

Electronic Supporting Information

Synthesis of (*E*)-vinyl sulfides via copper-catalyzed hydrothiolation of internal alkynes with thiosulfonates and silanes

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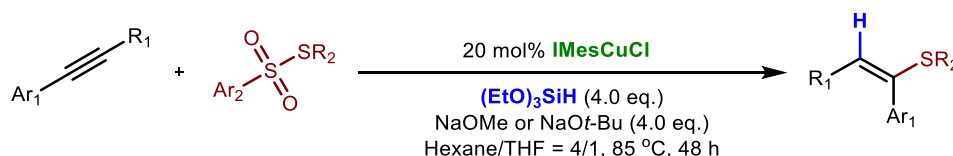
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1 General considerations

Unless otherwise noted, all reactions were performed under an argon atmosphere (purity \geq 99.999%) using standard Schlenk-type tubes on a dual-manifold Schlenk line. All the solvents were refluxed with CaH_2 for 12 h, then distilled, further degassed by bubbling with argon for 20 minutes at room temperature, and stored with activated 4 Å molecular sieves. Isolated yields were determined through purification of the crude product by column chromatography with 10 ~ 40 μm silica gel. Various reagents were purchased from commercial sources and used without further purification. The literature methods^[1] were used to synthesize the (NHC)CuCl catalysts including IMesCuCl, SIMesCuCl, IPrCuCl and SIPrCuCl. 1,2-Diarylethyne^[2-4] and thiosulfonates^[5-8] were synthesized according to the reported method. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance III HD 500 spectrometer. All NMR data were obtained in CDCl_3 at ambient temperature. High-resolution mass spectrometry (HRMS) was recorded on a Thermo Scientific Q Exactive.

2 General procedure for copper-catalyzed *syn*-hydrothiolation of internal alkynes with thiosulfonates and silanes



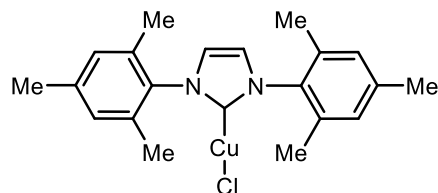
Into a flame-dried Schlenk tube fitted with a magnetic stir bar, IMesCuCl (0.04 mmol, 16.2 mg), NaOMe (0.8 mmol, 44 mg) or NaOt-Bu (0.8 mmol, 76.8 mg), and alkyne **1** (0.2 mmol, *if solid*) were charged. The tube was evacuated and backfilled with argon (this process was repeated three times). Then, 1.6 mL of hexane was introduced (if reaction time is 24 h, the amount of hexane is 0.8 mL), and the resulting mixture was stirred at room temperature for 5 minutes. Subsequently, alkyne **1** (0.2 mmol, *if liquid*) and $(\text{EtO})_3\text{SiH}$ (0.8 mmol, 148 μL) were added under a flow of argon. The resulting mixture was stirred at room temperature for an additional 5 minutes. The solution of thiosulfonate **2** (0.8 mmol) in 0.4 mL of THF (if reaction time is 24 h, the amount of THF is 0.2 mL) was introduced into the tube under an argon flow. The reaction tube was then sealed and stirred at 85 °C for 48 hours in the absence of light. After cooling to room temperature, the reaction mixture was purified through column chromatography on silica gel using petroleum ether as the eluent,

resulting in the isolation the designed products **3**. Notably, the processing operations needs to be conducted in the dark.

3 Characterization data of compounds

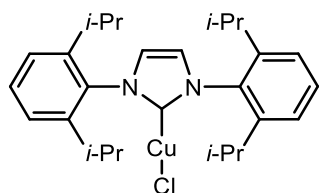
3.1 Characterization of catalysts

[1,3-Bismesitylimidazol-2-ylidene]copper(I) chloride (IMesCuCl)^[1]:



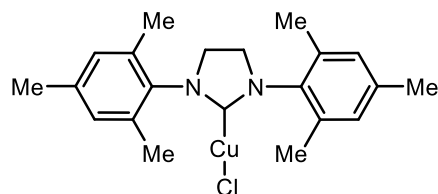
¹H NMR (500 MHz, CDCl₃) δ 7.05 (s, 2H), 7.00 (s, 4H), 2.34 (s, 6H), 2.10 (s, 12H).

[1,3-Bis[2,6-diisopropylphenyl]imidazol-2-ylidene]copper(I) chloride (IPrCuCl)^[1]:



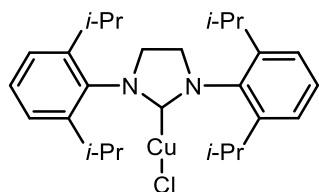
¹H NMR (500 MHz, CDCl₃) δ 7.49 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 4H), 7.13 (s, 2H), 2.60 – 2.52 (m, 4H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H).

[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]copper(I) chloride (SIMesCuCl)^[1]:



¹H NMR (500 MHz, CDCl₃) δ 6.95 (s, 4H), 3.95 (s, 4H), 2.31 (d, *J* = 8.7 Hz, 18H).

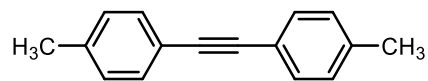
[1,3-Bis[2,6-(diisopropylphenyl)]imidazolidin-2-ylidene]copper(I) chloride (SIPrCuCl)^[1]:



¹H NMR (500 MHz, DMSO) δ 7.44 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 4H), 4.07 (s, 4H), 3.09 (dt, *J* = 13.5, 6.7 Hz, 4H), 1.31 (d, *J* = 6.8 Hz, 12H), 1.26 (d, *J* = 6.8 Hz, 12H).

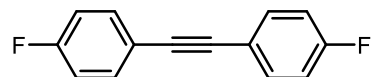
3.2 Characterization of 1,2-diarylethyne (1)

1,2-Di-*p*-tolylethyne (1b)^[2]:



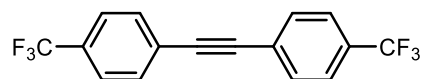
¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 4H), 2.36 (s, 6H).

1,2-Bis(4-fluorophenyl)ethyne (1c)^[2]:



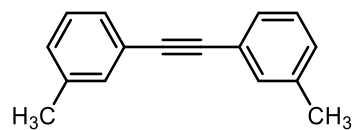
¹H NMR (500 MHz, CDCl₃) δ 7.49 (dd, *J* = 8.8, 5.4 Hz, 4H), 7.04 (t, *J* = 8.7 Hz, 4H).

1,2-Bis(4-(trifluoromethyl)phenyl)ethyne (1d)^[2]:



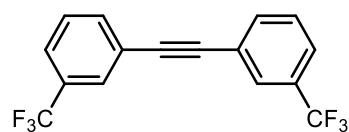
¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 8.6 Hz, 4H), 7.62 (d, *J* = 8.6 Hz, 4H).

1,2-Di-*m*-tolylethyne (1e)^[3]:



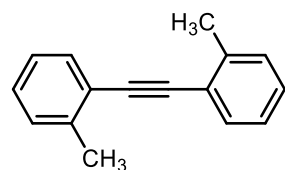
¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.32 (m, 4H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 2.32 (s, 6H).

1,2-Bis(3-(trifluoromethyl)phenyl)ethyne (1f)^[3]:



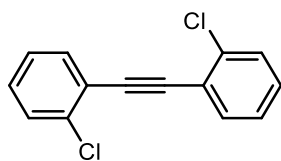
¹H NMR (500 MHz, CDCl₃) δ 7.81 (s, 2H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H).

1,2-Di-*o*-tolylethyne (1g)^[3]:



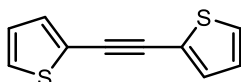
¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.23 (dd, *J* = 6.5, 5.6 Hz, 4H), 7.19 – 7.16 (m, 2H), 2.53 (s, 6H).

1,2-Bis(2-chlorophenyl)ethyne (1h)^[2]:



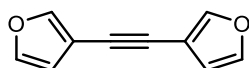
¹H NMR (500 MHz, CDCl₃) δ 7.53 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.36 (dd, *J* = 7.7, 1.2 Hz, 2H), 7.23 – 7.16 (m, 4H).

1,2-Di(thiophen-2-yl)ethyne (1i)^[2]:



¹H NMR (500 MHz, CDCl₃) δ 7.28 (dt, *J* = 13.4, 7.8 Hz, 4H), 7.01 (dd, *J* = 5.0, 3.7 Hz, 2H).

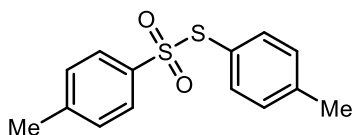
1,2-Di(furan-3-yl)ethyne (1j)^[4]:



¹H NMR (500 MHz, CDCl₃) δ 7.66 (m, *J* = 0.7 Hz, 2H), 7.39 (t, 2H), 6.49 (m, *J* = 1.2 Hz, 2H).

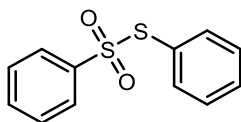
3.3 Characterization of thiosulfonates (2)

***S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (2a)^[6]:**



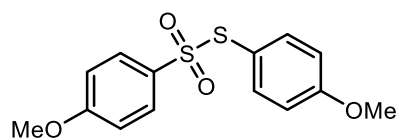
¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.14 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H).

***S*-phenyl benzenesulfonothioate (2b)^[6]:**



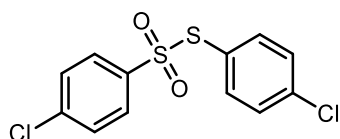
¹H NMR (500 MHz, CDCl₃) δ 7.56 (dd, *J* = 13.1, 7.4 Hz, 3H), 7.48 – 7.31 (m, 7H).

S-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate (2c)^[6]:



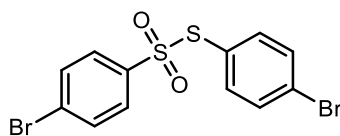
¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, *J* = 8.9 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.86 (dd, *J* = 14.2, 8.8 Hz, 4H), 3.87 (s, 3H), 3.83 (s, 3H).

S-(4-chlorophenyl) 4-chlorobenzenesulfonothioate (2d)^[6]:



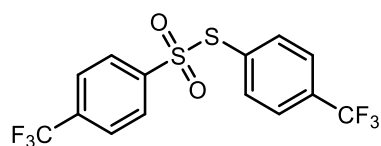
¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H).

S-(4-bromophenyl) 4-bromobenzenesulfonothioate (2e)^[6]:



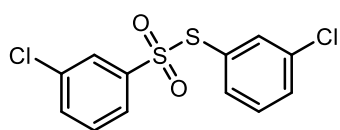
¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.57 (m, 1H), 7.54 – 7.49 (m, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.30 – 7.20 (m, 2H).

S-(4-(trifluoromethyl)phenyl) 4-(trifluoromethyl)benzenesulfonothioate (2f)^[7]:



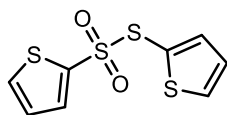
¹H NMR (500 MHz, CDCl₃) δ 7.75 – 7.71 (m, 4H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H).

S-(3-chlorophenyl) 3-chlorobenzenesulfonothioate (2g)^[6]:



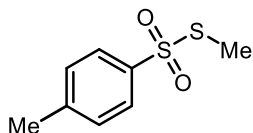
¹H NMR (500 MHz, CDCl₃) δ 7.60 – 7.57 (m, 1H), 7.54 (t, *J* = 1.8 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.46 (dd, *J* = 6.7, 1.3 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.29 (m, 3H).

S-(thiophen-2-yl) thiophene-2-sulfonylthioate (2h)^[6]:



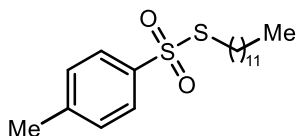
¹H NMR (500 MHz, CDCl₃) δ 7.69 – 7.64 (m, 2H), 7.41 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.11 (dd, *J* = 5.2, 3.8 Hz, 1H), 7.07 – 7.05 (m, 1H).

S-methyl 4-methylbenzenesulfonylthioate (2i)^[8]:



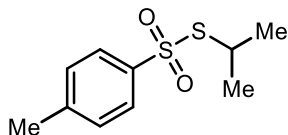
¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 2.49 (s, 3H), 2.45 (s, 3H).

S-dodecyl 4-methylbenzenesulfonylthioate (2j)^[8]:



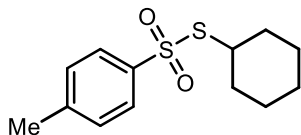
¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 1.58 – 1.52 (m, 2H), 1.20 (d, *J* = 25.3 Hz, 20H), 0.85 (t, *J* = 6.9 Hz, 3H).

S-isopropyl 4-methylbenzenesulfonylthioate (2k)^[8]:



¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.48 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.45 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 6H).

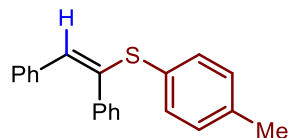
S-cyclohexyl 4-methylbenzenesulfonylthioate (2l)^[8]:



¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.37 – 3.31 (m, 1H), 2.44 (s, 3H), 1.93 – 1.90 (m, 2H), 1.65 (dd, *J* = 9.0, 4.1 Hz, 2H), 1.55 – 1.29 (m, 6H).

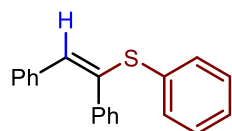
3.4 Characterization of (*E*)-vinyl sulfides (**3**) from copper-catalyzed *syn*-hydrothiolation of internal alkynes (**1**)

(*E*)-(1,2-diphenylvinyl)(*p*-tolyl)sulfane (**3aa**)^[9]:



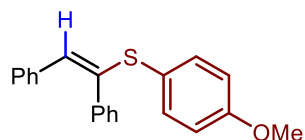
Purification by column chromatograph on silica gel (petroleum ether) gave **3aa** as a colorless oil (48.6 mg, 80 %). ¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.24 (m, 4H), 7.18 – 7.14 (m, 3H), 7.00 – 6.99 (m, 5H), 6.84 (dd, *J* = 7.4, 1.9 Hz, 2H), 6.56 (s, 1H), 2.22 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.99, 138.05, 137.88, 136.74, 133.16, 129.90, 129.86, 129.75, 129.01, 128.49, 128.33, 128.24, 128.08, 126.77, 21.28; HRMS (ESI) *m/z*: calculated for [C₂₁H₁₈S + H]⁺ 303.1202, found 303.1208.

(*E*)-(1,2-diphenylvinyl)(*p*-tolyl)sulfane (**3ab**)^[10]:



Purification by column chromatograph on silica gel (petroleum ether) gave **3ab** as a colorless oil (46.2 mg, 80 %). ¹H NMR (500 MHz, CDCl₃) δ 7.39 (d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.20 (dd, *J* = 16.2, 9.1 Hz, 6H), 7.08 (d, *J* = 5.3 Hz, 3H), 6.95 – 6.94 (m, 2H), 6.79 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 138.09, 137.93, 136.65, 133.73, 132.51, 129.94, 129.13, 129.02, 128.49, 128.31, 128.14, 128.12, 127.57, 127.01; HRMS (ESI) *m/z*: calculated for [C₂₀H₁₆S + H]⁺ 289.1045, found 289.1045.

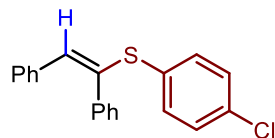
(*E*)-(1,2-diphenylvinyl)(4-methoxyphenyl)sulfane (**3ac**):



Purification by column chromatograph on silica gel (petroleum ether) gave **3ac** as a colorless oil (32.6 mg, 54%). ¹H NMR (500 MHz, CDCl₃) δ 7.32 (d, *J* = 8.7 Hz, 2H), 7.24 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.19 – 7.14 (m, 3H), 6.98 (d, *J* = 7.3 Hz, 3H), 6.82 – 6.78 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.40 (s, 1H), 3.70 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 145.73, 141.69, 139.40, 134.07, 132.17,

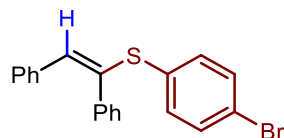
129.87, 129.68, 129.57, 128.90, 128.86, 128.76, 128.48, 125.60, 21.55; HRMS (ESI) m/z : calculated for $[C_{21}H_{18}OS + H]^+$ 319.1152, found 319.1142.

(E)-(4-chlorophenyl)(1,2-diphenylvinyl)sulfane (3ad)^[11]:



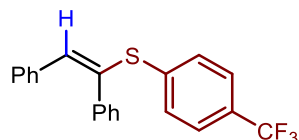
Purification by column chromatograph on silica gel (petroleum ether) gave **3ad** as a colorless oil (40.0 mg, 62%). ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.27 (m, 4H), 7.22 – 7.15 (m, 5H), 7.12 – 7.09 (m, 3H), 6.97 (dd, $J = 5.7, 2.5$ Hz, 2H), 6.87 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 137.56, 137.29, 136.42, 133.54, 133.42, 132.44, 130.96, 129.93, 129.21, 129.16, 128.57, 128.29, 128.21, 127.28; HRMS (ESI) m/z : calculated for $[C_{20}H_{15}ClS + H]^+$ 323.0656, found 323.0656.

(E)-(4-bromophenyl)(1,2-diphenylvinyl)sulfane (3ae):



Purification by column chromatograph on silica gel (petroleum ether) gave **3ae** as a colorless oil (43.4 mg, 59%). ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.23 (m, 4H), 7.18 – 7.12 (m, 5H), 7.08 – 7.01 (m, 3H), 6.91 (dd, $J = 6.7, 2.9$ Hz, 2H), 6.84 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 137.52, 136.99, 136.37, 133.46, 133.19, 132.05, 131.30, 129.92, 129.22, 128.56, 128.30, 128.20, 127.31, 121.52; HRMS (ESI) m/z : calculated for $[C_{20}H_{15}BrS + H]^+$ 367.0151, found 367.0140.

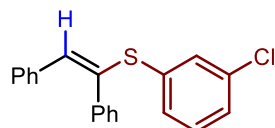
(E)-(1,2-diphenylvinyl)(4-(trifluoromethyl)phenyl)sulfane (3af):



Purification by column chromatograph on silica gel (petroleum ether) gave **3af** as a colorless oil (18.4 mg, 26%). ¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.36 (m, 6H), 7.24 – 7.17 (m, 3H), 7.17 – 7.13 (m, 3H), 7.12 (s, 1H), 7.04 (dd, $J = 6.5, 2.9$ Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 139.95, 137.38, 136.21, 135.16, 134.21, 130.24, 129.99, 129.39, 128.63 (q, $J = 32.8$ Hz), 128.60, 128.44,

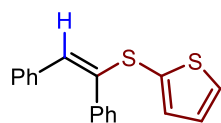
128.30, 127.71, 125.68 (q, $J = 3.7$ Hz), 124.15 (q, $J = 272.2$ Hz); HRMS (ESI) m/z : calculated for $[C_{21}H_{15}F_3S + H]^+$ 357.0920, found 357.0938.

(*E*)-(3-chlorophenyl)(1,2-diphenylvinyl)sulfane (3ag):



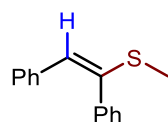
Purification by column chromatograph on silica gel (petroleum ether) gave **3ag** as a colorless oil (42.5 mg, 66%). 1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 3H), 7.15 – 7.10 (m, 4H), 7.05 – 7.01 (m, 5H), 6.91 (dd, $J = 6.5, 2.8$ Hz, 2H), 6.88 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.48, 136.47, 136.33, 136.21, 134.56, 132.23, 131.23, 129.95, 129.90, 129.59, 129.28, 128.54, 128.29, 128.22, 127.42, 127.32; HRMS (ESI) m/z : calculated for $[C_{20}H_{15}ClS + H]^+$ 323.0656, found 323.0645.

(*E*)-2-((1,2-diphenylvinyl)thio)thiophene (3ah):



Purification by column chromatograph on silica gel (petroleum ether) gave **3ah** as a colorless oil (13.5 mg, 23%). 1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, $J = 5.3$ Hz, 1H), 7.28 (dd, $J = 10.0, 5.4, 3.1$ Hz, 6H), 7.14 (d, $J = 3.5$ Hz, 1H), 7.09 – 7.04 (m, 3H), 6.96 (dd, $J = 5.3, 3.6$ Hz, 1H), 6.92 – 6.87 (m, 2H), 6.56 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.98, 137.45, 136.41, 136.12, 131.32, 130.95, 129.78, 128.97, 128.67, 128.31, 128.14, 127.75, 126.90, 126.62; HRMS (ESI) m/z : calculated for $[C_{18}H_{14}S_2 + H]^+$ 295.0610, found 295.0618.

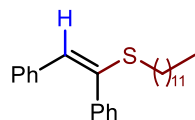
(*E*)-(1,2-diphenylvinyl)(methyl)sulfane (3ai):



Purification by column chromatograph on silica gel (petroleum ether) gave **3ai** as a colorless oil (8.3 mg, 18%). 1H NMR (500 MHz, $CDCl_3$) δ 7.32 (s, 5H), 7.11 – 7.02 (m, 3H), 6.91 (d, $J = 7.0$ Hz, 2H), 6.50 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.75, 138.24, 136.96, 129.66,

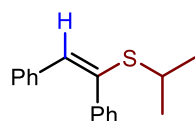
128.84, 128.18, 126.37, 123.69, 15.92; HRMS (ESI) m/z: calculated for $[C_{15}H_{14}S + H]^+$ 227.0889, found 227.0887.

(E)-(1,2-diphenylvinyl)(dodecyl)sulfane (3aj):



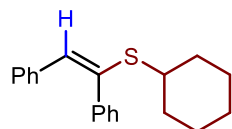
Purification by column chromatograph on silica gel (petroleum ether) gave **3aj** as a colorless oil (31.7 mg, 42%). 1H NMR (500 MHz, $CDCl_3$) δ 7.31 (dq, $J = 13.5, 6.1$ Hz, 5H), 7.06 (dd, $J = 9.2, 7.2$ Hz, 3H), 6.92 (d, $J = 7.2$ Hz, 2H), 6.72 (s, 1H), 2.52 (t, $J = 7.4$ Hz, 2H), 1.60 – 1.51 (m, 2H), 1.35 – 1.21 (m, 21H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.60, 138.29, 136.99, 129.76, 128.99, 128.73, 128.10, 128.09, 126.65, 126.51, 32.07, 32.05, 29.79, 29.77, 29.72, 29.61, 29.53, 29.50, 29.29, 28.90, 22.84, 14.28; HRMS (ESI) m/z: calculated for $[C_{26}H_{36}S + H]^+$ 381.2610, found 381.2606.

(E)-(1,2-diphenylvinyl)(isopropyl)sulfane (3ak):



Purification by column chromatograph on silica gel (petroleum ether) gave **3ak** as a colorless oil (11.2 mg, 22%). 1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 3H), 7.33 – 7.27 (m, 3H), 7.11 – 7.05 (m, 3H), 6.94 (dd, $J = 7.5, 1.3$ Hz, 2H), 6.89 (s, 1H), 2.91 – 2.81 (m, 1H), 1.22 (d, $J = 6.7$ Hz, 6H), 1.14 (d, $J = 6.7$ Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.61, 138.11, 136.93, 129.78, 129.57, 129.17, 128.67, 128.10, 128.02, 126.76, 35.31, 23.04; HRMS (ESI) m/z: calculated for $[C_{17}H_{18}S + H]^+$ 255.1202, found 255.1209.

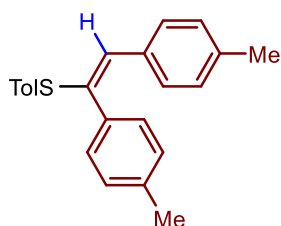
(E)-cyclohexyl(1,2-diphenylvinyl)sulfane (3al)^[12]:



Purification by column chromatograph on silica gel (petroleum ether) gave **3al** as a colorless oil (22.0 mg, 38%). 1H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, $J = 7.1, 1.6$ Hz, 2H), 7.32 – 7.27 (m, 3H),

7.07 (q, $J = 6.3$ Hz, 3H), 6.95 – 6.91 (m, 2H), 6.86 (s, 1H), 2.64 (tt, $J = 10.4, 3.6$ Hz, 1H), 1.95 – 1.85 (m, 2H), 1.75 – 1.67 (m, 2H), 1.58 – 1.51 (m, 1H), 1.42 – 1.12 (m, 7H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.75, 137.60, 136.98, 129.73, 129.24, 129.12, 128.63, 128.08, 127.98, 126.67, 43.56, 33.21, 25.90; HRMS (ESI) m/z : calculated for $[\text{C}_{20}\text{H}_{22}\text{S} + \text{H}]^+$ 295.1515, found 295.1525.

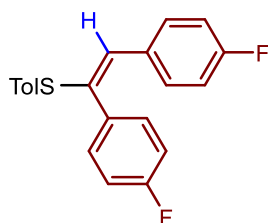
(*E*)-(1,2-di-*p*-tolylvinyl)(*p*-tolyl)sulfane (3ba):



Purification by column chromatograph on silica gel (petroleum ether) gave **3ba** as a white solid (46.4 mg, 70%).

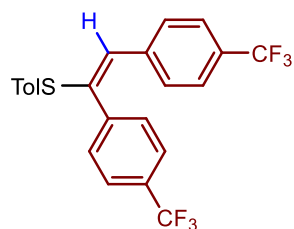
^1H NMR (500 MHz, CDCl_3) δ 7.22 (d, $J = 8.1$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.96 (dd, $J = 12.4, 7.9$ Hz, 4H), 6.82 (d, $J = 8.1$ Hz, 2H), 6.76 (d, $J = 8.2$ Hz, 2H), 6.55 (s, 1H), 2.21 (d, $J = 5.1$ Hz, 5H), 2.15 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 137.78, 137.56, 137.54, 136.57, 135.26, 134.08, 132.69, 130.35, 129.85, 129.73, 129.23, 128.93, 128.82, 128.72, 27.06, 21.45, 21.28; HRMS (ESI) m/z : calculated for $[\text{C}_{23}\text{H}_{22}\text{S} + \text{H}]^+$ 331.1515, found 331.1503.

(*E*)-(1,2-bis(4-fluorophenyl)vinyl)(*p*-tolyl)sulfane (3ca):



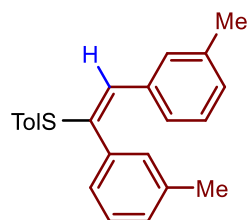
Purification by column chromatograph on silica gel (petroleum ether) gave **3ca** as a white solid (40.7 mg, 60%). ^1H NMR (500 MHz, CDCl_3) δ 7.23 – 7.18 (m, 4H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.86 – 6.78 (m, 4H), 6.71 (t, $J = 8.7$ Hz, 2H), 6.57 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.44 (d, $J = 248.2$ Hz), 161.63 (d, $J = 248.2$ Hz), 138.11, 137.68, 133.65 (d, $J = 3.3$ Hz), 133.10, 132.72 (d, $J = 3.4$ Hz), 131.68 (d, $J = 8.1$ Hz), 130.63 (d, $J = 7.9$ Hz), 129.97, 129.37, 127.61, 115.67 (d, $J = 21.6$ Hz), 115.17 (d, $J = 21.4$ Hz); HRMS (ESI) m/z : calculated for $[\text{C}_{21}\text{H}_{16}\text{F}_2\text{S} + \text{H}]^+$ 339.1014, found 339.0990.

(E)-(1,2-bis(4-(trifluoromethyl)phenyl)vinyl)(p-tolyl)sulfane (3da):



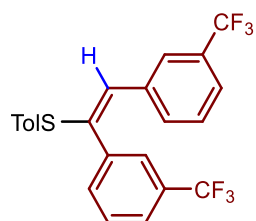
Purification by column chromatograph on silica gel (petroleum ether) gave **3da** as a white solid (35.2 mg, 40%). ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 4H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.59 (s, 1H), 2.33 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 141.25, 139.75, 139.03, 133.91, 130.29, 130.19, 129.93, 129.08, 128.68, 128.21, 127.01, 126.58, 125.74 (q, *J* = 3.7 Hz), 125.22 (q, *J* = 3.8 Hz), 123.07, 122.95, 21.36; HRMS (ESI) *m/z*: calculated for [C₂₃H₁₆F₆S + H]⁺ 439.0950, found 439.0933.

(E)-(1,2-di-m-tolylvinyl)(p-tolyl)sulfane (3ea):



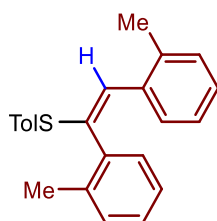
Purification by column chromatograph on silica gel (petroleum ether) gave **3ea** as a white solid (36.5 mg, 55%). ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.24 (s, 1H), 7.17 – 7.09 (m, 4H), 7.08 – 7.04 (m, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.55 (s, 1H), 2.33 (s, 3H), 2.29 (s, 3H), 2.18 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.93, 138.14, 138.08, 137.94, 137.52, 136.70, 133.30, 130.29, 129.93, 129.90, 128.86, 128.33, 127.97, 127.89, 127.48, 126.93, 125.86, 21.47, 21.42, 21.31; HRMS (ESI) *m/z*: calculated for [C₂₃H₂₂S + H]⁺ 331.1515, found 331.1513.

(E)-(1,2-bis(2-(trifluoromethyl)phenyl)vinyl)(p-tolyl)sulfane (3fa):



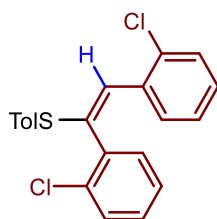
Purification by column chromatograph on silica gel (petroleum ether) gave **3fa** as a white solid (45.7 mg, 54%). ¹H NMR (500 MHz, CDCl₃) δ 7.59 (s, 1H), 7.49 (dd, *J* = 14.3, 7.8 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.13 – 7.10 (m, 3H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.60 (s, 1H), 2.32 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 140.71, 139.05, 138.27, 136.94, 134.09, 133.10, 131.89, 131.19 (q, *J* = 32.8 Hz), 130.68 (q, *J* = 31.5 Hz), 130.27, 129.26, 128.67, 128.15, 126.75 (q, *J* = 3.8 Hz), 126.32, 125.69 (q, *J* = 3.8 Hz), 125.19 (q, *J* = 3.7 Hz), 123.95 (q, *J* = 273.4 Hz), 123.91 (q, *J* = 273.2 Hz), 123.54 (q, *J* = 3.8 Hz), 21.34; HRMS (ESI) *m/z*: calculated for [C₂₃H₁₆F₆S + H]⁺ 439.0950, found 439.0970.

(*E*)-(1,2-di-*o*-tolylvinyl)(*p*-tolyl)sulfane (3ga):



Purification by column chromatograph on silica gel (petroleum ether) gave **3ga** as a white solid (14.5 mg, 22%). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.15 – 7.07 (m, 4H), 7.05 – 6.99 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.49 (s, 1H), 2.33 (s, 3H), 2.18 (s, 3H), 2.10 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 139.26, 138.78, 137.34, 136.38, 135.98, 135.80, 134.83, 130.36, 130.30, 130.04, 129.92, 129.09, 128.01, 127.98, 126.70, 125.82, 125.44, 125.14, 21.40, 20.11, 19.52; HRMS (ESI) *m/z*: calculated for [C₂₃H₁₆S + H]⁺ 331.1515, found 331.1504.

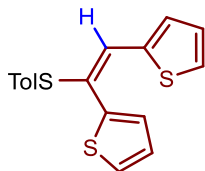
(*E*)-(1,2-bis(2-chlorophenyl)vinyl)(*p*-tolyl)sulfane (3ha):



Purification by column chromatograph on silica gel (petroleum ether) gave **3ha** as a white solid (57.6 mg, 78%). ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.06 – 7.02 (m, 4H), 6.92 (td, *J* = 7.8, 1.5 Hz, 1H), 6.78 (s, 1H), 6.76 – 6.73 (m, 1H), 6.63 (dd, *J* = 7.9, 1.4 Hz, 1H), 2.24 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.79, 138.56, 136.42, 134.90, 134.42,

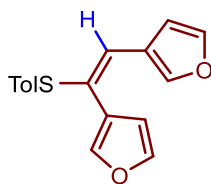
133.76, 131.67, 130.0, 129.95, 129.41, 129.38, 129.33, 128.46, 128.13, 126.80, 126.27, 126.21, 21.39; HRMS (ESI) m/z : calculated for $[C_{21}H_{16}Cl_2S + H]^+$ 371.0423, found 371.0406.

(E)-3,3'-(1-(p-tolylthio)ethene-1,2-diyl)dithiophene (3ia):



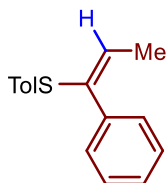
Purification by column chromatograph on silica gel (petroleum ether) gave **3ia** as a yellow solid (52.5 mg, 84%). 1H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 3H), 7.00 (d, $J = 7.9$ Hz, 2H), 6.98 – 6.93 (m, 2H), 6.88 (s, 1H), 6.85 (dd, $J = 5.0, 3.6$ Hz, 1H), 6.79 (d, $J = 3.1$ Hz, 1H), 6.78 – 6.75 (m, 1H), 2.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.78, 138.73, 138.11, 132.96, 129.92, 129.76, 129.33, 128.91, 128.49, 128.02, 127.84, 127.19, 126.36, 125.63, 21.32; HRMS (ESI) m/z : calculated for $[C_{17}H_{14}S_3 + H]^+$ 315.0331, found 315.0319.

(E)-3,3'-(1-(p-tolylthio)ethene-1,2-diyl)difuran (3ja):



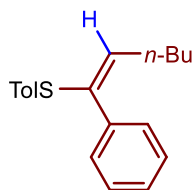
Purification by column chromatograph on silica gel (petroleum ether) gave **3ja** as a yellow oil (46.4 mg, 82%). 1H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.25 (dd, $J = 3.7, 1.9$ Hz, 2H), 7.18 (dd, $J = 12.9, 8.3$ Hz, 3H), 7.01 (d, $J = 7.9$ Hz, 2H), 6.45 (s, 1H), 6.31 (d, $J = 1.0$ Hz, 1H), 6.08 (d, $J = 1.2$ Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.83, 142.79, 142.17, 142.08, 137.64, 132.22, 130.42, 129.91, 127.10, 122.98, 122.56, 121.19, 111.53, 109.91, 21.27; HRMS (ESI) m/z : calculated for $[C_{17}H_{14}SO_2 + H]^+$ 283.0788, found 283.0778.

(E)-(1-phenylprop-1-en-1-yl)(p-tolyl)sulfane (3ka):



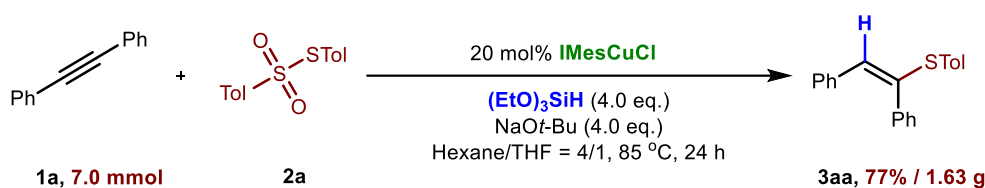
Purification by column chromatograph on silica gel (petroleum ether) gave **3ka** as an oil (14.4 mg, 30%). ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.24 (m, 4H), 7.19 (t, *J* = 8.1 Hz, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.10 (q, *J* = 7.1 Hz, 1H), 2.25 (s, 3H), 1.74 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 138.09, 136.74, 135.44, 131.36, 131.29, 129.65, 129.62, 129.28, 128.04, 127.50, 21.19, 16.19; HRMS (ESI) *m/z*: calculated for [C₁₆H₁₆S + H]⁺ 241.1046, found 241.1039.

(*E*)-(1-phenylhex-1-en-1-yl)(*p*-tolyl)sulfane (3la**):**



Purification by column chromatograph on silica gel (petroleum ether) gave **3la** as an oil (9.8 mg, 18%). ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.23 (m, 2H), 7.18 (dd, *J* = 9.9, 5.0 Hz, 2H), 7.13 – 7.09 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.96 (t, *J* = 7.6 Hz, 1H), 2.18 (s, 3H), 2.04 (dd, *J* = 14.8, 7.5 Hz, 2H), 1.28 (dd, *J* = 9.0, 6.3 Hz, 2H), 1.19 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.76 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 138.44, 136.69, 135.52, 134.52, 131.41, 131.24, 129.63, 129.53, 127.97, 127.46, 32.01, 30.02, 22.39, 21.19, 14.04. HRMS (ESI) *m/z*: calculated for [C₁₉H₂₂S + H]⁺ 283.1515, found 283.1503.

4 Gram-scale synthesis of (*E*)-vinyl sulfide

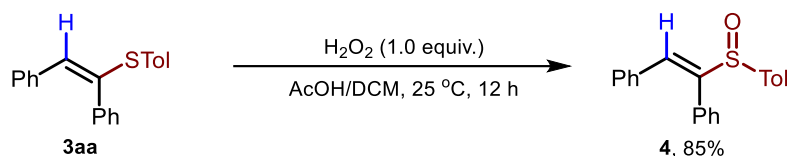


Into an eggplant shaped bottle fitted with a magnetic stir bar, IMesCuCl (1.4 mmol, 564.2 mg), NaOt-Bu (28.0 mmol, 2.69 g), and diphenylacetylene **1a** (7.0 mmol, 1.246 g) were charged. The bottle was evacuated and backfilled with argon (this process was repeated three times). Then, 28 mL of hexane was introduced, and the resulting mixture was stirred at room temperature for 5 minutes. Subsequently, (EtO)₃SiH (28.0 mmol, 5.2 mL) were added under a flow of argon. The resulting mixture was stirred at room temperature for an additional 5 minutes. The solution of S-(*p*-tolyl) 4-methylbenzenesulfonylthioate **2a** (28.0 mmol, 7.78 g) in 7 mL of THF was introduced into

the bottle under an argon flow. The reaction bottle was then sealed and stirred at 85°C for 24 hours. After cooling to room temperature, the reaction mixture was purified through column chromatography on silica gel using petroleum ether as the eluent. The desired product **3aa**, weighing 1.63 g with a yield of 77%, was successfully isolated.

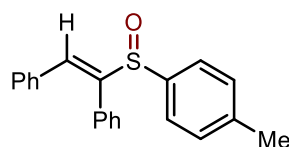
5 Further transformation reactions of (*E*)-vinyl sulfides (3)

5.1 Transformation of the (*E*)-vinyl sulfide to sulfoxide



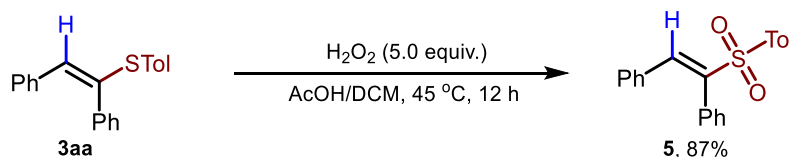
To a flame-dried Schlenk tube equipped with a magnetic stir bar, compound **3aa** (0.2 mmol), 30% hydrogen peroxide (0.2 mmol, 1.0 equiv.), glacial acetic acid (0.4 mL) and dichloromethane (0.2 mL) were charged.^[13a] The mixture was stirred at 25 °C for 12 h. Then, the reaction mixture was purified with column chromatography on silica gel, leading to the product **4** (the eluent of petroleum ether and ethyl acetate is in the ratio 10:1).

(*E*)-1-(*p*-tolylsulfinyl)ethene-1,2-diyldibenzene (4**)^[13b]:**



A white solid (54 mg, 85% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.33 (s, 1H), 7.25 – 7.15 (m, 2H), 7.09 (dd, *J* = 11.3, 3.9 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.1 Hz, 1H), 2.25 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 145.73, 141.69, 139.40, 134.07, 132.17, 129.87, 129.68, 129.57, 128.90, 128.76, 128.48, 125.60, 21.55.

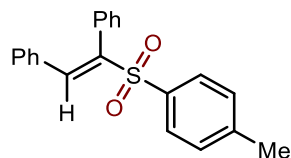
5.2 Transformation of the (*E*)-vinyl sulfide to sulfone



Into a flame-dried Schlenk tube equipped with a magnetic stir bar, compound **3aa** (0.2 mmol), 30% hydrogen peroxide (1.0 mmol, 5.0 equiv.), glacial acetic acid (0.4 mL) and dichloromethane (0.2 mL) were charged.^[13a] The mixture was stirred at 45 °C for 12 h. Then, the reaction mixture

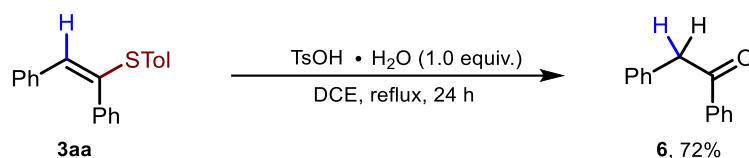
was purified with column chromatography on silica gel, resulting in the product **5** (the eluent of petroleum ether and ethyl acetate is in the ratio 10:1).

(E)-(1-tosylethene-1,2-diyl)dibenzene (5)^[13b]:



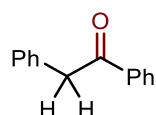
A white solid (58 mg, 87% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.95 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 14.8, 7.4 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.17 (dd, *J* = 14.9, 7.6 Hz, 1H), 7.05 (dd, *J* = 15.7, 7.4 Hz, 1H), 2.39 (s, 1H).

5.3 Hydrolysis of the (*E*)-vinyl sulfide to ketone



Into a round-bottom flask, (*E*)-vinyl sulfide **3aa** (0.2 mmol, 60.4 mg), *para*-toluenesulfonic acid monohydrate (0.2 mmol, 38 mg) and 1,2-dichloroethane (1.0 mL) were charged.^[14a] The mixture was refluxed at 80 °C for 24 h. Then, the reaction mixture underwent purification *via* column chromatography on silica gel, leading to the product **6**.

1,2-Diphenylethan-1-one (6)^[14b]:



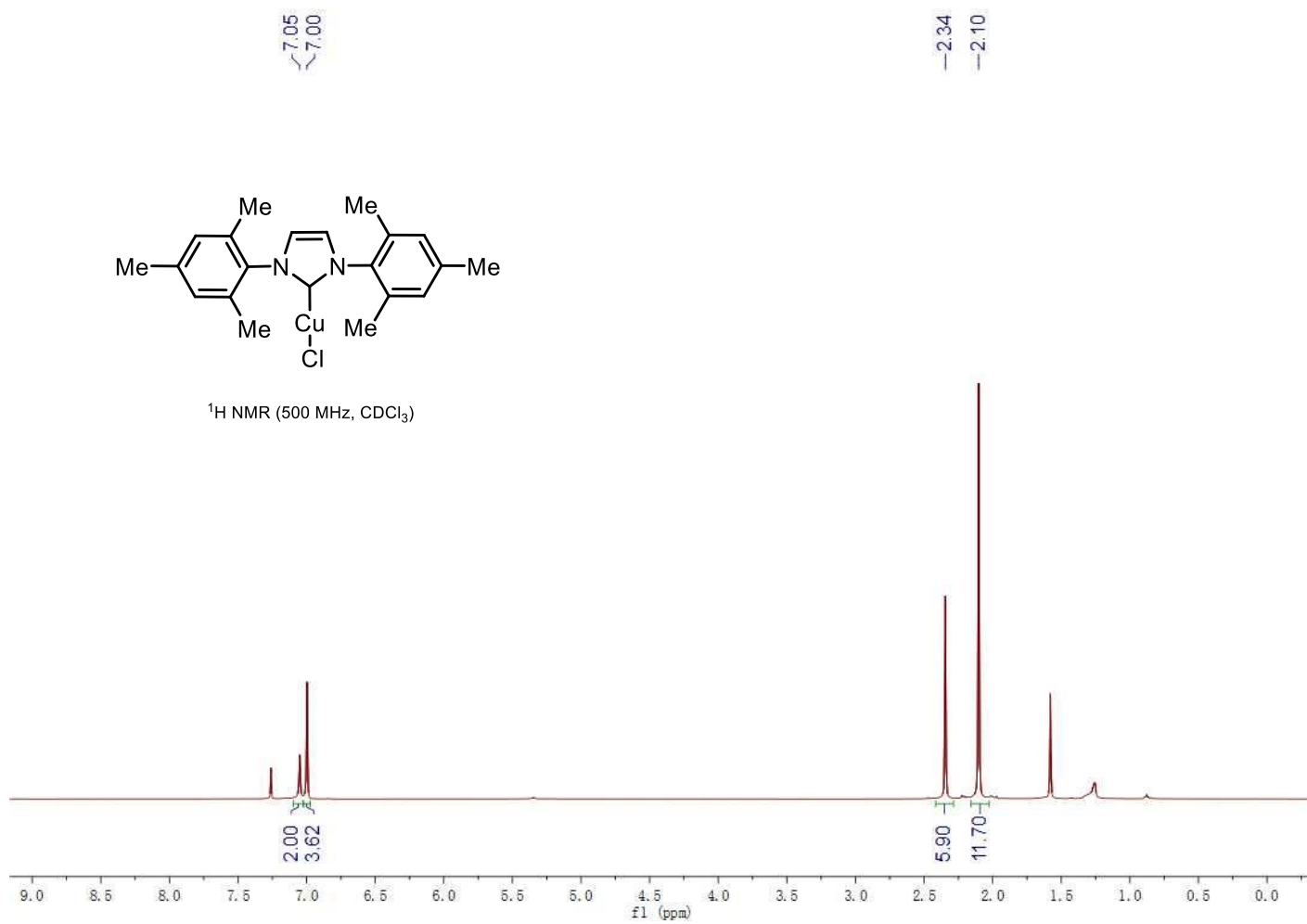
A white solid (28 mg, 72% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.96 – 7.91 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.12 (m, 5H), 4.20 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 197.72, 136.72, 134.65, 133.27, 129.58, 128.78, 128.75, 128.72, 127.00, 45.62.

6 References

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7 Spectroscopic data (NMR spectra)

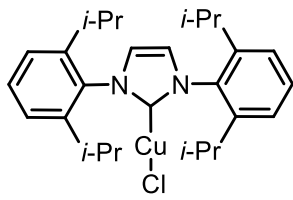


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7.47
7.30
7.29
7.26
7.13

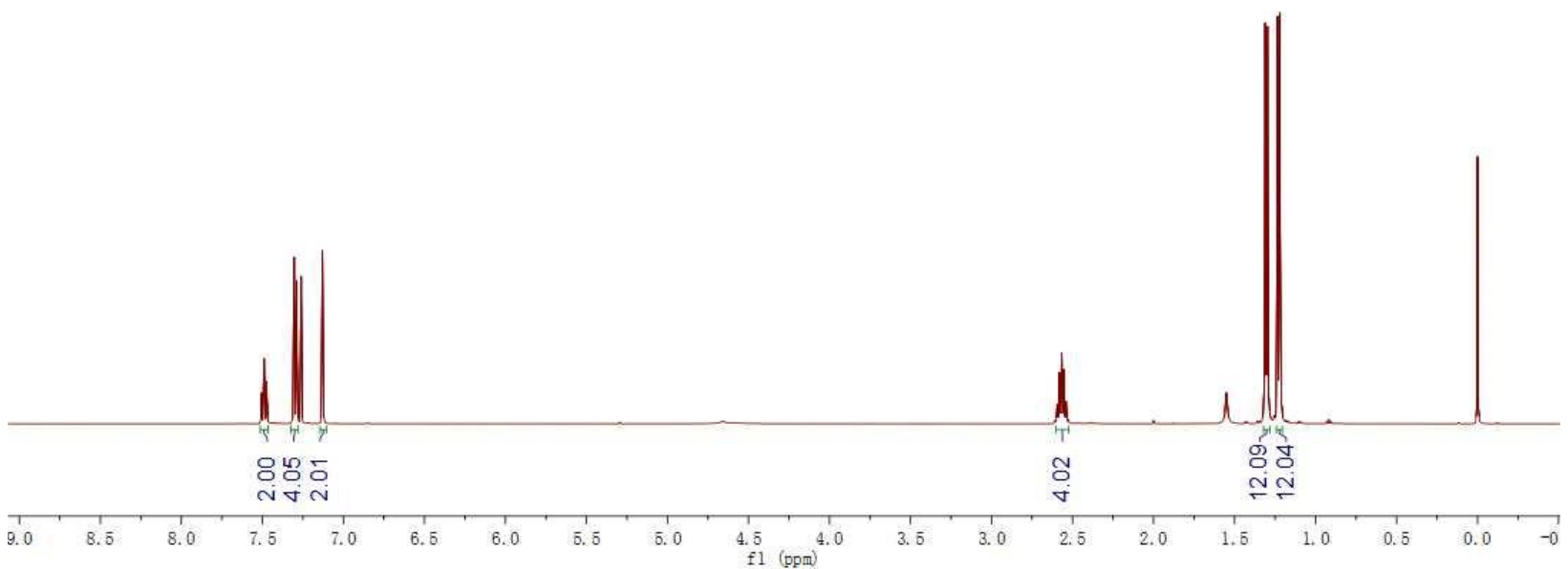
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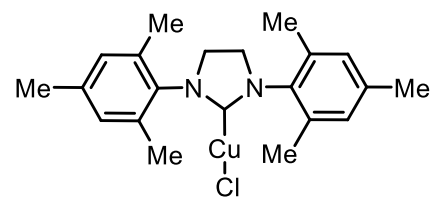
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1.22

-0.00

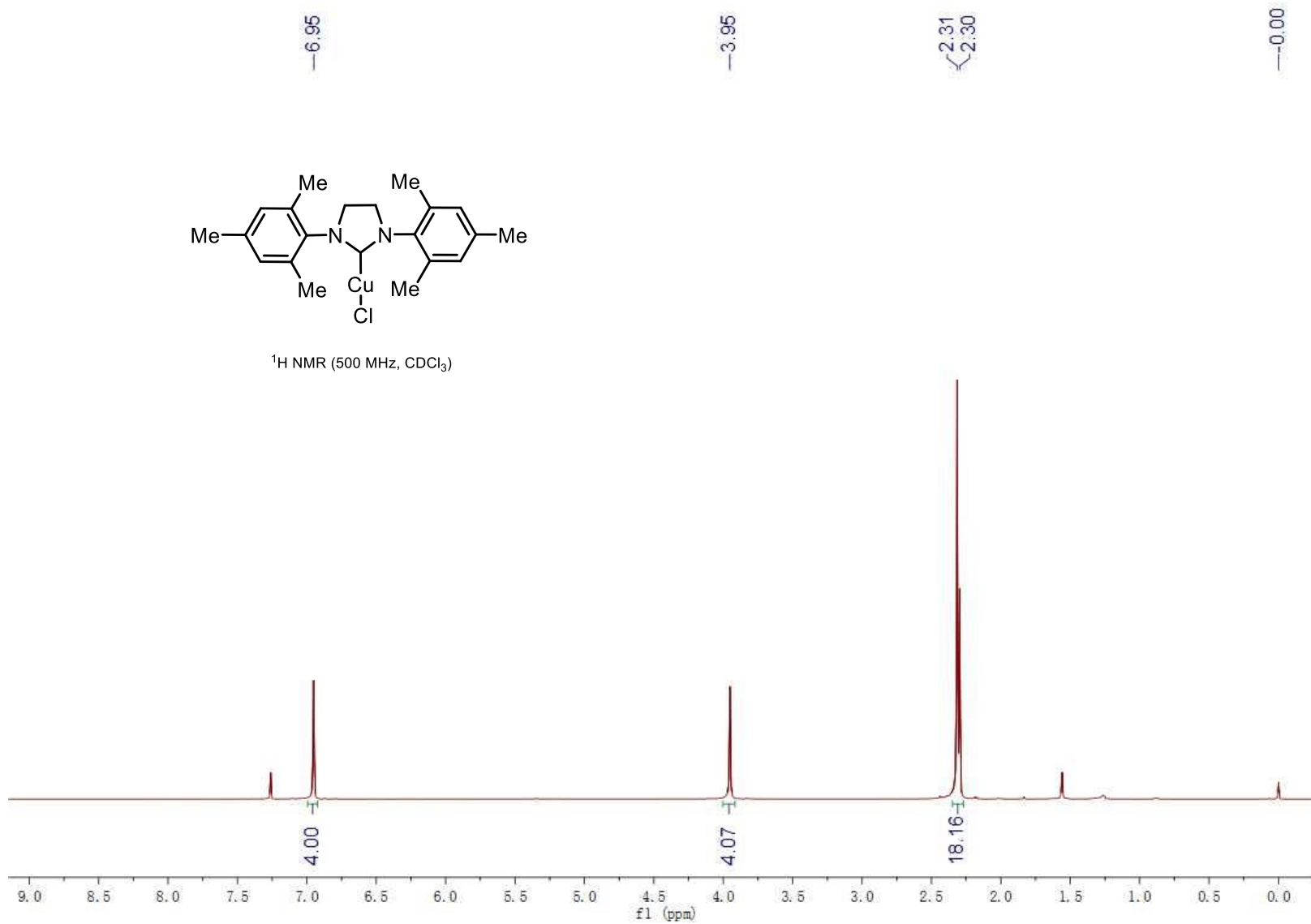


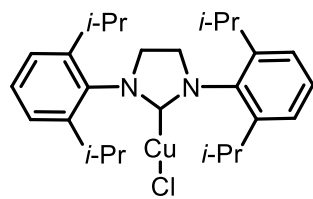
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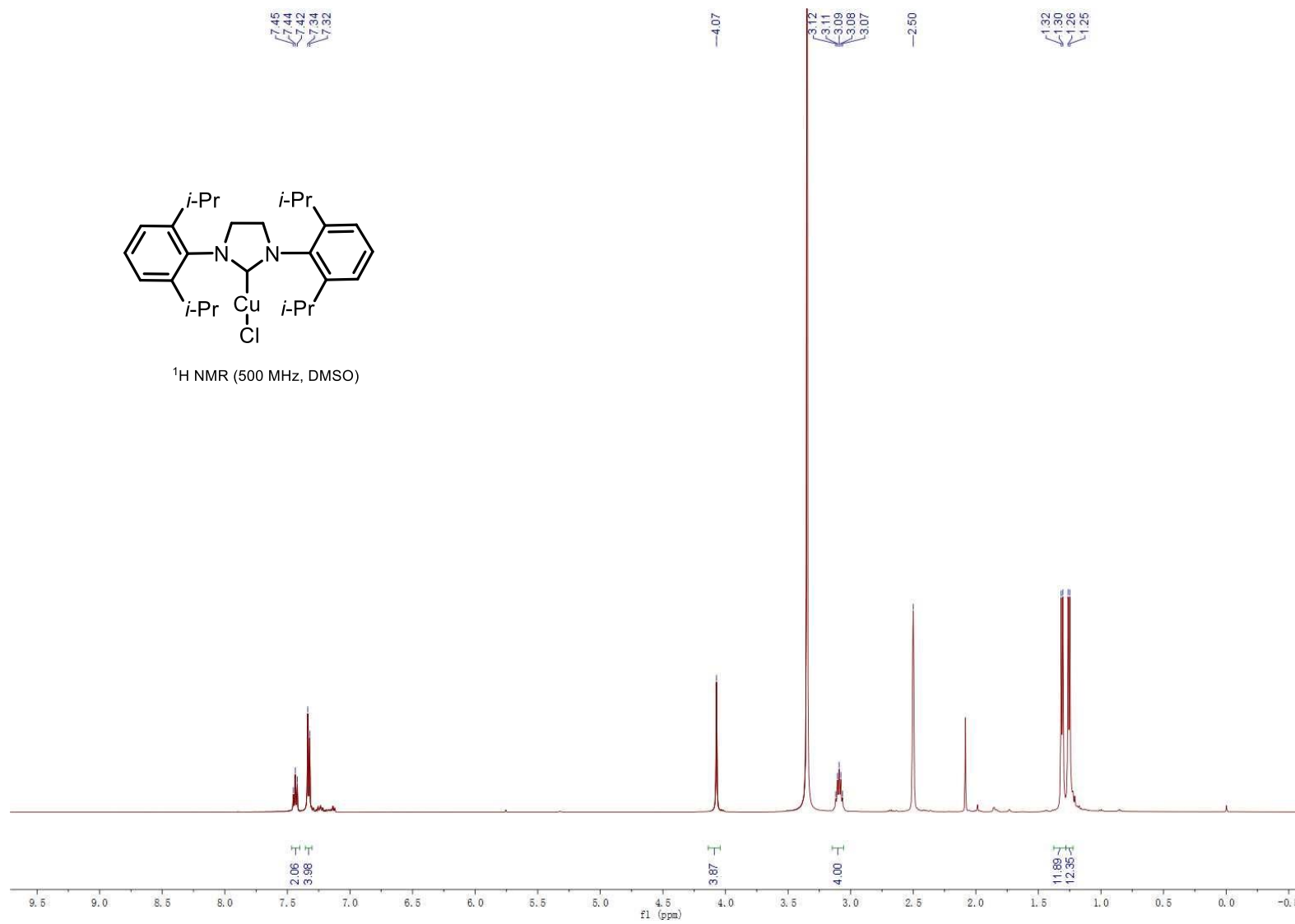


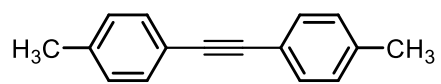
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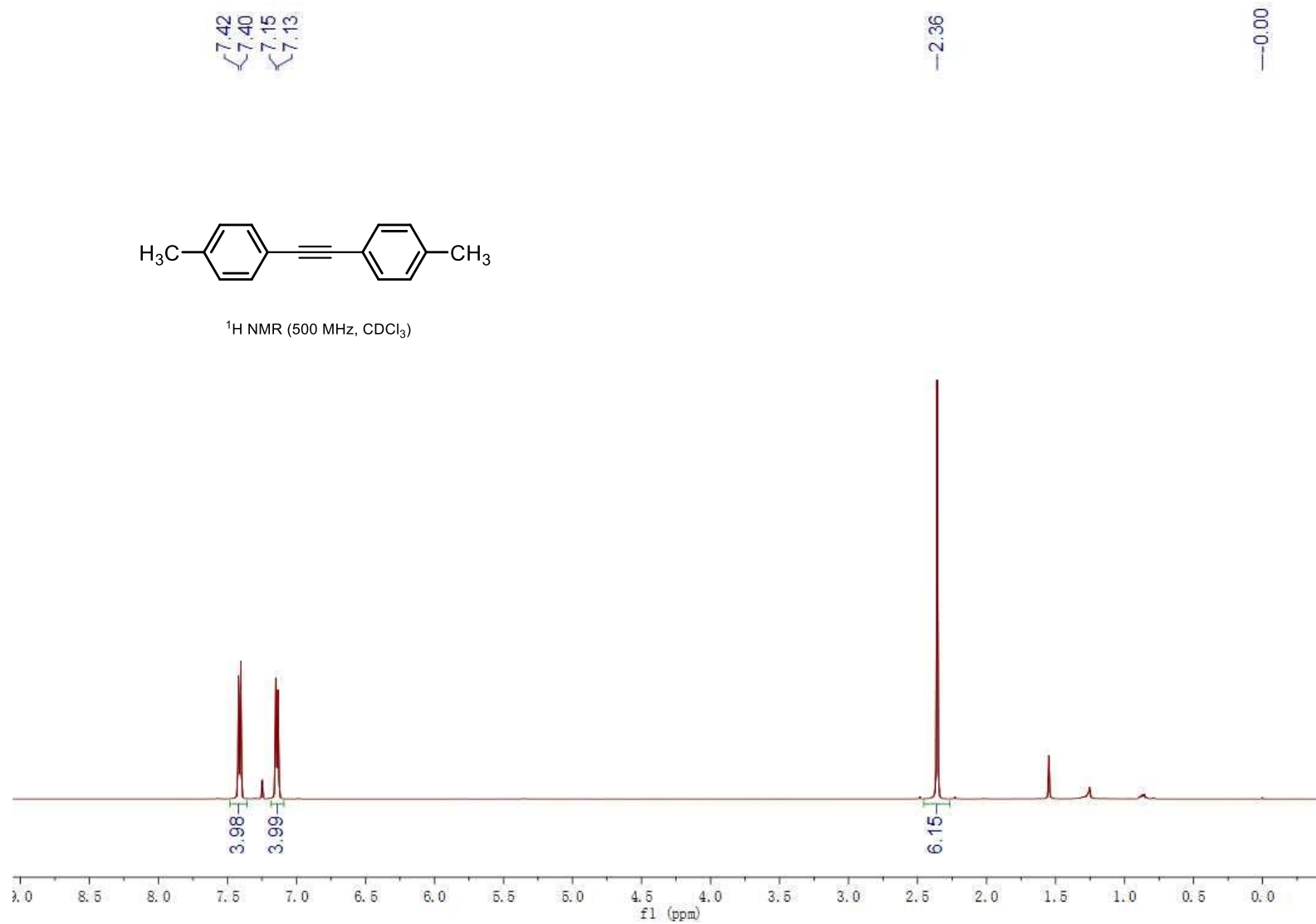


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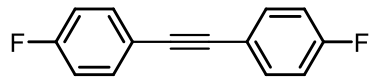


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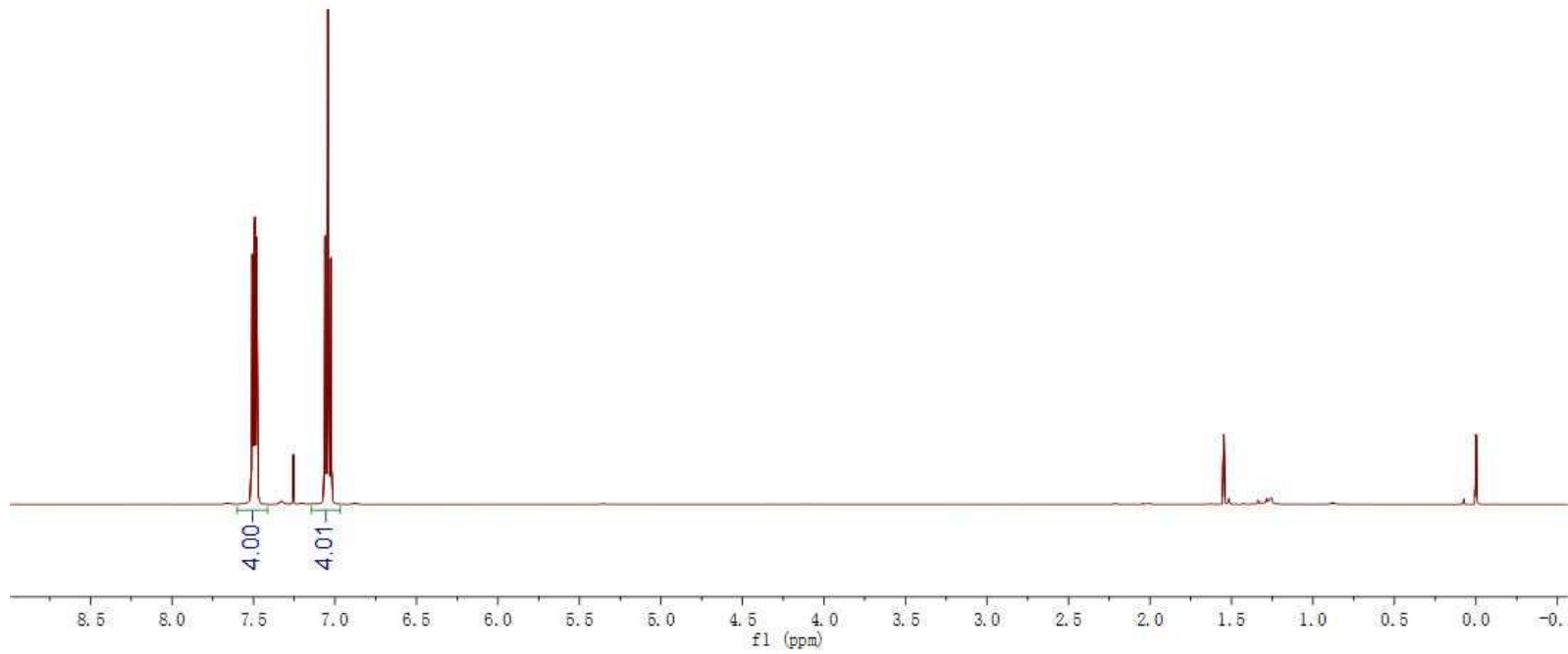


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7.04
7.02

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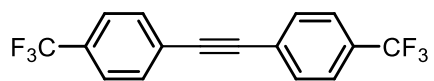


^1H NMR (500 MHz, CDCl_3)

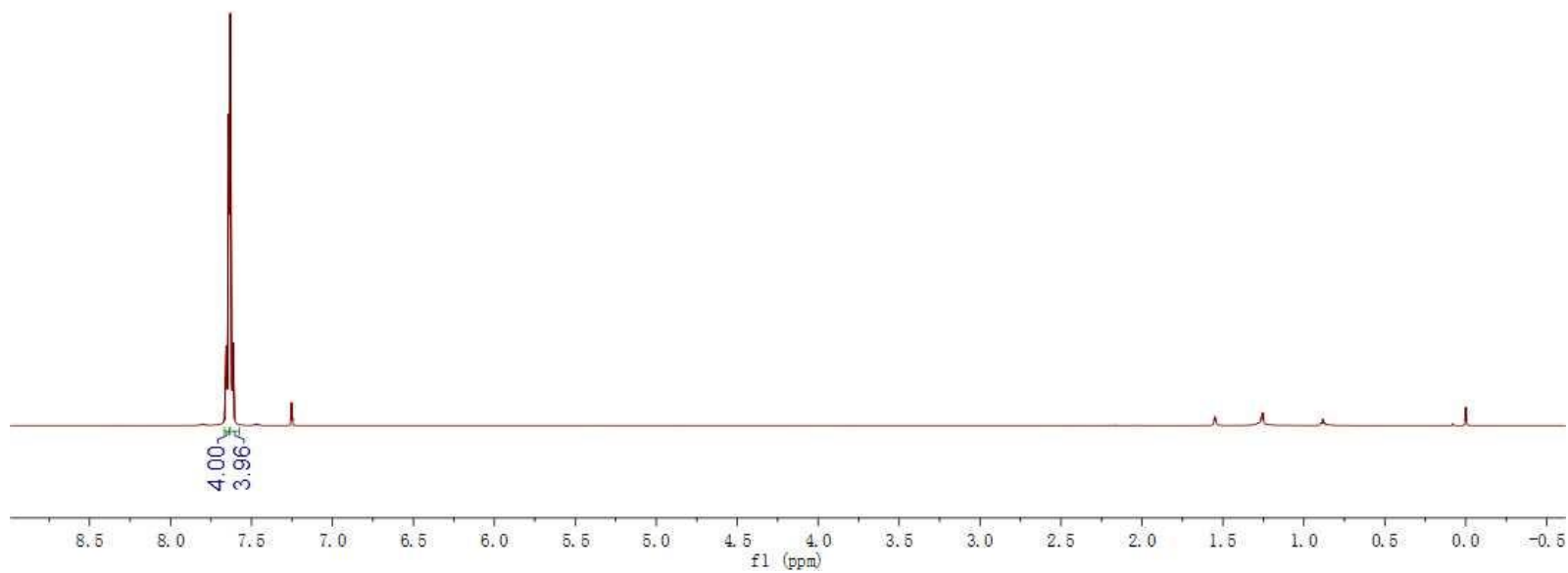


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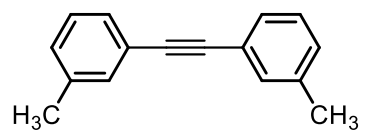
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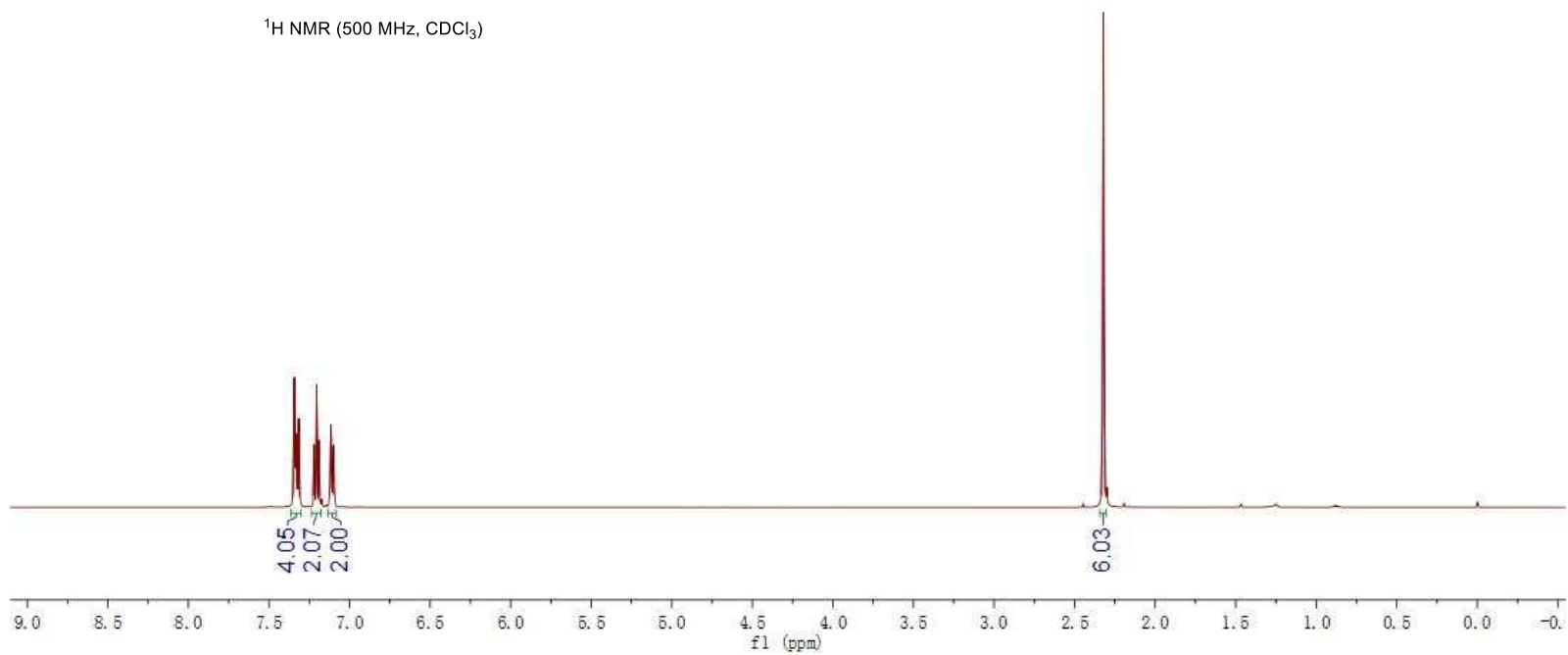
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7.10

-2.32

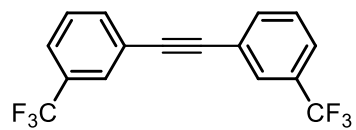
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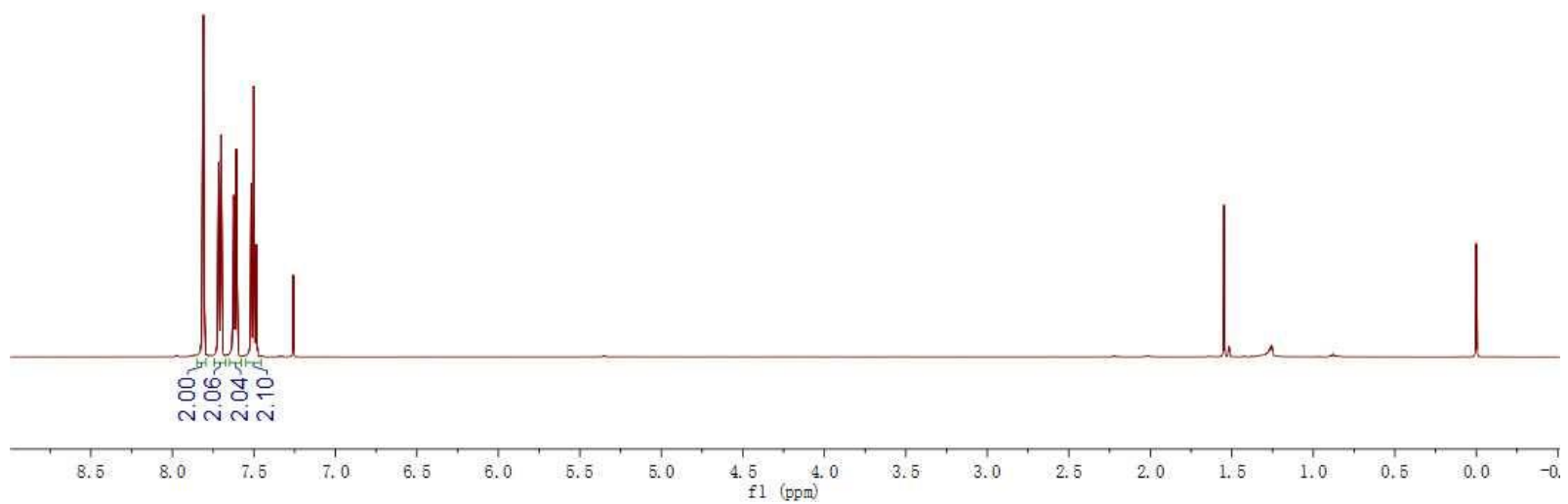
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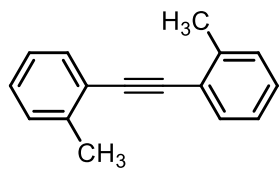
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7.50
7.48
7.26



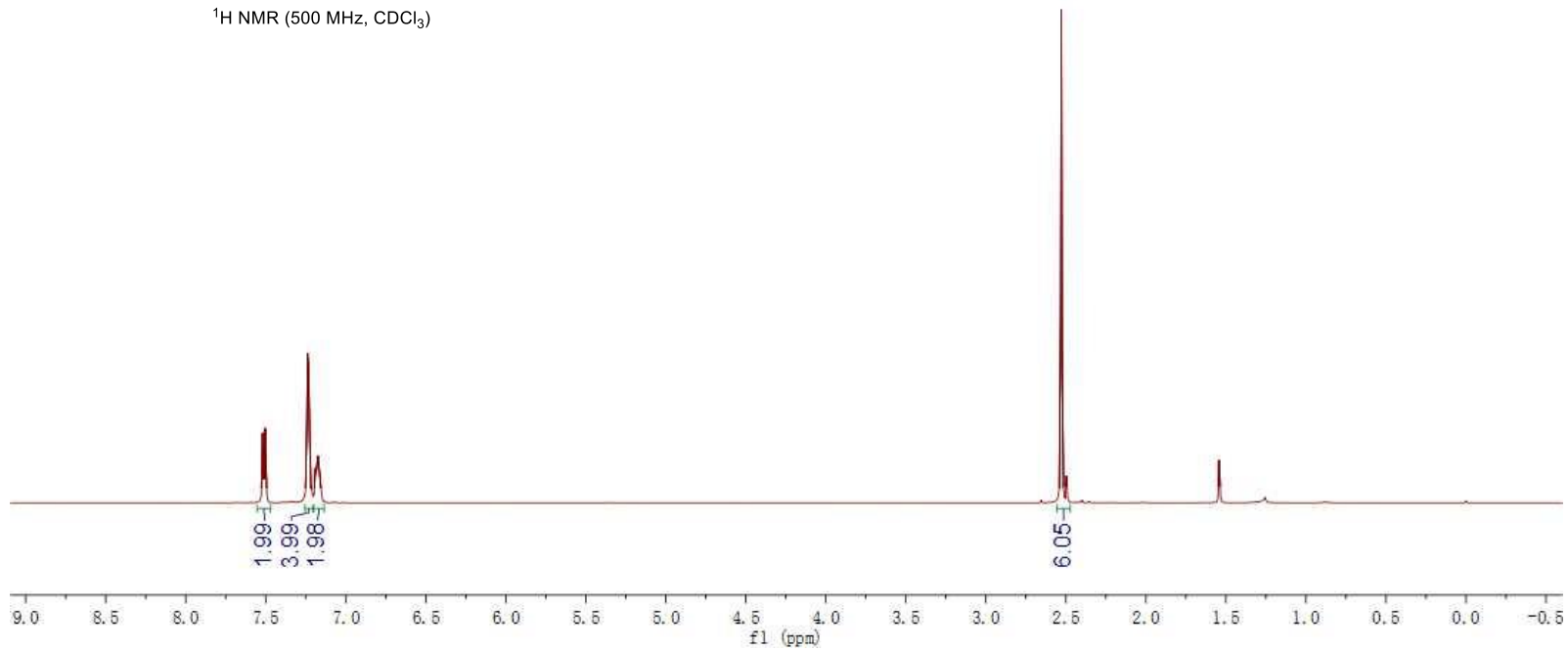
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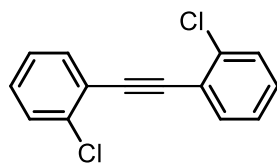
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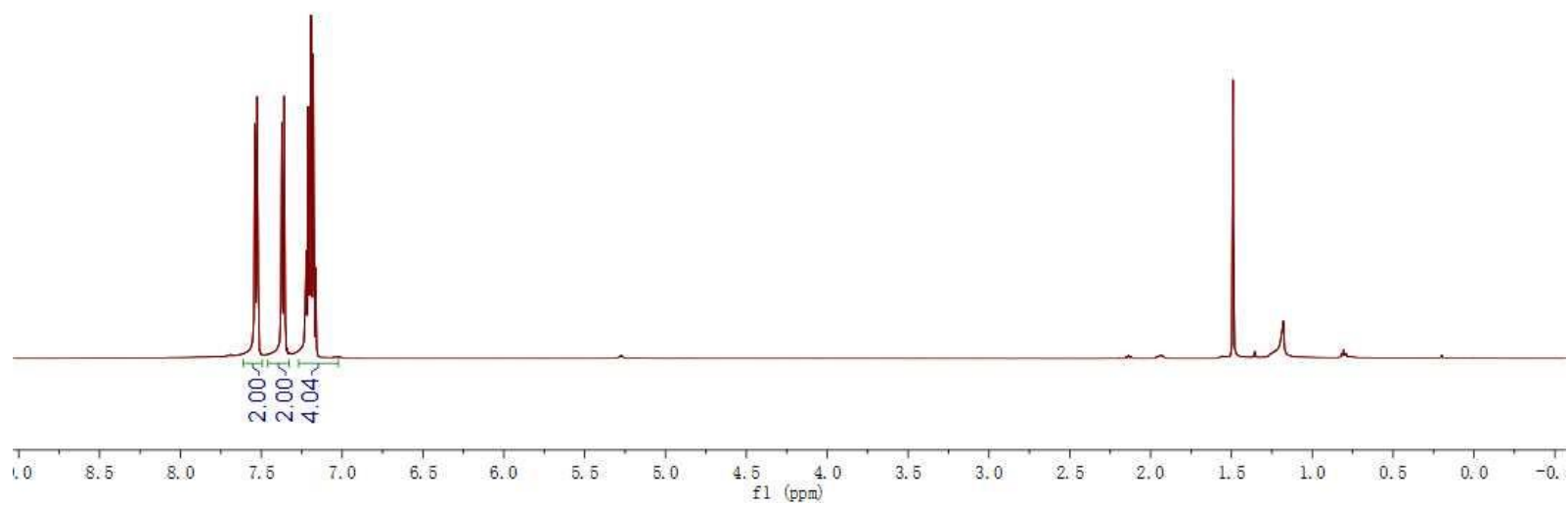
¹H NMR (500 MHz, CDCl₃)



7.54
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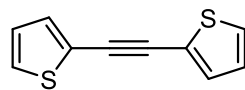


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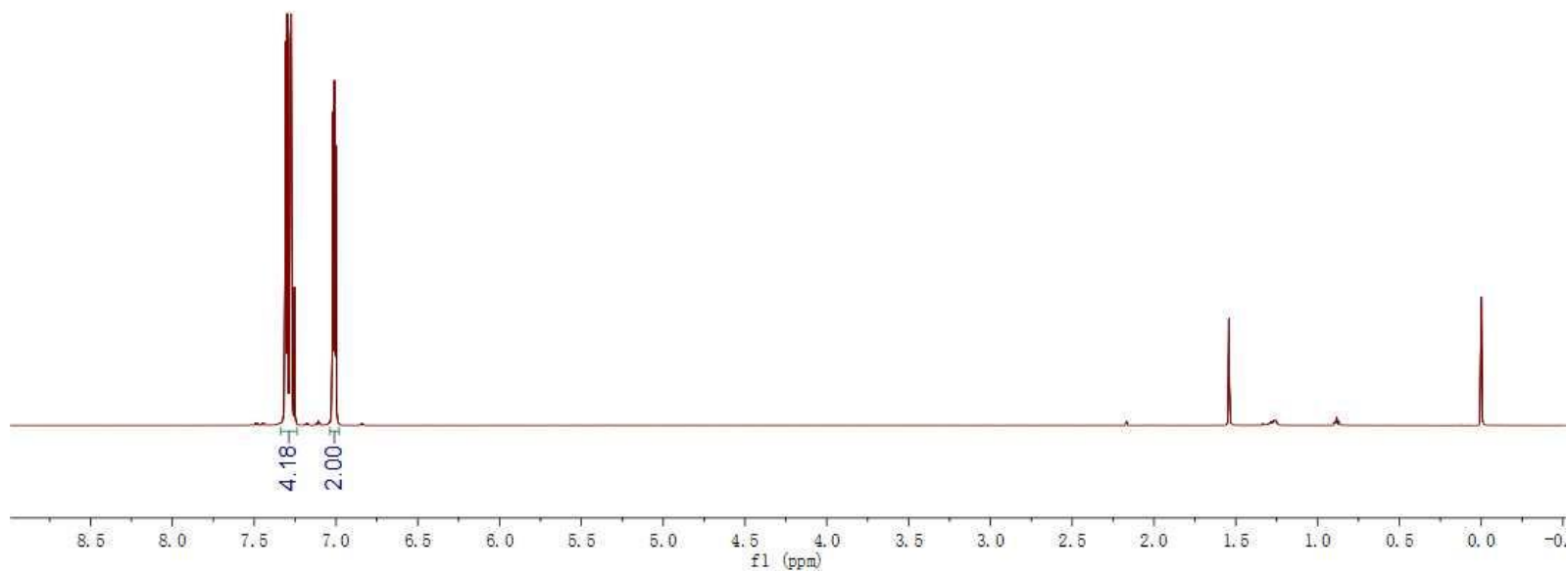


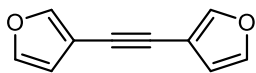
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¹H NMR (500 MHz, CDCl₃)

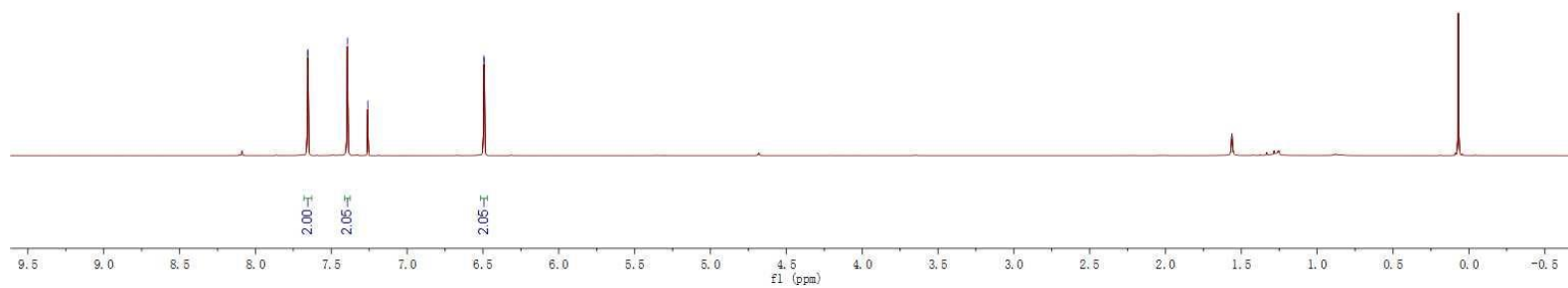


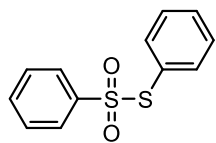


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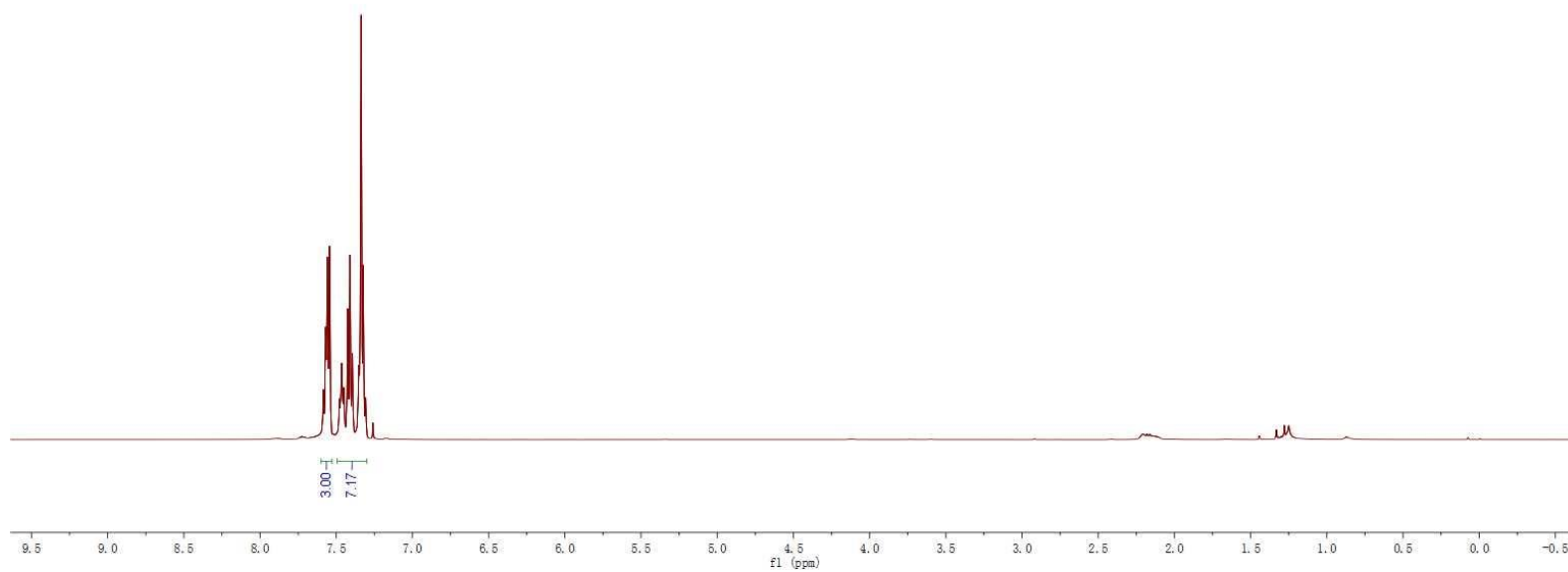
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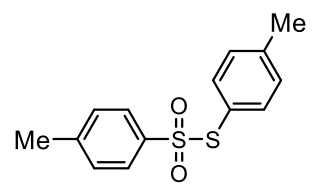




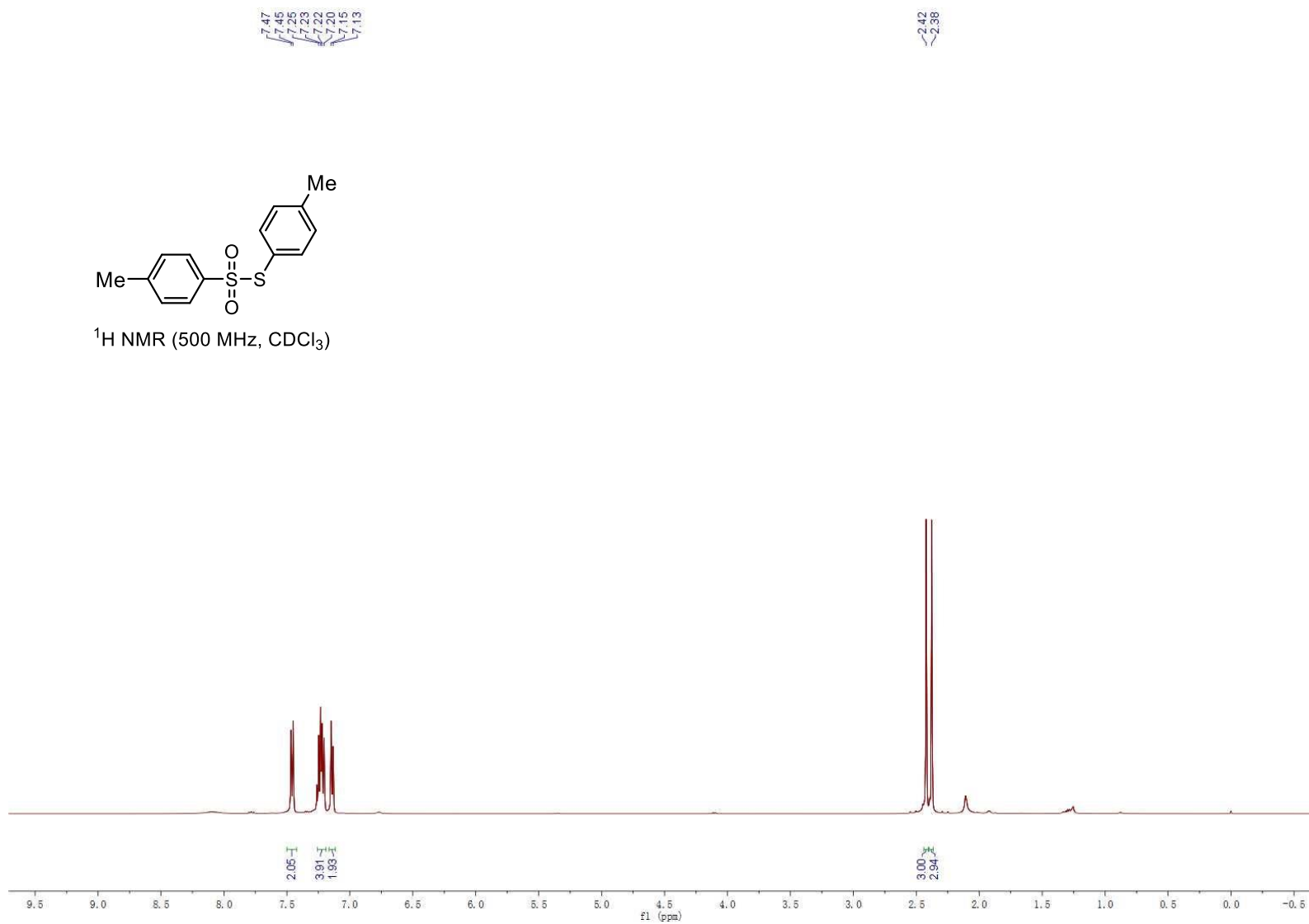
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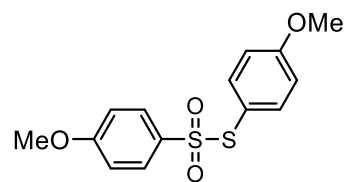
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7.31



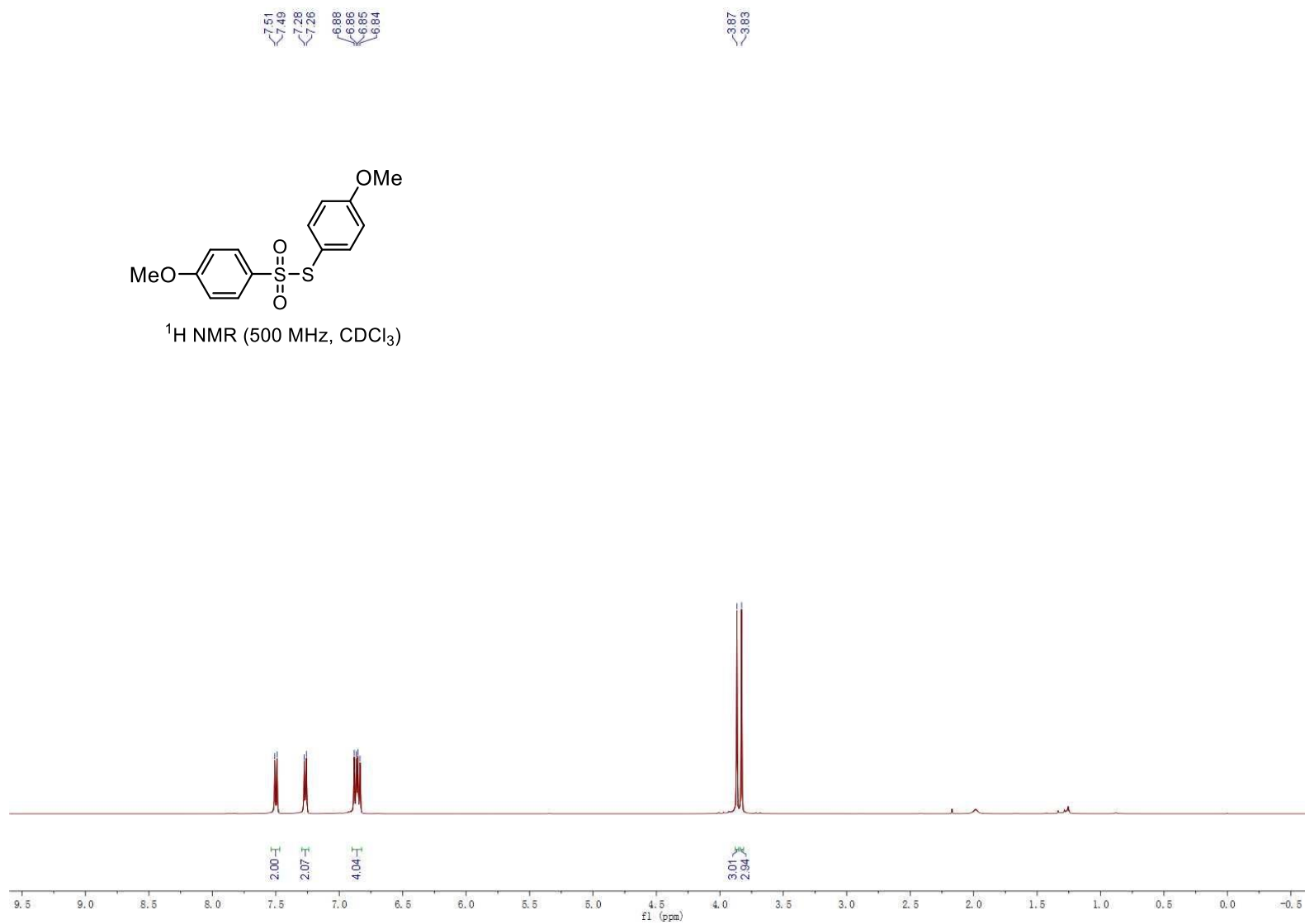


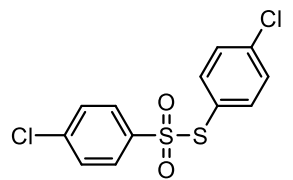
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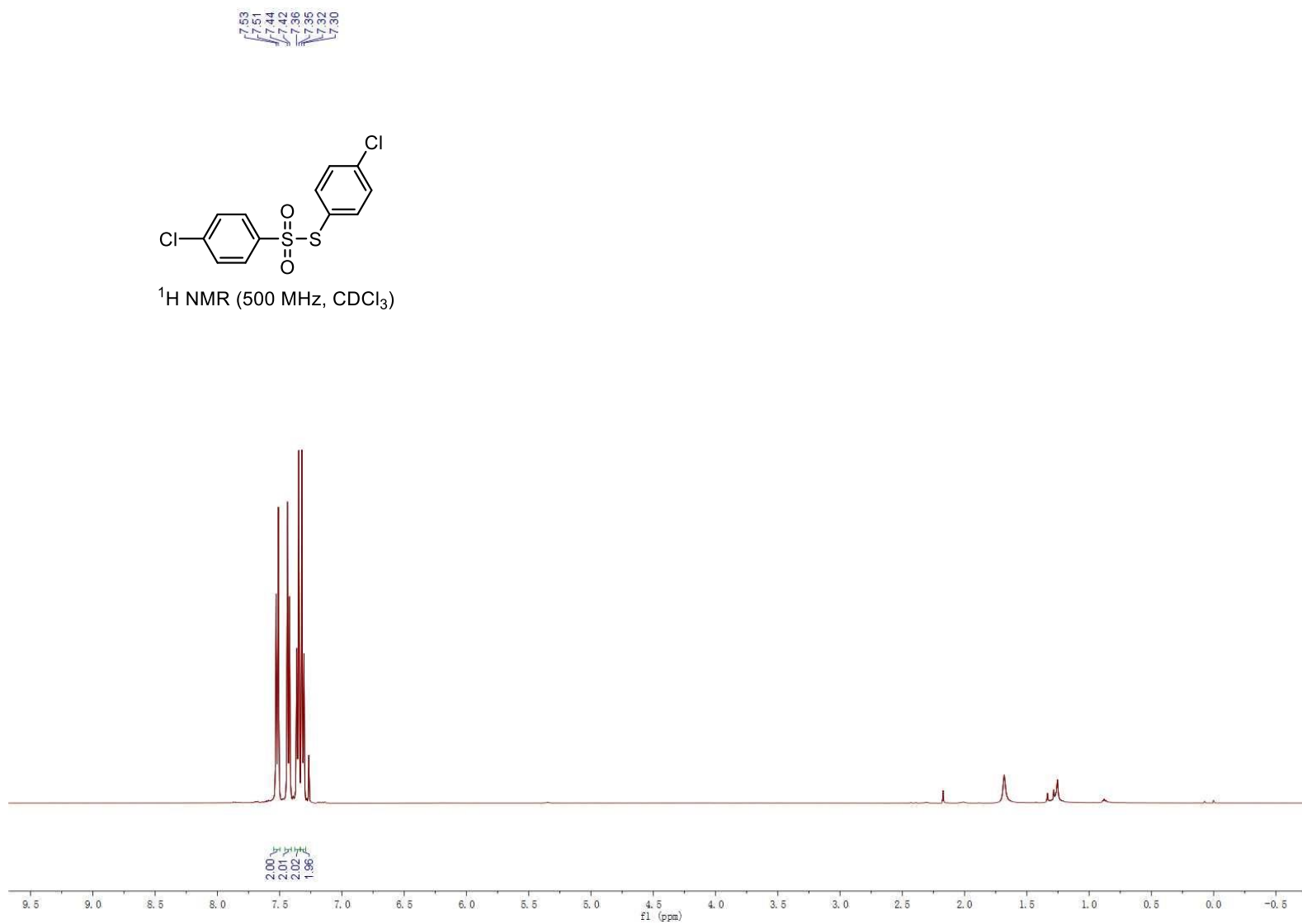


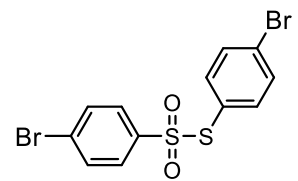
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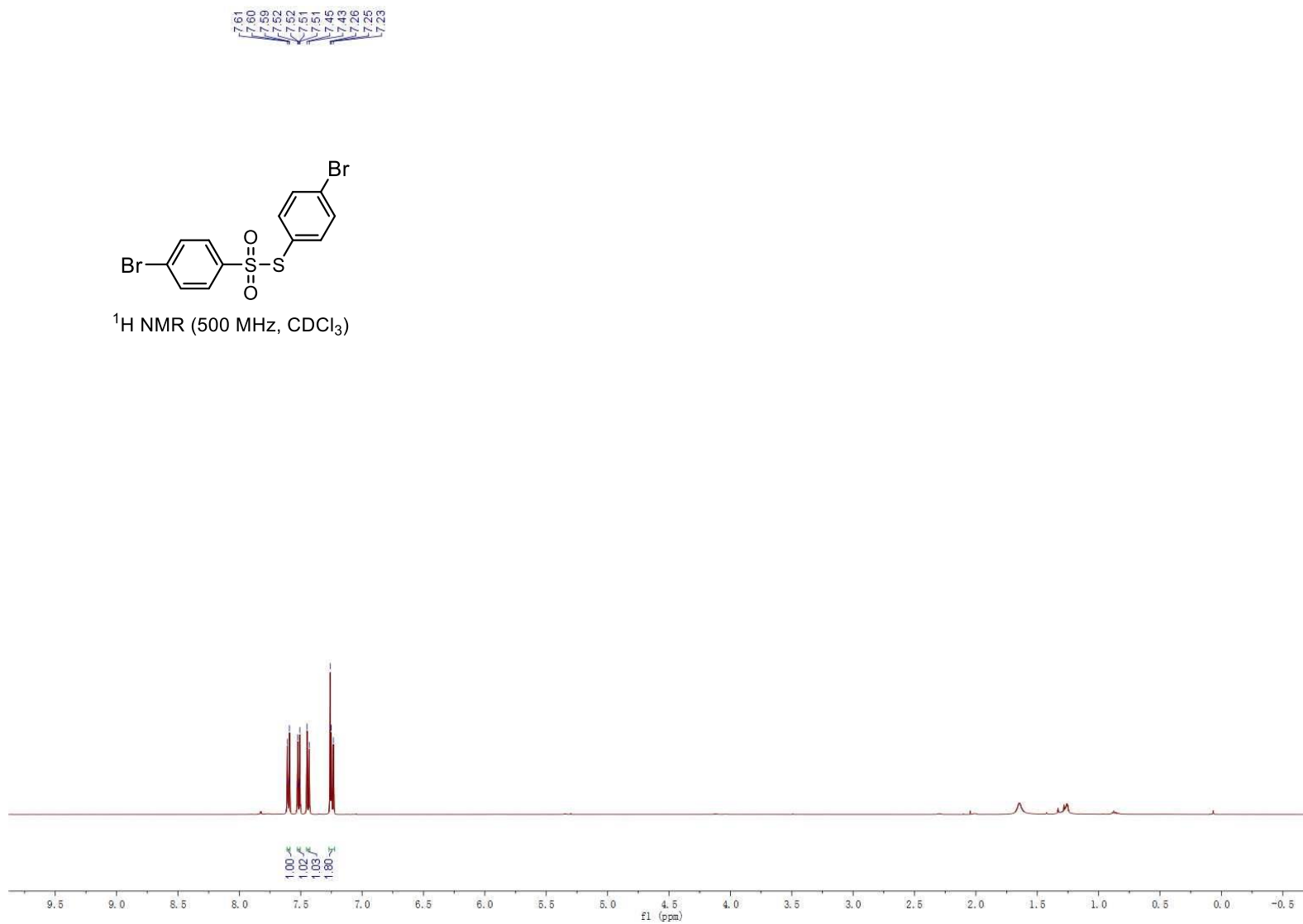


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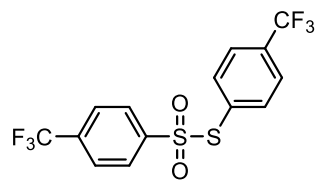




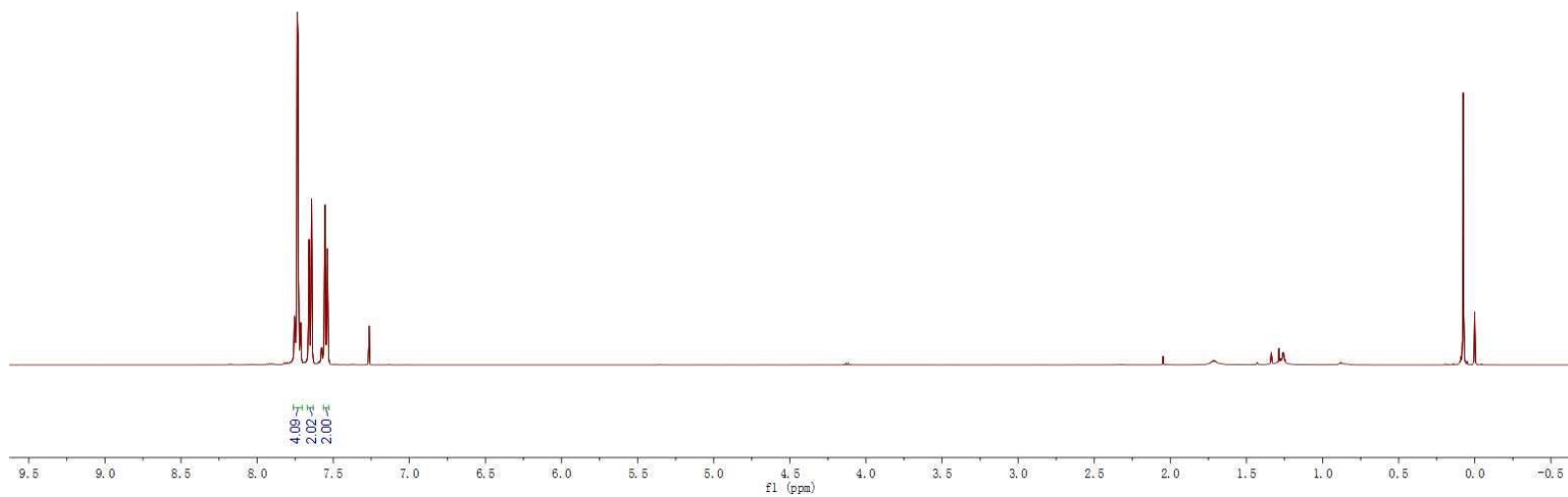
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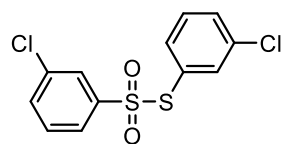
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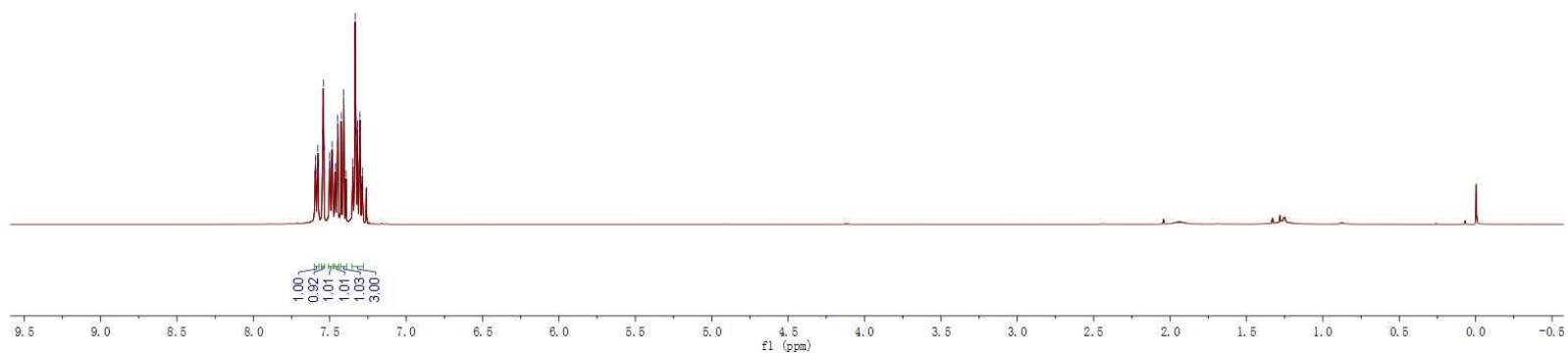
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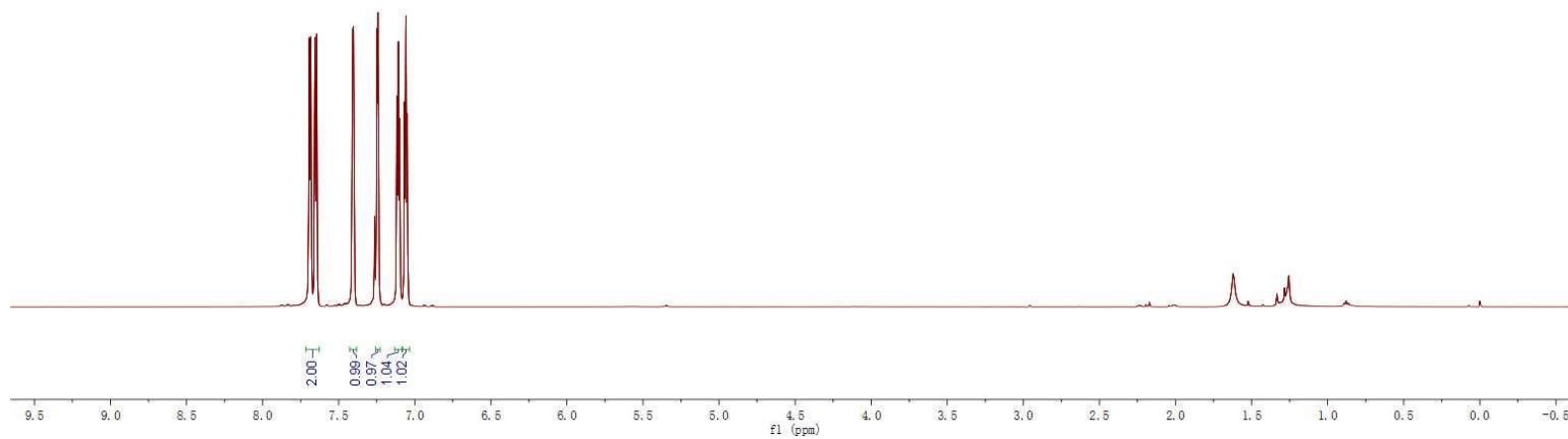
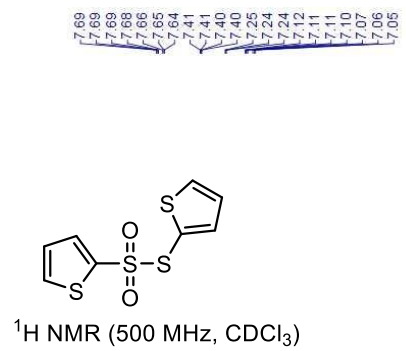


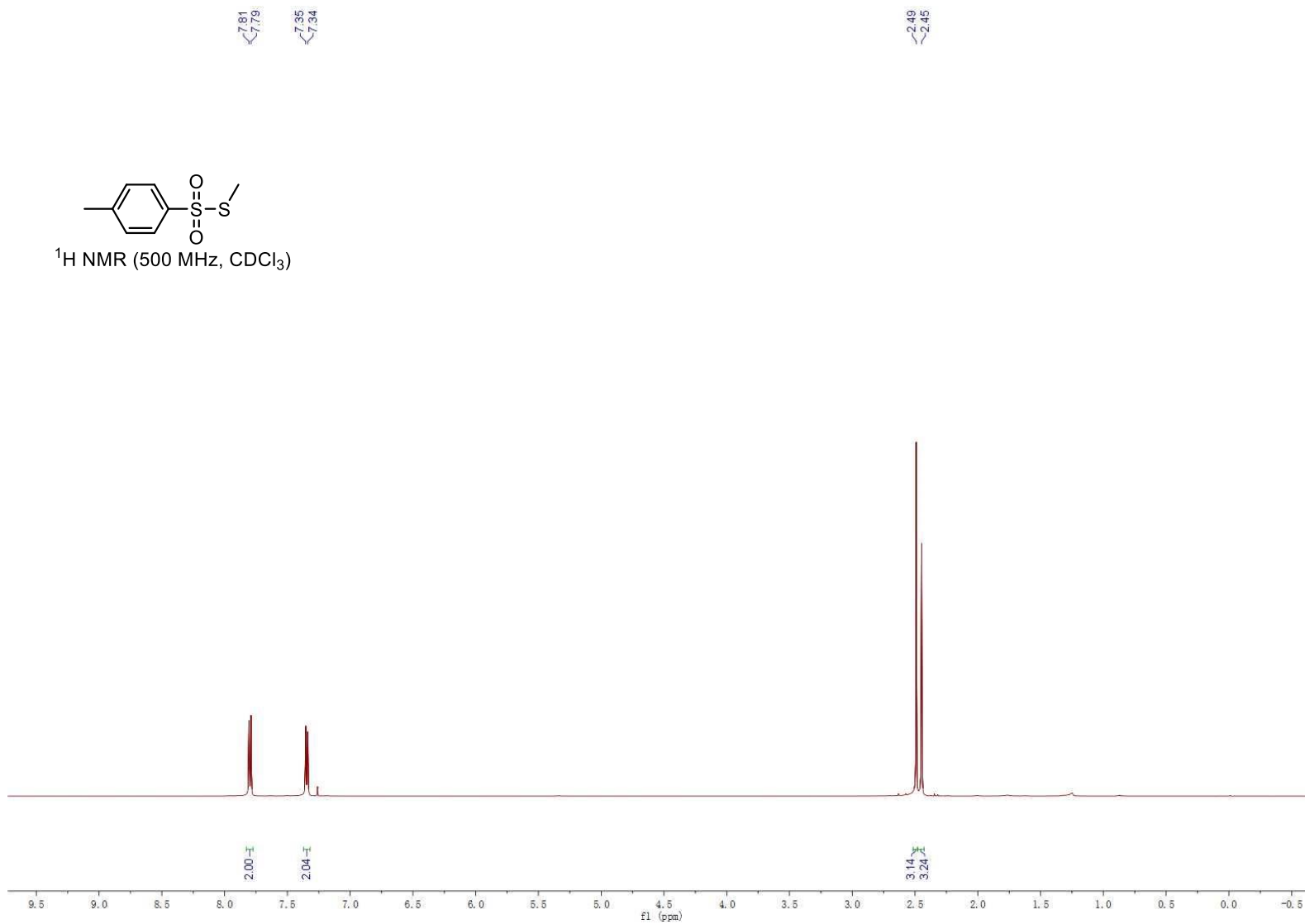
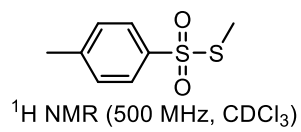
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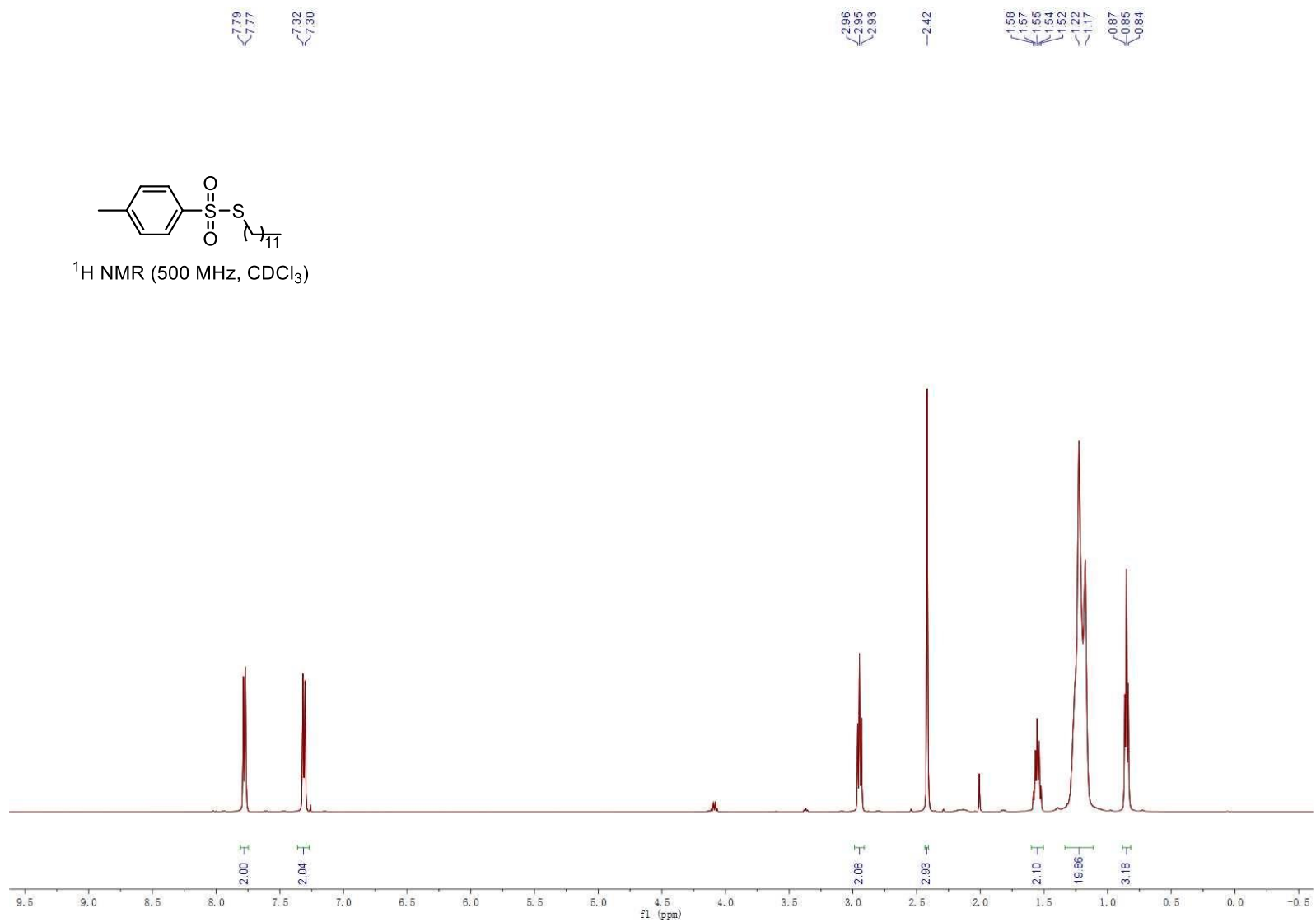
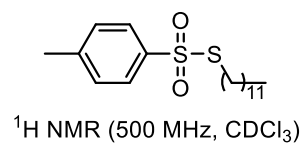


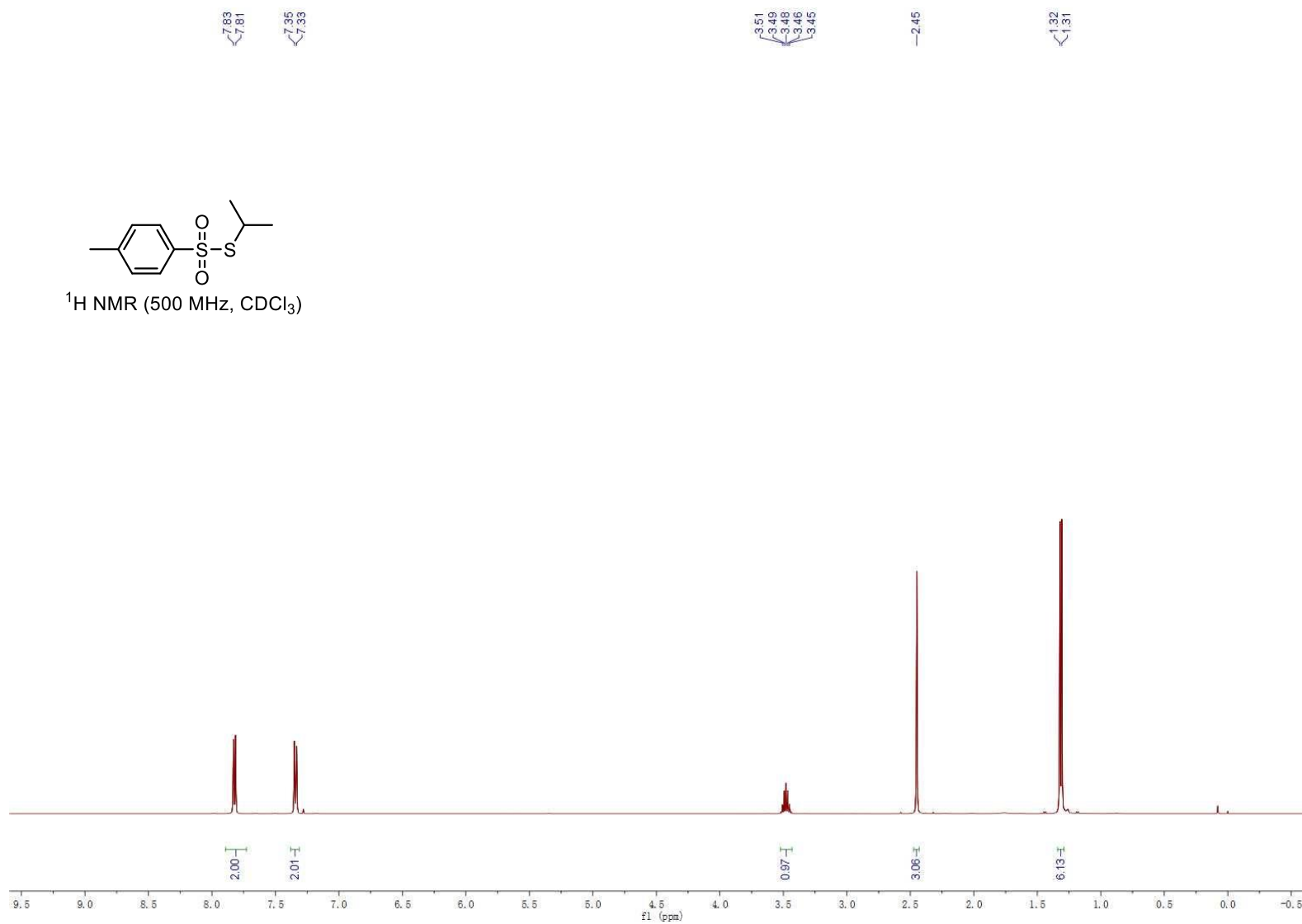
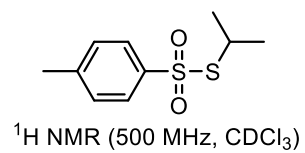
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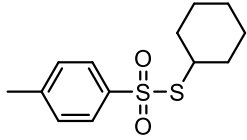




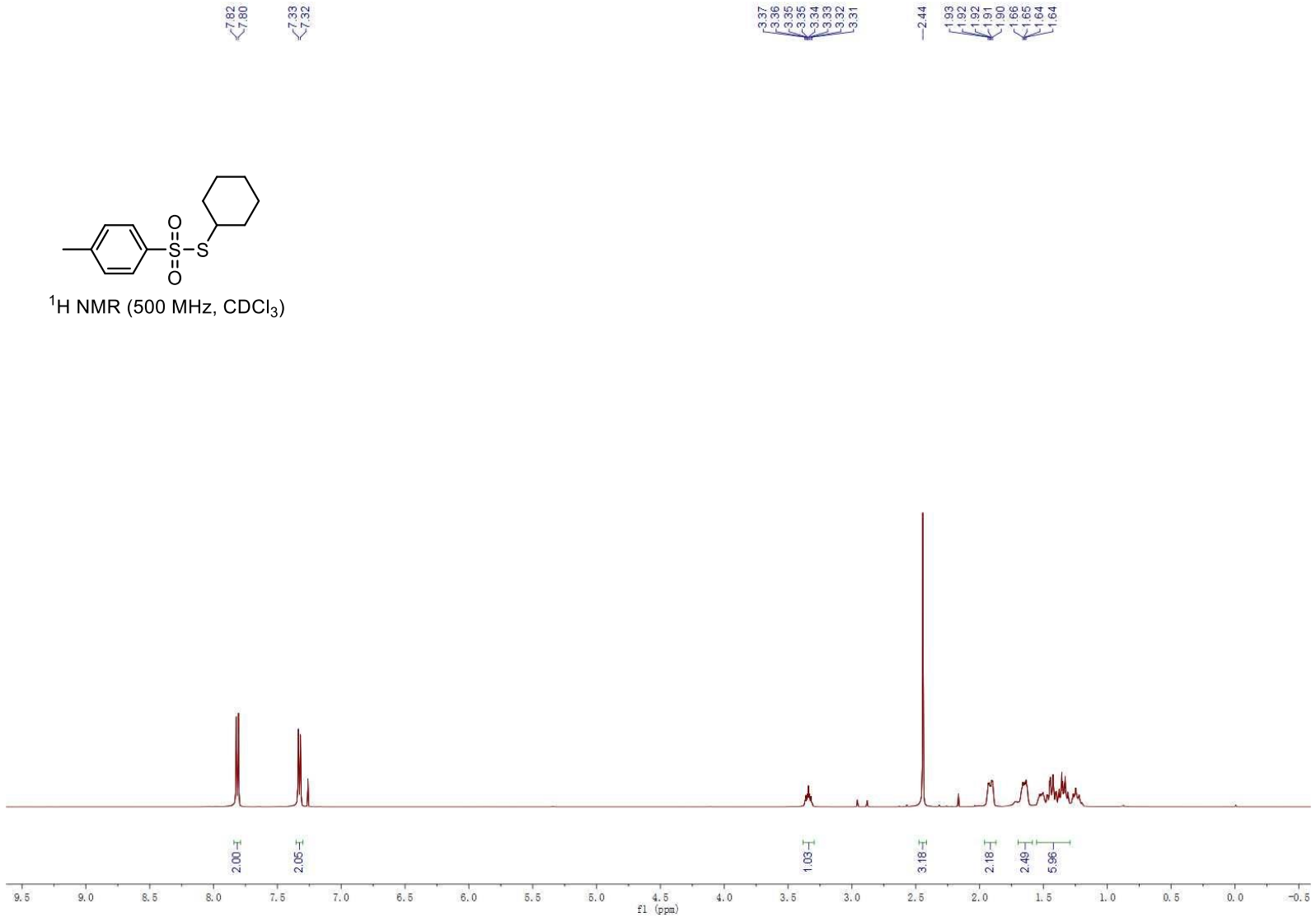


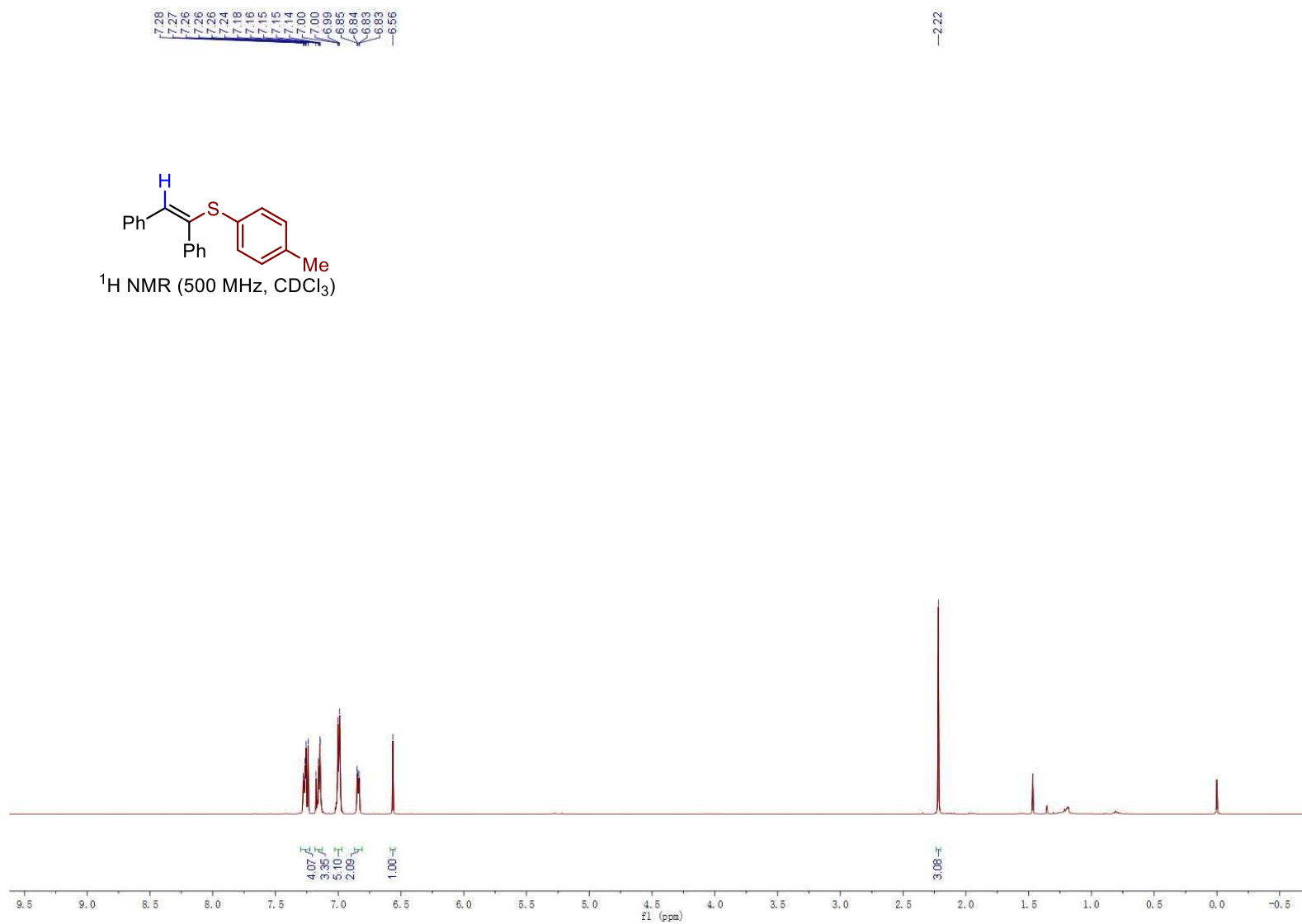
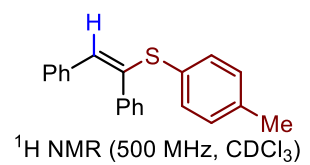


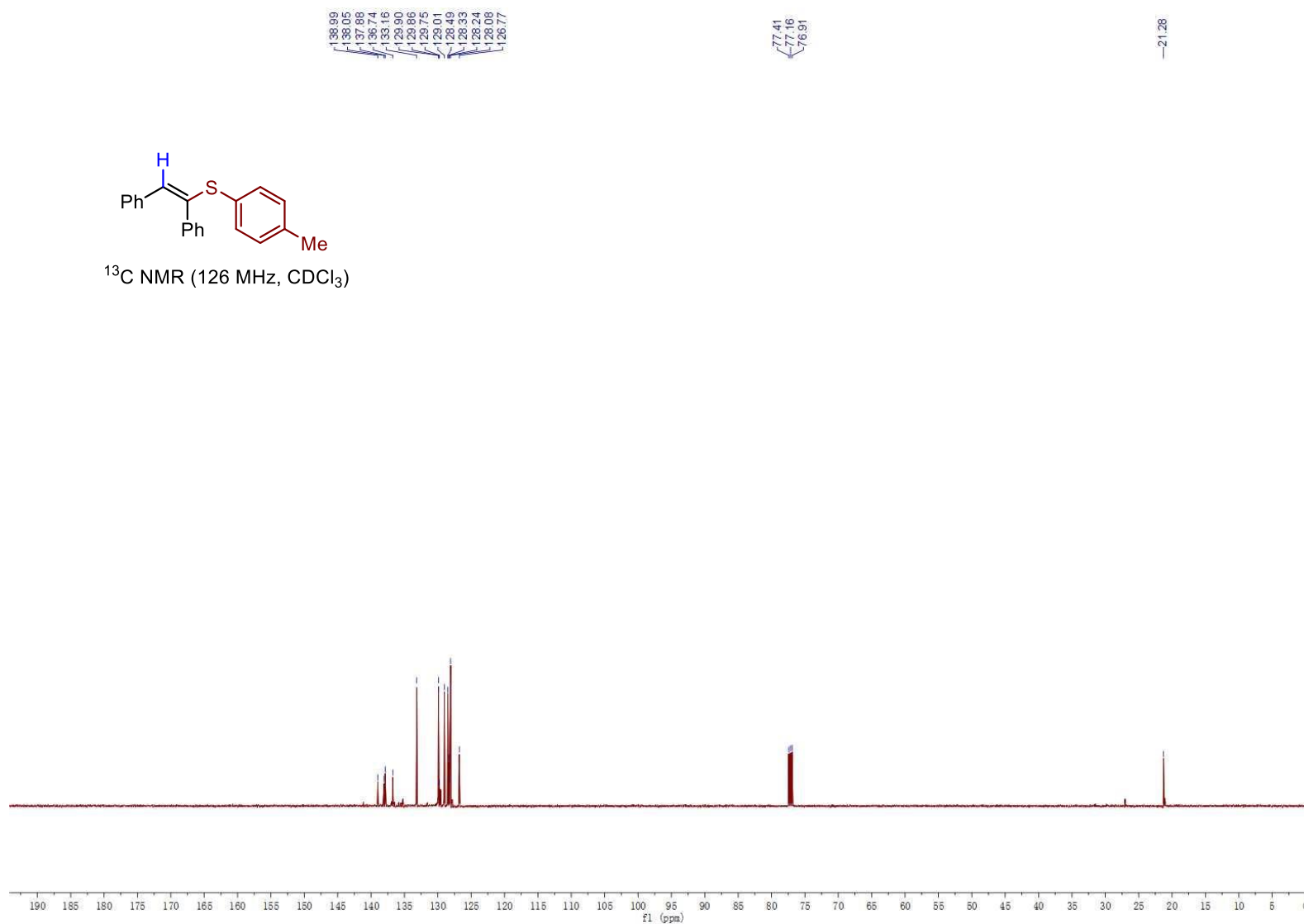
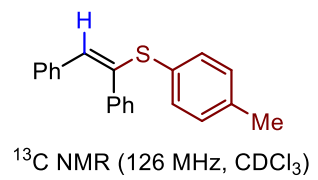




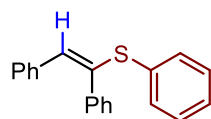
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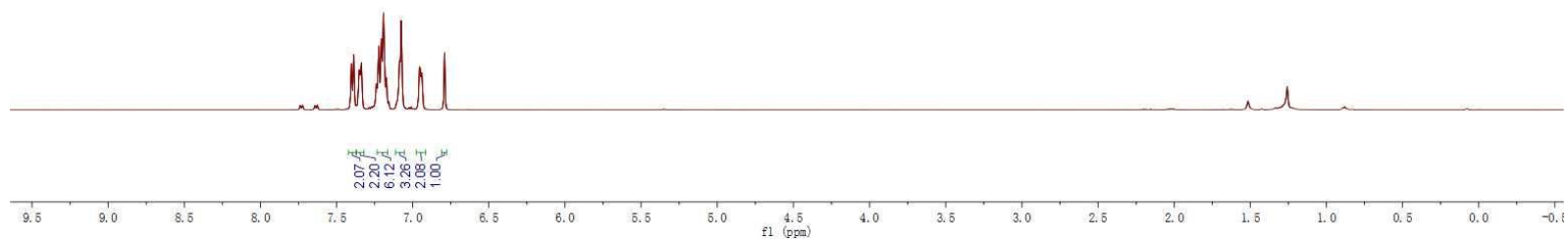


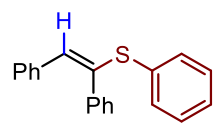


7.40
7.39
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7.17
7.08
6.95
6.94
6.79



$^1\text{H NMR}$ (500 MHz, CDCl_3)

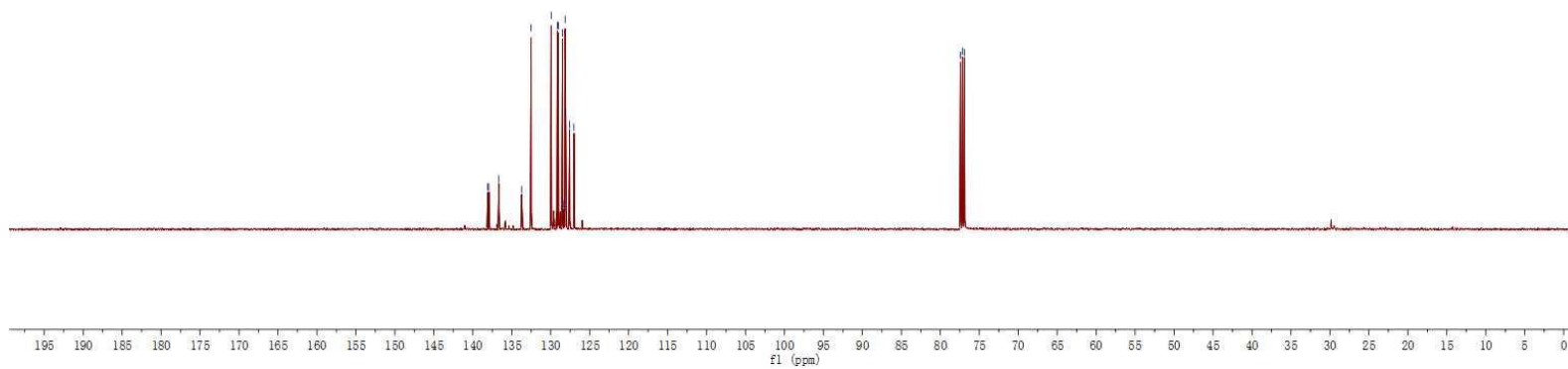


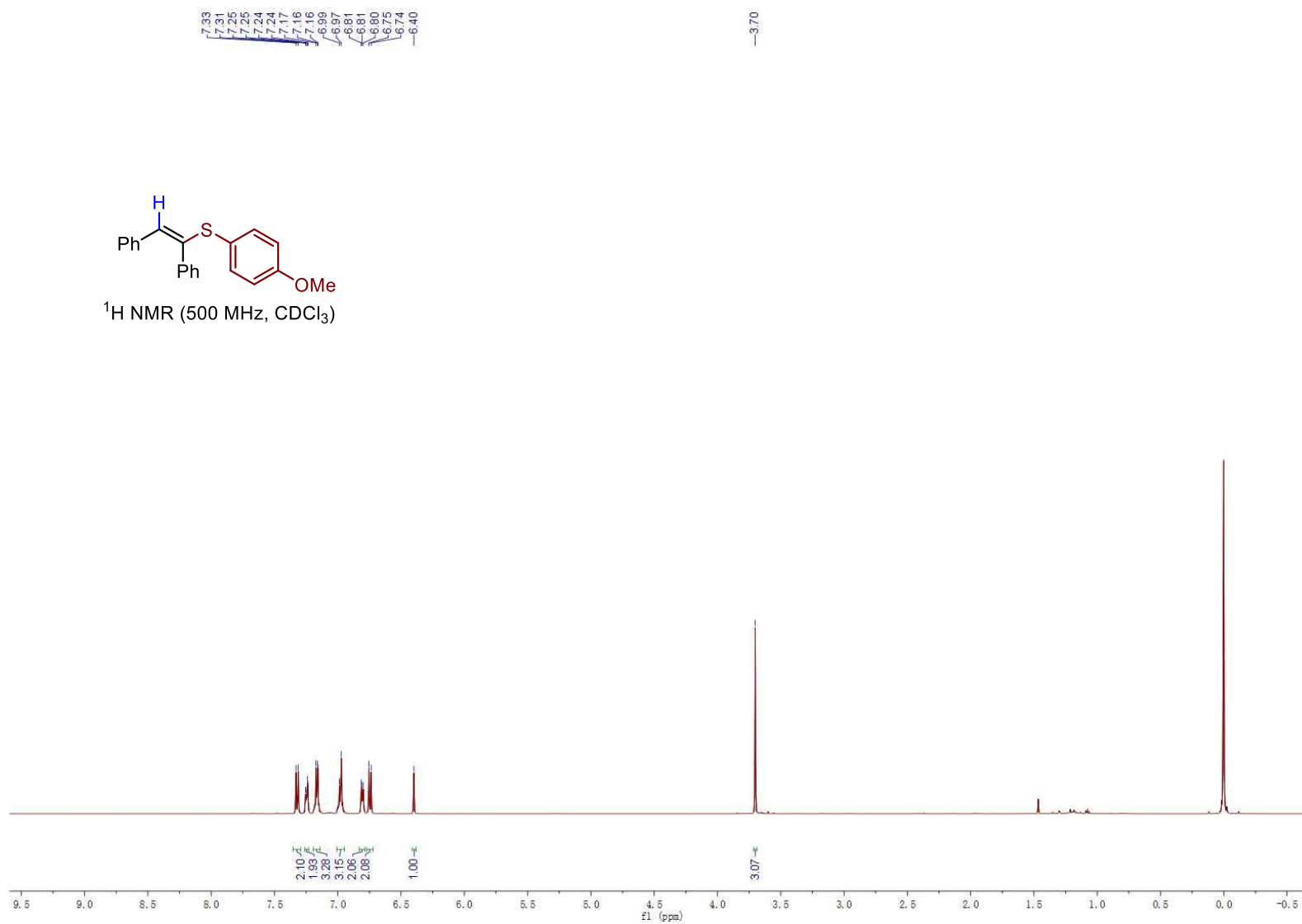
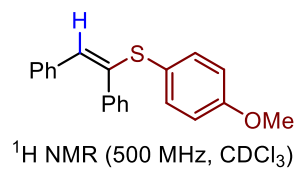


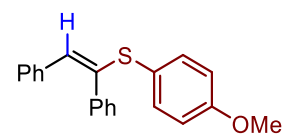
^{13}C NMR (126 MHz, CDCl_3)

138.09
137.09
136.65
133.73
133.51
133.94
133.13
133.02
128.49
128.31
128.14
128.12
127.57
127.01

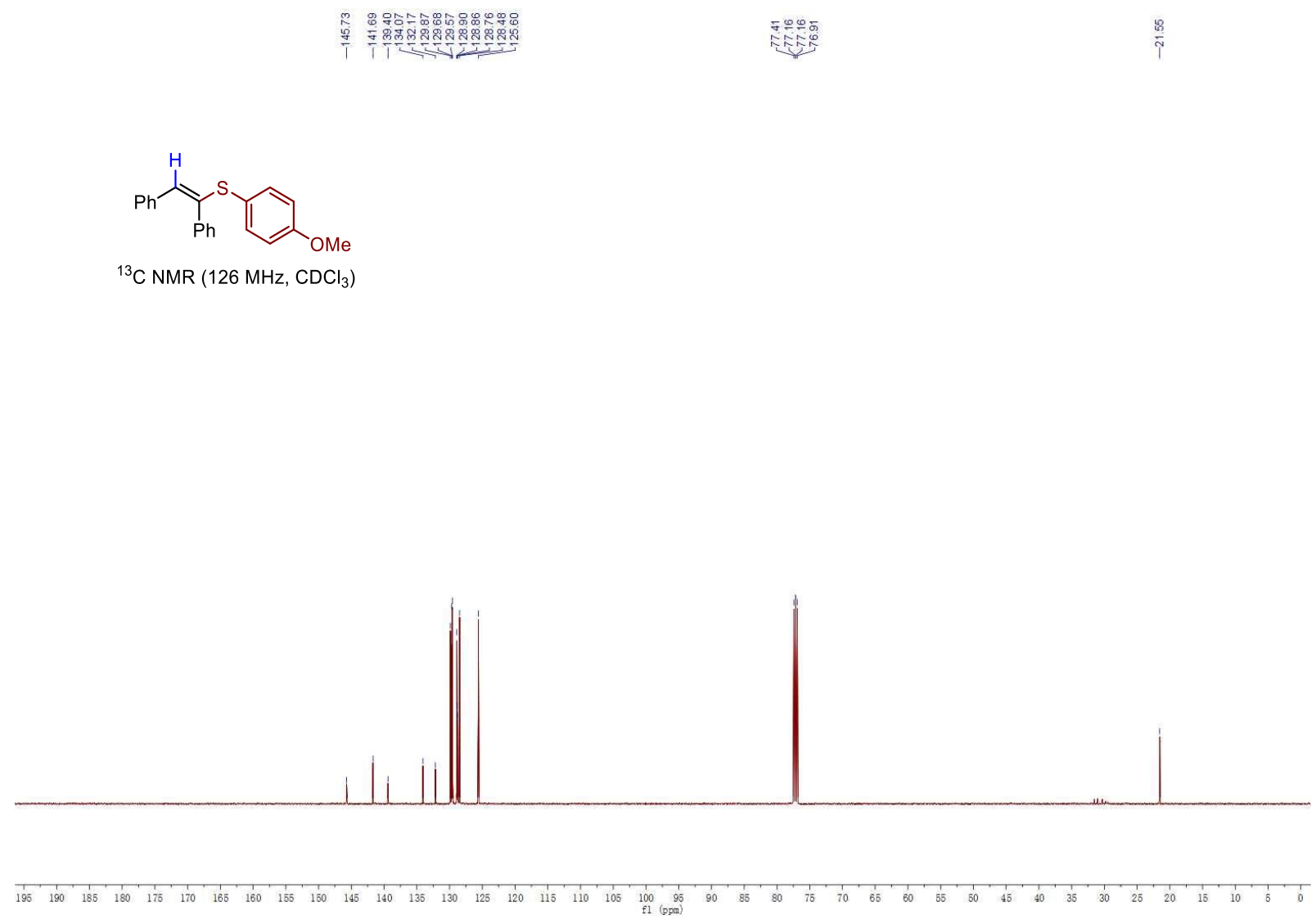
77.41
77.16
76.91



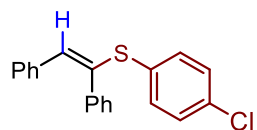




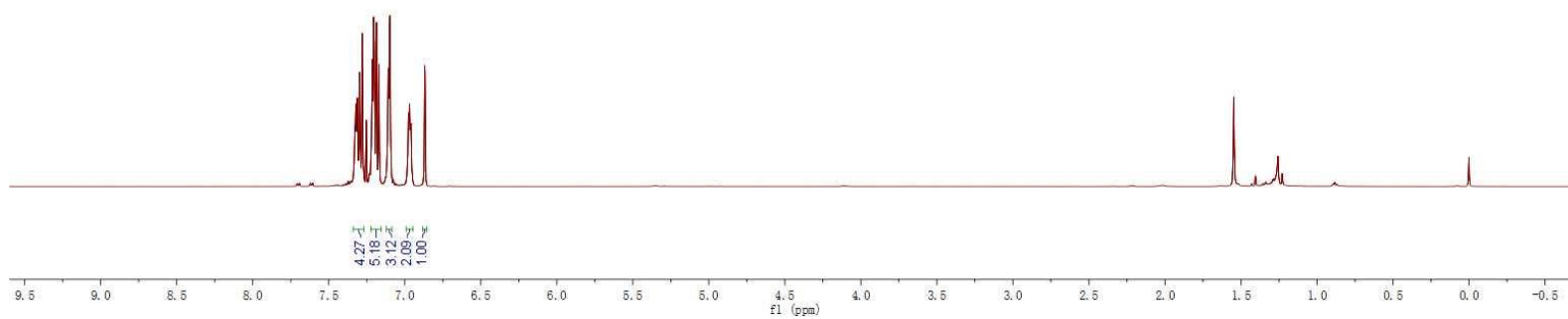
^{13}C NMR (126 MHz, CDCl_3)

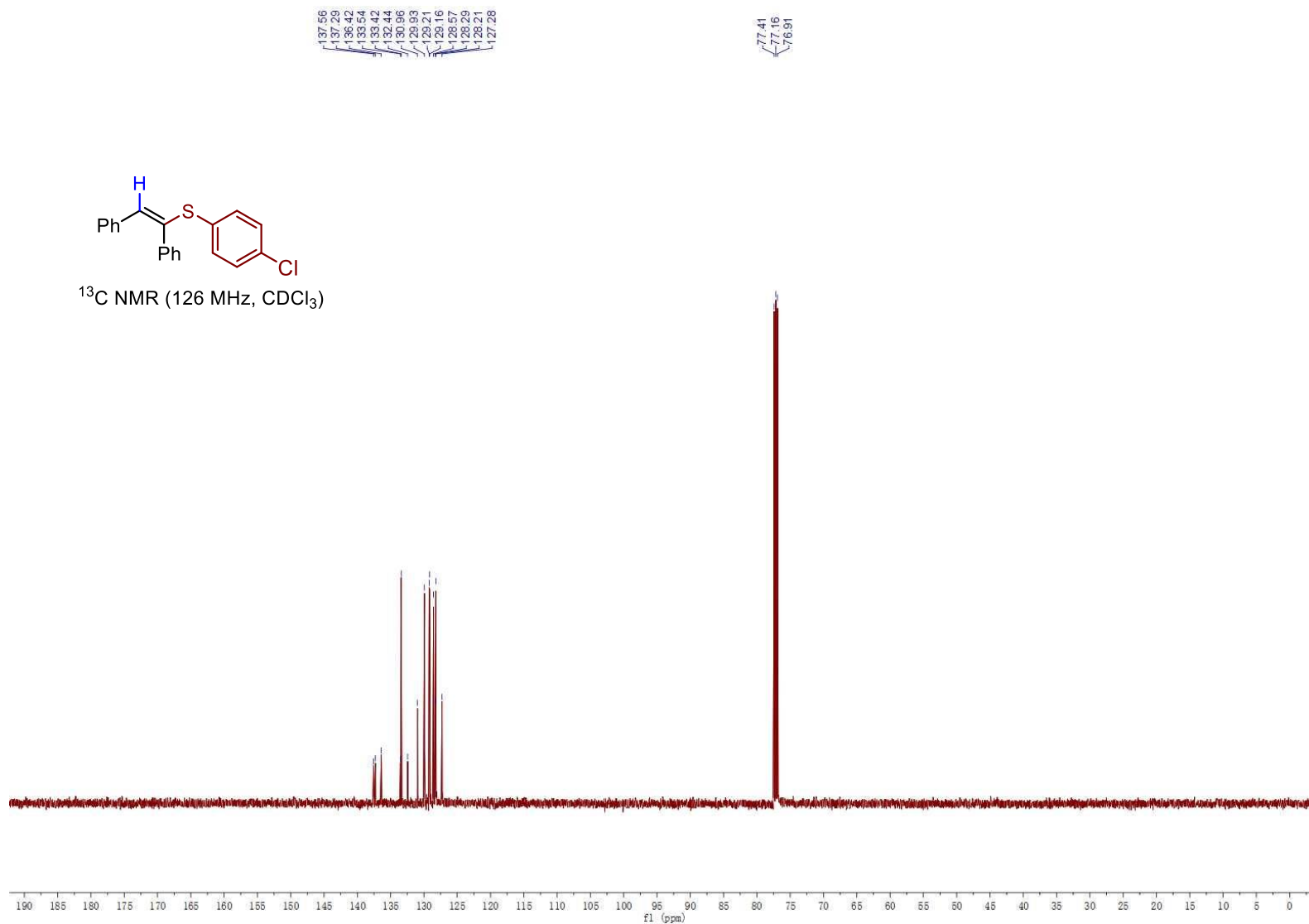
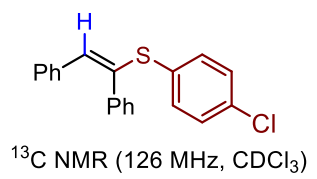


7.33
7.32
7.31
7.31
7.30
7.28
7.21
7.20
7.19
7.17
7.11
7.10
6.98
6.97
6.96
6.87

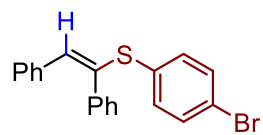


$^1\text{H NMR}$ (500 MHz, CDCl_3)

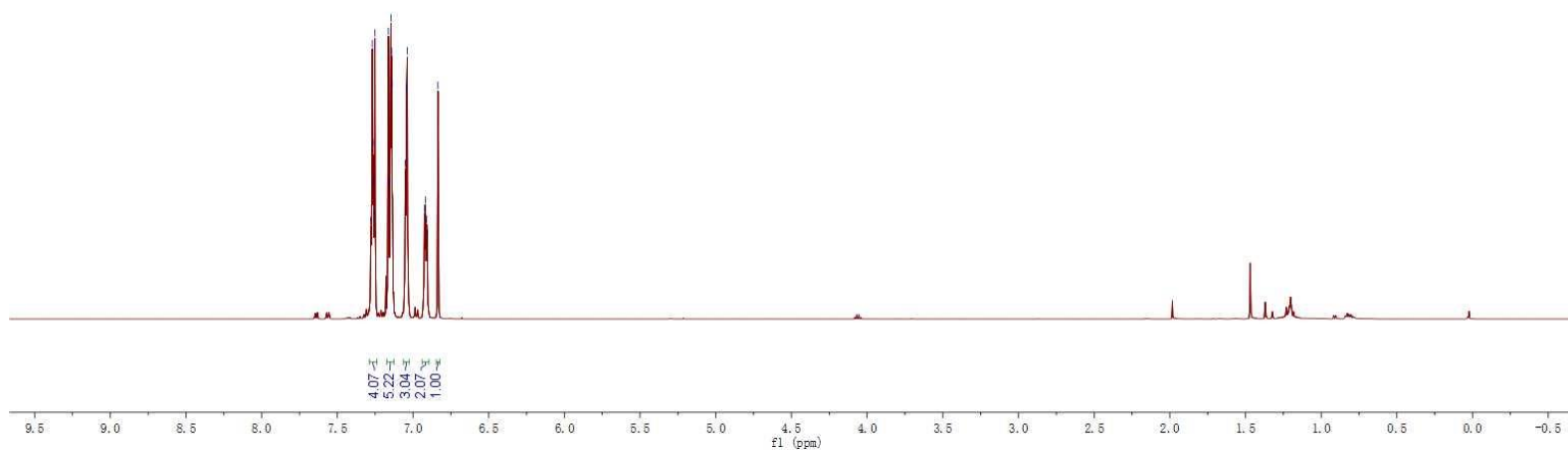


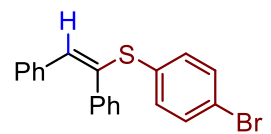


7.28
7.27
7.26
7.26
7.25
7.16
7.15
7.14
7.14
7.05
7.04
6.92
6.92
6.91
6.84

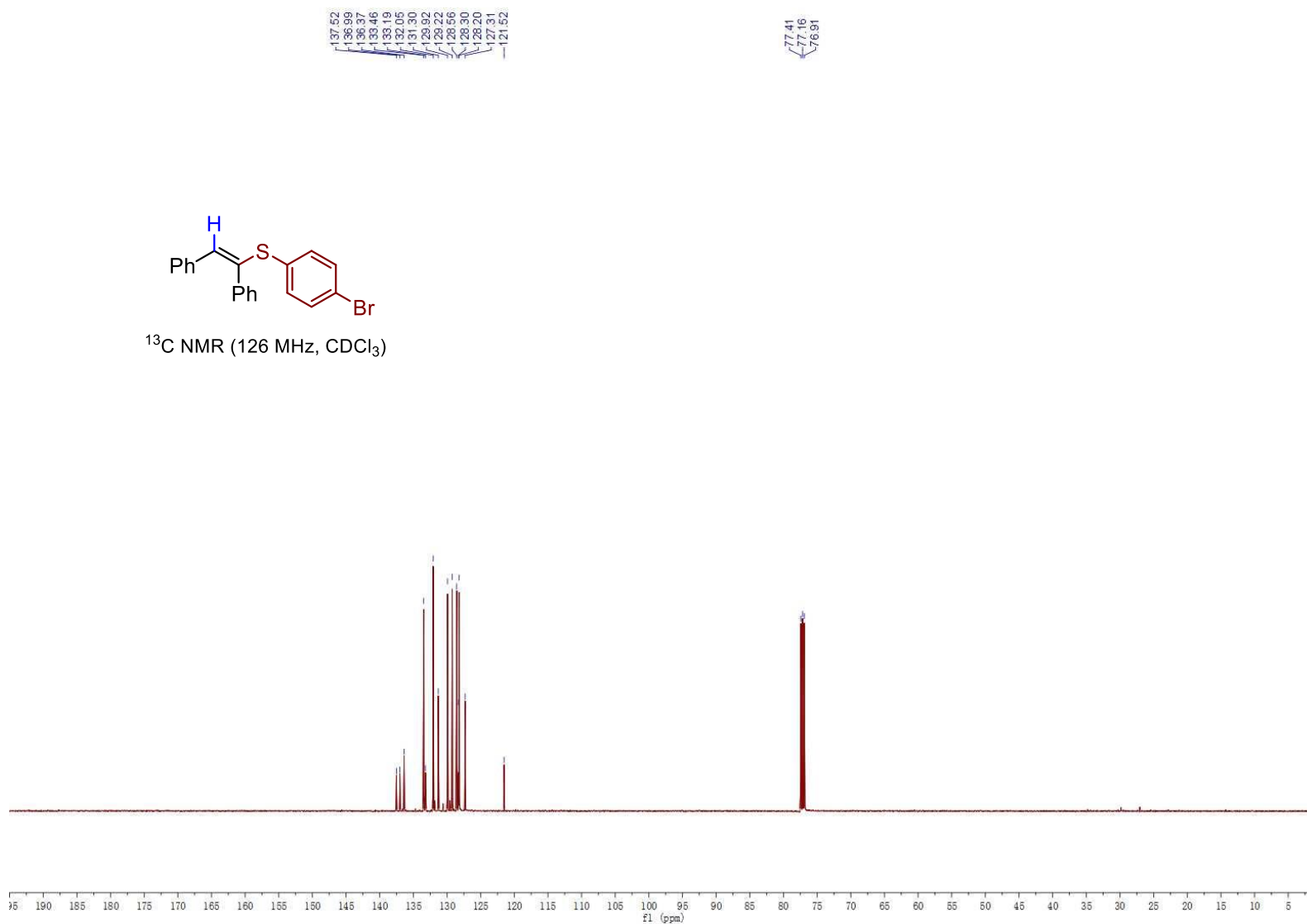


^1H NMR (500 MHz, CDCl_3)

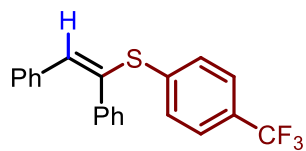




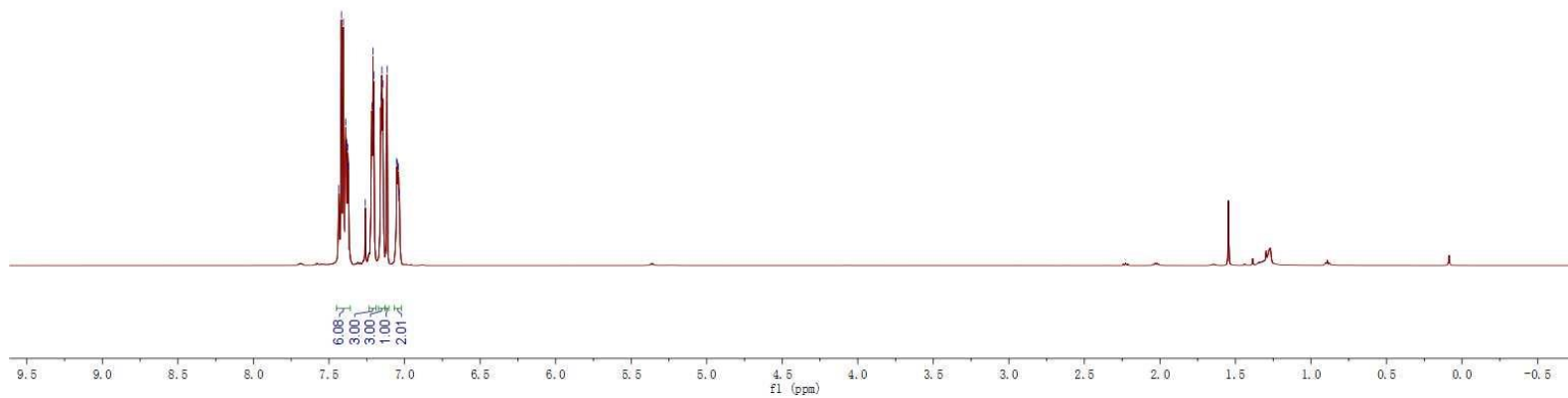
^{13}C NMR (126 MHz, CDCl_3)



7.44
7.42
7.41
7.39
7.38
7.37
7.26
7.22
7.21
7.20
7.16
7.15
7.14
7.12
7.08
7.06
7.04
7.03

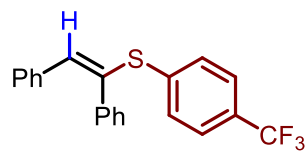


¹H NMR (500 MHz, CDCl₃)

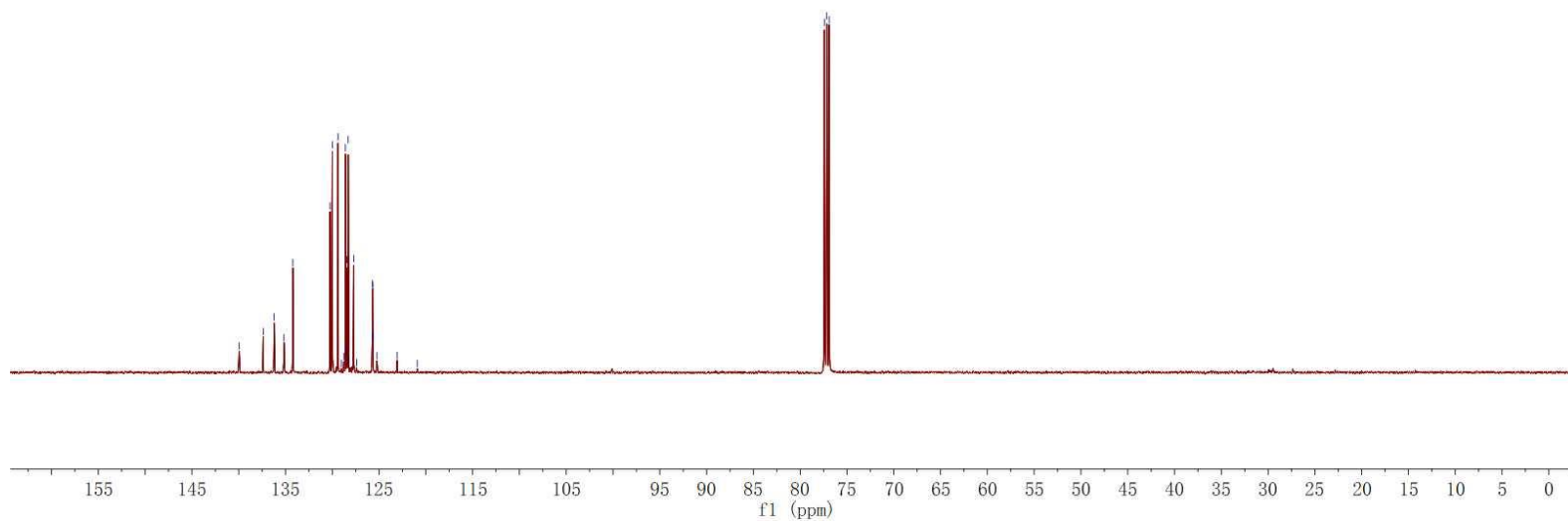


139.95
137.38
136.21
135.16
134.21
130.24
129.99
129.39
129.01
128.76
128.60
128.50
128.44
128.30
128.24
127.71
127.40
125.73
125.70
125.67
125.64
125.23
123.07
120.91

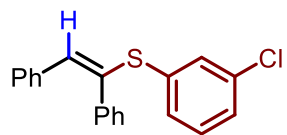
77.41
77.16
76.91



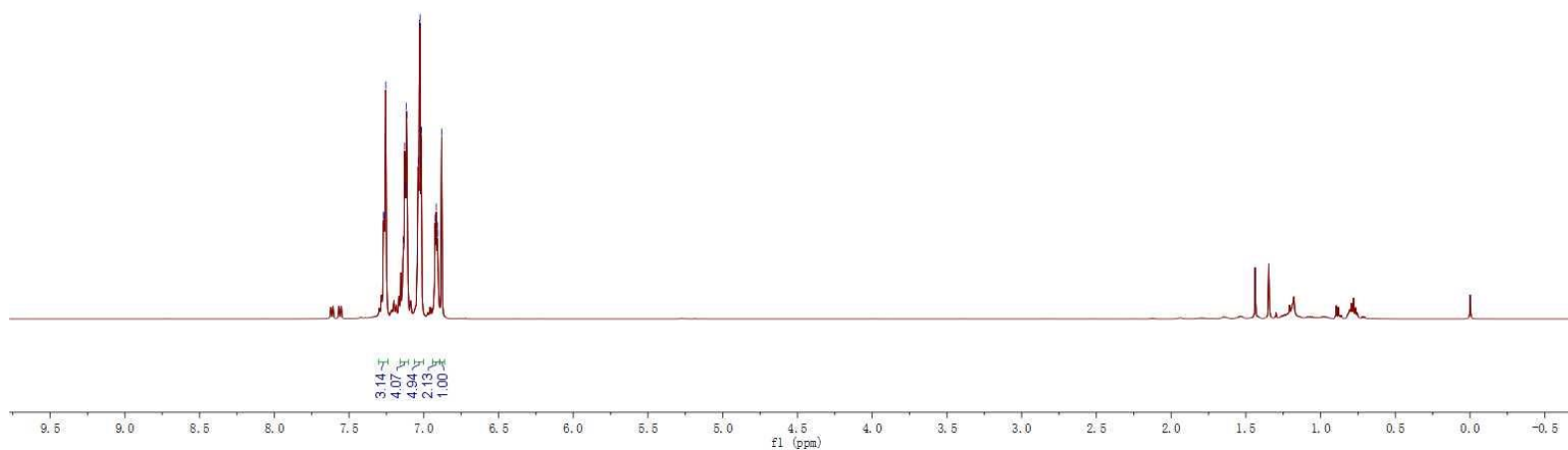
^{13}C NMR (126 MHz, CDCl_3)

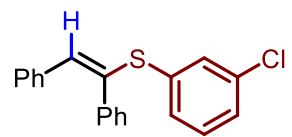


7.27
7.26
7.25
7.14
7.13
7.12
7.11
7.04
7.03
7.02
6.92
6.91
6.88

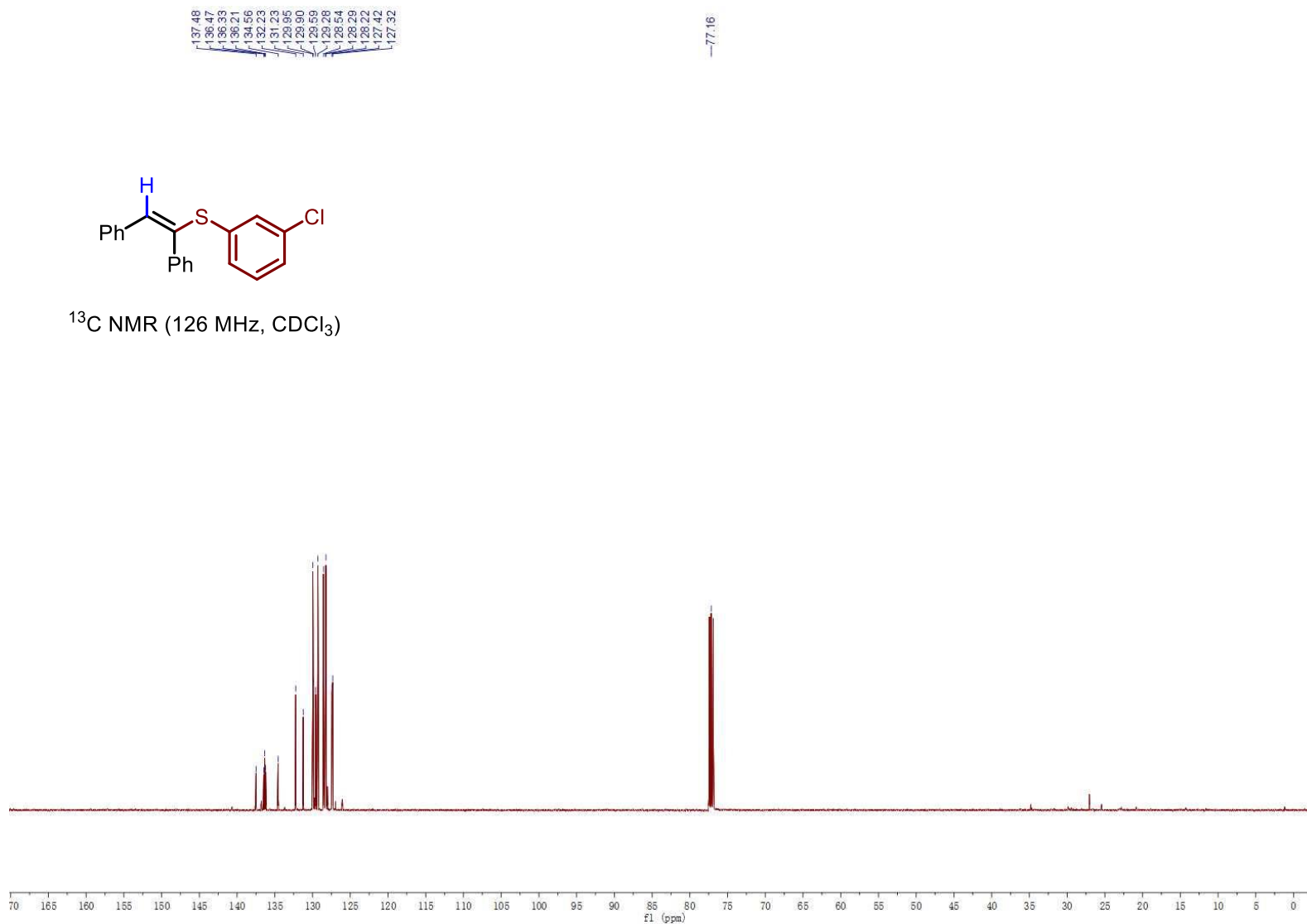


¹H NMR (500 MHz, CDCl₃)

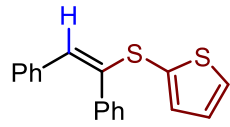




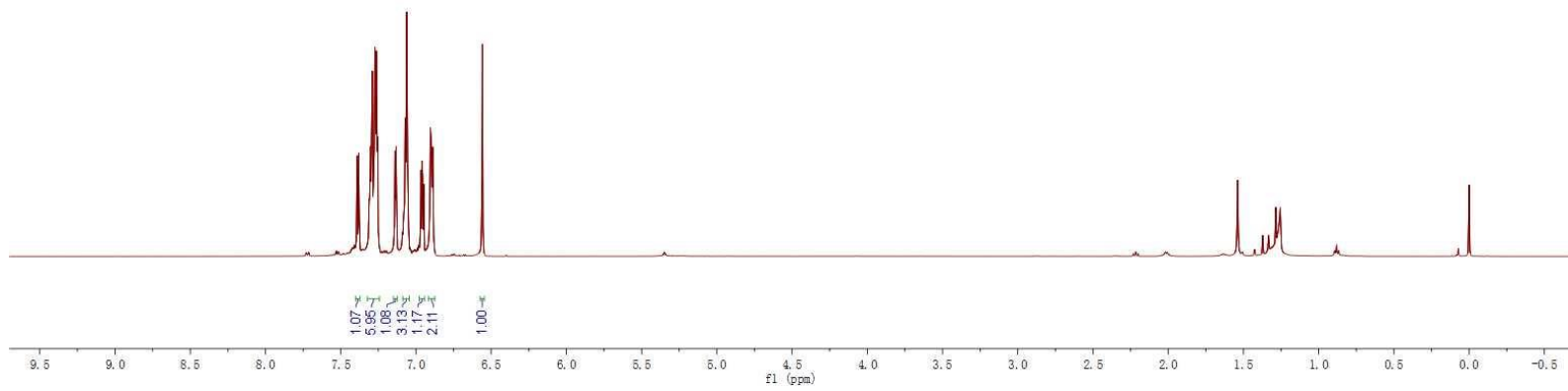
^{13}C NMR (126 MHz, CDCl_3)



7.39
7.38
7.30
7.29
7.29
7.28
7.27
7.26
7.26
7.25
7.14
7.13
7.07
7.06
6.97
6.96
6.95
6.90
6.89
6.56

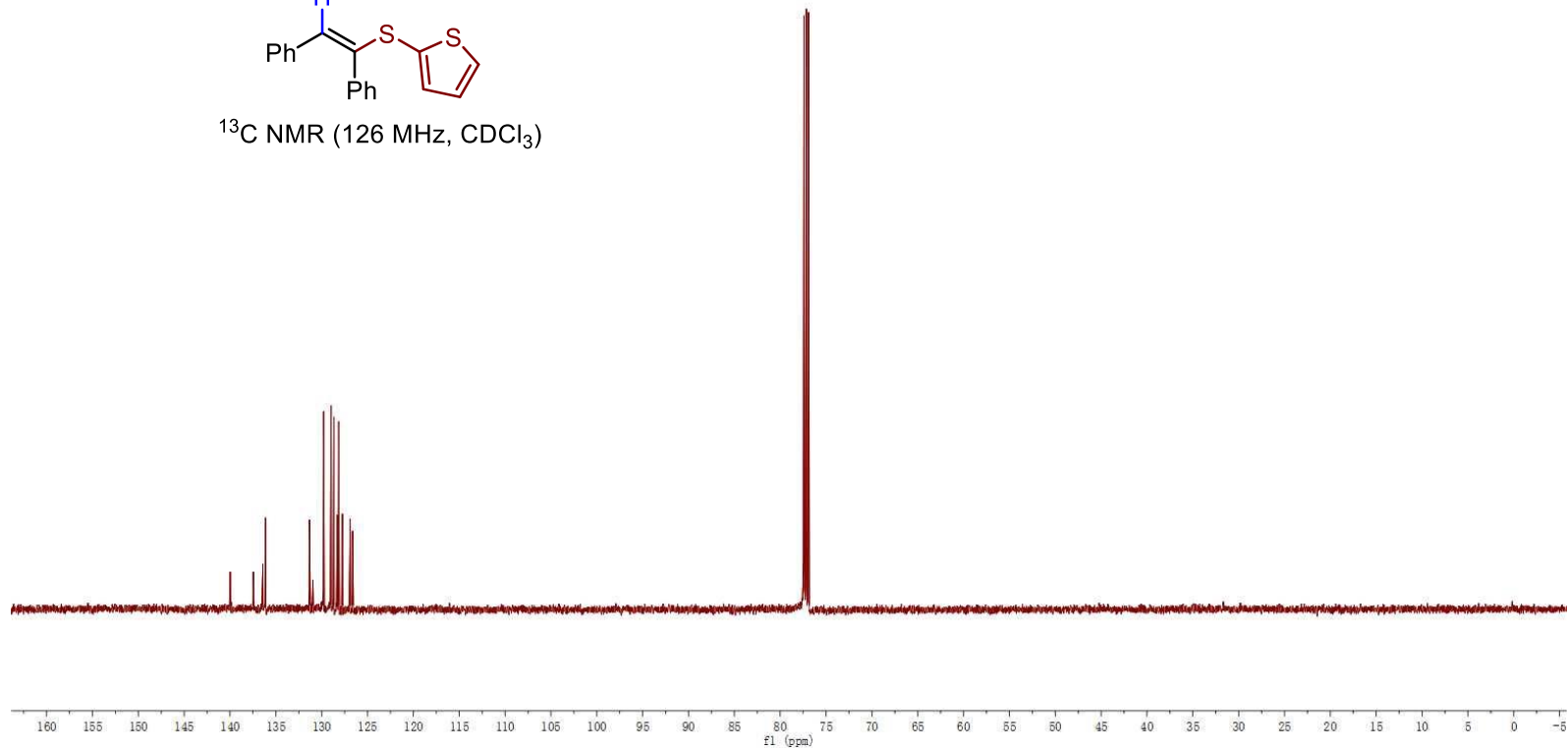
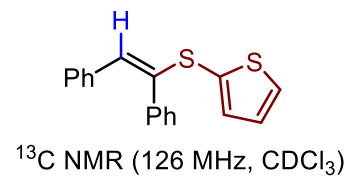


^1H NMR (500 MHz, CDCl_3)



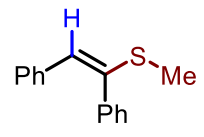
139.98
137.45
136.41
136.12
131.52
130.75
129.75
128.67
128.31
128.14
127.75
126.90
126.62

77.41
77.06
76.81

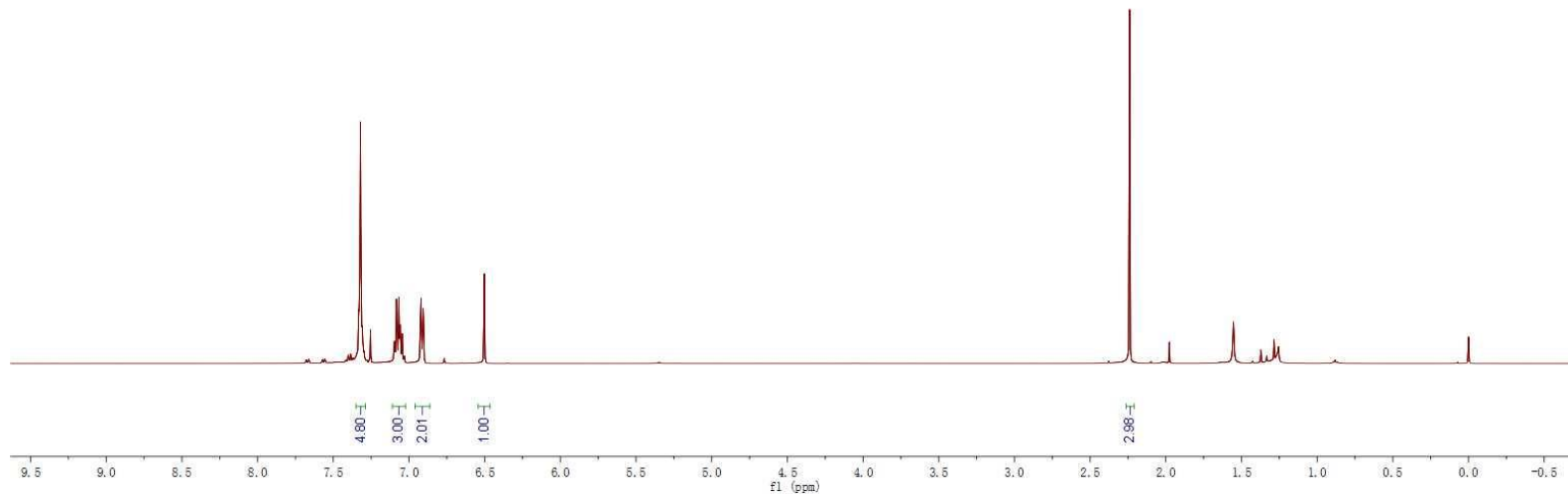


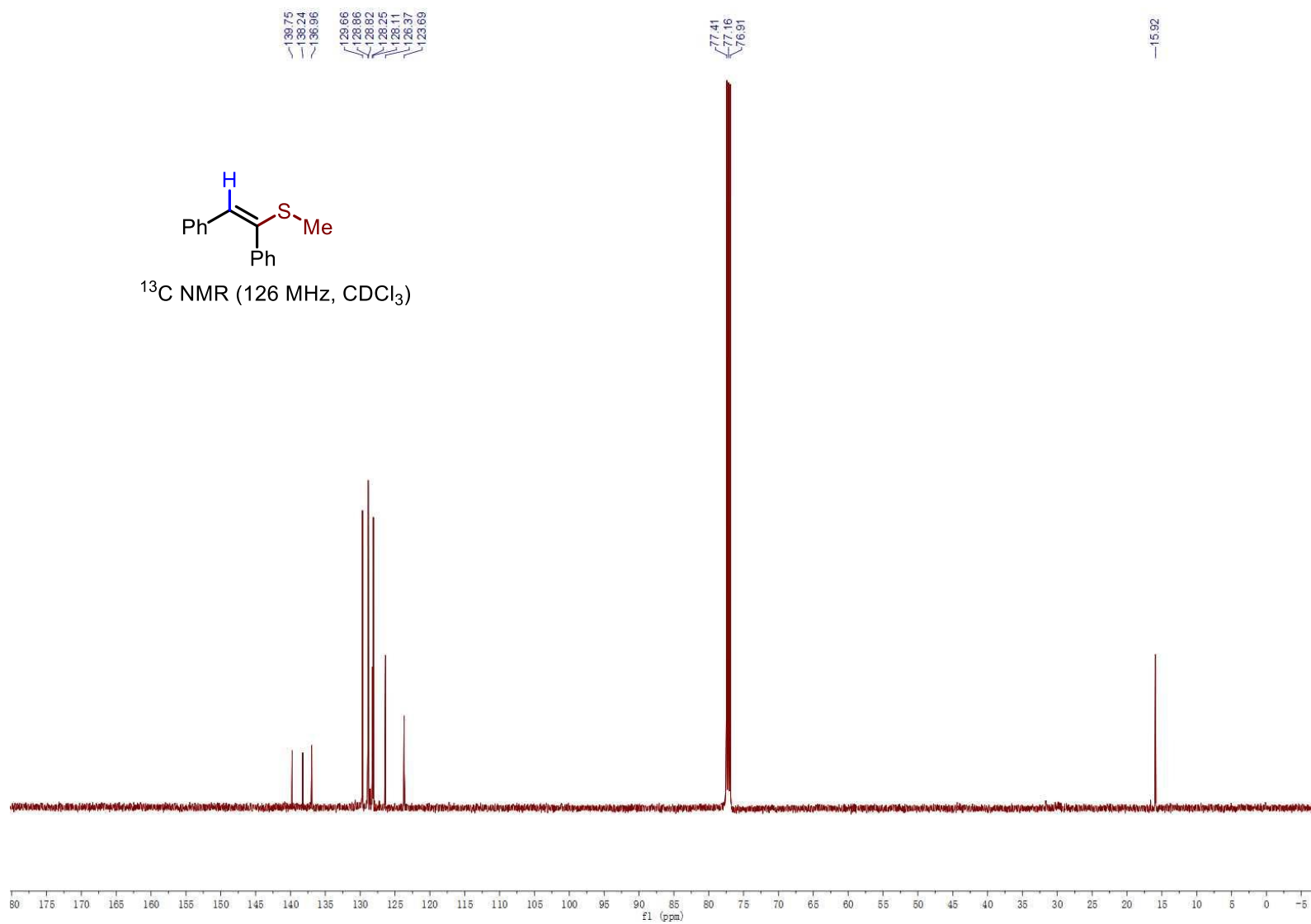
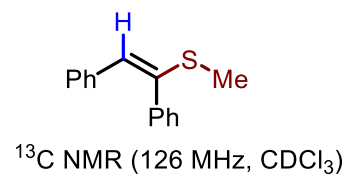
7.32
7.08
7.07
7.06
7.04
6.92
6.80

2.24



¹H NMR (500 MHz, CDCl₃)

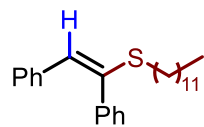




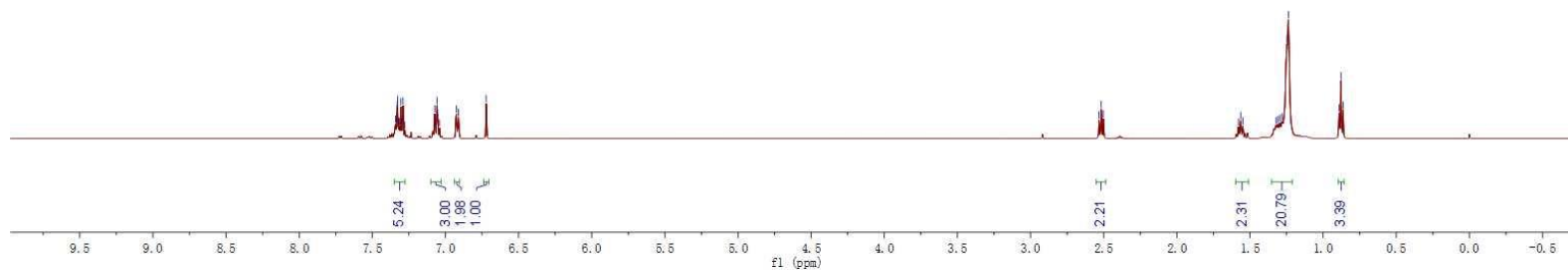
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.28
7.07
7.06
7.05
6.92
6.91
6.72

2.58
2.52
2.50

1.58
1.56
1.55
1.28
1.25
1.24
0.88
0.86



¹H NMR (500 MHz, CDCl₃)

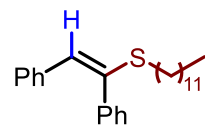


138.60
138.29
136.99
29.76
29.99
28.73
28.10
28.09
26.65
26.51

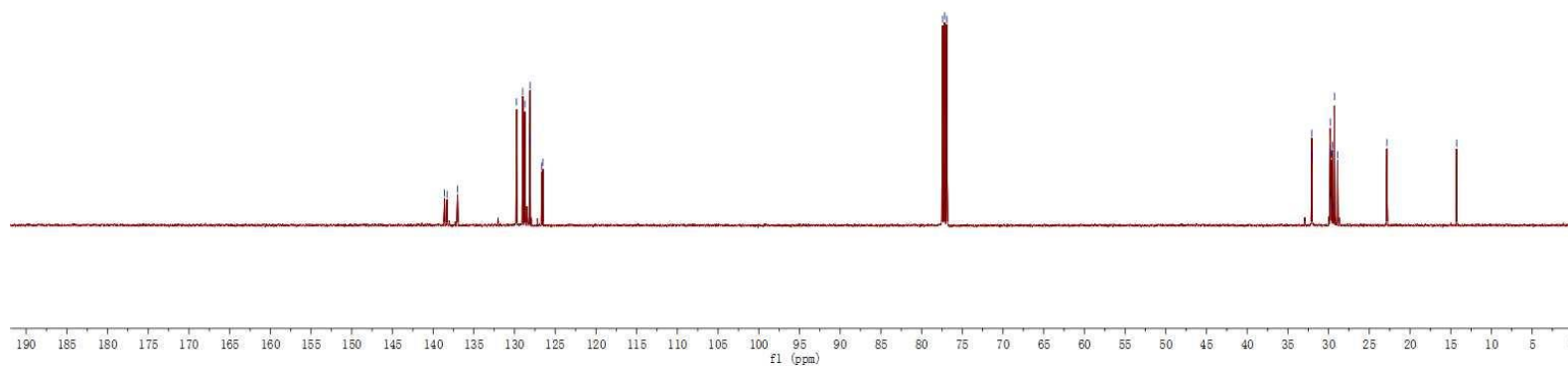
77.41
77.16
76.91

32.07
32.05
29.79
29.77
29.72
29.61
29.53
29.50
29.23
28.90
22.84

14.28



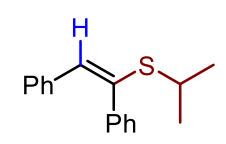
¹H NMR (500 MHz, CDCl₃)



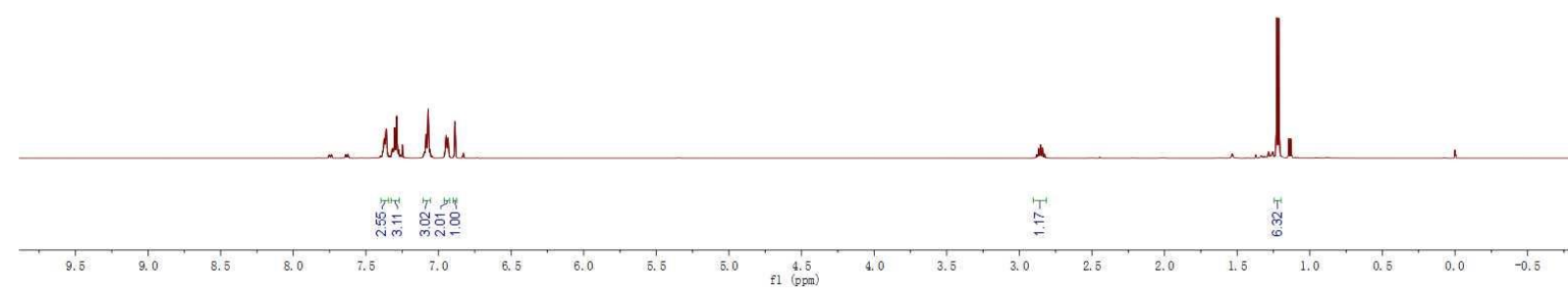
7.38
7.38
7.37
7.37
7.36
7.36
7.32
7.31
7.30
7.29
7.27
7.10
7.09
7.07
7.06
7.06
6.95
6.95
6.94
6.93
6.89

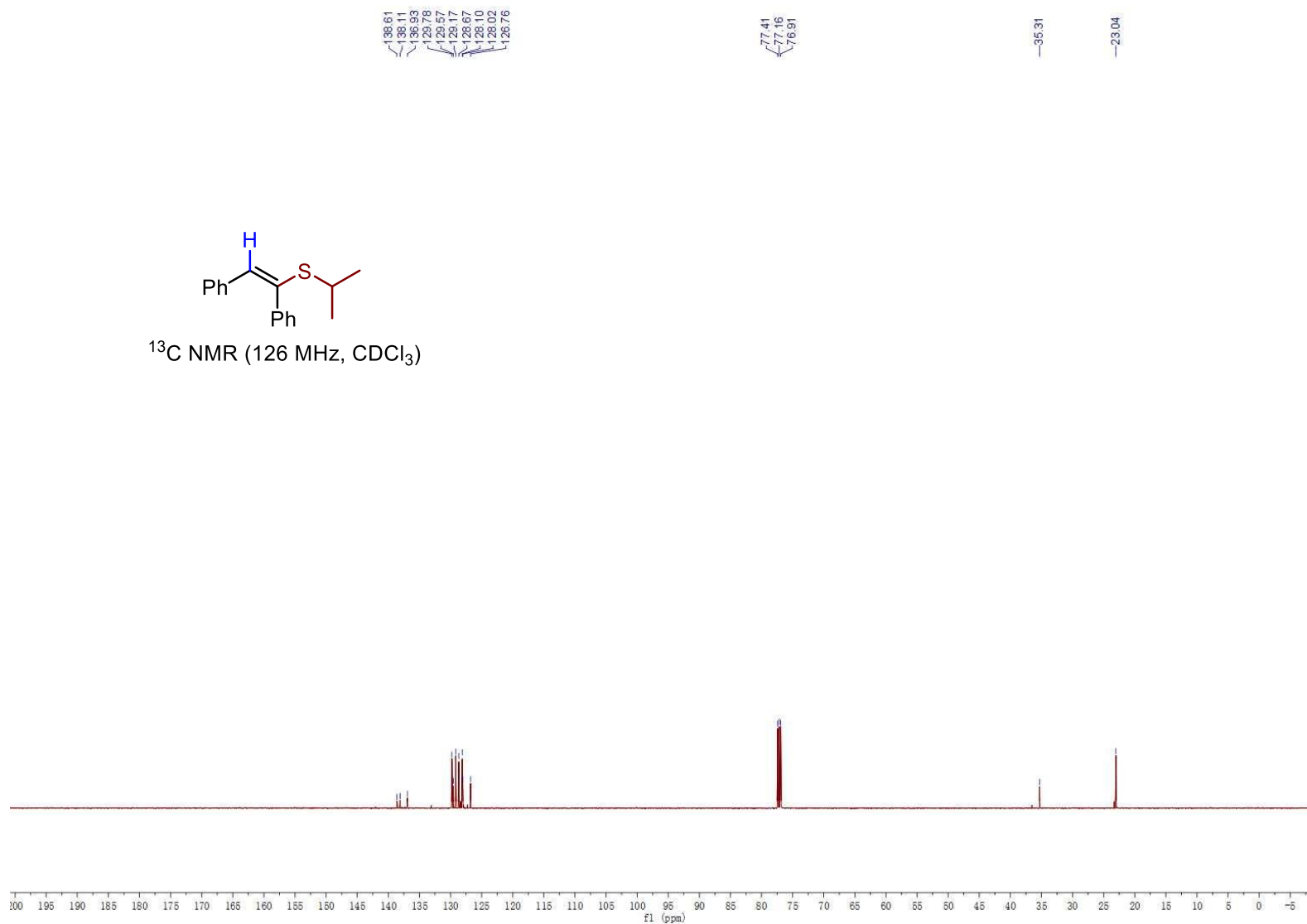
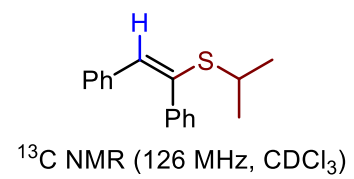
2.88
2.87
2.87
2.86
2.85
2.84
2.83

1.23
1.21



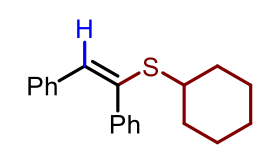
¹H NMR (500 MHz, CDCl₃)



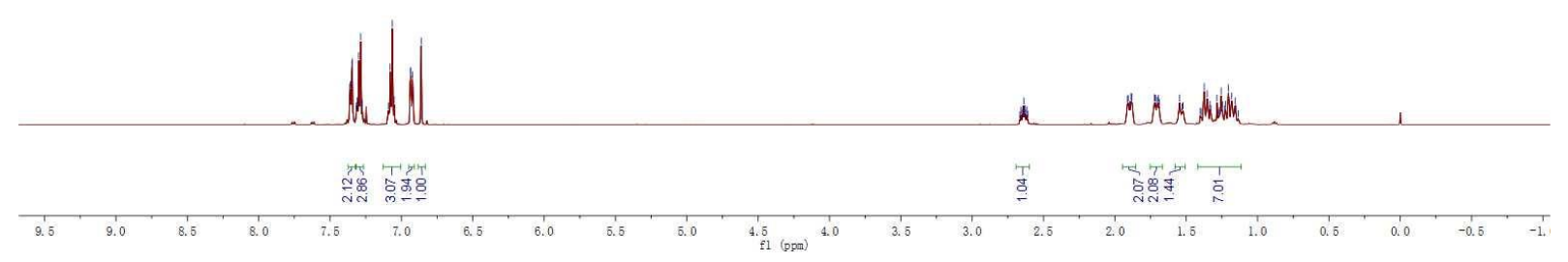


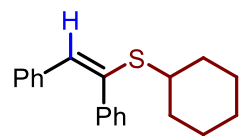
7.36
7.35
7.34
7.32
7.31
7.30
7.29
7.28
7.09
7.08
7.06
7.05
6.94
6.93
6.92
6.86

2.67
2.66
2.65
2.64
2.63
2.62
2.61
1.91
1.90
1.89
1.88
1.72
1.71
1.70
1.70
1.69
1.68
1.65
1.62
1.40
1.39
1.37
1.35
1.33
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1.25
1.23
1.22
1.20
1.18
1.15
1.14

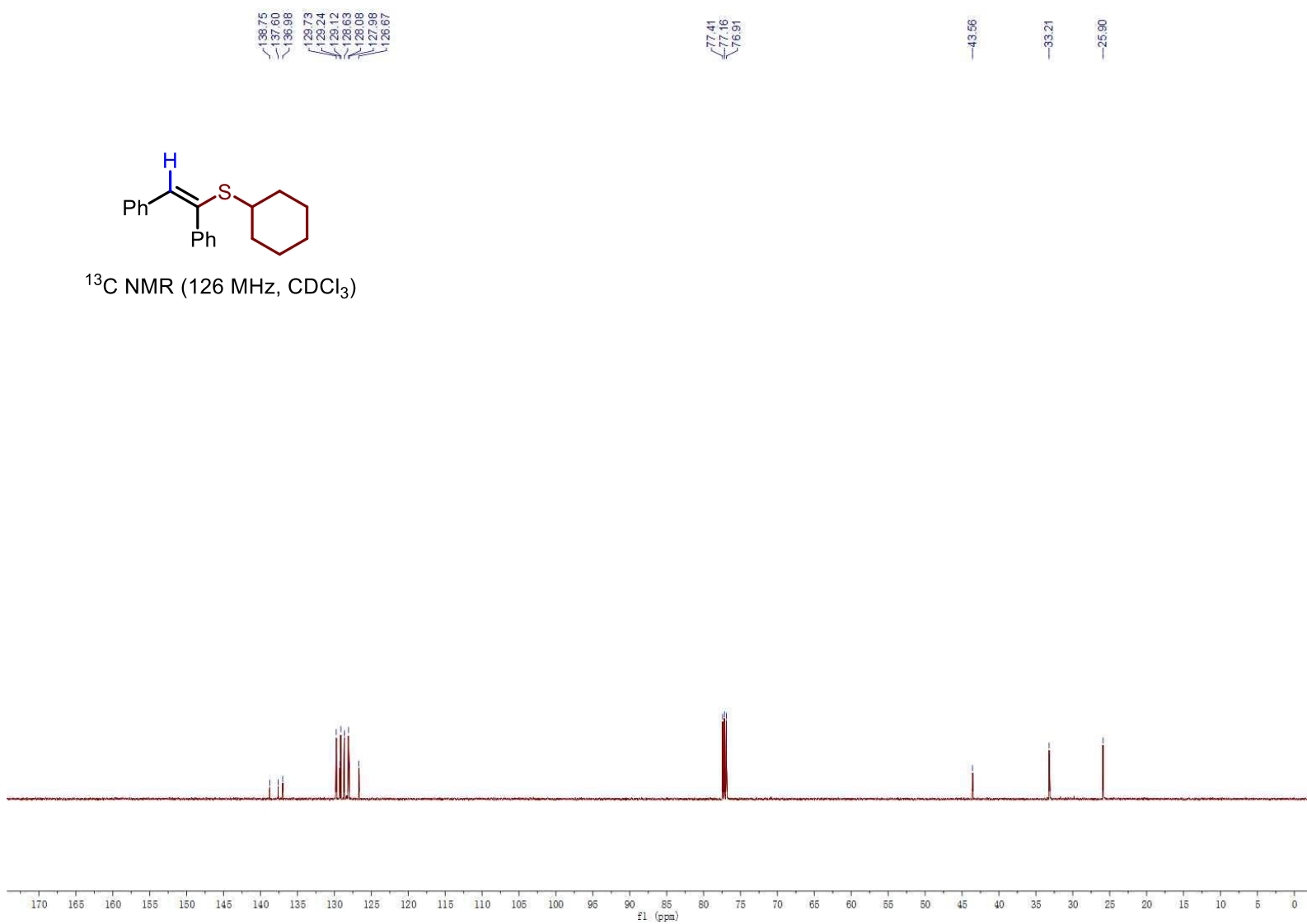


^1H NMR (500 MHz, CDCl_3)



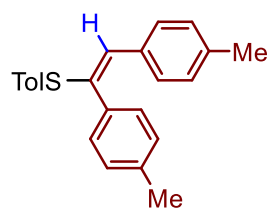


^{13}C NMR (126 MHz, CDCl_3)

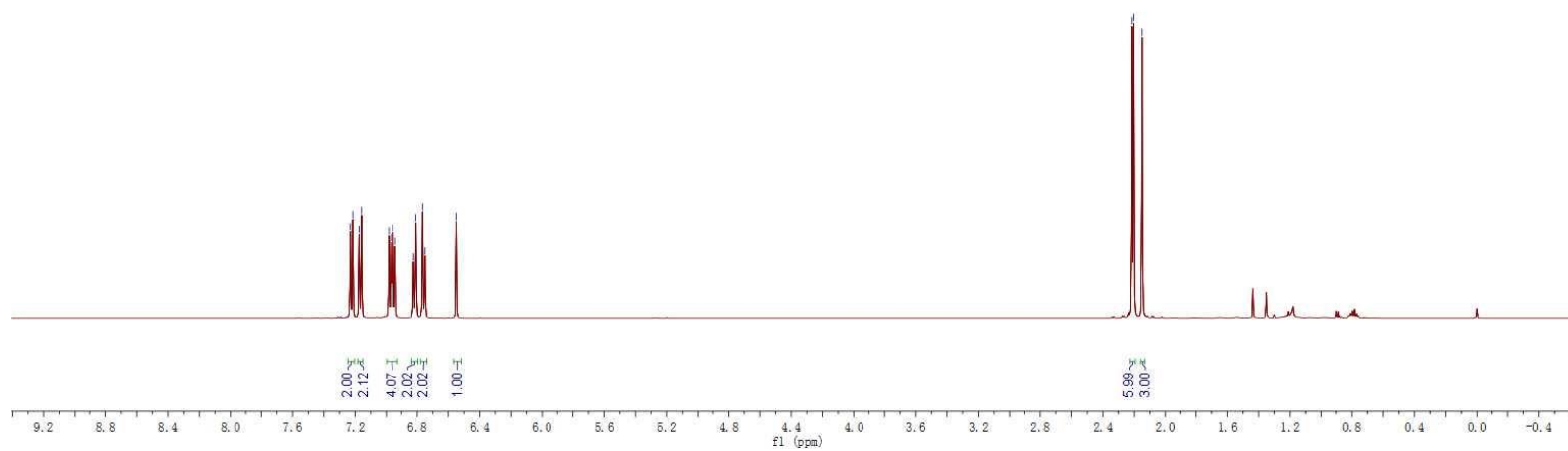


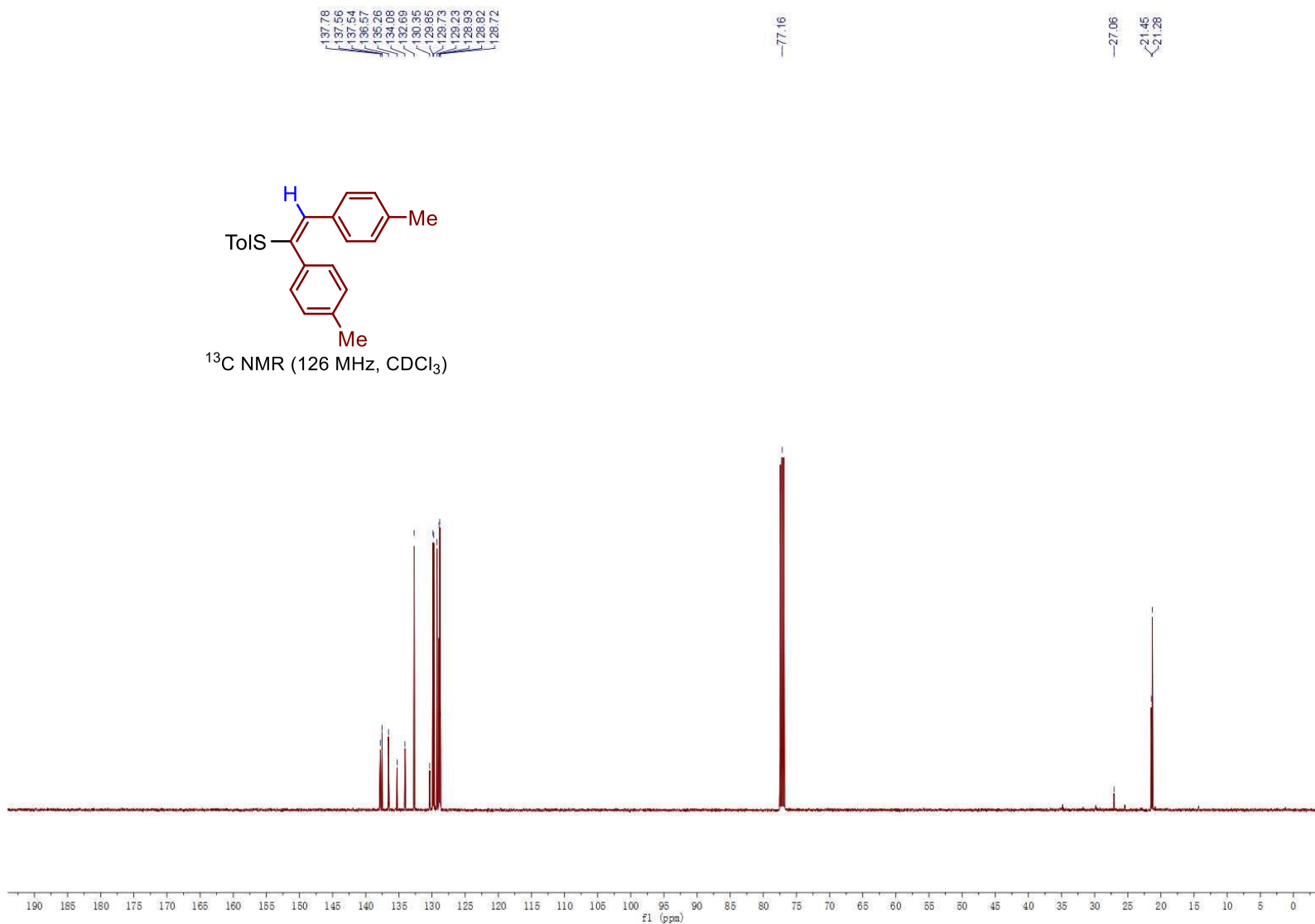
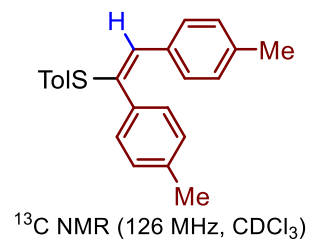
7.23
7.21
7.17
7.16
6.98
6.97
6.96
6.94
6.82
6.81
6.77
6.55

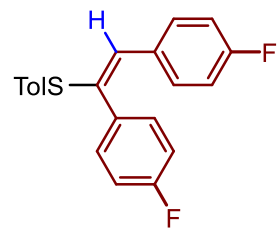
2.21
2.20
2.15



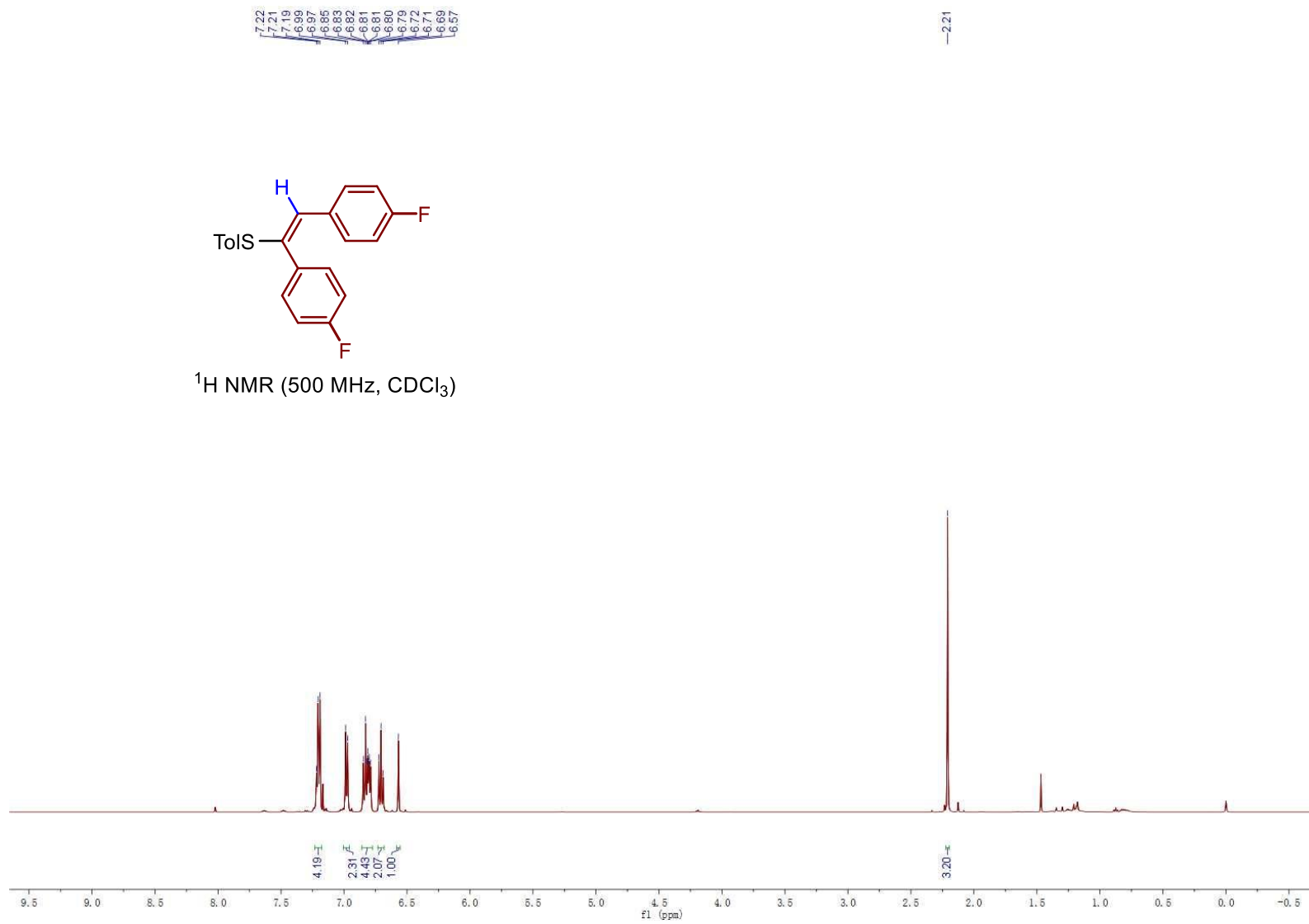
$^1\text{H NMR}$ (500 MHz, CDCl_3)







^1H NMR (500 MHz, CDCl_3)

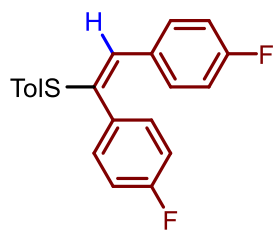


163.43
162.61
161.46
160.64

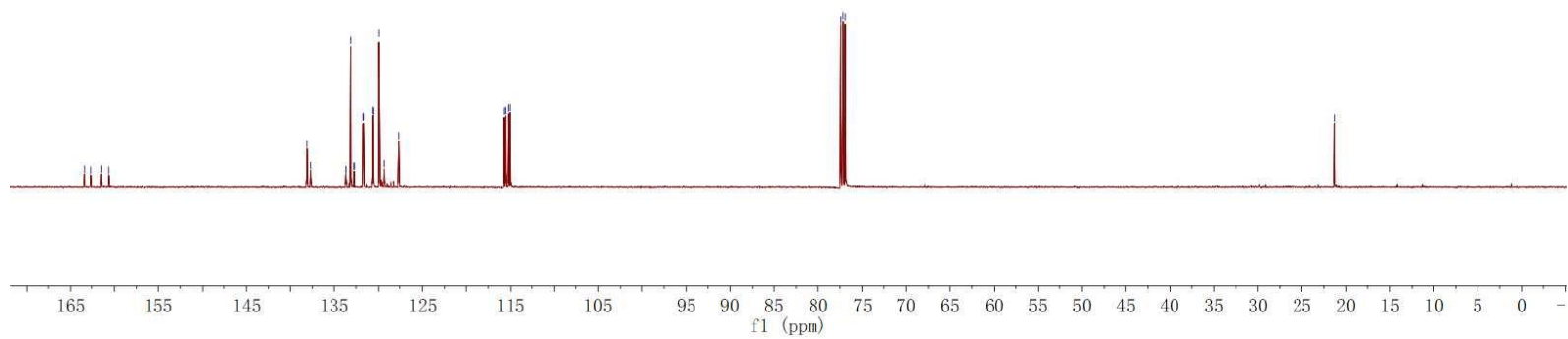
138.11
137.68
133.66
133.10
132.73
132.70
131.72
131.65
130.66
130.60
129.97
129.37
117.91
115.58
115.25
115.08

77.41
77.16
76.91

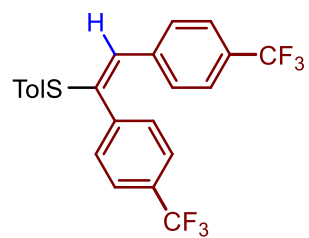
-21.30



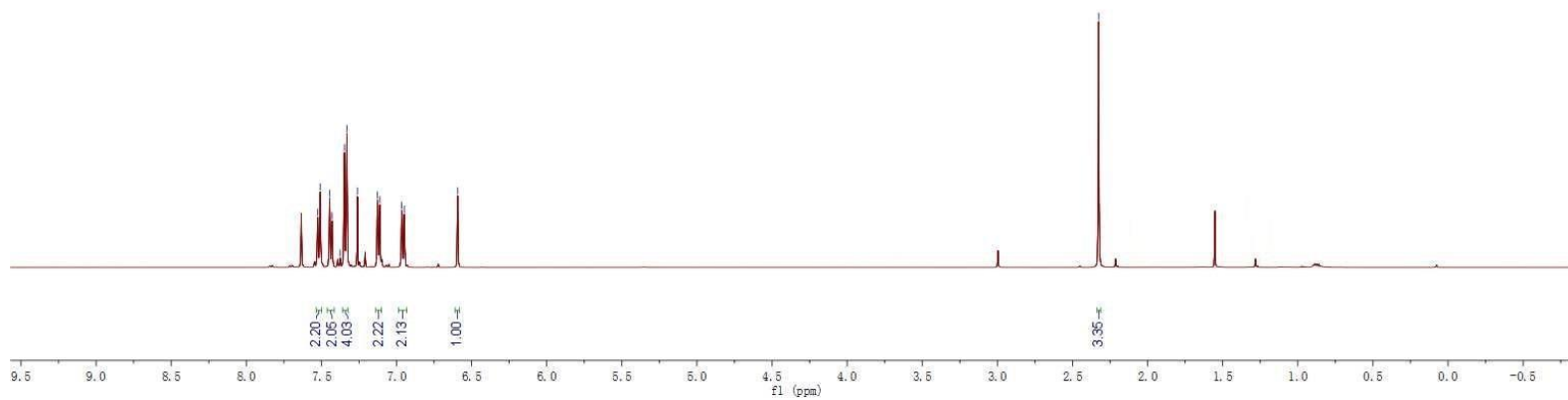
¹³C NMR (126 MHz, CDCl₃)

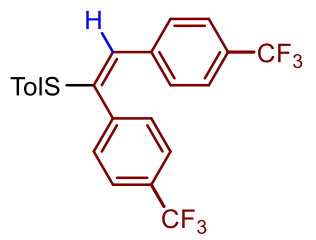
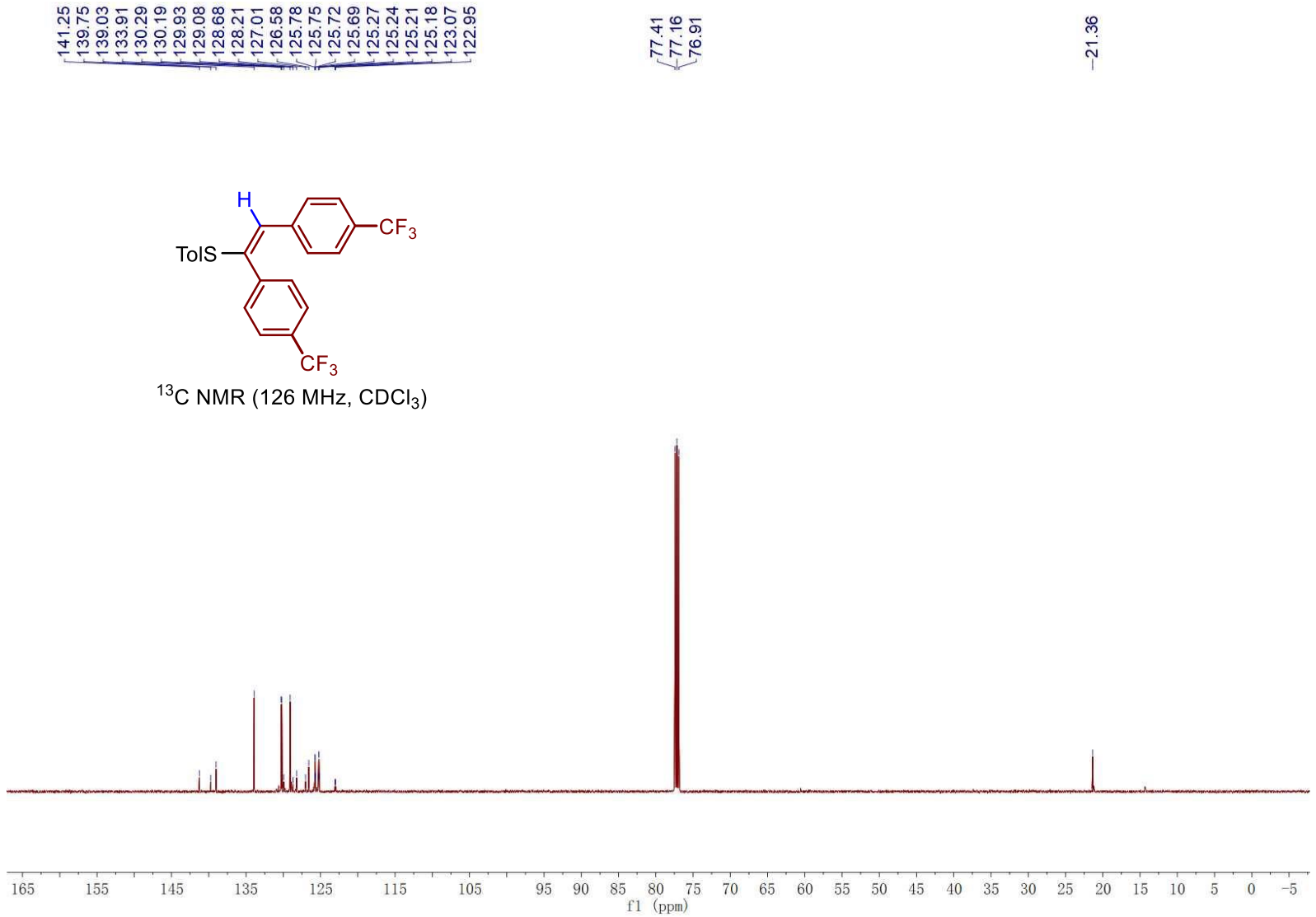


7.52
7.51
7.45
7.43
7.37
7.35
7.33
7.26
7.13
7.11
6.97
6.59



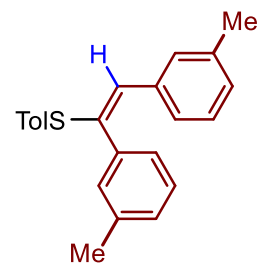
¹H NMR (500 MHz, CDCl₃)



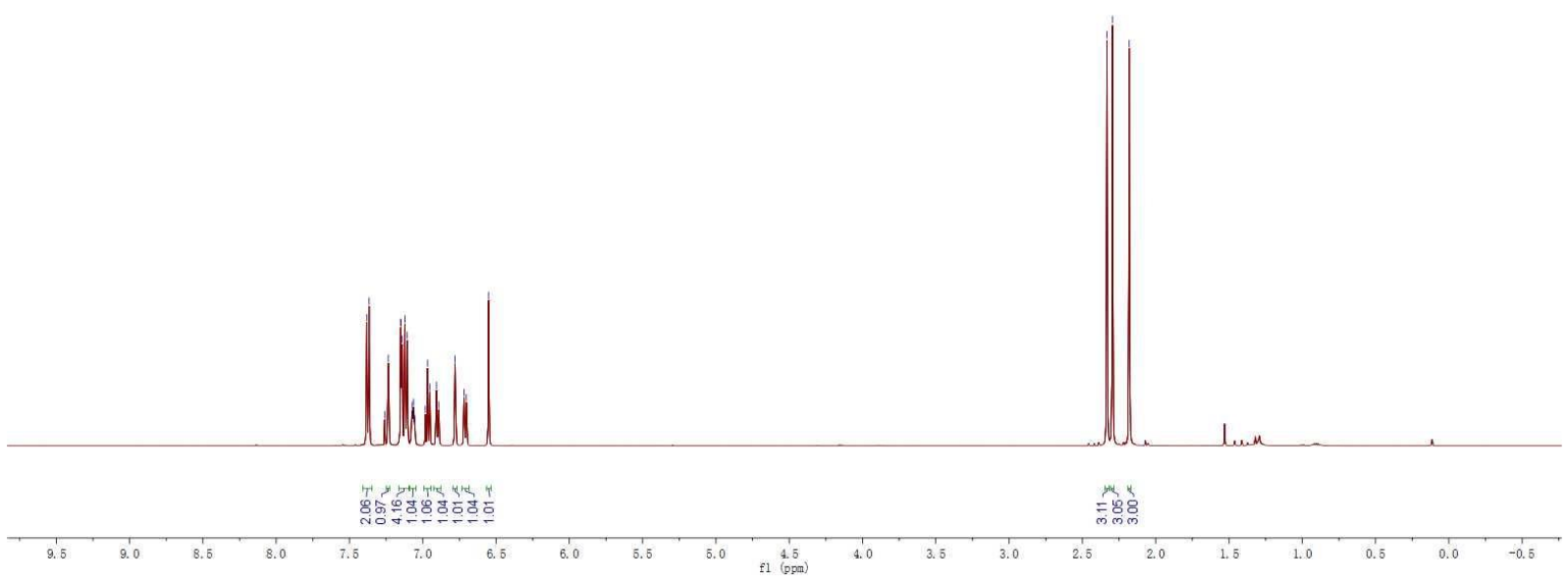


7.38
7.36
7.26
7.18
7.15
7.14
7.14
7.12
7.07
7.06
7.06
7.06
6.98
6.97
6.95
6.91
6.89
6.78
6.72
6.70
6.55

2.33
2.28
2.18



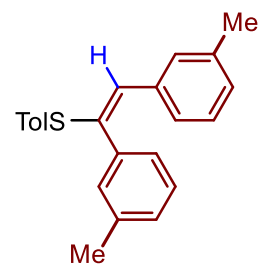
¹H NMR (500 MHz, CDCl₃)



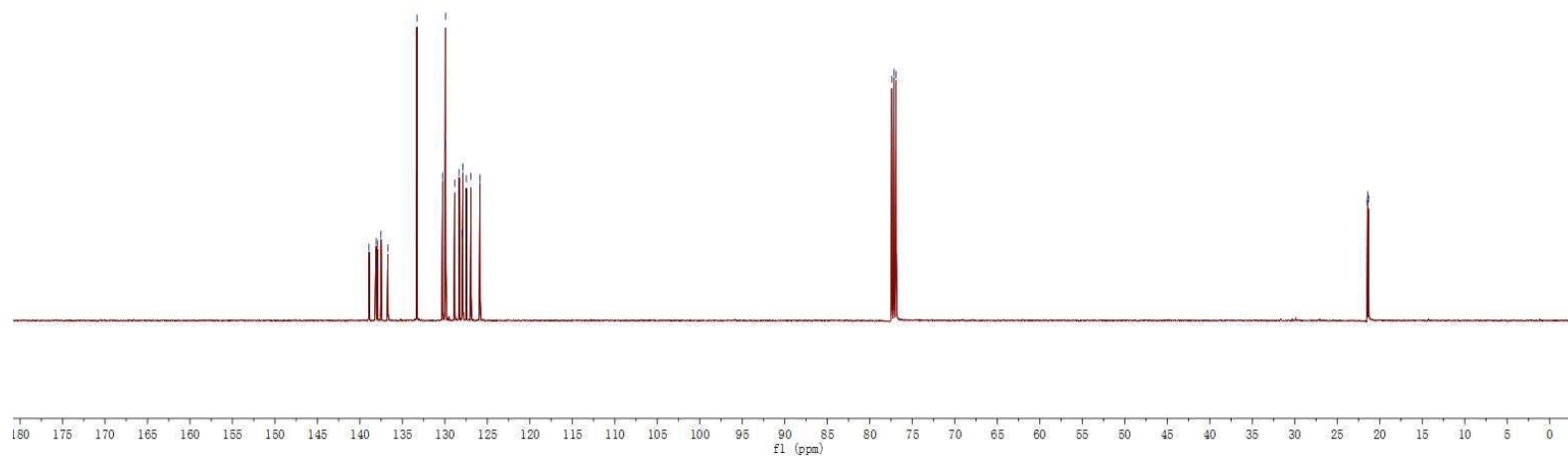
138.93
138.14
138.08
137.94
137.52
136.70
133.30
130.27
129.93
129.90
128.86
128.33
127.97
127.89
127.48
126.93
125.86

77.41
77.16
76.91

21.47
21.42
21.31

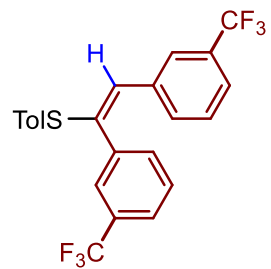


^{13}C NMR (126 MHz, CDCl_3)

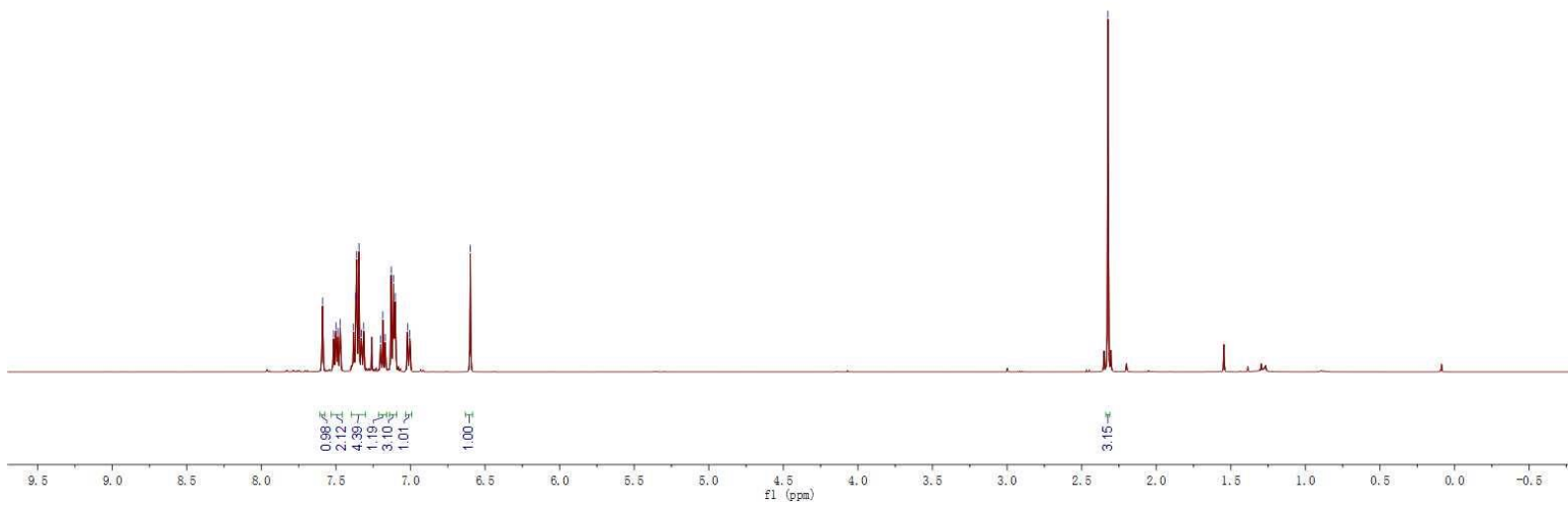


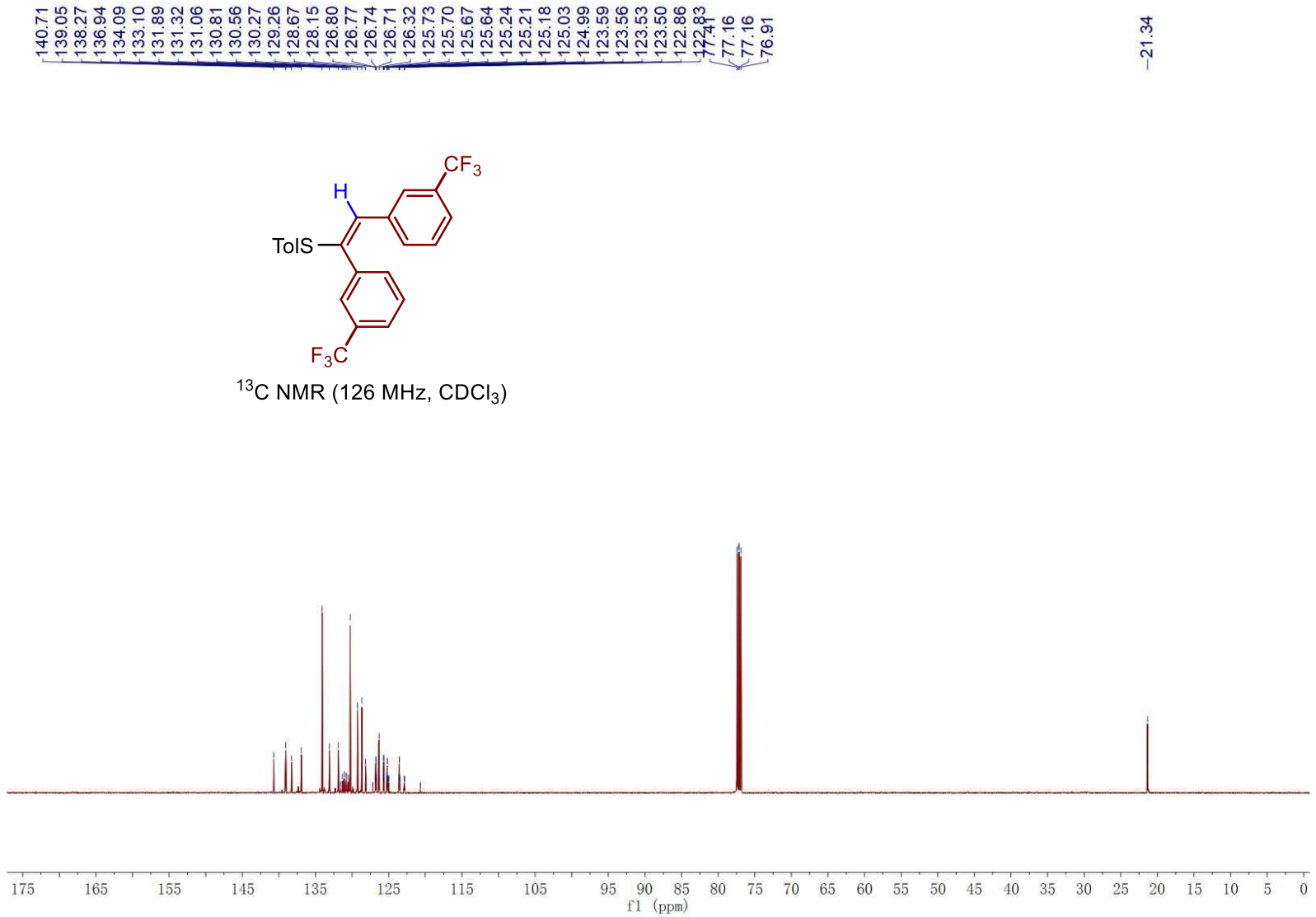
7.69
7.51
7.50
7.49
7.47
7.38
7.37
7.36
7.35
7.33
7.30
7.20
7.19
7.17
7.13
7.11
7.10
7.02
7.00
6.80

-2.32



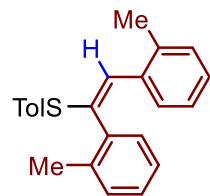
¹H NMR (500 MHz, CDCl₃)



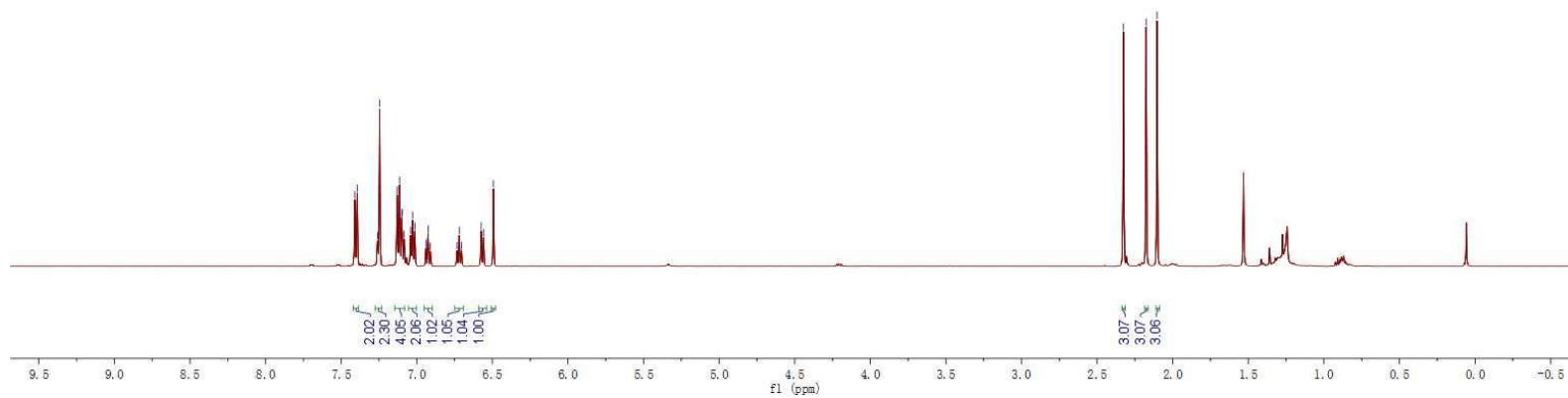


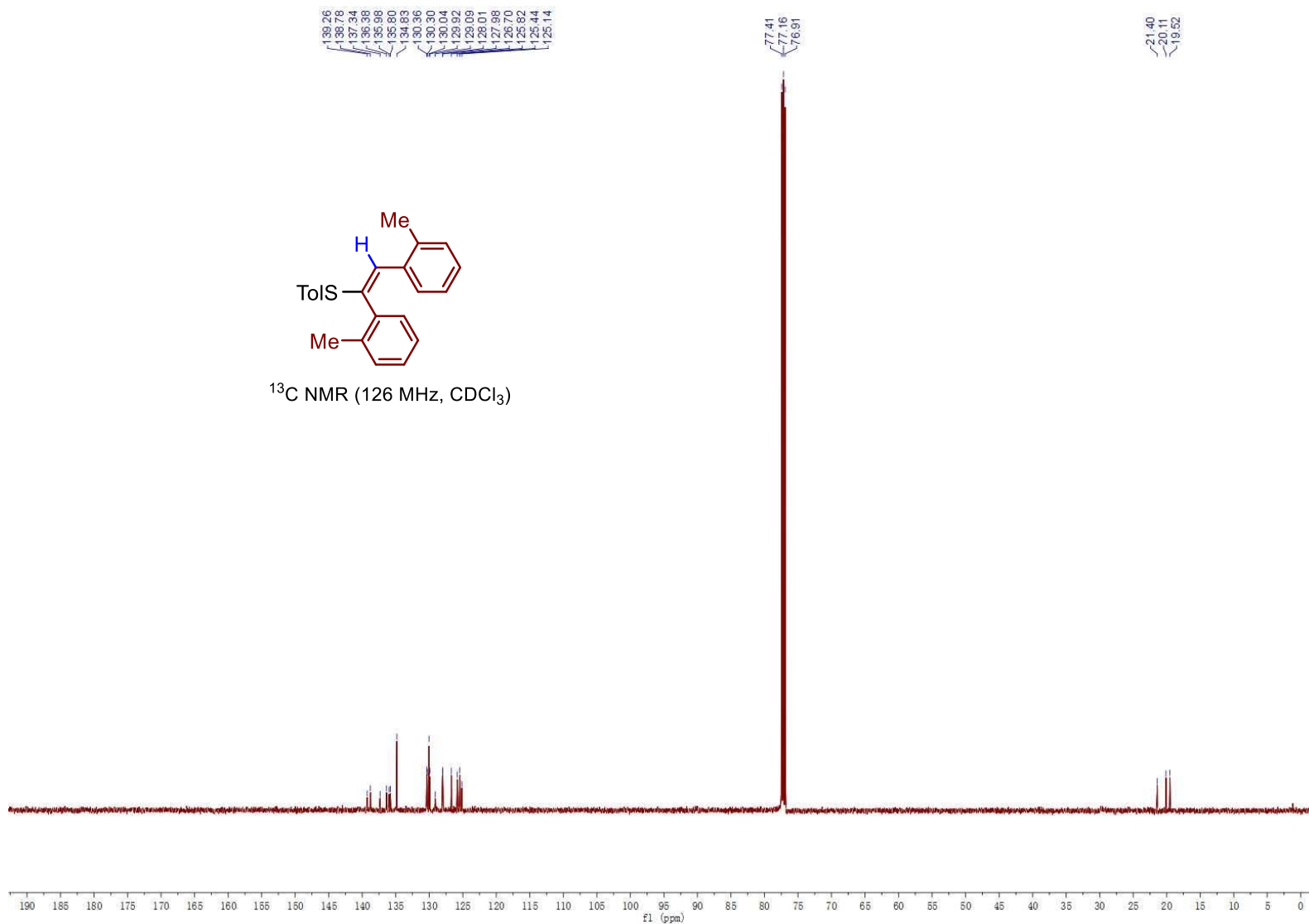
7.41
7.39
7.26
7.25
7.13
7.11
7.10
7.08
7.04
7.03
7.01
6.94
6.92
6.91
6.73
6.72
6.70
6.57
6.56
6.49

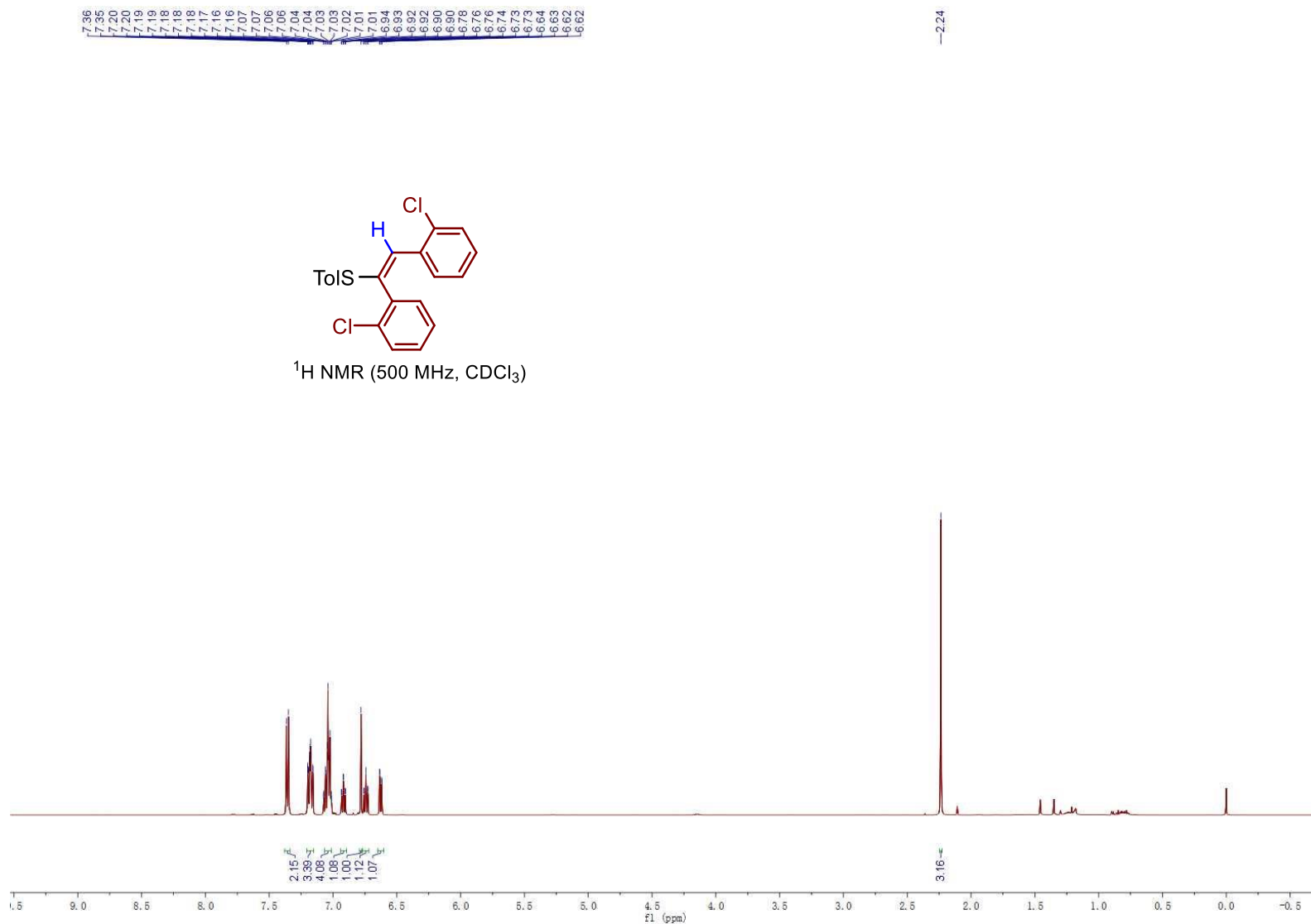
2.33
2.18
2.10

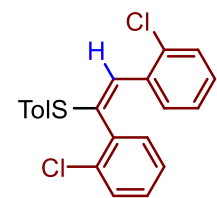


$^1\text{H NMR}$ (500 MHz, CDCl_3)

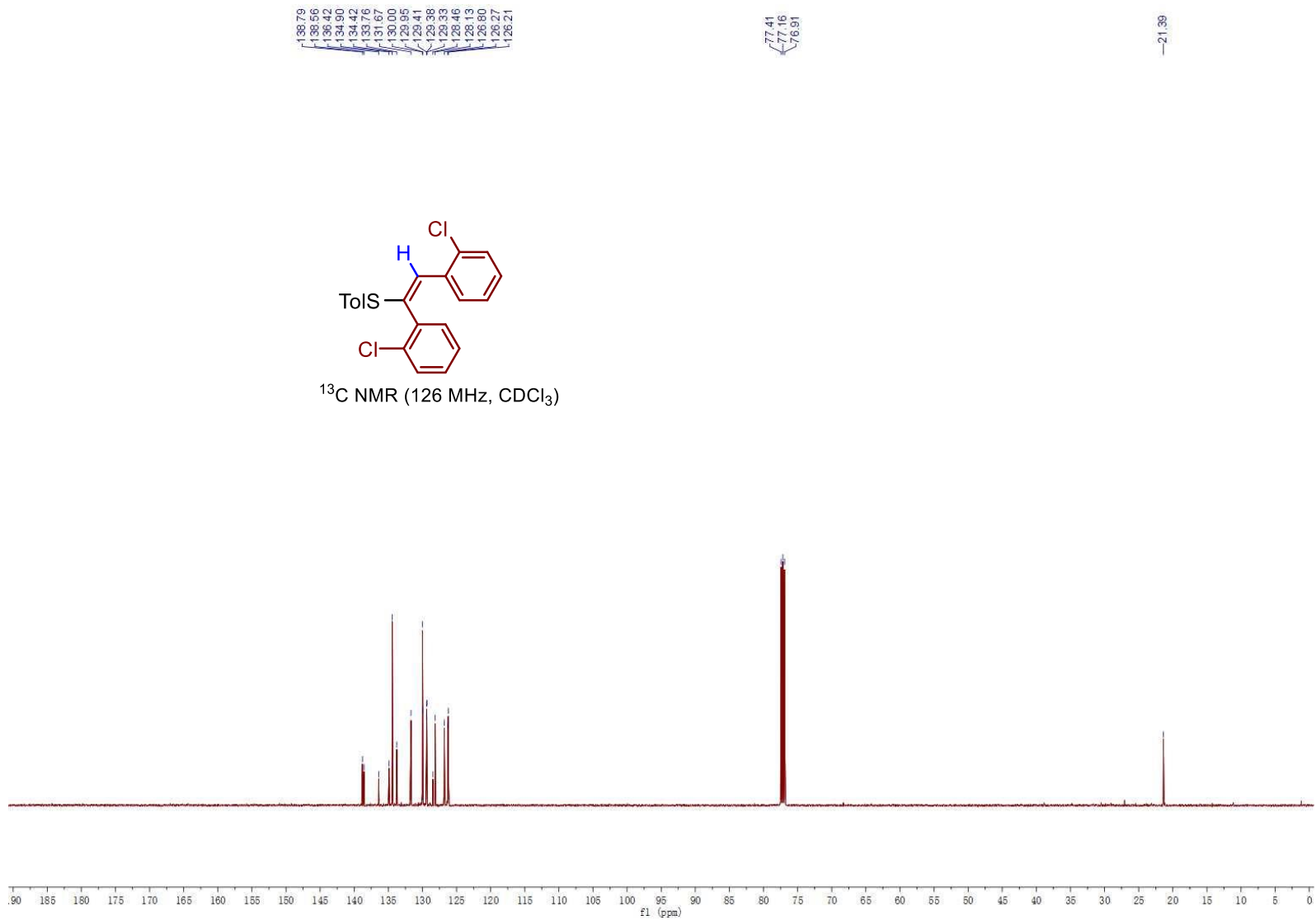






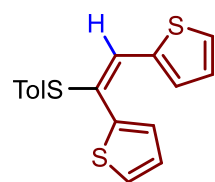


^{13}C NMR (126 MHz, CDCl_3)

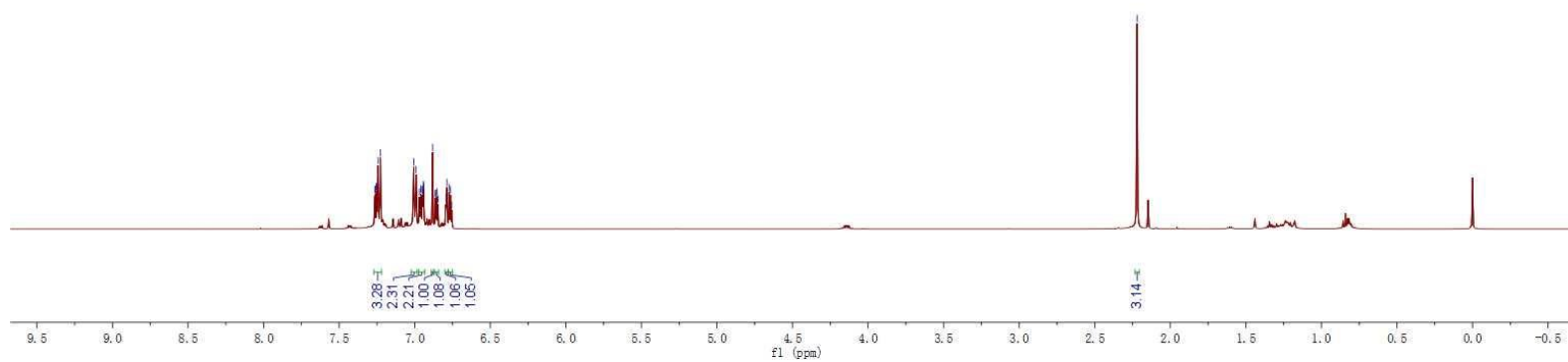


7.26
7.26
7.25
7.25
7.24
7.23
6.99
6.97
6.96
6.95
6.94
6.94
6.88
6.86
6.86
6.85
6.85
6.79
6.79
6.77
6.76
6.76

-2.22



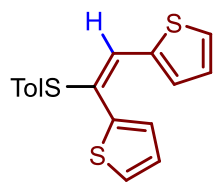
¹H NMR (500 MHz, CDCl₃)



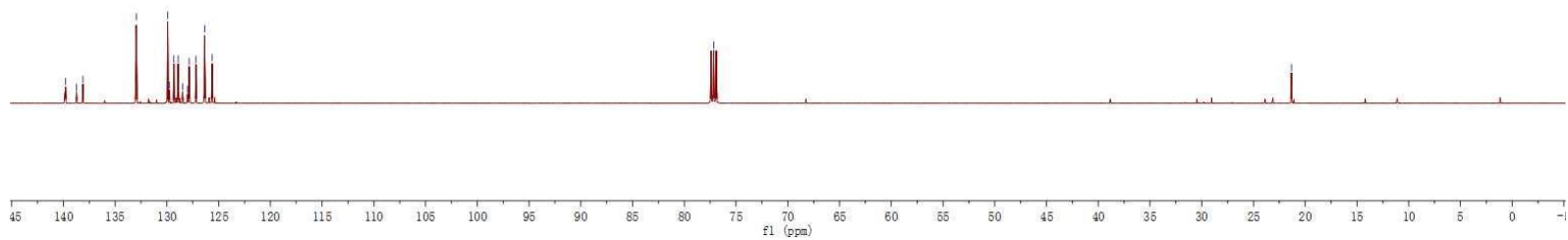
130.78
130.73
130.11
132.96
129.92
129.76
129.33
128.90
128.49
128.02
127.84
127.19
126.36
25.63

77.16

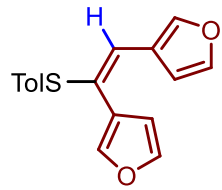
21.32



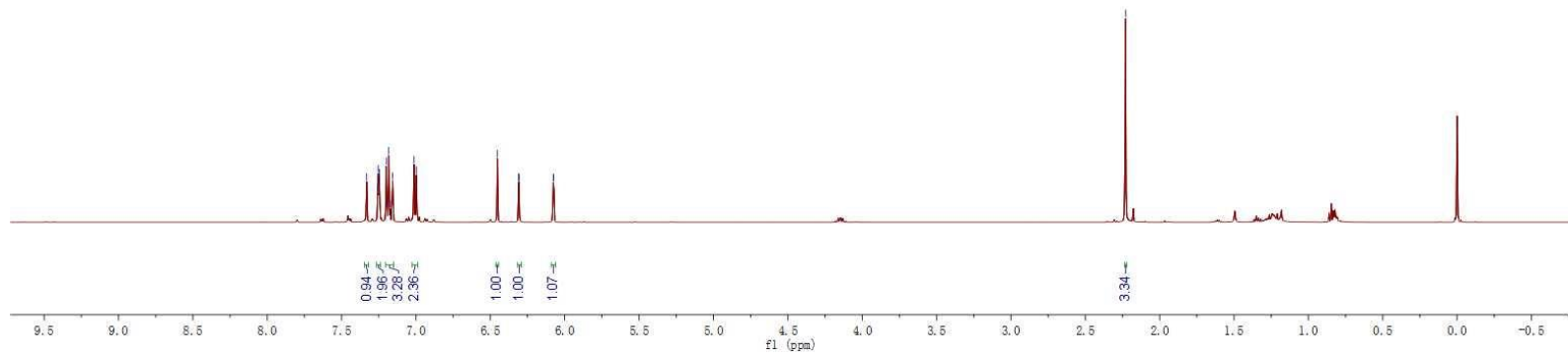
^{13}C NMR (126 MHz, CDCl_3)

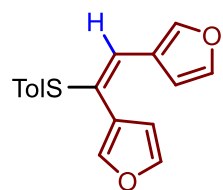


7.33
7.26
7.25
7.25
7.20
7.18
7.17
7.16
7.01
6.45
6.31
6.08
6.07

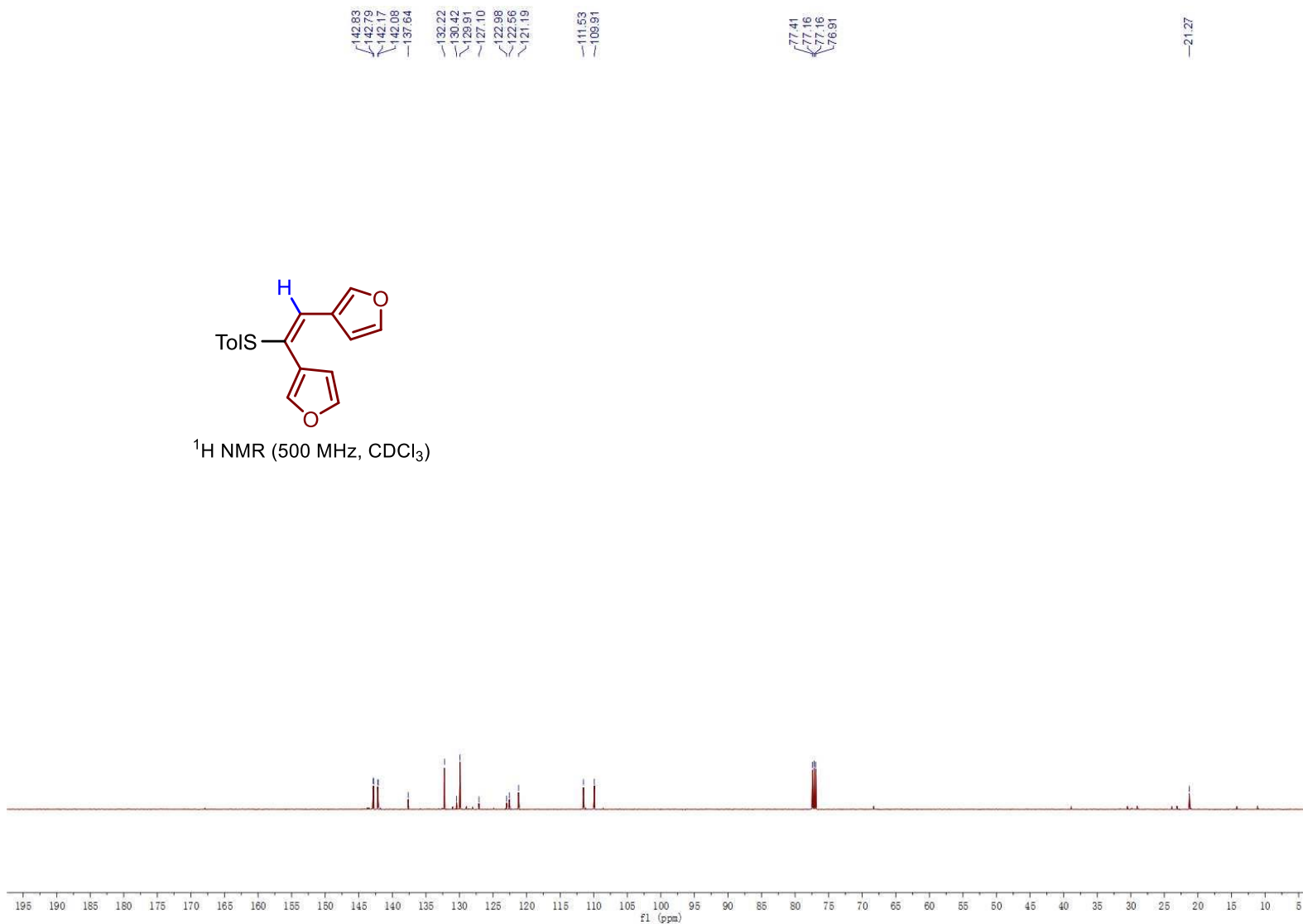


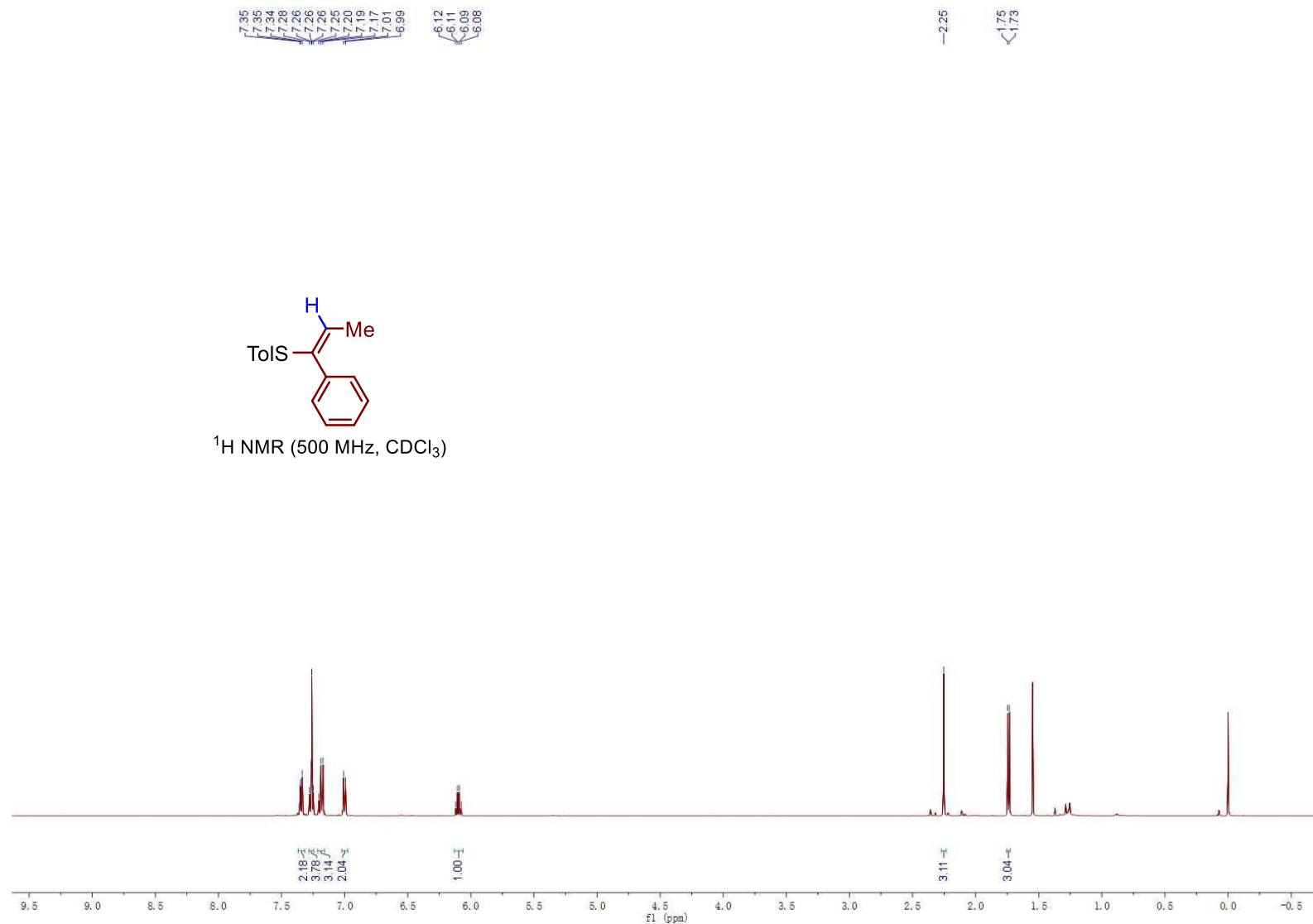
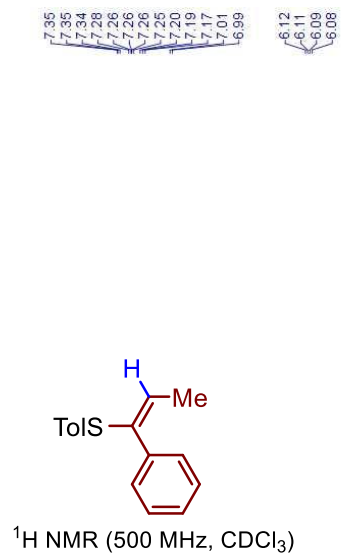
¹H NMR (500 MHz, CDCl₃)

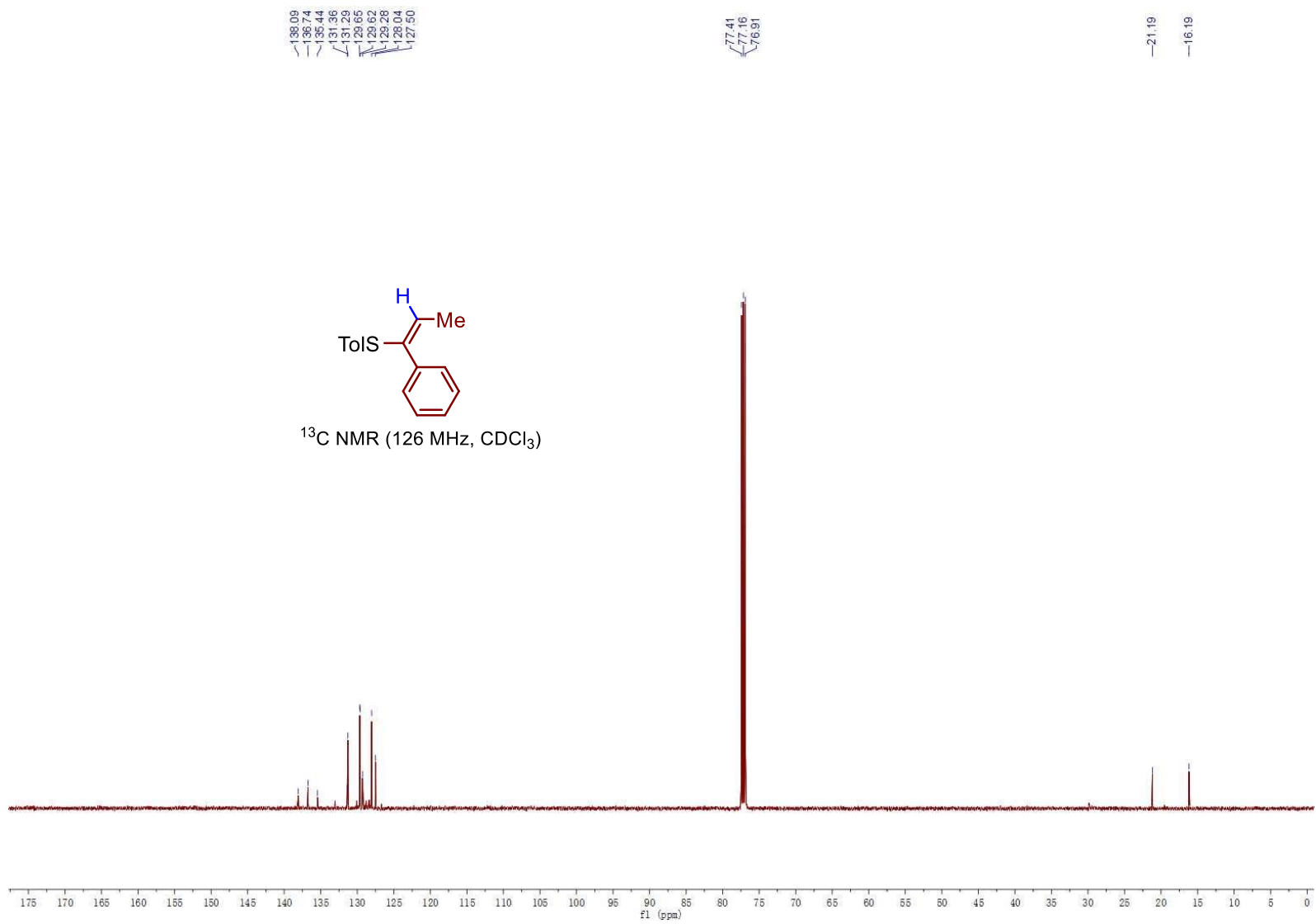




^1H NMR (500 MHz, CDCl_3)





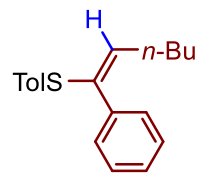


7.26
7.26
7.24
7.19
7.19
7.18
7.16
7.13
7.12
7.11
7.10
6.93
6.92

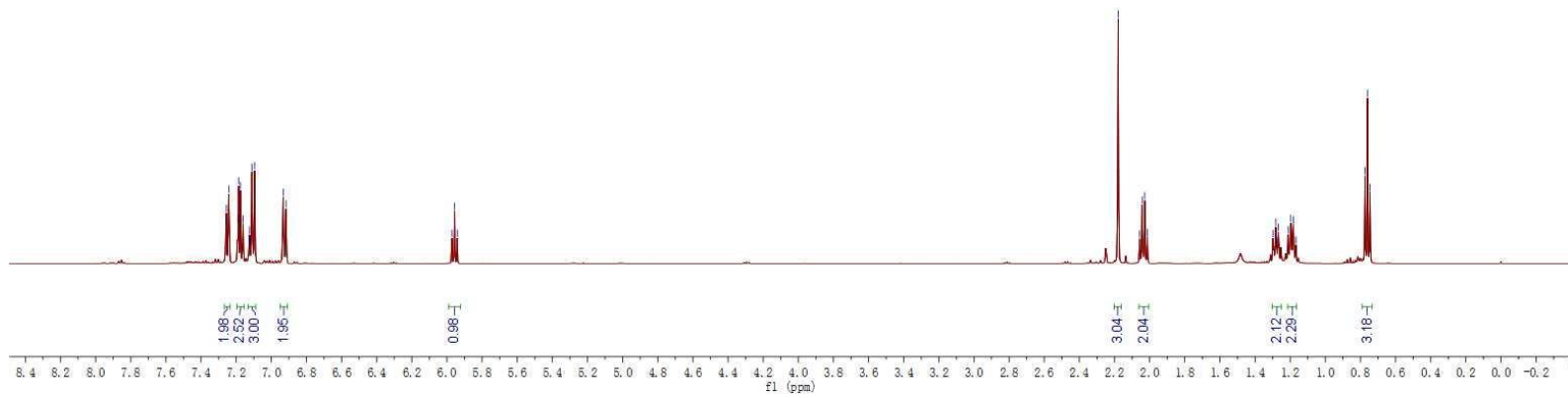
5.97
5.96
5.94

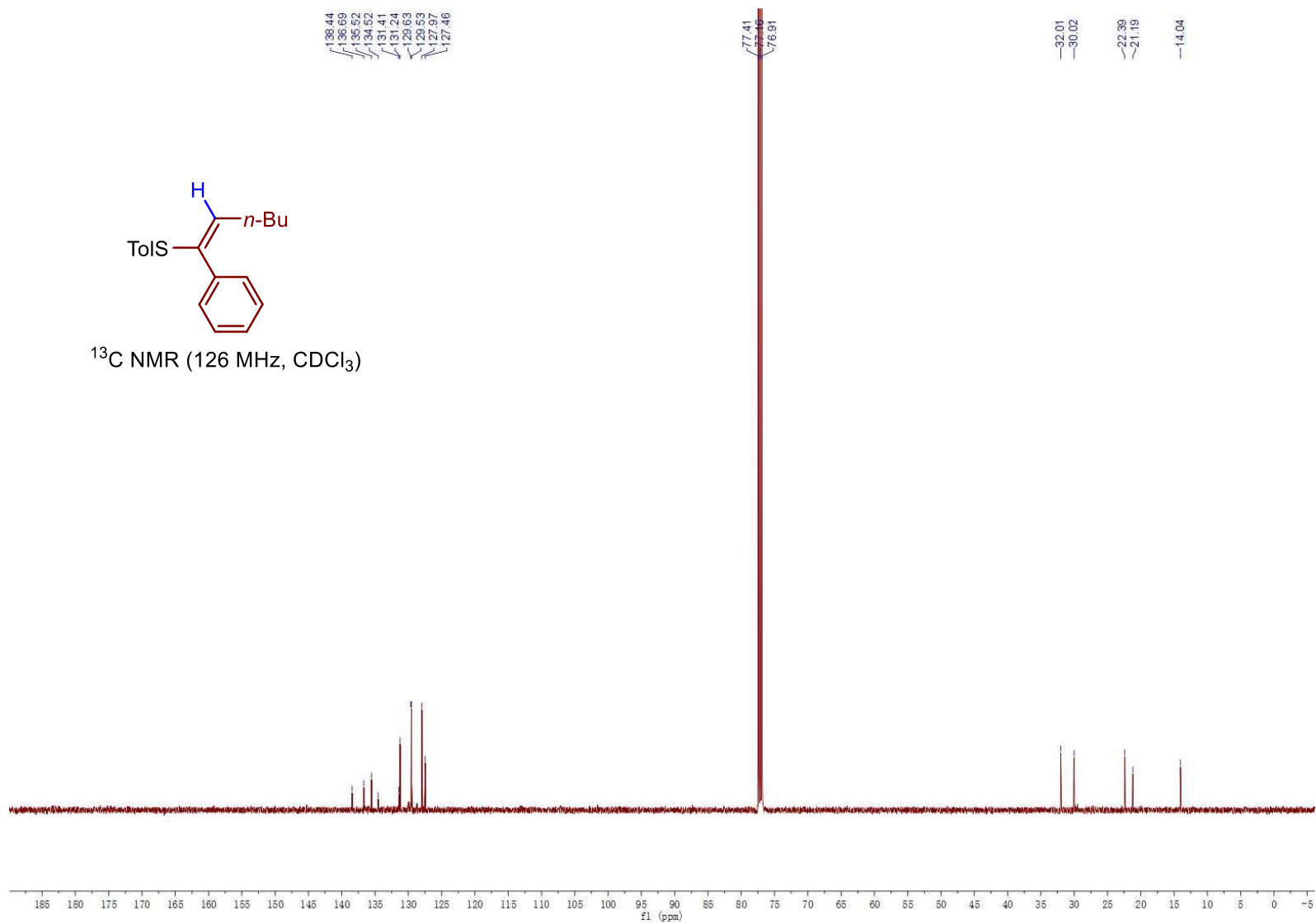
2.18
2.06
2.04
2.03
2.01

1.30
1.28
1.27
1.21
1.20
1.18
1.17
0.77
0.76
0.75



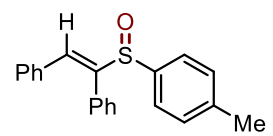
¹H NMR (500 MHz, CDCl₃)



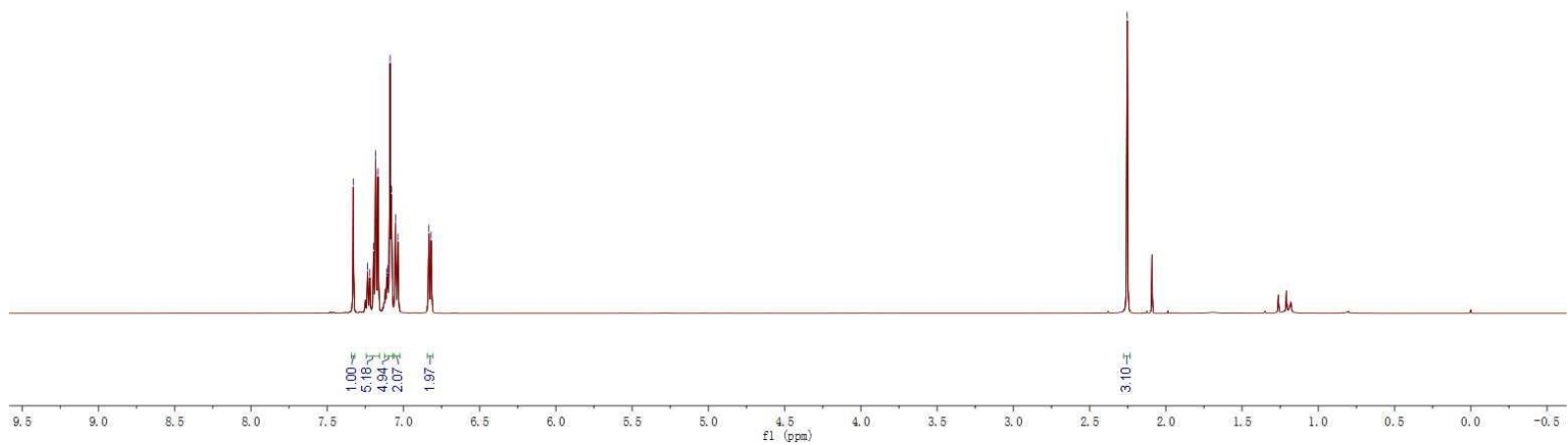


7.33
7.25
7.22
7.20
7.18
7.17
7.11
7.10
7.09
7.05
7.04
6.83
6.82

-2.25



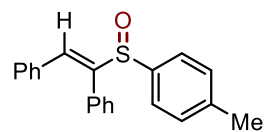
¹H NMR (500 MHz, CDCl₃)



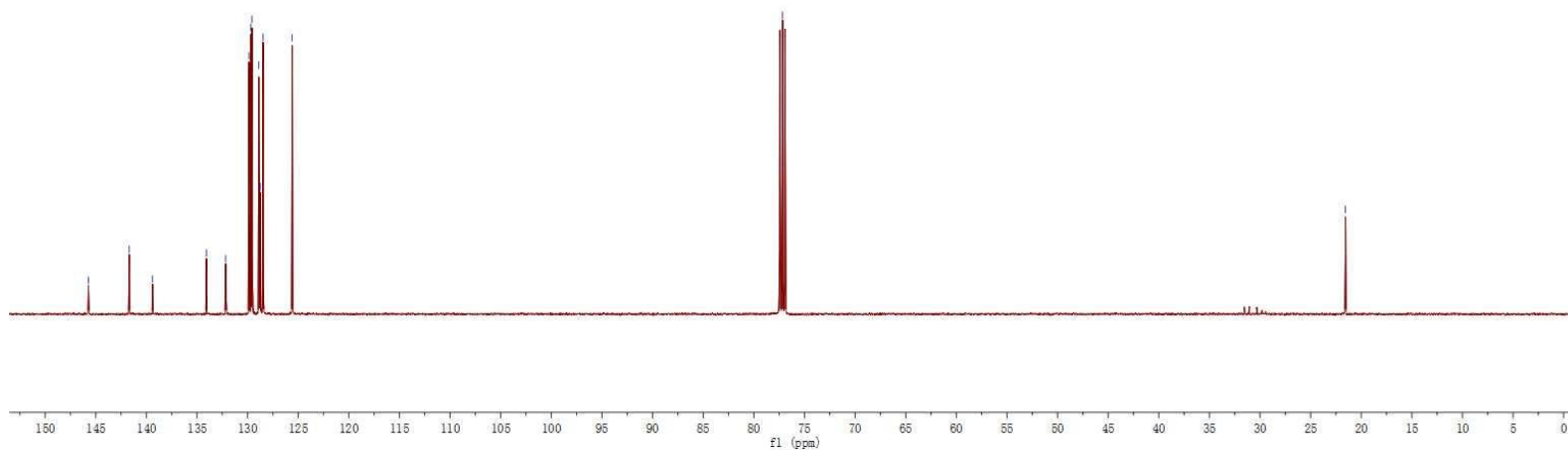
—145.73
—141.69
—139.40
—134.07
—132.17
—129.87
—129.68
—129.57
—128.90
—128.76
—128.48
—125.60

—77.16

—21.55

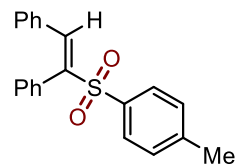


^{13}C NMR (126 MHz, CDCl_3)

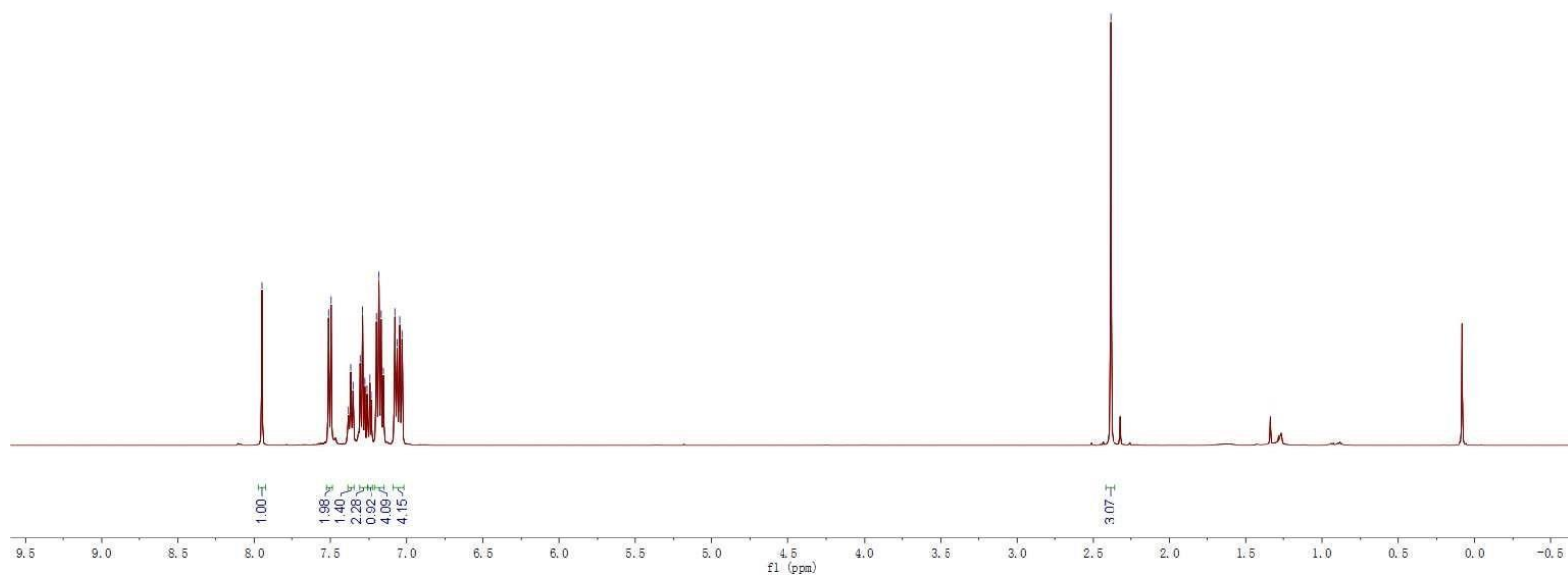


7.95
7.51
7.50
7.38
7.37
7.35
7.31
7.29
7.28
7.26
7.24
7.23
7.20
7.18
7.16
7.08
7.06
7.04

-2.39

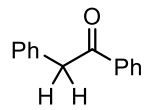


¹H NMR (500 MHz, CDCl₃)

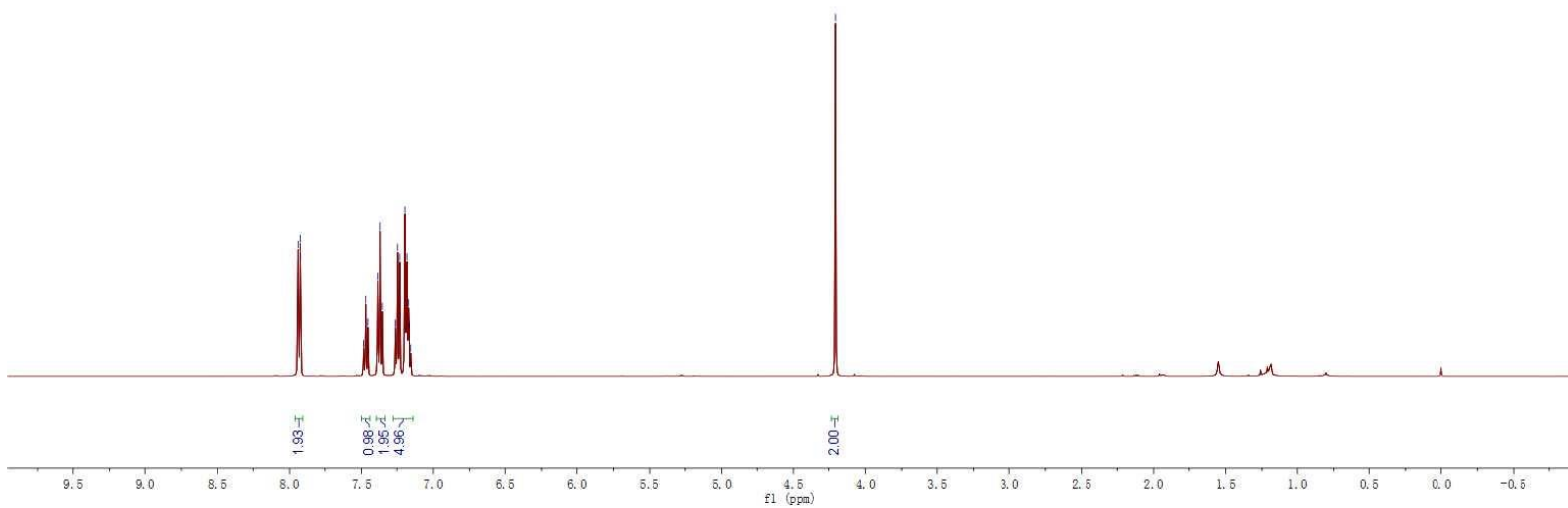


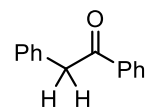
7.94
7.93
7.92
7.78
7.77
7.746
7.739
7.737
7.736
7.726
7.725
7.723
7.719
7.718
7.717
7.716
7.715

-4.20



¹H NMR (500 MHz, CDCl₃)





^{13}C NMR (126 MHz, CDCl_3)

