Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Selective Arylsulfonation of 1,3-Enynes via Photoredox/Nickel dual catalysis

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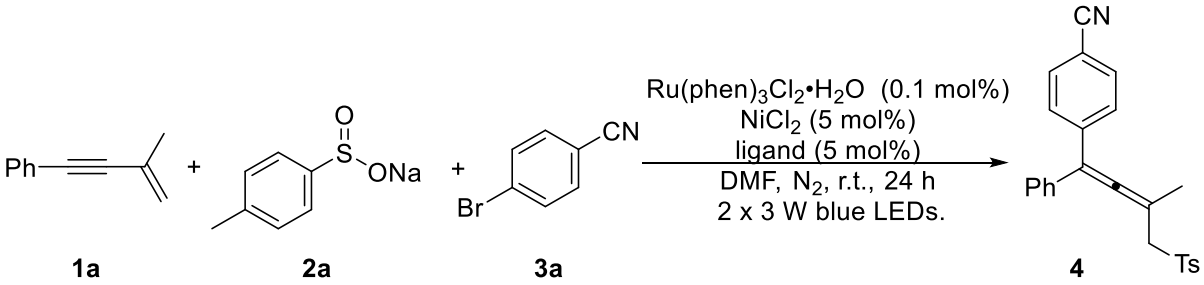
Contents

General Information:

NMR spectra were recorded on Bruker-400 (400 MHz for ^{1}H; 101 MHz for ^{13}C and 376 MHz for ^{19}F) or Bruker 500 MHz spectrometer(500 MHz for ^{1}H; 126 MHz for ^{13}C and 470 MHz for ^{19}F) instruments internally referenced to $SiMe_4$ signal. High resolution mass spectra (HRMS) were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight) or Micromass GCT using EI (electron impact). Super Dry N,N-dimethylformamide and 4,4‘-di-*tert*-butyl-2,2‘-bipyridine were purchased from J&K and used as received. $Ru(phen)Cl_2•H_2O$ was purchased from Bidepharmatech and used as received. Nickel(II) chloride was obtained from Infinity-Scientific and used as received. Sodium 4-toluenesulfinate was purchased from Energy and used as received. Sodium methanesulfinate and 4-bromobenzonitrile were obtained from Accela and used as received. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification.

Tables of the Optimization Reaction Conditions

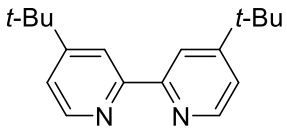
Table S1. Ligand Screening



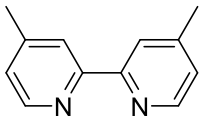
1a **2a** **3a** **4**

entry	ligand	yield[b]
1	L1	88%
2	L2	83%
3	L3	82%
4	L4	85%
5	L5	35%

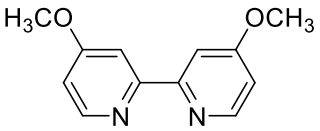
[a]Unless otherwise noted, the reaction conditions as follows: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol, 1.0 equiv), **3a** (0.4 mmol, 2.0 equiv), $Ru(phen)_3Cl_2•H_2O$ (0.1 mol%), $NiCl_2$ (5 mol%), ligand (5 mol%), DMF (2 mL), N_2, r.t., 2 x 3 W blue LEDs, 24 h. [b]isolated yield.



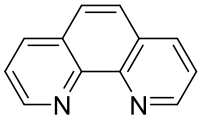
L1



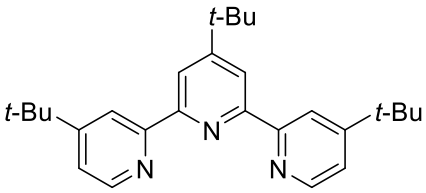
L2



L3

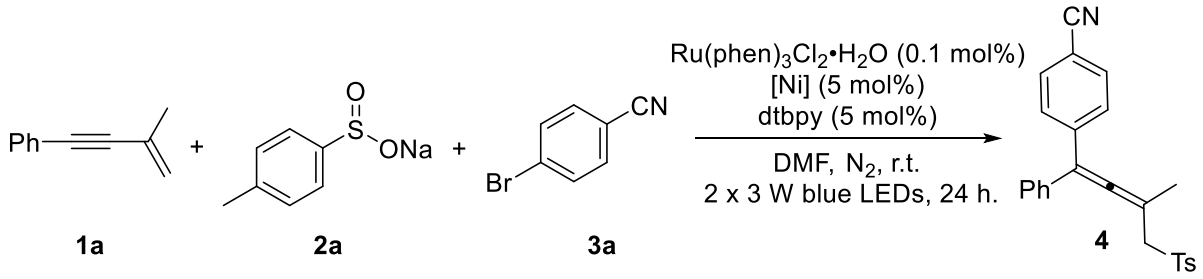


L4



L5

Table S2. Ni-Source Screening

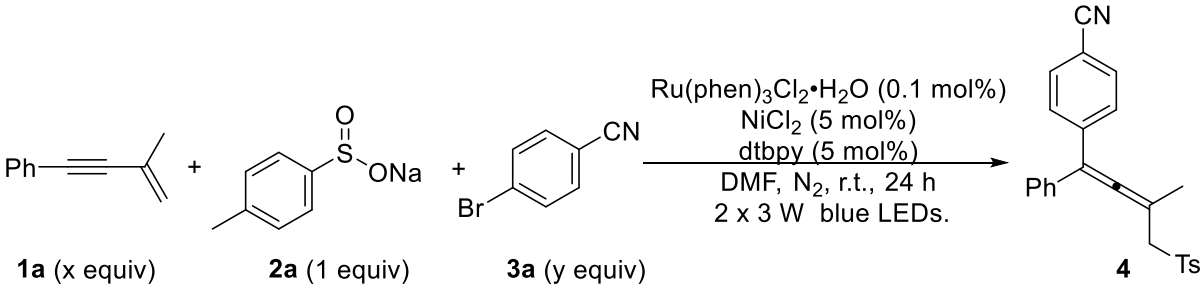


1a **2a** **3a** **4**

entry	[Ni]	yield[b]
1	$NiCl_2$	88%
2	$NiBr_2$	79%
3	$NiCl_2$(dme)	83%
4	$NiBr_2$(dme)	77%
5	$Ni(NO_3)_2•6H_2O$	78%
6	$Ni(OAc)_2$	73%
7	$Ni(PPh_3)_2Cl_2$	70%
8	$Ni(OTf)_2$	20%

[a]Unless otherwise noted, the reaction conditions as follows: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol, 1.0 equiv), **3a** (0.4 mmol, 2.0 equiv), $Ru(phen)_3Cl_2•H_2O$ (0.1 mol%), [Ni] (5 mol%), dtbpy (5 mol%), DMF (2 mL), N_2, r.t., 2 x 3 W blue LED, 24 h. [b]isolated yield.

Table S3. Optimization the amount of reactants

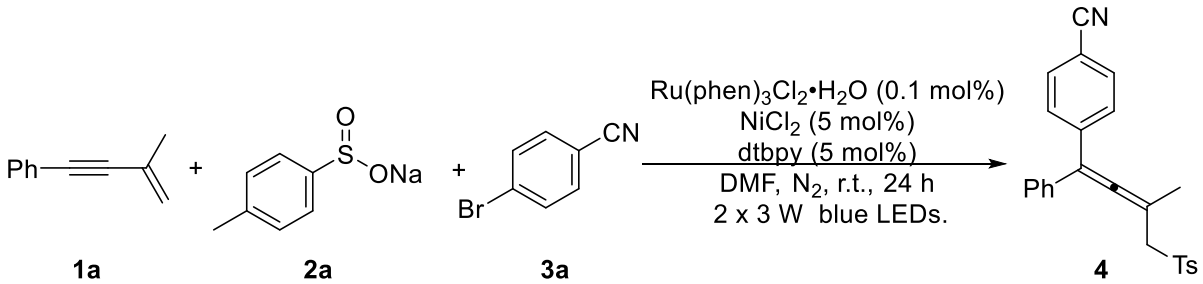


1a (x equiv) **2a** (1 equiv) **3a** (y equiv) **4**

entry	**1a** (equiv)	**3a** (equiv)	yield[b]
1	1.5	2	84%
2	1	2	82%
3	2	1.5	86%
4	2	1	81%

[a]Unless otherwise noted, the reaction conditions as follows: **1a**, **2a** (0.2 mmol, 1.0 equiv), **3a**, $Ru(phen)_3Cl_2•H_2O$ (0.1 mol%), $NiCl_2$ (5 mol%), dtbpy (5 mol%), DMF (2 mL), N_2, r.t., 2 x 3 W blue LEDs, 24 h. [b] isolated yield.

Table S4. Control experiment



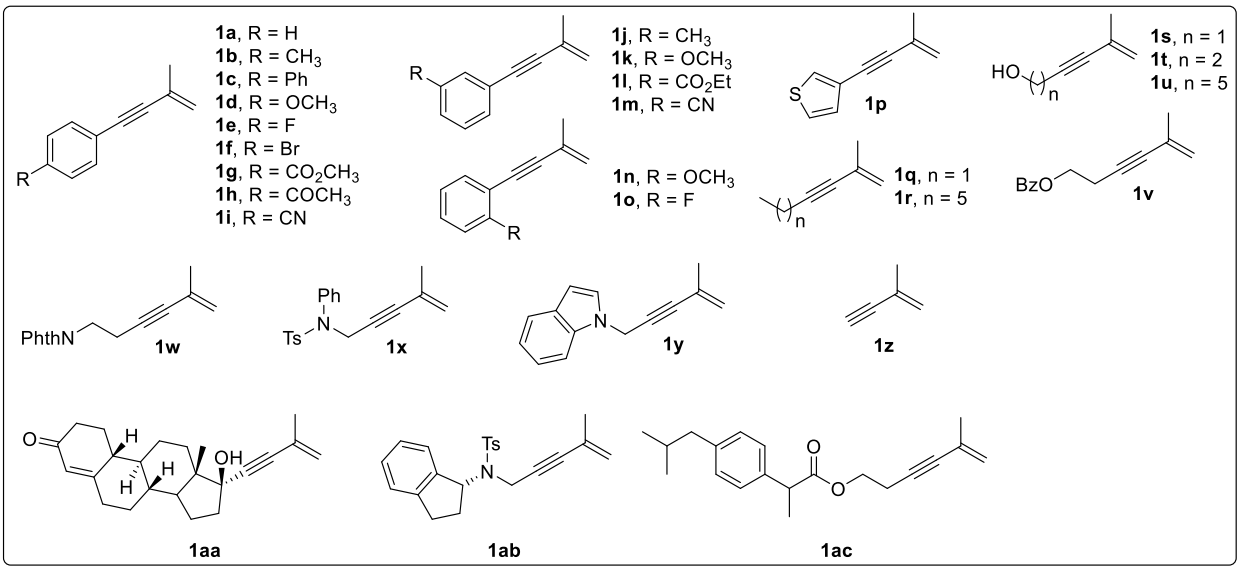
1a **2a** **3a** **4**

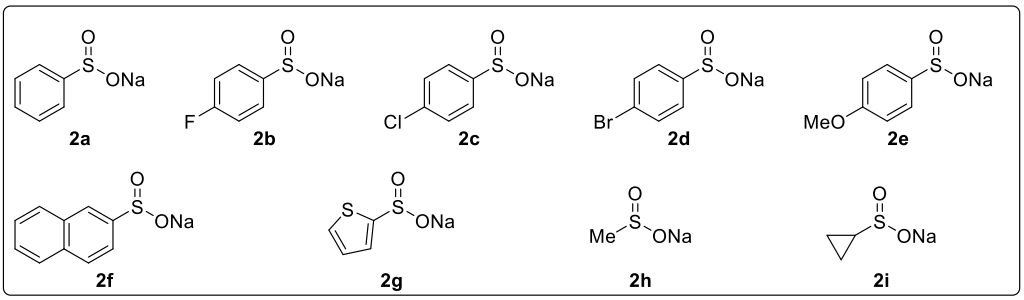
entry	change conditions	yield[b]
1	without light	ND
2	without $Ru(phen)_3Cl_2•H_2O$	10%
3	without $NiCl_2$	ND
4	without dtbpy	ND

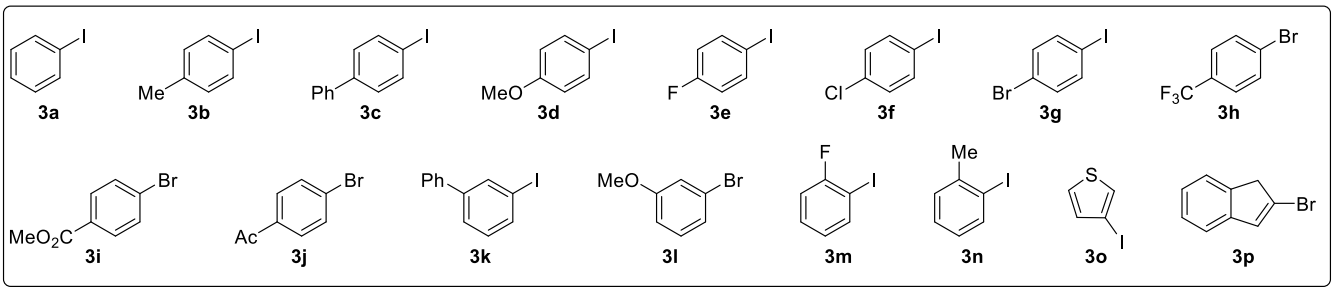
[a]Unless otherwise noted, the reaction conditions as follows: **1a** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol, 1.0 equiv), **3a** (0.4 mmol, 2.0 equiv), $Ru(phen)_3Cl_2•H_2O$ (0.1 mol%), $NiCl_2$ (5 mol%), dtbpy (5 mol%), DMF (2 mL), N_2, r.t., 2 x 3 W blue LEDs, 24 h. [b] isolated yield. ND means no reaction.

Preparation of Substrates:

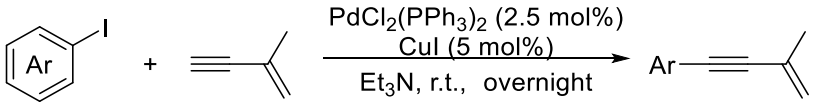
All of 1,3-enynes were prepared through the reported procedures, and 1,3-enynes **1a**-**1k**, **1n**-**1w** and **1z** were reported in the literature.[1] Sodium sulfinates **2e**-**2g** were synthesized according to the previous reports,[2] and others were the commercial available. Aryl halides were all purchased from commercial sources.



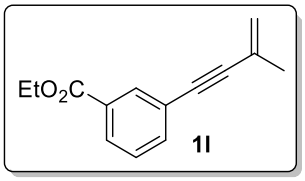




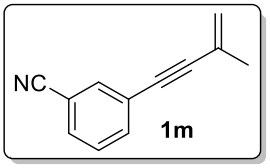
General procedure A for preparation of 1,3-enynes



$Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol, 2.5 mol%) and CuI (47.6 mg, 0.25 mmol, 5 mol%) were dissolved in Et_3N (10 mL) and then ArI (5.0 mmol) and 2-methylbut-1-en-3yne (396.6 mg, 6.0 mmol, 1.2 equiv) were added. The mixture was stirred under N_2 at room temperature for 12 h and then filtered through celite washed with petroleum ether. The solvent was removed in vacuo and purified by flash chromatography using petroleum ether as the eluent to afford product.

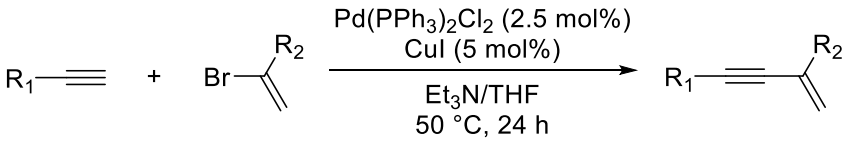


The product **1l** was purified by flash chromatography (PE/EA = 100 : 1) with 56% yield**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, *J* = 1.5 Hz, 1H), 7.97 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.60 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 5.45 – 5.39 (m, 1H), 5.36 – 5.30 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.03 – 1.96 (m, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.08, 135.70, 132.77, 130.85, 129.24, 128.51, 126.72, 123.78, 122.68, 91.50, 87.49, 61.32, 23.53, 14.44. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{15}O_2$ 215.1067, found 215.1068. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{15}O_2$ 215.1067, found 215.1068.

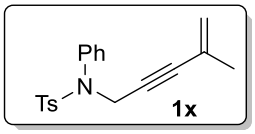


The product **1m** was purified by flash chromatography (PE/EA = 100 : 1) with 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 5.44 (s, 1H), 5.38 – 5.35 (m, 1H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.71, 134.97, 131.38, 129.32, 126.28, 125.03, 123.55, 118.20, 112.91, 93.04, 85.98, 23.32. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{10}N$ 168.0808, found 168.0808.

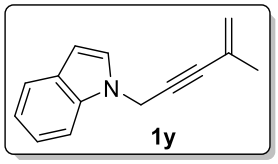
General procedure B for preparation of 1,3-enynes



A three-necked flask charged with $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol, 2.0 mol%) and CuI (47.6 mg, 0.25 mmol, 5.0 mol%) was evacuated and backfilled with N_2 (repeated for 3 times), then THF (10 mL), Et_3N (10 mL), alkyne (5.0 mmol) and 2-bromoalkene (6.0 mmol, 1.2 equiv) was added sequentially. The reaction mixture was heated at 50 ℃ for 24 h, and saturated aq. NH_4Cl (10 mL) was added to the mixture. The aqueous layer was extracted with EtOAc (3 ×15 mL). The combined organic phase was washed with 10% HCl (20 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was then purified by flash column chromatography to give 1,3-enynes.

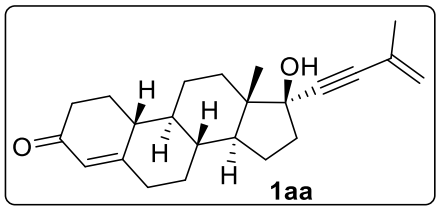


The product **1x** was purified by flash chromatography (PE/EA = 15 : 1) with 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.28 – 7.24 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.17 – 5.12 (m, 1H), 5.06 (s, 1H), 4.55 (s, 2H), 2.40 (s, 3H), 1.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.61, 139.79, 136.01, 129.35, 129.08, 128.64, 128.21, 128.20, 126.14, 122.18, 86.93, 82.76, 42.04, 23.09, 21.66. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{19}NO_2SNa$ 348.1029, found 348.1032.



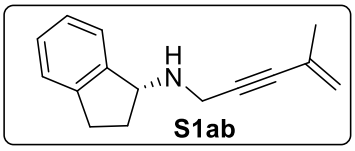
1y

The product **1y** was purified by flash chromatography (PE/EA = 15 : 1) with 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.44 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.20 – 7.11 (m, 1H), 6.59 – 6.51 (m, 1H), 5.32 (s, 1H), 5.29 – 5.24 (m, 1H), 5.00 (s, 2H), 1.92 – 1.87 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.97, 128.99, 127.41, 126.22, 122.82, 121.89, 121.17, 119.86, 109.54, 101.90, 86.54, 82.19, 36.63, 23.40. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{14}N$ 196.1121, found 196.1122.



1aa

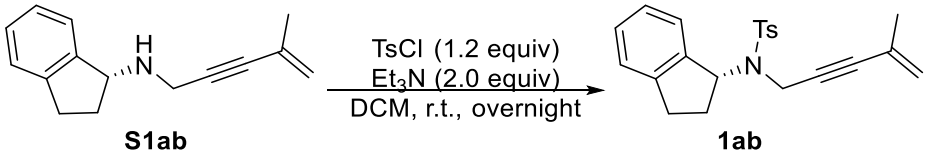
The product **1aa** was purified by flash chromatography (PE/EA = 5 : 1) with 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82 (s, 1H), 5.26 (s, 1H), 5.21 (s, 1H), 2.54 – 2.36 (m, 2H), 2.34 – 2.20 (m, 4H), 2.10 (s, 1H), 2.01 (t, *J* = 10.9 Hz, 2H), 1.88 (s, 3H), 1.77 – 1.41 (m, 6H), 1.41 – 1.20 (m, 3H), 1.15 – 1.01 (m, 1H), 0.91 (s, 3H), 0.90 – 0.81 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.12, 166.81, 126.54, 124.70, 121.90, 91.58, 87.33, 80.07, 49.46, 49.31, 47.34, 42.68, 41.20, 38.99, 36.64, 35.61, 32.79, 30.78, 26.67, 26.37, 23.72, 23.08, 12.97. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{23}H_{31}O_2$ 339.2319, found 339.2325.



S1ab

The product **S1ab** was purified by flash chromatography (PE/EA = 10 : 1) with 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 1H), 7.26 – 7.23 (m, 1H), 7.23 – 7.17 (m, 2H), 5.28 (s, 1H), 5.23 – 5.18 (m, 1H), 4.42 (s, 1H), 3.65 (s, 2H), 3.14 – 2.98 (m, 1H), 2.90 – 2.78 (m, 1H), 2.50 – 2.35 (m, 1H), 1.90 (s, 3H), 1.89 – 1.85 (m, 1H), 1.74 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.96, 127.75, 126.87, 126.37, 124.99, 124.36, 121.61, 84.89, 77.36, 62.13, 37.07, 33.54, 30.61, 23.73. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{18}N$ 212.1434, found 212.1434.

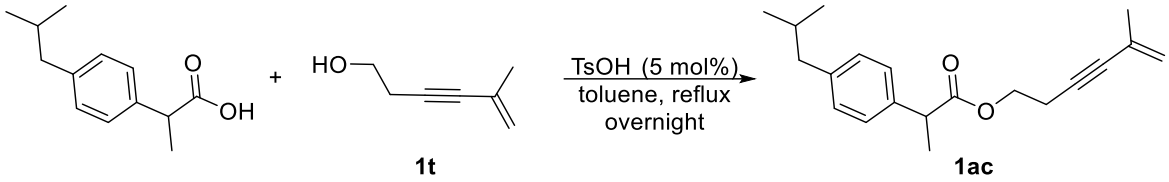
General procedure for preparation of 1ab



S1ab **1ab**

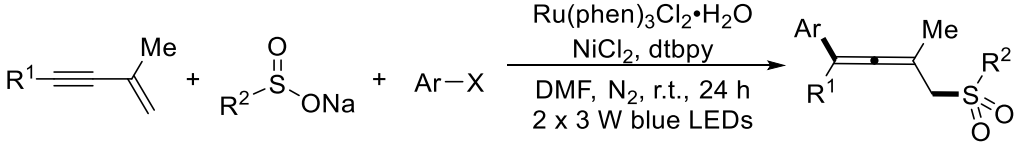
To a solution of **S1ab** (211.3 mg, 1 mmol, 1.0 equiv) in dichloromethane (5 mL) at 0 °C, triethylamine (0.25 mL, 2 mmol) and 4- methoxybenzenesulfonyl chloride (229 mg, 1.2 mmol, 1.2 equiv) were added. Then the solution was stirred at room temperature overnight. It was washed with water and brine, and dried over Na_2SO_4, and concentrated on a rotary evaporator. After evaporation of the solvent, the residue was subjected to flash column chromatography (PE/EA = 15/1) to give **1ab** (136 mg, 37% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.11 (m, 4H), 5.57 (t, *J* = 7.7 Hz, 1H), 5.13 (s, 1H), 5.04 (s, 1H), 4.32 (d, *J* = 18.7 Hz, 1H), 3.67 (d, *J* = 18.7 Hz, 1H), 3.00 (dt, *J* = 15.8, 6.7 Hz, 1H), 2.78 (dt, *J* = 16.1, 8.0 Hz, 1H), 2.44 (s, 3H), 2.19 (dd, *J* = 14.8, 7.7 Hz, 2H), 1.70 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.78, 143.35, 139.93, 138.18, 129.58, 128.55, 127.83, 126.97, 126.36, 125.08, 125.06, 121.83, 85.09, 84.56, 63.40, 33.40, 30.42, 29.27, 23.08, 21.68. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{24}NO_2S$ 366.1522, found 366.1523.

General procedure for preparation of 1ac



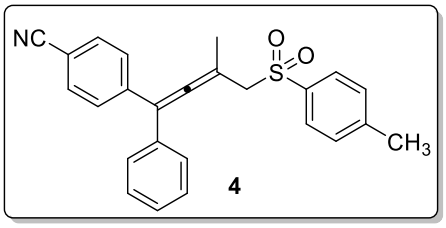
To a solution of buluofen (1.031 g, 5 mmol, 1.0 equiv) in 20 mL toluene, **1t** (550.0 mg, 5 mmol, 1.0 equiv) and *p*-Toluenesulfonic acid (43.1 mg, 0.25 mmol, 5 mol%) were added. The mixture was stirred under reflux with water trap overnight. The solvent was removed in vacuo and purified by flash chromatography (PE/EA = 20/1) to afford product **1ac** (933 mg, 63%)**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 7.8 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 5.20 (s, 1H), 5.16 (s, 1H), 4.31 – 4.11 (m, 2H), 3.72 (q, J = 7.1 Hz, 1H), 2.59 (t, J = 6.9 Hz, 2H), 2.44 (d, J = 7.2 Hz, 2H), 1.89 – 1.85 (m, 1H), 1.84 (s, 3H), 1.50 (d, J = 7.2 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.62, 140.67, 137.71, 129.45, 127.30, 126.96, 121.32, 84.55, 83.32, 62.67, 45.21, 45.18, 30.31, 23.73, 22.54, 19.81, 18.69. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{26}O_2Na$ 321.1825, found 321.1829.

General procedure for visible light induced arylsulfonation of 1,3-enynes



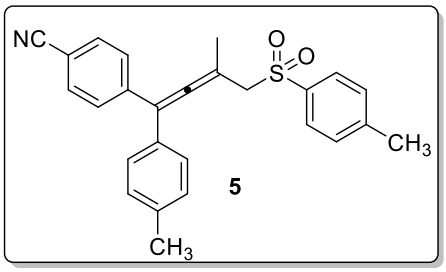
In a 25 mL oven-dried Schlenk tube, 1.84 mL DMF was added to a mixture of $NiCl_2$ (1.3 mg, 0.01 mmol, 5 mol%), dtbpy (2.7 mg, 0.01 mmol, 5 mol%), sodium sulfinate **2** (0.2 mmol, 1.0 equiv), 1,3-enyne **1** (0.4 mmol, 2.0 equiv) and aryl halide **3** (0.4 mmol, 2.0 equiv) under N_2 atmosphere. Then the solution of $Ru(phen)Cl_2•H_2O$ (1mg/mL, 0.16 mg, 0.002 mmol, 0.1 mol%) in dry DMF (0.16 mL) was added via

syringe under a stream of nitrogen. The tube was sealed with a Teflon lined cap and the reaction was stirred and irradiated with two 3 W blue LED lamps (with cooling fan to keep the reaction temperature near 25 °C) for 24 h. The reaction mixture was extracted with EtOAc (2 x 10 mL), and the combined organic phase was washed with brine (20 mL), dried over Na_2SO_4, concentrated in vacuo. The residue as purified by flash column chromatography to give the allene product.



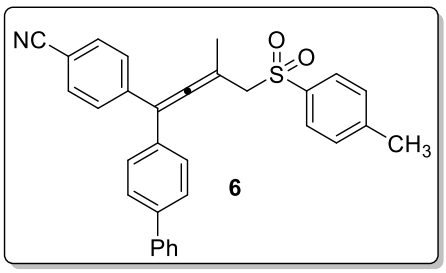
4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.30 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 6.6, 3.0 Hz, 2H), 3.94 (d, *J* = 13.9 Hz, 1H), 3.89 (d, *J* = 13.9 Hz, 1H), 2.37 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.24, 144.85, 141.48, 135.65, 135.14, 132.20, 129.90, 129.19, 128.74, 128.24, 128.14, 118.98, 110.96, 109.49, 94.13, 61.18, 21.83, 19.31. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{21}NO_2SNa$ 422.1185, found 422.1185.



5

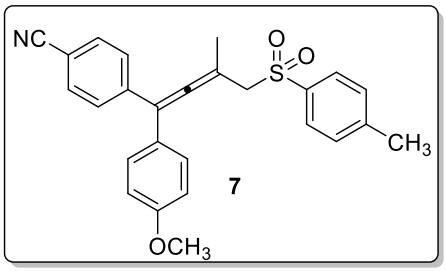
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 3.94 (d, *J* = 13.9 Hz, 1H), 3.89 (d, *J* = 13.9 Hz, 1H), 2.37 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.11, 144.77, 141.64, 138.01, 135.64, 132.12, 132.07, 129.85, 129.40, 129.14, 128.61, 128.21, 118.97, 110.82, 109.33, 93.86, 61.20, 21.77, 21.31, 19.27. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{23}NO_2SNa$ 436.1342, found 436.1349.



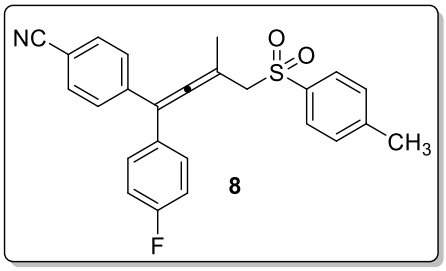
6

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.55 (m, 4H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 3.97 (d, *J* = 13.9 Hz, 1H), 3.93 (d, *J* = 13.9 Hz, 1H), 2.35 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.28, 144.83, 141.39, 140.90, 140.34, 135.65, 133.98, 132.20, 129.86,

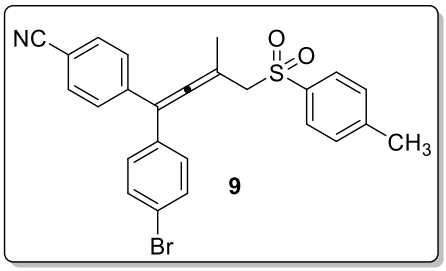
129.23, 129.10, 129.00, 128.19, 127.70, 127.32, 127.01, 118.92, 110.97, 109.20, 94.19, 61.09, 21.76, 19.31. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{31}H_{25}NO_2SNa$ 498.1498, found 498.1501.



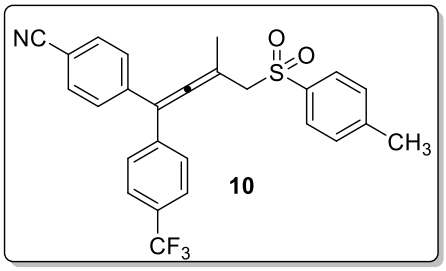
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.16 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.92 (d, *J* = 13.9 Hz, 1H), 3.88 (d, *J* = 13.9 Hz, 1H), 3.83 (s, 3H), 2.38 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.07, 159.56, 144.82, 141.84, 135.75, 132.17, 129.94, 129.89, 129.17, 128.25, 127.22, 119.00, 114.16, 110.89, 109.11, 93.78, 61.32, 55.47, 21.79, 19.38. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{24}NO_3S$ 430.1471, found 430.1473.



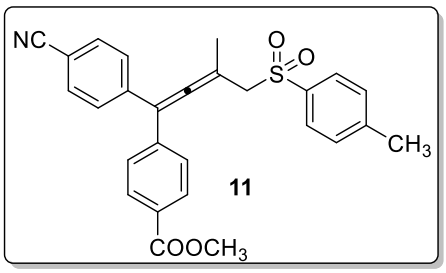
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 3.91 (s, 2H), 2.38 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.05, 162.49 (d, *J* = 248.0 Hz), 144.90, 141.29, 135.65, 132.24, 131.06 (d, *J* = 3.0 Hz), 130.41 (d, *J* = 8.2 Hz), 129.87, 129.04, 128.16, 118.84, 115.68 (d, *J* = 21.7 Hz), 111.06, 108.58, 94.26, 61.05, 21.74, 19.26. ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.29 – -116.61 (m). HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{25}H_{21}FNO_2S$ 418.1272, found 418.1277.



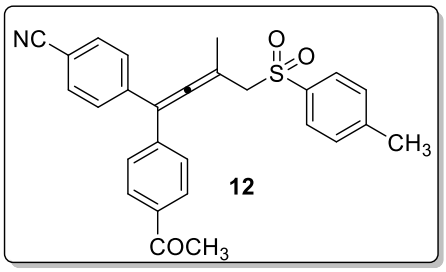
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 2H), 2.38 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.01, 144.93, 140.86, 135.51, 134.07, 132.25, 131.80, 130.26, 129.84, 129.03, 128.12, 122.07, 118.77, 111.13, 108.59, 94.57, 60.87, 21.76, 19.15. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{20}BrNO_2SNa$ 500.0290, found 500.0298.



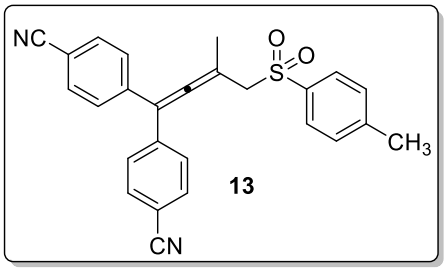
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.55 (m, 4H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 2H), 2.37 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.43, 145.05, 140.65, 139.03, 135.66, 132.40, 129.94, 129.13, 129.01, 128.21, 125.66 (q, *J* = 3.6 Hz), 124.07 (q, *J* = 272.1 Hz), 118.75, 111.41, 108.64, 95.00, 60.85, 21.71, 19.25. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.53 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{20}F_3NO_2SNa$ 490.1059, found 490.1058.



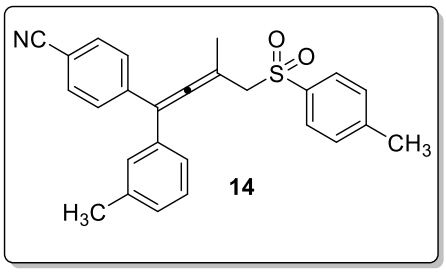
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2*2H), 4.13 – 3.71 (m, 5H), 2.36 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.49, 166.63, 144.97, 140.72, 139.87, 135.54, 132.31, 129.91, 129.61, 129.17, 128.55, 128.17, 118.76, 111.27, 108.90, 94.85, 60.85, 52.32, 21.71, 19.11. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{23}NO_4SNa$ 480.1240, found 480.1243.



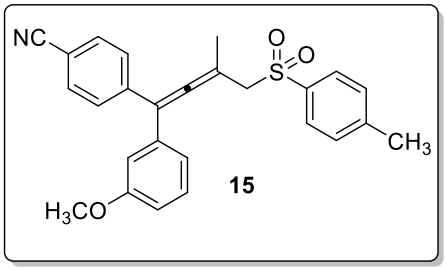
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 3.92 (s, 2H), 2.60 (s, 3H), 2.36 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.57, 197.43, 144.97, 140.67, 140.03, 136.45, 135.65, 132.30, 129.91, 129.18, 128.75, 128.69, 128.15, 118.73, 111.27, 108.88, 94.83, 60.81, 26.72, 21.74, 19.16. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{27}H_{23}NO_3SNa$ 464.1291, found 464.1291.



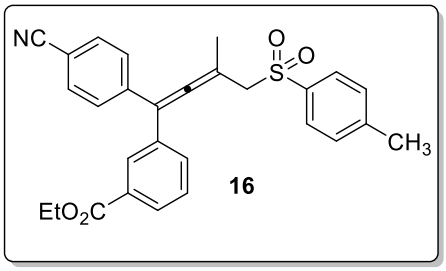
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 4H), 7.29 (d, *J* = 8.6 Hz, 4H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.90 (s, 2H), 2.40 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.69, 145.16, 140.21, 135.86, 132.52, 130.02, 129.25, 128.20, 118.65, 111.69, 108.62, 95.36, 60.77, 21.83, 19.31. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{20}N_2O_2SNa$ 447.1138, found 447.1133.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.17 – 7.06 (m, 3H), 6.96 (s, 1H), 6.90 (d, *J* = 6.6 Hz, 1H), 3.95 (d, *J* = 13.7 Hz, 1H), 3.89 (d, *J* = 13.8 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.13, 144.72, 141.55, 138.35, 135.64, 135.01, 132.09, 129.79, 129.29, 129.13, 128.86, 128.56, 128.12, 125.83, 118.94, 110.77, 109.45, 93.84, 61.12, 21.72, 21.49, 19.26. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{23}NO_2SNa$ 436.1342, found 436.1349.

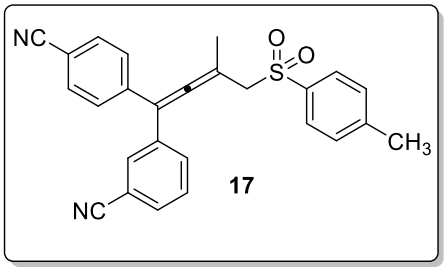


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.86 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.75 (t, *J* = 2.1 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 3.92 (d, *J* = 13.9 Hz, 1H), 3.89 (d, *J* = 13.9 Hz, 1H), 3.79 (s, 3H), 2.37 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.14, 159.85, 144.85, 141.39, 136.54, 135.73, 132.17, 129.88, 129.67, 129.19, 128.18, 121.14, 118.95, 114.51, 113.51, 110.94, 109.40, 94.07, 61.14, 55.44, 21.76, 19.33. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{23}NO_3SNa$ 452.1291, found 452.1295.



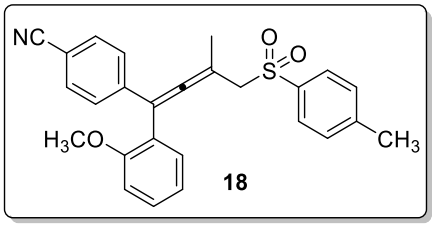
16

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 1H), 7.80 (s, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 6.3 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 13.9 Hz, 1H), 3.90 (d, *J* = 14.0 Hz, 1H), 2.34 (s, 3H), 2.06 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.33, 166.25, 144.87, 140.97, 135.67, 133.12, 132.33, 131.11, 129.87, 129.67, 129.16, 129.02, 128.85, 128.18, 118.85, 111.18, 108.85, 94.65, 61.34, 61.00, 21.74, 19.28, 14.42. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{25}NO_4SNa$ 494.1397, found 494.1399.



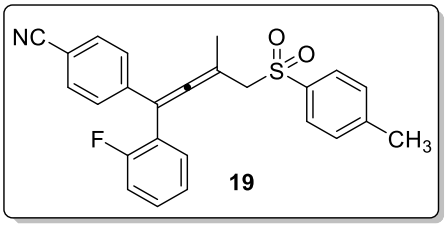
17

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 7.65 – 7.57 (m, 3H), 7.49 – 7.41 (m, 3H), 7.31 – 7.27 (m, 2H), 7.25 – 7.16 (m, 2H), 3.92 (s, 2H), 2.39 (d, *J* = 5.8 Hz, 3H), 2.06 (d, *J* = 3.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.30, 145.07, 140.21, 136.82, 135.74, 132.97, 132.51, 132.01, 131.51, 129.97, 129.66, 129.08, 128.14, 118.66, 118.47, 113.01, 111.61, 108.04, 95.39, 60.73, 21.79, 19.33. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{20}N_2O_2SNa$ 447.1138, found 447.1146.



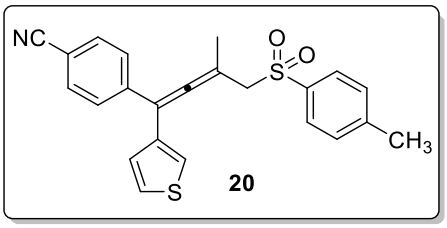
18

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.11 (d, *J* = 8.2 Hz, 2*2H), 7.01 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.96 (d, *J* = 13.9 Hz, 1H), 3.87 (d, *J* = 13.9 Hz, 1H), 3.65 (s, 3H), 2.35 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.50, 157.02, 144.61, 141.71, 135.49, 131.90, 131.29, 129.76, 129.73, 128.17, 127.67, 123.62, 120.83, 119.20, 111.28, 110.08, 105.19, 93.24, 61.04, 55.53, 21.80, 18.81. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{23}NO_3SNa$ 452.1291, found 452.1291.



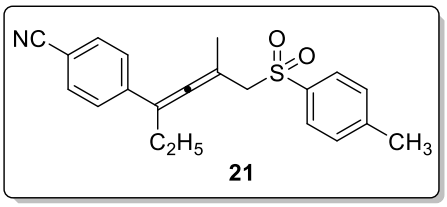
19

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.31 (m, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.03 (m, 5H), 3.96 (d, *J* = 13.9 Hz, 1H), 3.88 (d, *J* = 13.9 Hz, 1H), 2.34 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.59, 160.06 (d, *J* = 248.8 Hz), 144.76, 140.76, 135.40, 132.16, 131.47 (d, *J* = 2.6 Hz), 130.14 (d, *J* = 8.1 Hz), 129.80, 128.14, 127.89, 124.45 (d, *J* = 3.5 Hz), 122.58 (d, *J* = 14.1 Hz), 118.96, 116.16 (d, *J* = 21.7 Hz), 110.71, 103.08, 94.32, 60.72, 21.79, 18.88. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.66 (dd, *J* = 14.1, 7.7 Hz). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{20}FNO_2SNa$ 440.1091, found 440.1096.



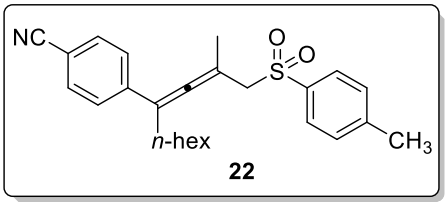
20

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.90 (dd, *J* = 5.0, 1.2 Hz, 1H), 3.90 (s, 2H), 2.40 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.11, 144.91, 141.38, 135.77, 135.41, 132.20, 129.92, 128.91, 128.19, 127.87, 126.10, 123.70, 118.86, 111.07, 104.86, 93.79, 61.12, 21.78, 19.30. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{23}H_{19}NO_2S_2Na$ 428.0749, found 428.0752.



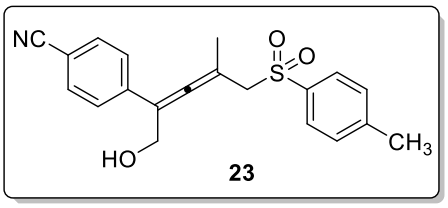
21

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.20 (m, 4H), 3.84 (d, *J* = 13.8 Hz, 1H), 3.78 (d, *J* = 13.7 Hz, 1H), 2.38 (s, 3H), 2.25 (q, *J* = 7.3 Hz, 2H), 1.94 (s, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.19, 144.86, 141.39, 136.14, 132.04, 129.92, 128.20, 126.86, 119.06, 110.10, 107.43, 94.28, 61.32, 23.00, 21.68, 19.01, 12.32. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{21}NO_2SNa$ 374.1185, found 374.1188.



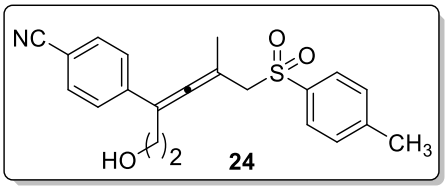
22

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (t, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 6.9 Hz, 2H), 7.33 – 7.25 (m, 4H), 3.85 (d, *J* = 13.8 Hz, 1H), 3.80 (d, *J* = 13.8 Hz, 1H), 2.41 (s, 3H), 2.22 (ddd, *J* = 21.7, 14.9, 7.6 Hz, 2H), 1.96 (s, 3H), 1.40 – 1.30 (m, 2H), 1.30 – 1.21 (m, 6H), 0.87 (t, *J* = 5.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.47, 144.83, 141.43, 136.13, 132.08, 129.92, 128.25, 126.98, 119.09, 110.12, 105.69, 93.41, 71.57, 61.29, 31.66, 29.01, 27.68, 22.72, 21.73, 18.93, 14.15. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{29}NO_2SNa$ 430.1811, found 430.1817.



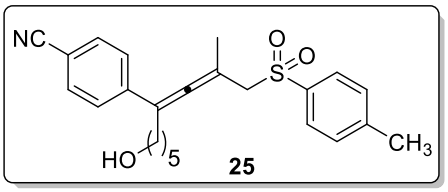
23

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.60 – 4.39 (m, 2H), 3.88 (d, *J* = 13.7 Hz, 1H), 3.75 (d, *J* = 13.7 Hz, 1H), 3.01 (s, 1H), 2.43 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.71, 145.44, 139.17, 135.90, 132.34, 130.17, 128.28, 127.01, 118.93, 110.72, 107.28, 95.51, 61.36, 60.90, 21.78, 19.32. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{19}NO_3SNa$ 376.0978, found 376.0976.



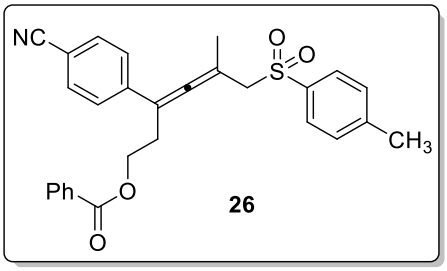
24

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.84 (s, 2H), 3.82 – 3.72 (m, 2H), 2.66 (s, 1H), 2.62 – 2.54 (m, 2H), 2.42 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.50, 145.24, 141.11, 136.20, 132.21, 130.09, 128.13, 126.91, 118.98, 110.42, 103.11, 94.12, 61.16, 60.22, 33.05, 21.74, 19.24. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{21}NO_3SNa$ 390.1134, found 390.1134.



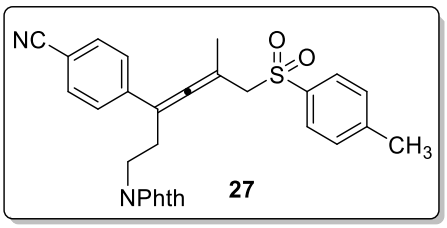
25

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.7 Hz, 2H), 7.50 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.32 – 7.25 (m, 4H), 3.85 (d, *J* = 13.7 Hz, 1H), 3.80 (d, *J* = 13.8 Hz, 1H), 3.66 – 3.52 (m, 2H), 2.41 (d, *J* = 1.4 Hz, 3H), 2.33 – 2.18 (m, 2H), 1.95 (d, *J* = 1.8 Hz, 3H), 1.82 (s, 1H), 1.60 – 1.48 (m, 2H), 1.47 – 1.31 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.47, 144.91, 141.37, 136.17, 132.11, 129.96, 128.20, 126.96, 119.07, 110.14, 105.58, 93.50, 62.66, 61.25, 32.45, 29.79, 27.42, 25.46, 21.73, 19.05. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{27}NO_3SNa$ 432.1604, found 432.1611.



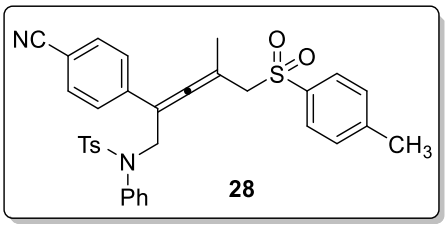
26

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.51 (m, 3H), 7.44 – 7.35 (m, 4H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.38 (td, *J* = 6.6, 1.1 Hz, 2H), 3.81 (d, *J* = 13.7 Hz, 1H), 3.75 (d, *J* = 13.7 Hz, 1H), 2.85 – 2.67 (m, 2H), 2.39 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.46, 166.40, 144.99, 140.68, 136.06, 133.24, 132.26, 129.98, 129.92, 129.54, 128.49, 128.20, 126.94, 118.92, 110.57, 102.20, 94.78, 62.86, 60.99, 29.22, 21.71, 19.02. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{25}NO_4SNa$ 494.1397, found 494.1403.



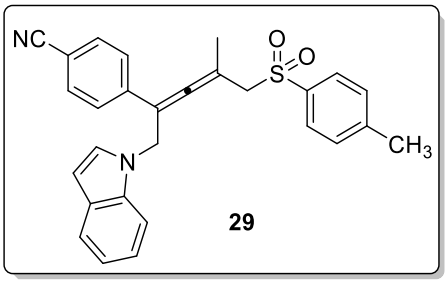
27

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 5.0, 3.1 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.72 (dd, *J* = 5.1, 3.0 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.27 (m, 4H), 3.84 (d, *J* = 13.7 Hz, 1H), 3.80 (d, *J* = 13.7 Hz, 1H), 3.78 – 3.65 (m, 2H), 2.70 (dt, *J* = 14.2, 7.0 Hz, 1H), 2.60 (dt, *J* = 14.9, 7.6 Hz, 1H), 2.38 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.59, 168.16, 144.97, 140.46, 136.08, 134.28, 132.26, 131.98, 130.04, 128.37, 126.98, 123.33, 118.91, 110.56, 102.59, 94.58, 61.04, 36.65, 28.74, 21.75, 18.89. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{24}N_2O_4SNa$ 519.1349, found 519.1357.



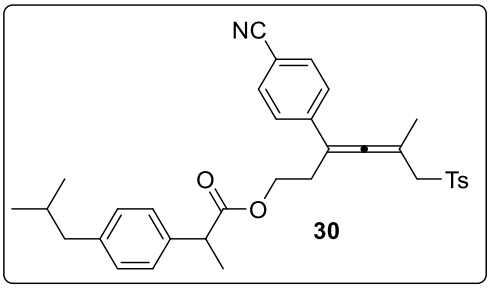
28

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.25 – 7.19 (m, 5H), 6.81 – 6.76 (m, 2H), 4.53 (d, *J* = 13.5 Hz, 1H), 4.40 (d, *J* = 13.5 Hz, 1H), 3.46 (d, *J* = 13.7 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.73, 145.05, 144.10, 138.63, 138.26, 136.02, 134.62, 132.26, 129.94, 129.73, 129.12, 129.10, 128.34, 128.07, 127.91, 127.45, 119.01, 110.79, 100.54, 94.24, 60.15, 51.10, 21.78, 21.71, 18.30. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{33}H_{30}N_2O_4S_2Na$ 605.1539, found 605.1548.



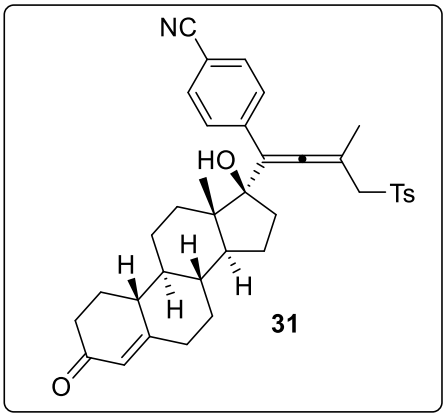
29

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.17 (m, 4H), 7.12 – 7.06 (m, 1H), 6.97 (d, *J* = 3.1 Hz, 1H), 6.45 (d, *J* = 3.1 Hz, 1H), 5.02 (s, 2H), 3.20 (d, *J* = 13.8 Hz, 1H), 3.13 (d, *J* = 13.9 Hz, 1H), 2.37 (s, 3H), 1.50 (s, 3H).. ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.88, 144.95, 138.91, 136.31, 135.83, 132.35, 129.94, 128.79, 128.11, 128.00, 126.81, 121.95, 121.24, 119.79, 118.80, 110.92, 109.37, 103.31, 101.96, 97.37, 59.94, 45.87, 21.69, 18.40. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{25}N_2O_2S$ 453.1631, found 453.1629.



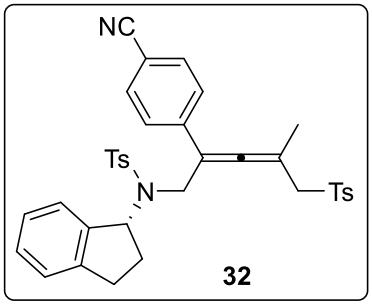
30

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.22 (m, 4H), 7.13 (dd, *J* = 10.4, 8.1 Hz, 2H), 7.05 (dd, *J* = 12.6, 8.0 Hz, 2H), 4.18 – 4.00 (m, 2H), 3.80 (d, *J* = 13.8 Hz, 0.50H), 3.77 (d, *J* = 13.8 Hz, 0.50H), 3.75 (d, *J* = 13.8 Hz, 0.50H), 3.67 (d, *J* = 13.8 Hz, 0.50H), 3.62 (q, *J* = 7.1 Hz, 1H), 2.66 – 2.46 (m, 2H), 2.46 – 2.41 (m, 2H), 2.40 (s, 1.5H), 2.39 (s, 1.5H), 1.89 (s, 1.5H), 1.89 (s, 1.5H), 1.86 – 1.77 (m, 1H), 1.44 (d, *J* = 7.1 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.33, 174.68, 144.99, 140.72, 140.70, 140.60, 137.66, 137.57, 136.06, 135.98, 132.18, 129.97, 129.45, 128.23, 127.11, 127.08, 126.87, 118.93, 110.51, 102.09, 102.07, 94.77, 94.72, 62.72, 62.69, 60.94, 60.89, 45.14, 45.13, 45.04, 30.24, 28.96, 22.45, 21.72, 18.91, 18.90, 18.85, 18.75. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{34}H_{37}NO_4SNa$ 578.2336, found 578.2336.



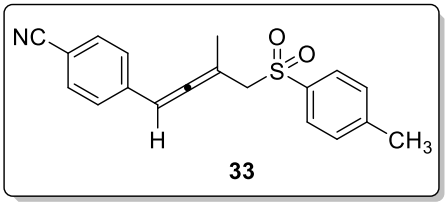
31

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 1.36H), 7.65 (d, *J* = 8.1 Hz, 1.52H), 7.62 (d, *J* = 7.8 Hz, 1.04H), 7.49 (d, *J* = 8.2 Hz, 0.63H), 7.46 (d, *J* = 8.2 Hz, 1.36H), 7.23 (d, *J* = 7.9 Hz, 1.42H), 7.14 (d, *J* = 7.9 Hz, 0.64H), 5.83 (s, 0.30H), 5.79 (s, 0.76H), 3.88 (d, *J* = 13.8 Hz, 0.67H), 3.80 (d, J = 13.7 Hz, 0.67H), 3.78 (d, *J* = 13.4 Hz, 0.32H), 3.70 (d, *J* = 13.7 Hz, 0.32H), 2.40 (s, 2.09H), 2.37 (s, 1.12H), 2.30 – 2.15 (m, 5H), 1.97 (s, 1.02H), 1.95 (s, 2.16H), 1.89 – 1.78 (m, 1H), 1.62 – 1.14 (m, 9H), 1.02 (s, 3H), 1.01 – 0.90 (m, 2H), 0.72 – 0.60 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.20, 207.67, 199.94, 199.82, 166.34, 166.16, 145.13, 145.10, 141.19, 141.05, 136.26, 136.11, 131.46, 131.42, 130.31, 130.14, 130.00, 129.97, 128.09, 128.01, 124.86, 124.77, 119.14, 113.18, 112.63, 110.16, 110.06, 92.84, 92.67, 86.88, 86.70, 61.28, 49.56, 49.42, 49.01, 48.58, 48.37, 48.21, 42.46, 42.44, 41.36, 41.14, 41.01, 40.93, 36.61, 36.55, 35.42, 35.38, 34.99, 34.82, 31.09, 30.92, 26.71, 26.56, 26.43, 26.33, 23.48, 23.43, 21.78, 21.74, 19.69, 19.15, 14.62. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{37}H_{42}NO_4S$ 596.2829, found 596.2836.



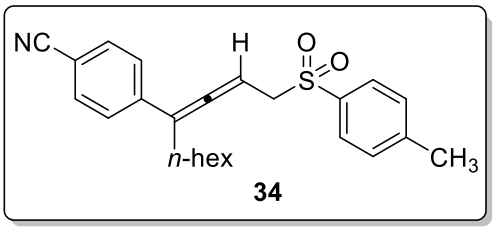
32

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.67 (m, 4H), 7.46 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.34 (dd, *J* = 8.0, 4.1 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.17 – 7.08 (m, 3H), 6.98 – 6.91 (m, 0.56H), 6.88 – 6.80 (m, 0.52H), 6.42 (d, *J* = 7.6 Hz, 0.47H), 6.06 (d, *J* = 7.6 Hz, 0.50H), 5.38 (q, *J* = 8.3 Hz, 1H), 4.12 (d, *J* = 16.4 Hz, 0.54H), 4.04 (d, *J* = 16.0 Hz, 0.50H), 4.03 (d, *J* = 13.8 Hz, 0.50H), 3.98 (d, *J* = 16.0 Hz, 0.53H), 3.93 (d, *J* = 16.4 Hz, 0.50H), 3.80 (d, *J* = 13.7 Hz, 0.50H), 3.70 (d, *J* = 13.7 Hz, 1H), 2.86 – 2.77 (m, 1H), 2.77 – 2.64 (m, 1H), 2.46 (s, 3H), 2.42 (s, 1.53H), 2.38 (s, 1.54H), 2.25 – 2.14 (m, 0.56H), 2.09 – 1.99 (m, 0.60H), 1.96 (s, 1.46H), 1.92 (s, 1.42H), 1.90 – 1.81 (m, 0.59H), 1.76 – 1.65 (m, 0.64H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.20, 208.07, 144.90, 144.75, 143.93, 143.91, 143.02, 142.83, 139.86, 139.71, 139.49, 139.30, 137.58, 137.13, 136.37, 136.16, 132.02, 130.17, 130.10, 129.95, 129.90, 128.40, 128.24, 128.19, 128.07, 127.46, 127.30, 127.27, 127.08, 126.67, 126.60, 125.22, 125.12, 124.73, 124.01, 119.01, 110.54, 110.49, 104.98, 104.51, 96.64, 95.92, 63.39, 63.32, 60.50, 60.45, 44.29, 44.04, 30.65, 30.14, 29.94, 29.38, 21.80, 21.74, 21.69, 18.65, 18.55. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{36}H_{34}N_2O_4S_2Na$ 645.1852, found 645.1860.



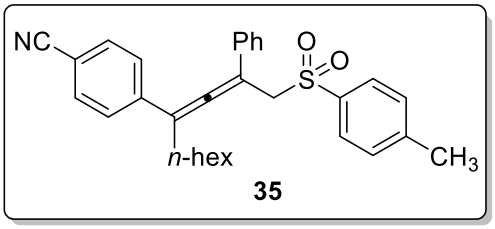
33

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.03 – 5.93 (m, 1H), 3.84 (d, *J* = 13.7 Hz, 1H), 3.79 (d, *J* = 13.7 Hz, 1H), 2.45 (s, 3H), 2.00 (d, *J* = 3.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.81, 145.05, 138.89, 135.77, 132.38, 130.04, 128.39, 127.72, 119.02, 110.52, 94.74, 94.11, 60.88, 21.81, 18.86. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{17}NO_2SNa$ 346.0872, found 346.0879.



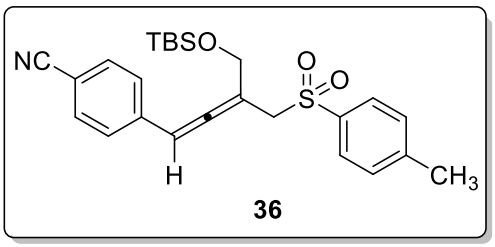
34

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.49 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 9.8 Hz, 2H), 5.64 – 5.58 (m, 1H), 3.86 (dd, *J* = 12.2, 5.6 Hz, 1H), 3.82 (dd, *J* = 12.2, 6.6 Hz, 1H), 2.47 (s, 3H), 2.32 – 2.25 (m, 2H), 1.39 – 1.33 (m, 2H), 1.32 – 1.23 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.13, 145.07, 140.49, 135.60, 132.24, 130.06, 128.65, 126.92, 119.01, 110.62, 107.53, 84.31, 57.04, 31.67, 29.55, 29.08, 27.68, 22.76, 21.85, 14.20. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{27}NO_2SNa$ 416.1655, found 416.1649.



35

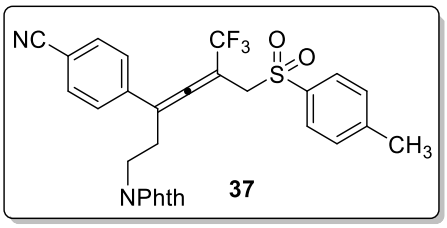
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.57 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.35 (d, *J* = 14.4 Hz, 1H), 4.29 (d, *J* = 14.4 Hz, 1H), 2.49 – 2.40 (m, 2H), 2.37 (s, 3H), 1.54 – 1.44 (m, 2H), 1.36 – 1.28 (m, 2H), 1.29 – 1.21 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.72, 144.85, 140.47, 136.31, 133.77, 132.41, 129.83, 128.81, 128.50, 127.85, 127.20, 126.28, 119.05, 110.90, 109.79, 100.12, 58.12, 31.72, 30.28, 29.34, 27.87, 22.76, 21.74, 14.16. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{31}NO_2SNa$ 492.1967, found 492.1970.



36

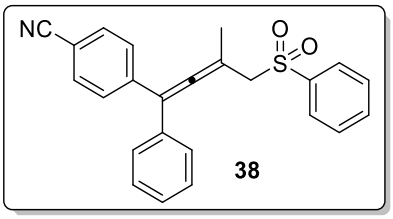
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 3H), 6.18 (s, 1H), 4.37 (dd, *J* = 12.3, 2.8 Hz, 1H), 4.33 (dd, *J* = 12.3, 2.5 Hz,

1H), 3.92 (dd, *J* = 13.8, 1.8 Hz, 1H), 3.88 (dd, *J* = 13.8, 1.3 Hz, 1H), 2.43 (s, 3H), 0.85 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.86, 145.06, 138.42, 136.00, 132.44, 130.06, 128.34, 127.89, 119.00, 110.83, 99.51, 96.58, 62.77, 55.89, 25.88, 21.79, 18.37, 5.23, 5.28. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{31}NO_3SSiNa$ 476.1686, found 476.1685.



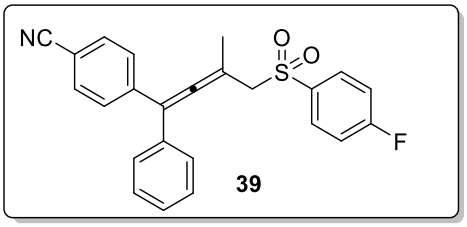
37

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 2H), 7.75 – 7.71 (m, 4H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.97 (d, *J* = 14.8 Hz, 1H), 3.94 – 3.87 (m, 3H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.54 (q, *J* = 3.4 Hz), 168.16, 145.53, 137.24, 135.53, 134.32, 132.74, 132.00, 130.14, 129.42, 128.52, 128.36, 127.74, 123.44, 118.46, 112.60, 111.80, 93.51, 93.07 (q, *J* = 36.9 Hz), 53.75, 36.05, 29.12, 21.83. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.40. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{21}F_3N_2O_4SNa$ 573.1066, found 573.1078.



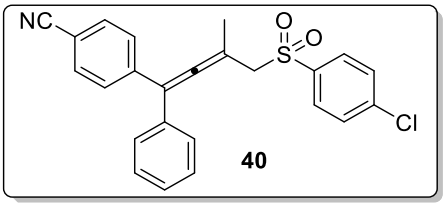
38

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.26 (t, *J* = 4.2 Hz, 2H), 7.13 – 7.07 (m, 2H), 3.96 (d, *J* = 13.9 Hz, 1H), 3.91 (d, *J* = 13.9 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.26, 141.42, 138.70, 135.10, 133.89, 132.28, 129.28, 129.18, 128.81, 128.75, 128.24, 128.19, 118.97, 111.02, 109.60, 94.00, 61.25, 19.33. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{19}NO_2SNa$ 408.1029, found 408.1037.



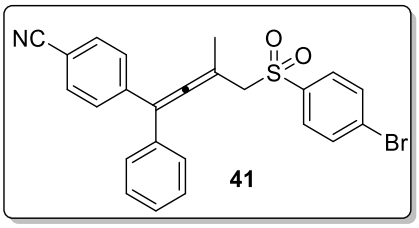
39

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.29 – 7.23 (m, 2H), 7.11 – 7.00 (m, 2H), 6.97 (t, *J* = 8.3 Hz, 2H), 3.94 (s, 2H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.13, 165.81 (d, J = 256.6 Hz), 141.27, 134.96, 134.30 (d, J = 2.9 Hz), 132.25, 131.05 (d, J = 9.8 Hz), 129.08, 128.79, 128.68, 128.28, 118.84, 116.53 (d, J = 22.3 Hz), 111.16, 109.62, 93.93, 61.29, 19.24. ^{19}F NMR (471 MHz, $CDCl_3$) δ -100.69 – -104.24 (m). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{18}FNO_2SNa$ 426.0934, found 426.0944.



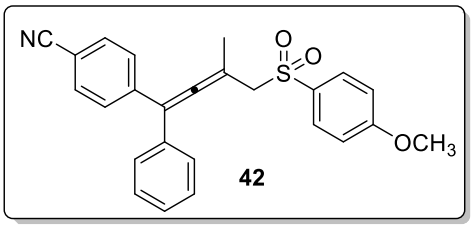
40

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.28 – 7.25 (m, 2H), 7.05 – 6.95 (m, 2H), 4.02 (d, *J* = 14.1 Hz, 1H), 3.96 (d, *J* = 14.1 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.11, 142.12, 140.99, 134.81, 132.75, 132.38, 129.00, 128.97, 128.81, 128.72, 118.75, 117.58, 117.07, 111.47, 109.99, 93.51, 61.05, 19.40. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{18}ClNO_2SNa$ 442.0639, found 442.0639.



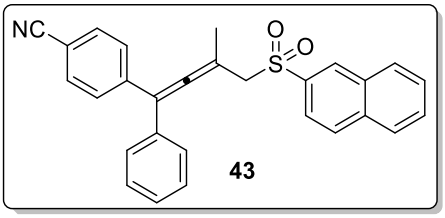
41

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.32 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.09 – 7.03 (m, 2H), 3.96 (d, *J* = 14.2 Hz, 1H), 3.93 (d, *J* = 14.2 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.08, 141.19, 137.22, 134.93, 132.51, 132.32, 129.71, 129.33, 129.08, 128.86, 128.64, 128.37, 118.88, 111.28, 109.73, 93.86, 61.11, 19.29. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{18}BrNO_2SNa$ 486.0134, found 486.0139.



42

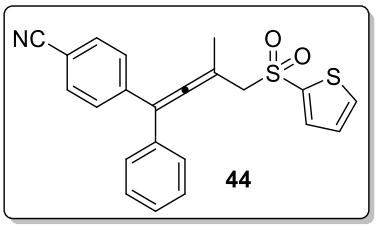
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.09 (dd, *J* = 6.7, 3.0 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.94 (d, *J* = 13.9 Hz, 1H), 3.89 (d, *J* = 13.9 Hz, 1H), 3.83 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.24, 163.84, 141.47, 135.16, 132.20, 130.42, 129.93, 129.17, 128.75, 128.71, 128.15, 118.98, 114.46, 110.99, 109.42, 94.37, 61.40, 55.72, 19.16. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{21}NO_3SNa$ 438.1134, found 438.1142.



43

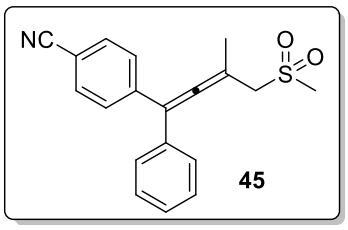
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.76 – 7.69 (m, 1H), 7.69 – 7.62 (m, 1H), 7.24 – 7.14 (m, 5H), 7.02 – 6.95 (m, 4H), 4.12 (d, *J* =

14.0 Hz, 1H), 4.01 (d, *J* = 14.0 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.18, 140.97, 135.33, 135.16, 134.90, 132.08, 131.88, 130.09, 129.63, 129.61, 129.56, 128.76, 128.65, 128.43, 128.15, 128.14, 127.94, 122.63, 118.87, 110.89, 109.42, 94.15, 60.96, 19.09. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{21}NO_2SNa$ 458.1185, found 458.1191.



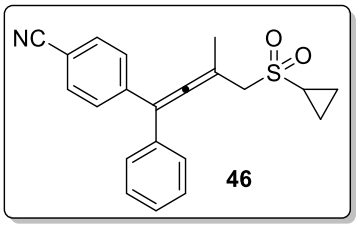
44

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 4H), 7.38 – 7.30 (m, 5H), 7.17 – 7.13 (m, 2H), 6.94 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.05 (d, *J* = 13.8 Hz, 1H), 4.00 (d, *J* = 13.8 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.35, 141.38, 139.34, 135.07, 134.63, 134.38, 132.26, 129.20, 128.78, 128.20, 127.93, 118.94, 111.03, 109.68, 94.02, 62.72, 19.23. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{17}NO_2S_2Na$ 414.0593, found 414.0600.



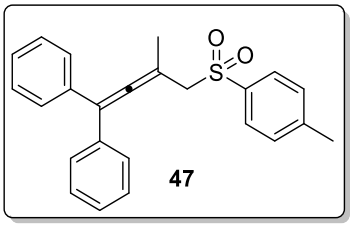
45

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 3.83 (d, *J* = 13.9 Hz, 1H), 3.79 (d, *J* = 14.0 Hz, 1H), 2.73 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.91, 141.03, 134.76, 132.48, 129.13, 129.02, 128.70, 128.51, 118.86, 111.39, 110.12, 94.49, 59.54, 40.10, 19.50. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{17}NO_2SNa$ 346.0872, found 346.0875.

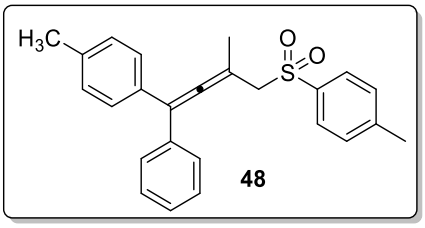


46

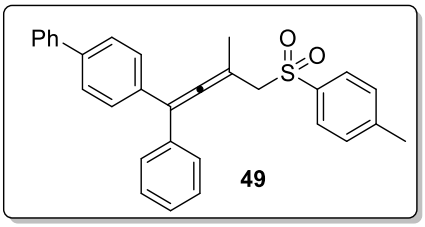
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.32 (m, 3H), 7.32 – 7.27 (m, 2H), 3.84 (d, *J* = 14.0 Hz, 1H), 3.80 (d, *J* = 14.0 Hz, 1H), 2.25 (tt, *J* = 8.0, 4.8 Hz, 1H), 2.17 (s, 3H), 1.22 – 1.05 (m, 2H), 0.83 – 0.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.29, 141.30, 135.07, 132.38, 129.13, 128.90, 128.72, 128.34, 118.91, 111.16, 109.67, 94.03, 58.49, 29.40, 19.47, 5.05. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{19}NO_2SNa$ 372.1029, found 372.1033.



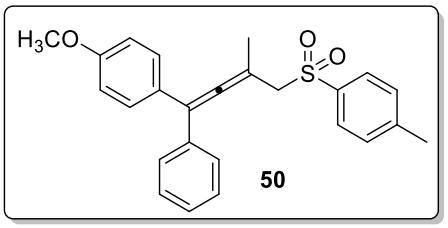
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.27 (m, 6H), 7.15 – 7.11 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.95 (s, 2H), 2.35 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.64, 144.50, 136.27, 135.41, 129.76, 128.71, 128.36, 128.22, 127.52, 110.24, 92.91, 61.59, 21.78, 19.34. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{22}O_2SNa$ 397.1233, found 397.1237.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.25 (m, 3H), 7.15 – 7.06 (m, 6H), 7.01 (d, *J* = 7.2 Hz, 2H), 3.94 (s, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.56, 144.47, 137.33, 136.45, 135.46, 133.28, 129.75, 129.09, 128.71, 128.62, 128.32, 128.25, 127.46, 110.11, 92.70, 61.69, 21.76, 21.29, 19.36. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}O_2SNa$ 411.1389, found 411.1391.

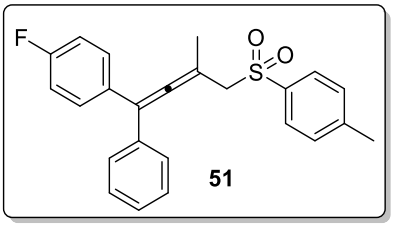


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.20 (dd, *J* = 7.1, 1.9 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.98 (s, 2H), 2.33 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.77, 144.54, 140.61, 140.31, 136.22, 135.48, 135.23, 129.76, 129.10, 128.95, 128.79, 128.41, 128.24, 127.61, 127.51, 127.03, 127.00, 110.00, 93.02, 61.56, 21.77, 19.40. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{26}O_2SNa$ 473.1546, found 473.1546.

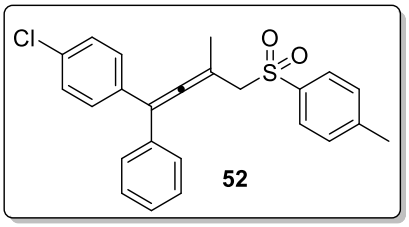


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.21 (m, 3H), 7.13 –7.06 (m, 4H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 2H), 3.81 (s, 3H), 2.33 (s, 3H), 2.04 (s, 3H). ^{13}C NMR

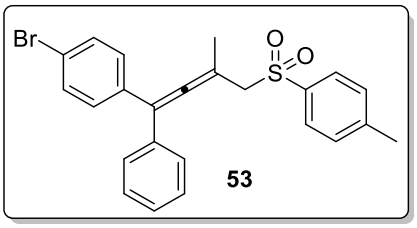
(126 MHz, $CDCl_3$) δ 207.46, 159.12, 144.48, 136.57, 135.48, 129.85, 129.75, 128.69, 128.41, 128.33, 128.23, 127.47, 113.79, 109.81, 92.58, 61.73, 55.38, 21.76, 19.43. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}O_3SNa$ 427.1338, found 427.1346.



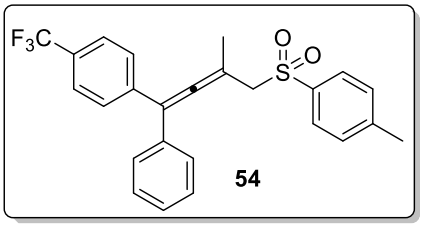
^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.34-7.26 (m, 3H), 7.17 – 7.03 (m, 6H), 7.03 – 6.91 (m, 2H), 3.95 (d, *J* = 14.0 Hz, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 2.35 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.50, 162.25 (d, *J* = 246.8 Hz), 144.61, 136.17, 135.51, 132.24 (d, *J* = 3.2 Hz), 130.34 (d, *J* = 8.1 Hz) , 129.78, 128.59, 128.47, 128.22, 127.69, 115.29 (d, *J* = 21.7 Hz), 109.39, 93.08, 61.54, 21.74, 19.35. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.13 – -116.61 (m). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{21}FO_2SNa$ 415.1138, found 415.1143.



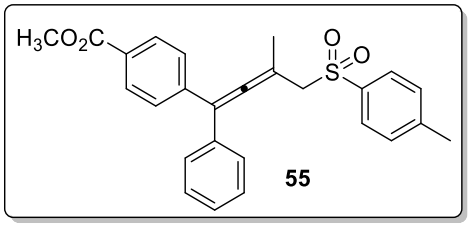
^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.08 (m, 4H), 7.05 (d, *J* = 8.4 Hz, 2H), 3.96 (d, *J* = 14.0 Hz, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.54, 144.66, 135.84, 135.40, 134.81, 133.29, 129.97, 129.76, 128.59, 128.52, 128.49, 128.19, 127.75, 109.38, 93.33, 61.41, 21.75, 19.26. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{21}ClO_2SNa$ 431.0843, found 431.0844.



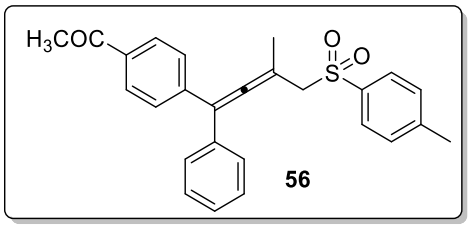
^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.15 – 7.08 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.96 (d, *J* = 14.0 Hz, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 2.36 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.51, 144.68, 135.77, 135.38, 135.30, 131.48, 130.31, 129.76, 128.59, 128.50, 128.19, 127.77, 121.48, 109.44, 93.39, 61.38, 21.80, 19.25. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{22}BrO_2S$ 453.0518, found 453.0517.



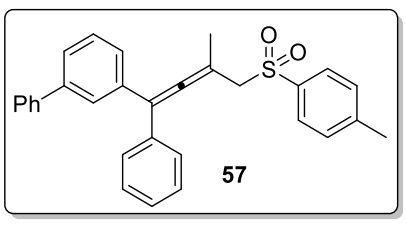
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.25 (d, *J* = 9.2 Hz, 2H), 7.16 – 7.08 (m, 4H), 3.97 (d, *J* = 14.0 Hz, 1H), 3.92 (d, *J* = 14.0 Hz, 1H), 2.35 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.91, 144.74, 140.25, 135.56, 135.50, 129.82, 129.48 (q, *J* = 32.3 Hz), 128.95, 128.65, 128.61, 128.24, 127.93, 125.29 (q, *J* = 3.6 Hz), 124.20 (d, *J* = 261.1 Hz), 109.48, 93.78, 61.28, 21.67, 19.28. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.41 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{21}F_3O_2SNa$ 465.1107, found 465.1111.



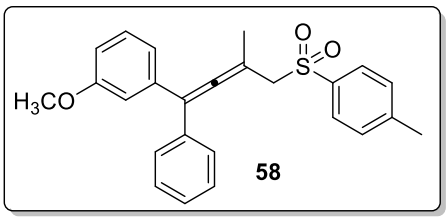
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.03 (m, 4H), 3.96 (d, *J* = 14.0 Hz, 1H), 3.92 (d, *J* = 14.0 Hz, 1H), 3.92 (s, 3H), 2.33 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.04, 166.86, 144.70, 141.18, 135.61, 135.38, 129.81, 129.63, 129.04, 128.69, 128.53, 128.21, 127.82, 109.77, 93.64, 61.31, 52.23, 21.70, 19.15. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}O_4SNa$ 455.1288, found 455.1291.



1H NMR (500 MHz, CDCl3) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.14 – 7.08 (m, 4H), 3.95 (d, *J* = 13.9 Hz, 1H), 3.92 (d, *J* = 14.0 Hz, 1H), 2.60 (s, 3H), 2.34 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.16, 197.64, 144.73, 141.39, 136.03, 135.57, 135.51, 129.84, 128.73, 128.56, 128.46, 128.23, 127.87, 109.78, 93.64, 61.30, 26.74, 21.77, 19.24. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}O_3SNa$ 439.1338, found 439.1344.

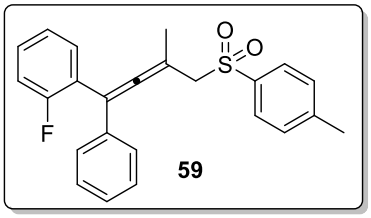


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.38 (dd, *J* = 17.1, 8.1 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.19 (d, *J* = 6.3 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 2H), 3.98 (s, 2H), 2.30 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.73, 144.50, 141.28, 140.84, 136.90, 136.22, 135.47, 129.73, 128.91, 128.85, 128.68, 128.43, 128.18, 127.80, 127.59, 127.53, 127.46, 127.18, 126.36, 110.29, 93.02, 61.57, 21.73, 19.44. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{30}H_{27}O_2S$ 451.1726, found 451.1733.



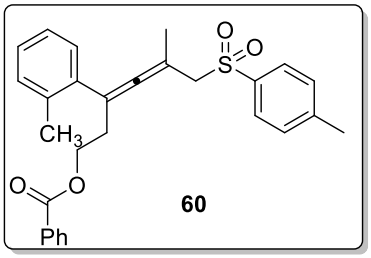
58

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.79 (s, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 3.93 (s, 2H), 3.79 (s, 3H), 2.34 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.63, 159.65, 144.55, 137.78, 136.21, 135.55, 129.77, 129.29, 128.75, 128.37, 128.20, 127.55, 121.26, 114.37, 113.13, 110.22, 92.87, 61.60, 55.39, 21.75, 19.41. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{24}O_3SNa$ 427.1338, found 427.1340.



59

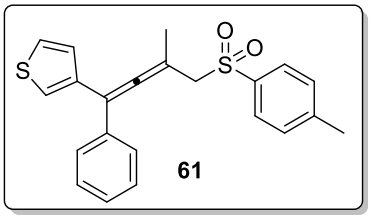
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.30 (mz, 1H), 7.26 – 7.20 (m, 3H), 7.12 – 7.08 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 3H), 7.04 – 6.98 (m, 2H), 3.97 (d, *J* = 14.0 Hz, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 2.31 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.77, δ 160.24 (d, *J* = 248.5 Hz), 144.44, 135.75, 135.20, 131.63 (d, *J* = 2.7 Hz), 129.68, 129.45 (d, *J* = 8.2 Hz), 128.39, 128.20, 127.46, 124.07 (d, *J* = 3.6 Hz), 123.83 (d, *J* = 14.1 Hz), 115.94 (d, *J* = 22.1 Hz), 103.62, 93.11, 61.23, 21.80, 18.95. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{21}FO_2SNa$ 415.1138, found 415.1147.



60

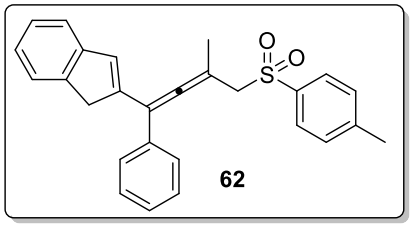
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.19 – 7.08 (m, 3H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 1H), 4.32 – 4.16 (m, 2H), 3.73 (s, 2H), 2.64 – 2.46 (m, 2H), 2.28 (s, 3H), 2.17 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (126

MHz, $CDCl_3$) δ 205.30, 166.34, 144.43, 136.02, 135.55, 135.07, 133.06, 130.47, 130.07, 129.53, 129.51, 128.40, 128.12, 128.02, 127.26, 125.86, 101.29, 90.42, 62.89, 61.63, 33.11, 21.67, 20.38, 18.73. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{28}H_{28}O_4SNa$ 483.1601, found 483.1606.



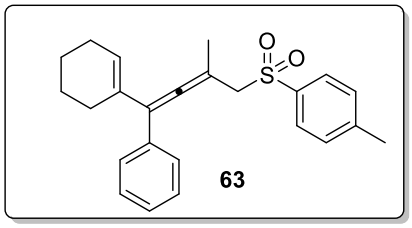
61

^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.28 (m, 3H), 7.25 (d, *J* = 3.0 Hz, 1H), 7.20 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.95 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.91 (dd, *J* = 5.0, 1.3 Hz, 1H), 3.93 (d, *J* = 13.9 Hz, 1H), 3.89 (d, *J* = 13.9 Hz, 1H), 2.38 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.69, 144.66, 136.86, 136.31, 135.67, 129.87, 128.46, 128.43, 128.28, 128.12, 127.70, 125.48, 123.24, 105.69, 92.60, 61.66, 21.82, 19.42. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{20}O_2S_2Na$ 403.0797, found 403.0799.



62

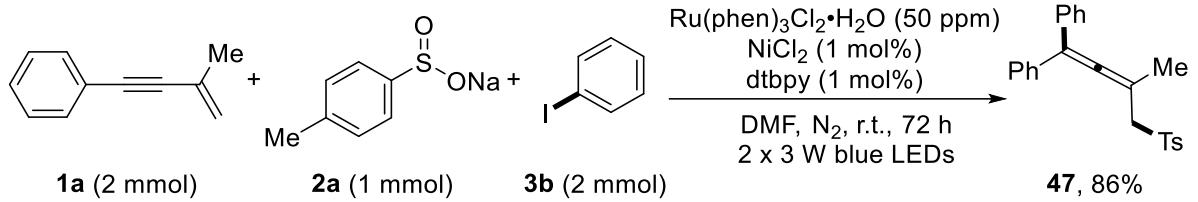
^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.29 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 7.17 (d, *J* = 7.1 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.60 (s, 1H), 3.96 (d, *J* = 14.0 Hz, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 3.38 (d, *J* = 22.6 Hz, 1H), 3.27 (d, *J* = 22.5 Hz, 1H), 2.30 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.81, 145.18, 144.70, 143.19, 143.06, 135.96, 135.65, 130.47, 129.81, 128.88, 128.40, 128.22, 127.68, 126.49, 124.99, 123.60, 120.88, 107.71, 92.26, 61.51, 40.15, 21.71, 19.40. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{24}O_2S$ 413.1570, found 413.1578.



63

^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.22 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.01 (m, 2H), 5.44 (t, *J* = 4.0 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 1H), 3.82 (d, *J* = 14.0 Hz, 1H), 2.37 (s, 3H), 2.07 – 2.00 (m, 2H), 1.95 (s, 3H), 1.94 – 1.88 (m, 1H), 1.87 – 1.78 (m, 1H), 1.66 – 1.58 (m, 2H), 1.58 – 1.51 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.74, 144.47, 136.33, 135.70, 132.86, 129.75, 129.34, 128.38, 128.06, 127.97, 127.09, 111.96, 91.93, 62.24, 27.34, 25.98, 22.94, 22.24, 21.83, 19.50. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{26}O_2SNa$ 401.1546, found 401.1555.

General Procedure for Large-Scale

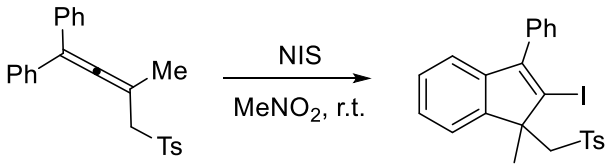


1a (2 mmol) **2a** (1 mmol) **3b** (2 mmol) **47**, 86%

In a 25 mL oven-dried Schlenk tube, 10 mL DMF was added to a mixture of $NiCl_2$ (1.3 mg, 0.01 mmol, 1 mol%), dtbpy (2.7 mg, 0.01 mmol, 1 mol%), sodium 4-toluenesulfinate **2a** (178.2 mg, 0.2 mmol, 1.0 equiv), 1,3-enyne **1a** (284.4 mg, 0.4 mmol, 2.0 equiv) and iodobenzene **3b** (408.0 mg, 0.4 mmol, 2.0 equiv) under N_2 atmosphere. Then the solution of $Ru(phen)Cl_2•H_2O$ (0.1mg/mL, 50 ppm) in dry DMF (0.4 mL,) was added via syringe under a stream of nitrogen. The tube was sealed with a Teflon lined cap and the reaction was stirred and irradiated with two 3 W blue LED lamps (with cooling fan to keep the reaction temperature near 25 ℃) for 72 h. The reaction mixture was extracted with EtOAc (2 x 20 mL), and the combined organic phase was washed with brine (40 mL), dried over Na_2SO_4, concentrated in vacuo. The residue was then analyzed by ^1H NMR with CH_2Br_2 as internal standard, giving 86% yield.

General Procedure for Further Transformations

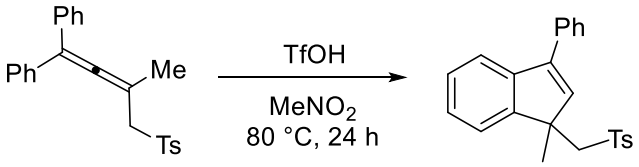
Synthesis of 64[3]:



47 **64**, 86%

To a 25 mL oven-dried sealed tube was added **47** (74.9 mg, 0.2 mmol,), NIS (54.0 mg, 0.24 mmol) and $MeNO_2$ (2.5 mL). The tube was sealed with a Teflon lined cap and reacted at room temperature. The reaction mixture was detected with TLC, then concentrated under vacuum. The residue was then purified by flash column chromatography (PE/EA = 5:1) to give product 64 as white solid (86.5 mg, 86% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 5H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.98 (td, *J* = 7.5, 1.9 Hz, 1H), 3.80 (d, *J* = 14.8 Hz, 1H), 3.73 (d, *J* = 14.8 Hz, 1H), 2.35 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.76, 146.43, 144.13, 142.99, 137.08, 135.03, 129.50, 129.06, 128.52, 128.40, 127.98, 127.32, 125.56, 123.59, 120.51, 111.97, 62.48, 54.23, 26.77, 21.64. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{21}IO_2SNa$ 523.0199, found 523.0200.

Synthesis of 65[4]:

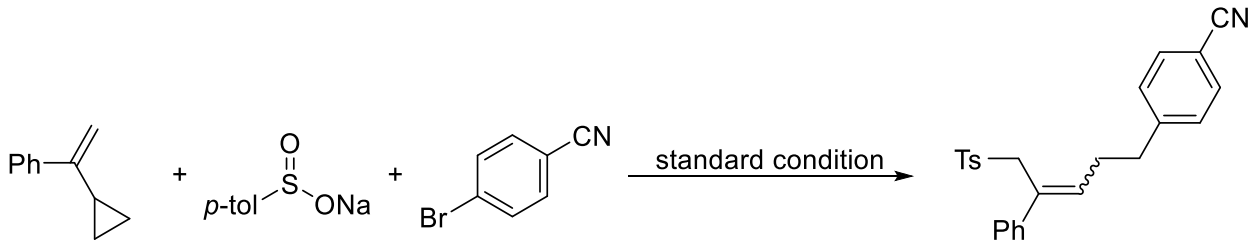


47 **65**, quantitive

To a 25 mL oven-dried sealed tube was added **47** (74.9 mg, 0.2 mmol), trifluoromethanesulfonic acid (6.0 mg, 0.04 mmol, 20 mol%) and $MeNO_2$ (2.5 mL). The tube was sealed with a Teflon lined cap and moved into a preheated oil bath at 80 ℃ for 24 h. The reaction mixture was then cooled to room temperature, and concentrated under vacuum. The residue was then purified by flash column chromatography (PE/EA = 5:1) to give product **6**5 as white solid in quantitive yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.9 Hz, 2H), 7.58 (d, *J* = 7.1 Hz, 2H), 7.51-7.43 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 2.1 Hz, 1H), 3.76 (dd, *J* = 14.3, 2.5 Hz, 1H), 3.28 (dd, *J* = 14.2, 2.4 Hz, 1H), 2.38 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.89, 144.49, 142.52, 141.54, 139.00, 137.55, 135.13, 129.74, 128.66, 128.04, 127.92, 127.79, 127.31, 125.88, 121.90, 121.14, 63.70, 49.78, 23.14, 21.64. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{22}O_2SNa$ 397.1233, found 397.1231.

Mechanistic Studies

1. Radical Clock Experiment:



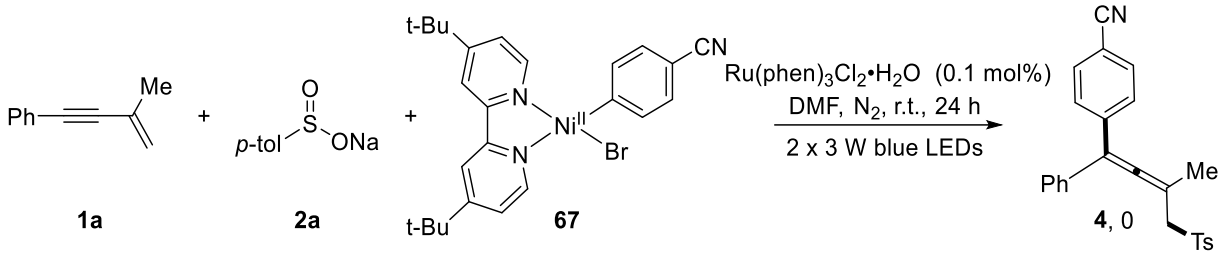
1ad **2a** **3a** **66**, 57%

In a 25 mL oven-dried Schlenk tube, 1.84 mL DMF was added to a mixture of $NiCl_2$ (1.3 mg, 0.01 mmol, 5 mol%), dtbpy (2.7 mg, 0.01 mmol, 5 mol%), sodium 4-toluenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), 1,3-enyne **1ad** (57.7 mg, 0.4 mmol, 2.0 equiv) and 4-bromobenzonitrile **3a** (72.8 mg, 0.4 mmol, 2.0 equiv) under N_2 atmosphere. Then the solution of $Ru(phen)Cl_2•H_2O$ (1 mg/mL, 0.16 mg, 0.002 mmol, 0.1 mol%) in dry DMF (0.16 mL) was added via syringe under a stream of nitrogen. The tube was sealed with a Teflon lined cap and the reaction was stirred and irradiated with two 3 W blue LED lamps (with cooling fan to keep the reaction temperature near 25 ℃) for 24 h. The reaction mixture was extracted with EtOAc (2 x 10 mL), and the combined organic phase was washed with brine (20 mL), dried over Na_2SO_4, concentrated in vacuo. The residue as purified by flash column chromatography to give the allene product **66** with 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 15.6, 8.0 Hz, 3.52H), 7.51 (d, *J* = 6.9 Hz, 0.67H), 7.30 (d, *J* = 7.8 Hz, 0.67H), 7.19 (dd, *J* = 7.3, 4.8 Hz, 1.51H), 7.17 – 7.10 (m, 4.18H),

7.07 (dd, *J* = 6.6, 2.8 Hz, 1.61H), 6.90 (dd, *J* = 6.4, 2.9 Hz, 0.52H), 5.96 (t, *J* = 7.4 Hz, 0.72H), 5.72 (t, *J* = 7.4 Hz, 0.27H), 4.25 (s, 1.42H), 4.06 (s, 0.52H), 2.80 (t, *J* = 7.6 Hz, 1.46H), 2.66 (t, *J* = 7.5 Hz, 0.61H), 2.55 – 2.47 (m, 1.49H), 2.39 (s, 0.80H), 2.38 – 2.29 (m, 2.74H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.01, 146.80, 144.66, 144.53, 140.73, 138.11, 136.36, 136.28, 136.18, 136.09, 132.32, 132.20, 129.83, 129.61, 129.58, 129.42, 129.37, 129.34, 128.43, 128.37, 128.33, 128.23, 127.38, 127.28, 126.45, 119.12, 110.03, 109.88, 64.91, 57.90, 35.63, 35.41, 30.87, 30.56, 21.65, 21.60. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{23}NO_2SNa$ 424.1342, found 424.1350.

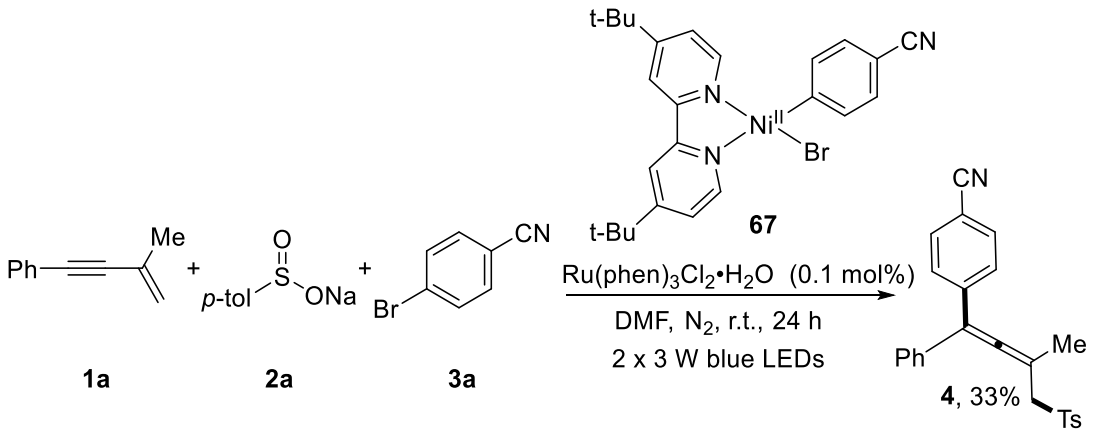
2. Stoichiometric and catalytic amount experiment with Ni(II) complex

(a) catalytic amount reactions of Ni(II) complex **67**



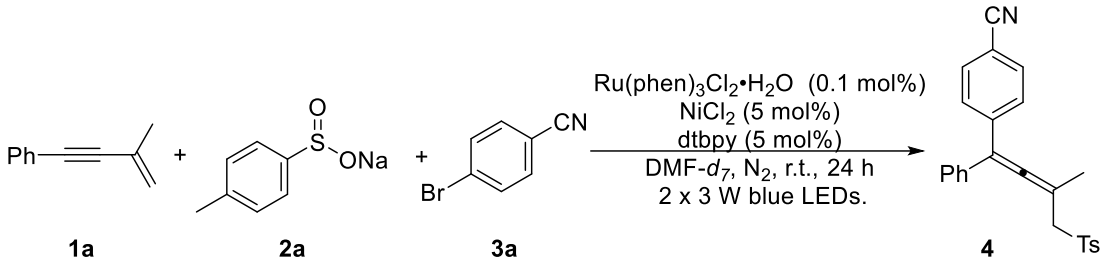
In glove box, Ni(II) complex **67**[5] (101.8 mg, 0.2 mmol, 1.0 equiv), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv) were combined in a 25 mL oven-dried sealed tube, and after that **1a** (56.8 mg, 0.4 mmol, 2.0 equiv), DMF (1.84 mL) were then added via syringe. Then the solution of $Ru(phen)Cl_2•H_2O$ (1 mg/mL, 0.16 mg, 0.002 mmol, 0.1 mol%) in dry DMF (0.16 mL) was added via syringe under a stream of nitrogen. The tube was sealed with a Teflon lined cap and the reaction was stirred and irradiated with two 3 W blue LED lamps (with cooling fan to keep the reaction temperature near 25 ℃) for 24 h. The reaction mixture was diluted with EtOAc (2 x 10 mL), then the organic phase was washed with brine (20 mL), dried over Na_2SO_4, concentrated in vacuo. The crude residue was analyzed by ^{1}H NMR, which demonstrated that none of the allene product was given.

(b) Stoichiometric reactions of Ni(II) complex **67**



In glove box, Ni(II) complex **67** (5.1 mg, 0.01 mmol, 5 mol%), **2a** (35.6 mg, 0.2 mmol, 1.0 equiv), **3a** (72.8 mg, 0.4 mmol, 2.0 equiv) were combined in a 25 mL oven-dried sealed tube, and after that 1a (56.8 mg, 0.4 mmol, 2.0 equiv), DMF (1.84 mL) were then added via syringe. Then the solution of $Ru(phen)Cl_2•H_2O$ (1 mg/mL, 0.16 mg, 0.002 mmol, 0.1 mol%) in dry DMF (0.16 mL) was added via syringe under a stream of nitrogen. The tube was sealed with a Teflon lined cap and the reaction was stirred and irradiated with two 3 W blue LED lamps (with cooling fan to keep the reaction temperature near 25 ℃) for 24 h. The reaction mixture was diluted with EtOAc (2 x 10 mL), then the organic phase was washed with brine (20 mL), dried over Na_2SO_4, concentrated in vacuo. Allene **4** was detected and its yield was analyzed by ^{1}H NMR with CH_2Br_2 as internal standard.

3. Light on/off experiment



In a NMR tube, 0.5 mL DMF-d_7 was added to a mixture of $NiCl_2$•dtbpy (1 mg, 0.0025 mmol, 5 mol%), **2a** (8.9 mg, 0.05 mmol, 1.0 equiv), **3a** (18.2 mg, 0.1 mmol, 2.0 equiv), **1a** (14.2 mg, 0.1 mmol, 2.0 equiv) and 1,4-dioxane (2.0 μL, 0.025 mmol, 0.5 equiv, as internal standard) under N_2 atmosphere. Then the solution of $Ru(phen)_3Cl_2•H_2O$ (1 mg/mL, 0.04 mg, 0.00005 mmol, 0.1 mol%) in dry DMF (0.04 mL) was added via syringe under a stream of nitrogen. The tube was sealed with an NMR cap and the reaction was stirred and irradiated with two 3 W blue LED lamps (with cooling fan to keep the reaction temperature near 25℃, and switching lights alternately). At each sampling time, the reaction was analyzed by ^{1}H NMR.

Table S1 The yield of product **8** with light on/off at different time intervals.

Time (h)	0	1	2	3	4	5	6
Yield (%)	0	13.3	13.4	19.9	20	31.6	31.6

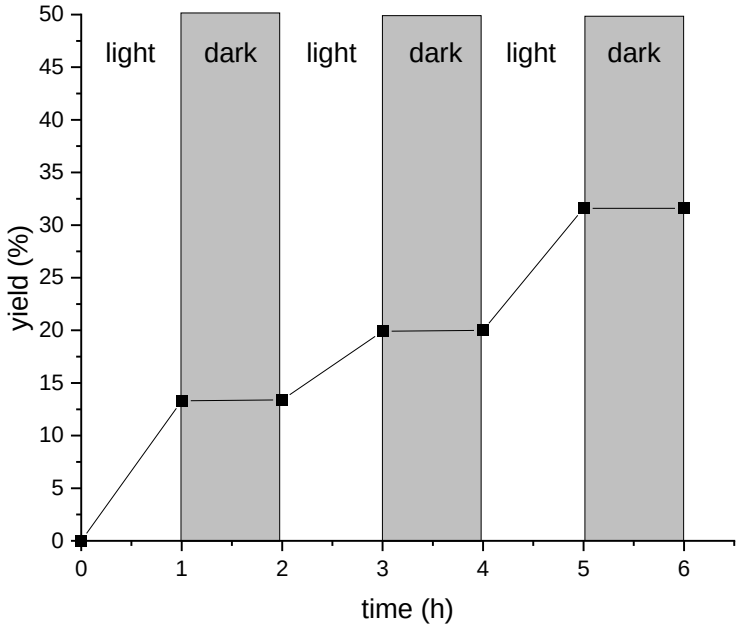


Fig. S1 Light on/off experiment

4. Stern-Volmer quenching experiments

Stern-Volmer quenching experiments were carried out using a 0.1 mM solution of $Ru(phen)_3Cl_2•H_2O$ and variable concentrations (0.1, 0.2, 0.5, 1.0 mM) of 1,3-enyne **1a**, sodium 4-methylbenzenesulfinate **2a**, and 4-bromobenzonitrile **3a** in anhydrous DMF. The samples were prepared in 3 mL quartz cuvettes. The intensity of the emission peak at 601.4 nm (λ_{ex} = 422 nm) expressed as the ratio I_0/I, where I_0 is the emission intensity of $Ru(phen)_3Cl_2•H_2O$ at 601.4 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured. Fluorescence emission spectra and Stern-Volmer plots for each component are given in the Supplementary Figures below

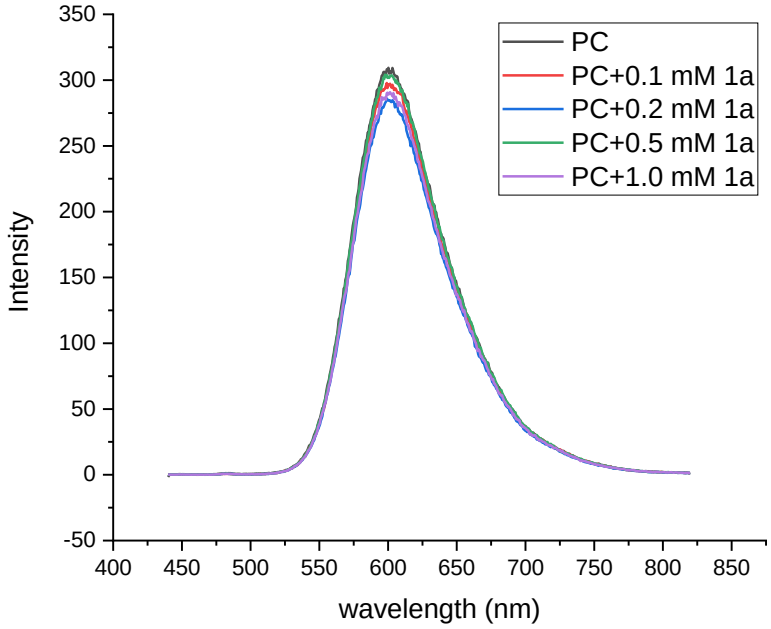


Fig. S2 Emission spectra of $Ru(phen)_3Cl_2•H_2O$ (0.1 mM) at different concentrations of 1,3-enyne **1a**.

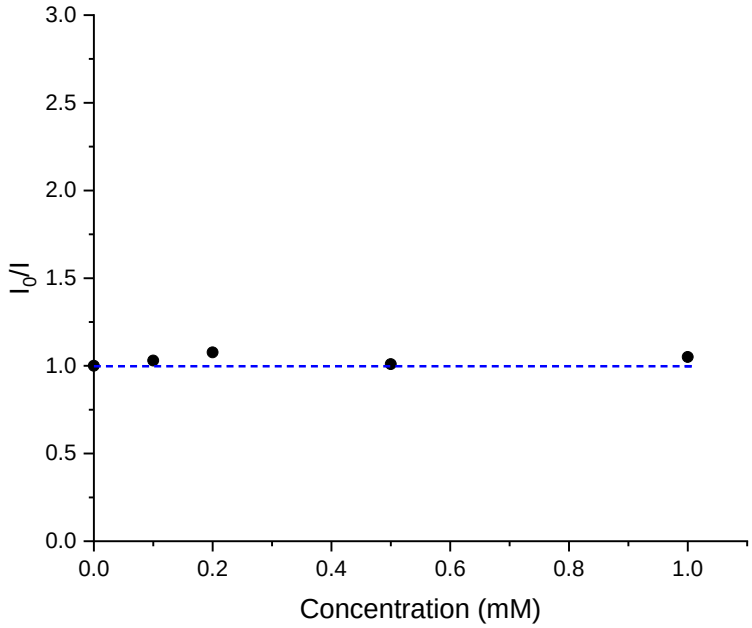


Fig. S3 Stern-Volmer plot of $Ru(phen)_3Cl_2•H_2O$ (0.1 mM) at different concentrations of 1,3-enyne **1a**.

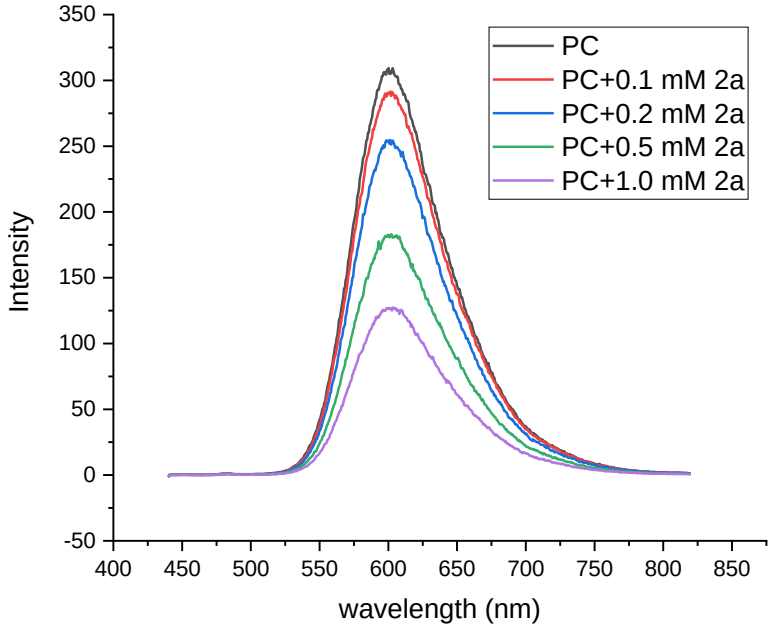


Fig. S4 Emission spectra of $Ru(phen)_3Cl_2•H_2O$ (0.1 mM) at different concentrations of sodium 4-methylbenzenesulfinate **2a.**

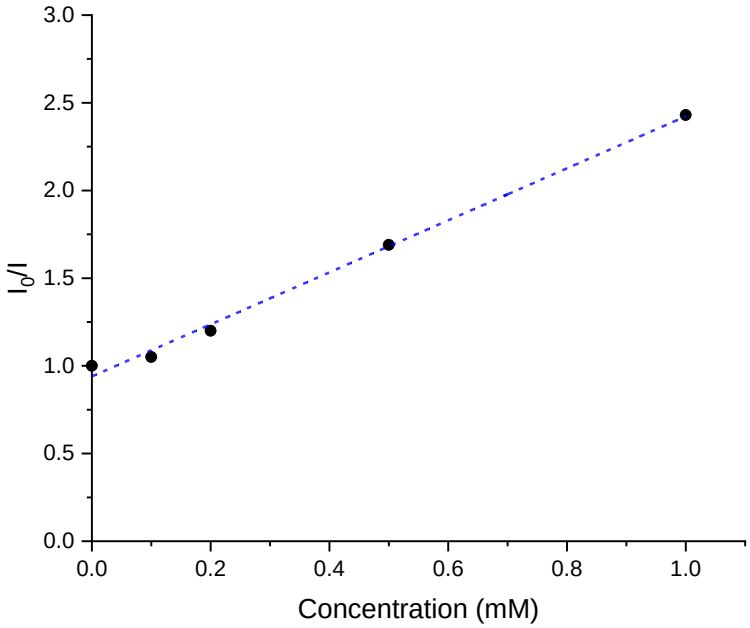


Fig. S5 Stern-Volmer plot of $Ru(phen)_3Cl_2•H_2O$ (0.1 mM) at different concentrations of sodium 4-methylbenzenesulfinate **2a.**

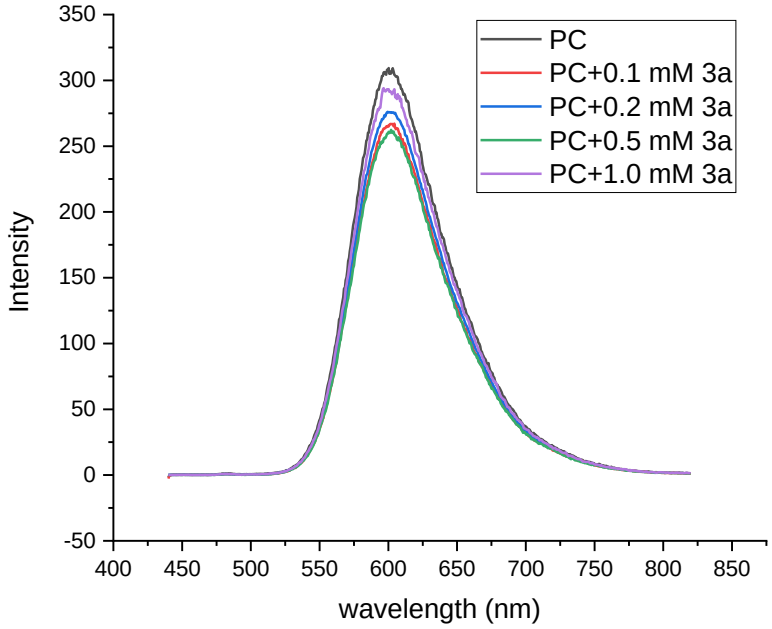


Fig. S6 Emission spectra of $Ru(phen)_3Cl_2•H_2O$ (0.1 mM) at different concentrations of 4-bromobenzonitrile **3a.**

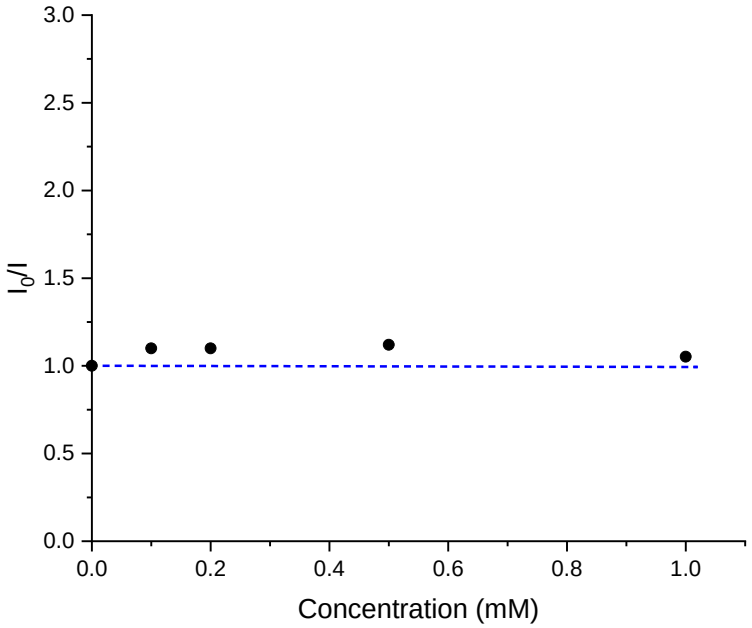


Fig. S7 Stern-Volmer plot of $Ru(phen)_3Cl_2•H_2O$ (0.1 mM) at different concentrations of 4-bromobenzonitrile **3a.**

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2647. (b) Pourjavadi, A.; Marandi, G. B. *J. Chem. Res. (S)* **2002**, 378-380. (c) Pourjavadi, A.; Marandi, G. B. *J. Chem. Res. (S)* **2002**, 552-555. (d) Hashmi, A. S. K.; Sinha, P. *Adv. Synth. Catal.* **2004**, *346*, 432-438. (e) Lee, C.-L.; Huang, C.-H.; Wang, H.-C.; Chuang D.-W.; Wu, M.-J.; Wang, S.-Y.; Hwang, T.-L.; Wu, C.-C.; Chen, Y.-L.; Chang, F.-R.; Wu, Y.-C. *Org. Biomol. Chem.* **2011**, *9*, 70-73. (f) Ho, K. Y. T.; Aïssa, C. *Chem.-Eur. J.* **2012**, *18*, 3486-3489. (g) Rotsides, C. Z.; Hu, C.; Woerpel, K. A. *Angew. Chem. Int. Ed.* **2013**, *52*, 13033-13036. (h) Barday, M.; Ho, K. Y. T.; Halsall, C. T.; Aïssa, C. *Org. Lett.* **2016**, *18*, 1756-1759. (i) Kleinhans, G.; Guisado-Barrios, G.; Liles, D. C.; Bertrand, G.; Bezuidenhout, D. I. *Chem. Comm.* **2016**, *52*, 3504-3507. (j) Wang, F.; Wang, D.; Zhou, Y.; Liang, L.; Lu, R.; Chen, P.; Lin, Z.; Liu, G. *Angew. Chem. Int. Ed.* **2018**, *57*, 7140-7145. (k) Zhang, K.-F.; Bian, K.-J.; Li, C.; Sheng, J.; Li, Y.; Wang, X.-S. *Angew. Chem. Int. Ed.* **2019**, *58*, 5069-5074. (l) Song, Y.; Song, S.; Duan, X.; Wu, X.; Jiang, F.; Zhang, Y.; Fan, J.; Huang, X.; Fu, C.; Ma, S. *Chem. Commun.* **2019**, *55*, 11774-11777. (m) Zeng, Y.; Chiou, M.-F.; Zhu, X.; Cao, J.; Lv, D.; Jian, W.; Li, Y.; Zhang, X.; Bao, H. *J. Am. Chem. Soc.* **2020**, *142*, 18014-18021.

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3. Grandclaudon, C.; Michelet, V.; Toullec, P. Y. *Org. Lett*. **2016**, *18*, 676.
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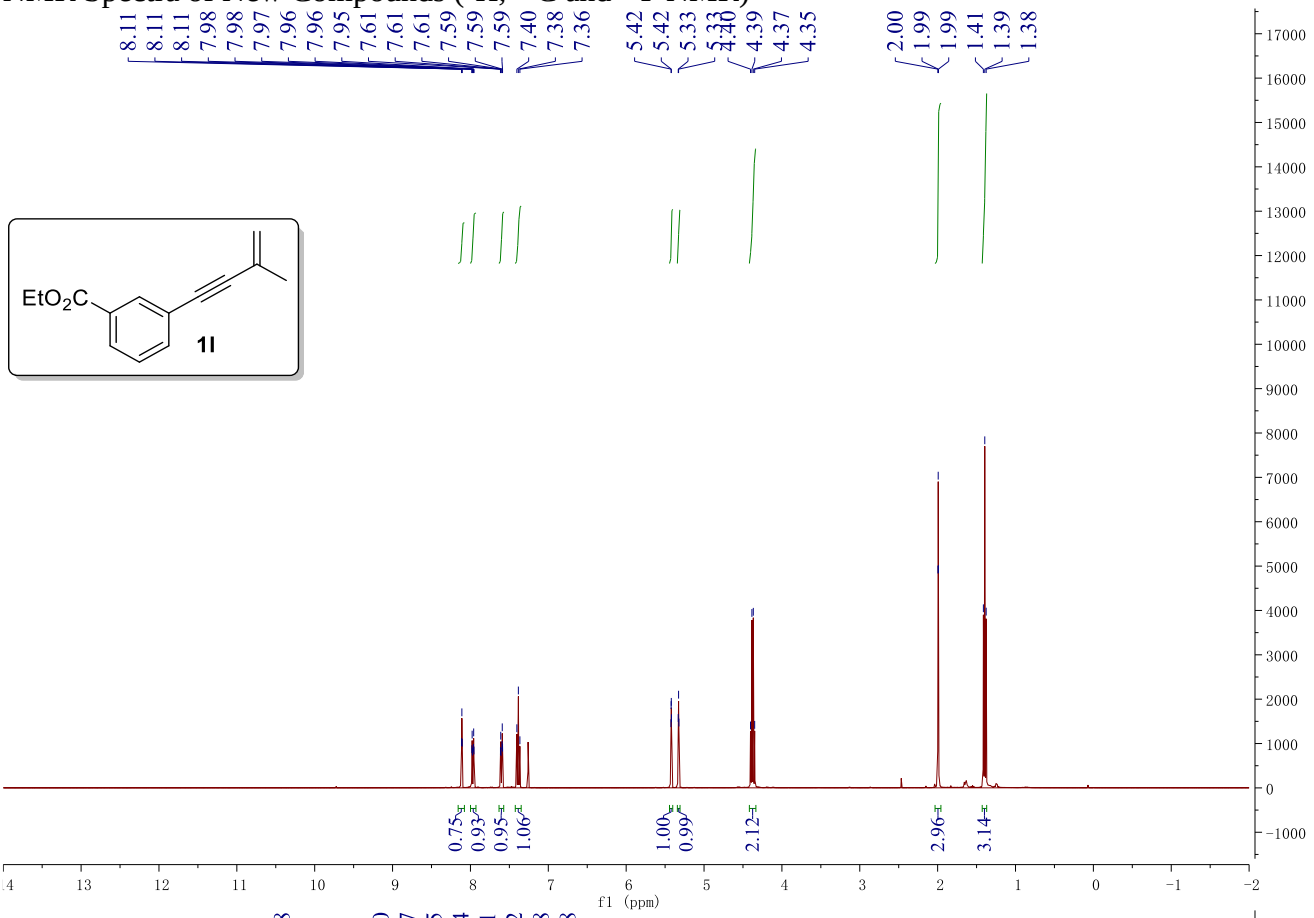
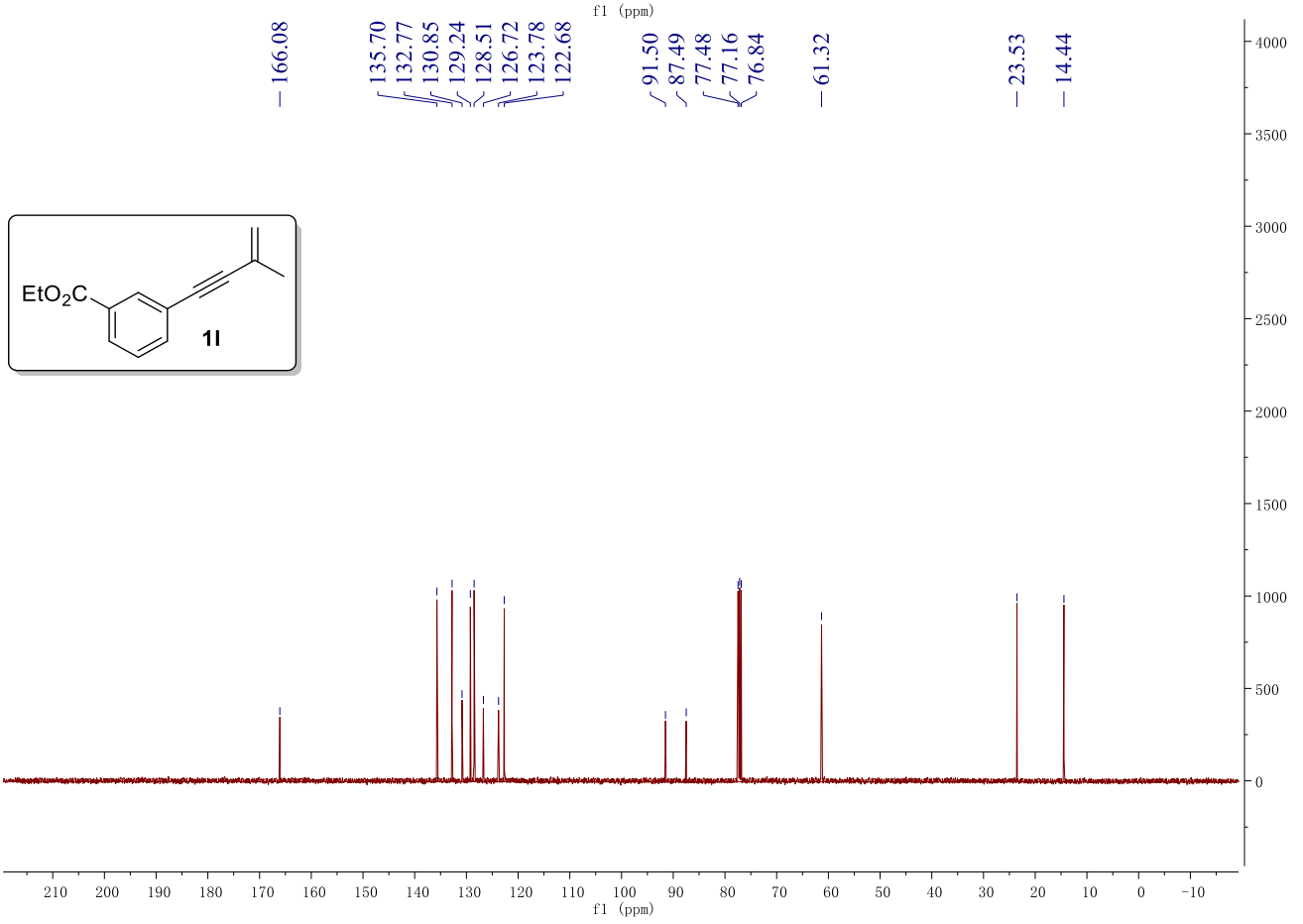
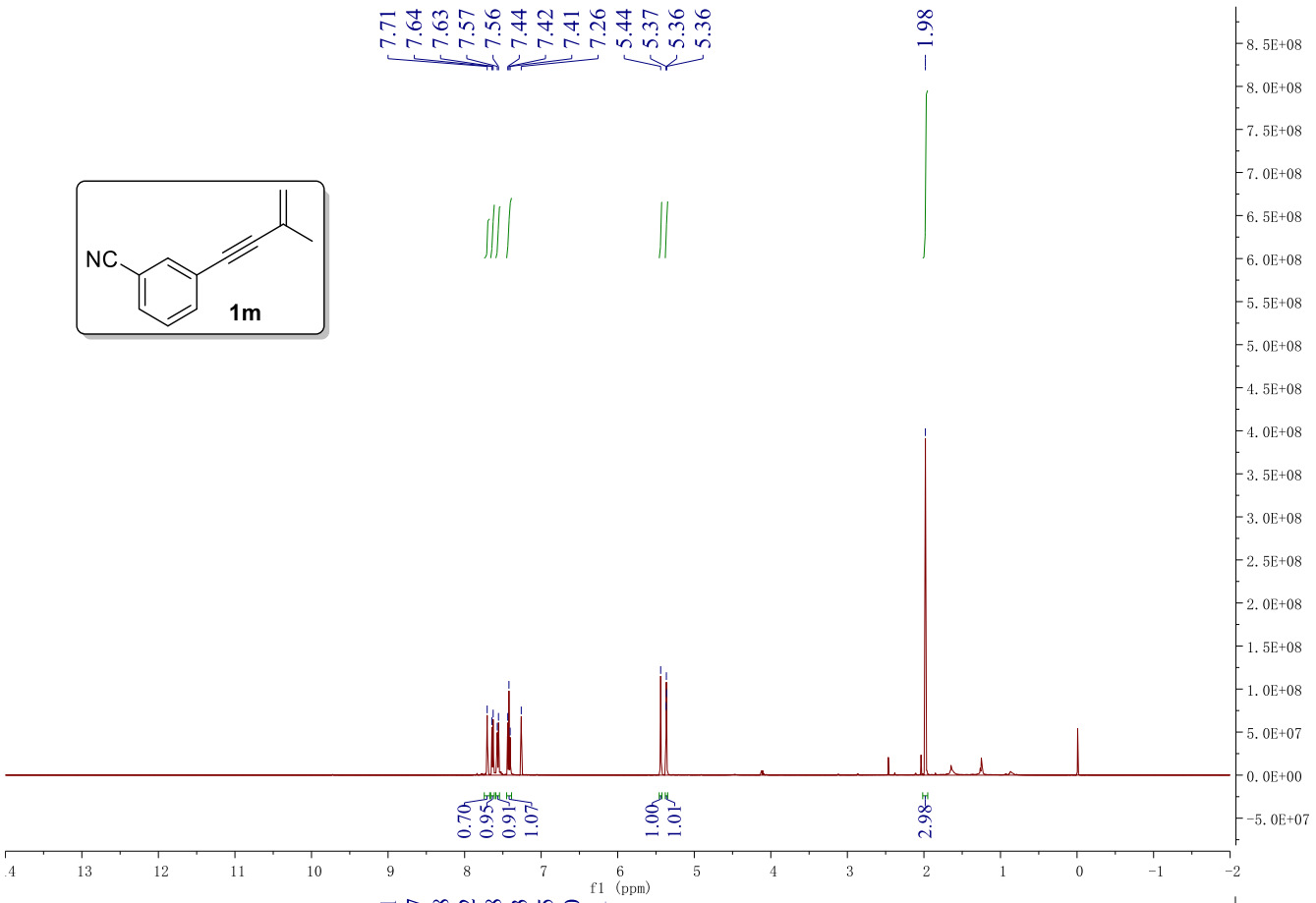
NMR Spectra of New Compounds (^{1}H, ^{13}C and ^{19}F NMR)



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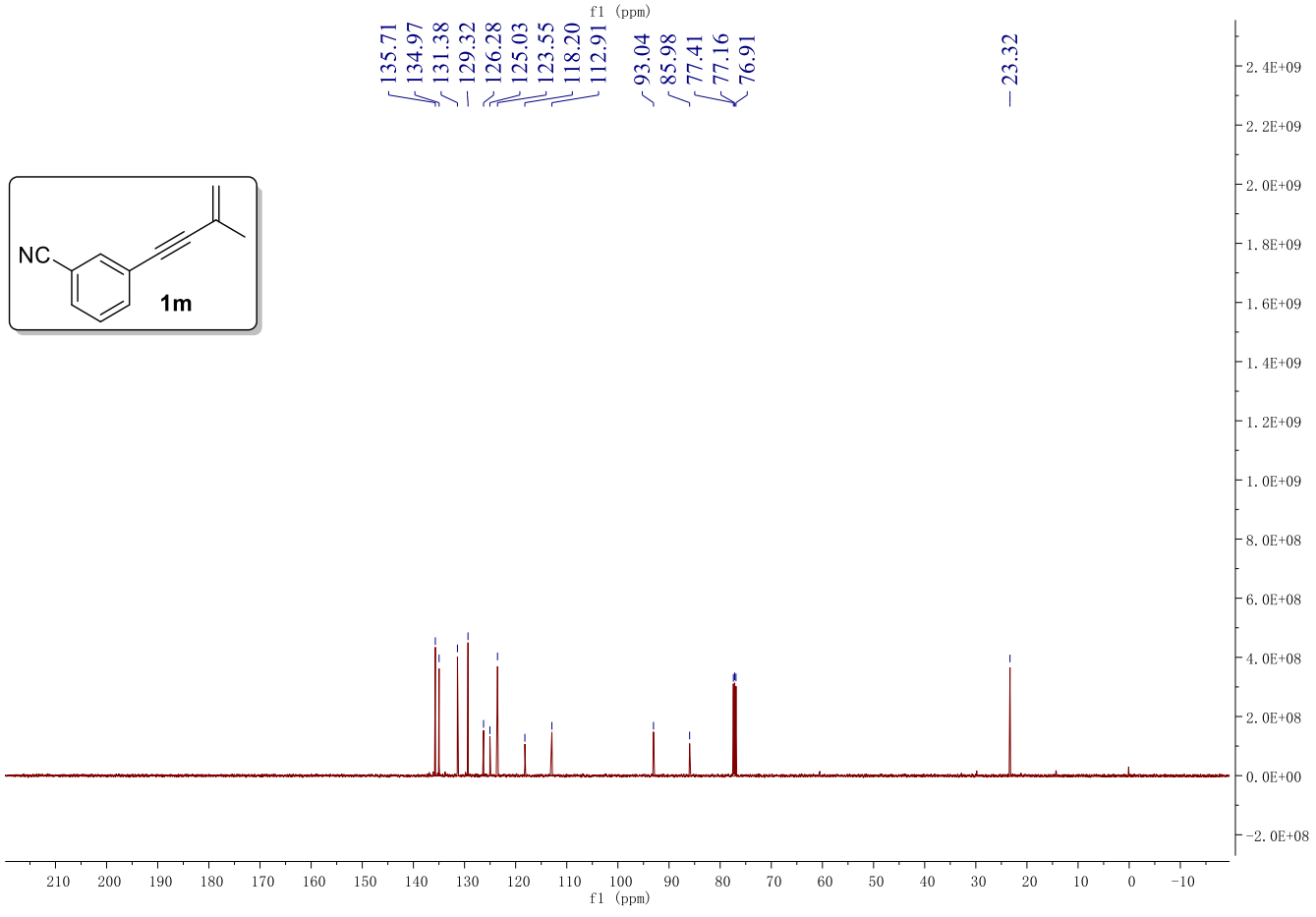
f1 (ppm)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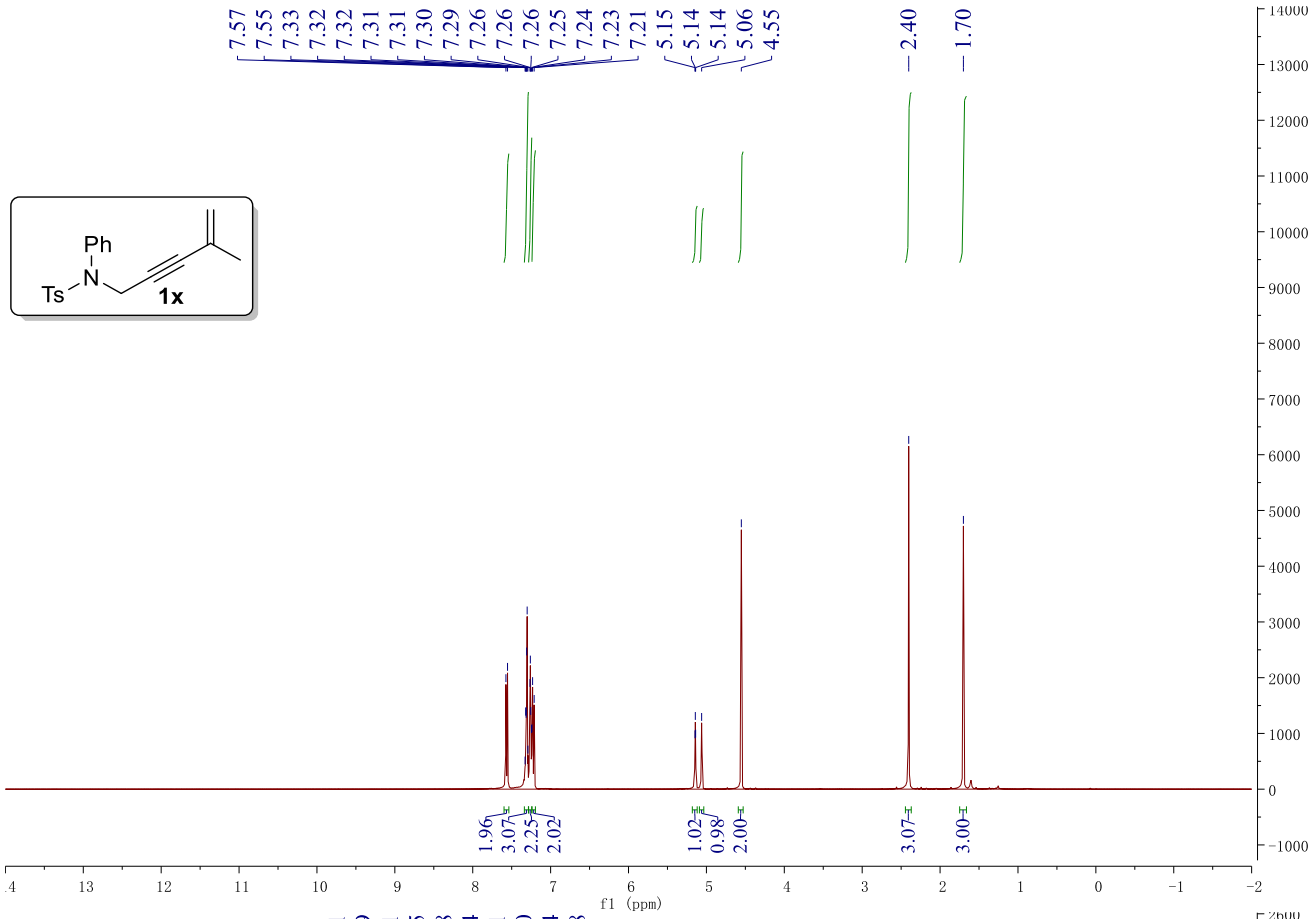
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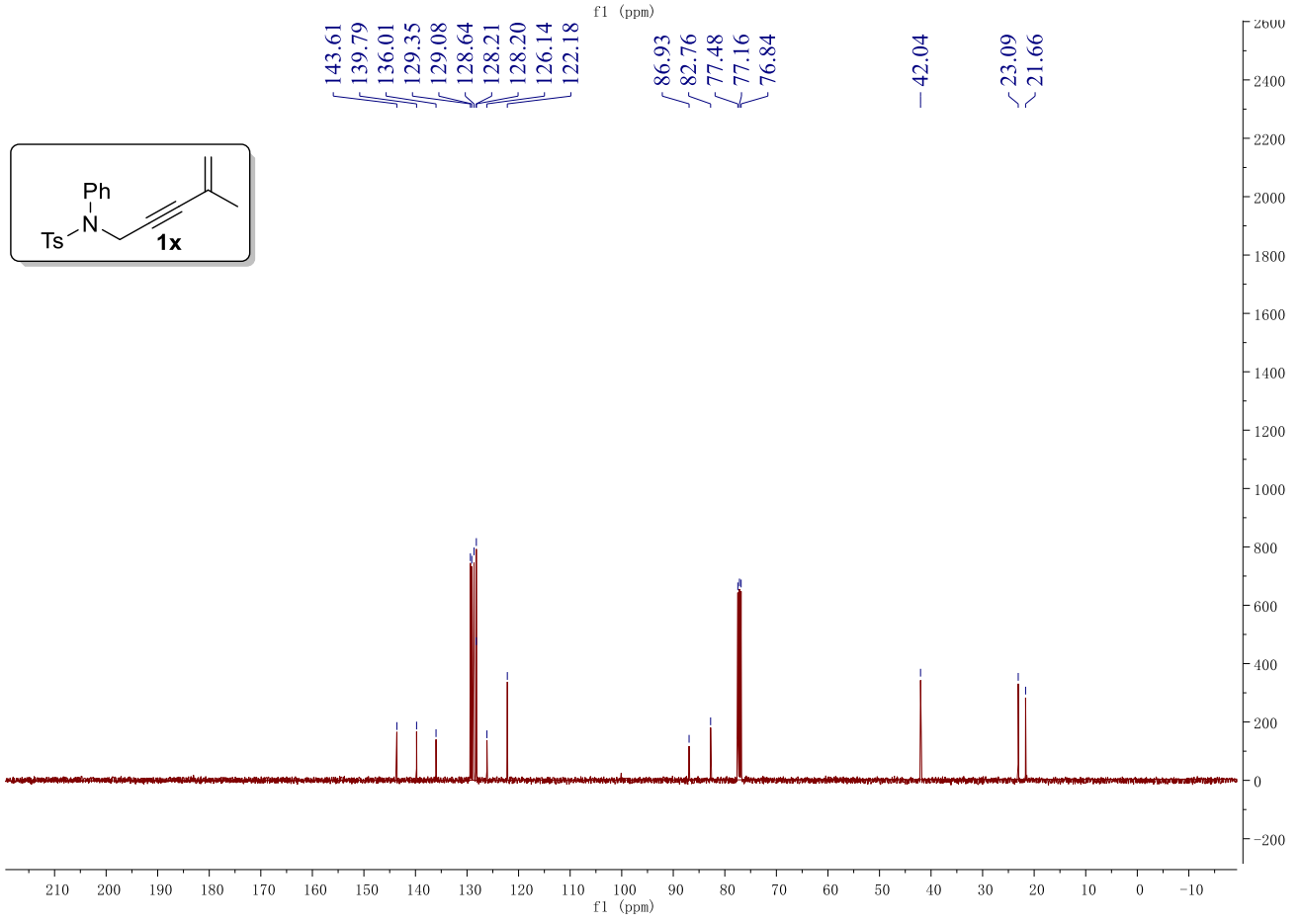
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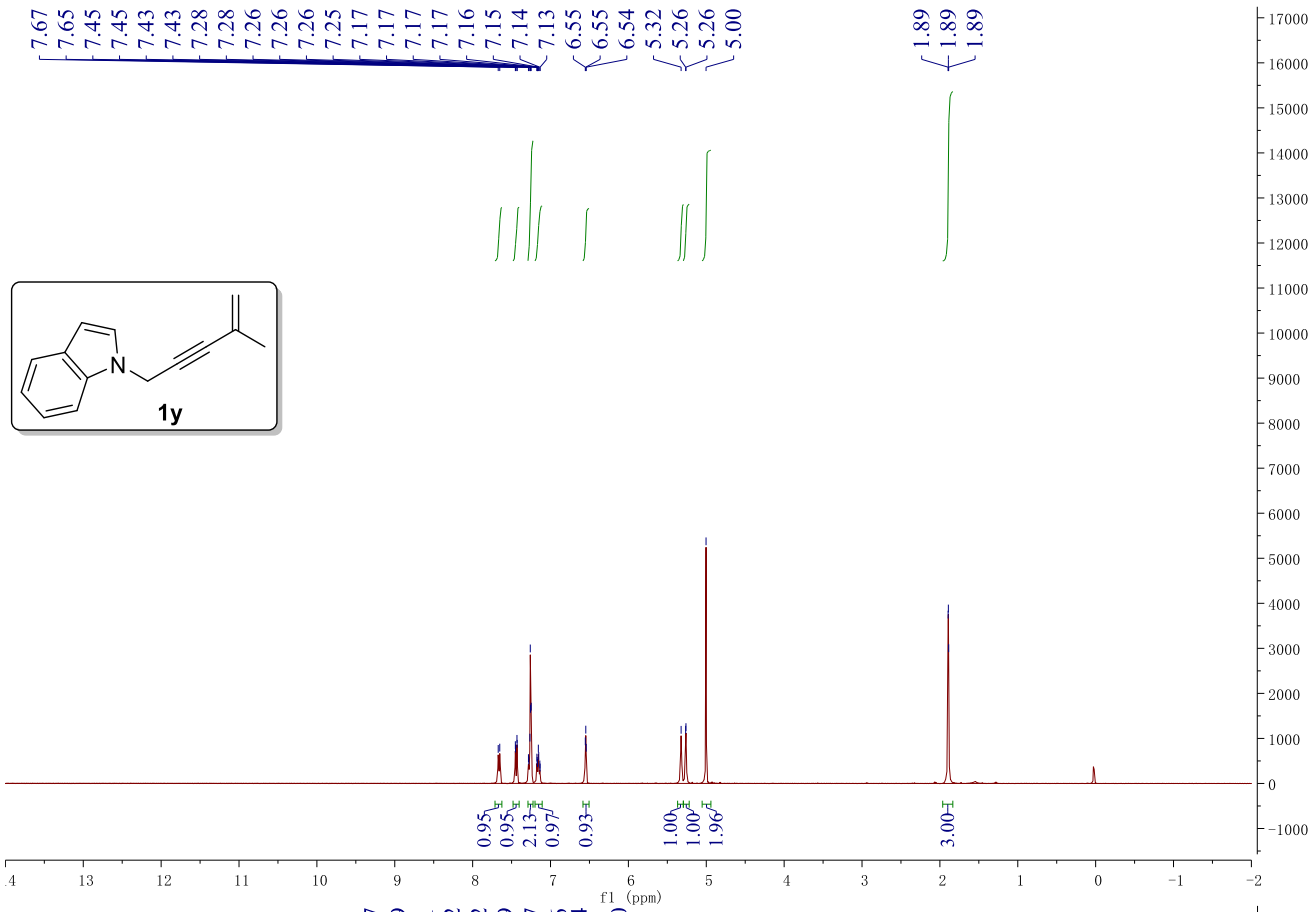
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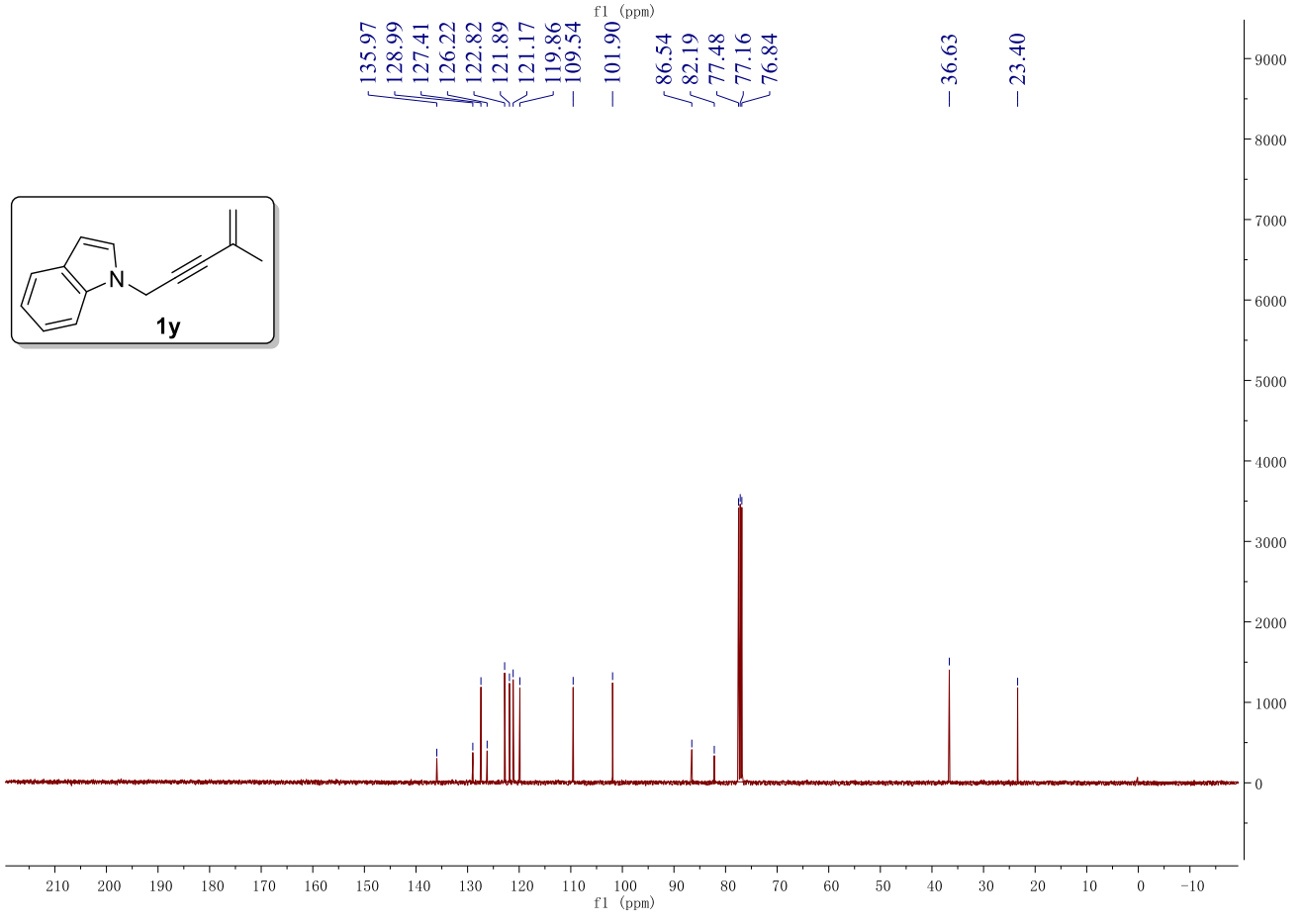
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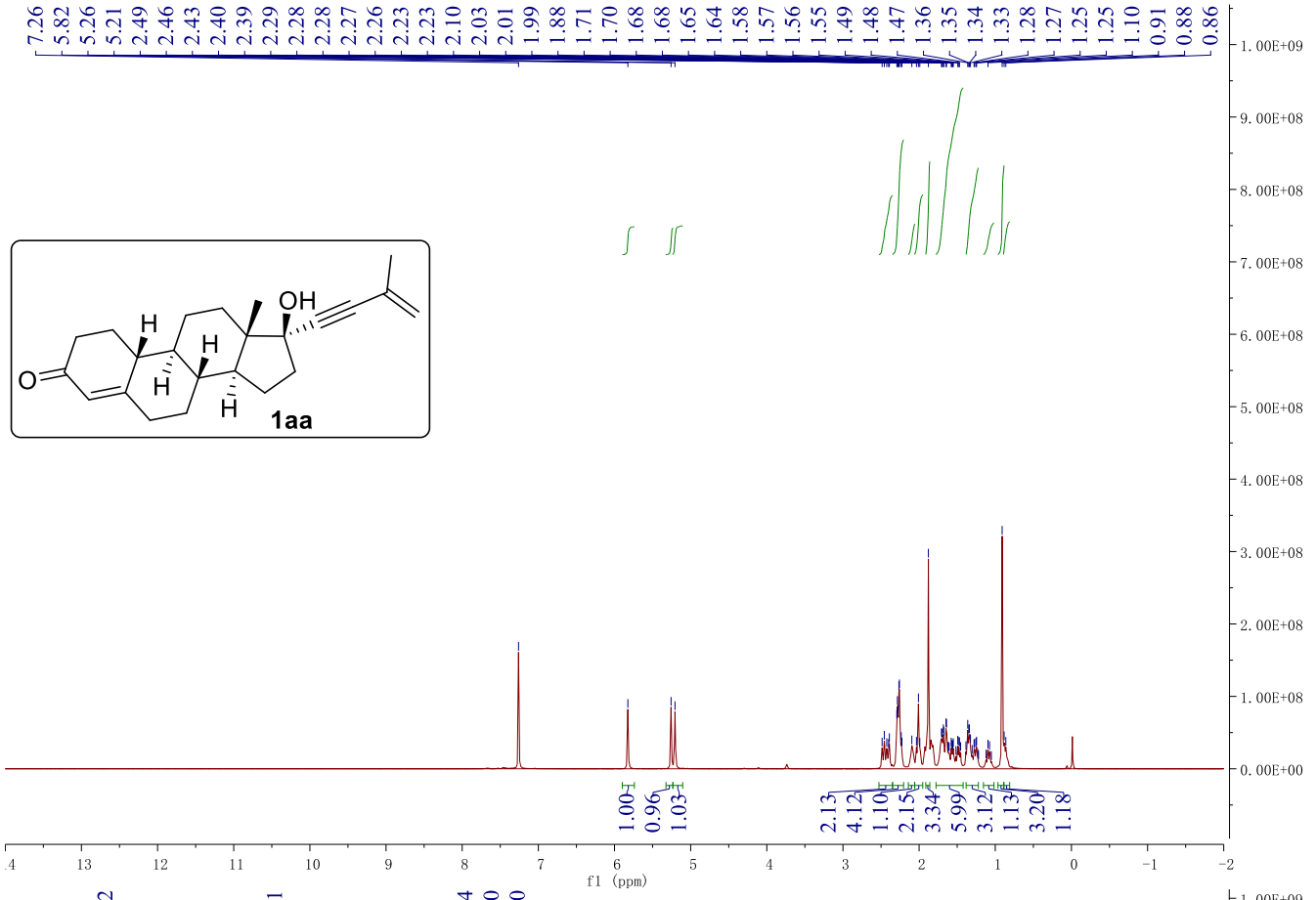
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H
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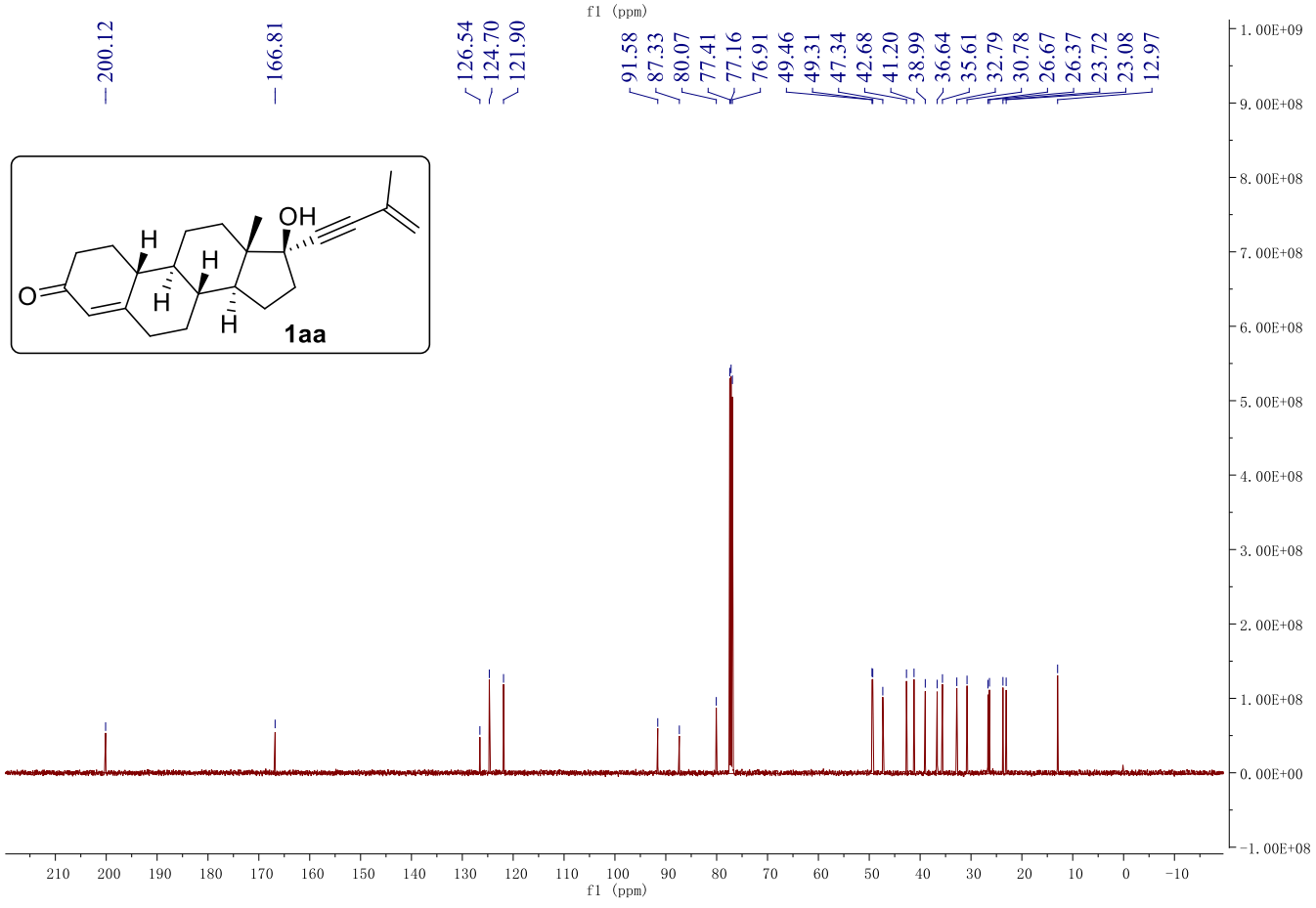
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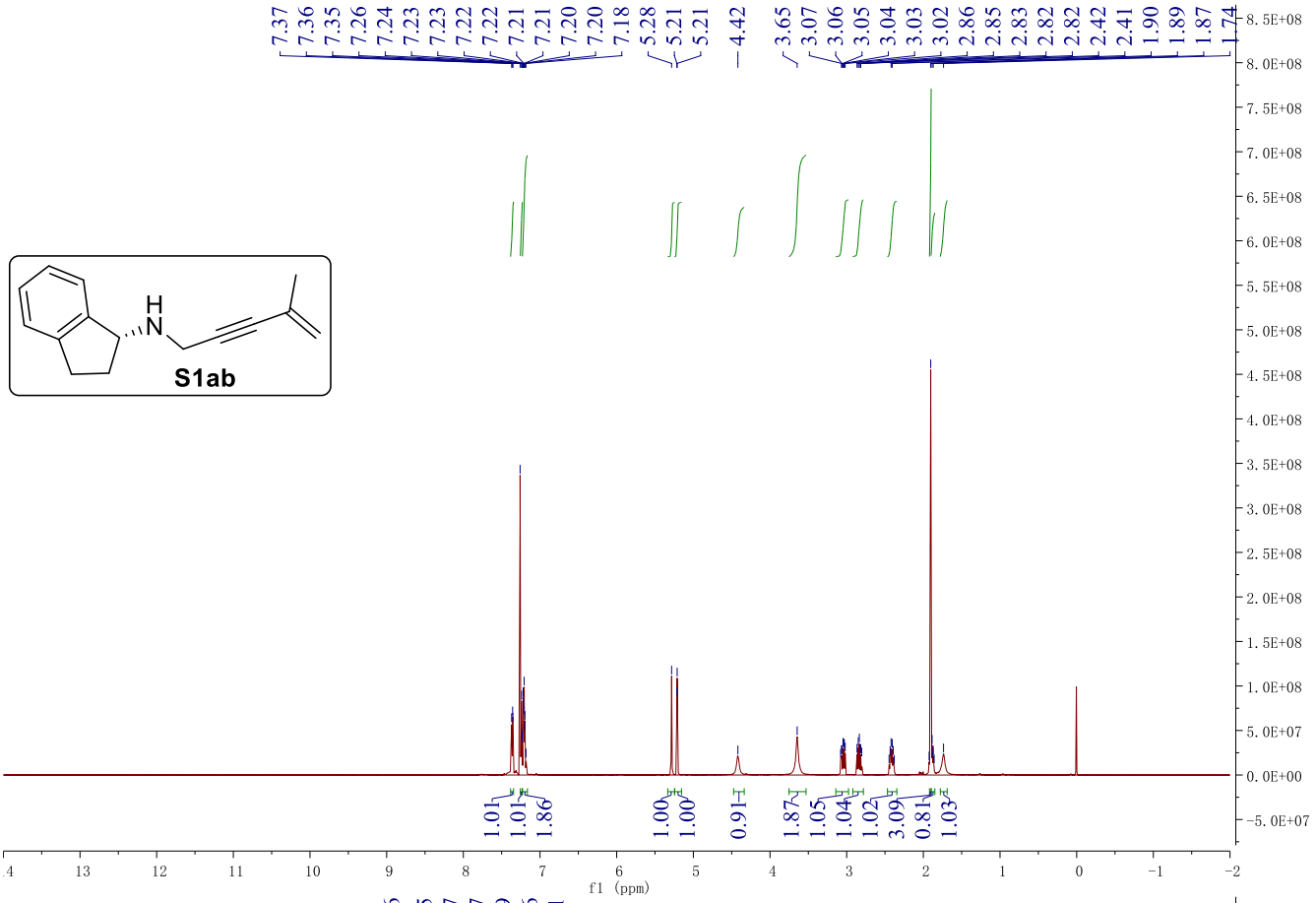
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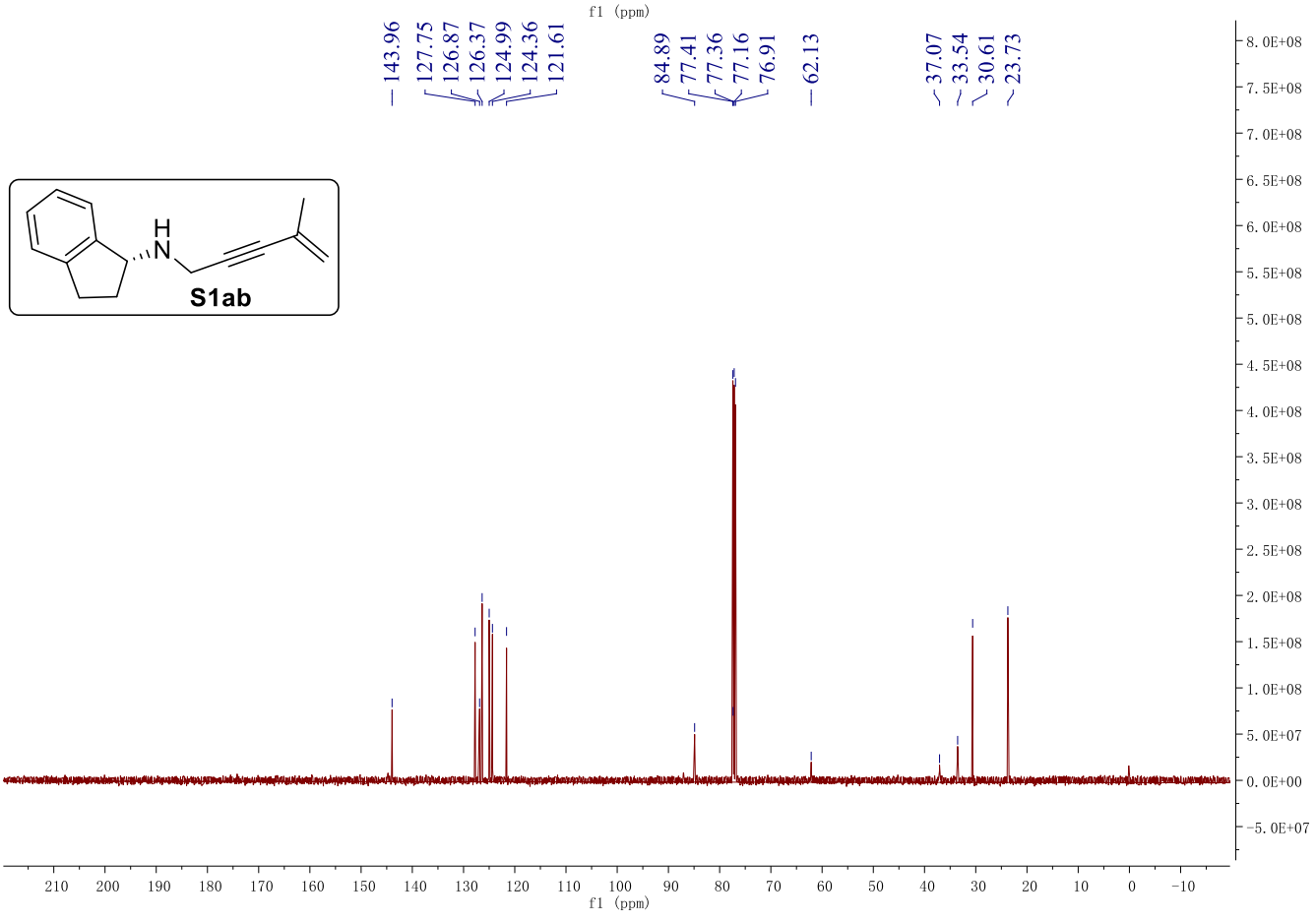
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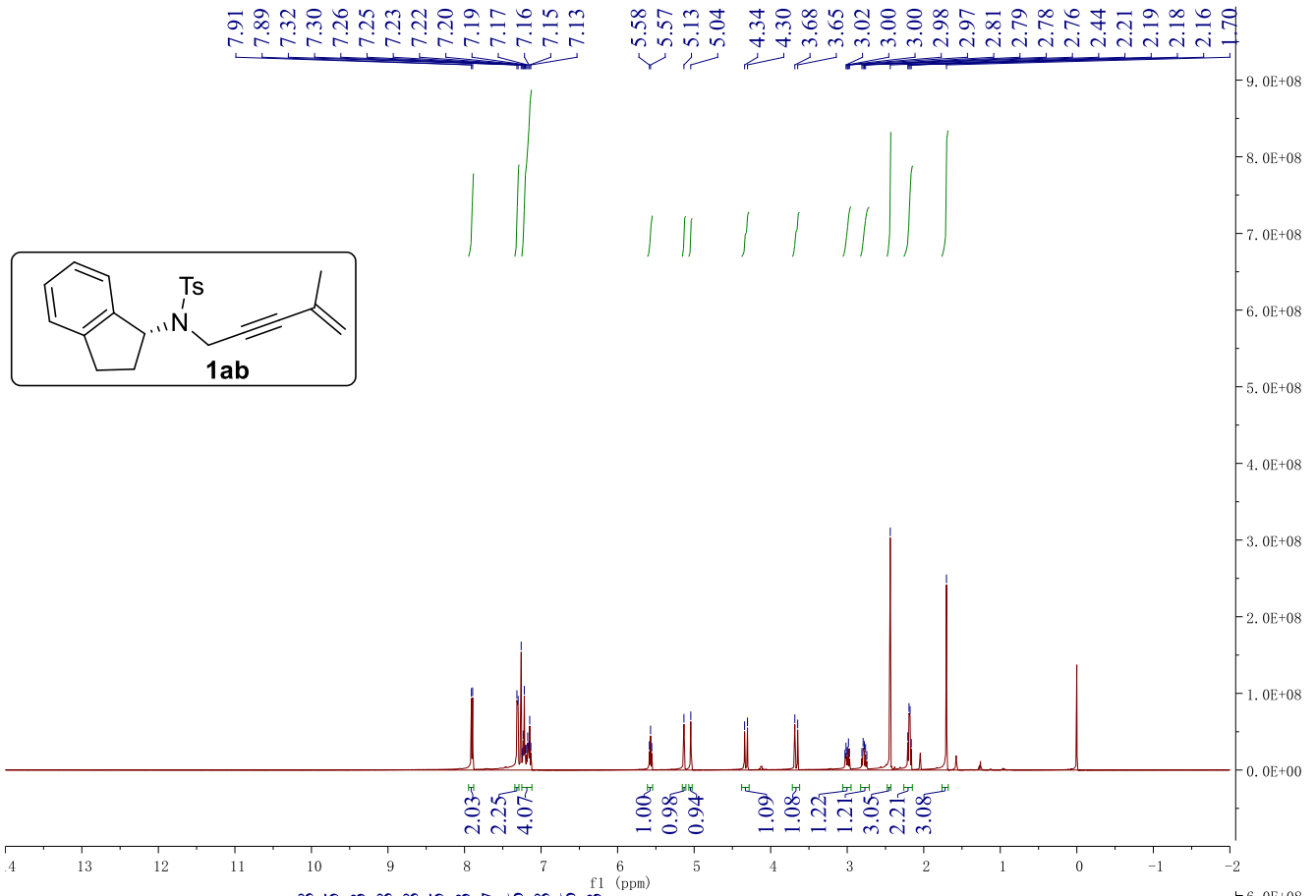
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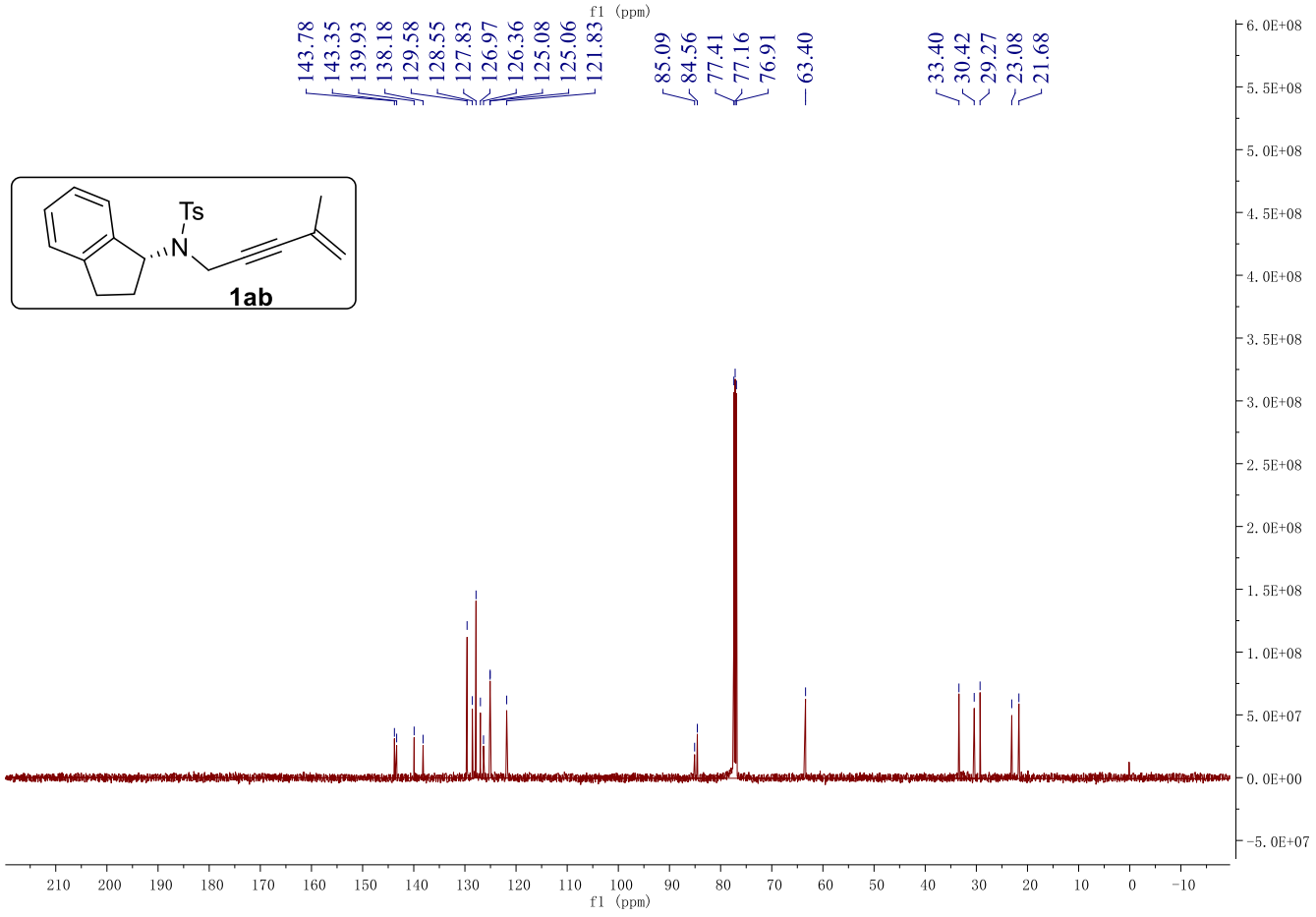
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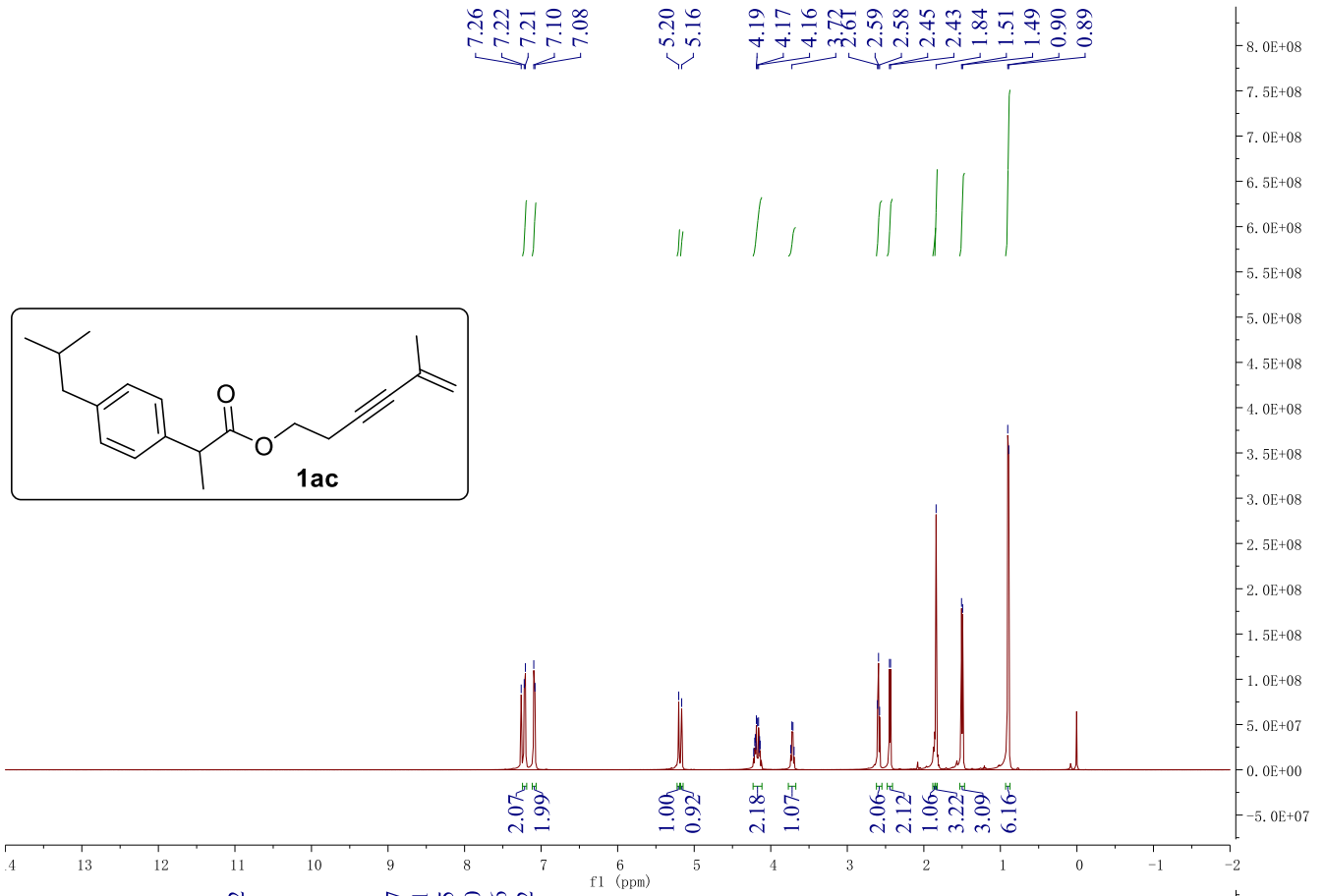
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f1 (ppm)

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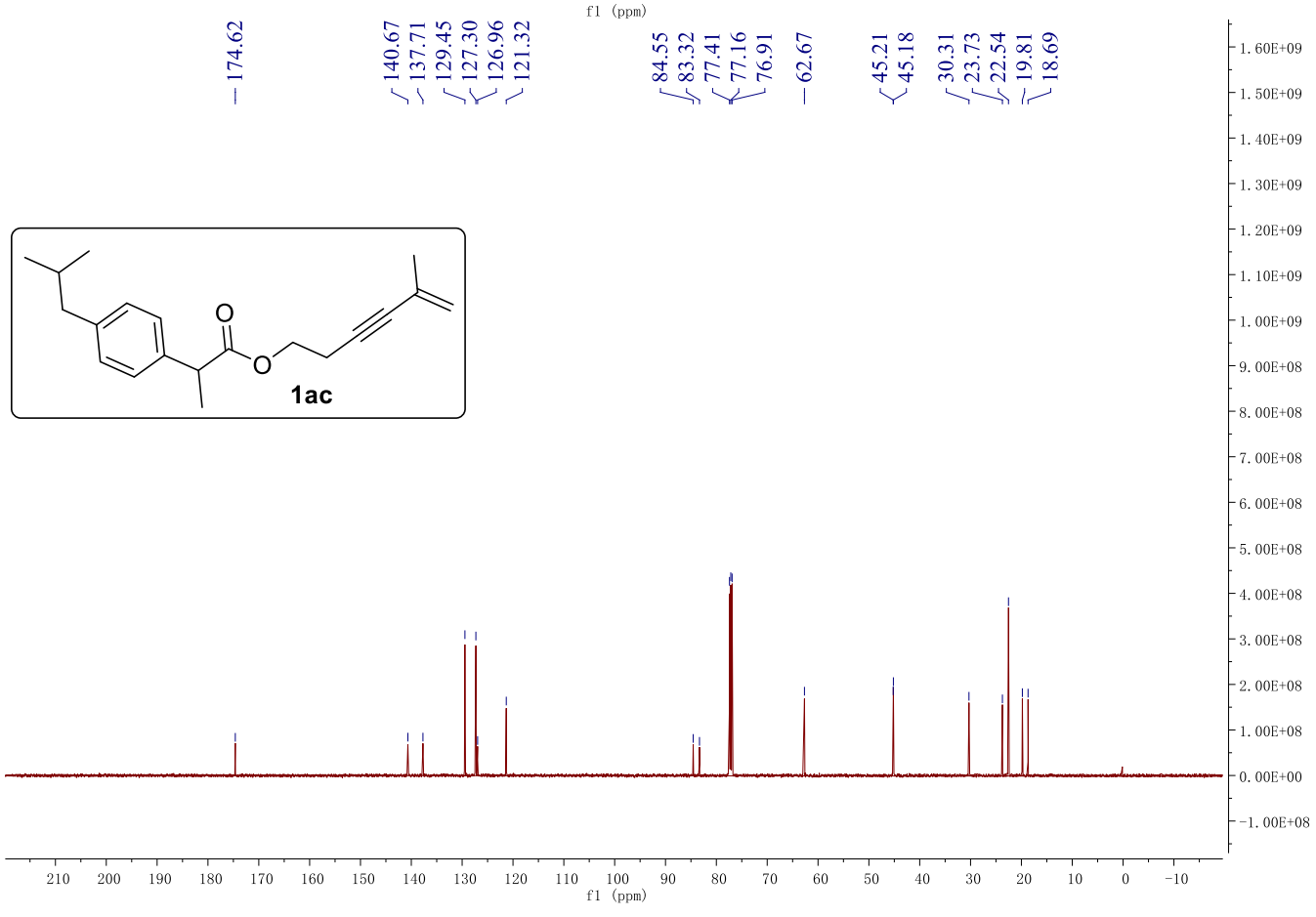
1ac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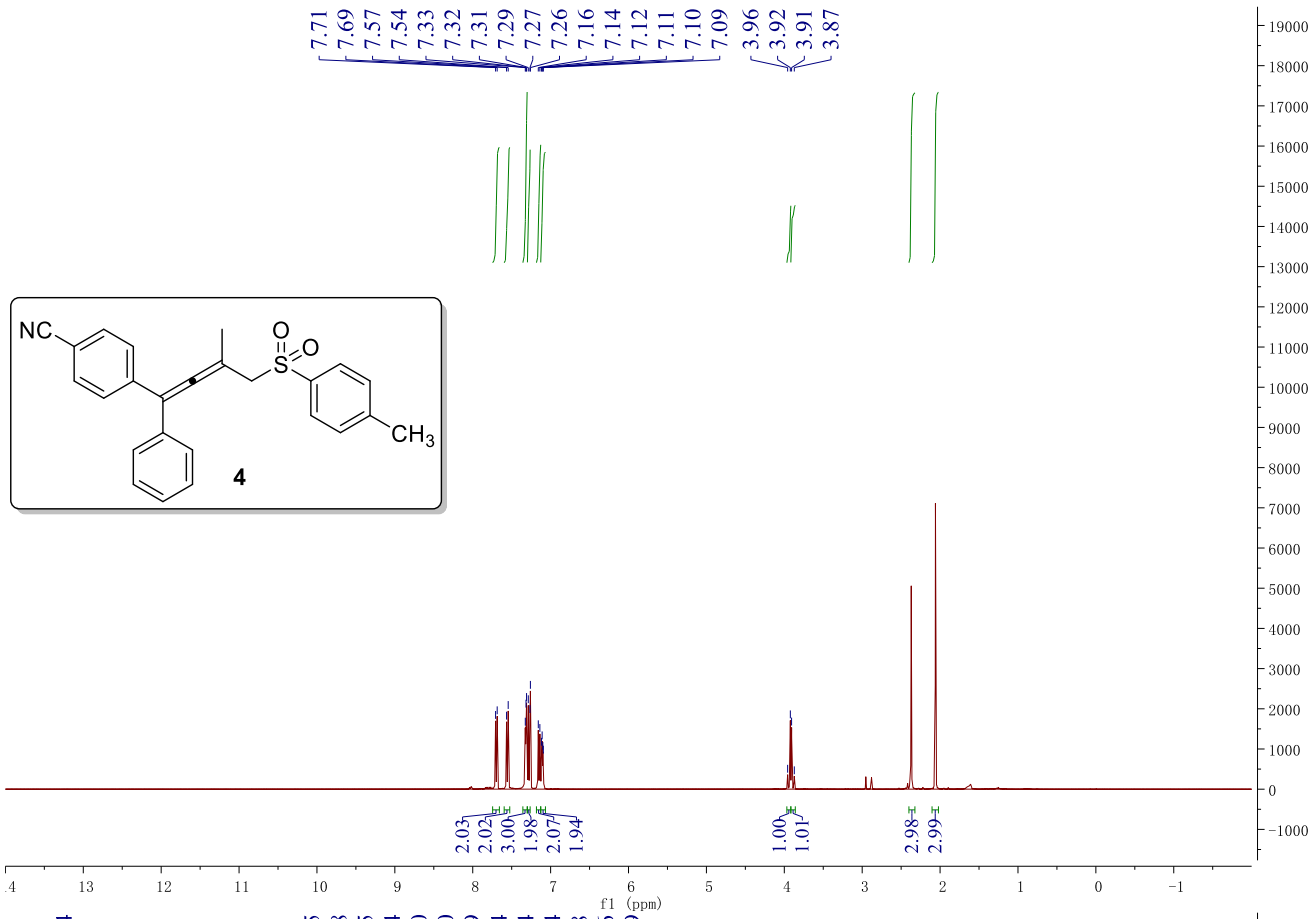
O
1ac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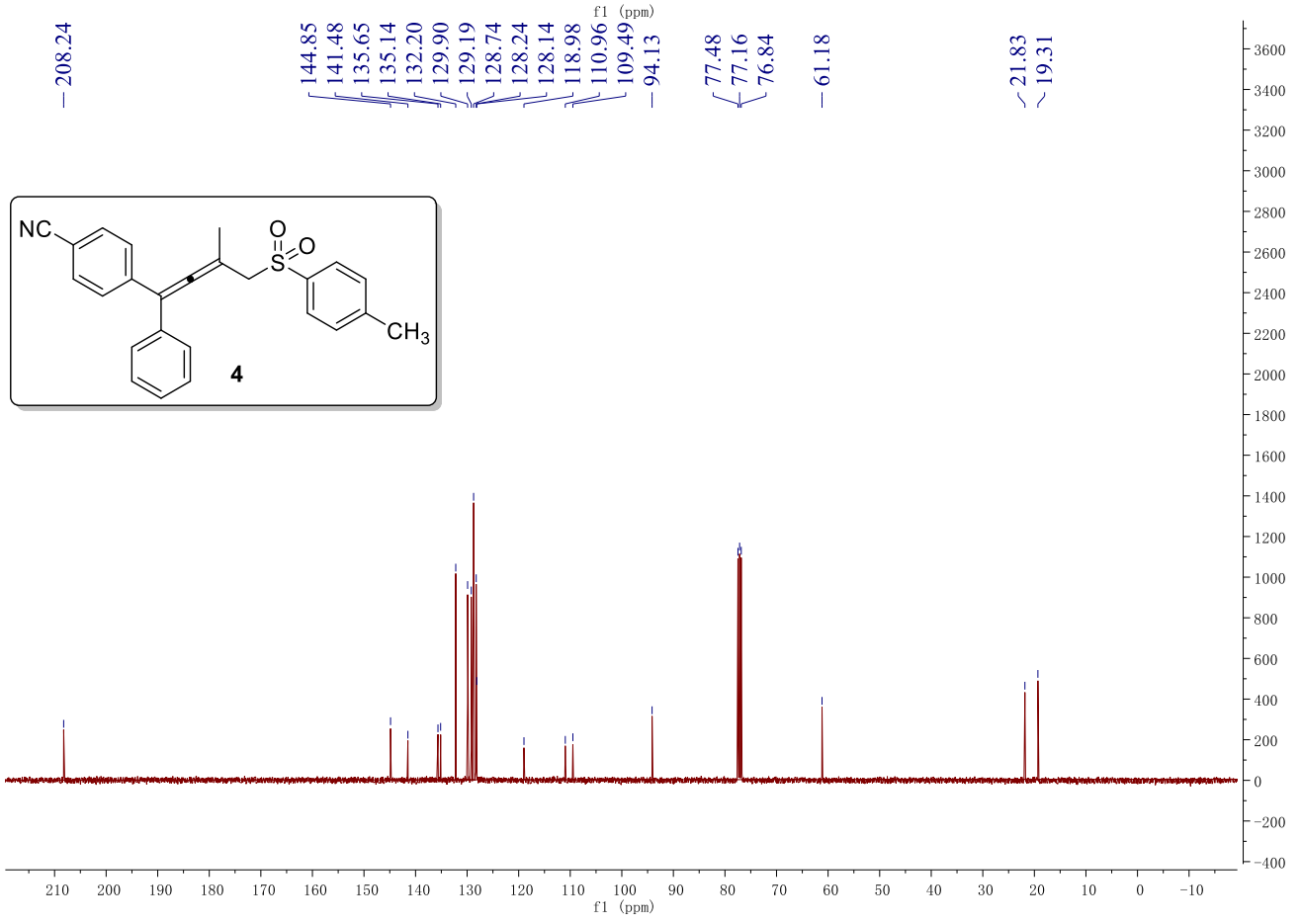
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135.65
135.14
132.20
129.90
129.19
128.74
128.24
128.14
118.98
110.96
109.49
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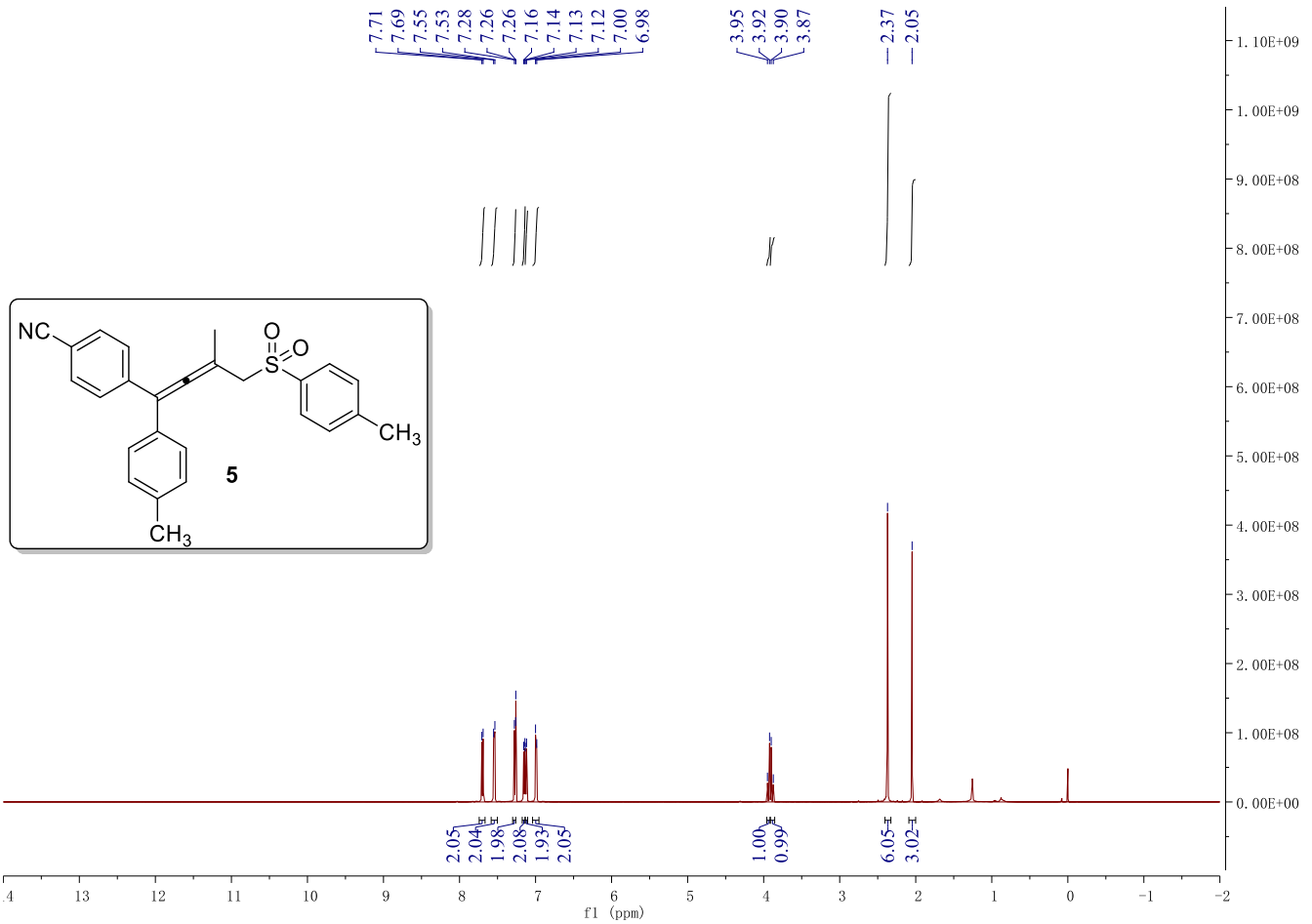
76.84
61.18
21.83
19.31
NC
O
S
O
CH3
4
f1 (ppm)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7.16
7.14
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7.12
7.00
6.98
3.95
3.92
3.90
3.87
2.37
2.05
NC
O
O
S
CH3
5
CH3
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
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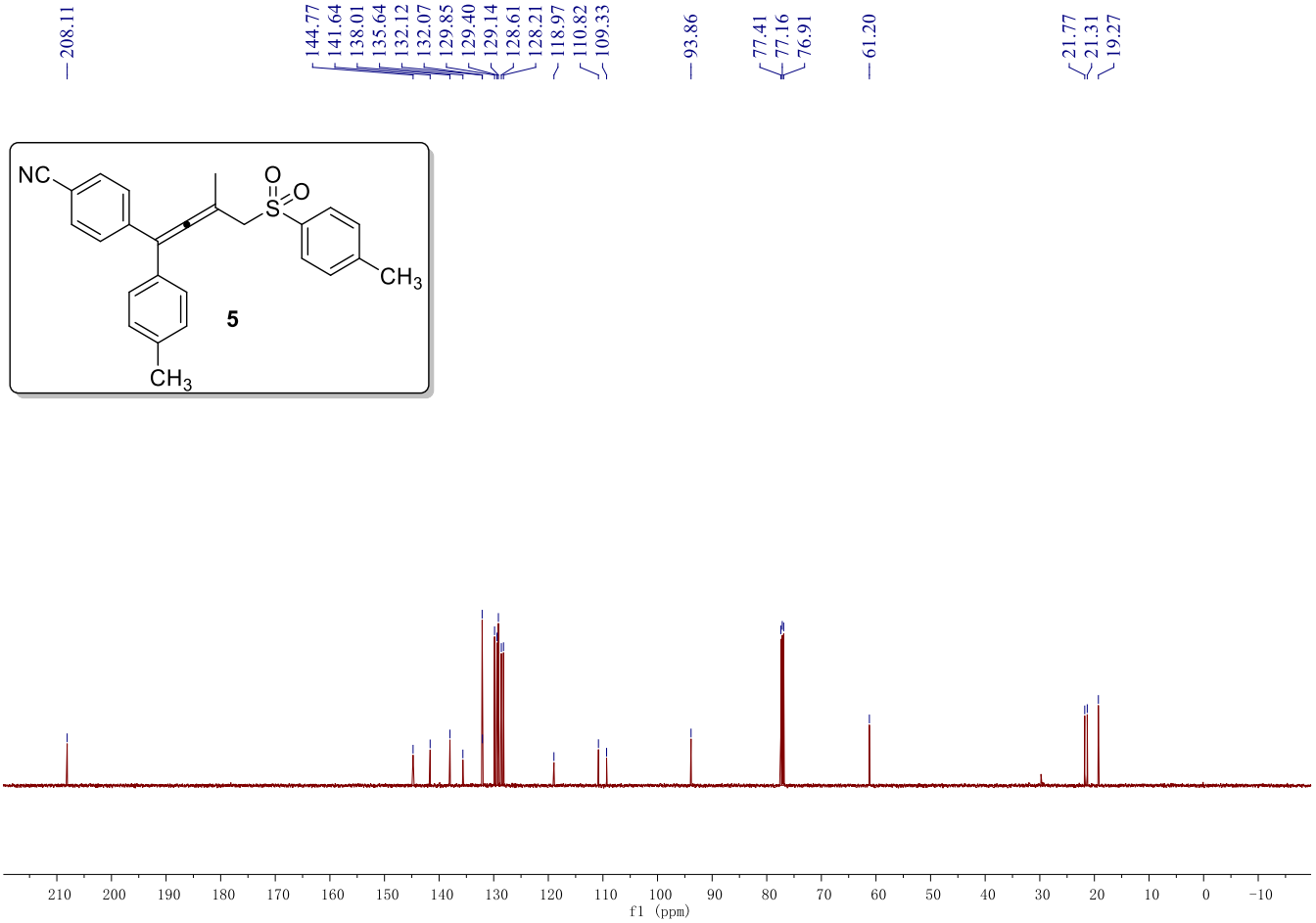
1.98
2.08
1.93
2.05
1.00
0.99
6.05
3.02
f1 (ppm)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128.21
118.97
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109.33
93.86
77.41
77.16
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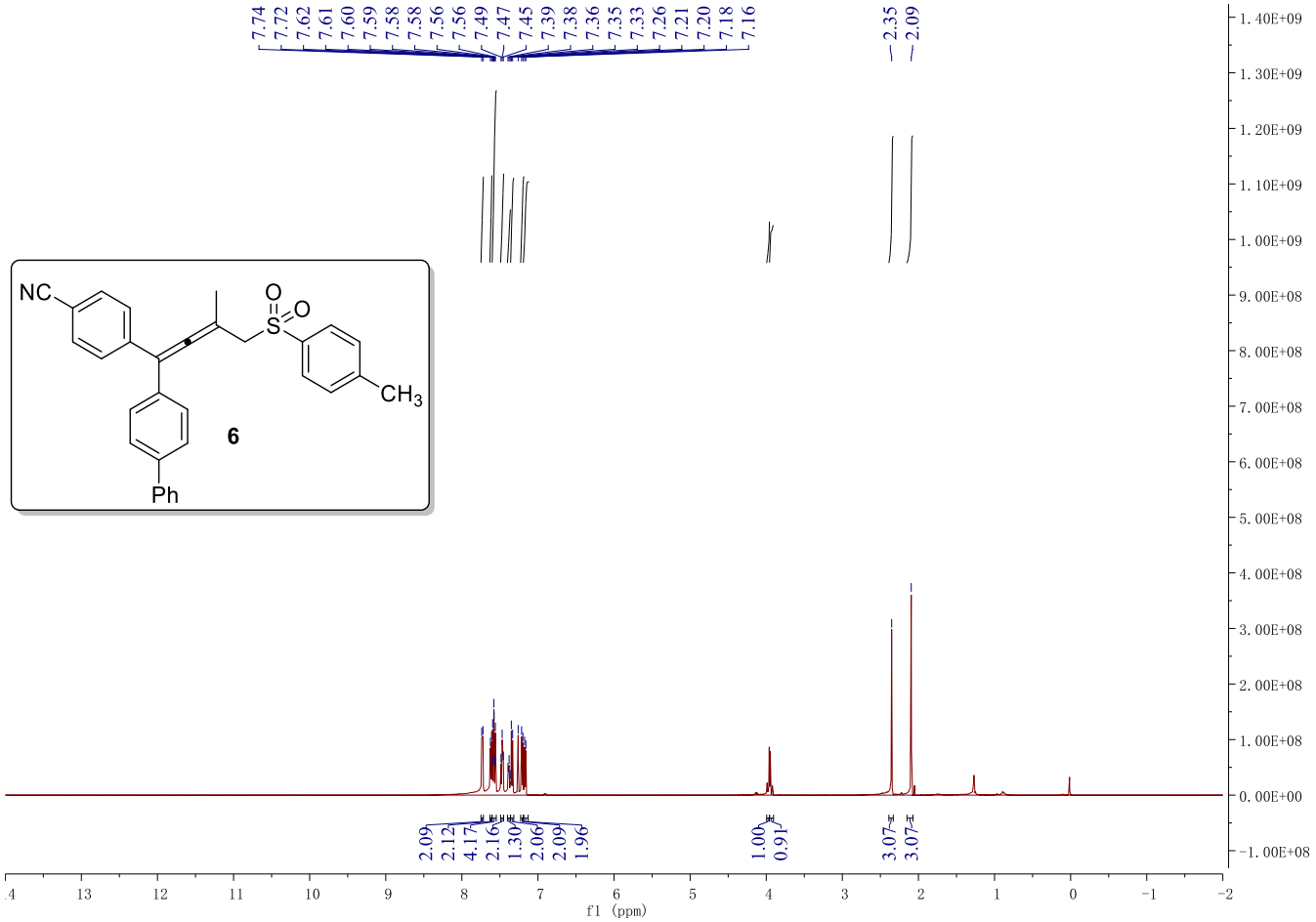
61.20
21.77
21.31
19.27
NC
O
O
S
CH3
5
CH3
f1 (ppm)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7.47
7.45
7.39
7.38
7.36
7.35
7.33
7.26
7.21
7.20
7.18
7.16
2.35
2.09
NC
O
O
S
CH3
6
Ph
2.09
2.12
4.17
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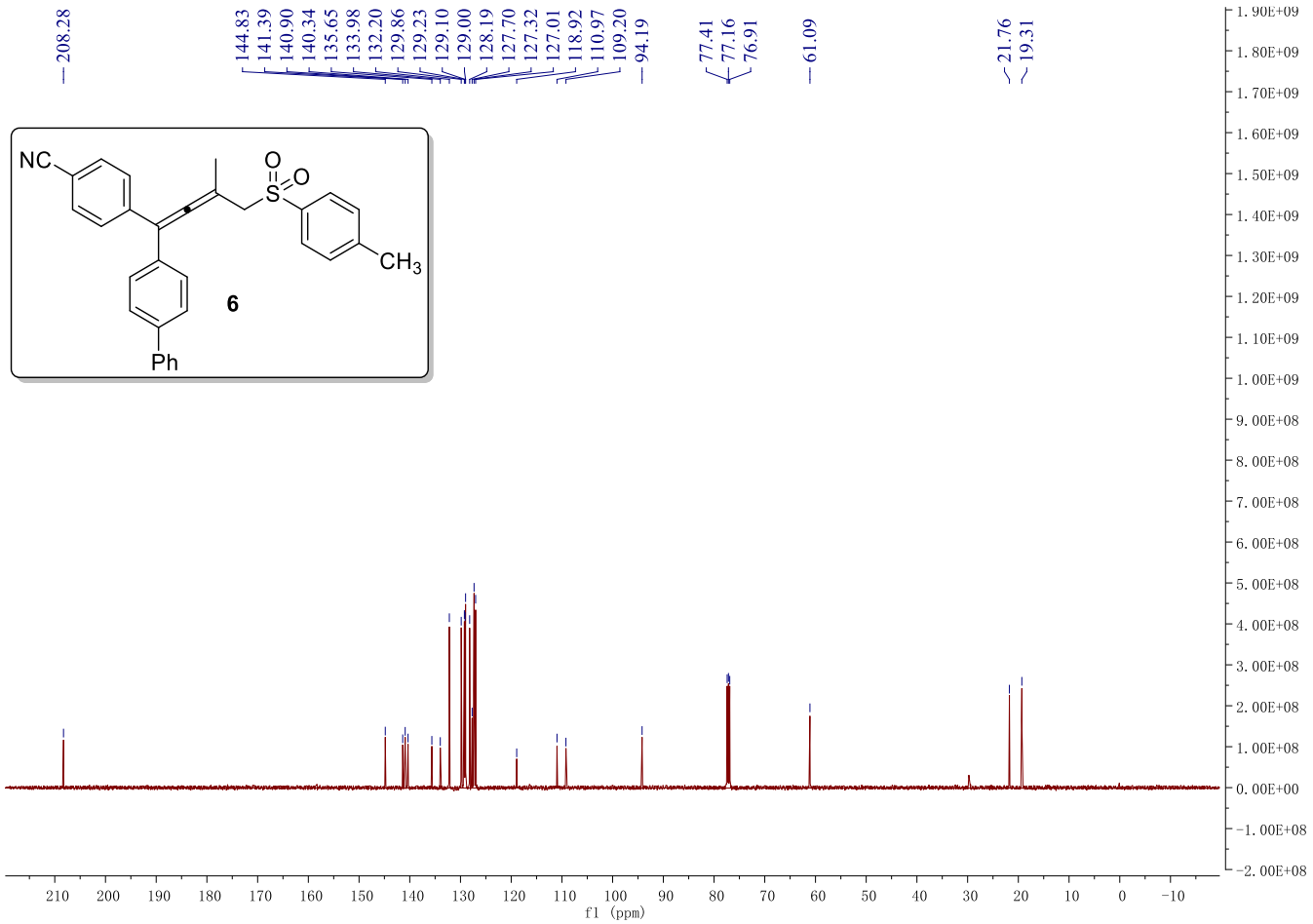
2.06
2.09
1.96
1.00
0.91
3.07
3.07
f1 (ppm)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132.20
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129.10
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128.19
127.70
127.32
127.01
118.92
110.97
109.20
94.19
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61.09
21.76
19.31
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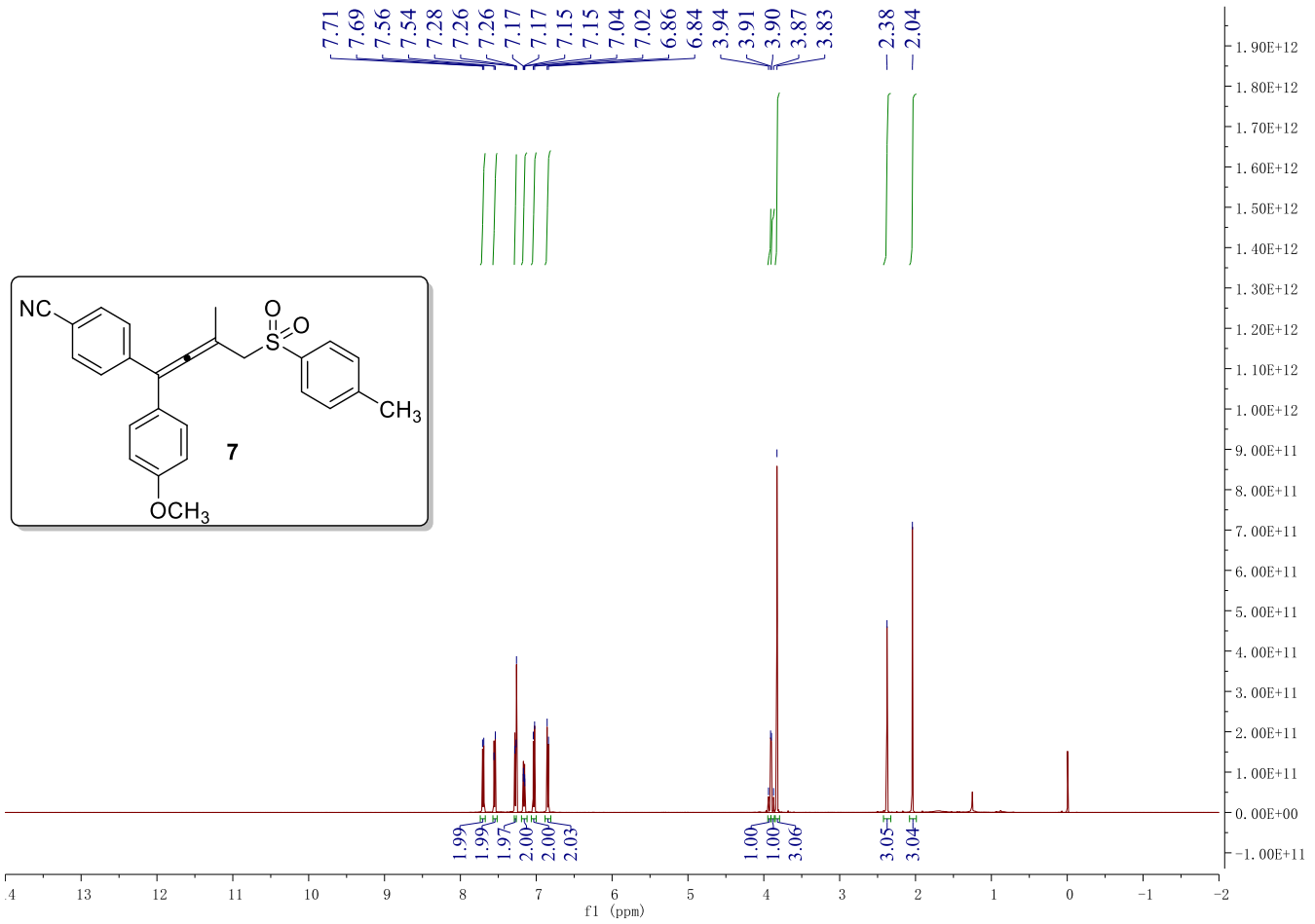
O
O
S
CH3
6
Ph
f1 (ppm)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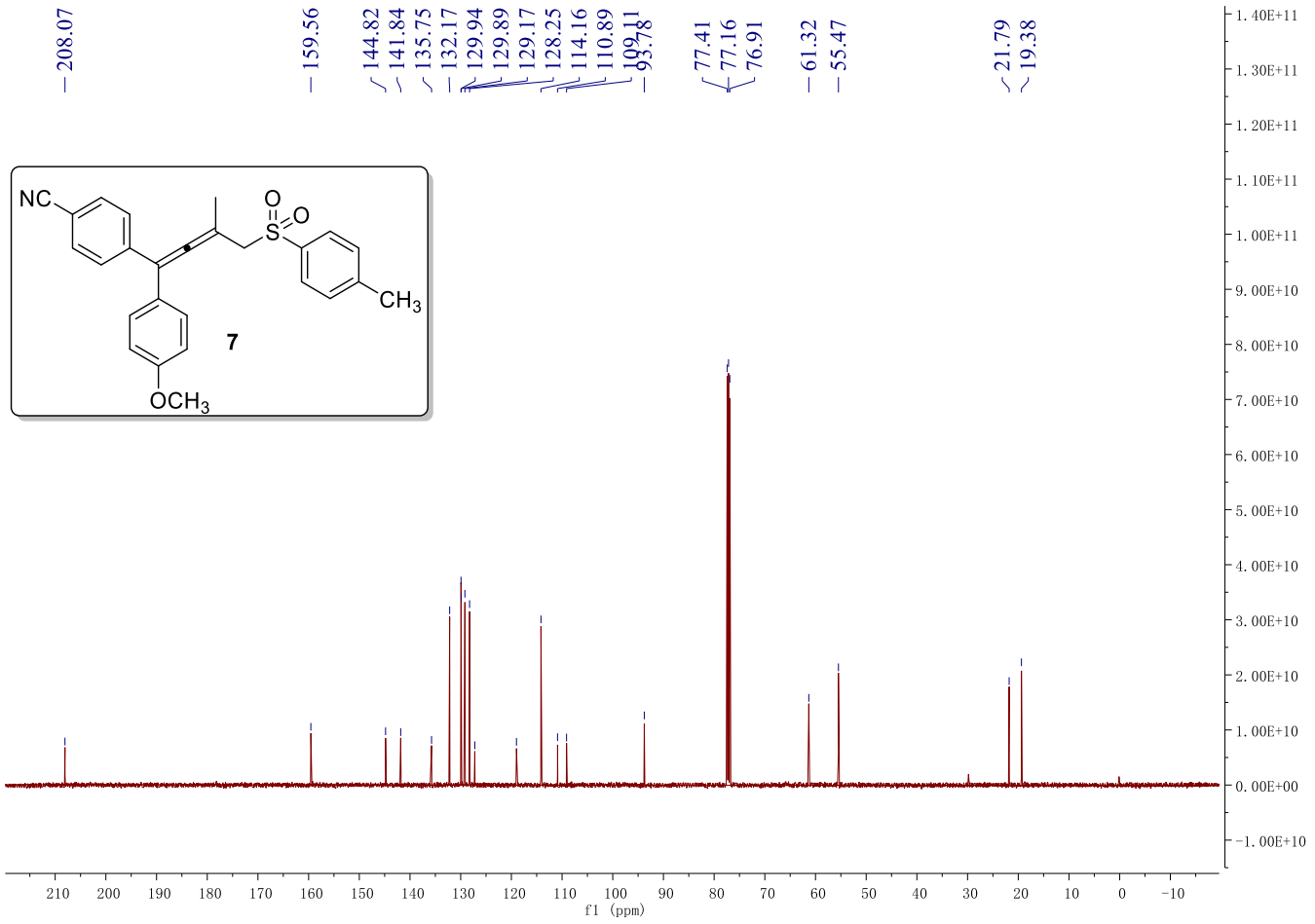
7.15
7.04
7.02
6.86
6.84
3.94
3.91
3.90
3.87
3.83
2.38
2.04
NC
O
S
O
CH3
7
OCH3
1.99
1.99
1.97
2.00
2.00
2.03
1.00
1.00
3.06
3.05
3.04
f1 (ppm)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114.16
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93.78
77.41
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55.47
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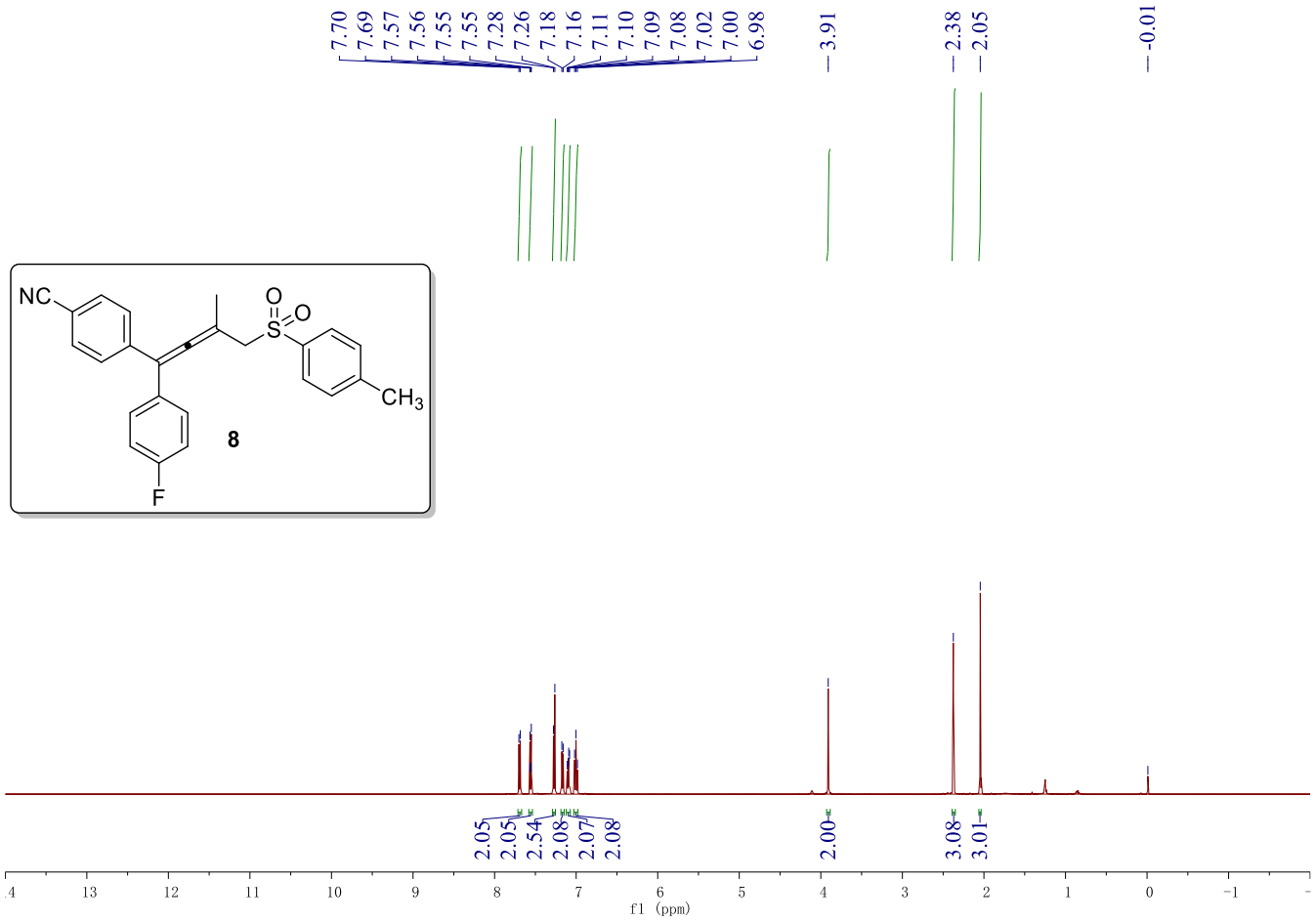
19.38
NC
O
S
O
CH3
7
OCH3
f1 (ppm)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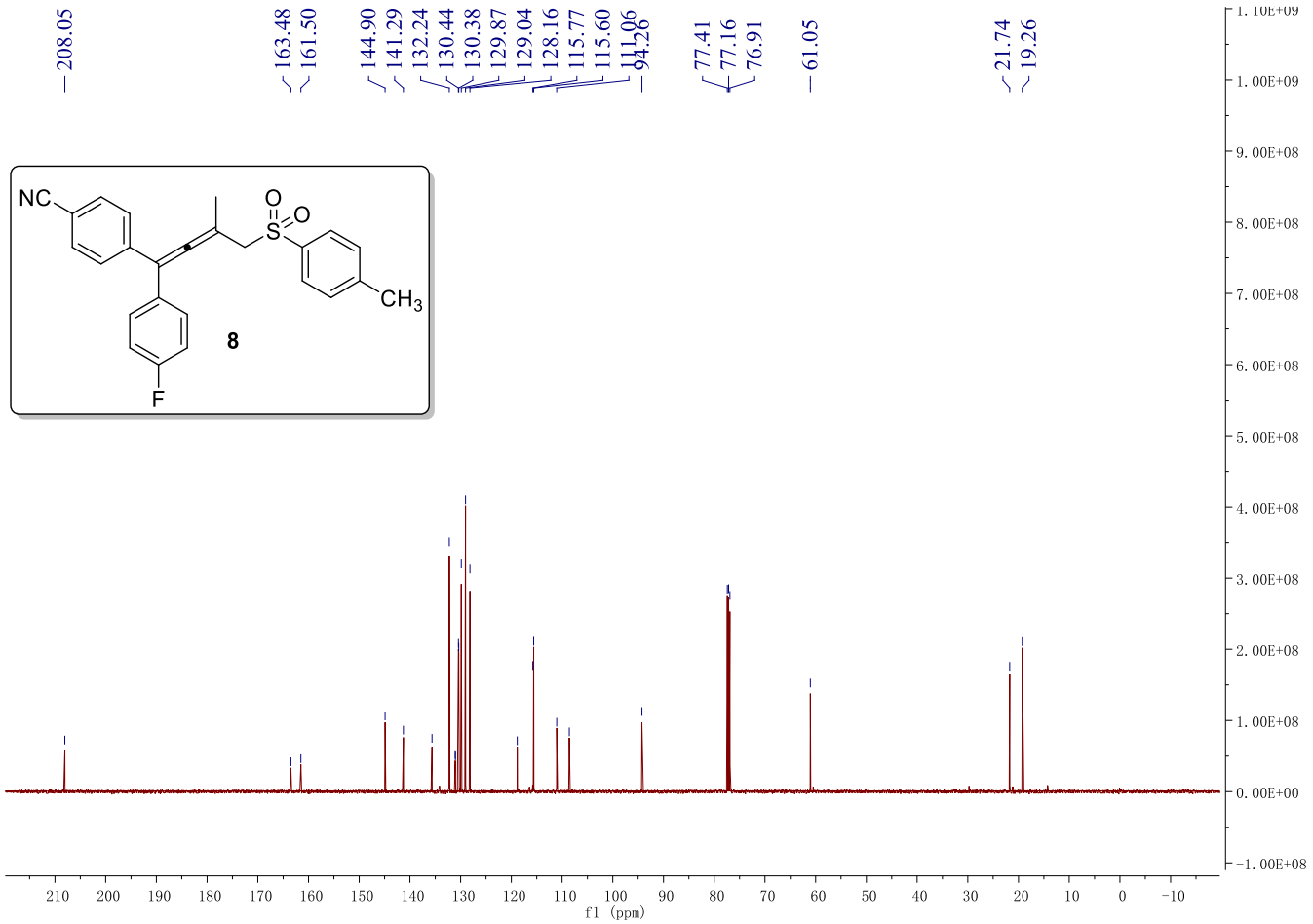
7.55
7.28
7.26
7.18
7.16
7.11
7.10
7.09
7.08
7.02
7.00
6.98
3.91
2.38
2.05
-0.01
NC
O
O
S
CH3
8
F
2.05
2.05
2.54
2.08
2.07
2.08
2.00
3.08
3.01
f1 (ppm)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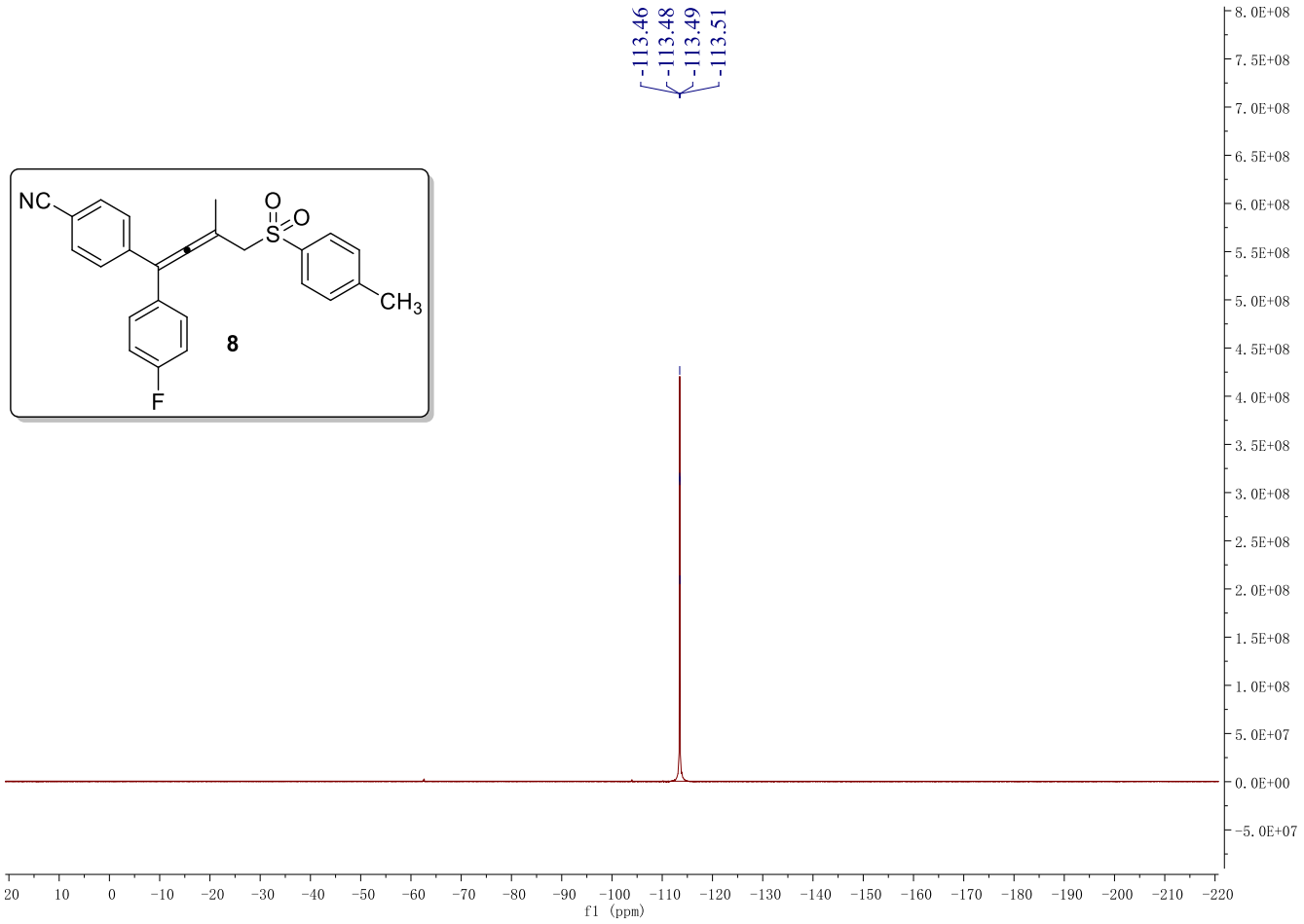
141.29
132.24
130.44
130.38
129.87
129.04
128.16
115.77
115.60
111.06
94.26
77.41
77.16
76.91
61.05
21.74
19.26
NC
O
O
S
CH3
8
F
f1 (ppm)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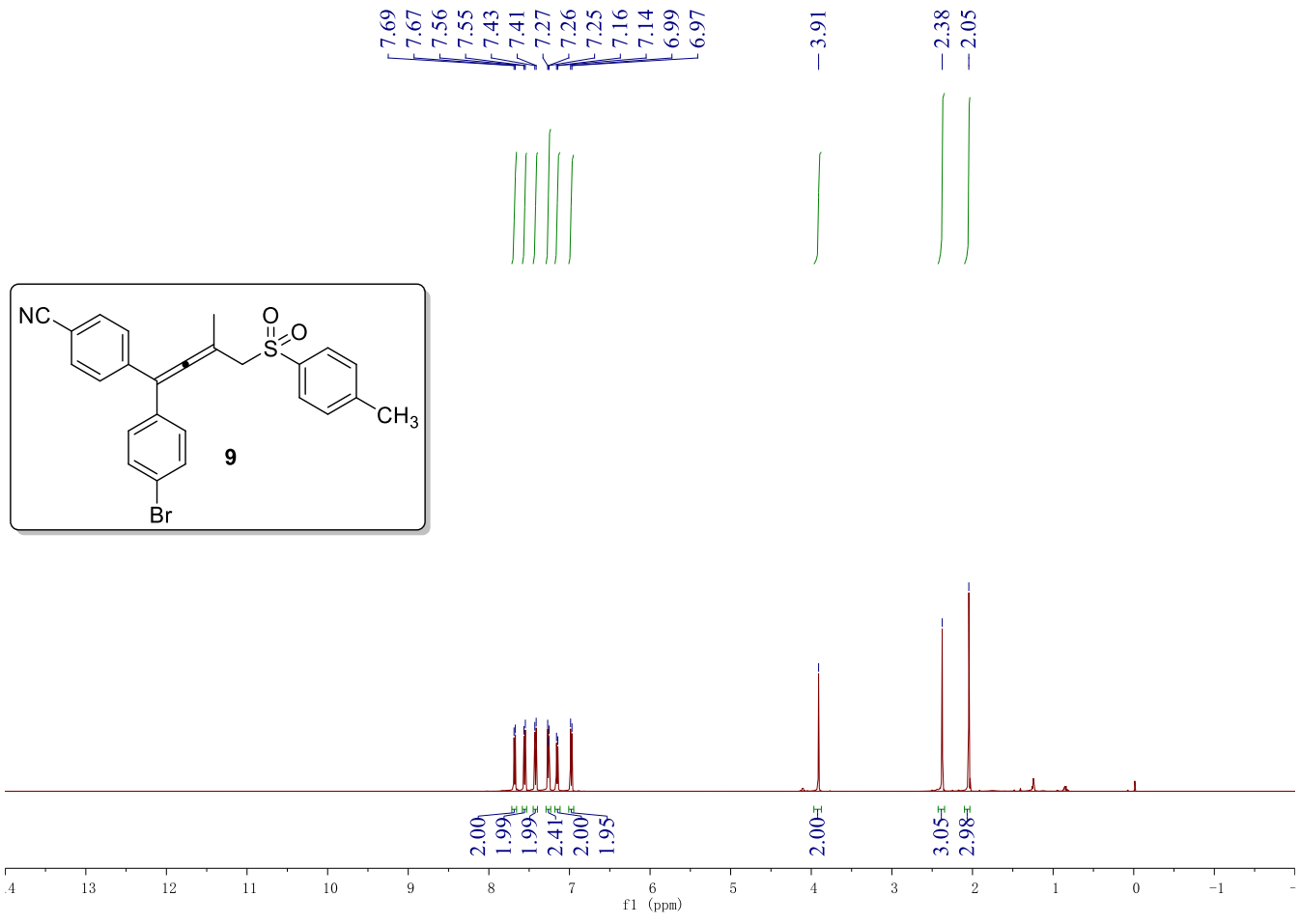
-113.48
-113.49
-113.51
NC
O
O
S
CH3
8
F
f1 (ppm)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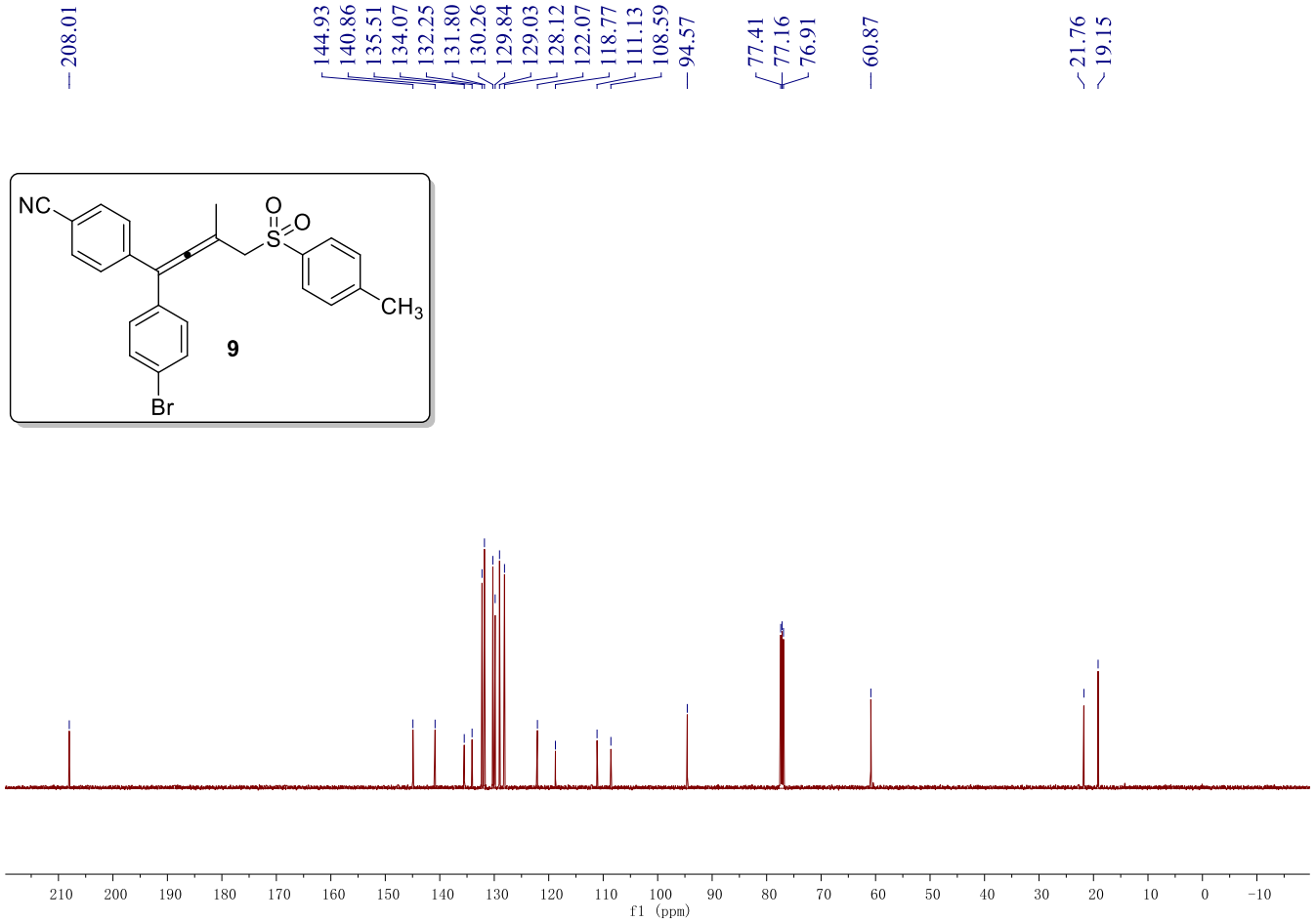
7.26
7.25
7.16
7.14
6.99
6.97
3.91
2.38
2.05
NC
O
O
S
CH3
9
Br
2.00
1.99
1.99
2.41
2.00
1.95
2.00
3.05
2.98
f1 (ppm)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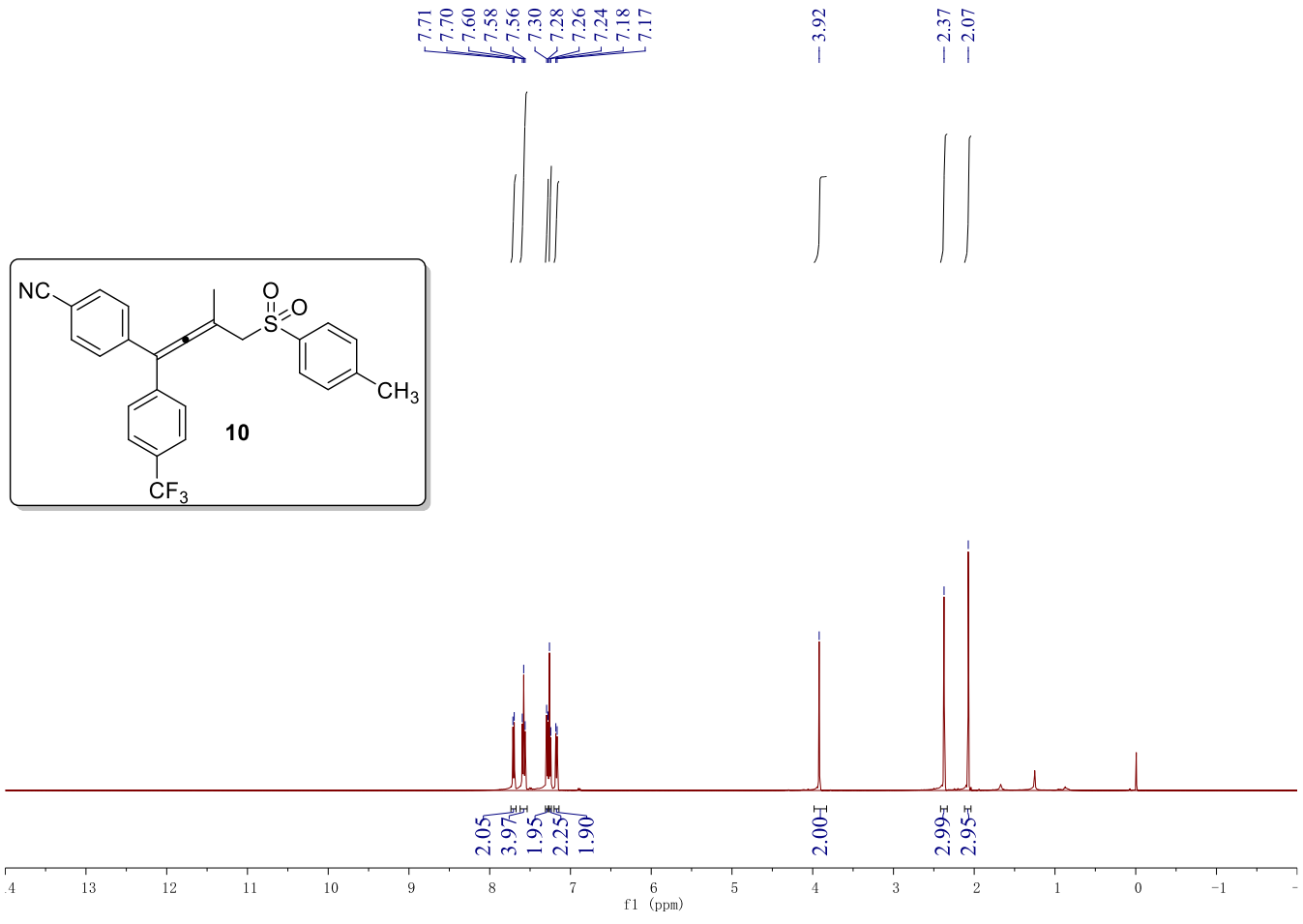
130.26
129.84
129.03
128.12
122.07
118.77
111.13
108.59
94.57
77.41
77.16
76.91
60.87
21.76
19.15
NC
O
O
S
CH3
9
Br
f1 (ppm)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7.70
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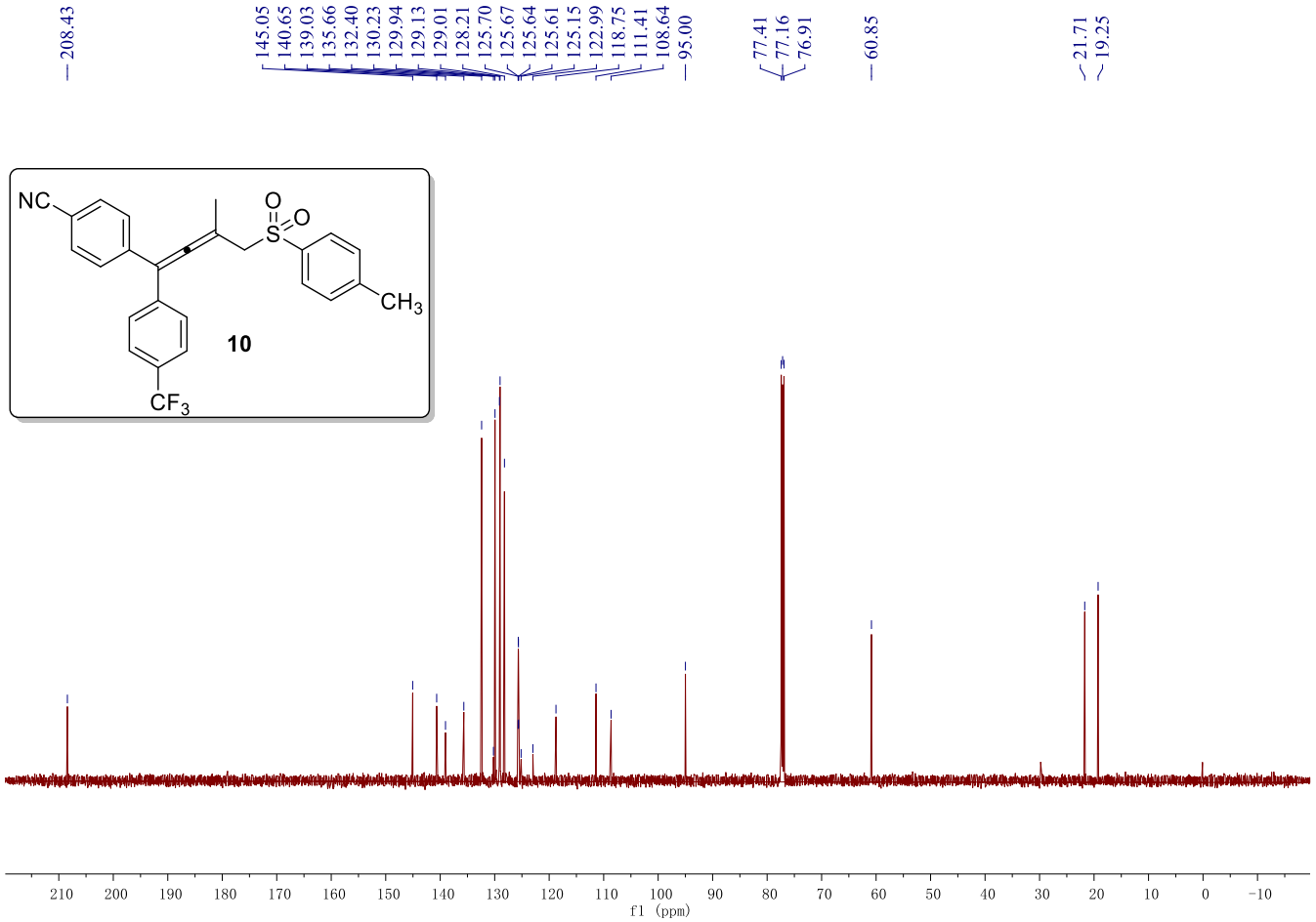
7.58
7.56
7.30
7.28
7.26
7.24
7.18
7.17
3.92
2.37
2.07
NC
O
O
S
CH3
10
CF3
2.05
3.97
1.95
2.25
1.90
2.00
2.99
2.95
f1 (ppm)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140.65
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135.66
132.40
130.23
129.94
129.13
129.01
128.21
125.70
125.67
125.64
125.61
125.15
122.99
118.75
111.41
108.64
95.00
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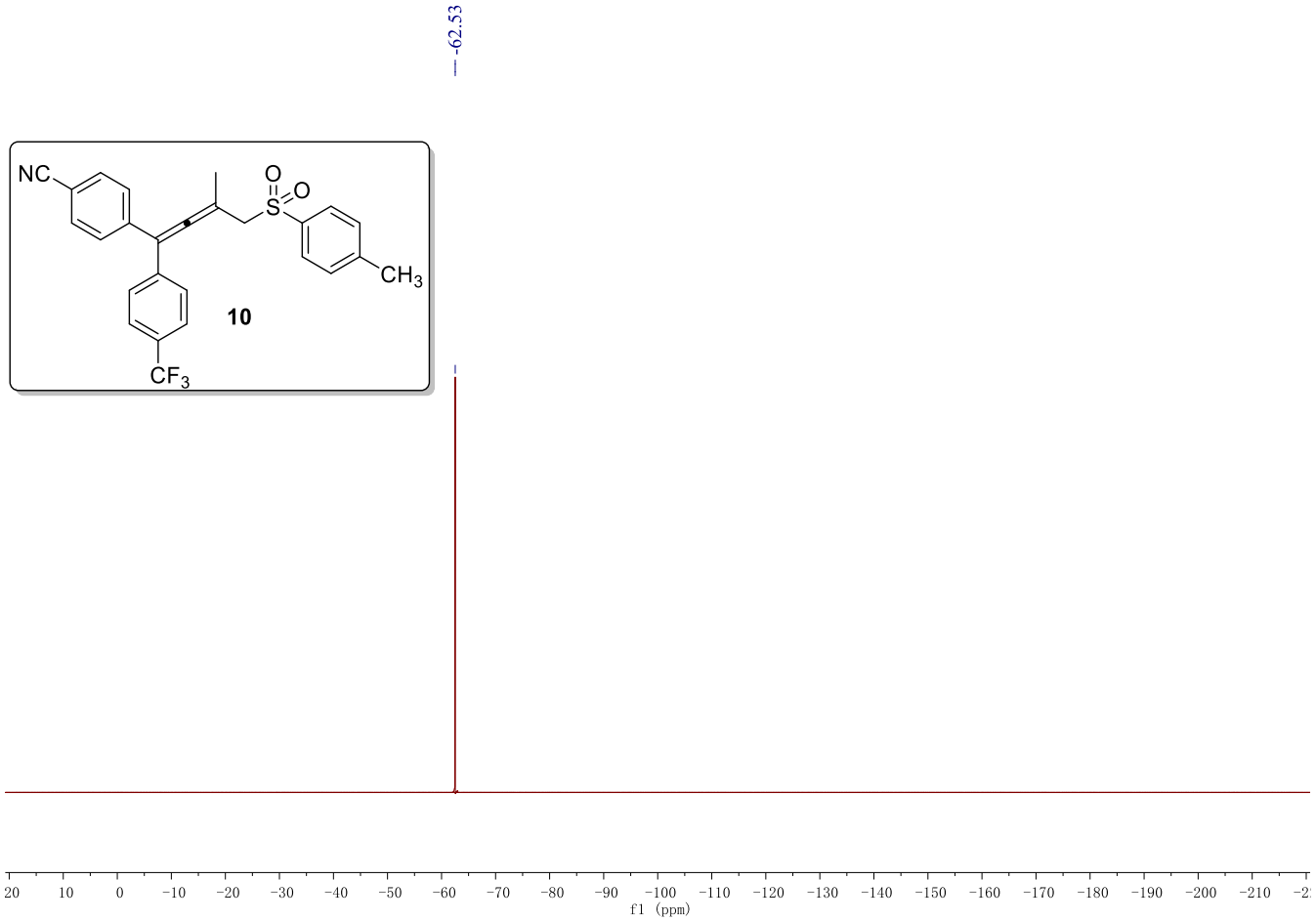
77.16
76.91
60.85
21.71
19.25
NC
O
O
S
CH3
10
CF3
f1 (ppm)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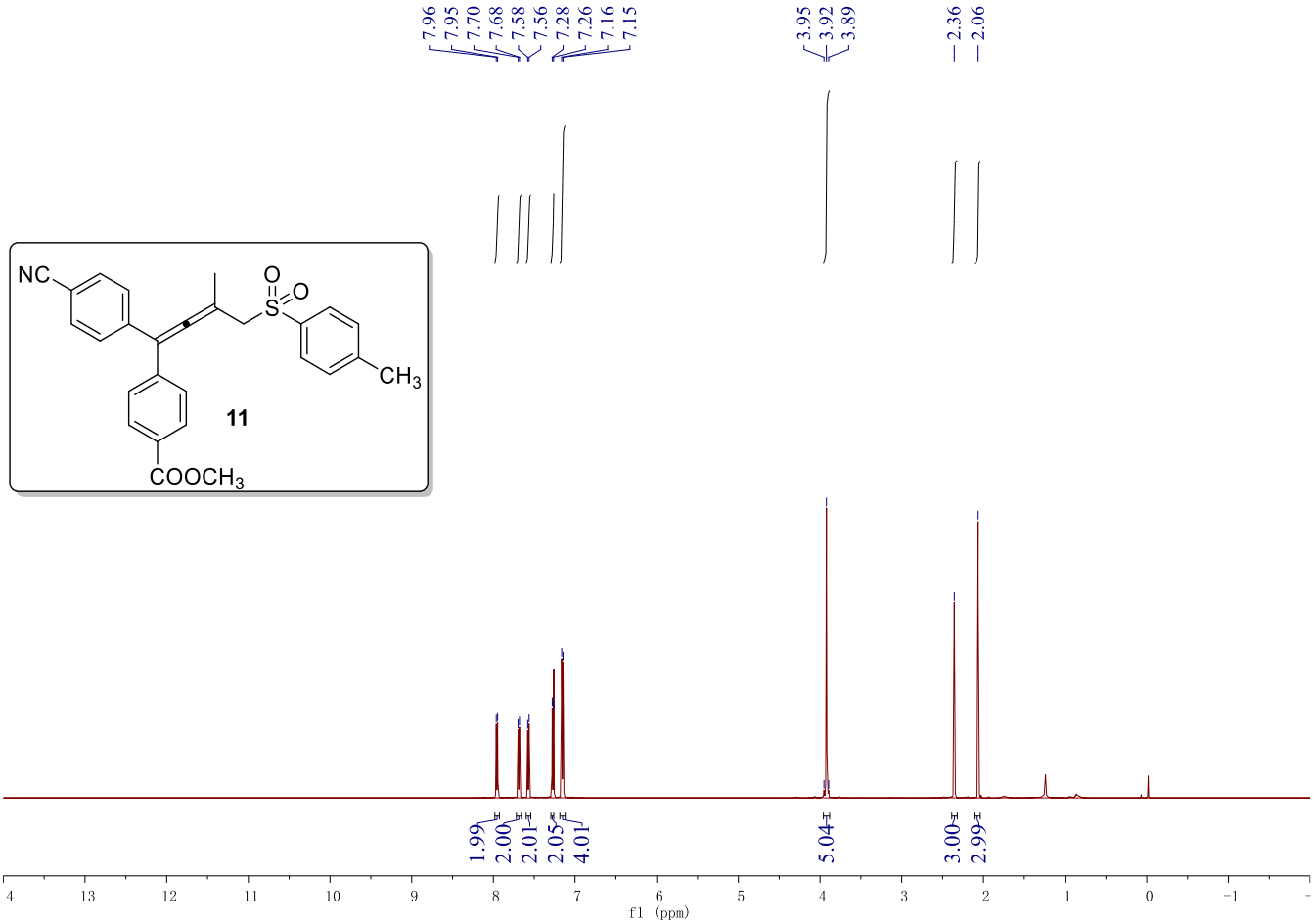
NC
O
O
S
CH3
10
CF3
f1 (ppm)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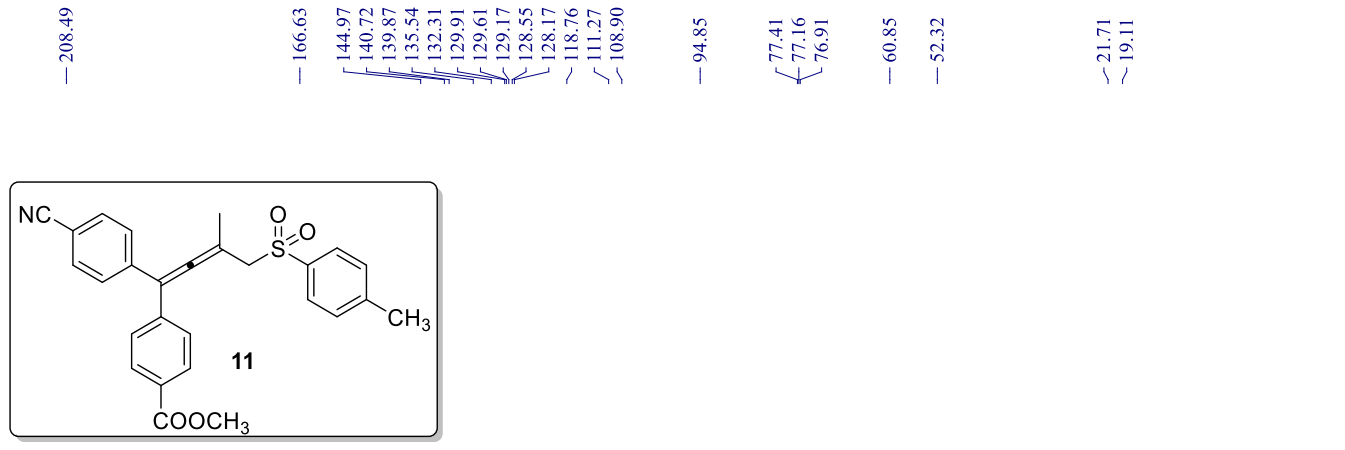
7.28
7.26
7.16
7.15
3.95
3.92
3.89
2.36
2.06
NC
O
O
S
CH3
11
COOCH3
1.99
2.00
2.01
2.05
4.01
5.04
3.00
2.99
f1 (ppm)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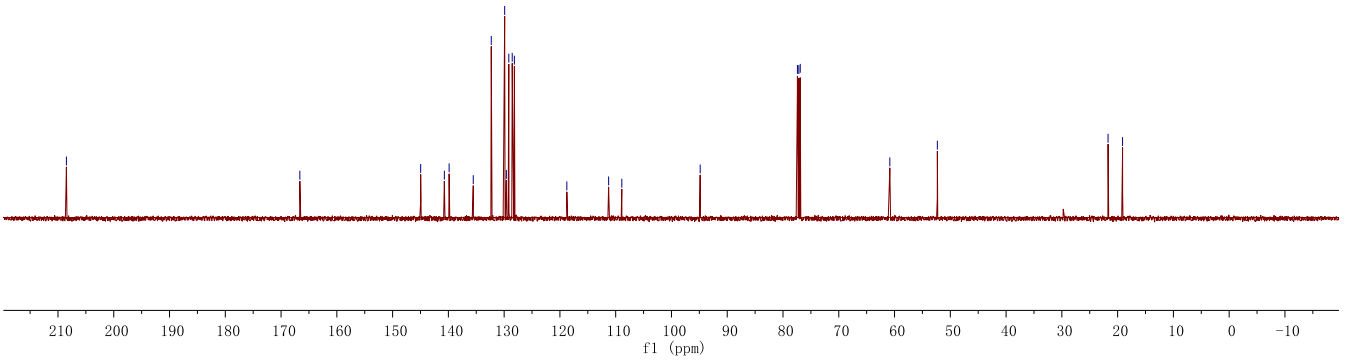
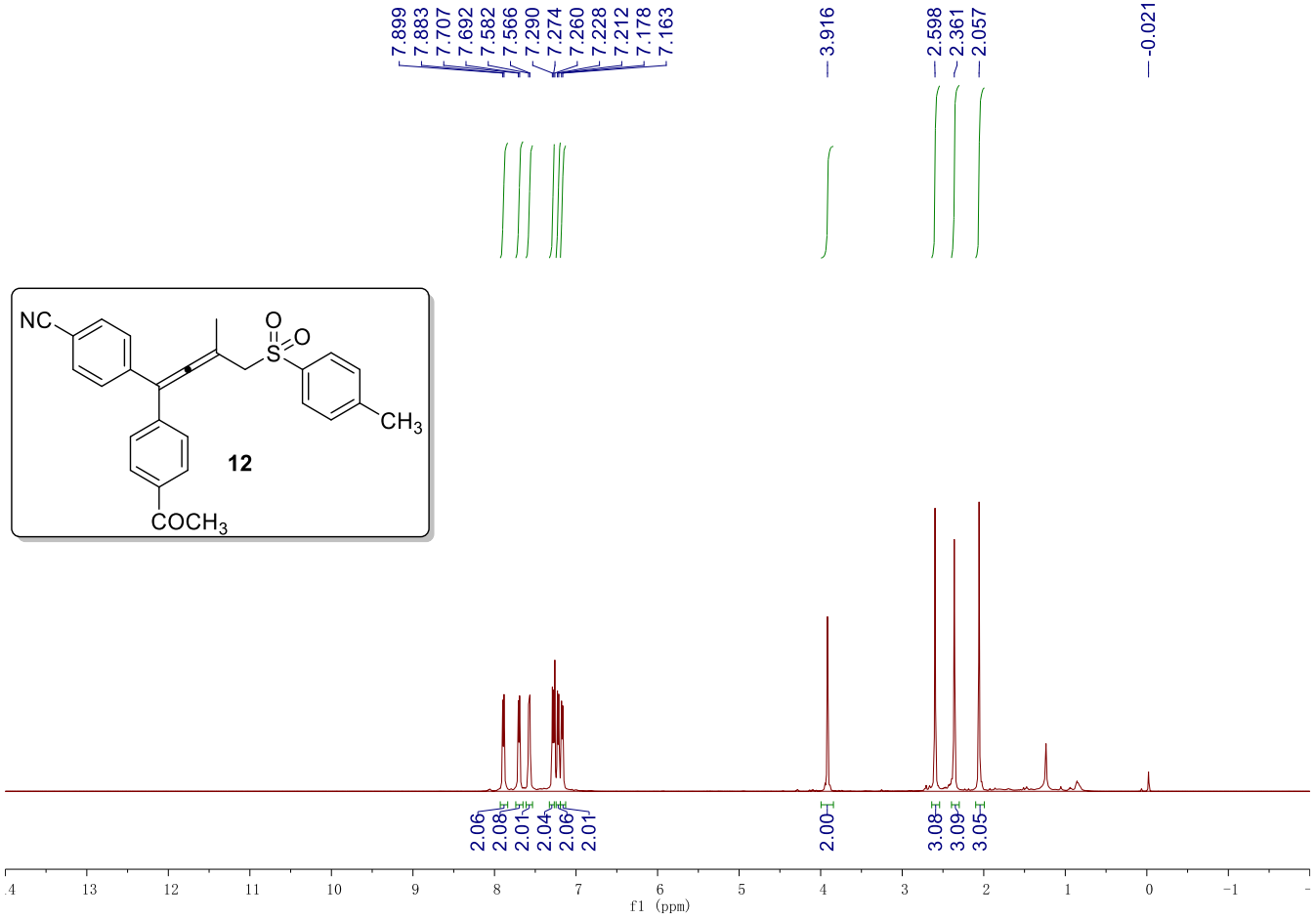
139.87
135.54
132.31
129.91
129.61
129.17
128.55
128.17
118.76
111.27
108.90
94.85
77.41
77.16
76.91
60.85
52.32
21.71
19.11

NC
O
O
S
CH3
11
COOCH3


f1 (ppm)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7.707
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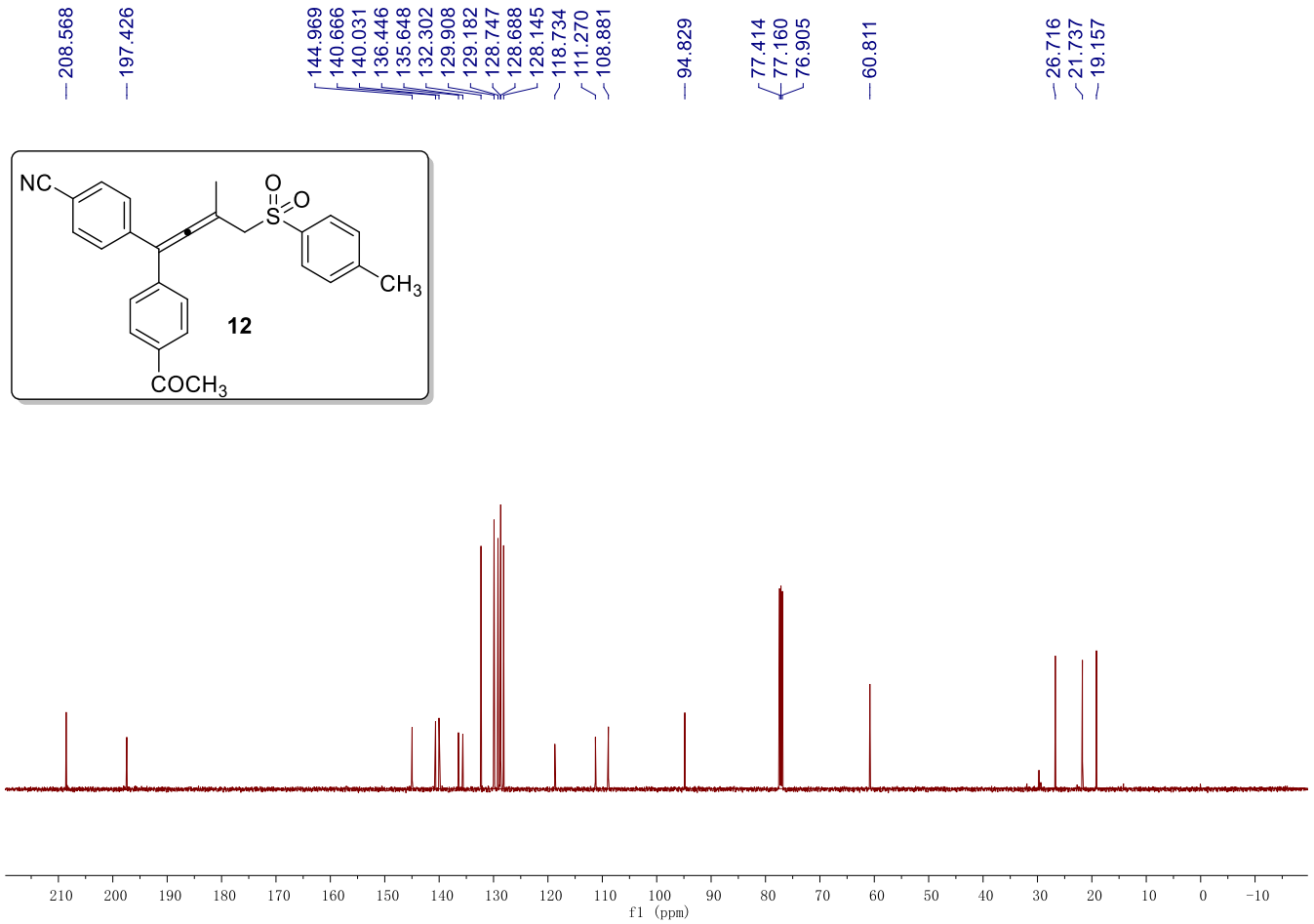
7.582
7.566
7.290
7.274
7.260
7.228
7.212
7.178
7.163
3.916
2.598
2.361
2.057
-0.021
NC
O
O
S
CH3
12
COCH3
2.06
2.08
2.01
2.04
2.06
2.01
2.00
3.08
3.09
3.05
f1 (ppm)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128.747
128.688
128.145
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111.270
108.881
94.829
77.414
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26.716
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19.157
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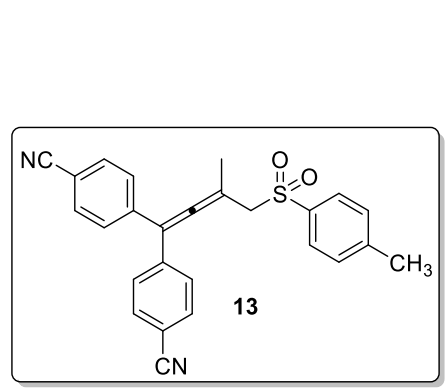
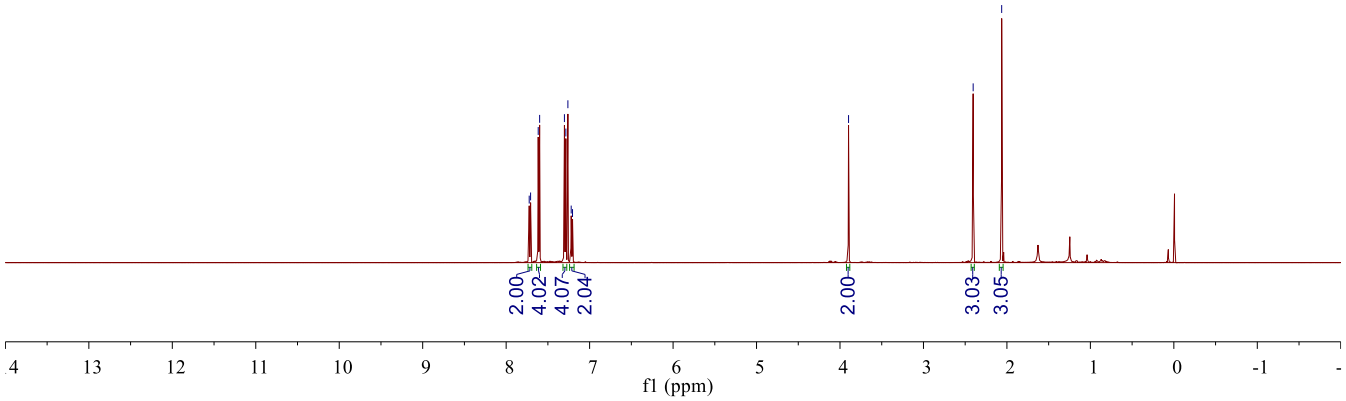
O
S
CH3
12
COCH3
f1 (ppm)


NC
O
O
S
CH3
13
CN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7.26
7.22
7.20
3.90
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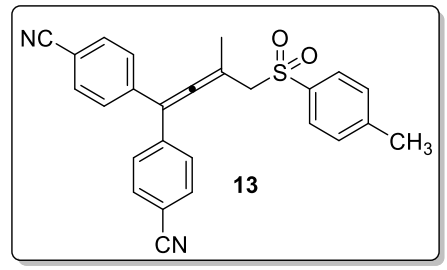
2.06
2.00
4.02
4.07
2.04
2.00
3.03
3.05
f1 (ppm)


NC
O
O
S
CH3
13
CN

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135.86
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129.25
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108.62
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77.16
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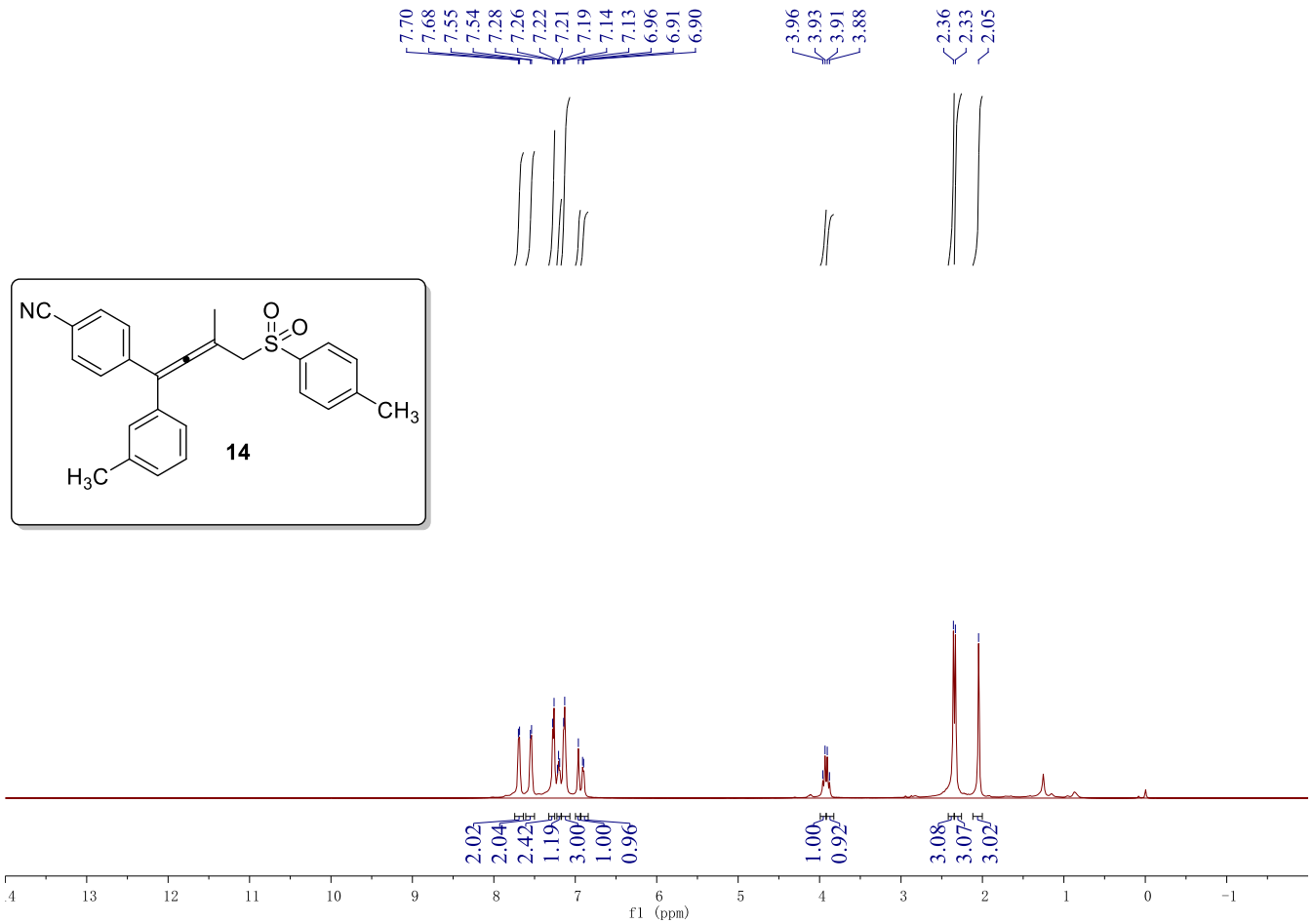
60.77
21.83
19.31
f1 (ppm)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7.14
7.13
6.96
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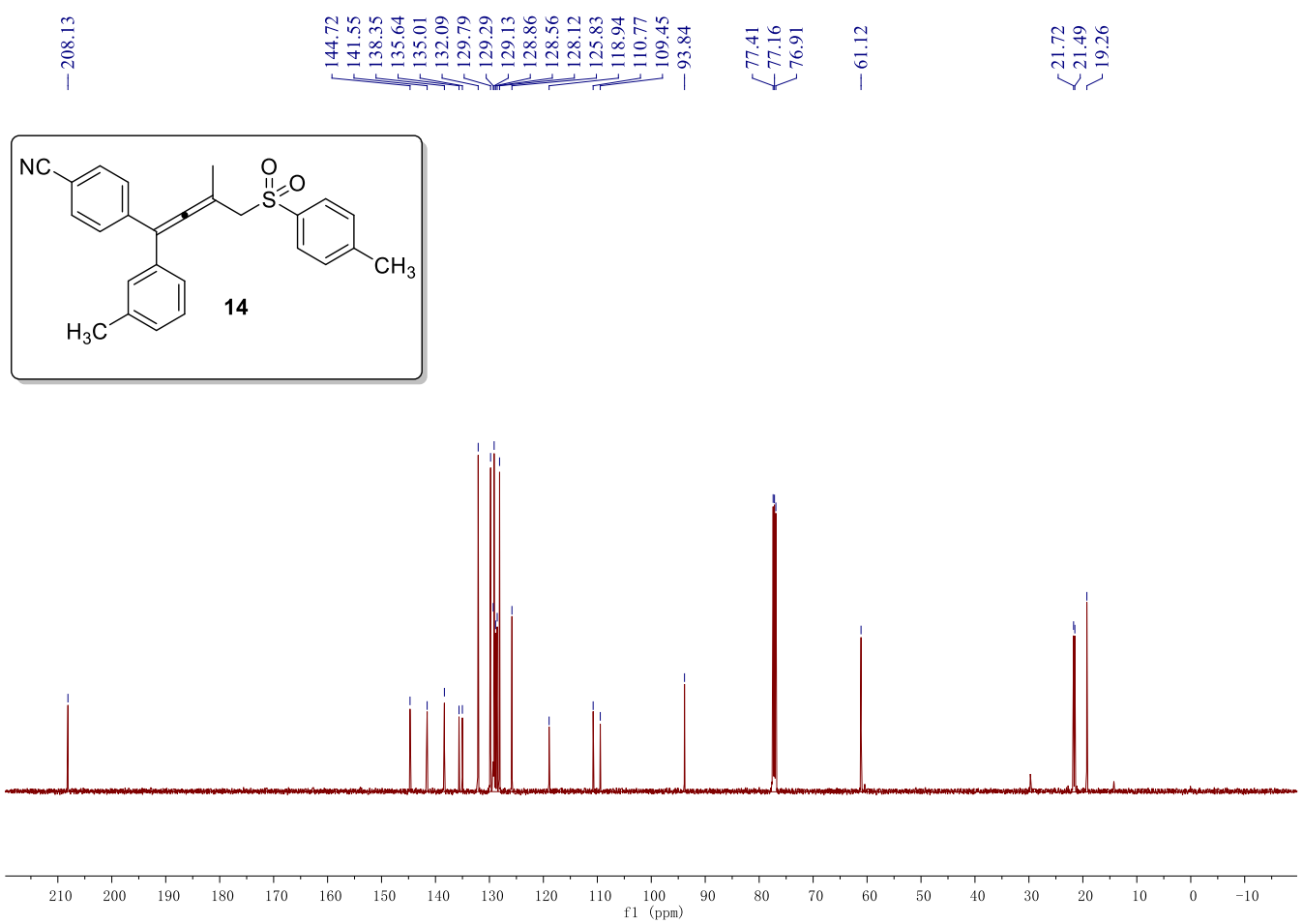
6.90
3.96
3.93
3.91
3.88
2.36
2.33
2.05
NC
O
O
S
CH3
H3C
14
2.02
2.04
2.42
1.19
3.00
1.00
0.96
1.00
0.92
3.08
3.07
3.02
f1 (ppm)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129.29
129.13
128.86
128.56
128.12
125.83
118.94
110.77
109.45
93.84
77.41
77.16
76.91
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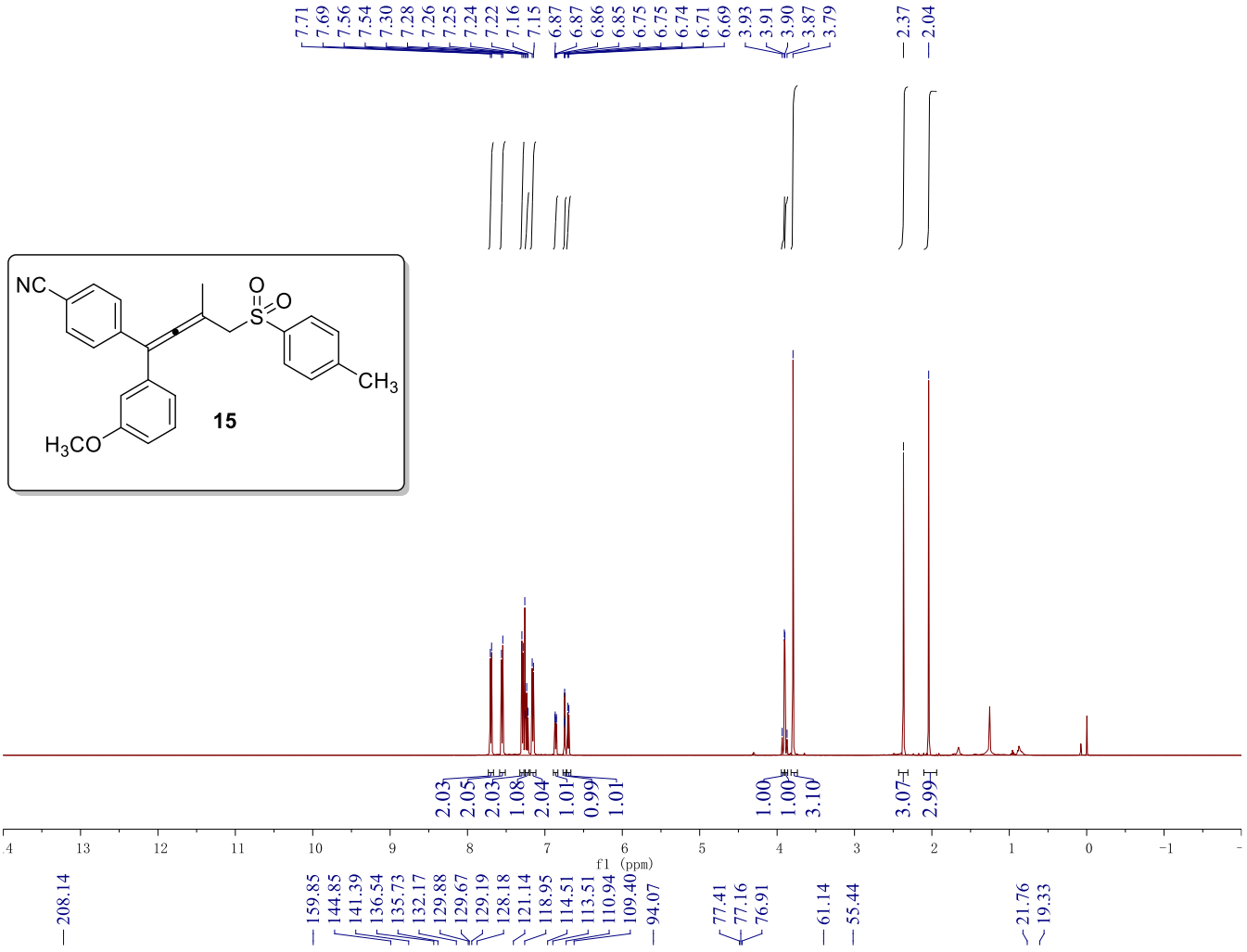
21.72
21.49
19.26
NC
O
O
S
CH3
H3C
14
f1 (ppm)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7.25
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7.22
7.16
7.15
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6.87
6.86
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6.75
6.74
6.71
6.69
3.93
3.91
3.90
3.87
3.79
2.37
2.04
NC
O
O
S
CH3
H3CO
15
2.03
2.05
2.03
1.08
2.04
1.01
0.99
1.01
1.00
1.00
3.10
3.07
2.99
f1 (ppm)
208.14
159.85
144.85
141.39
136.54
135.73
132.17
129.88
129.67
129.19
128.18
121.14
118.95
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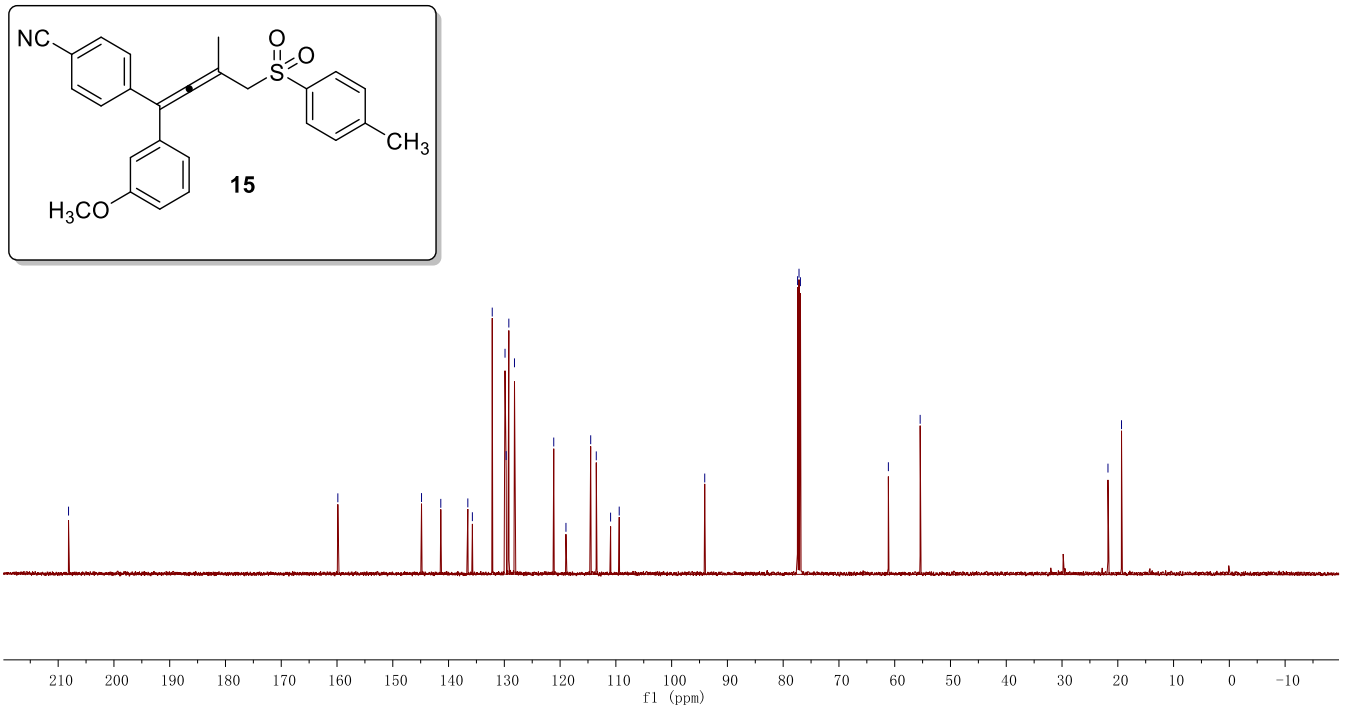
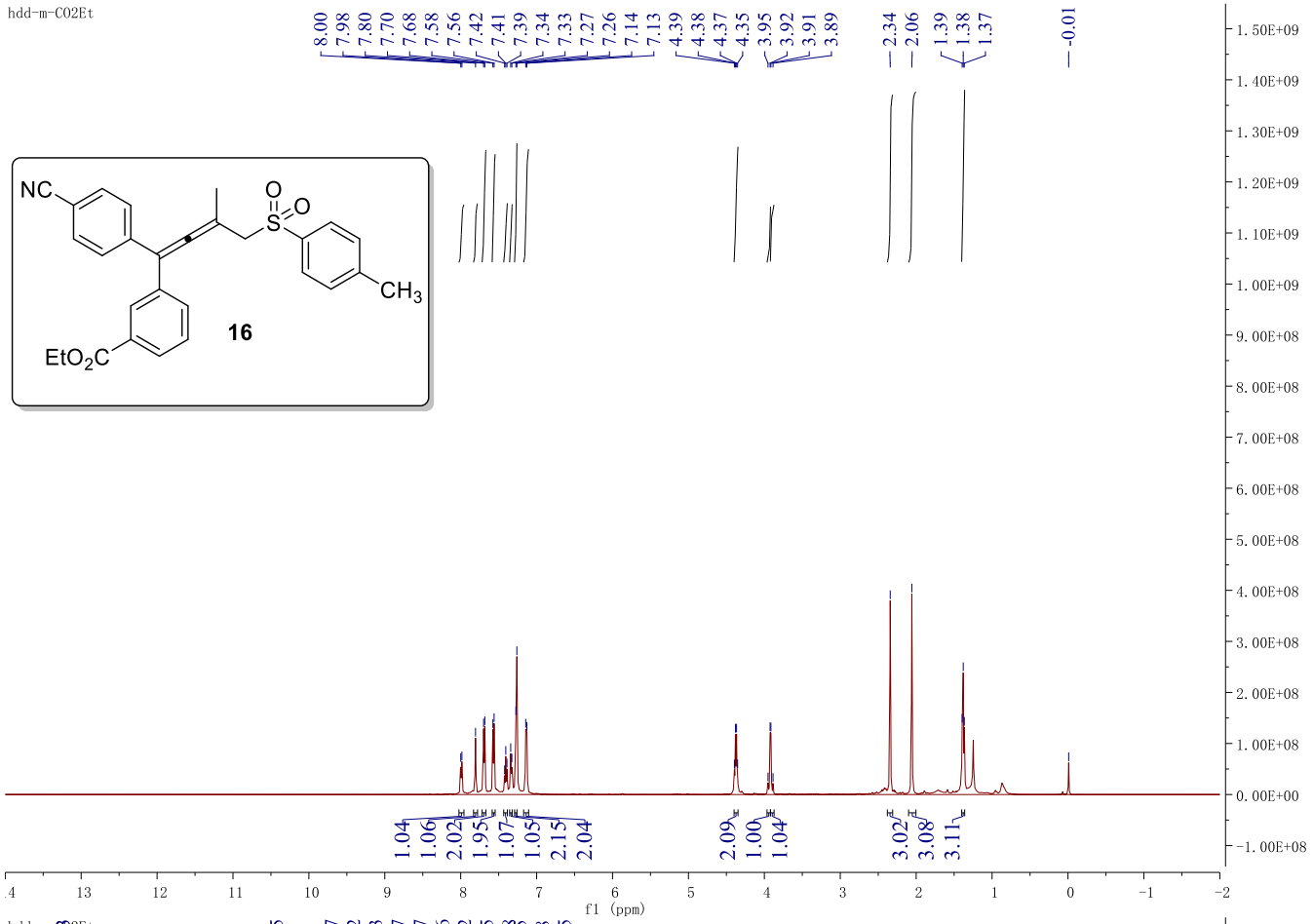
77.16
76.91
61.14
55.44
21.76
19.33


NC
O
O
S
CH3
H3CO
15
f1 (ppm)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7.70
7.68
7.58
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7.42
7.41
7.39
7.34
7.33
7.27
7.26
7.14
7.13
4.39
4.38
4.37
4.35
3.95
3.92
3.91
3.89
2.34
2.06
1.39
1.38
1.37
-0.01
NC
O
S
O
CH3
16
EtO2C
1.04
1.06
2.02
1.95
1.07
1.05
2.15
2.04
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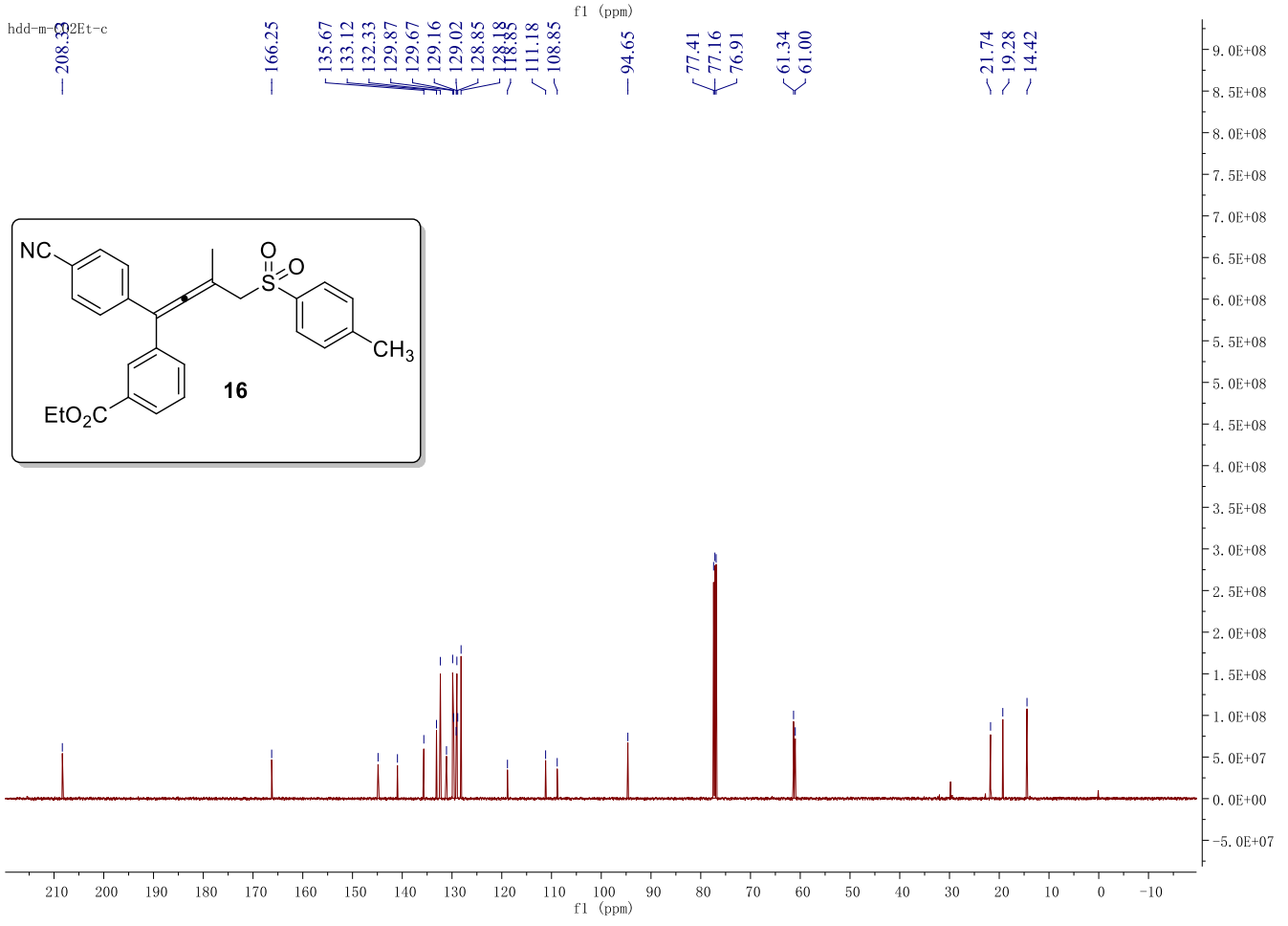
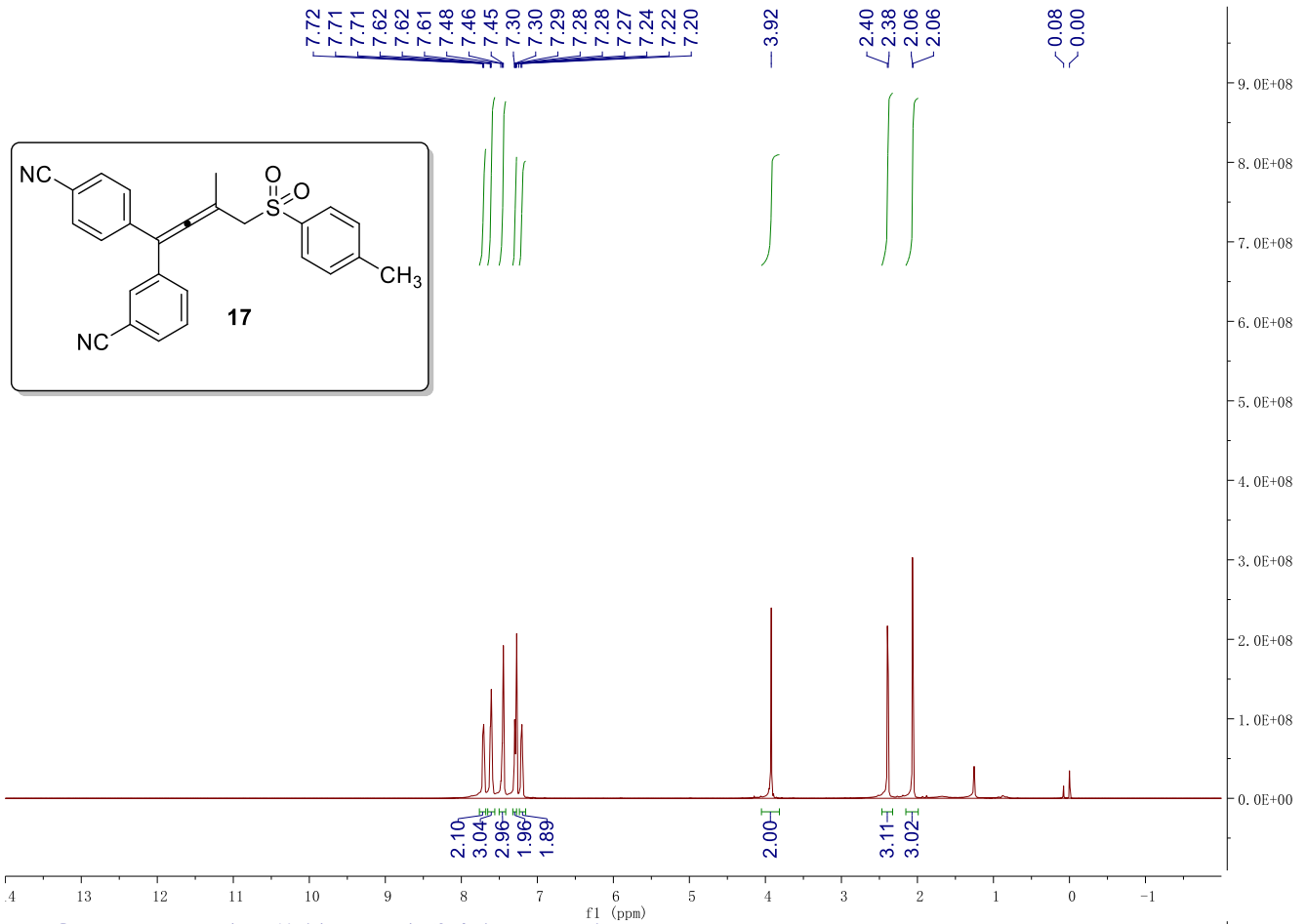
1.00
1.04
3.02
3.08
3.11
f1 (ppm)


hdd-m-CO2Et-c
208.33
166.25
135.67
133.12
132.33
129.87
129.67
129.16
129.02
128.85
128.18
118.85
111.18
108.85
94.65
77.41
77.16
76.91
61.34
61.00
21.74
19.28
14.42
NC
O
S
O
CH3
16
EtO2C
f1 (ppm)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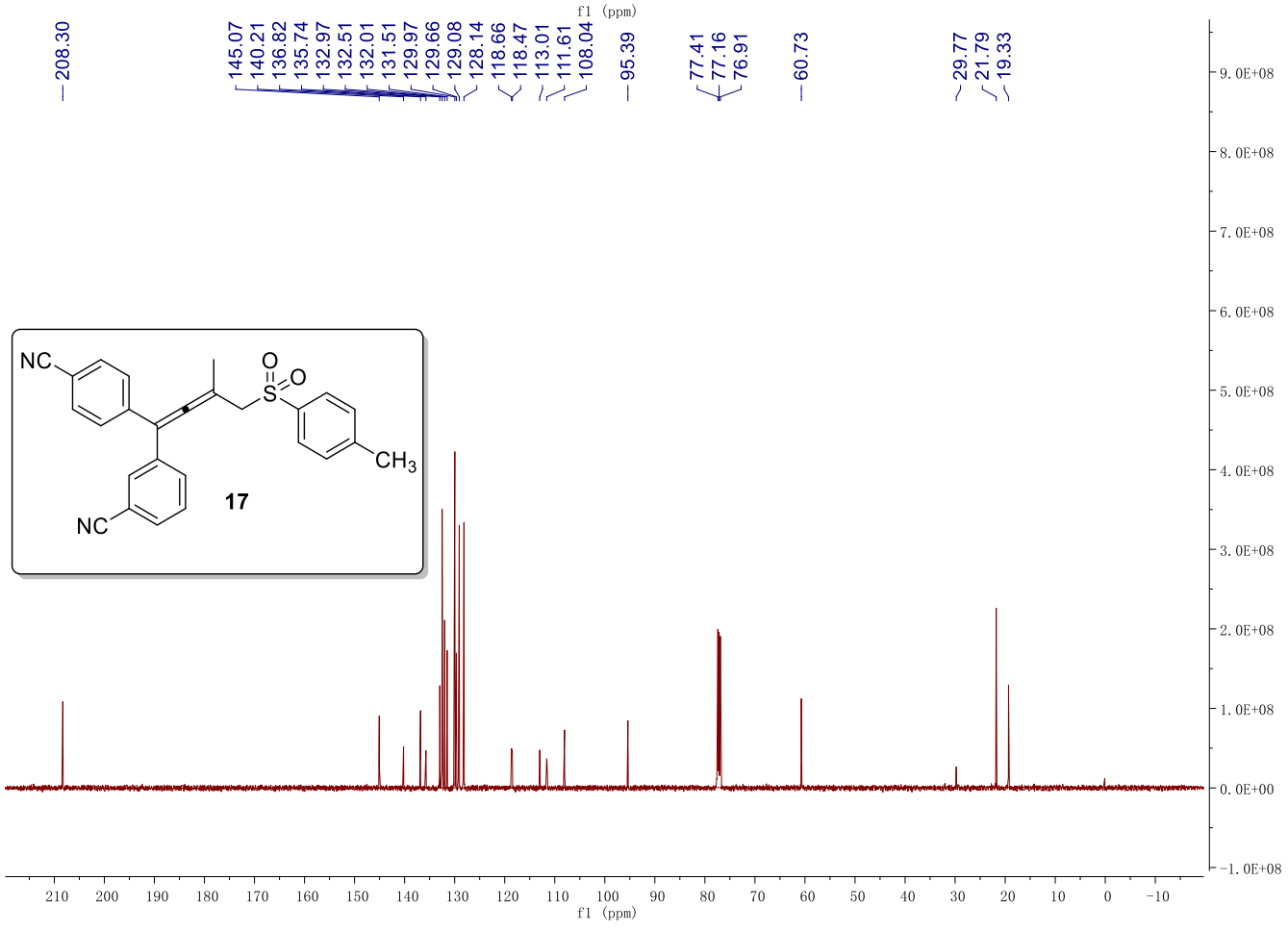
7.30
7.29
7.28
7.28
7.27
7.24
7.22
7.20
3.92
2.40
2.38
2.06
2.06
0.08
0.00
NC
O
O
S
CH3
NC
17
2.10
3.04
2.96
1.96
1.89
2.00
3.11
3.02
f1 (ppm)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140.21
136.82
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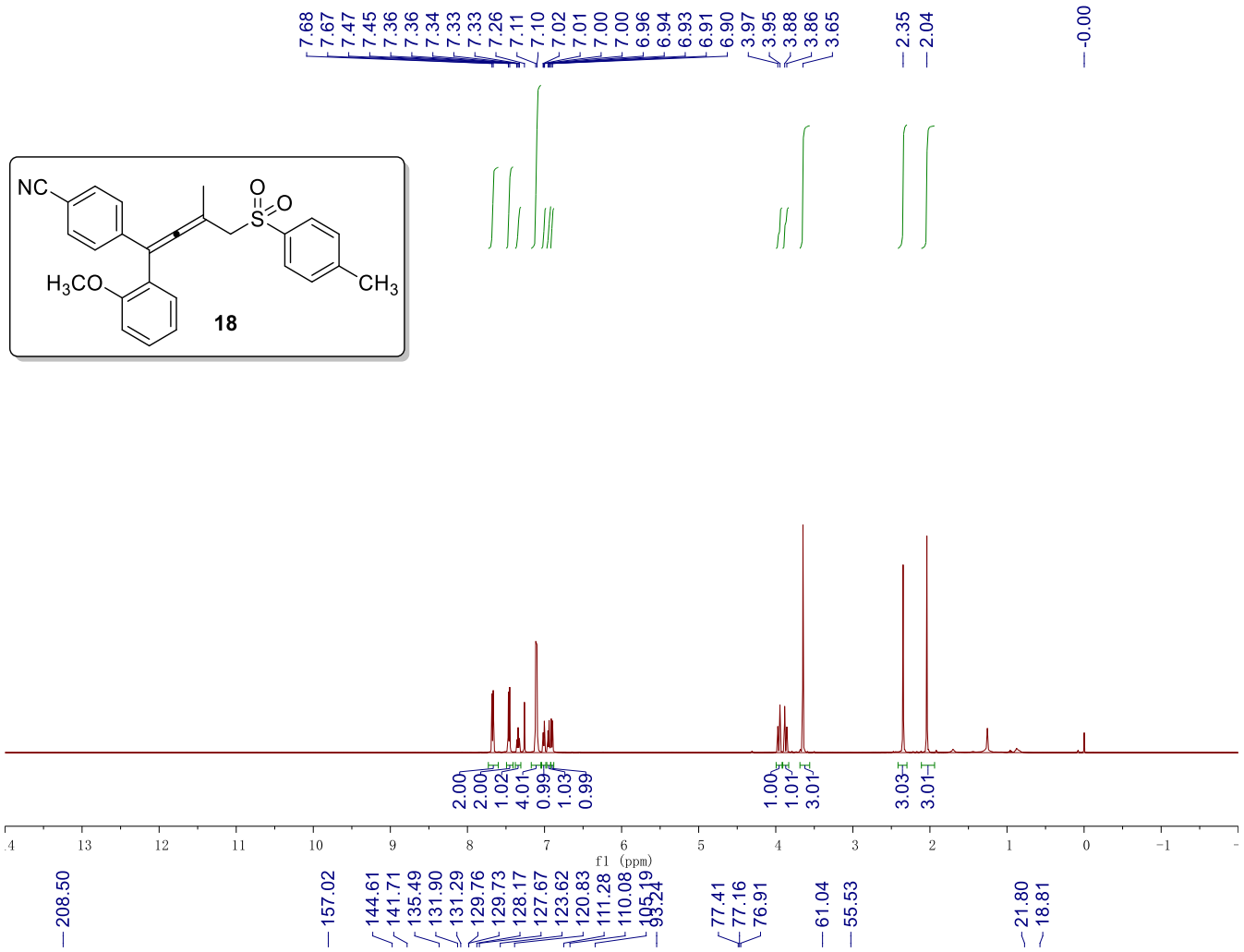
132.97
132.51
132.01
131.51
129.97
129.66
129.08
128.14
118.66
118.47
113.01
111.61
108.04
95.39
77.41
77.16
76.91
60.73
29.77
21.79
19.33
NC
O
O
S
CH3
NC
17
f1 (ppm)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7.67
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7.36
7.34
7.33
7.33
7.26
7.11
7.10
7.02
7.01
7.00
7.00
6.96
6.94
6.93
6.91
6.90
3.97
3.95
3.88
3.86
3.65
2.35
2.04
-0.00
NC
O
O
S
H3CO
CH3
18
2.00
2.00
1.02
4.01
0.99
1.03
0.99
1.00
1.01
3.01
3.03
3.01
f1 (ppm)

208.50
157.02
144.61
141.71
135.49
131.90
131.29
129.76
129.73
128.17
127.67
123.62
120.83
111.28
110.08
105.19
93.24
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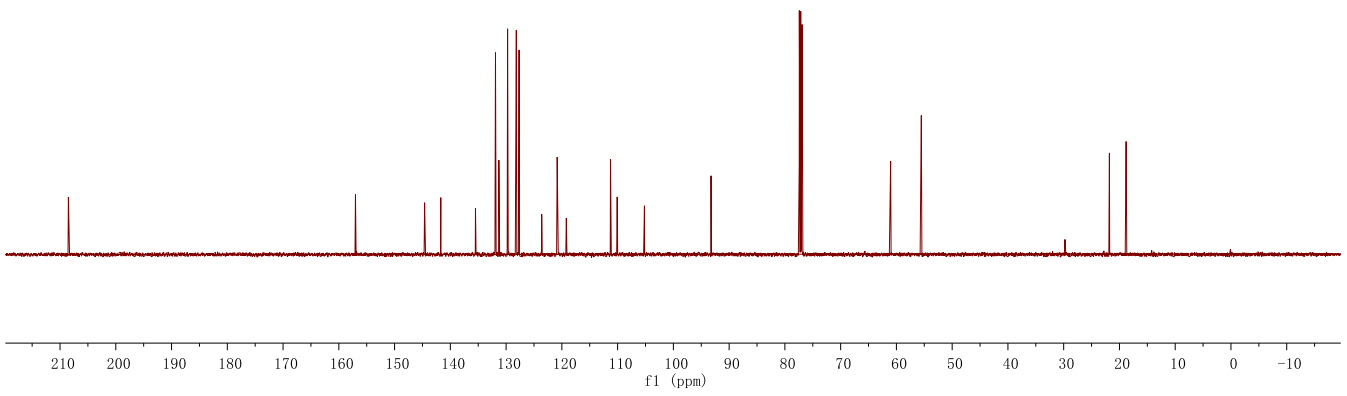
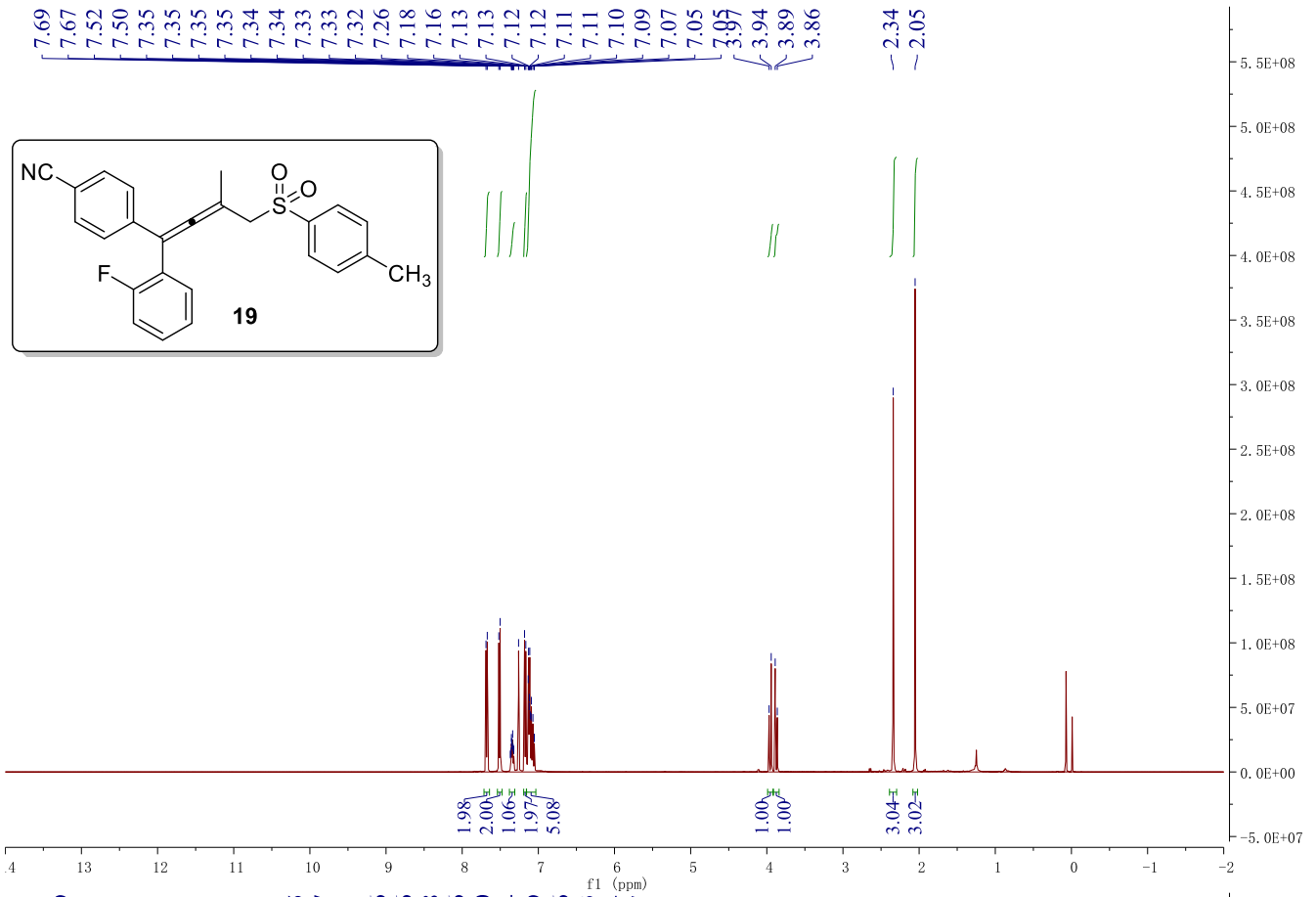
77.16
76.91
61.04
55.53
21.80
18.81


NC
O
O
S
H3CO
CH3
18


f1 (ppm)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7.35
7.35
7.35
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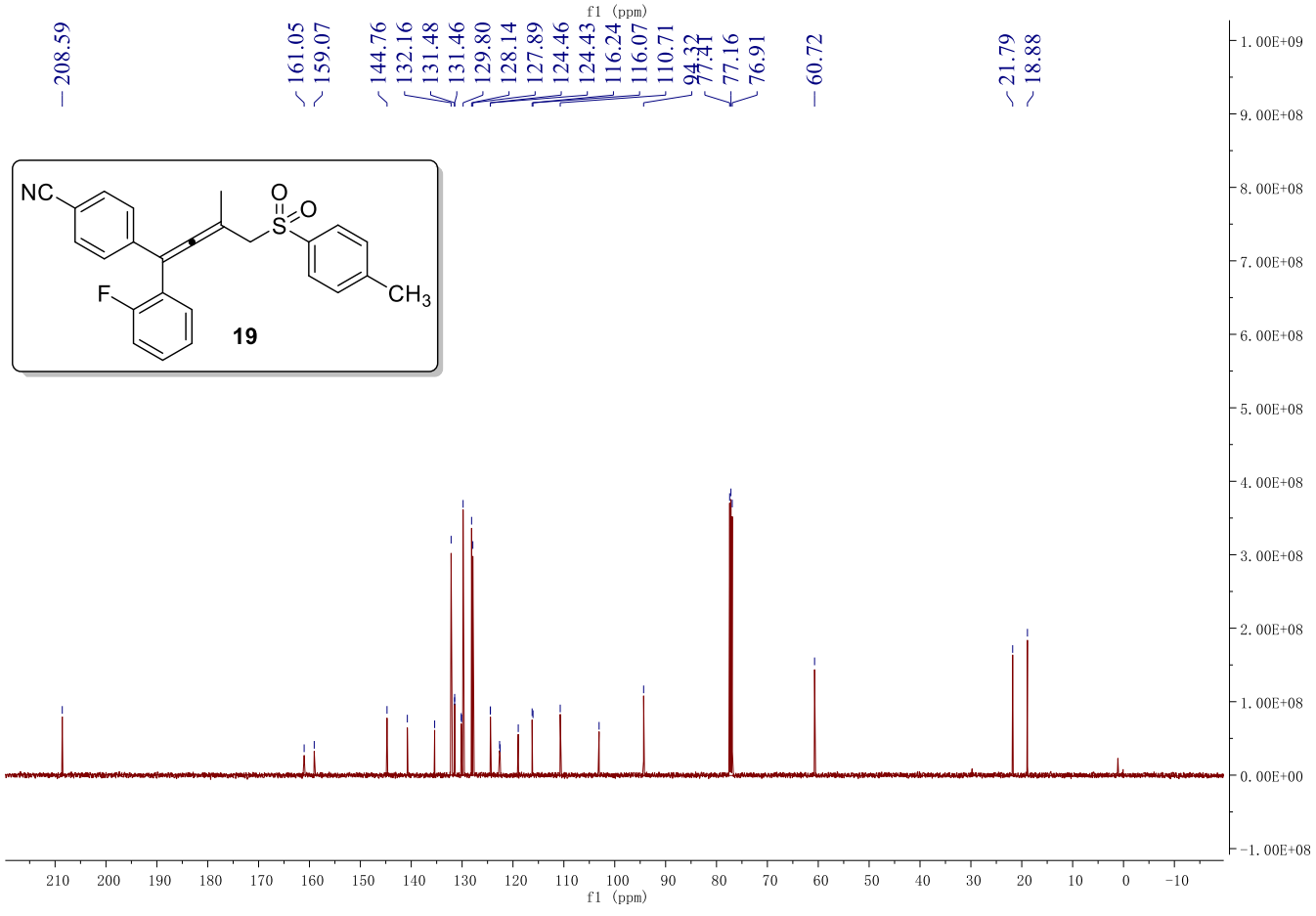
7.34
7.33
7.33
7.32
7.26
7.18
7.16
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.09
7.07
7.05
3.94
3.89
3.86
2.34
2.05
NC
O
S
O
F
CH3
19
1.98
2.00
1.06
1.97
5.08
1.00
1.00
3.04
3.02
f1 (ppm)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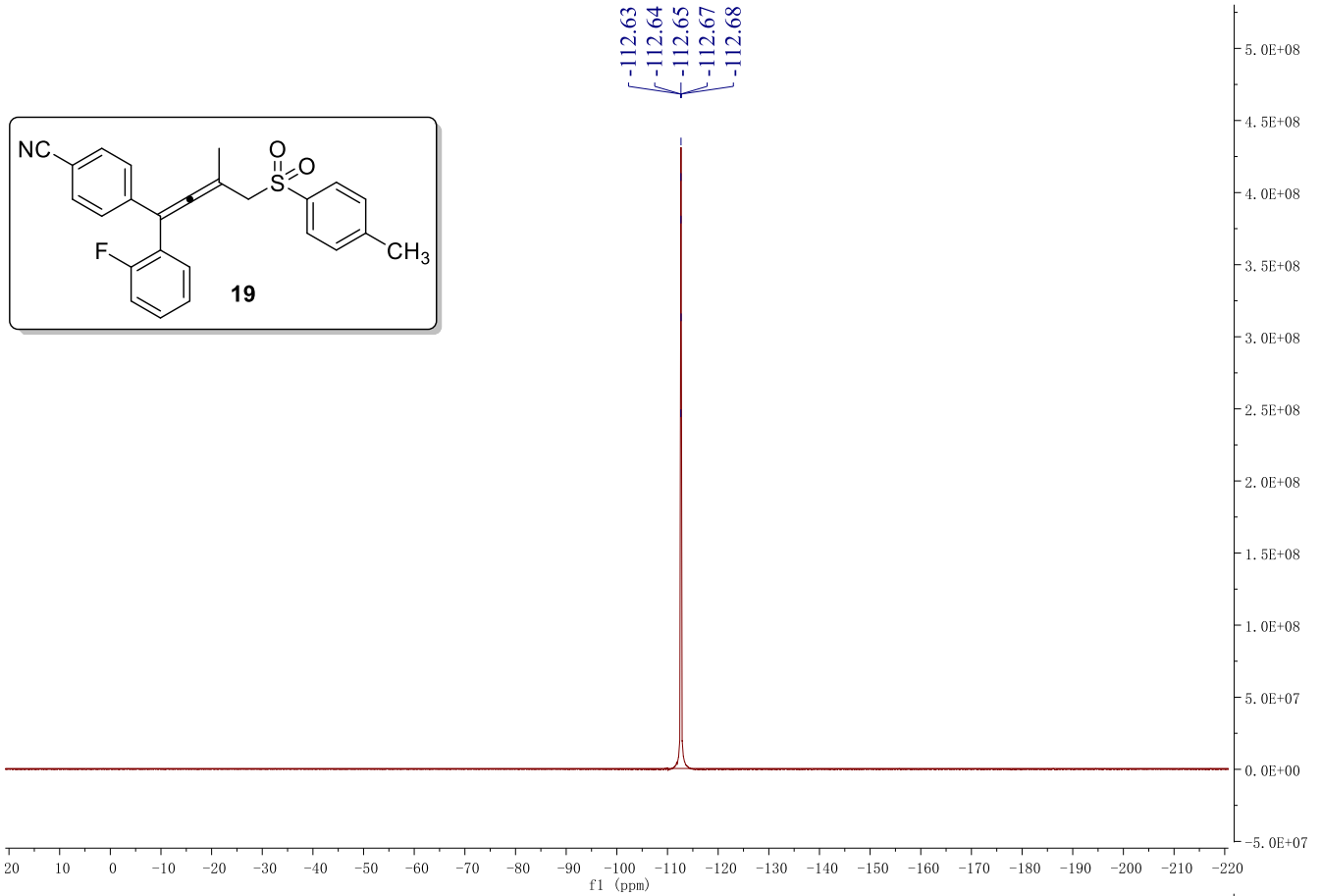
131.48
131.46
129.80
128.14
127.89
124.46
124.43
116.24
116.07
110.71
77.41
77.16
76.91
60.72
21.79
18.88
NC
O
S
O
F
CH3
19
f1 (ppm)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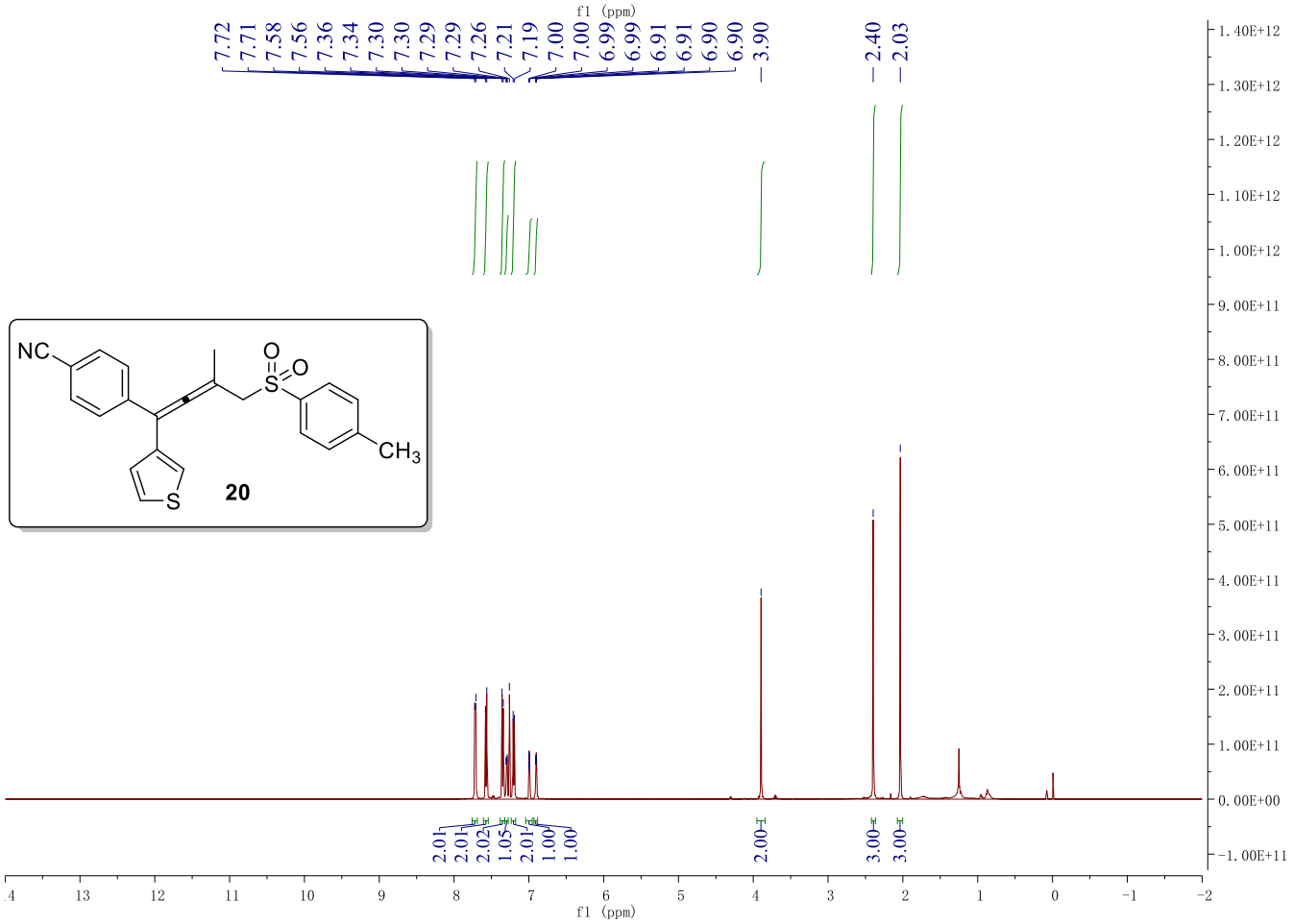
-112.65
-112.67
-112.68
NC
O
S
O
F
CH3
19
f1 (ppm)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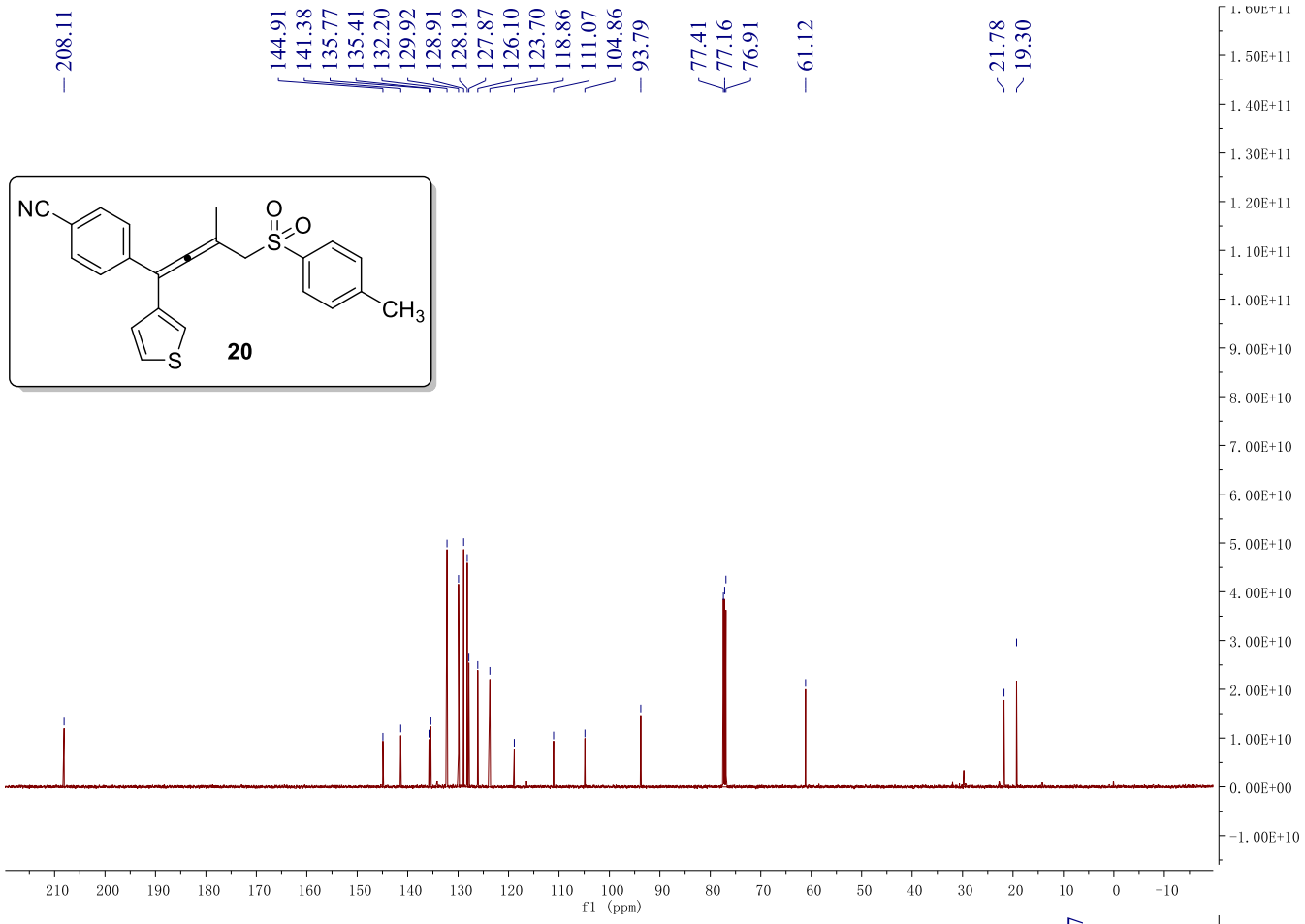
7.34
7.30
7.30
7.29
7.29
7.26
7.21
7.19
7.00
7.00
6.99
6.99
6.91
6.91
6.90
6.90
3.90
2.40
2.03
NC
O
S
O
CH3
S
20
2.01
2.01
2.02
1.05
2.01
1.00
1.00
2.00
3.00
3.00
f1 (ppm)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144.91
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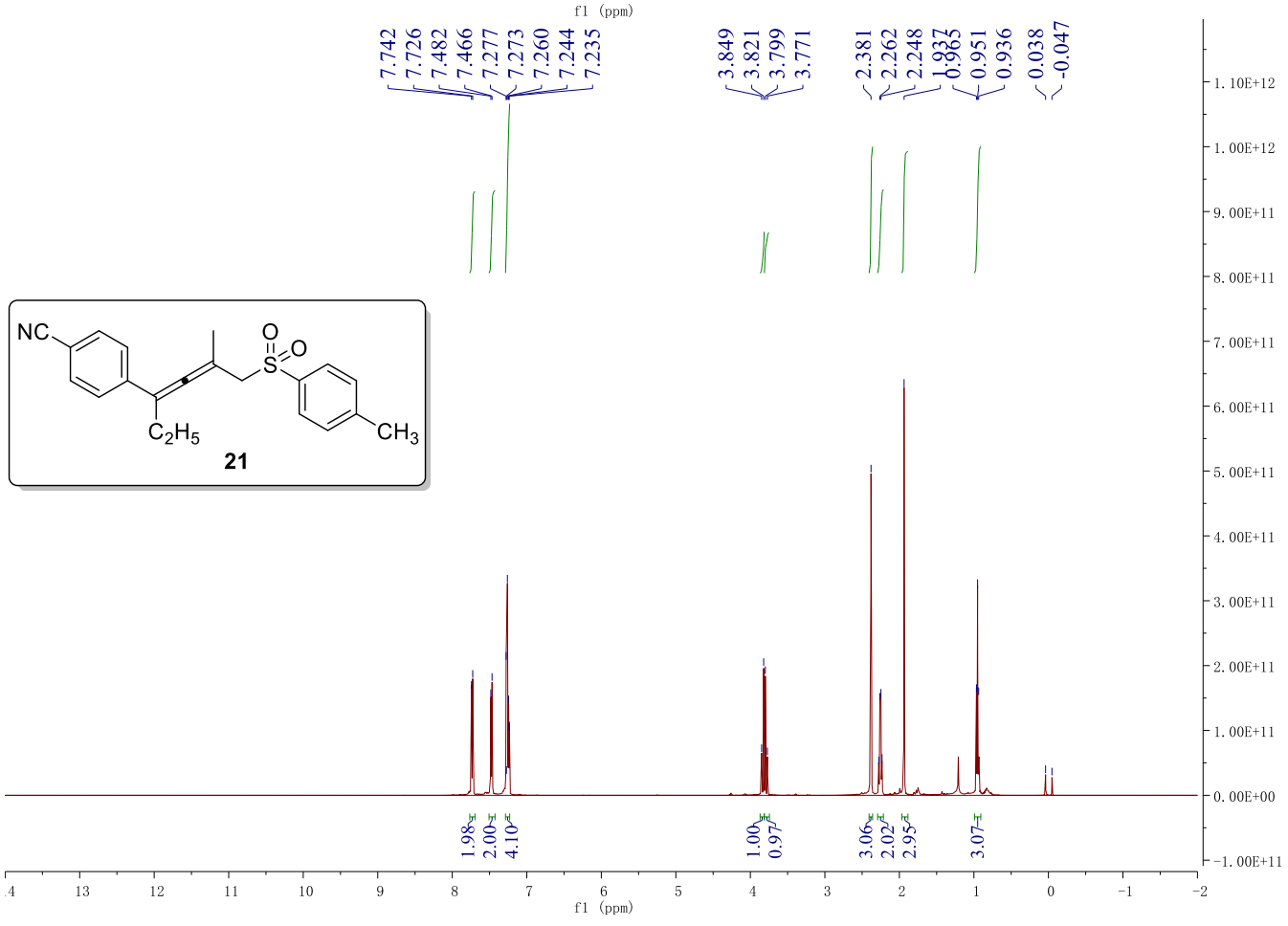
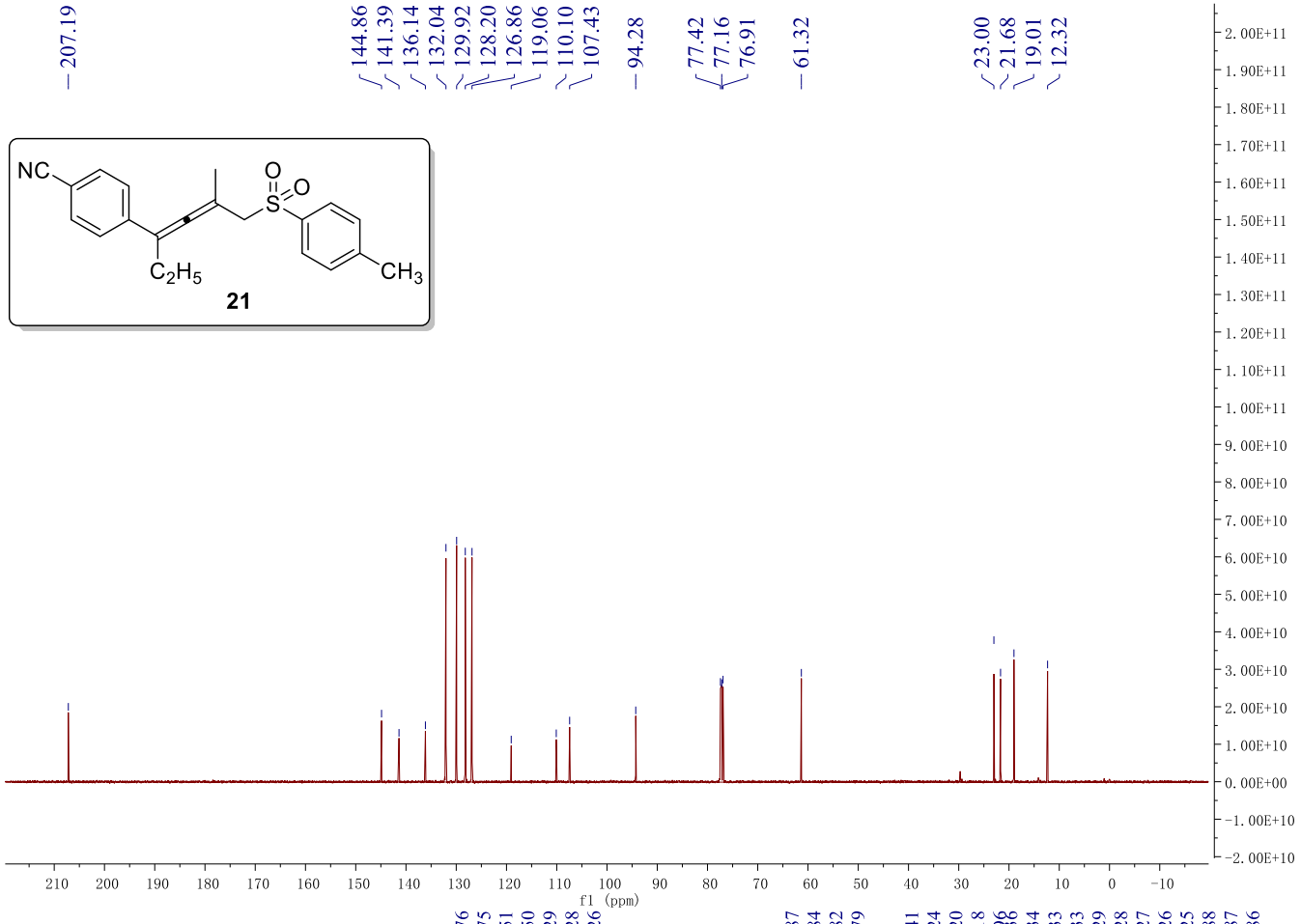
135.77
135.41
132.20
129.92
128.91
128.19
127.87
126.10
123.70
118.86
111.07
104.86
93.79
77.41
77.16
76.91
61.12
21.78
19.30
NC
O
S
O
CH3
S
20
f1 (ppm)


7.742
7.726
7.482
7.466
7.277
7.273
7.260
7.244
7.235
3.849
3.821
3.799
3.771
2.381
2.262
2.248
1.937
0.965
0.951
0.936
0.038
-0.047
NC
O
S
O
C2H5
CH3
21
1.98
2.00
4.10
1.00
0.97
3.06
2.02
2.95
3.07
f1 (ppm)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136.14
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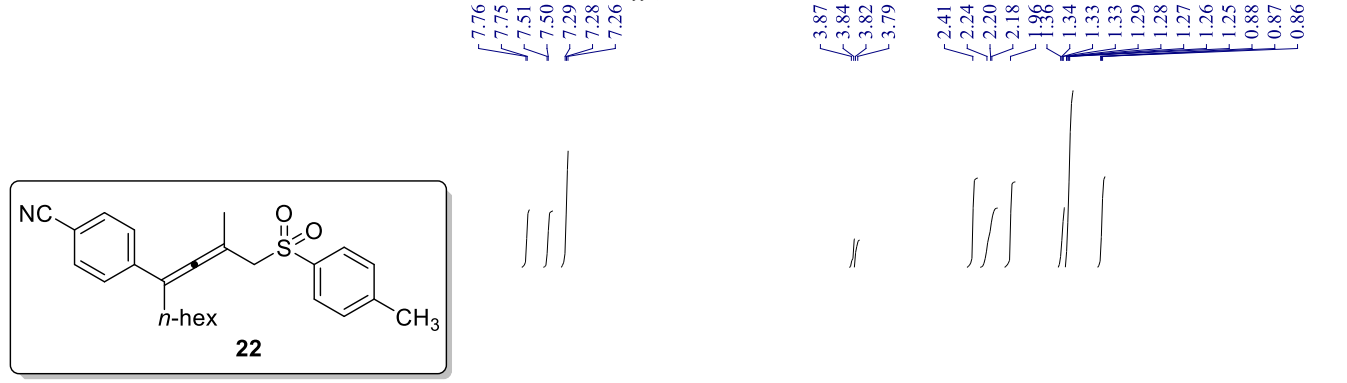
129.92
128.20
126.86
119.06
110.10
107.43
94.28
77.42
77.16
76.91
61.32
23.00
21.68
19.01
12.32
NC
O
S
O
C_2H_5
CH_3
21
f1 (ppm)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7.75
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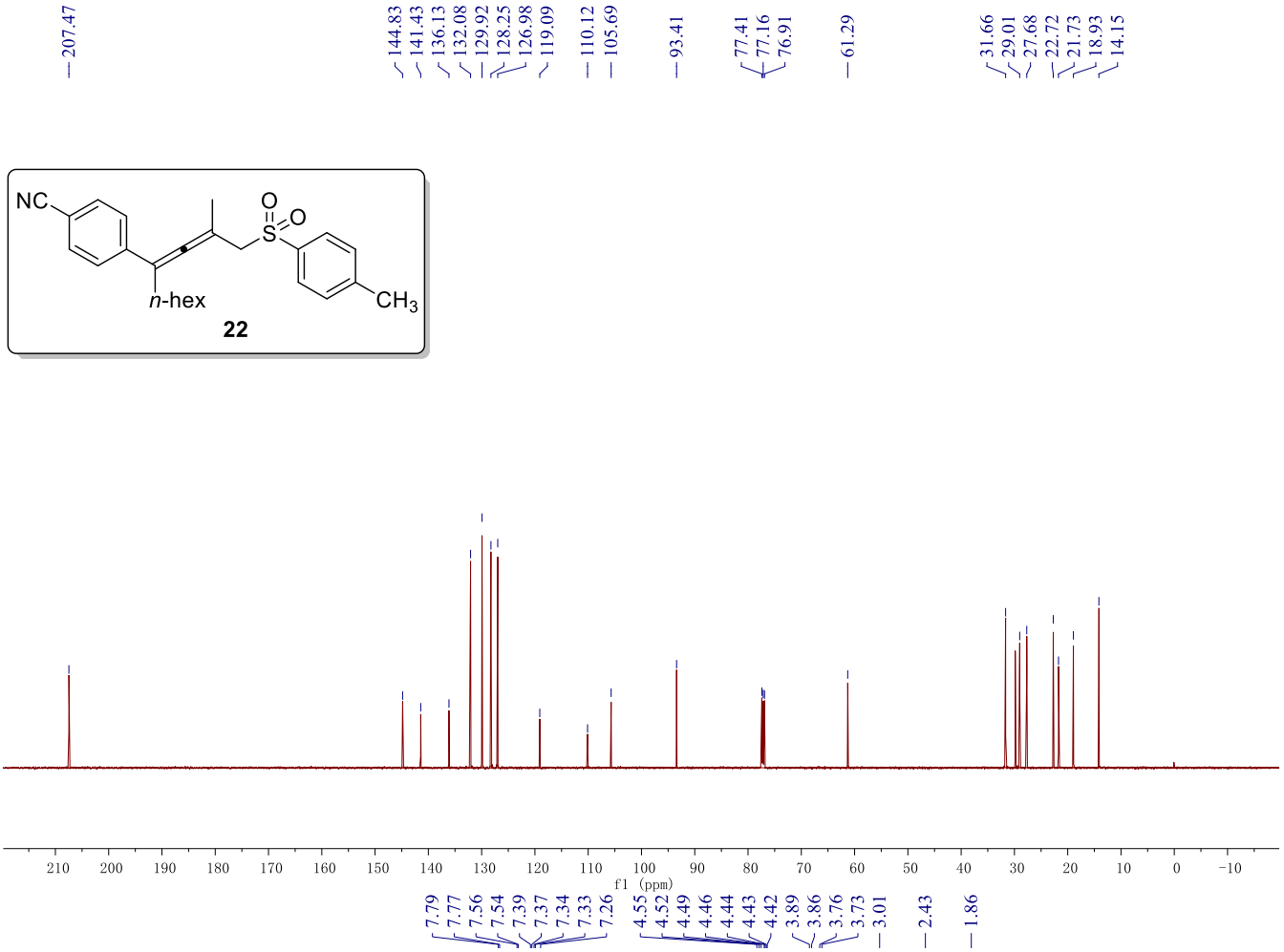
7.50
7.29
7.28
7.26
3.87
3.84
3.82
3.79
2.41
2.24
2.20
2.18
1.96
1.36
1.34
1.33
1.33
1.29
1.28
1.27
1.26
1.25
0.88
0.87
0.86

NC
O
S
O
n-hex
CH_3
22
2.01
1.97
4.05
1.00
0.95
3.11
2.07
2.98
2.09
6.15
3.16
f1 (ppm)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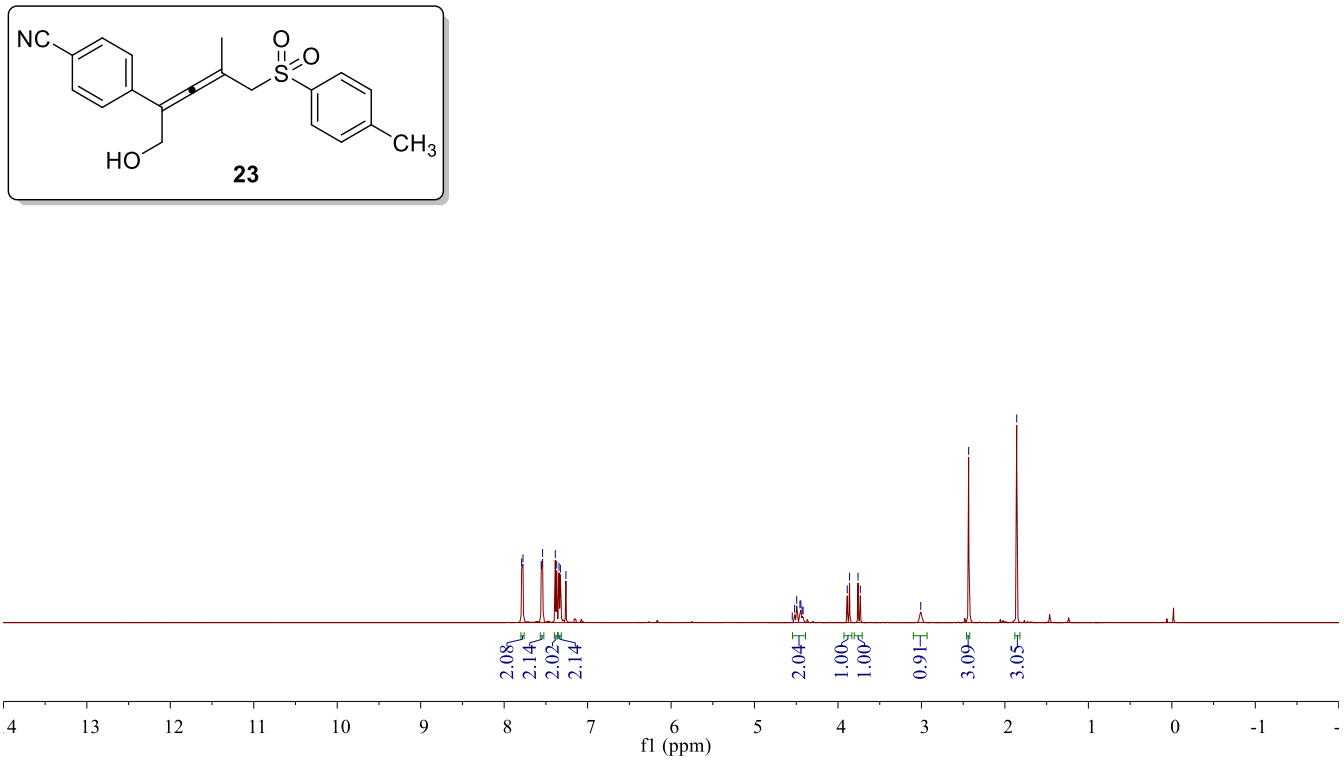
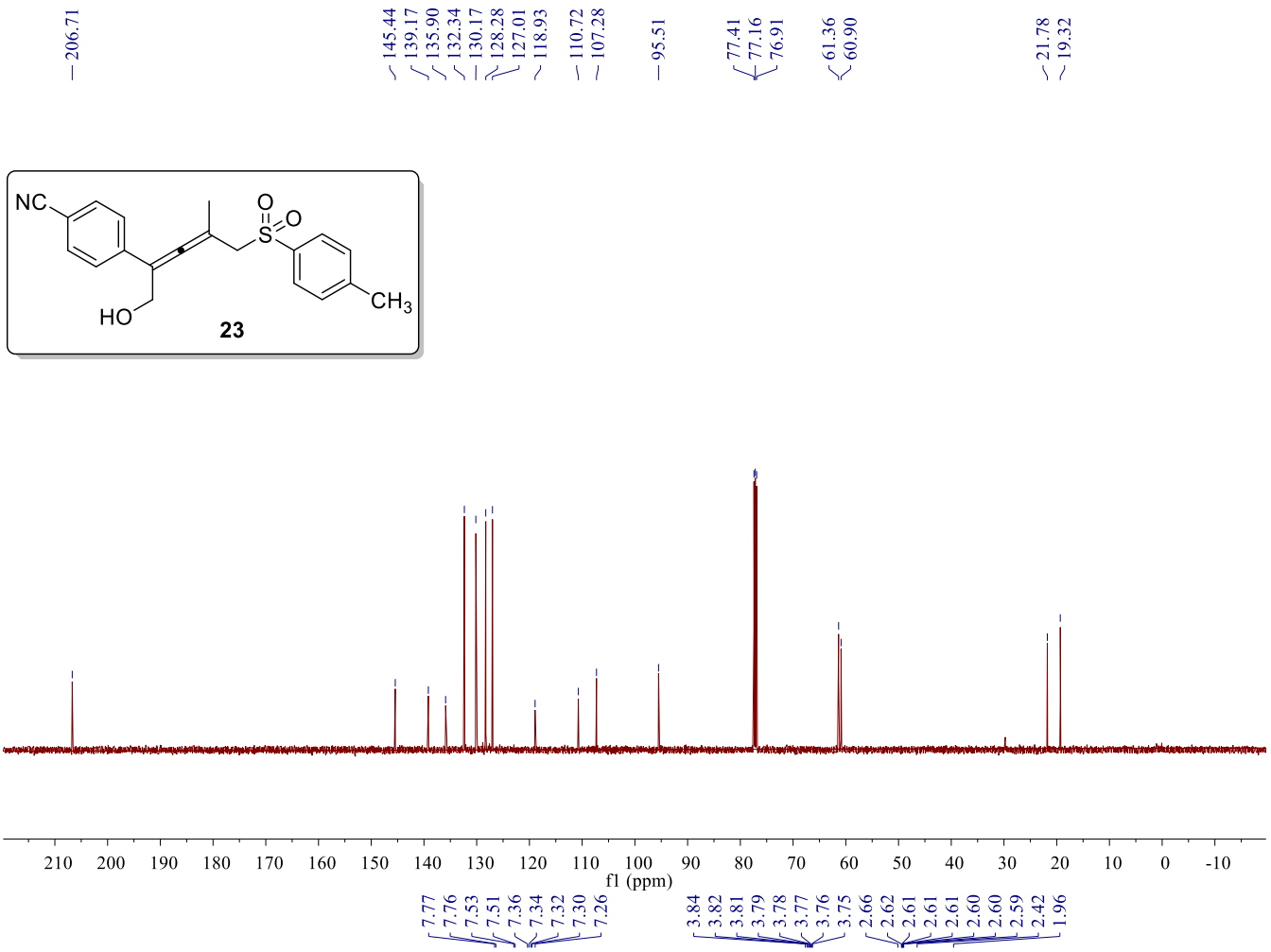
136.13
132.08
129.92
128.25
126.98
119.09
110.12
105.69
93.41
77.41
77.16
76.91
61.29
31.66
29.01
27.68
22.72
21.73
18.93
14.15
NC
O
S
O
n-hex
CH3
22
f1 (ppm)
7.79
7.77
7.56
7.54
7.39
7.37
7.34
7.33
7.26
4.55
4.52
4.49
4.46
4.44
4.43
4.42
3.89
3.86
3.76
3.73
3.01
2.43
1.86


NC
O
S
O
HO
CH3
23
2.08
2.14
2.02
2.14
2.04
1.00
1.00
0.91
3.09
3.05
f1 (ppm)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132.34
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128.28
127.01
118.93
110.72
107.28
95.51
77.41
77.16
76.91
61.36
60.90
21.78
19.32
NC
O
S
O
CH3
HO
23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
7.77
7.76
7.53
7.51
7.36
7.34
7.32
7.30
7.26
3.84
3.82
3.81
3.79
3.78
3.77
3.76
3.75
2.66
2.62
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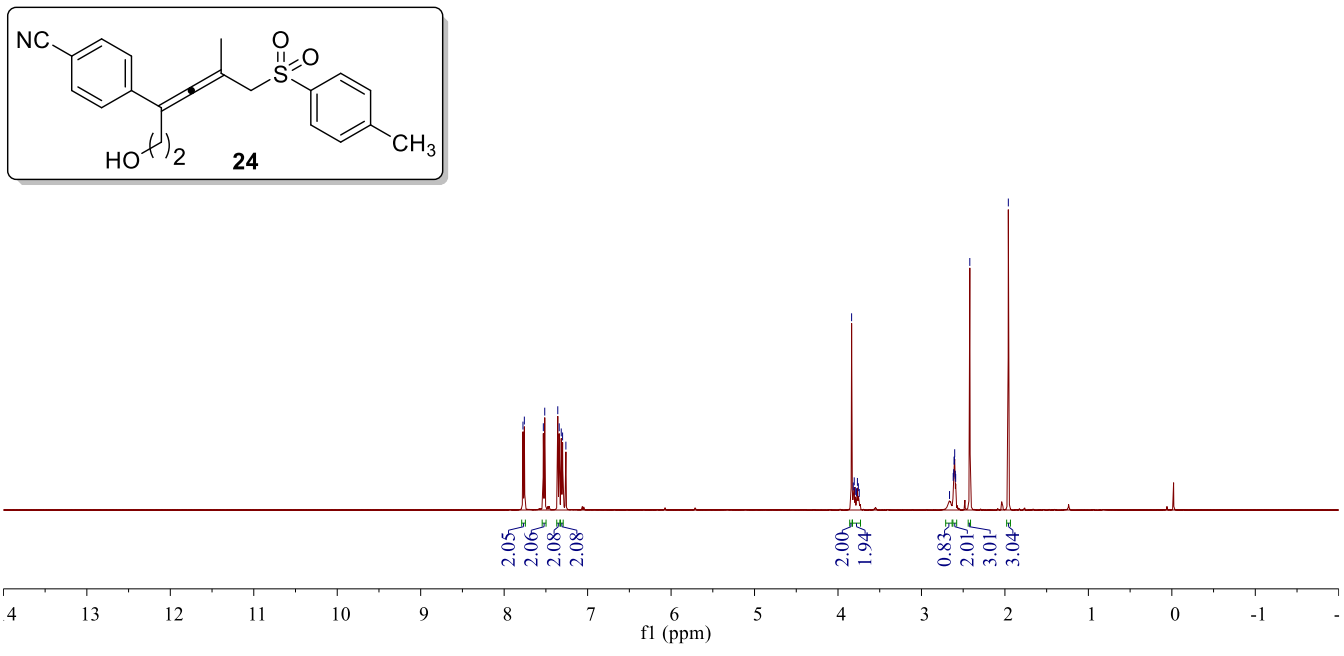
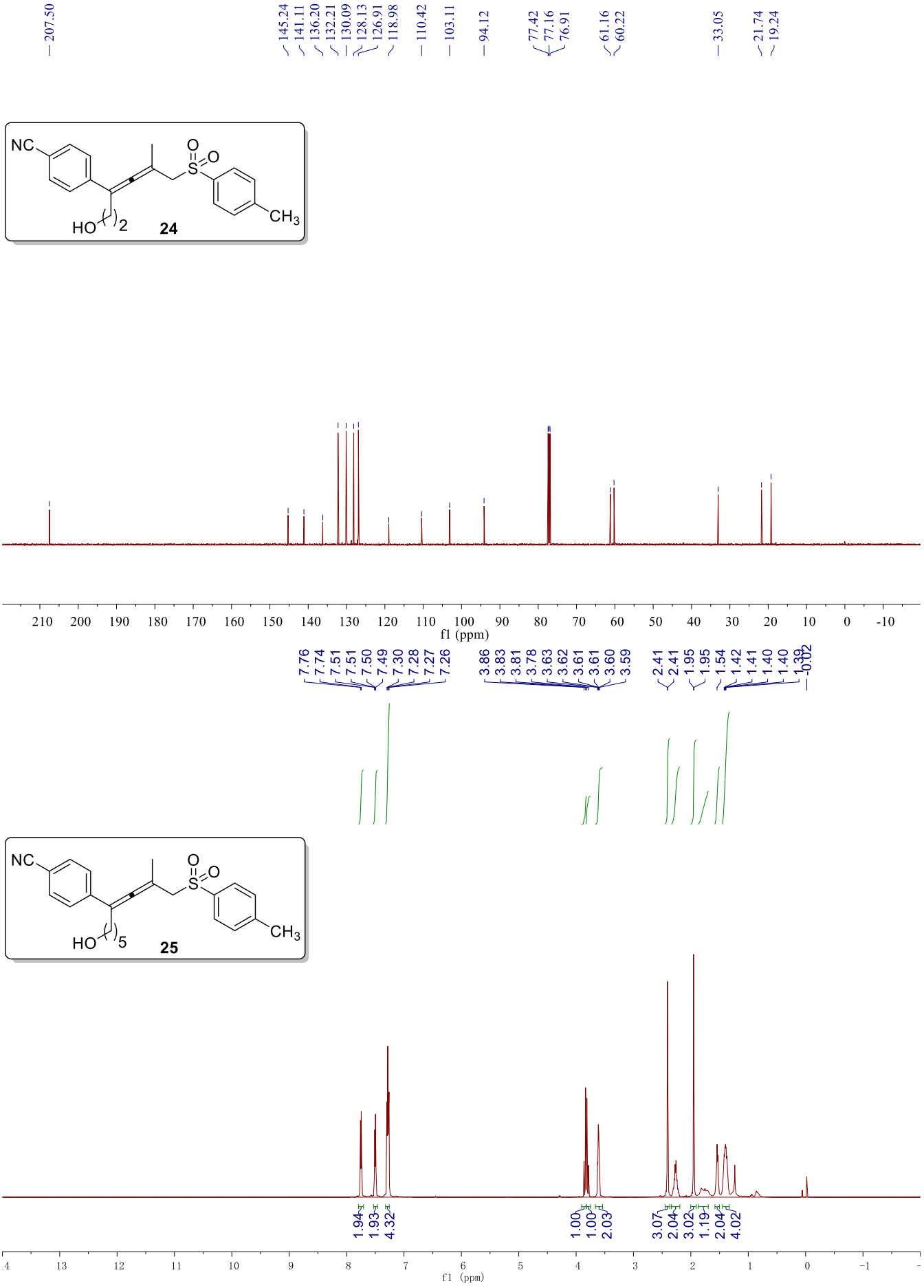
2.61
2.60
2.60
2.59
2.42
1.96


NC
O
S
O
CH3
HO
2
24
2.05
2.06
2.08
2.08
2.00
1.94
0.83
2.01
3.01
3.04
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -
f1 (ppm)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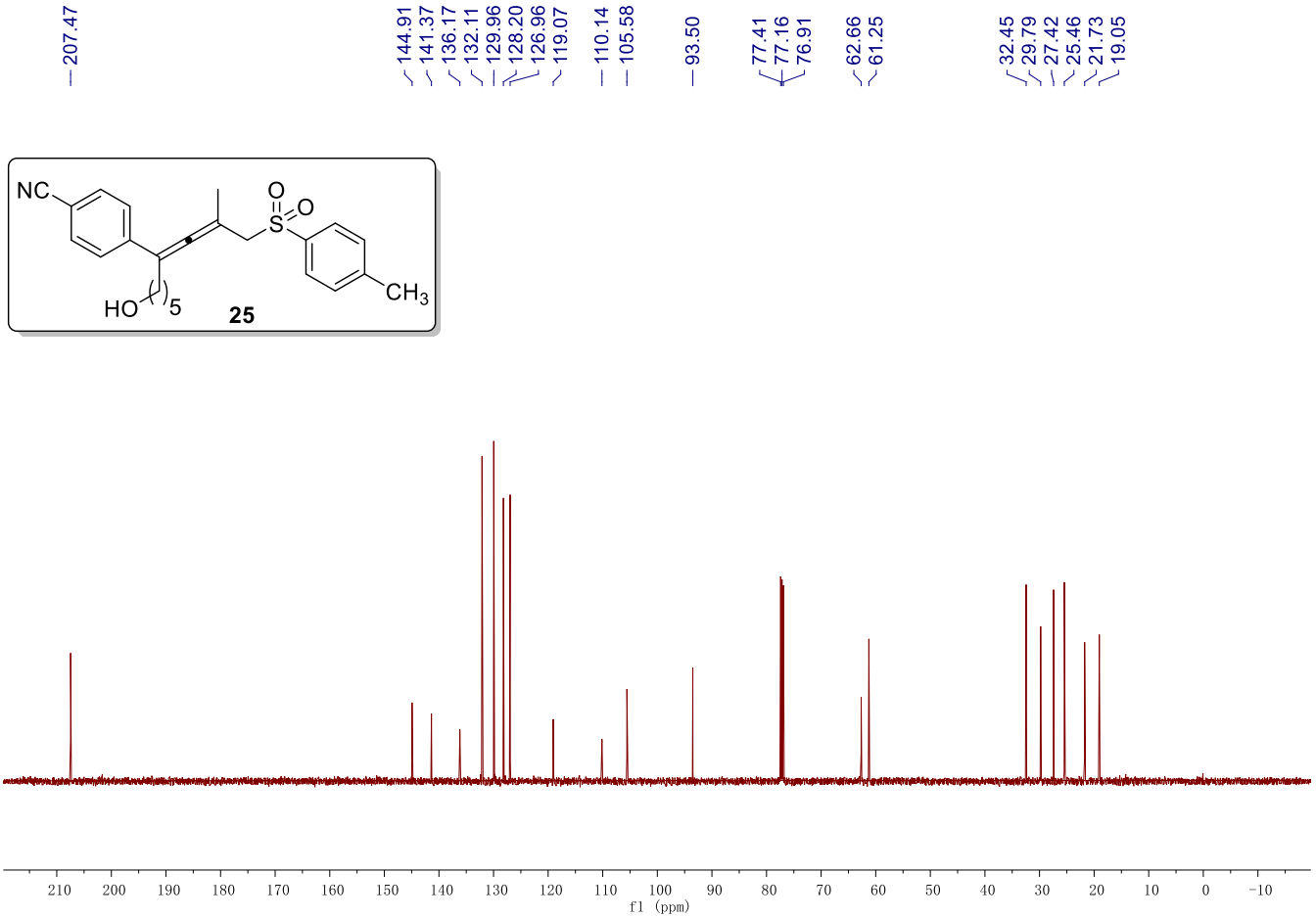
130.09
128.13
126.91
118.98
110.42
103.11
94.12
77.42
77.16
76.91
61.16
60.22
33.05
21.74
19.24
NC
O
S
O
CH3
HO
2
24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
7.76
7.74
7.51
7.51
7.50
7.49
7.30
7.28
7.27
7.26
3.86
3.83
3.81
3.78
3.63
3.62
3.61
3.61
3.60
3.59
2.41
2.41
1.95
1.95
1.54
1.42
1.41
1.40
1.40
1.39
0.02
NC
O
S
O
CH3
HO
5
25
1.94
1.93
4.32
1.00
1.00
2.03
3.07
2.04
3.02
1.19
2.04
4.02
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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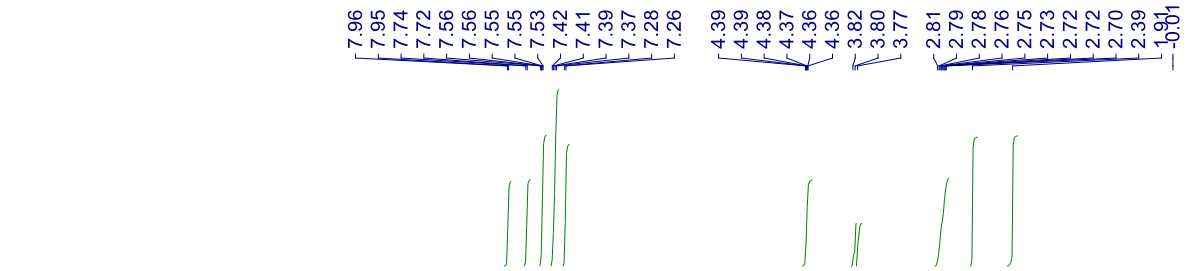
129.96
128.20
126.96
119.07
110.14
105.58
93.50
77.41
77.16
76.91
62.66
61.25
32.45
29.79
27.42
25.46
21.73
19.05
NC
O
S
O
CH3
HO
5
25
f1 (ppm)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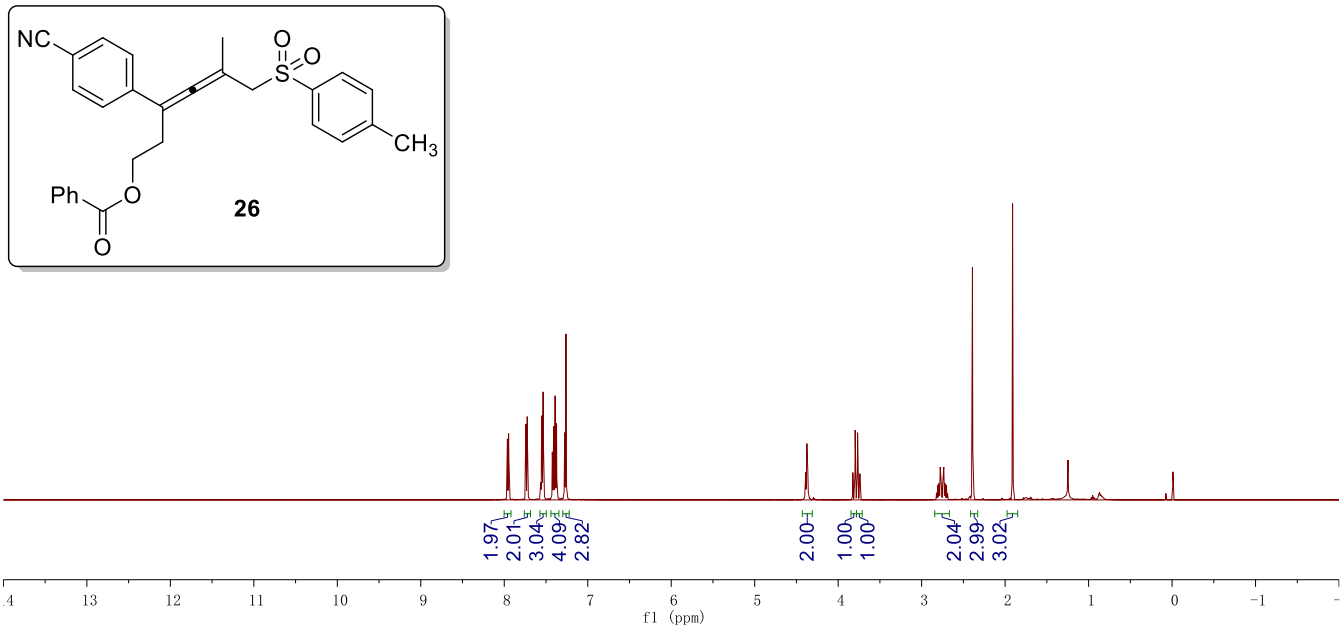
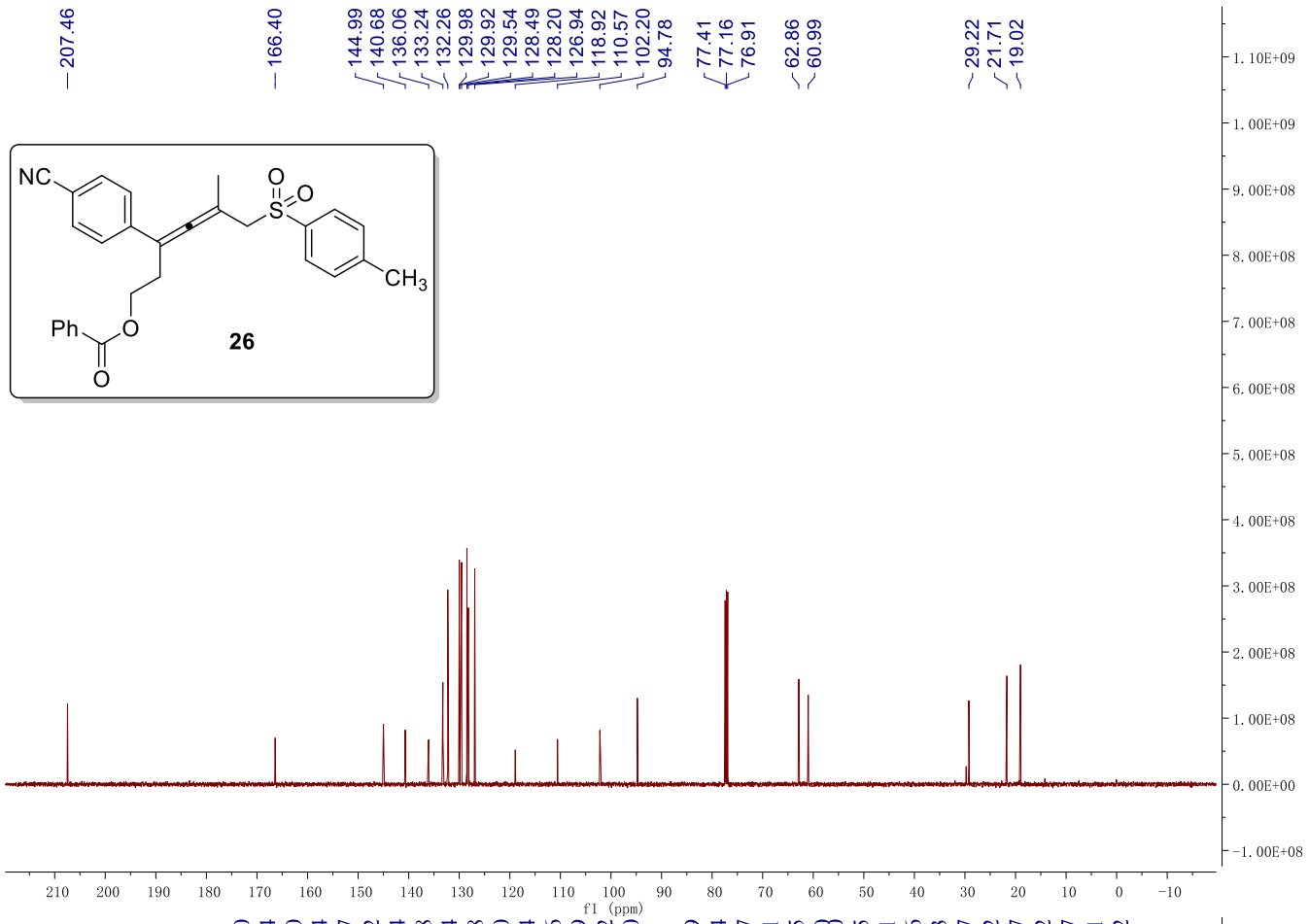
7.56
7.55
7.55
7.53
7.42
7.41
7.39
7.37
7.28
7.26
4.39
4.39
4.38
4.37
4.36
4.36
3.82
3.80
3.77
2.81
2.79
2.78
2.76
2.75
2.73
2.72
2.72
2.70
2.39
1.91
0.01


NC
O
S
O
CH3
Ph
O
O
26
1.97
2.01
3.04
4.09
2.82
2.00
1.00
1.00
2.04
2.99
3.02
f1 (ppm)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129.98
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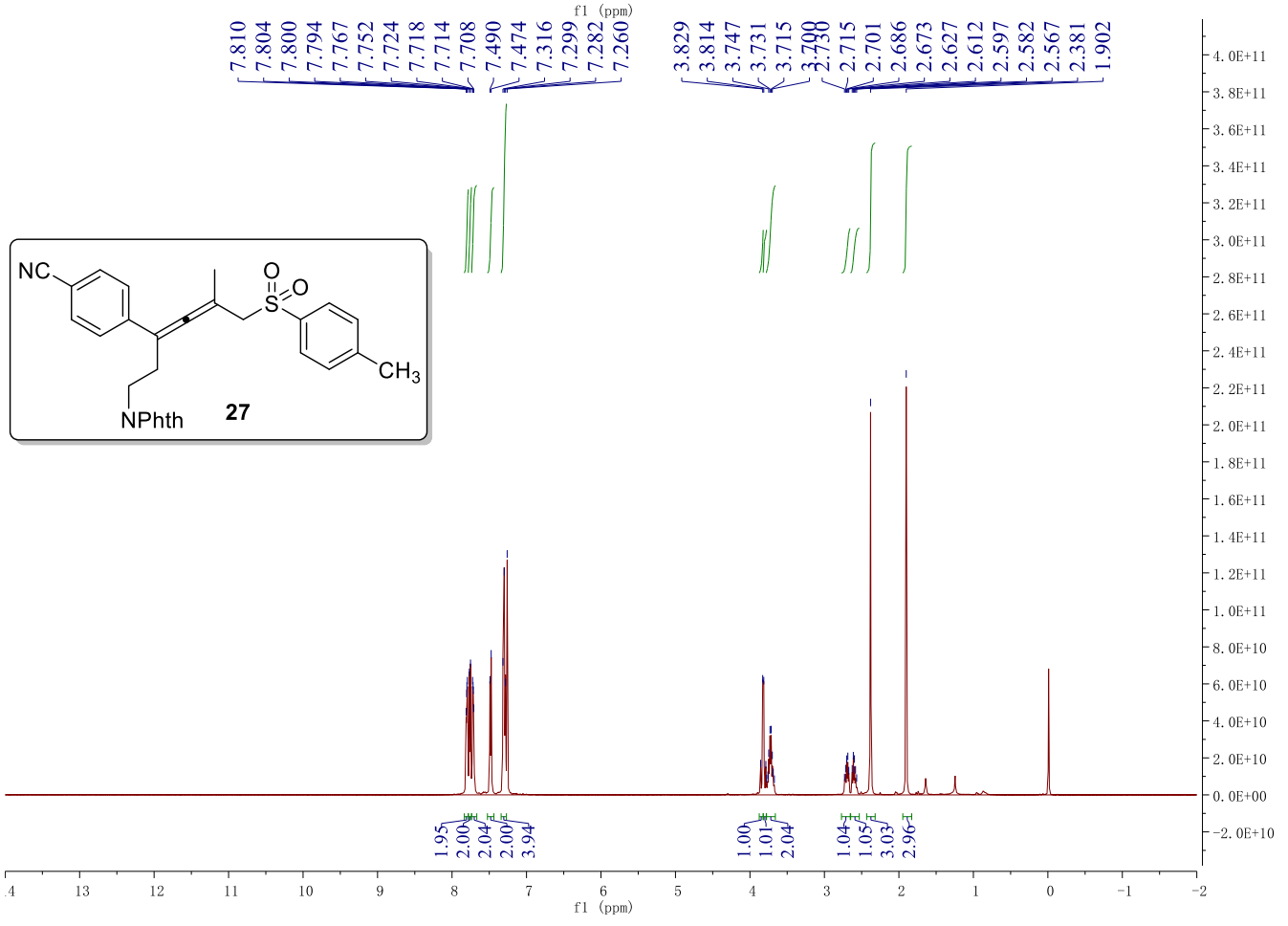
129.54
128.49
128.20
126.94
118.92
110.57
102.20
94.78
77.41
77.16
76.91
62.86
60.99
29.22
21.71
19.02
NC
O
S
O
CH3
Ph
O
O
26
f1 (ppm)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7.718
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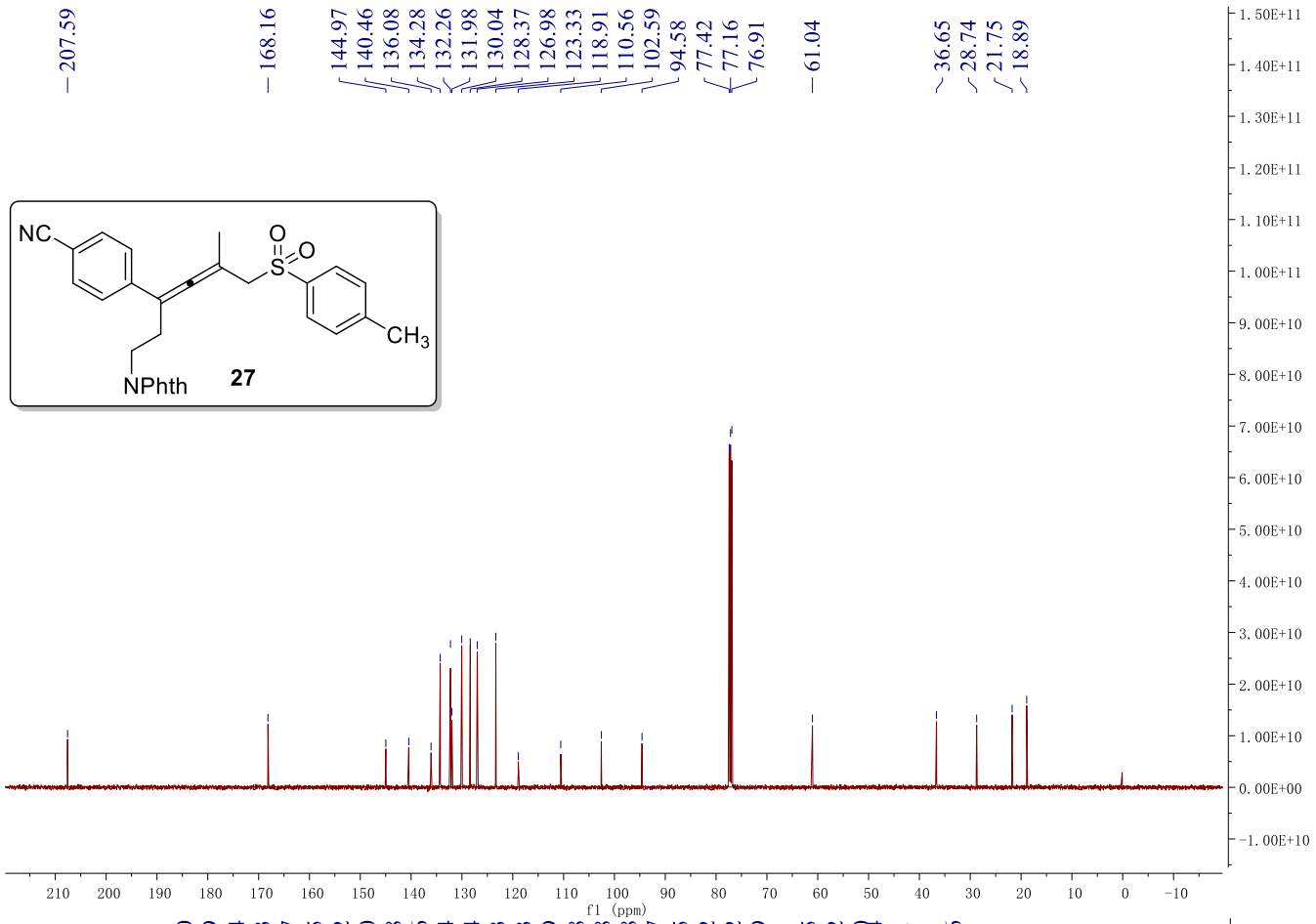
7.708
7.490
7.474
7.316
7.299
7.282
7.260
3.829
3.814
3.747
3.731
3.715
2.715
2.701
2.686
2.673
2.627
2.612
2.597
2.582
2.567
2.381
1.902
1.95
2.00
2.04
2.00
3.94
1.00
1.01
2.04
1.04
1.05
3.03
2.96
NC
O
S
O
CH3
NPhth
27
f1 (ppm)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136.08
134.28
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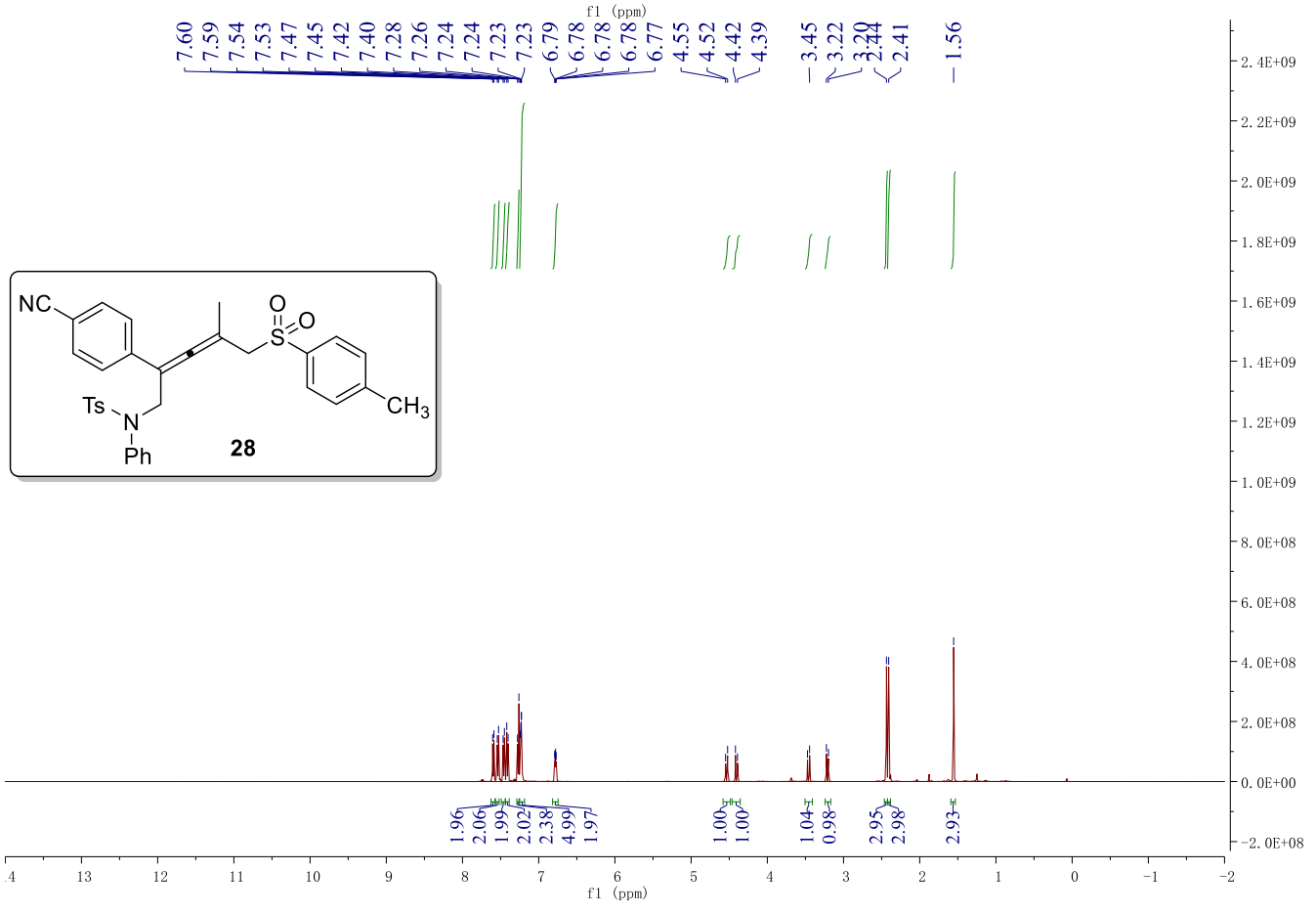
131.98
130.04
128.37
126.98
123.33
118.91
110.56
102.59
94.58
77.42
77.16
76.91
61.04
36.65
28.74
21.75
18.89
NC
O
S
O
CH3
NPhth
27
f1 (ppm)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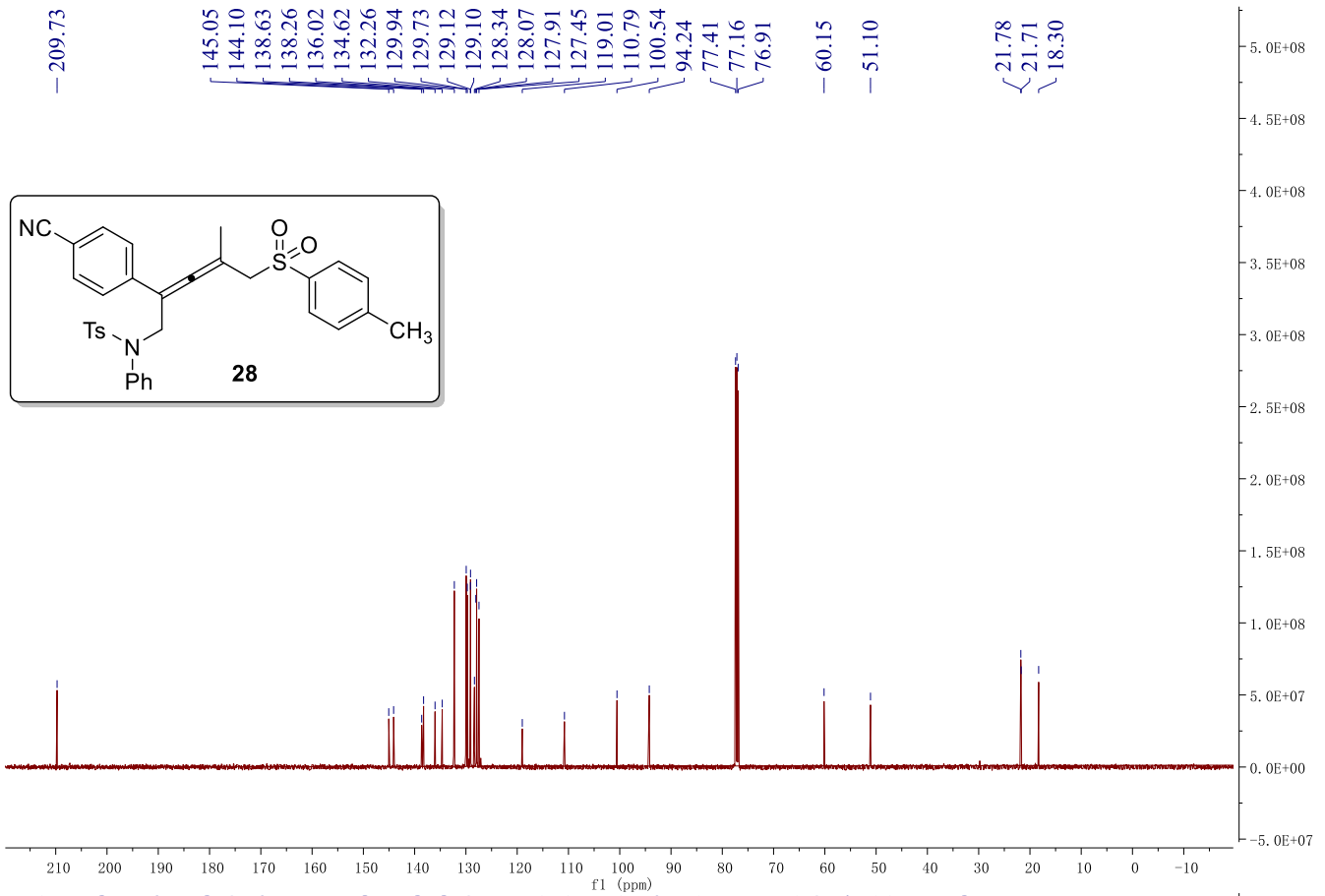
7.23
7.23
6.79
6.78
6.78
6.78
6.77
4.55
4.52
4.42
4.39
3.45
3.22
3.20
2.44
2.41
1.56
NC
O
S
O
CH3
Ts
N
Ph
28
1.96
2.06
1.99
2.02
2.38
4.99
1.97
1.00
1.00
1.04
0.98
2.95
2.98
2.93
f1 (ppm)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136.02
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132.26
129.94
129.73
129.12
129.10
128.34
128.07
127.91
127.45
119.01
110.79
100.54
94.24
77.41
77.16
76.91
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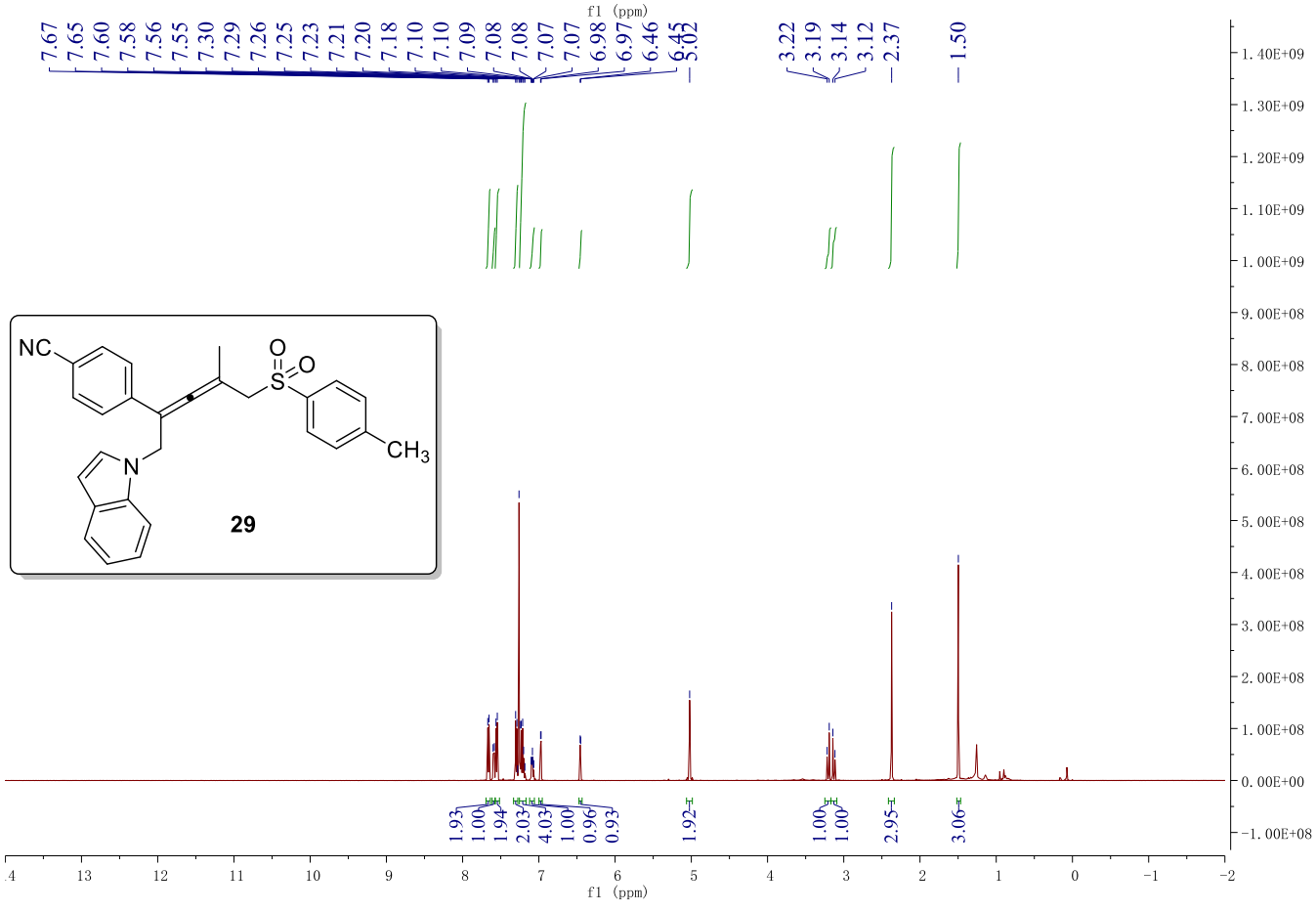
51.10
21.78
21.71
18.30
NC
O
S
O
Ts
N
Ph
CH3
28
f1 (ppm)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7.29
7.26
7.25
7.23
7.21
7.20
7.18
7.10
7.10
7.09
7.08
7.08
7.07
7.07
6.98
6.97
6.46
6.45
5.02
3.22
3.19
3.14
3.12
2.37
1.50
NC
O
S
O
N
CH3
29
1.93
1.00
1.94
2.03
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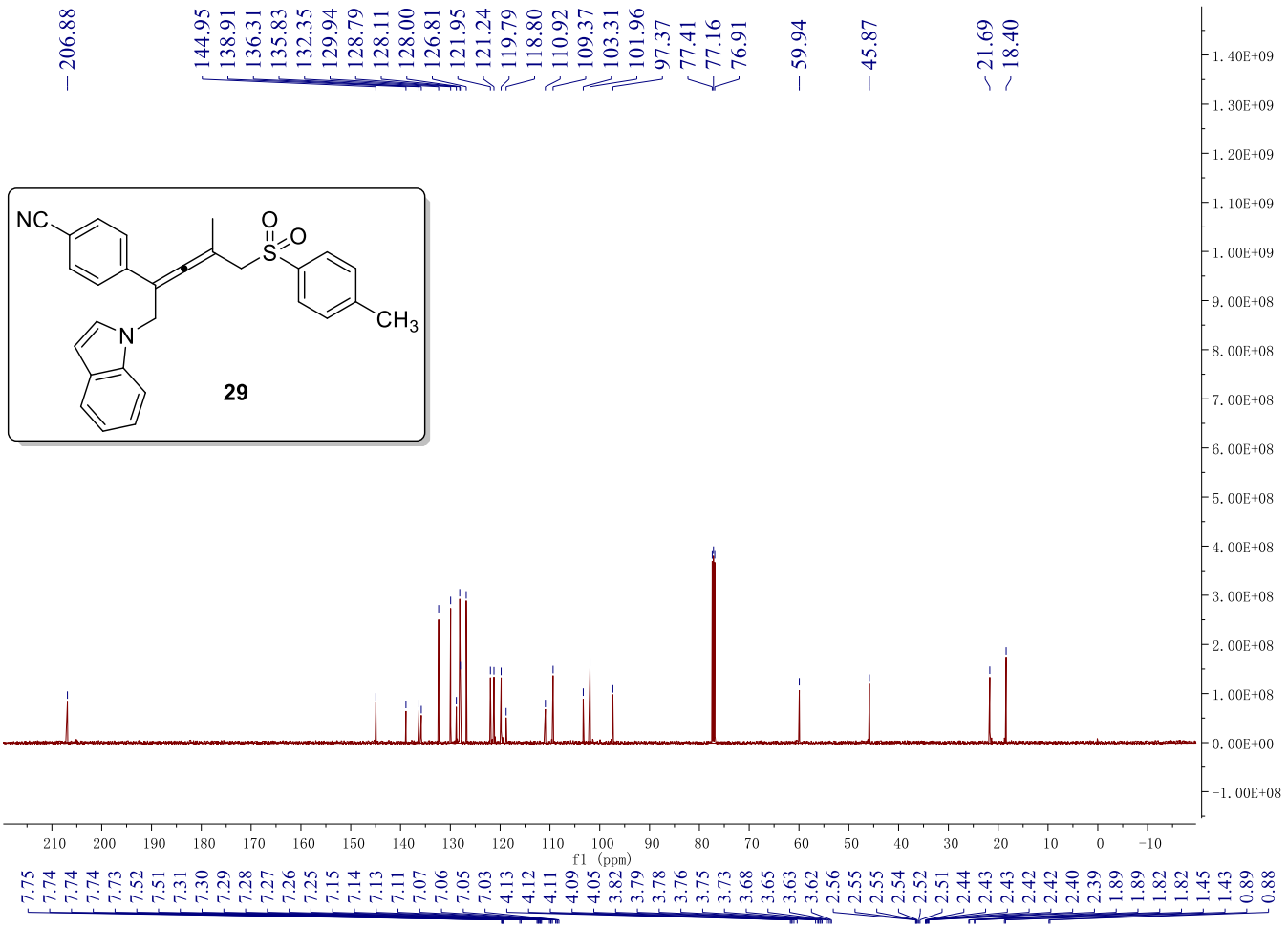
1.00
0.96
0.93
1.92
1.00
1.00
2.95
3.06
f1 (ppm)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132.35
129.94
128.79
128.11
128.00
126.81
121.95
121.24
119.79
118.80
110.92
109.37
103.31
101.96
97.37
77.41
77.16
76.91
59.94
45.87
21.69
18.40
NC
O
S
O
CH3
N
29
f1 (ppm)
7.75
7.74
7.74
7.74
7.73
7.52
7.51
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.15
7.14
7.13
7.11
7.07
7.06
7.05
7.03
4.13
4.12
4.11
4.09
4.05
3.82
3.79
3.78
3.76
3.75
3.73
3.68
3.65
3.63
3.62
2.56
2.55
2.55
2.54
2.52
2.51
2.44
2.43
2.43
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2.39
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1.82
1.82
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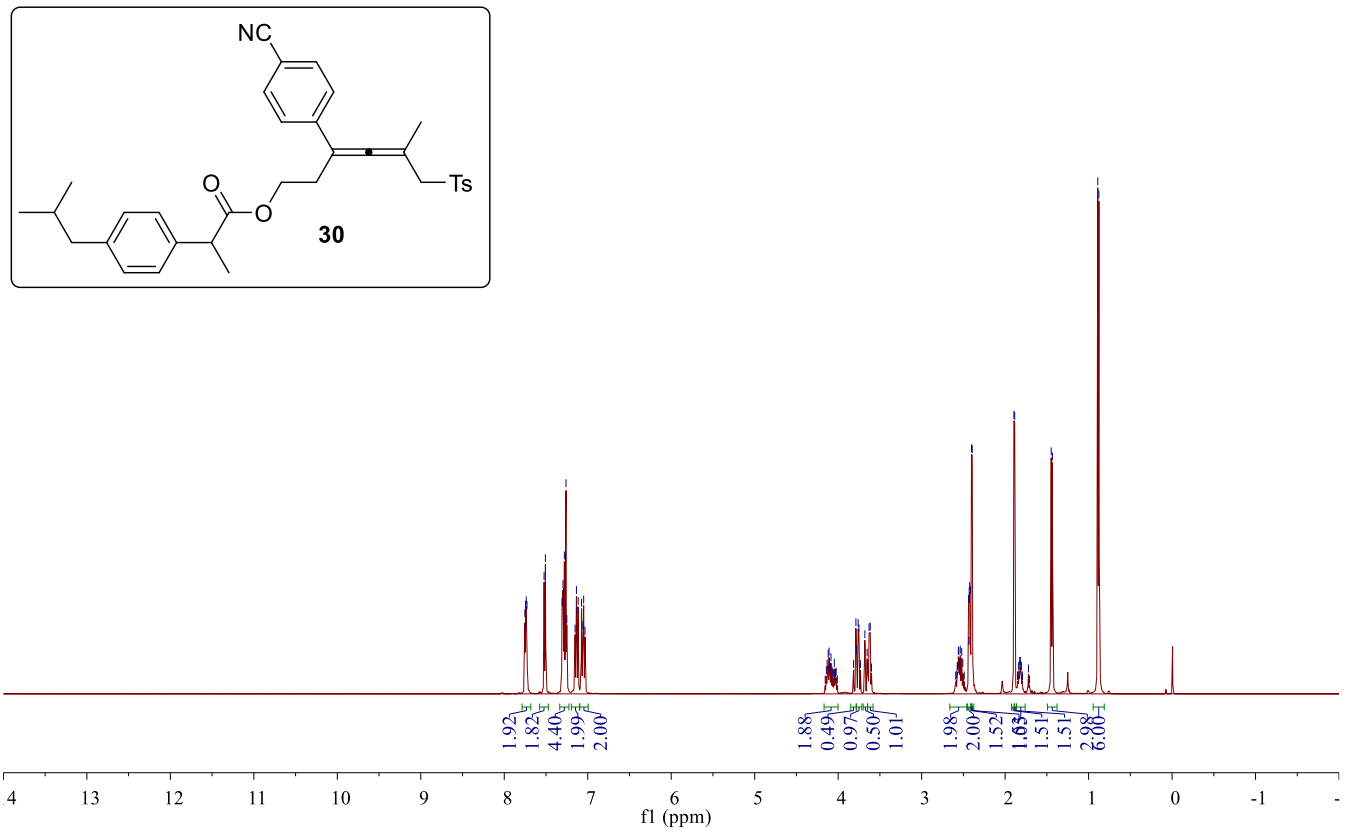
0.88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O
O
Ts
30
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1.82
4.40
1.99
2.00
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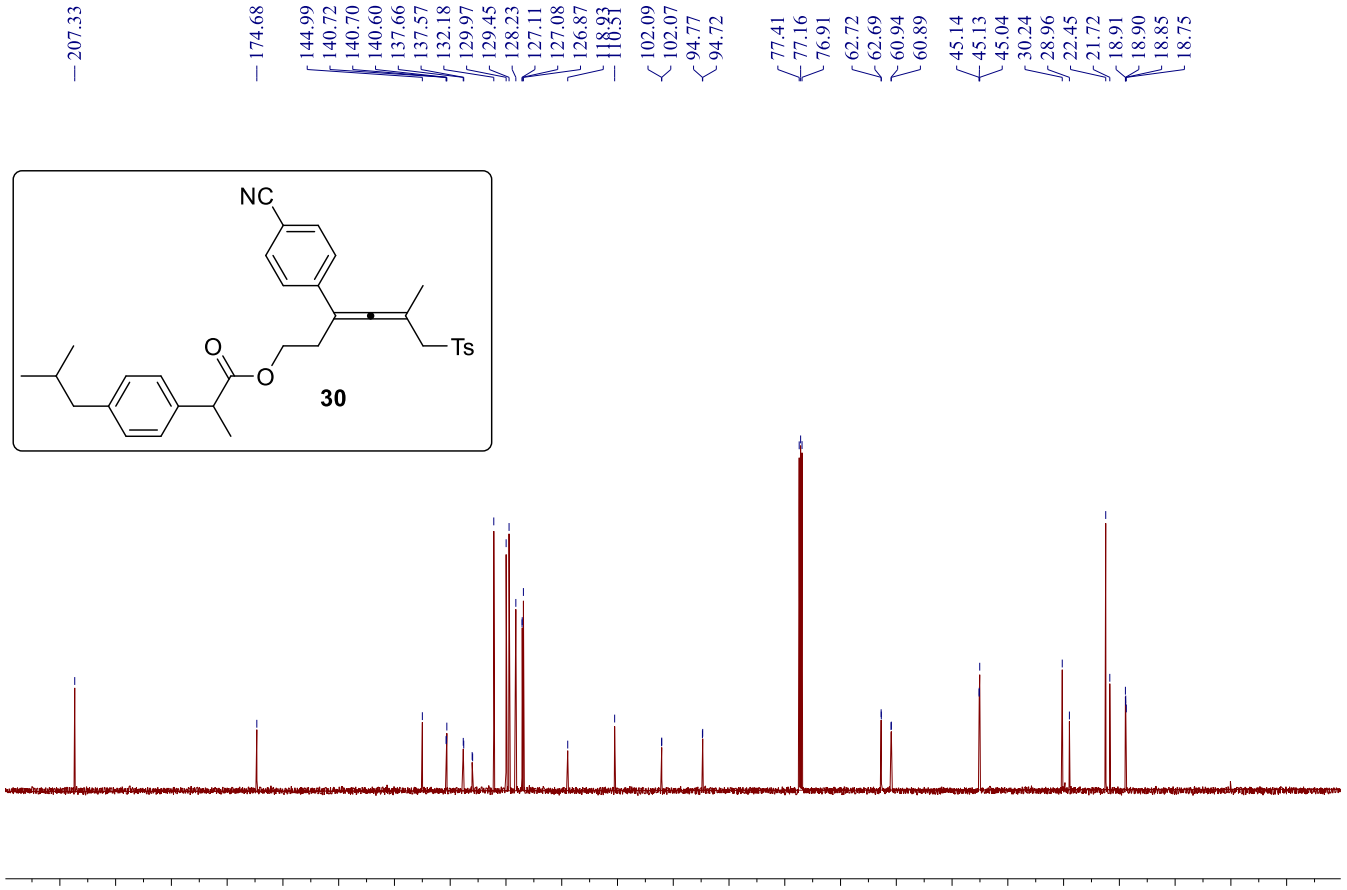
1.01
1.98
2.00
1.52
1.51
1.51
2.08
6.00
f1 (ppm)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140.60
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137.57
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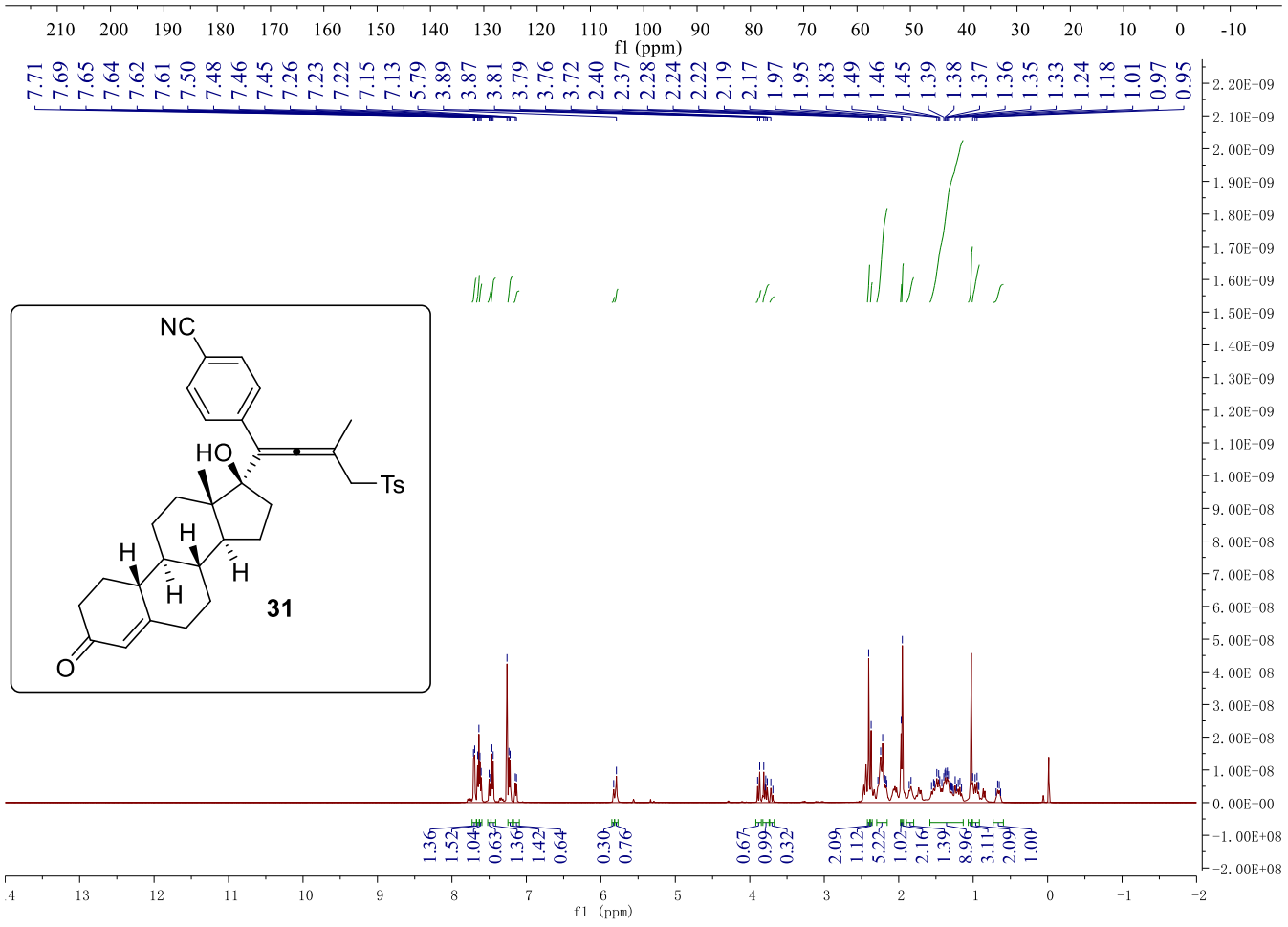
129.97
129.45
128.23
127.11
127.08
126.87
118.93
118.51
102.09
102.07
94.77
94.72
77.41
77.16
76.91
62.72
62.69
60.94
60.89
45.14
45.13
45.04
30.24
28.96
22.45
21.72
18.91
18.90
18.85
18.75
NC
O
O
Ts
30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.69
7.65
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7.62
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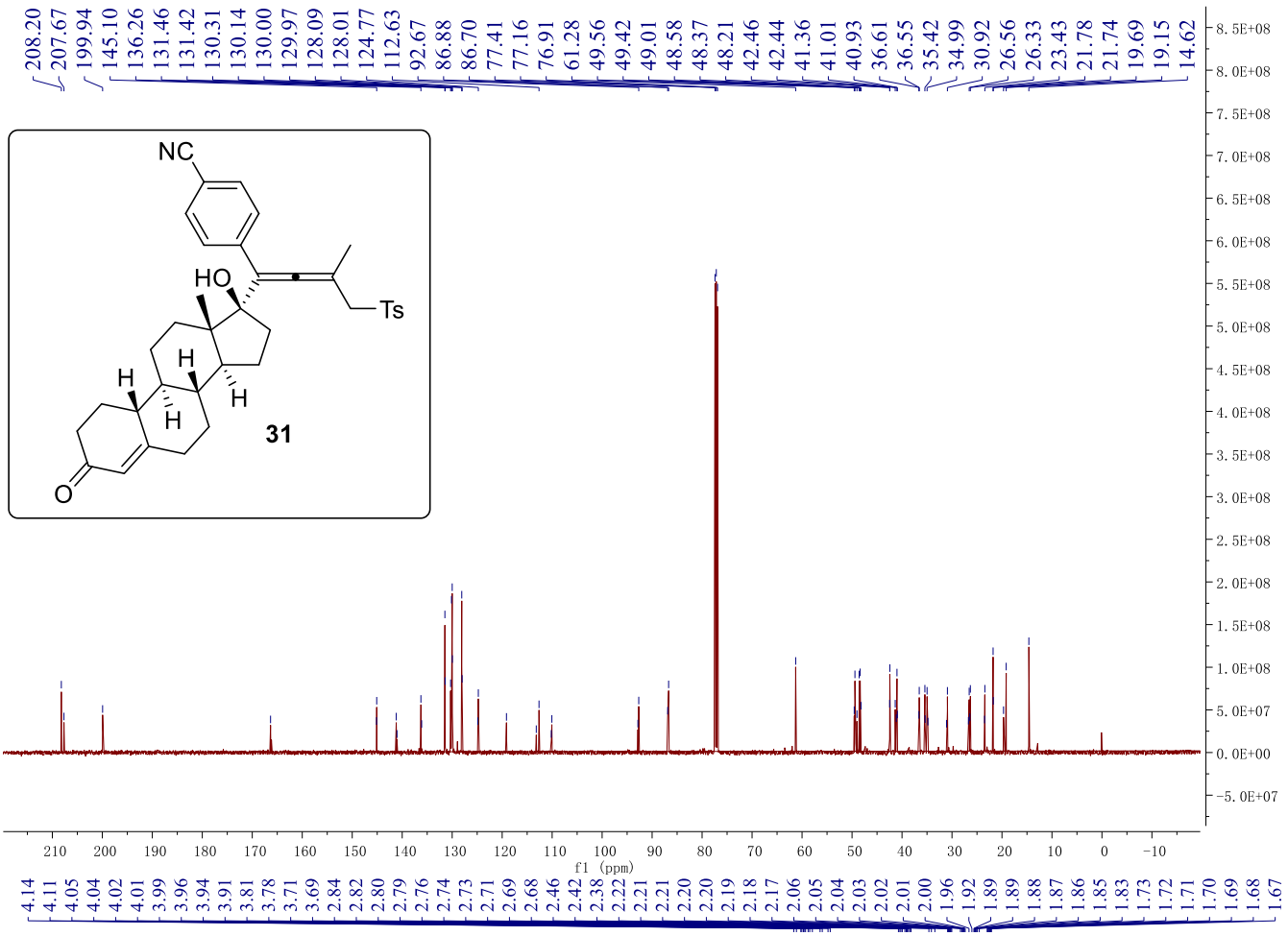
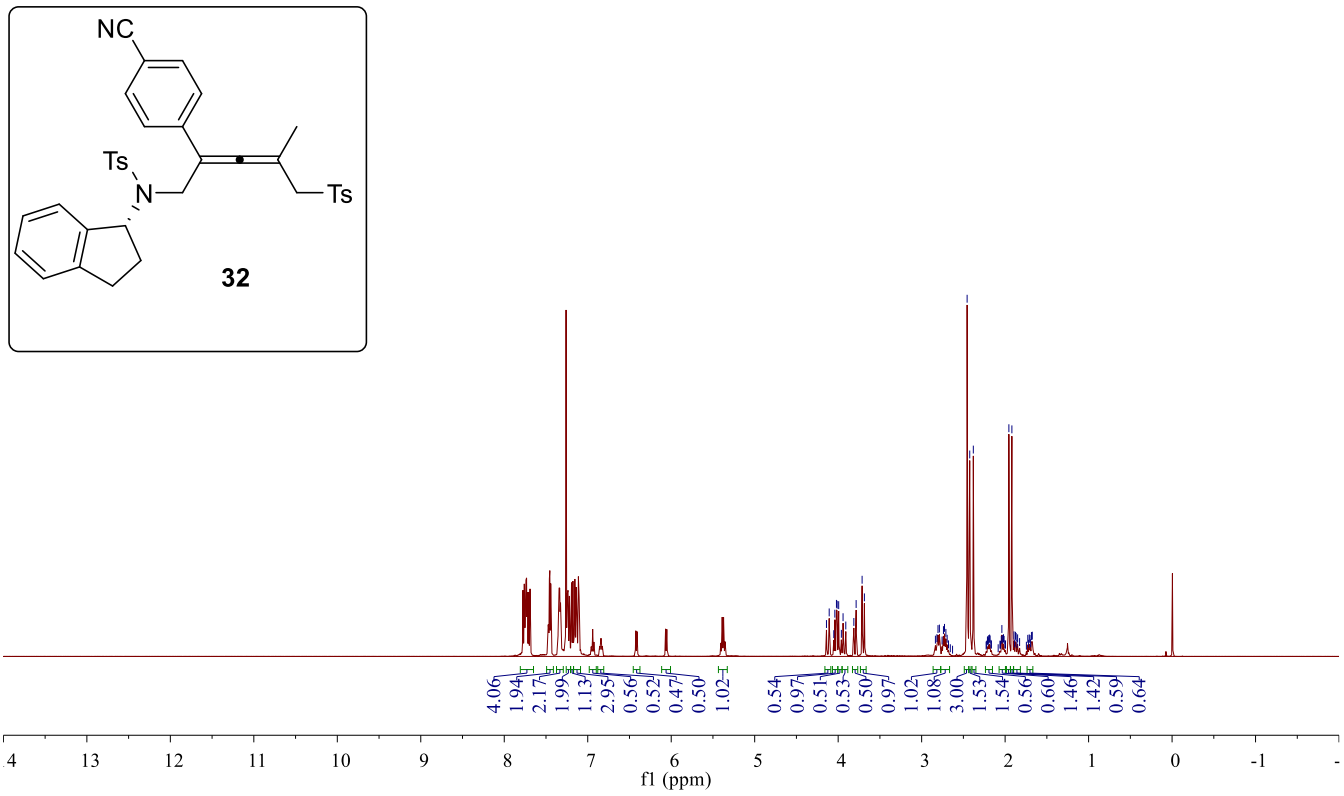
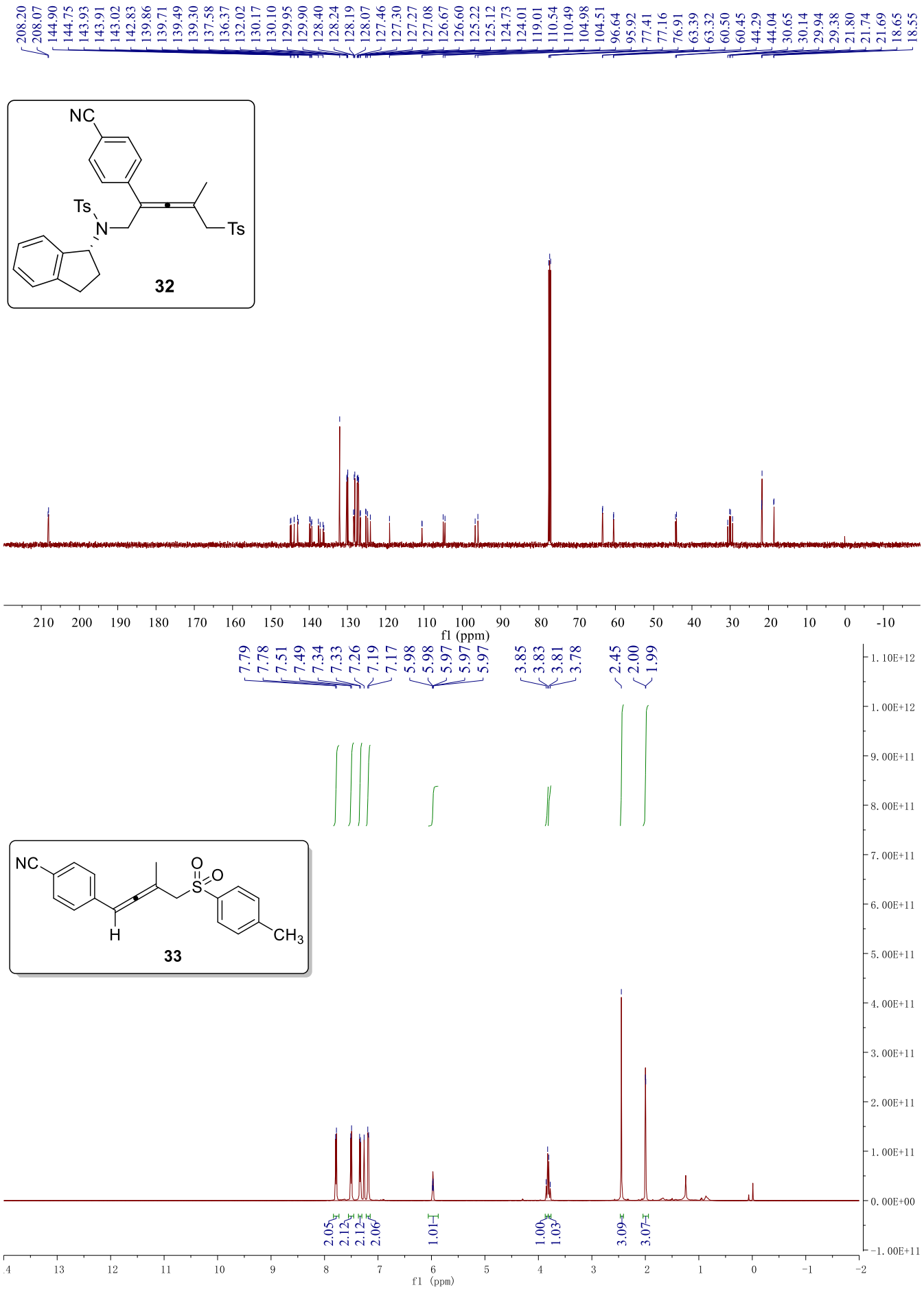
7.26
7.23
7.22
7.15
7.13
5.79
3.89
3.87
3.81
3.79
3.76
3.72
2.40
2.37
2.28
2.24
2.22
2.19
2.17
1.97
1.95
1.83
1.49
1.46
1.45
1.39
1.38
1.37
1.36
1.35
1.33
1.24
1.18
1.01
0.97
0.95
NC
HO
Ts
H
H
H
H
O
31
1.36
1.52
1.04
0.63
1.36
1.42
0.64
0.30
0.76
0.67
0.99
0.32
2.09
1.12
5.22
1.02
2.16
1.39
8.96
3.11
2.09
1.00
f1 (ppm)


NC
HO
Ts
H
H
H
H
O
31
f1 (ppm)


NC
Ts
N
Ts
32
f1 (ppm)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208.07
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143.91
143.02
142.83
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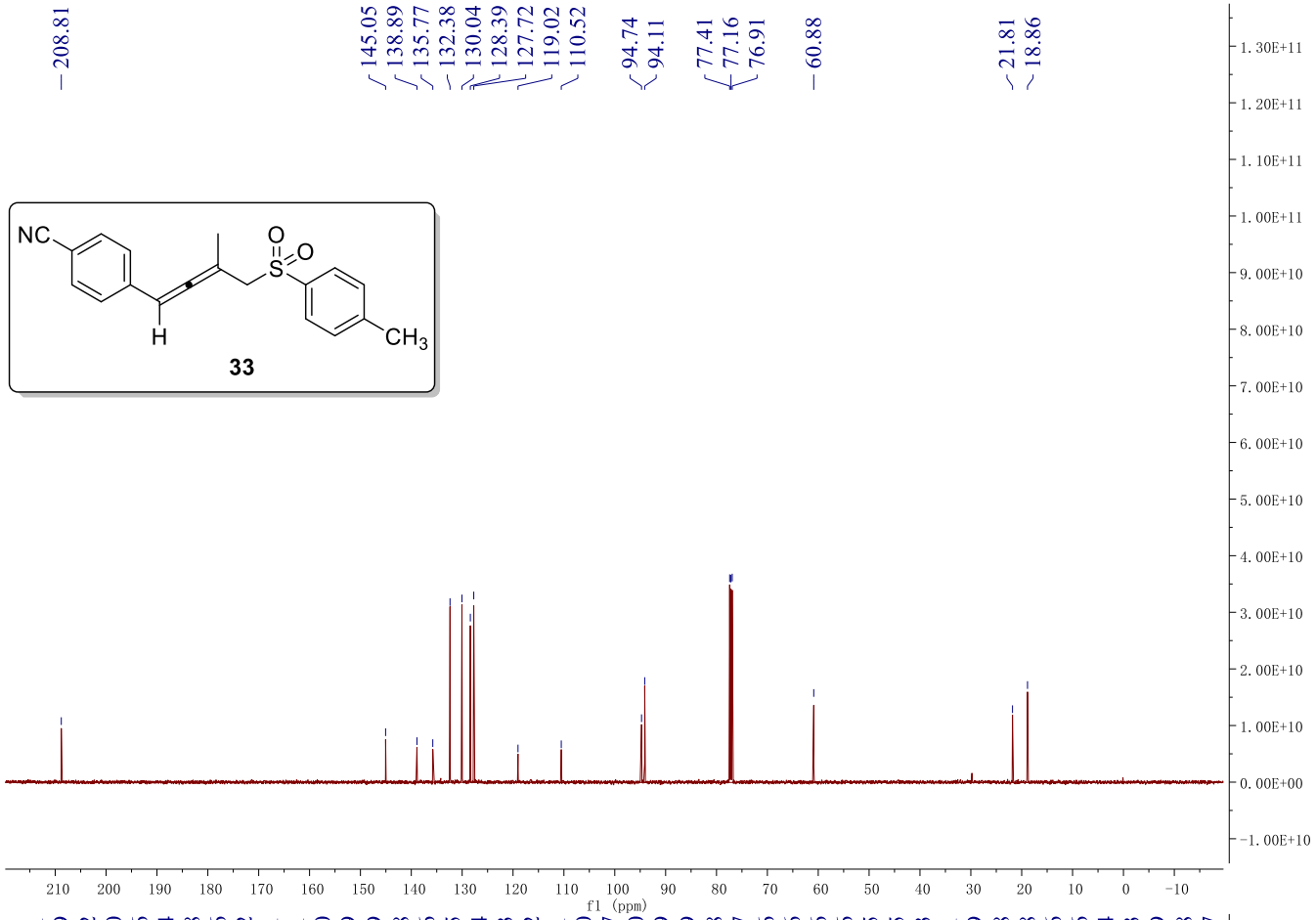
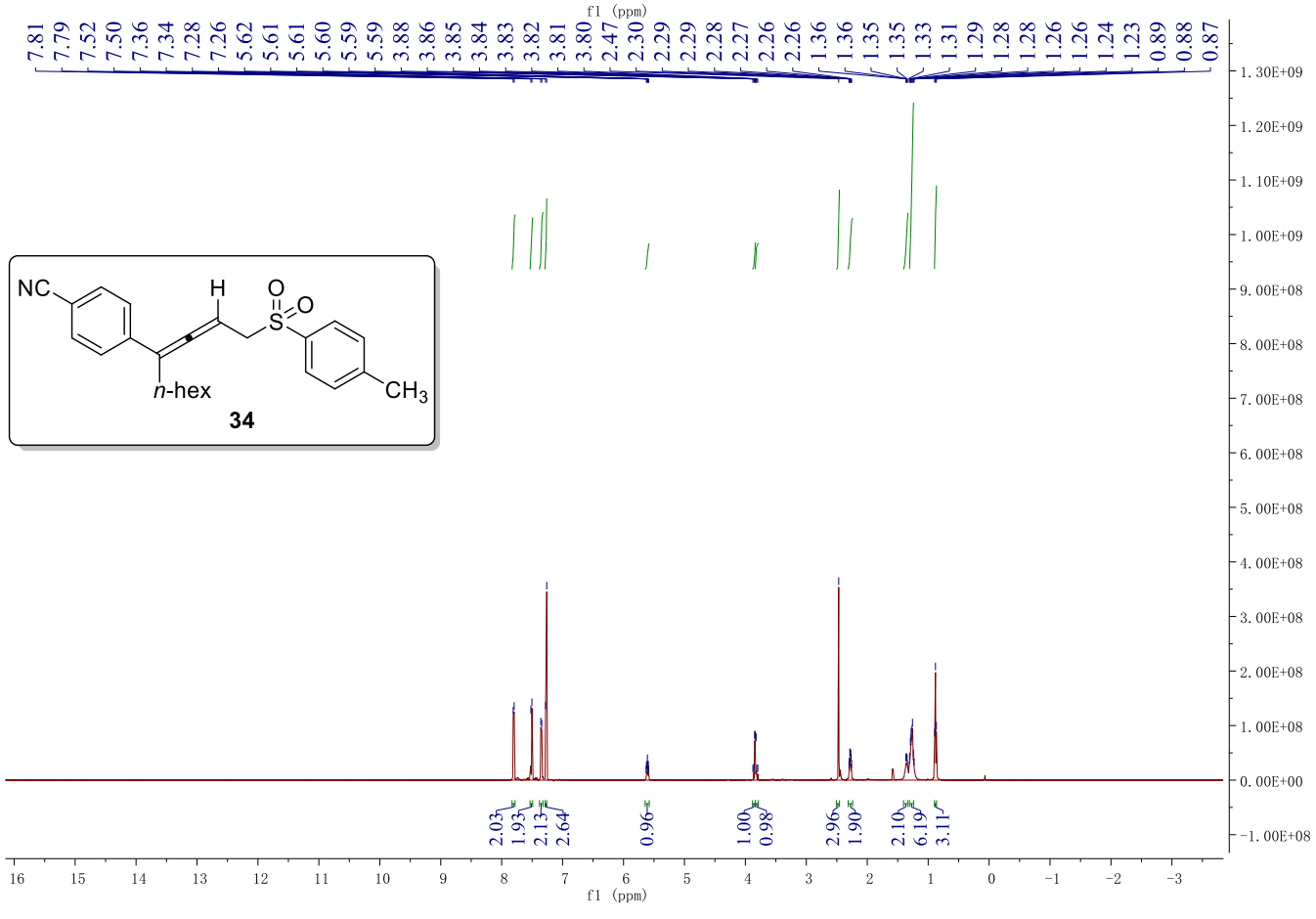
139.71
139.49
139.30
137.58
136.37
132.02
130.17
130.10
129.95
129.90
128.40
128.24
128.19
128.07
127.46
127.30
127.27
127.08
126.67
126.60
125.22
125.12
124.73
124.01
119.01
110.54
110.49
104.98
104.51
96.64
95.92
77.41
77.16
76.91
63.39
63.32
60.50
60.45
44.29
44.04
30.65
30.14
29.94
29.38
21.80
21.74
21.69
18.65
18.55
NC
Ts
N
Ts
32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
7.79
7.78
7.51
7.49
7.34
7.33
7.26
7.19
7.17
5.98
5.98
5.97
5.97
5.97
3.85
3.83
3.81
3.78
2.45
2.00
1.99
NC
O
O
S
H
CH3
33
2.05
2.12
2.12
2.06
1.01
1.00
1.03
3.09
3.07
1.10E+12
1.00E+12
9.00E+11
8.00E+11
7.00E+11
6.00E+11
5.00E+11
4.00E+11
3.00E+11
2.00E+11
1.00E+11
0.00E+00
-1.00E+11
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


208.81
145.05
138.89
135.77
132.38
130.04
128.39
127.72
119.02
110.52
94.74
94.11
77.41
77.16
76.91
60.88
21.81
18.86
NC
O
O
S
H
CH3
33
f1 (ppm)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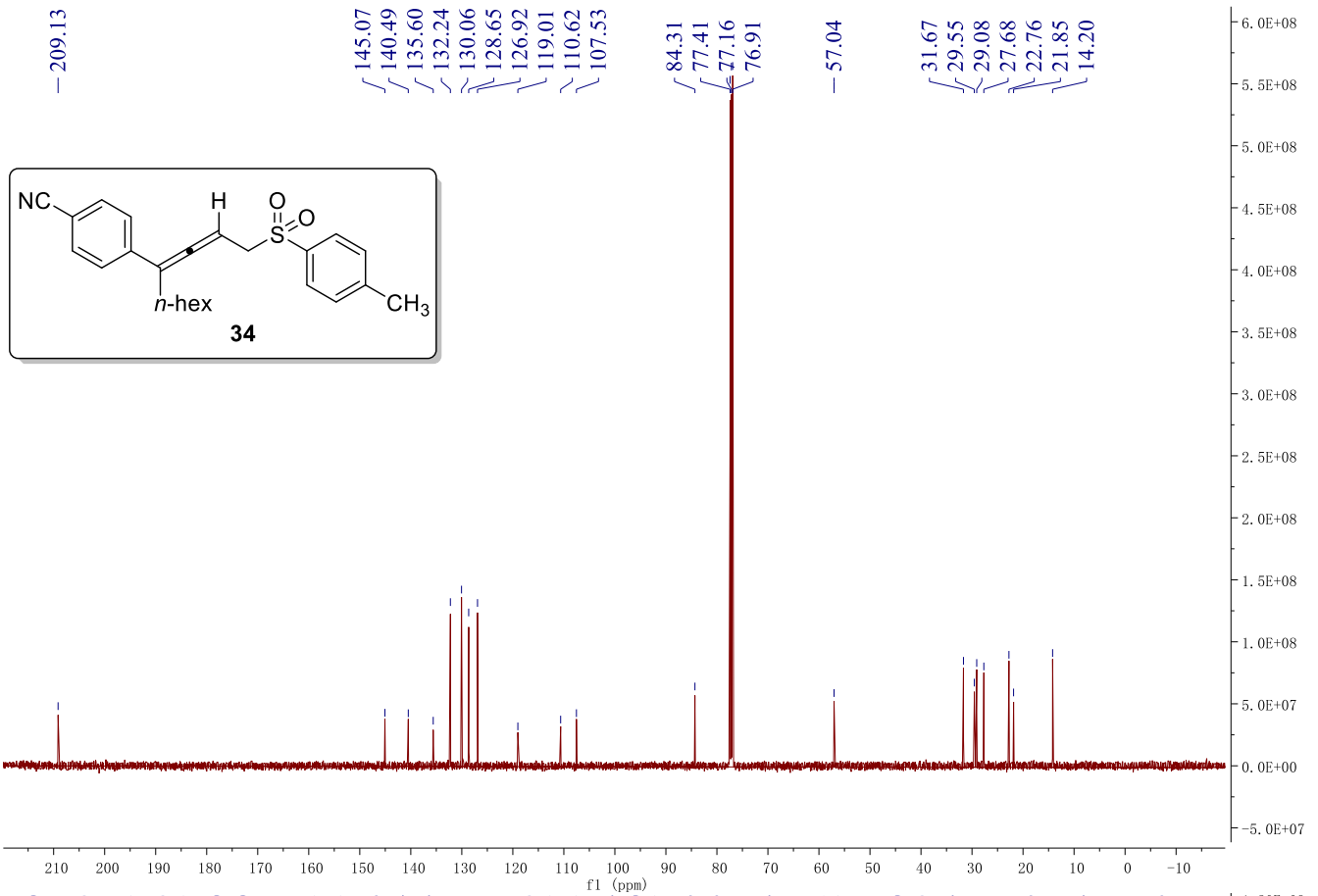
7.79
7.52
7.50
7.36
7.34
7.28
7.26
5.62
5.61
5.61
5.60
5.59
5.59
3.88
3.86
3.85
3.84
3.83
3.82
3.81
3.80
2.47
2.30
2.29
2.29
2.28
2.27
2.26
2.26
1.36
1.36
1.35
1.35
1.33
1.31
1.29
1.28
1.28
1.26
1.26
1.24
1.23
0.89
0.88
0.87
NC
H
O
O
S
n-hex
CH3
34
2.03
1.93
2.13
2.64
0.96
1.00
0.98
2.96
1.90
2.10
6.19
3.11
f1 (ppm)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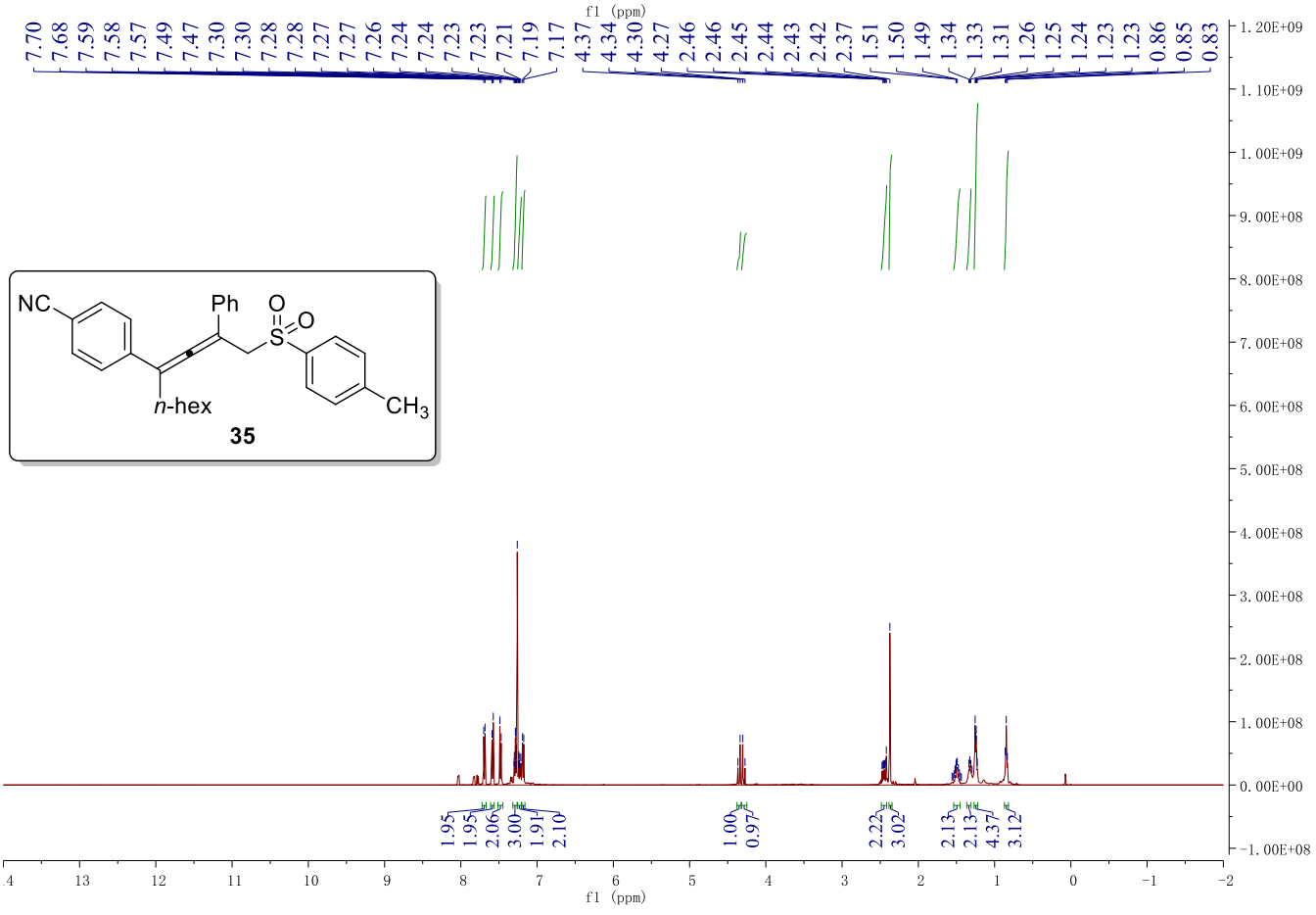
145.07
140.49
135.60
132.24
130.06
128.65
126.92
119.01
110.62
107.53
84.31
77.41
77.16
76.91
57.04
31.67
29.55
29.08
27.68
22.76
21.85
14.20
NC
H
O
S
O
n-hex
CH3
34
f1 (ppm)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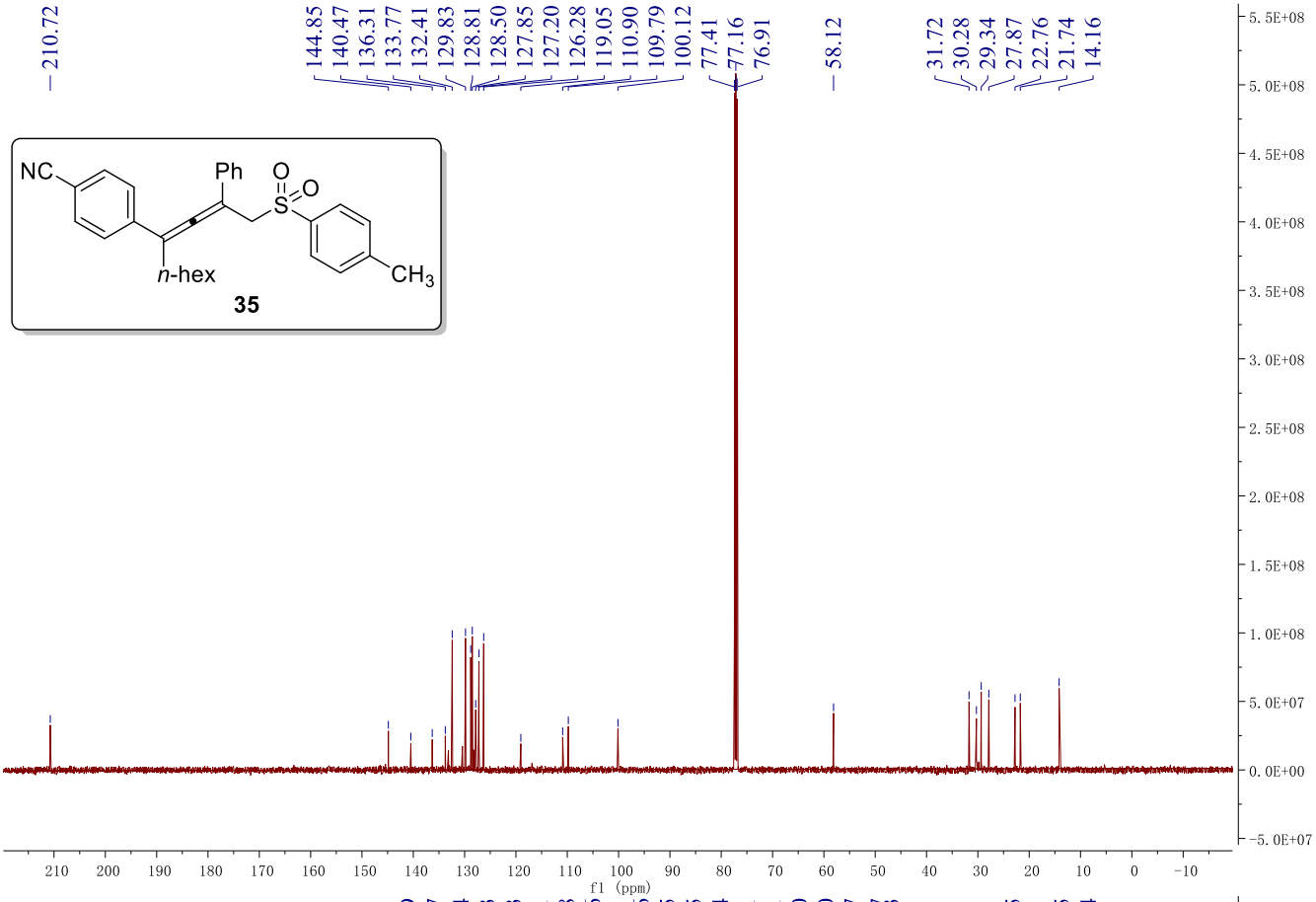
7.68
7.59
7.58
7.57
7.49
7.47
7.30
7.28
7.28
7.27
7.27
7.26
7.24
7.24
7.23
7.23
7.21
7.19
7.17
4.37
4.34
4.30
4.27
2.46
2.46
2.45
2.44
2.43
2.42
2.37
1.51
1.50
1.49
1.34
1.33
1.31
1.26
1.25
1.24
1.23
1.23
0.86
0.85
0.83
NC
Ph
O
S
O
n-hex
CH3
35
1.95
1.95
2.06
3.00
1.91
2.10
1.00
0.97
2.22
3.02
2.13
2.13
4.37
3.12
f1 (ppm)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136.31
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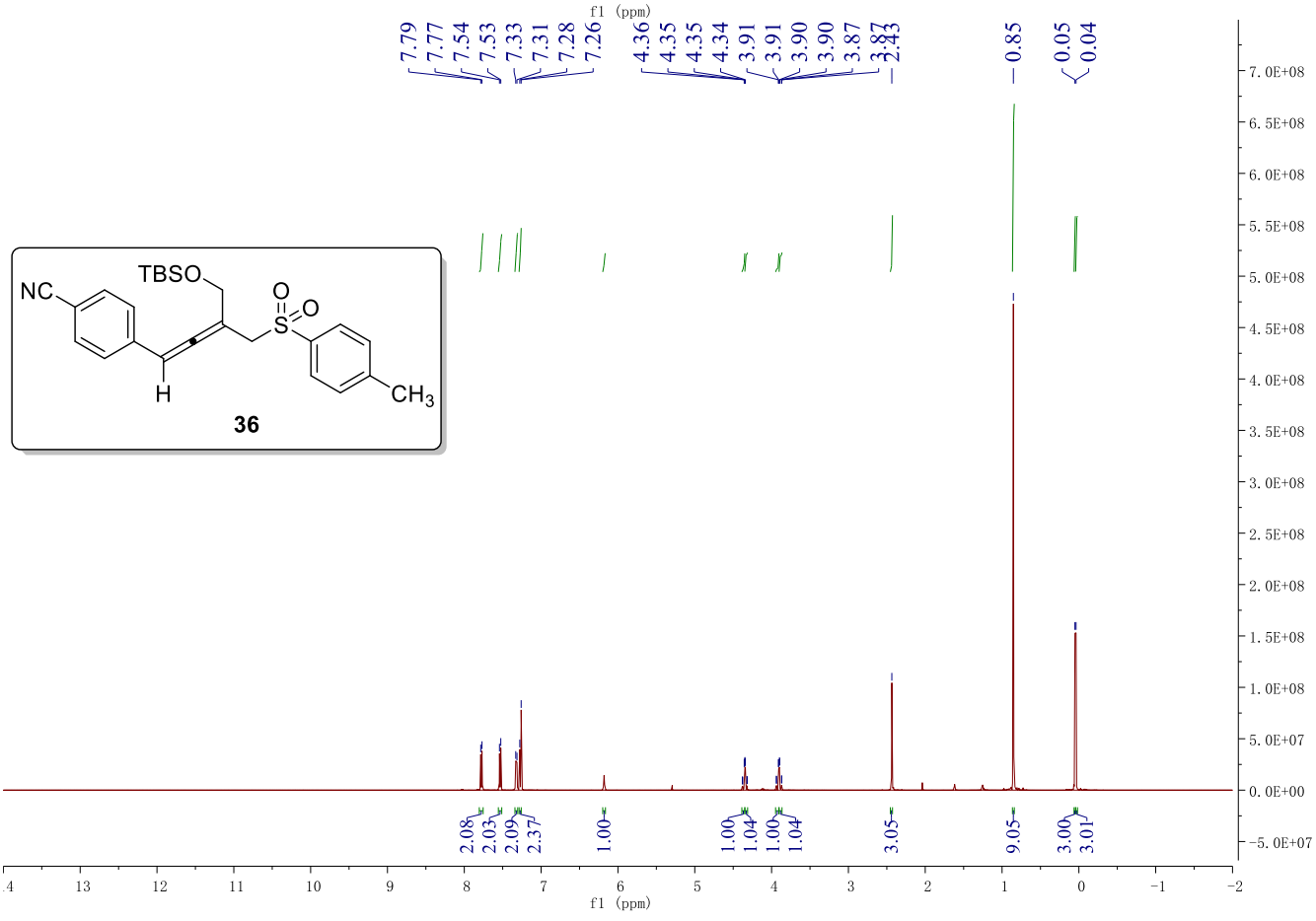
132.41
129.83
128.81
128.50
127.85
127.20
126.28
119.05
110.90
109.79
100.12
77.41
77.16
76.91
58.12
31.72
30.28
29.34
27.87
22.76
21.74
14.16
NC
Ph
O
S
O
n-hex
CH3
35
f1 (ppm)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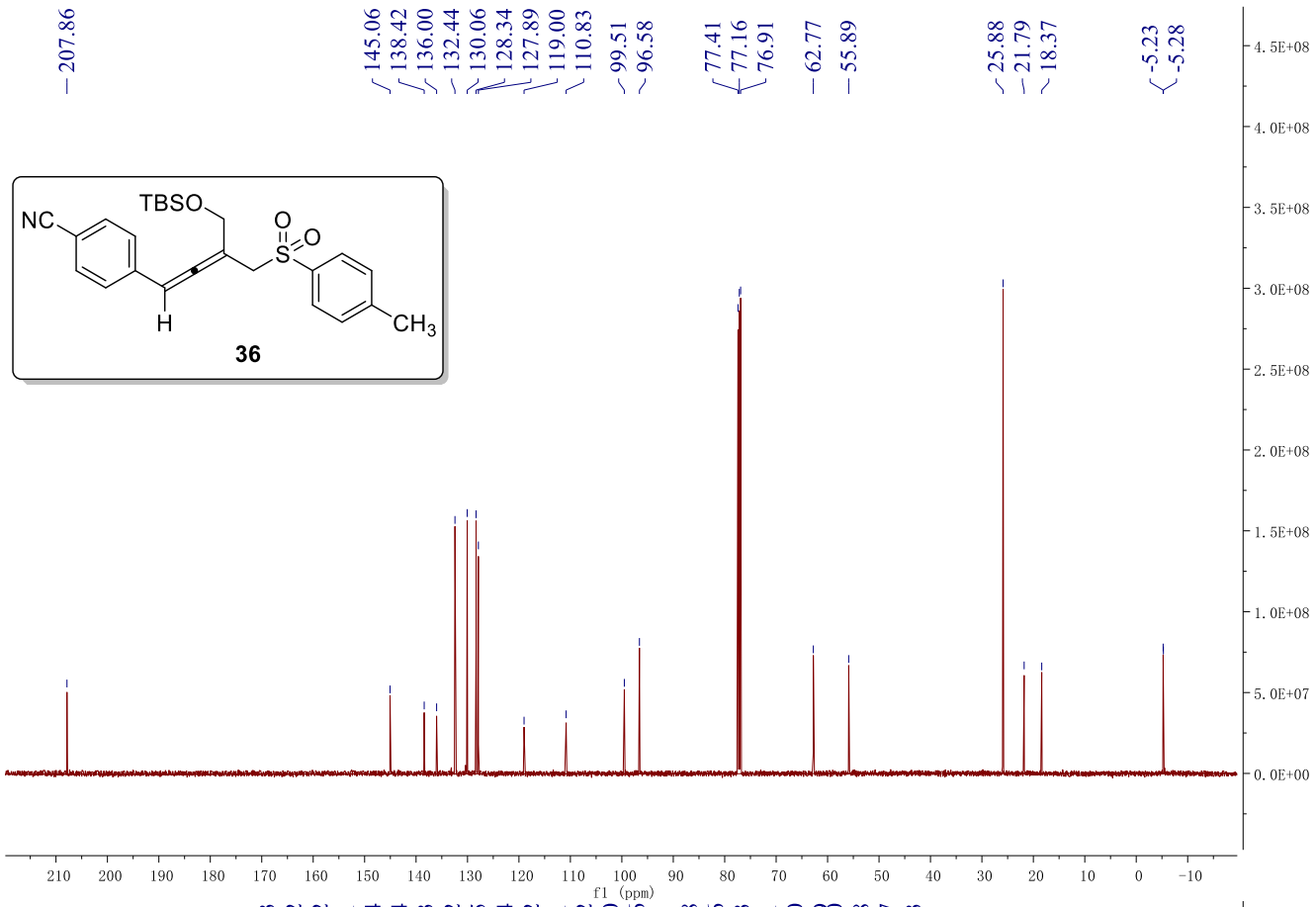
7.31
7.28
7.26
4.36
4.35
4.35
4.34
3.91
3.91
3.90
3.90
3.87
3.87
3.83
2.43
0.85
0.05
0.04
TBSO
NC
O
S
O
H
CH3
36
2.08
2.03
2.09
2.37
1.00
1.00
1.04
1.00
1.04
3.05
9.05
3.00
3.01
f1 (ppm)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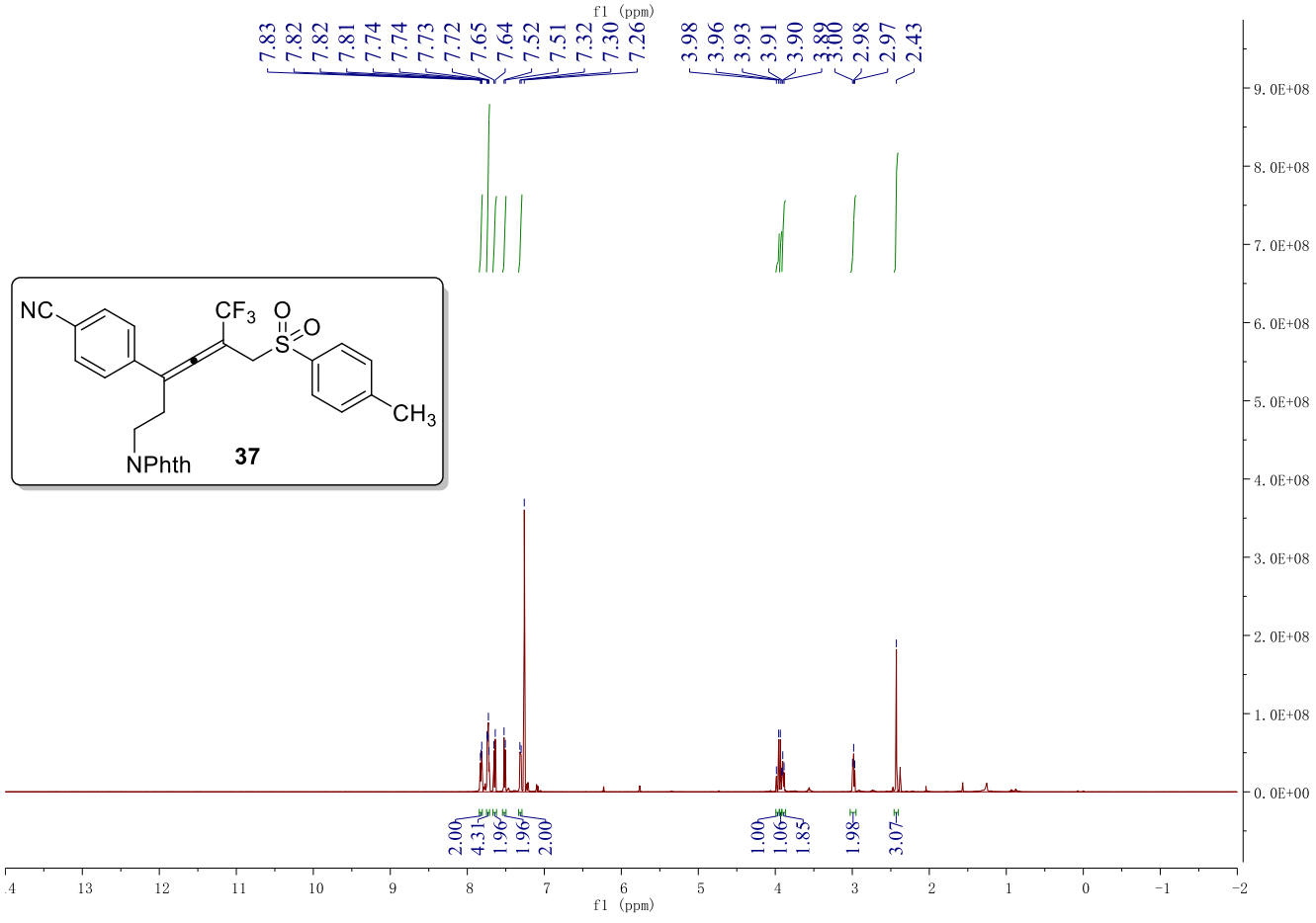
130.06
128.34
127.89
119.00
110.83
99.51
96.58
77.41
77.16
76.91
62.77
55.89
25.88
21.79
18.37
-5.23
-5.28
NC
TBSO
O
O
S
H
CH3
36
f1 (ppm)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7.82
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7.74
7.73
7.72
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7.64
7.52
7.51
7.32
7.30
7.26
3.98
3.96
3.93
3.91
3.90
2.98
2.97
2.43
NC
CF3
O
O
S
CH3
NPhth
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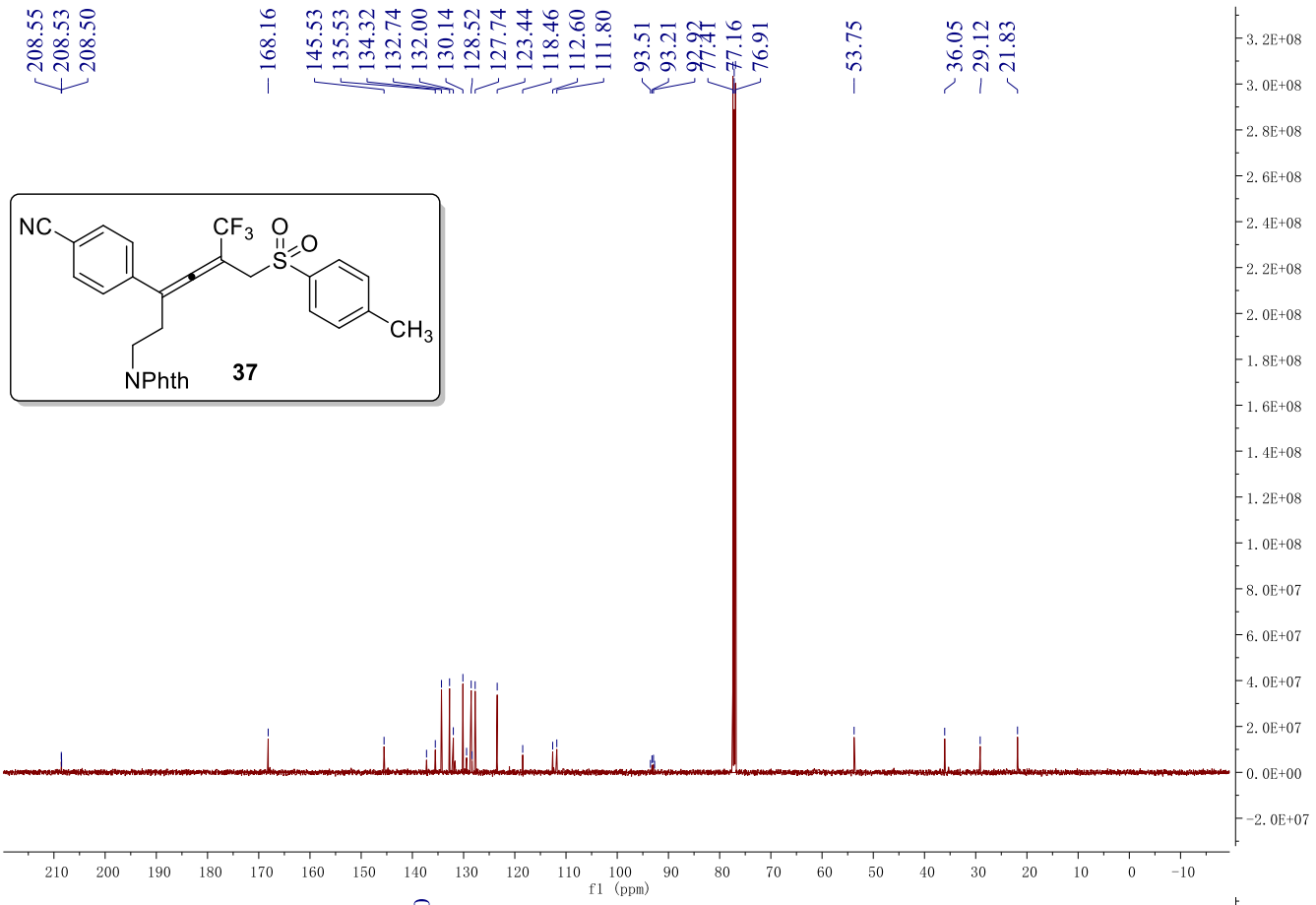
1.96
1.96
2.00
1.00
1.06
1.85
1.98
3.07
f1 (ppm)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127.74
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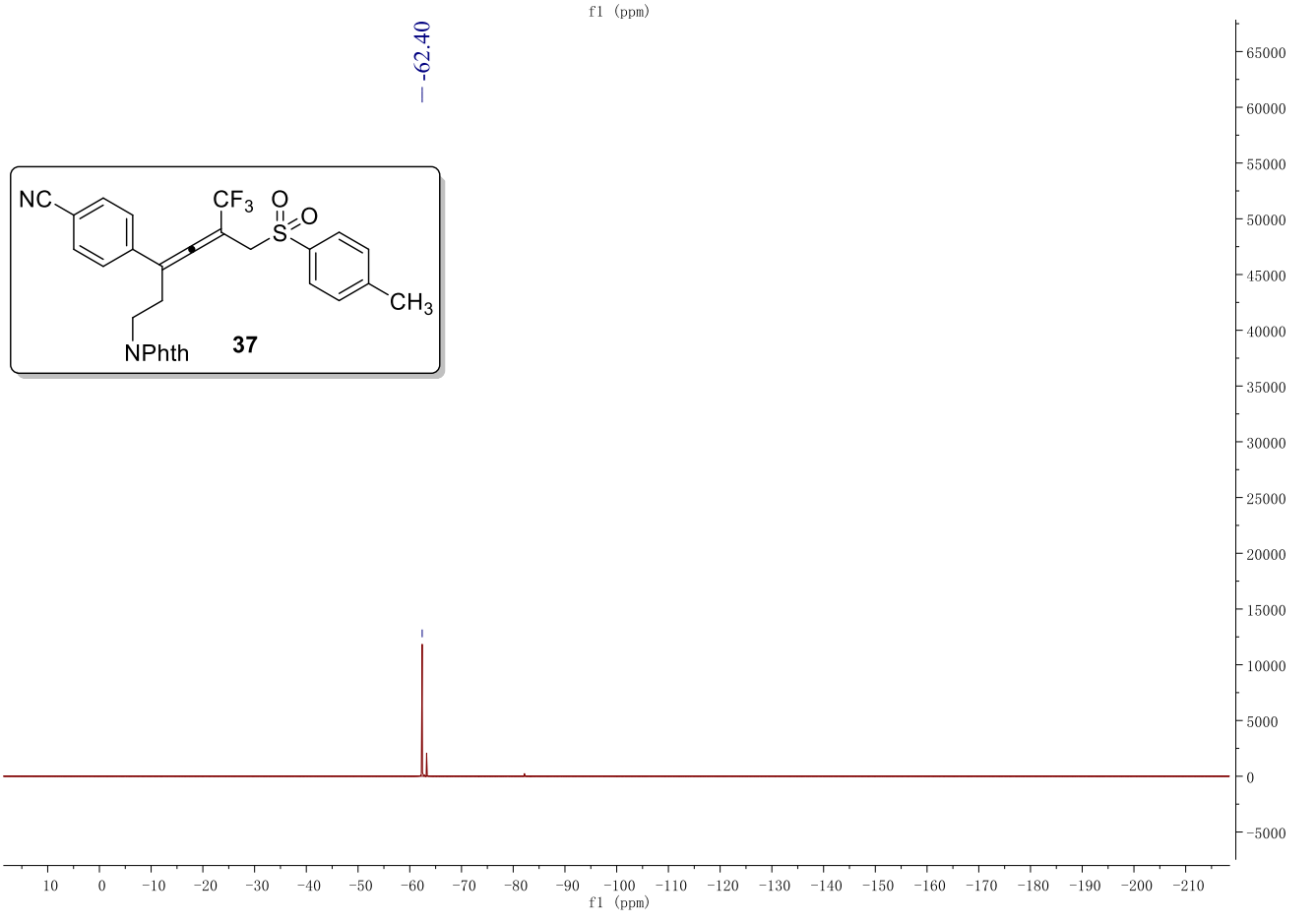
112.60
111.80
93.51
93.21
92.92
77.41
77.16
76.91
53.75
36.05
29.12
21.83
NC
CF3
O
S
O
CH3
NPhth
37
f1 (ppm)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CF3
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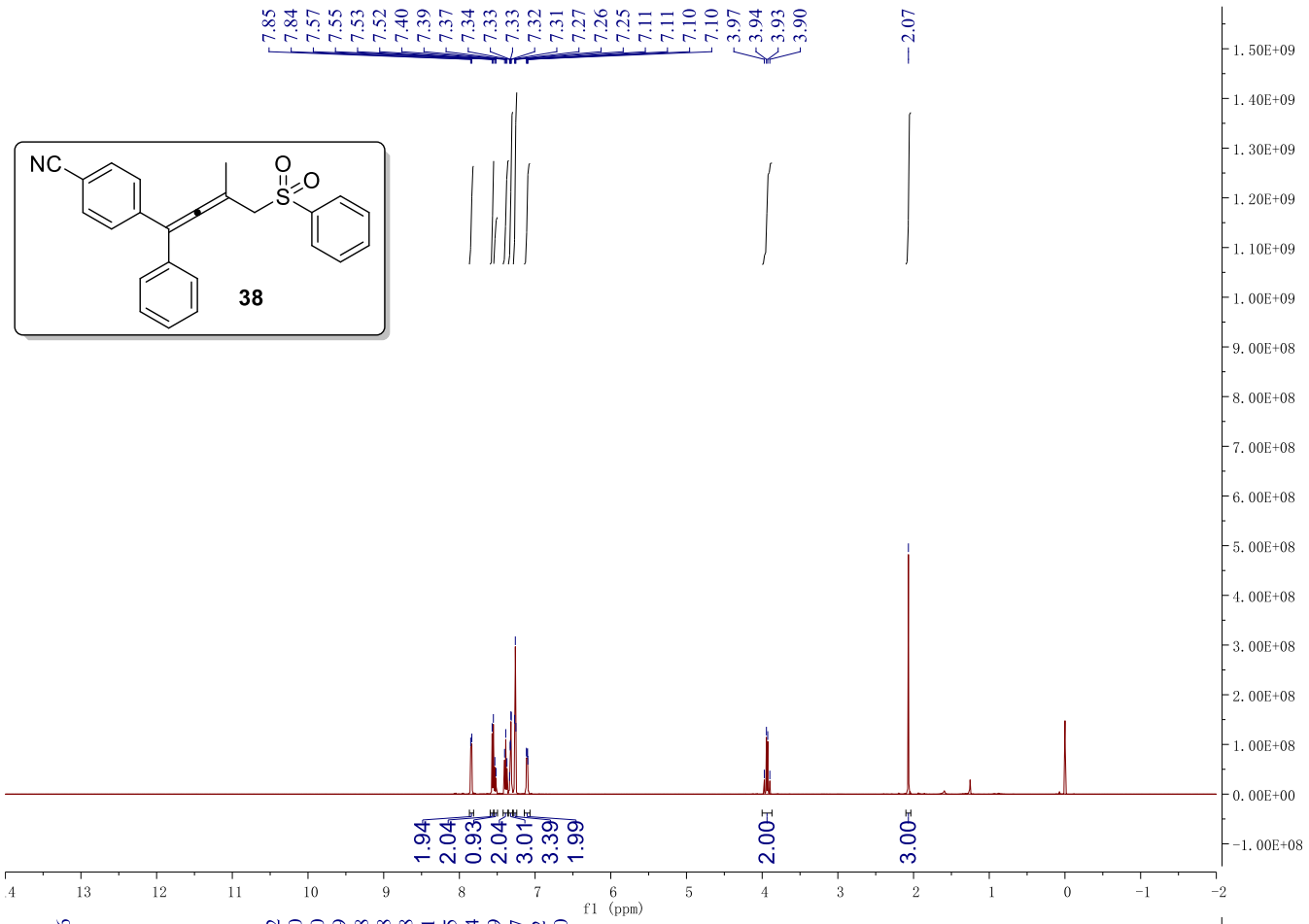
S
O
CH3
NPhth
37
f1 (ppm)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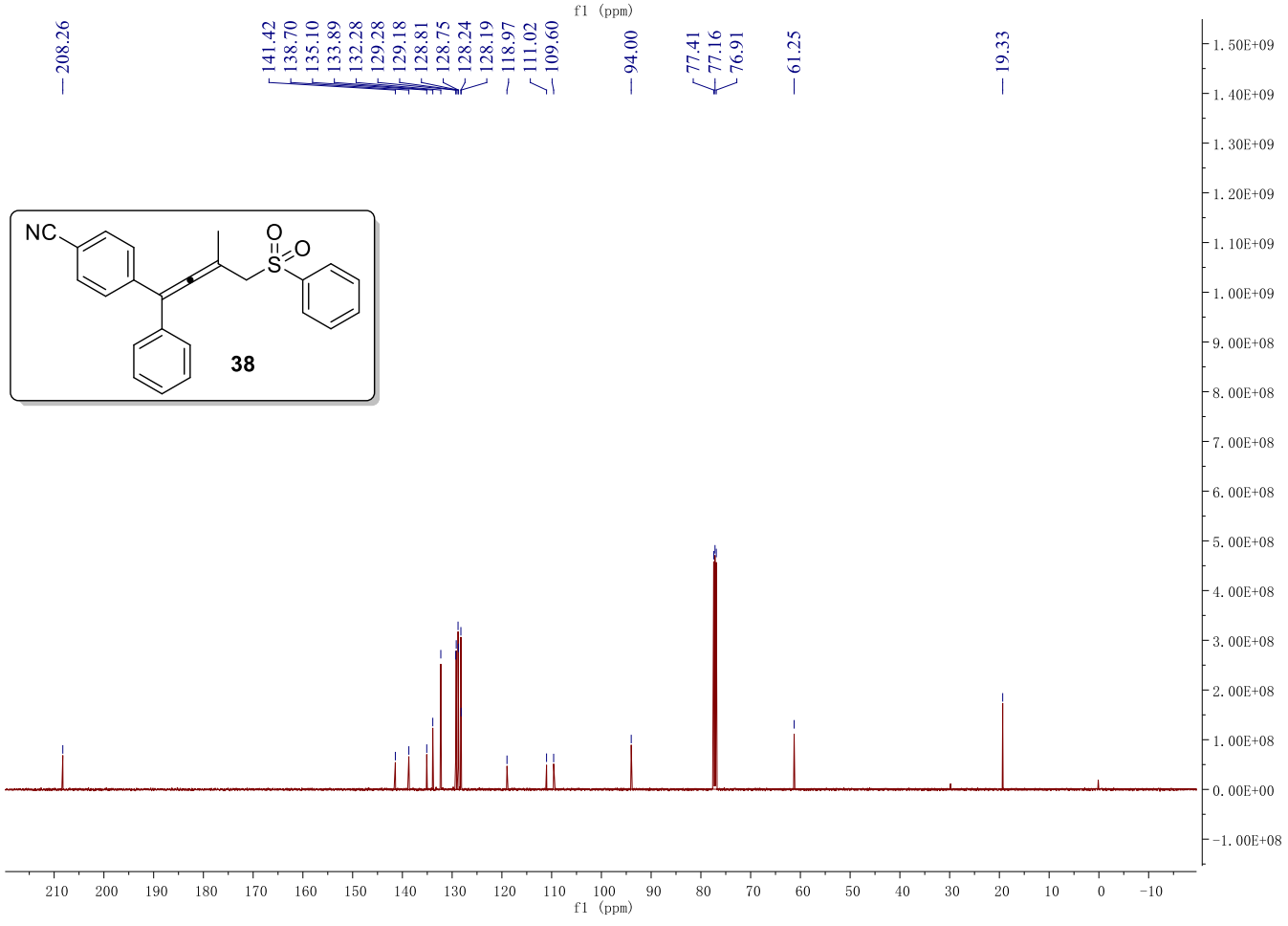
7.33
7.32
7.31
7.27
7.26
7.25
7.11
7.11
7.10
7.10
3.97
3.94
3.93
3.90
2.07
NC
O
S
O
38
1.94
2.04
0.93
2.04
3.01
3.39
1.99
2.00
3.00
f1 (ppm)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132.28
129.28
129.18
128.81
128.75
128.24
128.19
118.97
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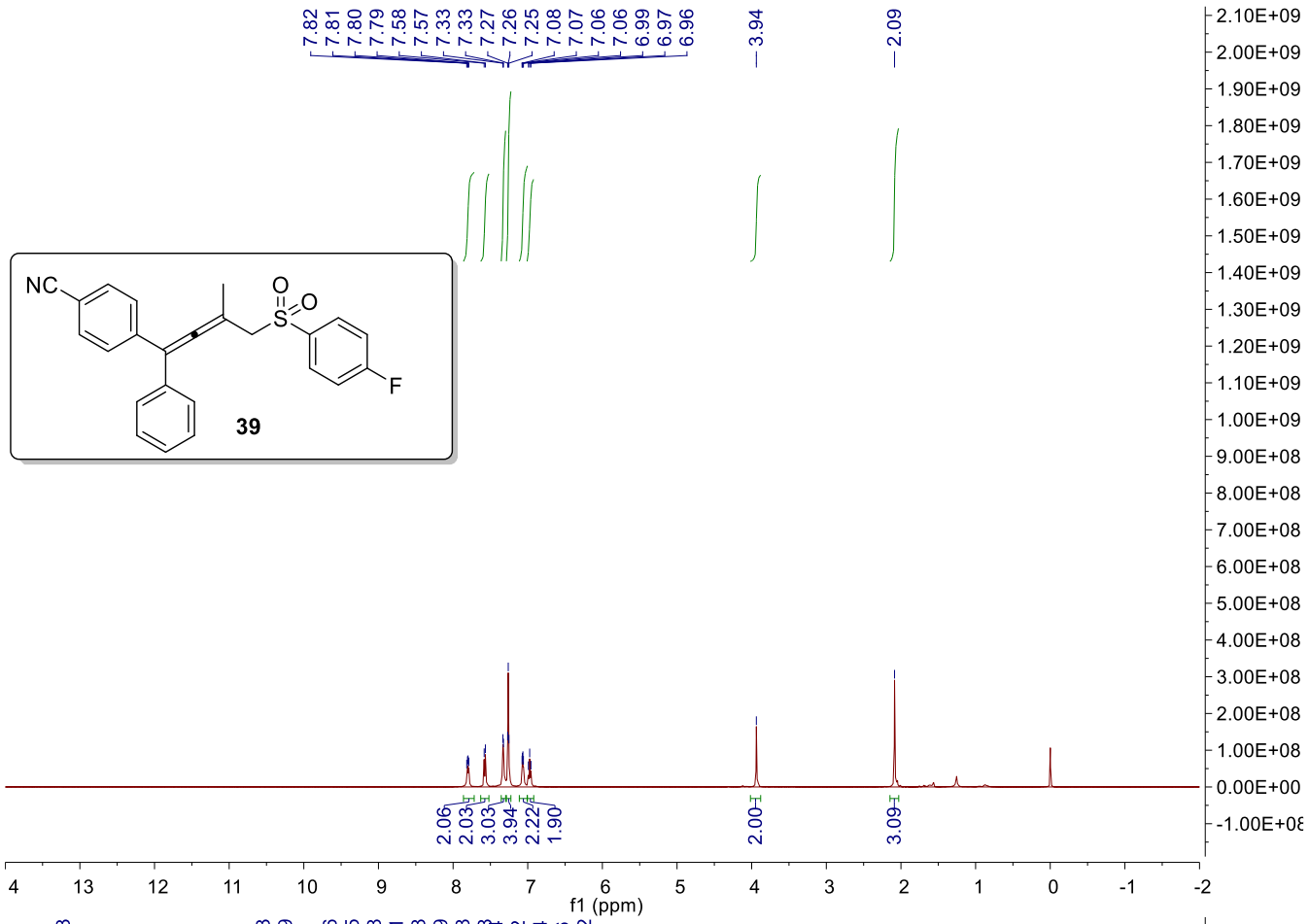
94.00
77.41
77.16
76.91
61.25
19.33
NC
O
S
O
38
f1 (ppm)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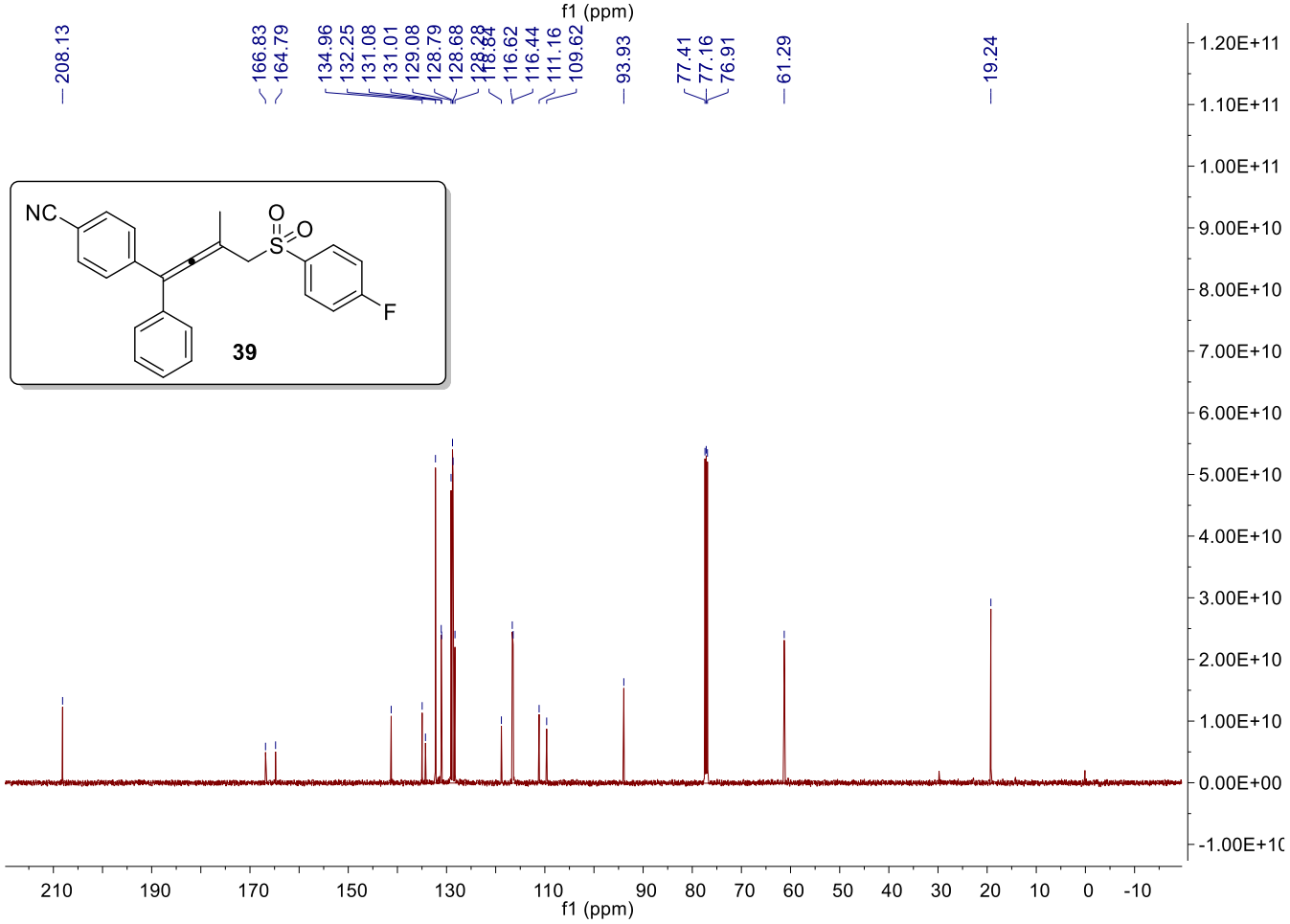
7.57
7.33
7.33
7.27
7.26
7.25
7.08
7.07
7.06
7.06
6.99
6.97
6.96
3.94
2.09
NC
O
S
O
F
39
2.06
2.03
3.03
3.94
2.22
1.90
2.00
3.09
f1 (ppm)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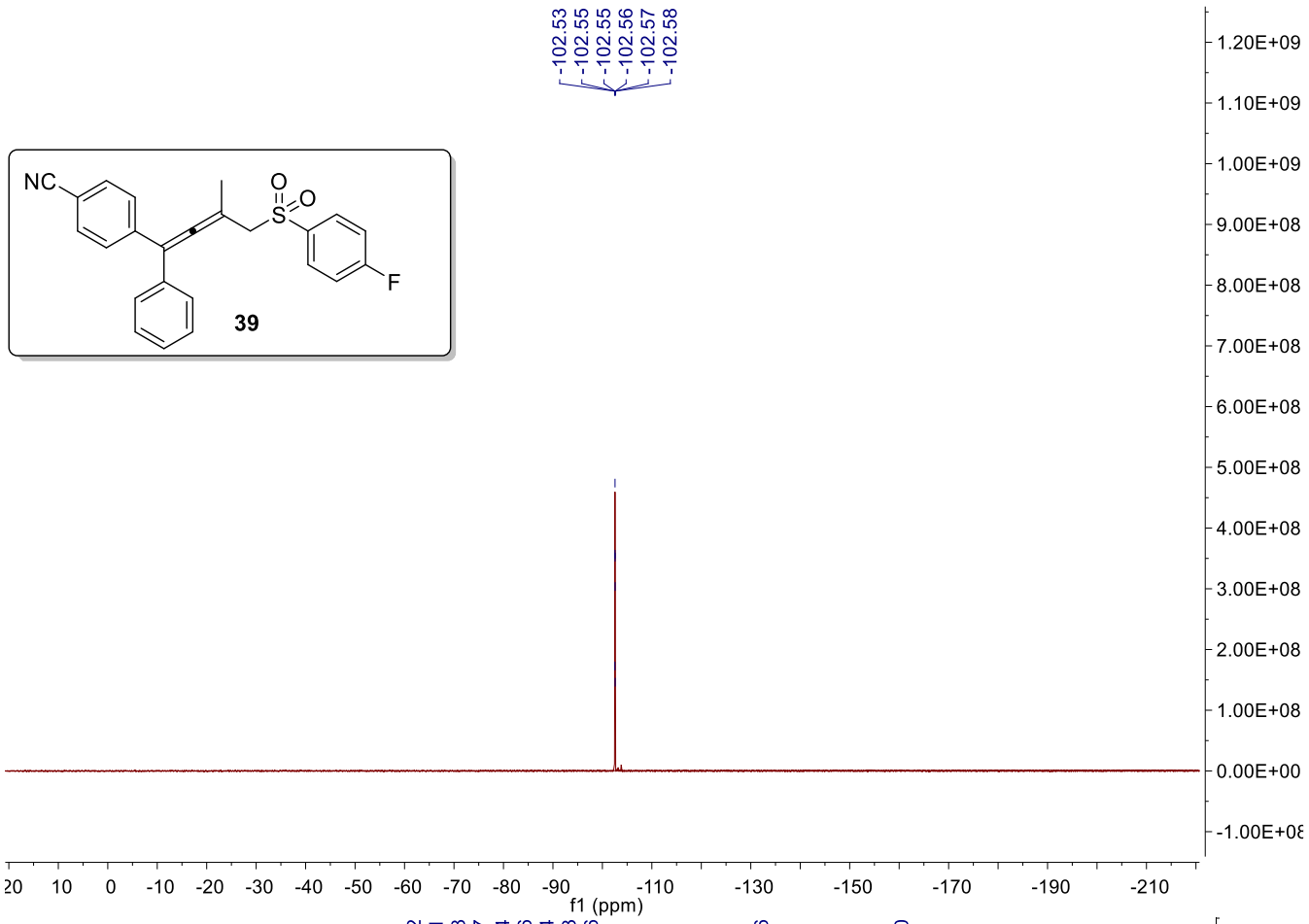
132.25
131.08
131.01
129.08
128.79
128.68
116.62
116.44
111.16
109.62
93.93
77.41
77.16
76.91
61.29
19.24
NC
O
S
O
F
39
f1 (ppm)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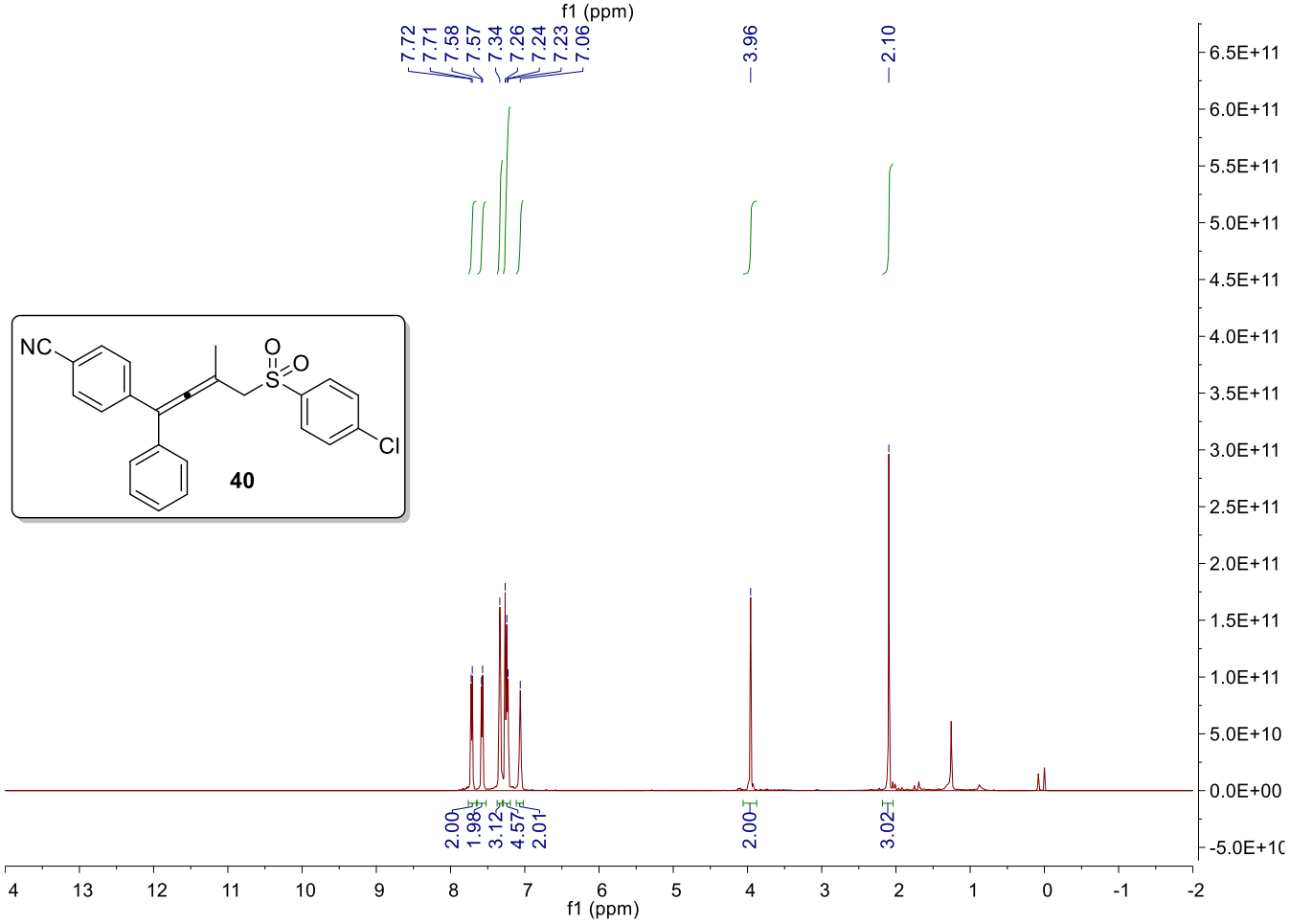
-102.55
-102.56
-102.57
-102.58
NC
O
S
O
F
39
f1 (ppm)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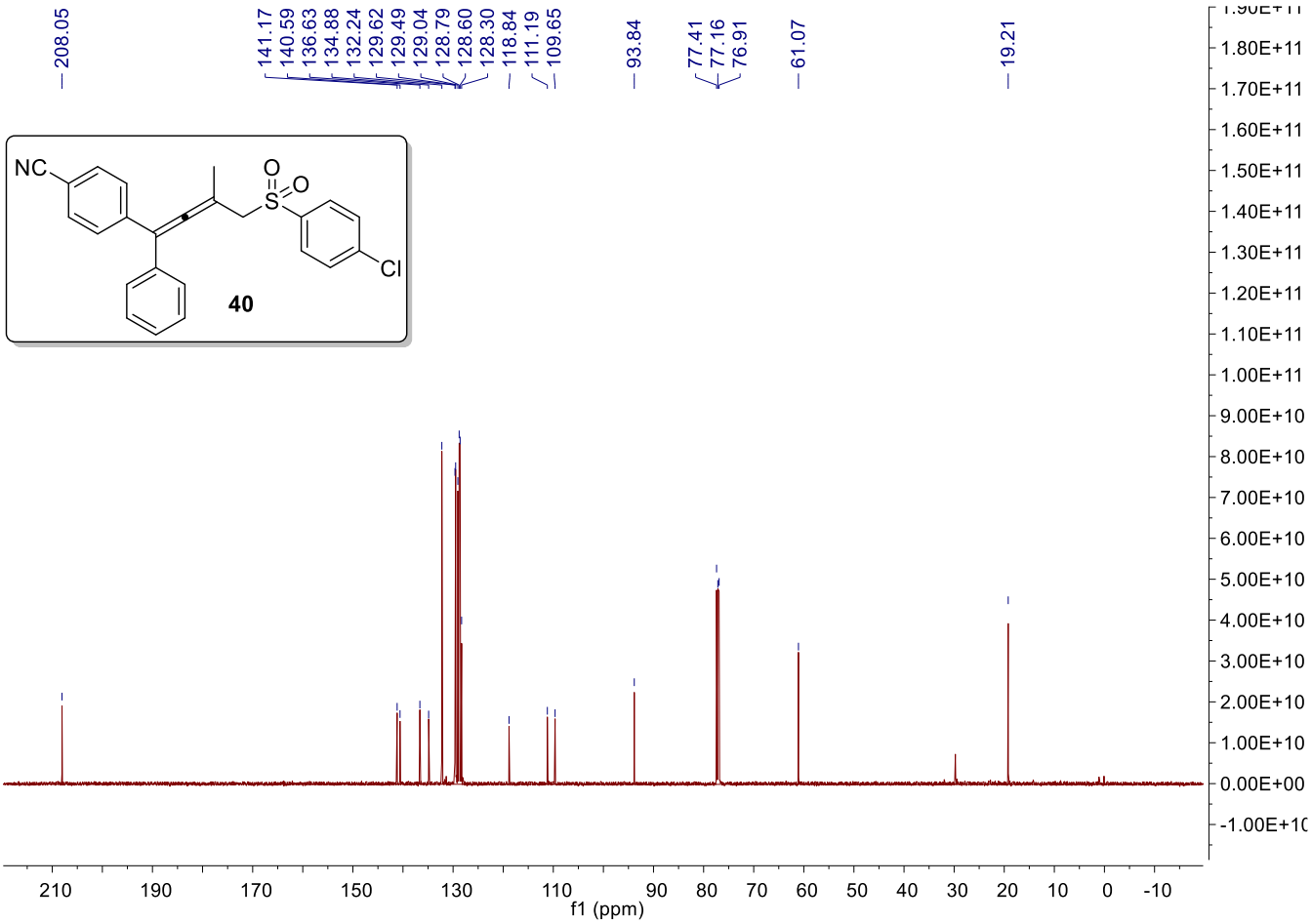
7.71
7.58
7.57
7.34
7.26
7.24
7.23
7.06
3.96
2.10
NC
O
S
O
Cl
40
2.00
1.98
3.12
4.57
2.01
2.00
3.02
f1 (ppm)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129.49
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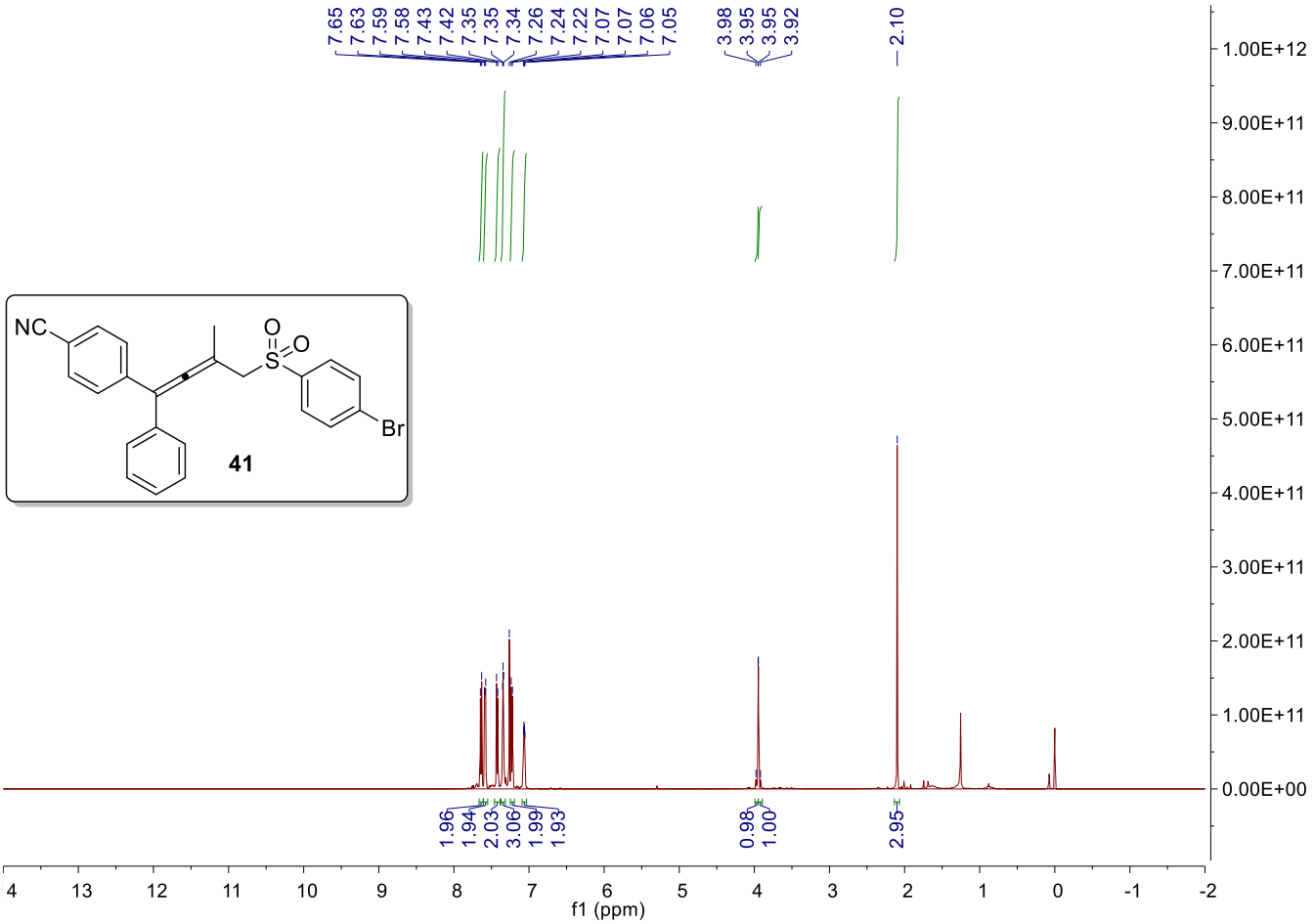
128.79
128.60
128.30
118.84
111.19
109.65
93.84
77.41
77.16
76.91
61.07
19.21
NC
O
O
S
Cl
40
f1 (ppm)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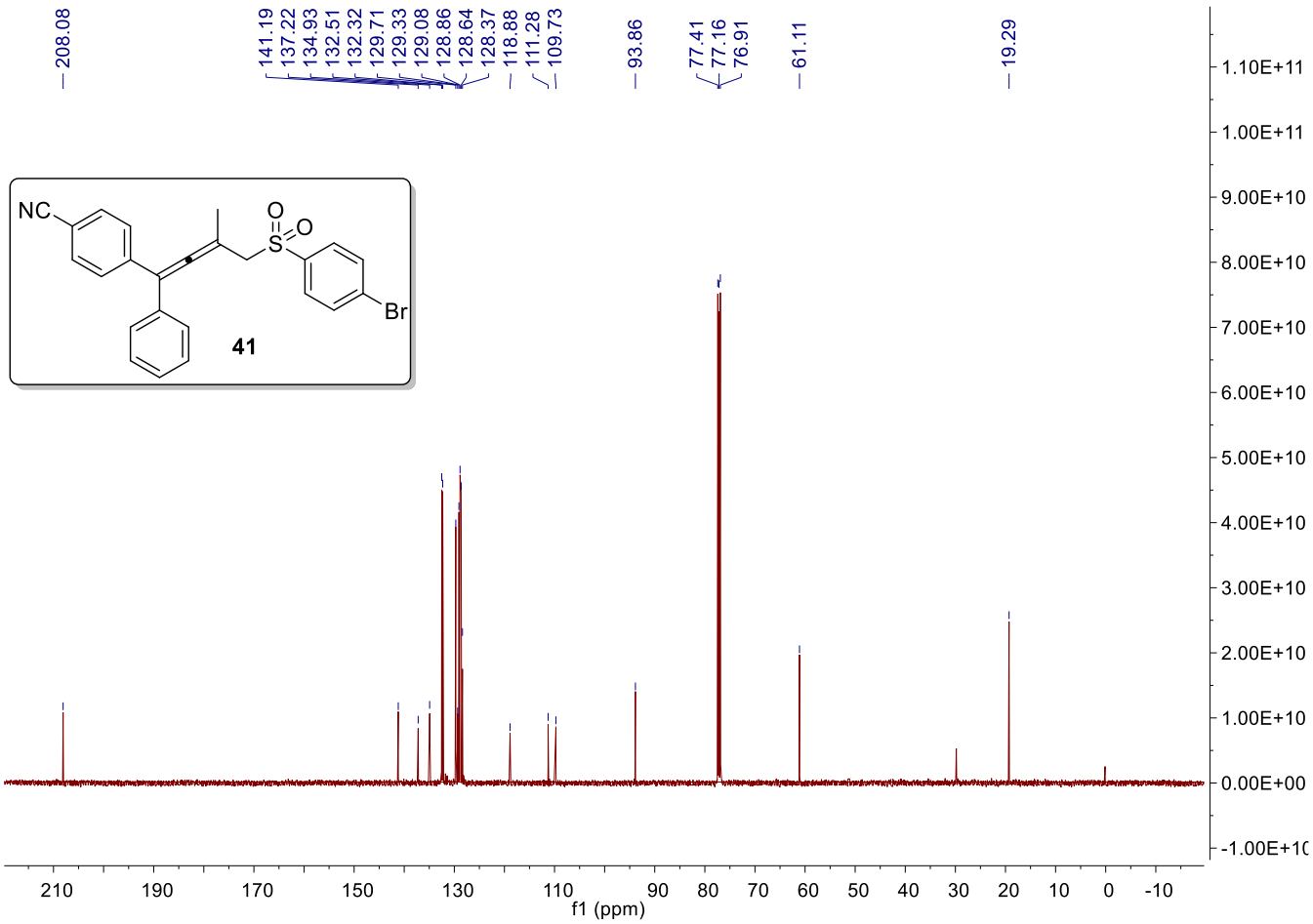
7.26
7.24
7.22
7.07
7.07
7.06
7.05
3.98
3.95
3.95
3.92
2.10
NC
O
O
S
Br
41
1.96
1.94
2.03
3.06
1.99
1.93
0.98
1.00
2.95
f1 (ppm)


208.08
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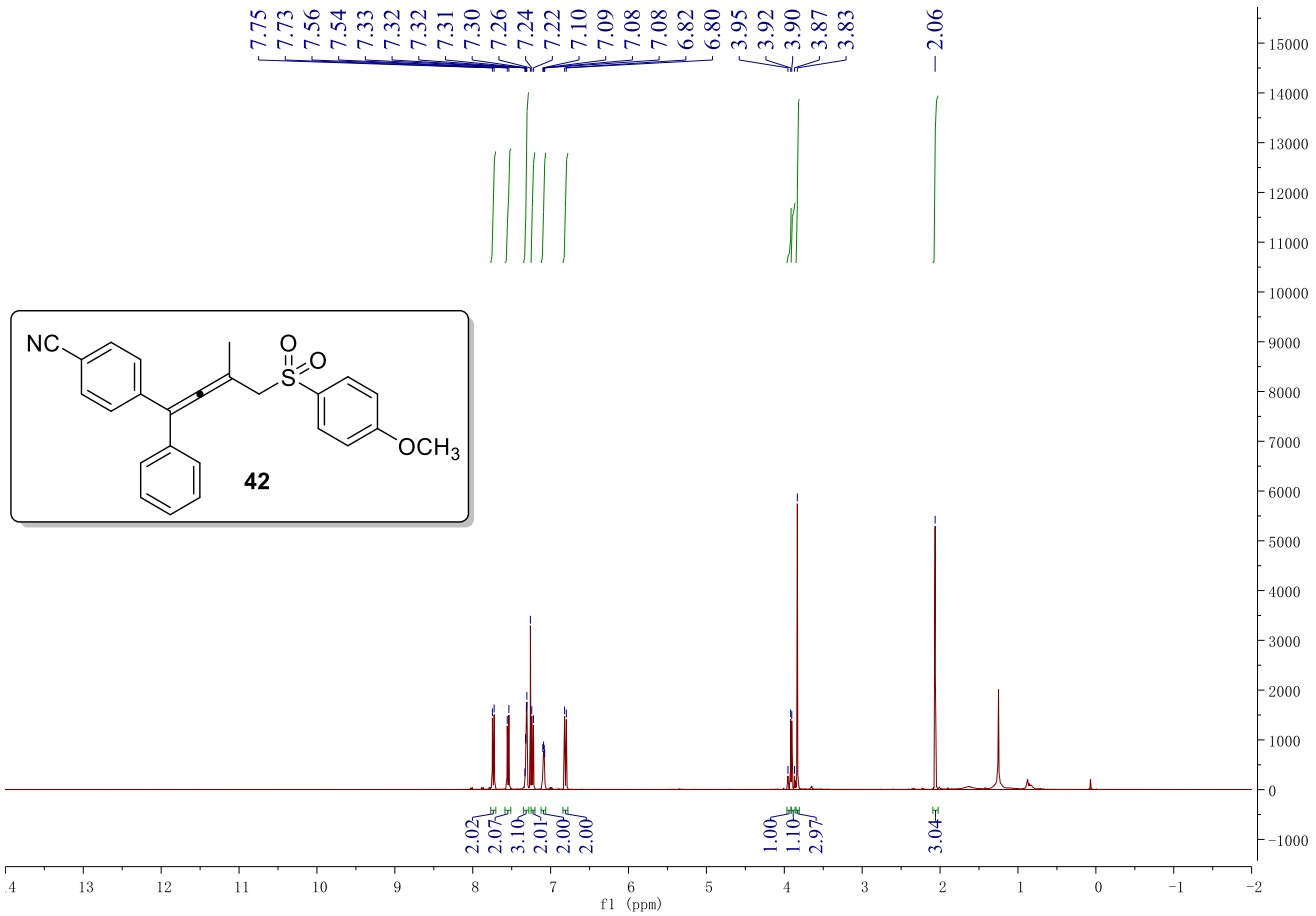
132.51
132.32
129.71
129.33
129.08
128.86
128.64
128.37
118.88
111.28
109.73
93.86
77.41
77.16
76.91
61.11
19.29
NC
O
S
O
Br
41
1.10E+11
1.00E+11
9.00E+10
8.00E+10
7.00E+10
6.00E+10
5.00E+10
4.00E+10
3.00E+10
2.00E+10
1.00E+10
0.00E+00
-1.00E+10
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.73
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7.31
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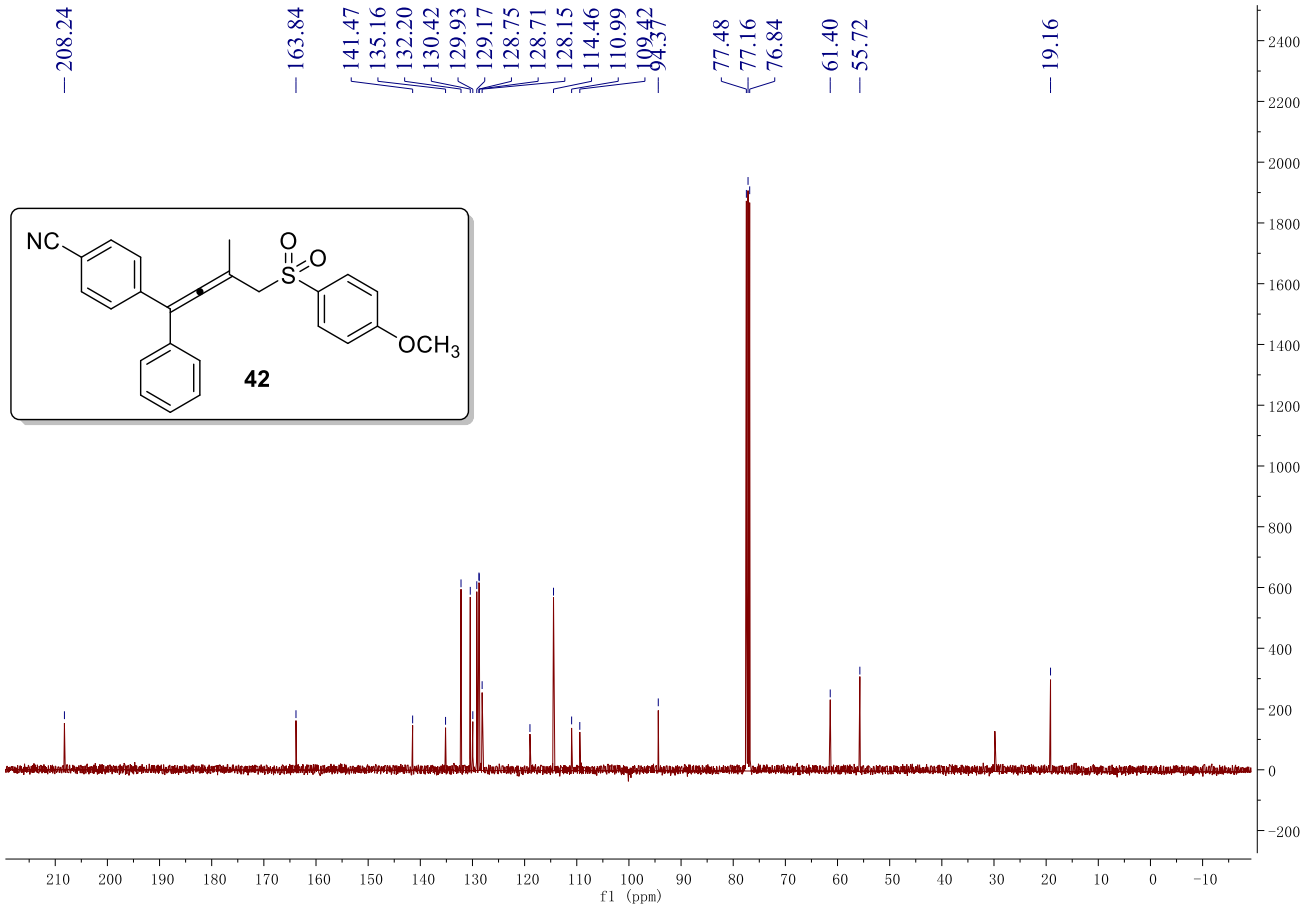
7.24
7.22
7.10
7.09
7.08
7.08
6.82
6.80
3.95
3.92
3.90
3.87
3.83
2.06
NC
O
S
O
OCH3
42
2.02
2.07
3.10
2.01
2.00
2.00
1.00
1.10
2.97
3.04
f1 (ppm)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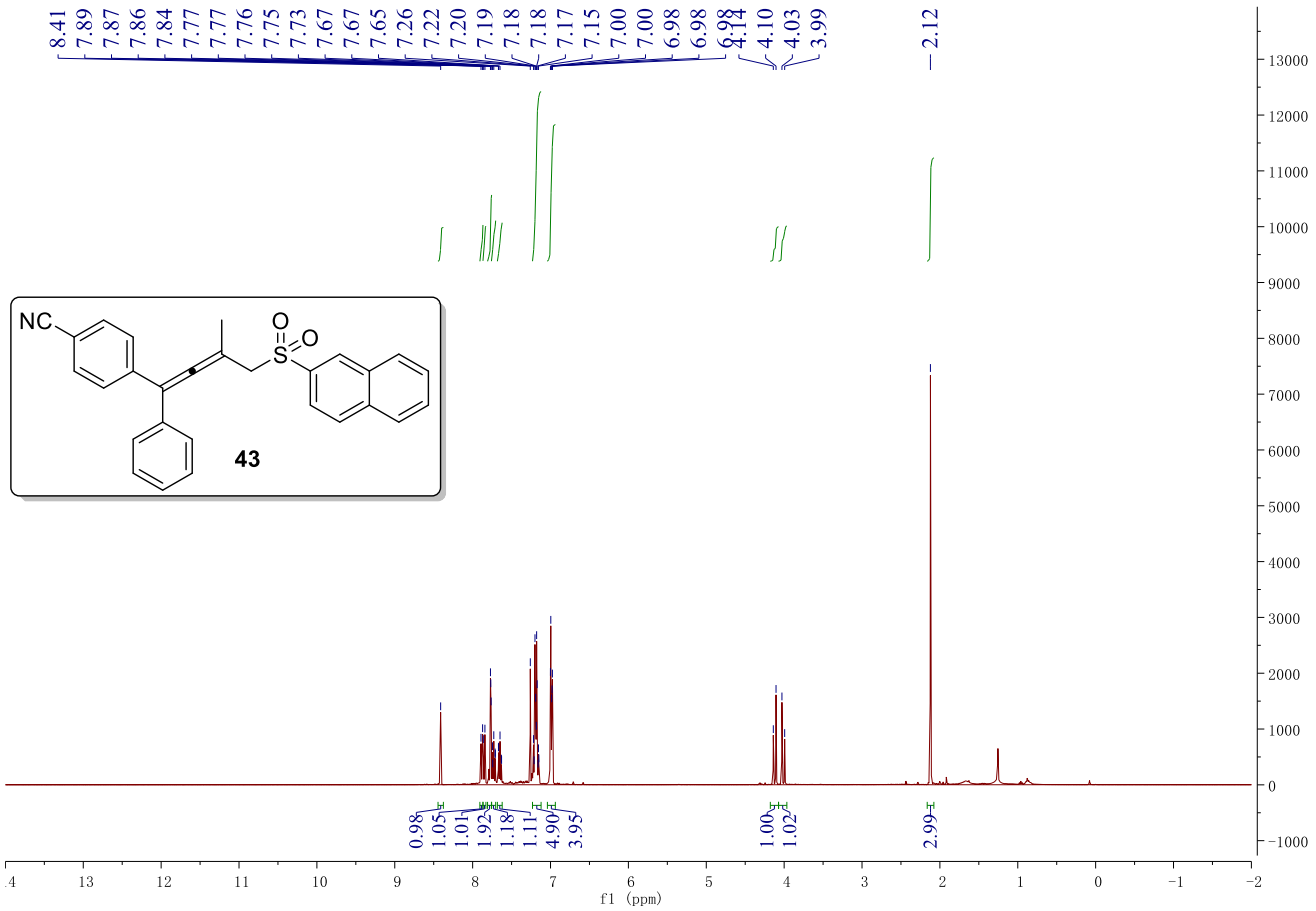
141.47
135.16
132.20
130.42
129.93
129.17
128.75
128.71
128.15
114.46
110.99
109.42
94.37
77.48
77.16
76.84
61.40
55.72
19.16
NC
O
S
O
OCH3
42
f1 (ppm)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7.77
7.76
7.75
7.73
7.67
7.67
7.65
7.26
7.22
7.20
7.19
7.18
7.18
7.17
7.15
7.00
7.00
6.98
6.98
4.14
4.10
4.03
3.99
2.12
NC
O
S
O
43
0.98
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1.92
1.18
1.11
4.90
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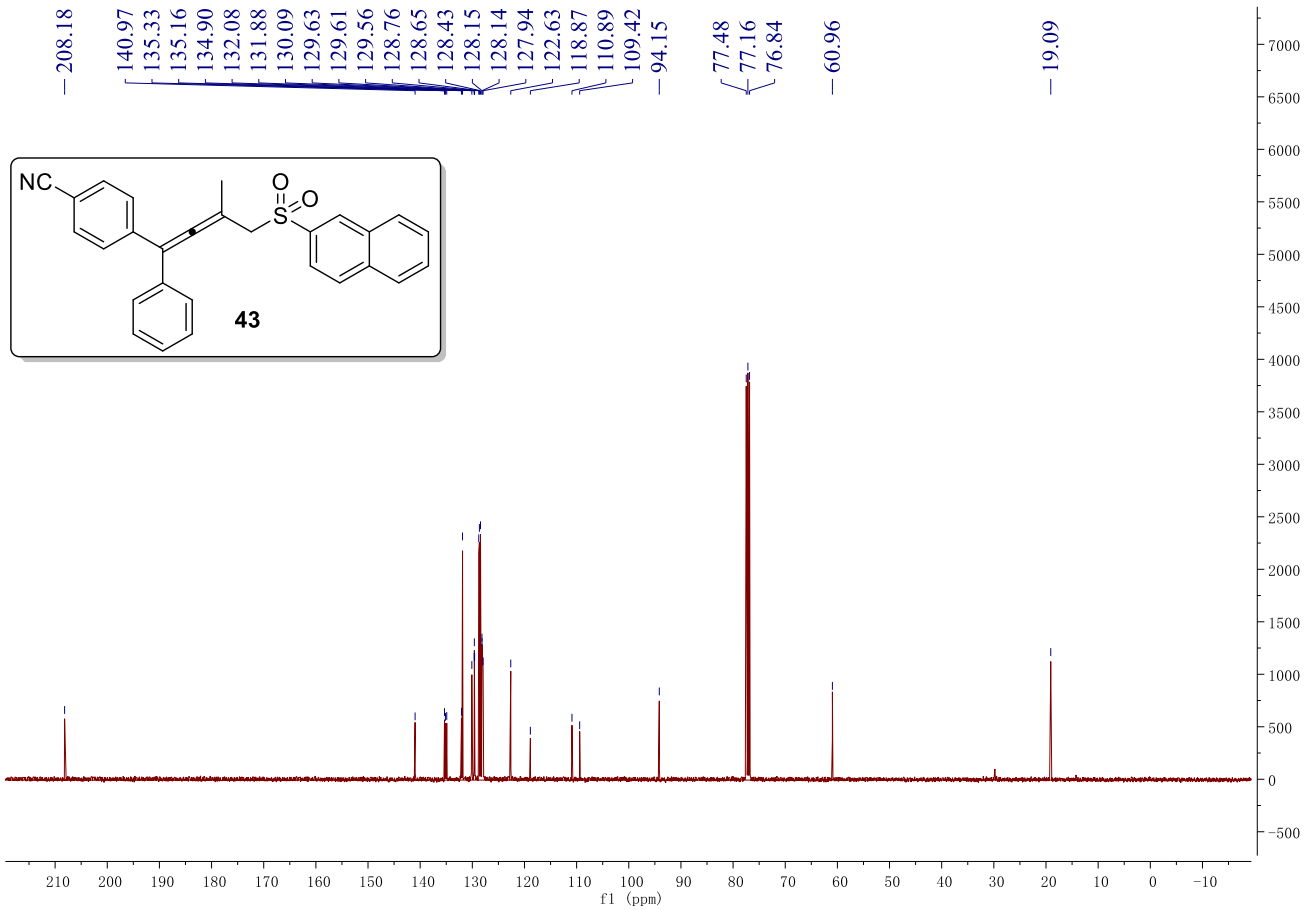
1.00
1.02
2.99
f1 (ppm)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130.09
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129.56
128.76
128.65
128.43
128.15
128.14
127.94
122.63
118.87
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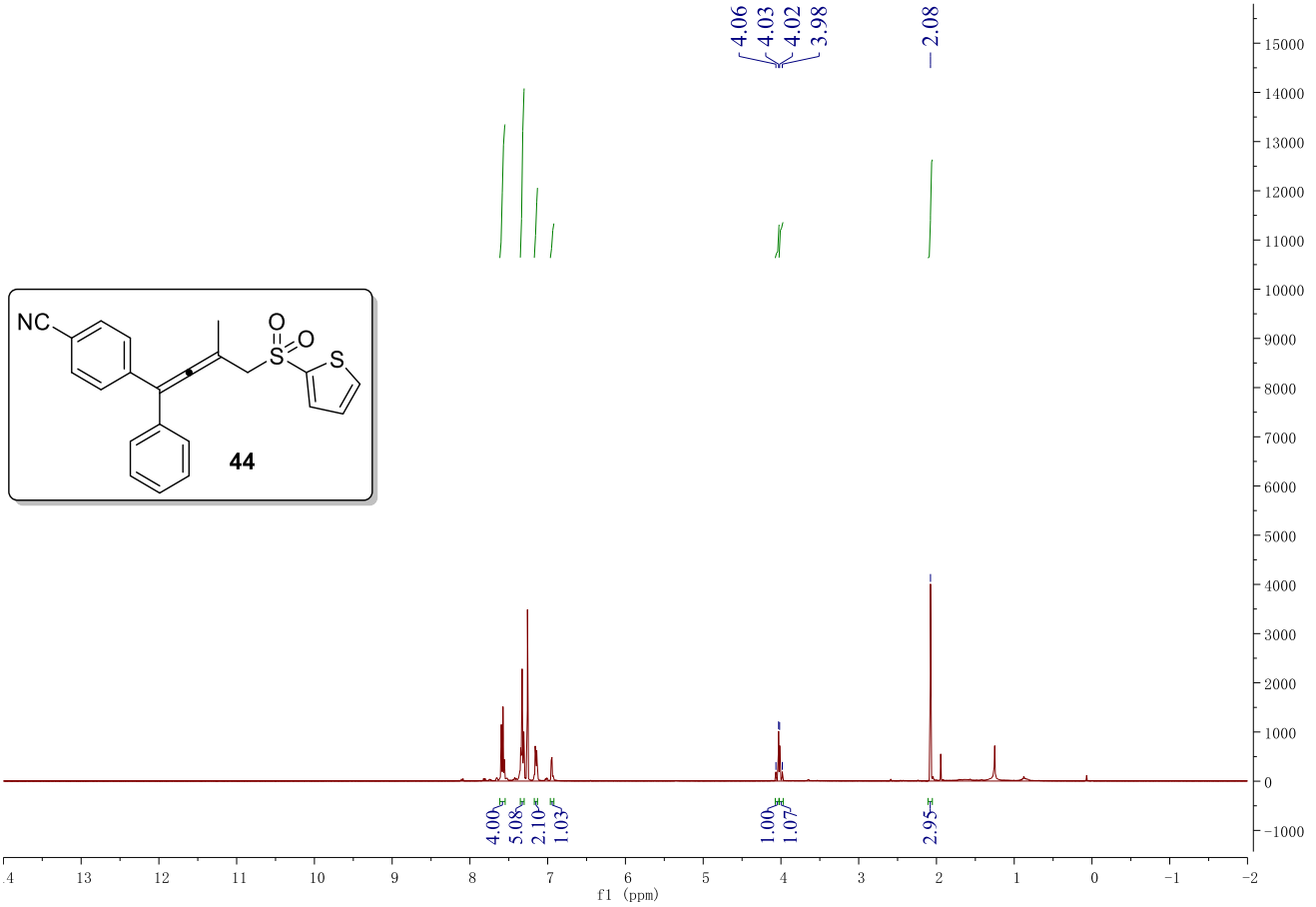
77.48
77.16
76.84
60.96
19.09
NC
O
S
O
43
f1 (ppm)


4.06
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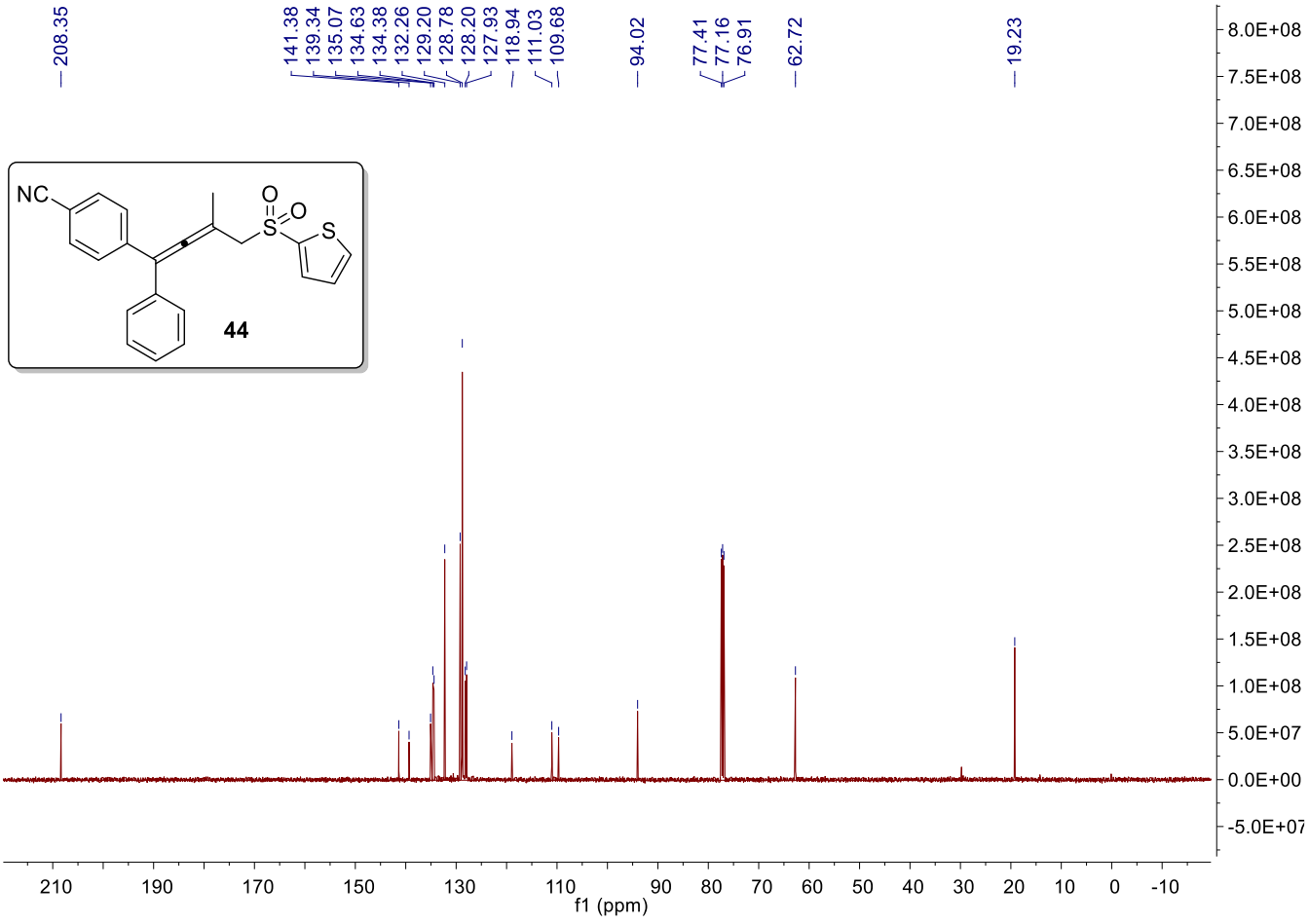
S
S
44
4.00
5.08
2.10
1.03
1.00
1.07
2.95
f1 (ppm)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129.20
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128.20
127.93
118.94
111.03
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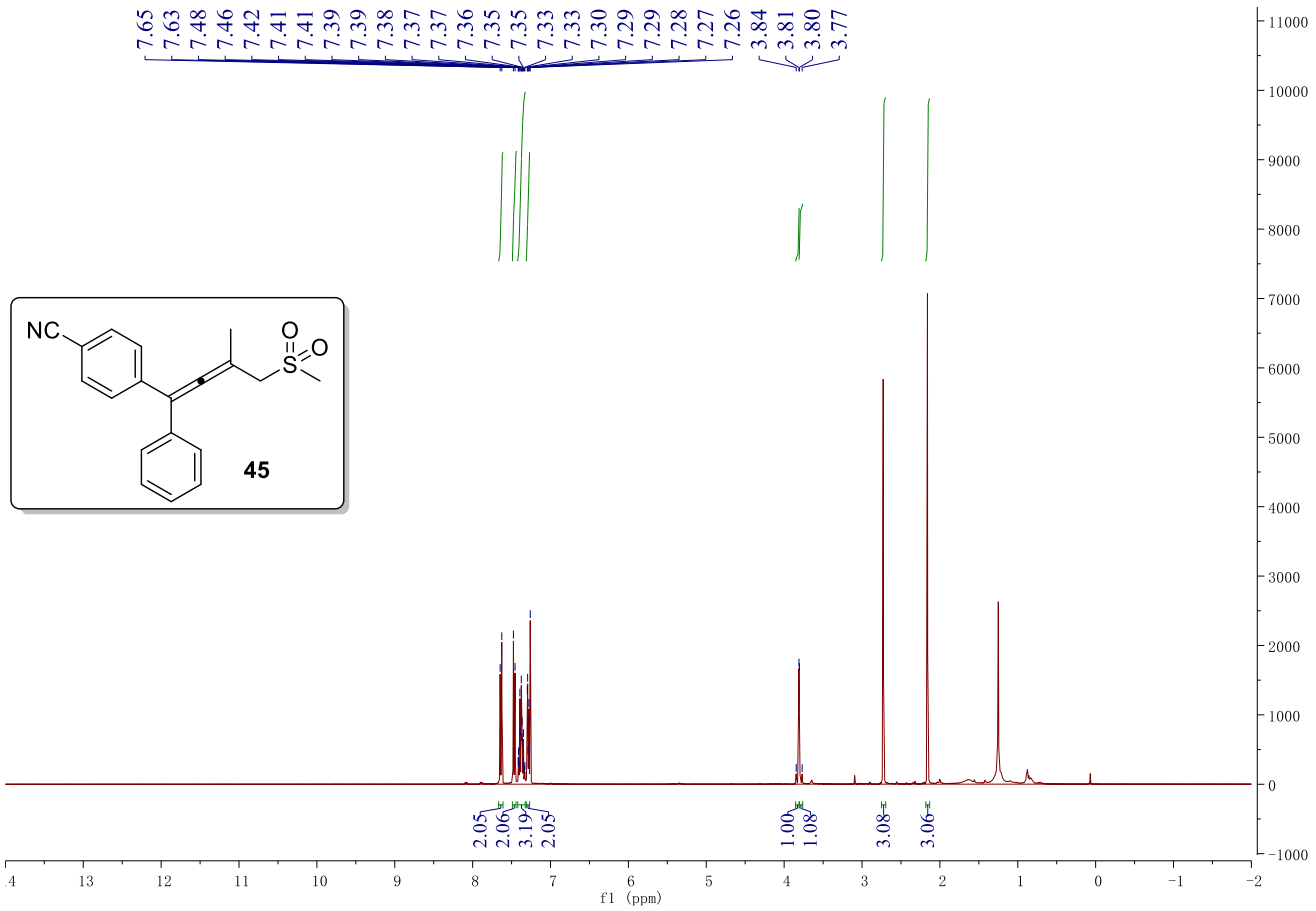
77.16
76.91
62.72
19.23
NC
O
O
S
S
44
f1 (ppm)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7.41
7.39
7.39
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7.37
7.37
7.36
7.35
7.35
7.33
7.33
7.30
7.29
7.29
7.28
7.27
7.26
3.84
3.81
3.80
3.77
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O
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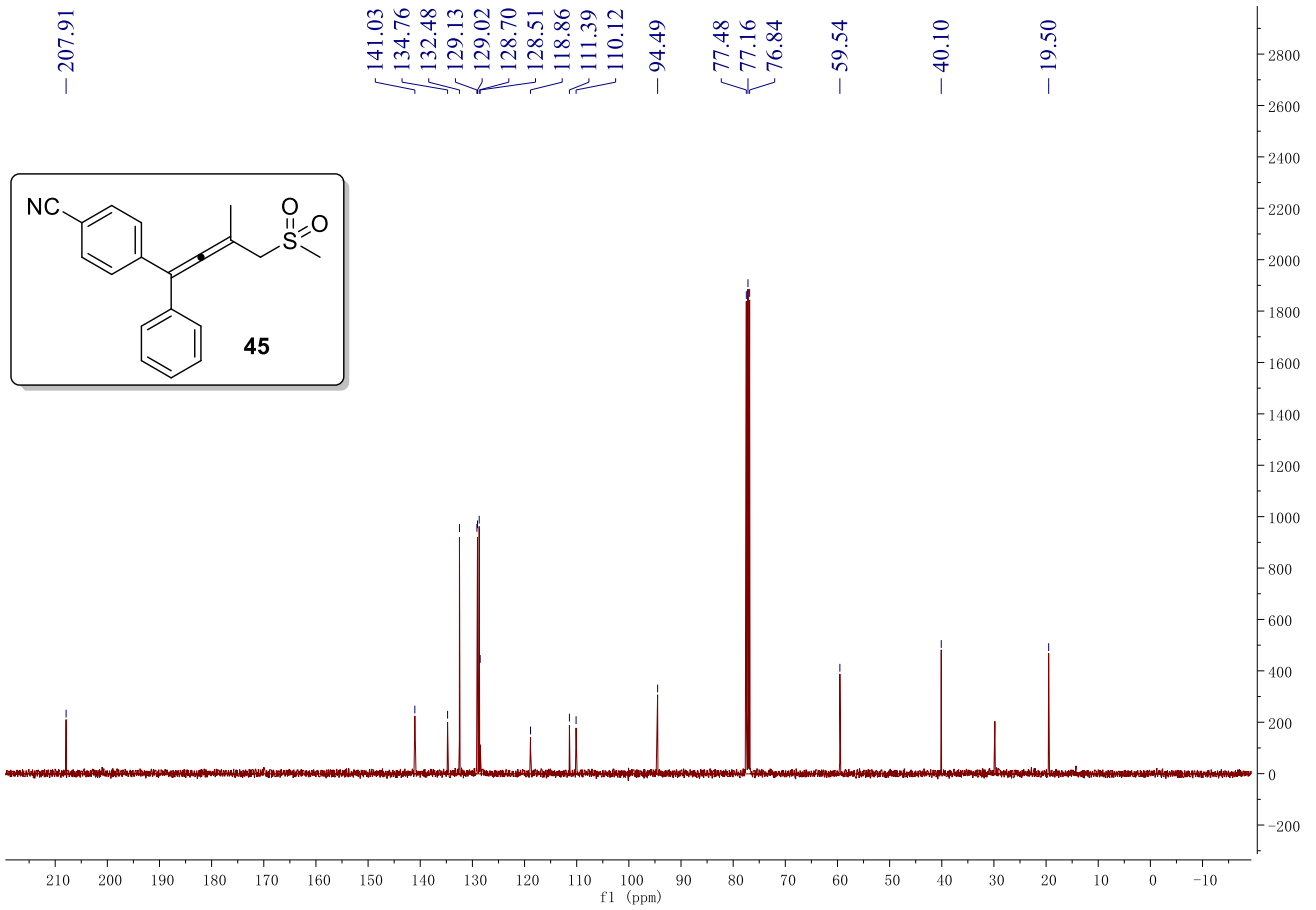
45
2.05
2.06
3.19
2.05
1.00
1.08
3.08
3.06
f1 (ppm)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129.02
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128.51
118.86
111.39
110.12
94.49
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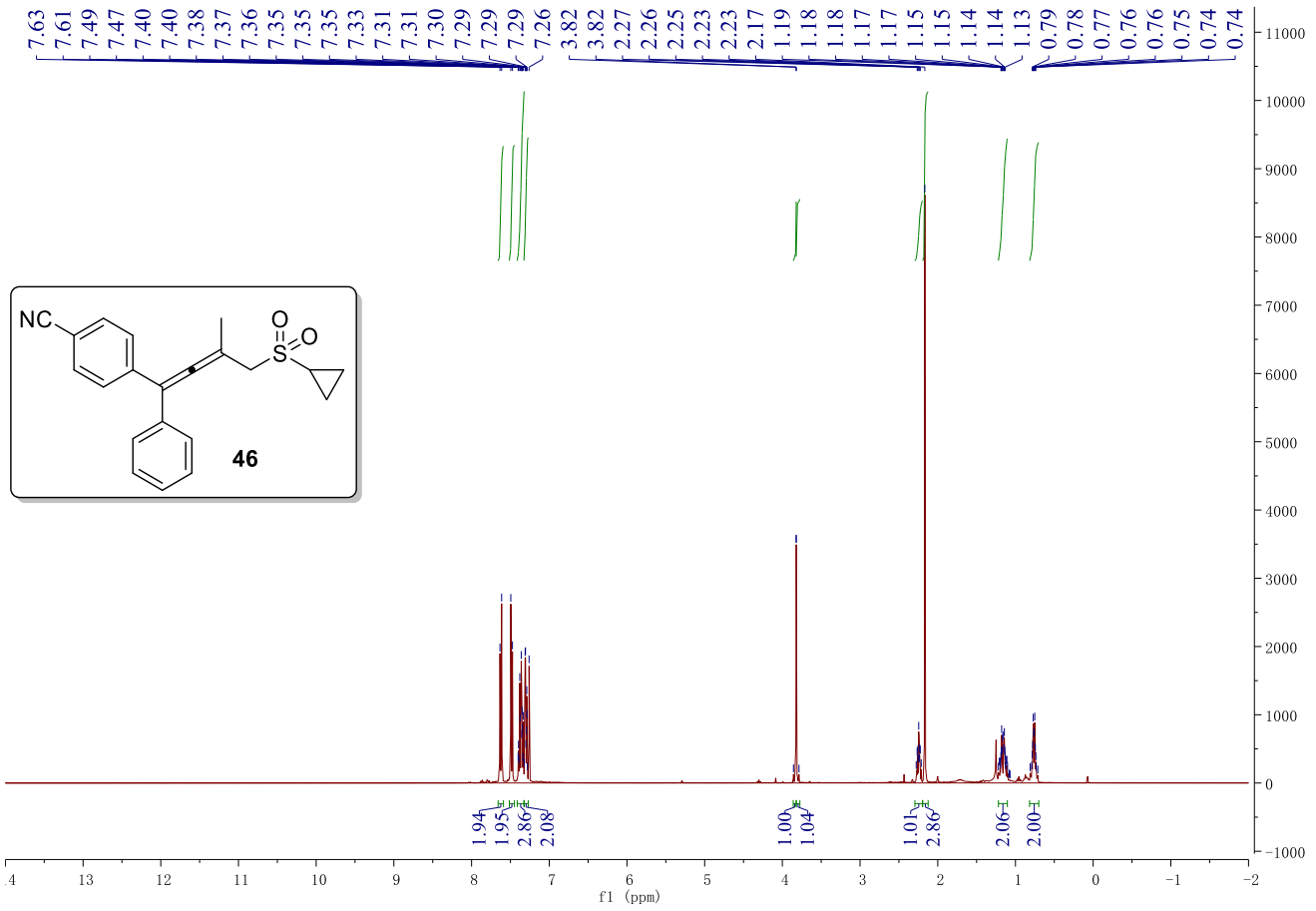
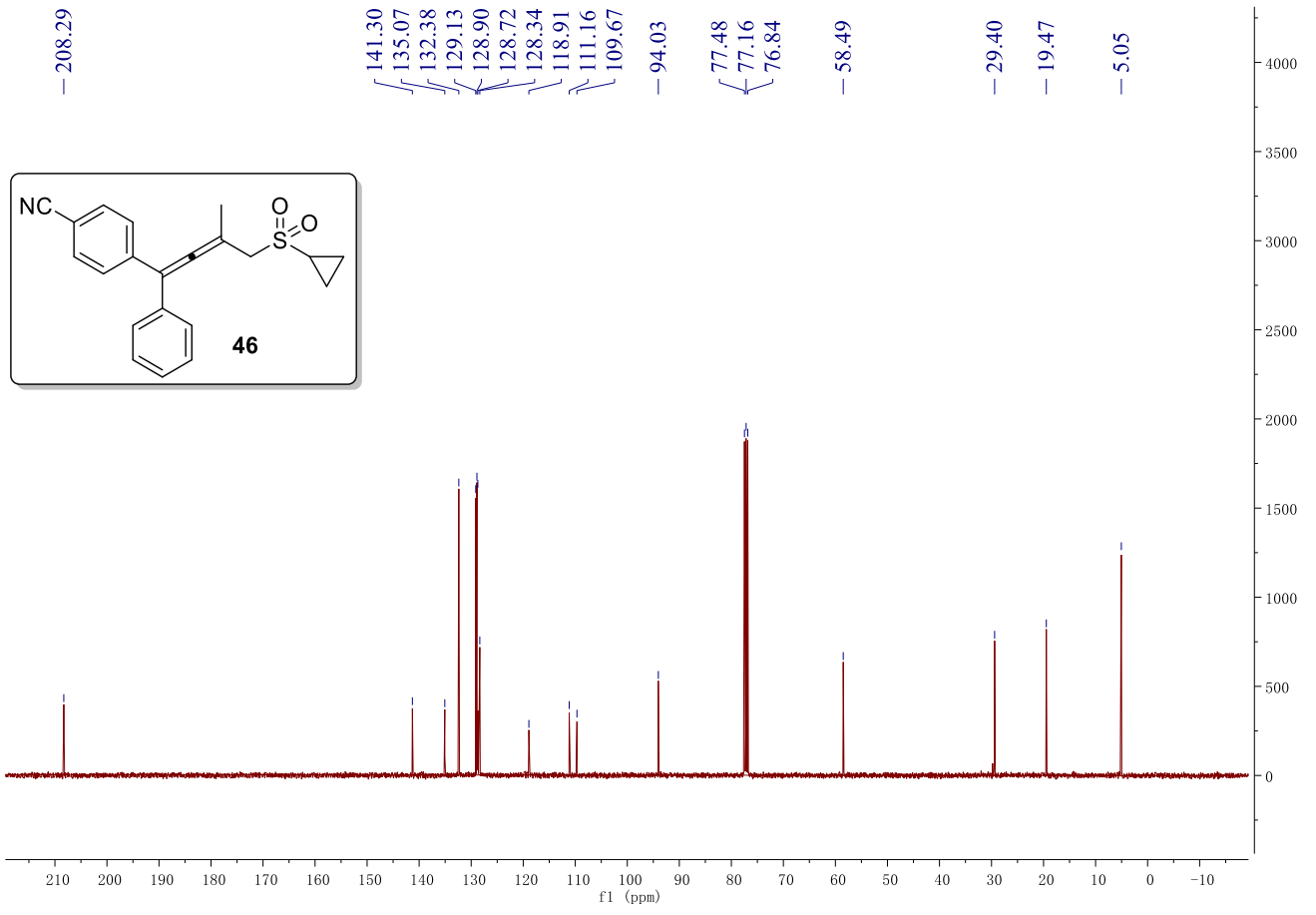
77.16
76.84
59.54
40.10
19.50
NC
O
O
S
45
f1 (ppm)


7.63 7.61 7.49 7.47 7.40 7.40 7.38 7.37 7.36 7.35 7.35 7.35 7.33 7.31 7.31 7.30 7.29 7.29 7.29 7.26
3.82 3.82 2.27 2.26 2.25 2.23 2.23 2.17 1.19 1.18 1.18 1.17 1.17 1.15 1.15 1.14 1.14 1.13
0.79 0.78 0.77 0.76 0.76 0.75 0.74 0.74
NC
O
O
S
46
1.94 1.95 2.86 2.08
1.00 1.04
1.01 2.86
2.06 2.00
f1 (ppm)


208.29
141.30 135.07 132.38 129.13 128.90 128.72 128.34 118.91 111.16 109.67
94.03
77.48 77.16 76.84
58.49
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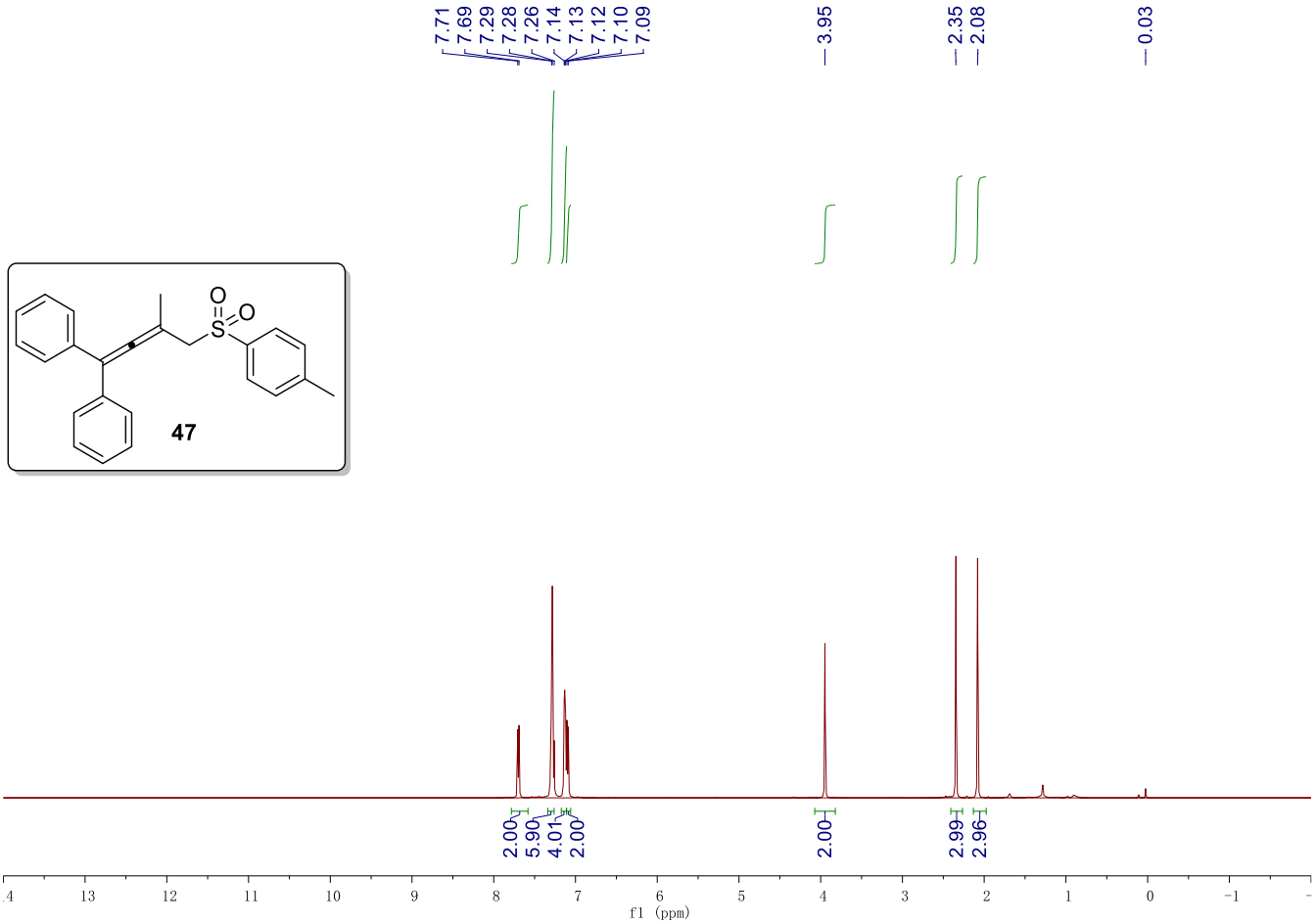
5.05
NC
O
O
S
46
f1 (ppm)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7.69
7.29
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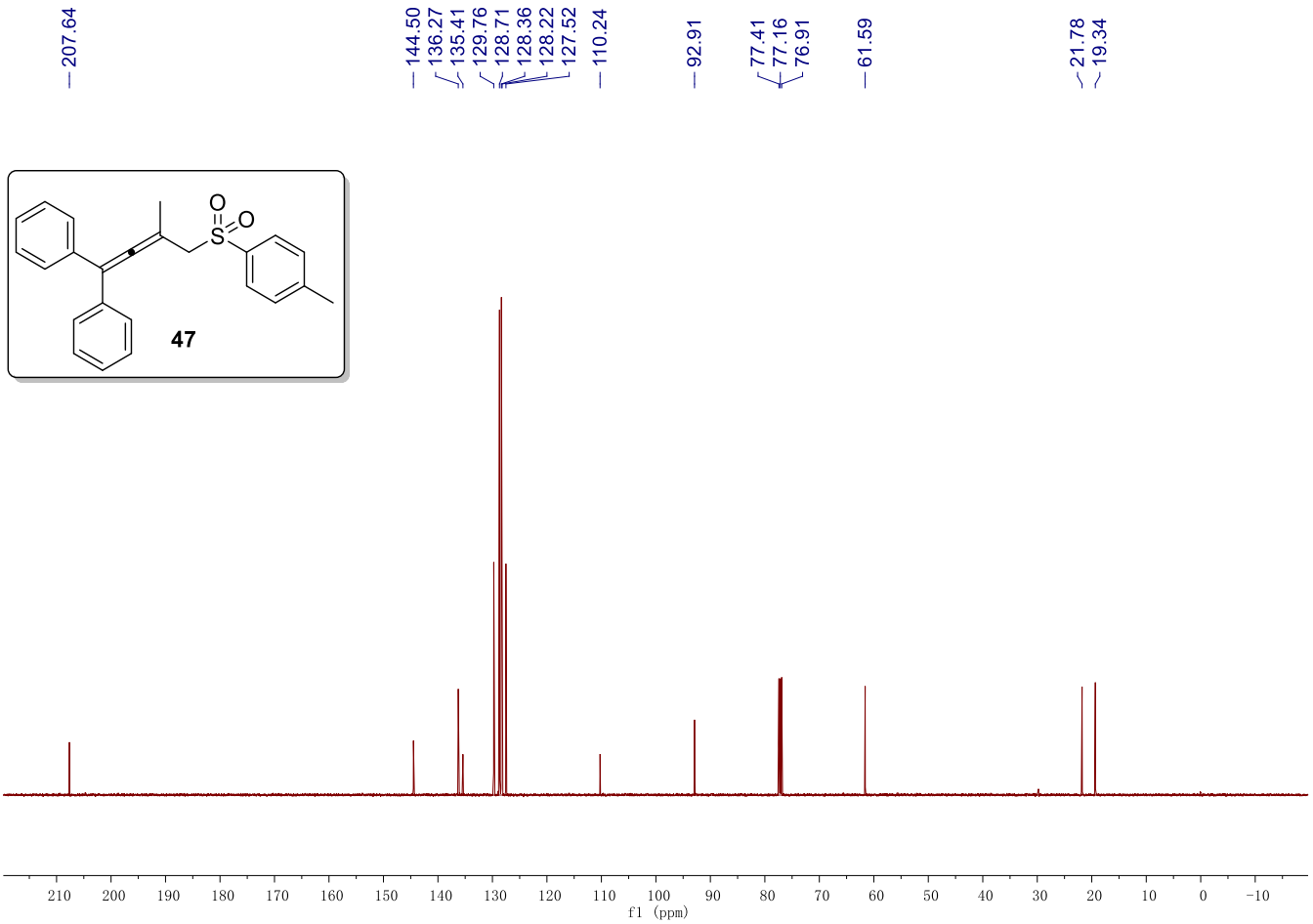
7.26
7.14
7.13
7.12
7.10
7.09
3.95
2.35
2.08
0.03
47
2.00
5.90
4.01
2.00
2.00
2.99
2.96
f1 (ppm)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129.76
128.71
128.36
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127.52
110.24
92.91
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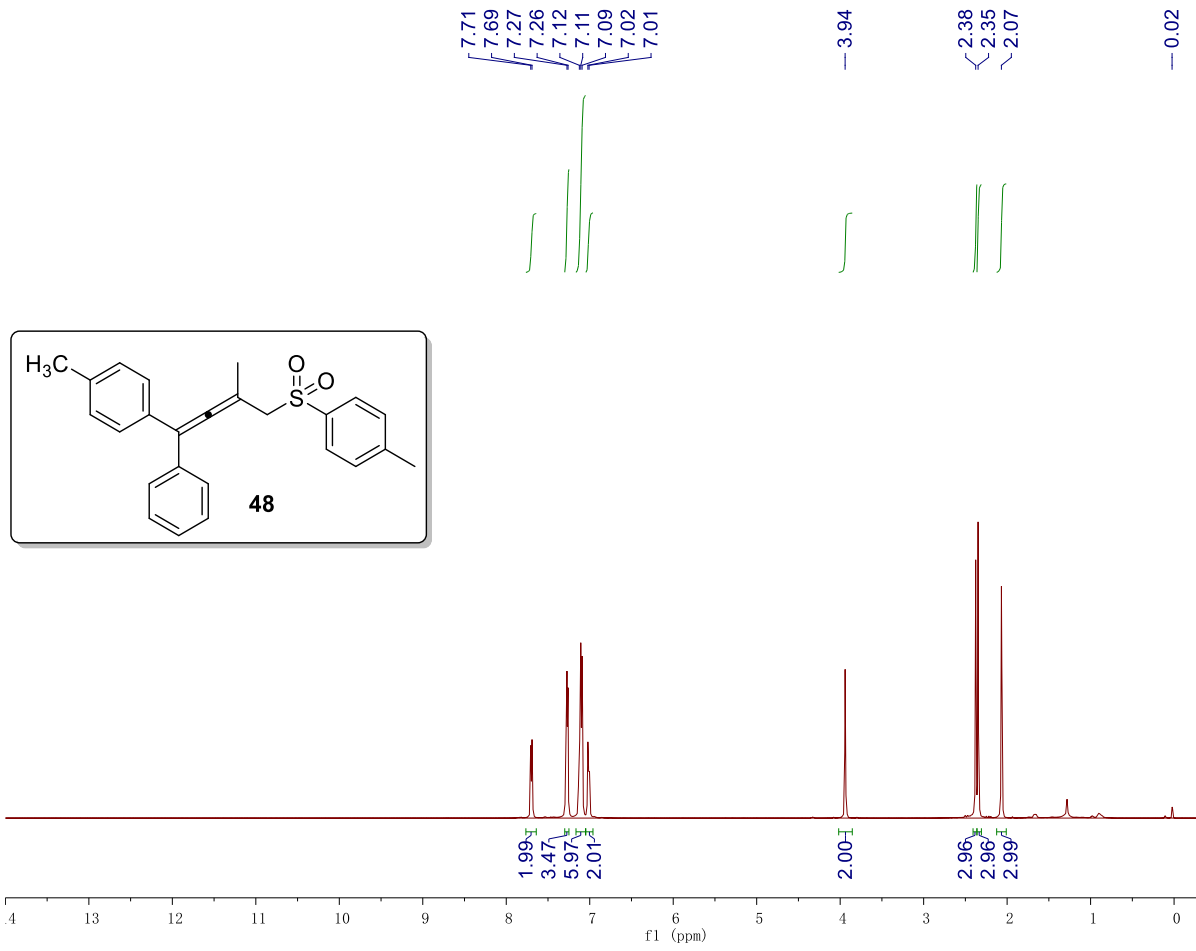
76.91
61.59
21.78
19.34
47
f1 (ppm)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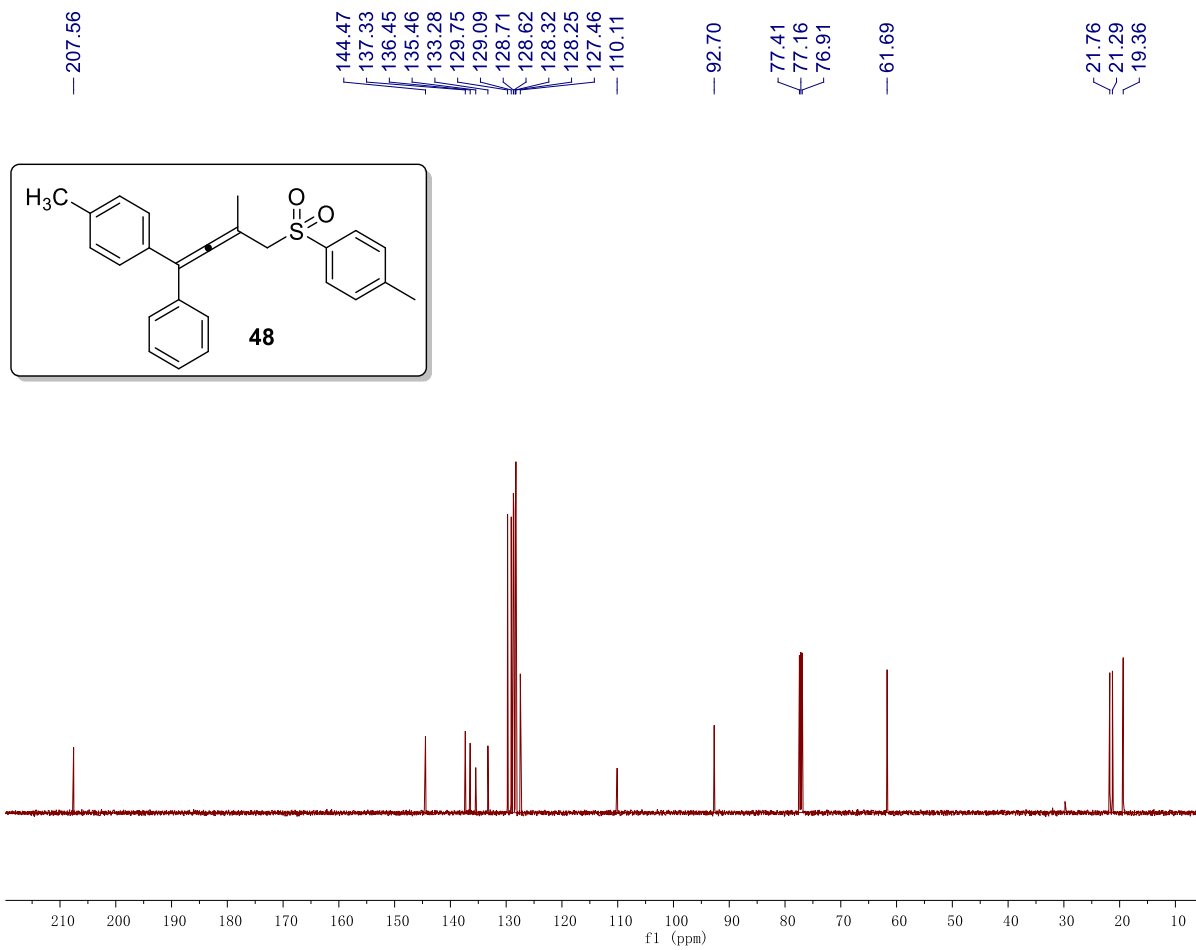
7.69
7.27
7.26
7.12
7.11
7.09
7.02
7.01
3.94
2.38
2.35
2.07
0.02
H3C
O
S
O
48
1.99
3.47
5.97
2.01
2.00
2.96
2.96
2.99
f1 (ppm)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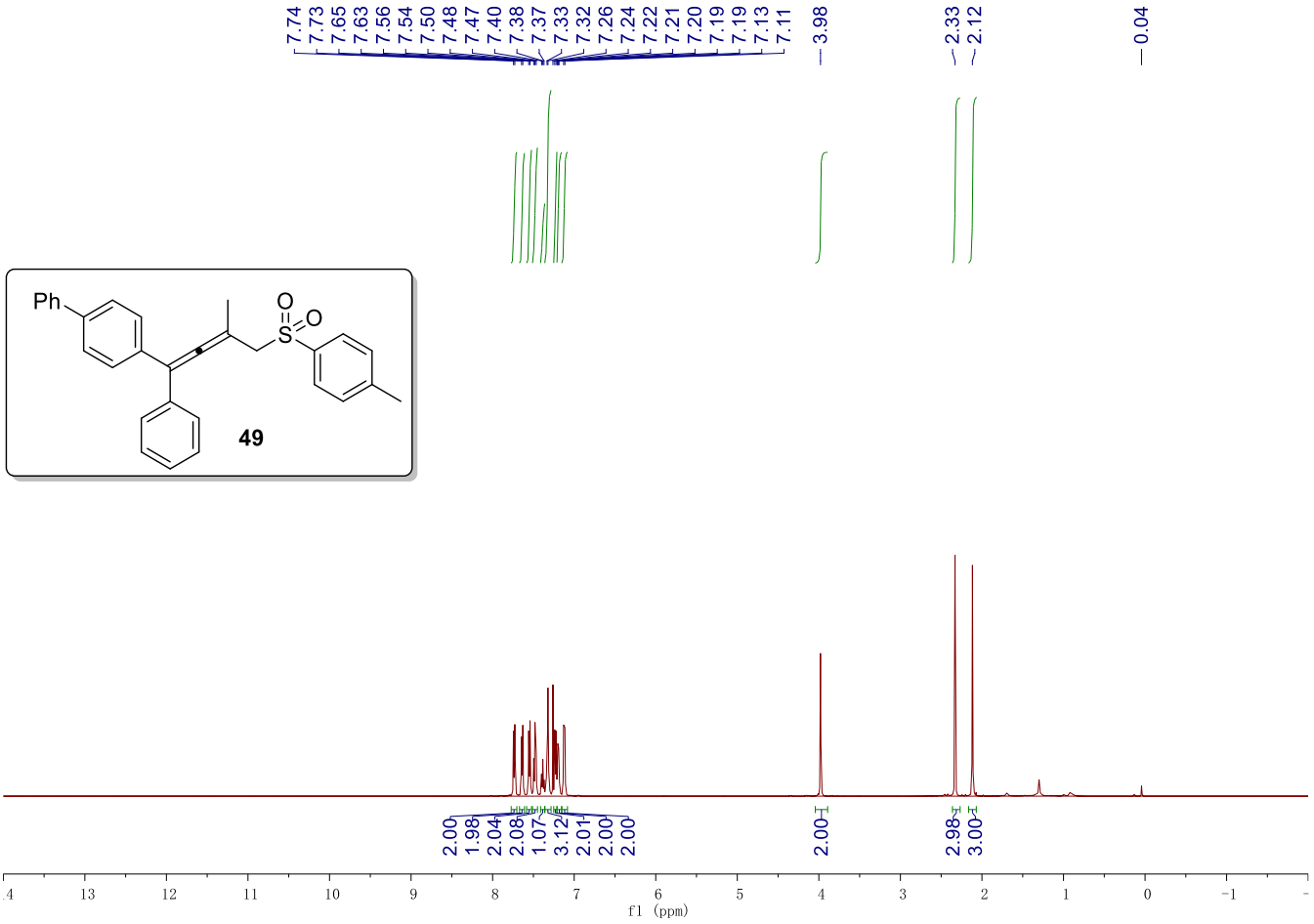
135.46
133.28
129.75
129.09
128.71
128.62
128.32
128.25
127.46
110.11
92.70
77.41
77.16
76.91
61.69
21.76
21.29
19.36
H3C
O
S
O
48
f1 (ppm)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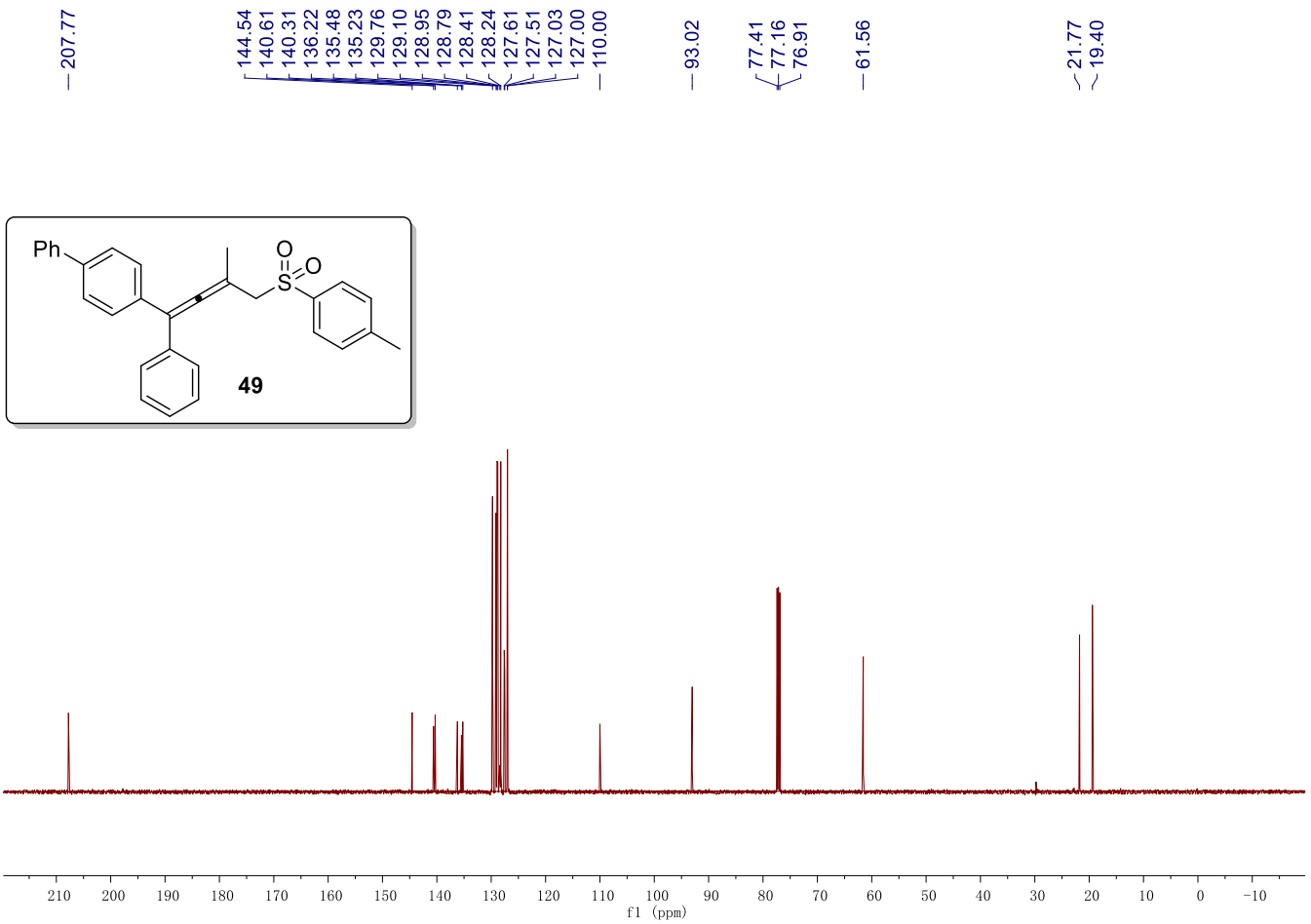
7.50
7.48
7.47
7.40
7.38
7.37
7.33
7.32
7.26
7.24
7.22
7.21
7.20
7.19
7.19
7.13
7.11
3.98
2.33
2.12
0.04
Ph
O
S
O
49
2.00
1.98
2.04
2.08
1.07
3.12
2.01
2.00
2.00
2.00
2.98
3.00
f1 (ppm)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135.23
129.76
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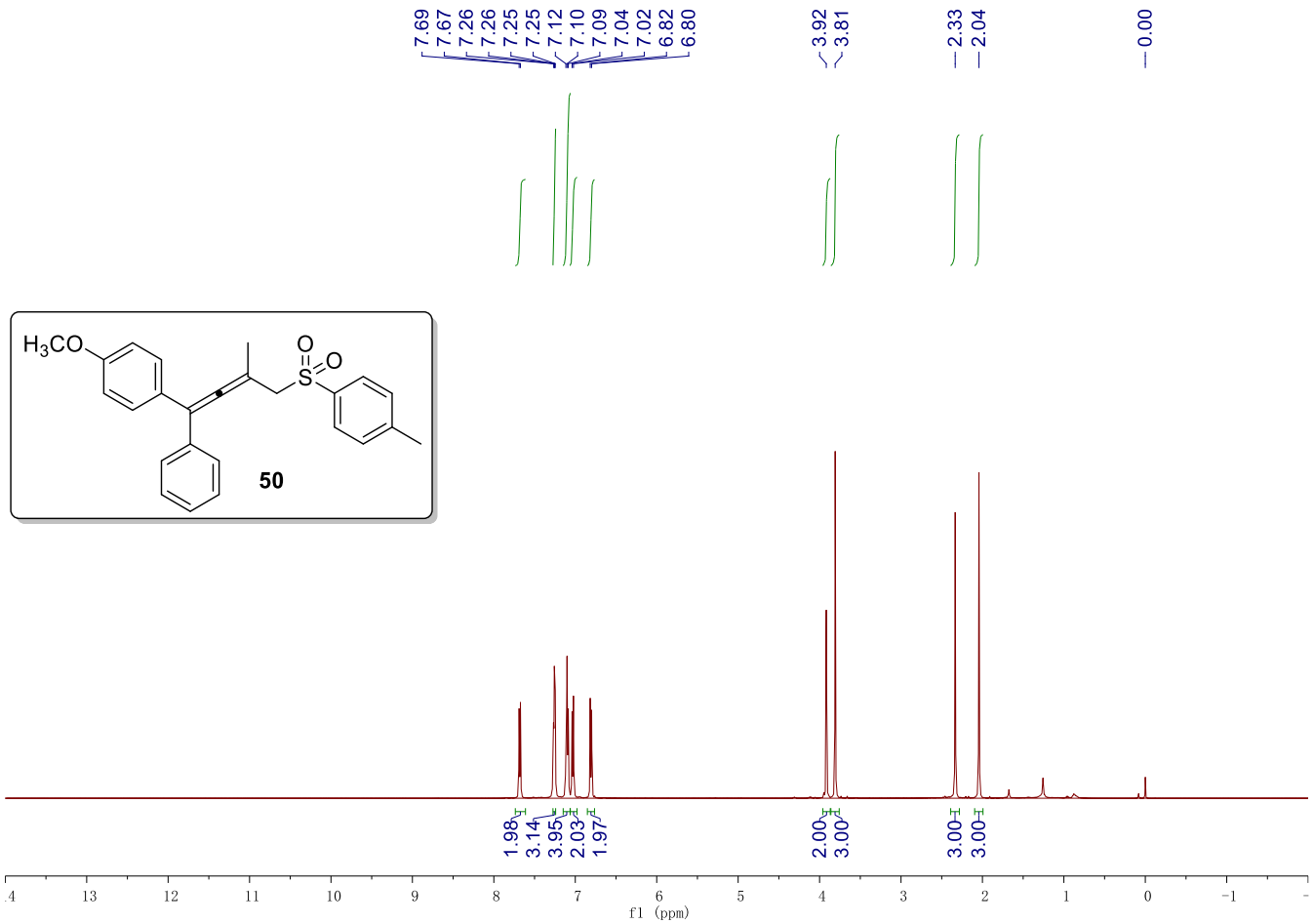
128.95
128.79
128.41
128.24
127.61
127.51
127.03
127.00
110.00
93.02
77.41
77.16
76.91
61.56
21.77
19.40
Ph
O
S
O
49
f1 (ppm)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7.67
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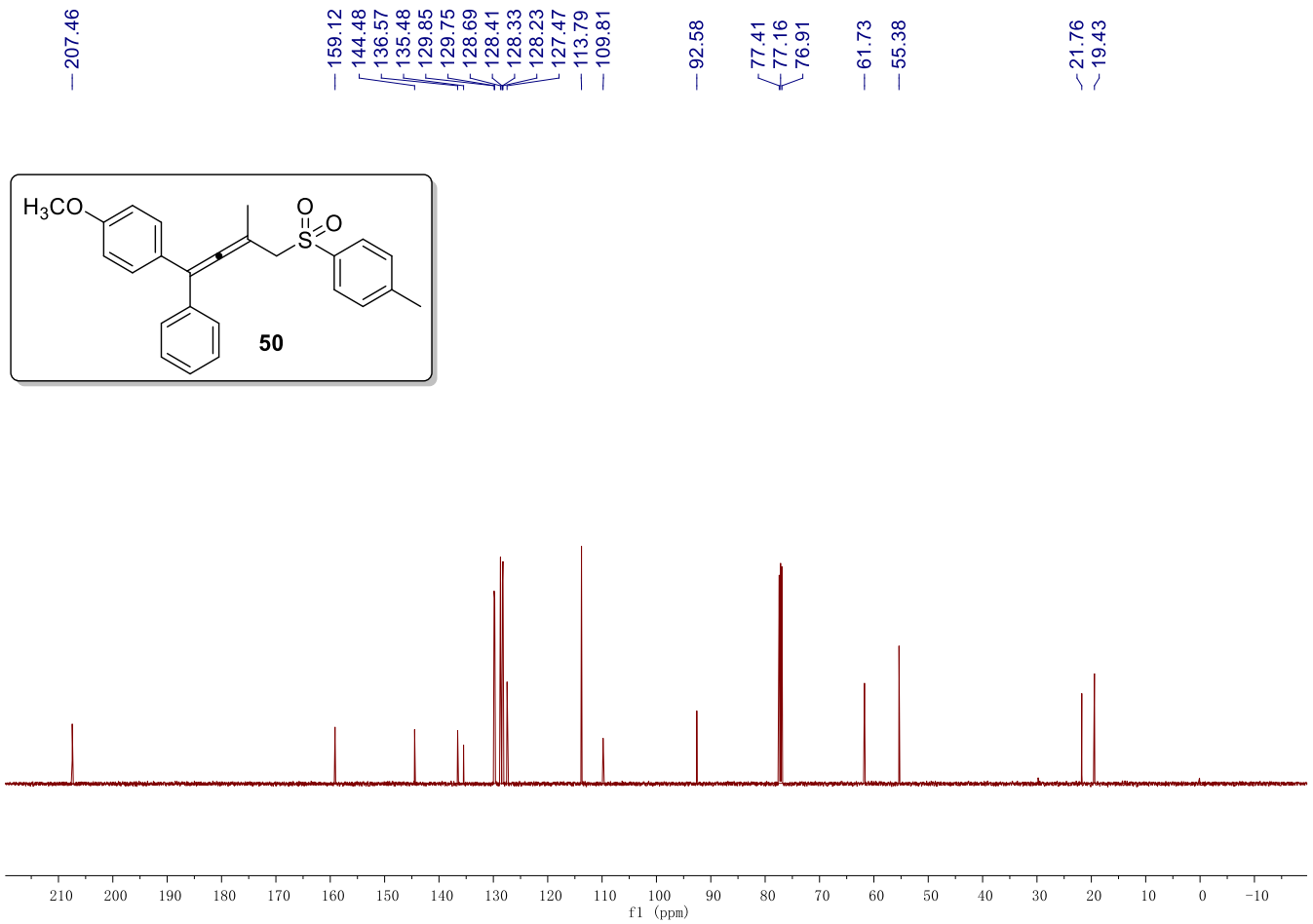
7.26
7.25
7.25
7.12
7.10
7.09
7.04
7.02
6.82
6.80
3.92
3.81
2.33
2.04
0.00
H3CO
O
S
O
50
1.98
3.14
3.95
2.03
1.97
2.00
3.00
3.00
3.00
f1 (ppm)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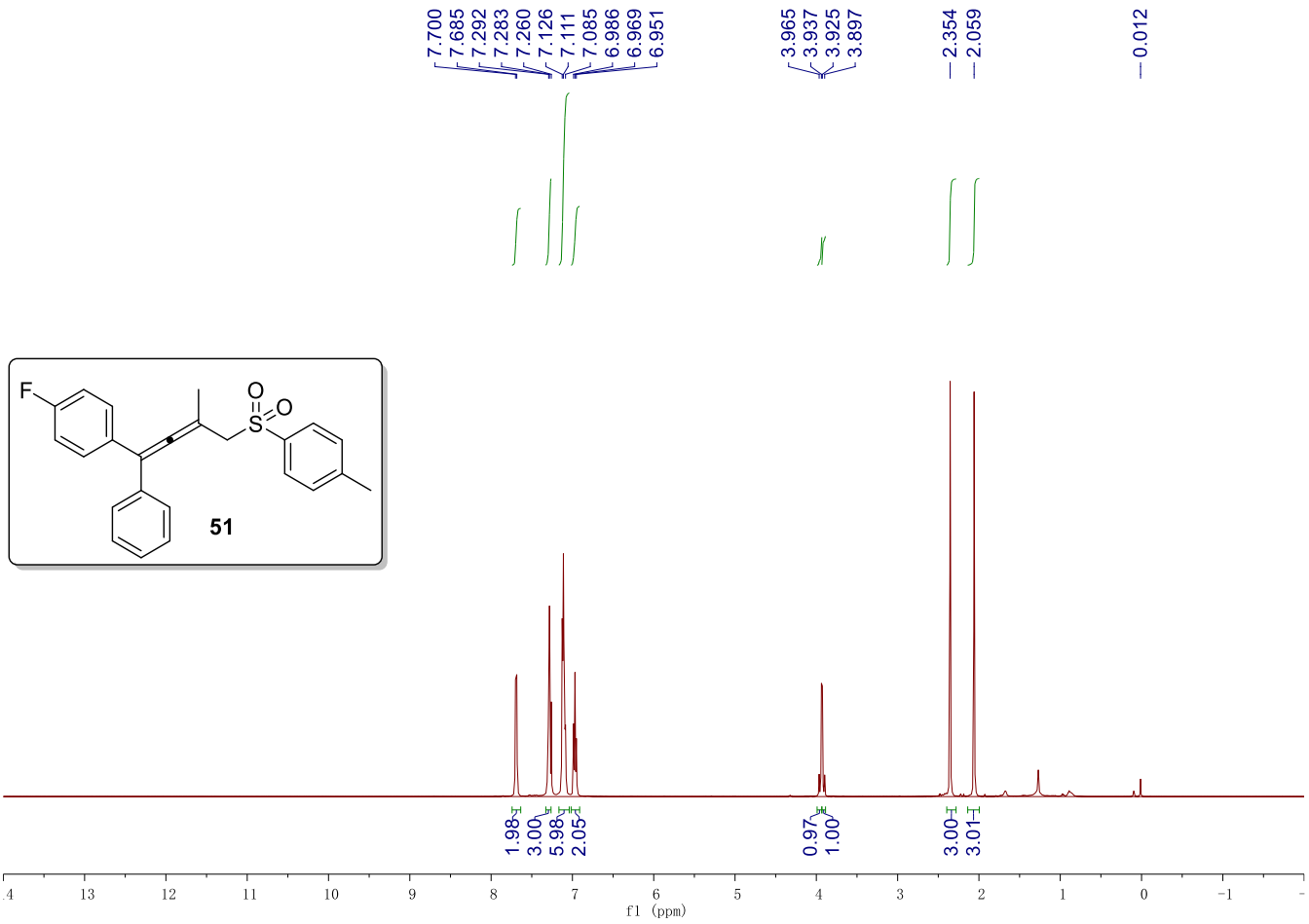
128.41
128.33
128.23
127.47
113.79
109.81
92.58
77.41
77.16
76.91
61.73
55.38
21.76
19.43
H3CO
O
S
O
50
f1 (ppm)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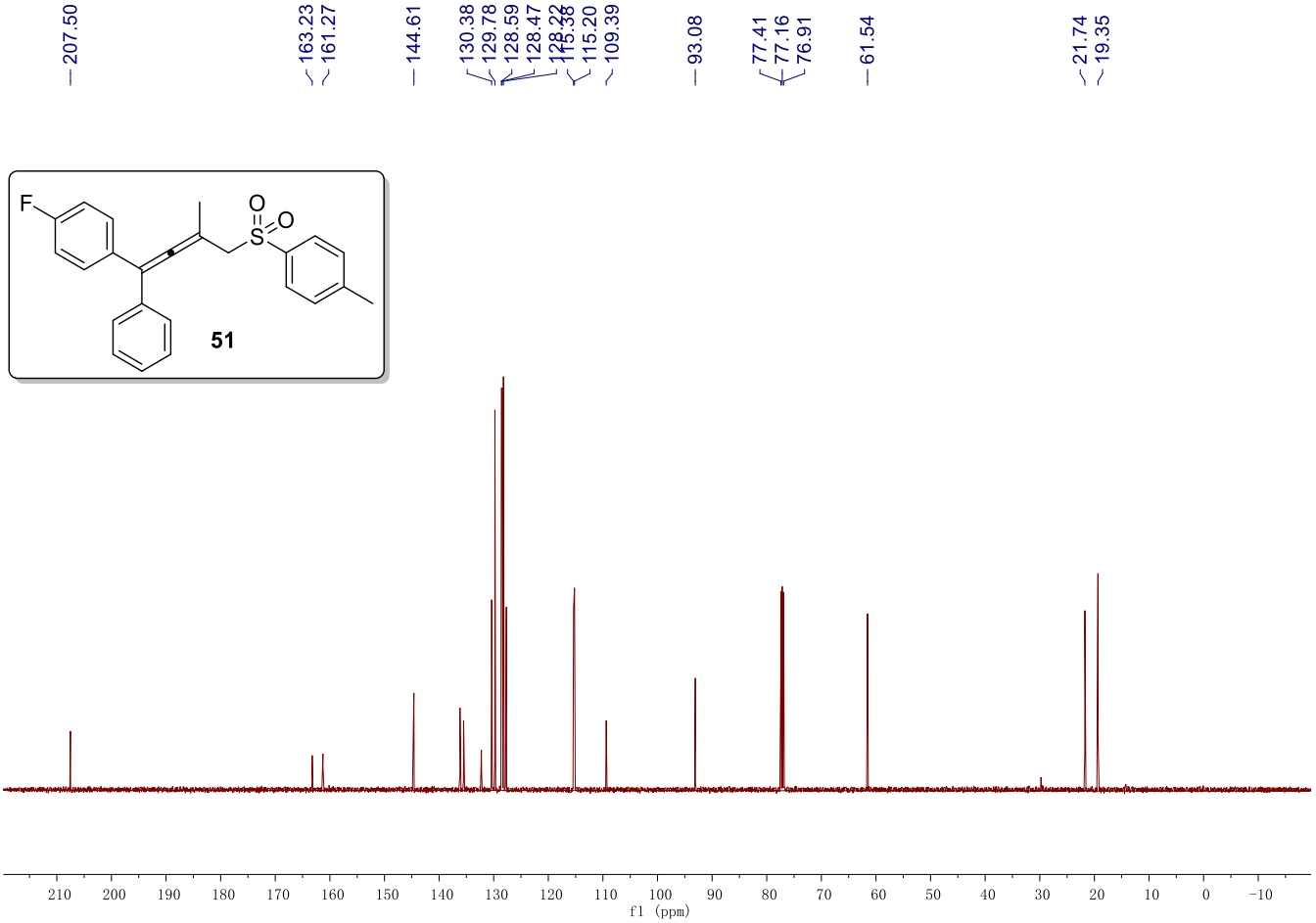
7.283
7.260
7.126
7.111
7.085
6.986
6.969
6.951
3.965
3.937
3.925
3.897
2.354
2.059
0.012
F
O
O
S
51
1.98
3.00
5.98
2.05
0.97
1.00
3.00
3.01
f1 (ppm)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129.78
128.59
128.47
115.20
109.39
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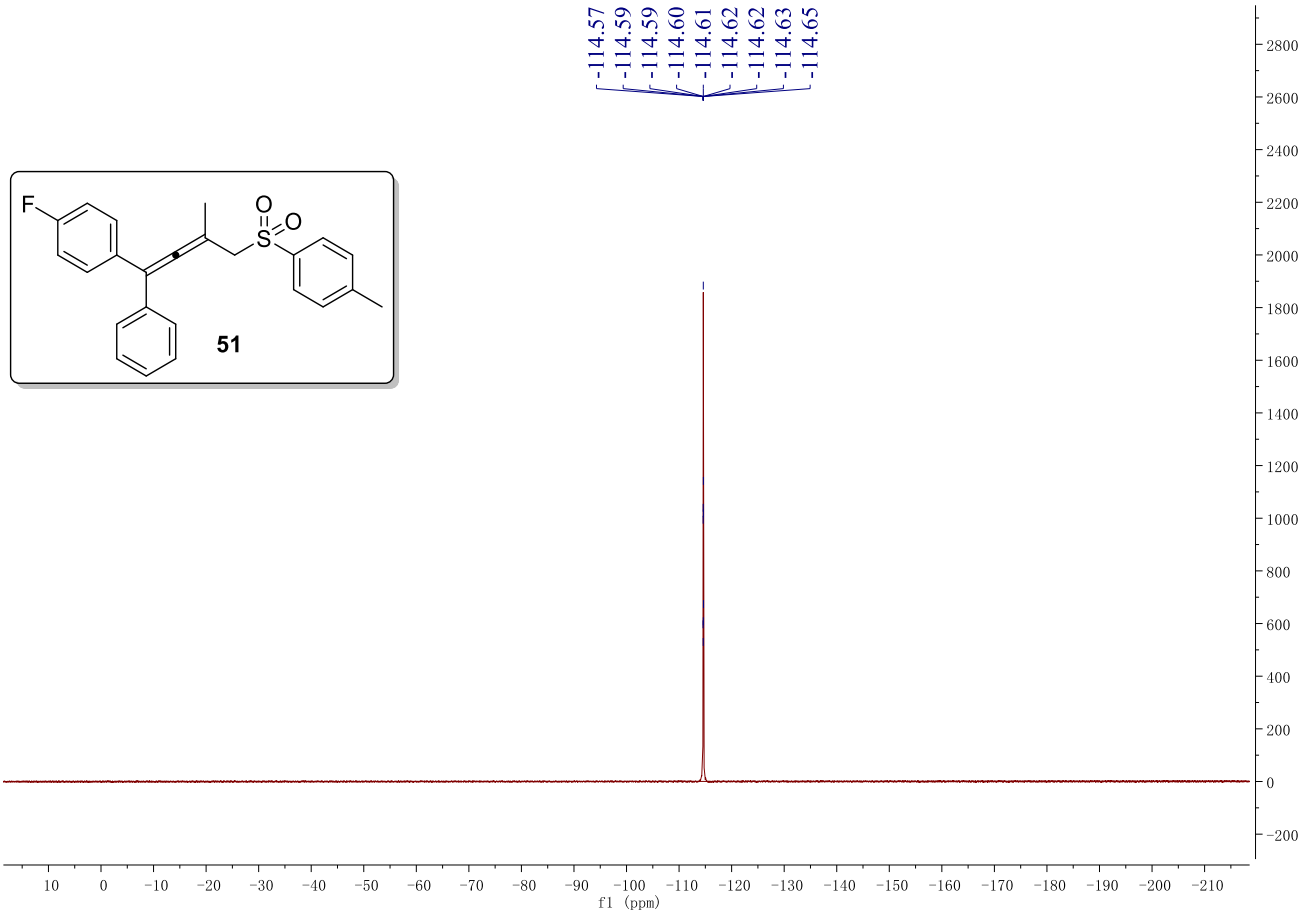
77.16
76.91
61.54
21.74
19.35
F
O
O
S
51
f1 (ppm)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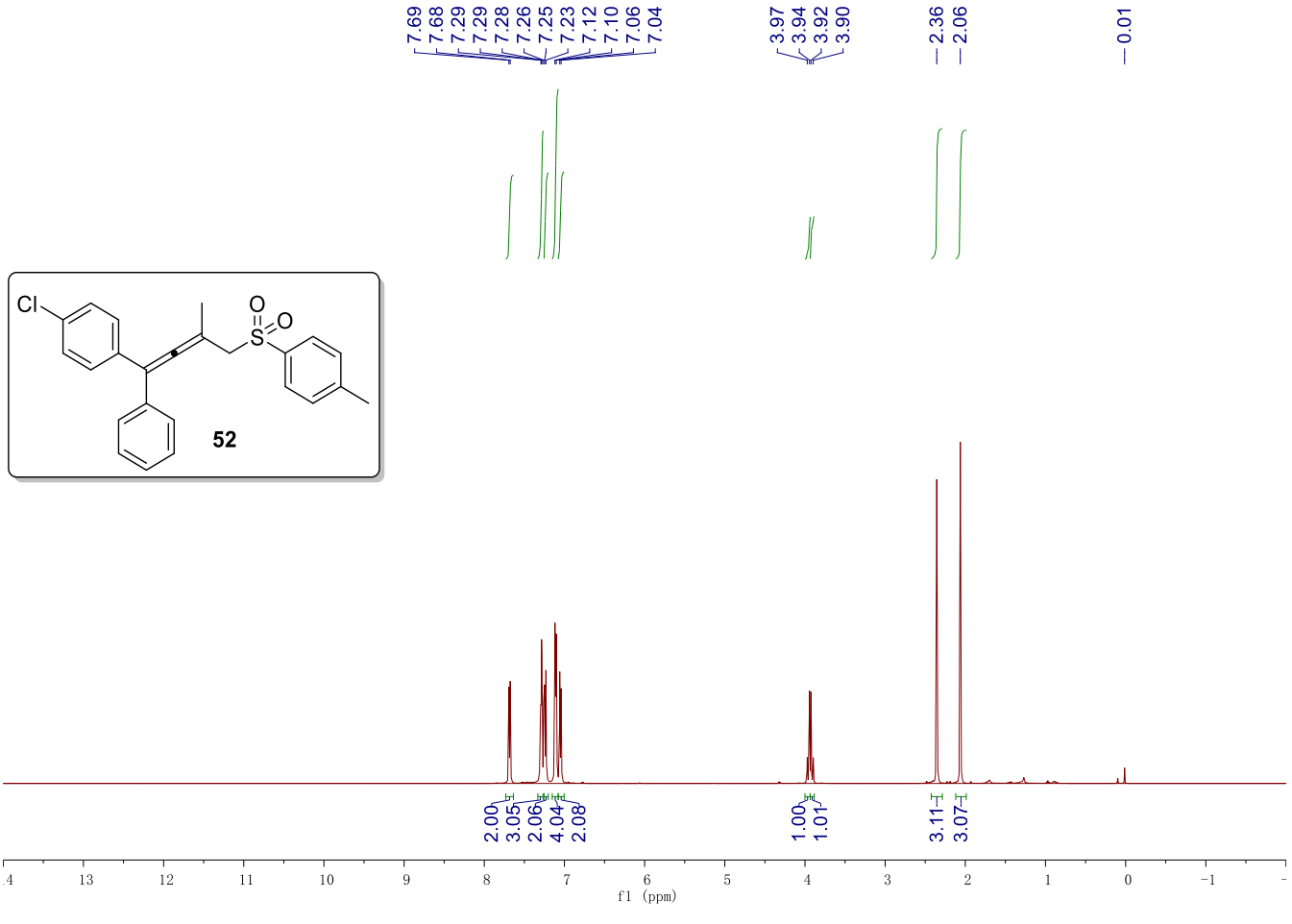
-114.59
-114.59
-114.60
-114.61
-114.62
-114.62
-114.63
-114.65
F
O
S
O
51
f1 (ppm)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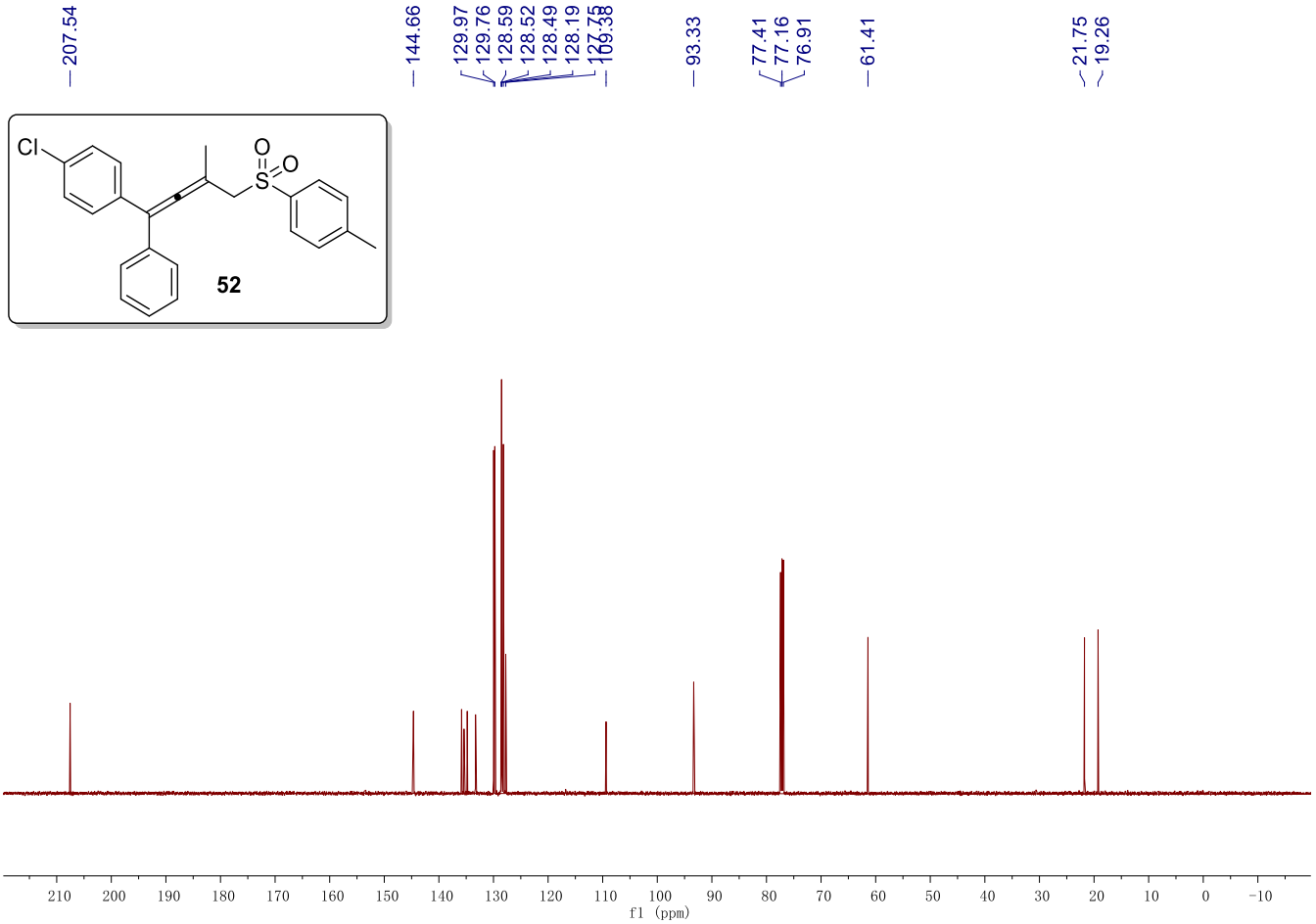
7.68
7.29
7.29
7.28
7.26
7.25
7.23
7.12
7.10
7.06
7.04
3.97
3.94
3.92
3.90
2.36
2.06
0.01
Cl
O
S
O
52
2.00
3.05
2.06
4.04
2.08
1.00
1.01
3.11
3.07
f1 (ppm)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128.19
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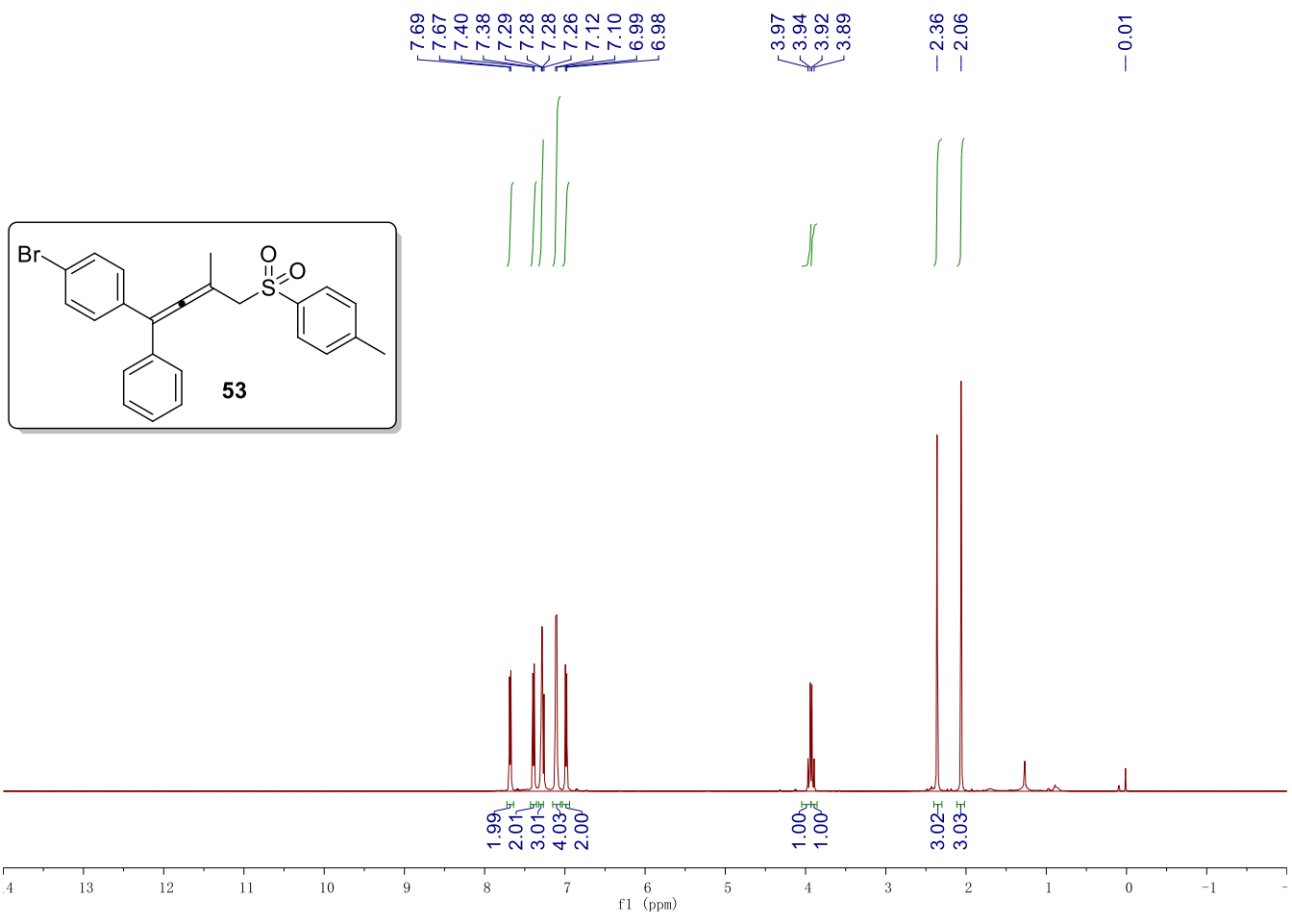
77.16
76.91
61.41
21.75
19.26
Cl
O
S
O
52
f1 (ppm)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7.28
7.28
7.26
7.12
7.10
6.99
6.98
3.97
3.94
3.92
3.89
2.36
2.06
0.01
Br
O
S
O
53
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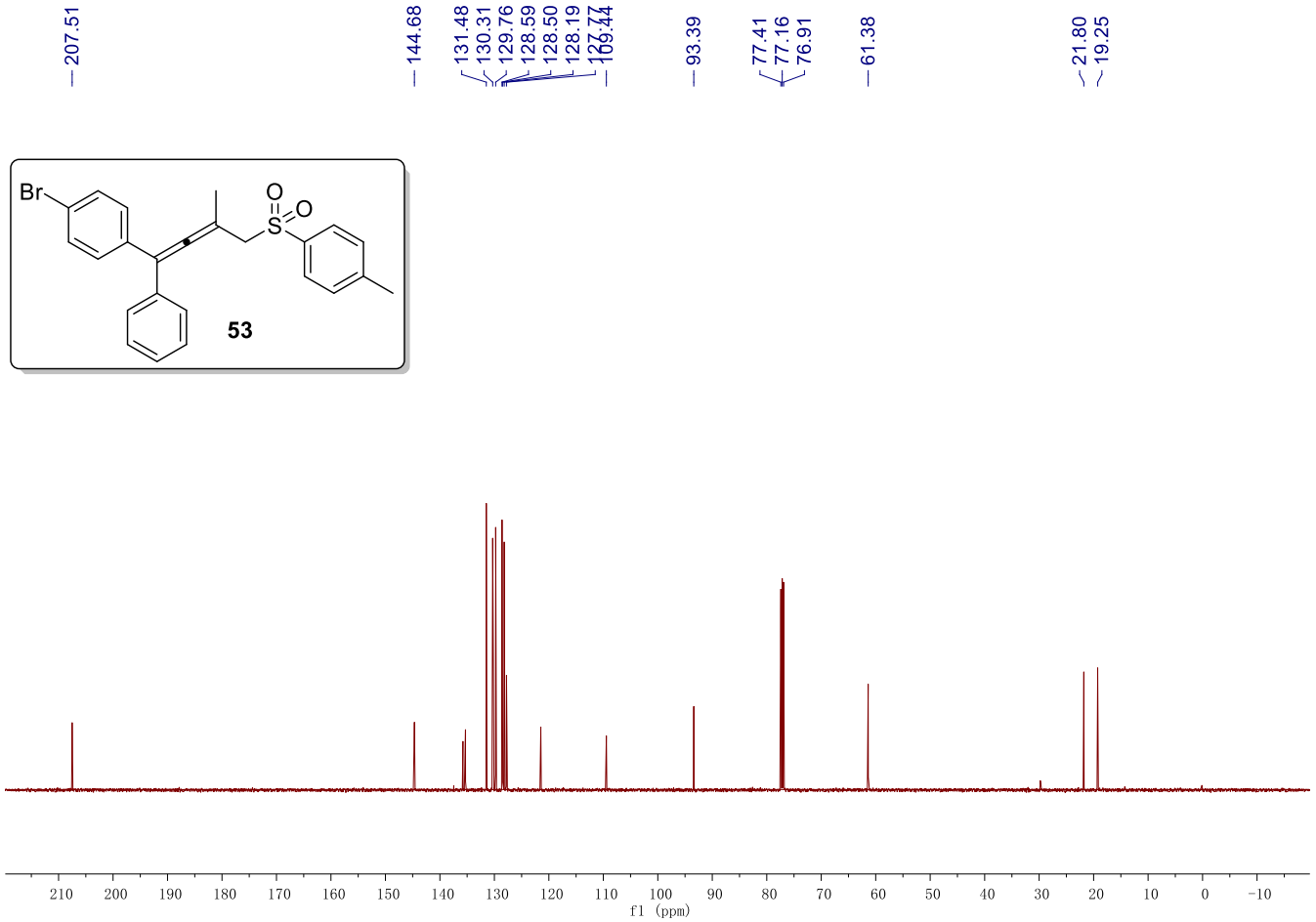
2.01
3.01
4.03
2.00
1.00
1.00
3.02
3.03
f1 (ppm)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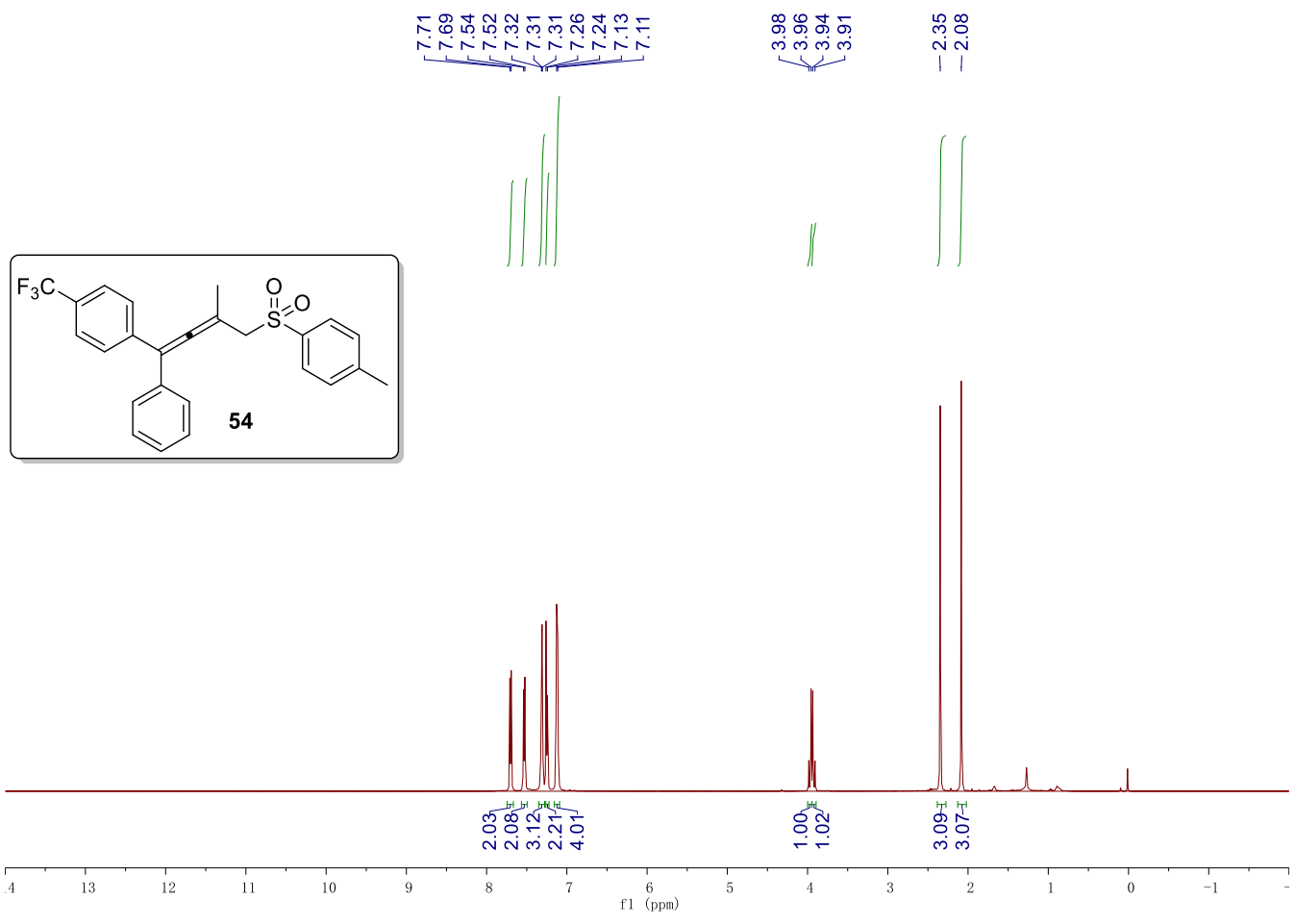
77.16
76.91
61.38
21.80
19.25
Br
O
S
O
53
f1 (ppm)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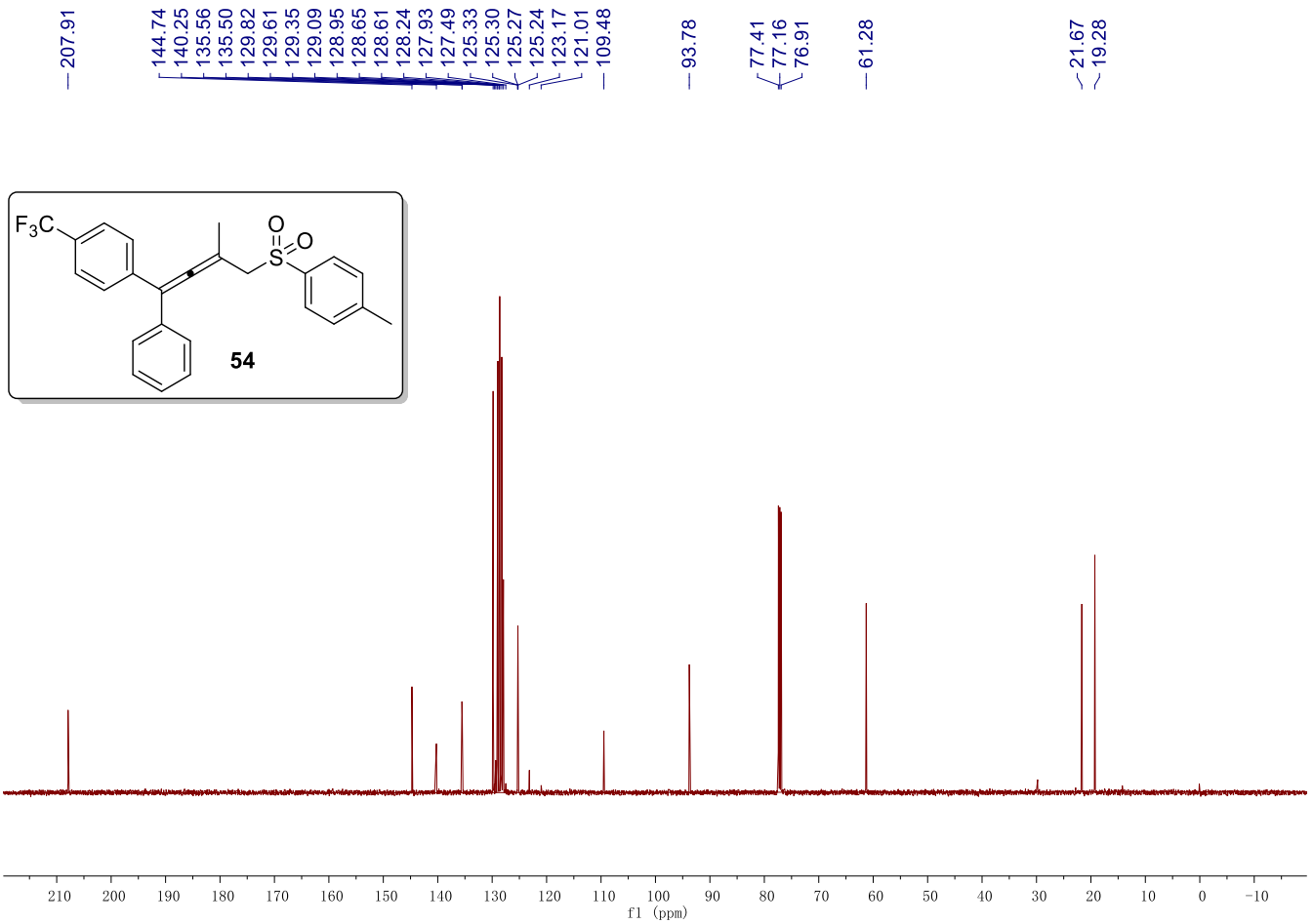
7.69
7.54
7.52
7.32
7.31
7.31
7.26
7.24
7.13
7.11
3.98
3.96
3.94
3.91
2.35
2.08
F3C
O
S
O
54
2.03
2.08
3.12
2.21
4.01
1.00
1.02
3.09
3.07
f1 (ppm)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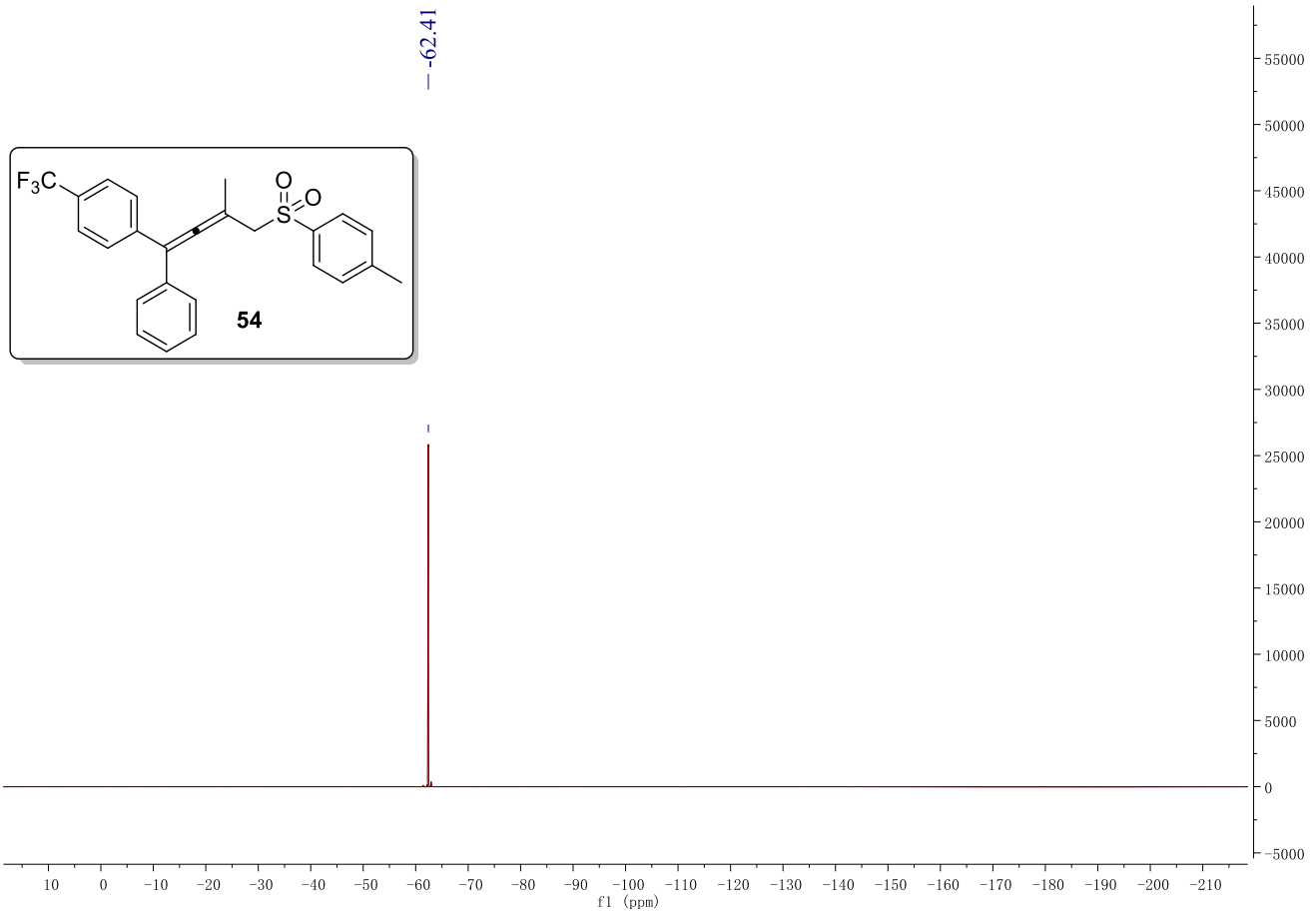
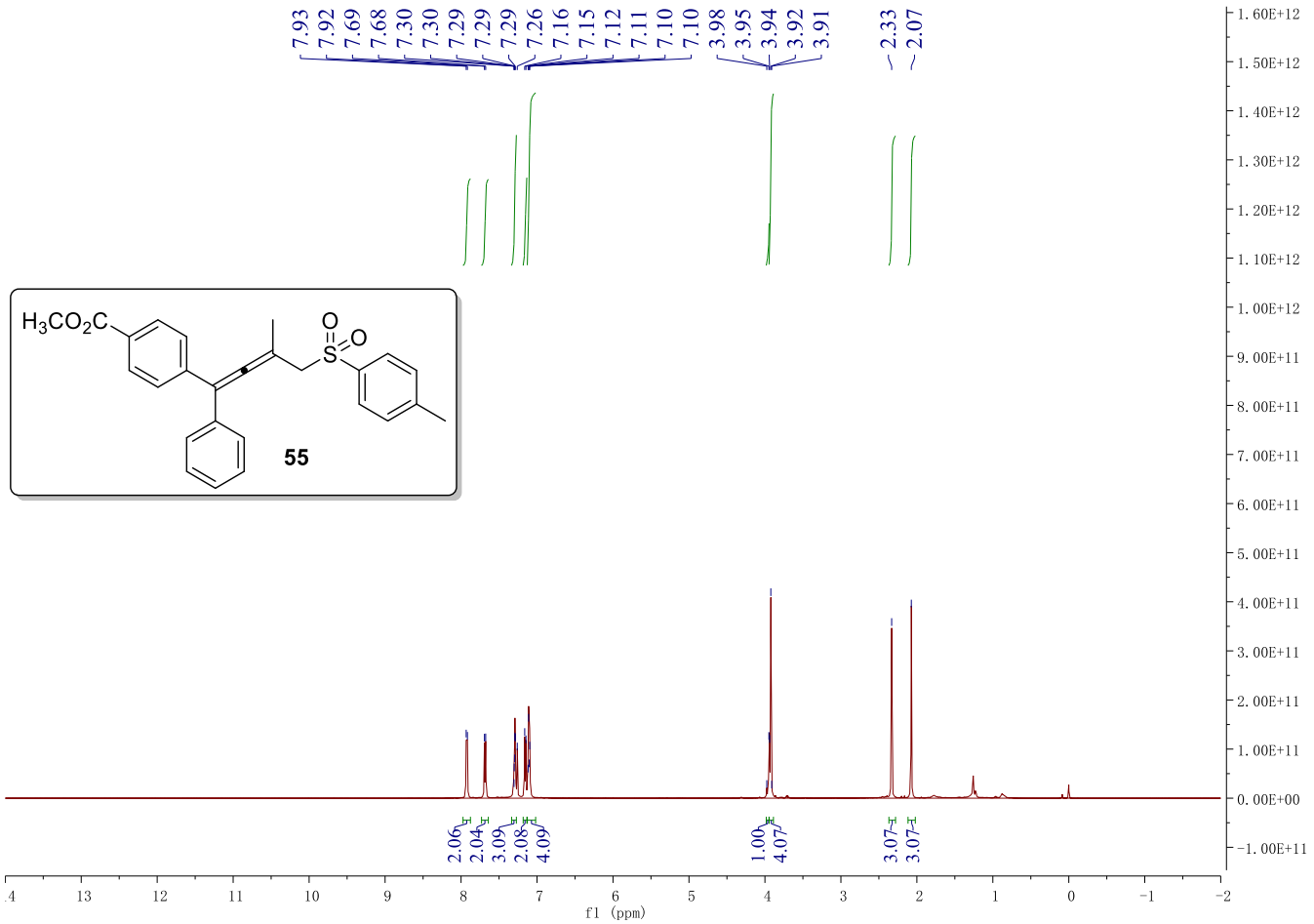
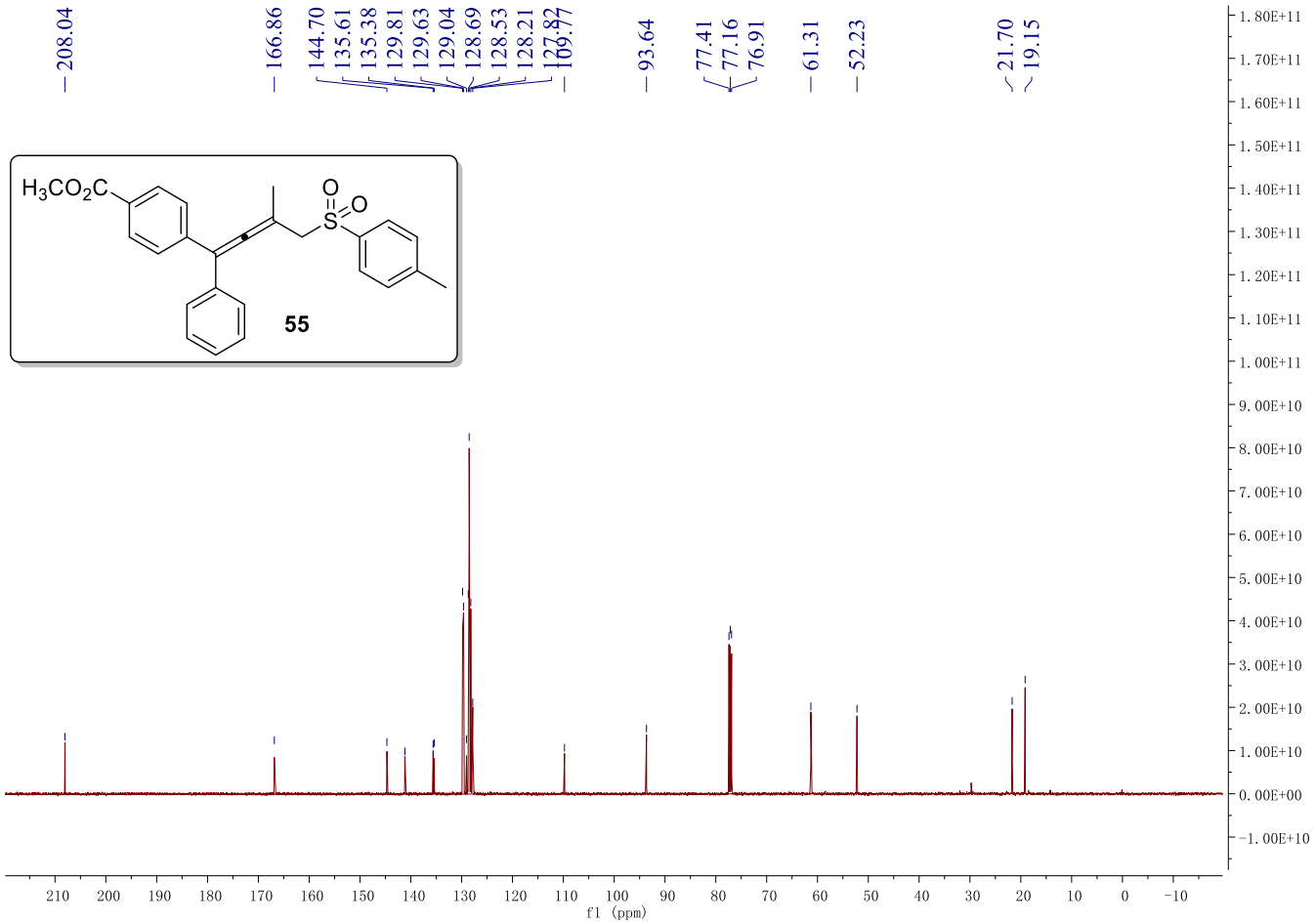
129.61
129.35
129.09
128.95
128.65
128.61
128.24
127.93
127.49
125.33
125.30
125.27
125.24
123.17
121.01
109.48
93.78
77.41
77.16
76.91
61.28
21.67
19.28
F3C
O
S
O
54
f1 (ppm)


-62.41
F3C
O
S
O
54
f1 (ppm)


7.93
7.92
7.69
7.68
7.30
7.30
7.29
7.29
7.29
7.26
7.16
7.15
7.12
7.11
7.10
7.10
3.98
3.95
3.94
3.92
3.91
2.33
2.07
H3CO2C
O
S
O
55
2.06
2.04
3.09
2.08
4.09
1.00
4.07
3.07
3.07
f1 (ppm)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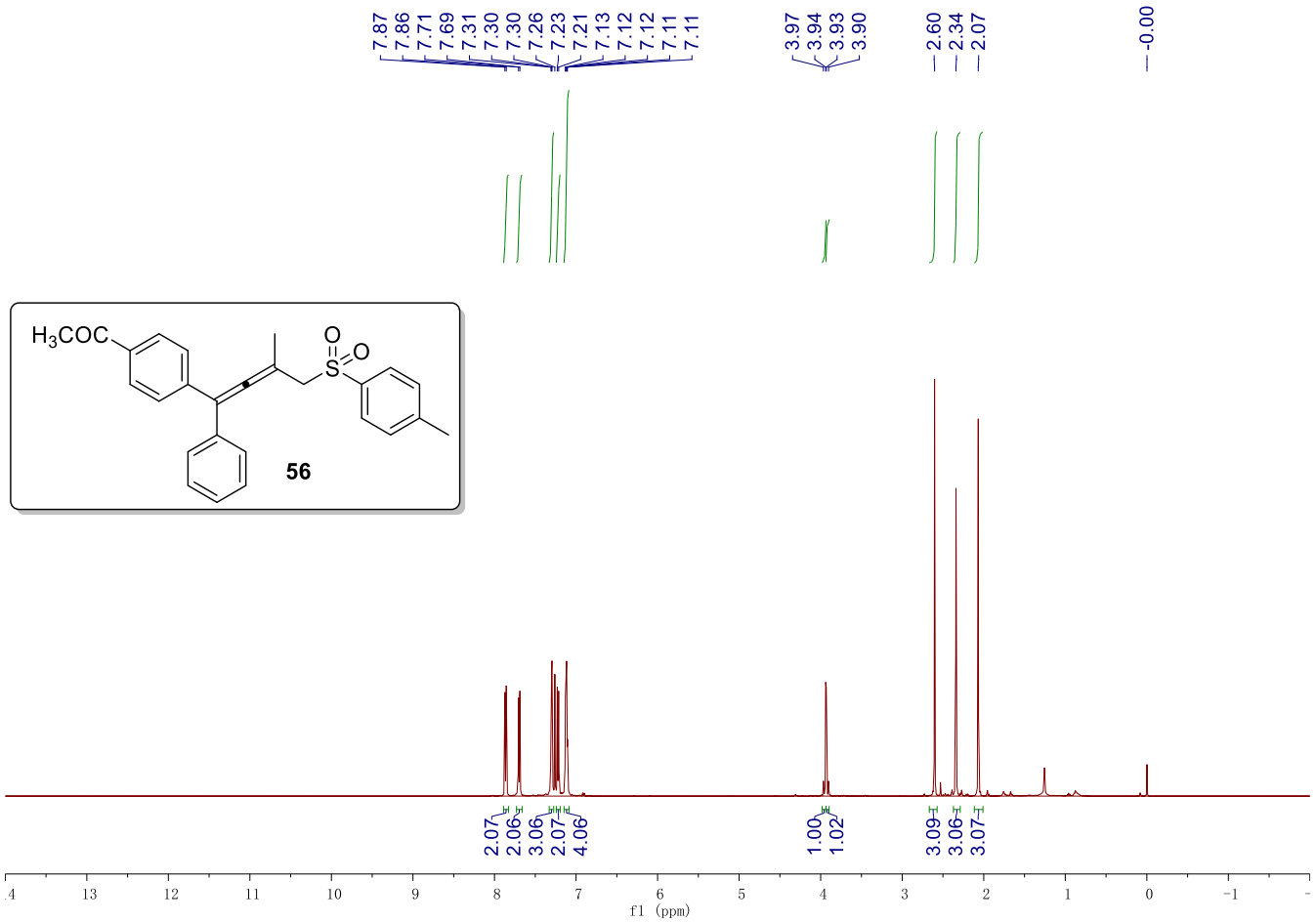
129.04
128.69
128.53
128.21
127.82
93.64
77.41
77.16
76.91
61.31
52.23
21.70
19.15
H3CO2C
O
S
O
55
f1 (ppm)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7.86
7.71
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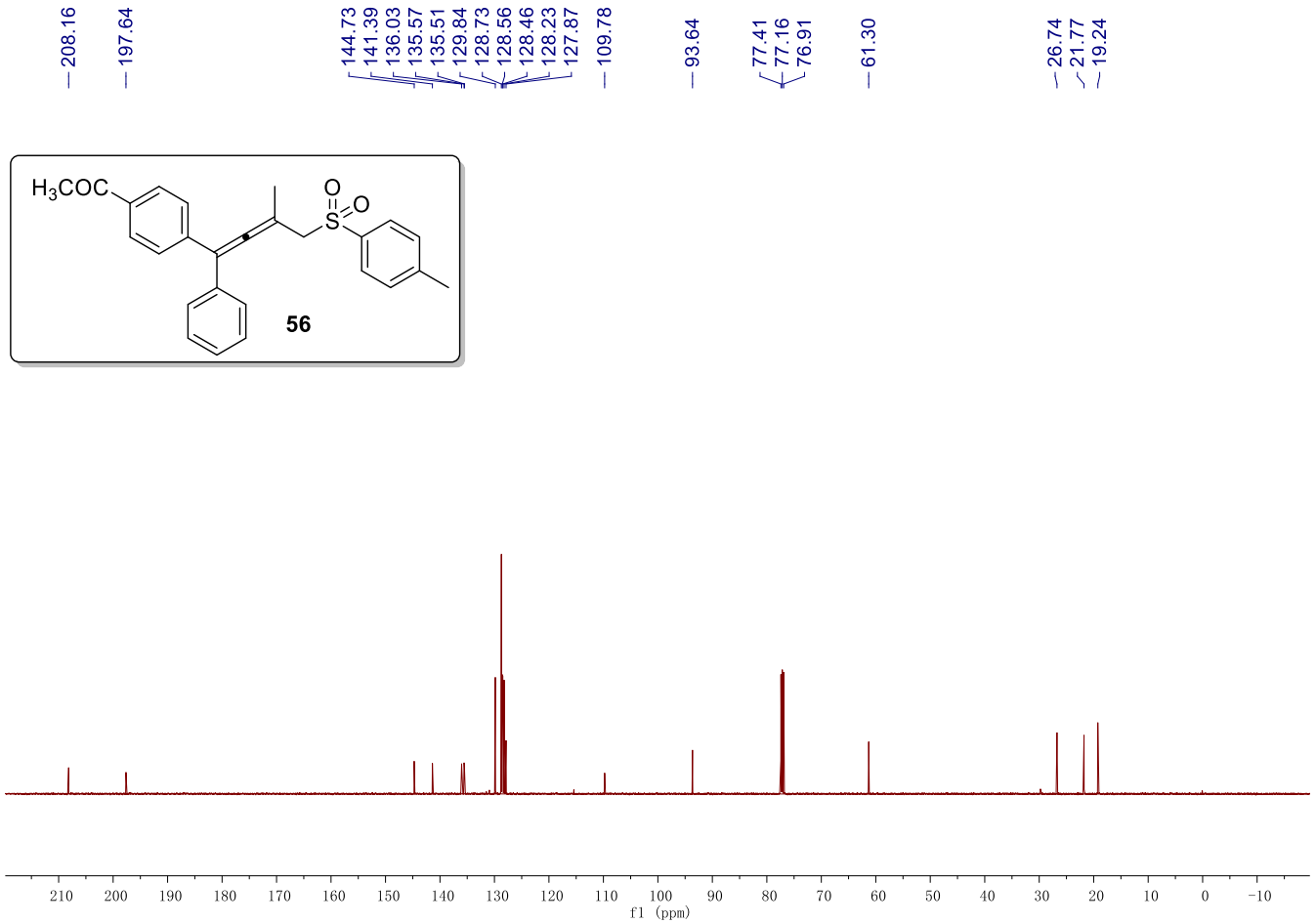
7.30
7.26
7.23
7.21
7.13
7.12
7.12
7.11
7.11
3.97
3.94
3.93
3.90
2.60
2.34
2.07
-0.00
H3COC
O
S
O
56
2.07
2.06
3.06
2.07
4.06
1.00
1.02
3.09
3.06
3.07
f1 (ppm)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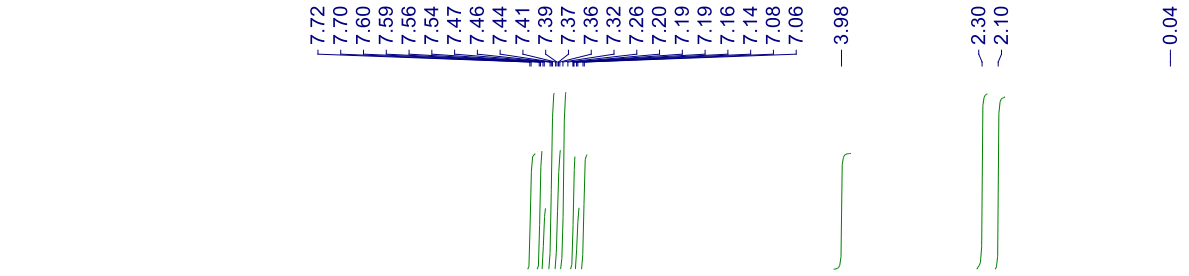
136.03
135.57
135.51
129.84
128.73
128.56
128.46
128.23
127.87
109.78
93.64
77.41
77.16
76.91
61.30
26.74
21.77
19.24
H3COC
O
S
O
56
f1 (ppm)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7.46
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7.41
7.39
7.37
7.36
7.32
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7.19
7.19
7.16
7.14
7.08
7.06
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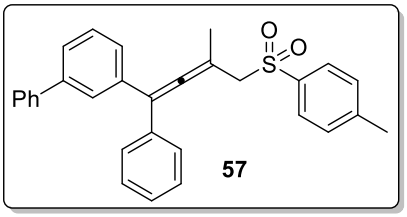
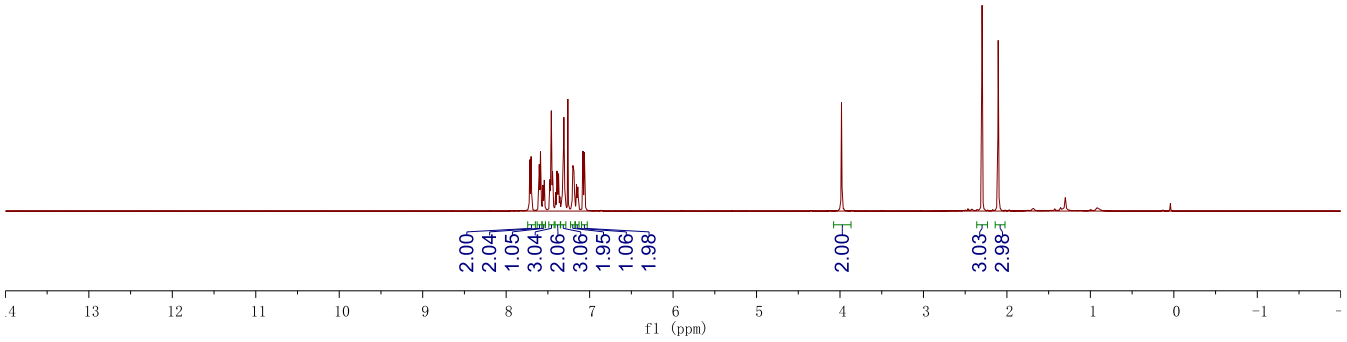
2.30
2.10
0.04


Ph
O
O
S
57


2.00
2.04
1.05
3.04
2.06
3.06
1.95
1.06
1.98
2.00
3.03
2.98
f1 (ppm)


207.73
144.50
141.28
140.84
136.90
136.22
135.47
129.73
128.91
128.85
128.68
128.43
128.18
127.80
127.59
127.53
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127.18
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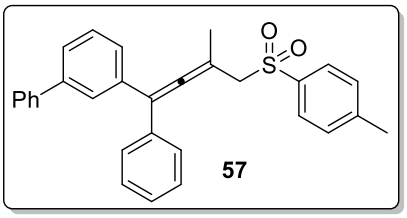
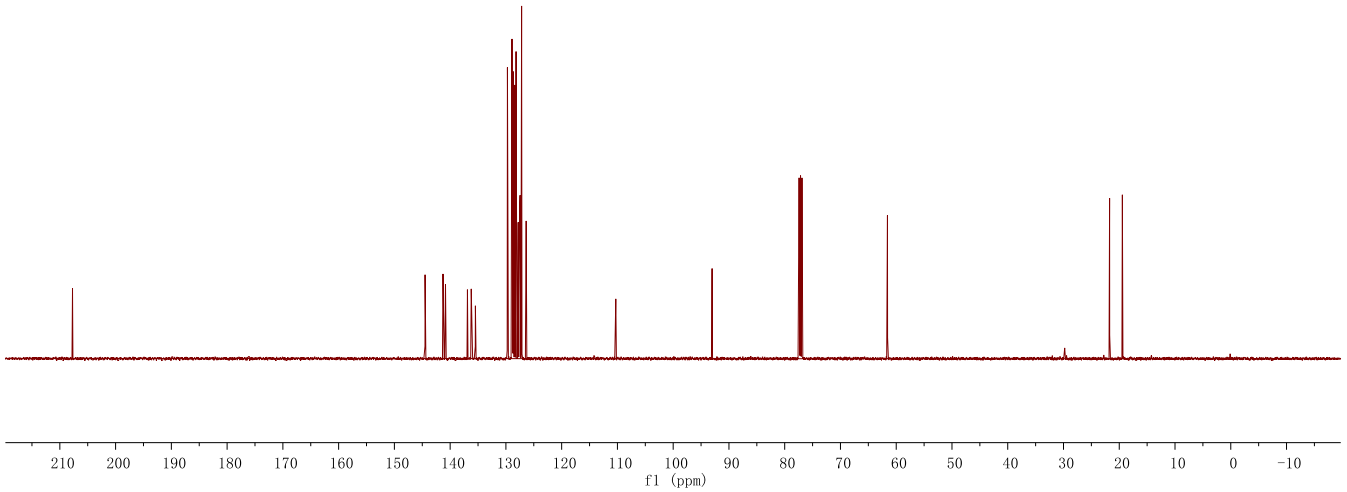
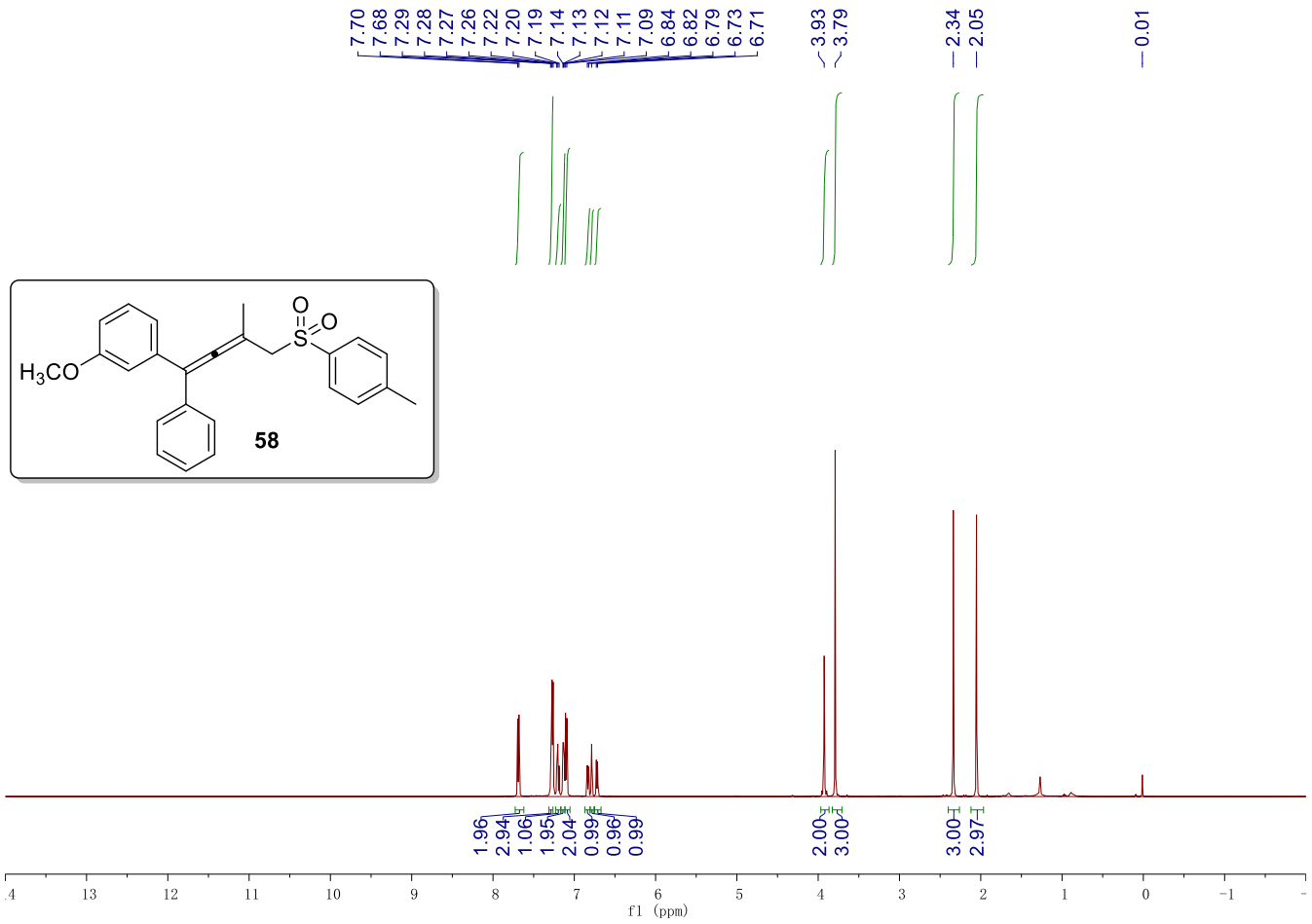
77.41
77.16
76.91
61.57
21.73
19.44


Ph
O
O
S
57


f1 (ppm)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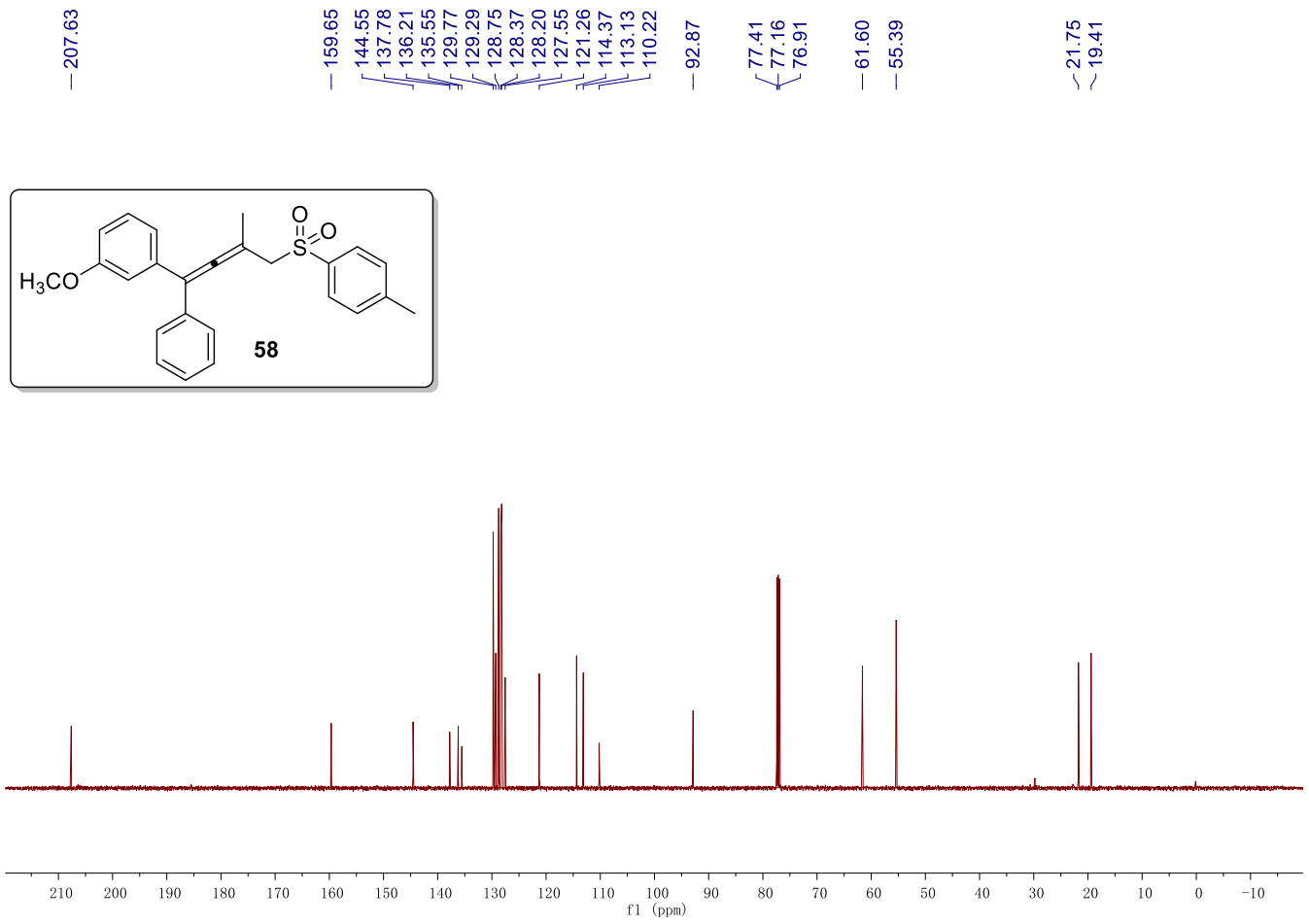
7.19
7.14
7.13
7.12
7.11
7.09
6.84
6.82
6.79
6.73
6.71
3.93
3.79
2.34
2.05
0.01
H3CO
O
O
S
58
1.96
2.94
1.06
1.95
2.04
0.99
0.96
0.99
2.00
3.00
3.00
2.97
f1 (ppm)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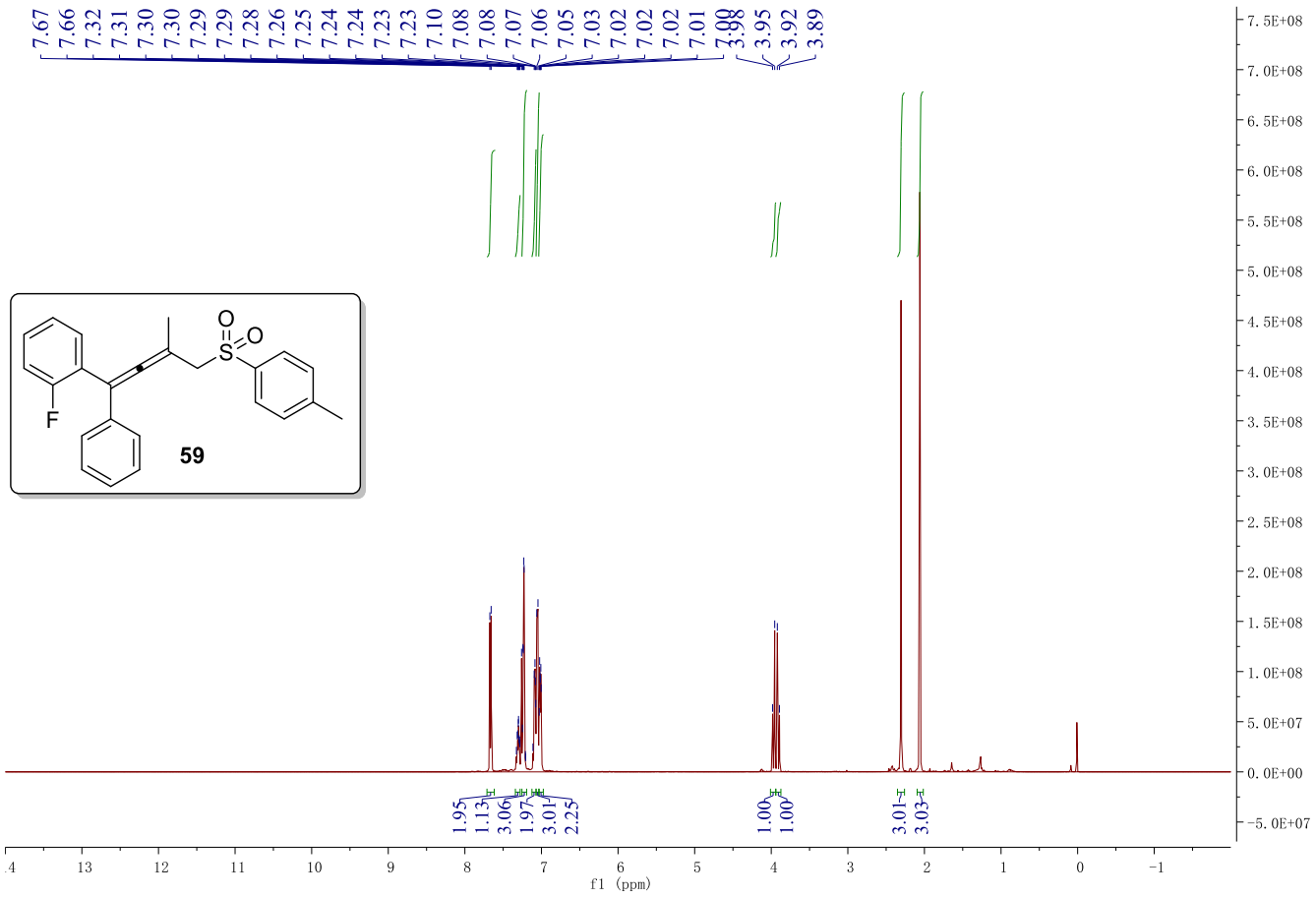
129.29
128.75
128.37
128.20
127.55
121.26
114.37
113.13
110.22
92.87
77.41
77.16
76.91
61.60
55.39
21.75
19.41
H3CO
O
O
S
58
f1 (ppm)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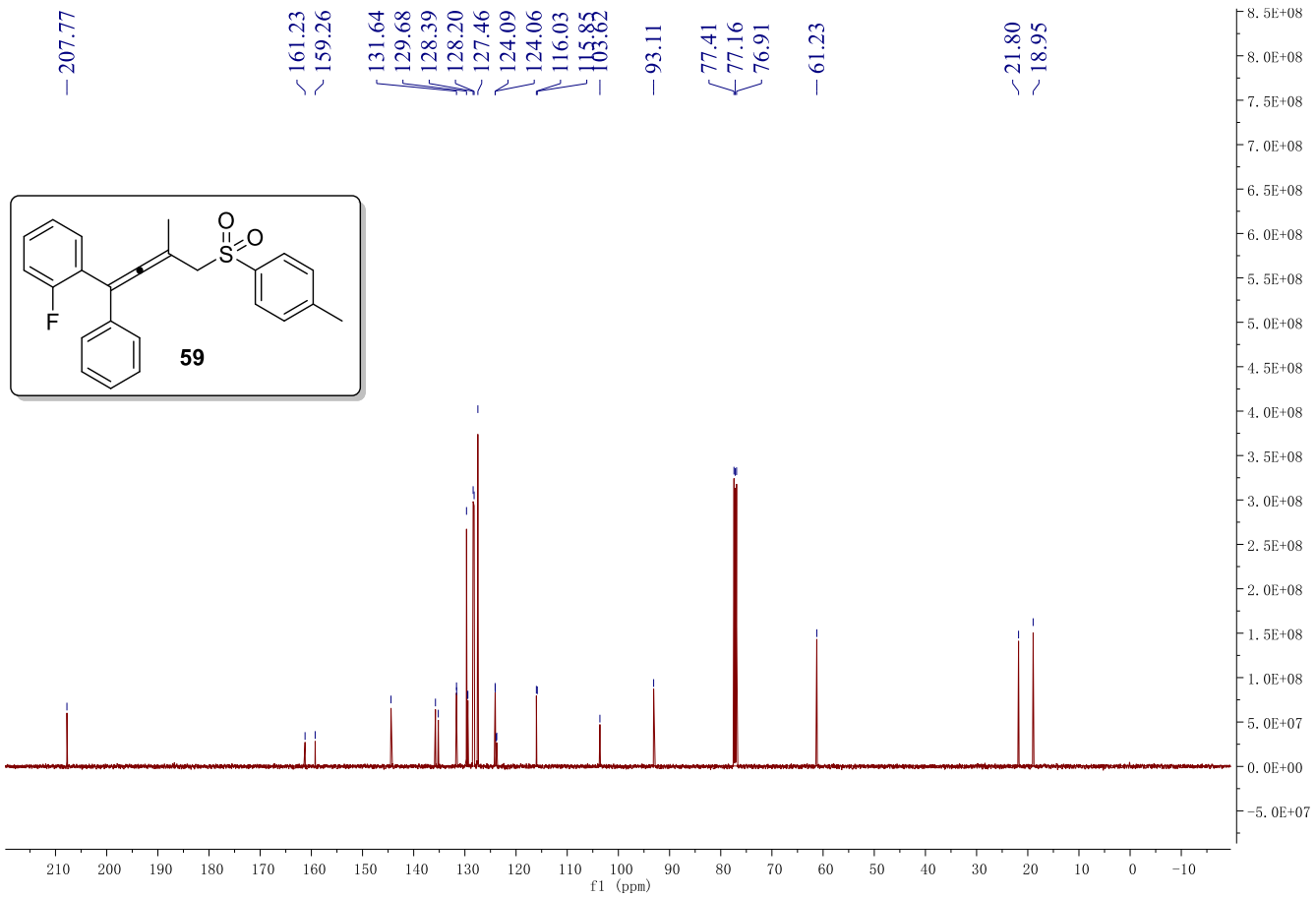
7.26
7.25
7.24
7.24
7.23
7.23
7.10
7.08
7.08
7.07
7.06
7.05
7.03
7.02
7.02
7.02
7.01
7.00
3.98
3.95
3.92
3.89
1.95
1.13
3.06
1.97
3.01
2.25
1.00
1.00
3.01
3.03
f1 (ppm)
59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128.20
127.46
124.09
124.06
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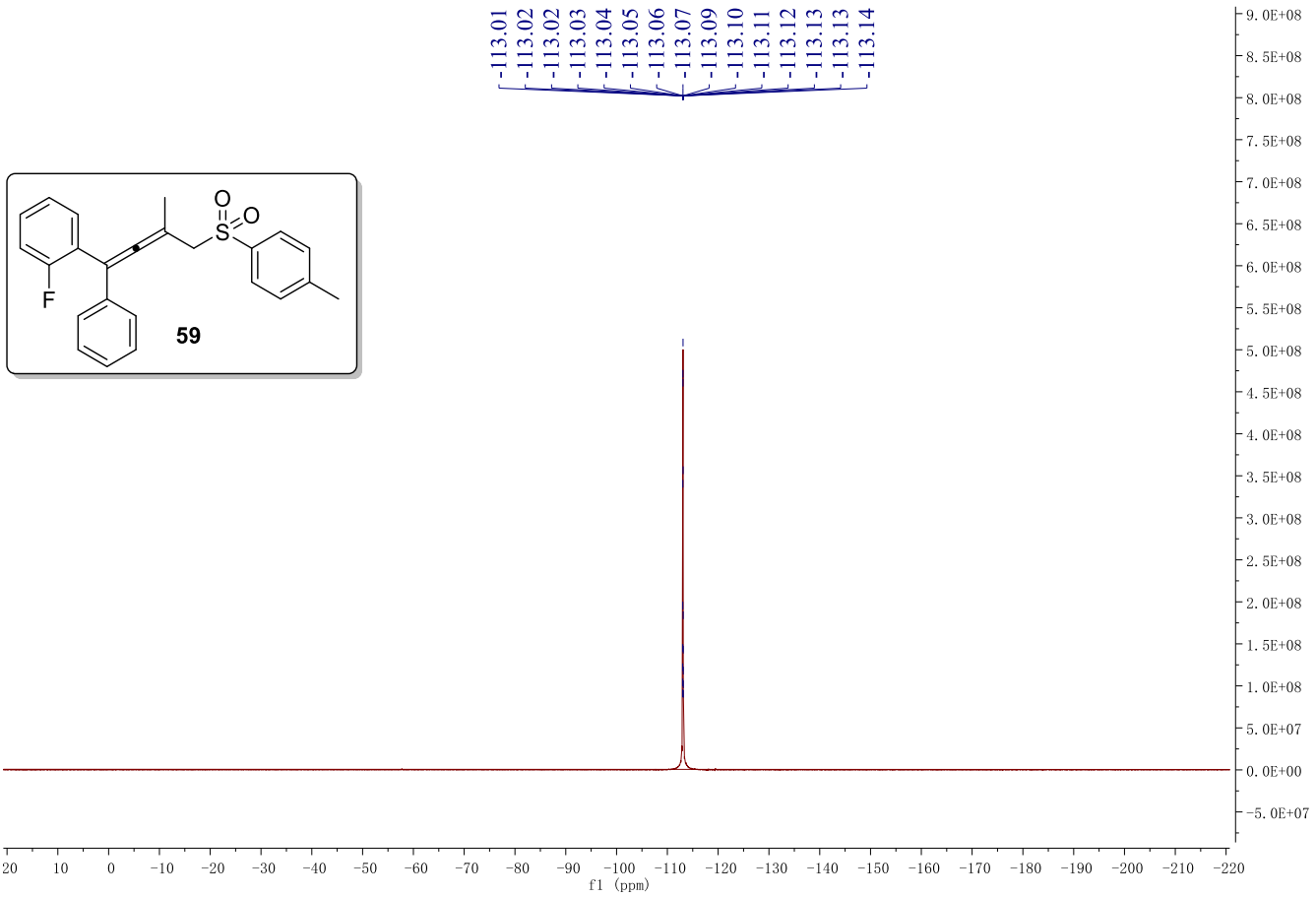
115.62
93.11
77.41
77.16
76.91
61.23
21.80
18.95
f1 (ppm)
59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-113.02
-113.03
-113.04
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-113.06
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-113.09
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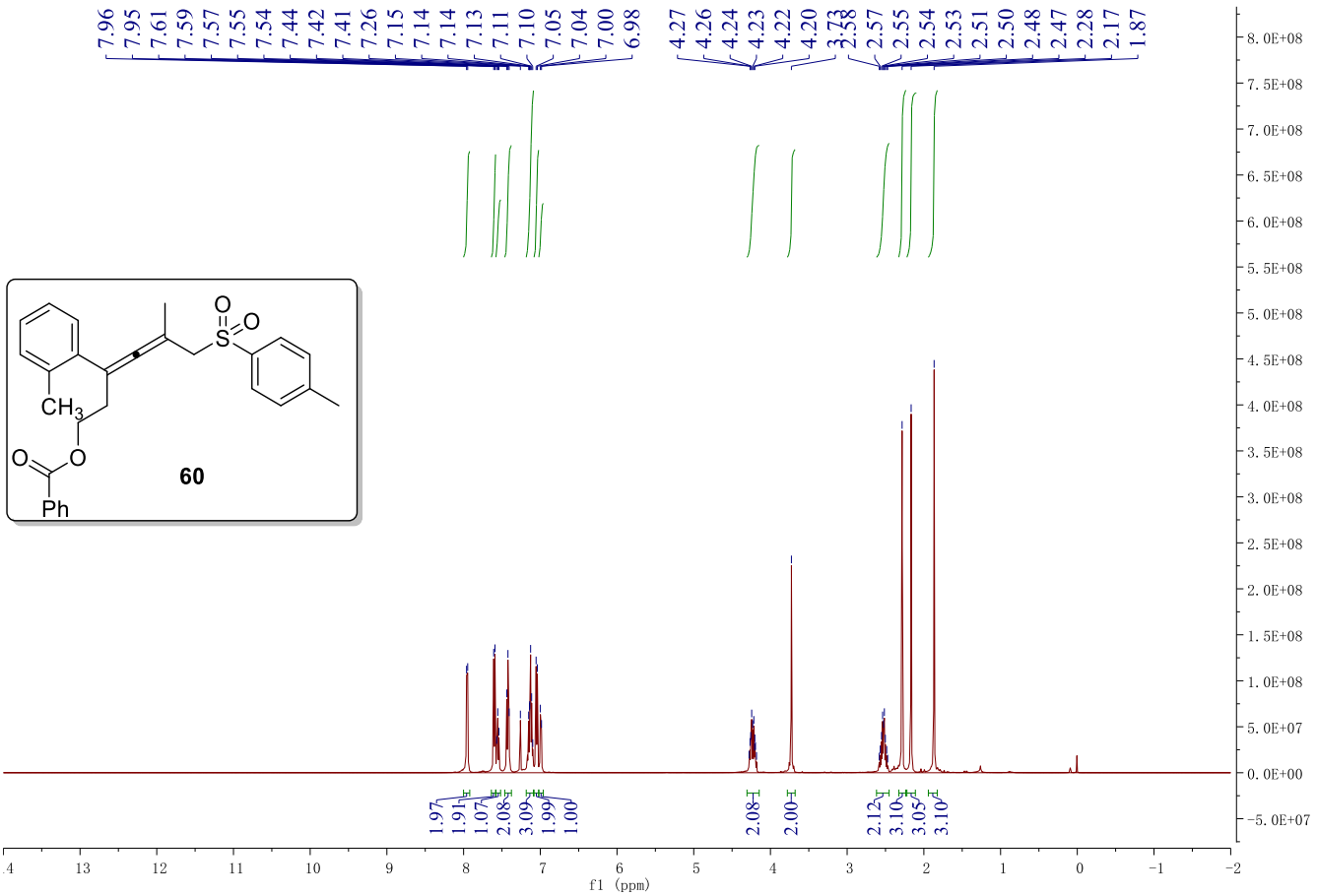
-113.13
-113.13
-113.14
O
O
S
F
59
f1 (ppm)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7.26
7.15
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7.14
7.13
7.11
7.10
7.05
7.04
7.00
6.98
4.27
4.26
4.24
4.23
4.22
4.20
3.73
3.58
2.57
2.55
2.54
2.53
2.51
2.50
2.48
2.47
2.28
2.17
1.87
O
O
S
CH3
O
O
Ph
60
1.97
1.91
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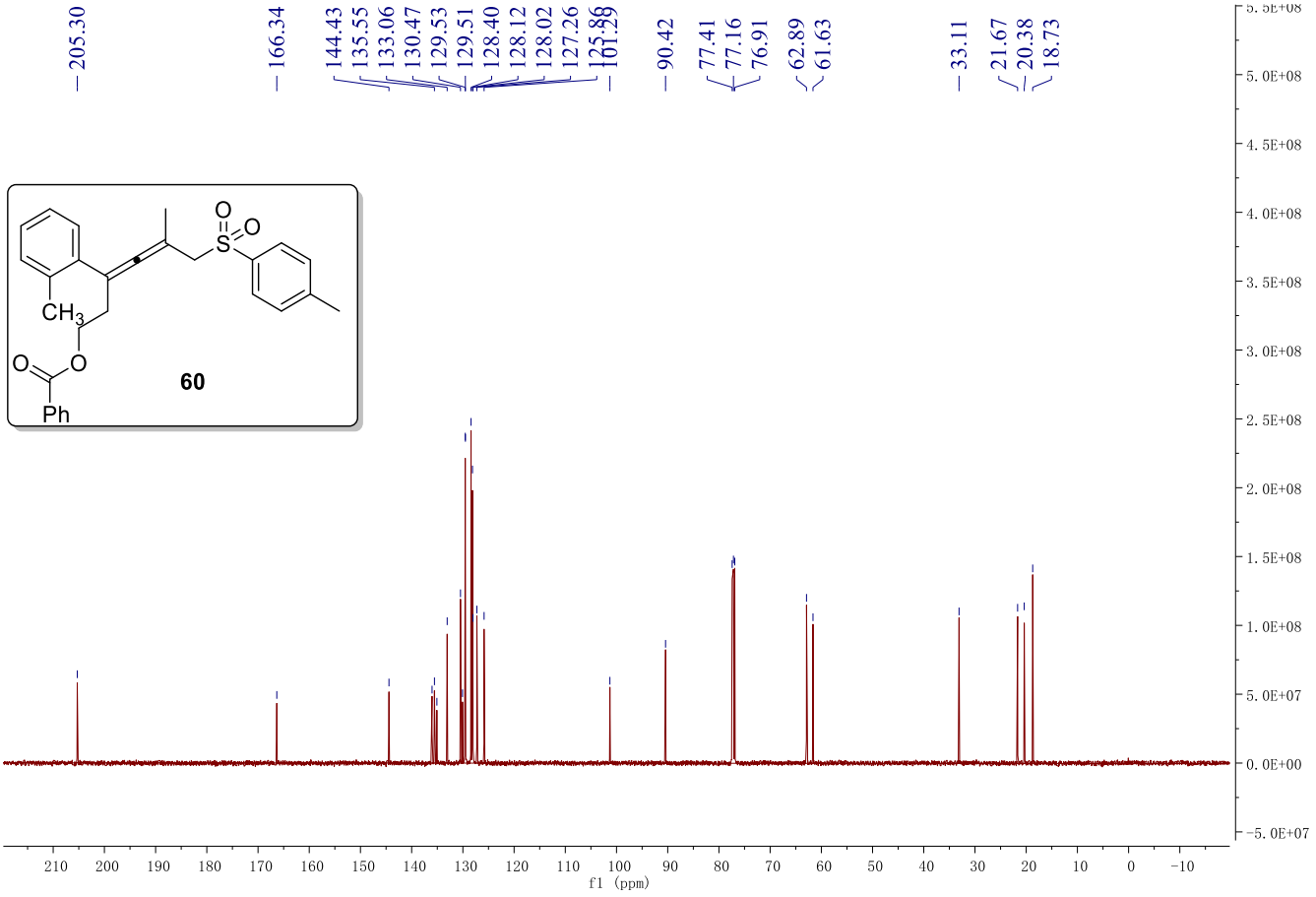
1.99
1.00
2.08
2.00
2.12
3.10
3.05
3.10
f1 (ppm)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128.12
128.02
127.26
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101.29
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76.91
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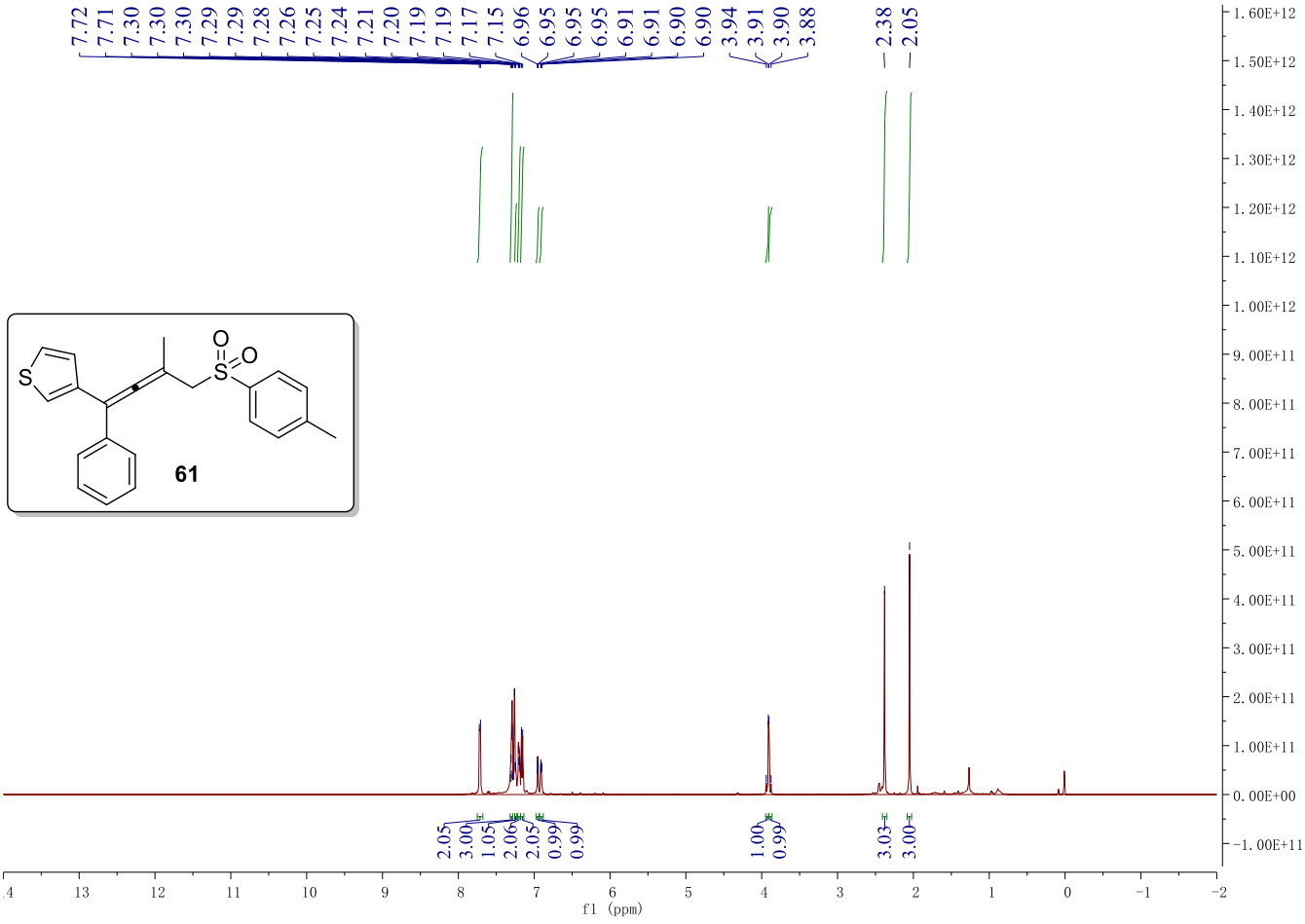
61.63
33.11
21.67
20.38
18.73
60
f1 (ppm)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7.24
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7.19
7.19
7.17
7.15
6.96
6.95
6.95
6.95
6.91
6.91
6.90
6.90
3.94
3.91
3.90
3.88
2.38
2.05
61
2.05
3.00
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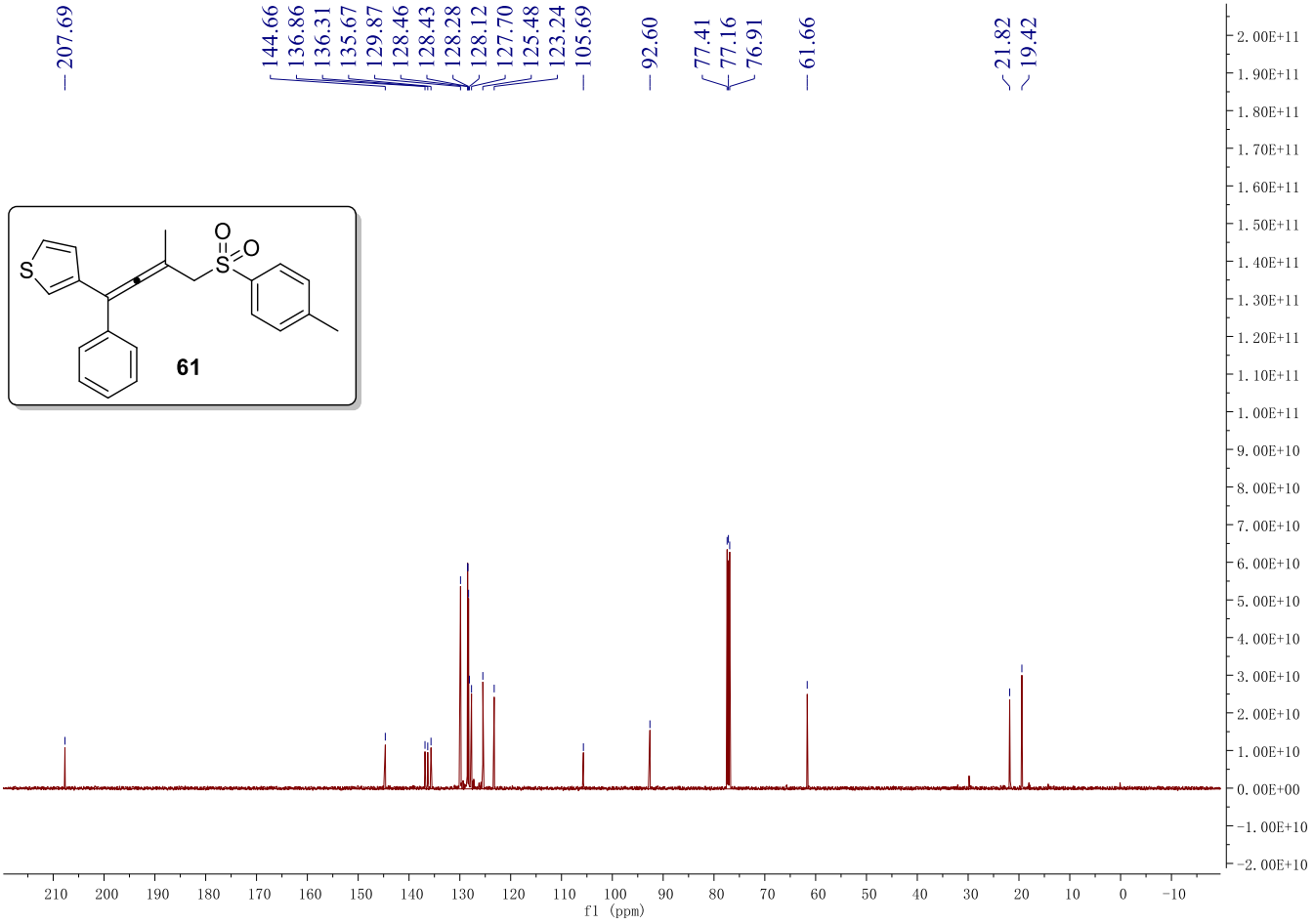
2.06
2.05
0.99
0.99
1.00
0.99
3.03
3.00
f1 (ppm)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77.16
76.91
61.66
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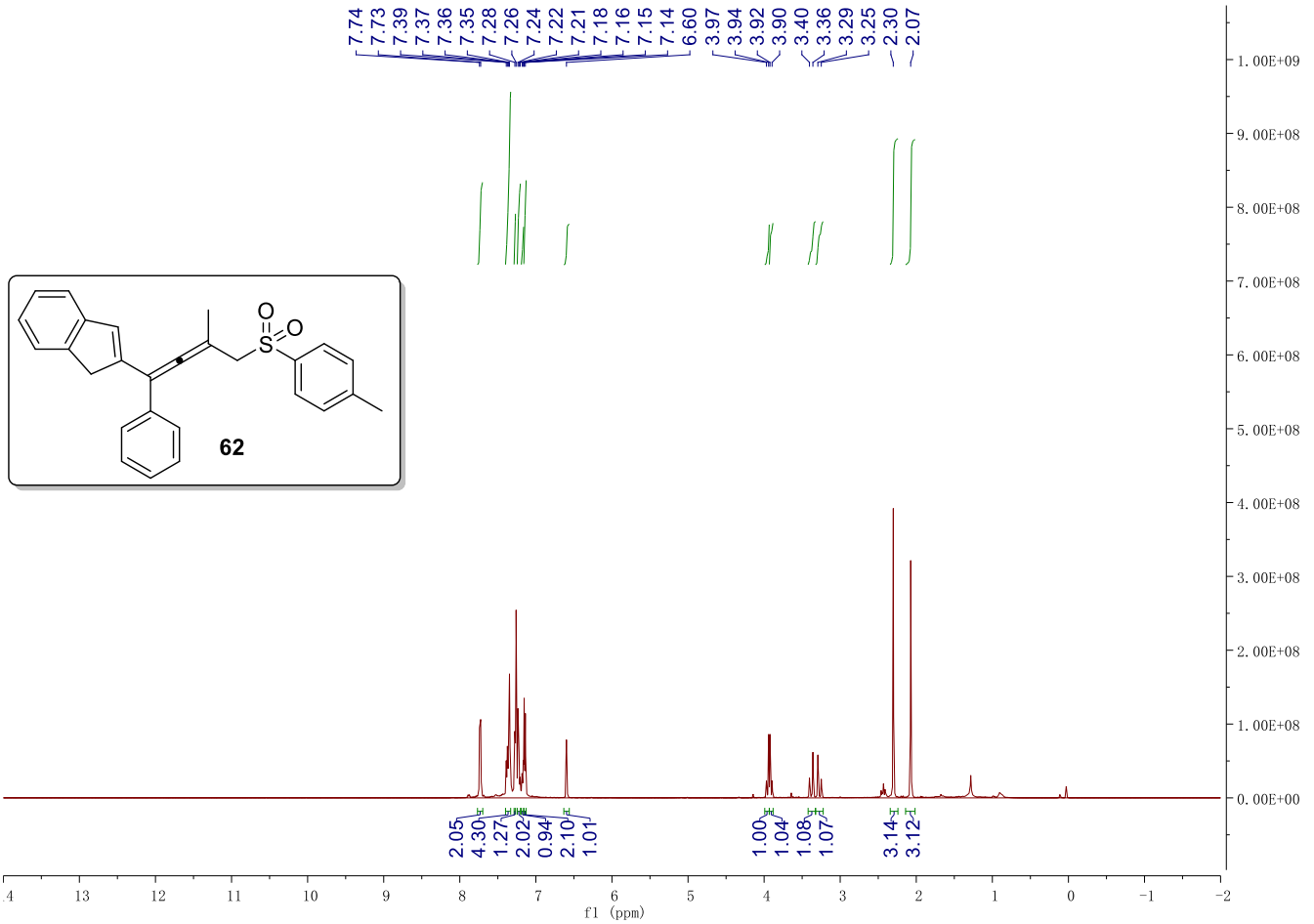
19.42
61
f1 (ppm)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7.24
7.22
7.21
7.18
7.16
7.15
7.14
6.60
3.97
3.94
3.92
3.90
3.40
3.36
3.29
3.25
2.30
2.07
2.05
4.30
1.27
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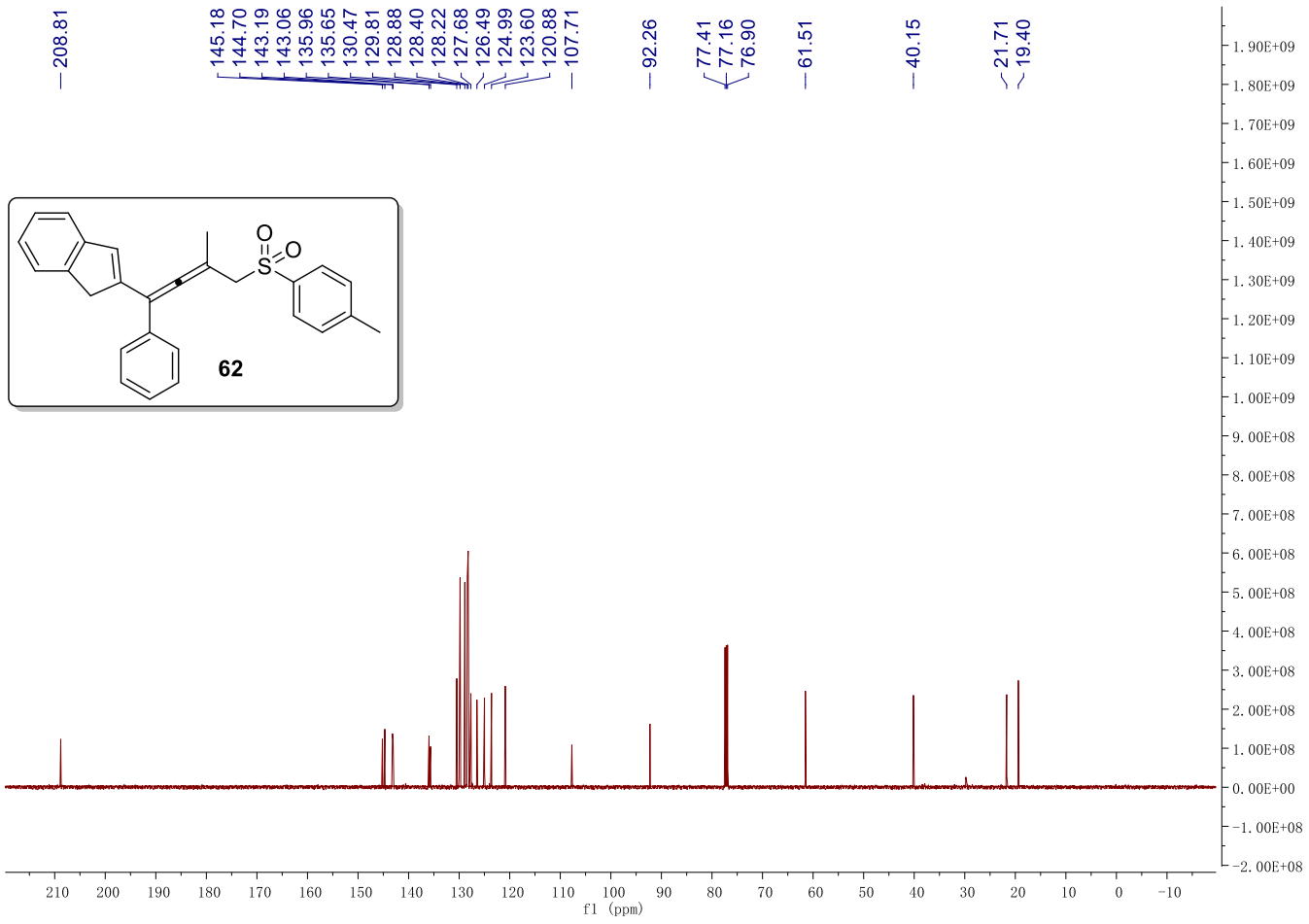
2.10
1.01
1.00
1.04
1.08
1.07
3.14
3.12
62
f1 (ppm)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124.99
123.60
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77.41
77.16
76.90
61.51
40.15
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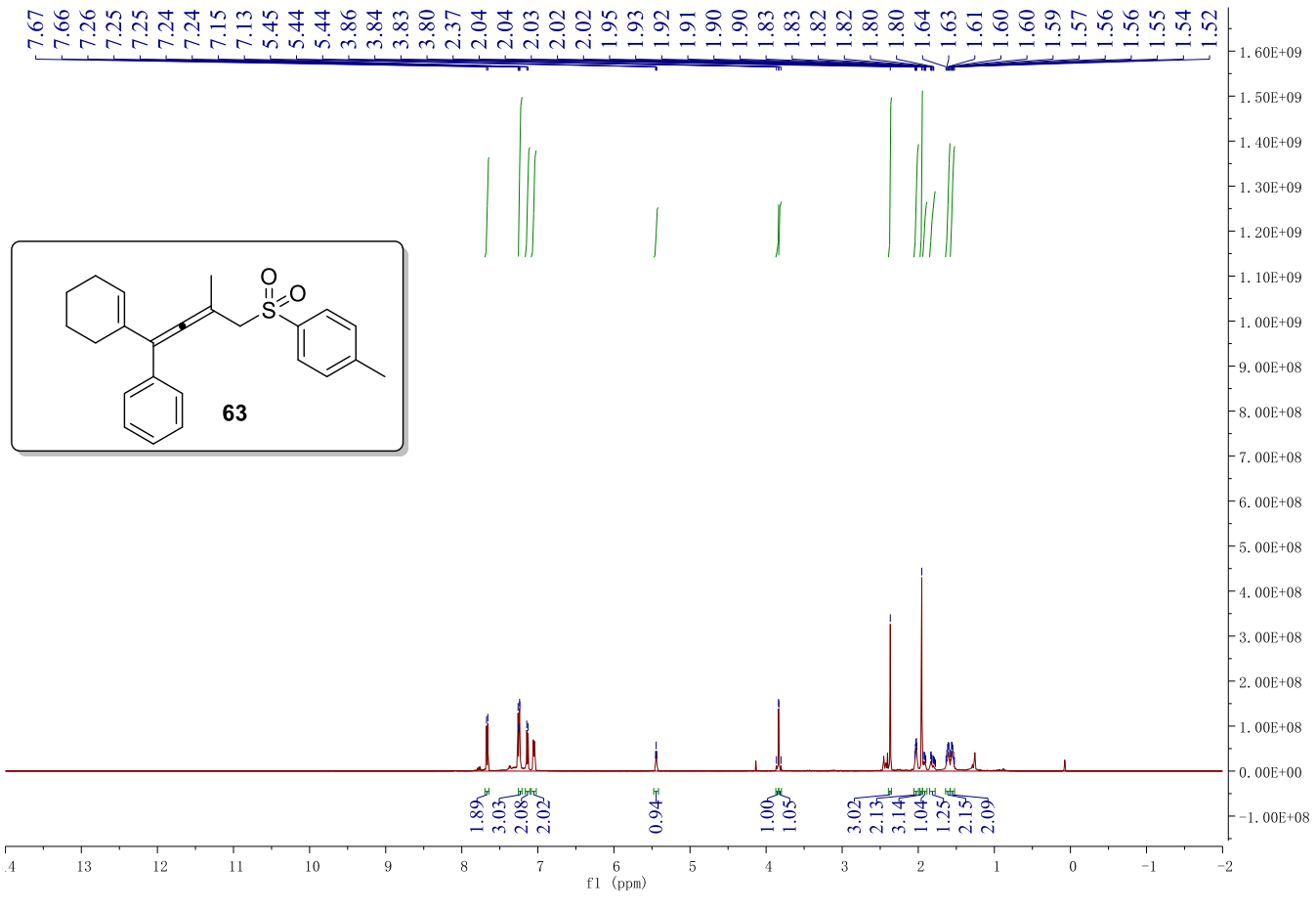
19.40
62
f1 (ppm)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5.44
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3.83
3.80
2.37
2.04
2.04
2.03
2.02
2.02
1.95
1.93
1.92
1.91
1.90
1.90
1.83
1.83
1.82
1.82
1.80
1.80
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1.63
1.61
1.60
1.60
1.59
1.57
1.56
1.56
1.55
1.54
1.52
63
1.89
3.03
2.08
2.02
0.94
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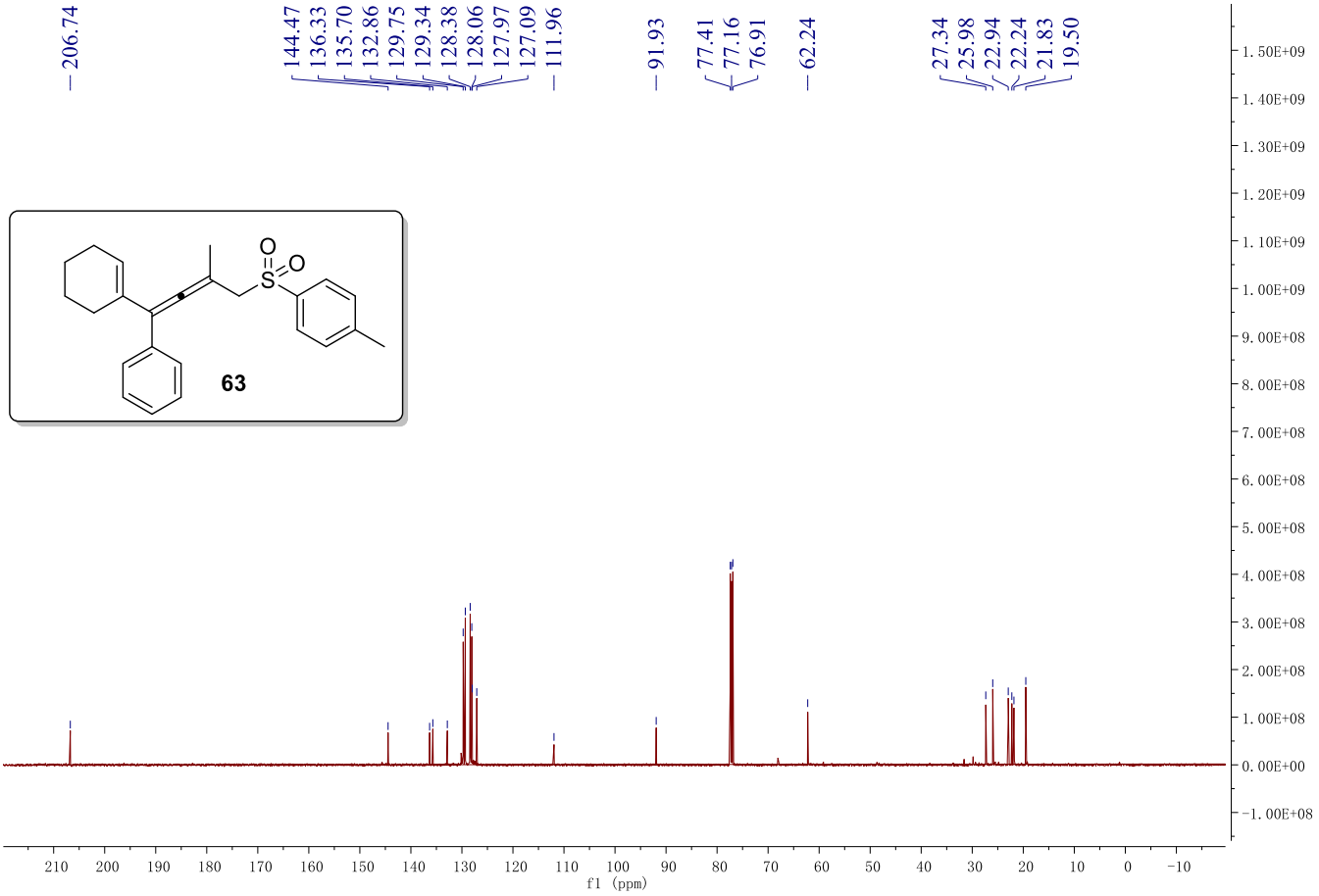
1.05
3.02
2.13
3.14
1.04
1.25
2.15
2.09
f1 (ppm)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127.97
127.09
111.96
91.93
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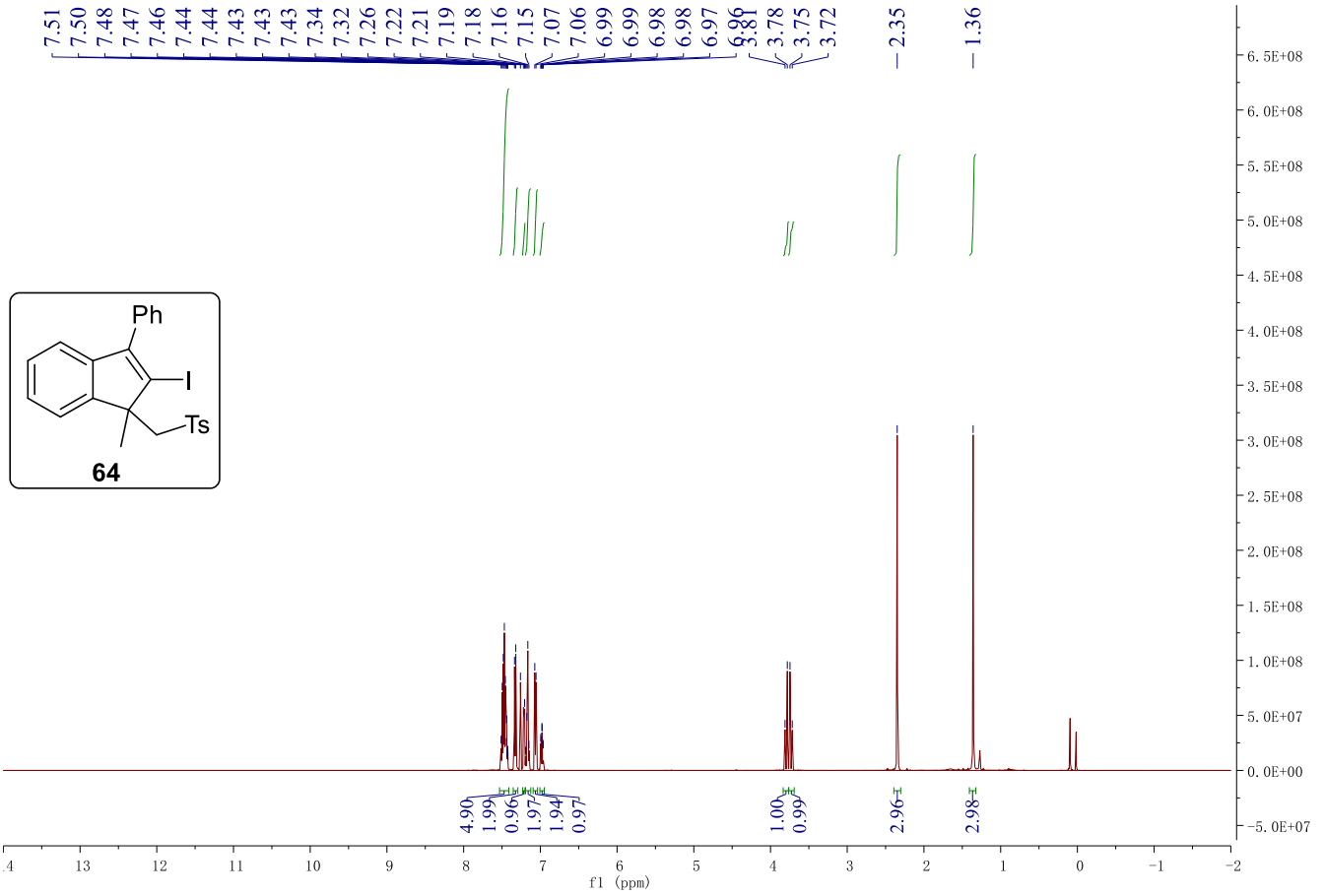
77.16
76.91
62.24
27.34
25.98
22.94
22.24
21.83
19.50
63
f1 (ppm)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7.43
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7.43
7.34
7.32
7.26
7.22
7.21
7.19
7.18
7.16
7.15
7.07
7.06
6.99
6.99
6.98
6.98
6.97
6.96
3.81
3.78
3.75
3.72
2.35
1.36
Ph
I
Ts
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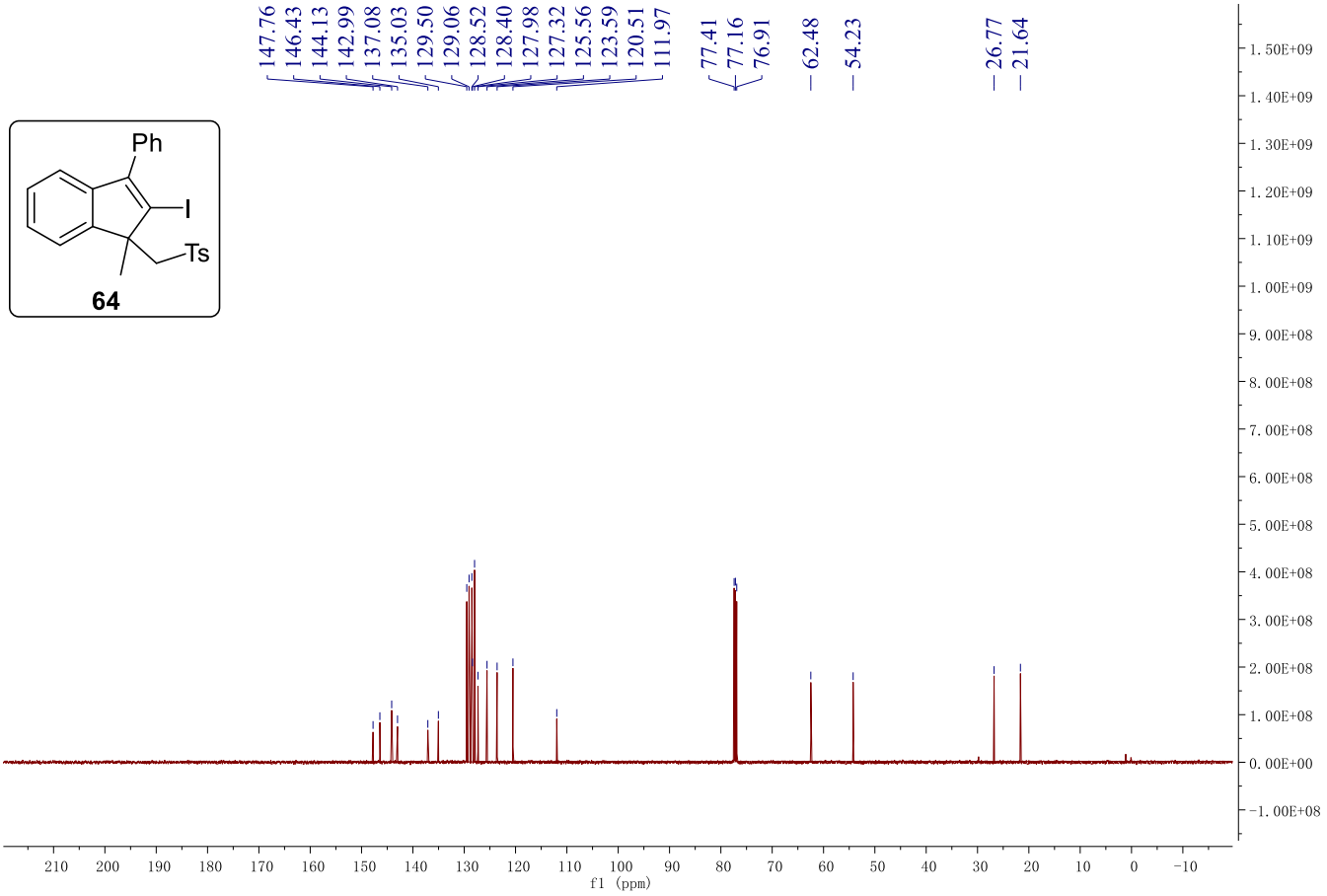
0.96
1.97
1.94
0.97
1.00
0.99
2.96
2.98
f1 (ppm)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127.32
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123.59
120.51
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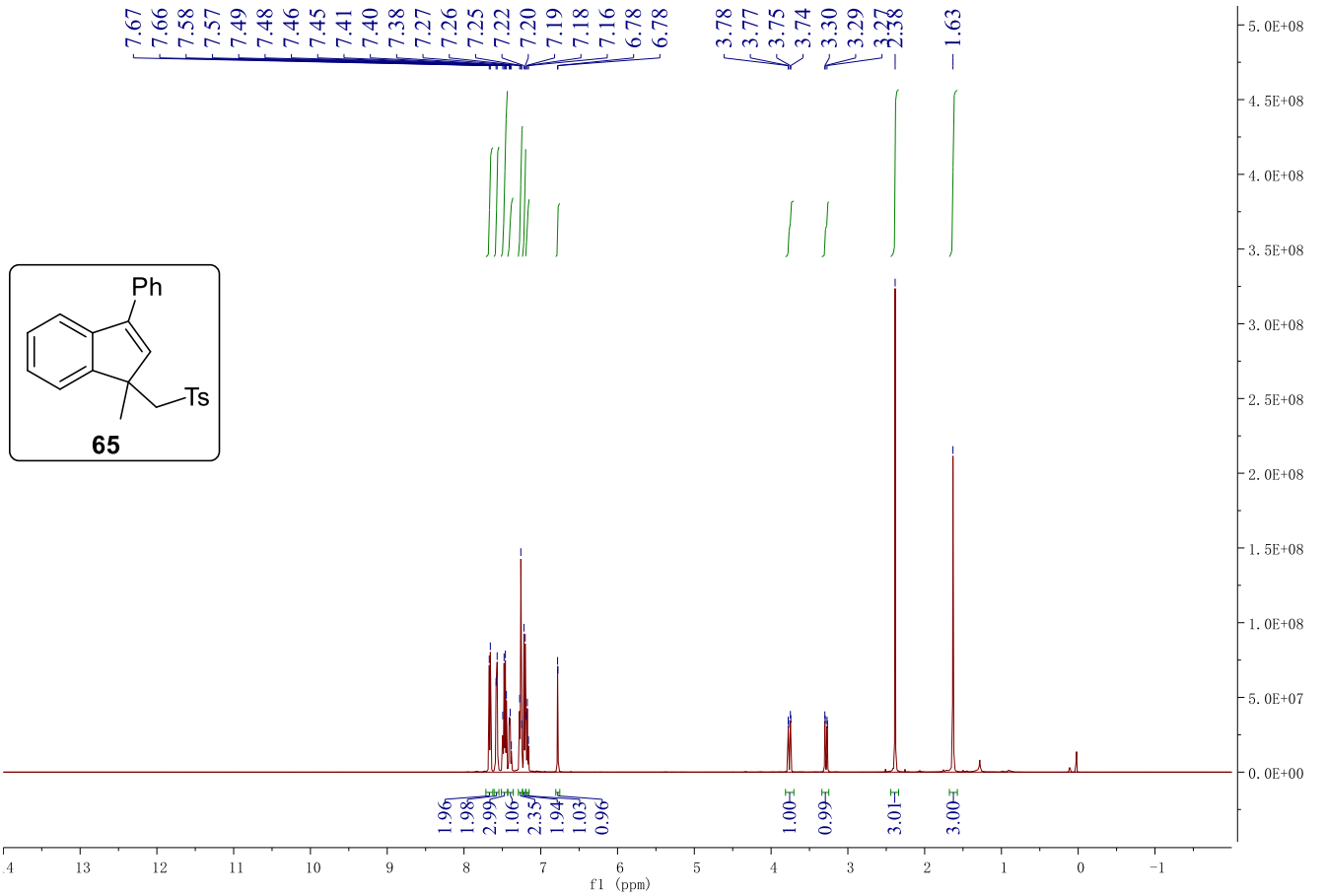
26.77
21.64
Ph
I
Ts
64
f1 (ppm)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7.26
7.25
7.22
7.20
7.19
7.18
7.16
6.78
6.78
3.78
3.77
3.75
3.74
3.30
3.29
3.27
2.38
1.63
Ph
Ts
65
1.96
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2.99
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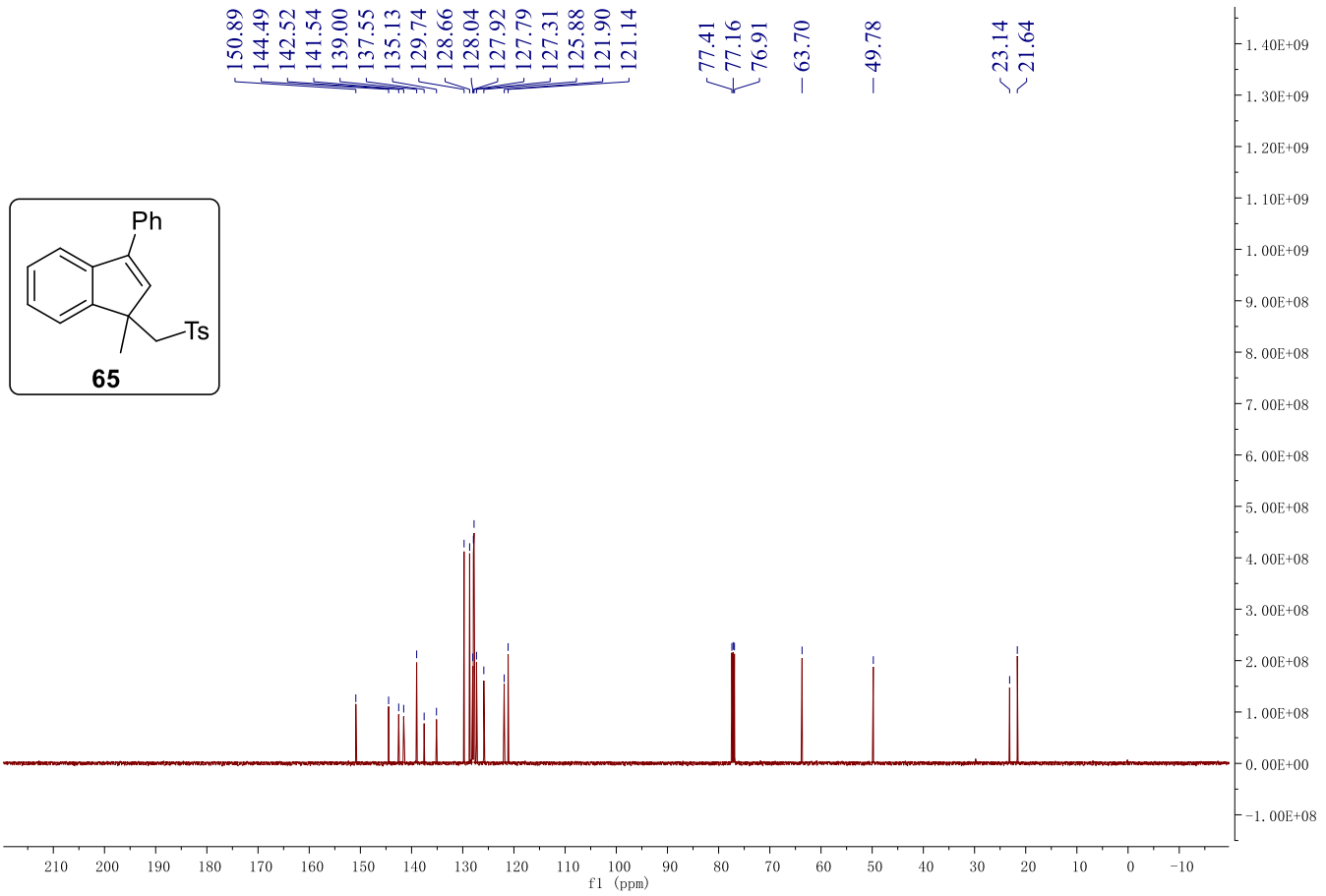
2.35
1.94
1.03
0.96
1.00
0.99
3.01
3.00
f1 (ppm)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127.79
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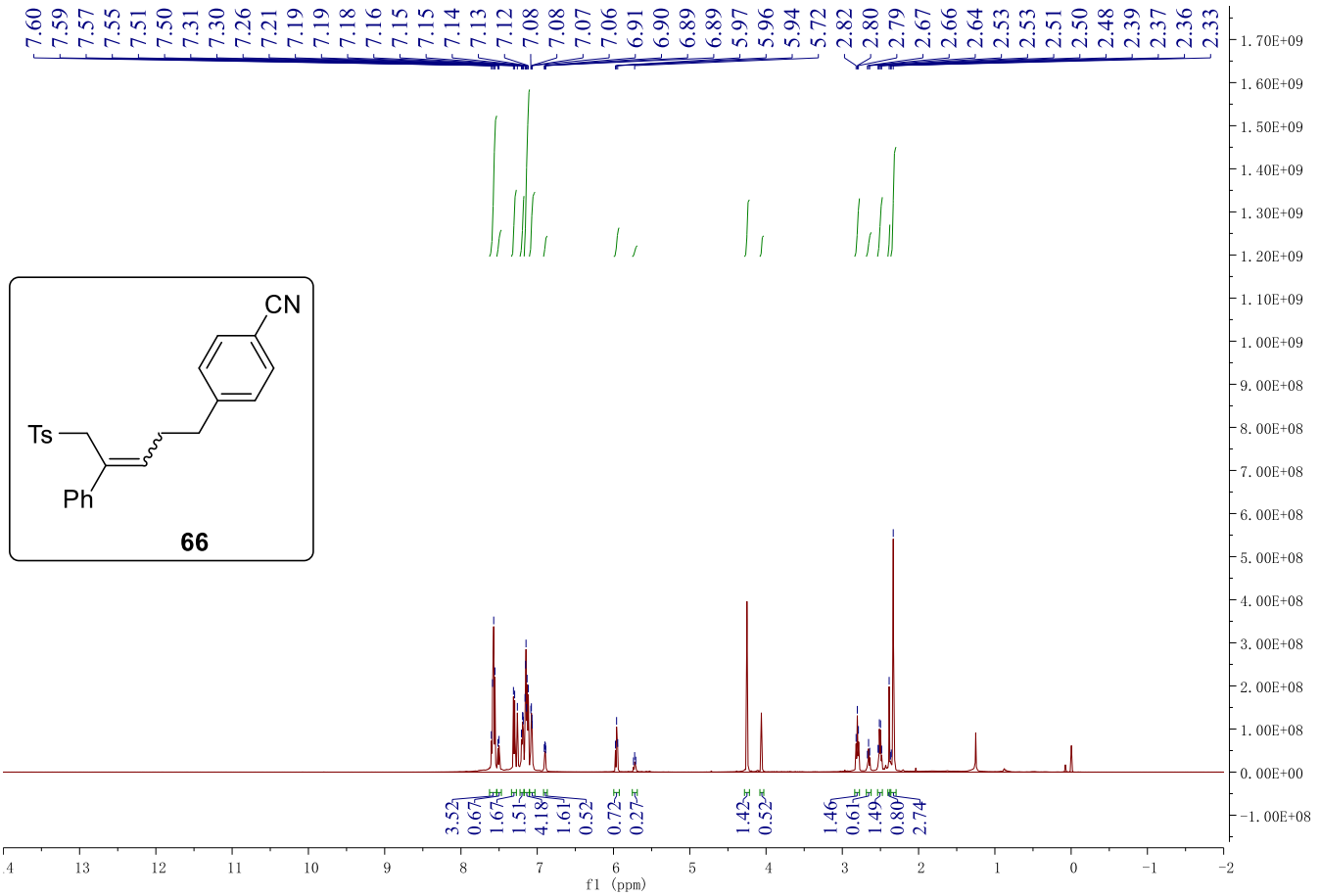
23.14
21.64
Ph
Ts
65
f1 (ppm)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5.94
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2.37
2.36
2.33
CN
Ts
Ph
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1.67
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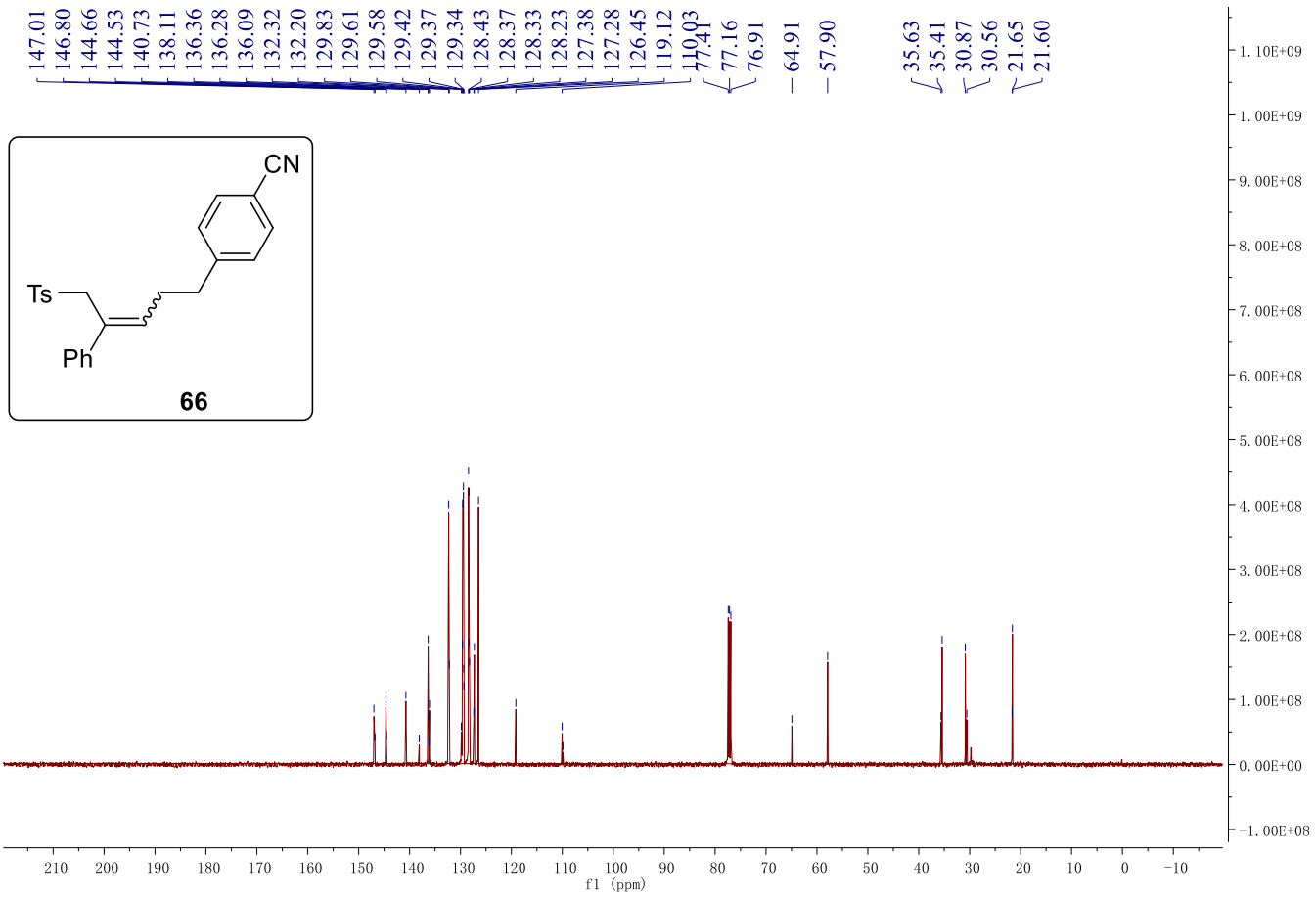
f1 (ppm)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129.34
128.43
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128.33
128.23
127.38
127.28
126.45
119.12
110.03
77.41
77.16
76.91
64.91
57.90
35.63
35.41
30.87
30.56
21.65
21.60
CN
Ts
Ph
66
f1 (ppm)