Copper-Catalyzed Three-Component Radical Relay Alkenylation of Sulfenamides

Renkang Wei,[+] Jing Zhong,[+] Qian Wang, Yixin Wang, Hequan Yao,* and Aijun Lin*

State Key Laboratory of Natural Medicines (SKLNM) and Department of Medicinal Chemistry, School of Pharmacy, China Pharmaceutical University, Nanjing 210009, P. R. China

*E-mail: hyao@cpu.edu.cn; ajlin@cpu.edu.cn.

Contents

1.General Information

Reagents and Solvents: PE refers to petroleum ether b.p. 60–90 °C, EA refers to ethyl acetate, and DCM refers to dichloromethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Chromatography: Flash column chromatography was carried out using commercially available 200–300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they were listed as volume/volume ratios.

Data collection: ^{1}H, ^{13}C and ^{19}F NMR Spectrum were collected on BRUKER AV-300 (300 MHz) or BRUKER AV-400 (400 MHz) spectrometer using $CDCl_3$ as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.16 ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus. Optical rotations were measured on an Anton Paar MCP 100 automatic polarimeter with $[\alpha]_{25}^{D}$ values reported in degrees; concentration (c) is in g/100 mL. The enantiomeric excess values were determined by chiral HPLC using Agilent 1200 LC or Shimadzu LC-40D instrument with Daicel CHIRALPAK® IA-3, IB-3, IC-3, AD-H, OD-H and AS-H columns. X-ray diffraction analyses were carried out on a microcrystalline powder using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer using or Cu radiation (λ = 1.54184 Å)

2. General Procedure for the Preparation of Substrates

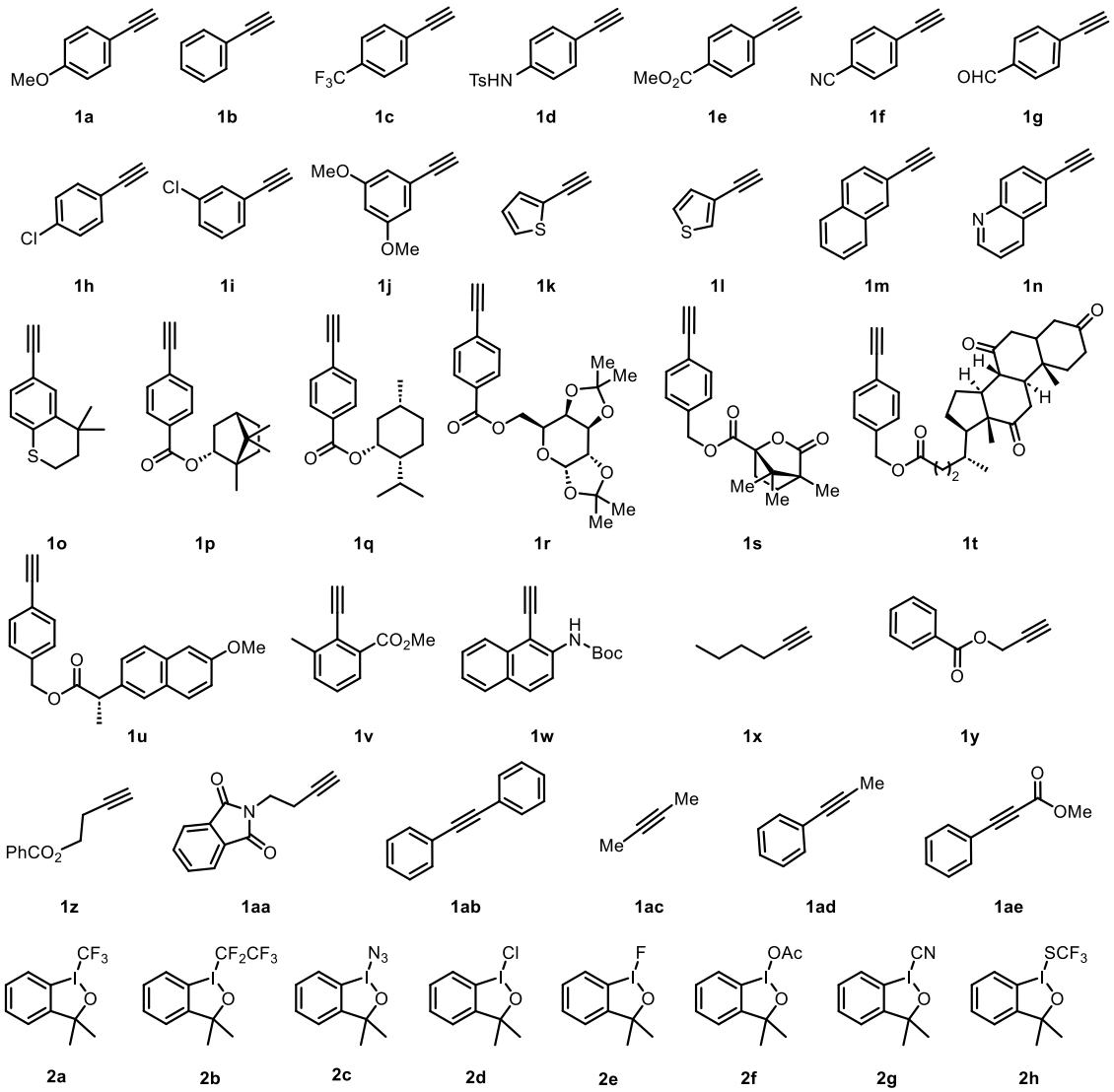
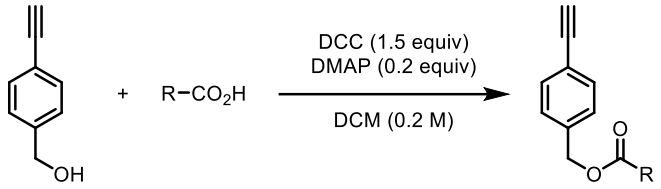


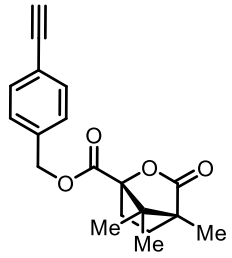
Figure S1. Structures of Substrates **1** and Substrates **2**

Except for **1s**, **1t** all other alkynes are known compounds. **1a**–**1o** are commercially available, **1p**–**1r** were prepared according to the reported procedures. [1] Both **2a** and **2b** are known compounds**. 2a** are commercially available, **2b** were prepared according to the reported procedures. [2]

General procedure A for the synthesis **1s**–**1u** [3]



In a 50 mL round bottom flask, a mixture of dicyclohexylcarbodiimide (DCC) (1.55 g, 7.5 mmol), 4-dimethylaminopyridine (DMAP) (0.12 g, 1.0 mmol), acid (6.0 mmol, 1.2 equiv) and (4-ethynylphenyl) methanol (5.0 mmol) in CH_2Cl_2 (25.0 mL) was stirred at room temperature for 12 h. After the completion of the reaction, the reaction was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to afford the corresponding ester compounds.



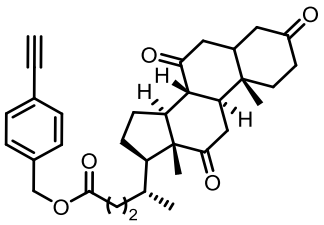
4-ethynylbenzyl(1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (1s)

Prepared according to General Procedure A. White solid, m.p. 92–94 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.35 – 7.33 (m, 2H), 5.26 (s, 2H), 3.12 (s, 1H), 2.47 – 2.40 (m, 1H), 2.07 – 2.01 (m, 1H), 1.96 – 1.89 (m, 1H), 1.72 – 1.65 (m, 1H), 1.10 (s, 3H), 1.02 (s, 3H), 0.90 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 167.3, 135.8, 132.4, 128.3, 122.4, 91.0, 83.1, 78.0, 66.6, 54.8, 54.4, 30.7, 28.9, 16.8, 16.7, 9.7 ppm.

HRMS (ESI) calcd for $[C_{19}H_{20}O_4+H]^+$ 313.1434, found 313.1430.



4-ethynylbenzyl(4R)-4-((8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (1t)

Prepared according to General Procedure A. White solid, m.p. 175–176 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.32 – 7.30 (m, 2H), 5.14 – 5.06 (m, 2H), 3.10 (s, 1H), 2.94 – 2.80 (m, 3H), 2.49 – 2.42 (m, 1H), 2.38 – 2.23 (m, 6H), 2.16 – 2.09 (m, 2H), 2.06 – 1.99 (m, 3H), 1.95 – 1.93 (m, 1H), 1.88 – 1.80 (m, 2H), 1.66 – 1.57 (m, 1H), 1.45 – 1.22 (m, 8H), 1.03 (s, 3H), 0.84 (d, J = 6.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.0, 209.2, 208.8, 173.8, 136.9, 132.4, 128.1, 122.0, 83.3, 65.6, 57.0, 51.8, 49.1, 46.9, 45.7, 45.6, 45.1, 42.9, 38.7, 36.6, 36.1, 35.5, 35.4, 34.1, 31.6, 30.5, 27.7, 25.7, 25.2, 25.1, 22.0, 18.7, 11.9 ppm.
HRMS (ESI) calcd for $[C_{33}H_{40}O_5+H]^+$ 517.2949, found 517.2943.

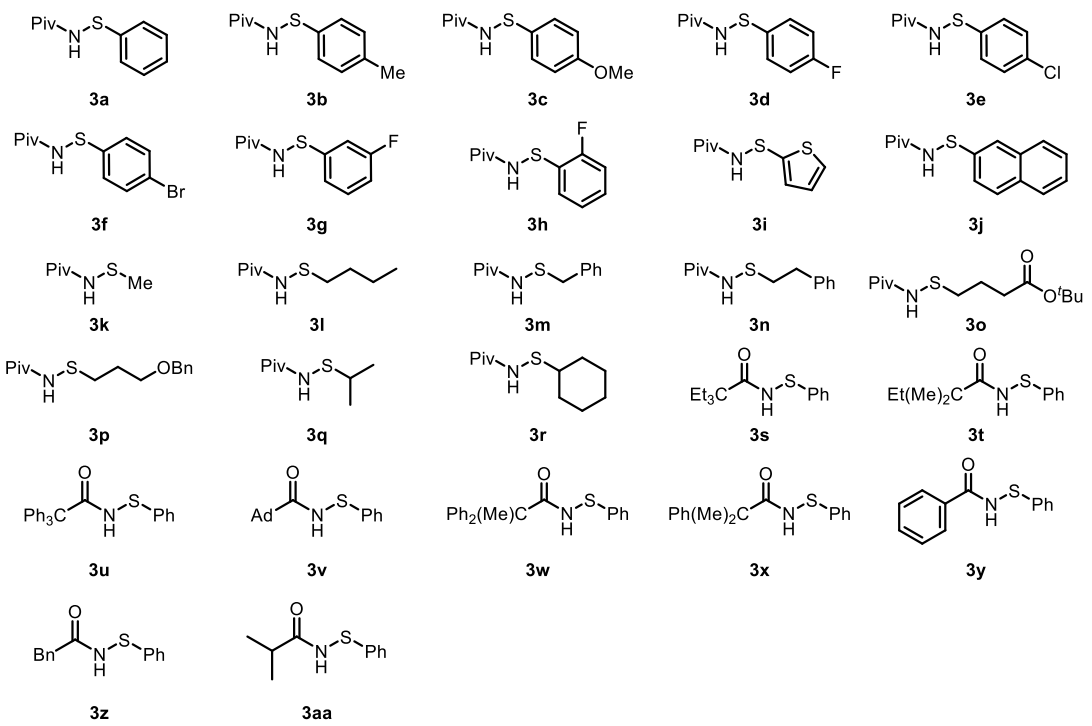
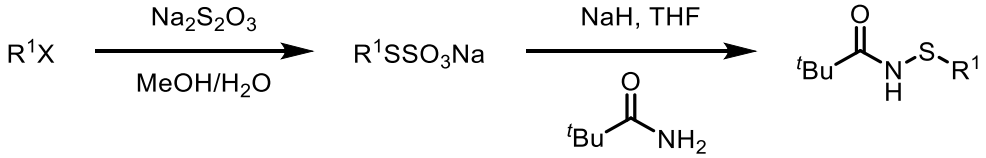


Figure S2. Structures of Substrates **3**

All sulfenamides are known compounds. **3a**–**3j**, **3l**, **3m**, **3r** were prepared according to the reported procedures.[4] **3k** were prepared according to the reported procedures.[5] **3q** were prepared according to the reported procedures.[6] **3s**, **3t** were prepared according to the reported procedure.[7] **3u** were prepared according to the reported procedures.[8] **3v** were prepared according to the reported procedures.[9] **3y**–**3aa** were prepared according to the reported procedure.[10]

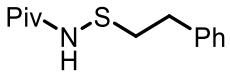
General procedure B for the synthesis **3n**–**3p**



A flask was charged with alkyl halide (50.0 mmol), sodium thiosulfate pentahydrate (14.9 g, 60.0 mmol), water (25.0 mL) and MeOH (75.0 mL). The reaction mixture was stirred and heated to 65 ℃, and then was cooled to room temperature until the reaction was complete determined via HPLC-MS analysis. The solution was concentrated to remove MeOH and water. The resultant solid was treated with MeOH (250.0 mL), heated to 50 ℃ (most solid dissolves), and filtered through a medium stone frit filter. This removes excess sodium thiosulfate and sodium halide. The filtrate was concentrated to a white solid, the crude Bunte salt was used in the next step without purification.

To a flame-dried round bottom flask under N_2 was added the pivalamide (10.0 mmol) and dry THF (100.0 mL). The flask was cooled to 0 ºC and NaH (60% dispersion in mineral oil, 1.0 g, 25.0 mmol) was added. The solution was warmed to room

temperature for 30 min, then cooled to 0 ºC. Bunte salt (30.0 mmol) was added in three batches until the reaction was complete as determined by TLC. The reaction was quenched with saturated NH_4Cl before water was added. The mixture was extracted with ethyl acetate (three times). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. Purification of the residue by the flash silica gel column chromatography afforded the desired *S*-alkyl sulfenamides.



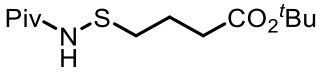
N-(phenethylthio)pivalamide (3n)

Prepared according to General Procedure C. White solid, m.p. 68–70 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 2H), 7.26 – 7.18 (m, 3H), 6.35 (s, 1H), 3.06 – 2.95 (m, 2H), 2.95 – 2.86 (m, 2H), 1.16 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.3, 140.2, 128.68, 128.65, 126.6, 40.1, 39.8, 35.0, 27.7 ppm.

HRMS (ESI) calcd for $[C_{13}H_{19}NOS+H]^+$ 238.1260, found 238.1260.



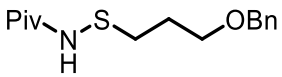
tert-butyl 4-(pivalamidothio) butanoate (3o)

Prepared according to General Procedure C. White solid, m.p. 50–52 ℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.73 (s, 1H), 2.70 (t, J = 6.7 Hz, 2H), 2.37 (t, J = 6.6 Hz, 2H), 1.88 (p, J = 6.6 Hz, 2H), 1.46 (s, 9H), 1.25 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 180.5, 173.5, 80.7, 39.9, 38.0, 34.1, 28.1, 27.8, 21.9 ppm.

HRMS (ESI) calcd for $[C_{13}H_{25}NO_3S+H]^+$ 298.1447, found 298.1446.



N-((3-(benzyloxy)propyl)thio) pivalamide (3p)

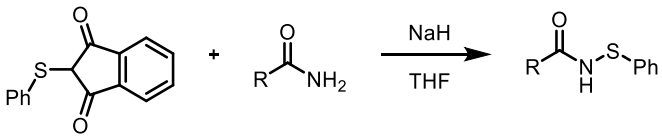
Prepared according to General Procedure C. light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 5H), 6.56 (s, 1H), 4.50 (s, 2H), 3.61 (t, J = 5.9 Hz, 2H), 2.83 (t, J = 7.0 Hz, 2H), 1.96 – 1.80 (m, 2H), 1.18 (s, 9H) ppm.

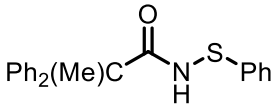
^{13}C NMR (75 MHz, $CDCl_3$) δ 180.5, 138.3, 128.5, 127.8, 127.7, 73.1, 68.7, 39.8, 35.9, 27.9, 27.7 ppm.

HRMS (ESI) calcd for $[C_{15}H_{23}NO_2S+H]^+$ 282.1522, found 282.1522.

General procedure C for the synthesis **3w, 3s**



To a flame-dried round bottom flask under N_2 was added the Amines (5.0 mmol) and dry THF (50.0 mL). The flask was cooled to 0 ºC before NaH (60% dispersion in mineral oil, 0.5 g, 12.5 mmol) was added. The resulting mixture warmed to r.t. and stirred for 30 min and then *N*-thiosuccinimide (5.0 mmol) was added at 0 ºC. The mixture was warmed to room temperature. and stirred until reaction completion as assessed by TLC. The reaction mixture was added saturated NH_4Cl and water, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. Purification by the flash silica gel column chromatography afforded the desired sulfonamides.



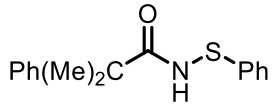
2,2-diphenyl-N-(phenylthio)propanamide (3w)

Prepared according to General Procedure C. white solid. m.p. 118–120 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.12 (m, 15H), 6.63 (s, 1H), 2.01 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 144.1, 138.4, 129.0, 128.8, 128.2, 127.4, 127.2, 126.3, 58.0, 27.8 ppm.

HRMS (ESI) calcd for $[C_{21}H_{19}NOS + H]^+$ 334.1260, found 334.1267.



2-methyl-2-phenyl-N-(phenylthio)propanamide (3x)

Prepared according to General Procedure C. white solid. m.p. 96–98 ℃.

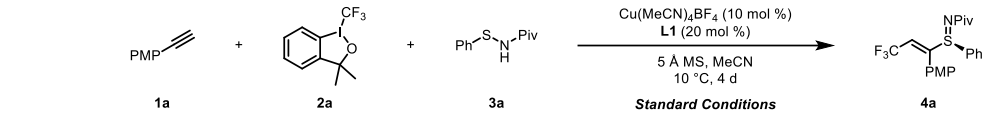
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.06 (m, 10H), 6.37 (s, 1H), 1.62 (s, 6H) ppm.

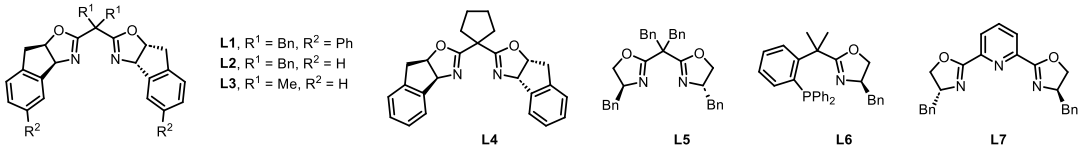
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.9, 144.1, 138.9, 129.0, 128.9, 127.5, 126.7, 126.4, 125.2, 48.0, 27.1 ppm.

HRMS (ESI) calcd for $[C_{16}H_{17}NOS + H]^+$ 272.1104, found 272.1103.

3. Copper-Catalyzed Three-Component Radical Relay Alkenylation of Sulfenamides

3.1 Optimization of reaction conditions[a]





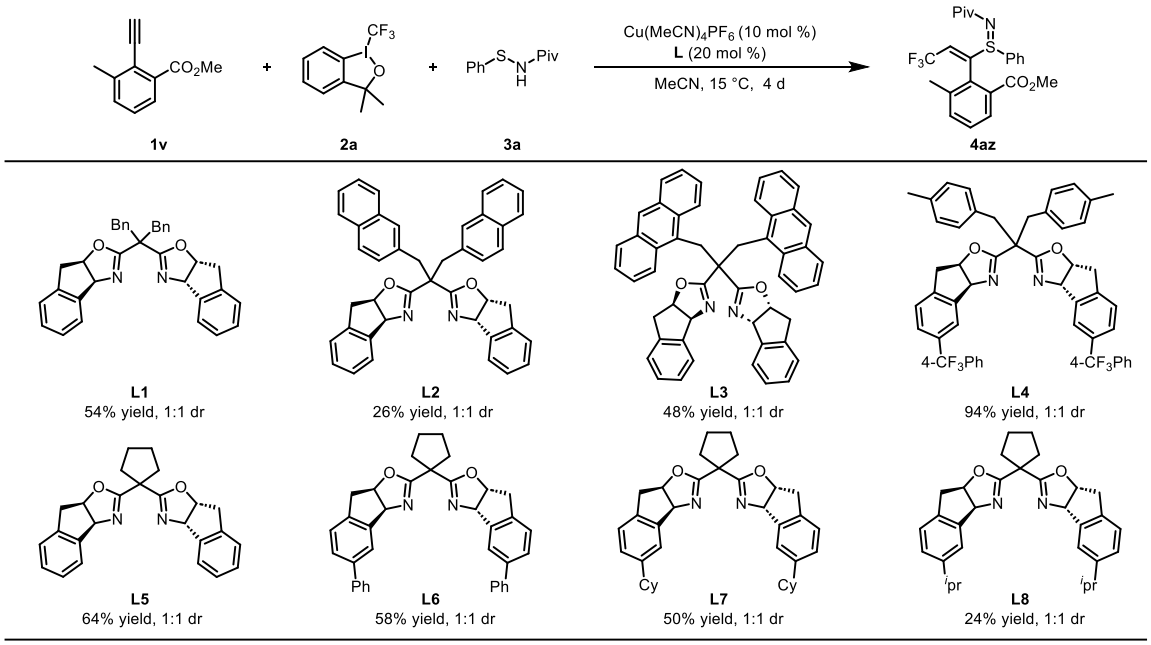
Entry	Variation from standard conditions	Yield (%) *E*/*Z* [b]	Ee (%)[c]
1	none	86[d] (> 20:1)	96
2	**L2** instead of **L1**	68 (> 20:1)	89
3	**L3** instead of **L1**	48 (> 20:1)	7
4	**L4** instead of **L1**	32 (> 20:1)	5
5	**L5** instead of **L1**	58 (> 20:1)	82
6	**L6** instead of **L1**	ND	-
7	**L7** instead of **L1**	ND	-
8	CuI instead of $Cu(MeCN)_4BF_4$	18 (3:1)	70
9	$Cu(OTf)_2$ instead of $Cu(MeCN)_4BF_4$	62 (> 20:1)	95
10	DCM as solvent	96 (> 20:1)	70
11	THF as solvent	38 (7:1)	75
12	25 °C	87 (> 20:1)	88
13	w/o 5 Å MS	72 (> 20:1)	96
14	2 d	70 (> 20:1)	96

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.20 mmol), $Cu(MeCN)_4BF_4$ (10 mol %), **L1** (20 mol %) and 5 Å MS (50 mg) in MeCN (1.0 mL) at 10 °C under Ar atmosphere, 4 d. [b]Yields were determined by ^{19}F NMR using CF_3-DMAc as internal standard. The *E*/*Z* ratio determined by ^{19}F NMR analysis. [c]Determined by chiral HPLC analysis. [d]Isolated yield. PMP = *p*-methoxyphenyl. Piv = *tert*-butylcarbonyl. ND = not detected. w/o = without.

Table S1. Optimization of reaction conditions

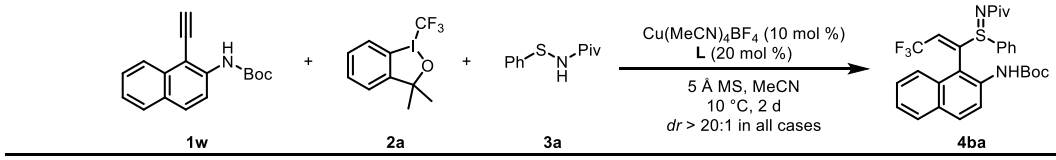
We initiated our study with p-methoxyphenylacetylene (**1a**), Togni reagent (**2a**), and sulfenamide (**3a**) as the model substrates. After systematic optimization, we determined that the combination of $Cu(MeCN)_4BF_4$ (10 mol %), **L1** (20 mol %) and 5 Å molecular sieves (50 mg) in MeCN (1.0 mL) at 10 °C for 4 days was the optimal condition, delivering **4a** in 86% isolated yield with 96% ee and > 20:1 *E*-selectivity (**Table S1**, entry 1). Bulky substituents at the ligand's methylene position were critical for

enantiocontrol, replacement of the benzyl group with other substituents gave nearly racemic products (**Table S1**, entries 3 and 4). Moreover, reducing the steric bulk of the overall ligand framework lowered enantioselectivity (**Table S1**, entries 2 and 5). No desired product was observed when N-P or Pybox-type ligands were employed (**Table S1**, entries 6 and 7). Utilizing CuI as the catalyst afforded **4a** in 18% yield with 70% ee and 3:1 *E*-selectivity (**Table S1**, entry 8), whereas $Cu(OTf)_2$ gave 62% yield and > 20:1 *E*-selectivity (**Table S1**, entry 9). Other solvents, such as DCM and THF furnished **4a** with 70% and 75% ee, respectively (**Table S1**, entries 10 and 11). Conducting the reaction at 25 °C diminished enantioselectivity (**Table S1**, entry 12). Omitting 5 Å molecular sieves or shortening the reaction time compromised the product yield (**Table S1**, entries 13 and 14).

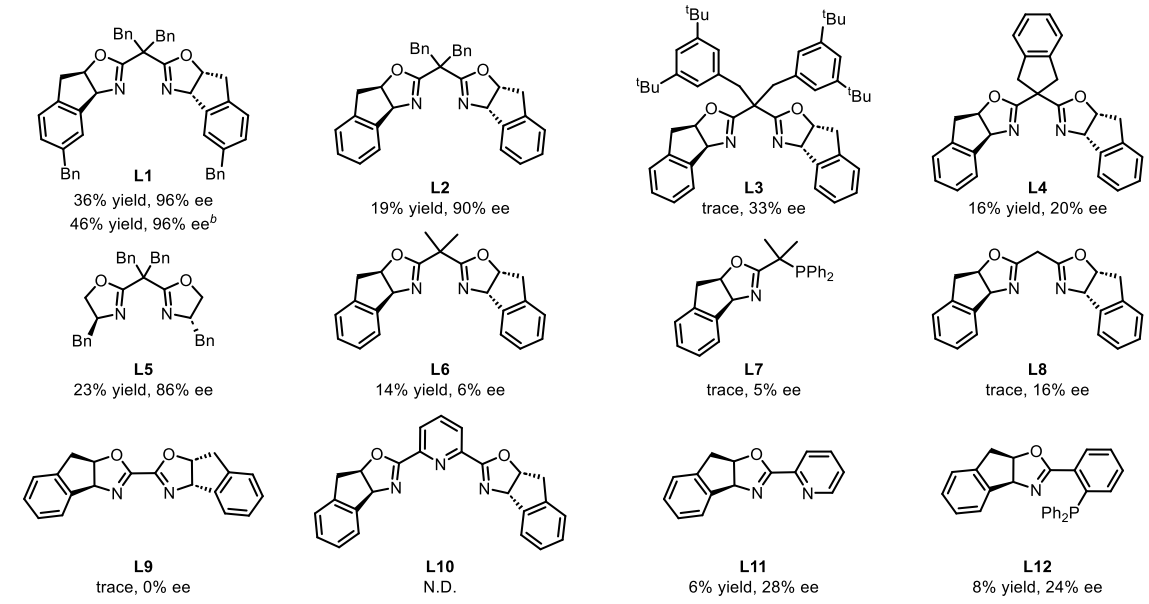


[a]Reaction conditions: **1v** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.20 mmol), $Cu(MeCN)_4PF_6$ (10 mol %), **L** (20 mol %) and in MeCN (1.0 mL) at 10 °C under Ar atmosphere, 4 d. The *dr* ratio was determined by ^{19}F NMR analysis.

Table S2. Ligand screening with **1v**

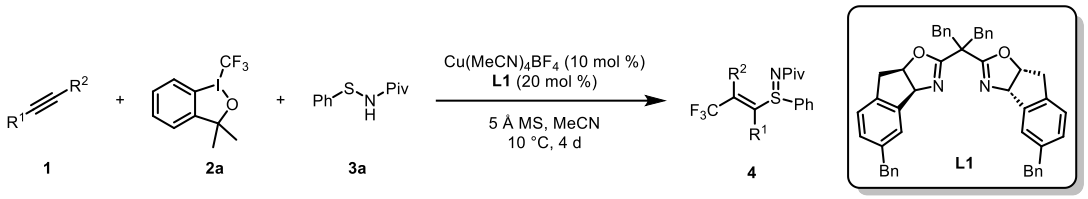


1w 2a 3a 4ba



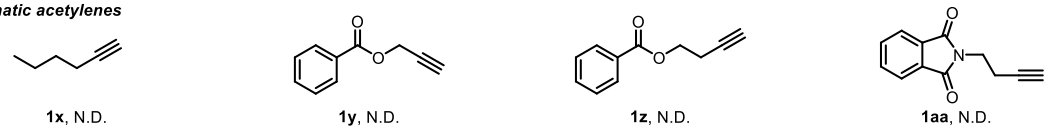
[a]Reaction conditions: **1w** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.20 mmol), $Cu(MeCN)_4BF_4$ (10 mol %), **L** (20 mol %) and 5 Å MS (50 mg) in MeCN (1.0 mL) at 10 °C under Ar atmosphere, 2 d. N.D. = not detected. The *ee* values were determined by chiral HPLC analysis. Yields were determined by ^{19}F NMR using CF_3-DMAc as internal standard. The *dr* ratio was determined by ^{19}F NMR analysis. [b]4d, Isolated yields were given.

Table S3. Ligand screening with **1w**



1 2a 3a 4 L1

Aliphatic acetylenes



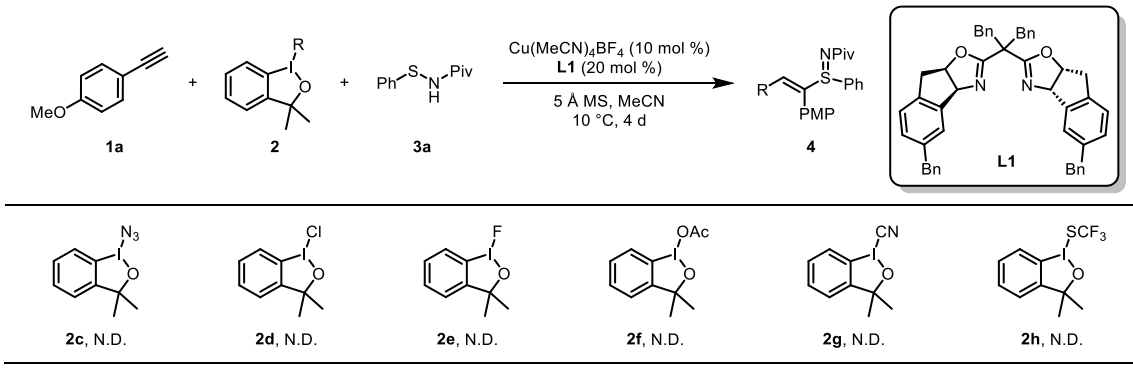
1x, N.D. **1y**, N.D. **1z**, N.D. **1aa**, N.D.

Internal alkynes

1ab, N.D. **1ac**, N.D. **1ad**, N.D. **1ae**, N.D.

[a]Reaction conditions: **1** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.20 mmol), $Cu(MeCN)_4BF_4$ (10 mol %), **L1** (20 mol %) and in MeCN (1.0 mL) at 10 °C under Ar atmosphere, 4 d. N.D. = not detected.

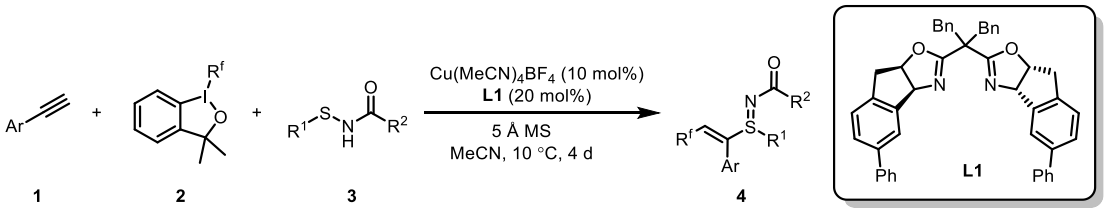
Table S4. Aliphatic acetylenes and interal alkynes screening



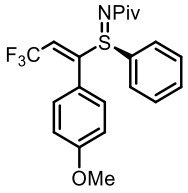
[a]Reaction conditions: **1a** (0.10 mmol), **2** (0.15 mmol), **3a** (0.20 mmol), $Cu(MeCN)_4BF_4$ (10 mol %), **L1** (20 mol %) and in MeCN (1.0 mL) at 10 °C under Ar atmosphere, 4 d. N.D. = not detected.

Table S5. Hypervalent iodine reagents screening

3.2 General Procedure



A sealed tube was charged with **2** (0.15 mmol, 1.5 equiv), **3** (0.2 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (3.2 mg, 0.01 mmol, 10 mol%), **L1** (13.2 mg, 0.02 mmol, 20 mol%), 5 Å MS (50.0 mg), the vial was thoroughly flushed with Ar, **1** (0.1 mmol, 1.0 equiv) and MeCN (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 10 ℃ for 4 d. The reaction mixture was diluted with EA (2.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel to afford products **4**.



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ^4-sulfaneylidene)pivalamide (4a)

35.2 mg, 86% yield, 96% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +87.1 (*c* = 0.071, $CHCl_3$).

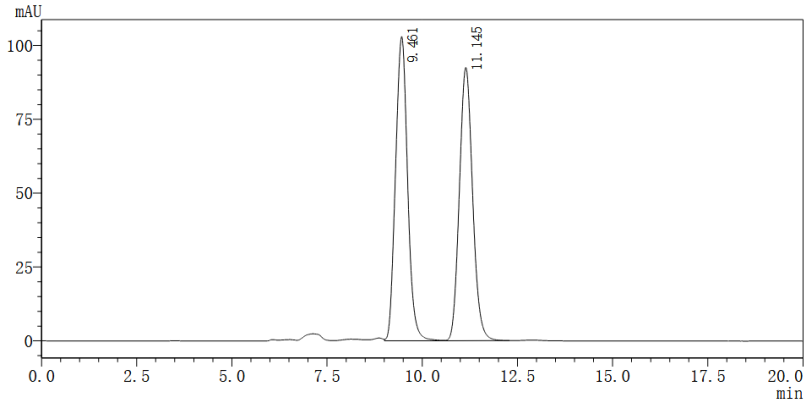
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.43 (m,3H), 7.39 – 7.32 (m, 2H), 7.00 – 6.95 (m, 2H), 6.82 – 6.69 (m, 3H), 3.80 (s, 3H), 1.31 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 161.2, 150.2 (q, $^3J_{C\text{-}F}$ =5.4 Hz), 132.5, 130.8 (q, $^4J_{C\text{-}F}$ = 1.6 Hz) 129.6, 128.4,122.2 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.5, 120.0 (q, $^2J_{C\text{-}F}$ = 35.7 Hz), 114.0, 55.4, 40.6, 28.7 ppm.

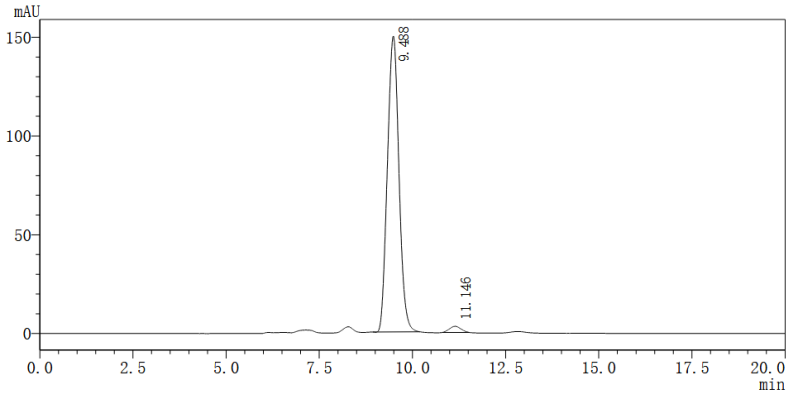
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.02 ppm.

HRMS (ESI) calcd for $[C_{21}H_{22}F_3NO_2S + H]^+$ 410.1396, found 410.1396.

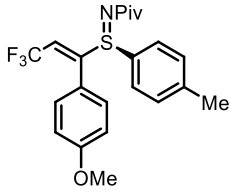
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 9.5 min (major), t_{R2} = 11.1 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.461	102989	0.586	2276501	50.357
2	11.145	92499	0.638	2244199	49.643



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.488	149780	0.579	3236120	97.977
2	11.146	3089	0.596	66817	2.023



N-((S)-p-tolyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4b)

33.5 mg,79% yield, 95% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +85.7 (*c* = 0.07, $CHCl_3$).

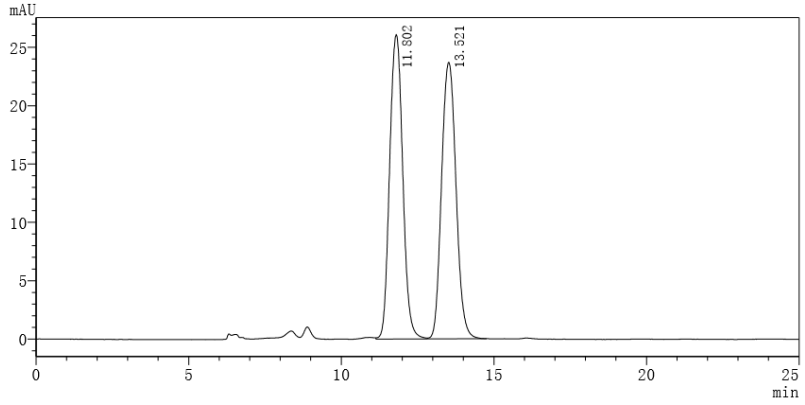
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.17 – 7.14 (m, 2H), 7.00 – 6.98 (m, 2H), 6.81 – 6.79 (m, 2H), 6.71 (q, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 2.35 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 161.2, 150.2 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 143.3, 130.7 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 130.3, 129.0, 128.4, 122.3 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 121.6, 119.7 (q, $^2J_{C\text{-}F}$ = 35.6 Hz), 114.0, 55.4, 40.6, 28.7, 21.6 ppm.

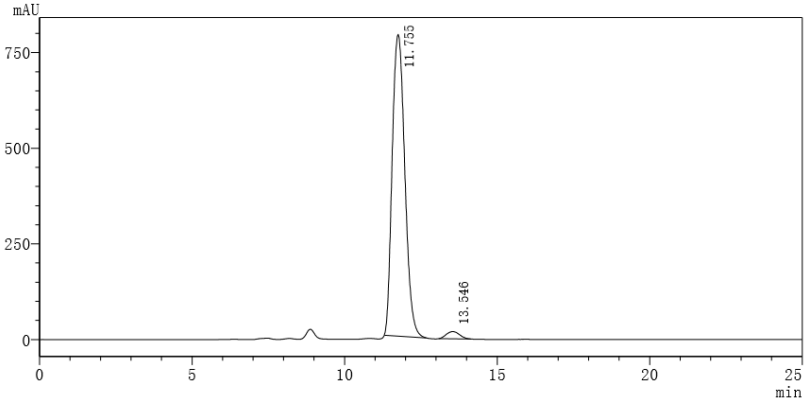
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.97 ppm.

HRMS (ESI) calcd for $[C_{21}H_{24}F_3NO_2S+H]^+$ 424.1553, found 424.1550.

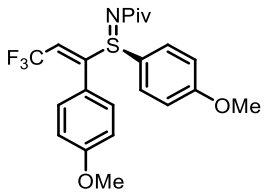
HPLC: Daicel Chiralpak OD-H, n-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 11.8 min (major), t_{R2} = 13.5 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.802	26085	0.770	778544	49.939
2	13.521	23695	0.853	780447	50.061



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.755	787875	0.748	22684908	97.545
2	13.546	18793	0.810	570955	2.455



N-((S)-(4-methoxyphenyl)((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4c)

31.4 mg,72% yield, 96% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +89.5 (*c* = 0.084, $CHCl_3$).

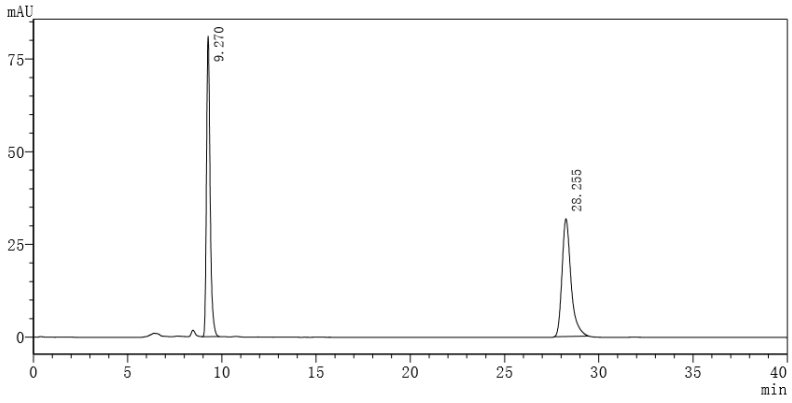
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.00 – 6.96 (m, 2H), 6.88 – 6.84 (m, 2H), 6.82 – 6.79 (m, 2H), 6.70 (q, *J* = 7.6 Hz, 1H), 4.10 – 3.51 (m, 6H), 1.29 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.4, 162.9, 161.1, 150.3 (q, $^3J_{C\text{-}F}$ = 5.2 Hz),130.8 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 130.5, 122.7, 122.3 (q, $^1J_{C\text{-}F}$ = 271.0 Hz),121.7,119.6 (q, $^2J_{C\text{-}F}$ = 35.6 Hz), 115.1, 114.0, 55.7, 55.3, 40.6, 28.7 ppm.

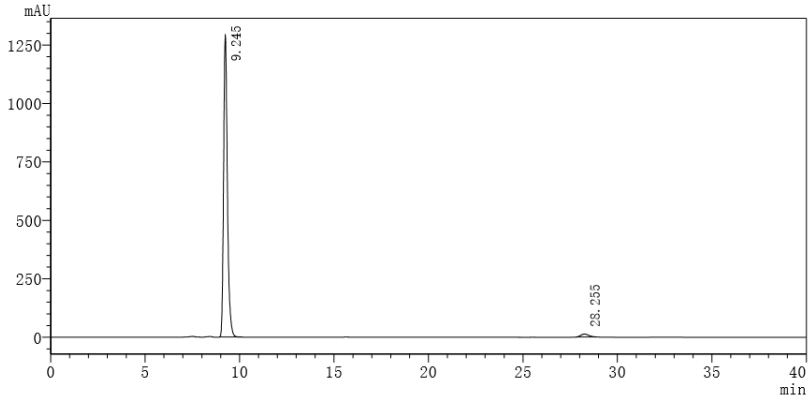
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.95 ppm.

HRMS (ESI) calcd for $[C_{21}H_{24}F_3NO_3S+H]^+$ 440.1502, found 440.1507.

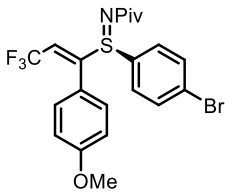
HPLC: Daicel Chiralpak IA-3, n-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 9.2 min (major), t_{R2} = 28.2 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.270	81044	0.345	1082837	50.761
2	28.255	31734	0.828	1050356	49.239



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.245	1291412	0.362	18076446	98.008
2	28.255	12473	0.794	367449	1.992



N-((S)-(4-bromophenyl)((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4d)

41.9 mg, 86% yield, 97% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +97.9 (*c* = 0.098, $CHCl_3$).

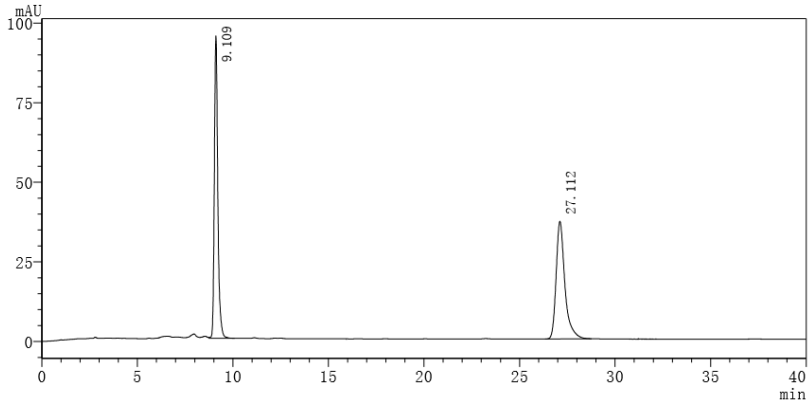
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.32 – 7.28 (m, 2H), 7.03 – 6.99 (m, 2H), 6.86 – 6.81 (m, 2H), 6.73 (q, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 161.4, 149.7 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 132.9, 131.8, 130.8 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 129.7, 127.4, 122.1 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.2, 120.3 (q, $^2J_{C\text{-}F}$ = 35.9 Hz), 114.2, 55.5, 40.7, 28.6 ppm.

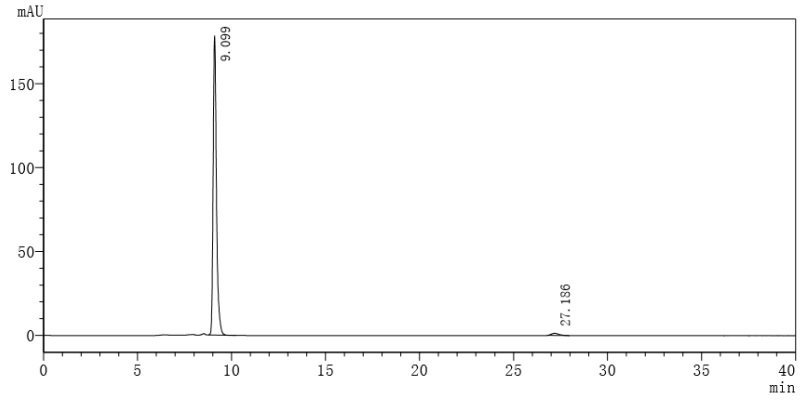
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.05 ppm.

HRMS (ESI) calcd for $[C_{21}H_{21}BrF_3NO_2S+H]^+$ 488.0502, found 488.0504.

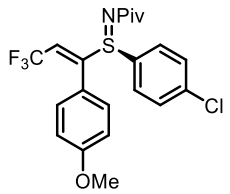
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 9.1 min (major), t_{R2} = 27.2 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.109	95084	0.322	1197331	50.443
2	27.112	36931	0.785	1176300	49.557



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.099	178354	0.315	2184625	98.506
2	27.186	1231	0.708	33125	1.494



N-((S)-(4-chlorophenyl)((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4e)

35.1 mg,79% yield, 97% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +82.2 (*c* = 0.062, $CHCl_3$).

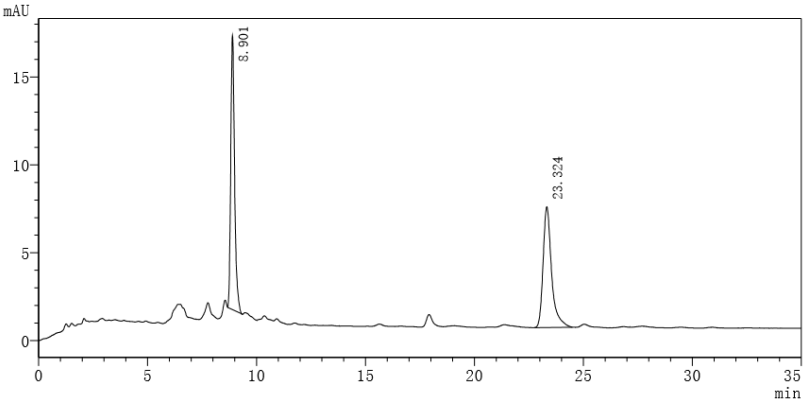
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.03 – 6.98 (m, 2H), 6.86 – 6.81 (m, 2H), 6.73 (q, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 161.4, 149.8 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 139.0, 131.1, 130.8 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 129.9, 129.6, 122.1 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.2, 120.3 (q, $^2J_{C\text{-}F}$ = 35.8 Hz), 114.2, 55.4, 40.6, 28.6 ppm.

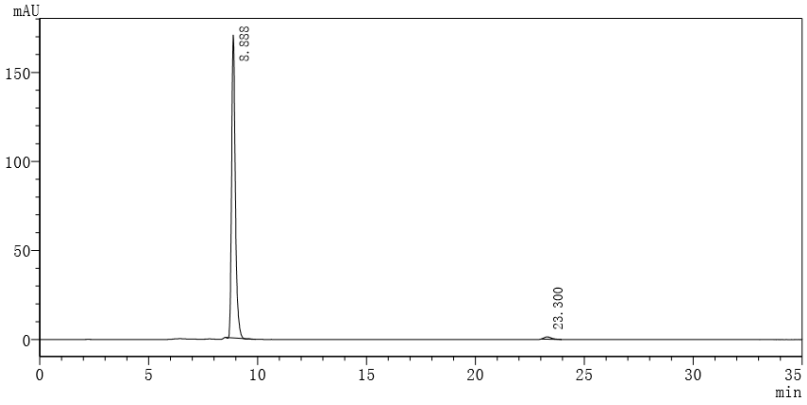
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.05 ppm.

HRMS (ESI) calcd for $[C_{21}H_{21}ClF_3NO_2S+H]^+$ 444.1007, found 444.1014.

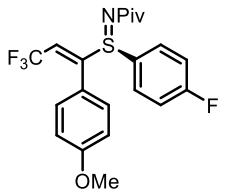
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 8.9 min (major), t_{R2} = 23.3 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.901	15593	0.317	189569	50.442
2	23.324	6867	0.667	186249	49.558



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.888	169864	0.308	2013170	98.686
2	23.300	1244	0.583	26803	1.314



N-((S)-(4-fluorophenyl)((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4f)

31.2 mg,73% yield, 96% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +120.7 (*c* = 0.082, $CHCl_3$).

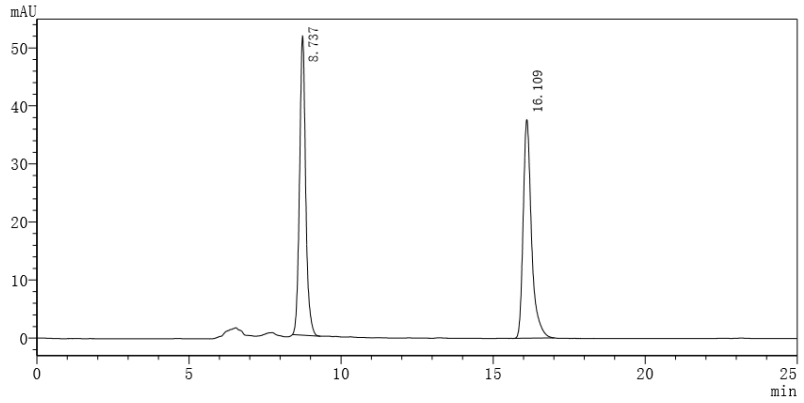
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.09 – 7.03 (m, 2H), 7.00 – 6.97 (m, 2H), 6.84 – 6.69 (m, 2H), 6.73 (q, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 165.1 (d, $^1J_{C\text{-}F}$ = 253.1 Hz), 161.4, 150.0 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 130.78 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 130.76 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 128.0 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 122.2 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.3, 120.2 (q, $^2J_{C\text{-}F}$ = 35.8 Hz), 117.1 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 114.2, 55.4, 40.6, 28.6 ppm.

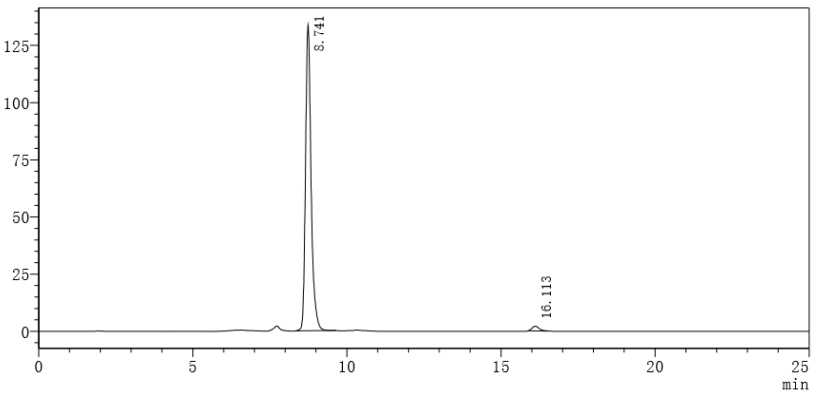
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.05 (3F), -105.38 (1F) ppm.

HRMS (ESI) calcd for $[C_{21}H_{21}F_4NO_2S+H]^+$ 428.1302, found 428.1304.

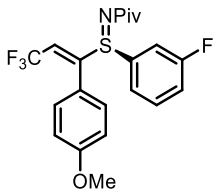
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 8.7 min (major), t_{R2} = 16.1 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.737	51530	0.360	720836	50.156
2	16.109	37657	0.473	716351	49.844



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.741	133693	0.323	1687841	98.100
2	16.113	2027	0.431	32684	1.900



N-((S)-(3-fluorophenyl)((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4g)

32.1 mg, 75% yield, 94% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +29.0 (*c* = 0.062, $CHCl_3$).

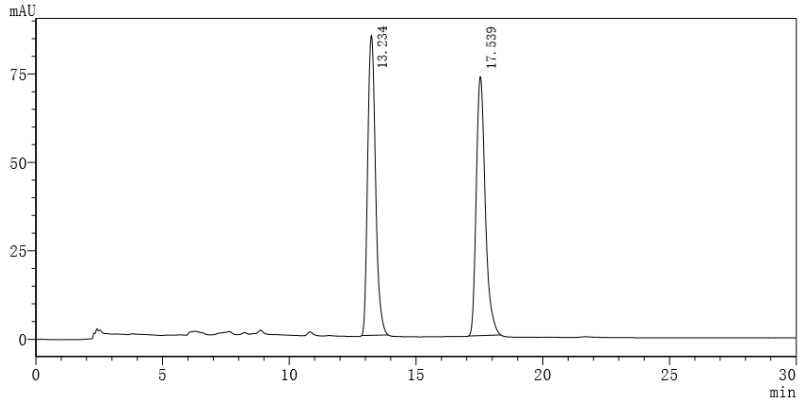
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 2H), 7.20 – 7.10 (m, 2H), 7.04 – 6.99 (m, 2H), 6.86 – 6.81 (m, 2H), 6.74 (q, *J* = 7.5 Hz, 1H) 3.81 (s, 3H), 1.31 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 162.8 (d, $^1J_{C\text{-}F}$ = 251.0 Hz), 149.8 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 134.8 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 131.0 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 130.8 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 124.2 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 122.1 (q, $^1J_{C\text{-}F}$ = 270.9 Hz), 121.2, 120.5 (q, $^2J_{C\text{-}F}$ = 35.9 Hz), 119.8 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 24.6 Hz), 114.2, 55.5, 40.7, 28.6 ppm.

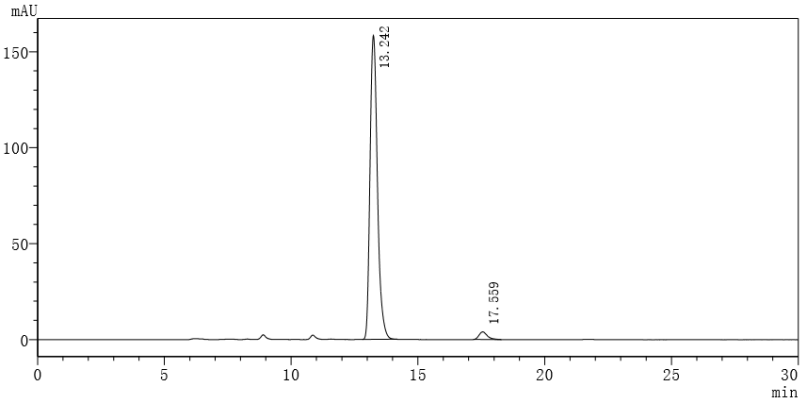
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.09 (3F), -108.57 (1F) ppm.

HRMS (ESI) calcd for $[C_{21}H_{21}F_4NO_2S+H]^+$ 428.1302, found 428.1309.

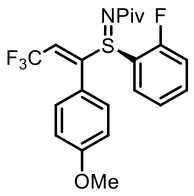
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 13.2 min (major), t_{R2} = 17.6 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	13.234	84765	0.553	1833152	50.316
2	17.539	73238	0.631	1810095	49.684



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	13.242	158428	0.520	3225582	97.273
2	17.559	3973	0.585	90432	2.727



N-((S)-(2-fluorophenyl)((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4h)

35.0 mg, 82% yield, 96% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +112.5 (*c* = 0.064, $CHCl_3$).

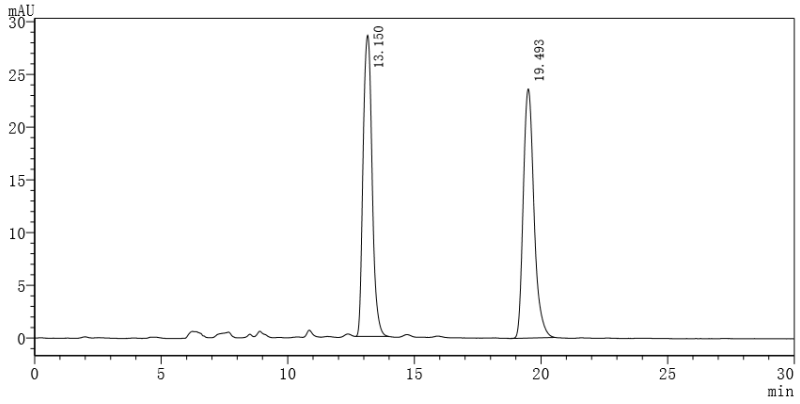
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 1H), 7.50 – 7.42 (m, 1H), 7.28 – 7.23 (m, 1H), 7.04 – 6.94 (m, 3H), 6.83 – 6.75 (m, 3H), 3.79 (s, 3H), 1.28 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 160.7 (d, $^1J_{C\text{-}F}$ = 252.7 Hz), 161.3, 149.3 (q, $^3J_{C\text{-}F}$ = 4.6 Hz), 134.5 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 130.7 (q, $^4J_{C\text{-}F}$ = 1.2 Hz), 129.4, 125.7 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 122.1 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 122.0 (q, $^1J_{C\text{-}F}$ =270.9 Hz), 120.4 (d, $^3J_{C\text{-}F}$ = 10.2 Hz), 120.3 (d, $^2J_{C\text{-}F}$ = 24.9 Hz), 116.5 (d, $^2J_{C\text{-}F}$ = 20.4 Hz), 113.7, 55.4, 40.6, 28.6 ppm.

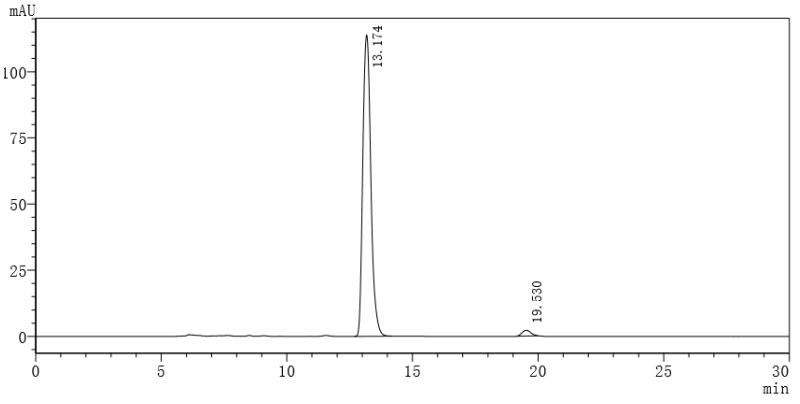
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.23 (3F), -109.96 (1F) ppm.

HRMS (ESI) calcd for $[C_{21}H_{21}F_4NO_2S+H]^+$ 428.1302, found 428.1305.

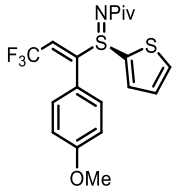
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 13.2 min (major), t_{R2} = 19.5 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	13.150	28560	0.620	707371	50.355
2	19.493	23626	0.746	697400	49.645



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	13.174	113815	0.562	2535736	97.990
2	19.530	2162	0.643	52002	2.010



N-((S)-thiophen-2-yl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4i)

34.0 mg, 82% yield, 96% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +44.3 (*c* = 0.07, $CHCl_3$).

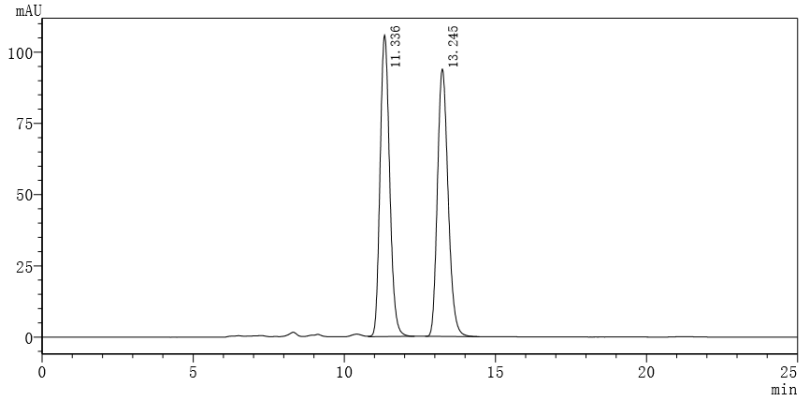
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 1H), 7.11 – 7.02 (m, 3H), 6.94 – 6.84 (m, 1H), 6.86 – 6.84 (m, 2H), 6.60 (q, *J* = 7.4 Hz, 1H), 3.82 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 161.4, 151.0 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 133.8, 133.4, 132.1, 130.8 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 127.5, 122.2 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.1, 119.0 (q, $^2J_{C\text{-}F}$ = 35.9 Hz), 114.1, 55.4, 40.6, 28.6 ppm.

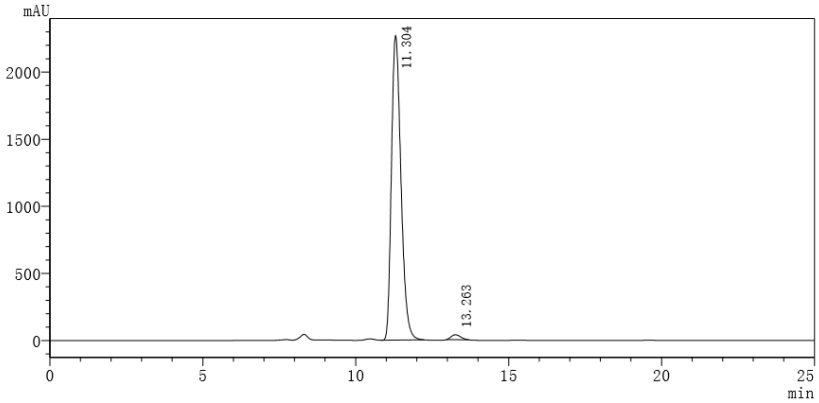
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.19 ppm.

HRMS (ESI) calcd for $[C_{19}H_{20}F_3NO_2S_2+H]^+$ 416.0960, found 416.0958.

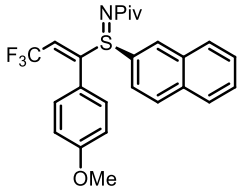
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 11.3 min (major), t_{R2} = 13.3 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.336	105804	0.577	2331009	50.169
2	13.245	93885	0.646	2315265	49.831



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.304	2269050	0.570	49237277	98.385
2	13.263	36966	0.600	808334	1.615



N-((S)-naphthalen-2-yl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4j)

30.8 mg, 67% yield, 96% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +100.0 (*c* = 0.098, $CHCl_3$).

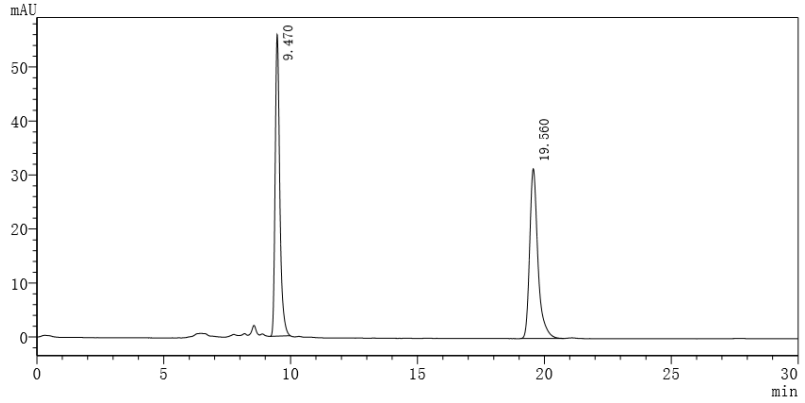
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 3H), 7.77 – 7.74 (m, 1H), 7.62 – 7.50 (m, 3H), 7.02 – 6.97 (m, 2H), 6.85 – 6.73 (m, 3H), 3.75 (s, 3H), 1.32 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 161.2, 149.9 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 134.9, 132.6, 130.8 (q, $^4J_{C\text{-}F}$ =1.4 Hz), 130.5, 130.1, 129.1, 128.8, 128.1, 127.6, 122.8, 122.3 (q, $^1J_{C\text{-}F}$ = 269.8 Hz) 121.5, 120.2 (q, $^2J_{C\text{-}F}$ = 35.5 Hz), 114.0, 55.4, 40.7, 28.7 ppm.

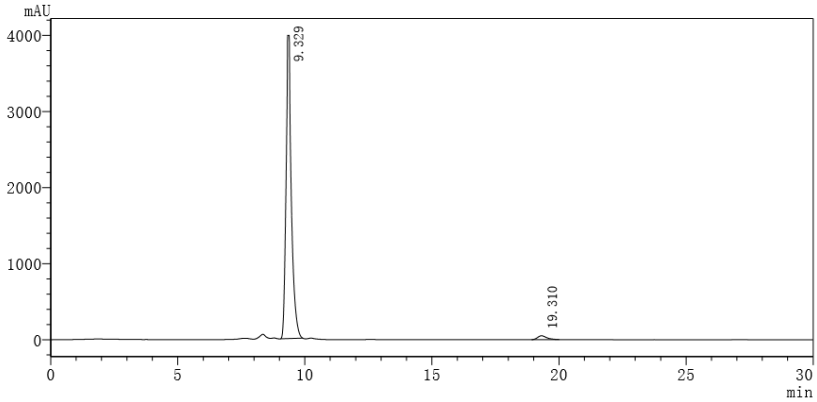
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.94 ppm.

HRMS (ESI) calcd for $[C_{25}H_{24}F_3NO_2S+H]^+$ 460.1553, found 460.1556.

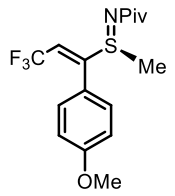
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 9.3 min (major), t_{R2} = 19.3 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.470	55843	0.327	708883	50.023
2	19.560	31435	0.560	708243	49.977



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.329	3984898	0.316	58016542	97.895
2	19.310	50231	0.642	1247279	2.105



N-((S)-methyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4k)

26.4 mg, 76% yield, 95% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +121.0 (*c* = 0.076, $CHCl_3$).

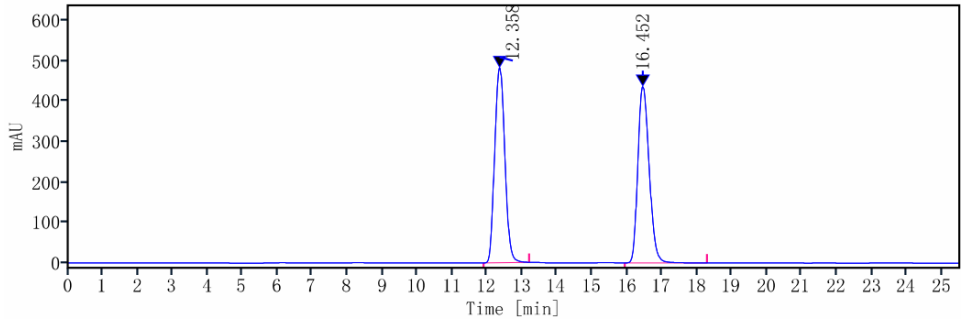
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.00 – 6.95 (m, 2H), 6.44 (q, *J* = 7.6 Hz, 1H), 3.85 (s, 3H), 2.48 (s, 3H), 1.27 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 161.7, 149.2 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 130.4 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 122.1 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.4, 120.1 (q, $^2J_{C\text{-}F}$ = 35.8 Hz), 114.7, 55.5, 40.3, 30.6, 28.6 ppm.

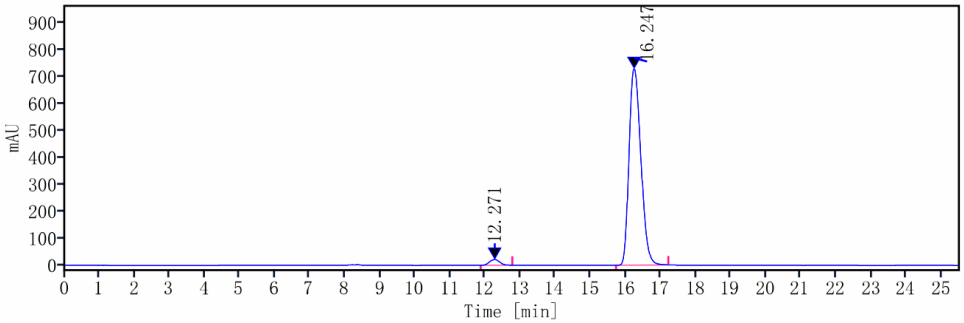
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.07 ppm.

HRMS (ESI) calcd for $[C_{16}H_{20}F_3NO_2S + H]^+$ 348.1240, found 348.1243

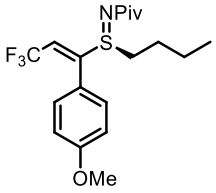
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 12.3 min (minor), t_{R2} = 16.2 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.358	BB	1.3042	9764.1870	481.7695	49.8570
16.452	BB	2.3533	9820.2127	435.8034	50.1430



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.271	VM m	0.3253	432.3033	21.2575	2.4620
16.247	VM m	0.3693	17126.8632	731.1185	97.5380



N-((S)-butyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4l)

35.2 mg, 87% yield, 99% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +54.7 (*c* = 0.064, $CHCl_3$).

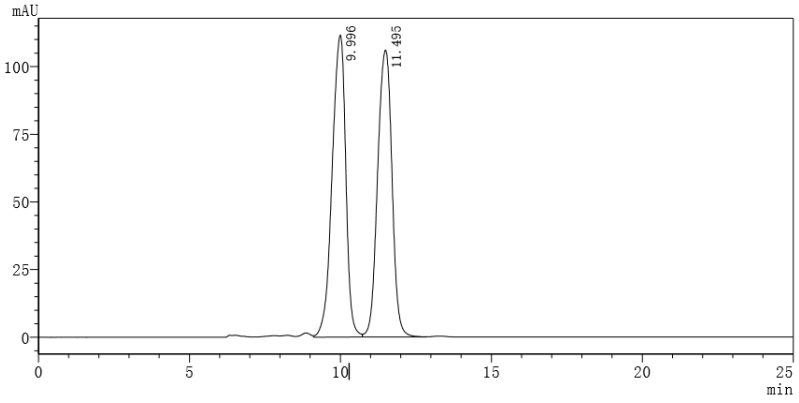
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.00 – 6.95 (m, 2H), 6.39 (q, *J* = 7.7 Hz, 1H), 3.85 (s, 3H), 2.81 – 2.71 (m, 1H), 2.67 – 2.58 (m, 1H), 1.72 – 1.47 (m, 2H), 1.41 – 1.25 (m, 11H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 161.6, 147.7 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 130.3 (q, $^4J_{C\text{-}F}$ = 1.8 Hz), 122.2 (q, $^1J_{C\text{-}F}$ =270.5 Hz), 121.7, 120.6 (q, $^2J_{C\text{-}F}$ = 35.8 Hz), 114.7, 55.5, 44.3, 40.6, 28.7, 24.7, 21.5, 13.6 ppm.

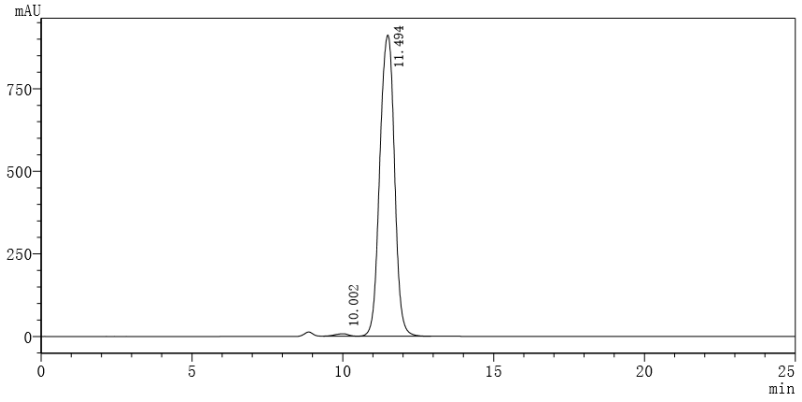
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.89 ppm.

HRMS (ESI) calcd for $[C_{19}H_{26}F_3NO_2S+H]^+$ 390.1709, found 390.1705.

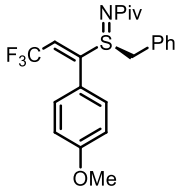
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 10.0 min (minor), t_{R2} = 11.5 min (major).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.996	111548	0.805	3500641	49.938
2	11.495	106029	0.841	3509329	50.062



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.002	6988	0.785	206231	0.663
2	11.494	911463	0.859	30876868	99.337



N-((S)-benzyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4m)

36.8 mg, 87% yield, 96% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +137.8 (*c* = 0.074, $CHCl_3$).

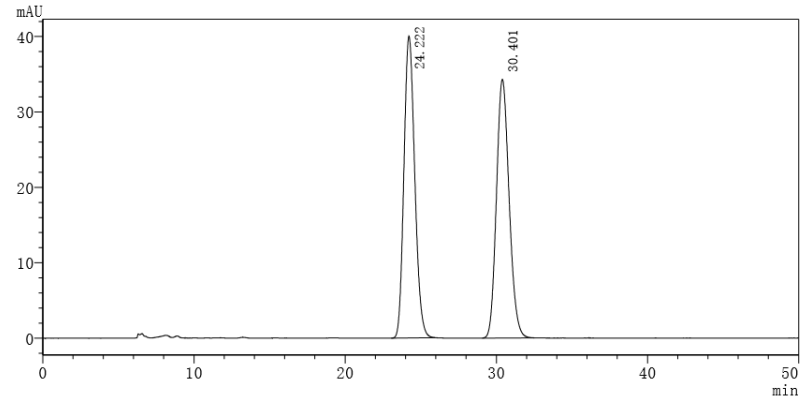
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.34 – 7.28 (m, 3H), 7.15 – 7.12 (m, 2H), 7.02 – 6.97 (m, 2H), 6.18 (q, *J* = 7.9 Hz, 1H), 4.18 (d, *J* = 12.8 Hz, 1H), 3.87 (s, 3H), 3.81 (d, *J* = 12.8 Hz, 1H), 1.23 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 161.8, 146.1 (q, $^3J_{C\text{-}F}$ = 5.5 Hz), 131.1, 130.7 (q, $^4J_{C\text{-}F}$ = 1.9 Hz), 129.2, 128.4, 128.1, 121.9, 121.7 (q, $^2J_{C\text{-}F}$ = 35.5 Hz), 122.1 (q, $^1J_{C\text{-}F}$ = 270.5 Hz), 114.7, 55.6, 50.0, 40.5, 28.6 ppm.

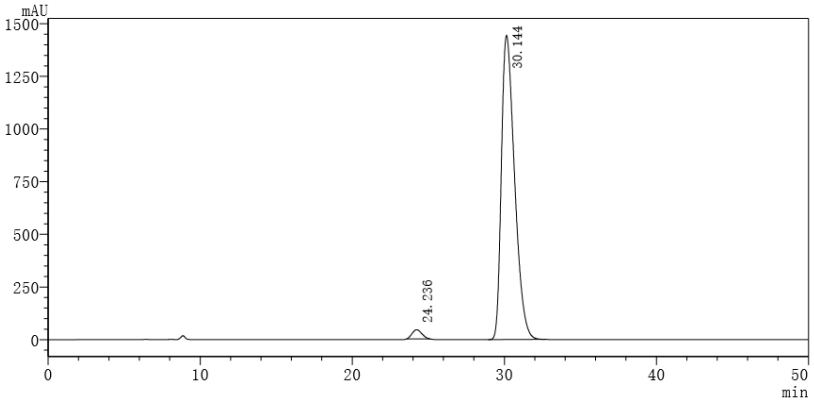
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.06 ppm.

HRMS (ESI) calcd for $[C_{22}H_{24}F_3NO_2S+H]^+$ 424.1553, found 424.1558.

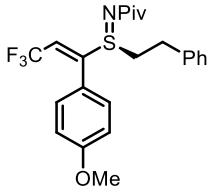
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 24.2 min (minor), t_{R2} = 30.1 min (major).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	24.222	40026	1.311	1992339	49.911
2	30.401	34302	1.537	1999407	50.089



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	24.236	43652	1.221	1955004	2.199
2	30.144	1444161	1.588	86956083	97.801



N-((S)-phenethyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4n)

37.5 mg, 86% yield, 99% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +28.1 (*c* = 0.11, $CHCl_3$).

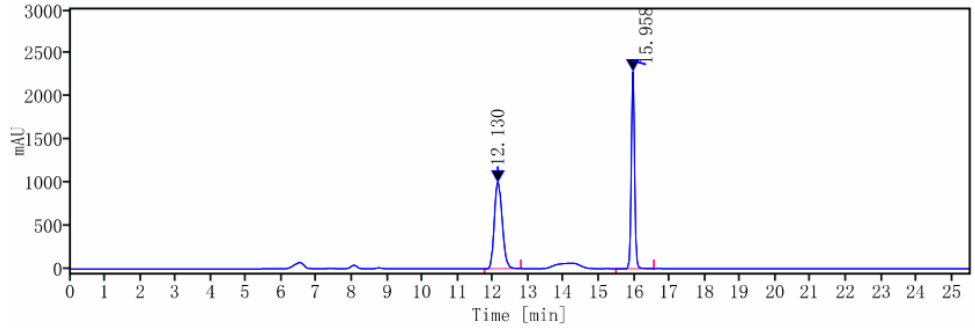
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.18 (m, 5H), 7.07 – 7.04 (m, 2H), 6.97 – 6.94 (m, 2H), 6.44 (q, *J* = 7.7 Hz, 1H), 3.84 (s, 3H), 3.09 – 2.80 (m, 4H), 1.32 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 161.7, 147.2 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 137.7, 130.2 (q, $^4J_{C\text{-}F}$ = 1.9 Hz), 128.9, 128.7, 127.2, 122.2 (q, $^1J_{C\text{-}F}$ = 270.6 Hz), 121.5, 121.0 (q, $^2J_{C\text{-}F}$ = 35.9 Hz), 114.7, 55.5, 45.3, 40.6, 28.8, 28.7 ppm.

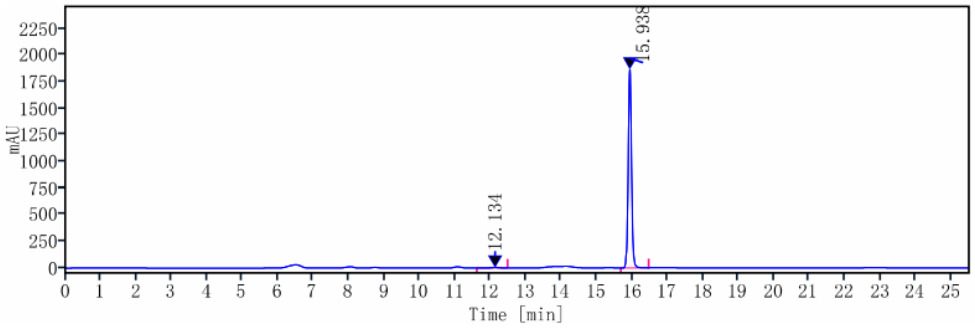
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.82 ppm.

HRMS (ESI) calcd for $[C_{23}H_{26}F_3NO_2S + H]^+$ 438.1709, found 438.1713.

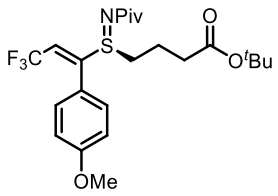
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 12.1 min (minor), t_{R2} = 15.9 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.130	VM m	0.2469	15697.7916	1001.0533	50.4451
15.958	MV m	0.1045	15420.7782	2292.5607	49.5549



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.134	BB	0.8681	94.4079	5.5959	0.7495
15.938	BV	0.7859	12501.6557	1864.9413	99.2505



tert-butyl4-((S)-N-pivaloyl-S-((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)sulfinimidoyl)butanoate (4o)

30.9 mg, 65% yield, 98% ee, *E/Z* > 20/1, as a colorless oil.

$[\alpha]_{25}^{D}$ = +40.6 (*c* = 0.064, $CHCl_3$).

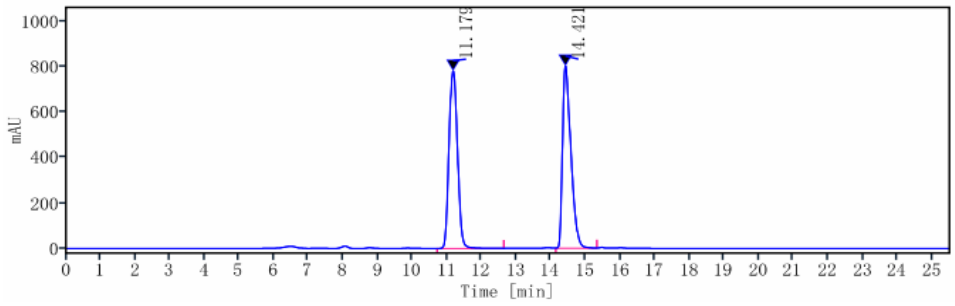
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.00 – 6.94 (m, 2H), 6.37 (q, *J* = 7.7 Hz, 1H), 3.85 (s, 3H), 2.87 – 2.77 (m, 1H), 2.74 – 2.65 (m, 1H), 2.38 – 2.20 (m, 2H), 2.03 – 1.81 (m, 2H), 1.38 (s, 9H), 1.28 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 171.3, 161.6, 147.5 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 130.3 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 122.1 (q, $^1J_{C\text{-}F}$ = 270.6 Hz), 121.5, 120.7 (q, $^2J_{C\text{-}F}$ = 35.9 Hz), 114.7, 81.0, 55.5, 43.5, 40.6, 33.5, 28.6, 28.1, 18.8 ppm.

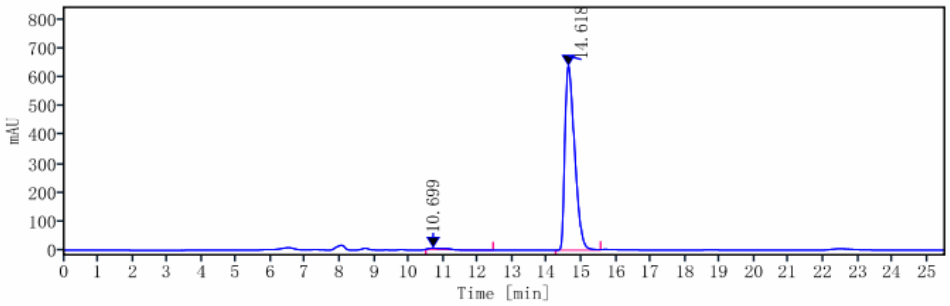
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.93 ppm.

HRMS (ESI) calcd for $[C_{23}H_{32}F_3NO_4S + H]^+$ 476.2077, found 476.2083.

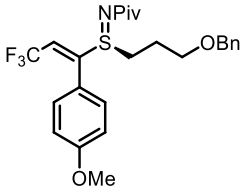
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 10.7 min (minor), t_{R2} = 14.6 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.179	BB	1.9289	13342.3950	780.8948	49.6650
14.421	VV	1.1840	13522.3737	802.2299	50.3350



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.699	MM m	0.3778	113.9194	4.5858	0.8987
14.618	BV	1.3016	12562.4469	638.6626	99.1013



N-((S)-(3-(benzyloxy)propyl)((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4p)

29.8 mg, 62% yield, 99% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +31.6 (*c* = 0.06, $CHCl_3$).

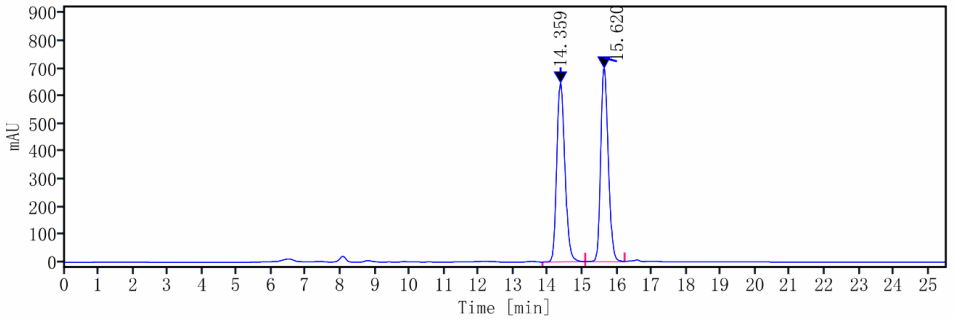
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 5H), 7.28 – 7.24 (m, 2H), 6.94 – 6.89 (m, 2H), 6.38 (q, *J* = 7.7 Hz, 1H), 4.44 – 4.36 (m, 2H), 3.82 (s, 3H), 3.57 – 3.44 (m, 2H), 3.00 – 2.91 (m, 1H), 2.77 – 2.68 (m, 1H), 2.04 – 1.83 (m, 2H), 1.28 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 161.6, 147.6 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 137.9, 130.3 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 128.5, 127.8, 127.7, 122.2 (q, $^1J_{C\text{-}F}$ =270.5 Hz), 121.5, 120.8 (q, $^2J_{C\text{-}F}$ = 35.8 Hz), 114.6, 73.0, 67.6, 55.4, 41.5, 40.5, 28.6, 23.4 ppm.

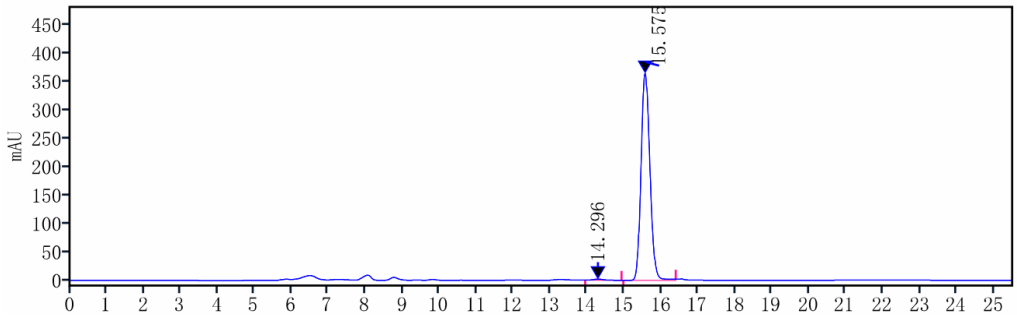
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.88 ppm.

HRMS (ESI) calcd for $[C_{25}H_{30}F_3NO_3S+H]^+$ 482.1971, found 482.1978.

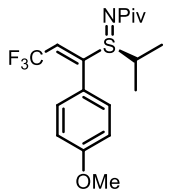
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 14.3 min (minor), t_{R2} = 15.6 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.359	BB	1.2388	10638.4227	646.0899	49.9767
15.620	BV	1.1372	10648.3312	699.1362	50.0233



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.296	BB	0.9800	43.3810	2.0904	0.7032
15.575	BV	1.4135	6125.3786	365.1566	99.2968



N-((S)-isopropyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4q)

24.7 mg, 66% yield, 99% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +48.6 (*c* = 0.07, $CHCl_3$).

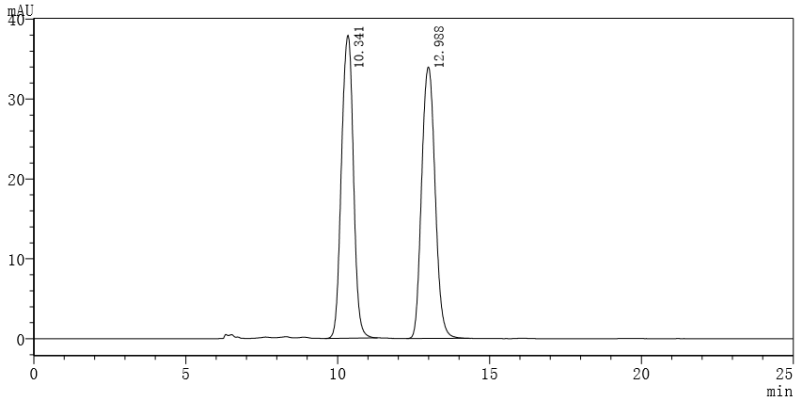
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 6.98 – 6.95 (m, 2H), 6.26 (q, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 2.88 – 2.79 (m, 1H), 1.29 – 1.27 (m, 12H), 1.20 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 161.6, 146.3 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 130.2 (q, $^4J_{C\text{-}F}$ = 1.9 Hz), 122.3 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 122.2, 121.3 (q, $^2J_{C\text{-}F}$ = 35.8 Hz), 114.7, 55.5, 46.1, 41.0, 28.7, 18.3, 14.4 ppm.

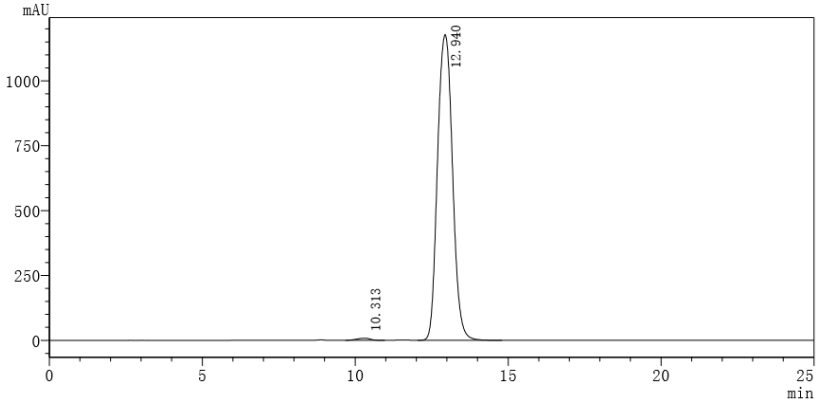
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.71 ppm.

HRMS (ESI) calcd for $[C_{18}H_{24}F_3NO_2S+H]^+$ 376.1553, found 376.1559.

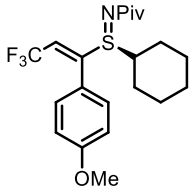
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 10.3 min (minor), t_{R2} = 12.9 min (major).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.341	37930	0.702	1040671	49.804
2	12.988	33987	0.795	1048856	50.196



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.313	7739	0.800	239163	0.592
2	12.940	1177453	0.869	40151946	99.408



N-((S)-cyclohexyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4r)

31.5 mg, 76% yield, 98% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +50.0 (*c* = 0.064, $CHCl_3$).

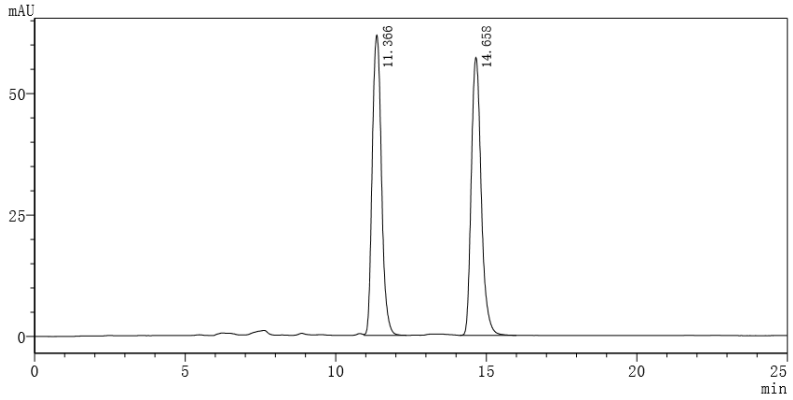
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 6.99 – 6.94 (m, 2H), 6.25 (q, *J* = 7.8 Hz, 1H), 3.86 (s, 3H), 2.61 – 2.51 (m, 1H), 1.86 – 1.49 (m, 7H), 1.28 (s, 9H), 1.18 – 1.10 (m, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.5, 161.6, 145.8 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 130.2 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 122.33, 122.28 (q, $^1J_{C\text{-}F}$ = 270.6 Hz), 121.4 (q, $^2J_{C\text{-}F}$ = 35.7 Hz) 114.7, 55.5, 54.0, 40.9, 28.7, 28.5, 26.0, 25.7, 25.2, 24.4 ppm.

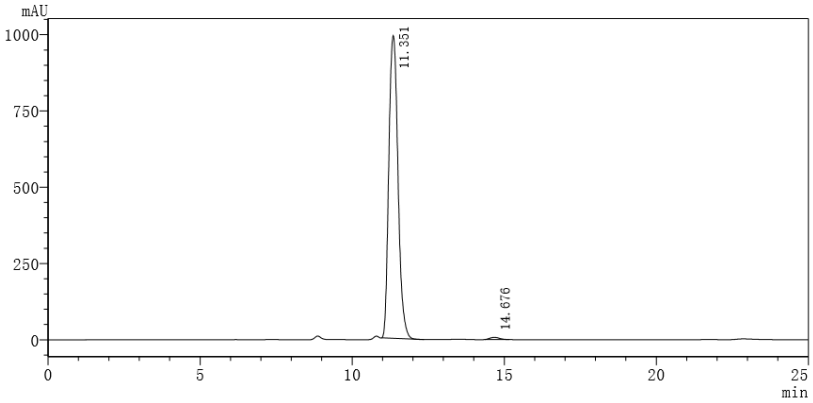
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.67 ppm.

HRMS (ESI) calcd for $[C_{21}H_{28}F_3NO_2S+H]^+$ 416.1866, found 416.1867.

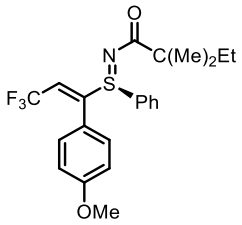
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 11.4 min (major), t_{R2} = 14.7 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.366	61816	0.542	1320316	50.096
2	14.658	57216	0.584	1315256	49.904



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.351	992336	0.536	20796329	99.249
2	14.676	7142	0.583	157419	0.751



2,2-dimethyl-N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)butanamide (4s)

34.3 mg, 81% yield, 96% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +108.1 (*c* = 0.086, $CHCl_3$).

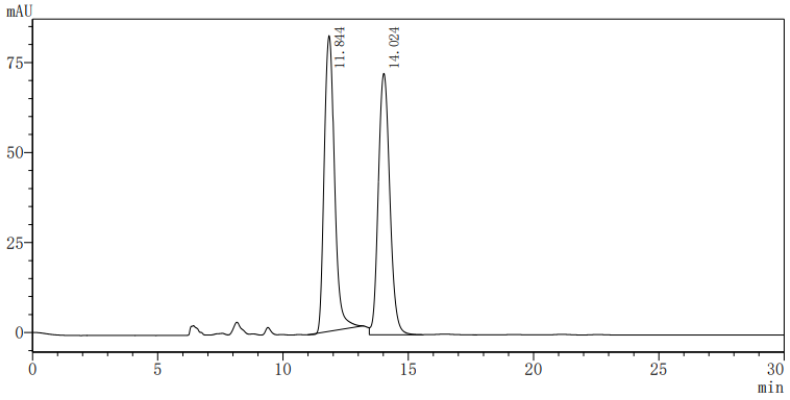
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 3H), 7.38 – 7.33 (m, 2H), 7.02 – 6.97 (m, 2H), 6.81 – 6.72 (m, 3H), 3.80 (s, 3H), 1.69 (q, *J* = 7.6 Hz, 2H), 1.26 – 1.25 (m, 6H), 0.88 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.0, 161.3, 150.2 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 132.7, 132.4, 130.8 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 129.6, 128.4, 122.3 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.59, 120.0 (q, $^4J_{C\text{-}F}$ = 35.7 Hz), 114.0, 55.4, 44.3, 34.5, 26.2, 26.0, 9.7 ppm.

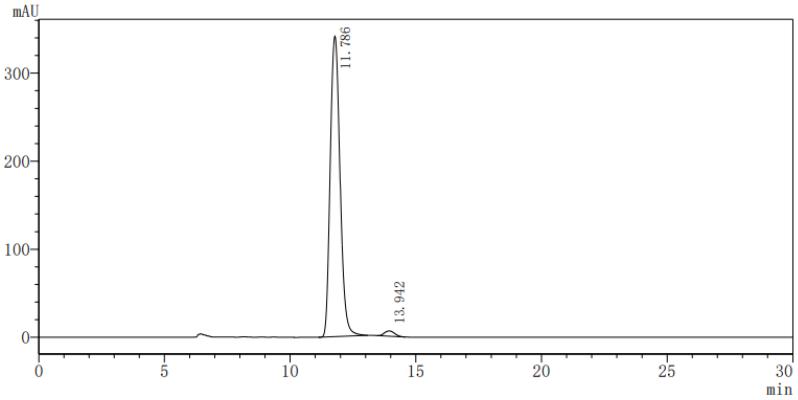
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.00 ppm.

HRMS (ESI) calcd for $[C_{22}H_{24}F_3NO_2S + H]^+$ 424.1553, found 424.1553.

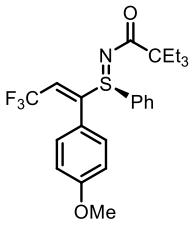
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 11.8 min (major), t_{R2} = 14.0 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.844	82081	0.717	2328621	50.107
2	14.024	72608	0.822	2318634	49.893



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.786	341232	0.693	9178682	98.219
2	13.942	5958	0.746	166459	1.781



2,2-diethyl-N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)butanamide (4t)

36.1 mg, 80% yield, 94% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +118.4 (*c* = 0.076, $CHCl_3$).

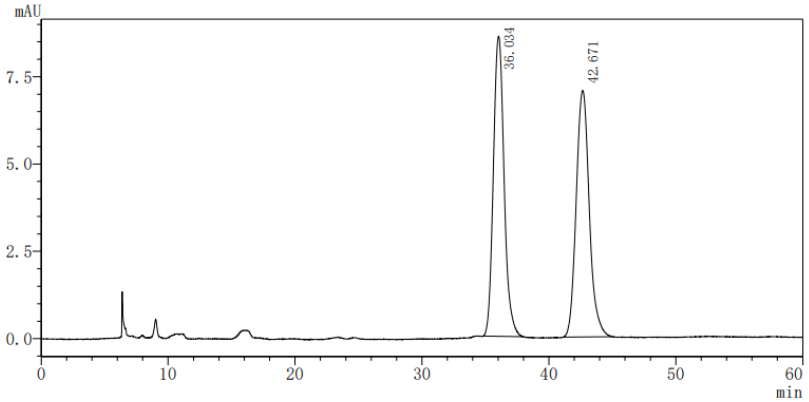
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 3H), 7.37 – 7.33 (m, 2H), 7.03 – 7.00 (m, 2H), 6.85 – 6.78 (m, 3H), 3.79 (s, 3H), 1.76 – 1.66 (m, 6H), 0.79 (t, *J* = 7.5 Hz, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1, 161.2, 150.3 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 133.2, 132.3, 130.8 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 129.5, 128.4, 122.3 (q, $^1J_{C\text{-}F}$ = 273.3 Hz), 121.7, 120.0 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 114.0, 55.4, 51.2, 27.2, 8.7 ppm.

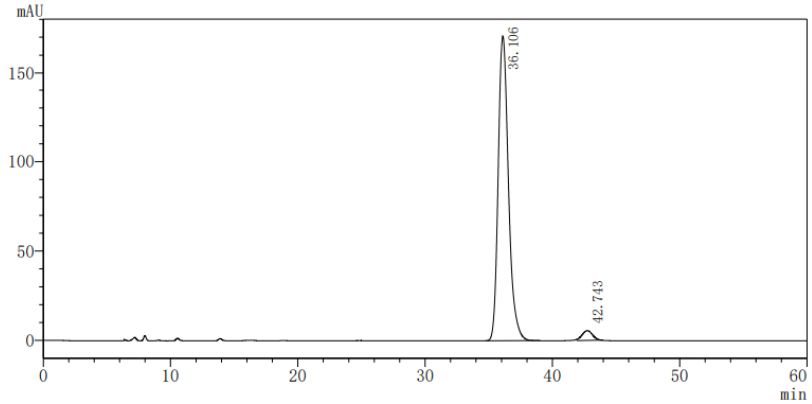
^{19}F NMR (376 MHz, $CDCl_3$) δ -56.93 ppm.

HRMS (ESI) calcd for $[C_{24}H_{28}F_3NO_2S + H]^+$ 452.1866, found 452.1864.

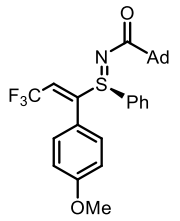
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 97/3, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 36.0 min (major), t_{R2} = 42.7 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	36.034	8595	1.483	501308	49.771
2	42.671	7049	1.811	505916	50.229



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	36.106	170797	1.409	9498897	96.816
2	42.743	5453	1.542	312354	3.184



(3S,5S,7S)-N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene) adamantane-1-carboxamide (4u)

35.6 mg, 73% yield, 94% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +45.8 (*c* = 0.07, $CHCl_3$).

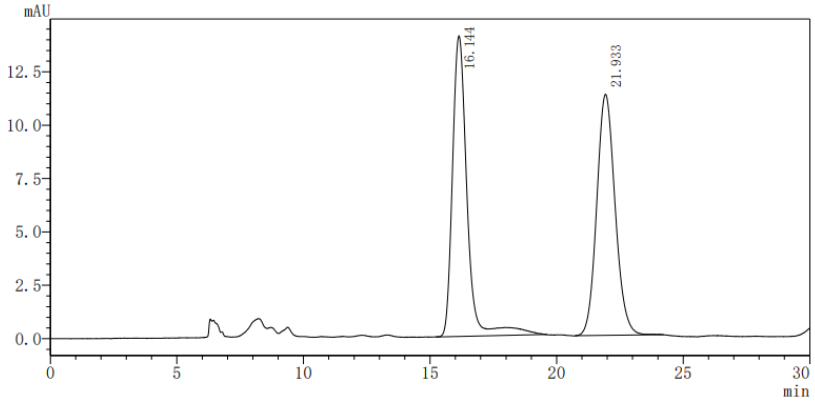
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 3H), 7.41 – 7.35 (m, 2H), 7.02 – 6.97 (m, 2H), 6.83 – 6.80 (m, 2H), 6.73 (q, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 2.04 (s, 9H), 1.77 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.8, 161.2, 150.2 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 132.5, 132.4, 130.8 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 129.6, 128.5, 122.3 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.6, 119.9 (q, $^2J_{C\text{-}F}$ = 35.7 Hz), 114.0, 55.4, 42.7, 40.4, 37.0, 28.7 ppm.

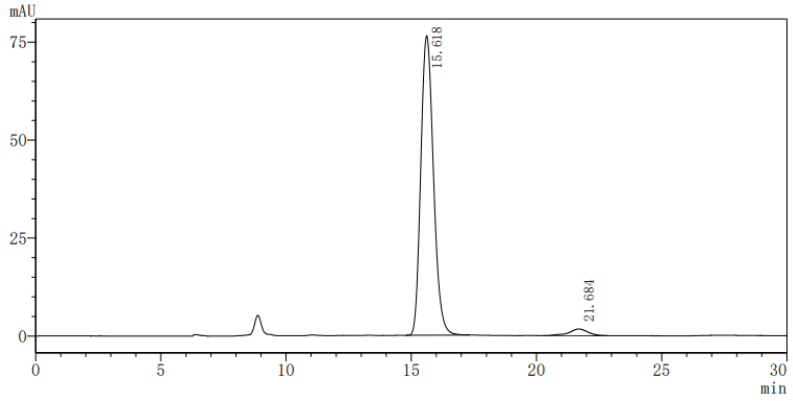
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.97 ppm.

HRMS (ESI) calcd for $[C_{27}H_{28}F_3NO_2S + H]^+$ 488.1866, found 488.1864.

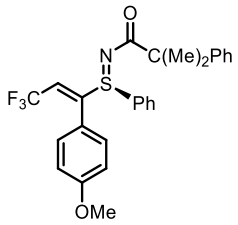
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 15.6 min (major), t_{R2} = 21.7 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	16.144	14073	0.980	566919	49.838
2	21.933	11288	1.322	570595	50.162



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	15.618	76434	0.921	2696435	96.805
2	21.684	1684	1.281	89004	3.195



2-methyl-2-phenyl-N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)propanamide (4v)

36.3 mg, 77% yield, 94% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +87.5 (*c* = 0.088, $CHCl_3$).

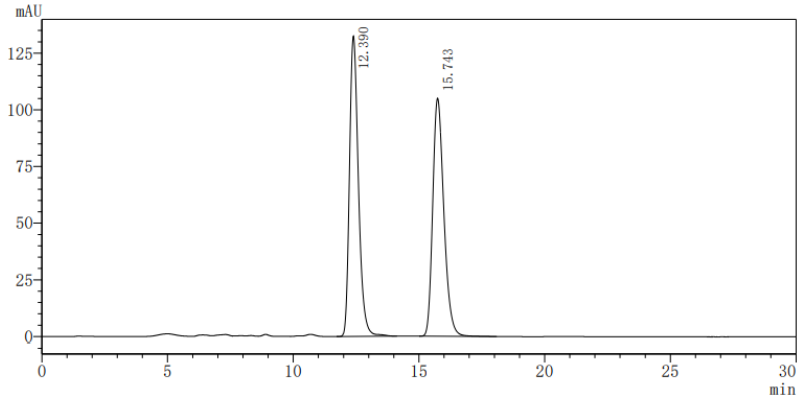
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.45 – 7.41 (m, 1H), 7.35 – 7.28 (m, 7H), 7.23 – 7.21 (m, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.40 (q, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 1.98 – 1.64 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.2, 161.2, 150.0 (q, $^3J_{C\text{-}F}$ = 5.4 Hz), 147.5, 132.5, 132.2, 130.8 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 129.5, 128.4, 128.2, 126.09, 126.06, 122.1 (q, $^1J_{C\text{-}F}$ = 270.9 Hz), 121.4, 120.1 (q, $^2J_{C\text{-}F}$ = 35.6 Hz), 114.0, 55.4, 48.2, 27.7, 27.3 ppm.

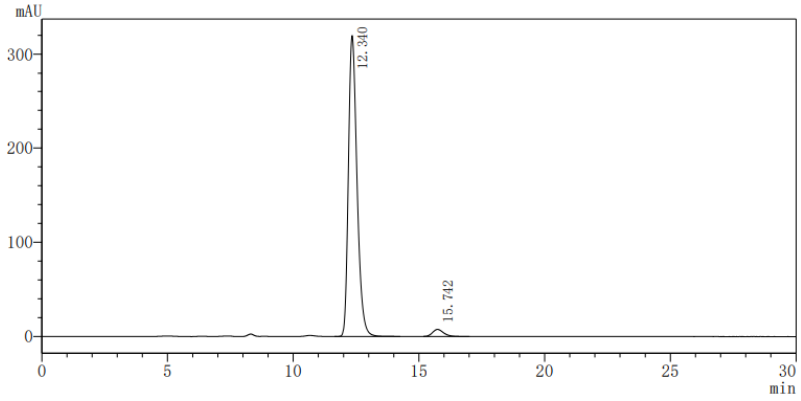
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.03 ppm.

HRMS (ESI) calcd for $[C_{26}H_{24}F_3NO_2S + H]^+$ 472.1553, found 472.1548.

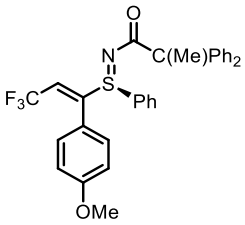
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 12.3 min (major), t_{R2} = 15.7 min (minor)



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	12.390	132467	0.639	3277219	50.272
2	15.743	105046	0.805	3241774	49.728



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	12.340	319473	0.620	7605983	97.077
2	15.742	7470	0.799	229008	2.923



2,2-diphenyl-N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)propanamide (4w)

39.5 mg, 74% yield, 95% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +76.9 (*c* = 0.078, $CHCl_3$).

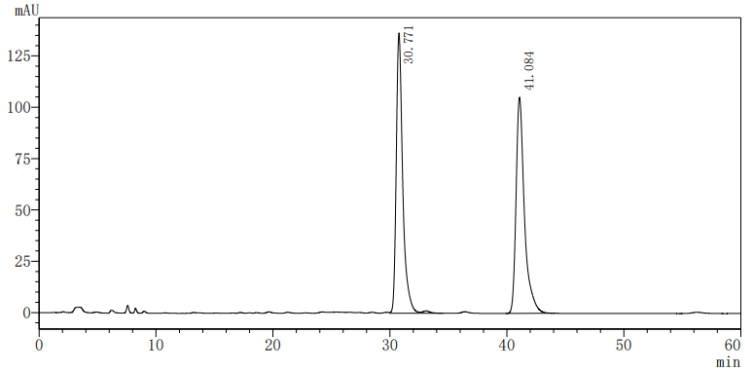
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 1H), 7.37 – 7.35 (m, 3H), 7.34 – 7.31 (m, 5H), 7.29 – 7.26 (m, 4H), 7.25 – 7.19 (m, 3H), 6.92 – 6.89 (m, 2H), 6.76 – 6.74 (m, 2H), 6.43 (q, *J* = 7.5 Hz, 1H), 3.77 (s, 3H), 2.05 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.1, 161.2, 149.5 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 147.3, 146.9, 132.5, 132.3, 130.8 (q, $^4J_{C\text{-}F}$ = 1.3 Hz), 129.6, 128.7, 128.5, 128.4, 127.8, 127.7, 126.2, 126.1, 122.0 (q, $^1J_{C\text{-}F}$ = 273.7 Hz), 121.3, 120.6 (q, $^2J_{C\text{-}F}$ = 35.9 Hz), 114.0, 58.4, 55.4, 28.3 ppm.

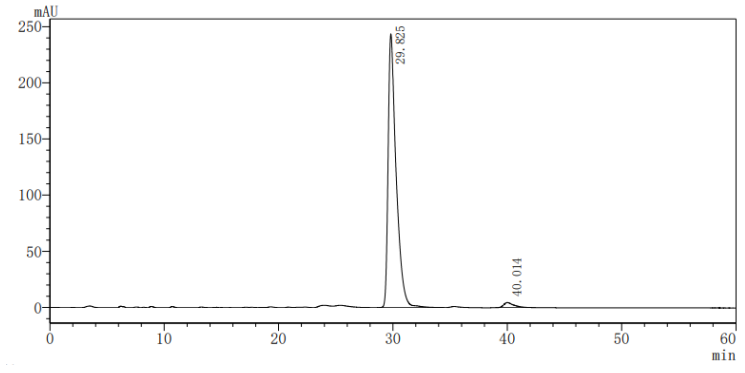
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.05 ppm.

HRMS (ESI) calcd for $[C_{31}H_{26}F_3NO_2S + H]^+$ 534.1709, found 534.1713.

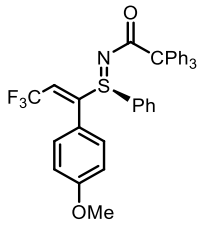
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 29.8 min (major), t_{R2} = 40.0 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	30.771	136316	0.945	5291819	50.224
2	41.084	105221	1.209	5244706	49.776



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	29.825	243473	1.189	11804749	97.621
2	40.014	4562	1.834	287721	2.379



2,2,2-triphenyl-N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)acetamide (4x)

44.1 mg, 75% yield, 94% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +104.8 (*c* = 0.062, $CHCl_3$).

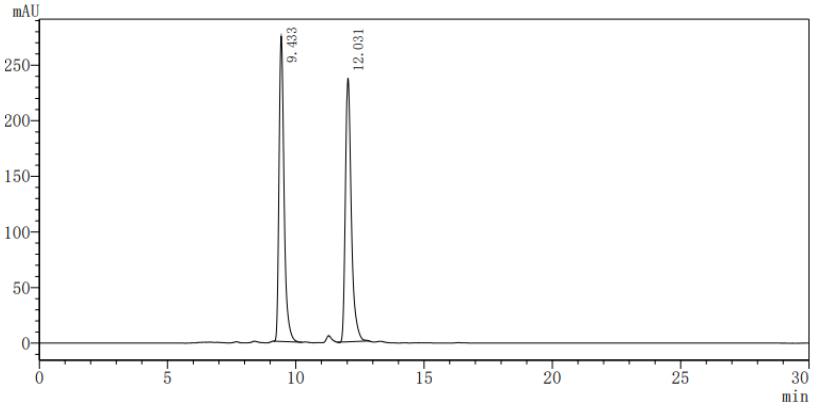
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 1H), 7.36 – 7.31 (m, 6H), 7.30 – 7.27 (m, 4H), 7.25 – 7.17 (m, 7H), 6.93 – 6.89 (m, 2H), 6.77 – 6.72 (m, 2H), 6.46 (q, *J* = 7.6 Hz, 1H), 3.77 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 184.2, 161.3, 149.0 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 145.3, 132.55, 132.49, 130.9, 130.8 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 129.6, 128.5, 127.3, 126.3, 122.0 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 121.32, 121.30 (q, $^2J_{C\text{-}F}$ = 35.3 Hz), 114.1, 69.5, 55.4 ppm.

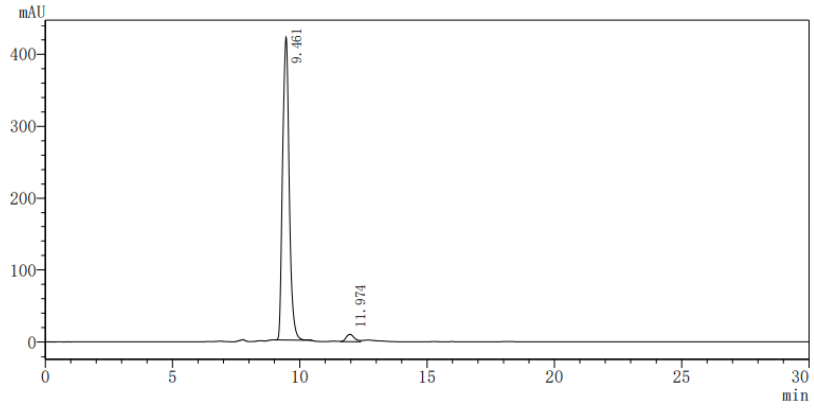
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.99 ppm.

HRMS (ESI) calcd for $[C_{36}H_{28}F_3NO_2S + H]^+$ 596.1866, found 596.1860.

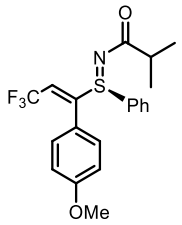
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 9.5 min (major), t_{R2} = 12.0 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.433	274456	0.350	3764764	50.253
2	12.031	236930	0.398	3726833	49.747



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.461	421317	0.469	7630285	97.135
2	11.974	10062	0.559	225059	2.865



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)isobutyramide (4y)

30.8 mg, 78% yield, 94% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +111.7 (*c* = 0.06, $CHCl_3$).

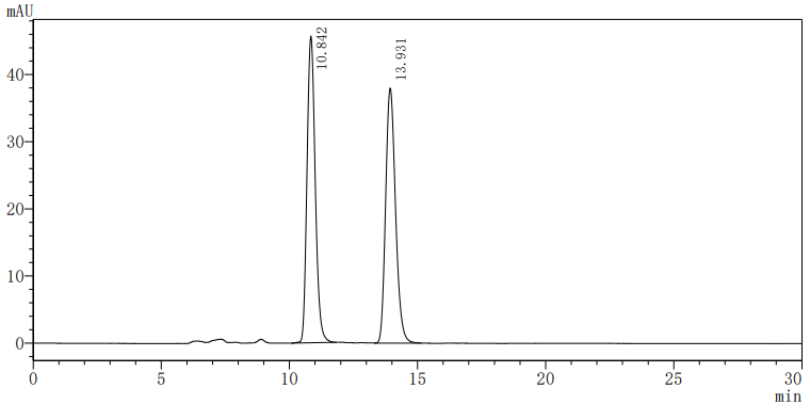
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.41 – 7.35 (m, 2H), 7.01 – 6.97 (m, 2H), 6.81 – 6.70 (m, 2H), 6.73 (q, *J* = 7.5 Hz, 1H), 3.79 (s, 3H), 2.82 – 2.75 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 161.3, 149.7 (q, $^3J_{C\text{-}F}$ = 5.3Hz), 132.7, 132.0,130.8 (q, $^4J_{C\text{-}F}$ = 1.6Hz), 129.8, 128.8, 122.2 (q, $^1J_{C\text{-}F}$ = 273.6Hz), 121.4, 120.1 (q, $^2J_{C\text{-}F}$ = 36.1Hz), 114.1, 55.4, 37.0, 20.8, 20.4 ppm.

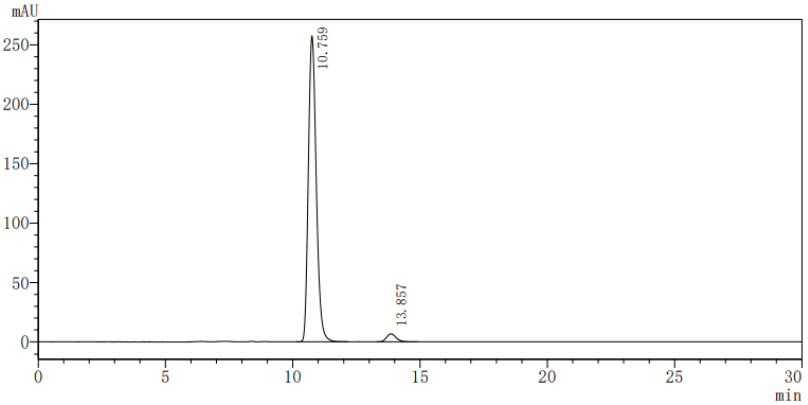
^{19}F NMR (376 MHz, $CDCl_3$) δ -56.98 ppm.

HRMS (ESI) calcd for $[C_{20}H_{20}F_3NO_2S + H]^+$ 396.1240, found 396.1238.

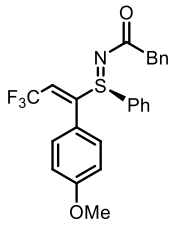
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 10.8 min (major), t_{R2} = 13.9 min (minor)



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.842	45600	0.583	1020418	50.038
2	13.931	37978	0.702	1018884	49.962



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.759	257048	0.565	5571080	96.933
2	13.857	6702	0.689	176281	3.067



2-phenyl-N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)acetamide (4z)

29.7 mg, 67% yield, 93% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +100.0 (*c* = 0.064, $CHCl_3$).

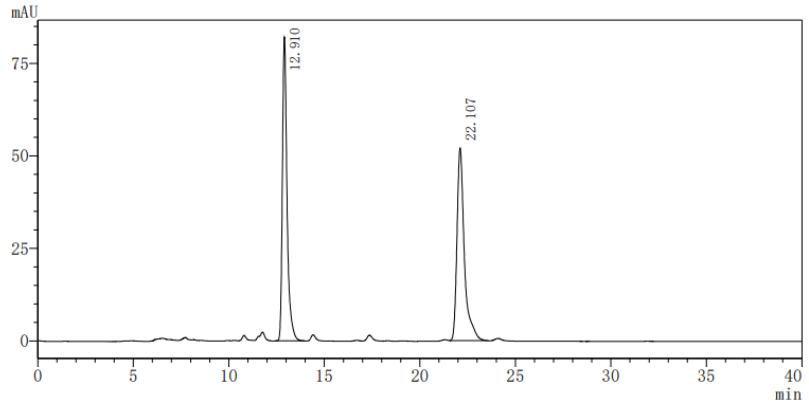
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 9H), 7.26 – 7.22 (m, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.58 (q, *J* = 7.5 Hz, 1H), 3.84 – 3.73 (m, 5H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 182.8, 161.2, 149.3 (q, $^3J_{C\text{-}F}$ = 5.3Hz), 137.4, 132.8, 131.7, 130.8 (q, $^4J_{C\text{-}F}$ = 1.4Hz), 129.8, 129.4, 128.8, 128.5, 126.5, 122.1 (q, $^1J_{C\text{-}F}$ = 273.6Hz), 121.1, 120.4 (q, $^2J_{C\text{-}F}$ = 36.1Hz), 118.0, 114.07, 55.4, 45.3 ppm.

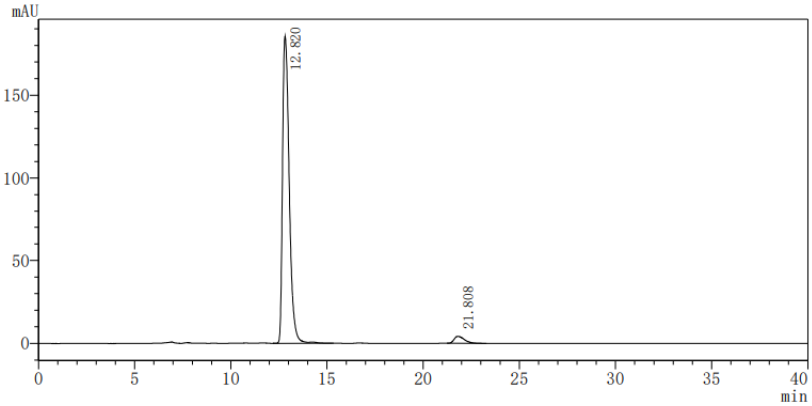
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.02 ppm.

HRMS (ESI) calcd for $[C_{24}H_{20}F_3NO_2S + H]^+$ 444.1240, found 444.1238.

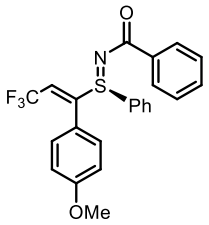
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 12.8 min (major), t_{R2} = 21.8 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	12.910	82067	0.421	1387302	49.930
2	22.107	52069	0.640	1391169	50.070



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	12.820	185389	0.606	4503690	96.650
2	21.808	4205	0.953	156093	3.350



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)benzamide (4aa)

37.8 mg, 88% yield, 89% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +119.4 (*c* = 0.072, $CHCl_3$).

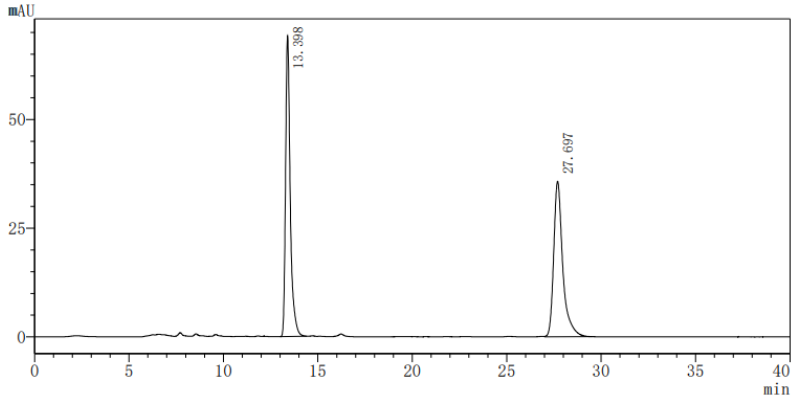
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 – 8.25 (m, 2H), 7.57 – 7.51 (m, 2H), 7.52 – 7.36 (m, 6H), 7.06 – 6.99 (m, 2H), 6.89 (q, *J* = 7.4 Hz, 1H), 6.84 – 6.79 (m, 2H), 3.80 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 161.3, 149.7 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 136.0, 132.8, 132.3, 131.4, 130.8 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 129.8, 129.1, 128.7, 128.1, 122.2 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 121.2, 120.6 (q, $^2J_{C\text{-}F}$ = 35.6 Hz), 114.1, 55.4 ppm.

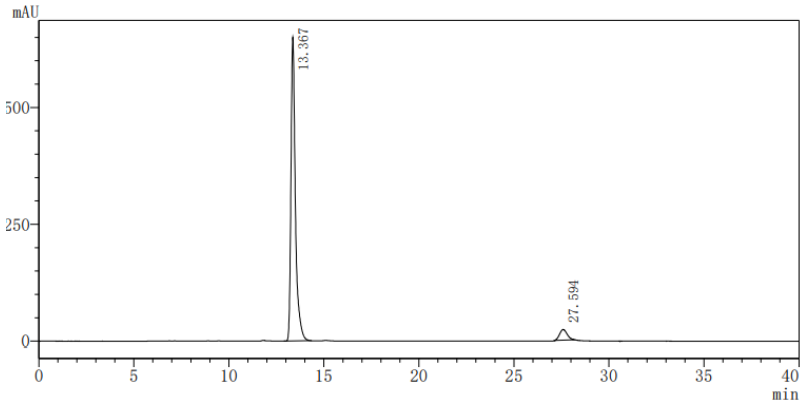
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.82 ppm.

HRMS (ESI) calcd for $[C_{23}H_{18}F_3NO_2S + H]^+$ 430.1083, found 430.1081.

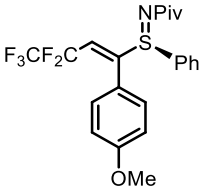
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 13.4 min (major), t_{R2} = 27.7 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	13.398	69193	0.428	1194499	50.064
2	27.697	35748	0.809	1191466	49.936



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	13.367	649763	0.397	10504246	94.337
2	27.594	22803	0.745	630568	5.663



N-((S)-((E)-3,3,4,4,4-pentafluoro-1-(4-methoxyphenyl)but-1-en-1-yl)(phenyl)-λ^4-sulfaneylidene)pivalamide (4ab)

32.6 mg, 71% yield, 93% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +55.8 (*c* = 0.068, $CHCl_3$).

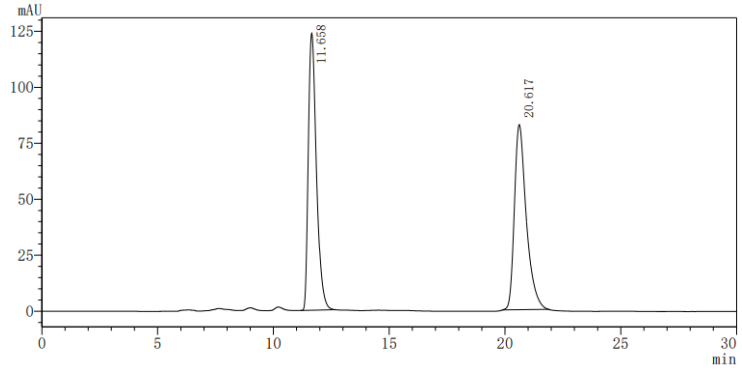
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 3H), 7.40 – 7.34 (m, 2H), 7.00 – 6.92 (m, 2H), 6.85 – 6.76 (m, 2H), 6.69 (dd, *J* = 15.8, 11.6 Hz, 1H), 3.80 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 161.2, 152.2 (dd, *J* = 5.6, 2.6 Hz), 132.5, 132.3, 130.9 (t, *J* = 1.9 Hz), 129.6, 128.5, 121.6, 118.7 (qt, *J* = 287.6, 36.2 Hz), 117.2 (t, *J* = 23.0 Hz), 113.8, 112.0 (ddt, *J* = 257.1, 254.3, 39.1 Hz), 55.4, 40.7, 28.6 ppm.

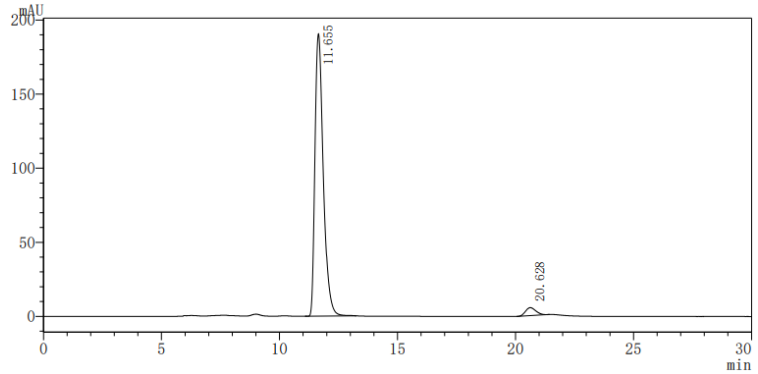
^{19}F NMR (282 MHz, $CDCl_3$) δ -85.00 (t, *J* = 2.6 Hz, 3F), -106.91 (ddq, *J* = 271.2, 11.8, 2.9 Hz, 1F), -112.51 (ddq, *J* = 271.1, 15.6, 2.5 Hz, 1F) ppm.

HRMS (ESI) calcd for $[C_{22}H_{22}F_5NO_2S + H]^+$ 460.1364, found 460.1366.

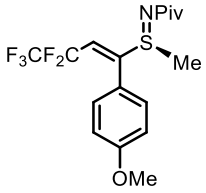
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 11.7 min (major), t_{R2} = 20.6 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.658	123674	0.621	3002195	50.298
2	20.617	82724	0.904	2966592	49.702



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.655	190453	0.621	4661784	96.590
2	20.628	5386	0.821	164558	3.410



N-((S)-methyl((E)-3,3,4,4,4-pentafluoro-1-(4-methoxyphenyl)but-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4ac)

26.2 mg, 66% yield, 94% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +71.9 (*c* = 0.064, $CHCl_3$).

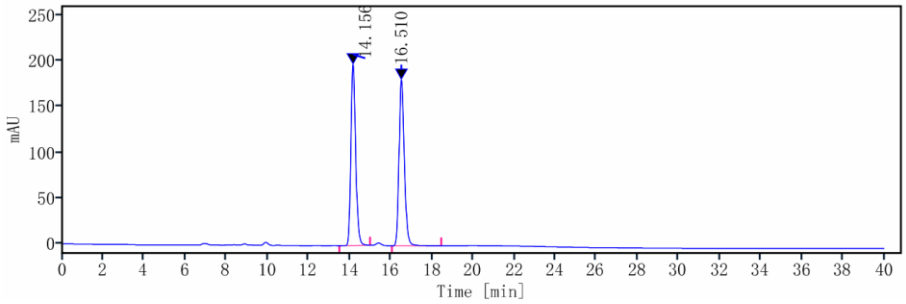
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 6.99 – 6.94 (m, 2H), 6.39 (dd, *J* = 16.2, 11.3 Hz, 1H), 3.85 (s, 3H), 2.49 (s, 3H), 1.26 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 161.6, 151.4 (dd, *J* = 5.9, 2.4 Hz), 130.5 (t, *J* = 2.3 Hz), 121.5, 118.7 (qt, *J* = 287.4, 36.6 Hz), 117.4 (t, *J* = 23.3 Hz), 114.5, 111.9 (ddt, *J* = 257.1, 253,6, 39.3 Hz), 55.5, 40.2, 30.3, 28.5 ppm.

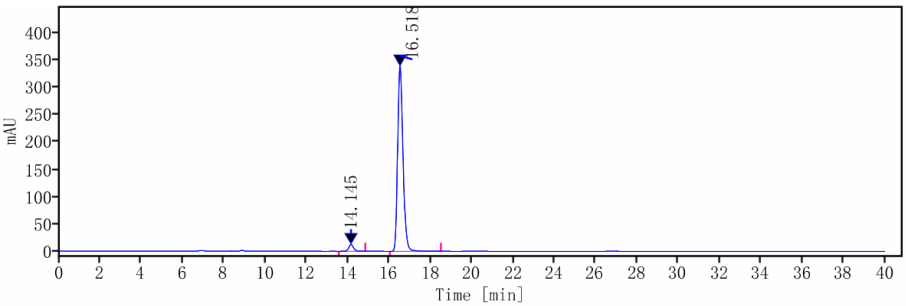
^{19}F NMR (282 MHz, $CDCl_3$) δ -85.06 (t, *J* = 2.6 Hz, 3F), -105.73 (dq, *J* = 272.1, 2.8 Hz, 1F), -113.16 (dq, *J* = 271.7, 2.2 Hz, 1F) ppm.

HRMS (ESI) calcd for $[C_{17}H_{20}F_5NO_2S + H]^+$ 398.1208, found 398.1205.

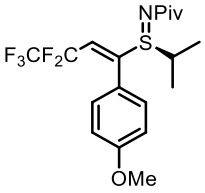
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 14.1 min (minor), t_{R2} = 16.5 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.156	BB	1.4919	3242.5079	198.4528	49.7945
16.510	BB	2.3933	3269.2706	181.8090	50.2055



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.145	BB	1.2900	204.8254	12.5146	3.2350
16.518	BB	2.4617	6126.6668	340.3341	96.7650



N-((S)-isopropyl((E)-3,3,4,4,4-pentafluoro-1-(4-methoxyphenyl)but-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4ad)

31.3 mg, 74% yield, 98% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +23.3 (*c* = 0.06, $CHCl_3$).

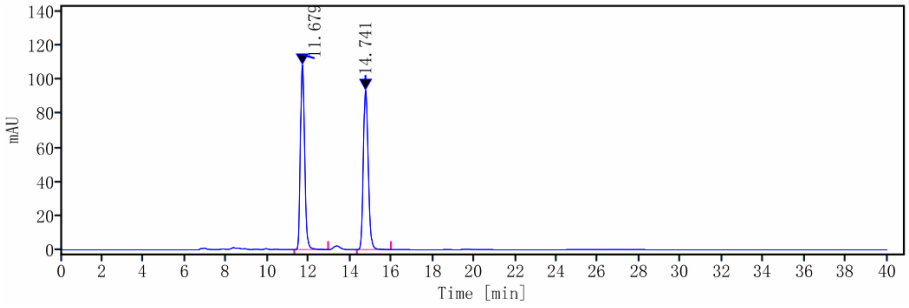
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 6.99 – 6.94 (m, 2H), 6.24 (dd, *J* = 16.5, 11.7 Hz, 1H), 3.85 (s, 3H), 2.91 – 2.78 (m, 1H), 1.30 – 1.27 (m, 12H), 1.20 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 161.6, 148.3 (dd, *J* = 5.7, 2.4 Hz), 130.3 (t, *J* = 2.4 Hz), 122.3, 118.8 (qt, *J* = 287.4, 36.7 Hz), 118.6 (t, *J* = 22.3 Hz), 114.5, 112.0 (ddt, *J* = 257.1, 253,5, 38.9 Hz), 55.5, 45.9, 40.9, 28.6, 18.3, 14.3 ppm.

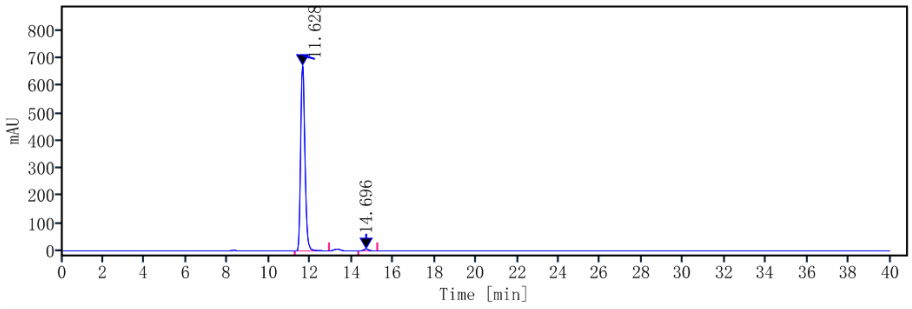
^{19}F NMR (282 MHz, $CDCl_3$) δ -85.13 (t, *J* = 2.6 Hz, 3F), -105.11 (dq, *J* = 271.9, 3.1 Hz, 1F), -113.30 (dq, *J* = 271.7, 2.2 Hz, 1F) ppm.

HRMS (ESI) calcd for $[C_{19}H_{24}F_5NO_2S + H]^+$ 426.1521, found 426.1524.

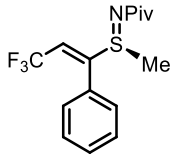
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 11.6 min (minor), t_{R2} = 14.7 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.679	BB	1.6333	1554.4429	108.8643	50.1170
14.741	BB	1.6567	1547.1856	93.9250	49.8830



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.628	BV	1.6428	9588.7824	672.5602	98.8508
14.696	BB	0.9200	111.4798	6.9155	1.1492



N-((S)-methyl((E)-3,3,3-trifluoro-1-phenylprop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4ae)

21.8 mg, 70% yield, 95% ee, *E/Z* > 20/1, as a colorless oil.

$[\alpha]_{25}^{D}$ = +98.6 (*c* = 0.074, $CHCl_3$).

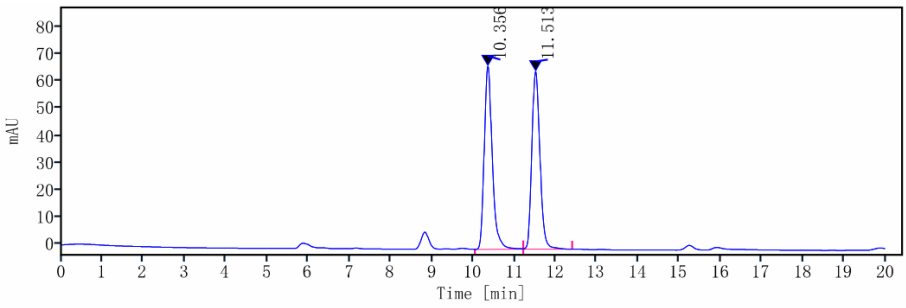
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 3H), 7.42 – 7.38 (m, 2H), 6.48 (q, *J* = 7.5 Hz, 1H), 2.49 (s, 3H), 1.28 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.2, 149.2 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 131.0, 129.5, 129.2, 128.8 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 122.0 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 121.2 (q, $^2J_{C\text{-}F}$ = 36.1 Hz), 40.3, 30.4, 28.6 ppm.

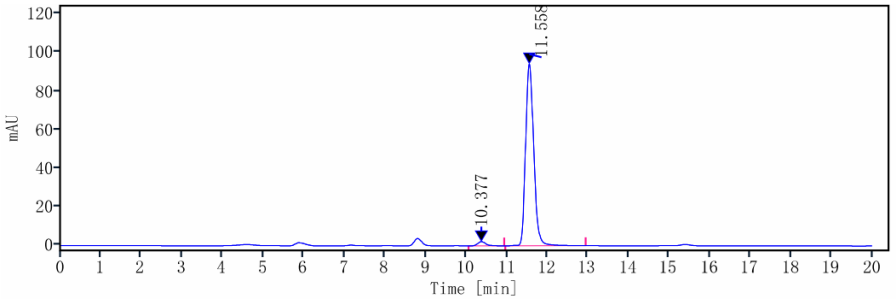
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.10 ppm.

HRMS (ESI) calcd for $[C_{15}H_{18}F_3NOS + H]^+$ 318.1134, found 318.1135.

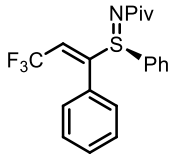
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 10.4 min (minor), t_{R2} = 11.6 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.356	BV	1.1726	920.6461	67.2553	50.8847
11.513	VB	1.1907	888.6316	65.2347	49.1153



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.377	BB	0.8800	30.0090	2.1816	2.2440
11.558	BB	1.9793	1307.3108	94.2613	97.7560



N-((S)-phenyl((E)-3,3,3-trifluoro-1-phenylprop-1-en-1-yl)-λ⁴-sulfaneylidene)-pivalamide (4af)

27.7 mg, 73% yield, 95% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +98.6 (*c* = 0.074, $CHCl_3$).

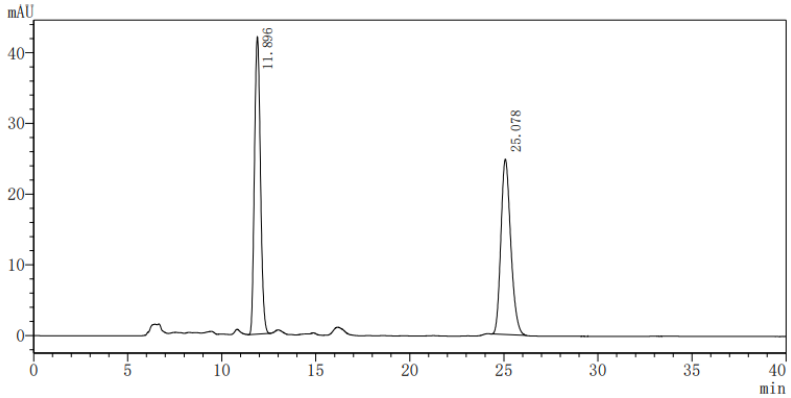
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 3H), 7.38 – 7.32 (m, 3H), 7.30 – 7.24 (m, 2H), 7.02 – 6.98 (m, 2H), 6.78 (q, *J* = 7.5 Hz, 1H), 1.31 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 150.2 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 132.6, 132.1, 130.4, 129.6, 129.4, 129.2 (q, $^4J_{C\text{-}F}$ =1.4 Hz), 128.4, 122.0 (q, $^1J_{C\text{-}F}$ = 270.9 Hz), 120.7 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 40.6, 28.6 ppm.

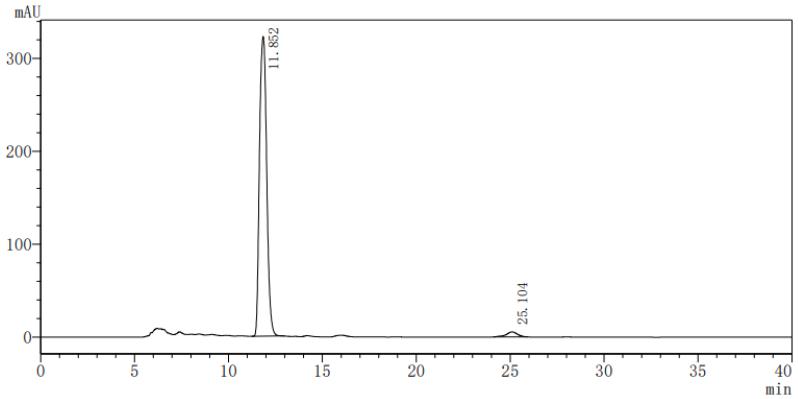
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.06 ppm.

HRMS (ESI) calcd for $[C_{20}H_{20}F_3NOS + H]^+$ 380.1290, found 380.1293.

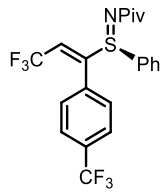
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 11.8 min (major), t_{R2} = 25.1 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.896	42043	0.580	926640	50.627
2	25.078	24786	0.960	903682	49.373



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.852	322264	0.664	8564232	97.495
2	25.104	5337	1.035	220003	2.505



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4ag)

28.6 mg, 64% yield, 95% ee, *E/Z* > 20/1, colorless oil.

$[\alpha]_{25}^{D}$ = +38.5 (*c* = 0.078, $CHCl_3$).

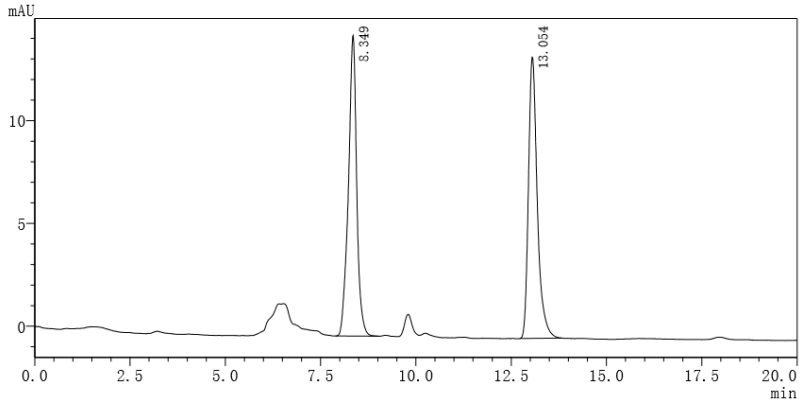
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.39 (m, 7H), 7.09 – 7.07 (m, 2H), 6.82 (q, *J* = 7.3 Hz, 1H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 149.3 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 133.0, 132.4 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 131.3, 129.9, 129.7 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 128.5, 125.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $^1J_{C\text{-}F}$ = 269.8 Hz), 122.8 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 121.7 (q, $^1J_{C\text{-}F}$ =271.2 Hz), 40.7, 28.6 ppm.

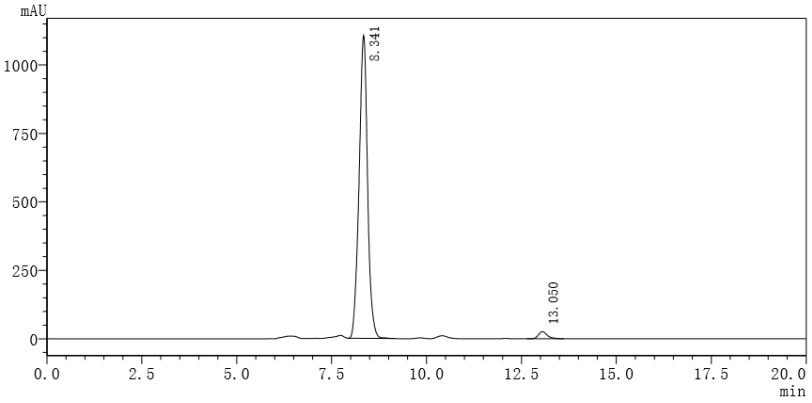
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.25 (3F), -63.03 (3F) ppm.

HRMS (ESI) calcd for $[C_{21}H_{19}F_6NOS+H]^+$ 448.1164, found 448.1160.

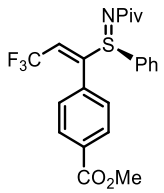
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 8.3 min (major), t_{R2} = 13.0 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.349	14612	0.385	222014	50.130
2	13.054	13682	0.409	220863	49.870



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.341	1106896	0.406	17228839	97.615
2	13.050	25923	0.418	420884	2.385



Methyl4-((S)-3,3,3-trifluoro-1-((E)-S-phenyl-N-pivaloylsulfinimidoyl)prop-1-en-1-yl) benzoate (4ah)

31.2 mg, 71% yield, 96% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +14.5 (*c* = 0.062, $CHCl_3$).

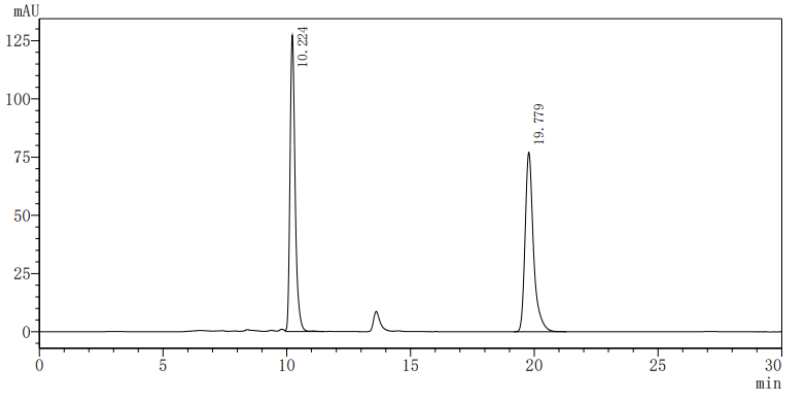
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.35 (m, 5H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.80 (q, *J* = 7.3 Hz, 1H), 3.92 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 166.2, 149.6 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 133.8, 132.9, 131.8, 131.5, 129.8, 129.5, 129.4 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 128.5, 121.81 (q, $^1J_{C\text{-}F}$ =271.1 Hz), 121.80 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 52.5, 40.7, 28.6 ppm.

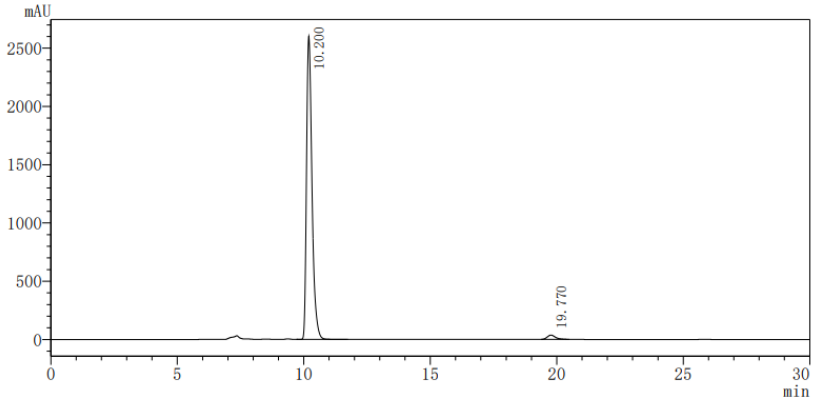
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.23 ppm.

HRMS (ESI) calcd for $[C_{22}H_{22}F_3NO_3S + H]^+$ 438.1345, found 438.1346.

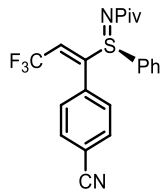
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 10.2 min (major), t_{R2} = 19.8 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.224	127252	0.368	1826874	50.191
2	19.779	77085	0.582	1812953	49.809



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.200	2600377	0.388	39071007	97.920
2	19.770	36882	0.577	829879	2.080



N-((S)-((E)-1-(4-cyanophenyl)-3,3,3-trifluoroprop-1-en-1-yl)(phenyl)-λ⁴-sulfaneylidene)pivalamide (4ai)

30.7 mg, 76% yield, 96% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +14.5 (*c* = 0.062, $CHCl_3$).

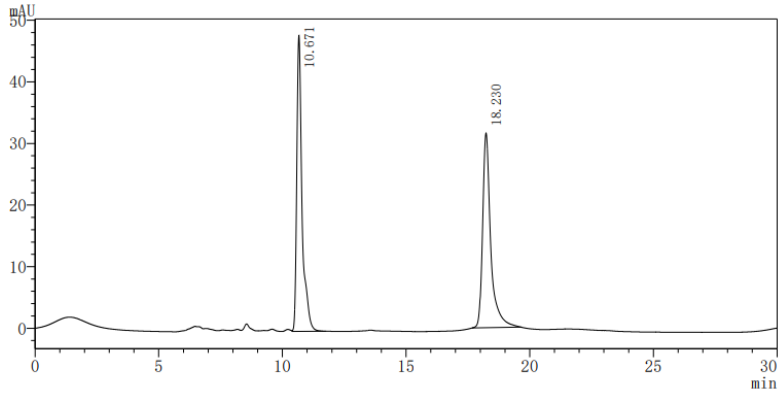
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.40 (m, 7H), 7.07 – 7.04 (m, 2H), 6.82 (q, *J* = 7.2 Hz, 1H), 1.29 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 149.1 (q, $^3J_{C\text{-}F}$ = 5.1 Hz), 133.8, 133.1, 132.0, 131.0, 130.0, 128.5, 122.8 (q, $^2J_{C\text{-}F}$ = 36.1 Hz), 121.6 (q, $^1J_{C\text{-}F}$ =271.3 Hz), 117.8, 114.3, 40.7, 28.6 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.31 ppm.

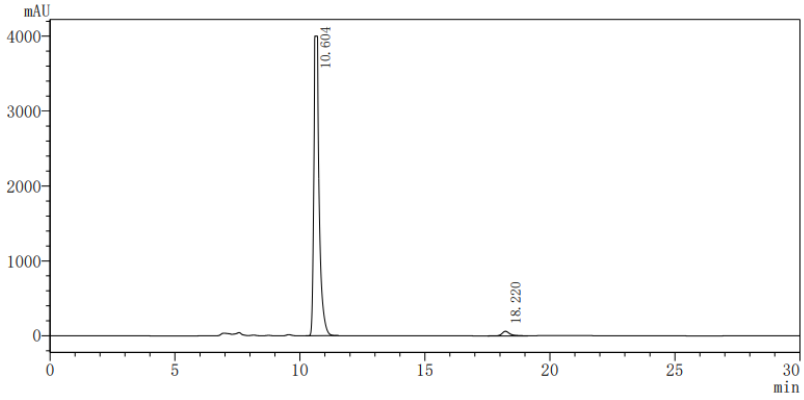
HRMS (ESI) calcd for $[C_{21}H_{19}F_3N_2OS+H]^+$ 405.1243, found 405.1244.

HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 10.6 min (major), t_{R2} = 18.2 min (minor).



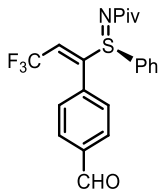
检测器A Ch1 280nm

Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.671	48027	0.349	715178	49.907
2	18.230	31596	0.532	717839	50.093



检测器A Ch1 280nm

Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	10.604	3999224	0.306	60009509	97.767
2	18.220	61237	0.533	1370480	2.233



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-formylphenyl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4aj)

31.8 mg, 78% yield, 93% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +17.1 (*c* = 0.07, $CHCl_3$).

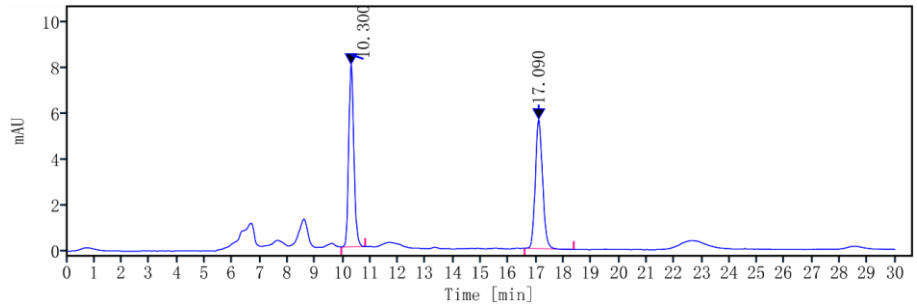
^{1}H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.81 – 7.78 (m, 2H), 7.55 – 7.37 (m, 5H), 7.15 – 7.13 (m, 2H), 6.82 (q, *J* = 7.3 Hz, 1H), 1.31 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 191.0, 149.5 (q, $^3J_{C\text{-}F}$ = 5.0 Hz), 137.2, 135.2, 133.0, 131.3, 130.0 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 129.9, 129.4, 128.5, 122.2 (q, $^2J_{C\text{-}F}$ = 36.1 Hz), 121.7 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 40.7, 28.6 ppm.

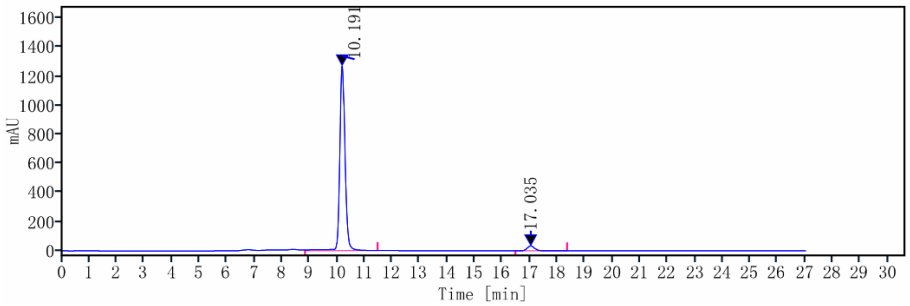
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.25 ppm.

HRMS (ESI) calcd for $[C_{21}H_{20}F_3NO_2S + H]^+$ 408.1240, found 408.1236.

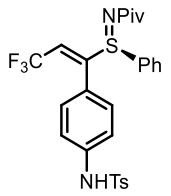
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 10.2 min (major), t_{R2} = 17.0 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.300	BB	0.8633	103.0814	7.9473	49.9748
17.090	BB	1.7733	103.1854	5.6283	50.0252



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.191	BB	2.5200	7154.9334	546.3278	96.2867
17.035	BB	1.9067	275.9292	14.7783	3.7133



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(4-((4-methylphenyl)sulfonamido)phenyl)prop-1-en-1-yl)- λ⁴-sulfaneylidene)pivalamide (4ak)

36.2 mg, 66% yield, 95% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +38.9 (*c* = 0.072, $CHCl_3$).

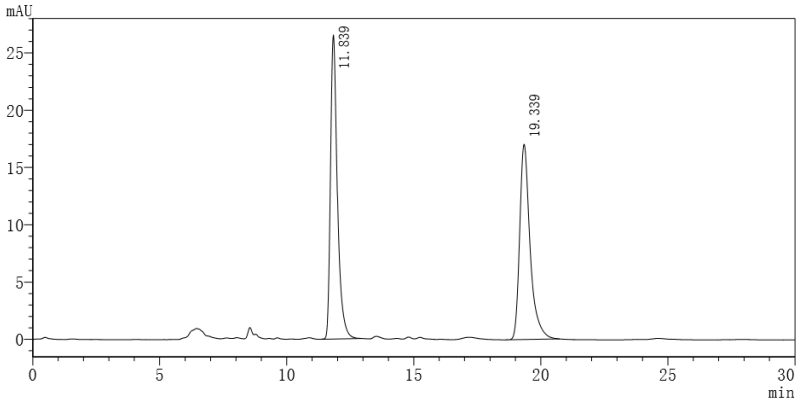
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.73 – 7.60 (m, 2H), 7.50 – 7.40 (m, 1H), 7.37 – 7.17 (m, 6H), 7.11 – 7.02 (m, 2H), 6.88 – 6.79 (m, 2H), 6.73 (q, *J* = 7.4 Hz, 1H), 2.38 (s, 3H), 1.29 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 149.5 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 144.2, 139.5, 136.0, 132.7, 131.9, 130.3 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 129.7, 129.6, 128.3, 127.3, 125.1, 122.0 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 120.9 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 120.2, 40.7, 28.6, 21.6 ppm.

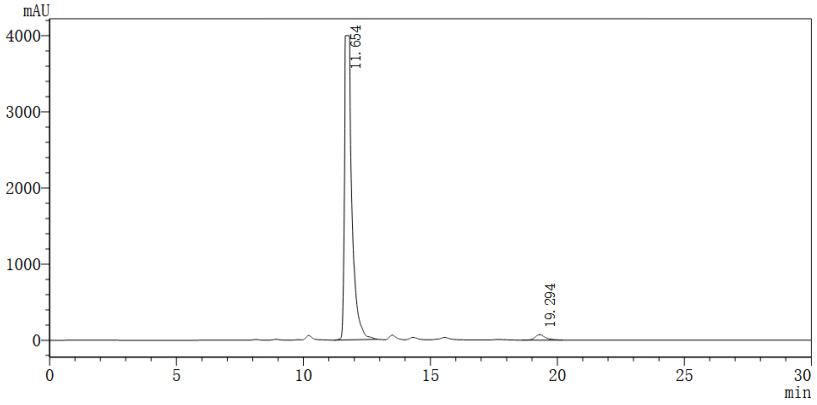
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.16 ppm.

HRMS (ESI) calcd for $[C_{27}H_{27}F_3N_2O_3S_2 + H]^+$ 548.1415, found 549.1504.

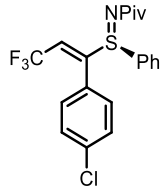
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 11.7 min (major), t_{R2} = 19.3 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.839	26505	0.471	496757	50.527
2	19.339	17038	0.707	486391	49.473



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	11.654	3995438	0.363	81215130	97.588
2	19.294	71648	0.702	2007051	2.412



N-((S)-((E)-1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)(phenyl)-λ⁴-sulfaneylidene)pivalamide (4al)

26.5 mg, 64% yield, 95% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +42.2 (*c* = 0.064, $CHCl_3$).

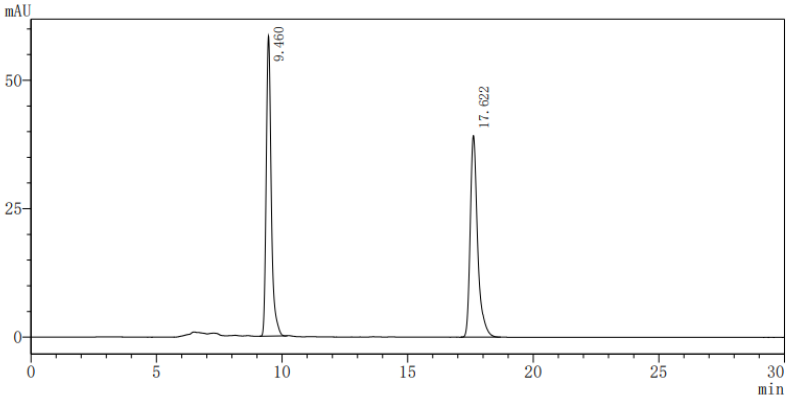
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.37 (m, 5H), 7.29 – 7.25 (m, 2H), 6.94 – 6.89 (m, 2H), 6.78 (q, *J* = 7.4 Hz, 1H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 149.5 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 136.9, 132.8, 131.7, 130.6 (q, $^4J_{C\text{-}F}$ = 1.5 Hz), 129.8, 128.8, 128.5, 127.8, 121.9 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 121.6 (q, $^2J_{C\text{-}F}$ = 36.1 Hz), 40.7, 28.6 ppm.

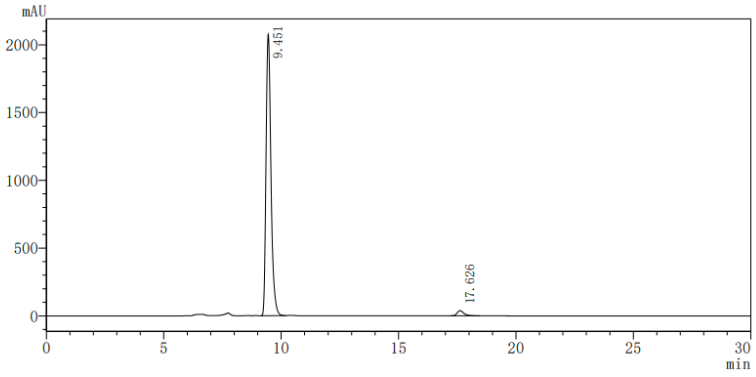
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.17 ppm.

HRMS (ESI) calcd for $[C_{20}H_{19}ClF_3NOS + H]^+$ 414.0901, found 414.0901.

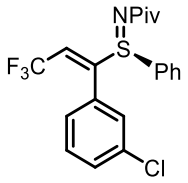
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 9.5 min (major), t_{R2} = 17.6 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.460	58438	0.356	818445	50.542
2	17.622	39254	0.508	800887	49.458



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.451	2074012	0.376	30293231	97.476
2	17.626	38581	0.511	784352	2.524



N-((S)-((E)-1-(3-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)(phenyl)-λ⁴-sulfaneylidene)pivalamide (4am)

28.1 mg, 68% yield, 95% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +13.3 (*c* = 0.06, $CHCl_3$).

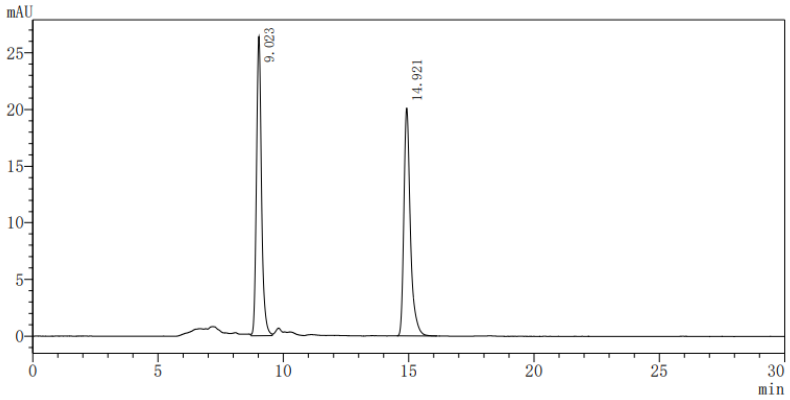
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.34 (m, 6H), 7.24 – 7.18 (m, 1H), 6.96 – 6.95 (m, 1H), 6.84 – 6.75 (m, 2H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 149.2 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 134.5, 132.9, 131.5, 130.8, 130.6, 129.8, 129.7, 129.2 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 128.5, 127.4 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 122.0 (q, $^2J_{C\text{-}F}$ =36.0 Hz), 121.8 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 40.7, 28.6 ppm.

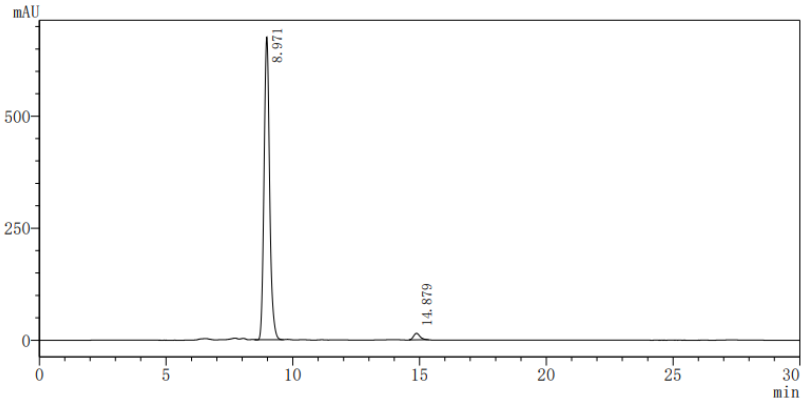
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.27 ppm.

HRMS (ESI) calcd for $[C_{20}H_{19}ClF_3NOS + H]^+$ 414.0901, found 414.0905.

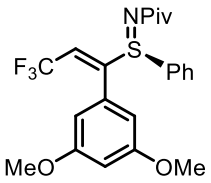
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 9.0 min (major), t_{R2} = 14.9 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.023	26383	0.360	370159	50.506
2	14.921	20090	0.450	362745	49.494



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.971	675114	0.399	10386358	97.595
2	14.879	14548	0.465	255920	2.405



N-((S)-((E)-1-(3,5-dimethoxyphenyl)-3,3,3-trifluoroprop-1-en-1-yl)(phenyl)-λ⁴-sulfaneylidene)pivalamide (4an)

25 mg, 57% yield, 95% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +75.0 (*c* = 0.084, $CHCl_3$).

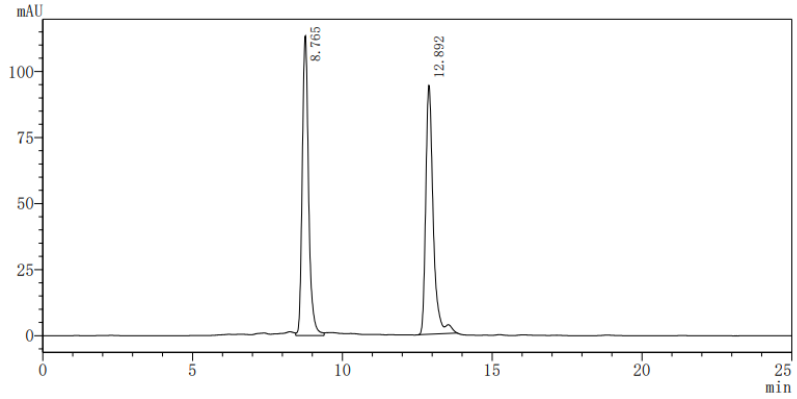
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 3H), 7.44 – 7.35 (m, 2H), 6.73 (q, *J* = 7.5 Hz, 1H), 6.52 – 6.40 (m, 1H), 6.22 – 6.08 (m, 2H), 3.67 (s, 6H), 1.31 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 160.6, 149.9 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 132.6, 132.3, 131.1, 129.6, 128.6, 122.1 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 120.5 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 107.1 (q, $^4J_{C\text{-}F}$ = 1.8 Hz), 102.9, 55.6, 40.7, 28.7 ppm.

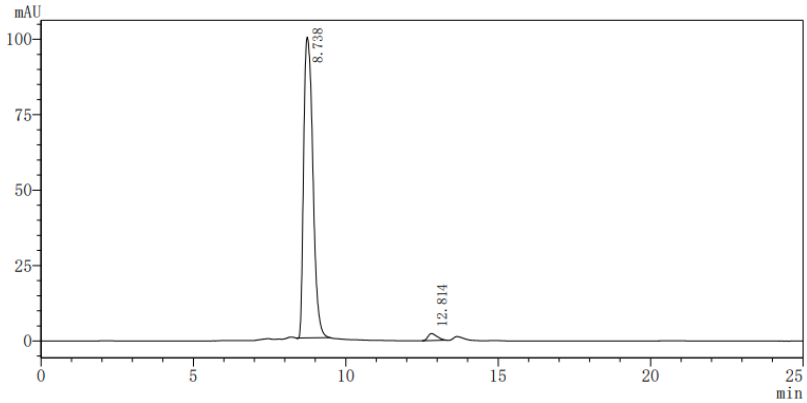
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.17 ppm.

HRMS (ESI) calcd for $[C_{22}H_{24}F_3NO_3S + H]^+$ 420.1502, found 420.1507.

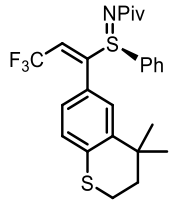
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 8.7 min (major), t_{R2} = 12.8 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.765	113375	0.375	1668148	50.356
2	12.892	94286	0.430	1644573	49.644



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	8.738	99675	0.524	2093763	97.770
2	12.814	2310	0.586	47761	2.230



N-((S)-((E)-1-(4,4-dimethylthiochroman-6-yl)-3,3,3-trifluoroprop-1-en-1-yl)(phenyl)-λ⁴-sulfaneylidene)pivalamide (4ao)

36.9 mg, 77% yield, 95% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +8.1 (*c* = 0.062, $CHCl_3$).

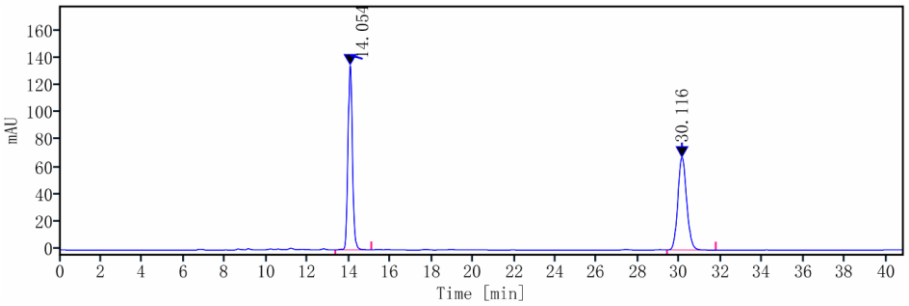
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.34 (m, 5H), 7.01 – 6.98 (m, 1H), 6.86 – 6.85 (m, 1H), 6.76 – 6.69 (m, 2H), 3.02 – 2.98 (m, 2H), 1.92 – 1.88 (m, 2H), 1.31 (s, 9H), 1.20 (s, 3H), 1.07 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 150.2 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 142.2, 135.8, 132.6, 132.4, 129.6, 128.5, 127.6 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 126.6, 126.35, 126.33, 124.8, 122.2 (q, $^1J_{C\text{-}F}$ = 270.9 Hz), 120.2 (q, $^2J_{C\text{-}F}$ =35.7 Hz), 40.7, 37.1, 33.0, 30.1, 30.0, 28.7, 23.2 ppm.

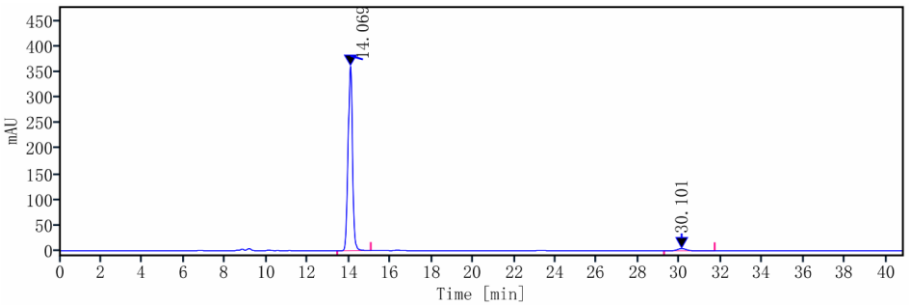
^{19}F NMR (282 MHz, $CDCl_3$) δ -56.89 ppm.

HRMS (ESI) calcd for $[C_{25}H_{28}F_3NOS_2 + H]^+$ 480.1637, found 480.1633.

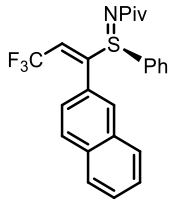
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 14.1 min (major), t_{R2} = 30.1 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.054	BB	1.7433	2034.9585	135.4613	50.1925
30.116	BB	2.3533	2019.3502	67.7866	49.8075



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.069	BB	1.6247	5377.3887	362.0443	97.5787
30.101	BB	2.4533	133.4338	4.4292	2.4213



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(naphthalen-2-yl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4ap)

32.1 mg, 75% yield, 92% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +45.9 (*c* = 0.074, $CHCl_3$).

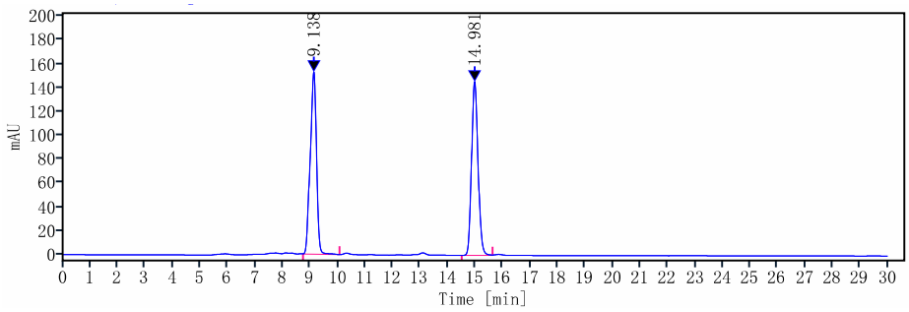
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 1H), 7.77 – 7.71 (m, 2H), 7.59 – 7.50 (m, 3H), 7.47 – 7.43 (m, 3H), 7.34 – 7.30 (m, 2H), 7.02 – 7.00 (m, 1H), 6.83 (q, *J* = 7.4 Hz, 1H), 1.33 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 150.4 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 133.7, 132.6, 132.4, 132.0, 129.7, 129.5, 128.6, 128.5, 128.3, 127.9, 127.8, 127.1, 126.8, 125.9 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 122.1 (q, $^1J_{C\text{-}F}$ = 273.6 Hz), 120.8 (q, $^2J_{C\text{-}F}$ = 36.4 Hz), 40.7, 28.7 ppm.

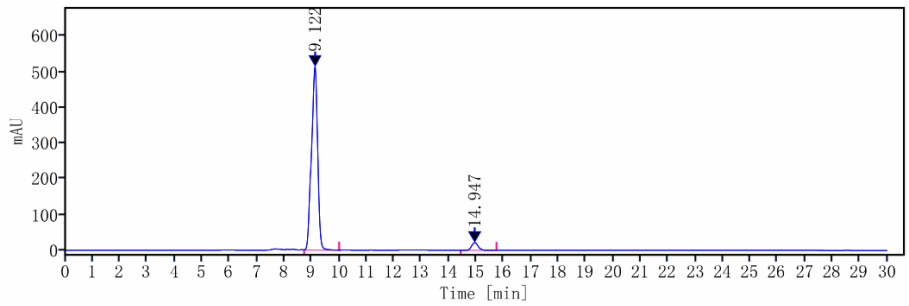
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.07 ppm.

HRMS (ESI) calcd for $[C_{24}H_{22}F_3NOS+H]^+$ 430.1447, found 430.1447.

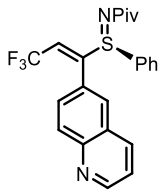
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 9.1 min (major), t_{R2} = 14.9 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
9.138	VB	1.3364	2408.5512	153.0464	50.1479
14.981	BV	1.1167	2394.3485	145.8381	49.8521



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
9.122	VB	1.2807	8015.8144	514.5143	95.7276
14.947	BB	1.3067	357.7541	21.8099	4.2724



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(quinolin-6-yl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4aq)

30.5 mg, 71% yield, 94% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +7.8 (*c* = 0.064, $CHCl_3$).

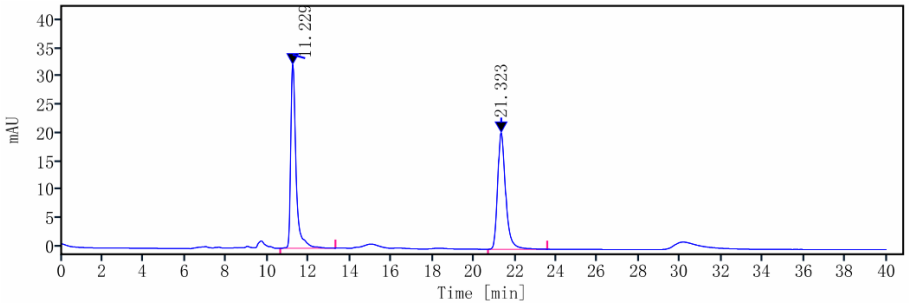
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 – 8.07 (m, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.38 – 7.32 (m, 2H), 7.17 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.85 (q, *J* = 7.4 Hz, 1H), 1.32 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 152.2, 150.0 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 148.4, 136.6, 132.8, 131.7, 129.9, 129.8, 129.6 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 129.42, 129.40, 128.6, 127.7, 127.5, 122.3, 122.0 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 121.7 (q, $^2J_{C\text{-}F}$ = 35.9 Hz), 40.7, 28.7 ppm.

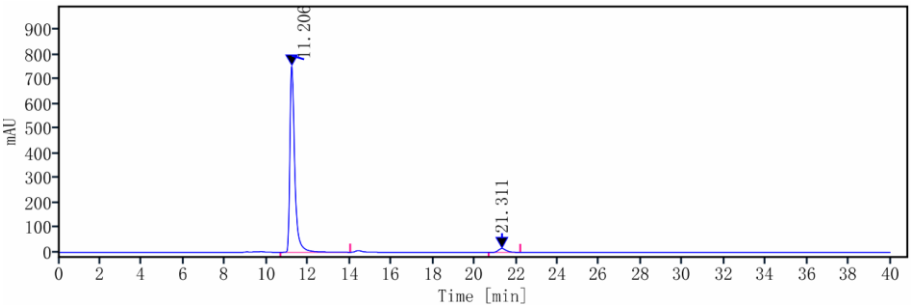
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.18 ppm.

HRMS (ESI) calcd for $[C_{23}H_{21}F_3N_2OS + H]^+$ 431.1399, found 431.1403.

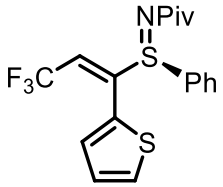
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 11.2 min (major), t_{R2} = 21.3 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.229	BB	2.6633	572.8101	32.4134	50.6368
21.323	BB	2.8700	558.4026	20.5500	49.3632



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.206	BV	3.3575	12184.7352	753.7278	96.7429
21.311	BM m	0.3997	410.2259	15.6560	3.2571



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(thiophen-2-yl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)pivalamide (4ar)

30.1mg, 78% yield, 95% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +87.1 (*c* = 0.062, $CHCl_3$).

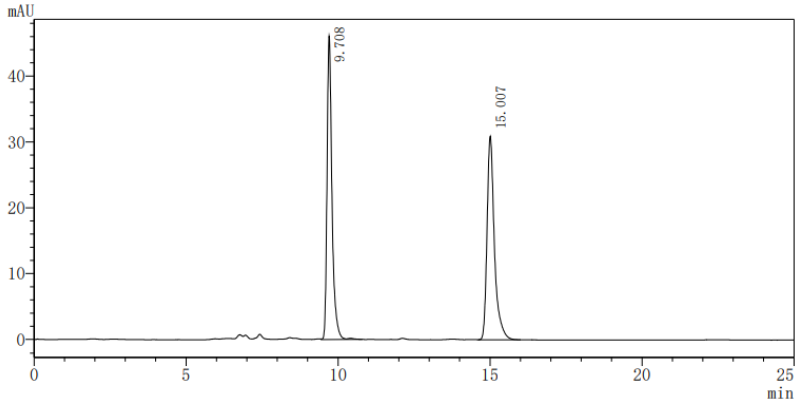
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 4H), 7.42 – 7.35 (m, 2H), 7.01 – 6.97 (m, 2H), 6.83 (q, *J* = 7.5 Hz, 1H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 144.0 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 132.7, 132.6, 131.4 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 130.5, 129.6, 128.8, 128.2, 127.6, 121.9 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.5 (q, $^2J_{C\text{-}F}$ = 36.4 Hz), 40.6, 28.5 ppm.

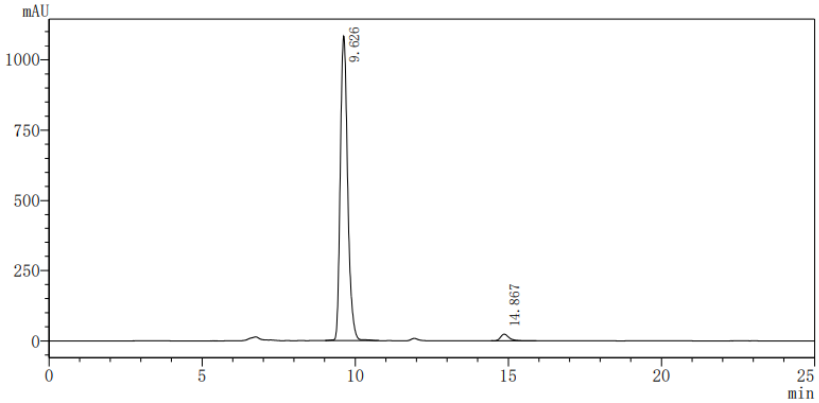
^{19}F NMR (282 MHz, $CDCl_3$) δ -57.19 ppm.

HRMS (ESI) calcd for $[C_{18}H_{18}F_3NO_2S_2 + H]^+$ 402.0804, found 402.0809.

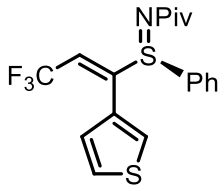
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 9.6 min (major), t_{R2} = 14.9 min (minor).



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.708	46036	0.288	521417	50.134
2	15.007	30894	0.416	518639	49.866



Peak	RetTime [min]	Height	Width [min]	Area [mAU*s]	Area%
1	9.626	1083094	0.432	18238083	97.521
2	14.867	23914	0.486	463693	2.479



N-((S)-phenyl((E)-3,3,3-trifluoro-1-(thiophen-3-yl)prop-1-en-1-yl)-λ⁴-sulfaneylidene)-pivalamide (4as)

17.7 mg, 46% yield, 92% ee, *E/Z* > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = -3.1 (*c* = 0.064, $CHCl_3$).

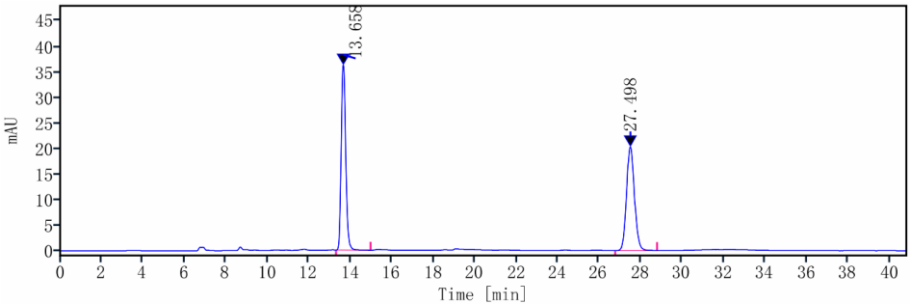
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 3H), 7.40 – 7.36 (m, 2H), 7.29 – 7.27 (m, 1H), 7.24 – 7.23 (m, 1H), 6.85 – 6.83 (m, 1H), 6.79 (q, *J* = 7.5 Hz, 1H), 1.30 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 145.6 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 132.7, 132.6, 129.7, 129.2, 128.2, 128.0 (q, $^4J_{C\text{-}F}$ = 1.8 Hz), 127.9 (q, $^5J_{C\text{-}F}$ = 1.7 Hz), 126.7, 122.1 (q, $^1J_{C\text{-}F}$ =273.5 Hz), 120.7 (q, $^2J_{C\text{-}F}$ = 37.0 Hz), 40.7, 28.7 ppm.

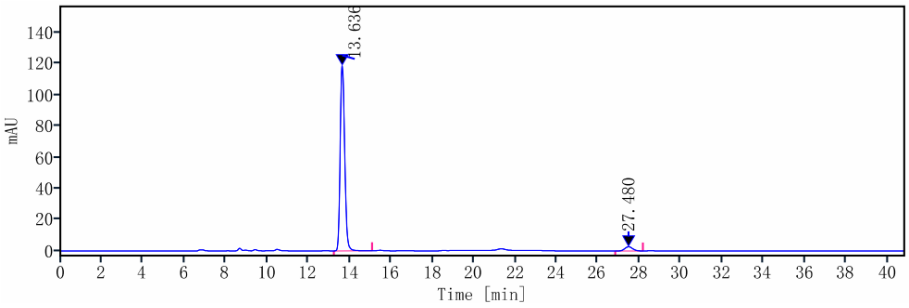
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.38 ppm.

HRMS (ESI) calcd for $[C_{18}H_{18}F_3NO_2S_2 + H]^+$ 402.0804, found 402.0808.

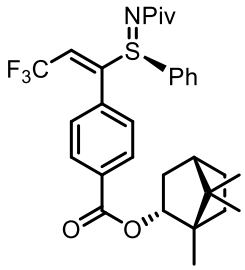
HPLC: Daicel Chiralpak IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 13.6 min (major), t_{R2} = 27.5 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.658	BB	1.6667	540.1580	36.2296	50.0227
27.498	BB	2.0122	539.6681	20.3163	49.9773



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.636	BB	1.8456	1768.7697	118.7441	96.1251
27.480	BB	1.3256	71.3003	2.7228	3.8749



(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl4-((E)-3,3,3-trifluoro-1-((S)-S-phenyl-N-pivaloylsulfinimidoyl)prop-1-en-1-yl)benzoate (4at)

24.1 mg, 43% yield, >20:1 dr, *E/Z* > 20/1, yellow oil.

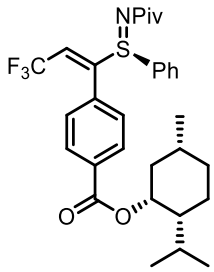
$[\alpha]_{25}^{D}$ = +3.2 (*c* = 0.093, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.56 – 7.39 (m, 6H), 7.10 – 7.06 (m, 2H), 6.82 (q, *J* = 7.4 Hz, 1H), 5.14 – 5.09 (m, 1H), 2.53 – 2.43 (m, 1H), 2.14 – 2.05 (m, 1H), 1.88 – 1.75 (m, 3H), 1.47 – 1.38 (m, 1H), 1.33 (s, 9H), 1.12 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.98 (s, 3H), 0.94 – 0.93 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 165.9, 149.6 (q, $^3J_{C\text{-}F}$ = 5.2 Hz) , 133.7, 132.9, 132.6, 131.6, 129.9, 129.4, 129.37 (q, $^4J_{C\text{-}F}$ = 1.6 Hz), 128.6, 121.8 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 121.7 (q, $^2J_{C\text{-}F}$ = 36.1 Hz), 81.4, 49.2, 48.1, 45.0, 40.7, 37.0, 28.7, 28.2, 27.5, 19.8, 19.0, 13.8 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.11 ppm.

HRMS (ESI) calcd for $[C_{31}H_{36}F_3NO_3S + H]^+$ 560.2441, found 560.2440.



(1R,2R,5R)-2-isopropyl-5-methylcyclohexyl4-((E)-3,3,3-trifluoro-1-((S)-S-phenyl-N-pivaloylsulfinimidoyl)prop-1-en-1-yl)benzoate (4au)

25.8 mg, 46% yield, >20:1 dr, *E/Z* > 20/1, yellow oil.

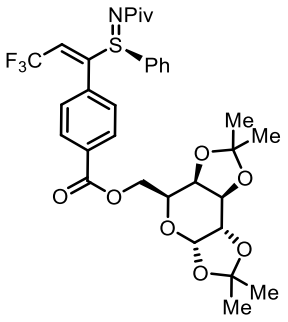
$[\alpha]_{25}^{D}$ = +40.0 (*c* = 0.06, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.38 (m, 5H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.80 (q, *J* = 7.4 Hz, 1H), 5.46 – 5.45 (m, 1H), 2.10 – 2.02 (m, 1H), 1.88 – 1.81 (m, 4H), 1.55 – 1.43 (m, 1H), 1.31 (s, 9H), 1.20 – 1.04 (m, 2H), 0.94 – 0.86 (m, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 165.1, 149.6 (q, $^3J_{C\text{-}F}$ = 5.1 Hz), 133.7, 132.9, 132.8, 131.6, 129.9, 129.4, 129.39 (q, $^4J_{C\text{-}F}$ = 1.7 Hz), 128.6, 121.9 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 121.7 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 72.6, 47.2, 40.7, 39.2, 34.9, 29.4, 28.6, 26.9, 25.5, 22.3, 21.1, 21.0 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.10 ppm.

HRMS (ESI) calcd for $[C_{31}H_{38}F_3NO_3S + H]^+$ 562.2597, found 562.2603.



((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl4-((E)-3,3,3-trifluoro-1-((S)-S-phenyl-N-pivaloylsulfinimidoyl)prop-1-en-1-yl)benzoate (4av)

37.9 mg, 57% yield, >20:1 dr, *E/Z* > 20/1, yellow oil.

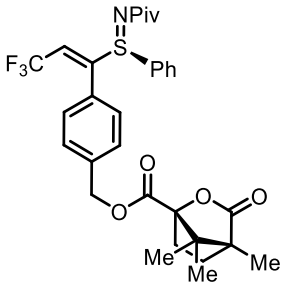
$[\alpha]_{25}^{D}$ = -25.8 (*c* = 0.062, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.52 – 7.36 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.79 (q, *J* = 7.3 Hz, 1H), 5.57 (d, *J* = 4.9 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.47 – 4.41 (m, 2H), 4.37 – 4.30 (m, 2H), 4.20 – 4.11 (m, 1H), 1.52 (s, 3H), 1.47 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 165.5, 149.5 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 133.8, 132.8, 131.7, 131.4, 129.7, 129.5, 129.2 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 128.4, 121.7 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 121.6 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 109.8, 108.9, 96.3, 71.1, 70.7, 70.5, 66.1, 64.4, 40.6, 28.5, 26.0, 25.97, 25.0, 24.5 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.18 ppm.

HRMS (ESI) calcd for $[C_{33}H_{38}F_3NO_8S + H]^+$ 666.2343, found 666.2347.



4-((E)-3,3,3-trifluoro-1-((S)-S-phenyl-N-pivaloylsulfinimidoyl)prop-1-en-1-yl)benzyl(1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (4aw)

42.4 mg, 72% yield, >20:1 dr, *E/Z* > 20/1, yellow oil.

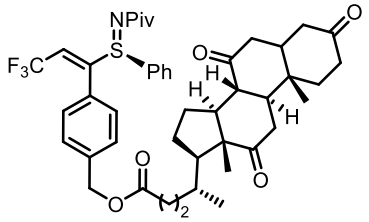
$[\alpha]_{25}^{D}$ = +23.3 (*c* = 0.133, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.35 (m, 5H), 7.31 – 7.29 (m, 2H), 7.01 – 6.98 (m, 2H), 6.78 (q, *J* = 7.4 Hz, 1H), 5.25 (s, 2H), 2.49 – 2.39 (m, 1H), 2.09 – 1.88 (m, 2H), 1.74 – 1.65 (m, 2H), 1.30 (s, 9H), 1.11 (s, 3H), 1.01 (s, 3H), 0.86 (s, 3H) ppm

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 178.1, 167.4, 149.8 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 137.6, 132.7, 131.8, 129.7, 129.6 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 128.5, 128.1, 124.8, 121.9 (q, $^1J_{C\text{-}F}$ = 271.1 Hz), 121.3 (q, $^2J_{C\text{-}F}$ = 35.8 Hz), 91.0, 66.3, 54.9, 54.5, 40.6, 30.8, 29.0, 28.6, 27.2, 16.8, 16.7, 9.8 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.12 ppm.

HRMS (ESI) calcd for $[C_{31}H_{34}F_3NO_5S + Na]^+$ 612.2002, found 612.2008.



4-((1E)-3,3,3-trifluoro-1-((S)-S-phenyl-N-pivaloylsulfinimidoyl)prop-1-en-1-yl)benzyl(4R)-4-((8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (4ax)

53.2 mg, 67% yield, >20:1 dr, *E/Z* > 20/1, yellow oil.

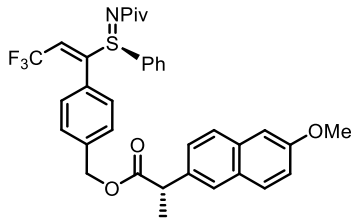
$[\alpha]_{25}^{D}$ = +27.4 (*c* = 0.062, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.34 (m, 5H), 7.28 – 7.24 (m, 2H), 7.05 – 6.96 (m, 2H), 6.77 (q, *J* = 7.4 Hz, 1H), 5.10 (s, 2H), 2.99 – 2.80 (m, 3H), 2.53 – 2.41 (m, 1H), 2.40 – 2.29 (m, 4H), 2.27 – 2.23 (m, 2H), 2.21 – 2.15 (m, 2H), 2.14 – 2.10 (m, 1H), 2.09 – 1.98 (m, 4H), 1.96 – 1.92 (m, 1H), 1.91 – 1.79 (m, 3H), 1.69 – 1.55 (m, 1H), 1.44 – 1.38 (m, 4H), 1.32 – 1.28 (m, 10H), 1.05 (s, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 212.1, 209.2, 208.8, 190.7, 173.8, 145.0 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 138.7, 132.7, 131.9, 129.7, 129.4 (q, $^4J_{C\text{-}F}$ = 1.3 Hz), 129.1, 128.5, 127.7, 122.0 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 121.4 (q, $^2J_{C\text{-}F}$ = 31.7 Hz), 65.2, 57.0, 51.9, 49.1, 46.9, 45.7, 45.6, 45.1, 42.9, 40.7, 38.7, 36.6, 36.1, 35.6, 35.4, 31.5, 30.5, 28.6, 27.7, 25.2, 22.0, 18.7, 11.9 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.00 ppm.

HRMS (ESI) calcd for $[C_{45}H_{54}F_3NO_6S + H]^+$ 794.3697, found 794.3698.



4-((E)-3,3,3-trifluoro-1-((S)-S-phenyl-N-pivaloylsulfinimidoyl)prop-1-en-1-yl)benzyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (4ay)

39.7 mg, 64% yield, >20:1 dr, *E/Z* > 20/1, yellow oil.

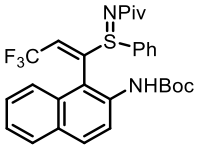
$[\alpha]_{25}^{D}$ = +42.7 (*c* = 0.082, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 3H), 7.45 – 7.28 (m, 6H), 7.16 – 7.09 (m, 4H), 6.94 – 6.88 (m, 2H), 6.74 (q, *J* = 7.4 Hz, 1H), 5.09 (s, 2H), 3.94 – 3.88 (m, 4H), 1.60 (d, *J* = 7.2 Hz, 2H), 1.30 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 174.4, 157.9, 149.9 (q, $^3J_{C\text{-}F}$ = 5.2 Hz), 138.6, 135.4, 133.9, 132.6, 131.9, 129.6, 129.35 (q, $^4J_{C\text{-}F}$ = 1.9 Hz), 129.33, 129.04, 129.00, 128.4, 127.48, 127.44, 127.3, 126.2, 126.1, 122.0 (q, $^1J_{C\text{-}F}$ = 270.9 Hz), 120.8 (q, $^2J_{C\text{-}F}$ = 36.2 Hz), 119.3, 105.7, 65.5, 55.4, 45.5, 40.7, 28.6, 18.6 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -57.05 ppm.

HRMS (ESI) calcd for $[C_{35}H_{34}F_3NO_4S + H]^+$ 622.2233, found 622.2238.



tert-butyl (1-((E)-3,3,3-trifluoro-1-((E)-S-phenyl-N-pivaloylsulfinimidoyl)prop-1-en-1-yl)naphthalen-2-yl)carbamate (4ba)

24.9 mg, 46% yield, 96% ee, *E/Z* > 20/1, dr > 20/1, yellow oil.

$[\alpha]_{25}^{D}$ = +177.9 (*c* = 0.113, $CHCl_3$).

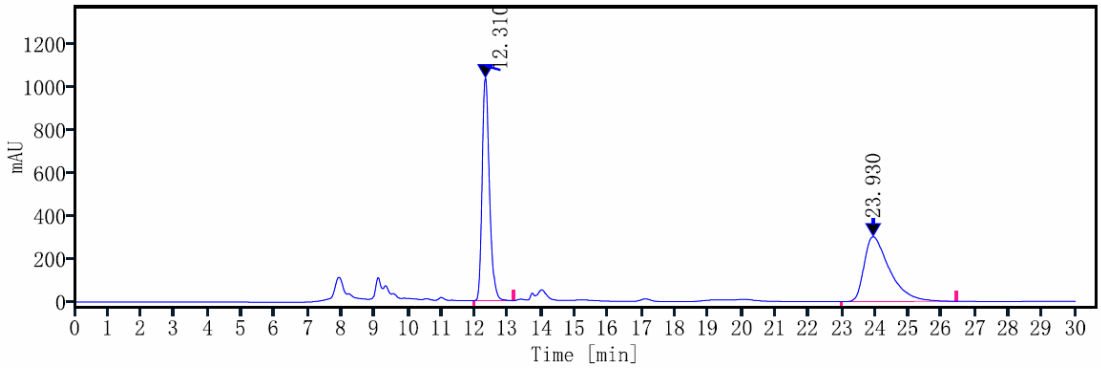
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 1H), 7.86 – 7.75 (m, 3H), 7.51 – 7.46 (m, 1H), 7.44 – 7.34 (m, 4H), 7.29 – 7.25 (m, 2H), 7.02 (q, *J* = 7.0 Hz, 1H), 6.49 (s, 1H), 1.44 (s, 9H), 1.38 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 152.1, 146.9 (q, $^3J_{C\text{-}F}$ = 4.6 Hz), 136.12 (q, $^4J_{C\text{-}F}$ = 1.1 Hz), 133.2, 131.8, 131.5, 130.8, 129.7, 129.6, 128.1, 128.1, 128.0, 125.7 (q, $^2J_{C\text{-}F}$ = 36.3 Hz), 125.4, 124.7, 121.5 (q, $^1J_{C\text{-}F}$ = 274.4 Hz), 80.9, 40.8, 28.8, 18.4 ppm.

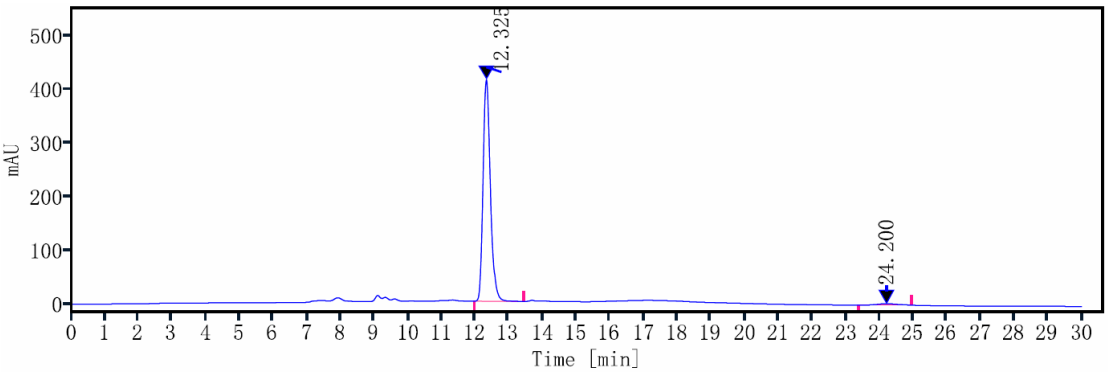
^{19}F NMR (377 MHz, $CDCl_3$) δ -60.80 ppm.

HRMS (ESI) calcd for $[C_{29}H_{31}F_3N_2O_3S+H]^+$ 545.2080, found 545.2076.

HPLC: Daicel Chiralpak IC-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 12.3 min (major), t_{R2} = 24.2 min (minor).

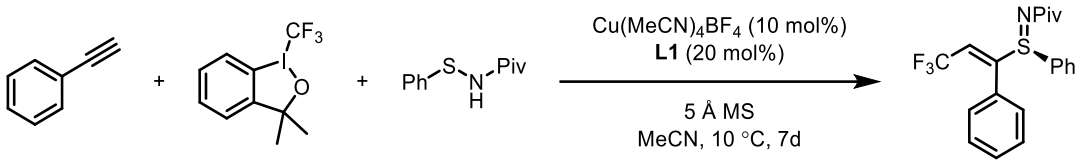


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.310	VB	1.1775	15729.5356	1036.5203	49.6402
23.930	BM m	0.7908	15957.5793	301.8120	50.3598



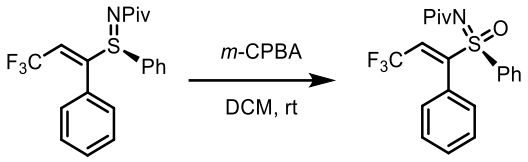
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.325	VB	1.4592	6211.6669	413.2567	98.0952
24.200	BM m	0.7114	120.6154	2.7196	1.9048

4. Synthetic Applications



1b 4 mmol | **2a** | **3a** | **4af** 1.24 g, 82%, 96% ee

An oven-dried 250 mL Schlenk tube was charged with **2a** (6.0 mmol, 1.5 equiv), **3a** (8 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (125.8 mg, 0.4 mmol, 10 mol%), **L1** (529.8 mg, 0.8 mmol, 20 mol%), 5 Å MS (2.0 g), the vial was thoroughly flushed with Ar, **1b** (4.0 mmol, 1.0 equiv) and MeCN (40.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 10 ℃ for 4 d. After cooling to room temperature, the reaction mixture was diluted with EA (10.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel to afford products **4af** (1.24 g, 82%, 96% ee).



4af **5**

To a 50 mL round-bottom flask was charged with **4af** (0.5 mmol, 1.0 equiv, 189.7 mg), followed by the addition of DCM (10.0 mL, 0.05 M) and *m*-CPBA (5.0 mmol, 10.0 equiv, 1.0 g). The reaction mixture was stirred at room temperature for 24 hours, then quenched with saturated sodium bicarbonate solution. The mixture was extracted with 10.0 mL DCM three times, and the combined organic layers were concentrated under reduced pressure. Purification was performed by column chromatography.

(R)-N-(oxo(phenyl)(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)-λ^6-sulfaneylidene)pivalamide (5)

85.2 mg, 43% yield, 95% ee, yellow oil.

$[\alpha]_{25}^{D}$ = -18.7 (*c* = 0.064, $CHCl_3$).

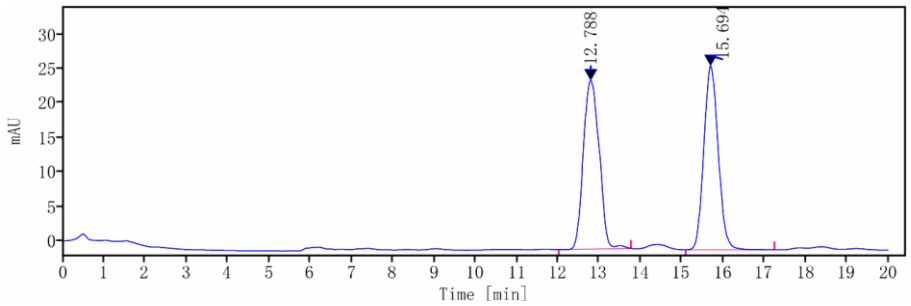
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 3H), 7.55 – 7.46 (m, 1H), 7.40 – 7.26 (m, 1H), 7.24 – 7.19 (m, 1H), 6.82 – 6.71 (m, 1H), 1.19 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2, 153.0 (q, $^3J_{C\text{-}F}$ = 5.1 Hz), 134.5, 134.4, 130.3, 129.8 (q, $^4J_{C\text{-}F}$ = 1.3 Hz), 129.41, 129.39,127.9, 127.6, 127.5 (q, $^2J_{C\text{-}F}$ = 36.2 Hz), 121.5 (q, $^1J_{C\text{-}F}$ = 273.5 Hz), 41.8, 27.7 ppm.

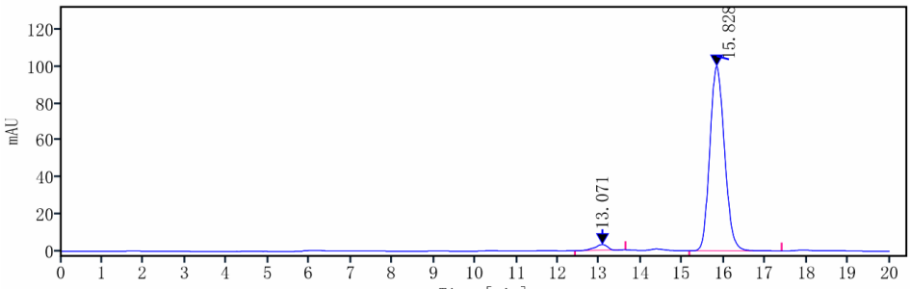
^{19}F NMR (376 MHz, $CDCl_3$) δ -58.24 ppm.

HRMS (ESI) calcd for $[C_{20}H_{20}F_3NO_2S + H]^+$ 396.1240, found 396.1245.

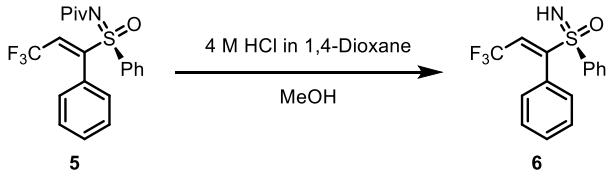
HPLC: Daicel Chiralpak AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 13.1 min (minor), t_{R2} = 15.8 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.788	BM m	0.4076	653.8907	24.4835	50.2591
15.694	BB	2.1467	647.1478	26.6892	49.7409



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.071	BM m	0.3222	64.7853	3.0703	2.5522
15.828	BB	2.2333	2473.5769	100.1346	97.4478



5 **6**

5 (39.5 mg) was placed in a 25 mL round-bottom flask, followed by the addition of 4.0 M HCl in 1,4-Dioxane (1.0 mL) and methanol (1.0 mL). The reaction mixture was stirred at room temperature for 24 hours, then quenched with a saturated sodium bicarbonate solution. The mixture was extracted three times with dichloromethane (DCM). The combined organic layers were concentrated under reduced pressure, and the crude product was purified by column chromatography.

(R)-imino(phenyl)(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)-λ^6-sulfanone (6)

19.9 mg, 64% yield, 92% ee, white solid. m.p. 79–81 °C.

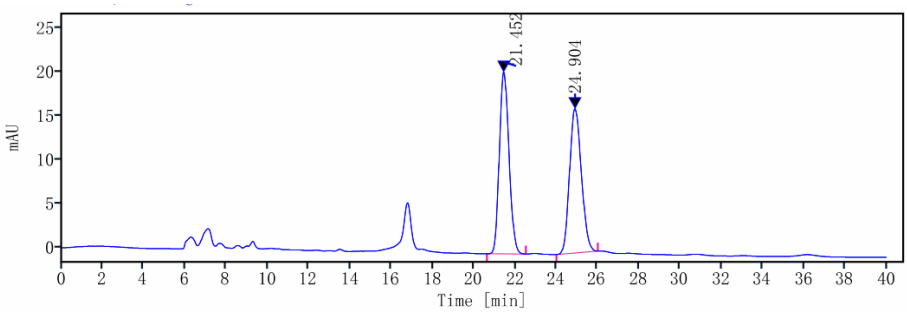
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 2H), 7.60 – 7.55 (m, 1H), 7.44 – 7.40 (m, 2H), 7.38 – 7.33 (m, 1H), 7.27 – 7.22 (m, 2H), 7.13 (q, J = 7.2 Hz, 1H), 6.95 – 6.93 (m, 2H), 3.05 (br s, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0 (q, $^3J_{C\text{-}F}$ = 4.9 Hz), 137.3, 133.8, 129.8,129.7 (q, $^4J_{C\text{-}F}$ = 1.4 Hz), 129.4, 129.0, 128.7, 127.9, 124.0 (q, $^2J_{C\text{-}F}$ = 35.6 Hz), 121.9 (q, $^1J_{C\text{-}F}$ = 273.3 Hz) ppm.

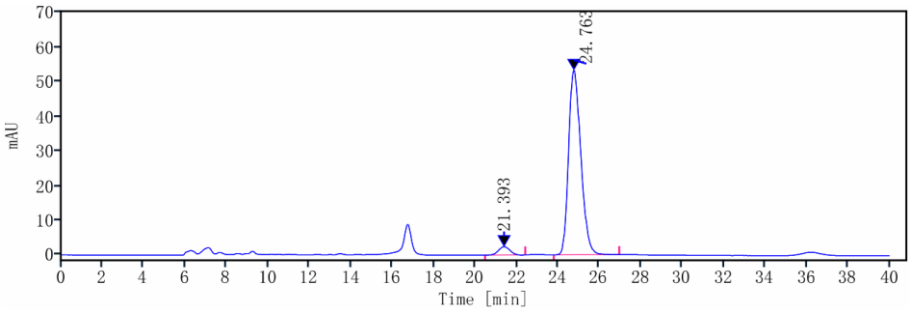
^{19}F NMR (376 MHz, $CDCl_3$) δ -58.11 ppm.

HRMS (ESI) calcd for $[C_{15}H_{12}F_3NOS + H]^+$ 312.0664, found 312.0667.

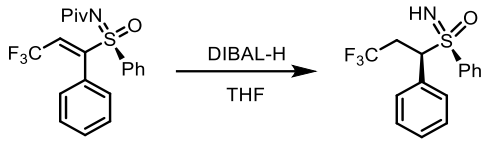
HPLC: Daicel Chiralpak OD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 280 nm, t_{R1} = 21.4 min (minor), t_{R2} = 24.7 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
21.452	BB	1.8867	675.5312	20.7155	50.7287
24.904	BB	2.0017	656.1243	16.4394	49.2713



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
21.393	BM m	0.5813	90.4938	2.4141	3.9728
24.763	BB	3.1533	2187.3457	53.2332	96.0272



5 **7**

5 (39.5 mg, 0.1 mmol, 1.0 equiv) was charged into a 25 mL round-bottom flask under an argon atmosphere. Anhydrous THF was introduced, and the mixture was cooled to 0 °C. A solution of 1 M DIBAL-H in THF (1.6 mL, 1.6 mmol, 16.0 equiv) was then added dropwise. The reaction was maintained at 0 °C for 24 hours, then quenched with a saturated sodium bicarbonate solution. The mixture was extracted three times with dichloromethane (DCM). The combined organic layers were concentrated under reduced pressure, and the crude product was purified by column chromatography.

(S)-imino(phenyl)((R)-3,3,3-trifluoro-1-phenylpropyl)-λ⁶-sulfanone (7)

21.9 mg, 70% yield, 95% ee, 11:1 dr, white solid. m.p. 110–112 ℃.

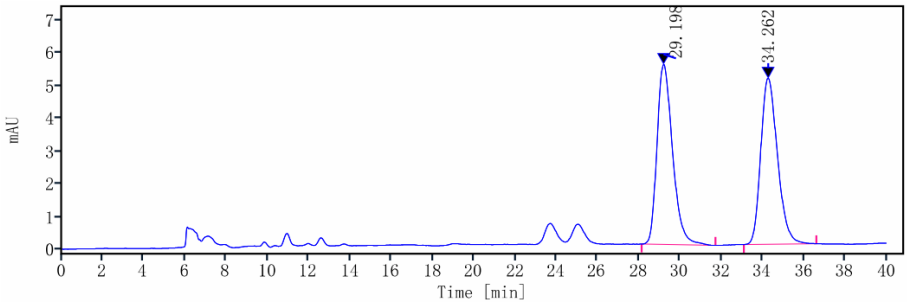
$[\alpha]_{25}^{D}$ = +61.6 (*c* = 0.06, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.63 – 7.59 (m, 1H), 7.52 – 7.46 (m, 2H), 7.40 – 7.26 (m, 5H), 4.24 (dd, *J* = 10.0, 4.1 Hz, 1H), 3.11 – 2.98 (m, 2H), 2.76 (br s, 1H) ppm.

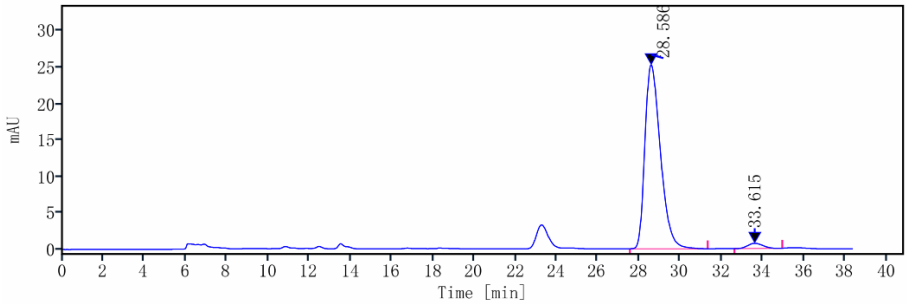
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 133.7, 130.7, 130.0, 129.6, 129.4, 129.2, 128.8, 125.5 (q, $^1J_{C\text{-}F}$ = 277.9 Hz), 67.6 (q, $^3J_{C\text{-}F}$ = 2.4 Hz), 34.3 (q, $^2J_{C\text{-}F}$ = 29.5 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.44 ppm.

HRMS (ESI) calcd for $[C_{15}H_{14}F_3NOS + Na]^+$ 336.0640, found 336.0642.
HPLC: Daicel Chiralpak AS-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 28.6 min (major), t_{R2} = 33.6 min (minor).



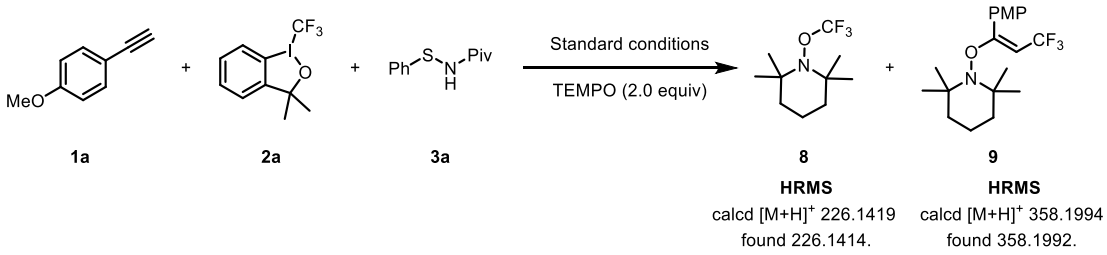
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
29.198	BB	3.5800	287.3306	5.4833	50.1805
34.262	BB	3.5133	285.2637	5.0537	49.8195



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
28.586	BB	3.7667	1323.3877	25.2603	97.4251
33.615	MM m	0.7391	34.9769	0.7047	2.5749

5. Mechanistic Studies

5.1 Radical trapping experiment



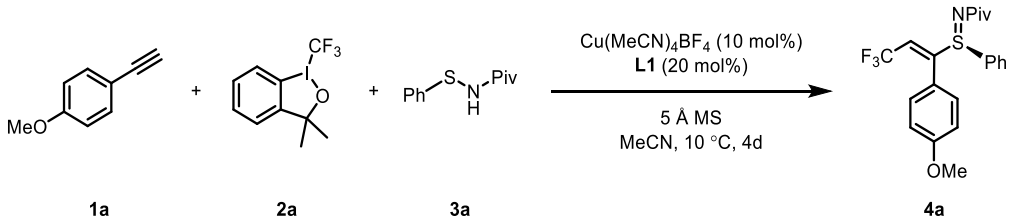
1a **2a** **3a** **8** **9**

HRMS calcd $[M+H]^+$ 226.1419 found 226.1414.

HRMS calcd $[M+H]^+$ 358.1994 found 358.1992.

A sealed tube was charged with **2a** (49.5 mg, 0.15 mmol, 1.5 equiv), **3a** (41.8 mg, 0.2 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (3.2 mg, 0.01 mmol, 10 mol%), **L1** (13.2 mg, 0.02 mmol, 20 mol%), 5 Å MS (50.0 mg), TEMPO (32.2 mg, 0.2 mmol, 2.0 equiv). The vial was thoroughly flushed with Ar, **1a** (0.1 mmol, 1.0 equiv) and MeCN (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was vigorously stirred at 10 ℃ for 4 d. After cooling to room temperature, the reaction mixture was diluted with MeOH filtered through a plug of Celite. The reaction mixture was analyzed by HRMS. The trifluoromethyl radical and alkenyl radical captured by TEMPO was detected by HRMS. This result suggests that a radical mechanism might be operative. The trifluoromethyl radical and alkenyl radical was generated under the current reaction conditions.

5.2 Nonlinear effect (NLE) experiments



1a **2a** **3a** **4a**

A sealed tube was charged with **2a** (49.5 mg, 0.15 mmol, 1.5 equiv), **3a** (41.8 mg, 0.2 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (3.2 mg, 0.01 mmol, 10 mol%), **L1** (13.2 mg, 0.02 mmol, 20 mol%, mixtures of two enantiomers determined by weight), 5 Å MS (50.0 mg). The vial was thoroughly flushed with Ar, **1a** (0.1 mmol, 1.0 equiv) and MeCN (1.0 mL) was added via a syringe under Ar atmosphere. The reaction mixture was diluted with EA (2.0 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give dark residue, which was purified by flash chromatography on silica gel to afford products **4a**. Analysis of the pure samples by chiral HPLC provided the reported enantiomeric excesses.

The results were listed as follows in **Table S6** and **Figure S3**.

Entry	1	2	3	4	5	6
Ligad ee (%)	0	20	40	60	80	>99
Product ee (%)	0	22	37	62	85	96

Table S6. The ee of **4a** at different ee of **L1**

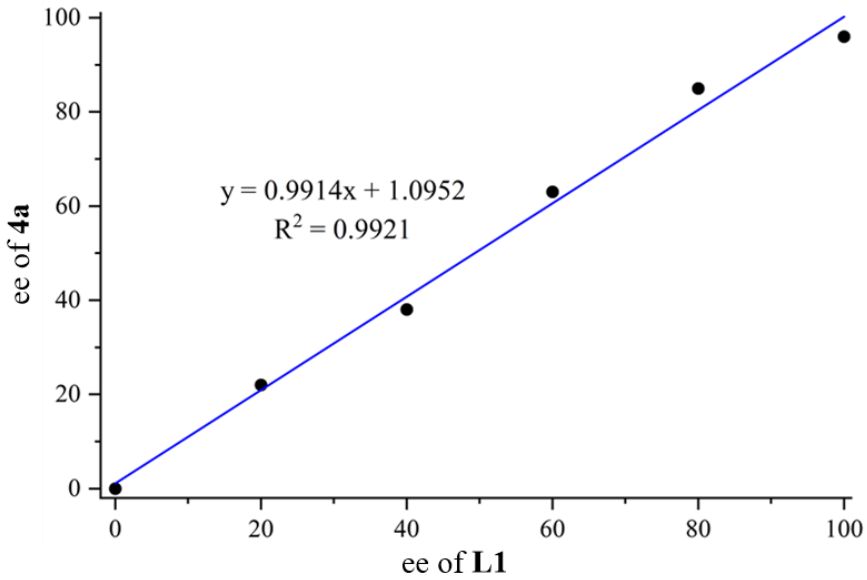


Figure S3. The ee of **4a** at different ee of **L1**

5.3 EPR experiments

Conditions A: All operations were conducted in a N_2-filled glove-box. A sealed tube was charged with **2a** (49.5 mg, 0.15 mmol, 1.5 equiv), **3a** (41.8 mg, 0.2 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (3.2 mg, 0.01 mmol, 10 mol%), **L1** (13.2 mg, 0.02 mmol, 20 mol%), **1a** (0.1 mmol, 1.0 equiv) and MeCN (1.0 mL) was added via a syringe under N_2 atmosphere. React at room temperature for 30 minutes, DMPO (0.4 mmol, 4.0 equiv) were added to the resulting mixture. After the reaction finished, the electron paramagnetic resonance (EPR) analysis of the reaction mixture revealed a strong radical signal (**Figure S4**), which would be assigned to the trapped alkenyl radical by DMPO according to the simulated spectrum (fitting results: for the alkenyl radical, g = 2.0063 A_H = 16.2 G, A_N = 13.6 G).

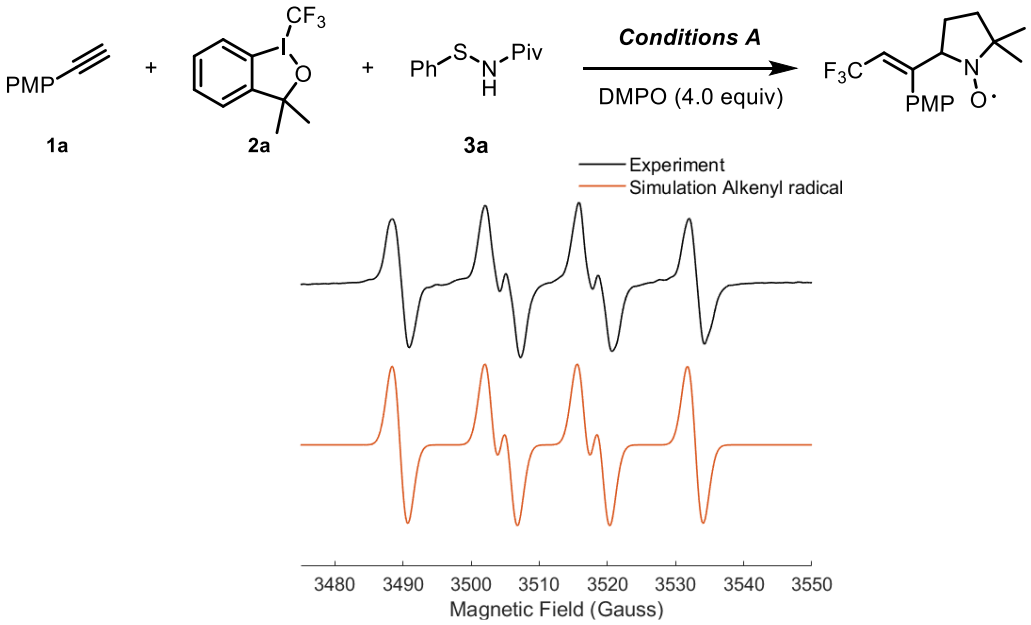


Figure S4. EPR spectra of trapped alkenyl radical by DMPO

Conditions B: All operations were conducted in a N_2-filled glove-box. A sealed tube was charged with **2a** (49.5 mg, 0.15 mmol, 1.5 equiv), **3a** (41.8 mg, 0.2 mmol, 2.0 equiv), $Cu(MeCN)_4BF_4$ (3.2 mg, 0.01 mmol, 10 mol%), **L1** (13.2 mg, 0.02 mmol, 20 mol%), **1a** (0.1 mmol, 1.0 equiv) and MeCN (1.0 mL) was added via a syringe under N_2 atmosphere. React at room temperature for 30 minutes, PBN (0.4 mmol, 4.0 equiv) were added to the resulting mixture. After the reaction finished, the electron paramagnetic resonance (EPR) analysis of the reaction mixture revealed a strong radical signal (**Figure S5**), which would be assigned to the trapped trifluoromethyl radical and alkenyl radical by PBN according to the simulated spectrum (fitting results: for the alkenyl radical, g = 2.006, A_H = 2.1 G, A_N = 14.2 G; for the trifluoromethyl radical g = 2.006, A_N = 14.2 G, A_H = 1.5 G, A_F = 1.6 G).

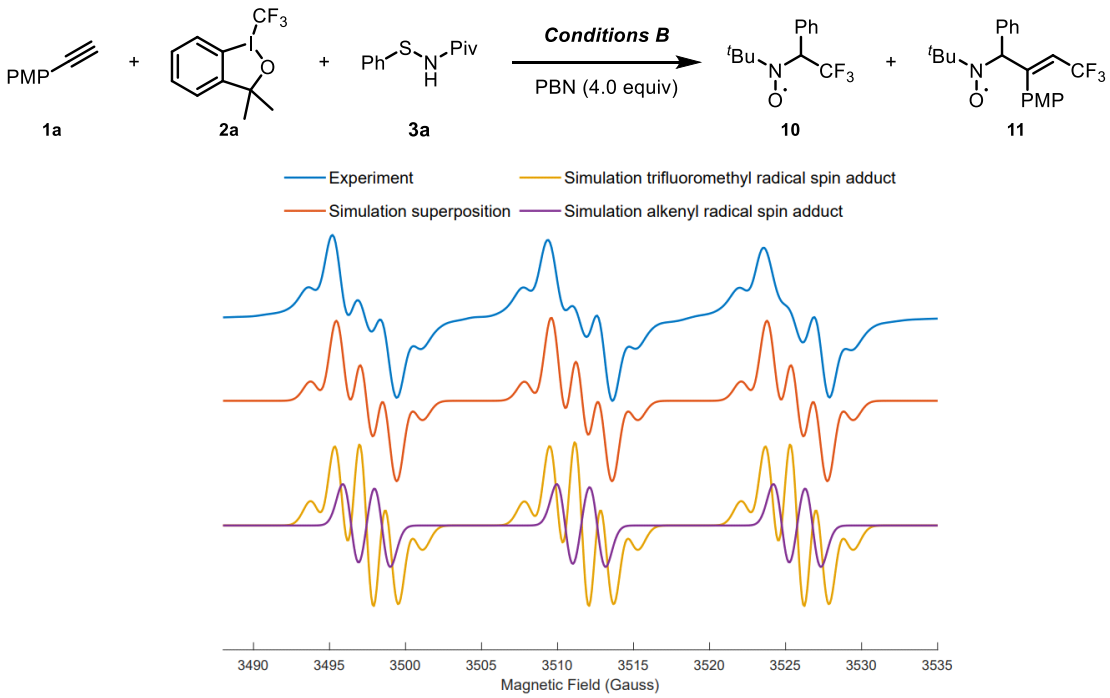
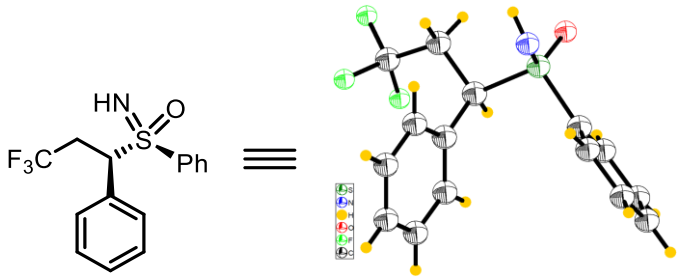


Figure S5. EPR spectra of trapped trifluoromethyl radical and alkenyl radical by PBN

6. Determination of the absolute configurations of 7

Experimental: Single Crystal **7** was grown by slow evaporation of concentrated solution in the mixed solution of DCM and *n*-Hexane in glass vial, which was then sealed by plug with needle on it.



7 **CCDC 2499850**

ORTEP plot of the crystal structure of 7 (50% ellipsoid probability)

X-ray crystallographic data of **7**

CCDC number	2499850
Bond precision	C-C = 0.0041 Å
Cell	a=5.93442(8) b=16.8551 (3) c=28.1750 (4) alpha=90 beta=90 gamma=90
Temperature	150 K
Volume	2818.21 (7)
Space group	P 21 21 21
Sum formula	$C_{15}H_{14}F_3NOS$
Mr	313.33
Dx, g cm-3	1.477
Z	8
Mu (mm-1)	2.356
F000	1296.0
h, k, lmax	7,21,35
Tmin, Tmax	0.441, 1.000
Correction method	# Reported T Limits: Tmin=0.441 Tmax=1.000
AbsCorr	MULTI-SCAN
Data completeness	1.66/0.96
Theta(max)	75.882
R(reflections)	0.0320 (5482)
wR2(reflections)	0.0853 (5640)
S	1.049

7. DFT calculations

7.1 Computational methods

All density functional theory (DFT) calculations were performed with Gaussian 16 program.[11] Geometry optimizations were performed using the (U)B3LYP functional,[12] employing the D3 version of Grimme's dispersion corrections[13] with Becke-Johnson damping.[14] The LANL2DZ basis set[15] was used for Cu and I, and the 6-31G(d) basis set was used for all other light atoms. After optimization, frequency calculations were performed at the same level of theory to characterize the stationary points as either minima (no imaginary frequencies) or saddle points (one imaginary frequency) on the potential energy surface, as well as to evaluate zero-point vibrational energies and thermodynamic corrections for free energies at 283.15 K, 1 atm. For all transition states, Intrinsic Reaction Coordinate (IRC)[16] calculations were performed to confirm that the transition state connects with its respective reactant and product. Single-point energies of optimized structures were calculated using the (U)PBE0 functionals[17] employing the D3 version of Grimme's dispersion corrections and Becke-Johnson damping with def2-TZVP basis set[18] was used for all atoms (assigned def2-ECP for I). SMD solvation model[19] (solvent = Acetonitrile) was used in single-point energy calculations to consider solvent effect. The final Gibbs free energy was calculated as the sum of Gibbs free energy correction (from frequency calculation) and the single point energy in solution. For each species, extensive conformational search was done and the reported value is from the conformer with the lowest Gibbs free energy. A wavefunction stability test at the same level of theory as the geometry optimizations was employed to ensure that the SCF-converged wavefunction was stable. Graphics of the transition states were rendered using CYLview[20]. The visualizations of energy barriers were performed by EnePro v1.6 script[21].

The reaction involving **1b**, **2a**, and **3k** was selected for computational analysis, and the energy profile were presented in **Figure S6** and **Figure S7**. The conformations of transition states and intermediates were carefully examined; the relative electronic

energy and Gibbs free energy of transition states and intermediates were listed in **Table S7.**

7.2 Gibbs energy profiles

The energy profile for the activation of the Togni reagent by the cationic Cu(I) complex is presented in **Figure S6**. The profile starts from **Int1**, in which Cu(I) is coordinated to the chiral ligand **L1** and substrate **3k**. Solvent-coordinated intermediates **CuL*2MeCN** and **CuL*MeCN** were also considered, with the latter being lower in relative Gibbs free energy. Given the complexity of solvent coordination for CuL*, only selected examples are provided here without detailed discussion. Following ligand exchange, **Int2** forms with a free energy increase of 1.7 kcal/mol. A subsequent single-electron transfer (SET) from **Int2** proceeds via transition state ^{OSS}**TS**$_{SET}$ with a free energy barrier of 17.3 kcal/mol, giving the Cu(II) species **Int3** and a trifluoromethyl radical (CF_3). The relative free energy of **Int3** is 2.9 kcal/mol higher than that of **Int2**. **3k** was then coordinated with copper in **Int3** to form the intermediate **Int4**.

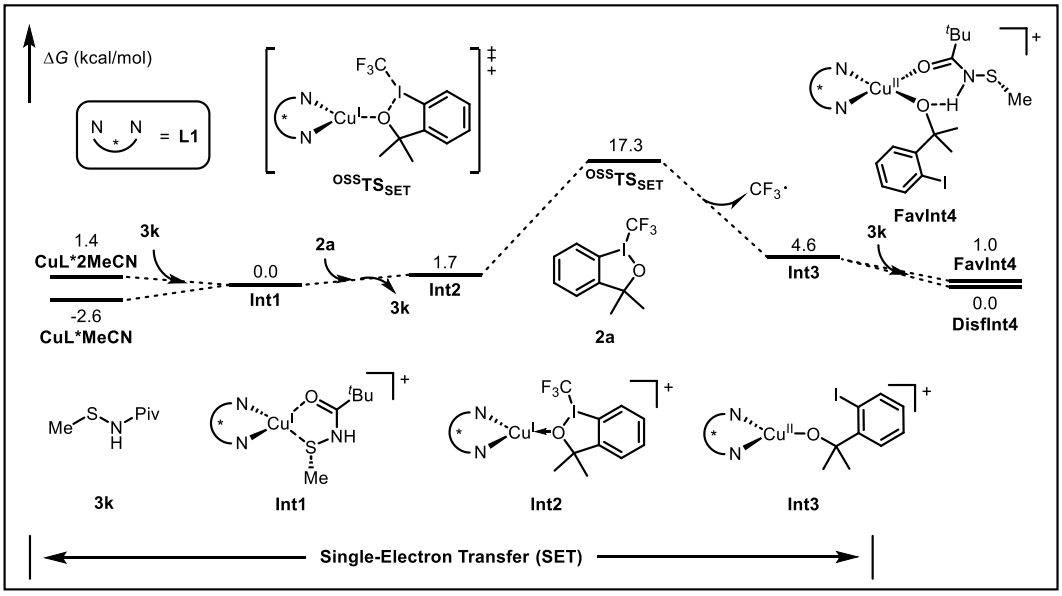


Figure S6. The energy profile for the activation of the Togni reagent

From the **Int4**, an O,S-chelation intermediate formation followed by an SH2 process involving an outer-sphere-generated radical directly attack was first considered.

However, numerous attempts to locate the transition state for this pathway failed. Instead, the O,S-chelated copper species appeared to directly lead to product formation. Subsequently, we scanned the distance between the alkenyl radical and the sulfur atom, starting from the proposed intermediate **IntO_S**. The potential energy was found to decrease as the carbon atom of the alkynyl radical approached the sulfur atom, indicating that a transition state for this C-S bond formation step cannot be located on the potential energy surface.

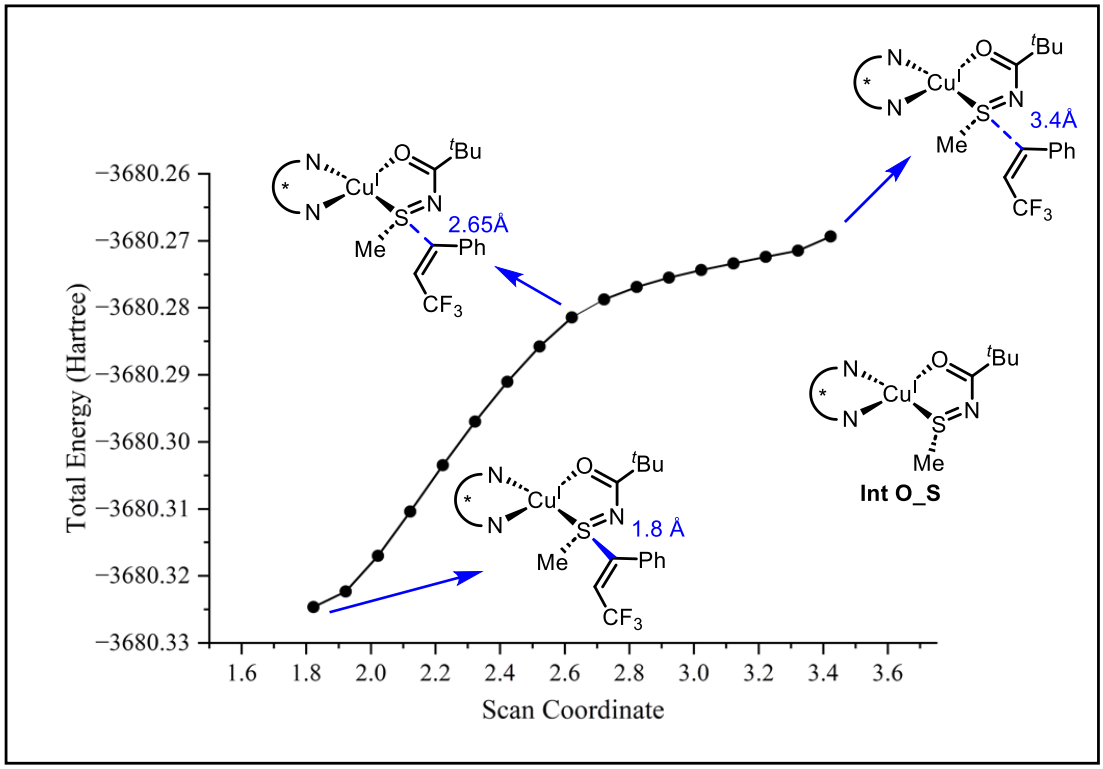


Figure S7. Electronic energy profile

We then considered a concerted hydrogen-atom transfer (HAT) and radical coupling (RC) process, and the energy profiles were given in **Figure S8**. The combination of **Int3** and **3k** leads to generation of intermediates: **FavInt4** and **DisfInt4**, which is endergonic by 3.6 kcal/mol and 4.6 kcal/mol, respectively. **Int4** subsequently undergoes concerted hydrogen atom transfer reaction (HAT) and radical coupling reaction (RC) to yield **Int5**. Among the pathways examined, the blue path via the transition states ^{OSS}**FavTS**$_{HAT\_RC}$**-2** exhibits the lowest energy barrier of 15.5 kcal/mol.

Under the Curtin-Hammett assumption, the cooper species with different coordination

modes are in rapid equilibrium before the insertion step. The Gibbs energies of the intermediates **Int5** were much lower than the corresponding transition states, hence the reverse reactions were considered unlikely under the reaction conditions and the enantioselectivities of the products were mainly determined by this step. The enantioselectivity was rationalized using the Curtin-Hammett principle, with the enantiomeric excess (ee) calculated as:

$$ee_{calc} = \frac{\exp(-\Delta\Delta G^{\ddagger}/RT) - 1)}{\exp(-\Delta\Delta G^{\ddagger}/RT) + 1)} = \frac{\exp\left(-(G^{\ddagger}_{Fav} - G^{\ddagger}_{Disf})/RT\right) - 1)}{\exp\left(-(G^{\ddagger}_{Fav} - G^{\ddagger}_{Disf})/RT\right) + 1)}$$

$G^{\ddagger}_{Fav}$ and $G^{\ddagger}_{Disf}$ correspond to the relative Gibbs energies of the lowest-energy transition states that produce the different enantiomers. **Figure S9** shows the relative energies of the competing transition states. With $\Delta\Delta G^{\ddagger} = 1.8\ kcal/mol$, the calculated $er_{calc} = 96{:}4$, which is consistent with the experimental value ($er_{exp} = 97.5{:}2.5$).

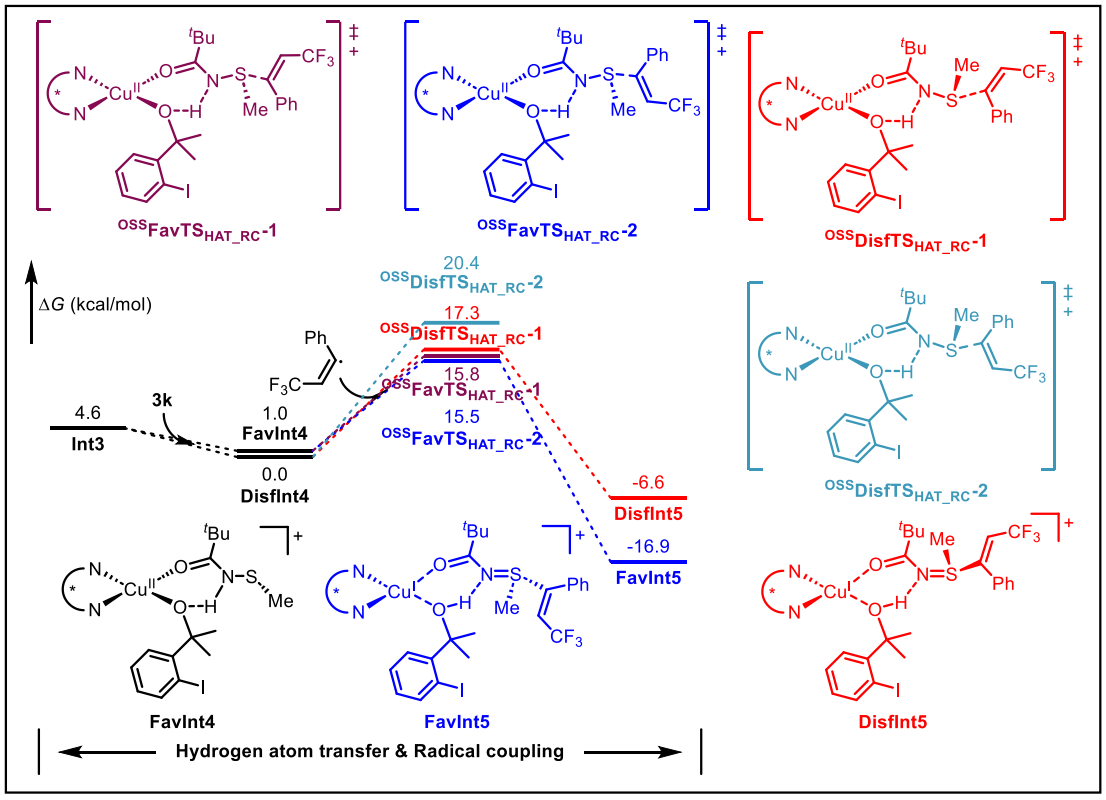


Figure S8. The energy profile of the hydrogen atom transfer and radical coupling

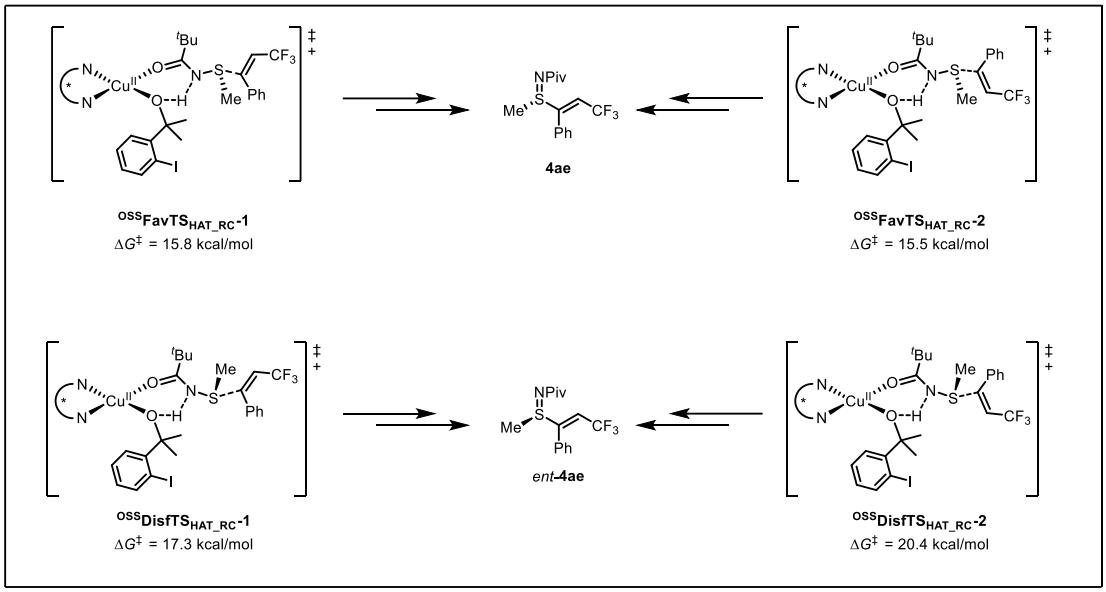


Figure S9. The relative energies of the competing transition states

In addition, Mulliken spin population analysis of **FavInt4** reveals a spin density of 0.00 on the N3 (the nitrogen of the sulfenamide **3k** portion), indicating that no nitrogen radical is generated in the sulfenamide (**3k**) portion of intermediate **FavInt4 (Figure S10)**.

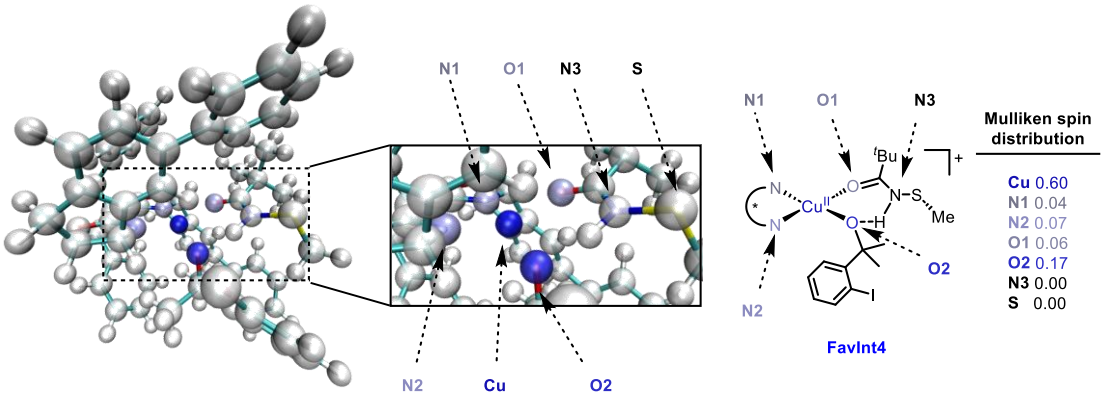


Figure S10. Mulliken spin density distribution of **FavInt4**

Furthermore, analysis of transition state **^{OSS}FavTS$_{HAT_RC}$-2** shows spin densities of -0.47 on the copper center, 0.07 on the sulfenamide S atom, and -0.39 on the alkenyl radical C1 position. These results suggest that C−S bond formation occurs via a HAT-induced concerted radical−radical coupling, and that the radical coupling step follows an outer-sphere pathway (i.e., the two radical centers couple directly without direct

metal coordination) (**Figure S11)**.

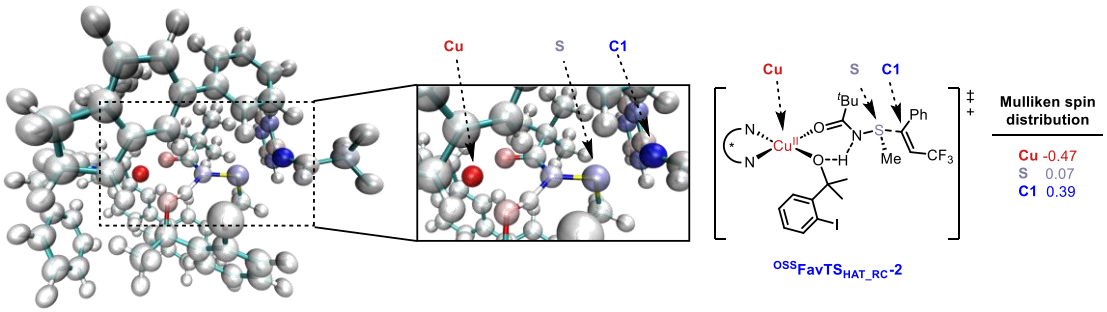


Figure S11. Mulliken spin density distribution of ^{OSS}**FavTS$_{HAT_RC}$-2**

According to the mechanism studies and the DFT calculations, a proposed catalytic cycle was given (**Figure S12**).

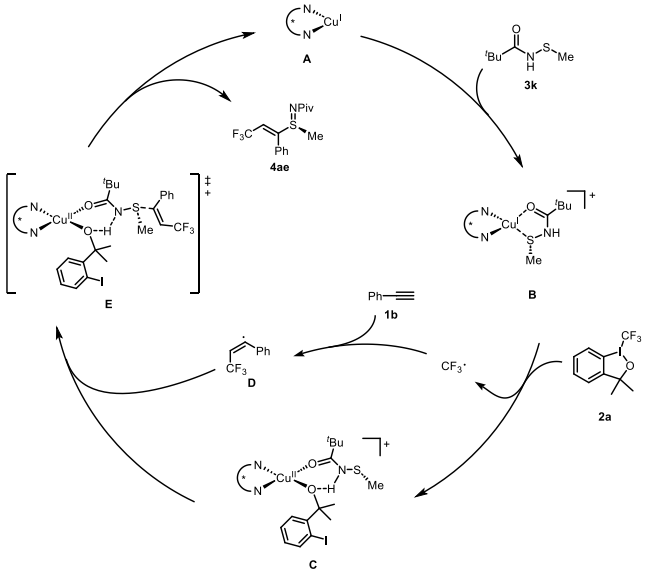


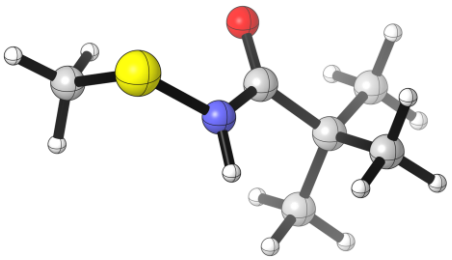
Figure S12. Proposed catalytic cycle

Cartesian coordinates and visualization

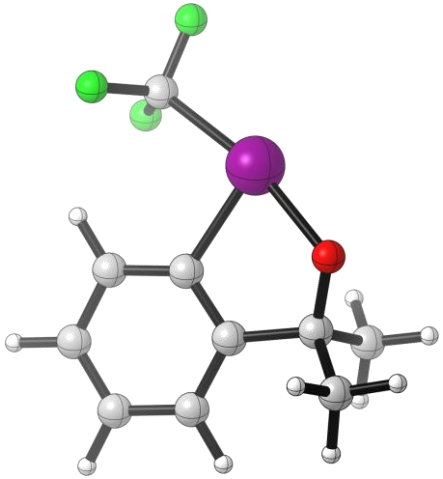
Name (in manuscript)	Name (in SI)	Electronic Energy (a.u.)	Gibbs Energy (a.u.)	Relative Gibbs Energy (kcal/mol)
3k	**3k**	**-764.2581960**	**-764.1090204**	
2a	**2a**	**-1058.9890040**	**-1058.8514767**	
	MeCN	**-3845.2442490**	**-3844.5546040**	
	CF_3·	**-337.3903380**	**-337.4025837**	
	Alkene_radical	**-645.6137041**	**-645.5276682**	
CuL*2MeCN	**CuL*2MeCN**	**-3977.9124909**	**-3977.1791540**	**1.4**
CuL*MeCN	**CuL*MeCN**	**-3845.2442490**	**-3844.5546040**	**-2.6**
Int1	**Int1**	**-4476.8529318**	**-4476.0287661**	**0.0**
Int2	**Int2**	**-4771.5841802**	**-4770.7685196**	**1.7**
^{TS}SET	**^{OSS}TS$_{SET}$**	**-4771.5547753**	**-4770.7436057**	**17.3**
Int3	**Int3**	**-4434.1649077**	**-4433.3613094**	**4.6**
FavInt4	**FavInt4**	**-5198.4579108**	**-5197.4760510**	**1.0**
DisfInt4	**DisfInt4**	**-5198.4598688**	**-5197.4777328**	**0.0**
	^{OSS}FavTS$_{HAT_RC}$-1	**-5844.0728403**	**-5842.9800952**	**15.8**
FavTS$_{HAT_RC}$	**^{OSS}FavTS$_{HAT_RC}$-2**	**-5844.0720440**	**-5842.9805477**	**15.5**
DisfTS$_{HAT_RC}$	**^{OSS}DisfTS$_{HAT_RC}$-1**	**-5844.0659480**	**-5842.9778307**	**17.3**
	^{OSS}DisfTS$_{HAT_RC}$-2	**-5844.0642992**	**-5842.9728027**	**20.4**
FavInt5	**FavInt5**	**-5844.1282555**	**-5843.0323204**	**-16.9**
DisfInt5	**DisfInt5**	**-5844.1094110**	**-5843.0158148**	**-6.6**

Table S7. Electronic energy and Gibbs energy of transition states and intermediates

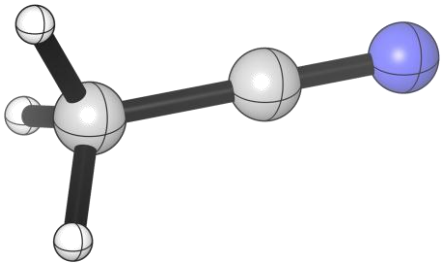
3k



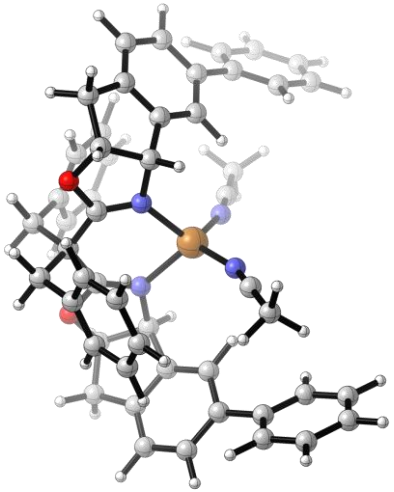
2a



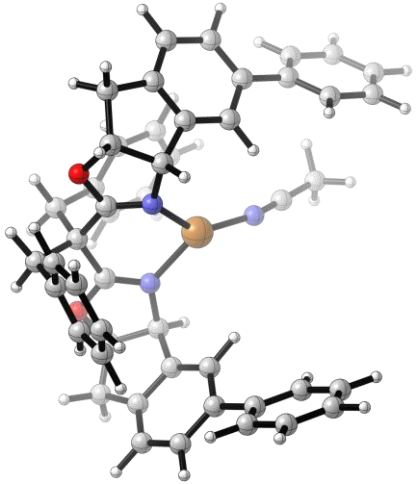
MeCN



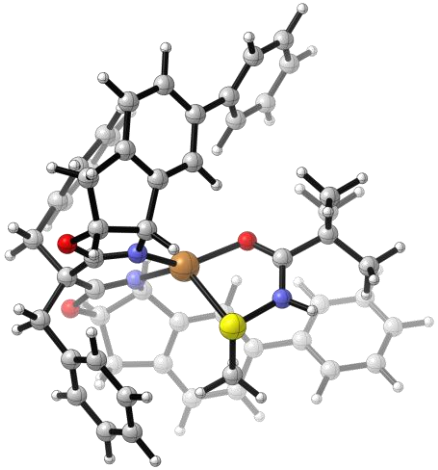
CuL*2MeCN



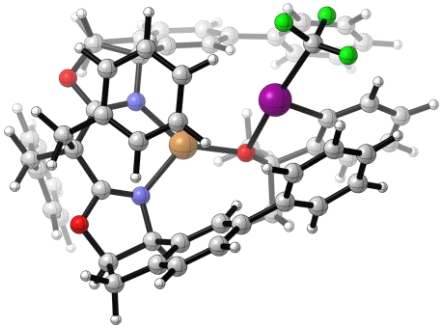
CuL*MeCN



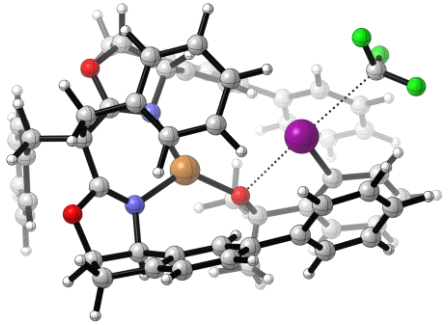
Int1



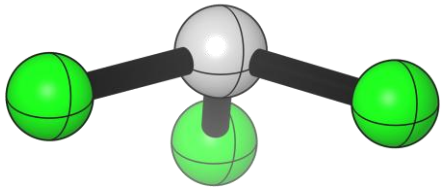
Int2



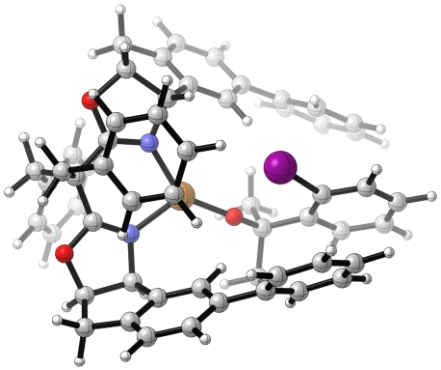
$^{OSS}TS_{SET}$



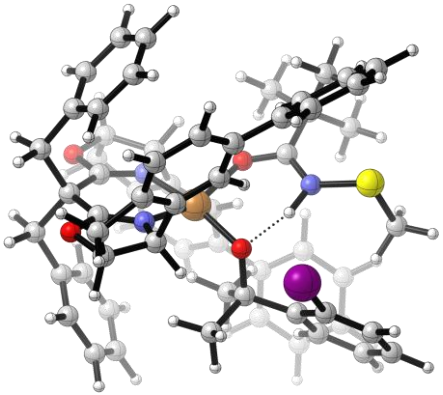
CF_3 radical



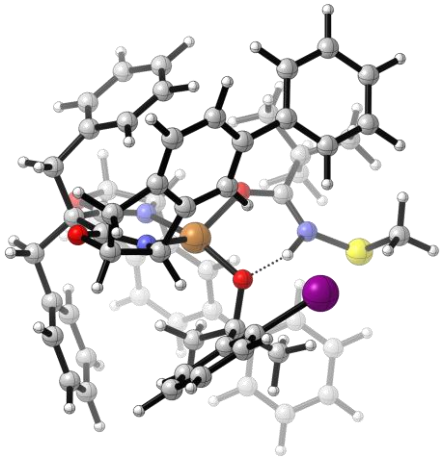
Int3



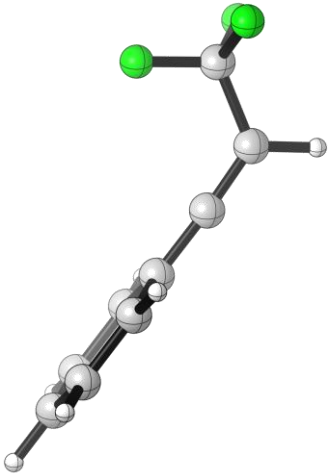
FavInt4



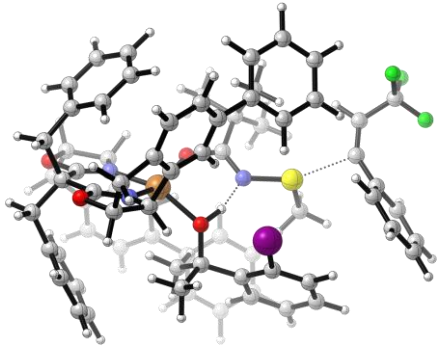
DisfInt4



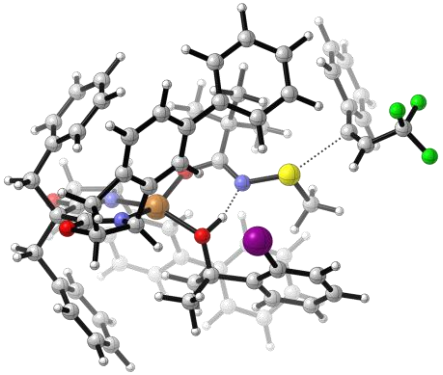
Alkene_radical



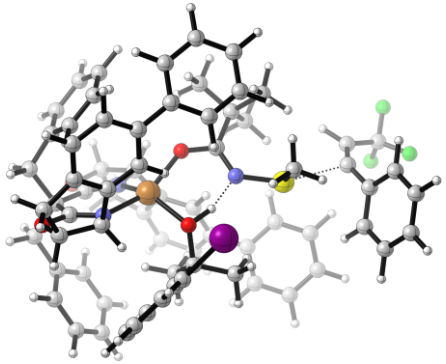
$^{OSS}FavTS_{HAT\_RC}$-1

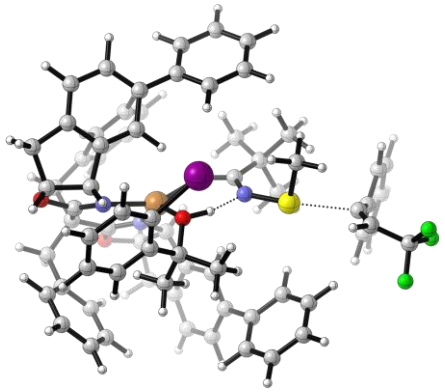
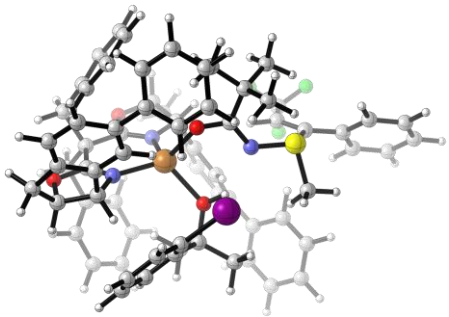
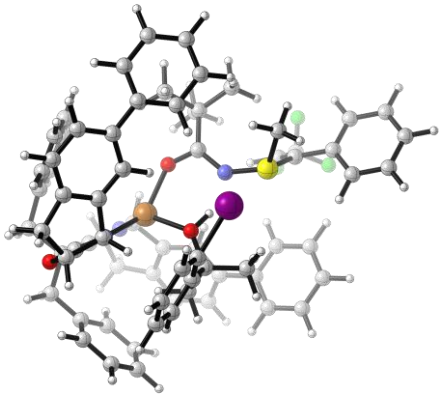


$^{OSS}FavTS_{HAT\_RC}$-2



$^{OSS}DisfTS_{HAT\_RC}$-1



$^{OSS}DisfTS_{HAT\_RC}$-2	FavInt5	DisfInt5
		

Cartesian Coordinates

3k

C	-0.22251300	-0.29168800	0.32576700
O	0.09315900	-1.34927200	0.84339400
N	0.70754900	0.69543700	0.04736500
H	0.42444100	1.50075500	-0.49412900
C	-1.67073300	0.04783700	-0.09359700
C	-2.12202700	1.36754600	0.56400600
C	-1.73889700	0.16999700	-1.63088400
C	-2.58323400	-1.09633800	0.36903000
H	-2.03561700	1.31271300	1.65432700
H	-1.53592200	2.22854900	0.22402600
H	-3.17093600	1.56527800	0.31568300
H	-1.38495400	-0.74757500	-2.11329800
H	-2.77506400	0.34007000	-1.94443500
H	-1.13866600	1.00471200	-2.01091000
H	-3.61769100	-0.88714300	0.07400600
H	-2.27566000	-2.04700100	-0.07391300
H	-2.54561700	-1.21281100	1.45567500
S	2.37677000	0.55196400	0.40929100
C	2.88805900	-0.71105000	-0.80515400
H	3.95711600	-0.88134700	-0.64213400
H	2.33901900	-1.63573600	-0.61787700
H	2.72918800	-0.36359300	-1.82938900

2a

C	0.52029700	0.82366400	-0.11901000
C	1.85976300	0.50451600	-0.00061300
C	2.75552000	1.57903600	0.07741200
C	2.29902500	2.89507100	0.01478100
C	0.93668400	3.16400100	-0.12379200
C	0.01763900	2.11320000	-0.18770900
C	2.27839600	-0.97882400	0.08288500
H	3.81713200	1.38143600	0.18618500
H	3.01024700	3.71397200	0.06934400
H	0.57992600	4.18752500	-0.18716900
H	-1.03710700	2.31736700	-0.30432600
O	1.26629400	-1.78086900	-0.45205300
I	-0.72491300	-0.96835500	-0.16428200
C	3.53742000	-1.23852200	-0.76048900
H	3.35723900	-0.94850200	-1.79942400
H	4.41189700	-0.69690600	-0.38325000
H	3.75803200	-2.30946700	-0.73309500
C	2.53263300	-1.32741100	1.56607700
H	1.62712400	-1.15903700	2.15944000
H	2.80127100	-2.38572000	1.64284600
H	3.33846500	-0.72233900	1.99730100
C	-2.61387700	0.32789300	0.13866500
F	-3.62106900	-0.55926300	0.27730000
F	-2.92052200	1.13121000	-0.90482900
F	-2.58231800	1.09646300	1.24378000

MeCN

C	0.00000000	0.00000000	0.28035500
C	0.00000000	0.00000000	-1.18073600
H	0.00000000	1.02666800	-1.56029000
H	0.88912100	-0.51333400	-1.56029000
H	-0.88912100	-0.51333400	-1.56029000
N	0.00000000	0.00000000	1.44045100

CF3 •

C	0.00000000	0.00000000	0.32922500
F	0.00000000	1.26431500	-0.07316100
F	-1.09492900	-0.63215700	-0.07316100
F	1.09492900	-0.63215700	-0.07316100

Alkene_radical

C	3.18242300	1.21344000	0.15547700
C	1.84210900	1.22868400	-0.18736200
C	1.12947500	0.00000100	-0.36887900
C	1.84211100	-1.22868300	-0.18737600
C	3.18242500	-1.21344000	0.15546300
C	3.86500400	0.00000000	0.32948300
H	3.70889000	2.15380200	0.29182600
H	1.31134300	2.16543300	-0.32048600
H	1.31134700	-2.16543100	-0.32051100
H	3.70889400	-2.15380300	0.29180100
H	4.91659300	-0.00000100	0.59862300
C	-0.19683000	0.00000100	-0.71575100
C	-1.47214800	0.00000300	-0.97472900
H	-1.87458900	0.00000700	-1.99052700
C	-2.53333000	0.00000000	0.09475300
F	-2.01604000	-0.00000900	1.33513600
F	-3.33252800	1.08555200	-0.02073900
F	-3.33253300	-1.08554800	-0.02075300

CuL*2MeCN

C	1.49943500	-0.51383200	-2.50840300
C	1.63129400	-1.92280200	-3.15423400
C	0.62682000	-2.01850200	-1.11383000
H	0.98544500	-2.09146600	-4.01757400
C	-0.00003300	-2.82687100	-0.00012900
C	-0.62684000	-2.01870800	1.11374900
C	-1.63142800	-1.92326400	3.15409500
C	-1.49965400	-0.51421200	2.50841100
H	-0.98568000	-2.09187500	4.01752000
H	-0.95603600	0.21101600	3.12027200
C	1.12015700	-3.72442400	0.63877100
H	0.63201200	-4.41185600	1.33321000
H	1.56280900	-4.31699400	-0.16543200
C	-1.12026000	-3.72418100	-0.63927200
H	-0.63212700	-4.41161700	-1.33373000
H	-1.56309400	-4.31678800	0.16479700

O	1.14616300	-2.80069100	-2.09456300
O	-1.14604900	-2.80100800	2.09445500
N	0.73933700	-0.75545500	-1.26395200
N	-0.73952900	-0.75568800	1.26392200
H	0.95580700	0.21144300	-3.12020000
C	3.12144300	-2.17313500	-3.43775400
H	3.41420300	-3.17971500	-3.12108900
C	3.82851000	-1.06839100	-2.68376100
C	2.92610600	-0.11092000	-2.21231300
C	3.35460500	0.99378200	-1.48883300
C	4.72019800	1.15068000	-1.20671400
C	5.62571800	0.18919300	-1.69477200
C	5.19100100	-0.91395800	-2.43000800
H	2.63310400	1.70089100	-1.09664100
H	6.68749200	0.32035100	-1.51053000
H	5.91130400	-1.63922700	-2.79787500
H	3.31547900	-2.10944800	-4.51582100
C	-3.35482100	0.99346100	1.48901000
C	-4.72041100	1.15036100	1.20687400
C	-5.62591800	0.18881300	1.69481900
C	-5.19118500	-0.91441100	2.42995900
C	-3.82869200	-1.06887600	2.68366800
C	-2.92631000	-0.11131500	2.21235000
H	-2.63334000	1.70064400	1.09691600
H	-6.68769600	0.31997600	1.51060000
H	-5.91149700	-1.63970900	2.79775300
C	-5.18826300	2.28842900	0.38131800
C	-6.23078800	2.12373100	-0.54645200
C	-4.59136400	3.55511500	0.49468500
C	-6.66536000	3.19011600	-1.33229300
H	-6.69331200	1.14787900	-0.66270200
C	-5.02544900	4.62301300	-0.29046600
H	-3.80383800	3.71027600	1.22593200
C	-6.06437100	4.44509300	-1.20824300
H	-7.47308800	3.04117900	-2.04294200
H	-4.56259300	5.59877400	-0.17440000
H	-6.40792800	5.27829800	-1.81384000
C	5.18809500	2.28869300	-0.38110400
C	4.59113100	3.55536400	-0.49429200
C	6.23075800	2.12397200	0.54651300
C	5.02529300	4.62322400	0.29087300
H	3.80348600	3.71055200	-1.22540300
C	6.66542000	3.19031900	1.33234800
H	6.69331600	1.14812400	0.66265000
C	6.06436800	4.44528500	1.20847100
H	4.56237400	5.59897200	0.17495100
H	7.47325200	3.04136200	2.04287400
H	6.40798200	5.27846000	1.81407800
C	-3.12160500	-2.17376400	3.43743400
H	-3.31578100	-2.11053100	4.51549700
H	-3.41424400	-3.18024300	3.12033500
C	2.17195300	-2.90208100	1.34844800

C	2.06606100	-2.63394300	2.71970200
C	3.24026100	-2.34364000	0.63649400
C	3.00210300	-1.82336700	3.36237500
H	1.25433000	-3.07977700	3.28759200
C	4.17674400	-1.52956500	1.27241800
H	3.34864400	-2.55101600	-0.42231000
C	4.06030400	-1.26856600	2.63884200
H	2.91685400	-1.64227200	4.43022000
H	4.99668800	-1.11281000	0.69760800
H	4.80732200	-0.66234700	3.14460400
C	-2.17182100	-2.90160300	-1.34902400
C	-3.24010800	-2.34301000	-0.63717000
C	-2.06572300	-2.63341900	-2.72025500
C	-4.17637900	-1.52873100	-1.27315900
H	-3.34864700	-2.55043400	0.42160300
C	-3.00154500	-1.82263900	-3.36299400
H	-1.25400800	-3.07937800	-3.28806600
C	-4.05972200	-1.26767500	-2.63954900
H	-4.99631100	-1.11185800	-0.69841800
H	-2.91613800	-1.64147800	-4.43081500
H	-4.80657300	-0.66129000	-3.14536200
Cu	-0.00030800	0.71405000	0.00035700
C	-2.22314900	2.02334800	-1.82465600
N	-1.33386600	1.72824300	-1.14312700
C	-3.35122100	2.38267100	-2.66906800
H	-3.81224600	3.30465500	-2.30384300
H	-3.01956700	2.51965900	-3.70276100
H	-4.09442300	1.58297000	-2.62859500
C	2.22369300	2.02252200	1.82530700
N	1.33440300	1.72710700	1.14393400
C	3.35167300	2.38217500	2.66970200
H	4.09454900	1.58212100	2.63027300
H	3.81322100	3.30357900	2.30367800
H	3.01974800	2.52032900	3.70315100

CuL*MeCN

C	1.89955600	-0.17344000	-2.54287200
C	2.47523300	-1.48708800	-3.13949900
C	1.27217600	-1.87428600	-1.24537700
H	2.00767600	-1.81953900	-4.06786800
C	0.69281400	-2.81054300	-0.21140400
C	-0.03726400	-2.12447900	0.92527400
C	-1.05819700	-2.22509800	2.95404200
C	-1.10963300	-0.78428100	2.36679900
H	-0.41818100	-2.33419400	3.82986300
H	-0.62294400	-0.03060200	2.99135600
C	1.85442700	-3.65481100	0.42142100
H	1.39885600	-4.46962300	0.98782300
H	2.42700100	-4.09524700	-0.39769400
C	-0.33774100	-3.73876800	-0.96196100
H	0.22518100	-4.31517800	-1.70111700
H	-0.74172200	-4.43815700	-0.22538600

O	2.11142400	-2.47317800	-2.11709100
O	-0.42062800	-2.98742300	1.88567300
N	1.02837100	-0.63307600	-1.44217300
N	-0.36048000	-0.89317900	1.08910900
H	1.31295000	0.42132200	-3.24810200
C	3.99976500	-1.32939100	-3.22786700
H	4.50832600	-2.24763400	-2.91650800
C	4.28944800	-0.13943700	-2.33918500
C	3.11658000	0.53781600	-1.99406100
C	3.13586000	1.64116800	-1.15072200
C	4.35850500	2.09773300	-0.63381900
C	5.53869100	1.42449300	-1.00559200
C	5.51336400	0.31278800	-1.84781700
H	2.20805700	2.11793400	-0.84728500
H	6.49118100	1.78974100	-0.63462600
H	6.43908500	-0.19138800	-2.11055200
H	4.29256100	-1.13934000	-4.26840100
C	-3.15986600	0.59539800	1.55835100
C	-4.54148900	0.61474400	1.31200000
C	-5.30824000	-0.50646300	1.68191200
C	-4.72522700	-1.62146500	2.28531000
C	-3.34985600	-1.63090100	2.51341000
C	-2.57968400	-0.52728400	2.13509700
H	-2.54602900	1.43911500	1.26417200
H	-6.38202500	-0.48838900	1.52393300
H	-5.34396000	-2.46432800	2.57979100
C	-5.17728400	1.78876700	0.66876300
C	-6.21845600	1.62524300	-0.26109700
C	-4.76252800	3.09428000	0.98183400
C	-6.83464300	2.73136000	-0.84762600
H	-6.54200100	0.62409200	-0.53084500
C	-5.37968700	4.20037700	0.39757500
H	-3.98083000	3.24252800	1.72093200
C	-6.41985600	4.02418400	-0.51775800
H	-7.64192400	2.58304500	-1.55893700
H	-5.06103500	5.20150800	0.67367000
H	-6.90813400	4.88519900	-0.96399400
C	4.39853100	3.24230400	0.30494700
C	3.54927000	4.34657700	0.12927200
C	5.27791200	3.24127100	1.39941900
C	3.57847200	5.41713100	1.02098700
H	2.88682400	4.37884000	-0.73125300
C	5.30722000	4.31157900	2.29126300
H	5.92574600	2.38526200	1.56470200
C	4.45732000	5.40341800	2.10573600
H	2.92410400	6.26931300	0.86138800
H	5.99045000	4.29048900	3.13525400
H	4.48234000	6.23872100	2.79906900
C	-2.50554700	-2.69989000	3.17160600
H	-2.72513900	-2.77352400	4.24363800
H	-2.65131000	-3.69960700	2.74869200
C	2.72933300	-2.80748400	1.32152400

C	2.56929600	-2.85127700	2.71271000
C	3.65530800	-1.90513700	0.78185100
C	3.29650400	-1.99607300	3.54194400
H	1.87284800	-3.56348800	3.14587900
C	4.37685100	-1.04293200	1.60623600
H	3.82043600	-1.87243300	-0.28847600
C	4.19352400	-1.08021900	2.98947800
H	3.16647900	-2.04943000	4.61915800
H	5.07958300	-0.34657500	1.16080300
H	4.75457900	-0.40925800	3.63313600
C	-1.43527900	-2.93355600	-1.61642200
C	-2.55342200	-2.52604200	-0.87847700
C	-1.30438200	-2.48548500	-2.93730300
C	-3.50335200	-1.66763400	-1.43149800
H	-2.68272300	-2.87598500	0.14012000
C	-2.25479800	-1.63242000	-3.49868500
H	-0.45252900	-2.81128300	-3.52912100
C	-3.35153700	-1.21280800	-2.74228600
H	-4.35482000	-1.36005700	-0.83408500
H	-2.14341700	-1.30320300	-4.52788700
H	-4.09507900	-0.55228800	-3.17991300
Cu	-0.44147600	0.37030700	-0.48267700
C	-2.43444400	2.33202700	-1.69623200
N	-1.58992700	1.72749800	-1.18243200
C	-3.50226500	3.07437200	-2.34434700
H	-3.32519800	3.12292400	-3.42315100
H	-4.45886700	2.58104800	-2.14596000
H	-3.55339900	4.08682700	-1.93591000

Int1

C	-0.88255900	-1.57964600	2.36254100
C	-0.76471700	-3.04641900	2.85720500
C	0.75365500	-2.61347600	1.23423000
H	-0.55143400	-3.14515000	3.92074100
C	2.01488500	-2.96768900	0.47309400
C	2.37717400	-2.01485800	-0.64375000
C	3.72742700	-1.39106500	-2.37141300
C	2.56028100	-0.38748500	-2.15534900
H	3.65614300	-1.99393000	-3.27853900
H	1.94237500	-0.21830400	-3.04233800
C	1.88701500	-4.40364000	-0.13661600
H	2.82775200	-4.62596100	-0.64719600
H	1.78472100	-5.10670500	0.69275600
C	3.17968100	-2.92844600	1.54077200
H	3.01072600	-3.75568400	2.23428600
H	4.11478600	-3.11883400	1.00853400
O	0.41378800	-3.54423800	2.15676400
O	3.55372100	-2.31449600	-1.24817400
N	0.06548500	-1.53251600	1.22505100
N	1.73650000	-1.00900900	-1.10179300
H	-0.54912300	-0.83172200	3.08892300
C	-2.06265200	-3.77266200	2.43022000

H	-1.84570600	-4.48712200	1.63056000
C	-2.97181200	-2.65998600	1.95487500
C	-2.32022300	-1.42312000	1.95227600
C	-2.97557000	-0.25455900	1.57712300
C	-4.32010900	-0.31999900	1.17387300
C	-4.96671700	-1.57036800	1.16828800
C	-4.30578900	-2.73588900	1.55775600
H	-2.44628000	0.69353200	1.55789100
H	-6.01194400	-1.61874700	0.87868700
H	-4.83582800	-3.68425700	1.56380800
H	-2.49888300	-4.33885800	3.25990900
C	2.62397900	1.96564400	-1.06646300
C	3.41460900	2.98703500	-0.52028300
C	4.81565600	2.87293200	-0.59675800
C	5.42599100	1.75037800	-1.15880800
C	4.62813900	0.72407800	-1.66448700
C	3.23783800	0.85633400	-1.63233800
H	1.54263400	2.03545000	-1.01686200
H	5.43200300	3.65478800	-0.16340800
H	6.50939900	1.67155500	-1.17286900
C	2.77803700	4.12151000	0.18755300
C	3.25111900	5.43386400	0.03843400
C	1.69379900	3.88732900	1.05067900
C	2.65487900	6.48703000	0.73045000
H	4.07722700	5.62998900	-0.63905400
C	1.10493400	4.94131900	1.74817000
H	1.33000000	2.87368600	1.18800000
C	1.58104800	6.24428000	1.58910300
H	3.02768000	7.49829600	0.59715000
H	0.28015800	4.74326500	2.42705100
H	1.12216100	7.06400000	2.13381000
C	-5.04124000	0.89835600	0.73620900
C	-4.95463700	2.08937600	1.47304600
C	-5.83695800	0.88046900	-0.42063200
C	-5.65031300	3.22878700	1.06891800
H	-4.36300800	2.10945100	2.38382000
C	-6.52823900	2.02113300	-0.82814400
H	-5.90645600	-0.03265600	-1.00520500
C	-6.43802400	3.19941000	-0.08332700
H	-5.58439400	4.13733200	1.66017500
H	-7.13987900	1.98952500	-1.72521000
H	-6.98224700	4.08553100	-0.39544800
C	5.04457600	-0.60533100	-2.25758000
H	5.49380700	-0.48556500	-3.25148200
H	5.77099600	-1.14852100	-1.64397900
C	0.71114800	-4.53297200	-1.07846100
C	0.75623100	-4.00573800	-2.37699200
C	-0.46672800	-5.15902300	-0.65409900
C	-0.35310100	-4.08169400	-3.21879700
H	1.67419000	-3.55632200	-2.74239300
C	-1.57959300	-5.24196600	-1.49278800
H	-0.49887400	-5.60352100	0.33585800

C	-1.52730300	-4.69812100	-2.77755700
H	-0.29511600	-3.67842900	-4.22567700
H	-2.47903300	-5.74475000	-1.14926300
H	-2.38577200	-4.77316700	-3.43870900
C	3.21305400	-1.60952200	2.27768100
C	3.79957200	-0.47898300	1.69726800
C	2.55938500	-1.47048200	3.50923400
C	3.70314800	0.76968900	2.31142900
H	4.33213600	-0.56815900	0.75665100
C	2.46252000	-0.22404500	4.12860700
H	2.12248200	-2.34634500	3.98198600
C	3.02313200	0.90291100	3.52307400
H	4.15910900	1.63345400	1.84085800
H	1.95949100	-0.13461700	5.08750600
H	2.94663200	1.87592600	3.99920300
Cu	0.01143900	-0.23961700	-0.31560700
N	-2.01499100	1.16958700	-2.23129100
S	-1.45973000	-0.45429600	-2.43069300
C	-1.55439000	2.02151300	-1.26993300
O	-0.77987600	1.64167800	-0.37571000
C	-1.95055400	3.49635000	-1.38063800
C	-0.75952600	4.20579300	-2.07116200
H	-0.99039800	5.27037200	-2.18049500
H	0.15147300	4.11602500	-1.47302900
H	-0.57041200	3.79580300	-3.07004400
C	-2.12838100	4.05977000	0.03952100
H	-1.22241900	3.91539000	0.62840100
H	-2.33293200	5.13345800	-0.02239000
H	-2.96789400	3.58000300	0.54850700
C	-3.23985500	3.71040000	-2.19274000
H	-4.07641200	3.12916000	-1.79237400
H	-3.51929300	4.76707700	-2.14533100
H	-3.11120200	3.47546000	-3.25770900
C	-2.90321300	-1.41279700	-1.86585600
H	-3.75109900	-1.26768000	-2.53913900
H	-2.58109000	-2.45726700	-1.90170300
H	-3.15987100	-1.14128200	-0.84509100
H	-2.60142600	1.54839600	-2.96318900

Int2

C	-2.58476100	-2.12805800	-2.09132700
C	-3.99375200	-2.77905200	-1.97720200
C	-3.69445100	-1.14116100	-0.42421200
H	-4.67540300	-2.54787600	-2.79762900
C	-4.18138100	-0.37975400	0.78874400
C	-3.30472900	0.77297700	1.22007400
C	-2.90856200	2.61388700	2.46067800
C	-1.58133600	1.97976800	1.98644200
H	-2.98644100	2.74804900	3.53868300
H	-1.02228100	1.45552700	2.76797300
C	-4.16628000	-1.39111400	2.01686700
H	-4.77436600	-0.93888600	2.80470000

H	-4.67071100	-2.30240500	1.68560400
C	-5.64453800	0.10456300	0.52887100
H	-6.24208200	-0.77838000	0.28977300
H	-6.02507800	0.51831900	1.46465500
O	-4.54029300	-2.13373400	-0.78678800
O	-3.90179500	1.60955100	2.09751700
N	-2.61714900	-1.01826100	-1.10529000
N	-2.04567500	0.93990000	1.02989600
H	-2.35704600	-1.72112000	-3.08002900
C	-3.80346000	-4.28406000	-1.73280100
H	-4.47852700	-4.63892900	-0.94730800
C	-2.33770900	-4.41261400	-1.38368500
C	-1.64248800	-3.22936800	-1.65294300
C	-0.27680800	-3.12659700	-1.42213200
C	0.41848700	-4.22313000	-0.88900600
C	-0.28631100	-5.40611800	-0.60429700
C	-1.65578900	-5.50921900	-0.85560300
H	0.23988200	-2.18697600	-1.57856900
H	0.24999800	-6.25915900	-0.19943300
H	-2.17930100	-6.43595600	-0.63838000
H	-4.04822900	-4.84603800	-2.64286800
C	0.50705000	3.12670400	0.99215600
C	1.05140500	4.27113400	0.38940300
C	0.21376100	5.38610700	0.20187000
C	-1.12789400	5.37113300	0.59401100
C	-1.65592800	4.22055400	1.17778100
C	-0.82637800	3.11154800	1.36428500
H	1.11933200	2.24455000	1.13159800
H	0.62768200	6.28982800	-0.23460900
H	-1.74193200	6.25577200	0.45052000
C	2.45717800	4.24866900	-0.07617100
C	2.83148400	4.88841700	-1.26842100
C	3.43312100	3.52377800	0.62768200
C	4.13881100	4.80188400	-1.74364800
H	2.08472000	5.42899400	-1.84226300
C	4.73854300	3.43592900	0.15188100
H	3.17392300	3.04100800	1.56467300
C	5.09648100	4.07235100	-1.03755700
H	4.40720700	5.29801100	-2.67184300
H	5.47514900	2.86987100	0.71330000
H	6.11346000	4.00073800	-1.41078000
C	1.86379100	-4.08112000	-0.59245900
C	2.71565300	-3.44434700	-1.50866200
C	2.40114700	-4.51882800	0.62843700
C	4.06103400	-3.23780100	-1.21122500
H	2.31863000	-3.12762400	-2.46754000
C	3.74443800	-4.30016600	0.93365200
H	1.75678700	-5.01234500	1.35083200
C	4.57820200	-3.65666200	0.01606900
H	4.70310400	-2.74582500	-1.93527000
H	4.14096800	-4.63216900	1.88865600
H	5.62419900	-3.49042100	0.25440000

C	-3.06126300	3.93992000	1.67137900
H	-3.46736800	4.74369500	2.29352100
H	-3.75338300	3.79280300	0.83427800
C	-2.77234900	-1.67193900	2.52662000
C	-2.28194200	-0.97811100	3.64114800
C	-1.91010200	-2.53799300	1.84338000
C	-0.95257400	-1.11337700	4.04227600
H	-2.94689000	-0.31593300	4.19016200
C	-0.57730900	-2.67031400	2.23588200
H	-2.26990200	-3.10977900	0.99557300
C	-0.09047700	-1.95053600	3.32944100
H	-0.59258600	-0.57318200	4.91339300
H	0.07574200	-3.33728600	1.68559500
H	0.94609000	-2.05608900	3.63662400
C	-5.73654000	1.13738600	-0.57239800
C	-5.85760600	2.49693200	-0.25846000
C	-5.67648300	0.76555700	-1.92237900
C	-5.88805500	3.46406400	-1.26422500
H	-5.93762000	2.79409400	0.78247000
C	-5.70256700	1.72937200	-2.93030600
H	-5.63409000	-0.28650100	-2.18668600
C	-5.79939100	3.08337700	-2.60394500
H	-5.99258500	4.51291300	-1.00141700
H	-5.66223900	1.42228200	-3.97144100
H	-5.82547100	3.83363200	-3.38840200
Cu	-0.98135000	0.08466700	-0.41831000
C	3.54391600	0.16134600	-0.91728900
C	2.90110800	0.56619100	-2.07498500
C	3.73377500	1.02326400	-3.10895700
C	5.11903300	1.02869400	-2.97776000
C	5.71600200	0.56816200	-1.80376500
C	4.92101700	0.12842400	-0.74622900
C	1.37481300	0.49404300	-2.25135000
H	3.28207300	1.37217700	-4.03170900
H	5.73455500	1.38400800	-3.79791600
H	6.79630100	0.55147900	-1.70067600
H	5.38015900	-0.23506800	0.16156900
O	0.82248400	-0.17994000	-1.13389800
I	2.21436800	-0.48620100	0.67136700
C	0.79120100	1.90890000	-2.36990400
H	0.98004700	2.47797700	-1.46156800
H	1.22501500	2.45493800	-3.21375500
H	-0.29260700	1.84158500	-2.52220000
C	1.03530700	-0.32616800	-3.50907900
H	1.48765900	-1.31927600	-3.45860700
H	-0.05214500	-0.43846200	-3.57089200
H	1.37882200	0.16644300	-4.42371600
C	3.83302100	-0.44309700	2.24998800
F	3.19310800	-0.69309600	3.40306300
F	4.40738000	0.76550900	2.33036600
F	4.79480900	-1.35842900	2.09088200

$^{OSS}TS_{SET}$			
C	-2.74542500	-2.05215900	-2.05912100
C	-4.18201600	-2.63471600	-1.92864400
C	-3.79262900	-1.03490800	-0.35473000
H	-4.86697000	-2.35695000	-2.73117700
C	-4.20188600	-0.27328900	0.88377900
C	-3.24960700	0.82503200	1.29375900
C	-2.67110000	2.58761700	2.57607700
C	-1.41283400	1.93059300	1.96370400
H	-2.65732900	2.66059500	3.66235500
H	-0.81585700	1.34514500	2.66944600
C	-4.18705300	-1.30589300	2.09597600
H	-4.77535600	-0.85338600	2.89819400
H	-4.71458900	-2.20185100	1.75870600
C	-5.64513600	0.28974300	0.68175300
H	-6.29599600	-0.55558100	0.44494200
H	-5.97251900	0.70150100	1.63842300
O	-4.68005300	-1.97775100	-0.71696800
O	-3.73707800	1.64274000	2.24325000
N	-2.72637400	-0.94878000	-1.06337100
N	-2.00443200	0.95746800	1.00375700
H	-2.51334900	-1.64519600	-3.04643200
C	-4.06053900	-4.14828200	-1.70271100
H	-4.74488900	-4.47989300	-0.91508600
C	-2.59906200	-4.34845300	-1.37045000
C	-1.84863900	-3.19860500	-1.63803300
C	-0.47562800	-3.16529300	-1.42398700
C	0.17203600	-4.30037400	-0.91079000
C	-0.58940600	-5.44987100	-0.63160600
C	-1.96518300	-5.48302300	-0.86413600
H	0.08914300	-2.25384600	-1.58131700
H	-0.09113300	-6.33377100	-0.24525700
H	-2.53055200	-6.38581200	-0.65115300
H	-4.34140200	-4.68570600	-2.61713500
C	0.63499200	3.05137800	0.85886500
C	1.17380000	4.20883200	0.27470000
C	0.36677200	5.35988600	0.20951700
C	-0.93952100	5.37158600	0.70690900
C	-1.46364100	4.21102600	1.27358200
C	-0.66611600	3.06471100	1.33444500
H	1.22414800	2.14332300	0.90823600
H	0.78092500	6.27054100	-0.21204200
H	-1.52742400	6.28392700	0.65951200
C	2.54217400	4.16858800	-0.28996800
C	2.85362200	4.85229500	-1.47572500
C	3.54123100	3.39037100	0.31720000
C	4.12463900	4.75531400	-2.03960400
H	2.08601900	5.43684400	-1.97443300
C	4.81059200	3.29442100	-0.24565900
H	3.33150700	2.87049400	1.24595600
C	5.10635300	3.97341300	-1.42858900
H	4.34559200	5.28491700	-2.96182300

H	5.56445400	2.68644700	0.24322900
H	6.09485000	3.89441300	-1.87078700
C	1.62590300	-4.24034700	-0.63019700
C	2.49898500	-3.60677200	-1.52802500
C	2.15263700	-4.76206600	0.56176800
C	3.85595500	-3.48499600	-1.23924800
H	2.10955400	-3.21965500	-2.46439700
C	3.50865900	-4.62870700	0.85820400
H	1.49068000	-5.25082200	1.27153200
C	4.36392000	-3.98596600	-0.03906700
H	4.51384700	-2.99051400	-1.94689000
H	3.89701700	-5.02517100	1.79179500
H	5.41971900	-3.88273000	0.19324500
C	-2.83272900	3.95901400	1.87304400
H	-3.14787400	4.74148700	2.57042300
H	-3.60051100	3.88616600	1.09446800
C	-2.79116300	-1.61861300	2.58283400
C	-2.28316500	-0.95928500	3.71037700
C	-1.94617500	-2.47833400	1.86923600
C	-0.95314900	-1.12637000	4.09862300
H	-2.93476600	-0.30390000	4.28263300
C	-0.61205200	-2.63866300	2.24678800
H	-2.32109800	-3.02587300	1.01155800
C	-0.10899600	-1.95604000	3.35703100
H	-0.57937900	-0.61582300	4.98160700
H	0.03215100	-3.29431600	1.67277600
H	0.92716800	-2.08914300	3.65650900
C	-5.71088100	1.35137600	-0.39347300
C	-5.74706700	2.70703700	-0.04392200
C	-5.70198600	1.01024200	-1.75291100
C	-5.74376000	3.69944500	-1.02520400
H	-5.78903300	2.98189600	1.00550400
C	-5.69496900	1.99932000	-2.73649500
H	-5.72761900	-0.03549400	-2.04414500
C	-5.70609300	3.34800900	-2.37528200
H	-5.78224500	4.74550800	-0.73517000
H	-5.69669000	1.71717800	-3.78538500
H	-5.70628300	4.11801800	-3.14067700
Cu	-1.09120200	0.10443000	-0.53706300
C	3.36064700	-0.03210200	-1.01378200
C	2.72079400	0.43254000	-2.16437900
C	3.55619000	0.87239100	-3.20572400
C	4.94231900	0.81012600	-3.12275600
C	5.54439400	0.28906700	-1.97873200
C	4.74989700	-0.12790700	-0.91482000
C	1.19677100	0.46765600	-2.39157200
H	3.10171200	1.26520500	-4.10930400
H	5.54762600	1.15764400	-3.95383400
H	6.62477700	0.21412800	-1.90369800
H	5.21157600	-0.53115600	-0.02329800
O	0.54397500	-0.19914500	-1.33671600
I	2.26653100	-0.63231300	0.73817500

C	0.69798200	1.91172500	-2.53250700
H	0.85805600	2.46093800	-1.60586800
H	1.21387500	2.44561500	-3.33570500
H	-0.37576800	1.90573700	-2.75865700
C	0.85187200	-0.34464300	-3.66314700
H	1.23841400	-1.36329700	-3.58364700
H	-0.23694200	-0.38569100	-3.77319000
H	1.26838000	0.12010200	-4.56080400
C	4.54563400	-0.11857600	2.52747000
F	4.01585900	-0.36180700	3.71896800
F	4.89993300	1.16114200	2.41890200
F	5.59165600	-0.91118000	2.30420900

Int3

C	-2.46382900	-1.27366000	-2.30474800
C	-4.00137200	-1.44817000	-2.44818400
C	-3.48975500	-0.12070900	-0.67208500
H	-4.44753400	-0.92368600	-3.29377600
C	-3.88365300	0.69024400	0.53692700
C	-2.73050100	1.36939500	1.23700000
C	-1.91153100	2.64192700	2.92642800
C	-0.76037200	1.89562600	2.19560900
H	-2.02624700	2.36379900	3.97282300
H	-0.27493900	1.12251800	2.79728700
C	-4.49578200	-0.29524100	1.61479500
H	-5.04917900	0.31563600	2.33201500
H	-5.21018100	-0.94092300	1.09826900
C	-4.92257300	1.76003500	0.05924600
H	-5.83815300	1.23412900	-0.22159300
H	-5.15231400	2.40383300	0.91172100
O	-4.50723200	-0.77725200	-1.24162600
O	-3.11525700	2.15647000	2.24983700
N	-2.33839300	-0.26782200	-1.22014700
N	-1.46624200	1.20348500	1.08399400
H	-1.96925300	-0.89604300	-3.20278300
C	-4.30916800	-2.94958300	-2.38980800
H	-5.19512000	-3.14329500	-1.77652200
C	-3.03706100	-3.55624700	-1.83991300
C	-1.98280500	-2.63679800	-1.85101500
C	-0.71769600	-2.97827300	-1.38628100
C	-0.48987000	-4.27066600	-0.88631800
C	-1.55471600	-5.19100100	-0.87850500
C	-2.82056200	-4.84493300	-1.35301000
H	0.07787200	-2.24366000	-1.34459100
H	-1.38089600	-6.19633200	-0.50761800
H	-3.62444900	-5.57539000	-1.33889100
H	-4.53077200	-3.32134900	-3.39820200
C	1.40900900	2.82467300	1.13694800
C	2.13804100	3.95729300	0.74057000
C	1.57548200	5.22794000	0.96679900
C	0.33198300	5.38066800	1.58272300
C	-0.37836000	4.24664600	1.97556000

C	0.16746300	2.98291900	1.73636400
H	1.80814700	1.83131500	0.96786600
H	2.14105500	6.11163500	0.68836000
H	-0.06061700	6.37624700	1.76994000
C	3.45451800	3.78985100	0.08372100
C	3.84935900	4.63503200	-0.96525200
C	4.30709700	2.73685900	0.45521500
C	5.05696000	4.42712300	-1.62965600
H	3.19080800	5.43746600	-1.28447600
C	5.51305800	2.52951200	-0.20864600
H	4.02938400	2.08293800	1.27589500
C	5.89069000	3.37112600	-1.25646500
H	5.34257200	5.08541800	-2.44495100
H	6.15300500	1.70636100	0.09009700
H	6.82977400	3.20739000	-1.77672900
C	0.84049500	-4.61652400	-0.33407100
C	2.01259900	-4.15713300	-0.95358500
C	0.95682200	-5.36591200	0.84710500
C	3.26400200	-4.42581600	-0.40583700
H	1.94125500	-3.59835300	-1.88078300
C	2.20878600	-5.63056500	1.40035400
H	0.06051500	-5.72120800	1.34827800
C	3.36578600	-5.15879100	0.77771800
H	4.15730900	-4.05631500	-0.89965000
H	2.28013200	-6.20208400	2.32110800
H	4.34017200	-5.36504500	1.21042500
C	-1.69900800	4.15738400	2.71157200
H	-1.66648500	4.68621400	3.67057200
H	-2.53843700	4.58254600	2.14941600
C	-3.40569500	-1.08256600	2.30980100
C	-2.95247500	-0.68568300	3.57507100
C	-2.73270400	-2.11910500	1.64916400
C	-1.82834500	-1.28058000	4.15047200
H	-3.48156800	0.09989000	4.10773900
C	-1.60158400	-2.70739000	2.21554700
H	-3.08097000	-2.46958600	0.68340000
C	-1.13913600	-2.28153400	3.46256400
H	-1.49559900	-0.96672600	5.13578400
H	-1.07829900	-3.49050000	1.68001200
H	-0.25970000	-2.74344700	3.90184300
C	-4.37201600	2.54483100	-1.11133800
C	-3.38150800	3.51753200	-0.91822200
C	-4.75991700	2.23195200	-2.41986600
C	-2.77497200	4.14465000	-2.00602300
H	-3.08536000	3.79401200	0.08842800
C	-4.16046600	2.86263900	-3.51140400
H	-5.53996500	1.49270200	-2.58152500
C	-3.15873100	3.81331700	-3.30758900
H	-2.01094600	4.89747900	-1.83521300
H	-4.48151200	2.61778700	-4.51972000
H	-2.69250500	4.30541100	-4.15574000
Cu	-0.62257800	0.33009400	-0.46049100

C	3.56252900	-0.88355200	-0.06968000
C	3.34142400	-0.36622500	-1.35518800
C	4.46956200	-0.25061200	-2.18918300
C	5.74195500	-0.64024500	-1.79339000
C	5.93185300	-1.16303800	-0.51500900
C	4.84287300	-1.27659100	0.34324900
C	1.99722700	0.09144500	-1.96536400
H	4.33942800	0.16240400	-3.18379100
H	6.57729500	-0.53380100	-2.47830600
H	6.91581300	-1.47883600	-0.18184700
H	4.98277700	-1.68143100	1.33875400
O	0.96284800	-0.22741000	-1.08520000
I	2.07356800	-1.19289600	1.47356500
C	2.00688700	1.59474200	-2.27732400
H	2.10802700	2.17158300	-1.35985600
H	2.83098800	1.87507200	-2.93841500
H	1.06273100	1.86697300	-2.76450200
C	1.70938200	-0.71463400	-3.25779400
H	1.73302600	-1.78744500	-3.05763400
H	0.71574400	-0.44365000	-3.62994000
H	2.44028800	-0.48653700	-4.03728900

FavInt4

C	-2.65048300	-1.62020400	2.09161400
C	-3.48046400	-2.92632200	2.25343700
C	-2.09073400	-3.06137700	0.46090600
H	-3.23264600	-3.51301300	3.13826100
C	-1.52239500	-3.84150900	-0.69659200
C	-0.41689400	-3.12973700	-1.43084800
C	1.13290700	-3.02151700	-3.09080100
C	1.24530600	-1.79877400	-2.14263600
H	0.73934000	-2.79878700	-4.08348500
H	1.17603700	-0.83120600	-2.62962900
C	-2.67541100	-4.13649100	-1.71871900
H	-2.27187900	-4.80751700	-2.48068100
H	-3.45985200	-4.67372500	-1.18001700
C	-0.93360200	-5.17704400	-0.10148800
H	-1.77499000	-5.75968100	0.28038500
H	-0.48439300	-5.73280600	-0.92783300
O	-3.06212900	-3.72662100	1.10506900
O	0.11523300	-3.84967400	-2.42852600
N	-1.77551900	-1.90592300	0.91954000
N	0.08549300	-1.96610500	-1.23365400
H	-2.01155100	-1.38262200	2.94043900
C	-4.97268600	-2.56297100	2.14725000
H	-5.48249200	-3.22914800	1.44305600
C	-4.97050200	-1.10927400	1.72941700
C	-3.68506200	-0.56274300	1.78924000
C	-3.46321900	0.78085400	1.52637000
C	-4.52886300	1.60203300	1.12815400
C	-5.81535400	1.03974000	1.04116200
C	-6.04439000	-0.30235400	1.35412300

H	-2.46017300	1.17806900	1.58585100
H	-6.65130300	1.67130700	0.75613900
H	-7.05238400	-0.70494700	1.30853000
H	-5.46436600	-2.69449600	3.11879400
C	3.11627600	-1.19804600	-0.44071800
C	4.39749000	-1.49654000	0.04985100
C	5.07016900	-2.62449000	-0.46114900
C	4.51149200	-3.42018400	-1.46081000
C	3.25535400	-3.08887500	-1.96646800
C	2.56838700	-1.99088200	-1.44206700
H	2.58485400	-0.32111900	-0.09127200
H	6.04550500	-2.88190400	-0.06062100
H	5.05686500	-4.27935100	-1.84115200
C	5.05112100	-0.61980600	1.04832500
C	4.31562200	-0.00156900	2.07205200
C	6.43136900	-0.37213200	0.97251400
C	4.94769600	0.82937900	2.99540800
H	3.24949900	-0.19336000	2.15415100
C	7.06108500	0.46225700	1.89331800
H	7.00922100	-0.81407600	0.16662300
C	6.32078800	1.06510700	2.91034400
H	4.37344200	1.28643200	3.79315600
H	8.12791000	0.64754100	1.81053500
H	6.80836600	1.71423600	3.63140700
C	-4.26388100	3.01416300	0.76714100
C	-3.32870200	3.77268200	1.48995800
C	-4.88813700	3.60442200	-0.34239100
C	-3.02107100	5.07806500	1.11349400
H	-2.86066400	3.33899900	2.36848500
C	-4.58328500	4.91234100	-0.71938700
H	-5.59487400	3.02463000	-0.92892600
C	-3.64833300	5.65369400	0.00641800
H	-2.29959400	5.65014600	1.68962900
H	-5.07334900	5.35129200	-1.58344100
H	-3.41576600	6.67376100	-0.28435800
C	2.49121200	-3.73791600	-3.09982400
H	2.99240800	-3.57770200	-4.06228800
H	2.36094700	-4.81977100	-2.98712800
C	-3.20921400	-2.86793100	-2.34488200
C	-4.13534600	-2.06895600	-1.66092100
C	-2.73620800	-2.43156800	-3.58862400
C	-4.56682800	-0.85572300	-2.19506900
H	-4.52989000	-2.39834500	-0.70630500
C	-3.17644500	-1.22425600	-4.13405000
H	-2.02931800	-3.04868400	-4.13721400
C	-4.08720900	-0.43032700	-3.43524600
H	-5.27489500	-0.24966900	-1.63827900
H	-2.80887900	-0.90522700	-5.10478200
H	-4.42515400	0.51100600	-3.85813100
C	0.07309100	-4.89168700	0.99031800
C	1.39802600	-4.57572100	0.66825400
C	-0.32426400	-4.83180400	2.33286000

C	2.29707400	-4.16677400	1.65273000
H	1.73383100	-4.64466300	-0.36014300
C	0.57272600	-4.42945900	3.32308000
H	-1.33936000	-5.11040100	2.60179500
C	1.88228100	-4.08185700	2.98298600
H	3.31540000	-3.91630000	1.37533500
H	0.25292900	-4.39876300	4.36092500
H	2.58119700	-3.76739000	3.75245700
Cu	-0.45367400	-0.58237600	0.10397600
C	1.44898300	3.38022400	-2.05008800
C	0.09977200	3.03854200	-1.84237500
C	-0.80561200	4.11250400	-1.75109300
C	-0.40936800	5.44194900	-1.87555200
C	0.93168200	5.74683200	-2.09027000
C	1.86040300	4.71102500	-2.17080000
C	-0.43147800	1.58879100	-1.78298500
H	-1.85434500	3.91460400	-1.57575300
H	-1.15283800	6.22889200	-1.79657900
H	1.26208900	6.77619400	-2.19155000
H	2.90852200	4.93600700	-2.33068400
O	0.38205400	0.83807200	-0.88449400
I	3.05504400	1.95659800	-2.21980400
C	-1.88503000	1.54486200	-1.29275300
H	-1.98582200	2.04586400	-0.33093600
H	-2.58570000	2.00615000	-1.99338200
H	-2.20712900	0.50181100	-1.19225900
C	-0.40233800	1.00020900	-3.20896800
H	-1.01907100	1.60927900	-3.87808600
H	0.61121000	0.97853900	-3.61460000
H	-0.81647900	-0.01274500	-3.20320900
C	0.31516700	1.27017900	2.36015700
O	-0.36736300	0.30181100	1.91139400
N	1.02170300	1.99939000	1.48363000
H	0.89121100	1.68355900	0.49096900
C	0.26620700	1.52146400	3.87607000
C	1.64724100	1.22112900	4.49661000
C	-0.14963000	2.97468300	4.18626500
C	-0.76931700	0.57014100	4.50264900
H	1.97933500	0.20574300	4.25469900
H	2.39942900	1.93117400	4.15236700
H	1.57413800	1.30079100	5.58631500
H	-1.06650800	3.25018700	3.65440000
H	-0.34625800	3.06622500	5.25916100
H	0.63492100	3.68550900	3.92802400
H	-0.80515200	0.74896500	5.58167800
H	-1.77120100	0.73690800	4.09585000
H	-0.49746700	-0.47621200	4.33898800
S	2.18321200	3.24943700	1.75293200
C	1.17561800	4.72112600	1.37777200
H	1.88286100	5.55188100	1.29585500
H	0.66618800	4.59556000	0.42399300
H	0.45505200	4.93087800	2.17167300

DisfInt4

C	2.23950800	-0.80862800	-2.58652100
C	3.28692100	-1.88340100	-2.99808100
C	2.32096400	-2.40530000	-1.01024900
H	3.00249100	-2.48435100	-3.86128200
C	2.08838600	-3.36722500	0.12467200
C	1.06246400	-2.89574400	1.12356200
C	-0.21968100	-3.21868500	2.97784900
C	-0.61245500	-1.91108700	2.24657800
H	0.27923900	-3.07359100	3.93643400
H	-0.60056700	-1.02690500	2.87359600
C	3.43002700	-3.62528500	0.88655600
H	3.24963400	-4.43470400	1.59831800
H	4.15536000	-3.98381100	0.15196600
C	1.56294200	-4.70221100	-0.54465300
H	2.43369000	-5.21177300	-0.96422200
H	1.15806200	-5.33117400	0.25152700
O	3.28728100	-2.79646400	-1.85326900
O	0.78250100	-3.80045600	2.07244200
N	1.67728900	-1.34217100	-1.32073100
N	0.41824800	-1.78688000	1.18433100
H	1.41983300	-0.67938700	-3.29408900
C	4.65104300	-1.18735800	-3.13005700
H	5.43179800	-1.76385900	-2.62301000
C	4.42017800	0.18802500	-2.54400000
C	3.05887500	0.43468700	-2.33941400
C	2.61020600	1.66243100	-1.86909600
C	3.54082400	2.66179000	-1.54280100
C	4.91015300	2.39661700	-1.72407400
C	5.35415400	1.17547600	-2.23411200
H	1.55421800	1.84271200	-1.70136700
H	5.63124100	3.17322800	-1.48848900
H	6.41573500	1.00529200	-2.39055600
H	4.94005700	-1.12353200	-4.18644700
C	-2.65468800	-1.45283900	0.70647000
C	-3.81419700	-1.97808400	0.11461000
C	-4.24802900	-3.26218600	0.49573300
C	-3.55484000	-4.01816200	1.44150000
C	-2.39421400	-3.49429100	2.00830700
C	-1.95572200	-2.22162300	1.62937000
H	-2.29427500	-0.46845400	0.42941100
H	-5.15674200	-3.66262800	0.05744800
H	-3.91836700	-5.00221400	1.72336600
C	-4.55756400	-1.20211100	-0.90571500
C	-5.10261000	-1.83405100	-2.03552200
C	-4.74432000	0.18107900	-0.75601900
C	-5.81670100	-1.10650500	-2.98682400
H	-4.95998500	-2.90210200	-2.17351100
C	-5.47959600	0.90259000	-1.69468900
H	-4.34346600	0.67840000	0.12088800
C	-6.01544400	0.26437900	-2.81581900

H	-6.22539700	-1.61243100	-3.85652500
H	-5.65156800	1.96388900	-1.54156600
H	-6.58697500	0.82943500	-3.54596700
C	3.07540300	3.94664400	-0.97482200
C	1.95333500	4.60046300	-1.50630300
C	3.72642700	4.51464700	0.13115300
C	1.49429500	5.79118600	-0.94616100
H	1.45487500	4.18333800	-2.37655000
C	3.26307800	5.70199000	0.69470400
H	4.58162900	4.00509100	0.56573400
C	2.14511700	6.34370700	0.15806800
H	0.62798600	6.28610900	-1.37297800
H	3.77101500	6.12350000	1.55711900
H	1.78434100	7.26880200	0.59709700
C	-1.46506200	-4.11460900	3.02950900
H	-1.89993600	-4.08447900	4.03660900
H	-1.20820000	-5.15839700	2.82228500
C	3.94548800	-2.39420400	1.59802700
C	4.63318700	-1.39500100	0.89446700
C	3.71936600	-2.21651100	2.96827500
C	5.08825600	-0.24882900	1.54366200
H	4.82669100	-1.51856400	-0.16562300
C	4.18686500	-1.07632700	3.62497400
H	3.19438600	-2.98724600	3.52681300
C	4.87237900	-0.08985200	2.91422600
H	5.61135000	0.51491000	0.97610100
H	4.02545800	-0.96555900	4.69353200
H	5.23869600	0.79528200	3.42563700
C	0.54698900	-4.42325500	-1.62946600
C	-0.74493600	-3.98234400	-1.31573900
C	0.92949900	-4.48359200	-2.97591000
C	-1.61738100	-3.57016100	-2.32236800
H	-1.07772100	-3.95145300	-0.28413700
C	0.05370200	-4.08360100	-3.98630100
H	1.92311600	-4.84231700	-3.23078200
C	-1.21829000	-3.61120300	-3.65909300
H	-2.60409000	-3.20969300	-2.05799600
H	0.36280700	-4.14631100	-5.02589200
H	-1.89939600	-3.28822900	-4.44059200
Cu	0.36329900	-0.32388900	-0.18521200
C	-1.33806600	1.22345200	3.64912900
C	0.01012300	1.20943600	3.24995500
C	0.91418800	0.63980300	4.16573300
C	0.51259000	0.08692900	5.37988200
C	-0.83463600	0.09396300	5.73044300
C	-1.75920200	0.67413100	4.86309900
C	0.51756500	1.69700300	1.87601500
H	1.96421600	0.59855400	3.91009900
H	1.25408100	-0.34608300	6.04523600
H	-1.17146400	-0.33233400	6.67054800
H	-2.80936600	0.69787000	5.13042100
O	-0.28519600	1.11920500	0.85395600

I	-2.95525300	2.04212900	2.48039500
C	0.41745000	3.23338700	1.77092800
H	-0.60904900	3.58372900	1.87780900
H	1.02743200	3.70454900	2.54842700
H	0.79295900	3.55855600	0.79753000
C	1.99011600	1.32195700	1.64537700
H	2.66309400	1.83780000	2.33537300
H	2.16435700	0.24748600	1.74501500
H	2.27250500	1.62972500	0.63800000
C	-1.10913500	1.34477500	-2.26785600
O	-0.57649300	0.26576900	-1.88787100
N	-1.26524000	2.31879000	-1.34952600
H	-0.92891100	2.03258000	-0.40107500
C	-1.46879000	1.46336300	-3.75427200
C	-2.81889300	2.15755900	-4.01404400
C	-0.32000500	2.24656200	-4.43366000
C	-1.54830700	0.04101700	-4.34370400
H	-3.61992300	1.68413100	-3.43999100
H	-2.78973500	3.22247400	-3.78465000
H	-3.06476600	2.05271200	-5.07597800
H	0.64981100	1.77015300	-4.25140200
H	-0.48909100	2.26999100	-5.51530200
H	-0.27358200	3.27915500	-4.07572700
H	-1.77032300	0.11361000	-5.41320800
H	-0.61681500	-0.51361100	-4.21823600
H	-2.34476100	-0.53626300	-3.86364800
S	-1.60833700	3.99442800	-1.55524800
C	-3.36531800	4.06333400	-1.08506400
H	-3.98792700	3.52660700	-1.80232400
H	-3.50267700	3.66447200	-0.07857500
H	-3.63167500	5.12511200	-1.08960000

IntO_S

C	-1.84503100	-1.00147100	2.28316700
C	-2.45194100	-2.39053700	2.63782100
C	-1.04760800	-2.54902000	0.85705200
H	-2.14861600	-2.78888700	3.60583900
C	-0.41900800	-3.33227700	-0.26678700
C	0.29796500	-2.48148800	-1.28878000
C	1.36402100	-2.21254400	-3.28103700
C	1.33569400	-0.87791400	-2.47992400
H	0.73025900	-2.23236100	-4.16818300
H	0.86279200	-0.03968900	-2.99512400
C	-1.54735800	-4.15563000	-0.97747200
H	-1.12942800	-4.53912800	-1.91299900
H	-1.76255000	-5.02089700	-0.34646400
C	0.64348200	-4.30606900	0.37511000
H	0.09187200	-4.98787500	1.02772500
H	1.07690800	-4.89562400	-0.43703100
O	-1.85430200	-3.27629600	1.63167300
O	0.76600700	-3.16871100	-2.33789200
N	-0.90302900	-1.31307800	1.17887000

N	0.52283400	-1.21772800	-1.28454300
H	-1.29536000	-0.52897200	3.10043100
C	-3.97650100	-2.30215600	2.44528000
H	-4.32759100	-3.12007500	1.80876000
C	-4.19492800	-0.94243900	1.82283000
C	-3.01738300	-0.19306400	1.77753800
C	-2.99834900	1.09286900	1.24750600
C	-4.18069500	1.65240000	0.74067400
C	-5.36223600	0.88986700	0.78893600
C	-5.37758500	-0.39544000	1.32867300
H	-2.08428700	1.67405900	1.19839700
H	-6.28486000	1.32720400	0.42005800
H	-6.30380800	-0.96121300	1.36036700
H	-4.48740400	-2.39539600	3.41105400
C	3.29044300	0.35714700	-1.29469000
C	4.65244600	0.35276900	-0.95852500
C	5.48241800	-0.63910800	-1.51320800
C	4.97394900	-1.61736500	-2.36967900
C	3.61085800	-1.62190500	-2.66671200
C	2.78391000	-0.63622100	-2.12169400
H	2.62419300	1.10803500	-0.89005700
H	6.54272000	-0.63219600	-1.27945000
H	5.63774400	-2.36522300	-2.79418700
C	5.16198800	1.33843600	0.02225000
C	6.04040200	0.94399700	1.04395200
C	4.71473100	2.66873200	-0.00303300
C	6.44815800	1.85198700	2.02038000
H	6.38661200	-0.08490700	1.08638400
C	5.12283900	3.57695200	0.97151100
H	4.05713600	2.99197200	-0.80322100
C	5.98720600	3.16999400	1.99043800
H	7.12294300	1.52923000	2.80780100
H	4.77192000	4.60396700	0.93104700
H	6.30563100	3.87646100	2.75096900
C	-4.17555500	3.02420400	0.18208200
C	-3.47015400	4.05325400	0.82668100
C	-4.87495800	3.32295500	-0.99748600
C	-3.47607200	5.34824100	0.31069400
H	-2.93673700	3.84252600	1.74865900
C	-4.86887200	4.61547300	-1.51988800
H	-5.40913600	2.53191500	-1.51646300
C	-4.17208600	5.63305800	-0.86559400
H	-2.94245400	6.13694300	0.83238300
H	-5.40721800	4.82757100	-2.43887800
H	-4.17337100	6.64138500	-1.26820400
C	2.83341000	-2.57036600	-3.55230700
H	3.06655500	-2.41138300	-4.61231400
H	3.01967700	-3.62888500	-3.34216700
C	-2.83611100	-3.39109400	-1.21710200
C	-4.05554100	-3.99931800	-0.89442200
C	-2.85892100	-2.08934900	-1.73843800
C	-5.26506700	-3.33188100	-1.08973000

H	-4.05635500	-5.00674200	-0.48598200
C	-4.06516500	-1.41270900	-1.91902500
H	-1.93719700	-1.58219500	-1.99983100
C	-5.27231800	-2.03202600	-1.59734600
H	-6.19929200	-3.82618600	-0.83973000
H	-4.05778400	-0.39798100	-2.30538800
H	-6.21064200	-1.50485700	-1.73797200
C	1.70504900	-3.56161900	1.14845700
C	2.85950100	-3.09397700	0.51091900
C	1.51468900	-3.26023700	2.50394600
C	3.79479900	-2.32597200	1.20381700
H	3.03395100	-3.33140300	-0.53348800
C	2.44907900	-2.49436200	3.20180400
H	0.63486200	-3.64023300	3.01762300
C	3.58934900	-2.01852800	2.54925600
H	4.68035800	-1.97431700	0.68844400
H	2.29544700	-2.28400300	4.25654600
H	4.32124400	-1.42340000	3.08761400
Cu	0.08777800	0.07117900	0.19478000
N	0.42210100	3.03780700	0.99605800
S	0.46235100	1.62119000	1.97186500
C	0.38339200	2.80134300	-0.29182200
O	0.40604500	1.62738900	-0.86231200
C	0.28755500	3.98771400	-1.25534900
C	0.21739300	5.32345900	-0.50422600
H	0.15091600	6.14308700	-1.22829000
H	-0.65975600	5.36312400	0.14465300
H	1.10458300	5.47872300	0.11605600
C	-0.98662500	3.78826400	-2.10586500
H	-1.87980400	3.74814200	-1.47685400
H	-1.09892300	4.62943500	-2.79795000
H	-0.92684800	2.86365600	-2.68677800
C	1.52920300	3.96677100	-2.16991700
H	1.63824900	3.00204600	-2.67372400
H	1.43799400	4.74764800	-2.93211600
H	2.44054400	4.16739200	-1.59604900
C	2.24596300	1.37344000	2.27662300
H	2.63990100	2.28494600	2.73123800
H	2.33867400	0.53037400	2.96467200
H	2.78428500	1.15943500	1.35524000

^{OSS}FavTS$_{HAT_RC}$-1

C	-3.50787300	0.47257800	2.60327400
C	-4.99550600	0.23782300	3.00215900
C	-4.55500300	-0.63688700	0.95337900
H	-5.13456400	-0.43952600	3.84442200
C	-4.97207900	-1.44611800	-0.24923700
C	-3.87446600	-1.66195200	-1.26337200
C	-3.10408200	-2.53859800	-3.21738500
C	-1.96106100	-1.83952900	-2.43108300
H	-3.40936400	-2.03006900	-4.13262300
H	-1.43792000	-1.06140700	-2.98220300

C	-6.15499400	-0.71310000	-0.96960400
H	-6.53147200	-1.37869200	-1.75007300
H	-6.95055400	-0.57554800	-0.23309700
C	-5.41559900	-2.85592500	0.30472200
H	-6.35232100	-2.70966600	0.84749900
H	-5.61909100	-3.49955900	-0.55432400
O	-5.55182100	-0.44821200	1.83562100
O	-4.24245600	-2.43630600	-2.29599400
N	-3.40739000	-0.16961100	1.26919000
N	-2.66690400	-1.23028300	-1.27717200
H	-2.77679100	-0.00255000	3.25867700
C	-5.65871300	1.61440000	3.19659400
H	-6.58852900	1.67873500	2.62109200
C	-4.59899200	2.60364300	2.76396000
C	-3.37509400	1.97319700	2.52130600
C	-2.23859700	2.69973000	2.19312300
C	-2.32261400	4.09410500	2.05265100
C	-3.56409900	4.72006400	2.27117700
C	-4.69592200	3.98866700	2.63577800
H	-1.30700800	2.17881900	2.00947000
H	-3.63321200	5.80044200	2.19020400
H	-5.63415800	4.50132000	2.82884200
H	-5.92963000	1.76063600	4.24920100
C	0.05737800	-2.89821600	-1.16522200
C	0.72657800	-4.08064600	-0.81128300
C	0.24642900	-5.30812300	-1.30646300
C	-0.86289600	-5.37251100	-2.14916400
C	-1.51512900	-4.19180100	-2.50003100
C	-1.05715500	-2.97054700	-1.99573900
H	0.40746100	-1.94466800	-0.78470000
H	0.77453700	-6.22031100	-1.04668500
H	-1.20213900	-6.33119800	-2.53121300
C	1.92627800	-4.05297500	0.05859400
C	2.95817900	-3.12843200	-0.16946900
C	2.07013300	-4.98038200	1.10256800
C	4.11180700	-3.15438300	0.61206100
H	2.86452900	-2.41040500	-0.97871400
C	3.21412000	-4.98510700	1.90006700
H	1.27346300	-5.69343700	1.29684400
C	4.24304600	-4.07546900	1.65273500
H	4.91606600	-2.45488200	0.42033900
H	3.30287700	-5.70256600	2.71067200
H	5.13930400	-4.07339900	2.26365300
C	-1.12957200	4.87458000	1.64786700
C	0.15158500	4.52176100	2.10322400
C	-1.24774800	5.96115800	0.76577200
C	1.27548300	5.23952300	1.69859900
H	0.26245200	3.69565900	2.79952800
C	-0.12310800	6.67756200	0.35801400
H	-2.22614600	6.23071400	0.37930900
C	1.14345300	6.32107100	0.82589900
H	2.25504800	4.96198100	2.07548700

H	-0.23656800	7.51421500	-0.32523900
H	2.01893400	6.88546700	0.51896300
C	-2.70510600	-4.00819400	-3.41633300
H	-2.43267600	-4.18350300	-4.46450100
H	-3.54542300	-4.67327300	-3.19093600
C	-5.71299900	0.60989600	-1.55469300
C	-5.57432400	1.74146000	-0.73896600
C	-5.36065400	0.71026800	-2.90617500
C	-5.08192400	2.93951400	-1.25420200
H	-5.85838400	1.69029400	0.30614500
C	-4.88021500	1.91213200	-3.42968000
H	-5.47596500	-0.15561000	-3.55318000
C	-4.73355400	3.02756900	-2.60342700
H	-4.97226900	3.79791300	-0.59796500
H	-4.62396800	1.97749500	-4.48306900
H	-4.35663800	3.96102700	-3.01064000
C	-4.35259600	-3.43841900	1.20997300
C	-3.20845900	-4.03874100	0.67151700
C	-4.43453000	-3.27657100	2.59955700
C	-2.14938200	-4.42433800	1.49302400
H	-3.13482700	-4.20575700	-0.39705000
C	-3.37888400	-3.66354100	3.42598000
H	-5.33134500	-2.84308900	3.03302500
C	-2.22554800	-4.22388100	2.87229100
H	-1.27045800	-4.87810300	1.04902700
H	-3.46016100	-3.53560000	4.50167800
H	-1.40058900	-4.52077400	3.51317300
Cu	-1.71725700	-0.20771700	0.13875200
C	2.00043400	1.70120500	-2.65701400
C	0.89946300	2.41097600	-2.14198500
C	1.11728000	3.77001900	-1.84728700
C	2.34815700	4.39061400	-2.04073600
C	3.42417300	3.65422500	-2.52716000
C	3.24555000	2.30793700	-2.83594700
C	-0.49535900	1.81185100	-1.90123900
H	0.31087700	4.36298700	-1.43671700
H	2.45944800	5.44016200	-1.78886000
H	4.40039400	4.10860400	-2.66621100
H	4.08039300	1.72795800	-3.20639600
O	-0.33915100	0.55737200	-1.17795200
I	1.95962000	-0.37317700	-3.25099500
C	-1.38899300	2.71622700	-1.05287300
H	-0.89651000	2.98409400	-0.11977700
H	-1.66735000	3.63602300	-1.57379500
H	-2.31900700	2.18712000	-0.82626200
C	-1.20408200	1.52279000	-3.22894200
H	-1.34233400	2.46038200	-3.77584700
H	-0.62811200	0.84382600	-3.85927900
H	-2.19374500	1.09754100	-3.03787000
C	0.64670100	0.02487400	1.85950600
O	-0.63881800	-0.06920800	1.75657300
N	1.30606100	0.42011500	0.79354200

H	0.42963300	0.60980500	-0.47511000
C	1.21853700	-0.36246300	3.23643400
C	2.01607500	-1.67305900	3.08570800
C	2.12003900	0.75420000	3.79789800
C	0.05966900	-0.59946600	4.22341200
H	1.38931900	-2.47712200	2.68742000
H	2.86663800	-1.55799600	2.41382100
H	2.39111400	-1.99007500	4.06554400
H	1.59555000	1.71685300	3.82036500
H	2.40656000	0.50776500	4.82604600
H	3.03446700	0.87291500	3.21475000
H	0.47243400	-0.89298100	5.19462500
H	-0.53571900	0.30827500	4.36685100
H	-0.60559000	-1.39367300	3.87459900
S	3.02619000	0.53619300	0.56784300
C	3.18720600	2.33833800	0.78083400
H	4.10376700	2.65999700	0.28692600
H	2.33356700	2.80959300	0.29658000
H	3.21223700	2.60392100	1.84011200
C	7.16069100	2.37970600	-1.34462600
C	6.65487300	1.90114600	-0.14400300
C	5.96843000	0.65994500	-0.10114500
C	5.78609000	-0.06073200	-1.30929900
C	6.30916600	0.42522300	-2.49984000
C	6.99381200	1.64623700	-2.52660300
H	7.70094900	3.32151700	-1.36233500
H	6.79444900	2.45638500	0.77788600
H	5.23643600	-0.99469200	-1.29330200
H	6.17831800	-0.14590300	-3.41407400
H	7.39880800	2.02229700	-3.46104400
C	5.39381700	0.20009300	1.10641700
C	5.64532800	-0.41943800	2.23655000
H	4.88158600	-0.61016100	2.98542000
C	6.98870700	-1.01802100	2.55846400
F	7.97543200	-0.53538300	1.78665000
F	7.31392900	-0.79695200	3.84757400
F	6.96125400	-2.36617900	2.38224700

^{OSS}FavTS$_{HAT_RC}$-2

C	-3.20345700	0.89940900	2.69679500
C	-4.63535700	0.75070900	3.29299100
C	-4.41708000	-0.46213700	1.38566900
H	-4.67224900	0.23397800	4.25174500
C	-4.95640500	-1.46302200	0.39352600
C	-3.98045000	-1.85329600	-0.69141200
C	-3.42540900	-3.06245500	-2.53781600
C	-2.21363200	-2.23120300	-2.03067900
H	-3.84171800	-2.73165000	-3.48991500
H	-1.78293700	-1.55526400	-2.76678400
C	-6.22754400	-0.86073200	-0.29643100
H	-6.68106900	-1.64859800	-0.90260400
H	-6.93419600	-0.59674500	0.49433400

C	-5.30792000	-2.75661800	1.22675700
H	-6.17136600	-2.51492600	1.85079900
H	-5.60758500	-3.53387200	0.51986400
O	-5.30934700	-0.12548100	2.33529200
O	-4.45459600	-2.79151500	-1.52735600
N	-3.24916500	0.04811800	1.48272000
N	-2.78996400	-1.43650700	-0.91955000
H	-2.40009700	0.52719600	3.33439500
C	-5.28766400	2.14679300	3.31679300
H	-6.26938200	2.12098100	2.83145400
C	-4.28357900	3.04072500	2.62248700
C	-3.08861500	2.36492200	2.35921000
C	-1.99587400	3.01479600	1.80224400
C	-2.09973800	4.36952900	1.44905400
C	-3.31435300	5.03792600	1.69154800
C	-4.39910500	4.38845300	2.28376700
H	-1.08742600	2.45816100	1.60803600
H	-3.39659900	6.09215300	1.44576500
H	-5.31426700	4.93733200	2.48779500
H	-5.45688000	2.47073100	4.35076700
C	-0.01386800	-3.04335200	-0.88517100
C	0.72880500	-4.14359700	-0.42765400
C	0.21411500	-5.43998900	-0.62027300
C	-0.99850600	-5.65502800	-1.27436800
C	-1.72034900	-4.55673800	-1.73803200
C	-1.23086500	-3.26415100	-1.52529800
H	0.36221900	-2.03689700	-0.73646700
H	0.79730200	-6.29052100	-0.28114100
H	-1.36227900	-6.66682000	-1.42953300
C	2.05276300	-3.97313200	0.21894700
C	3.03080900	-3.14755200	-0.35760700
C	2.37542300	-4.69170700	1.38115500
C	4.31114300	-3.07857600	0.19133100
H	2.79912400	-2.59438400	-1.26236400
C	3.64548200	-4.59748800	1.94783900
H	1.62241400	-5.32363600	1.84417300
C	4.62167200	-3.80195700	1.34468500
H	5.07673500	-2.48187800	-0.29002800
H	3.87701400	-5.15763500	2.84910600
H	5.62457000	-3.75897600	1.76045100
C	-0.95805400	5.05731500	0.80094200
C	0.36523400	4.75502000	1.16303200
C	-1.17093300	5.99585200	-0.22209300
C	1.43858500	5.37866400	0.52986200
H	0.55164600	4.04512500	1.96352700
C	-0.09706100	6.61791900	-0.85795700
H	-2.18548400	6.22096600	-0.53710700
C	1.21303000	6.31335800	-0.48227300
H	2.45327700	5.14377600	0.83641500
H	-0.28413600	7.34000500	-1.64745600
H	2.05014700	6.80513500	-0.96874200
C	-3.02210100	-4.54436700	-2.50913200

H	-2.88206700	-4.91562900	-3.53187200
H	-3.81180700	-5.15291100	-2.05588600
C	-5.87991000	0.34126400	-1.14640900
C	-5.65910900	1.59381900	-0.55703200
C	-5.69799900	0.20922000	-2.52848100
C	-5.25155200	2.68425700	-1.32391100
H	-5.81220600	1.72206200	0.50859500
C	-5.30434700	1.30229600	-3.30274800
H	-5.87805400	-0.75323400	-3.00061800
C	-5.07345100	2.54055400	-2.70126600
H	-5.07505800	3.64083100	-0.84077000
H	-5.18028600	1.18668400	-4.37550700
H	-4.76329900	3.38915600	-3.30368700
C	-4.13123000	-3.18643100	2.07487100
C	-3.05932600	-3.88243300	1.50421400
C	-4.03381600	-2.78623900	3.41429200
C	-1.89723400	-4.13088800	2.23402700
H	-3.12369000	-4.23147000	0.48012400
C	-2.87460500	-3.03505300	4.15005700
H	-4.87177000	-2.27490900	3.87948500
C	-1.79593500	-3.69403400	3.55590400
H	-1.07798000	-4.66313000	1.76327000
H	-2.81642800	-2.72162300	5.18856100
H	-0.89087000	-3.88302200	4.12566600
Cu	-1.70176100	-0.18526700	0.17703900
C	1.60502600	1.22571600	-3.36064300
C	0.58530200	2.01884000	-2.80213100
C	0.83616700	3.40197600	-2.73565800
C	2.01957800	3.97147600	-3.19632600
C	3.01354300	3.15986700	-3.73500100
C	2.80324600	1.78479300	-3.81332500
C	-0.75954400	1.48009400	-2.28857800
H	0.09471100	4.05854800	-2.30029900
H	2.15952300	5.04461300	-3.11760700
H	3.94570300	3.58300700	-4.09712200
H	3.56934200	1.14421600	-4.23469700
O	-0.49648500	0.35140100	-1.41017500
I	1.49730600	-0.91294100	-3.62066000
C	-1.54035600	2.51485800	-1.47839300
H	-0.93330600	2.90969600	-0.66560600
H	-1.88652700	3.35148900	-2.09105900
H	-2.43111200	2.03901600	-1.05845300
C	-1.63918400	0.99670900	-3.44683300
H	-1.87199000	1.84130800	-4.10233300
H	-1.14552300	0.22899200	-4.04402800
H	-2.58310000	0.60570800	-3.05593800
C	0.86253100	0.29095400	1.53025300
O	-0.42251200	0.21954300	1.59827100
N	1.38919300	0.51466500	0.34129200
H	0.34888000	0.51166600	-0.82715500
C	1.59819100	0.08905600	2.86784200
C	2.38751700	-1.23354400	2.80071600

C	2.53499200	1.27501500	3.16333100
C	0.56625000	-0.01421500	4.00721400
H	1.72108200	-2.07835200	2.60134200
H	3.14890400	-1.21786900	2.02097800
H	2.88694800	-1.41045300	3.75927800
H	1.98839300	2.22559200	3.13644900
H	2.96674900	1.16291600	4.16297600
H	3.36295000	1.32738800	2.45905200
H	1.09619600	-0.17775500	4.95195100
H	-0.01979600	0.90590300	4.10070400
H	-0.12576400	-0.84538000	3.84786800
S	3.06045500	0.55971900	-0.06741300
C	3.29377500	2.36054900	-0.18064800
H	4.15806200	2.54202700	-0.82258900
H	2.40529900	2.79819900	-0.63509800
H	3.46590200	2.79478600	0.80814900
C	5.96340300	-0.07309600	4.25192100
C	5.77097500	-0.37969100	2.91324500
C	5.83595100	0.64400700	1.93270600
C	6.08407400	1.97852400	2.34762300
C	6.27271400	2.26687100	3.69187800
C	6.21088700	1.24716600	4.64933900
H	5.92419300	-0.86428400	4.99468800
H	5.56619400	-1.39669100	2.59891500
H	6.13592000	2.76230800	1.59905200
H	6.47427500	3.28836700	3.99970800
H	6.35957000	1.47936900	5.69925500
C	5.56657400	0.35569500	0.58707400
C	6.01459800	-0.01548200	-0.58632600
H	5.36681600	-0.14389100	-1.45314400
C	7.45231000	-0.38803200	-0.84153100
F	8.24483900	-0.15839800	0.21603100
F	7.53450200	-1.70636200	-1.14451000
F	7.94654700	0.29345300	-1.89500600

^{OSS}DisfTS$_{HAT_RC}$-1

C	1.62348200	2.70733300	-2.20951900
C	2.76320900	3.64037400	-2.72040200
C	3.58440400	2.02123100	-1.35863600
H	2.95054700	3.57850600	-3.79193100
C	4.75019900	1.27914100	-0.75483700
C	4.36120700	0.12409700	0.13432500
C	4.91085400	-1.64132900	1.46408100
C	3.38145000	-1.57931600	1.21554200
H	5.21394900	-1.41727500	2.48707800
H	2.78232400	-1.54611800	2.11964400
C	5.62478000	2.26524800	0.08680900
H	6.54065200	1.73806400	0.36401800
H	5.90248600	3.09389800	-0.56907100
C	5.57373800	0.70537500	-1.97933800
H	6.13428200	1.54026100	-2.40699800
H	6.29391400	-0.01435600	-1.58263300

O	3.95568900	3.10226300	-2.06816500
O	5.41630700	-0.54265700	0.63284100
N	2.34208200	1.72032100	-1.36885700
N	3.20071000	-0.31920800	0.45262300
H	1.09584600	2.15903500	-2.99211600
C	2.46989600	5.06406200	-2.21518200
H	3.35581700	5.49463400	-1.73664300
C	1.28673800	4.89419500	-1.28827600
C	0.74290600	3.60850700	-1.37805600
C	-0.42505600	3.27013500	-0.70326000
C	-1.03816800	4.22003200	0.12865200
C	-0.45095400	5.49039300	0.26317300
C	0.69591100	5.83938900	-0.45158400
H	-0.84448100	2.27286100	-0.77687400
H	-0.93051600	6.22409800	0.90398200
H	1.10668400	6.84173400	-0.36695500
H	2.21571700	5.72094100	-3.05608100
C	1.90765700	-3.05247800	-0.33229000
C	1.87498600	-4.09517200	-1.27114800
C	3.04901500	-4.83812900	-1.49846100
C	4.23490200	-4.55854000	-0.81820600
C	4.26117900	-3.50536900	0.09502100
C	3.09868100	-2.76305900	0.32256400
H	1.01799500	-2.46047600	-0.14699800
H	3.02336000	-5.66014600	-2.20692500
H	5.12342000	-5.15380200	-1.00858100
C	0.63327900	-4.38319200	-2.02582900
C	0.68175100	-4.71352900	-3.38999800
C	-0.61841500	-4.32954000	-1.39271200
C	-0.48624500	-4.98335100	-4.10186400
H	1.64066000	-4.74700000	-3.89934200
C	-1.78311800	-4.62197900	-2.09977600
H	-0.66925600	-4.09158300	-0.33503700
C	-1.72368200	-4.94521100	-3.45735600
H	-0.42876600	-5.22918400	-5.15809900
H	-2.73981100	-4.61383100	-1.58621200
H	-2.63319700	-5.17002800	-4.00628700
C	-2.28845300	3.89433200	0.85576800
C	-3.39908400	3.38600300	0.16596900
C	-2.39709000	4.12713900	2.23523000
C	-4.60038100	3.14599100	0.83177500
H	-3.33166600	3.22857300	-0.90594200
C	-3.58896500	3.86040100	2.90764000
H	-1.53751900	4.50888300	2.77908800
C	-4.69645500	3.38003900	2.20540600
H	-5.46401500	2.80682600	0.27087100
H	-3.65768500	4.04091900	3.97644100
H	-5.63484000	3.20238900	2.72294600
C	5.41526500	-2.99151300	0.92948100
H	5.63427700	-3.66509200	1.76761900
H	6.34674300	-2.86661500	0.36789000
C	4.90730700	2.76834900	1.32027300

C	3.93523600	3.77469900	1.22480200
C	5.17645100	2.21357400	2.57720800
C	3.24807800	4.21522000	2.35427600
H	3.72095300	4.22660600	0.26305100
C	4.50253700	2.66470000	3.71376000
H	5.93260000	1.43821000	2.66693500
C	3.53430600	3.66438800	3.60551000
H	2.49359900	4.98973400	2.25273200
H	4.74246300	2.24216100	4.68539100
H	3.01305800	4.01745600	4.49051900
C	4.66383500	0.09374800	-3.02022200
C	4.03223400	-1.13635000	-2.79549800
C	4.33557200	0.81806000	-4.17351000
C	3.06177800	-1.60767600	-3.67909300
H	4.28753900	-1.73117400	-1.92536300
C	3.37425800	0.34224500	-5.06629900
H	4.83384300	1.76422800	-4.36671400
C	2.72369700	-0.86597900	-4.81181400
H	2.56536300	-2.54869500	-3.47481600
H	3.13750000	0.91240900	-5.96024700
H	1.96519500	-1.23334800	-5.49610600
Cu	1.44535800	0.16666400	-0.39512200
C	0.84929900	-1.90975600	3.64225900
C	1.00979400	-0.52844200	3.42385100
C	2.06507700	0.08677100	4.12053400
C	2.92368900	-0.61466400	4.96316000
C	2.74723900	-1.98297100	5.14611300
C	1.70191400	-2.62715800	4.48642500
C	0.16798300	0.31292500	2.45086600
H	2.24404200	1.14323900	3.98035900
H	3.72681200	-0.08755800	5.46940500
H	3.40398600	-2.55085700	5.79816800
H	1.55091100	-3.69140300	4.62520100
O	0.21677700	-0.36763800	1.16750600
I	-0.65243200	-3.14122500	2.71078400
C	-1.28978000	0.44565500	2.91784400
H	-1.78443700	-0.52054500	3.01622400
H	-1.31403900	0.94653900	3.89042400
H	-1.85712000	1.05411200	2.20757100
C	0.73557300	1.72071600	2.24612800
H	0.68196800	2.32172100	3.15810500
H	1.77474900	1.69837100	1.90934700
H	0.13891900	2.22584600	1.48750300
C	-1.20083400	-0.19019200	-1.71557800
O	0.07516500	-0.05067300	-1.78237100
N	-1.73415400	-0.31343700	-0.51339200
H	-0.68100800	-0.34533600	0.64547300
C	-1.93284100	-0.12054400	-3.07287800
C	-3.01531200	-1.20475300	-3.22736800
C	-2.55808500	1.28591600	-3.18879300
C	-0.90721800	-0.31649600	-4.20622000
H	-2.59760500	-2.20035600	-3.05194300

H	-3.86021500	-1.05261100	-2.55484800
H	-3.39877500	-1.18130900	-4.25350800
H	-1.79174900	2.06694500	-3.13395400
H	-3.07591600	1.38640200	-4.14930500
H	-3.27918400	1.46711500	-2.38677200
H	-1.42071600	-0.23832200	-5.17085900
H	-0.11078600	0.42907900	-4.17224800
H	-0.43923800	-1.30363200	-4.14220000
S	-3.40190000	-0.35363500	-0.08141800
C	-3.59605900	-2.15489000	0.12255100
H	-3.63947200	-2.64653600	-0.85055800
H	-2.73414200	-2.51458300	0.68530000
H	-4.50989400	-2.34405300	0.68603700
C	-6.60462800	-0.73318900	2.97173900
C	-6.11229800	-0.08595300	1.84741600
C	-6.43651000	-0.56930500	0.55103600
C	-7.24560600	-1.73195000	0.43163400
C	-7.72948400	-2.36227600	1.56761900
C	-7.41119800	-1.86989300	2.84081200
H	-6.35924300	-0.35364200	3.95900200
H	-5.47486300	0.78482500	1.94241900
H	-7.48687700	-2.10401700	-0.55844300
H	-8.36094700	-3.23981500	1.46789700
H	-7.79074000	-2.37130200	3.72559000
C	-5.88658100	0.01826300	-0.59992400
C	-6.09710000	0.75127900	-1.66571400
H	-5.33676100	0.93587500	-2.41905800
C	-7.39098100	1.48816200	-1.89766400
F	-8.39431000	1.03348900	-1.13003500
F	-7.23244200	2.80784500	-1.62388400
F	-7.76873000	1.39357700	-3.18760200

^{OSS}DisfTS$_{HAT_RC}$-2

C	1.07991800	2.36142900	-2.54454900
C	2.05135300	3.28329400	-3.34035100
C	3.17407400	2.02474600	-1.82011000
H	2.16115300	3.02212000	-4.39261300
C	4.46899900	1.51774800	-1.23480100
C	4.30319800	0.47012100	-0.16002200
C	5.17890500	-1.01527600	1.32930200
C	3.63627100	-1.14782700	1.24165800
H	5.54833100	-0.61473400	2.27376400
H	3.12243300	-1.04872600	2.19306500
C	5.26965900	2.71394000	-0.62233100
H	6.26059100	2.34266000	-0.35024300
H	5.39707800	3.45816700	-1.41222100
C	5.26010900	0.86723200	-2.44135400
H	5.68330600	1.68681200	-3.02721300
H	6.08880300	0.29255000	-2.02076900
O	3.34731600	3.01416400	-2.71782600
O	5.47259000	-0.00413600	0.30706200
N	1.98210800	1.59534400	-1.65567700

N	3.23854300	-0.03777500	0.34172600
H	0.52320500	1.64929100	-3.15616000
C	1.62647200	4.74009300	-3.09328600
H	2.49315400	5.35986200	-2.84049700
C	0.59651200	4.64288800	-1.98982400
C	0.21564300	3.31726000	-1.75742700
C	-0.77494100	3.00017200	-0.83471100
C	-1.36621800	4.02595200	-0.07933600
C	-0.95482900	5.35370600	-0.29594500
C	0.00907600	5.67036200	-1.25372900
H	-1.05692100	1.96797500	-0.65415600
H	-1.42319000	6.14823000	0.27686300
H	0.28930000	6.70647000	-1.42254600
H	1.18840300	5.16558700	-4.00474900
C	2.21189600	-2.95955300	0.04860600
C	2.21641000	-4.11543900	-0.74768300
C	3.44240900	-4.76393900	-0.98992100
C	4.64261500	-4.27855800	-0.46907000
C	4.62885200	-3.11293600	0.29593600
C	3.41365400	-2.46824100	0.54396300
H	1.28126600	-2.43719100	0.24179800
H	3.45015800	-5.67233600	-1.58405400
H	5.57272800	-4.80246800	-0.67024000
C	0.95688000	-4.61275400	-1.34860500
C	0.93922900	-5.13364000	-2.65289100
C	-0.24843200	-4.56415300	-0.63060000
C	-0.24696500	-5.59318500	-3.22341300
H	1.85912200	-5.16604000	-3.22963700
C	-1.42922900	-5.04365300	-1.19379800
H	-0.24762500	-4.17914600	0.38371800
C	-1.43590000	-5.55594100	-2.49329000
H	-0.24075200	-5.98559500	-4.23602800
H	-2.34498600	-5.03357500	-0.61023700
H	-2.35781700	-5.92795200	-2.93020900
C	-2.37124000	3.71113900	0.96249100
C	-3.41690000	2.80847800	0.71384300
C	-2.28475000	4.30815200	2.23014800
C	-4.35974600	2.52636900	1.70204900
H	-3.50285400	2.35133000	-0.26770600
C	-3.21824900	4.01373100	3.22246500
H	-1.46579900	4.98987600	2.44093900
C	-4.26187600	3.12507300	2.95910300
H	-5.17835700	1.84752400	1.49524400
H	-3.13099000	4.47877300	4.20007300
H	-4.99814400	2.90076900	3.72496200
C	5.78550000	-2.37088100	0.93151200
H	6.15254400	-2.89050900	1.82567800
H	6.64368100	-2.23559300	0.26533700
C	4.57613200	3.31501100	0.58058000
C	3.50064200	4.20060000	0.41980000
C	4.96968400	2.96670300	1.87829500
C	2.83535400	4.72596100	1.52586100

H	3.18642400	4.49045200	-0.57678300
C	4.31550100	3.50316100	2.98924000
H	5.80611500	2.28679900	2.01729500
C	3.24579000	4.38305000	2.81611100
H	1.99942500	5.40248700	1.37465400
H	4.65045800	3.24260700	3.98942600
H	2.73962700	4.80315400	3.68033600
C	4.35140300	0.02030000	-3.30391200
C	3.86390400	-1.21228200	-2.85001200
C	3.87456600	0.52501600	-4.52050400
C	2.88748200	-1.89845700	-3.57123400
H	4.23545100	-1.64101200	-1.92585800
C	2.90787400	-0.16682500	-5.25177000
H	4.25953300	1.47152400	-4.89032000
C	2.39994800	-1.37371000	-4.76892200
H	2.50163600	-2.83611200	-3.18998100
H	2.55512500	0.23529400	-6.19741700
H	1.63651000	-1.90815800	-5.32594900
Cu	1.36660500	0.12563100	-0.37559000
C	1.27258500	-1.49446500	3.88675200
C	1.30170200	-0.13211700	3.53634300
C	2.35133500	0.62469000	4.08752900
C	3.32799200	0.07097800	4.91158600
C	3.28308700	-1.28546500	5.22076700
C	2.24662500	-2.06557200	4.71047600
C	0.32448400	0.54367400	2.56153200
H	2.42792900	1.67462900	3.84166100
H	4.11990600	0.70191900	5.30437600
H	4.03497600	-1.73991000	5.85879600
H	2.19614200	-3.12092300	4.95194500
O	0.32202800	-0.27161100	1.35821500
I	-0.20942800	-2.90848500	3.21671200
C	-1.09593400	0.63821700	3.13692600
H	-1.50445100	-0.33789500	3.39885200
H	-1.08262800	1.25940200	4.03722600
H	-1.76342500	1.11038200	2.41065600
C	0.77739100	1.94894500	2.15750200
H	0.74953300	2.64635300	2.99860700
H	1.78702200	1.94778400	1.74076100
H	0.09331500	2.32864200	1.40052600
C	-1.33669900	-0.66590700	-1.38954300
O	-0.08910000	-0.45721300	-1.57620900
N	-1.76886800	-0.66755900	-0.13417000
H	-0.60839900	-0.41550600	0.94736300
C	-2.17410500	-0.80997100	-2.67668200
C	-3.17271900	-1.97732700	-2.61420700
C	-2.92202400	0.52282300	-2.88867700
C	-1.22669500	-1.06439800	-3.86509900
H	-2.66331600	-2.91598700	-2.37705900
H	-3.96439900	-1.80145300	-1.88704300
H	-3.65171400	-2.09055000	-3.59256800
H	-2.22230300	1.36284100	-2.96319900

H	-3.50876600	0.48051700	-3.81232300
H	-3.61582100	0.72496700	-2.07007500
H	-1.82022100	-1.13966300	-4.78299800
H	-0.49465000	-0.26409300	-3.98739800
H	-0.67385800	-1.99938100	-3.73204300
S	-3.37190400	-0.75854600	0.44777300
C	-3.51582000	-2.54384600	0.79323100
H	-3.57284500	-3.11723900	-0.13268700
H	-2.63810300	-2.84405200	1.36823600
H	-4.41897700	-2.70157100	1.38653400
C	-6.78368900	-0.54670600	-3.67838000
C	-6.50969200	-0.96677600	-2.38428800
C	-6.20344200	-0.01774500	-1.37909000
C	-6.17060000	1.35940600	-1.71831500
C	-6.44797300	1.76325800	-3.01654600
C	-6.75019800	0.81527700	-4.00149500
H	-7.02994500	-1.27931000	-4.44082200
H	-6.53624500	-2.02028600	-2.12673700
H	-5.93840800	2.08885000	-0.94927800
H	-6.43428600	2.81997400	-3.26520600
H	-6.96593100	1.13691400	-5.01562400
C	-5.87019900	-0.41989500	-0.07095000
C	-6.30848000	-0.50432700	1.16246400
H	-5.67689000	-0.78054100	2.00572500
C	-7.71017300	-0.12628800	1.57279200
F	-8.50525700	0.14522700	0.52845100
F	-8.28103900	-1.10865200	2.29606900
F	-7.66351100	0.97699300	2.35903100

FavInt5

C	-0.94510200	1.78151800	-2.39829400
C	-0.69403500	2.78912700	-3.55454100
C	1.03848400	2.73431800	-2.08410700
H	-0.49344700	2.32866800	-4.52322900
C	2.40681200	3.21128000	-1.66051700
C	3.00404900	2.48923000	-0.47459400
C	4.65601400	2.27680500	1.07539100
C	3.65640400	1.09186800	1.13674400
H	4.59853800	2.96221300	1.92343200
H	3.21016200	0.94161200	2.11493900
C	2.32247100	4.73742300	-1.31573400
H	3.34296900	5.09357100	-1.15911700
H	1.92298400	5.24620700	-2.19621900
C	3.37117200	2.99871100	-2.89070900
H	3.09590300	3.73832000	-3.64654400
H	4.38515800	3.22755900	-2.55266500
O	0.54322700	3.43728400	-3.13605200
O	4.19486700	3.01771400	-0.09379700
N	0.31571400	1.78343000	-1.63148300
N	2.59717200	1.46311200	0.17276400
H	-1.15536500	0.76579200	-2.74109600
C	-1.85932800	3.78854000	-3.56537400

H	-1.49991800	4.81202700	-3.71371500
C	-2.54404100	3.56417000	-2.23546100
C	-2.07442200	2.40508500	-1.60961600
C	-2.59288200	1.98063700	-0.39332500
C	-3.60927100	2.73059300	0.21767200
C	-4.05798900	3.91070500	-0.39852500
C	-3.53365000	4.33060200	-1.62244400
H	-2.18676300	1.10827300	0.10667700
H	-4.85033800	4.48432700	0.07344300
H	-3.90575700	5.23682000	-2.09215700
H	-2.53669200	3.56084400	-4.39822100
C	3.99638500	-1.37654200	0.38132800
C	4.88644800	-2.32812400	-0.14278200
C	6.22162300	-1.95613500	-0.38446000
C	6.68088100	-0.67068400	-0.09914400
C	5.79233900	0.26380300	0.42975400
C	4.45906300	-0.09472800	0.65604400
H	2.94927200	-1.62823300	0.51292100
H	6.91109800	-2.69635800	-0.77888900
H	7.71893100	-0.40920300	-0.28484700
C	4.42368800	-3.70217000	-0.44624700
C	4.79081600	-4.34072000	-1.64114100
C	3.60578600	-4.39360200	0.46081400
C	4.34325900	-5.63007500	-1.92657000
H	5.41526500	-3.81453600	-2.35770100
C	3.16936900	-5.68733300	0.18102800
H	3.33106700	-3.91847400	1.39693700
C	3.53098500	-6.30849800	-1.01628100
H	4.62945300	-6.10482200	-2.86058200
H	2.55405300	-6.21576900	0.90391000
H	3.19002800	-7.31632700	-1.23412500
C	-4.21790100	2.25761600	1.48298400
C	-4.66683400	0.93189600	1.58592900
C	-4.37007700	3.10525200	2.58913700
C	-5.25764700	0.46586600	2.75967500
H	-4.57180400	0.28361500	0.72287600
C	-4.94573000	2.63555200	3.77005300
H	-4.01553200	4.13012300	2.52621400
C	-5.39320400	1.31588200	3.85971200
H	-5.62629600	-0.55515000	2.81124800
H	-5.04607400	3.30161400	4.62196300
H	-5.85015900	0.95562100	4.77636600
C	6.05724900	1.69831200	0.83042400
H	6.65221900	1.75208100	1.75112800
H	6.59211900	2.27702200	0.07019200
C	1.46779400	5.02719800	-0.10239700
C	0.07469300	5.12374900	-0.21752500
C	2.04854600	5.18959600	1.16230200
C	-0.72004800	5.38078700	0.89854100
H	-0.39311500	5.00947600	-1.18904300
C	1.25736900	5.45764400	2.28081500
H	3.12867100	5.12831700	1.26249300

C	-0.12923500	5.55639100	2.15108000
H	-1.79729300	5.44591500	0.78113500
H	1.72589300	5.60345600	3.25039800
H	-0.74444700	5.77007900	3.02038600
C	3.27712300	1.60385200	-3.46337100
C	3.90786500	0.52155100	-2.83719300
C	2.49203400	1.36086800	-4.59807900
C	3.73796500	-0.77601100	-3.31826700
H	4.53732200	0.68622000	-1.96975300
C	2.32883200	0.06520000	-5.08915100
H	2.01476300	2.19685300	-5.10213900
C	2.94755100	-1.00781800	-4.44502500
H	4.22021600	-1.60244000	-2.80837100
H	1.72974000	-0.10405200	-5.97969400
H	2.82591900	-2.01758000	-4.82576500
Cu	0.87866200	0.44434100	-0.15913100
C	1.61578500	-0.77027400	3.55460300
C	1.00033900	0.49092900	3.47786800
C	1.72088800	1.55353700	4.05787800
C	2.96617600	1.38568800	4.65868700
C	3.55732400	0.12555200	4.68565300
C	2.87590800	-0.95505100	4.13013700
C	-0.37841700	0.78623400	2.84775900
H	1.30346500	2.55054500	4.02223100
H	3.47195700	2.24259100	5.09334700
H	4.53293700	-0.02731600	5.13647500
H	3.32129400	-1.94265100	4.15130900
O	-0.46459000	0.23296600	1.51654700
I	0.72925000	-2.60840800	2.84809900
C	-1.50751800	0.24291300	3.73270100
H	-1.43255700	-0.83783800	3.87733400
H	-1.46362700	0.71359800	4.71939700
H	-2.47596200	0.48137800	3.28449600
C	-0.59583600	2.28251100	2.61160900
H	-0.65453000	2.84422400	3.54633800
H	0.19752500	2.70236300	1.98992100
H	-1.54100700	2.41341000	2.08738700
C	-0.31454500	-2.29772100	-0.78723200
O	0.65221900	-1.51680300	-0.78741600
N	-1.40017500	-1.92365100	-0.02926700
H	-0.81962200	-0.67602600	1.45008400
C	-0.19348100	-3.59571500	-1.62077600
C	-0.21033900	-4.82393300	-0.68423500
C	-1.31987200	-3.68421100	-2.67391600
C	1.15337600	-3.56685400	-2.36314100
H	0.56376100	-4.72997000	0.08226700
H	-1.17590100	-4.97925800	-0.19477100
H	0.01312100	-5.72442100	-1.26565700
H	-1.36607600	-2.77297000	-3.28070200
H	-1.11409900	-4.52256600	-3.34734700
H	-2.31173600	-3.85935800	-2.24725400
H	1.26232100	-4.48524000	-2.94938600

H	1.21397700	-2.70784900	-3.03537500
H	1.99001400	-3.50313200	-1.66788000
S	-2.74806300	-2.86163200	0.06860100
C	-3.30587100	-2.46433600	1.74861800
H	-2.61935400	-2.96259700	2.43489600
H	-3.27082600	-1.38331800	1.88357200
H	-4.32060000	-2.84709200	1.86832400
C	-7.74828600	-2.22656300	-0.22472000
C	-6.48413300	-1.68892500	-0.45076900
C	-5.39297900	-2.53832000	-0.70475700
C	-5.59219300	-3.93026400	-0.71942200
C	-6.86110600	-4.45990600	-0.49623900
C	-7.94010400	-3.61002000	-0.24515600
H	-8.58471600	-1.56271300	-0.02996100
H	-6.33995500	-0.61541100	-0.43117500
H	-4.76101100	-4.59595300	-0.93274100
H	-7.00769800	-5.53503800	-0.52405400
H	-8.92761700	-4.02442300	-0.06765600
C	-4.04608900	-1.97799000	-0.88889600
C	-3.61048800	-0.95374300	-1.62417000
H	-2.57142000	-0.65247000	-1.54175700
C	-4.44544000	-0.14275000	-2.57079500
F	-5.37124100	-0.87451400	-3.21141900
F	-5.09099700	0.86508700	-1.93824400
F	-3.64738900	0.42189900	-3.50744000

DisfInt5

C	1.39919000	2.55488400	-2.63498400
C	2.54009700	3.35469900	-3.33288400
C	3.36431700	1.87707800	-1.81035900
H	2.64541600	3.15783700	-4.40023600
C	4.54567100	1.20656400	-1.14274000
C	4.19822400	0.18223700	-0.08522600
C	4.82322800	-1.27858000	1.54266900
C	3.28876600	-1.31590300	1.29880700
H	5.11289800	-0.86588400	2.51008800
H	2.69266300	-1.08504200	2.17968600
C	5.44476200	2.30323900	-0.47926200
H	6.37012700	1.81910600	-0.16002300
H	5.69915300	3.03087000	-1.25348800
C	5.34653800	0.46778300	-2.28234100
H	5.73005200	1.23431900	-2.96027400
H	6.20103200	-0.02405600	-1.81050200
O	3.74287500	2.83518000	-2.69634100
O	5.29257500	-0.33336900	0.53189600
N	2.11223100	1.64466000	-1.71334900
N	3.06235700	-0.27134200	0.27951200
H	0.78968600	1.94941800	-3.31182600
C	2.33668100	4.84643000	-3.00197000
H	3.26758900	5.29164700	-2.63534700
C	1.21229400	4.85588300	-1.98881300
C	0.62132700	3.59484600	-1.86741100

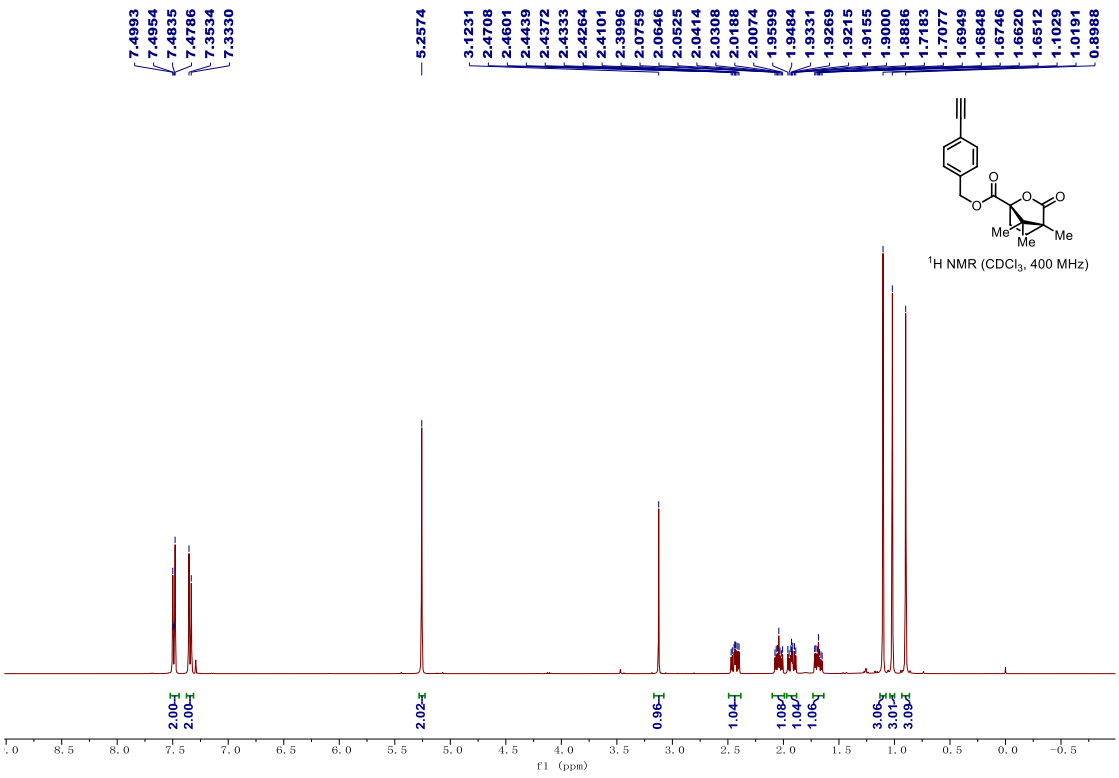
C	-0.47643100	3.38588700	-1.04152900
C	-0.97288100	4.45124700	-0.27255300
C	-0.35115000	5.70868200	-0.37044400
C	0.72538600	5.92187400	-1.23318700
H	-0.90855500	2.39375800	-0.93855400
H	-0.74220800	6.53506200	0.21552400
H	1.17024100	6.90990300	-1.31375900
H	2.05598500	5.40169900	-3.90550400
C	1.81658200	-3.19563400	0.27224900
C	1.78113600	-4.48229000	-0.28893200
C	2.97239200	-5.22930800	-0.35510400
C	4.17915800	-4.72146300	0.12674800
C	4.20270500	-3.44295400	0.68193300
C	3.02421800	-2.69377300	0.74358700
H	0.92029500	-2.58525900	0.30928000
H	2.94277400	-6.23367000	-0.76658500
H	5.08227300	-5.32312400	0.07334000
C	0.51450100	-5.05012600	-0.80707400
C	0.48847200	-5.78442000	-2.00340500
C	-0.68863400	-4.87590600	-0.10403100
C	-0.70316900	-6.32305500	-2.48721300
H	1.40649900	-5.91416100	-2.56895800
C	-1.87807900	-5.42534000	-0.58239100
H	-0.67451700	-4.33849300	0.83815300
C	-1.89285000	-6.14620000	-1.77896700
H	-0.70260500	-6.87966800	-3.41971800
H	-2.79285500	-5.32145600	-0.00402600
H	-2.81902500	-6.57560600	-2.14899900
C	-2.10769100	4.23121500	0.65417200
C	-3.25284400	3.54603400	0.22259200
C	-2.05390400	4.68094000	1.98221800
C	-4.31389600	3.30552500	1.09498200
H	-3.32355600	3.24959700	-0.81770200
C	-3.11035900	4.43508900	2.85830800
H	-1.16645800	5.20032000	2.33210200
C	-4.24120500	3.74265500	2.41940700
H	-5.20597200	2.80584300	0.73152300
H	-3.04948600	4.78129900	3.88596000
H	-5.06757100	3.56057600	3.10028300
C	5.37381500	-2.69185500	1.27947900
H	5.70413900	-3.15170000	2.21917700
H	6.24892200	-2.65054700	0.62188000
C	4.77626300	2.98290000	0.69572000
C	3.83694700	4.00418800	0.49601200
C	5.06742600	2.58989900	2.00803700
C	3.20809600	4.62120700	1.57562400
H	3.60255900	4.32749800	-0.51143700
C	4.44941300	3.21419800	3.09342300
H	5.79700700	1.80306900	2.17712000
C	3.51839100	4.23225400	2.88047400
H	2.47778600	5.40379200	1.39249800
H	4.70651500	2.91374500	4.10561800

H	3.04218700	4.72205400	3.72500300
C	4.48141300	-0.52545200	-3.02126600
C	4.29023700	-1.81575200	-2.51420400
C	3.78206900	-0.14652100	-4.17439800
C	3.40232100	-2.70026500	-3.12440700
H	4.83457600	-2.13330100	-1.63158400
C	2.89705200	-1.02971000	-4.79295400
H	3.93992300	0.84475400	-4.59145500
C	2.69918800	-2.30701000	-4.26397900
H	3.26425600	-3.69068100	-2.70432600
H	2.36992700	-0.72485900	-5.69281600
H	2.01183200	-2.99644900	-4.74527600
Cu	1.25239500	0.21262100	-0.54201400
C	0.58897900	-1.26093900	3.85172400
C	0.87656200	0.06647000	3.49236100
C	2.00459300	0.63695700	4.10871100
C	2.81147800	-0.06571000	5.00055300
C	2.50945000	-1.38784800	5.31328900
C	1.38699100	-1.98410600	4.73996700
C	0.10442700	0.87147600	2.43257100
H	2.28188000	1.65182900	3.85848700
H	3.67560700	0.42275500	5.44122500
H	3.12821900	-1.95661000	6.00067100
H	1.13564000	-3.00990000	4.98272700
O	0.07568200	0.03488200	1.25628100
I	-1.09258700	-2.39904400	3.10147000
C	-1.31889900	1.22165800	2.88958300
H	-1.89336800	0.34160100	3.18071900
H	-1.27935700	1.90173800	3.74480700
H	-1.84724900	1.73675200	2.08142100
C	0.82597300	2.16353500	2.04414600
H	0.86685000	2.87845800	2.87003300
H	1.84201200	1.96497800	1.69786900
H	0.27944300	2.63263400	1.22763300
C	-1.43888200	-0.93692600	-1.58089800
O	-0.23660000	-0.65083800	-1.70442000
N	-2.00627200	-0.51760700	-0.39086100
H	-0.81889700	-0.04514400	0.84184300
C	-2.05738200	-1.63774000	-2.81947800
C	-3.41393000	-2.32610300	-2.64412500
C	-2.16460200	-0.56439000	-3.93114100
C	-1.03629600	-2.70539400	-3.27121500
H	-3.34180100	-3.17620600	-1.96199300
H	-4.20287400	-1.64605900	-2.31700200
H	-3.72455500	-2.72591200	-3.61494100
H	-1.21869100	-0.02674600	-4.03955400
H	-2.39033800	-1.05899400	-4.88169200
H	-2.96561700	0.15786200	-3.74630200
H	-1.41755300	-3.21576800	-4.16214500
H	-0.07192400	-2.25197200	-3.50236600
H	-0.88373100	-3.45339500	-2.49184200
S	-3.42247000	-0.69637600	0.37340000

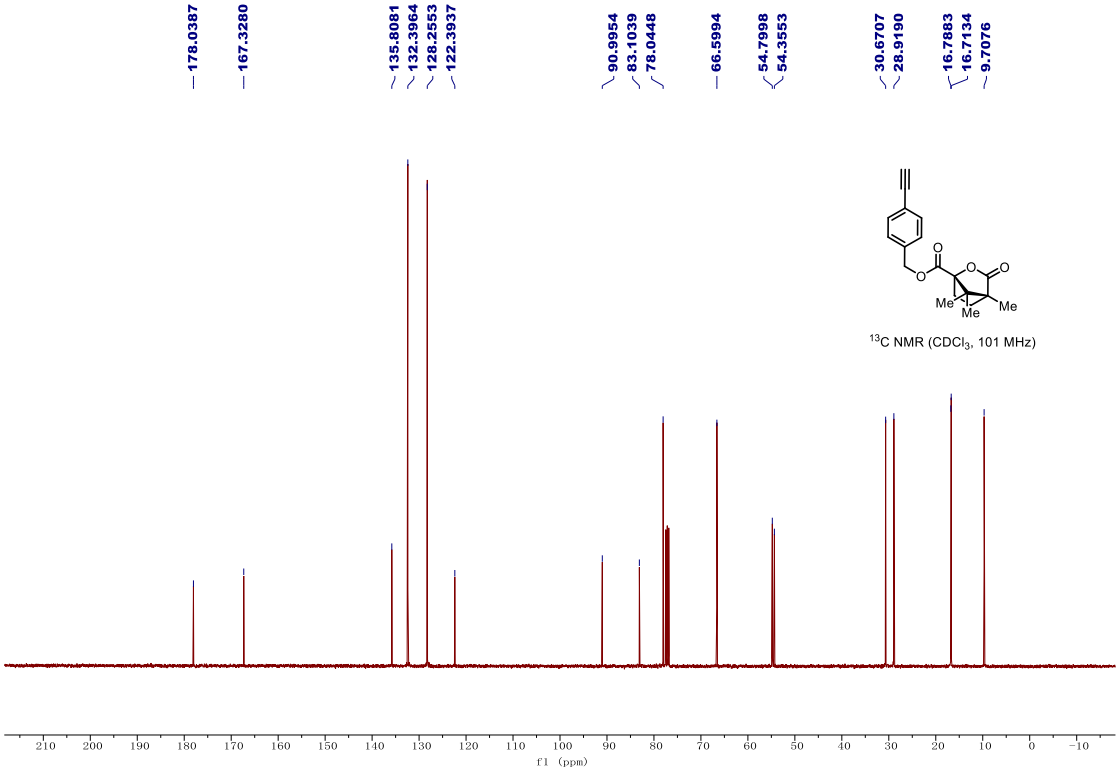
C	-4.06360700	-2.42433300	0.46193200
H	-4.77321500	-2.64361300	-0.33182600
H	-3.18651100	-3.06895100	0.39798700
H	-4.53598800	-2.51492400	1.44139100
C	-7.52129700	-0.19085700	2.04361400
C	-6.27852900	0.06366500	1.46822500
C	-6.10152000	-0.09318100	0.08247500
C	-7.17709900	-0.51578500	-0.71397300
C	-8.41564800	-0.77012600	-0.12936300
C	-8.58927600	-0.61123900	1.24731300
H	-7.65769000	-0.05554900	3.11198300
H	-5.45445600	0.41459700	2.08306200
H	-7.03887600	-0.63209400	-1.78347000
H	-9.24563300	-1.09343900	-0.74966400
H	-9.55605900	-0.81125400	1.69863100
C	-4.78034800	0.13632200	-0.52200900
C	-4.42137900	0.91459800	-1.54144100
H	-3.38505000	0.95497700	-1.85219900
C	-5.34605900	1.77688800	-2.34539600
F	-6.33055200	2.32653400	-1.61297100
F	-4.64356300	2.77837400	-2.91632500
F	-5.92302900	1.07040300	-3.34644900

8. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Title Compounds

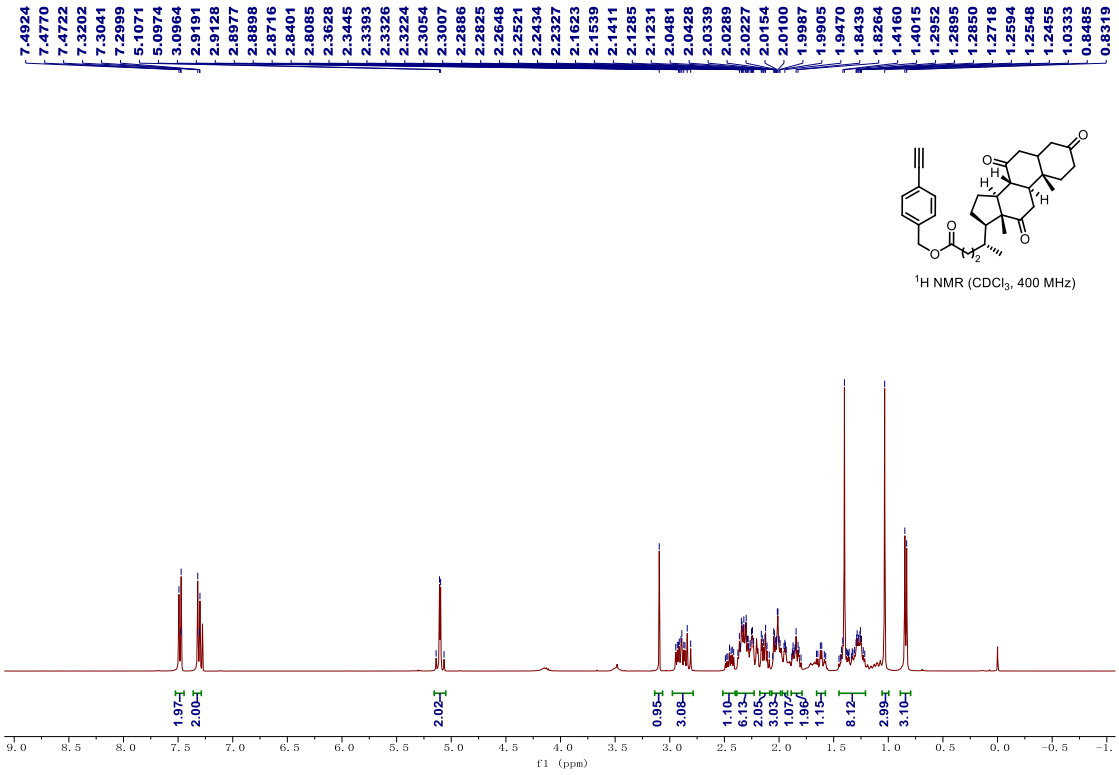
^{1}H NMR Spectrum of 1s



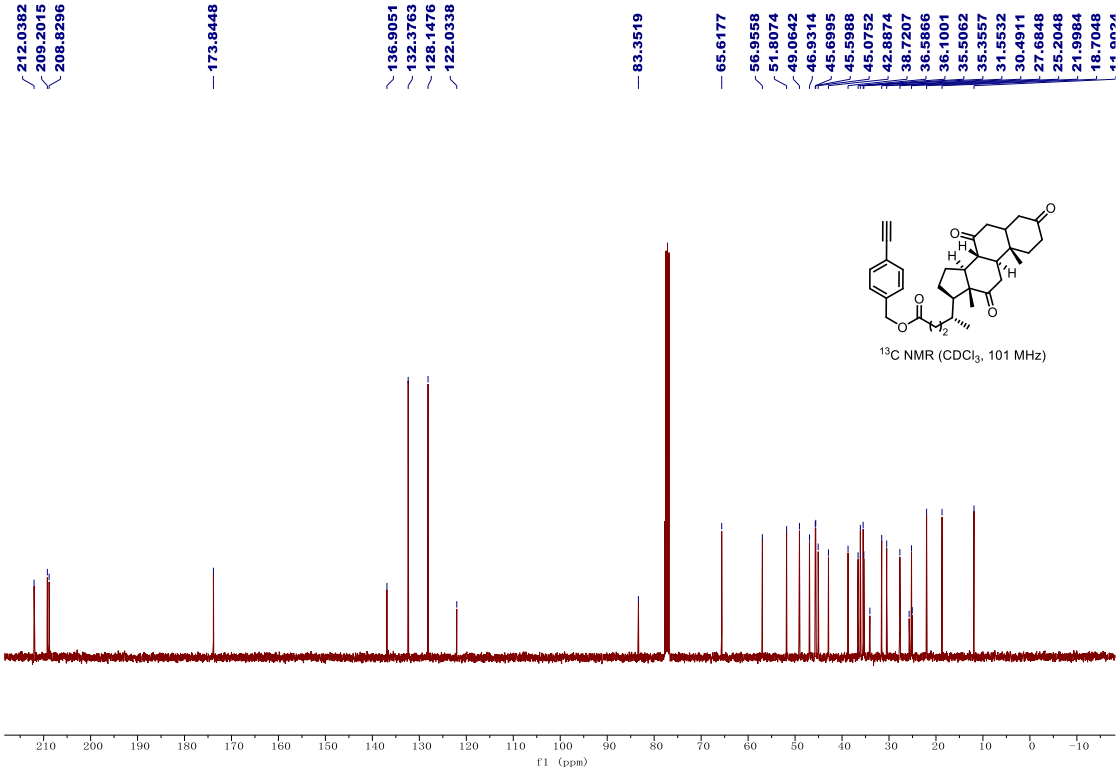
^{13}C NMR Spectrum of 1s



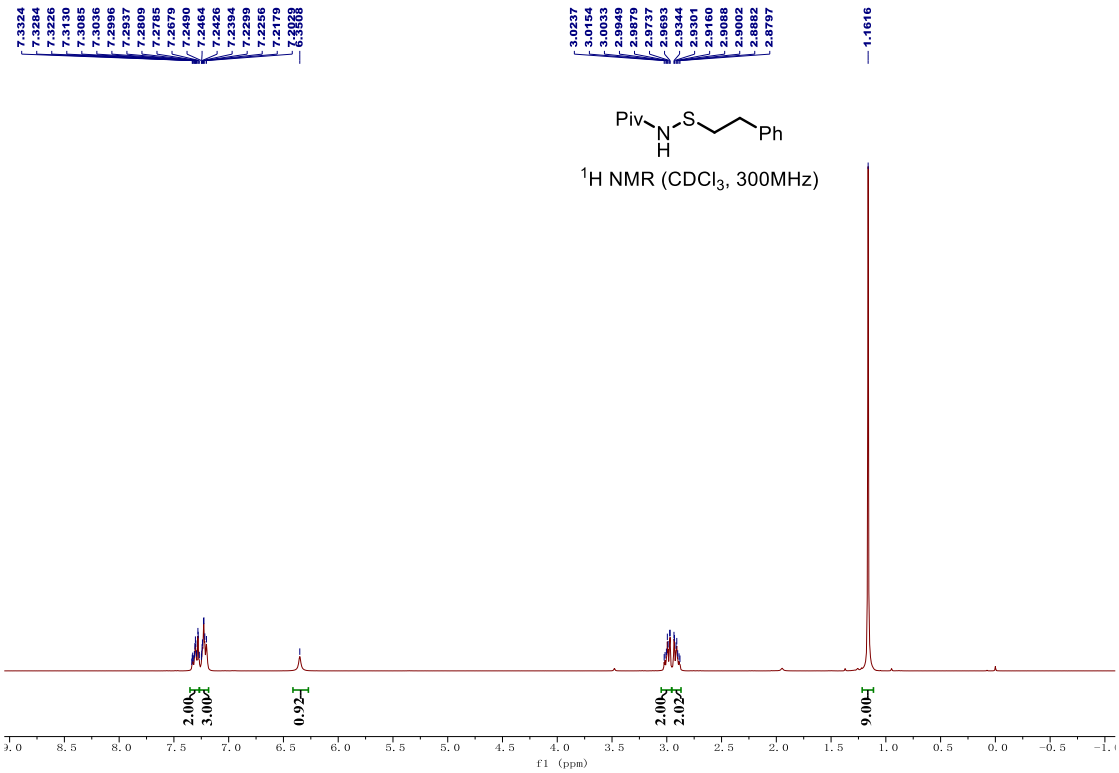
^{1}H NMR Spectrum of 1t



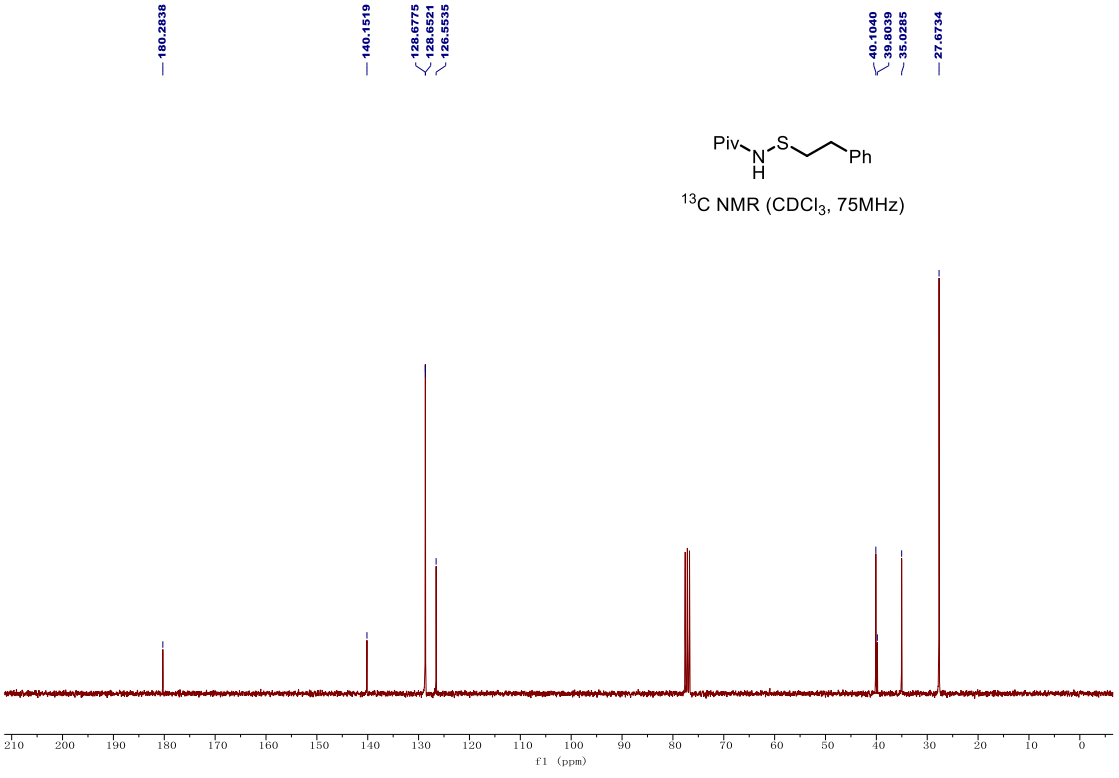
^{13}C NMR Spectrum of 1t



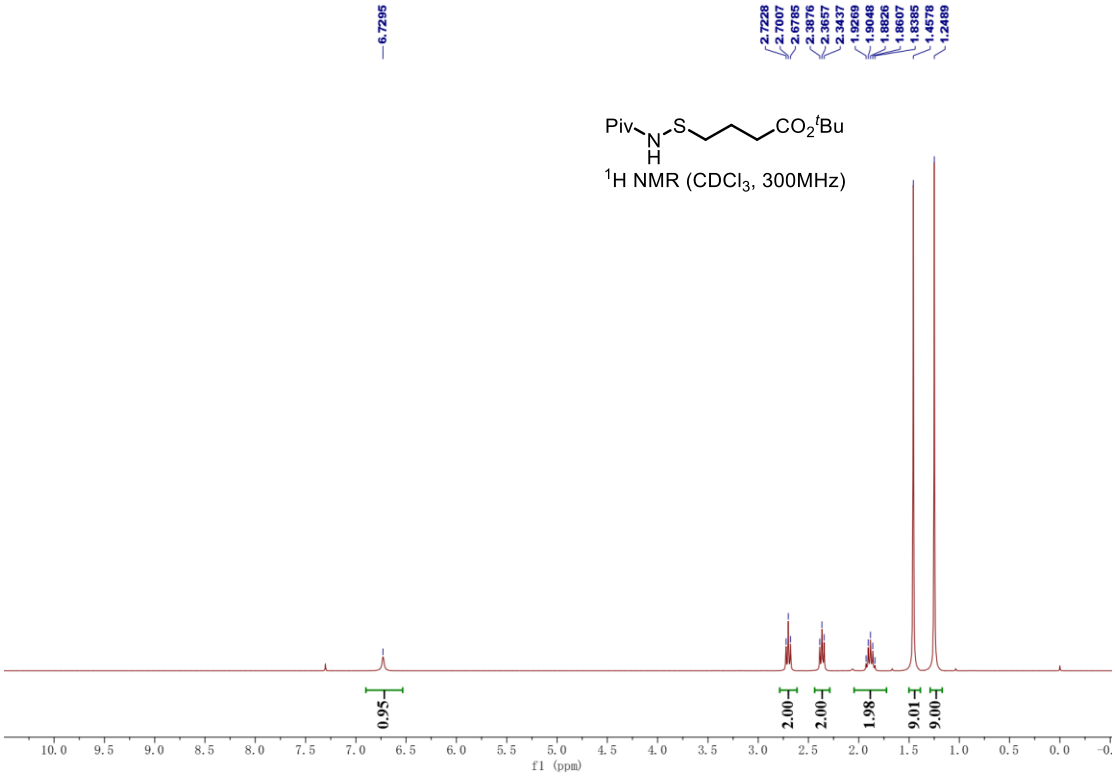
^{1}H NMR Spectrum of 3n



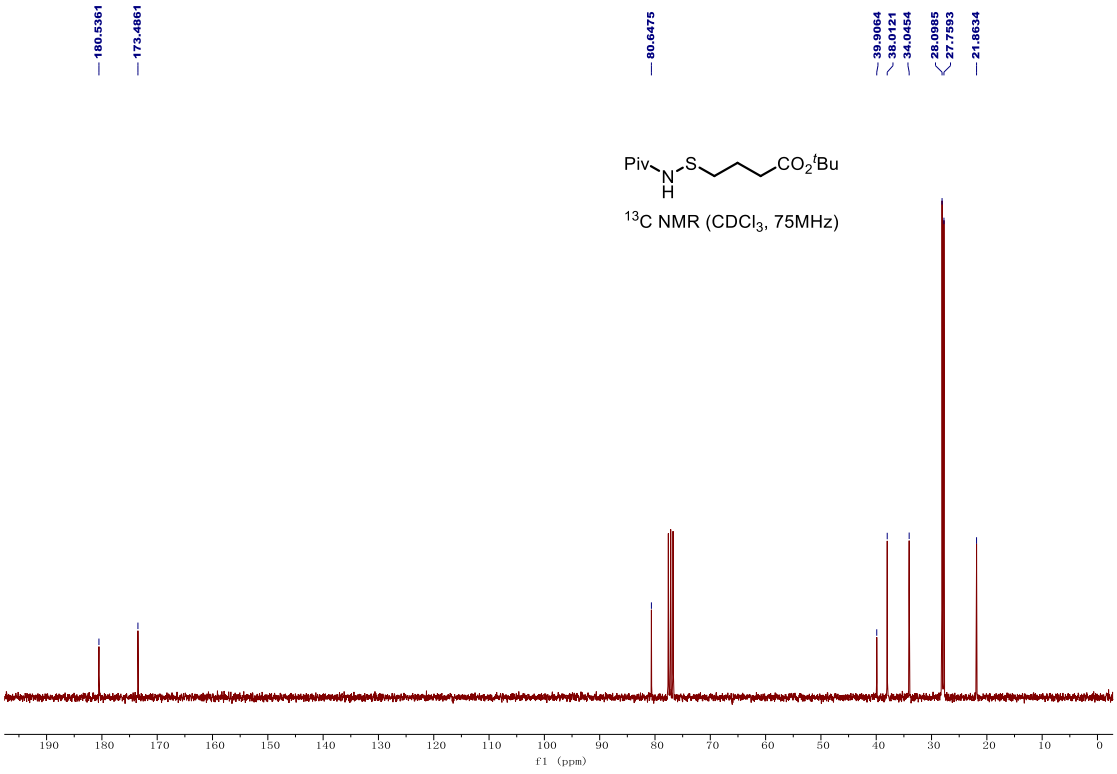
^{13}C NMR Spectrum of 3n



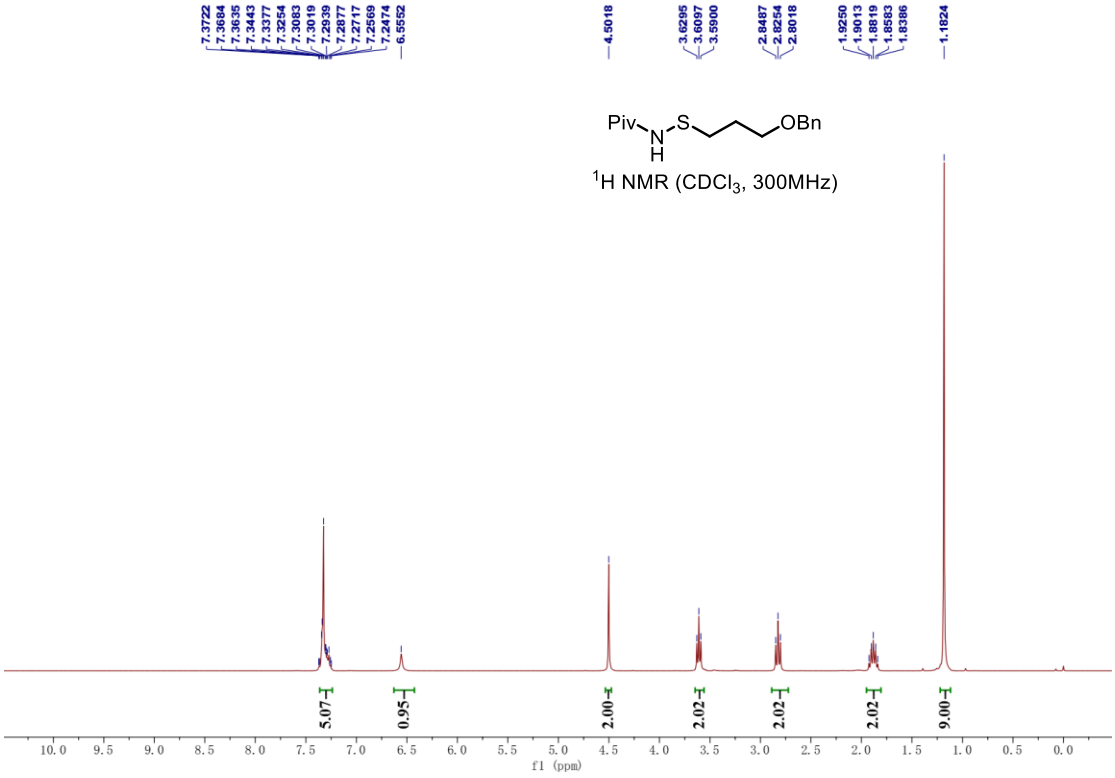
^{1}H NMR Spectrum of 3o



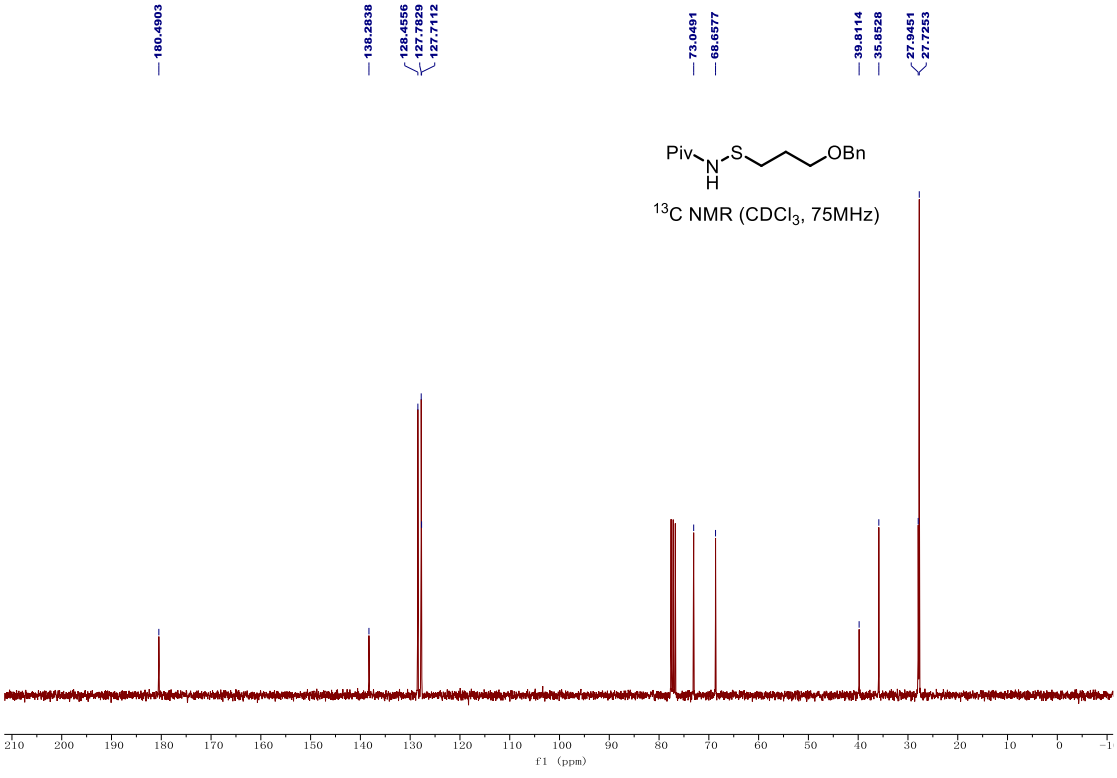
^{13}C NMR Spectrum of 3o



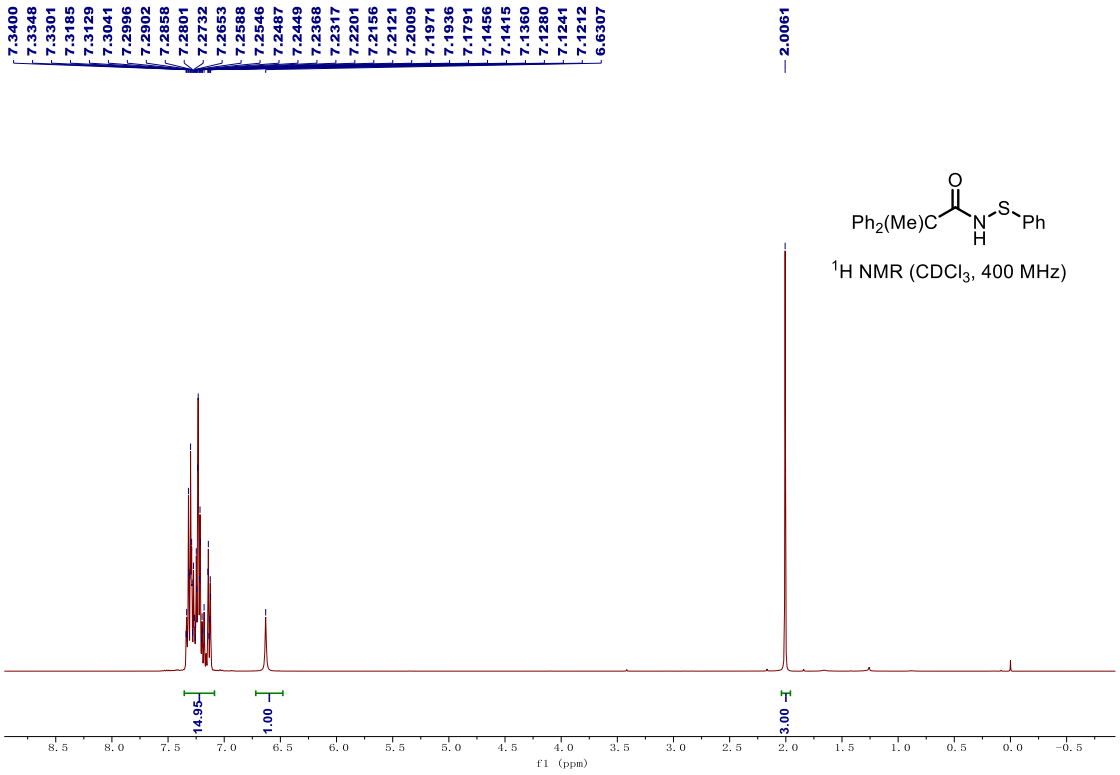
^{1}H NMR Spectrum of 3p



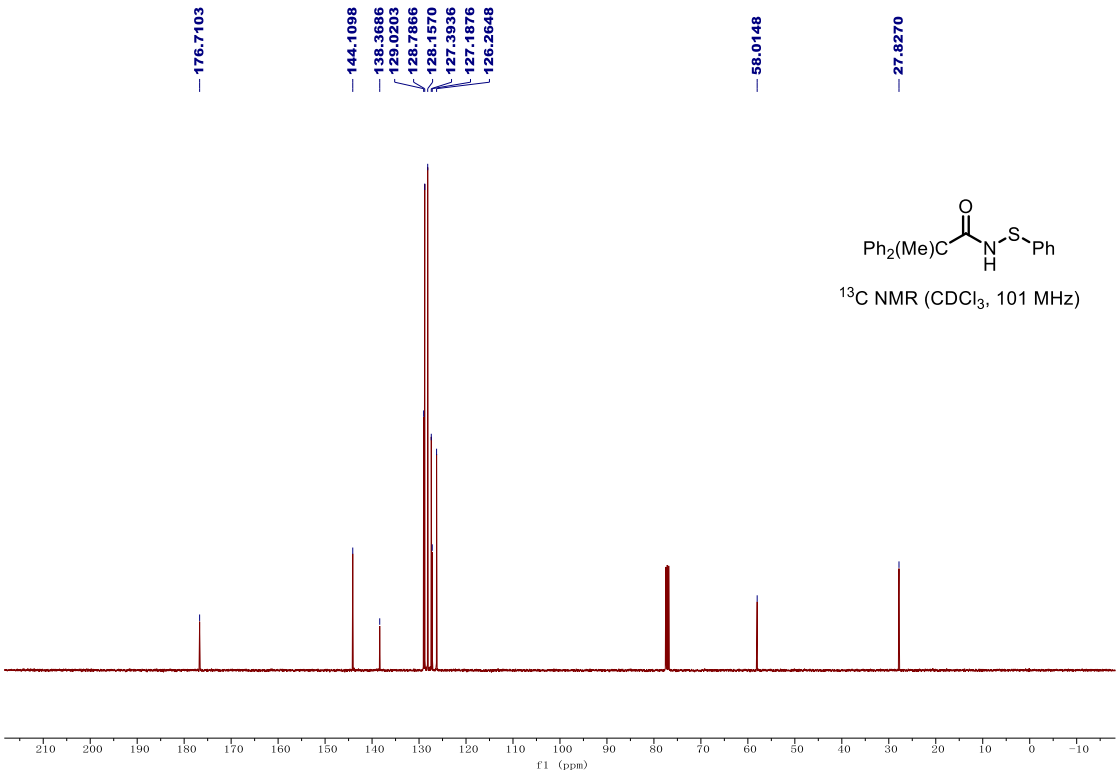
^{13}C NMR Spectrum of 3p



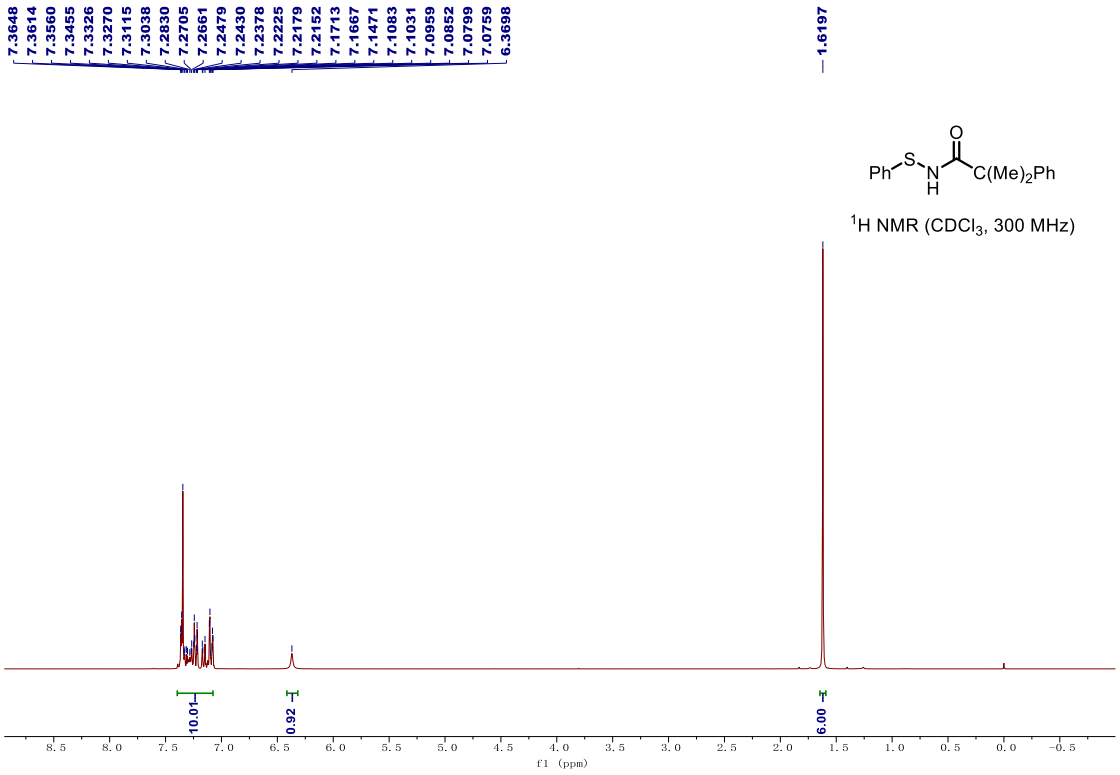
^{1}H NMR Spectrum of 3w



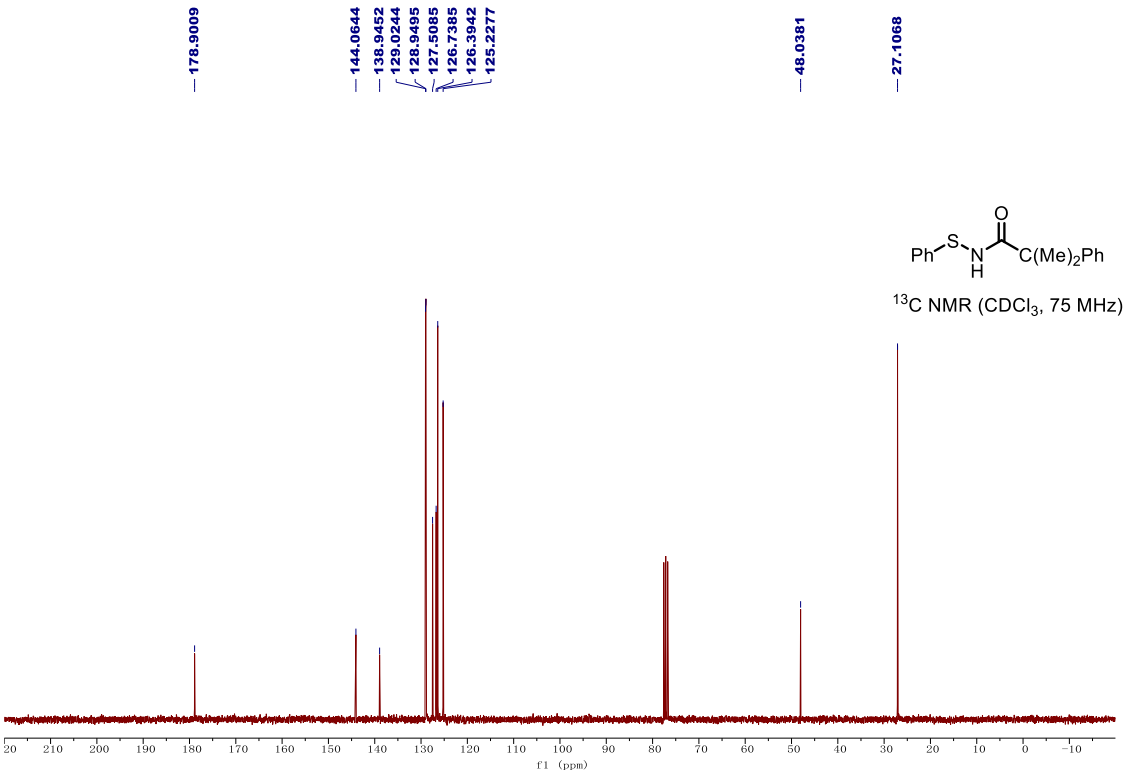
^{13}C NMR Spectrum of 3w



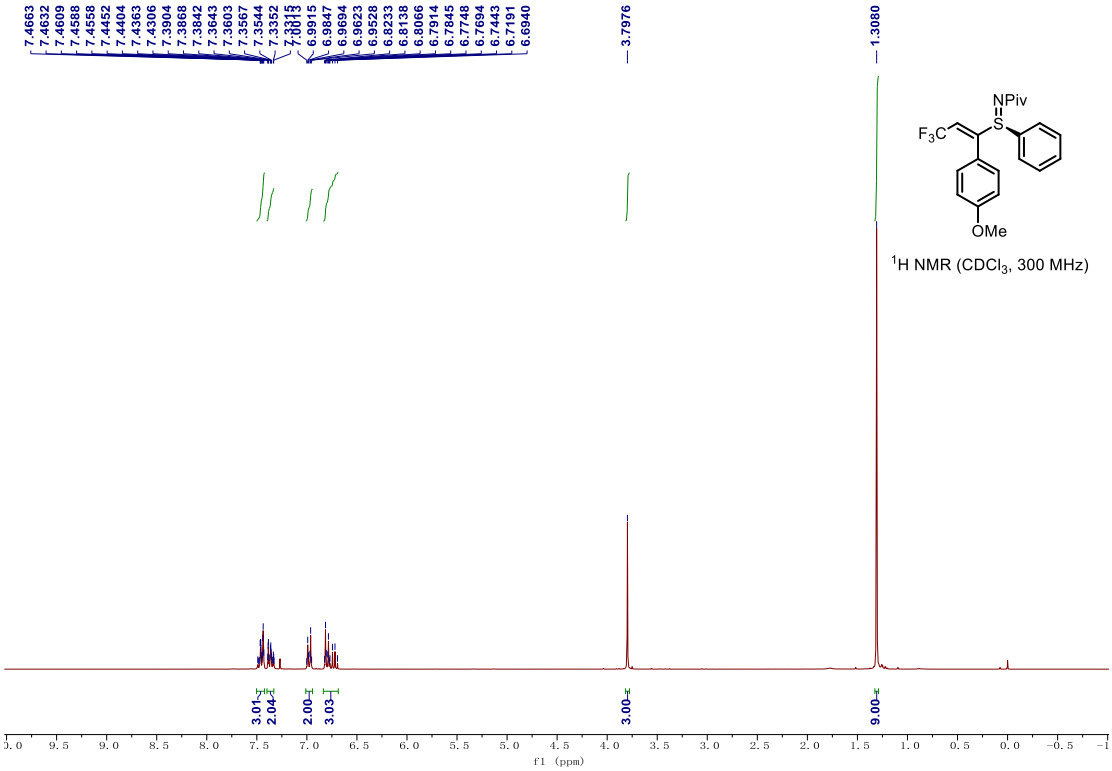
^{1}H NMR Spectrum of 3x



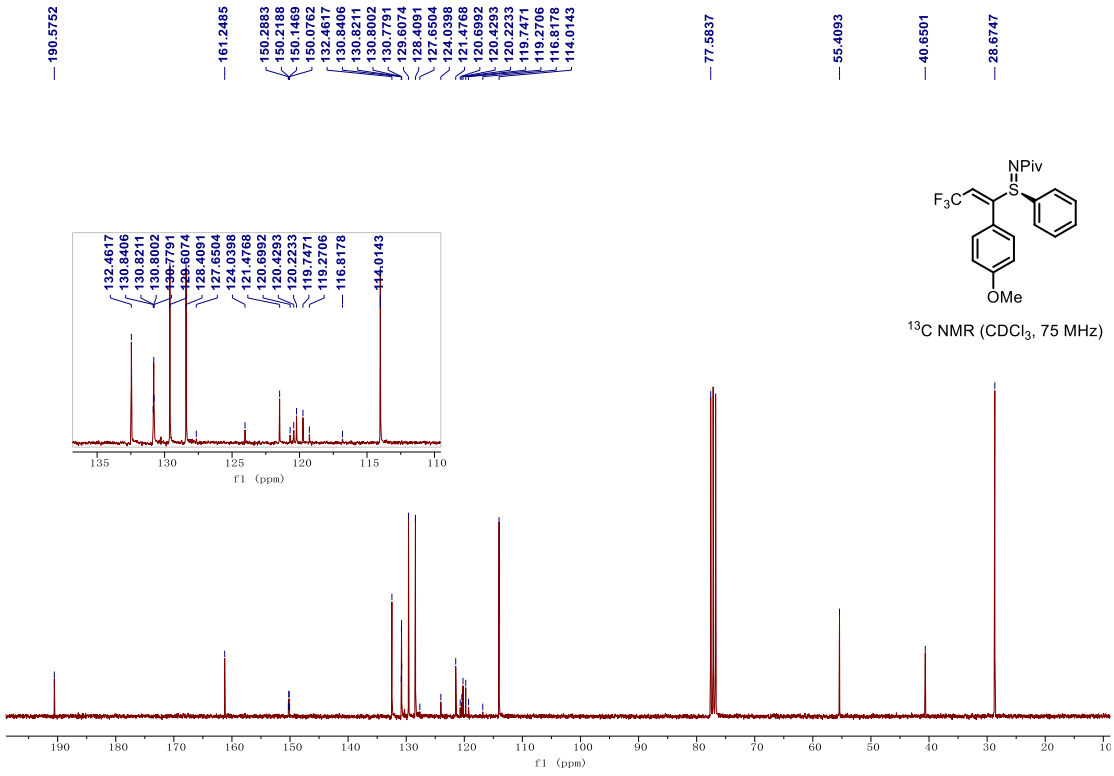
^{13}C NMR Spectrum of 3x



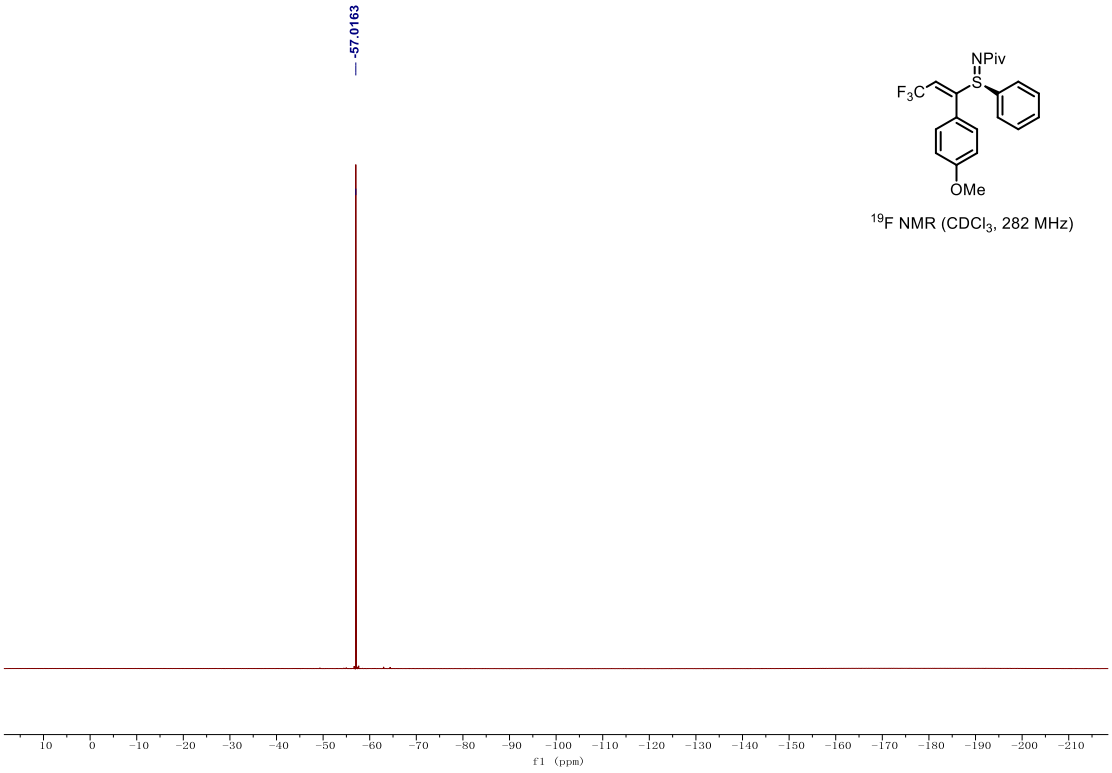
^{1}H NMR Spectrum of 4a



^{13}C NMR Spectrum of 4a

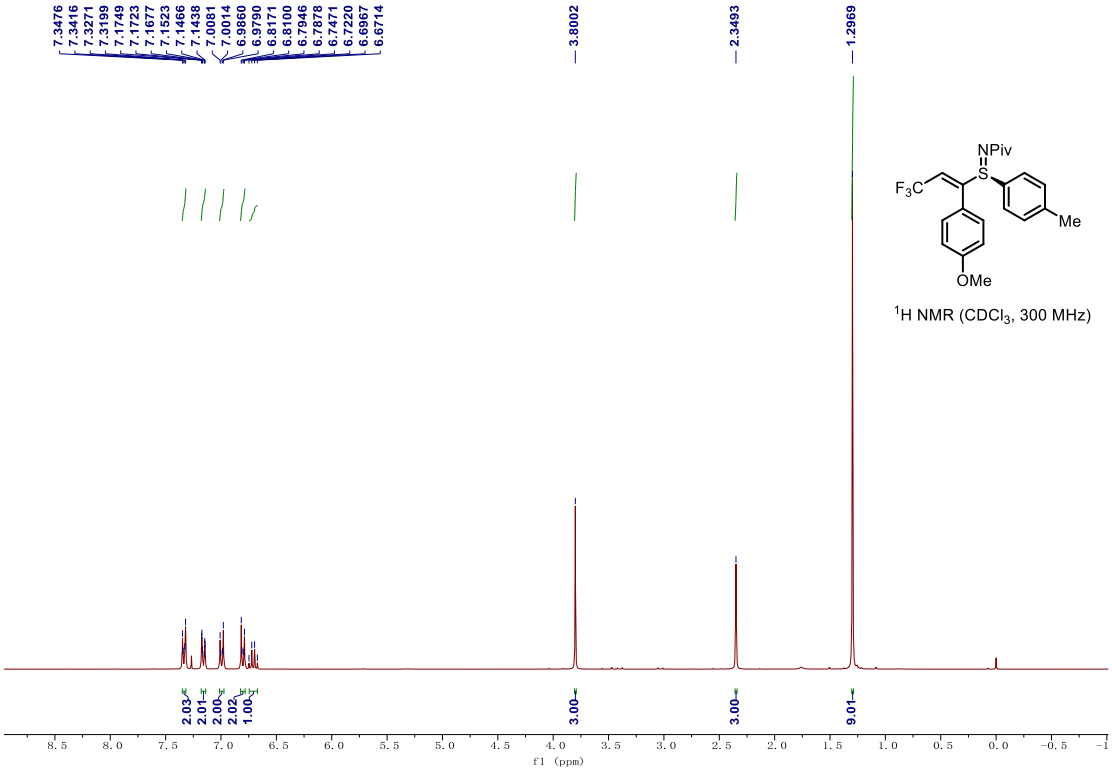


^{19}F NMR Spectrum of 4a



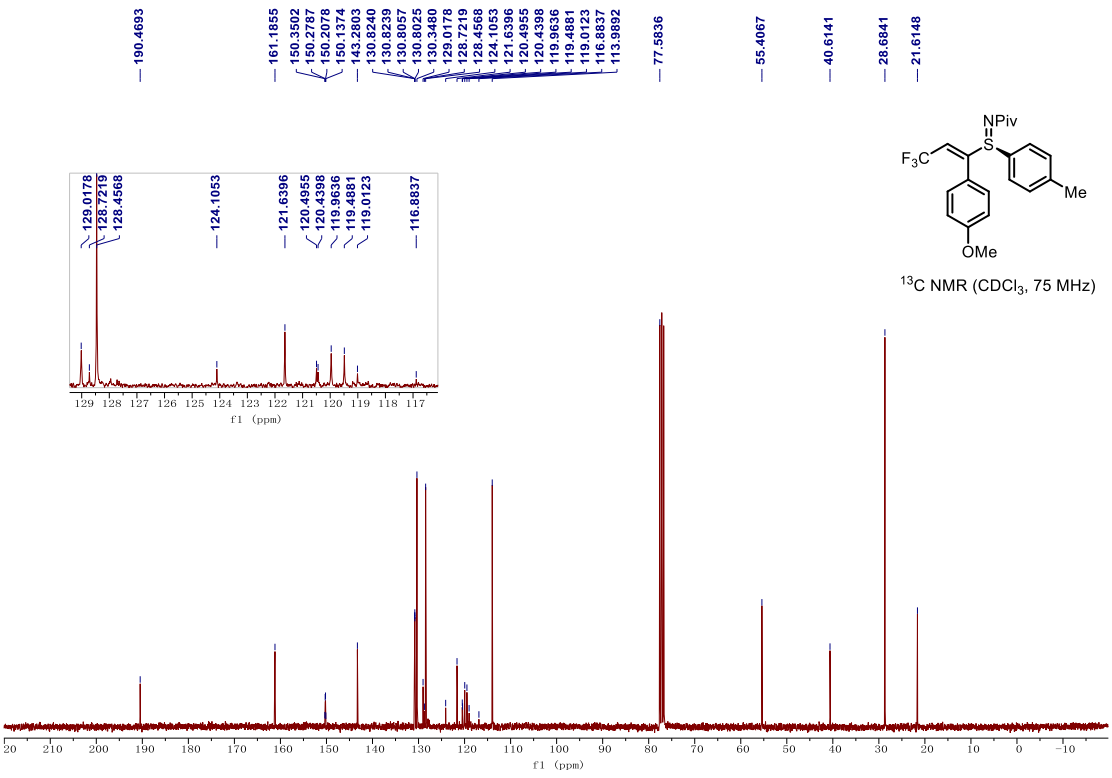
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4b



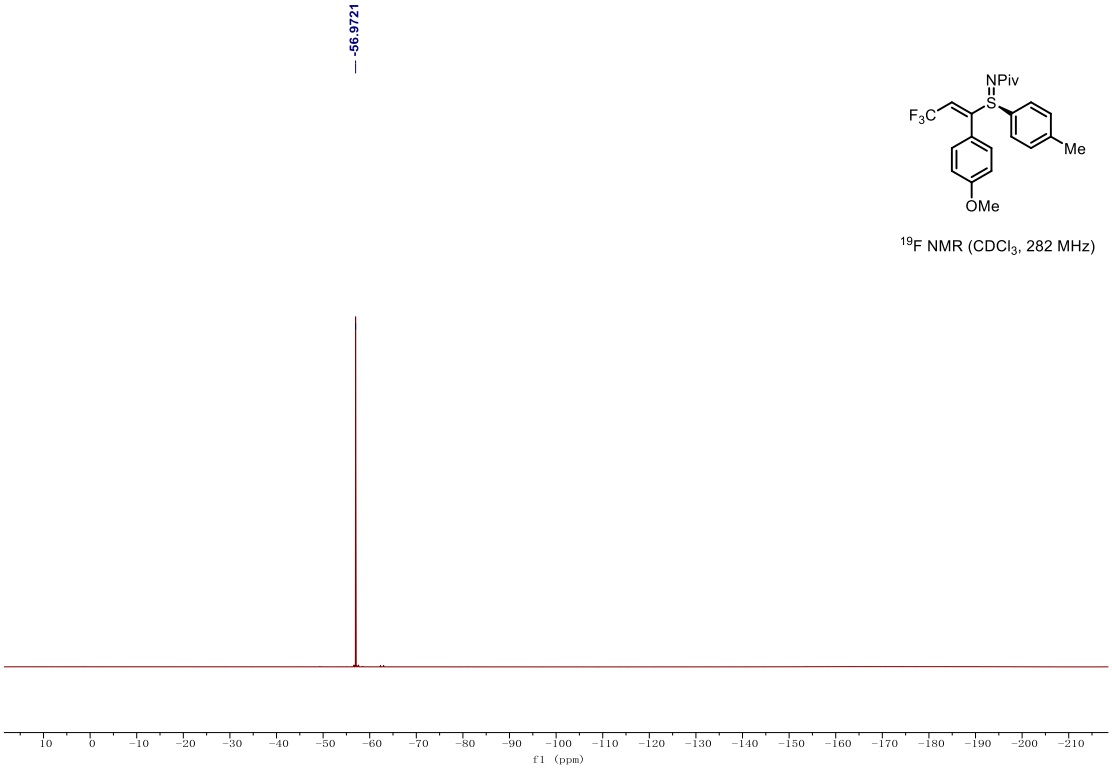
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4b

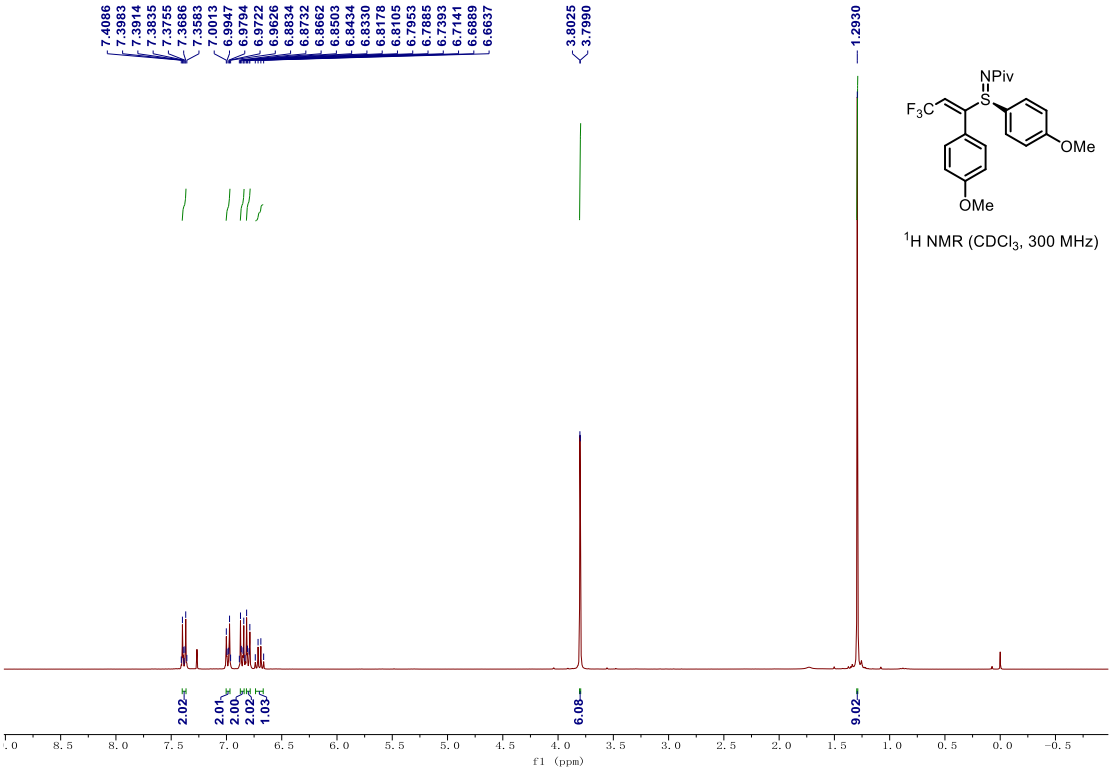


^{13}C NMR ($CDCl_3$, 75 MHz)

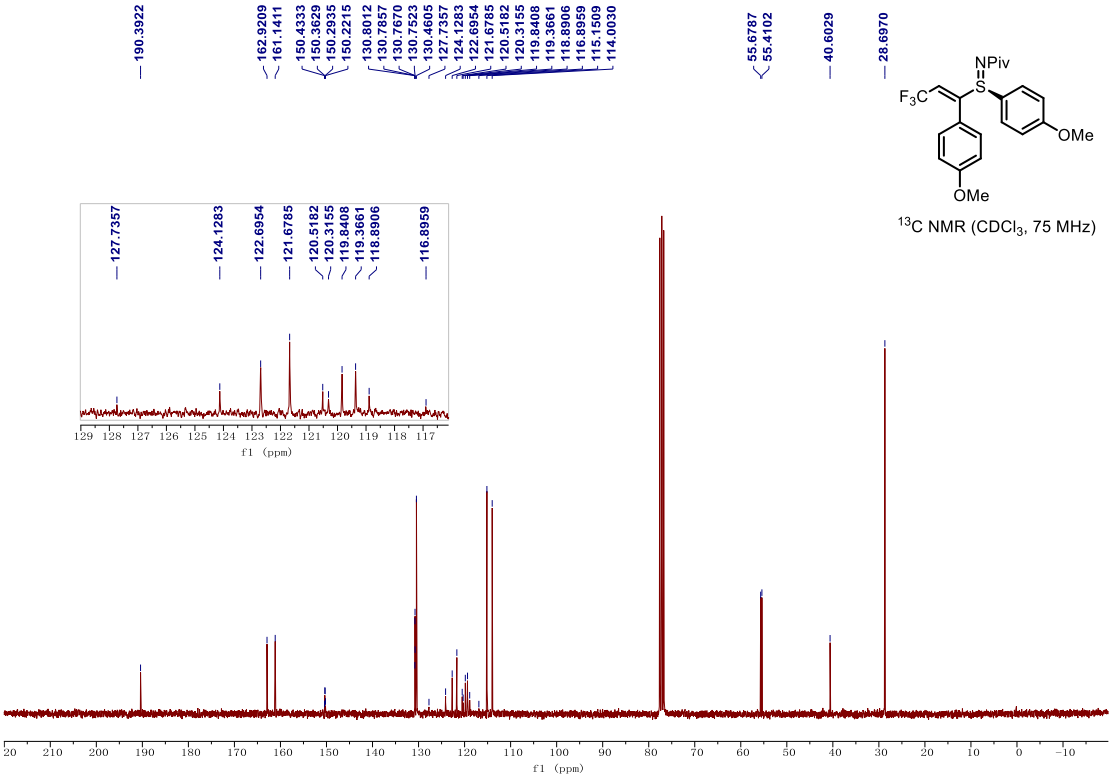
^{19}F NMR Spectrum of 4b



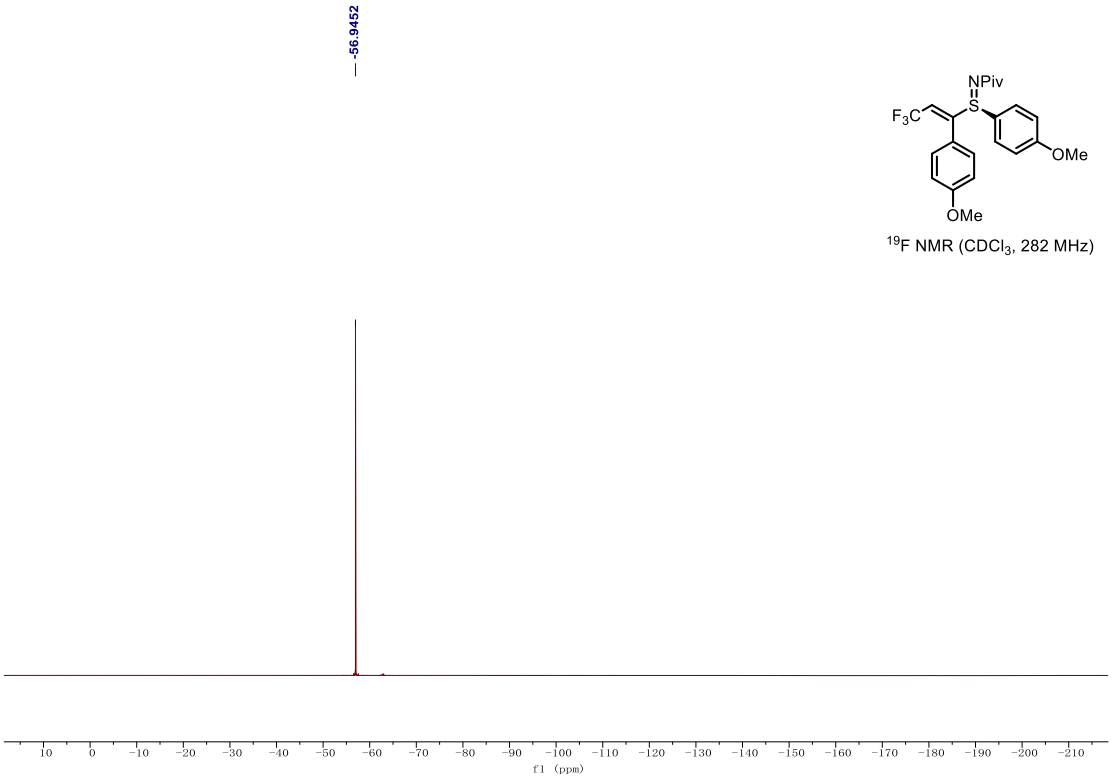
^{1}H NMR Spectrum of 4c



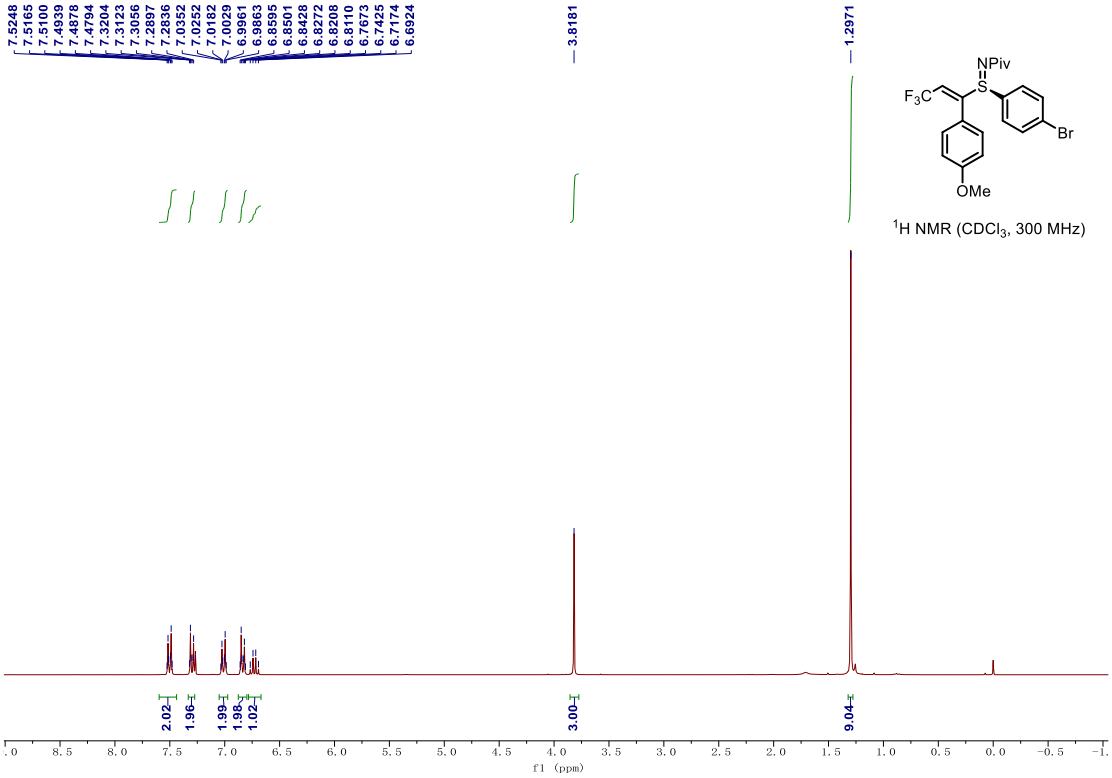
^{13}C NMR Spectrum of 4c



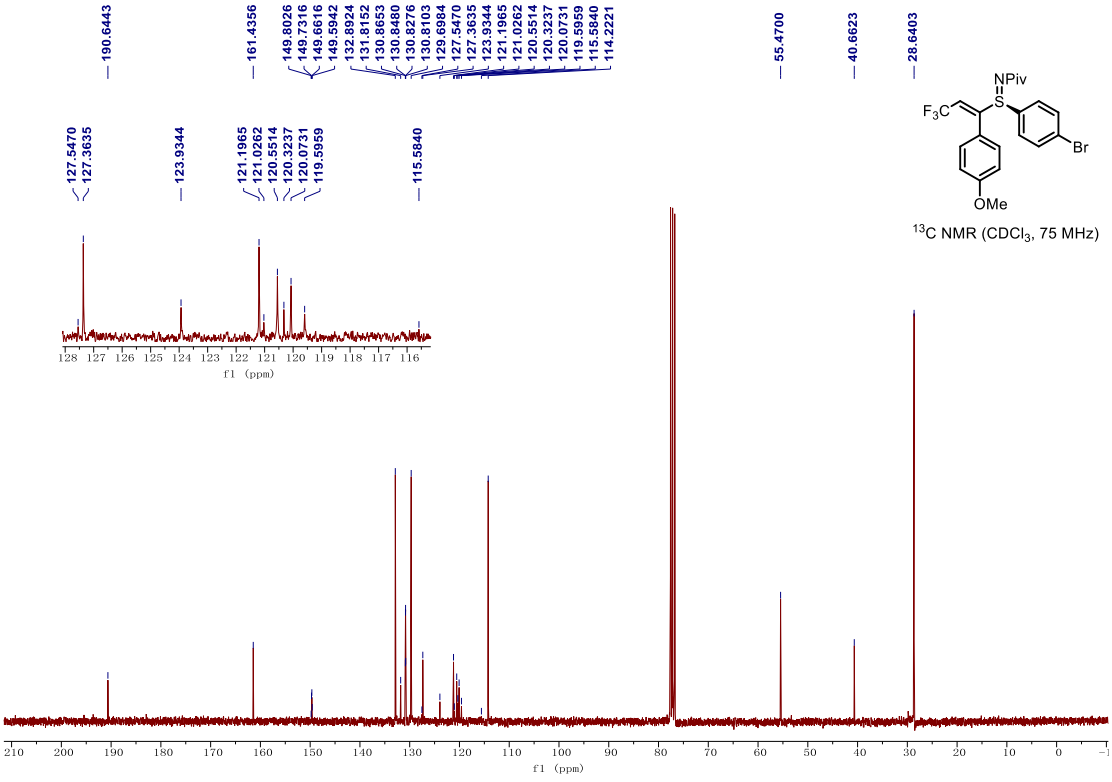
^{19}F NMR Spectrum of 4c



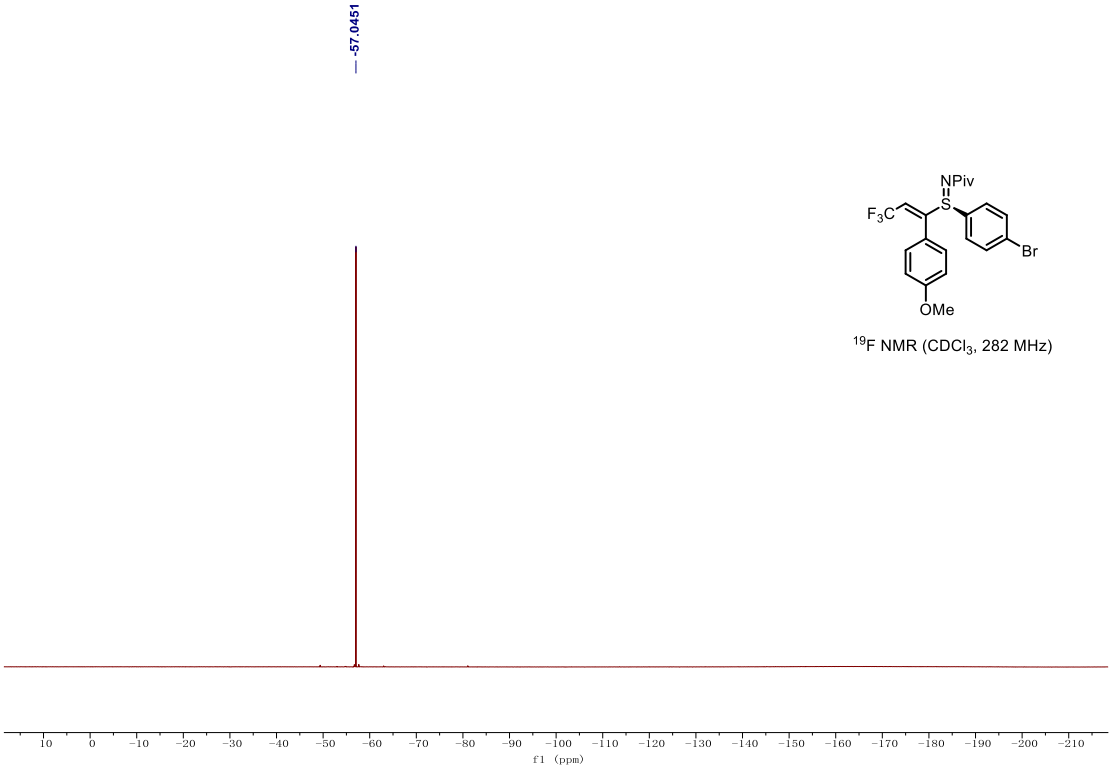
^{1}H NMR Spectrum of 4d



^{13}C NMR Spectrum of 4d

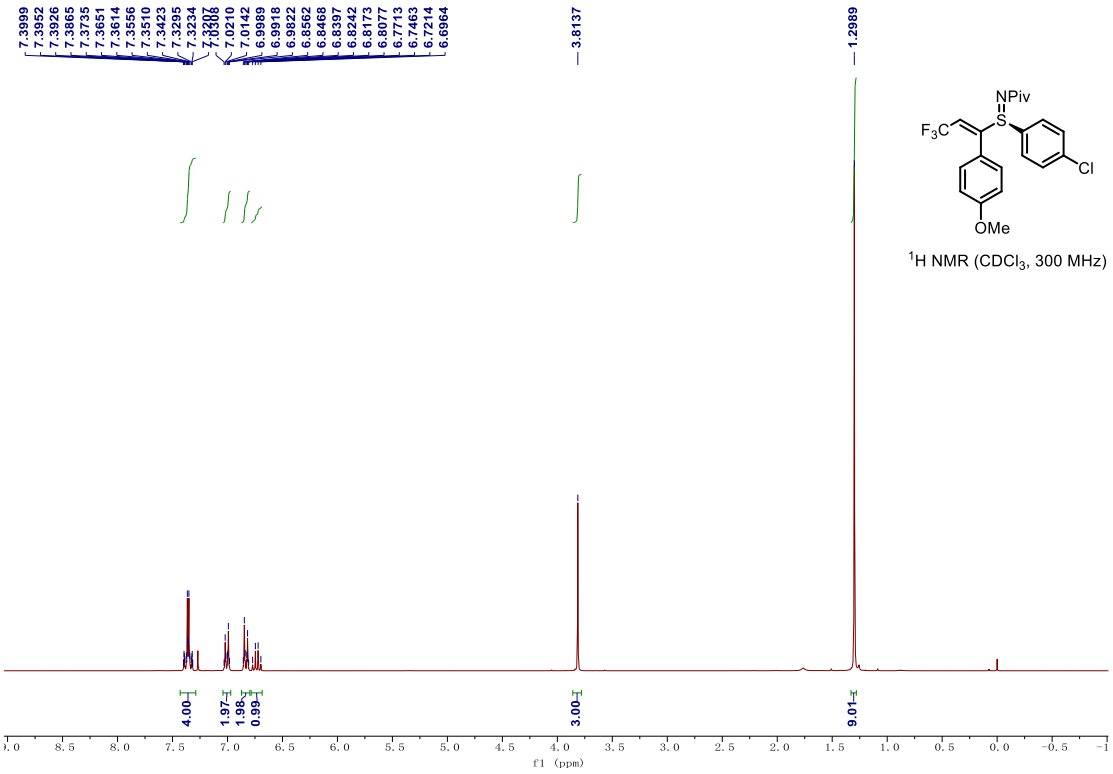


^{19}F NMR Spectrum of 4d



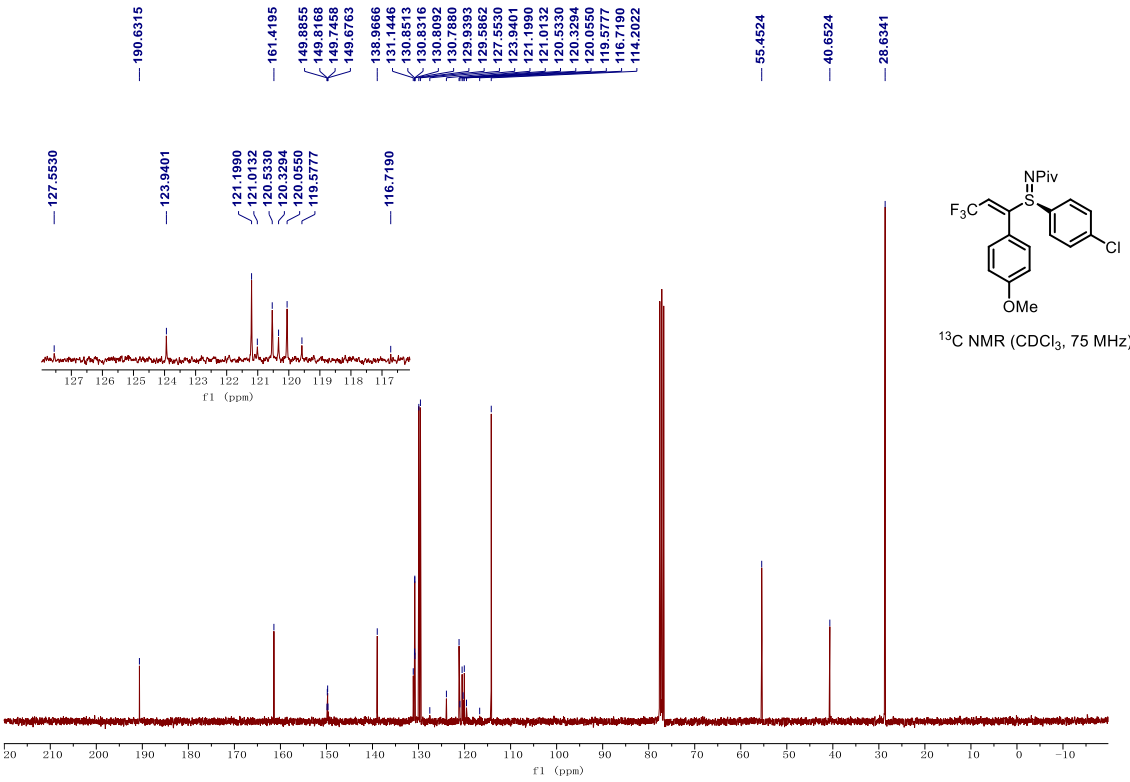
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4e



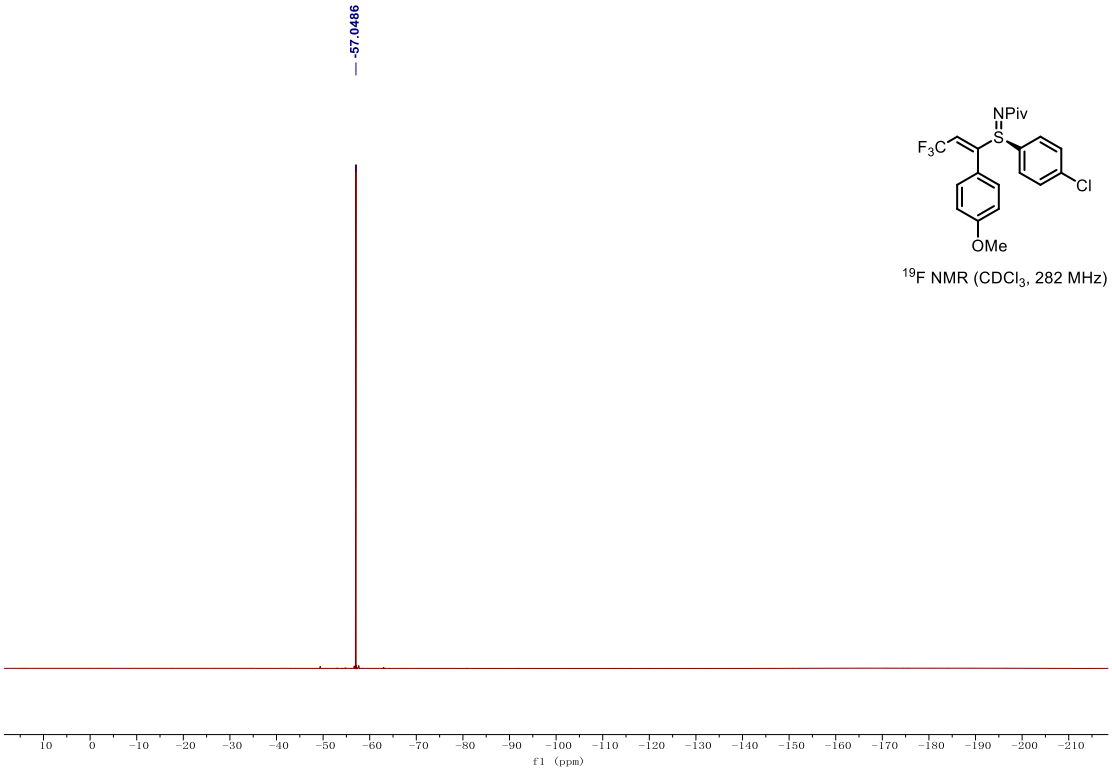
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4e



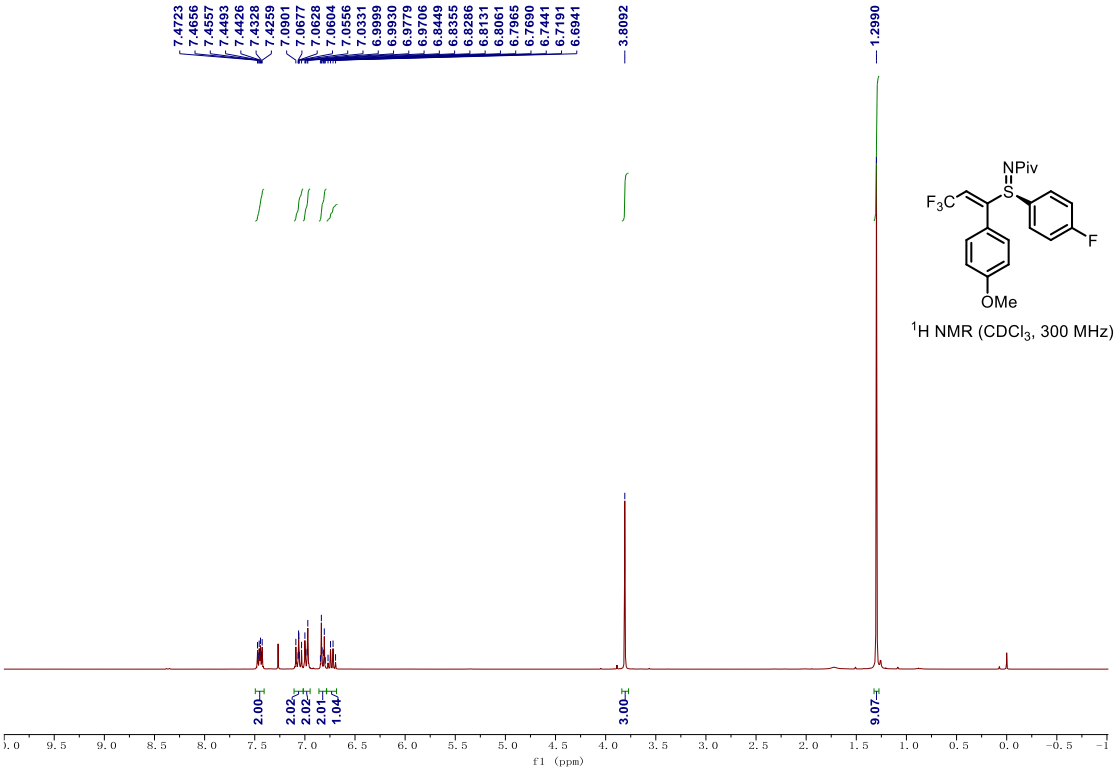
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4e

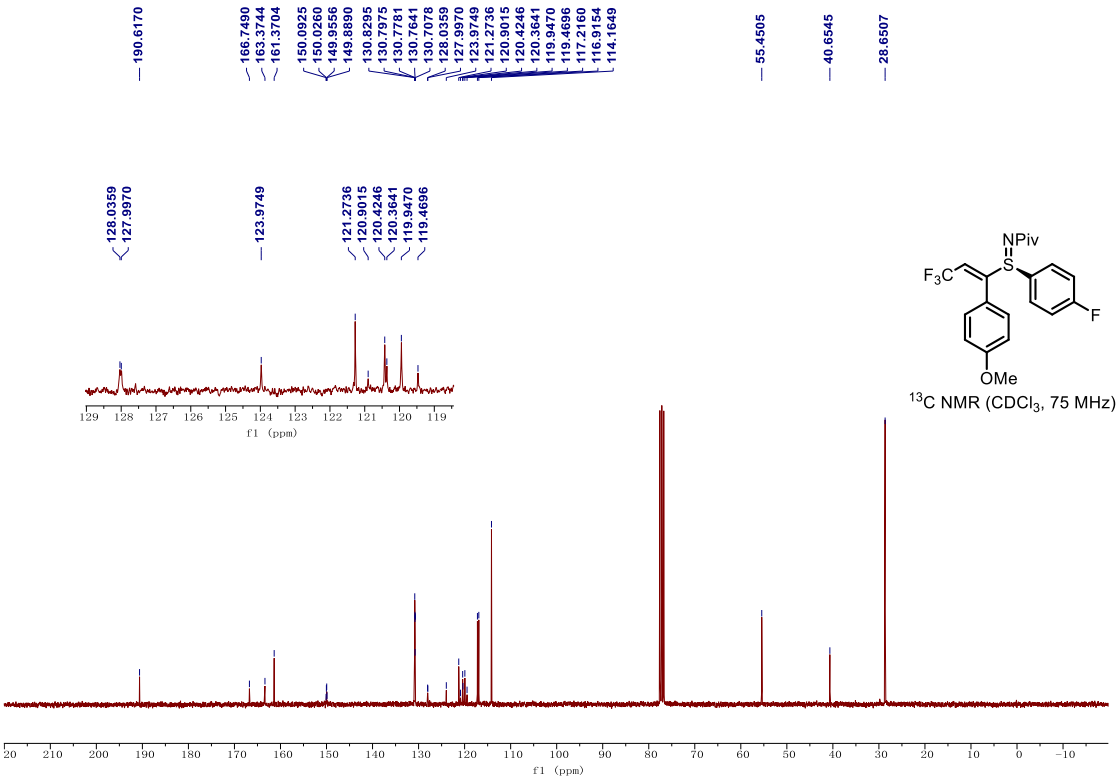


^{19}F NMR ($CDCl_3$, 282 MHz)

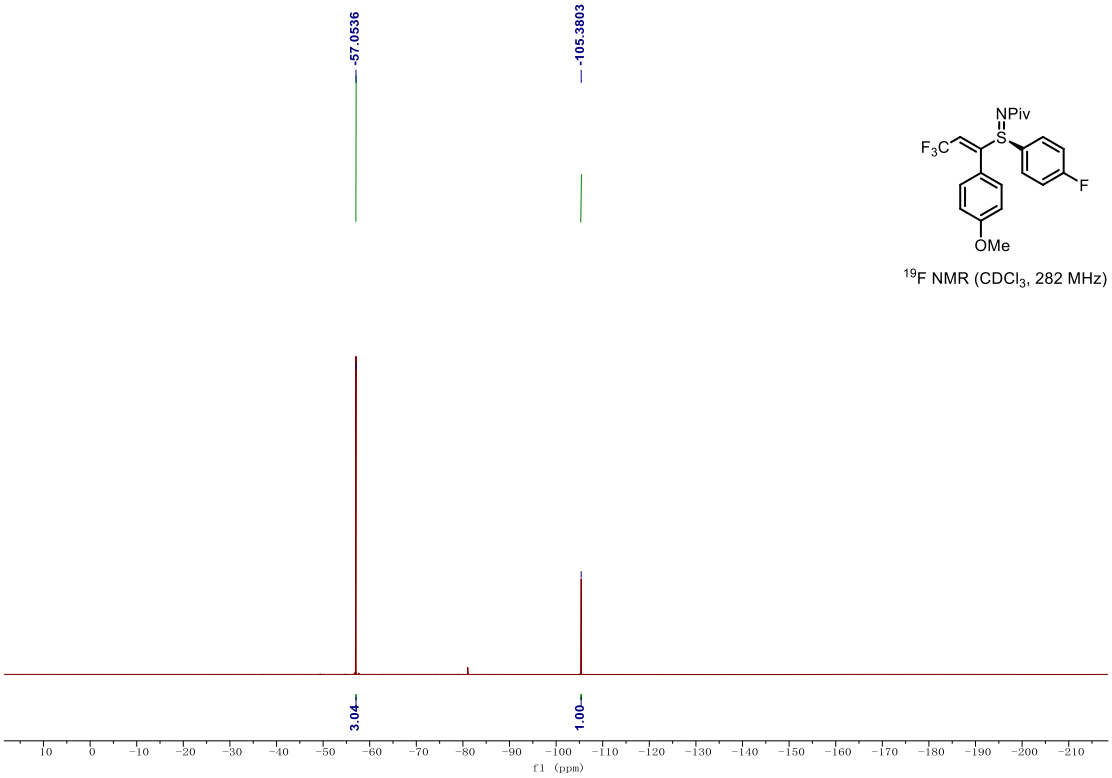
^{1}H NMR Spectrum of 4f



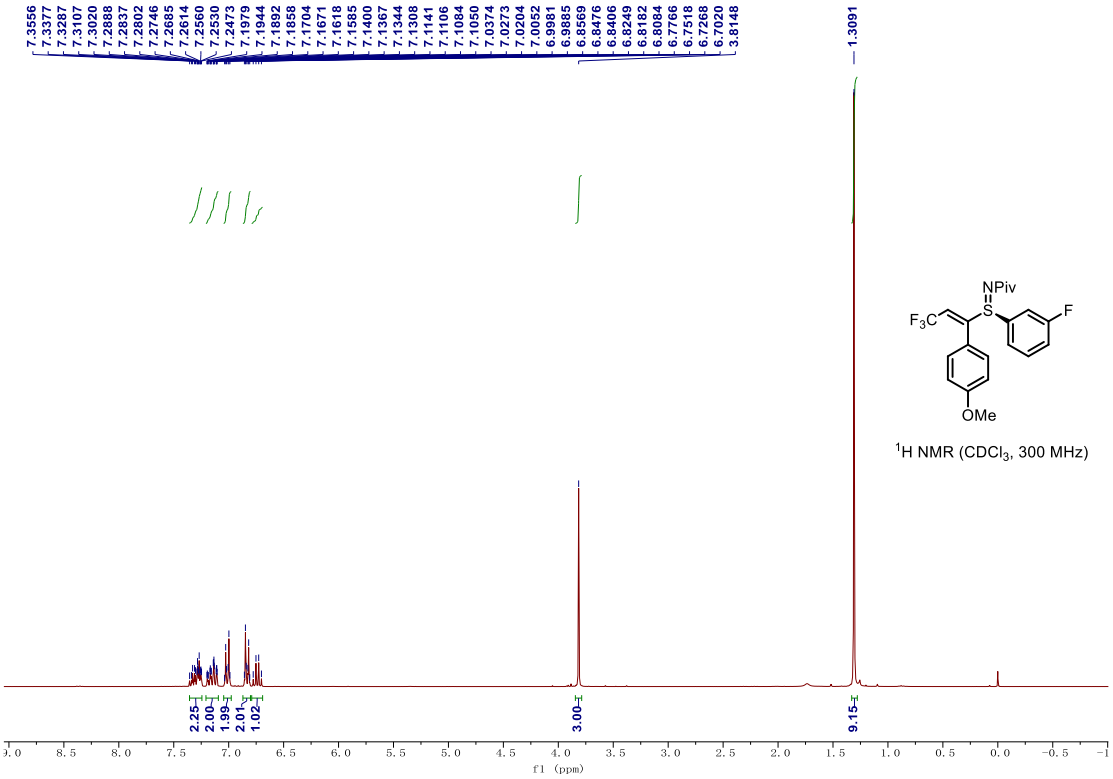
^{13}C NMR Spectrum of 4f



^{19}F NMR Spectrum of 4f

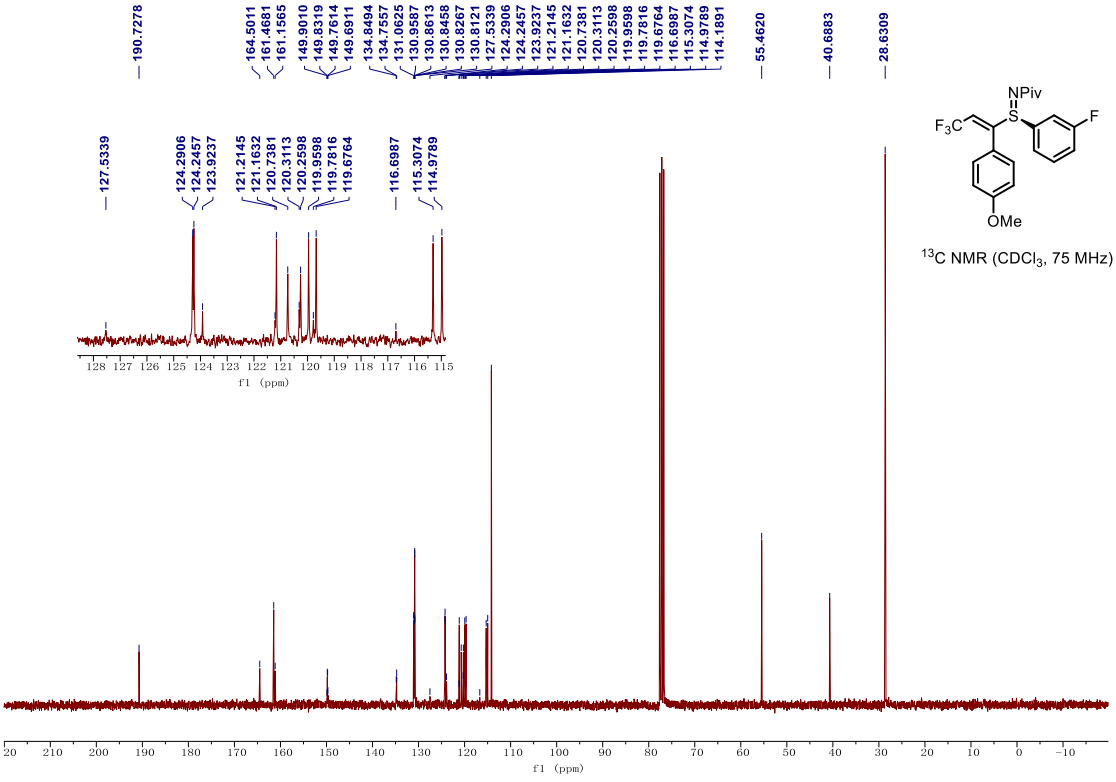


^{1}H NMR Spectrum of 4g



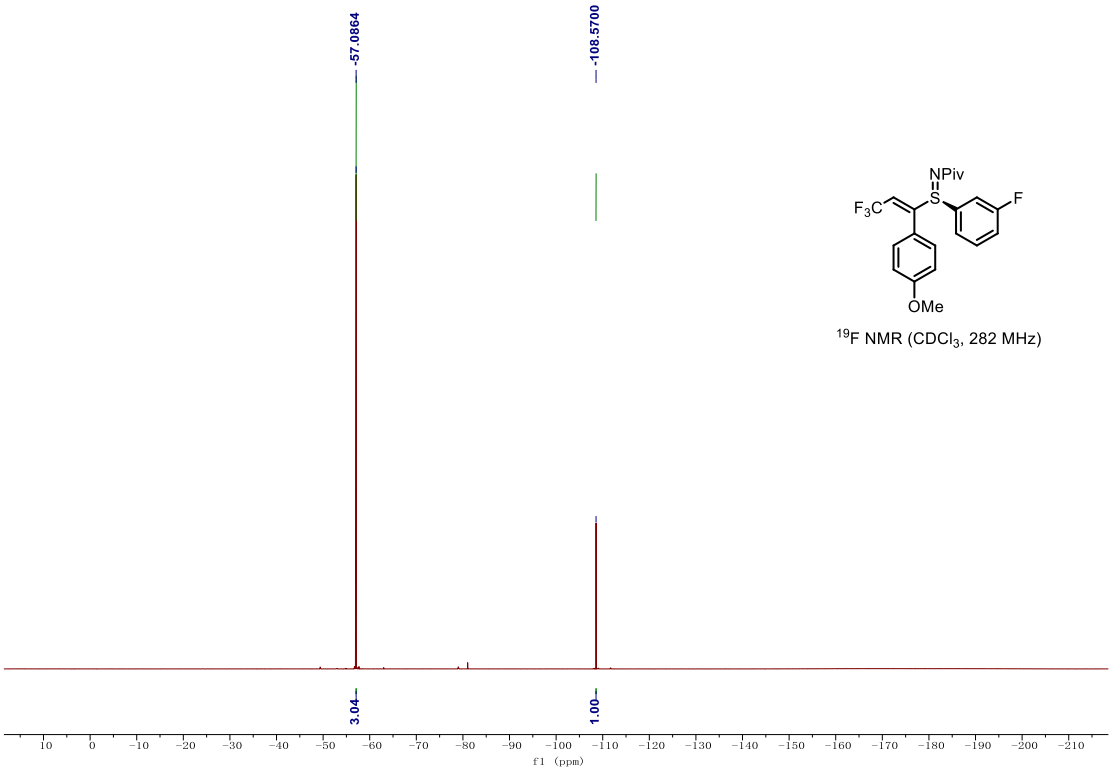
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4g

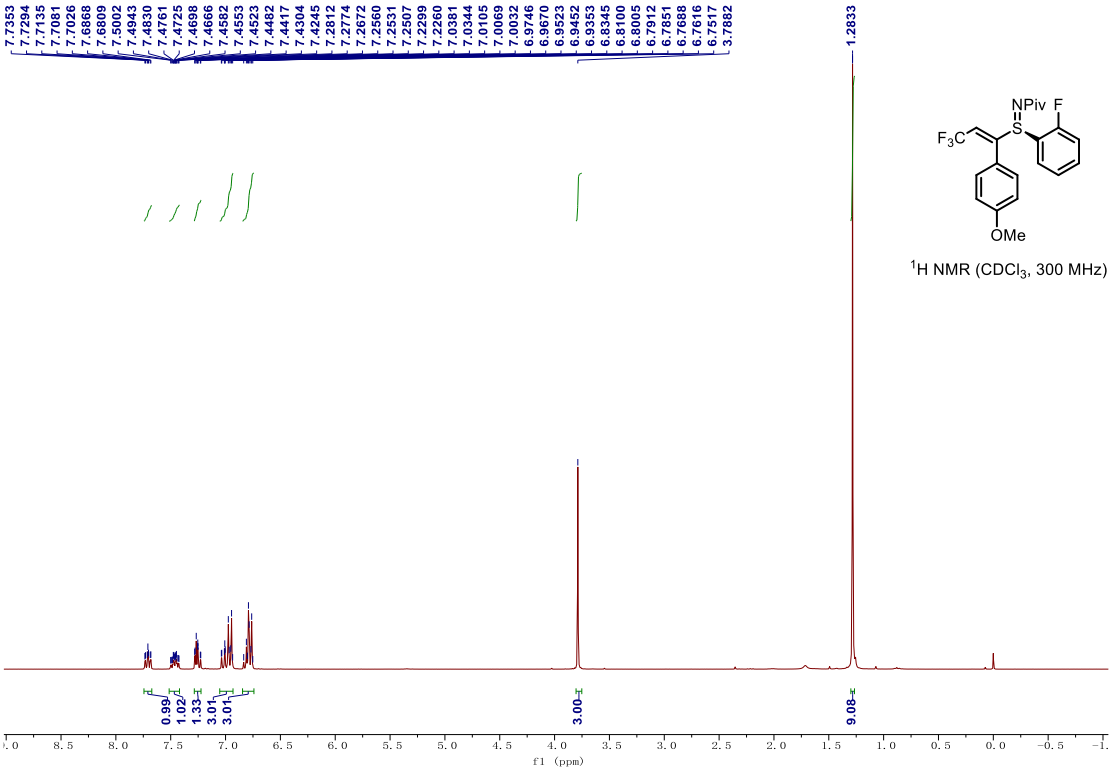


^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4g

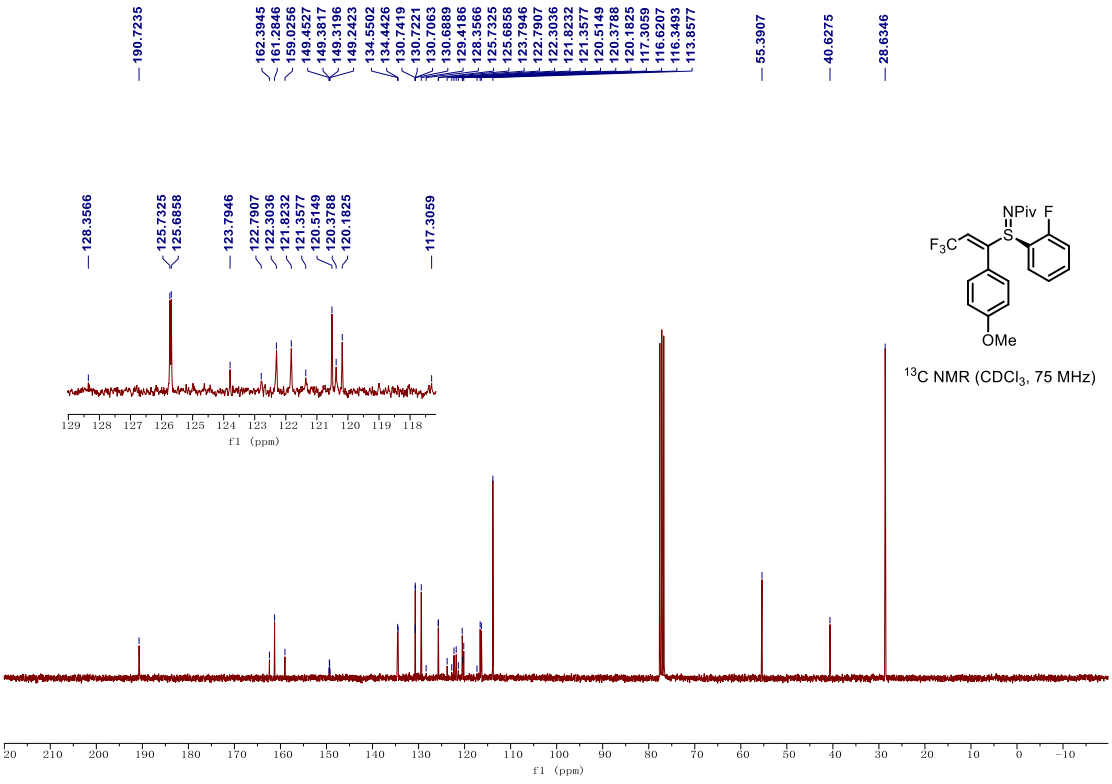


^{1}H NMR Spectrum of 4h



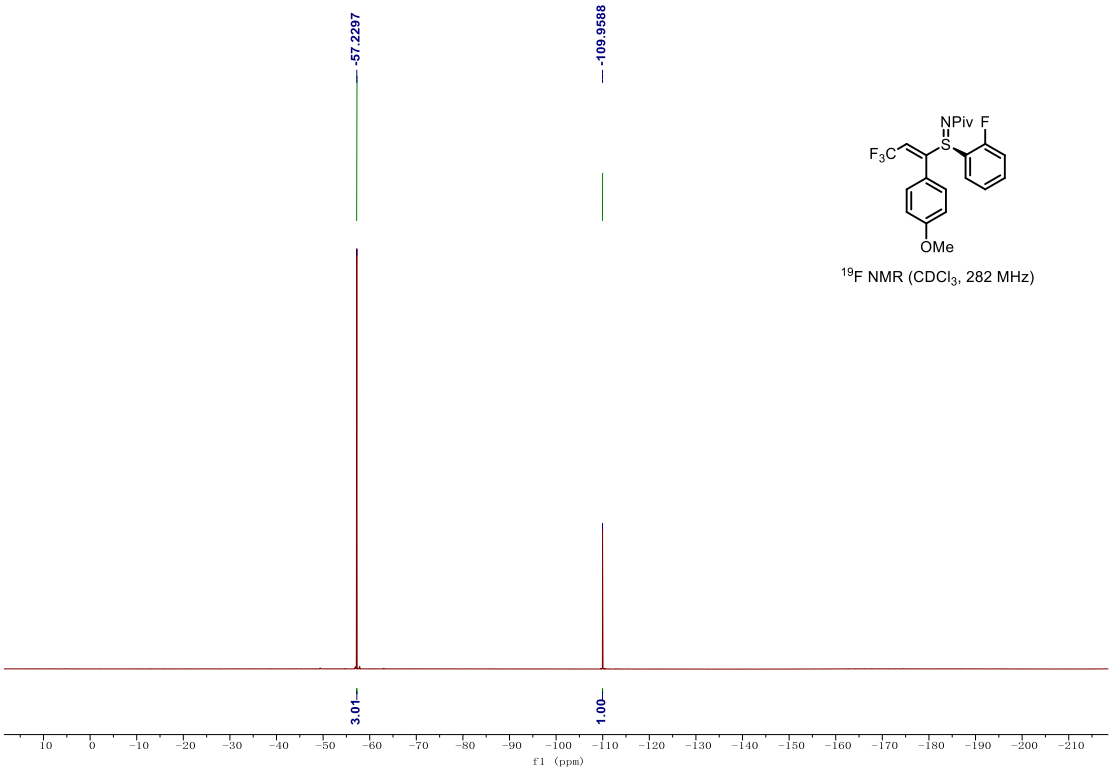
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4h



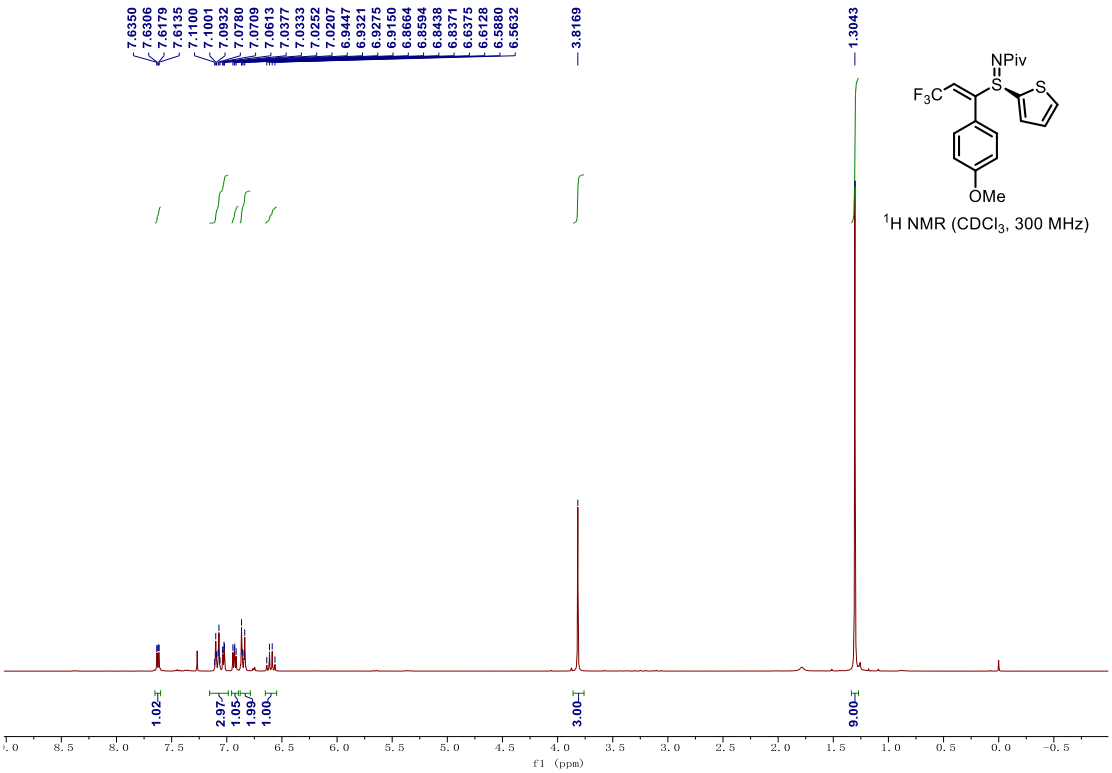
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4h

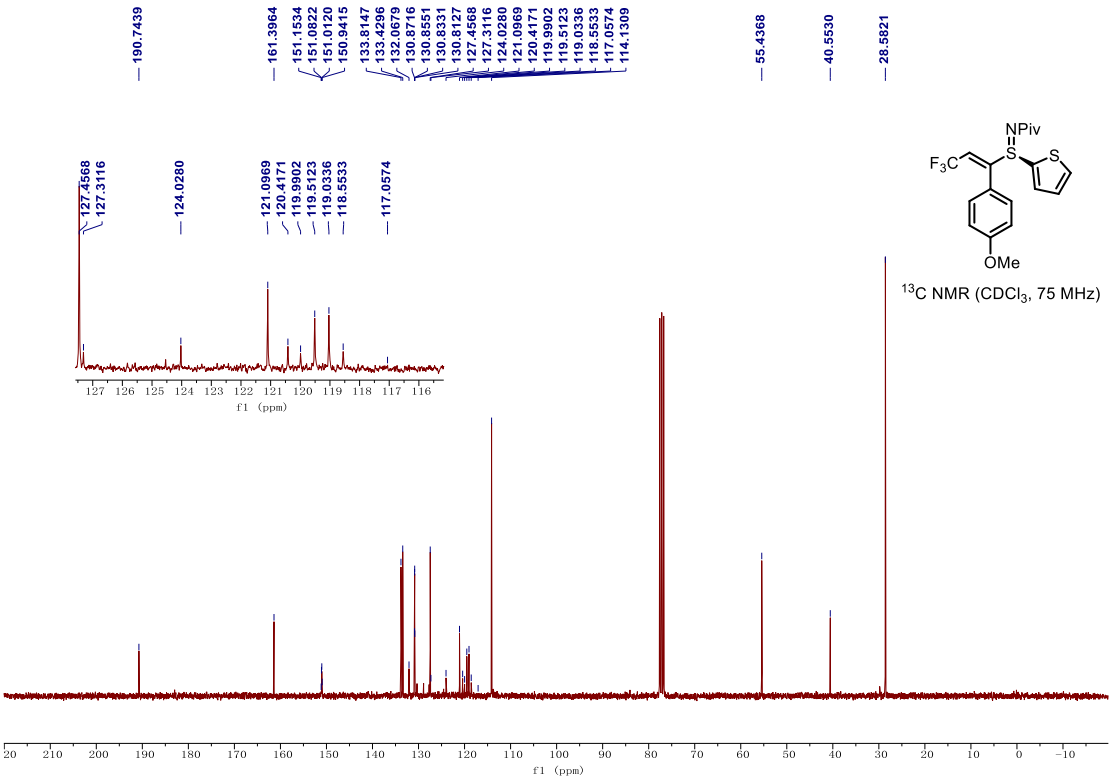


^{19}F NMR ($CDCl_3$, 282 MHz)

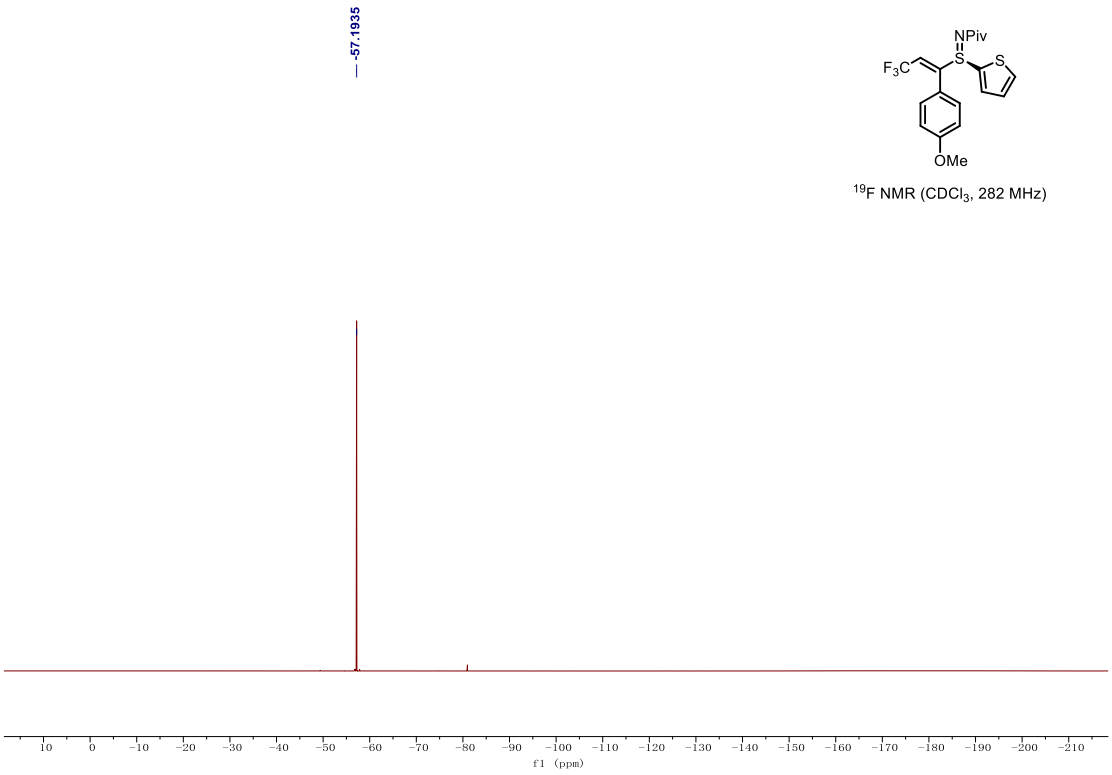
^{1}H NMR Spectrum of 4i



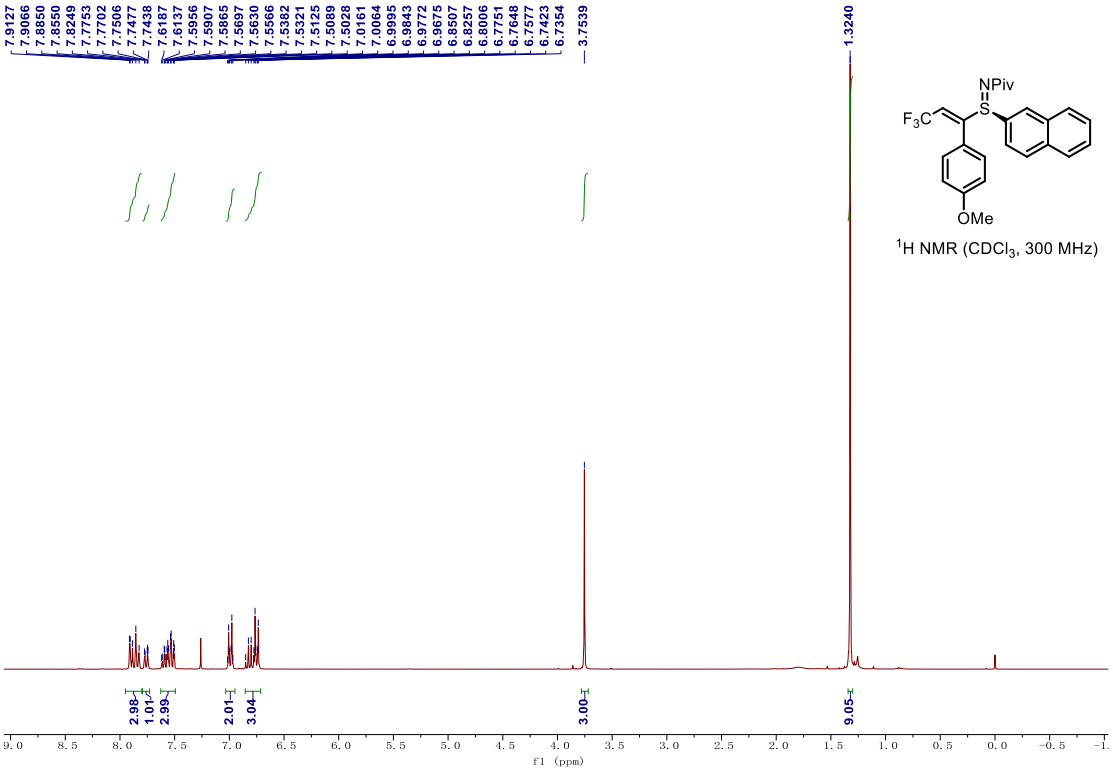
^{13}C NMR Spectrum of 4i



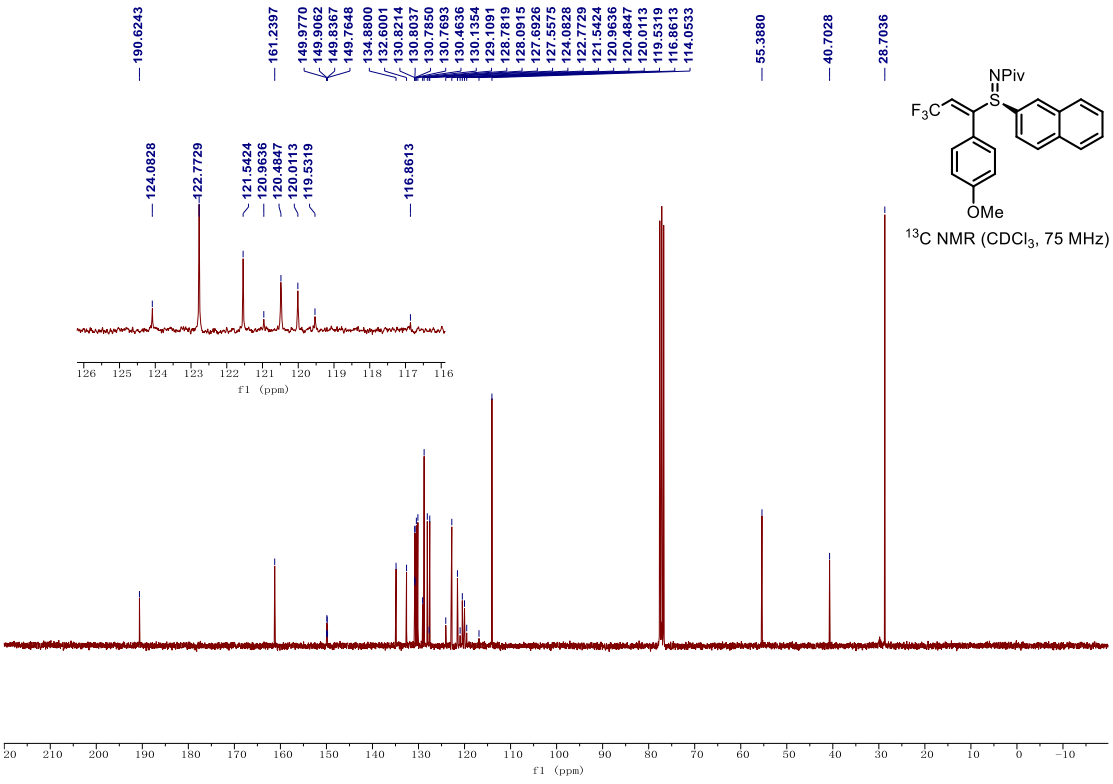
^{19}F NMR Spectrum of 4i



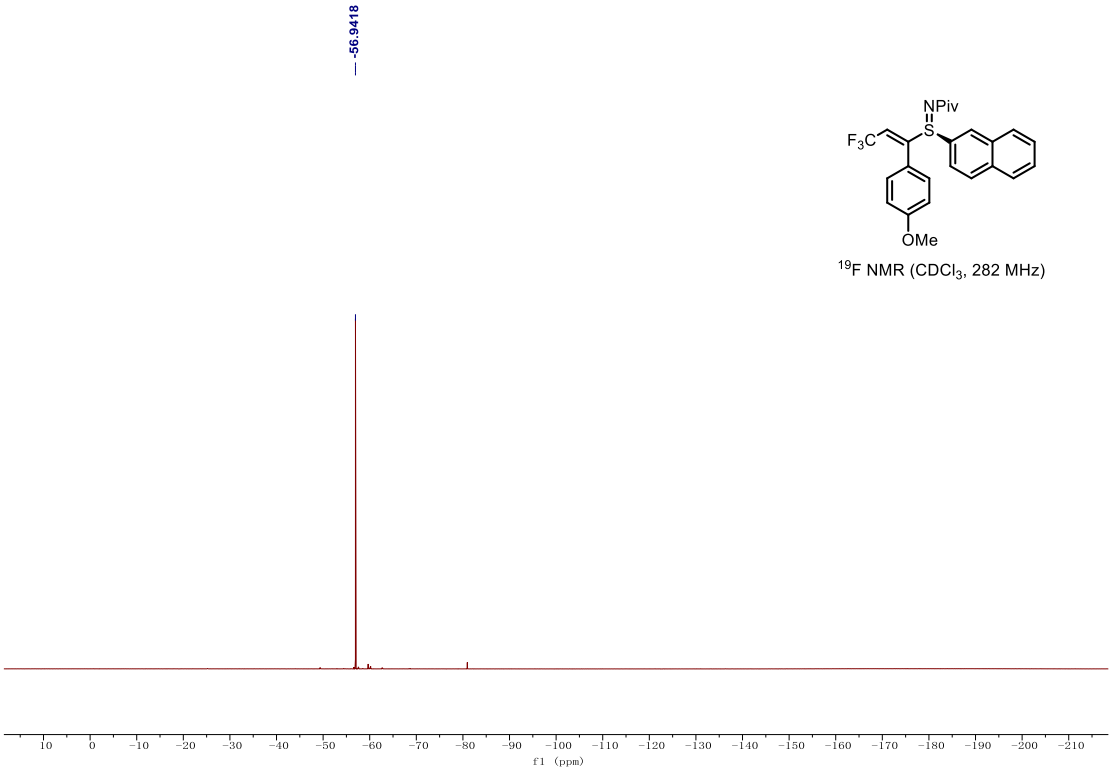
^{1}H NMR Spectrum of 4j



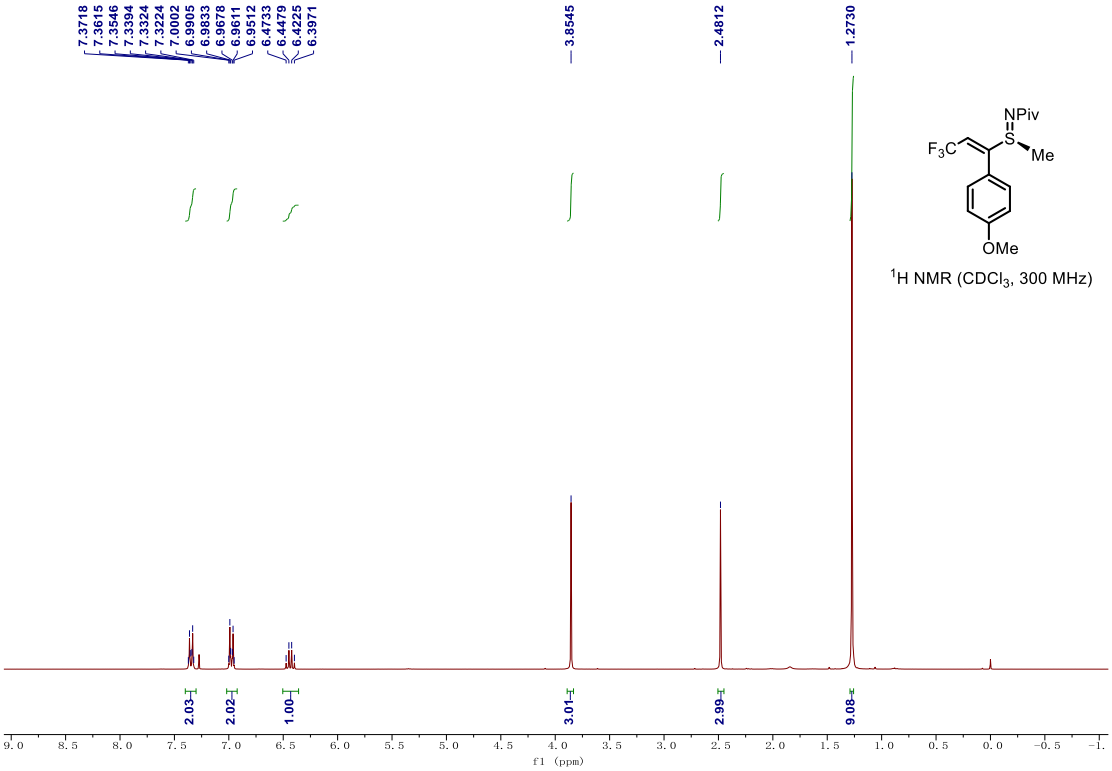
^{13}C NMR Spectrum of 4j



^{19}F NMR Spectrum of 4j

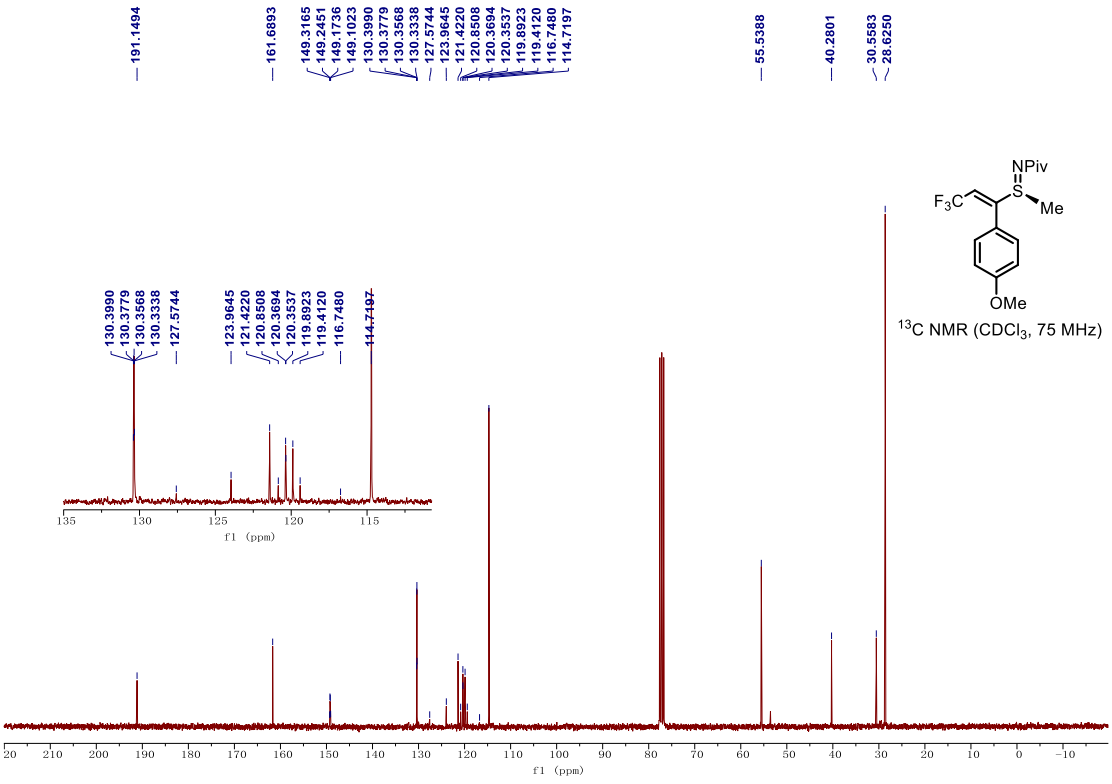


^{1}H NMR Spectrum of 4k



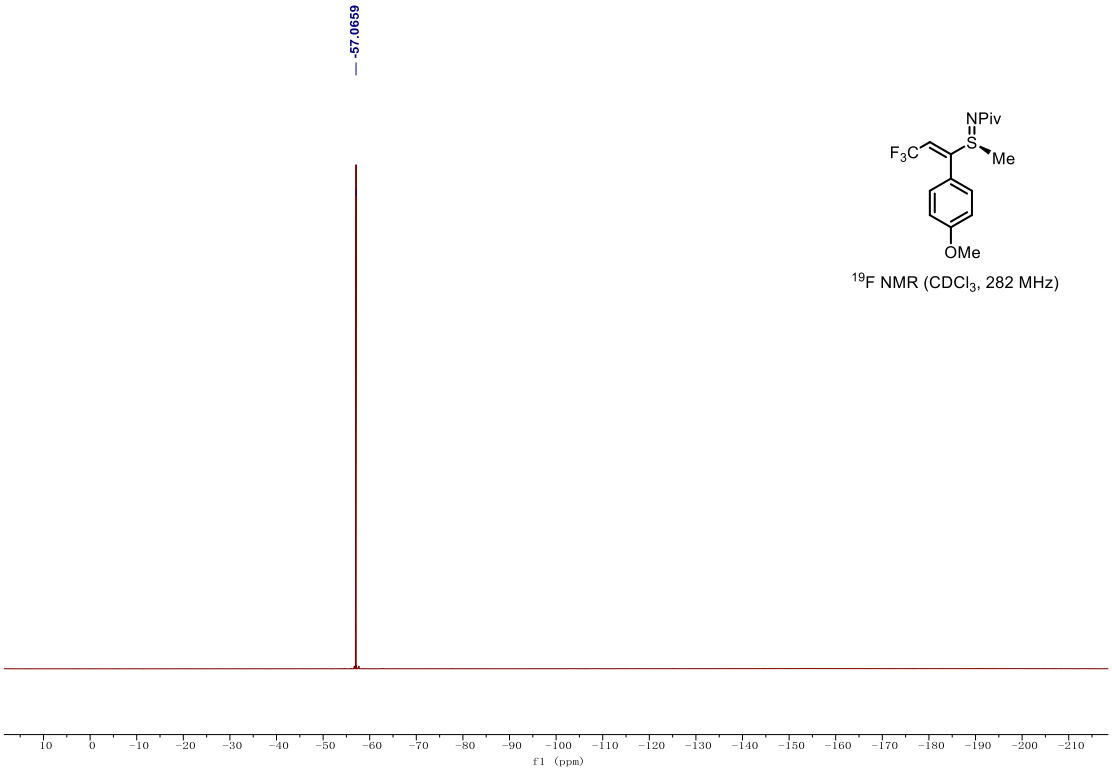
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4k



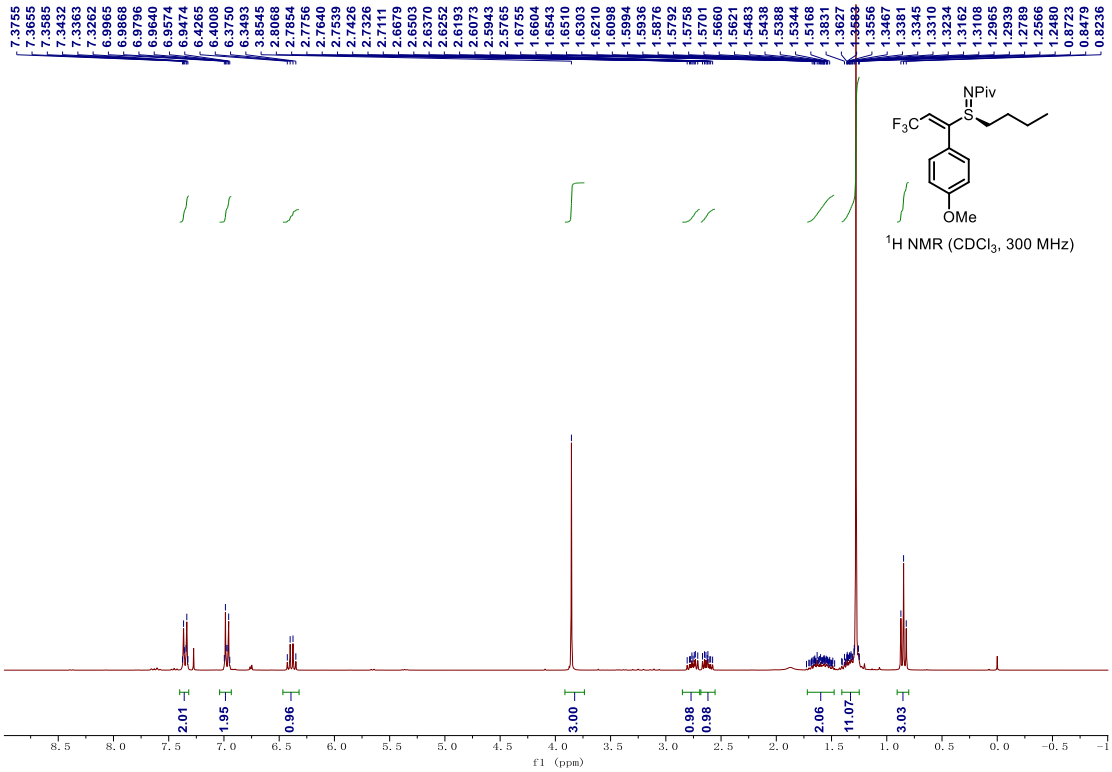
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4k

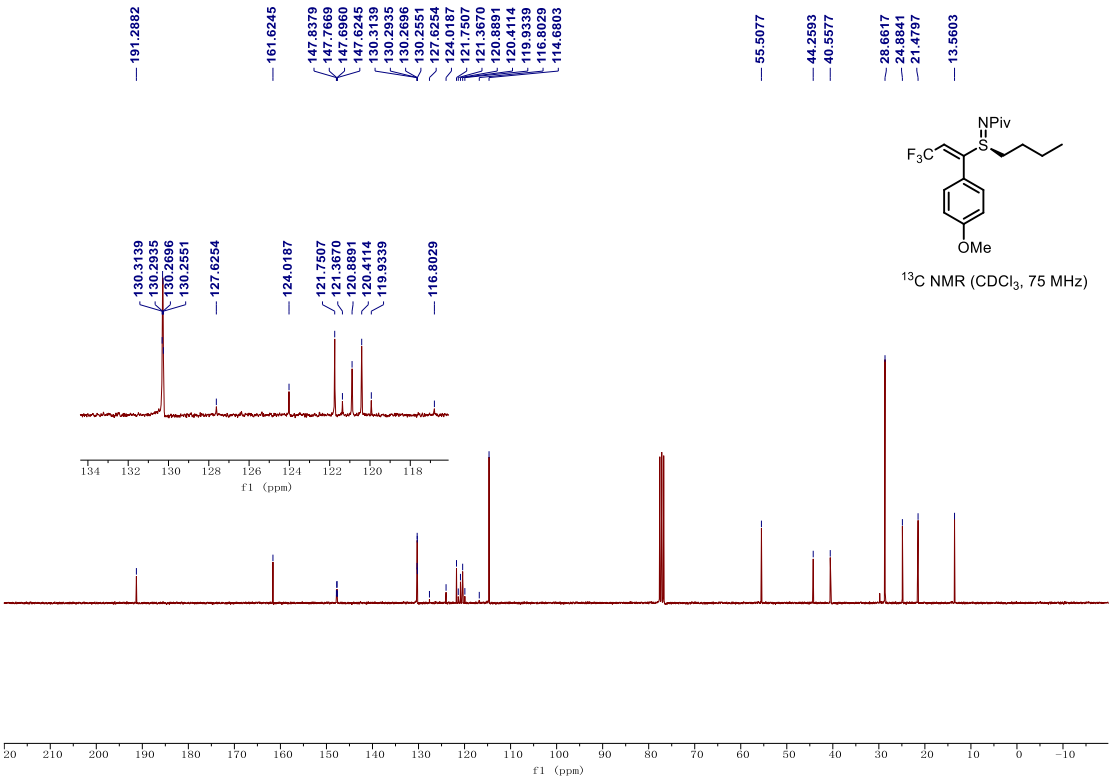


^{19}F NMR ($CDCl_3$, 282 MHz)

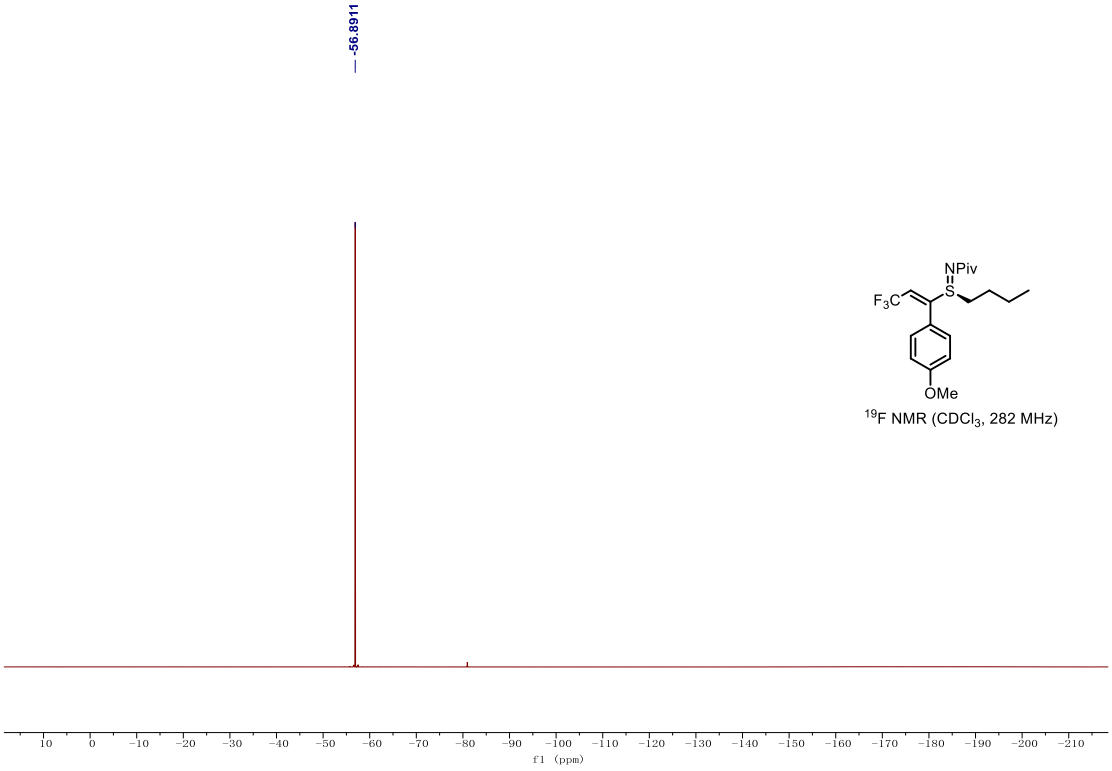
^{1}H NMR Spectrum of 4l



^{13}C NMR Spectrum of 4l

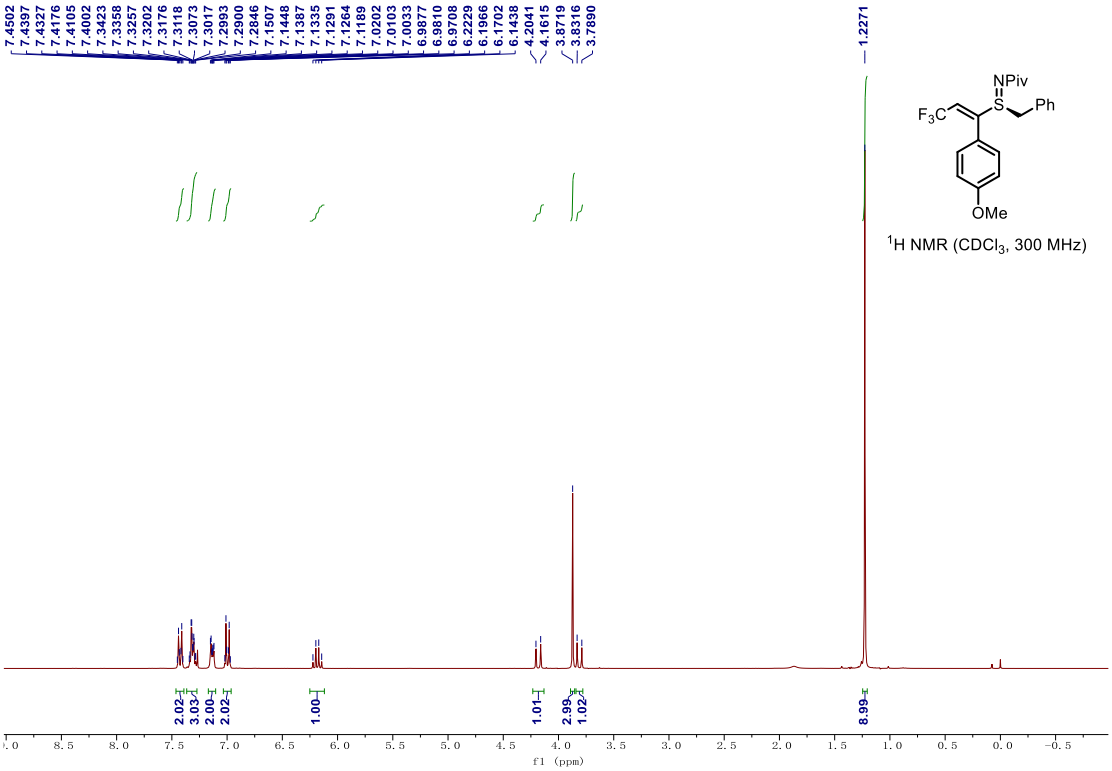


^{19}F NMR Spectrum of 4l

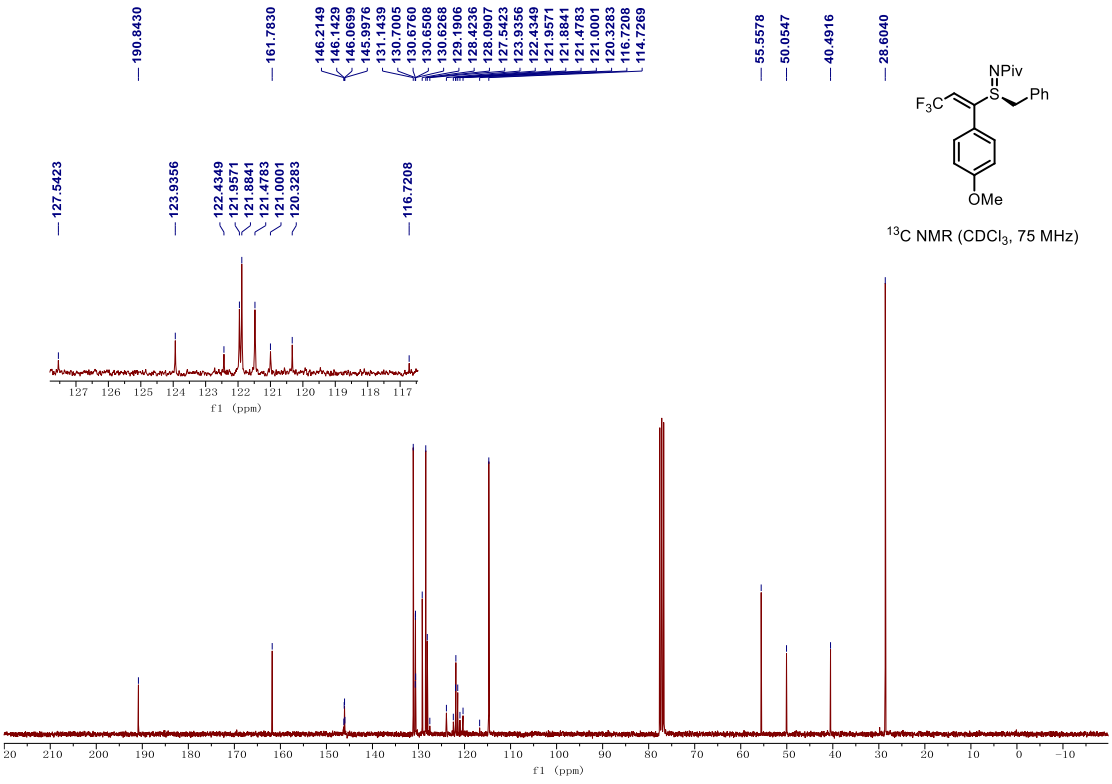


^{19}F NMR ($CDCl_3$, 282 MHz)

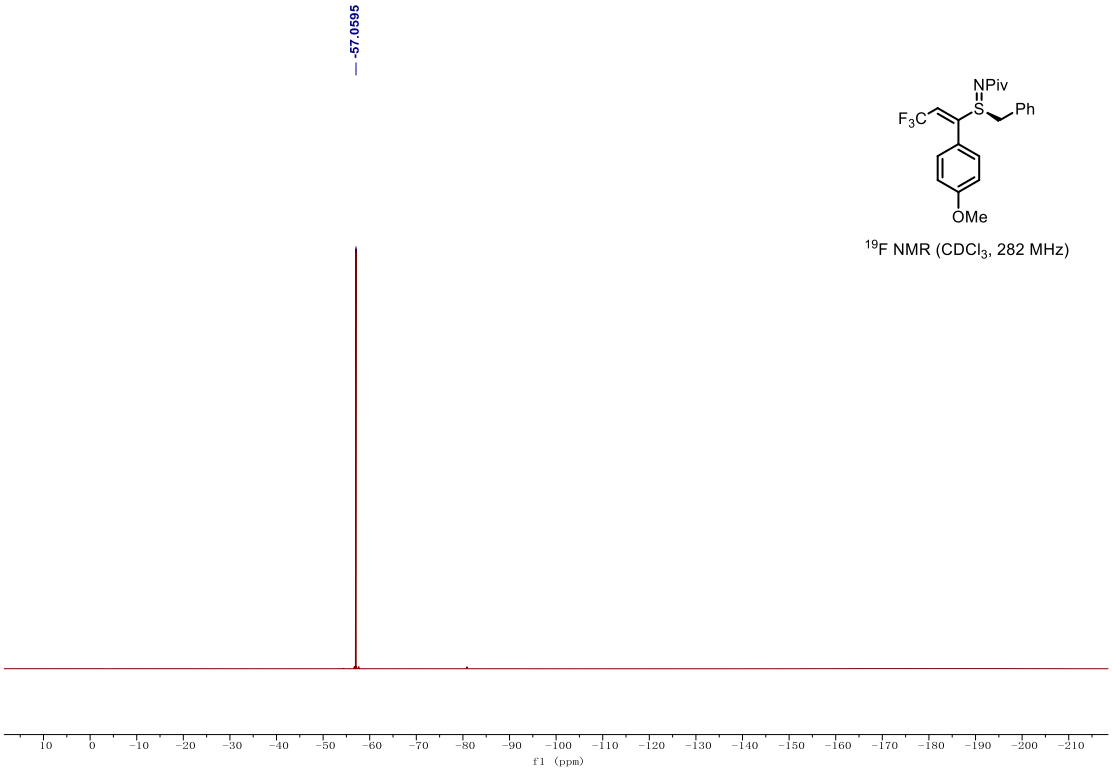
^{1}H NMR Spectrum of 4m



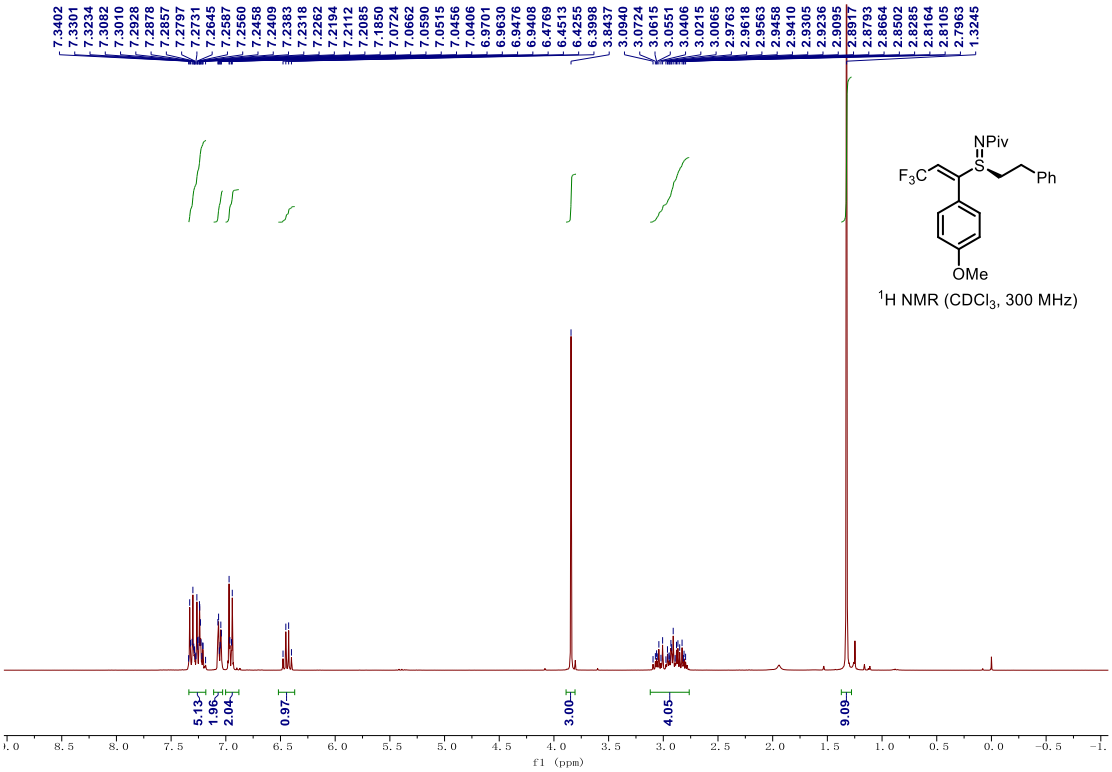
^{13}C NMR Spectrum of 4m



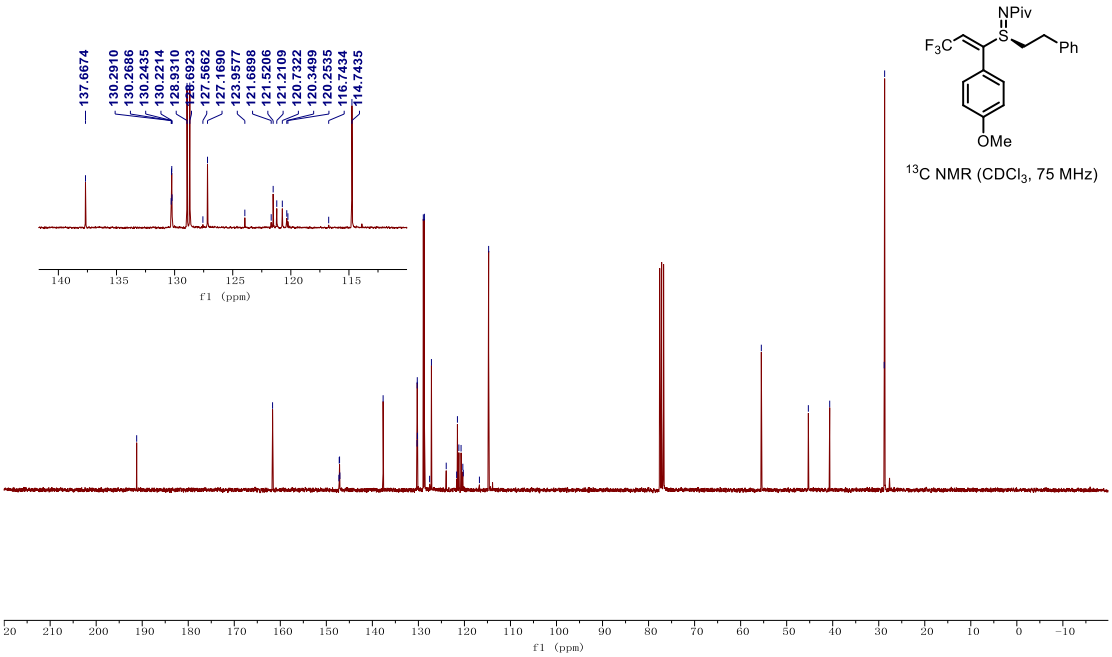
^{19}F NMR Spectrum of 4m



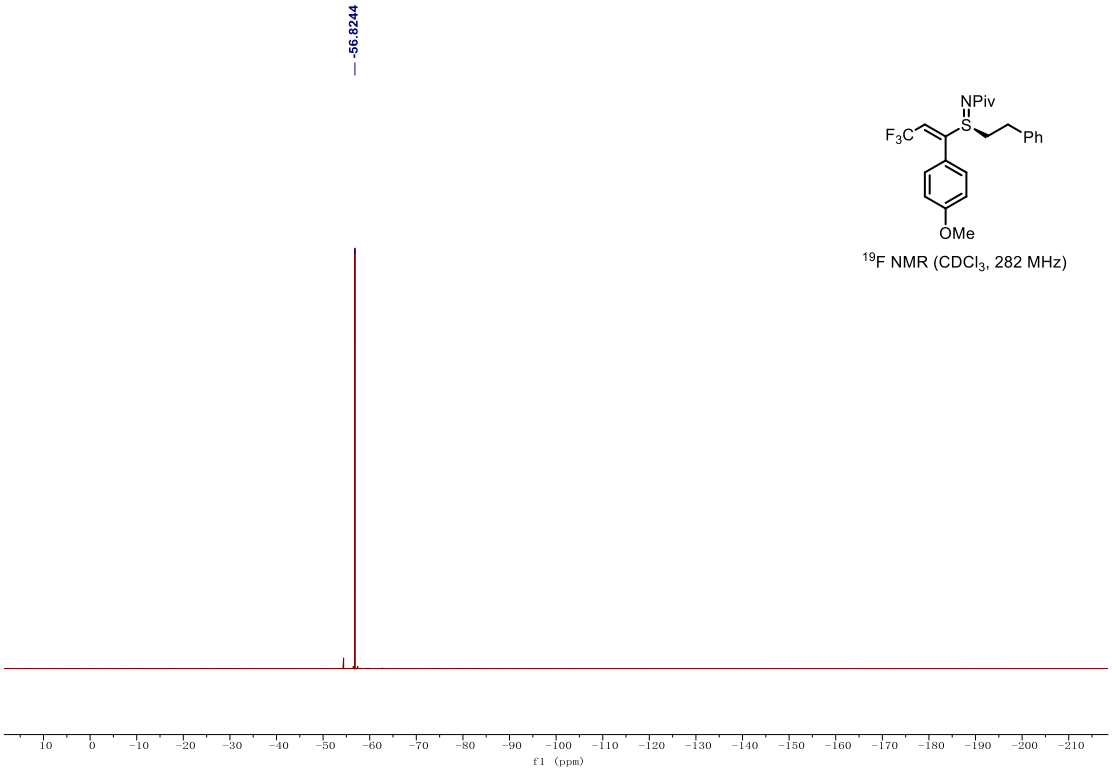
^{1}H NMR Spectrum of 4n



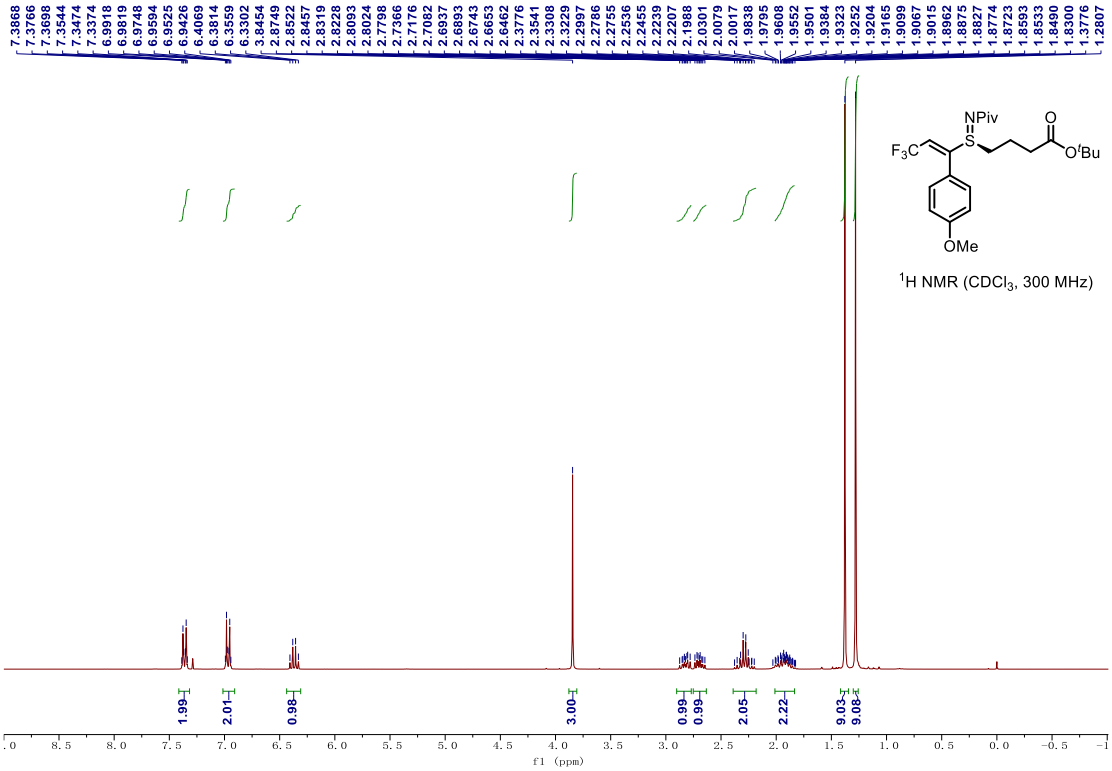
^{13}C NMR Spectrum of 4n



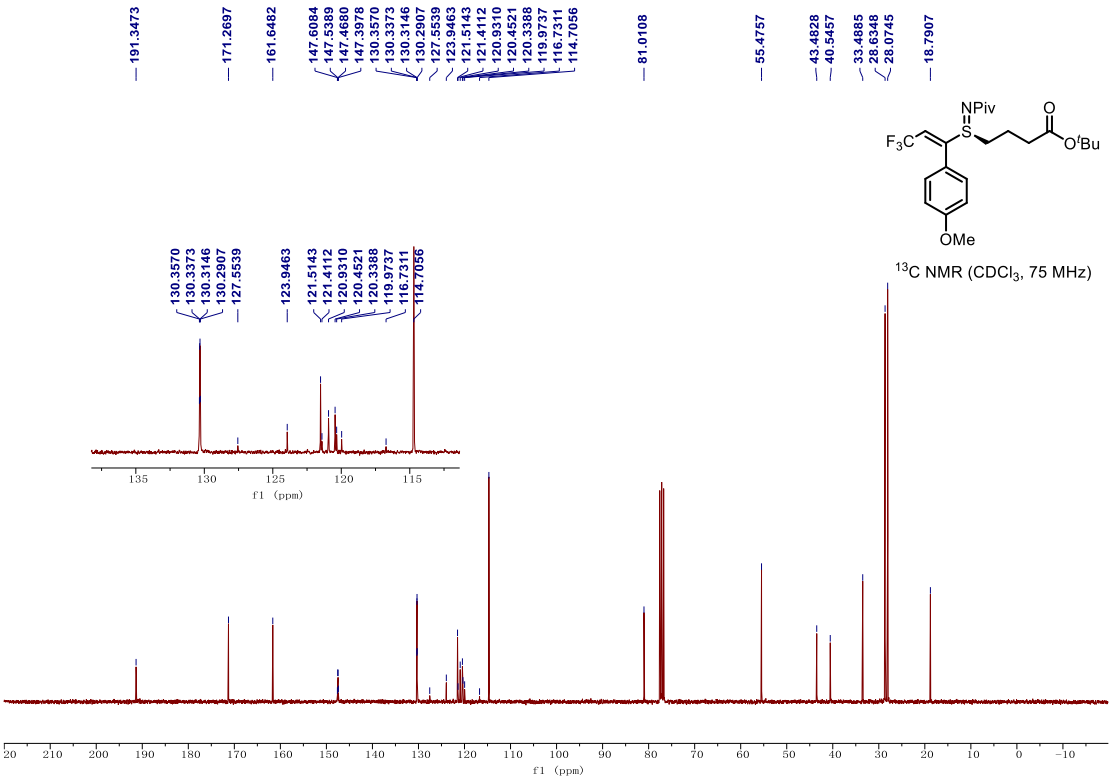
^{19}F NMR Spectrum of 4n



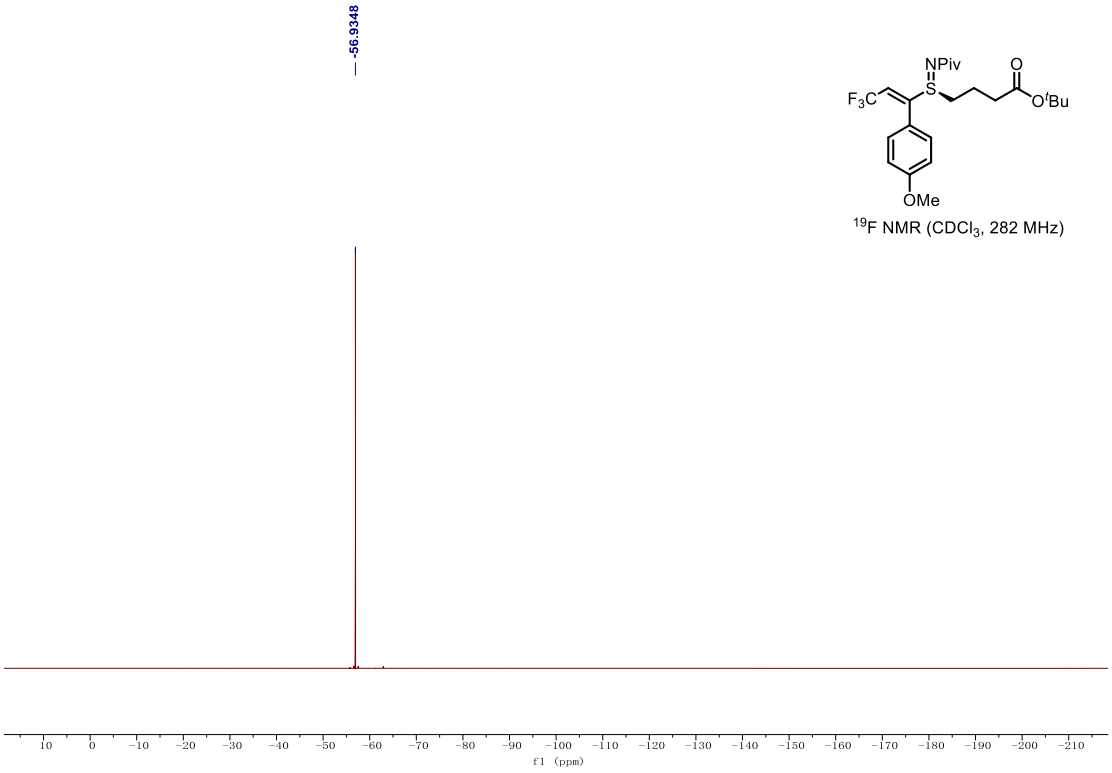
^{1}H NMR Spectrum of 4o



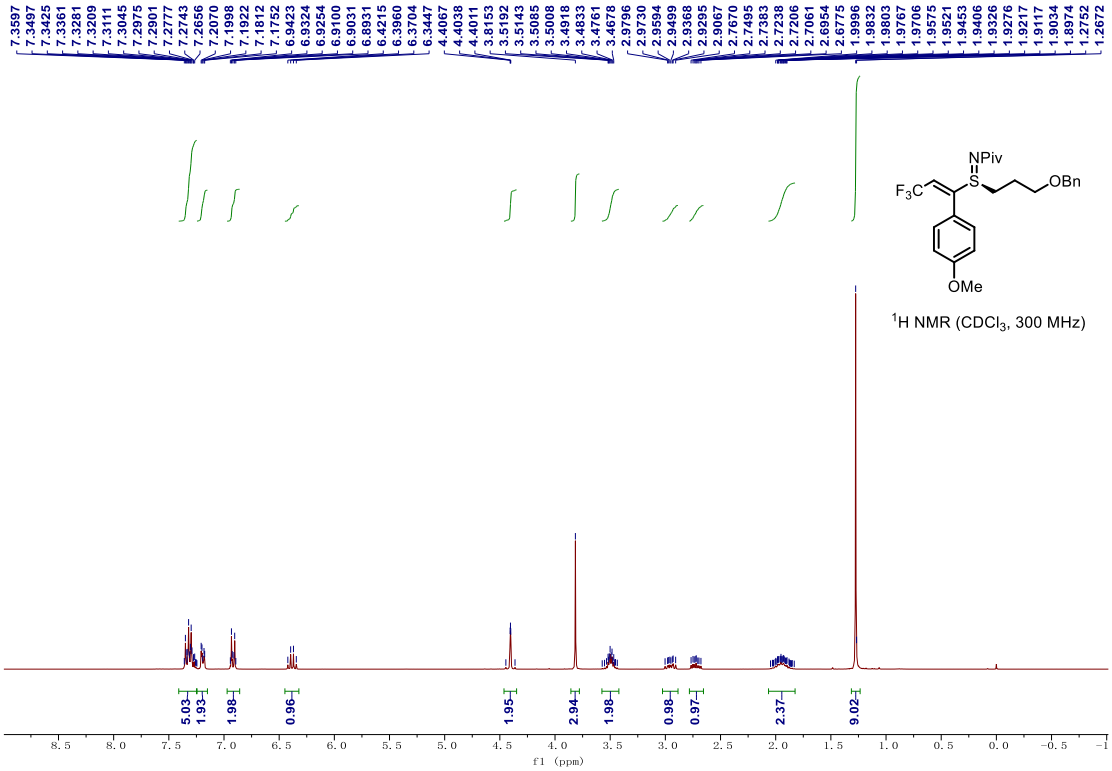
^{13}C NMR Spectrum of 4o



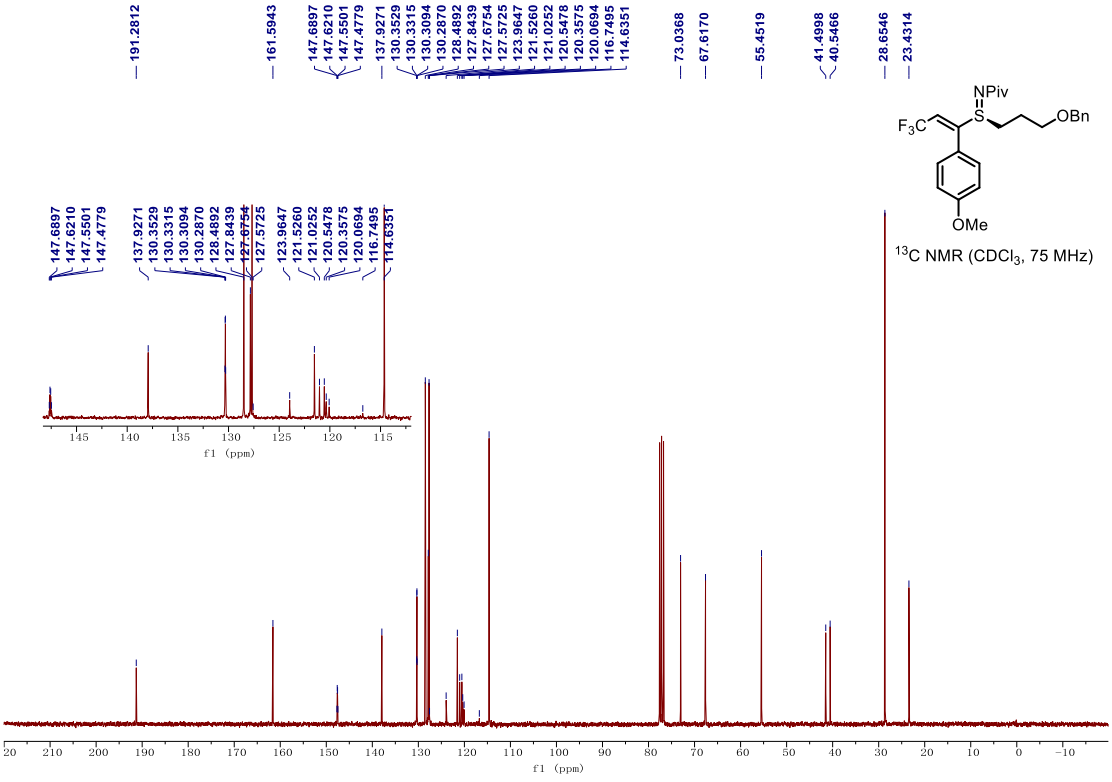
^{19}F NMR Spectrum of 4o



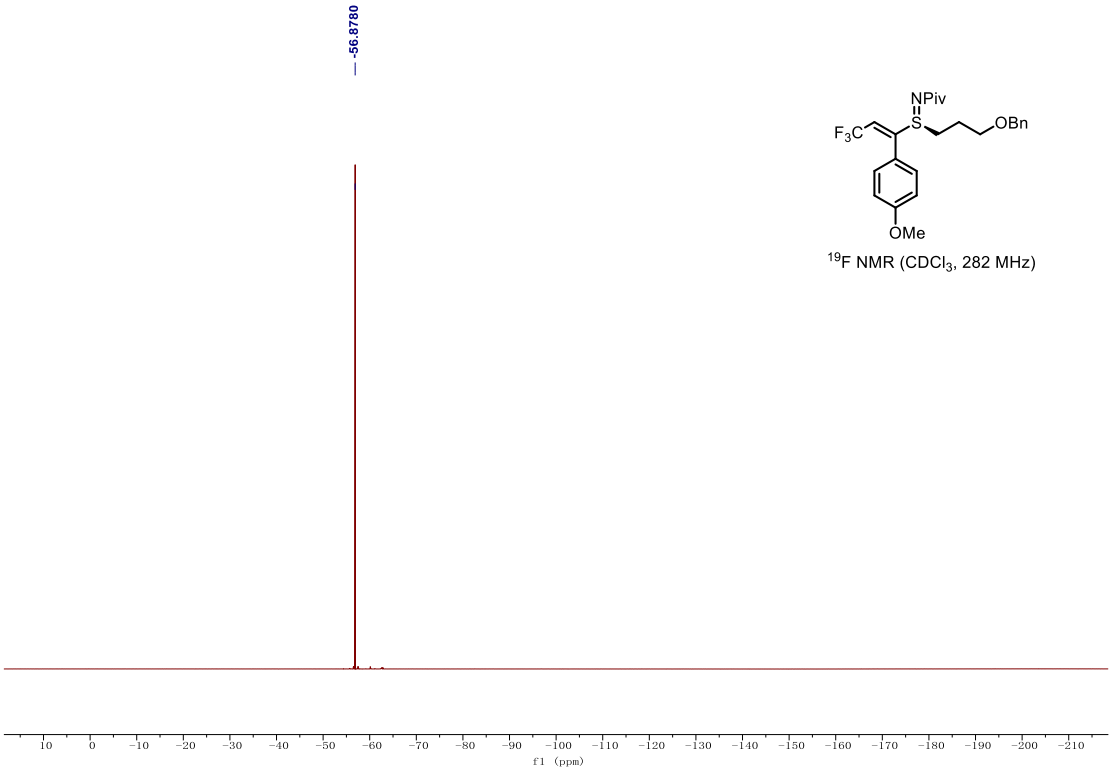
^{1}H NMR Spectrum of 4p



^{13}C NMR Spectrum of 4p

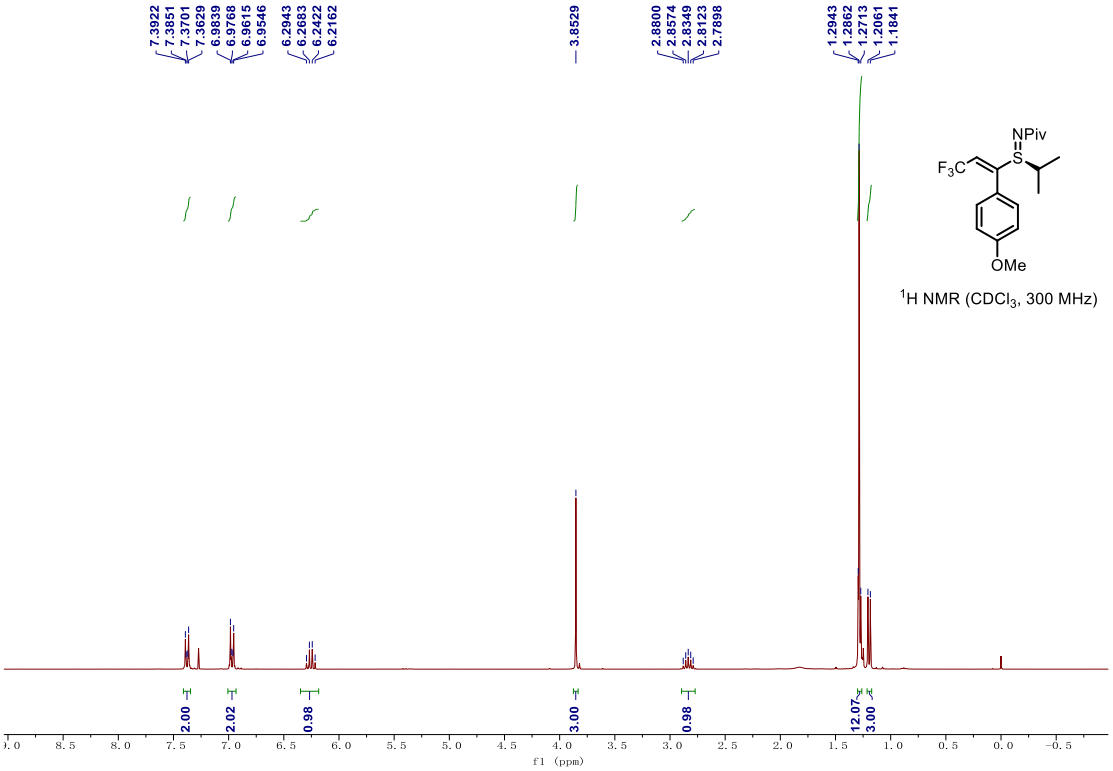


^{19}F NMR Spectrum of 4p

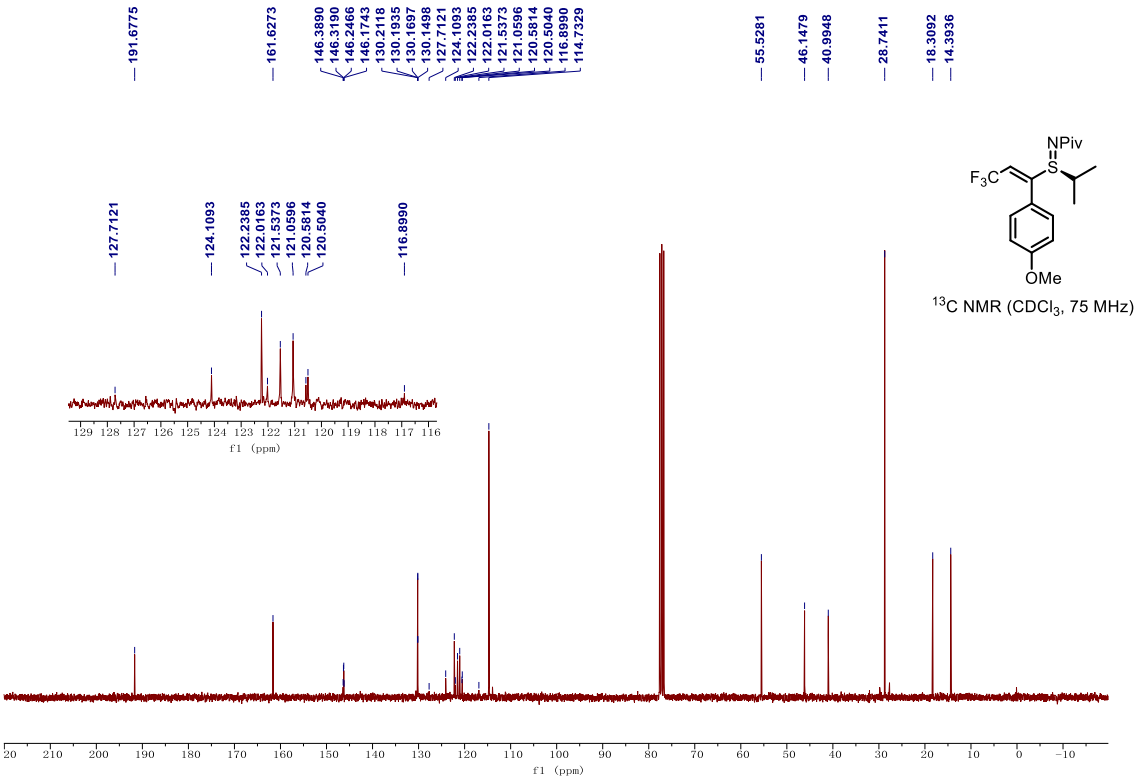


^{19}F NMR ($CDCl_3$, 282 MHz)

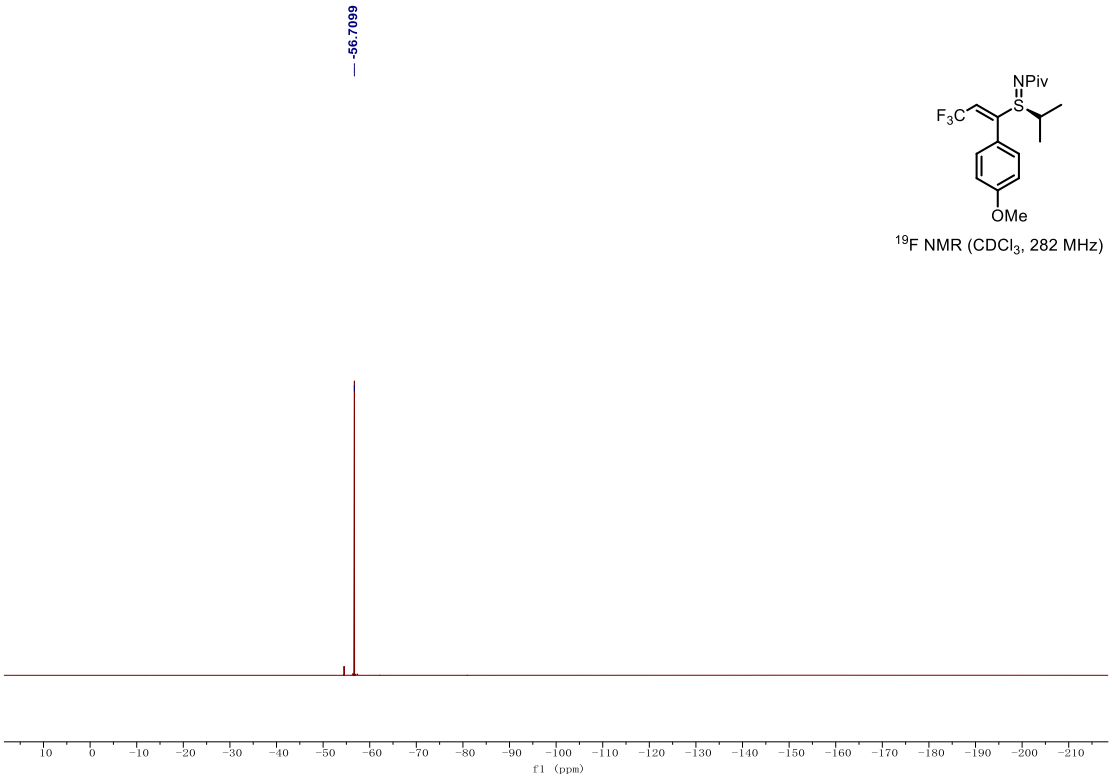
^{1}H NMR Spectrum of 4q



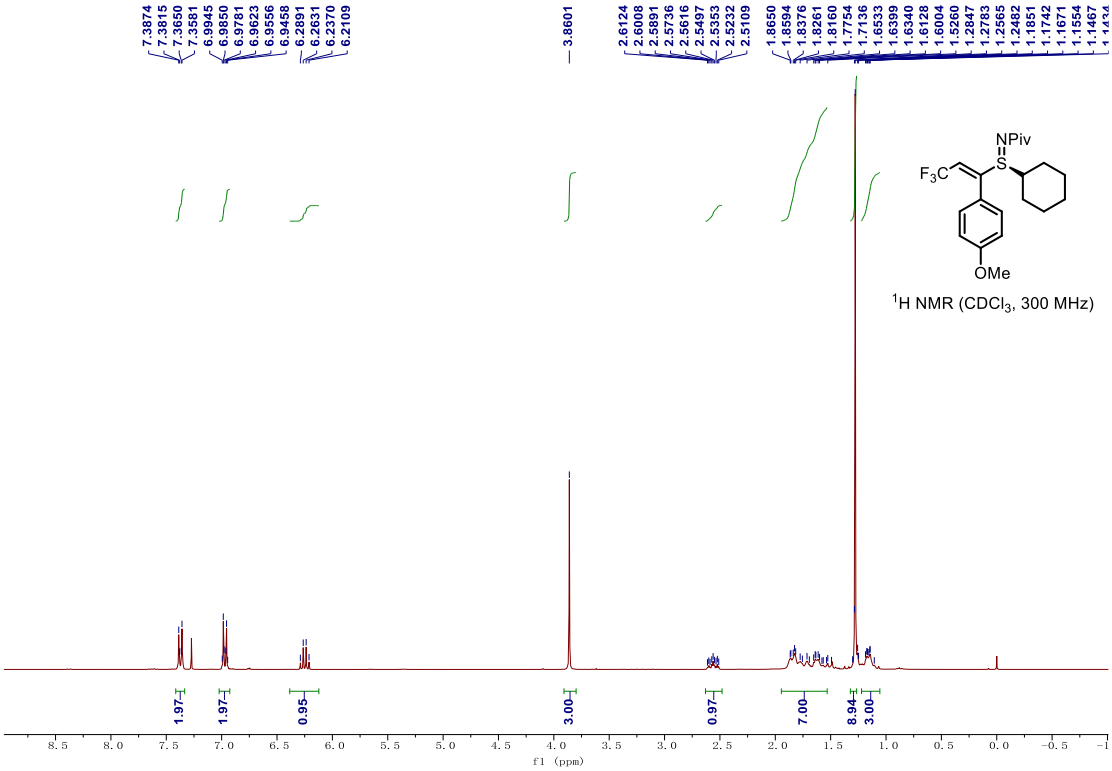
^{13}C NMR Spectrum of 4q



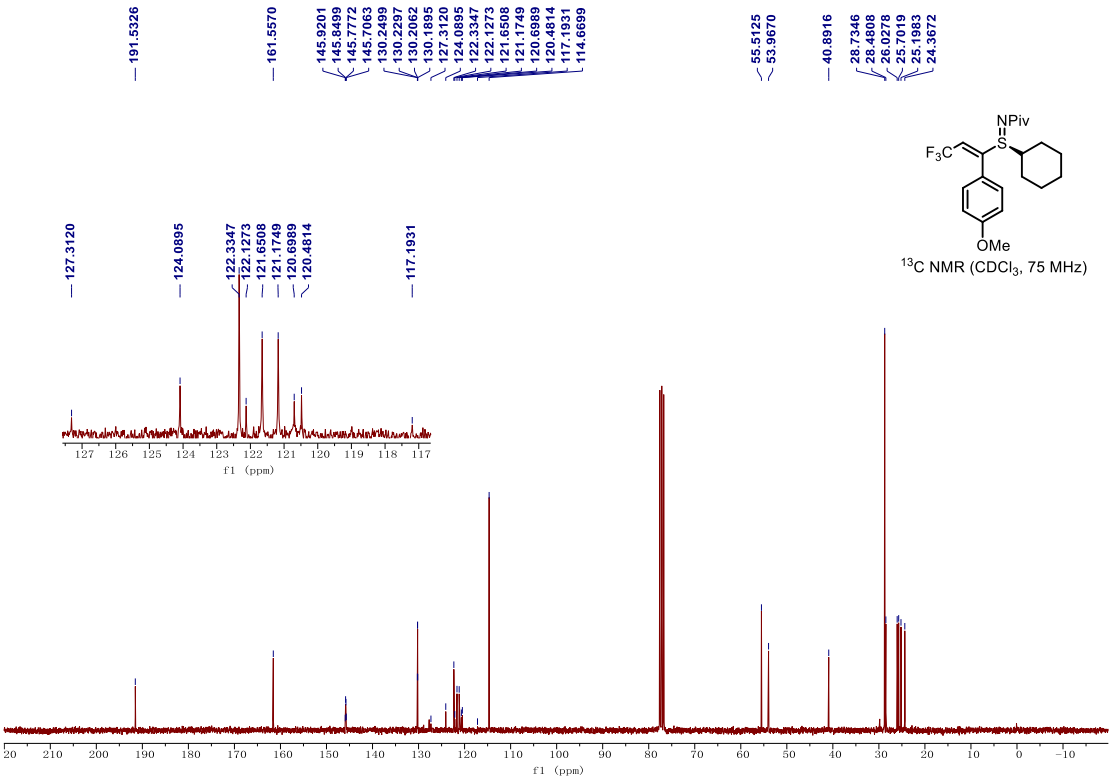
^{19}F NMR Spectrum of 4q



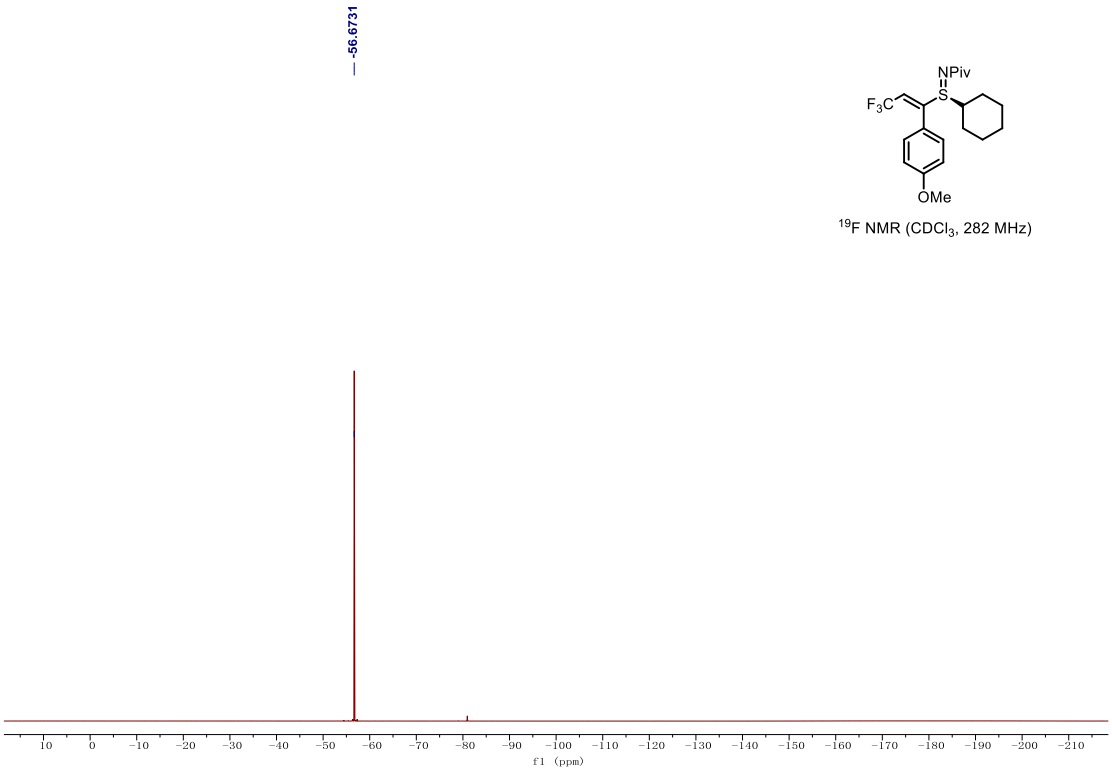
^{1}H NMR Spectrum of 4r



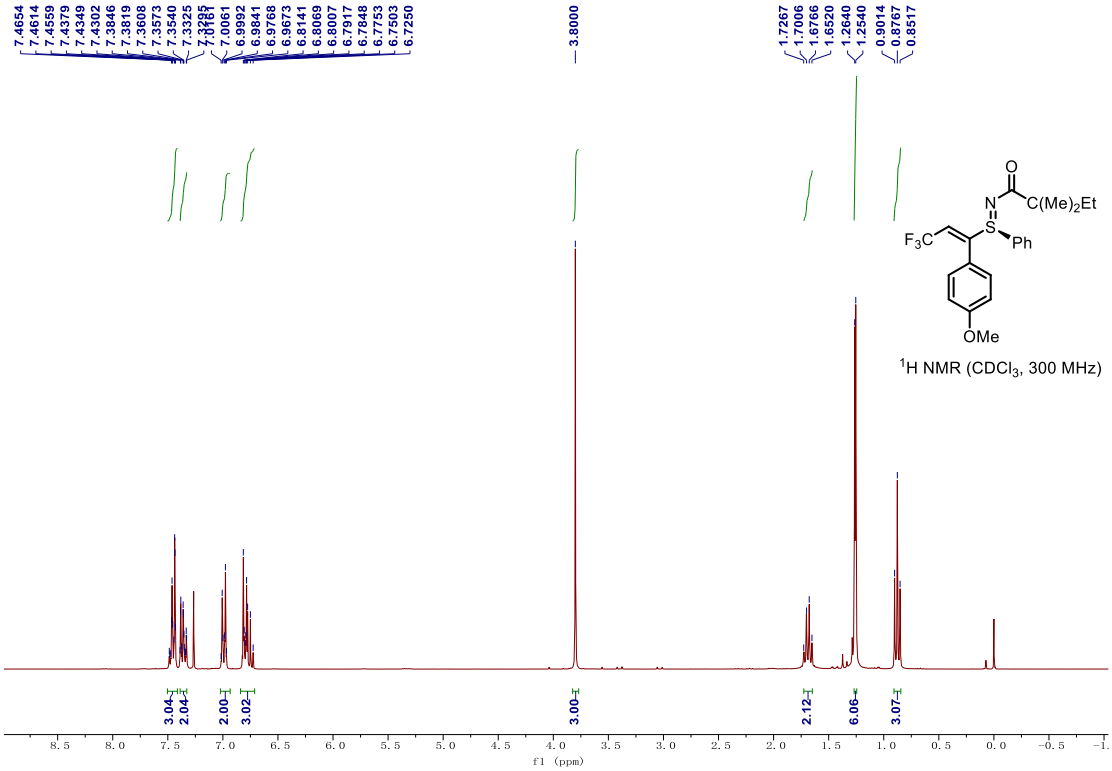
^{13}C NMR Spectrum of 4r



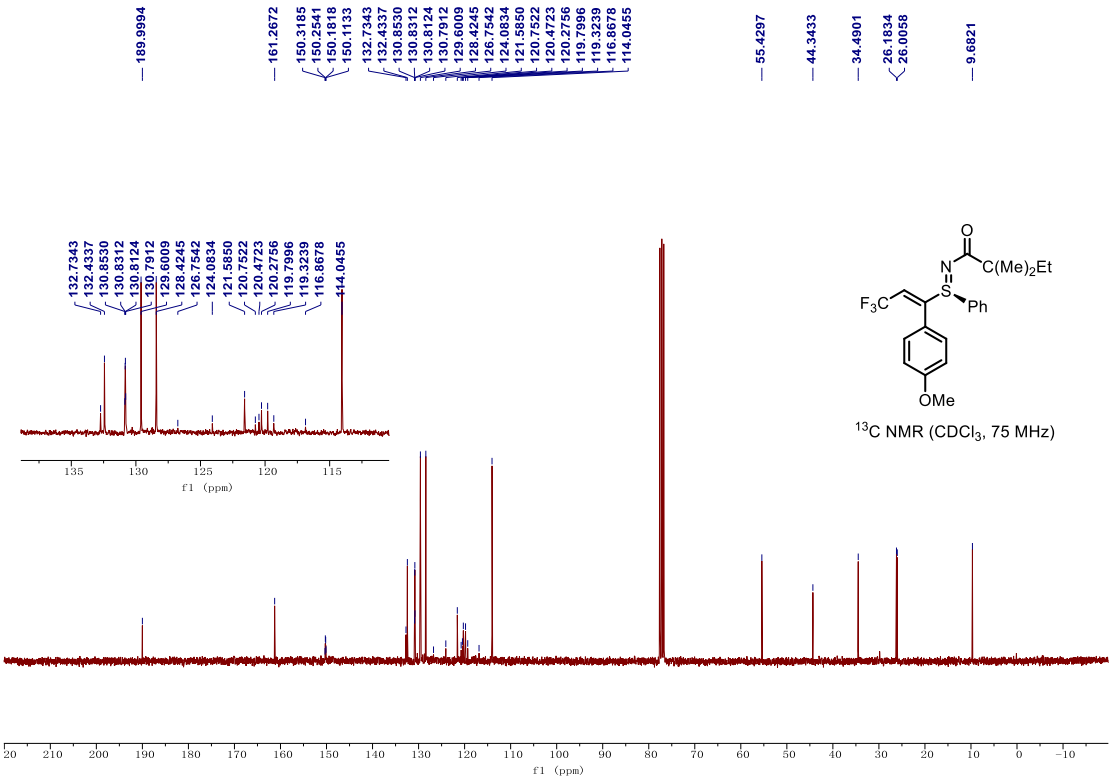
^{19}F NMR Spectrum of 4r



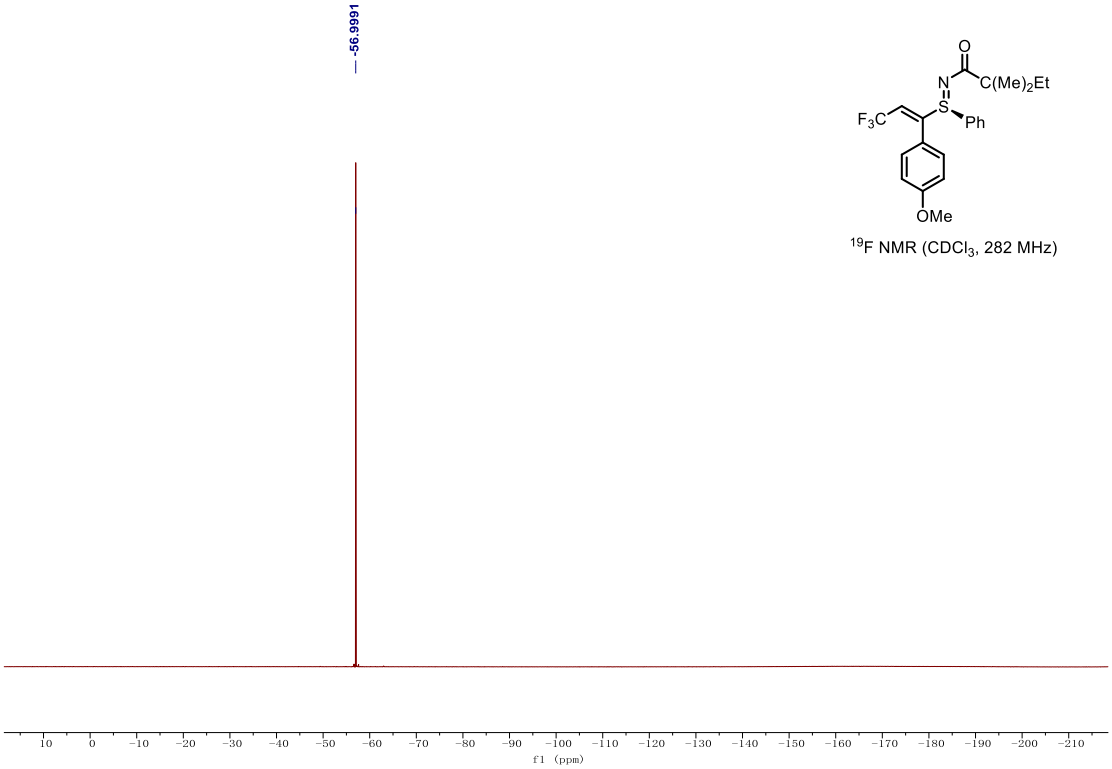
^{1}H NMR Spectrum of 4s



^{13}C NMR Spectrum of 4s

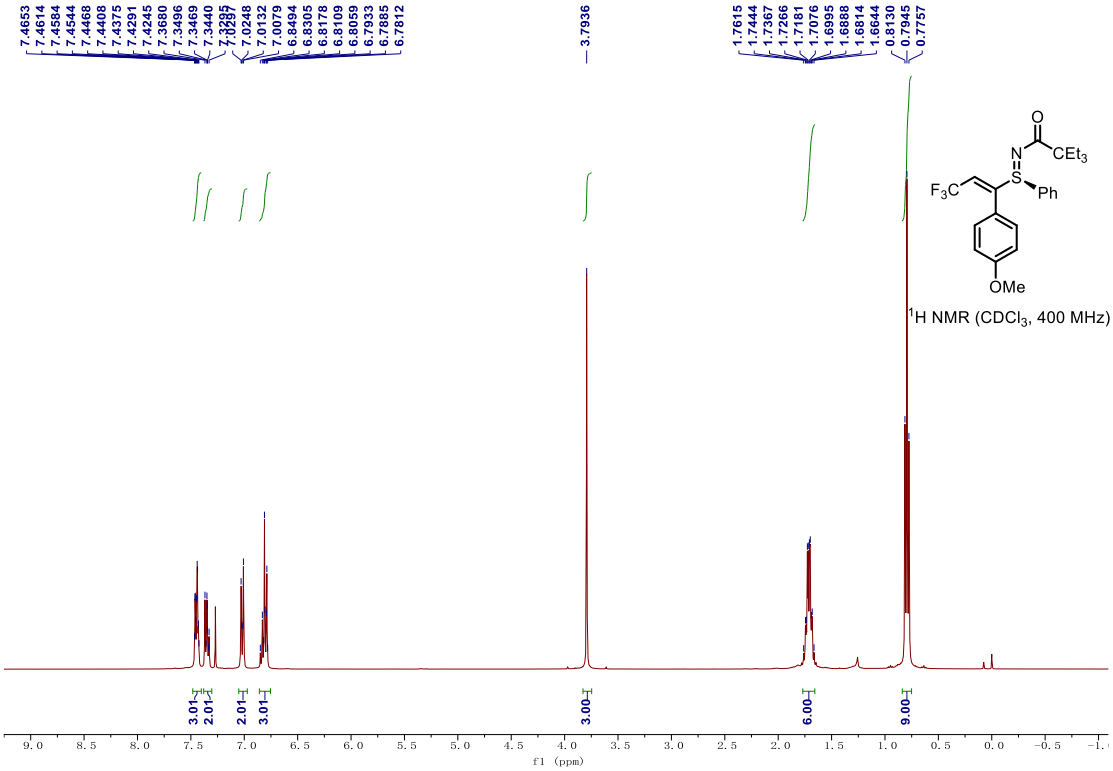


^{19}F NMR Spectrum of 4s

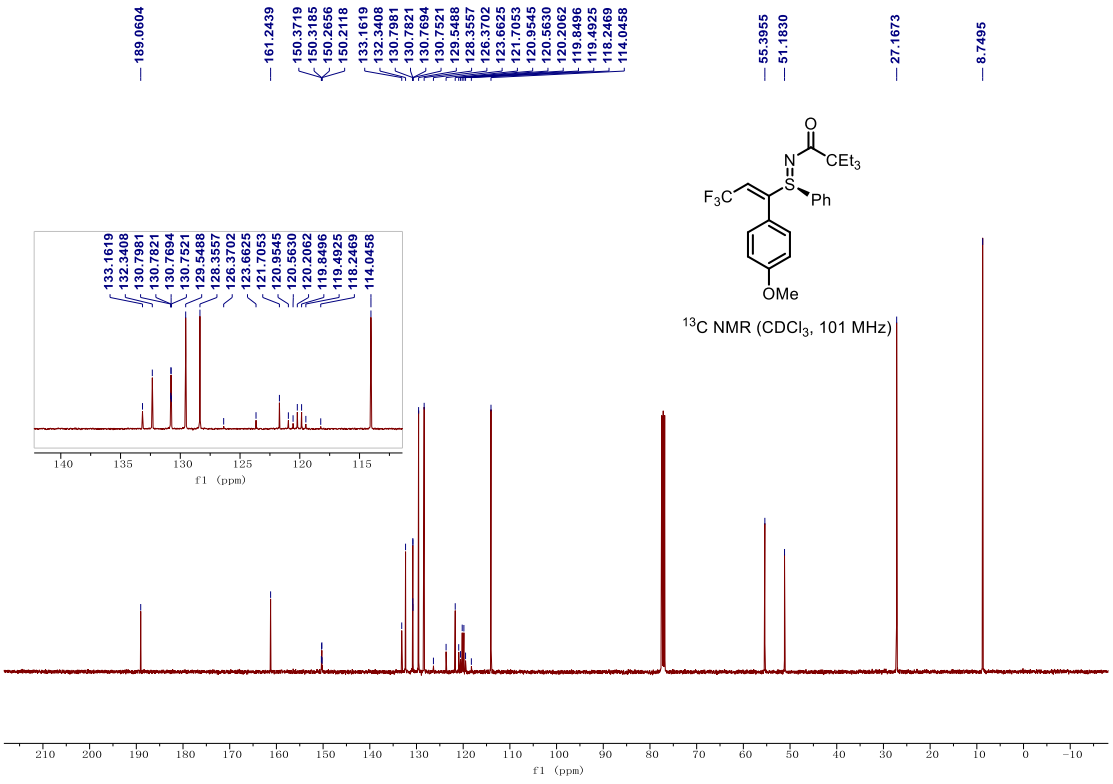


^{19}F NMR ($CDCl_3$, 282 MHz)

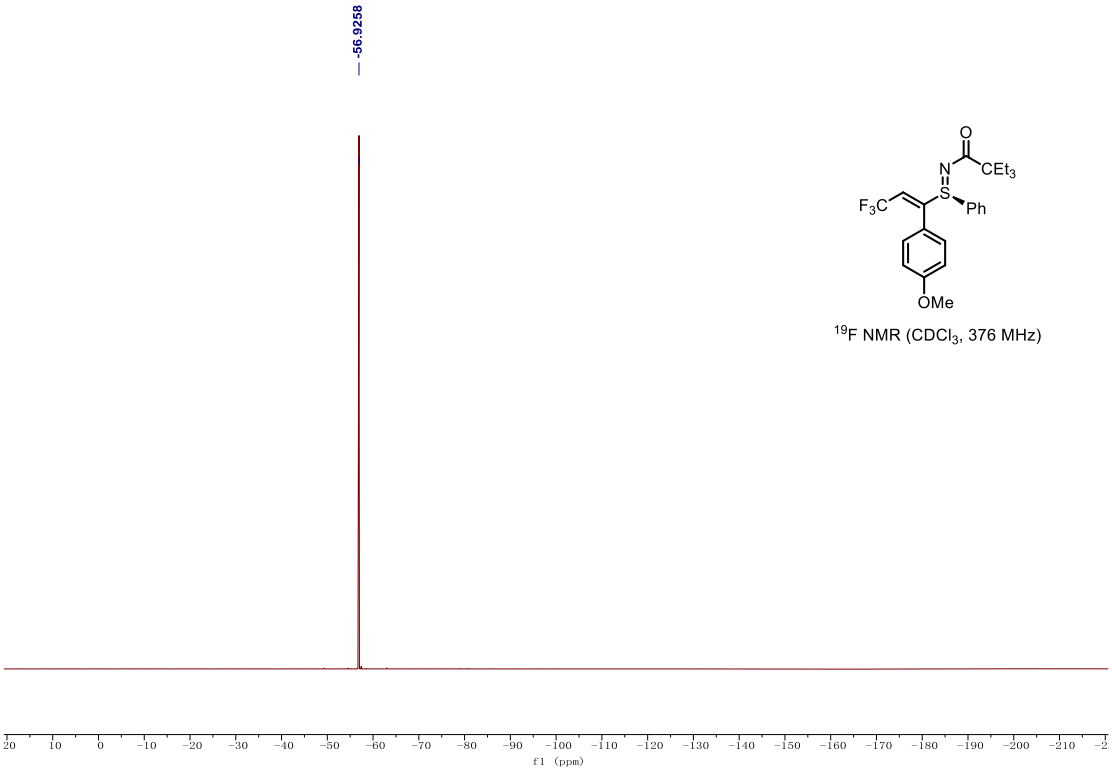
^{1}H NMR Spectrum of 4t



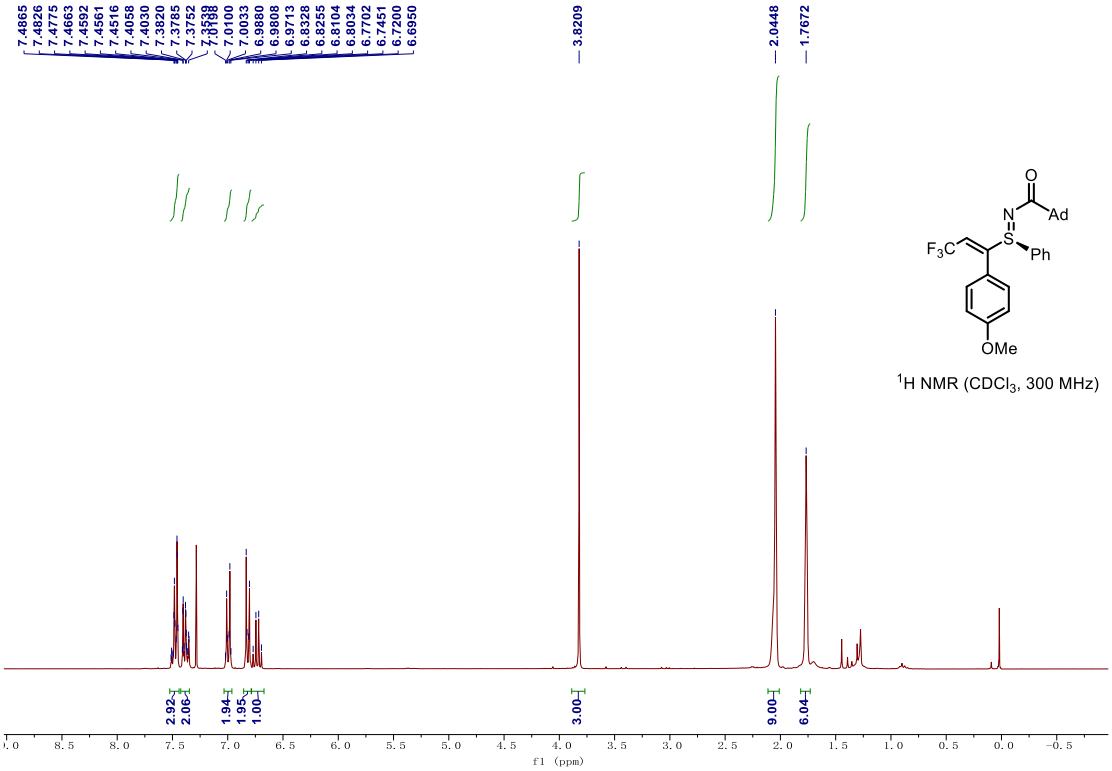
^{13}C NMR Spectrum of 4t



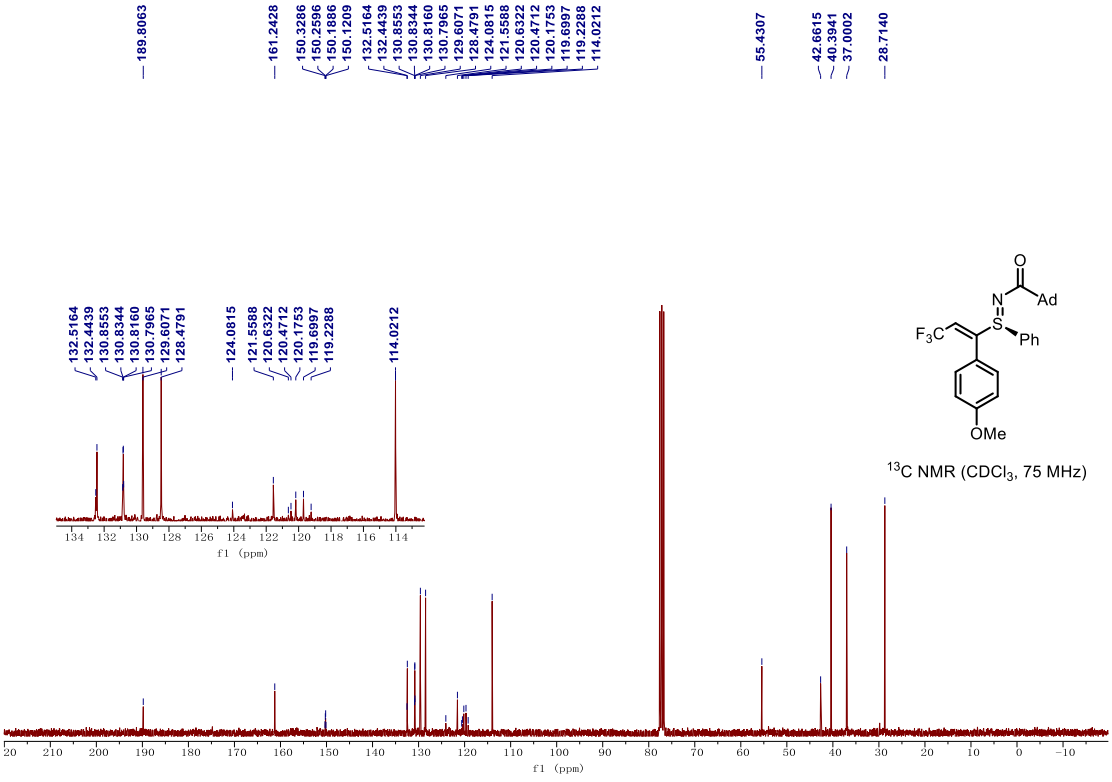
^{19}F NMR Spectrum of 4t



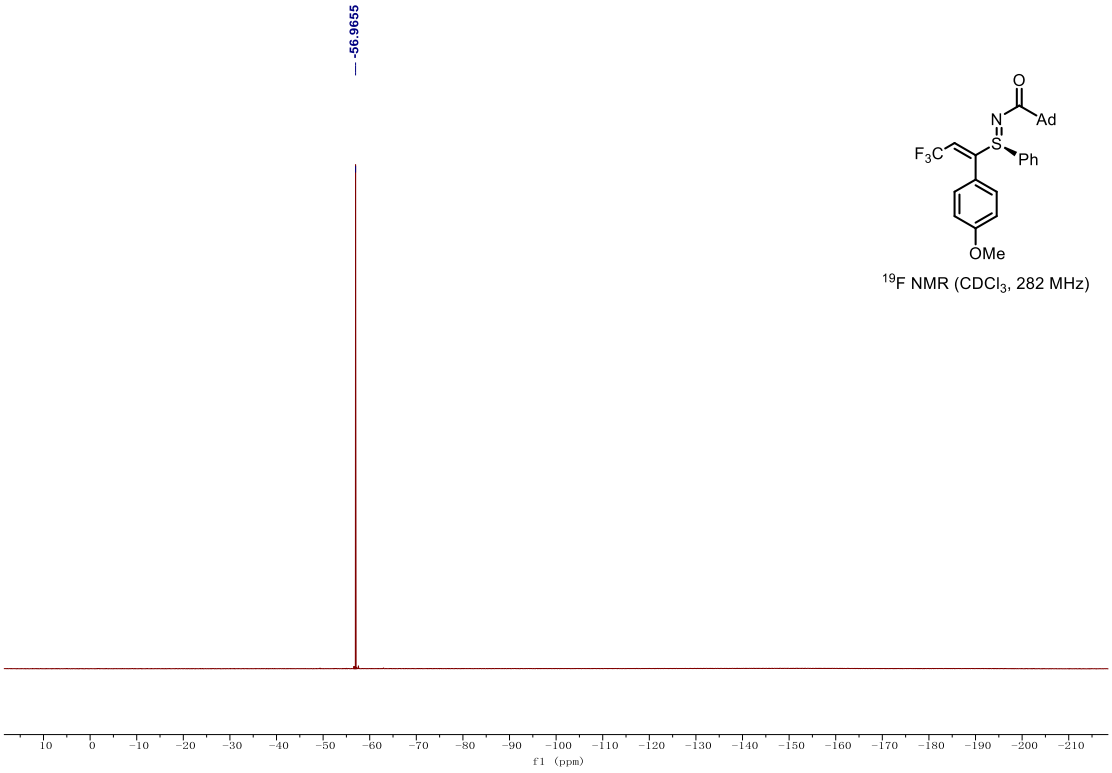
^{1}H NMR Spectrum of 4u



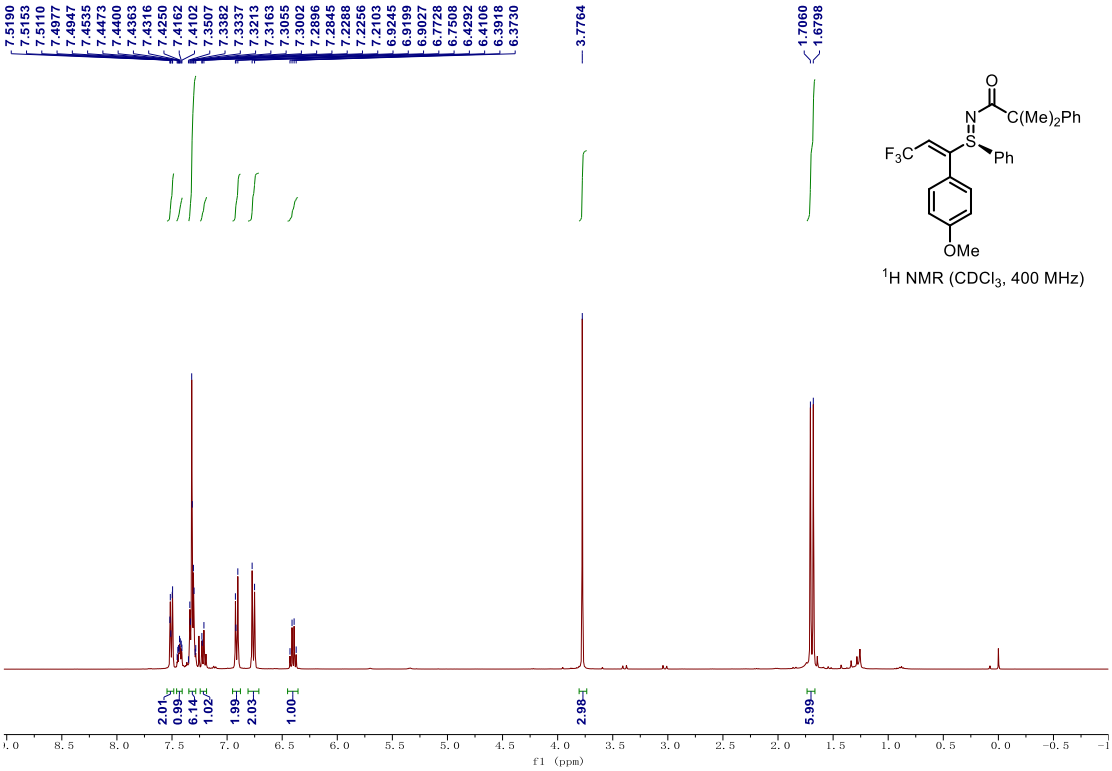
^{13}C NMR Spectrum of 4u



^{19}F NMR Spectrum of 4u

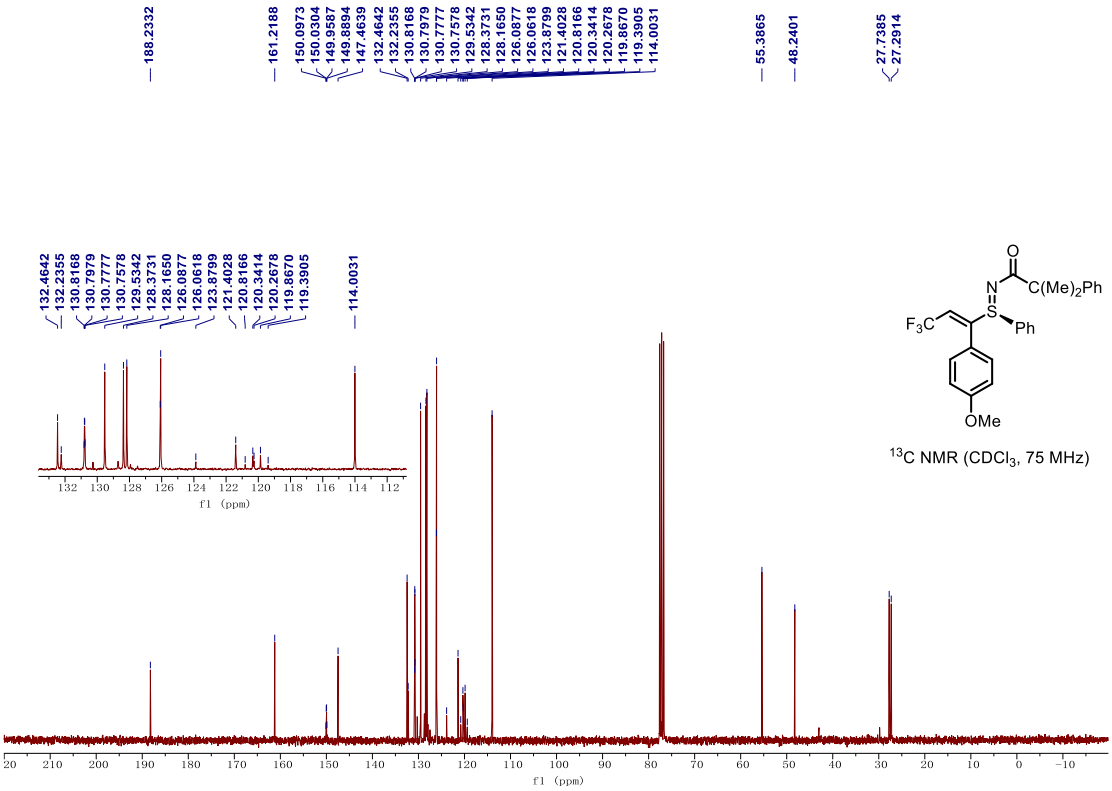


^{1}H NMR Spectrum of 4v



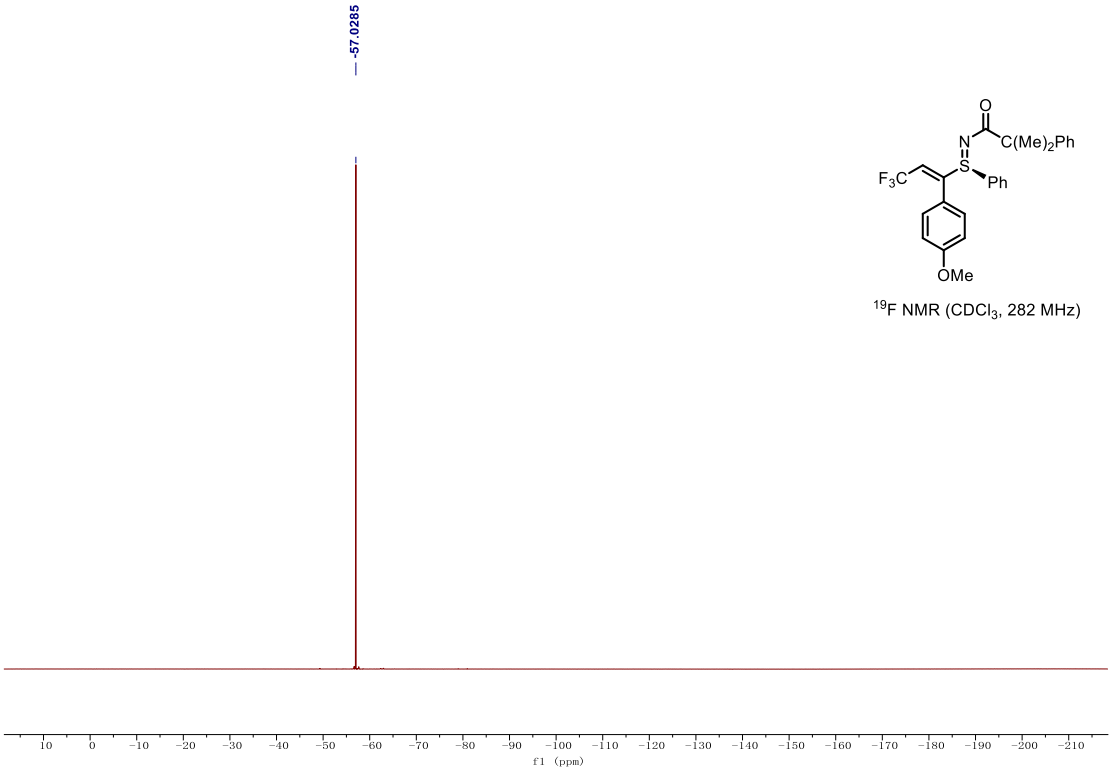
^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR Spectrum of 4v

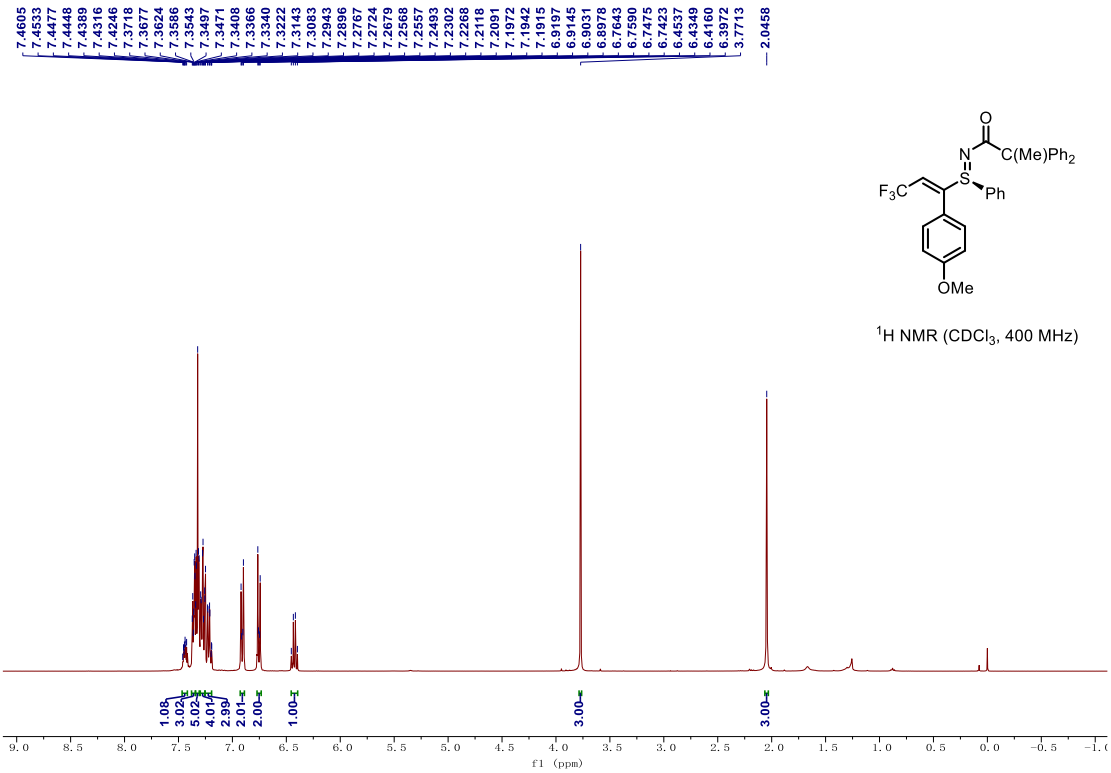


^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4v

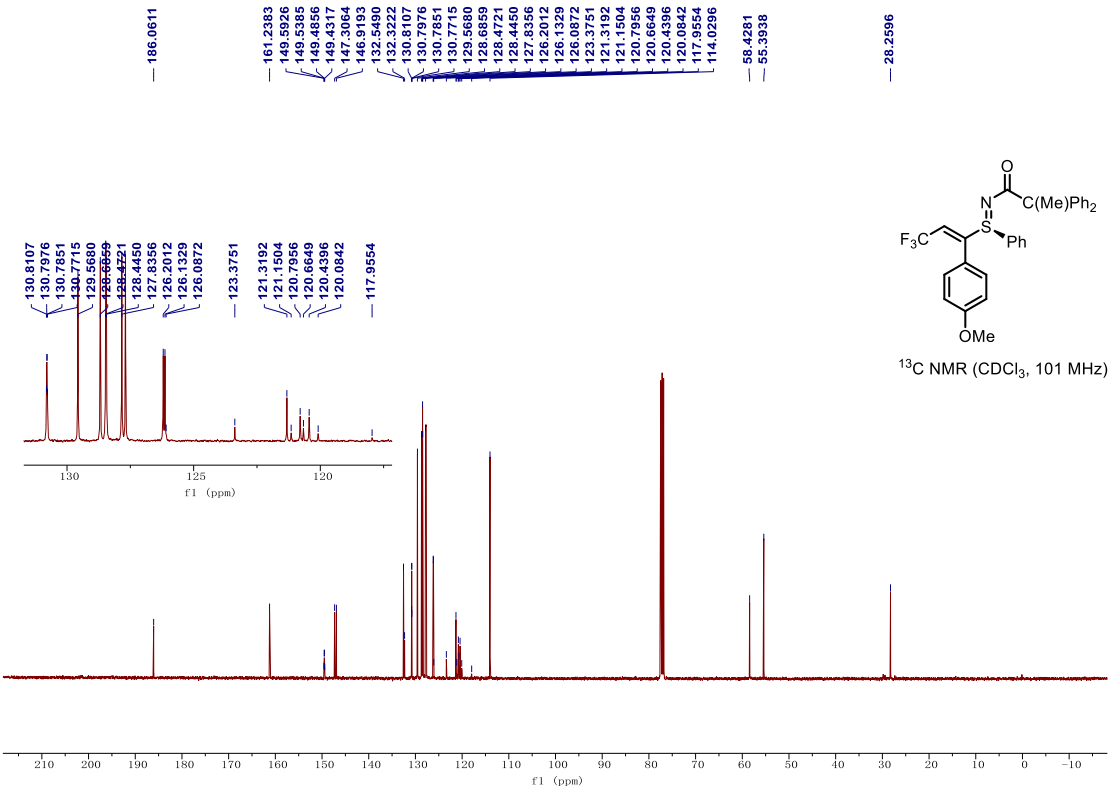


^{1}H NMR Spectrum of 4w



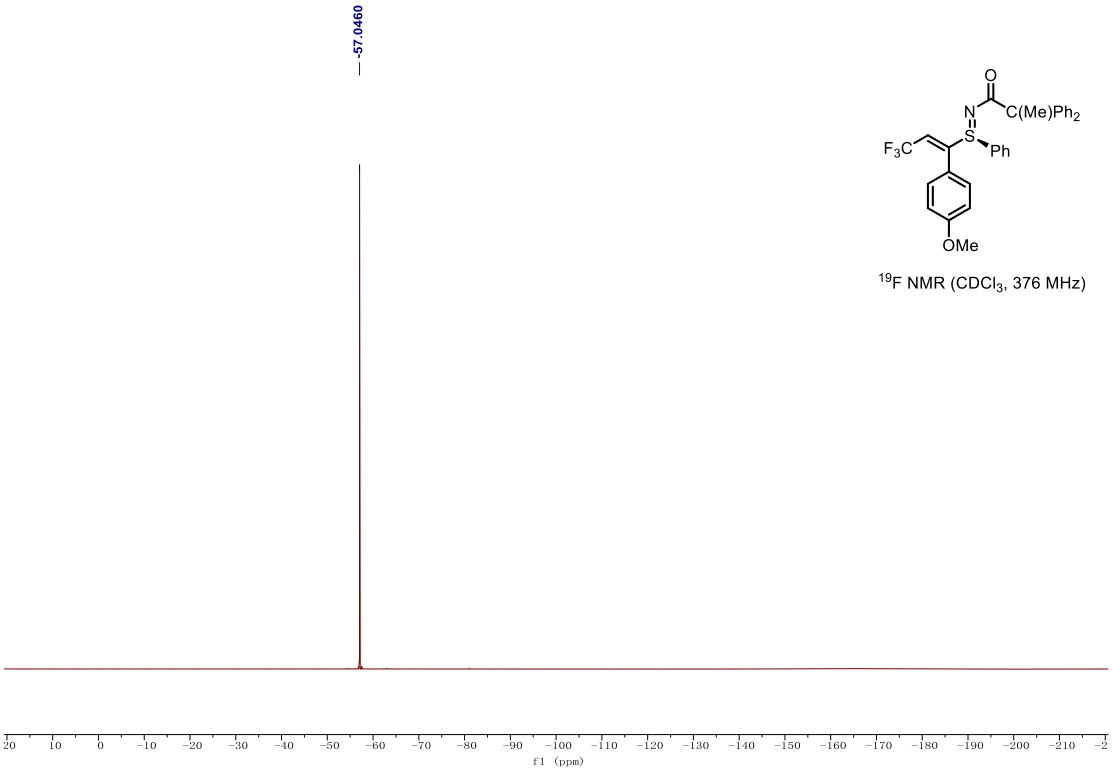
^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR Spectrum of 4w

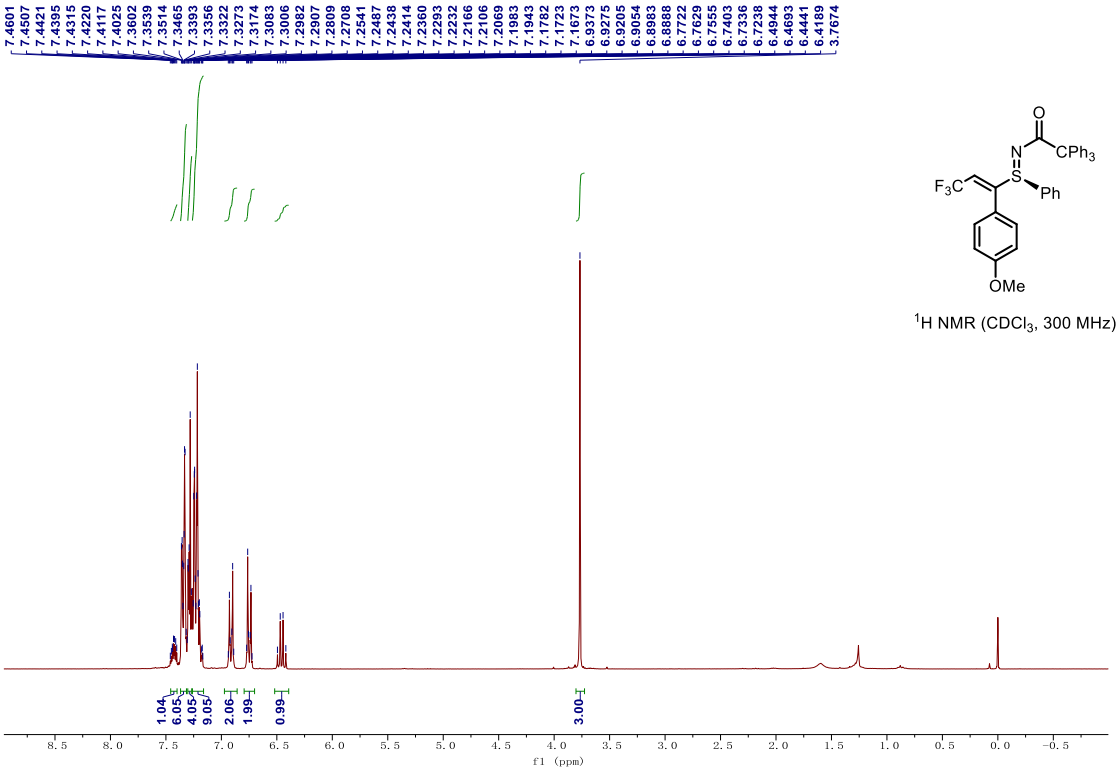


^{13}C NMR ($CDCl_3$, 101 MHz)

^{19}F NMR Spectrum of 4w

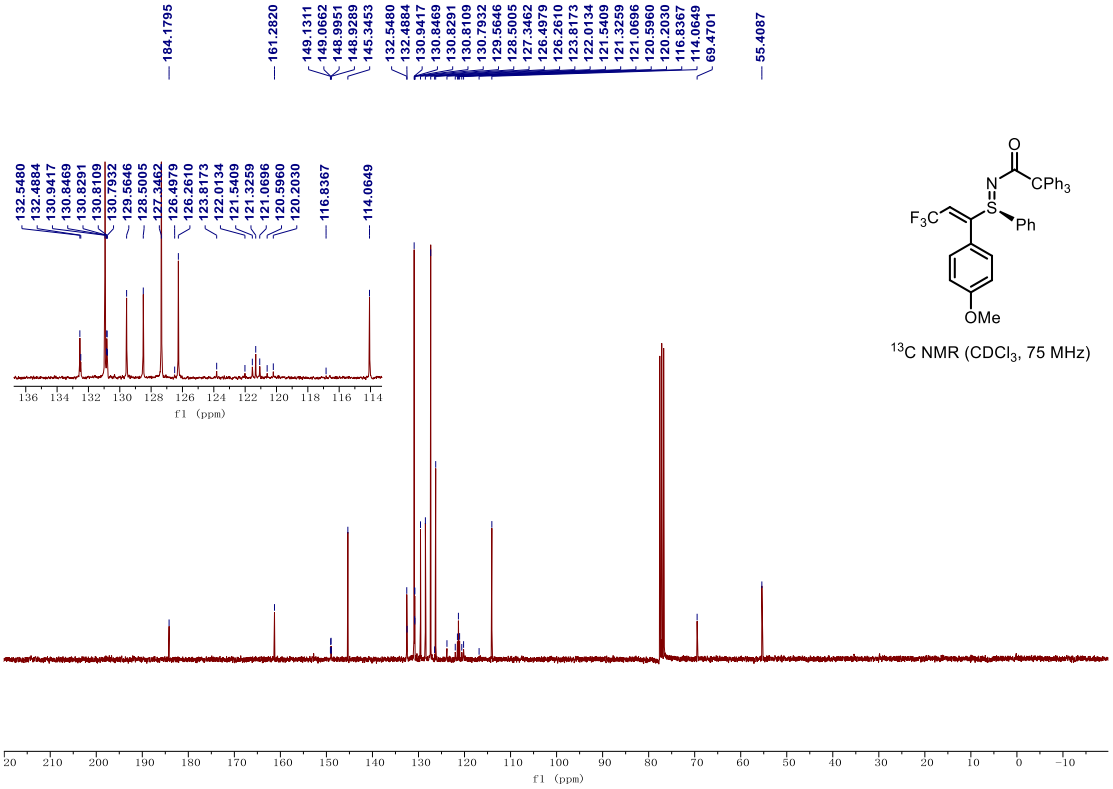


^{1}H NMR Spectrum of 4x



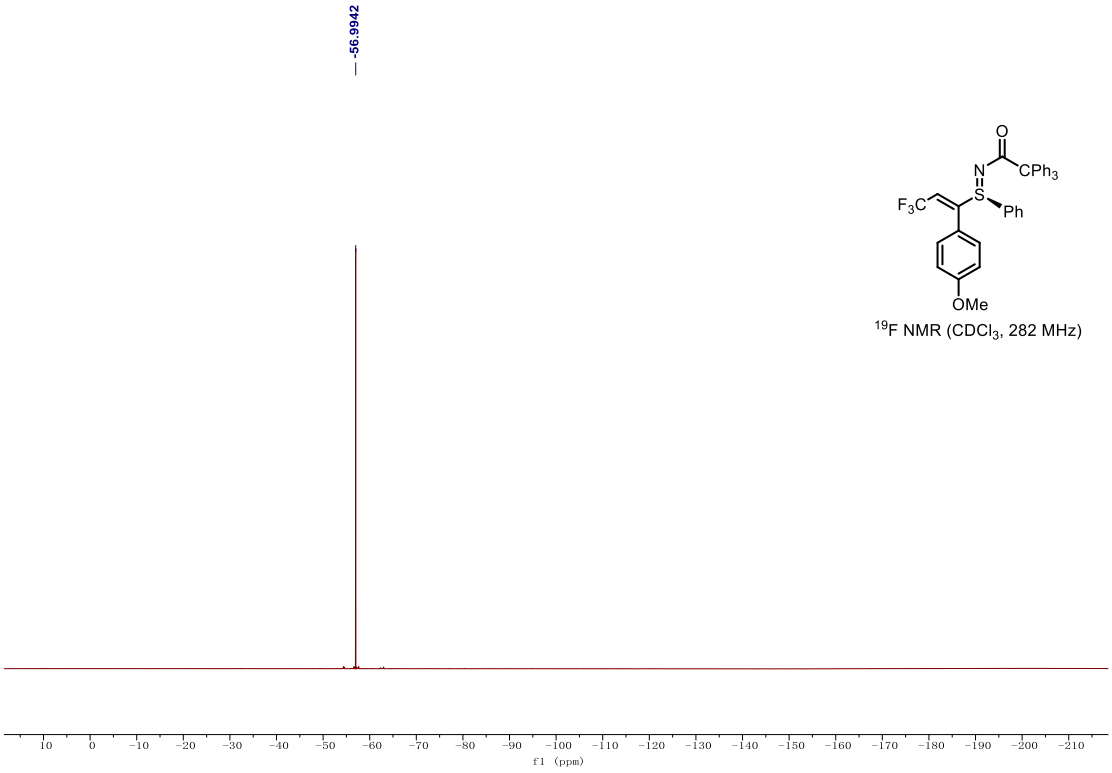
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4x



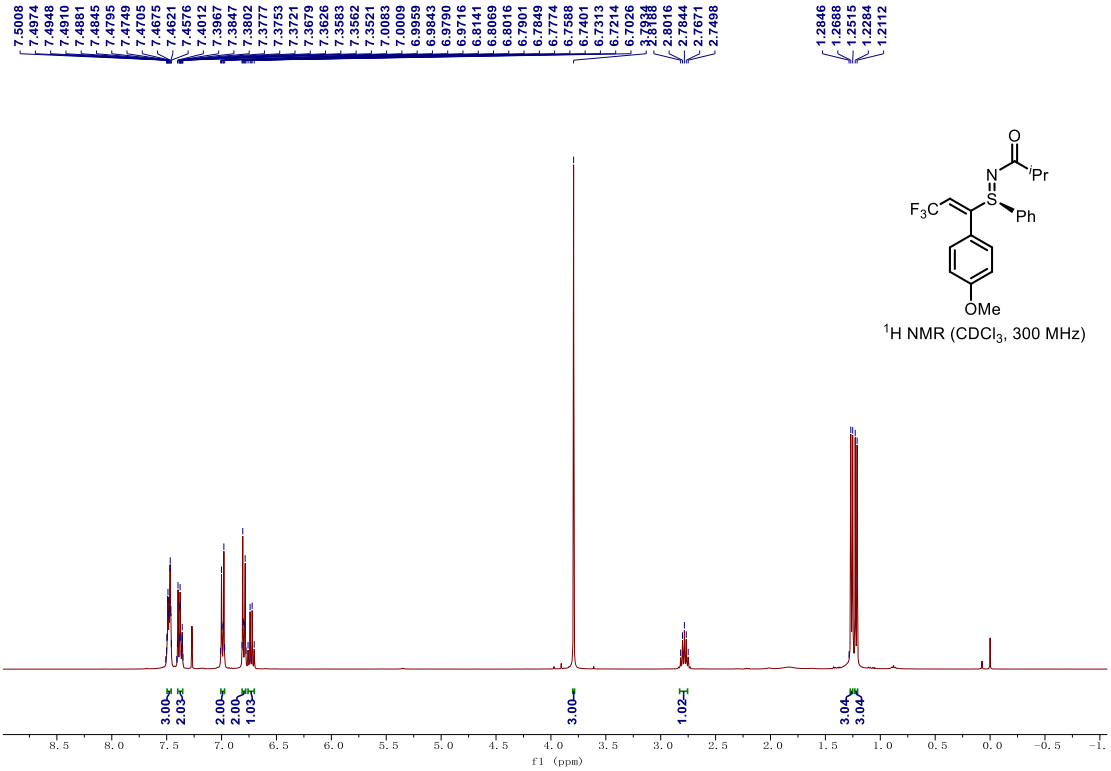
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4x

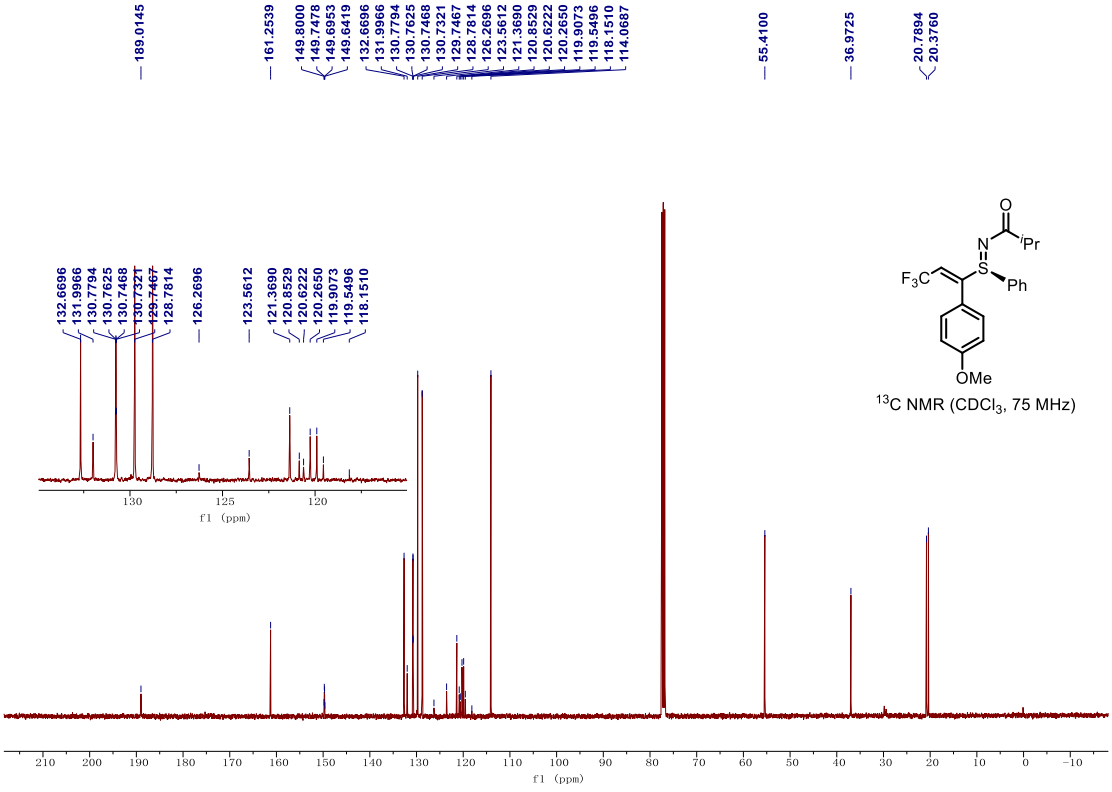


^{19}F NMR ($CDCl_3$, 282 MHz)

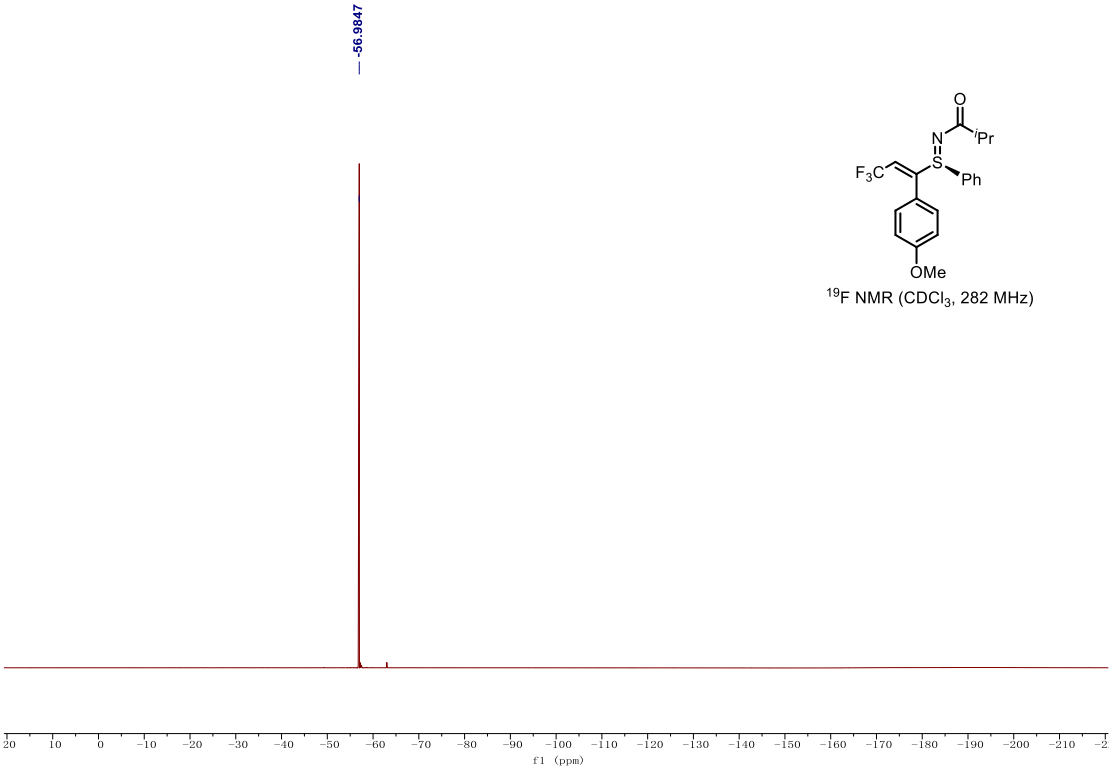
^{1}H NMR Spectrum of 4y



^{13}C NMR Spectrum of 4y

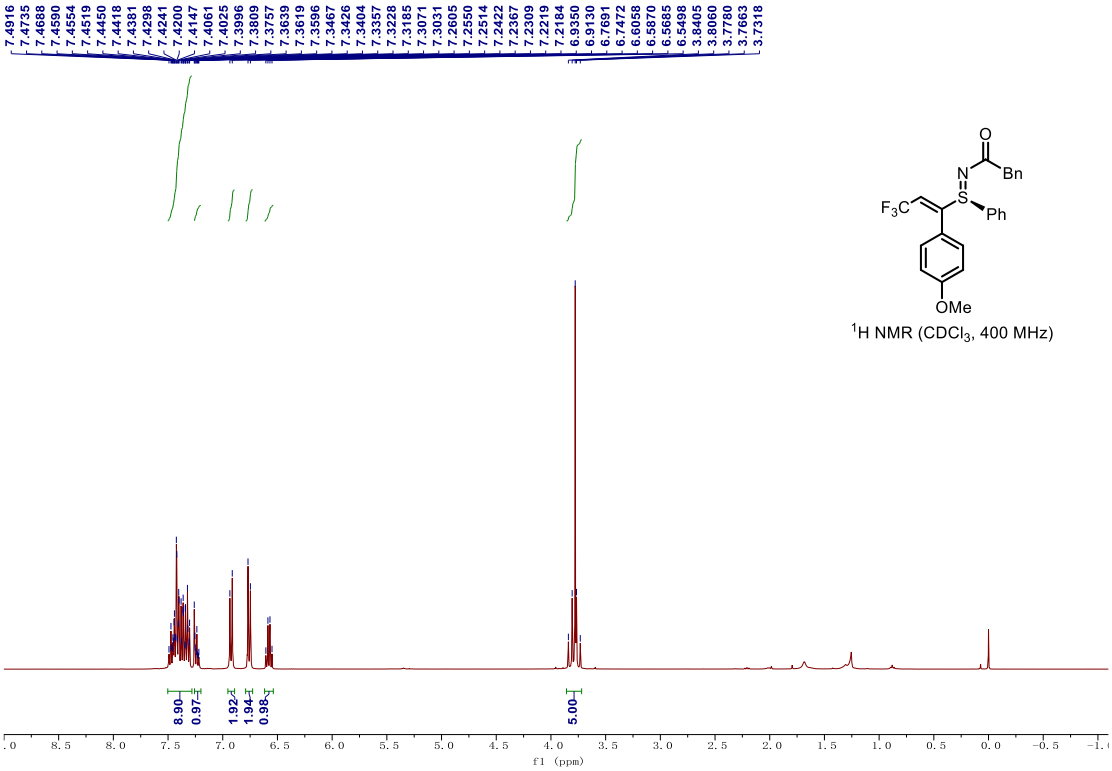


^{19}F NMR Spectrum of 4y



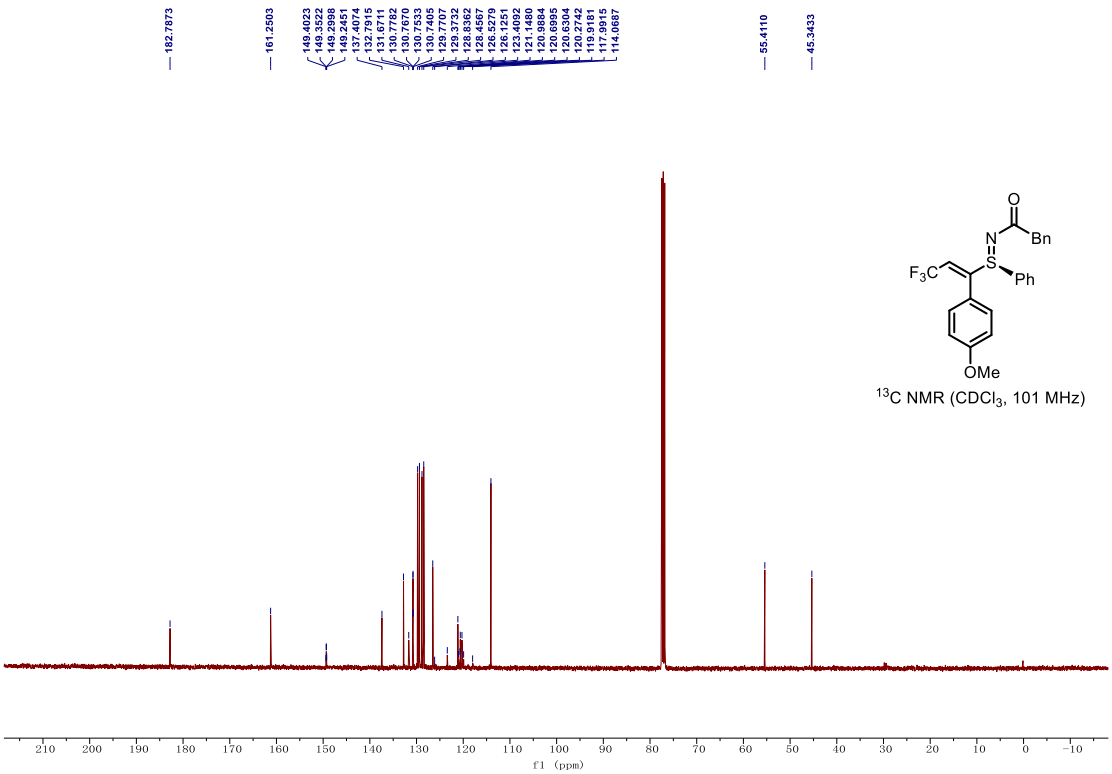
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4z



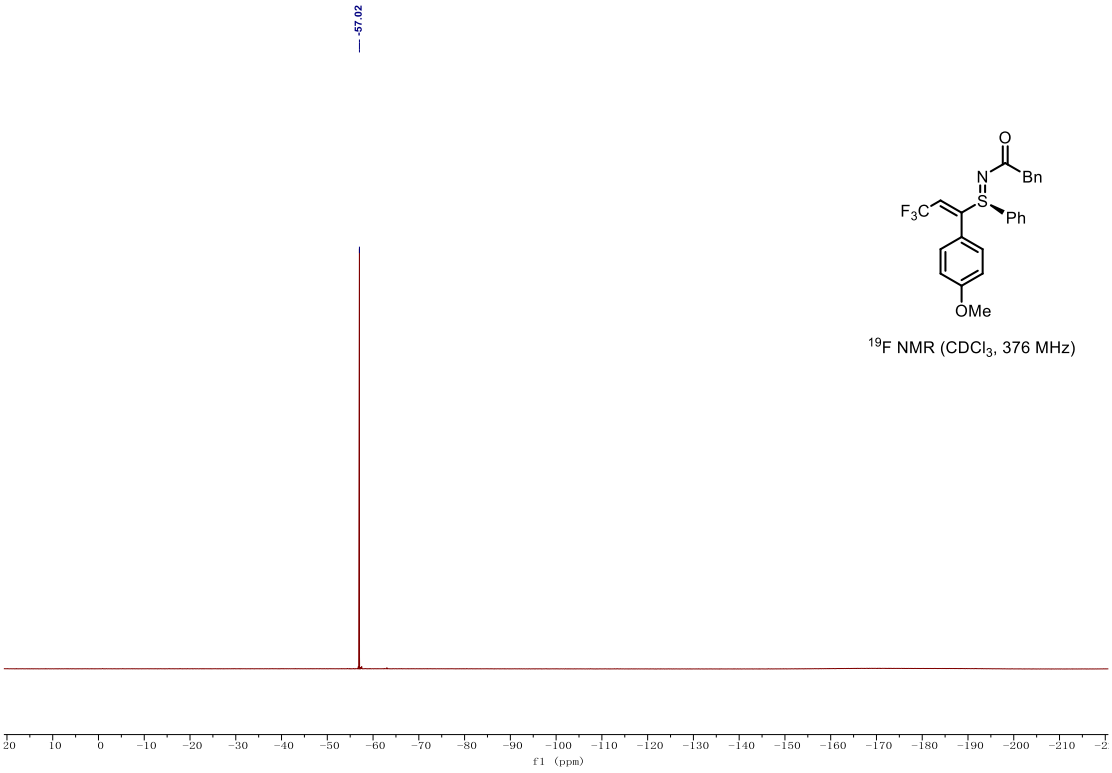
^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR Spectrum of 4z



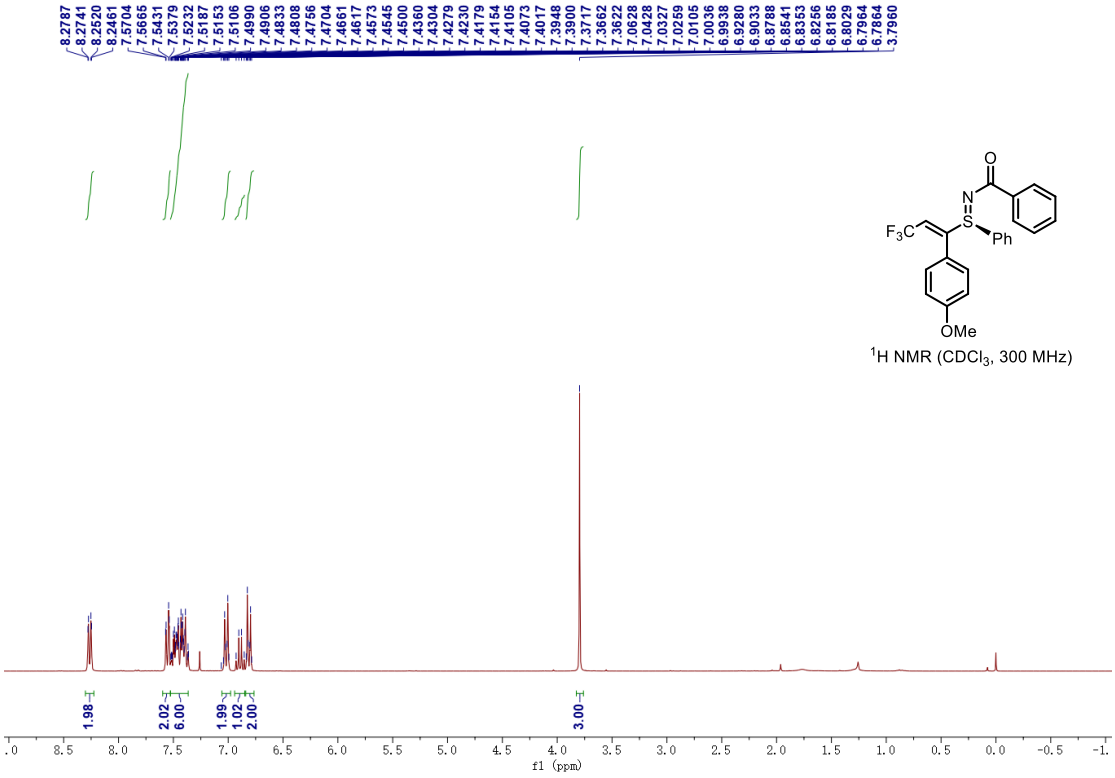
^{13}C NMR ($CDCl_3$, 101 MHz)

^{19}F NMR Spectrum of 4z



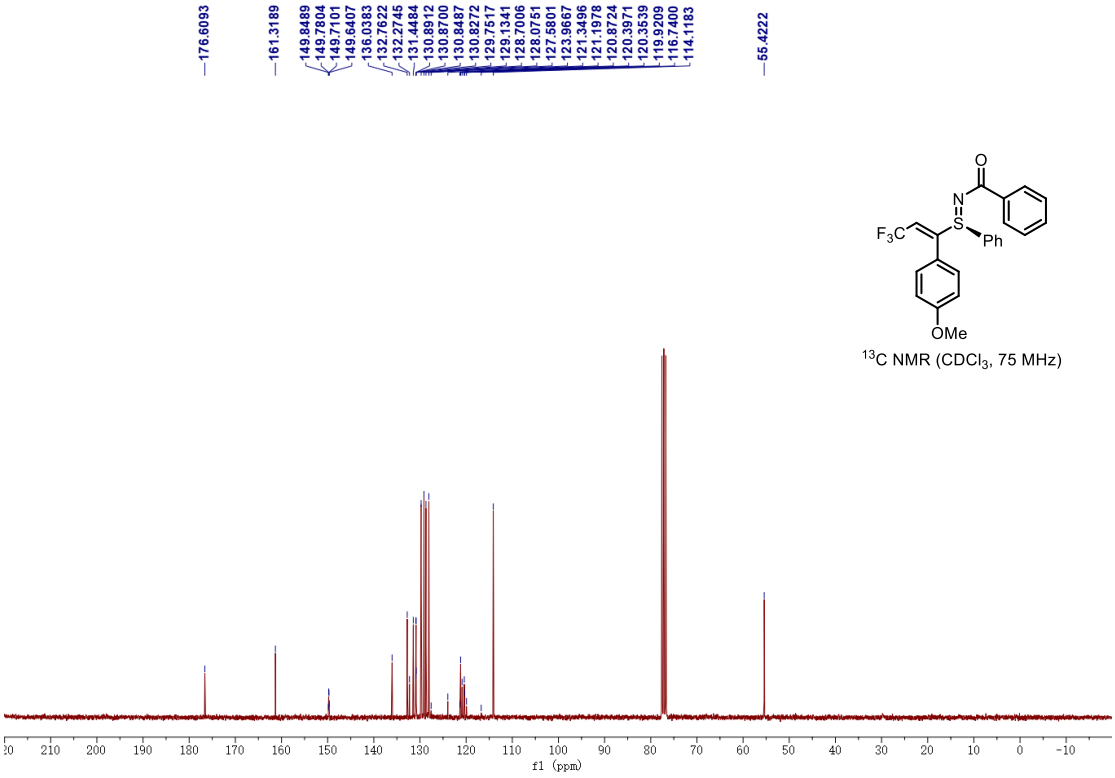
^{19}F NMR ($CDCl_3$, 376 MHz)

^{1}H NMR Spectrum of 4aa



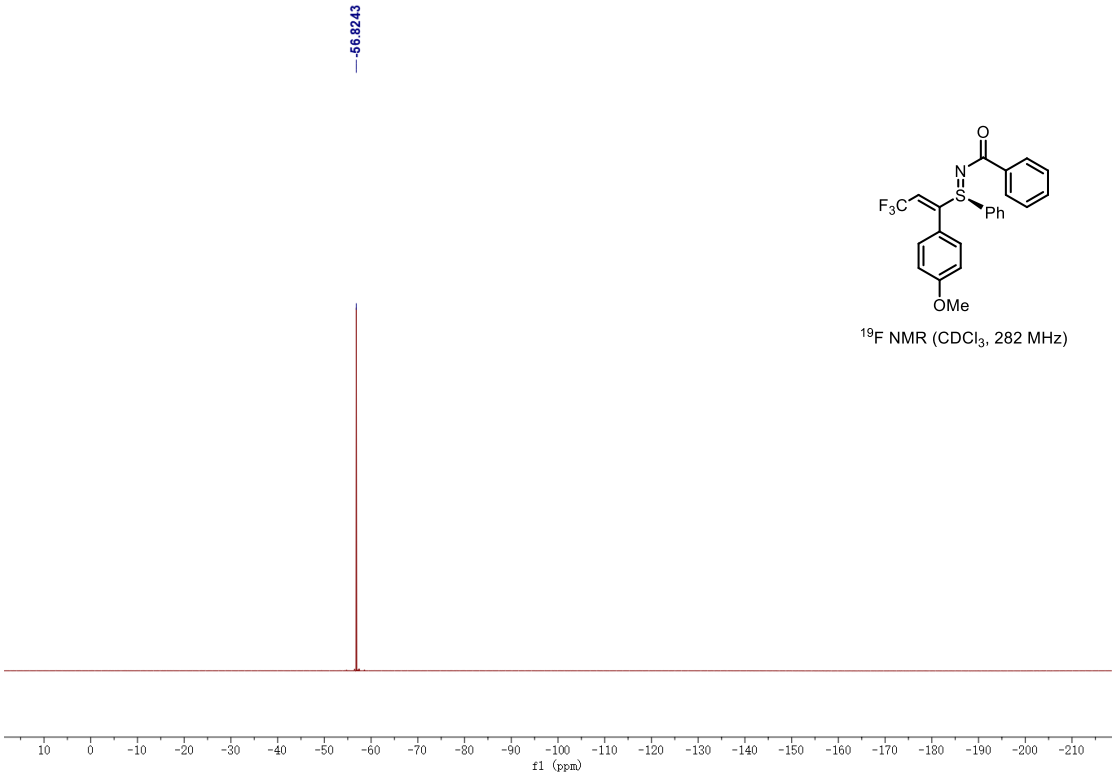
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4aa

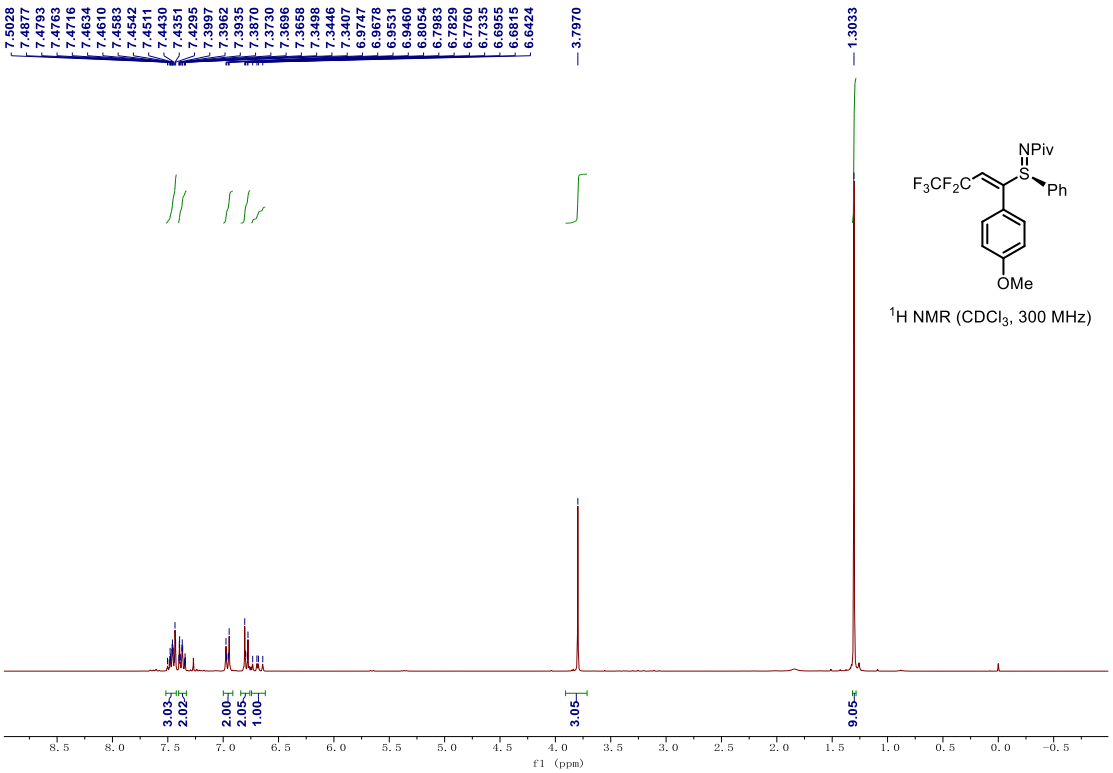


^{13}C NMR ($CDCl_3$, 75 MHz)

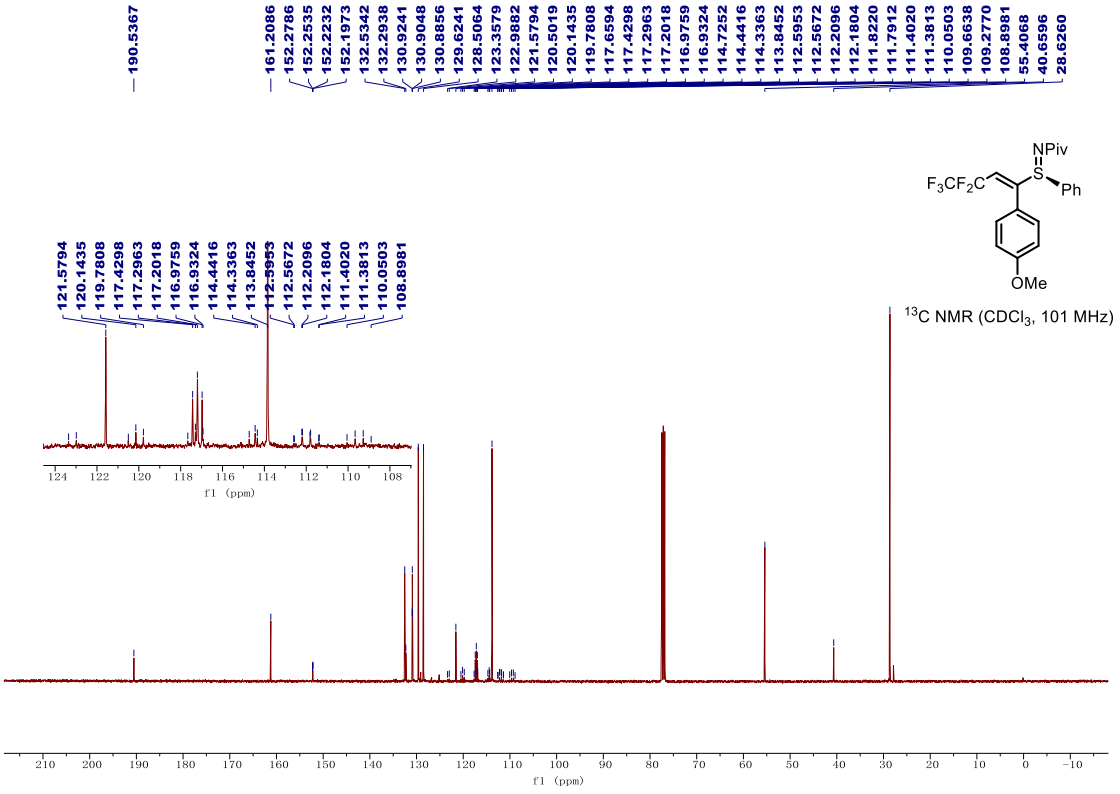
^{19}F NMR Spectrum of 4aa



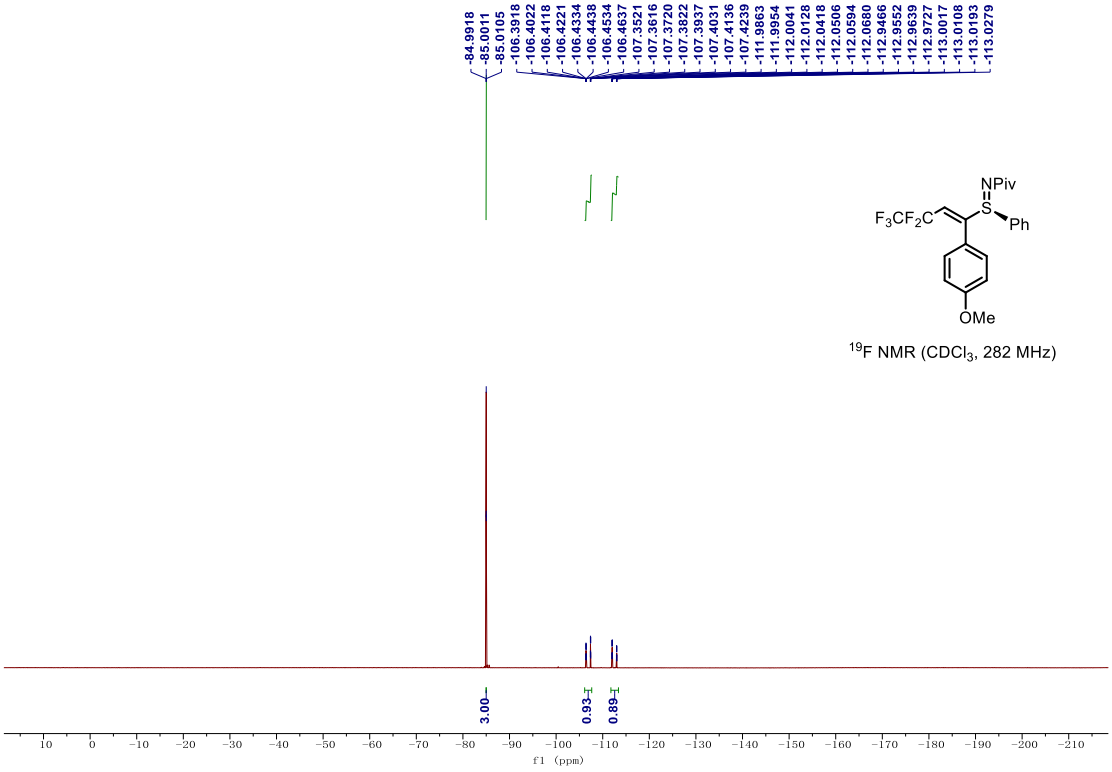
^{1}H NMR Spectrum of 4ab



^{13}C NMR Spectrum of 4ab

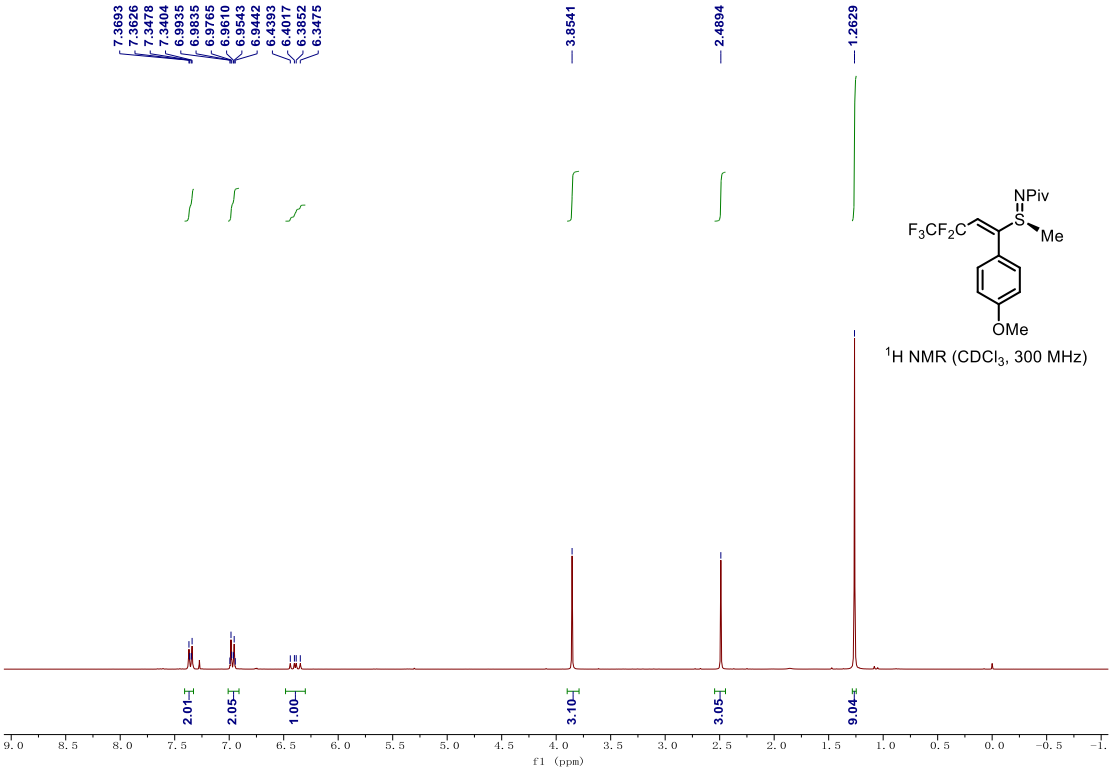


^{19}F NMR Spectrum of 4ab

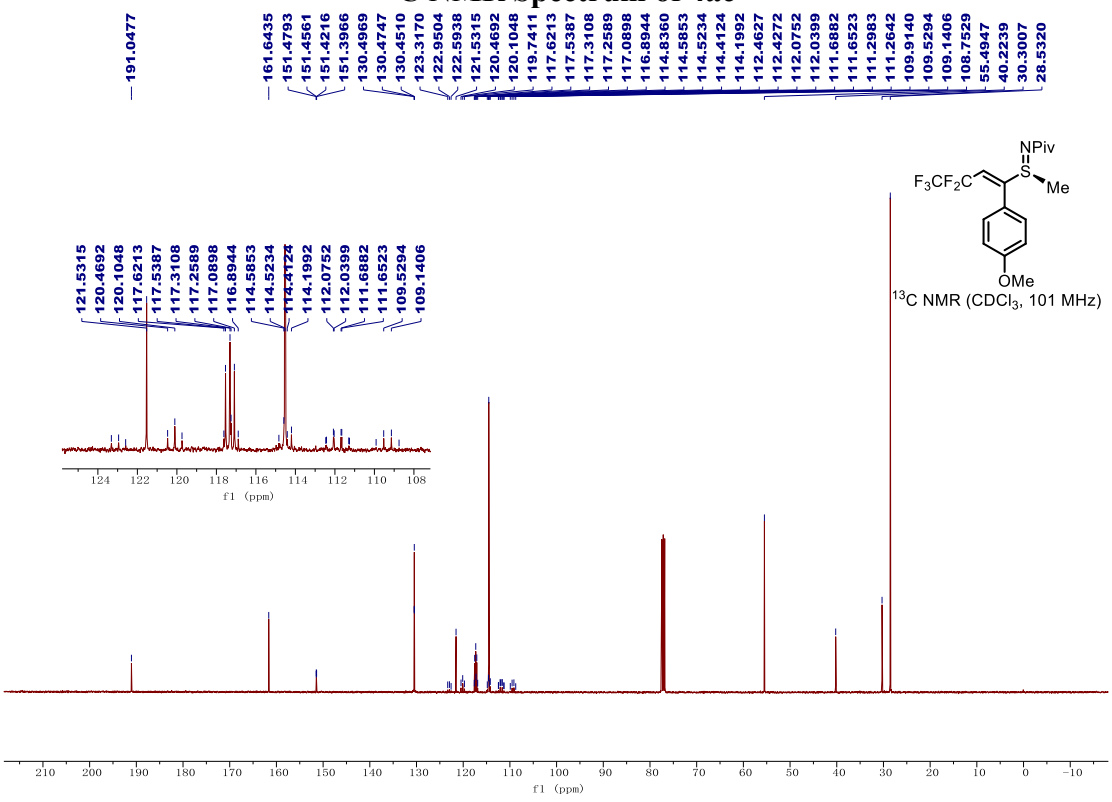


^{19}F NMR ($CDCl_3$, 282 MHz)

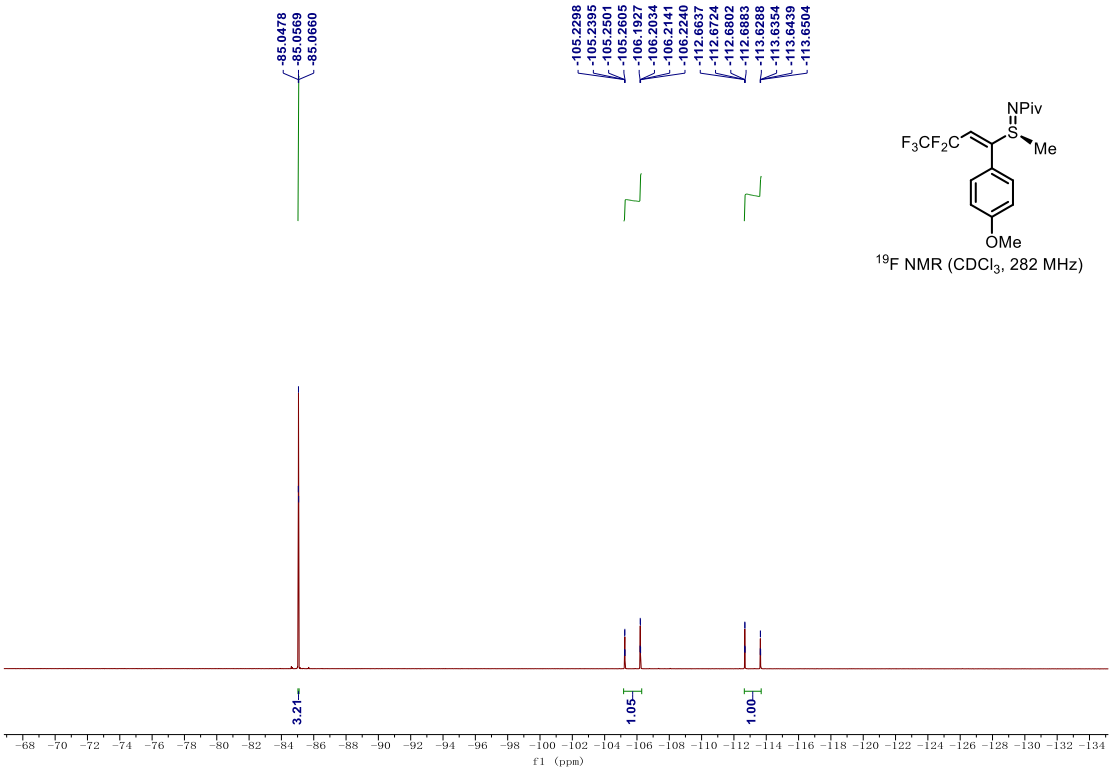
^{1}H NMR Spectrum of 4ac



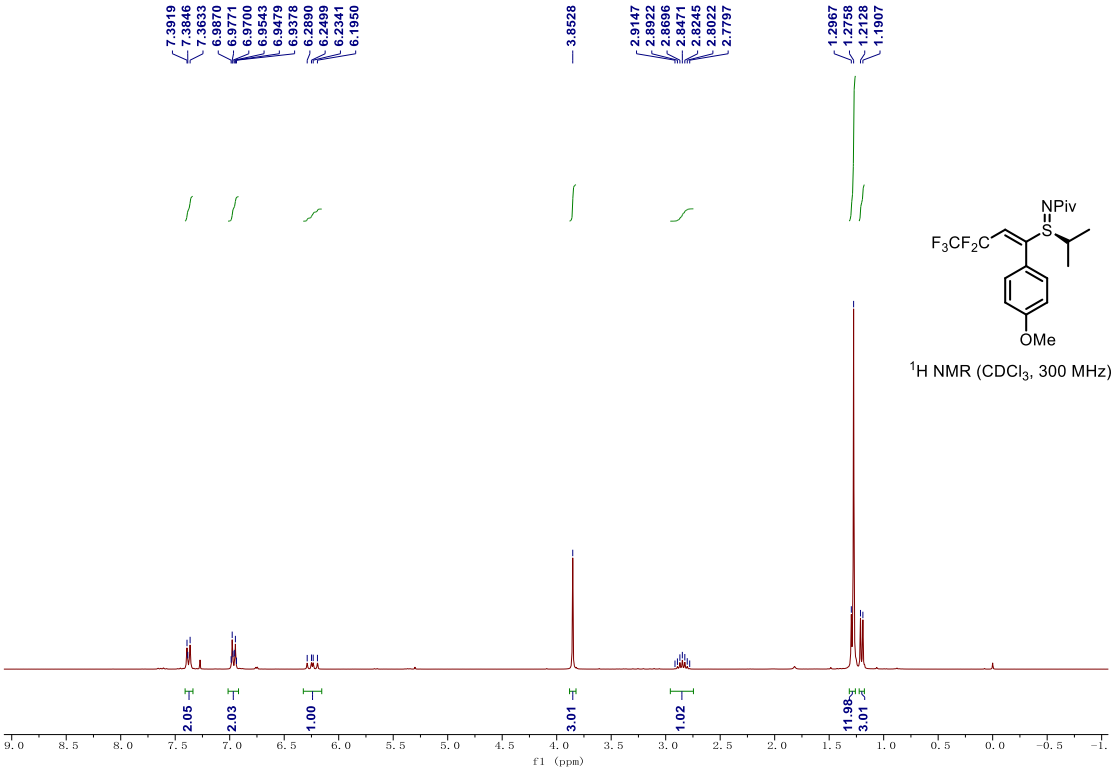
^{13}C NMR Spectrum of 4ac



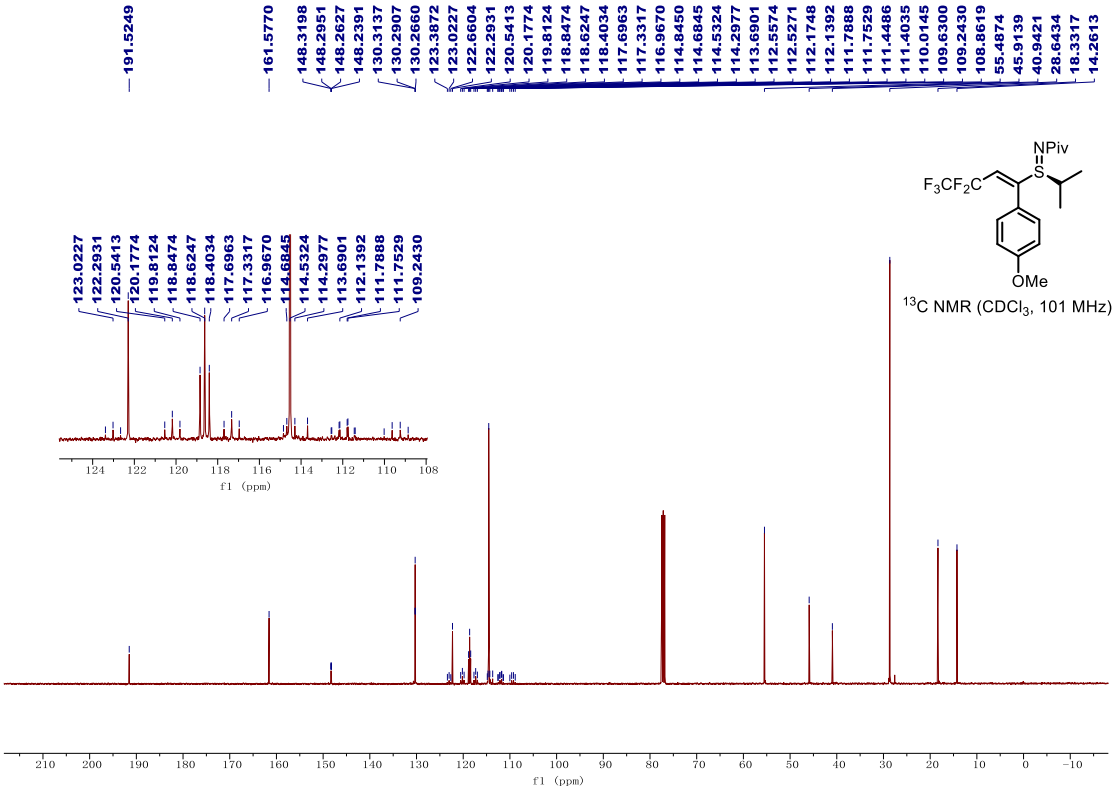
^{19}F NMR Spectrum of 4ac



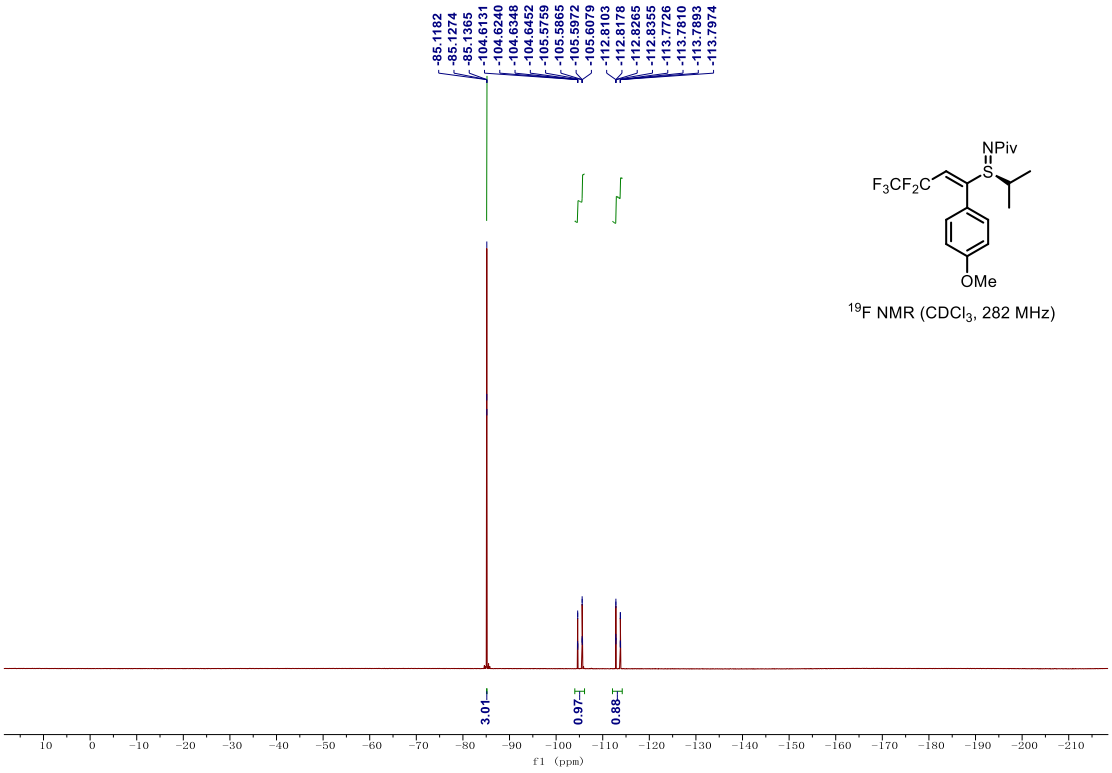
^{1}H NMR Spectrum of 4ad



^{13}C NMR Spectrum of 4ad

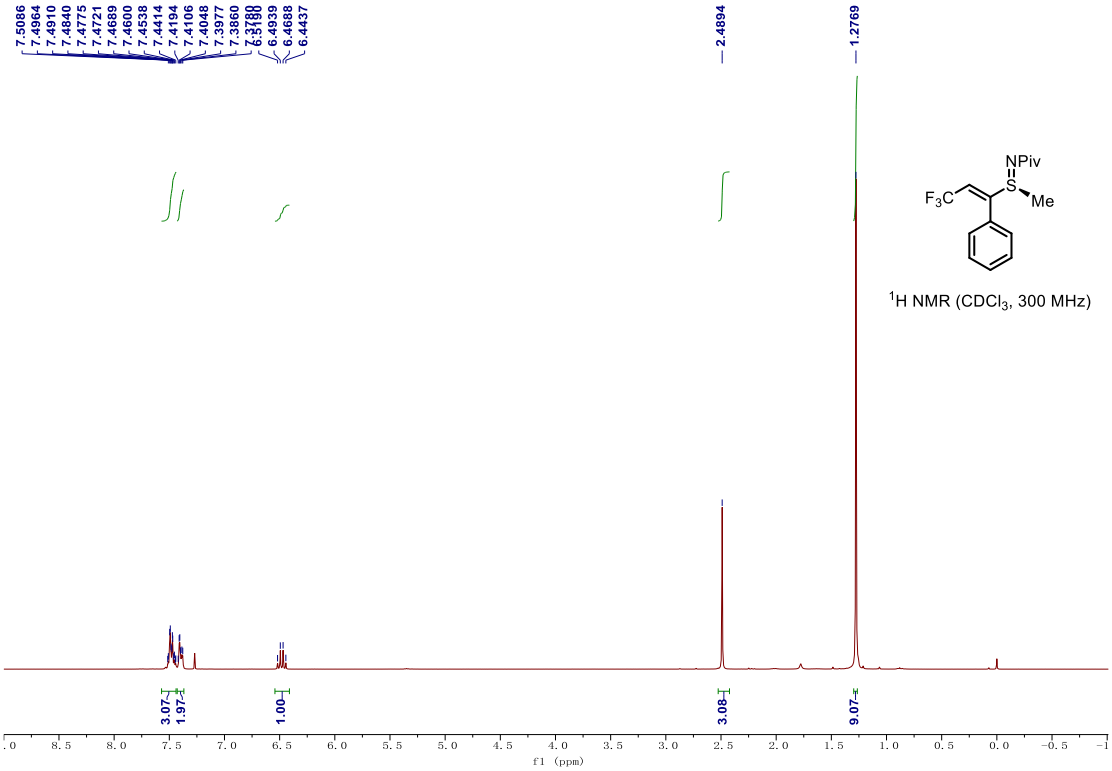


^{19}F NMR Spectrum of 4ad



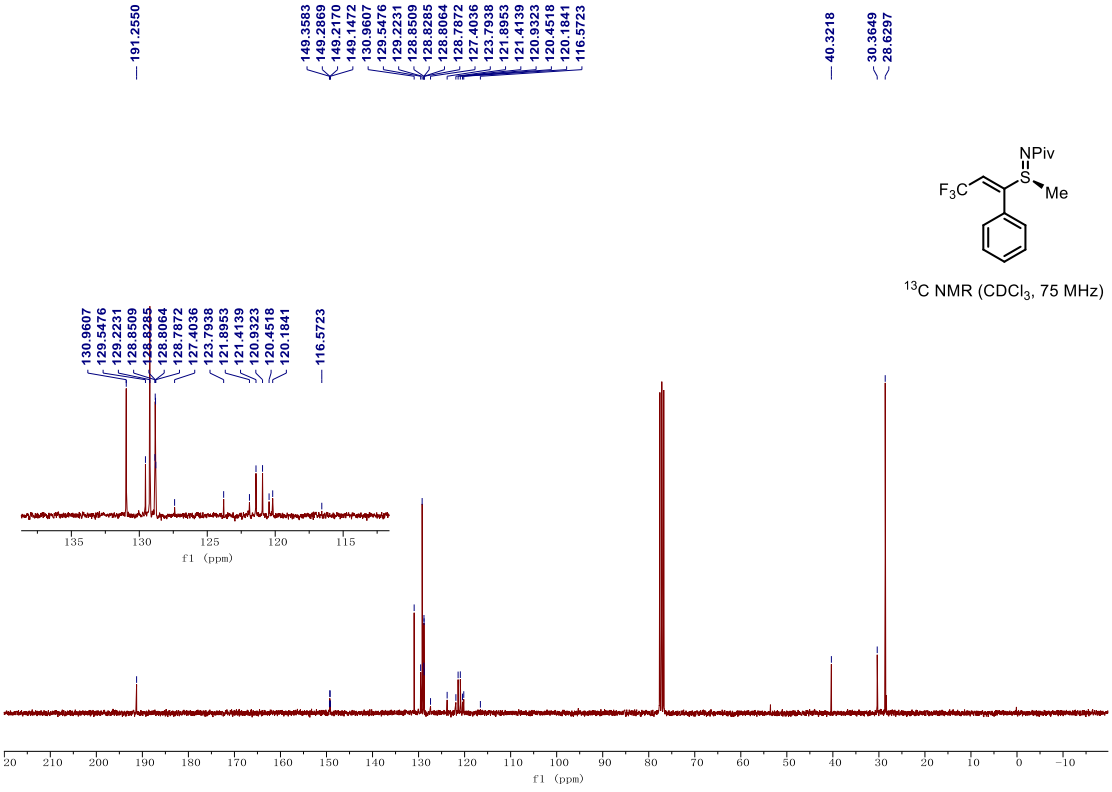
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4ae



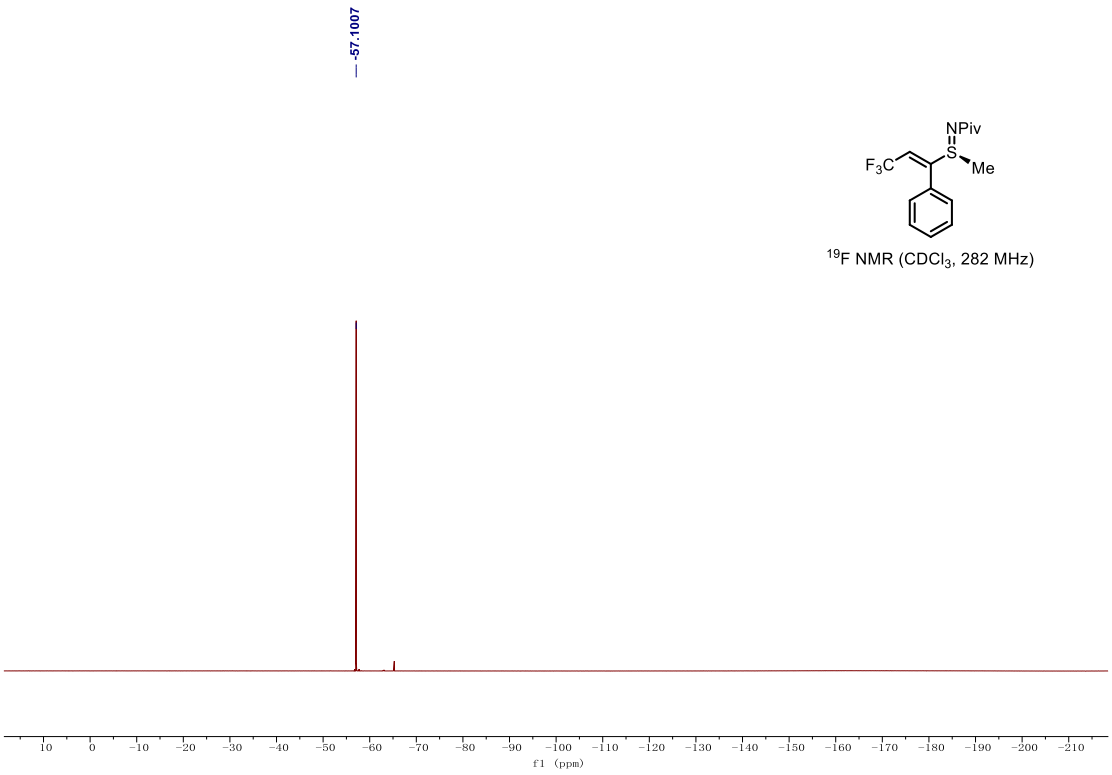
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4ae

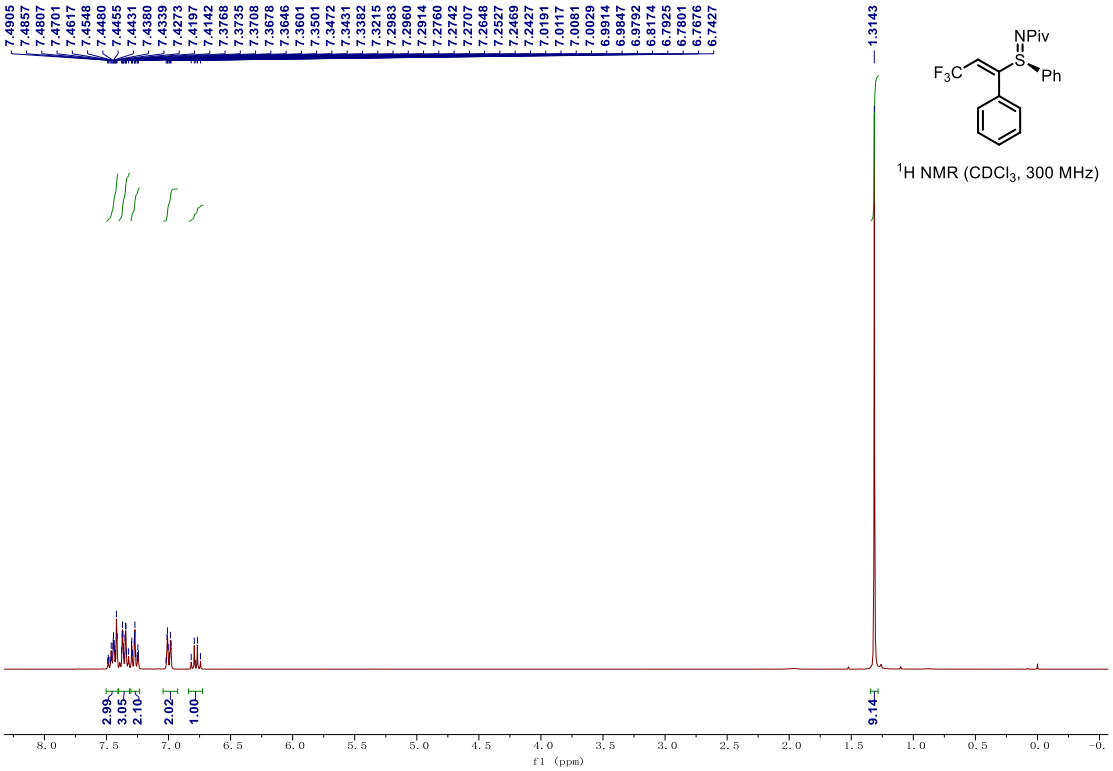


^{13}C NMR ($CDCl_3$, 75 MHz)

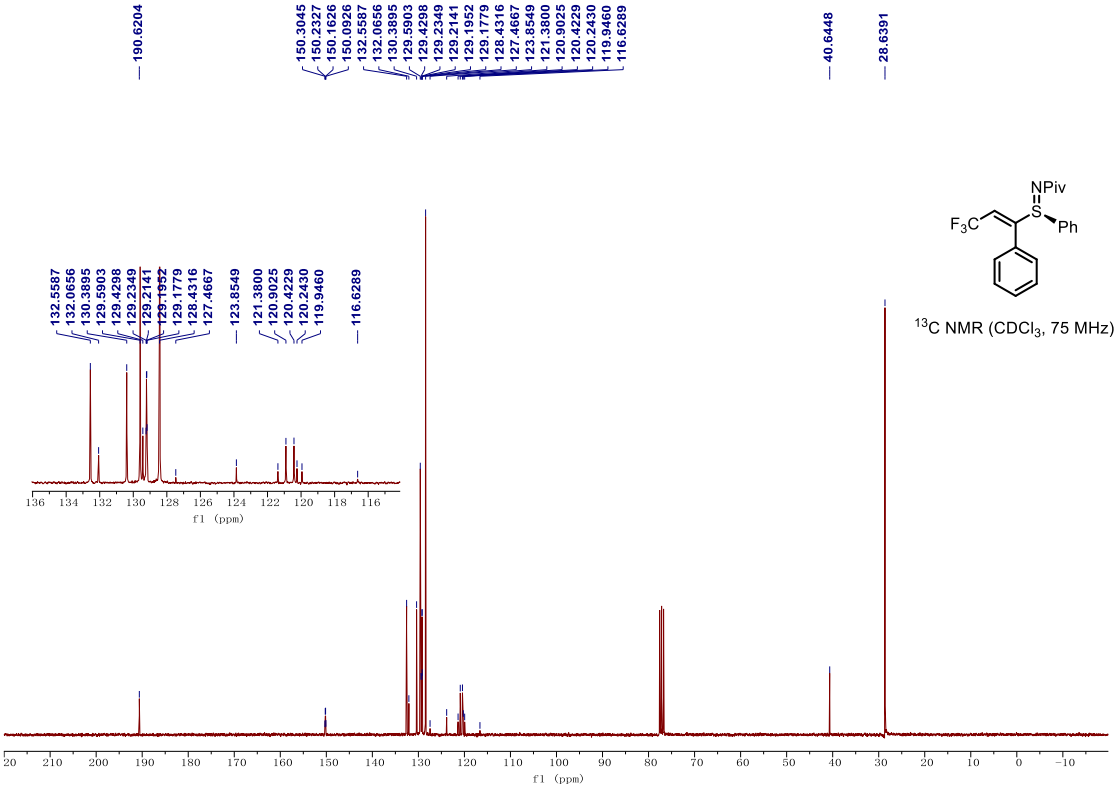
^{19}F NMR Spectrum of 4ae



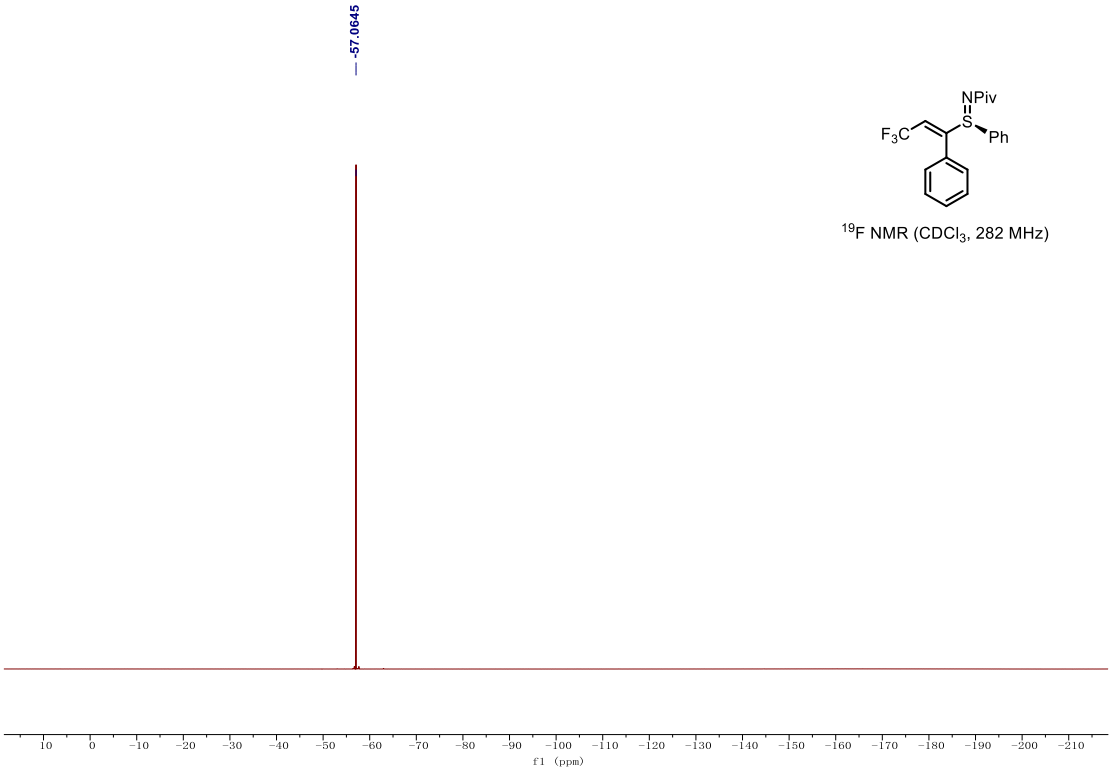
^{1}H NMR Spectrum of 4af



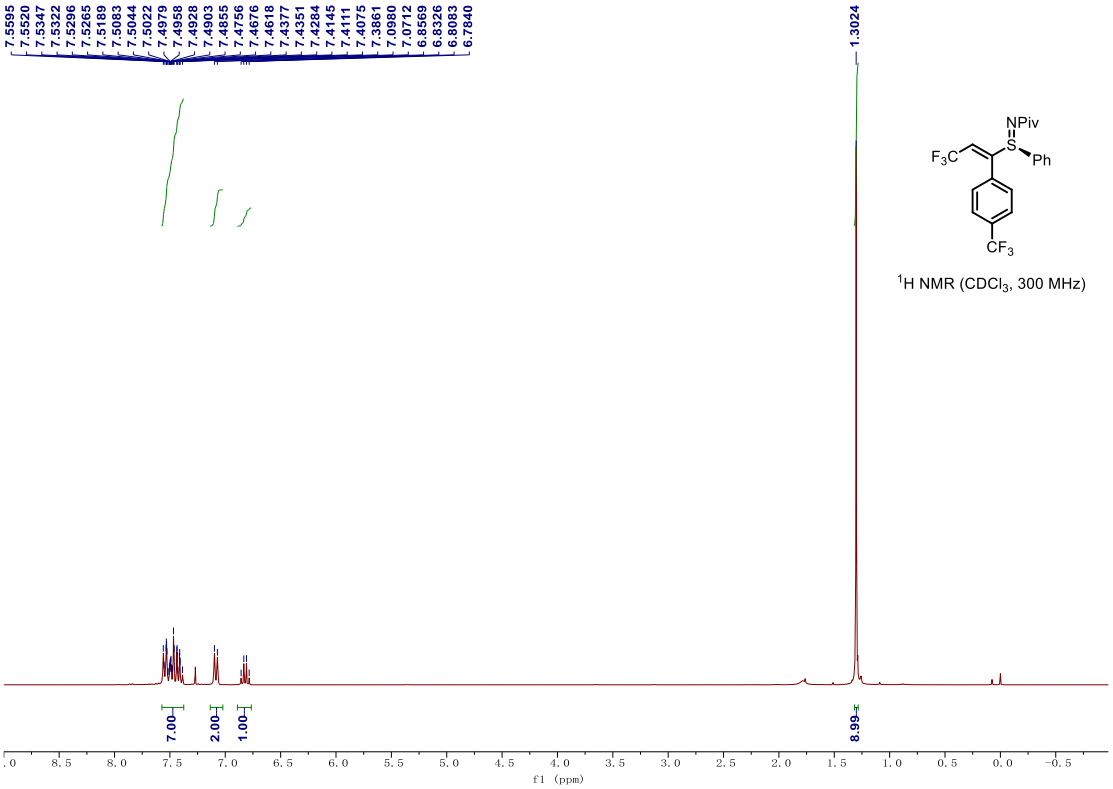
^{13}C NMR Spectrum of 4af



^{19}F NMR Spectrum of 4af

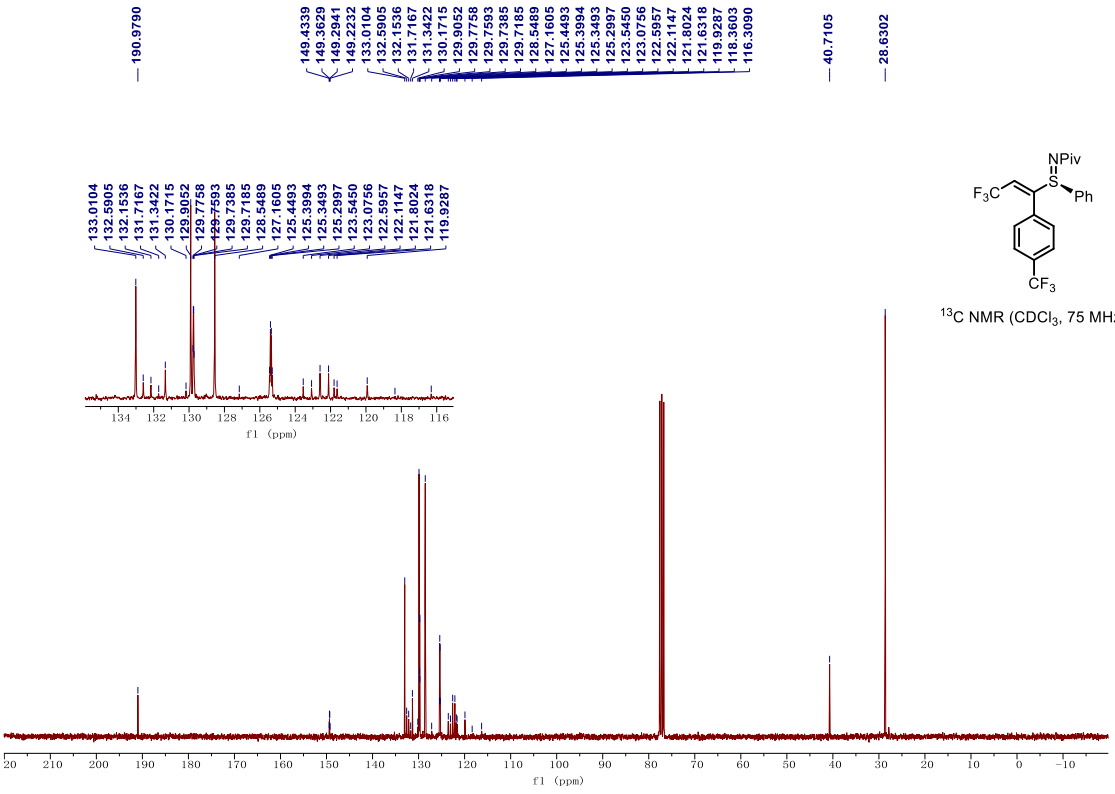


^{1}H NMR Spectrum of 4ag



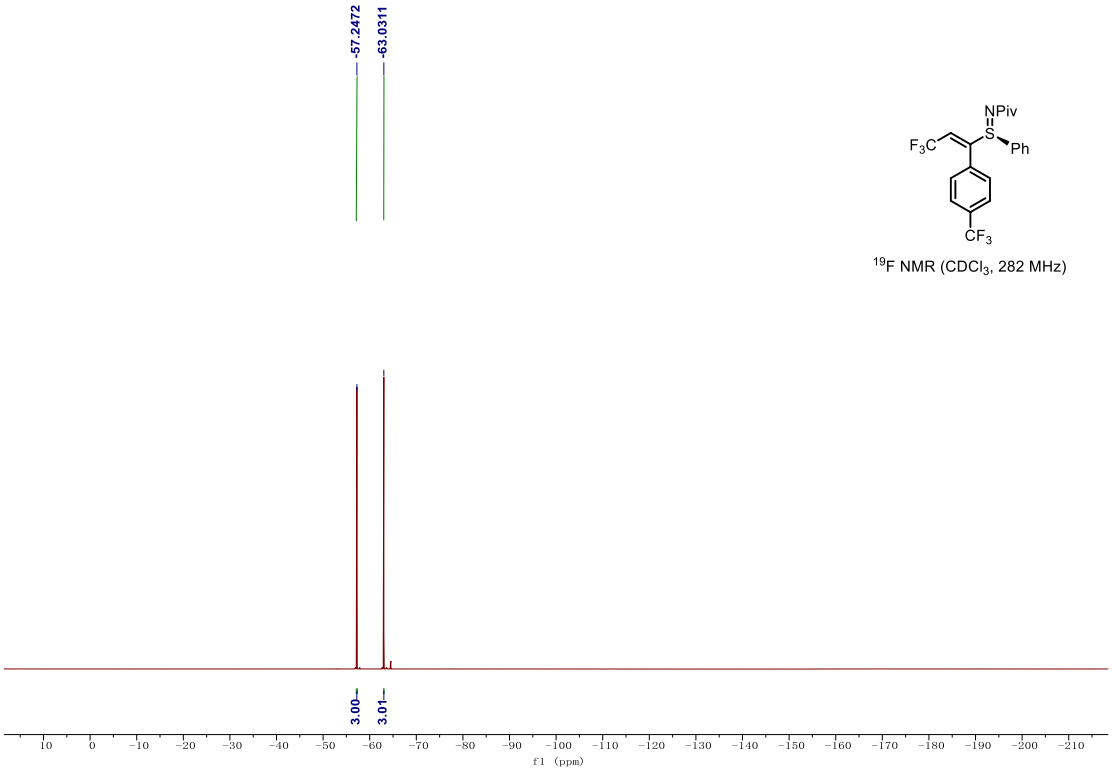
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4ag

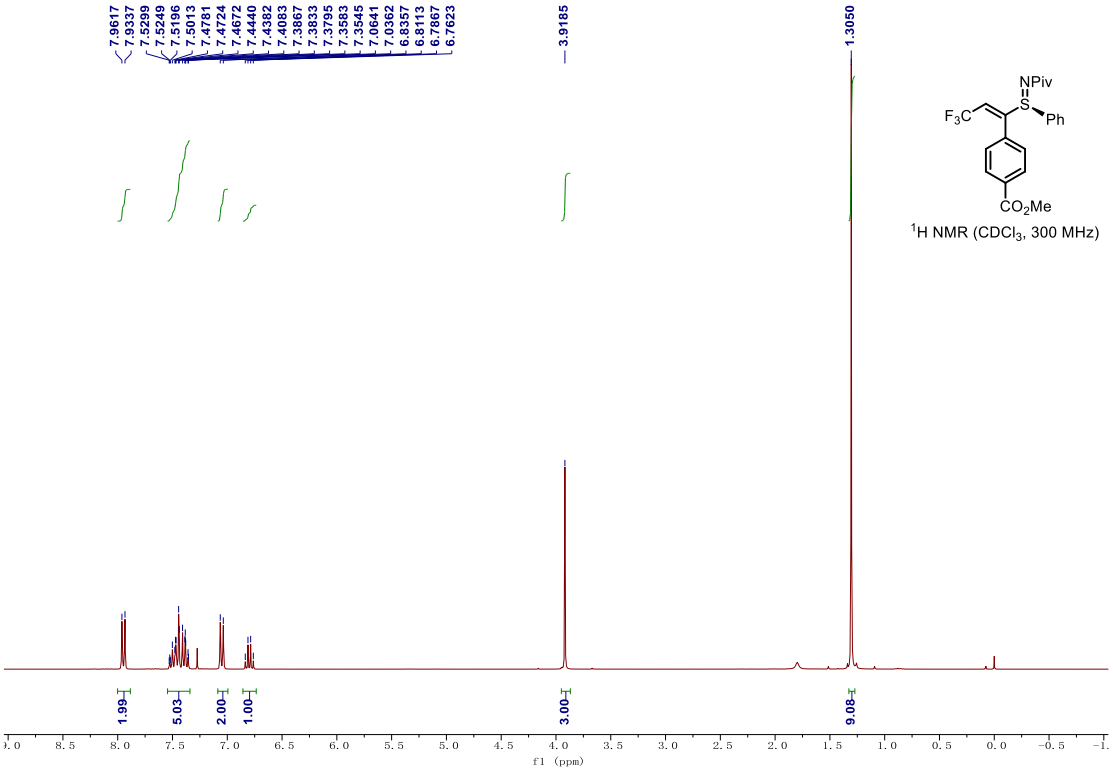


^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4ag

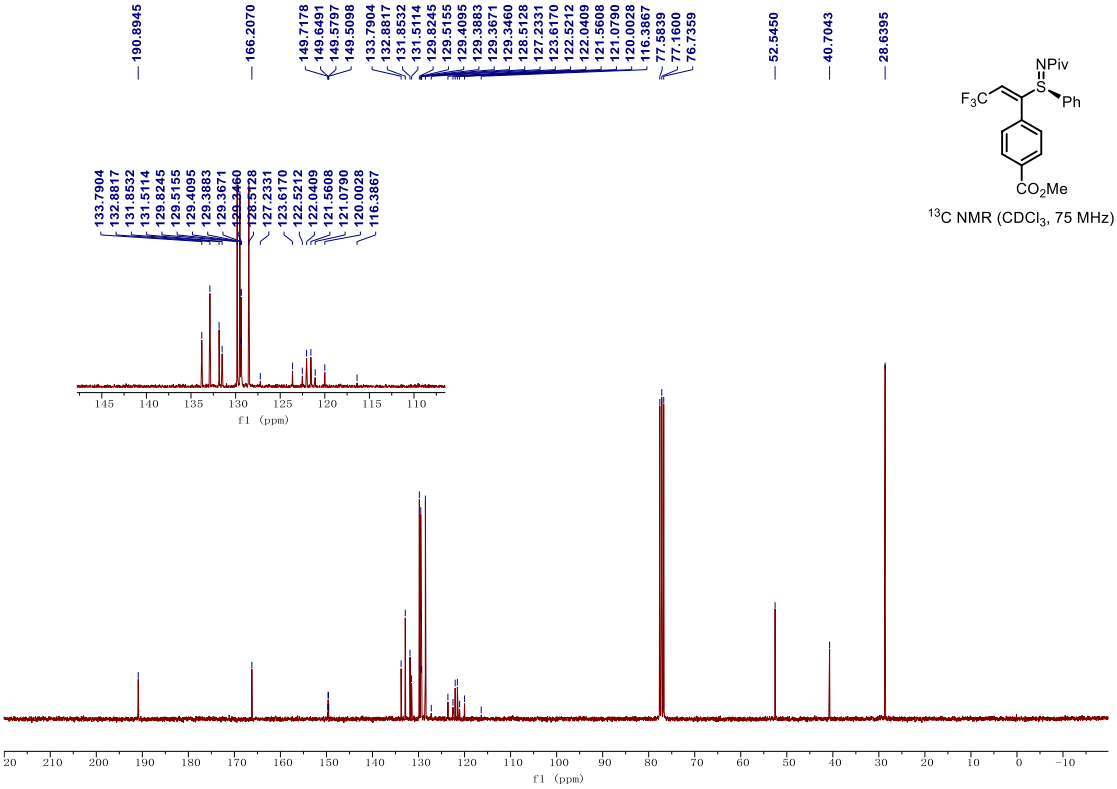


^{1}H NMR Spectrum of 4ah



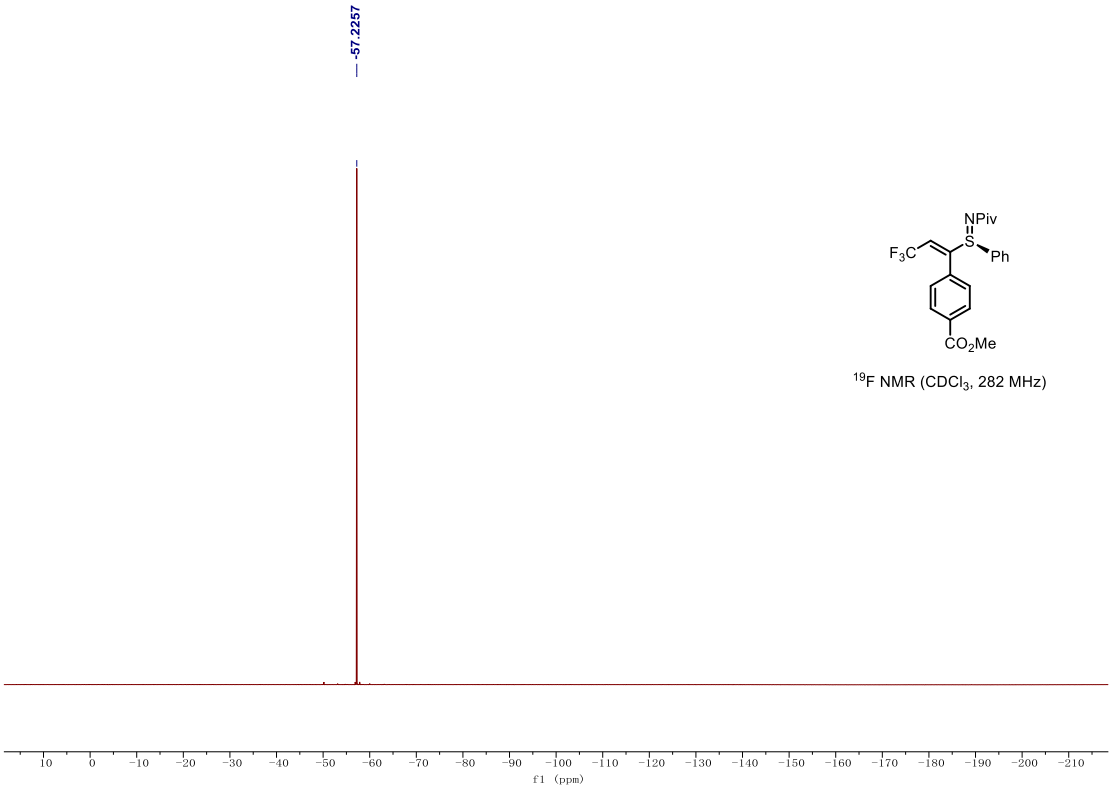
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4ah



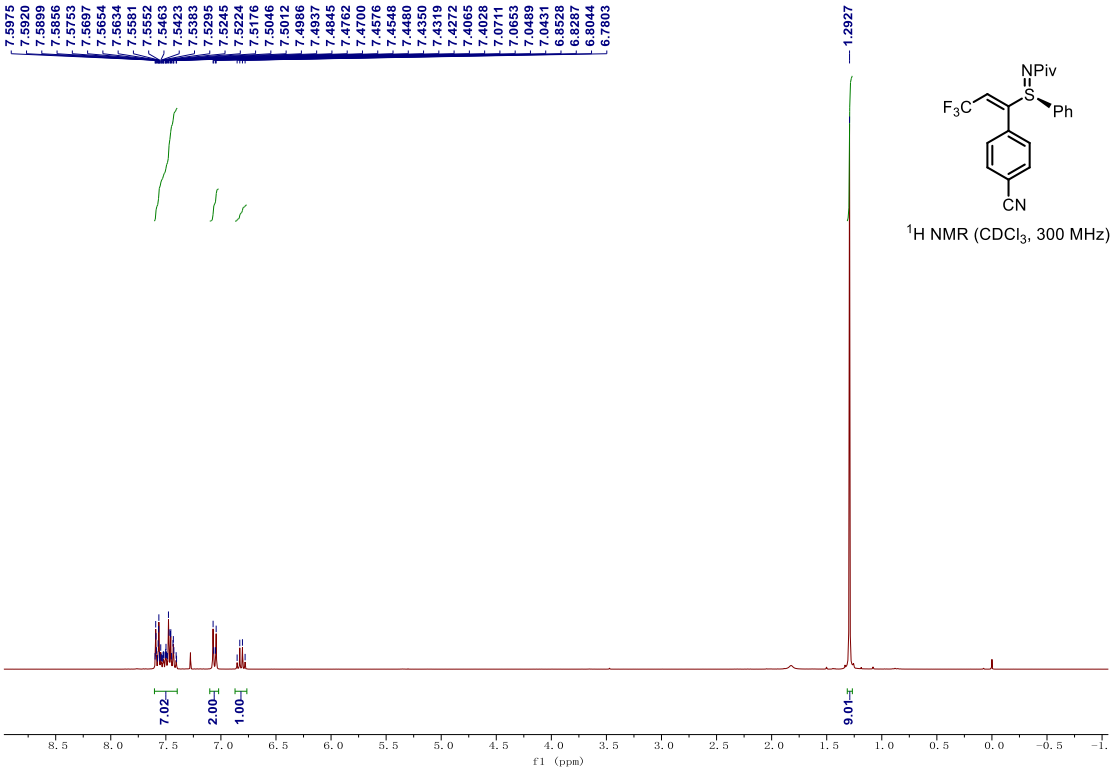
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4ah



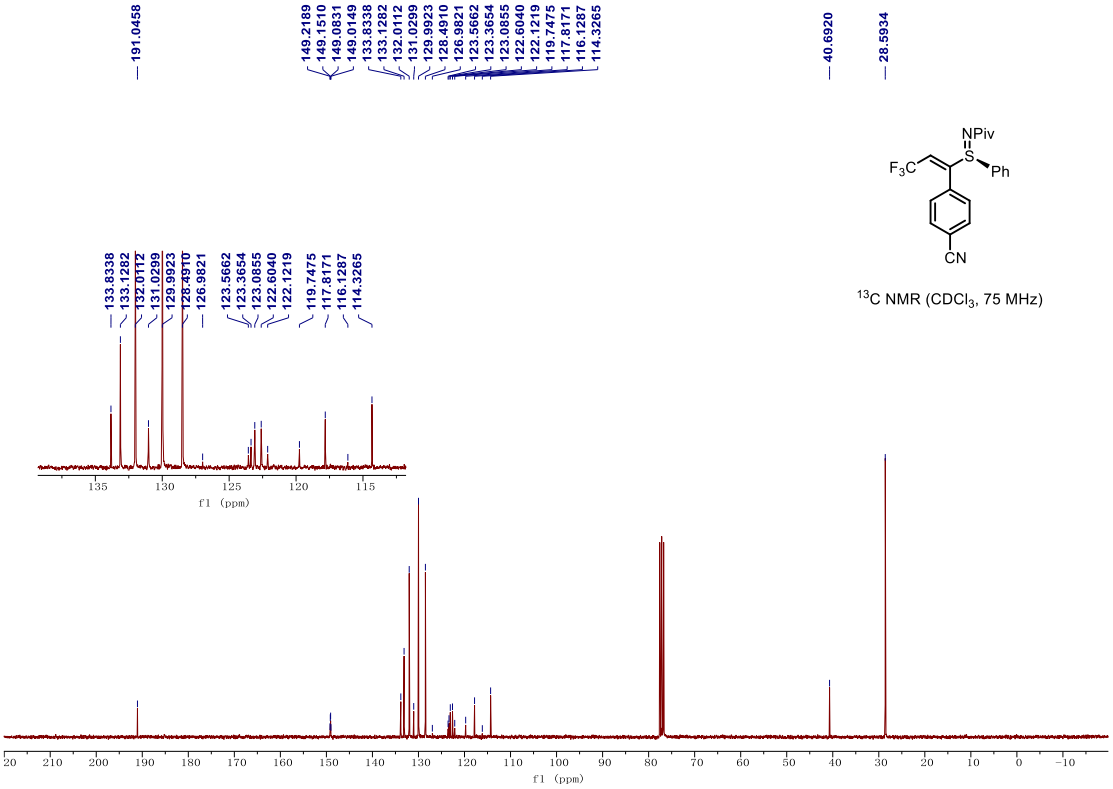
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4ai



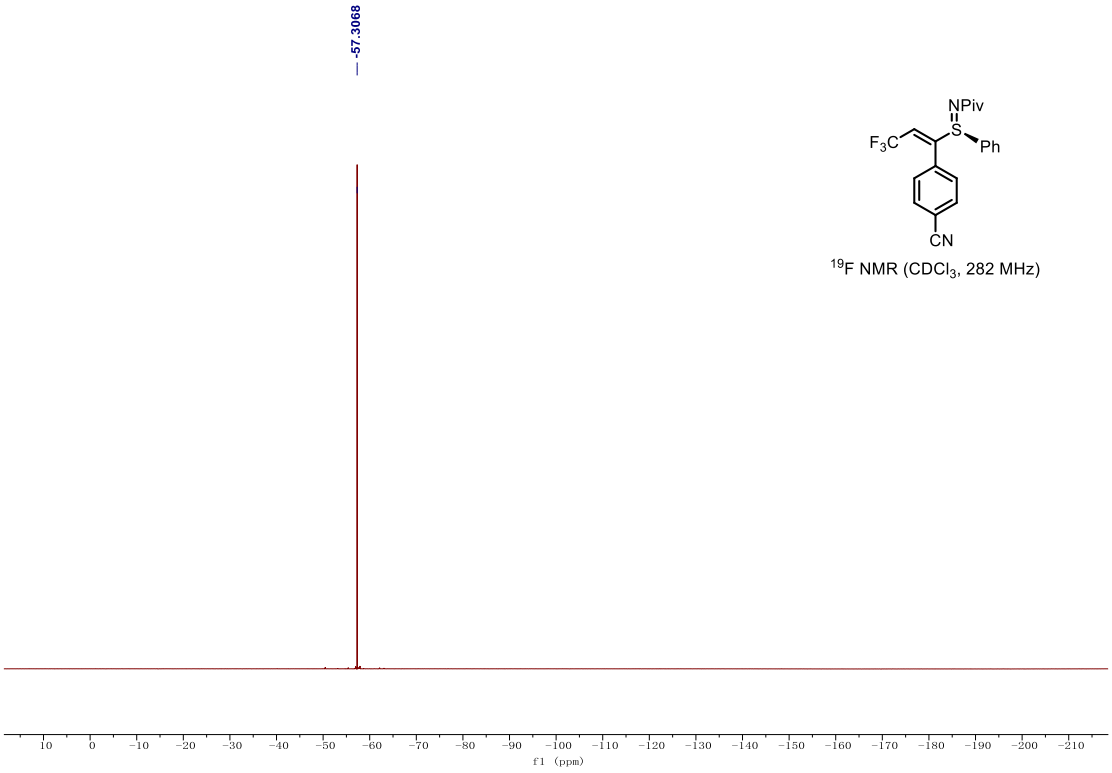
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4ai

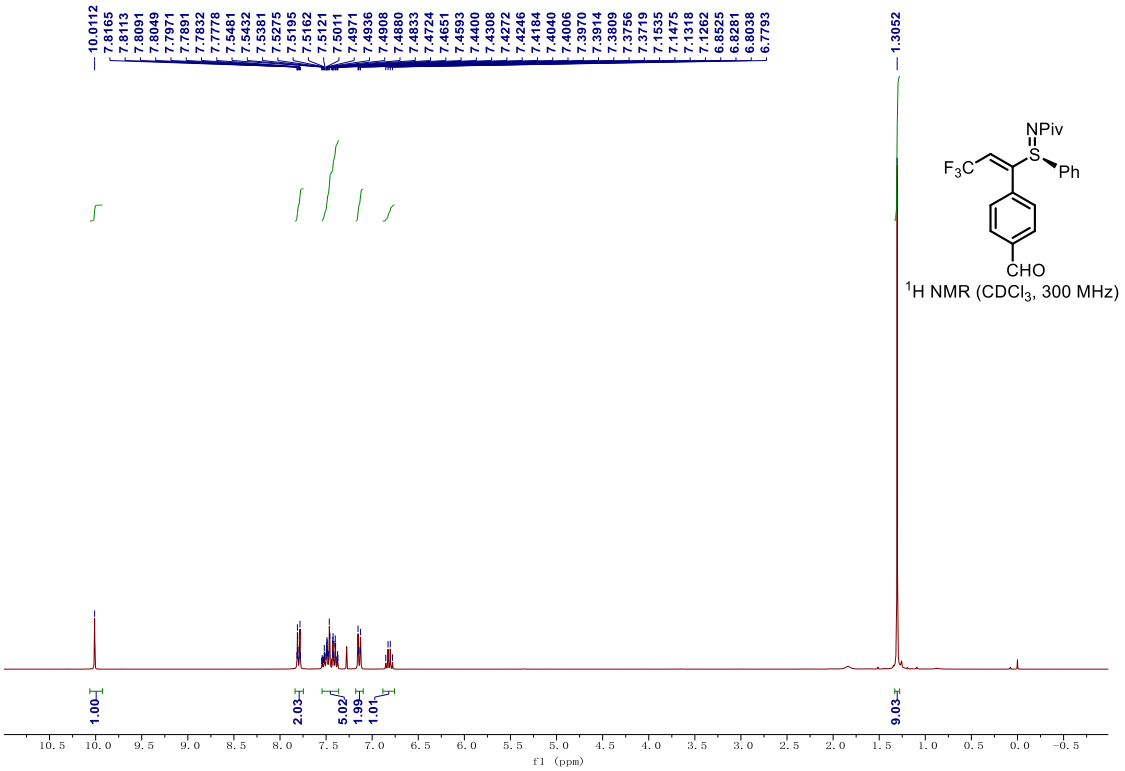


^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4ai

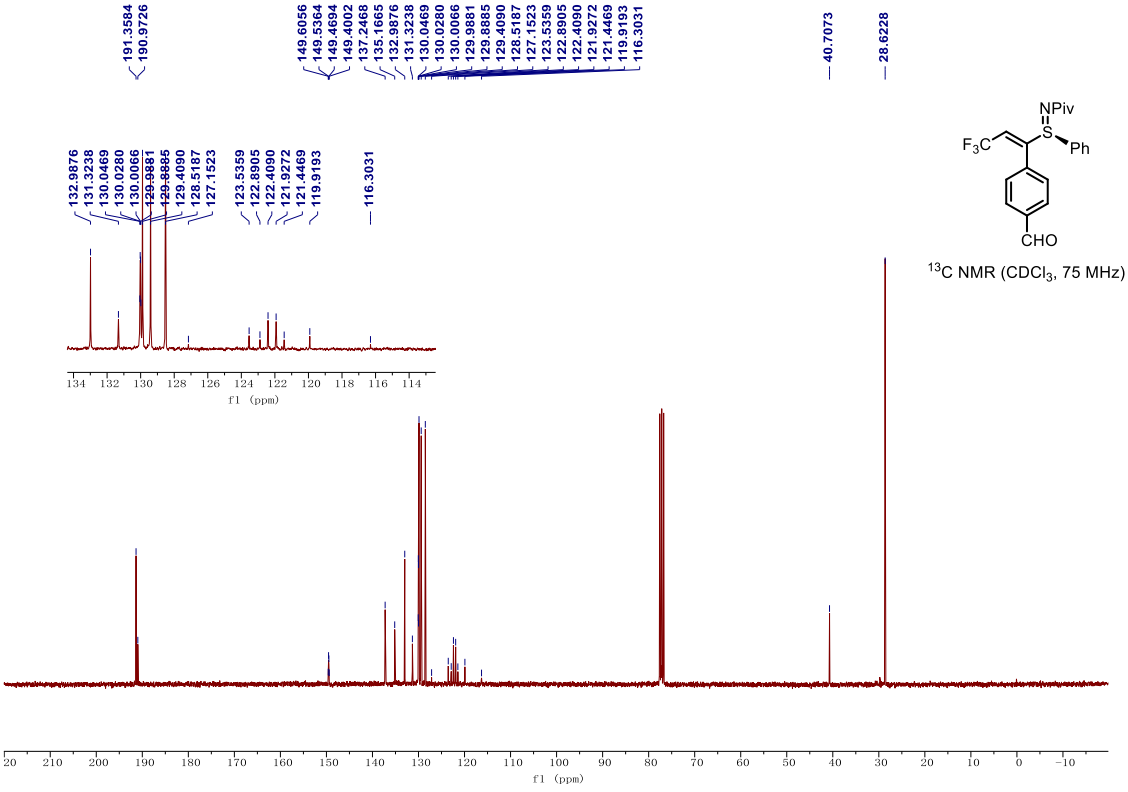


^{1}H NMR Spectrum of 4aj



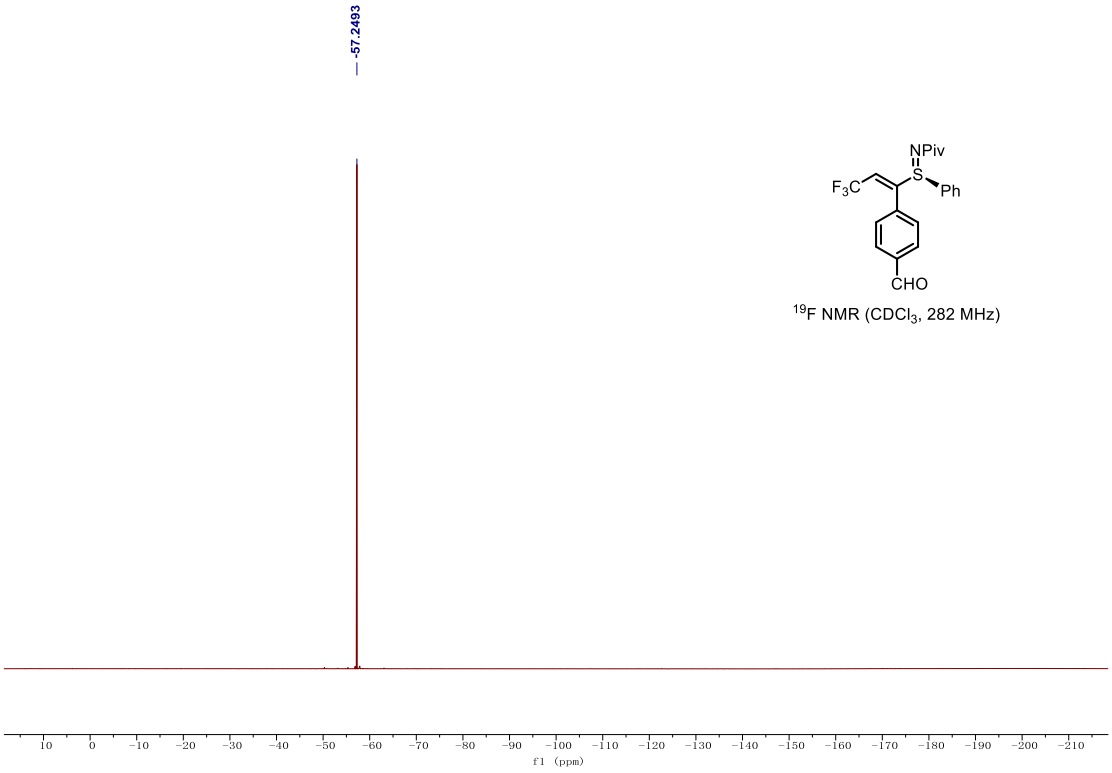
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4aj



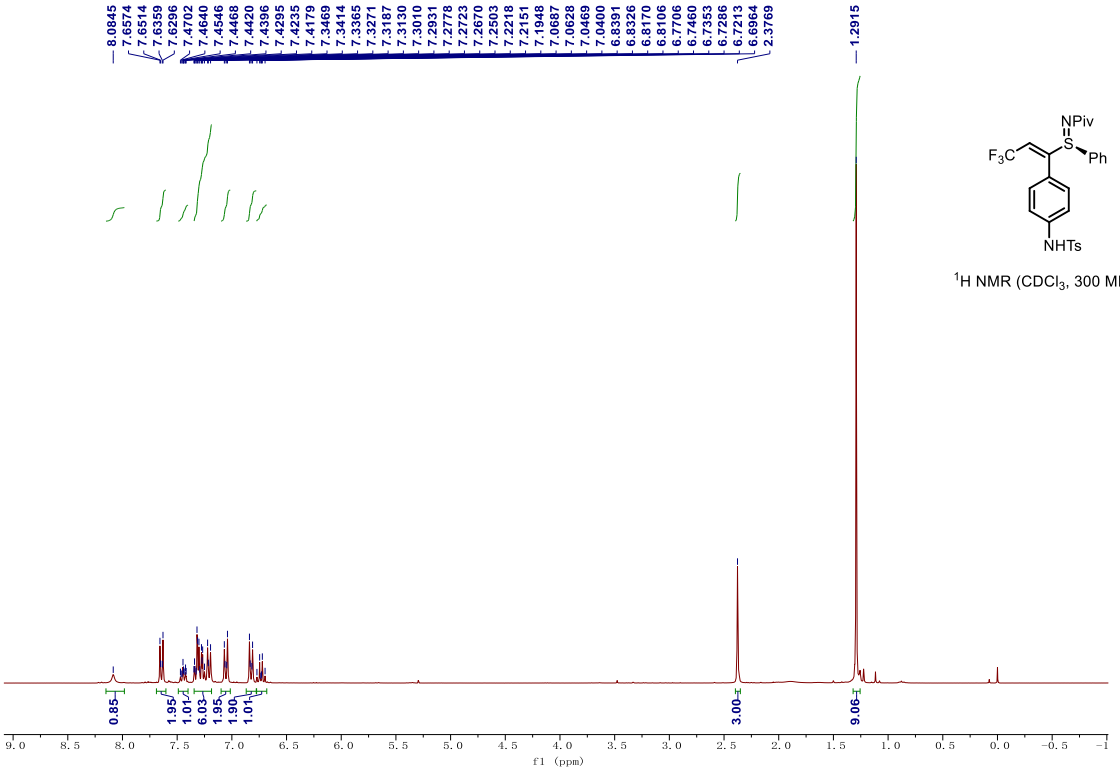
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4aj



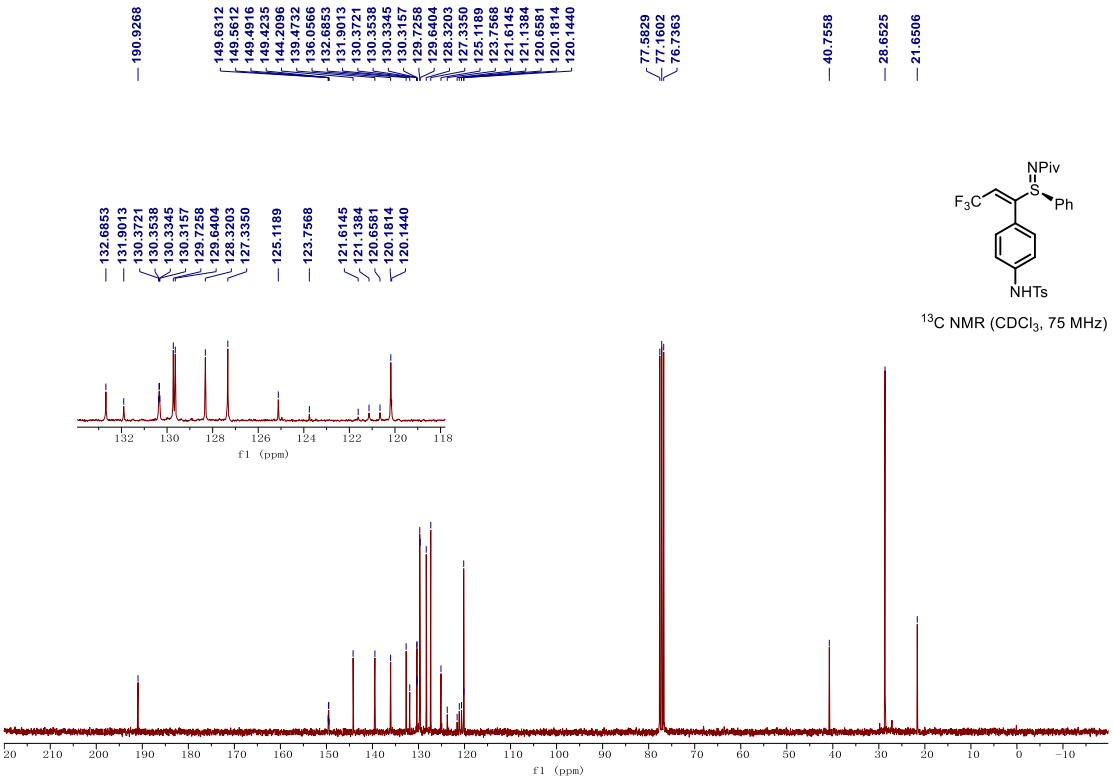
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4ak



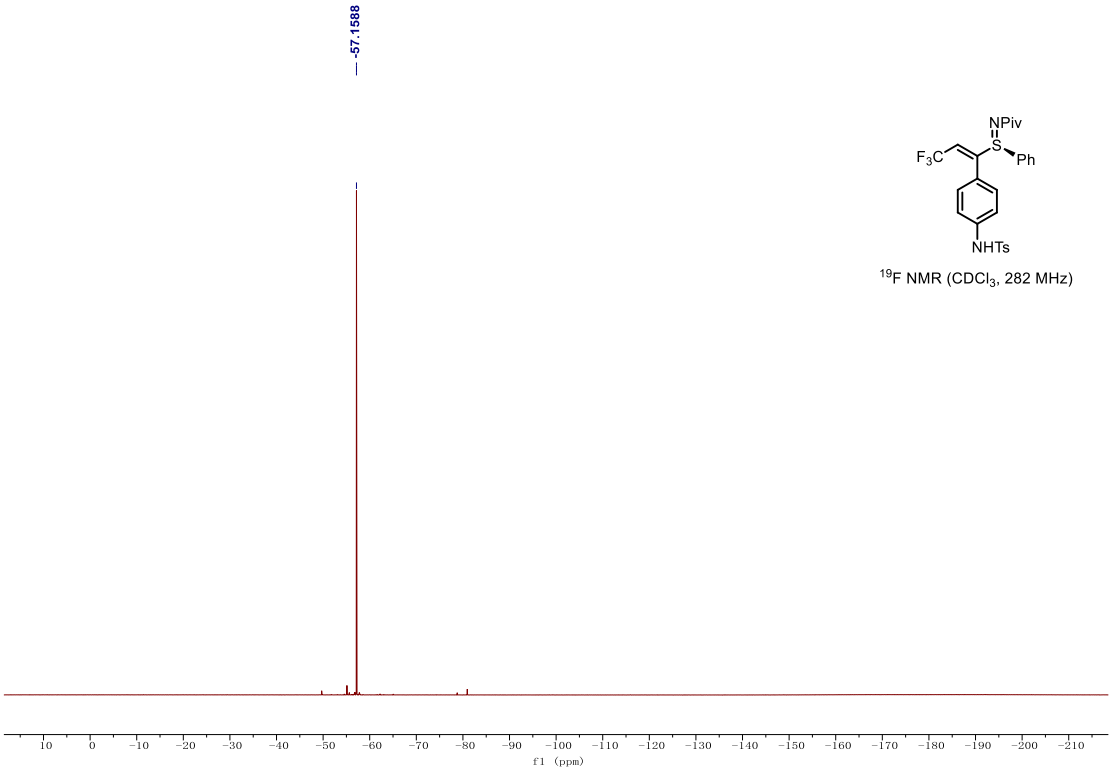
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4ak

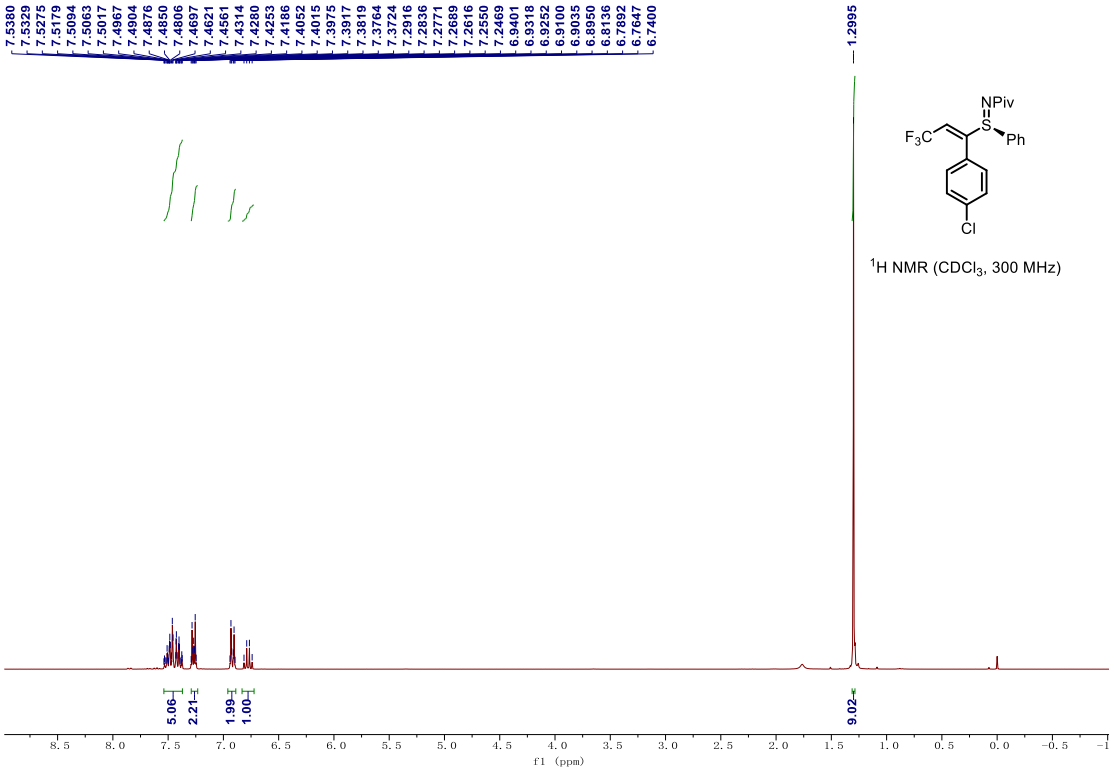


^{13}C NMR ($CDCl_3$, 75 MHz)

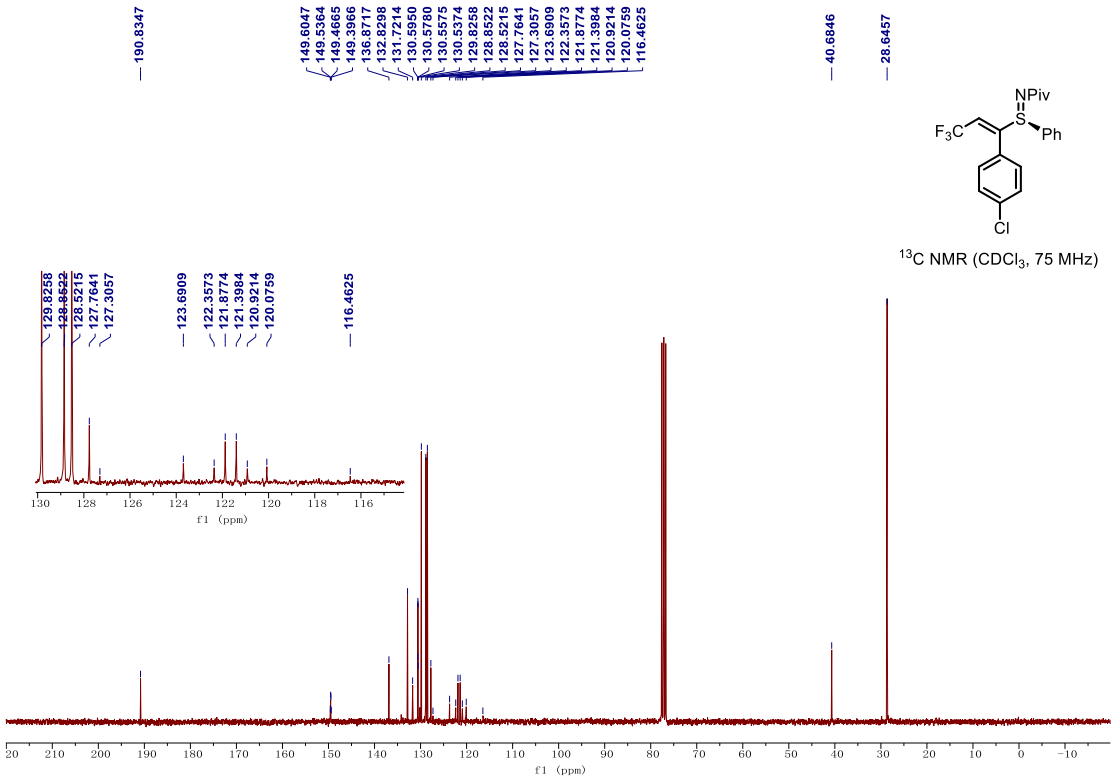
^{19}F NMR Spectrum of 4ak



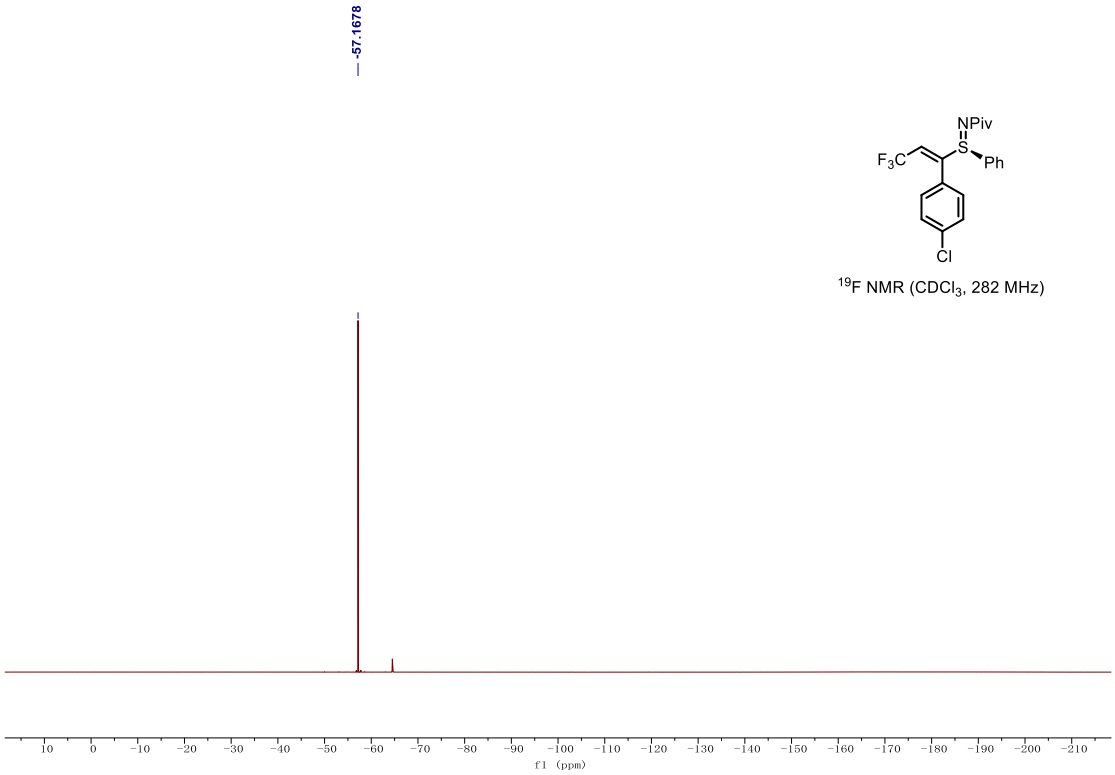
^{1}H NMR Spectrum of 4al



^{13}C NMR Spectrum of 4al

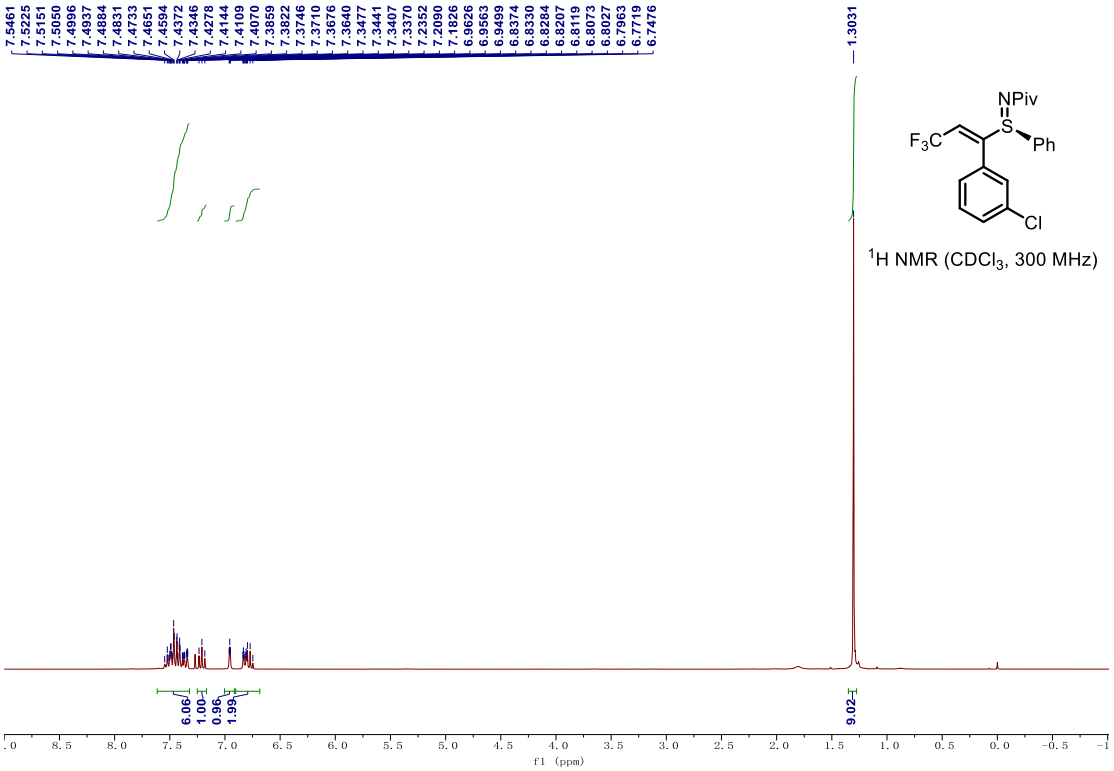


^{19}F NMR Spectrum of 4al



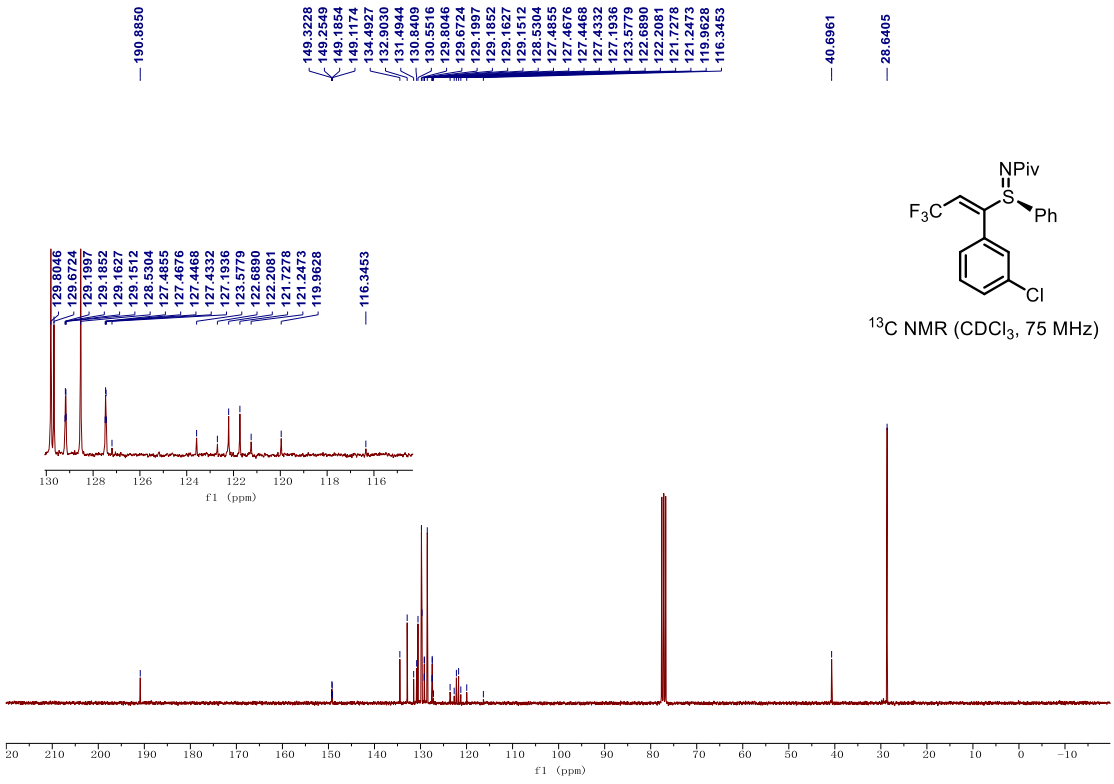
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4am



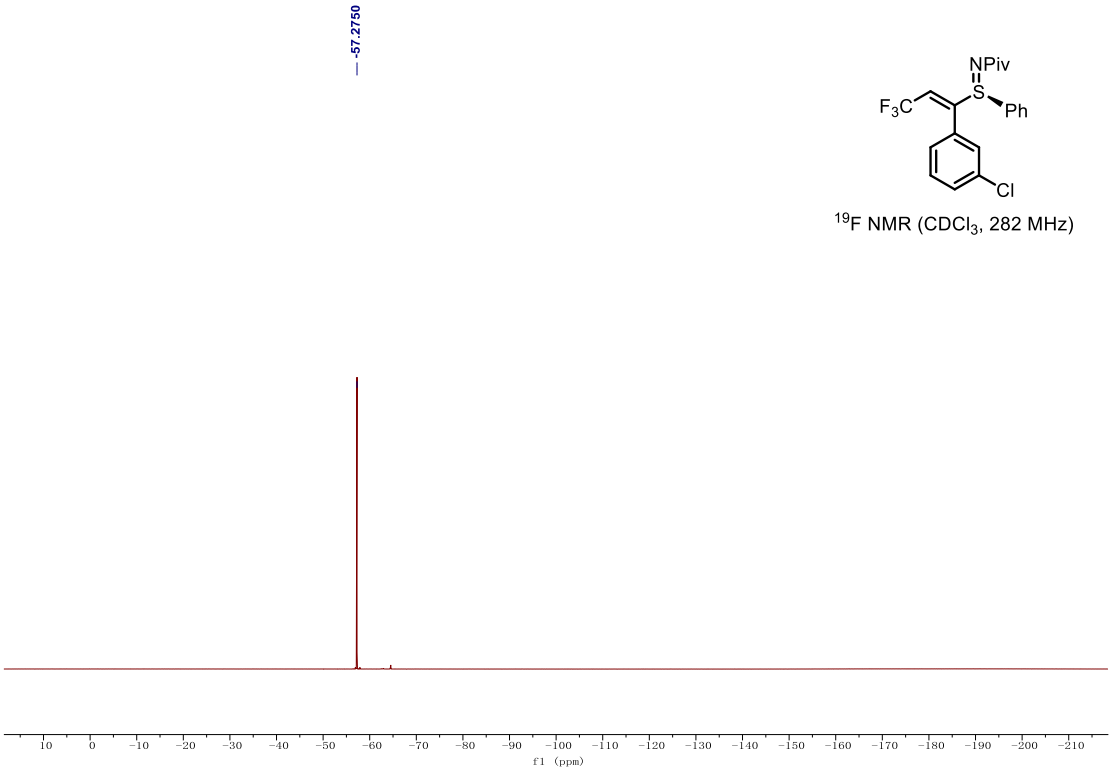
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4am



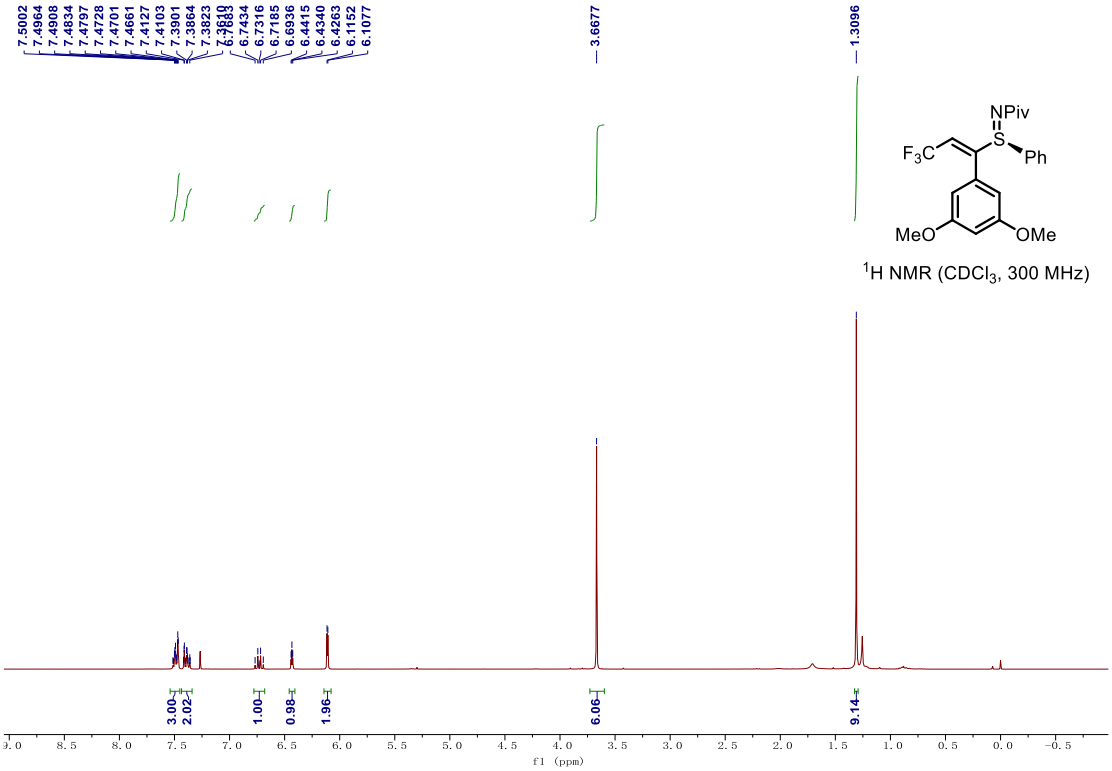
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4am



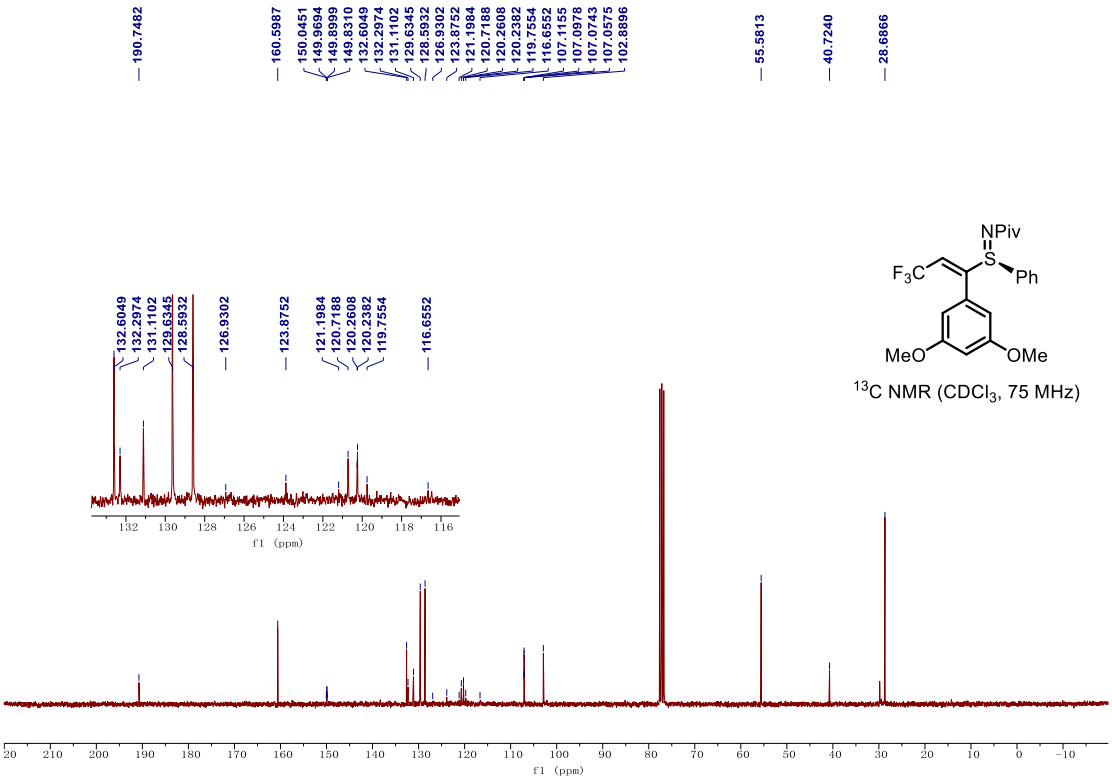
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4an



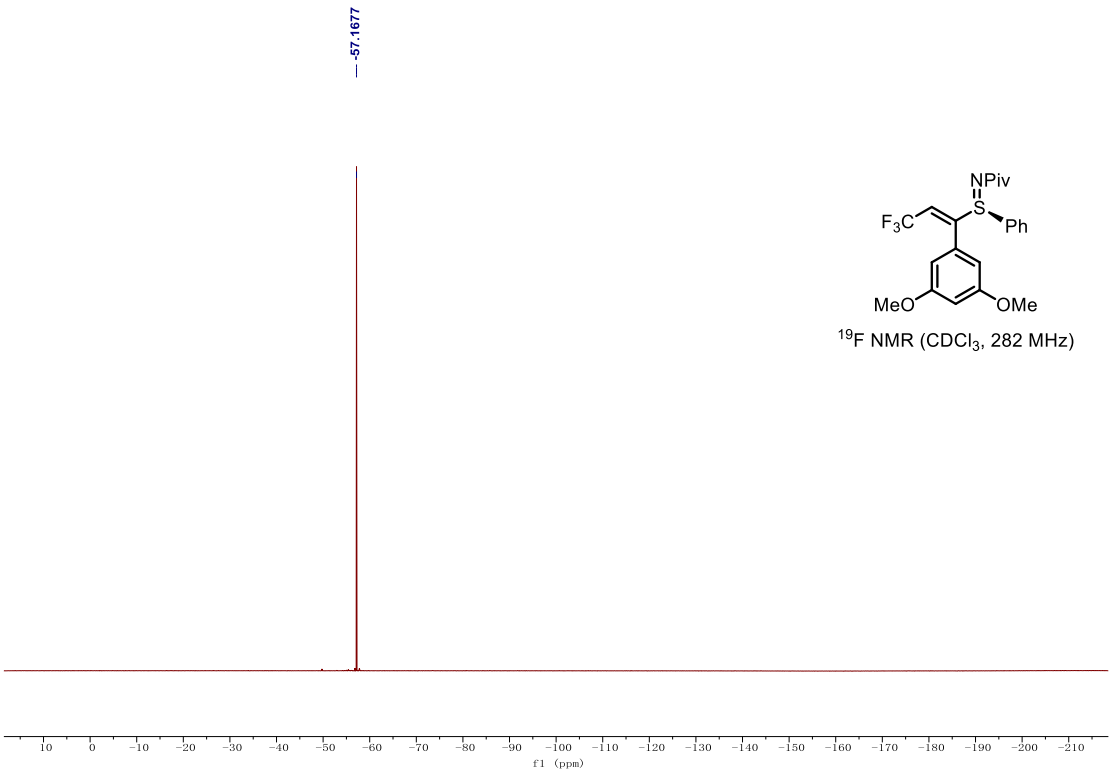
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4an

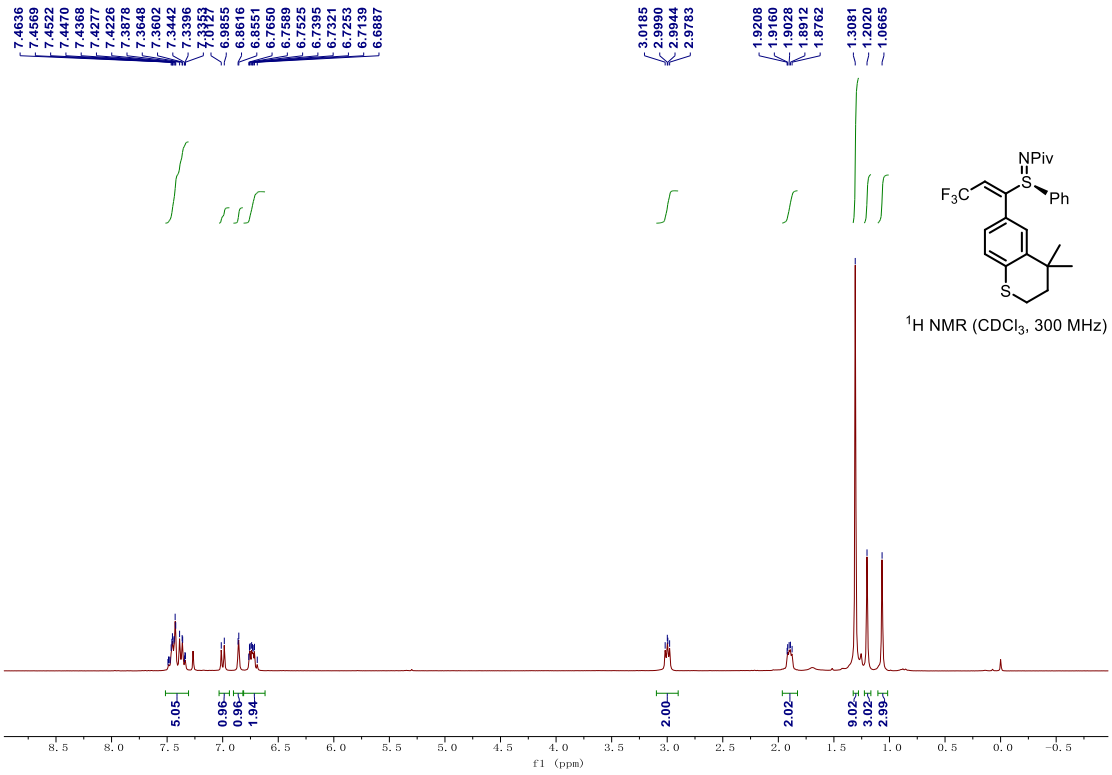


^{13}C NMR ($CDCl_3$, 75 MHz)

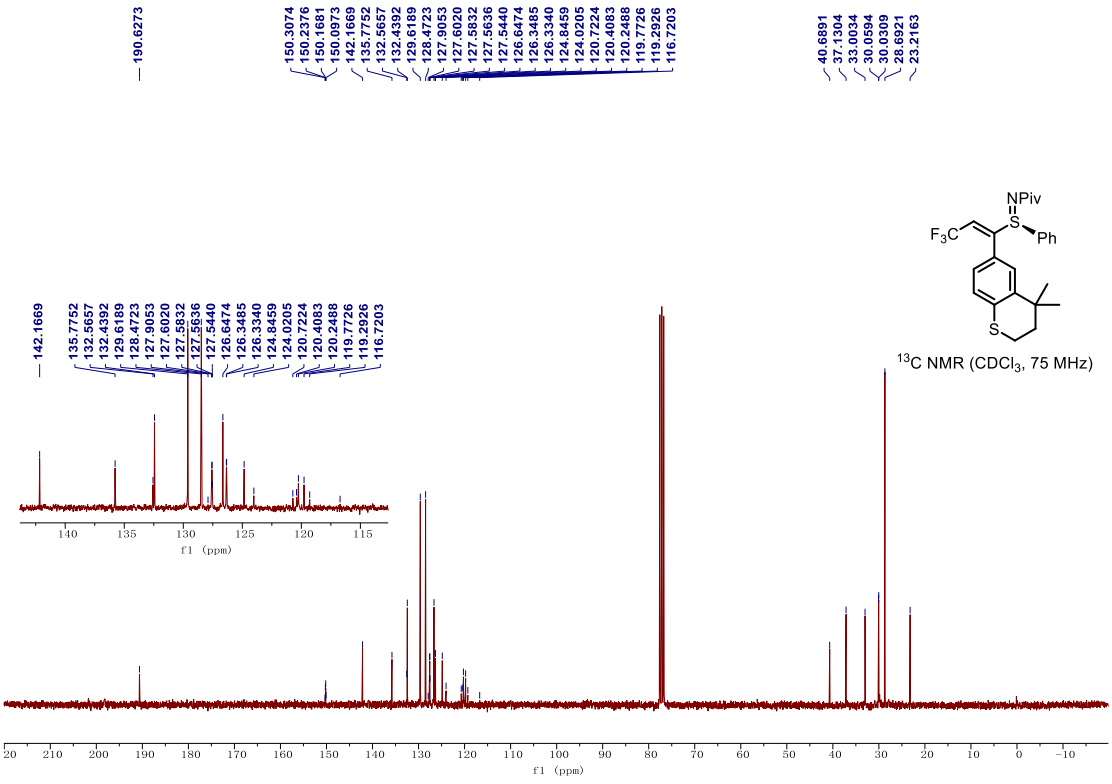
^{19}F NMR Spectrum of 4an



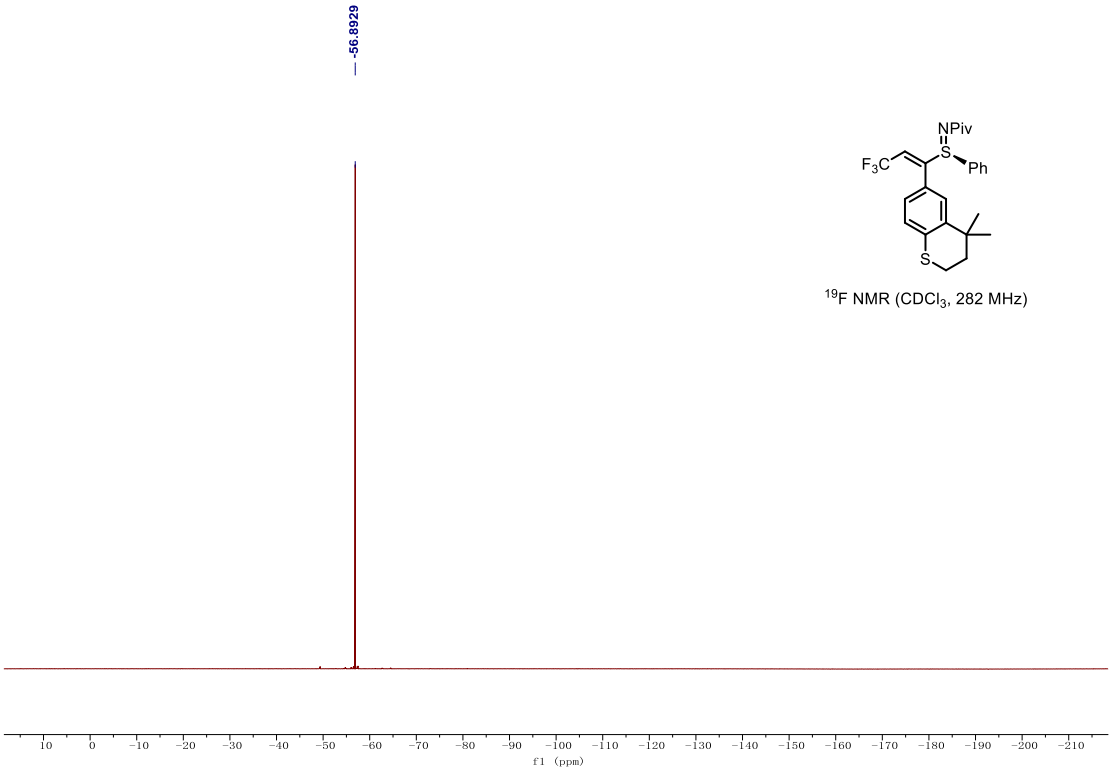
^{1}H NMR Spectrum of 4ao



^{13}C NMR Spectrum of 4ao

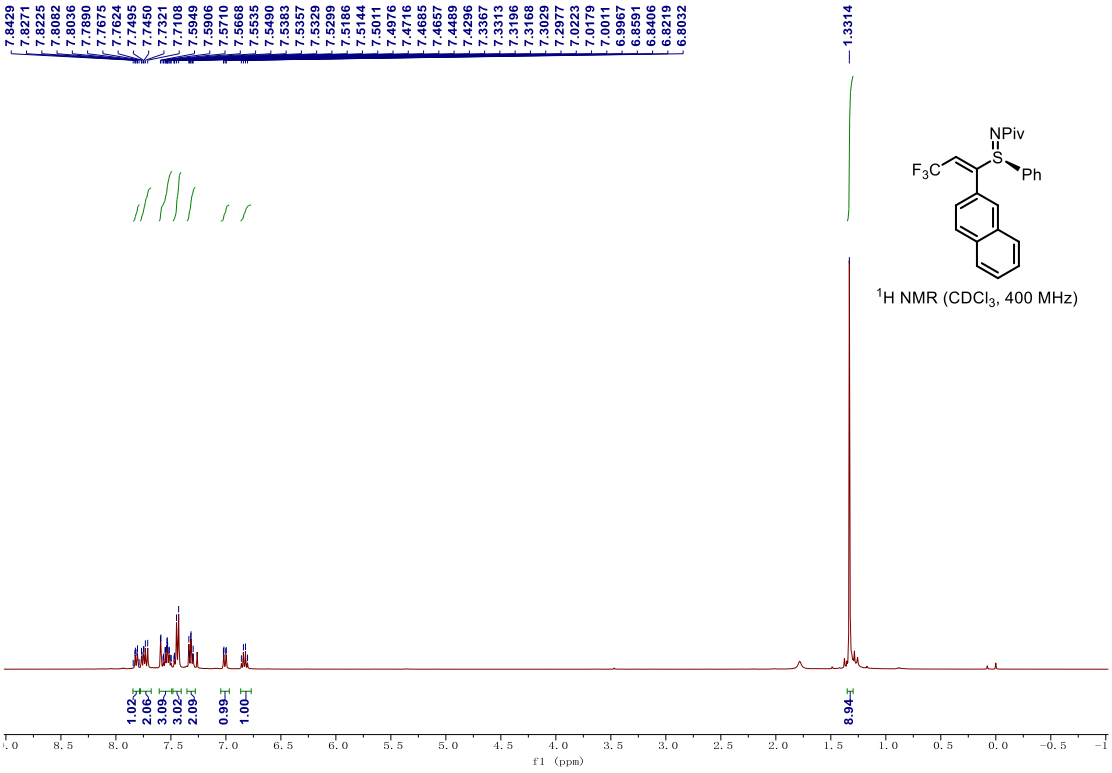


^{19}F NMR Spectrum of 4ao



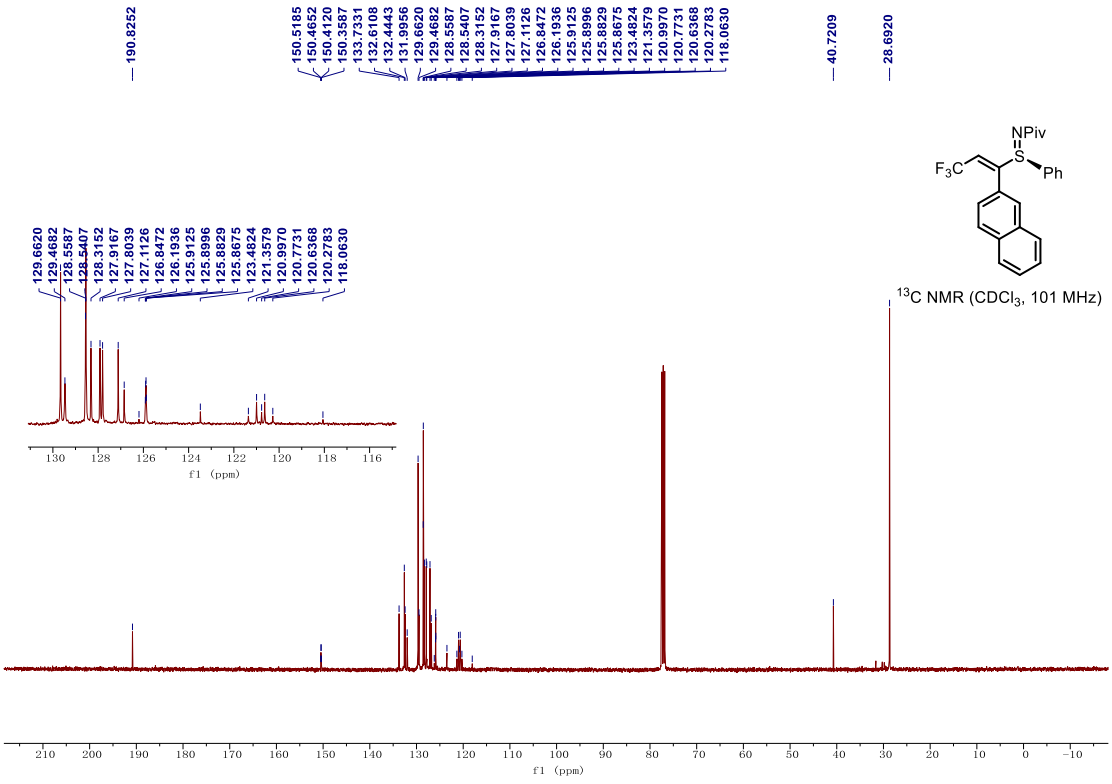
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4ap



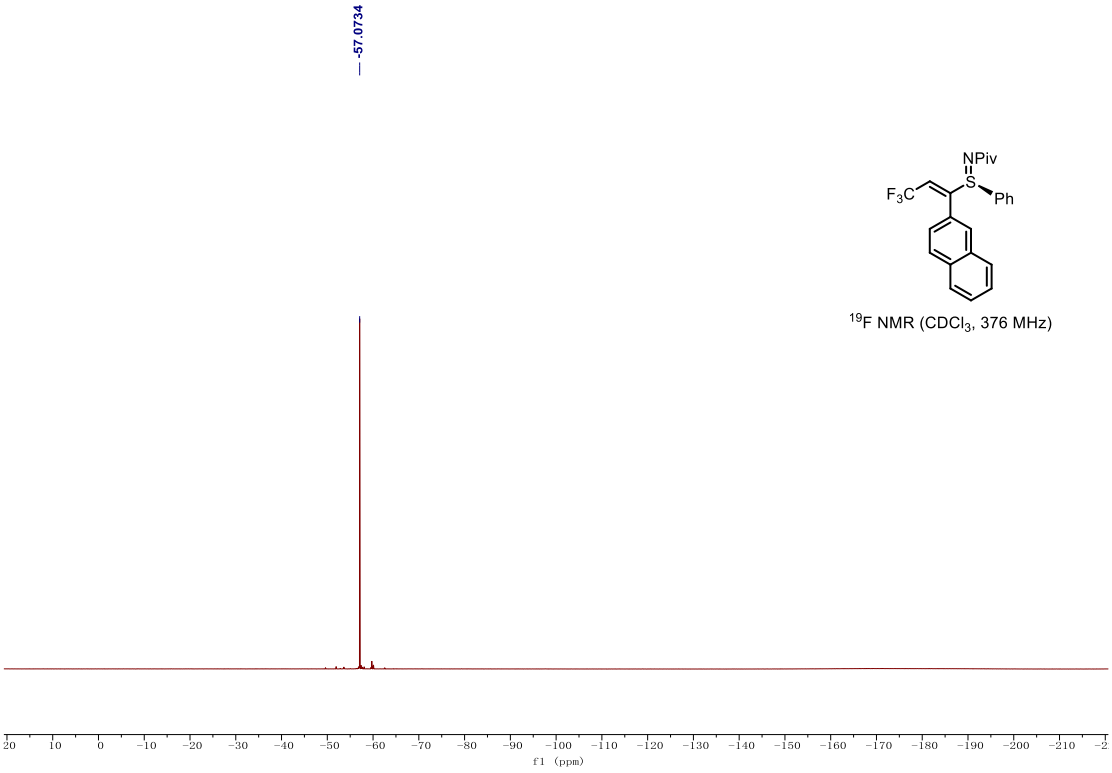
^{1}H NMR ($CDCl_3$, 400 MHz)

^{13}C NMR Spectrum of 4ap

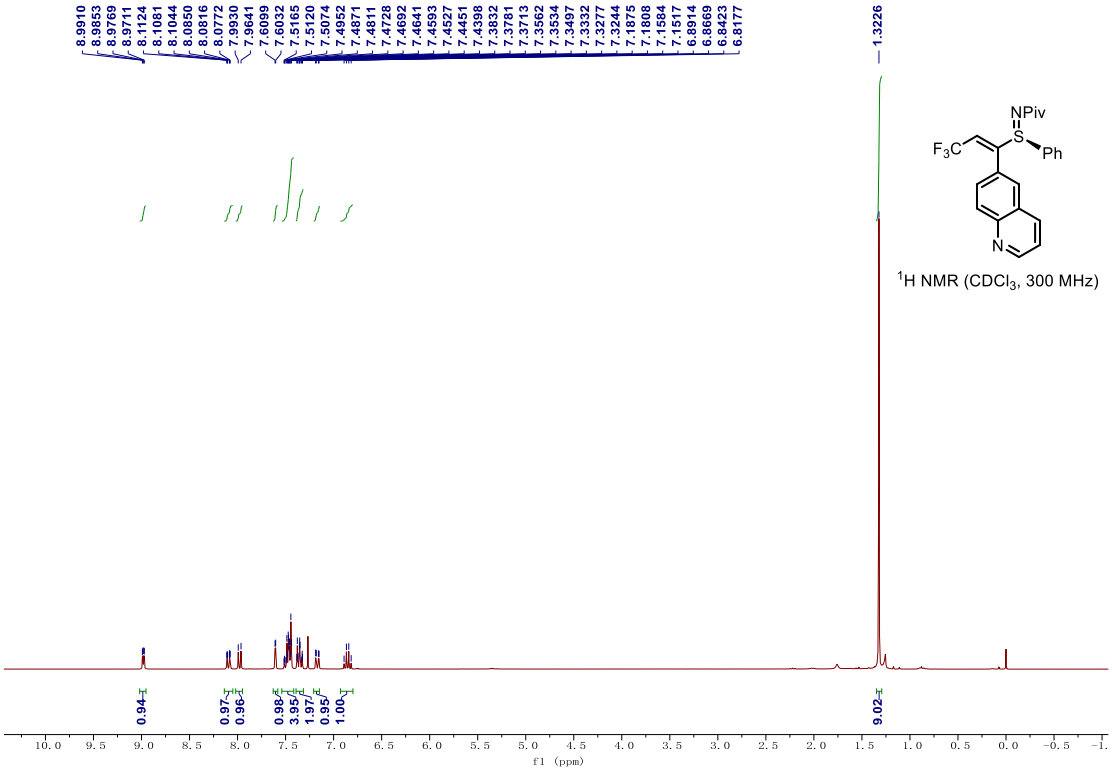


^{13}C NMR ($CDCl_3$, 101 MHz)

^{19}F NMR Spectrum of 4ap

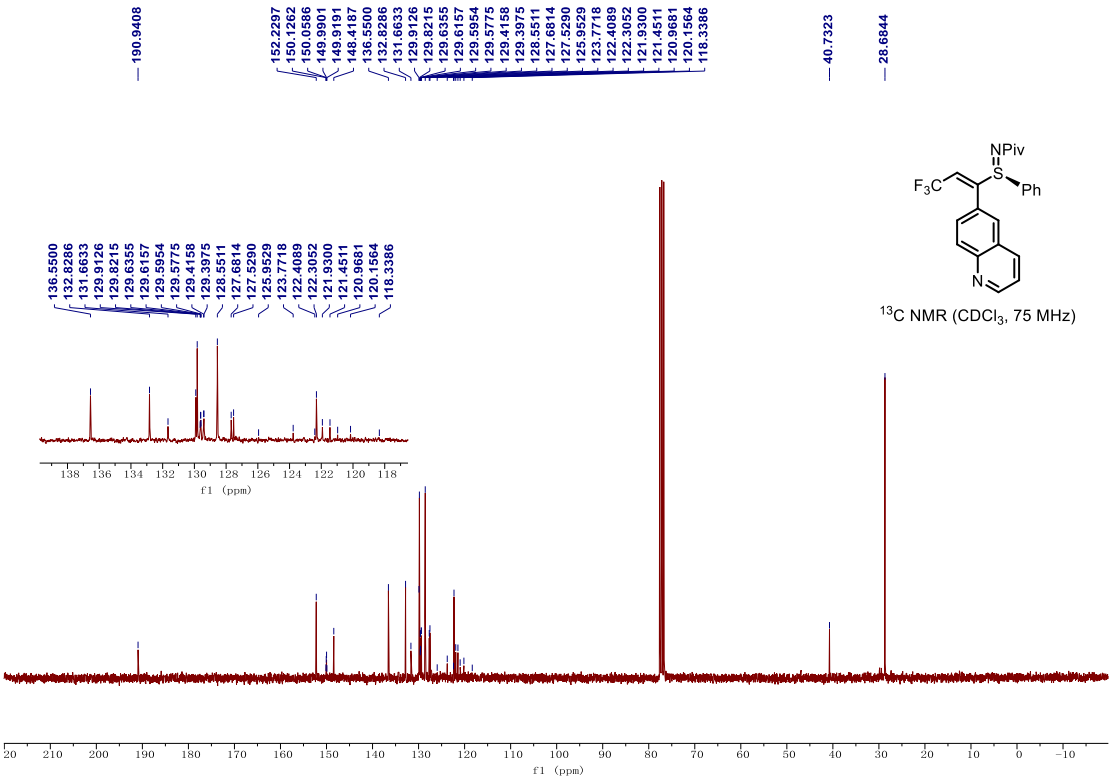


^{1}H NMR Spectrum of 4aq



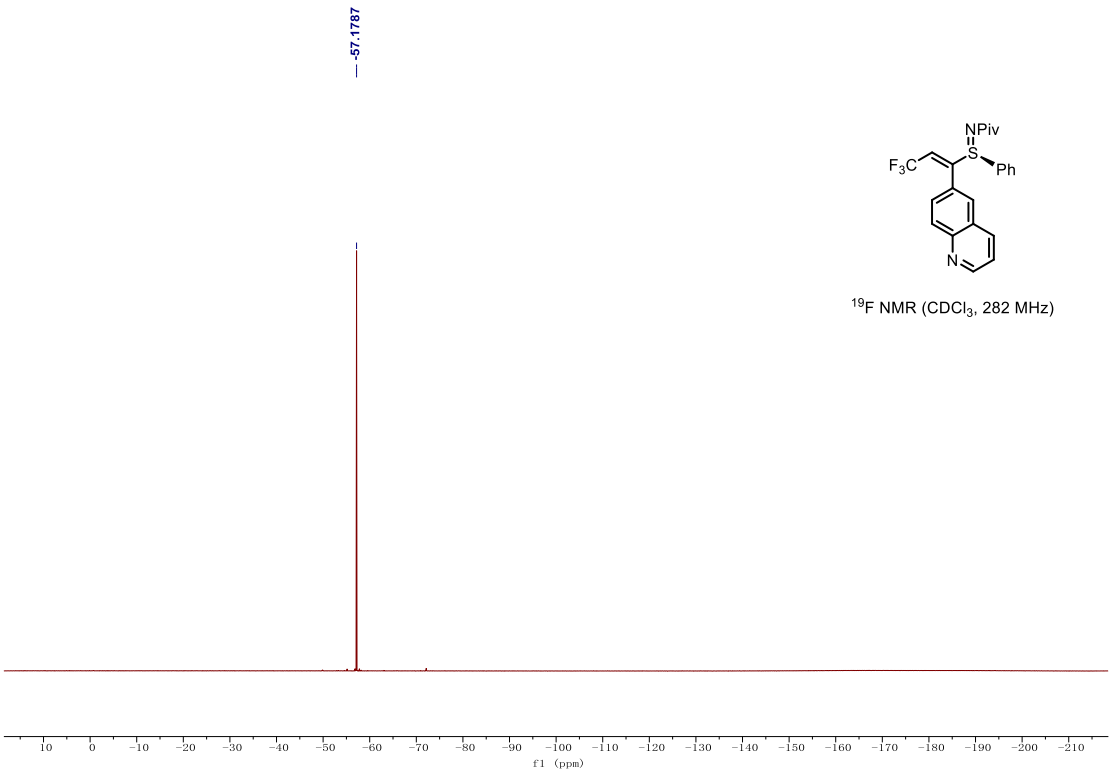
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4aq



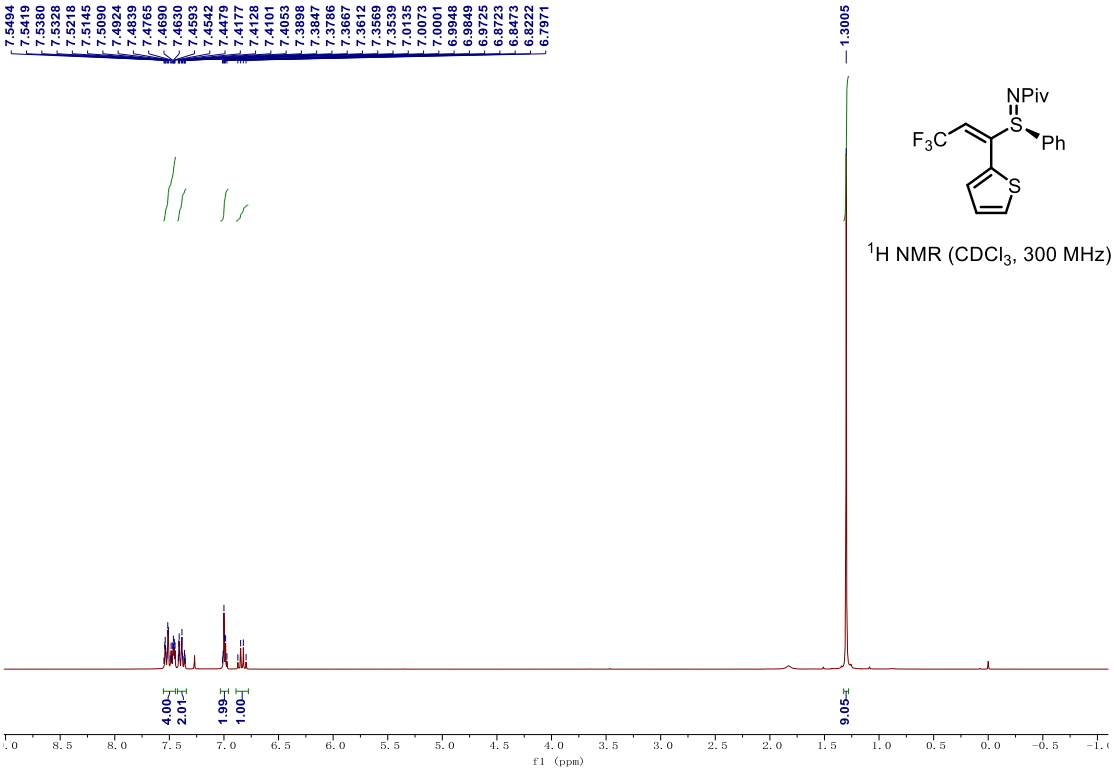
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4aq



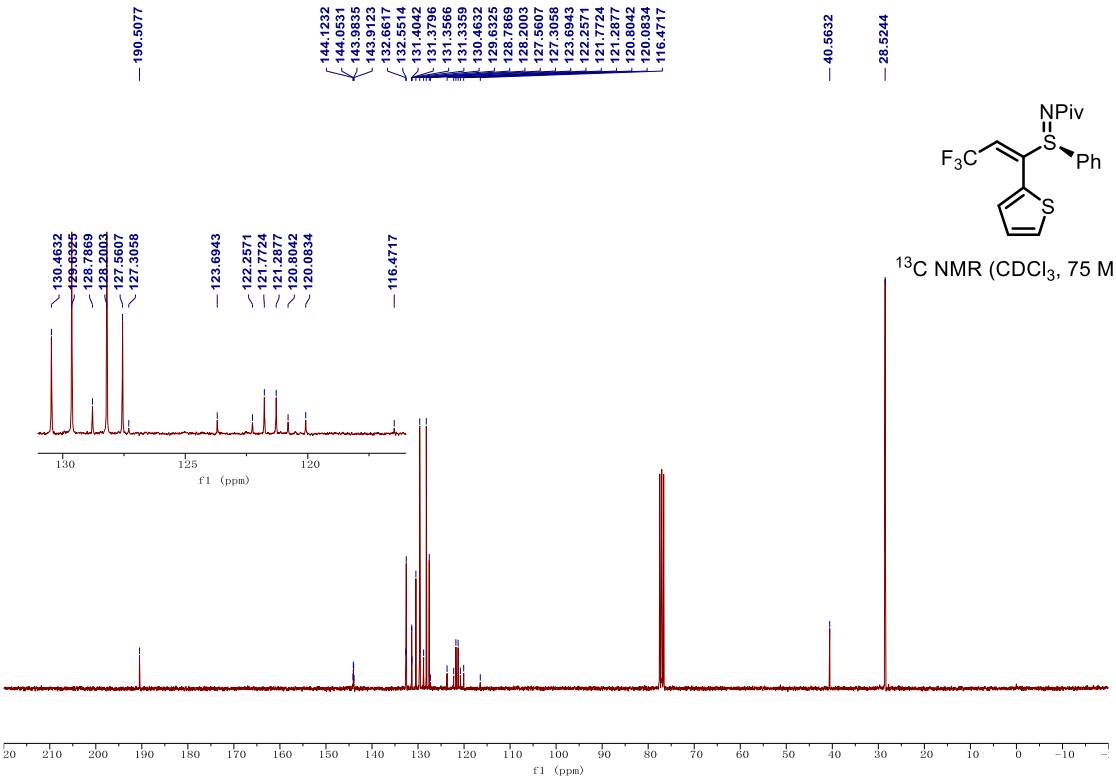
^{19}F NMR ($CDCl_3$, 282 MHz)

^{1}H NMR Spectrum of 4ar



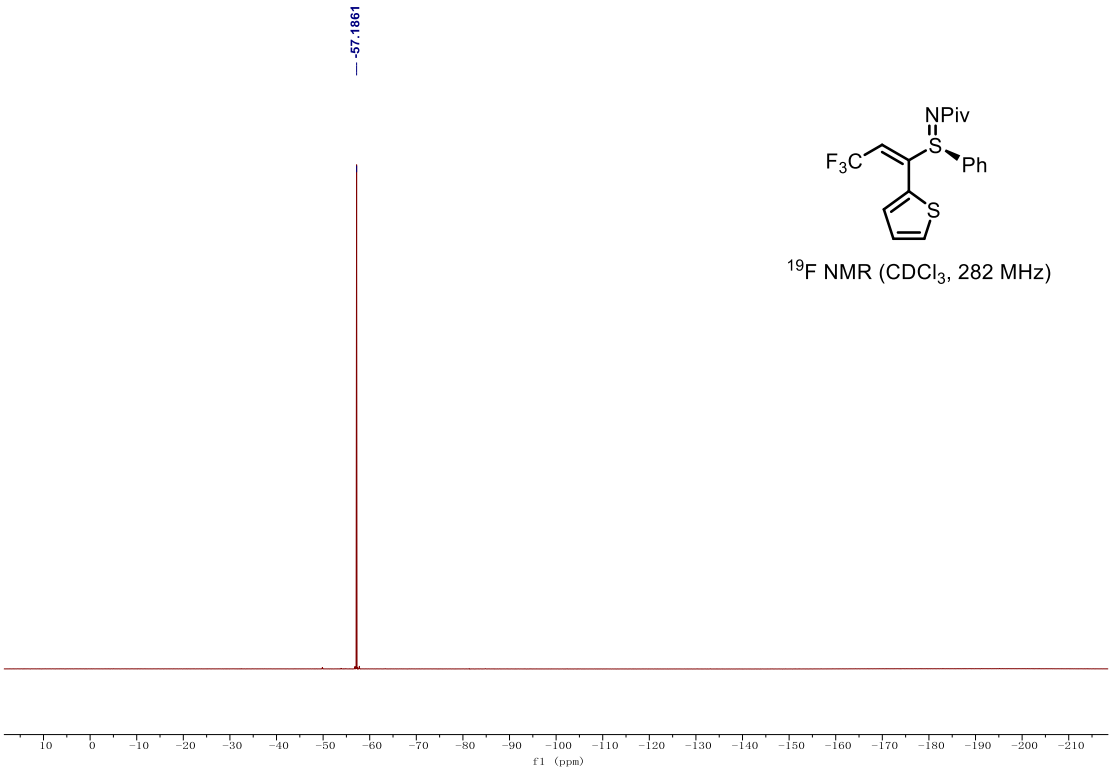
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4ar



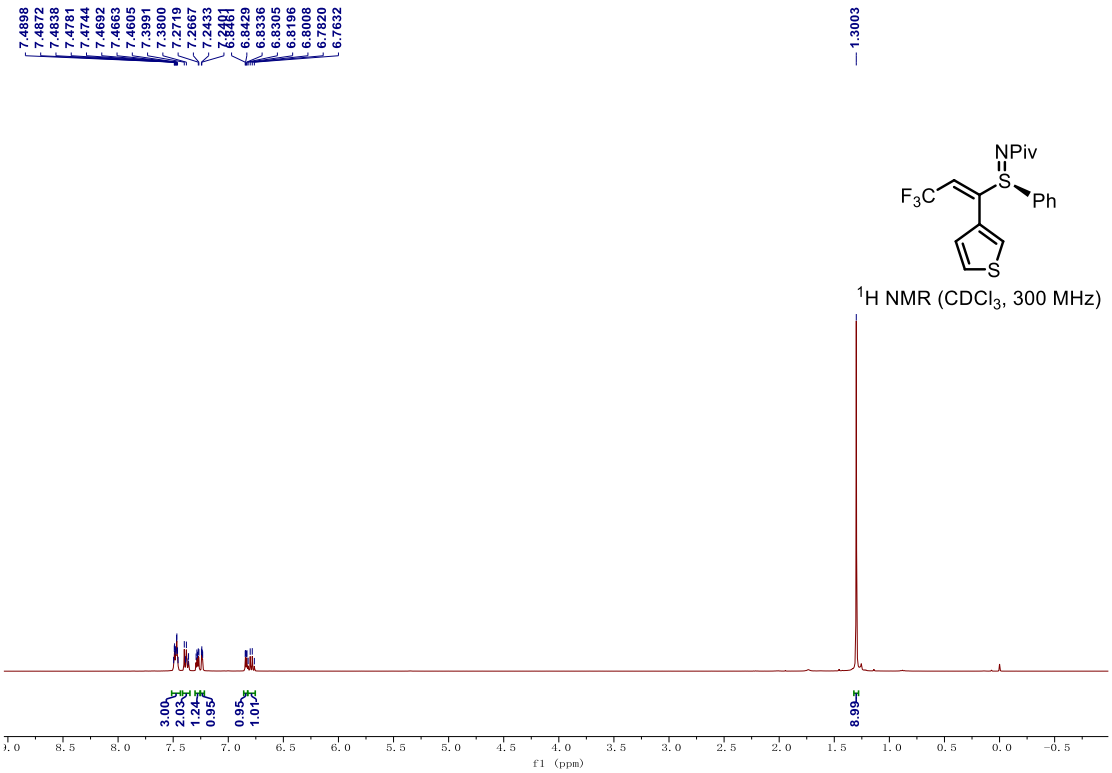
^{13}C NMR ($CDCl_3$, 75 MHz)

^{19}F NMR Spectrum of 4ar

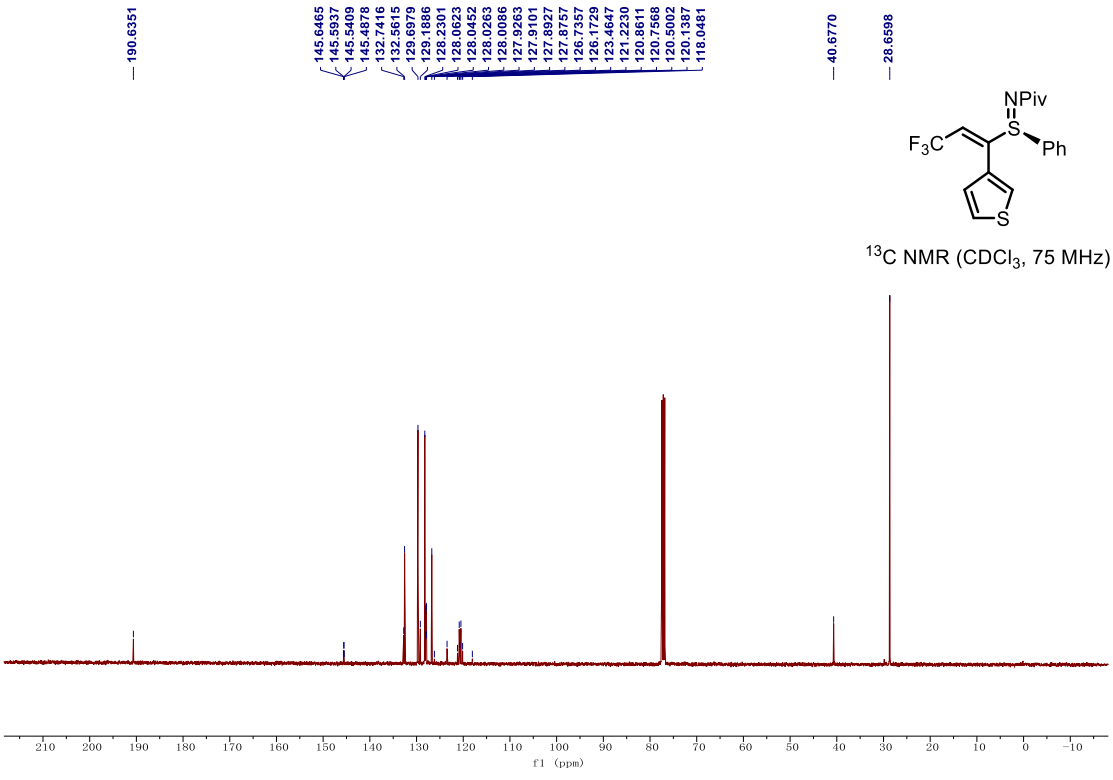


^{19}F NMR ($CDCl_3$, 282 MHz)

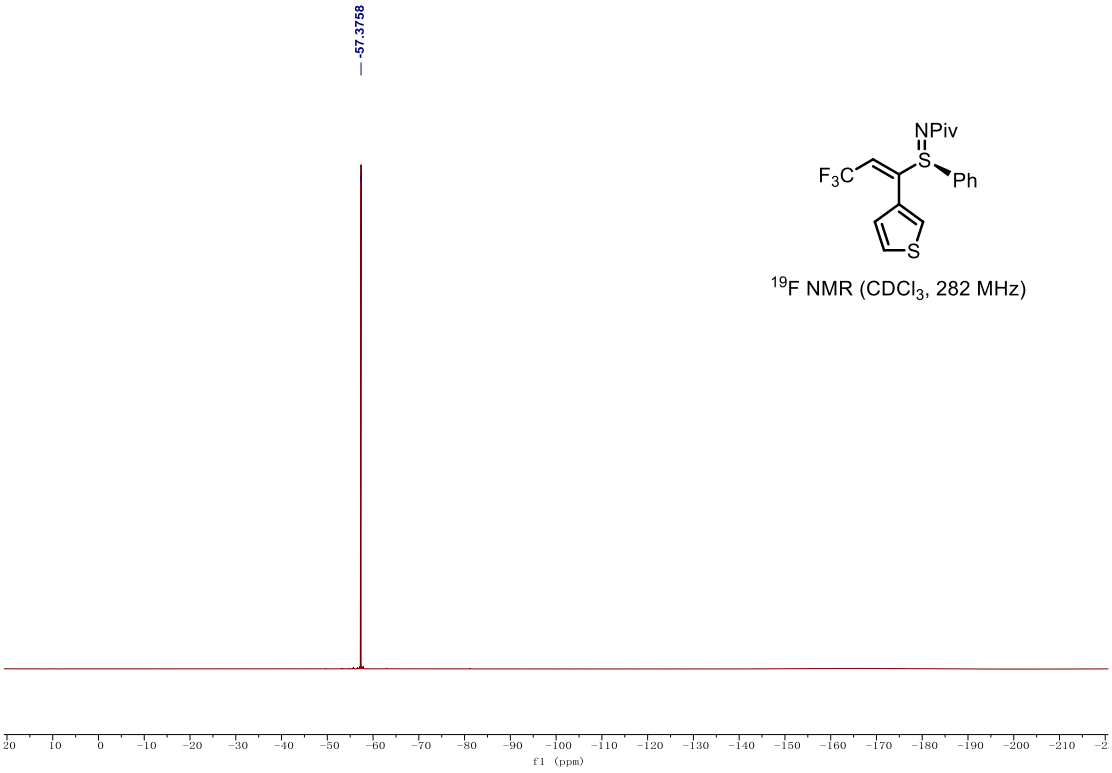
^{1}H NMR Spectrum of 4as



^{13}C NMR Spectrum of 4as

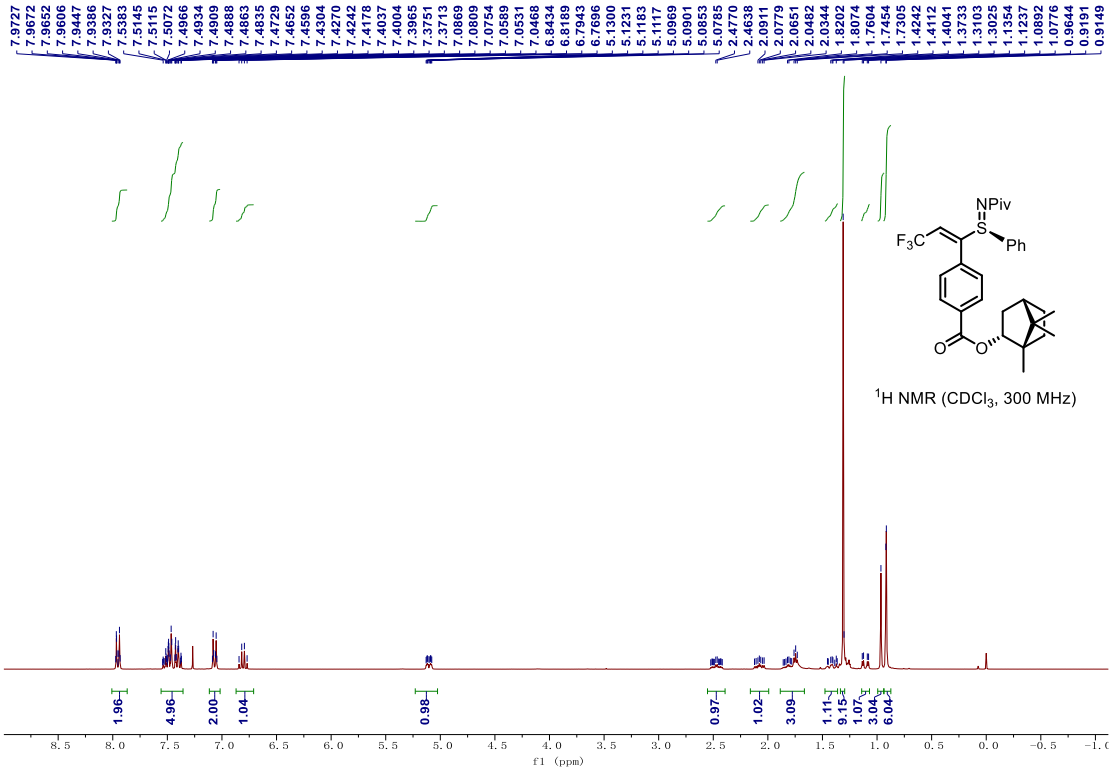


^{19}F NMR Spectrum of 4as

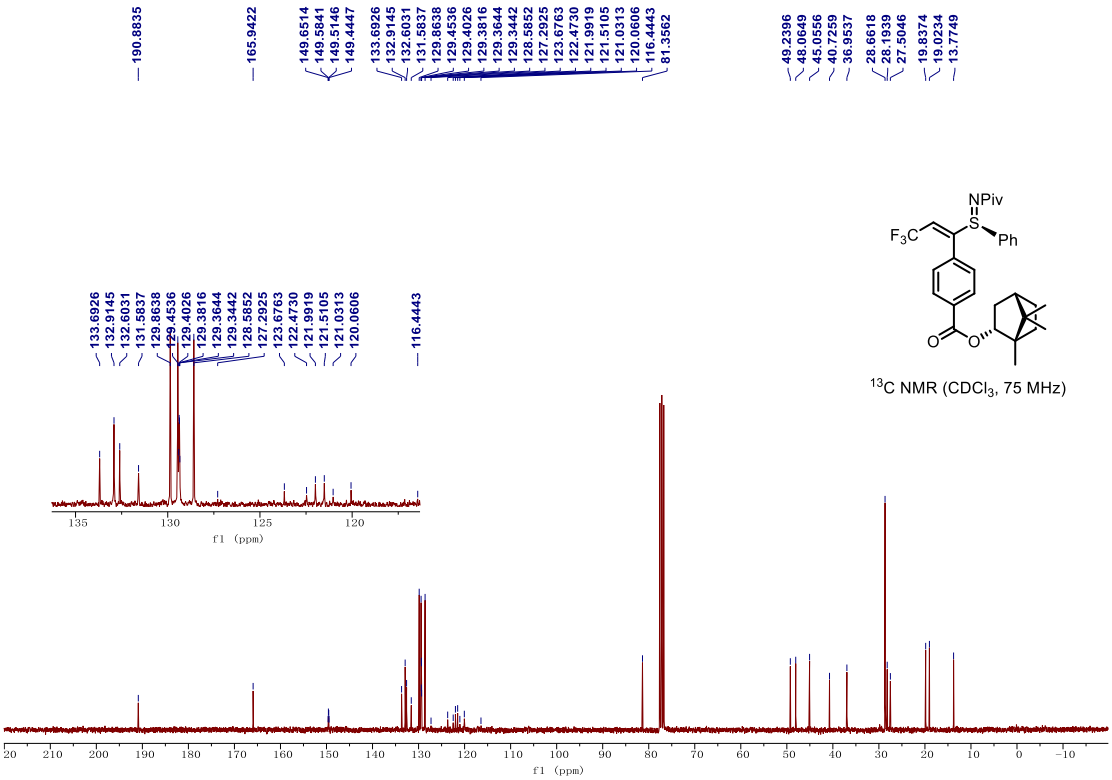


^{19}F NMR ($CDCl_3$, 282 MHz)

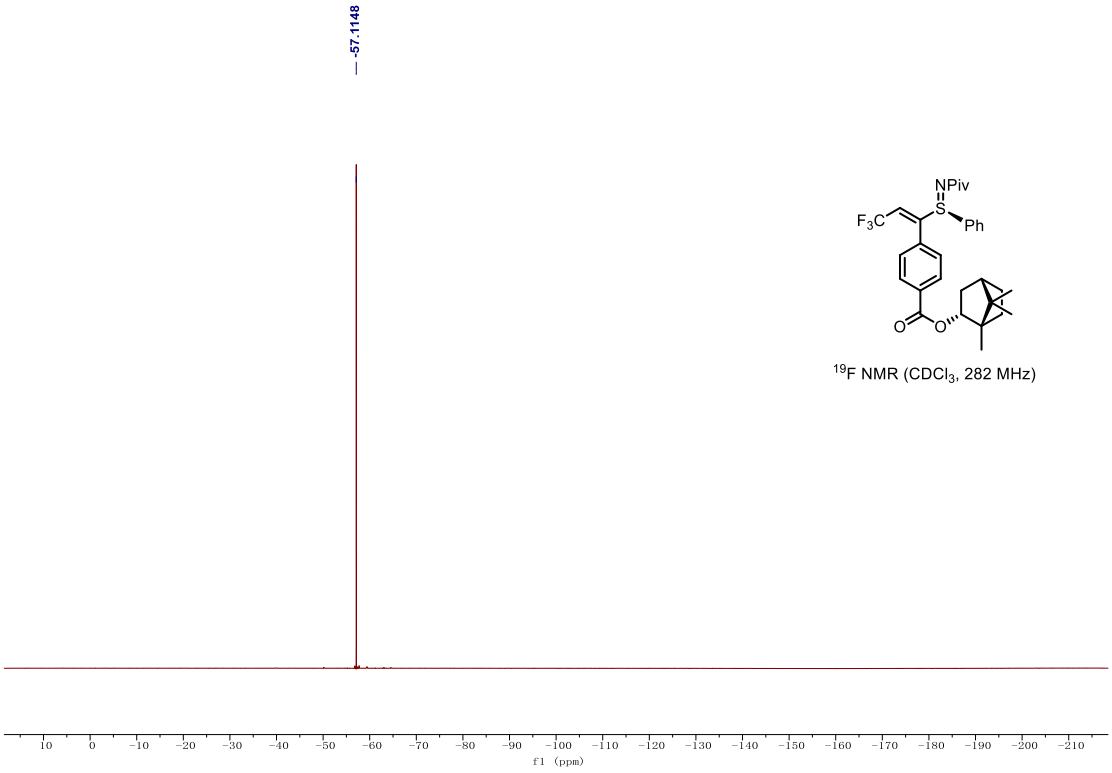
^{1}H NMR Spectrum of 4at



^{13}C NMR Spectrum of 4at

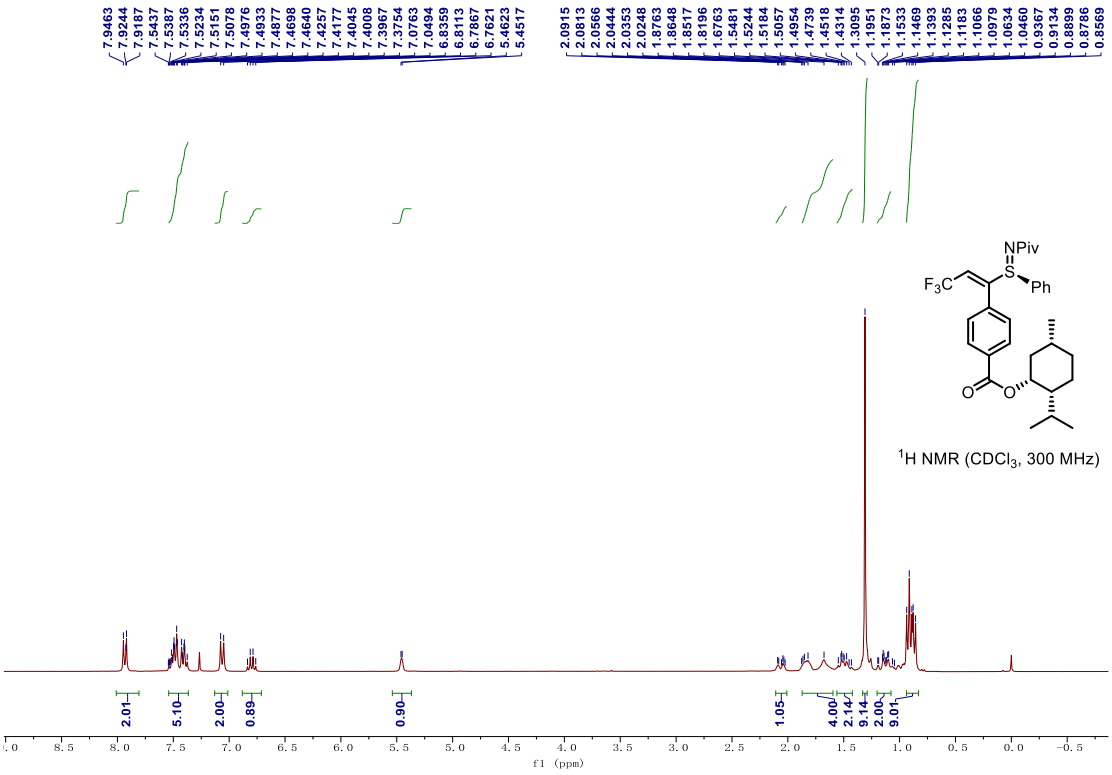


^{19}F NMR Spectrum of 4at

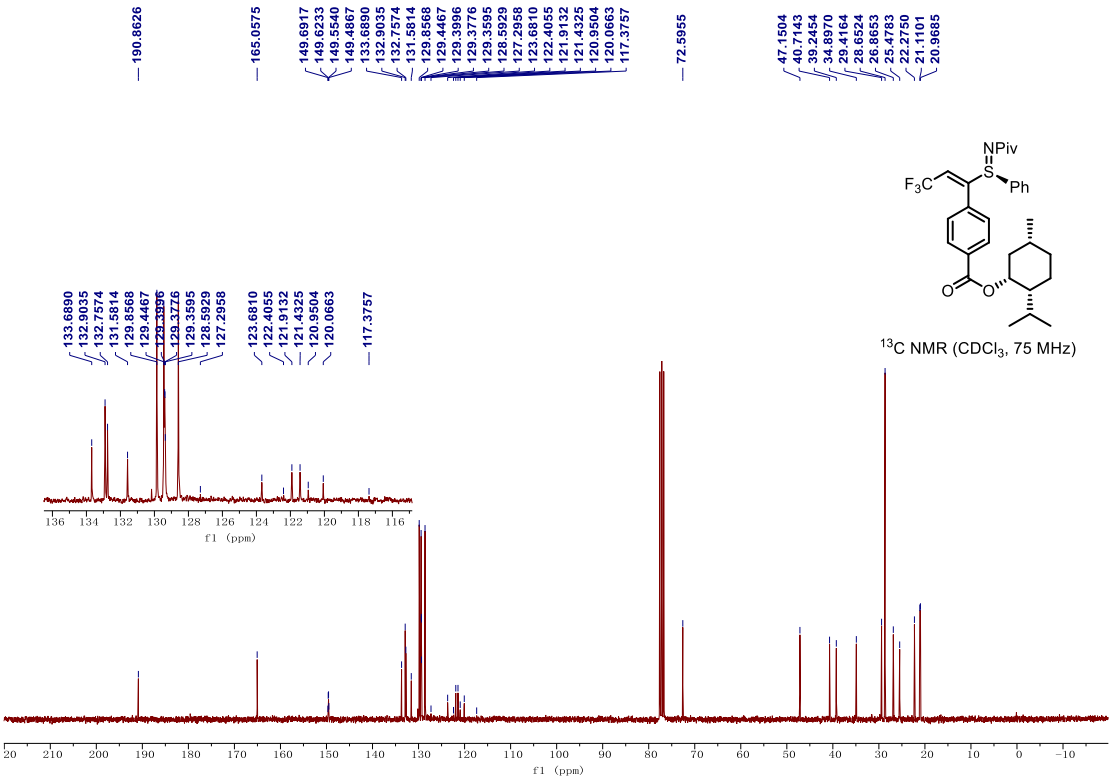


^{19}F NMR ($CDCl_3$, 282 MHz)

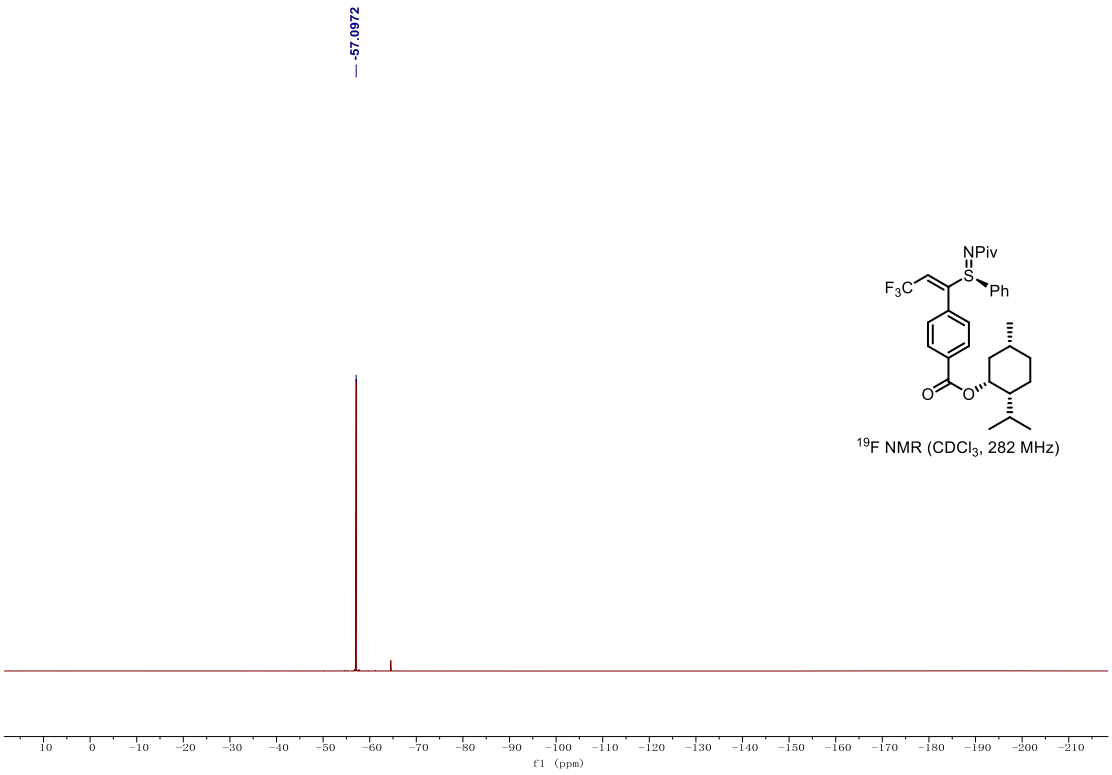
^{1}H NMR Spectrum of 4au



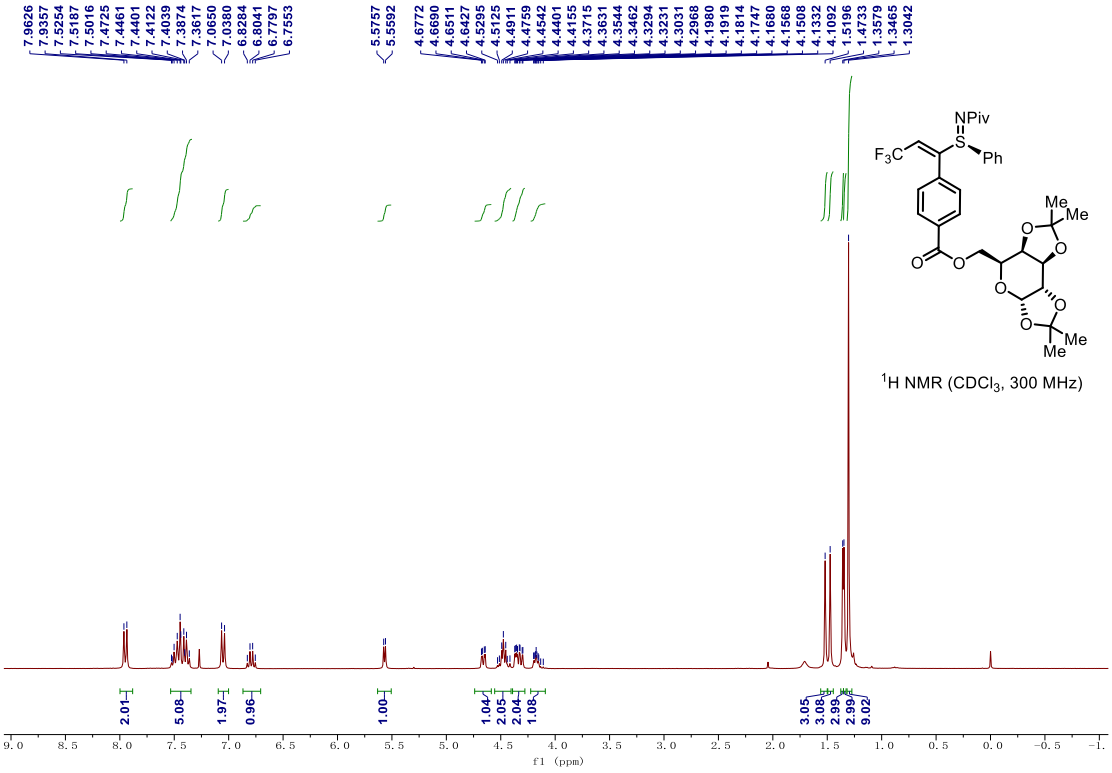
^{13}C NMR Spectrum of 4au



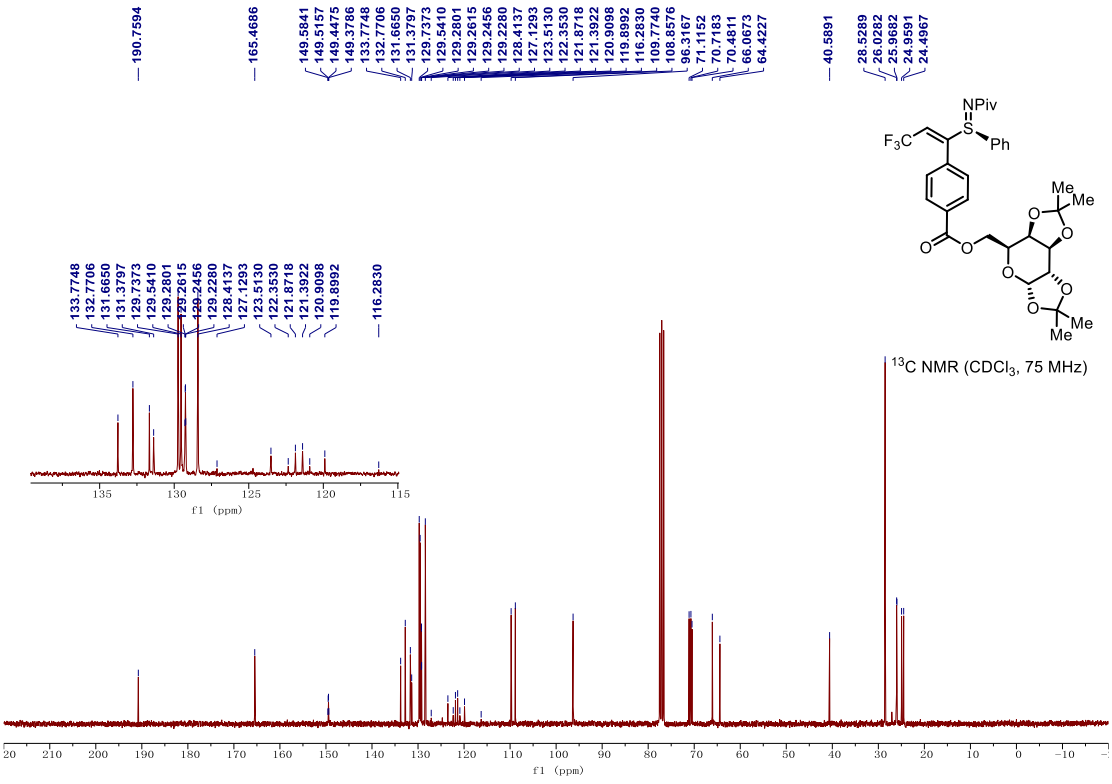
^{19}F NMR Spectrum of 4au



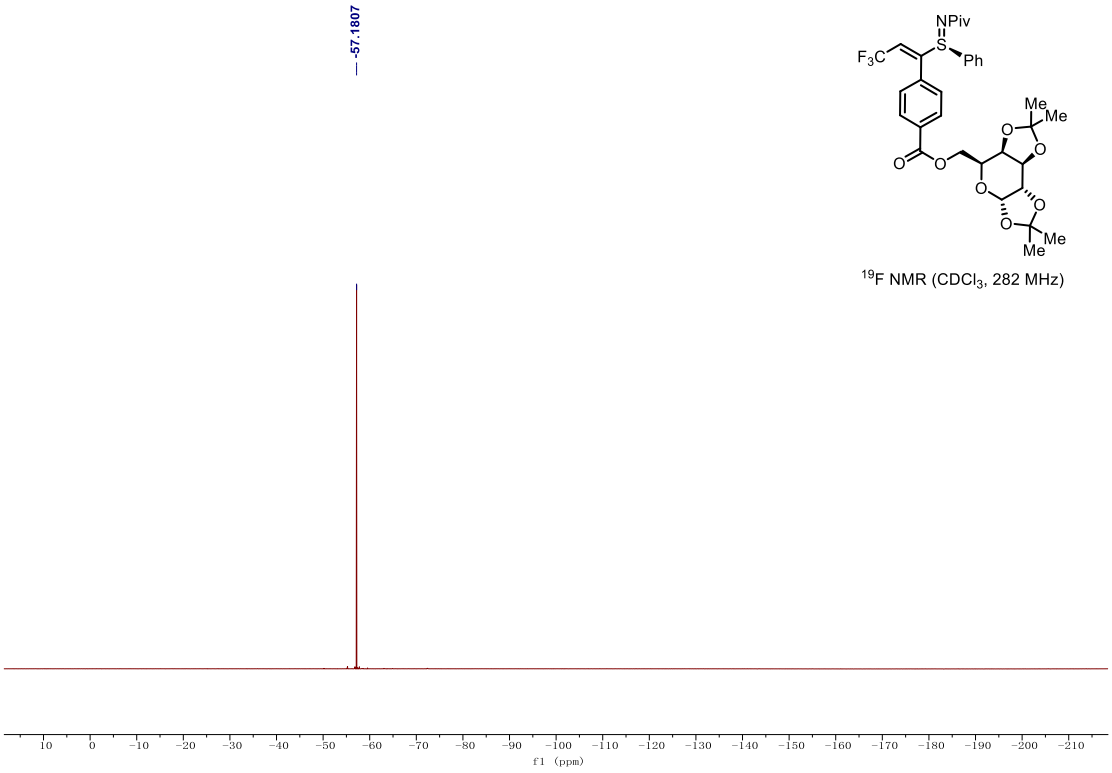
^{1}H NMR Spectrum of 4av



^{13}C NMR Spectrum of 4av

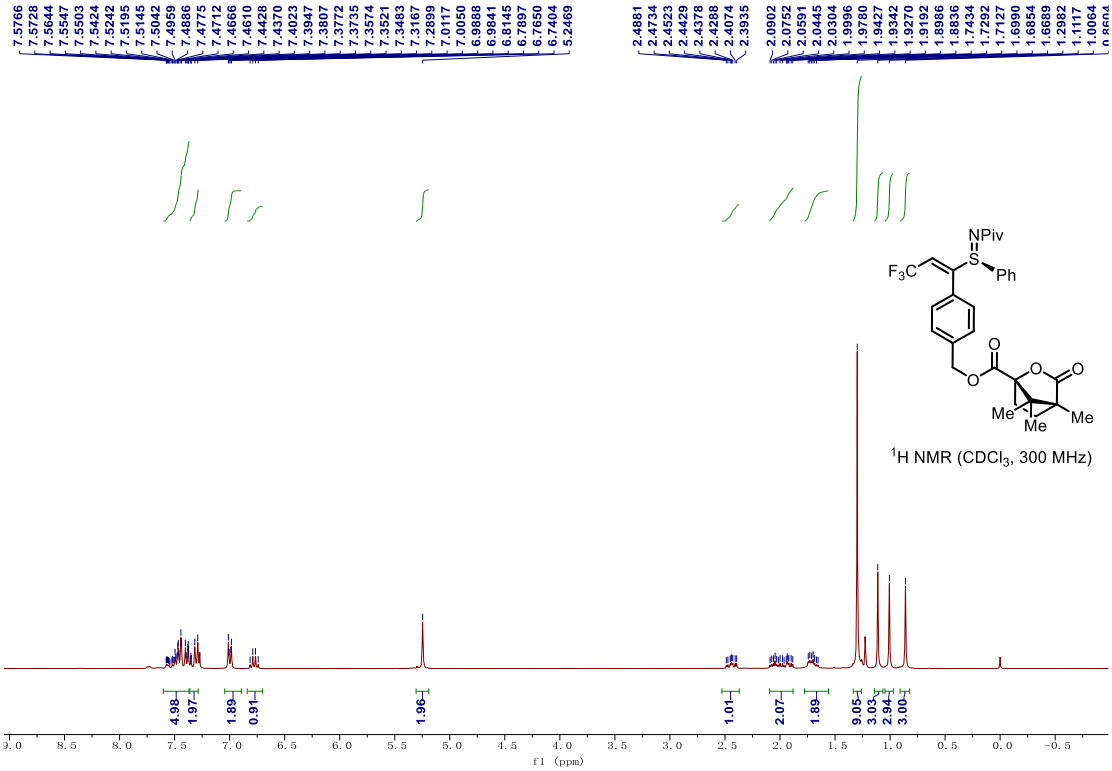


^{19}F NMR Spectrum of 4av

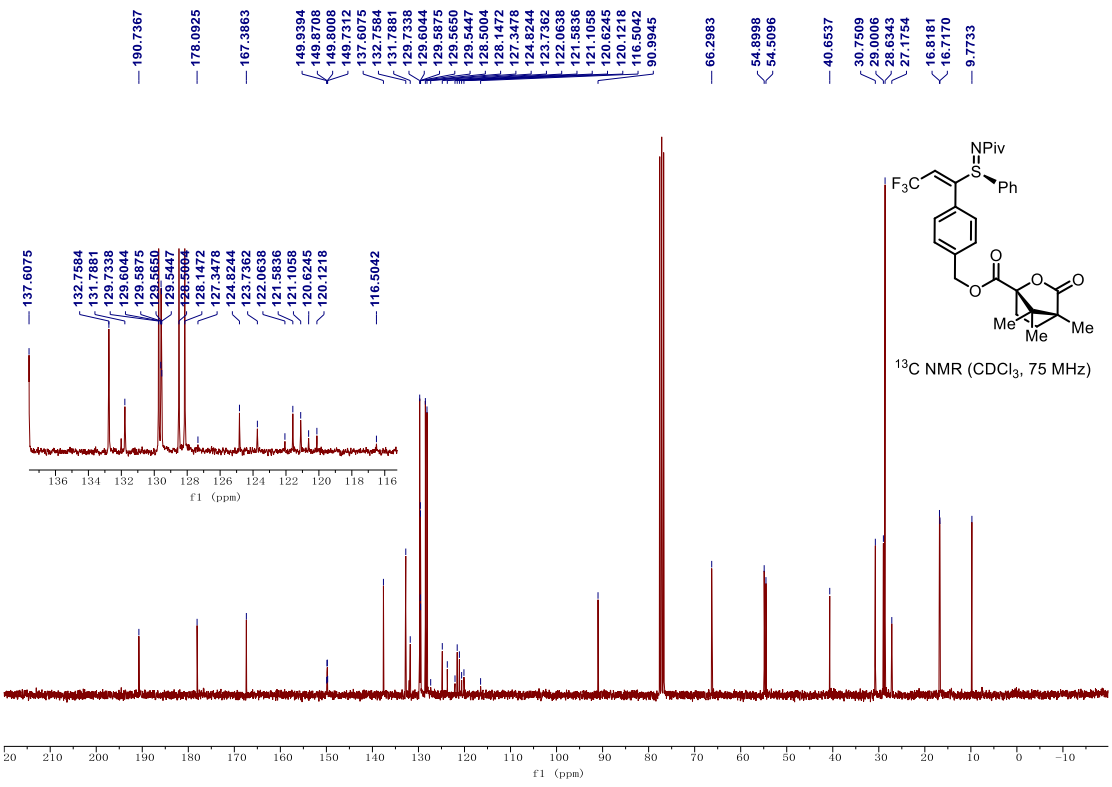


^{19}F NMR ($CDCl_3$, 282 MHz)

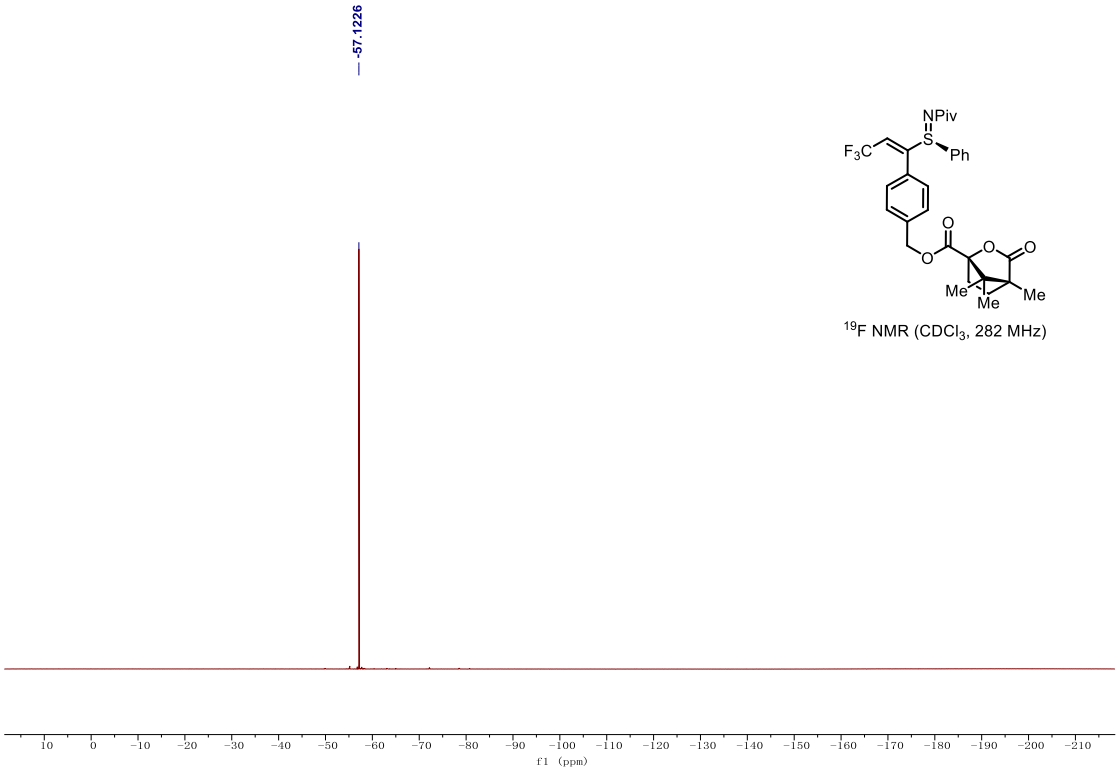
^{1}H NMR Spectrum of 4aw



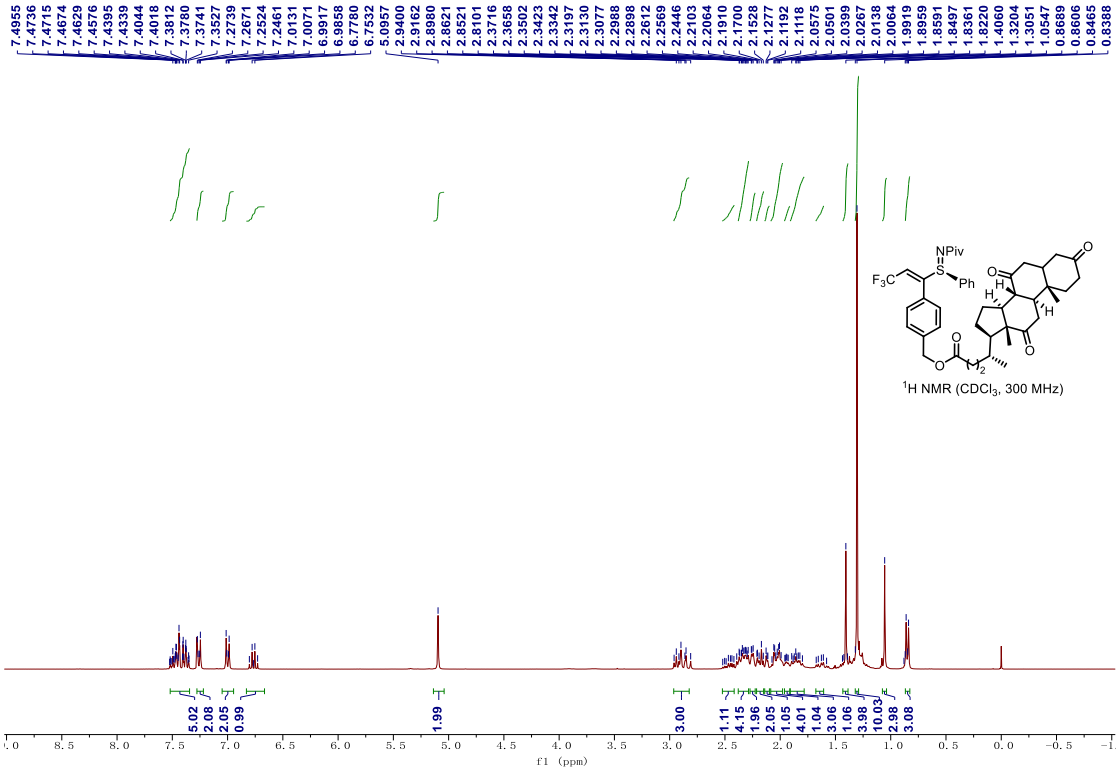
^{13}C NMR Spectrum of 4aw



^{19}F NMR Spectrum of 4aw

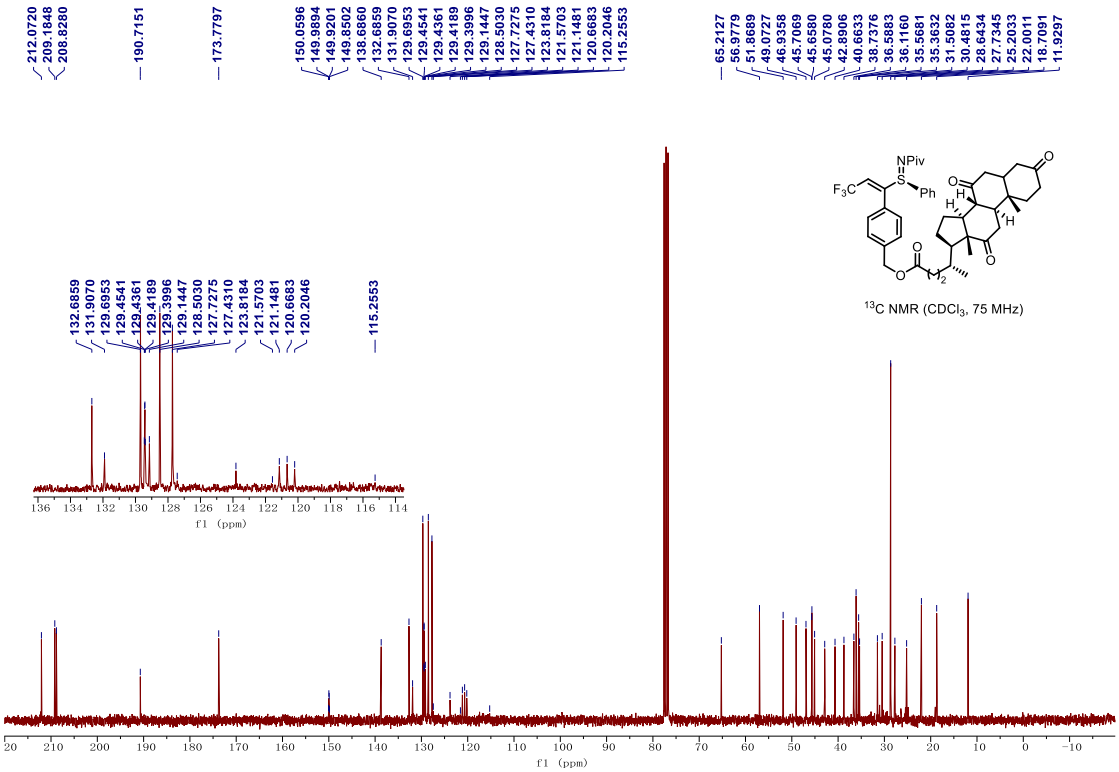


^{1}H NMR Spectrum of 4ax



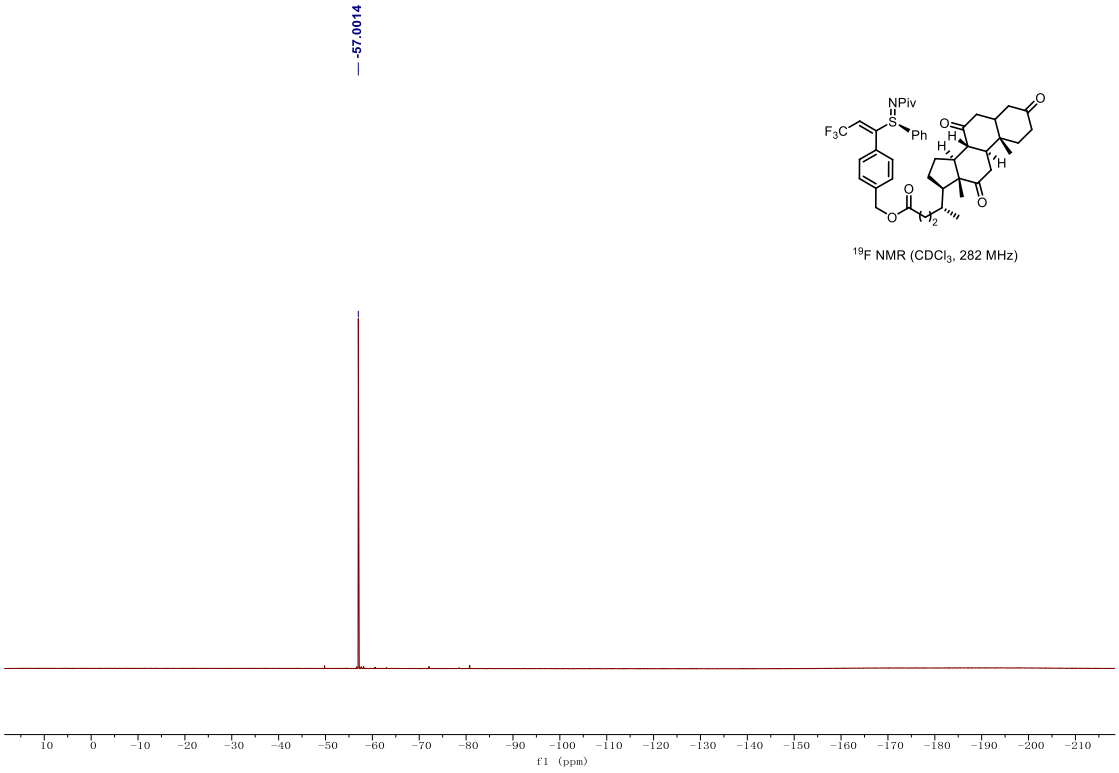
^{1}H NMR ($CDCl_3$, 300 MHz)

^{13}C NMR Spectrum of 4ax

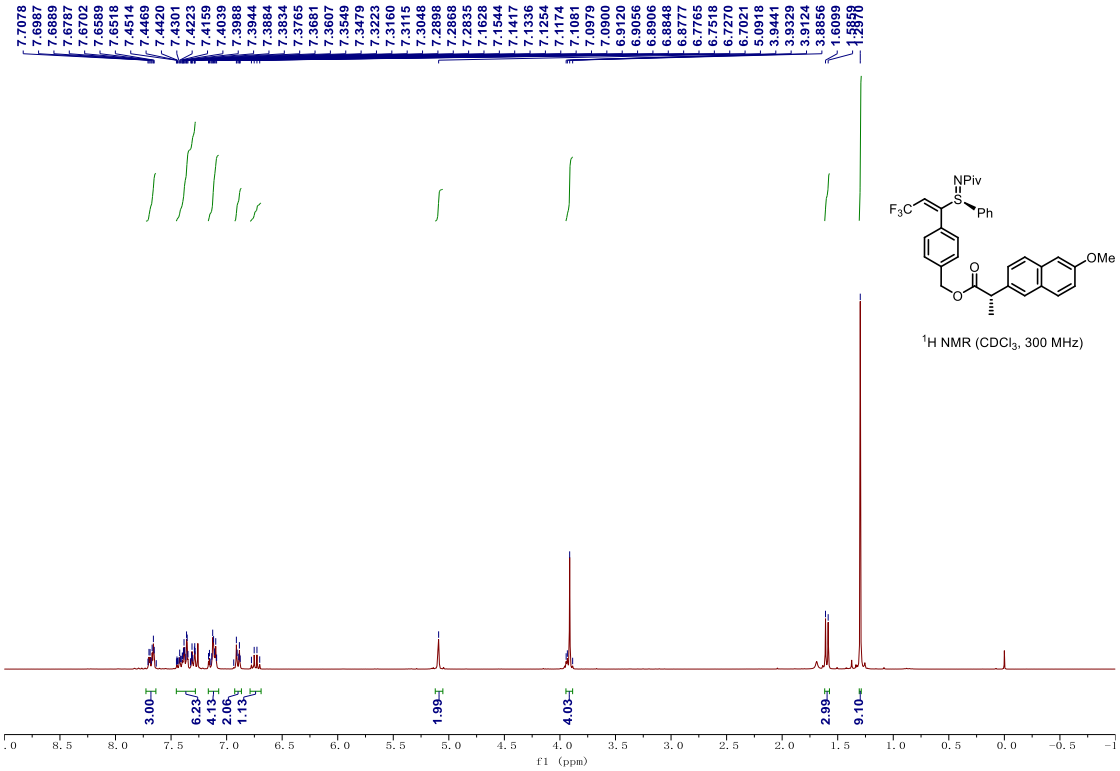


^{13}C NMR ($CDCl_3$, 75 MHz)

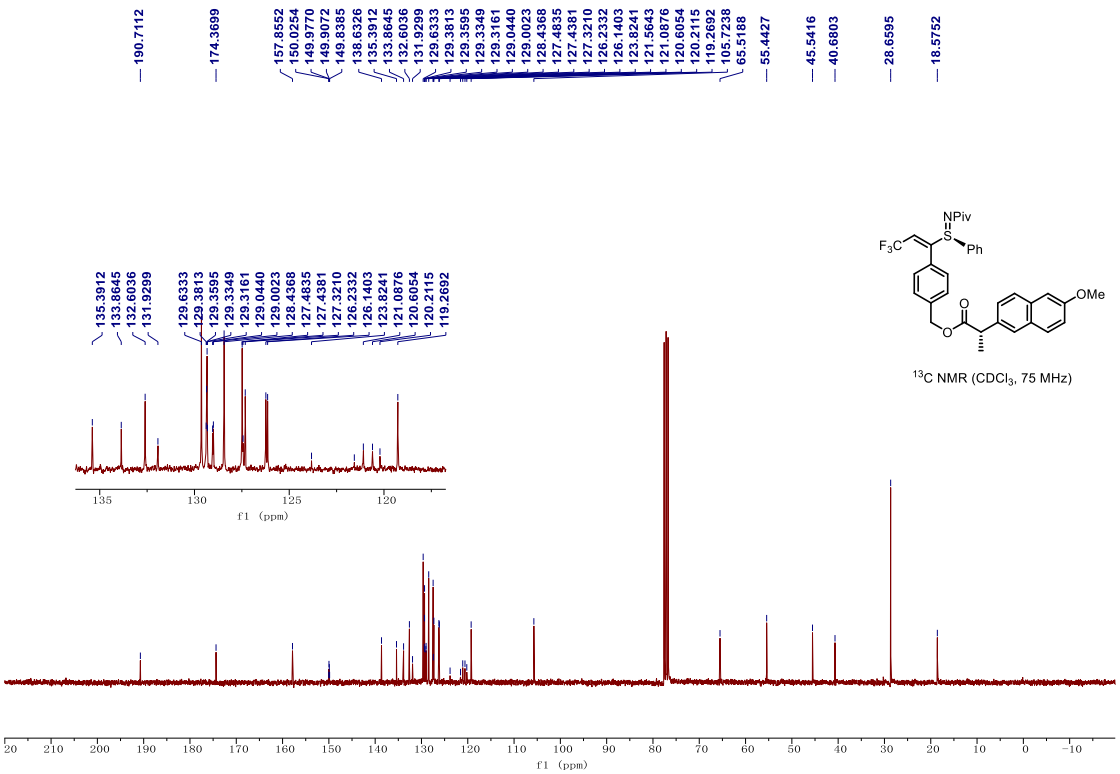
^{19}F NMR Spectrum of 4ax



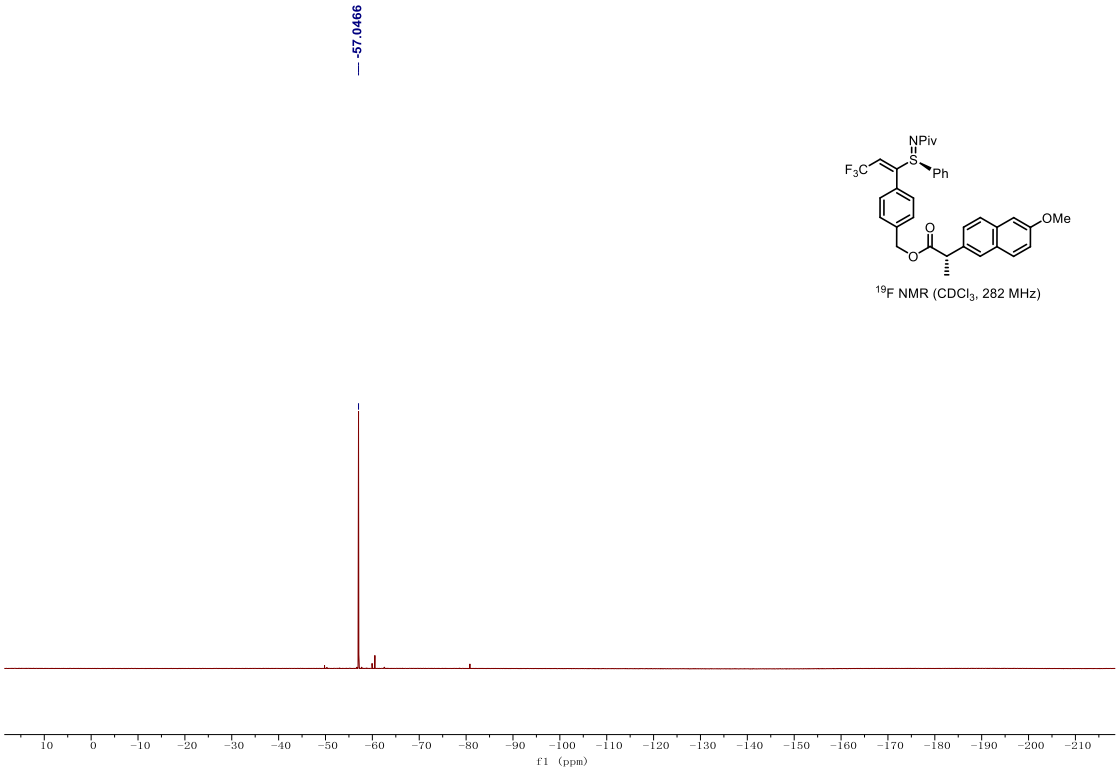
^{1}H NMR Spectrum of 4ay



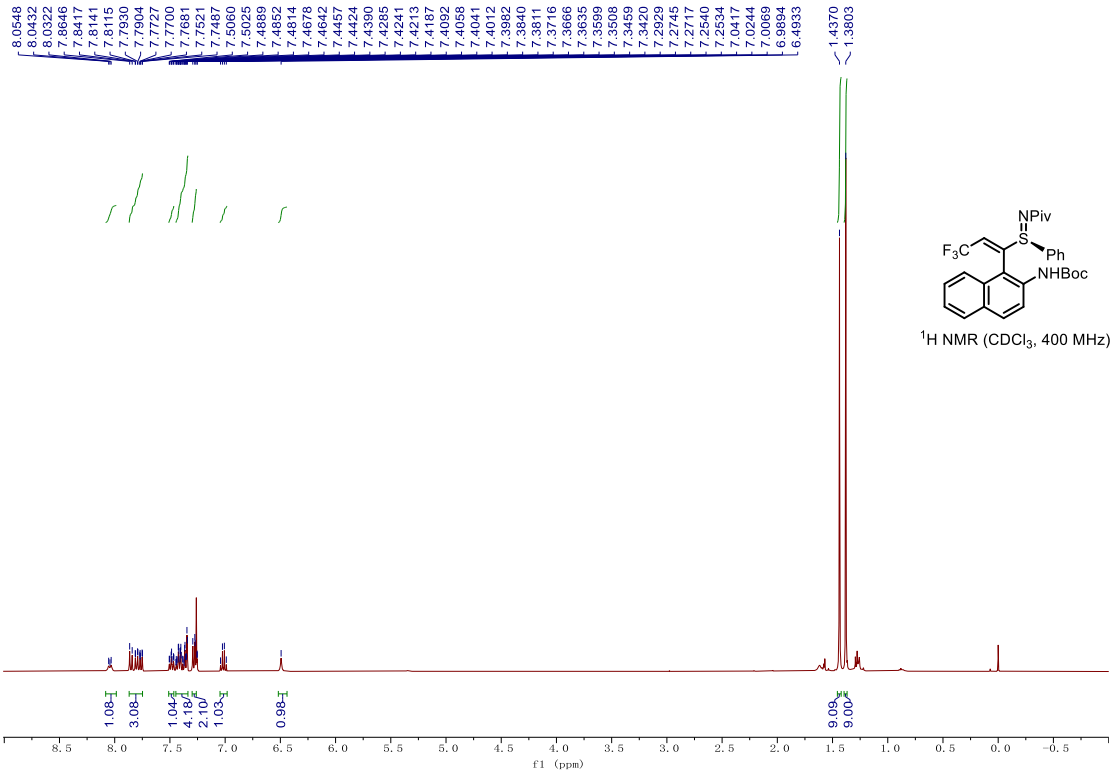
^{13}C NMR Spectrum of 4ay



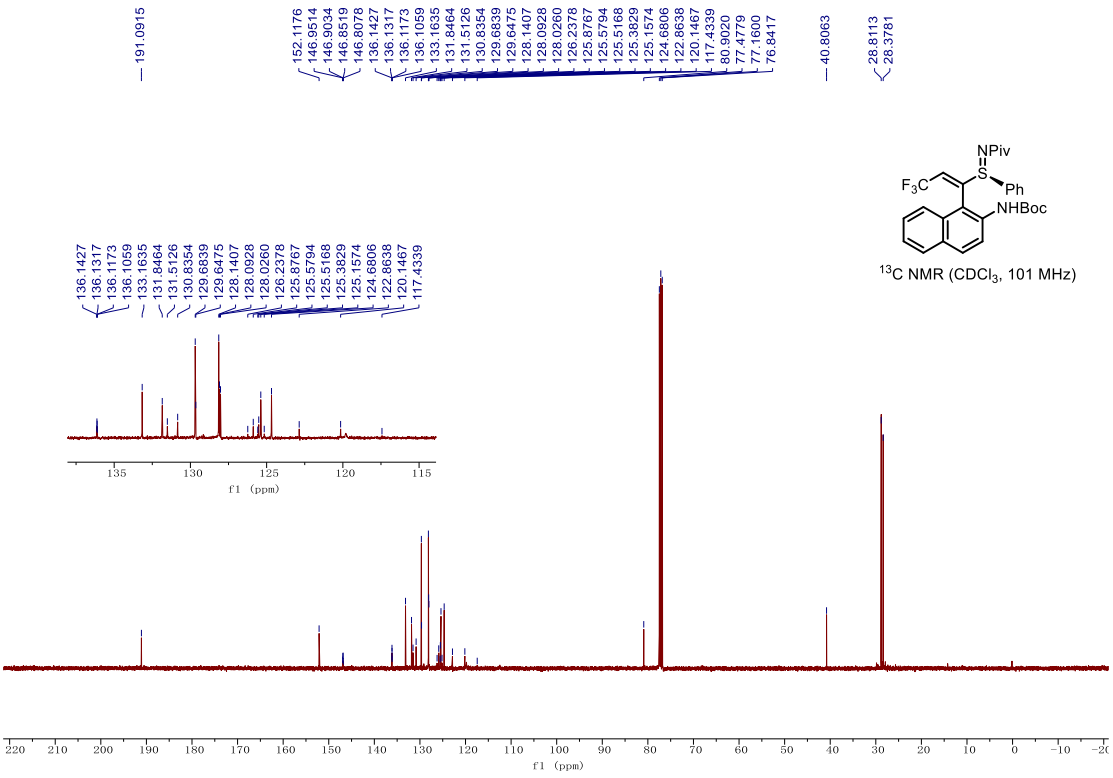
^{19}F NMR Spectrum of 4ay



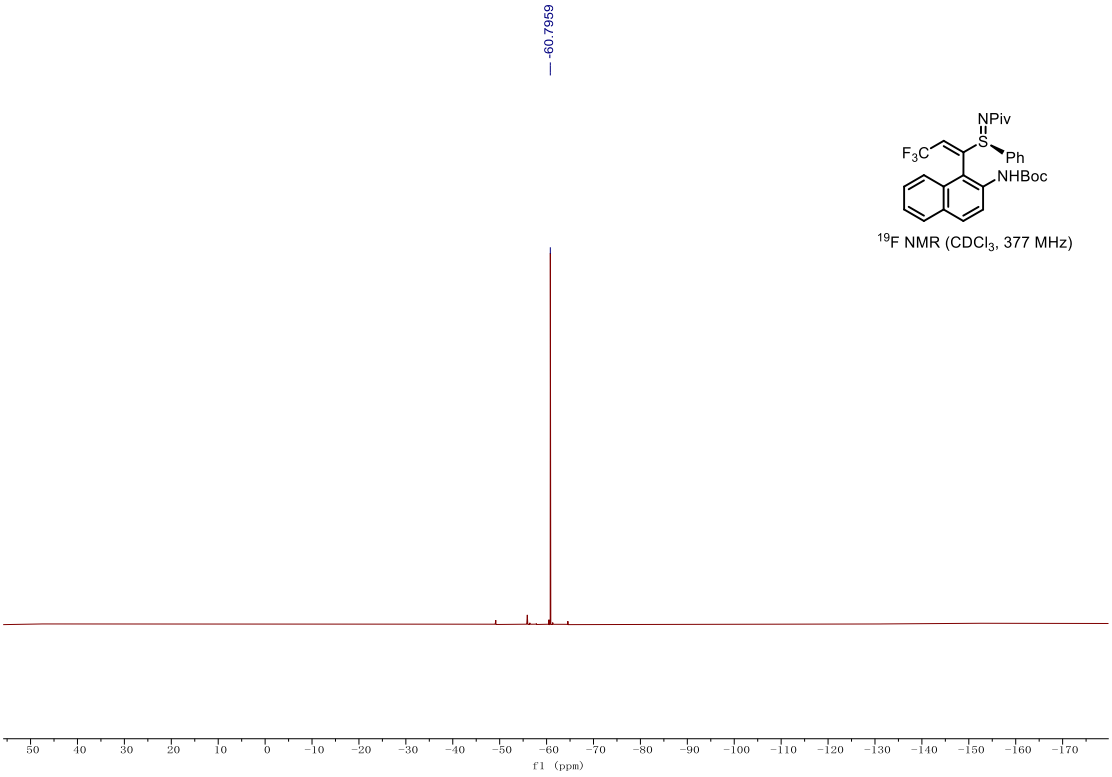
^{1}H NMR Spectrum of 4ba



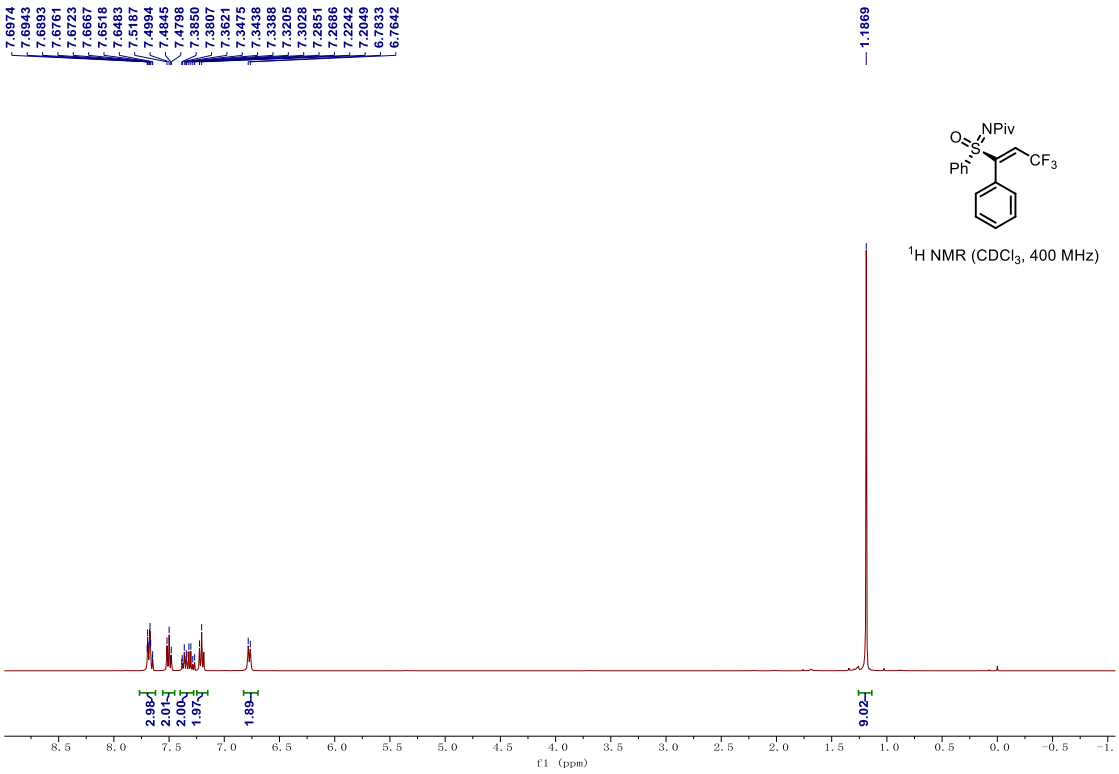
^{13}C NMR Spectrum of 4ba



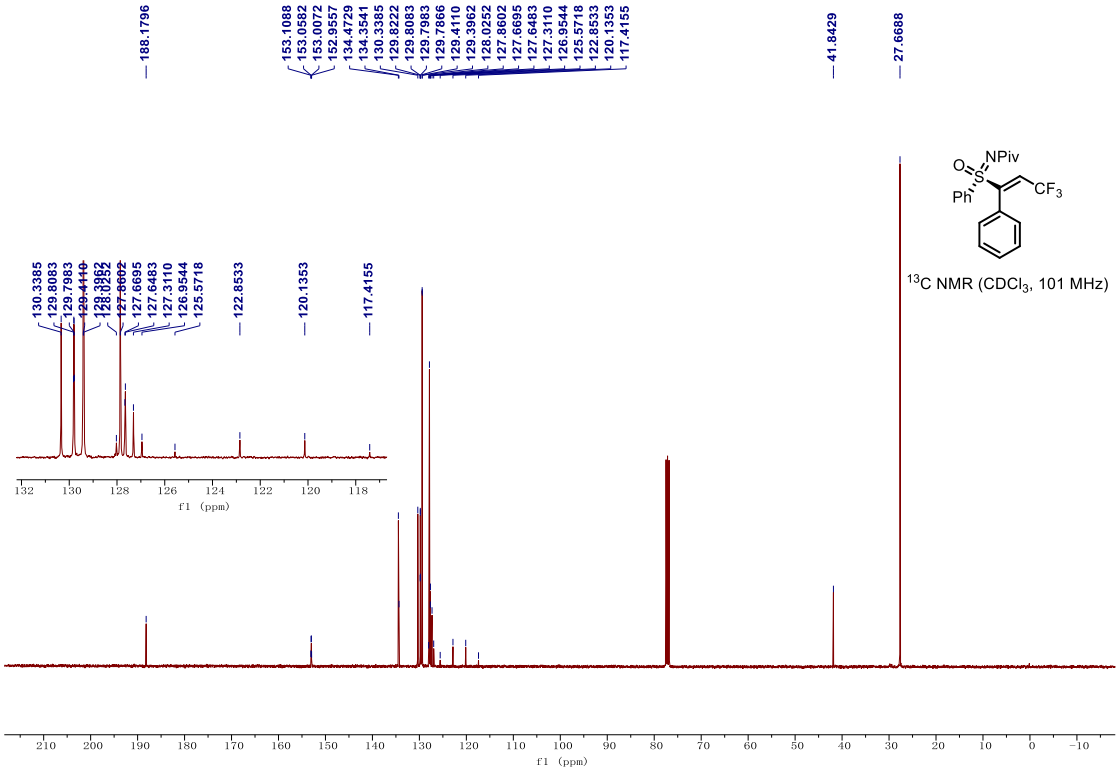
^{19}F NMR Spectrum of 4ba



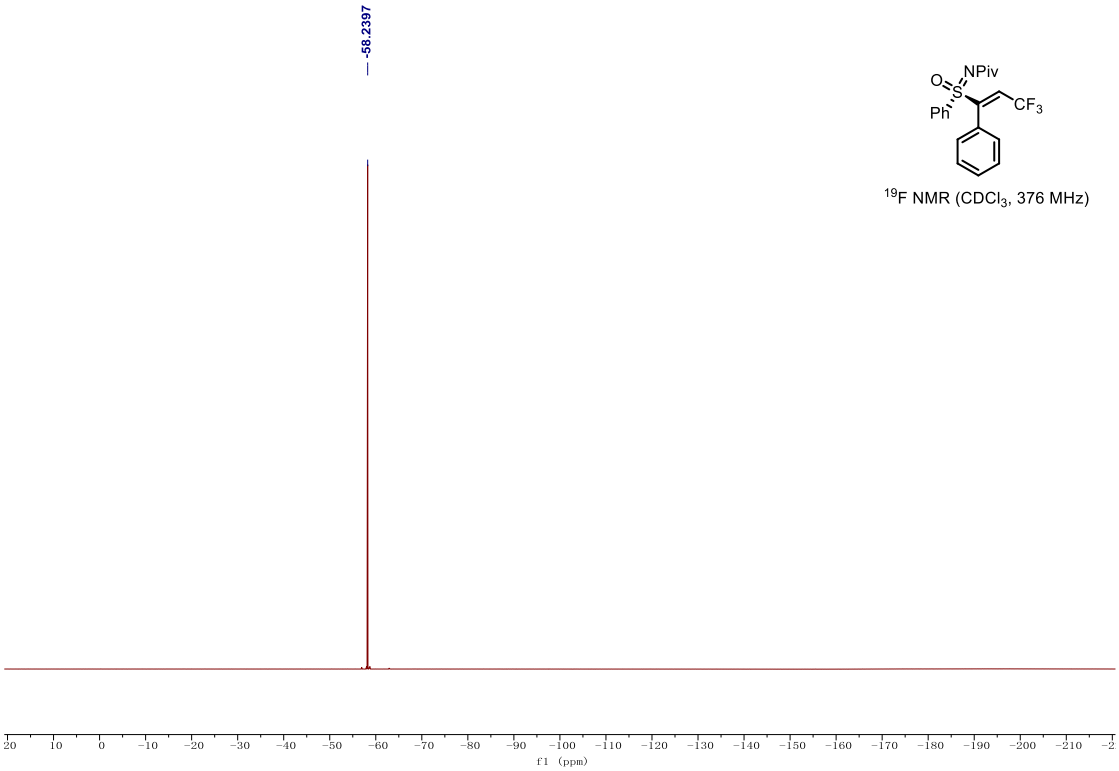
^{1}H NMR Spectrum of 5



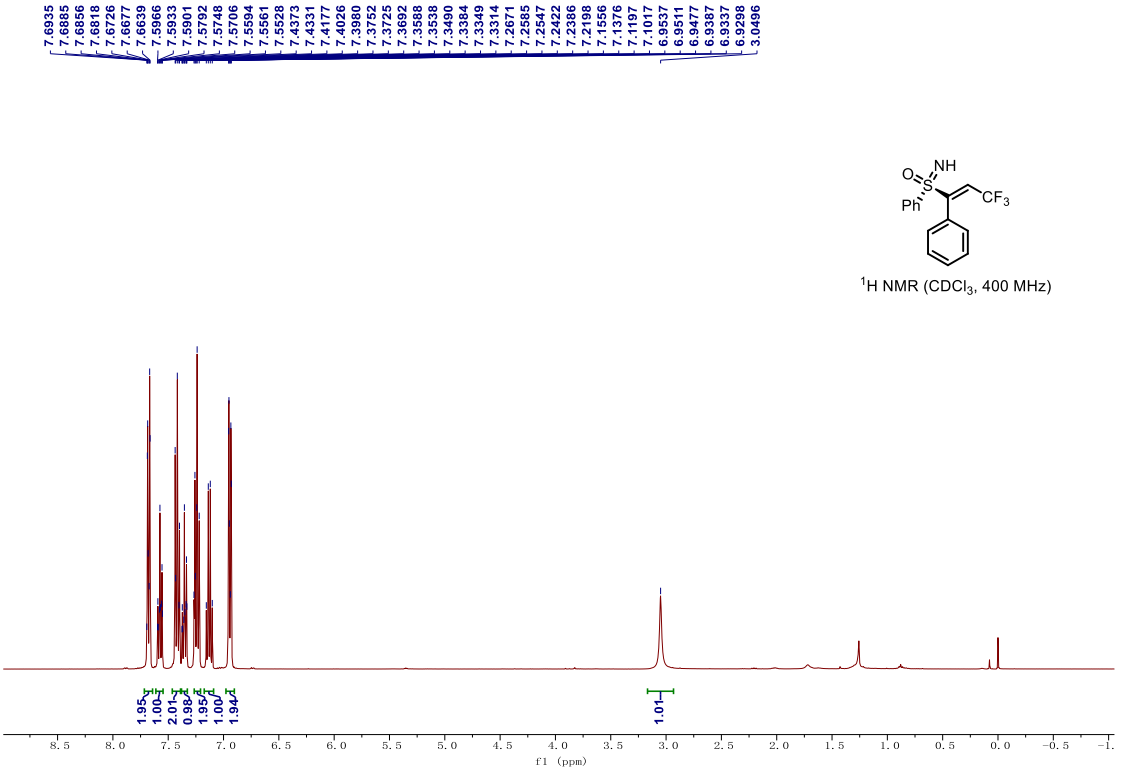
^{13}C NMR Spectrum of 5



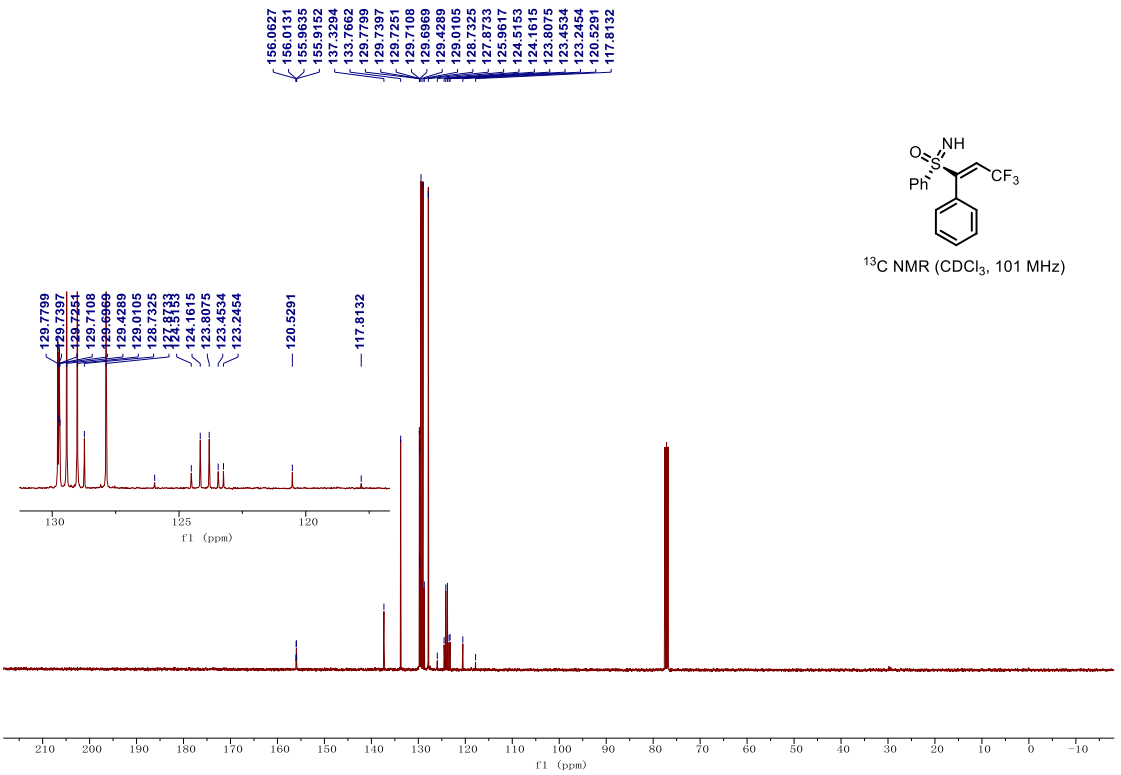
^{19}F NMR Spectrum of 5



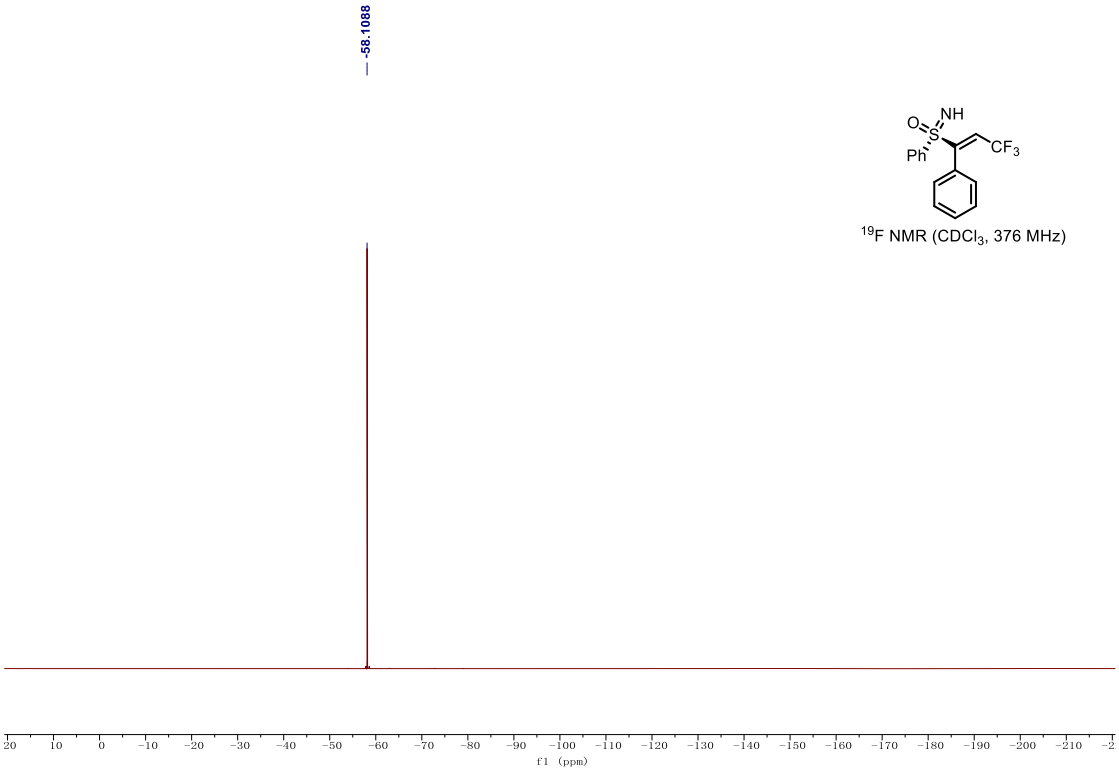
^{1}H NMR Spectrum of 6



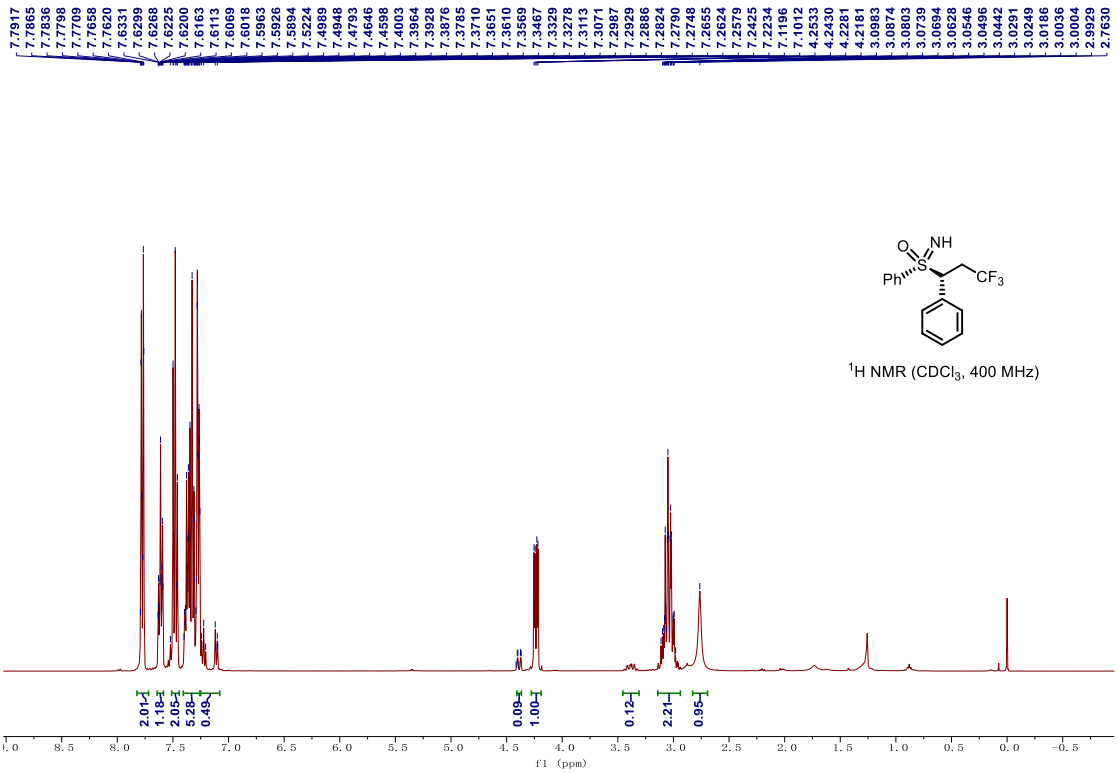
^{13}C NMR Spectrum of 6



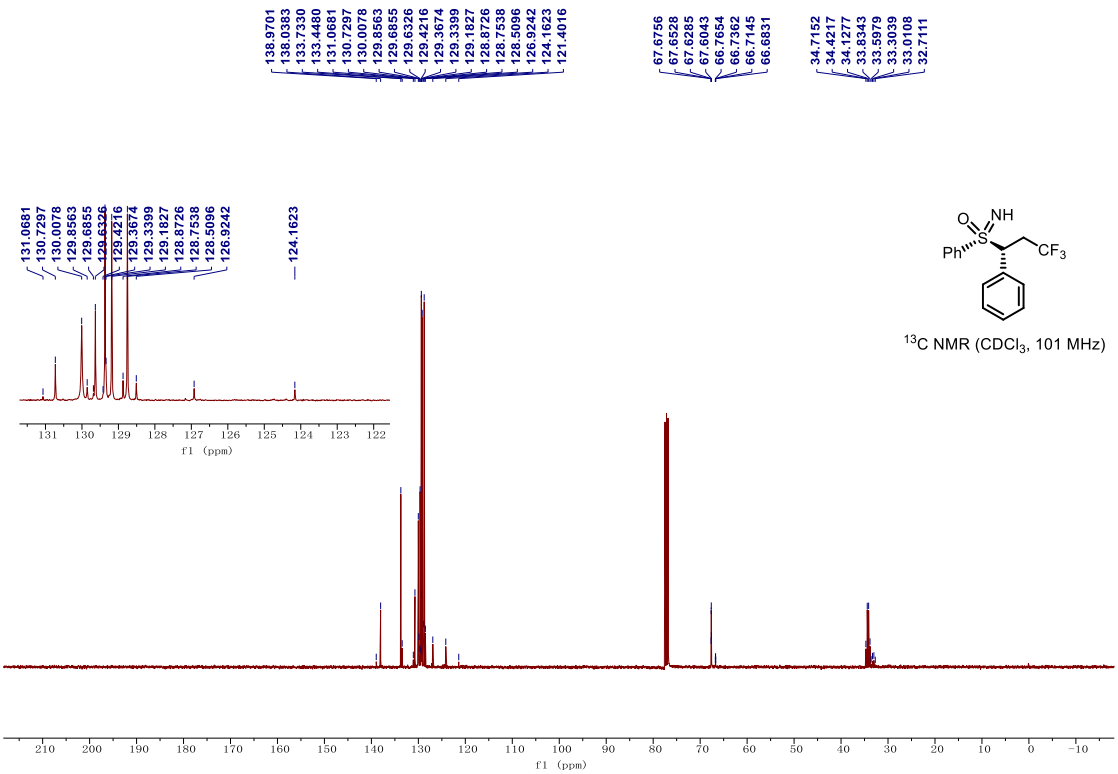
^{19}F NMR Spectrum of 6



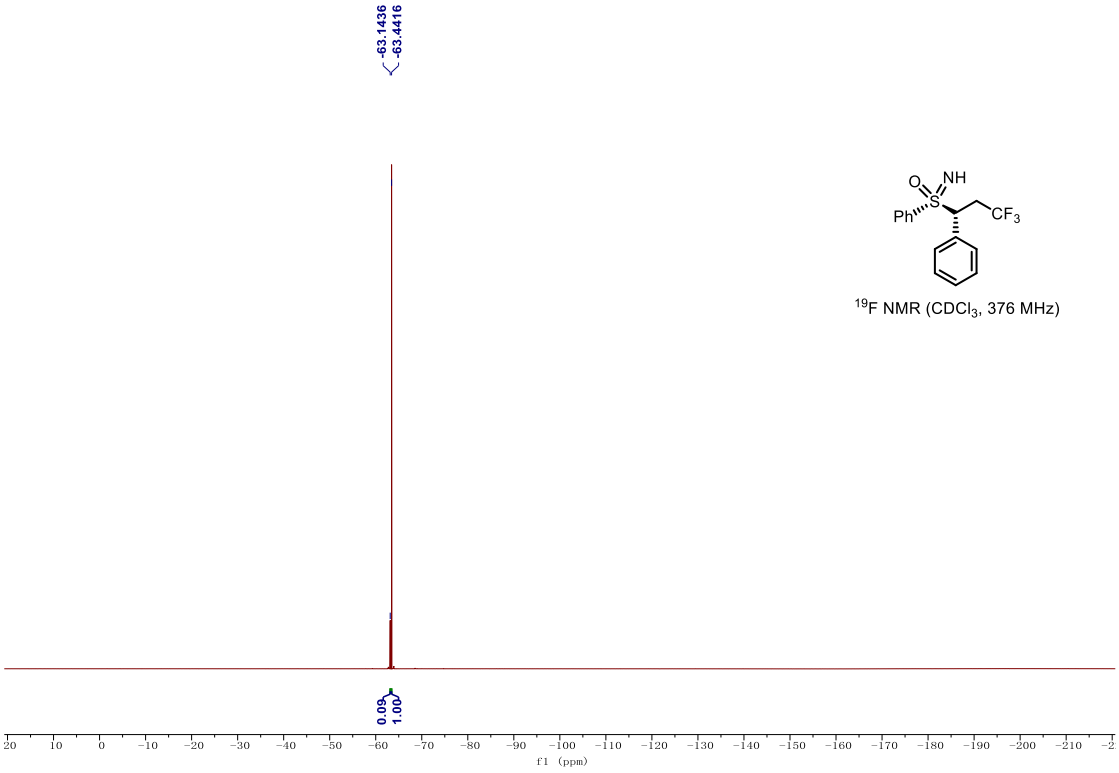
^{1}H NMR Spectrum of 7



^{13}C NMR Spectrum of 7



^{19}F NMR Spectrum of 7



^{19}F NMR ($CDCl_3$, 376 MHz)

9. References

(1). S. Li, J. Li, H. Zhang, G. Zhang and R. Guo, *Org. Lett*. 2025, **27**, 5057–5062.
(2). R. Muta, T. Torigoe and Y. Kuninobu, *Org. Lett*. 2022, **24**, 8218–8222.
(3). R. Ma, X. Qiu, H. Jiang and W. Wu, *Chem. Commun.*, 2024, **60**, 9578–9 581.
(4). Y. Zhang, H. Cao, S. Wei, Y. Li, L. Wang and L. Zong, *Chem. Commun.*, 2025, **15**, 13929–13937.
(5). N. S. Greenwood and J. A. Ellman, *Org. Lett.*, 2023, **25**, 4759–4764.
(6). Z.-K. Zhang, Y. Yuan, H. Peng, Y. Han, J. Zhang and J. Yang, *J. Org. Chem.*, 2024, **89**, 17609–17614.
(7). A. T. Champlin, N. Y. Kwon and J. A. Ellman, *Angew. Chem., Int. Ed.* 2 024, **63**, e202410773.
(8). Q. Xiong, M. Liao, S. Zhao, S. Wu, Y. Hong, Y. R. Chi, X. Zhang and X. Wu, *Angew. Chem., Int. Ed.* 2025, **64**, e202500170.
(9). Y. Chen, D.-M. Fang, H.-S. Huang, X.-K. Nie, S.-Q. Zhang, X. Cui, Z. T ang and G.-X. Li, *Org. Lett.*, 2023, **25**, 2134–2138.
(10). M. Han, S.-Q. Zhang, X. Cui, Z. Tang and G.-X. Li, *J. Org. Chem.*, 2025, **90**, 13440–13448.
(11). M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16, Revision A.03.* Gaussian, Inc., Wallingford CT, 2016.
(12). (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
(13). S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **1 32**, 154104.
(14). S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 145 6–1465.
(15). P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270–283.
(16). K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363–368.
(17). Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.
(18). D. Andrae, U. Haussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Ch im. Acta*, 1990, **77**, 123–141.

(19). A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 200 9, **113**, 6378–6396.
(20). C. Y. Legault, *CYLview, 1.0b.* Université de Sherbrooke, 2009 (http://ww w.cylview.org).
(21). Z. Wang, EnePro1.6 (github.com/wongzit/EnePro).