The Facile Synthesis of α-trifluoromethylthio Phosphonium Ylides with a Constrained Trifluoromethylthiooxide via Proton-Transfer Procedure

Chengyao Kimmy Cao,[a] Yue Zhang,[b] Tianlei Lan, [b] Wei Liu,[c] Chao Chen*[a]
Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084

Supporting information

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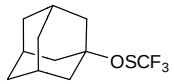
1. General information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with JEOL AL - 600 MHz, AL - 400 MHz and AL - 300 MHz spectrometer. $CDCl_3$ was selected as the solvent and residual proton resonance of $CDCl_3$ was referenced using the 7.26 ppm in ^{1}H NMR and 77.16 ppm in ^{13}C NMR. Data are reported in the following order: multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and Coupling constants (*J*) are in Hertz (Hz). HRMS were recorded on a high-resolution mass spectrometer in the EI or ESI mode. IR spectra was recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer.

Materials: Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents were purified by solvent purification system. Reactions were performed under an atmosphere of N_2 using glassware that was flame-dried under vacuum. n-BuLi was purchased from Energy (1,6 M in hexane). $AgSCF_3$ [1] and compounds **A1,**[2] **A2,** [3] **A3,** [2] **A4,** [4] **A5** [5] were prepared following the literature.

2. Synthesis of compound A[1]

A 200 mL round-bottomed flask charged with 1-adamantanemethanol (4.5 mmol, 686 mg), N-trifluoromethylthiosaccharin (5.9 mmol, 1.65 g), and Et_3N (10.4 mmol, 1.5 mL) was added DCM (90 mL). The mixture was stirred at room temperature for 10 min. The mixture was concentrated to (15 mL). The resulting mixture was then purified by flash column chromatography (Eluent: pentane) to give trifluoromethyl substituted thioperoxide **A** as a colorless liquid in 87% yield.



A

^{1}H NMR (400 MHz, CHLOROFORM-D) δ 2.23 (s, 3H), 1.82 (s, 6H), 1.62 (q, J = 12.4 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ130.69 (q, J = 312.5 Hz), 83.10, 41.60, 35.88, 31.41. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -52.50 (s). IR (FTIR): ν = 2912, 2856, 1456, 1117, 1047, 892, 798 cm^{-1}. Anal. Calcd for $C_{11}H_{15}F_3OS$: C, 52.37; H, 5.99. Found: C, 52.52; H, 6.17.

3. Studies of compound $Ph_3P{=}CHSCF_3$ by trifluoromethylthiolated of methylenetriphenylphosphorane

Initial observation of $Ph_3P{=}CHSCF_3$. To a solution of Methyltriphenylphosphonium bromide (71.4 mg, 0.2 mmol) in THF (2 mL) was added n-BuLi (1.6 M in hexane, 125 μL, 0.2 mmol) at -78 °C, and stirred for 1 h. Then trifluoromethylthiolationg reagent **A** – **A5** (0.1 mmol) was added to the reaction mixture independently. The mixture was allowed to warm to 30 °C and stirred for 4 h. As shown in Figure **S1**, a strong signal at around δ = –52.6 ppm was observed by ^{19}F NMR spectroscopy at room temperature using reagent **A5** and **A** (1.0 equiv) as the trifluoromethylthiolating reagents (5, 6). When **A1** to **A4** was used as the functional reagent, no change was occurred (Figure **S1**, 1 – 4).

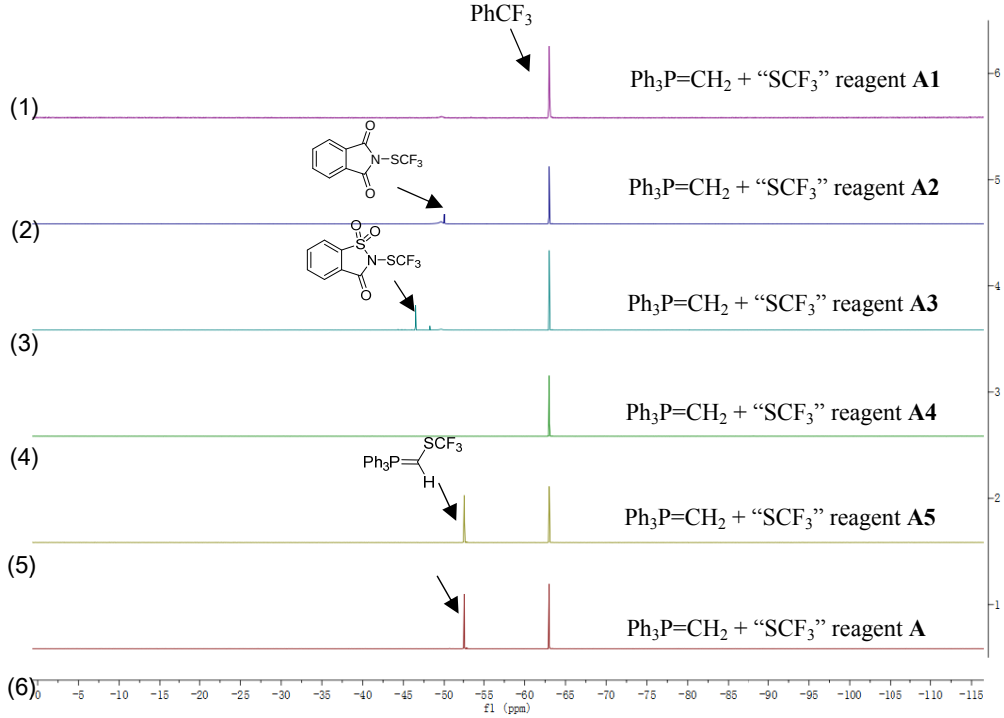


Figure S1 ^{19}F NMR of the mixture of methylenetriphenylphosphorane with "SCF_3" reagents **A - A5**

The identification and reactivity of $Ph_3P=CHSCF_3$. In order to further affirm the new intermediate was our trifluoromethylthiolated ylide, aldehyde was added into the mixture in one-pot, ^{19}F NMR spectra was recorded for different hours. As we can see the peak at -52.6 ppm decreased quickly in 10 min, and two new signals at -43.2 ppm emerged, which is exactly the same signal of the corresponding trifluoromethylthiolated olefin products (Figure S2). Prolonging the reaction time, the intermediate was almost consumed completely. The above information obviously indicated that compound $Ph_3P=CHSCF_3$ was produced and can finish Wittig reaction smoothly. It should be noted that compound $Ph_3P=CHSCF_3$ was not stable enough to be separated because of its high activity.

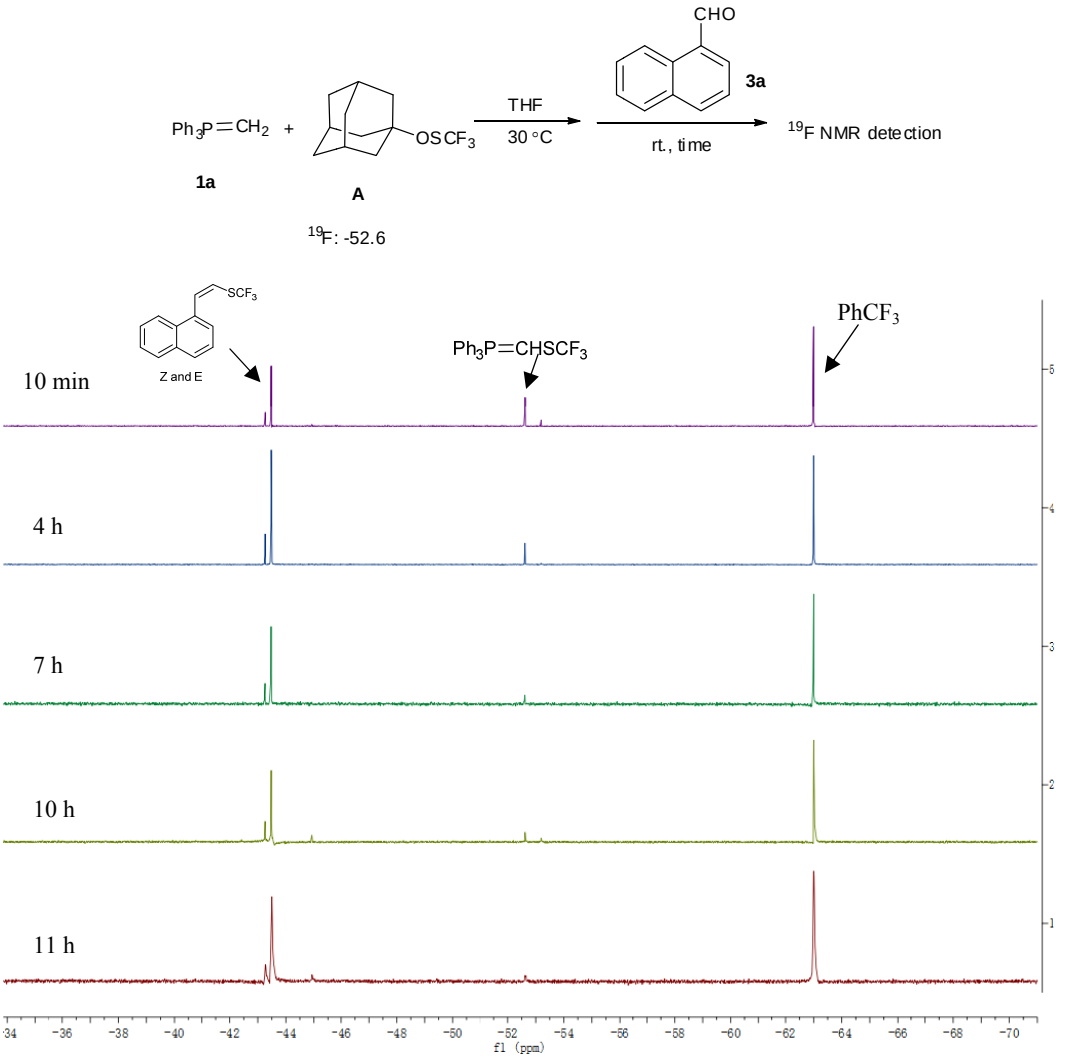
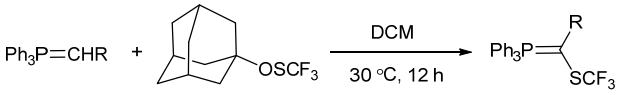
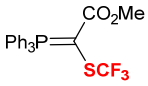


Figure S2. ^{19}F NMR spectrum of the mixture of $Ph_3P=CHSCF_3$ and 1-Naphthaldehyde in THF

4. General procedure for the synthesis of compound 2b-2d

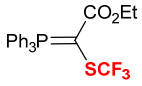
Phosphonium ylide (0.2 mmol) was added to a dry seal tube. The tube was evacuated and backfilled with pure N_2 for 3 times. DCM (2 mL) was added, then "SCF_3" reagent **A** (0.2 mmol) was added, the reaction was stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel by using a 5:1 mixture of Petroleum ether/EtOAc as an eluent to provide the trifluoromethylthiolated ylides **2b**, **2c**, **2d**.





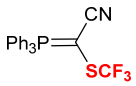
2b

methyl 2-((trifluoromethyl)thio)-2-(triphenyl-λ^5-phosphanylidene)acetate **2b** was obtained as white solid in 90% yield; R_f(PE/EA=5:1)=0.54. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.60 (m, 9H), 7.49 (m, 6H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 134.01 (d, *J* = 9.5 Hz), 132.43 (d, *J* = 2.6 Hz), 128.77 (d, *J* = 12.4 Hz). ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -49.53 (d, *J* = 440.3 Hz). ^{31}P NMR (243 MHz, CHLOROFORM-D) δ 29.47 (s). HRMS (ESI) calcd for $C_{22}H_{18}F_3O_2PS$ $(M+H)^+$ 435.0790, found 435.0788. MP: 164.2 - 165.7 °C.



2c

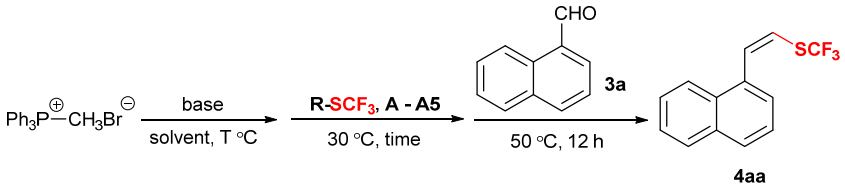
ethyl 2-((trifluoromethyl)thio)-2-(triphenyl-λ^5-phosphanylidene)acetate **2c** was obtained as white solid in 92% yield; R_f(PE/EA=5:1)=0.54. ^{1}H NMR (600 MHz, CHLOROFORM-D) δ 7.64 – 7.53 (m, 9H), 7.51 – 7.43 (m, 6H), 4.43 – 3.58 (m, 2H), 1.70 – 0.96 (m, 3H). ^{13}C NMR (151 MHz, CHLOROFORM-D) δ 133.94 (d, *J* = 9.6 Hz), 132.34 (d, *J* = 1.6 Hz), 128.67 (d, *J* = 12.4 Hz), 126.21 (m), 59.51 (m), 14.08 (m). ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -49.51 (d, *J* = 379.6 Hz). ^{31}P NMR (243 MHz, CHLOROFORM-D) δ 29.60 (s). HRMS (ESI) calcd for $C_{23}H_{20}F_3O_2PS$ $(M+H)^+$ 449.0946, found 449.0941. MP: 165. – 166.4 °C.



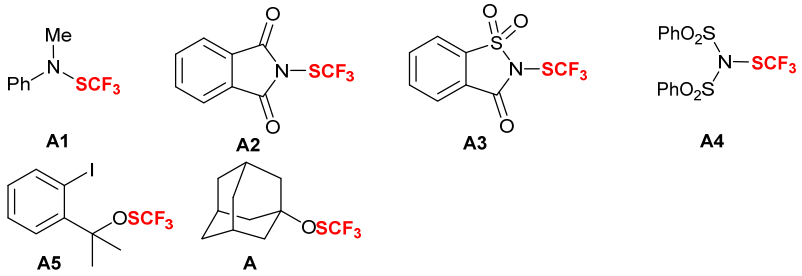
2d

2-((trifluoromethyl)thio)-2-(triphenyl-l5-phosphanylidene)acetonitrile **2d** was obtained as white solid in 60% yield; R_f(PE/EA=5:1)=0.35. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.71 – 7.61 (m, 9H), 7.56 (m, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 134.08 (d, *J* = 9.7 Hz), 133.57 (d, *J* = 2.3 Hz), 129.30 (d, *J* = 12.5 Hz), 126.58 (d, *J* = 25.6 Hz), 123.72 (d, *J* = 92.3 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -49.08 (s). ^{31}P NMR (243 MHz, CHLOROFORM-D) δ 30.41 (s). HRMS (ESI) calcd for $C_{21}H_{15}F_3NPS$ $(M+H)^+$ 402.0688, found 402.0685. MP: 161.5 – 162 °C.

5. Table S1. Optimization of Wittig-Horner reaction conditions



Entry	SCF_3 reagent	Base	T°C	Solvent	Yield of 4aa (%) [b]	*Z*/*E*[b]
1	**A1-A4**	n-BuLi	- 78 to rt	THF	0	----
2	**A5**	n-BuLi	- 78 to rt	THF	69	80:20
3	**A**	**n-BuLi**	**- 78 to rt**	**THF**	**98 (96)[c]**	**80:20**
4	**A**	NaH	70	THF	50	78:22
5	**A**	t-BuOK	70	THF	22	79:21
6	**A**	$NaNH_2$	rt	THF	7	67:33
7	**A**	$N(TMS)_2Na$	- 78 to rt	THF	44	60:40
8	**A**	n-BuLi	- 78 to rt	Et_2O	30	70:30
9	**A**	n-BuLi	- 78 to rt	toluene	10	67:33

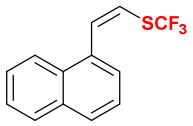


[a] Reaction conditions: preparation of the phosphonium ylide: methyltriphenylphosphoniu bromide (0.2 mmol), base (0.2 mmol), solvent; **A - A5** (0.2 mmol) was added dropwise to the reaction mixture, 30°C, 4 h. then aldehyde (0.17 mmol) was added, 50°C, 12 h. [b] Yields and *Z*/*E* ratio were determined by ^{19}F-NMR using trifluoromethylbenzene as an internal standard. [c] Value in parentheses refers to isolated yield.

6. Typical procedures for the synthesis of compound 4

Methyltriphenylphosphonium bromide (71.4 mg, 0.2 mmol, 1.2 equiv) was added to a dry Seal tube. The tube was evacuated and backfilled with pure N_2 for 3 times. THF (2 mL) was added with syringe and the solution was cooled to -78 ^{o}C, then n-BuLi (1.6 M in hexane, 125 μL, 0.2 mmol, 1.2 equiv) was added, the mixture was allowed to stirred for 1 h. "SCF_3" reagent **A** (52.0 mg, 0.2 mmol, 1.2 equiv) was added, the reaction was stirred for additional 4 h at 30^{o}C. With the prepared trifluoromethylthiolated phosphonium ylides in hand, aldehydes (0.17mmol, 1equiv) was added in situ. The reaction mixture was stirred at corresponding temperature. The reaction was monitored by TLC. After completed the reaction, the reaction was treated with H_2O and extracted three times with EtOAc. The combined organic layers were dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography to give the products.

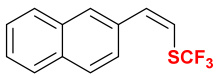
Analytic Data for products



4aa

Z:E= 80:20

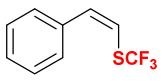
(2-(Naphthalen-1-yl)vinyl)(trifluoromethyl)sulfane 4aa was obtained as colorless oil in 96% yield (*Z:E*=80:20, 41.5 mg); R_f(n-pentane)=0.80. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.98 – 7.94 (m, 1H), 7.93 – 7.90 (m, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 10.1 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 1H), 6.72 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ133.70, 132.21, 131.18, 130.95, 129.85 (q, *J* = 307.6 Hz), 129.16, 128.77, 126.67, 126.41, 126.36, 125.23, 124.26, 117.40 (q, *J* = 3.2 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ-43.21(s). HRMS (ESI) calcd for $C_{13}H_9F_3S$ $[M]^+$: 254.0377; found, 254.0374.



4ab

Z:E= 84:16

(2-(Naphthalen-2-yl)vinyl)(trifluoromethyl)sulfane 4ab was obtained as white solid in 82% yield (*Z:E*=84:16, 35.4 mg); R_f(n-pentane)=0.80. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.89 – 7.81 (m, 3H), 7.78 (s, 1H), 7.50 (m, 3H), 7.00 (d, *J* = 10.5 Hz, 1H), 6.49 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 133.25, 132.97, 132.70, 132.35, 129.72 (q, *J* = 307.9 Hz), 128.39, 128.37, 128.29, 127.81, 126.82, 126.71, 126.25, 114.36 (q, *J* = 3.6 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -43.00 (s). HRMS (ESI) calcd for $C_{13}H_9F_3S$ $[M]^+$: 254.0377; found, 254.0372.

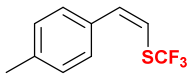


4ac

Z:E= 83:17

Styryl(trifluorometyl)sulfane 4ac was obtained as light yellow oil in 81% yield (*Z:E*=83:17, 28.1 mg); R_f(n-pentane)=0.82. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.43 – 7.29 (m, 5H), 6.85 (d, *J* = 10.4 Hz, 1H), 6.40 (d, *J* = 10.4 Hz, 1H). ^{13}C NMR (151 MHz,

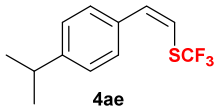
CHLOROFORM-D) δ135.17, 132.32, 129.67 (q, *J* = 307.8 Hz), 128.79, 128.71, 128.39, 114.01 (q, *J* = 3.0 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -42.81(s). HRMS (ESI) calcd for $C_9H_7F_3S$ [M]$^+$: 204.0221; found, 204.0220.



4ad

Z:E= 84:16

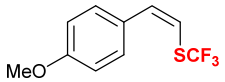
(4-methylstyryl)(trifluoromethyl)sulfane 4ad was obtained as colorless oil in 80% yield (*Z:E*=84:16, 29.7 mg); R_f(n-pentane)=0.82. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 10.5 Hz, 1H), 6.34 (d, *J* = 10.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ138.46, 132.46, 132.40, 129.73 (q, *J* = 307.7 Hz), 129.39, 128.78, 112.89 (q, *J* = 3.5 Hz), 21.42. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -43.15 (s). HRMS (ESI) calcd for $C_{10}H_9F_3S$ [M]$^+$: 218.0377; found, 218.0379.



4ae

Z:E= 84:16

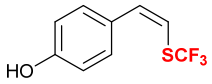
(4-isopropylstyryl)(trifluoromethyl)sulfane 4ae was obtained as colorless oil in 83% yield (*Z:E*=84:16, 34.7 mg); R_f(n-pentane)=0.82. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 10.5 Hz, 1H), 6.35 (d, *J* = 10.5 Hz, 1H), 2.94 (m, 1H), 1.28 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 149.37, 132.40, 129.74 (q, *J* = 307.7 Hz), 128.91, 127.06, 126.79, 112.87 (q, *J* = 3.5 Hz), 34.11, 23.97. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -43.17 (s). HRMS (ESI) calcd for $C_{12}H_{13}F_3S$ [M]$^+$: 246.0690; found, 246.0688.



4af

Z:E= 78:22

(4-methoxystyryl)(trifluoromethyl)sulfane 4af was obtained as pale yellow oil in 68% yield (*Z:E*=78:22, 27.1 mg); R_f(n-pentane/EA 10:1)=0.74. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.31 (d, *J* = 7.4 Hz, 2H), 6.93 (d, *J* = 7.4 Hz, 2H), 6.80 (d, *J* = 10.4 Hz, 1H), 6.27 (dd, *J* = 10.4, 1.4 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 159.62, 132.42, 130.36, 129.74 (q, *J* = 307.5 Hz), 127.86, 114.09, 111.38 (q, *J* = 3.3 Hz), 55.42. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -43.16 (s). HRMS (ESI) calcd for $C_{10}H_9F_3OS$ [M]$^+$: 234.0326; found, 234.0328.

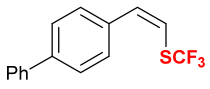


4ag

Z:E= 86:14

(4-methoxystyryl)(trifluoromethyl)sulfane 4ag was obtained as white solid in 83% yield (*Z:E*=86:14, 31.1 mg); R_f(n-pentane/EA 10:1)=0.45. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.25 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 10.4 Hz, 1H), 6.26 (dd, *J* = 10.4, 0.9 Hz, 1H), 5.15 (s, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D)

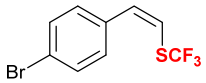
δ 155.61, 132.31, 130.59, 129.71 (q, *J* = 307.7 Hz), 128.12, 115.60, 111.57 (q, *J* = 3.4 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -43.19 (s). HRMS (ESI) calcd for $C_9H_7F_3OS$ $[M]^+$: 220.0170; found, 220.0169 . MP: 52.2 – 54.7 °C.



4ah

Z:E= 82:18

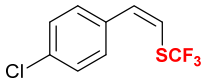
(2-([1,1'-biphenyl]-4-yl)vinyl)(trifluoromethyl)sulfane 4ah was obtained as white solid in 91% yield (*Z:E*=82:18, 43.3 mg); R_f(n-pentane)=0.77. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.69 – 7.65 (m, 4H), 7.51 – 7.40 (m, 5H), 6.91 (d, *J* = 10.5 Hz, 1H), 6.47 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 141.11, 140.41, 134.11, 131.89, 129.68 (q, *J* = 307.9 Hz), 129.30, 129.01, 127.77, 127.32, 127.17, 125.09, 113.88 (q, *J* = 3.3 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -45.49 (s). HRMS (ESI) calcd for $C_{15}H_{11}F_3S$ $[M]^+$: 280.0534; found, 280.0529.



4ai

Z:E= 79:21

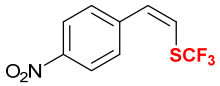
(4-bromostyryl)(trifluoromethyl)sulfane 4ai was obtained as colorless oil in 98% yield (*Z:E*=79:21, 47.0 mg); R_f(n-pentane)=0.60. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.51 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 10.4 Hz, 1H), 6.43 (dd, *J* = 10.5, 1.2 Hz, 1H).^{13}C NMR (101 MHz, CHLOROFORM-D) δ 134.01, 131.89, 131.21, 130.30, 129.50 (q, *J* = 308.0 Hz), 122.45, 114.92 (q, *J* = 3.4 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -42.93 (s). HRMS (ESI) calcd for $C_9H_6BrF_3S$ $[M]^+$: 281.9326; found, 281.9327.



4aj

Z:E= 74:26

(4-chlorostyryl)(trifluoromethyl)sulfane 4aj was obtained as colorless oil in 99% yield (*Z:E*=74:26, 40.1 mg); R_f(n-pentane)=0.60. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 10.5 Hz, 1H), 6.34 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ134.25, 133.58, 131.20, 130.05, 129.53 (q, *J* = 307.7 Hz), 128.94, 114.77 (q, *J* = 3.6 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -42.94 (s). HRMS (ESI) calcd for $C_9H_6ClF_3S$ $[M]^+$: 237.9831; found, 237.9828.

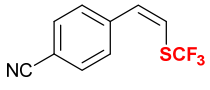


4ak

Z:E= 75:25

(4-nitrostyryl)(trifluoromethyl)sulfane 4ak was obtained as pale yellow oil in 99% yield (*Z:E*=75:25, 41.9 mg); R_f(n-pentane/EA 10:1)=0.30. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 10.7 Hz, 1H), 6.64 (d, *J* = 10.7 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ-147.08, 141.34, 129.70, 129.42, 129.19 (q, *J* =

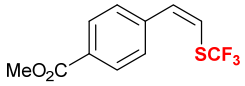
308.1 Hz), 123.99, 118.75 (q, *J* = 3.7 Hz). ^{19}F NMR (565 MHz, CHLOROFORM-D) δ -42.74 (s). HRMS (ESI) calcd for $C_9H_6F_3NO_2S$ $[M]^+$: 249.0071; found, 249.0072.



4al

Z:E=88:12

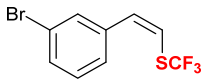
4-(2-((trifluoromethyl)thio)vinyl)benzonitrile 4al was obtained as yellow oil in 91% yield (*Z:E*=88:12, 35.4 mg); R_f(n-pentane/EA 10:1)=0.33. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 10.7 Hz, 1H), 6.59 (d, *J* = 10.7 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 139.43, 132.44, 130.13, 129.21, 129.21 (d, *J* = 308.3 Hz), 118.57, 117.99 (q, *J* = 3.5 Hz), 111.71. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -45.17 (s). HRMS (ESI) calcd for $C_{10}H_6F_3NS$ $[M]^+$: 229.0173; found, 229.0171.



4am

Z:E=86:14

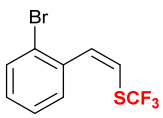
Methyl-4-(2-((trifluoromethyl)thio)vinyl)benzoate 4am was obtained as white solid in 92% yield (*Z:E*=86:14, 41.1 mg); R_f(n-pentane/EA 10:1)=0.46. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 10.6 Hz, 1H), 6.51 (d, *J* = 10.6 Hz, 1H), 3.92 (s, 3H).^{13}C NMR (101 MHz, CHLOROFORM-D) δ 166.58, 139.43, 130.93, 129.93, 129.67, 129.44 (q, *J* = 307.9 Hz), 128.62, 116.55 (q, *J* = 3.7 Hz), 52.29. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -45.17 (s). HRMS (ESI) calcd for $C_{11}H_9F_3O_2S$ $[M]^+$: 262.0275; found, 262.0278.



4an

Z:E= 80:20

(3-bromostyryl)(trifluoromethyl)sulfane 4an was obtained as yellow oil in 65% yield (*Z:E*=80:20, 31.2 mg); R_f(n-pentane)=0.60. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (s, 1H), 7.44 (td, *J* = 5.1, 2.1 Hz, 1H), 7.26 (d, *J* = 5.1 Hz, 2H), 6.76 (d, *J* = 10.6 Hz, 1H), 6.46 (d, *J* = 10.6 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 137.12, 131.66, 131.33, 130.69, 130.20, 129.48 (q, *J* = 307.9 Hz), 127.19, 122.83, 115.86 (q, *J* = 3.6 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -45.32 (s). HRMS (ESI) calcd for $C_9H_6BrF_3S$ $[M]^+$: 281.9326; found, 281.9325.

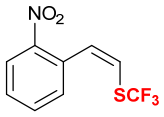


4ao

Z:E= 75:25

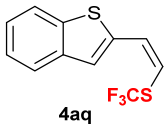
(2-bromostyryl)(trifluoromethyl)sulfane 4ao was obtained as colorless oil in 99% yield (*Z:E*=75:25, 47.5 mg); R_f(n-pentane)=0.60. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.63 (d, *J* = 8.3 Hz, 1H), 7.34 (m, 2H), 7.23 – 7.15 (m, 1H), 7.00 (d, *J* = 10.4 Hz, 1H), 6.54 (d, *J* = 10.4 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 135.11,

133.16, 132.17, 129.94, 129.66, 129.60 (q, J = 308.0 Hz), 127.40, 123.93, 116.75 (q, J = 3.5 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -42.73 (s). HRMS (ESI) calcd for $C_9H_6BrF_3S$ $[M]^+$: 281.9326; found, 281.9322.



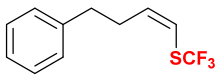
4ap
Z:E= 66:34

(2-nitrostyryl)(trifluoromethyl)sulfane 4ap was obtained as pale yellow oil in 82% yield (*Z:E*=66:34, 34.7 mg); R_f(n-pentane/EA 10:1)=0.34. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.13 (d, J = 8.2 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.53 (t, J = 8.1 Hz, 1H), 7.46 (d, J = 7.4 Hz, 1H), 7.29 (d, J = 10.2 Hz, 1H), 6.60 (d, J = 10.2 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 147.39, 134.0, 133.64, 130.93, 130.54, 129.51, 129.49 (q, J = 308.0 Hz), 125.29, 117.60 (q, J = 3.1 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -42.26 (s). HRMS (ESI) calcd for $C_9H_6F_3NO_2S$ $[M]^+$: 249.0071; found, 249.0074.



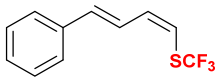
4aq
Z:E= 82:18

2-(2-((trifluoromethyl)thio)vinyl)benzo[b]thiophene 4aq was obtained as white solid in 68% yield (*Z:E*=82:18, 30.1 mg); R_f(n-pentane)=0.85. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.85 – 7.82 (m, 1H), 7.77 –7.79(m 1H), 7.40 – 7.36 (m, 2H), 7.33 (s, 1H), 7.07 (d, J = 10.1 Hz, 1H), 6.41 (d, J = 10.2 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ139.59, 138.87, 138.16, 130.97 (t, J = 308.7 Hz), 127.51, 126.85, 125.44, 124.90, 124.09, 122.36, 113.28 (d, J = 3.4 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -42.43 (s). HRMS (ESI) calcd for $C_{11}H_7F_3S_2$ $[M]^+$: 259.9941; found, 259.9944.



4ar
Z:E= 50:50

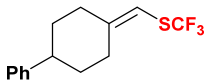
(4-phenylbut-1-en-1-yl)(trifluoromethyl)sulfane 4ar was obtained as colorless oil in 35% yield (*Z:E*= 50:50, 13.8 mg); R_f(n-pentane)=0.88. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.32 (d, J = 7.2 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.26 –7.16 (m, 3H), 6.33 – 6.05 (m, 2H), 2.78 – 2.72 (m, 2H), 2.59 – 2.49 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ140.75, 138.83, 129.75 (d, J = 307.0 Hz), 128.56, 128.5, 126.29, 113.69 (d, J = 2.8 Hz), 34.74, 30.91. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -43.08 (s). HRMS (ESI) calcd for $C_{11}H_{11}F_3S$ $[M]^+$: 232.0534; found, 232.0536.



4as
Z:E= 61:39

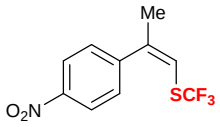
***3E*-4-phenylbuta-1,3-dien-1-yl)(trifluoromethyl)sulfane 4as** was obtained as colorless oil in 85% yield (*Z:E*= 61:39, 33.3 mg); R_f(n-pentane)=0.85. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (d, J = 7.3 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.10 (dd, J = 15.3, 11.1 Hz,

1H), 6.78 – 6.72 (m, 2h), 6.17 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ137.39, 136.43, 129.61 (q, *J* = 307.5 Hz), 128.91, 128.79, 128.08, 127.10, 126.95, 122.94, 112.63 (q, *J* = 2.8 Hz). ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -42.26 (s). HRMS (ESI) calcd for $C_{11}H_9F_3S$ $[M]^+$: 230.0377; found, 230.0373.



4at

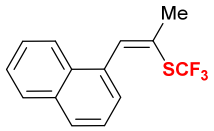
((4-phenylcyclohexylidene)methyl)(trifluoromethyl)sulfane 4at was obtained as colorless oil in 42% yield (19.4 mg); R_f(n-pentane)=0.76. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.19 (m, 3H), 5.91 (s, 1H), 3.09 (d, *J* = 14.7 Hz, 1H), 2.76 (t, *J* = 12.2 Hz, 1H), 2.55 (d, *J* = 13.7 Hz, 1H), 2.41 – 2.29 (m, 1H), 2.13 – 2.04 (m, 3H), 1.66 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 155.07, 146.00, 130.03 (q, *J* = 306.9 Hz), 128.61, 126.92, 126.42, 103.63 (q, *J* = 2.0 Hz), 44.14, 36.67, 35.31, 34.43, 30.50. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -43.02 (s). HRMS (ESI) calcd for $C_{14}H_{15}F_3S$ $[M]^+$: 272.0847; found, 272.0851.



4au

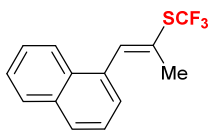
Z:*E*= 55:45

(2-(4-nitrophenyl)prop-1-en-1-yl)(trifluoromethyl)sulfane 4au was obtained as pale yellow oil in 65% yield (*Z*:*E*= 55:45, 29 mg); R_f(n-pentane/EA 10:1)=0.30. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 6.57 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 146.87, 146.11, 143.44, 129.55 (q, *J* = 307.7 Hz), 126.63, 124.05, 114.81 (q, *J* = 3.0 Hz), 25.43. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -42.75 (s). HRMS (ESI) calcd for $C_{10}H_8F_3NO_2S$ $[M]^+$: 263.0228; found, 263.0226.



4ea

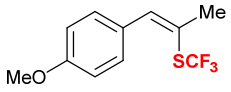
(*Z*)-(1-(naphthalen-1-yl)prop-1-en-2-yl)(trifluoromethyl)sulfane 4ea was obtained as colorless oil in 37% yield (17.0 mg); R_f(n-pentane)=0.78. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.89 – 7.85 (m, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.52 (m, 2H), 7.54 – 7.50 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.33 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 135.35, 133.45, 133.21, 131.47, 129.74 (d, *J* = 308.9 Hz), 128.62, 128.56, 127.59, 127.37, 126.38, 126.15, 125.23, 124.59, 25.86. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -37.97 (s). HRMS (ESI) calcd for $C_{14}H_{11}F_3S$ $[M]^+$: 268.0534; found, 268.0533.



4ea'

(*E*)-(1-(naphthalen-1-yl)prop-1-en-2-yl)(trifluoromethyl)sulfane 4ea' was obtained as colorless oil in 32% yield (14.0 mg); R_f(n-pentane)=0.82. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.92

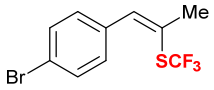
– 7.86 (m, 2H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.59 (s, 1H), 7.57 – 7.51 (m, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 141.09, 133.65, 133.12, 131.40, 130.35 (q, *J* = 308.8 Hz), 128.76, 128.68, 126.86, 126.69, 126.60, 126.34, 125.32, 124.63, 21.89. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -40.56 (s). HRMS (ESI) calcd for $C_{14}H_{11}F_3S$ $[M]^+$: 268.0534; found, 268.0531.



4ef

Z:*E* = 63:37

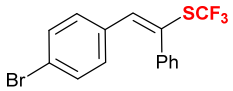
(1-(4-methoxyphenyl)prop-1-en-2-yl)(trifluoromethyl)sulfane 4ef was obtained as colorless oil in 85% yield (*Z*:*E*= 63:37, 35.8 mg); R_f(n-pentane/EA 10:1)=0.56. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.86 (s, 1H), 3.83 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ159.45, 137.75, 130.81, 129.95 (q, *J* = 309.5 Hz), 128.20, 121.63, 113.73, 55.39, 27.10. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -38.29 (s). HRMS (ESI) calcd for $C_{11}H_{11}F_3OS$ $[M]^+$: 248.0483; found, 248.0485.



4ei

Z:*E* = 62:38

(1-(4-bromophenyl)prop-1-en-2-yl)(trifluoromethyl)sulfane 4ei was obtained as colorless oil in 89% yield (*Z*:*E*= 62:38, 44.8 mg); R_f(n-pentane)=0.86. NMR of the major isomer: ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 136.75, 134.50, 131.53, 130.90, 129.69 (q, *J* = 309.3 Hz), 125.00, 122.19, 26.96. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -38.07 (s). HRMS (ESI) calcd for $C_{10}H_8BrF_3S$ $[M]^+$: 295.9482; found, 295.9483.



4fi

(*E*)-(2-(4-bromophenyl)-1-phenylvinyl)(trifluoromethyl)sulfane 4fi was obtained as colorless oil in 20% yield (12.3 mg); R_f(n-pentane)=0.84. ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.38 – 7.31 (m, 5H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.20 (s, 1H), 6.88 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 139.46, 137.50, 134.30, 131.64, 131.06, 129.49, 129.02, 128.98, 128.91, 122.72. ^{19}F NMR (283 MHz, CHLOROFORM-D) δ -40.81 (s). HRMS (ESI) calcd for $C_{15}H_{10}BrF_3S$ $[M]^+$: 357.9639; found, 357.9635.

7. References

[1] G. Teverovskiy, D. S. Surry and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2011, **50**, 7312.

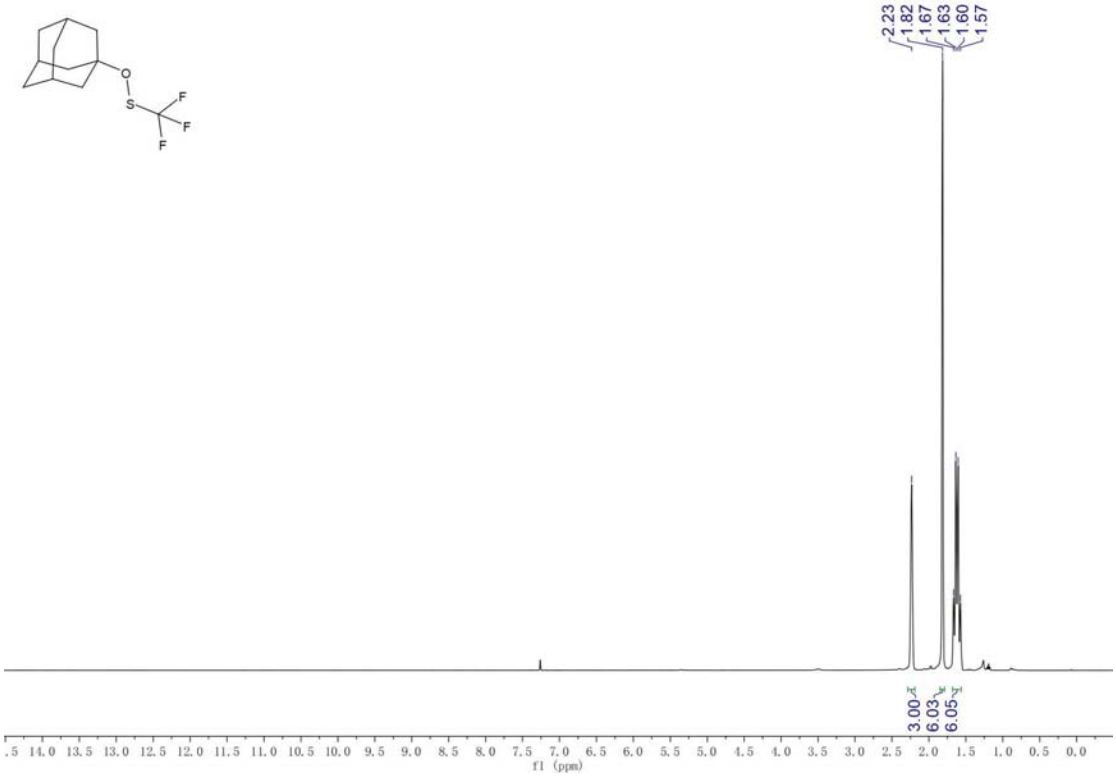
[2] C. Xu, B. Ma and Q. Shen, *Angew. Chem. Int. Ed.*, 2014, **53**, 9316.

[3] R. Pluta, P. Nikolaienko and M. Rueping, *Angew. Chem. Int. Ed.*, 2014, **53**, 1650.

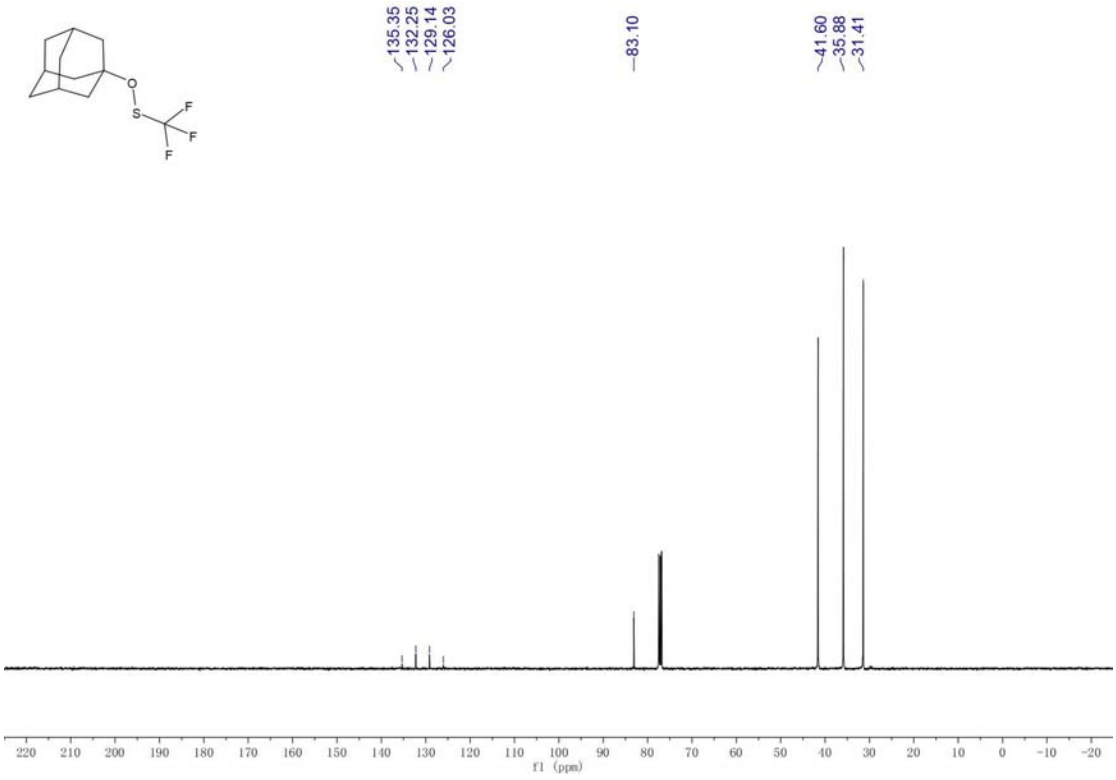
[4] P. Zhang, M. Li, X. -S. Xue, C. Xu, Q. Zhao, Y. Liu, H. Wang, Y. Guo, L. Lu and Q. Shen, *J. Org. Chem*. 2016, **81**, 7486.

[5] X. Shao, X. Wang, T. Yang, L. Lu and Q. Shen, *Angew. Chem. Int. Ed.*, 2013, **52**, 3457.

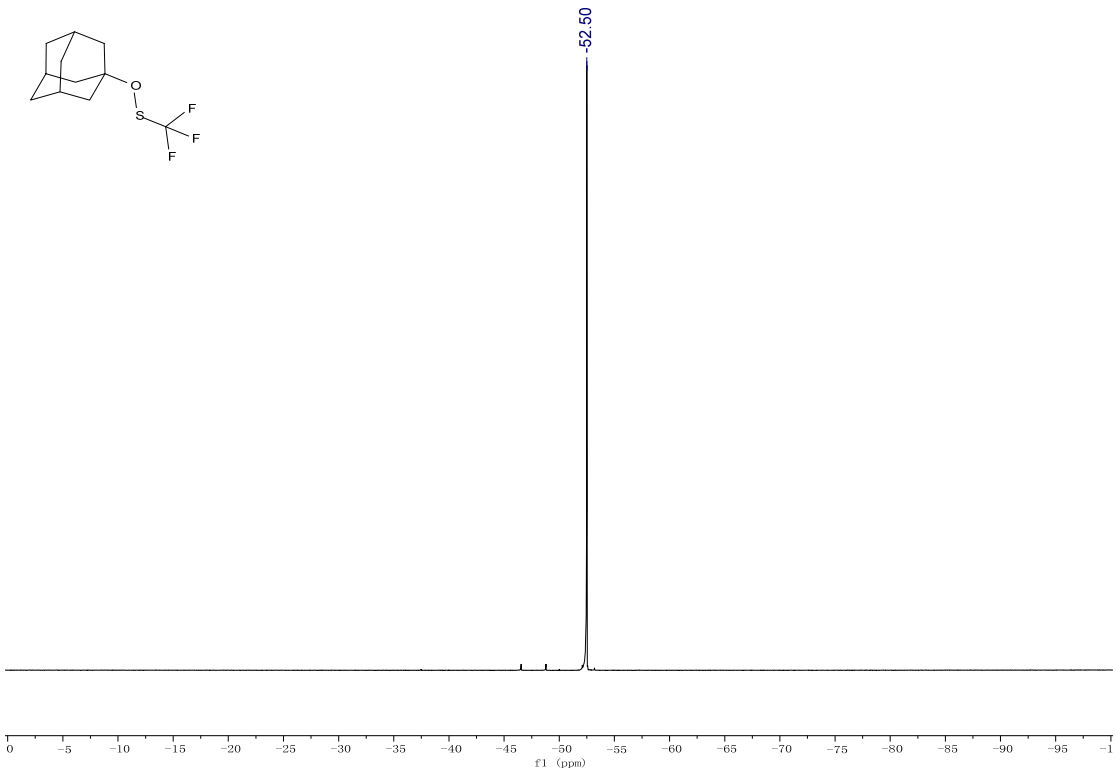
8. Copies of ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra of the products.



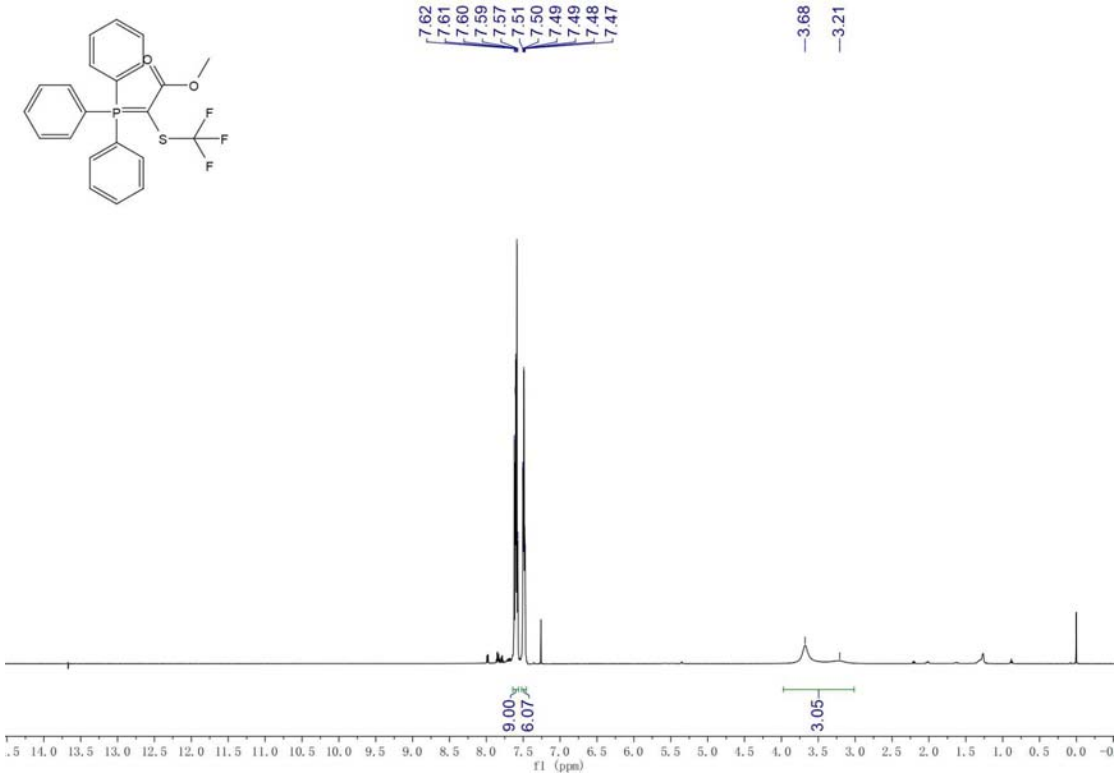
^{1}H NMR spectrum of **A** in $CDCl_3$ (400 MHz)



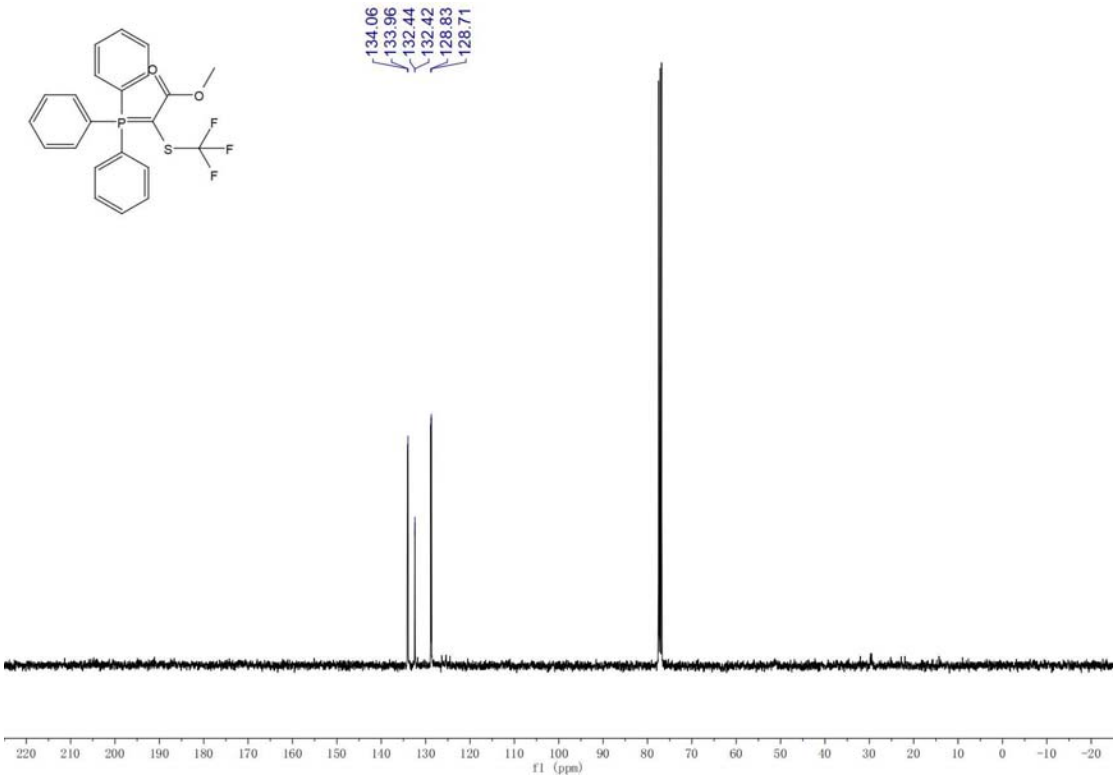
^{13}C NMR spectrum of **A** in $CDCl_3$ (101 MHz)



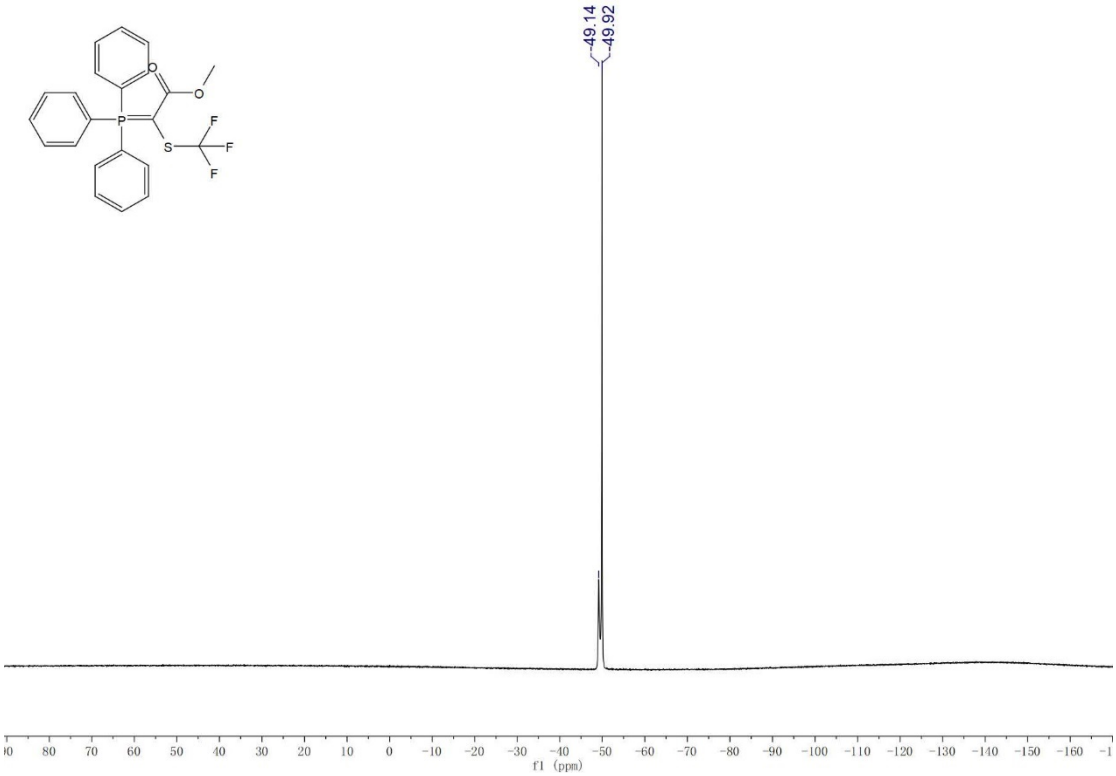
^{19}F NMR spectrum of **A** in $CDCl_3$ (283 MHz)



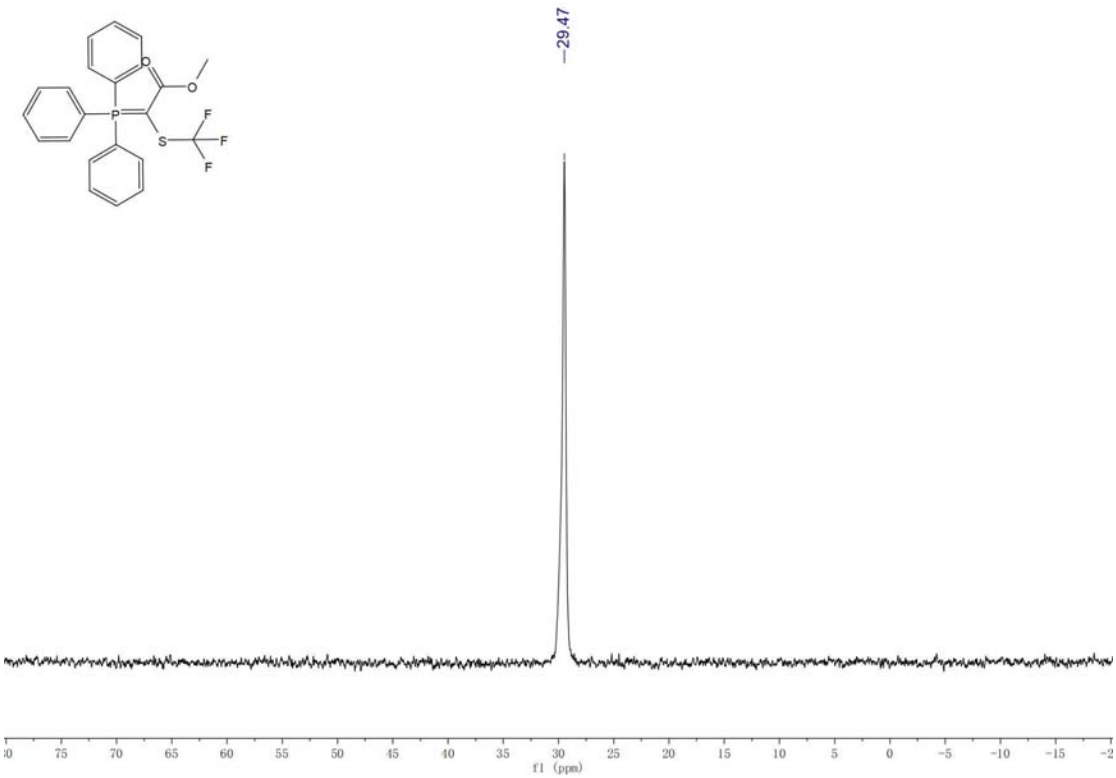
^{1}H NMR spectrum of **2b** in $CDCl_3$ (400 MHz)



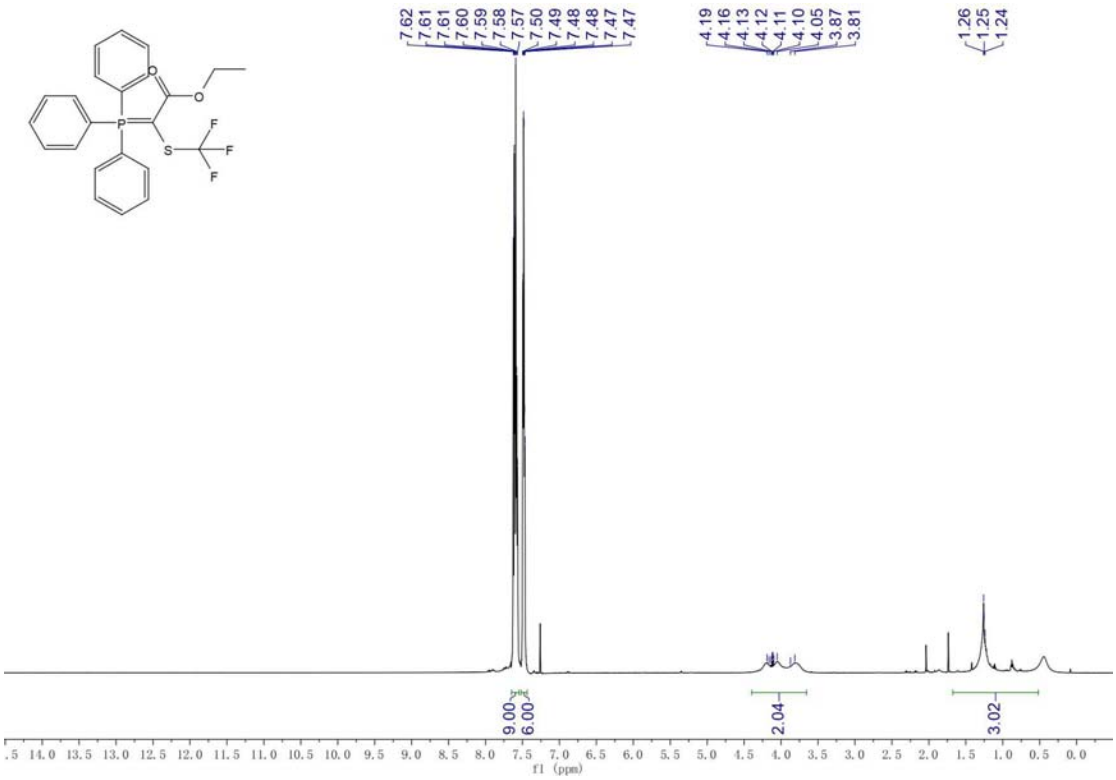
^{13}C NMR spectrum of **2b** in $CDCl_3$ (101 MHz)



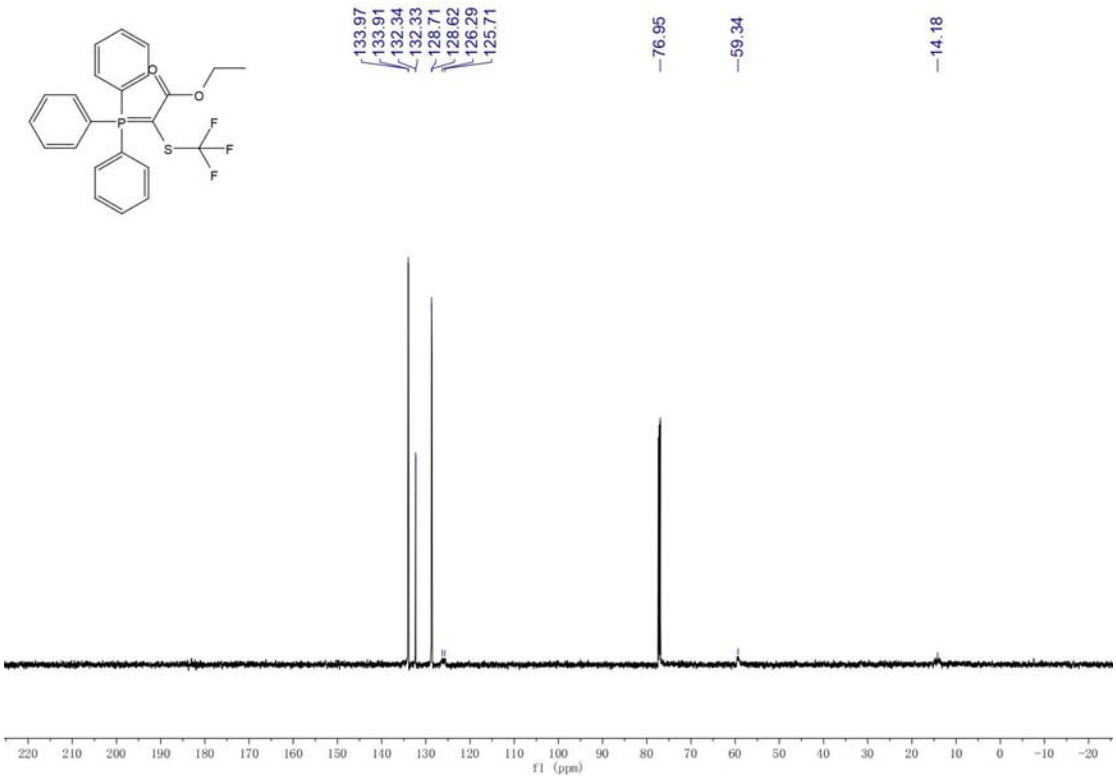
^{19}F NMR spectrum of **2b** in $CDCl_3$ (565 MHz)



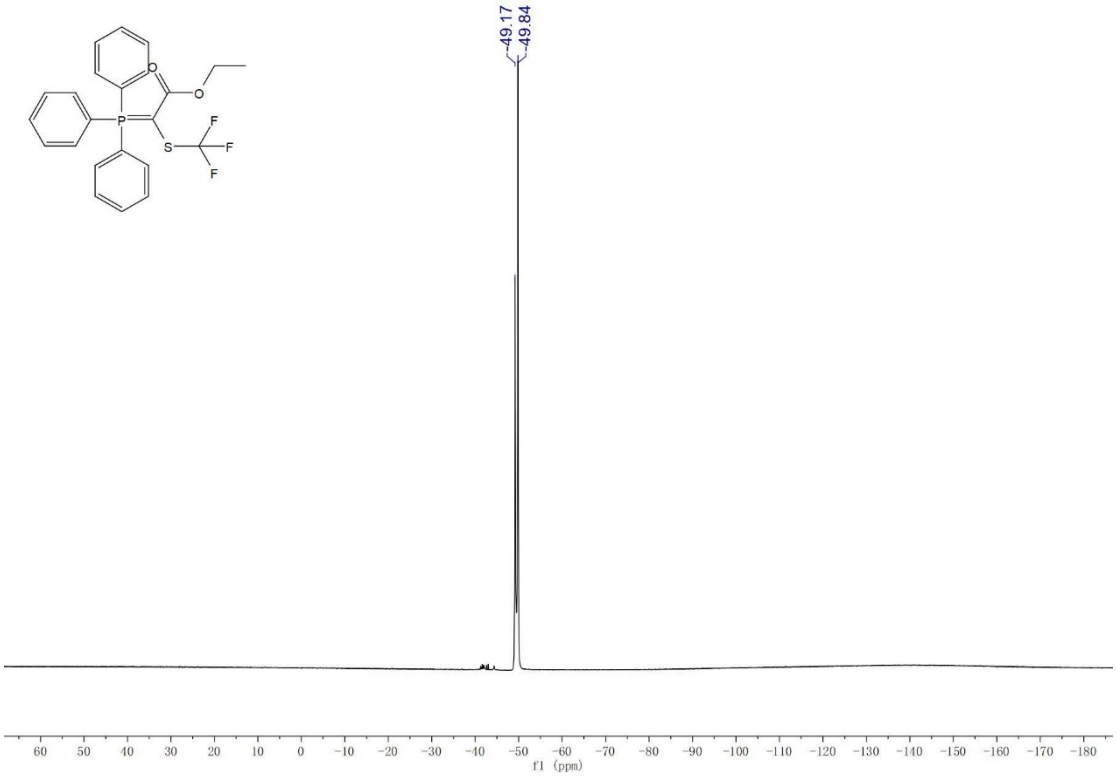
^{31}P NMR spectrum of **2b** in $CDCl_3$ (243 MHz)



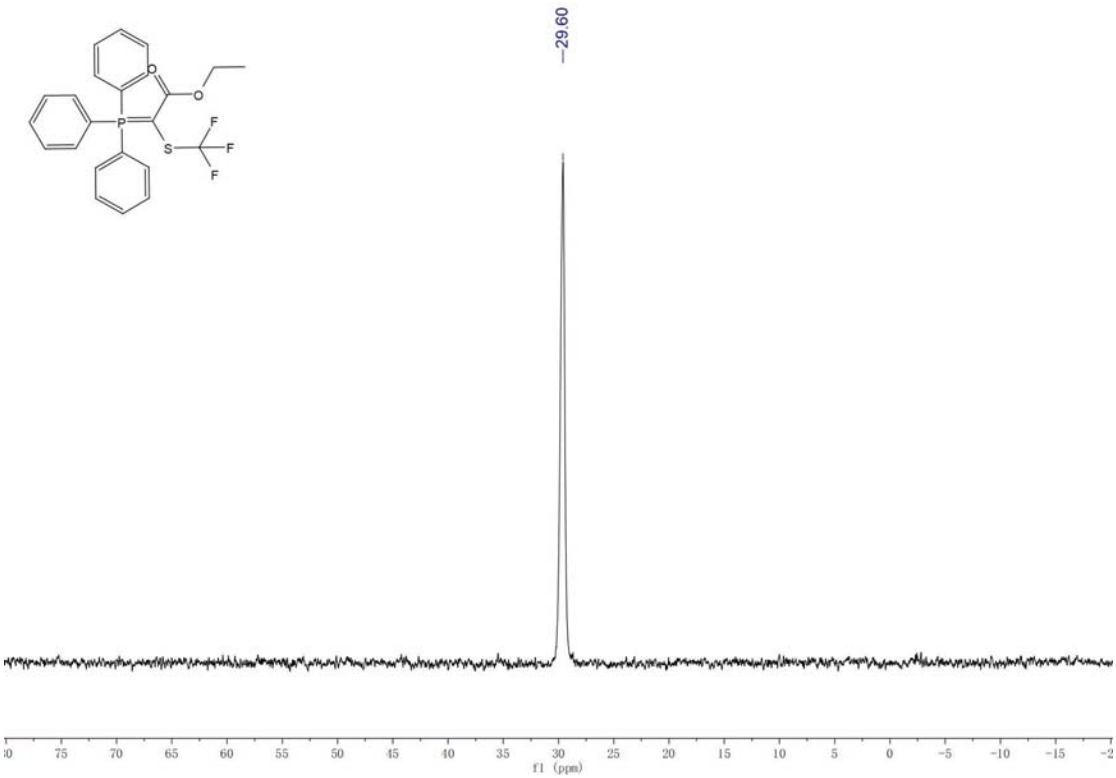
^{1}H NMR spectrum of **2c** in $CDCl_3$ (600 MHz)



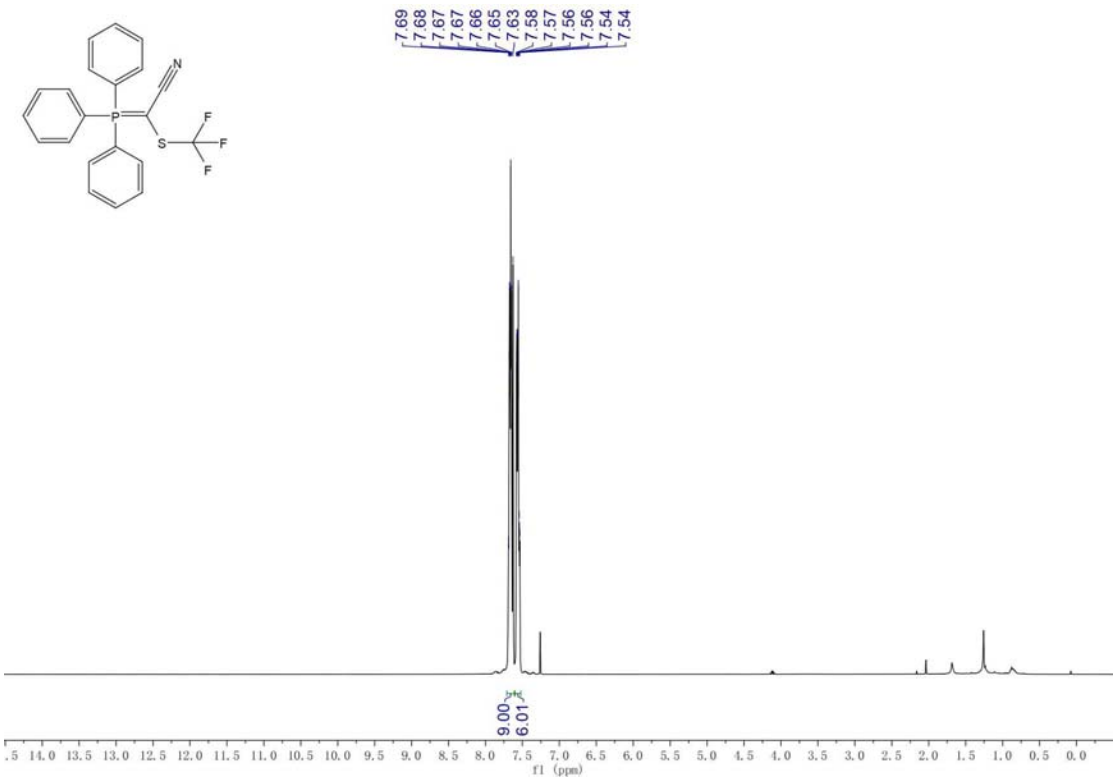
^{13}C NMR spectrum of **2c** in $CDCl_3$ (151 MHz)



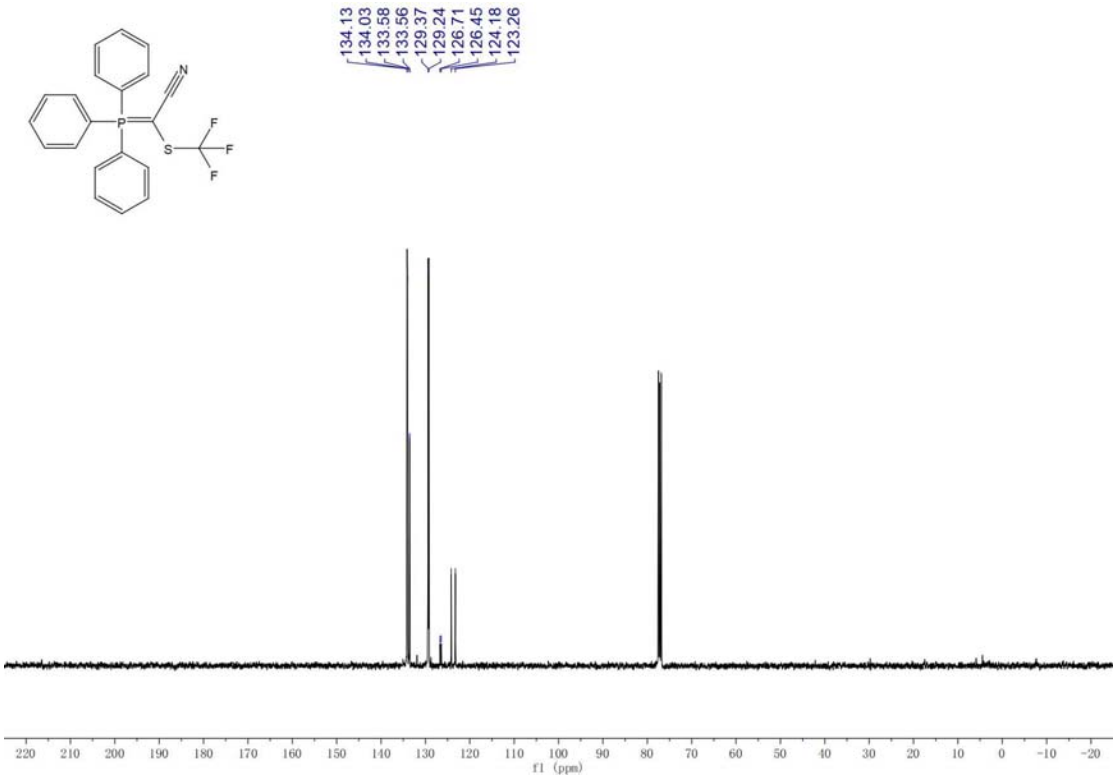
^{19}F NMR spectrum of **2c** in $CDCl_3$ (565 MHz)



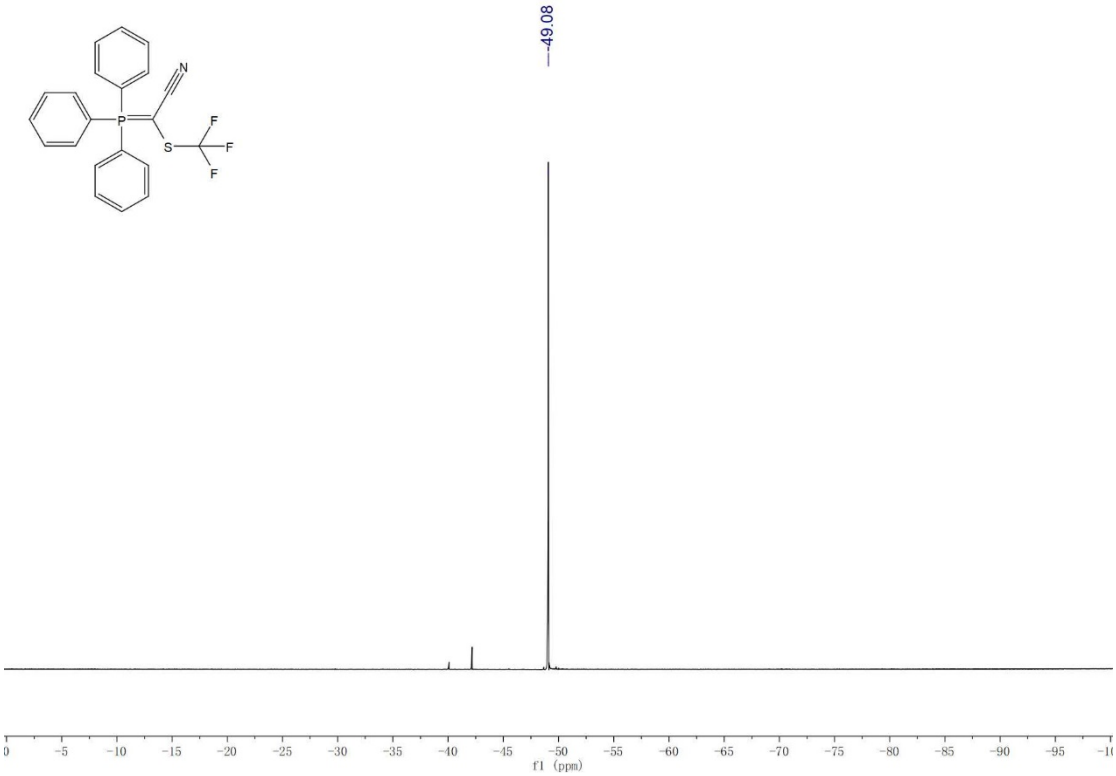
^{31}P NMR spectrum of **2c** in $CDCl_3$ (243 MHz)



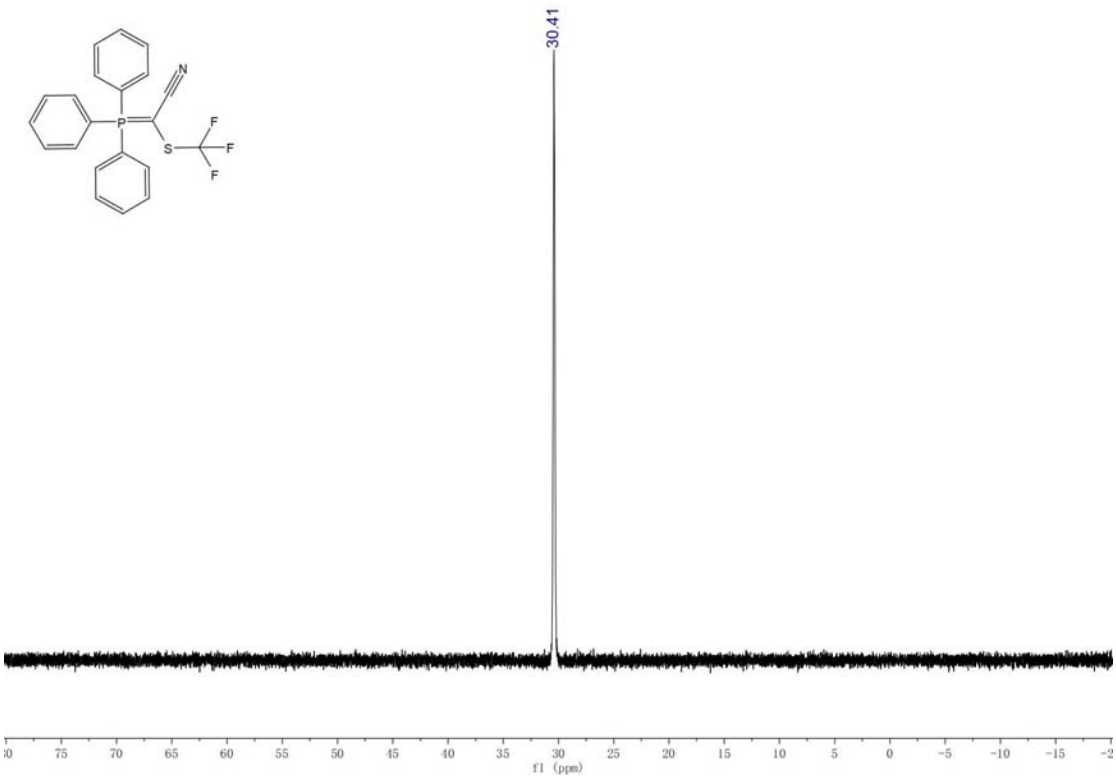
^{1}H NMR spectrum of **2d** in $CDCl_3$ (400 MHz)



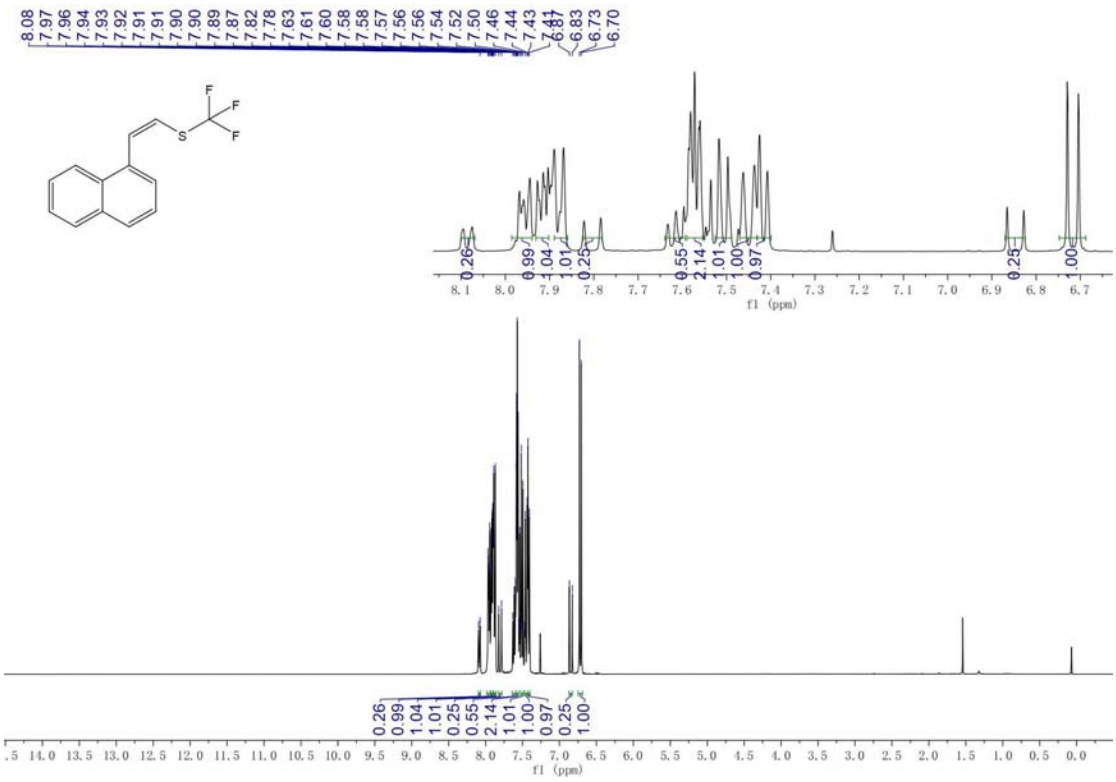
^{13}C NMR spectrum of **2d** in $CDCl_3$ (101 MHz)



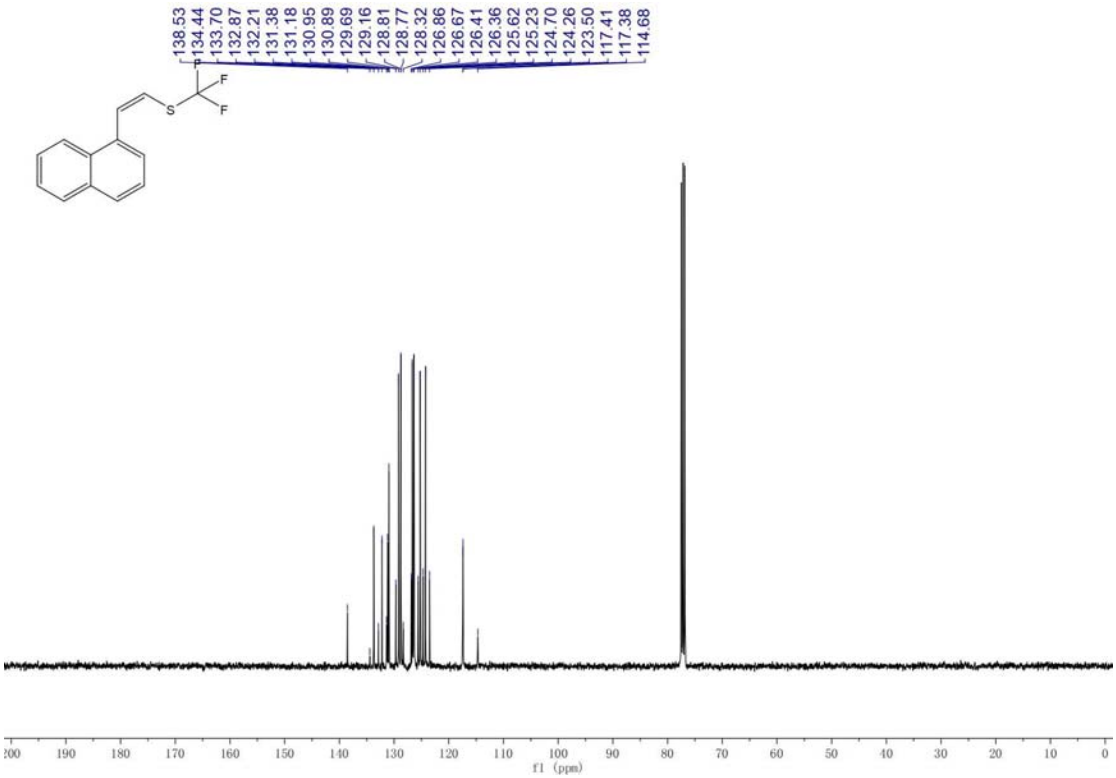
^{19}F NMR spectrum of **2d** in $CDCl_3$ (283 MHz)



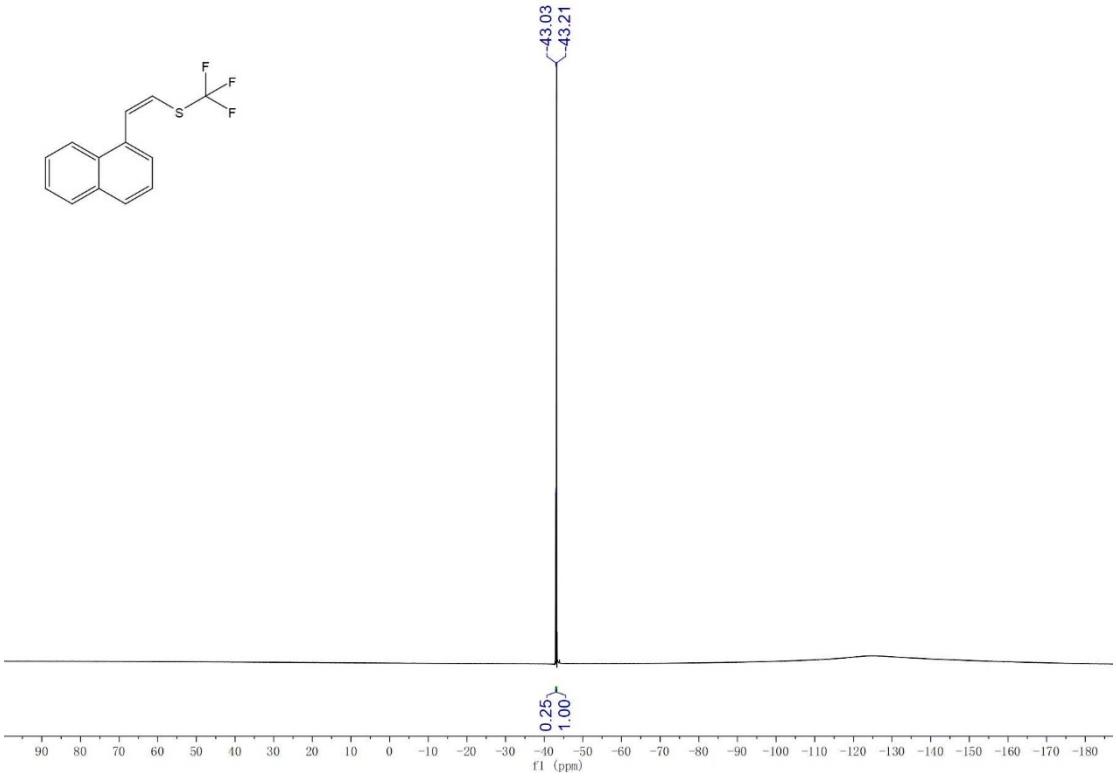
^{31}P NMR spectrum of **2d** in $CDCl_3$ (243 MHz)



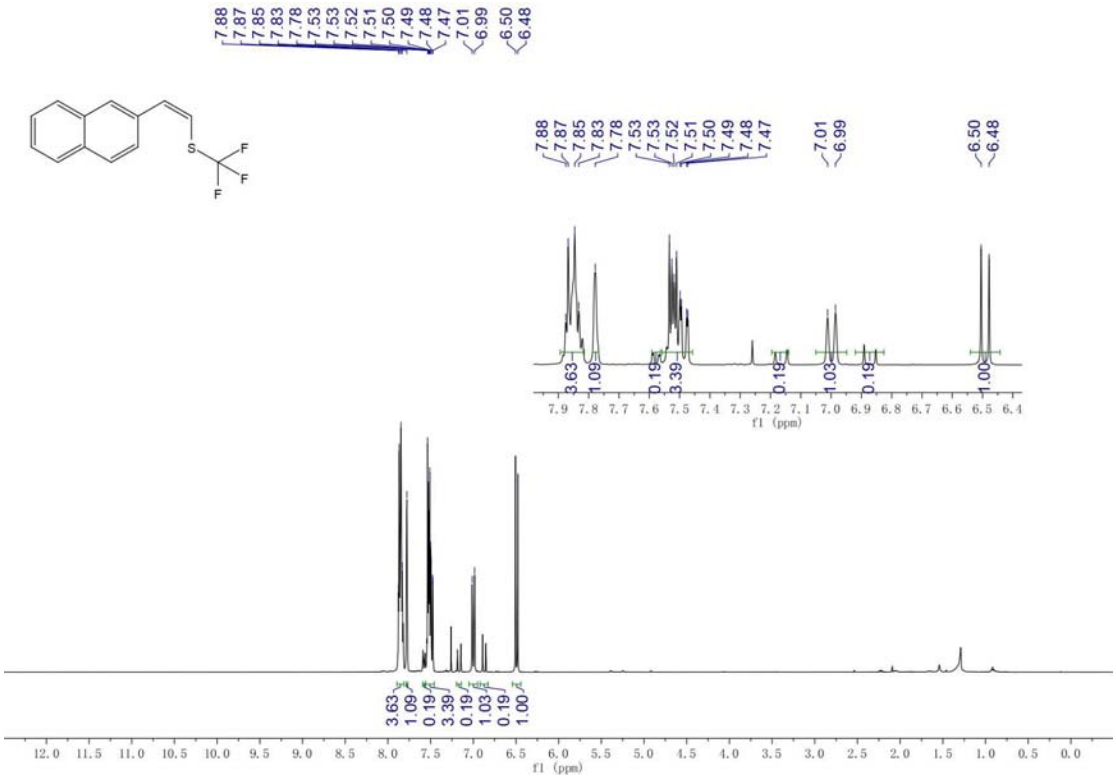
^{1}H NMR spectrum of **4aa** in $CDCl_3$ (400 MHz)



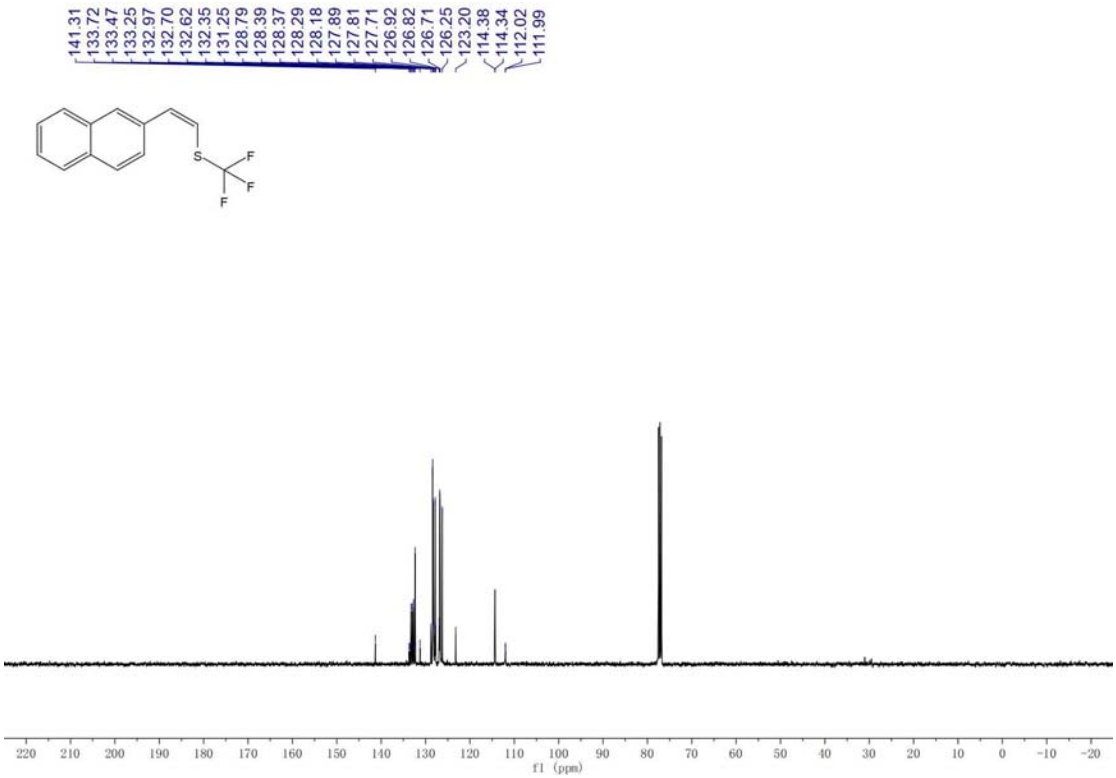
^{13}C NMR spectrum of **4aa** in $CDCl_3$ (101 MHz)



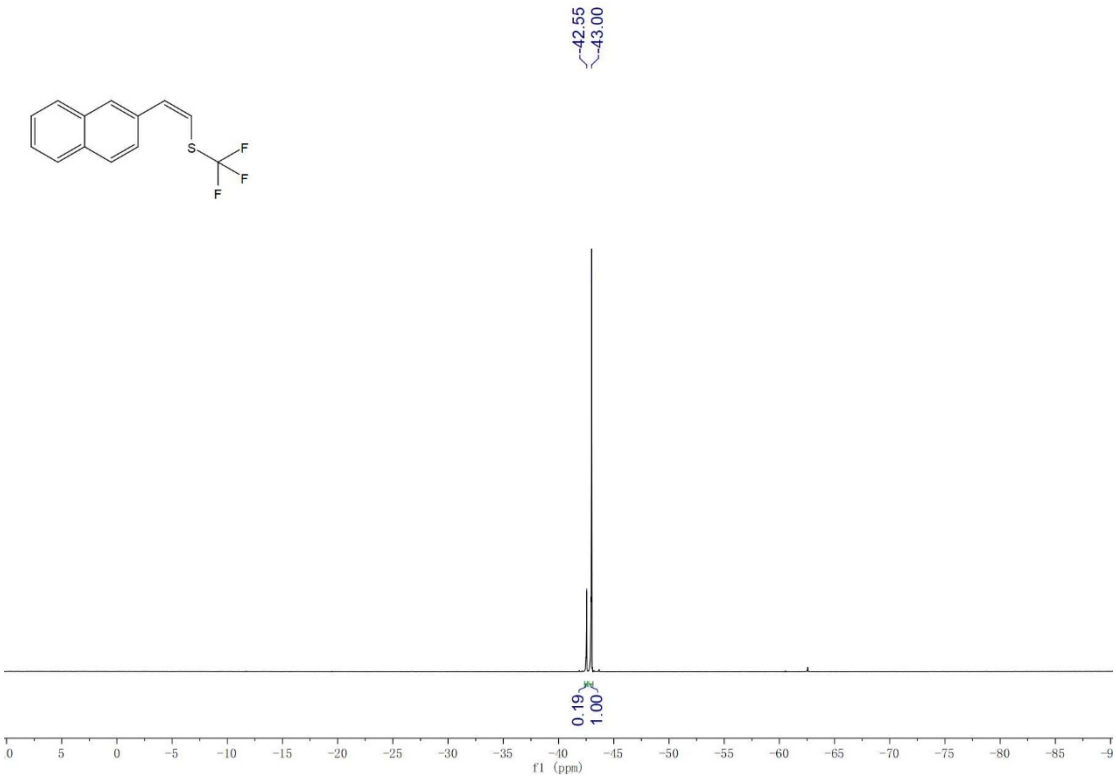
^{19}F NMR spectrum of **4aa** in $CDCl_3$ (283 MHz)



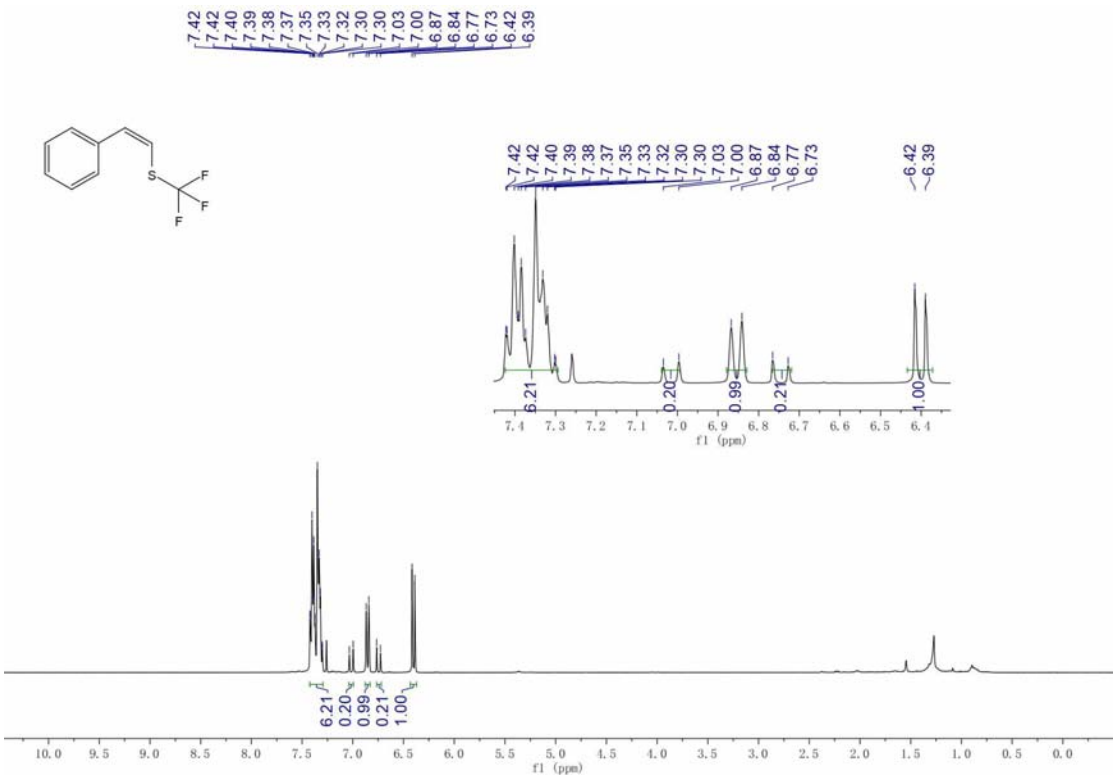
^{1}H NMR spectrum of **4ab** in $CDCl_3$ (400 MHz)



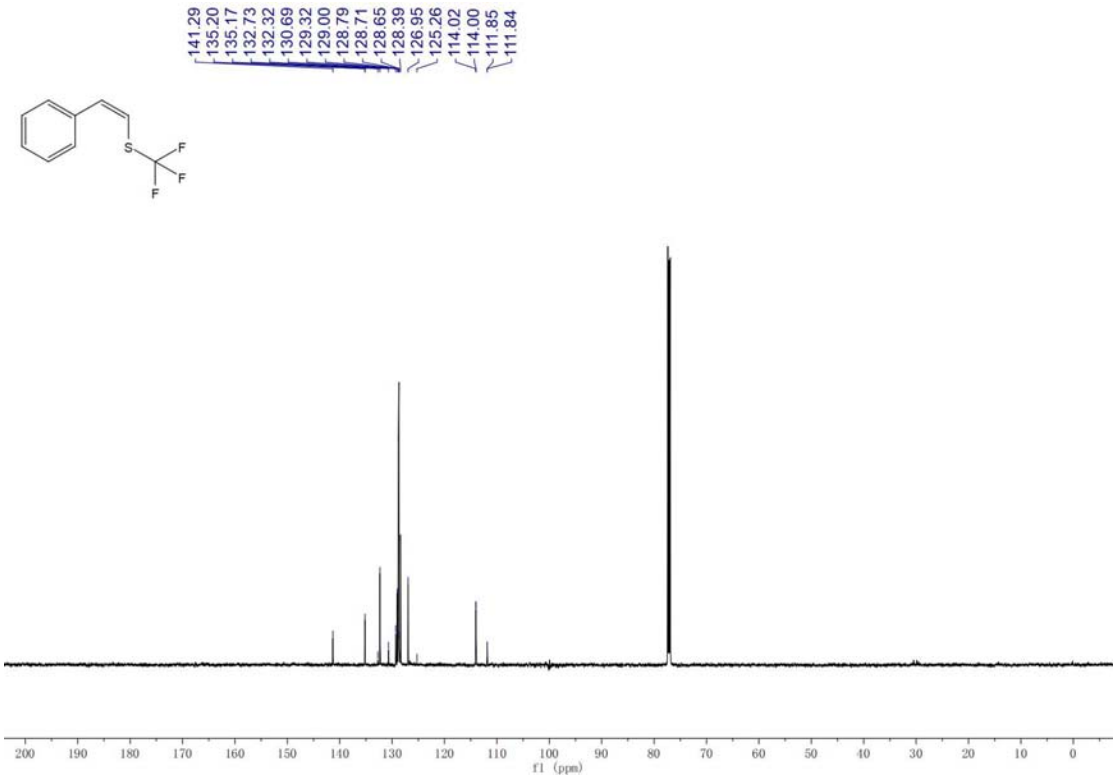
^{13}C NMR spectrum of **4ab** in $CDCl_3$ (101 MHz)



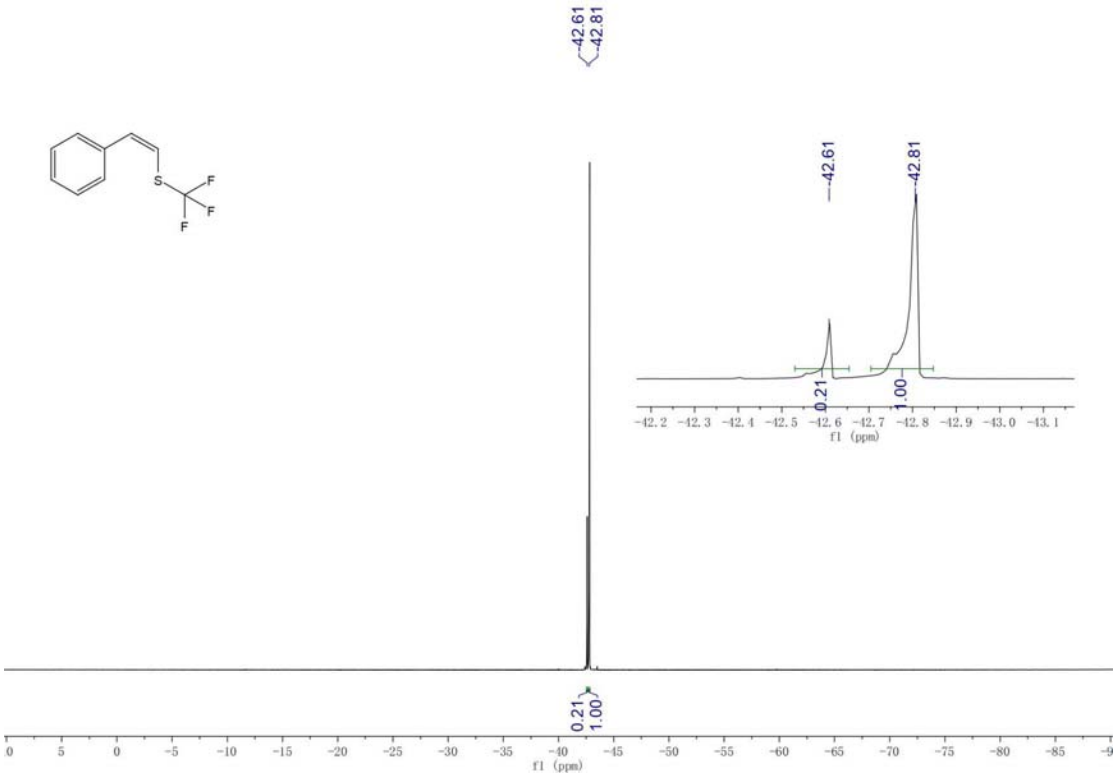
^{19}F NMR spectrum of **4ab** in $CDCl_3$ (283 MHz)



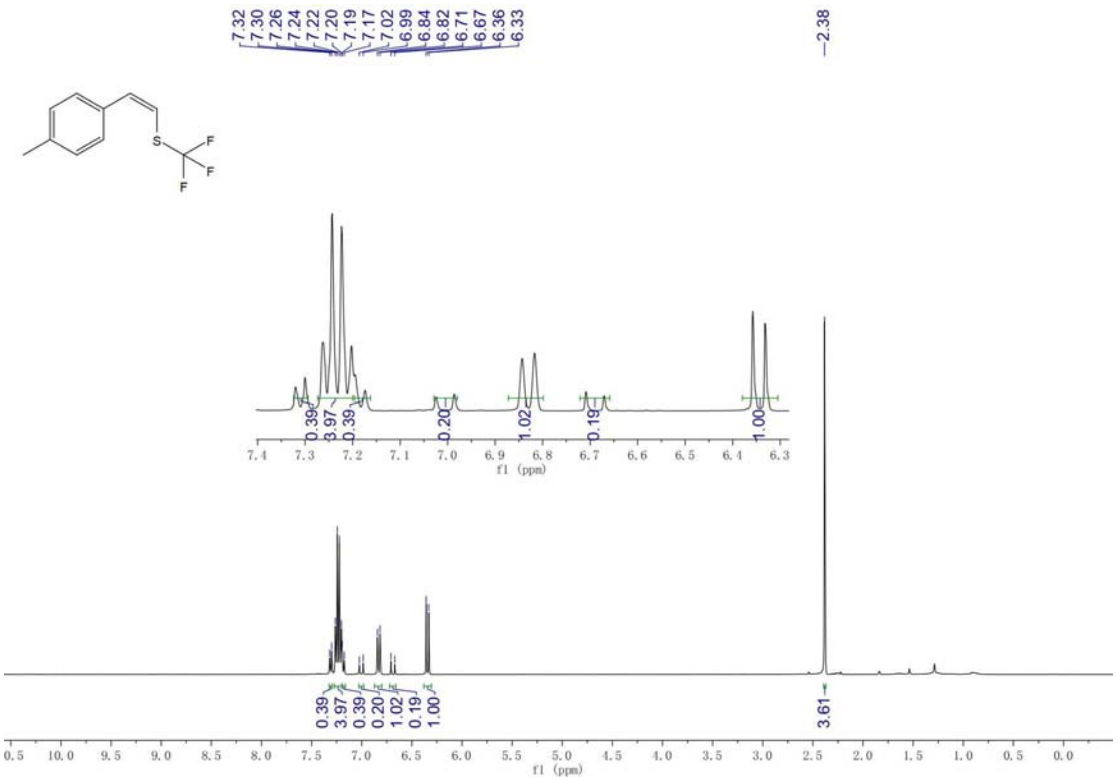
^{1}H NMR spectrum of **4ac** in $CDCl_3$ (400 MHz)



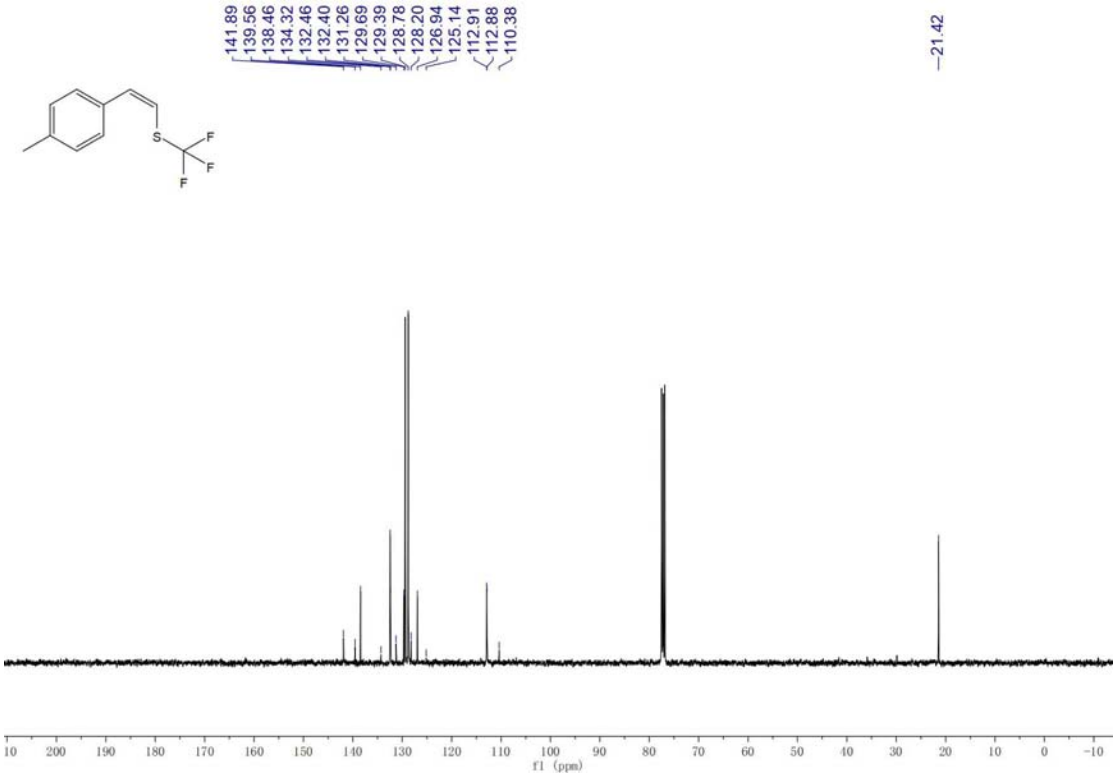
^{13}C NMR spectrum of **4ac** in $CDCl_3$ (151 MHz)



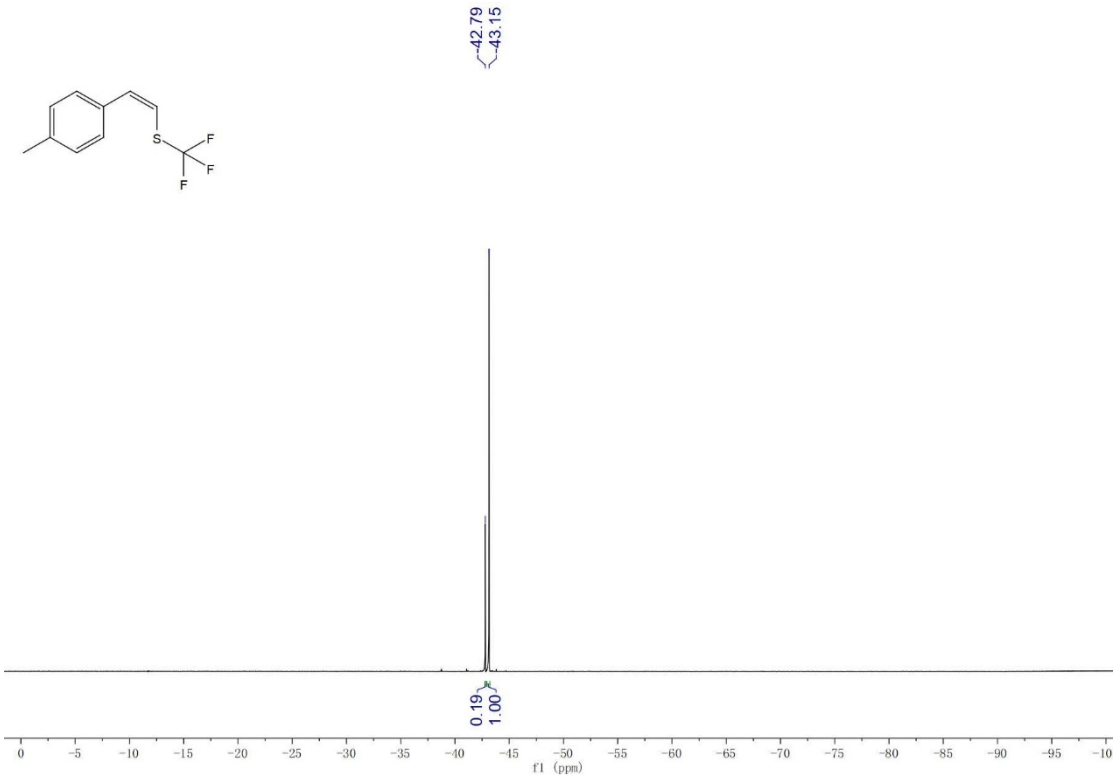
^{19}F NMR spectrum of **4ac** in $CDCl_3$ (283 MHz)



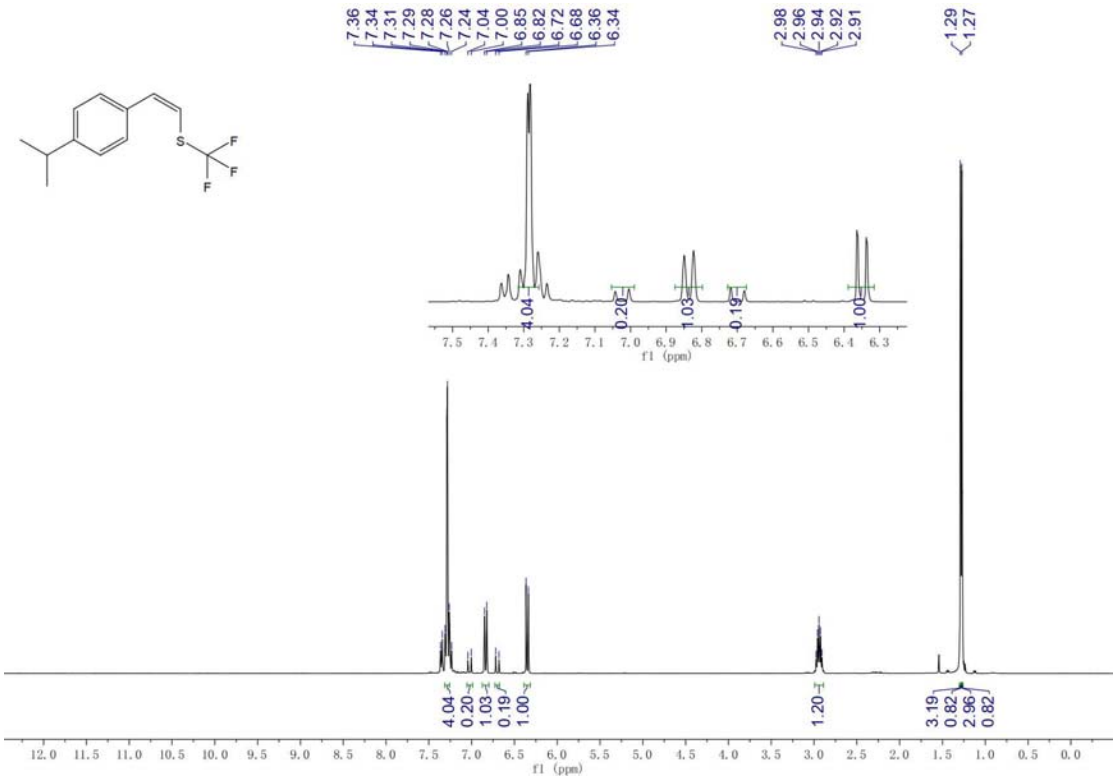
^{1}H NMR spectrum of **4ad** in $CDCl_3$ (400 MHz)



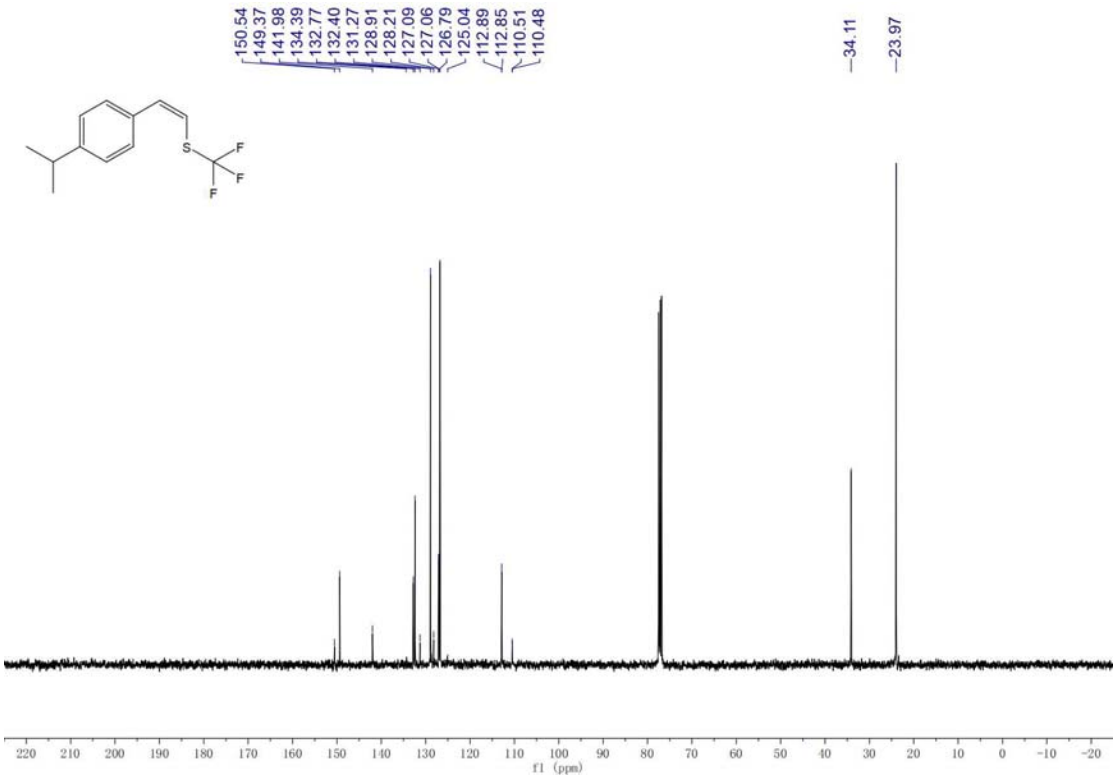
^{13}C NMR spectrum of **4ad** in $CDCl_3$ (101 MHz)



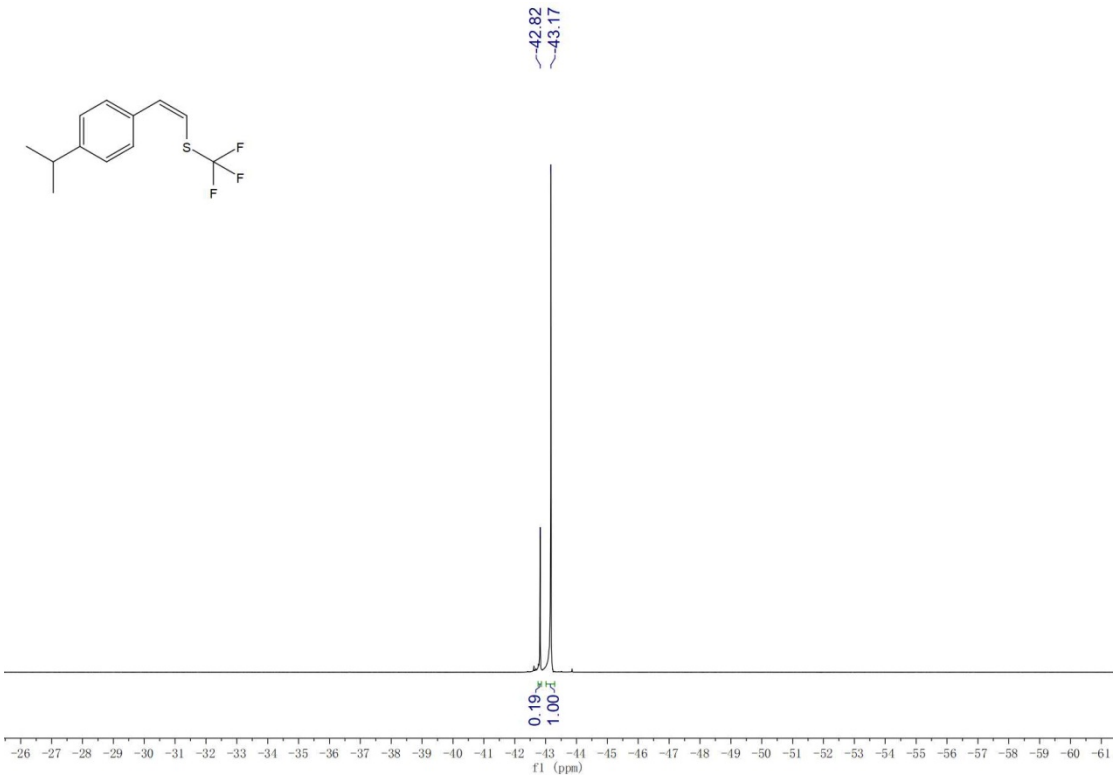
^{19}F NMR spectrum of **4ad** in $CDCl_3$ (283 MHz)



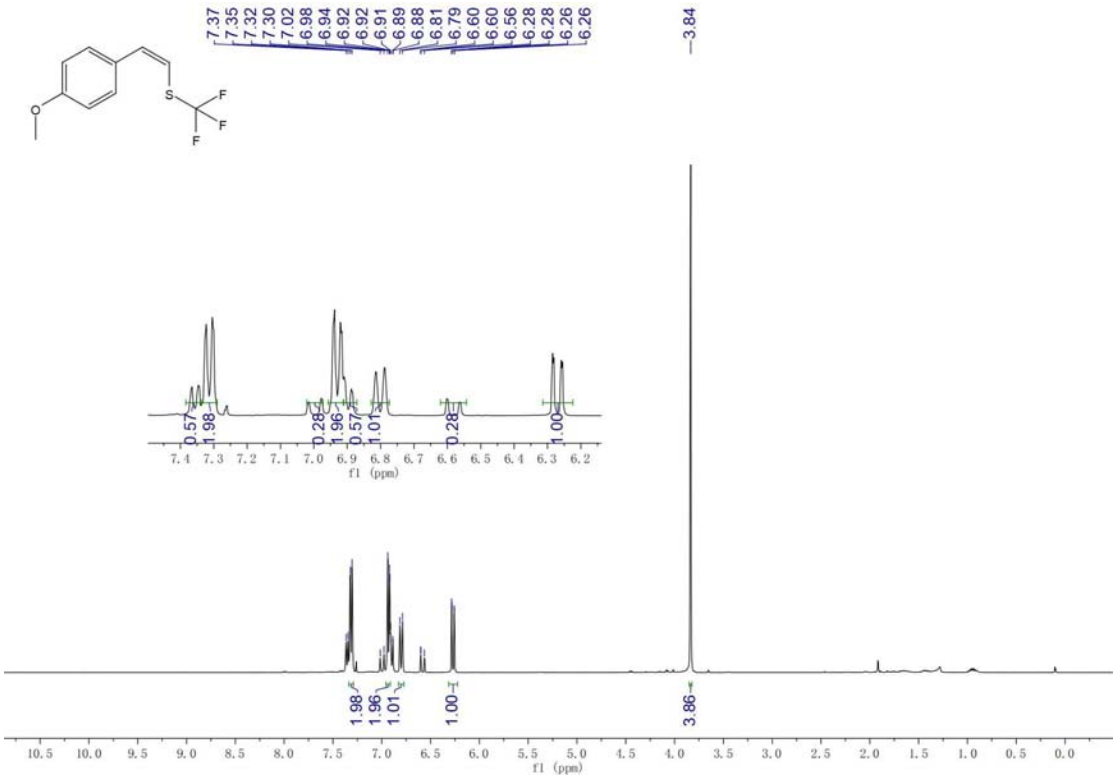
^{1}H NMR spectrum of **4ae** in $CDCl_3$ (400 MHz)



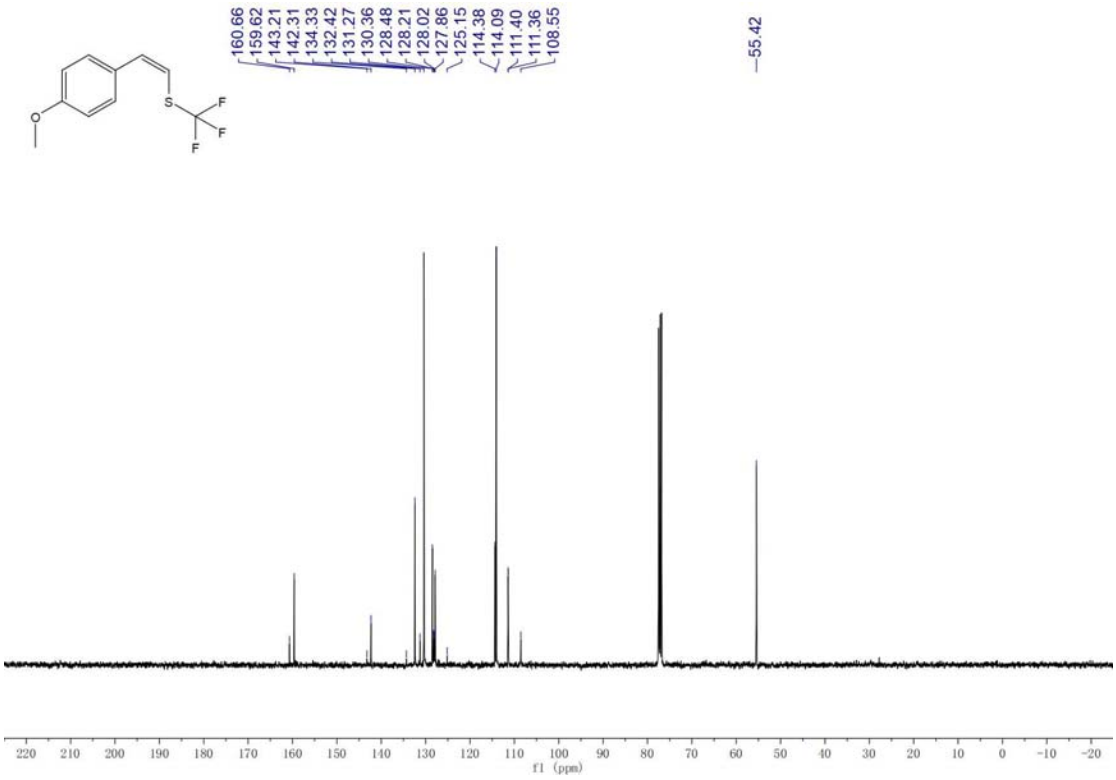
^{13}C NMR spectrum of **4ae** in $CDCl_3$ (101 MHz)



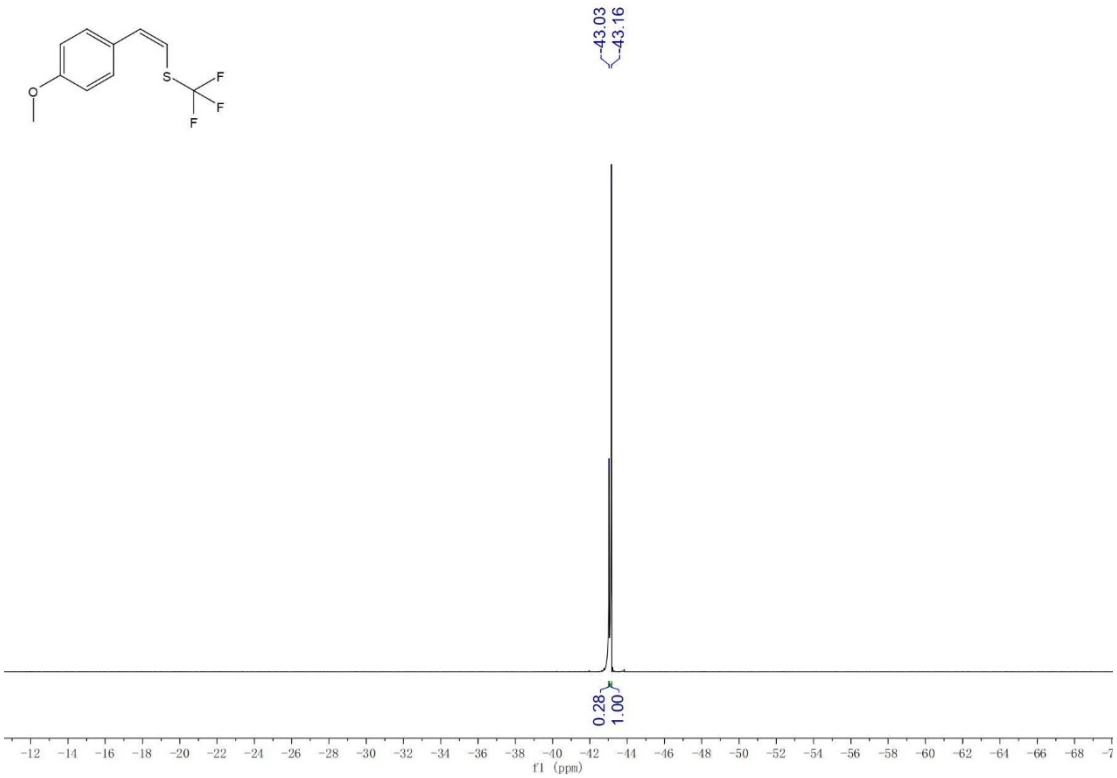
^{19}F NMR spectrum of **4ae** in $CDCl_3$ (283 MHz)



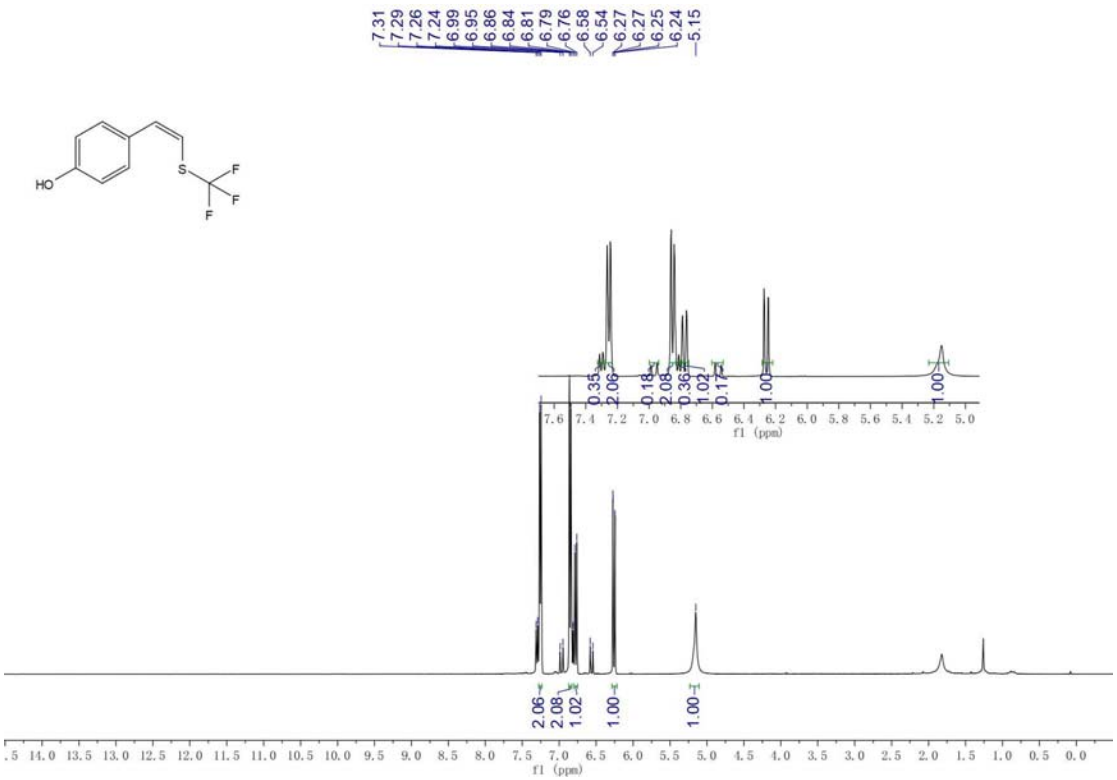
^{1}H NMR spectrum of **4af** in $CDCl_3$ (400 MHz)



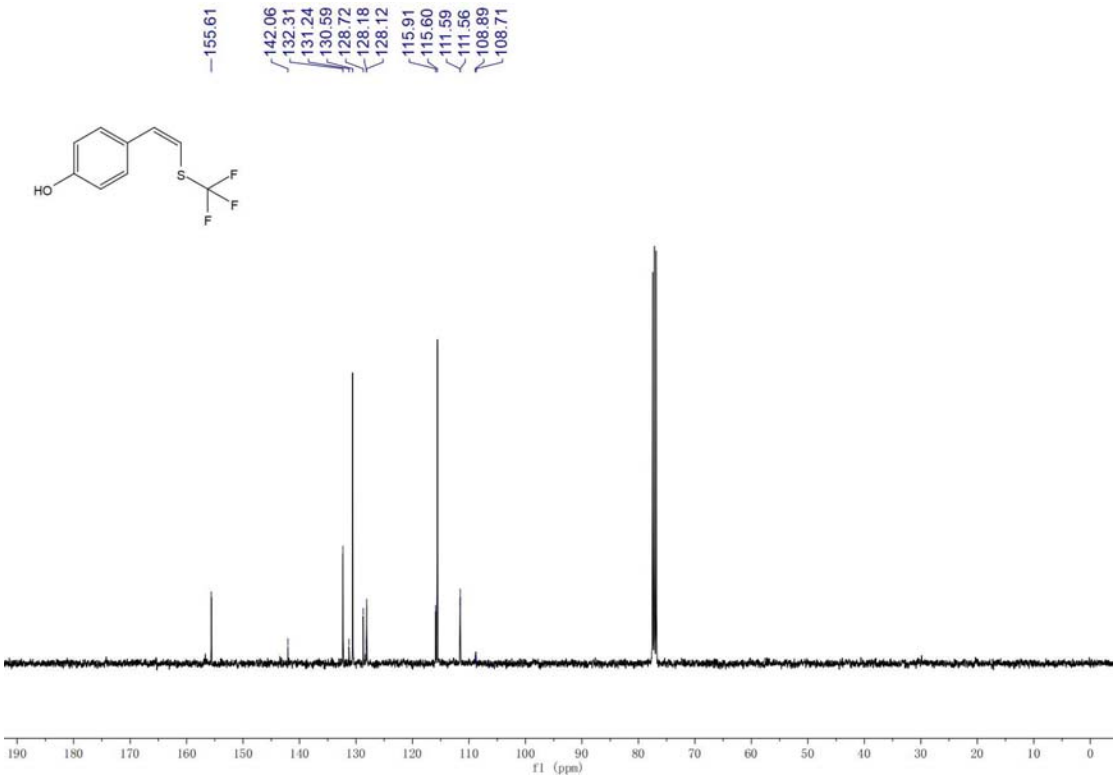
^{13}C NMR spectrum of **4af** in $CDCl_3$ (101 MHz)



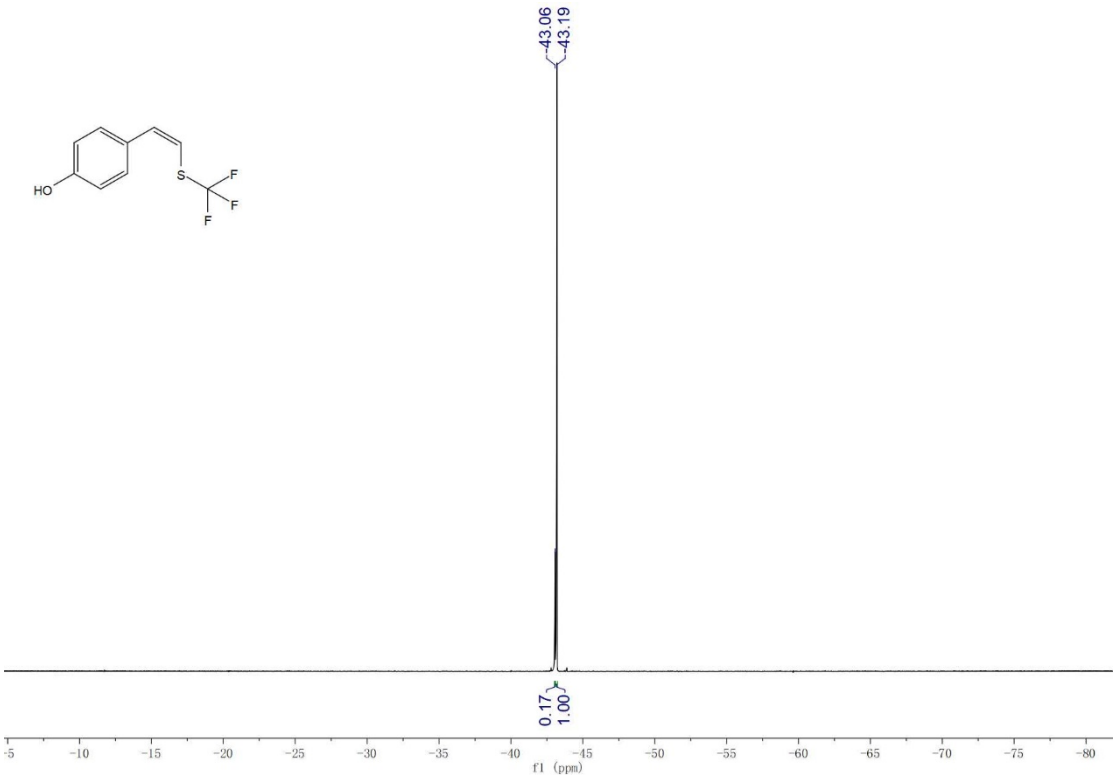
^{19}F NMR spectrum of **4af** in $CDCl_3$ (283 MHz)



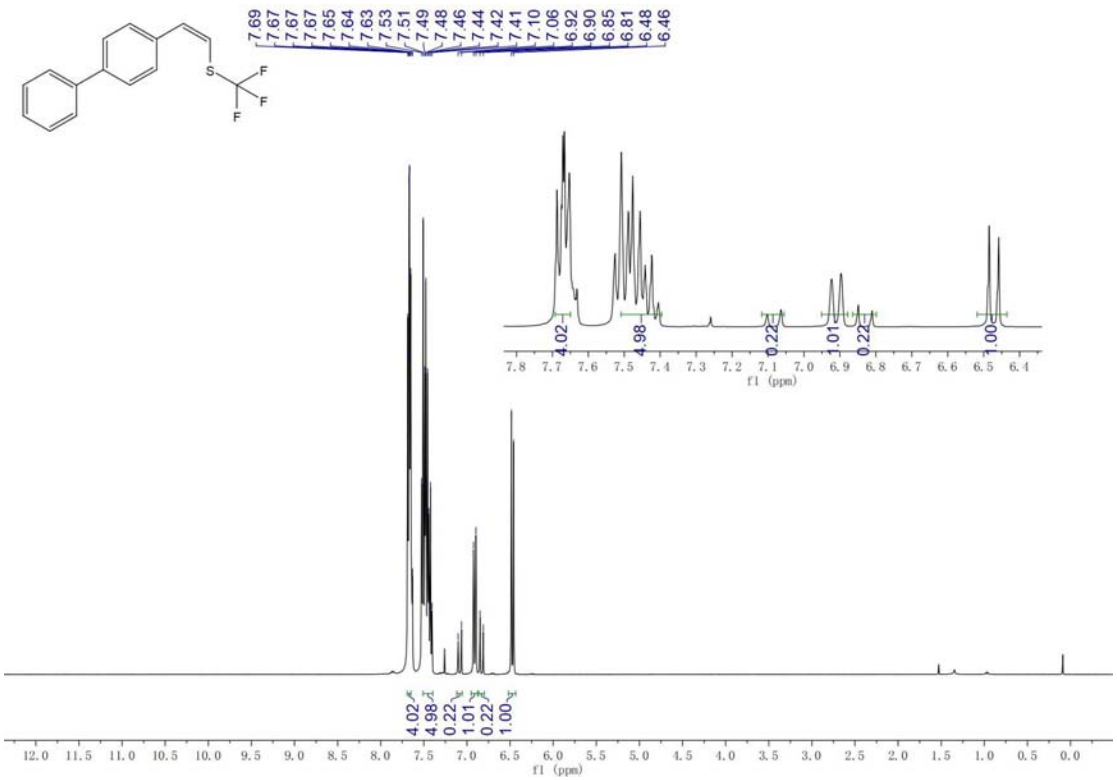
^{1}H NMR spectrum of **4ag** in $CDCl_3$ (400 MHz)



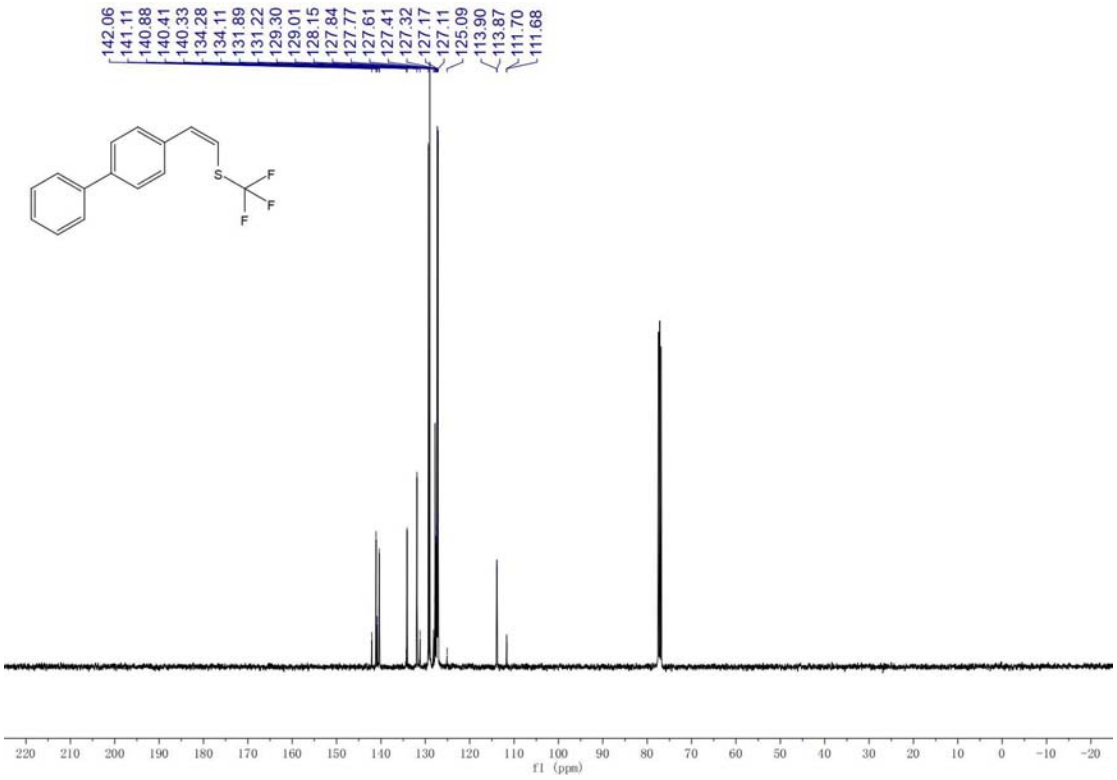
^{13}C NMR spectrum of **4ag** in $CDCl_3$ (101 MHz)



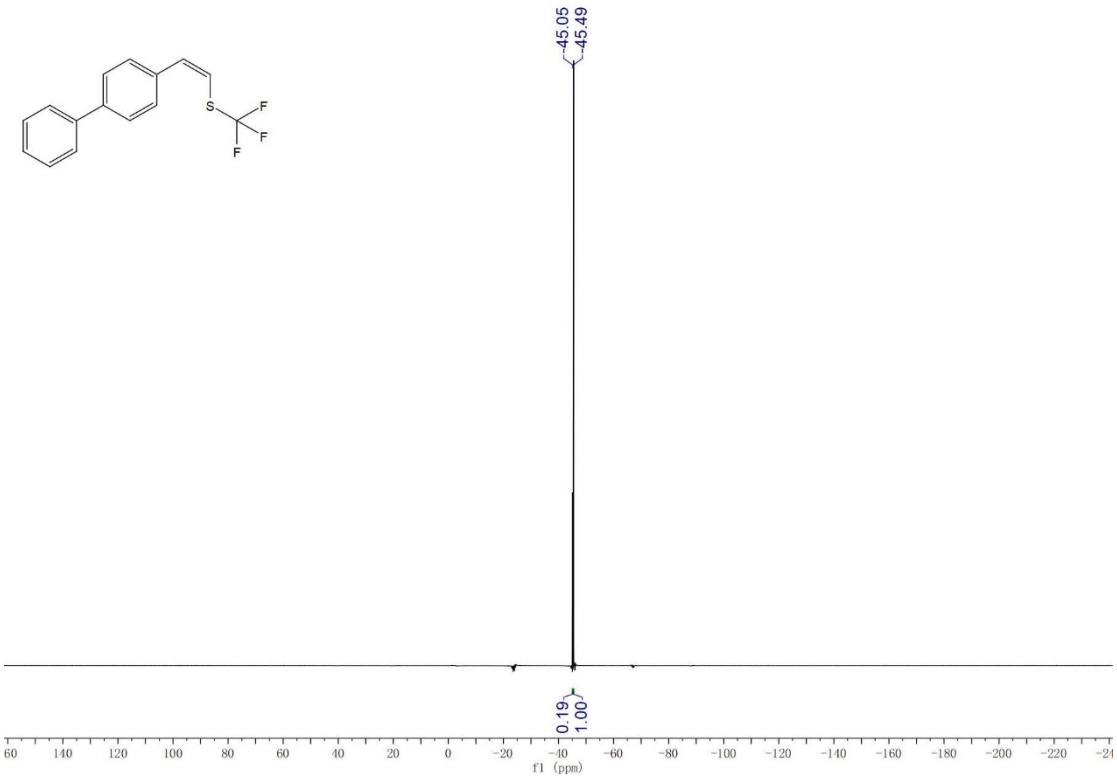
^{19}F NMR spectrum of **4ag** in $CDCl_3$ (4283 MHz)



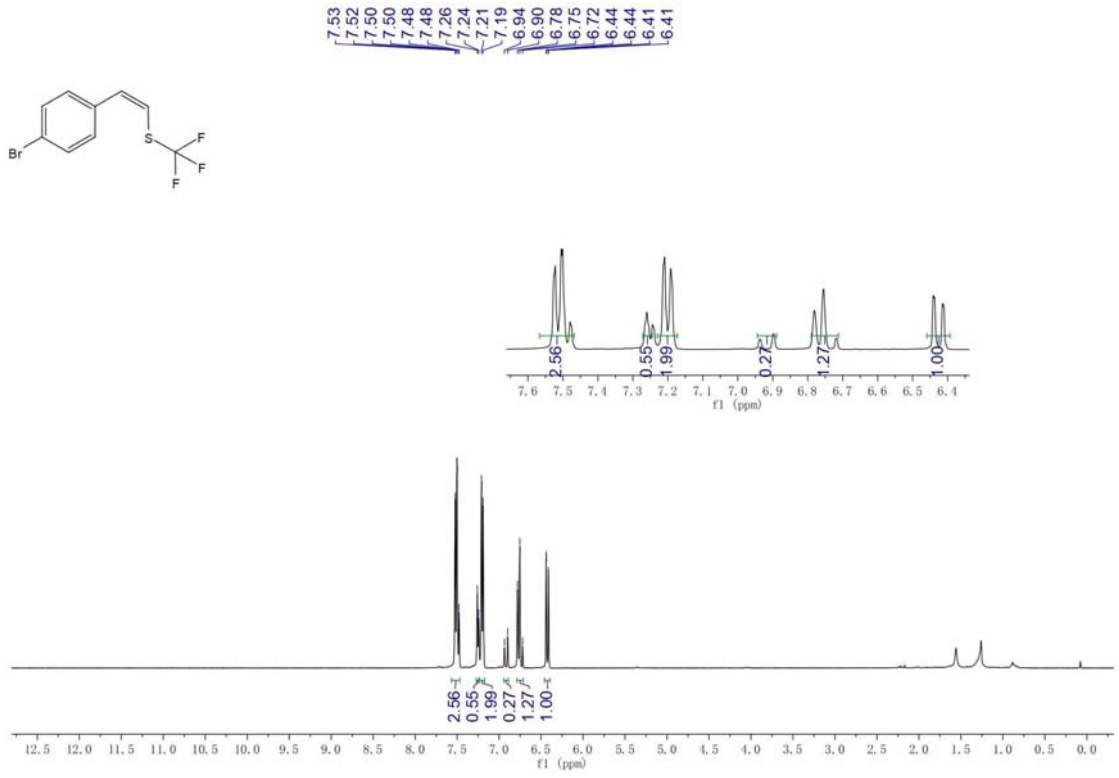
^{1}H NMR spectrum of **4ah** in $CDCl_3$ (400 MHz)



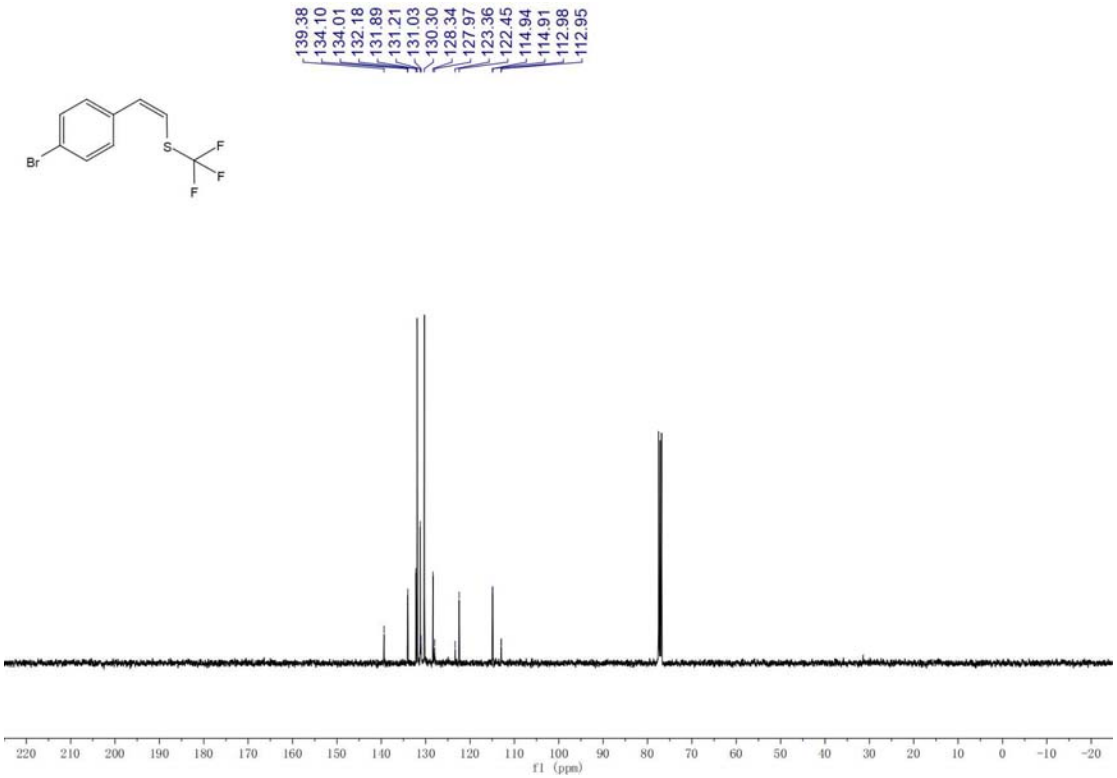
^{13}C NMR spectrum of **4ah** in $CDCl_3$ (101 MHz)



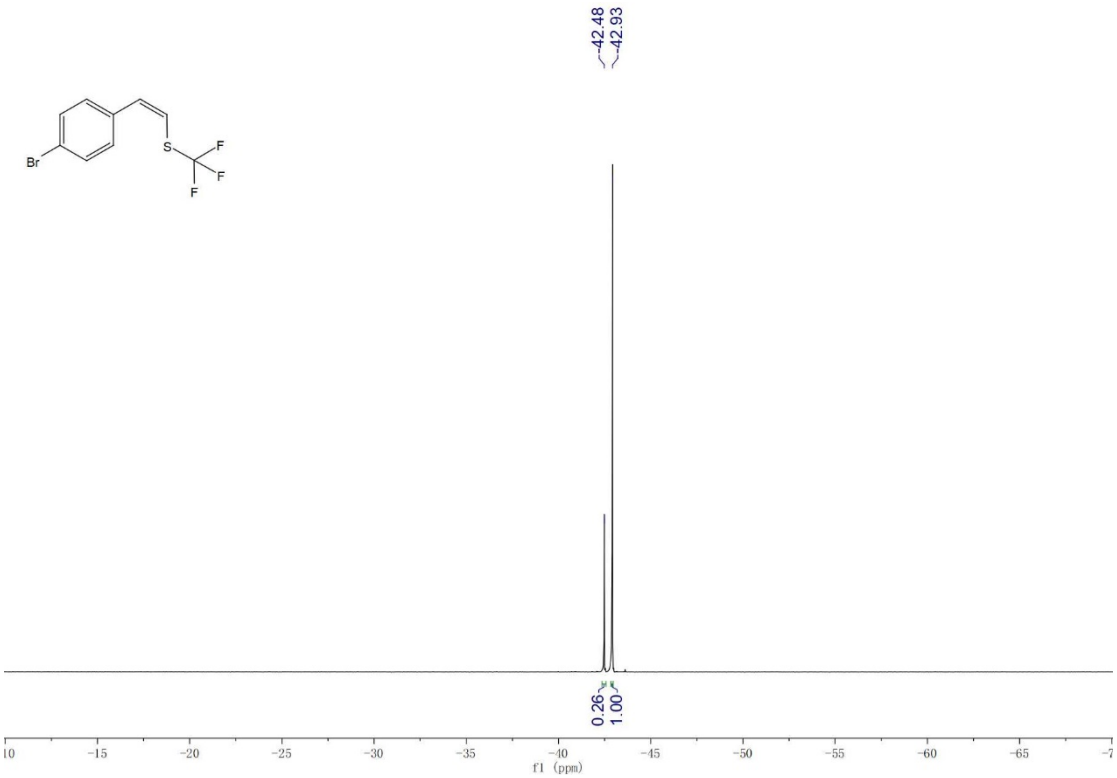
^{19}F NMR spectrum of **4ah** in $CDCl_3$ (376 MHz)



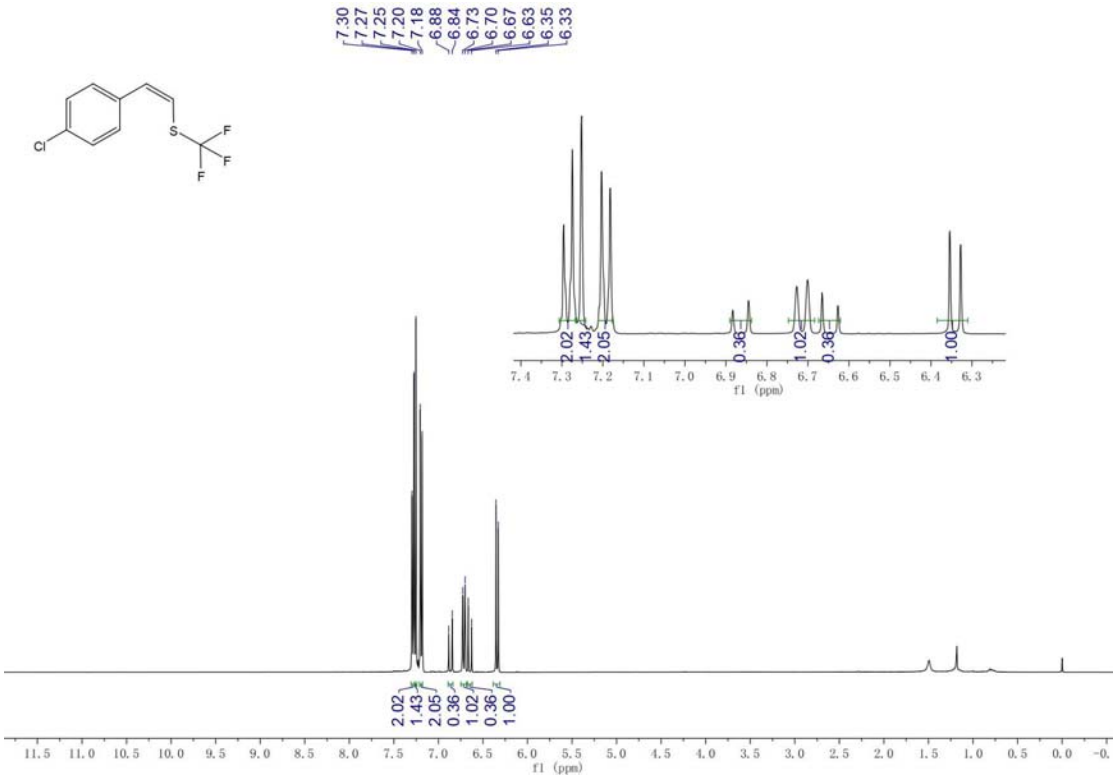
^{1}H NMR spectrum of **4ai** in $CDCl_3$ (400 MHz)



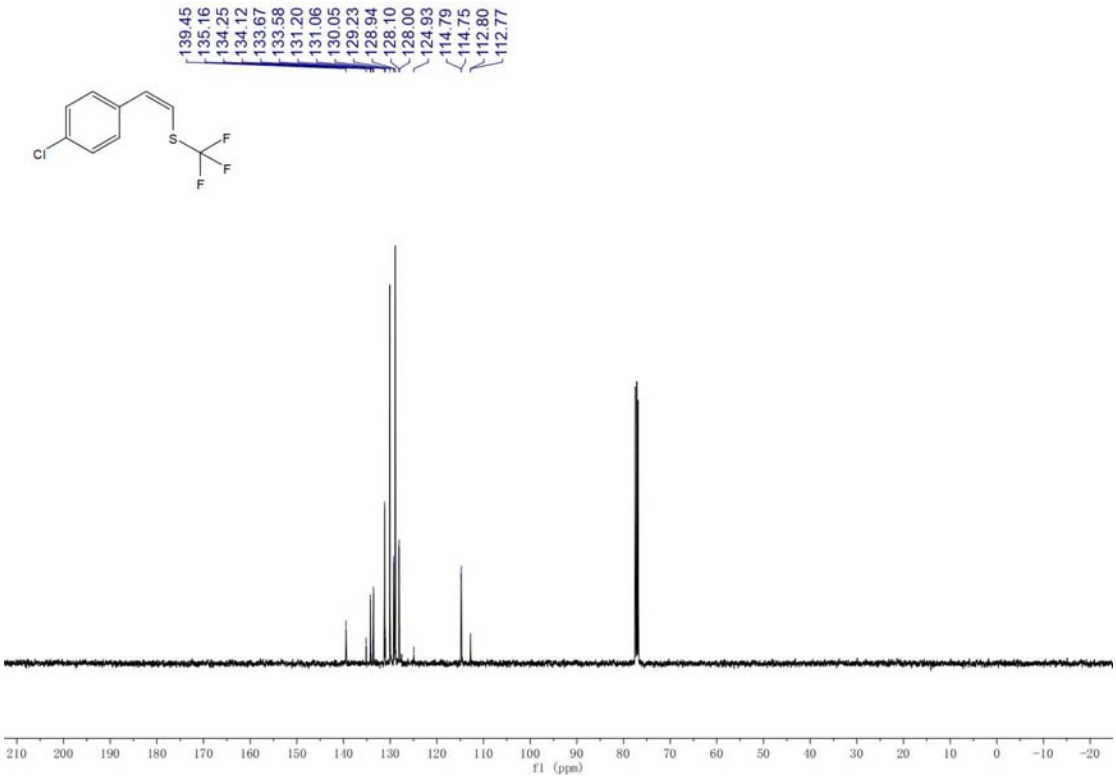
^{13}C NMR spectrum of **4ai** in $CDCl_3$ (101 MHz)



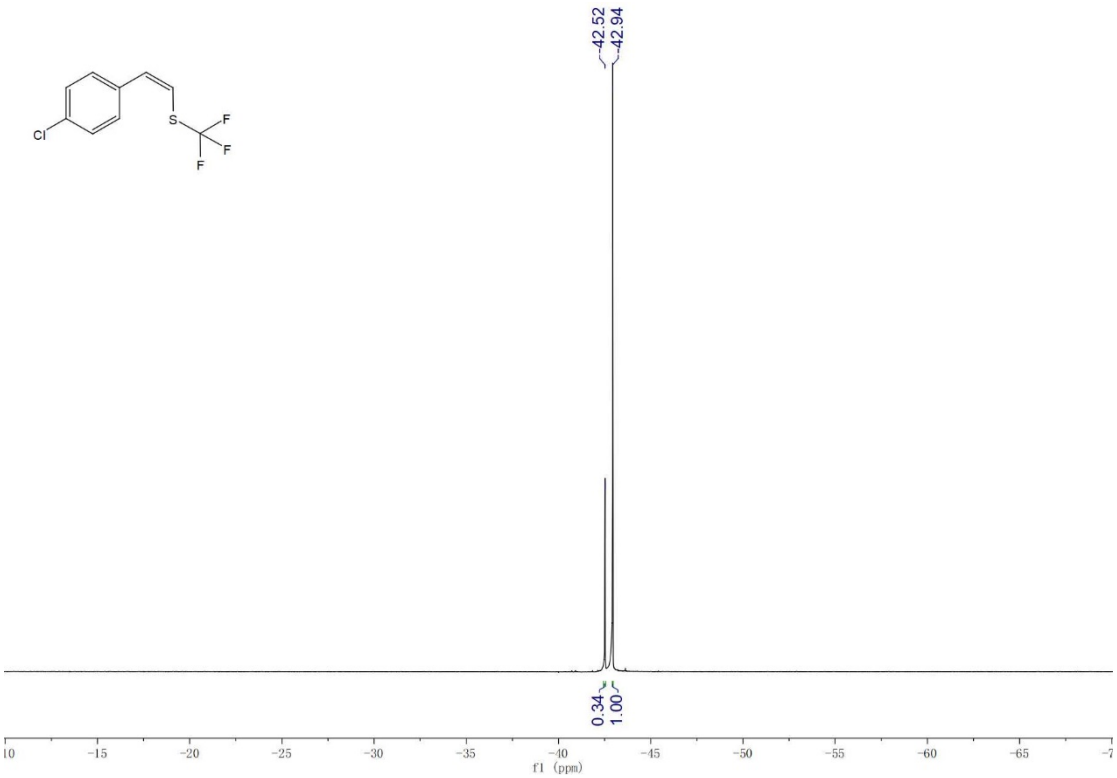
^{13}F NMR spectrum of **4ai** in $CDCl_3$ (283 MHz)



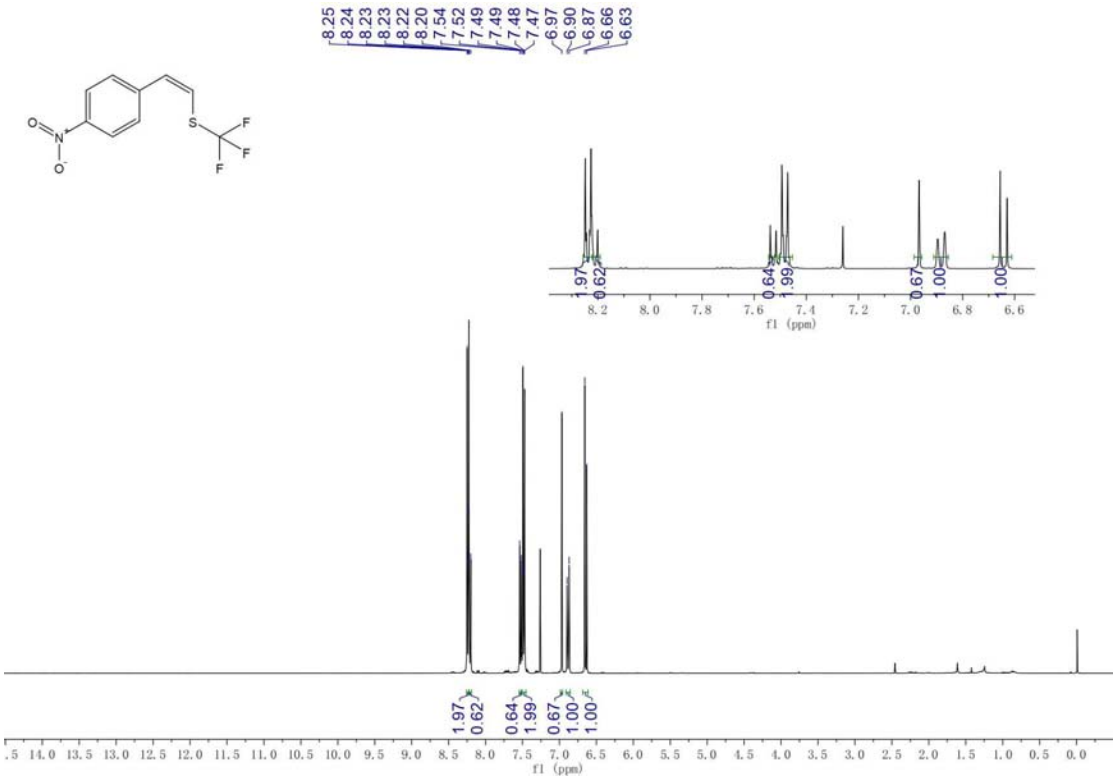
^{1}H NMR spectrum of **4aj** in $CDCl_3$ (400 MHz)



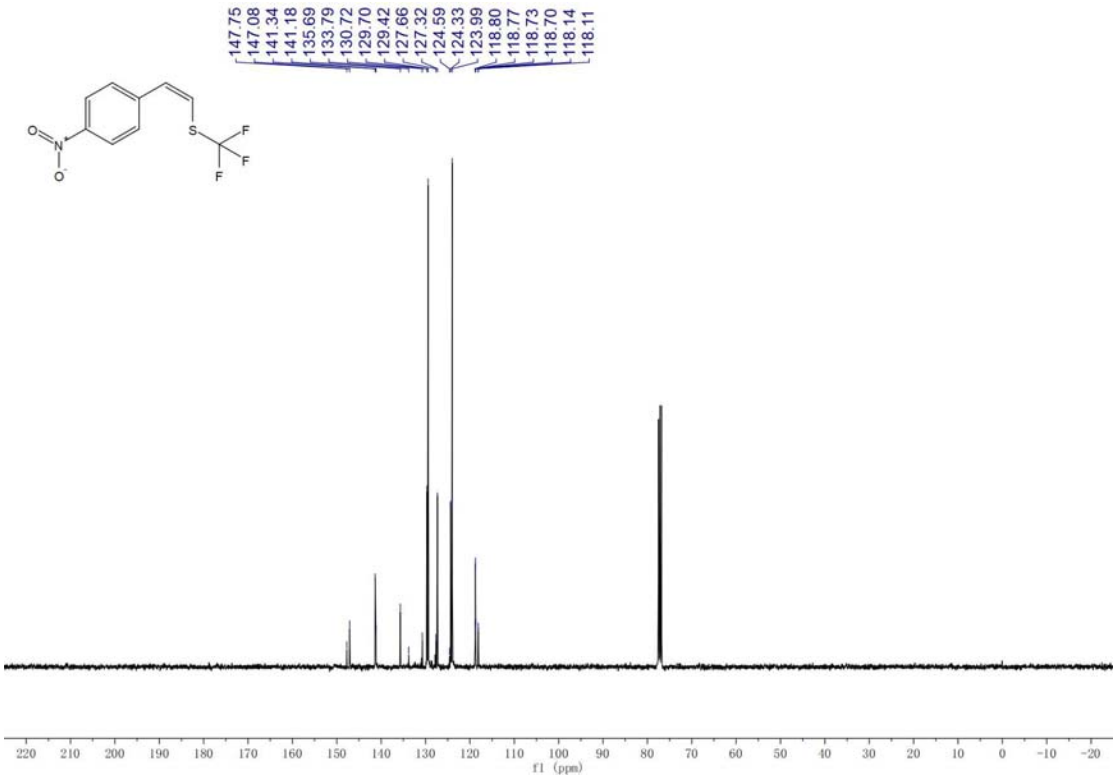
^{13}C NMR spectrum of **4aj** in $CDCl_3$ (101 MHz)



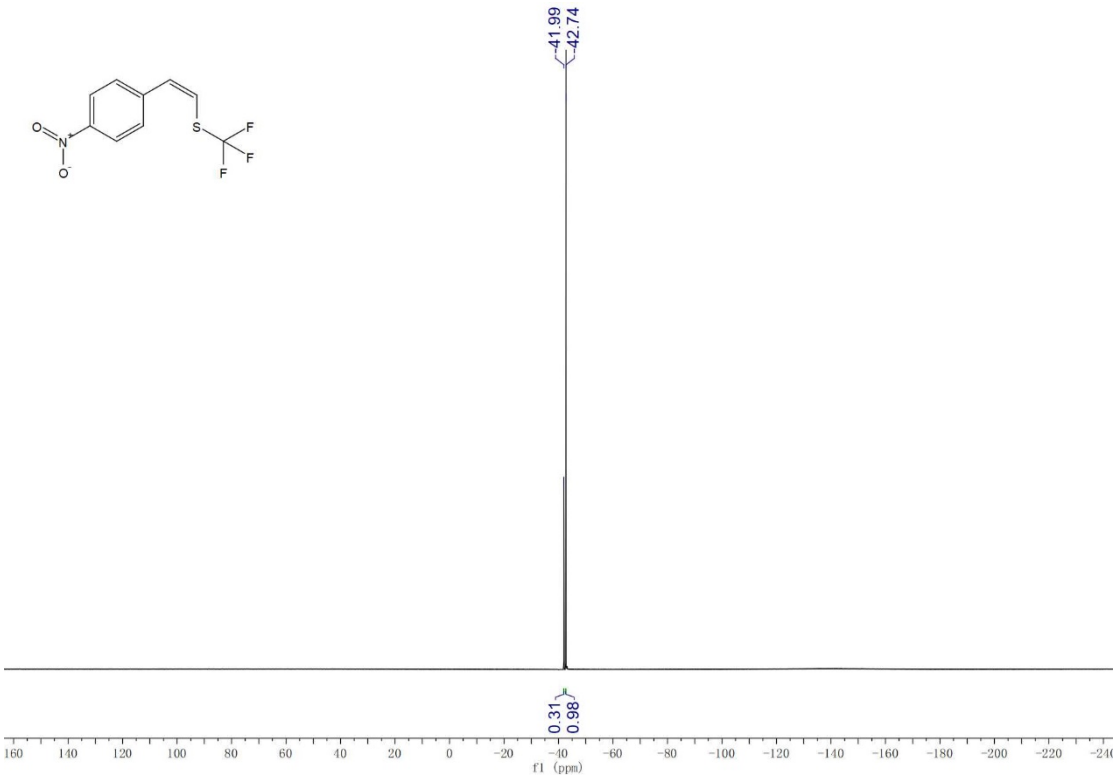
^{19}F NMR spectrum of **4aj** in $CDCl_3$ (283 MHz)



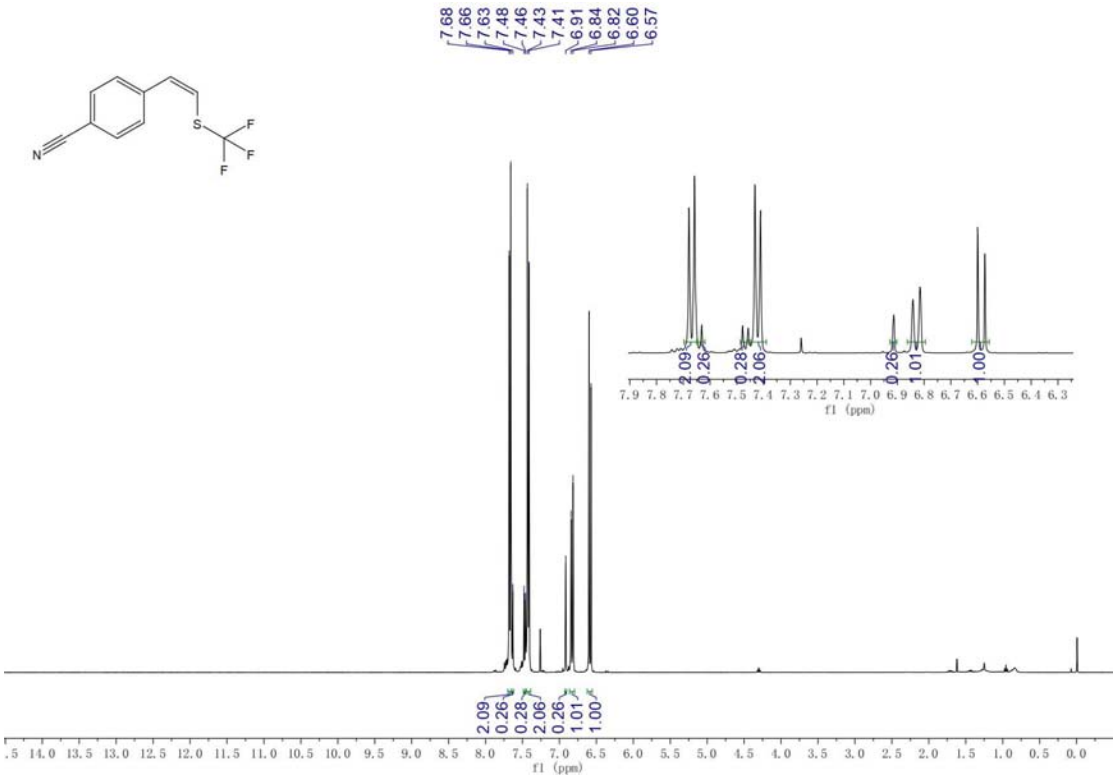
^{1}H NMR spectrum of **4ak** in $CDCl_3$ (400 MHz)



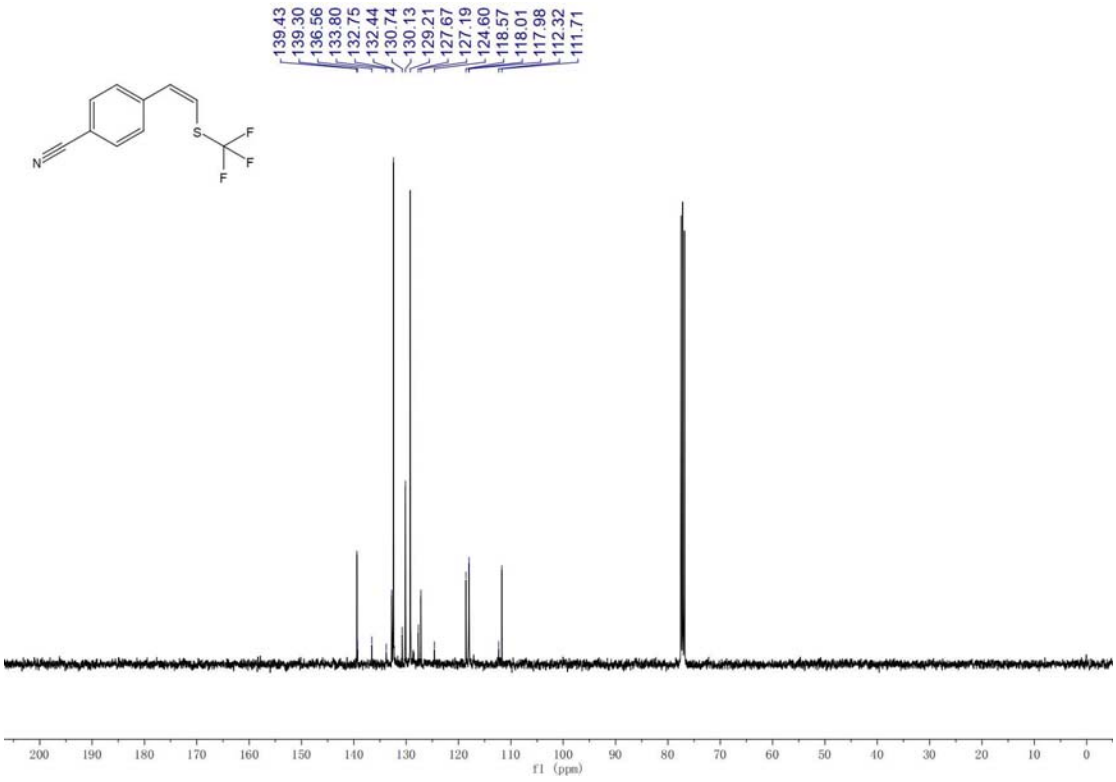
^{13}C NMR spectrum of **4ak** in $CDCl_3$ (101 MHz)



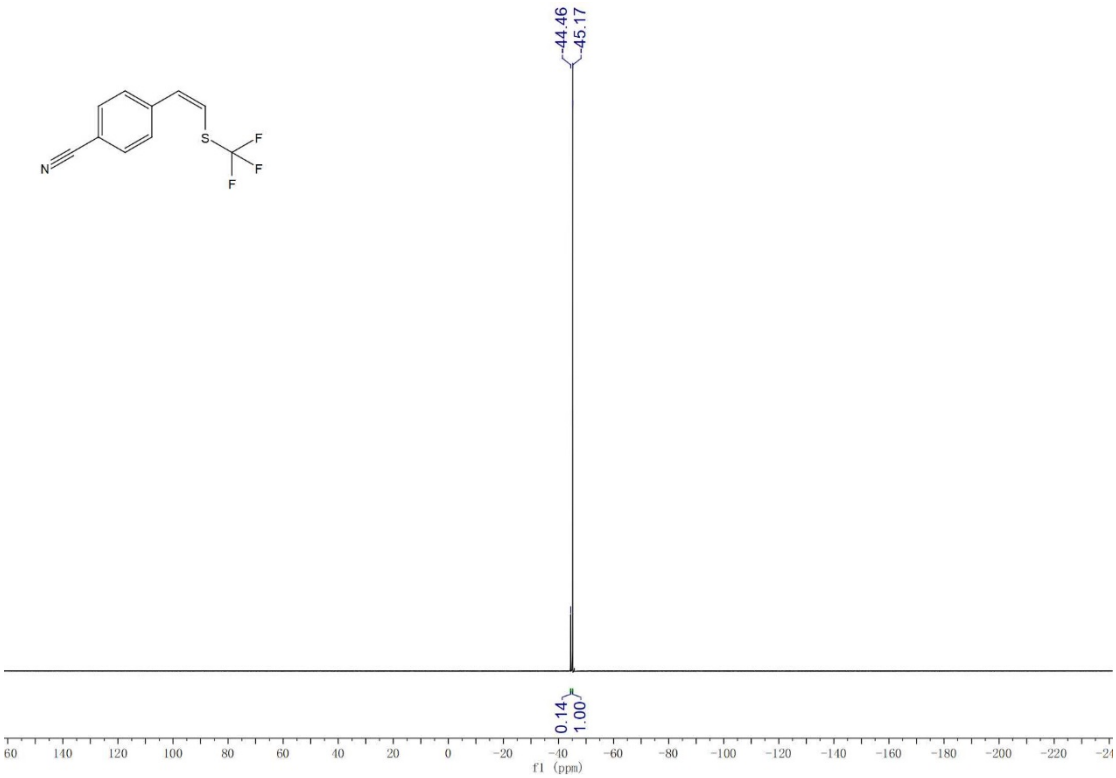
^{19}F NMR spectrum of **4ak** in $CDCl_3$ (565 MHz)



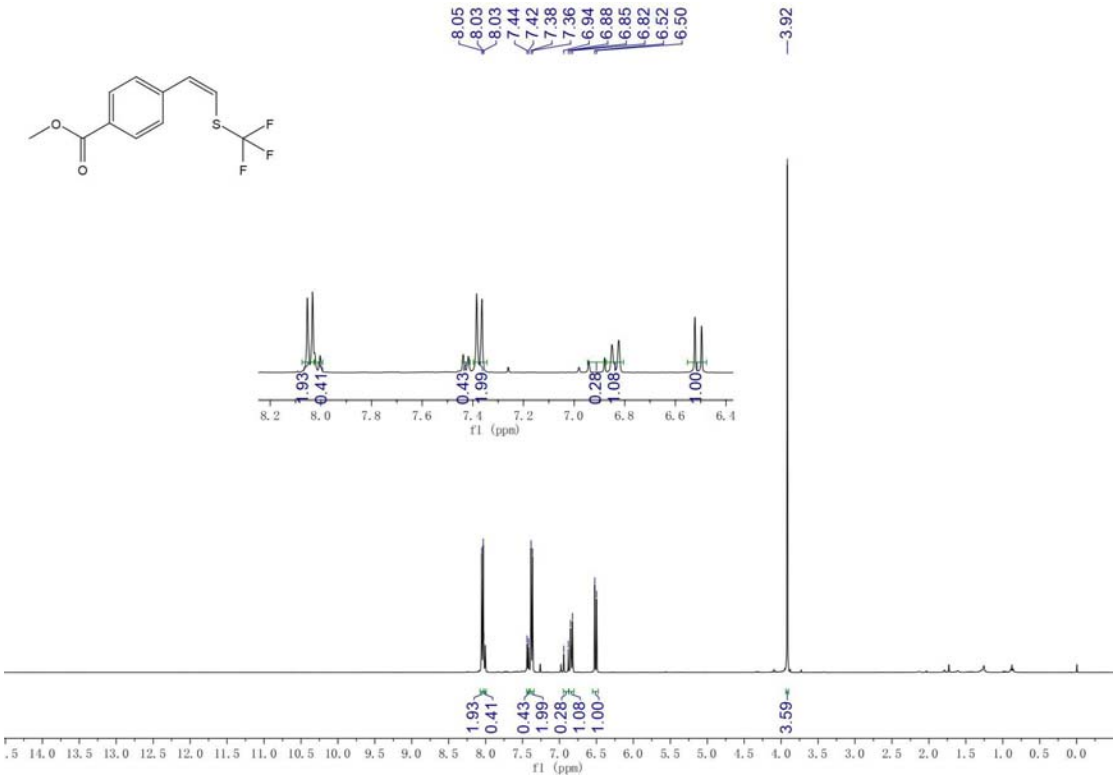
^{1}H NMR spectrum of **4al** in $CDCl_3$ (400 MHz)



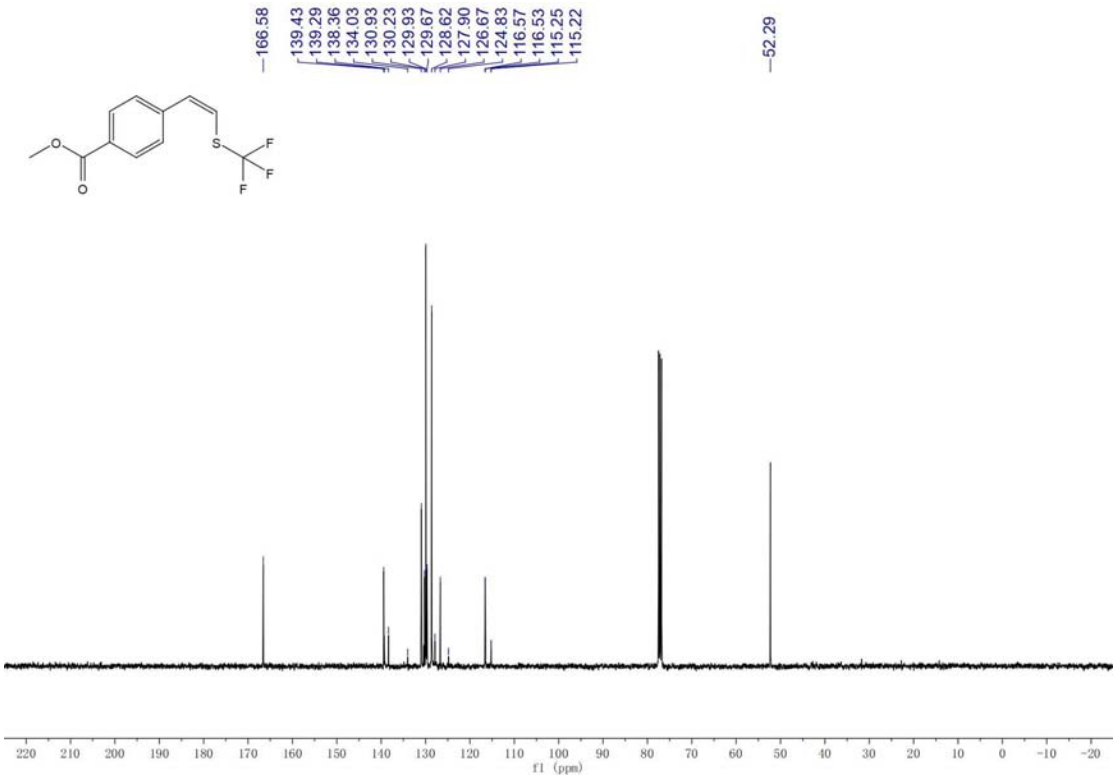
^{13}C NMR spectrum of **4al** in $CDCl_3$ (101 MHz)



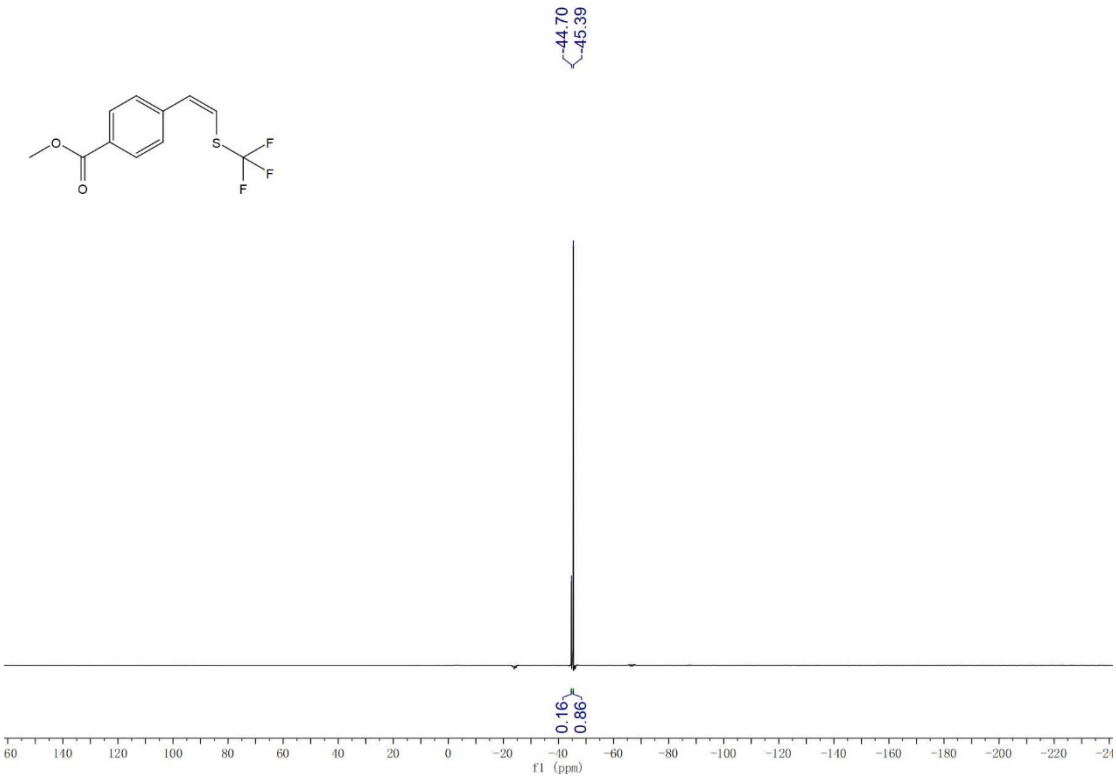
^{19}F NMR spectrum of **4al** in $CDCl_3$ (376 MHz)



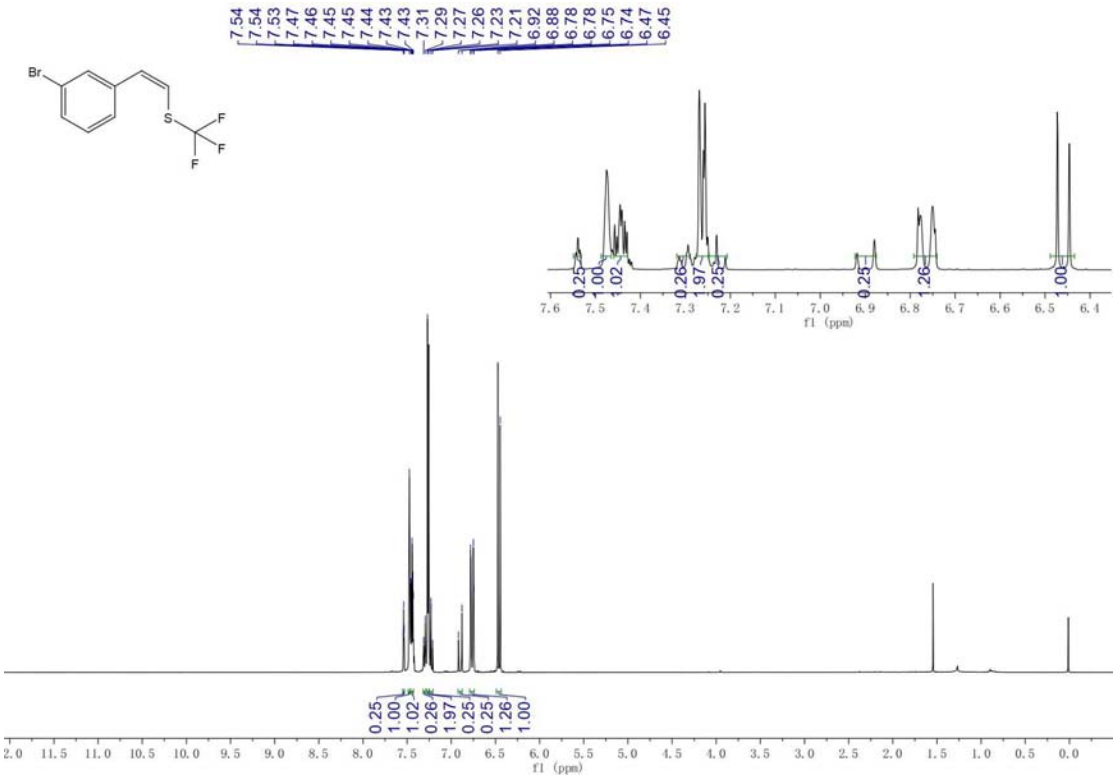
^{1}H NMR spectrum of **4am** in $CDCl_3$ (400 MHz)



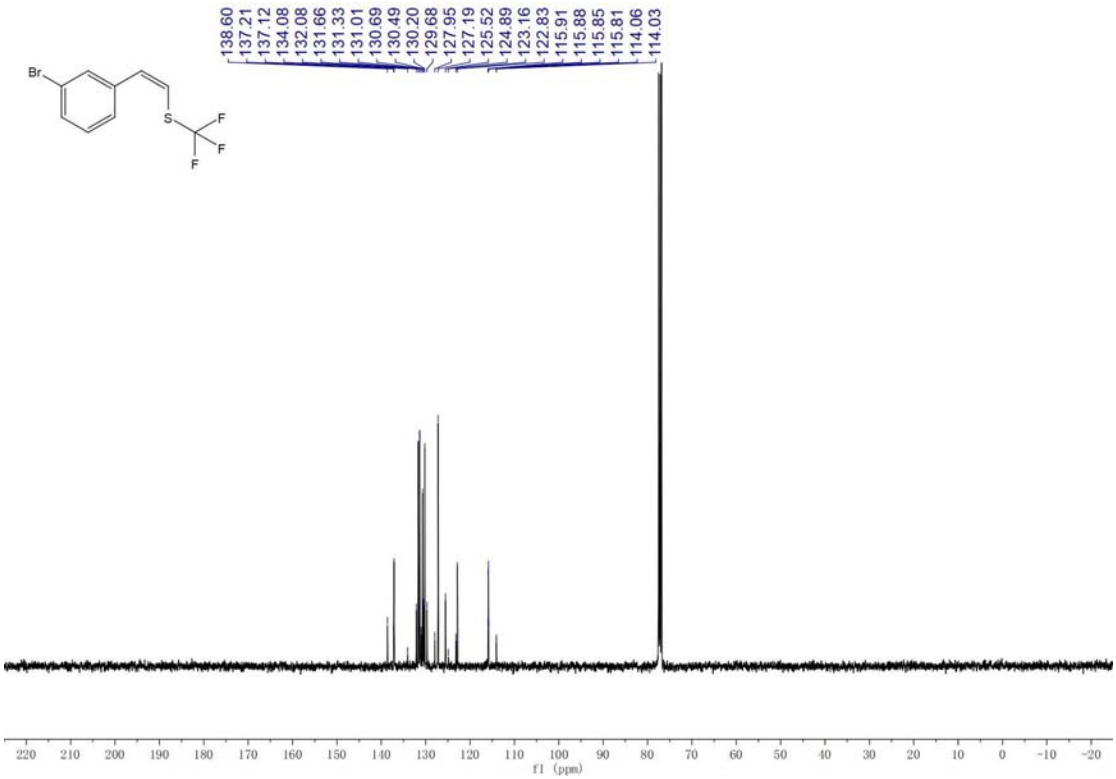
^{13}C NMR spectrum of **4am** in $CDCl_3$ (101 MHz)



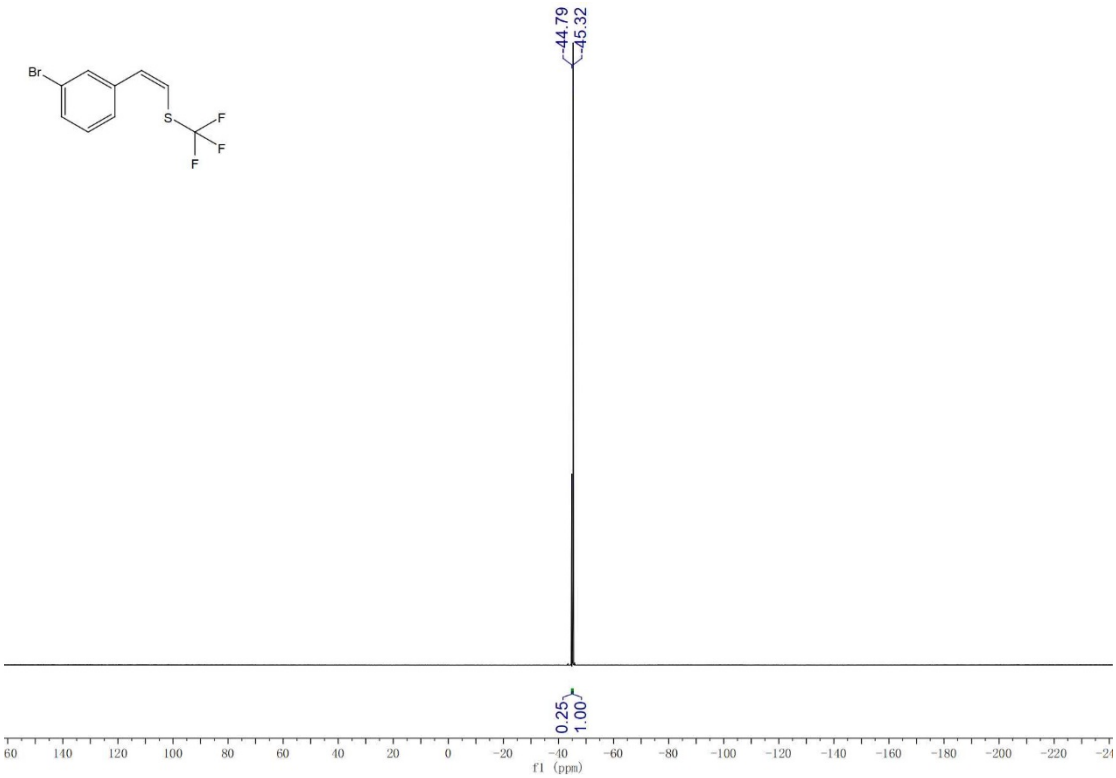
^{19}F NMR spectrum of **4am** in $CDCl_3$ (376 MHz)



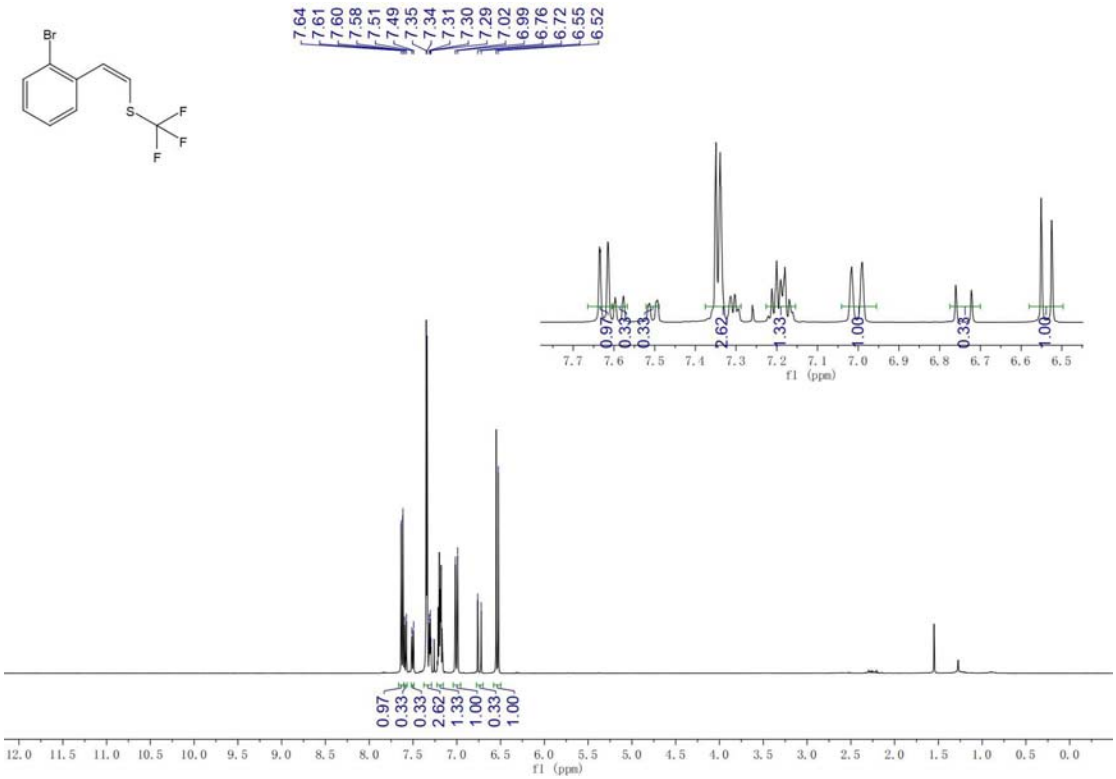
^{1}H NMR spectrum of **4an** in $CDCl_3$ (400 MHz)



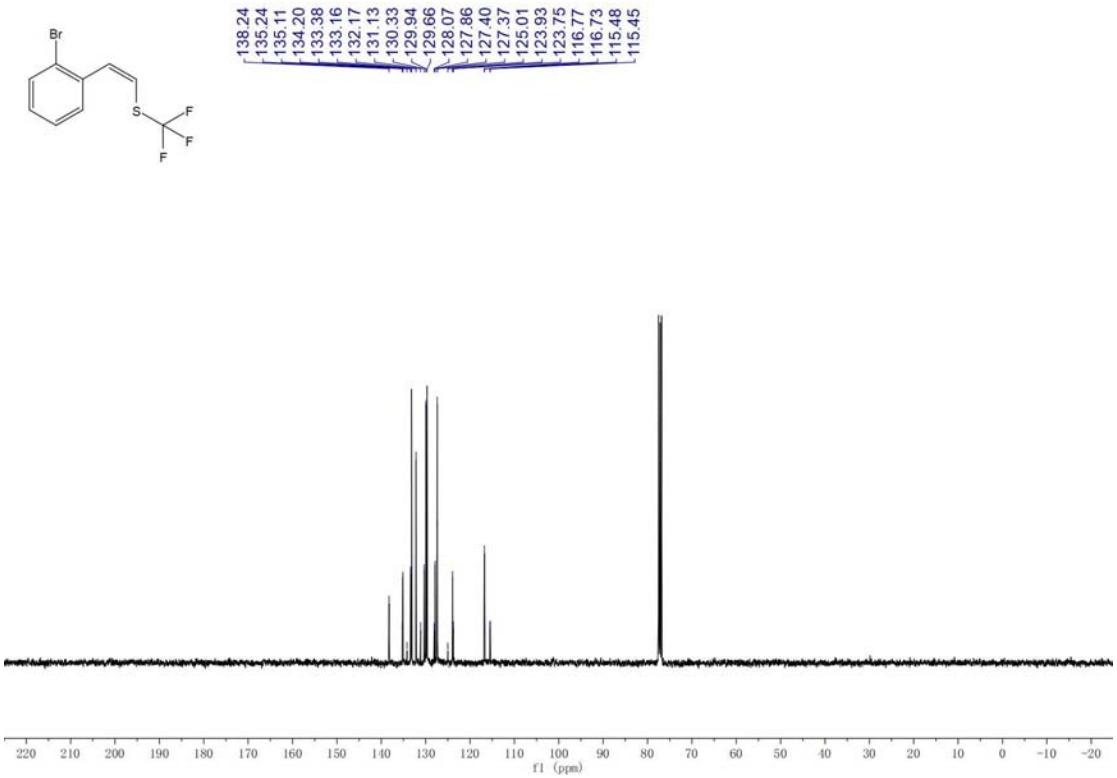
^{13}C NMR spectrum of **4an** in $CDCl_3$ (101 MHz)



^{19}F NMR spectrum of **4an** in $CDCl_3$ (376 MHz)

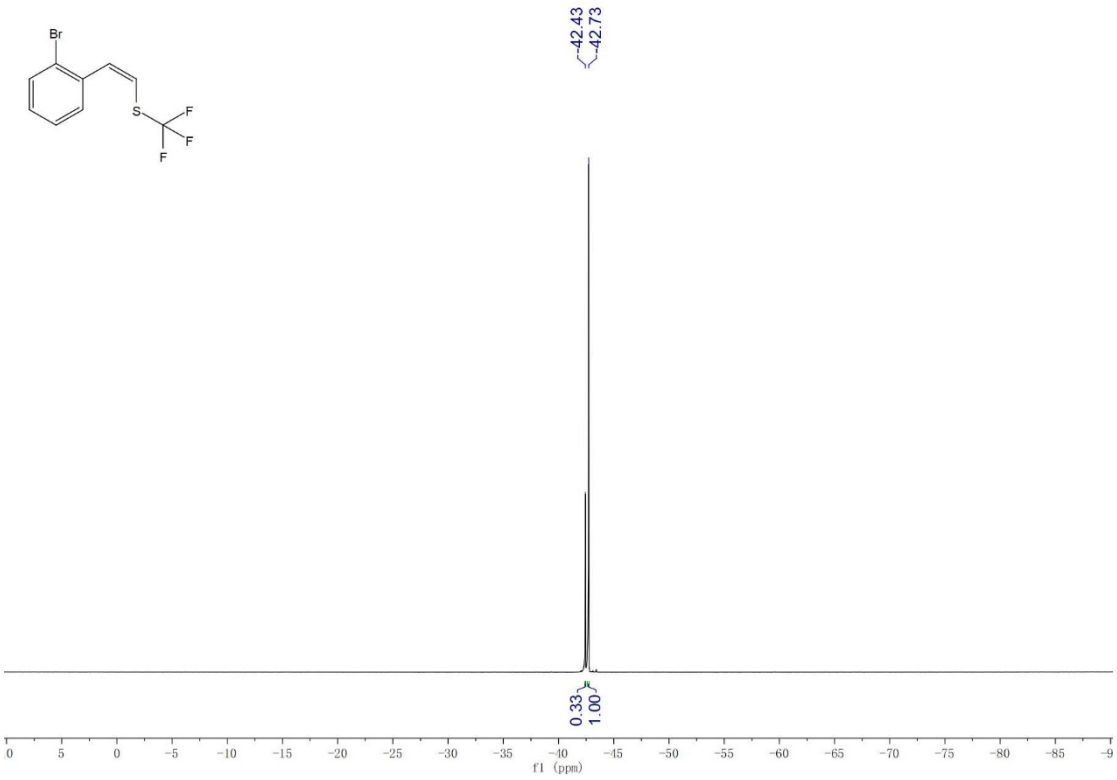


^{1}H NMR spectrum of **4ao** in $CDCl_3$ (400 MHz)

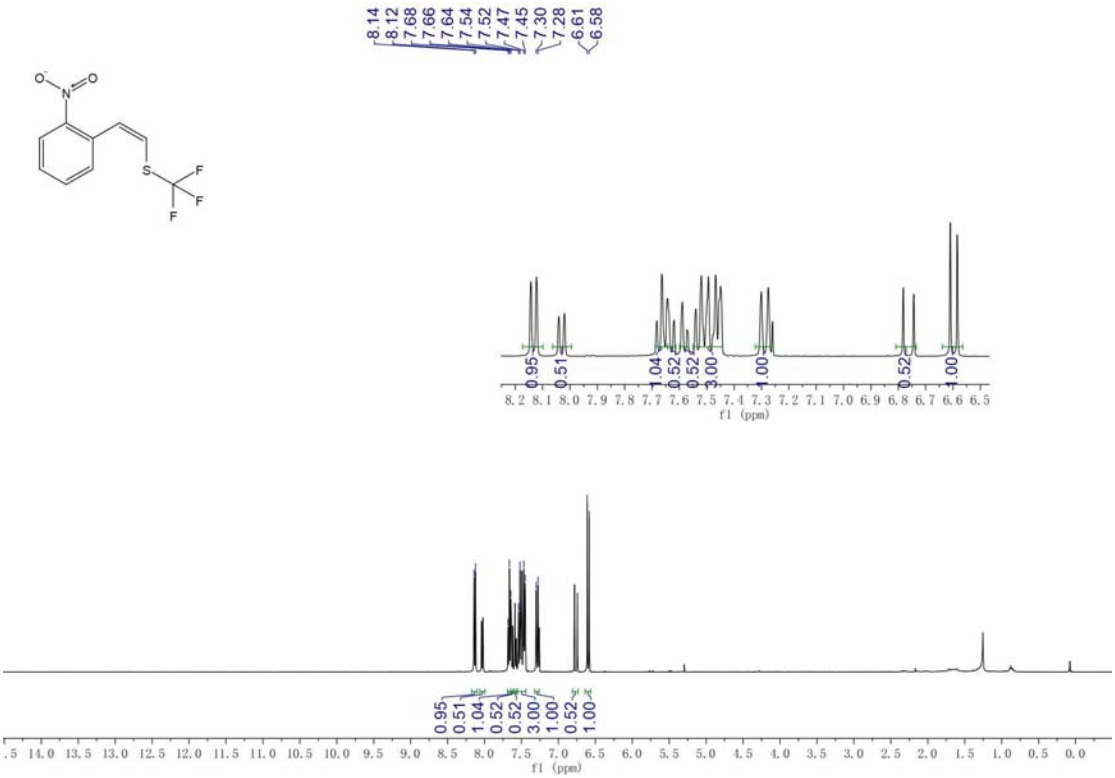


^{13}C NMR spectrum of **4ao** in $CDCl_3$ (101 MHz)

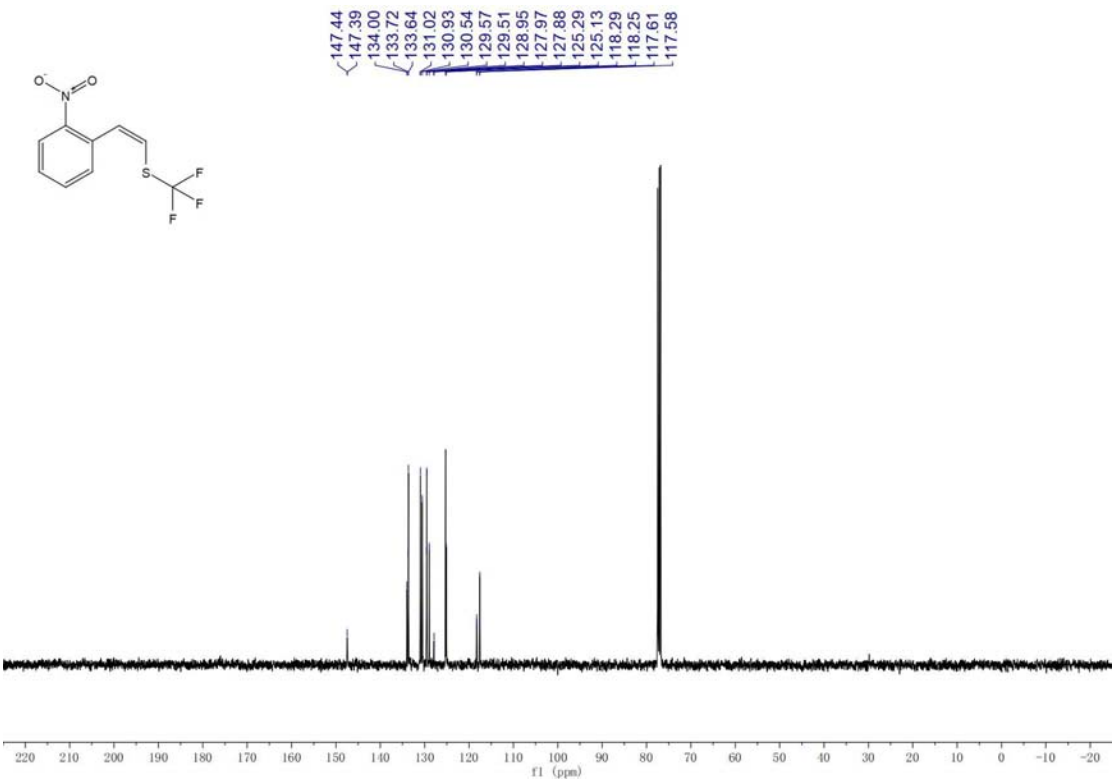
1



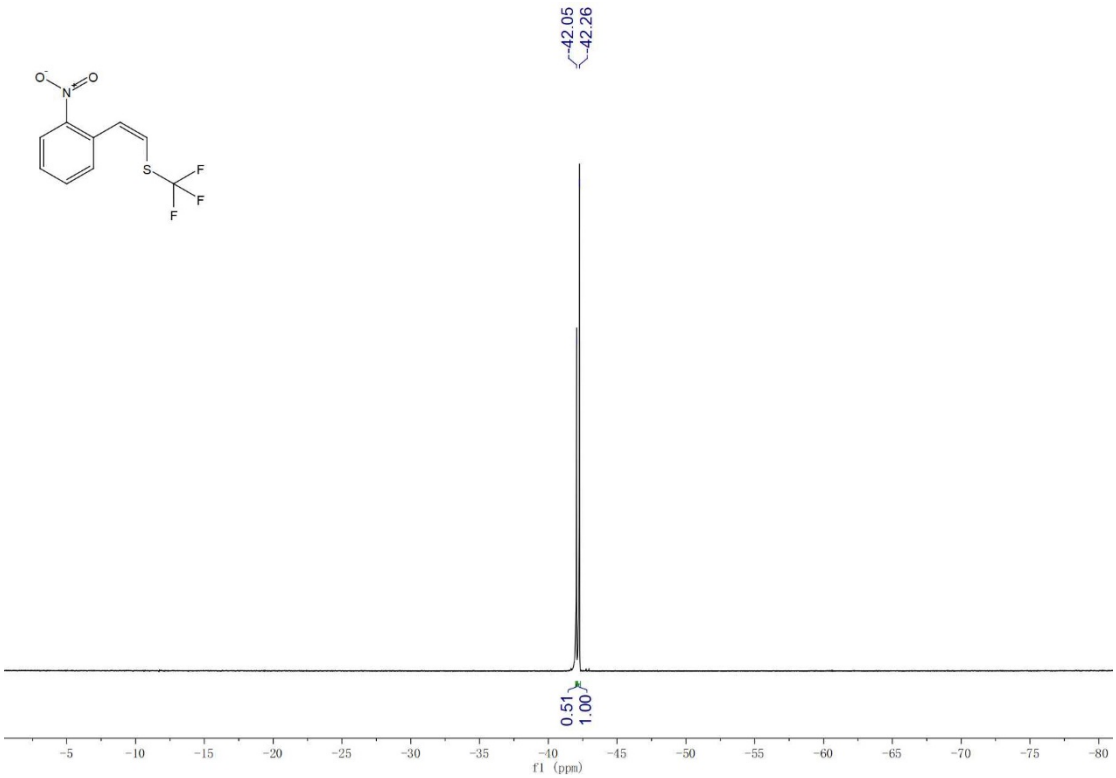
^{9}F NMR spectrum of **4ao** in $CDCl_3$ (283 MHz)



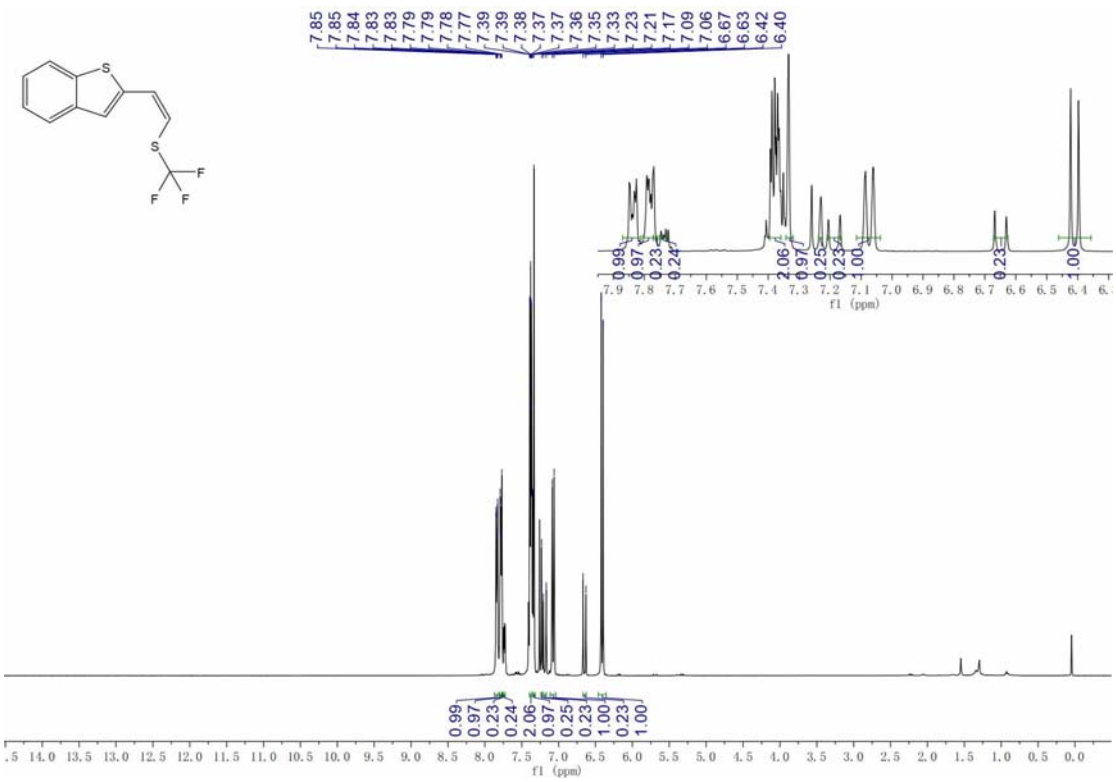
^{1}H NMR spectrum of **4ap** in $CDCl_3$ (400 MHz)



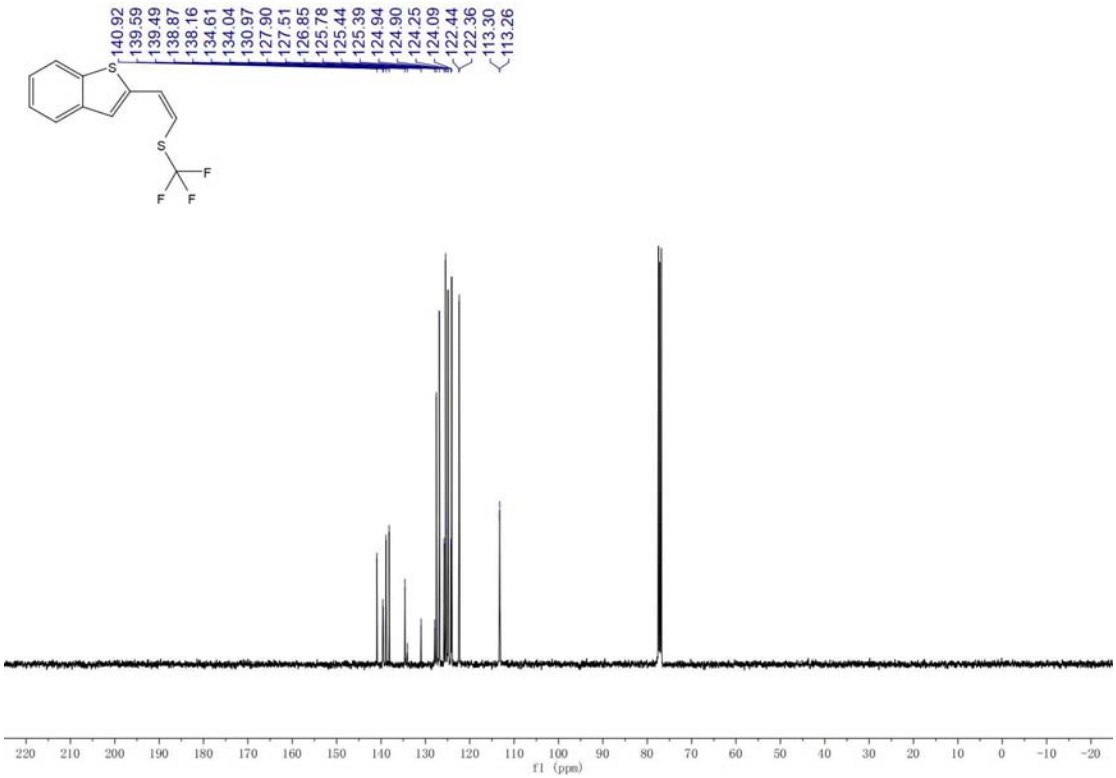
^{13}C NMR spectrum of **4ap** in $CDCl_3$ (101 MHz)



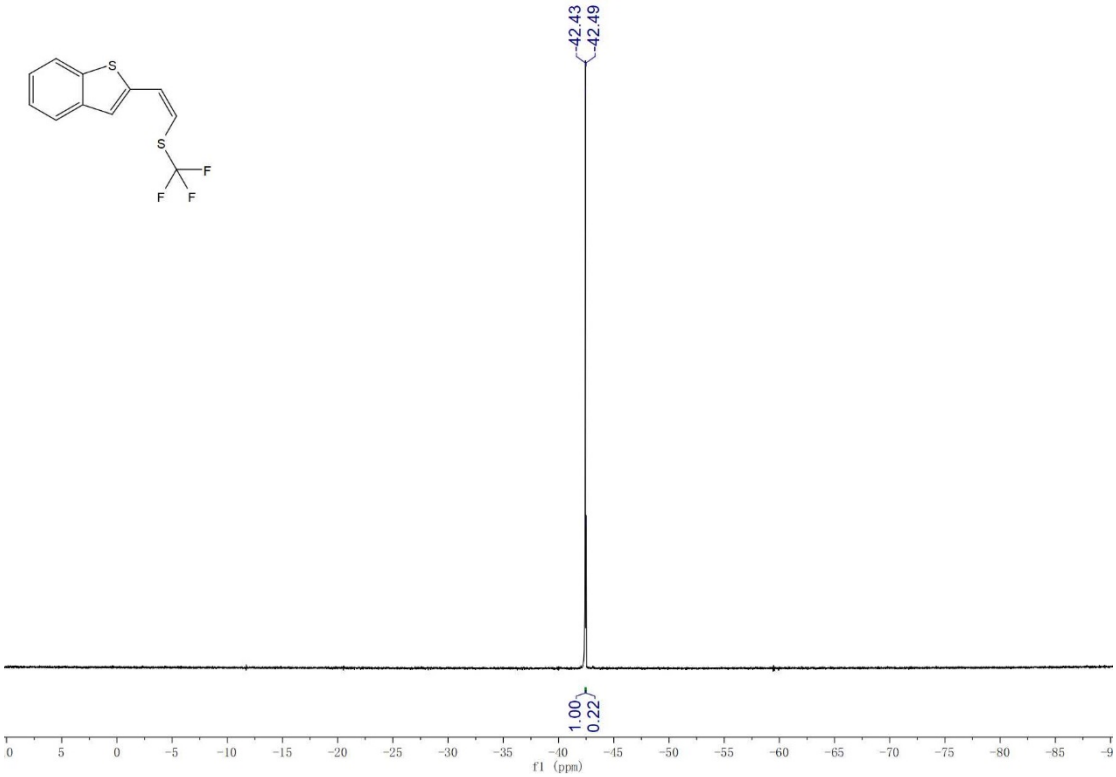
^{19}F NMR spectrum of **4ap** in $CDCl_3$ (283 MHz)



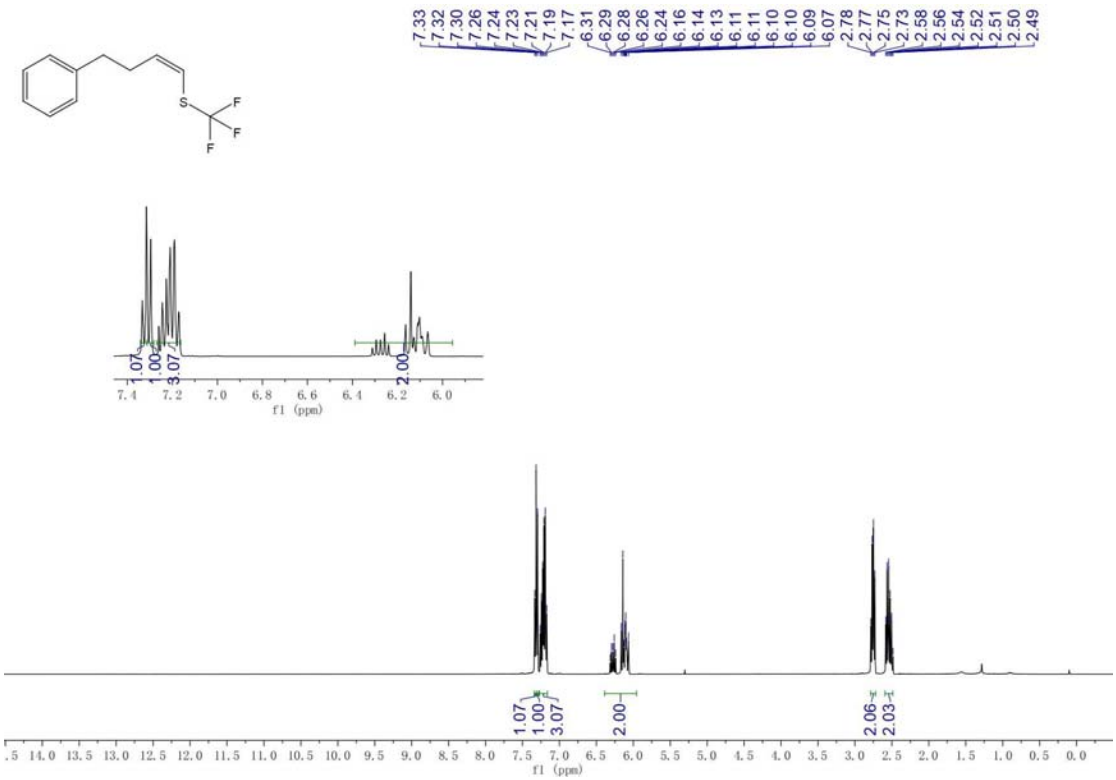
^{1}H NMR spectrum of **4aq** in $CDCl_3$ (400 MHz)



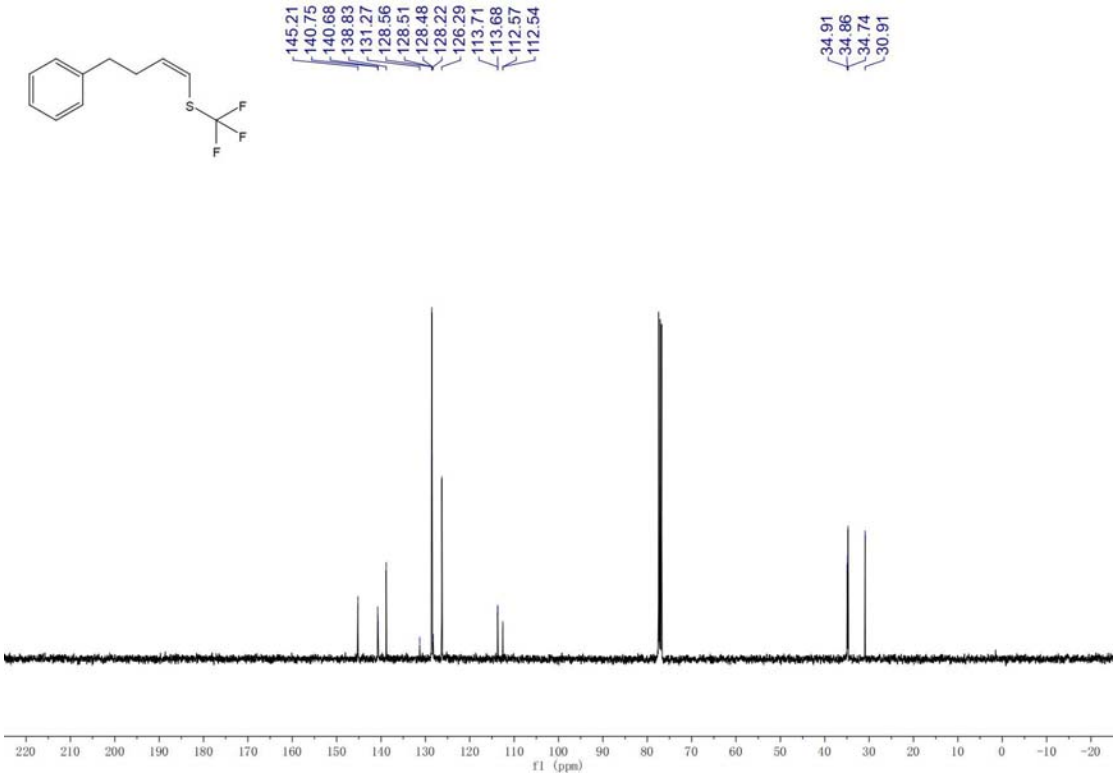
^{13}C NMR spectrum of **4aq** in $CDCl_3$ (101 MHz)



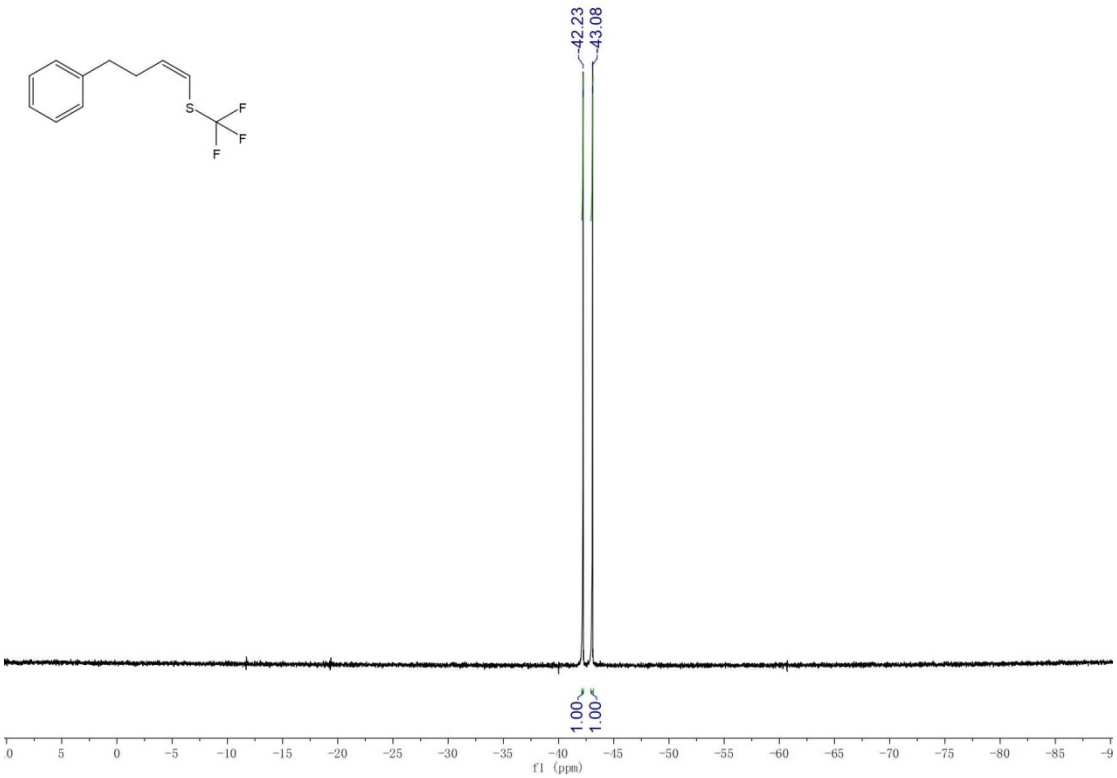
^{19}F NMR spectrum of **4aq** in $CDCl_3$ (283 MHz)



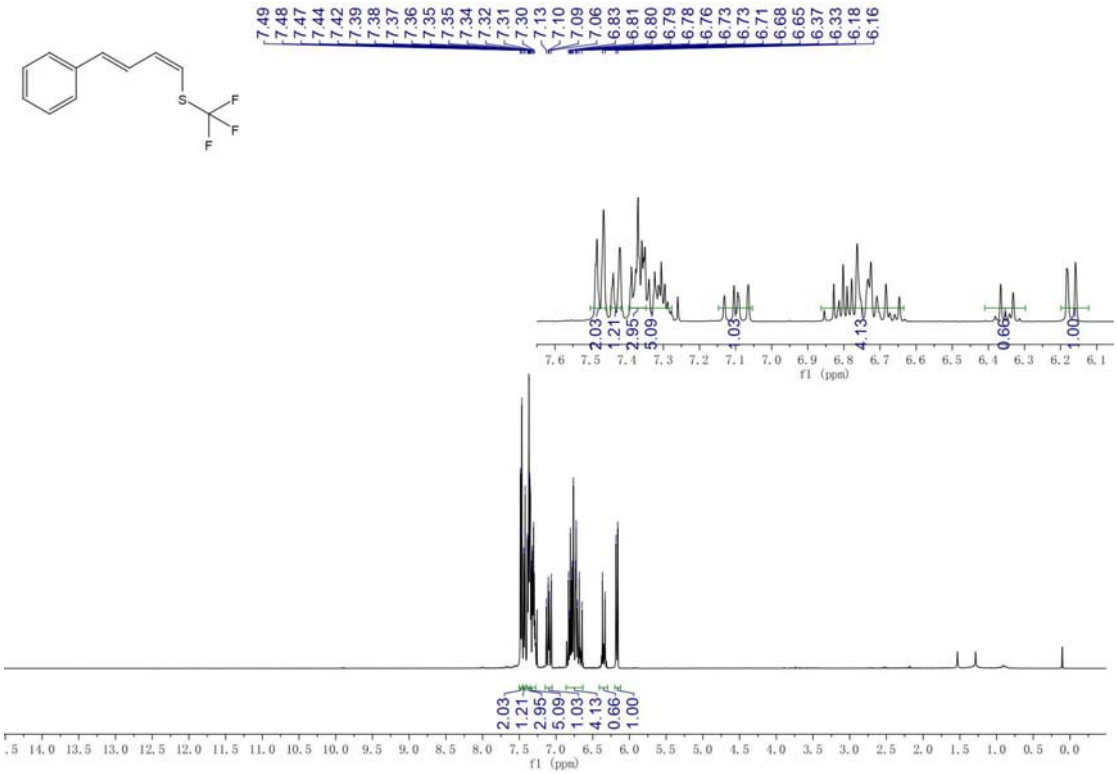
^{1}H NMR spectrum of **4ar** in $CDCl_3$ (400 MHz)



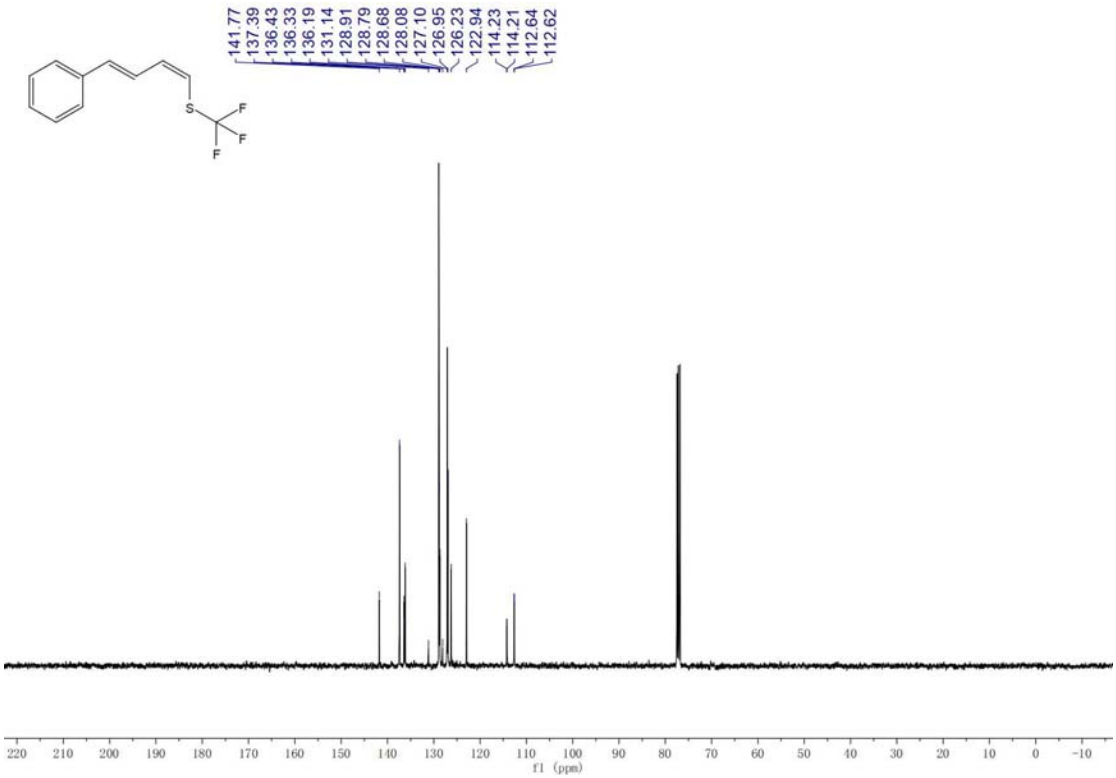
^{13}C NMR spectrum of **4ar** in $CDCl_3$ (101 MHz)



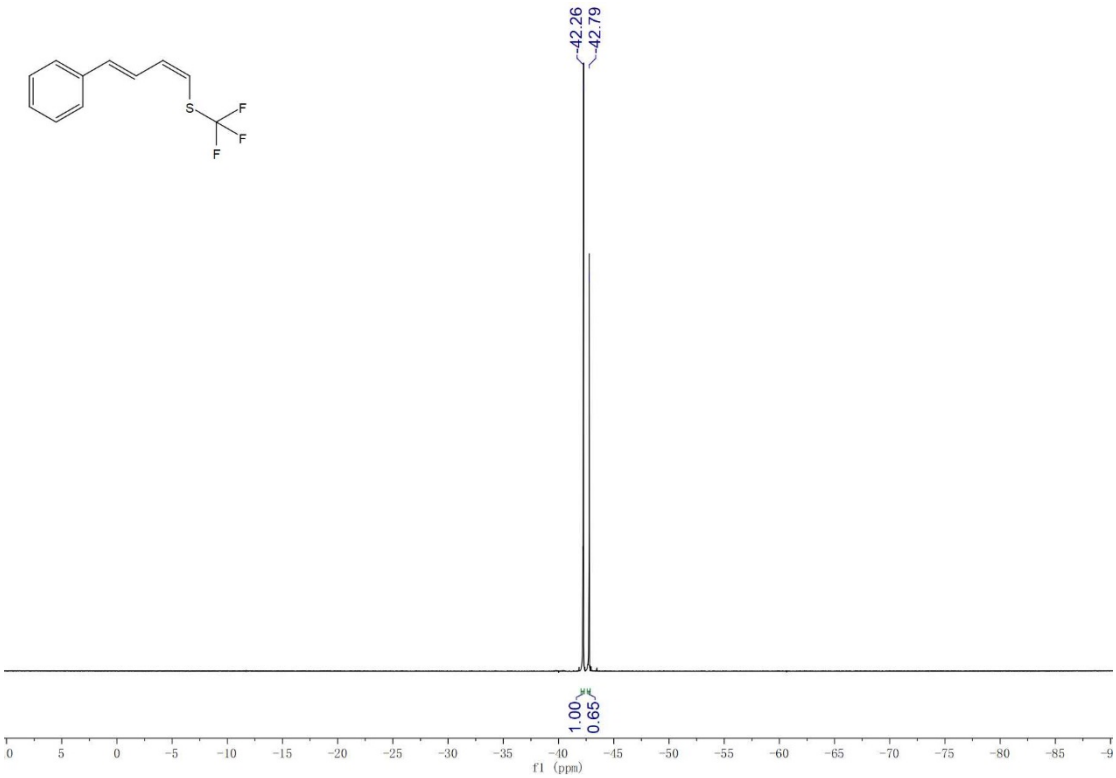
^{19}F NMR spectrum of **4ar** in $CDCl_3$ (283 MHz)



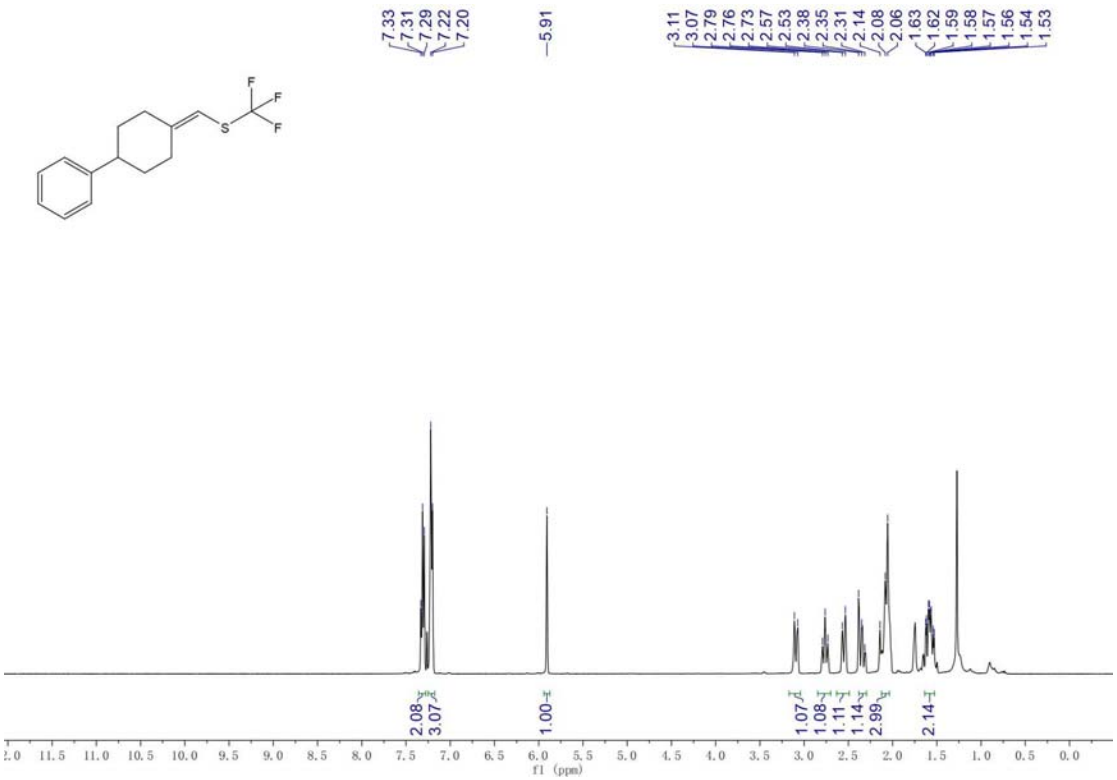
^{1}H NMR spectrum of **4as** in $CDCl_3$ (400 MHz)



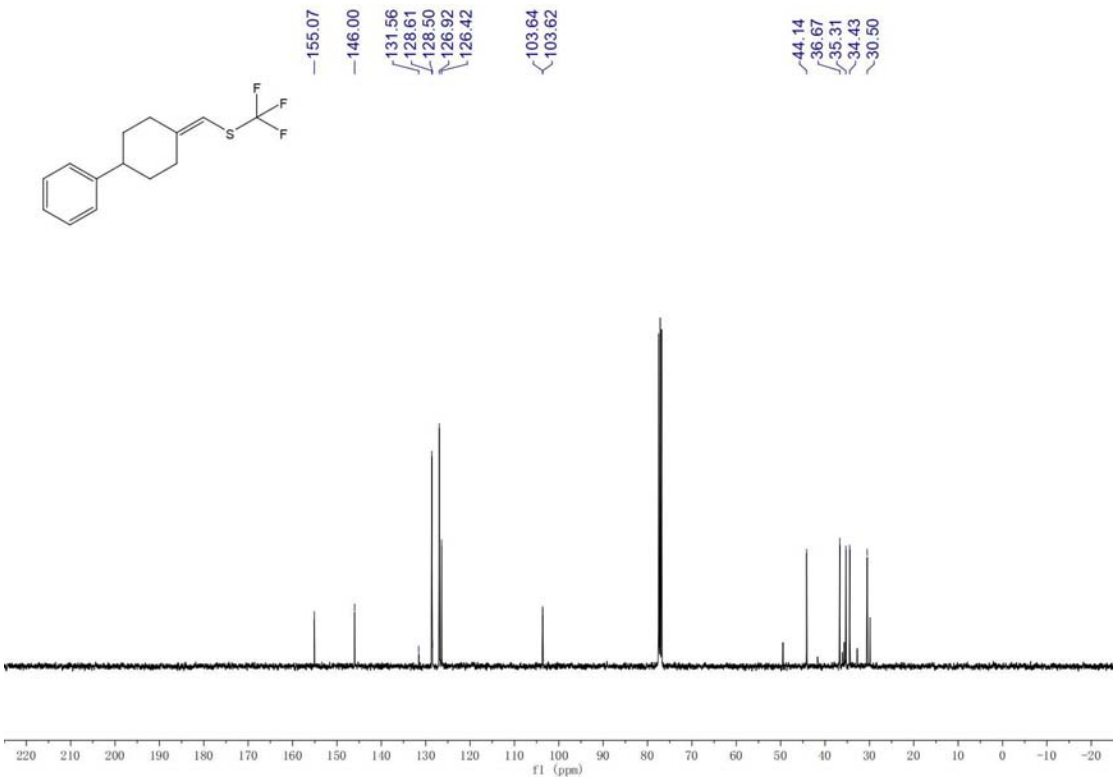
^{13}C NMR spectrum of **4as** in $CDCl_3$ (101 MHz)



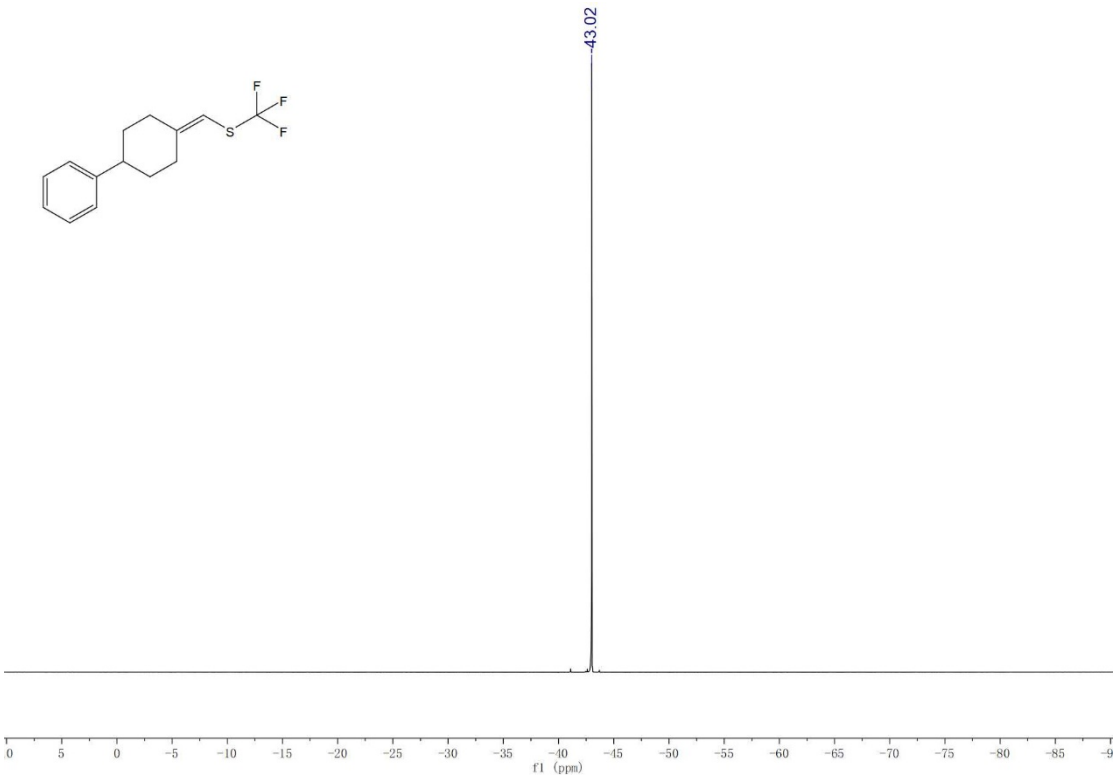
^{19}F NMR spectrum of **4as** in $CDCl_3$ (283 MHz)



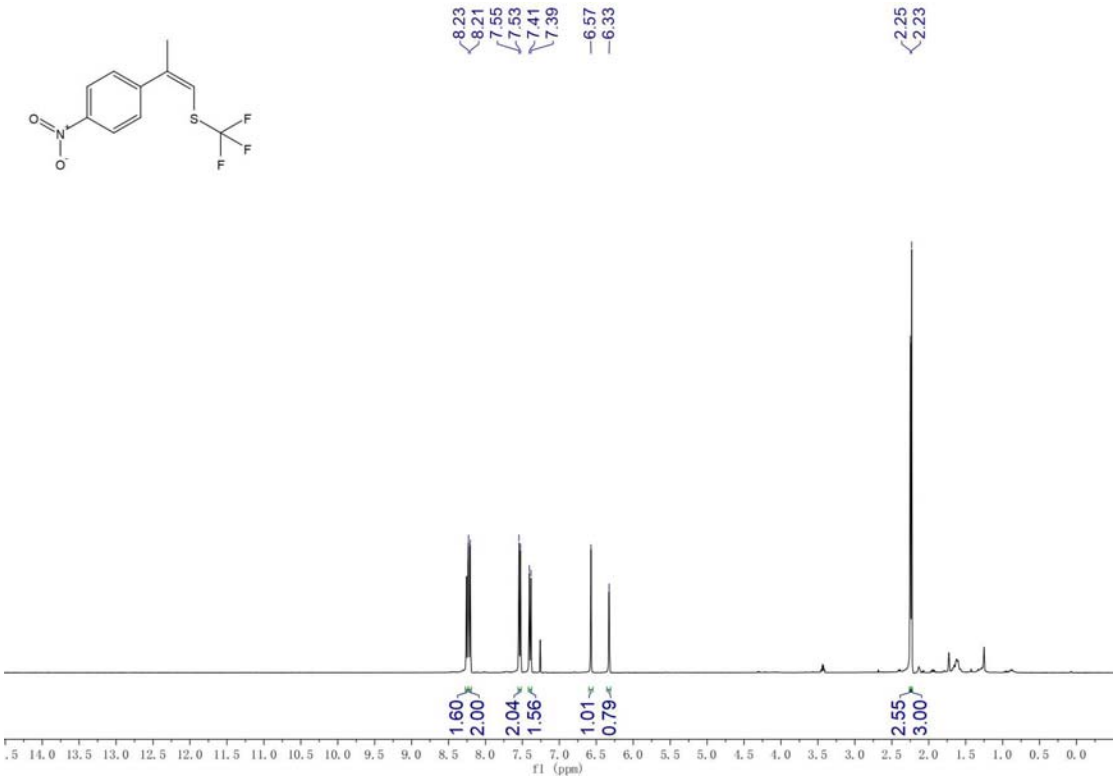
^{1}H NMR spectrum of **4at** in $CDCl_3$ (400 MHz)



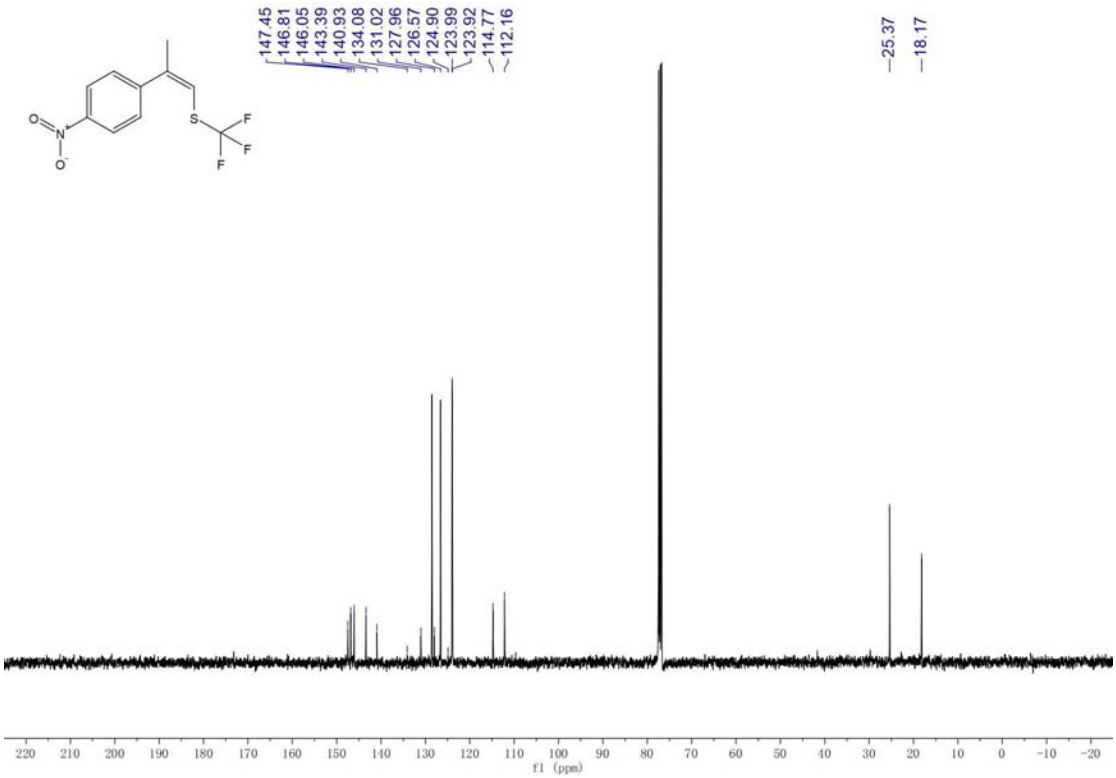
^{13}C NMR spectrum of **4at** in $CDCl_3$ (101 MHz)



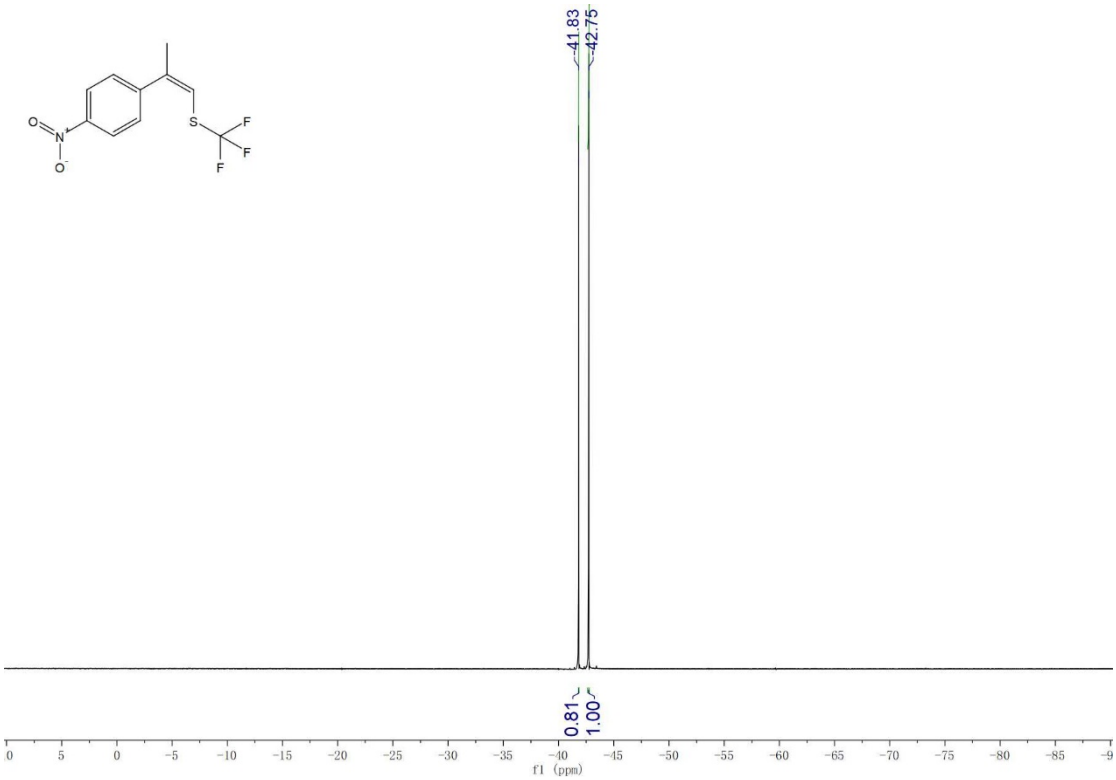
^{19}F NMR spectrum of **4at** in $CDCl_3$ (283 MHz)



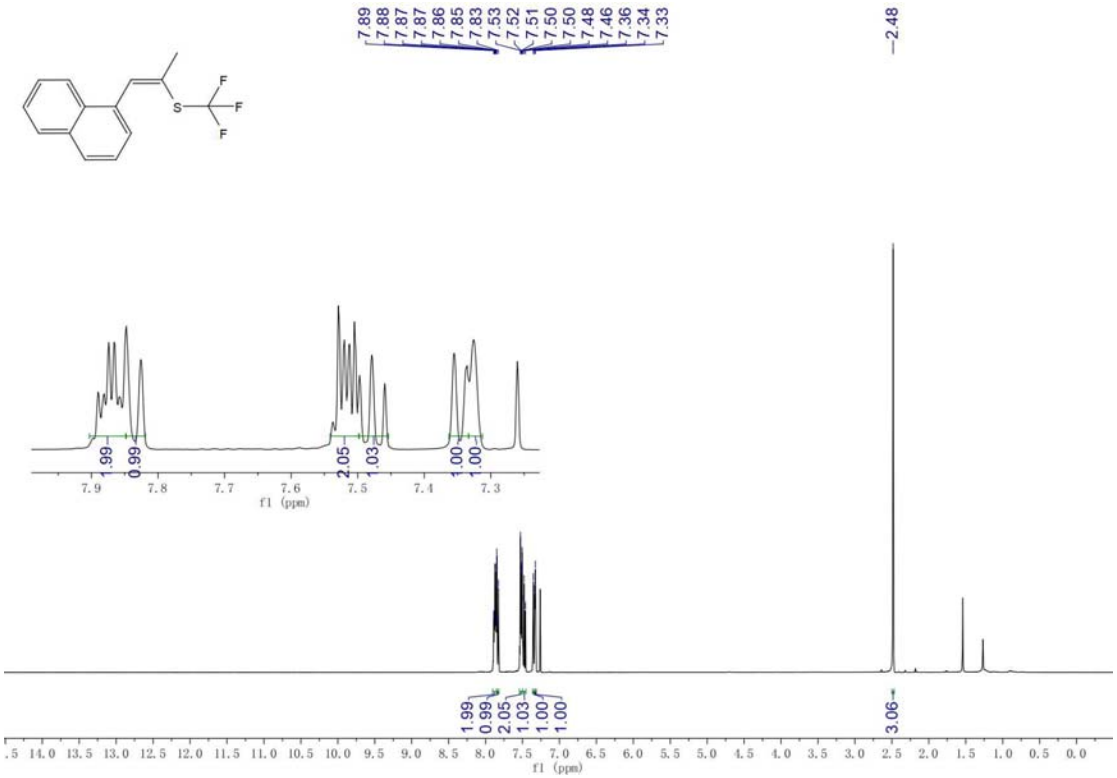
^{1}H NMR spectrum of **4au** in $CDCl_3$ (400 MHz)



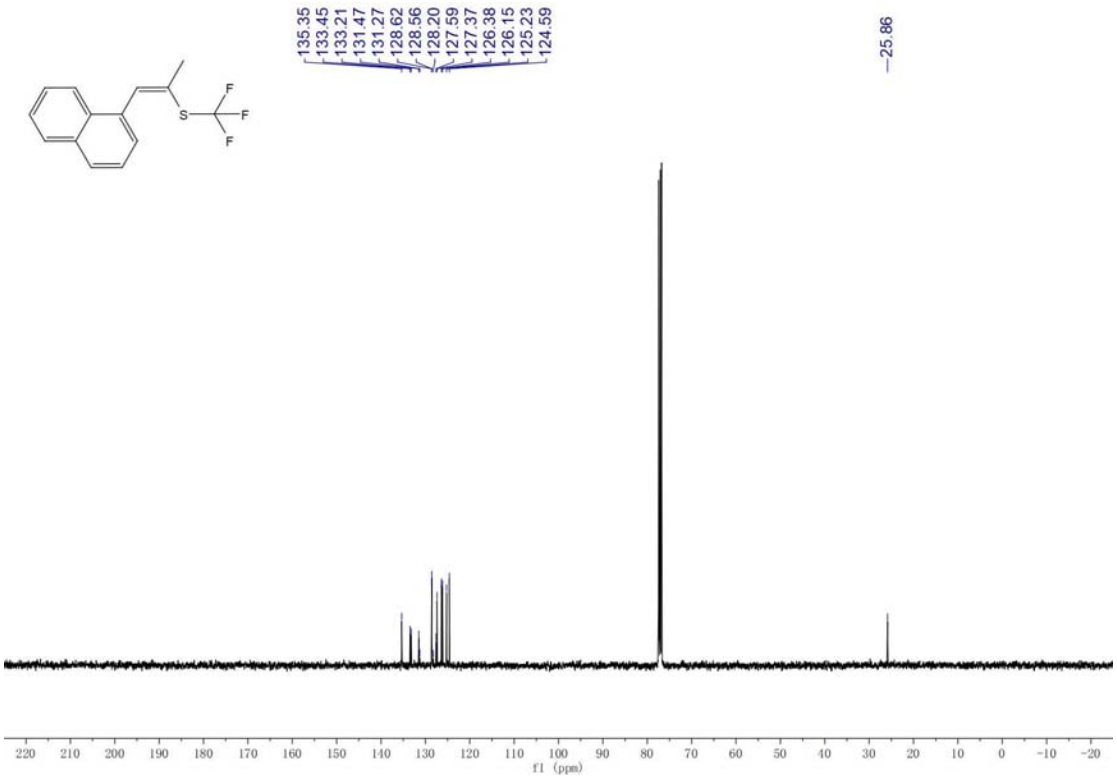
^{13}C NMR spectrum of **4au** in $CDCl_3$ (101 MHz)



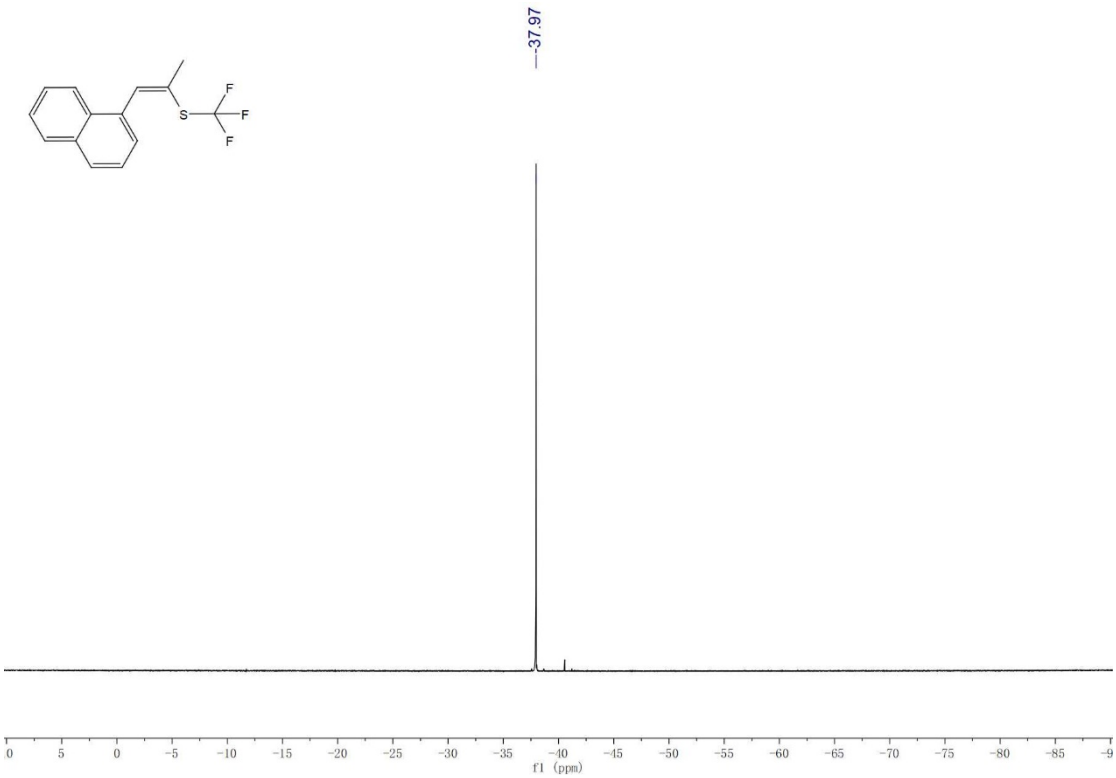
^{19}F NMR spectrum of **4au** in $CDCl_3$ (283 MHz)



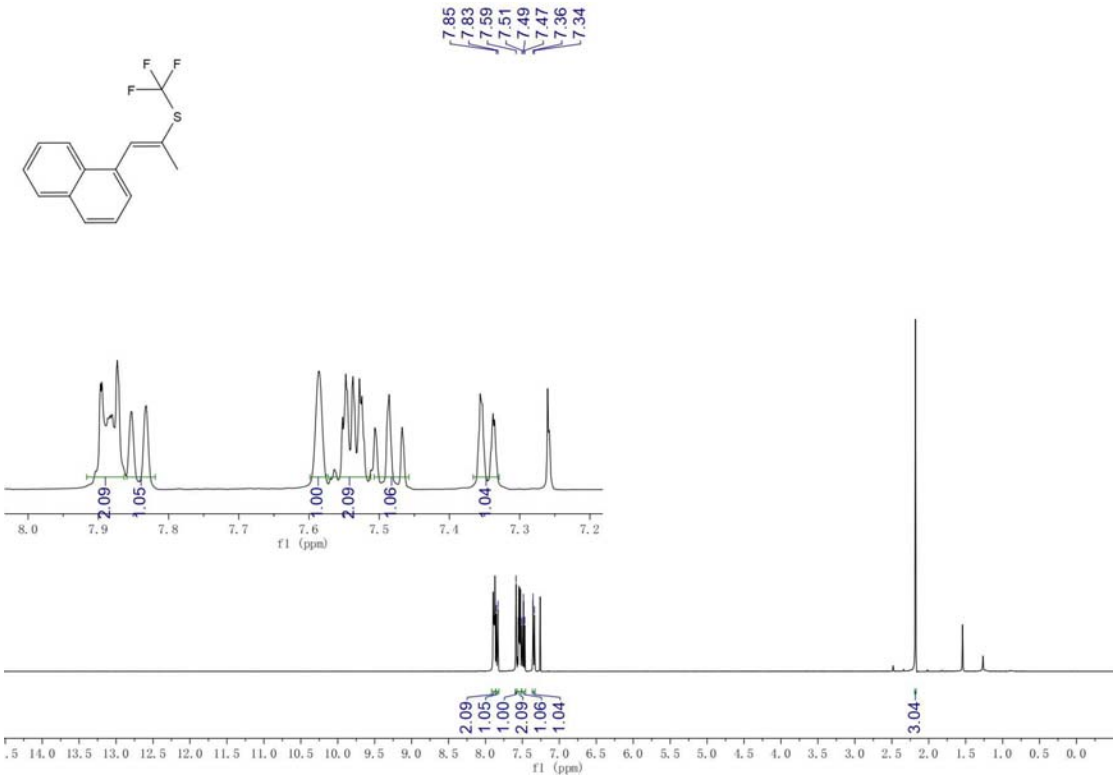
^{1}H NMR spectrum of **4ea** in $CDCl_3$ (400 MHz)



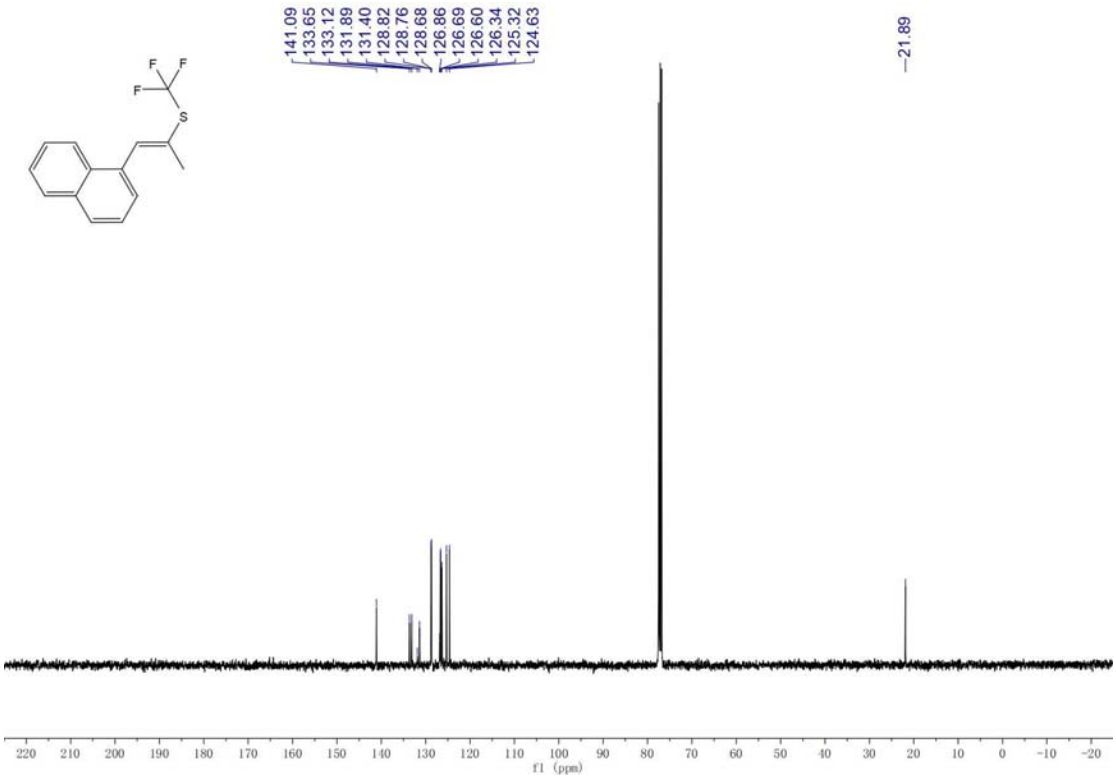
^{13}C NMR spectrum of **4ea** in $CDCl_3$ (101 MHz)



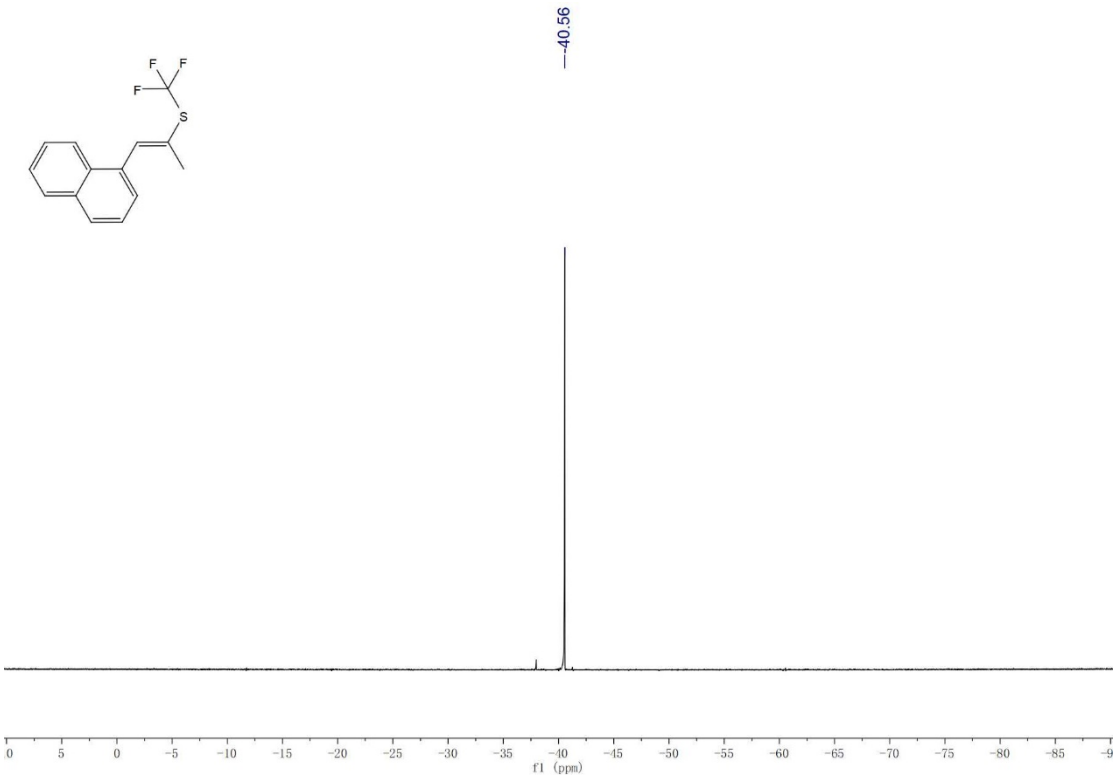
^{19}F NMR spectrum of **4ea** in $CDCl_3$ (283 MHz)



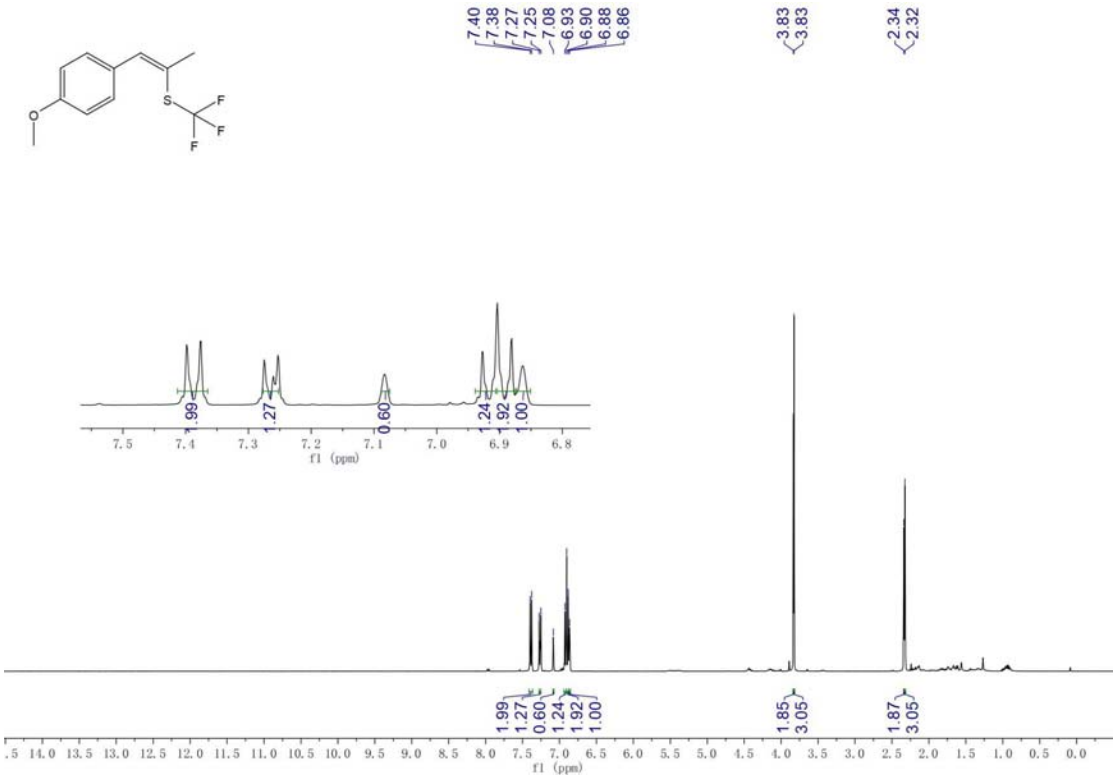
^{1}H NMR spectrum of **4ea'** in $CDCl_3$ (400 MHz)



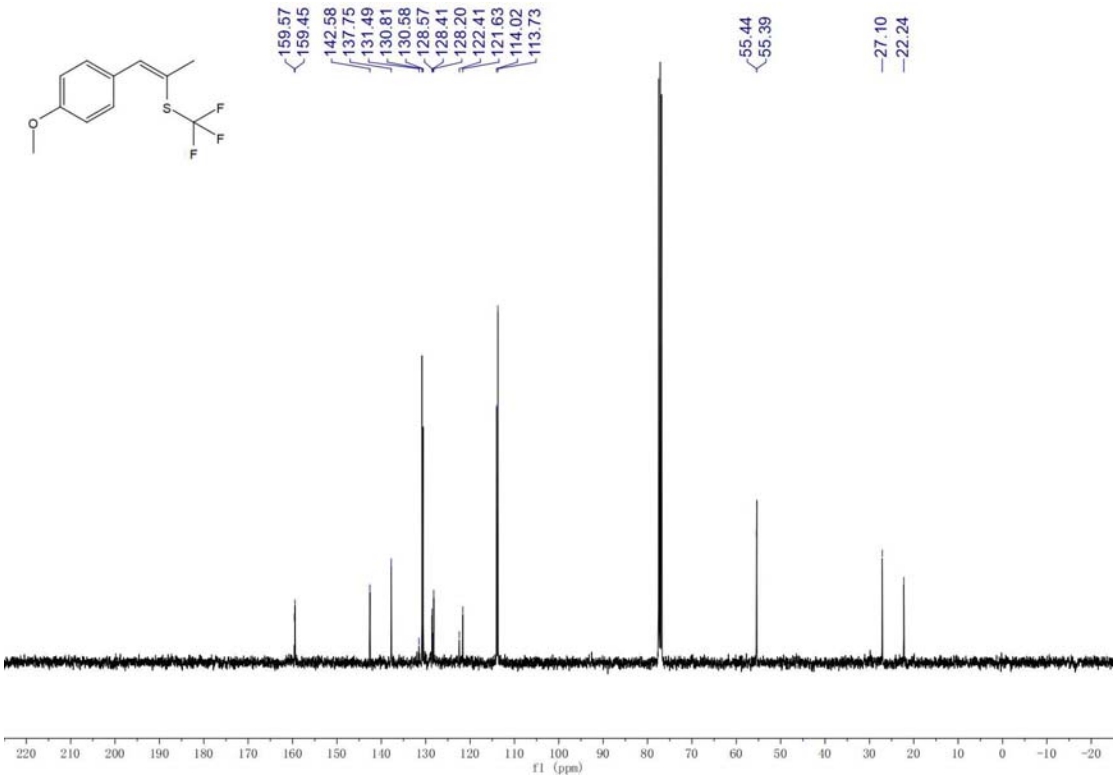
^{13}C NMR spectrum of **4ea'** in $CDCl_3$ (101 MHz)



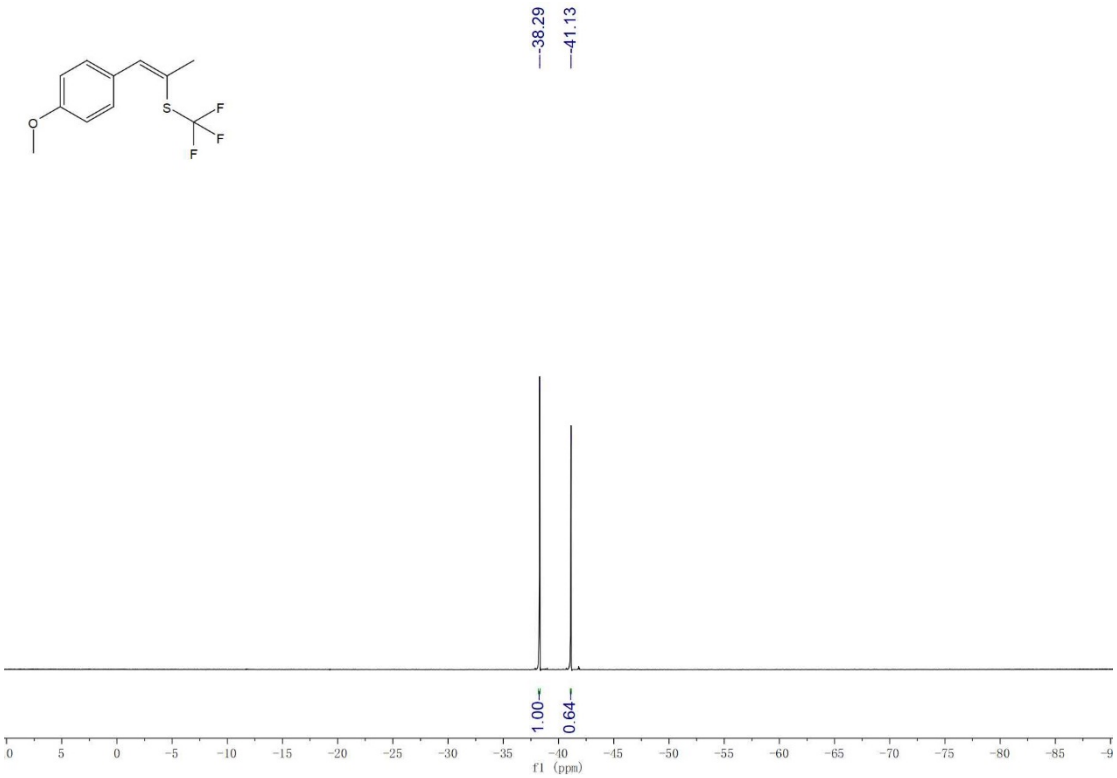
^{19}F NMR spectrum of **4ea'** in $CDCl_3$ (283 MHz)



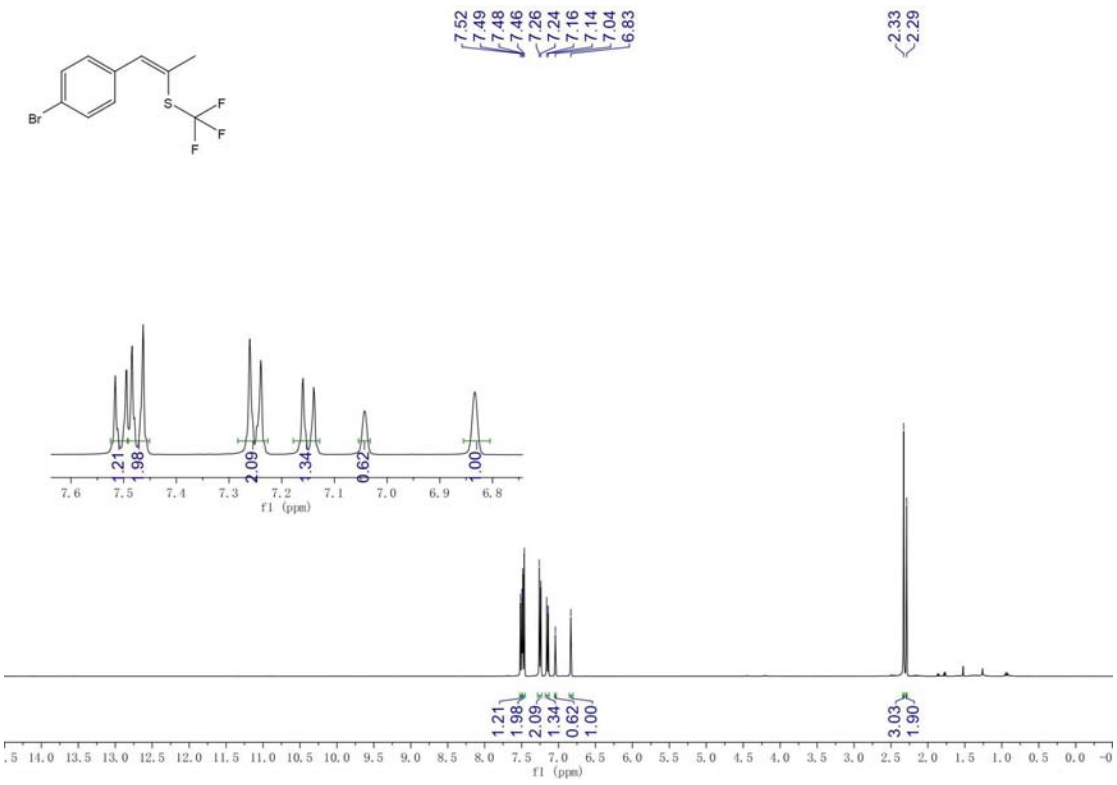
^{1}H NMR spectrum of **4ef** in $CDCl_3$ (400 MHz)



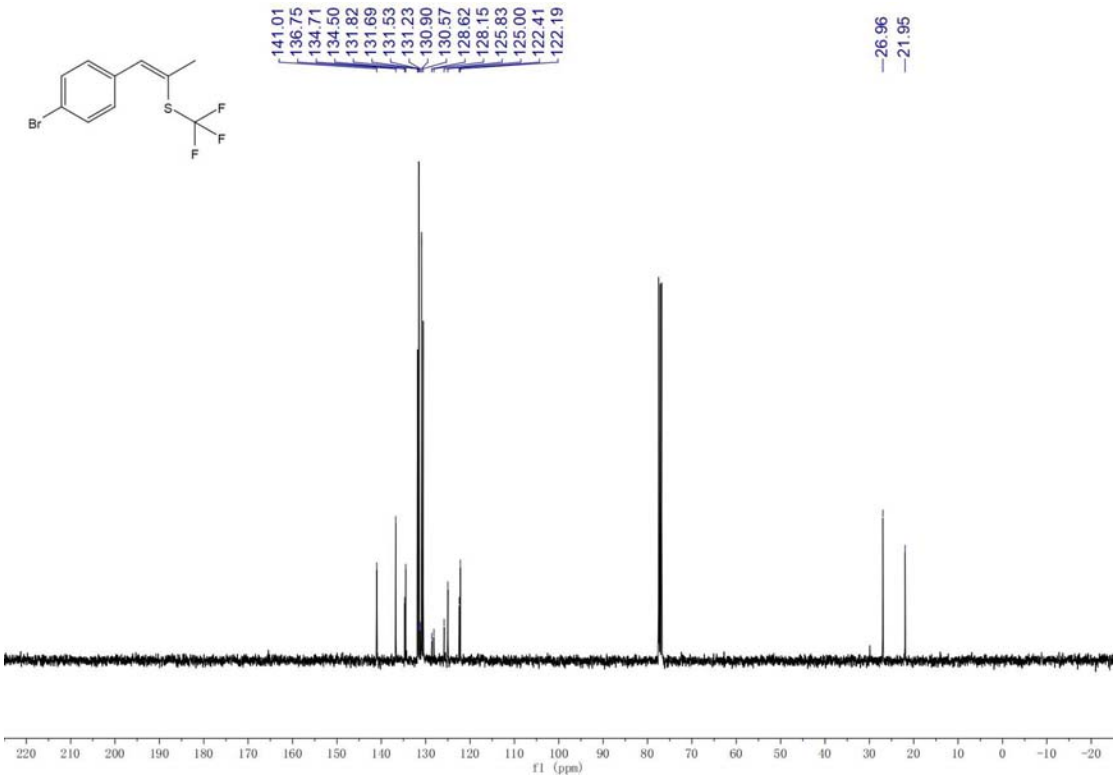
^{13}C NMR spectrum of **4ef** in $CDCl_3$ (101 MHz)



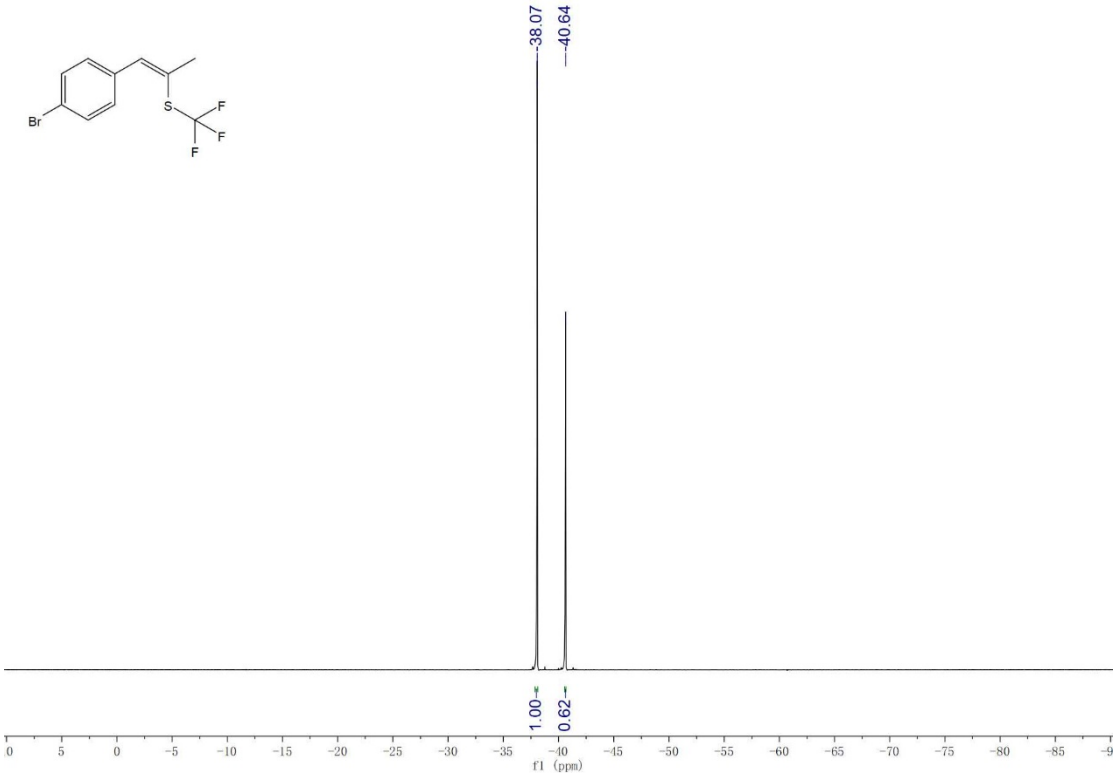
^{19}F NMR spectrum of **4ef** in $CDCl_3$ (283 MHz)



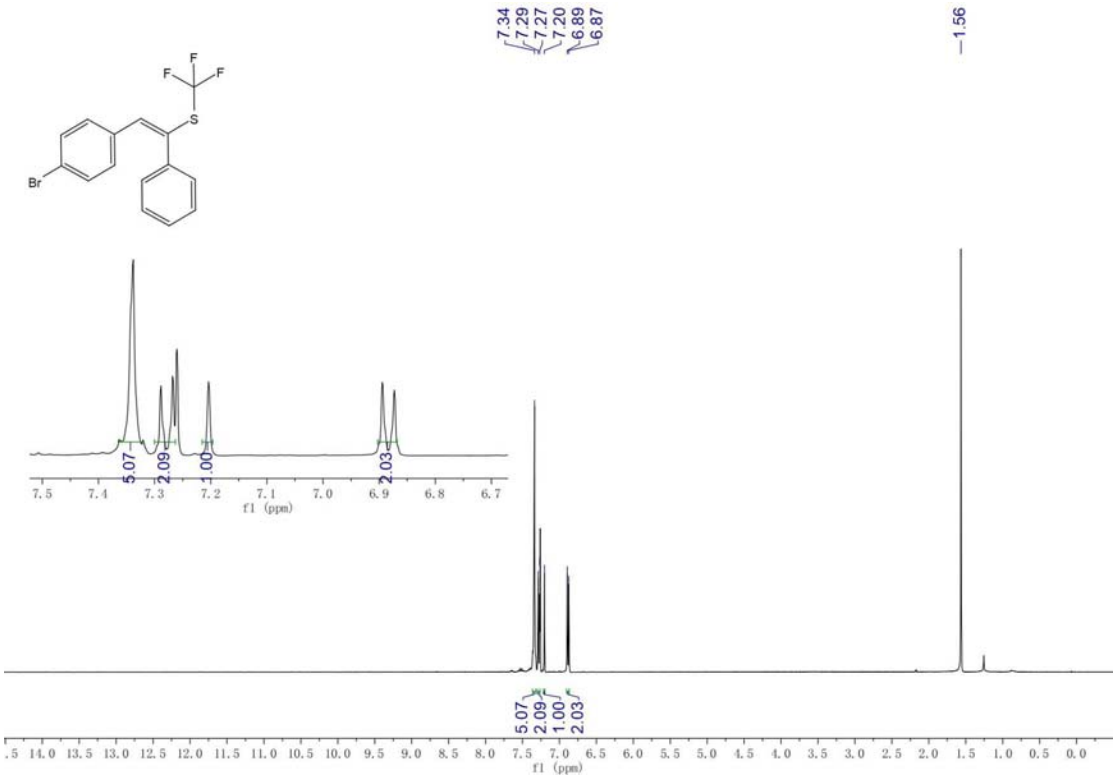
^{1}H NMR spectrum of **4ei** in $CDCl_3$ (400 MHz)



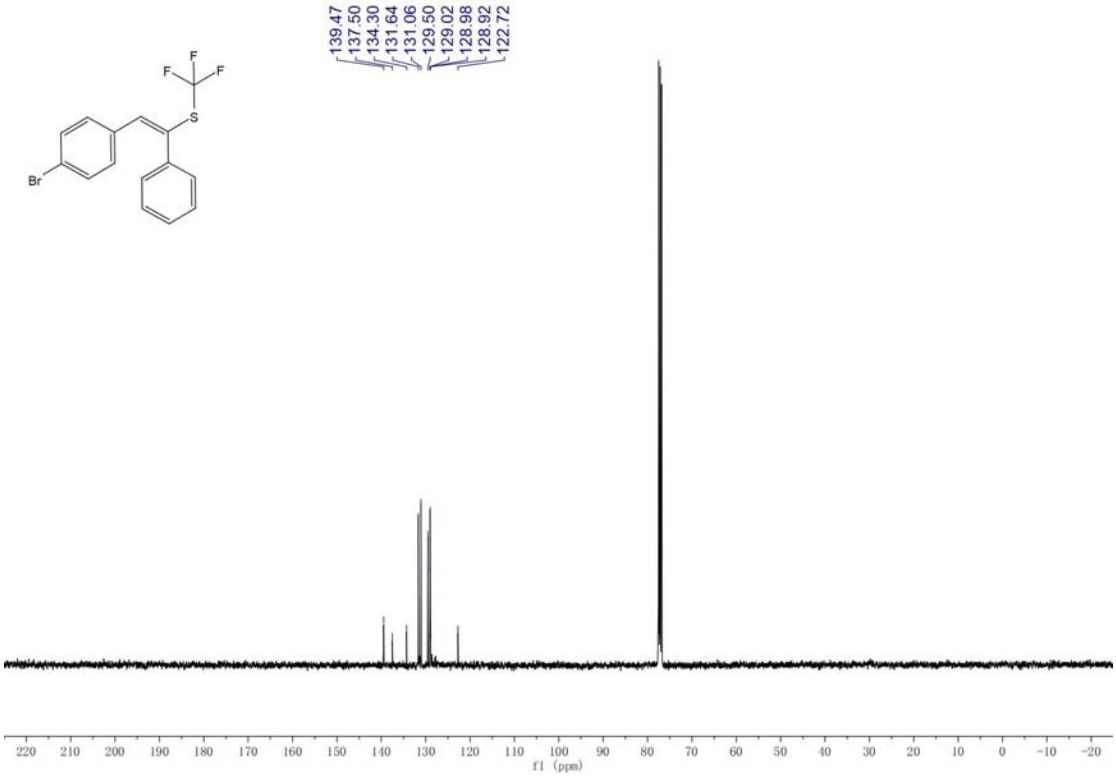
^{13}C NMR spectrum of **4ei** in $CDCl_3$ (101 MHz)



^{19}F NMR spectrum of **4ei** in $CDCl_3$ (283 MHz)



^{1}H NMR spectrum of **4fi** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of **4fi** in $CDCl_3$ (101 MHz)

^{19}F NMR spectrum of **4fi** in $CDCl_3$ (283 MHz)

9. X-ray single crystallographic data of compound 2b

The trifluoromethylthiolated phosphonium ylide **2b** was recrystallized from a solution in DCM/PE. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 1914419).

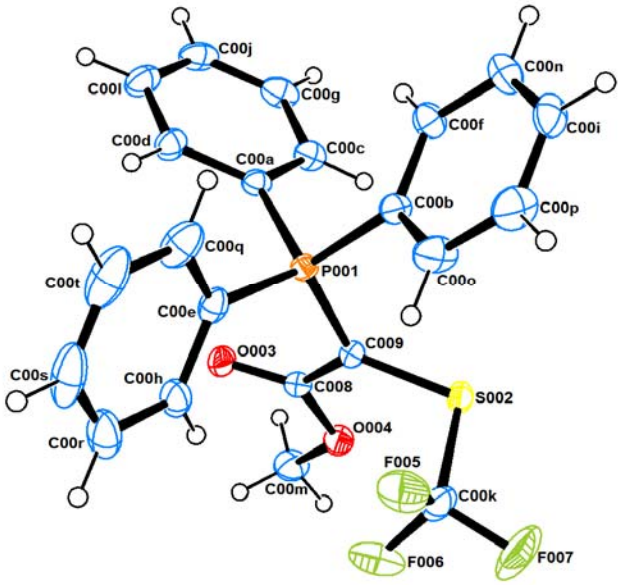


Table 1 Crystal data and structure refinement for compound 2b.

Empirical formula	$C_{22}H_{18}F_3O_2PS$
Formula weight	434.39
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.7335(2)
b/Å	20.6854(3)
c/Å	10.7411(2)
α/°	90
β/°	103.192(2)
γ/°	90
Volume/Å^3	2105.56(7)
Z	4
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	2.459
F(000)	896.0
Crystal size/mm^3	0.6 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.55 to 153.408
Index ranges	$-12 \le h \le 12$, $-17 \le k \le 25$, $-13 \le l \le 13$

Reflections collected	10455
Independent reflections	4378 [R_{int} = 0.0264, R_{sigma} = 0.0295]
Data/restraints/parameters	4378/0/263
Goodness-of-fit on F^2	1.132
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.1350
Final R indexes [all data]	R_1 = 0.0437, wR_2 = 0.1407
Largest diff. peak/hole / e $Å^{-3}$	0.57/-0.48