Supporting information

Visible-Light-Initiated Manganese-Catalyzed Hydrosulfonylation of Alkenes

Chun-Min Li, Xin-Xin Dong, Zhe Wang,* and Bo Zhang*

State Key Laboratory of Natural Medicines, China Pharmaceutical University, 24 Tongjia Xiang, Nanjing 210009, China

E-mail: zb3981444@cpu.edu.cn; wangzhe@cpu.edu.cn

Table of contents

General

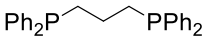
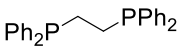
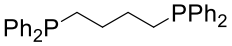
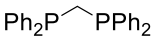
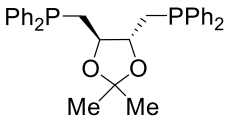
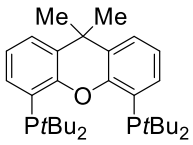
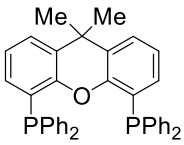
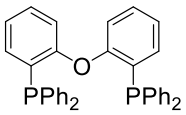
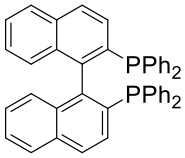
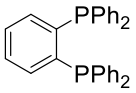
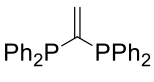
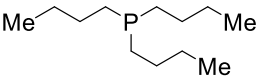
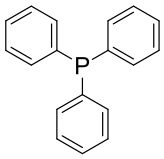
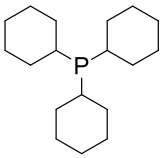
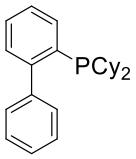
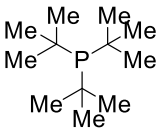
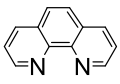
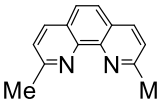
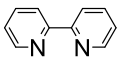
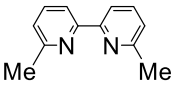
All manipulations were conducted with a standard *Schlenk* tube under a nitrogen atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous decalin, cyclohexane, EtOAc, THF, CH_3CN, and CH_2Cl_2 were purchased from J&K Chemical or Energy Chemical and used as received. These solvents were dried and degassed by commercial suppliers.

Flash column chromatography was carried out on silica gel (200-300 mesh). Thin layer chromatography (TLC) was performed using silica gel 60 F_{254} plates.

^1H NMR spectra were recorded on a *Bruker AV-300 or AV-400* spectrometer at room temperature. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). ^{19}F NMR spectra were obtained by the same NMR spectrometer and using $CFCl_3$ as external standard. Data for ^1H NMR are reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad singlet), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift and multiplicity where appropriate. Mass spectra (MS) were performed on an *Aglient 5977A*. High-Resolution Mass Spectrometry (HRMS) were performed on an *Aglient 6545 Q-TOF*. The yields were determined on a *METTLER TOLEDO ME 104* balance (accuracy: 0.1 mg).

Optimization of reaction conditions

Table S1. Evaluation of ligand[a,b]

 **L1**, 64%	 **L2**, 46%	 **L3**, 60%	 **L4**, 39%
 **L5**, 54%	 **L6**, 25%	 **L7**, 31%	 **L8**, 42%
 **L9**, 32%	 **L10**, 36%	 **L11**, 34%	 **L12**, 45%
 **L13,** 43%	 **L14,** 32%	 **L15,** 40%	 **L16**, 28%
 **L17**, 28%	 **L18**, 24%	 **L19**, 26%	 **L20**, 26%

[a]Reaction conditions: **1** (0.5 mmol), **2** (0.2 mmol), $(Me_3Si)_3SiH$ (0.3 mmol), $Mn_2(CO)_{10}$ (10 mol%), and ligand (20 mol%) in CH_2Cl_2 (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under N_2 for 12 h. [b]Isolated yields.

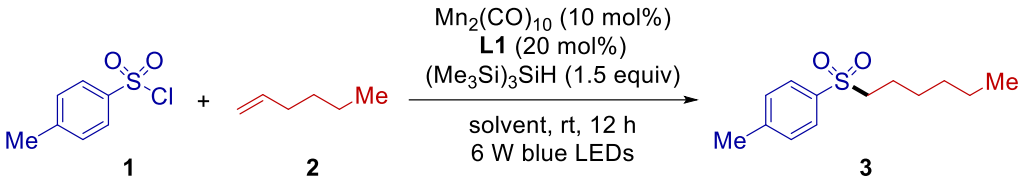
Table S2. Evaluation of H-atom donor[a]

1 **2** **3**

entry	H-atom donor (equiv)	solvent	yield[b] (%)
1	$(Me_3Si)_3SiH$ (1.5)	CH_2Cl_2	64
2	Et_3SiH (1.5)	CH_2Cl_2	trace
3	Ph_3SiH (1.5)	CH_2Cl_2	trace
4	$(iPr)_3SiH$ (1.5)	CH_2Cl_2	trace
5	$(EtO)_3SiH$ (1.5)	CH_2Cl_2	trace
6	$(MeO)_3SiH$ (1.5)	CH_2Cl_2	trace
7	Hantzsch ester (1.5)	CH_2Cl_2	0
8	nBu_3SnH (1.5)	CH_2Cl_2	0

[a]Reaction conditions: **1** (0.5 mmol), **2** (0.2 mmol), H-atom donor (0.3 mmol), $Mn_2(CO)_{10}$ (10 mol%), and **L1** (20 mol%) in CH_2Cl_2 (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under N_2 for 12 h. [b]Isolated yields.

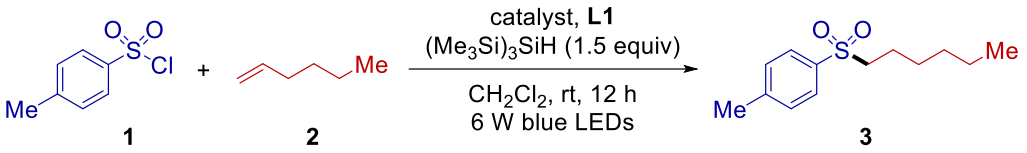
Table S3. Evaluation of solvent[a]



entry	H-atom donor (equiv)	solvent	yield[b] (%)
1	$(Me_3Si)_3SiH$ (1.5)	CH_2Cl_2	64
2	$(Me_3Si)_3SiH$ (1.5)	decalin	trace
3	$(Me_3Si)_3SiH$ (1.5)	cyclohexane	trace
4	$(Me_3Si)_3SiH$ (1.5)	EtOAc	30
5	$(Me_3Si)_3SiH$ (1.5)	THF	50
6	$(Me_3Si)_3SiH$ (1.5)	CH_3CN	43

[a]Reaction conditions: **1** (0.5 mmol), **2** (0.2 mmol), $(Me_3Si)_3SiH$ (0.3 mmol), $Mn_2(CO)_{10}$ (10 mol%), and **L1** (20 mol%) in solvent (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under N_2 for 12 h. [b]Isolated yields.

Table S4. Evaluation of different reaction parameters[a]



entry	catalyst (mol%)	ligand (mol%)	H-atom donor (equiv)	**1** (equiv)	yield[b] (%)
1	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	3.0	62
2	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	2.5	64
3	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	2.0	66
4	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	1.5	72
5	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	1.2	55
6	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.2)	1.5	65
7	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (2.0)	1.5	62
8	$Mn_2(CO)_{10}$ (5)	**L1** (10)	$(Me_3Si)_3SiH$ (1.5)	1.5	46
9	$Mn_2(CO)_{10}$ (15)	**L1** (30)	$(Me_3Si)_3SiH$ (1.5)	1.5	52
10	$Mn(CO)_5Br$ (10)	**L1** (10)	$(Me_3Si)_3SiH$ (1.5)	1.5	51
11[c]	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	1.5	55

[a]Reaction conditions: **1**, **2** (0.2 mmol), $(Me_3Si)_3SiH$, $Mn_2(CO)_{10}$, and **L1** in CH_2Cl_2 (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under N_2 for 12 h. [b]Isolated yields. [c]The reaction was conducted under the irradiation of 6 W 390 nm LED source.

Table S5. Control experiments[a]

entry	catalyst (mol%)	ligand (mol%)	H-atom donor (equiv)	yield[b] (%)
1[c]	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	0
2	$Mn_2(CO)_{10}$ (10)	none	$(Me_3Si)_3SiH$ (1.5)	19
3	$Mn_2(CO)_{10}$ (10)	**L1** (20)	none	0
4	none	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	23
5	none	none	$(Me_3Si)_3SiH$ (1.5)	0
6[d]	$Mn_2(CO)_{10}$ (10)	**L1** (20)	$(Me_3Si)_3SiH$ (1.5)	trace

[a]Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), $(Me_3Si)_3SiH$ (0.3 mmol), $Mn_2(CO)_{10}$ (10 mol%), and **L1** (20 mol%) in CH_2Cl_2 (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under N_2 for 12 h. [b]Isolated yields. [c]The reaction was conducted in the dark. [d]The reaction was conducted under air.

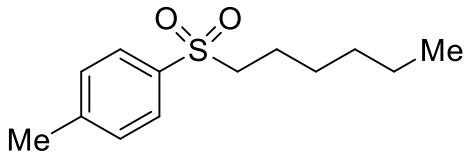
General procedure for hydrosulfonylation of alkenes (GP):

Alkene (0.2 mmol, 1.0 equiv), sulfonyl chloride (0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product.

Reaction setup (4x6 W blue LEDs)

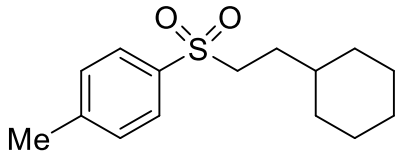
Physical data of the compounds

1-(Hexylsulfonyl)-4-methylbenzene (3)[1]



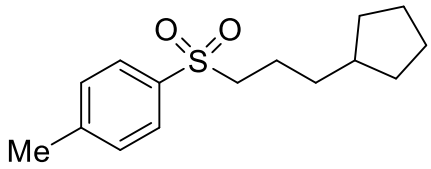
According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.5 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.1 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **3** as pale yellow oil (34.7 mg, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74-7.67 (m, 2H), 7.32-7.24 (m, 2H), 3.00-2.96 (m, 2H), 2.37 (s, 3H), 1.65-1.57 (m, 2H), 1.30-1.23 (m, 2H), 1.21-1.14 (m, 4H), 0.77 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 136.2, 129.8, 128.0, 56.3, 31.1, 27.8, 22.6, 22.2, 21.5, 13.8. **MS** (ESI) m/z 241.2 $[M+H]^+$.

1-((2-Cyclohexylethyl)sulfonyl)-4-methylbenzene (4)[2]



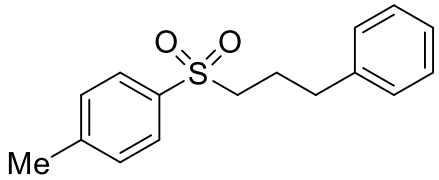
According to **GP** with vinylcyclohexane (28 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.4 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **4** as white solid (43.4 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H), 7.38-7.32 (m, 2H), 3.09-3.05 (m, 2H), 2.45 (s, 3H), 1.69-1.57 (m, 7H), 1.32-1.07 (m, 4H), 0.90-0.81 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.5, 136.2, 129.8, 128.0, 54.4, 36.6, 32.8, 29.7, 26.2, 26.0, 21.6. **MS** (ESI) m/z 267.1 $[M+H]^+$.

1-((3-cyclopentylpropyl)sulfonyl)-4-methylbenzene (5)



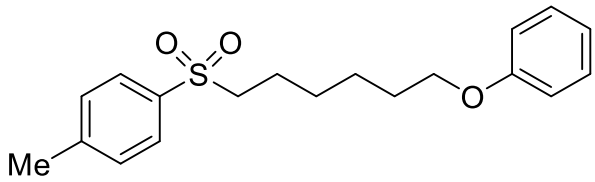
According to **GP** with allylcyclopentane (28 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.4 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.6 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **5** as pale yellow oil (37.3 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 2H), 7.39-7.33 (m, 2H), 3.08-3.04 (m, 2H), 2.45 (s, 3H), 1.75-1.67 (m, 5H), 1.59-1.45 (m, 4H), 1.37-1.32 (m, 2H), 1.07-0.96 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.5, 136.2, 129.8, 128.0, 56.6, 39.6, 34.6, 32.4, 25.0, 21.9, 21.6. **HRMS** (ESI) calculated for $C_{15}H_{22}NaO_2S$ $[M+Na]^+$ m/z 289.1233, found 289.1231.

1-Methyl-4-((3-phenylpropyl)sulfonyl)benzene (6)[3]



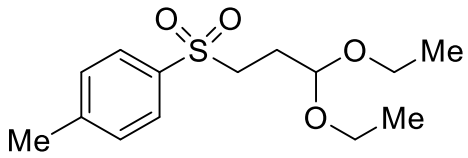
According to **GP** with allylbenzene (27 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.6 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **6** as yellow oil (39.0 mg, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.80-7.71 (m, 2H), 7.38-7.31 (m, 2H), 7.35-7.17 (m, 3H), 7.13-7.06 (m, 2H), 3.08-3.03 (m, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 2.08-1.98 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.6, 139.9, 136.1, 129.8, 128.5, 128.3, 128.0, 126.3, 55.5, 34.0, 24.2, 21.6. **MS** (ESI) m/z 275.1 $[M+H]^+$.

1-Methyl-4-((4-phenoxybutyl)sulfonyl)benzene (7)



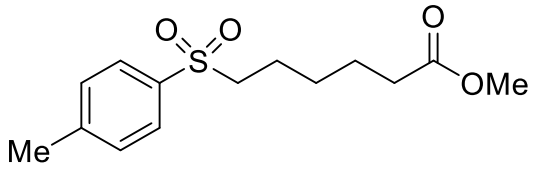
According to **GP** with (but-3-en-1-yloxy)benzene (35.6 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.4 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **7** as pale yellow oil (34.6 mg, 52%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H), 7.38-7.31 (m, 2H), 7.29-7.23 (m, 2H), 6.94-6.89 (m, 1H), 6.88-6.81 (m, 2H), 3.90 (t, *J* = 6.3 Hz, 2H), 3.09-3.04 (m, 2H), 2.43 (s, 3H), 1.77-1.71 (m, 4H), 1.44-1.41 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.8, 144.5, 136.0, 129.8, 129.3, 127.9, 120.4, 114.3, 67.2, 56.1, 28.8, 27.9, 25.5, 22.6, 21.5. **HRMS** (ESI) calculated for $C_{19}H_{24}NaO_3S$ $[M+Na]^+$ m/z 355.1338, found 355.1362.

1-((3,3-Diethoxypropyl)sulfonyl)-4-methylbenzene (8)



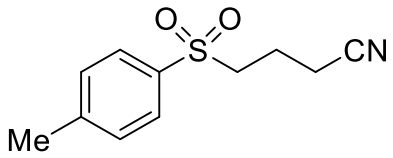
According to **GP** with 3,3-diethoxyprop-1-ene (31 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.8 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **8** as pale yellow oil (34.0 mg, 60%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.83-7.74 (m, 2H), 7.41-7.30 (m, 2H), 4.54 (t, *J* = 5.3 Hz, 1H), 3.65-3.55 (m, 2H), 3.50-3.39 (m, 2H), 3.20-3.15 (m, 2H), 2.45 (s, 3H), 2.03-1.96 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.5, 135.8, 129.7, 127.8, 100.5, 61.8, 51.6, 27.1, 21.4, 15.0. **HRMS** (ESI) calculated for $C_{14}H_{22}NaO_4S$ $[M+Na]^+$ m/z 309.1131, found 309.1131.

Methyl 6-tosylhexanoate (9)



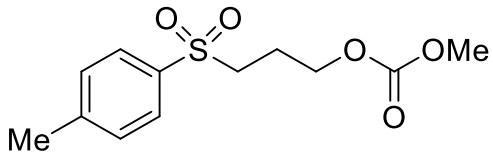
According to **GP** with methyl hex-5-enoate (28 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.5 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.5 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **9** as yellow oil (45.7 mg, 80%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H), 7.41-7.33 (m, 2H), 3.65 (s, 3H), 3.09-3.04 (m, 2H), 2.46 (s, 3H), 2.28 (t, *J* = 7.3 Hz, 2H), 1.77-1.65 (m, 2H), 1.62-1.55 (m, 2H), 1.45-1.34 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.6, 144.6, 136.0, 129.8, 128.0, 56.0, 51.5, 33.4, 27.6, 24.2, 22.4, 21.5. **HRMS** (ESI) calculated for $C_{14}H_{20}NaO_4S$ $[M+Na]^+$ m/z 307.0975, found 307.0971.

4-Tosylbutanenitrile (10)[4]



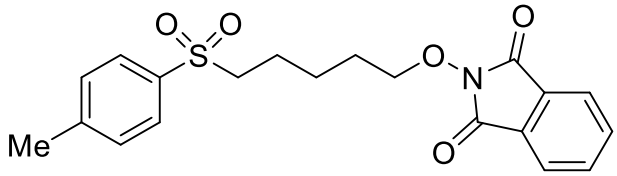
According to **GP** with but-3-enenitrile (16 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (115.2 mg, 0.6 mmol, 3.0 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (17.0 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The reaction was conducted for 24 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **10** as yellow oil (17.9 mg, 40%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 2H), 7.42-7.36 (m, 2H), 3.21 (t, *J* = 7.4 Hz, 2H), 2.57 (t, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 2.14-2.07 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.1, 135.2, 129.9, 127.7, 118.1, 54.0, 21.4, 18.9, 15.8. **MS** (ESI) m/z 224.3 $[M+H]^+$.

Methyl (3-tosylpropyl) carbonate (11)



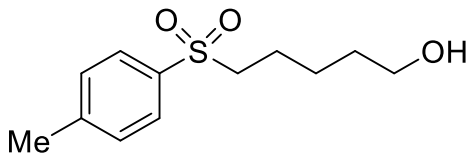
According to **GP** with allyl methyl carbonate (23 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (114.9 mg, 0.6 mmol, 3.0 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (17.1 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The reaction was conducted for 24 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **11** as white solid (28.4 mg, 50%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82-7.75 (m, 2H), 7.41-7.34 (m, 2H), 4.20 (t, *J* = 6.1 Hz, 2H), 3.77 (s, 3H), 3.21-3.15 (m, 2H), 2.46 (s, 3H), 2.15-2.05 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.3, 144.9, 135.7, 130.0, 128.0, 65.6, 54.9, 52.9, 22.5, 21.6. **HRMS** (ESI) calculated for $C_{12}H_{16}NaO_5S$ $[M+Na]^+$ m/z 295.0611, found 295.0609.

2-(Pent-4-en-1-yloxy)isoindoline-1,3-dione (12)



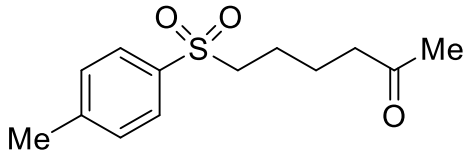
According to **GP** with 2-(pent-4-en-1-yloxy)isoindoline-1,3-dione (46.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (115.7 mg, 0.6 mmol, 3.0 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The reaction was conducted for 24 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **12** as white solid (60.6 mg, 80%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.84-7.74 (m, 6H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.16 (t, *J* = 6.1 Hz, 2H), 3.15-3.10 (m, 2H), 2.44 (s, 3H), 1.85-1.72 (m, 4H), 1.67-1.57 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5, 144.5, 136.0, 134.5, 129.8, 128.8, 128.0, 123.4, 77.8, 56.0, 27.5, 24.4, 22.4, 21.5. **HRMS** (ESI) calculated for $C_{20}H_{21}NNaO_5S$ $[M+Na]^+$ m/z 410.1033, found 410.1034.

5-Tosylpentan-1-ol (13)



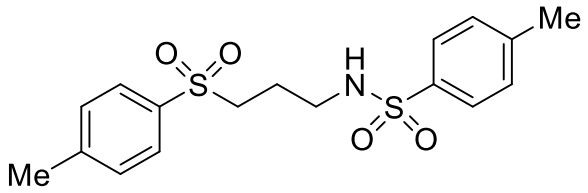
According to **GP** with pent-4-en-1-ol (21 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.8 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.1 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **13** as white solid (27.4 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 3.57 (t, *J* = 6.2 Hz, 2H), 3.09-3.05 (m, 2H), 2.45 (s, 3H), 2.18 (brs, 1H), 1.76-1.68 (m, 2H), 1.55-1.49 (m, 2H), 1.47-1.39 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.6, 136.0, 129.8, 128.0, 62.1, 56.2, 31.9, 24.5, 22.4, 21.6. **HRMS** (ESI) calculated for $C_{12}H_{18}NaO_3S$ $[M+Na]^+$ m/z 265.0869, found 265.0864.

6-Tosylhexan-2-one (14)



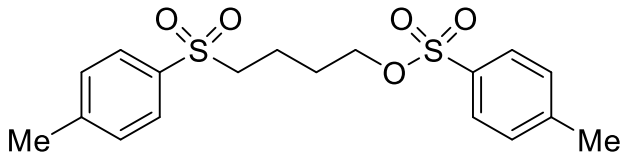
According to **GP** with hex-5-en-2-one (23 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (115.1 mg, 0.6 mmol, 3.0 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.6 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The reaction was conducted for 24 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **14** as pale yellow oil (35.6 mg, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.72 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.10-3.06 (m, 2H), 2.48-2.40 (m, 2H), 2.45 (s, 3H), 2.11 (s, 3H), 1.73-1.60 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.5, 144.5, 135.9, 129.7, 127.8, 55.8, 42.5, 29.7, 22.1, 22.0, 21.4. **HRMS** (ESI) calculated for $C_{13}H_{18}NaO_3S$ $[M+H]^+$ m/z 277.0869, found 277.0864.

4-Methyl-*N*-(3-tosylpropyl)benzenesulfonamide (15)



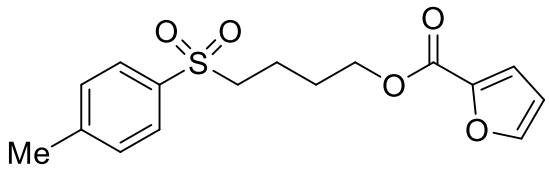
According to **GP** with *N*-allyl-4-methylbenzenesulfonamide (42.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **15** as white solid (46.3 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.73 (m, 2H), 7.72-7.67 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.85 (t, *J* = 6.5 Hz, 1H), 3.16-3.12 (m, 2H), 3.10-3.05 (m, 2H), 2.46 (s, 3H), 2.43 (s, 3H), 1.99-1.92 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 143.6, 136.6, 135.9, 130.0, 129.8, 128.0, 127.0, 53.2, 41.4, 23.1, 21.6, 21.5. **HRMS** (ESI) calculated for $C_{17}H_{22}NO_4S_2$ $[M+H]^+$ m/z 368.0985, found 368.0980.

4-Tosylbutyl 4-methylbenzenesulfonate (16)



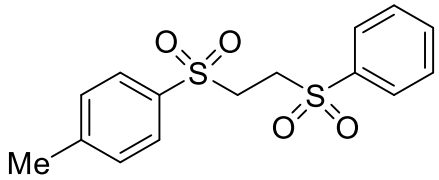
According to **GP** with but-3-en-1-yl 4-methylbenzenesulfonate (45.7 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.4 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.6 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **16** as white solid (57.2 mg, 75%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.81-7.75 (m, 2H), 7.74-7.70 (m, 2H), 7.41-7.36 (m, 2H), 7.35-7.31 (m, 2H), 4.00 (t, *J* = 7.4 Hz, 2H), 3.06-3.00 (m, 2H), 2.46 (s, 6H), 1.78-1.74 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 144.8, 135.9, 132.7, 130.0, 129.9, 128.0, 127.8, 69.3, 55.3, 27.4, 21.62, 31.61, 19.2. **HRMS** (ESI) calculated for $C_{18}H_{26}NO_5S_2$ $[M+NH_4]^+$ m/z 400.1247, found 400.1238.

4-Tosylbutyl furan-2-carboxylate (17)



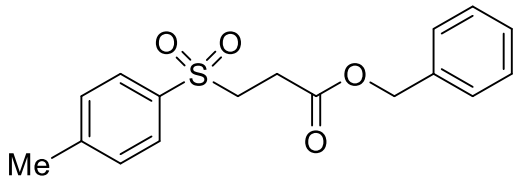
According to **GP** with but-3-en-1-yl furan-2-carboxylate (33.5 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.3 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **17** as white solid (44.6 mg, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.84-7.73 (m, 2H), 7.61-7.55 (m, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 3.2 Hz, 1H), 6.58-6.45 (m, 1H), 4.35-4.20 (m, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 1.95-1.76 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.3, 146.3, 144.6, 144.2, 135.7, 129.8, 127.9, 117.9, 111.7, 63.6, 55.5, 27.1, 21.5, 19.5. **HRMS** (ESI) calculated for $C_{16}H_{18}NaO_5S$ $[M+Na]^+$ m/z 345.0767, found 345.0765.

1-Methyl-4-((2-(phenylsulfonyl)ethyl)sulfonyl)benzene (18)



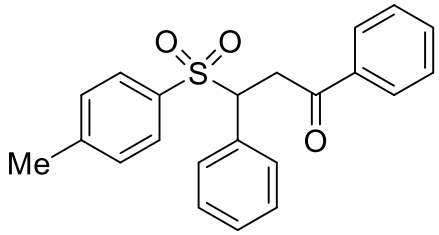
According to **GP** with (vinylsulfonyl)benzene (33.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (115.4 mg, 0.6 mmol, 3.0 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.1 mg, 0.02 mmol, 0.1 equiv). The reaction was conducted for 24 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **18** as white solid (43.4 mg, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.61-7.57 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.43 (s, 4H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7, 138.0, 134.9, 134.4, 130.2, 129.6, 128.0, 127.98, 49.54, 49.50, 21.6. **HRMS** (ESI) calculated for $C_{15}H_{16}NaO_4S_2$ $[M+Na]^+$ m/z 347.0382, found 347.0383.

Benzyl 3-tosylpropanoate (19)



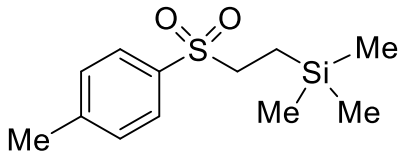
According to **GP** with benzyl acrylate (30 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **19** as white solid (63.1 mg, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2H), 7.38-7.30 (m, 7H), 5.06 (s, 2H), 3.42 (t, *J* = 7.8 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 145.0, 135.4, 135.1, 129.9, 128.5, 128.4, 128.3, 128.1, 67.0, 51.4, 27.9, 21.5. **HRMS** (ESI) calculated for $C_{17}H_{18}NaO_4S$ $[M+Na]^+$ m/z 341.0818, found 341.0812.

1,3-Diphenyl-3-tosylpropan-1-one (20)[5]



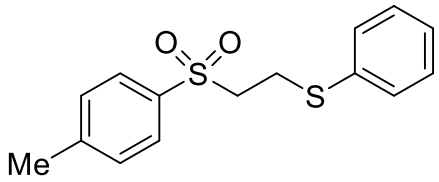
According to **GP** with (*E*)-chalcone (41.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.8 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (7.9 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **20** as white solid (58.3 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97-7.90 (m, 2H), 7.59-7.56 (m, 1H), 7.48-7.41 (m, 4H), 7.26-7.16 (m, 7H), 4.91 (dd, *J* = 9.7, 3.5 Hz, 1H), 4.11 (dd, *J* = 17.8, 3.5 Hz, 1H), 3.93 (dd, *J* = 17.8, 9.7 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.9, 144.7, 136.2, 134.0, 133.6, 132.6, 129.8, 129.4, 129.0, 128.7, 128.4, 128.1, 66.5, 37.0, 21.6. **MS** (ESI) m/z 365.2 $[M+H]^+$.

Trimethyl(2-tosylethyl)silane (21)



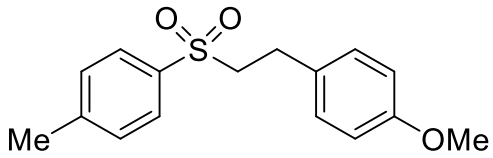
According to **GP** with trimethyl(vinyl)silane (29 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.1 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **21** as pale yellow oil (51.0 mg, 97%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02-7.88 (m, 2H), 7.58-7.48 (m, 2H), 3.15-3.11 (m, 2H), 2.61 (s, 3H), 1.09-1.04 (m, 2H), 0.15 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 135.7, 129.8, 128.2, 52.7, 21.6, 9.1, -2.1. **HRMS** (ESI) calculated for $C_{21}H_{24}NO_2SSi$ $[M+NH_4]^+$ m/z 274.1292, found 274.1288.

Phenyl(2-tosylethyl)sulfane (22)



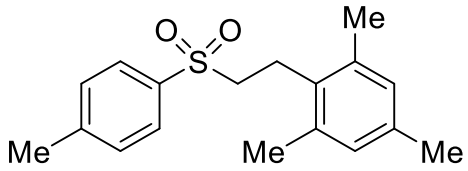
According to **GP** with phenyl(vinyl)sulfane (26 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **22** as white solid (49.5 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80-7.71 (m, 2H), 7.40-7.33 (m, 2H), 7.30-7.21 (m, 5H), 3.31-3.26 (m, 2H), 3.17-3.13 (m, 2H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.1, 135.6, 133.5, 130.2, 130.0, 129.3, 128.1, 127.2, 55.8, 26.4, 21.6. **HRMS** (ESI) calculated for $C_{15}H_{16}NaO_2S_2$ $[M+Na]^+$ m/z 315.0484, found 315.0481.

1-Methoxy-4-(2-tosylethyl)benzene (23)



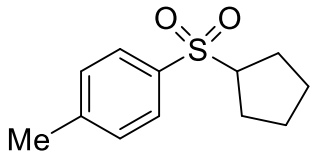
According to **GP** with 1-methoxy-4-vinylbenzene (27 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.7 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **23** as white solid (41.3 mg, 71%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.85-7.77 (m, 2H), 7.40-7.33 (m, 2H), 7.07-6.99 (m, 2H), 6.83-6.76 (m, 2H), 3.76 (s, 3H), 3.33-3.28 (m, 2H), 3.00-2.94 (m, 2H), 2.46 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.4, 144.7, 136.0, 129.9, 129.4, 129.2, 128.1, 114.1, 57.8, 55.2, 27.9, 21.6. **MS** (ESI) m/z 291.2 $[M+H]^+$.

1,3,5-Trimethyl-2-(2-tosylethyl)benzene (24)



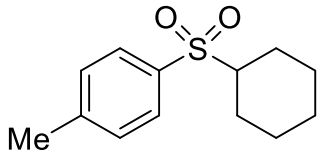
According to **GP** with 1,3,5-trimethyl-2-vinylbenzene (32 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **24** as white solid (47.8 mg, 79%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.91-7.80 (m, 2H), 7.45-7.33 (m, 2H), 6.79 (s, 2H), 3.15-3.06 (m, 2H), 3.03-2.94 (m, 2H), 2.47 (s, 3H), 2.21 (s, 3H), 2.13 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.7, 136.3, 136.0, 135.8, 131.0, 129.9, 129.1, 128.1, 54.7, 22.5, 21.6, 20.7, 19.3. **HRMS** (ESI) calculated for $C_{18}H_{22}NaO_2S$ $[M+Na]^+$ m/z 325.1233, found 325.1230.

1-(Cyclopentylsulfonyl)-4-methylbenzene (25)[6]



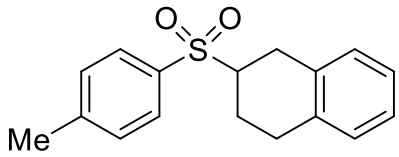
According to **GP** with cyclopentene (18 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.6 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.3 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **25** as colourless oil (35.8 mg, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.74 (m, 2H), 7.38-7.31 (m, 2H), 3.51-3.43 (m, 1H), 2.45 (s, 3H), 2.10-2.01 (m, 2H), 1.91-1.85 (m, 2H), 1.82-1.71 (m, 2H), 1.64-1.54 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.3, 136.0, 129.7, 128.4, 64.2, 27.2, 25.8, 21.6. **MS** (ESI) m/z 225.2 $[M+H]^+$.

1-(Cyclohexylsulfonyl)-4-methylbenzene (26)[7]



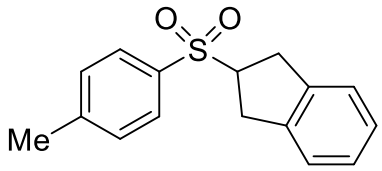
According to **GP** with cyclohexene (20 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.1 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **26** as pale yellow oil (22.0 mg, 46%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.70 (m, 2H), 7.38-7.32 (m, 2H), 2.91-2.84 (m, 1H), 2.45 (s, 3H), 2.07-2.05 (m, 2H), 1.87-1.83 (m, 2H), 1.70-1.65 (m, 1H), 1.44-1.34 (m, 2H), 1.29-1.07 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 134.2, 129.6, 129.0, 63.5, 25.5, 25.1, 25.0, 21.6. **MS** (ESI) m/z 239.1 $[M+H]^+$.

2-Tosyl-1,2,3,4-tetrahydronaphthalene (27)



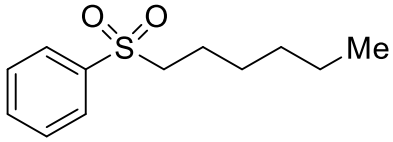
According to **GP** with 1,2-dihydronaphthalene (26 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.3 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **27** as white solid (31.9 mg, 55%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.85-7.77 (m, 2H), 7.42-7.34 (m, 2H), 7.12-7.02 (m, 4H), 3.36-3.26 (m, 1H), 3.09-2.89 (m, 3H), 2.86-2.75 (m, 1H), 2.46 (s, 3H), 2.41-2.33 (m, 1H), 1.87-1.72 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.8, 134.7, 133.8, 132.8, 129.8, 129.00, 128.98, 128.6, 126.3, 126.1, 60.5, 28.7, 28.2, 22.6, 21.6. **HRMS** (ESI) calculated for $C_{17}H_{18}NaO_2S$ $[M+H]^+$ m/z 309.0920, found 309.0917.

2-Tosyl-2,3-dihydro-1*H*-indene (28)



According to **GP** with 1*H*-indene (23 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.8 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **28** as white solid (29.2 mg, 54%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.84-7.76 (m, 2H), 7.37-7.29 (m, 2H), 7.17-7.09 (m, 4H), 4.05-3.94 (m, 1H), 3.49-3.41 (m, 2H), 3.20-3.12 (m, 2H), 2.42 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.6, 139.4, 134.9, 129.7, 128.3, 126.9, 124.1, 63.2, 33.5, 21.4. **HRMS** (ESI) calculated for $C_{16}H_{20}NO_2S$ $[M+HH_4]^+$ m/z 290.1209, found 290.1205.

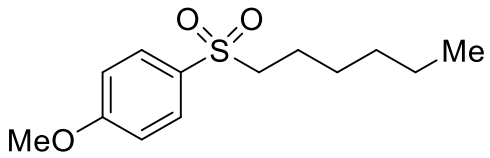
(Hexylsulfonyl)benzene (29)[8]



According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), benzenesulfonyl chloride (38 μL, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv),

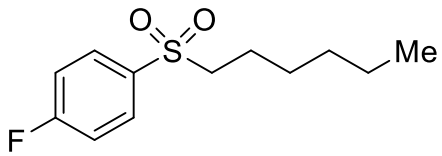
1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **29** as pale yellow oil (34.1 mg, 75%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97-7.87 (m, 2H), 7.69-7.64 (m, 1H), 7.60-7.55 (m, 2H), 3.11-3.06 (m, 2H), 1.76-1.65 (m, 2H), 1.40-1.34 (m, 2H), 1.31-1.22 (m, 4H), 0.85 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.1, 133.6, 129.2, 128.0, 56.2, 31.1, 27.9, 22.5, 22.2, 13.9. **MS** (ESI) m/z 227.0 $[M+H]^+$.

1-(Hexylsulfonyl)-4-methoxybenzene (30)



According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-methoxybenzenesulfonyl chloride (62.5 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **30** as pale yellow oil (37.3 mg, 73%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87-7.78 (m, 2H), 7.06-6.98 (m, 2H), 3.89 (s, 3H), 3.08-3.03 (m, 2H), 1.74-1.63 (m, 2H), 1.39-1.23 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6, 130.7, 130.1, 114.4, 56.6, 55.6, 31.1, 27.9, 22.7, 22.2, 13.9. **HRMS** (ESI) calculated for $C_{13}H_{20}NaO_3S$ $[M+Na]^+$ m/z 279.1025, found 279.1022.

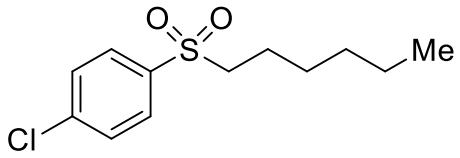
1-Fluoro-4-(hexylsulfonyl)benzene (31)[9]



According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-fluorobenzenesulfonyl chloride (58.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.6 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.4 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **31** as pale yellow oil (44.4 mg,

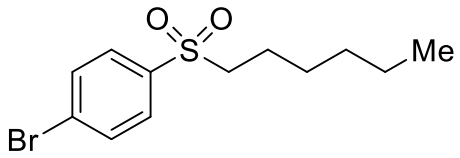
90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98-7.88 (m, 2H), 7.29-7.21 (m, 2H), 3.10-3.06 (m, 2H), 1.74-1.66 (m, 2H), 1.40-1.32 (m, 2H), 1.31-1.20 (m, 4H), 0.86 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.7 (d, *J* = 256.1 Hz), 135.2 (d, *J* = 3.3 Hz), 130.9 (d, *J* = 9.6 Hz), 116.5 (d, *J* = 22.6 Hz), 56.4, 31.1, 27.9, 22.6, 22.2, 13.9. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -103.73; **MS** (ESI) m/z 245.5 $[M+H]^+$.

1-Chloro-4-(hexylsulfonyl)benzene (32)



According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-chlorobenzenesulfonyl chloride (63.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **32** as colourless oil (31.6 mg, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2H), 7.58-7.52 (m, 2H), 3.10-3.06 (m, 2H), 1.74-1.66 (m, 2H), 1.40-1.32 (m, 2H), 1.31-1.21 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.3, 137.6, 129.55, 129.52, 56.3, 31.1, 27.9, 22.6, 22.2, 13.8. **HRMS** (ESI) calculated for $C_{12}H_{21}ClNO_2S$ $[M+NH_4]^+$ m/z 278.0976, found 278.0971.

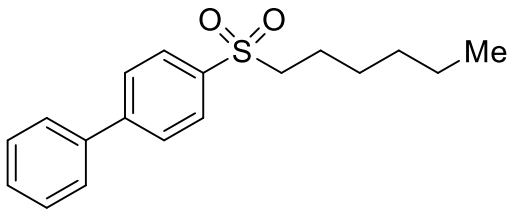
1-Bromo-4-(hexylsulfonyl)benzene (33)



According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-bromobenzenesulfonyl chloride (76.7 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.3 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **33** as colourless oil (40.6 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 2H), 7.74-7.69 (m, 2H), 3.10-3.06 (m, 2H), 1.73-1.65 (m, 2H), 1.39-1.29 (m, 2H), 1.26-1.20 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.1, 132.5, 129.6, 128.8, 56.2, 31.0, 27.8, 22.5,

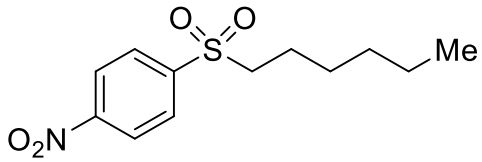
22.2, 13.8. **HRMS** (ESI) calculated for $C_{12}H_{17}BrNaO_2S$ $[M+Na]^+$ m/z 327.0025, found 327.0023.

4-(Hexylsulfonyl)-1,1'-biphenyl (34)[10]



According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), [1,1'-biphenyl]-4-sulfonyl chloride (75.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.6 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **34** as white solid (39.6 mg, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.51-7.41 (m, 3H), 3.15-3.10 (m, 2H), 1.80-1.69 (m, 2H), 1.48-1.32 (m, 2H), 1.31-1.16 (m, 4H), 0.86 (t, *J* = 5.8 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 146.5, 139.1, 137.6, 129.0, 128.6, 128.5, 127.8, 127.3, 56.4, 31.1, 27.9, 22.6, 22.2, 13.9. **MS** (ESI) m/z 303.2 $[M+H]^+$.

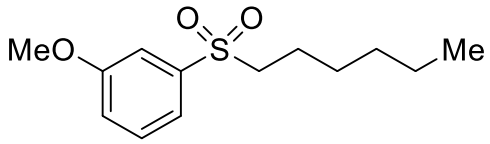
1-(Hexylsulfonyl)-4-nitrobenzene (35)



According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-nitrobenzenesulfonyl chloride (66.5 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (7.9 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **35** as brown yellow oil (22.1 mg, 41%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.49-8.39 (m, 2H), 8.16-8.09 (m, 2H), 3.17-3.12 (m, 2H), 1.78-1.67 (m, 2H), 1.43-1.34 (m, 2H), 1.33-1.22 (m, 4H), 0.86 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.8, 144.7, 129.6, 124.4, 56.2, 31.0, 27.8, 22.4, 22.2, 13.8. **HRMS** (ESI) calculated for $C_{12}H_{17}NNaO_4S$ $[M+Na]^+$ m/z 294.0770, found

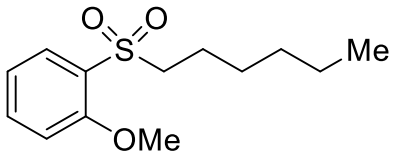
294.0774.

1-(Hexylsulfonyl)-3-methoxybenzene (36)



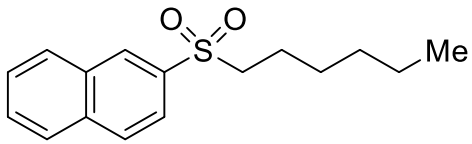
According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 3-methoxybenzenesulfonyl chloride (43 μL, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (17.0 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **36** as colourless oil (42.2 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.42-7.38 (m, 1H), 7.20-7.14 (m, 1H), 3.88 (s, 3H), 3.10-3.06 (m, 2H), 1.75-1.67 (m, 2H), 1.39-1.32 (m, 2H), 1.31-1.23 (m, 4H), 0.86 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.0, 140.4, 130.3, 120.1, 120.0, 112.4, 56.2, 55.7, 31.1, 27.9, 22.5, 22.2, 13.9. **HRMS** (ESI) calculated for $C_{13}H_{20}NaO_3S$ $[M+Na]^+$ m/z 279.1025, found 279.1023.

1-(Hexylsulfonyl)-2-methoxybenzene (37)



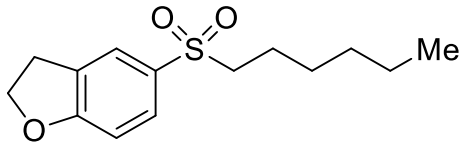
According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 2-methoxybenzenesulfonyl chloride (63.2 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.3 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **37** as pale yellow oil (34.4 mg, 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.61-7.57 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 3.36-3.32 (m, 2H), 1.72-1.64 (m, 2H), 1.40-1.33 (m, 2H), 1.30-1.21 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.2, 135.4, 130.5, 126.8, 120.7, 122.2, 56.2, 54.3, 31.1, 27.9, 22.3, 22.2, 13.9. **HRMS** (ESI) calculated for $C_{13}H_{20}NaO_3S$ $[M+Na]^+$ m/z 279.1025, found 279.1030.

2-(Hexylsulfonyl)naphthalene (38)[9]



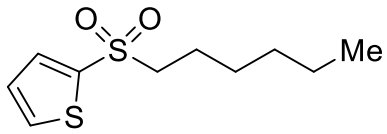
According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), naphthalene-2-sulfonyl chloride (68.4 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **38** as white solid (40.9 mg, 74%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.49 (d, *J* = 0.6 Hz, 1H), 8.03-7.99 (m, 2H), 7.95-7.92 (m, 1H), 7.87 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.70-7.60 (m, 2H), 3.19-3.14 (m, 2H), 1.79-1.68 (m, 2H), 1.40-1.28 (m, 2H), 1.25-1.19 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.0, 135.2, 132.1, 129.7, 129.5, 129.3, 129.2, 127.9, 127.6, 122.7, 56.3, 31.1, 27.9, 22.6, 22.2, 13.8. **MS** (ESI) m/z 277.1 $[M+H]^+$.

5-(Hexylsulfonyl)-2,3-dihydrobenzofuran (39)



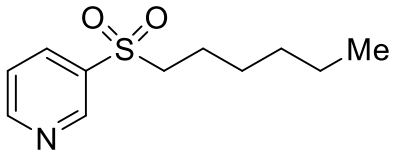
According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 2,3-dihydrobenzofuran-5-sulfonyl chloride (65.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.4 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **39** as yellow oil (54.8 mg, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.70 (t, *J* = 8.8 Hz, 2H), 3.28 (t, *J* = 8.8 Hz, 2H), 3.06-3.02 (m, 2H), 1.73-1.65 (m, 2H), 1.39-1.31 (m, 2H), 1.30-1.20 (m, 4H), 0.86 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 130.7, 129.7, 128.5, 125.2, 109.6, 72.3, 56.7, 31.1, 28.9, 27.9, 22.8, 22.3, 13.9. **HRMS** (ESI) calculated for $C_{14}H_{20}NaO_3S$ $[M+H]^+$ m/z 291.1025, found 291.1024.

2-(Hexylsulfonyl)thiophene (40)



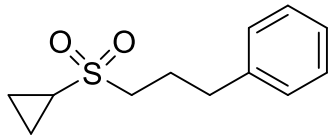
According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), thiophene-2-sulfonyl chloride (55.1 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.1 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **40** as yellow oil (44.2 mg, 95%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 5.0 Hz, 1H), 7.69 (d, *J* = 3.8 Hz, 1H), 7.18-7.15 (m, 1H), 3.22-3.17 (m, 2H), 1.82-1.72 (m, 2H), 1.43-1.34 (m, 2H), 1.33-1.26 (m, 4H), 0.87 (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.2, 133.9, 133.8, 127.8, 57.7, 31.1, 27.8, 22.9, 22.2, 13.9. **HRMS** (ESI) calculated for $C_{10}H_{20}NO_2S_2$ $[M+NH_4]^+$ m/z 250.0930, found 250.0930.

3-(Hexylsulfonyl)pyridine (41)



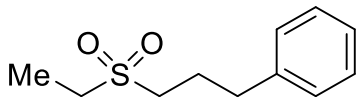
According to **GP** with hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), pyridine-3-sulfonyl chloride (36 μL, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **41** as yellow oil (30.0 mg, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.12 (d, *J* = 1.8 Hz, 1H), 8.89 (dd, *J* = 4.6, 1.0 Hz, 1H), 8.20 (dt, *J* = 8.0, 1.7 Hz, 1H), 7.54 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.15-3.11 (m, 2H), 1.77-1.70 (m, 2H), 1.42-1.34 (m, 2H), 1.33-1.26 (m, 4H), 0.86 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.2, 149.1, 135.9, 135.6, 123.8, 56.6, 31.1, 27.8, 22.5, 22.2, 13.8. **HRMS** (ESI) calculated for $C_{11}H_{18}NO_2S$ $[M+Na]^+$ m/z 228.1053, found 228.1052.

(3-(Cyclopropylsulfonyl)propyl)benzene (42)



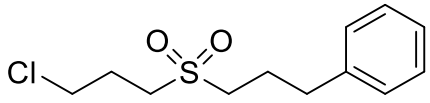
According to **GP** with allylbenzene (27 μL, 0.2 mmol, 1.0 equiv), cyclopropanesulfonyl chloride (31 μL, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.6 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **42** as pale yellow oil (28.8 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.24-7.18 (m, 3H), 3.04-3.00 (m, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.37-2.31 (m, 1H), 2.25-2.18 (m, 2H), 1.24-1.20 (m, 2H), 1.03-0.98 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.9, 128.6, 128.4, 126.4, 53.1, 34.3, 29.2, 23.7, 4.5. **HRMS** (ESI) calculated for $C_{12}H_{16}NaO_2S$ $[M+Na]^+$ m/z 247.0763, found 247.0759.

(3-(Ethylsulfonyl)propyl)benzene (43)[11]



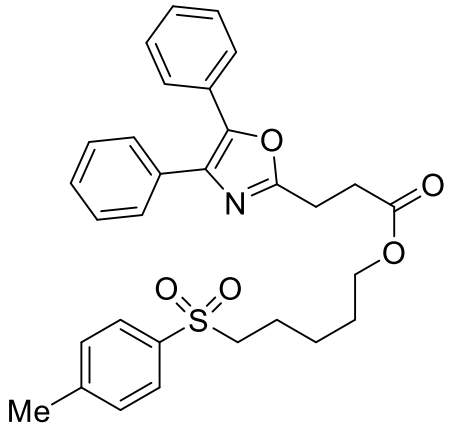
According to **GP** with allylbenzene (27 μL, 0.2 mmol, 1.0 equiv), ethanesulfonyl chloride (57 μL, 0.6 mmol, 3.0 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The reaction was conducted for 24 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **43** as pale yellow oil (15.7 mg, 37%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.24-7.17 (m, 3H), 2.98-2.89 (m, 4H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.21-2.11 (m, 2H), 1.34 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.7, 128.5, 128.3, 126.3, 50.8, 46.9, 34.1, 23.3, 6.4. **MS** (ESI) m/z 213.0 $[M+H]^+$.

(3-((3-Chloropropyl)sulfonyl)propyl)benzene (44)



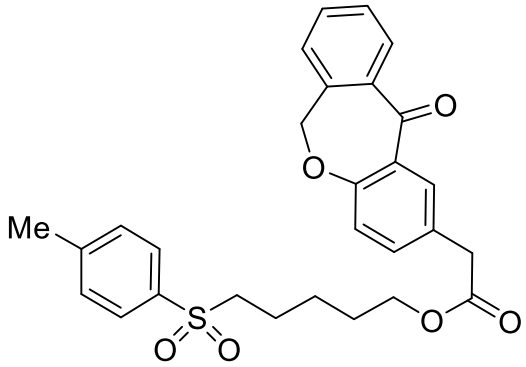
According to **GP** with allylbenzene (27 μL, 0.2 mmol, 1.0 equiv), 3-chloropropane-1-sulfonyl chloride (73 μL, 0.6 mmol, 3.0 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.1 mg, 0.02 mmol, 0.1 equiv). The reaction was conducted for 24 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **44** as yellow solid (18.2 mg, 35%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.25-7.17 (m, 3H), 3.64 (t, *J* = 6.2 Hz, 2H), 3.10-3.06 (m, 2H), 2.97-2.93 (m, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.28-2.21 (m, 2H), 2.20-2.13 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.6, 128.5, 128.2, 126.3, 52.1, 49.6, 42.8, 33.9, 24.7, 23.3. **HRMS** (ESI) calculated for $C_{12}H_{17}ClNaO_2S$ $[M+Na]^+$ m/z 283.0530, found 283.0528.

5-Tosylpentyl 3-(4,5-diphenyloxazol-2-yl)propanoate (45)



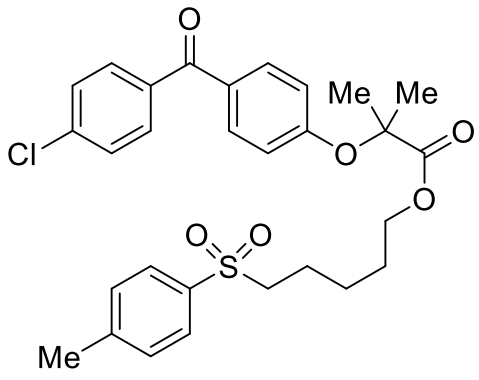
According to **GP** with pent-4-en-1-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (72.6 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3:1) to afford the desired product **45** as white solid (57.7 mg, 56%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82-7.71 (m, 2H), 7.63-7.60 (m, 2H), 7.58-7.54 (m, 2H), 7.38-7.27 (m, 8H), 4.08 (t, *J* = 6.4 Hz, 2H), 3.16 (t, *J* = 7.4 Hz, 2H), 3.02-2.97 (m, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.44 (s, 3H), 1.75-1.56 (m, 4H), 1.45-1.37 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.9, 161.6, 145.3, 144.6, 136.0, 135.0, 132.3, 129.8, 128.8, 128.6, 128.5, 128.4, 128.0, 127.9, 127.7, 126.3, 64.1, 56.0, 31.0, 28.0, 24.7, 23.4, 22.3, 21.5. **HRMS** (ESI) calculated for $C_{30}H_{31}NNaO_5S$ $[M+Na]^+$ m/z 540.1815, found 540.1805.

5-Tosylpentyl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (46)



According to **GP** with pent-4-en-1-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (67.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.8 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **46** as white solid (72.7 mg, 74%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 7.3 Hz, 1H), 7.80-7.72 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.42-7.32 (m, 4H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.61 (s, 2H), 3.09-3.04 (m, 2H), 2.43 (s, 3H), 1.77-1.66 (m, 2H), 1.63-1.56 (m, 2H), 1.46-1.36 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.8, 171.3, 160.4, 144.6, 140.3, 136.3, 136.0, 135.5, 132.8, 132.3, 129.8, 129.4, 129.2, 128.0, 127.8, 127.7, 125.0, 121.0, 73.5, 64.3, 56.0, 40.1, 28.0, 24.7, 22.4, 21.6. **HRMS** (ESI) calculated for $C_{28}H_{28}NaO_6S$ $[M+Na]^+$ m/z 515.1499, found 515.1490.

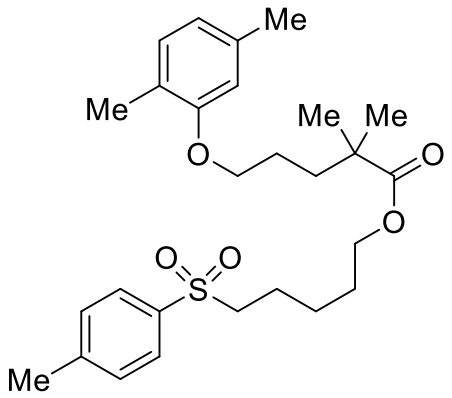
5-Tosylpentyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (47)



According to **GP** with pent-4-en-1-yl

2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (77.6 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (58.0 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.4 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **47** as white solid (91.7 mg, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.68 (m, 6H), 7.49-7.41 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.90-6.78 (m, 2H), 4.12 (t, *J* = 6.4 Hz, 2H), 2.99-2.95 (m, 2H), 2.44 (s, 3H), 1.70-1.55 (m, 4H), 1.66 (s, 6H), 1.33-1.25 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 194.0, 173.5, 159.5, 144.6, 138.2, 136.1, 135.9, 131.9, 131.0, 130.2, 129.8, 128.4, 127.9, 117.0, 79.2, 65.0, 55.8, 27.8, 25.3, 24.5, 22.2, 21.5. **HRMS** (ESI) calculated for $C_{29}H_{31}ClNaO_6S$ $[M+Na]^+$ m/z 565.1422, found 565.1413.

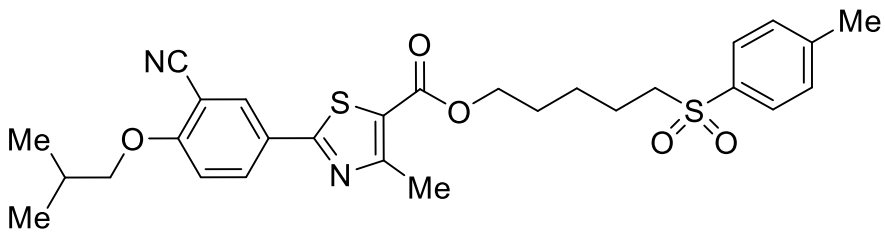
5-Tosylpentyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (48)



According to **GP** with pent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (63.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.9 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **48** as yellow oil (74.3 mg, 78%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.80-7.72 (m, 2H), 7.38-7.30 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.92-3.89 (m, 2H), 3.07-3.02 (m, 2H), 2.44 (s, 3H), 2.30 (s, 3H), 2.15 (s, 3H), 1.78-1.73 (m, 6H), 1.65-1.56 (m, 2H), 1.47-1.38 (m, 2H), 1.19 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 156.9, 144.6, 136.5, 136.2, 130.3, 129.9, 128.0, 123.5, 120.7, 111.9, 67.9, 63.8, 56.2, 42.0, 37.0, 28.2, 25.2, 25.1, 24.9, 22.5, 21.6, 21.4, 15.7. **HRMS** (ESI) calculated

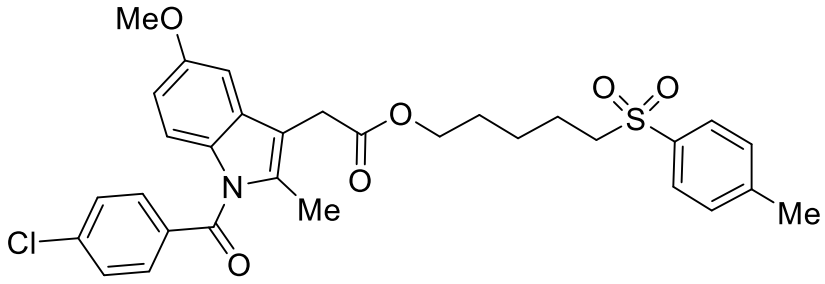
for $C_{27}H_{38}NaO_5S$ $[M+Na]^+$ m/z 497.2332, found 497.2325.

5-Tosylpentyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (49)



According to **GP** with pent-4-en-1-yl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (77.5 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.7 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.4 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 4:1) to afford the desired product **49** as white solid (67.5 mg, 62%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.84-7.74 (m, 2H), 7.40-7.32 (m, 2H), 7.02 (d, *J* = 8.9 Hz, 1H), 4.26 (t, *J* = 6.3 Hz, 2H), 3.90 (d, *J* = 6.4 Hz, 2H), 3.13-3.09 (m, 2H), 2.74 (s, 3H), 2.45 (s, 3H), 2.25-2.15 (m, 1H), 1.84-1.71 (m, 4H), 1.57-1.50 (m, 2H), 1.09 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.1, 162.4, 161.8, 161.1, 144.6, 136.0, 132.5, 131.9, 129.8, 127.9, 125.7, 121.4, 115.3, 112.5, 102.7, 75.5, 64.6, 56.0, 28.1, 28.0, 24.8, 22.4, 21.5, 18.9, 17.3. **HRMS** (ESI) calculated for $C_{28}H_{32}N_2NaO_5S_2$ $[M+Na]^+$ m/z 563.1645, found 563.1639.

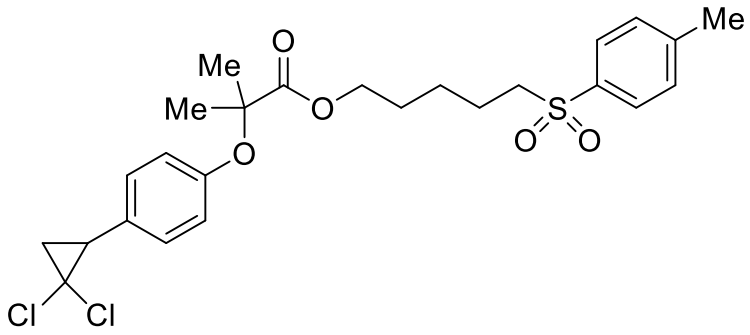
5-Tosylpentyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (50)



According to **GP** with pent-4-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (85.6 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.8

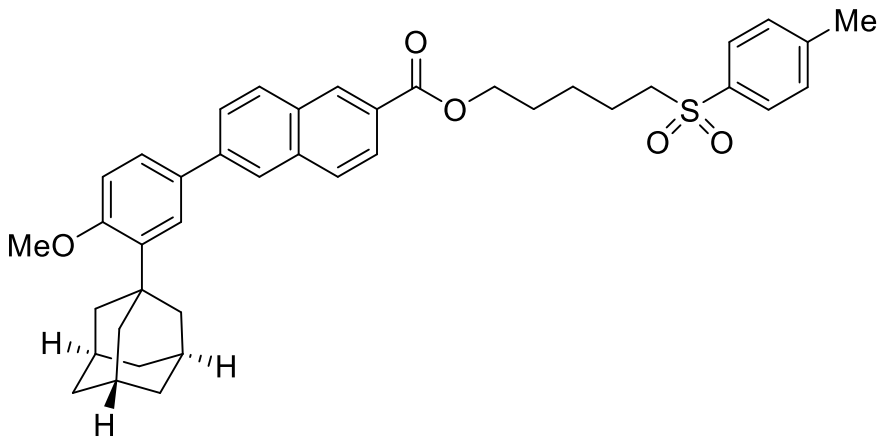
mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.3 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3:1) to afford the desired product **50** as white solid (66.6 mg, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.72 (m, 2H), 7.68-7.62 (m, 2H), 7.50-7.44 (m, 2H), 7.38-7.31 (m, 2H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.65 (d, *J* = 9.0, 2.5 Hz, 1H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 3.64 (s, 2H), 2.99-2.95 (m, 2H), 2.44 (s, 3H), 2.37 (s, 3H), 1.71-1.63 (m, 2H), 1.62-1.55 (m, 2H), 1.39-1.31 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.8, 168.2, 155.9, 144.6, 139.2, 136.0, 135.9, 133.8, 131.1, 130.7, 130.6, 129.9, 129.1, 128.0, 114.9, 112.5, 111.3, 101.4, 64.3, 56.0, 55.6, 30.3, 28.0, 24.7, 22.3, 21.6, 13.3. **HRMS** (ESI) calculated for $C_{31}H_{32}ClNNaO_6S$ $[M+Na]^+$ m/z 604.1531, found 604.1523.

5-Tosylpentyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (51)



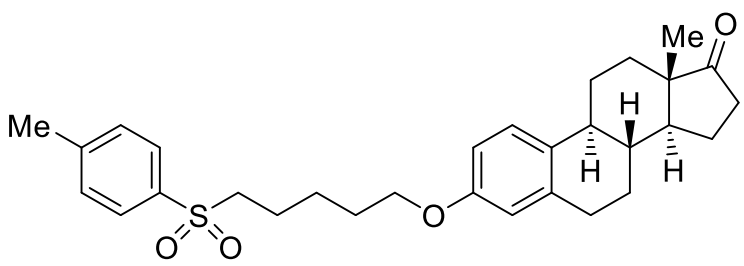
According to **GP** with pent-4-en-1-yl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (71.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.6 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.6 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (7.9 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **51** as white solid (70.2 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.71 (m, 2H), 7.43-7.31 (m, 2H), 7.16-7.02 (m, 2H), 6.82-6.70 (m, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 2.99-2.94 (m, 2H), 2.84-2.79 (m, 1H), 2.45 (s, 3H), 1.92 (dd, *J* = 10.6, 7.5 Hz, 1H), 1.77 (t, *J* = 7.9 Hz, 1H), 1.68-1.52 (m, 4H), 1.58 (s, 6H), 1.30-1.23 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 154.9, 144.6, 136.0, 129.8, 129.5, 127.9, 118.2, 78.9, 64.7, 60.8, 56.0, 34.7, 27.8, 25.7, 25.3, 24.5, 22.2, 21.5. **HRMS** (ESI) calculated for $C_{25}H_{30}Cl_2NaO_5S$ $[M+Na]^+$ m/z 535.1083, found 535.1075.

5-Tosylpentyl 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (52)



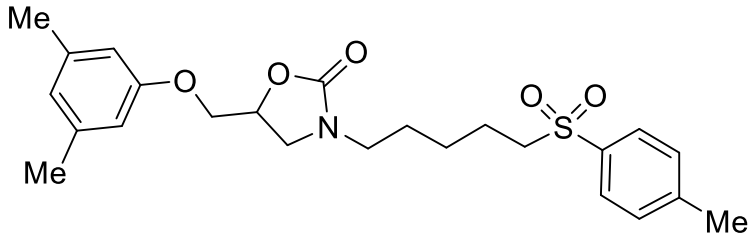
According to **GP** with pent-4-en-1-yl 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (96.7 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (58.1 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.1 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **52** as white solid (76.8 mg, 60%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.97-7.89 (m, 3H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.73-7.68 (m, 3H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.46 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.28-7.20 (m, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 3.06-3.01 (m, 2H), 2.34 (s, 3H), 2.15-2.07 (m, 6H), 2.06-1.97 (m, 3H), 1.79-1.68 (m, 10H), 1.54-1.44 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.7, 158.9, 144.6, 141.3, 138.9, 136.0, 135.9, 132.4, 131.1, 130.7, 129.9, 129.6, 128.2, 128.0, 126.9, 126.4, 125.9, 125.7, 125.4, 124.6, 112.0, 64.5, 56.2, 55.1, 40.5, 37.1, 37.0, 29.0, 28.3, 25.0, 22.6, 21.6. **HRMS** (ESI) calculated for $C_{40}H_{44}NaO_5S$ $[M+Na]^+$ m/z 659.2802, found 659.2803.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-((5-tosylpentyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (53)



According to **GP** with (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(pent-4-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (67.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.8 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.3 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **53** as white solid (90.2 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.74 (m, 2H), 7.39-7.32 (m, 2H), 7.17 (d, *J* = 8.6 Hz, 1H), 6.65 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.59 (d, *J* = 2.0 Hz, 1H), 3.89 (t, *J* = 6.1 Hz, 2H), 3.11-3.07 (m, 2H), 2.94-2.83 (m, 2H), 2.53-2.37 (m, 2H), 2.48 (s, 3H), 2.26-1.93 (m, 5H), 1.81-1.70 (m, 4H), 1.64-1.37 (m, 8H), 0.90 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 220.9, 156.7, 144.5, 137.6, 136.0, 131.9, 129.8, 127.9, 126.2, 114.3, 111.9, 67.0, 56.1, 50.2, 47.9, 43.8, 38.2, 35.8, 31.4, 29.5, 28.6, 26.4, 25.8, 24.9, 22.5, 21.53, 21.46, 13.7. **HRMS** (ESI) calculated for $C_{30}H_{42}NO_4S$ $[M+NH_4]^+$ m/z 512.2829, found 512.2816.

5-((3,5-Dimethylphenoxy)methyl)-3-(5-tosylpentyl)oxazolidin-2-one (54)

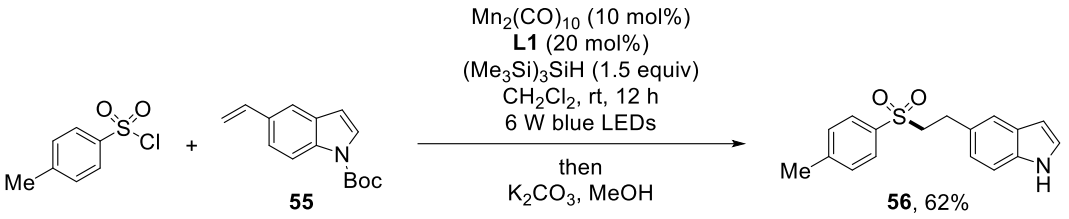


According to **GP** with 5-((3,5-dimethylphenoxy)methyl)-3-(pent-4-en-1-yl)oxazolidin-2-one (58.4 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.8 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3:1) to afford the desired product **54** as colourless oil (72.2 mg, 81%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82-7.69 (m, 2H), 7.41-7.29 (m, 2H), 6.62 (s, 1H), 6.50 (s, 2H), 4.83-4.75 (m, 1H), 4.06 (d, *J* = 4.5 Hz, 2H), 3.65 (t, *J* = 8.8 Hz, 1H), 3.48 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.32-3.15 (m, 2H), 3.08-3.03 (m, 2H), 2.44 (s, 3H), 2.27 (s, 6H), 1.78-1.68 (m, 2H), 1.60-1.50 (m, 2H), 1.46-1.38 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.0, 157.4, 144.5, 139.2, 135.9, 129.8, 127.8, 123.1, 112.1, 70.6,

67.8, 55.8, 46.3, 43.5, 26.6, 25.1, 22.3, 21.4, 21.2. **HRMS** (ESI) calculated for $C_{24}H_{31}NNaO_5S$ $[M+Na]^+$ m/z 468.1815, found 468.1808.

Synthesis of an intermediate for the preparation of Eletriptan:

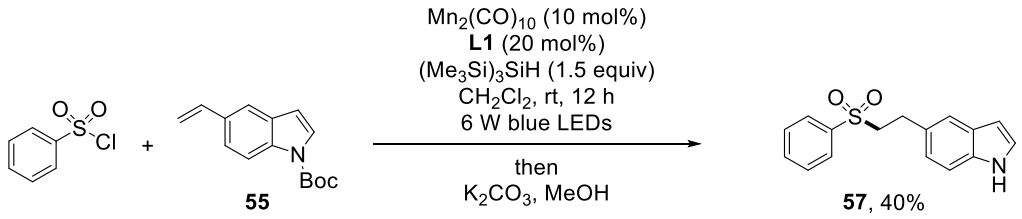
5-(2-Tosylethyl)-1*H*-indole (56)



tert-Butyl 5-vinyl-1*H*-indole-1-carboxylate (48.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (58.1 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane **L1** (16.5 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20/1) to afford hydrosulfonylated product (55.9 mg, 69%).

Then, hydrosulfonylated product (79.7 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (82.9 mg, 0.6 mmol, 3.0 equiv) were placed in a dry 10 mL tube. Then MeOH (10.0 mL) was added with a syringe. The reaction mixture was refluxed for 6 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford the desired product **56** as white solid (60.3 mg, 90%). Two steps: 62% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.36 (brs, 1H), 7.85-7.76 (m, 2H), 7.37-7.29 (m, 3H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.15 (t, *J* = 2.9 Hz, 1H), 6.88 (d, *J* = 8.4, 1.6 Hz, 1H), 6.43-6.41 (m, 1H), 3.40-3.35 (m, 2H), 3.12-3.06 (m, 2H), 2.43 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.7, 135.9, 134.6, 129.8, 128.4, 128.0, 127.9, 124.9, 122.1, 119.8, 111.4, 101.9, 58.3, 28.9, 21.5. **HRMS** (ESI) calculated for $C_{17}H_{17}NNaO_2S$ $[M+Na]^+$ m/z 322.0872, found 322.0873.

5-(2-(Phenylsulfonyl)ethyl)-1*H*-indole (57)[13]

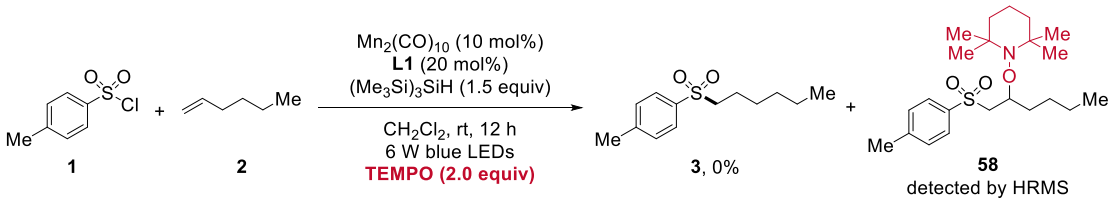


tert-Butyl 5-vinyl-1*H*-indole-1-carboxylate (48.8 mg, 0.2 mmol, 1.0 equiv), benzenesulfonyl chloride (38 μL, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane **L1** (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20/1) to afford hydrosulfonylated product (39.1 mg, 50%).

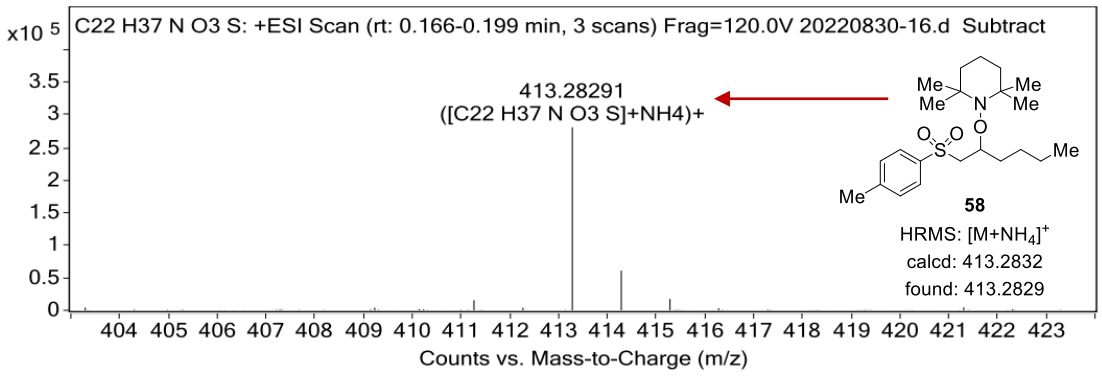
Then, hydrosulfonylated product (77.3 mg, 0.2 mmol, 1.0 equiv), K_2CO_3 (138.5 mg, 1.0 mmol, 5.0 equiv) were placed in a dry 10 mL tube. Then MeOH (10.0 mL) was added with a syringe. The reaction mixture was refluxed for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford the desired product **57** as white solid (45.9 mg, 80%). Two steps: 40% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.27 (brs, 1H), 7.99-7.91 (m, 2H), 7.68-7.63 (m, 1H), 7.58-7.53 (m, 2H), 7.34 (s, 1H), 7.27 (d, J = 8.3 Hz, 1H), 7.17 (t, J = 2.8 Hz, 1H), 6.90 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.45-6.43 (m, 1H), 3.43-3.37 (m, 2H), 3.14-3.09 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.0, 134.7, 133.7, 129.3, 128.5, 128.1, 128.0, 124.9, 122.3, 120.0, 111.3, 102.1, 58.3, 28.8. **HRMS** (ESI) calculated for $C_{16}H_{15}NNaO_2S$ $[M+Na]^+$ m/z 308.0716, found 308.0708.

Mechanistic studies

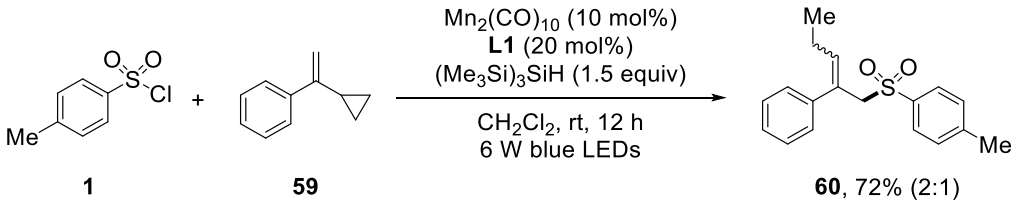
1) Radical trapping experiment:



Hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane **L1** (16.7 mg, 0.04 mmol, 0.2 equiv), $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (62.8 mg, 0.4 mmol, 2.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. In this reaction, the formation of **3** was completely suppressed. Moreover, high-resolution mass spectra (HRMS) analysis of this reaction mixture showed that the TEMPO-trapped product **58** was formed. This result indicated that a stepwise mechanism that proceeds through a carbon-centered radical intermediate was involved in this reaction.

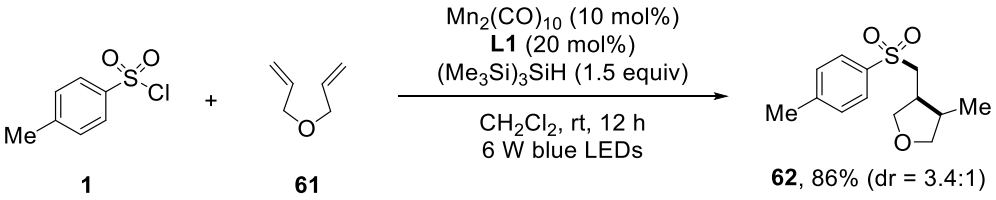


2) Radical clock experiments:



(1-Cyclopropylvinyl)benzene (29.9 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.8 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane **L1** (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.0 mg, 0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 35/1) to afford the ring-opening product **60** (42.4 mg, 72%, major isomer/minor isomer = 2:1).

1-Methyl-4-((2-phenylpent-2-en-1-yl)sulfonyl)benzene (60): white solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ major isomer: 7.62-7.60 (m, 2H), 7.26-7.14 (m, 7H), 5.94 (t, *J* = 7.4 Hz, 1H), 4.34 (s, 2H), 2.35 (s, 3H), 2.12-2.02 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); minor isomer: 7.65-7.62 (m, 2H), 7.26-7.14 (m, 5H), 7.06-7.02 (m, 2H), 5.58 (t, *J* = 7.5 Hz, 1H), 4.10 (s, 2H), 2.39 (s, 3H), 2.02-1.94 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); **HRMS** (ESI) calculated for $C_{18}H_{20}NaO_2S$ $[M+Na]^+$ m/z 323.1076, found 323.1071.



3-(Allyloxy)prop-1-ene (24 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.4 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane **L1** (16.5 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.4 mg, 0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20/1) to afford the ring-opening product **62** (42.1 mg, 86%, dr = 3.4:1).

3-Methyl-4-(tosylmethyl)tetrahydrofuran (62): yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ major isomer: 7.88-7.72 (m, 2H), 7.44-7.32 (m, 2H), 3.99-3.95 (m, 1H), 3.91-3.87 (m, 1H), 3.60-3.56 (m, 1H), 3.44-3.41 (m, 1H), 3.26-3.21 (m, 1H), 3.08-3.01 (m, 1H), 2.72-2.63 (m, 1H), 2.46 (s, 3H), 2.42-2.36 (m, 1H), 0.92 (d, *J* =

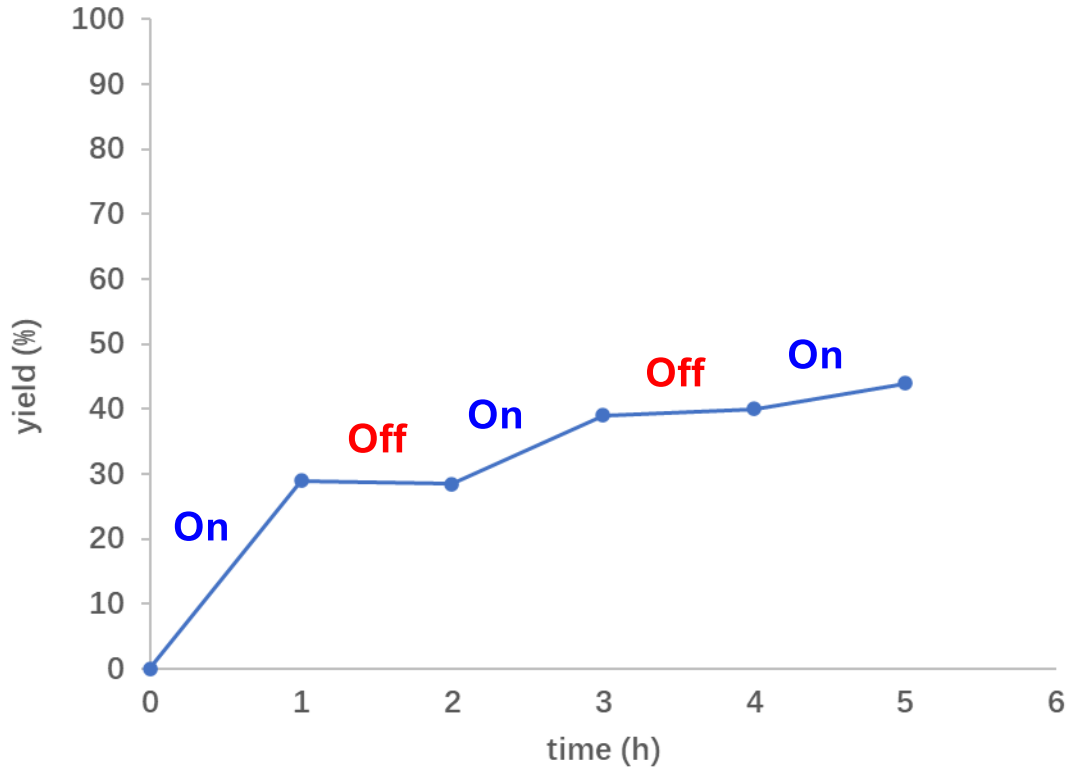
7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ major isomer: 144.9, 136.3, 130.0, 127.9, 74.5, 70.9, 55.3, 36.6, 35.9, 21.6, 13.3; **HRMS** (ESI) calculated for $C_{13}H_{18}NaO_3S$ $[M+H]^+$ m/z 277.0869, found 277.0865.

3) Formation of $(Me_3Si)_3Si$ Cl:

Hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.9 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane **L1** (16.5 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (7.9 mg, 0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 50/1) to afford **63** as colourless oil (48.6 mg, 65%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 0.20 (s, 27H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ -0.60. **MS** (ESI) m/z 283.2 $[M+H]^+$. The spectroscopic data were in accordance with those reported in the literature.[12] This result is consistent with Cl-atom abstraction by the silyl radical.

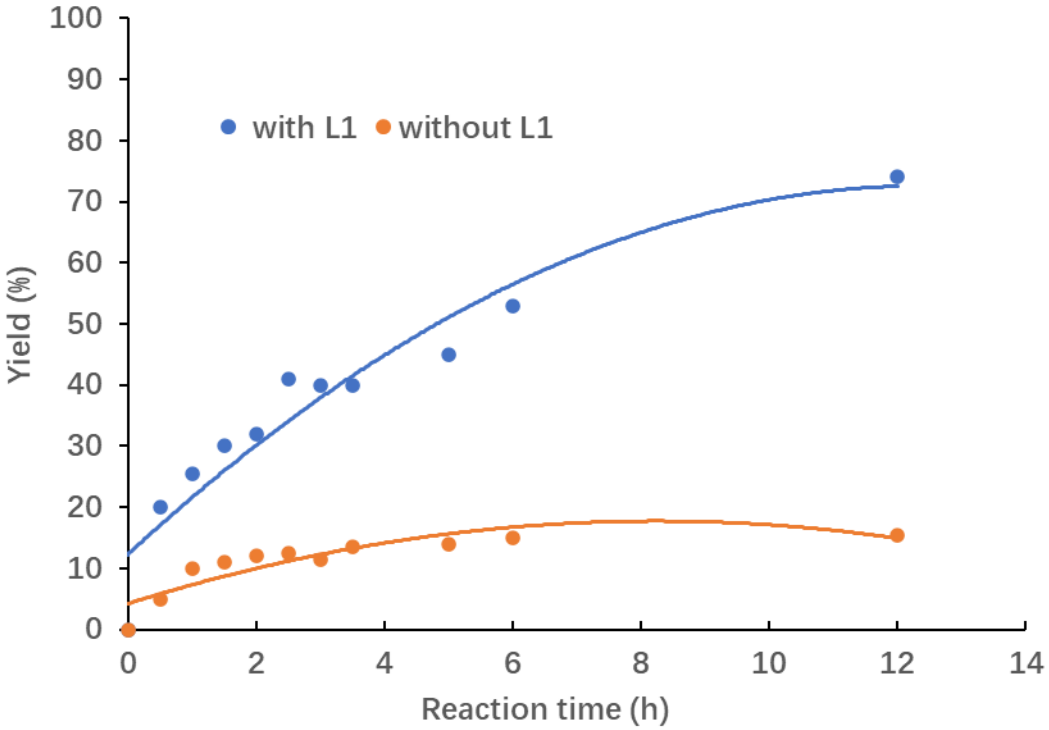
4) Visible light on/off experiments:

Hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (58.1 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane **L1** (16.8 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. The process of photocatalytic reaction with and without light was monitored by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. The results suggest that the formation of product **3** requires continuous visible light irradiation.



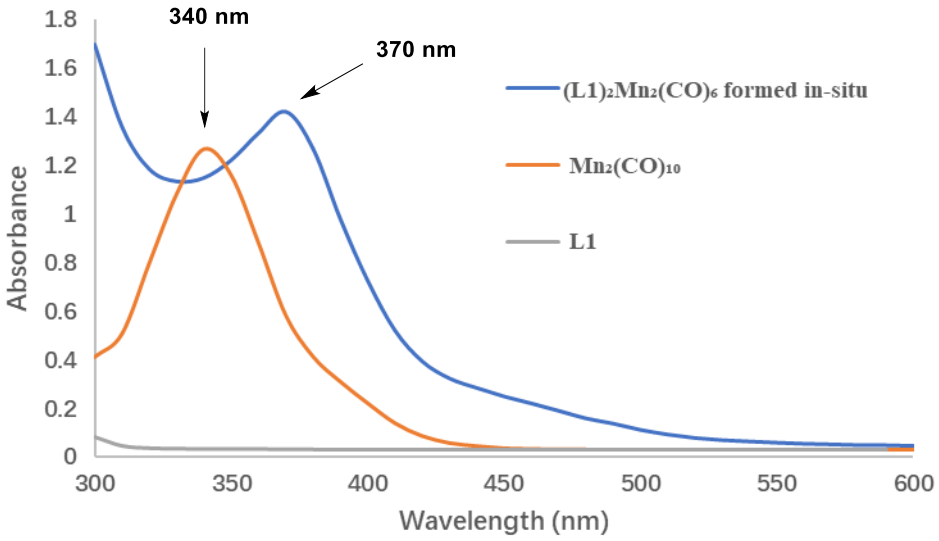
5) The time profile of model reaction with and without ligand L1:

Hex-1-ene (25 μL, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (57.7 mg, 0.3 mmol, 1.5 equiv), $(Me_3Si)_3SiH$ (93 μL, 0.3 mmol, 1.5 equiv), 1,3-bis(diphenylphosphanyl)propane **L1** (16.7 mg, 0.04 mmol, 0.2 equiv), and $Mn_2(CO)_{10}$ (8.2 mg, 0.02 mmol, 0.1 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous CH_2Cl_2 (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. In addition, the same reaction was conducted again, but without **L1**. The processes of these two reactions were monitored by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard. The time profile of model reaction indicates that the inclusion of **L1** helpes in accelerating this radical transformation.



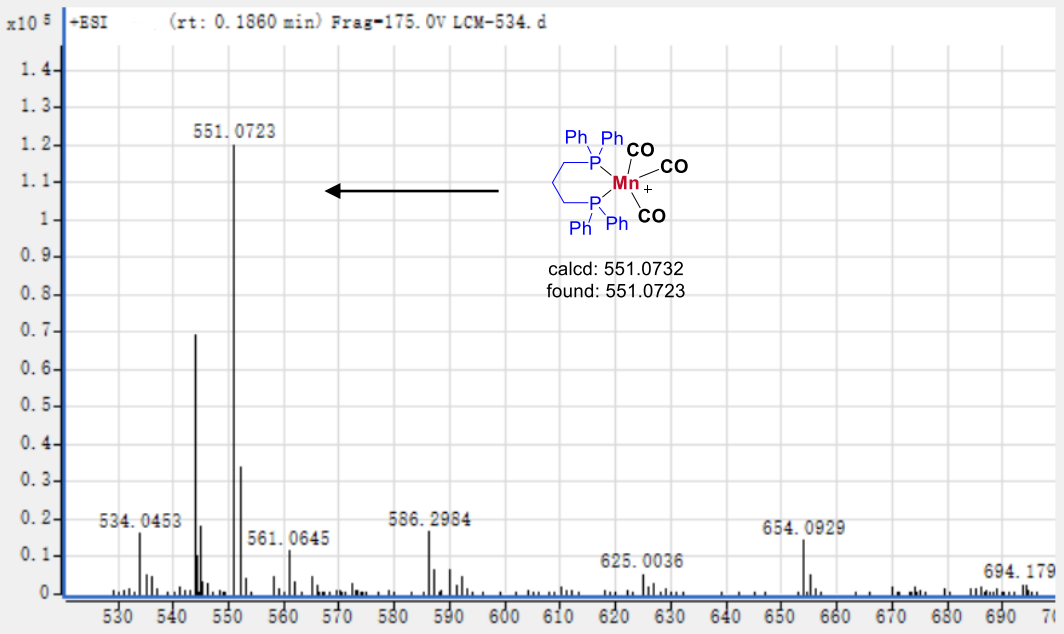
6) UV-vis spectroscopic measurements:

The UV-vis experiments were performed on an Agilent Cary 100 UV-visible spectrophotometer with a quartz cuvette (10 mm path length). The reaction mixture of $Mn_2(CO)_{10}$ and **L1** was stirred in hexafluorobenzene and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the mixture was filtered to give the crude (**L1**)$_2Mn_2(CO)_6$. (**L1**)$_2Mn_2(CO)_6$ was are measured in DCM with 800 μM concentration. $Mn_2(CO)_6$ and **L1** are measured in DCM with 80 μM concentration. The full spectras were collected, and we observed that the optical absorption spectrum of in situ formed (**L1**)$_2Mn_2(CO)_6$ generated a bathochromic shift compared to the spectra of $Mn_2(CO)_{10}$, which indicated that the (**L1**)$_2Mn_2(CO)_6$ complex could be an effective complex for the generation of manganese radicals under blue LEDs irradiation (λ ranging from 420 to 500 nm, λ_{max} = 450 nm).



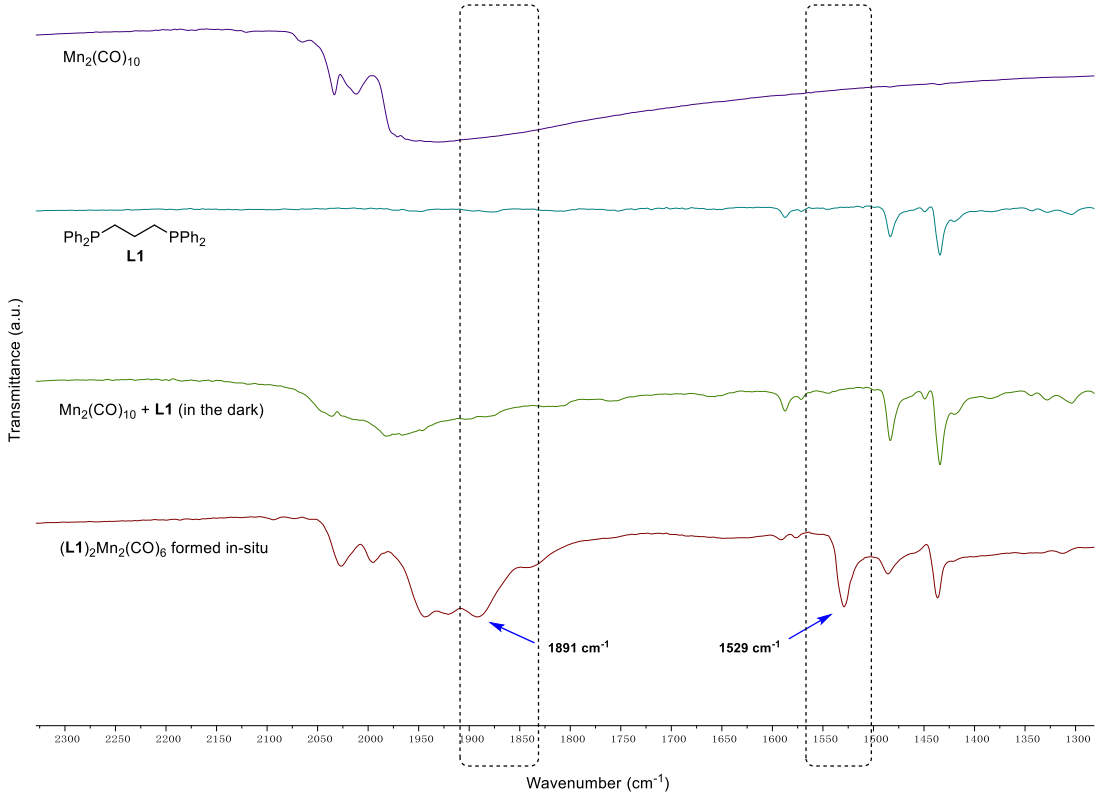
7) HRMS analysis of reaction mixture of $Mn_2(CO)_{10}$ and L1:

We performed high-resolution mass spectrometry (HRMS) analysis. The reaction mixture of $Mn_2(CO)_{10}$ and **L1** in CH_2Cl_2 was irradiated with 6 W blue LEDs at room temperature under N_2 for 1 h. When the mixture was subjected to HRMS analysis, the mass of $[\mathbf{L1}Mn(CO)_3]^+$ could be detected, since the $\mathbf{L1}Mn(CO)_3^{\cdot}$ readily loses one electron during the HRMS analysis. This result supports the existence of $\mathbf{L1}Mn(CO)_3^{\cdot}$.

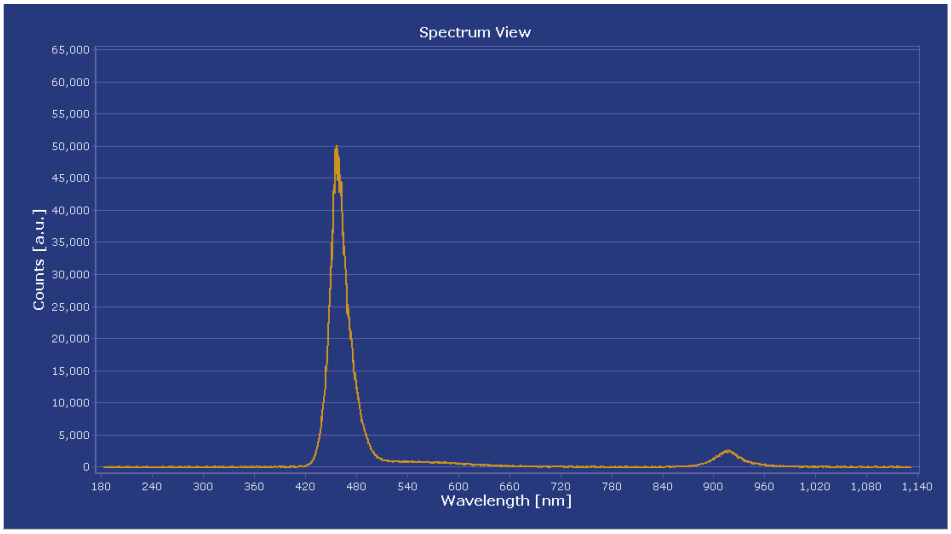


8) Infrared spectroscopic measurements:

The infrared spectra were measured on a Shimazu IRAffinity-15 spectrometer. The reaction mixture of $Mn_2(CO)_{10}$ and **L1** was stirred in hexafluorobenzene and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the mixture was filtered to give the crude $(\mathbf{L1})_2Mn_2(CO)_6$. The infrared spectra of $(\mathbf{L1})_2Mn_2(CO)_6$ generated a new infrared vibrational band at the 1891 cm^{-1} compared to that of $Mn_2(CO)_{10}$ + **L1** (in the dark), which might be attributed to the CO stretching mode of $(\mathbf{L1})_2Mn_2(CO)_6$. Moreover, a new infrared vibrational band appeared at the 1529 cm^{-1} compared to that of **L1** or $Mn_2(CO)_{10}$ + **L1** (in the dark), which might be attributed to the aromatic C-C stretching mode of **L1** in $(\mathbf{L1})_2Mn_2(CO)_6$.



9) The emission spectra for the light source:



The emission spectra for 6 W blue LEDs

References:

[1] B. T. V. Srinivas, V. S. Rawat, K. Konda, B. Sreedhar, *Adv. Synth. Catal.* **2014**, *356*, 805.

[2] T. Miura, D. Moriyama, S. Miyakawa, M. Murakami, *Chem. Lett.* **2020**, *49*, 1382.

[3] F. Wang, W. Rao, S.-Y. Wang, *J. Org. Chem.* **2021**, *86*, 8970.

[4] X.-S. Zhou, Y. Cheng, J. Chen, X.-Y. Yu, W.-J. Xiao, J.-R. Chen, *ChemCatChem* **2019**, *11*, 5300.

[5] G-P. Lu, C. Cai, F. Chen, R.-L. Ye, B.-J. Zhou, *ACS Sustainable Chem. Eng.* **2016**, *4*, 1804.

[6] W. Liu, H. Li, H. Qin, W. Zhao, C. Zhou, S. Jiang, C. Yang, *Chem. Res. Chin. Univ.* **2017**, *33*, 213.

[7] J. He, G. Chen, B. Zhang, Y. Li, J.-R. Chen, W.-J. Xiao, F. Liu, C. Li, *Chem* **2020**, *6*, 1149.

[8] D. Li, T.-K. Ma, R. J. Scott, J. D. Wilden, *Chem. Sci.* **2020**, *11*, 5333.

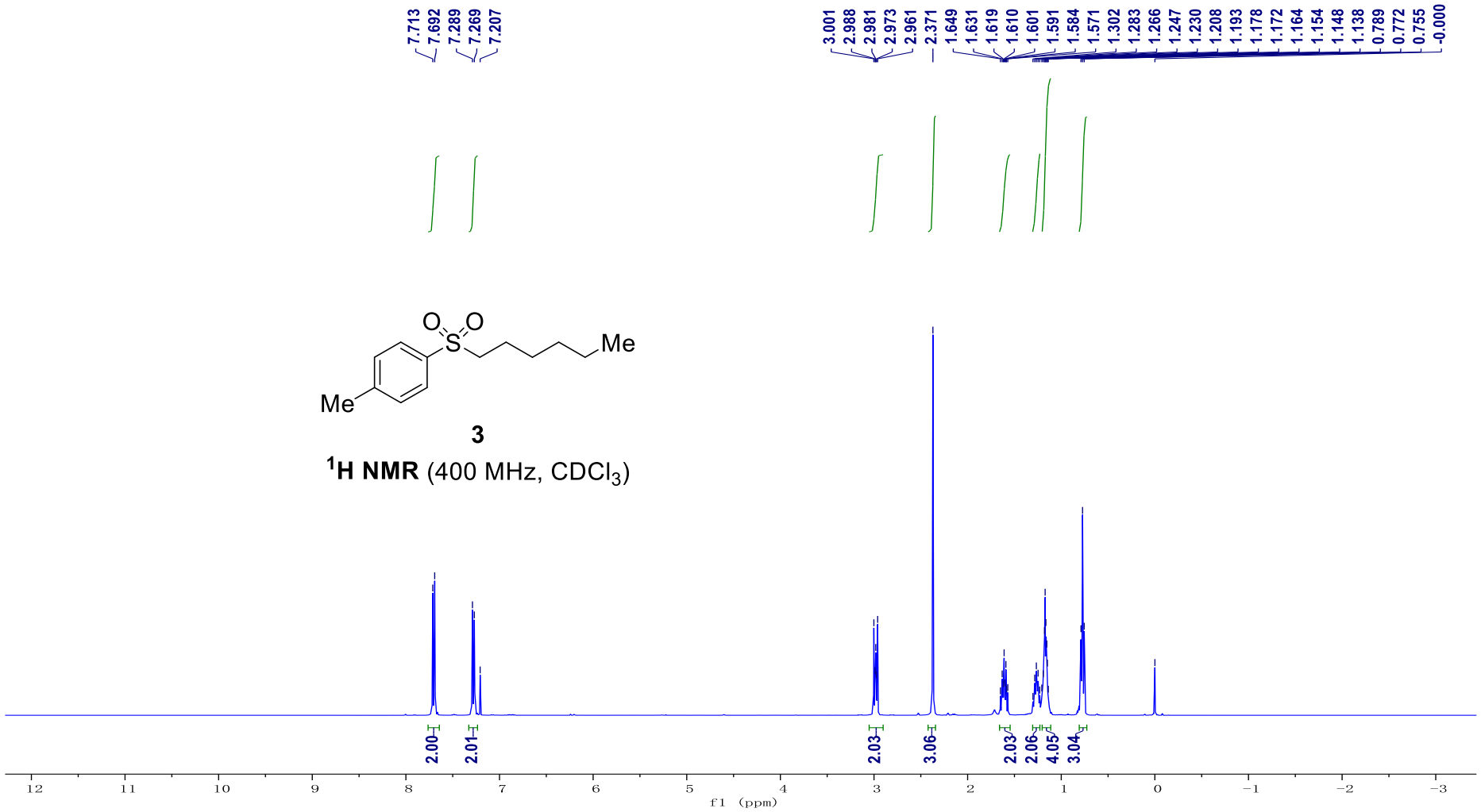
[9] Y. Fu, Q.-S. Xu, Q.-Z. Li, Z. Du, K.-H. Wang, D. Huang, Y. Hu, *Org. Biomol. Chem.* **2017**, *15*, 2841.

[10] S. Chen, Y. Li, M. Wang, X. Jiang, *Green Chem.* **2020**, *22*, 322.

[11] S. Luo, M. Peng, P. Querard, C.-C. Li, C.-J. Li, *J. Org. Chem.* **2021**, *86*, 13111.

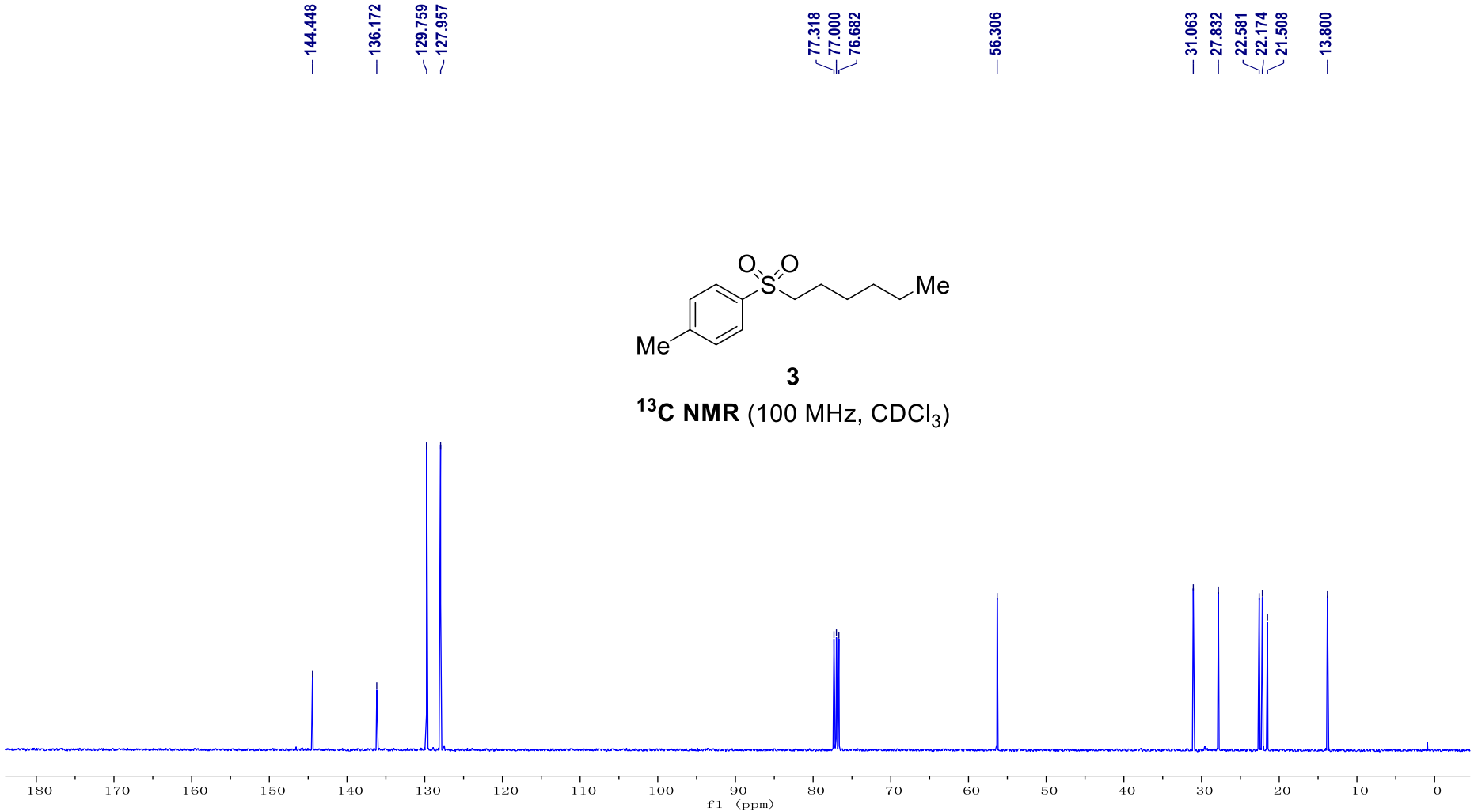
[12] S. M. Hell, C. F. Meyer, A. Misale, J. B. I. Sap, K. E. Christensen, M. C. Willis, A. A. Trabanco, V. Gouverneur, *Angew. Chem. Int. Ed.* **2020**, *59*, 11620.

[13] P. Das, S. Das, K. Varalaxmi, R. Jana, *Adv. Synth. Catal.* **2021**, *363*, 575.



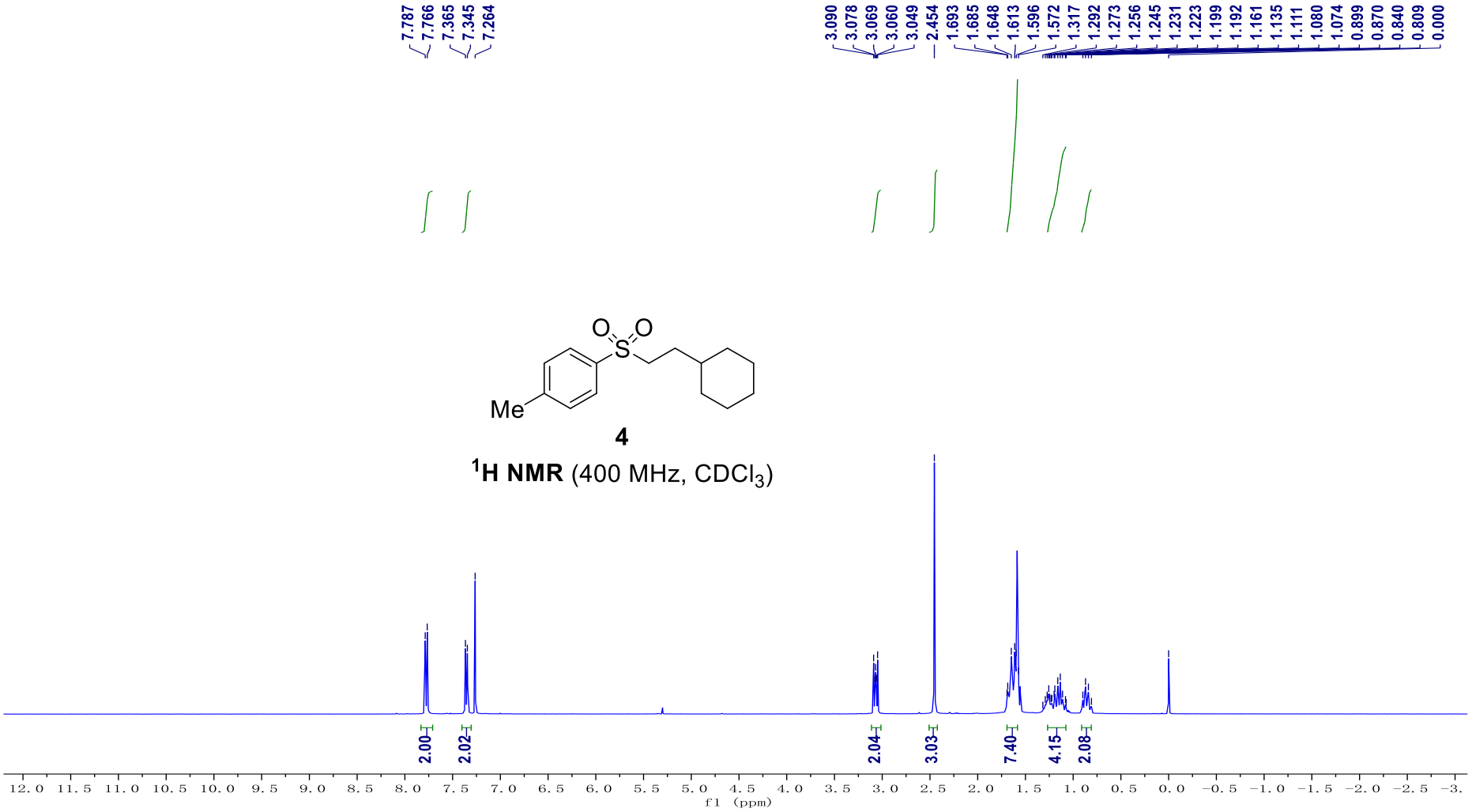
3

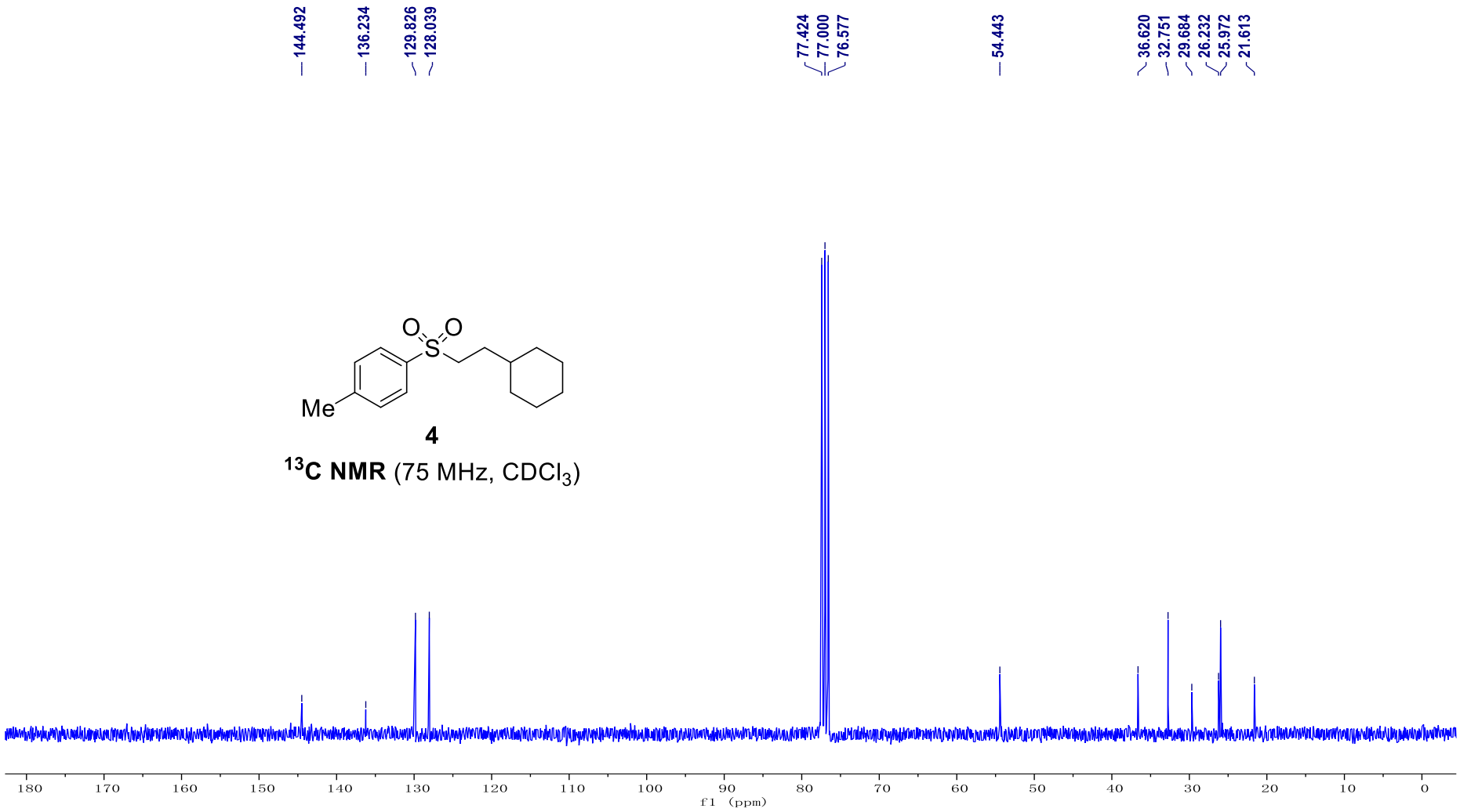
^{1}H NMR (400 MHz, $CDCl_3$)

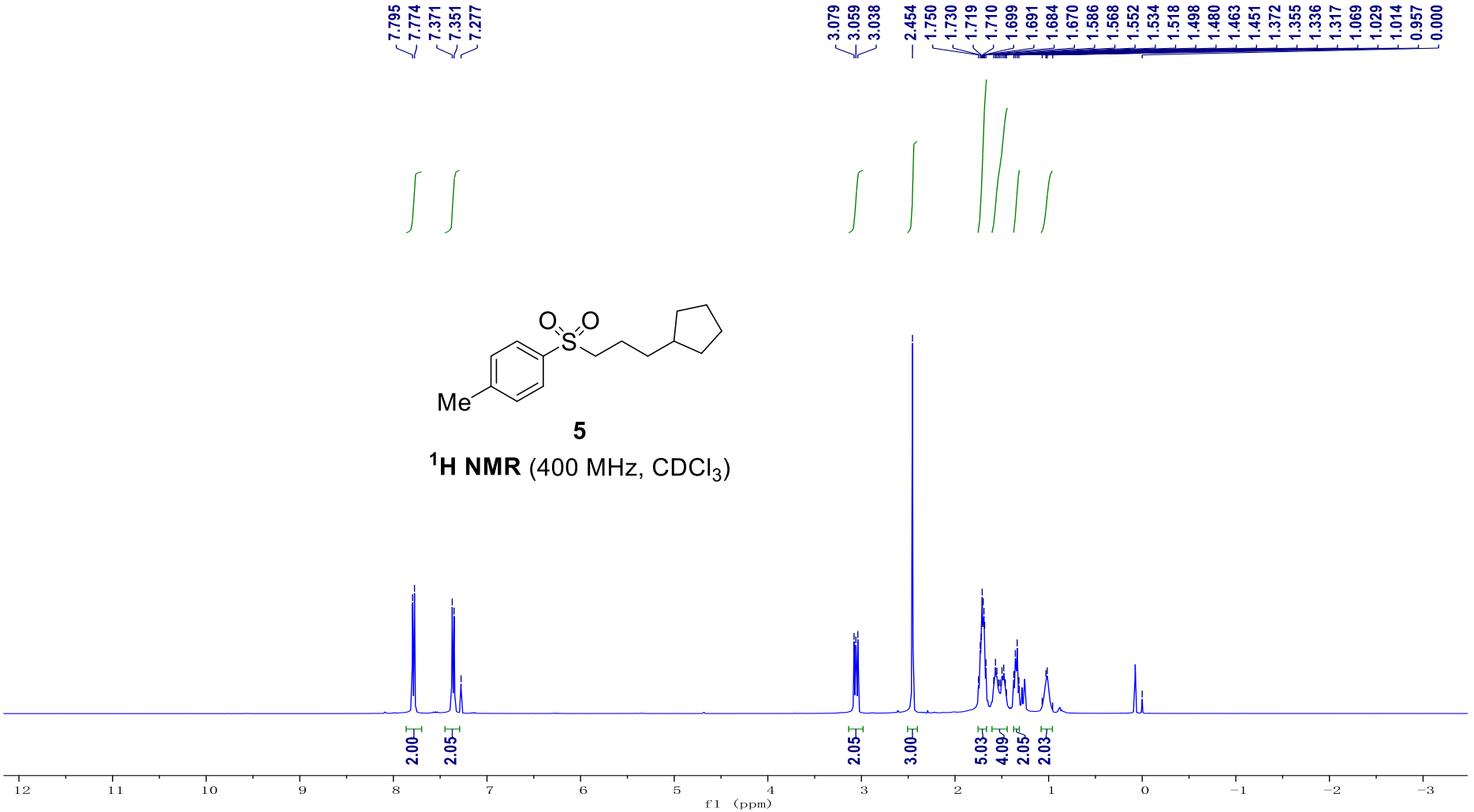


3

^{13}C NMR (100 MHz, $CDCl_3$)

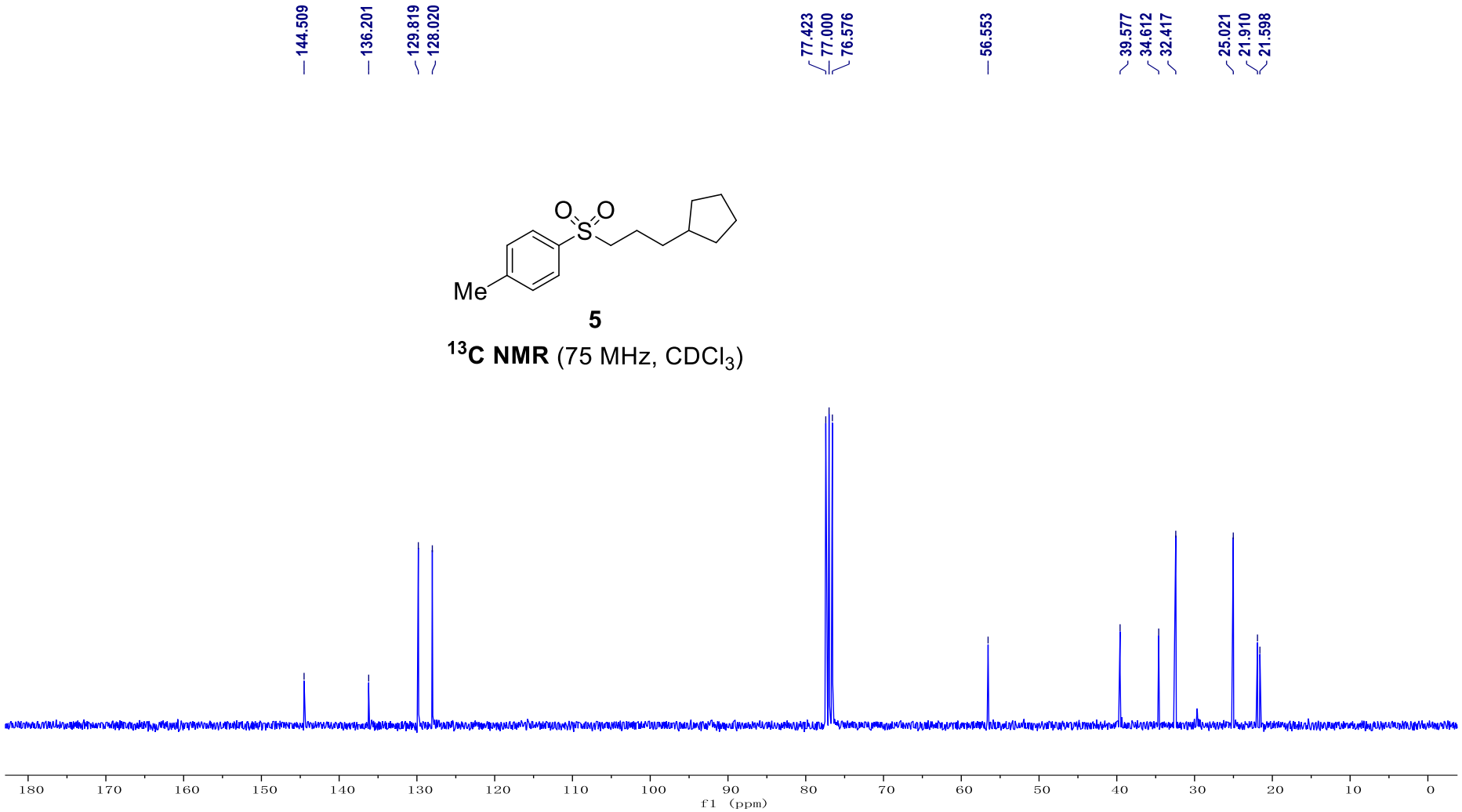

7.787
7.766
7.365
7.345
7.264
3.090
3.078
3.069
3.060
3.049
2.454
1.693
1.685
1.648
1.613
1.596
1.572
1.317
1.292
1.273
1.256
1.245
1.231
1.223
1.199
1.192
1.161
1.135
1.111
1.080
1.074
0.899
0.870
0.840
0.809
0.000
O
O
S
Me
4
1H NMR (400 MHz, CDCl3)
2.00
2.02
2.04
3.03
7.40
4.15
2.08
f1 (ppm)


144.492
136.234
129.826
128.039
77.424
77.000
76.577
54.443
36.620
32.751
29.684
26.232
25.972
21.613
O
O
S
Me
4
13C NMR (75 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



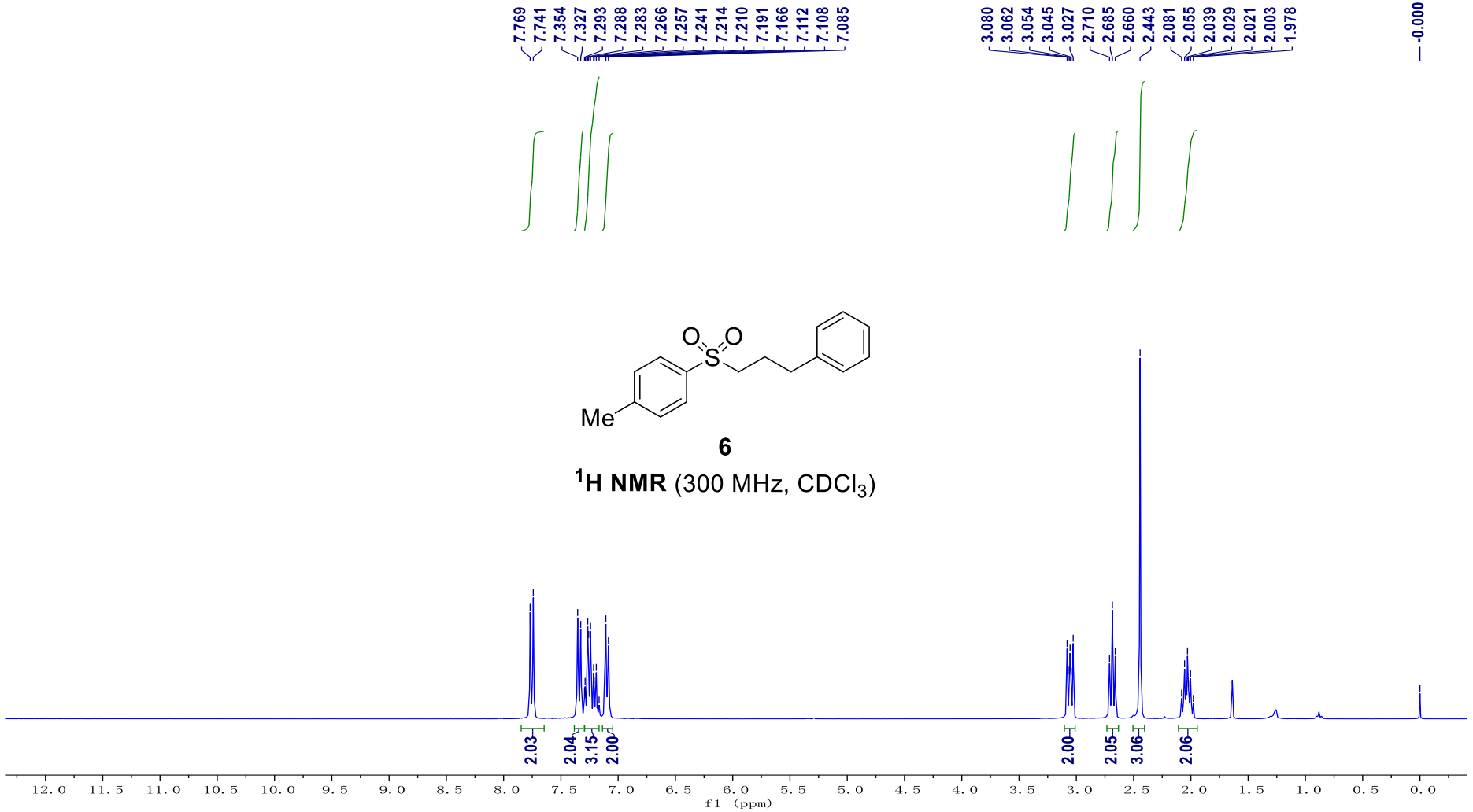
5

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



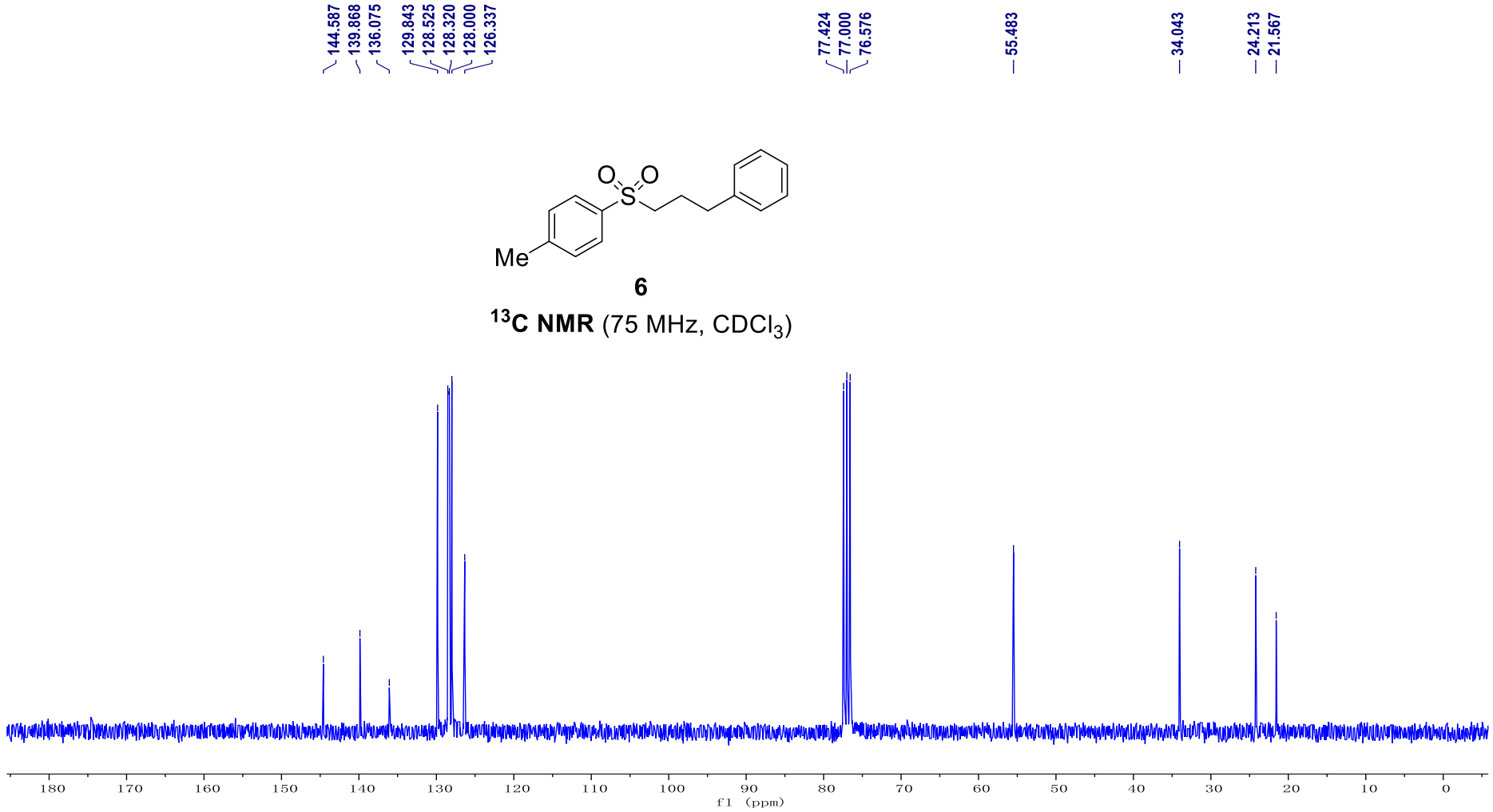
5

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



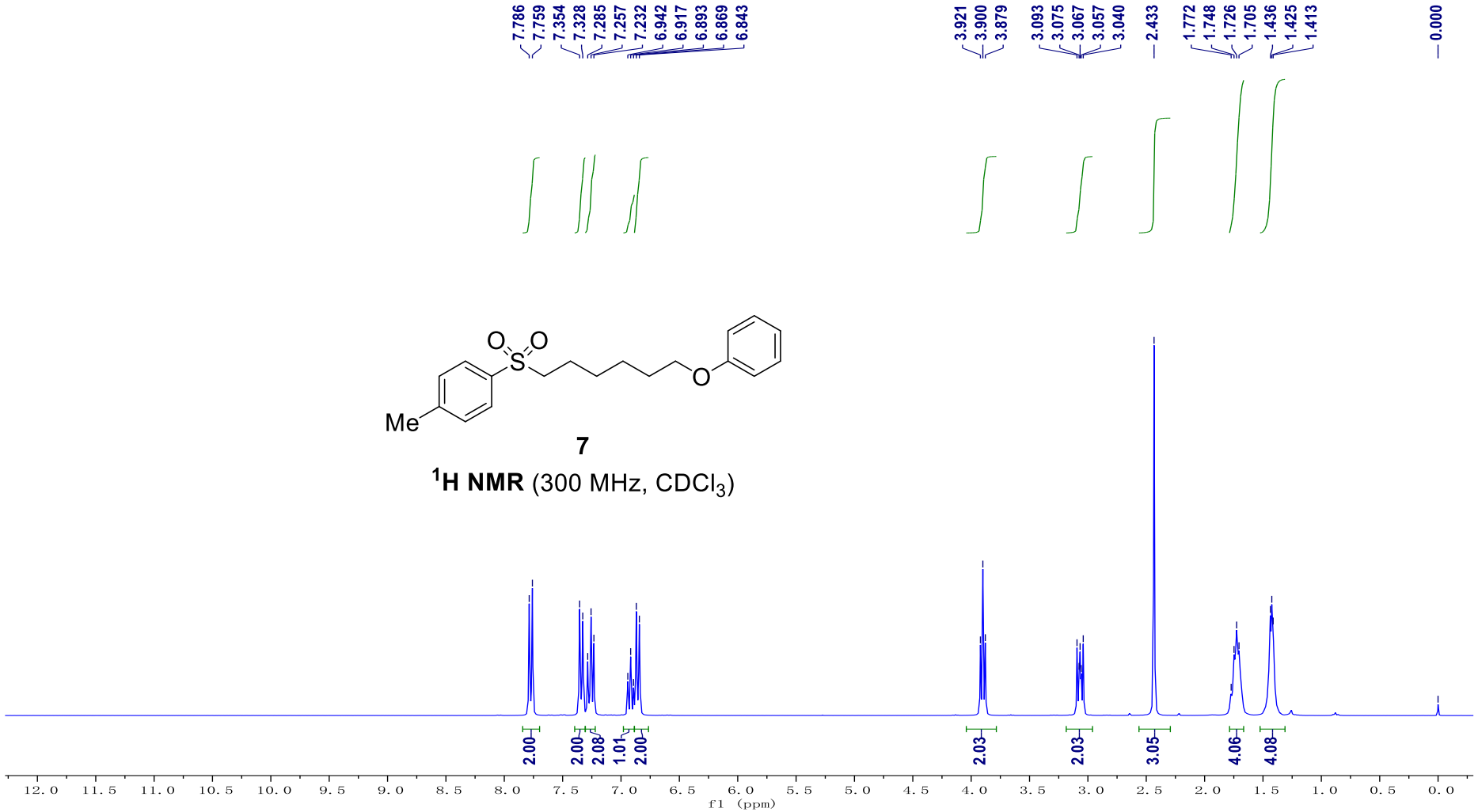
6

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



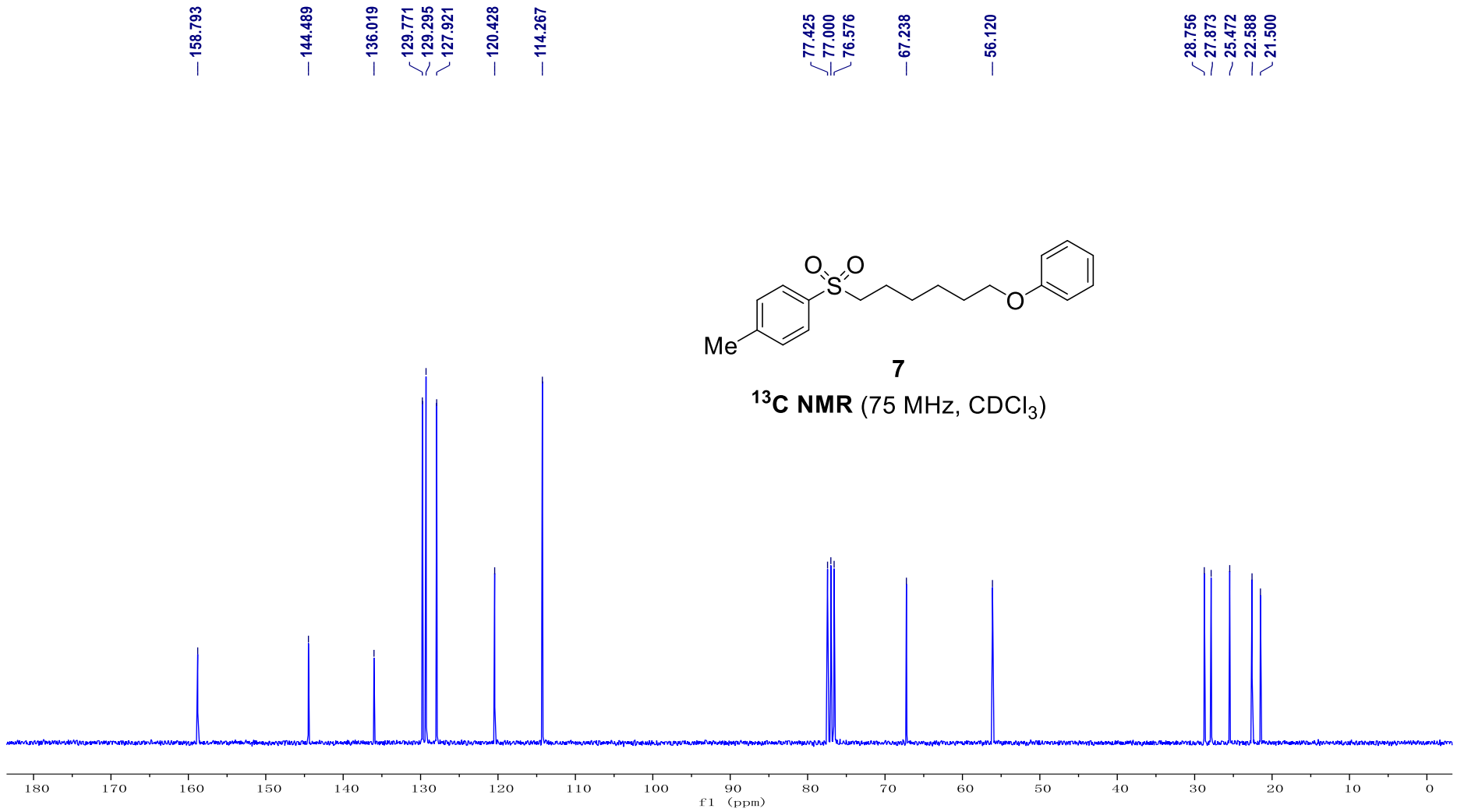
6

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



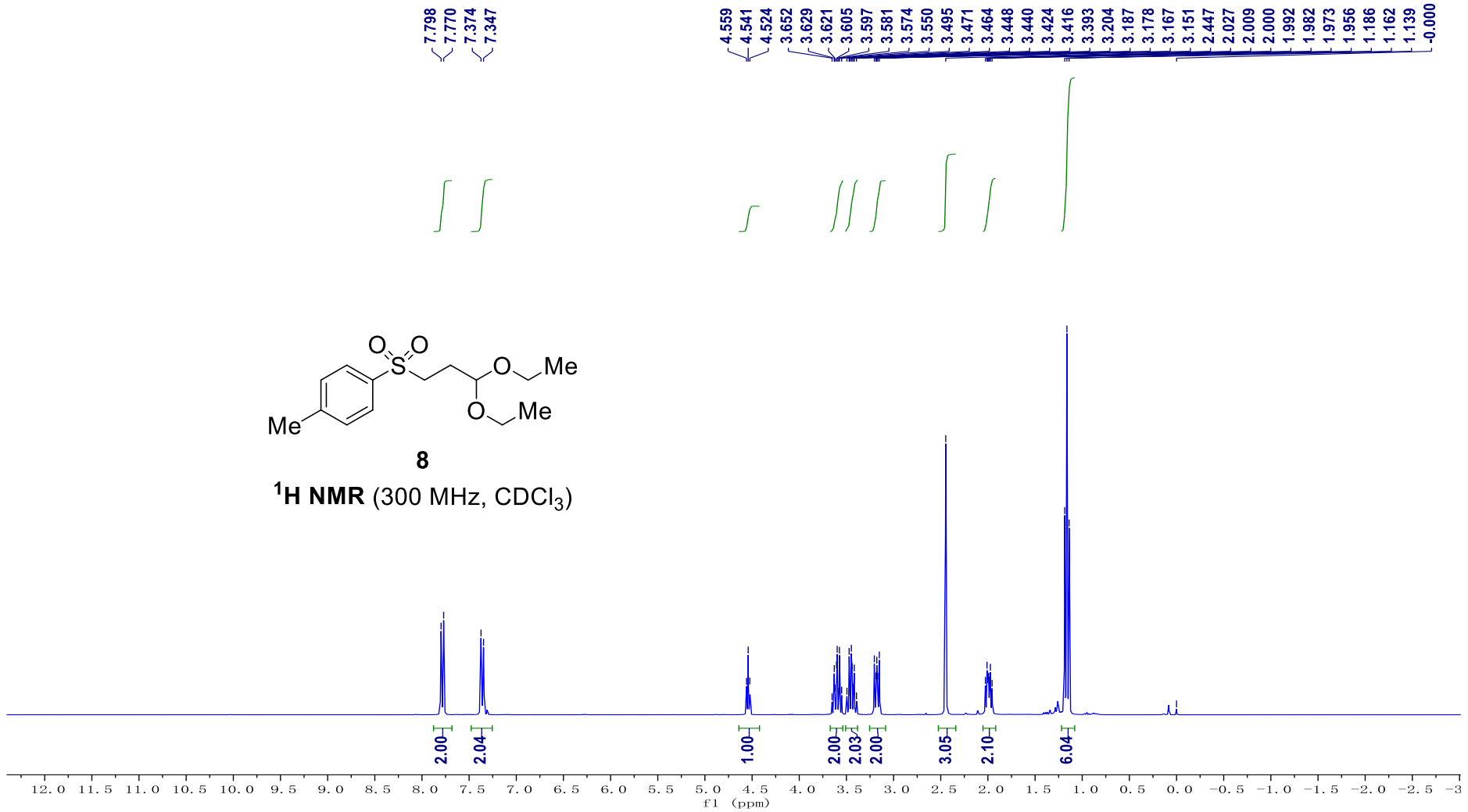
7

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



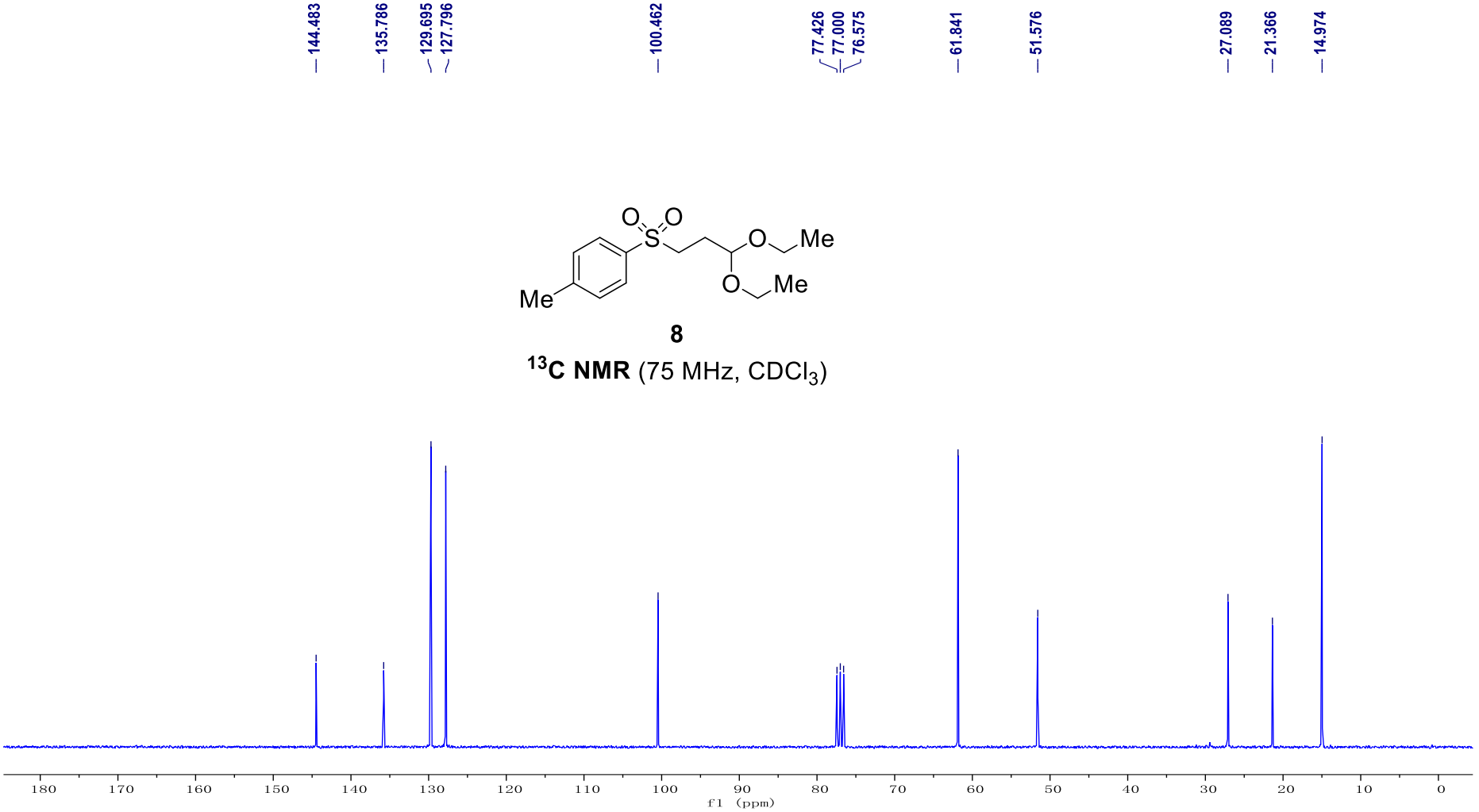
7

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



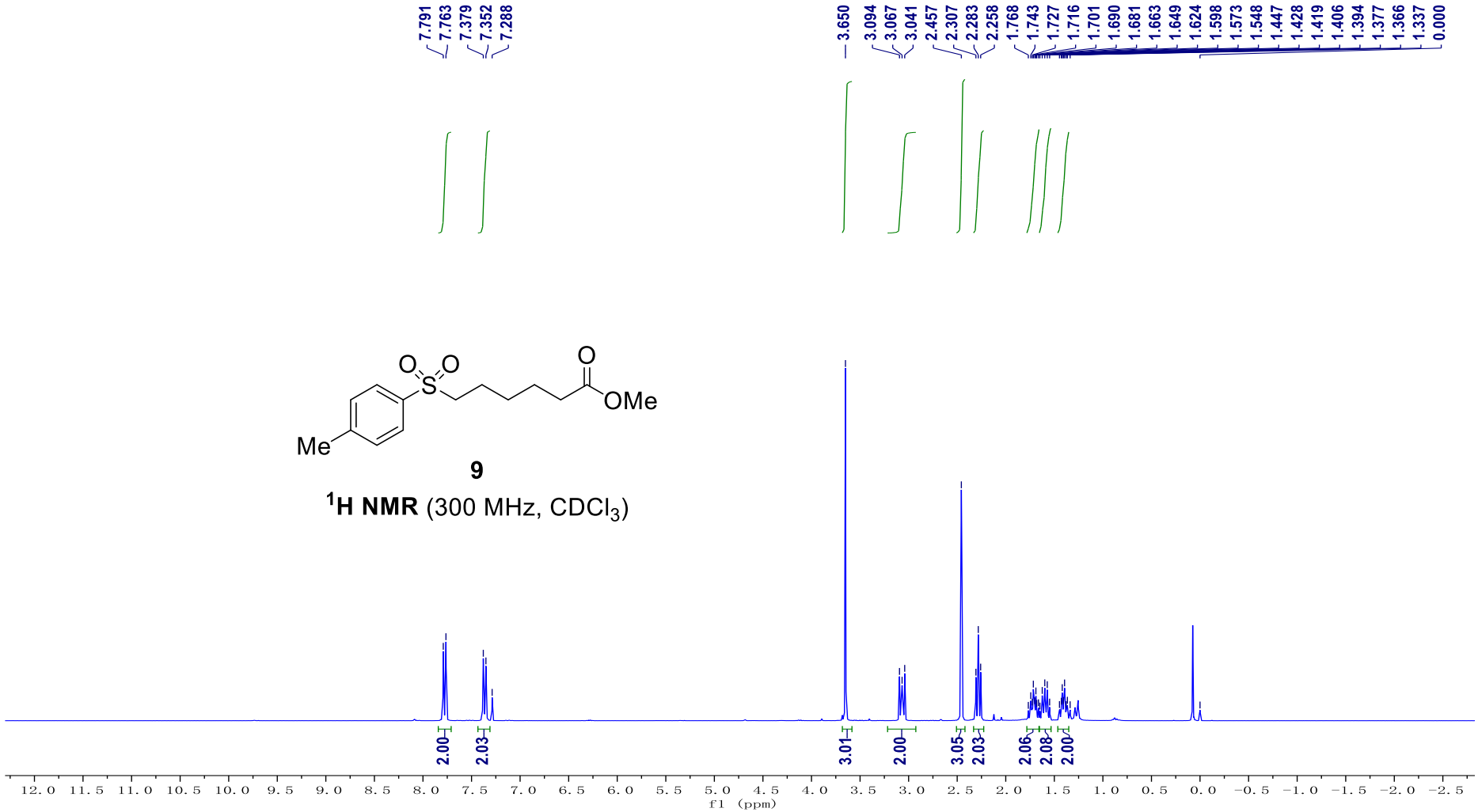
8

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



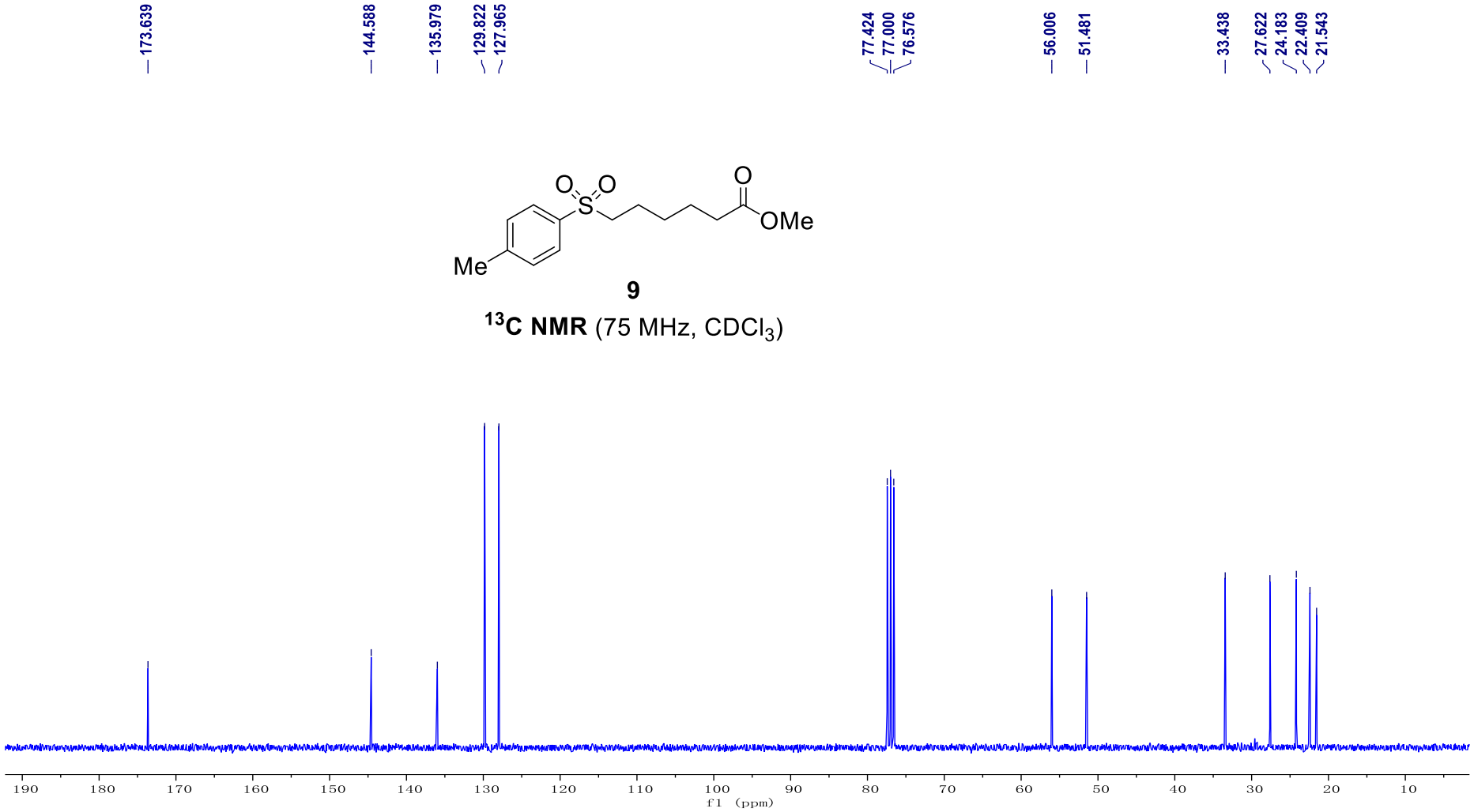
8

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



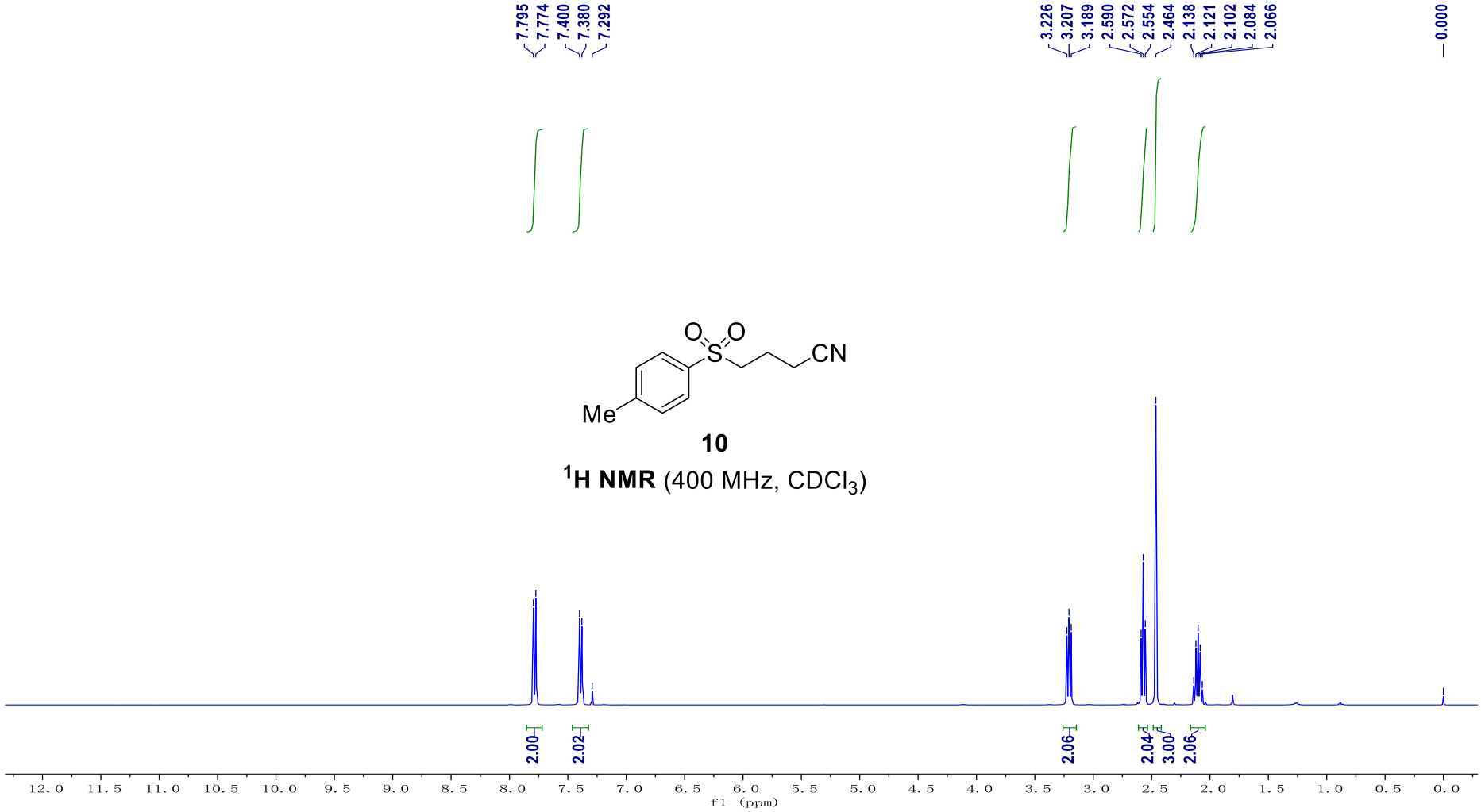
9

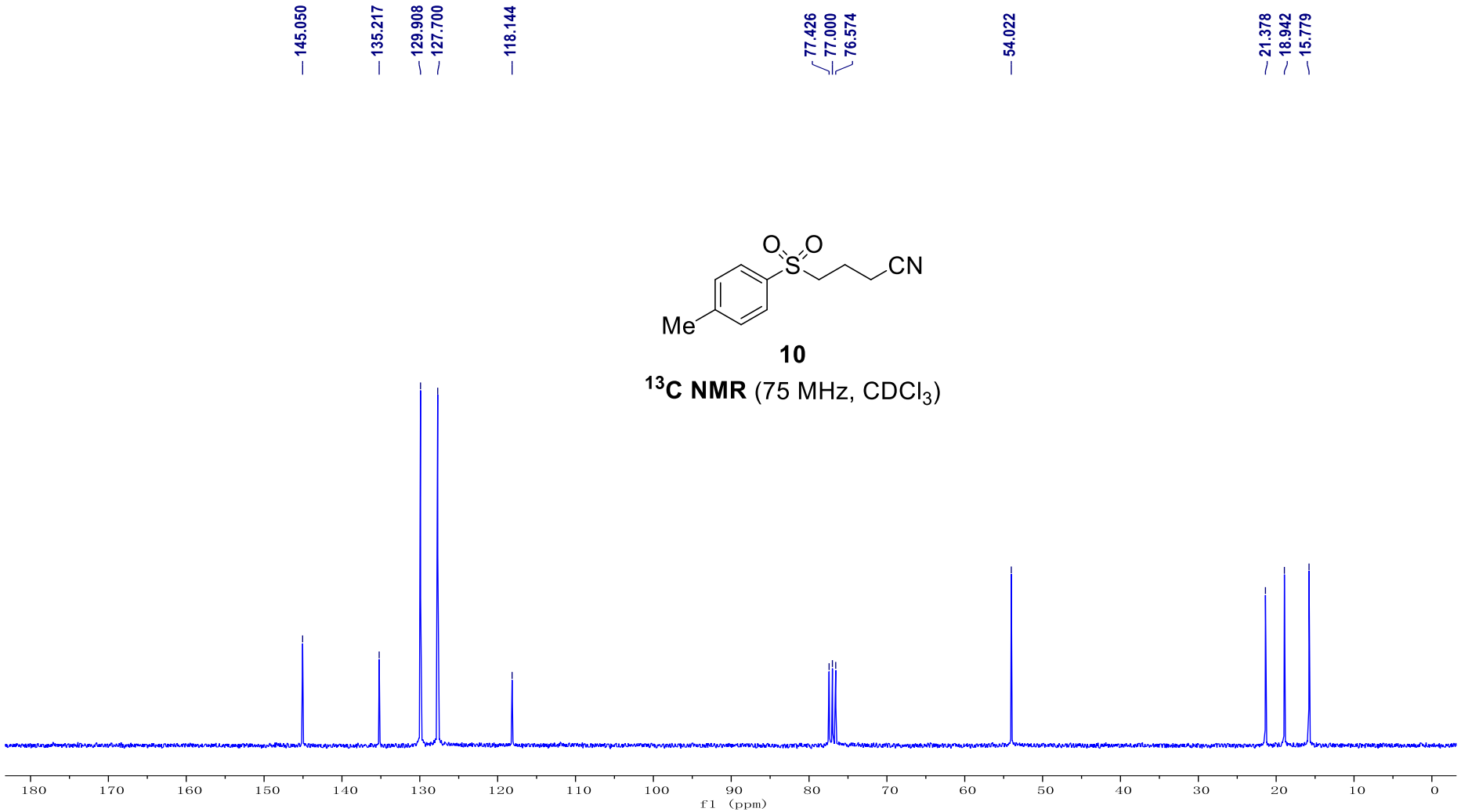
^{1}H NMR (300 MHz, $CDCl_3$)

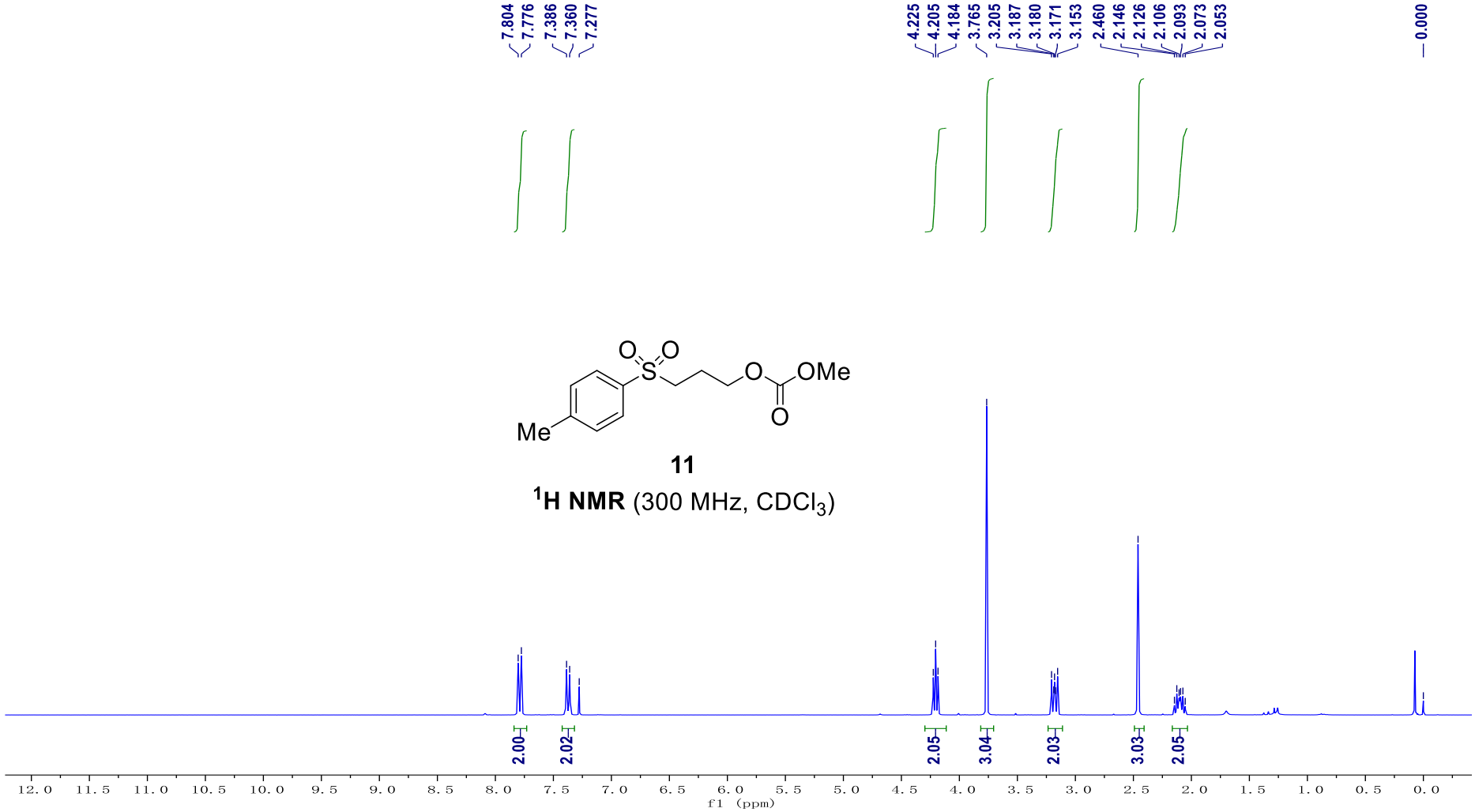


9

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

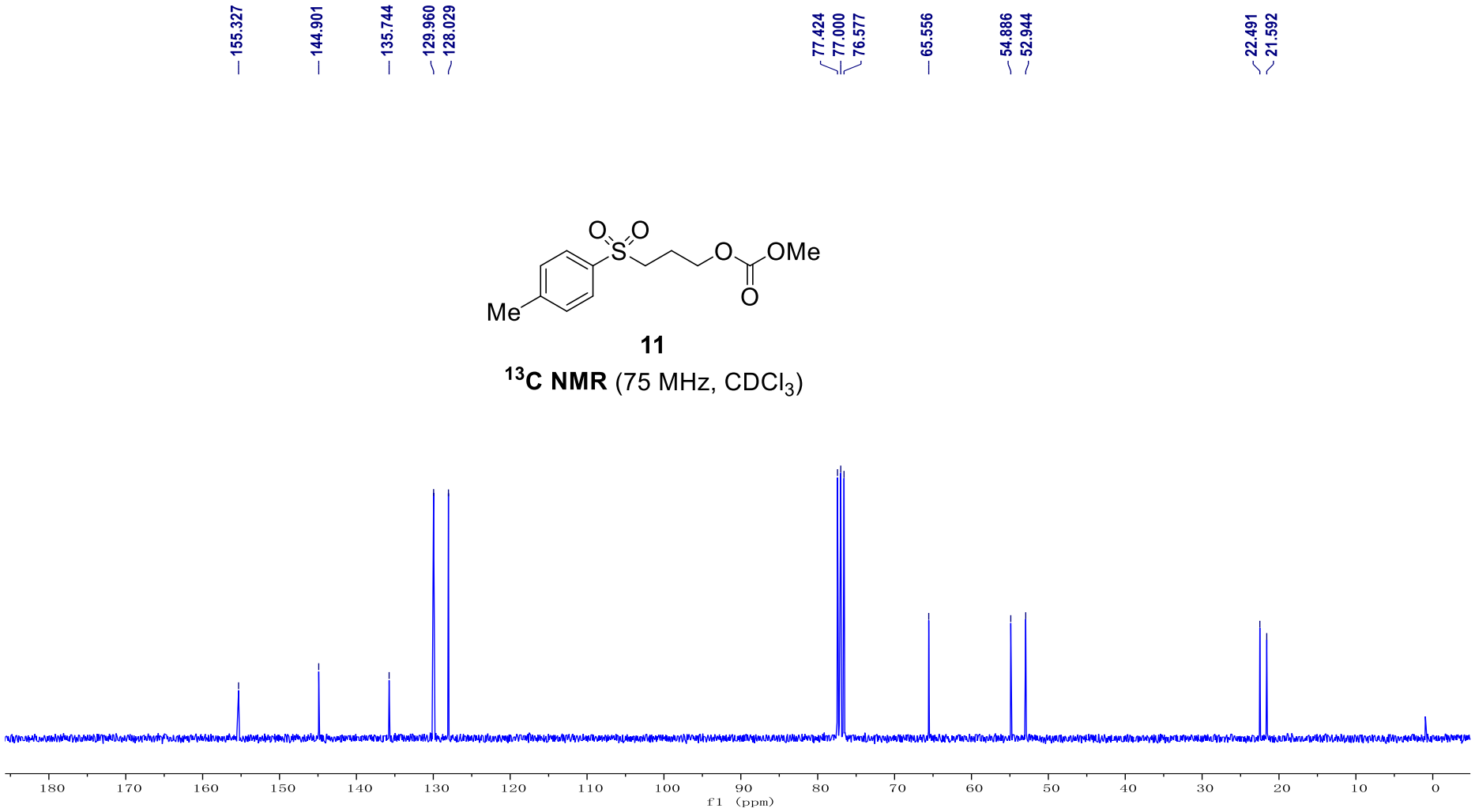

7.795
7.774
7.400
7.380
7.292
3.226
3.207
3.189
2.590
2.572
2.554
2.464
2.138
2.121
2.102
2.084
2.066
0.000
O
O
S
CN
Me
10
1H NMR (400 MHz, CDCl3)
2.00
2.02
2.06
2.04
3.00
2.06
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.050
135.217
129.908
127.700
118.144
77.426
77.000
76.574
54.022
21.378
18.942
15.779
O
O
S
CN
Me
10
13C NMR (75 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



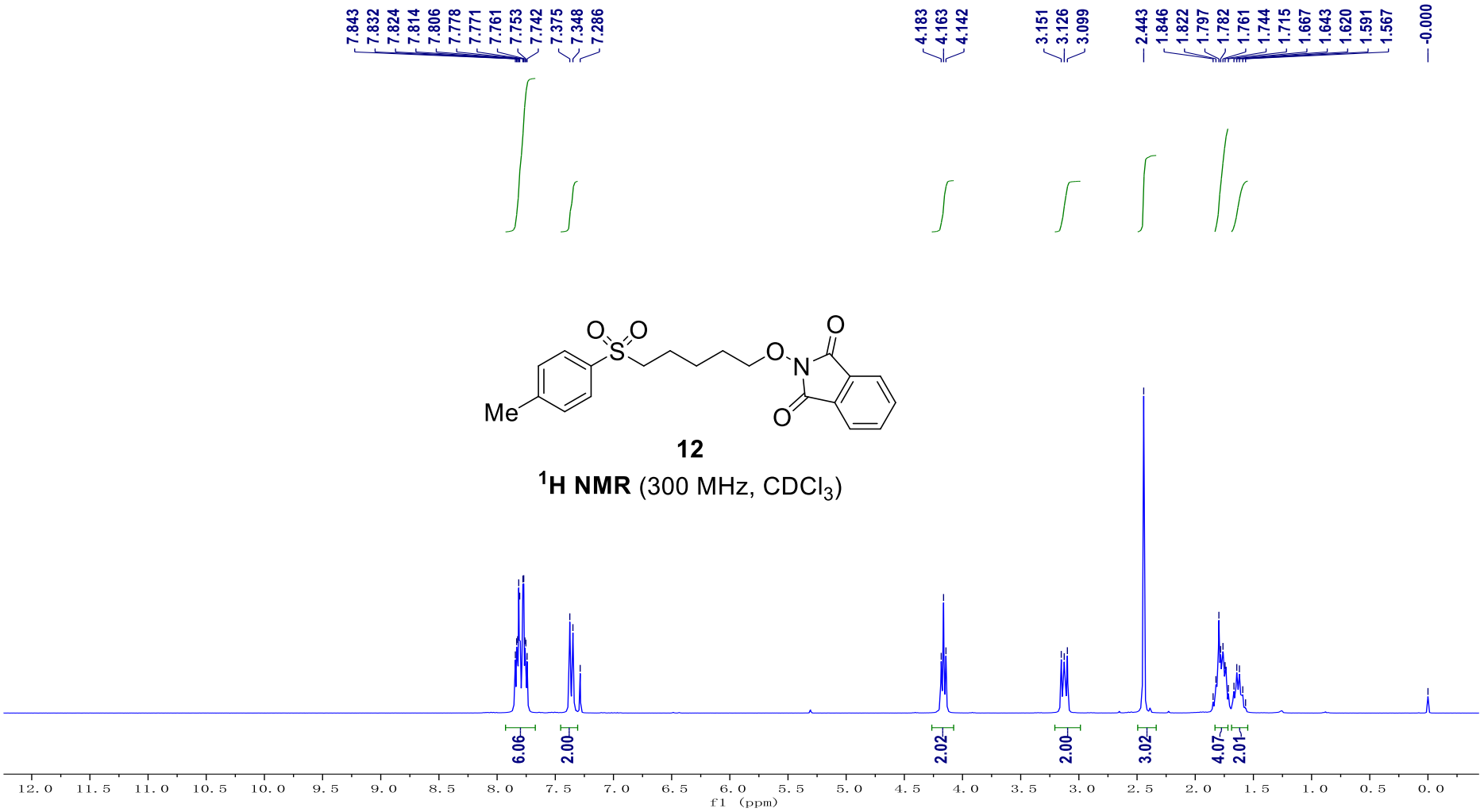
11

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



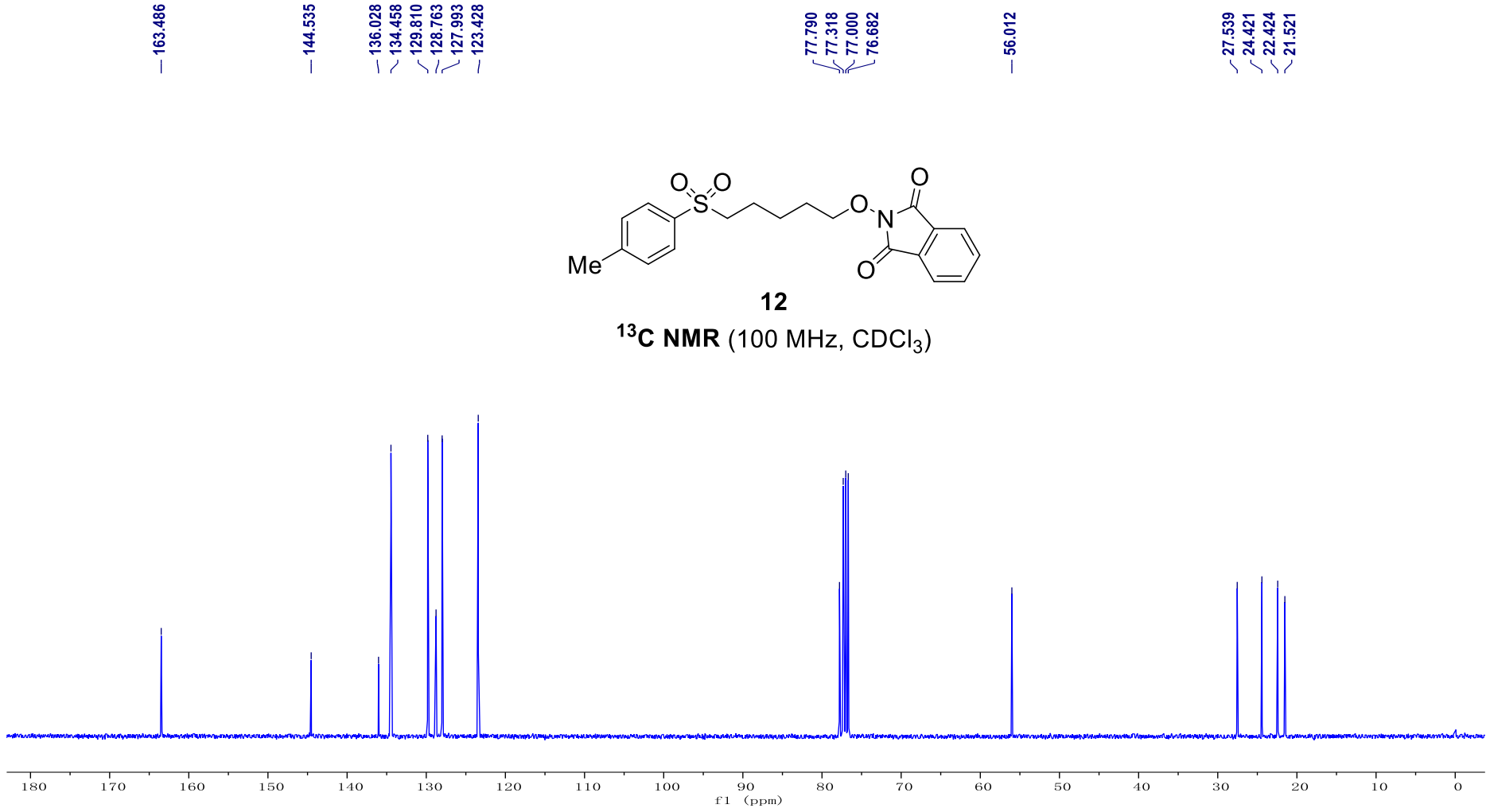
11

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



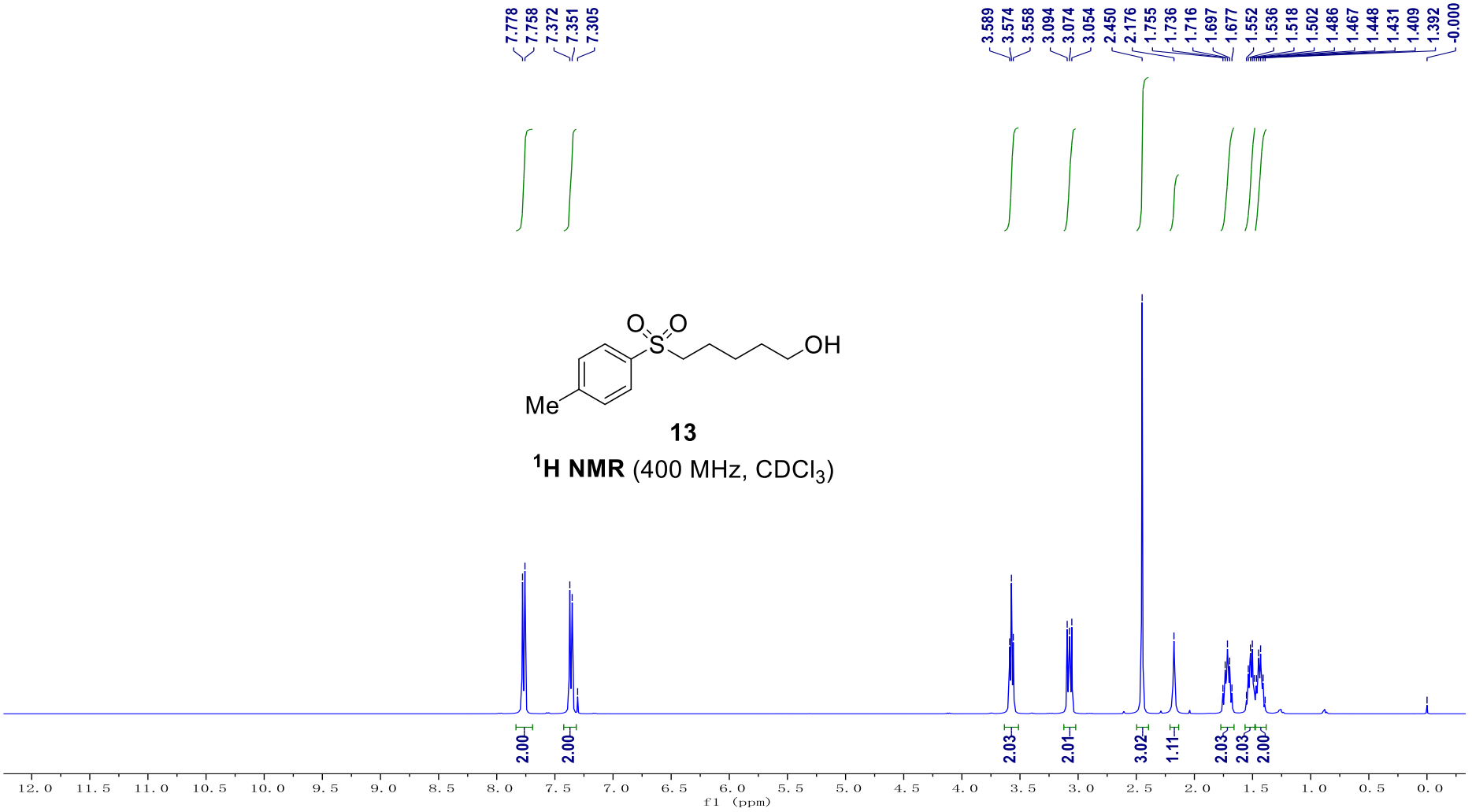
12

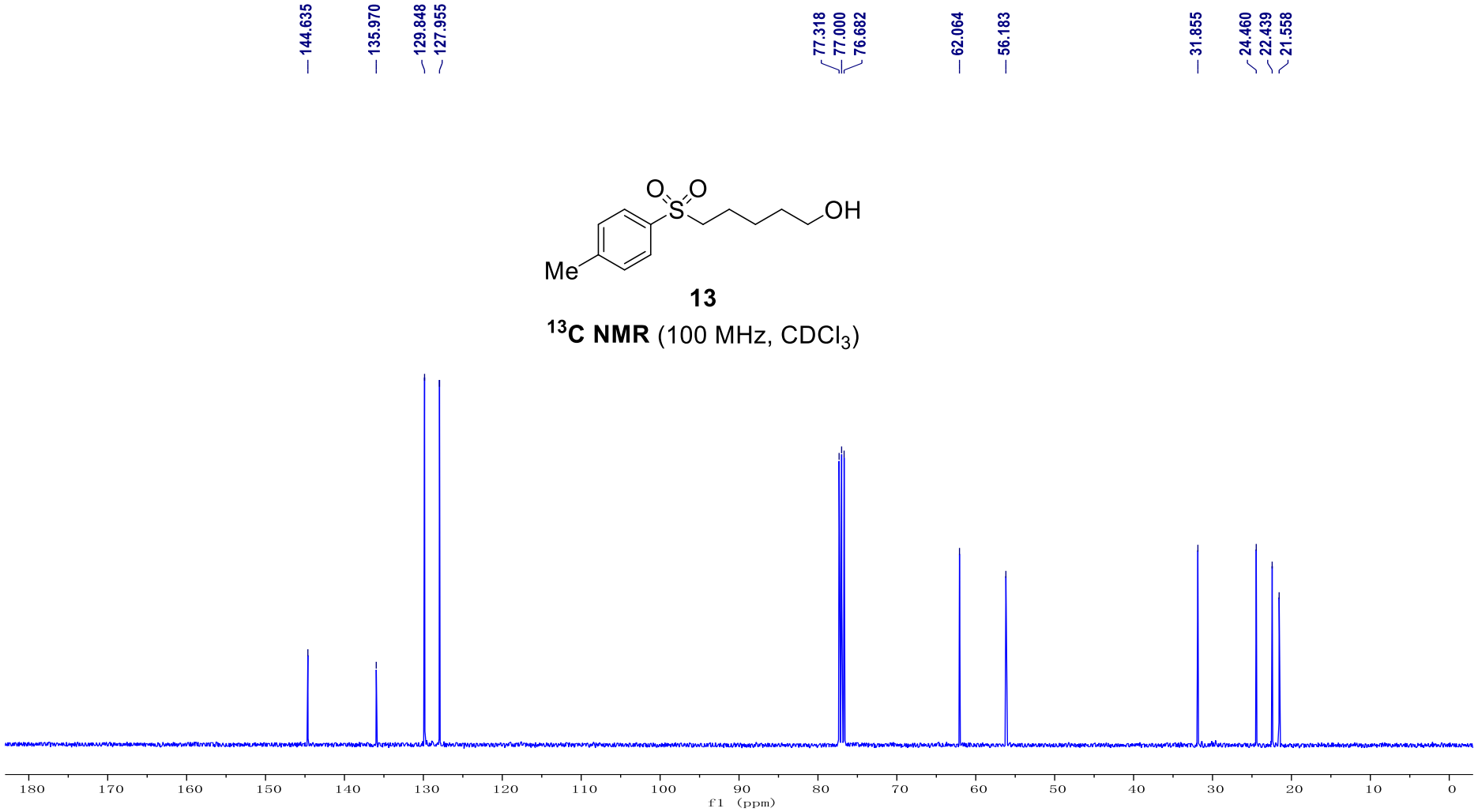
^{1}H NMR (300 MHz, $CDCl_3$)



12

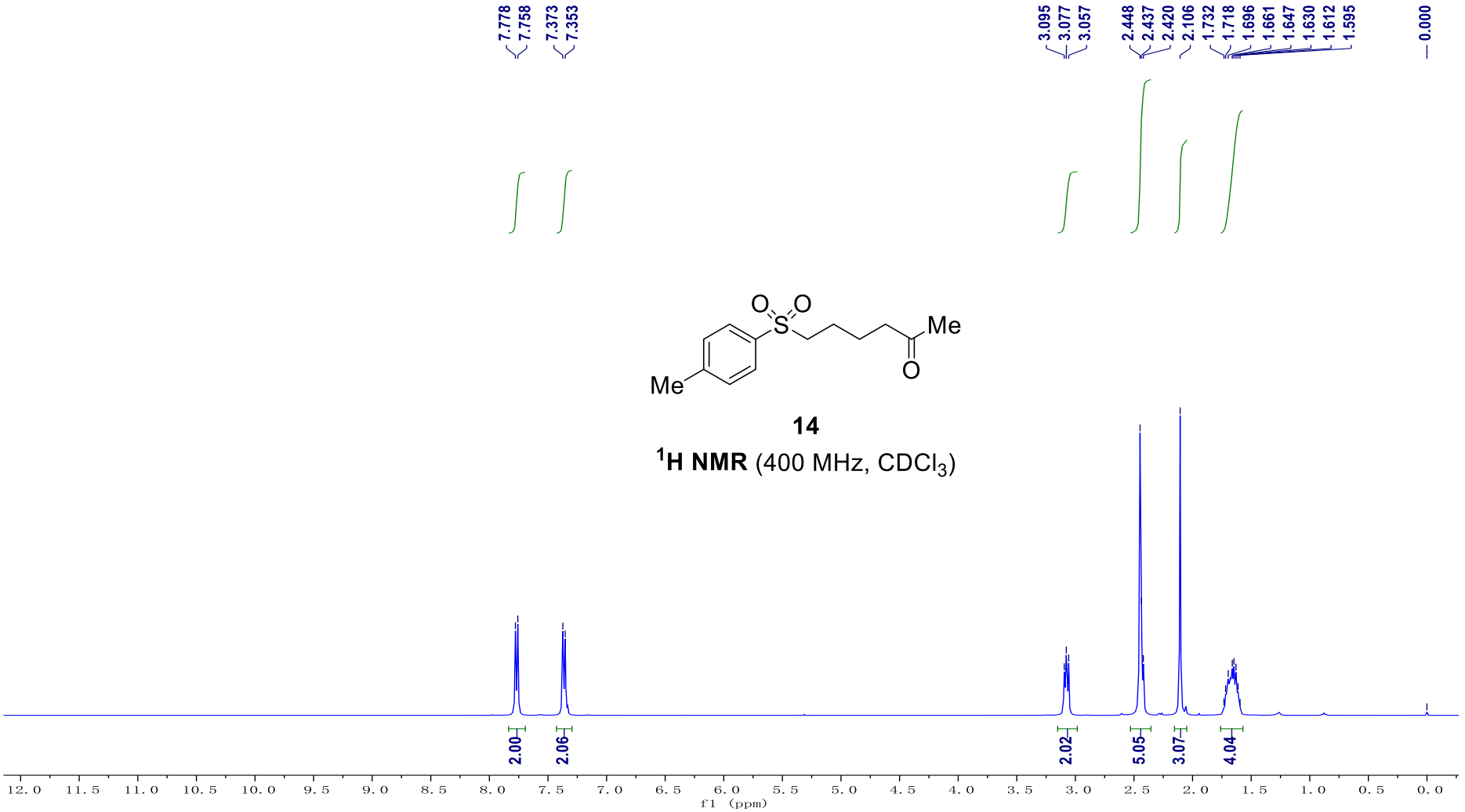
^{13}C NMR (100 MHz, $CDCl_3$)


7.778
7.758
7.372
7.351
7.305
3.589
3.574
3.558
3.094
3.074
3.054
2.450
2.176
1.755
1.736
1.716
1.697
1.677
1.552
1.536
1.518
1.502
1.486
1.467
1.448
1.431
1.409
1.392
-0.000
O
O
S
OH
Me
13
1H NMR (400 MHz, CDCl3)
2.00
2.00
2.03
2.01
3.02
1.11
2.03
2.03
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



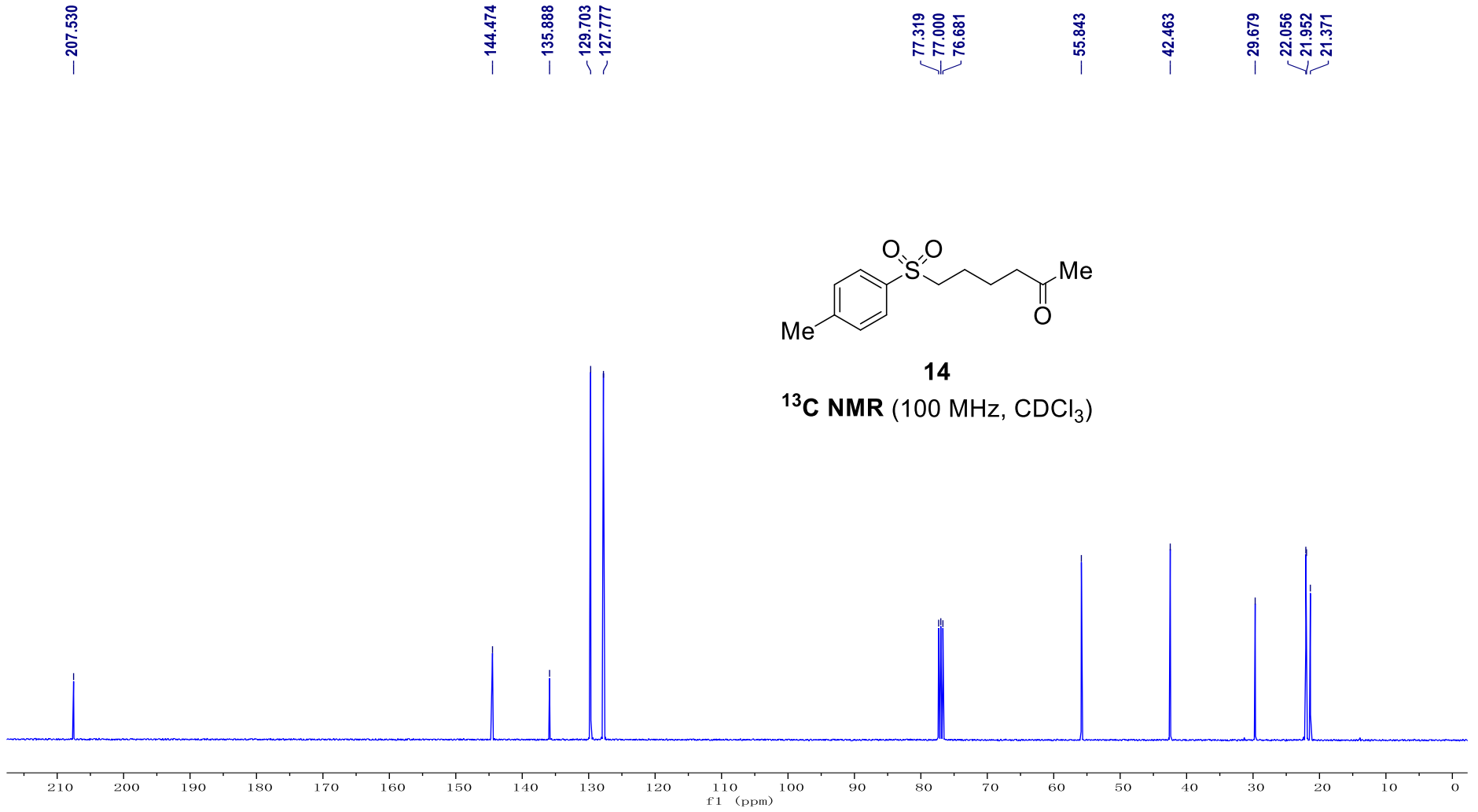
13

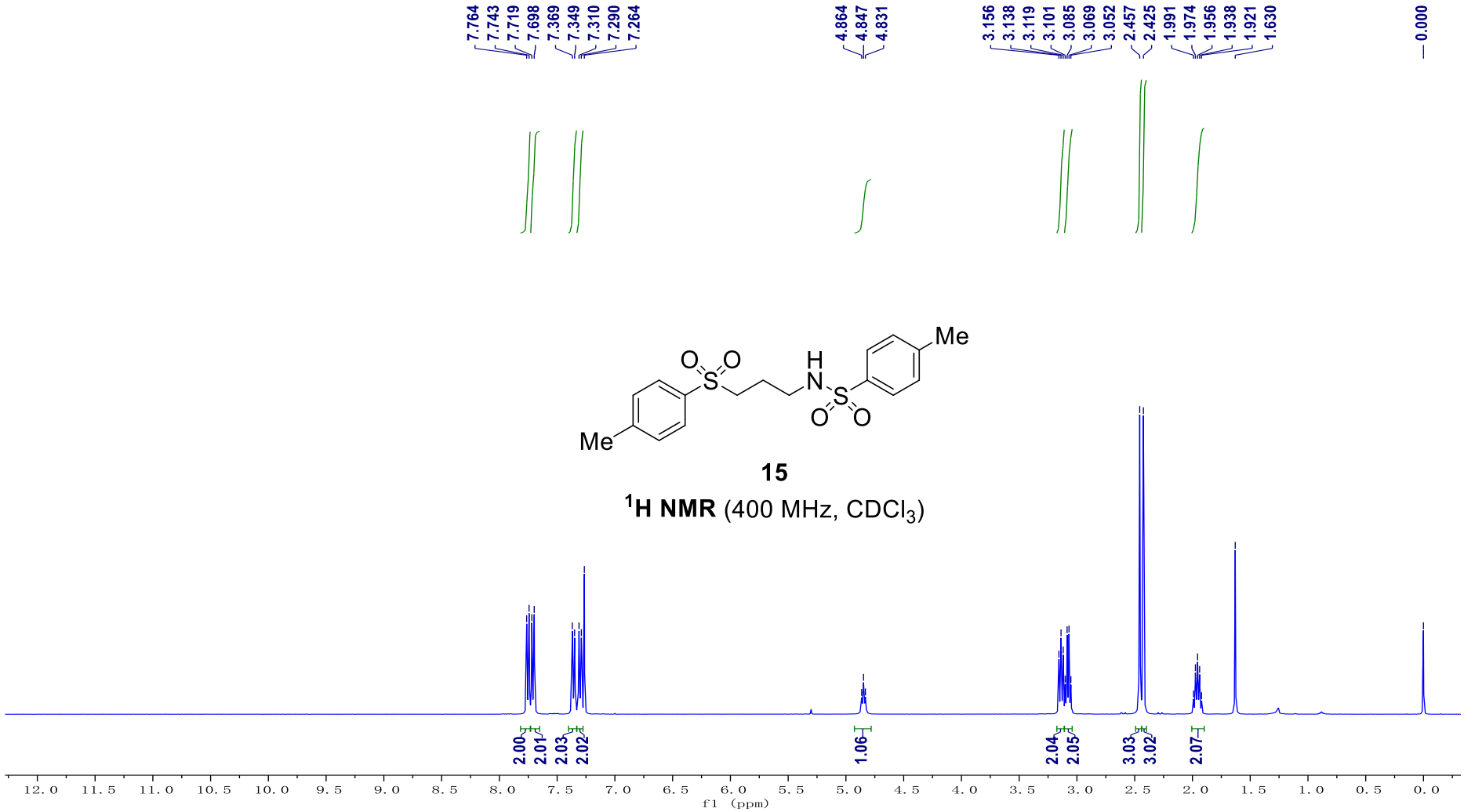
^{13}C NMR (100 MHz, $CDCl_3$)

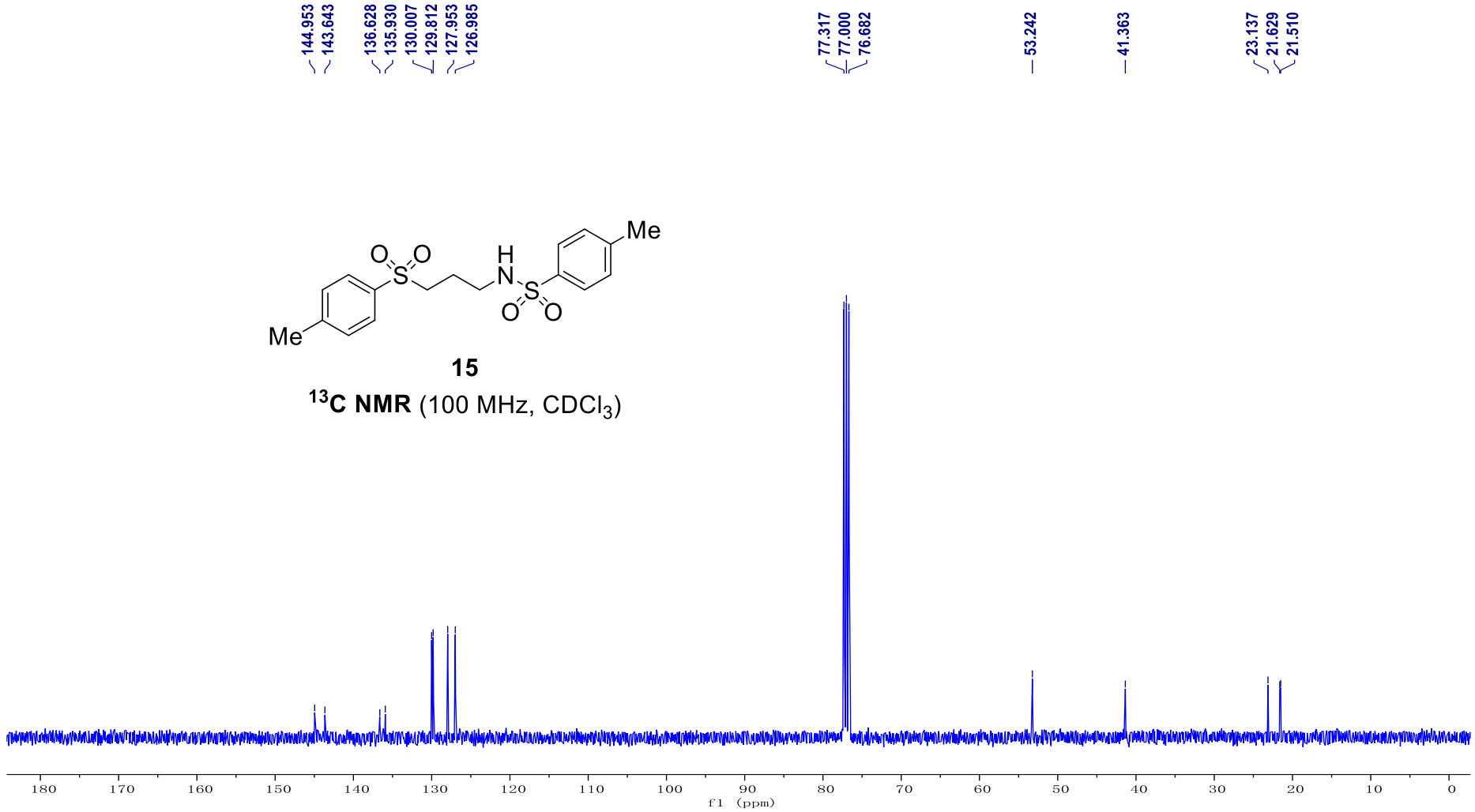


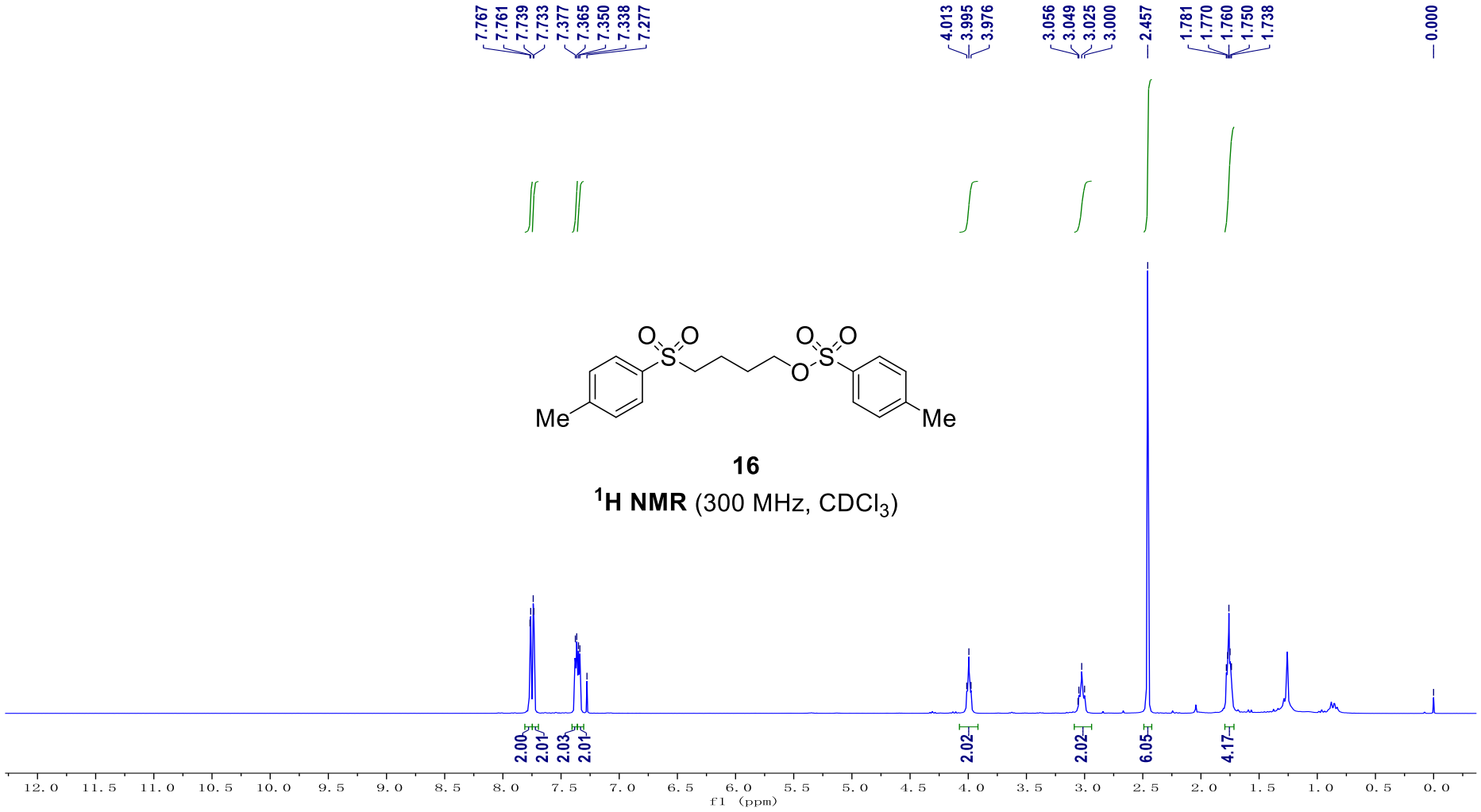
14

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


207.530
144.474
135.888
129.703
127.777
77.319
77.000
76.681
55.843
42.463
29.679
22.056
21.952
21.371
O
O
S
Me
Me
O
14
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

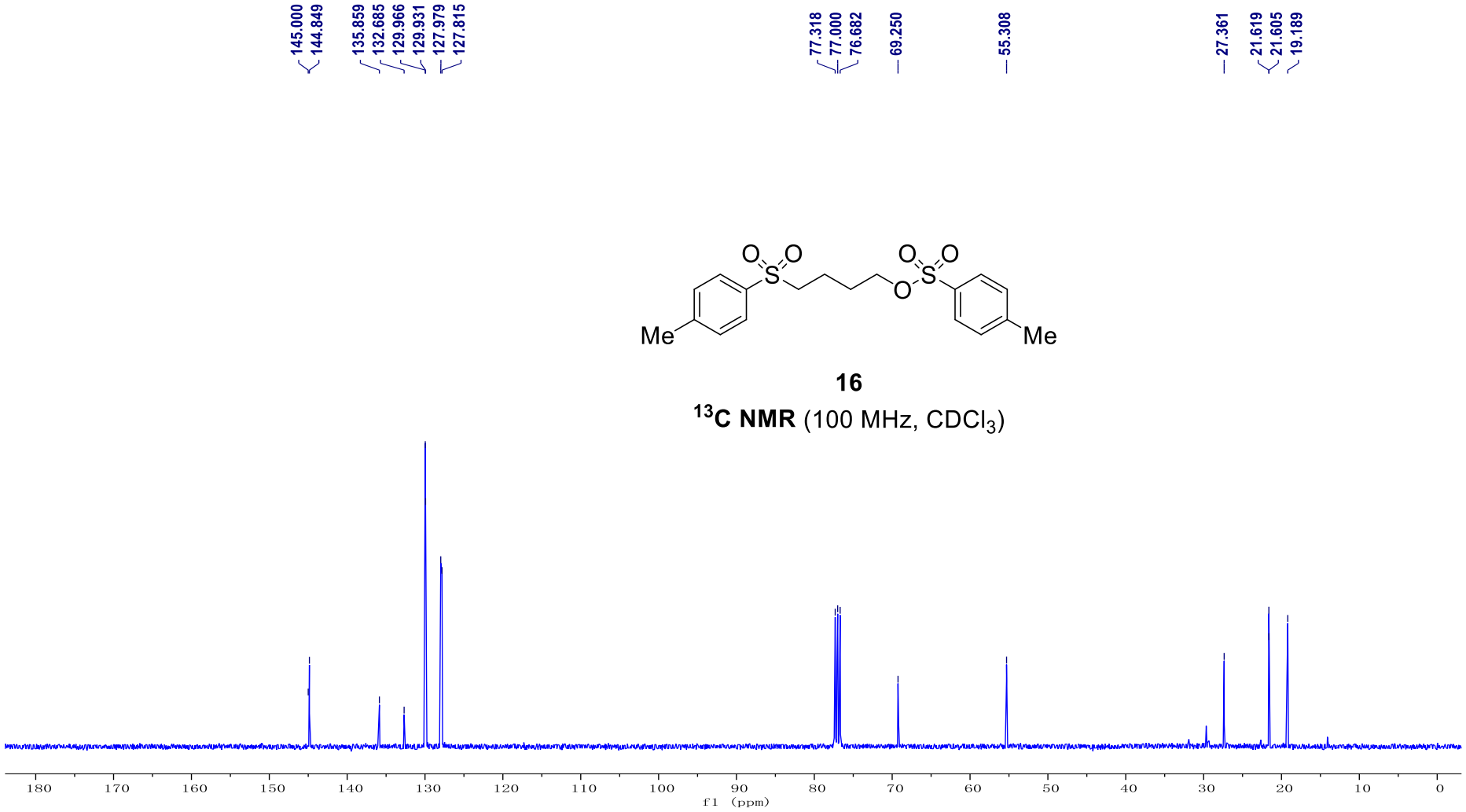

7.764
7.743
7.719
7.698
7.369
7.349
7.310
7.290
7.264
4.864
4.847
4.831
3.156
3.138
3.119
3.101
3.085
3.069
3.052
2.457
2.425
1.991
1.974
1.956
1.938
1.921
1.630
0.000
Me
H
N
O
S
Me
15
1H NMR (400 MHz, CDCl3)
2.00
2.01
2.03
2.02
1.06
2.04
2.05
3.03
3.02
2.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

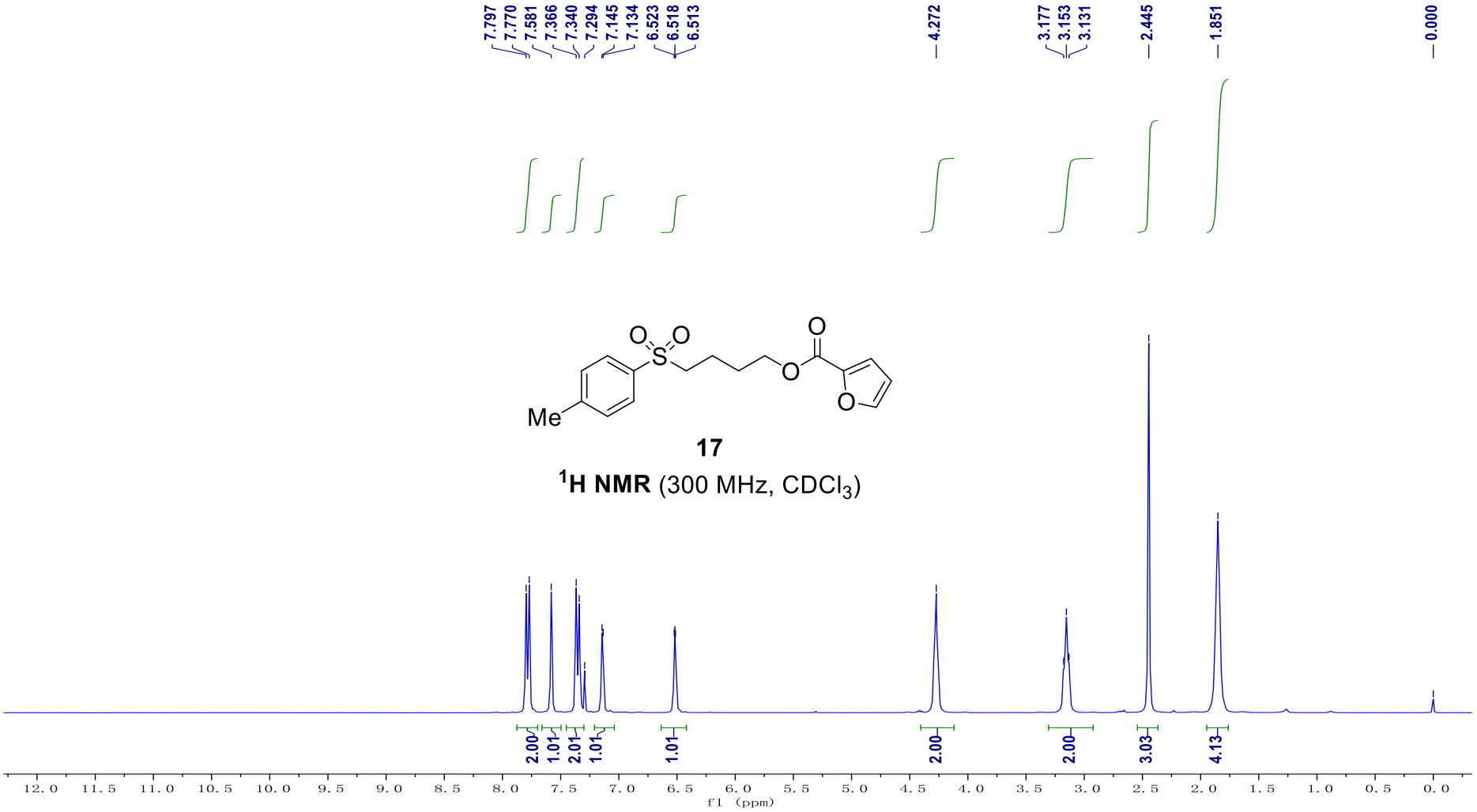

144.953
143.643
136.628
135.930
130.007
129.812
127.953
126.985
77.317
77.000
76.682
53.242
41.363
23.137
21.629
21.510
Me
Me
15
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



16

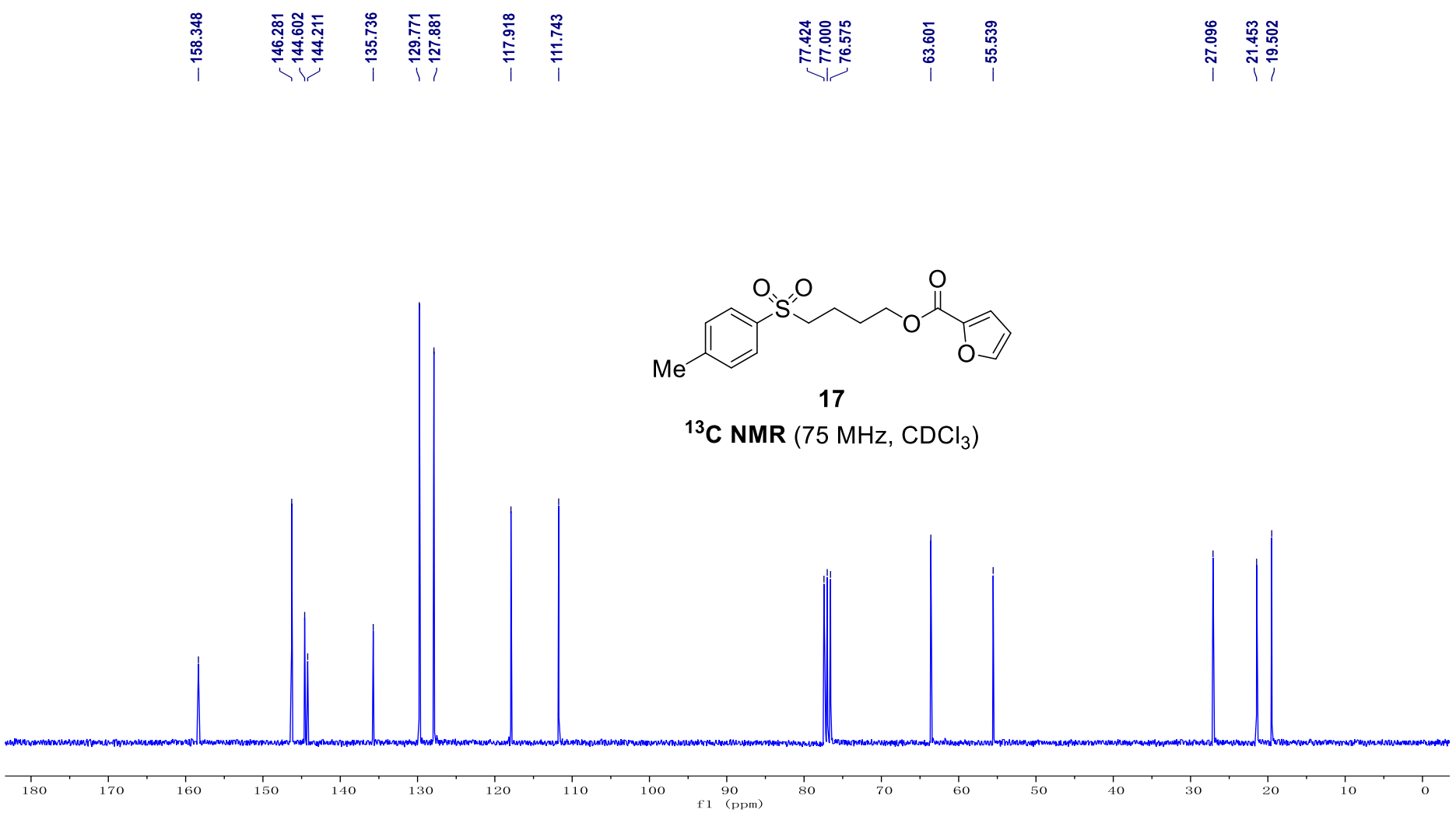
^{1}H NMR (300 MHz, $CDCl_3$)


145.000
144.849
135.859
132.685
129.966
129.931
127.979
127.815
77.318
77.000
76.682
69.250
55.308
27.361
21.619
21.605
19.189
O
O
S
O
O
S
O
Me
Me
16
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



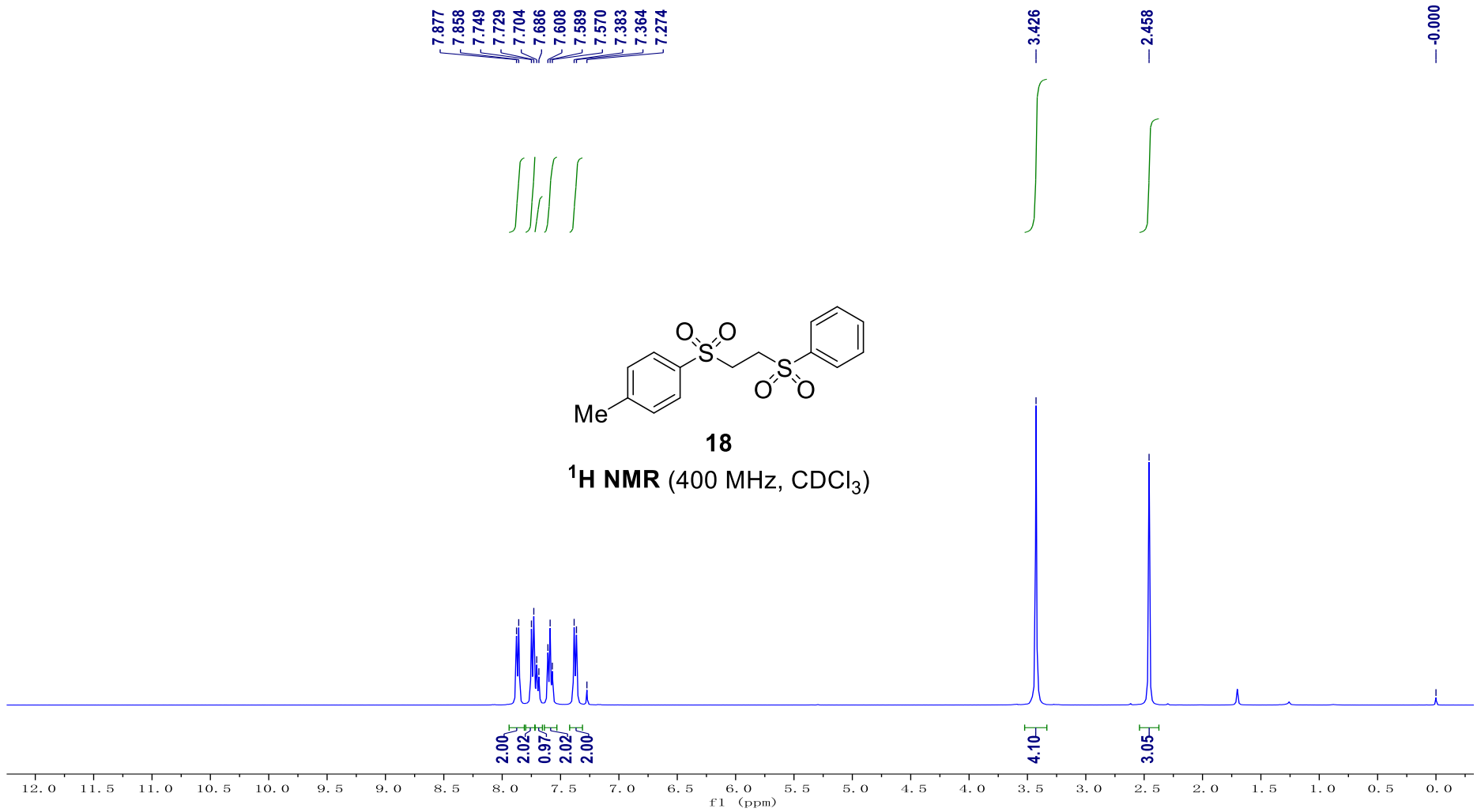
17

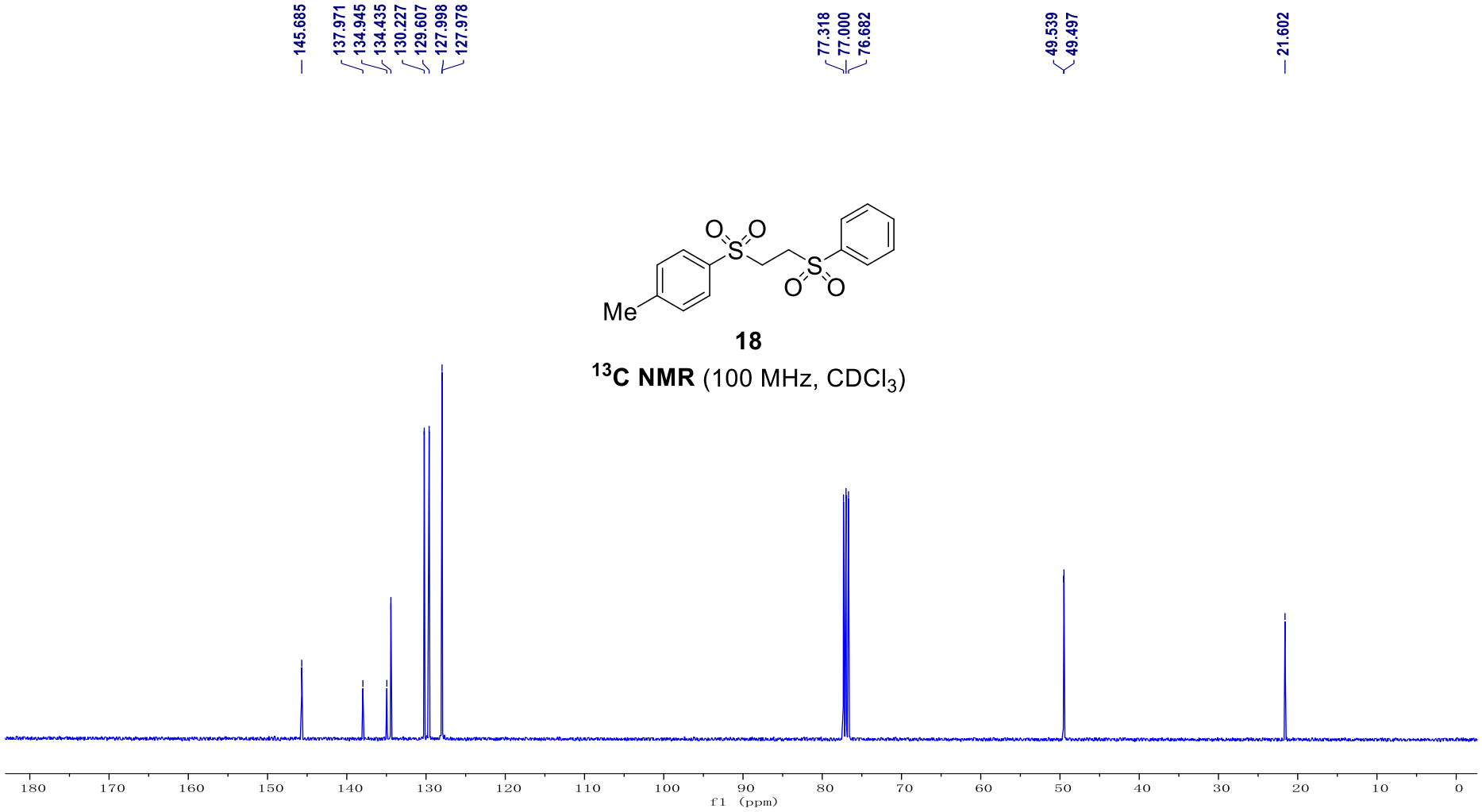
^{1}H NMR (300 MHz, $CDCl_3$)



17

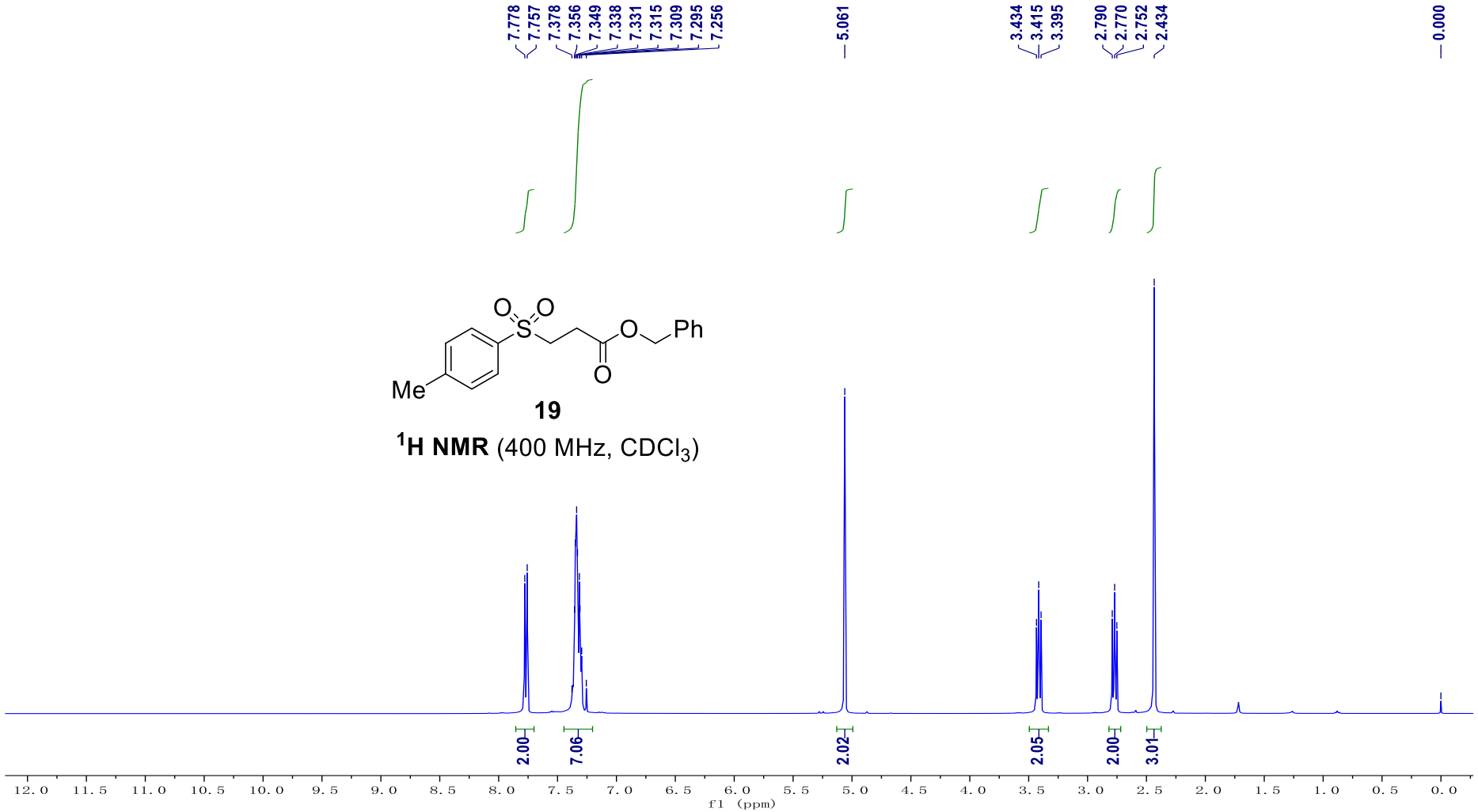
^{13}C NMR (75 MHz, $CDCl_3$)

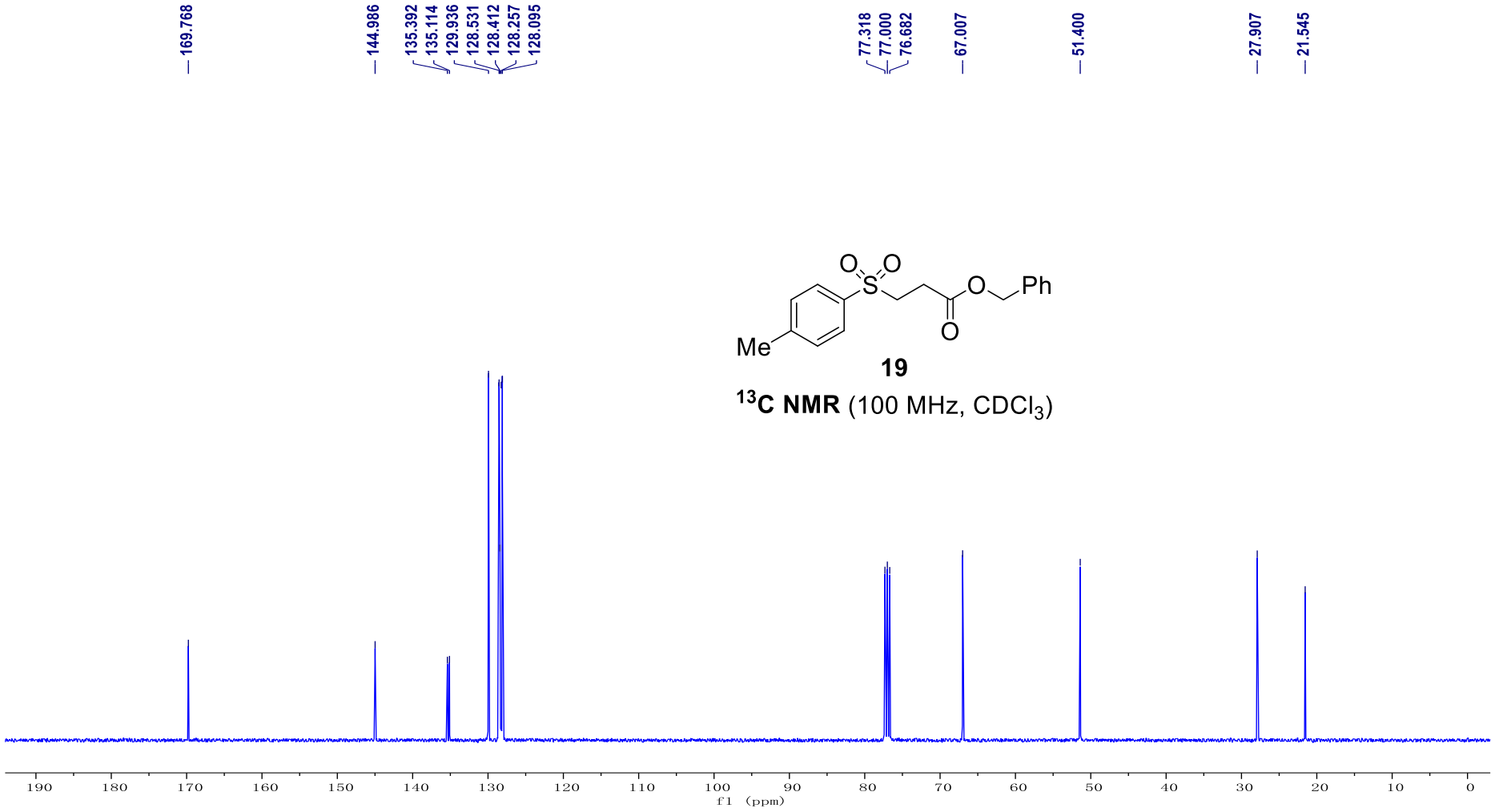

7.877
7.858
7.749
7.729
7.704
7.686
7.608
7.589
7.570
7.383
7.364
7.274
3.426
2.458
-0.000
Me
18
1H NMR (400 MHz, CDCl3)
2.00
2.02
0.97
2.02
2.00
4.10
3.05
f1 (ppm)

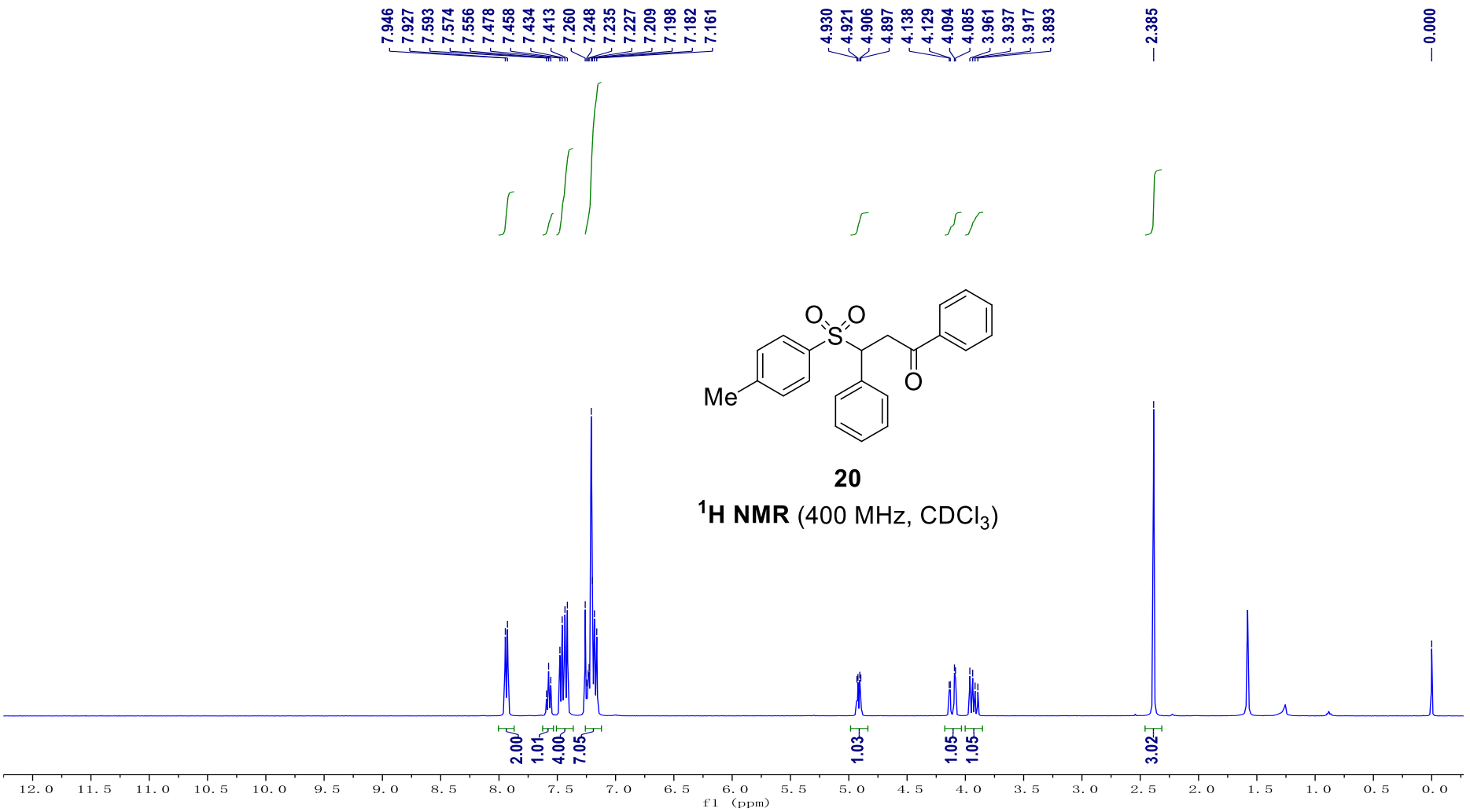


18

^{13}C NMR (100 MHz, $CDCl_3$)

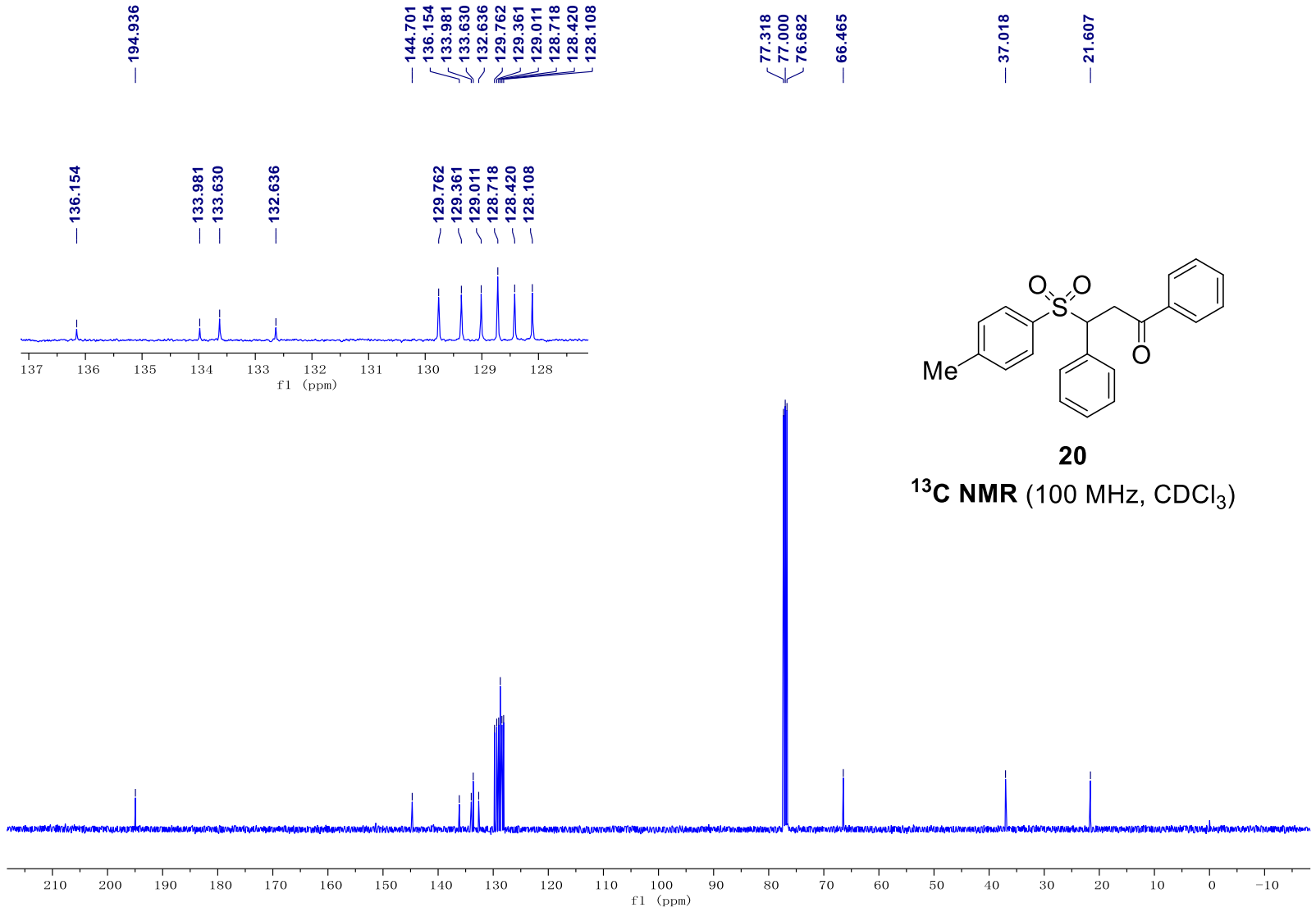

7.778
7.757
7.378
7.356
7.349
7.338
7.331
7.315
7.309
7.295
7.256
5.061
3.434
3.415
3.395
2.790
2.770
2.752
2.434
0.000
O
O
S
O
Ph
O
Me
19
1H NMR (400 MHz, CDCl3)
2.00
7.06
2.02
2.05
2.00
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.768
144.986
135.392
135.114
129.936
128.531
128.412
128.257
128.095
77.318
77.000
76.682
67.007
51.400
27.907
21.545
O
O
S
O
Ph
O
Me
19
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



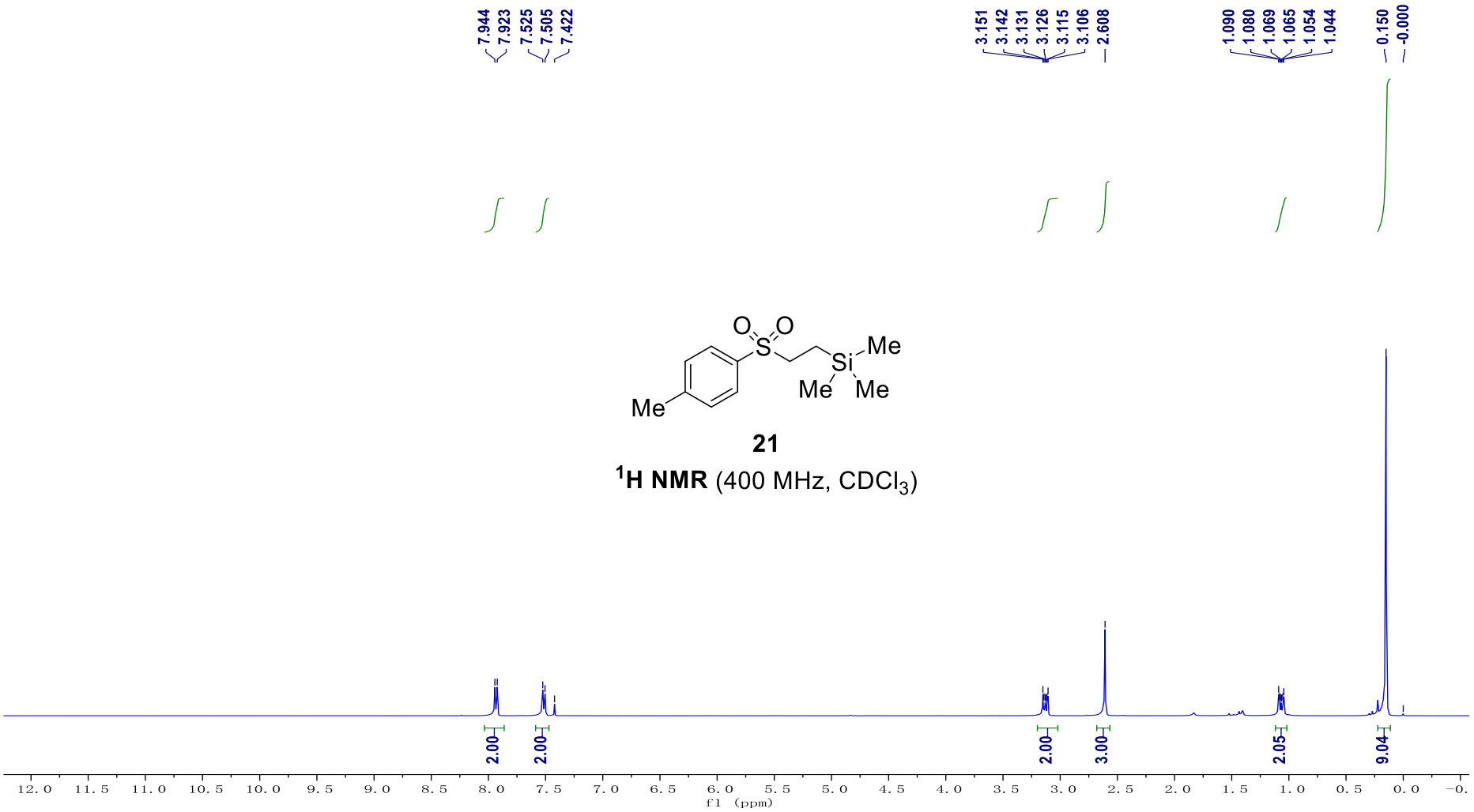
20

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



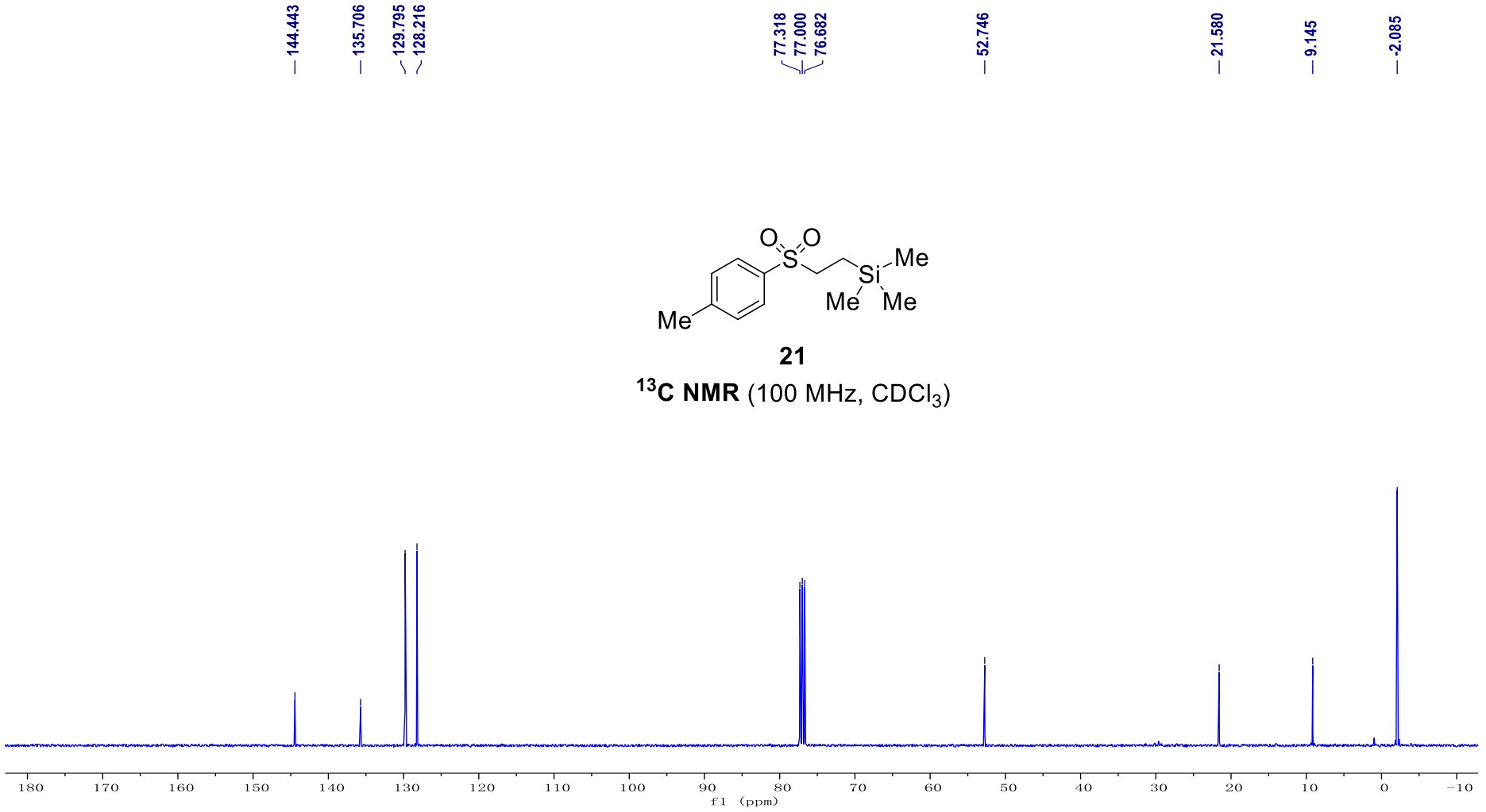
20

^{13}C NMR (100 MHz, $CDCl_3$)



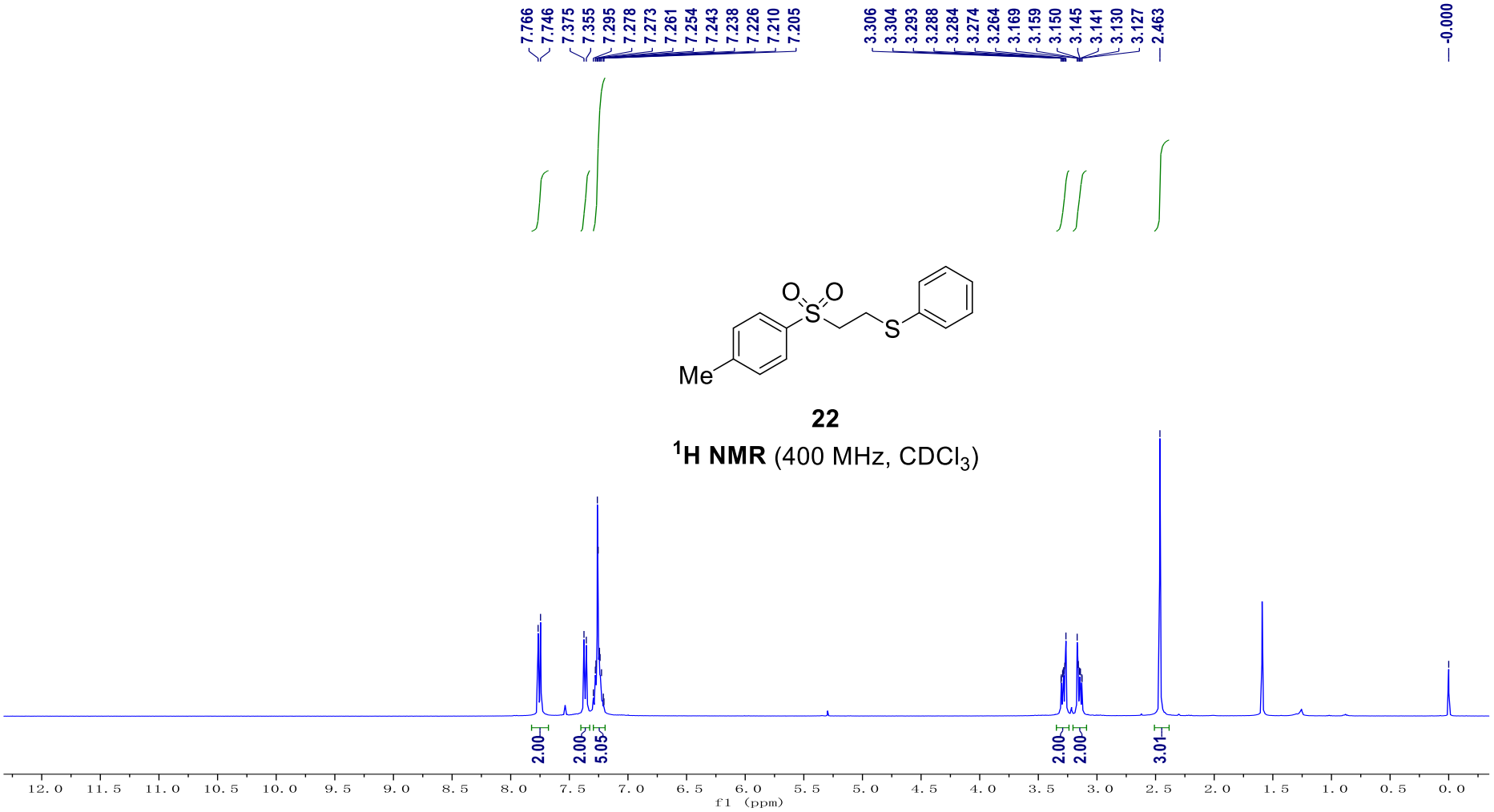
21

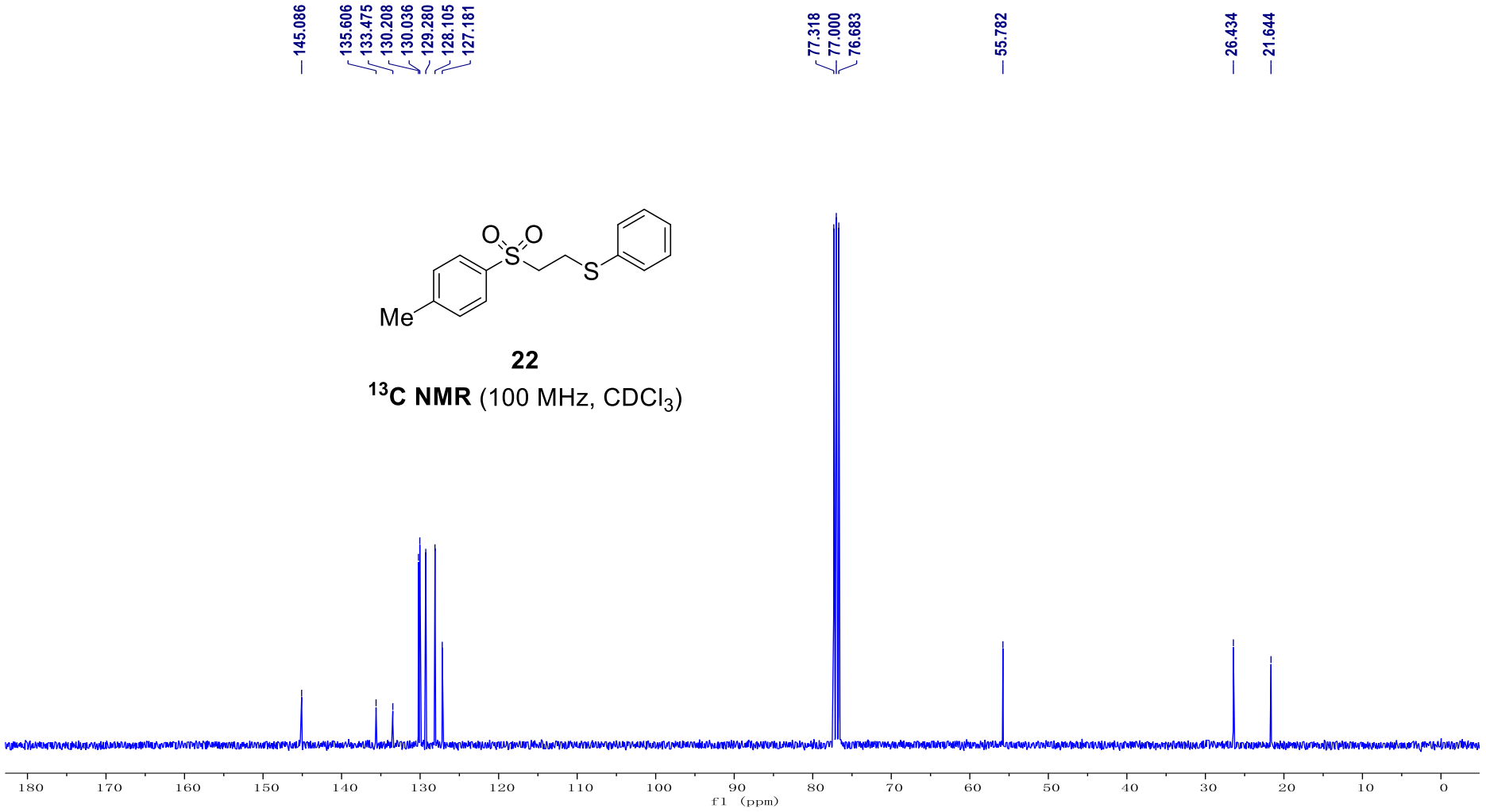
^{1}H NMR (400 MHz, $CDCl_3$)

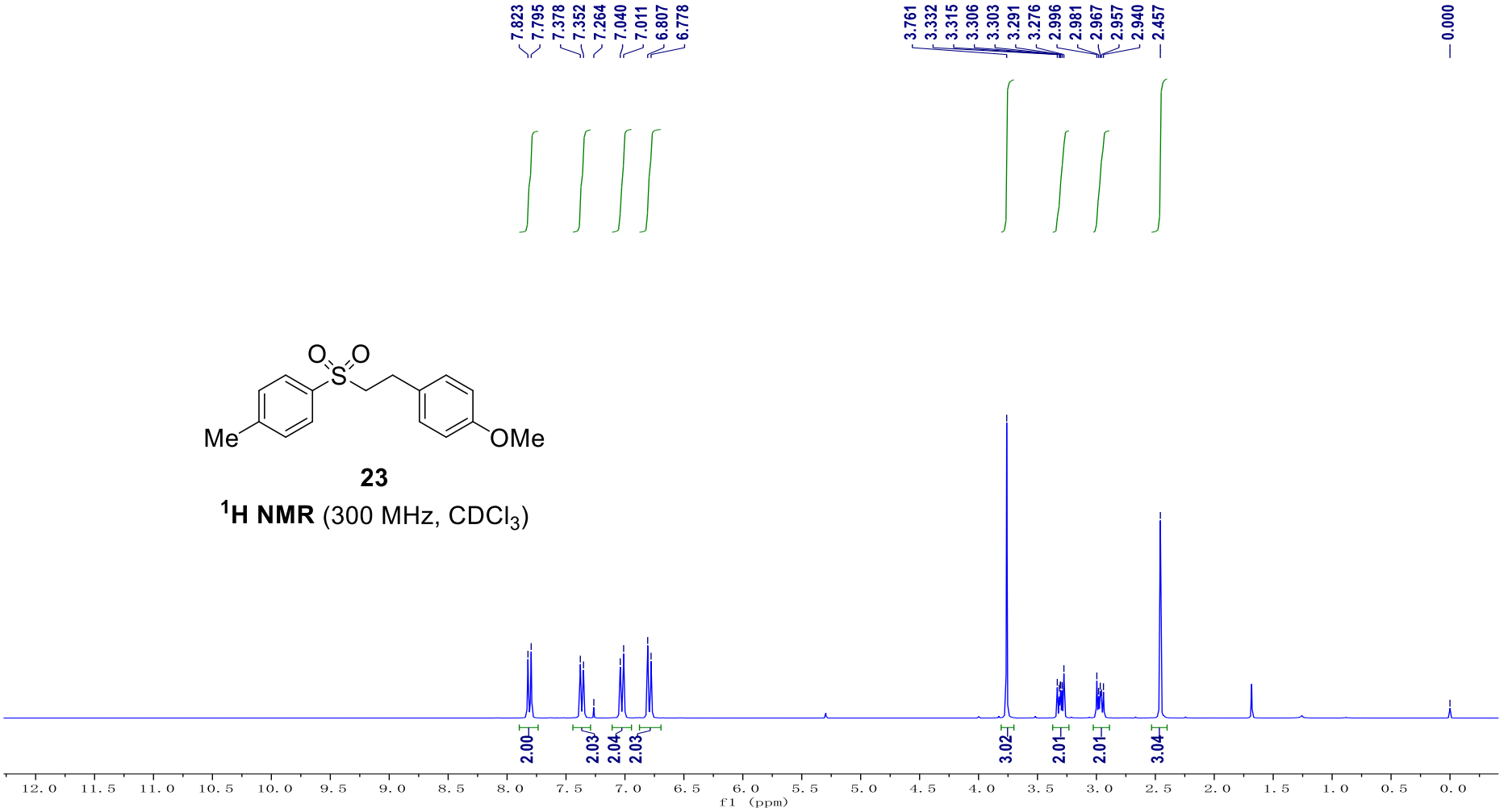


21

^{13}C NMR (100 MHz, $CDCl_3$)

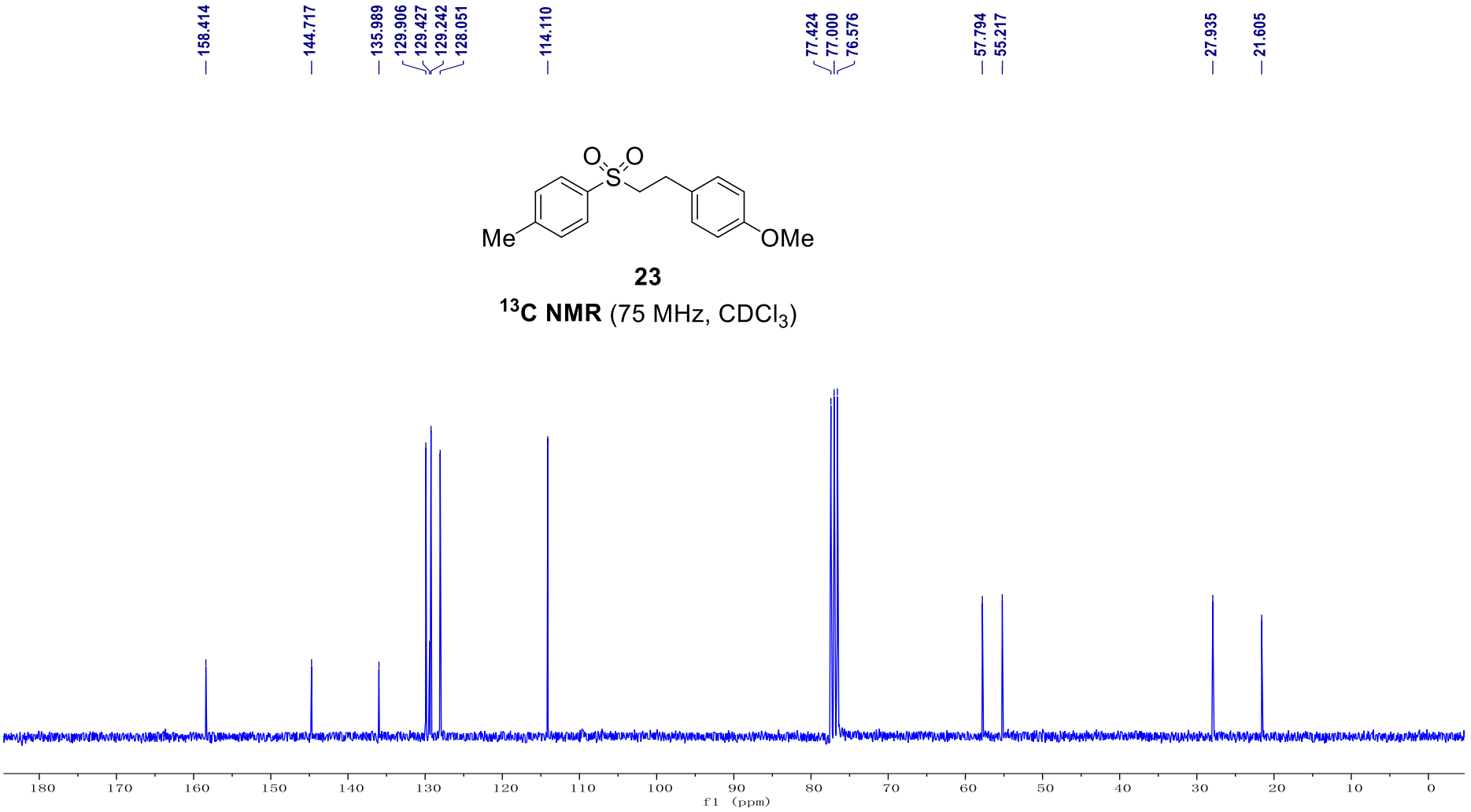

7.766
7.746
7.375
7.355
7.295
7.278
7.273
7.261
7.254
7.243
7.238
7.226
7.210
7.205
3.306
3.304
3.293
3.288
3.284
3.274
3.264
3.169
3.159
3.150
3.145
3.141
3.130
3.127
2.463
-0.000
O
O
S
S
Me
22
1H NMR (400 MHz, CDCl3)
2.00
2.00
5.05
2.00
2.00
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.086
135.606
133.475
130.208
130.036
129.280
128.105
127.181
77.318
77.000
76.683
55.782
26.434
21.644
O
O
S
S
Me
22
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



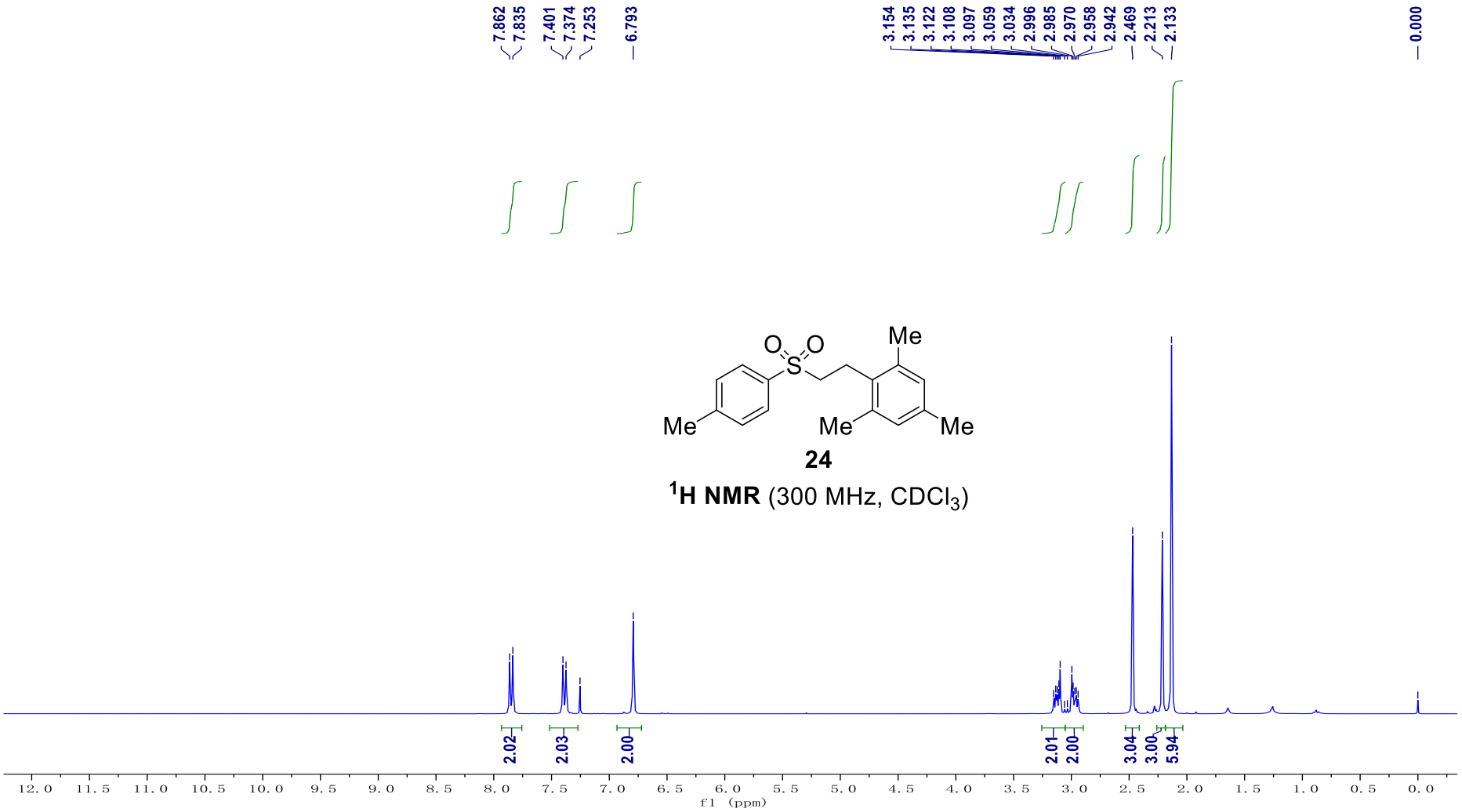
23

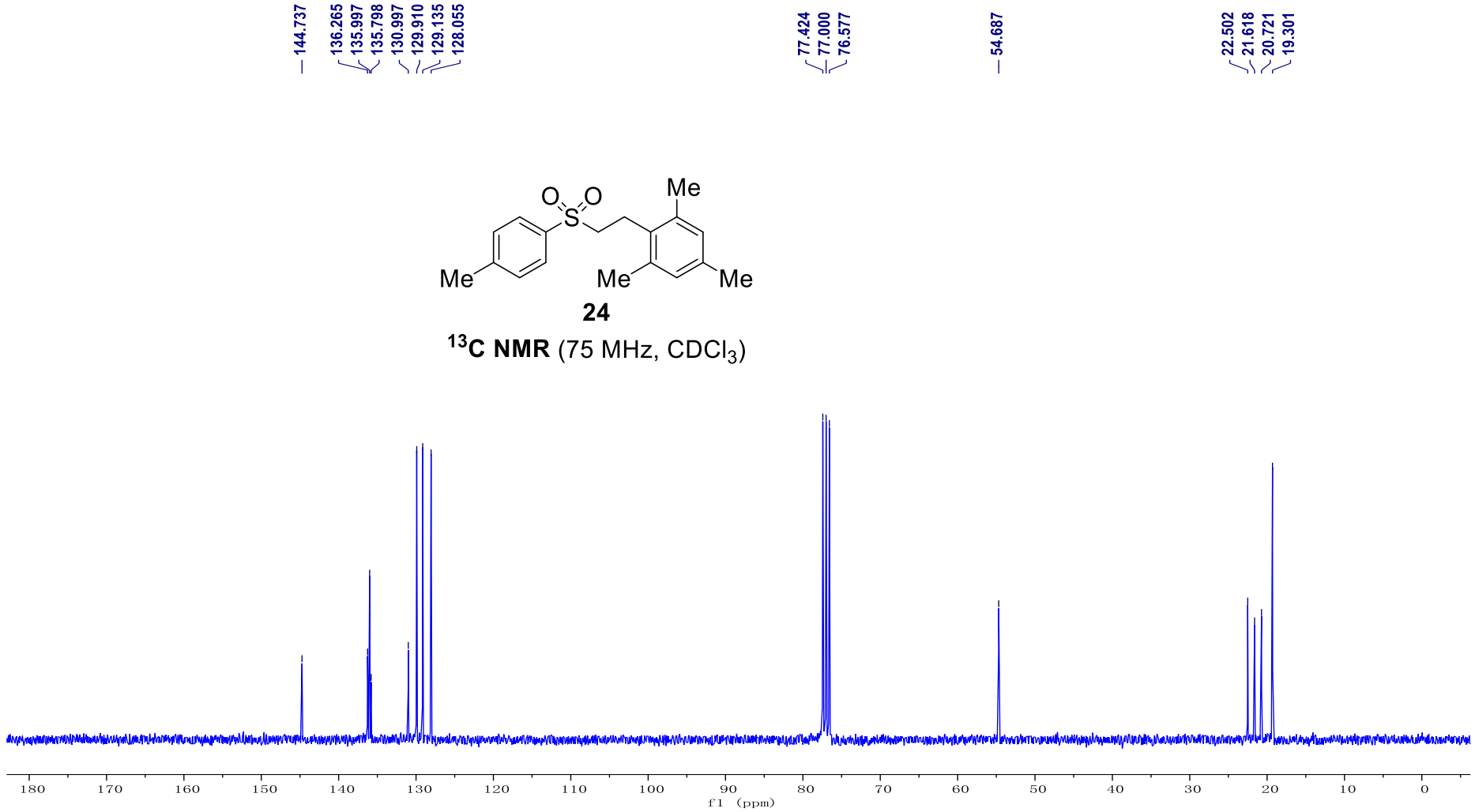
^{1}H NMR (300 MHz, $CDCl_3$)



23

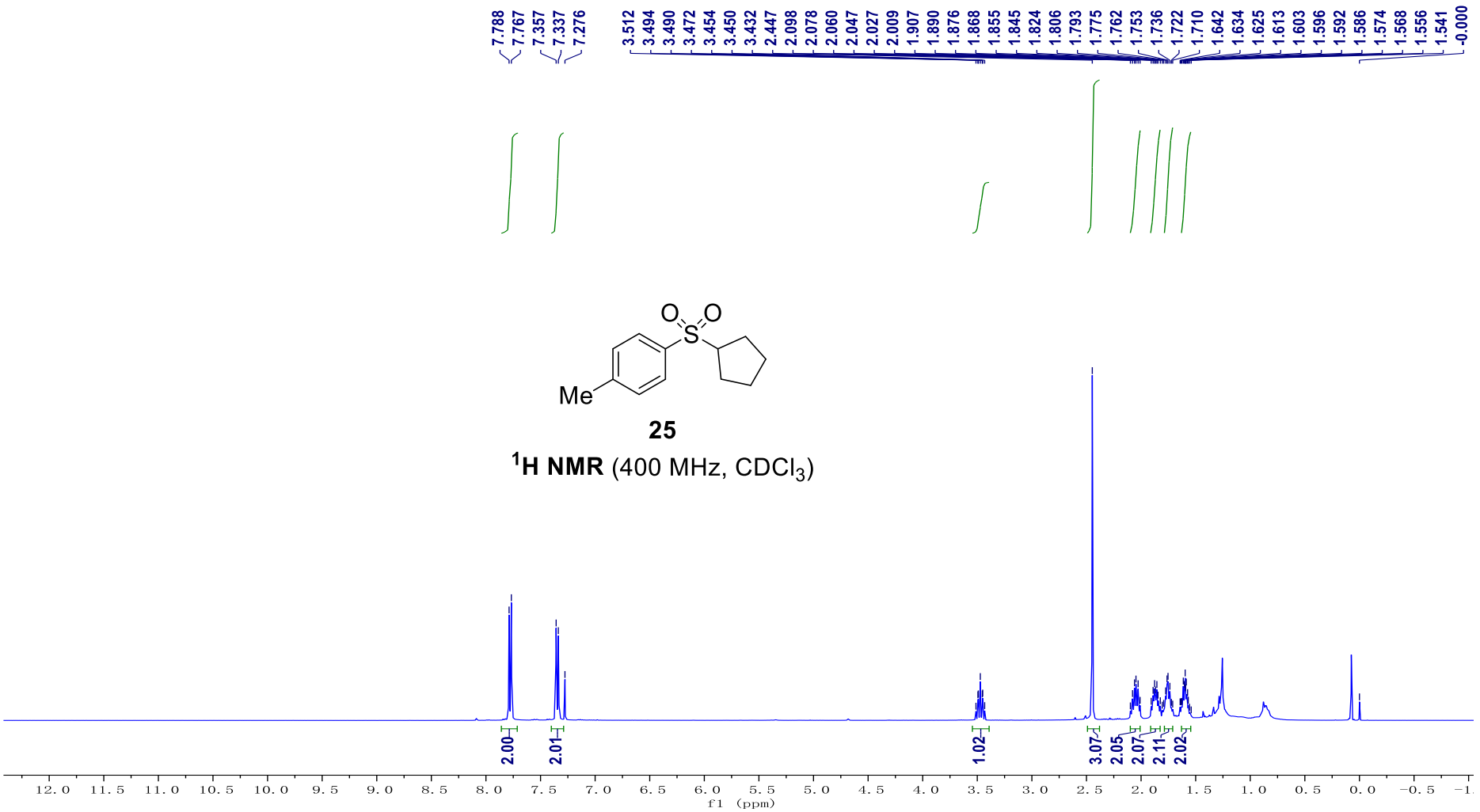
^{13}C NMR (75 MHz, $CDCl_3$)


7.862
7.835
7.401
7.374
7.253
6.793
3.154
3.135
3.122
3.108
3.097
3.059
3.034
2.996
2.985
2.970
2.958
2.942
2.469
2.213
2.133
0.000
Me
Me
Me
Me
24
1H NMR (300 MHz, CDCl3)
2.02
2.03
2.00
2.01
2.00
3.04
3.00
5.94
f1 (ppm)



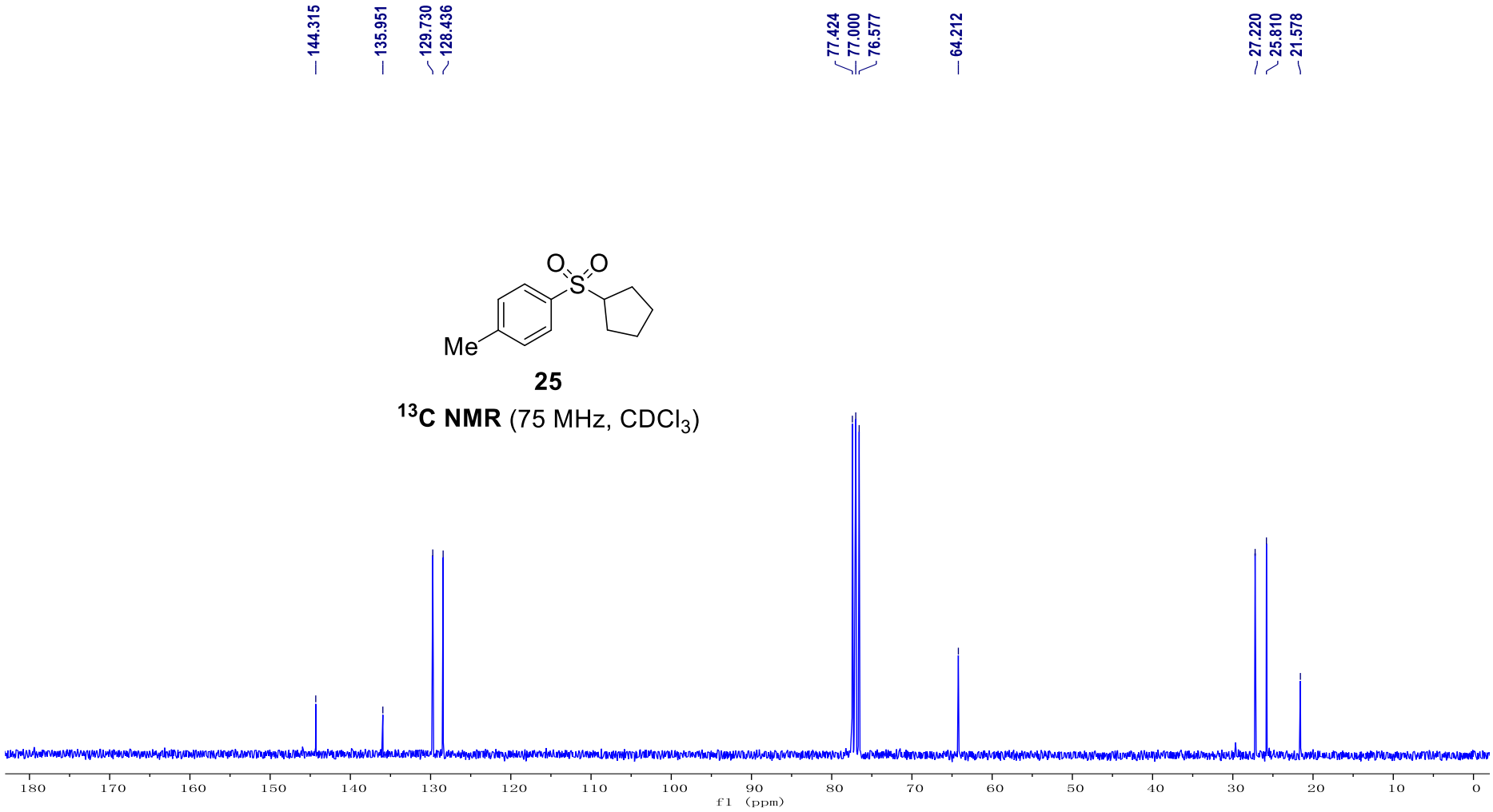
24

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



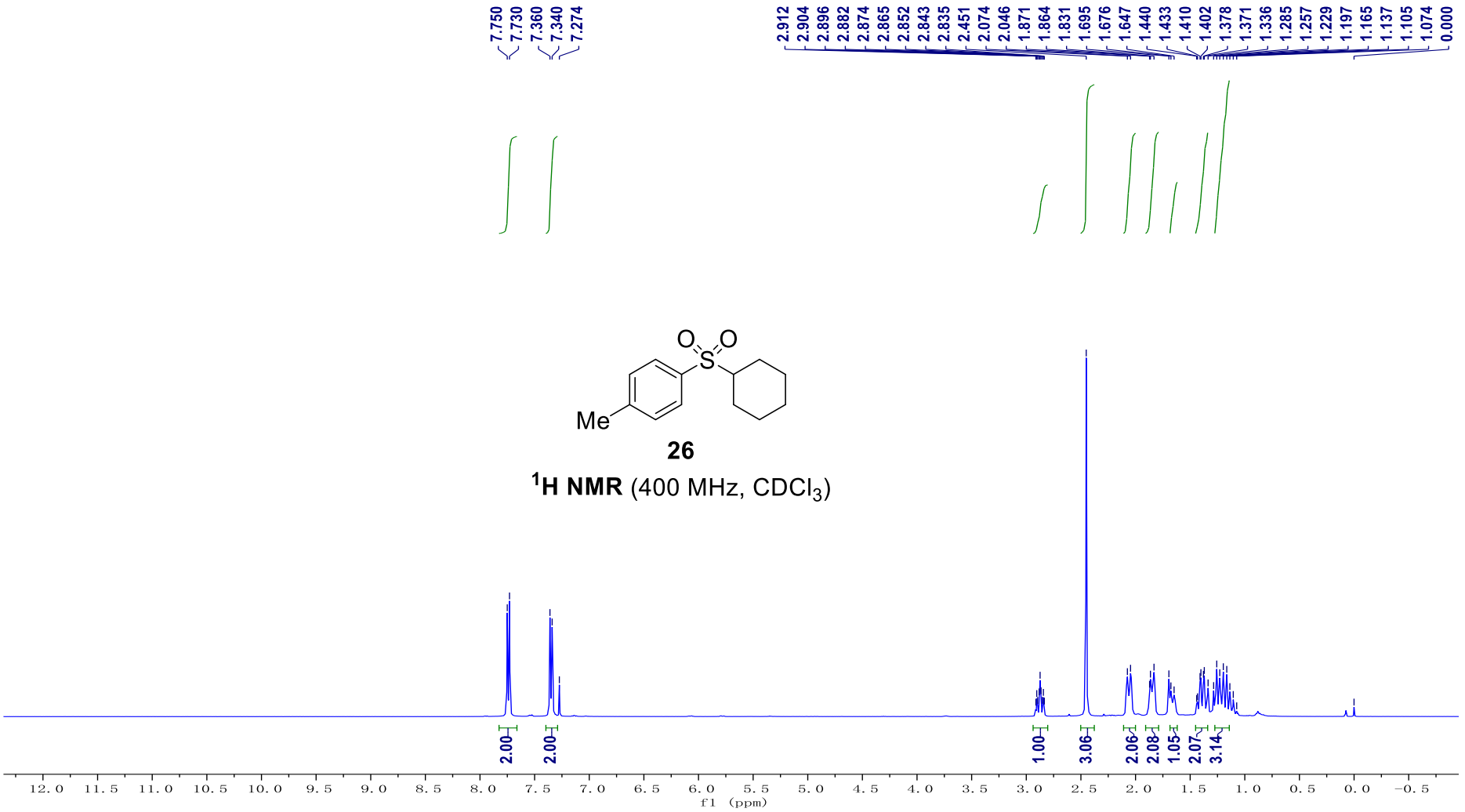
25

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



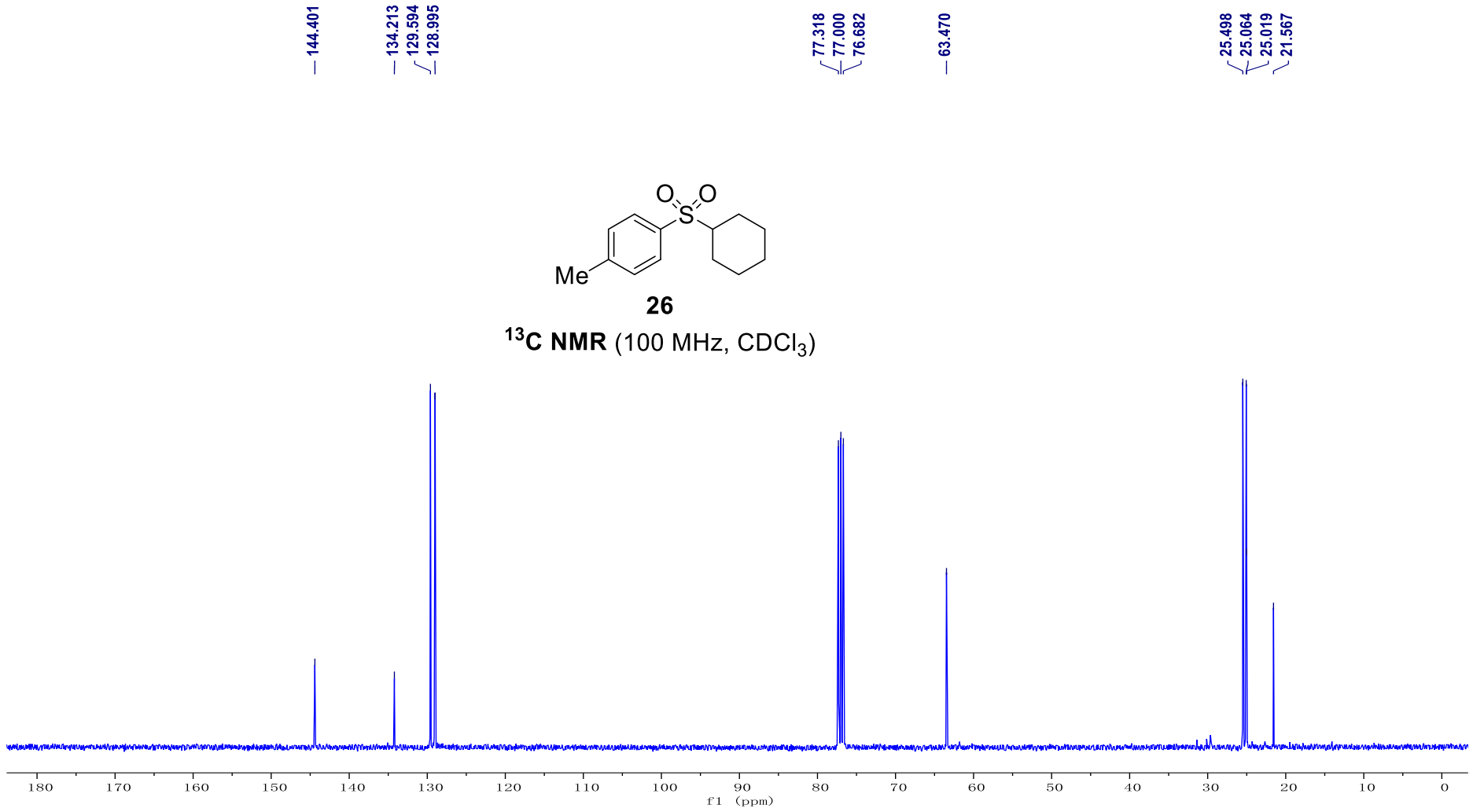
25

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



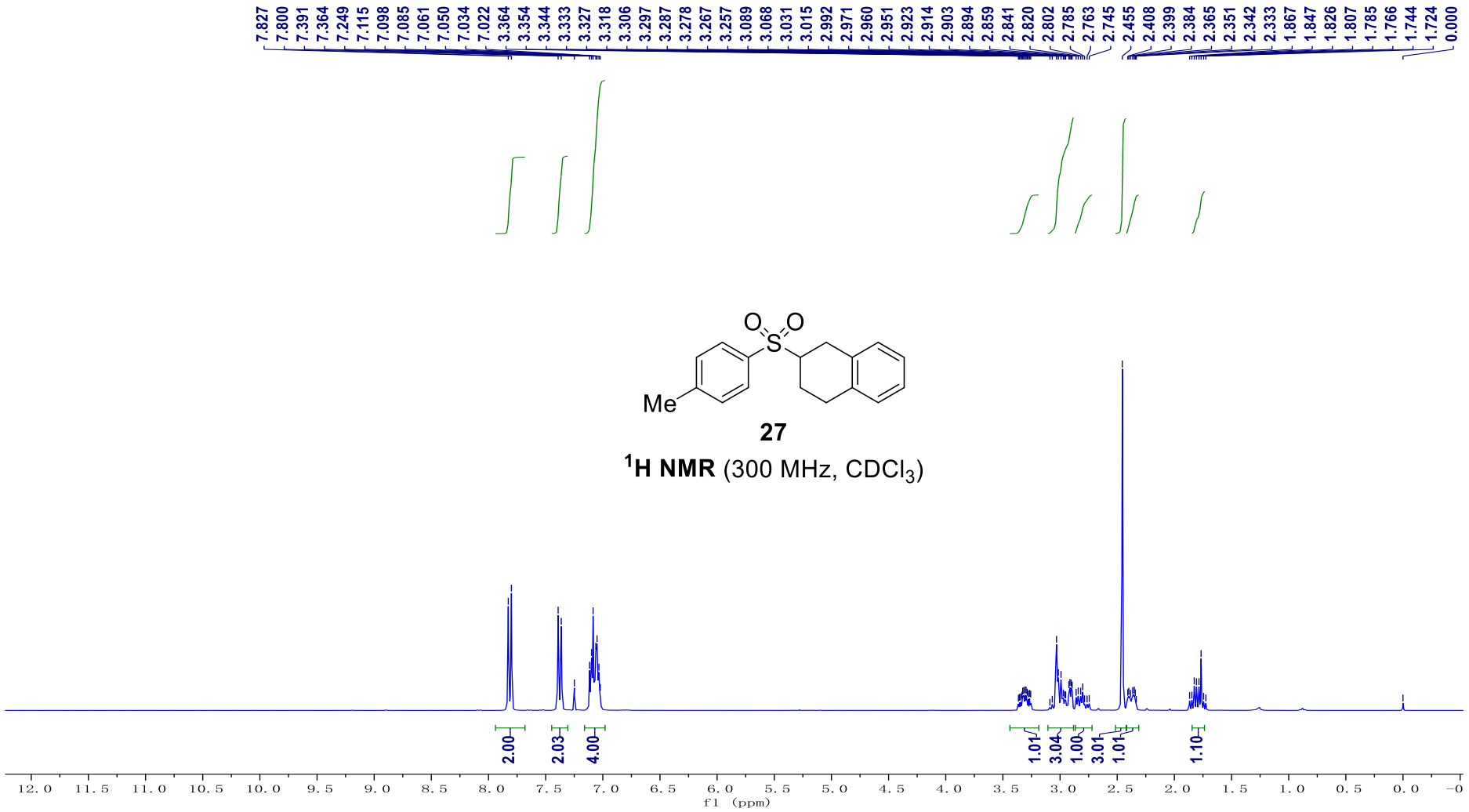
26

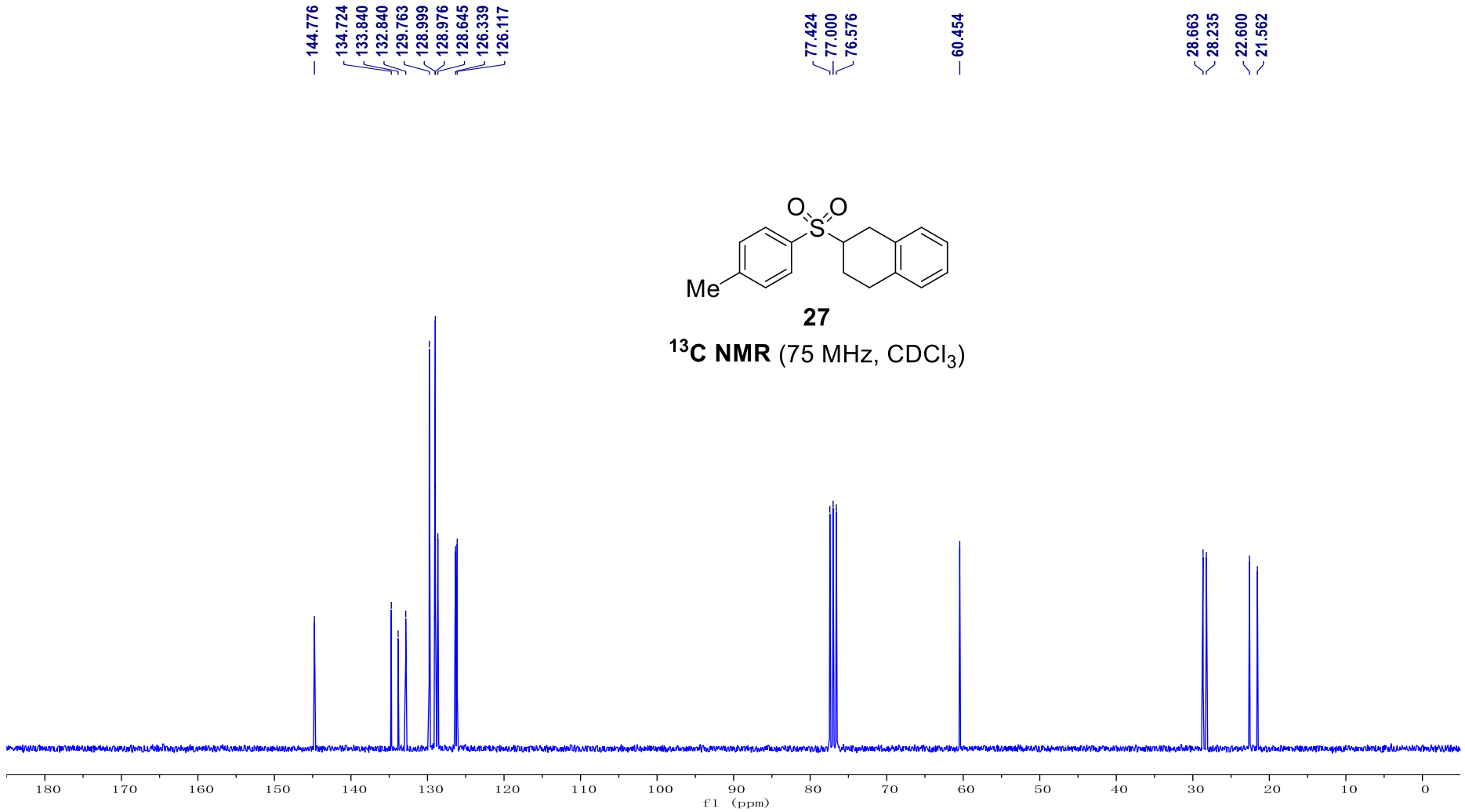
^{1}H NMR (400 MHz, $CDCl_3$)



26

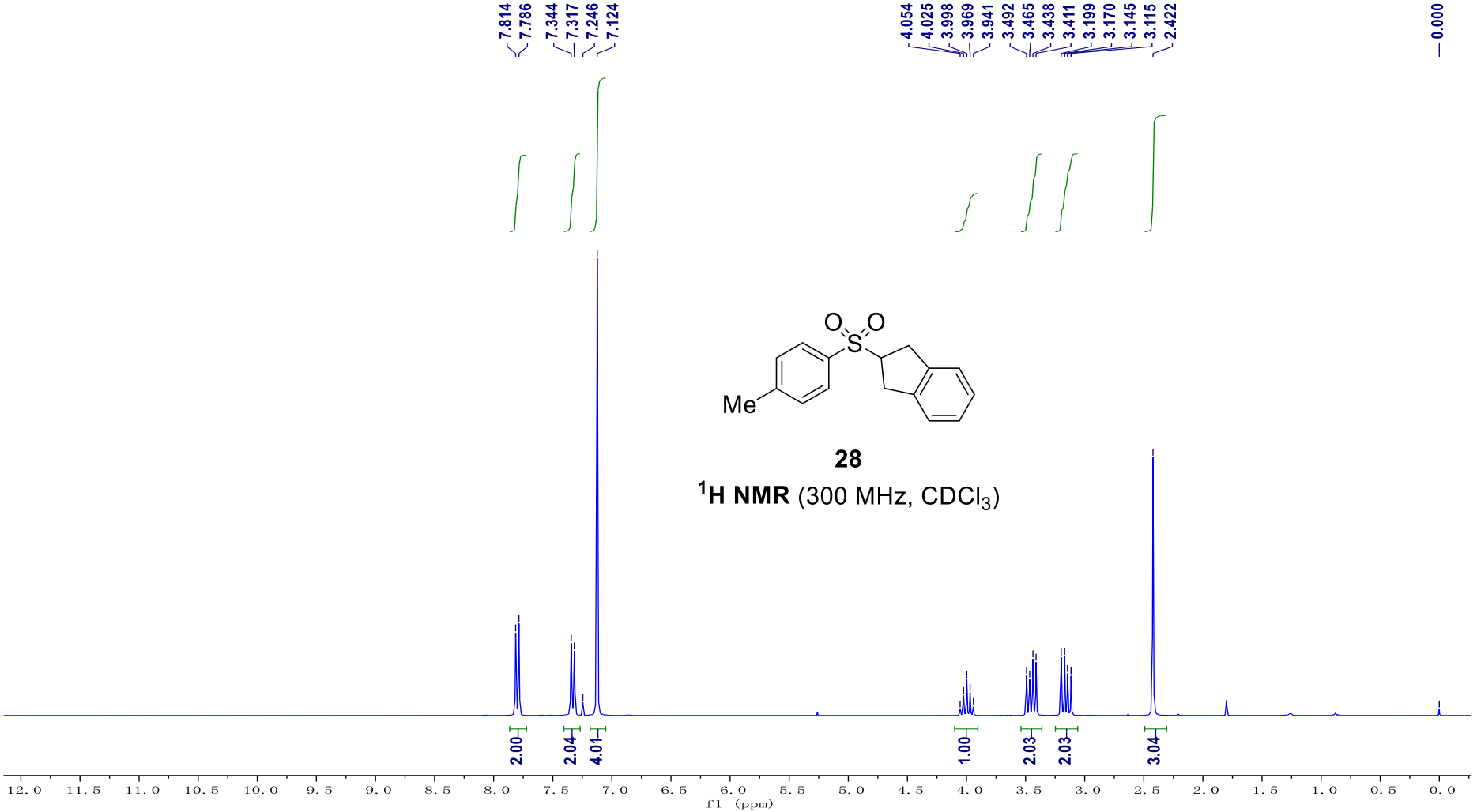
^{13}C NMR (100 MHz, $CDCl_3$)

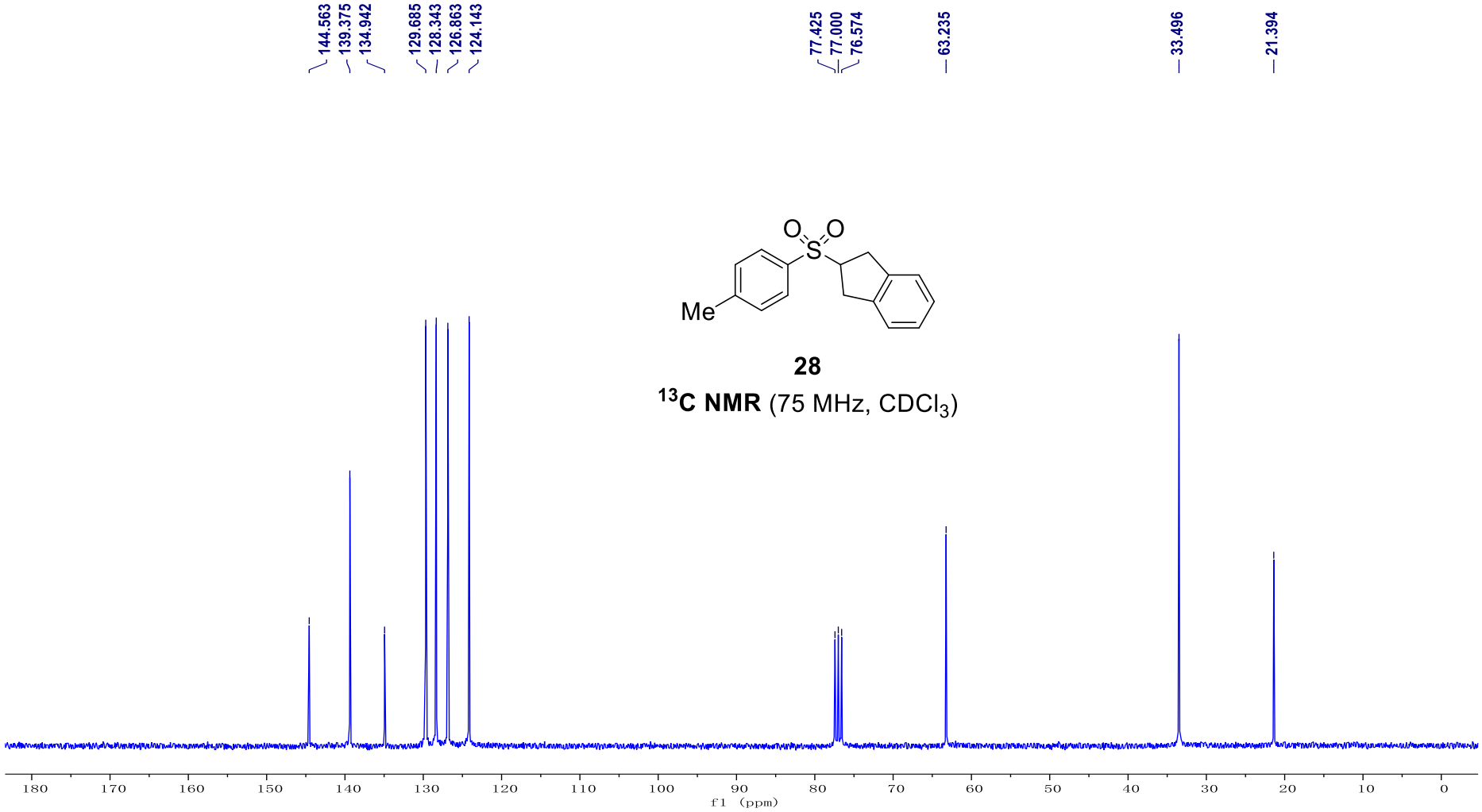

7.827
7.800
7.391
7.364
7.249
7.115
7.098
7.085
7.061
7.050
7.034
7.022
3.364
3.354
3.344
3.333
3.327
3.318
3.306
3.297
3.287
3.278
3.267
3.257
3.089
3.068
3.031
3.015
2.992
2.971
2.960
2.951
2.923
2.914
2.903
2.894
2.859
2.841
2.820
2.802
2.785
2.763
2.745
2.455
2.408
2.399
2.384
2.365
2.351
2.342
2.333
1.867
1.847
1.826
1.807
1.785
1.766
1.744
1.724
0.000
O
O
S
Me
27
1H NMR (300 MHz, CDCl3)
2.00
2.03
4.00
1.01
3.04
1.00
3.01
1.01
1.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)



27

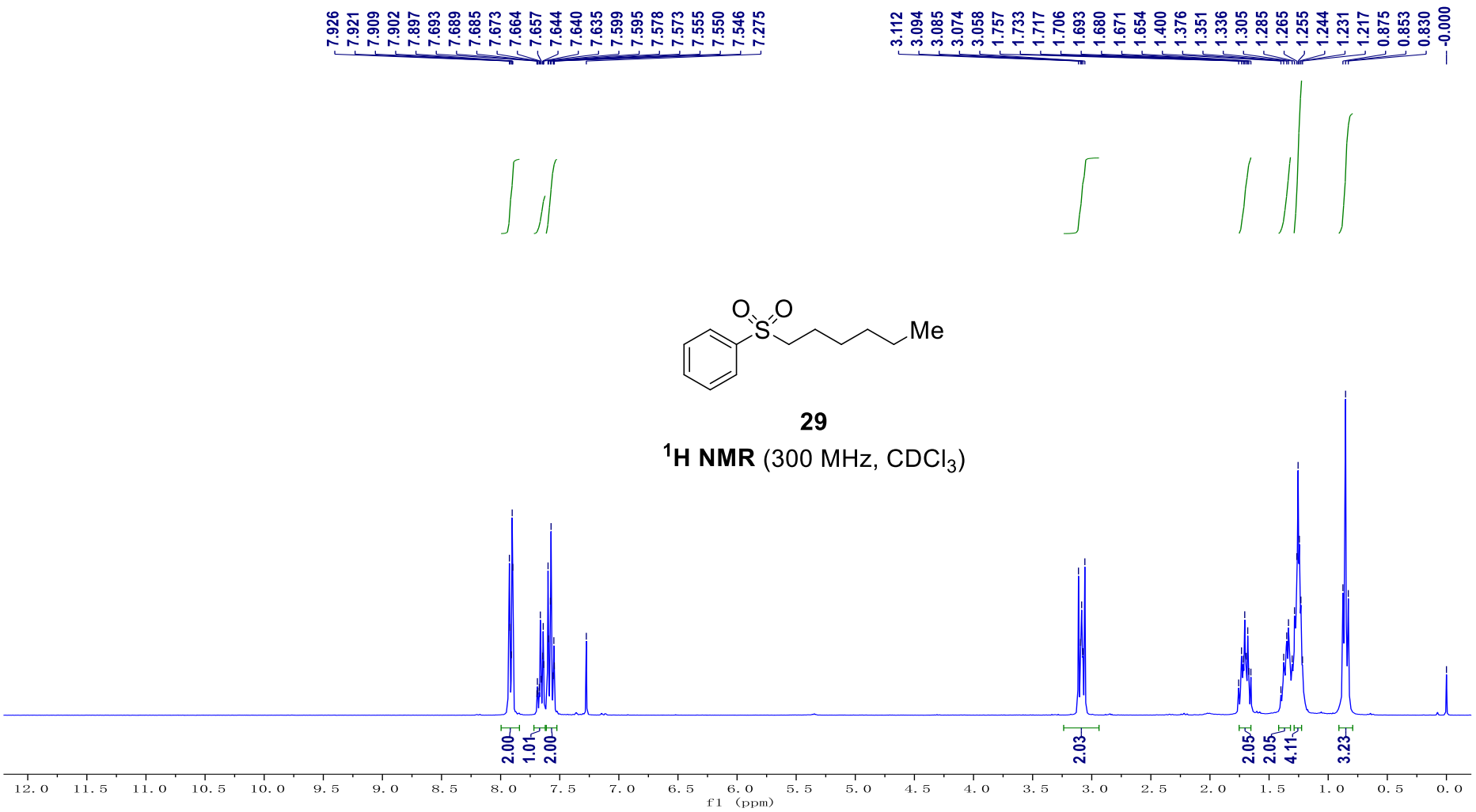
^{13}C NMR (75 MHz, $CDCl_3$)

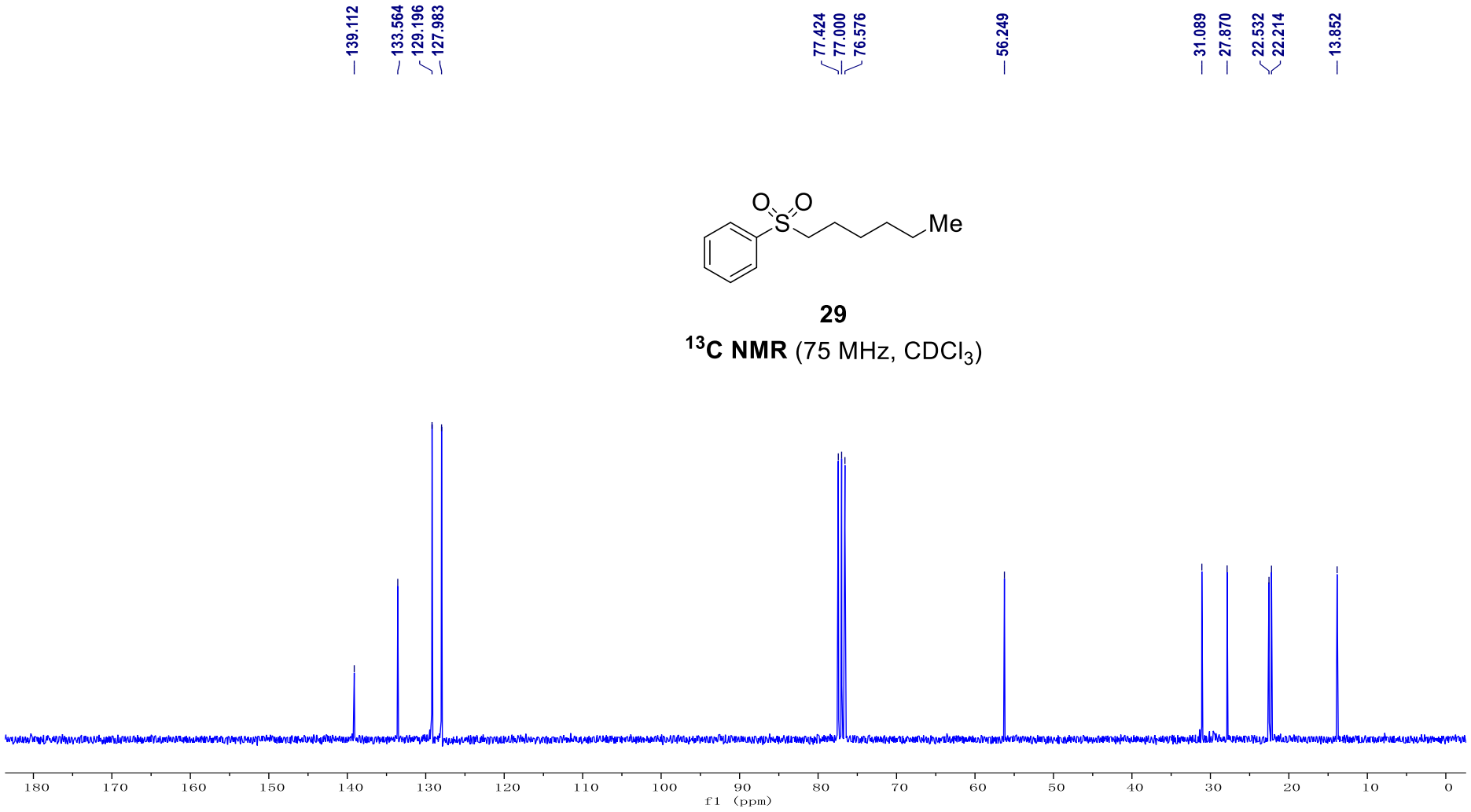

7.814
7.786
7.344
7.317
7.246
7.124
4.054
4.025
3.998
3.969
3.941
3.492
3.465
3.438
3.411
3.199
3.170
3.145
3.115
2.422
0.000
O
O
S
Me
28
1H NMR (300 MHz, CDCl3)
2.00
2.04
4.01
1.00
2.03
2.03
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



28

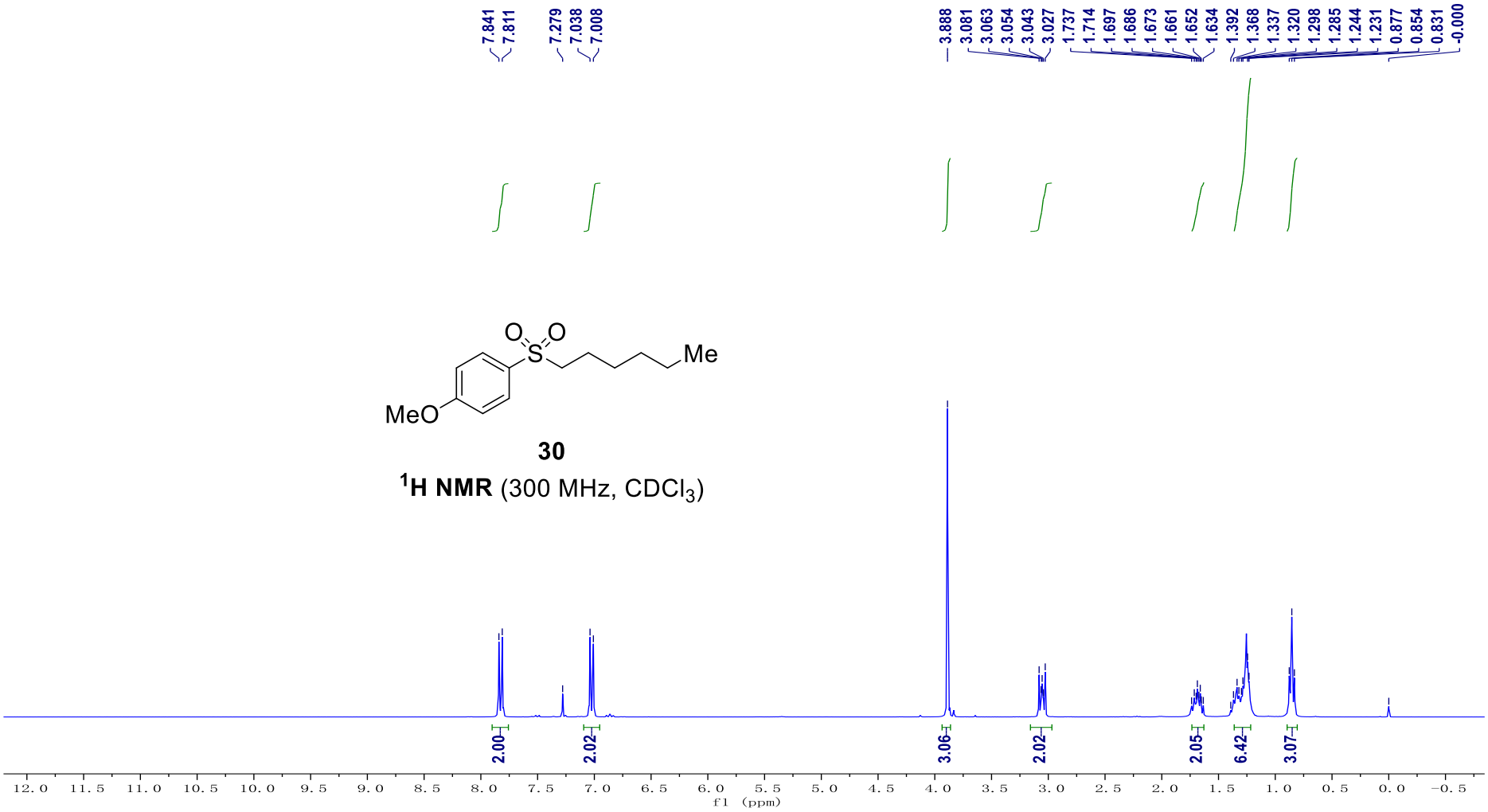
^{13}C NMR (75 MHz, $CDCl_3$)


7.926
7.921
7.909
7.902
7.897
7.693
7.689
7.685
7.673
7.664
7.657
7.644
7.640
7.635
7.599
7.595
7.578
7.573
7.555
7.550
7.546
7.275
3.112
3.094
3.085
3.074
3.058
1.757
1.733
1.717
1.706
1.693
1.680
1.671
1.654
1.400
1.376
1.351
1.336
1.305
1.285
1.265
1.255
1.244
1.231
1.217
0.875
0.853
0.830
-0.000
O
O
S
Me
29
1H NMR (300 MHz, CDCl3)
2.00
1.01
2.00
2.03
2.05
2.05
4.11
3.23
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



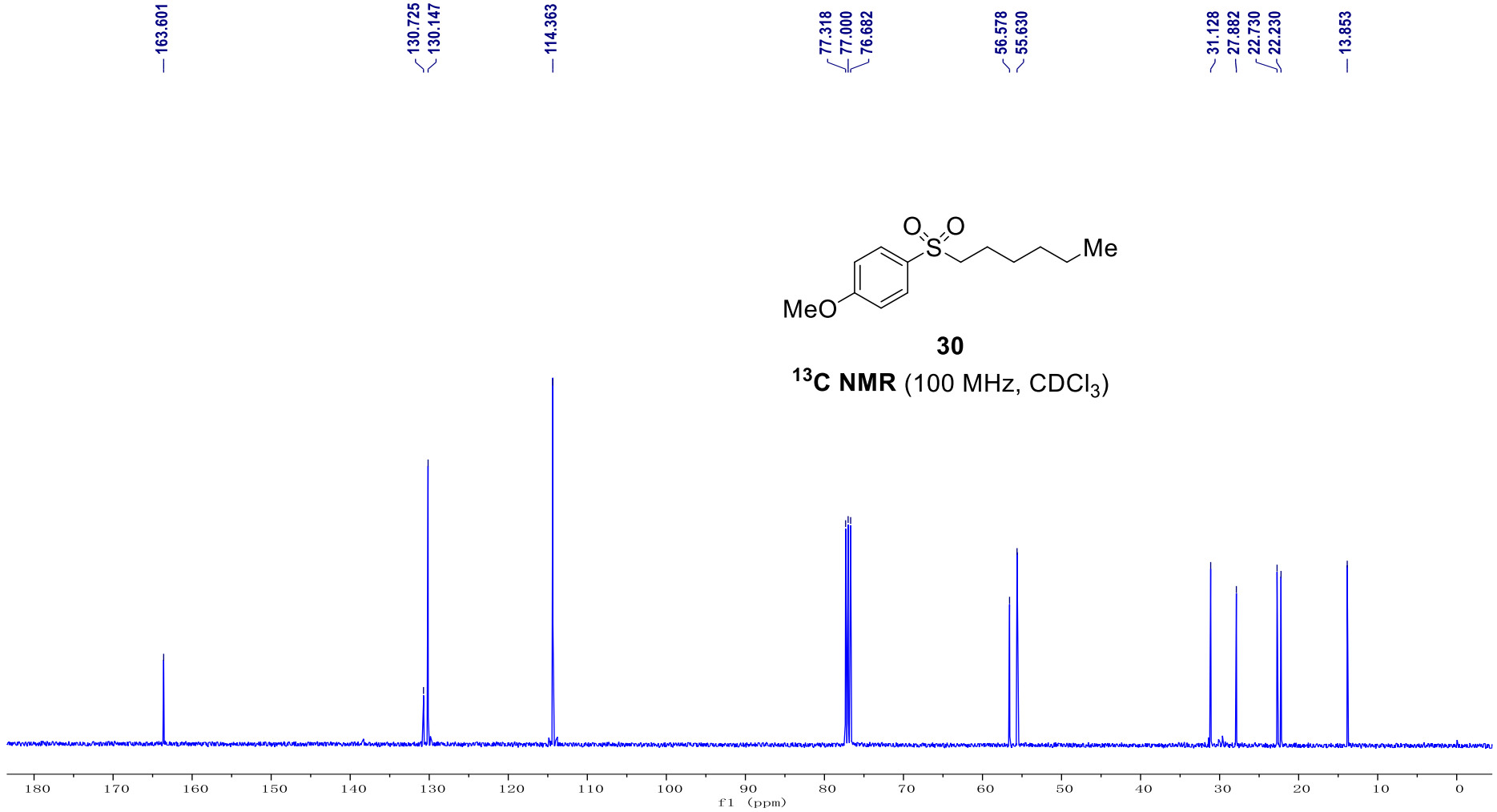
29

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



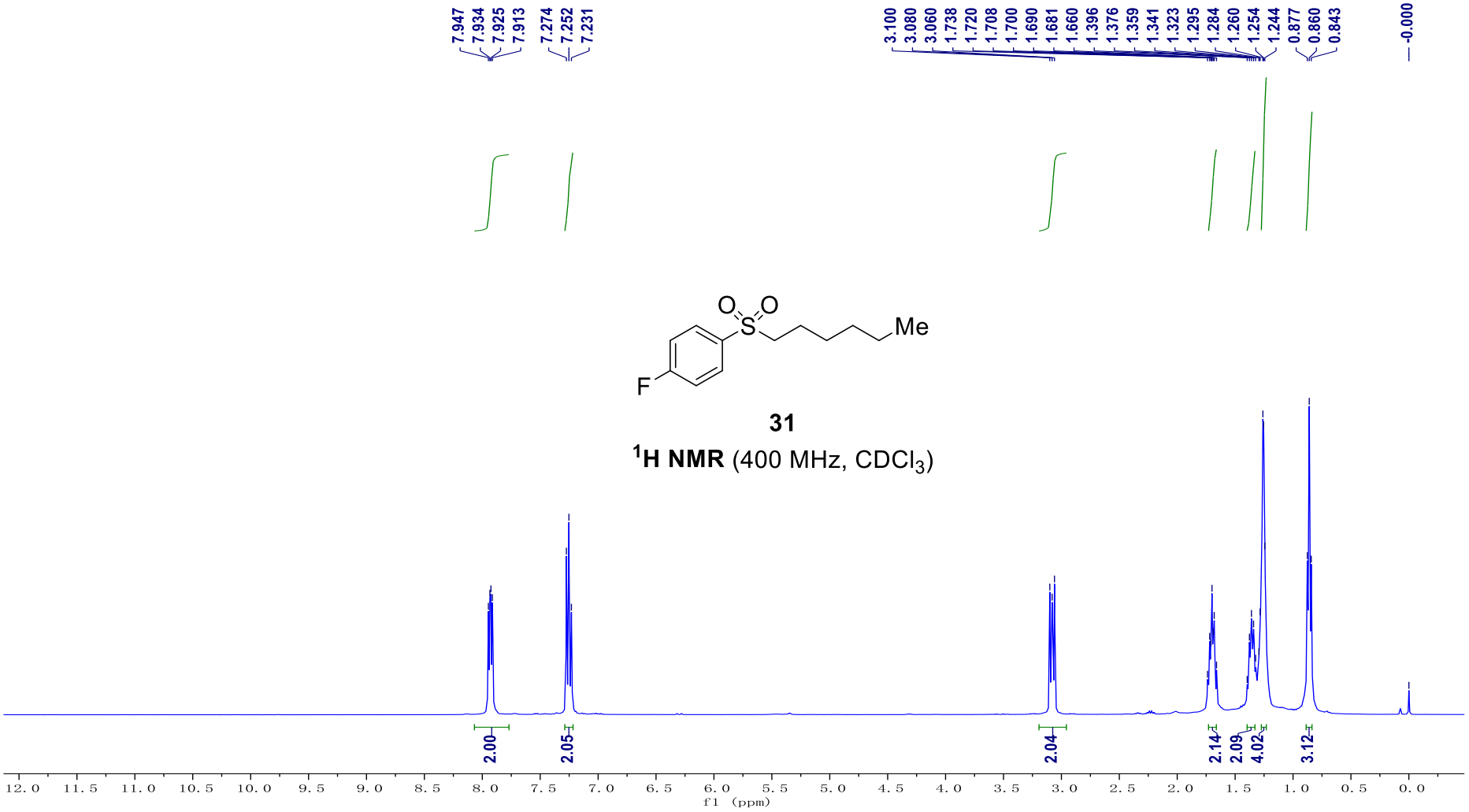
30

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



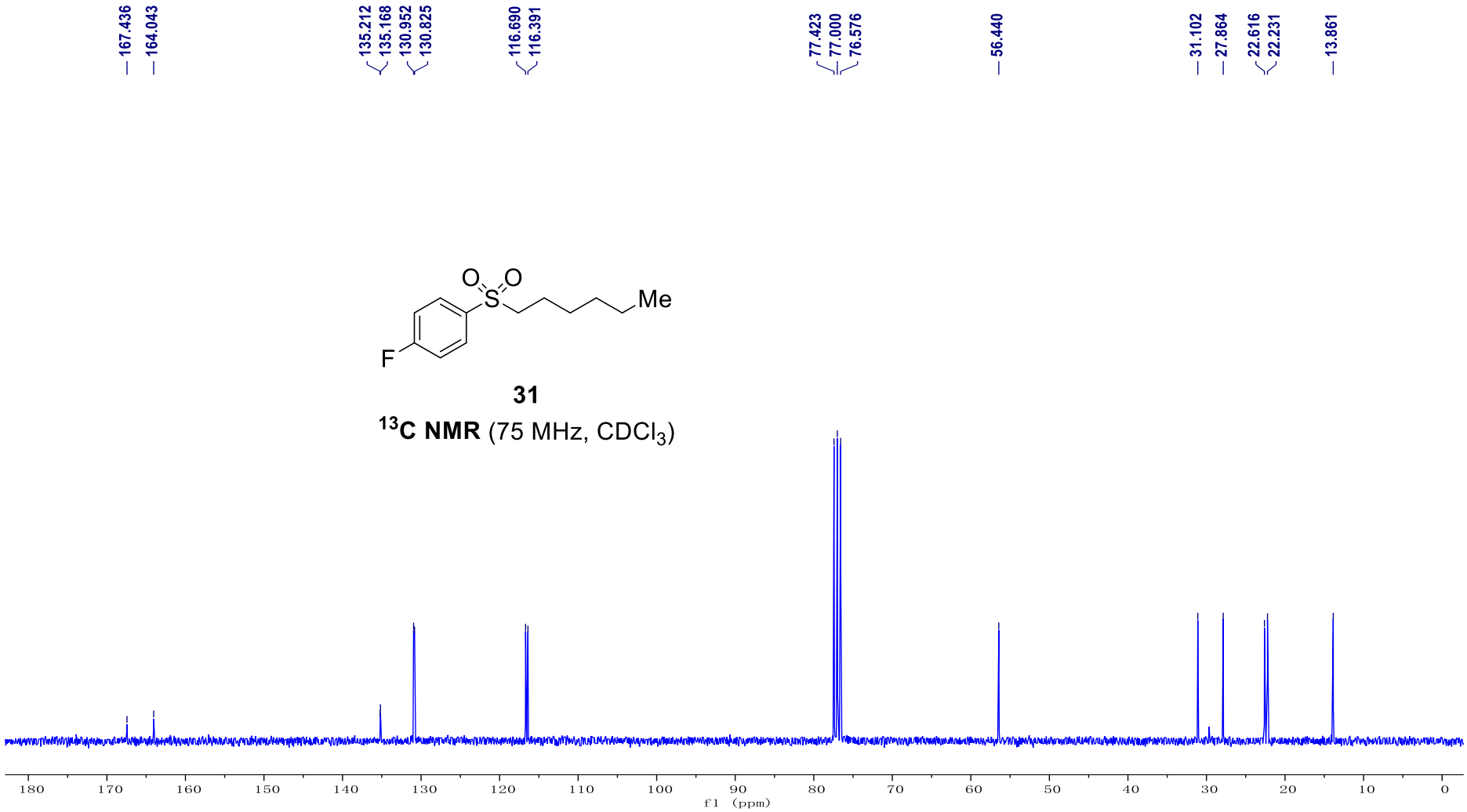
30

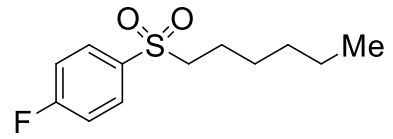
^{13}C NMR (100 MHz, $CDCl_3$)



31

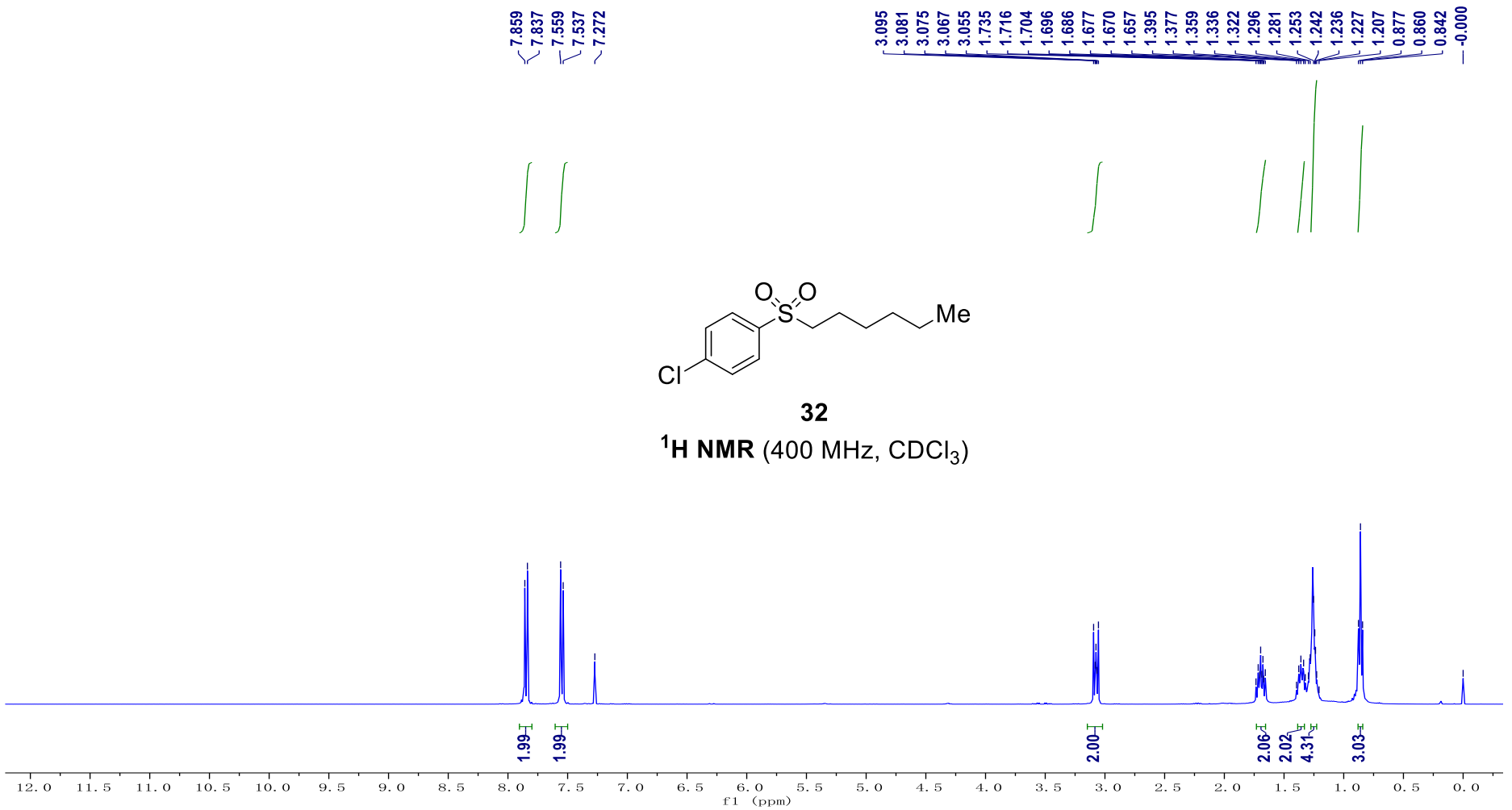
^{1}H NMR (400 MHz, $CDCl_3$)


167.436
164.043
135.212
135.168
130.952
130.825
116.690
116.391
77.423
77.000
76.576
56.440
31.102
27.864
22.616
22.231
13.861
O
O
S
Me
F
31
13C NMR (75 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



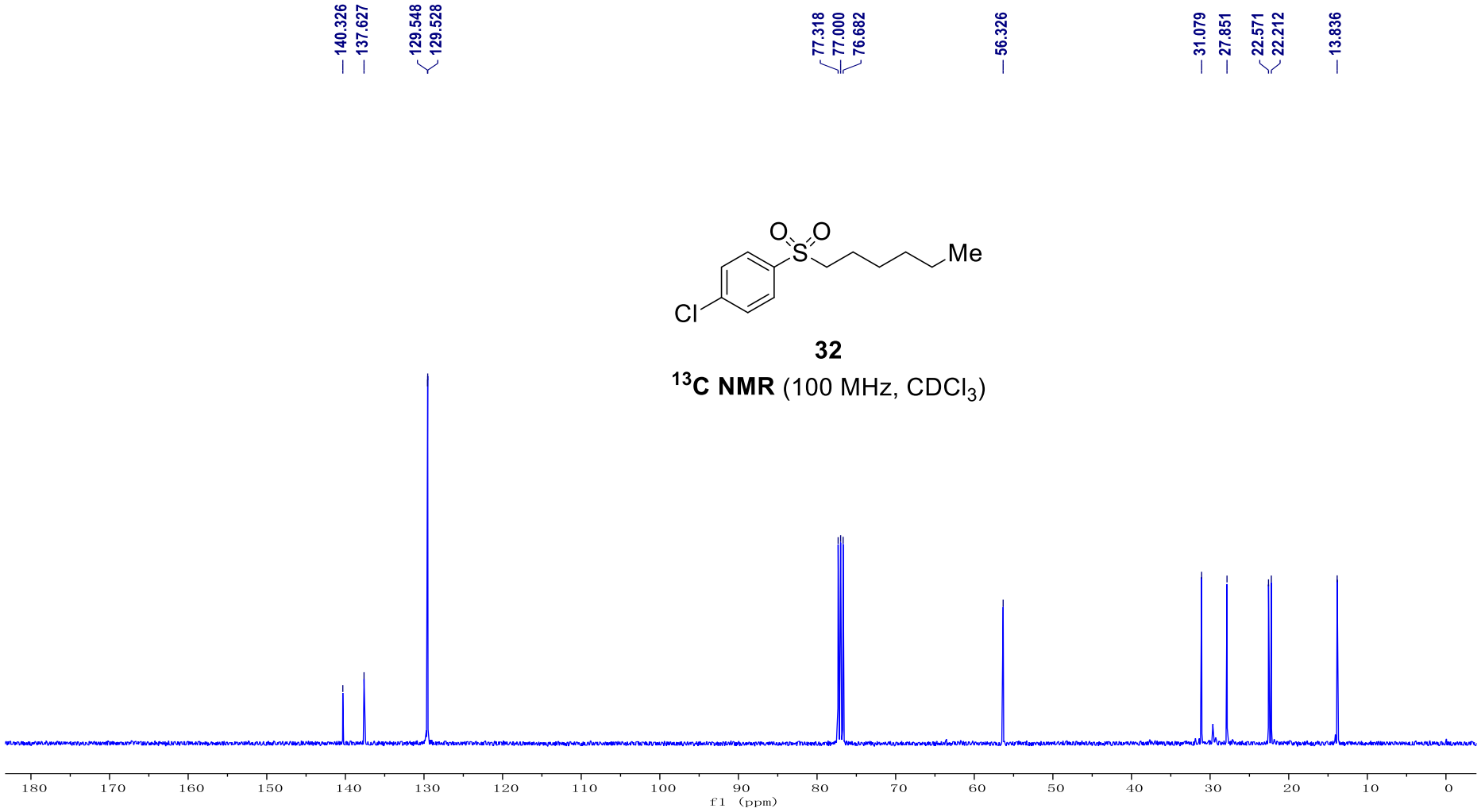
31

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



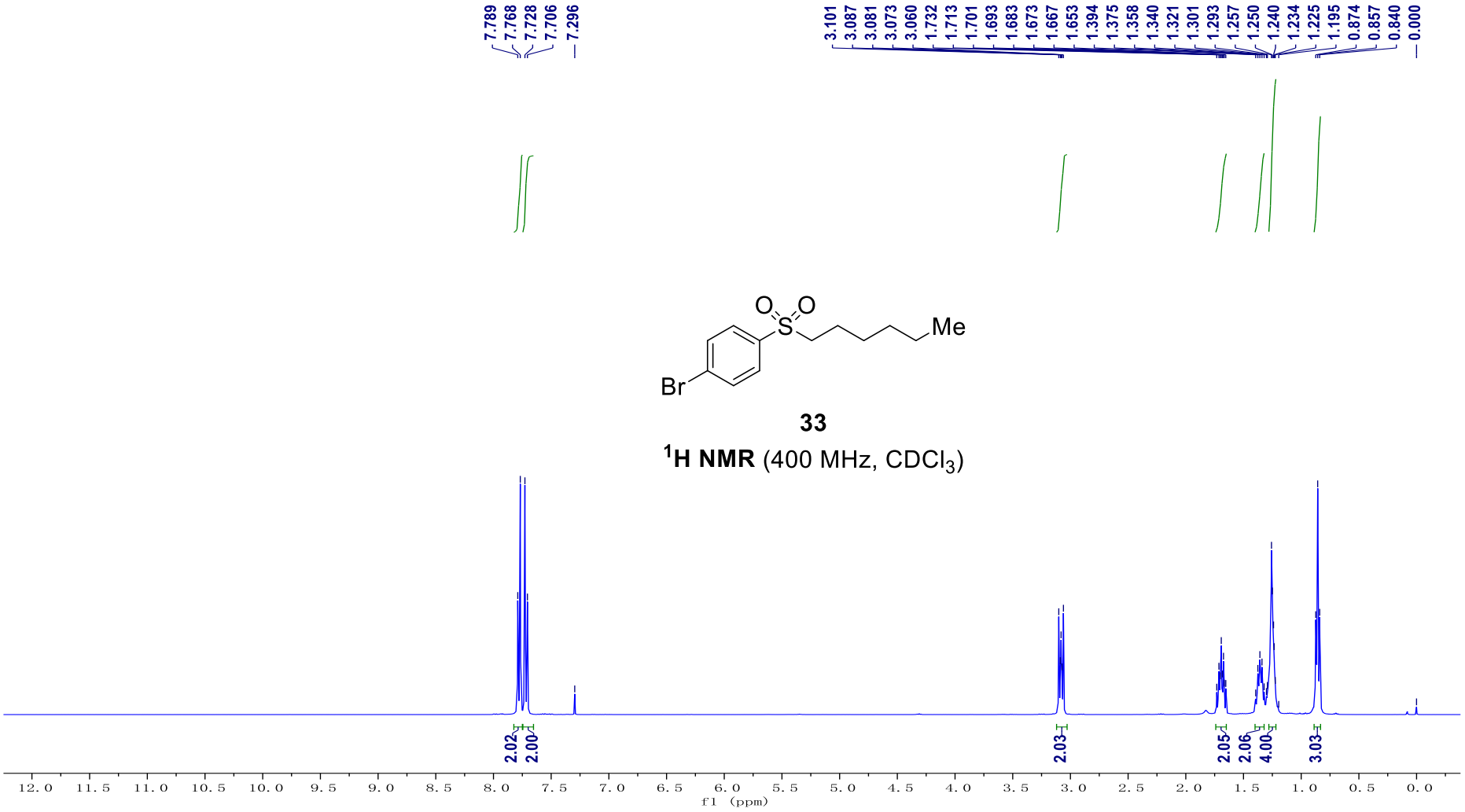
32

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



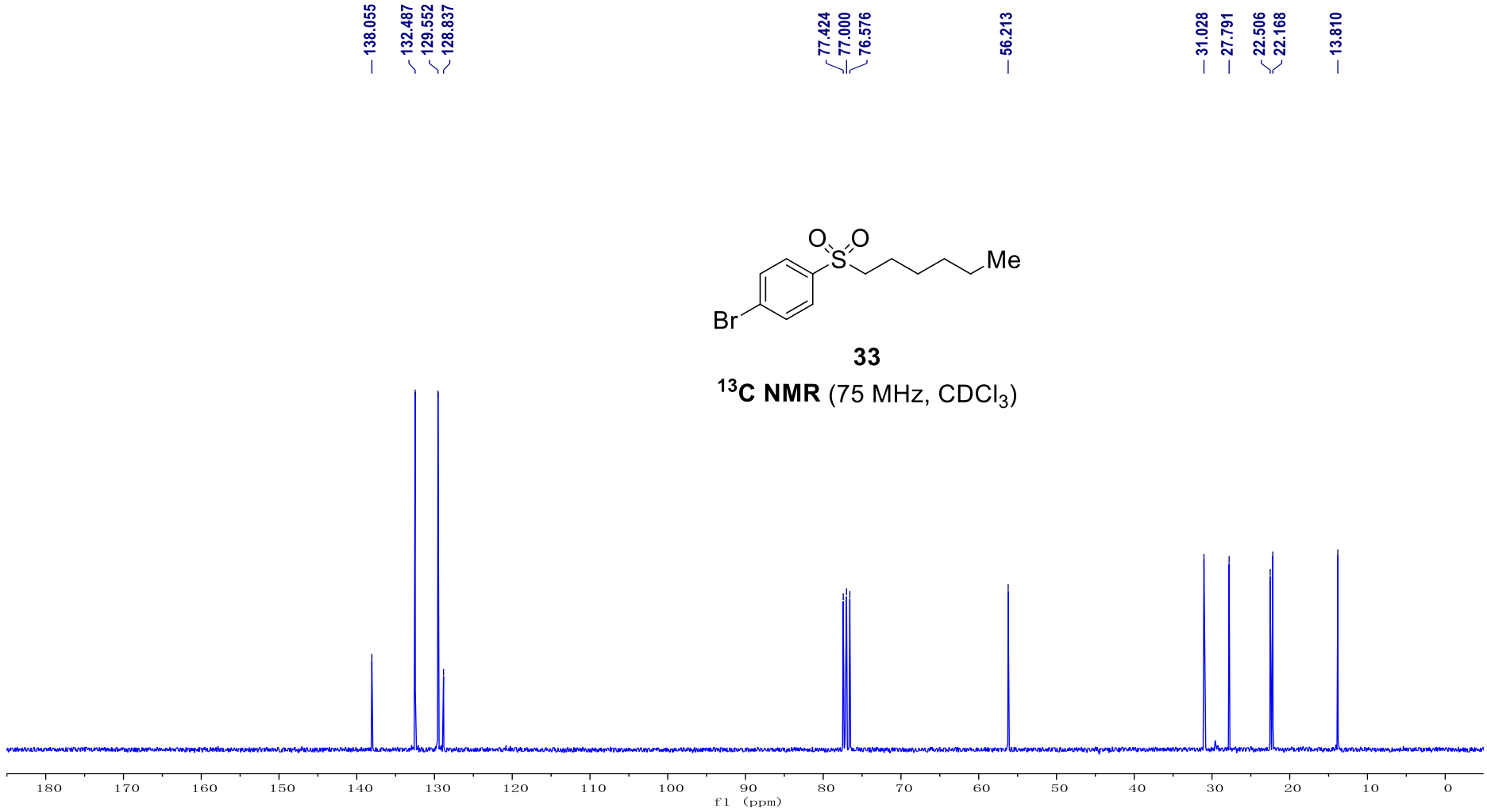
32

^{13}C NMR (100 MHz, $CDCl_3$)



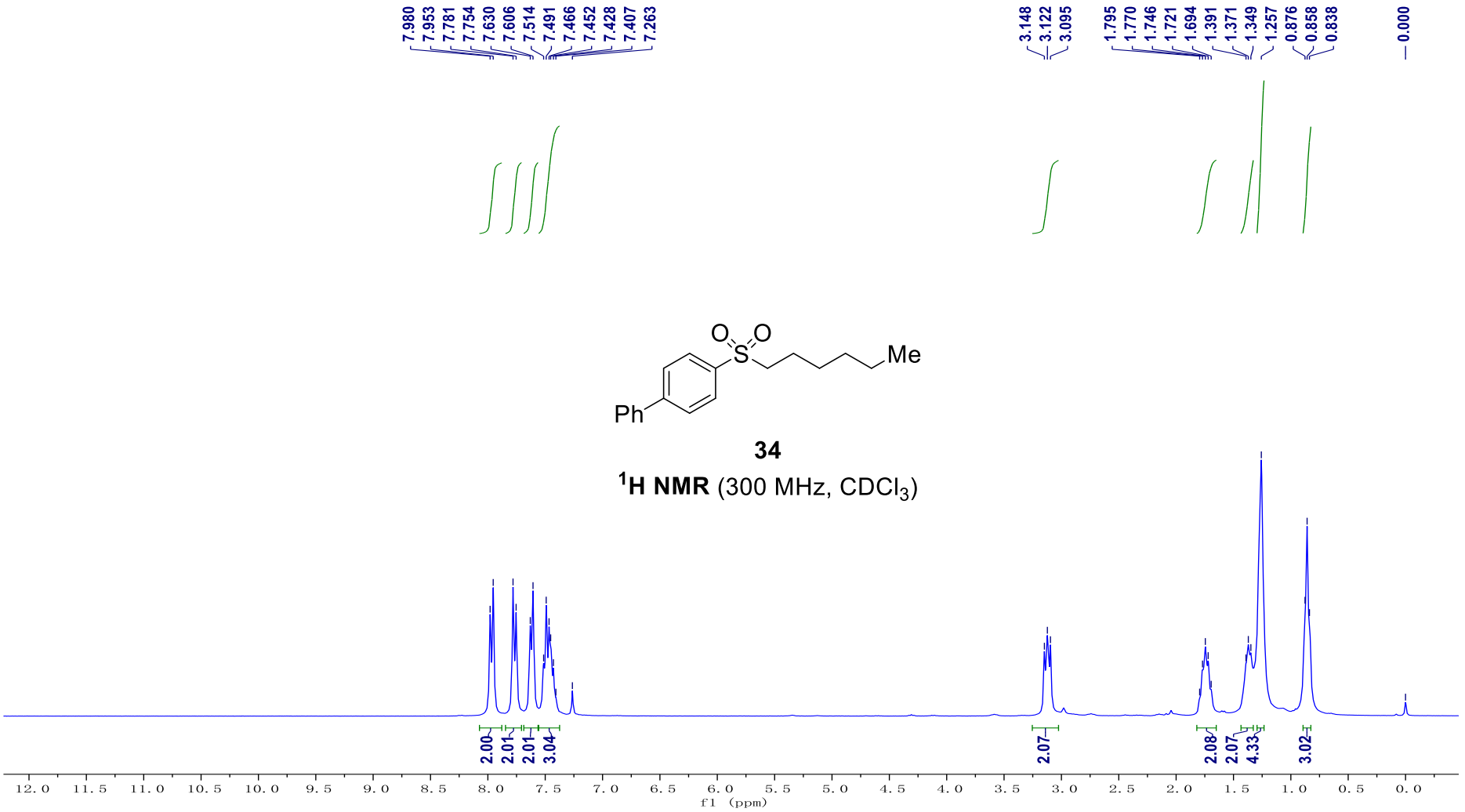
33

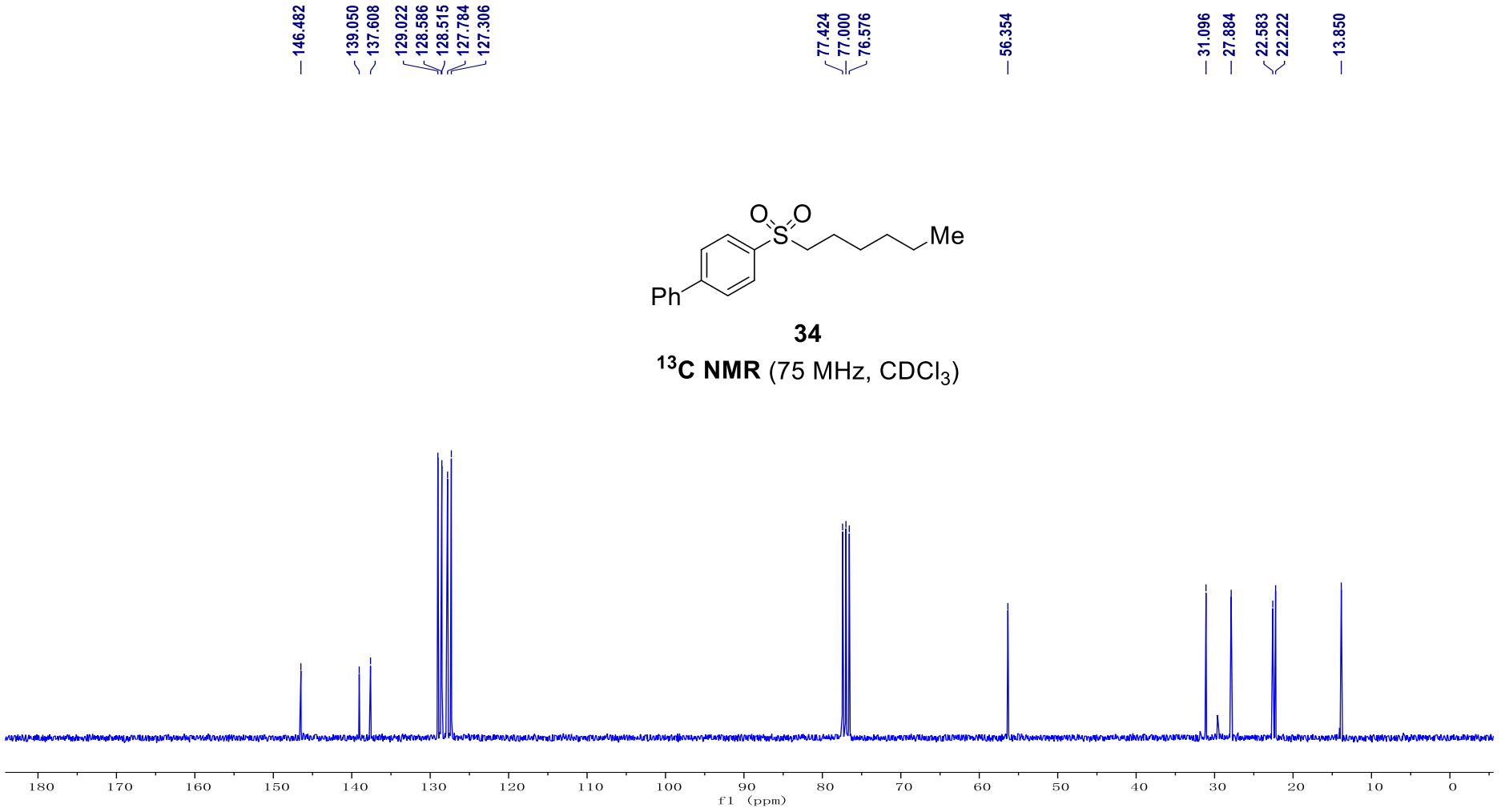
^{1}H NMR (400 MHz, $CDCl_3$)



33

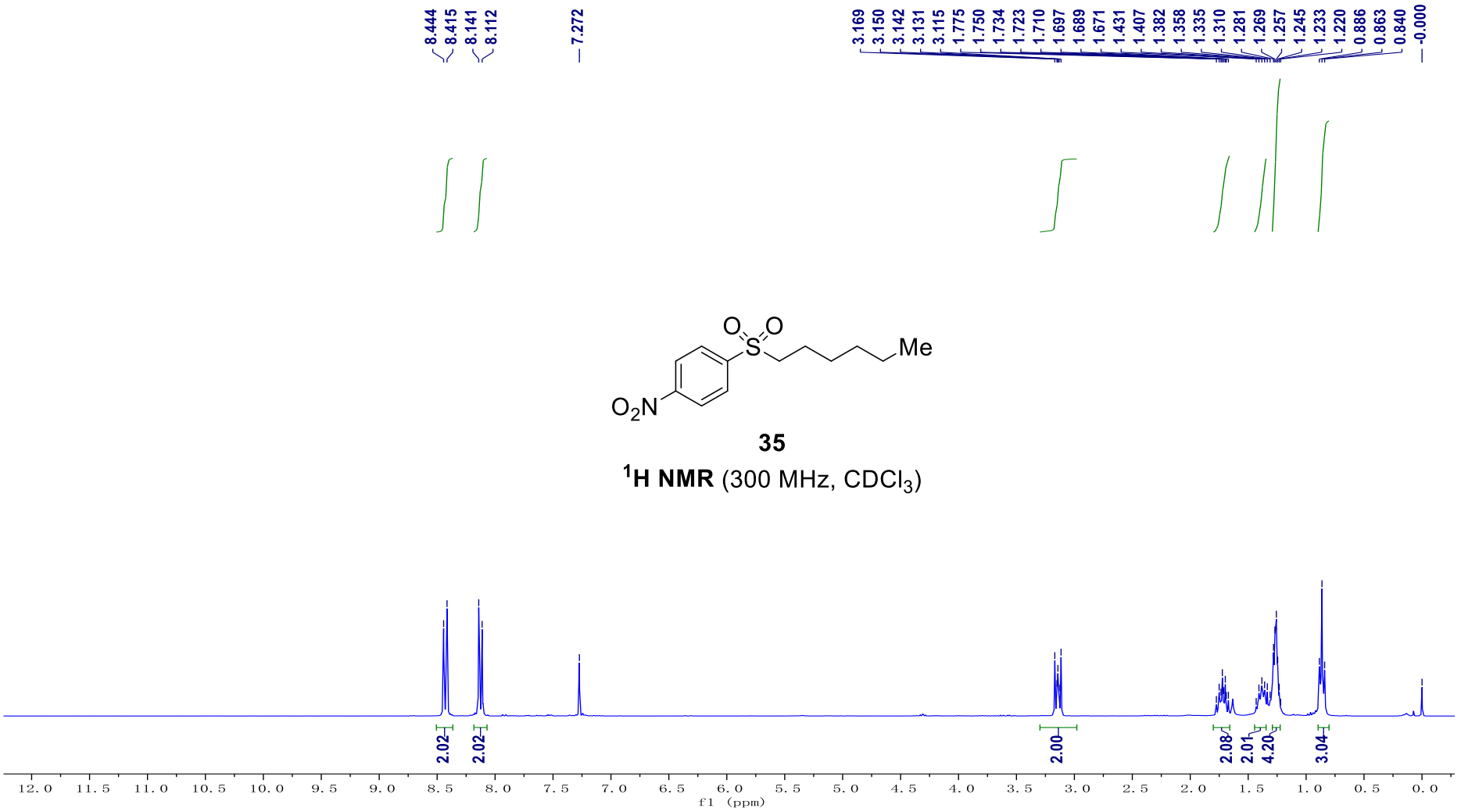
^{13}C NMR (75 MHz, $CDCl_3$)


7.980
7.953
7.781
7.754
7.630
7.606
7.514
7.491
7.466
7.452
7.428
7.407
7.263
3.148
3.122
3.095
1.795
1.770
1.746
1.721
1.694
1.391
1.371
1.349
1.257
0.876
0.858
0.838
0.000
O
O
S
Me
Ph
34
1H NMR (300 MHz, CDCl3)
2.00
2.01
2.01
3.04
2.07
2.08
2.07
4.33
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



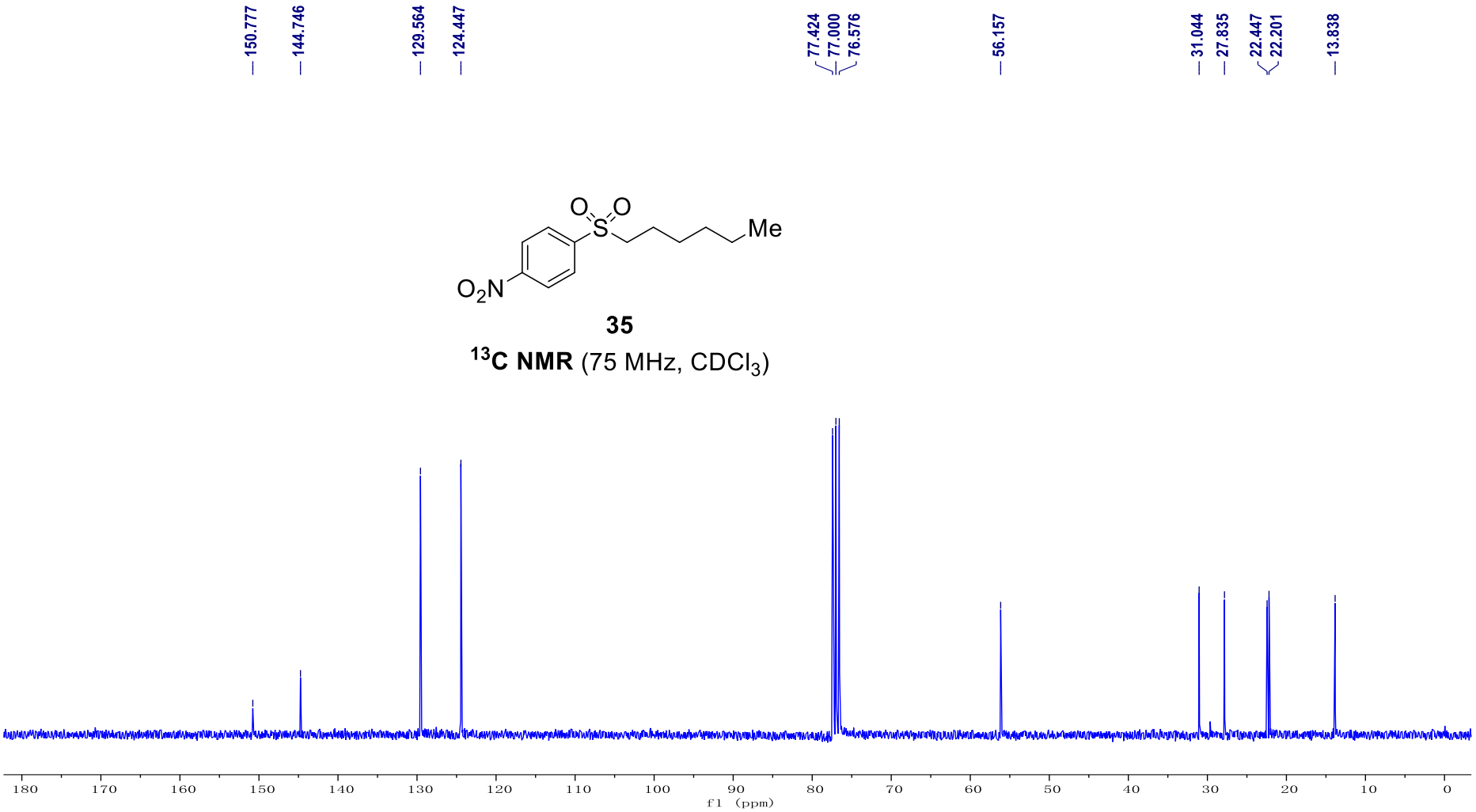
34

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



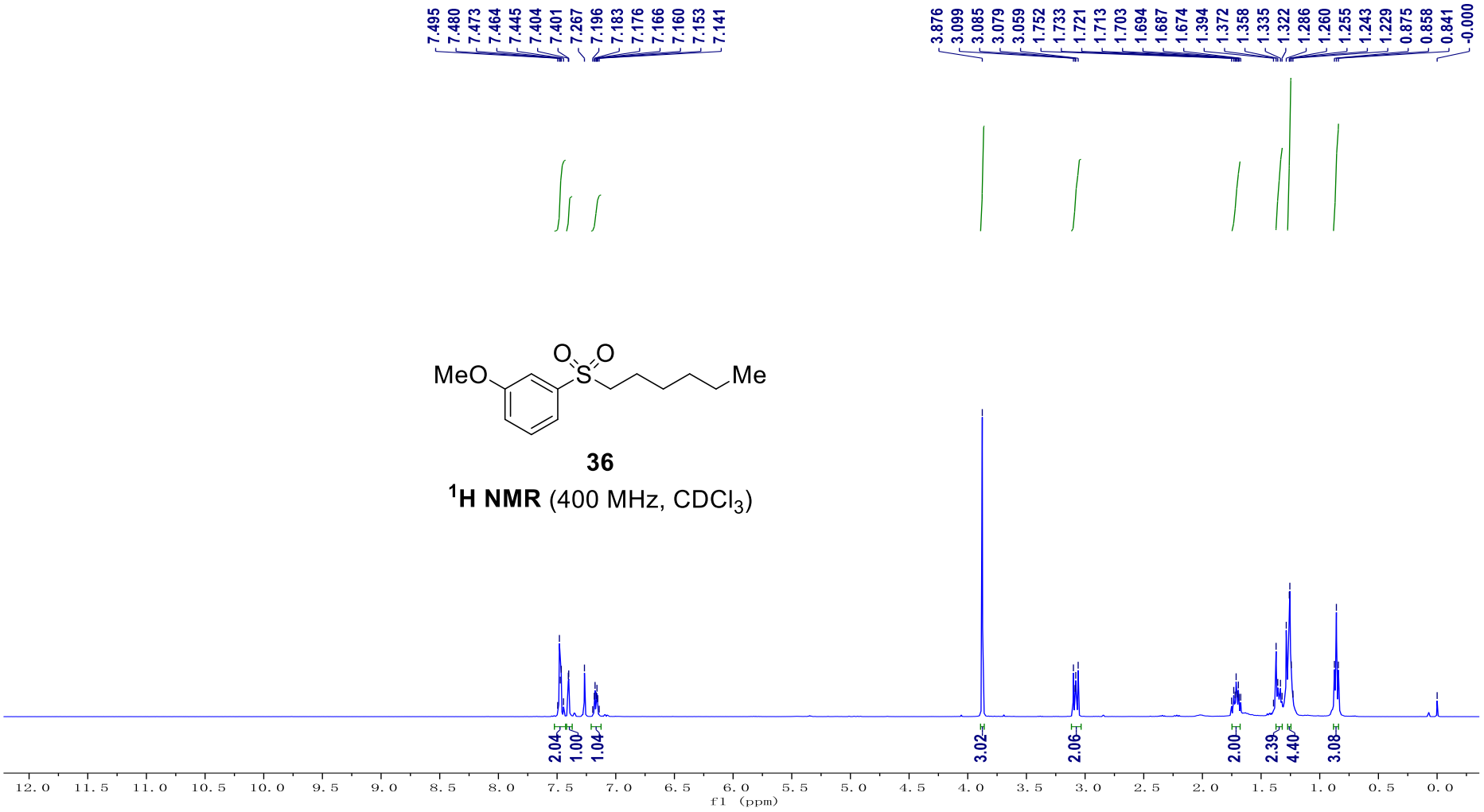
35

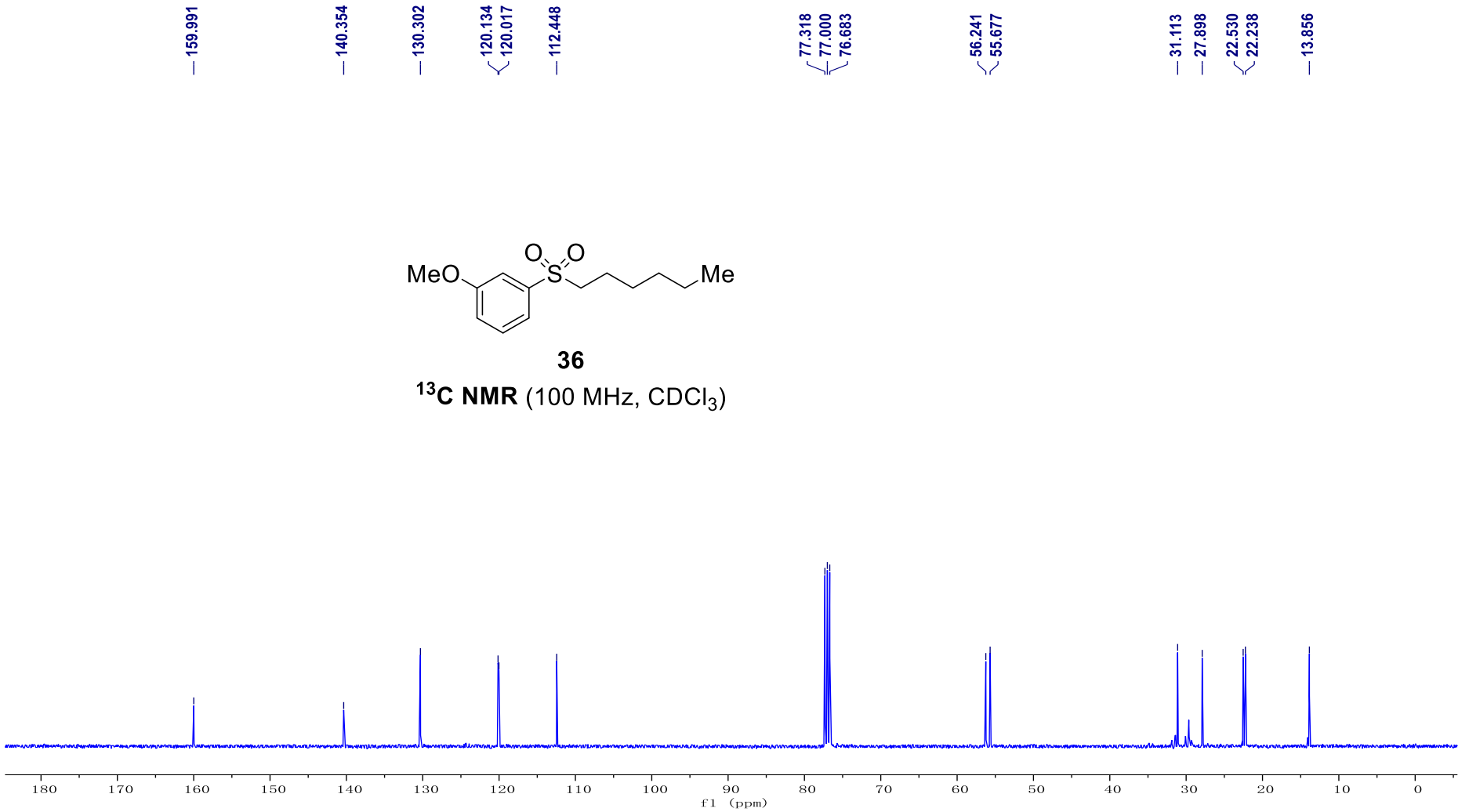
^{1}H NMR (300 MHz, $CDCl_3$)



35

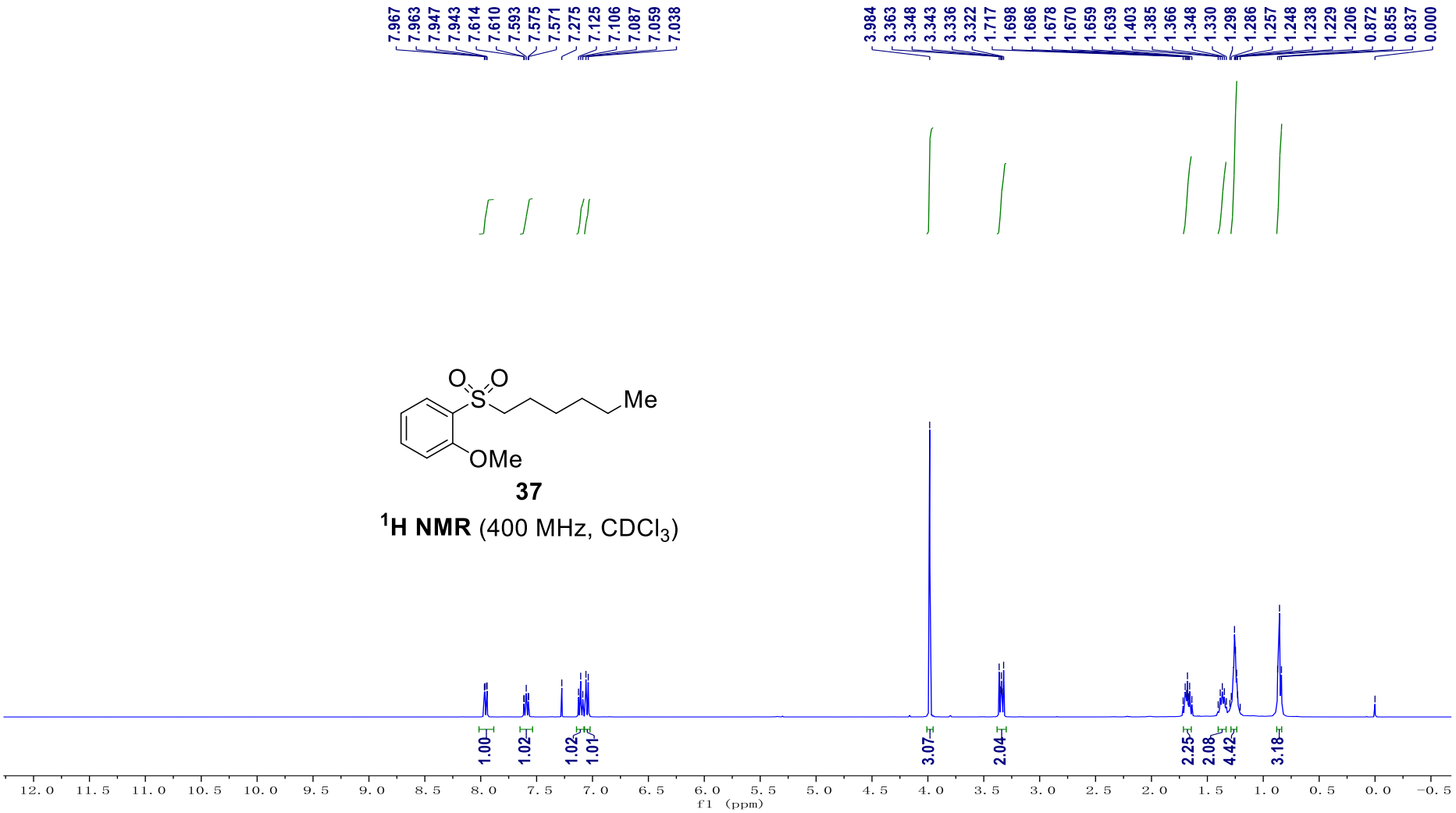
^{13}C NMR (75 MHz, $CDCl_3$)

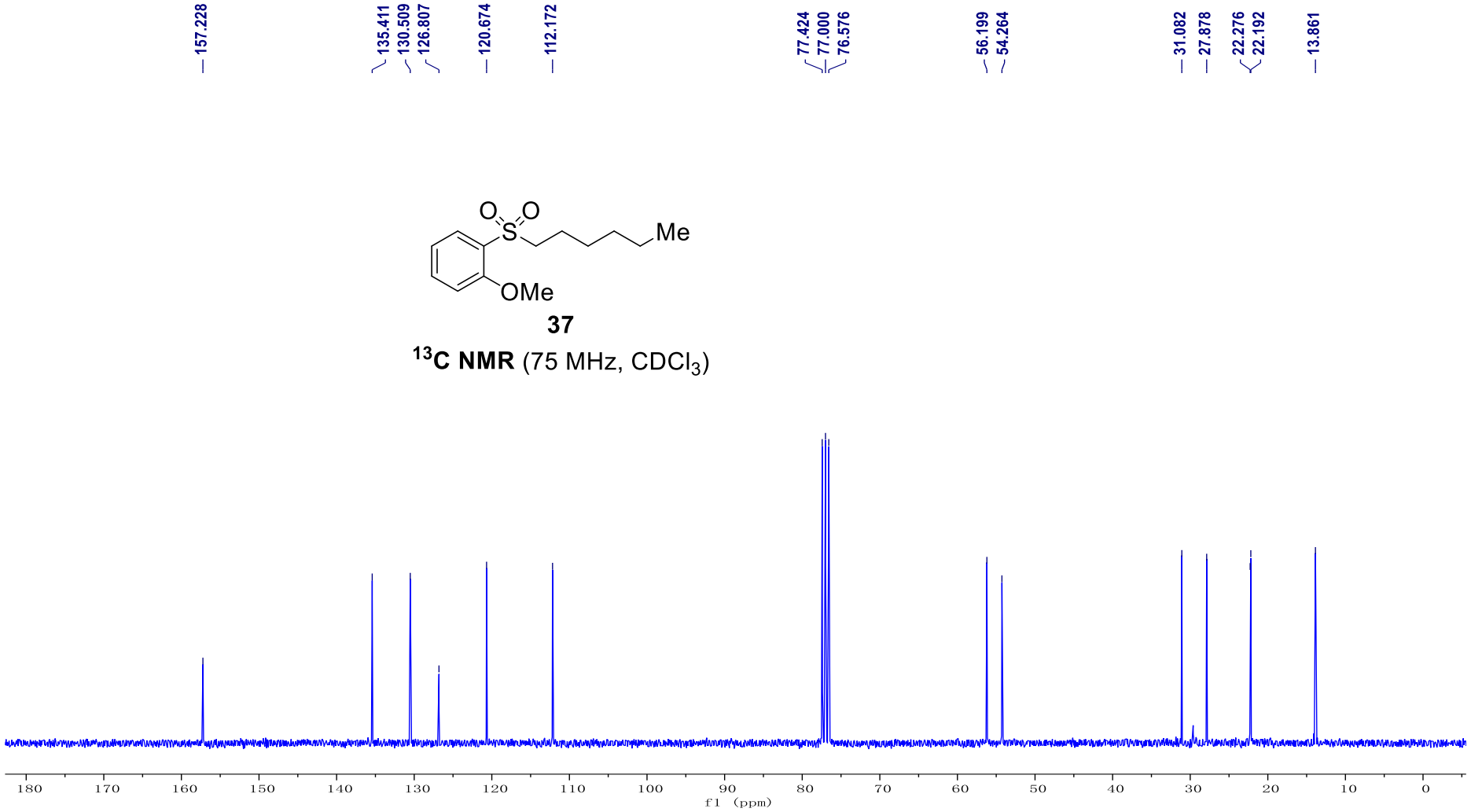

7.495
7.480
7.473
7.464
7.445
7.404
7.401
7.267
7.196
7.183
7.176
7.166
7.160
7.153
7.141
3.876
3.099
3.085
3.079
3.059
1.752
1.733
1.721
1.713
1.703
1.694
1.687
1.674
1.394
1.372
1.358
1.335
1.322
1.286
1.260
1.255
1.243
1.229
0.875
0.858
0.841
-0.000
MeO
O
O
S
Me
36
1H NMR (400 MHz, CDCl3)
2.04
1.00
1.04
3.02
2.06
2.00
2.39
4.40
3.08
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



36

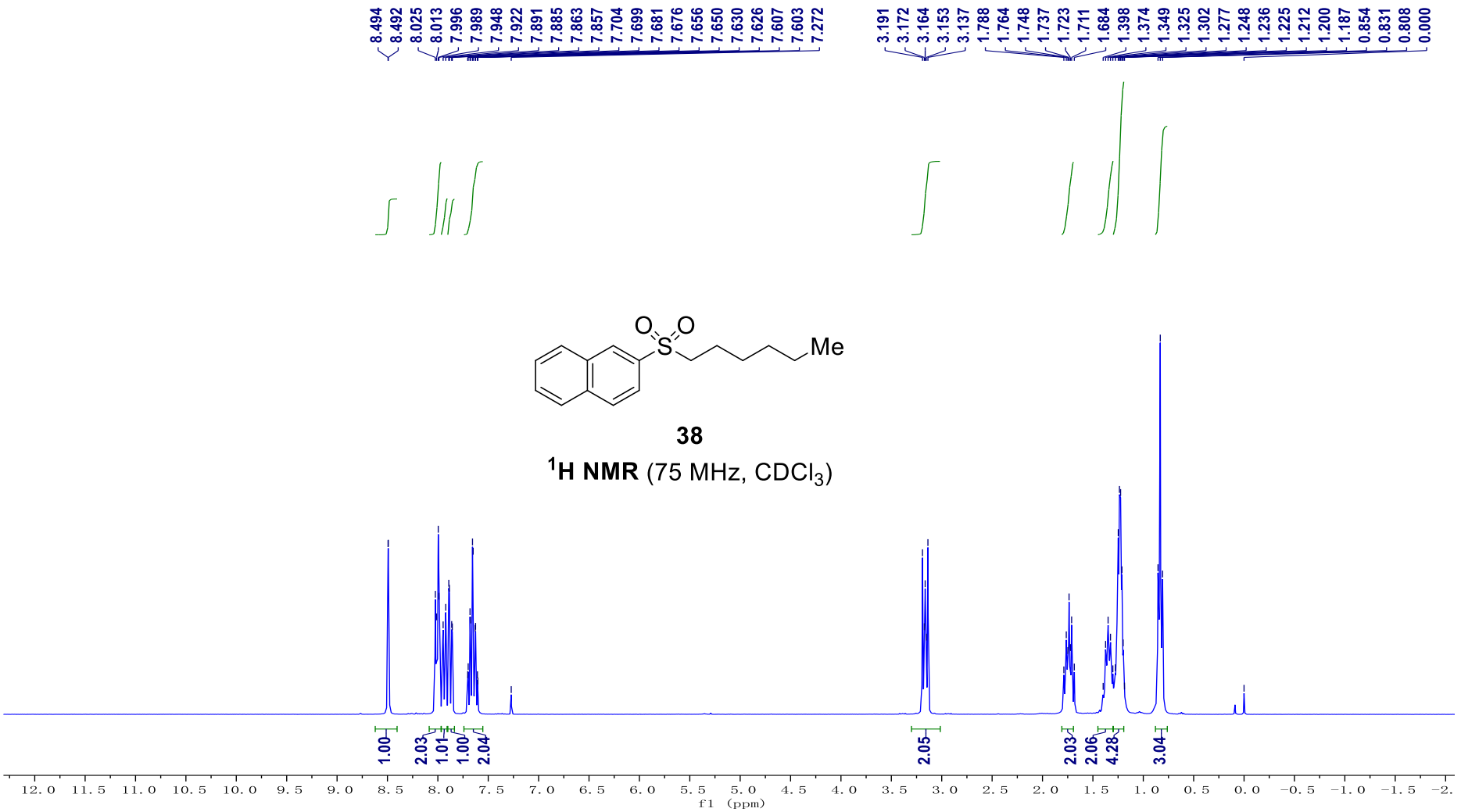
^{13}C NMR (100 MHz, $CDCl_3$)

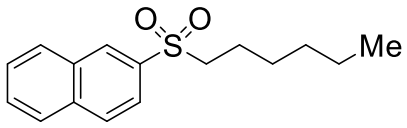

7.967
7.963
7.947
7.943
7.614
7.610
7.593
7.575
7.571
7.275
7.125
7.106
7.087
7.059
7.038
3.984
3.363
3.348
3.343
3.336
3.322
1.717
1.698
1.686
1.678
1.670
1.659
1.639
1.403
1.385
1.366
1.348
1.330
1.298
1.286
1.257
1.248
1.238
1.229
1.206
0.872
0.855
0.837
0.000
O
O
S
Me
OMe
37
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.02
1.01
3.07
2.04
2.25
2.08
4.42
3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)



37

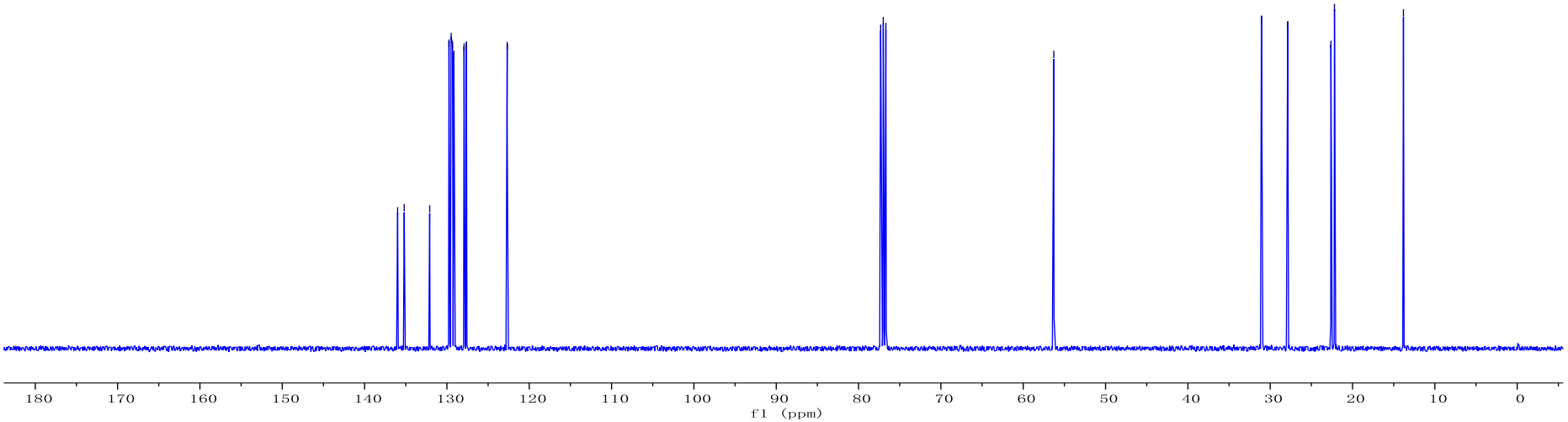
^{13}C NMR (75 MHz, $CDCl_3$)

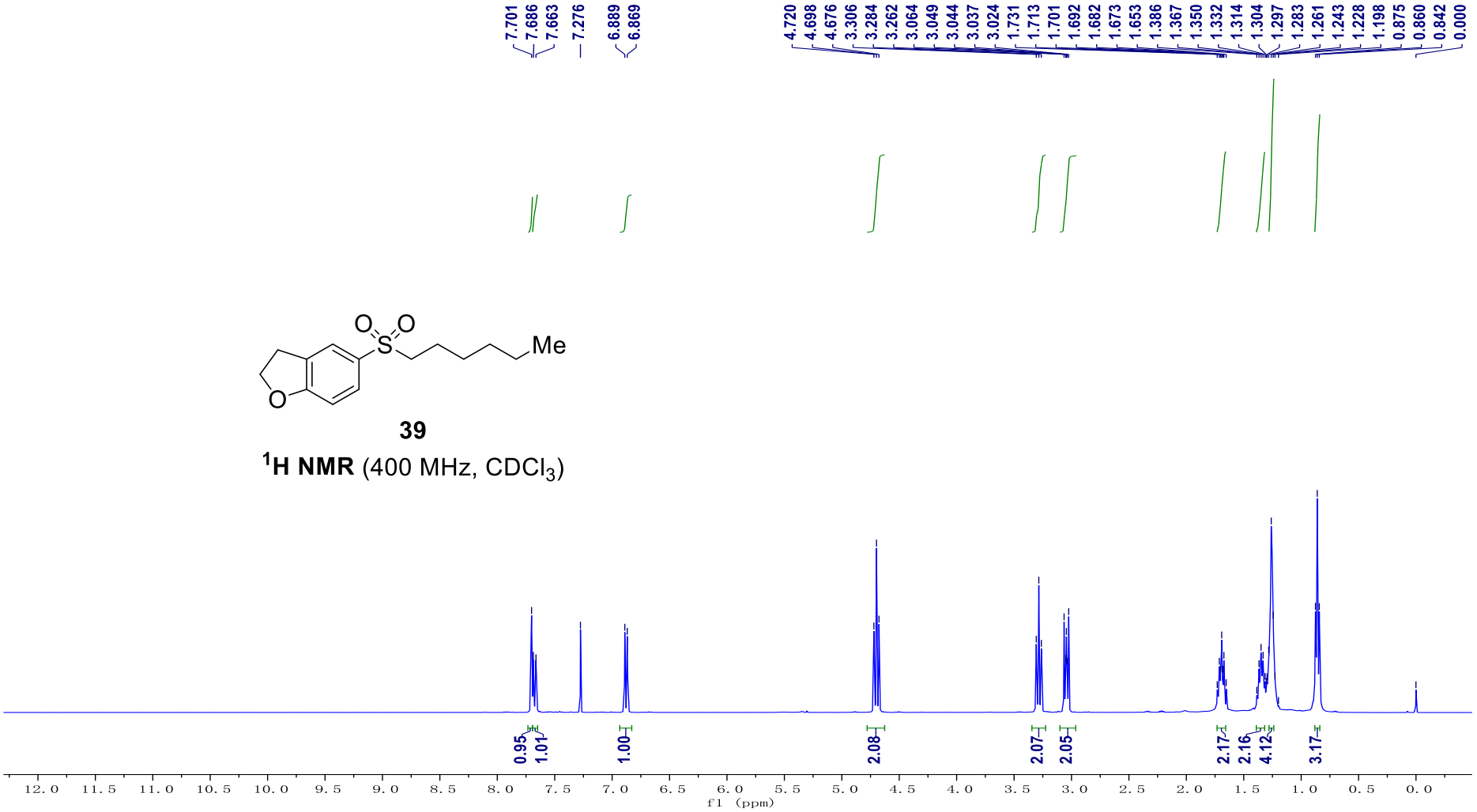

8.494
8.492
8.025
8.013
7.996
7.989
7.948
7.922
7.891
7.885
7.863
7.857
7.704
7.699
7.681
7.676
7.656
7.650
7.630
7.626
7.607
7.603
7.272
3.191
3.172
3.164
3.153
3.137
1.788
1.764
1.748
1.737
1.723
1.711
1.684
1.398
1.374
1.349
1.325
1.302
1.277
1.248
1.236
1.225
1.212
1.200
1.187
0.854
0.831
0.808
0.000
O
O
S
Me
38
1H NMR (75 MHz, CDCl3)
1.00
2.03
1.01
1.00
2.04
2.05
2.03
2.06
4.28
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2.
f1 (ppm)

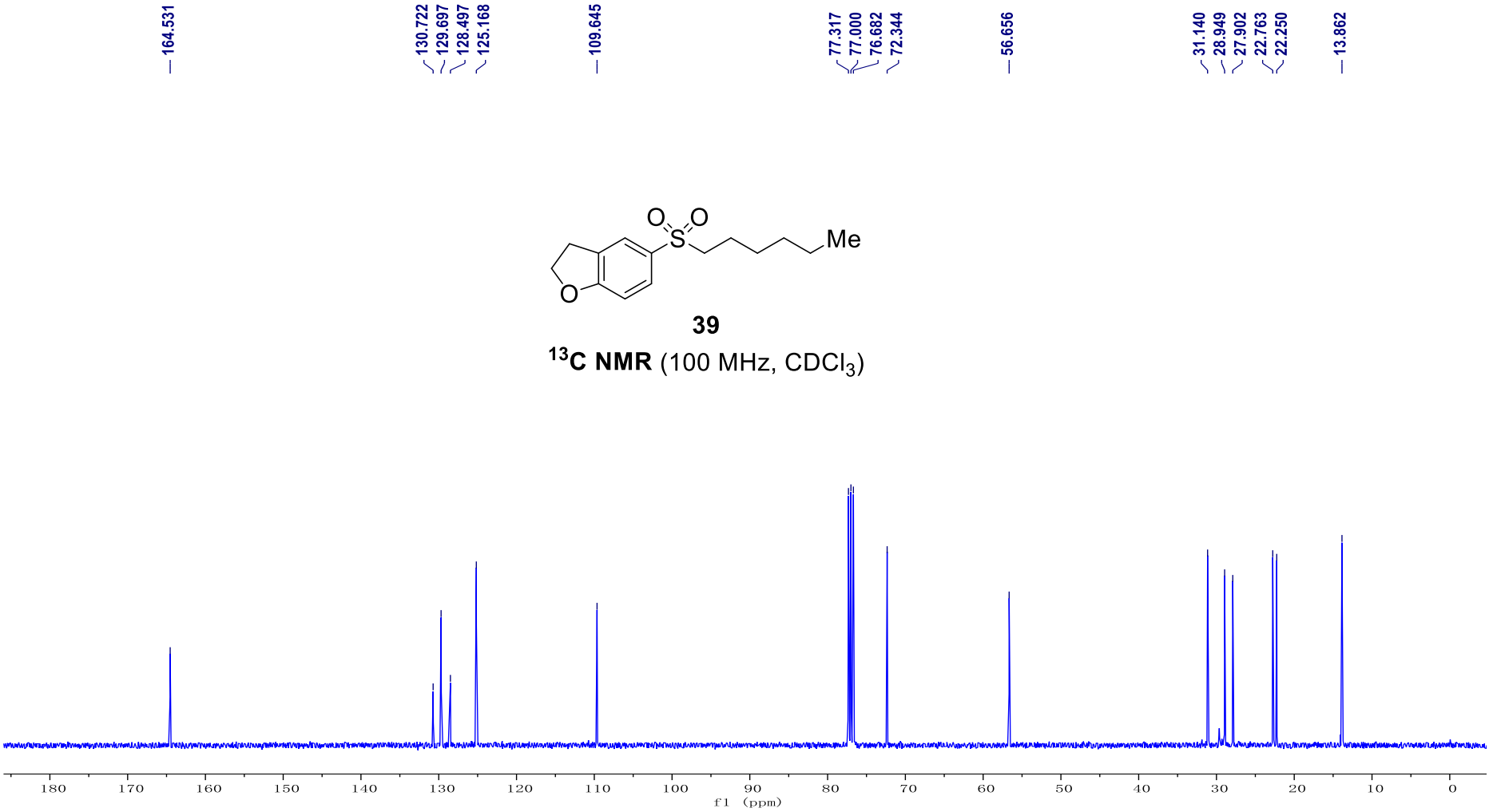


38

^{13}C NMR (100 MHz, $CDCl_3$)

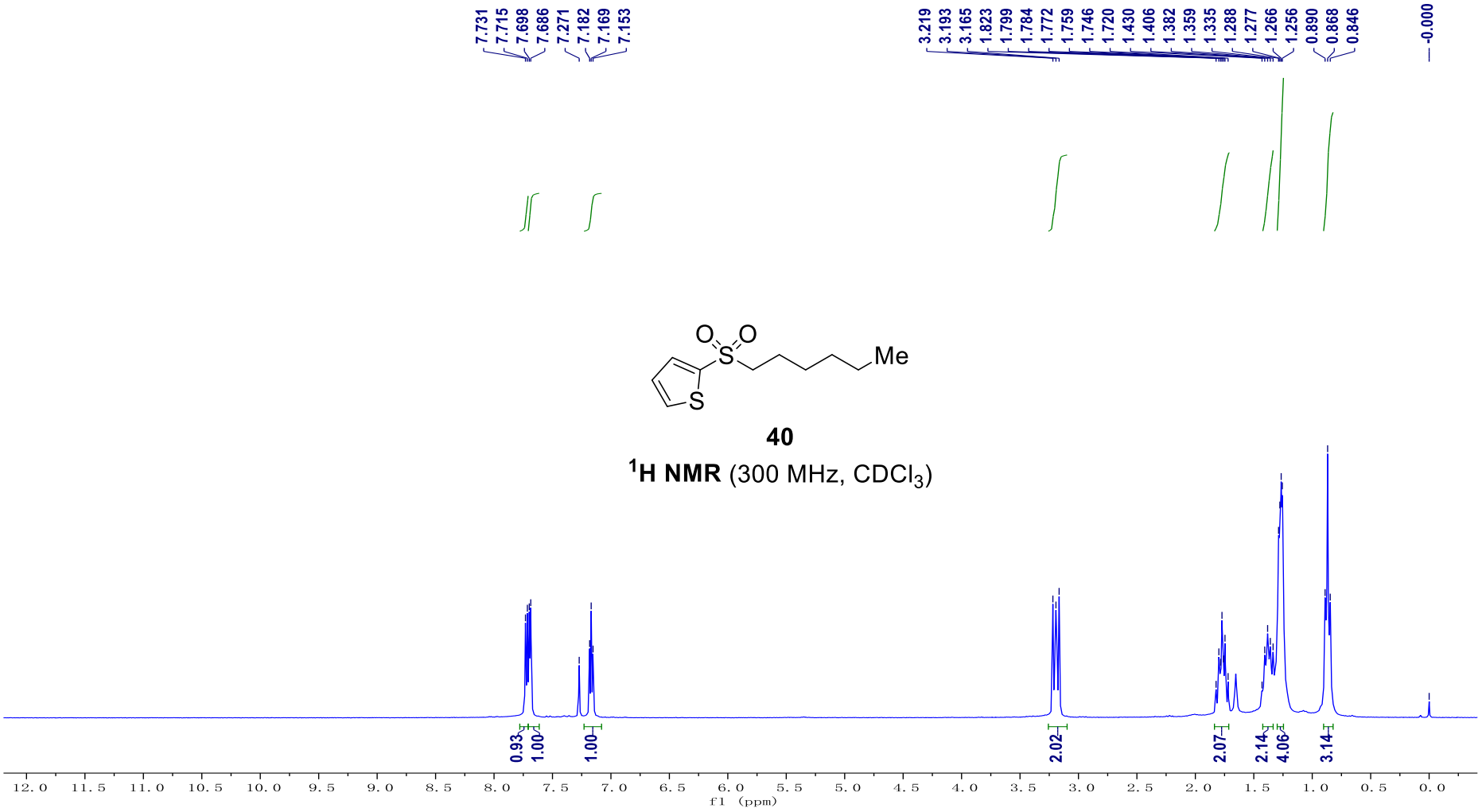


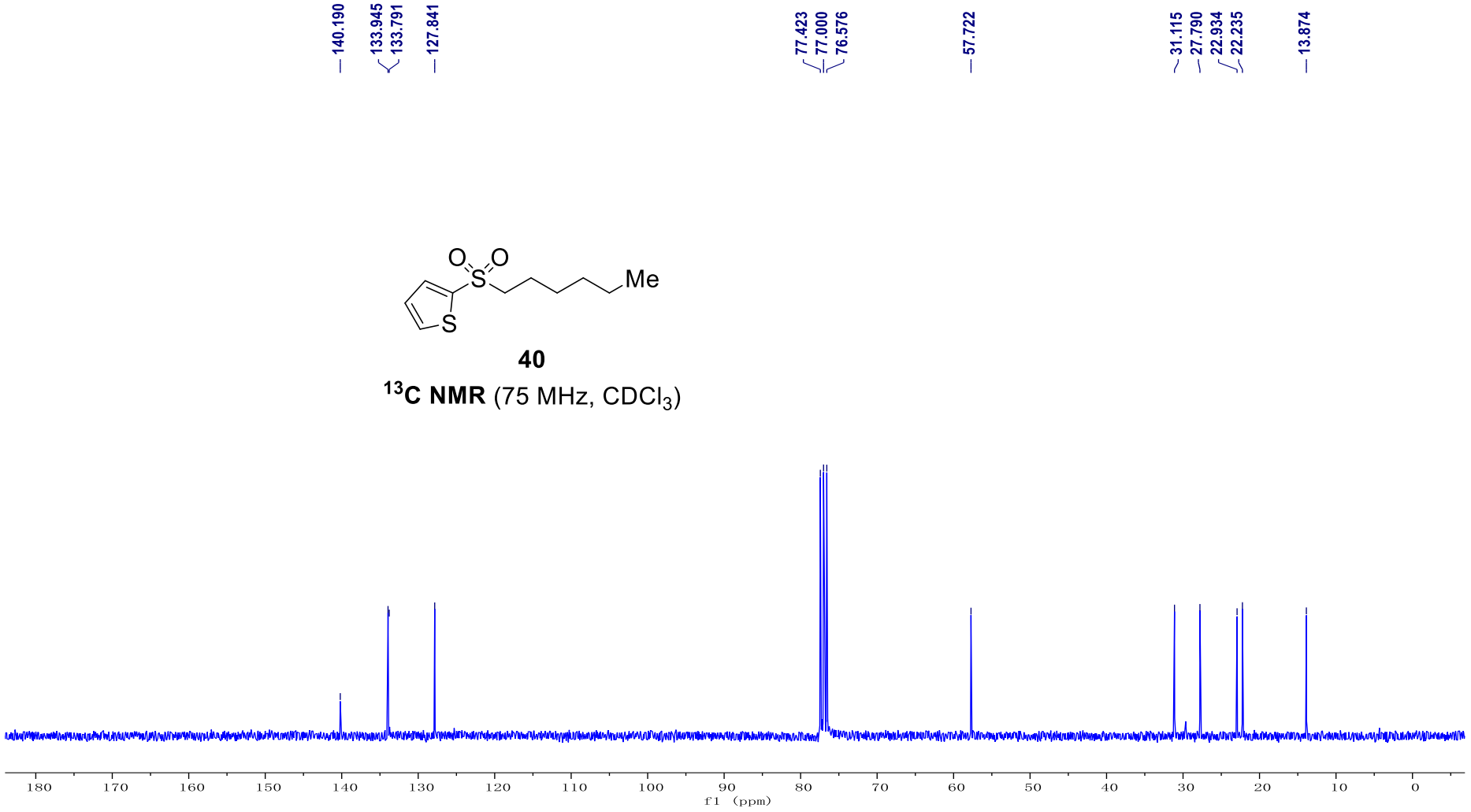

7.701
7.686
7.663
7.276
6.889
6.869
4.720
4.698
4.676
3.306
3.284
3.262
3.064
3.049
3.044
3.037
3.024
1.731
1.713
1.701
1.692
1.682
1.673
1.653
1.386
1.367
1.350
1.332
1.314
1.304
1.297
1.283
1.261
1.243
1.228
1.198
0.875
0.860
0.842
0.000
O
O
S
Me
O
39
1H NMR (400 MHz, CDCl3)
0.95
1.01
1.00
2.08
2.07
2.05
2.17
2.16
4.12
3.17
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



39

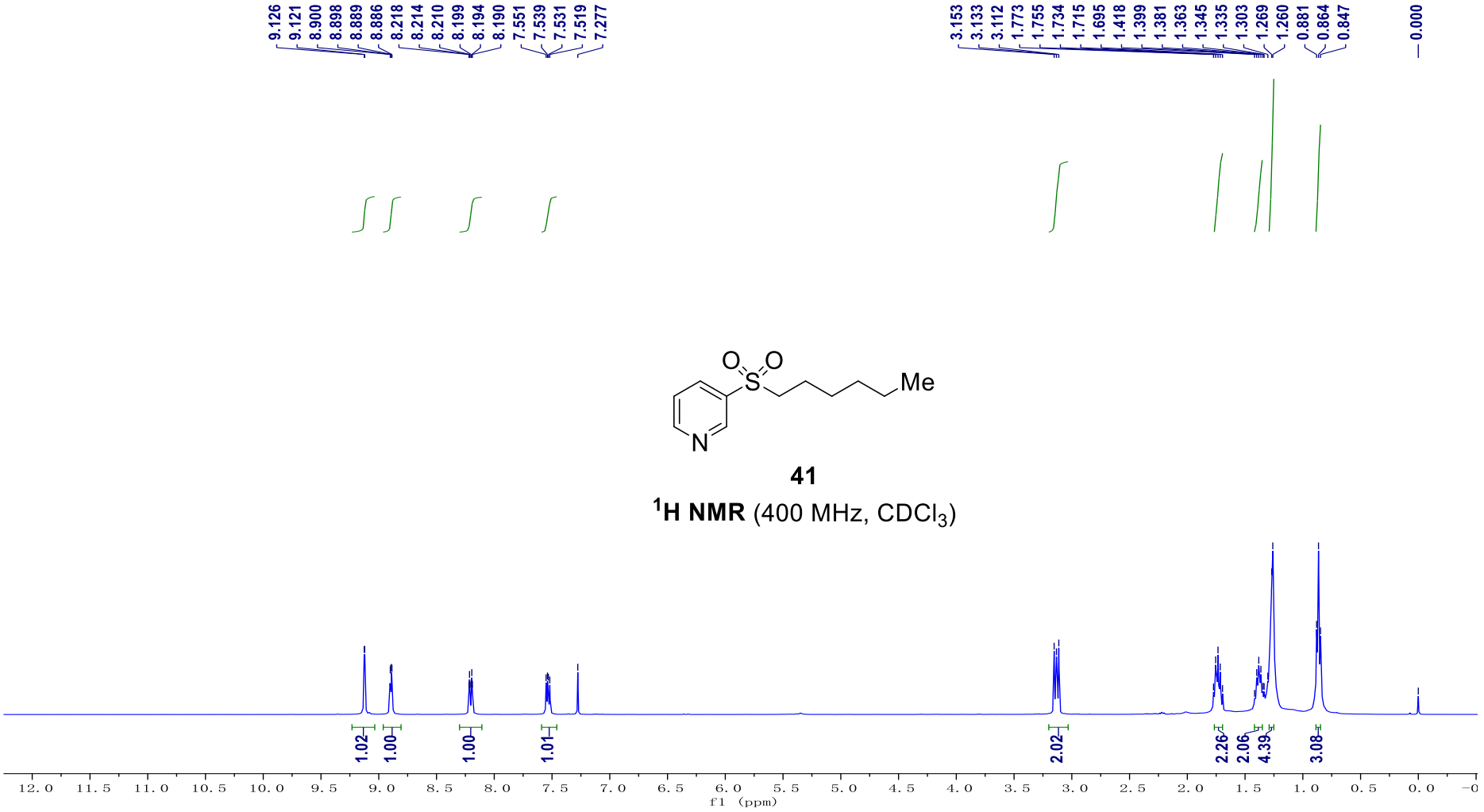
^{13}C NMR (100 MHz, $CDCl_3$)


7.731
7.715
7.698
7.686
7.271
7.182
7.169
7.153
3.219
3.193
3.165
1.823
1.799
1.784
1.772
1.759
1.746
1.720
1.430
1.406
1.382
1.359
1.335
1.288
1.277
1.266
1.256
0.890
0.868
0.846
-0.000
O
O
S
Me
S
40
1H NMR (300 MHz, CDCl3)
0.93
1.00
1.00
2.02
2.07
2.14
4.06
3.14
f1 (ppm)



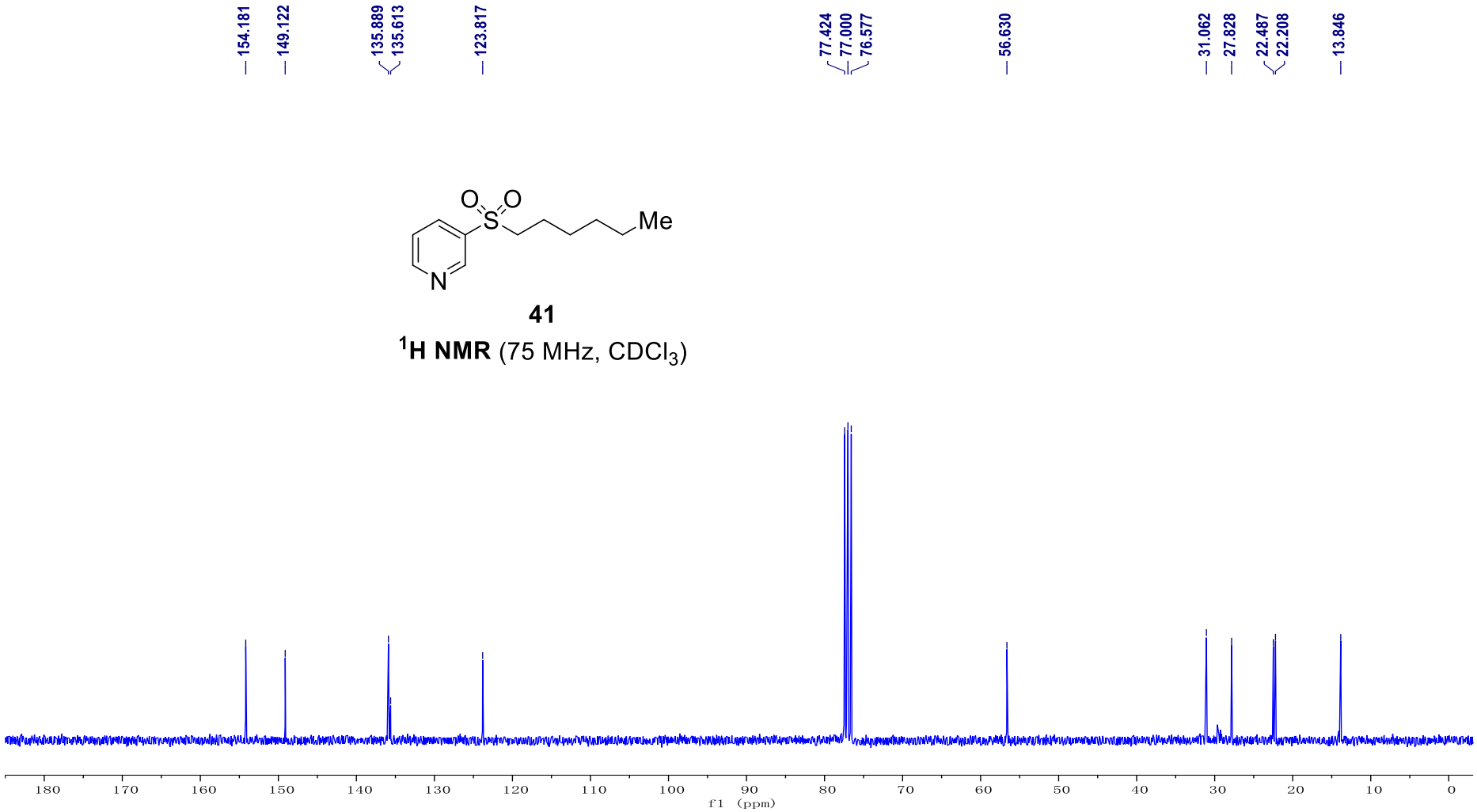
40

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



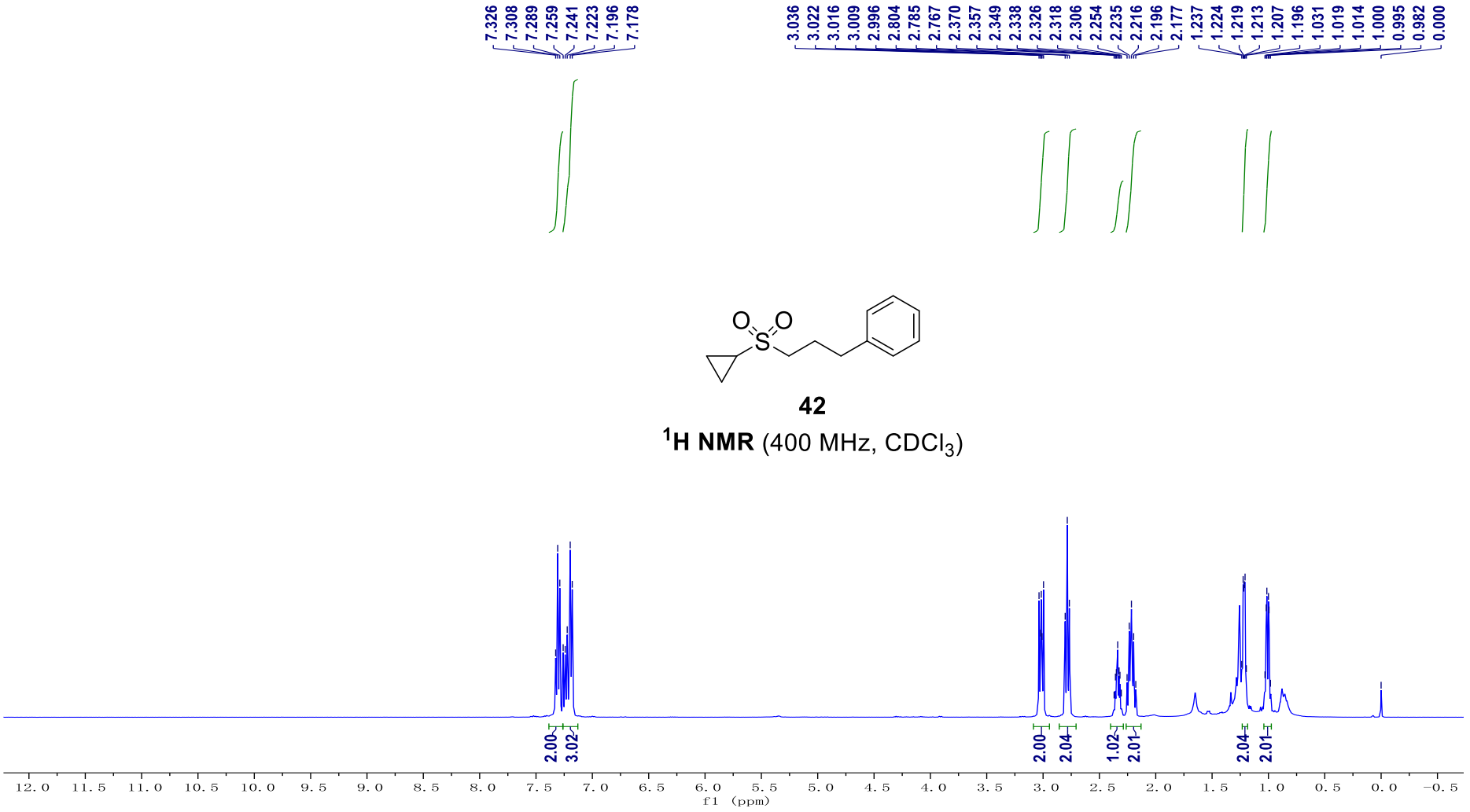
41

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



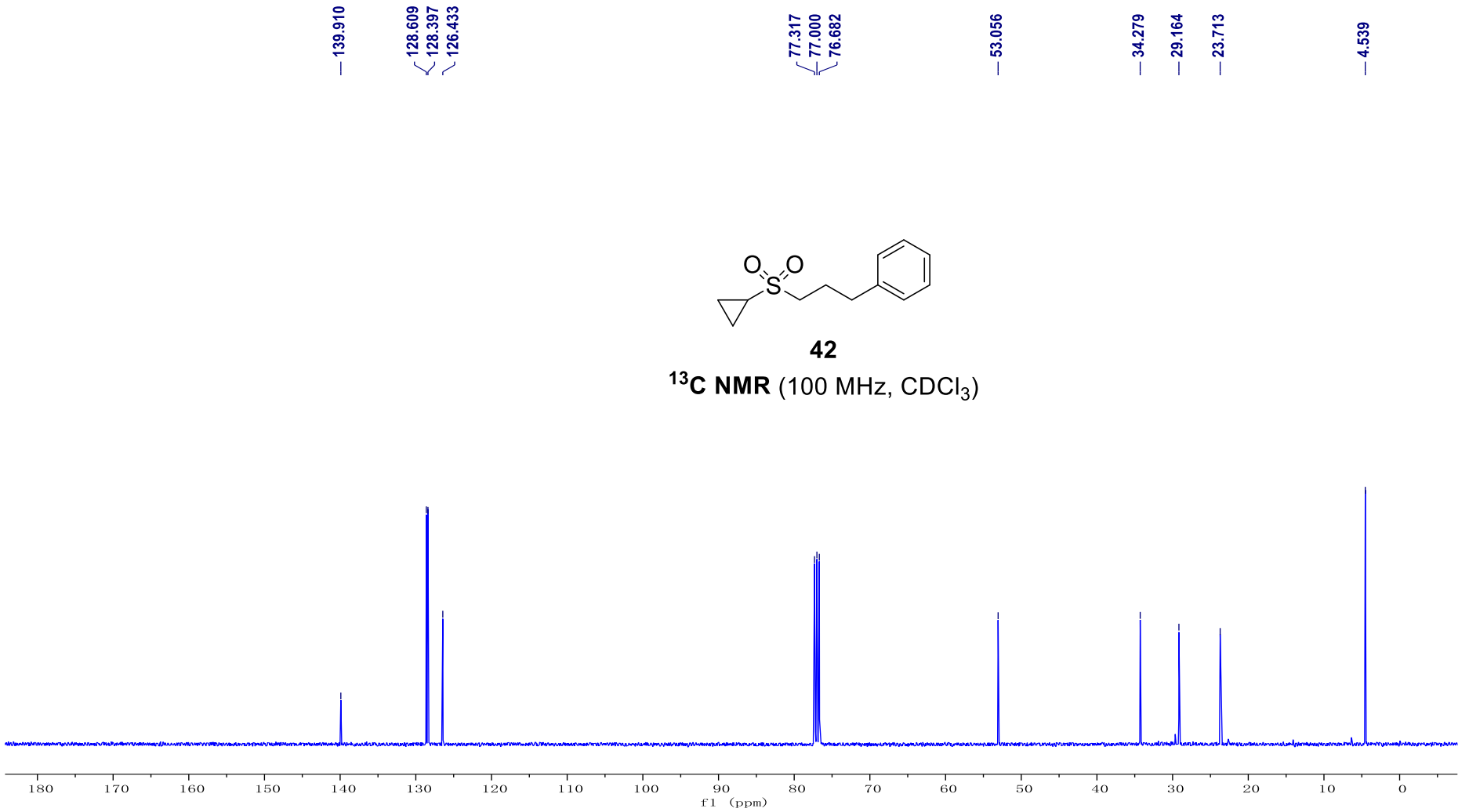
41

^{1}H NMR (75 MHz, $CDCl_3$)



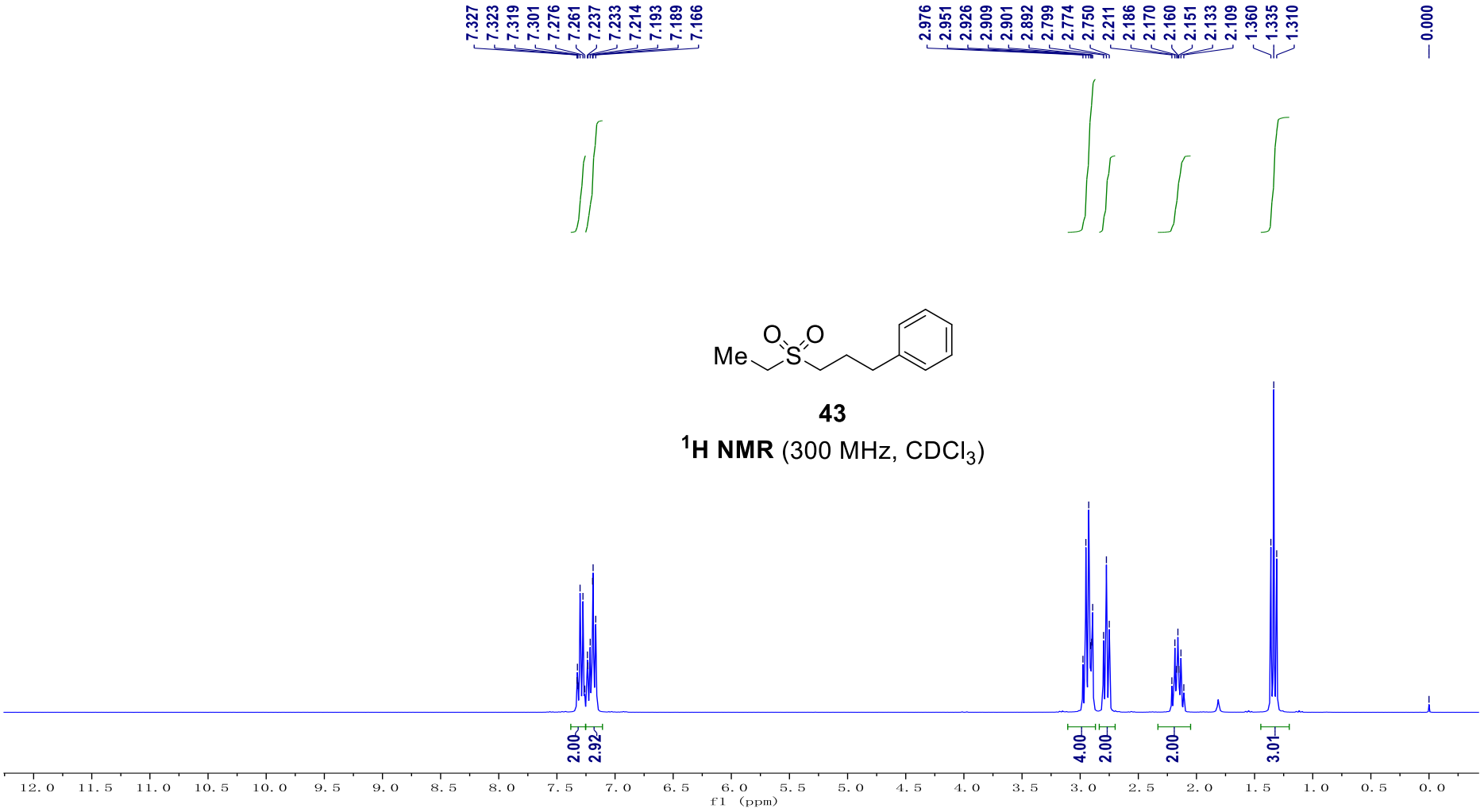
42

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



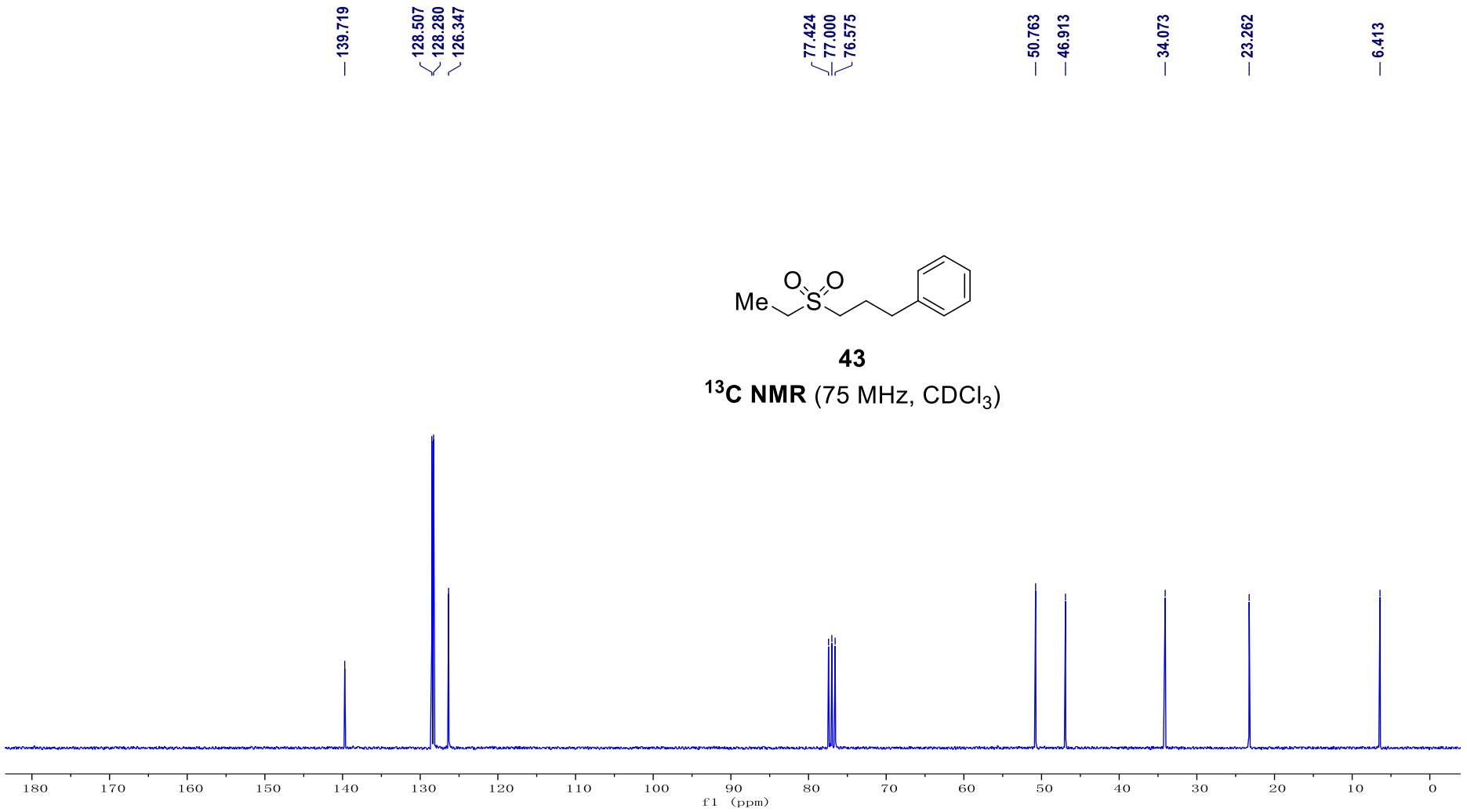
42

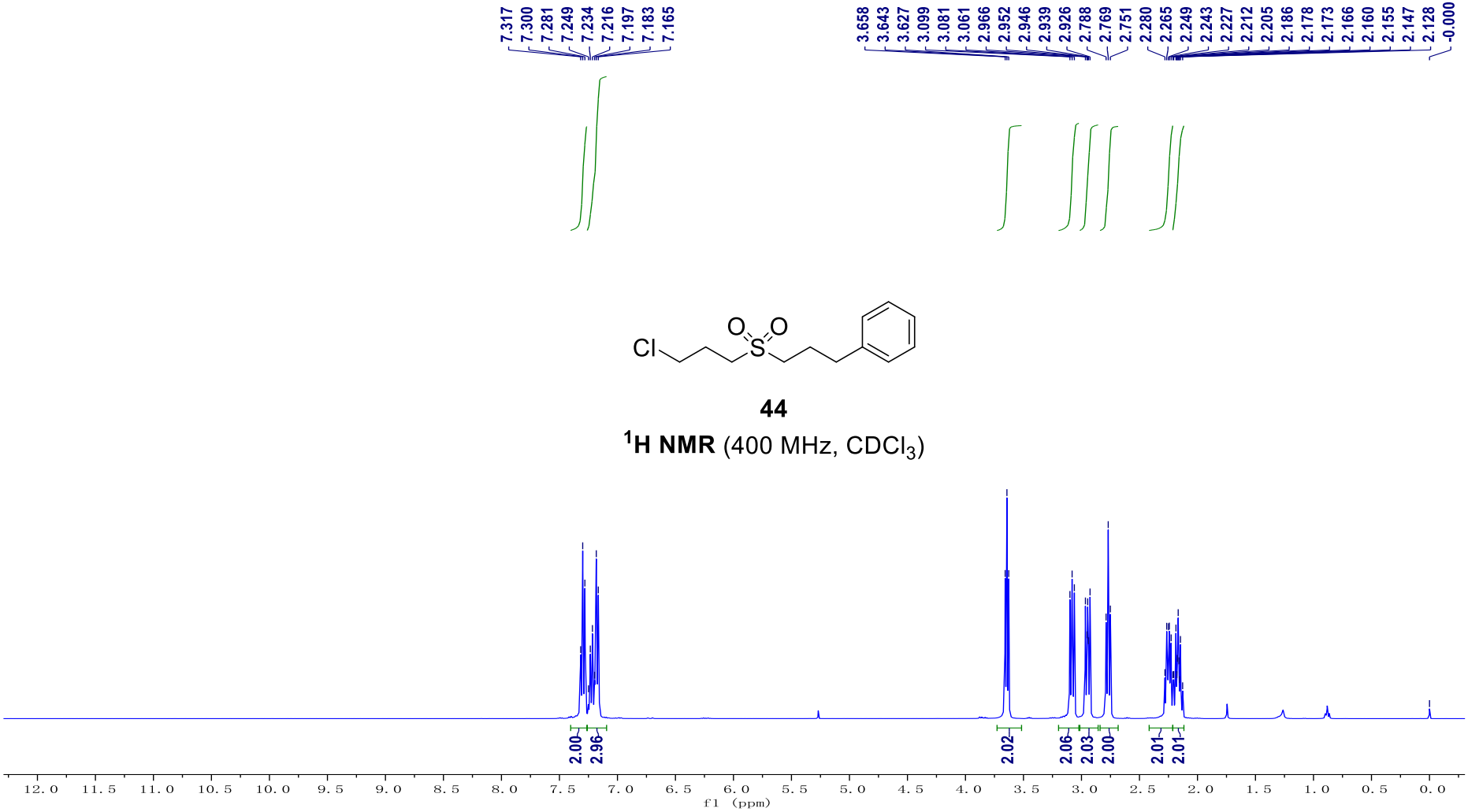
^{13}C NMR (100 MHz, $CDCl_3$)



43

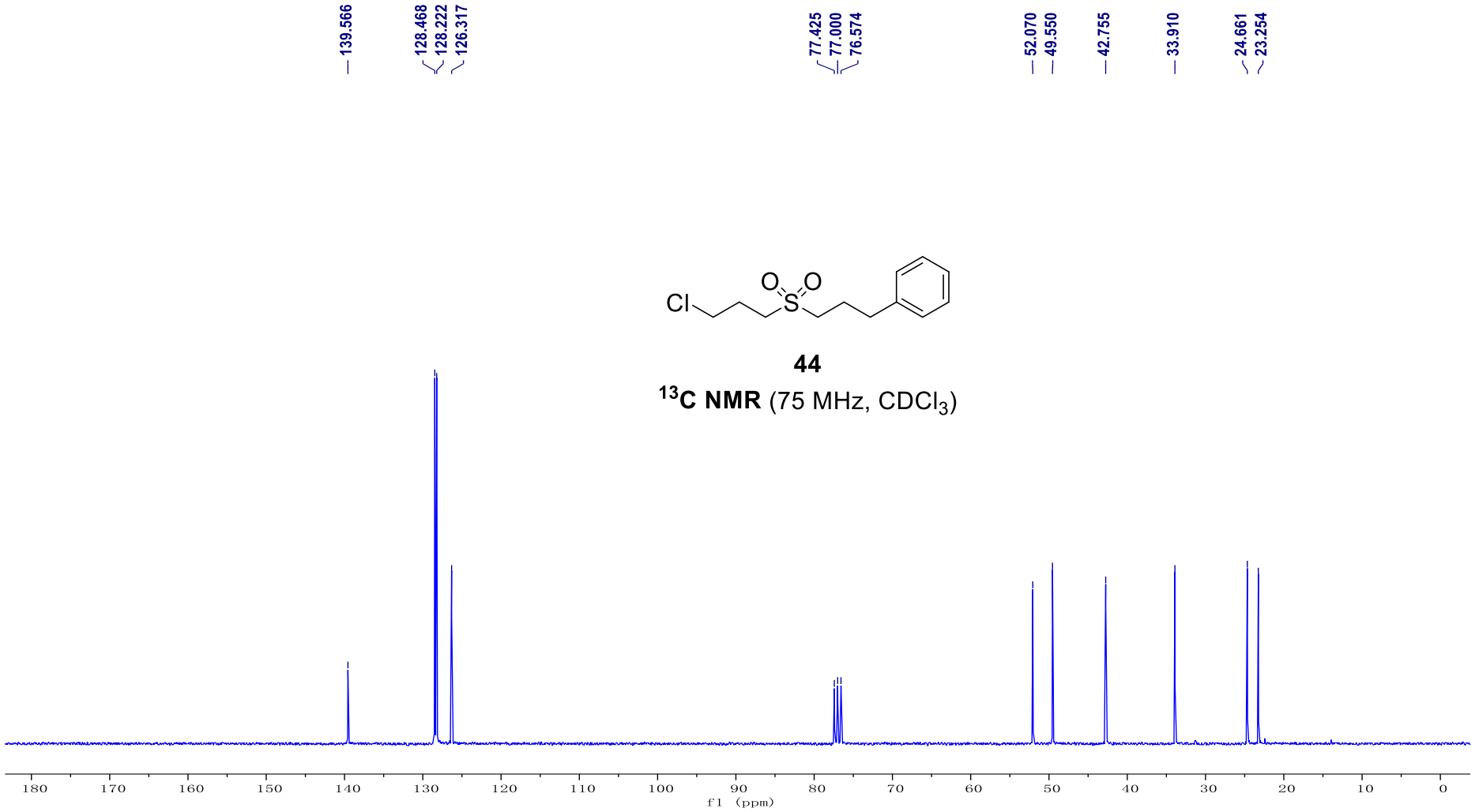
^{1}H NMR (300 MHz, $CDCl_3$)


139.719
128.507
128.280
126.347
77.424
77.000
76.575
50.763
46.913
34.073
23.262
6.413
Me
O
O
S
43
13C NMR (75 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



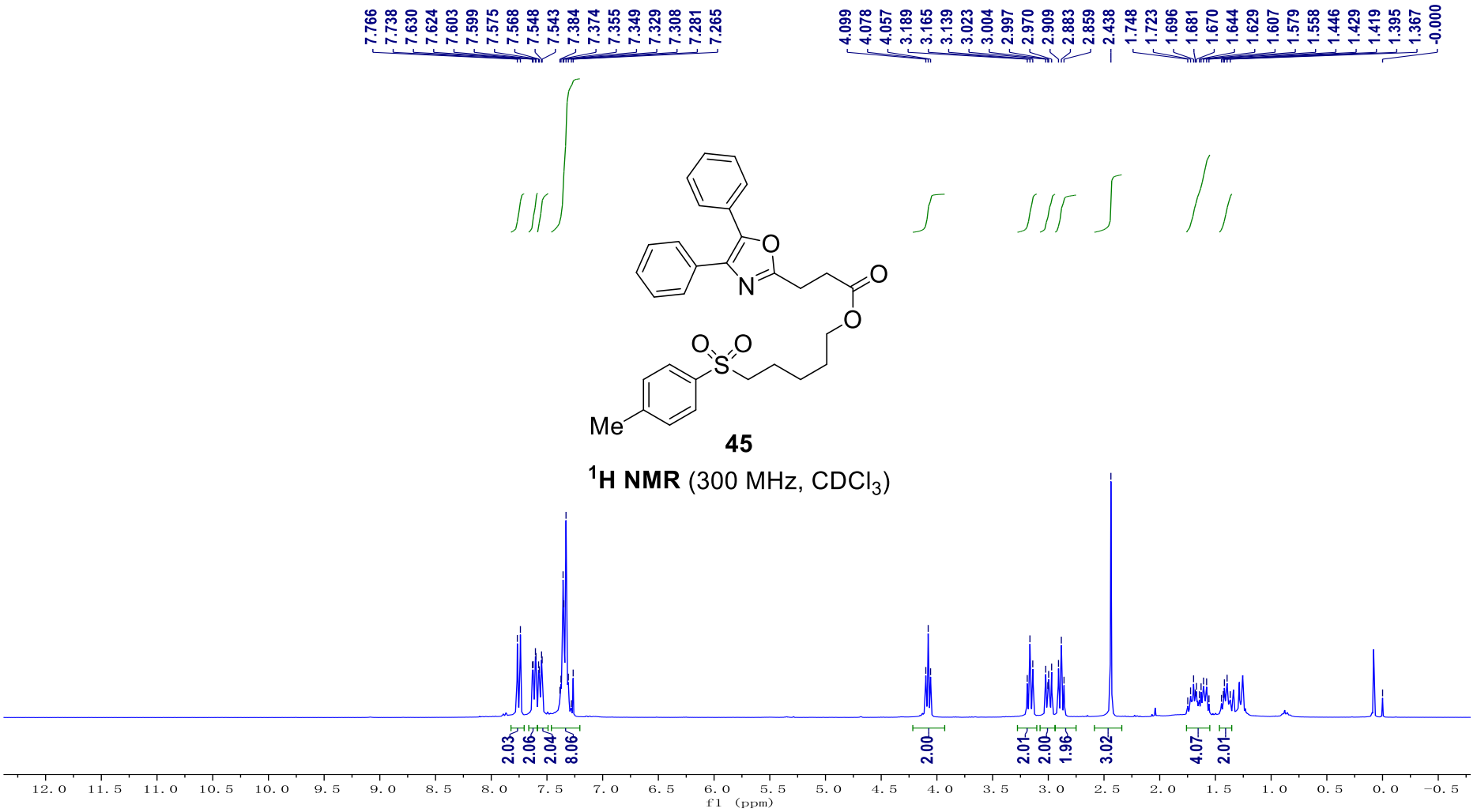
44

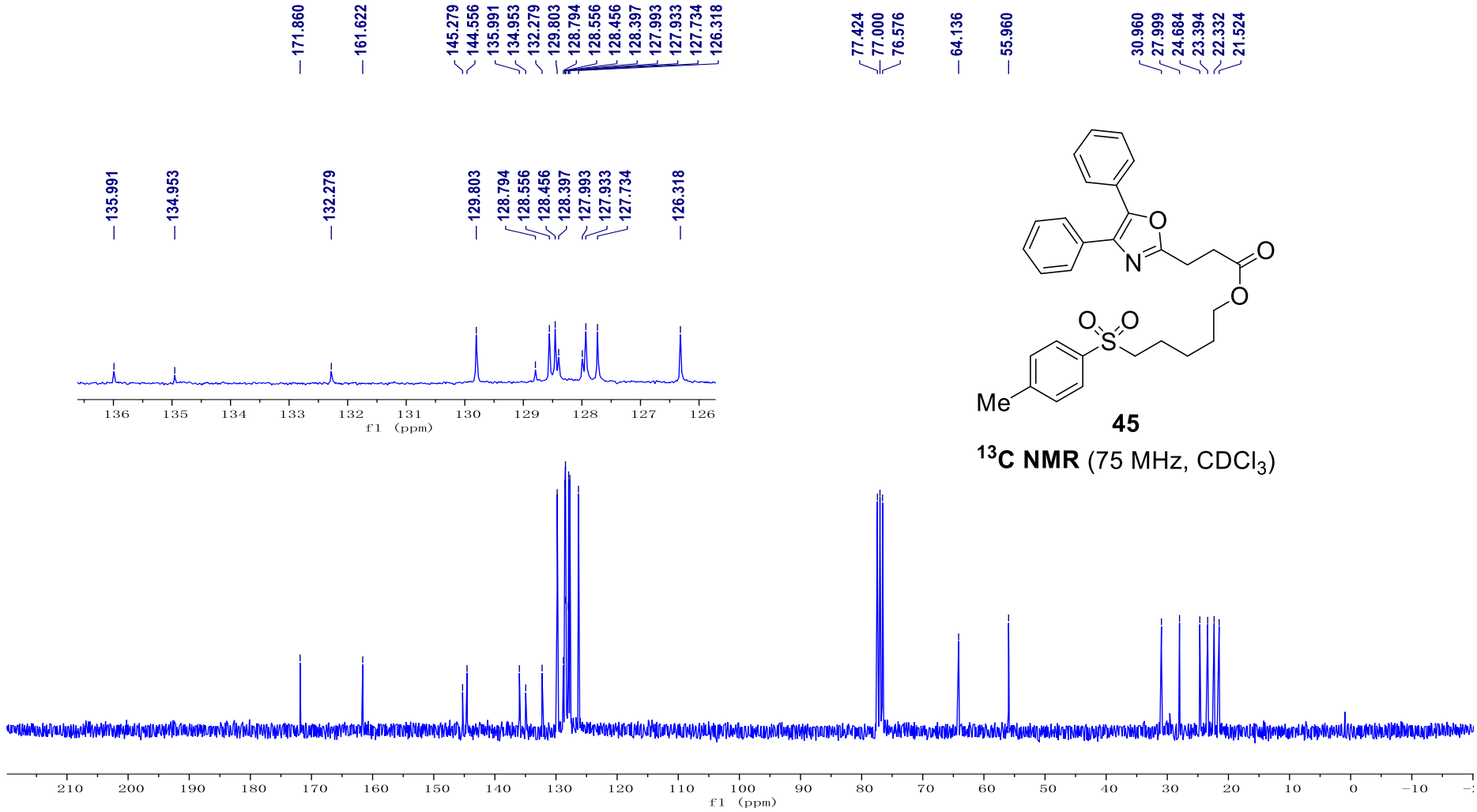
^{1}H NMR (400 MHz, $CDCl_3$)

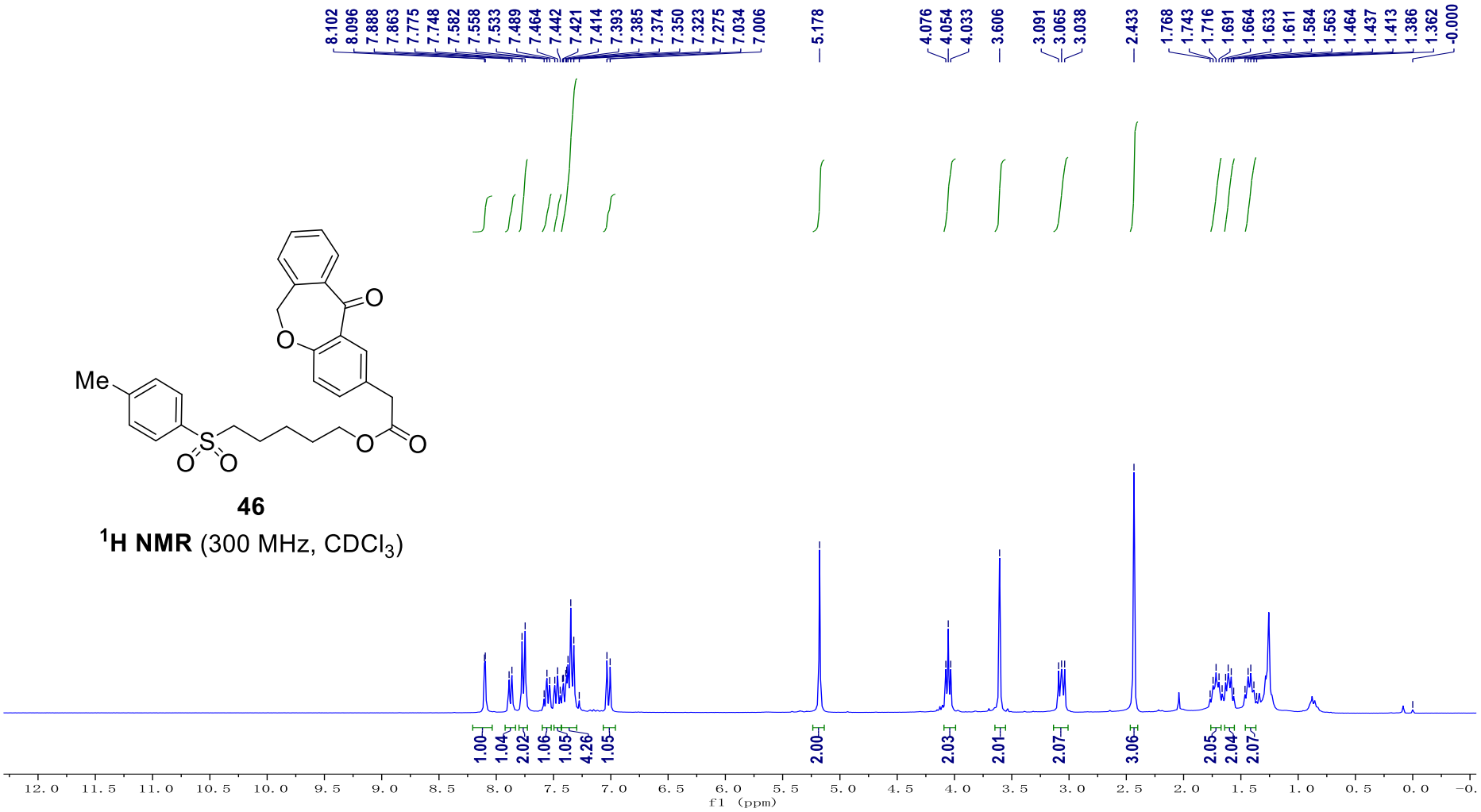


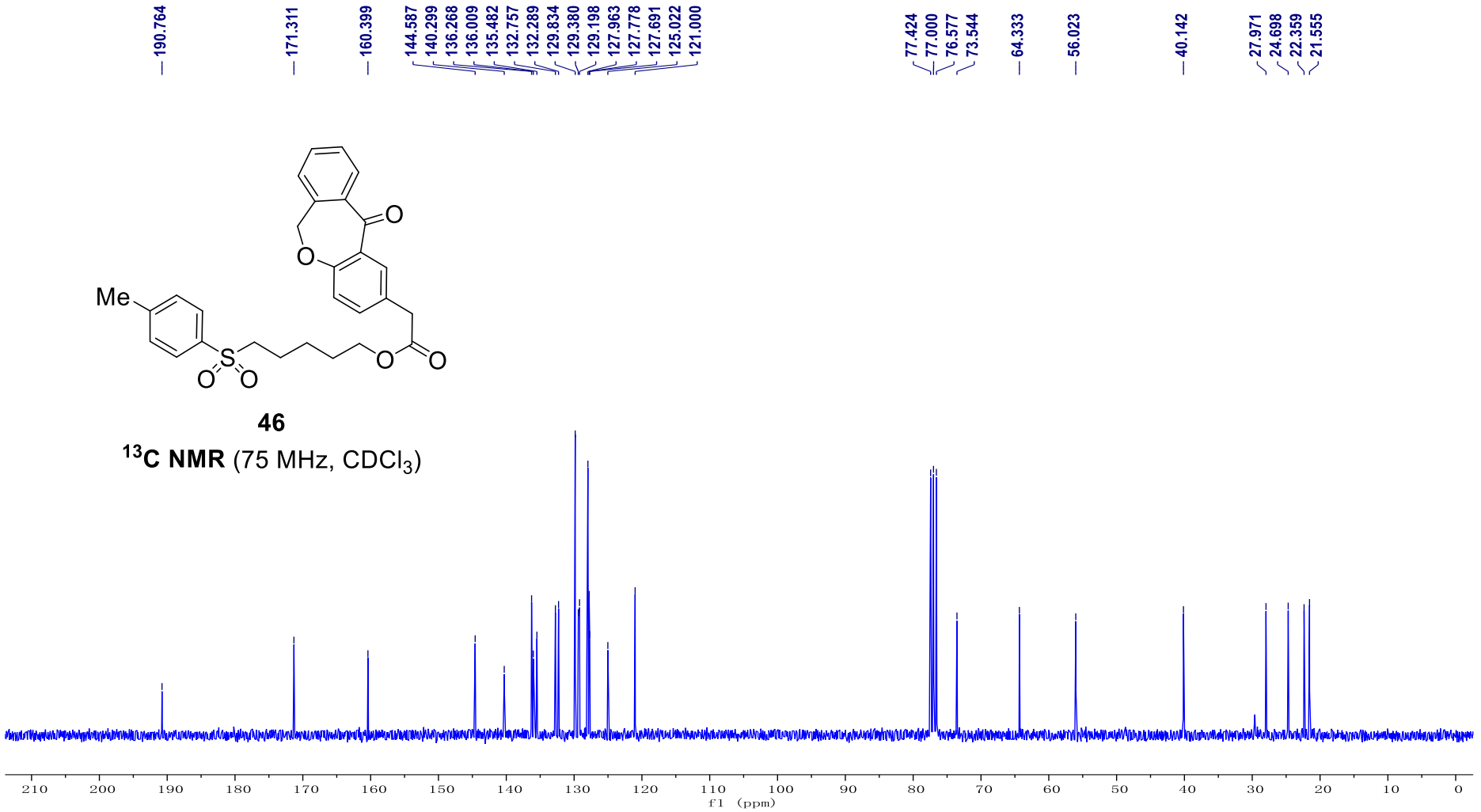
44

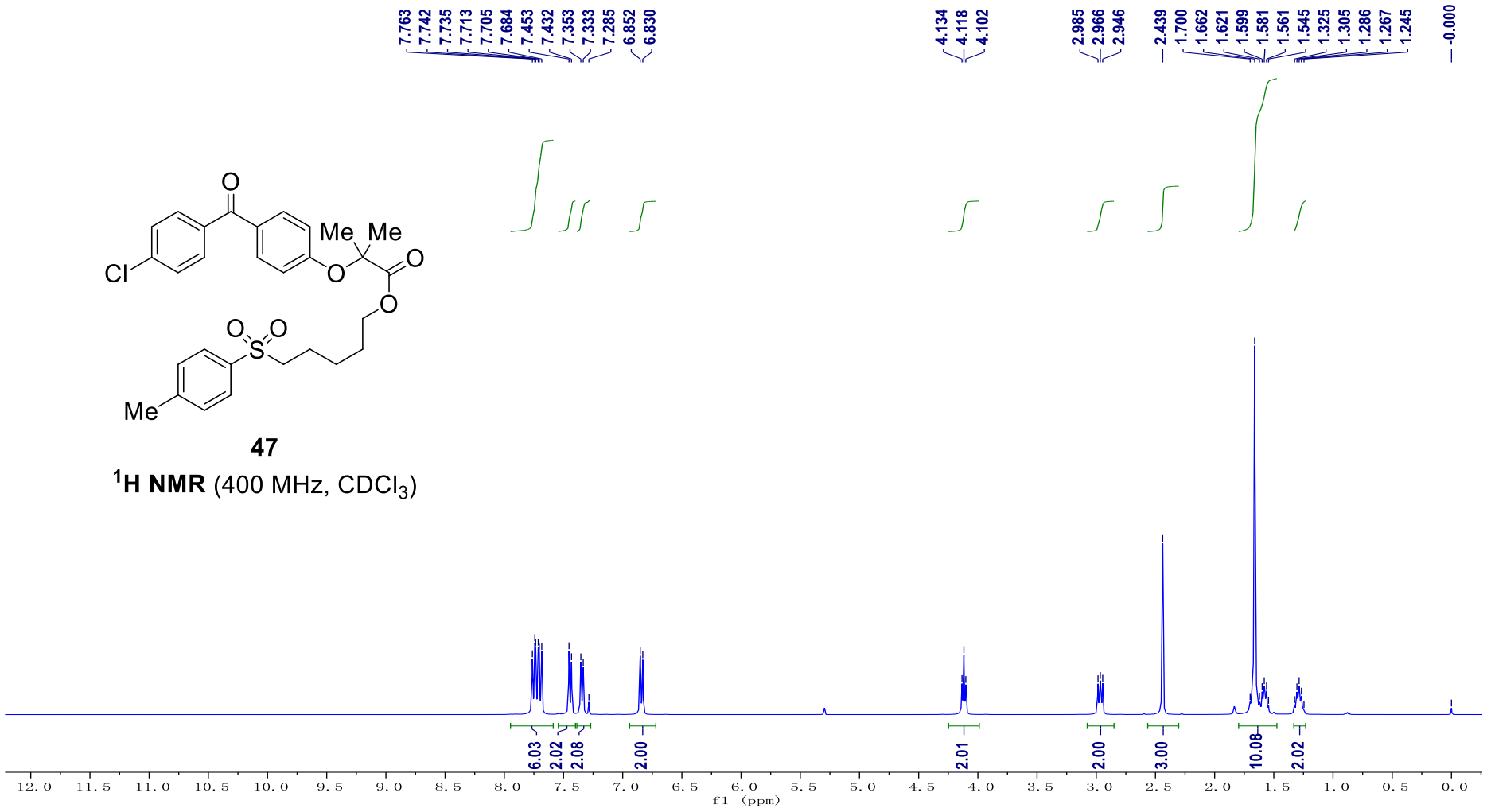
^{13}C NMR (75 MHz, $CDCl_3$)


7.766
7.738
7.630
7.624
7.603
7.599
7.575
7.568
7.548
7.543
7.384
7.374
7.355
7.349
7.329
7.308
7.281
7.265
4.099
4.078
4.057
3.189
3.165
3.139
3.023
3.004
2.997
2.970
2.909
2.883
2.859
2.438
1.748
1.723
1.696
1.681
1.670
1.644
1.629
1.607
1.579
1.558
1.446
1.429
1.419
1.395
1.367
-0.000
O
N
O
O
O
O
S
Me
45
1H NMR (300 MHz, CDCl3)
2.03
2.06
2.04
8.06
2.00
2.01
2.00
1.96
3.02
4.07
2.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


171.860
161.622
145.279
144.556
135.991
134.953
132.279
129.803
128.794
128.556
128.456
128.397
127.993
127.933
127.734
126.318
77.424
77.000
76.576
64.136
55.960
30.960
27.999
24.684
23.394
22.332
21.524
O
N
O
O
O
O
S
Me
45
13C NMR (75 MHz, CDCl3)
f1 (ppm)

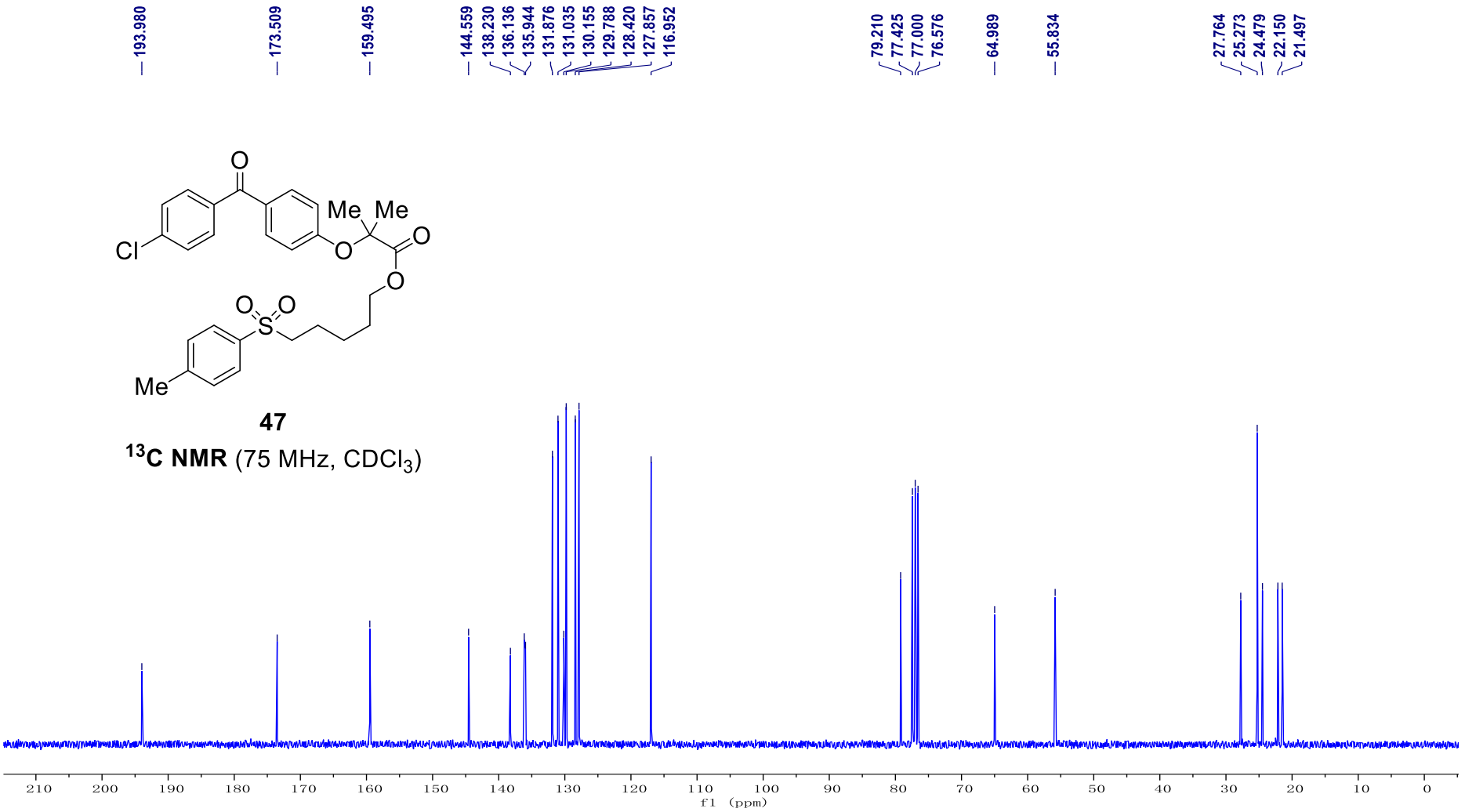

8.102
8.096
7.888
7.863
7.775
7.748
7.582
7.558
7.533
7.489
7.464
7.442
7.421
7.414
7.393
7.385
7.374
7.350
7.323
7.275
7.034
7.006
5.178
4.076
4.054
4.033
3.606
3.091
3.065
3.038
2.433
1.768
1.743
1.716
1.691
1.664
1.633
1.611
1.584
1.563
1.464
1.437
1.413
1.386
1.362
-0.000
Me
O
O
S
O
O
O
O
46
1H NMR (300 MHz, CDCl3)
1.00
1.04
2.02
1.06
1.05
4.26
1.05
2.00
2.03
2.01
2.07
3.06
2.05
2.04
2.07
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.
f1 (ppm)

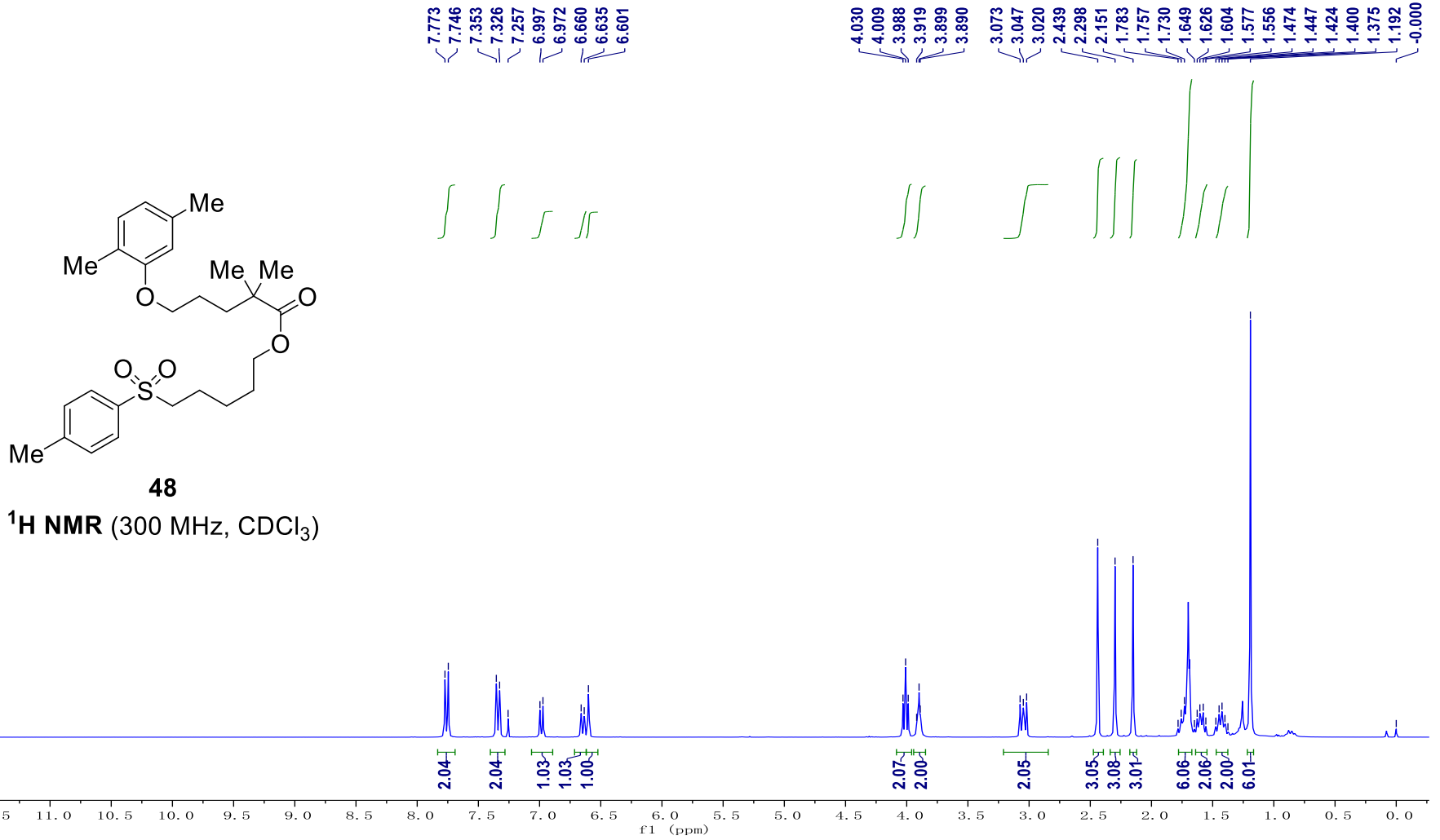

190.764
171.311
160.399
144.587
140.299
136.268
136.009
135.482
132.757
132.289
129.834
129.380
129.198
127.963
127.778
127.691
125.022
121.000
77.424
77.000
76.577
73.544
64.333
56.023
40.142
27.971
24.698
22.359
21.555
Me
O
O
S
O
O
O
O
46
13C NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



47

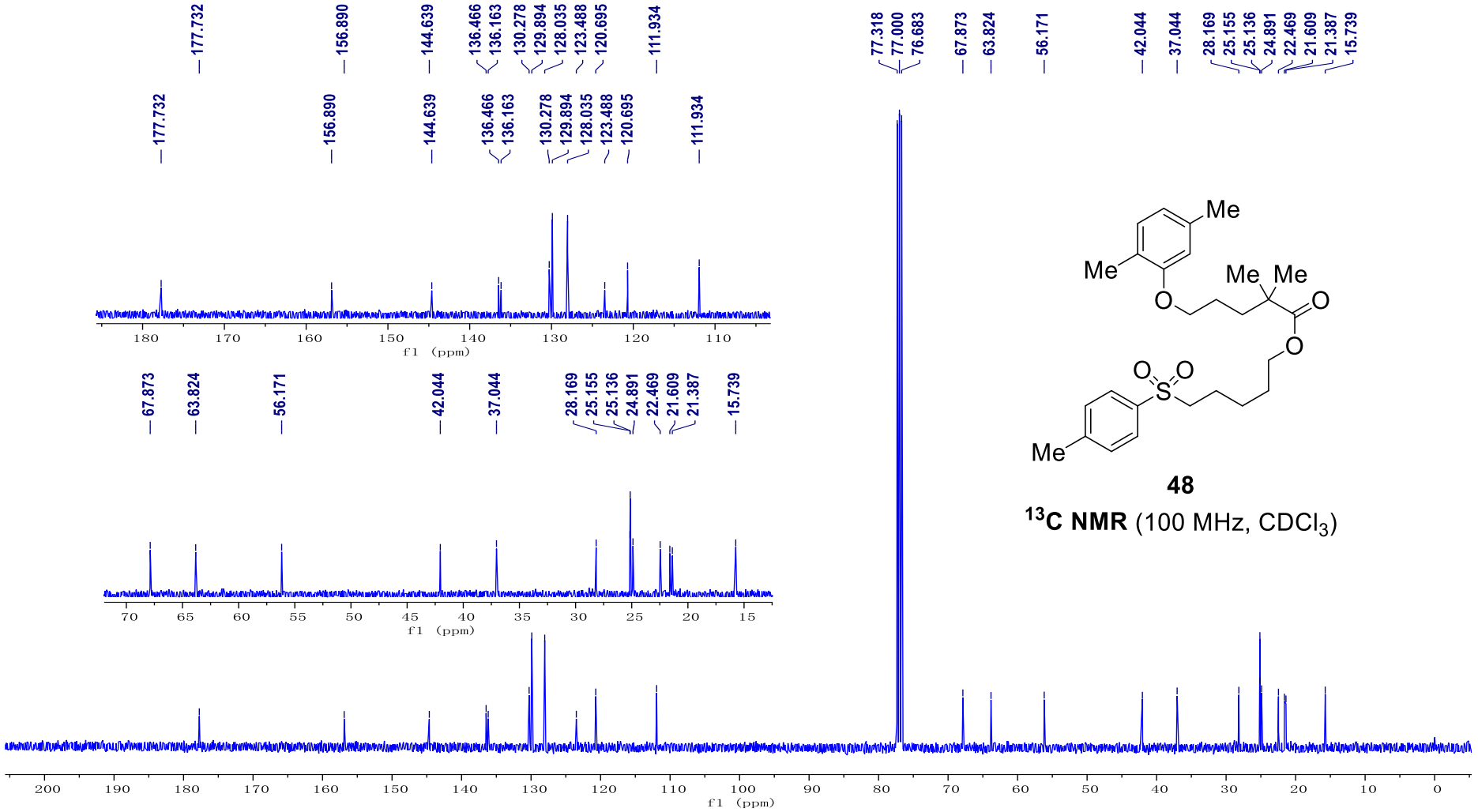
^{1}H NMR (400 MHz, $CDCl_3$)


193.980
173.509
159.495
144.559
138.230
136.136
135.944
131.876
131.035
130.155
129.788
128.420
127.857
116.952
79.210
77.425
77.000
76.576
64.989
55.834
27.764
25.273
24.479
22.150
21.497
O
Me Me
Cl
O
O
O
O
S
O
Me
47
13C NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



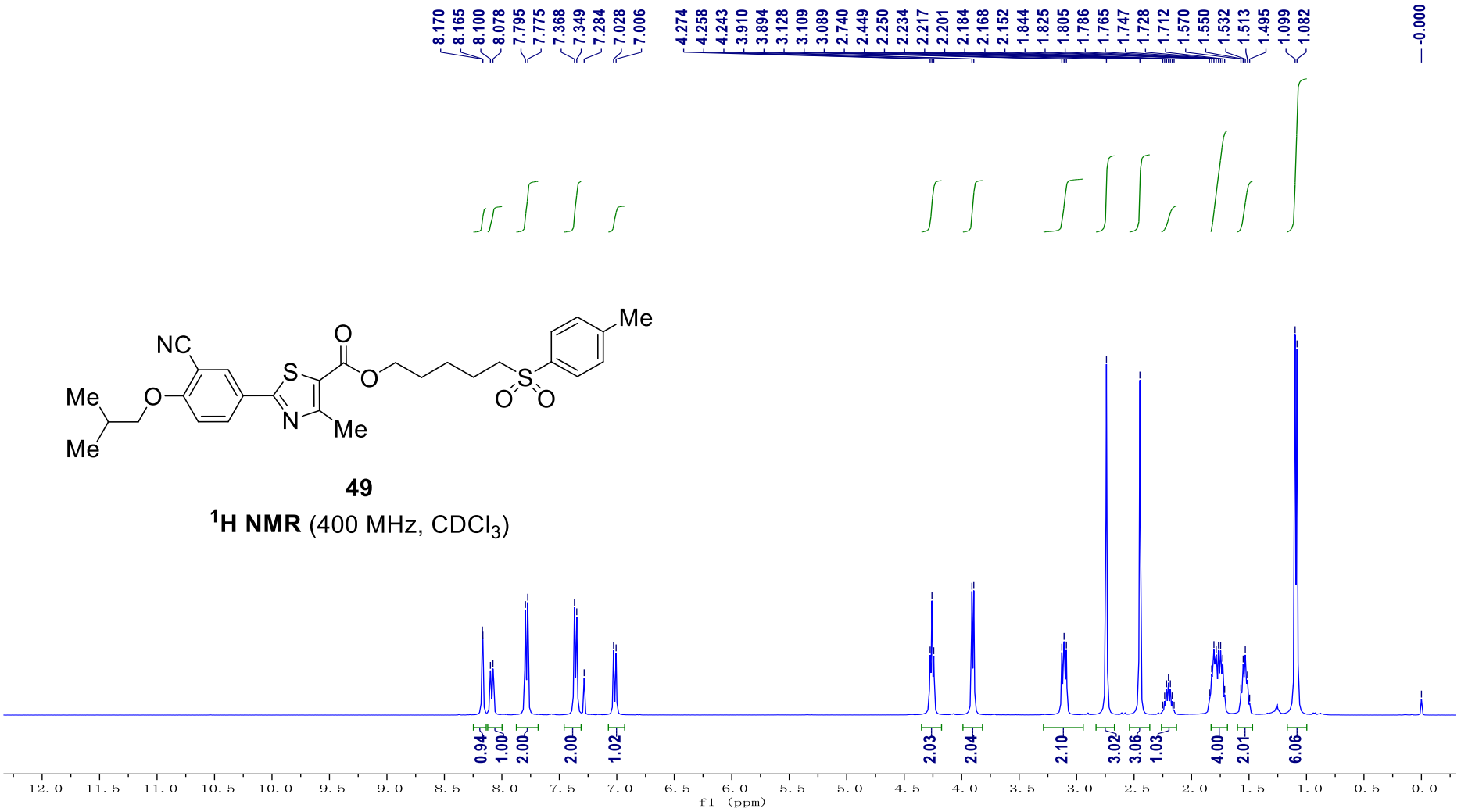
48

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



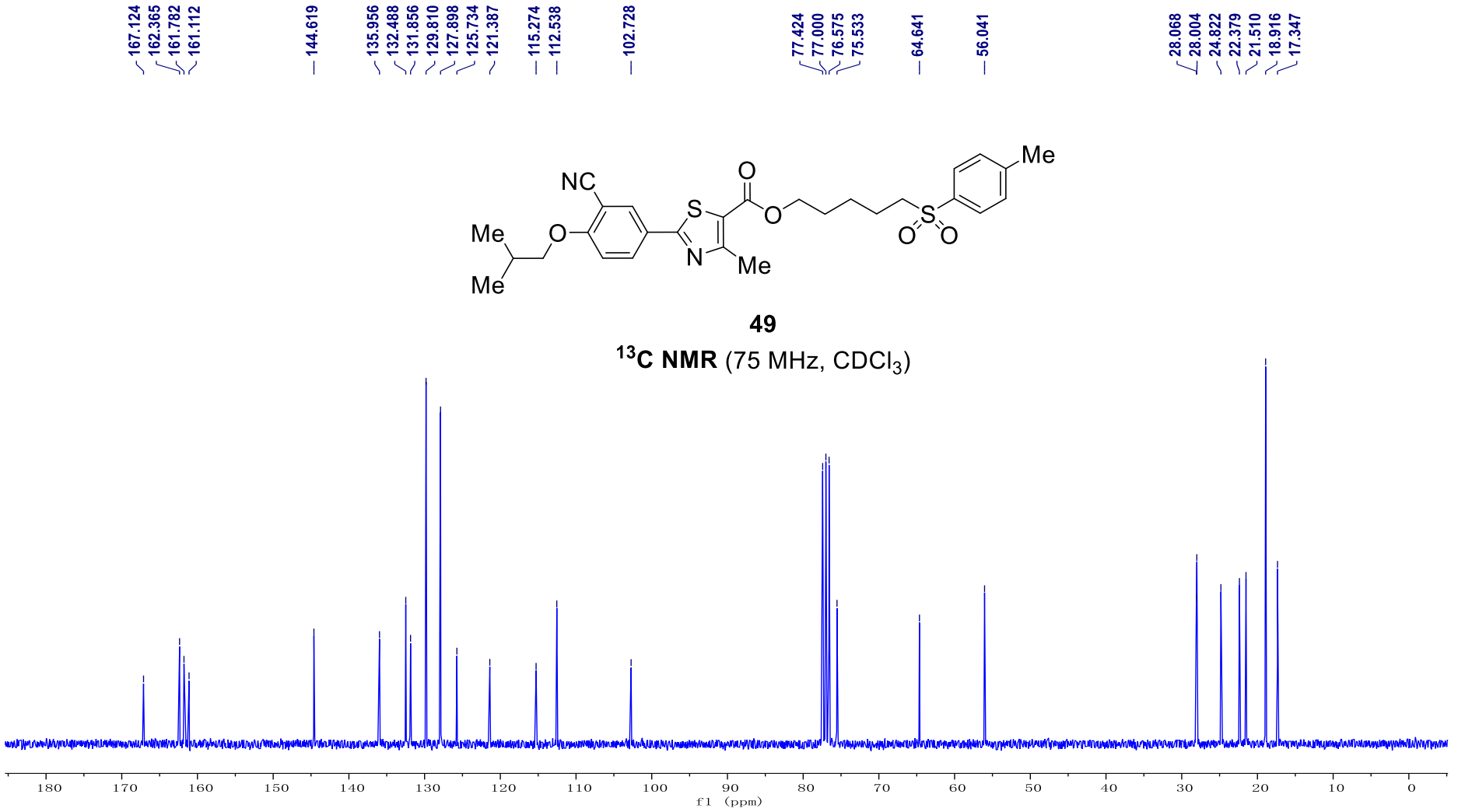
48

^{13}C NMR (100 MHz, $CDCl_3$)



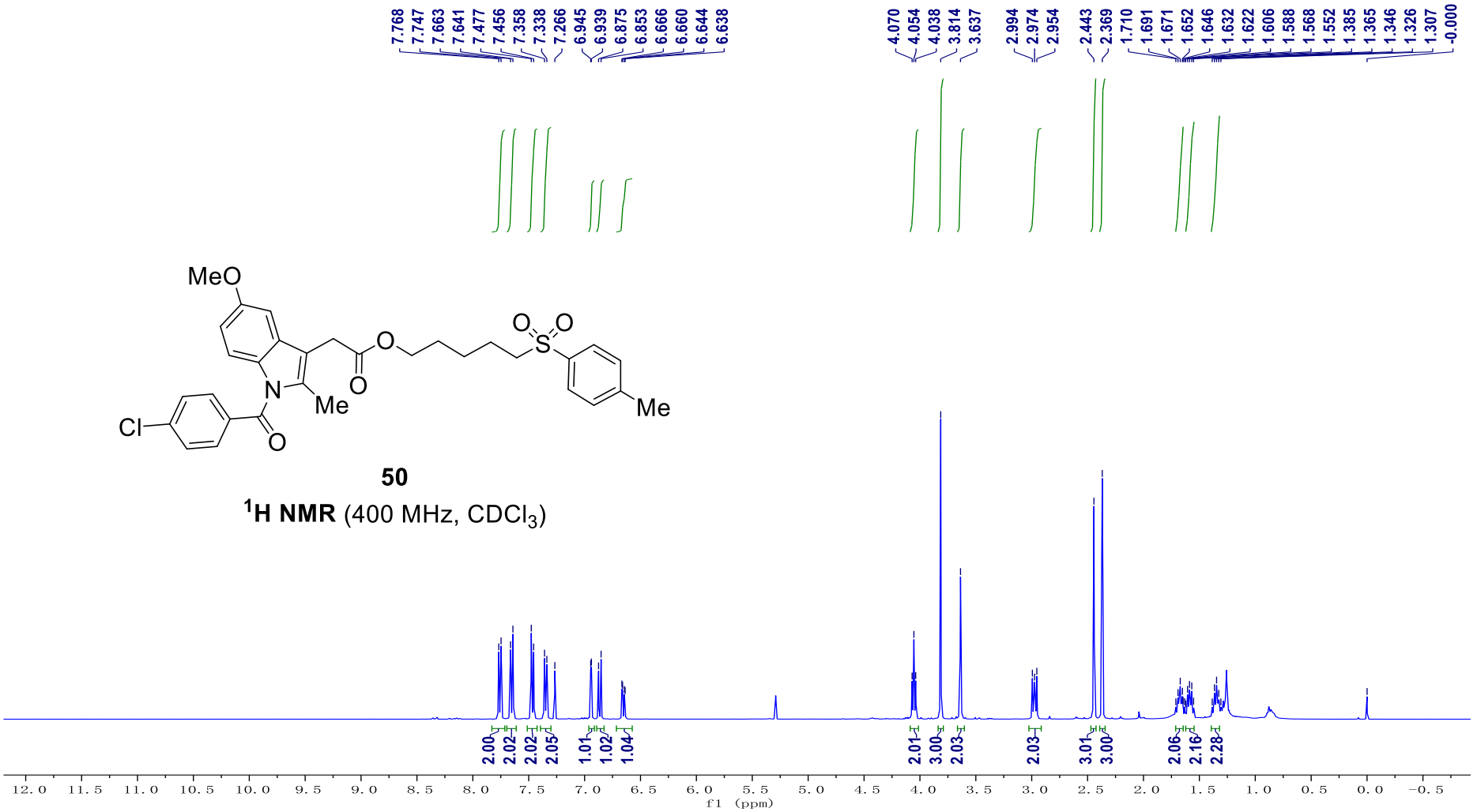
49

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



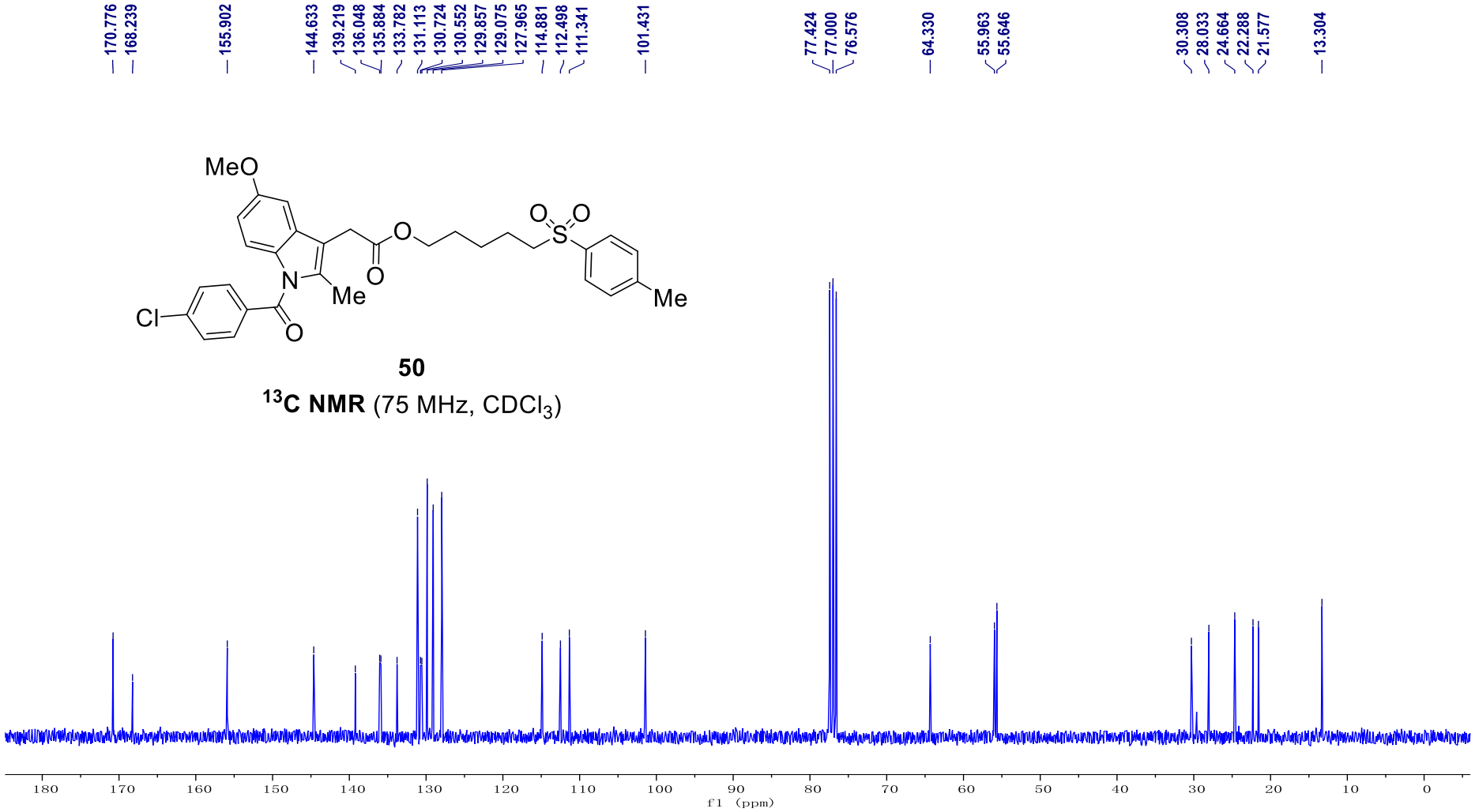
49

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



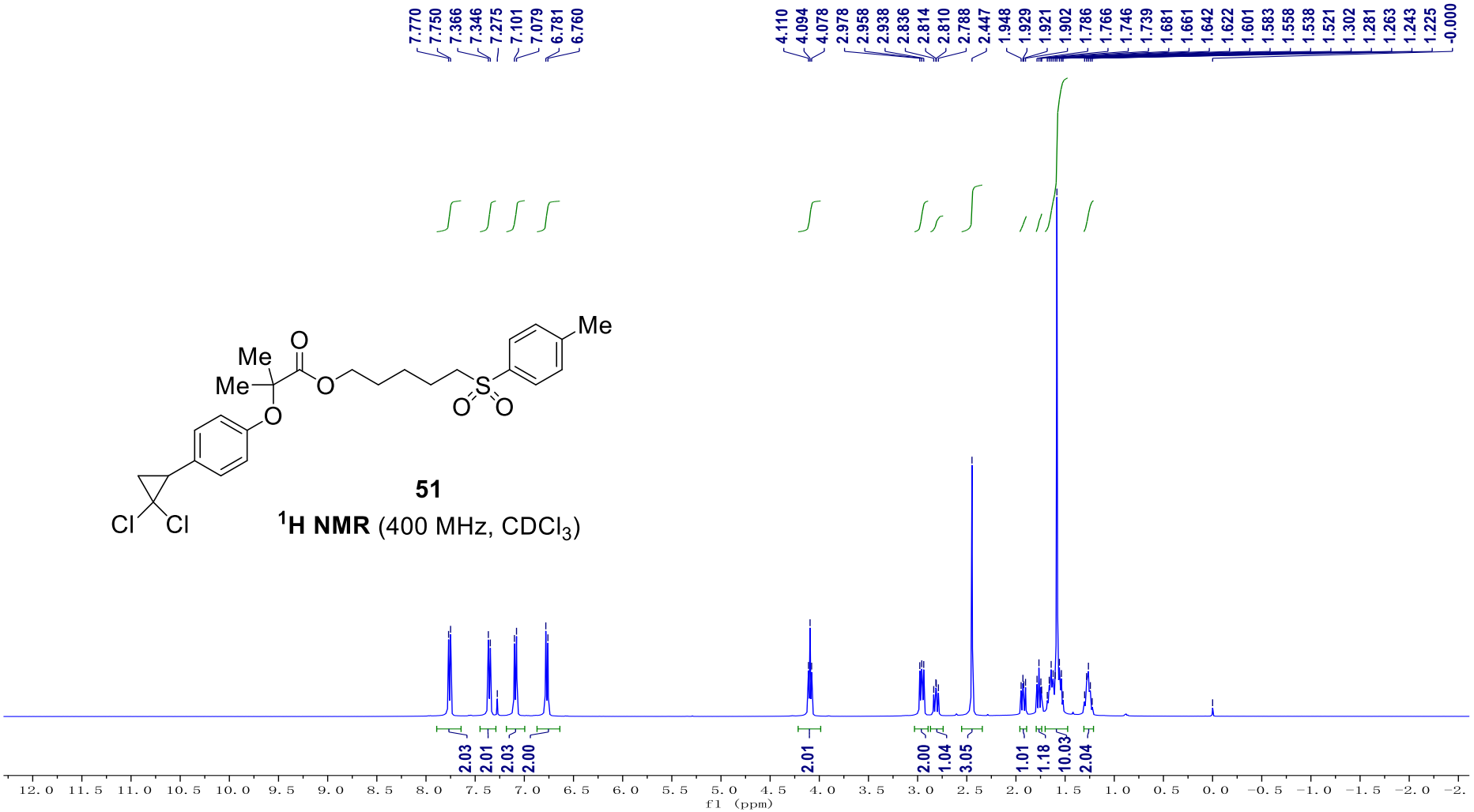
50

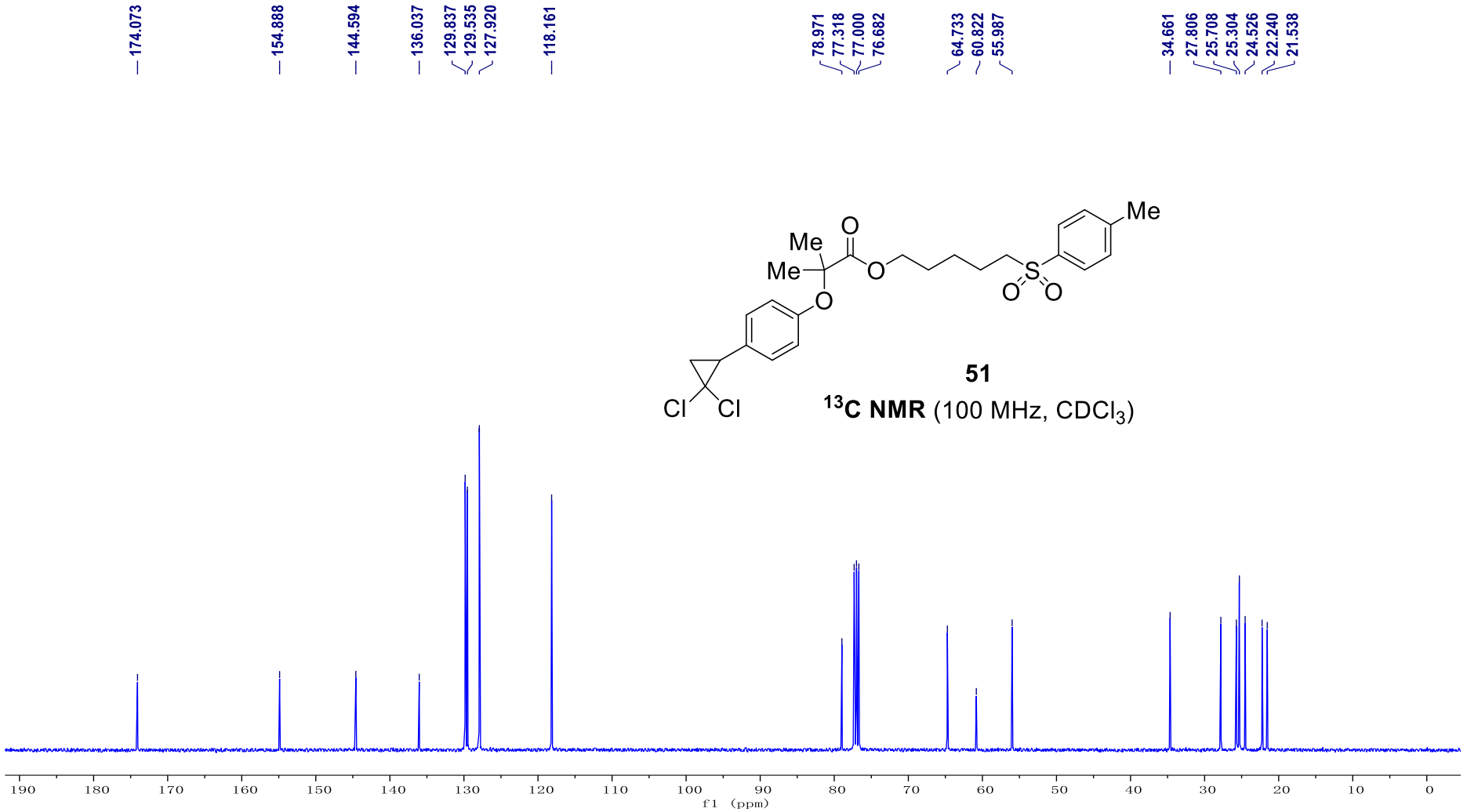
^{1}H NMR (400 MHz, $CDCl_3$)

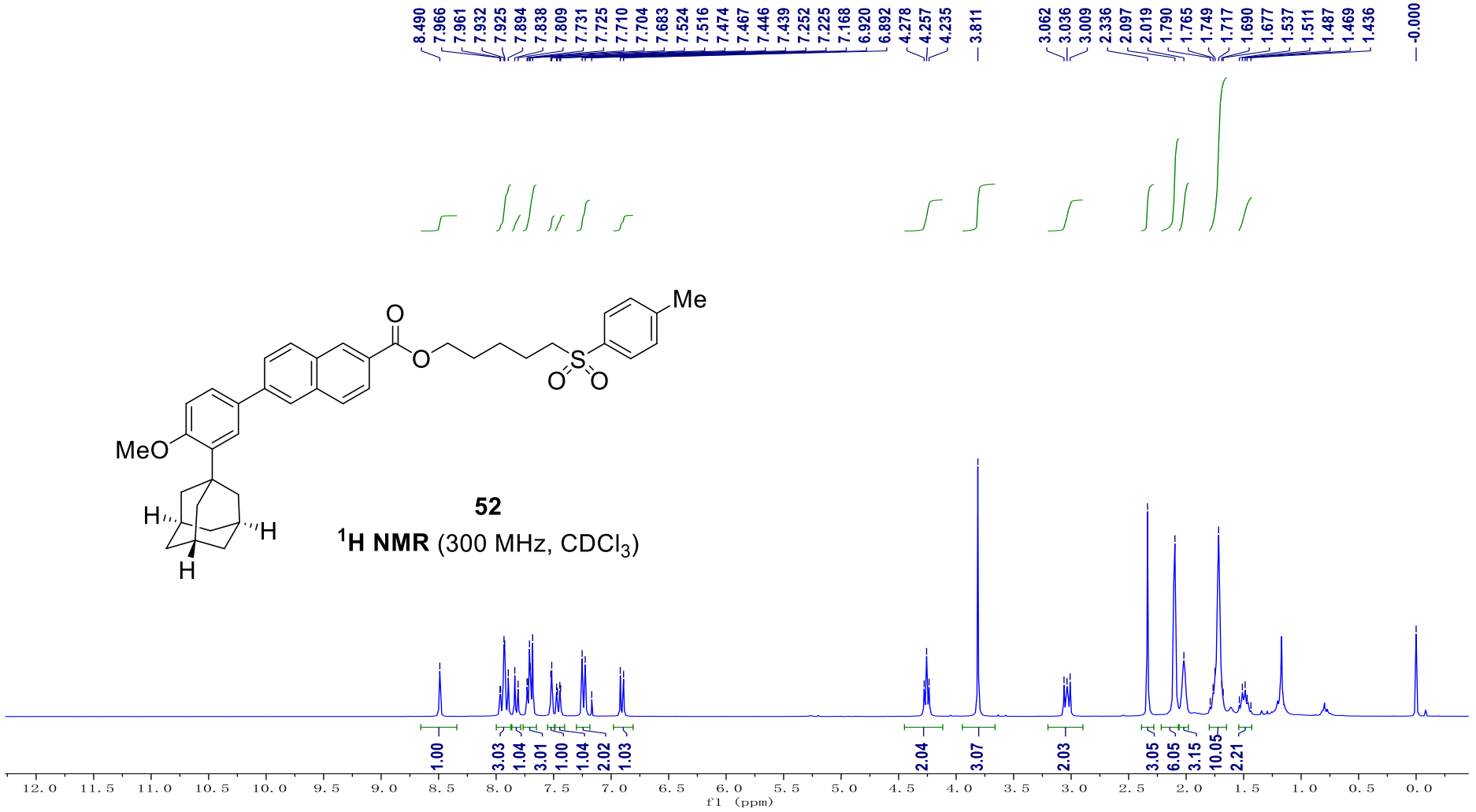


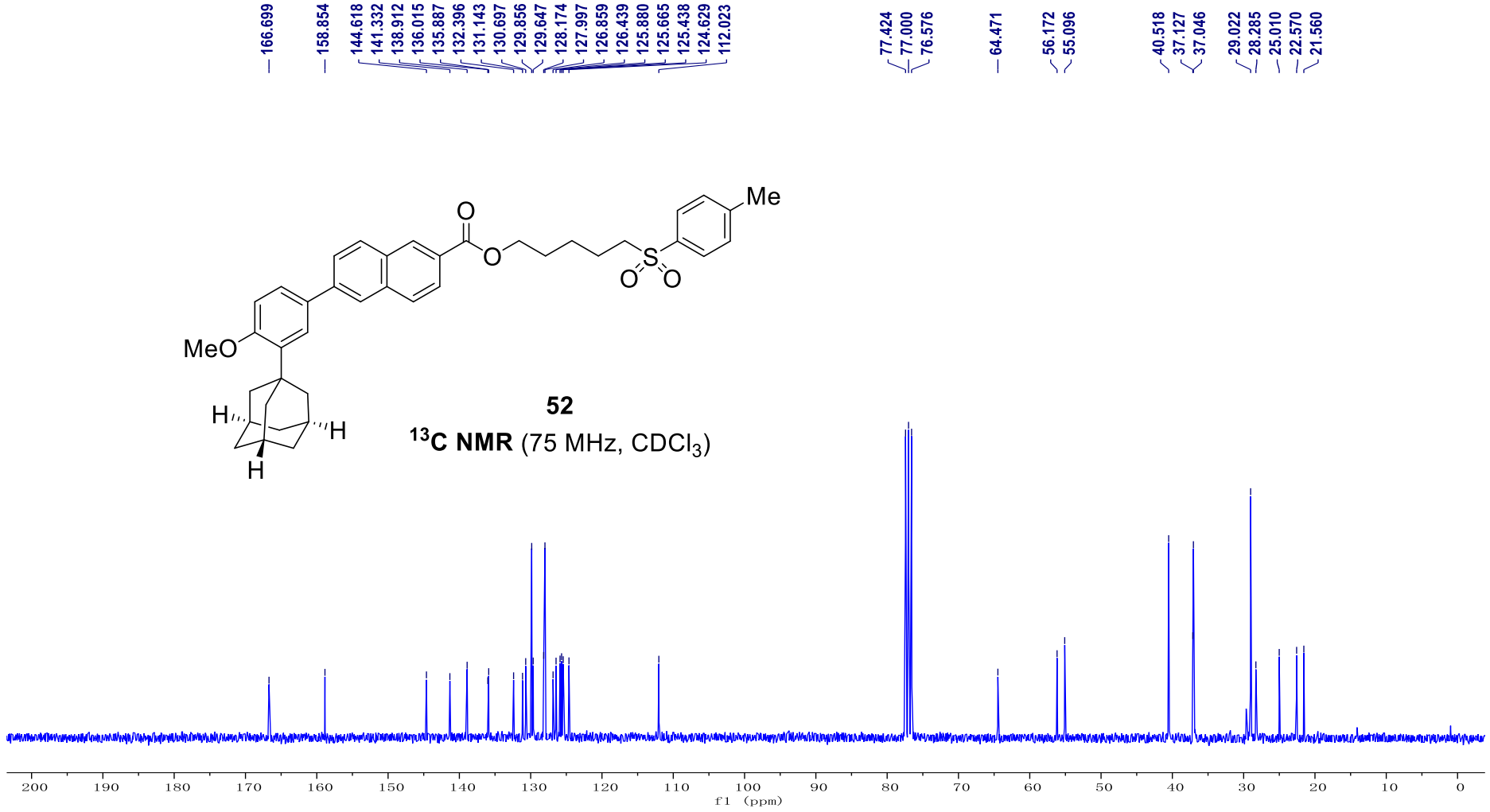
50

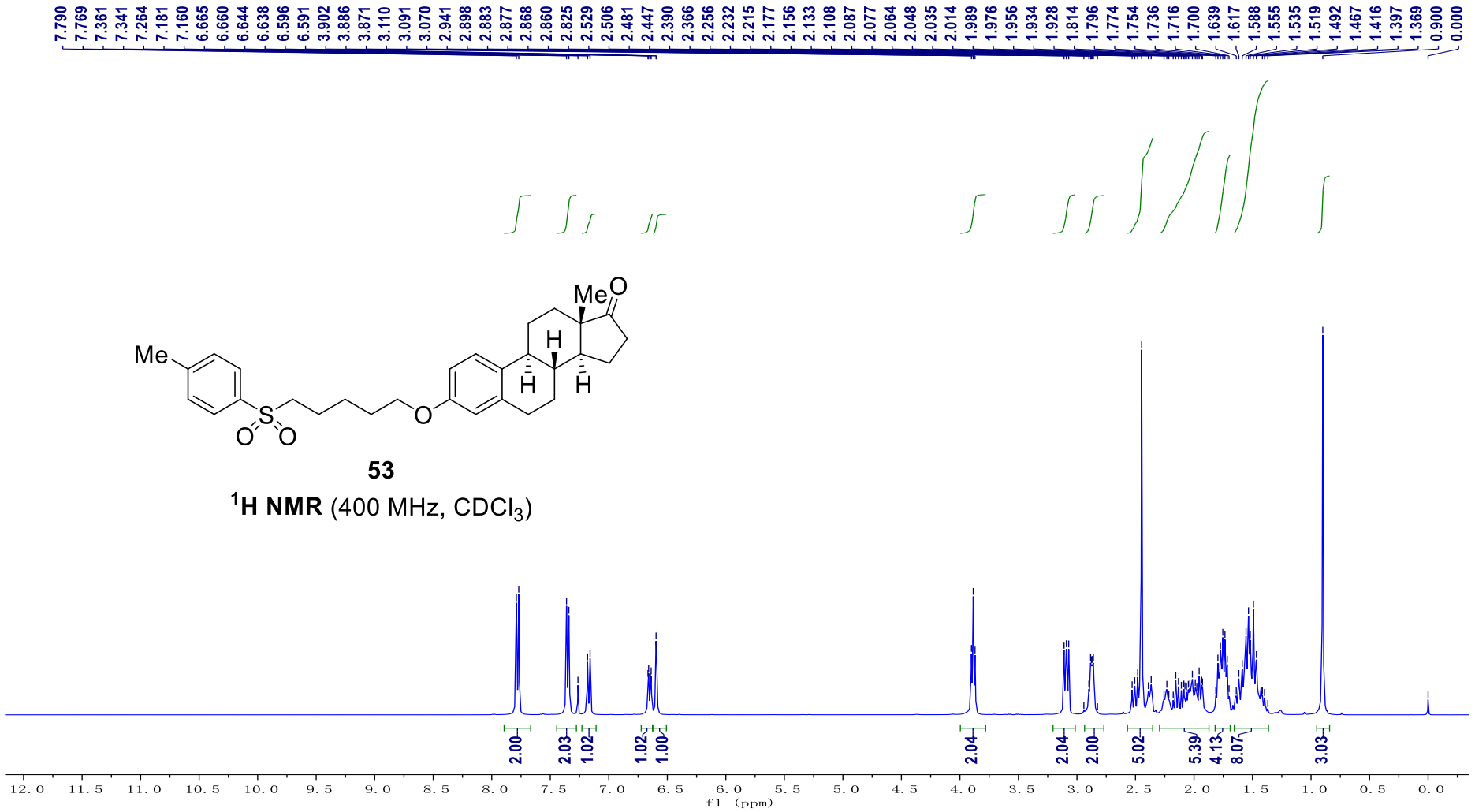
^{13}C NMR (75 MHz, $CDCl_3$)


7.770
7.750
7.366
7.346
7.275
7.101
7.079
6.781
6.760
4.110
4.094
4.078
2.978
2.958
2.938
2.836
2.814
2.810
2.788
2.447
1.948
1.929
1.921
1.902
1.786
1.766
1.746
1.739
1.681
1.661
1.642
1.622
1.601
1.583
1.558
1.538
1.521
1.302
1.281
1.263
1.243
1.225
-0.000
Me
Me
Me
O
O
O
O
S
O
Cl
Cl
51
1H NMR (400 MHz, CDCl3)
2.03
2.01
2.03
2.00
2.01
2.00
1.04
3.05
1.01
1.18
10.03
2.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.
f1 (ppm)


174.073
154.888
144.594
136.037
129.837
129.535
127.920
118.161
78.971
77.318
77.000
76.682
64.733
60.822
55.987
34.661
27.806
25.708
25.304
24.526
22.240
21.538
Me
Me
Me
O
O
O
O
S
O
O
Cl
Cl
51
13C NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

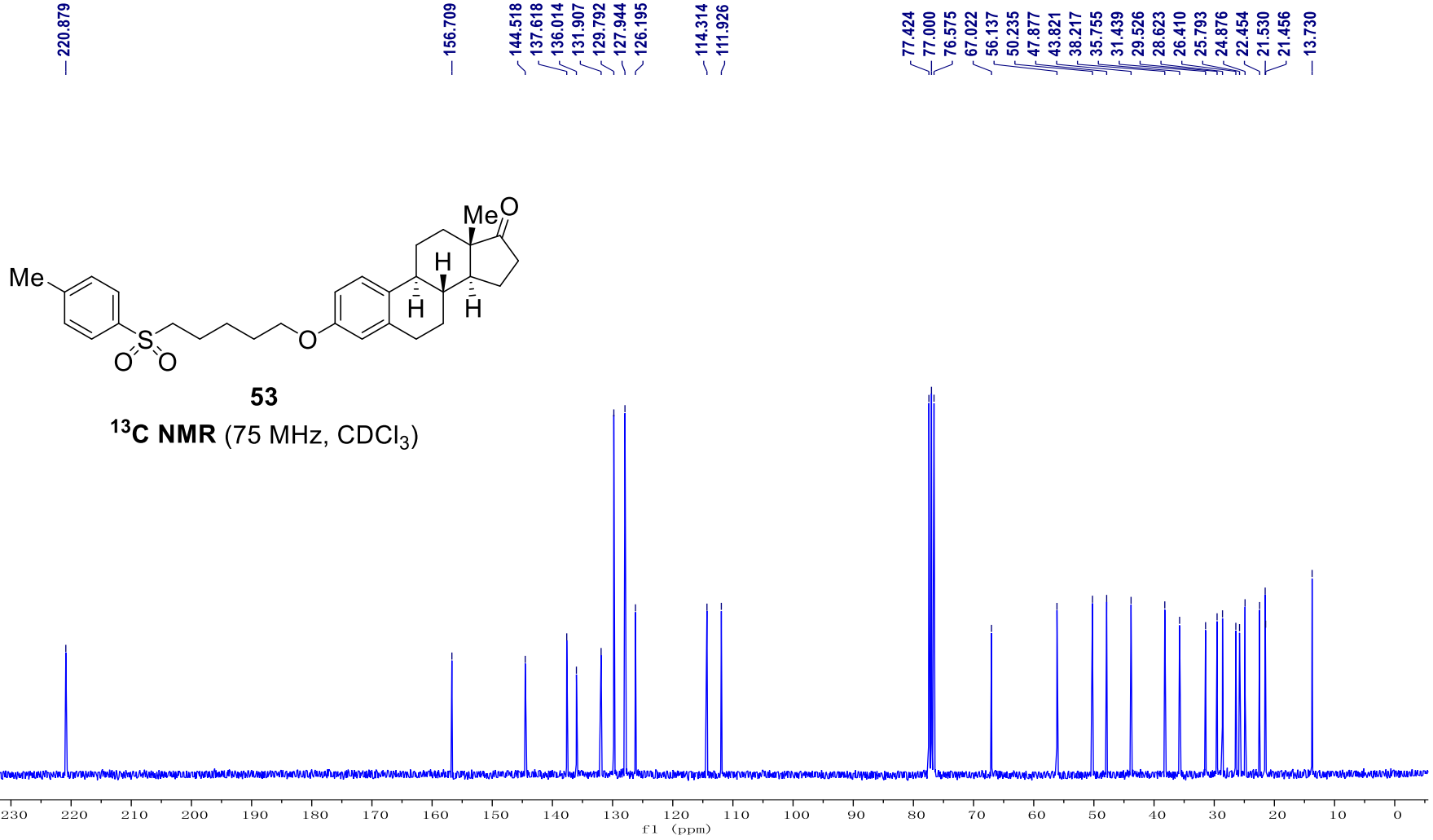

8.490
7.966
7.961
7.932
7.925
7.894
7.838
7.809
7.731
7.725
7.710
7.704
7.683
7.524
7.516
7.474
7.467
7.446
7.439
7.252
7.225
7.168
6.920
6.892
4.278
4.257
4.235
3.811
3.062
3.036
3.009
2.336
2.097
2.019
1.790
1.765
1.749
1.717
1.690
1.677
1.537
1.511
1.487
1.469
1.436
-0.000
Me
O
O
S
O
O
MeO
H
H
H
52
1H NMR (300 MHz, CDCl3)
1.00
3.03
1.04
3.01
1.00
1.04
2.02
1.03
2.04
3.07
2.03
3.05
6.05
3.15
10.05
2.21
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

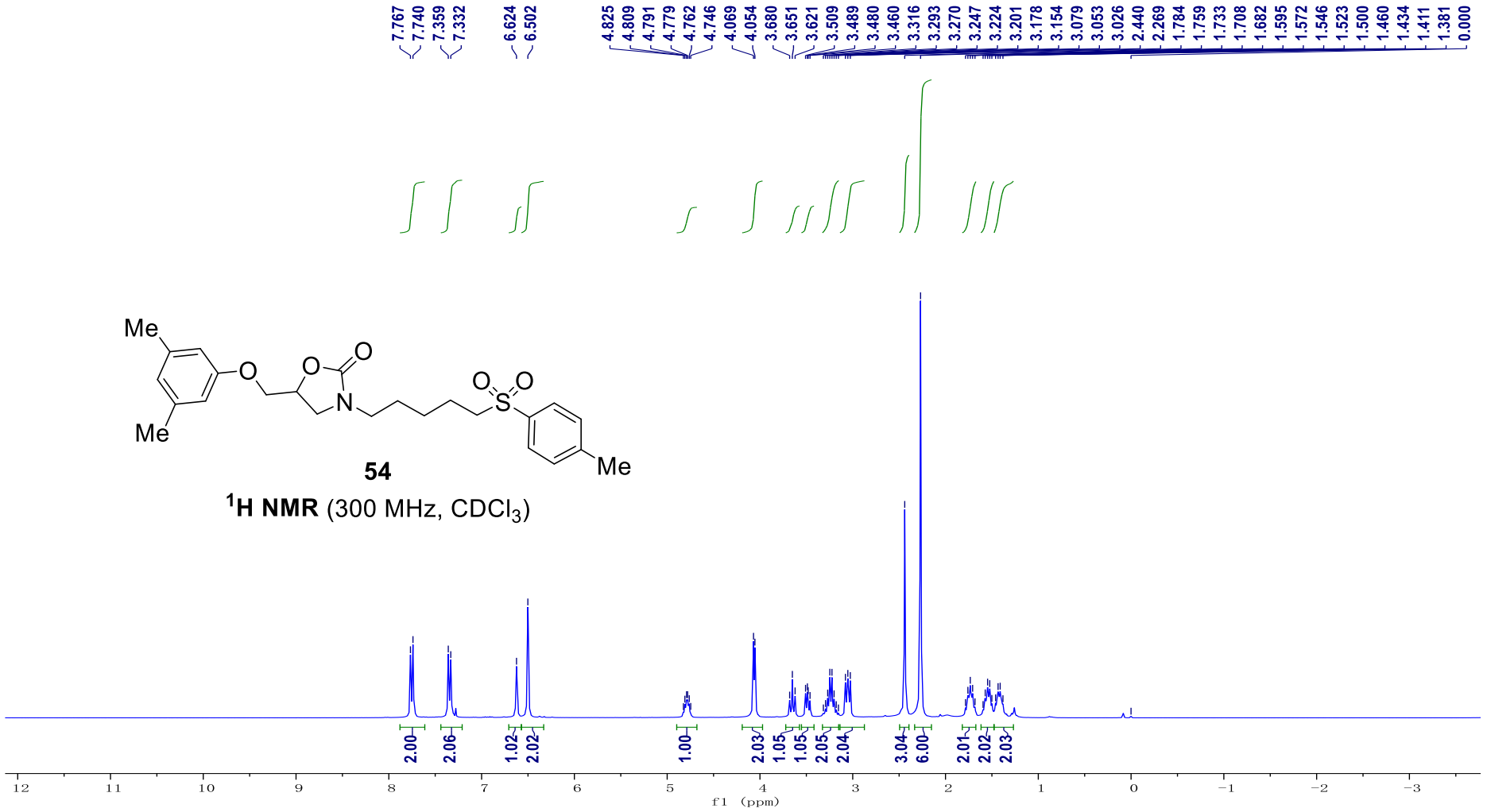

166.699
158.854
144.618
141.332
138.912
136.015
135.887
132.396
131.143
130.697
129.856
129.647
128.174
127.997
126.859
126.439
125.880
125.665
125.438
124.629
112.023
77.424
77.000
76.576
64.471
56.172
55.096
40.518
37.127
37.046
29.022
28.285
25.010
22.570
21.560
Me
O
O
S
O
O
MeO
H
H
H
52
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

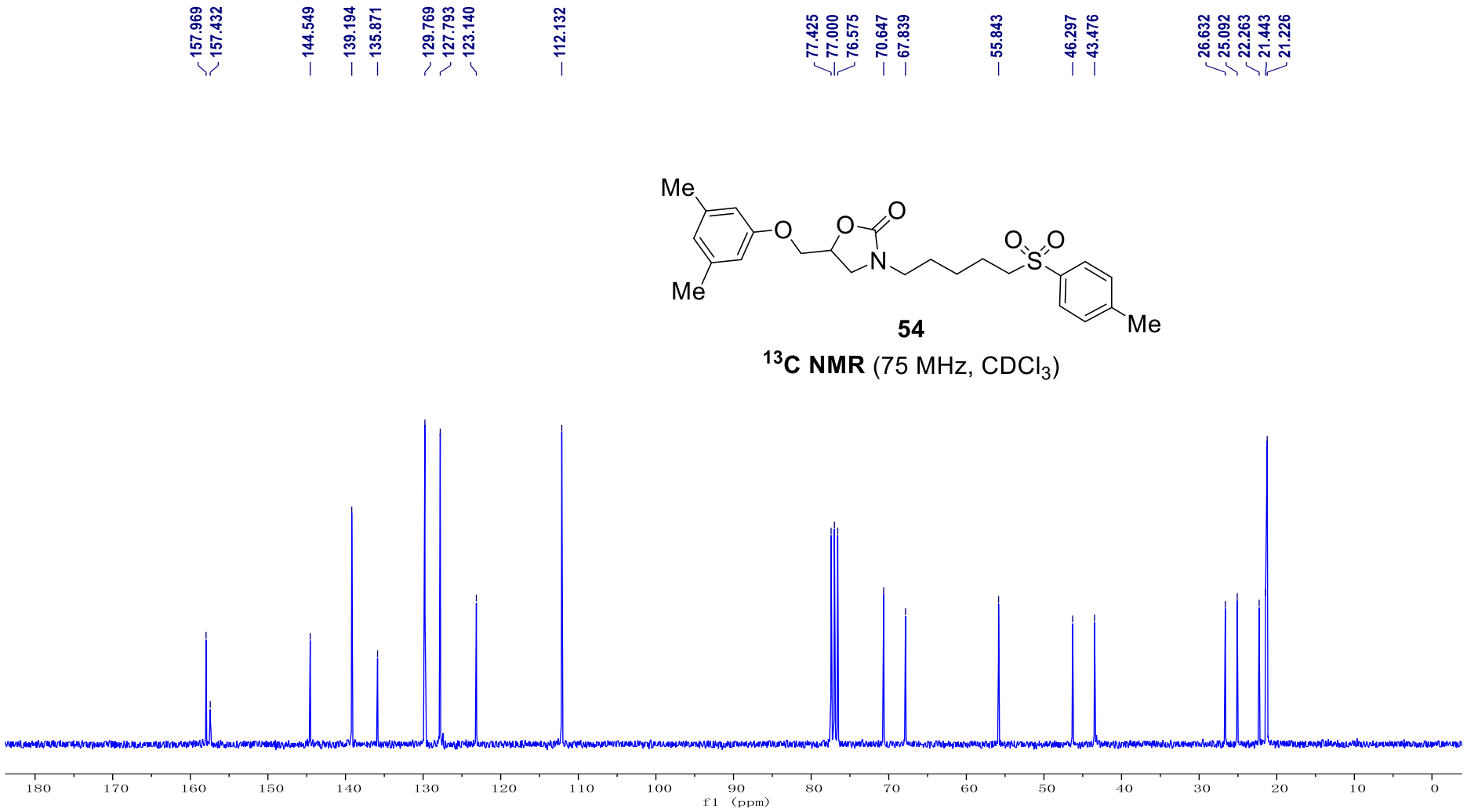


53

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

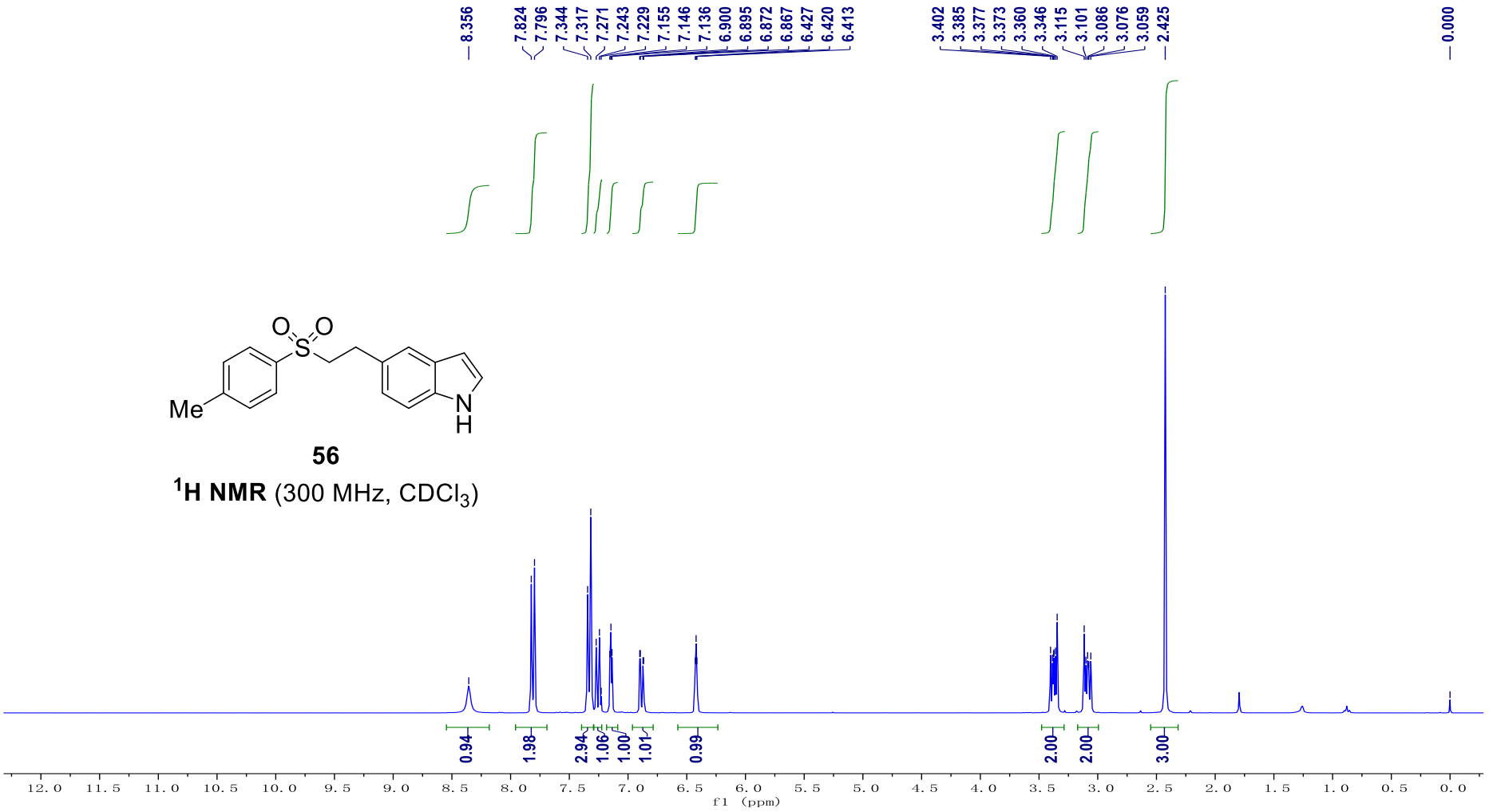

220.879
156.709
144.518
137.618
136.014
131.907
129.792
127.944
126.195
114.314
111.926
77.424
77.000
76.575
67.022
56.137
50.235
47.877
43.821
38.217
35.755
31.439
29.526
28.623
26.410
25.793
24.876
22.454
21.530
21.456
13.730
Me
O
H
H
H
Me
S
O
O
O
53
13C NMR (75 MHz, CDCl3)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

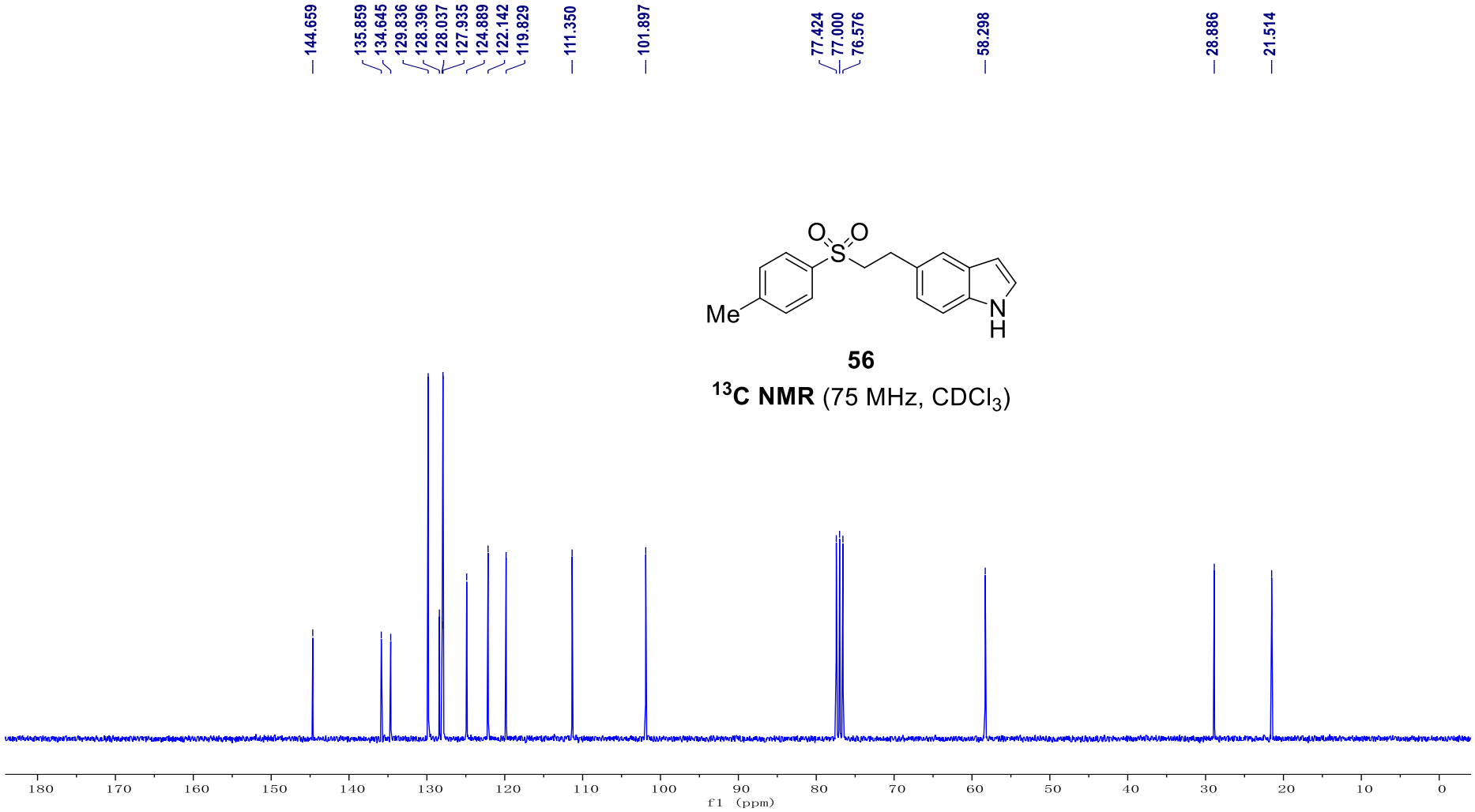

7.767
7.740
7.359
7.332
6.624
6.502
4.825
4.809
4.791
4.779
4.762
4.746
4.069
4.054
3.680
3.651
3.621
3.509
3.489
3.480
3.460
3.316
3.293
3.270
3.247
3.224
3.201
3.178
3.154
3.079
3.053
3.026
2.440
2.269
1.784
1.759
1.733
1.708
1.682
1.595
1.572
1.546
1.523
1.500
1.460
1.434
1.411
1.381
0.000
Me
O
O
O
N
O
O
S
Me
Me
54
1H NMR (300 MHz, CDCl3)
2.00
2.06
1.02
2.02
1.00
2.03
1.05
1.05
2.05
2.04
3.04
6.00
2.01
2.02
2.03
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

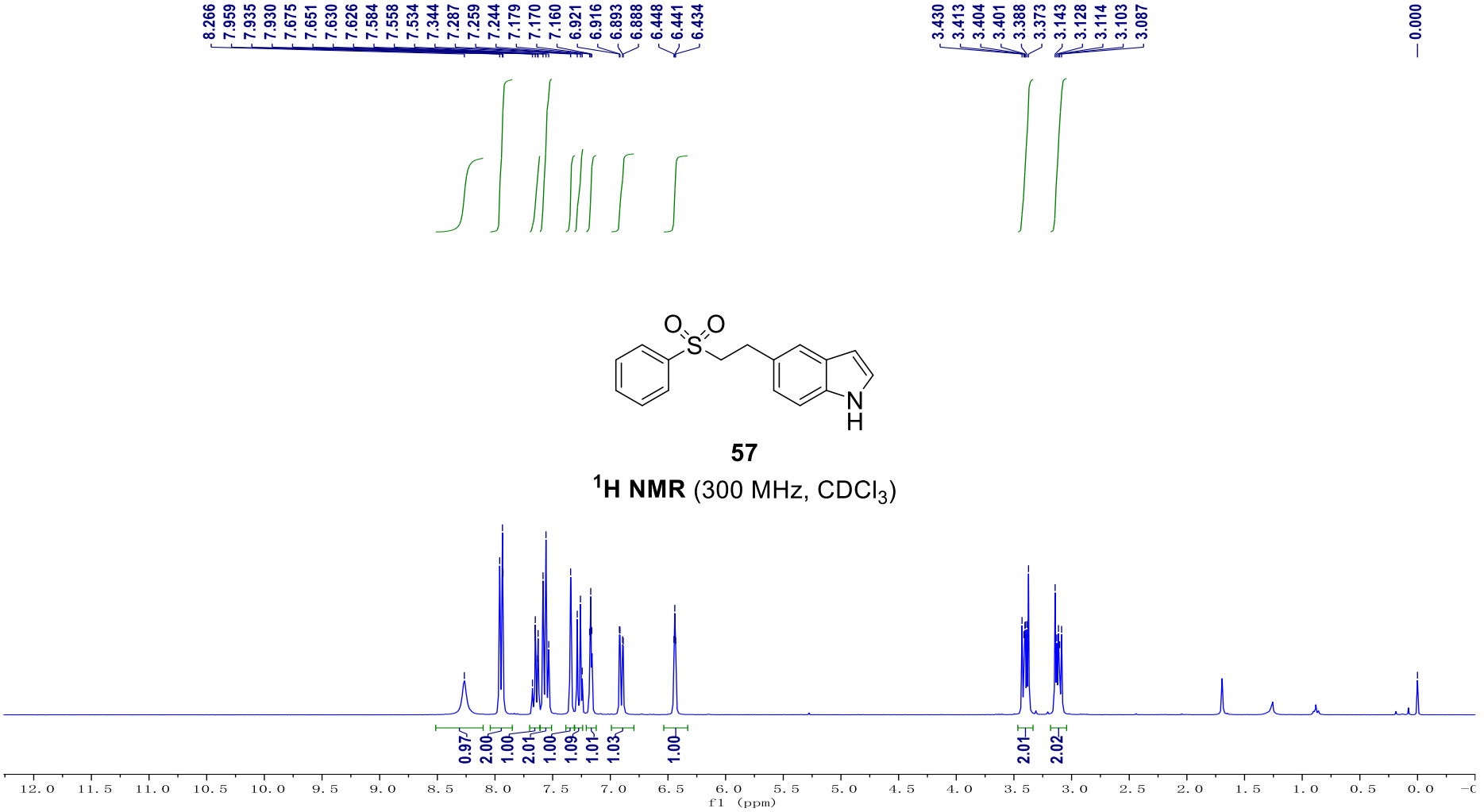


54

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

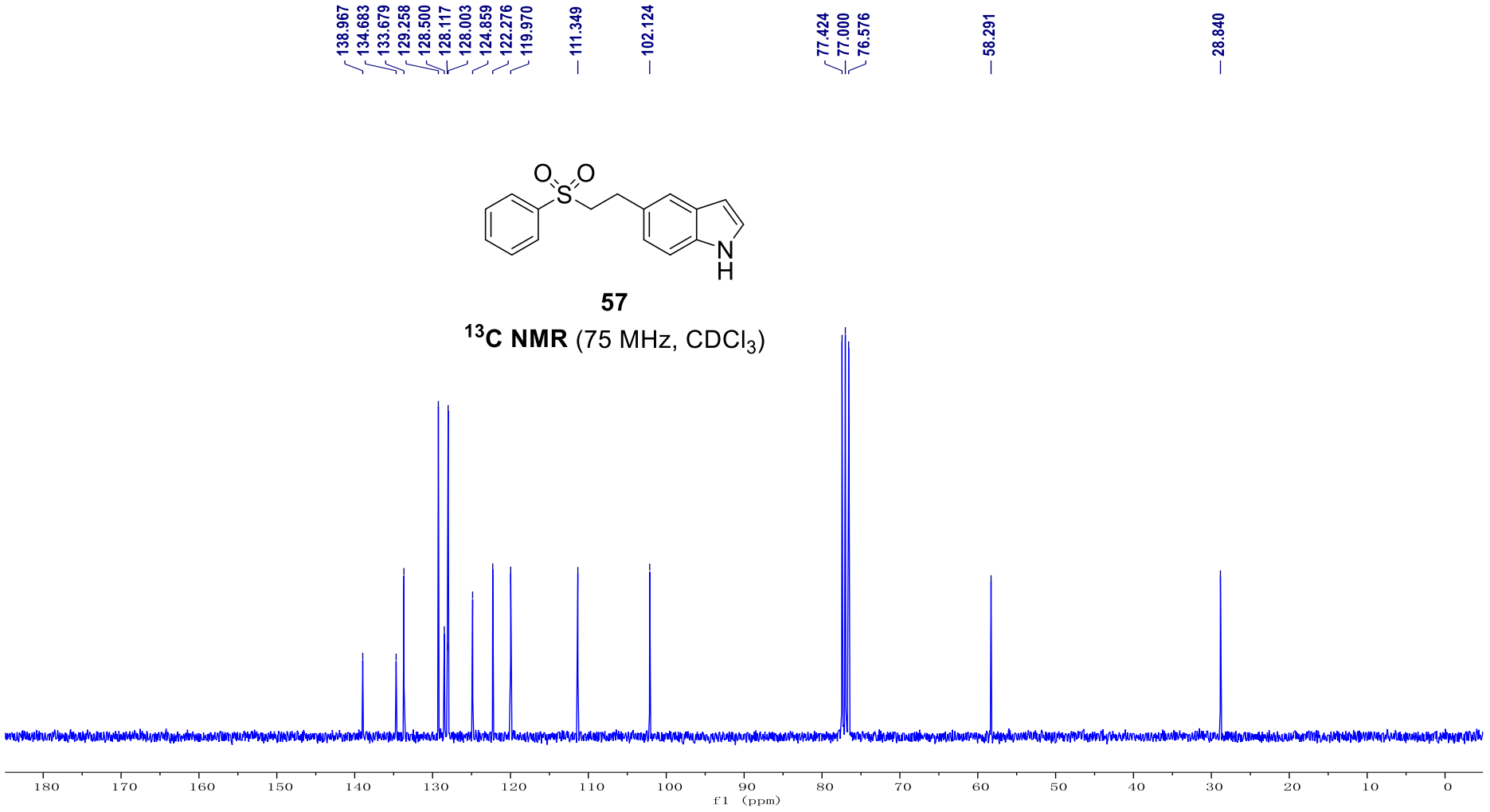

8.356
7.824
7.796
7.344
7.317
7.271
7.243
7.229
7.155
7.146
7.136
6.900
6.895
6.872
6.867
6.427
6.420
6.413
3.402
3.385
3.377
3.373
3.360
3.346
3.115
3.101
3.086
3.076
3.059
2.425
0.000
O
O
S
Me
N
H
56
1H NMR (300 MHz, CDCl3)
0.94
1.98
2.94
1.06
1.00
1.01
0.99
2.00
2.00
3.00
f1 (ppm)


144.659
135.859
134.645
129.836
128.396
128.037
127.935
124.889
122.142
119.829
111.350
101.897
77.424
77.000
76.576
58.298
28.886
21.514
O
O
S
Me
N
H
56
13C NMR (75 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



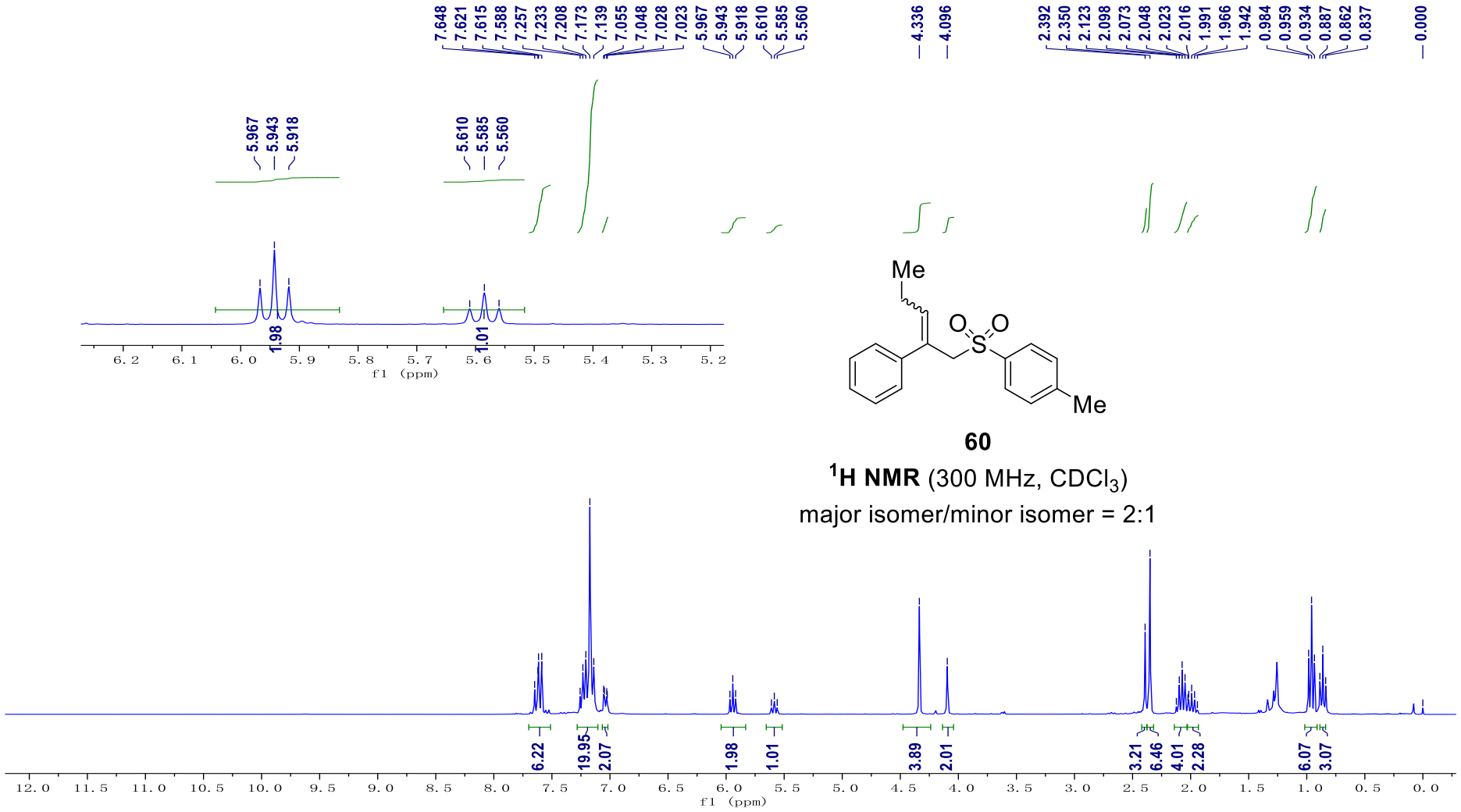
57

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



57

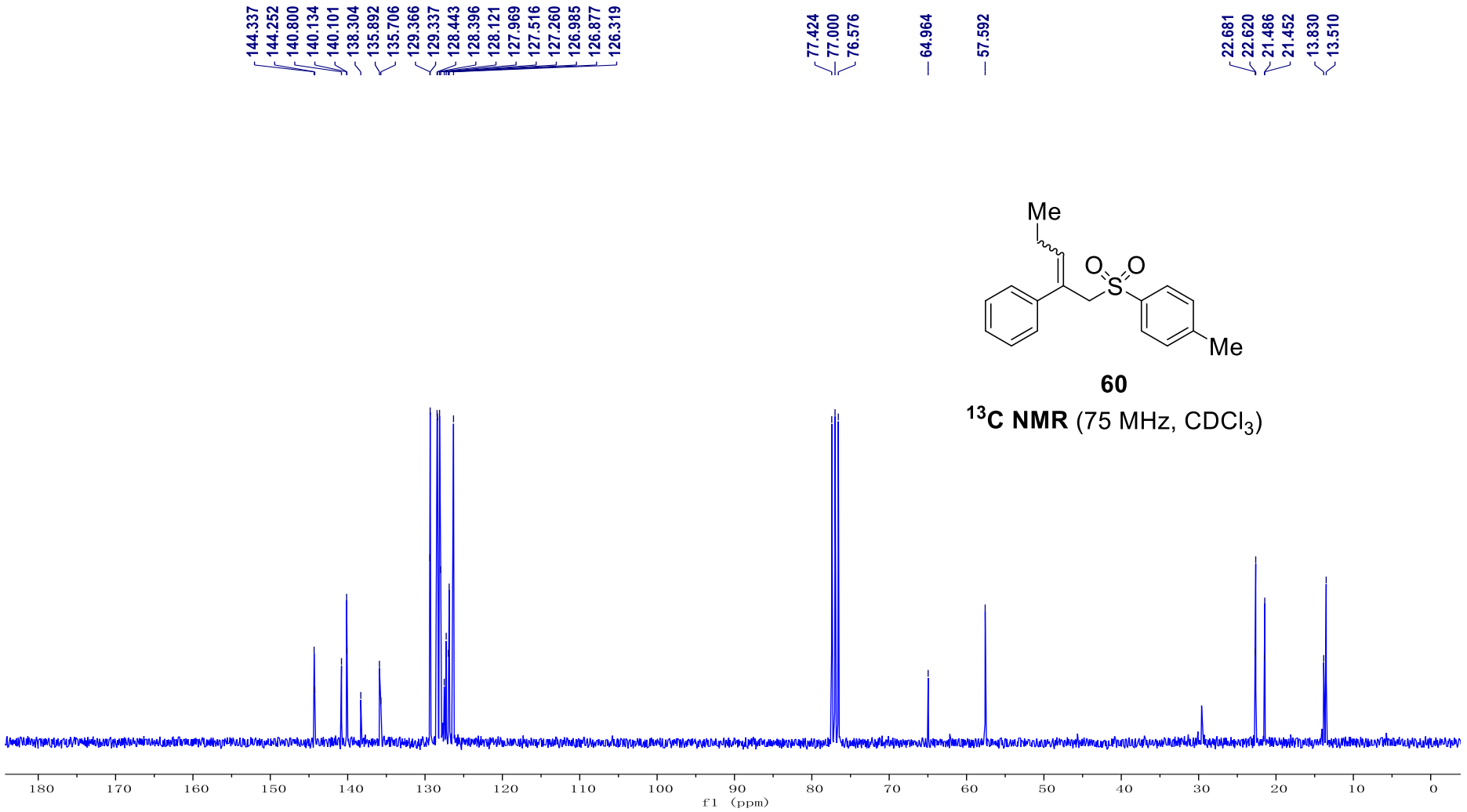
^{13}C NMR (75 MHz, $CDCl_3$)

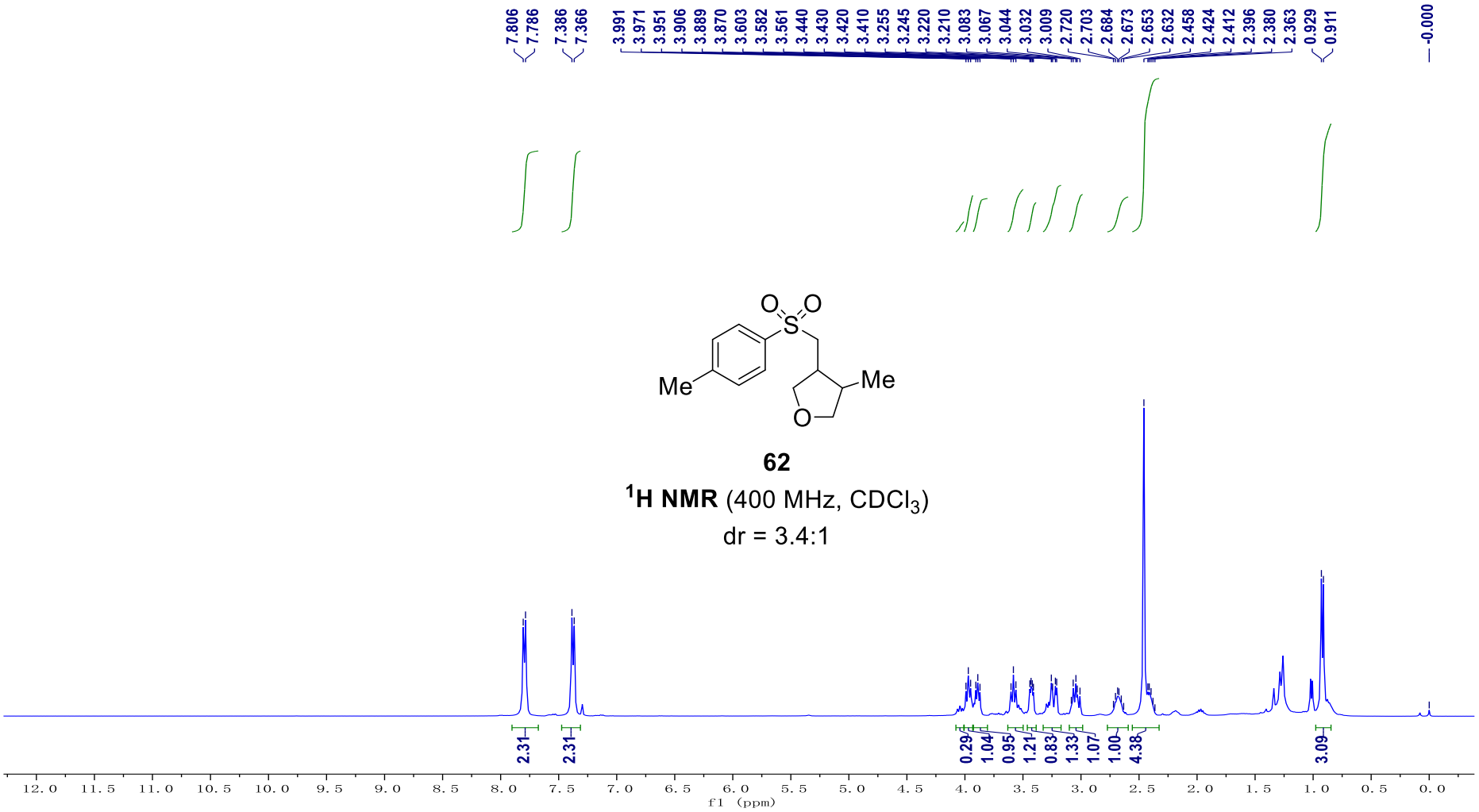


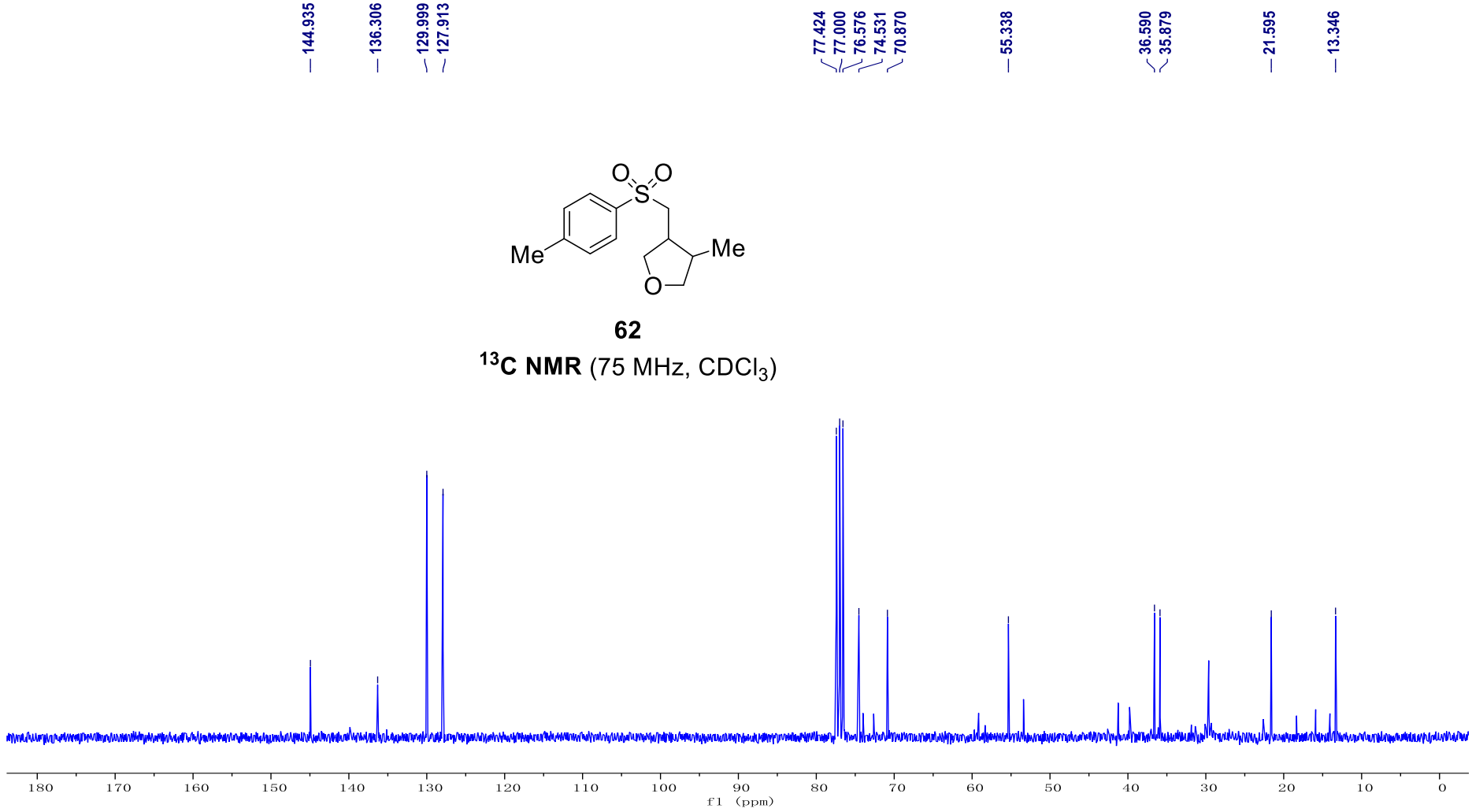
60

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

major isomer/minor isomer = 2:1


144.337
144.252
140.800
140.134
140.101
138.304
135.892
135.706
129.366
129.337
128.443
128.396
128.121
127.969
127.516
127.260
126.985
126.877
126.319
77.424
77.000
76.576
64.964
57.592
22.681
22.620
21.486
21.452
13.830
13.510
Me
O
O
S
Me
60
13C NMR (75 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.806
7.786
7.386
7.366
3.991
3.971
3.951
3.906
3.889
3.870
3.603
3.582
3.561
3.440
3.430
3.420
3.410
3.255
3.245
3.220
3.210
3.083
3.067
3.044
3.032
3.009
2.720
2.703
2.684
2.673
2.653
2.632
2.458
2.424
2.412
2.396
2.380
2.363
0.929
0.911
-0.000
O
O
S
Me
Me
O
62
1H NMR (400 MHz, CDCl3)
dr = 3.4:1
2.31
2.31
0.29
1.04
0.95
1.21
0.83
1.33
1.07
1.00
4.38
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



62

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