Intramolecular Hydrofunctionalization Reactions of Alkenyl Amines Catalyzed by Disulfonimides

（ジスルホンイミドを用いたアルケニルアミンのヒドロアミノ化反応）

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Chapter 1. General Introduction

1-1. Introduction

Chirality is a geometric property of many organic molecules which are nonsuperimposable with its mirror image in the same way as a right hand can not be superimposed on a left hand. A chiral molecule and its mirror image are defined as being a pair of enantiomers. Chirality is at the base of life on Earth because all living beings are composed of chiral molecules in a pure enantiomeric form. That has significant effects on the production of medicine, which interacts specifically with receptors in living organisms like cellular receptors, or proteins, or nucleic acids. Thus, just one enantiomer of a drug has a desired pharmacological activity, whereas the other enantiomer can cause serious effects. Therefore, it is very essential to create bioactive compounds in a single and pure enantiomeric form.

Nitrogen-atom containing heterocycles are the structural cores of enormous drugs and biologically active natural products[1]. Indeed, it is estimated that currently about 40% of the chiral drugs sold on the market having a chiral cyclic amine as the structural motif. Especially, cyclic amines with an alpha-tetrasubstituted carbon stereocenter as a core structure are often found in many drugs and bioactive natural products such as chiral isoindolinones **A-C** (**A**: renin inhibitor[2], **B**: drug for the treatment of cardiac arrhythmias[3], **C**: modulator of serotonin receptors[4]). Some more complex C_2-arylindoline, such as phalarine[5], hinckdentine **A**[6], and tabernaebovine[7], have been also isolated from natural products (Figure 1).

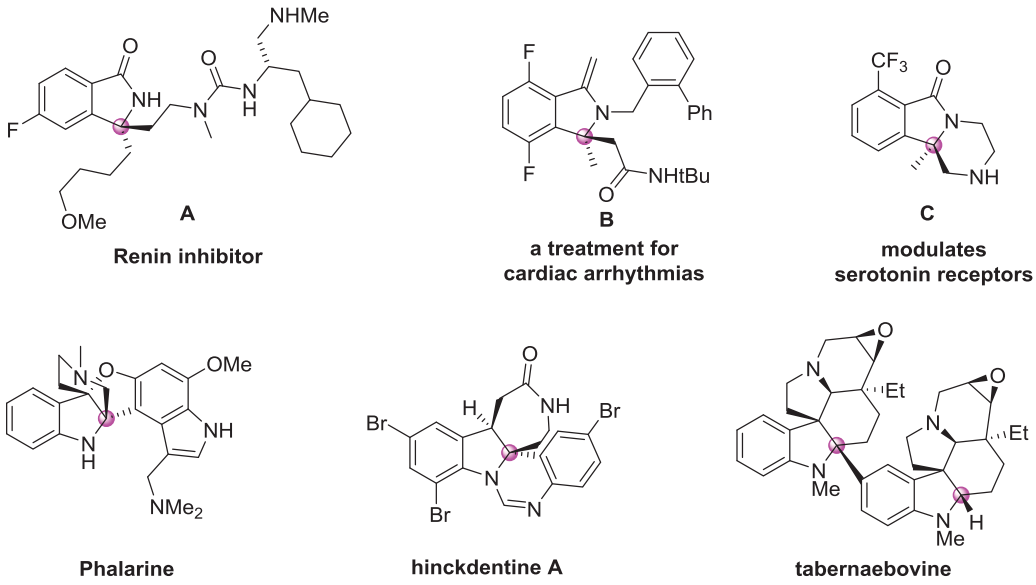
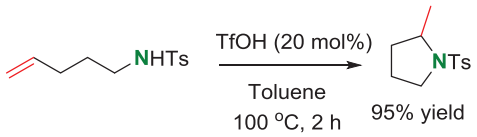


Figure 1. Several cyclic amines with an alpha-tetrasubstituted carbon stereocenter to the nitrogen atom.

Among the various approaches to the synthesis of nitrogen-containing heterocycles, the Brønsted acid-catalyzed hydroamination reaction of alkenyl amines is one of the atom-economical and effective methods. Because the addition of a nucleophilic amine to the

protonated olefin with Brønsted acid provides directly highly substituted nitrogen-containing heterocycles in a single step[8–11] (Scheme 1). In 2002, Hartwig et al. performed the hydroamination of alkenyl amine (RNHTs) in the presence of strong acids such as triflic acid, they found that cyclic amines were formed in excellent yields[4]. After the pioneering work, other Brønsted acids such as perfluorous superacid ($C_8F_{17}SO_3H$)[9] and triflic acid (TfOH)[12,13] have been also reported to catalyze the hydroamination. Moreover, Lewis acid-mediated hydroamination using $BF_3{\cdot}Et_2O$[10] and $Ca(NTf_2)_2$[11] have been also developed. However, these Brønsted acids and Lewis acids have some drawbacks as corrosivity and moisture sensitivity, and so on.



Scheme 1. Brønsted acid-catalyzed hydroamination of alkenyl amine.

On asymmetric hydroamination, there have been many reports using metal Lewis acids as catalysts. Because Lewis acidic metals can directly activate the olefin or amine moiety of alkenyl amine[14]. For these Lewis acidic metals, rare and/or toxic elements have been often used. In addition, some chiral metal catalysts used on hydroamination have generally a lower activity, and higher temperatures and high catalyst loadings are needed for good results. As a result, asymmetric hydroamination catalyzed by metal Lewis acid might be non-environmentally friendly.

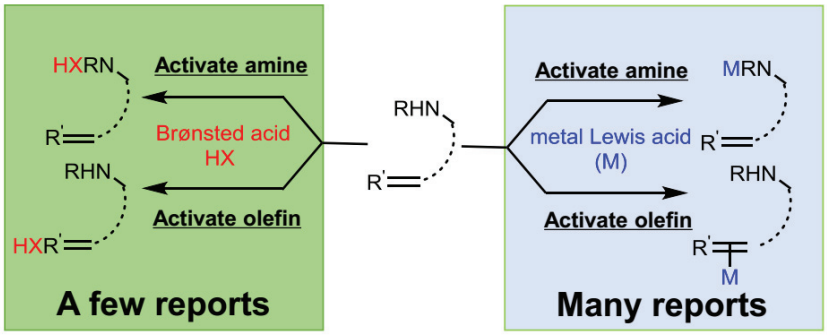
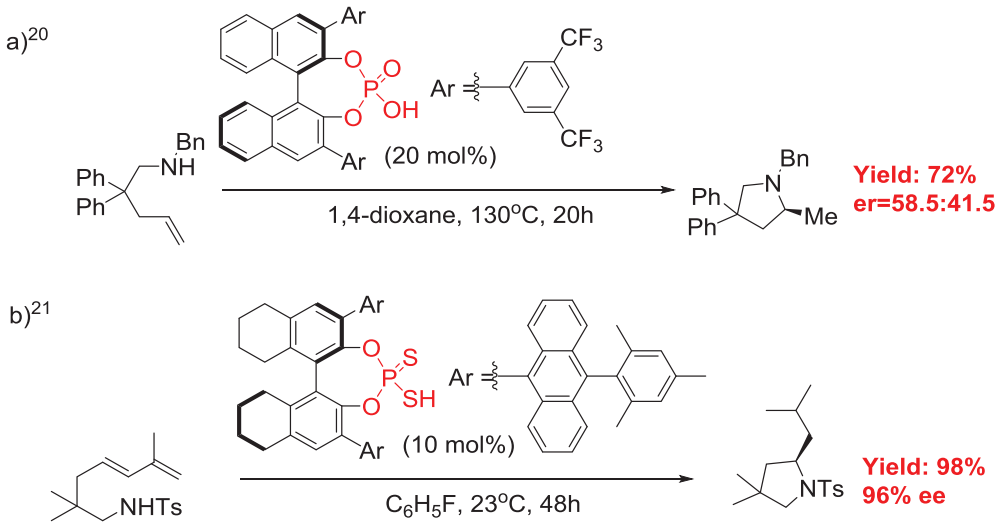


Figure 2. Activation modes in asymmetric hydroamination of alkenyl amines catalyzed by metal Lewis acid or Brønsted acid.

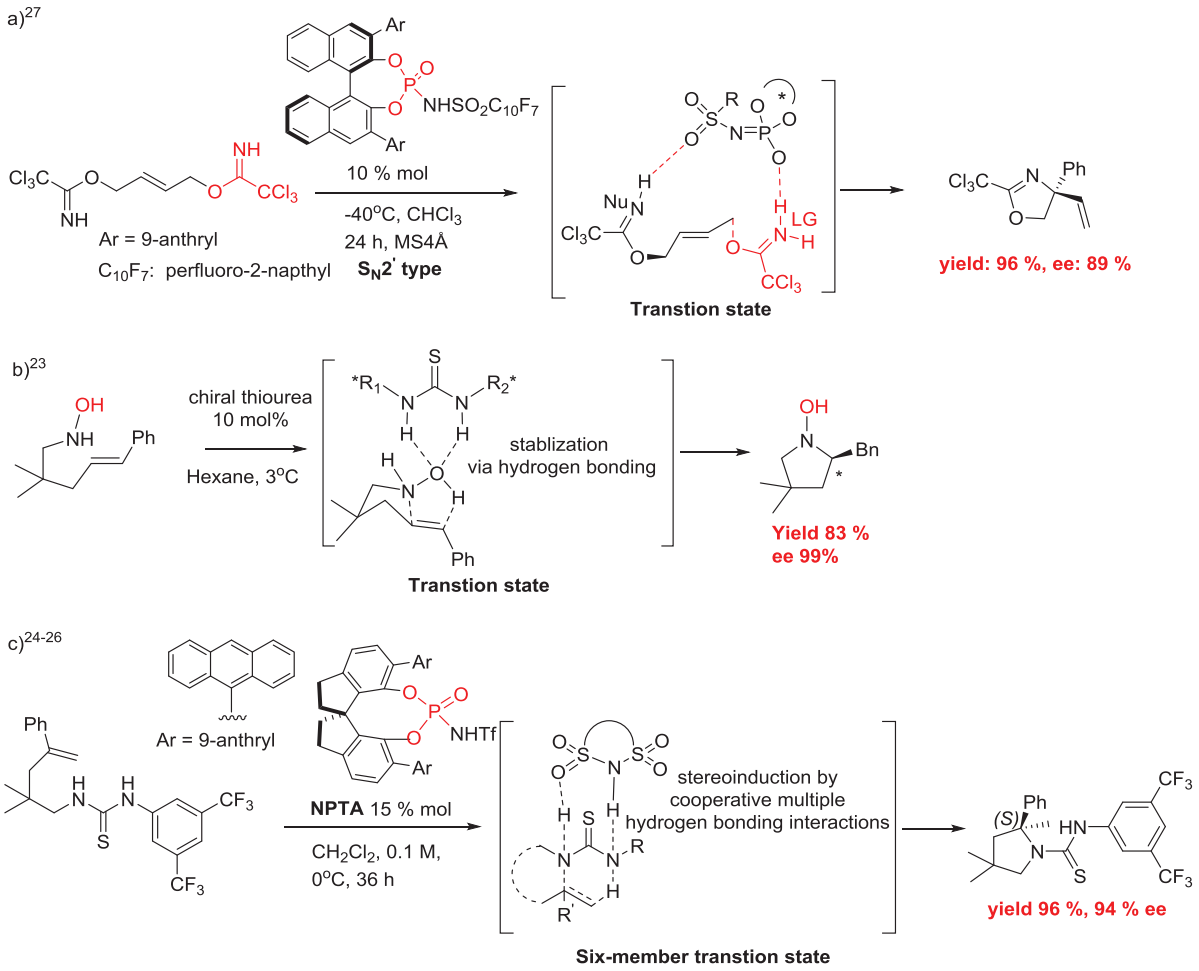
In contrast to these drawbacks of metal Lewis catalysts, organic Brønsted acids are consisted of organic elements, environmentally friendly, and not sensitive to moisture and oxygen[15–18]. Their tunability and their tolerance toward diverse functional groups are also advantageous points. Despite their superior advantages, the use of chiral organic Brønsted acids

on hydroamination reaction of alkenyl amines has been less studied because Brønsted acids are not sufficiently acidic to activate the olefin moiety. So far, only a limited number of examples have been reported for chiral organic Brønsted acid-catalyzed asymmetric hydroamination of alkenyl amine via direct activation of the olefin moiety (Scheme 2)[19–22]. The hydroamination of terminal alkenyl amine catalyzed by chiral phosphoric acid needed high temperature and the hydroamination product was obtained with low enantioselectivity (Scheme 2a)[20]. Toste et al. have reported that the hydroamination of dienyl amine catalyzed by dithiophosphoric acid affords hydroamination product with good yield and high enantioselectivity under mild reaction conditions (Scheme 2b)[21]. In this reaction, more nucleophilic diene and more acidic dithiophosphoric acid were used as a substrate and Brønsted acid, respectively, in order to accelerate the hydroamination.



Scheme 2. Chiral Brønsted acid-catalyzed hydroamination of alkenyl amine via the direct activation of the olefin moiety.

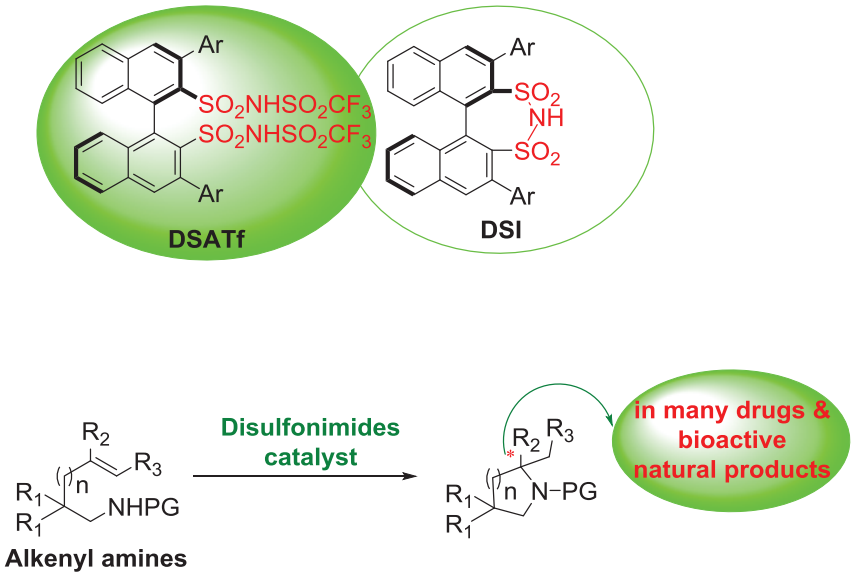
In order to avoid the acidity limitation in chiral Brønsted acid catalyzed hydroamination of alkenyl amines, a few asymmetric hydroamination of alkenyl amines with specific protecting groups, which are activated by Brønsted acid, have been developed (Scheme 3)[23–27]. The introduction of a leaving group at the allylic position of an alkenyl amine enables the activation of the leaving group and the nitrogen atom via hydrogen bonding with the chiral phosphoric acid, leading to formal enantioselective hydroamination via an intramolecular S_N2' reaction (Scheme 3a)[27]. The enantioselective hydroamination of alkenyl amines *N*-substituted with basic functional groups, such as hydroxyl amine[23] or thiourea group[24–26], have been developed (Scheme 3b and c). In these reactions, chiral Brønsted acid coordinates to the functional groups on the amine moiety to create an asymmetric environment and promote the protonation of alkene via the activated functional group.



Scheme 3. Chiral Brønsted acid-catalyzed hydroamination via the activation of amine moiety.

1-2. Purpose of this Study

In this study, in order to overcome the acidity limitations of Brønsted acids for the direct olefine activation on hydroamination, a new chiral BINOL-derived disulfonamide trifluoromethanesulfonate (**DSATf**) was designed, based on the strong acidity of Tf_2NH. **DSATf**-catalyzed hydroamination of alkenyl amines was examined. Hydroamination of alkenyl thiourea catalyzed by a cyclic **DSI** catalyst[28], which was developed by List et al., was also examined. The mechanism of the hydroamination reaction was also investigated using density functional theory calculations to understand the behavior of the reactions and the origin of enantioselectivity.

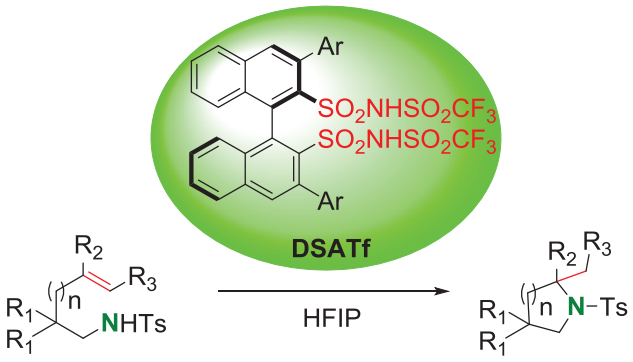


Chapter 2

Synthesis of New Strong Brønsted Acids

and

its Application to Hydroamination



2-1. Design of a New Strong Brønsted Acid

Brønsted acid catalysts with high acidity had the possibility to give the product with good yield and enantioselectivity in some reported asymmetric reactions [29]. Thus, many chiral organic Brønsted acids have been developed in order to create a strong chiral Brønsted acid (Figure 1) [30–33].

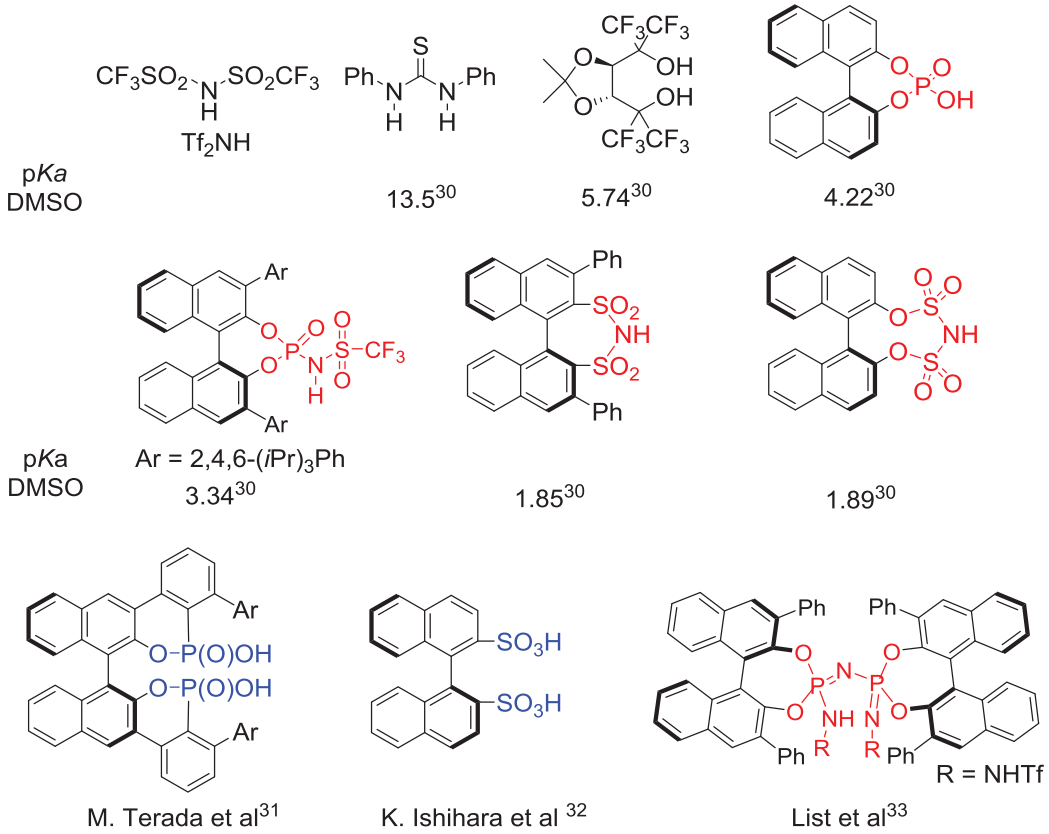


Figure 1. Some chiral strong Brønsted acids and experimental pK_a values

So far, there are two strategies for the design of Brønsted acids. The first one is the introduction of strongly electron-withdrawing groups, such as *N*-triflyl phosphoramide[10], disulfonimide[34–36], imidodiphosphate[37–41], and imidodiphosphorimidate[22,33] onto the chiral binaphthol (BINOL) skeleton to increase the acidity of the Brønsted acids. The second strategy is the stabilization of the conjugated base of Brønsted acids by intramolecular hydrogen bonds from the adjacent functional groups. Based on the second strategy, chiral Brønsted acids bearing two strongly electron-withdrawing groups, such as dicarboxylic acid[42], disulfonic acid[32,43–45], diphosphoric acid[31,46,47], tether-linked diphosphoric acid[48–50] and conjugate-base-stabilized carboxylic acids[51–54] have been developed. Terada and co-workers used X-ray diffraction analysis to reveal an intramolecular hydrogen bond between the two phosphoric acid moieties in diphosphoric acid (Figure 2)[31]. This suggests that intramolecular hydrogen bonds in a

Brønsted acid bearing two adjacent strongly electron-withdrawing groups possibly play an important role in attaining high reactivity and stereoselectivity.

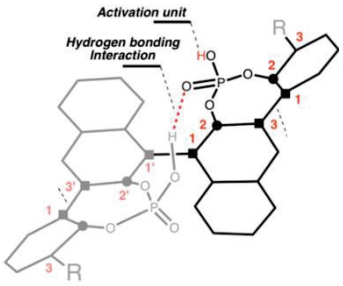


Figure 2. X-ray analysis bis-phosphoric acid

On the basis of these hypotheses, a new BINOL-derived disulfonamide trifluoromethanesulfonate (**DSATf**) was designed, based on the strong acidity of a superacid Tf_2NH[55] (Figure 3).

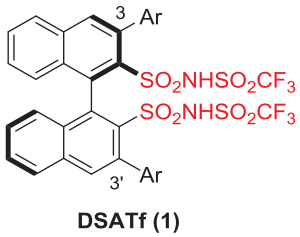
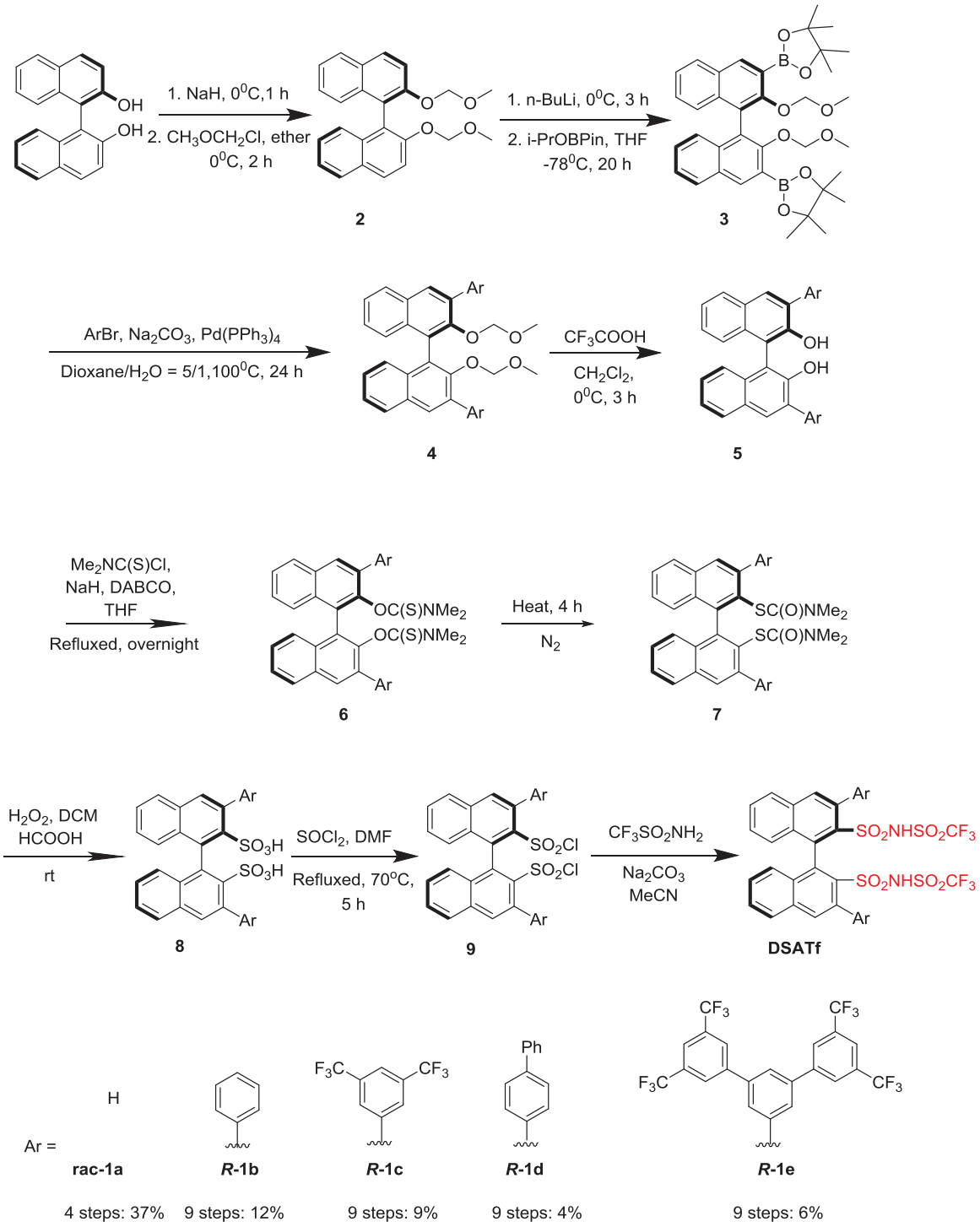


Figure 3. DSATf (**1**)

2-2. Synthesis of New Strong Brønsted Acids DSATf

DSATf 1 was prepared according to the literature method (Scheme 1)[36,56]. Two hydroxy groups of *R*-binapthanol were protected with methoxymethyl group in diethyl ether to produce compound **2** and then was coupled with dioxaborolane to give compound **3**. The compound **3** coupled with ArBr using Na_2CO_3 and $Pd[(Ph)_3P]_4$ in dioxane: H_2O to produce the desired product **4**. Next, compound **4** went through the deprotection to get compound **5**. Compound **5** was carbamothioated to produce compound **6** and S-rearranged via Newman−Kwart rearrangement by heating at 60ºC to get compound **7**. The compound **7** was easily oxidized in dichloromethane by a perfomic acid solution to give sulfonic acid **8**. After chlorination of sulfonic acid, compound **9** was formed. Lastly, the introduction of trifluoromethanesulfonamide group to **9** was conducted via substitution reaction with $TfNH_2$ in MeCN to give **DSATf** (**1**). An observation was that non-substituted disulfonamide **1a** absorbed moisture from the air so much like Tf_2NH, but disulfonamides **1b-d** were not so.



Scheme 1. Synthesis of **DSATf (1a-e)**

2-3. pK_a value of DSATf

In order to evaluate the acidic strength of **DSATf**, the computational prediction of p*K*a value using the direct method at the SMD/M06-2x/6-311++G(2df,2p)//B3LYP/6-31+G(d) level of theory[57,58] and the experimental measurement of the pK_a value by an overlapping indicator method via UV-Vis spectrophotometric titrations in DMSO[30] were performed (Figure 4). The predicted pK_a value (-5.26) of **1a** suggested that the acidity of **DSATf 1a** was stronger than that of **NPTA** and weaker than that of **BINSA**. The optimized structure of **1a** and its conjugated base indicated that the intramolecular hydrogen bond between the two sulfonimides plays an important role in high acidity, as our hypothesis (Figure 5).

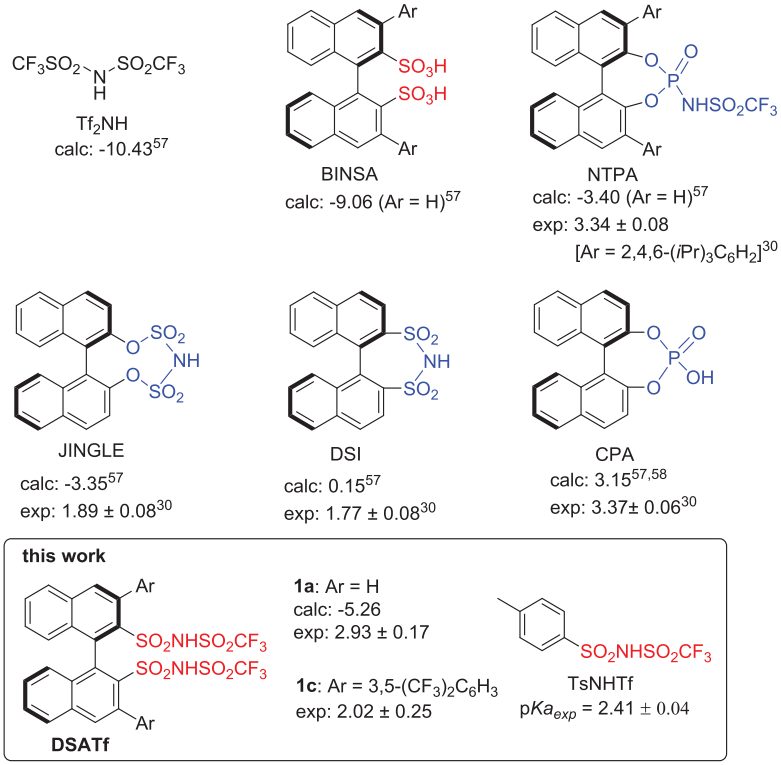


Figure 4. Computational and experimental pK_a values of **DSATf** and Brønsted Acids in DMSO.

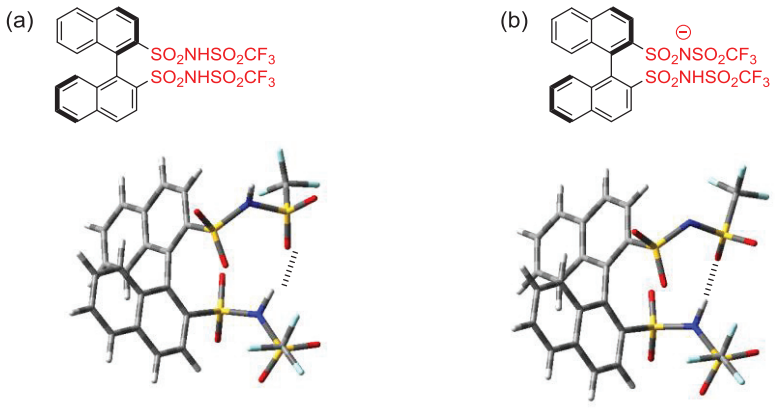


Figure 5. Optimized structure of (a) **1a** and (b) anion of **1a** at the B3LYP/6-31+G(d) level of theory.

The experimental pK_a values of **DSATf 1a** and **1c** were measured with an overlapping indicator method via UV-Vis spectrophotometric titrations reported by O'Donoghue and Berkessel using 2,4-dinitronaphthol as an indicator (Figure 6)[30]. The experimental pK_a value (2.02) of **1c** suggested that the acidity of **DSATf 1c** was stronger than that of **NPTA** and was similar to that of **DSI**. The experimental pK_a value (2.41) of monosulfonamide TsNHTf is larger than that (2.02) of **DSATf 1c**. That indicated the adjacent sulfonamide groups contributed considerably to enhance the acidity of **DSATf 1c**. From the experimental measurement and the computational calculation, it showed that the acidity of **DSATf 1** was one of the strong Brønsted acids.

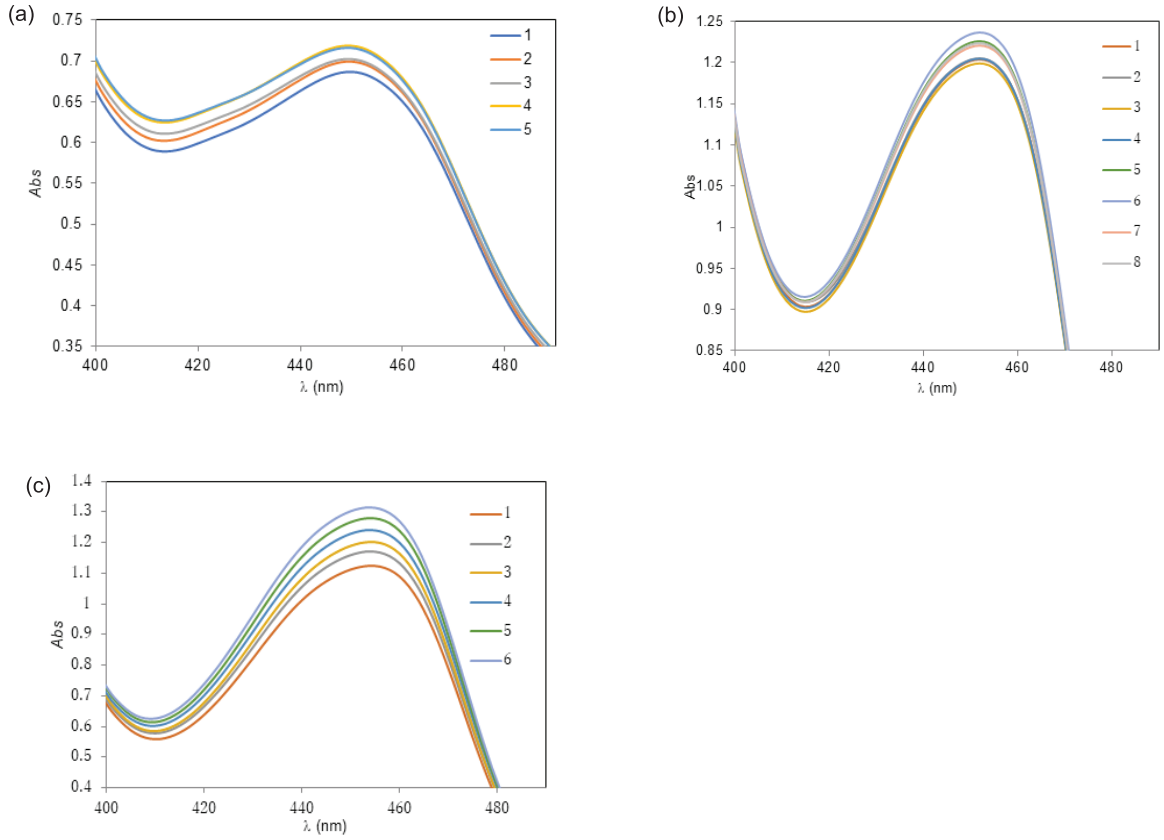


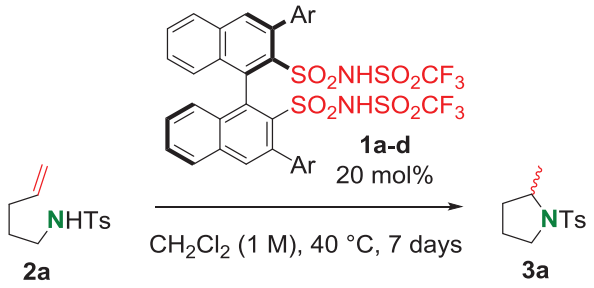
Figure 6. UV/Vis spectra of 2,4-dinitronaphthol in DMSO containing **DSATf** (a: **1a**, b: **1c**, c: TsNHTf) and conjugate base.

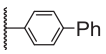
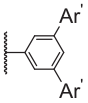
2-4. DSATf Catalyzed Hydroamination of Alkenyl Amines

2-4.1. Optimization of 3,3'-substituents (Ar) of BINOL Backbone of DSATf

After the estimation of the acidity of **DSATf**, the efficiency of **DSATf** as a catalyst in the hydroamination of alkenyl amines was evaluated. First, the catalyst was optimized by increasing the size of the 3,3'-substituents of the BINOL backbone (Table 1). The hydroamination reaction using 20 mol% catalysts was performed in DCM at 40°C for 7 days. **DSATf 1a** and **1b** provided the product in low yield (23% and 26%) and enantioselectivity (0% ee and 15% ee) (entries 1-2). The results showed that catalysts **1a** and **1b** were not sufficiently acidic for this reaction. Increasing the size of 3,3'-substituents (Ar) slightly affected the enantioselectivity (entries 1-4) but too large substituents decreased the enantioselectivity (entry 5). Introducing two CF_3 groups to the phenyl ring of catalyst could give the product with the best yield (81%) because of increased acidity of the catalyst by introducing two electron-withdrawing groups CF_3 (entry 3).

Table 1. Asymmetric hydroamination using **DSATf 1a-e**



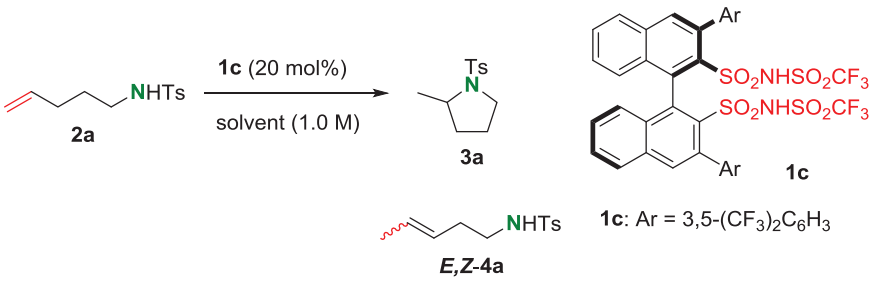
entry	catalyst	yield (%)[a)]	e.e. (%)[b]
1	*rac*-**1a**: Ar =H	23	-
2	*R*-**1b**: Ar = 	26	15
3	*R*-**1c** : Ar = 	**81**	3
4	*R*-**1d**: Ar = 	23	19
5	*R*-**1e** : Ar =  Ar' = 3.5-$(CF_3)_2C_6H_3$	37	10

[a] Isolated yield. [b] Determined by chiral HPLC analysis. Ts = $SO_2C_6H_4$*p*-Me.

2-4.2. Optimization of Solvents

The reaction solvent in the hydroamination of alkenyl amine **2a** catalyzed **1c** was next evaluated (Table 2). In DCM and benzene, the reaction needed 7 days at 40°C to consume **2a** (entries 1 and 2). Under these conditions, the product was obtained with a good yield (81% and 70%) but no enantioselectivity was observed. The hydroamination in HFIP solvent proceeded smoothly and effectively even at 20°C (entry 3). Because polyfluorinated alcohols have unique properties, including their protic and non-nucleophilic character, excellent hydrogen bonding donor ability, high ionizability beneficial for stabilizing cationic species, and high polarity[11,59,60]. Unfortunately, TFE is not effective in the reaction with the chemical yield 25% (entry 4). At a higher temperature 60°C, the reaction in HFIP was accelerated and gave the product **3a** in 73% for 12 h (entry 5). In the reaction, the olefin-isomerized product **4a** was also obtained as a byproduct. Thus, performing the reaction at 60°C in HFIP is the best synthetic condition. No enantioselectivity was observed in these reactions because two functional groups $SO_2NHSO_2CF_3$ were so flexible that led to being difficult to control conformation. Therefore, only the catalytic ability of catalyst **1c** was focused on further examinations.

Table 2. Optimization of reaction conditions of hydroamination.



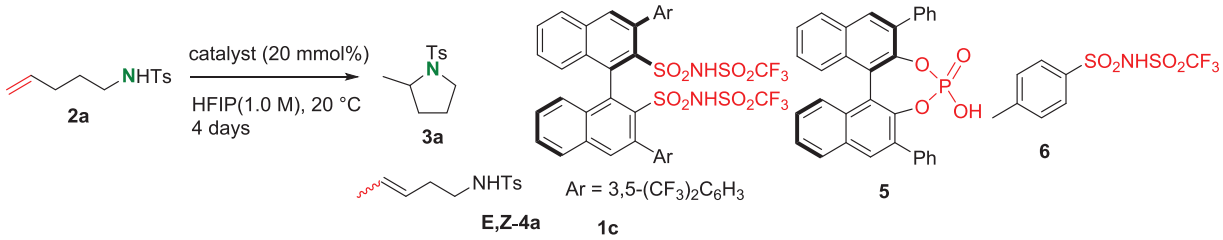
entry	conditions	yield (%)[a]	e.e.(%)[b]
1	DCM, 40°C, 7 days	81	3
2	Benzene 40°C, 7 days	70	0
3	HFIP, 20°C, 4 days	82[c]	N.D.
4	TFE, 20°C, 4 days	25	0
5	HFIP, 60°C, 12 h	73	N.D

[a] Isolated yield. [b] Determined by chiral stationary phase HPLC analysis. [c] Alkene **4a**, which was generated from olefin isomerization of **2a**, was also obtained: *E*-**4a**: 2.5% yield, *Z*-**4a**: 1.8% yield. Ts = *p*-$MeC_6H_4SO_2$. DCM = CH_2Cl_2. HFIP = $(CF_3)_2CHOH$. TFE = CF_3CH_2OH, N.D. = not determined.

2-4.3. Comparison of catalytic efficiency of some Brønsted acids with DSATf

The hydroamination reaction of alkenyl amine **2a** using 20 mol% of **DSATf 1c** and several common Brønsted acids was performed in HFIP at 20°C for 4 days in order to compare the catalytic efficiencies (Table 3). The hydroamination catalyzed by $TsOH.H_2O$, Tf_2NH, TfOH, and **1c** produced pyrrolidine **3a** in good chemical with the small amount of the isomerized product **4** (entries 1-4). When using phosphoric acid **5**, the olefin-isomerized product **4a** became the major product (entry 5). Because the nucleophilicity of the conjugated base of **5** was stronger than that of **1c**, the isomerization reaction was promoted to form the olefin-isomerized product **4a**.

Table 3. Comparison of the catalytic efficiency of some Brønsted acids with **DSATf**.



entry	catalyst	con(%)[a]	Yield (%)[b]		
			3a	***E*-4a**	***Z*-4a**
1	$TsOH.H_2O$	96	89	3.9	3.2
2	Tf_2NH	94	88	3.6	2.3
3	TfOH	97	85	1	0.6
4	**1c**	86	82	2.5	1.8
5	**5**	81	7	61	6
6	**6**	48	33	9.4	3.3

[a] Determined by ^1H NMR measurement of the crude product using 1,3,5-trimethoxybenzene as an internal standard. [b] Isolated yield. HFIP = $(CF_3)_2CHOH$. Tf_2NH = $(CF_3SO_2)_2NH$. TfOH = CF_3SO_3H

The time profile of the chemical yield of pyrrolidine **3a** in the several Brønsted acid catalyzed hydroamination reactions of **2a** was investigated (Figure 7). The result showed that the order of the catalytic efficiency of Brønsted acid was $TsOH\cdot H_2O$, Tf_2NH > TfOH ≈ **DSATf** >> TsNHTf (**6**). The poor hydroamination result catalyzed by monosulfonamide **6** showed the importance of adjacent sulfonamide groups for the high acidity of **DSATf**. This result is consistent with the experimental pK_a of **DSATf** and TsNHTf (**6**) (Figure 4).

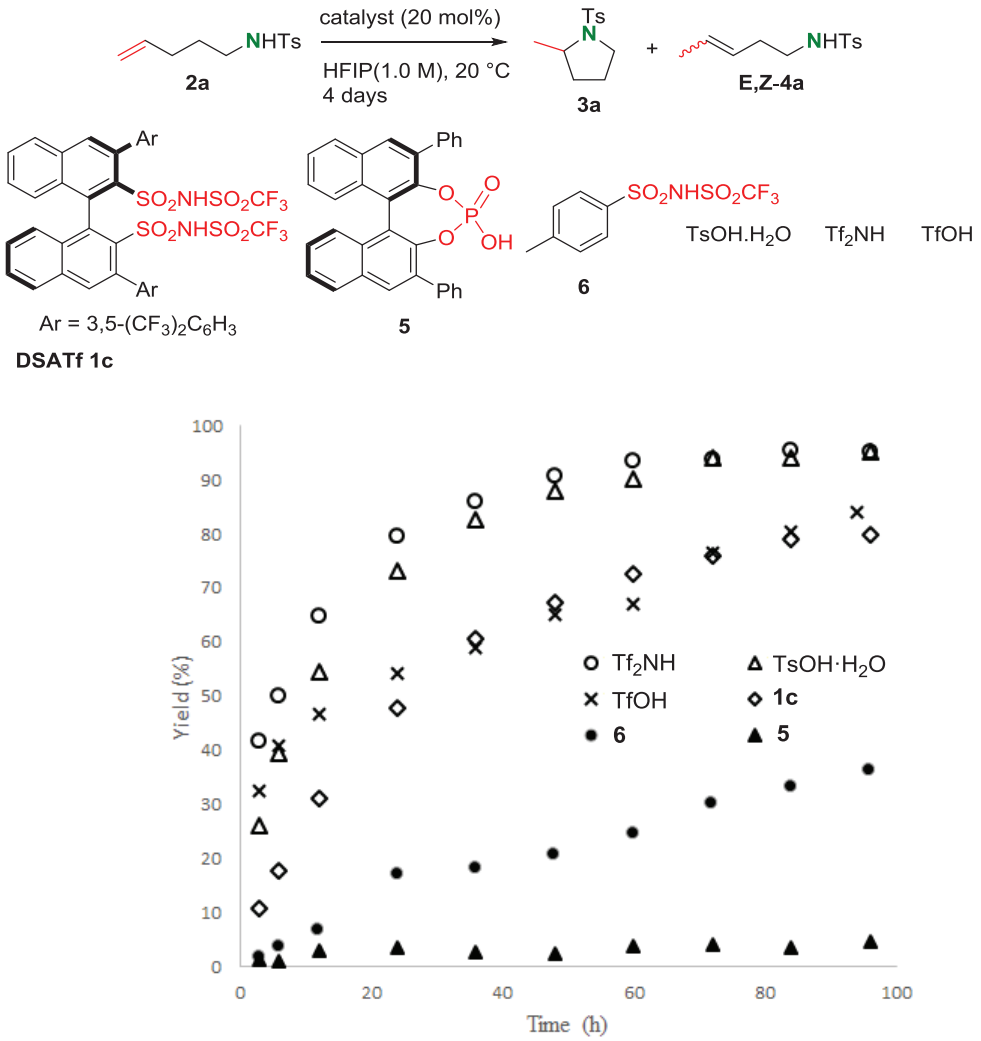
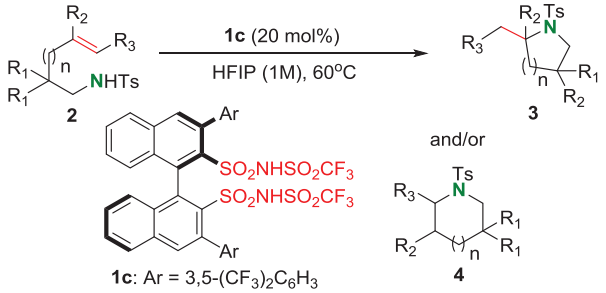


Figure 7. The time profile of chemical yield of pyrrolidine **3a** in the hydroamination of **2a**.

2-5. Scope of Hydroamination Catalyzed by DSATf

The scope of **1c**-catalyzed hydroamination was next examined under the optimized conditions at 60°C in 1M HFIP (Table 4). With substrate substituted with a *gem*-dimethyl group (**2b**), the reaction proceeded quickly only 3h (entry 1). Because of the conformational effect by the *gem*-dimethyl group, the product was obtained with a good yield (92%). In entries 2 and 3, the hydroamination of alkenyl amine **2c** containing an internal olefin required a longer reaction time to consume the starting material. In entry 2, the hydroamination of *E*-**2c** produced pyrrolidine **3c** as a single product with a high yield (91%). Unlike *E*-**2c** substrate, the formation of the two products (**3c** and **4c**) was observed during the hydroamination of *Z*-**2c** alkenyl amine (entry 3). In entry 4, pyrrolidine **3c** was formed as a major product with a chemical yield 50%. Because the olefin-isomerization of alkenyl amine was a competing reaction under hydroamination. On the hydroamination of **2e** with the phenyl substituent at the olefin moiety, the six-membered ring piperidine **4e** was formed with the chemical yield 61% as a single product through an intermediate with the benzylic stabilization (entry 5). These data suggested that the reaction rate of the cyclization at 60°C followed the order of 5-*exo* > 5-*endo* > olefin-isomerization > 6-*exo* (entries 0-4) and the benzylic cation intermediate was generated from **2e** and **2f** as a stable cation intermediate at that temperature (entries 5-6).

Table 4. Scope of hydroamination catalyzed by **DSATf 1c**.



entry	substrate	time	product [a]	ee[b]
0	NHTs **2a**	12 h	NTs **3a**: 73%	
1	NHTs **2b**	3 h	NTs **3b**: 92%	3%
2	NHTs *E*-**2c**	24 h	NTs **3c**: 91%	2%
3	NHTs *Z*-**2c**	96 h	NTs **3c**: 83% + NHTs **4c**: 2%	

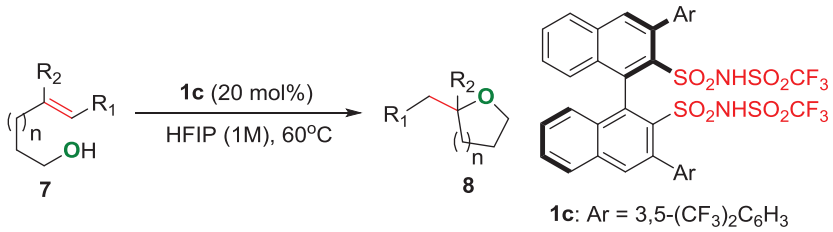
entry	substrate	time	product [a]
4[c]	NHTs **2d**	7 h	NTs **3c**: 50% + NHTs **4c**: 14%
5[d]	Ph NHTs **2e**	1 h	Ph NTs **3e**: 0% + Ph NTs **4e**: 61%
6	Ph NHTs **2f**	9 h	Ph NTs **3f**: 85%

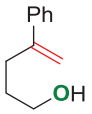
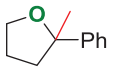
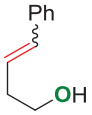
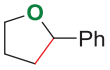
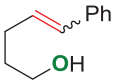
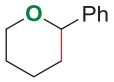
[a] Isolated yield. [b] Determined by chiral stationary phase HPLC analysis.
[c] A mixture of *E*- and *Z*-N-toluenesulfonyl 4-hexen-1-amine was also obtained in 8% yield.
[d] When the reaction was carried out at 20°C for 4 h, a mixture of pyrrolidine derivative and piperidine derivative was obtained (pyrrolidine derivative **3e**: 20% yield, piperidine derivative **4e**: 5% yield).

2-6. Scope of Hydroalkoxylation Catalyzed by DSATf

The scope of hydroalkoxylation of alkenyl alcohol catalyzed by **DSATf 1c** was conducted (Table 5). The results showed that the hydroalkoxylation of alkenyl alcohol containing an internal olefin needed a longer reaction time to completely consume the starting material than that of terminal olefin derivatives. The cyclization occurred at the benzylic position, in which the most stable benzylic cation was generated. These results indicate **DSATf** can also catalyze the hydroalkoxylation of alkenyl alcohols in HFIP with high efficiency.

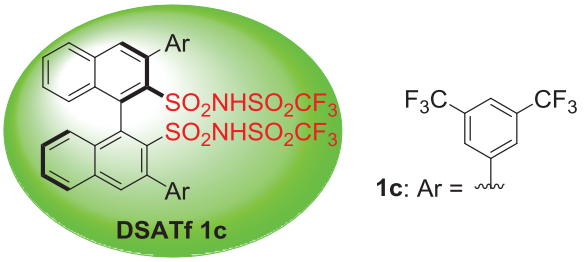
Table 5. Scope of hydroalkoxylation catalyzed by **DSATf 1c**.



entry	substrate	time	product [a]
1	 **7a**	1 h	 **8a**: 78%
2 [b]	 **7b**	4 h	 **8b**: 47%
3 [c]	 **7c**	4 h	 **9c**: 62 %

[a] Isolated yield. [b] A mixture of *E*- and *Z*-isomer (*E*:*Z* = 5.3:1) was used as the substrate.
[c] A mixture of *E*- and *Z*-isomer (*E*:*Z* = 22:1) was used as the substrate.

2-7. Conclusion



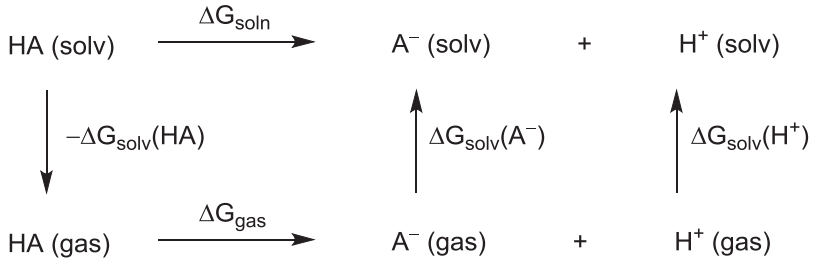
Our new designed disulfonamide

In summary, a new Brønsted acid containing disulfonamide trifluoromethanesulfonate (**DSATf**) functionality has been developed. The computational prediction and experimental measurement of the pK_a value of **DSATf** categorized it as a strong Brønsted acid. The **DSATf** catalyzed hydroamination reaction proceeded smoothly in HFIP solvent. The catalytic ability order of Brønsted acid in hydroamination: $TsOH{\cdot}H_2O$, Tf_2NH > TfOH ≈ **DSATf** >> TsNHTf. However, the enantioselectivity in the hydroamination was not observed. A comparison of the catalytic efficiency of **DSATf** and TsNHTf indicated the importance of adjacent sulfonimide groups for enhancing the acidity of **DSATf**. **DSATf** also catalyzed the hydroalkoxylation of alkenyl alcohols in HFIP with high efficiency. The advantages of **DSATf** is including its strong Brønsted acidity, reusability, and ease of handling than $TsOH{\cdot}H_2O$, Tf_2NH, and TfOH.

2-8. Experimental Section

2-8-1. Details of computational methods

The structures of all species were carried out with the Gaussian 09 package[61]. Geometry optimizations were conducted at the B3LYP/6-31+G(d) level. The nature of the stationary points was confirmed by frequency calculations at the same level of theory. The solution phase free energy calculations were performed by virtue of SMD model at the M06-2x/6-311++G(2df,2p) level. The direct method was applied to predict pK_a values (Scheme S1)[58,62–69]. As a proton solvation free energy ($\Delta G_{solv}(H^+)$) in DMSO, −268.34 kcal/mol was used[30]. The free energy of acid dissociation in DMSO (ΔG_{soln}) can be obtained through eq. 1. Then, pK_a can be obtained through the thermodynamic relationship (eq. 2). In the equations below, asterisks (*) indicate a standard state of 1 mol/L in any phase[70].



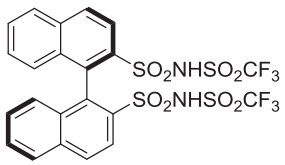
$$\Delta G^*_{solv} = \Delta G^*_{gas} + \Delta G^*_{solv}(A^-) + \Delta G^*_{solv}(H^+) - \Delta G^*_{solv}(HA) \quad \text{(eq 1)}$$

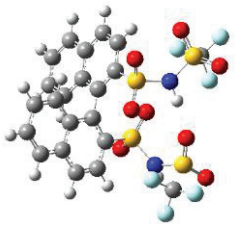
$$\Delta G^*_{solv}(H^+) = -268.34 \text{ kcal/mol}$$

$$pK_a = \frac{\Delta G^*_{soln}}{RT\ln(10)} \quad \text{(eq 2)}$$

Scheme S1. pK_a Calculation via the direct method.

B3LYP/6-31+G(d) Optimized cartesian coordinates and energies for DSATf 1a



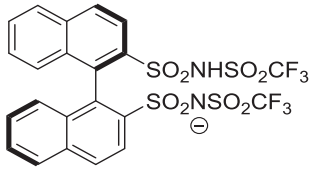


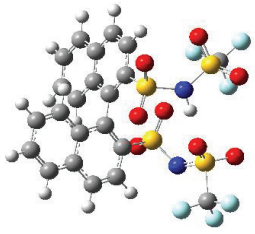
Zero-point correction = 0.355716 (Hartree/Particle)
Thermal correction to Energy = 0.393704
Thermal correction to Enthalpy = 0.394648
Thermal correction to Gibbs Free Energy = 0.281805
Sum of electronic and zero-point Energies = -3749.303256
Sum of electronic and thermal Energies = -3749.265268
Sum of electronic and thermal Enthalpies = -3749.264324
Sum of electronic and thermal Free Energies = -3749.377167

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.882229	-1.736623	0.710540
2	6	0	-1.727950	-0.974390	-0.083854
3	6	0	-1.566025	-3.803378	-0.328070
4	6	0	-2.537337	-1.659790	-1.057833
5	6	0	-0.804562	-3.148660	0.605713
6	6	0	-2.440056	-3.085766	-1.185058
7	6	0	-3.447940	-0.971199	-1.910776
8	1	0	-3.146576	-4.836628	-2.239523
9	1	0	-1.506212	-4.885142	-0.415754
10	6	0	-4.204158	-1.651273	-2.840731
11	1	0	-3.544548	0.106176	-1.835544
12	1	0	-4.885478	-1.101961	-3.484582
13	6	0	-4.097906	-3.057118	-2.967379
14	1	0	-4.698710	-3.580523	-3.706165
15	6	0	-3.234512	-3.756294	-2.153761
16	6	0	-1.700909	2.859725	-0.580501
17	1	0	-2.933424	4.302321	0.393750
18	6	0	-2.663037	3.252789	0.312179

19	6	0	-1.957336	0.502906	0.087806
20	6	0	-3.318003	2.301117	1.137502
21	6	0	-1.341778	1.489888	-0.671092
22	6	0	-2.976931	0.913851	1.018109
23	6	0	-4.314182	2.698512	2.068588
24	1	0	-3.433631	-1.076386	1.765055
25	6	0	-4.958490	1.767581	2.853101
26	1	0	-4.558175	3.754861	2.151040
27	1	0	-5.717339	2.082706	3.564081
28	6	0	-4.632272	0.395776	2.732927
29	1	0	-5.142125	-0.335934	3.353375
30	6	0	-3.670215	-0.020968	1.838158
31	16	0	-0.139009	1.082307	-1.941999
32	8	0	0.544345	-0.165554	-1.640772
33	8	0	-0.710741	1.351767	-3.262101
34	16	0	0.206230	-1.022227	1.956943
35	8	0	0.018478	0.424214	2.031570
36	8	0	0.159580	-1.872249	3.137257
37	7	0	1.785120	-1.147880	1.258997
38	1	0	2.140745	-0.250729	0.912944
39	7	0	1.015955	2.414267	-1.837829
40	1	0	1.125324	2.837642	-2.761330
41	16	0	2.907492	-2.386765	1.341430
42	8	0	4.184396	-1.845845	1.782820
43	8	0	2.282648	-3.561458	1.930762
44	16	0	2.431009	2.536631	-0.933107
45	8	0	2.575124	1.391580	-0.046995
46	8	0	3.483561	3.001032	-1.824594
47	6	0	3.150915	-2.776652	-0.494075
48	6	0	2.021228	4.003384	0.186013
49	9	0	4.076930	-3.736305	-0.598186
50	9	0	3.567551	-1.686009	-1.142868
51	9	0	2.008939	-3.208456	-1.036384
52	9	0	3.114027	4.318735	0.880626
53	9	0	1.653242	5.048659	-0.567261
54	9	0	1.031828	3.687731	1.019426
55	1	0	-0.142279	-3.697363	1.266276
56	1	0	-1.206328	3.589532	-1.210885

Anion of DSATf 1a





Zero-point correction = 0.343323 (Hartree/Particle)
Thermal correction to Energy = 0.380463
Thermal correction to Enthalpy = 0.381407
Thermal correction to Gibbs Free Energy = 0.271869
Sum of electronic and zero-point Energies = -3748.839328
Sum of electronic and thermal Energies = -3748.802188
Sum of electronic and thermal Enthalpies = -3748.801243
Sum of electronic and thermal Free Energies = -3748.910782

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000001607	0.000003464	0.000002238
2	6	-0.000003130	-0.000001905	-0.000004954
3	6	-0.000003506	-0.000000843	-0.000003442
4	6	0.000001143	-0.000001398	0.000001519
5	6	-0.000002705	-0.000003143	-0.000000203
6	6	0.000000111	-0.000001709	-0.000000180
7	6	0.000001536	-0.000001961	-0.000001373
8	1	-0.000001592	-0.000003093	-0.000002338
9	1	-0.000002826	-0.000001592	-0.000001883
10	6	0.000001291	-0.000004035	-0.000001428
11	1	0.000001808	-0.000002795	-0.000000049
12	1	0.000001702	-0.000003806	-0.000001731
13	6	0.000000184	-0.000002941	-0.000002141
14	1	0.000000350	-0.000004310	-0.000002662
15	6	-0.000001556	-0.000003451	-0.000002781
16	6	0.000001905	-0.000002542	0.000003292
17	1	0.000002943	-0.000000389	0.000000725

18	6	0.000002385	0.000000911	0.000000334
19	6	0.000000551	-0.000001771	0.000000608
20	6	0.000001492	-0.000000620	-0.000000470
21	6	0.000002445	-0.000000426	-0.000000070
22	6	-0.000000004	0.000000035	-0.000002050
23	6	0.000001719	-0.000001378	0.000000253
24	1	-0.000001181	-0.000001667	-0.000001455
25	6	0.000000621	-0.000002163	-0.000000706
26	1	0.000002688	-0.000001412	-0.000000196
27	1	0.000000947	-0.000002019	-0.000000857
28	6	0.000000076	-0.000002179	-0.000001069
29	1	-0.000000926	-0.000002500	-0.000001773
30	6	-0.000000022	-0.000001985	-0.000001165
31	16	-0.000003285	-0.000000421	-0.000005126
32	8	0.000000636	-0.000003198	0.000002374
33	8	0.000004975	0.000002063	0.000005275
34	16	0.000007917	0.000001921	-0.000011095
35	8	-0.000000321	0.000001949	0.000001331
36	8	-0.000004003	0.000003246	0.000002598
37	7	-0.000014269	-0.000000185	0.000007515
38	1	0.000004508	-0.000004589	0.000002187
39	7	0.000008543	0.000005869	0.000005656
40	16	0.000003425	0.000008426	-0.000002435
41	8	-0.000003561	0.000001618	0.000001158
42	8	-0.000006921	0.000001294	0.000001775
43	16	-0.000006350	-0.000010395	-0.000018917
44	8	-0.000002540	0.000011244	0.000016495
45	8	0.000001758	0.000007604	0.000003175
46	6	-0.000004158	0.000001260	-0.000001611
47	6	0.000007217	0.000011141	0.000010245
48	9	-0.000003204	0.000002976	0.000001589
49	9	-0.000002462	0.000005500	0.000001454
50	9	0.000000643	0.000002888	-0.000000936
51	9	0.000001171	0.000002047	0.000000956
52	9	0.000006744	0.000000032	-0.000002880
53	9	-0.000003616	0.000000607	0.000006142
54	1	-0.000003773	0.000000125	-0.000001649
55	1	0.000004083	0.000000600	0.000000734

2-8-2. Details of the determination of pK_a value in DMSO via UV-Vis spectrophotometric titration

$$HIn + A^- \underset{}{\overset{K_{eq}}{\rightleftharpoons}} In^- + HA \qquad \text{(eq 3)}$$

$$pK_a(HA) = \log_{10}K_{eq} + pK_a(HIn) \qquad \text{(eq 4)}$$

$$K_{eq} = \frac{[HA]}{[A^-]} \times \frac{[In^-]}{[HIn]} = \frac{[HA]}{[A^-]} \times \frac{(Abs - Abs_{min})}{(Abs_{max} - Abs)} \qquad \text{(eq 5)}$$

The overlapping indicator method involves the experimental determination of the equilibrium constant K_{eq} for the equilibrium in eq. 3 using UV/Vis spectrophotometry, in which HA and A^- are the Brønsted acid and corresponding conjugate base, and HIn and In^- are the indicator and indicator anion. The pK_a values of the Brønsted acids could be calculated from the K_{eq} values and known indicator pK_a values by the application of eq. 4. In this study, 2,4-dinitronaphthol (DNN) was used as an indicator: pK_a(HIn)= 2.11.

In a typical experiment, UV/Vis spectra of the indicator (1.5×10^{-5} M) in DMSO buffered with Brønsted acid and conjugate base were recorded at 25°C. The conjugate base of the Brønsted acid was generated in situ by adding and varying amounts of a solution of sodium hydroxide (1.0×10^{-5} M) in DMSO. The solution of sodium hydroxide in DMSO was prepared by dilution of aqueous sodium hydroxide solution for volumetric analysis into DMSO so that the final concentration of water was < 2 vol %. The [InH]/[In^-] ratio was determined by comparing the observed absorbance at a given buffer ratio with the maximal and minimal absorbance values for the indicator at 454 nm. The values for K_{eq} were determined using eq. 5. For strong Brønsted acids, the natural ionization of HA was significant. O'Donoghue and Berkessel et al. carried out the correction of values of [HA] and [A^-].[30] However, in this study, the correction was not carried out, and the pK_a value of the acid was roughly determined. The standard deviation of pK_a values (^{s}pK_a), given in parentheses, was calculated using eq. 6.

$$ {}^{s}pK_a = \sqrt{S_a^2 + S_b^2} \qquad \text{(eq 6)} $$

S_a: standard deviation quoted for pK_a (HIn) by Bordwell[5]

$$ S_a = 0.04 \quad \text{for DNN} $$

$$ S_b = \frac{0.434 \times {}^{s}K_{eq}}{K^{av}_{eq}} $$

K^{av}_{eq}: mean values of K_{eq}

${}^{s}K_{eq}$: standard deviation of K_{eq}

$$ {}^{s}K_{eq} = \sqrt{\frac{\sum (K_{eq} - K^{av}_{eq})^2}{n - 1}} $$

DSATf 1a

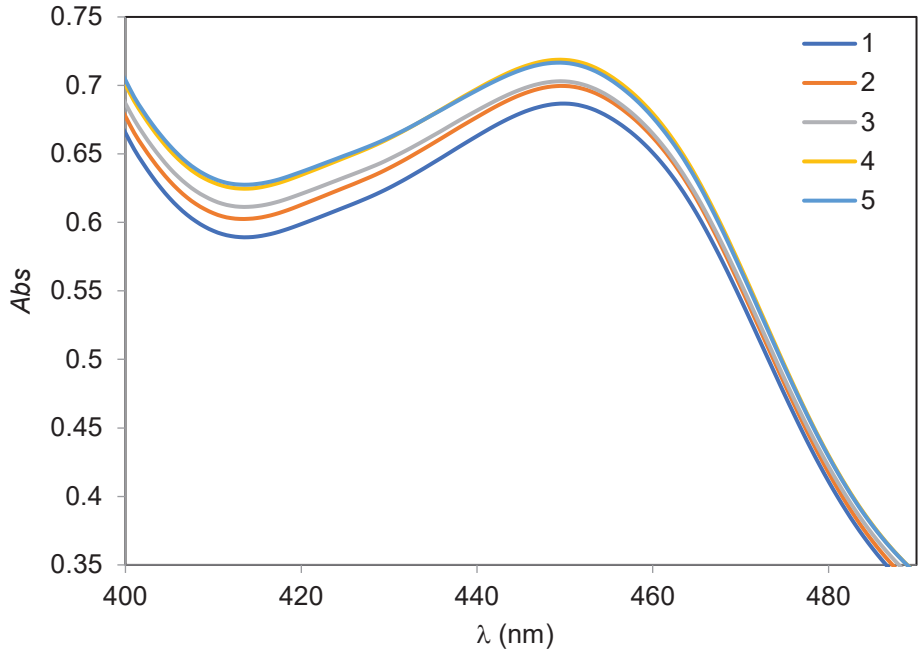


Figure S1. UV/Vis spectra of 2,4-dinitronaphthol in DMSO containing **DSATf 1a** and conjugate base: spectra 1–5 correspond to the conditions given in Table S1.

Table S1. Absorbance data for 2,4-dinitronaphthol (DNN)[a] in DMSO containing acid (**1a**) and anion[b] (**1a**$^-$) at 454 nm and 25°C.

Spectrum	[**1a**] (M)	[**1a**$^-$][b] (M)	*Abs*	[In$^-$]/[HIn][c]	K_{eq}[d]
1	0.28 x 10^{-3}	0.20 x 10^{-3}	0.680	3.33	4.71
2	0.23 x 10^{-3}	0.25 x 10^{-3}	0.693	6.25	1.10
3	0.18 x 10^{-3}	0.30 x 10^{-3}	0.696	7.63	4.66
4	0.13 x 10^{-3}	0.35 x 10^{-3}	0.705	21.8	8.32
5	0.08 x 10^{-3}	0.40 x 10^{-3}	0.709	52.4	10.9

[a] The concentration of 2,4-dinitronaphthol was 1.5 × 10^{-5} M. [b] Anion **1a**$^-$ was generated by addition of NaOH in water solution in DMSO such that the content of water was < 2 vol %. [c] The ratio of phenolate to phenol was obtained using the relationship [(*Abs* – 0.578)/(0.711 – *Abs*)]. [d] K_{eq} = ([**1a**]/[**1a**$^-$]) x ((*Abs* – Abs_{min})/(Abs_{max} – *Abs*)).

The pK_a value was calculated using equation eq 4: pK_a = 2.93 ± 0.17.

DSATf 1c

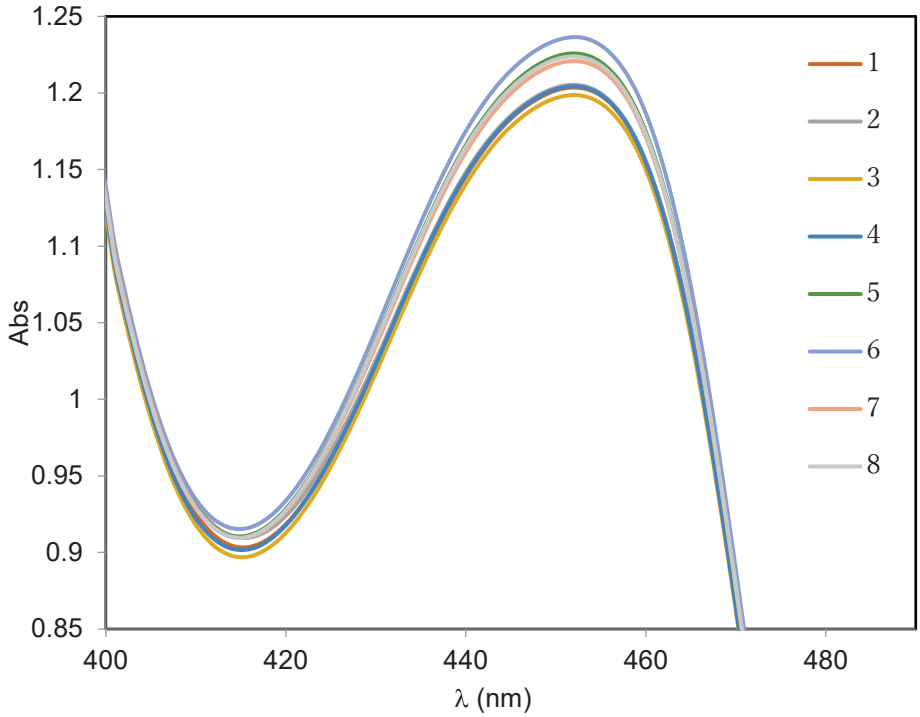


Figure S2. UV/Vis spectra of 2,4-dinitronaphthol in DMSO containing **DSATf 1c** and conjugate base: spectra 1–8 correspond to the conditions given in Table S2.

Table S2. Absorbance data for 2,4-dinitronaphthola (DNN)[a] in DMSO containing acid (**1c**) and anion[b] (**1c**$^-$) at 454 nm and 25°C.

Spectrum	[**1c**] (M)	[**1c**$^-$][b] (M)	*Abs*	[In$^-$]/[HIn][c]	K_{eq}[d]
1	2.8 x 10^{-3}	6.0 x 10^{-4}	1.203	0.42	1.97
2	2.5 x 10^{-3}	9.0 x 10^{-4}	1.205	0.46	1.29
3	2.2 x 10^{-3}	1.2 x 10^{-3}	1.199	0.31	0.57
4	1.9 x 10^{-3}	1.5 x 10^{-3}	1.204	0.44	0.55
5	1.6 x 10^{-3}	1.8 x 10^{-3}	1.221	1.02	0.90
6	1.3 x 10^{-3}	2.1 x 10^{-3}	1.224	1.18	0.73
7	1.0 x 10^{-3}	2.4 x 10^{-3}	1.226	1.29	0.54
8	7.0 x 10^{-4}	2.7 x 10^{-3}	1.237	2.25	0.58

[a] The concentration of 2,4-dinitronaphthol was 1.5 × 10^{-5} M. [b] Anion **1c**$^-$ was generated by addition of NaOH in water solution in DMSO such that the content of water was < 2 vol %. [c] The ratio of phenolate to phenol was obtained using the relationship [(*Abs* – 1.262)/(1.179 – *Abs*)]. [d] K_{eq} = ([**1c**]/[**1c**$^-$]) x ((*Abs* – Abs_{min})/(Abs_{max} – *Abs*)).

The pK_a value was calculated using equation eq 4: pK_a = 2.02 ± 0.25

Monosulfonamide 6

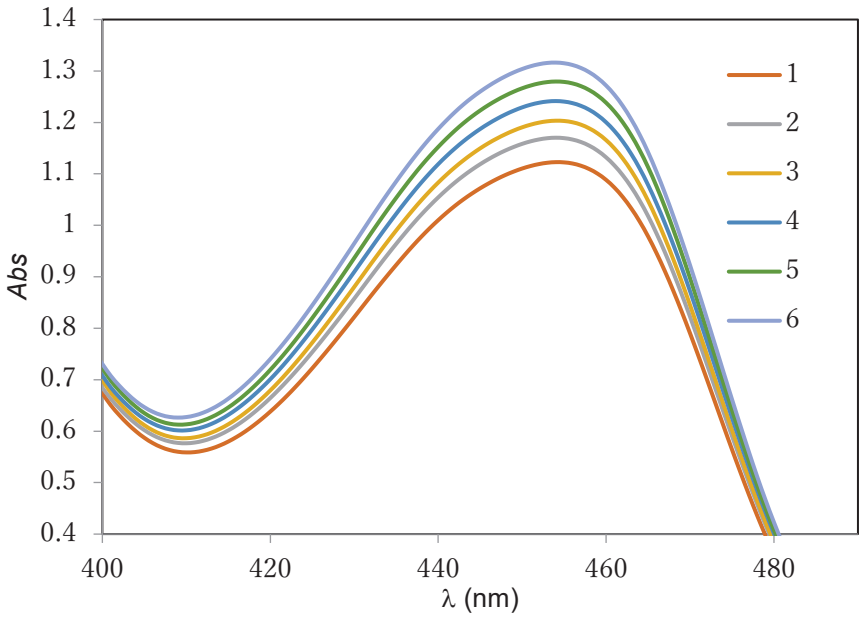


Figure S3. UV/Vis spectra of 2,4-dinitronaphthol in DMSO containing **6** and conjugate base: spectra 1–8 correspond to the conditions given in Table S3.

Table S3. Absorbance data for 2,4-dinitronaphthol (DNN)[a] in DMSO containing acid (**6**) and anion[b] (**6**$^-$) at 454 nm and 25°C.

Spectrum	[**6**] (M)	[**6**$^-$][b] (M)	*Abs*	[In$^-$]/[HIn][c]	K_{eq}[d]
1	9.2 x 10^{-3}	1.0 x 10^{-4}	1.123	1.44	13.2
2	8.7 x 10^{-3}	1.5 x 10^{-4}	1.170	1.93	11.1
3	8.2 x 10^{-3}	2.0 x 10^{-3}	1.203	2.40	9.78
4	7.7 x 10^{-3}	2.5 x 10^{-3}	1.242	3.18	9.76
5	7.2 x 10^{-3}	3.0 x 10^{-3}	1.280	4.41	10.5
6	6.7 x 10^{-4}	3.5 x 10^{-3}	1.316	6.57	12.5

[a] The concentration of 2,4-dinitronaphthol was 1.5 × 10^{-5} M. [b] Anion **6**$^-$ was generated by addition of NaOH in water solution in DMSO such that the content of water was < 2 vol %. [c] The ratio of phenolate to phenol was obtained using the relationship [(*Abs* – 1.408)/(0.712 – *Abs*)]. [d] K_{eq} = ([**6**]/[**6**$^-$]) x ((*Abs* – Abs_{min})/(Abs_{max} – *Abs*)).

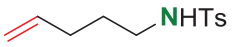
The pK_a value was calculated using equation eq 4: pK_a = 3.16 ± 0.07

2-8-3. General Information.

Internal references for ^{1}H NMR spectra were 0.0 ppm (Me_4Si) for $CDCl_3$ and CD_3OD (3.31 ppm). Chemical shifts for ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm) and CD_3OD (49.0 ppm). The chemical shift for ^{19}F NMR spectra was reported on the basis of CF_3CO_2H (-76.0 ppm) as an external standard. High resolution mass spectral (HRMS) data were recorded with an LTQ Orbitrap trap mass spectrometer using electrospray ionization (ESI) method. Optical rotations were measured on a digital polarimeter with a 0.1 dm cell at room temperature. All reactions involving air- and moisture-sensitive reagents were carried out under N_2. All reactions were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm).

2-8-4. Preparation of alkenyl amines and alcohols

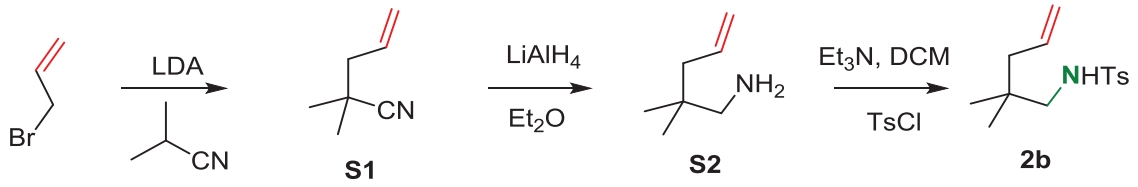
Preparation of 2a

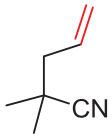


2a

A mixture of 5-bromo-1-pentene (0.80m, 6.75mmol), *p*-toluenesulfonamide (1.20 g, 7.01 mmol) and potassium carbonate (1.84 g, 13.3 mmol) was dissolved in acetone (7.0 ml) and stirred for 1 day at 40°C. The reaction mixture was cooled and passed through a pad of celite. The filtrate was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. The organic phase was washed with water and brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated under vacuum. The crude product was purified by column chromatography on silica gel (hexane: EtOAc= 5: 1) to give 4-methyl-*N*-(pent-4-en-1-yl) benzenesulfonamide **2a**[71] (1.20 g, 75%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.53 (m, 2H), 7.31 (d, J = 7.9 Hz, 2H), 5.70 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.08–4.84 (m, 2H), 4.59 (s, 1H), 2.95 (dd, J = 13.5, 6.9 Hz, 2H), 2.43 (s, 3H), 2.04 (td, J = 7.0, 1.2 Hz, 2H), 1.62–1.45 (m, 2H).

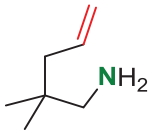
Preparation of 2b





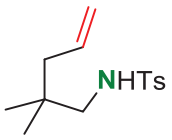
S1

A mixture of diisopylamine (3.4 ml, 24.0 mmol) in THF (32 mL) was added n-BuLi (13 ml, 16.7 mmol) at 0°C and stirred at 0°C for 30 min and then added isobutyronitrile (1.5 ml, 16.7 mmol) to this mixture at -78°C and stirred for 1 h. Next, allyl bromide (2.5 ml, 28.9 mmol) was also added to this mixture at -78°C and stirred at room temperature overnight. The reaction mixture was added to saturated NH_4Cl and extracted by diethyl ether. The organic layer was washed by water, brine, and dried over Na_2SO_4. The reaction mixture was evaporated to obtain the crude **S1** (2.55 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (m,1 H), 5.22 (dt, *J* = 1.0, 10 Hz, 1 H), 5.18 (dt, J = 1.0, 17.0 Hz, 1 H), 2.28 (dd, J = 1.0, 7.4 Hz, 2 H), 1.34 (s, 6 H).



S2

S1 (crude, 2.55 g) was dissolved in dry diethyl ether (20 ml), and then added lithium aluminum hydride (1.86 g, 49.1 mmol) at 0°C and refluxed for 2 h. The reaction mixture was added to water and filtered. The filtrate was extracted by diethyl ether. The organic layer was dried over Na_2SO_4. The reaction mixture was evaporated to obtain **S2** (1.62 g, 0.014 mmol, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77-5.86 (m, 1 H), 5.00-5.04 (m, 2 H), 2.45 (s, 2 H), 1.96 (d, *J* = 7.6 Hz, 2 H), 0.88 (s, 6 H).

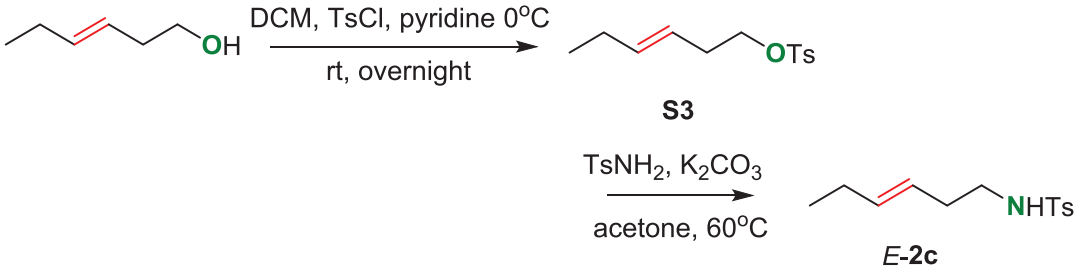


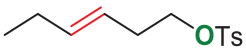
2b

S2 (1.62 g, 14.3 mmol) and triethylamine (4.0 ml, 28.7 mmol) were dissolved in CH_2Cl_2 (30 ml). To the reaction mixture was added TsCl (2.74 g, 14.4 mmol) at 0°C, and stirred at room

temperature for 7 h. The reaction mixture was washed by saturated $NaHCO_3$, saturated NaCl and dried over Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (hexane: EtOAc= 5: 1) to give **2b**[72] (2.72 g, 10.2 mmol, 60%) as yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 5.68-5.77 (m,1 H), 4.98-5.04 (m, 2 H), 4.45 (t, *J* = 6.8 Hz, 1 H), 2.68 (d, *J* = 7.1 Hz, 2 H), 2.43 (s, 3 H), 1.96 (d, *J* = 7.6 Hz, 2 H), 0.86 (s, 6 H).

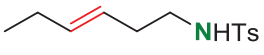
Preparation of *E*-2c





S3

p-toluenesulfonyl chloride (4.51 g, 0.024 mmol) and pyridine (2.6 mL) were added to a solution of (*E*)-hex-3-en-1-ol (1.57 g, 0.016 mmol) in CH_2Cl_2 (26 mL) at 0°C. The reaction was warmed up to room temperature and stirred overnight. The reaction was diluted with ether and washed with water, 1 M HCl, saturated $NaHCO_3$, and brine. The organic extracts were combined, dried over Na_2SO_4, filtered, and concentrated under vacumn to afford a yellow oil. The crude product was purified by column chromatography (Hexane: AcOEt= 5: 1) to give the desired product (3.39 g, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.72 (m, 2H), 97.34 (d, *J* = 8.0 Hz, 2H), 5.57 – 5.43 (m, 1H), 5.23 (dtt, *J* = 15.2, 6.8, 1.5 Hz, 1H), 4.01 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 2.33 (qd, *J* = 6.8, 1.1 Hz, 2H), 1.96 (qdd, *J* = 7.5, 6.4, 1.3 Hz, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).

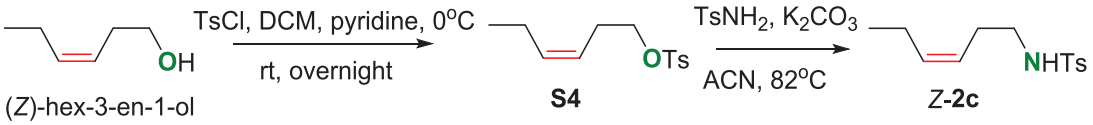


E-**2c**

To a solution of *p*-toluenesulfonamide (4.57 g, 0.027 mmol) in acetone (14 mL), (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate (3.4 g, 0.013 mmol) and K_2CO_3 (3.7 g, 0.027 mmol) were added. The reaction mixture was refluxed at 60°C for 2 days. The reaction mixture was quenched with saturated NH_4Cl and the mixture was extracted with Et_2O. The organic phase was washed with brine, dried over $NaSO_4$, and filtered. The filtrate was concentrated under vacumn. The crude

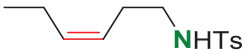
residue was purified by column chromatography (Hexane: AcOEt= 2: 1) to afford the desired product *E*-**2c**[73] (2.28 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.70 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.55–5.42 (m, 1H), 5.25–5.06 (m, 1H), 4.37 (s, 1H), 2.97 (q, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 2.13 (qd, *J* = 6.7, 1.0 Hz, 2H), 2.08–1.89 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).

Preparation fo *Z*-2c



S4

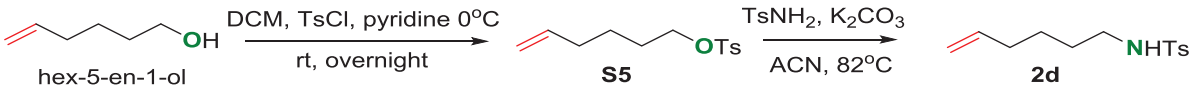
p-toluenesulfonyl chloride (4.47 g, 0.023 mol) and pyridine (2.5 mL) were added to a solution of (*Z*)-hex-3-en-1-ol (1.55 g, 0.015 mol) in CH_2Cl_2 (25 mL) at 0°C. The reaction was warmed up to room temperature and stirred overnight. The reaction was diluted with ether and washed with water, 1 M HCl, saturated $NaHCO_3$, and brine. The organic extracts were combined and dried over $NaSO_4$, filtered, and concentrated under vacumn to afford a yellow oil. The crude product was purified by column chromatography (Hexane: AcOEt= 5: 1) to give the desired product (3.4 g, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.46–7.29 (m, 2H), 5.63–5.35 (m, 1H), 5.29–5.04 (m, 1H), 4.00 (t, *J* = 7.0 Hz, 2H), 2.66–2.23 (m, 5H), 2.13–1.84 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).

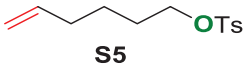


***Z*-2c**

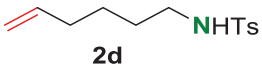
To a solution of *p*-toluenesulfonylamide (3.56 g, 0.02 mol) in acetonitrile (14 mL), (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate (3.4 g, 0.013 mol) and K_2CO_3 (3.59 mg, 0.026 mmol) were added. The reaction mixture was refluxed at 82°C for 20 h. The reaction mixture was quenched with saturated NH_4Cl and extracted with Et_2O. The organic phase was washed with brine, dried over $NaSO_4$, and filtered. The filtrate was concentrated under vacumn. The crude residue was purified by column chromatography (Hexane: AcOEt= 2: 1) to afford the desired product *Z*-**2c**[73] (2.7 g, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.70 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.47 (dt, *J* = 10.7, 7.3 Hz, 1H), 5.21–5.06 (m, 1H), 4.82 (s, 1H), 2.95 (q, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 2.20 (q, *J* = 7.0 Hz, 2H), 2.03–1.86 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H).

Preparation fo 2d

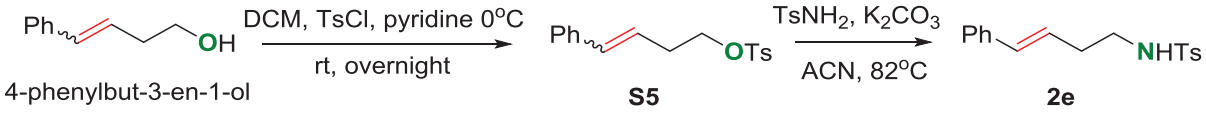


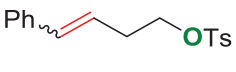


p-toluenesulfonyl chloride (4.42 g, 0.023 mol) and pyridine (2.5 mL) were added to a solution of hex-5-en-1-ol (1.52 g, 0.015 mol) in CH_2Cl_2 (2.5 mL) at 0°C. The reaction was warmed up to room temperature and stirred overnight. The reaction was diluted with ether and washed with water, 1 M HCl, saturated $NaHCO_3$, and brine. The organic extracts were combined and dried, filtered, and concentrated under vacumn to afford a yellow oil. The crude product was purified by column chromatography (Hexane: AcOEt= 5: 1) to give the desired product (3.2 g, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.74 (m, 2H), 7.40–7.30 (m, 2H), 5.72 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.03–4.86 (m, 2H), 4.03 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H), 2.09–1.91 (m, 2H), 1.72–1.58 (m, 2H), 1.49–1.30 (m, 2H).



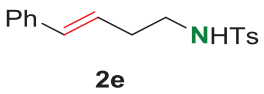
To a solution of *p*-toluenesulfonamide (3.28 g, 0.019 mol) in acetonitrile (13 mL), (*E*)-hex-3-en-1-yl 4-methylbenzenesulfonate (3.24 g, 0.013 mol) and K_2CO_3 (3.57 g,0.026 mol) were added. The reaction mixture was refluxed at 82°C for 12 h. The reaction mixture was quenched with saturated NH_4Cl and the mixture was extracted with Et_2O. The organic phase was washed with brine, dried over $NaSO_4$, and filtered. The filtrate was concentrated under vacumn. The crude residue was purified by column chromatography (Hexane: AcOEt= 20: 1) to afford the desired product **2d**[71] (2.9 g, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.71 (m, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.71 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.94 (ddt, J = 6.0, 2.0, 1.3 Hz, 2H), 4.53 (s, 1H), 2.93 (dd, J = 13.4, 6.7 Hz, 2H), 2.43 (s, 3H), 2.12–1.86 (m, 2H), 1.57–1.23 (m, 4H).





p-toluenesulfonyl chloride (0.29 g, 0.0015 mol) and pyridine (0.17 mL, 0.0021 mol) were added to a solution of 4-phenylbut-3-en-1-ol (1.55 g, 0.001 mol) in CH_2Cl_2 (1.7 mL) at 0°C. The

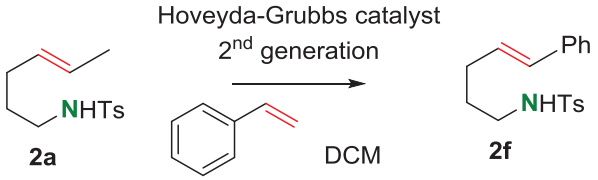
reaction was warmed up to room temperature and stirred overnight. The reaction was diluted with ether and washed with water, 1 M HCl, saturated $NaHCO_3$, and brine. The organic extracts were combined and dried, filtered, and concentrated under vacumn to afford a yellow oil. The crude product was purified by column chromatography (Hexane: AcOEt= 10: 1) to give the mixture of inseparable *Z* and *E* isomers (0.23 g, 76%) as a colorless oil **S5** (*E*: *Z*= 5.3: 1) 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.74 (m, 2H), 7.35–7.24 (m, 7H), 6.39 (d, *J* = 15.9 Hz, 1H), 5.99 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.13 (dd, *J* = 10.8, 4.2 Hz, 2H), 2.60–2.40 (m, 5H).



2e

To a solution of *p*-toluenesulfonamide (3.28 g, 0.019 mol) in acetonitrile (0.75 mL), hex-3-en-1-yl 4-methylbenzenesulfonate (230 mg, 0.76 mol) and K_2CO_3 (210 mg, 1.51 mol) were added. The reaction mixture was refluxed at 82°C for 12 h. The reaction mixture was quenched with saturated NH_4Cl and extracted with Et_2O. The organic phase was washed with brine, dried over $NaSO_4$, and filtered. The filtrate was concentrated under vacumn. The crude residue was purified by column chromatography (Hexane: AcOEt= 5: 1) to afford the mixture of inseparable *Z* and *E* isomers **2e**[74] (*E*: *Z*= 5.3: 1) (0.15 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 20.9, 8.3 Hz, 2H), 7.34–7.25 (m, 7H), 6.36 (d, *J* = 15.9 Hz, 1H), 5.97 (dt, *J* = 15.9, 7.1 Hz, 1H), 3.11 (dd, *J* = 12.9, 6.5 Hz, 2H), 2.44–2.31 (m, 5H).

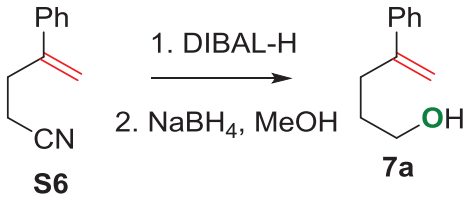
Preparation of 2f



2a **2f**

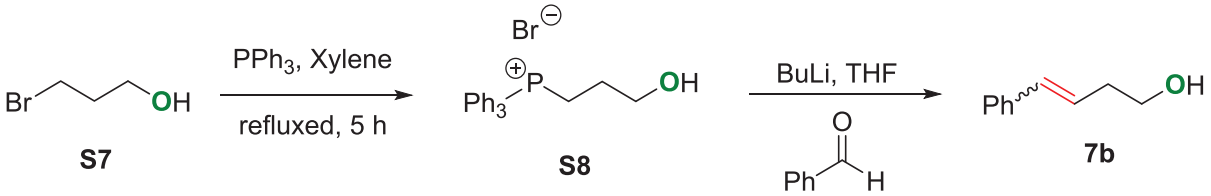
A mixture of **2a** (51.0 mg, 0.23 mmol), Hoveyda-Grubbs catalyst 2nd generation (20.0 mg, 24.3 mmol), CH_2Cl_2 (4.0 ml) and styrene (90 µl, 0.78 mmol) was refluxed for 15 h. The reaction mixture was evaporated to obtain the crude product. The crude product was purified by column chromatography on silica gel (CH_2Cl_2) and GPC machine to give **2f**[75] (36.6 mg, 51%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.26 (dt, *J* = 17.0, 10.3 Hz, 1H), 5.99 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.67–5.45 (m, 1H), 5.09 (d, *J* = 17.0 Hz, 1H), 4.98 (d, *J* = 10.1 Hz, 1H), 4.40 (s, 1H), 2.95 (dd, *J* = 13.5, 6.7 Hz, 2H), 2.43 (s, 3H), 2.08 (dd, *J* = 14.8, 7.7 Hz, 2H), 1.71–1.40 (m, 2H).

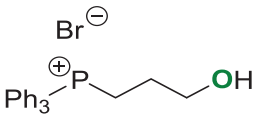
Preparation of 7a



3-Phenyl-3-butenyl-1-cyanide **S6** was prepared according to known procedure[76]. Diisobutylaluminum hydride (DIBAL-H) (1.0 M in hexane, 2.4 ml, 2.4 mmol) was added dropwise to **S6** (240 mg, 1.5 mmol) in CH_2Cl_2 (4.4 ml) at -78°C. After the reaction mixture was stirred at the temperature for 2 h, the mixture was quenched by saturated NH_4Cl at -78°C. The reaction mixture was extracted with EtOAc, dried over Na_2SO_4, filtered, and concentrated in vacuo. $NaBH_4$ (66.0 mg, 1.7 mmol) was added slowly to the obtained crude product in MeOH (4.4 ml) at r.t., and the reaction mixture was stirred overnight. The mixture was quenched by saturated NH_4Cl, extracted with EtOAc, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, EtOAc: hexane= 15: 1) to give **7a**[77] (50 mg, 20 % for 2 steps) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.26 (m, 5H), 5.30 (d, *J* = 1.4 Hz, 1H), 5.10 (d, *J* = 1.4 Hz, 1H), 3.83–3.55 (m, 2H), 2.67–2.55 (m, 2H), 1.73 (ddd, *J* = 13.9, 10.3, 6.5 Hz, 2H).

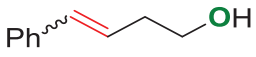
Preparation of 7b





S8

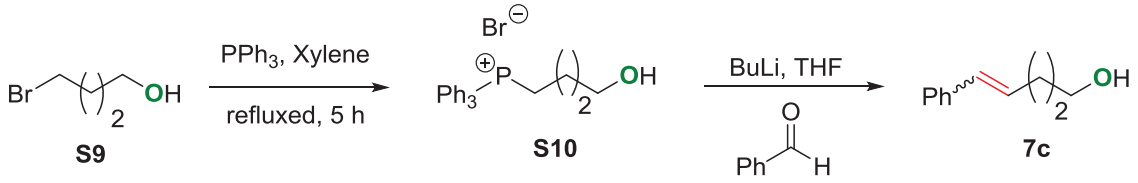
Under nitrogen atmosphere, the solution of triphenylphosphine (6.21 g, 23.67 mmol), 3-bromopropane-1-ol (3.27 g, 23.6 mg) in xylene (21 mL) was stirred under reflux for 5 h. Then the reaction mixture was cooled to room temperature and ether was added. The solids were collected by filtration and evaporated under vacuum to afford the desired product **S8** (8.99 g, 96%) as a white powder which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.65 (m, 15H), 3.92–3.71 (m, 4H), 1.90 – 1.79 (m, 2H).



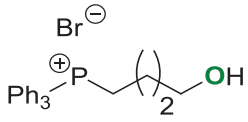
7b

n-BuLi (4.5 mL, 10.35 mmol) was added dropwise to a suspension of (3-propan-1-ol) triphenylphosphonium bromide (1.58 g, 6.71 mmol) in THF (12 mL) at -78°C. The mixture reaction was stirred at -78°C for 1 h and then benzaldehyde (0.3 mL, 7 mmol) was added dropwise at -78°C and stirred at -78°C for 2 hours. The mixture was warmed up to room temperature and stirred overnight at r.t, and then saturated NH_4Cl solution was added. This reaction mixture was extracted with EtOAc, dried over sodium sulfate, and concentrated. The crude product was purified by column chromatography (Hexene: AcOEt= 5: 1) and GPC machine to give a colorless oil of the mixture of inseparable *Z* and *E* isomers **7b**[78] (220 mg, 34%) *(E*: *Z*= 5.3: 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.21 (m, 5H), 6.59 (d, *J* = 11.7 Hz, 1H, *cis* isomer), 6.50 (d, *J* = 15.9 Hz, 1H, *trans* isomer), 6.21 (dt, *J* = 15.8, 7.1 Hz, 1H, *trans* isomer), 5.69 (dt, *J* = 11.7, 7.4 Hz, 1H *cis* isomer), 3.85–3.60 (m, 1H *cis* isomer and 2H *trans* isomer), 2.62 (ddd, *J* = 13.9, 6.5, 1.8 Hz, 1H *cis* isomer), 2.59–2.36 (m, 2H).

Preparation of 7c

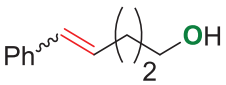


S9 **S10** **7c**



S10

Under nitrogen atmosphere, the solution of triphenylphosphine (3.41 g, 0.013 mol), 3-bromopropane-1-ol (2.08 g, 0.014 mol) in xylene (21 mL) was stirred under reflux for 5 h. Then, the reaction mixture was cooled to room temperature and ether was added. The solids were collected by filtration and dried under vacuum to afford the crude product **S10** (4.5 g, 83%) as a white powder which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.37 (m, 15H), 4.14–3.37 (m, 4H), 2.19 (d, *J* = 117.7 Hz, 4H).



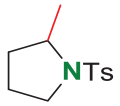
7c

n-BuLi (9 mL, 20.7 mmol) was added dropwise to a suspension of (4-butan-1-ol) triphenylphosphonium bromide (3 g, 7 mmol) in THF at -78°C. The reaction mixture was stirred

at -78°C for 1 h and benzaldehyde (0.8 mL, 8 mmol) was added dropwise. After 2 h, the mixture was warmed up to room temperature and stirred overnight at r.t, and then saturated NH_4Cl solution was added. This mixture was extracted with EtOAc, dried over sodium sulfate and concentrated. The crude product was purified by column chromatography (Hexene: AcOEt= 5: 1) and GPC machine to give a colorless oil of the mixture of inseparable *Z* and *E* isomers **7c**[79] (30 mg, 2.6 %) (*E*: *Z* = 22: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.23 (m, 5H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.71 (t, *J* = 6.5 Hz, 2H), 2.42–2.19 (m, 2H), 1.82–1.67 (m, 2H).

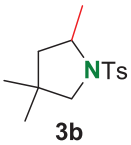
2-8-5. Typical procedure for hydrofunctionalization

Alkenyl amine 4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide **2a** (41.0 mg, 0.17 mmol) was charged in a crew-cap vial equipped with a stir bar. A solution of **DSATf 1c** (37.7 mg, 34 mmol) in HFIP (0.17 ml) was added and the tube was sealed. The reaction mixture was stirred at 60°C and the progress of the reaction was monitored by thin layer chromatography. After the starting material was consumed, the reaction was quenched with solid $NaHCO_3$ and filtered. The filtrate was evaporated and the crude product was purified by column chromatography (SiO_2, EtOAc: hexane= 15: 1) to give the hydrofunctionalization product **3a** (30 mg, 73%).



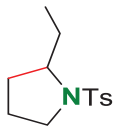
3a

3a[8]: 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.80–3.59 (m, 1H), 3.51–3.35 (m, 1H), 3.15 (dt, *J* = 10.1, 7.2 Hz, 1H), 2.43 (s, 3H), 1.89–1.75 (m, 1H), 1.75–1.63 (m, 1H), 1.58–1.42 (m, 2H), 1.31 (d, *J* = 6.4 Hz, 3H).



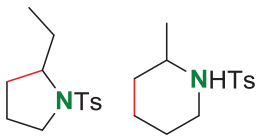
3b

3b[80]: 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.69 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 3.65 (ddq, *J* = 12.4, 8.5, 6.2 Hz, 1H), 3.17 (d, *J* = 10.4 Hz, 1H), 3.07 (dd, *J* = 10.3, 1.2 Hz, 1H), 2.43 (s, 3H), 1.73 (ddd, *J* = 12.5, 7.2, 1.2 Hz, 1H), 1.57 (s, 1H), 1.41 (d, *J* = 6.1 Hz, 3H), 1.04 (s, 3H), 0.55 (s, 3H).



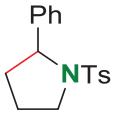
3c

3c[81]: 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.69 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 3.54 (dt, *J* = 10.4, 5.8 Hz, 1H), 3.38 (ddd, *J* = 10.4, 7.0, 5.1 Hz, 1H), 3.19 (dt, *J* = 10.4, 7.2 Hz, 1H), 2.43 (s, 3H), 1.93–1.68 (m, 2H), 1.55–1.43 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 3H).



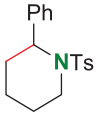
3c **4c**

A mixture of **3c** and **4c**[82]: **3c**: 83% yield, **4c**: 2% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.23 (s, **4c**-1H), 3.70 (d, J = 13.3 Hz, **4c**-1H), 3.54 (td, *J* = 10.2, 5.7 Hz, 1H), 3.38 (ddd, *J* = 10.5, 7.0, 5.2 Hz, 1H), 3.19 (dt, *J* = 10.4, 7.2 Hz, 1H), 3.03–2.92 (m, **4c**-1H), 2.43 (s, 3H), 1.94–1.69 (m, 2H), 1.67–1.46 (m, 4H), 1.07 (d, *J* = 6.9 Hz, **4c**-3H), 0.91 (t, *J* = 7.5 Hz, 3H).



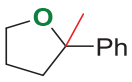
3f

3f[83]: 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.40–7.20 (m, 7H), 4.79 (dd, *J* = 7.9, 3.6 Hz, 1H), 3.62 (ddd, *J* = 9.8, 7.1, 4.9 Hz, 1H), 3.43 (dt, *J* = 10.2, 7.2 Hz, 1H), 2.43 (s, 3H), 2.10–1.91 (m, 1H), 1.93–1.74 (m, 2H), 1.73–1.57 (m, 1H).



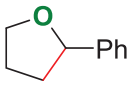
4e

4e[8]: 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.40–7.24 (m, 7H), 5.29 (d, *J* = 3.9 Hz, 1H), 3.86 (d, *J* = 14.3 Hz, 1H), 3.13–2.94 (m, 1H), 2.46 (s, 3H), 2.24 (d, *J* = 13.0 Hz, 1H), 1.77–1.24 (m, 5H).



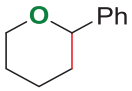
8a

8a[84]: 78 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.18 (m, 5H), 4.07–3.96 (m, 1H), 3.96–3.84 (m, 1H), 2.26–2.13 (m, 1H), 1.98 (tdt, *J* = 10.7, 7.9, 6.7 Hz, 2H), 1.87–1.72 (m, 1H), 1.52 (s, 3H).



8b

8b[85]: 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.22 (m, 5H), 4.92 (t, *J* = 7.2 Hz, 1H), 4.16 (ddd, *J* = 14.9, 14.1, 6.7 Hz, 1H), 3.97 (td, *J* = 7.8, 6.6 Hz, 1H), 2.45–2.25 (m, 1H), 2.12–1.93 (m, 2H), 1.84 (ddd, *J* = 16.0, 12.1, 7.6 Hz, 1H).



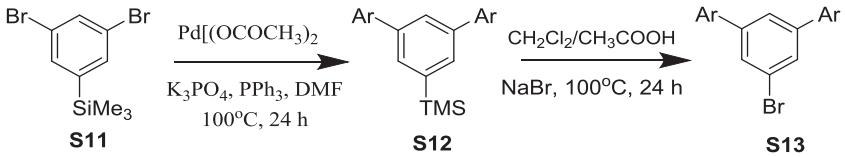
9c

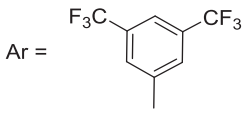
9c[86]: 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.16 (m, 5H), 4.40–4.24 (m, 1H), 4.23–4.04 (m, 1H), 3.61 (ddd, *J* = 11.5, 5.3, 2.5 Hz, 1H), 2.03–1.59 (m, 5H).

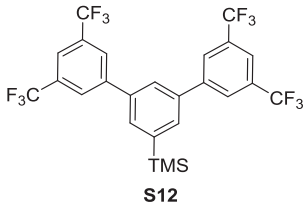
2-8-6. The typical procedure for the synthesis of the catalyst DSATf

According to the literature procedure, the corresponding sulfonyl chloride was prepared by *N*-chlorosuccinimide (NCS) and the corresponding thiocarbamoyl derivative (for **1a**)[56] or thionyl chloride and the corresponding sulfuric acid derivative (for **1b-e**)[36].

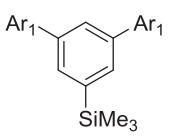
2-8-6-1. Preparation of Ar substituent





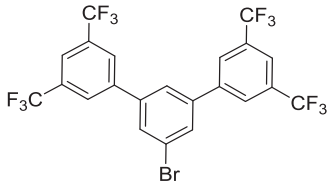


3,5-bis (3,5 - di (3,5 - trifluoromethyl phenyl) -1-trimethyl silyl benzene[87]



3,5-dibromo trisilyl benzene (3.1151 g, 10.1 mmol), PPh_3 (516.7 mg,1.97 mmol), K_3PO_4 (6.8315 g, 32.2 mmol), Ar-OH (6.4712 g, 25.1 mmol), $Pd(OCOCH_3)_2$ (197.2 mg, 0.878 mmol) were mixed in DMF. The mixture was stirred at 100°C for 15 h under a nitrogen atmosphere, cooled to room temperature, quenched with saturated NH_4Cl, and extracted with EtOAc. The organic layer was washed with brine and

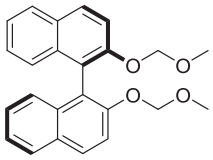
dried with Na_2SO_4. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane) to give 3,5-bis (3,5 - di (3,5 - trifluoromethyl phenyl) -1-trimethyl silyl benzene as a white solid (54% yield). R_f = 0.63 (hexane), ^{1}H NMR (500MHz, $CDCl_3$) δ 8.03 (s, 4H), 7.92 (s, 2H), 7.74 (d, *J*= 1.8 Hz, 2H), 7.69 (t, *J* = 1.8 Hz, 1H), 0.40 (s, 9H)



S13

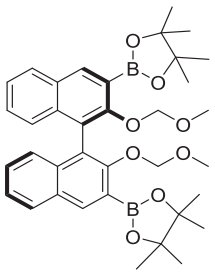
S12 (999.2 mg, 1.74 mmol) in CH_2Cl_2/CH_3COOH = 6/1 (4.1 ml) was added NaBr (663.4 mg, 6.45 mmol), *N*-bromosuccinimide (819.1 mg, 4.60 mmol) at room temperature. The mixture was stirred at 100 °C for 25 h, quenched with saturated $NaHSO_3$ and extracted with Et_2O. The organic layer was washed with brine and dried with Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by recrystallization (hexane) to give the product (384.3 mg, 38%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 4H), 7.94 (s, 2H), 7.81 (d, *J* = 1.6 Hz, 2H), 7.67 (t, *J* = 1.8 Hz, 1H), ^{13}C NMR ($CDCl_3$, 101 MHz) δ 141.4, 141.3, 132.6 (q, *J* = 33.6 Hz), 130.7, 127.5 (q, *J* = 3.5 Hz), 125.0, 124.2, 123.1 (q, *J* = 272.4 Hz), 122.1 (q, *J* = 3.9 Hz), ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.8, HRMS (APCI–) *m*/*z* calcd for $C_{22}H_9F_{12}BrCl[M+Cl]^-$ 614.93900, found 614.93964, m.p. 98-99°C.

2-8-6-2. Preparation of DSATf



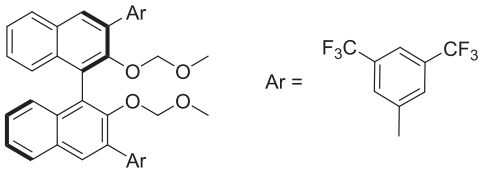
2

(*R*)-Binaphthol (5 g, 17 mmol) in dry THF (70 ml) was added to the mixture of NaH (1.7 g, 68 mmol) was mixed in dry THF (100 ml) at 0°C under an N_2 atmosphere. After the addition, the mixture was warmed up to room temperature for 1 h. After the mixture was cooled to 0°C, chloromethyl methyl ether was slowly added. Then, the mixture was warmed up to room temperature for 3 h. Water was added to the flask, then extracted by EtOAc, washed with brine, dried over Na_2SO_4, and concentrated. The crude product was used for the next step (7 g, 107 %). R_f=0.46 (hexane: EtOAc= 3: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*=9.0 Hz, 2H), 7.87 (d, *J*=8.1 Hz, 2H), 7.58 (d, *J*= 9.0 Hz, 2H), 7.34 (t, *J*=8.0Hz, 2H), 7.28-7.18 (m, 4H), 5.08 (dd, *J*=6.8Hz, 4H), 3.14 (s, 6H).



3

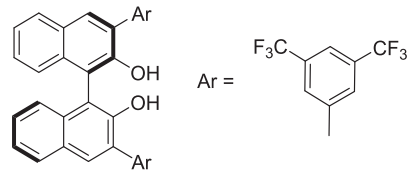
n-BuLi (27.3 ml, 73.4 mmol) was added to **2** in dry THF (150 ml) at 0°C under nitrogen. This mixture was kept at room temperature for 3h, then the mixture was cooled to -78°C, and i-PrOBPin (20 ml, 98 mmol) was added slowly to the mixture at -78°C and then kept at room temperature overnight. The reaction mixture was cooled to 0°C, and then 1N HCl was added for 1 h, extracted with EtOAc, washed with brine, and dried over $MgSO_4$. The crude product was recrystallized by hexane to give the product (9.5 g, 93%). R_f= 0.3 (hexane: EtOAc= 3: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 2H), 7.89 (d, *J*=8.1Hz, 2H), 7.36 (t, *J*=7.4Hz, 2 H), 7.25 (d, *J*=9.1Hz, H), 7.18 (d, *J*=8.5Hz, 2H), 4.39-4.8 (m, 4H), 2.28 (s, 6H), 1.38 (s, 24H).



4

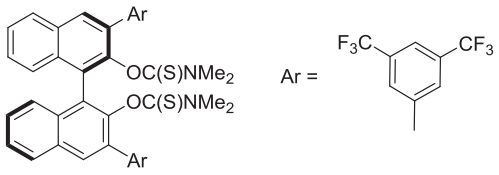
(*R*)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl-3,3'-bis(boronic acid pinacol ester) (161.2 mg, 0.257 mmol), 3,5 - bis (3,5 - di (3,5 - trifluoromethyl phenyl) -1-bromo benzene **3** (308.5 mg, 0.53 mmol), barium hydroxide deoctahydrate (285.4 mg, 0.91 mmol), Tetrakis(triphenylphosphine)palladium(0) (23.8 mg, 0.0201 mmol) were mixed in dioxane/H_2O= 5/1 (4.2 ml). The mixture was stirred at 100°C for 22 h under nitrogen atmosphere, cooled to room temperature, quenched with 1M HCl. The reaction mixture was extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane: benzene= 4: 1) to give (*R*)-3,3'-bis(3,5-di(3,5-trifluoromethylphenyl)phenyl)-2,2'-dimethoxymethoxy-1,1'-binaphthalene **4** (75% yield) as a white solid. R_f = 0.30 (hexane: benzene= 3: 1), ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.14 (s, 10H), 8.09 (d, *J* = 1.7 Hz, 4H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.96 (s, 4H), 7.79 (t, *J* = 1.7 Hz, 2H), 7.50 – 7.54 (m, 2H), 7.38 – 7.39 (m, 4H), 4.48 4.59 (d, AB, J_{AB} = 5.6 Hz, 4H), 2.58 (s, 6H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151, 143, 141, 140, 134, 133 x 2, 132 x 2, 131 x 2, 129, 128 x 2, 127 x 3, 126 x 2, 125 x 2, 122 x 3, 120, 99, ^{19}F NMR($CDCl_3$, 376 MHz) δ -62.78, HRMS(ESI-MS(FTMS, Positive)), m/z calcd for

$C_{68}H_{38}F_{24}O_4$[M+Na]$^+$1397.24 Found 1397.22754, $[\alpha]_D^{25}$ (*c* 7.01, $CHCl_3$) -5.4, m.p 132-133^{o}C.



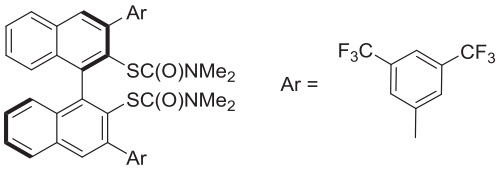
5

To a side-arm flask containing (*R*)-3,3'-bis(3,5-di(3,5-trifluoromethylphenyl)phenyl)-2,2'-dimethoxymethoxy-1,1'-binaphthalene **4** (257.6 mg, 0.19 mmol) in CH_2Cl_2 (0.40 ml) was added trifluoroacetate (0.15 ml, 1.94 mmol) at 0^{o}C. After stirred 3 h, saturated $NaHCO_3$ was added and then extracted with CH_2Cl_2. The organic layer was washed with brine and dried with Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (hexane: benzene= 3: 1) to give (*R*)-3,3'-bis(3,5-di(3,5-trifluoromethylphenyl)phenyl)-1,1'-binaphthalene -2,2'-diol (83% yield) as a white solid. R_f= 0.30 (hexane: benzene= 3: 1), ^{1}H NMR (400MHz,$CDCl_3$) δ 8.19 (s, 2H), 8.11 (s, 8H), 8.01-8.05 (m, 6H), 7.93 (s, 4H), 7.78 (t, *J* = 1.8 Hz, 2H), 7.30 - 7.49 (m, 4H) 7.26 – 7.30 (m, 2H), 5.45 (s, 2H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150, 143, 140, 133 x 3, 132 x 3, 130, 129 x 2, 128 x 3, 126, 125 x 2, 124, 122 x 3, ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.70, HRMS(ESI-MS(FTMS, Negative)), m/z calcd for $C_{64}H_{30}F_{24}O_2$[M-H]$^-$1258.19 Found 1285.17700, $[\alpha]_D^{25}$ (*c* 9.23, $CHCl_3$) + 0.35, m.p 158-159^{o}C.



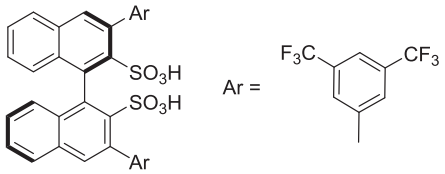
6

NaH (198.1 mg, 4.95 mmol) was added to a solution of (*R*)-3,3'-bis (3,5-di(3,5-trifluoromethylphenyl)phenyl)-1,1'-binaphthalene -2,2'-diol **5** (1.23 g, 0.96 mmol) in THF (10.6 mL) at 0°C and stirred for 1 h at the temperature. To this solution, was added *N*, *N*-dimethylthiocarbamoylchloride (482.2 mg, 3.90 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (137.7 mg, 1.23 mmol). The reaction mixture was heated at 60°C for 15 h, then cooled to room temperature, quenched with 2% KOH solution, and extracted by EtOAc. The combined organic layer was washed with brine, and dried with Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (SiO_2, hexane: EtOAc= 8: 1) to give the product **6** (1.40 g) quantitatively as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-7.31 (m, 28H), 2.99-1.99 (m, 12H), ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8; HRMS (ESI+) *m*/*z* calcd for $C_{70}H_{40}F_{25}N_2O_2S_2$ [M+H]$^+$ 1461.22207, found 1461.22314, $[\alpha]_D^{25}$ (*c* 0.31, $CHCl_3$) –8.5, m.p. 129-130°C.



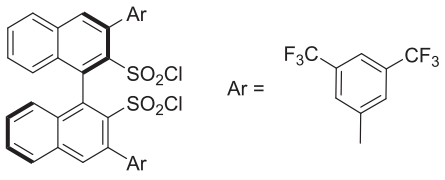
7

(*R*)-O,O'-(3,3'-bis(3,3",5,5"-tetrakis(trifluoromethyl)-[1,1':3',1"-terphenyl]-5'-yl)-[1,1'-binaphthalene]-2,2'-diyl) bis(dimethylcarbamothioate) **6** (1.37 g, 0.94 mmol) was placed into a round flask and heated to 230°C for 8 h under N_2 atmosphere. The resulting crude product was purified by column chromatography (SiO_2, hexane: CH_2Cl_2= 1: 1) to give the product **7** (875.3 mg, 64% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 10H), 7.99-7.91 (m, 10H), 7.76 (s, 2H), 7.58-7.52 (m, 2H), 7.33 (s, 4H), 2.45 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 145.0, 144.1, 143.0, 142.8, 138.6, 133.6, 132.8, 132.4 (q, J = 33.4 Hz), 129.8, 129.6, 127.8, 127.7, 127.5, 126.9, 124.6, 123.3 (q, J = 272.7 Hz), 121.4, 36.6, ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.7, HRMS (ESI+) m/z calcd for $C_{70}H_{40}F_{24}N_2O_2S_2Na$ $[M+Na]^+$ 1483.20402, found 1483.20288, $[\alpha]_D^{25}$ (*c* 6.53, $CHCl_3$) −5.6, m.p. 127-128°C.



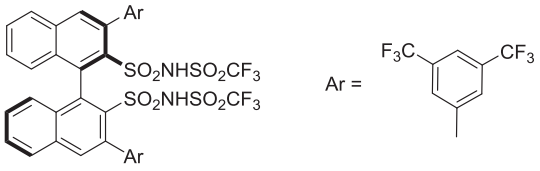
8

A performic acid solution was prepared by mixing and stirring 30 % H_2O_2 (3.0 mL, 32.0 mmol) and formic acid (17 ml, 447.0 mmol) at 0°C for 1 h. To this solution was added dropwise a solution of **7** (736.4 mg, 0.51 mmol) in (8.0 ml) at 0°C. After stirring for 12 h at 0°C to room temperature, the reaction mixture was extracted by CH_2Cl_2, washed with brine, dried with Na_2SO_4, and evaporated. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2: MeOH= 20: 1). The resultant solid was dissolved in CH_2Cl_2 and washed with 1N HCl. Remaining water traces were removed by azeotropic distillation with benzene to give the product **8** (519.2 mg, 72% yield) as a white solid. ^{1}H NMR (400 MHz, CD_3OD) δ 8.40 (s, 10H), 8.13-7.94 (m, 12H), 7.54 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), ^{13}C NMR (101 MHz, CD_3OD) δ 146.4, 145.1, 139.6, 139.0, 138.6, 138.4, 134.4, 133.3 (q, J = 32.8 Hz), 132.6, 131.3, 129.1, 128.8, 128.6, 128.0, 125.7, 125.1 (q, J= 274.9 Hz), 121.9, ^{19}F NMR (376 MHz, $CDCl_3$) δ −64.1, HRMS(ESI−) calcd for $C_{64}H_{28}F_{24}O_6S_2$ $[M-2H]^{2-}$ 706.04775, found 706.04742.



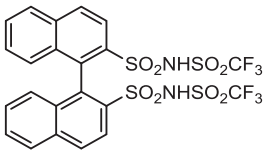
9

To a solution of (*R*)-3,3'-bis(3,3",5,5"-tetrakis(trifluoromethyl)-[1,1':3',1"-terphenyl]-5'-yl)-[1,1'-binaphthalene]-2,2'-disulfonic acid **8** (471.3 mg, 0.33 mmol) in $SOCl_2$ (0.4 ml) was added several drops of dry DMF. After the mixture was refluxed for 2 h, $SOCl_2$ was removed under reduced pressure. The resulting crude product was purified by column chromatography (SiO_2, hexane: EtOAc= 8: 1) to give the product **9** (426.2 mg, 89% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.35 (m, 10H), 8.20-8.10 (m, 6H), 8.03-7.97 (m, 6H), 7.79 (t, *J*= 7.7 Hz, 2H), 7.54 (t, *J*= 7.0 Hz, 2H), 7.30 (d, *J*= 8.0 Hz, 2H), ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.7, HRMS (ESI+) calcd for $C_{64}H_{28}O_4Cl_2F_{24}NaS_2$ 1473.03150, found 1473.03296, $[\alpha]_D^{25}$ (*c* 1.23, $CHCl_3$) +3.1.



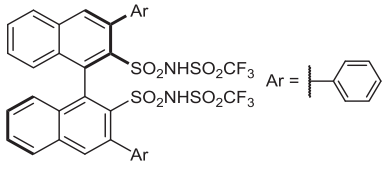
DSATf 1e

A mixture of (*R*)-3,3'-Bis(2,2",5,5"-tetrakis(trifluoromethyl) [1,1':3',1"-terphenyl]-5'-yl)-[1,1'-binaphthalene]-2,2'-disulfonyl dichloride **9** (392.0 mg, 0.27 mmol), trifluoromethanesulfonamide (148.5 mg, 0.10 mmol), K_2CO_3 (161.4 mg, 1.17 mmol) was dissolved in MeCN (1.3 ml). The reaction mixture was stirred at 70°C for 12 h, quenched with 1N HCl, and extracted by EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and evaporated to obtain the crude product which was purified by column chromatography (SiO_2, hexane: EtOAc= 3: 1). The resultant solid was dissolved in CH_2Cl_2 and washed with 1N HCl. Remaining water traces were removed by azeotropic distillation with benzene to give **DSATf 1e** (270.1 mg, 60% yield) as a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.48 (s, 4H), 8.40 (s, 4H), 8.17 (s, 2H), 8.07 (s, 2H), 8.01-7.89 (m, 10H), 7.54 (t, *J*= 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 2H), ^{13}C NMR (CD_3OD, 101 MHz) δ 145.5, 145.2, 139.3, 139.0, 138.7, 138.3, 134.7, 134.1, 133.5, 133.1 (q, *J* = 33.6 Hz), 131.9, 131.8, 130.1, 129.2, 128.4, 128.1, 125.9, 125.0 (q, *J*= 271.3 Hz), 121.3 (q, *J* = 319.1 Hz), 121.0 (q, *J*= 322.2 Hz), 120.9, ^{19}F NMR (376 MHz, CD_3OD) δ −64.1, −79.4, HRMS (ESI−) m/z calcd for $C_{66}H_{28}F_{30}N_2O_8S_4$ $[M-2H]^{2-}$ 837.01302, found 837.01172, $[\alpha]_D^{25}$ (*c* 0.04, $CHCl_3$) +75.8.



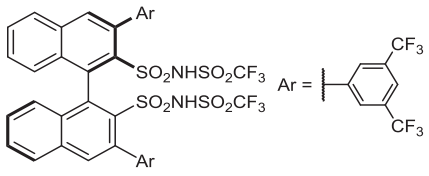
DSATf-1a

1,1’-Binaphthalene-2,2’-disulfonyl chloride (303.3 mg, 0.672 mmol), $TfNH_2$ (245.9 mg, 1.649 mmol) and K_2CO_3 (241.9 mg, 1.75 mmol) were dissolved in MeCN 0.61 ml and stirred for 25 h at r.t.. The reaction mixture was quenched with water and extracted by CH_2Cl_2. The water layer was added 1 M HCl and extracted by EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated to obtain N^2, $N^{2'}$-bis((trifluoromethyl)sulfonyl)-[1,1'-binaphthalene]-2,2'-disulfonamide **DSATf-1a** (424.6 mg, 0.628 mmol, 93%). R_f= 0.15 (EtOAc: MeOH = 20:1), ^{1}H NMR (500 MHz, CD_3OD) δ *J* = 9.0 Hz, 2 H), 8.18 (d, *J* = 7.6 Hz, 2 H), 7.98 (d, *J* = 8.4 Hz, 2 H), 7.61 (t, *J* = 7.6 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 6.99 (d, *J* = 8.6 Hz, 2 H) ^{13}C NMR(125MHz,CD_3OD) 140.5, 135.2, 134.7, 133.7, 129.1, 129.0, 128.3, 128.1, 127.4, 124.9, 120.8 (q, *J* = 320 Hz), 120.7 (q, *J* = 320 Hz), ^{19}F NMR (400 MHz, CD_3OD), δ -79.65, IR (KBr): ν= 3391, 3250, 1638, 1321, 1192 cm^{-1}. HRMS(APCl+) *m*/*z* calcd for $C_{22}H_{14}O_8N_2F_6NaS_4$ $[M+Na]^+$ 698.94110 Found 698.94294, $[\alpha]_D^{23}$ = -35.7^o (c 1.25 in MeOH), m.p.186~189^{o}C.



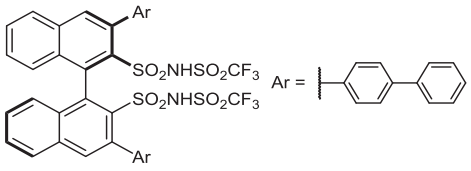
DSATf-1b

A mixture of 3, 3’-diphenyl-[1, 1’-binaphthalene]-2, 2’-disulfonyl dichloride (101.9 mg, 0.17 mmol), trifluoromethanesulfonamide (47.7 mg, 0.320 mmol), K_2CO_3 (67.0 mg, 0.491 mmol) was dissolved in MeCN 0.5 ml. The reaction mixture was stirred at 35^{o}C for 48 h, quenched with 1 M HCl, extracted by EtOAc, washed with brine, dried over Na_2SO_4, evaporated, and purified by column chromatography (SiO_2, EtOAc) to get (*R*)-3, 3’-diphenyl-N2, N2’-bis ((trifluoromethyl) sulfonyl)-[1, 1’-binaphthalene]-2, 2’-disulfonamide **DSATf-1b** (969.7 mg, 1.58 mmol, 91%). R_f=0.10 (EtOAc), ^{1}H NMR (500 MHz, CD_3OD) δ 7.85 (d, *J* = 8.2Hz, 2 H), 7.77 (s, 2 H), 7.69 (d, *J* = 6.1 Hz, 4 H), 7.49 (dt, *J* = 7.5, 1.0 Hz, 2 H), 7.29-7.37 (m, 6 H), 7.23 (dt, *J* = 7.8, 1.0 Hz, 2 H), 7.12 (d, *J* = 8.7 Hz, 2 H), ^{13}C NMR (125 MHz, $CDCl_3$) δ 142, 139, 138 x 2, 133 x 2, 130 x 2, 129, 126, 119 (q, *J* = 323 Hz), ^{19}F NMR (400 MHz, CD_3OD) d -77.8, IR (KBr): ν = 3434, 1620, 1308, 1190 cm^{-1}, HRMS (ESI-) calcd for $C_{34}H_{20}O_8N_2F_6NaS_4$ 848.99099, found 848.99127, $[\alpha]_D^{23}$ = 55.9 (*c* 1.26 in $CHCl_3$), m.p.104-105^{o}C.



DSATf-1c

A mixture of 3, 3'- bis(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2, 2'-disulfonyl dichloride (814.9 mg, 0.93 mmol), trifluoromethanesulfonamide (386.3 mg, 2.59 mmol), K_2CO_3 (479.6 mg, 3.47 mmol) was dissolved in MeCN 5.0 ml. The reaction mixture was stirred at r.t. for 48 h, quenched with 1 M HCl, and extracted by EtOAc, washed with brine, dried over Na_2SO_4, evaporated, and purified by column chromatography (SiO_2, EtOAc) to get (*R*)-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-N2,N2'-bis((trifluoromethyl)sulfonyl)-[1,1'-binaphthalene]-2,2'-disulfonamide **DSATf-1c** (1.08 g, 0.98 mmol, 98%). R_f = 0.3 (CH_2Cl_2: MeOH= 6: 1), ^{1}H NMR (400 MHz, CD_3OD) δ 8.19 (s, 4 H), 7.84 (d, *J* = 8.1 Hz, 2 H), 7.78 (s, 2 H), 7.73 (s, 2 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 7.22 (t, *J* = 7.8 Hz, 2 H), 7.11 (d, *J* = 8.1 Hz, 2 H), ^{13}C NMR (125 MHz, $CDCl_3$) 145, 138, 137, 135, 133 x 2, 132 x 2, 130, 129, 128, 127 x 2, 125, 120, 119 (q, *J* = 322 Hz), ^{19}F NMR (400 MHz, CD_3OD) δ -62.10, -78.29, IR (KBr): ν = 3468, 1621, 1311, 1280, 1185 cm^{-1}, $[\alpha]_D^{23}$ = 48.5 (*c* 1.27, $CHCl_3$), m.p.141~143ºC.

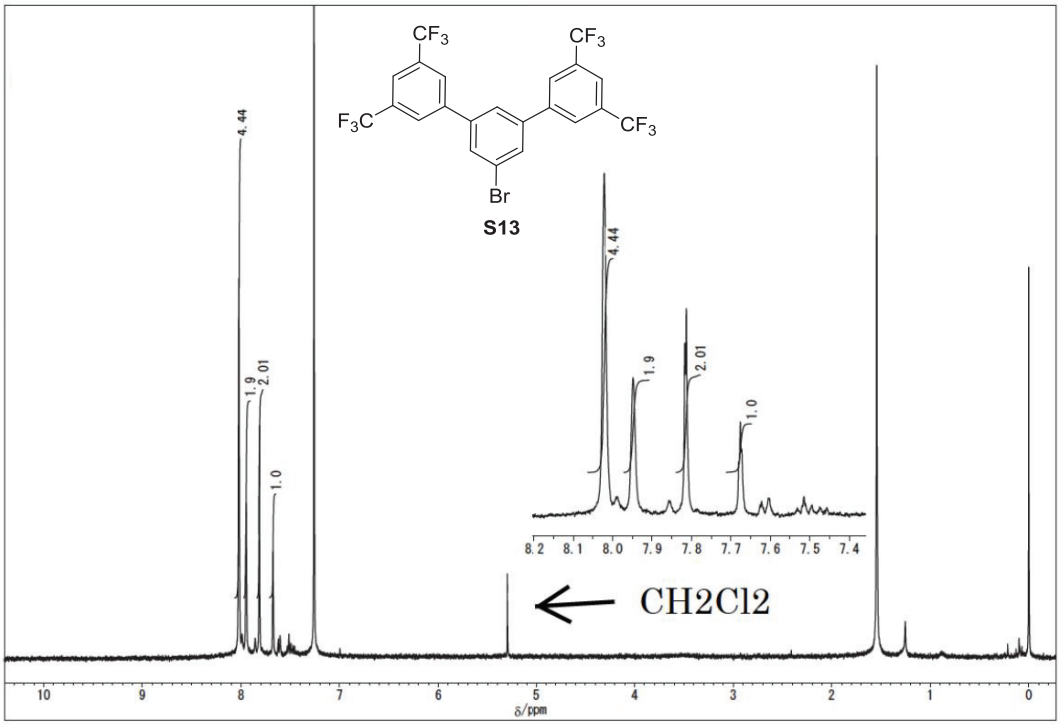


DSATf-1d

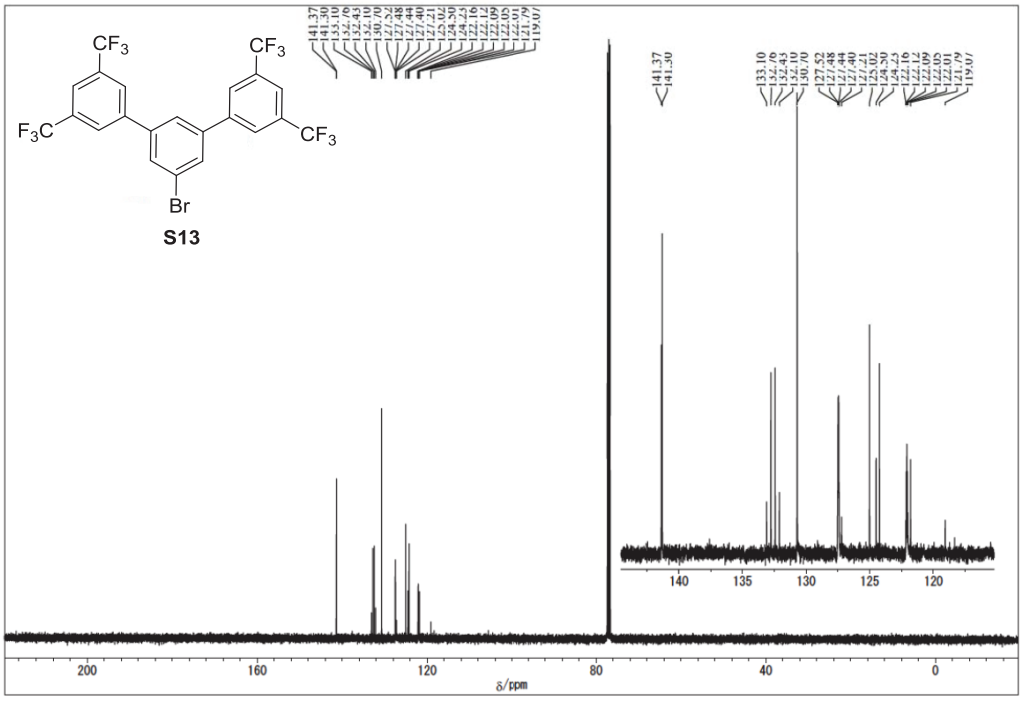
A mixture of 3, 3'- di([1,1'-biphenyl]-4-yl**)**-[1, 1'-binaphthalene]-2, 2'-disulfonyl dichloride (295.4 mg, 0.391 mmol), trifluoromethanesulfonamide (182.5 mg, 1.22 mmol), K_2CO_3 (140.9 mg, 1.02 mmol) was dissolved in MeCN (3.0 ml). The reaction mixture was stirred at r.t. for 48 h, quenched with 1 M HCl, and extracted by EtOAc, washed with brine, dried over Na_2SO_4, evaporated, and purified by column chromatography (SiO_2, EtOAc) to get *(R)*-3,3'-di([1,1'-biphenyl]-4-yl)-N2,N2'-bis((trifluoromethyl)sulfonyl)-[1,1'-binaphthalene]-2,2'-disulfonamide **DSATf-1d** (192.5 mg, 0.20 mmol, 50%). R_f = 0.3 (CH_2Cl_2/MeOH = 6/1), ^{1}H NMR (400 MHz, CD_3OD) δ 7.86-7.91 (m, 2 H), 7.78 (d, *J* = 7.6 Hz, 2 H), 7.70 (d, *J* = 7.7 Hz, 2 H), 7.65 (d, *J* = 8.4 Hz, 2 H), 7.53 (t, *J* = 7.3 Hz, 2 H), 7.46 (t, *J* = 7.2 Hz, 2 H), 7.33-7.36 (m, 2 H), 7.26 (t, *J* = 7.3 Hz, 2 H), 7.10 (d, *J* = 8.2 Hz, 2 H), ^{13}C NMR (125 MHz,$CDCl_3$) d 145, 143, 142 x 2, 141, 138, 137, 136, 135, 133, 132 x 2, 131 x 4, 130 x 3, 128, 123 (q, *J* = 322 Hz), ^{19}F NMR (400 MHz, CD_3OD) δ-77.72, IR (KBr): ν = 3435, 1629, 1307, 1190 cm^{-1}, $[\alpha]_D^{23}$ = 71.9 (c 1.56 in $CHCl_3$), m.p.190~192ºC.

2-8-7. NMR spectra of new compounds

^{1}H NMR

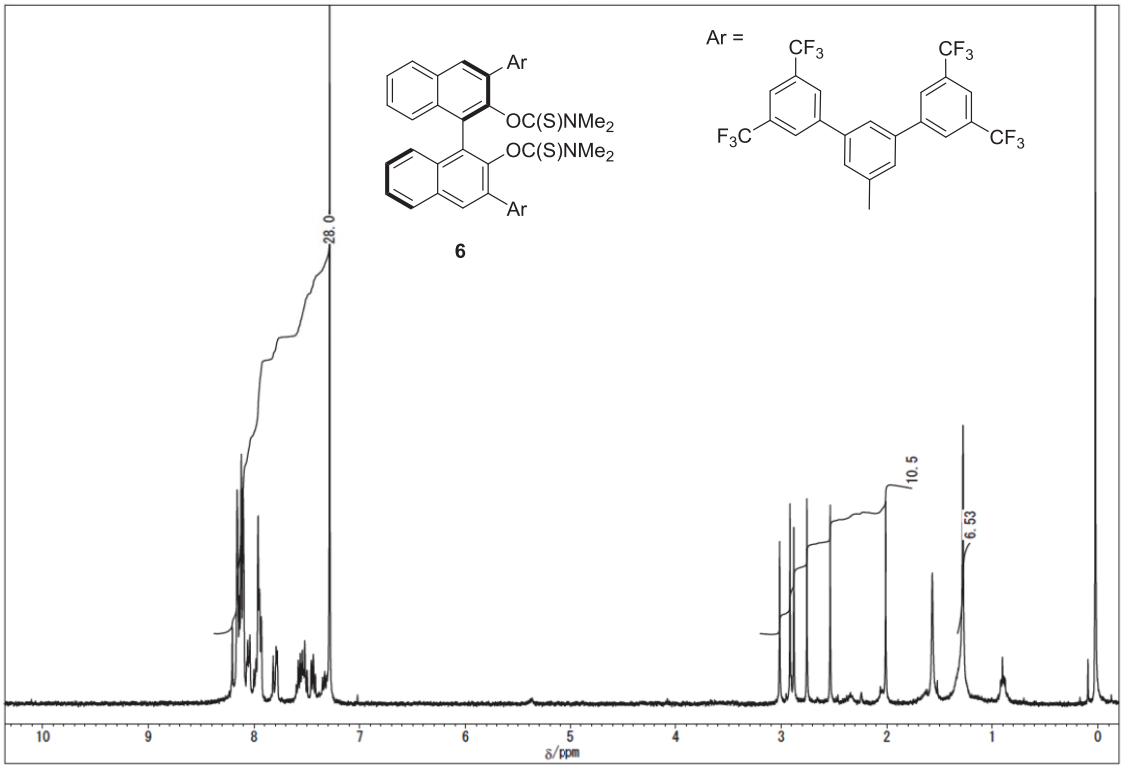


^{13}C NMR



^{19}F NMR

^{1}H NMR



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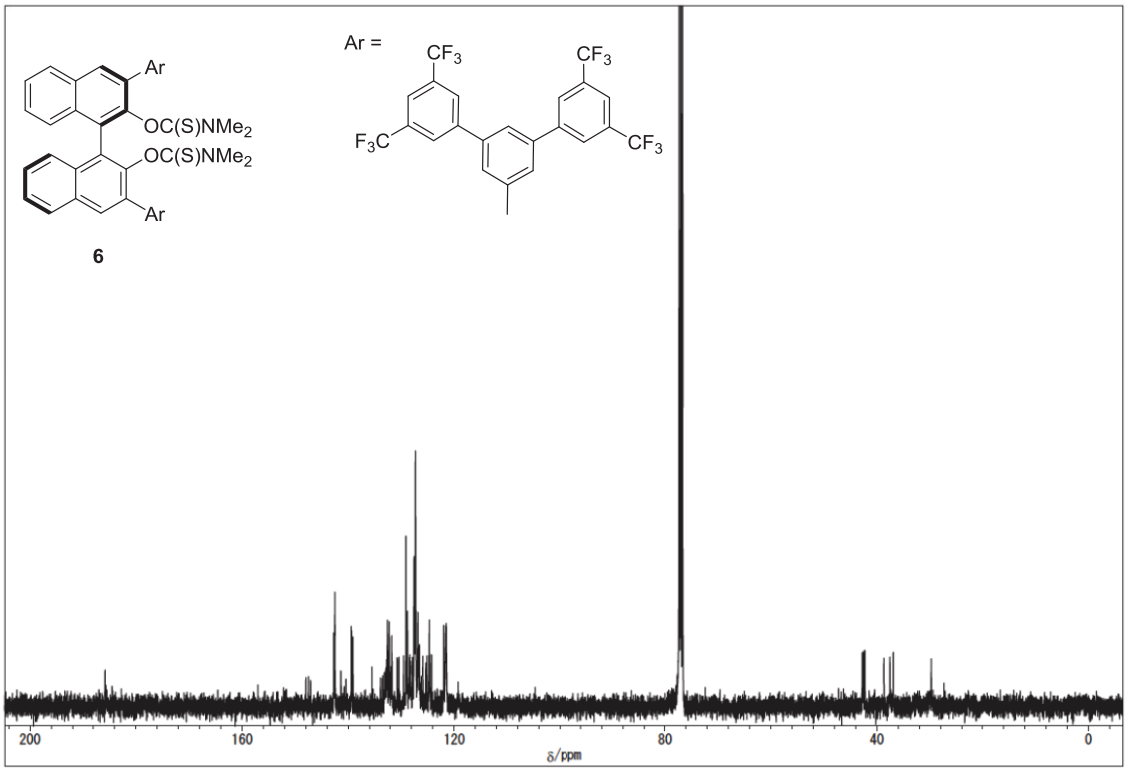

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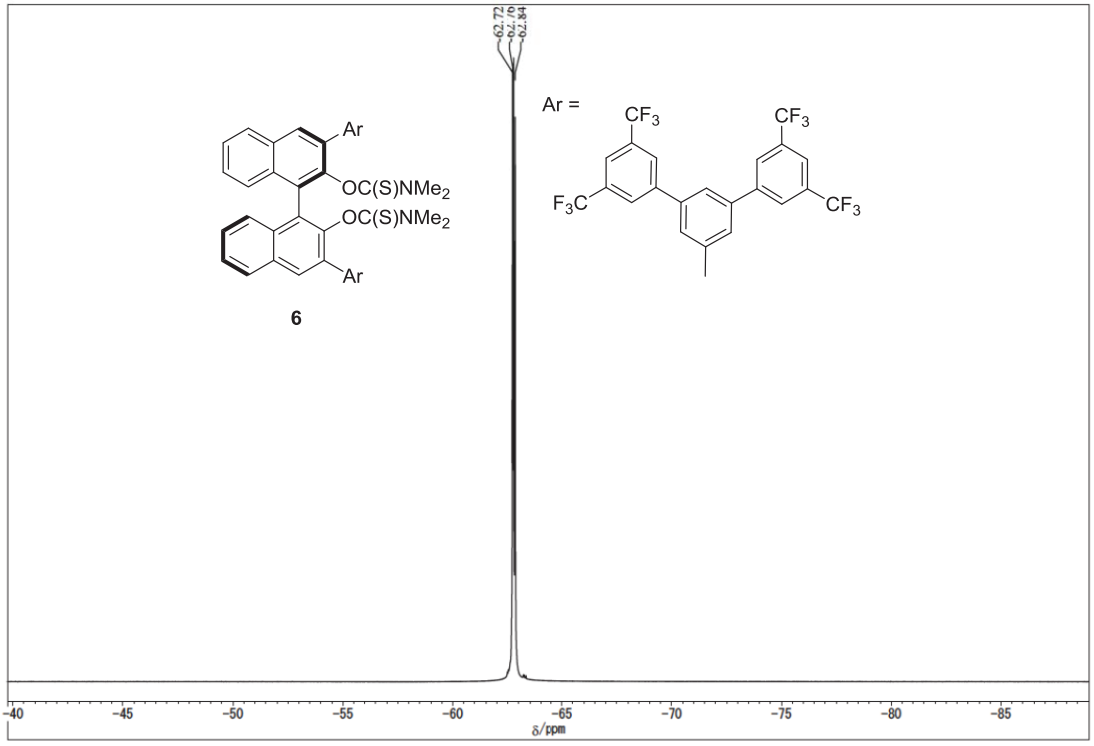

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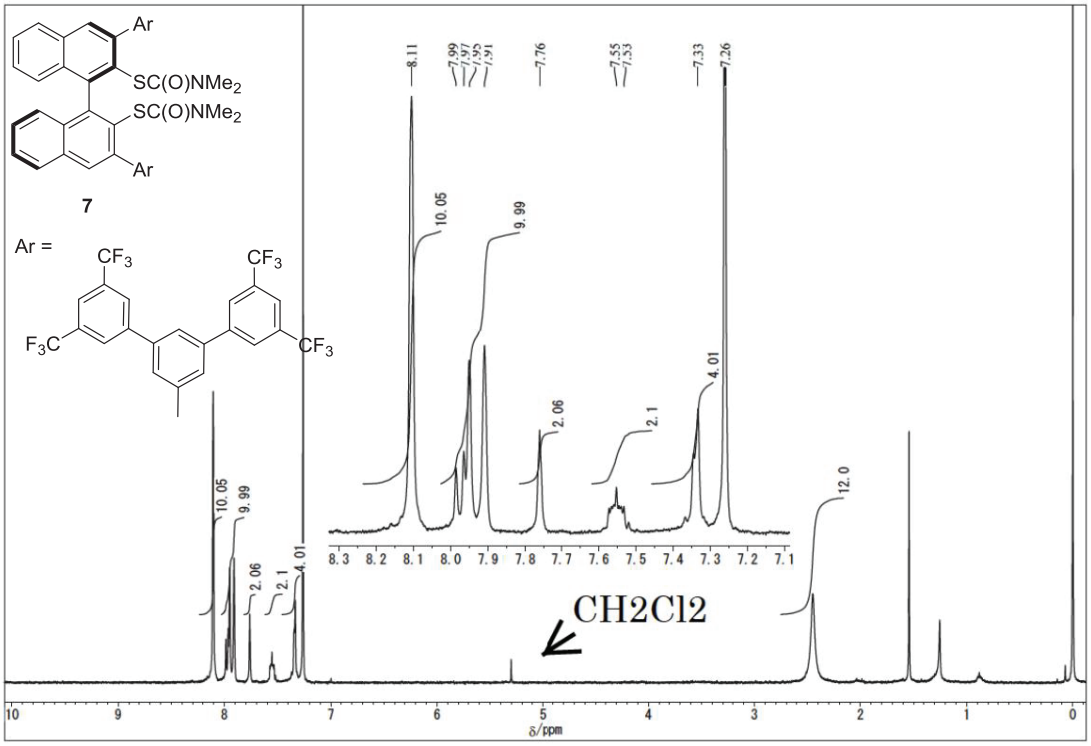

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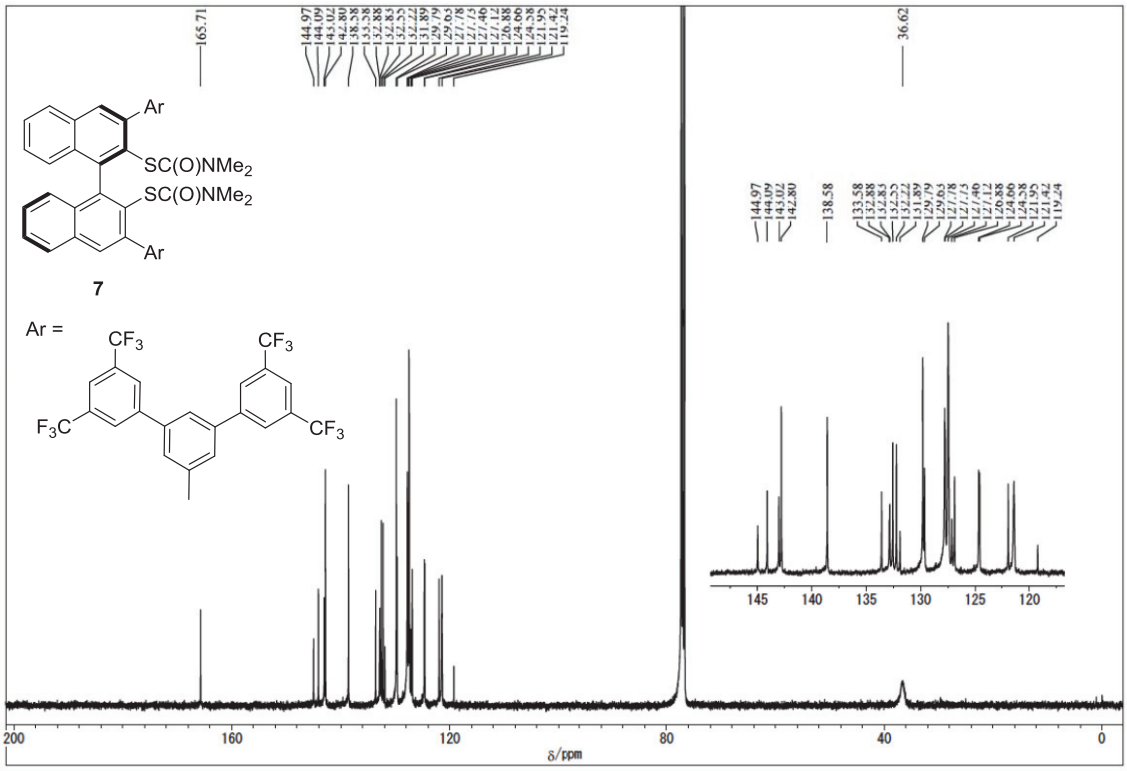
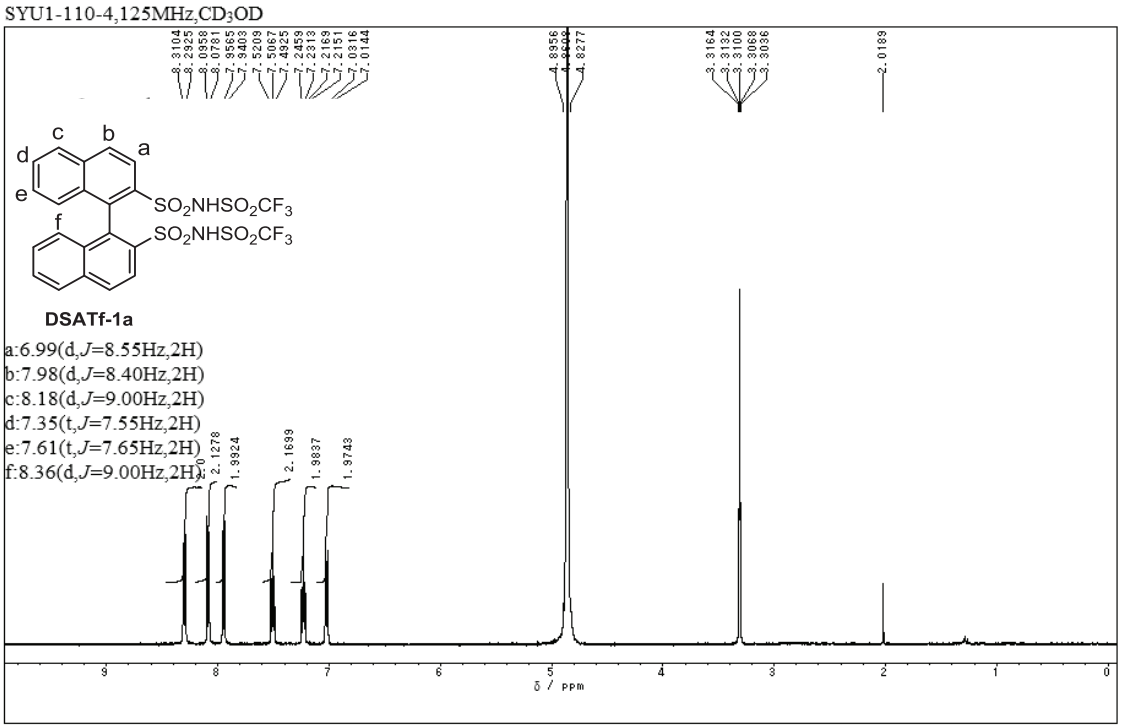
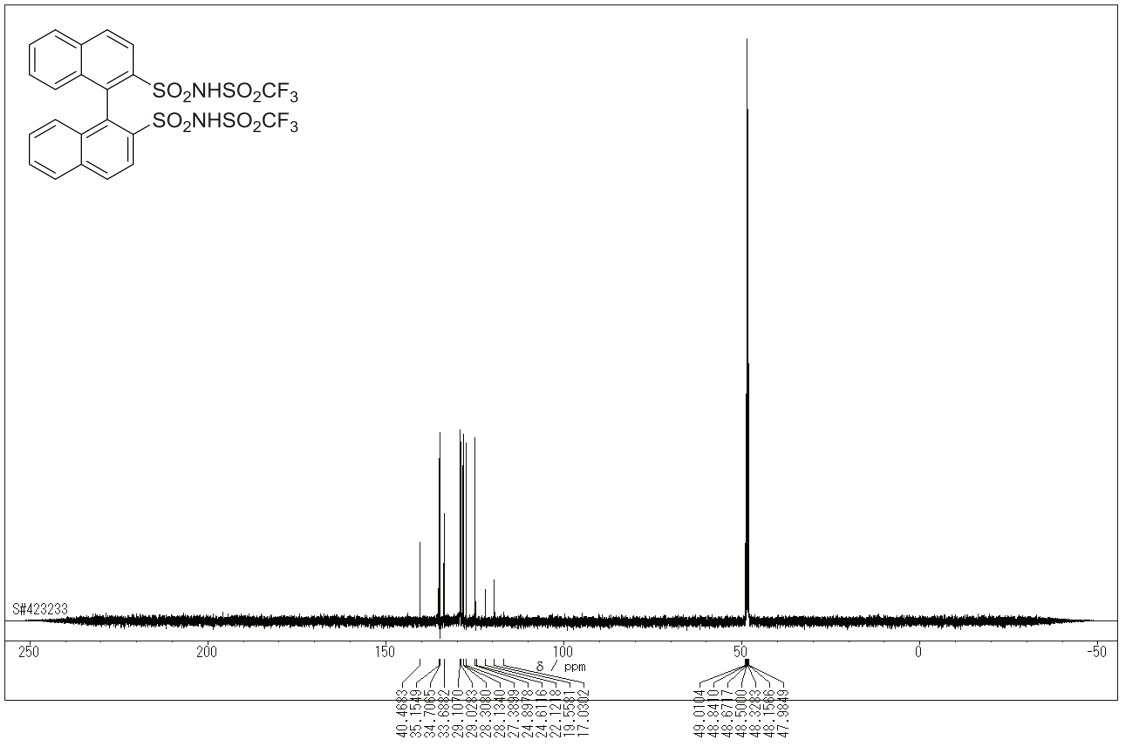


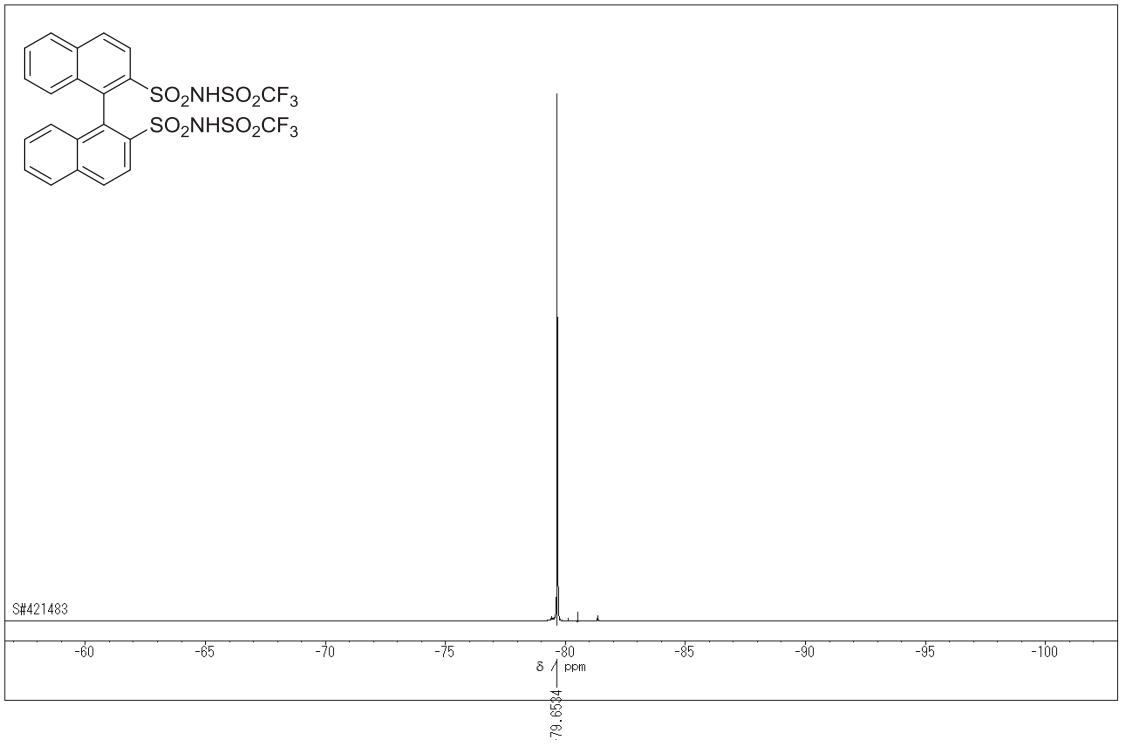
^{1}H NMR



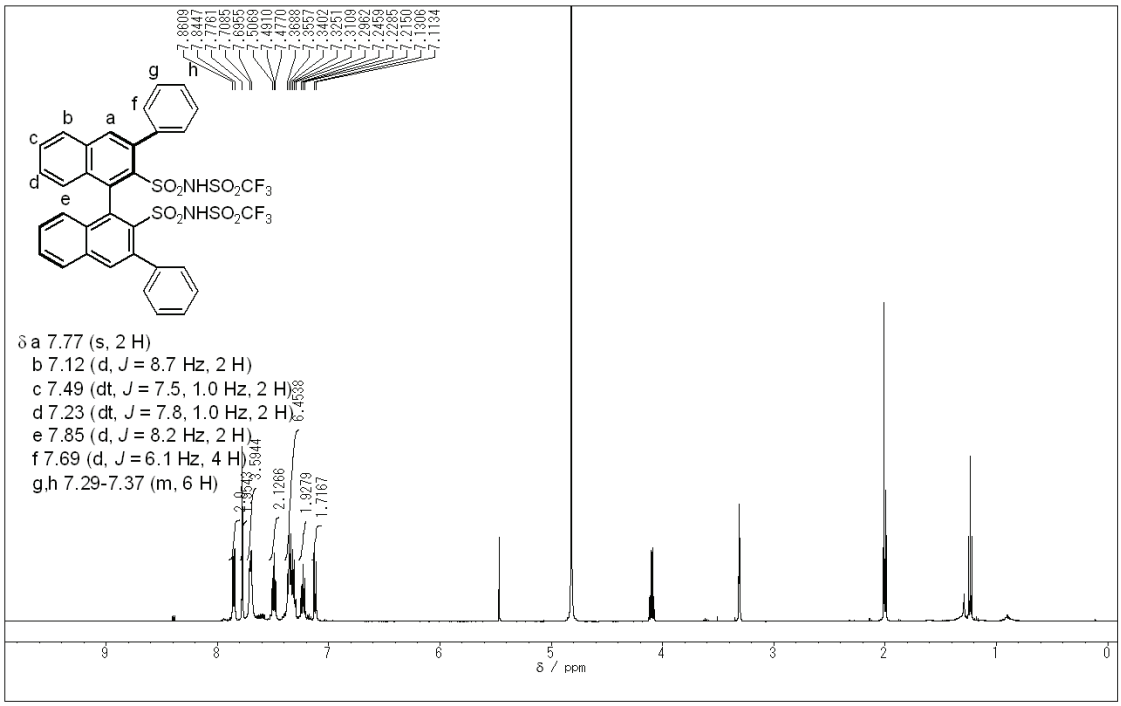
^{13}C NMR



^{19}F NMR

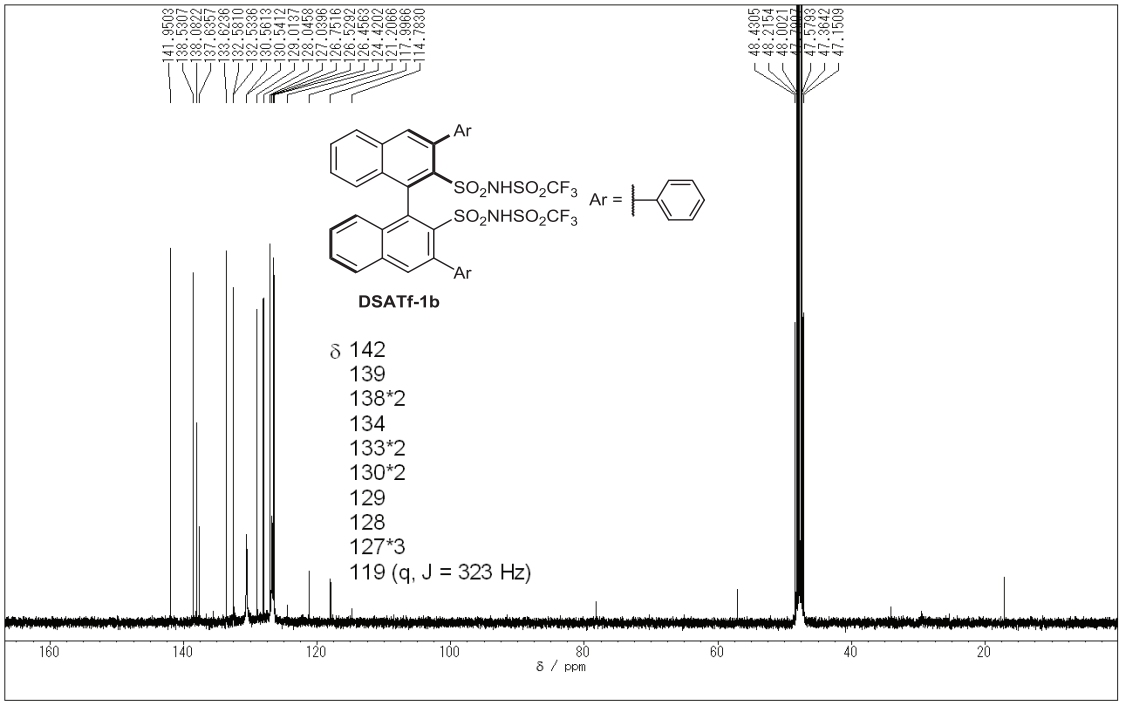


^{1}H NMR



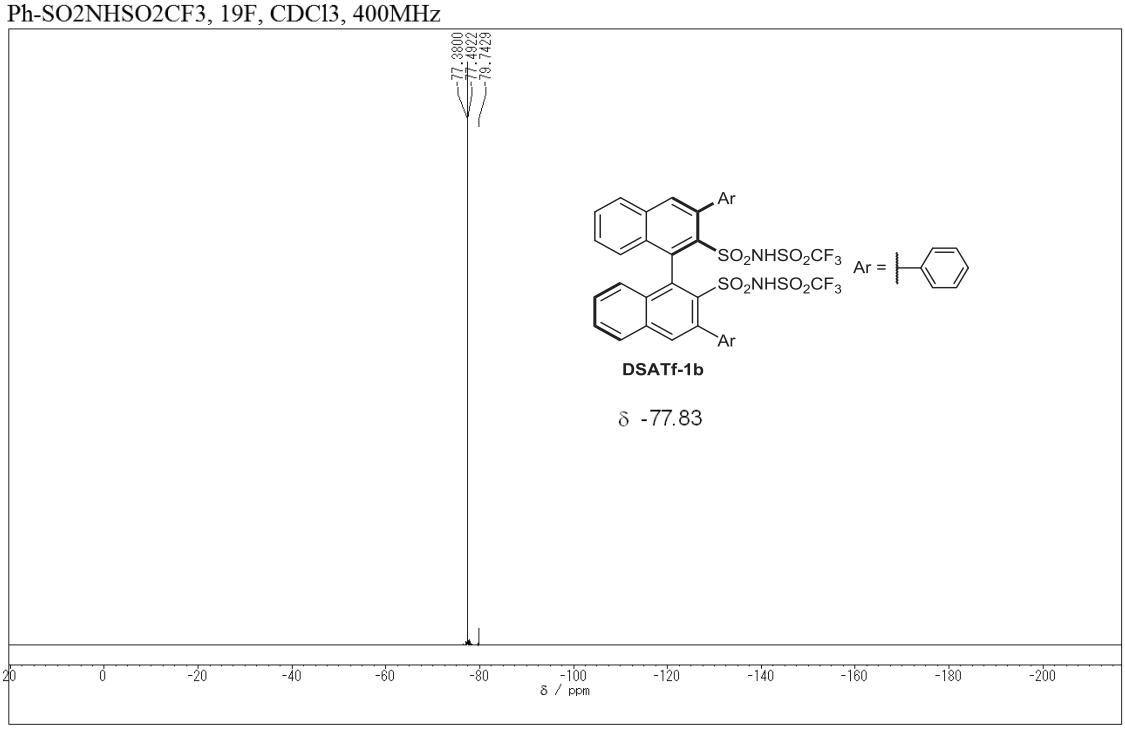
^{13}C NMR

Ph-$SO_2NHSO_2CF_3$, CD_3OD, 100MHz



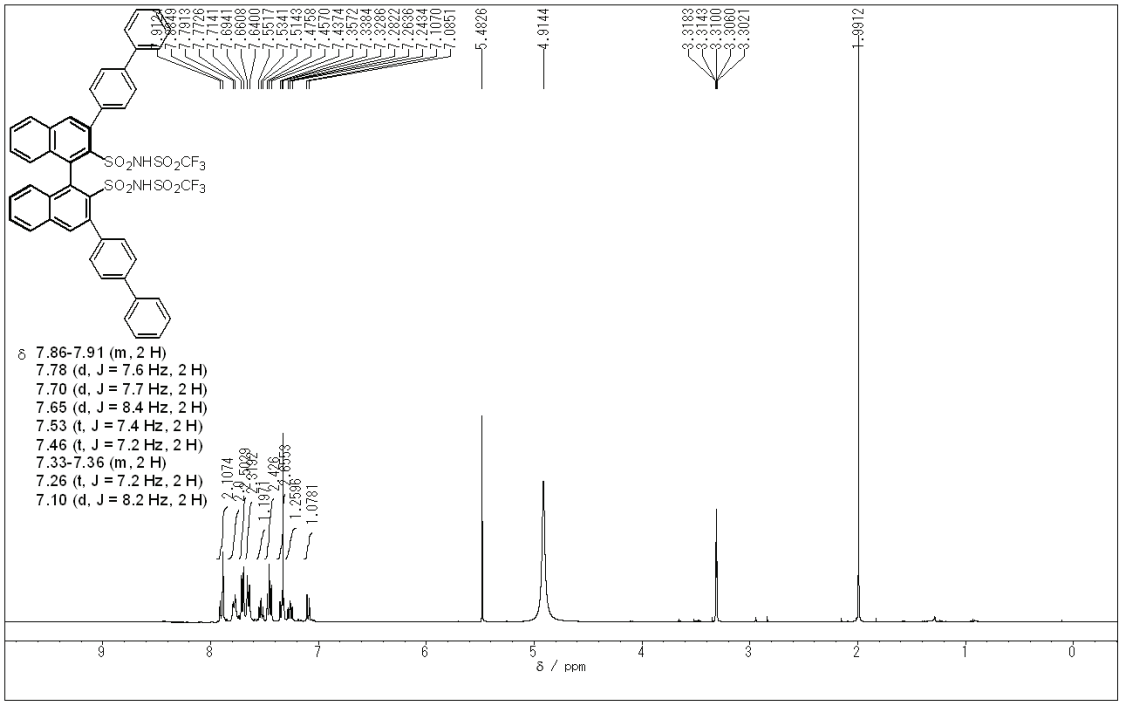
^{19}F NMR

Ph-SO2NHSO2CF3, 19F, CDCl3, 400MHz



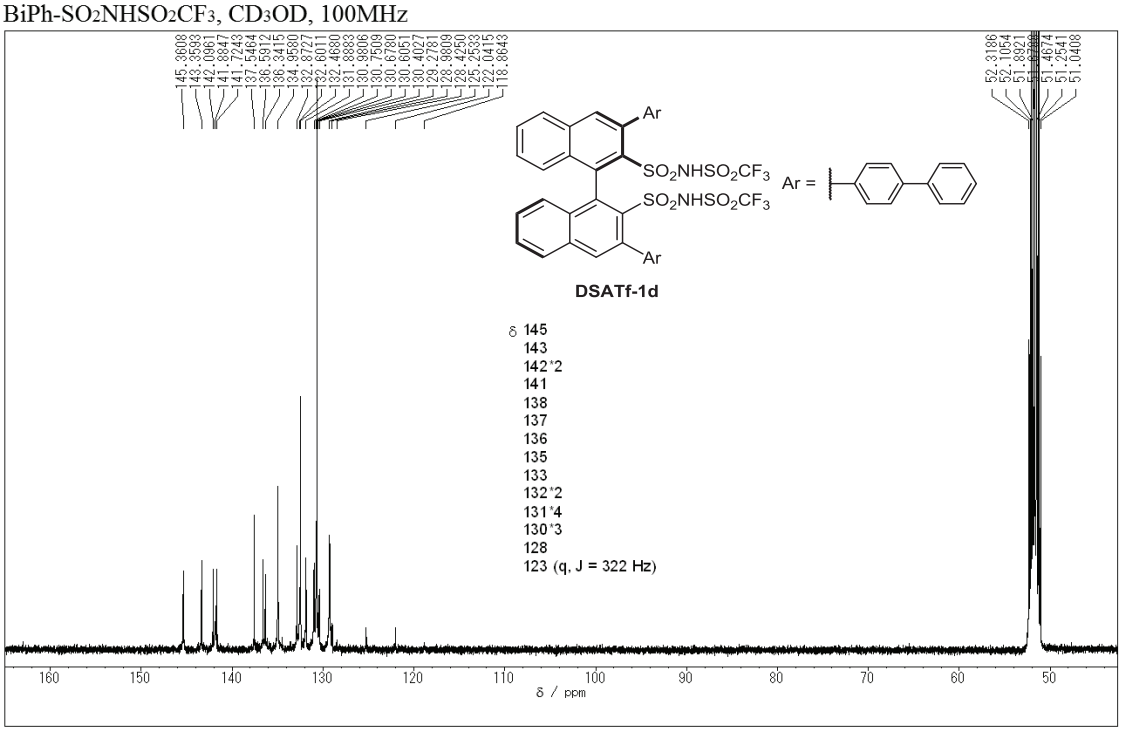
^{1}H NMR

SYU419196, CD_3OD, 400MHz



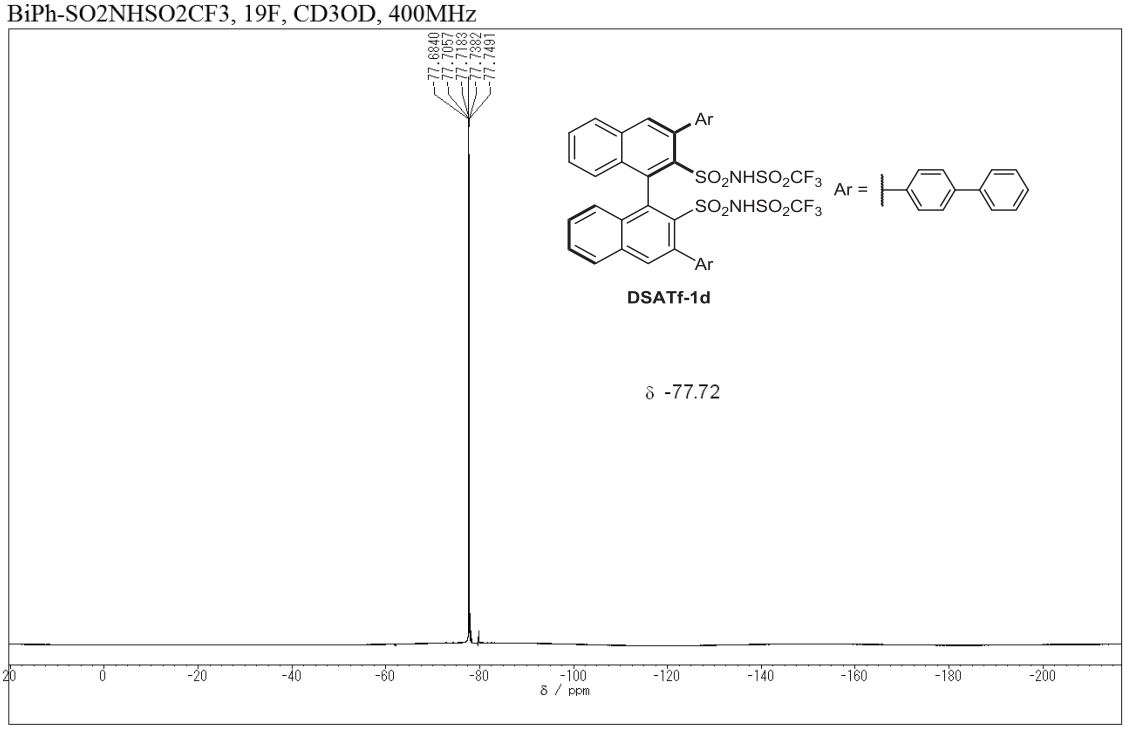
^{13}C NMR

BiPh-$SO_2NHSO_2CF_3$, CD_3OD, 100MHz

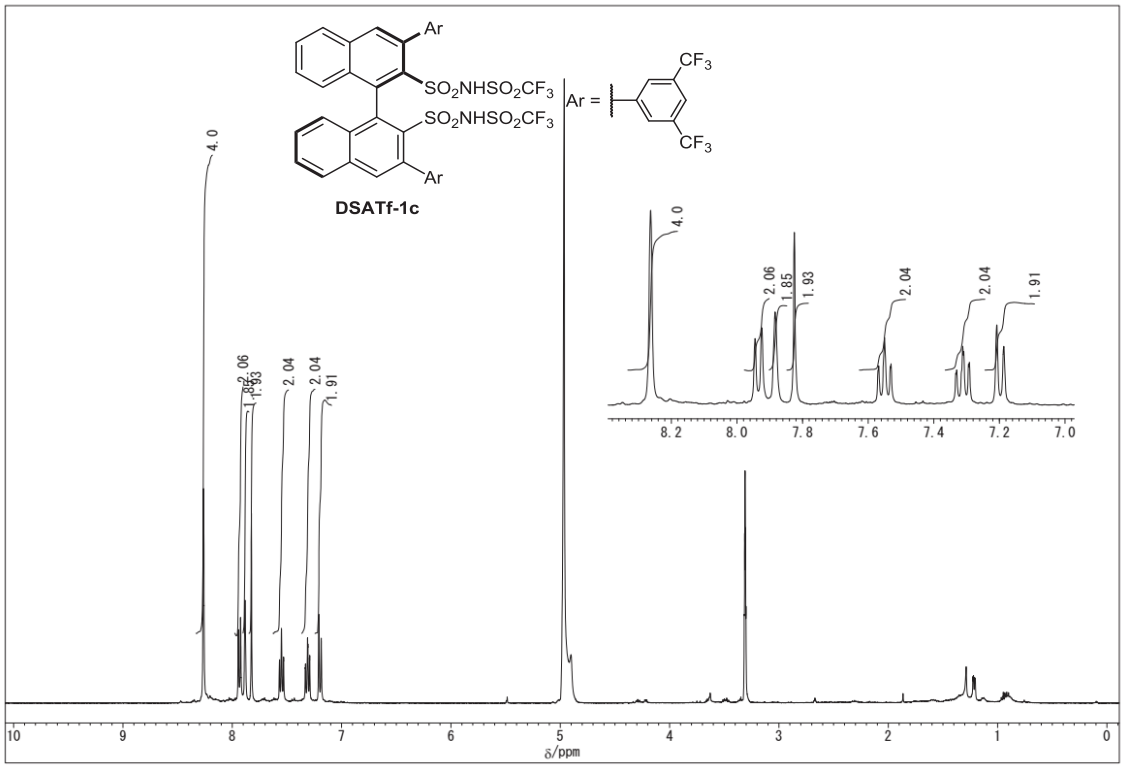


^{19}F NMR

BiPh-SO2NHSO2CF3, 19F, CD3OD, 400MHz

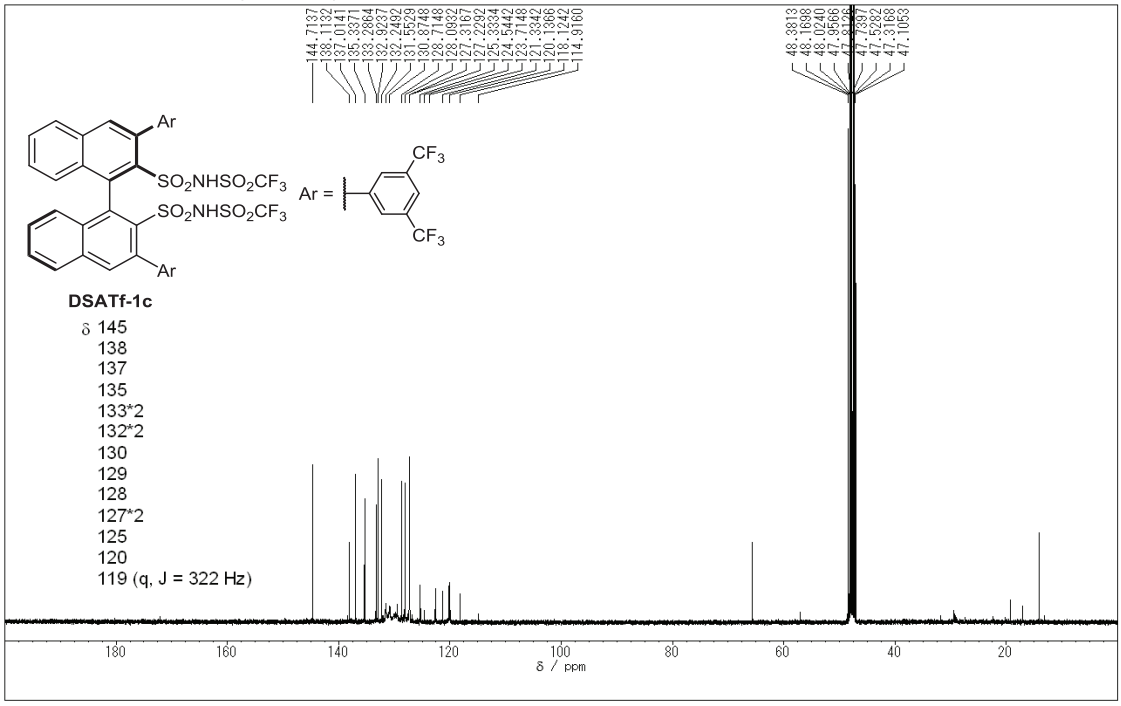


^{1}H NMR



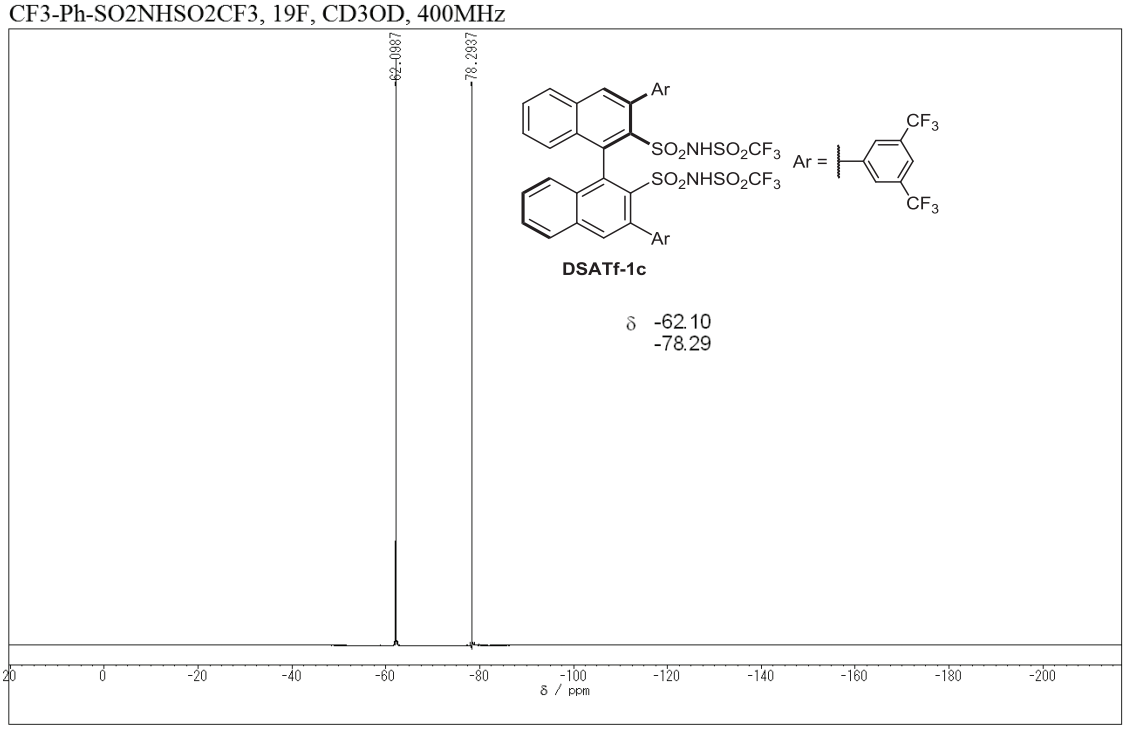
^{13}C NMR

CF3-Ph-SO2NHSO2CF3, CD3OD, 100MHz



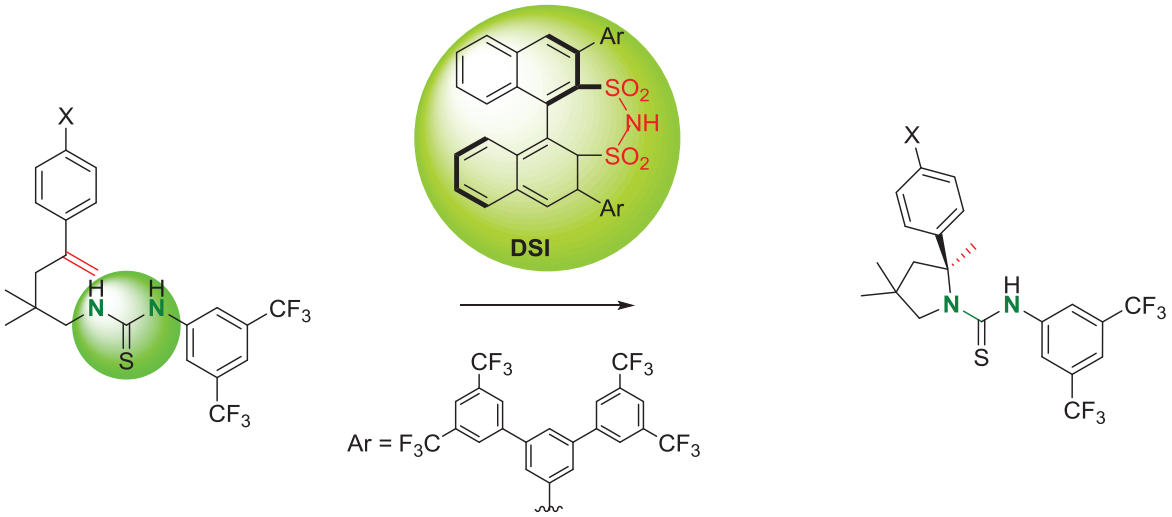
^{19}F NMR

CF3-Ph-SO2NHSO2CF3, 19F, CD3OD, 400MHz



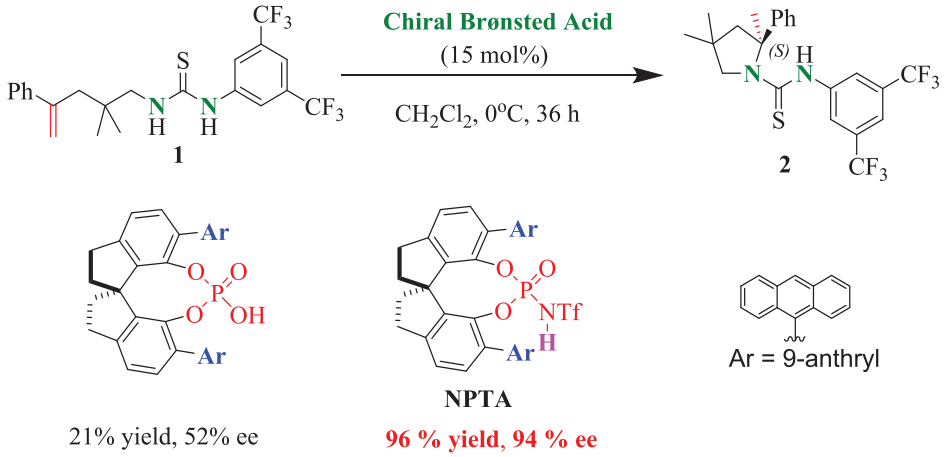
Chapter 3.

DSI Catalyzed Hydroamination Reaction



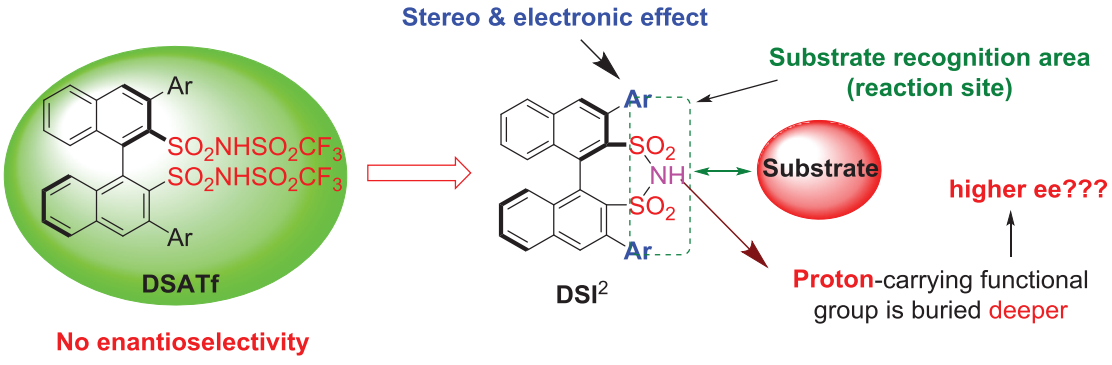
3-1. DSI Catalyzed Asymmetric Intramolecular Hydroamination Reaction

Liu and co-workers reported enantioselective hydroamination of alkenyl thioureas by **NPTA** (Scheme 1)[24–26]. The authors believe that the reaction proceeded by the activation of thiourea moiety by **NPTA**. In their research, the importance of acidity of Brønsted acid for good results was shown.



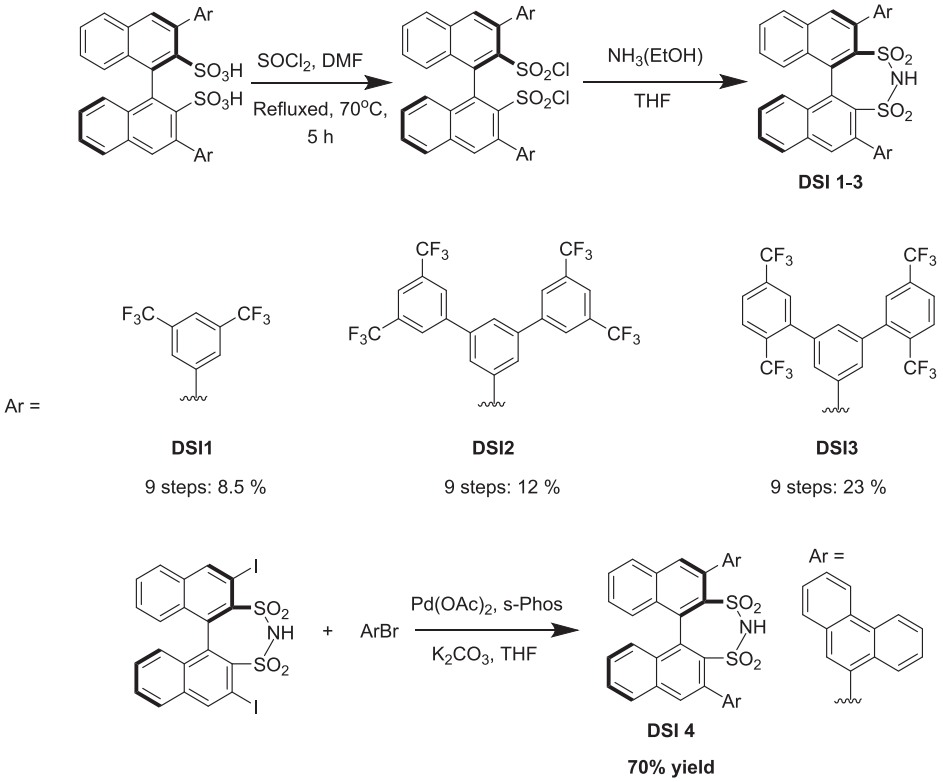
Scheme 1. NPTA-catalyzed hydroamination of alkenyl thiourea by Liu et al.

In chapter 2, **DSATf** was not effective for an asymmetric reaction in hydroamination of alkenyl amines. The flexibility of sulfonamide moiety is a reason for the no asymmetric induction. So a cyclic disulfonimide **DSI**[28] was focused as an asymmetric catalyst in order to achieve the enantioselective hydroamination. Because the proton-carrying functional group of **DSI** is buried deeper in the reaction site of the disulfonimide, leading to higher enantioselectivity by an enhanced stereochemical communication between catalyst and substrate (Scheme 2). In this study, **DSI**-catalyzed hydroamination of alkenyl thiourea was examined with an expectation of improving catalytic efficiency.



Scheme 2. Comparison of **DSATf** and **DSI**.

3-1.1. Synthesis of Brønsted Acid DSI



Scheme 3. Synthesis of **DSI**

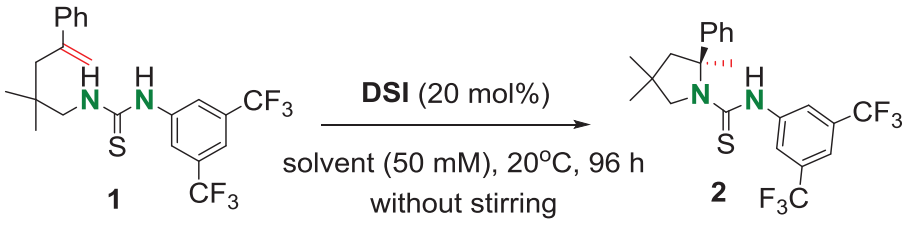
DSI 1-3 were prepared according to the literature procedure from corresponding disulfonic acid (Scheme 3)[28,88].

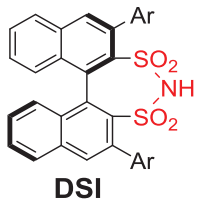
3-1.2. Optimization of 3,3'- substituents (Ar) of DSI and Solvent

At first, the aryl (Ar) group of **DSI** and solvents for the hydroamination reaction were screened (Table 1). The hydroamination reaction was performed using 20 mol% of **DSI** in 5-mm NMR tube without stirring at 20°C for 4 days. The screening of Ar group indicated that the size of Ar group affected the enantioselectivity, and the reaction using **DSI2** gave the hydroamination product with better enantioselectivity than **DSI1** (entries 1-2). The hydroamination using **DSI3** substituted with bulkier Ar group than **DSI2** gave hydroamination product **2** with lower chemical yield and enantioselectivity (entry 9). As other types of bulky Ar group, **DSI4** bearing 9-phenanthrenyl group was also examined (entry 10). On the hydroamination, the product was obtained with a good chemical yield (81%) but low enantioselectivity (18%ee).

The results of the solvent screening on the hydroamination catalyzed by **DSI2** showed that the use of benzene derived solvents led to better enantioselectivity than DCM (entries 2-8). When electron-donating benzene derivatives such as *o*-xylene and mesitylene were used as a solvent, the formation of a byproduct seemed to result from the reaction of the thiourea moiety on the alkenyl amine with the solvent was observed (entries 2 and 3). Toluene was selected as a suitable solvent on the basis of chemical yield and enantioselectivity (entry 4).

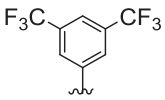
Table 1. Screening of aryl (Ar) group and solvent[a].



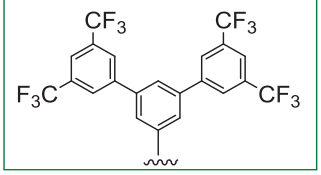


DSI

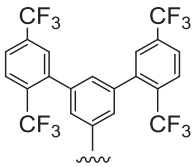
DSI1: Ar =



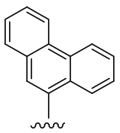
DSI2: Ar =



DSI3: Ar =



DSI4: Ar =



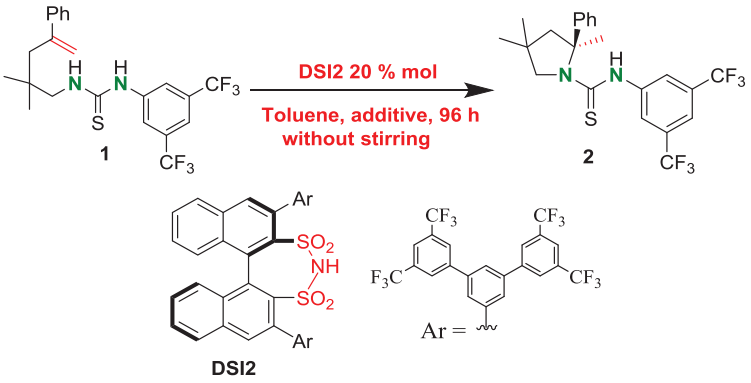
entry	DSI	Solvent	yield (%)[b]	e.e.(%)[c]
1	**DSI1**	o-xylene	43	50
2	**DSI2**	o-xylene	31(45)[d]	62
3	**DSI2**	mesitylene	56(64)[d]	64
4	**DSI2**	toluene	68(68)[d]	67
5	**DSI2**	benzene	66(66)[d]	63
6	**DSI2**	C_6H_5F	75(75)[d]	50
7	**DSI2**	$C_6H_5CF_3$	70(70)[d]	38
8	**DSI2**	DCM	56(56)[d]	25
9	**DSI3**	toluene	44	57
10	**DSI4**	toluene	81	18

[a]Reactions were performed with alkenyl thiourea (44 mmol), **DSI** (20 mol%) in solvent (0.88 mL) at 20°C for 96 h.
The reactions were performed in a 5-mm NMR tube under non-stirring.
b. Isolated yield. c. Determined by chiral stationary phase HPLC analysis.
d. Conversion.

3-1.3. Effect of Additives

With the suitable Aryl group on **DSI** and solvent in hand, the effect of the additive was investigated (Table 2). Although the enantioselectivities were not affected by the use of the additives, the chemical yield increased in the presence of MS4Å as a drying agent (entry 2).

Table 2. Screening of Additives[a].



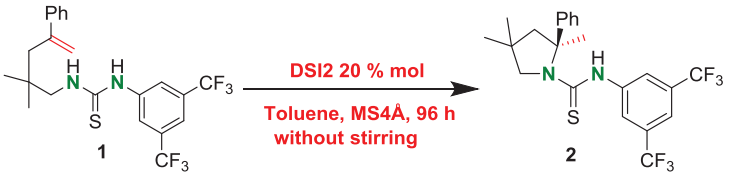
Entry	Additive	yield (%)[b]	e.e.(%)[c]
	-	68	67
1	Na_2SO_4	69	62
2	MS4Å	78	66
3	MS3Å	72	67

[a] Reactions were performed with alkenyl thiourea (44 mmol), **DSI2** (20 mol%), additive (50 mg) in toluene (0.88 mL) at 20°C for 96 h.
The reactions were performed in a 5-mm NMR tube under non-stirring.
b. Isolated yield. c. Determined by chiral stationary phase HPLC.

3-1.4. Optimization of Reaction Conditions

The optimization of reaction conditions including concentration, temperature, and stirring of the reaction mixture on the **DSI** catalyzed hydroamination was performed (Table 3). When the reaction was conducted without stirring, the enantioselectivity of the product remained almost unchanged (70%ee) even when the reaction concentration decreased from 50 mM to 2.5 mM of concentration (entries 1, 4-7). The high concentration of 200 mM led to a decrease in enantioselectivity (entry 2). In entry 8, to improve the chemical yield, the amount of **DSI** was increased from 20 mol% to 30 mol%, the chemical yield increased and the product with the best chemical yield (86%) was obtained. At low temperature (0°C), the enantioselectivity could not be improved and the chemical yield also decreased (entries 3 and 9). When the reaction mixture was stirred, interestingly the chemical yield was dropped, but there was no change in enantioselectivity (entries 1, 3, and 8-9). These results showed that dilute (2.5 mM) concentration and non-stirring of the reaction mixture were important factors in controlling enantioselectivity.

Table 3. Optimization of Reaction Conditions[a].



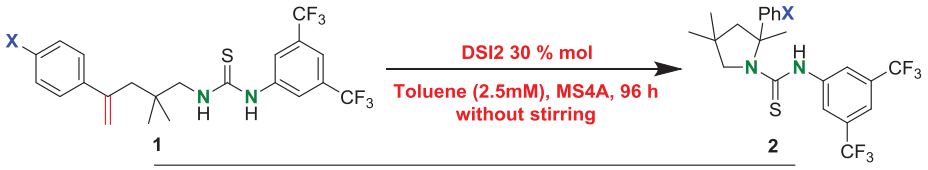
entry	Conc. (mM)	temp. (°C)	yield (%)[b]	e.e.(%)[c]
1	50	20	78(63)[d]	68(69)[d]
2	200	20	75	57
3	50	0	56(25)[d]	66(73)[d]
4[e]	20	20	64	68
5[e]	10	20	80	69
6[e]	5	20	77	70
7[e]	2.5	20	64	70
8[e,f]	2.5	20	86 (27)[d]	70(70)[d]
9[e,f]	2.5	0	24(0)[d]	75(---)[d]

a Unless otherwise noted, reactions were performed with alkenyl thiourea (44 mmol), **DSI2** (20 mol%), MS4Å (50 mg) in toluene at 20°C for 96 h. The reactions were performed in a 5-mm NMR tube under non-stirring. b. Isolated yield. c. Determined by chiral stationary phase HPLC. d. The reaction was performed in a test tube under stirring with a stirring bar. e. The reaction was performed in a test tube under non-stirring. f. 30 mol% of **DSI2** was used.

3-1.5. Scope of Substituent on Alkenyl Amine

Next, the substrate scope with a variety of X on the phenyl ring of alkenyl amines was examined (Table 4). The results showed that at 20°C the hydroamination of alkenyl amines with electron-donating groups (EDG) (MeO and Me) gave a product with excellent yields (98%, 84%) but low enantioselectivities (22%ee, 52%ee) (entries 1 and 3). In contrast, the hydroamination of alkenyl amines substituted with electron-withdrawing groups (EWG) (F, Cl, and Br) at room temperature gave a product with moderate enantioselectivity but low chemical yield (33%, 22%, 17%) (entries 6, 8, and 11). On the reaction of EWG-substituted alkenyl amines, increasing the reaction temperature to 50°C improved the chemical yield and interestingly, the enantioselectivity remained constant (entries 7, 9, and 12). However, when the reaction was performed at 70°C, a decline in both chemical yield and enantioselectivity was observed (entries 10 and 13). From these results, it was found that cation intermediate generated from protonation of the olefin moiety of alkenyl thiourea was affected by the substituent (X) on the phenyl ring of alkenyl thiourea.

Table 4. Scope of substituent on alkenyl amines[a]



1 2

entry	X	temp. (°C)	yield (%)[b]	e.e.(%)[c]
1	MeO	20	98	22
2	MeO	-20	28	12
3	Me	20	84	52
4	Me	0	45	49
5	H	20	86	70
6	F	20	33	70
7[e]	F	50	81	70
8	Cl	20	22(0)[d]	73(---)[d]
9	Cl	50	66(58)[e]	64(---)[e]
10	Cl	70	74	61
11	Br	20	17(0)[d]	71(---)[d]
12	Br	50	43(45)[e]	71(67)[e]
13	Br	70	40	61

[a]Unless otherwise noted, reactions were performed with alkenyl thiourea (44 mmol), **DSI2** (30 mol%), MS4Å (50 mg) in toluene (17.4 mL) at 20°C for 96 h. The reactions were performed in a test tube under non-stirring with a stirring bar. b. Isolated yield. c. Determined by chiral stationary phase HPLC.
d. The reaction was conducted at 10 mM of the reaction mixture.
e. The reaction was performed in a test tube under sitrring with a stirring bar.

3-1.6. Determination of Absolute Configuration

To determine the absolute configuration of the hydroamination product, the retention time on the chiral stationary phase HPLC analysis of the product obtained from the hydroamination of alkenyl thiourea derivative (X= Me) was compared with the reported value[26] (Figures 1 and 2). The HPLC column using the same chiral selector with the literature was used as a stationary phase in this study. In the literature, the absolute stereochemistry of the product was determined by X-ray analysis. The comparison of the retention time on the HPLC analysis indicated that the **DSI**-catalyzed hydroamination afforded the hydroamination product having the same absolute stereochemistry as the literature.

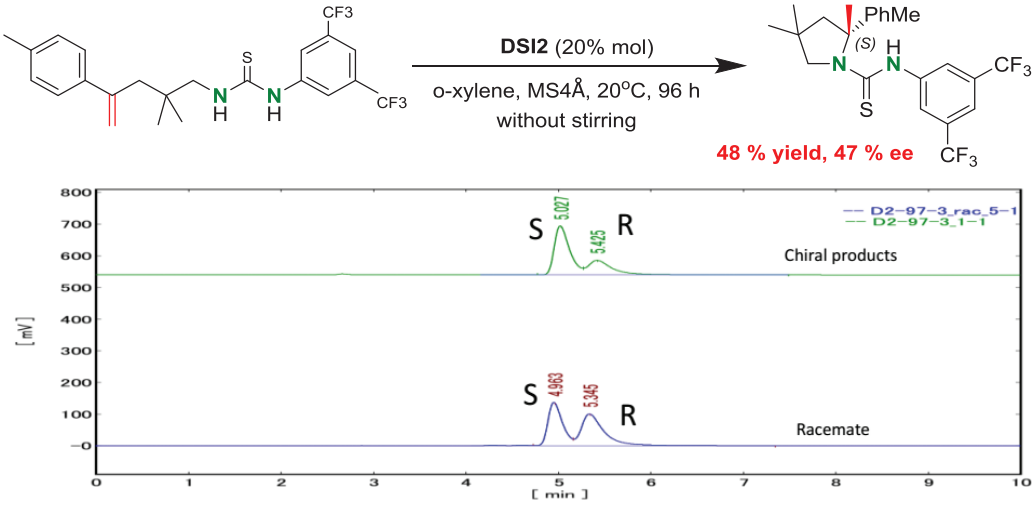


Figure 1. Chiral HPLC analysis using chiralpak IA column of the product on the hydroamination of alkenyl thiourea derivative (X = Me).

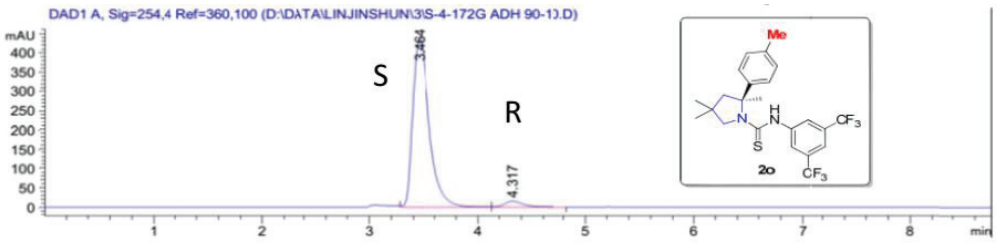
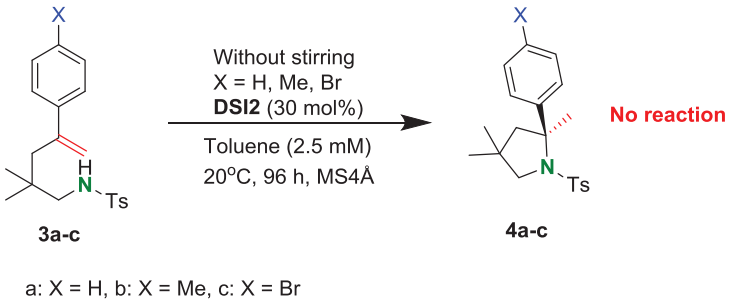


Figure 2. The reported chiral HPLC analysis using chiralpak AD-H column of the product on the hydroamination of alkenyl thiourea derivative (X = Me).

3-1.7. Hydroamination of *N*-Toluenesulfonyl (Ts) Alkenyl Amines and Effect of Thiourea Moiety

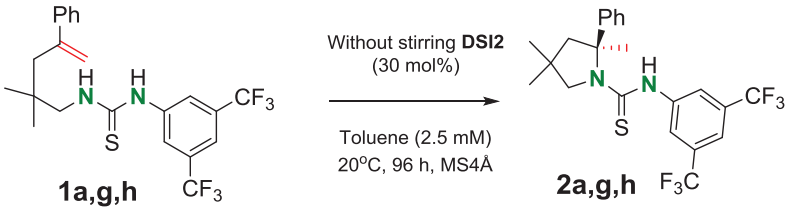
To understand the reaction mechanism, the hydroamination of alkenyl amines bearing several types of *N*-protective groups was examined. In the case of the hydroamination of *N*-toluenesulfonyl alkenyl amines **3a-c**, no reaction was observed (Scheme 4). It showed that the acidity of **DSI** was not sufficiently acidic to directly activate the alkene moiety of the alkenyl amines, even when the phenyl ring on the alkenyl amine was substituted with electron-donating groups (X). The results in Table 5 showed the importance of the 3,5-$(CF_3)_2C_6H_3$ substituted thiourea moiety for the activation of the alkene moiety of the alkenyl thiourea and asymmetric induction in the hydroamination reaction. This suggested that the thiourea moiety acted as a hydrogen bond donor rather than as a hydrogen bond acceptor.



a: X = H, b: X = Me, c: X = Br

Scheme 4. Hydroamination of *N*-Toluenesulfonyl (Ts) alkenyl amines.

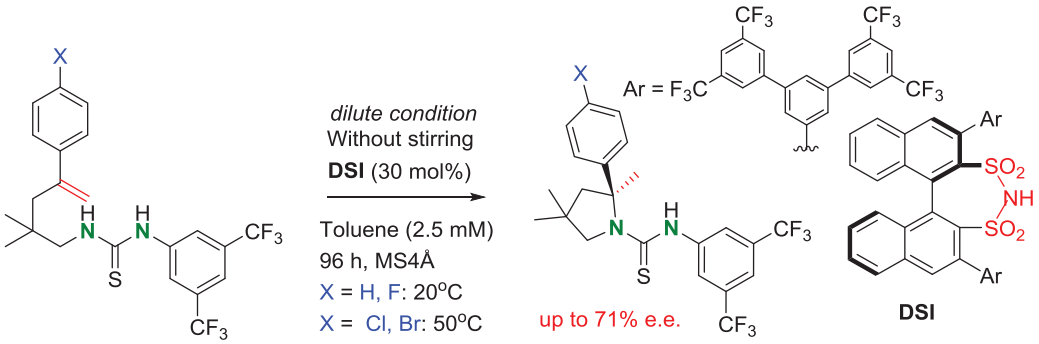
Table 5. Effect of Thiourea Moiety[a].



entry	substituent	yield (%)[b]	e.e.(%)[c]
1	Y = S, R = CF_3 (**a**)	86	70
2	Y = S, R = H (**g**)	0	---
3	Y = O, R = CF_3 (**h**)	10	58

[a]Reactions were performed with alkenyl amine (44 mmol), **DSI2** (30 mol%), MS4Å (50 mg) in toluene (17.4 mL) at 20°C for 96 h. The reactions were performed in a 5-mm NMR tube under non-stirring. b. Isolated yield.
c. Determined by chiral stationary phase HPLC.

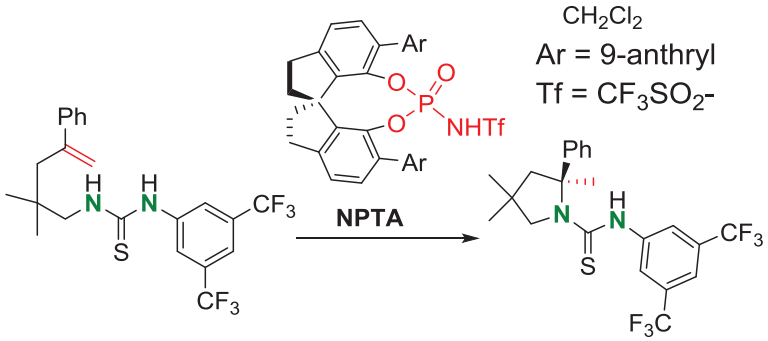
3-1.8. Conclusion



In conclusion, **DSI**-catalyzed hydroamination of alkenyl thiourea afforded the hydroamination product with good yield and moderate enantioselectivity under dilute concentration (2.5 mM) without stirring of the reaction mixture. The substituent on the phenyl ring of alkenyl thiourea significantly affected the reaction rate. When the electron-withdrawing group was introduced on the phenyl ring, the moderate enantioselectivity on the hydroamination product remained constant, although a higher reaction temperature was needed for the reaction progress.

3-2. Computational Mechanistic Study on DSI-catalyzed Asymmetric Intramolecular Hydroamination

3-2.1. Possible Mechanisms on DSI-Catalyzed Asymmetric Intramolecular Hydroamination



In previous work, Liu and coworkers proposed three possible mechanisms for hydroamination of alkenyl thiourea using **NPTA** (Figure 3)[24–26]. In modes **a** and **b**, the thiourea moiety of substrate acted as a hydrogen bond acceptor from **NPTA**. In mode **a**, the nitrogen atom of the thiourea moiety was activated by the hydrogen bonding from **NPTA**, then the acidity of the N-H bond of thiourea moiety was enhanced. The olefin of alkenyl thioureas was protonated by the activated N-H bond of the thiourea moiety. In mode **b**, the sulfur atom of the thiourea moiety made a hydrogen bond with **NPTA**, and the acidity of the S-H bond is enhanced. The olefin of alkenyl thioureas was protonated by the activated S-H bond. However, from considering the valency of the nitrogen atom in mode **a** and the nucleophilicity of the sulfur atom in mode **b**, it appeared that these structures were unsuitable. In mode **c**, thiourea acted as a dual hydrogen bond donor to activate **NPTA**. The olefin of alkenyl thioureas was activated by the activated **NPTA**. Liu and coworker only proposed three mechanisms and the detail of the mechanisms was not clear.

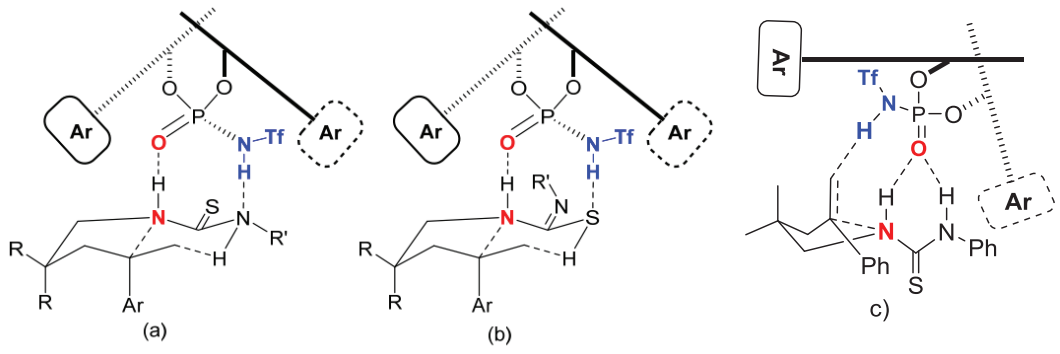


Figure 3. Possible mechanisms of **NPTA** catalyzed hydroamination of alkenyl thioureas: (a) and (b): Thiourea hydrogen bond acceptor, (c): thiourea hydrogen bond donor proposed by Liu et al.

3-2.2. DFT Calculation on HBr-Catalyzed Asymmetric Intramolecular Hydroamination

In order to determine hydrogen bond mode between alkenyl thiourea and Brønsted acid, density functional theory (DFT) calculations on the HBr-catalyzed intramolecular hydroamination of alkenyl thiourea as a simplified model were performed (Figure 4). Chiral phosphoric acids are generally known to create a chiral environment by dual hydrogen bonding with a substrate for the creation of high enantioselectivity[48,89–91], and it was assumed that HBr forms dual hydrogen bonding with alkenyl thiourea during hydroamination. In this model study, five possible hydrogen bonding modes **A**-**E** based on differing complexation between HBr and the thiourea moiety were considered. Among these, structures **B**, **D**, and **E** were the same hydrogen bond mode mentioned by Liu et al. in their reports[24,25]. Additionally, modes **A** and **C** as the transition state structure were proposed as applicable structures. The exploration of transition state structures based on the possible hydrogen bond modes **A–E** was carried out at the B3LYP/6‐31G(d,p) level of theory. The transition state structures (TS^{HBr}_{A-C} and TS^{HBr}_{D, E_TS1}) having a single imaginary frequency related to the olefin protonation from the hydrogen bond donor moiety were optimized. The intrinsic reaction coordinate (IRC) calculation of the transition state structures and the estimation of the Gibbs energy profile for the reaction pathway via hydrogen bonding modes **D** and **E** indicated that the reaction pathways via hydrogen bond modes **A**–**D** proceeded through a concerted mechanism in which olefin protonation and C−N bond formation occur more synchronously. The reaction pathway via mode **E** involved the formation of cation intermediate. The relative Gibbs energies suggested that hydrogen bond modes **C** or **E** were favoured for the hydroamination reaction pathway.

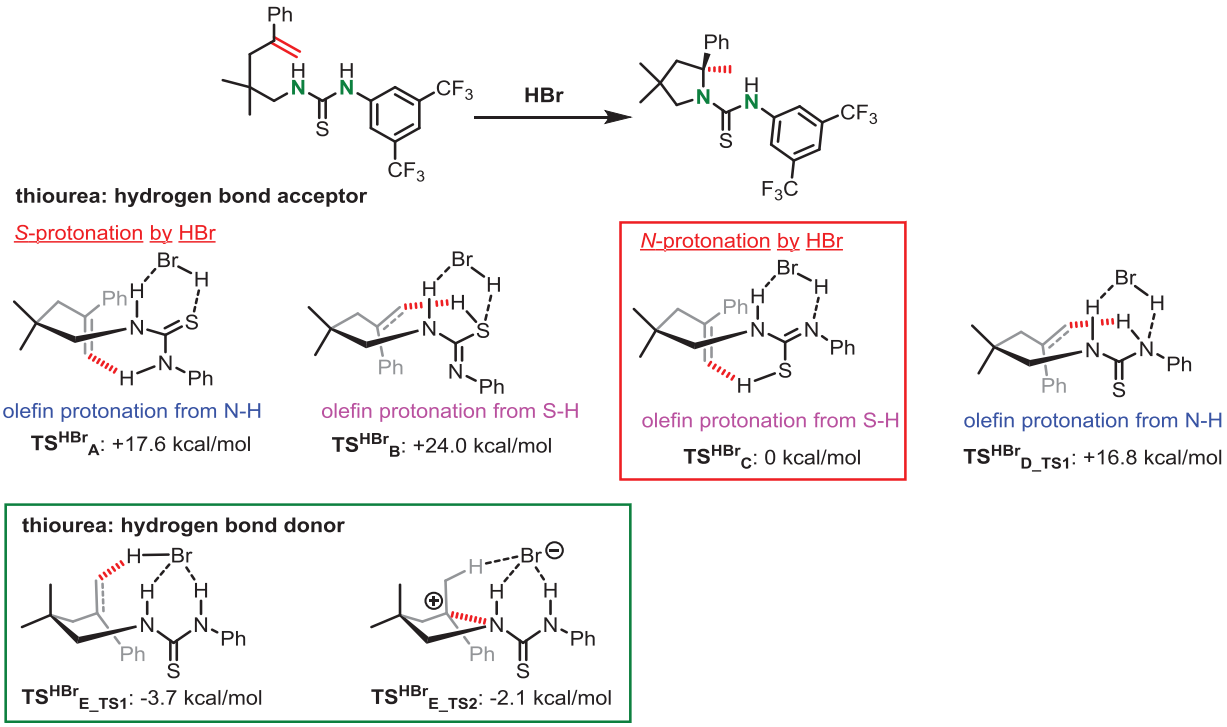


Figure 4. Schematic transition state structures based on possible hydrogen bonding modes in the HBr - catalyzed hydroamination of alkenyl thiourea and the relative Gibbs energies of transition states at 298.15 K at the B3LYP/6 - 31G(d,p) level of theory.

3-2.3. DFT Calculation on DSI-Catalyzed Asymmetric Intramolecular Hydroamination

Based on the above finding, computational studies on the enantioselective hydroamination of alkenyl thiourea catalyzed by **DSI** were conducted. There are 12 possible hydrogen bond modes for both enantiomers of the product (Figure 5). In the first 10 modes, thiourea acted as a hydrogen bonding acceptor from the catalyst and olefin was protonated by the activated S-H bond. In the last 2 cases, thiourea acted as a dual hydrogen bond donor and the olefin of alkenyl amine was protonated by the activated **DSI**. From the relative Gibbs energies of these structures, the transition state structure TSs was energetically most favoured for the hydroamination reaction pathway. The structure TSs gave the hydroamination product in agreement with the experimentally determined (*S*)-configuration.

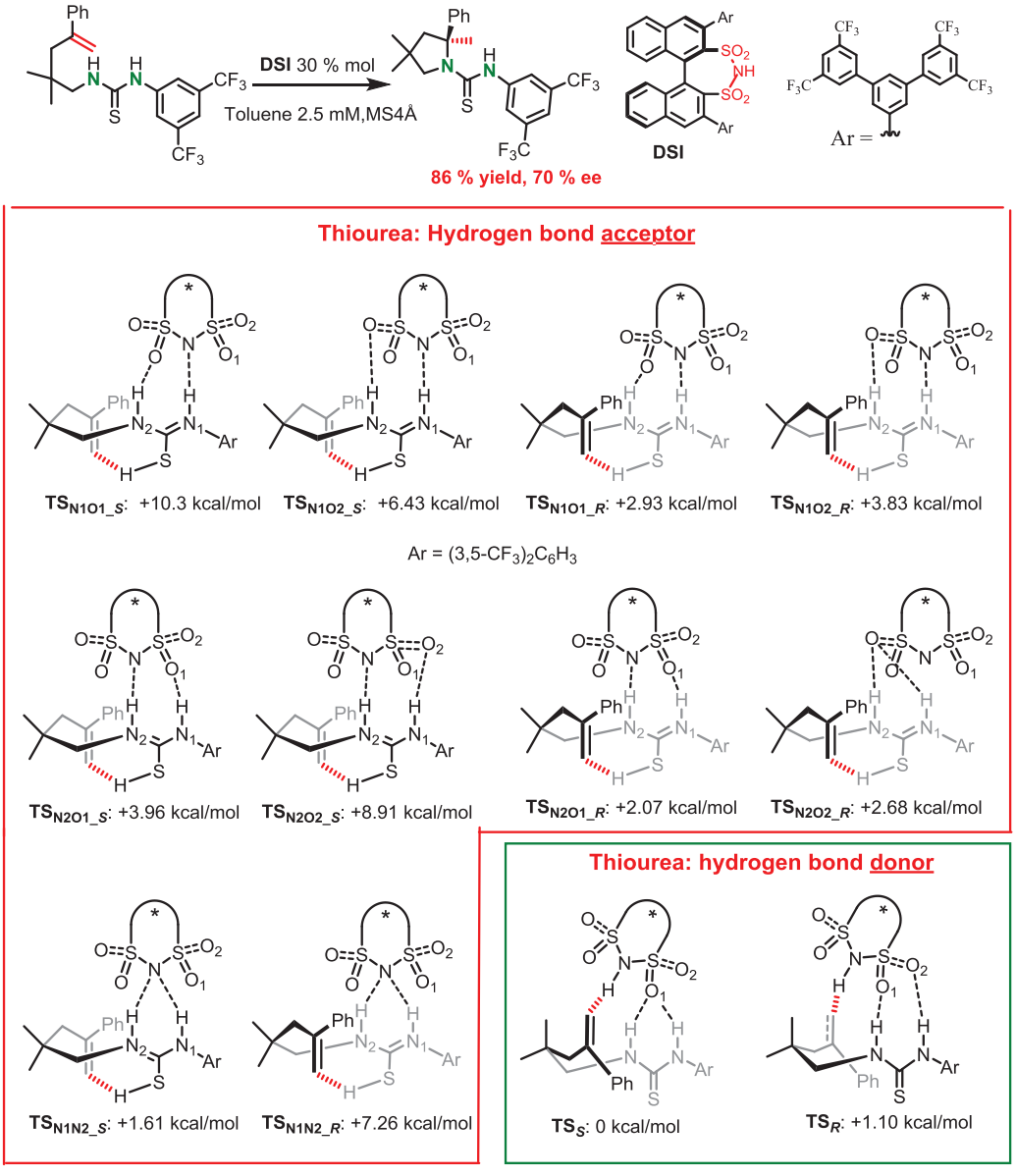


Figure 5. Schematic structures and relative energies of possible transition states (298.15 K in toluene) of the **DSI**-catalyzed hydroamination at the M06-2X/6-311+G(d,p)/SMD(toluene) //ONIOM(B3LYP/6-31G(d): HF/3-21G*) level of theory.

The Gibbs energy profile in toluene via TS_S and TS_R was examined to gain insights into the lowest energy path on the **DSI**-catalyzed hydroamination (Figure 6). The results showed that the reaction pathways proceeded through a stepwise mechanism in which the protonation of the olefin was a rate-determining step. **DSI** was activated by the dual hydrogen bond from thiourea moiety and then the olefin of alkenyl thiourea was protonated by the activated **DSI** to form the carbocation intermediate. In the second transition state, the carbocation was then attracted by the nucleophilic nitrogen to give the cyclized product.

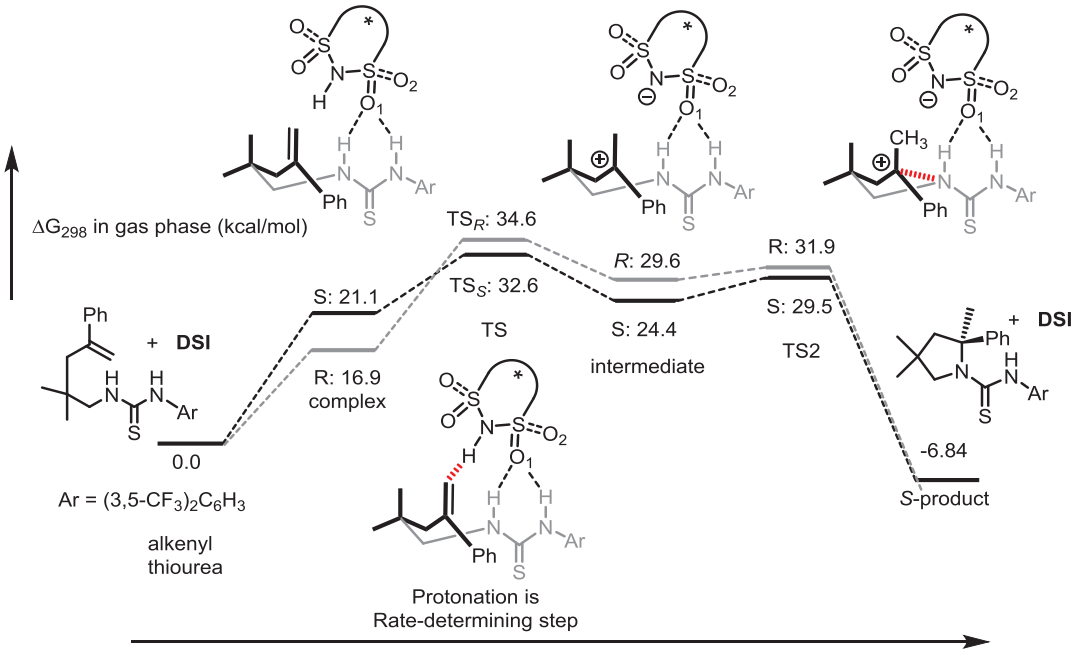


Figure 6. Calculated Gibbs energy profile for the **DSI**-catalysed hydroamination of alkenyl thiourea at 298.15 K in toluene at the M06-2X/6 311+G(d, p)/SMD (toluene)//ONIOM(M06-2X/6-31G(d): HF/3-21G*) level of theory.

3-2.4. Distortion/interaction analysis for TS_R and TS_S

Distortion/interaction analysis for TS_R and TS_S was conducted to understand the origin of enantioselectivity (Figure 7). The analysis indicated that the total distortion energy of substrate ($\Delta\Delta G^{\ddagger}_{dist\_sub}$) and catalyst ($\Delta\Delta G^{\ddagger}_{dist\_cat}$) was 0.2 kcal/mol and noncovalent interactions ($\Delta\Delta G^{\ddagger}_{int}$) between substrate and catalyst predominantly contributed to the enantioselectivity. The visualization of noncovalent interactions of TS_R and TS_S using IMGPlot showed the presence of the dual hydrogen bond and other noncovalent interactions between **DSI** and alkenyl thiourea (Figure 8).

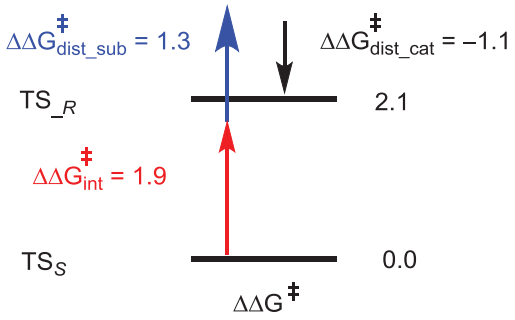


Figure 7. Distortion/interaction analysis for TS_R and TS_S.

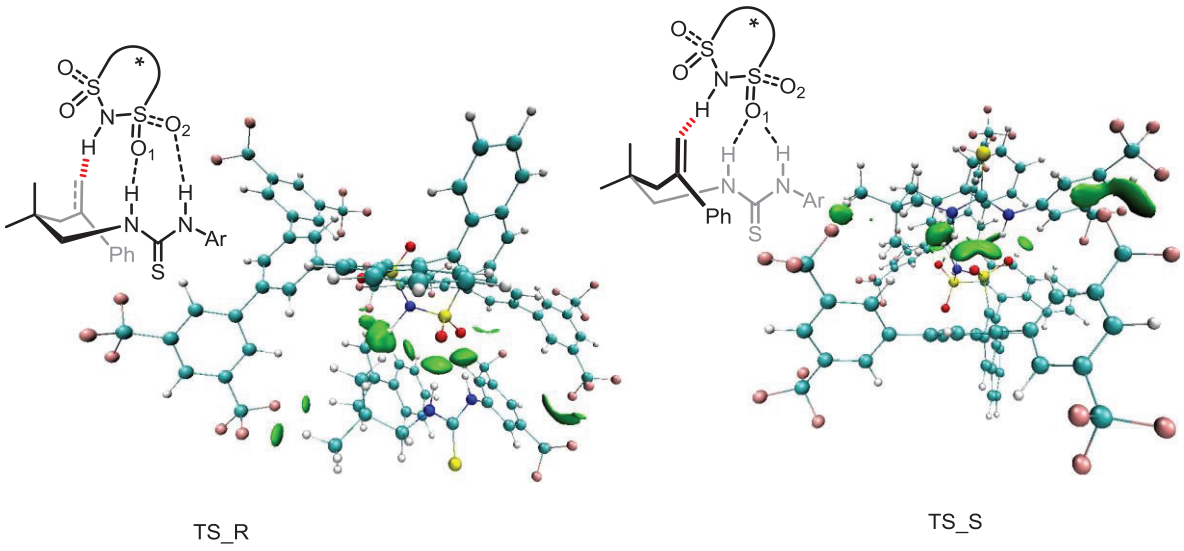


Figure 8. Nonbonding interactions visualized by IGMPlot.

3-2.5. Concentration Effect on Alkenyl Thiourea

To support the calculational result, the ^{1}H-NMR measurement of alkenyl amines from high concentration 100 mM to low concentration 2.5 mM was carried out (Figure 9). The spectra showed that the peak of the N_1-H moiety appeared at a higher magnetic field in a high concentration. The phenomena suggested that the self-association of thiourea was possible at high concentration[92,93]. In the diluted condition of the **DSI**-catalyzed hydroamination, the self-association of alkenyl thiourea can be avoided and **DSI** can be activated by a dual hydrogen bond from the thiourea moiety.

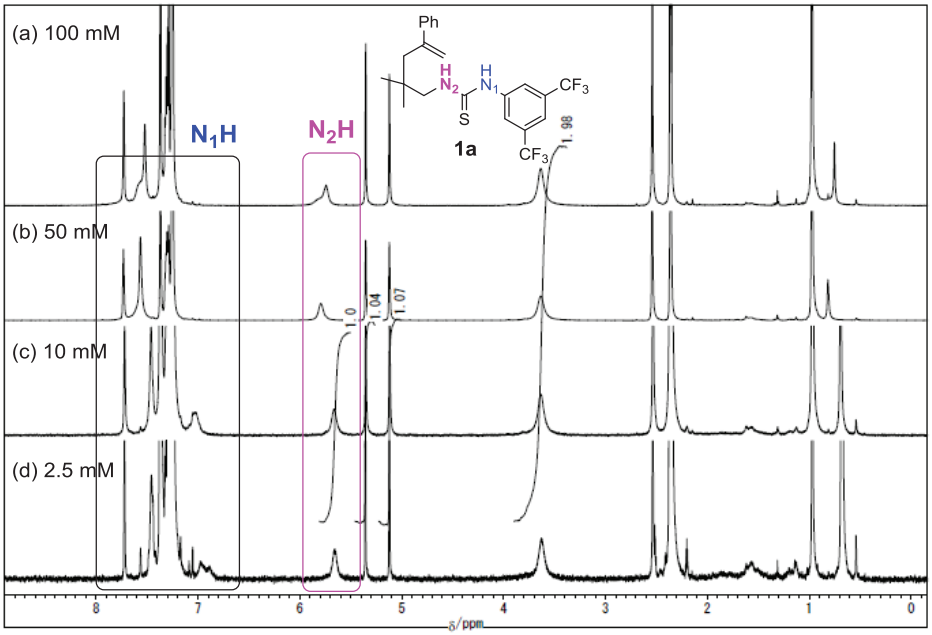
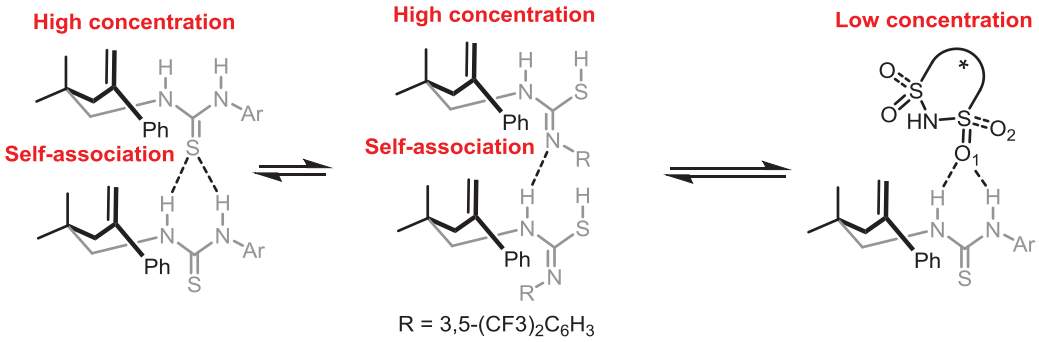
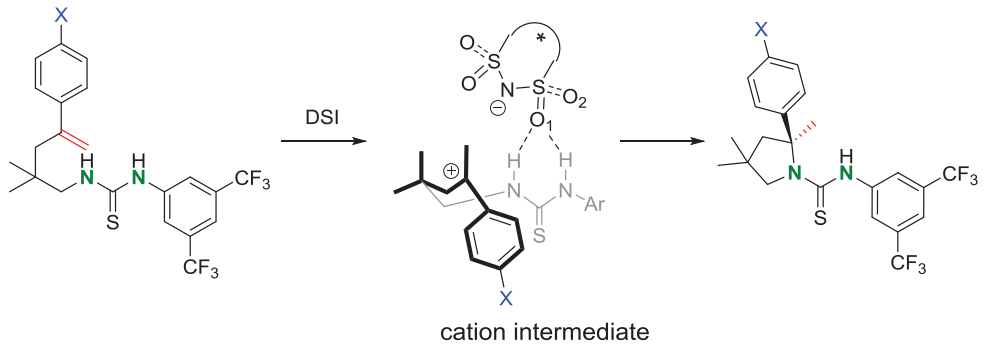


Figure 9. ^{1}H NMR spectra of alkenyl thiourea **1a** in toluene-d_8 at 25°C, (a) 100 mM, (b) 50 mM, (c) 10 mM, and (d) 2.5 mM.



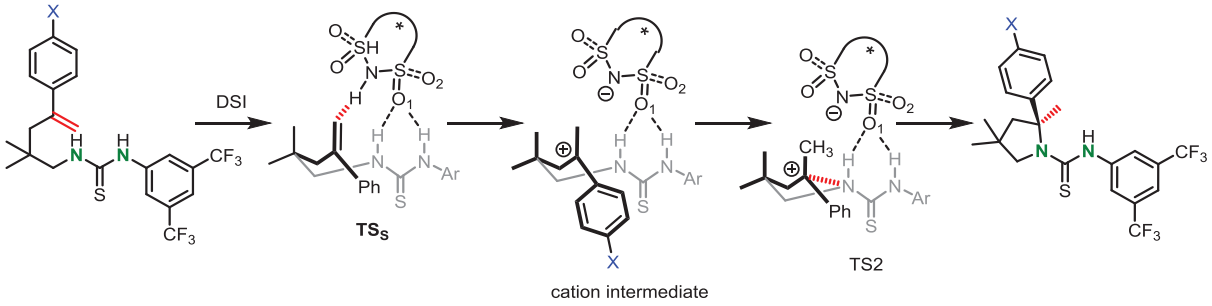
Scheme 5. Concentration effect on the **DSI**-catalyzed hydroamination.

3-2.6. Substituent Effect



The substituent effect of the phenyl ring of alkenyl thiourea on the **DSI**-catalyzed hydroamination is able to be explained by the stepwise mechanism. The electron-donating groups (MeO, Me) on the phenyl ring stabilized the cation intermediate and the reaction rate was accelerated. As a result, the asymmetric induction was not generated. In the case of the electron-withdrawing group (F, Cl, Br), although the intermediate was destabilized by the substituents, the hydroamination product was obtained with moderate enantioselectivity.

3-2.7. Conclusion



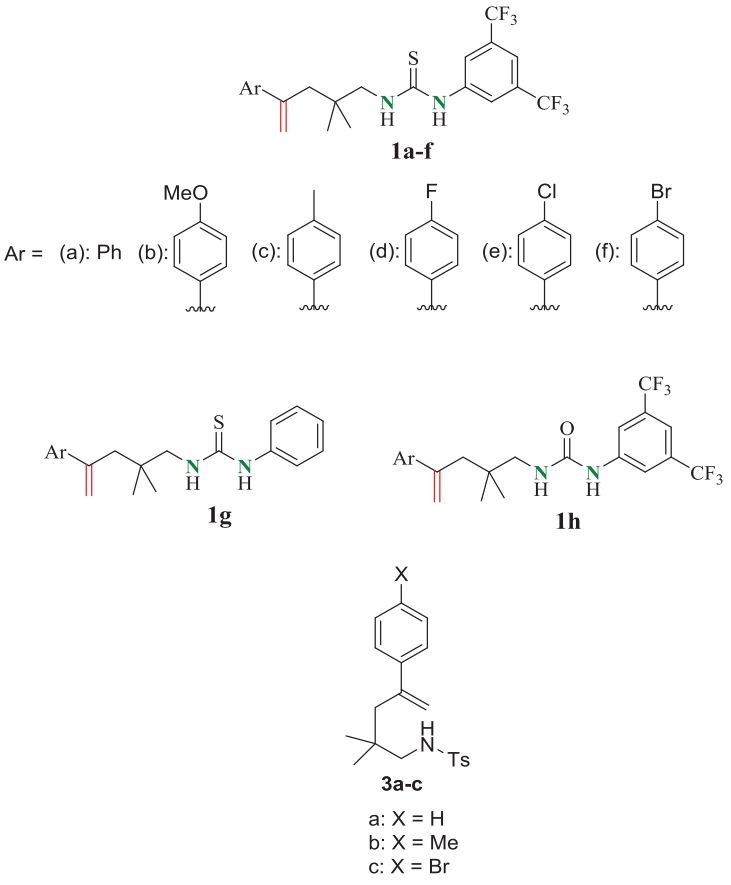
The mechanism for the intramolecular hydroamination of alkenyl thioureas catalyzed by **DSI** was investigated. The DFT calculations on the reaction supported the stepwise mechanism, in which thiourea moiety of alkenyl amines acted as a dual hydrogen bond donor to **DSI**.

3-2.8. Experimental Section

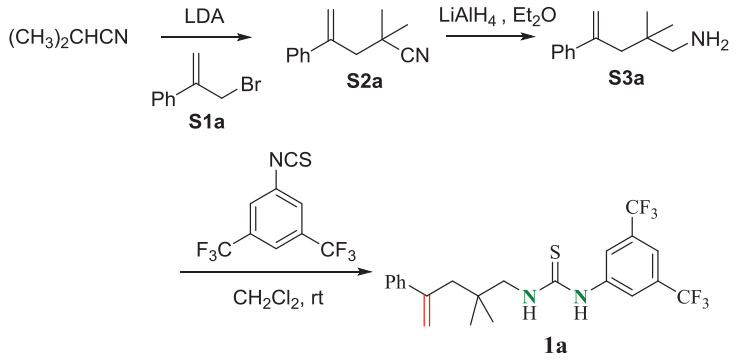
General experiment

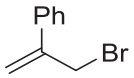
Internal references for ^{1}H NMR spectra were 0.0 ppm (Me_4Si) for $CDCl_3$, $(CD_3)_2CO$ (2.05 ppm) and MeOD (3.31 ppm and 4.78 ppm). Chemical shifts for ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm). High resolution mass spectral (HRMS) data were recorded with an LTQ Orbitrap trap mass spectrometer using the electrospray ionization (ESI) method. The enantiomeric excess (ee) of the products was determined by high performance liquid chromatography (HPLC) measured on a digital polarimeter with a 0.1 dm cell at room temperature. All reactions were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm).

3-2.8.1. Preparation of alkenyl amine



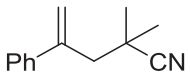
Preparation of 1a





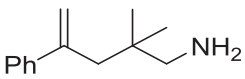
S1a

Alpha-methylstyrene (7 ml, 53.9 mmol) and $TsOH.H_2O$ (0.15 g, 0.77 mmol) were mixed in THF (140 ml). The mixture was refluxed at 100°C for 4 h. The reaction mixture was extracted with EtOAc, washed with 1N HCl and water, and dried over Na_2SO_4. The crude product was purified by hexane to give the desired product **S1a** (6.53 g, 62% yield). R_f= 0.8 (hexane), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.29 (m, 5H), 5.56 (s, 1H), 5.49 (s, 1H), 4.39 (s, 2H).



S2a

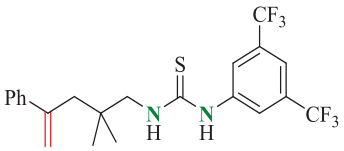
Isobutyronitrile (3.8 ml, 42 mmol) was added to a solution of LDA [generated in situ from *n*-BuLi (31 ml, 81 mmol) (in hexane, 2.6 M) and diisopropylamine (8.4 ml, 60 mmol) in THF (115 ml)] at -78°C and stirred for 45 min. To the resulting solution was added (3-bromoprop-1-en-2-yl)benzene **S1a** (6.53 g, 33 mmol) at -78°C. The solution was warmed up to room temperature overnight with stirring. The mixture was extracted with DCM, washed with water, dried over Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography (Hexane: EtOAc= 20:1) to give the desired product **S2a** as a liquid (6 g, 98 % yield). R_f= 0.3 (hexane: EtOAc= 5: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 5.44 (d, J = 1.2 Hz, 1H), 5.29 (d, J = 1.0 Hz, 1H), 2.77 (d, J = 0.8 Hz, 2H), 1.26 (s, 6H).



S3a

$LiAlH_4$ (2.5 g, 66 mmol) was added slowly to Et_2O (75 ml) at 0°C and then added 2,2-dimethyl-

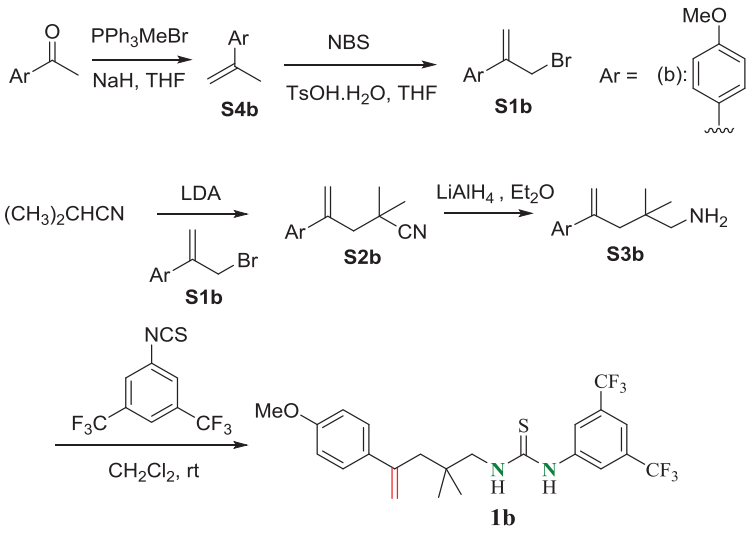
4-phenylpent-4-enenitrile **S2a** (6 g, 32 mmol) slowly to this mixture at 0°C. This mixture was stirred at room temperature overnight. The reaction mixture was quenched by adding dropwise KOH until the grey solid changed completely to the white solid, and then was filtrated. The filtrate was evaporated and 2,2-dimethyl-4-phenylpent-4-en-1-amine **S3a** was used for the next step (6.1 g, 100 %). R_f= 0.3 (hexane: EtOAc= 5: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 5H), 5.24 (d, *J* = 2.0 Hz, 1H), 5.10 – 4.98 (m, 1H), 2.48 (d, *J* = 0.5 Hz, 2H), 2.34 (d, *J* = 9.2 Hz, 2H), 0.74 (s, 6H).



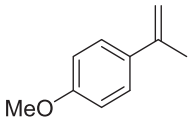
1a

To a stirred solution 2,2-dimethyl-4-phenylpent-4-en-1-amine **S3a** (0.94 g, 5 mmol) in CH_2Cl_2 (37 ml) was added aryl isothiocyanates (1 ml, 5 mmol) at room temperature. The reaction mixture was stirred overnight. The reaction mixture was concentrated to obtain the solid. The solid was washed with hexane and filtrated. The filtrate was concentrated to give the desired product **1a**[7] (2 g, 88 % yield). R_f= 0.58 (hexane: EtOAc= 5: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 19.2 Hz. 3H), 7.21 (s, 5H), 5.89 (s, 1H), 5.04 (s, 1H), 3.37 (s, 2H), 2.51 (s, 2H), 0.92 (s, 6H).

Preparation of 1b

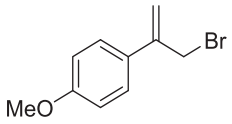


1b



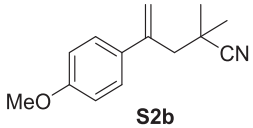
S4b

S4b was prepared according to the preparation of **S4a**. 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 2H), 6.93 – 6.77 (m, 2H), 5.28 (dd, *J* = 1.5, 0.7 Hz, 1H), 5.05 – 4.89 (m, 1H), 3.82 (s, 3H), 2.13 (dd, *J* = 1.4, 0.8 Hz, 3H).



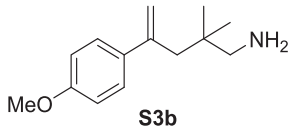
S1b

S1b was prepared according to the preparation of **S1a**. 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.41 (m, 2H), 6.93-6.88 (m, 2H), 5.48 (s, 1H), 5.40 (m, 1H), 4.37 (m, 2H), 3. 83 (m, 3H).



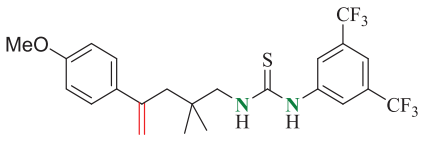
S2b

S2b was prepared according to the preparation of **S2a**. 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 6.89 – 6.84 (m, 2H), 5.37 (d, *J* = 1.3 Hz, 1H), 5.19 (d, *J* = 1.0 Hz, 1H), 3.81 (s, 3H), 2.74 (d, *J* = 0.6 Hz, 2H), 1.26 (s, 6H).



S3b

S3b was prepared according to the preparation of **S3a**. 100% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.17 (d, *J* = 2.0 Hz, 1H), 5.00 – 4.90 (m, 1H), 3.78 (s, 3H), 2.43 (s, 2H), 2.33 (s, 2H), 0.74 (s, 6H).

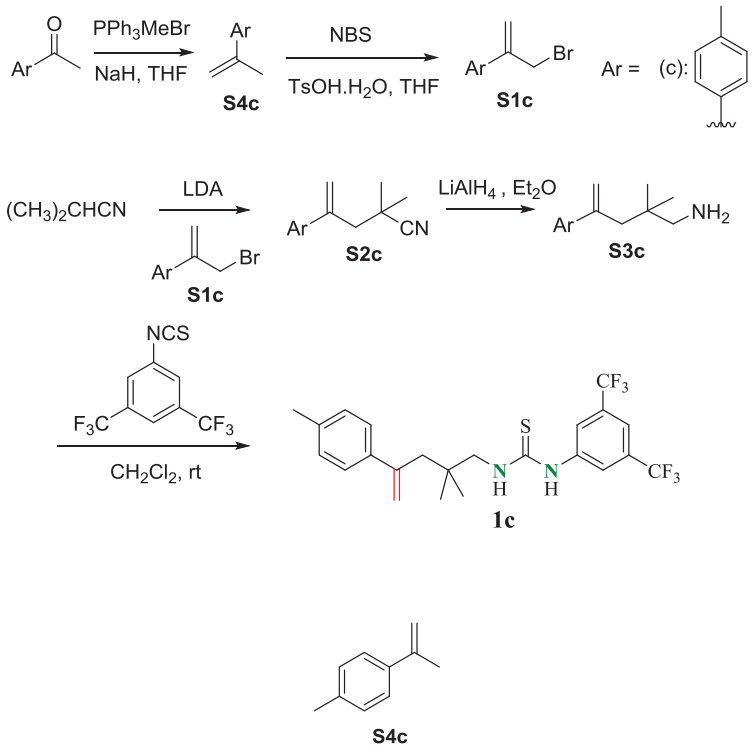


1b

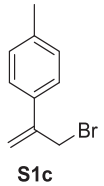
1b was prepared according to the preparation of **3a**. 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 9.3 Hz, 3H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 5.95 (s, 1H), 5.15 (s, 1H), 4.95 (s, 1H), 3.75 (s, 3H), 3.38 (s, 2H), 2.47 (s, 2H), 0.92 (s, 6H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 180.79, 159.13, 145.29, 138.98, 135.07, 133.25 (q, J = 34.9 Hz) (x2), 127.33 (x2), 123.86, 122.79 (q, J= 273.0 Hz) (x2), 119.26, 116.18, 113.80 (x2), 55.16, 54.89, 45.54, 35.76, 26.16 (x2).^{19}F NMR (376 MHz, $CDCl_3$) δ -63.01 (s). HRMS (ESI+) calcd for $C_{23}H_{24}ON_2F_6NaS$ $[M+Na]^+$ 513.14057, found 513.14112.

Preparation of 1c

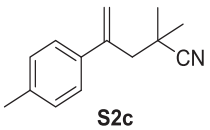


NaH (2 g, 0.083 mol) was added to the mixture of Ph_3PCH_3Br in THF at room temperature and stirred for 1 hour. Then the solution of 4'-methylacetophenone (5 ml, 0.037 mol) in THF was added dropwise to the reaction mixture at 0°C and refluxed overnight at 66°C. The reaction mixture was diluted with hexane and filtrated with silica gel. The filtrate was concentrated and purified by column chromatography (hexane) to give the product **S4c** (2.8 g, 64% yield). R_f= 0.55 (hexane), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.33 (s, 1H), 5.07 – 4.98 (m, 1H), 2.34 (s, 3H), 2.14 (s, 3H).



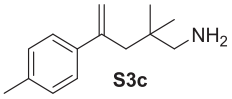
S1c

S1c was prepared according to the preparation of **S1a**. 59% yield. R_f= 0.55 (hexane), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.32 (m, 2H), 7.18 (d, J = 7.9 Hz, 2H), 5.52 (s, 1H), 5.44 (s, 1H), 4.38 (s, 2H), 2.36 (s, 3H).



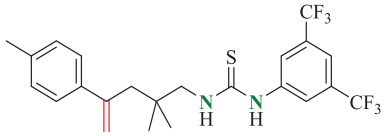
S2c

S2c was prepared according to the preparation of **S2a**. 62% yield. R_f= 0.59 (hexane: EtOAc= 5: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J*=*8.2*Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 5.41 (d, *J* = 1.1 Hz, 1H), 2.75 (s, 2H), 1.26 (s, 6H).



S3c

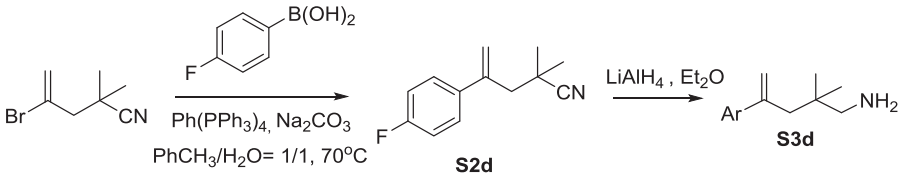
S3c was prepared according to the preparation of **S3a**. 100% yield. R_f= 0.28 ($CHCl_3$: MeOH= 5: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 1.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.21 (d, *J* = 2.0 Hz, 1H), 4.99 (d, *J* = 1.9 Hz, 1H), 2.45 (s, 2H), 2.34 (d, *J* = 4.6 Hz, 4H), 0.75 (s, 6H).



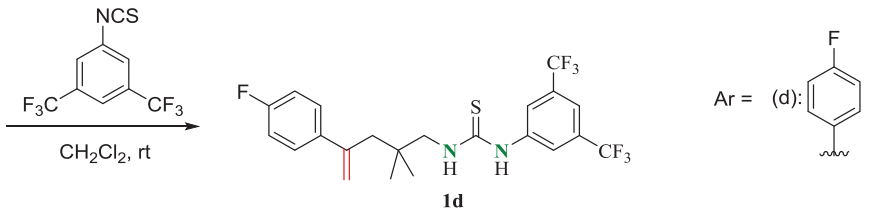
1c

1c[26] was prepared according to the preparation of **1a**. 95% yield. R_f= 0.14 (hexane: EtOAc= 10: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 17.9 Hz, 3H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 5.88 (s, 1H), 5.19 (s, 1H), 4.99 (s, 1H), 3.36 (s, 2H), 2.48 (s, 2H),2.26 (s, 3H), 0.92 (s, 6H).

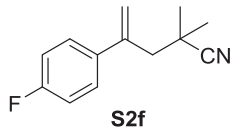
Preparation of 1d



S2d **S3d**

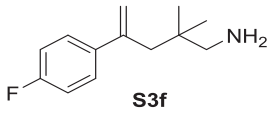


1d



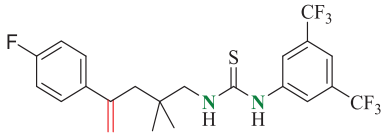
S2f

4-fluorophenylboronic acid (0.77 g, 5.5 mmol), sodium carbonate (1.78 g, 16.8 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.24 g, 0.21 mmol) were added to 4-bromo-2,2-dimethylpent-4-enenitrile (0.79 g, 4.2 mmol) in toluene/water (1/1) (12 ml) and then this mixture was degassed and refluxed at 70ºC for 18 h under nitrogen atmosphere. The reaction mixture was diluted by ethyl acetate and washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography (Hexane: EtOAc= 40: 1) to give the desired product **S2f** as a colorless liquid (0.51 g, 60 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 2H), 7.08 – 6.97 (m, 1H), 5.39 (d, J = 0.9 Hz, 1H), 5.26 (s, 2H), 2.73 (d, J = 0.5 Hz, 2H), 1.26 (s, 6H).



S3f

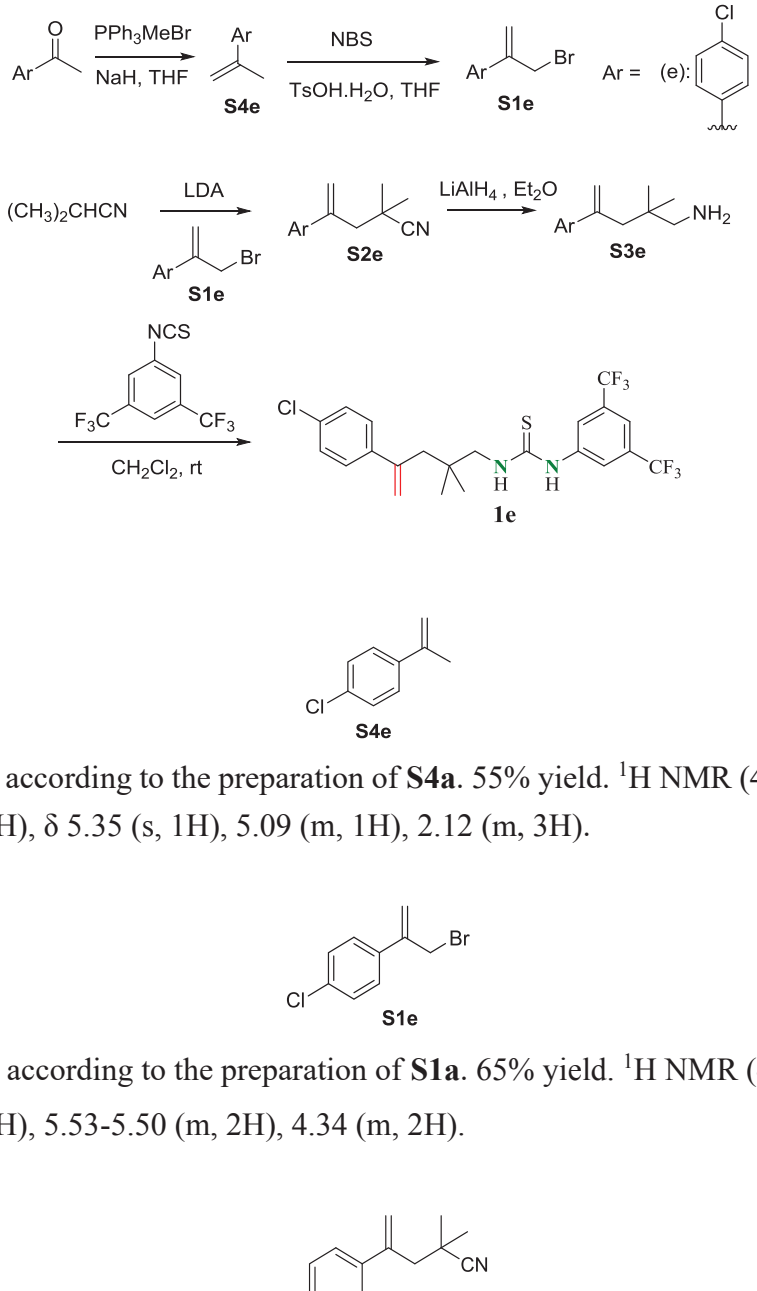
S3f was prepared according to the preparation of **S3a**. 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.08 – 6.90 (m, 2H), 5.20 (d, J = 1.8 Hz, 1H), 5.03 (d, J = 0.8 Hz, 1H), 2.45 (s, 2H), 2.35 (s, 2H), 0.73 (s, 6H).



1f

1b[26] was prepared according to the preparation of **1a**. 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 15.5 Hz, 3H), 7.25 – 7.18 (m, 2H), 6.92 (t, J = 8.5 Hz, 2H), 5.99 (s, 1H), 5.19 (s, 1H), 5.01 (s, 1H), 3.42 (s, 2H), 2.48 (s, 2H), 0.87 (s, 6H).

Preparation of 1e



S4e

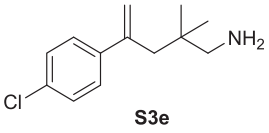
S4e was prepared according to the preparation of **S4a**. 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.30 (m, 4H), δ 5.35 (s, 1H), 5.09 (m, 1H), 2.12 (m, 3H).

S1e

S1e was prepared according to the preparation of **S1a**. 65% yield. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.44-7.30 (m, 4H), 5.53-5.50 (m, 2H), 4.34 (m, 2H).

S2e

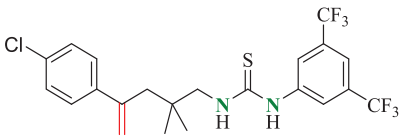
S2e was prepared according to the preparation of **S2a**. 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 5.43 (d, 1H), 5.30 (d, 1H), 2.73 (s, 2H), 1.26 (s, 6H).



S3e

S3e was prepared according to the preparation of **S3a**. 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 5.23 (d, J = 1.8 Hz, 1H), 5.06 (dd, J = 1.9, 1.0Hz, 1H), 2.45 (d, J = 0.9

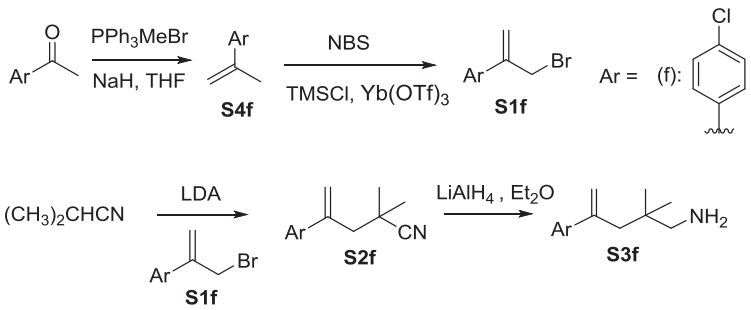
Hz, 2H), 2.35 (s, 2H), 0.73 (s, 6H).

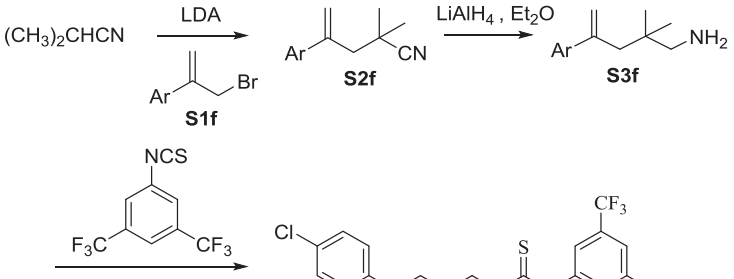


1e

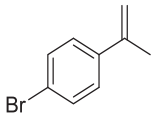
1e was prepared according to the preparation of **1a**. 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 14.7 Hz, 3H), 7.20 (s, 4H), 5.96 (s, 1H), 5.23 (s, 1H), 5.05 (s, 1H), 3.41 (s, 2H), 2.49 (s, 2H), 0.87 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.83, 144.79, 141.24, 138.85, 133.34, 133.13(q, *J* = 30.7 Hz) (x2), 128.57(x2), 127.57(x2), 123.85(x2), 122.74 (q, *J* =273.1 Hz) (x2), 119.48 – 118.33, 118.10, 55.09, 45.34, 35.81, 25.92(x2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.02 (s). HRMS (ESI+) *m/z* calcd for $C_{22}H_{22}N_2ClF_6S$ $[M+H]^+$ 495.10909 found 495.10904.

Preparation of 1f



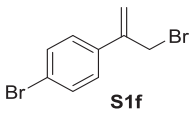


1f



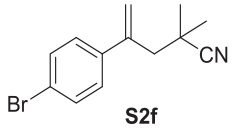
S4f

S4f was prepared according to the preparation of **S4a**. 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.36 – 7.28 (m, 2H), 5.39 – 5.33 (m, 1H), 5.12 – 5.07 (m, 1H), 2.13 (dd, J = 1.4, 0.8 Hz, 3H).



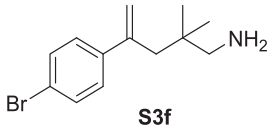
S1f

To a mixture of the 1-bromo-4-(prop-1-en-2-yl)benzene (0.98 g, 5 mmol) **S4f** and TMSCl (6.7 mg, 0.06 mmol) in CH_2Cl_2/THF (4:1) (15 ml) under an nitrogen atmosphere were added NBS (1 g, 5.8 mmol) and $Yb(OTf)_3$ (39 mg, 0.06 mmol) in one portion. After stirring for 1.5 h, the mixture was concentrated under reduced pressure. The resulting residue was filtered three times with hexane, and the combined filtrates were concentrated under reduced pressure. The crude product mixture was then purified by silica gel chromatography (hexane) to give the product **S1f** (0.54 g, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 5.54 (s, 1H), 5.50 (s, 1H), 4.33 (s, 2H).



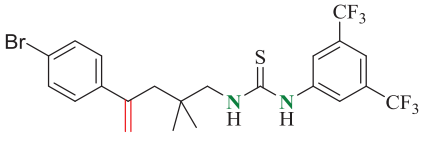
S2f

S2f was prepared according to the preparation of **S2a**. 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 5.44 (d, *J* = 1.0 Hz, 1H), 5.30 (d, *J* = 0.8 Hz, 1H), 2.73 (d, *J* = 0.6 Hz, 2H), 1.26 (s, 6H).



S3f

S3f was prepared according to the preparation of **S3a**. 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.27 – 7.22 (m, 2H), 5.24 (d, *J* = 1.7 Hz, 1H), 5.07 – 5.02 (m, 1H), 2.44 (s, 2H), 2.34 (s, 2H), 0.73 (d, *J* = 5.3 Hz, 6H).

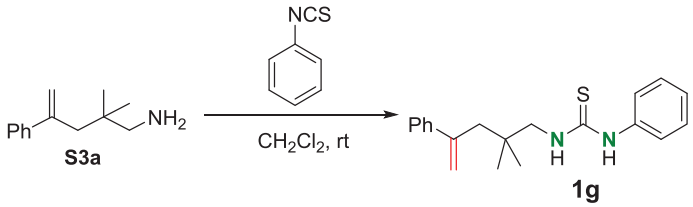


1f

1f was prepared according to the preparation of **1a**. 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.75 (s, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.05 (s, 1H), 5.23 (s, 1H), 5.04 (s, 1H), 3.42 (s, 2H), 2.47 (s, 2H), 0.85 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.99, 144.88, 141.74, 138.69, 133.32 (q, *J* = 67.0, 33.4 Hz) (x2),131.59 (x2) , 127.92 (x2) , 123.93 (x2), 122.51 (q, *J* = 128.4 Hz) (x2), 121.51, 119.65 – 119.51, 118.22, 55.12, 45.40,

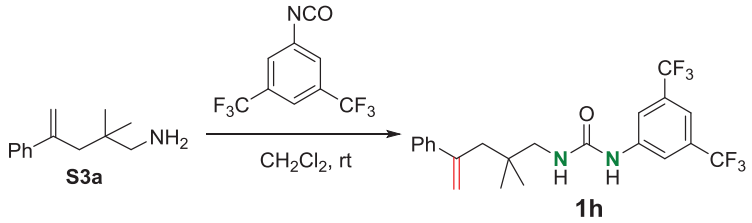
35.87, 26.03(x2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.00 (s). HRMS (ESI+), *m/z* calcd for $C_{22}H_{22}N_2BrF_6S$ $[M+H]^+$ 539.05858, found 539.05908.

Preparation of 1g



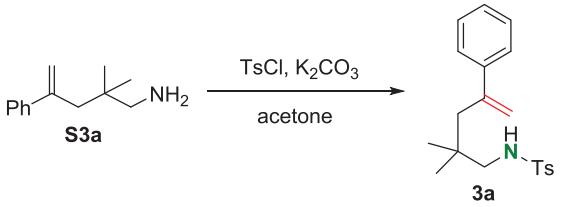
To a stirred solution amine (0.23 g, 0.0012 mol) in CH_2Cl_2 (9.4 ml) was added aryl isothiocyanates (0.2 g, 0.0002 mol) at room temperature. The reaction mixture was stirred overnight. The reaction mixture was concentrated and purified by column chromatography (Hexane: EtOAc= 5: 1) give the product **1g** (0.32 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.73 (bs, 2H), 7.20 (bs, 4H), 5.96 (s, 1H), 5.23 (s, 1H), 5.05 (s, 1H), 3.41 (bs, 2H), 2.49 (s, 2H), 0.87 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 144.8, 141.2, 138.9, 133.3, 133.1 (q, *J* = 29.3 Hz, x2), 128.6 (x2), 127.6 (x2), 123.8 (x2), 122.7 (q, *J* = 273.3 Hz, x2), 119.3, 118.1, 55.1, 45.3, 35.8, 26.0 (x2). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0. HRMS (ESI+) *m/z* calcd for $C_{22}H_{22}N_2ClF_6S$ $[M+H]^+$ 495.10909, found 495.10904.

Preparation of 1h



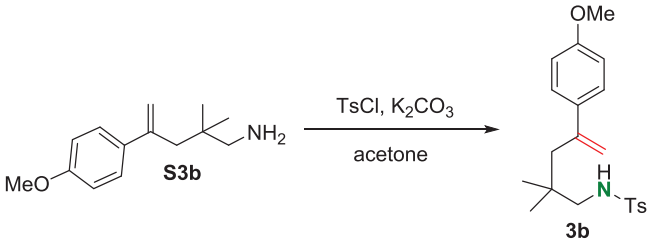
1h[94] was prepared according to the preparation of **1g**. 95% yield. ^{1}H NMR (400 MHz, CDCl3) δ 7.89 – 7.29 (m, 7H), 6.41 (d, *J* = 75.3 Hz, 1H), 5.28 (s, 1H), 5.08 (s, 1H), 4.50 (d, *J* = 41.4 Hz, 1H), 2.99 (d, *J* = 6.3 Hz, 2H), 2.51 (s, 2H), 0.84 (d, *J* = 3.2 Hz, 5H).

Preparation of 3a



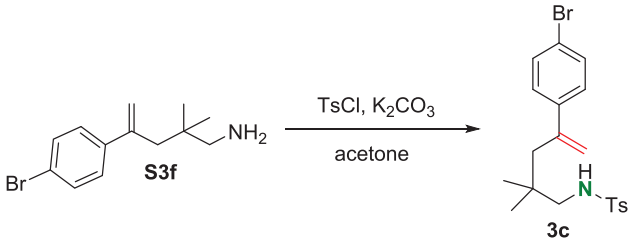
2,2-Dimethyl-4-phenylpent-4-en-1-amine (100.6 mg, 0.56 mmol) **S2a**, K_2CO_3 (144 mg, 1 mmol), and 4-methylbenzenesulfonyl chloride (111 mg, 0.58 mmol) in acetone (0.53 ml) were refluxed at 60°C for 12 h, quenched with saturated NH_4Cl, extracted with EtOAc and brine, dried over Na_2SO_4, and then concentrated in vacuo. The crude products were isolated by column chromatography on silica gel using EtOAc: hexane= 5: 1 to give the product **3a**[26] (84 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.31 – 7.22 (m, 7H), 5.22 (d, *J* = 1.8 Hz, 1H), 5.04 – 4.99 (m, 1H), 4.13 (dd, *J* = 8.7, 5.6 Hz, 1H), 2.46 (dd, *J* = 22.9, 10.8 Hz, 7H), 0.79 (s, 6H).

Preparation of 3b



3b was prepared according to the preparation of **3a**. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.37 (m, 2H), 7.26 (s, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.18 (d, *J* = 1.8 Hz, 1H), 5.03 – 4.87 (m, 1H), 4.08 (t, *J* = 7.2 Hz, 1H), 2.79 – 1.89 (m, 10H), 0.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.89, 143.06, 140.40, 137.02, 129.53(x2), 129.19(x2), 126.95(x2), 126.28(x2), 116.83, 52.97, 44.82, 35.18(x2), 25.65(x2), 21.52, 21.12. HRMS (ESI+) *m/z* calcd for $C_{21}H_{27}O_2NNaS$ $[M+Na]^+$ 380.16547, found 380.16580.

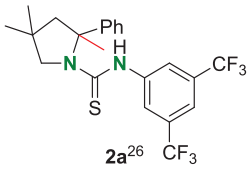
Preparation of 3c



3c was prepared according to the preparation of **3a**. 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.34 – 7.24 (m, 2H), 7.21 – 7.12 (m, 2H), 5.22 (d, *J* = 1.6 Hz, 1H), 5.05 (s, 1H), 4.14 (t, *J* = 7.2 Hz, 1H), 2.47 (dd, *J* = 27.4, 4.9 Hz, 6H), 0.79 (d, *J* = 5.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.96, 143.30, 142.18, 136.79(x2), 131.59(x2), 129.67(x2), 128.03(x2), 126.90(x2), 121.36, 118.22, 53.05, 44.85, 35.24, 25.52(x2), 21.54. HRMS (ESI+), *m*/*z* calcd for $C_{20}H_{24}O_2NBrNaS$ $[M+Na]^+$ 444.06033, found 444.06042.

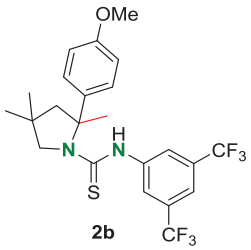
3-2.8.2. Typical procedure for asymmetric hydroamination of alkenyl thioureas

The substrate (20.2 mg, 44 mmol), **DSI** (12.3 mg, 8.8 mmol), and molecular sieves MS4Å (55.8 mg) and toluene (17.4 mL) were added to the test tube and was kept for 1 h at 20°C and then alkenyl thiourea (20.2 mg, 44 mmol) was added and kept for 4 days. The reaction mixture was added $NaHCO_3$ and kept for 15 min and filtered. The filtrate was concentrated and purified by column chromatography (Hexane: EtOAc= 40: 1) to give the chiral product (17.4 mg, 86%). The ee value was determined by the chiral stationary phase HPLC of the isolated product.



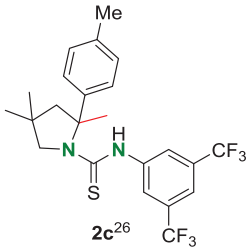
2a[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.27 (m, 8H), 6.84 (s, 1H), 4.37 (d, *J* = 12.6 Hz, 1H), 4.04 (d, *J* = 12.6 Hz, 1H), 2.36 (dd, *J* = 33.1, 13.7 Hz, 2H), 2.04 (s, 3H), 1.33 (s, 3H), 1.17 (s, 3H).



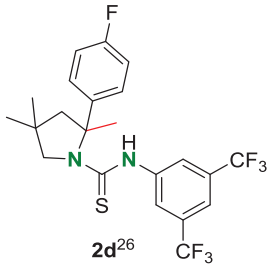
2b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.45 – 7.29 (m, 4H), 7.06 – 6.99 (m, 2H), 6.98 (s, 1H), 4.34 (d, *J* = 12.6 Hz, 1H), 4.02 (d, *J* = 12.7 Hz, 1H), 3.86 (s, 3H), 2.33 (dd, *J* = 31.1, 13.5 Hz, 2H), 2.00 (s, 3H), 1.32 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.28, 159.73, 140.76, 136.73, 131.44 (q, *J* =33.5 Hz) (x2),126.85(x2), 123.07 (q, *J* =272.8 Hz) (x2),124.12-124.09(x2), 118.23-118.09, 115.11(x2), 69.00, 68.58, 61.44, 55.44, 34.99, 29.07, 28.92, 26.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.04 (s). HRMS (ESI+) *m*/*z* cacld for $C_{23}H_{25}ON_2F_6S$ $[M+H]^+$ 491.15863, found 491.15918.



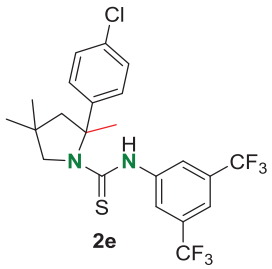
2c[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 3H), 7.79 (dd, *J* = 13.8, 5.0 Hz, 4H), 7.71 (s, 2H), 7.43 (ddd, *J* = 8.1, 4.8, 3.2 Hz, 1H), 7.32 (s, 1H), 7.31 – 7.27 (m, 2H), 4.43 (dd, *J* = 15.7, 5.7 Hz, 2H), 2.41 (s, 3H).



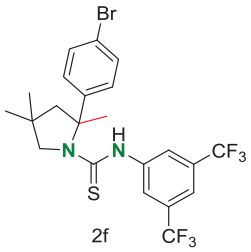
2d[26]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.35 (m, 4H), 7.19 (t, *J* = 8.5 Hz, 3H), N-H: 6.81 (s, 1H), 4.35 (d, *J* = 12.4 Hz, 1H), 4.02 (d, *J* = 12.6 Hz, 1H), 2.32 (s, 2H), 2.04 (s, 3H), 1.31 (s, 3H), 1.14 (s, 3H).



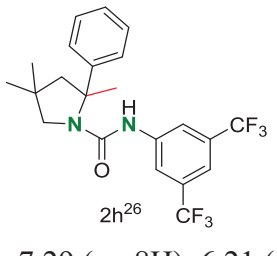
2e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.47 (d, *J* = 8.6 Hz, 3H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.77 (s, 1H), 4.33 (d, *J* = 12.8 Hz, 1H), 4.02 (d, *J* = 12.6 Hz, 1H), 2.32 (s, 2H), 2.04 (s, 3H), 1.30 (s, 3H), 1.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.68, 143.75, 140.52, 134.59, 131.66 (q, *J* = 33.6 Hz) (x2), 129.95 (x2), 126.85 (x2), 124.59-124.56 (x2), 122.99 (q, *J* =272.8 Hz) (x2), 121.63, 118.78-118.63, 68.79 (d, *J* = 20.2 Hz), 61.57, 35.16, 28.88, 28.57, 26.73. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.01 (s). HRMS (ESI+) calcd for $C_{22}H_{22}N_2ClF_6S$ $[M+H]^+$ 495.10909, found 495.10909.



2f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 2H), 7.48 (s, 2H), 7.33 – 7.23 (m, 3H), 6.76 (s, 1H), 4.32 (d, *J* = 12.6 Hz, 1H), 4.02 (d, *J* = 12.6 Hz, 1H), 2.32 (s, 2H), 2.03 (s, 3H), 1.30 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.71(x2), 144.30, 140.50, 132.93(x2), 131.67 (q, *J* = 33.6 Hz) (x2), 127.14(x2), 123.25 (q, *J* = 272.7 Hz) (x2), 124.63-124.60(x2), 122.58, 118.82-118.67(x2), 68.75 (d, *J* = 24.9 Hz), 61.53, 35.17, 28.88, 28.56, 26.71. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99. HRMS (ESI+) *m/z* calcd for $C_{22}H_{22}N_2BrF_6S$ $[M+H]^+$ 539.05858, found 539.05865.



2h[26]

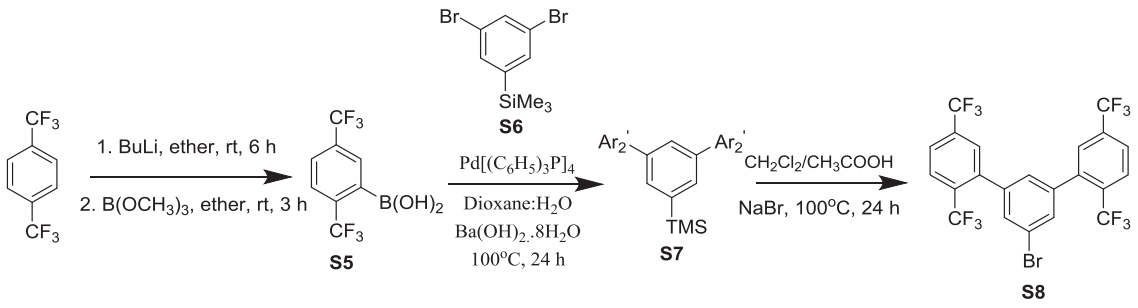
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.29 (m, 8H), 6.21 (s, 1H), 3.74 (d, *J* = 10.6 Hz, 1H), 3.64 (d, *J* = 10.6 Hz, 1H), 2.35 – 2.07 (m, 2H), 1.94 (s, 3H), 1.27 (d, *J* = 6.0 Hz, 3H), 1.12 (s, 3H).

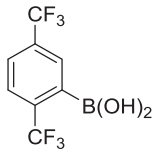
3-2.8.3. Preparation of DSI

DSIs were prepared according to the literature procedure[28,88] and the preparation of **DSATf**. **DSI** was dried in vacuo at 50°C for 3 h before using.

Preparation of DSI via the final sulfonimide formation

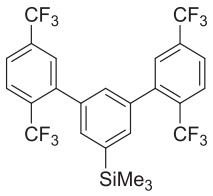
Preparation of Ar substituent for DSI3





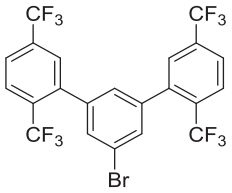
S5

n-BuLi (2.7 M in hexane, 37 mL, 0.1 mol) in hexane was mixed with bis(trifluoromethyl)benzene (14 ml, 0.09 mol) was added dropwise to this solution at room temperature. After refluxing for 6 h, this solution was added dropwise, over a 1 h period, from a dropping funnel to a flask in an ice bath containing trimethyl borate (25 ml, 0.23 mol) mixed with ether (180 ml). The mixture was further stirred for 2 h at room temperature. Then, the mixture was poured into 1N HCl. The ether layer was separated and washed with water. The product was dried over $MgSO_4$. The solvent was evaporated and the crude product was washed with hexane to give the product (11.6 g, 50%). R_f= 0.27 (hexane: EtOAc= 4: 1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.81 (q, *J* = 8.*4* Hz, 2H), 4.81 (s, 2H).



S7

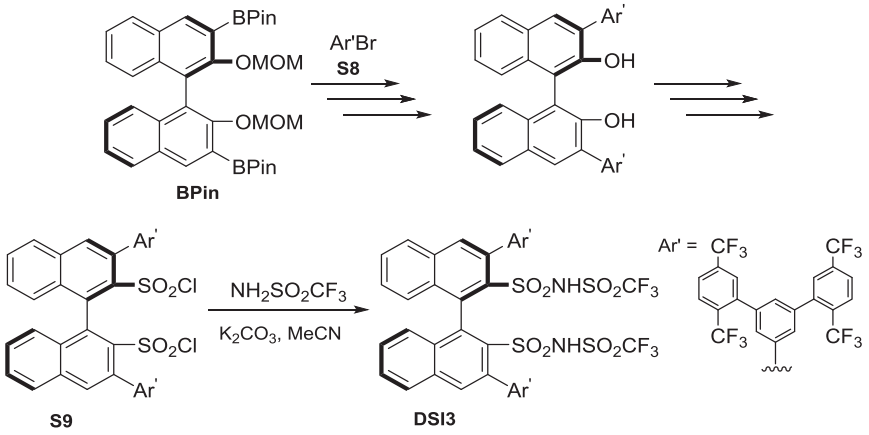
3,5-dibromo trisilyl benzene **S6** (0.85 g, 2.75 mmol), barium hydroxide octahydrate (3 g, 9.6 mmol), $ArB(OH)_2$ **S5** (2.86 g, 11 mmol), and $Pd[(C_6H_5)_3P]_4$ (0.26 g, 0.2 mmol) were mixed in dioxane: H_2O (5:1) (48 ml). The mixture was stirred at 100°C for 24 h under nitrogen atmosphere. The reaction mixture was quenched with 1M HCl for 1 h, extracted with CH_2Cl_2, washed with brine, and dried with Na_2SO_4. The crude product was purified by column chromatography (hexane) to give the desired product **S7** (1.4 g, 89%). R_f= 0.45 (hexane), ^{1}H NMR (400 MHz, Acetone) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 (s, 2H), 7.50 (d, *J* = 1.4 Hz, 2H), 7.29 (s, 1H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.02 (s), 139.73 (s), 134.29 (s), 133.96 (s), 133.67 (s), 133.47 (d, *J* = 33.3 Hz), 132.45 (s), 132.14 (s), 131.83 (s), 131.64 (d, *J* = 22.4 Hz), 128.71 (q, *J* = 3.6 Hz), 128.19 (s), 127.76 – 126.71 (m), 125.15 (q, *J* = 3.7 Hz), 124.47 (d, *J* = 4.3 Hz), 121.75 (s), 119.03 (s).^{19}F NMR (376 MHz, $CDCl_3$) δ -57.54 (s), -63.19 (s). HRMS (ESI+) *m/z* calcd for $C_{25}H_{18}F_{12}Si_1[M]^{+\cdot}$574.09861, found 574.09898, m.p 98-108°C.

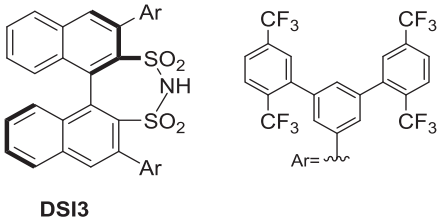


S8

Trimethyl(2,2",5,5"-tetrakis(trifluoromethyl)-[1,1':3',1"-terphenyl]-5'-yl)silane **S7** (1 g, 1.76 mmol) in CH_2Cl_2/CH_3COOH (8 ml) was added NaBr (0.8 g, 7.83 mmol), NBS (1 g, 5.85 mmol) at r.t.. The mixture was stirred at 100°C for 1 day, quenched with aqueous $NaHSO_3$, extracted with Et_2O, washed with brine, dried over Na_2SO_4 and concentrated. The crude product was purified by washing with hexane to give the product **S8** (0.99 g, 98%). R_f= 0.33 (hexane), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.66 (s, 2H), 7.59 (d, *J* = 1.5 Hz, 2H), 7.27 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.02 (s), 139.73 (s), 134.29 (s), 133.79 (d, *J* = 33.3 Hz), 131.95 (d, *J* = 38.1 Hz), 131.57 – 131.08 (m), 128.74 (dd, *J* = 7.3, 3.7 Hz), 128.21 (s), 127.14 (d, *J* = 5.4 Hz), 125.19 (d, *J* = 3.7 Hz), 124.49 (d, *J* = 3.6 Hz), 121.78 (s), 119.05 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.52 (s), -63.15 (s). HRMS (ESI+) *m/z* calcd for $C_{22}H_{10}BrF_{12}[M]^{2+\cdot}$580.09861, found 580.96674, m.p 125-132°C.

Preparation of DSI3

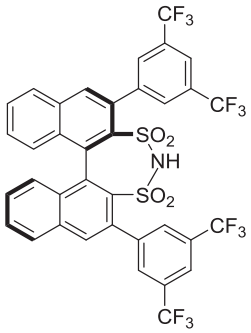




DSI3

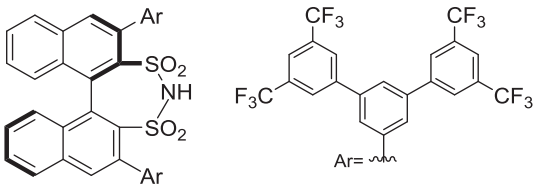
A mixture of **S8** (0.13 g, 0.09 mmol) in THF (14 ml) was kept at -20°C for 20 minutes and then NH_3 in EtOH (1.5 ml, 3 mmol) was added to this solution and was continued to stir overnight

at -20^{0}C. The crude product was purified by column chromatography (Hexane: AcOEt= 3: 1) and the obtained product was extracted with 1N HCl to give **DSI3** (0.07 g, 60%). R_f= 0.6 ($CHCl_3$: MeOH= 5: 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.90 (dd, *J* = 24.0, 8.2 Hz, 2H), 7.82 – 7.65 (m, 5H), 7.61 (s, 1H), 7.49 (s, 1H), 7.39 (dd, *J* = 16.7, 9.2 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.26 (s), 137.70 (d, *J* = 43.4 Hz), 136.72 (s), 136.11 (s), 134.52 (s), 133.32 (s), 132.67 (d, *J* = 33.0 Hz), 132.44 – 131.78 (m), 131.01 (t, *J* = 15.3 Hz), 129.99 (s), 128.93 (s), 127.75 (d, *J* = 42.6 Hz), 127.06 (s), 126.81 – 124.92 (m), 123.67 (d, *J* = 17.9 Hz), 121.40 – 120.43 (m), 118.25 – 117.28 (m).



DSI1

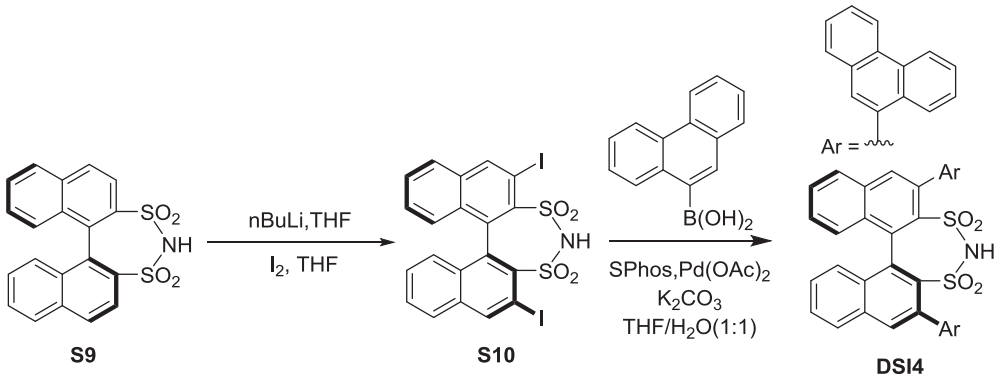
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.1 Hz, 4H), 8.05 – 7.89 (m, 6H), 7.84 – 7.76 (m, 2H), 7.54 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H).



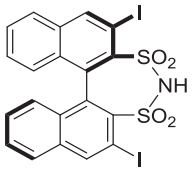
DSI2

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 8.15 (s, 4H), 8.09 (d, *J* = 12Hz, 6H), 7.82 (ddd, *J* = 20.2, 8.3 Hz, 12H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.28 (s, 2H).

Preparation of DSI via the direct introduction of Ar-group to DSI skeleton (Preparation of DSI4)

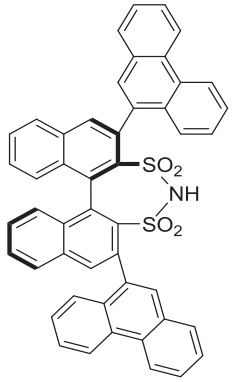


S9 S10 DSI4



S10

To a dry-ice-cooled solution of **S9** (149 mg, 0.38 mmol) in dry THF at –40ºC under N_2 was dropwise added n-BuLi (10.4 ml, 3.45 mmol). After this dark green solution was kept stirring at –40ºC for 2.5 h. After the mixture was cooled at –78ºC, a solution of I_2 (1 g, 3.94 mmol) in THF (4.5 ml) was slowly added dropwise. After the addition, the reddish-brown solution was warmed to r.t and stirred for 12 h. The resulting solution was quenched by saturated NH_4Cl. The mixture was then acidified with 4 N HCl and extracted with AcOEt three times. The combined organic layers were washed with saturated $Na_2S_2O_3$, brine, and dried over anhydrous Na_2SO_4. After the removal of the solvent under reduced pressure, the crude product was purified by a flash column chromatography (hexane: AcOEt= 1:6) to give the desired product **S10** (87.3 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 2H), 7.96 (d, J = 8.3 Hz, 2H), 7.60 – 7.51 (m, 2H), 7.31 – 7.21 (m, 2H), 6.78 (d, J = 8.6 Hz, 2H).

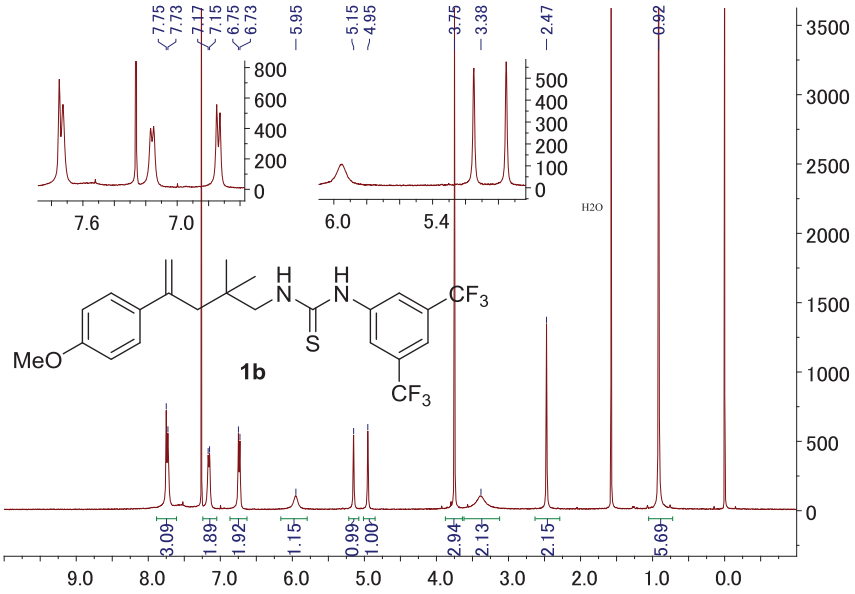


DSI4

(*S*)-3,3'-diiododisulfonimide (87.3 mg, 0.13 mmol) **S10**, 9-phenanthracenyl boronic acid (124 mg, 0.56 mmol), K_2CO_3 (77 mg, 0.56 mmol), palladium(II)-acetate (3.3 mg, 0.015 mmol) were suspended in THF/water (3 ml) under an atmosphere of nitrogen was heated for 1 day at 70°C. The reaction was poured into HCl 1M and extracted with DCM, and the combined organic layers were washed with water and brine. The organic layer was dried over Na_2SO_4, and the product was purified by flash column chromatography (hexane: AcOEt= 1: 6). The purified product was dissolved in DCM, acidified with HCl and the solvent was removed in vacuo to obtain **DSI4** (68.2 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 18.0, 8.2 Hz, 2H), 8.27 – 8.11 (m, 1H), 8.03 (dd, *J* = 12.5, 7.9 Hz, 1H), 7.96 – 7.81 (m, 2H), 7.73 – 7.49 (m, 6H), 7.46 – 7.33 (m, 2H).

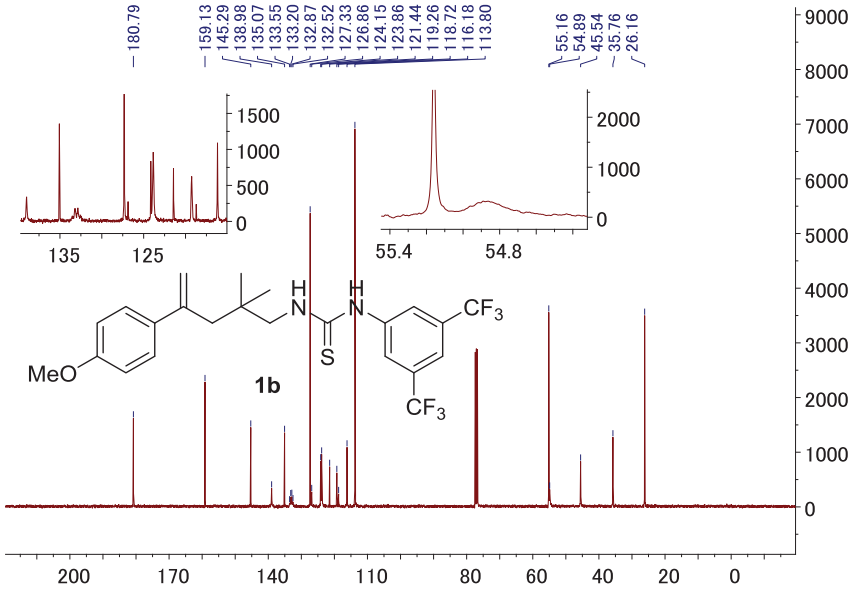
NMR spectra of new compounds

^{1}H NMR



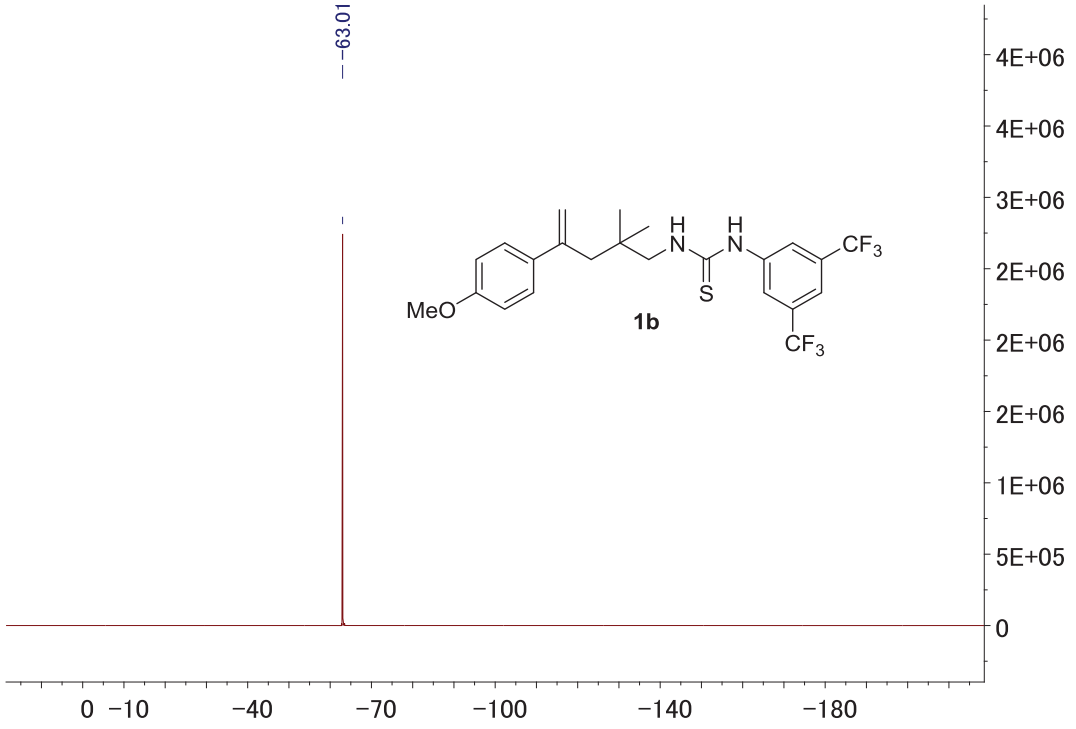
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 9.3 Hz, 3H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 5.95 (s, 1H), 5.15 (s, 1H), 4.95 (s, 1H), 3.75 (s, 3H), 3.38 (s, 2H), 2.47 (s, 2H), 0.92 (s, 6H).

^{13}C NMR



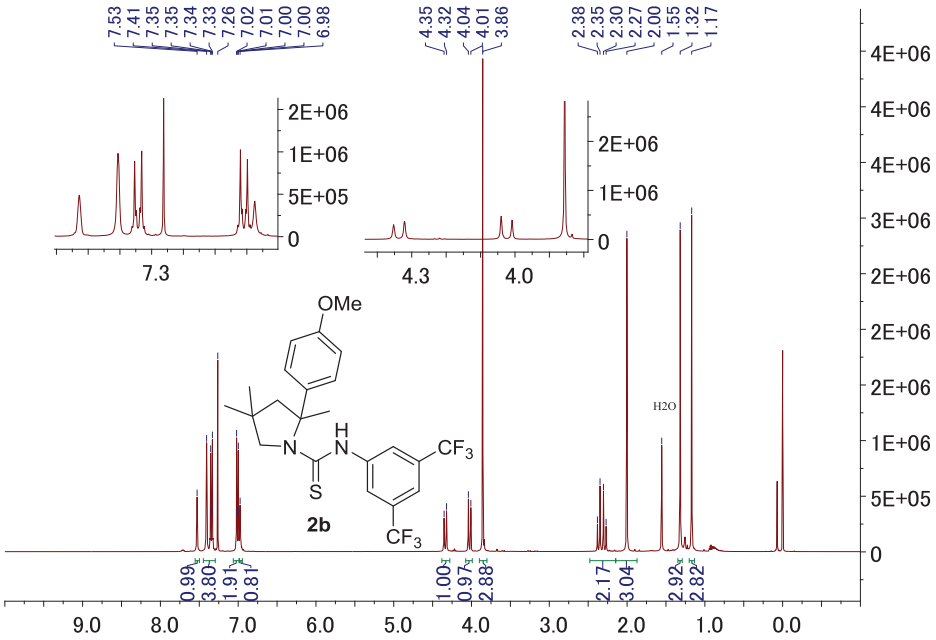
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.79, 159.13, 145.29, 138.98, 135.07, 133.25 (q, *J* = 34.9 Hz) (x2), 127.33 (x2), 123.86, 122.79 (q, *J*= 242.7 Hz) (x2), 119.26, 116.18, 113.80 (x2), 55.16, 54.89, 45.54, 35.76, 26.16 (x2).

^{19}F NMR



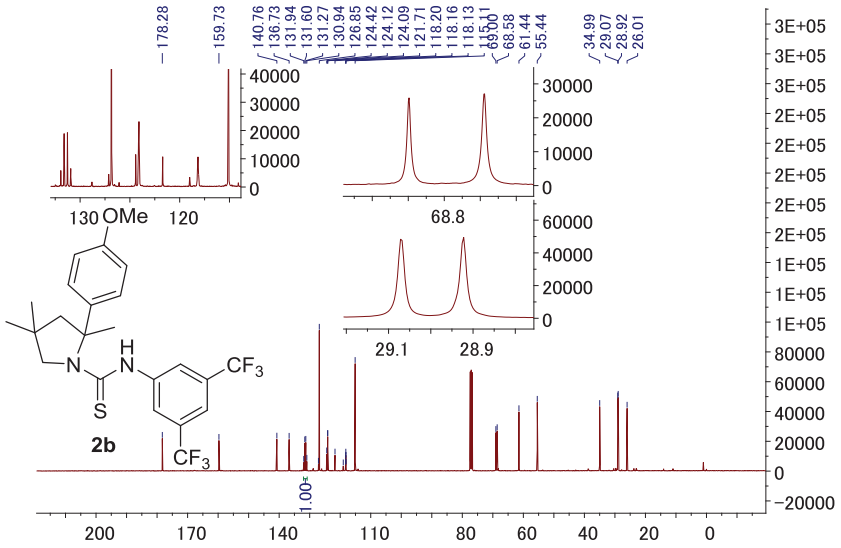
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.01 (s).

^{1}H NMR



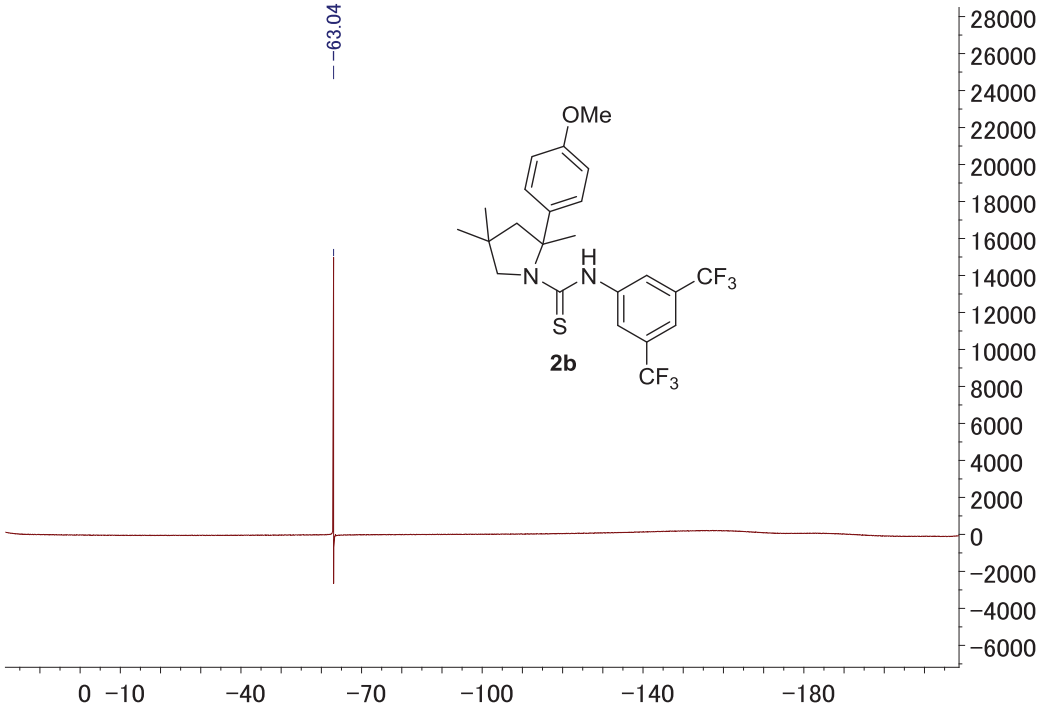
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.45 – 7.29 (m, 4H), 7.06 – 6.99 (m, 2H), 6.98 (s, 1H), 4.34 (d, *J* = 12.6 Hz, 1H), 4.02 (d, *J* = 12.7 Hz, 1H), 3.86 (s, 3H), 2.33 (dd, *J* = 31.1, 13.5 Hz, 2H), 2.00 (s, 3H), 1.32 (s, 3H), 1.17 (s, 3H).

^{13}C NMR



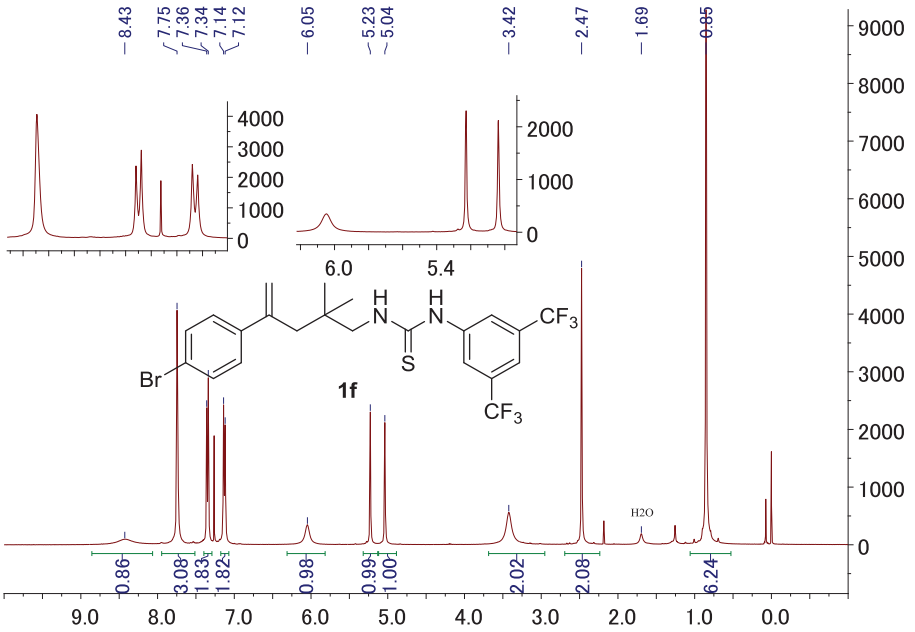
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.28, 159.73, 140.76, 136.73, 131.44 (q, *J* =33.5 Hz) (x2),126.85(x2), 123.07 (q, *J* =272.8 Hz) (x2),124.12-124.09(x2), 118.23-118.09, 115.11(x2), 69.00, 68.58, 61.44, 55.44, 34.99, 29.07, 28.92, 26.0.

^{19}F NMR



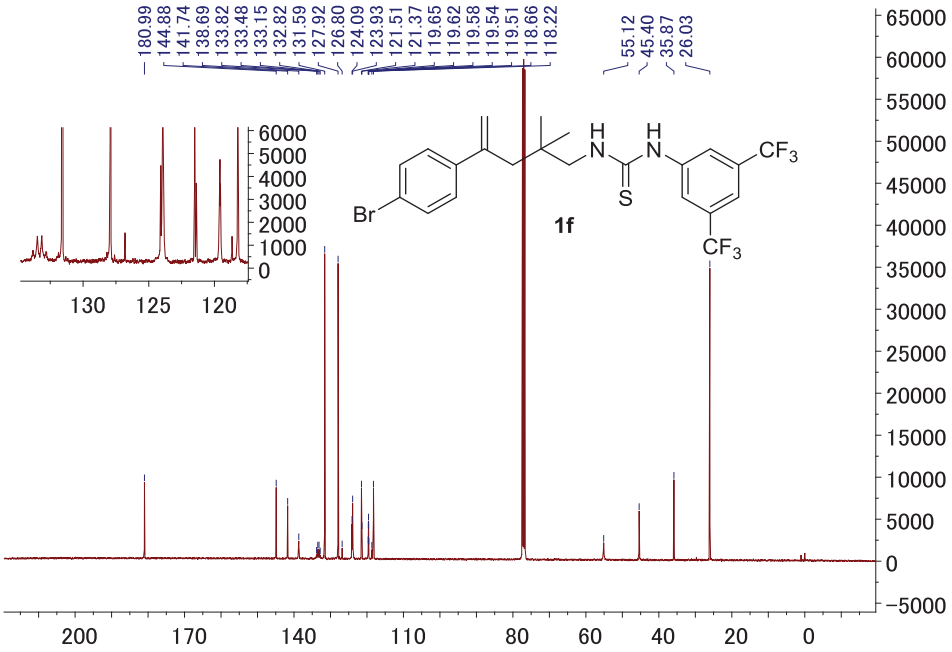
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.04 (s).

^{1}H NMR



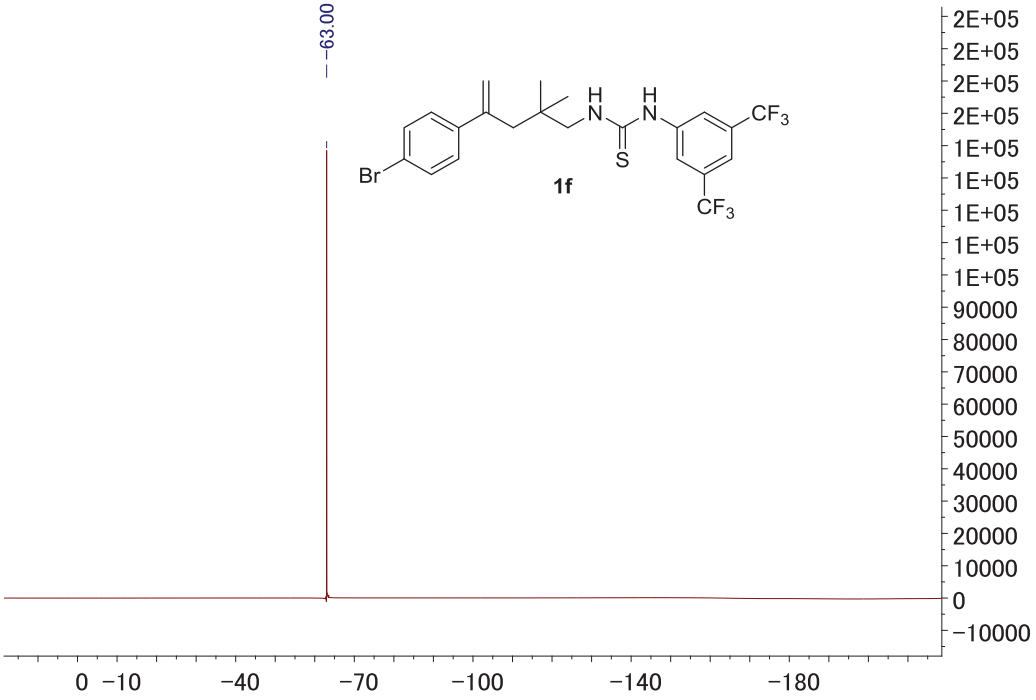
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.75 (s, 3H), 7.35 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 6.05 (s, 1H), 5.23 (s, 1H), 5.04 (s, 1H), 3.42 (s, 2H), 2.47 (s, 2H), 0.85 (s, 6H).

^{13}C NMR



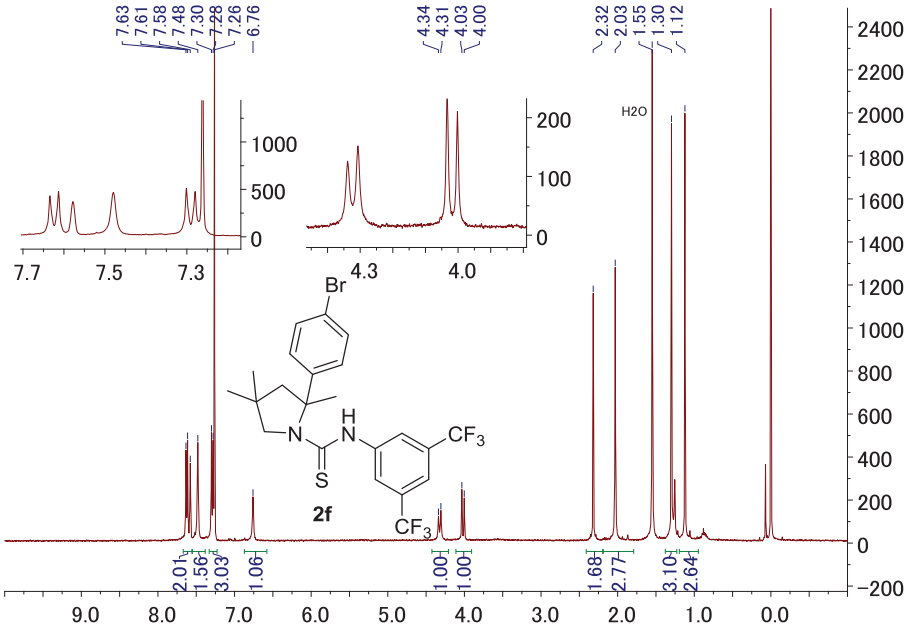
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.99, 144.88, 141.74, 138.69, 133.32 (q, J = 67.0, 33.4 Hz) (x2),131.59 (x2) , 127.92 (x2) , 123.93 (x2), 122.51 (q, J = 128.4 Hz) (x2), 121.51, 119.65 – 119.51, 118.22, 55.12, 45.40, 35.87, 26.03(x2).

^{19}F NMR



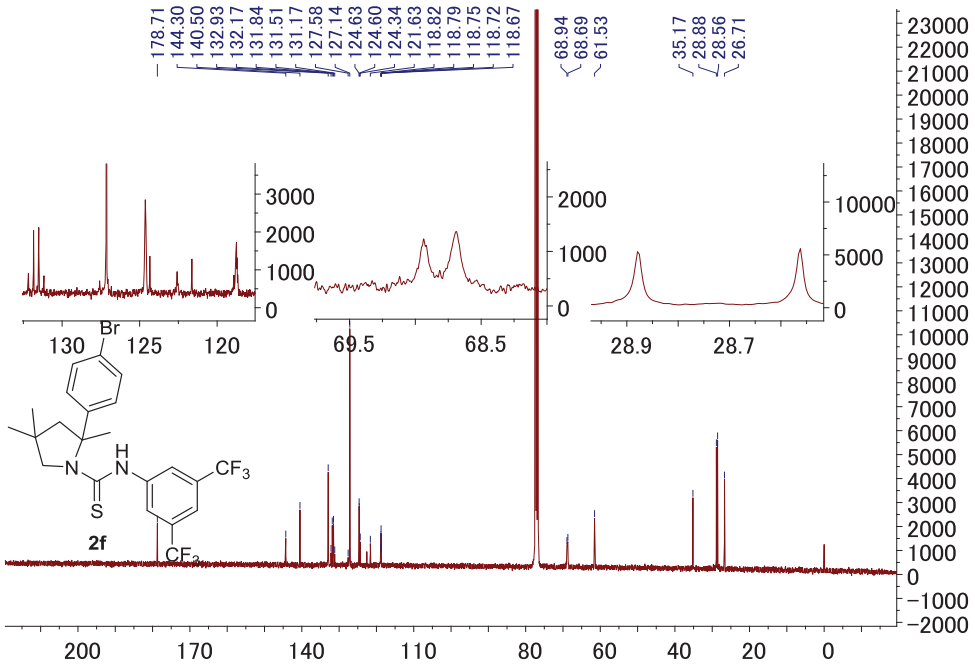
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.00 (s).

^{1}H NMR



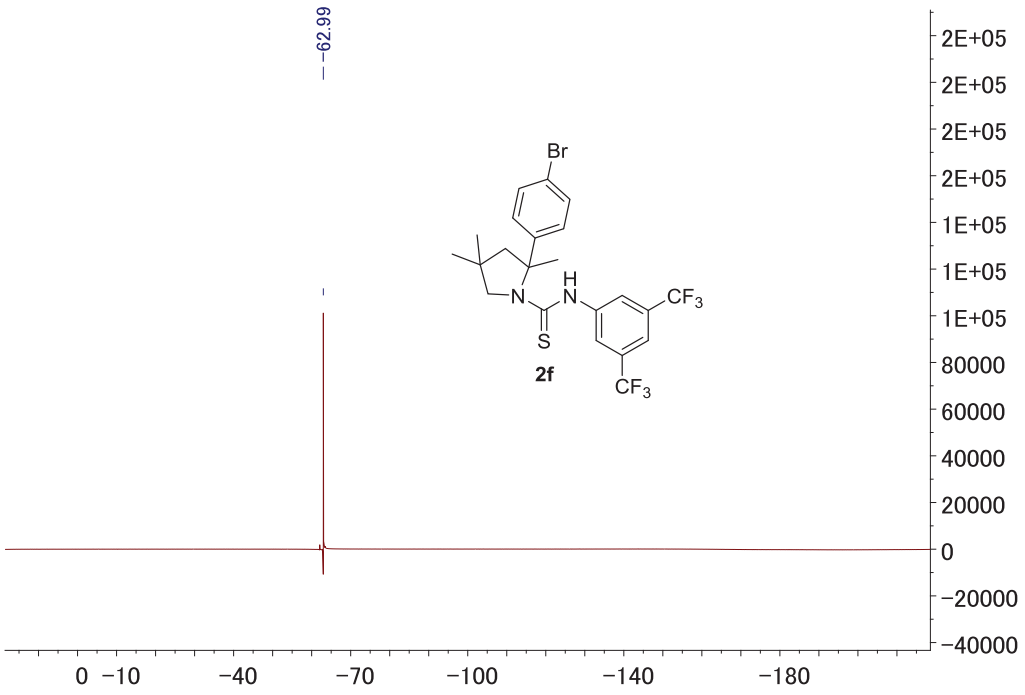
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 2H), 7.48 (s, 2H), 7.33 – 7.23 (m, 3H), 6.76 (s, 1H), 4.32 (d, J = 12.6 Hz, 1H), 4.02 (d, J = 12.6 Hz, 1H), 2.32 (s, 2H), 2.03 (s, 3H), 1.30 (s, 3H), 1.12 (s, 3H).

^{13}C NMR



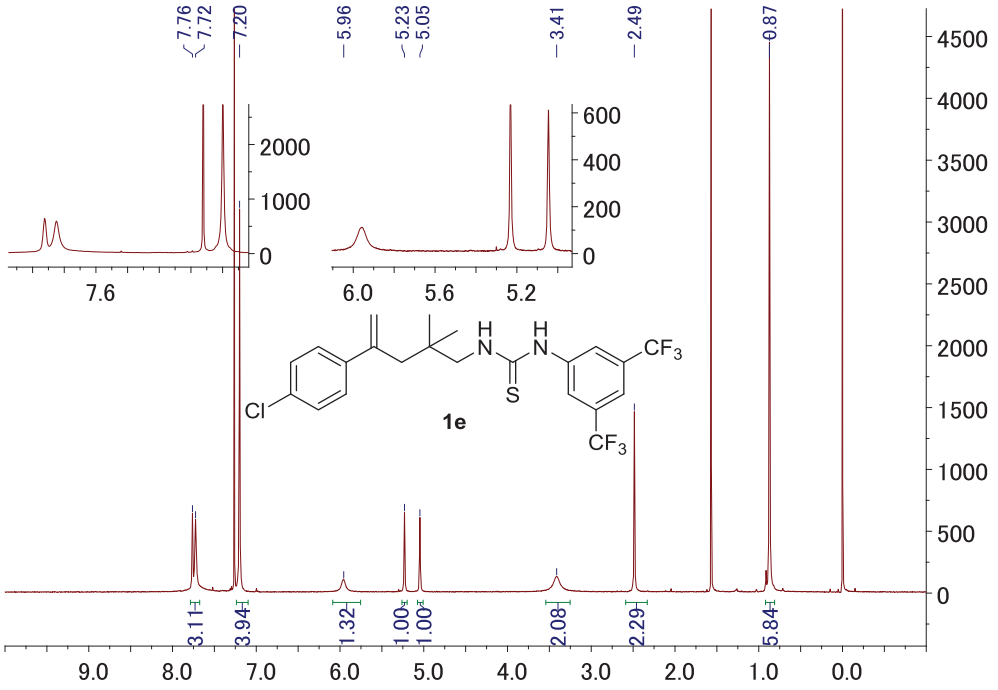
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.71(x2), 144.30, 140.50, 132.93(x2), 131.67 (q, J = 33.6 Hz) (x2), 127.14(x2), 123.25 (q, J = 272.7 Hz) (x2), 124.63-124.60 (x2), 122.58, 118.82-118.67 (x2), 68.75 (d, J = 24.9 Hz), 61.53, 35.17, 28.88, 28.56, 26.71.

^{19}F NMR



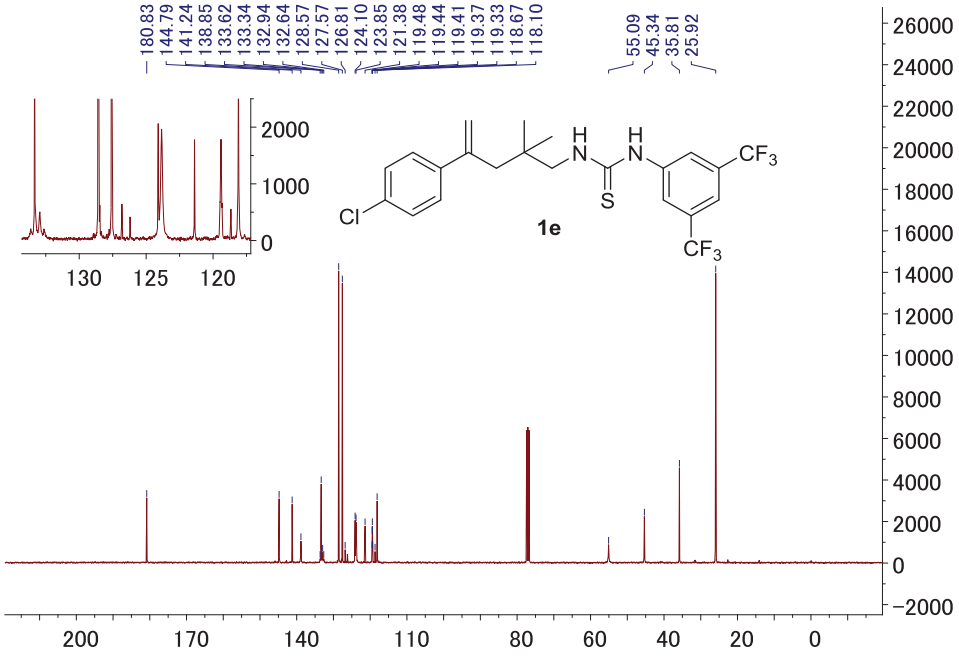
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99 (s)

^{1}H NMR



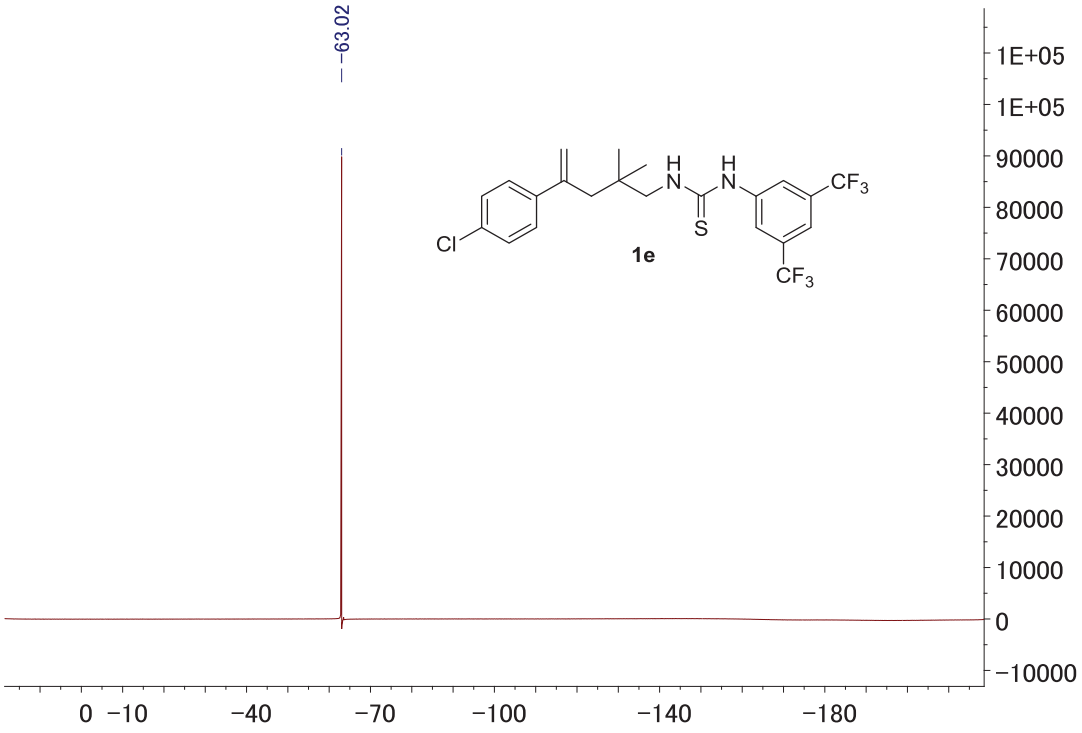
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 14.7 Hz, 3H), 7.20 (s, 4H), 5.96 (s, 1H), 5.23 (s, 1H), 5.05 (s, 1H), 3.41 (s, 2H), 2.49 (s, 2H), 0.87 (s, 6H).

^{13}C NMR



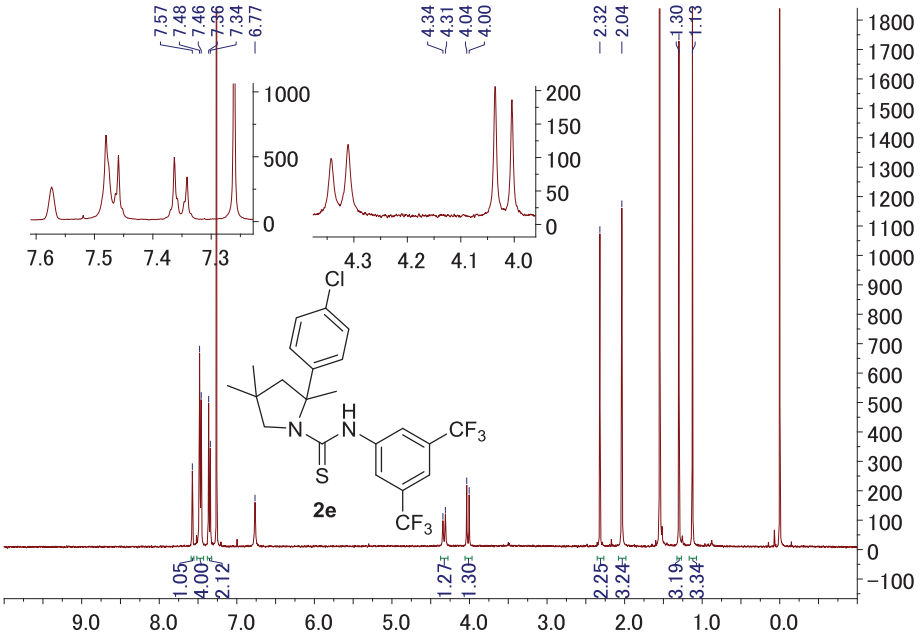
^{13}C NMR (101 MHz, $CDCl_3$) δ 180.83, 144.79, 141.24, 138.85, 133.34, 133.13 (q, J = 30.7 Hz) (x2), 128.57(x2), 127.57(x2), 123.85(x2), 122.74 (q, J =273.1 Hz) (x2), 119.48 – 118.33, 118.10, 55.09, 45.34, 35.81, 25.92(x2).

^{19}F NMR



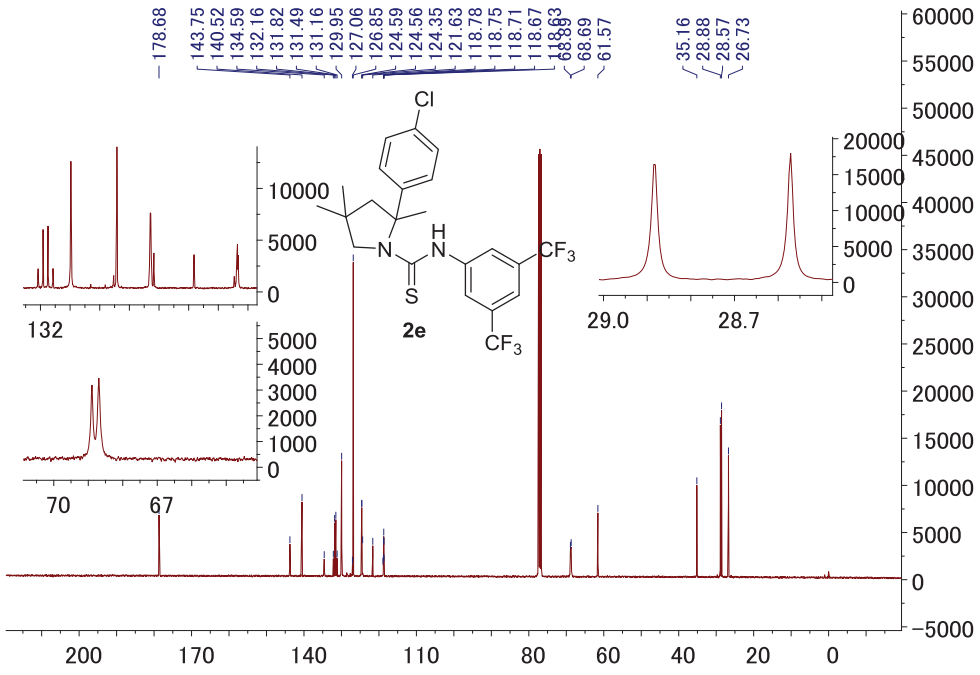
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.02 (s).

^{1}H NMR



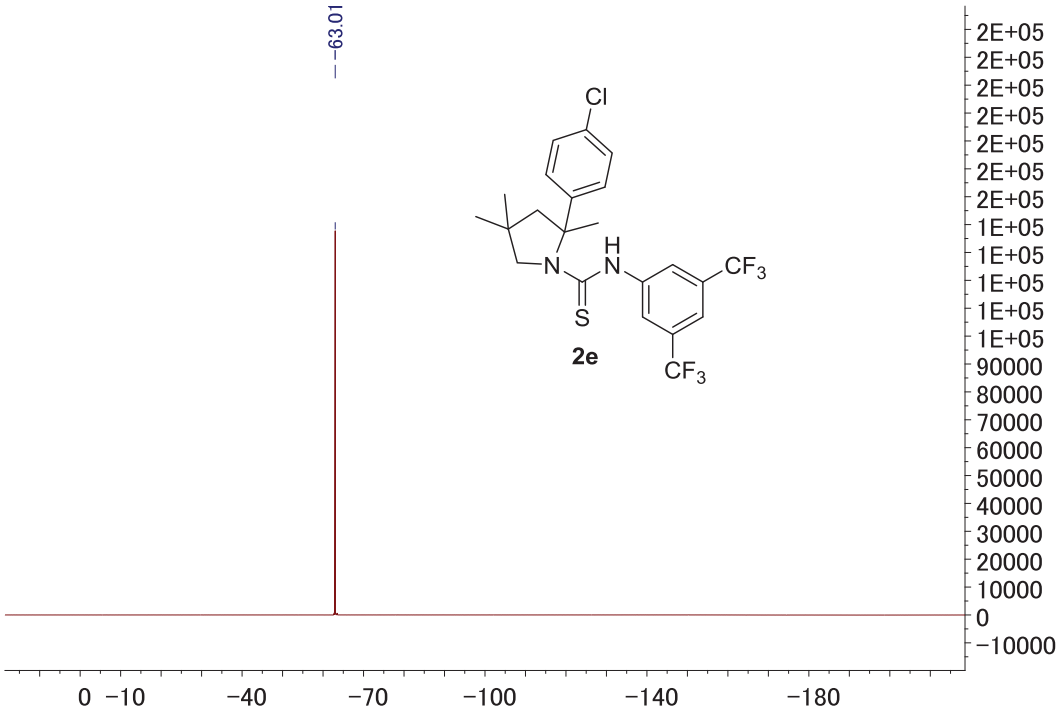
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.47 (d, *J* = 8.6 Hz, 4H), 7.35 (d, *J* = 8.7 Hz, 2H), 4.33 (d, *J* = 12.8 Hz, 1H), 4.02 (d, *J* = 12.6 Hz, 1H), 2.32 (s, 2H), 2.04 (s, 3H), 1.30 (s, 3H), 1.13 (s, 3H).

^{13}C NMR



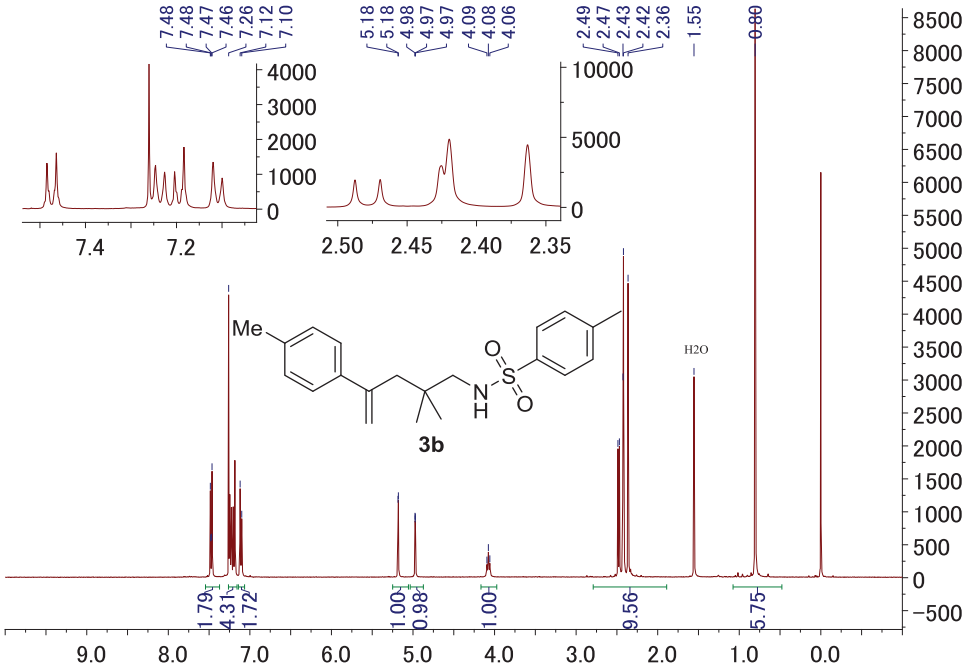
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.68, 143.75, 140.52, 134.59, 131.66 (q, *J* = 33.6 Hz) (x2) , 129.95 (x2), 126.85 (x2),124.59-124.56 (x2), 122.99 (q, *J* =272.8 Hz) (x2), 121.63, 118.78-118.63, 68.79 (d, *J* = 20.2 Hz), 61.57, 35.16, 28.88, 28.57, 26.73.

^{19}F NMR



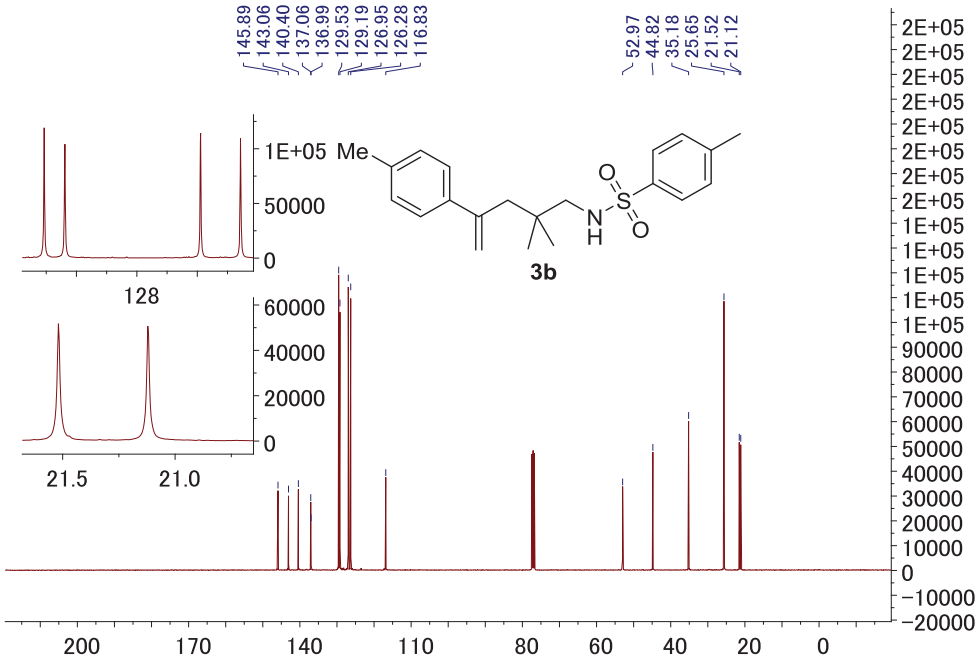
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.01 (s).

^{1}H NMR



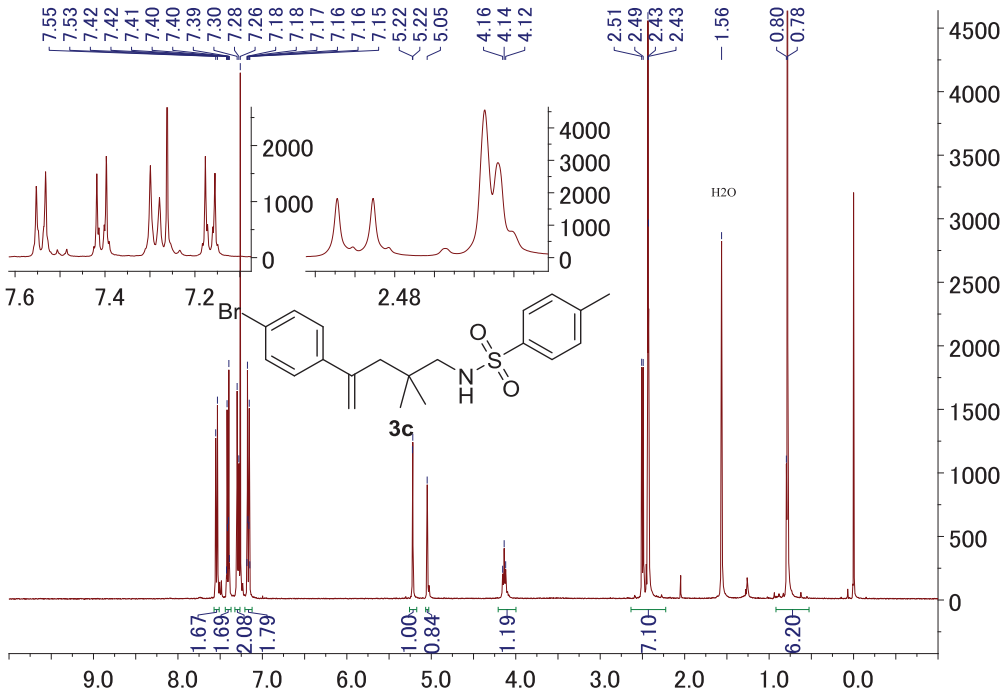
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.37 (m, 2H), 7.26 (s, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.18 (d, *J* = 1.8 Hz, 1H), 5.03 – 4.87 (m, 1H), 4.08 (t, *J* = 7.2 Hz, 1H), 2.79 – 1.89 (m, 10H), 0.80 (s, 6H).

^{13}C NMR



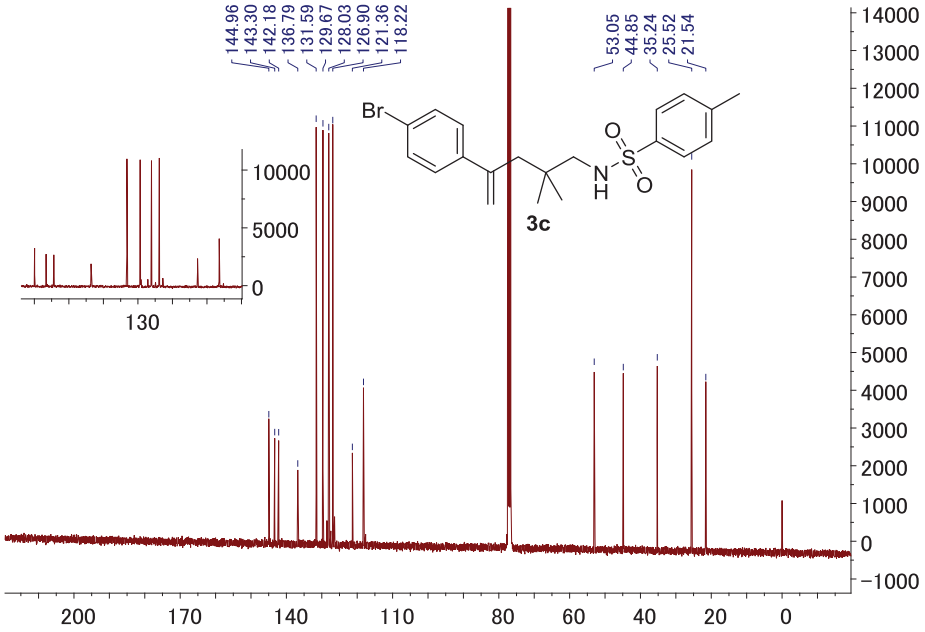
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.89, 143.06, 140.40, 137.02, 129.53(x2), 129.19(x2), 126.95(x2), 126.28(x2), 116.83, 52.97, 44.82, 35.18(x2), 25.65(x2), 21.52, 21.12.

^{1}H NMR



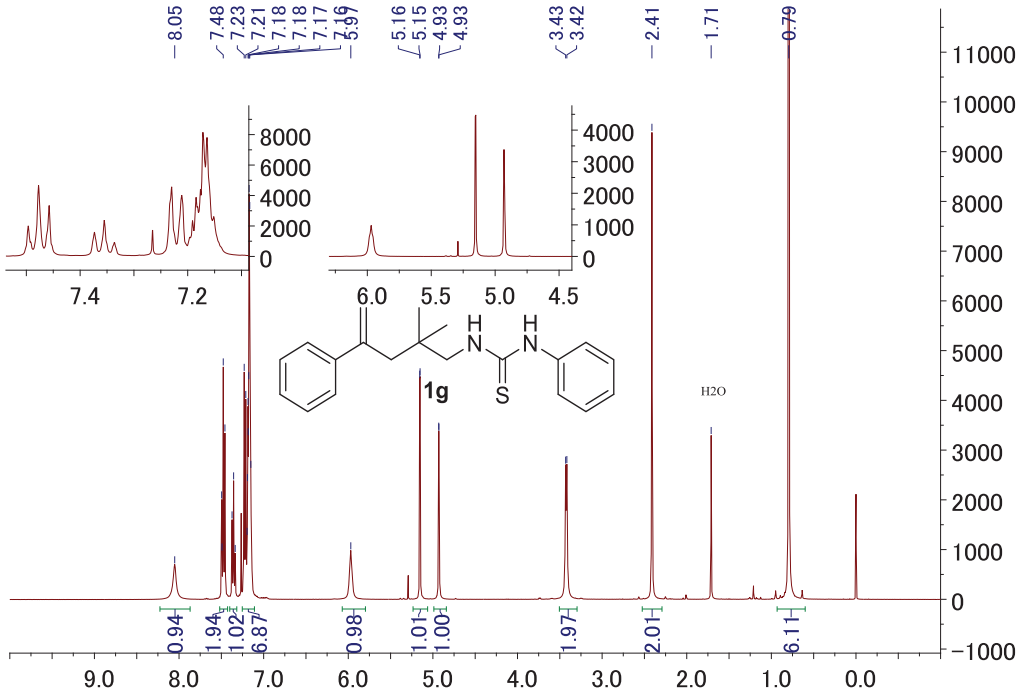
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.34 – 7.24 (m, 2H), 7.21 – 7.12 (m, 2H), 5.22 (d, *J* = 1.6 Hz, 1H), 5.05 (s, 1H), 4.14 (t, *J* = 7.2 Hz, 1H), 2.47 (dd, *J* = 27.4, 4.9 Hz, 6H), 0.79 (d, *J* = 5.3 Hz, 6H).

^{13}C NMR



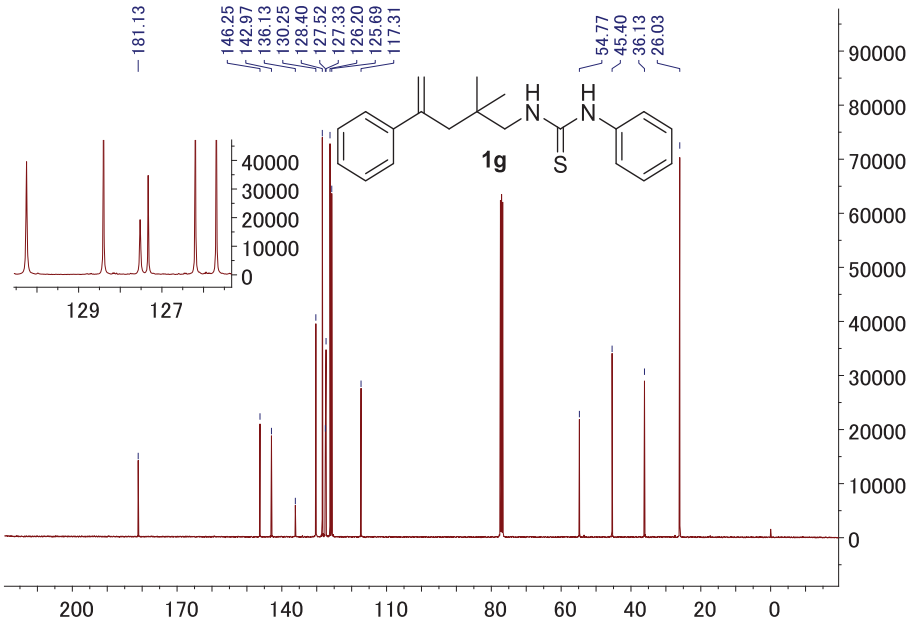
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.96, 143.30, 142.18, 136.79(x2), 131.59(x2), 129.67(x2), 128.03(x2), 126.90(x2), 121.36, 118.22, 53.05, 44.85, 35.24, 25.52(x2), 21.54.

^{1}H NMR



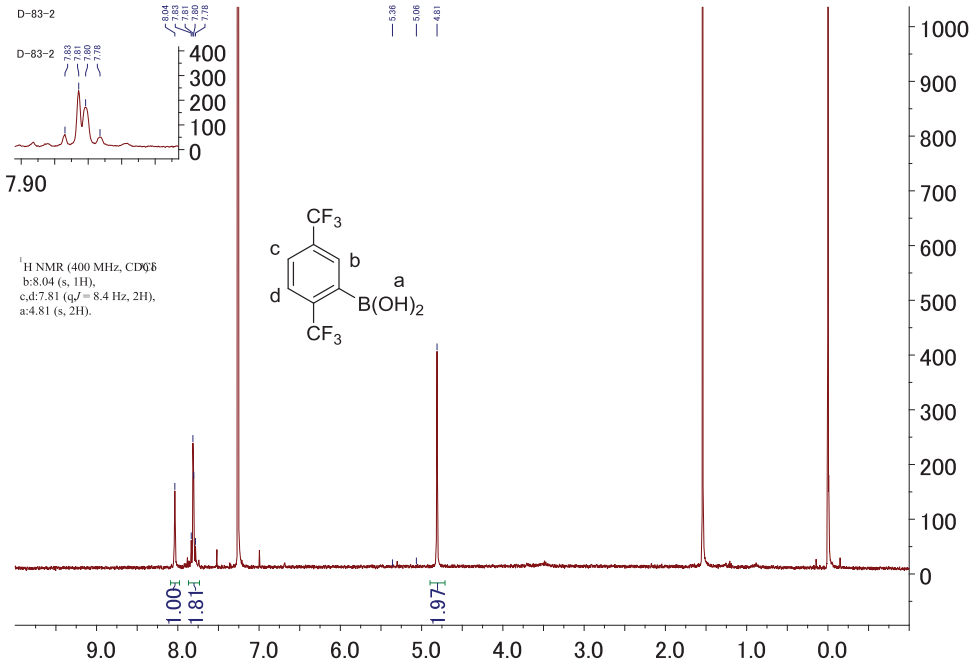
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.48 (dd, *J* = 10.6, 4.9 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.11 (m, 7H), 5.97 (s, 1H), 5.15 (d, *J* = 1.7 Hz, 1H), 4.93 (d, *J* = 0.7 Hz, 1H), 3.42 (d, *J* = 5.7 Hz, 2H), 2.41 (s, 2H), 0.79 (s, 6H).

^{13}C NMR

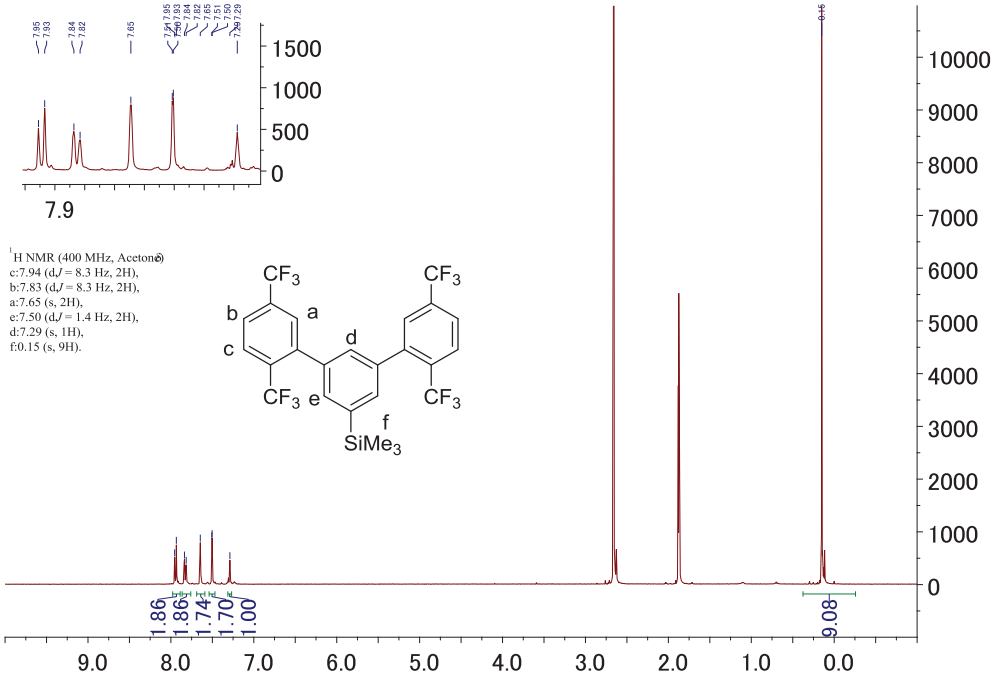


^{13}C NMR (101 MHz, $CDCl_3$) δ 181.13, 146.25, 142.9, 136.13, 130.25 (x2), 128.40 (x2), 127.52, 127.33, 126.20(x2)

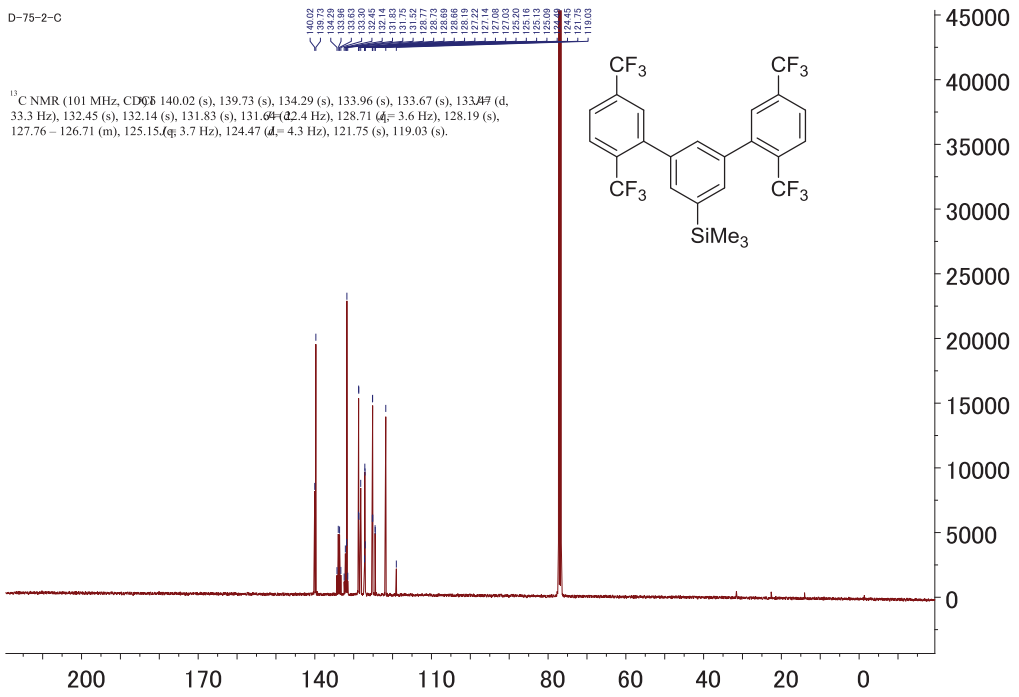
^{1}H NMR


D-83-2
D-83-2
7.90
^{1}H NMR (400 MHz, CD$_3$OD)
b:8.04 (s, 1H),
c,d:7.81 (q,J = 8.4 Hz, 2H),
a:4.81 (s, 2H).
CF$_3$
B(OH)$_2$
1.00
1.81
1.97

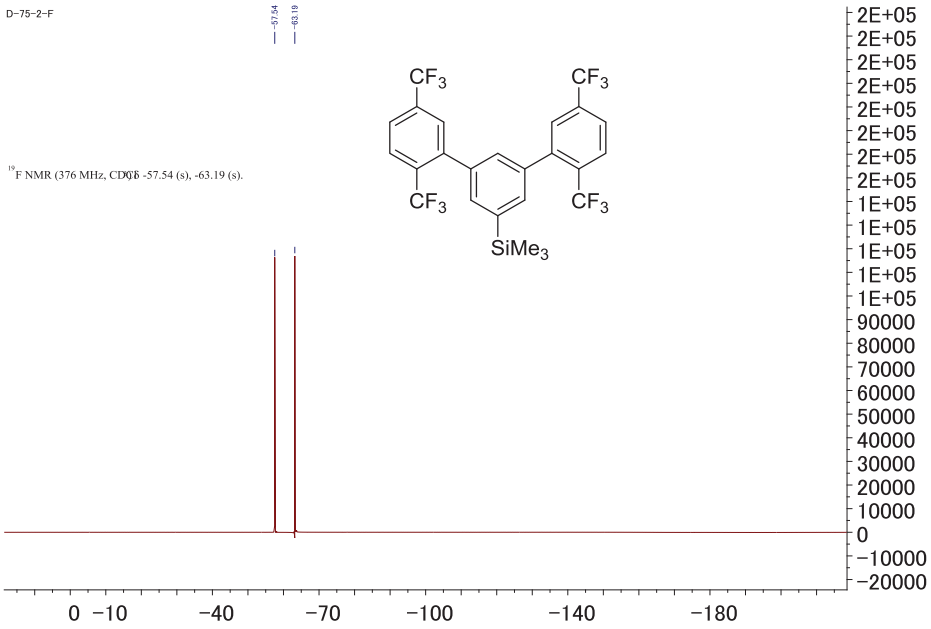
^{1}H NMR


7.9
^{1}H NMR (400 MHz, Acetone)
c:7.94 (d,J = 8.3 Hz, 2H),
b:7.83 (d,J = 8.3 Hz, 2H),
a:7.65 (s, 2H),
e:7.50 (d,J = 1.4 Hz, 2H),
d:7.29 (s, 1H),
f:0.15 (s, 9H).
CF$_3$
SiMe$_3$
1.86
1.86
1.74
1.70
1.00
9.08

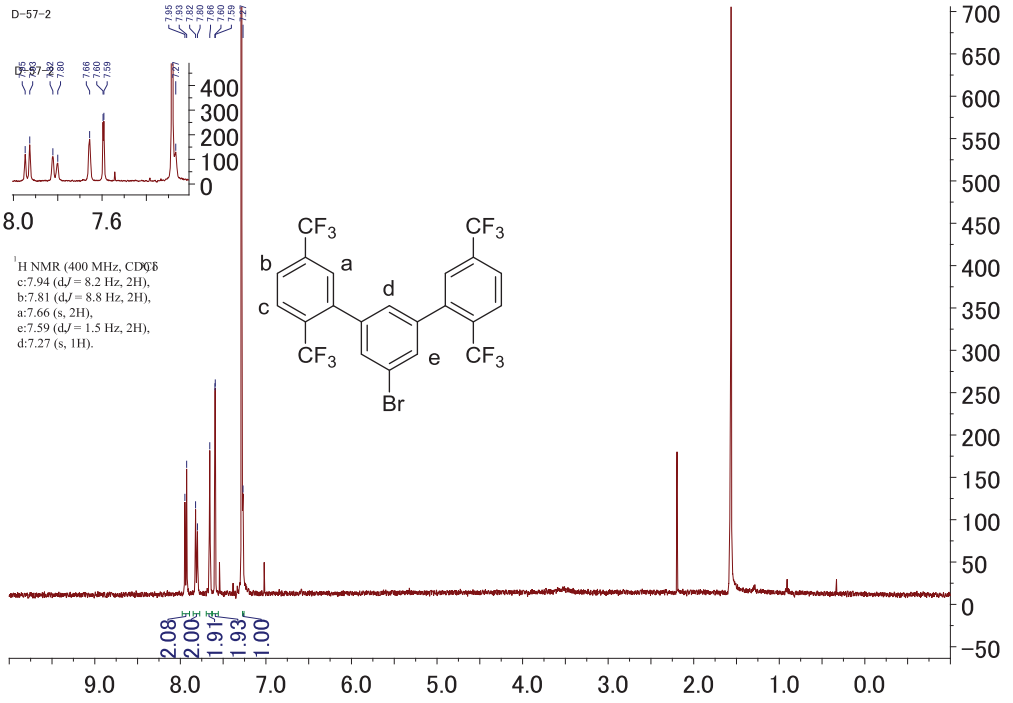
^{13}C NMR



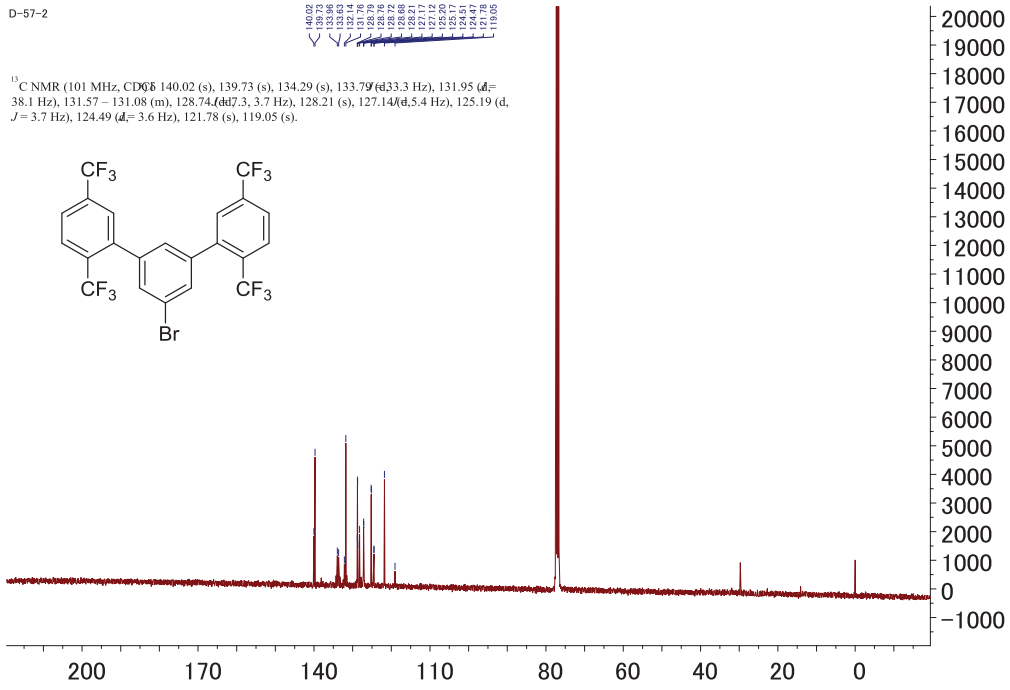
^{19}F NMR



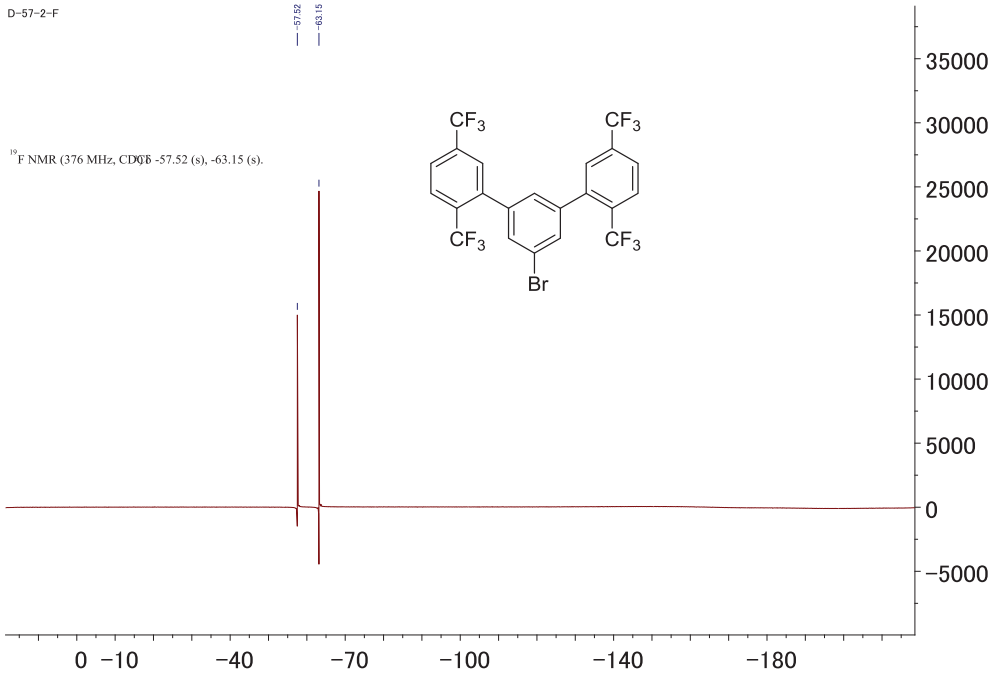
^{1}H NMR



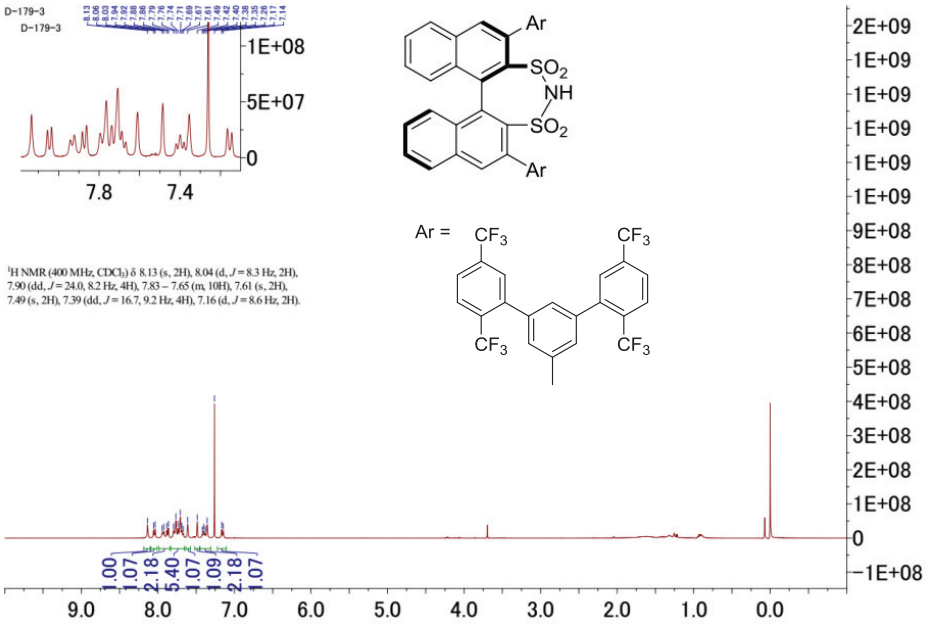
^{13}C NMR



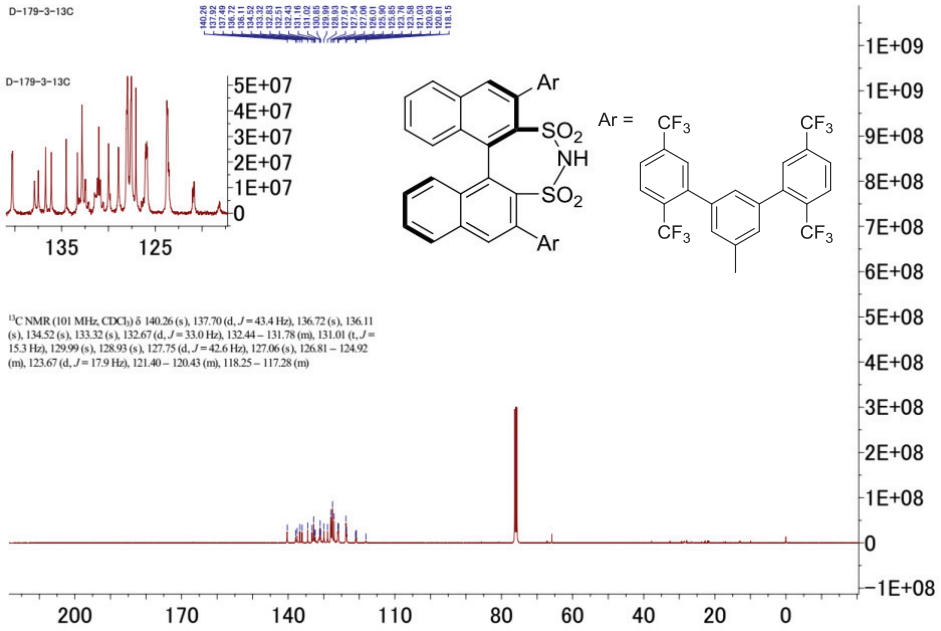
^{19}F NMR


D-57-2-F
-57.52
-63.15
^{19}F NMR (376 MHz, CDCl3 -57.52 (s), -63.15 (s).
CF3
CF3
CF3
CF3
Br
35000
30000
25000
20000
15000
10000
5000
0
−5000
0 −10
−40
−70
−100
−140
−180

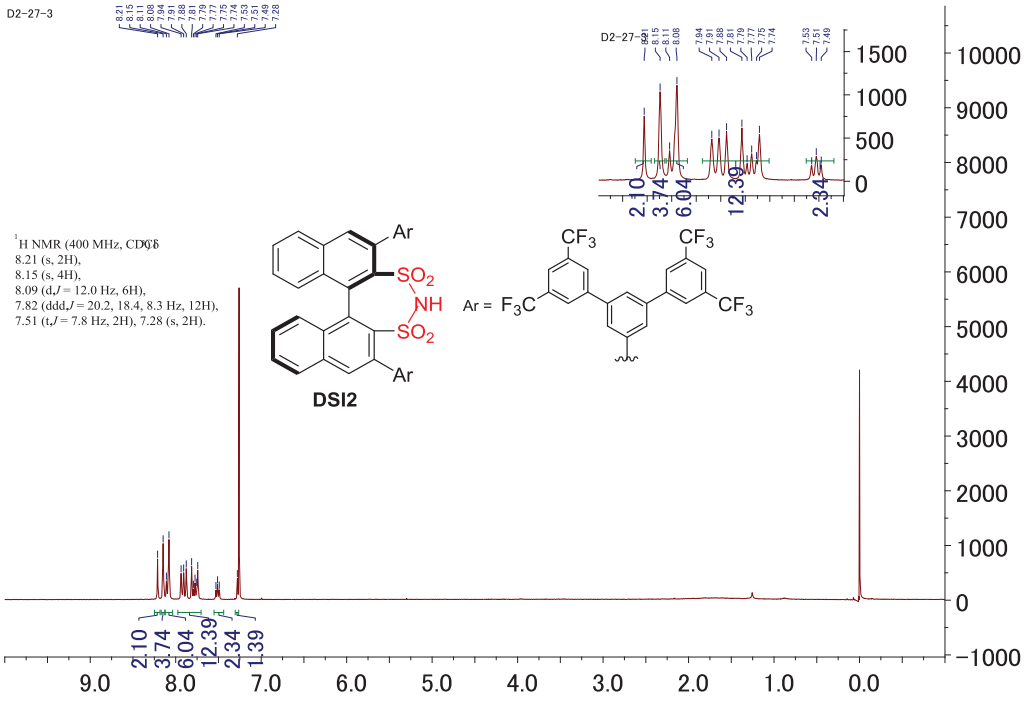
^{1}H NMR



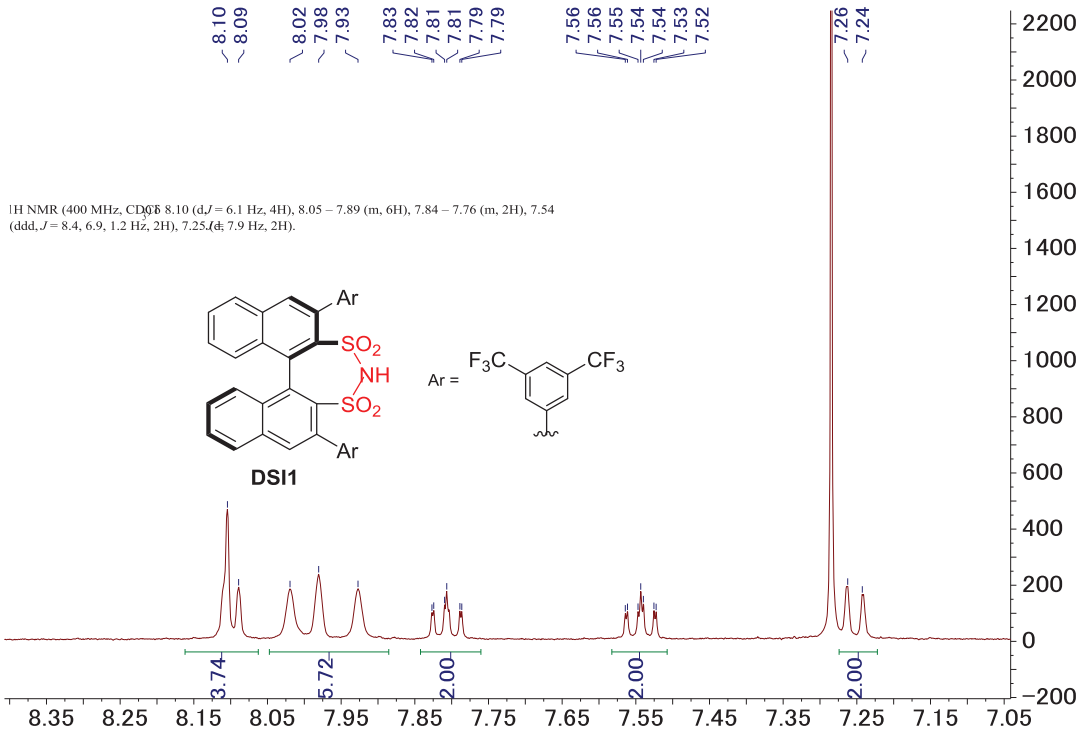
^{13}C NMR



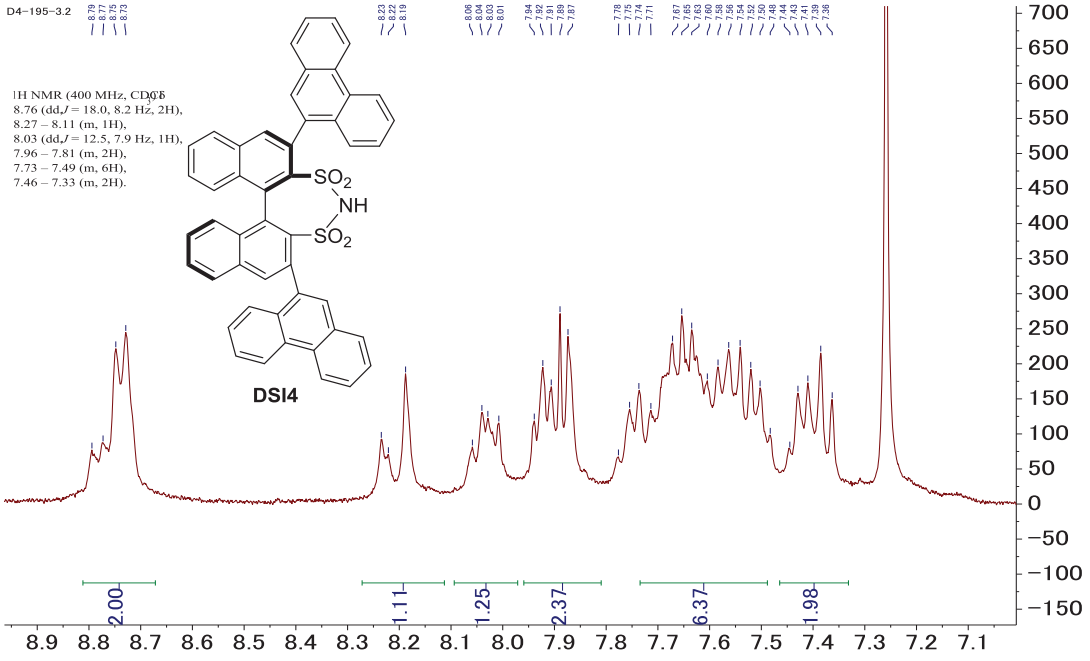
^{1}H NMR


D2-27-3
1H NMR (400 MHz, CDCl3) δ
8.21 (s, 2H),
8.15 (s, 4H),
8.09 (d, J = 12.0 Hz, 6H),
7.82 (ddd, J = 20.2, 18.4, 8.3 Hz, 12H),
7.51 (t, J = 7.8 Hz, 2H), 7.28 (s, 2H).
Ar
SO2
NH
SO2
Ar
DSI2
Ar = F3C
CF3
CF3
CF3
2.10
3.74
6.04
12.39
2.34
1.39

^{1}H NMR


1H NMR (400 MHz, CD2Cl2) δ 8.10 (d, J = 6.1 Hz, 4H), 8.05 – 7.89 (m, 6H), 7.84 – 7.76 (m, 2H), 7.54 (ddd, J = 8.4, 6.9, 1.2 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H).
Ar
SO2
NH
SO2
Ar
DSI1
Ar =
F3C
CF3
3.74
5.72
2.00
2.00
2.00

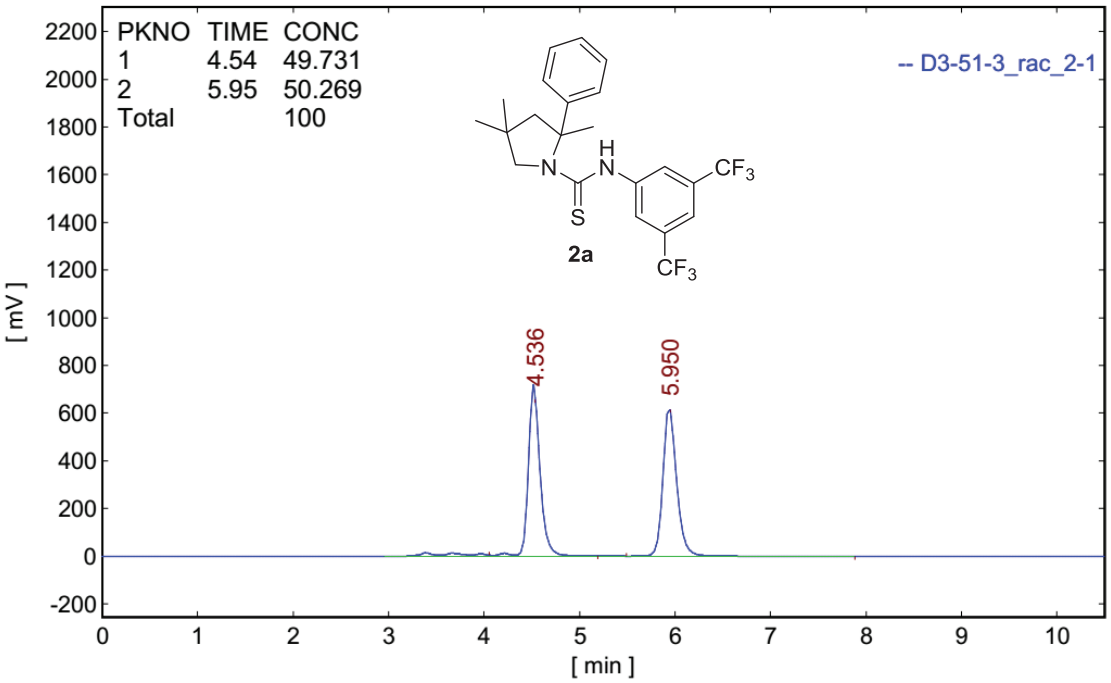
^{1}H NMR


D4-195-3.2
8.79
8.77
8.75
8.73
8.23
8.22
8.19
8.06
8.04
8.03
8.01
7.94
7.92
7.91
7.89
7.87
7.78
7.75
7.74
7.71
7.67
7.65
7.63
7.60
7.58
7.56
7.54
7.52
7.50
7.48
7.44
7.43
7.41
7.39
7.38
1H NMR (400 MHz, CD2Cl2) δ
8.76 (dd, J = 18.0, 8.2 Hz, 2H),
8.27 – 8.11 (m, 1H),
8.03 (dd, J = 12.5, 7.9 Hz, 1H),
7.96 – 7.81 (m, 2H),
7.73 – 7.49 (m, 6H),
7.46 – 7.33 (m, 2H).
SO2
NH
SO2
DSI4
2.00
1.11
1.25
2.37
6.37
1.98
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1

HPLC spectra

Table 3

Entry 8: *Rac*-**2a** Chiralpak IB, hexane: EtOH= 10: 1, 1.0 mL/ min 254 nm



2a: 70% ee

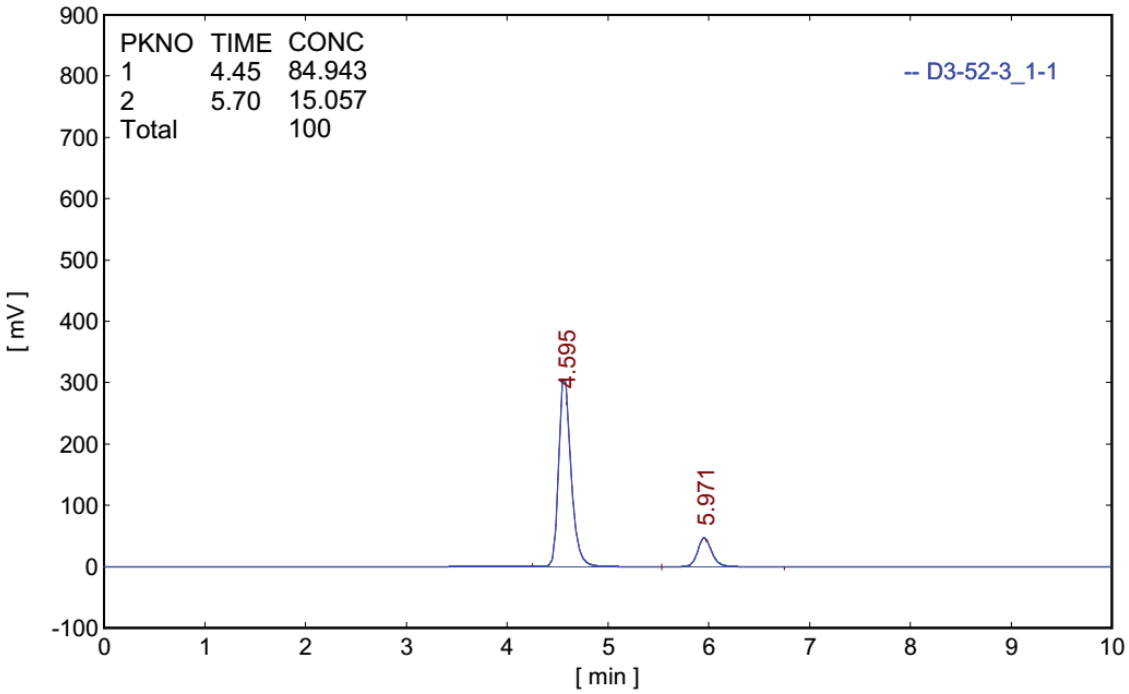
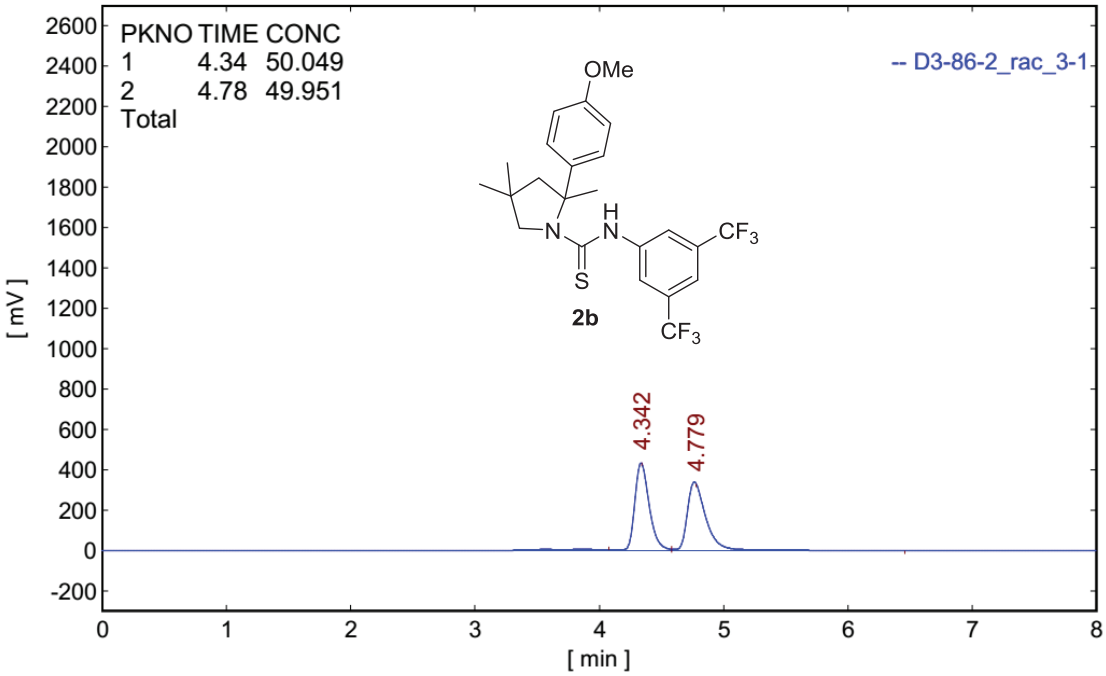
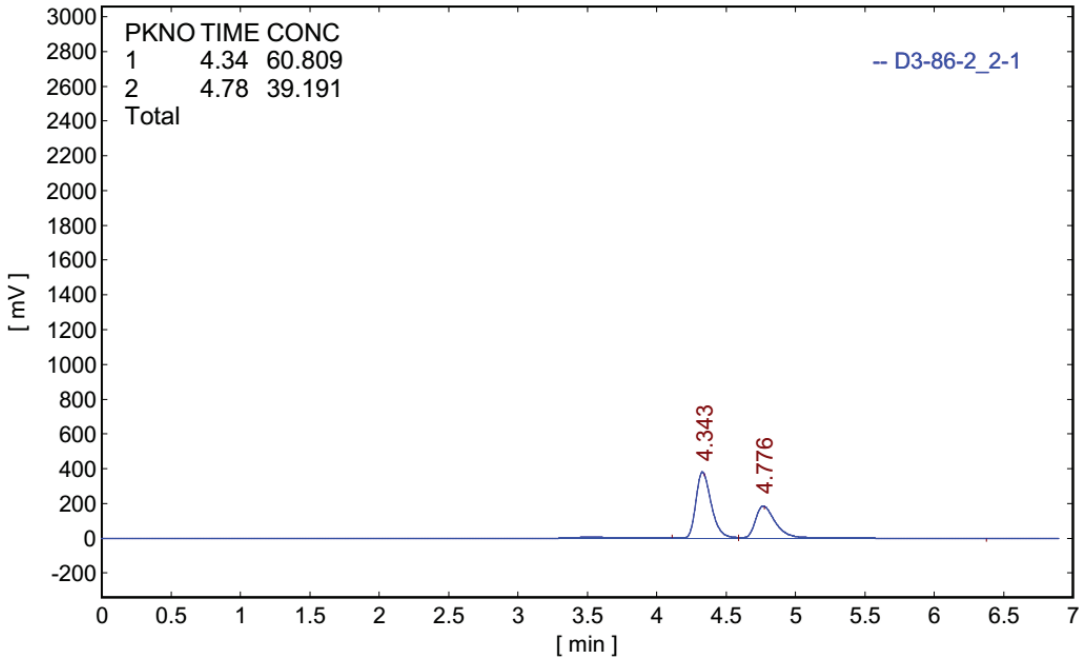


Table 4

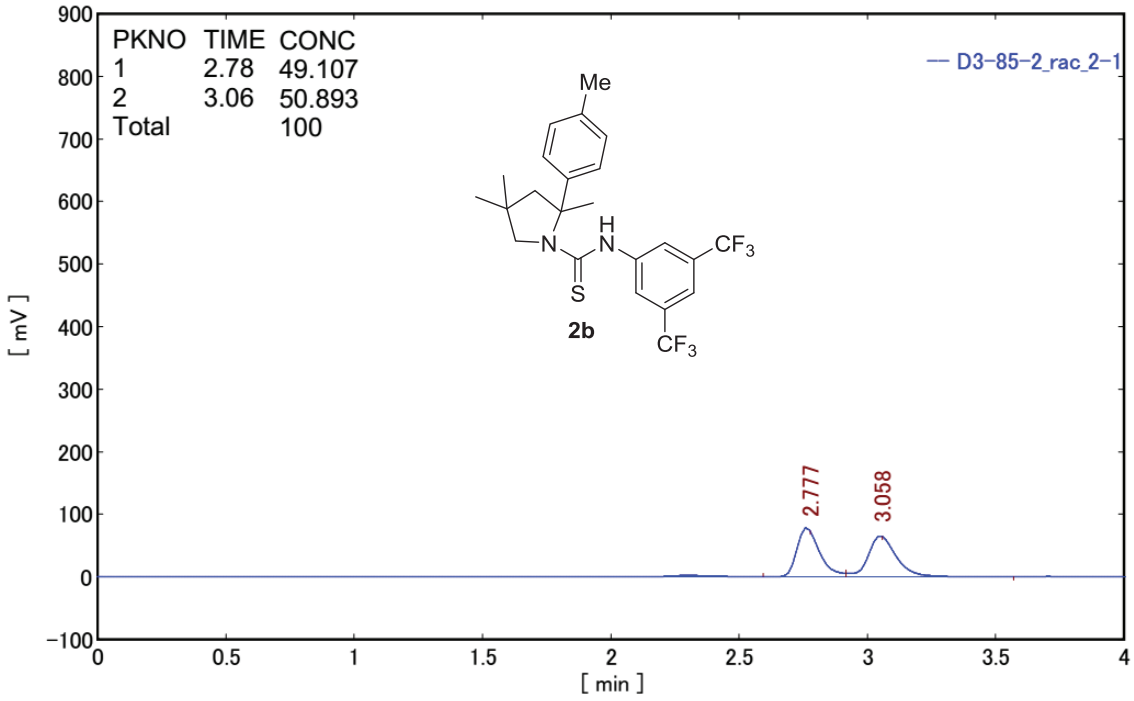
Rac-**2b** Chiralpak ID, hexane: EtOH= 20: 1, 1.0 mL/ min 254 nm



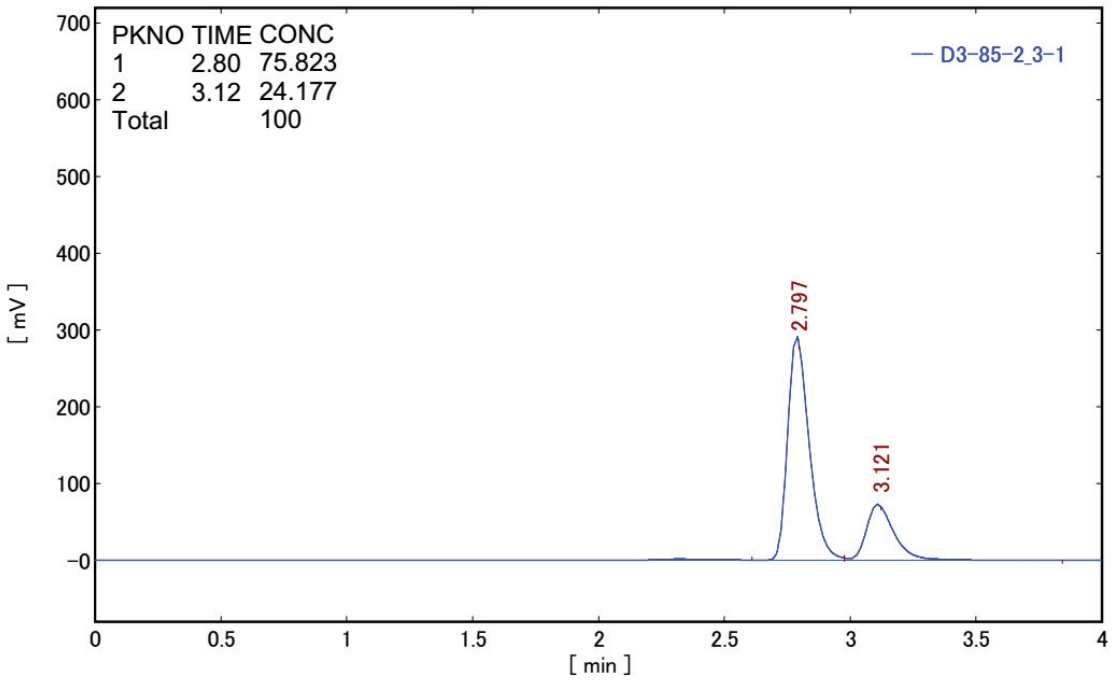
2b: 22% ee (Table 4, entry 1)



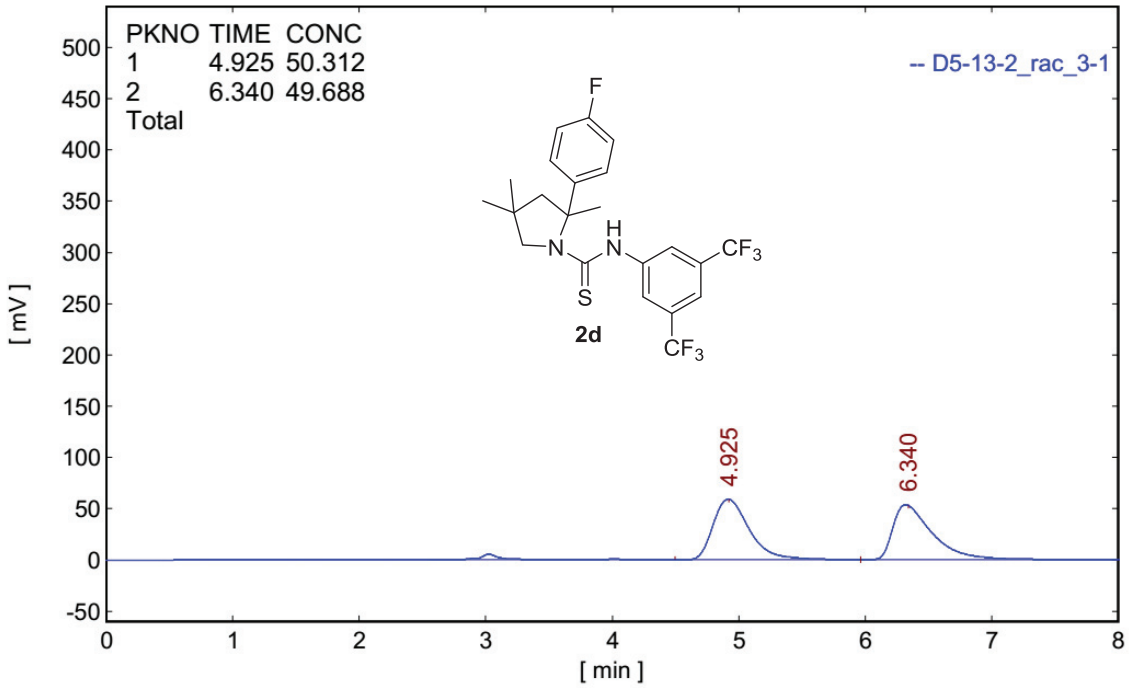
Rac-**2c** Chiralpak ID, hexane: EtOH= 40: 1, 1.5 mL/ min 254 nm



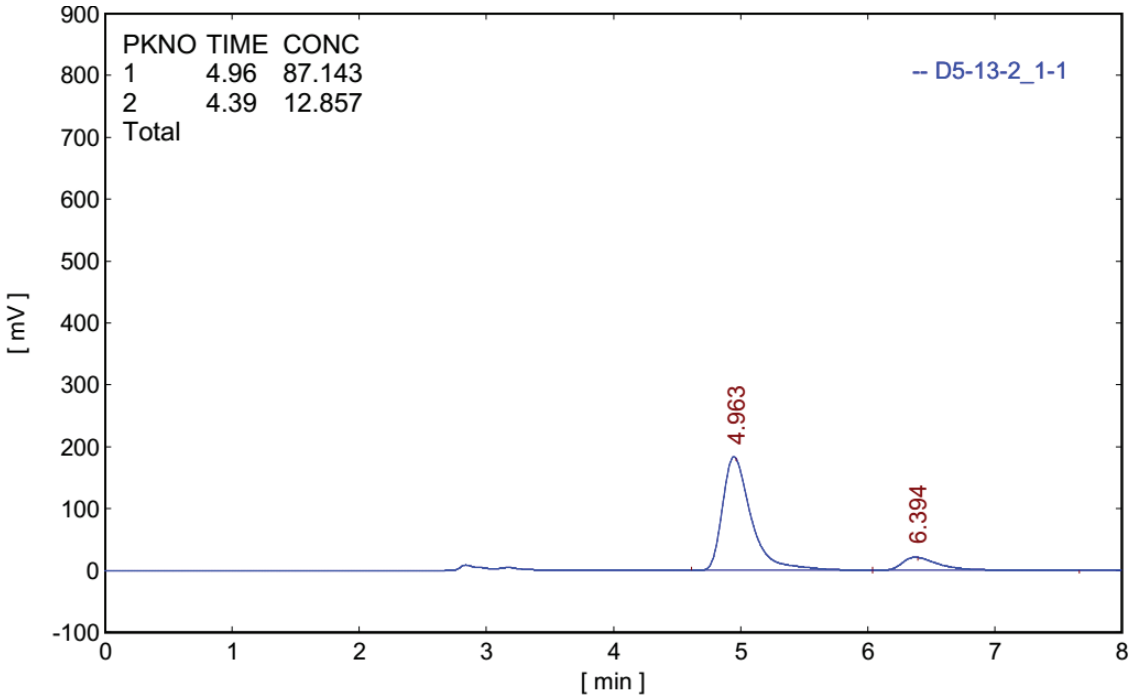
2c: 52% ee (Table 4, entry 3)



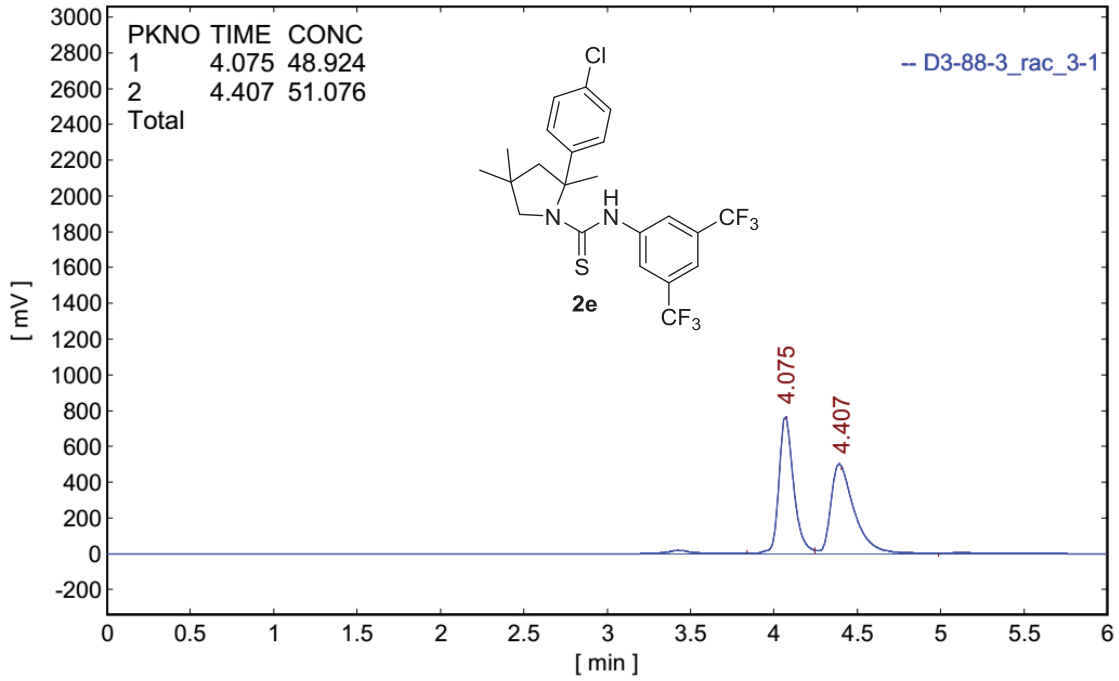
Rac-**2d** Chiralpak IG-3, hexane: EtOH= 80: 1, 1.1 mL/ min 254 nm



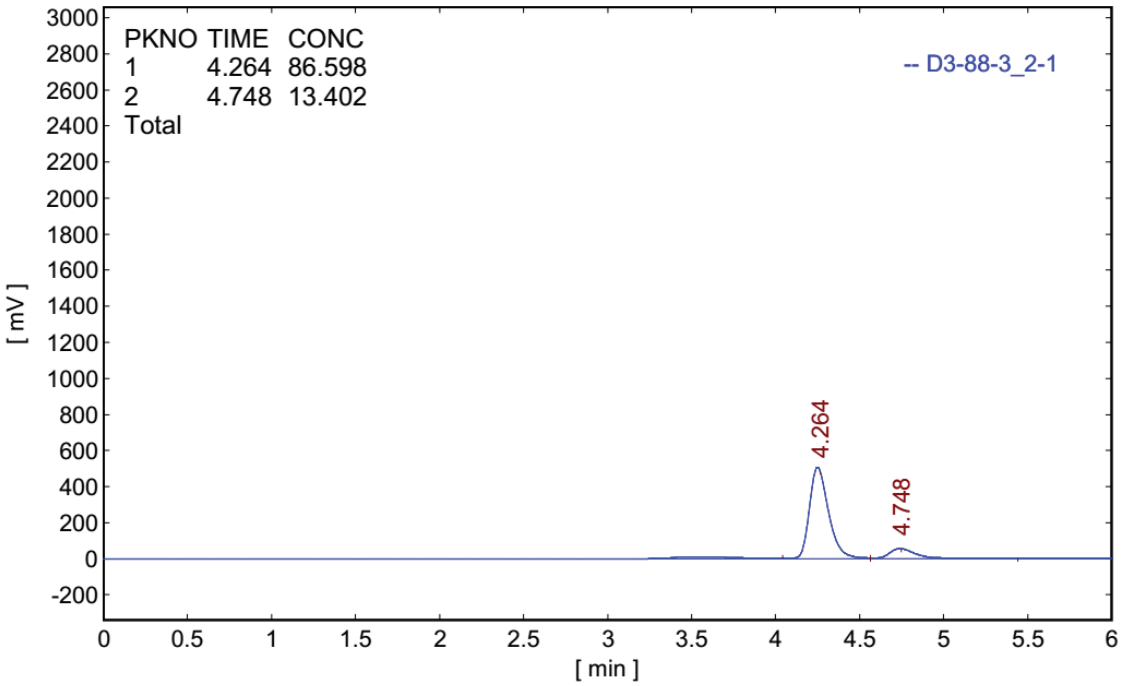
2d: 74% ee (Table 4, entry 6)



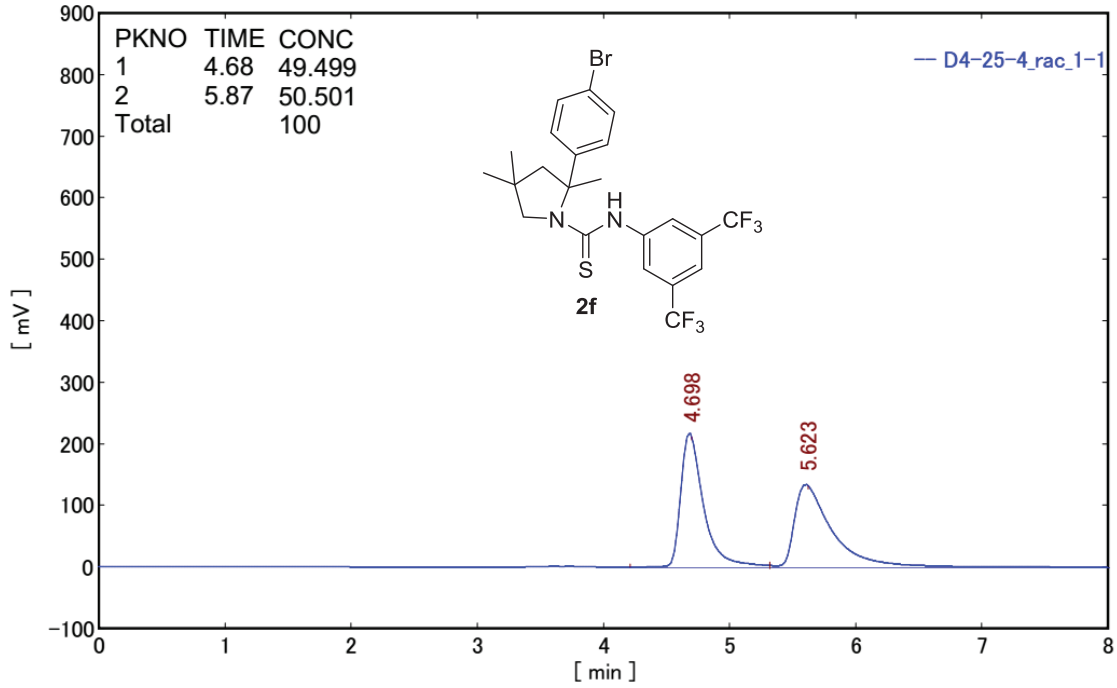
Rac-**2e** Chiralpak ID, hexane: EtOH= 20: 1, 1.0 mL/ min 254 nm



2e: 73% ee (Table 4, entry 8)



Entry 11: *Rac*-**2f** Chiralpak ID, hexane: EtOH= 40: 1, 1.0 mL/ min 254 nm



2f: 71% ee

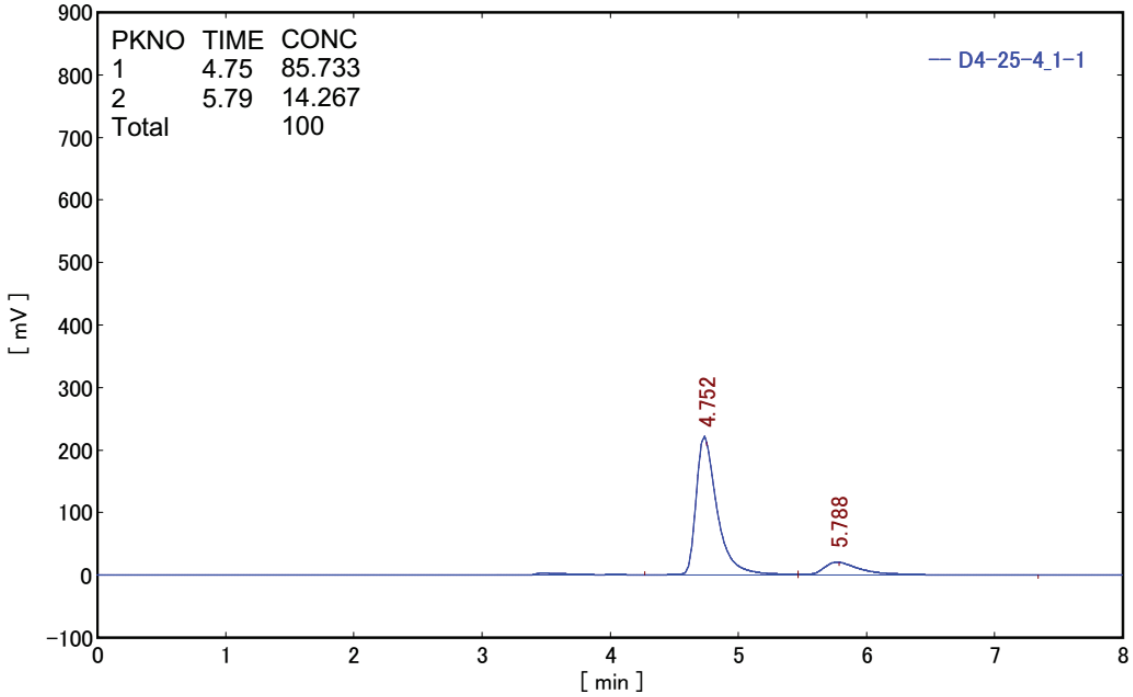
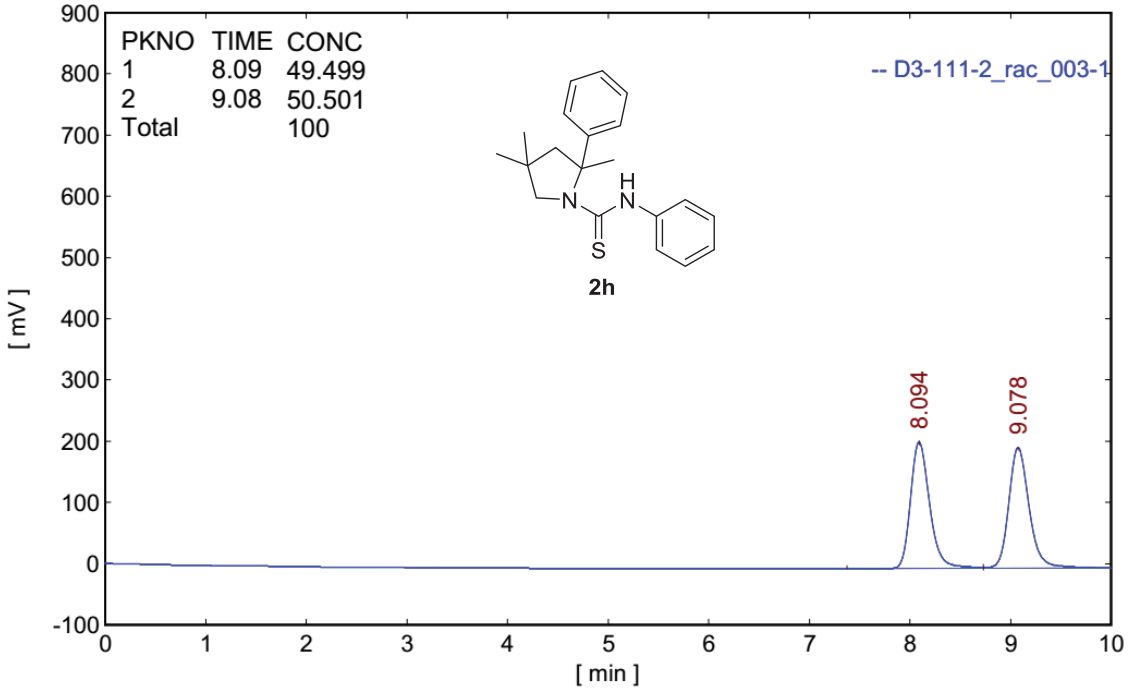
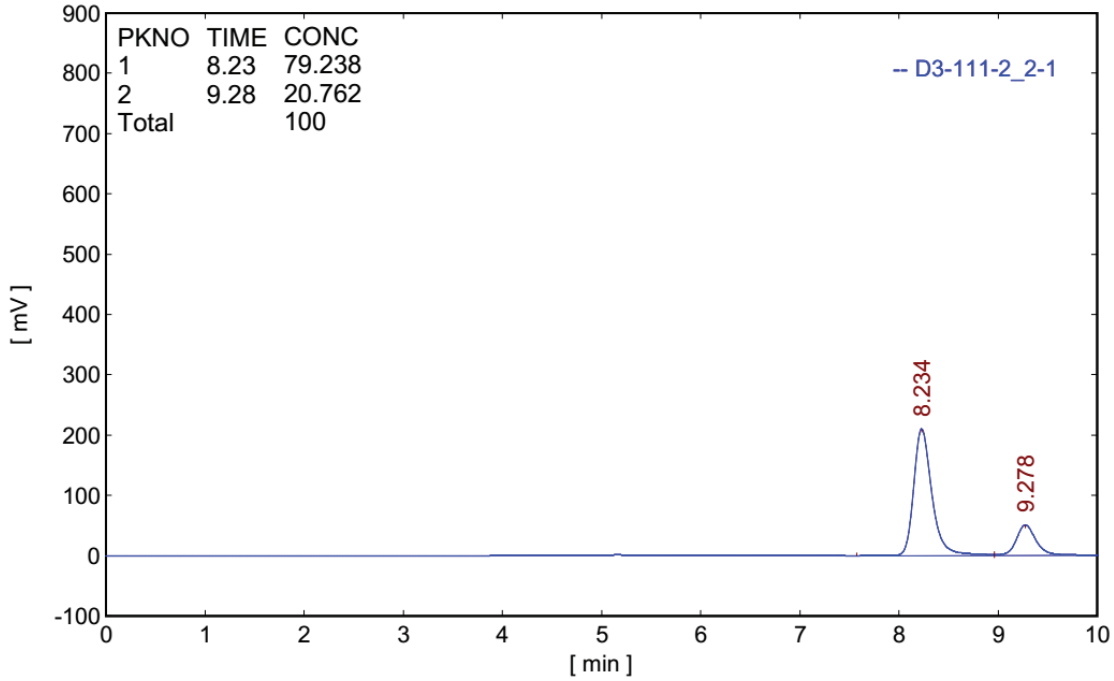


Table 5

Entry 3: *Rac*-**2h** Chiralpak IB, hexane: EtOH= 50: 1, 0.75 mL/min 254 nm



2h: 58% ee



Computational Study

Summary of the calculated energies

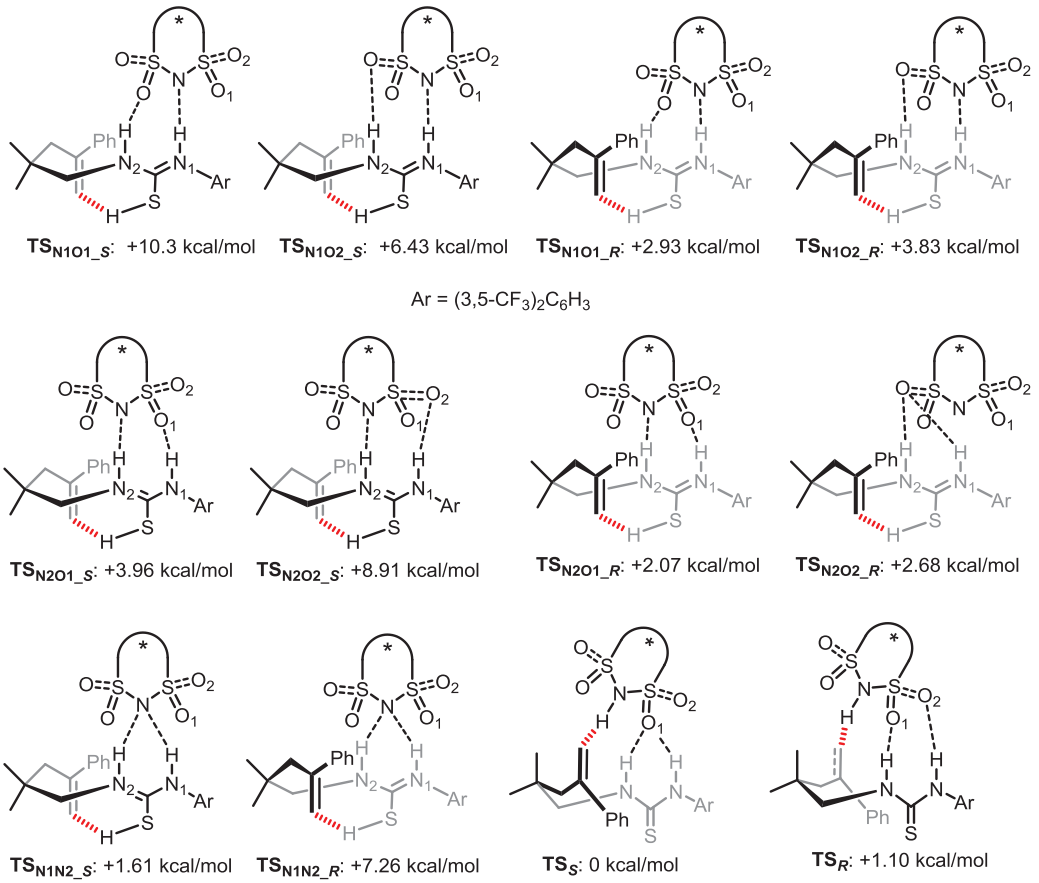


Figure S1. Schematic structures and relative energies of possible transition states (298.15 K in toluene) of the **DSI**-catalyzed hydroamination at the M06-2X/6-311+G(d,p)/SMD(toluene)//ONIOM(B3LYP/6-31G(d):HF/3-21G*) level of theory.

Table S1. Electronic energies of possible transtion states at 298.15 K in toluene at the M06-2X/6-311+G(d,p)/SMD (toluene)//ONIOM(B3LYP/6-31G(d): HF/3-21G*) level of theory.

	$E_{sp}^{toluene}$ (a.u.)	ΔE (kcal/mol)		$E_{sp}^{toluene}$ (a.u.)	ΔE (kcal/mol)
TS_{N1O2_S}	-7962.461166	+10.312	TS_{N1O1_R}	-7962.472932	+2.939
TS_{N1O2_S}	-7962.467356	+6.427	TS_{N1O2_R}	-7962.471501	+3.826
TS_{N2O1_S}	-7962.471295	+3.956	TS_{N2O1_R}	-7962.474300	+2.070
TS_{N2O2_S}	-7962.463404	+8.907	TS_{N2O2_R}	-7962.473332	+2.678
TS_{N1N2_S}	-7962.475041	+1.605	TS_{N1N2_R}	-7962.466025	+7.263
TS_S	-7962.477599	0	TS_R	-7962.475851	+1.097

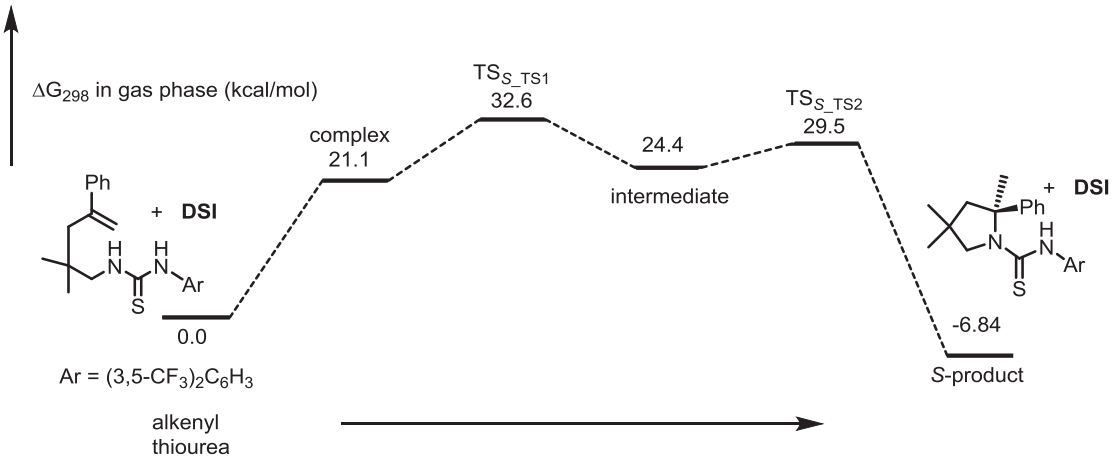


Figure. S2 Calculated Gibbs energy profile for the **DSI**-catalyzed hydroamination of alkenyl thiourea via transition state structure TS_S at 298.15 K in toluene at the M06-2X/6-311+G(d,p)/SMD(toluene)// ONIOM(M06-2X/6-31G(d): HF/3-21G*) level of theory.

Table S3. Calculated Gibbs energies for the **DSI**-catalyzed hydroamination via transition state TS_S at 298.15 K in toluene at the M06-2X/6-311+G(d,p)/SMD (toluene)//ONIOM(M06-2X/6-31G(d):HF/3-21G*) level of theory.

	G_{298} (a.u.)	ΔG_{298} (kcal/mol)
thiourea + **DSI**	-7961.397859	0
complex	-7961.364227	21.104080
TS_{S_TS1}	-7961.345959	32.567187
intermediate	-7961.358931	24.427320
TS_{S_TS2}	-7961.350799	29.530150
product + **DSI**	-7961.408841	-6.891205

Table S4. Calculated Gibbs energies for the **DSI**-catalyzed hydroamination via transition state TS_R at 298.15 K in toluene at the M06-2X/6-311+G(d,p)/SMD (toluene)//ONIOM(M06-2X/6-31G(d):HF/3-21G*) level of theory.

	G_{298} (a.u.)	ΔG_{298} (kcal/mol)
thiourea + **DSI**	-7961.397859	0
complex	-7961.370872	16.934343
TS_{S_TS1}	-7961.342649	34.644275
intermediate	-7961.350616	29.6449825
TS_{S_TS2}	-7961.347031	31.89457
product + **DSI**	-7961.408841	-6.891205

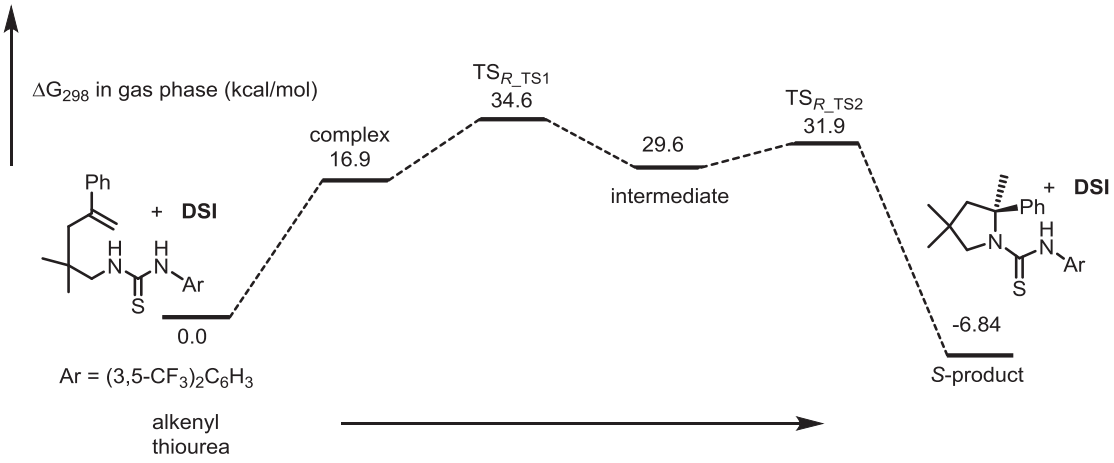
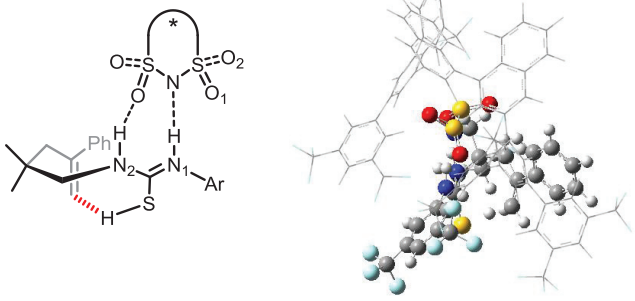


Figure. S3 Calculated Gibbs energy profile for the **DSI**-catalyzed hydroamination of alkenyl thiourea via transition state structure TS_R at 298.15 K in toluene at the M06-2X/6-311+G(d,p)/SMD(toluene)//ONIOM(M06-2X/6-31G(d):HF/3-21G*) level of theory.

Cartesian coordinates of the structures

TS_{N1O2_S}



E (ONIOM(B3LYP/6-31G(d):HF/3-21G*)) = -7911.096155 a.u.
Imaginary Freq = 1: -832.46 cm-1
Zero-point Energy Correction = 1.285824
Thermal Correction to Energy = 1.38963
Thermal Correction to Enthalpy = 1.390574
Thermal Correction to Free Energy = 1.120923
EE + Zero-point Energy = -7909.810331
EE + Thermal Energy Correction = -7909.706525
EE + Thermal Enthalpy Correction = -7909.705581
EE + Thermal Free Energy Correction = -7909.975232

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.461166

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	2.453948	-1.749989	3.813709
3	6	0	3.496447	-2.470015	2.908859
4	7	0	1.734926	-2.500346	1.042901
5	1	0	2.943414	-1.539375	4.779416
6	1	0	2.273409	-0.760416	3.387729
7	6	0	4.470905	-1.374203	2.416424
8	1	0	4.896800	-0.829084	3.267328

9	1	0	3.984251	-0.650390	1.755945
10	1	0	5.305111	-1.831026	1.870670
11	6	0	4.337357	-3.523205	3.664825
12	1	0	4.945243	-3.044770	4.440955
13	1	0	5.017526	-4.027938	2.968541
14	1	0	3.732845	-4.297631	4.146810
15	6	0	0.037712	-1.436091	4.549535
16	6	0	-2.001987	0.326329	5.377773
17	6	0	-0.926700	-1.830786	5.508309
18	6	0	-0.056514	-0.131433	4.014603
19	6	0	-1.065799	0.735489	4.427201
20	6	0	-1.931514	-0.963125	5.914016
21	1	0	-0.856228	-2.808081	5.974214
22	1	0	0.620360	0.220552	3.244190
23	1	0	-1.108823	1.730631	3.992990
24	1	0	-2.663559	-1.269247	6.652368
25	1	0	-2.787393	0.991204	5.718704
26	6	0	0.890906	-3.738392	4.159106
27	1	0	0.531471	-4.060547	2.883714
28	1	0	1.745871	-4.405007	4.237252
29	6	0	0.593214	-3.090356	0.655781
30	7	0	-0.185045	-2.454550	-0.244374
31	6	0	-1.262617	-3.084465	-0.935368
32	6	0	-3.327344	-4.312927	-2.370913
33	6	0	-1.020664	-4.265226	-1.647798
34	6	0	-2.529070	-2.500291	-0.957807
35	6	0	-3.550908	-3.122304	-1.682894
36	6	0	-2.053567	-4.881203	-2.348655
37	1	0	-0.024705	-4.691845	-1.668575
38	1	0	-2.700346	-1.557128	-0.452307
39	1	0	-4.125616	-4.780444	-2.934218
40	16	0	0.070925	-4.607272	1.352710
41	1	0	-0.011673	-4.113510	4.639012
42	6	0	2.852993	-3.194349	1.697083
43	1	0	2.497203	-4.181127	1.984681
44	1	0	3.633255	-3.365584	0.947902
45	1	0	1.967057	-1.594290	0.607580
46	1	0	-0.015005	-1.446156	-0.434980

47	6	0	-1.204044	2.826374	-0.129441
48	6	0	-0.124194	3.661315	-0.082545
49	6	0	-2.301096	4.088993	1.581992
50	6	0	-0.066618	4.719260	0.873486
51	6	0	-2.337375	3.054762	0.700695
52	6	0	-1.172069	4.925589	1.715037
53	6	0	1.070729	5.556591	1.027441
54	1	0	-1.992661	6.123418	3.300306
55	1	0	-3.160756	4.285066	2.191884
56	6	0	1.081681	6.542617	1.958596
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58	1	0	1.946909	7.164471	2.070163
59	6	0	-0.040182	6.759211	2.790738
60	1	0	-0.014231	7.546878	3.516701
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62	6	0	3.144055	2.505634	-1.697018
63	1	0	4.200932	3.495065	-3.217785
64	6	0	3.305692	3.481360	-2.628451
65	6	0	1.043860	3.521624	-1.026178
66	6	0	2.336222	4.482969	-2.850823
67	6	0	1.955031	2.509564	-0.908881
68	6	0	1.195466	4.519383	-2.034159
69	6	0	2.499501	5.456857	-3.867727
70	1	0	-0.658481	5.548272	-1.661968
71	6	0	1.555831	6.410464	-4.062970
72	1	0	3.377362	5.418315	-4.482056
73	1	0	1.677038	7.141998	-4.836379
74	6	0	0.398564	6.440933	-3.252441
75	1	0	-0.346327	7.190653	-3.427402
76	6	0	0.222096	5.526638	-2.266131
77	16	0	1.487330	1.141887	0.173980
78	8	0	1.296677	1.663564	1.541854
79	8	0	2.515466	0.071774	0.065489
80	16	0	-1.060278	1.366280	-1.186302
81	8	0	-0.719623	1.821926	-2.538220
82	8	0	-2.267875	0.544490	-1.034934
83	7	0	0.155304	0.489636	-0.486756
84	6	0	-3.621732	2.285773	0.624776

85	6	0	-6.076301	0.996429	0.566633
86	6	0	-3.971400	1.411907	1.636725
87	6	0	-4.512101	2.528544	-0.408457
88	6	0	-5.736428	1.885014	-0.444052
89	6	0	-5.199590	0.763824	1.613665
90	1	0	-3.279368	1.209678	2.429004
91	1	0	-4.244435	3.205151	-1.195092
92	1	0	-7.032119	0.511328	0.549931
93	6	0	4.314556	1.586004	-1.498879
94	6	0	6.582237	0.025911	-1.169973
95	6	0	4.356850	0.305138	-2.025470
96	6	0	5.411889	2.080962	-0.817620
97	6	0	6.554945	1.307630	-0.650929
98	6	0	5.481255	-0.482272	-1.850567
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101	1	0	7.465980	-0.573037	-1.067860
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104	6	0	5.195808	-2.255645	-3.617839
105	6	0	5.748922	-2.901295	-1.392100
106	6	0	5.701946	-4.227325	-1.765432
107	6	0	5.167449	-3.586299	-3.982651
108	1	0	4.984202	-1.501197	-4.347444
109	1	0	5.951581	-2.643486	-0.373842
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112	6	0	9.907124	2.884336	1.488045
113	6	0	8.288224	3.070621	-0.271609
114	6	0	8.278694	1.156910	1.151023
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116	6	0	9.366126	3.574093	0.426008
117	1	0	7.880763	3.627338	-1.090150
118	1	0	7.843517	0.231086	1.466039
119	1	0	10.724231	3.293369	2.043375
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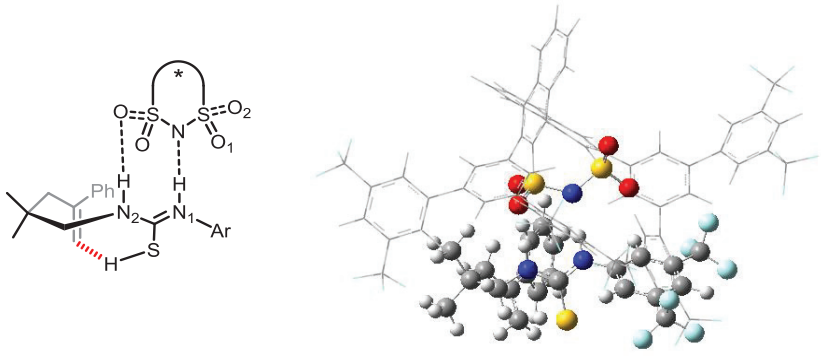
124	6	0	-8.210450	3.635887	-2.681313
125	6	0	-7.829864	1.460804	-3.545160
126	1	0	-6.426784	0.262215	-2.480700
127	1	0	-7.137193	4.144674	-0.918214
128	1	0	-9.122618	2.888962	-4.454400
129	6	0	-5.570363	-0.150930	2.730296
130	6	0	-6.226333	-1.840425	4.847551
131	6	0	-5.633481	0.331710	4.027121
132	6	0	-5.843838	-1.492198	2.501894
133	6	0	-6.177083	-2.317979	3.556443
134	6	0	-5.947587	-0.511972	5.072857
135	1	0	-5.451630	1.369828	4.217260
136	1	0	-5.775166	-1.890888	1.511355
137	1	0	-6.475929	-2.490637	5.658337
138	6	0	4.913066	-3.948926	-5.402137
139	6	0	5.981799	-5.266525	-0.742699
140	6	0	9.979771	4.857187	-0.004780
141	6	0	9.952390	0.889099	2.953216
142	6	0	-5.932533	0.018997	6.456875
143	6	0	-6.520435	-3.740127	3.292324
144	6	0	-8.922027	4.937848	-2.734370
145	6	0	-8.126672	0.404180	-4.546464
146	6	0	-1.801428	-6.185993	-3.059507
147	6	0	-4.925548	-2.511869	-1.684104
148	9	0	4.350478	-5.171396	-5.502353
149	9	0	4.099323	-3.053094	-5.999550
150	9	0	6.050291	-3.983917	-6.133381
151	9	0	7.302682	-5.455413	-0.532971
152	9	0	5.462211	-4.910189	0.463967
153	9	0	5.459276	-6.459507	-1.084630
154	9	0	9.012412	0.164970	3.600412
155	9	0	10.884997	0.007571	2.525917
156	9	0	10.560797	1.692614	3.850554
157	9	0	10.577082	5.487775	1.028494
158	9	0	9.056369	5.689624	-0.533804
159	9	0	10.927497	4.684055	-0.953649
160	9	0	-8.501856	0.938703	-5.729335

161	9	0	-9.137012	-0.406776	-4.154225
162	9	0	-7.058063	-0.390979	-4.759977
163	9	0	-8.159134	5.937493	-2.238282
164	9	0	-9.271111	5.260332	-3.998146
165	9	0	-10.063668	4.935898	-2.007414
166	9	0	-5.781256	-4.250450	2.286843
167	9	0	-7.816087	-3.901336	2.940372
168	9	0	-6.321416	-4.502102	4.391668
169	9	0	-6.652666	-0.745421	7.300416
170	9	0	-4.670190	0.073167	6.972888
171	9	0	-6.401651	1.282941	6.515009
172	9	0	-5.569845	-2.727500	-0.500339
173	9	0	-5.717188	-3.013535	-2.648069
174	9	0	-4.880604	-1.170139	-1.849463
175	9	0	-2.589074	-6.320313	-4.147139
176	9	0	-2.051724	-7.243303	-2.255518
177	9	0	-0.517394	-6.292525	-3.465501

TS_{N102_S}



E (ONIOM(B3LYP/6-31G(d):HF/3-21G*)) = -7911.104351 a.u.
Imaginary Freq = 1: -820.27 cm-1
Electronic Energy (EE) = -7911.1044
Zero-point Energy Correction = 1.286352
Thermal Correction to Energy = 1.389699
Thermal Correction to Enthalpy = 1.390643
Thermal Correction to Free Energy = 1.127158
EE + Zero-point Energy = -7909.817999

EE + Thermal Energy Correction = -7909.714652

EE + Thermal Enthalpy Correction - -7909.713708

EE + Thermal Free Energy Correction = -7909.977193

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.467356

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.892911	-3.533619	-3.588126
2	6	0	2.130445	-3.701446	-2.738272
3	6	0	3.463357	-2.953514	-3.009685
4	7	0	2.228198	-0.776128	-2.460976
5	1	0	2.351734	-4.781263	-2.749325
6	1	0	1.854418	-3.503280	-1.698602
7	6	0	4.328824	-3.158751	-1.742886
8	1	0	4.392258	-4.224249	-1.491130
9	1	0	3.921383	-2.633185	-0.873597
10	1	0	5.346744	-2.806512	-1.926345
11	6	0	4.262472	-3.537769	-4.196076
12	1	0	4.448096	-4.606172	-4.036484
13	1	0	5.239741	-3.047913	-4.270524
14	1	0	3.761262	-3.429065	-5.162916
15	6	0	-0.364088	-4.049615	-3.024155
16	6	0	-2.718055	-5.215070	-1.995160
17	6	0	-0.581391	-4.138523	-1.629370
18	6	0	-1.372182	-4.549058	-3.884030
19	6	0	-2.533308	-5.117046	-3.377098
20	6	0	-1.742226	-4.722030	-1.127486
21	1	0	0.126070	-3.727799	-0.917019
22	1	0	-1.220197	-4.538008	-4.957986
23	1	0	-3.299382	-5.500247	-4.041502
24	1	0	-1.873947	-4.783293	-0.050865
25	1	0	-3.622367	-5.680967	-1.620854
26	6	0	0.919817	-2.940119	-4.852664
27	1	0	0.874902	-1.594697	-4.671020
28	1	0	1.856495	-2.951820	-5.403706

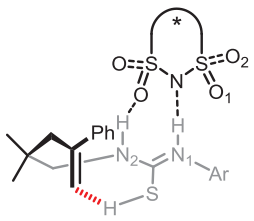
29	6	0	1.263111	0.033526	-2.921168
30	7	0	0.566536	0.761076	-2.022072
31	6	0	-0.350249	1.798853	-2.370228
32	6	0	-2.108336	3.875278	-3.009268
33	6	0	-1.673208	1.741697	-1.927900
34	6	0	0.105337	2.903019	-3.096241
35	6	0	-0.779768	3.927510	-3.426913
36	6	0	-2.540548	2.789139	-2.248790
37	1	0	-2.012038	0.908392	-1.323552
38	1	0	1.148153	2.985359	-3.373462
39	1	0	-2.794882	4.671520	-3.269486
40	16	0	0.853461	0.099752	-4.619883
41	1	0	0.035467	-3.028455	-5.481401
42	6	0	3.265973	-1.431044	-3.267083
43	1	0	3.040727	-1.232488	-4.313400
44	1	0	4.218147	-0.927852	-3.051032
45	1	0	2.403620	-0.755677	-1.443921
46	1	0	0.587317	0.480025	-1.021369
47	6	0	-1.288012	-1.462485	2.563188
48	6	0	-0.321942	-2.066301	3.322151
49	6	0	-2.700431	-3.385740	2.778008
50	6	0	-0.481303	-3.414880	3.757946
51	6	0	-2.525584	-2.121585	2.307657
52	6	0	-1.687367	-4.076657	3.476786
53	6	0	0.541561	-4.124562	4.442103
54	1	0	-2.797974	-5.904608	3.698072
55	1	0	-3.642140	-3.873973	2.622032
56	6	0	0.349499	-5.409890	4.829728
57	1	0	1.469932	-3.634392	4.639932
58	1	0	1.130198	-5.938796	5.338137
59	6	0	-0.875139	-6.065311	4.566009
60	1	0	-1.010543	-7.078686	4.886829
61	6	0	-1.866337	-5.416522	3.907450
62	6	0	3.055655	-0.259332	3.317482
63	1	0	4.056458	0.538661	4.982142
64	6	0	3.185016	0.016587	4.640063
65	6	0	0.920926	-1.329894	3.756167
66	6	0	2.189586	-0.327792	5.578903

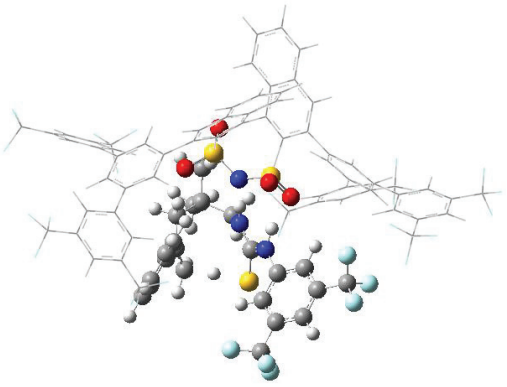
67	6	0	1.901705	-0.965239	2.876767
68	6	0	1.031023	-0.988946	5.137882
69	6	0	2.323267	0.012127	6.949149
70	1	0	-0.889974	-1.743687	5.754175
71	6	0	1.334830	-0.278566	7.829424
72	1	0	3.215647	0.512289	7.270032
73	1	0	1.434859	-0.015355	8.863201
74	6	0	0.156239	-0.920066	7.385572
75	1	0	-0.626099	-1.127065	8.087515
76	6	0	0.006224	-1.265490	6.082882
77	16	0	1.558107	-1.265518	1.133521
78	8	0	1.226980	-2.696870	0.971368
79	8	0	2.720579	-0.822445	0.318363
80	16	0	-0.876451	0.126528	1.785301
81	8	0	-0.457217	1.057175	2.839024
82	8	0	-1.989625	0.539039	0.922111
83	7	0	0.354292	-0.253087	0.743541
84	6	0	-3.702435	-1.494149	1.624041
85	6	0	-5.965910	-0.438936	0.417816
86	6	0	-4.131990	-1.980781	0.403543
87	6	0	-4.421005	-0.487888	2.250027
88	6	0	-5.546702	0.044989	1.649231
89	6	0	-5.265955	-1.458313	-0.204782
90	1	0	-3.566204	-2.740889	-0.095276
91	1	0	-4.090983	-0.103499	3.194173
92	1	0	-6.845316	-0.033280	-0.041360
93	6	0	4.141024	0.233622	2.409898
94	6	0	6.152873	1.192064	0.770143
95	6	0	4.078454	1.526184	1.919584
96	6	0	5.218131	-0.573261	2.093483
97	6	0	6.223481	-0.101896	1.263236
98	6	0	5.081948	2.011340	1.094016
99	1	0	3.241783	2.146371	2.173856
100	1	0	5.248919	-1.582898	2.451614
101	1	0	6.923248	1.556227	0.118996
102	6	0	-6.312059	1.135083	2.323764
103	6	0	-7.747394	3.161526	3.576296
104	6	0	-6.201592	2.445605	1.884544

105	6	0	-7.139493	0.850728	3.396345
106	6	0	-7.853803	1.859784	4.010078
107	6	0	-6.915764	3.444206	2.515474
108	1	0	-5.552130	2.683094	1.068203
109	1	0	-7.225534	-0.154872	3.753855
110	1	0	-8.299752	3.941235	4.055814
111	6	0	-5.719725	-2.007556	-1.513646
112	6	0	-6.529426	-3.068731	-3.961967
113	6	0	-5.818010	-1.196748	-2.636646
114	6	0	-6.035055	-3.350392	-1.633204
115	6	0	-6.422427	-3.872950	-2.851219
116	6	0	-6.231151	-1.728922	-3.839776
117	1	0	-5.541443	-0.166346	-2.572172
118	1	0	-5.990332	-3.985819	-0.772351
119	1	0	-6.835307	-3.474876	-4.902519
120	6	0	7.314581	-1.011271	0.819519
121	6	0	9.266590	-2.788800	-0.081665
122	6	0	7.504898	-1.229901	-0.535444
123	6	0	8.121830	-1.688708	1.720355
124	6	0	9.084268	-2.567308	1.266050
125	6	0	8.468228	-2.112214	-0.976029
126	1	0	6.874522	-0.732166	-1.242781
127	1	0	8.009576	-1.521844	2.772010
128	1	0	10.011331	-3.474847	-0.424811
129	6	0	4.996773	3.378413	0.511121
130	6	0	4.863180	5.898302	-0.673452
131	6	0	3.874349	3.764165	-0.204758
132	6	0	6.048293	4.275135	0.635333
133	6	0	5.971385	5.522752	0.054237
134	6	0	3.820418	5.009489	-0.797442
135	1	0	3.050561	3.086904	-0.310434
136	1	0	6.924324	4.000037	1.185948
137	1	0	4.815065	6.860497	-1.136264
138	6	0	-8.788061	1.525384	5.114000
139	6	0	-6.747173	4.853804	2.075919
140	6	0	-6.387398	-0.838301	-5.018990
141	6	0	-6.669449	-5.330163	-2.963862
142	6	0	2.637281	5.358907	-1.626790

143	6	0	7.079304	6.491781	0.256617
144	6	0	8.640080	-2.315291	-2.436744
145	6	0	9.898113	-3.328759	2.249191
146	6	0	-3.953603	2.769223	-1.733347
147	6	0	-0.271797	5.132979	-4.175745
148	9	0	-8.971644	2.575070	5.943234
149	9	0	-8.333999	0.483129	5.845467
150	9	0	-10.014889	1.168373	4.667004
151	9	0	-7.831998	5.596810	2.391897
152	9	0	-5.685738	5.456902	2.656539
153	9	0	-6.555533	4.935928	0.742659
154	9	0	-5.510404	-6.036719	-3.108783
155	9	0	-7.432749	-5.634309	-4.031132
156	9	0	-7.259927	-5.827181	-1.856887
157	9	0	-7.622440	-0.292585	-5.094745
158	9	0	-5.513029	0.188465	-4.982172
159	9	0	-6.196436	-1.516570	-6.172870
160	9	0	-4.472040	1.513795	-1.714304
161	9	0	-4.026797	3.221948	-0.455849
162	9	0	-4.782417	3.531637	-2.470954
163	9	0	0.287578	6.039566	-3.338841
164	9	0	0.665254	4.800414	-5.085610
165	9	0	-1.269461	5.768510	-4.828488
166	9	0	1.491559	4.968598	-1.032854
167	9	0	2.670205	4.722817	-2.829655
168	9	0	2.578698	6.678917	-1.872616
169	9	0	7.160414	7.367494	-0.767421
170	9	0	8.268625	5.859977	0.369619
171	9	0	6.927472	7.225018	1.382634
172	9	0	9.294130	-4.475378	2.638152
173	9	0	10.112343	-2.609872	3.371909
174	9	0	11.094723	-3.678603	1.732207
175	9	0	7.437348	-2.305273	-3.072413
176	9	0	9.374659	-1.344361	-3.021303
177	9	0	9.244756	-3.488159	-2.709857

TS_{N101_R}





E (ONIOM(B3LYP/6-31G(d): HF/3-21G*)) = -7911.129054 a.u.
Imaginary Freq = 1: -842.02 cm-1
Zero-point Energy Correction = 1.28867
Thermal Correction to Energy = 1.391795
Thermal Correction to Enthalpy = 1.39274
Thermal Correction to Free Energy = 1.128899
EE + Zero-point Energy = -7909.840385
EE + Thermal Energy Correction = -7909.737259
EE + Thermal Enthalpy Correction = -7909.736315
EE + Thermal Free Energy Correction = -7910.000155

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.472932

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.069499	2.034052	-3.738580
2	6	0	-1.988307	2.958284	-2.547188
3	6	0	-0.718230	3.817402	-2.262122
4	7	0	0.558315	1.599211	-2.097809
5	1	0	-2.840391	3.650295	-2.628113
6	1	0	-2.206746	2.378660	-1.647457
7	6	0	-0.809121	4.284579	-0.791775
8	1	0	-1.768677	4.761423	-0.582117
9	1	0	-0.691423	3.465568	-0.077594
10	1	0	-0.021126	5.018990	-0.585599

11	6	0	-0.626567	5.093582	-3.128436
12	1	0	-1.456960	5.769174	-2.895255
13	1	0	0.310024	5.617927	-2.913129
14	1	0	-0.646849	4.899255	-4.204539
15	6	0	-2.835741	0.783683	-3.608787
16	6	0	-4.173436	-1.697484	-3.434017
17	6	0	-3.525099	0.245410	-4.719962
18	6	0	-2.859736	0.058635	-2.398433
19	6	0	-3.506908	-1.171156	-2.326004
20	6	0	-4.190717	-0.971487	-4.629445
21	1	0	-3.571411	0.806586	-5.647943
22	1	0	-2.346704	0.419915	-1.515028
23	1	0	-3.478628	-1.711625	-1.386068
24	1	0	-4.724307	-1.358391	-5.492728
25	1	0	-4.673133	-2.659294	-3.372696
26	6	0	-1.396795	2.278883	-4.934047
27	1	0	-1.034541	3.278868	-5.150242
28	1	0	-1.675996	1.698048	-5.812268
29	6	0	1.012496	0.588399	-2.864714
30	7	0	1.324615	-0.546460	-2.212223
31	6	0	1.691789	-1.818763	-2.718390
32	6	0	2.456296	-4.401595	-3.493100
33	6	0	1.046809	-2.442865	-3.791682
34	6	0	2.696894	-2.494369	-2.021489
35	6	0	3.070879	-3.779929	-2.409254
36	6	0	1.444293	-3.722527	-4.176089
37	1	0	0.237717	-1.947416	-4.310735
38	1	0	3.161079	-2.018709	-1.164664
39	1	0	2.744086	-5.402794	-3.789538
40	16	0	1.215888	0.739770	-4.584067
41	1	0	-0.201890	1.621142	-4.727922
42	6	0	0.603440	3.022722	-2.456257
43	1	0	0.972451	3.088962	-3.477899
44	1	0	1.360009	3.507404	-1.831737
45	1	0	0.343989	1.359293	-1.118565
46	6	0	-1.759882	0.052519	3.029931
47	6	0	-0.730868	-0.138330	3.913824
48	6	0	-3.096933	-1.550470	4.207827

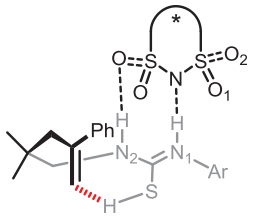
49	6	0	-0.826507	-1.127360	4.939239
50	6	0	-2.989520	-0.659918	3.184458
51	6	0	-2.030548	-1.832776	5.083564
52	6	0	0.253738	-1.445030	5.806307
53	1	0	-3.083810	-3.335183	6.203653
54	1	0	-4.028367	-2.057979	4.359784
55	6	0	0.115063	-2.396933	6.762136
56	1	0	1.182813	-0.931900	5.691379
57	1	0	0.939465	-2.635164	7.403404
58	6	0	-1.108349	-3.087201	6.919594
59	1	0	-1.198881	-3.832890	7.683615
60	6	0	-2.153323	-2.812290	6.102040
61	6	0	2.751631	1.140283	2.974492
62	1	0	3.946129	2.454487	4.097118
63	6	0	2.990293	1.975647	4.019148
64	6	0	0.549489	0.661994	3.877222
65	6	0	2.016443	2.243956	5.004860
66	6	0	1.488894	0.488575	2.899761
67	6	0	0.777895	1.585312	4.939831
68	6	0	2.264466	3.163941	6.055286
69	1	0	-1.158359	1.405468	5.863326
70	6	0	1.309314	3.423774	6.981091
71	1	0	3.217493	3.653490	6.096220
72	1	0	1.496243	4.123519	7.770711
73	6	0	0.053613	2.778920	6.905955
74	1	0	-0.698229	3.005491	7.634691
75	6	0	-0.205822	1.885455	5.919334
76	16	0	0.968651	-0.460225	1.458786
77	8	0	0.548247	-1.795716	1.896383
78	8	0	2.071833	-0.426932	0.461123
79	16	0	-1.401116	1.165551	1.636881
80	8	0	-0.980693	2.445839	2.228491
81	8	0	-2.553183	1.243235	0.711028
82	7	0	-0.209816	0.438226	0.769622
83	6	0	-4.211446	-0.466030	2.343954
84	6	0	-6.546548	-0.158978	0.872953
85	6	0	-4.835467	-1.568568	1.780050
86	6	0	-4.780666	0.785708	2.185508

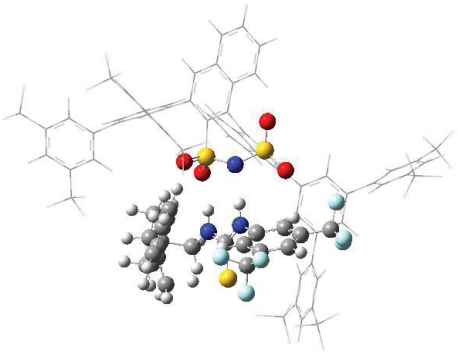
87	6	0	-5.921066	0.951373	1.421538
88	6	0	-6.016497	-1.425471	1.061526
89	1	0	-4.400215	-2.540416	1.903458
90	1	0	-4.315881	1.640868	2.627529
91	1	0	-7.409843	-0.029988	0.250384
92	6	0	3.880657	0.944864	2.006399
93	6	0	6.112587	0.726936	0.375126
94	6	0	4.194056	1.954911	1.116644
95	6	0	4.696718	-0.171743	2.089896
96	6	0	5.818102	-0.284363	1.281676
97	6	0	5.303816	1.849473	0.288074
98	1	0	3.579498	2.832205	1.081107
99	1	0	4.471845	-0.942499	2.799694
100	1	0	6.957002	0.622976	-0.277523
101	1	0	1.477011	-0.455061	-1.192825
102	6	0	5.609281	2.943126	-0.674363
103	6	0	6.142951	5.034763	-2.445216
104	6	0	6.884632	3.485585	-0.769151
105	6	0	4.612135	3.459492	-1.485310
106	6	0	4.879953	4.498890	-2.354357
107	6	0	7.139867	4.517488	-1.645294
108	1	0	7.674702	3.107593	-0.153795
109	1	0	3.630727	3.033385	-1.445390
110	1	0	6.350424	5.830679	-3.127383
111	6	0	6.725054	-1.461131	1.406308
112	6	0	8.445562	-3.633091	1.700141
113	6	0	6.246569	-2.758283	1.298527
114	6	0	8.076071	-1.266703	1.656515
115	6	0	8.922990	-2.344799	1.793985
116	6	0	7.106856	-3.828918	1.448555
117	1	0	5.214739	-2.939720	1.084304
118	1	0	8.460854	-0.274474	1.772235
119	1	0	9.099573	-4.466741	1.838602
120	6	0	-6.678096	-2.603211	0.436643
121	6	0	-7.935530	-4.751037	-0.830658
122	6	0	-8.040799	-2.820456	0.590336
123	6	0	-5.954993	-3.488966	-0.345742
124	6	0	-6.584770	-4.538379	-0.981776

125	6	0	-8.652622	-3.889261	-0.029641
126	1	0	-8.623011	-2.156521	1.195415
127	1	0	-4.901482	-3.352766	-0.473507
128	1	0	-8.418957	-5.565342	-1.326707
129	6	0	-6.386104	2.321986	1.080330
130	6	0	-7.200388	4.874218	0.324827
131	6	0	-7.705999	2.714476	1.235658
132	6	0	-5.472682	3.222092	0.547365
133	6	0	-5.888679	4.483831	0.171305
134	6	0	-8.102372	3.980242	0.857659
135	1	0	-8.418807	2.043527	1.669709
136	1	0	-4.450379	2.914674	0.429990
137	1	0	-7.510730	5.858686	0.048532
138	6	0	4.184876	-4.455105	-1.650282
139	6	0	0.795025	-4.369253	-5.373156
140	6	0	10.372578	-2.111930	2.018232
141	6	0	6.582957	-5.215167	1.313109
142	6	0	8.495216	5.126467	-1.683032
143	6	0	3.776822	5.034036	-3.192260
144	6	0	-5.792488	-5.389645	-1.903312
145	6	0	-10.097966	-4.141388	0.207214
146	6	0	-9.530151	4.368726	0.987007
147	6	0	-4.907429	5.418364	-0.434191
148	9	0	5.390776	-5.358521	1.925278
149	9	0	7.439181	-6.112210	1.851882
150	9	0	6.403517	-5.581698	0.022591
151	9	0	10.939283	-3.135838	2.691228
152	9	0	10.586264	-0.975320	2.717686
153	9	0	11.061366	-1.981929	0.860993
154	9	0	8.763410	5.651149	-2.897444
155	9	0	9.450158	4.218229	-1.390017
156	9	0	8.632921	6.131760	-0.788596
157	9	0	3.244319	4.094780	-4.008274
158	9	0	4.176542	6.064988	-3.959136
159	9	0	2.740358	5.472078	-2.426067
160	9	0	-4.560465	-5.640211	-1.414583
161	9	0	-5.600175	-4.782843	-3.107324
162	9	0	-6.402920	-6.562988	-2.155665

163	9	0	-10.662092	-4.782983	-0.837948
164	9	0	-10.315678	-4.910932	1.297687
165	9	0	-10.770366	-2.987935	0.411492
166	9	0	-5.415251	6.657704	-0.583668
167	9	0	-4.498320	5.010239	-1.665774
168	9	0	-3.779090	5.518741	0.306109
169	9	0	-9.666821	5.703091	1.140214
170	9	0	-10.113441	3.757813	2.041084
171	9	0	-10.258277	4.028912	-0.101992
172	9	0	3.997703	-4.319690	-0.309750
173	9	0	4.270101	-5.765850	-1.926753
174	9	0	5.376723	-3.886524	-1.932018
175	9	0	0.754234	-5.713216	-5.253450
176	9	0	-0.471520	-3.935223	-5.553441
177	9	0	1.472586	-4.094193	-6.510732

TS_{N1O2_R}





E (ONIOM(B3LYP/6-31G(d): HF/3-21G*)) = -7911.100988 a.u.
Imaginary Freq = 1: -671.87 cm-1
Electronic Energy (EE) = -7911.101
Zero-point Energy Correction = 1.28567
Thermal Correction to Energy = 1.389474
Thermal Correction to Enthalpy = 1.390418
Thermal Correction to Free Energy = 1.119879
EE + Zero-point Energy = -7909.815318
EE + Thermal Energy Correction = -7909.711514
EE + Thermal Enthalpy Correction = -7909.710570
EE + Thermal Free Energy Correction = -7909.981109

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.471501

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.194573	4.371739	0.697289
2	6	0	2.625199	3.927167	-0.678685
3	6	0	1.780721	4.218255	-1.959287
4	7	0	-0.026130	2.733937	-0.932067
5	1	0	3.624415	4.360325	-0.840477
6	1	0	2.810275	2.850085	-0.642182
7	6	0	2.366523	3.319909	-3.074389
8	1	0	3.429202	3.528514	-3.225035
9	1	0	2.243013	2.255945	-2.854262
10	1	0	1.857259	3.521282	-4.024437
11	6	0	1.903236	5.676080	-2.455570
12	1	0	2.952764	5.926038	-2.646535
13	1	0	1.361602	5.796444	-3.401149
14	1	0	1.500966	6.418818	-1.761197
15	6	0	2.607678	3.573422	1.859471
16	6	0	3.220142	2.059032	4.160813
17	6	0	2.862525	4.201144	3.102666
18	6	0	2.698505	2.164412	1.796376
19	6	0	2.979994	1.425096	2.940850
20	6	0	3.176452	3.454718	4.232544
21	1	0	2.851939	5.284349	3.169770
22	1	0	2.495156	1.622431	0.879627
23	1	0	2.993242	0.343709	2.885985
24	1	0	3.380052	3.960485	5.171730
25	1	0	3.433355	1.457298	5.037915
26	6	0	1.347280	5.466315	0.907071
27	1	0	1.255735	6.218759	0.129777
28	1	0	1.260957	5.856958	1.920534
29	6	0	-0.782978	2.710694	0.178818
30	7	0	-1.050301	1.510819	0.729337
31	6	0	-1.682622	1.310409	1.997742

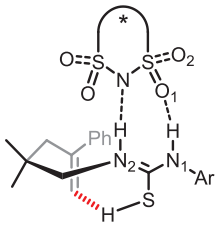
32	6	0	-2.904270	0.847876	4.470277
33	6	0	-1.082761	1.776072	3.171837
34	6	0	-2.871614	0.586932	2.055112
35	6	0	-3.478773	0.366985	3.296566
36	6	0	-1.698263	1.548701	4.400020
37	1	0	-0.138985	2.304651	3.123310
38	1	0	-3.299864	0.187726	1.143549
39	1	0	-3.379100	0.670326	5.427322
40	16	0	-1.423711	4.168578	0.896366
41	1	0	0.145967	4.897284	0.853870
42	6	0	0.263547	3.902334	-1.766736
43	1	0	-0.264845	4.751876	-1.335750
44	1	0	-0.171511	3.723872	-2.758040
45	1	0	0.287752	1.836054	-1.329649
46	6	0	1.789581	-2.158077	-2.199725
47	6	0	0.842918	-2.684332	-3.034921
48	6	0	3.172965	-4.092196	-2.478857
49	6	0	1.004492	-3.998241	-3.566382
50	6	0	2.999803	-2.861416	-1.933248
51	6	0	2.182367	-4.705491	-3.275809
52	6	0	0.003926	-4.632894	-4.349568
53	1	0	3.262735	-6.540754	-3.564849
54	1	0	4.089436	-4.618700	-2.300523
55	6	0	0.190911	-5.891260	-4.819343
56	1	0	-0.905053	-4.110665	-4.554009
57	1	0	-0.574270	-6.365611	-5.399860
58	6	0	1.386695	-6.591921	-4.542245
59	1	0	1.516325	-7.584688	-4.923914
60	6	0	2.356027	-6.015013	-3.790537
61	6	0	-2.562761	-0.939370	-3.051308
62	1	0	-3.509874	-0.059458	-4.707555
63	6	0	-2.628363	-0.556569	-4.353986
64	6	0	-0.376195	-1.904569	-3.458360
65	6	0	-1.570189	-0.781218	-5.258710
66	6	0	-1.401282	-1.626918	-2.597816
67	6	0	-0.421286	-1.454217	-4.811989
68	6	0	-1.640889	-0.331339	-6.602370
69	1	0	1.540881	-2.130922	-5.387997

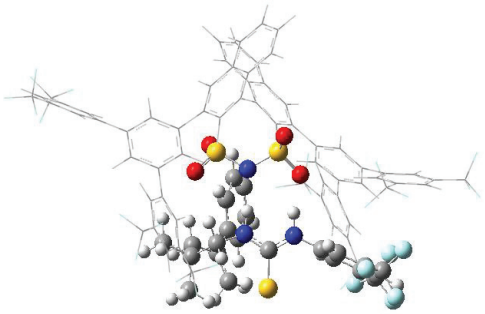
70	6	0	-0.602273	-0.529523	-7.449828
71	1	0	-2.529410	0.171694	-6.929906
72	1	0	-0.656203	-0.186624	-8.463553
73	6	0	0.565300	-1.186402	-6.998137
74	1	0	1.384885	-1.325811	-7.673968
75	6	0	0.655184	-1.636569	-5.722097
76	16	0	-1.126836	-2.026564	-0.850641
77	8	0	-0.716871	-3.431431	-0.776676
78	8	0	-2.300196	-1.614642	-0.071313
79	16	0	1.366854	-0.645886	-1.311587
80	8	0	1.045341	0.406389	-2.320241
81	8	0	2.465056	-0.276070	-0.399609
82	7	0	0.063371	-0.973430	-0.401363
83	6	0	4.149121	-2.299383	-1.153854
84	6	0	6.360925	-1.348634	0.218538
85	6	0	4.420875	-2.755067	0.122952
86	6	0	4.987656	-1.368430	-1.743798
87	6	0	6.090858	-0.886413	-1.060507
88	6	0	5.522547	-2.275522	0.817123
89	1	0	3.763700	-3.465778	0.583016
90	1	0	4.773984	-1.011681	-2.731766
91	1	0	7.190876	-0.947847	0.766283
92	6	0	-3.750848	-0.612000	-2.198857
93	6	0	-5.988543	0.051405	-0.703134
94	6	0	-3.981723	0.701917	-1.836358
95	6	0	-4.656217	-1.593651	-1.830827
96	6	0	-5.771596	-1.267430	-1.080791
97	6	0	-5.101795	1.045405	-1.086893
98	1	0	-3.273607	1.457628	-2.113123
99	1	0	-4.475764	-2.614531	-2.100243
100	1	0	-6.859359	0.301155	-0.131308
101	1	0	-0.714068	0.644593	0.260677
102	6	0	6.938871	0.184601	-1.657258
103	6	0	8.501046	2.230678	-2.723290
104	6	0	6.404514	1.446213	-1.861840
105	6	0	8.265561	-0.041475	-1.989895
106	6	0	9.033429	0.977251	-2.514312
107	6	0	7.183901	2.455106	-2.392712

108	1	0	5.385693	1.635004	-1.588810
109	1	0	8.692971	-1.013657	-1.853675
110	1	0	9.100523	3.013560	-3.135674
111	6	0	5.748723	-2.655751	2.239340
112	6	0	6.168904	-3.195897	4.940536
113	6	0	6.915609	-3.273381	2.659974
114	6	0	4.792533	-2.323453	3.184762
115	6	0	5.007965	-2.586402	4.520871
116	6	0	7.115174	-3.538786	3.999587
117	1	0	7.660976	-3.556742	1.945387
118	1	0	3.891968	-1.838944	2.869360
119	1	0	6.334482	-3.397453	5.977235
120	6	0	-5.337759	2.466847	-0.710269
121	6	0	-5.776207	5.133003	-0.024650
122	6	0	-5.271197	3.465497	-1.669192
123	6	0	-5.628206	2.820427	0.601218
124	6	0	-5.840816	4.142179	0.930018
125	6	0	-5.484096	4.783749	-1.322628
126	1	0	-5.081668	3.212976	-2.692124
127	1	0	-5.685687	2.067513	1.358142
128	1	0	-5.968930	6.152150	0.235136
129	6	0	-6.740291	-2.326731	-0.675708
130	6	0	-8.555730	-4.292070	0.086817
131	6	0	-7.524819	-2.963813	-1.621483
132	6	0	-6.865129	-2.687424	0.657450
133	6	0	-7.765307	-3.665493	1.025011
134	6	0	-8.428208	-3.934004	-1.235767
135	1	0	-7.433779	-2.703900	-2.656200
136	1	0	-6.250759	-2.220247	1.396143
137	1	0	-9.255383	-5.045181	0.381291
138	6	0	-5.359367	5.837512	-2.360681
139	6	0	-6.089170	4.515318	2.346589
140	6	0	-9.310982	-4.554924	-2.255067
141	6	0	-7.847429	-4.086237	2.447760
142	6	0	-4.771103	-0.402015	3.342973
143	6	0	-1.082463	2.106681	5.656643
144	6	0	3.965465	-2.200303	5.506327
145	6	0	8.397388	-4.148228	4.438268

146	6	0	10.468478	0.732451	-2.812983
147	6	0	6.578783	3.790318	-2.622643
148	9	0	-6.086890	6.930994	-2.049675
149	9	0	-5.763025	5.390252	-3.570899
150	9	0	-4.081748	6.257516	-2.522301
151	9	0	-6.864677	5.619351	2.432573
152	9	0	-6.697633	3.517524	3.021845
153	9	0	-4.948973	4.796561	3.016660
154	9	0	-8.689204	-4.652982	-3.451359
155	9	0	-10.438978	-3.838924	-2.471779
156	9	0	-9.705930	-5.790901	-1.881618
157	9	0	-9.078700	-4.558305	2.746895
158	9	0	-6.975048	-5.073571	2.750451
159	9	0	-7.574991	-3.060321	3.281486
160	9	0	-5.287916	-0.486310	4.578555
161	9	0	-4.626587	-1.661720	2.866142
162	9	0	-5.722736	0.174203	2.545990
163	9	0	-1.392237	1.361660	6.738576
164	9	0	-1.510680	3.364509	5.905887
165	9	0	0.266760	2.162450	5.570636
166	9	0	2.928868	-3.062673	5.542687
167	9	0	4.467532	-2.126544	6.755476
168	9	0	3.434849	-0.987347	5.198164
169	9	0	8.249045	-4.833317	5.591386
170	9	0	8.887092	-4.989768	3.502289
171	9	0	9.358448	-3.221473	4.659021
172	9	0	11.261712	0.945071	-1.738317
173	9	0	10.678941	-0.544488	-3.198102
174	9	0	10.913393	1.550836	-3.790091
175	9	0	7.508839	4.733573	-2.863030
176	9	0	5.842334	4.195101	-1.555717
177	9	0	5.722673	3.799935	-3.675455

TS_{N2O1_S}





E (ONIOM(B3LYP/6-31G(d): HF/3-21G*)) = -7911.099991 a.u.
Imaginary Freq = 1: -931.48 cm-1
Zero-point Energy Correction = 1.287466
Thermal Correction to Energy = 1.390238
Thermal Correction to Enthalpy = 1.391182
Thermal Correction to Free Energy = 1.131316
EE + Zero-point Energy = -7909.812525
EE + Thermal Energy Correction = -7909.709753
EE + Thermal Enthalpy Correction = -7909.708809
EE + Thermal Free Energy Correction = -7909.968675

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.471295

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.507610	-1.271484	-4.325260
2	6	0	0.985223	-1.030564	-4.229379
3	6	0	1.573180	0.407607	-4.150494
4	7	0	-0.156681	0.837848	-2.181509
5	1	0	1.417923	-1.501460	-5.126483
6	1	0	1.389204	-1.601946	-3.391117
7	6	0	3.107994	0.232950	-4.019145
8	1	0	3.517409	-0.263501	-4.906830
9	1	0	3.374555	-0.354420	-3.134213
10	1	0	3.588154	1.213491	-3.944748
11	6	0	1.350046	1.264676	-5.418001
12	1	0	1.629592	0.707521	-6.320641

13	1	0	1.990849	2.149460	-5.363195
14	1	0	0.328191	1.625800	-5.531970
15	6	0	-1.079709	-2.399227	-3.565089
16	6	0	-2.077775	-4.693971	-2.260891
17	6	0	-2.163269	-3.132908	-4.102624
18	6	0	-0.523690	-2.843763	-2.346809
19	6	0	-1.018196	-3.975786	-1.702676
20	6	0	-2.654422	-4.262469	-3.459164
21	1	0	-2.584812	-2.848313	-5.060949
22	1	0	0.289470	-2.311542	-1.868482
23	1	0	-0.559214	-4.284929	-0.767980
24	1	0	-3.474306	-4.829604	-3.884831
25	1	0	-2.458483	-5.595527	-1.790828
26	6	0	-1.293412	-0.516655	-5.185276
27	1	0	-0.816784	-0.033565	-6.034432
28	1	0	-2.330322	-0.804147	-5.345101
29	6	0	-1.310156	1.516131	-2.296251
30	7	0	-2.086844	1.639354	-1.208152
31	6	0	-3.373456	2.267283	-1.181447
32	6	0	-5.871891	3.508139	-1.078963
33	6	0	-4.496095	1.603263	-1.674244
34	6	0	-3.495965	3.536038	-0.609873
35	6	0	-4.746634	4.154779	-0.570951
36	6	0	-5.742525	2.228023	-1.616454
37	1	0	-4.389871	0.612845	-2.100815
38	1	0	-2.626451	4.035702	-0.200966
39	1	0	-6.839007	3.998008	-1.059489
40	16	0	-1.825461	2.163868	-3.826327
41	1	0	-1.498267	0.741749	-4.512871
42	6	0	1.115996	1.179234	-2.864447
43	1	0	1.120861	2.250303	-3.070241
44	1	0	1.855888	0.988704	-2.084477
45	1	0	0.015306	0.422846	-1.248843
46	6	0	2.735103	-0.992511	2.147328
47	6	0	1.937340	-1.500733	3.134293
48	6	0	4.335731	-0.268065	3.773063
49	6	0	2.281560	-1.326055	4.507805
50	6	0	3.985719	-0.387173	2.465547

51	6	0	3.496061	-0.697186	4.821992
52	6	0	1.432316	-1.735729	5.570292
53	1	0	4.789003	-0.029102	6.403550
54	1	0	5.279149	0.176364	4.020255
55	6	0	1.796053	-1.533116	6.860955
56	1	0	0.496196	-2.195973	5.341401
57	1	0	1.143779	-1.836218	7.654870
58	6	0	3.028536	-0.915601	7.173240
59	1	0	3.298381	-0.766156	8.199329
60	6	0	3.856025	-0.507840	6.180331
61	6	0	-1.657572	-2.476804	2.232035
62	1	0	-2.520470	-4.373862	2.500263
63	6	0	-1.617236	-3.799707	2.552804
64	6	0	0.686545	-2.292097	2.841361
65	6	0	-0.434883	-4.447659	2.963149
66	6	0	-0.460002	-1.710615	2.371590
67	6	0	0.738880	-3.692686	3.107280
68	6	0	-0.410906	-5.839952	3.234117
69	1	0	2.836436	-3.796567	3.583370
70	6	0	0.742067	-6.446721	3.607049
71	1	0	-1.319258	-6.400580	3.132065
72	1	0	0.760999	-7.499411	3.805842
73	6	0	1.932476	-5.694045	3.729624
74	1	0	2.840416	-6.188488	4.010225
75	6	0	1.933311	-4.358881	3.491781
76	16	0	2.071028	-1.026707	0.465729
77	8	0	2.993509	-0.324105	-0.444707
78	8	0	1.755742	-2.424587	0.119793
79	16	0	-0.265325	0.008402	1.819064
80	8	0	-1.556254	0.512399	1.272626
81	8	0	0.259162	0.783272	2.947913
82	7	0	0.718234	-0.083694	0.523550
83	6	0	5.013625	0.068003	1.471318
84	6	0	7.064460	0.938609	-0.178487
85	6	0	6.126457	-0.725691	1.262836
86	6	0	4.931807	1.305895	0.857178
87	6	0	5.947565	1.740182	0.024445
88	6	0	7.160576	-0.296532	0.438520

89	1	0	6.196659	-1.675730	1.753899
90	1	0	4.069808	1.919508	1.018520
91	1	0	7.833644	1.260051	-0.852940
92	6	0	-2.989395	-1.938109	1.817726
93	6	0	-5.523087	-1.051890	1.091014
94	6	0	-3.688297	-2.561639	0.799065
95	6	0	-3.576526	-0.879253	2.483329
96	6	0	-4.813304	-0.397909	2.091136
97	6	0	-4.976243	-2.159461	0.455644
98	1	0	-3.208686	-3.339574	0.243337
99	1	0	-3.056092	-0.401613	3.285648
100	1	0	-6.477863	-0.669394	0.790997
101	1	0	-1.736641	1.279087	-0.302131
102	6	0	8.345844	-1.166625	0.207574
103	6	0	10.564143	-2.799928	-0.227600
104	6	0	8.186475	-2.486886	-0.188771
105	6	0	9.631504	-0.676752	0.382154
106	6	0	10.723996	-1.491896	0.170552
107	6	0	9.288596	-3.286786	-0.407109
108	1	0	7.203645	-2.885775	-0.335412
109	1	0	9.780592	0.337493	0.690642
110	1	0	11.414563	-3.426259	-0.394380
111	6	0	5.810879	3.021853	-0.718811
112	6	0	5.557567	5.359073	-2.216090
113	6	0	6.789033	4.003997	-0.666046
114	6	0	4.700490	3.229024	-1.521043
115	6	0	4.587604	4.384398	-2.268586
116	6	0	6.651559	5.162001	-1.401610
117	1	0	7.655503	3.865297	-0.052664
118	1	0	3.944096	2.471284	-1.568214
119	1	0	5.468771	6.248652	-2.801691
120	6	0	-5.303522	0.869379	2.695160
121	6	0	-6.132318	3.304442	3.765299
122	6	0	-6.607699	1.037431	3.132613
123	6	0	-4.418115	1.934691	2.801011
124	6	0	-4.835975	3.134477	3.336111
125	6	0	-7.008993	2.245862	3.664102
126	1	0	-7.309353	0.231851	3.060773

127	1	0	-3.414856	1.818323	2.438126
128	1	0	-6.456360	4.246010	4.153080
129	6	0	-5.712192	-2.909689	-0.602570
130	6	0	-7.011818	-4.352188	-2.620995
131	6	0	-5.511989	-4.275023	-0.752296
132	6	0	-6.599109	-2.285524	-1.470955
133	6	0	-7.235161	-3.002433	-2.461791
134	6	0	-6.140777	-4.976169	-1.758816
135	1	0	-4.878767	-4.802689	-0.070925
136	1	0	-6.807753	-1.245877	-1.376654
137	1	0	-7.519307	-4.904871	-3.382467
138	6	0	-6.970163	1.487222	-2.068220
139	6	0	-4.915878	5.521159	0.046712
140	6	0	-3.853217	4.242532	3.453845
141	6	0	-8.393307	2.391056	4.182399
142	6	0	-5.813067	-6.410931	-1.939187
143	6	0	-8.131884	-2.296837	-3.416386
144	6	0	9.096686	-4.675508	-0.899598
145	6	0	12.088331	-0.966840	0.435589
146	6	0	7.676130	6.231459	-1.281210
147	6	0	3.431202	4.535146	-3.185376
148	9	0	-6.763579	-7.065193	-2.633189
149	9	0	-5.634176	-7.038508	-0.757293
150	9	0	-4.647133	-6.579112	-2.625552
151	9	0	-8.818594	3.670117	4.103356
152	9	0	-8.501473	2.028941	5.481719
153	9	0	-9.260286	1.613517	3.496878
154	9	0	-7.461431	-1.797725	-4.479300
155	9	0	-8.766404	-1.259467	-2.833116
156	9	0	-9.066539	-3.136816	-3.914949
157	9	0	-2.902211	3.976920	4.377053
158	9	0	-3.186335	4.442837	2.288268
159	9	0	-4.437766	5.402291	3.806797
160	9	0	-7.509333	0.786626	-1.019232
161	9	0	-6.685581	0.570469	-3.018853
162	9	0	-7.933588	2.295350	-2.531832
163	9	0	-5.463837	5.437289	1.282060
164	9	0	-3.752814	6.183811	0.154887

165	9	0	-5.755623	6.280952	-0.693254
166	9	0	7.746714	6.972408	-2.407764
167	9	0	8.899288	5.713581	-1.035868
168	9	0	7.412531	7.089260	-0.269764
169	9	0	3.501764	3.669824	-4.233993
170	9	0	2.256226	4.257802	-2.570185
171	9	0	3.348284	5.774815	-3.701714
172	9	0	12.165300	0.355830	0.172072
173	9	0	13.014800	-1.603600	-0.311625
174	9	0	12.459699	-1.121794	1.727171
175	9	0	7.957829	-5.215977	-0.414677
176	9	0	9.007701	-4.739213	-2.247575
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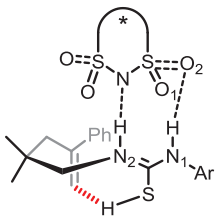
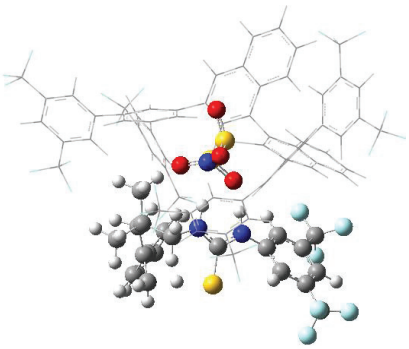
TS_{N2O2_S}





E (ONIOM(B3LYP/6-31G(d): HF/3-21G*)) = -7911.101681 a.u.
Imaginary Freq = 1: -807.61 cm-1
Zero-point Energy Correction = 1.286605
Thermal Correction to Energy = 1.39004
Thermal Correction to Enthalpy = 1.390985
Thermal Correction to Free Energy = 1.124268
EE + Zero-point Energy = -7909.815076
EE + Thermal Energy Correction = -7909.711641
EE + Thermal Enthalpy Correction = -7909.710697
EE + Thermal Free Energy Correction = -7909.977413

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.463404

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.696034	0.946904	-4.310333
2	6	0	2.288686	1.883055	-3.199931
3	6	0	0.931696	2.645206	-3.209464
4	7	0	-0.276859	0.438727	-2.791748
5	1	0	3.083276	2.644160	-3.142888
6	1	0	2.383571	1.338217	-2.253051
7	6	0	0.739467	3.277577	-1.810342
8	1	0	1.502418	4.034627	-1.622268
9	1	0	0.772268	2.535841	-1.007617
10	1	0	-0.229858	3.784148	-1.758018
11	6	0	0.922080	3.810632	-4.224949
12	1	0	1.711403	4.523910	-3.965174
13	1	0	-0.037973	4.330591	-4.186309
14	1	0	1.083797	3.498466	-5.261374
15	6	0	3.807548	0.014220	-4.051840
16	6	0	5.920020	-1.802157	-3.650108
17	6	0	3.912157	-0.706309	-2.843948
18	6	0	4.783507	-0.197144	-5.050685
19	6	0	5.842516	-1.074197	-4.840019
20	6	0	4.940313	-1.628903	-2.670277
21	1	0	3.178346	-0.581954	-2.055068
22	1	0	4.733773	0.371570	-5.974417
23	1	0	6.605117	-1.192621	-5.604358
24	1	0	4.978257	-2.236013	-1.772955
25	1	0	6.743794	-2.482945	-3.463444
26	6	0	2.045169	0.859613	-5.540322
27	1	0	1.018944	0.004006	-5.255156
28	1	0	1.453710	1.697328	-5.897316
29	6	0	-0.371590	-0.781794	-3.334839
30	7	0	-0.489356	-1.819098	-2.468826
31	6	0	-0.662731	-3.194185	-2.762054
32	6	0	-1.016961	-5.940512	-3.189349
33	6	0	-1.576419	-3.641334	-3.719520
34	6	0	0.049805	-4.122658	-1.987597

35	6	0	-0.135316	-5.484682	-2.206265
36	6	0	-1.735005	-5.011612	-3.937063
37	1	0	-2.177920	-2.936706	-4.279028
38	1	0	0.728340	-3.773461	-1.217844
39	1	0	-1.153780	-7.002853	-3.356366
40	16	0	-0.303150	-1.048321	-5.060181
41	1	0	2.520821	0.269430	-6.323326
42	6	0	-0.279660	1.718730	-3.512425
43	1	0	-0.366385	1.496507	-4.573717
44	1	0	-1.188823	2.258994	-3.238681
45	1	0	-0.302670	0.507221	-1.759956
46	1	0	-0.184674	-1.642119	-1.499785
47	6	0	-1.886821	-0.874631	1.510711
48	6	0	-0.975461	-1.721780	2.078015
49	6	0	-3.324209	-2.725489	1.004265
50	6	0	-1.149695	-3.135278	1.996436
51	6	0	-3.138828	-1.379189	1.035240
52	6	0	-2.325687	-3.636154	1.416538
53	6	0	-0.150215	-4.050822	2.415977
54	1	0	-3.392891	-5.405129	0.824545
55	1	0	-4.260907	-3.113690	0.656303
56	6	0	-0.323505	-5.385283	2.242153
57	1	0	0.752547	-3.673703	2.845679
58	1	0	0.448224	-6.068510	2.532793
59	6	0	-1.510519	-5.887883	1.662350
60	1	0	-1.618110	-6.942392	1.516508
61	6	0	-2.490006	-5.035934	1.269618
62	6	0	2.397597	-0.206826	3.116002
63	1	0	3.141906	-0.051259	5.073308
64	6	0	2.317479	-0.361284	4.462665
65	6	0	0.195042	-1.207130	2.882138
66	6	0	1.177092	-0.905328	5.090438
67	6	0	1.299852	-0.634935	2.318498
68	6	0	0.097276	-1.334248	4.300155
69	6	0	1.099763	-1.019284	6.501766
70	1	0	-1.887742	-2.168669	4.358604
71	6	0	-0.010466	-1.525868	7.090996
72	1	0	1.932863	-0.689646	7.090541

73	1	0	-0.069203	-1.606122	8.157784
74	6	0	-1.105007	-1.944536	6.300764
75	1	0	-1.981650	-2.331347	6.779777
76	6	0	-1.055475	-1.854176	4.948709
77	16	0	1.229722	-0.377281	0.542708
78	8	0	0.990225	-1.716584	-0.070428
79	8	0	2.454469	0.290009	0.063484
80	16	0	-1.318772	0.836312	1.245718
81	8	0	-0.972559	1.437091	2.535721
82	8	0	-2.281615	1.549023	0.394252
83	7	0	-0.028806	0.603691	0.242718
84	6	0	-4.337081	-0.524417	0.738878
85	6	0	-6.605497	1.023934	0.330383
86	6	0	-4.455709	0.250584	-0.398196
87	6	0	-5.380356	-0.550058	1.651995
88	6	0	-6.527379	0.205322	1.445903
89	6	0	-5.564214	1.059200	-0.585651
90	1	0	-5.298390	-1.162948	2.527333
91	1	0	-7.447941	1.675616	0.206141
92	6	0	3.679143	0.357158	2.577893
93	6	0	6.114614	1.365044	1.720937
94	6	0	3.804972	1.704377	2.278144
95	6	0	4.772057	-0.478744	2.446464
96	6	0	5.993547	0.018441	2.011090
97	6	0	5.018328	2.208560	1.844136
98	1	0	2.953106	2.348777	2.361313
99	1	0	4.672315	-1.521657	2.673390
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101	1	0	-3.659283	0.276982	-1.106299
102	6	0	-5.552075	2.061859	-1.683061
103	6	0	-5.493525	4.049239	-3.630878
104	6	0	-4.438866	2.887704	-1.811915
105	6	0	-6.624177	2.238796	-2.539196
106	6	0	-6.586987	3.225305	-3.506131
107	6	0	-4.420630	3.864396	-2.783543
108	1	0	-3.615473	2.769851	-1.133101
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110	1	0	-5.484703	4.832250	-4.359581

111	6	0	-7.637008	0.171879	2.437352
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115	6	0	-8.423358	0.343834	4.698879
116	6	0	-9.964920	-0.103502	2.955666
117	1	0	-9.158369	-0.228047	0.995549
118	1	0	-6.391029	0.569082	4.124197
119	1	0	-10.514479	0.074934	5.006016
120	6	0	7.125686	-0.912696	1.746959
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122	6	0	8.340231	-0.818405	2.403041
123	6	0	6.965296	-1.890199	0.776974
124	6	0	7.998384	-2.744804	0.464668
125	6	0	9.362410	-1.697733	2.097192
126	1	0	8.492146	-0.066477	3.150047
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128	1	0	10.005206	-3.330956	0.891865
129	6	0	5.143787	3.625766	1.397932
130	6	0	5.445096	6.225259	0.450916
131	6	0	4.505303	4.028844	0.235342
132	6	0	5.929256	4.536894	2.083823
133	6	0	6.075197	5.823824	1.607206
134	6	0	4.660238	5.319644	-0.228674
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142	6	0	-3.216908	4.713204	-2.952942
143	6	0	-7.725347	3.366729	-4.449703
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147	6	0	-2.672852	-5.481230	-5.019754
148	9	0	8.257915	6.663657	1.919219

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161	9	0	-6.916496	0.196833	6.487712
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163	9	0	-12.269627	0.099862	3.330112
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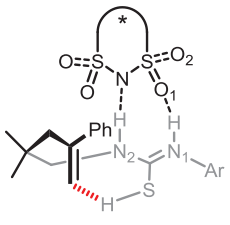
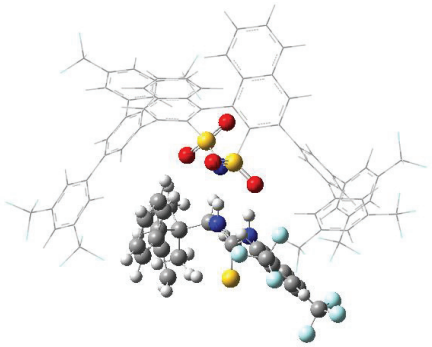
169	9	0	-3.156278	-6.715488	-4.760467
170	9	0	-3.729271	-4.650223	-5.158255
171	9	0	-2.055924	-5.540514	-6.220151
172	9	0	-2.364271	4.195802	-3.885434
173	9	0	-2.497945	4.818712	-1.816364
174	9	0	-3.525648	5.952779	-3.383134
175	9	0	-7.603949	2.562851	-5.531223
176	9	0	-8.896268	3.039103	-3.860982
177	9	0	-7.824111	4.629548	-4.917307

TS_{N2O1_R}





E (ONIOM(B3LYP/6-31G(d): HF/3-21G*)) = -7911.100950 a.u.
Imaginary Freq = 1: -889.01 cm-1
Zero-point Energy Correction = 1.286709
Thermal Correction to Energy = 1.390098
Thermal Correction to Enthalpy = 1.391043
Thermal Correction to Free Energy = 1.124413
EE + Zero-point Energy = -7909.814241
EE + Thermal Energy Correction = -7909.710852
EE + Thermal Enthalpy Correction = -7909.709908
EE + Thermal Free Energy Correction = -7909.976537

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.474300

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.070995	-3.955131	0.426521
2	6	0	3.001698	-2.964976	1.089089
3	6	0	2.731663	-2.414731	2.523300
4	7	0	0.374209	-1.742853	1.573774
5	1	0	3.965482	-3.488514	1.143320
6	1	0	3.157619	-2.112971	0.423608
7	6	0	3.883605	-1.424002	2.821312
8	1	0	4.840404	-1.955678	2.889153
9	1	0	3.954436	-0.647623	2.053260
10	1	0	3.721369	-0.931628	3.787408
11	6	0	2.792013	-3.502755	3.620818

12	1	0	3.662258	-4.152873	3.474566
13	1	0	2.897294	-3.025597	4.602406
14	1	0	1.891438	-4.117691	3.669248
15	6	0	1.775870	-3.802535	-1.008288
16	6	0	1.219285	-3.571448	-3.760669
17	6	0	1.639227	-4.949420	-1.822044
18	6	0	1.640665	-2.536467	-1.616730
19	6	0	1.346278	-2.423818	-2.973768
20	6	0	1.375800	-4.833705	-3.183014
21	1	0	1.787979	-5.934640	-1.392216
22	1	0	1.711894	-1.630193	-1.026047
23	1	0	1.183178	-1.438816	-3.398019
24	1	0	1.293810	-5.728933	-3.792926
25	1	0	0.996410	-3.481470	-4.820236
26	6	0	1.543794	-5.033283	1.129254
27	1	0	2.057474	-5.377860	2.022569
28	1	0	1.016160	-5.807639	0.575667
29	6	0	-0.773748	-2.431035	1.674350
30	7	0	-1.829420	-1.958581	0.974480
31	6	0	-3.059724	-2.622222	0.686982
32	6	0	-5.552740	-3.701559	0.018952
33	6	0	-3.424307	-2.755715	-0.654521
34	6	0	-3.933623	-3.024384	1.700379
35	6	0	-5.171325	-3.571435	1.355093
36	6	0	-4.669052	-3.294192	-0.980220
37	1	0	-2.747385	-2.422826	-1.433280
38	1	0	-3.671523	-2.877930	2.740876
39	1	0	-6.530203	-4.087419	-0.242991
40	16	0	-0.871531	-3.900145	2.592242
41	1	0	0.457998	-4.467548	1.804345
42	6	0	1.393448	-1.600085	2.631298
43	1	0	0.909379	-1.810605	3.585814
44	1	0	1.639331	-0.535966	2.608000
45	1	0	0.375605	-0.962257	0.894930
46	6	0	2.127691	1.919026	-1.967385
47	6	0	1.201368	2.537471	-2.760328
48	6	0	3.532136	1.509568	-3.866748
49	6	0	1.369811	2.566790	-4.177758

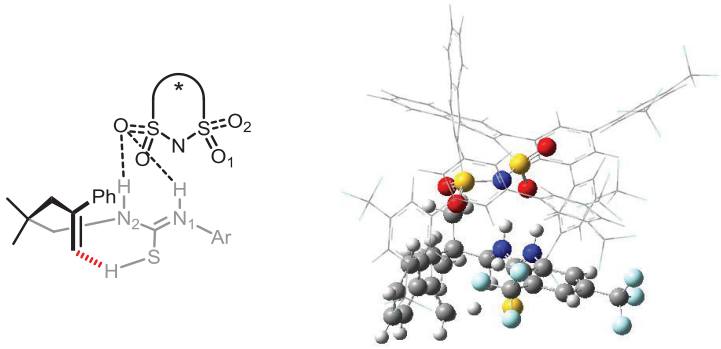
50	6	0	3.349320	1.436946	-2.522912
51	6	0	2.544173	2.031092	-4.730661
52	6	0	0.378587	3.082651	-5.053476
53	1	0	3.630346	1.640809	-6.543931
54	1	0	4.460822	1.178181	-4.287412
55	6	0	0.570226	3.070442	-6.396391
56	1	0	-0.527567	3.470034	-4.641533
57	1	0	-0.188342	3.452704	-7.049085
58	6	0	1.762637	2.550110	-6.947955
59	1	0	1.897434	2.553754	-8.010937
60	6	0	2.724031	2.044058	-6.136817
61	6	0	-2.188148	3.264388	-1.129214
62	1	0	-3.083111	5.149007	-0.891365
63	6	0	-2.223545	4.617020	-1.247613
64	6	0	-0.002037	3.241467	-2.184232
65	6	0	-1.149624	5.352666	-1.790692
66	6	0	-1.047314	2.568354	-1.615856
67	6	0	-0.013213	4.666831	-2.250645
68	6	0	-1.186666	6.769117	-1.856144
69	1	0	1.960995	4.913949	-3.076693
70	6	0	-0.129240	7.463032	-2.342221
71	1	0	-2.063153	7.277044	-1.505093
72	1	0	-0.156798	8.533222	-2.385791
73	6	0	1.025111	6.777989	-2.785771
74	1	0	1.860821	7.338994	-3.152612
75	6	0	1.083846	5.424014	-2.743955
76	16	0	-0.830120	0.786785	-1.443075
77	8	0	-0.509945	0.252640	-2.776771
78	8	0	-2.031351	0.193609	-0.803276
79	16	0	1.672598	1.596515	-0.240546
80	8	0	1.376782	2.880255	0.407222
81	8	0	2.711728	0.758319	0.384735
82	7	0	0.364228	0.599594	-0.348576
83	6	0	4.512948	0.978830	-1.701764
84	6	0	6.759357	0.208542	-0.272058
85	6	0	4.972794	-0.322556	-1.783239
86	6	0	5.187361	1.896185	-0.912533
87	6	0	6.307573	1.519012	-0.192743

88	6	0	6.092885	-0.715457	-1.060551
89	1	0	4.431488	-1.041152	-2.365964
90	1	0	4.836832	2.907693	-0.860855
91	1	0	7.620152	-0.092581	0.292121
92	6	0	-3.365979	2.617198	-0.465864
93	6	0	-5.574517	1.548050	0.816700
94	6	0	-3.316878	2.344186	0.890121
95	6	0	-4.526320	2.366837	-1.177357
96	6	0	-5.633242	1.826816	-0.538229
97	6	0	-4.415360	1.802760	1.534925
98	1	0	-2.416787	2.545359	1.436575
99	1	0	-4.562354	2.567319	-2.229415
100	1	0	-6.422005	1.110960	1.306777
101	1	0	-1.692527	-1.110105	0.398911
102	6	0	6.509793	-2.144022	-1.059057
103	6	0	7.128819	-4.864924	-0.994412
104	6	0	6.732612	-2.846824	-2.234829
105	6	0	6.620972	-2.818642	0.144824
106	6	0	6.907029	-4.167649	0.170105
107	6	0	7.053126	-4.187584	-2.193172
108	1	0	6.652460	-2.350524	-3.179821
109	1	0	6.452473	-2.294154	1.062534
110	1	0	7.346822	-5.911305	-0.971641
111	6	0	7.005111	2.505502	0.676251
112	6	0	8.301647	4.326944	2.337341
113	6	0	6.295038	3.216191	1.634125
114	6	0	8.369442	2.719908	0.559678
115	6	0	9.004566	3.625740	1.383862
116	6	0	6.944746	4.119127	2.449777
117	1	0	5.245144	3.041378	1.758668
118	1	0	8.936477	2.180602	-0.171127
119	1	0	8.803700	5.005692	2.993406
120	6	0	-4.328505	1.424554	2.971813
121	6	0	-4.156134	0.612622	5.632786
122	6	0	-5.175395	1.961405	3.928021
123	6	0	-3.394144	0.480371	3.363458
124	6	0	-3.321628	0.074623	4.678897
125	6	0	-5.075625	1.562468	5.246042

126	1	0	-5.909788	2.688247	3.647321
127	1	0	-2.741107	0.052259	2.632005
128	1	0	-4.096686	0.295951	6.652377
129	6	0	-6.876690	1.491539	-1.294522
130	6	0	-9.231595	0.810805	-2.610506
131	6	0	-7.795854	2.467408	-1.636245
132	6	0	-7.137394	0.173166	-1.634241
133	6	0	-8.308169	-0.158151	-2.283215
134	6	0	-8.963574	2.121886	-2.288173
135	1	0	-7.605507	3.492832	-1.393805
136	1	0	-6.421116	-0.586062	-1.410947
137	1	0	-10.141680	0.549282	-3.107312
138	6	0	-2.379613	-1.011571	5.039086
139	6	0	-5.941930	2.202676	6.269724
140	6	0	-8.567742	-1.572640	-2.662671
141	6	0	-9.969801	3.172690	-2.585896
142	6	0	6.165091	4.899472	3.446278
143	6	0	10.457500	3.879678	1.206847
144	6	0	7.356445	-4.907275	-3.457684
145	6	0	6.871992	-4.867634	1.477136
146	6	0	-5.068372	-3.367001	-2.430836
147	6	0	-6.092905	-4.045500	2.450489
148	9	0	-2.063266	-1.002122	6.346605
149	9	0	-1.231725	-0.928016	4.321093
150	9	0	-2.890918	-2.243874	4.770573
151	9	0	-6.148885	1.382266	7.321552
152	9	0	-5.401220	3.339044	6.765572
153	9	0	-7.142152	2.543926	5.753197
154	9	0	-6.021163	-3.246946	3.537992
155	9	0	-7.380808	-4.067938	2.046351
156	9	0	-5.779695	-5.295527	2.855352
157	9	0	-4.021881	-3.695891	-3.217601
158	9	0	-6.046187	-4.262116	-2.651851
159	9	0	-5.513095	-2.158262	-2.867381
160	9	0	-8.010123	-2.431467	-1.775668
161	9	0	-9.895217	-1.826444	-2.704156
162	9	0	-8.079326	-1.896108	-3.877772
163	9	0	-10.740225	2.834546	-3.641708

164	9	0	-10.810564	3.394822	-1.549195
165	9	0	-9.377910	4.357454	-2.855289
166	9	0	5.590483	-5.049251	1.908216
167	9	0	7.438614	-6.086752	1.416033
168	9	0	7.484275	-4.155150	2.445336
169	9	0	7.045393	-6.217874	-3.362290
170	9	0	6.673228	-4.383088	-4.497902
171	9	0	8.666426	-4.844000	-3.786453
172	9	0	11.029429	4.293654	2.357350
173	9	0	10.707042	4.836982	0.284186
174	9	0	11.103045	2.768969	0.787718
175	9	0	6.939914	5.277972	4.486266
176	9	0	5.644476	6.031467	2.920706
177	9	0	5.127088	4.185474	3.929319

TS_{N2O2_R}



E (ONIOM(B3LYP/6-31G(d): HF/3-21G*)) = -7911.104119 a.u.
Imaginary Freq = 1: -622.35 cm-1
Zero-point Energy Correction = 1.286952
Thermal Correction to Energy = 1.389983
Thermal Correction to Enthalpy = 1.390927
Thermal Correction to Free Energy = 1.132228
EE + Zero-point Energy = -7909.817166
EE + Thermal Energy Correction = -7909.714136
EE + Thermal Enthalpy Correction = -7909.713191
EE + Thermal Free Energy Correction = -7909.971891

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.473332

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.255778	-5.279831	-1.809018
2	6	0	0.287999	-5.224860	-0.651193
3	6	0	-1.256824	-5.111779	-0.836586
4	7	0	-1.055140	-2.718853	-1.686574
5	1	0	0.478851	-6.143907	-0.071614
6	1	0	0.604145	-4.424838	0.024812
7	6	0	-1.827325	-4.750659	0.554977
8	1	0	-1.550977	-5.510148	1.295142
9	1	0	-1.452863	-3.791852	0.925710
10	1	0	-2.922677	-4.709966	0.517548
11	6	0	-1.911251	-6.441260	-1.274678
12	1	0	-1.781548	-7.202607	-0.497251
13	1	0	-2.985789	-6.300987	-1.434155
14	1	0	-1.497817	-6.846839	-2.202836
15	6	0	2.663757	-4.953287	-1.564103
16	6	0	5.361529	-4.175548	-1.276280
17	6	0	3.045496	-4.000695	-0.593687
18	6	0	3.681347	-5.537200	-2.357876
19	6	0	5.008640	-5.159999	-2.207140
20	6	0	4.374835	-3.605542	-0.469627
21	1	0	2.312456	-3.513111	0.035710
22	1	0	3.429626	-6.315917	-3.070740
23	1	0	4.618959	-2.834594	0.254017
24	1	0	6.393539	-3.849884	-1.198602
25	6	0	0.843760	-5.512102	-3.126366
26	1	0	0.532418	-4.277437	-3.505073
27	1	0	-0.097520	-6.022304	-3.306777
28	6	0	-0.375717	-2.035572	-2.620762
29	7	0	-0.117234	-0.740967	-2.350575
30	6	0	0.806545	0.078163	-3.077155
31	6	0	2.603196	1.766047	-4.386980
32	6	0	2.173688	-0.036763	-2.821210
33	6	0	0.331162	1.024165	-3.984651

34	6	0	1.234008	1.865570	-4.635934
35	6	0	3.066311	0.804706	-3.486222
36	1	0	2.526056	-0.757285	-2.091930
37	1	0	-0.733156	1.117012	-4.161649
38	1	0	3.292557	2.464446	-4.848941
39	16	0	0.150956	-2.704797	-4.135863
40	1	0	1.609453	-5.710186	-3.875248
41	6	0	-1.692304	-4.022895	-1.857838
42	1	0	-1.522570	-4.340351	-2.885139
43	1	0	-2.775320	-3.897400	-1.759734
44	1	0	-1.297477	-2.185396	-0.842489
45	1	0	-0.564464	-0.321147	-1.531805
46	6	0	1.504455	-0.596777	3.418924
47	6	0	0.415378	-0.734295	4.223441
48	6	0	2.643051	0.733230	5.054591
49	6	0	0.407130	-0.110086	5.520904
50	6	0	2.604809	0.230030	3.799761
51	6	0	1.565557	0.559840	5.955062
52	6	0	-0.723486	-0.115803	6.381334
53	1	0	2.493167	1.646002	7.557617
54	1	0	3.462632	1.359661	5.346523
55	6	0	-0.670687	0.469996	7.604819
56	1	0	-1.625361	-0.584364	6.058133
57	1	0	-1.535241	0.460264	8.237492
58	6	0	0.509806	1.099659	8.052294
59	1	0	0.534769	1.550271	9.023986
60	6	0	1.596787	1.148588	7.243430
61	6	0	-3.059132	-1.459233	2.807942
62	1	0	-4.483500	-2.746023	3.662671
63	6	0	-3.455125	-2.443796	3.650583
64	6	0	-0.852814	-1.450475	3.822581
65	6	0	-2.543666	-3.081375	4.523686
66	6	0	-1.694932	-1.014306	2.834282
67	6	0	-1.239815	-2.574783	4.625868
68	6	0	-2.925710	-4.192781	5.314612
69	1	0	0.675205	-2.851362	5.564548
70	6	0	-2.031141	-4.786792	6.144132
71	1	0	-3.930847	-4.558406	5.237973

72	1	0	-2.320042	-5.632289	6.735737
73	6	0	-0.709647	-4.297107	6.229255
74	1	0	-0.007202	-4.784309	6.874885
75	6	0	-0.326227	-3.218229	5.499854
76	16	0	-1.174425	-0.007715	1.380600
77	8	0	-1.495753	1.419339	1.571944
78	8	0	-1.865929	-0.694460	0.247543
79	16	0	1.362286	-1.264980	1.746397
80	8	0	0.742687	-2.605882	1.841248
81	8	0	2.652053	-1.214457	1.050624
82	7	0	0.422090	-0.108140	1.111564
83	6	0	3.532529	0.762157	2.755664
84	6	0	4.910047	1.663002	0.534231
85	6	0	2.969383	1.705360	1.917473
86	6	0	4.822025	0.329243	2.535880
87	6	0	5.521121	0.793130	1.427120
88	6	0	3.623434	2.129675	0.775756
89	1	0	1.979515	2.051016	2.126122
90	1	0	5.258168	-0.415153	3.171862
91	1	0	5.414459	1.933634	-0.369651
92	6	0	-4.087802	-0.790202	1.957406
93	6	0	-5.987580	0.460465	0.368273
94	6	0	-4.873408	-1.532384	1.095185
95	6	0	-4.284540	0.576691	2.050443
96	6	0	-5.214618	1.212446	1.241674
97	6	0	-5.827355	-0.916746	0.299628
98	1	0	-4.728428	-2.591973	1.032341
99	1	0	-3.690091	1.155425	2.723177
100	1	0	-6.675923	0.951191	-0.291390
101	1	0	5.774068	-5.627053	-2.820066
102	6	0	6.889990	0.270673	1.159029
103	6	0	9.440651	-0.752522	0.685917
104	6	0	7.881587	0.364487	2.123393
105	6	0	7.191560	-0.340423	-0.050517
106	6	0	8.454575	-0.850055	-0.271113
107	6	0	9.141295	-0.145213	1.883619
108	1	0	7.677426	0.857270	3.051705
109	1	0	6.444241	-0.414726	-0.812632

110	1	0	10.424830	-1.124286	0.494756
111	6	0	2.876942	2.962292	-0.207003
112	6	0	1.411880	4.383221	-2.113819
113	6	0	3.496070	3.896794	-1.021877
114	6	0	1.511923	2.741449	-0.369630
115	6	0	0.794352	3.459924	-1.300016
116	6	0	2.766692	4.582738	-1.972280
117	1	0	4.544074	4.089607	-0.927913
118	1	0	1.021534	1.973617	0.193972
119	1	0	0.865011	4.896379	-2.872419
120	6	0	-6.614692	-1.742990	-0.654035
121	6	0	-8.048022	-3.406084	-2.377802
122	6	0	-7.995496	-1.647062	-0.743544
123	6	0	-5.964318	-2.670235	-1.453629
124	6	0	-6.676451	-3.495703	-2.296371
125	6	0	-8.695408	-2.466842	-1.605336
126	1	0	-8.527554	-0.959020	-0.119400
127	1	0	-4.897924	-2.740248	-1.409953
128	1	0	-8.602031	-4.064532	-3.012278
129	6	0	-5.338877	2.695046	1.292946
130	6	0	-5.572818	5.463996	1.404978
131	6	0	-4.201719	3.497411	1.233440
132	6	0	-6.582266	3.293989	1.403518
133	6	0	-6.692303	4.667978	1.461391
134	6	0	-4.333801	4.870175	1.288811
135	1	0	-3.230698	3.049580	1.140448
136	1	0	-7.465988	2.691629	1.455009
137	1	0	-5.661003	6.528322	1.453439
138	6	0	8.740209	-1.568682	-1.537027
139	6	0	10.173981	-0.071476	2.948664
140	9	0	8.018069	-1.086247	-2.566751
141	9	0	10.047317	-1.509316	-1.863766
142	9	0	8.436404	-2.895660	-1.449501
143	9	0	10.028563	1.039880	3.702224
144	9	0	10.109785	-1.120779	3.801655
145	9	0	11.420261	-0.072898	2.429861
146	6	0	-0.657429	3.185257	-1.459570
147	6	0	3.470826	5.455146	-2.942757

148	9	0	-1.442719	3.817344	-0.564490
149	9	0	-0.927671	1.858706	-1.326342
150	9	0	-1.092348	3.548832	-2.689711
151	9	0	4.601317	5.977580	-2.421297
152	9	0	3.849809	4.768683	-4.056020
153	9	0	2.691937	6.468038	-3.371571
154	6	0	0.743565	2.922876	-5.593492
155	6	0	4.550433	0.694335	-3.251367
156	9	0	-0.559752	2.773329	-5.893503
157	9	0	1.439987	2.895138	-6.749110
158	9	0	0.899244	4.170575	-5.080701
159	9	0	4.858164	-0.323196	-2.408174
160	9	0	5.063267	1.825507	-2.696543
161	9	0	5.224396	0.490949	-4.397755
162	6	0	-10.170824	-2.321370	-1.714905
163	6	0	-8.028041	5.285428	1.654195
164	6	0	-3.134316	5.744579	1.183905
165	9	0	-8.073531	6.536983	1.150027
166	9	0	-8.373133	5.383392	2.959572
167	9	0	-8.998530	4.554477	1.060725
168	9	0	-3.343108	6.920569	1.825501
169	9	0	-2.043142	5.168825	1.721612
170	9	0	-2.829358	6.065134	-0.092924
171	9	0	-10.752347	-3.482829	-2.083821
172	9	0	-10.714165	-1.928109	-0.542801
173	6	0	-5.941775	-4.473472	-3.137932
174	9	0	-4.870366	-4.981867	-2.469421
175	9	0	-5.446179	-3.931497	-4.270751
176	9	0	-6.726702	-5.505870	-3.504496
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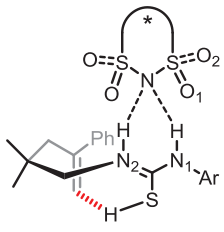
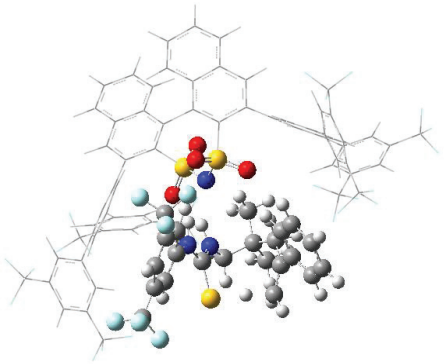
TS_{N1N2_S}





Imaginary Freq = 1: -747.33 cm-1
Electronic Energy (EE) at ONIOM(B3LYP/6-31G(d): HF/3-21G*=
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Zero-point Energy Correction = 1.287518 Hartree
Thermal Correction to Energy = 1.390557 Hartree
Thermal Correction to Enthalpy = 1.391501 Hartree
Thermal Correction to Free Energy = 1.129979 Hartree
EE + Zero-point Energy = -7909.821308 Hartree
EE + Thermal Energy Correction = -7909.718269 Hartree
EE + Thermal Enthalpy Correction = -7909.717325 Hartree
EE + Thermal Free Energy Correction = -7909.978847 Hartree

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.475041

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.327792	1.267907	-4.020686
2	6	0	1.356707	2.284298	-2.910488
3	6	0	0.167202	3.239885	-2.582053
4	7	0	-1.297510	1.284878	-1.879674
5	1	0	2.223791	2.926777	-3.127442
6	1	0	1.631901	1.759201	-1.991282
7	6	0	0.454038	3.787536	-1.163862
8	1	0	1.380954	4.367840	-1.162209
9	1	0	0.556665	2.986992	-0.423589

10	1	0	-0.341421	4.455344	-0.828008
11	6	0	0.096943	4.454822	-3.533574
12	1	0	-0.143020	4.183366	-4.567461
13	1	0	1.056755	4.980314	-3.539526
14	1	0	-0.675183	5.150095	-3.186903
15	6	0	2.211887	0.100482	-3.905249
16	6	0	3.835084	-2.197186	-3.728999
17	6	0	2.822618	-0.447632	-5.057163
18	6	0	2.443554	-0.526950	-2.663132
19	6	0	3.230374	-1.673117	-2.584190
20	6	0	3.635981	-1.570454	-4.964743
21	1	0	2.692627	0.041055	-6.017960
22	1	0	1.975090	-0.174970	-1.751399
23	1	0	3.350698	-2.149648	-1.616487
24	1	0	4.115995	-1.962557	-5.856742
25	1	0	4.460547	-3.081305	-3.658157
26	6	0	0.443094	1.341434	-5.097138
27	1	0	-0.012971	2.295911	-5.345995
28	1	0	0.613136	0.681365	-5.947358
29	6	0	-1.645075	0.078403	-2.346212
30	7	0	-1.721348	-0.897134	-1.403338
31	6	0	-2.046623	-2.271717	-1.529570
32	6	0	-2.584169	-5.024516	-1.643803
33	6	0	-1.410814	-3.154109	-0.641761
34	6	0	-2.992858	-2.763150	-2.437018
35	6	0	-3.230607	-4.139326	-2.502087
36	6	0	-1.689286	-4.517329	-0.701241
37	1	0	-0.699722	-2.784686	0.092881
38	1	0	-3.556096	-2.103704	-3.081328
39	1	0	-2.770727	-6.088847	-1.707469
40	16	0	-1.961655	-0.225063	-4.031115
41	1	0	-0.611093	0.683054	-4.571469
42	6	0	-1.226444	2.549673	-2.607352
43	1	0	-1.571156	2.373615	-3.625406
44	1	0	-1.937303	3.243945	-2.146295
45	1	0	-1.251000	1.371782	-0.857961
46	6	0	1.833066	-0.041949	2.994438
47	6	0	0.947250	0.154583	4.018747

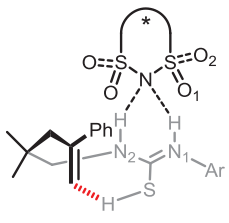
48	6	0	3.540868	1.125851	4.198021
49	6	0	1.328968	0.908354	5.169744
50	6	0	3.162486	0.463901	3.073017
51	6	0	2.649504	1.376467	5.260741
52	6	0	0.423594	1.227119	6.218294
53	1	0	4.070198	2.457202	6.458017
54	1	0	4.545458	1.491547	4.274731
55	6	0	0.834953	1.945693	7.292076
56	1	0	-0.589857	0.899038	6.149368
57	1	0	0.141524	2.185124	8.072783
58	6	0	2.173004	2.390350	7.391959
59	1	0	2.479447	2.952939	8.250819
60	6	0	3.055682	2.114957	6.401635
61	6	0	-2.787272	-0.278959	3.269877
62	1	0	-4.126640	-1.508427	4.323088
63	6	0	-3.103045	-1.212406	4.208261
64	6	0	-0.468136	-0.373131	3.993930
65	6	0	-2.131320	-1.818669	5.029318
66	6	0	-1.426596	0.141384	3.159395
67	6	0	-0.793607	-1.408214	4.919104
68	6	0	-2.477190	-2.838369	5.952926
69	1	0	1.209761	-1.770043	5.620651
70	6	0	-1.522456	-3.432373	6.708892
71	1	0	-3.504233	-3.136029	6.030434
72	1	0	-1.783351	-4.208892	7.399442
73	6	0	-0.170049	-3.039806	6.581878
74	1	0	0.577459	-3.531303	7.171134
75	6	0	0.185682	-2.057272	5.717961
76	16	0	1.195337	-0.831460	1.499240
77	8	0	2.267589	-0.922552	0.496187
78	8	0	0.564951	-2.101624	1.898716
79	16	0	-0.797998	1.218347	1.834627
80	8	0	-1.893632	1.635110	0.916933
81	8	0	-0.065063	2.324740	2.463001
82	7	0	0.085438	0.225675	0.891790
83	6	0	4.202521	0.354420	1.997292
84	6	0	6.226063	0.271787	0.105906
85	6	0	4.853298	-0.838604	1.728075

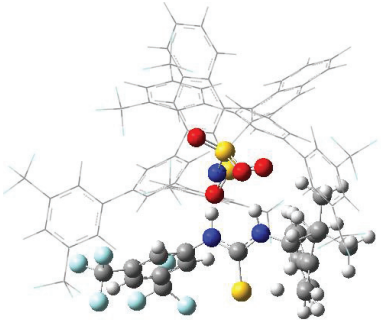
86	6	0	4.573777	1.502978	1.322985
87	6	0	5.584291	1.469429	0.368828
88	6	0	5.862518	-0.887174	0.781491
89	1	0	4.541852	-1.735106	2.224041
90	1	0	4.075626	2.425244	1.546612
91	1	0	7.001330	0.232584	-0.633701
92	6	0	-3.903367	0.239476	2.421982
93	6	0	-5.929914	1.148816	0.758320
94	6	0	-4.664463	-0.657410	1.689697
95	6	0	-4.183159	1.592550	2.336813
96	6	0	-5.163264	2.054390	1.478227
97	6	0	-5.690819	-0.210289	0.868097
98	1	0	-4.422581	-1.701287	1.714598
99	1	0	-3.593973	2.294407	2.888854
100	1	0	-6.681716	1.505679	0.081876
101	1	0	-1.297588	-0.640693	-0.501511
102	6	0	6.518137	-2.179882	0.443635
103	6	0	7.698066	-4.620752	-0.218645
104	6	0	6.629312	-2.578174	-0.879471
105	6	0	7.012524	-3.019421	1.431939
106	6	0	7.600514	-4.220349	1.096296
107	6	0	7.207591	-3.789600	-1.199220
108	1	0	6.246747	-1.949568	-1.657571
109	1	0	6.941472	-2.735314	2.461631
110	1	0	8.143100	-5.559360	-0.470870
111	6	0	5.955121	2.701457	-0.378769
112	6	0	6.633375	4.987270	-1.832857
113	6	0	4.973622	3.503594	-0.938943
114	6	0	7.284371	3.067026	-0.550164
115	6	0	7.610845	4.198555	-1.265221
116	6	0	5.316321	4.629964	-1.660865
117	1	0	3.942926	3.236500	-0.821226
118	1	0	8.062983	2.470260	-0.121695
119	1	0	6.894445	5.855871	-2.397972
120	6	0	-6.435377	-1.181969	0.021578
121	6	0	-7.725573	-3.042867	-1.604668
122	6	0	-7.136930	-2.239962	0.579117
123	6	0	-6.399456	-1.063026	-1.358092

124	6	0	-7.037169	-1.988410	-2.156590
125	6	0	-7.772574	-3.156361	-0.232349
126	1	0	-7.198607	-2.339959	1.643233
127	1	0	-5.852327	-0.257902	-1.806811
128	1	0	-8.209573	-3.760700	-2.230210
129	6	0	-5.252669	3.507819	1.169094
130	6	0	-5.338019	6.165366	0.344698
131	6	0	-4.113282	4.129028	0.675621
132	6	0	-6.429023	4.232434	1.260358
133	6	0	-6.458879	5.554545	0.863135
134	6	0	-4.170140	5.441150	0.254343
135	1	0	-3.202728	3.564054	0.612101
136	1	0	-7.319803	3.769209	1.632891
137	1	0	-5.377620	7.179913	0.010904
138	6	0	-6.939973	-1.834046	-3.629809
139	6	0	-8.471146	-4.313489	0.384038
140	6	0	-7.708614	6.339694	1.030078
141	6	0	-2.961809	6.042280	-0.361252
142	6	0	4.237594	5.441794	-2.277054
143	6	0	9.035792	4.605444	-1.380060
144	6	0	8.187811	-5.069844	2.164848
145	6	0	7.245926	-4.209521	-2.622295
146	6	0	-1.043703	-5.451442	0.292631
147	6	0	-4.223848	-4.660570	-3.511098
148	9	0	3.596014	4.771441	-3.275927
149	9	0	3.271165	5.756203	-1.382739
150	9	0	4.702913	6.586094	-2.809125
151	9	0	9.854293	3.531418	-1.381427
152	9	0	9.432762	5.390387	-0.353143
153	9	0	9.254605	5.308821	-2.511462
154	9	0	-2.672359	5.475454	-1.568839
155	9	0	-1.855334	5.849868	0.391635
156	9	0	-3.100529	7.364544	-0.574454
157	9	0	-7.786018	7.340275	0.126236
158	9	0	-7.800982	6.914845	2.250963
159	9	0	-8.802380	5.558713	0.892275
160	9	0	-8.994814	-3.987152	1.586603
161	9	0	-9.469621	-4.764515	-0.404248

162	9	0	-7.644761	-5.362262	0.600745
163	9	0	-7.460551	-0.653916	-4.040836
164	9	0	-7.580182	-2.814617	-4.288990
165	9	0	-5.647744	-1.821378	-4.049411
166	9	0	-4.039978	-4.112083	-4.726970
167	9	0	-5.503615	-4.386768	-3.144360
168	9	0	-4.141708	-6.000700	-3.651913
169	9	0	-1.764146	-5.521706	1.435585
170	9	0	-0.958854	-6.711046	-0.195575
171	9	0	0.198015	-5.057551	0.624951
172	9	0	8.122473	-5.210786	-2.829034
173	9	0	6.035511	-4.652162	-3.060566
174	9	0	7.572144	-3.181046	-3.435076
175	9	0	9.474341	-4.746445	2.430808
176	9	0	7.512067	-4.936621	3.326375
177	9	0	8.182164	-6.373514	1.815496

TS_{N1N2_R}





Imaginary Freq = 1: -603.16 cm-1
Electronic Energy (EE) at ONIOM(B3LYP/6-31G(d): HF/3-21G*)=
-7911.1038 Hartree
Zero-point Energy Correction = 1.286535 Hartree
Thermal Correction to Energy = 1.390098 Hartree
Thermal Correction to Enthalpy = 1.391042 Hartree
Thermal Correction to Free Energy = 1.12498 Hartree
EE + Zero-point Energy = -7909.8173259 Hartree
EE + Thermal Energy Correction = -7909.713696 Hartree
EE + Thermal Enthalpy Correction = -7909.712751 Hartree

EE + Thermal Free Energy Correction = -7909.978813 Hartree

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.466025

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.088599	-5.173450	-2.223077
2	6	0	-0.977374	-4.832913	-1.208022
3	6	0	-2.438907	-4.465781	-1.583133
4	7	0	-1.713592	-2.114312	-2.226412
5	1	0	-1.021694	-5.683456	-0.511266
6	1	0	-0.584771	-4.012748	-0.593458
7	6	0	-3.117003	-4.079550	-0.247936
8	1	0	-3.066627	-4.909772	0.465875
9	1	0	-2.648008	-3.210314	0.223106
10	1	0	-4.175458	-3.852151	-0.413395
11	6	0	-3.225740	-5.656875	-2.171145
12	1	0	-3.215136	-6.498005	-1.468123
13	1	0	-4.271309	-5.389747	-2.344913
14	1	0	-2.823122	-6.021349	-3.120909
15	6	0	1.439256	-5.424939	-1.712888
16	6	0	4.039622	-5.964191	-0.753557
17	6	0	1.855562	-4.965240	-0.439994
18	6	0	2.363604	-6.178030	-2.477333
19	6	0	3.643841	-6.437794	-2.007280
20	6	0	3.136681	-5.237129	0.025730
21	1	0	1.202573	-4.361834	0.180430
22	1	0	2.063051	-6.597640	-3.430945
23	1	0	4.331927	-7.020369	-2.612825
24	1	0	3.440444	-4.889594	1.005975
25	1	0	5.042398	-6.143376	-0.384100
26	6	0	-0.160201	-5.153522	-3.601382
27	1	0	-0.154982	-3.868129	-3.915844
28	1	0	-1.166852	-5.372900	-3.944533
29	6	0	-0.737082	-1.579440	-2.977030
30	7	0	-0.155840	-0.462398	-2.507393

31	6	0	0.958395	0.203666	-3.109574
32	6	0	3.131197	1.594558	-4.183009
33	6	0	2.231745	-0.359300	-3.059478
34	6	0	0.763542	1.461804	-3.681646
35	6	0	1.852460	2.154824	-4.208207
36	6	0	3.309578	0.334920	-3.612432
37	1	0	2.376002	-1.319585	-2.579266
38	1	0	-0.229672	1.895171	-3.701969
39	1	0	3.977161	2.145782	-4.573208
40	16	0	-0.225525	-2.242688	-4.510776
41	1	0	0.617035	-5.512918	-4.272851
42	6	0	-2.547370	-3.264660	-2.571276
43	1	0	-2.302048	-3.556320	-3.591135
44	1	0	-3.593072	-2.939649	-2.597688
45	1	0	-2.019549	-1.559195	-1.414897
46	1	0	-0.365886	-0.184051	-1.528036
47	6	0	0.986240	-0.018663	2.566251
48	6	0	-0.066272	0.063100	3.431391
49	6	0	2.194834	1.622073	3.815261
50	6	0	-0.045321	1.002741	4.510253
51	6	0	2.156257	0.765823	2.760163
52	6	0	1.106519	1.785106	4.695546
53	6	0	-1.149141	1.207854	5.383408
54	1	0	2.042780	3.313189	5.881687
55	1	0	3.079137	2.204744	3.980254
56	6	0	-1.081838	2.126756	6.378230
57	1	0	-2.039413	0.635511	5.245545
58	1	0	-1.923937	2.278184	7.022969
59	6	0	0.087773	2.896058	6.573457
60	1	0	0.120669	3.615108	7.366938
61	6	0	1.152825	2.729288	5.753265
62	6	0	-3.611367	-1.052172	2.611506
63	1	0	-4.843235	-2.252219	3.819062
64	6	0	-3.843675	-1.914085	3.629119
65	6	0	-1.311675	-0.781100	3.331891
66	6	0	-2.800041	-2.343571	4.486668
67	6	0	-2.280156	-0.564481	2.400084
68	6	0	-1.534734	-1.745529	4.369096

69	6	0	-3.020846	-3.310746	5.496320
70	1	0	0.459792	-1.695095	5.168321
71	6	0	-2.016213	-3.674065	6.334214
72	1	0	-3.994039	-3.752541	5.582974
73	1	0	-2.185231	-4.411346	7.093218
74	6	0	-0.740876	-3.083138	6.210991
75	1	0	0.045871	-3.384129	6.872876
76	6	0	-0.507230	-2.140341	5.261577
77	16	0	-1.938081	0.284890	0.828161
78	8	0	-2.110852	1.739410	0.993550
79	8	0	-2.832308	-0.366492	-0.167114
80	16	0	0.702689	-0.973015	1.066622
81	8	0	0.234039	-2.323344	1.448355
82	8	0	1.896671	-0.910304	0.216282
83	7	0	-0.420294	-0.058745	0.330995
84	6	0	3.405620	0.705667	1.930409
85	6	0	5.869913	0.777430	0.665161
86	6	0	3.711016	1.738730	1.060510
87	6	0	4.337583	-0.288796	2.166046
88	6	0	5.571187	-0.261527	1.532976
89	6	0	4.945219	1.783074	0.424944
90	1	0	2.980967	2.499692	0.870153
91	1	0	4.114031	-1.067586	2.867580
92	1	0	6.824787	0.806312	0.179365
93	6	0	-4.758919	-0.465612	1.859452
94	6	0	-6.831612	0.726479	0.452867
95	6	0	-5.644601	-1.243782	1.139928
96	6	0	-4.938360	0.906573	1.904790
97	6	0	-5.956341	1.513545	1.187712
98	6	0	-6.679683	-0.652010	0.430544
99	1	0	-5.509567	-2.305624	1.101818
100	1	0	-4.257044	1.510258	2.465999
101	1	0	-7.588513	1.187942	-0.150207
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103	6	0	-9.054453	-3.095388	-2.153180
104	6	0	-8.917893	-1.495132	-0.366507
105	6	0	-6.925264	-2.302360	-1.395286
106	6	0	-7.679450	-3.097556	-2.229837

107	6	0	-9.662533	-2.291832	-1.213788
108	1	0	-9.414212	-0.874581	0.351153
109	1	0	-5.860410	-2.277576	-1.492642
110	1	0	-9.640423	-3.689227	-2.822244
111	6	0	-6.037310	2.998221	1.150813
112	6	0	-6.158625	5.775674	1.026560
113	6	0	-4.884261	3.742650	0.921932
114	6	0	-7.242735	3.658994	1.319422
115	6	0	-7.295637	5.036422	1.259698
116	6	0	-4.957986	5.118962	0.866048
117	1	0	-3.944740	3.243121	0.774437
118	1	0	-8.140732	3.103716	1.497680
119	1	0	-6.208653	6.840879	0.952209
120	6	0	6.577715	-1.318664	1.822625
121	6	0	8.441366	-3.305306	2.425451
122	6	0	7.873628	-0.987644	2.190636
123	6	0	6.230209	-2.659567	1.752339
124	6	0	7.157510	-3.636406	2.052202
125	6	0	8.789138	-1.975199	2.489518
126	1	0	8.165623	0.040388	2.254190
127	1	0	5.238735	-2.930450	1.453795
128	1	0	9.155027	-4.065693	2.662197
129	6	0	5.295792	2.913746	-0.479503
130	6	0	6.001635	5.042780	-2.137321
131	6	0	5.871746	2.682481	-1.721204
132	6	0	5.076097	4.224884	-0.083444
133	6	0	5.430600	5.272681	-0.906450
134	6	0	6.216661	3.742056	-2.535367
135	1	0	6.025742	1.679695	-2.053742
136	1	0	4.635794	4.430557	0.870268
137	1	0	6.272897	5.859009	-2.772106
138	6	0	-6.985324	-3.985052	-3.194698
139	6	0	-11.142167	-2.320523	-1.075317
140	6	0	-3.716449	5.909872	0.656594
141	6	0	-8.587233	5.728093	1.498720
142	6	0	6.781025	-5.066632	1.937514
143	6	0	10.148708	-1.595287	2.953897
144	6	0	6.796213	3.479180	-3.878241

145	6	0	5.257017	6.667913	-0.426644
146	6	0	1.662827	3.504483	-4.852115
147	6	0	4.672665	-0.300031	-3.561371
148	9	0	7.576651	2.381498	-3.878674
149	9	0	5.845289	3.276003	-4.830637
150	9	0	7.533742	4.524905	-4.308148
151	9	0	4.188544	6.777970	0.391821
152	9	0	6.325534	7.104424	0.281027
153	9	0	5.098646	7.527718	-1.454189
154	9	0	5.467423	-5.259331	2.210627
155	9	0	6.970375	-5.565514	0.686277
156	9	0	7.501151	-5.845497	2.767998
157	9	0	11.051037	-2.558763	2.670741
158	9	0	10.559960	-0.444190	2.380946
159	9	0	10.200000	-1.398341	4.291263
160	9	0	5.120406	-0.416768	-2.279184
161	9	0	5.605337	0.431109	-4.212568
162	9	0	4.678485	-1.541193	-4.084784
163	9	0	0.463131	4.043514	-4.552865
164	9	0	1.743205	3.424788	-6.199186
165	9	0	2.614773	4.376778	-4.453236
166	9	0	-9.631567	4.984532	1.069385
167	9	0	-8.810739	5.973063	2.811124
168	9	0	-8.633010	6.922889	0.871793
169	9	0	-3.996794	7.133476	0.152995
170	9	0	-2.867564	5.291965	-0.187839
171	9	0	-3.036891	6.115030	1.808405
172	9	0	-11.620974	-1.126804	-0.665032
173	9	0	-11.738898	-2.640932	-2.242892
174	9	0	-11.555673	-3.232981	-0.166093
175	9	0	-7.756698	-4.286140	-4.255816
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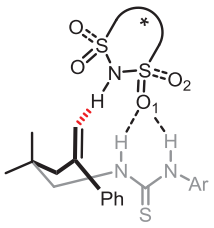
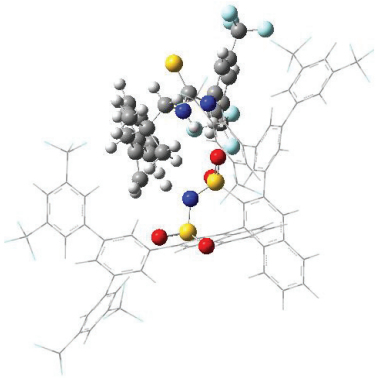
TS*S*





Imaginary Freq = 1: -1336.18 cm-1
Electronic Energy (EE) at ONIOM(B3LYP/6-31G(d): HF/3-21G*)=
-7911.0943 Hartree
Zero-point Energy Correction = 1.286001 Hartree
Thermal Correction to Energy = 1.389864 Hartree
Thermal Correction to Enthalpy = 1.390808 Hartree
Thermal Correction to Free Energy = 1.122679 Hartree
EE + Zero-point Energy = -7909.808269 Hartree
EE + Thermal Energy Correction = -7909.704404 Hartree
EE + Thermal Enthalpy Correction = -7909.703460 Hartree
EE + Thermal Free Energy Correction = -7909.971589 Hartree

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.477599

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.068870	-0.576082	-2.729139
2	6	0	-0.549708	0.016156	-4.023209
3	6	0	0.675990	1.004126	-4.047376
4	7	0	2.176932	-0.429626	-2.605612
5	1	0	-1.392468	0.577143	-4.445455
6	1	0	-0.315619	-0.775277	-4.736396
7	6	0	0.702744	1.613386	-5.467903
8	1	0	-0.186516	2.228957	-5.645026
9	1	0	0.734251	0.833894	-6.238561
10	1	0	1.584883	2.245820	-5.594378

11	6	0	0.547084	2.153313	-3.031910
12	1	0	-0.382813	2.713249	-3.183436
13	1	0	1.375557	2.856804	-3.170375
14	1	0	0.565609	1.820837	-1.990571
15	6	0	-0.909733	-1.997754	-2.418166
16	6	0	-0.729163	-4.747194	-1.790402
17	6	0	-1.218948	-2.478734	-1.117733
18	6	0	-0.484846	-2.942616	-3.378993
19	6	0	-0.410119	-4.298571	-3.069730
20	6	0	-1.120018	-3.826682	-0.808876
21	1	0	-1.482840	-1.785466	-0.328385
22	1	0	-0.223605	-2.634516	-4.382595
23	1	0	-0.086947	-5.000277	-3.831612
24	1	0	-1.315671	-4.166562	0.203116
25	1	0	-0.658697	-5.801907	-1.544040
26	6	0	-1.805017	0.256115	-1.867677
27	1	0	-2.086428	1.233464	-2.253377
28	1	0	-2.597838	-0.204392	-1.279572
29	6	0	2.726523	-1.668183	-2.451013
30	7	0	2.875507	-2.006692	-1.119125
31	16	0	3.158269	-2.668495	-3.735682
32	6	0	3.124777	-3.300258	-0.595935
33	6	0	3.570972	-5.824991	0.544465
34	6	0	2.275701	-3.780445	0.405393
35	6	0	4.224681	-4.067376	-1.000675
36	6	0	4.437943	-5.318389	-0.426251
37	6	0	2.497046	-5.043032	0.960986
38	1	0	1.440393	-3.174592	0.742906
39	1	0	4.914818	-3.681297	-1.735258
40	1	0	3.738862	-6.804983	0.974002
41	6	0	2.018996	0.256450	-3.876802
42	1	0	2.827703	0.988662	-4.014468
43	1	0	2.137867	-0.495795	-4.659218
44	1	0	2.033259	0.119221	-1.761990
45	1	0	2.421830	-1.372936	-0.462679
46	1	0	-1.103013	0.615077	-0.779872
47	6	0	-2.207996	0.504394	2.646653
48	6	0	-1.200232	0.352626	3.563554

49	6	0	-3.371618	-1.369108	3.581070
50	6	0	-1.224500	-0.720849	4.501260
51	6	0	-3.325727	-0.384952	2.642094
52	6	0	-2.336909	-1.577172	4.513929
53	6	0	-0.159541	-0.976623	5.407099
54	1	0	-3.250372	-3.284161	5.448442
55	1	0	-4.223775	-2.018197	3.609831
56	6	0	-0.229771	-2.012846	6.278454
57	1	0	0.702833	-0.347259	5.390197
58	1	0	0.582276	-2.202774	6.950587
59	6	0	-1.364222	-2.856230	6.305787
60	1	0	-1.400643	-3.667880	7.003992
61	6	0	-2.389910	-2.644768	5.446239
62	6	0	2.085547	2.127258	2.720068
63	1	0	3.082055	3.549893	3.898264
64	6	0	2.216546	2.923842	3.812054
65	6	0	-0.011219	1.278943	3.612521
66	6	0	1.238703	2.976753	4.827721
67	6	0	0.941454	1.285435	2.629718
68	6	0	0.101445	2.158528	4.727086
69	6	0	1.372333	3.854318	5.933515
70	1	0	-1.781619	1.658207	5.645945
71	6	0	0.403220	3.920341	6.878556
72	1	0	2.248323	4.468579	6.000282
73	1	0	0.502794	4.588272	7.710275
74	6	0	-0.753998	3.115491	6.768194
75	1	0	-1.519747	3.190856	7.513374
76	6	0	-0.902725	2.259674	5.727288
77	16	0	0.598635	0.303217	1.162131
78	8	0	0.280783	-1.076717	1.561499
79	8	0	1.709109	0.426352	0.193211
80	16	0	-1.934892	1.765529	1.369082
81	8	0	-1.529947	3.006983	2.025852
82	8	0	-3.056832	1.834866	0.425562
83	7	0	-0.682671	1.096331	0.458816
84	6	0	-4.474372	-0.320407	1.685411
85	6	0	-6.648693	-0.275470	-0.039176
86	6	0	-4.784885	-1.434832	0.920675

87	6	0	-5.274884	0.803655	1.598613
88	6	0	-6.337680	0.847681	0.715144
89	6	0	-5.883647	-1.426632	0.068926
90	1	0	-4.177386	-2.315003	0.995004
91	1	0	-5.050867	1.663373	2.193419
92	1	0	-7.454924	-0.236066	-0.744895
93	6	0	3.180552	2.208650	1.697874
94	6	0	5.265441	2.485207	-0.101240
95	6	0	3.119370	3.176211	0.710136
96	6	0	4.288625	1.384964	1.789599
97	6	0	5.336638	1.519207	0.889870
98	6	0	4.156849	3.313989	-0.199326
99	1	0	2.248773	3.796699	0.632111
100	1	0	4.342244	0.645883	2.564090
101	1	0	6.073640	2.589777	-0.798026
102	6	0	4.061419	4.307193	-1.303257
103	6	0	3.830953	6.125264	-3.405537
104	6	0	3.788498	5.644466	-1.054504
105	6	0	4.221646	3.895504	-2.616589
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107	6	0	3.673880	6.536632	-2.099826
108	1	0	3.681818	5.992089	-0.047609
109	1	0	4.414276	2.863672	-2.828341
110	1	0	3.740661	6.822719	-4.210768
111	6	0	6.535048	0.637501	0.980151
112	6	0	8.780213	-1.002967	1.142244
113	6	0	6.416756	-0.734273	0.830468
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115	6	0	8.898228	0.362911	1.284520
116	6	0	7.535706	-1.540656	0.912113
117	1	0	5.456164	-1.169425	0.638200
118	1	0	7.900354	2.236070	1.349348
119	1	0	9.637854	-1.635455	1.223041
120	6	0	-7.057025	2.133020	0.512323
121	6	0	-8.330375	4.569370	0.090541
122	6	0	-8.436609	2.223915	0.577705
123	6	0	-6.315733	3.274509	0.230099
124	6	0	-6.956470	4.478688	0.030737

125	6	0	-9.061894	3.435430	0.360938
126	1	0	-9.023355	1.360526	0.816478
127	1	0	-5.247739	3.201719	0.154538
128	1	0	-8.820092	5.505888	-0.071416
129	6	0	-6.224703	-2.634248	-0.733563
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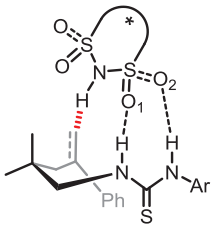
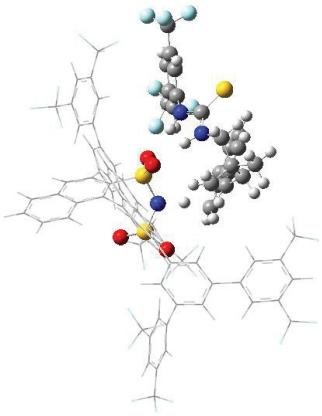
131	6	0	-5.276440	-3.259707	-1.529130
132	6	0	-7.509032	-3.159512	-0.694230
133	6	0	-7.830682	-4.274823	-1.437194
134	6	0	-5.610395	-4.384384	-2.257021
135	1	0	-4.282750	-2.865431	-1.594272
136	1	0	-8.251023	-2.710254	-0.066797
137	1	0	-7.138071	-5.768884	-2.789245
138	6	0	3.327519	7.954336	-1.816421
139	6	0	4.300909	4.324601	-5.045671
140	6	0	10.240519	0.967387	1.485384
141	6	0	7.377696	-3.007078	0.719389
142	6	0	-4.563677	-5.059308	-3.068406
143	6	0	-9.226651	-4.783995	-1.423700
144	6	0	-10.545500	3.503205	0.376318
145	6	0	-6.152297	5.704177	-0.214842
146	6	0	1.506758	-5.569129	1.962481
147	6	0	5.671682	-6.105983	-0.784619
148	9	0	3.811727	8.777324	-2.770514
149	9	0	3.819733	8.349614	-0.622720
150	9	0	1.992016	8.158741	-1.769458
151	9	0	5.602627	4.197176	-5.378964
152	9	0	3.748125	3.094316	-5.220135
153	9	0	3.740703	5.161780	-5.940515
154	9	0	10.166135	2.092285	2.230326
155	9	0	10.827974	1.319857	0.319080
156	9	0	11.081603	0.107817	2.097982
157	9	0	8.492287	-3.675784	1.067920
158	9	0	6.345845	-3.480491	1.448884
159	9	0	7.106899	-3.311158	-0.573416
160	9	0	6.671306	-5.900207	0.109551
161	9	0	6.150451	-5.788570	-2.000673
162	9	0	5.423892	-7.437841	-0.777405

163	9	0	1.951948	-6.671686	2.599010
164	9	0	1.202097	-4.649463	2.902530
165	9	0	0.329735	-5.909907	1.365399
166	9	0	-3.751481	-5.839785	-2.318416
167	9	0	-3.765798	-4.161621	-3.685825
168	9	0	-5.108539	-5.856731	-4.011492
169	9	0	-9.270132	-6.108020	-1.682099
170	9	0	-10.003872	-4.181859	-2.352527
171	9	0	-9.817826	-4.563962	-0.229228
172	9	0	-11.068897	2.615430	1.250438
173	9	0	-10.980998	4.735934	0.711831
174	9	0	-11.088702	3.215744	-0.829264
175	9	0	-6.865642	6.630124	-0.893236
176	9	0	-5.747358	6.294127	0.932767
177	9	0	-5.036532	5.429474	-0.921684

TS*R*





Imaginary Freq = 1: -1404.23 cm-1
Electronic Energy (EE) at ONIOM(B3LYP/6-31G(d): HF/3-21G*) = -7911.0993 Hartree
Zero-point Energy Correction = 1.28726 Hartree
Thermal Correction to Energy = 1.390473 Hartree
Thermal Correction to Enthalpy = 1.391417 Hartree
Thermal Correction to Free Energy = 1.129337 Hartree
EE + Zero-point Energy = -7909.812020 Hartree
EE + Thermal Energy Correction = -7909.708807 Hartree

EE + Thermal Enthalpy Correction = -7909.707863 Hartree
EE + Thermal Free Energy Correction = -7909.969943 Hartree

E_{sp} (RM06-2X/6-311+G(d,p)/SMD (toluene)) = -7962.475851

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.846994	-2.690366	-1.913894
2	6	0	-1.334194	-4.126236	-1.772590
3	6	0	-1.390876	-4.904667	-0.407788
4	7	0	1.031922	-4.384957	0.175225
5	1	0	-2.367028	-4.095207	-2.143763
6	1	0	-0.797573	-4.764395	-2.476102
7	6	0	-2.213804	-6.184878	-0.685873
8	1	0	-3.242586	-5.957728	-0.975550
9	1	0	-1.765555	-6.777538	-1.492185
10	1	0	-2.249122	-6.818174	0.208319
11	6	0	-2.088119	-4.118824	0.715339
12	1	0	-3.101309	-3.827241	0.414937
13	1	0	-2.183522	-4.752922	1.604775
14	1	0	-1.547482	-3.219890	1.016987
15	6	0	0.304812	-2.400514	-2.780551
16	6	0	2.565904	-1.828504	-4.381569
17	6	0	0.542103	-1.093964	-3.275815
18	6	0	1.225743	-3.410360	-3.141243
19	6	0	2.343111	-3.126212	-3.919926
20	6	0	1.653726	-0.817408	-4.061108
21	1	0	-0.152357	-0.289426	-3.076996
22	1	0	1.114125	-4.422708	-2.775982
23	1	0	3.046197	-3.921777	-4.145016
24	1	0	1.808714	0.192584	-4.429417
25	1	0	3.446795	-1.601754	-4.974203
26	6	0	-1.580580	-1.652671	-1.321170
27	1	0	-2.543449	-1.913543	-0.889038
28	1	0	-1.592601	-0.680609	-1.812760
29	6	0	2.321224	-4.551034	-0.248143

30	7	0	3.102921	-3.450636	0.007963
31	16	0	2.888693	-5.928405	-1.043882
32	6	0	4.413643	-3.228105	-0.478289
33	6	0	7.002247	-2.650996	-1.390677
34	6	0	4.650464	-2.082485	-1.240863
35	6	0	5.475078	-4.085520	-0.161688
36	6	0	6.757361	-3.787107	-0.612927
37	6	0	5.941268	-1.804454	-1.701705
38	1	0	3.828858	-1.414771	-1.476865
39	1	0	5.294916	-4.963134	0.443929
40	1	0	8.010266	-2.403349	-1.694954
41	6	0	0.004509	-5.405593	0.045080
42	1	0	-0.120034	-5.932349	1.002879
43	1	0	0.385422	-6.137962	-0.669200
44	1	0	0.858990	-3.657654	0.868841
45	1	0	2.618832	-2.594440	0.280838
46	1	0	-0.939367	-1.070585	-0.257610
47	6	0	-2.271951	-0.259476	2.798325
48	6	0	-1.365106	-0.566459	3.784614
49	6	0	-3.875357	-1.755236	3.768230
50	6	0	-1.650803	-1.599103	4.722522
51	6	0	-3.580127	-0.835554	2.809708
52	6	0	-2.921608	-2.196222	4.708671
53	6	0	-0.683564	-2.067402	5.651348
54	1	0	-4.199064	-3.659087	5.632131
55	1	0	-4.866148	-2.161368	3.812118
56	6	0	-0.990086	-3.061522	6.520624
57	1	0	0.294118	-1.636025	5.644567
58	1	0	-0.251315	-3.418643	7.209034
59	6	0	-2.280489	-3.641175	6.524356
60	1	0	-2.505061	-4.420390	7.224549
61	6	0	-3.220848	-3.220557	5.643595
62	6	0	1.963032	1.209776	3.115747
63	1	0	2.879517	2.658607	4.326303
64	6	0	2.086442	1.941920	4.249744
65	6	0	-0.101134	0.237978	3.962578
66	6	0	1.129134	1.876798	5.286459
67	6	0	0.895404	0.272122	3.030499

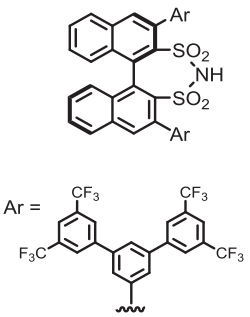
68	6	0	-0.018063	1.079042	5.116858
69	6	0	1.254077	2.685869	6.443655
70	1	0	-1.936690	0.584710	5.965752
71	6	0	0.268417	2.715674	7.373465
72	1	0	2.137446	3.281807	6.559965
73	1	0	0.364381	3.330820	8.245316
74	6	0	-0.902914	1.948262	7.188262
75	1	0	-1.686228	1.998915	7.917156
76	6	0	-1.045666	1.156925	6.096039
77	16	0	0.748348	-0.850705	1.637912
78	8	0	0.362475	-2.173729	2.174336
79	8	0	1.963135	-0.854265	0.807541
80	16	0	-1.693149	0.746558	1.391985
81	8	0	-1.157089	2.022632	1.879055
82	8	0	-2.691629	0.795597	0.321362
83	7	0	-0.474556	-0.201730	0.705938
84	6	0	-4.667137	-0.444919	1.861714
85	6	0	-6.642679	0.251636	0.039219
86	6	0	-5.311452	-1.419668	1.121585
87	6	0	-5.041709	0.879427	1.707630
88	6	0	-6.000097	1.235874	0.777921
89	6	0	-6.305569	-1.080545	0.212043
90	1	0	-5.026794	-2.446050	1.237691
91	1	0	-4.552110	1.644551	2.275218
92	1	0	-7.354498	0.531774	-0.711955
93	6	0	2.773717	1.600179	1.923100
94	6	0	4.094696	2.481786	-0.341621
95	6	0	2.073850	2.223747	0.905617
96	6	0	4.145731	1.469499	1.839062
97	6	0	4.814477	1.928727	0.709650
98	6	0	2.717627	2.638958	-0.246565
99	1	0	1.022132	2.382829	1.028182
100	1	0	4.695655	1.022636	2.643541
101	1	0	4.609032	2.748480	-1.242457
102	6	0	-6.915695	-2.141277	-0.633315
103	6	0	-7.996002	-4.140646	-2.252056
104	6	0	-6.093626	-3.013081	-1.330431
105	6	0	-8.289045	-2.280660	-0.761592

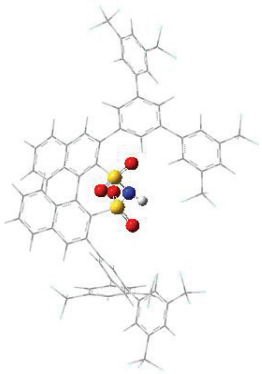
106	6	0	-8.815256	-3.273327	-1.563516
107	6	0	-6.632027	-4.004501	-2.120901
108	1	0	-5.031944	-2.893529	-1.278757
109	1	0	-8.947382	-1.617094	-0.239448
110	1	0	-8.411806	-4.891118	-2.890538
111	6	0	-6.223885	2.676371	0.473011
112	6	0	-6.575609	5.356078	-0.167624
113	6	0	-7.459778	3.277305	0.634590
114	6	0	-5.160852	3.424073	-0.017953
115	6	0	-5.347698	4.754326	-0.336092
116	6	0	-7.625131	4.610758	0.320977
117	1	0	-8.290206	2.711026	1.004067
118	1	0	-4.207764	2.954566	-0.165028
119	1	0	-6.712344	6.386262	-0.416528
120	6	0	1.898572	3.227696	-1.340458
121	6	0	0.255510	4.373762	-3.288126
122	6	0	0.634708	2.712510	-1.600946
123	6	0	2.332536	4.315128	-2.084604
124	6	0	1.520798	4.866172	-3.054427
125	6	0	-0.177144	3.293868	-2.551849
126	1	0	0.289618	1.856040	-1.058058
127	1	0	3.288683	4.754974	-1.889924
128	1	0	-0.379881	4.826605	-4.018572
129	6	0	6.300609	1.845351	0.633719
130	6	0	9.084756	1.745337	0.534185
131	6	0	7.042185	2.985775	0.369601
132	6	0	6.972840	0.648459	0.845929
133	6	0	8.349938	0.607169	0.788061
134	6	0	8.420592	2.931006	0.327199
135	1	0	6.545519	3.919842	0.205758
136	1	0	6.422939	-0.247989	1.041793
137	1	0	10.153352	1.707184	0.496613
138	6	0	-5.719022	-4.955168	-2.802233
139	6	0	-10.290312	-3.440805	-1.643381
140	6	0	-4.218722	5.539696	-0.903763
141	6	0	-8.937456	5.260802	0.565532
142	6	0	-1.553752	2.768153	-2.736771
143	6	0	2.030261	5.993599	-3.877376

144	6	0	9.193456	4.182292	0.117354
145	6	0	9.070387	-0.683516	0.947921
146	6	0	6.157383	-0.624264	-2.610117
147	6	0	7.911456	-4.697115	-0.277509
148	9	0	9.002254	-3.994078	0.101143
149	9	0	8.279090	-5.442115	-1.344753
150	9	0	7.611138	-5.551373	0.722708
151	9	0	5.826823	-0.917626	-3.894133
152	9	0	5.393870	0.437763	-2.254341
153	9	0	7.440333	-0.211762	-2.620223
154	9	0	10.198257	-0.529671	1.674523
155	9	0	9.461357	-1.198346	-0.243917
156	9	0	8.299674	-1.610538	1.550203
157	9	0	8.531123	5.039152	-0.689921
158	9	0	9.421735	4.846920	1.273795
159	9	0	10.401521	3.930510	-0.428731
160	9	0	2.695549	5.567895	-4.976402
161	9	0	2.895869	6.760916	-3.180334
162	9	0	1.024029	6.778478	-4.316623
163	9	0	-3.982029	5.247836	-2.202948
164	9	0	-3.066612	5.310477	-0.242754
165	9	0	-4.473156	6.867072	-0.845646
166	9	0	-9.133066	6.308035	-0.263490
167	9	0	-9.956541	4.389195	0.395559
168	9	0	-9.052938	5.739472	1.826065
169	9	0	-10.926183	-2.256698	-1.515655
170	9	0	-10.658133	-3.998783	-2.815704
171	9	0	-10.769632	-4.241860	-0.664651
172	9	0	-6.269395	-5.480706	-3.911948
173	9	0	-4.549754	-4.359572	-3.144947
174	9	0	-5.378746	-5.998564	-2.002435
175	9	0	-2.370994	3.068586	-1.704217
176	9	0	-2.126649	3.238975	-3.859289
177	9	0	-1.555992	1.405717	-2.821223

4.2.2 Structures optimized at the ONIOM(M06-2x/6-31G(d): HF/3-21G*) level of theory

DSI2





ONIOM(M06-2X/6-31G(d):HF/3-21G*) (Hartree)	
Imaginary Freq	0
Electronic Energy (EE)	-5952.539625
Zero-point Energy Correction	0.880399
Thermal Correction to Energy	0.954131
Thermal Correction to Enthalpy	0.955076
Thermal Correction to Free Energy	0.750302
EE + Zero-point Energy	-5951.659226
EE + Thermal Energy Correction	-5951.585493
EE + Thermal Enthalpy Correction	-5951.584549
EE + Thermal Free Energy Correction	-5951.789323

E_{sp} (RM06-2X/6-311+(d,p)/SMD (toluene)) -6004.254989

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.170289	-1.857381	-1.278963
2	6	0	-0.197641	-2.629115	-1.860010
3	6	0	-2.685936	-2.353874	-3.062562
4	6	0	-0.422285	-3.230369	-3.130480
5	6	0	-2.459513	-1.735939	-1.874499
6	6	0	-1.681931	-3.083304	-3.734403

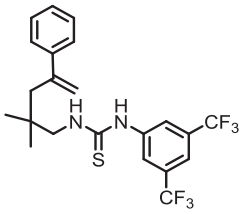
7	6	0	0.590805	-3.943134	-3.825815
8	1	0	-2.888382	-3.558170	-5.448733
9	1	0	-3.659097	-2.287524	-3.506401
10	6	0	0.338647	-4.485637	-5.042381
11	1	0	1.558520	-4.037845	-3.383042
12	1	0	1.110770	-5.013344	-5.564461
13	6	0	-0.937283	-4.354746	-5.637655
14	1	0	-1.117128	-4.792986	-6.598579
15	6	0	-1.920681	-3.672148	-5.001966
16	6	0	3.250987	-2.166203	-0.237318
17	1	0	4.370603	-3.642003	0.747286
18	6	0	3.481778	-3.435521	0.185677
19	6	0	1.119417	-2.884570	-1.169873
20	6	0	2.554360	-4.478855	-0.016012
21	6	0	2.056439	-1.905118	-0.977047
22	6	0	1.337304	-4.199797	-0.660143
23	6	0	2.801849	-5.784609	0.477812
24	1	0	-0.568565	-5.030747	-1.228351
25	6	0	1.866843	-6.757057	0.348132
26	1	0	3.736826	-5.982158	0.963379
27	1	0	2.054020	-7.742121	0.725370
28	6	0	0.630005	-6.474011	-0.274274
29	1	0	-0.107859	-7.246402	-0.353709
30	6	0	0.369901	-5.236012	-0.762694
31	16	0	1.635469	-0.278507	-1.614613
32	8	0	1.032394	-0.426811	-2.922568
33	8	0	2.678921	0.716130	-1.458382
34	16	0	-0.734392	-0.894635	0.171282
35	8	0	-0.142925	-1.752425	1.171123
36	8	0	-1.783639	0.036846	0.521181
37	7	0	0.492685	0.137619	-0.430324
38	6	0	-3.624701	-1.039452	-1.239385
39	6	0	-5.871892	0.162780	-0.158325
40	6	0	-4.089798	0.154281	-1.759842
41	6	0	-4.293224	-1.638231	-0.185018
42	6	0	-5.417523	-1.040757	0.362332
43	6	0	-5.213154	0.764775	-1.219138
44	1	0	-3.581408	0.606300	-2.588118

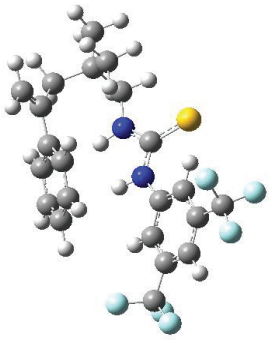
45	1	0	-3.927931	-2.559791	0.223295
46	1	0	-6.739390	0.630756	0.263509
47	6	0	4.205119	-1.103351	0.199979
48	6	0	5.893119	0.930725	1.044870
49	6	0	3.728200	-0.082322	0.998038
50	6	0	5.546436	-1.131529	-0.139212
51	6	0	6.401542	-0.127759	0.303945
52	6	0	4.547344	0.965643	1.374875
53	1	0	2.695399	-0.074486	1.279788
54	1	0	5.922228	-1.907127	-0.776827
55	1	0	6.538683	1.734461	1.340229
56	6	0	3.887954	2.154728	1.978948
57	6	0	2.443375	4.309196	2.989544
58	6	0	4.244255	2.726127	3.185501
59	6	0	2.820874	2.690585	1.268965
60	6	0	2.103030	3.746230	1.777534
61	6	0	3.519571	3.796632	3.679310
62	1	0	5.068409	2.338118	3.748743
63	1	0	2.570751	2.264986	0.319603
64	1	0	1.883033	5.128264	3.388363
65	6	0	7.844226	-0.163895	-0.063920
66	6	0	10.545070	-0.241001	-0.752759
67	6	0	8.614542	-1.282540	0.214633
68	6	0	8.444940	0.916420	-0.694017
69	6	0	9.780213	0.868636	-1.035967
70	6	0	9.951380	-1.312073	-0.124145
71	1	0	8.173592	-2.127382	0.702275
72	1	0	7.869191	1.788792	-0.925857
73	1	0	11.580893	-0.269881	-1.016724
74	6	0	-6.127791	-1.681405	1.503377
75	6	0	-7.457264	-2.881388	3.638632
76	6	0	-6.369820	-0.974486	2.672282
77	6	0	-6.557916	-2.996423	1.419306
78	6	0	-7.220420	-3.582374	2.477992
79	6	0	-7.023951	-1.577028	3.726219
80	1	0	-6.039068	0.039721	2.762715
81	1	0	-6.382578	-3.561526	0.527032
82	1	0	-7.968165	-3.341101	4.457840

83	6	0	-5.708296	2.053093	-1.777788
84	6	0	-6.629958	4.464619	-2.826750
85	6	0	-7.024918	2.186864	-2.190757
86	6	0	-4.858741	3.143633	-1.894480
87	6	0	-5.323957	4.335395	-2.409267
88	6	0	-7.472477	3.381796	-2.715156
89	1	0	-7.698917	1.358826	-2.110367
90	1	0	-3.839949	3.064744	-1.574881
91	1	0	-6.983128	5.389837	-3.230167
92	1	0	0.181518	1.112332	-0.489392
93	6	0	-4.418747	5.513250	-2.460685
94	6	0	-8.866079	3.479315	-3.221042
95	9	0	-3.135971	5.137065	-2.650461
96	9	0	-4.444570	6.234828	-1.317876
97	9	0	-4.767196	6.354959	-3.457365
98	9	0	-8.976484	3.080552	-4.509076
99	9	0	-9.321652	4.748498	-3.168578
100	9	0	-9.703346	2.696406	-2.506183
101	6	0	-7.212460	-0.826978	4.995539
102	6	0	-7.735101	-4.968846	2.337524
103	9	0	-7.835211	-5.581679	3.535710
104	9	0	-6.930713	-5.712588	1.545941
105	9	0	-8.965297	-5.010059	1.776664
106	9	0	-8.302429	-1.261982	5.663592
107	9	0	-6.163419	-0.962423	5.837225
108	9	0	-7.354415	0.496164	4.766439
109	6	0	0.973741	4.290722	0.981961
110	6	0	3.867072	4.353725	5.012149
111	6	0	10.386788	2.006799	-1.774552
112	6	0	10.771473	-2.493490	0.248333
113	9	0	11.278813	-2.399121	1.498398
114	9	0	10.037461	-3.628193	0.219504
115	9	0	11.821842	-2.647059	-0.585208
116	9	0	9.813202	3.178794	-1.427165
117	9	0	11.712810	2.095122	-1.536114
118	9	0	10.241601	1.889303	-3.113867
119	9	0	3.265812	3.688821	6.025111
120	9	0	5.196274	4.278319	5.243154

121	9	0	3.490152	5.645468	5.120194
122	9	0	0.356578	3.304908	0.271945
123	9	0	1.359481	5.213110	0.075005
124	9	0	0.048233	4.875789	1.767487

Alkenyl thiourea





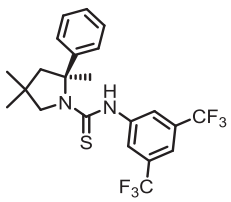
RM06-2X/6-31G(d) (Hartree)	
Imaginary Freq	0
Electronic Energy (EE)	-1957.728467
Zero-point Energy Correction	0.414555
Thermal Correction to Energy	0.443339
Thermal Correction to Enthalpy	0.444283
Thermal Correction to Free Energy	0.352738
EE + Zero-point Energy	-1957.313912
EE + Thermal Energy Correction	-1957.285128
EE + Thermal Enthalpy Correction	-1957.284184
EE + Thermal Free Energy Correction	-1957.375729
E_{sp} (RM06-2X/6-311+(d,p)/SMD (toluene))	-1958.245910

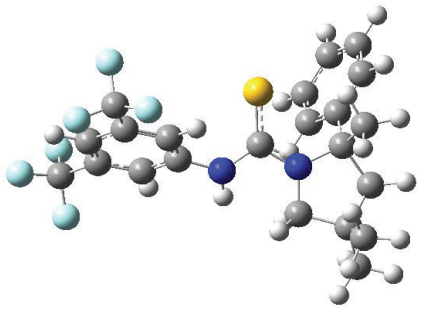
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.009241	-1.052511	1.316408
2	6	0	-4.911283	-0.583107	0.188951
3	6	0	-4.658831	0.847527	-0.395336
4	7	0	-2.458452	0.209439	-1.421424

5	1	0	-5.933126	-0.593615	0.583569
6	1	0	-4.906678	-1.306694	-0.639576
7	6	0	-6.011354	1.397639	-0.868145
8	1	0	-6.686942	1.539630	-0.018368
9	1	0	-6.494391	0.711203	-1.573827
10	1	0	-5.886493	2.365259	-1.365861
11	6	0	-4.063761	1.787509	0.653280
12	1	0	-4.693823	1.816725	1.549209
13	1	0	-3.980464	2.800957	0.248932
14	1	0	-3.062495	1.466978	0.958961
15	6	0	-2.697013	-1.703361	1.039478
16	6	0	-0.230244	-3.003954	0.632627
17	6	0	-2.572691	-2.728108	0.089681
18	6	0	-1.556507	-1.331450	1.764955
19	6	0	-0.339546	-1.977885	1.570524
20	6	0	-1.350699	-3.370923	-0.113958
21	1	0	-3.446102	-3.048824	-0.473774
22	1	0	-1.631545	-0.514683	2.477140
23	1	0	0.533457	-1.667933	2.137286
24	1	0	-1.280336	-4.173555	-0.842215
25	1	0	0.723992	-3.500161	0.480327
26	6	0	-4.393850	-0.900676	2.587939
27	1	0	-5.347034	-0.442043	2.836678
28	1	0	-3.779973	-1.241311	3.416439
29	6	0	-1.283524	0.864844	-1.273771
30	7	0	-0.260614	-0.014051	-1.011594
31	16	0	-1.108814	2.520208	-1.440859
32	6	0	1.079350	0.193313	-0.663436
33	6	0	3.778131	0.309701	0.138269
34	6	0	1.934708	-0.897278	-0.853099
35	6	0	1.586748	1.353295	-0.070613
36	6	0	2.926192	1.395136	0.304610
37	6	0	3.257193	-0.840906	-0.440130
38	1	0	1.555838	-1.802168	-1.321193
39	1	0	0.944200	2.207672	0.097678
40	1	0	4.812944	0.357524	0.454207
41	6	0	-3.757770	0.806398	-1.643945
42	1	0	-3.591757	1.819304	-2.018711

43	1	0	-4.260206	0.230511	-2.432490
44	1	0	-2.457956	-0.788865	-1.248124
45	1	0	-0.512167	-0.998943	-1.014813
46	6	0	4.090667	-2.077817	-0.610178
47	6	0	3.437302	2.672042	0.915564
48	9	0	3.592047	-3.094979	0.118997
49	9	0	5.357755	-1.894071	-0.227791
50	9	0	4.102341	-2.495398	-1.884028
51	9	0	4.687628	2.538098	1.379228
52	9	0	3.442960	3.672935	0.026602
53	9	0	2.665236	3.064015	1.939811

Product



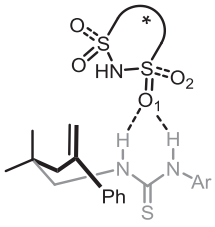


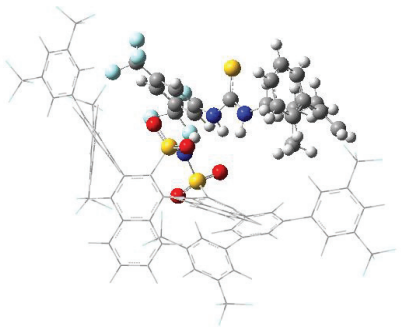
RM06-2X/6-31G(d) (Hartree)	
Imaginary Freq	0
Frequencies scaled by	1
Electronic Energy (EE)	-1957.742936
Zero-point Energy Correction	0.415338
Thermal Correction to Energy	0.443727
Thermal Correction to Enthalpy	0.444672
Thermal Correction to Free Energy	0.354185
EE + Zero-point Energy	-1957.327598
EE + Thermal Energy Correction	-1957.299209
EE + Thermal Enthalpy Correction	-1957.298265
EE + Thermal Free Energy Correction	-1957.388752
E_{sp} (RM06-2X/6-311+(d,p)/SMD (toluene))	-1958.258339

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	2.188584	-0.220110	-0.784501
2	6	0	3.520026	-0.585549	-0.209105
3	6	0	4.484975	0.099069	-1.217459
4	6	0	3.716983	0.305209	-2.532631
5	6	0	2.305137	0.581142	-2.006644
6	1	0	4.777778	1.078055	-0.822871
7	1	0	5.398573	-0.488133	-1.351213
8	1	0	1.533997	0.289333	-2.728376
9	1	0	2.186099	1.657064	-1.785822
10	6	0	4.267124	1.491584	-3.322387
11	1	0	4.291498	2.399257	-2.710079
12	1	0	3.656569	1.691740	-4.209934
13	1	0	5.287664	1.283878	-3.660796
14	6	0	3.709196	-0.941481	-3.424638
15	1	0	3.148068	-1.763749	-2.974286
16	1	0	4.730237	-1.286498	-3.617977
17	1	0	3.241930	-0.712273	-4.388730
18	6	0	3.741715	-2.104250	-0.189650
19	1	0	4.803206	-2.315786	-0.030227
20	1	0	3.452605	-2.545712	-1.144533
21	1	0	3.157653	-2.579201	0.597668
22	6	0	3.702469	0.050428	1.171342
23	6	0	4.118813	1.332737	3.635884
24	6	0	3.235529	1.349527	1.394156
25	6	0	4.387903	-0.592244	2.200273
26	6	0	4.595067	0.045123	3.422980
27	6	0	3.434052	1.985362	2.612437
28	1	0	2.693288	1.866354	0.604550
29	1	0	4.754681	-1.604012	2.067183
30	1	0	5.124996	-0.476976	4.213848
31	1	0	3.049278	2.989007	2.765992
32	1	0	4.274048	1.823719	4.591370
33	6	0	1.000041	-0.453820	-0.170546
34	16	0	0.789498	-1.426031	1.169752

35	7	0	-0.049765	0.230341	-0.766506
36	6	0	-1.414691	0.134573	-0.436851
37	6	0	-4.176145	0.023447	0.043083
38	6	0	-2.164980	1.303907	-0.357840
39	6	0	-2.050813	-1.103031	-0.284614
40	6	0	-3.413951	-1.141602	-0.038396
41	6	0	-3.537404	1.240668	-0.125854
42	1	0	-1.683534	2.271283	-0.475944
43	1	0	-1.481181	-2.019667	-0.366352
44	1	0	-5.244857	-0.023108	0.218233
45	1	0	0.192340	1.080664	-1.258350
46	6	0	-4.093237	-2.467175	0.171861
47	6	0	-4.302128	2.529966	-0.025823
48	9	0	-4.207621	-2.759866	1.473915
49	9	0	-3.419172	-3.470174	-0.404776
50	9	0	-5.334335	-2.463158	-0.338697
51	9	0	-5.624694	2.332919	-0.069268
52	9	0	-4.027961	3.176848	1.116505
53	9	0	-3.979850	3.364331	-1.027655

Complex_*S*





ONIOM(M06-2X/6-31G(d):HF/3-21G*) (Hartree)

Imaginary Freq = 0

Electronic Energy (EE)	-7910.289362
Zero-point Energy Correction	1.297289
Thermal Correction to Energy	1.401309
Thermal Correction to Enthalpy	1.402253

Thermal Correction to Free Energy	1.132658
EE + Zero-point Energy	-7908.992073
EE + Thermal Energy Correction	-7908.888053
EE + Thermal Enthalpy Correction	-7908.887109
EE + Thermal Free Energy Correction	-7909.156704

E_{sp} (RM06-2X/6-311+(d,p)/SMD (toluene))	-7962.496885

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.602951	-6.516539	-1.267194
2	6	0	-4.306600	-5.636884	-2.460608
3	6	0	-3.560671	-4.312354	-2.156661
4	7	0	-1.354973	-3.335090	-1.586181
5	1	0	-5.261694	-5.360183	-2.920491
6	1	0	-3.736373	-6.187640	-3.219967
7	6	0	-3.590858	-3.471810	-3.439380
8	1	0	-4.620615	-3.238108	-3.720900
9	1	0	-3.114754	-4.004480	-4.269402
10	1	0	-3.057725	-2.524055	-3.306816
11	6	0	-4.280997	-3.567612	-1.029374
12	1	0	-5.351015	-3.517134	-1.242938
13	1	0	-3.895789	-2.545846	-0.925137
14	1	0	-4.160385	-4.083869	-0.070415
15	6	0	-3.492546	-7.299669	-0.660268
16	6	0	-1.390466	-8.752868	0.507827
17	6	0	-3.352744	-7.367945	0.731604
18	6	0	-2.553795	-7.968178	-1.456225
19	6	0	-1.516387	-8.692014	-0.877827
20	6	0	-2.312945	-8.087853	1.311183
21	1	0	-4.056539	-6.826789	1.358105
22	1	0	-2.640989	-7.935767	-2.538362
23	1	0	-0.801816	-9.206912	-1.512356
24	1	0	-2.215152	-8.117949	2.392068
25	1	0	-0.573370	-9.307770	0.957722
26	6	0	-5.837228	-6.561237	-0.754509

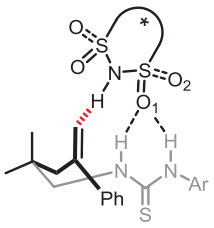
27	1	0	-6.641078	-5.969081	-1.183343
28	1	0	-6.079938	-7.198729	0.090957
29	6	0	-0.417952	-2.878183	-2.434329
30	7	0	-0.087685	-1.533209	-2.122831
31	16	0	0.269446	-3.729109	-3.678797
32	6	0	0.960629	-0.839076	-2.781467
33	6	0	3.035162	0.595808	-3.975279
34	6	0	2.267952	-1.326780	-2.712461
35	6	0	0.693808	0.366773	-3.418800
36	6	0	1.736703	1.080970	-4.002025
37	6	0	3.286656	-0.608325	-3.320194
38	1	0	2.477339	-2.250266	-2.184704
39	1	0	-0.319378	0.754673	-3.459066
40	1	0	3.840750	1.168682	-4.418402
41	6	0	-2.100466	-4.577782	-1.738921
42	1	0	-1.576748	-5.175310	-2.488337
43	1	0	-2.059168	-5.115925	-0.786762
44	1	0	-1.619737	-2.730441	-0.814619
45	1	0	-0.916187	-0.955380	-1.972662
46	1	0	0.302656	-1.264075	-0.318992
47	6	0	1.507242	-0.694723	3.006534
48	6	0	0.411785	-0.559211	3.811105
49	6	0	2.745642	0.868444	4.310952
50	6	0	0.459485	0.322313	4.937502
51	6	0	2.676371	0.087331	3.203456
52	6	0	1.667379	0.989361	5.213023
53	6	0	-0.655875	0.568906	5.785078
54	1	0	2.687454	2.334712	6.540676
55	1	0	3.623487	1.459948	4.477110
56	6	0	-0.543194	1.396740	6.853192
57	1	0	-1.588277	0.094085	5.578193
58	1	0	-1.391709	1.573876	7.482524
59	6	0	0.682562	2.035638	7.145368
60	1	0	0.751266	2.682730	7.996271
61	6	0	1.756873	1.840911	6.343130
62	6	0	-3.114370	-0.845534	2.467858
63	1	0	-4.737559	-1.773859	3.428432
64	6	0	-3.670910	-1.683419	3.377176

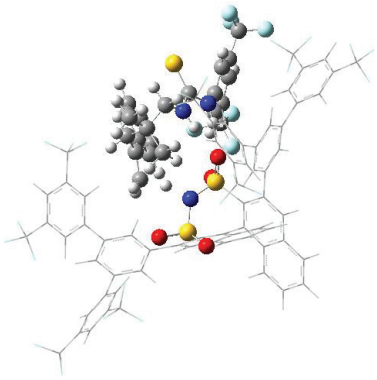
65	6	0	-0.936414	-1.165556	3.506755
66	6	0	-2.880889	-2.398675	4.312079
67	6	0	-1.689559	-0.687426	2.470858
68	6	0	-1.509761	-2.106617	4.411876
69	6	0	-3.451150	-3.343655	5.198209
70	1	0	0.319469	-2.571821	5.439441
71	6	0	-2.678185	-3.977182	6.117549
72	1	0	-4.499804	-3.553784	5.124968
73	1	0	-3.111482	-4.698706	6.780548
74	6	0	-1.297445	-3.695463	6.206814
75	1	0	-0.699198	-4.214496	6.927670
76	6	0	-0.727862	-2.779671	5.382155
77	16	0	-0.909077	0.104340	1.056243
78	8	0	-0.427657	1.430482	1.400927
79	8	0	-1.765847	-0.063955	-0.115018
80	16	0	1.349932	-1.830920	1.650682
81	8	0	0.611187	-2.987849	2.117661
82	8	0	2.578602	-2.029112	0.916193
83	7	0	0.390670	-0.883275	0.648136
84	6	0	3.759755	0.263076	2.181436
85	6	0	5.746086	0.834371	0.348700
86	6	0	3.637208	1.356674	1.341272
87	6	0	4.869985	-0.555684	2.097602
88	6	0	5.860012	-0.280687	1.167514
89	6	0	4.637908	1.665148	0.428417
90	1	0	2.745939	1.950761	1.389595
91	1	0	4.946875	-1.423566	2.720141
92	1	0	6.536818	1.060764	-0.337111
93	6	0	-3.982102	0.072206	1.671468
94	6	0	-5.580505	1.873221	0.287874
95	6	0	-5.085441	-0.376659	0.967821
96	6	0	-3.709358	1.432180	1.709775
97	6	0	-4.476020	2.335323	0.993812
98	6	0	-5.895664	0.523100	0.286102
99	1	0	-5.314943	-1.422607	0.941056
100	1	0	-2.882176	1.791849	2.287338
101	1	0	-6.168578	2.555130	-0.293787
102	6	0	-7.078050	0.011851	-0.464260

103	6	0	-9.285543	-1.064666	-1.784952
104	6	0	-8.361032	0.446836	-0.165123
105	6	0	-6.915196	-0.948105	-1.448539
106	6	0	-8.012843	-1.492324	-2.084654
107	6	0	-9.446439	-0.081680	-0.831708
108	1	0	-8.514831	1.175805	0.603791
109	1	0	-5.930645	-1.268726	-1.716789
110	1	0	-10.133879	-1.489375	-2.277251
111	6	0	-4.071089	3.767248	0.949320
112	6	0	-3.288498	6.436011	0.778828
113	6	0	-2.735352	4.102297	0.756093
114	6	0	-5.003717	4.785624	1.068075
115	6	0	-4.608358	6.104590	0.988288
116	6	0	-2.358471	5.425978	0.671601
117	1	0	-1.992480	3.335894	0.658078
118	1	0	-6.037748	4.555287	1.222378
119	1	0	-2.993159	7.458833	0.681153
120	6	0	7.033068	-1.187116	1.026329
121	6	0	9.225997	-2.874724	0.726454
122	6	0	7.294434	-1.791753	-0.195518
123	6	0	7.874888	-1.442892	2.094916
124	6	0	8.959048	-2.283992	1.940038
125	6	0	8.381565	-2.627010	-0.334031
126	1	0	6.649787	-1.610380	-1.027921
127	1	0	7.703836	-0.967563	3.038981
128	1	0	10.084781	-3.500002	0.603034
129	6	0	4.527771	2.880254	-0.425156
130	6	0	4.321323	5.170253	-2.006727
131	6	0	4.942659	2.866161	-1.750973
132	6	0	4.014912	4.060328	0.094519
133	6	0	3.903130	5.184311	-0.696088
134	6	0	4.847544	4.005821	-2.521109
135	1	0	5.307592	1.959370	-2.183080
136	1	0	3.718598	4.112940	1.121248
137	1	0	4.239852	6.046383	-2.614269
138	6	0	-10.808458	0.434563	-0.534924
139	6	0	-7.798717	-2.582501	-3.070412
140	6	0	-5.615967	7.179941	1.175382

141	6	0	-0.920803	5.763597	0.474353
142	6	0	5.375467	4.008312	-3.909693
143	6	0	3.292005	6.415102	-0.130050
144	6	0	8.622561	-3.306968	-1.633441
145	6	0	9.826466	-2.577064	3.109208
146	6	0	4.701975	-1.113599	-3.293595
147	6	0	1.464365	2.376293	-4.716567
148	9	0	-11.129184	1.507610	-1.291925
149	9	0	-10.913008	0.827837	0.753028
150	9	0	-11.750489	-0.502774	-0.771228
151	9	0	-6.815486	-2.278234	-3.948709
152	9	0	-7.403967	-3.739704	-2.469490
153	9	0	-8.915707	-2.861576	-3.766437
154	9	0	-5.264265	8.305916	0.520297
155	9	0	-5.772433	7.521198	2.475355
156	9	0	-6.833875	6.793977	0.734206
157	9	0	-0.786847	6.982252	-0.087494
158	9	0	-0.236818	5.787945	1.640396
159	9	0	-0.314363	4.852137	-0.312495
160	9	0	1.471113	2.215349	-6.045519
161	9	0	2.400789	3.294117	-4.429004
162	9	0	0.274253	2.889553	-4.380378
163	9	0	5.188136	-1.310029	-4.518718
164	9	0	5.532529	-0.218545	-2.691894
165	9	0	4.834236	-2.249501	-2.599708
166	9	0	6.681508	4.360372	-3.955790
167	9	0	4.715264	4.877568	-4.697393
168	9	0	5.306015	2.778418	-4.480594
169	9	0	3.756843	7.522954	-0.745937
170	9	0	3.547977	6.526357	1.191884
171	9	0	1.945542	6.437410	-0.262788
172	9	0	8.148739	-2.578607	-2.666032
173	9	0	9.941886	-3.520973	-1.834848
174	9	0	8.023934	-4.517050	-1.703595
175	9	0	11.077558	-2.909702	2.727340
176	9	0	9.905622	-1.515914	3.942713
177	9	0	9.361830	-3.608451	3.852506

TS*S* at ONIOM(M06-2X/6-31G(d): HF/3-21G*)





ONIOM(M06-2X/6-31G(d): HF/3-21G*) (Hatree)

Imaginary Freq = 1: -1214.90

Electronic Energy (EE)	-7910.273177
Zero-point Energy Correction	1.292317
Thermal Correction to Energy	1.395335
Thermal Correction to Enthalpy	1.396279
Thermal Correction to Free Energy	1.130681
EE + Zero-point Energy	-7908.980860
EE + Thermal Energy Correction	-7908.877842
EE + Thermal Enthalpy Correction	-7908.876898
EE + Thermal Free Energy Correction	-7909.142497

E_{sp} (RM06-2X/6-311+(d,p)/SMD (toluene))	-7962.485587

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.059570	-0.233406	-2.719696
2	6	0	-0.491784	0.316534	-4.002996
3	6	0	0.764877	1.247037	-3.961710
4	7	0	2.131585	-0.309760	-2.588414
5	1	0	-1.297734	0.910155	-4.448969
6	1	0	-0.267861	-0.490747	-4.703347
7	6	0	0.828816	1.949708	-5.325692
8	1	0	-0.021524	2.627512	-5.452170
9	1	0	0.811644	1.222663	-6.145178
10	1	0	1.749207	2.530850	-5.410455

11	6	0	0.677320	2.308508	-2.861034
12	1	0	-0.223503	2.920743	-2.976729
13	1	0	1.540493	2.977972	-2.932898
14	1	0	0.663869	1.889838	-1.849066
15	6	0	-0.845661	-1.614842	-2.303302
16	6	0	-0.498499	-4.273668	-1.462359
17	6	0	-1.239399	-2.026352	-1.007544
18	6	0	-0.255664	-2.570651	-3.150795
19	6	0	-0.089494	-3.885894	-2.733944
20	6	0	-1.062863	-3.334507	-0.593633
21	1	0	-1.642965	-1.309862	-0.301000
22	1	0	0.095348	-2.300563	-4.139175
23	1	0	0.384809	-4.597044	-3.400858
24	1	0	-1.324554	-3.620928	0.420202
25	1	0	-0.354649	-5.295737	-1.126857
26	6	0	-1.851942	0.619894	-1.939430
27	1	0	-2.096804	1.594117	-2.354304
28	1	0	-2.666574	0.182973	-1.362902
29	6	0	2.615888	-1.568195	-2.452340
30	7	0	2.598772	-1.977119	-1.141867
31	16	0	3.129891	-2.506715	-3.745309
32	6	0	2.800554	-3.269468	-0.620721
33	6	0	3.085729	-5.805905	0.544143
34	6	0	1.988903	-3.650886	0.449257
35	6	0	3.801672	-4.136119	-1.070344
36	6	0	3.930700	-5.386018	-0.478655
37	6	0	2.124899	-4.917226	1.006099
38	1	0	1.238697	-2.962522	0.831867
39	1	0	4.481832	-3.831217	-1.851572
40	1	0	3.189171	-6.793061	0.980177
41	6	0	2.054693	0.422730	-3.833116
42	1	0	2.910857	1.103965	-3.935604
43	1	0	2.125216	-0.302152	-4.647510
44	1	0	1.955323	0.213876	-1.734333
45	1	0	2.128672	-1.343007	-0.497270
46	1	0	-1.146879	0.873220	-0.867126
47	6	0	-2.222081	0.561393	2.646373
48	6	0	-1.211924	0.414301	3.561631

49	6	0	-3.378114	-1.314774	3.588027
50	6	0	-1.231855	-0.656185	4.503612
51	6	0	-3.334669	-0.334363	2.645393
52	6	0	-2.343307	-1.514057	4.522636
53	6	0	-0.164754	-0.908022	5.408406
54	1	0	-3.253537	-3.217470	5.466539
55	1	0	-4.225956	-1.969625	3.616236
56	6	0	-0.232689	-1.940020	6.284900
57	1	0	0.697276	-0.278534	5.387379
58	1	0	0.580886	-2.125984	6.956336
59	6	0	-1.366470	-2.783959	6.318903
60	1	0	-1.401108	-3.592127	7.021238
61	6	0	-2.393622	-2.577352	5.460084
62	6	0	2.098997	2.129898	2.700818
63	1	0	3.139126	3.517429	3.883735
64	6	0	2.252519	2.922248	3.792951
65	6	0	-0.015695	1.332837	3.597238
66	6	0	1.275046	3.003934	4.807257
67	6	0	0.928066	1.325249	2.604905
68	6	0	0.120928	2.209181	4.711503
69	6	0	1.429971	3.880246	5.911273
70	1	0	-1.769019	1.748454	5.636161
71	6	0	0.464920	3.967995	6.858769
72	1	0	2.318813	4.476150	5.974833
73	1	0	0.580467	4.635382	7.688875
74	6	0	-0.708766	3.186638	6.753382
75	1	0	-1.470818	3.279313	7.500401
76	6	0	-0.877664	2.331832	5.714697
77	16	0	0.542426	0.385773	1.128895
78	8	0	0.238639	-0.992487	1.504264
79	8	0	1.620386	0.521752	0.141669
80	16	0	-1.960238	1.822898	1.380913
81	8	0	-1.564286	3.049340	2.044486
82	8	0	-3.079618	1.893750	0.450841
83	7	0	-0.731501	1.175261	0.477398
84	6	0	-4.472791	-0.288669	1.674689
85	6	0	-6.605163	-0.278303	-0.102315
86	6	0	-4.738307	-1.401857	0.892436

87	6	0	-5.298638	0.816359	1.580880
88	6	0	-6.341734	0.842807	0.673502
89	6	0	-5.813556	-1.410645	0.010956
90	1	0	-4.111399	-2.267570	0.972796
91	1	0	-5.107107	1.676293	2.186691
92	1	0	-7.392968	-0.249062	-0.829059
93	6	0	3.212305	2.153030	1.695310
94	6	0	5.344359	2.305886	-0.063458
95	6	0	3.246917	3.147106	0.733386
96	6	0	4.249331	1.240038	1.781504
97	6	0	5.320890	1.312369	0.902930
98	6	0	4.307860	3.223423	-0.156557
99	1	0	2.430813	3.837903	0.658358
100	1	0	4.230477	0.480675	2.537860
101	1	0	6.170633	2.362699	-0.744371
102	6	0	4.310810	4.248301	-1.235359
103	6	0	4.259620	6.130730	-3.292804
104	6	0	4.130155	5.595337	-0.956783
105	6	0	4.470519	3.859355	-2.555897
106	6	0	4.443120	4.795130	-3.569319
107	6	0	4.103530	6.519436	-1.980072
108	1	0	4.027103	5.924614	0.056635
109	1	0	4.593652	2.822033	-2.791104
110	1	0	4.237894	6.852907	-4.080834
111	6	0	6.447346	0.339905	0.991074
112	6	0	8.563814	-1.464472	1.145364
113	6	0	6.229632	-1.016979	0.818100
114	6	0	7.738199	0.784216	1.240699
115	6	0	8.780769	-0.113573	1.312245
116	6	0	7.285489	-1.905162	0.895619
117	1	0	5.241507	-1.377161	0.610956
118	1	0	7.923361	1.826680	1.399812
119	1	0	9.371805	-2.159655	1.221913
120	6	0	-7.086475	2.112690	0.464556
121	6	0	-8.405754	4.522345	0.030830
122	6	0	-8.468828	2.171821	0.501250
123	6	0	-6.365642	3.272452	0.205052
124	6	0	-7.029199	4.463152	-0.000577

125	6	0	-9.116777	3.370350	0.278786
126	1	0	-9.040556	1.293675	0.721988
127	1	0	-5.294917	3.224010	0.151661
128	1	0	-8.913190	5.448560	-0.135723
129	6	0	-6.089217	-2.612814	-0.823645
130	6	0	-6.612427	-4.871877	-2.374461
131	6	0	-5.086962	-3.198755	-1.582176
132	6	0	-7.358540	-3.173598	-0.854616
133	6	0	-7.611586	-4.285348	-1.629117
134	6	0	-5.352215	-4.320546	-2.341373
135	1	0	-4.103011	-2.776284	-1.592774
136	1	0	-8.142601	-2.756028	-0.257149
137	1	0	-6.811802	-5.739447	-2.966056
138	6	0	3.853605	7.950814	-1.665767
139	6	0	4.636334	4.342916	-4.970532
140	6	0	10.161875	0.386671	1.535232
141	6	0	7.022837	-3.353306	0.678120
142	6	0	-4.245343	-4.950363	-3.108088
143	6	0	-8.991441	-4.833349	-1.691220
144	6	0	-10.601548	3.404509	0.262941
145	6	0	-6.247804	5.707695	-0.222395
146	6	0	1.138344	-5.330829	2.057158
147	6	0	5.068423	-6.283058	-0.882017
148	9	0	4.414369	8.760753	-2.588404
149	9	0	4.347888	8.279656	-0.452922
150	9	0	2.535149	8.248968	-1.638084
151	9	0	5.933538	4.136574	-5.281130
152	9	0	4.006202	3.157993	-5.188313
153	9	0	4.153175	5.238852	-5.853488
154	9	0	10.163081	1.502415	2.297480
155	9	0	10.786006	0.712547	0.380290
156	9	0	10.930721	-0.542133	2.141689
157	9	0	8.091604	-4.104637	1.002528
158	9	0	5.969052	-3.768838	1.411682
159	9	0	6.718471	-3.613602	-0.616059
160	9	0	6.095763	-6.187331	-0.020484
161	9	0	5.536133	-5.996931	-2.098820
162	9	0	4.690835	-7.572672	-0.881375

163	9	0	1.525108	-6.428702	2.716377
164	9	0	0.928491	-4.362362	2.956256
165	9	0	-0.065862	-5.608163	1.507452
166	9	0	-3.431875	-5.693805	-2.323366
167	9	0	-3.460991	-4.018825	-3.692794
168	9	0	-4.716203	-5.769178	-4.072097
169	9	0	-8.984657	-6.154164	-1.968821
170	9	0	-9.739064	-4.239668	-2.649435
171	9	0	-9.646666	-4.647121	-0.524723
172	9	0	-11.123100	2.499484	1.120240
173	9	0	-11.071903	4.624913	0.596477
174	9	0	-11.112296	3.112786	-0.955748
175	9	0	-6.968497	6.623066	-0.907288
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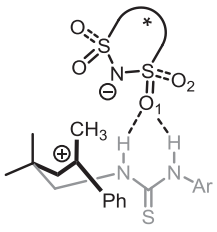
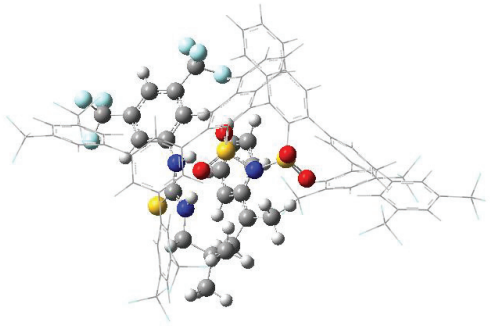
177	9	0	-5.113510	5.462578	-0.910730

Intermediate_*S*





ONIOM(M06-2X/6-31G(d): HF/3-21G*) (Hartree)	
Imaginary Freq	0
Electronic Energy (EE)	-7910.283873
Zero-point Energy Correction	1.297233
Thermal Correction to Energy	1.400645
Thermal Correction to Enthalpy	1.401589
Thermal Correction to Free Energy	1.136369
EE + Zero-point Energy	-7908.986640
EE + Thermal Energy Correction	-7908.883227
EE + Thermal Enthalpy Correction	-7908.882283

EE + Thermal Free Energy Correction -7909.147504

E_{sp} (RM06-2X/6-311+(d,p)/SMD (toluene)) -7962.495300

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.177779	-0.675137	-2.880420
2	6	0	-0.582224	-0.400243	-4.213796
3	6	0	0.544220	0.703415	-4.288555
4	7	0	1.865055	-0.555396	-2.572814
5	1	0	-1.407053	-0.038304	-4.842945
6	1	0	-0.162205	-1.298587	-4.671060
7	6	0	0.659069	1.106030	-5.764651
8	1	0	-0.241446	1.635538	-6.092548
9	1	0	0.798483	0.229684	-6.406934
10	1	0	1.511521	1.775150	-5.900990
11	6	0	0.294766	1.960816	-3.449670
12	1	0	-0.655861	2.441816	-3.698185
13	1	0	1.090037	2.674725	-3.679833
14	1	0	0.316110	1.772207	-2.370301
15	6	0	-1.043042	-1.918376	-2.199982
16	6	0	-0.822760	-4.332149	-0.802283
17	6	0	-1.355440	-1.985736	-0.811376
18	6	0	-0.622247	-3.102266	-2.860548
19	6	0	-0.536184	-4.298095	-2.164577
20	6	0	-1.224830	-3.172858	-0.123360
21	1	0	-1.630939	-1.083464	-0.276141
22	1	0	-0.408174	-3.095700	-3.920623
23	1	0	-0.220755	-5.196474	-2.681922
24	1	0	-1.392379	-3.196784	0.948626
25	1	0	-0.717239	-5.260410	-0.248962
26	6	0	-2.013612	0.387860	-2.282187
27	1	0	-2.293407	1.147236	-3.010059
28	1	0	-2.906439	-0.012576	-1.797029
29	6	0	2.228213	-1.846909	-2.352564
30	7	0	2.246689	-2.163697	-1.024010

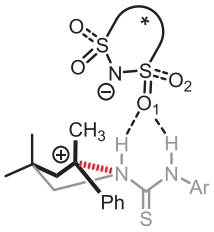
31	16	0	2.542176	-2.942182	-3.593819
32	6	0	2.567639	-3.396581	-0.422580
33	6	0	3.104822	-5.821277	0.885843
34	6	0	1.865035	-3.747962	0.730755
35	6	0	3.595218	-4.228316	-0.882106
36	6	0	3.848360	-5.422427	-0.222266
37	6	0	2.124191	-4.962393	1.358517
38	1	0	1.115227	-3.070825	1.128457
39	1	0	4.200086	-3.939858	-1.729154
40	1	0	3.297548	-6.771294	1.370958
41	6	0	1.885736	0.073635	-3.877898
42	1	0	2.642735	0.868028	-3.893405
43	1	0	2.183623	-0.685628	-4.602820
44	1	0	1.845919	0.059956	-1.755327
45	1	0	1.830555	-1.489448	-0.379984
46	1	0	-1.450609	0.882532	-1.466690
47	6	0	-2.021689	0.392635	2.521475
48	6	0	-0.981624	0.208778	3.394463
49	6	0	-3.098297	-1.583073	3.358219
50	6	0	-0.929366	-0.944118	4.234610
51	6	0	-3.121818	-0.521022	2.507100
52	6	0	-2.008927	-1.841929	4.214602
53	6	0	0.184177	-1.241273	5.066036
54	1	0	-2.816695	-3.663607	5.021764
55	1	0	-3.936839	-2.250459	3.381285
56	6	0	0.195227	-2.360468	5.831313
57	1	0	1.020813	-0.578030	5.073045
58	1	0	1.047008	-2.583363	6.441021
59	6	0	-0.905217	-3.247520	5.827420
60	1	0	-0.877712	-4.124113	6.442576
61	6	0	-1.979385	-2.994203	5.041505
62	6	0	2.249157	2.152770	2.723071
63	1	0	3.230892	3.454680	4.046436
64	6	0	2.367552	2.839654	3.887327
65	6	0	0.165538	1.184732	3.511700
66	6	0	1.379571	2.781601	4.894257
67	6	0	1.110178	1.320381	2.531465
68	6	0	0.262069	1.949893	4.711145

69	6	0	1.491545	3.549333	6.081122
70	1	0	-1.605163	1.313642	5.574194
71	6	0	0.521824	3.498859	7.026708
72	1	0	2.352423	4.175273	6.209571
73	1	0	0.605275	4.084869	7.919792
74	6	0	-0.613997	2.679293	6.836417
75	1	0	-1.380966	2.661641	7.584063
76	6	0	-0.741460	1.925783	5.716271
77	16	0	0.750941	0.529665	0.961695
78	8	0	0.584274	-0.912750	1.215785
79	8	0	1.819826	0.804585	-0.010762
80	16	0	-1.813871	1.732816	1.318689
81	8	0	-1.524617	2.944355	2.067672
82	8	0	-2.951312	1.777128	0.402150
83	7	0	-0.572085	1.224572	0.399424
84	6	0	-4.328565	-0.382103	1.633893
85	6	0	-6.572156	-0.162196	0.010864
86	6	0	-4.697788	-1.426886	0.802377
87	6	0	-5.110262	0.758582	1.670405
88	6	0	-6.208851	0.889318	0.841884
89	6	0	-5.825203	-1.329548	-0.006042
90	1	0	-4.105030	-2.318839	0.776601
91	1	0	-4.838887	1.568189	2.314098
92	1	0	-7.399704	-0.046795	-0.661163
93	6	0	3.359585	2.279076	1.725841
94	6	0	5.414271	2.501926	-0.114805
95	6	0	3.348819	3.305713	0.799095
96	6	0	4.409150	1.378402	1.745251
97	6	0	5.442756	1.482989	0.824982
98	6	0	4.368119	3.412240	-0.132225
99	1	0	2.519563	3.983794	0.768433
100	1	0	4.420292	0.591190	2.472876
101	1	0	6.194818	2.574249	-0.846549
102	6	0	4.277406	4.426275	-1.219175
103	6	0	4.003247	6.256651	-3.302755
104	6	0	4.283920	5.788043	-0.964250
105	6	0	4.134999	3.993705	-2.526922
106	6	0	3.998920	4.902982	-3.554147

107	6	0	4.147120	6.687909	-2.002218
108	1	0	4.406233	6.146408	0.037204
109	1	0	4.106081	2.943685	-2.732081
110	1	0	3.894312	6.960561	-4.100210
111	6	0	6.553589	0.491026	0.814180
112	6	0	8.628819	-1.369989	0.765327
113	6	0	6.285020	-0.864900	0.714029
114	6	0	7.876506	0.904109	0.889945
115	6	0	8.897124	-0.021399	0.861344
116	6	0	7.318519	-1.780635	0.689409
117	1	0	5.270626	-1.204341	0.645477
118	1	0	8.106755	1.944482	0.994420
119	1	0	9.422860	-2.085182	0.764531
120	6	0	-6.898557	2.204006	0.758839
121	6	0	-8.111943	4.696365	0.548269
122	6	0	-8.268590	2.330495	0.904863
123	6	0	-6.135163	3.337547	0.502540
124	6	0	-6.746527	4.569416	0.407759
125	6	0	-8.864840	3.570861	0.793067
126	1	0	-8.869243	1.471541	1.124545
127	1	0	-5.075353	3.235076	0.365489
128	1	0	-8.578809	5.654759	0.466994
129	6	0	-6.184683	-2.444759	-0.924423
130	6	0	-6.850741	-4.520606	-2.667890
131	6	0	-5.228986	-3.006731	-1.758185
132	6	0	-7.480052	-2.940147	-0.975913
133	6	0	-7.803045	-3.960943	-1.845033
134	6	0	-5.563484	-4.036187	-2.613191
135	1	0	-4.226610	-2.631552	-1.751246
136	1	0	-8.230879	-2.543728	-0.323850
137	1	0	-7.106700	-5.315659	-3.335155
138	6	0	4.100969	8.143670	-1.705242
139	6	0	3.862964	4.399935	-4.943308
140	6	0	10.307241	0.445280	0.897311
141	6	0	6.992083	-3.225356	0.550774
142	6	0	-4.505760	-4.645091	-3.460281
143	6	0	-9.209872	-4.433938	-1.924902
144	6	0	-10.342332	3.680912	0.892565

145	6	0	-5.919393	5.784310	0.186200
146	6	0	1.283253	-5.322127	2.547930
147	6	0	5.003445	-6.281816	-0.657258
148	9	0	4.531686	8.872648	-2.756810
149	9	0	4.864263	8.449638	-0.634063
150	9	0	2.850829	8.573326	-1.421828
151	9	0	5.045529	4.079028	-5.509650
152	9	0	3.116825	3.259536	-4.971593
153	9	0	3.269694	5.301947	-5.748561
154	9	0	10.431199	1.581662	1.617481
155	9	0	10.791539	0.719885	-0.335714
156	9	0	11.122115	-0.487696	1.433369
157	9	0	8.068913	-3.999522	0.778856
158	9	0	6.013844	-3.584815	1.408575
159	9	0	6.535630	-3.515568	-0.692253
160	9	0	6.084557	-6.076792	0.114129
161	9	0	5.362070	-6.050987	-1.921963
162	9	0	4.701094	-7.586466	-0.548715
163	9	0	1.499236	-6.575544	2.963332
164	9	0	1.502791	-4.508077	3.586469
165	9	0	-0.032532	-5.222259	2.253041
166	9	0	-3.767220	-5.560960	-2.792924
167	9	0	-3.633038	-3.709903	-3.904470
168	9	0	-5.029321	-5.272534	-4.533396
169	9	0	-9.273829	-5.719986	-2.329646
170	9	0	-9.945461	-3.714094	-2.802327
171	9	0	-9.830552	-4.332072	-0.729947
172	9	0	-10.848111	2.760998	1.743693
173	9	0	-10.720763	4.904880	1.317544
174	9	0	-10.957383	3.477220	-0.295878
175	9	0	-6.640318	6.764781	-0.403271
176	9	0	-5.439183	6.300718	1.339652
177	9	0	-4.851563	5.519821	-0.594142

TS2_*S*



ONIOM(M06-2X/6-31G(d): HF/3-21G*) (Hartree)

Imaginary Freq	1: -115.54 cm-1
Electronic Energy (EE)	-7910.280059
Zero-point Energy Correction	1.297659
Thermal Correction to Energy	1.400411
Thermal Correction to Enthalpy	1.401355
Thermal Correction to Free Energy	1.137054
EE + Zero-point Energy	-7908.982400
EE + Thermal Energy Correction	-7908.879649
EE + Thermal Enthalpy Correction	-7908.878705
EE + Thermal Free Energy Correction	-7909.143005

E_{sp} (RM06-2X/6-311+(d,p)/SMD (toluene)) -7962.487853

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.296116	0.165404	-3.179257
2	6	0	0.385691	0.402769	-4.486950
3	6	0	1.608770	1.363387	-4.470141
4	7	0	1.974385	-0.002932	-2.364366
5	1	0	-0.373427	0.839828	-5.154447
6	1	0	0.722758	-0.535670	-4.925780
7	6	0	2.329989	1.202479	-5.816273
8	1	0	1.677475	1.500391	-6.644179
9	1	0	2.645597	0.165613	-5.968509
10	1	0	3.212950	1.846822	-5.839390
11	6	0	1.259170	2.852505	-4.308541
12	1	0	0.495704	3.163245	-5.030347
13	1	0	2.159353	3.441038	-4.502476

14	1	0	0.913014	3.107149	-3.304816
15	6	0	-0.718803	-1.141652	-2.750259
16	6	0	-1.479033	-3.673204	-1.811808
17	6	0	-1.260353	-1.298977	-1.448376
18	6	0	-0.559533	-2.292152	-3.559527
19	6	0	-0.958440	-3.537036	-3.097777
20	6	0	-1.611807	-2.553237	-0.983325
21	1	0	-1.362104	-0.440407	-0.790331
22	1	0	-0.159099	-2.211610	-4.561682
23	1	0	-0.860283	-4.404854	-3.739920
24	1	0	-1.965607	-2.667416	0.036555
25	1	0	-1.806369	-4.643934	-1.456278
26	6	0	-0.837720	1.368161	-2.473881
27	1	0	-0.977814	2.183537	-3.183465
28	1	0	-1.783334	1.164689	-1.970495
29	6	0	2.288377	-1.355651	-2.399783
30	7	0	2.044236	-1.959896	-1.213891
31	16	0	2.803353	-2.101225	-3.803597
32	6	0	2.009193	-3.331150	-0.880243
33	6	0	1.798619	-6.002877	-0.063463
34	6	0	1.131580	-3.687235	0.145914
35	6	0	2.834103	-4.300628	-1.456303
36	6	0	2.723075	-5.617914	-1.029359
37	6	0	1.014304	-5.019400	0.522725
38	1	0	0.542293	-2.921996	0.646529
39	1	0	3.574253	-4.031251	-2.194569
40	1	0	1.709505	-7.040360	0.237613
41	6	0	2.567197	0.928715	-3.319360
42	1	0	2.866304	1.811655	-2.748454
43	1	0	3.460851	0.463877	-3.741538
44	1	0	1.841487	0.370617	-1.418149
45	1	0	1.776477	-1.338191	-0.445377
46	1	0	-0.163859	1.710752	-1.677670
47	6	0	-2.137884	0.828571	2.673996
48	6	0	-1.200684	0.681966	3.665364
49	6	0	-3.539549	-0.800902	3.739614
50	6	0	-1.378087	-0.283125	4.701958
51	6	0	-3.345100	0.065021	2.707254

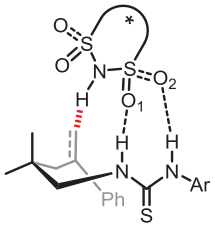
52	6	0	-2.573574	-1.017074	4.740366
53	6	0	-0.387732	-0.550972	5.686507
54	1	0	-3.704633	-2.514969	5.788511
55	1	0	-4.459886	-1.347288	3.792675
56	6	0	-0.605593	-1.478209	6.651303
57	1	0	0.536897	-0.018393	5.654963
58	1	0	0.151798	-1.677331	7.382299
59	6	0	-1.823438	-2.194684	6.701595
60	1	0	-1.977201	-2.920383	7.474614
61	6	0	-2.781174	-1.970573	5.770332
62	6	0	2.319851	2.002717	2.935829
63	1	0	3.410557	3.375888	4.092173
64	6	0	2.476951	2.862375	3.975324
65	6	0	0.074107	1.491536	3.716000
66	6	0	1.441906	3.121402	4.899757
67	6	0	1.083595	1.305006	2.811168
68	6	0	0.219668	2.441833	4.768627
69	6	0	1.607312	4.065575	5.944733
70	1	0	-1.772565	2.255336	5.562227
71	6	0	0.589242	4.329536	6.799738
72	1	0	2.548136	4.571270	6.037569
73	1	0	0.713864	5.048152	7.584638
74	6	0	-0.650566	3.666217	6.654780
75	1	0	-1.452712	3.898229	7.325759
76	6	0	-0.831913	2.749152	5.672441
77	16	0	0.674775	0.332113	1.365107
78	8	0	0.240482	-1.005849	1.776348
79	8	0	1.850554	0.296934	0.465986
80	16	0	-1.676714	1.924817	1.304120
81	8	0	-1.300130	3.198490	1.898366
82	8	0	-2.723511	1.960333	0.283015
83	7	0	-0.434027	1.165531	0.585579
84	6	0	-4.445870	0.147207	1.697157
85	6	0	-6.547503	0.228804	-0.119373
86	6	0	-4.881992	-1.011553	1.074634
87	6	0	-5.087790	1.340686	1.421522
88	6	0	-6.107802	1.396966	0.489470
89	6	0	-5.945255	-0.982611	0.180291

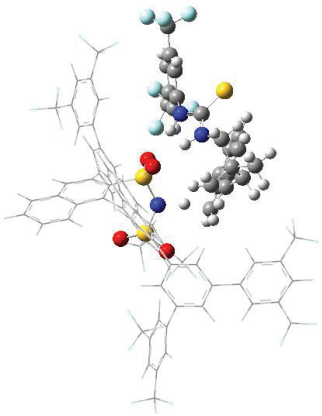
90	1	0	-4.397171	-1.942585	1.291063
91	1	0	-4.769115	2.239294	1.904220
92	1	0	-7.320486	0.271910	-0.861398
93	6	0	3.481117	1.854236	1.998228
94	6	0	5.669046	1.669290	0.308642
95	6	0	3.747906	2.865013	1.092566
96	6	0	4.316192	0.750457	2.061544
97	6	0	5.408193	0.651356	1.215476
98	6	0	4.839436	2.777391	0.237135
99	1	0	3.079830	3.700757	1.027719
100	1	0	4.111021	-0.033880	2.762384
101	1	0	6.517012	1.590720	-0.342952
102	6	0	5.077095	3.835015	-0.783240
103	6	0	5.469351	5.800978	-2.727200
104	6	0	5.058417	5.181262	-0.445314
105	6	0	5.302711	3.490566	-2.107667
106	6	0	5.485001	4.466884	-3.065090
107	6	0	5.253121	6.146131	-1.411159
108	1	0	4.917130	5.475950	0.573993
109	1	0	5.333426	2.459460	-2.393407
110	1	0	5.640262	6.553784	-3.467116
111	6	0	6.291783	-0.550101	1.240692
112	6	0	7.951184	-2.786657	1.223042
113	6	0	5.793359	-1.794316	0.890097
114	6	0	7.630820	-0.437836	1.585133
115	6	0	8.446177	-1.548841	1.573125
116	6	0	6.624169	-2.898441	0.879377
117	1	0	4.762014	-1.895936	0.615909
118	1	0	8.029603	0.511318	1.879293
119	1	0	8.583793	-3.647882	1.229976
120	6	0	-6.629054	2.724967	0.071144
121	6	0	-7.520000	5.222864	-0.767870
122	6	0	-7.982830	3.009416	0.030003
123	6	0	-5.719152	3.703677	-0.313826
124	6	0	-6.171653	4.940380	-0.721330
125	6	0	-8.417802	4.249631	-0.393173
126	1	0	-8.697521	2.276732	0.344907
127	1	0	-4.669936	3.476892	-0.302108

128	1	0	-7.862827	6.182680	-1.090739
129	6	0	-6.407175	-2.243456	-0.463956
130	6	0	-7.263727	-4.639204	-1.609770
131	6	0	-5.516141	-3.065483	-1.135200
132	6	0	-7.737868	-2.632270	-0.384622
133	6	0	-8.155306	-3.812349	-0.960711
134	6	0	-5.945677	-4.255003	-1.690847
135	1	0	-4.490840	-2.770742	-1.233227
136	1	0	-8.440381	-2.025524	0.148689
137	1	0	-7.589368	-5.563212	-2.036337
138	6	0	5.190774	7.582725	-1.032531
139	6	0	5.642581	4.062910	-4.484772
140	6	0	9.887947	-1.400351	1.899437
141	6	0	6.070343	-4.212647	0.454357
142	6	0	-4.953103	-5.128217	-2.367512
143	6	0	-9.593432	-4.182739	-0.909901
144	6	0	-9.875190	4.517684	-0.488251
145	6	0	-5.190941	5.996419	-1.083495
146	6	0	-0.019422	-5.358198	1.557727
147	6	0	3.703659	-6.636328	-1.541205
148	9	0	5.946505	8.339570	-1.855826
149	9	0	5.616448	7.775089	0.234245
150	9	0	3.933940	8.076621	-1.096283
151	9	0	6.312184	2.897587	-4.599750
152	9	0	4.440487	3.862102	-5.095575
153	9	0	6.283035	5.002036	-5.206248
154	9	0	10.089160	-0.414309	2.800854
155	9	0	10.632305	-1.083651	0.814871
156	9	0	10.401073	-2.544032	2.399604
157	9	0	6.936573	-5.214896	0.693080
158	9	0	4.913879	-4.485445	1.093792
159	9	0	5.786765	-4.224550	-0.870968
160	9	0	4.753689	-6.754759	-0.711913
161	9	0	4.180823	-6.317487	-2.747821
162	9	0	3.143245	-7.852824	-1.630178
163	9	0	-0.032320	-6.662314	1.853967
164	9	0	0.170619	-4.679635	2.692793
165	9	0	-1.256710	-5.036379	1.120664

166	9	0	-4.046596	-5.641885	-1.496075
167	9	0	-4.228583	-4.448182	-3.284407
168	9	0	-5.540130	-6.169182	-2.989651
169	9	0	-9.758615	-5.521792	-0.957356
170	9	0	-10.294855	-3.669551	-1.946435
171	9	0	-10.180836	-3.721606	0.215443
172	9	0	-10.562451	3.847400	0.462868
173	9	0	-10.146597	5.833751	-0.358862
174	9	0	-10.396015	4.131304	-1.676449
175	9	0	-5.735348	6.900797	-1.928691
176	9	0	-4.753201	6.689646	-0.008569
177	9	0	-4.097201	5.473551	-1.676802

TS_R at ONIOM(M06-2X/6-31G(d): HF/3-21G*)





ONIOM(M06-2X/6-31G(d):HF/3-21G*) (Hartree)

Imaginary Freq = 1: -1279.94 cm-1

Electronic Energy (EE)	-7910.275841
Zero-point Energy Correction	1.293665
Thermal Correction to Energy	1.39588
Thermal Correction to Enthalpy	1.396824
Thermal Correction to Free Energy	1.14004
EE + Zero-point Energy	-7908.982176
EE + Thermal Energy Correction	-7908.879961
EE + Thermal Enthalpy Correction	-7908.879017
EE + Thermal Free Energy Correction	-7909.135801

E_{sp} (RM06-2X/6-311+(d,p)/SMD (toluene))	-7962.482689

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.844257	-2.736269	-1.721265
2	6	0	-1.359956	-4.150406	-1.550671
3	6	0	-1.403924	-4.855189	-0.158698
4	7	0	0.993941	-4.318168	0.333891
5	1	0	-2.395833	-4.109590	-1.909497
6	1	0	-0.839328	-4.822517	-2.235180
7	6	0	-2.265235	-6.114973	-0.340322
8	1	0	-3.289940	-5.873508	-0.629410
9	1	0	-1.846319	-6.767344	-1.114379
10	1	0	-2.301221	-6.686145	0.593481
11	6	0	-2.029786	-3.982853	0.930832
12	1	0	-3.050719	-3.696569	0.655166
13	1	0	-2.087494	-4.547824	1.867458
14	1	0	-1.461108	-3.072804	1.135603
15	6	0	0.362055	-2.486847	-2.514780
16	6	0	2.693498	-2.012878	-4.014222
17	6	0	0.670515	-1.192033	-2.985601
18	6	0	1.247779	-3.532950	-2.833468
19	6	0	2.407874	-3.297149	-3.558588
20	6	0	1.816238	-0.964507	-3.730757
21	1	0	0.003801	-0.359558	-2.809460
22	1	0	1.069081	-4.541240	-2.481478
23	1	0	3.091982	-4.119376	-3.742449
24	1	0	2.033874	0.036826	-4.085816
25	1	0	3.603945	-1.820746	-4.575067
26	6	0	-1.599149	-1.676102	-1.206726
27	1	0	-2.575943	-1.915160	-0.794604
28	1	0	-1.579971	-0.716079	-1.722259
29	6	0	2.275540	-4.478517	-0.096894
30	7	0	3.024049	-3.351700	0.099473
31	16	0	2.854635	-5.870559	-0.837649
32	6	0	4.236747	-3.028645	-0.542841
33	6	0	6.576679	-2.257184	-1.874439

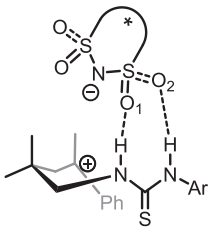
34	6	0	4.289880	-1.805982	-1.220635
35	6	0	5.357933	-3.854533	-0.512649
36	6	0	6.516482	-3.455136	-1.176122
37	6	0	5.448474	-1.439279	-1.891088
38	1	0	3.410831	-1.168593	-1.245075
39	1	0	5.322356	-4.800044	0.014380
40	1	0	7.486299	-1.965420	-2.385836
41	6	0	-0.012482	-5.357097	0.264477
42	1	0	-0.106008	-5.862173	1.236683
43	1	0	0.345576	-6.100933	-0.450827
44	1	0	0.814264	-3.564864	0.999434
45	1	0	2.518216	-2.523394	0.413465
46	1	0	-0.949164	-1.123469	-0.185726
47	6	0	-2.295623	-0.175020	2.805407
48	6	0	-1.416874	-0.464434	3.822126
49	6	0	-3.944278	-1.612662	3.791942
50	6	0	-1.735484	-1.467337	4.781791
51	6	0	-3.614504	-0.727627	2.812140
52	6	0	-3.015177	-2.044595	4.760662
53	6	0	-0.792941	-1.925397	5.740682
54	1	0	-4.332933	-3.461354	5.699470
55	1	0	-4.943398	-1.998469	3.830626
56	6	0	-1.130937	-2.891194	6.630060
57	1	0	0.191533	-1.509705	5.740388
58	1	0	-0.410379	-3.241364	7.341003
59	6	0	-2.430450	-3.450147	6.625707
60	1	0	-2.680161	-4.206553	7.342231
61	6	0	-3.347926	-3.038428	5.717046
62	6	0	1.949251	1.262097	3.211198
63	1	0	2.856920	2.713016	4.425641
64	6	0	2.051571	2.011736	4.335518
65	6	0	-0.151111	0.333896	4.012488
66	6	0	1.061792	1.981811	5.342400
67	6	0	0.868104	0.341962	3.104035
68	6	0	-0.090040	1.195444	5.153442
69	6	0	1.163655	2.811444	6.487370
70	1	0	-2.039786	0.743669	5.954290
71	6	0	0.151380	2.872508	7.386373

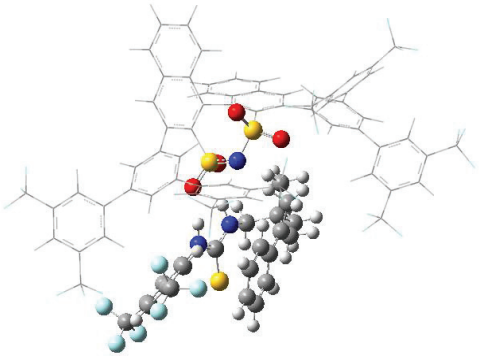
72	1	0	2.051454	3.397650	6.618600
73	1	0	0.229668	3.503280	8.248784
74	6	0	-1.024294	2.117022	7.180477
75	1	0	-1.828538	2.192520	7.884004
76	6	0	-1.145043	1.306055	6.100139
77	16	0	0.737944	-0.794511	1.728373
78	8	0	0.366992	-2.104150	2.277618
79	8	0	1.949870	-0.804389	0.911703
80	16	0	-1.671849	0.766140	1.384986
81	8	0	-1.145457	2.045543	1.834267
82	8	0	-2.639552	0.771918	0.300216
83	7	0	-0.463589	-0.200249	0.784834
84	6	0	-4.677806	-0.347157	1.833556
85	6	0	-6.607509	0.321611	-0.048794
86	6	0	-5.333544	-1.334571	1.121541
87	6	0	-5.019156	0.978423	1.621495
88	6	0	-5.954617	1.319317	0.663084
89	6	0	-6.303762	-1.009661	0.181331
90	1	0	-5.075750	-2.361864	1.283215
91	1	0	-4.520948	1.754073	2.166862
92	1	0	-7.299825	0.588418	-0.822727
93	6	0	2.812929	1.603101	2.042601
94	6	0	4.232833	2.335279	-0.216668
95	6	0	2.170854	2.223037	0.985803
96	6	0	4.177291	1.403840	2.001155
97	6	0	4.895270	1.788530	0.874158
98	6	0	2.861341	2.560617	-0.164191
99	1	0	1.122448	2.425852	1.071645
100	1	0	4.684156	0.951708	2.830530
101	1	0	4.782817	2.531903	-1.114057
102	6	0	-6.917632	-2.091967	-0.632912
103	6	0	-7.996003	-4.145368	-2.184834
104	6	0	-6.096771	-3.014920	-1.261729
105	6	0	-8.289556	-2.206739	-0.797172
106	6	0	-8.814530	-3.226020	-1.565843
107	6	0	-6.633950	-4.032727	-2.018404
108	1	0	-5.034667	-2.916028	-1.183208
109	1	0	-8.947613	-1.504283	-0.328264

110	1	0	-8.410224	-4.918063	-2.797229
111	6	0	-6.144789	2.751757	0.302502
112	6	0	-6.438159	5.413013	-0.437809
113	6	0	-7.373775	3.378034	0.416165
114	6	0	-5.059329	3.464933	-0.190318
115	6	0	-5.217142	4.786625	-0.557656
116	6	0	-7.510298	4.701794	0.052983
117	1	0	-8.221095	2.838239	0.786895
118	1	0	-4.110951	2.975927	-0.301066
119	1	0	-6.552655	6.435448	-0.726298
120	6	0	2.089747	3.121717	-1.305789
121	6	0	0.520845	4.219438	-3.341099
122	6	0	0.810808	2.642258	-1.559642
123	6	0	2.578029	4.147134	-2.102353
124	6	0	1.802024	4.673886	-3.114218
125	6	0	0.035687	3.199683	-2.554065
126	1	0	0.423840	1.831366	-0.976687
127	1	0	3.548752	4.558498	-1.917598
128	1	0	-0.086099	4.656474	-4.104582
129	6	0	6.373212	1.598427	0.833773
130	6	0	9.138005	1.264230	0.759121
131	6	0	7.211398	2.685224	0.644185
132	6	0	6.935801	0.340390	0.987879
133	6	0	8.304979	0.182222	0.938899
134	6	0	8.580347	2.514205	0.617611
135	1	0	6.797177	3.664663	0.520777
136	1	0	6.306916	-0.514157	1.128080
137	1	0	10.199236	1.134774	0.727981
138	6	0	-5.719782	-5.034418	-2.619977
139	6	0	-10.290099	-3.364747	-1.683203
140	6	0	-4.061367	5.534392	-1.122581
141	6	0	-8.816729	5.380677	0.245136
142	6	0	-1.355586	2.710419	-2.729546
143	6	0	2.366867	5.733187	-3.989929
144	6	0	9.462116	3.702568	0.489324
145	6	0	8.888317	-1.182572	1.006126
146	6	0	5.489858	-0.177313	-2.703929
147	6	0	7.724108	-4.349698	-1.090821

148	9	0	8.675227	-3.995412	-1.962064
149	9	0	7.393097	-5.624027	-1.348185
150	9	0	8.264806	-4.333595	0.134889
151	9	0	5.842072	-0.430730	-3.975517
152	9	0	4.303589	0.451049	-2.739421
153	9	0	6.379631	0.710375	-2.228927
154	9	0	10.117418	-1.168055	1.563468
155	9	0	9.035725	-1.730825	-0.226298
156	9	0	8.105434	-2.018215	1.716342
157	9	0	8.884561	4.665283	-0.261749
158	9	0	9.742156	4.269050	1.686157
159	9	0	10.647002	3.379790	-0.070888
160	9	0	3.026636	5.222183	-5.055271
161	9	0	3.254787	6.502260	-3.323546
162	9	0	1.398504	6.532840	-4.484644
163	9	0	-3.765716	5.156647	-2.387016
164	9	0	-2.941007	5.350341	-0.395839
165	9	0	-4.314381	6.862548	-1.162676
166	9	0	-8.977755	6.399398	-0.625831
167	9	0	-9.846108	4.519316	0.085219
168	9	0	-8.950897	5.907544	1.484395
169	9	0	-10.901661	-2.162246	-1.631746
170	9	0	-10.635671	-3.970543	-2.838465
171	9	0	-10.816997	-4.107024	-0.682823
172	9	0	-6.256833	-5.628483	-3.701012
173	9	0	-4.539515	-4.472235	-2.982144
174	9	0	-5.400379	-6.023151	-1.745790
175	9	0	-2.155739	3.039223	-1.691860
176	9	0	-1.921430	3.186401	-3.852539
177	9	0	-1.395986	1.347297	-2.802445

Intermediate_*R*





ONIOM(M062X/6-31G(d): HF/3-21G*) (Hartree)	
Imaginary Freq	0
Electronic Energy (EE)	-7910.289205
Zero-point Energy Correction	1.29876
Thermal Correction to Energy	1.401534
Thermal Correction to Enthalpy	1.402478
Thermal Correction to Free Energy	1.14361
EE + Zero-point Energy	-7908.990446
EE + Thermal Energy Correction	-7908.887672
EE + Thermal Enthalpy Correction	-7908.886727
EE + Thermal Free Energy Correction	-7909.145595
E_{sp}(RM06-2X/6-311+G(d,p)/SMD(toluene))	-7962.494226

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.940624	-3.228826	-1.265865
2	6	0	-1.391870	-4.545455	-0.733867
3	6	0	-1.416465	-4.780745	0.813950
4	7	0	0.908590	-3.847590	0.851424
5	1	0	-2.426558	-4.657147	-1.090416
6	1	0	-0.811160	-5.367390	-1.154624
7	6	0	-2.109052	-6.133188	1.031734
8	1	0	-3.157802	-6.098340	0.726417
9	1	0	-1.613111	-6.927202	0.462807

10	1	0	-2.071439	-6.406830	2.091481
11	6	0	-2.156973	-3.715859	1.626423
12	1	0	-3.188046	-3.598740	1.278056
13	1	0	-2.202729	-4.042222	2.670580
14	1	0	-1.661011	-2.742318	1.622728
15	6	0	0.100830	-3.099743	-2.235426
16	6	0	2.094995	-2.778306	-4.183338
17	6	0	0.495256	-1.802198	-2.672006
18	6	0	0.739592	-4.224171	-2.818312
19	6	0	1.723472	-4.056014	-3.784557
20	6	0	1.471770	-1.649411	-3.629917
21	1	0	0.025715	-0.918957	-2.261787
22	1	0	0.451184	-5.228785	-2.545717
23	1	0	2.206603	-4.927940	-4.210453
24	1	0	1.768162	-0.655896	-3.947265
25	1	0	2.874999	-2.645751	-4.926752
26	6	0	-1.722231	-2.026479	-0.890032
27	1	0	-2.663947	-2.281145	-0.412496
28	1	0	-1.912404	-1.366982	-1.739272
29	6	0	2.047538	-4.084992	0.138243
30	7	0	2.800828	-2.970527	-0.041216
31	16	0	2.427014	-5.588312	-0.524108
32	6	0	3.994808	-2.867029	-0.789166
33	6	0	6.346641	-2.543290	-2.283322
34	6	0	4.119124	-1.804743	-1.681827
35	6	0	5.060632	-3.754292	-0.621392
36	6	0	6.223214	-3.576360	-1.360050
37	6	0	5.280650	-1.667779	-2.439857
38	1	0	3.300291	-1.100682	-1.792456
39	1	0	4.979155	-4.571416	0.085309
40	1	0	7.260100	-2.410989	-2.846918
41	6	0	0.033554	-4.907687	1.317722
42	1	0	0.021986	-4.895037	2.414724
43	1	0	0.460579	-5.856484	0.989642
44	1	0	0.864544	-2.987717	1.407774
45	1	0	2.462880	-2.090735	0.364890
46	1	0	-1.148121	-1.400562	-0.178709
47	6	0	-2.236063	0.409790	2.872777

48	6	0	-1.409721	0.264723	3.962182
49	6	0	-3.940954	-0.862186	3.992712
50	6	0	-1.778258	-0.586750	5.044173
51	6	0	-3.558081	-0.140560	2.902969
52	6	0	-3.063189	-1.148314	5.057120
53	6	0	-0.881210	-0.909313	6.097440
54	1	0	-4.442110	-2.393191	6.141269
55	1	0	-4.945218	-1.232532	4.045443
56	6	0	-1.269190	-1.728340	7.106081
57	1	0	0.109050	-0.508538	6.076136
58	1	0	-0.582289	-1.975912	7.889939
59	6	0	-2.577029	-2.266545	7.133108
60	1	0	-2.867745	-2.903587	7.944193
61	6	0	-3.450788	-1.984467	6.136209
62	6	0	2.012960	1.817658	3.248020
63	1	0	2.919790	3.406734	4.277453
64	6	0	2.103536	2.712233	4.260789
65	6	0	-0.132039	1.055680	4.091745
66	6	0	1.083809	2.840367	5.231030
67	6	0	0.917481	0.907688	3.233744
68	6	0	-0.082710	2.063589	5.108571
69	6	0	1.172083	3.815381	6.255856
70	1	0	-2.070663	1.775683	5.887257
71	6	0	0.133119	4.023407	7.101382
72	1	0	2.071580	4.392843	6.338425
73	1	0	0.201567	4.763929	7.872688
74	6	0	-1.056375	3.276757	6.955847
75	1	0	-1.881800	3.467714	7.611496
76	6	0	-1.164514	2.329281	5.990740
77	16	0	0.755604	-0.354333	1.970760
78	8	0	0.284963	-1.583223	2.638366
79	8	0	2.022416	-0.553658	1.255703
80	16	0	-1.543655	1.181516	1.371206
81	8	0	-1.085098	2.523369	1.719208
82	8	0	-2.493948	1.074336	0.269694
83	7	0	-0.312866	0.211926	0.920455
84	6	0	-4.586542	0.056399	1.834256
85	6	0	-6.499532	0.348620	-0.163557

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128	1	0	0.175503	3.899925	-4.617053
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133	6	0	8.393492	0.572198	-0.066538
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135	1	0	6.843558	2.687973	2.704248
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169	9	0	-10.798244	-2.323810	-1.314180
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172	9	0	-6.264280	-6.376728	-2.275294
173	9	0	-4.532979	-5.066649	-1.987815
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175	9	0	-2.030773	2.811865	-2.186790
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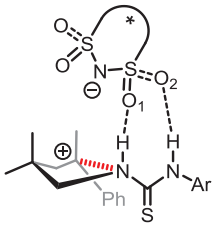
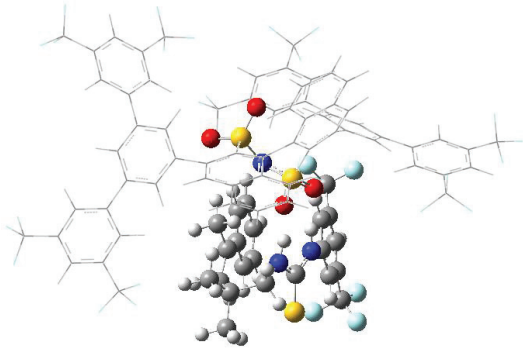
TS2_*R*





ONIOM(M062X/6-31G(d):HF/3-21G*) (Hartree)

Imaginary Freq	1: -75.05 cm-1
Electronic Energy (EE)	-7910.290823
Zero-point Energy Correction	1.299252
Thermal Correction to Energy	1.401322
Thermal Correction to Enthalpy	1.402266
Thermal Correction to Free Energy	1.14381
EE + Zero-point Energy	-7908.991571
EE + Thermal Energy Correction	-7908.889501

EE + Thermal Enthalpy Correction -7908.888557

EE + Thermal Free Energy Correction -7909.147013

E_{sp}(RM06-2X/6-311+(d,p)/SMD(toluene)) -7962.490841

Center Number	Atomic Number	Integrated Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000024115	-0.000015330	0.000002867
2	6	-0.000002499	-0.000002305	0.000006708
3	6	0.000000004	-0.000004299	-0.000007497
4	7	0.000035059	0.000015254	-0.000007554
5	1	0.000004064	0.000001377	-0.000001521
6	1	0.000001106	-0.000000488	-0.000001342
7	6	0.000013837	0.000003942	0.000002289
8	1	0.000000855	0.000003560	-0.000000979
9	1	-0.000002121	0.000003790	0.000001893
10	1	0.000000121	-0.000001995	0.000000004
11	6	-0.000003233	0.000003786	-0.000004948
12	1	0.000002668	-0.000002037	-0.000000024
13	1	0.000000573	-0.000000799	-0.000000268
14	1	-0.000004312	0.000004649	0.000003613
15	6	-0.000014778	-0.000005770	-0.000008154
16	6	-0.000009212	0.000002842	0.000008182
17	6	-0.000001082	-0.000001432	0.000003429
18	6	0.000000083	0.000019988	-0.000000753
19	6	-0.000006451	-0.000008778	-0.000007386
20	6	-0.000004249	0.000010555	0.000003223
21	1	-0.000004810	0.000011511	0.000007914
22	1	-0.000004601	0.000001919	0.000001026
23	1	-0.000007233	-0.000006521	0.000004520
24	1	-0.000000777	-0.000005485	0.000003595
25	1	0.000002550	-0.000004325	-0.000002543
26	6	0.000006893	-0.000009668	-0.000003847
27	1	-0.000000461	0.000013451	0.000010863
28	1	-0.000015566	0.000013807	-0.000004044
29	6	-0.000024241	-0.000000271	-0.000007493

30	7	-0.000010938	0.000002489	0.000008030
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32	6	-0.000001991	-0.000012395	0.000006147
33	6	-0.000001509	-0.000000143	-0.000010030
34	6	-0.000010545	0.000014892	0.000008925
35	6	0.000030648	-0.000050804	-0.000026131
36	6	-0.000007026	0.000012531	0.000004492
37	6	-0.000012273	0.000022909	0.000015260
38	1	0.000005408	-0.000003171	-0.000001218
39	1	-0.000005714	-0.000001135	-0.000009740
40	1	0.000006748	0.000004060	0.000001457
41	6	-0.000014333	-0.000012364	0.000010657
42	1	0.000007733	-0.000003296	0.000018131
43	1	-0.000012230	-0.000012918	-0.000010076
44	1	-0.000006601	0.000005978	0.000011837
45	1	0.000031911	-0.000000606	-0.000006281
46	1	-0.000006022	-0.000019727	-0.000016199
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48	6	0.000002918	0.000004110	-0.000003817
49	6	0.000001116	0.000000272	-0.000001106
50	6	-0.000000739	-0.000000892	0.000000387
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52	6	-0.000000219	0.000000569	-0.000000265
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55	1	-0.000000441	-0.000000433	0.000000456
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57	1	0.000000152	-0.000000075	-0.000000282
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65	6	-0.000003034	-0.000001370	0.000001590
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67	6	0.000003482	-0.000010461	0.000007984

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69	6	-0.000000196	0.000000023	-0.000000237
70	1	-0.000000203	0.000000191	0.000000320
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73	1	-0.000000164	0.000000228	-0.000000096
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75	1	-0.000000136	0.000000170	-0.000000059
76	6	0.000000097	0.000000088	0.000000123
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78	8	-0.000009204	0.000008458	-0.000017282
79	8	-0.000021346	-0.000002252	0.000014402
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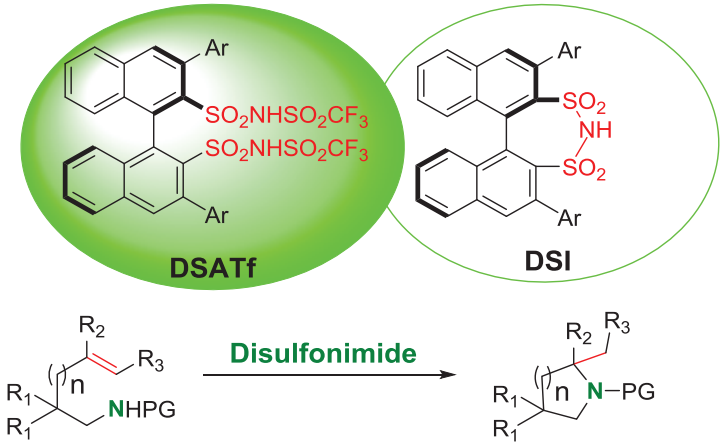
175	9	0.000002345	-0.000000447	0.000002521
176	9	0.000002282	0.000003079	-0.000003220
177	9	-0.000002954	0.000002937	-0.000005580

Chapter 4. Overall Conclusion

In chapter 2, a new strong brønsted acid **DSATf** bearing *N*-trifuoromethylsulfonamide groups has been developed. The computational prediction of pK_a value of **DSATf** categorized it as a strong Brønsted acid. Hydrofunctionalization of alkenyl amines proceeded with high efficiency but no enantioselectivity was observed. In chapter 3, a cyclic **DSI** catalyzed asymmetric intramolecular hydroamination of alkenyl thioureas was examined. It was found that the hydroamination product was obtained in good chemical yield and moderate enantioselectivity under dilute conditions without stirring. The DFT calculation on the hydroamination supported a mechanism, in which thiourea moiety of alkenyl amines acted as a hydrogen bond donor.



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List of Publications

(1) Bis(trifluoromethanesulfonimide) (BSI): Acidity and application to hydrofunctionalization as a Brønsted acid catalyst

Ryukichi Takagi, Yuichiro Sakai, Duyen Thi Duong

Tetrahedron. **2021**,132037.

(2) Disulfonimide catalyzed asymmetric intramolecular hydroamination of alkenyl thioureas: Concentration effect in the hydroamination

Ryukichi Takagi, Duyen Thi Duong, Toshiya Ichiki

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