Supporting Information

for

CO_2-Promoted Photoredox-Catalyzed Hydrosulfonylation of Alkenes with Sulfinates

Wanhui Huang,[a,b] Ge Liu,[b,c] Fangyuanhang Yang,[b] Yuxi Ren,[b] Yuzhen Gao,*[a,b,c] Weiping Su*[b,c]

[a]College of Chemistry & Materials Science, Fujian Normal University, Fuzhou 350007, P. R. China

[b]State Key Laboratory of Structural Chemistry, Center for Excellence in Molecular Synthesis, Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fujian Institute of Research on the Structure of Matter, 155 Yangqiao Road West, Fuzhou 350002, P. R. China

[c]University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

*E-mail: gyz@fjirsm.ac.cn, wpsu@fjirsm.ac.cn

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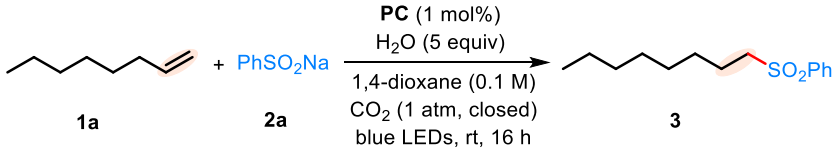
1. General Information

All chemical reagents and raw materials were sourced from commercial suppliers (including Accela, Acros, Adamas-beta®, Alfa Aesar, Aladdin, Bidepharmatech Energy Chemical, TCI Chemicals, Innochem, J&K Chemicals, Laajoo, Leyan, Sigma-Aldrich, Sinocompound, and 3A Chemicals) and used as received without further purification, unless otherwise noted. The Blue LED strips (1 meter, 5 W*8) were purchased from GeAo Chemical (China) without a light filter. The reaction contents were maintained at room temperature (around 30 ℃) without using additional cooling. The distance/path from the light source to the irradiation vessel is approximately 2.0 cm and there are no filters. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Bruker AVANCE III HD (400 MHz) spectrometer; JEOL ECZ600S 600M spectrometer and JEOL ECZ400S (400 MHz) spectrometer, using $CDCl_3$ as solution. Chemical shifts (δ) are given in parts per million (ppm) with the solvent resonance as the internal standard (for $CDCl_3$: 7.26 ppm, and 77.16 ppm). Spin multiplicity was abbreviated as follows: s - singlet, d - doublet, t - triplet, q - quartet, dd - doublet of doublet, td - triplet of doublet and m - multiplet. High-resolution mass spectra (HRMS) were obtained on an Impact II UHR-TOF mass spectrometry equipped with an ESI source from Bruker at Fujian Institute of Research on the Structure of Matter. Flash column chromatography (FCC) was carried out on silica gel (200 - 300 mesh). Single-crystal X-ray diffraction (SCXRD) data of all compounds were recorded using Bruker D8 ADVANCE with a graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation and XtaLAB Synergy R, HyPix. The structure was solved by the direct method using a SHELXL-97 program.

2. Experimental Section

2.1 Optimization of reaction condition

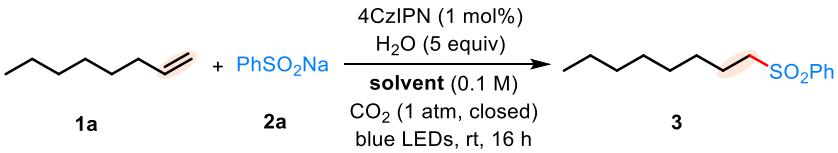
Table S1. Screening of the photocatalyst.[a]



Entry	PC (1 mol%)	Yield (%)[b]
1	**4CzIPN**	**29**
2	$Ir(ppy)_2(dtbbpy)PF_6$	42
3	$Ru(bpy)_3Cl_2$	11
4	Eosin Y	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), PC (1 mol%), H_2O (5.0 equiv), CH_3CN (2 mL, 0.1 M), CO_2 (1 atm, closed), 40 W blue LEDs, rt, 16 h. [b]Yield was determined by ^{1}H NMR with $CHCl_2CHCl_2$ as internal standard.

Table S2. Screening of the solvent.[a]

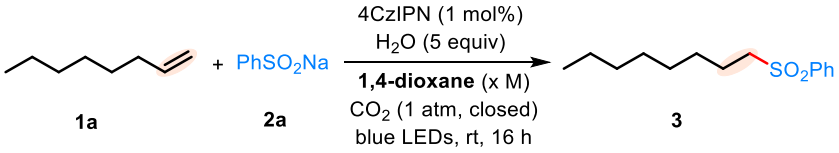


Entry	Solvent (2 mL)	Yield (%)[b]

1	DMSO	0
2	Actone	0
3	Chlorobenzene	0
4	Tetrahydrofuran	0
5	**1,4-dioxane**	**77**
6	DCM	0
7	CH_3CN	24
8	CH_3OH	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), 4CzIPN (1 mol%), H_2O (5.0 equiv), solvent (2 mL, 0.1 M), CO_2 (1 atm, closed), 40 W blue LEDs, rt, 16 h. [b]Yield was determined by ^1H NMR with $CHCl_2CHCl_2$ as internal standard.

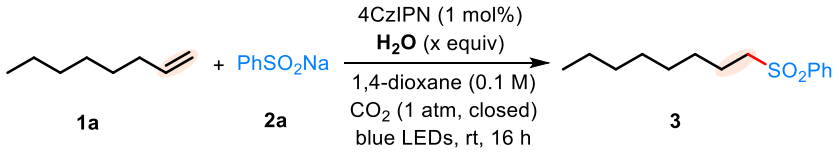
Table S3. Screening of the amount of solvent.[a]



Entry	1,4-dioxane (M)	Yield (%)[b]
1	0.05	90
2	**0.1**	**99**
3	0.15	89

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), 4CzIPN (1 mol%), H_2O (5.0 equiv), 1,4-dioxane (x M),CO_2 (1 atm, closed), 40 W blue LEDs, rt, 16 h. [b]Yield was determined by ^1H NMR with $CHCl_2CHCl_2$ as internal standard.

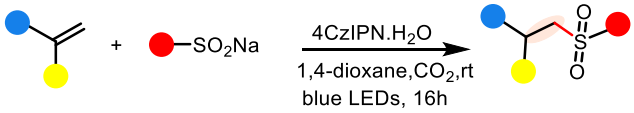
Table S4. Screening of the mount of H_2O.[a]



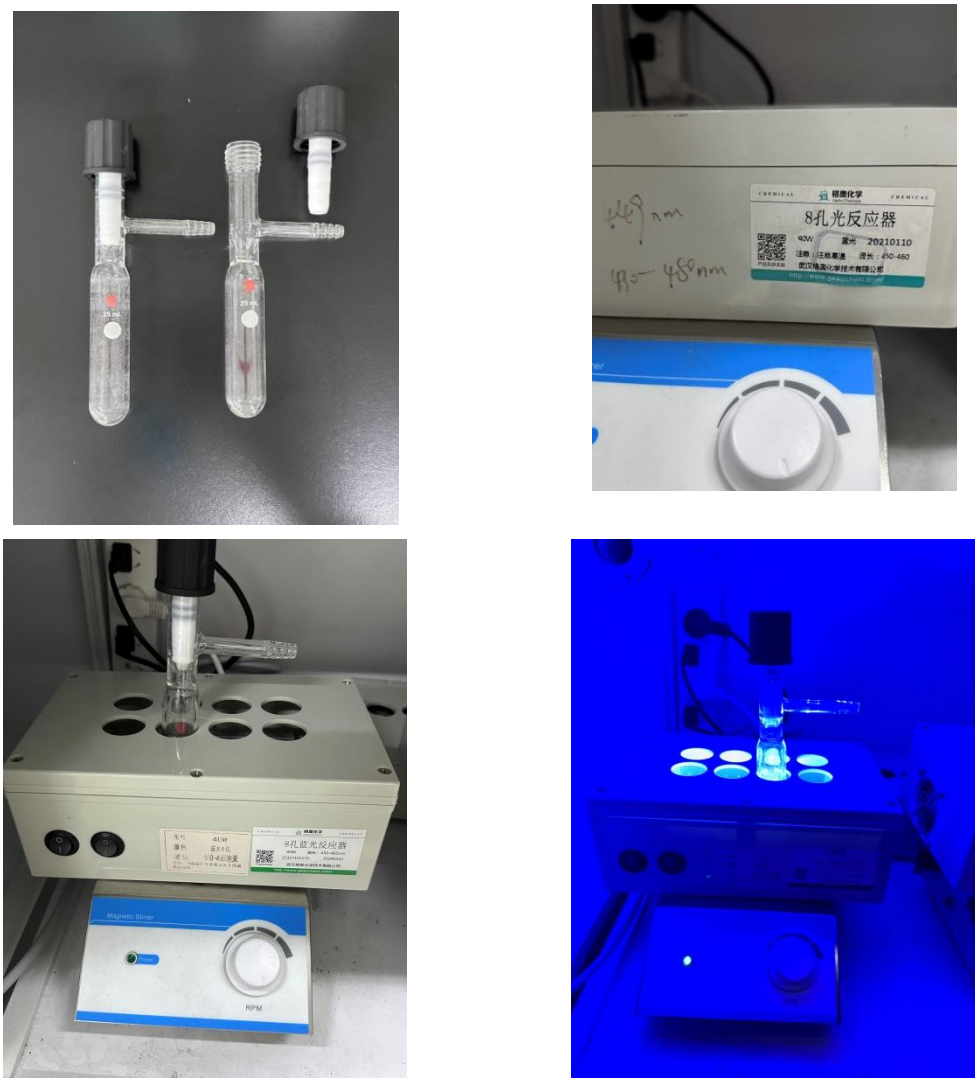
Entry	H_2O (equiv)	Yield (%)[b]
1	0	21
2	2	5
3	3	62
4	**5**	**99**
5	7	95
6	10	91
7	15	97
8	20	92

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv), 4CzIPN (1 mol%), H_2O(x equiv), 1,4-dioxane(2 mL, 0.1 M), CO_2 (1 atm, closed), 40 W blue LEDs, rt, 16 h. [b]Yield was determined by ^1H NMR with $CHCl_2CHCl_2$ as internal standard.

2.2 General procedures for synthesis of products



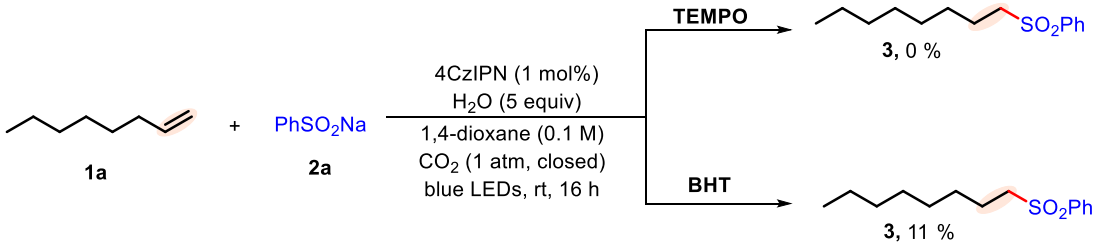
In clean and dry Schlenk tube (25 mL) reaction flask, a 1 cm Teflon magnetic stir bar was added, followed by the sequential addition of olefin (0.2 mmol, 1.0 equiv), sulfinate (1.5 equiv), 4CzIPN (1 mol%), H_2O (5.0 equiv), and 1,4-dioxane (2 mL). Then, the flask was filled with CO_2 and the system was subjected to three cycles of purging and refilling with CO_2. The mixture was placed under a 8*5 W blue LED light source (λ_{max} = 448 nm, 1.0 cm away, with cooling fan to keep the reaction temperature and stirred at ambient temperature for 16 h. After the reaction is complete, filter the reaction product mixture through a silica gel column (200 - 300 mesh) packed with small pieces of cotton at the bottom, and rinse it with EA solvent two to three times. After that, the mixture was concentrated on a rotary evaporator. The filtrate was concentrated in vacuo, and crude ^1H NMR spectrum was taken using $CHCl_2CHCl_2$ as internal standard. The resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using petroleum ether/ethyl acetate (from 15:1 to 1:1) as the elution to give the desired products.



Supplementary Figure 1. Photograph of the photocatalytic reactor used for reactions conducted under

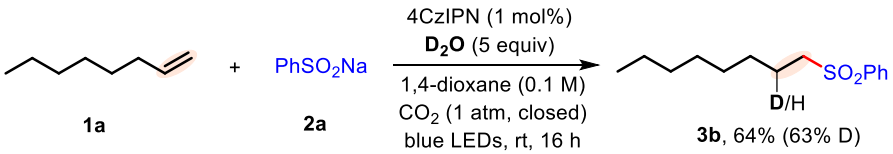
blue LED inrradiation.

2.3 Radical-trapping experiments



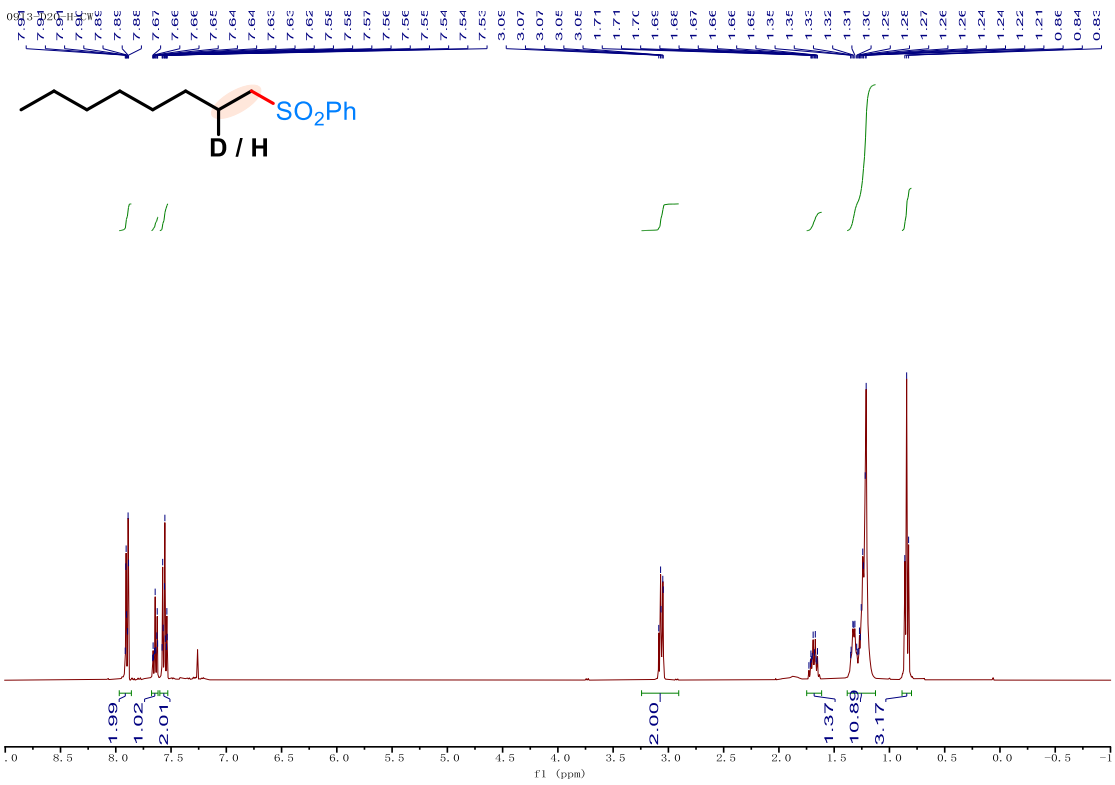
In clean and dry Schlenk tube (25 mL) reaction flask, a 1cm Teflon magnetic stir bar was added, followed by the sequential addition of **1a** (0.2 mmol, 1.0 equiv), **2a** (1.5 equiv), 4CzIPN (1 mol%), H_2O (5.0 equiv), BHT or TEMPO (2.0 equiv) and 1,4-dioxane (2 mL).Then, the flask was filled with CO_2 and the system was subjected to three cycles of purging and refilling with CO_2. The mixture was placed under a 8*5 W blue LED light source (λ_{max} = 448 nm, 1.0 cm away, with cooling fan to keep the reaction temperature at 15 - 40℃) and stirred at ambient temperature for 16 h. After the reaction is complete, filter the reaction product mixture through a silica gel column (200 - 300 mesh) packed with small pieces of cotton at the bottom, and rinse it with EA solvent two to three times. After that, the mixture was concentrated on a rotary evaporator. The yield was determined by ^{1}H NMR spectroscopy using $CHCl_2CHCl_2$ as the internal standard. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using petroleum ether/ethyl acetate (5:1) as the elution to give the desired product **3**.

2.4 Deuterium-labeling experiment



In clean and dry Schlenk tube (25 mL) reaction flask, a 1 cm Teflon magnetic stir bar was added, followed by the sequential addition of **1a** (0.2 mmol, 1.0 equiv), **2a** (1.5 equiv), 4CzIPN (1 mol%), D_2O (5.0 equiv) and 1,4-dioxane (2 mL). Then, the flask was filled with CO_2 and the system was subjected to three cycles of purging and refilling with CO_2. The mixture was placed under a 8*5 W blue LED light source (λ_{max} = 448 nm, 1.0 cm away, with cooling fan to keep the reaction temperature at 15 - 40°C) and stirred at ambient temperature for 16 h. After the reaction is complete, filter the reaction product mixture through a silica gel column (200 - 300 mesh) packed with small pieces of cotton at the bottom, and rinse it with EA solvent two to three times. The filtrate was concentrated in vacuo, and crude ^{1}H NMR spectrum was taken using $CHCl_2CHCl_2$ as internal standard. After that, the resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using PE/EA (7:1) as the elution to give the desired product. Yield = 64% (32.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.86 (m, 2H), 7.68 - 7.62 (m, 1H), 7.60 - 7.53 (m, 2H), 3.24 - 2.91 (m, 2H), 1.75 - 1.61 (m, 1.37H), 1.38 - 1.13 (m, 11H), 0.84 (t, *J* = 6.8 Hz, 3H).



Supplementary Figure 2. ^{1}H NMR Spectrum of **3b** ($CDCl_3$ as solvent, 400 MHz).

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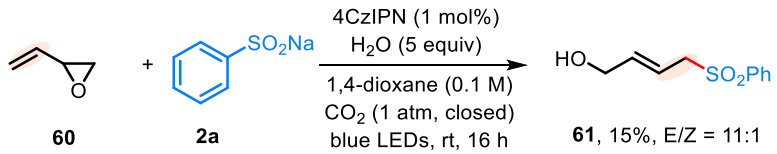
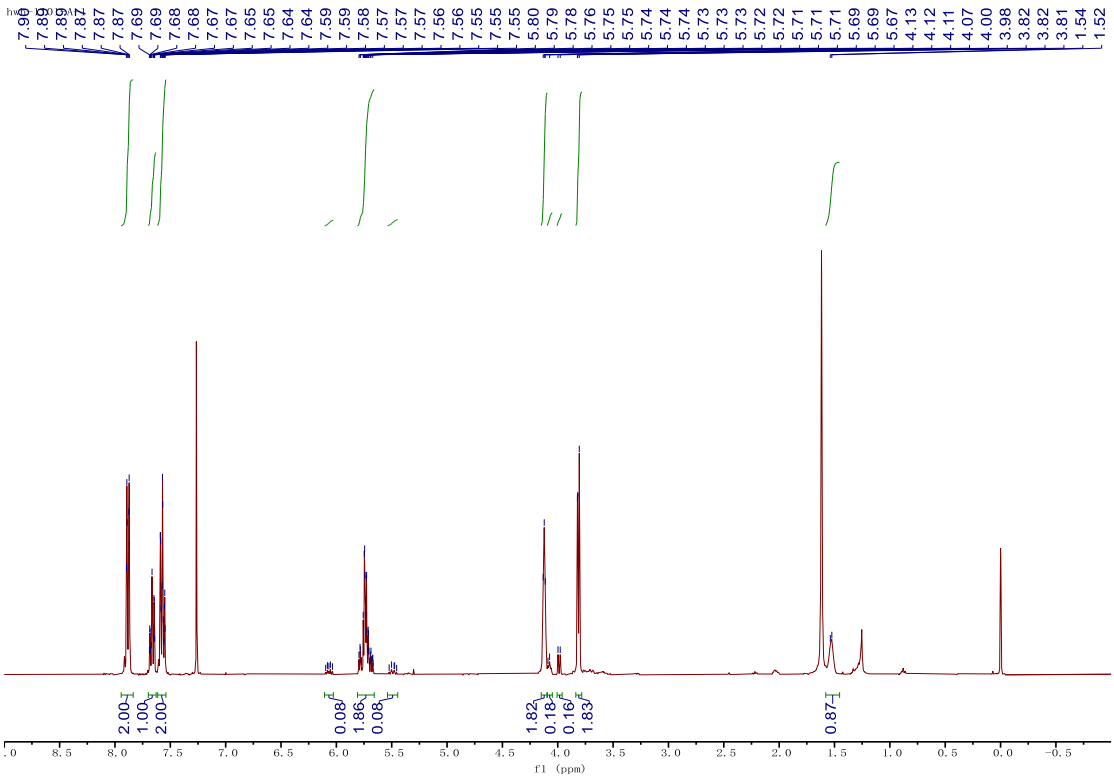
2.5 Reaction with radical clocks



60 **2a** **61**, 15%, E/Z = 11:1

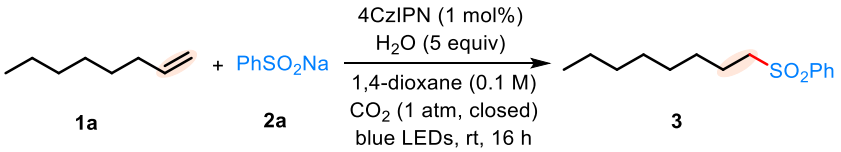
In clean and dry Schlenk tube (25 mL) reaction flask, a 1 cm Teflon magnetic stir bar was added, followed by the sequential addition of **60** (0.2 mmol, 1.0 equiv), **2a** (1.5 equiv), 4CzIPN (1 mol%), H_2O (5.0 equiv), and 1,4-dioxane (2 mL). Then, the flask was filled with CO_2 and the system was subjected to three cycles of purging and refilling with CO_2. The mixture was placed under an 8*5 W blue LED light source (λ_{max} = 448 nm, 1.0 cm away, with cooling fan to keep the reaction temperature at 15 - 40°C) and stirred at ambient temperature for 16 h. After the reaction is complete, filter the reaction product mixture through a silica gel column (200-300 mesh) packed with small pieces of cotton at the bottom, and rinse it with EA solvent two to three times. After that, the mixture was concentrated on a rotary evaporator. The filtrate was concentrated in vacuo, and crude ^{1}H NMR spectrum was taken using $CHCl_2CHCl_2$ as internal standard. The resulting residue was purified by flash silica gel chromatography or preparative thin layer chromatography using PE/EA (5/1) as the elution to give the desired product **61**[1].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.4, 1.2 Hz, 2H), 7.70 - 7.63 (m, 1H), 7.59 - 7.55 (m, 2H), 5.81 - 5.66 (m, 2H), 4.13 (d, *J* = 3.7 Hz, 2H), 3.84 - 3.78 (m, 2H), 1.58 - 1.45 (m, 1H).

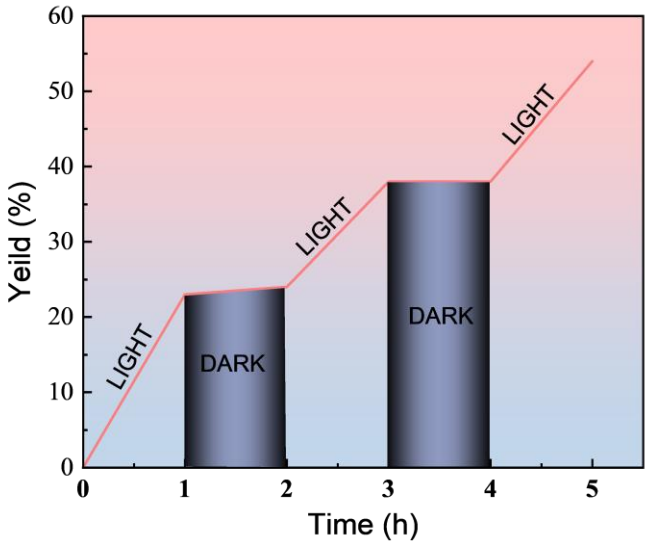


Supplementary Figure 3. ^{1}H NMR Spectrum of **61** ($CDCl_3$ as solvent, 400 MHz).

2.6 Light/Dark experiment

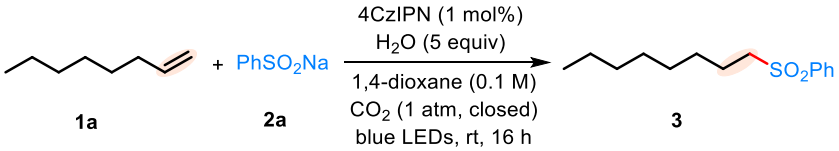


In a clean and dry 25 mL sample vial reaction flask, 1 cm Teflon magnetic stir bar was added, followed by the sequential addition of **1a** (0.2 mmol, 1.0 equiv), **2a** (1.5 equiv), 4CzIPN (1 mol%), H_2O (5.0 equiv) and 1,4-dioxane (2 mL). Subsequently, 1,3,5-trimethoxybenzene was introduced into the 2 mL standard reaction mixture as an internal standard. Gas exchange was carried out by purging the container with CO_2 three times, with additional CO_2 supplied using a gas bag. Prior to the reaction, 0.15 mL of the liquid mixture was collected and irradiated for one hour, followed by another 0.15 mL collection. The reaction was then conducted in the dark for 1 hour before collecting another 0.15 mL. The mixture was again irradiated for 1 hour, and 0.15 mL was collected. It was then reacted in the dark for an additional hour, followed by another 0.15 mL collection. Finally, the mixture underwent one last irradiation for 1 hour, and another 0.15 mL was collected. The solvent was subsequently removed under vacuum at elevated temperature, and the yield was determined by ^{1}H NMR spectroscopy.



Supplementary Figure 4. Light/Dark experiment.

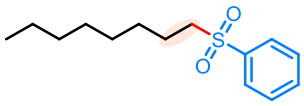
2.7 Gram-scale experiment



In clean and dry Schlenk tube (150 mL) reaction flask, a 5 cm Teflon magnetic stir bar was added, followed by the sequential addition of **1a** (5 mmol, 1.0 equiv, 0.561g), **2a** (1.5 equiv), 4CzIPN (1 mol%), H_2O (5.0 equiv) and 1,4-dioxane (50 mL). Then, the flask was filled with CO_2 and the system was subjected to ten cycles of purging and refilling with CO_2. The mixture was placed under a 8*5 W blue LED light source (λ_{max} = 448 nm, 1.0 cm away, with cooling fan) and stirred at ambient temperature for 16 h. Afterwards, the filtrate was concentrated under vacuum and purified by silica gel column chromatography using EA as the eluent to obtain the desired product. And crude ^{1}H NMR spectrum was taken using $CHCl_2CHCl_2$ as internal standard. The resulting residue was purified by flash silica gel chromatography using petroleum PE/EA (7:1) as the eluent to give the desired product **3**, yield = 78% (0.992 g).

3. Datas of Compounds and Product characteristics

(Octylsulfonyl)benzene (3)[2]

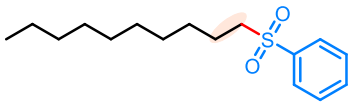


Colorless oil; Yield = 95% (48.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.83 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 3.12 - 3.01 (m, 2H), 1.70 -1.66 (m, 2H), 1.32 (p, *J* = 7.2 Hz, 2H), 1.27 - 1.16 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 133.7, 129.3, 128.1, 56.4, 31.7, 29.0, 29.0, 28.3, 22.7, 22.6, 14.1

(Decylsulfonyl)benzene (4)[3]

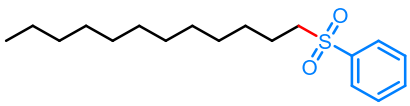


Orange yellow oily liquid; Yield = 96% (54.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 - 7.56 (m, 2H), 7.36 (dd, *J* = 8.8, 6.1 Hz, 1H), 7.30 - 7.25 (m, 2H), 2.90 - 2.70 (m, 2H), 1.47 - 1.35 (m, 2H), 1.09 - 0.87 (m, 14H), 0.59 - 0.55 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 133.7, 129.3, 128.1, 56.3, 31.9, 29.5, 29.3, 29.0, 28.3, 22.7, 22.7, 14.2.

(Dodecylsulfonyl)benzene (5)[4]

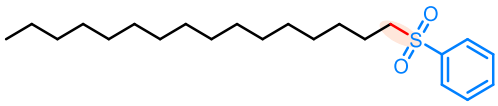


Orange yellow solid; Yield = 99% (61.4 mg).

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.88 (t, *J* = 9.0 Hz, 2H), 7.62 (p, *J* = 7.2 Hz, 1H), 7.54 (dt, *J* = 10.7, 7.3 Hz, 2H), 3.05 (td, *J* = 11.0, 7.4 Hz, 2H), 1.68 - 1.64 (m, 2H), 1.35 - 1.14 (m, 18H), 0.84 (dt, *J* = 11.2, 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 139.2, 133.7, 129.3, 128.1, 31.9, 29.6, 29.5, 29.3, 29.2, 29.0, 28.3, 22.7, 22.7.

(Hexadecylsulfonyl)benzene (6)



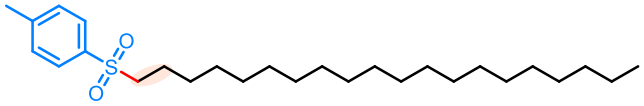
Yellow solid with a loose structure; Yield = 88% (64.5 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, *J* = 5.8 Hz, 2H), 7.64 (q, *J* = 6.2, 4.5 Hz, 1H), 7.56 (q, *J* = 7.1 Hz, 2H), 3.06 (td, *J* = 10.0, 4.6 Hz, 2H), 1.73 - 1.64 (m, 2H), 1.32 - 1.13 (m, 26H), 0.86 (q, *J* = 5.7, 5.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 133.2, 128.8, 127.6, 55.8, 31.5, 29.2, 29.1, 29.0, 28.9, 28.8, 28.5, 27.8, 22.2, 22.2, 13.7.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{38}NaO_2S$ 389.2486, found 389.2485.

1-(Icosylsulfonyl)-4-methylbenzene (7)



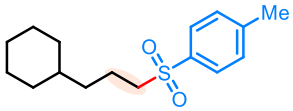
Lodine brown oily; Yield = 70% (61.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (q, *J* = 7.4, 6.9 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 3.03 (p, *J* = 7.5, 6.8 Hz, 2H), 2.42 (s, 3H), 1.67 (p, *J* = 7.5 Hz, 2H), 1.35 - 1.18 (m, 34H), 0.87 (q, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 135.5, 129.1, 127.4, 55.7, 31.2, 29.0, 28.9, 28.8, 28.7, 28.5, 28.3, 27.6, 22.0, 20.9, 13.4.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{27}H_{48}NaO_2S$ 459.3267, found 459.3269.

1-((3-Cyclohexylpropyl)sulfonyl)-4-methylbenzene (8)



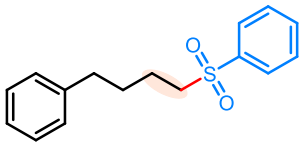
Light yellow solid; Yield = 98% (55.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.74 (m, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.06 - 2.98 (m, 2H), 2.44 (s, 3H), 1.77 - 1.57 (m, 8H), 1.23 - 1.11 (m, 5H), 0.81 (q, *J* = 10.2, 9.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 136.3, 130.1, 129.9, 128.3, 128.1, 56.7, 37.3, 36.0, 33.1, 26.6, 26.3, 21.8, 21.7, 20.3.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{24}NaO_2S$ 303.1389, found 303.1389.

((4-Phenylbutyl)sulfonyl)benzene (9)[2]

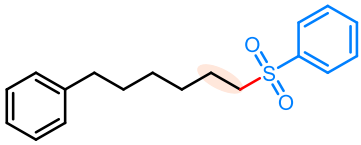


Cololess oild; Yield = 81% (44.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (t, *J* = 8.0 Hz, 2H), 7.65 (dd, *J* = 8.7, 6.5 Hz, 1H), 7.55 (q, *J* = 8.6, 8.1 Hz, 2H), 7.26 - 7.20 (m, 2H), 7.17 (dd, *J* = 8.9, 6.4 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 3.11 - 3.05 (dd, *J* = 9.0, 6.4 Hz, 2H), 2.57 (q, *J* = 8.1 Hz, 2H), 1.82 - 1.55 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.2, 133.8, 129.4, 128.6, 128.4, 128.2, 126.1, 56.2, 35.4, 30.1, 22.4.

((6-Phenylhexyl)sulfonyl)benzene (10)



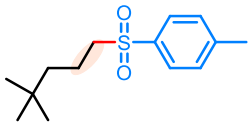
Lodine brown oily; Yield = 70% (42.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.67 - 7.59 (m, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.18 - 7.10 (m, 3H), 3.30 - 2.74 (m, 2H), 2.55 (q, *J* = 7.7 Hz, 2H), 1.74 - 1.62 (m, 2H), 1.56 (p, *J* = 7.8 Hz, 2H), 1.41 - 1.22 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 139.2, 133.7, 129.3, 128.4, 128.4, 128.1, 125.8, 56.3, 35.8, 31.1, 28.6, 28.2, 22.6.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{22}NaO_2S$ 325.1233, found 325.1234.

1-((4,4-Dimethylpentyl)sulfonyl)-4-methylbenzene (11)



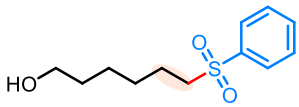
Colorless oil; Yield = 26% (13.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.71 (m, 2H), 7.39 - 7.31 (m, 2H), 3.09 - 2.90 (m, 2H), 2.43 (s, 3H), 1.75 - 1.61 (m, 2H), 1.26 - 1.14 (m, 2H), 0.83 (d, *J* = 8.4 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 136.4, 130.0, 128.1, 57.3, 42.7, 30.5, 29.3, 21.7, 18.2.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{14}H_{22}NaO_2S$ 277.1235, found 277.1233.

6-(Phenylsulfonyl)hexan-1-ol (12)[2]

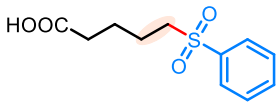


Greyish-green oil; Yield = 89% (43.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.86 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 3.13 - 3.01 (m, 2H), 1.71 - 1.65 (m,3H), 1.49 (p, *J* = 6.7 Hz, 2H), 1.39 - 1.31 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 133.8, 129.4, 128.1, 62.6, 56.2, 32.3, 28.1, 25.3, 22.7.

5-(Phenylsulfonyl)pentanoic acid (13) [2]

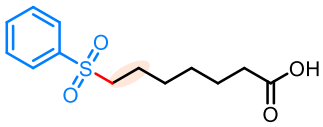


Colorless oil; Yield = 81% (39.3 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 - 7.86 (m, 2H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 3.21 - 3.03 (m, 2H), 2.34 (t, *J* = 6.9 Hz, 2H), 2.16 (s, 1H), 1.84 - 1.63 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ178.7, 138.9, 133.9, 129.5, 128.1, 55.9, 33.4, 23.3, 22.2.

7-(Phenylsulfonyl)heptanoic acid (14) [2]

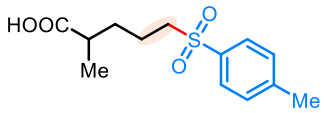


White solid; Yield = 99% (53.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.67 - 7.63 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 3.21 - 2.95 (m, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.74 - 1.66 (m, 2H), 1.64 - 1.48 (m, 2H), 1.37 - 1.29 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 139.1, 133.8, 129.4, 128.1, 56.2, 33.8, 28.5, 28.0, 24.3, 22.5.

2-Methyl-5-tosylpentanoic acid (15)



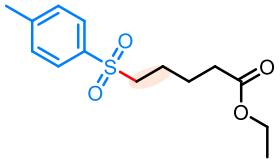
Feather shaped pale yellow crystal; Yield = 94% (50.8 mg);

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.06 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 2.43 - 2.40 (m, 1H), 1.81 - 1.42 (m, 4H), 1.14 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 182.1, 144.8, 136.0, 130.0, 128.1, 56.1, 38.9, 31.8, 21.7, 20.6, 16.8.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{13}H_{18}NaO_4S$ 293.0818, found 293.0818.

Ethyl 5-tosylpentanoate (16)



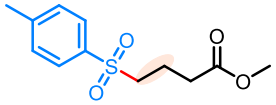
Green oil; Yield = 81% (46.1 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 1.99 (s, 3H), 1.73 - 1.68 (m, 2H), 1.60 - 1.55 (m, 2H), 1.41 (p, *J* = 7.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 144.6, 135.9, 129.8, 127.9, 63.7, 56.0, 27.9, 24.7, 22.3, 21.5, 20.8.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{14}H_{20}NaO_4S$ 307.0975, found 307.0973.

Methyl 4-tosylbutanoate (17)[5]

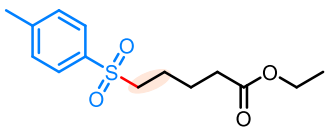


Reddish brown oily liquid; Yield = 62% (31.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 - 7.70 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.09 (t, *J* = 6.2 Hz, 2H), 3.42 - 2.93 (m, 2H), 2.43 (s, 3H), 2.10 - 2.01 (m, 2H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ170.0, 144.2, 135.0, 129.2, 127.3, 61.3, 52.5, 21.7, 20.9, 20.0.

Ethyl 4-tosylbutanoate (18) [5]

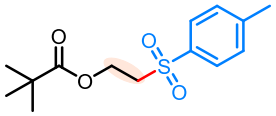


Orange yellow solid; Yield = 95% (54.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.69 (m, 2H), 7.37 - 7.29 (m, 2H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.13 - 2.97 (m, 2H), 2.42 (s, 3H), 2.25 (t, *J* = 6.8 Hz, 2H), 1.76 - 1.61 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 144.8, 136.0, 130.0, 128.1, 60.5, 56.0, 33.6, 23.6, 22.3, 21.7, 14.2.

2-Tosylethyl pivalate (19)



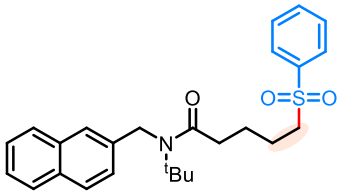
Colorless oil; Yield = 25% (14.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.79 (m, 2H), 7.43 - 7.31 (m, 2H), 4.39 - 4.35 (m, 2H), 3.45 - 3.41 (m, 2H), 2.45 (d, *J* = 2.3 Hz, 3H), 1.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 145.2, 136.4, 130.2, 128.3, 57.8, 55.4, 38.7, 27.2, 27.0, 21.8.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{14}H_{20}NaO_4S$ 307.0974, found 307.0975.

N-(Tert-butyl)-N-(naphthalen-2-ylmethyl)-5-(phenylsulfonyl)pentanamide (20)



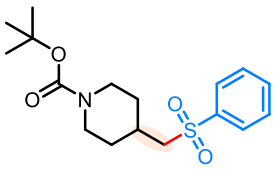
Grey green oil; Yield = 71% (65.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.80 (m, 5H), 7.59 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.49 (td, *J* = 7.8, 3.1 Hz, 4H), 7.27 (dd, *J* = 8.8, 3.4 Hz, 1H), 4.71 (d, *J* = 3.3 Hz, 2H), 3.07 - 3.02 (m, 2H), 2.37 - 2.22 (m, 2H), 1.68 (m, 4H), 1.44 (d, *J* = 3.4 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 139.0, 136.8, 133.7, 133.4, 132.6, 129.3, 128.8, 128.0, 127.8, 127.7, 126.6, 126.0, 124.0, 123.8, 58.0, 56.1, 48.8, 35.0, 28.8, 24.1, 22.4.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{26}H_{31}NNaO_3S$ 460.1917, found 460.1919.

Tert-butyl 4-((phenylsulfonyl)methyl)piperidine-1-carboxylate (21)



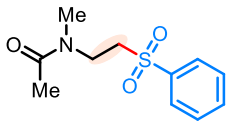
Yellow brown solid; Yield = 48% (32.5 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 - 7.88 (m, 2H), 7.67 - 7.63 (m, 1H), 7.59 - 7.54 (m, 2H), 4.17 - 3.88 (m, 2H), 3.00 (d, *J* = 6.4 Hz, 2H), 2.80 - 2.56 (m, 2H), 2.21 - 2.11 (m, 1H), 1.85 (d, *J* = 12.9 Hz, 2H), 1.42 (s, 9H), 1.30 - 1.14 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 140.2, 133.9, 129.5, 127.8, 62.0, 32.0, 31.3, 28.5.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{25}NNaO_4S$ 362.1399, found 362.1396.

N-Methyl-N-(2-(phenylsulfonyl)ethyl)acetamide (22)



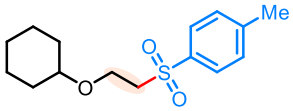
Light yellow transparent liquid; Yield = 69% (36.4 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 - 7.91 (m, 2H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 3.73 (t, *J* = 6.6 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 3.08 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (151 MHz, CDCl3) δ 171.3, 139.4, 134.0, 129.5, 127.8, 53.4, 42.9, 37.7, 21.8.

HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{11}H_{15}NNaO_3S$ 264.0065, found 264.0666.

1-((2-(Cyclohexyloxy)ethyl)sulfonyl)-4-methylbenzene (23)



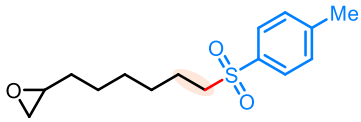
Yellow oil; Yield = 99% (60.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.72 (m, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.78 (t, *J* = 6.5 Hz, 2H), 3.38 (t, *J* = 6.4 Hz, 2H), 3.17 - 3.12 (m, 1H), 2.44 (s, 3H), 1.79 - 1.68 (m, 2H), 1.62 (d, *J* = 9.0 Hz, 2H), 1.53 - 1.43 (m, 1H), 1.49 - 1.10 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 137.0, 129.8, 128.2, 78.1, 61.2, 56.9, 31.8, 25.7, 23.9, 21.7.

HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{15}H_{22}NaO_3S$ 305.1182, found 305.1181.

2-(6-Tosylhexyl)oxirane (24)



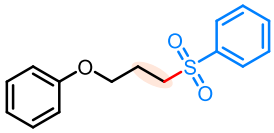
Orange red oil; Yield = 99% (60.5 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 - 7.73 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.07 - 2.97 (m, 2H), 2.84 - 2.83 (m, 1H), 2.71 - 2.68 (m, 1H), 2.41 (s, 3H), 1.70 - 1.62 (m, 2H), 1.52 - 1.24 (m, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7, 136.2, 129.9, 128.1, 56.3, 52.2, 47.0, 32.3, 28.8, 28.2, 25.7, 22.7, 21.6.

HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{15}H_{22}NaO_3S$ 305.1182, found 305.1181.

((3-Phenoxypropyl)sulfonyl)benzene (25)[6]



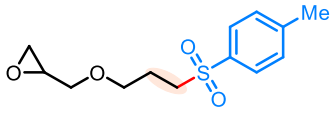
Colorless oil; Yield = 84% (46.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.8, 2.4 Hz, 2H), 7.68 - 7.61 (m, 1H), 7.58 - 7.54 (m, 2H), 7.27 - 7.23 (m, 2H), 6.96 - 6.91 (m, 1H), 6.82 (dd, *J* = 8.7, 2.3 Hz, 2H), 4.01 - 3.98 (m, 2H), 3.43 - 3.11 (m, 2H), 2.23 - 2.18 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 139.2, 133.8, 129.4, 128.5, 128.4, 128.2, 126.1, 56.2, 35.4, 30.1, 22.4.

HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{13}H_{18}NaO_4S$ 293.0819, found 293.0818.

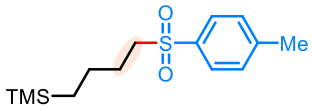
2-((3-Tosylpropoxy)methyl)oxirane (26)



Red brown oil; Yield = 90% (48.7 mg);

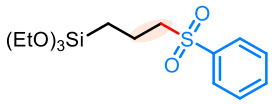
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 - 7.74 (m, 2H), 7.33 - 7.32 (m, 2H), 3.68 - 3.66 (m, 1H), 3.62 - 3.42 (m, 2H), 3.32 - 3.21 (m, 1H), 3.18 - 3.15 (m, 2H), 3.06 - 3.04 (m, 1H), 2.74 - 2.73 (m, 1H), 2.53 - 2.51 (m, 1H), 2.41 (s, 3H), 1.96 - 1.93 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.5, 135.9, 129.7, 127.8, 71.3, 68.7, 53.2, 50.5, 43.8, 23.1, 21.4.

Trimethyl (4-tosylbutyl)silane (27)



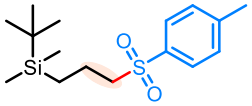
Colorless oil; Yield = 90% (51.2 mg).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.15 - 2.91 (m, 2H), 2.43 (s, 3H), 1.72 - 1.66 (m, 2H), 1.36 - 1.27 (m, 2H), 0.48 - 0.32 (m, 2H), -0.08 (d, *J* = 0.9 Hz, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 144.6, 136.4, 129.9, 128.1, 56.2, 26.4, 22.9, 21.7, 16.3, -1.8.
HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{14}H_{24}NaO_2SSi$ 307.1157, found 307.1158.

Triethoxy(3-(phenylsulfonyl)propyl)silane (28)[7]



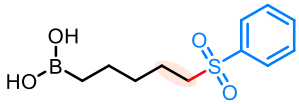
Yellow green oily liquid; Yield = 71% (49.2 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.86 (m, 2H), 7.66 - 7.58 (m, 1H), 7.58 - 7.49 (m, 2H), 4.01 - 3.49 (m, 6H), 3.37 - 2.86 (m, 2H), 1.83 - 1.78 (m, 2H), 1.25 - 1.09 (m, 9H), 0.67 - 0.63 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 133.7, 129.3, 128.2, 58.6, 58.4, 18.3, 16.9, 9.4.

Tert-butyldimethyl(3-tosylpropyl)silane (29)



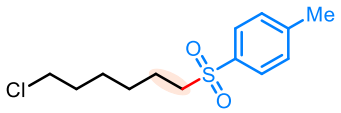
Orange yellow oil; Yield = 45% (28.1 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.08 (dd, *J* = 9.5, 6.3 Hz, 2H), 2.45 (s, 3H), 1.79 - 1.68 (m, 2H), 0.82 (s, 9H), 0.57 - 0.45 (m, 2H), -0.10 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 136.5, 130.0, 128.1, 59.8, 26.5, 21.7, 18.0, 16.5, 11.7, -6.3.
HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{28}NaO_2SSi$ 335.1471, found 335.1471.

(4-(Phenylsulfonyl)butyl)boronic acid (30)



Grey Solid; Yield = 60% (30.7 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.84 (m, 2H), 7.67 - 7.50(m, 3H), 3.06 (t, *J* = 8.1 Hz, 2H), 1.72 - 1.64 (m, 2H), 1.48 - 1.14 (m, 4H), 0.92 - 0.62 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 134.2, 129.7, 128.5, 56.5, 31.1, 24.0, 23.1, 22.8.
HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{11}H_{17}BNaO_4S$ 279.0834, found 279.0833.

1-((7-Chloroheptyl)sulfonyl)-4-methylbenzene (31)[8]

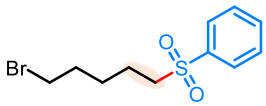


Lodine brown oily; Yield = 58% (31.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 3.11 - 2.97 (m, 2H), 2.43 (s, 3H), 1.73 - 1.68 (m, 4H), 1.41 - 1.35 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.8, 136.2, 130.0, 128.1, 56.3, 44.8, 32.1, 27.6, 26.3, 22.7, 21.7.

((5-Bromopentyl)sulfonyl)benzene (32)[2]

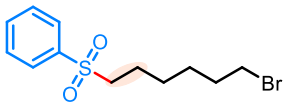


Yellow oil; Grey green oily liquid; Yield = 75% (43.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 - 7.58 (m, 2H), 7.37 (dt, *J* = 8.4, 6.6, 2.2 Hz, 1H), 7.36 - 7.25 (m, 2H), 3.06 (t, *J* = 6.5 Hz, 2H), 2.92 - 2.70 (m, 2H), 1.62 - 1.49 (m, 2H), 1.44 (dt, *J* = 10.7, 7.9, 3.9 Hz, 2H), 1.32 - 1.14 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 133.9, 129.4, 128.1, 56.1, 33.1, 32.1, 26.9, 22.0.

((6-Bromohexyl)sulfonyl)benzene (33)[9]



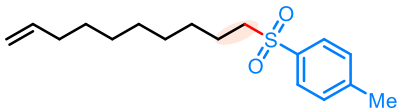
Orange yellow oil; Yield = 65% (39.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.84 (m, 2H), 7.70 - 7.63 (m, 1H), 7.57 (td, *J* = 7.8, 1.8 Hz, 2H), 3.36 (td, *J* = 6.7, 1.9 Hz, 2H), 3.15 - 3.02 (m, 2H), 1.89 - 1.77 (m, 2H), 1.75 - 1.68 (m, 2H), 1.44 - 1.38 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 133.8, 129.4, 128.1, 56.2, 33.7, 32.3, 27.6, 27.5, 22.6.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{12}H_{17}BrNaO_2S$ 327.0025, found 327.0024.

1-(Dec-9-en-1-ylsulfonyl)-4-methylbenzene (34)



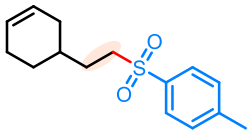
White solid; Yield = 80% (47.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.73 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.78 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.03 - 4.89 (m, 2H), 3.09 - 3.00 (m, 2H), 2.45 (s, 3H), 2.04 - 1.98 (m, 2H), 1.73 - 1.65 (m, 2H), 1.37 - 1.29 (m, 4H), 1.24 (q, *J* = 4.2, 3.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 139.2, 136.3, 130.0, 128.2, 114.3, 56.5, 33.8, 29.1, 29.0, 29.0, 28.9, 28.3, 22.8, 21.7.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{26}NaO_2S$ 317.1544, found 317.1546.

1-((2-(Cyclohex-3-en-1-yl)ethyl)sulfonyl)-4-methylbenzene (35)



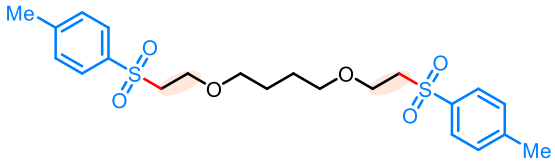
Colorless oil; Yield = 30% (17.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 5.74 - 5.48 (m, 2H), 3.10 (dd, *J* = 9.6, 6.8 Hz, 2H), 2.45 (s, 3H), 2.11 - 1.91 (m, 3H), 1.72 - 1.55 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 136.3, 130.0, 128.2, 127.2, 125.7, 54.6, 32.7, 31.4, 29.1, 28.5, 24.9, 21.8.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{26}NaO_2S$ 287.1077, found 287.1076.

1,4-Bis(2-tosylethoxy)butane (36)



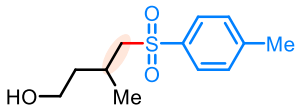
Orange yellow oil; Yield = 98% (89.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 10.4, 7.1 Hz, 4H), 7.42 (t, *J* = 8.8 Hz, 4H), 3.80 (dd, *J* = 11.4, 6.2 Hz, 4H), 3.47 - 3.40 (m, 4H), 3.36 - 3.29 (m, 4H), 2.59 - 2.35 (m, 6H), 1.43 - 1.36 (m, 4H).

13C NMR (101 MHz, CDCl3) δ 143.9, 136.1, 129.0, 127.3, 70.0, 63.2, 55.5, 25.1, 20.9.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{30}NaO_6S_2$ 477.1378, found 477.1376.

3-Methyl-4-tosylbutan-1-ol (37)



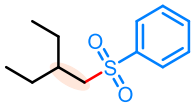
Colorless oil; Yield = 65% (31.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.73 - 3.57 (m, 2H), 3.06 (ddd, *J* = 93.2, 14.2, 6.1 Hz, 2H), 2.43 (s, 3H), 2.28 (q, *J* = 6.4 Hz, 1H), 2.10 (s, 1H), 1.75 - 1.52 (m, 2H), 1.05 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 136.9, 130.0, 127.9, 62.3, 59.9, 39.0, 25.7, 21.6, 20.3

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{12}H_{18}NaO_3S$ 265.0871, found 265.0869.

((2-Ethylbutyl)sulfonyl)benzene (38)[2]

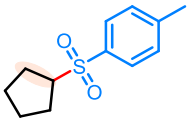


White solid; Yield = 50% (22.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 - 7.86 (m, 2H), 7.67 - 7.61 (m, 1H), 7.59 - 7.53 (m, 2H), 3.01 (d, *J* = 6.0 Hz, 2H), 1.89 - 1.85 (m, 1H), 1.52 - 1.37 (m, 4H), 0.80 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 133.7, 129.4, 128.0, 59.6, 35.8, 25.3, 10.3.

1-(Cyclopentylsulfonyl)-4-methylbenzene (39)[10]

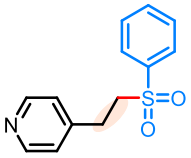


Colorless oil; Yield = 53% (23.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.48 - 3.42 (m, 1H), 2.43 (s, 3H), 2.09 - 1.99 (m, 2H), 1.90 - 1.81 (m, 2H), 1.79 - 1.70 (m, 2H), 1.63 - 1.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 136.1, 129.9, 128.6, 64.4, 27.4, 25.9, 21.7.

4-(2-(Phenylsulfonyl)ethyl)pyridine (41)[11]



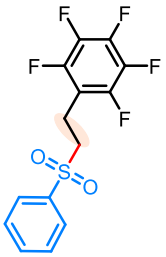
Colorless oil; Yield = 60% (29.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 - 8.42 (m, 2H), 8.02 - 7.84 (m, 2H), 7.71 - 7.63 (m, 1H), 7.62 - 7.51 (m, 2H), 7.13 - 6.98 (m, 2H), 3.41 - 3.33 (m, 2H), 3.13 - 3.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.8, 138.8, 134.2, 129.6, 128.2, 123.8, 56.3, 28.2.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{13}H_{14}NO_2S$ 248.0740, found 248.0740.

1,2,3,4,5-Pentafluoro-6-(2-(phenylsulfonyl)ethyl)benzene (42)[12]



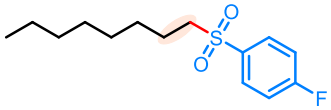
Yellow oil; Yield = 88% (59.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 - 7.84 (m, 2H), 7.71 - 7.64 (m, 1H), 7.62 - 7.53 (m, 2H), 3.34 (dd, *J* = 9.3, 6.3 Hz, 2H), 3.12 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4 (m), 143.9 (m), 138.9 (m), 138.5, 134.2, 129.6, 129.4 (m), 128.1, 127.8 (m), 110.9 (m), 54.1, 16.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.65 (dd, *J* = 21.9, 7.9 Hz), -155.06 (t, *J* = 20.6 Hz), -161.53 (td, *J* = 21.5, 8.3 Hz).

1-Fluoro-4-(octylsulfonyl)benzene (43)



Orange yellow solid; Yield = 96% (55.4 mg).

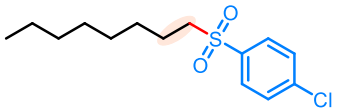
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (td, *J* = 9.1, 4.9 Hz, 2H), 7.26 (q, *J* = 9.4, 8.4 Hz, 2H), 3.12 - 3.07 (m, 2H), 1.72 - 1.69 (m, 2H), 1.41 - 1.20 (m, 10H), 0.88 (dd, *J* = 11.7, 6.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1 (d, *J* = 256.1 Hz), 135.6, 131.2 (d, *J* = 9.3 Hz), 116.9 (d, *J* = 22.3 Hz), 56.7, 31.9, 29.2, 29.2, 28.5, 23.0, 22.8, 14.3.

^{19}F NMR (565 MHz,) δ -105.02 (d, *J* = 10.1 Hz).

HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{14}H_{21}FNaO_2S$ 295.1139, found 295.1138.

1-Chloro-4-(octylsulfonyl)benzene (44)



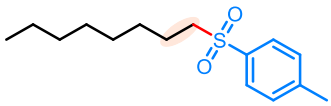
Brownish yellow oily liquid; Yield = 84% (48.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ **7**.93 - 7.74 (m, 2H), 7.64 - 7.44 (m, 2H), 3.13 - 2.98 (m, 2H), 1.71 - 1.65 (m, 2H), 1.39 - 1.16 (m, 10H), 0.84 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 137.7, 129.7, 129.7, 56.4, 31.7, 29.0, 29.0, 28.3, 22.7, 22.6, 14.1.

HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{14}H_{21}ClNaO_2S$ 311.0845, found 311.0843.

1-Methyl-4-(octylsulfonyl)benzene (45)[13]

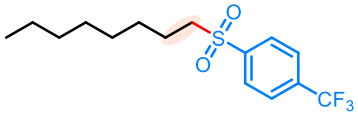


Orange yellow solid; Colorless oil; Yield = 99% (53.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.11 - 2.98 (m, 2H), 2.44 (s, 3H), 1.71 - 1.65 (m, 2H), 1.31 (q, *J* = 6.5 Hz, 2H), 1.23 (dd, *J* = 14.1, 4.7 Hz, 9H), 0.85 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 136.3, 130.0, 128.2, 56.5, 31.8, 29.1, 29.0, 28.4, 22.8, 22.7, 21.7, 14.2

1-(Octylsulfonyl)-4-(trifluoromethyl)benzene (46)



Yellow oil; Yield = 60% (38.7 mg).

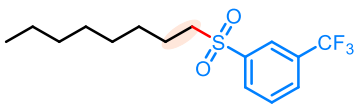
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.5, 2.3 Hz, 2H), 7.85 (dd, *J* = 8.5, 2.3 Hz, 2H), 3.25 – 3.00 (m, 2H), 1.75 - 1.67(m, 2H), 1.38 -1.33 (m, 2H), 1.29 - 1.20 (m, 8H), 0.86 (t, *J* = 6.9Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 135.5 (q, *J* = 32.1 Hz), 128.9, 126.6 (q, *J* = 17.1 Hz) , 123.3(q, *J* = 267.3 Hz), 56.3, 31.7, 29.0, 29.0, 28.3, 22.7, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.03.

HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{15}H_{21}F_3NaO_2S$ 345.1105, found 345.1107.

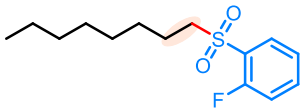
1-(Octylsulfonyl)-3-(trifluoromethyl)benzene (47)



Brown oil; Yield = 58% (37.4 mg);

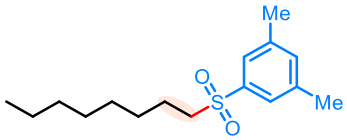
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 1H), 3.11 (t, *J* = 8.1 Hz, 2H), 1.72 (p, *J* = 7.8 Hz, 2H), 1.35 (q, *J* = 7.3 Hz, 2H), 1.24 (d, *J* = 7.3 Hz, 8H), 0.85 (t, J = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 132.2 (d, *J* = 33.7 Hz), 131.5, 130.5 (q, *J* = 3.6 Hz), 130.3, 125.4 (d, *J* = 3.9 Hz), 123.2 (d, *J* = 272.9 Hz), 56.4, 31.8, 29.0, 28.9, 28.3, 22.7, 22.6, 14.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.82.
HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{21}F_3NaO_2S$ 345.1105, found 345.1115.

1-Fluoro-2-(octylsulfonyl)benzene (48)



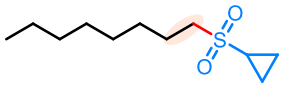
Colorless oil; Yield = 48% (26.6 mg);
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 8.11 (m, 1H), 7.87 - 7.79 (m, 1H), 7.56 - 7.50 (m, 1H), 7.47 - 7.40 (m, 1H), 3.48 (dd, *J* = 9.3, 6.8 Hz, 2H), 1.91 (t, *J* = 7.8 Hz, 2H), 1.61 - 1.35 (m, 10H), 1.08 - 1.01 (m, 3H).
^{13}C NMR (101 MHz, CDCl3) δ 159.7 (d, *J* = 245.0 Hz), 136.2 (d, *J* = 8.6 Hz), 130.7, 127.2 (d, *J* = 15.3 Hz), 124.9 (d, *J* = 3.8 Hz), 117.4, 117.2, 55.8, 55.7, 31.7, 29.0, 29.0, 28.3, 22.7, 22.4, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -109.1.
HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{14}H_{21}FNaO_2S$ 295.1139, found 295.1138.

1-(Heptylsulfonyl)-3,5-dimethylbenzene(49)



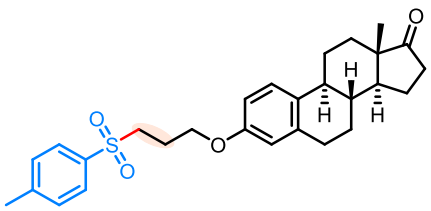
Colorless oil; Yield = 43% (24.3 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 11.2 Hz, 2H), 7.30 - 7.19 (m, 1H), 3.08 - 3.01 (m, 2H), 2.44 - 2.34 (m, 6H), 1.76 - 1.61 (m, 2H), 1.37 - 1.20 (m, 10H), 0.91 - 0.81 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 139.0, 135.4, 125.6, 56.4, 31.8, 29.1, 29.0, 28.4, 22.7, 21.4, 14.2.
HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{26}NaO_2S$ 305.1546, found 305.1546.

(Octylsulfonyl)cyclopropane (50)



Grass green oily substance; Yield = 44% (19.2 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10 - 2.86 (m, 2H), 2.38 - 2.30 (m, 1H), 1.87 - 1.80 (m, 2H), 1.44 - 1.35 (m, 2H), 1.31 - 1.15 (m, 10H), 1.03 - 0.94 (m, 2H), 0.85 (dt, *J* = 9.0, 5.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 54.0, 31.8, 29.2, 29.1, 29.0, 28.6, 22.7, 22.3, 14.2, 4.6.
HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{11}H_{22}NaO_2S$ 241.1233, found 241.1233.

(8R,9S,13S,14S)-13-Methyl-3-(3-tosylpropoxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (51)



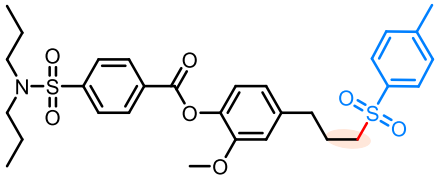
Colorless oil; Yield = 43% (40.2 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 - 7.77 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.63 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 3.98 (t, *J* = 6.0 Hz, 2H), 3.34 - 3.23 (m, 2H), 2.87 - 2.85 (m, 2H), 2.49 - 2.47 (m, 1H), 2.45 (s, 3H), 2.49 - 2.36 (m, 1H), 2.25 - 2.22 (m, 1H), 2.21 - 2.10 (m, 3H), 2.08 - 2.02 (m, 1H), 2.03 - 1.99 (m, 1H), 1.97 - 1.91 (m, 1H), 1.64 - 1.59 (m, 1H), 1.59 - 1.54 (m, 1H), 1.51 - 1.45 (m, 2H), 1.46 - 1.37 (m, 1H), 1.34 - 1.21 (m, 1H), 0.90 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 221.1, 156.6, 144.9, 138.0, 136.3, 132.7, 130.1, 128.2, 126.6, 114.7, 112.3, 65.7, 53.6, 50.5, 48.1, 44.1, 38.5, 36.0, 31.7, 29.8, 26.7, 26.1, 23.3, 21.8, 21.7, 14.0.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{28}H_{34}NaO_4S$ 489.2071, found 489.2070.

2-Methoxy-4-(3-tosylpropyl)phenyl 4-(N,N-dipropylsulfamoyl)benzoate (52)



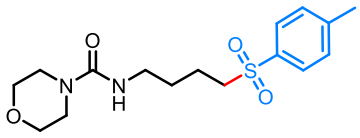
Colorless oil; Yield = 30% (35.3 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.85 - 6.60 (m, 2H), 3.78 (s, 3H), 3.23 - 2.99 (m, 6H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 2.17 - 1.97 (m, 2H), 1.61 - 1.54 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ163.6, 151.1, 144.9, 139.5, 138.2, 136.2, 132.8, 131.0, 130.1, 128.2, 127.2, 122.8, 120.7, 112.7, 56.0, 55.5, 50.1, 34.2, 24.4, 22.1, 21.8, 11.3, 1.1.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{30}H_{37}NNaO_7S_2$ 610.1904, found 610.1904.

N-(4-tosylbutyl)morpholine-4-carboxamide (53)



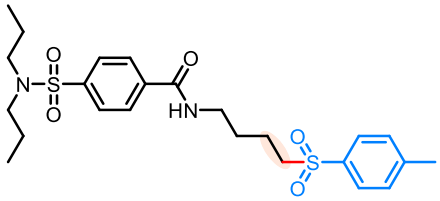
Grey Solid; Yield = 75% (51.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 5.76 (s, 1H), 4.05 - 3.86 (m, 2H), 3.37 (dt, *J* = 11.7, 5.8 Hz, 2H), 3.22 (q, *J* = 6.5 Hz, 2H), 3.09 (t, *J* = 7.7 Hz, 2H), 2.44 (s, 3H), 1.85 - 1.57 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 145.0, 136.1, 130.1, 128.1, 67.3, 55.8, 42.3, 38.5, 29.3, 28.3, 21.7, 20.1.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{16}H_{24}N_2O_4S$ 362.1396, found 362.1397.

4-(N,N-dipropylsulfamoyl)-N-(4-tosylbutyl)benzamide (54)



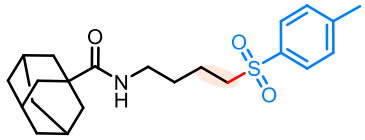
Grass green oily substance; Yield = 99% (98.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.74 (dd, *J* = 11.9, 8.1 Hz, 4H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.92 (t, *J* = 5.8 Hz, 1H), 3.40 (q, *J* = 6.3 Hz, 2H), 3.07 (dt, *J* = 15.7, 7.5 Hz, 6H), 2.42 (s, 3H), 1.80 - 7.70 (m, 4H), 1.56 – 1.46 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ166.4, 144.9, 142.5, 138.1, 135.9, 130.0, 128.0, 127.8, 127.1, 55.7, 50.0, 39.3, 27.9, 21.9, 21.7, 20.1, 11.2

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{34}N_2NaO_5S_2$ 517.1800, found 517.1801.

N-(4-tosylbutyl)adamantane-1-carboxamide (55)



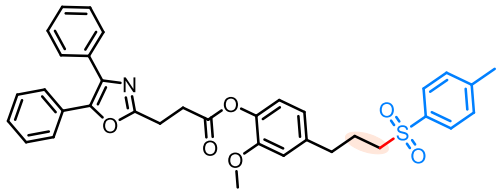
Grey oil; Yield = 56% (43.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 5.72 (s, 1H), 3.19 (q, *J* = 6.5 Hz, 2H), 3.13 - 3.03 (m, 2H), 2.42 (s, 3H), 2.03 - 1.96 (m, 3H), 1.76 (d, *J* = 2.9 Hz, 6H), 1.74 - 1.55 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ178.2, 144.7, 136.0, 129.9, 128.1, 55.7, 40.6, 39.2, 38.2, 36.5, 28.2, 28.1, 21.6, 20.0.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{22}H_{31}NNaO_3S$ 412.1919, found 412.1917.

2-Methoxy-4-(3-tosylpropyl)phenyl 3-(4,5-diphenyloxazol-2-yl)propanoate (56)



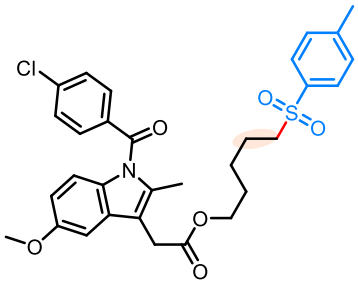
Colorless soild; Yield = 32% (38.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.41 - 7.30 (m, 8H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.75 - 6.58 (m, 2H), 3.73 (s, 3H), 3.31 (t, *J* = 7.4 Hz, 2H), 3.19 (t, *J* = 7.4 Hz, 2H), 3.13 - 2.99 (m, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 2.03 (p, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ170.4, 161.7, 151.1, 145.6, 144.8, 139.1, 138.2, 136.2, 135.3, 132.5, 130.1, 129.1, 128.8, 128.7, 128.6, 128.2, 128.2, 128.0, 126.6, 122.8, 120.5, 112.6, 55.9, 55.5, 34.1, 31.0, 24.4, 23.7, 21.7.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{35}H_{33}NNaO_6S$ 618.1923, found 618.1921.

5-Tosylpentyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (57)



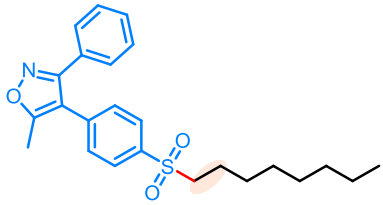
White solid; Yield = 59% (37.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.71 - 7.61 (m, 2H), 7.51 - 7.43 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 2.6 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.05 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H), 3.63 (s, 2H), 3.04 - 2.90 (m, 2H), 2.44 (s, 3H), 2.37 (s, 3H), 1.72 - 1.56 (m, 5H), 1.38 - 1.31 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 168.4, 156.1, 144.8, 139.4, 136.3, 136.1, 134.0, 131.3, 130.9, 130.7, 130.0, 129.3, 128.2, 115.1, 112.7, 111.5, 101.6, 64.5, 56.2, 55.8, 30.5, 28.2, 24.9, 22.5, 21.8, 13.5.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{17}H_{28}NaO_2S$ 319.1701, found 319.1702.

5-Methyl-4-(4-(octylsulfonyl)phenyl)-3-phenylisoxazole (58)



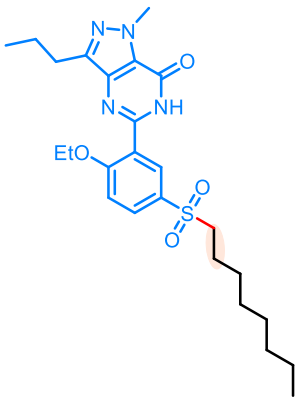
White solid; Yield = 63% (52 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.46 – 7.28 (m, 7H), 3.41 - 2.80 (m, 2H), 2.49 (s, 3H), 1.74 (p, *J* = 7.6 Hz, 2H), 1.37 (p, *J* = 7.1 Hz, 2H), 1.25 (d, *J* = 11.4 Hz, 8H), 0.85 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 161.2, 138.4, 136.3, 130.5, 129.9, 128.8, 128.5, 128.5, 114.5, 56.3, 31.7, 29.1, 29.0, 28.3, 22.6, 22.6, 14.1, 11.9.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{29}NNaO_3S$ 434.1760, found 434.1760.

5-(2-Ethoxy-5-((octylsulfonyl)methyl)phenyl)-1-methyl-3-propyl-1H-pyrazolo[4,3-d]pyrimidine (59)



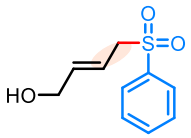
White solid; Yield = 74% (72.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.93 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.7 Hz, 1H), 4.39 - 4.36 (m, 2H), 4.27 (d, *J* = 2.7 Hz, 3H), 3.27 - 3.05 (m, 2H), 2.96 - 2.91(m, 2H), 1.86 - 1.84 (m, 2H), 1.75 - 1.73 (m, 2H), 1.49 - 1.11 (m, 13H), 1.03 (td, *J* = 7.5, 2.8 Hz, 3H), 0.84 (td, *J* = 7.0, 2.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 153.8, 147.2, 146.5, 138.4, 132.6, 132.2, 131.8, 124.6, 121.5, 113.3, 66.3, 56.6, 38.4, 31.8, 29.1, 29.0, 28.4, 27.7, 22.9, 22.7, 22.5, 14.7, 14.2.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{25}H_{36}N_4O_4S$ 511.2457, found 511.2349.

(E)-4-(Phenylsulfonyl)but-2-en-1-ol (61)[2]

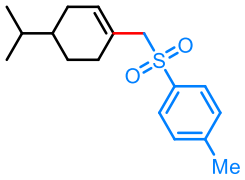


Colorless oil; Yield = 15% (6.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 8.4, 1.2 Hz, 2H), 7.70 - 7.63 (m, 1H), 7.59 - 7.55 (m, 2H), 5.81 - 5.66 (m, 2H), 4.13 (d, *J* = 3.7 Hz, 2H), 3.84 - 3.78 (m, 2H), 1.58 - 1.45 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 134.0, 129.3, 128.6, 117.0, 62.7, 59.7.

1-(((4-Isopropylcyclohex-1-en-1-yl)methyl)sulfonyl)-4-methylbenzene (62)[10]

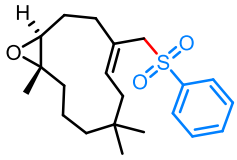


White solid; Yield = 98% (57.3 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.39 (dd, *J* = 4.9, 2.6 Hz, 1H), 3.65 (s, 2H), 2.43 (s, 3H), 2.10 (dd, *J* = 8.3, 4.3 Hz, 2H), 2.01 - 1.90 (m, 1H), 1.75 - 1.61 (m, 2H), 1.47 - 1.36 (m, 1H), 1.22 - 1.08 (m, 2H), 0.91 - 0.78 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.5, 135.8, 132.8, 129.6, 128.6, 126.1, 64.6, 39.3, 32.0, 29.5, 29.4, 26.2, 21.7, 20.0, 19.7.

(1S,11S,Z)-7,7,11-trimethyl-4-((phenylsulfonyl)methyl)-12-oxabicyclo[9.1.0]dodec-4-ene (63)



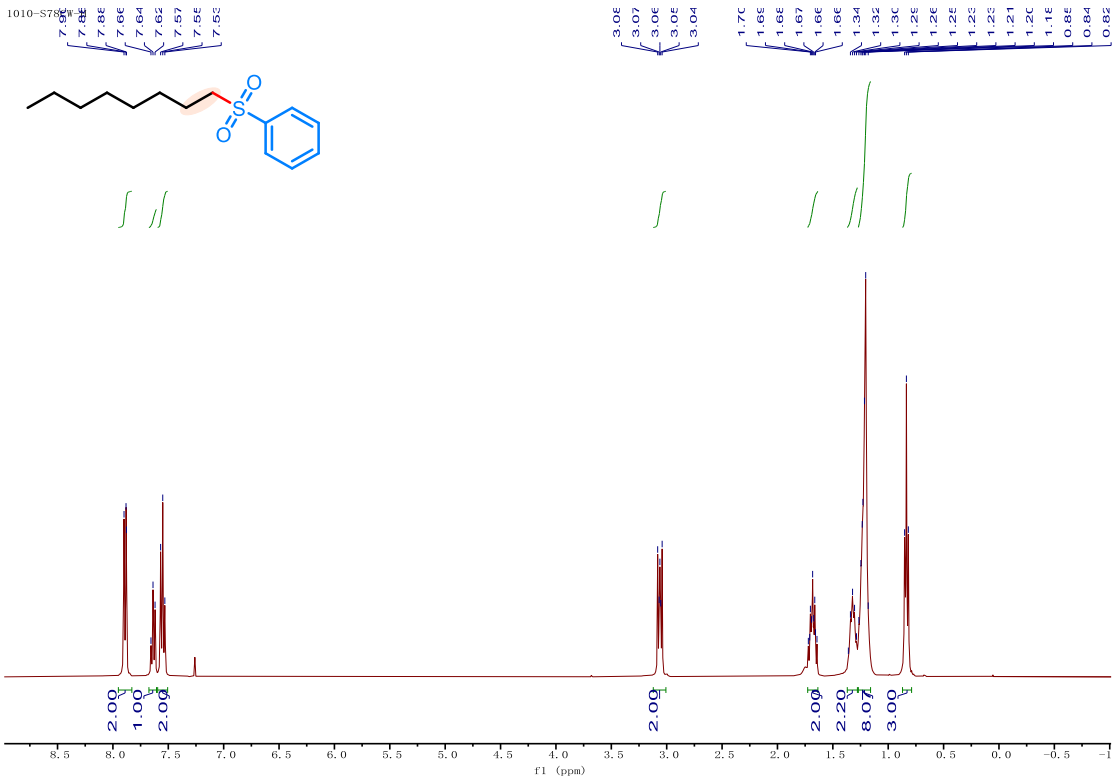
Yellow solid; Yield = 99% (71.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 - 7.79 (m, 2H), 7.67 - 7.59 (m, 1H), 7.59 - 7.50 (m, 2H), 5.53 - 5.50 (m, 1H), 3.94 (dd, *J* = 13.8, 4.4 Hz, 1H), 3.56 (dd, *J* = 14.2, 4.8 Hz, 1H), 2.66 (dt, *J* = 11.2, 2.9 Hz, 1H), 2.53 - 2.40 (m, 1H), 2.19 (tt, *J* = 13.6, 4.9 Hz, 1H), 2.03 - 1.90 (m, 2H), 1.70 - 1.64 (m, 1H), 1.44 - 1.27 (m, 2H), 1.19 - 0.92 (m, 6H), 0.84 - 0.50 (m, 8H).

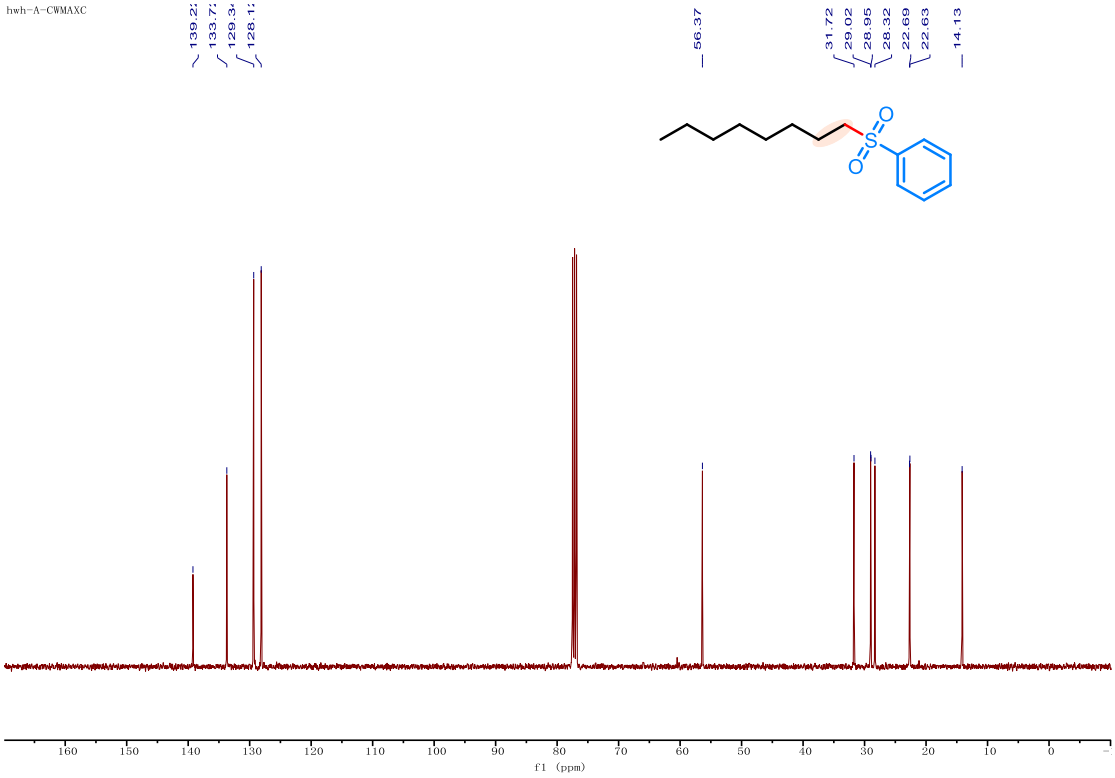
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.14, 134.30, 133.90, 129.22, 128.88, 125.35, 62.51, 62.35, 56.58, 40.57, 38.21, 37.28, 35.05, 32.94, 29.29, 27.94, 24.22, 18.40, 17.74.

4. ^{1}H, ^{13}C and ^{19}F spectra

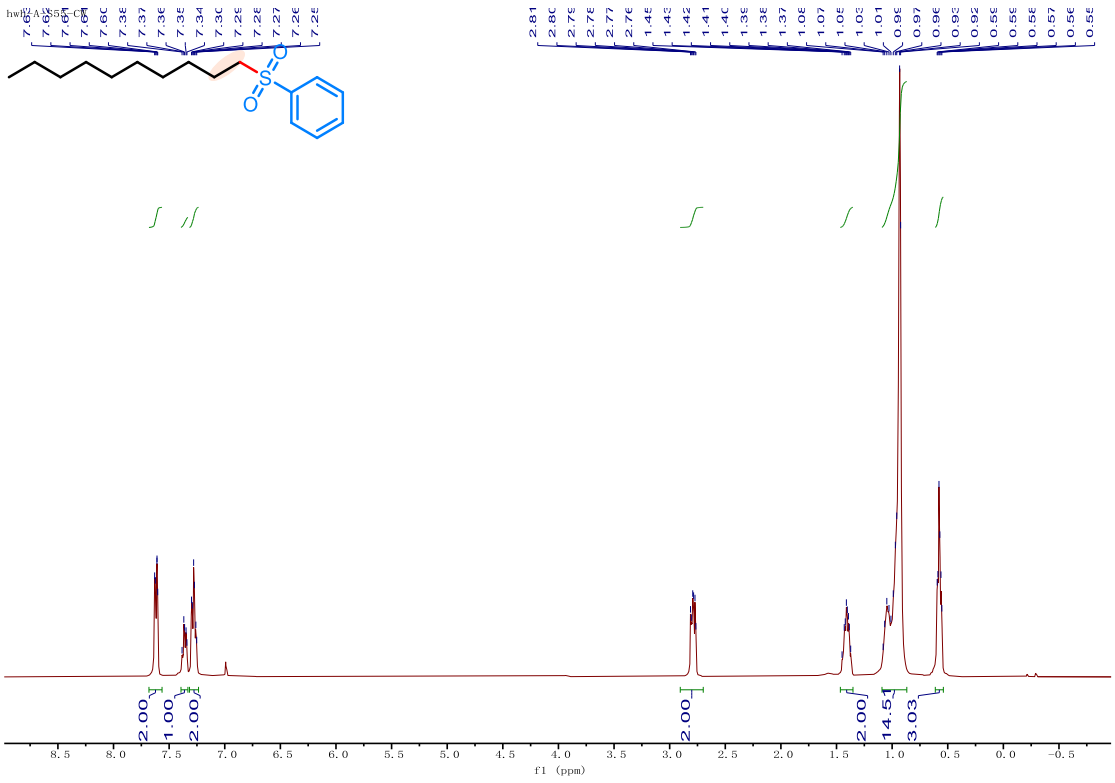
^{1}H NMR Spectrum of 3 ($CDCl_3$ as solvent, 400 MHz)



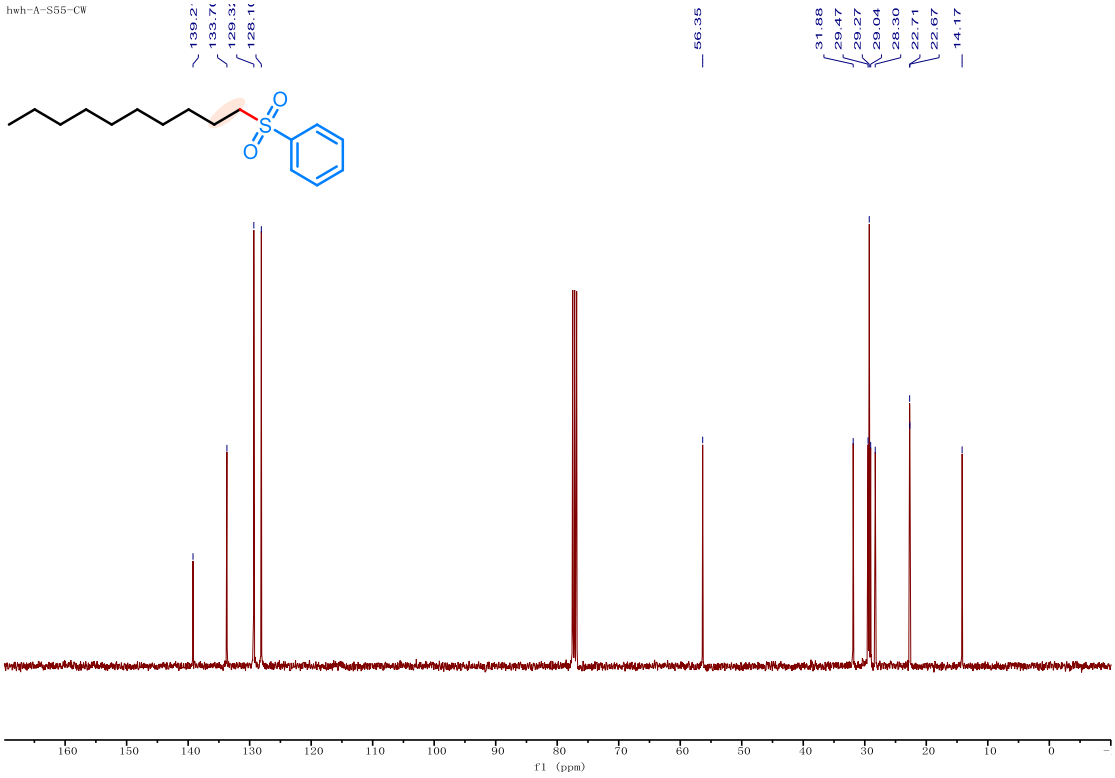
^{13}C {^{1}H} NMR Spectrum of 3 ($CDCl_3$ as solvent, 101 MHz)



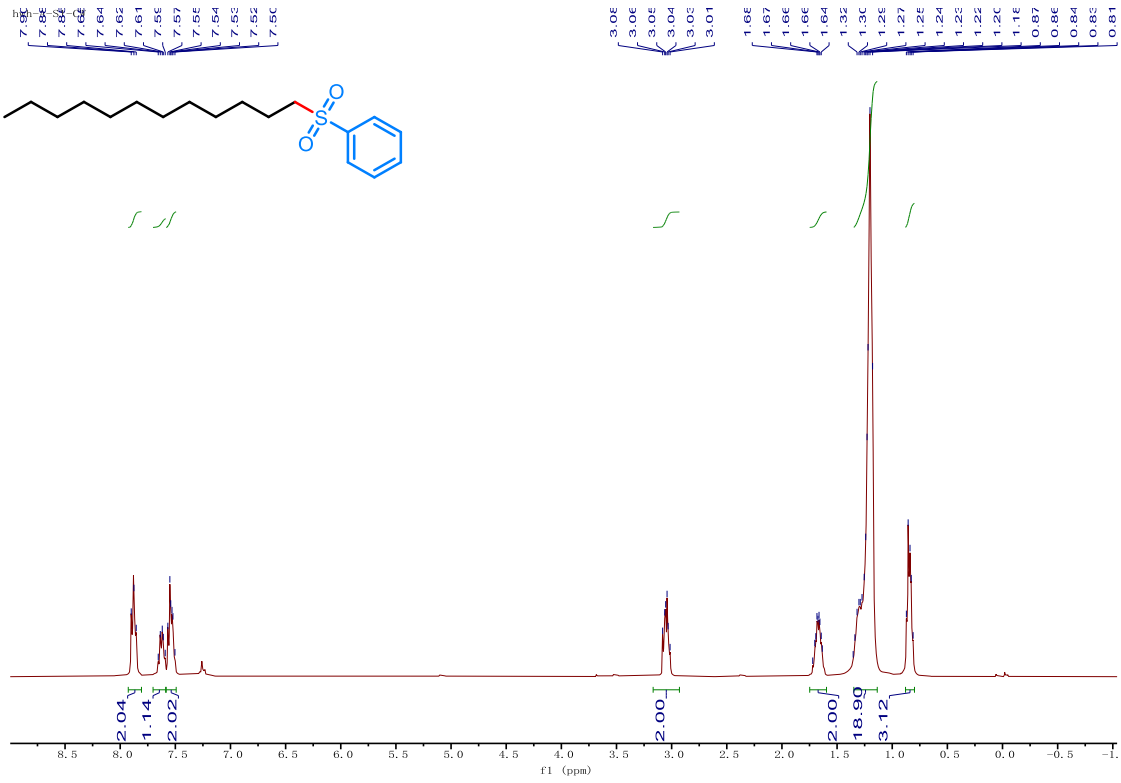
^{1}H NMR Spectrum of 4 ($CDCl_3$ as solvent, 400 MHz)



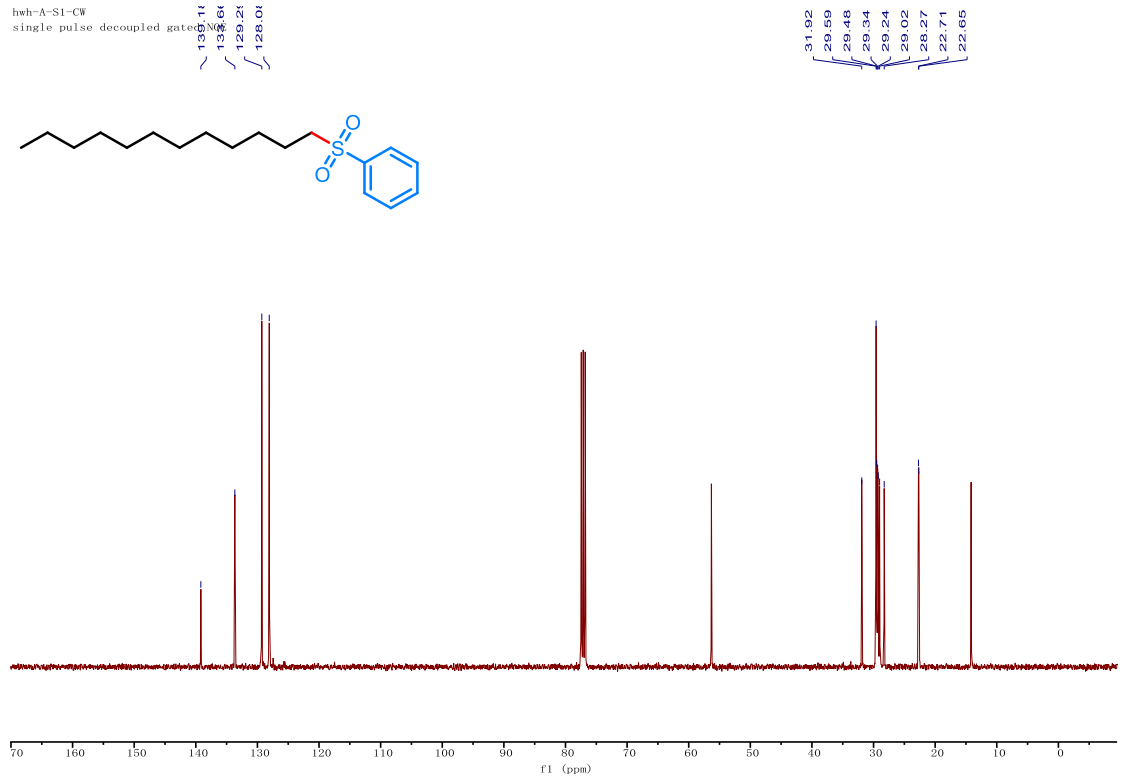
^{13}C {^{1}H} NMR Spectrum of 4 ($CDCl_3$ as solvent, 101 MHz)



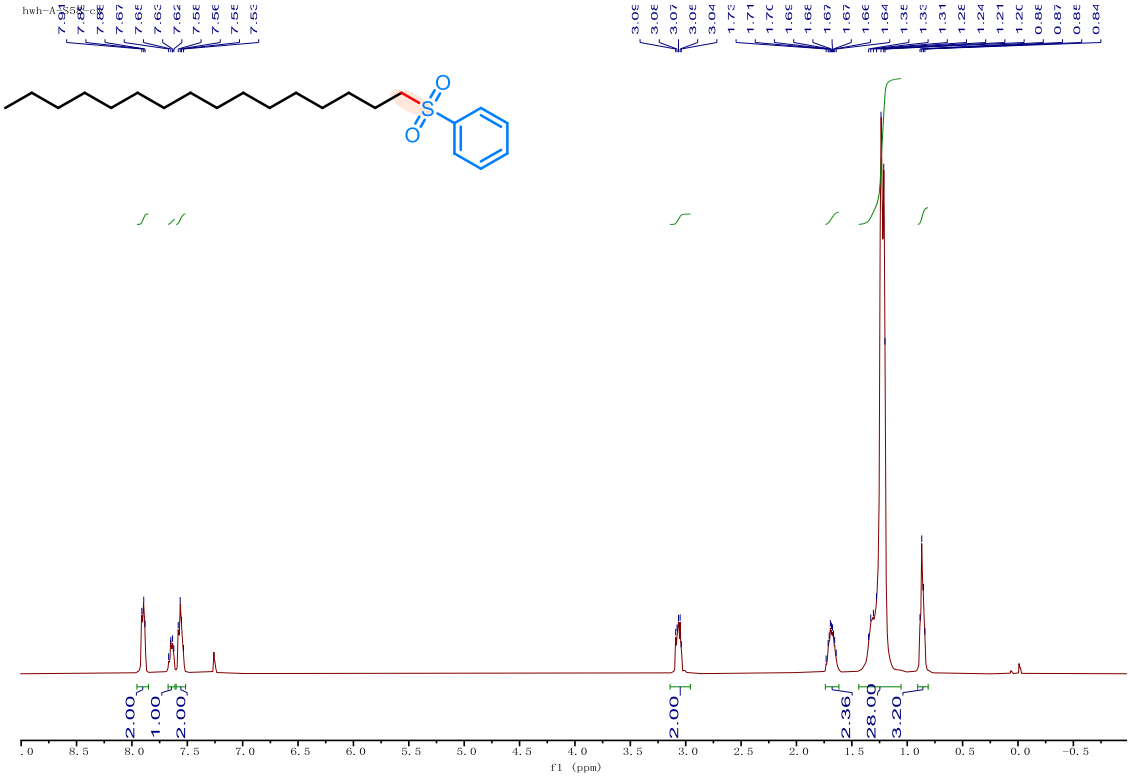
^{1}H NMR Spectrum of 5 ($CDCl_3$ as solvent, 400 MHz)



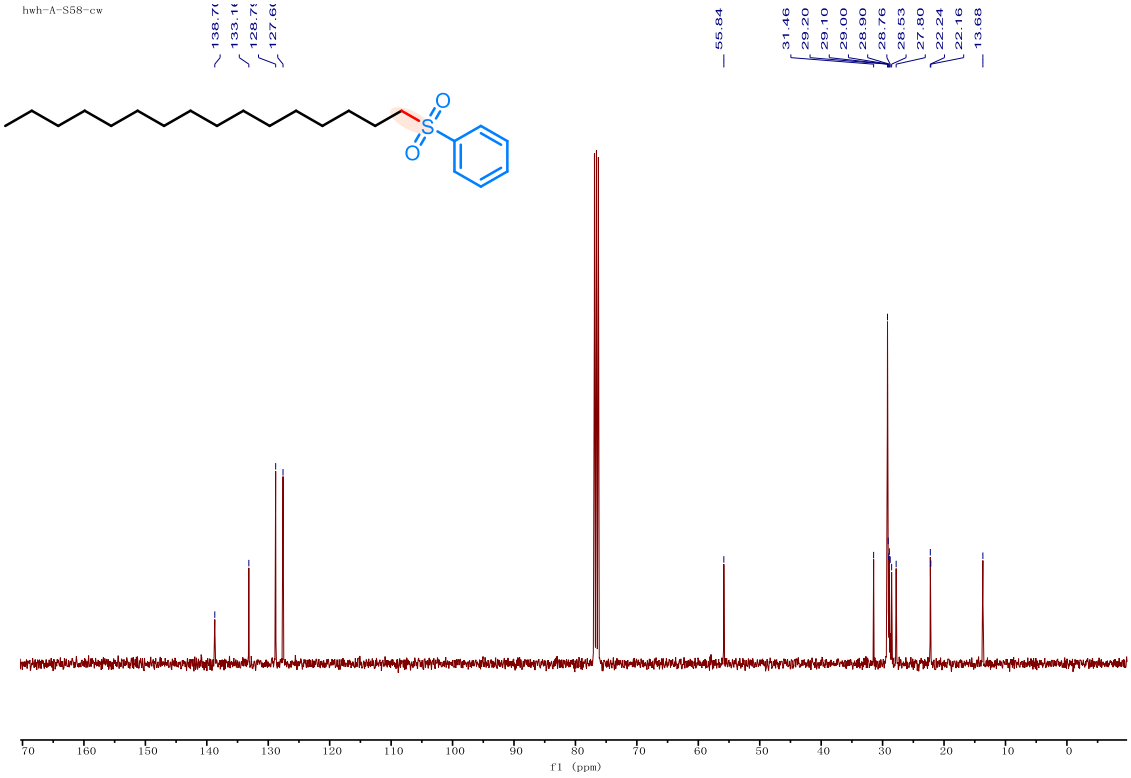
^{13}C {^{1}H} NMR Spectrum of 5 ($CDCl_3$ as solvent, 101 MHz)



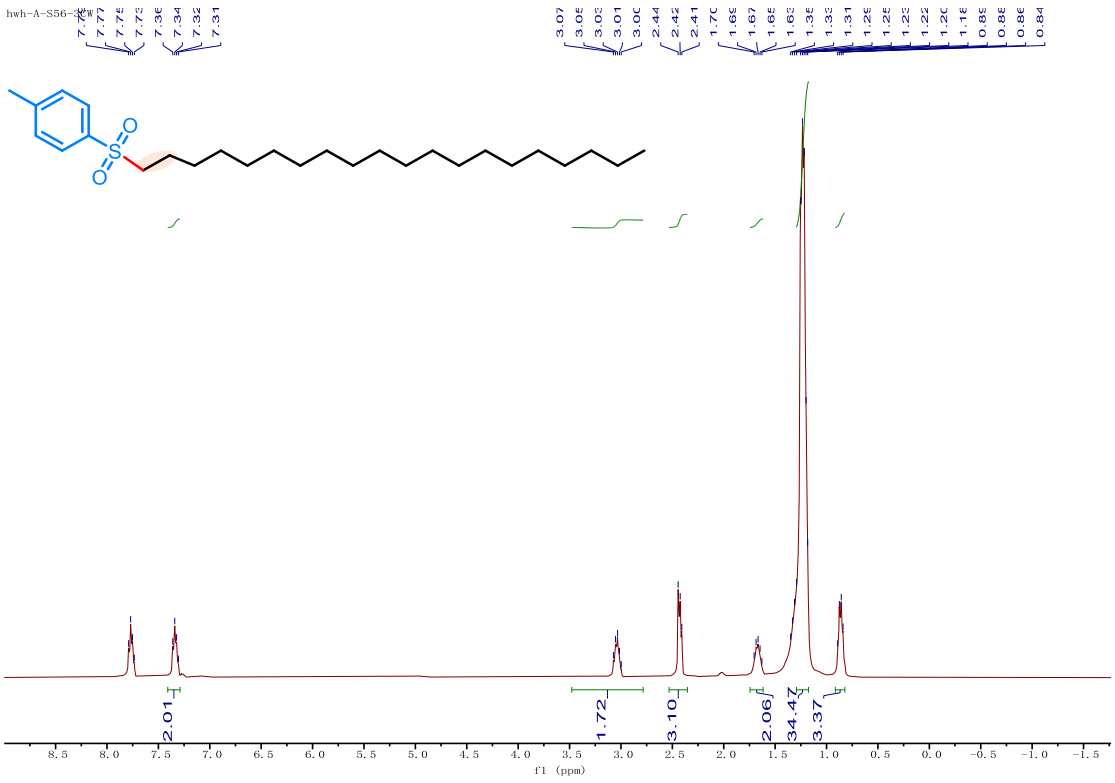
^{1}H NMR Spectrum of 6 ($CDCl_3$ as solvent, 400 MHz)



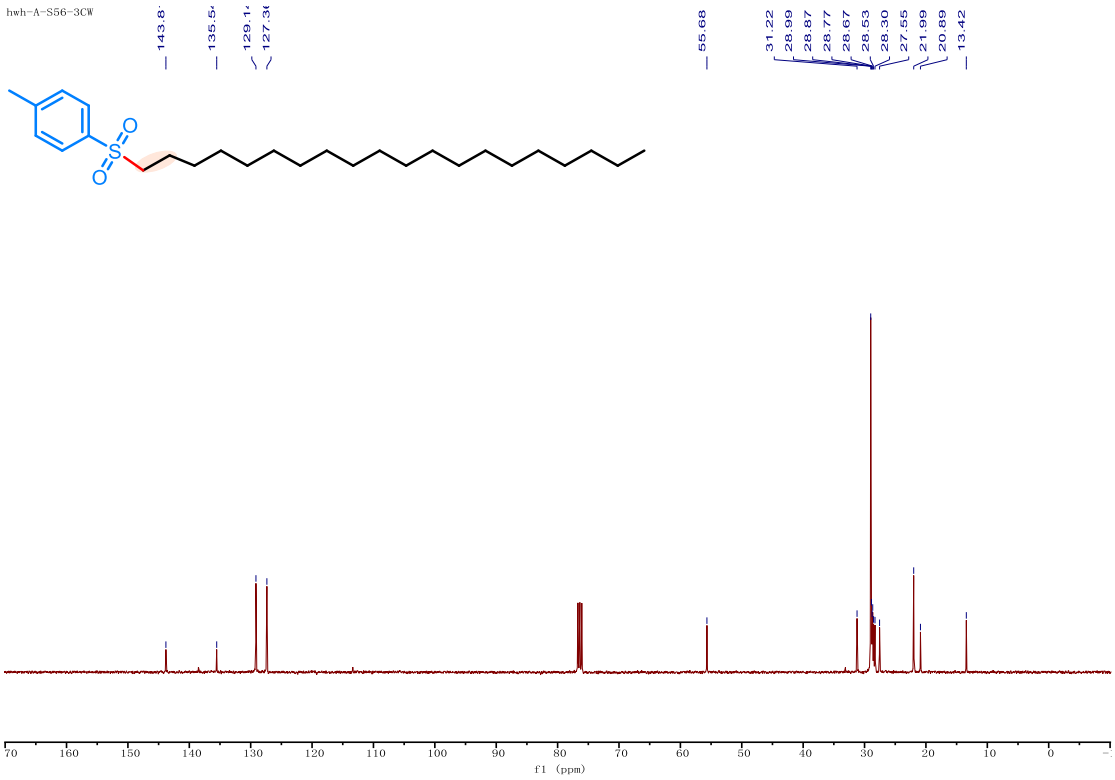
^{13}C {^{1}H} NMR Spectrum of 6 ($CDCl_3$ as solvent, 101 MHz)



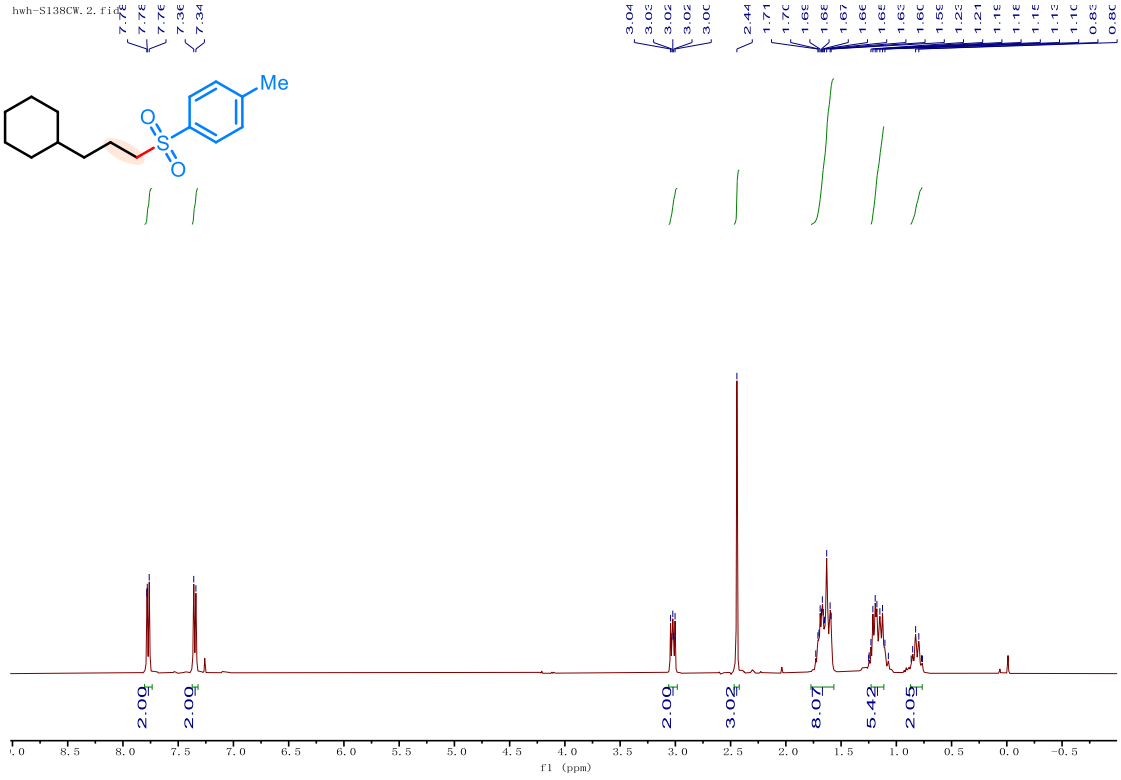
^{1}H NMR Spectrum of 7 ($CDCl_3$ as solvent, 400 MHz)



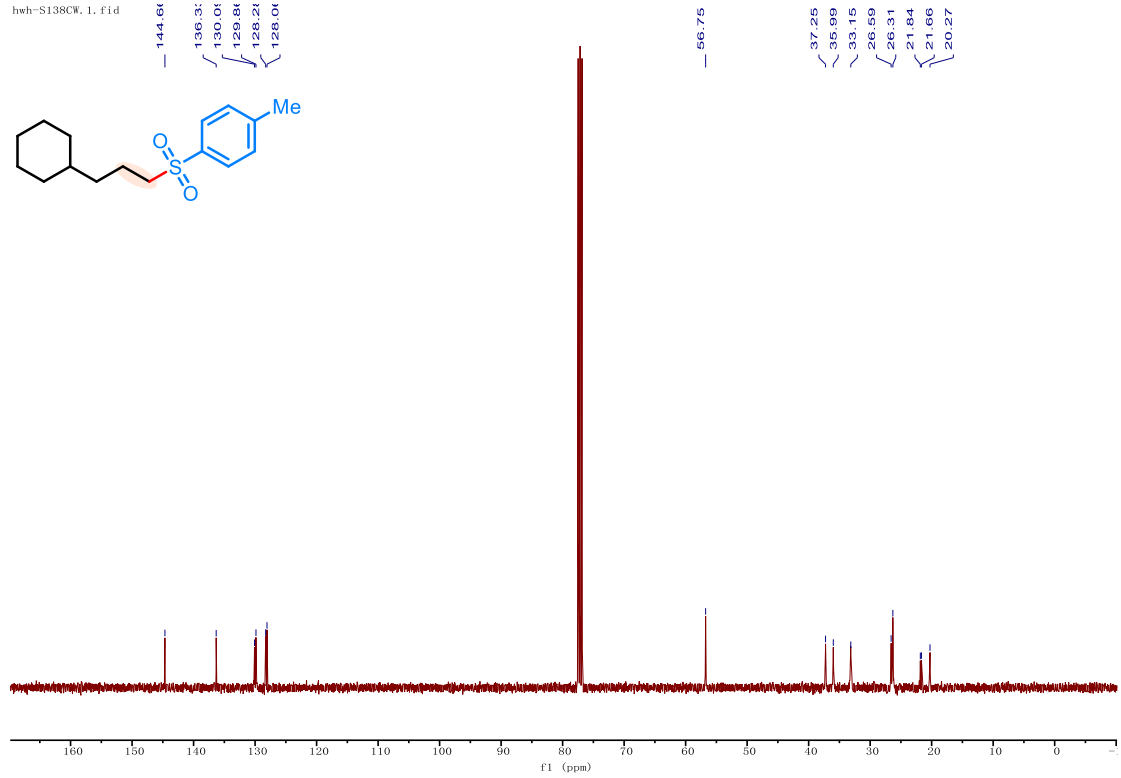
^{13}C {^{1}H} NMR Spectrum of 7 ($CDCl_3$ as solvent, 101 MHz)



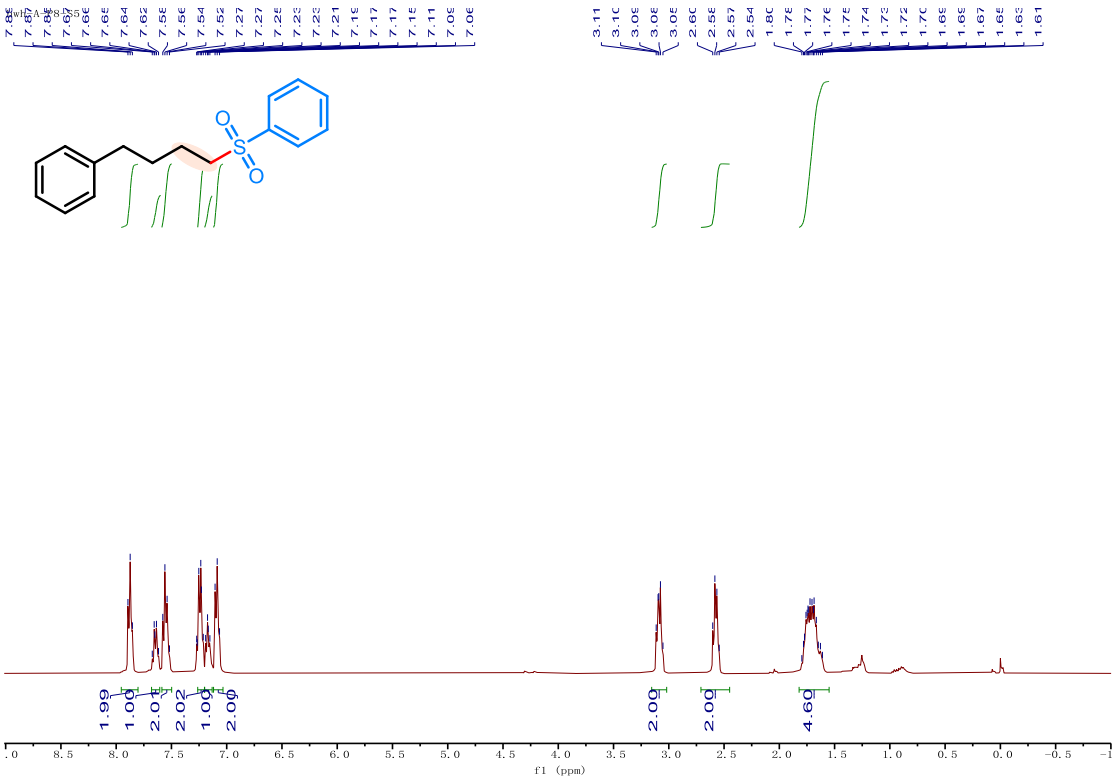
^{1}H NMR Spectrum of 8 ($CDCl_3$ as solvent, 400 MHz)



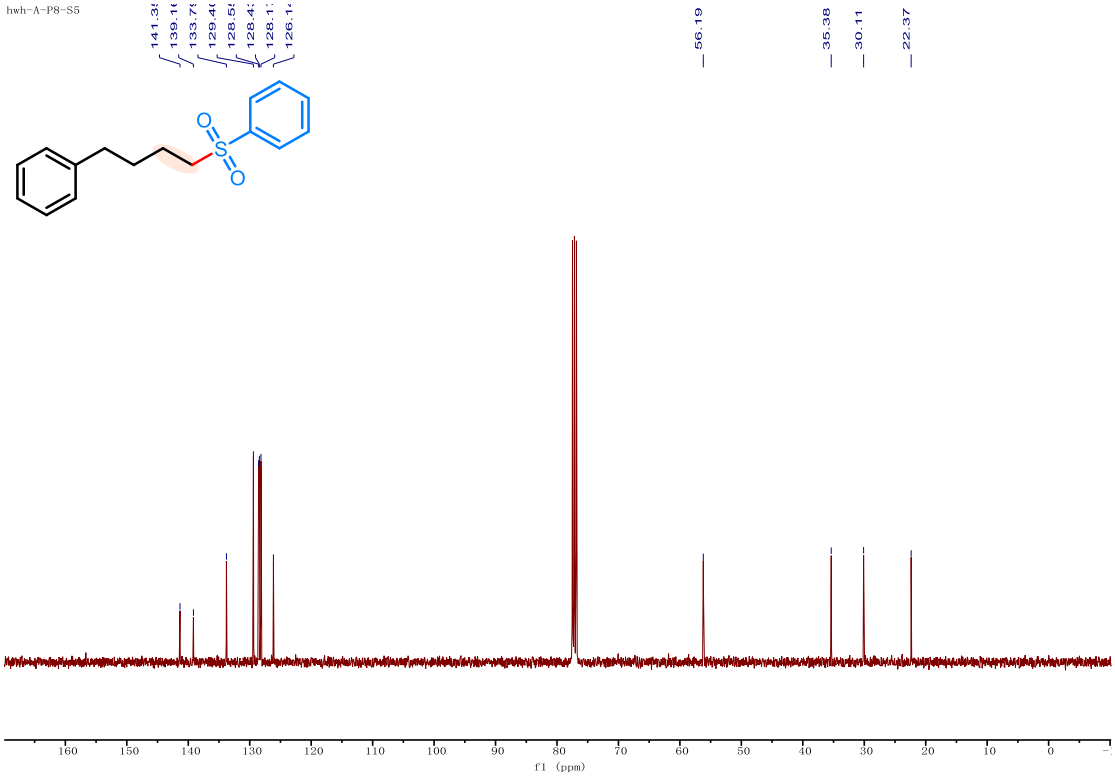
^{13}C {^{1}H} NMR Spectrum of 8 ($CDCl_3$ as solvent, 101 MHz)



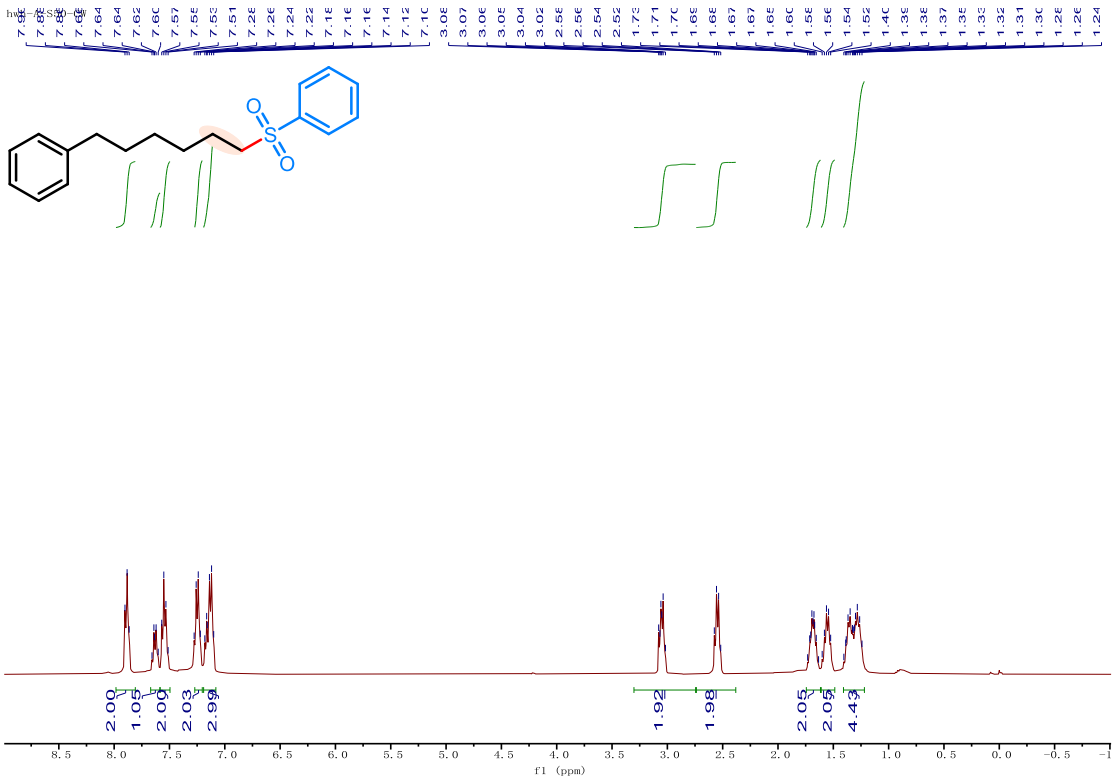
^{1}H NMR Spectrum of 9 ($CDCl_3$ as solvent, 400 MHz)



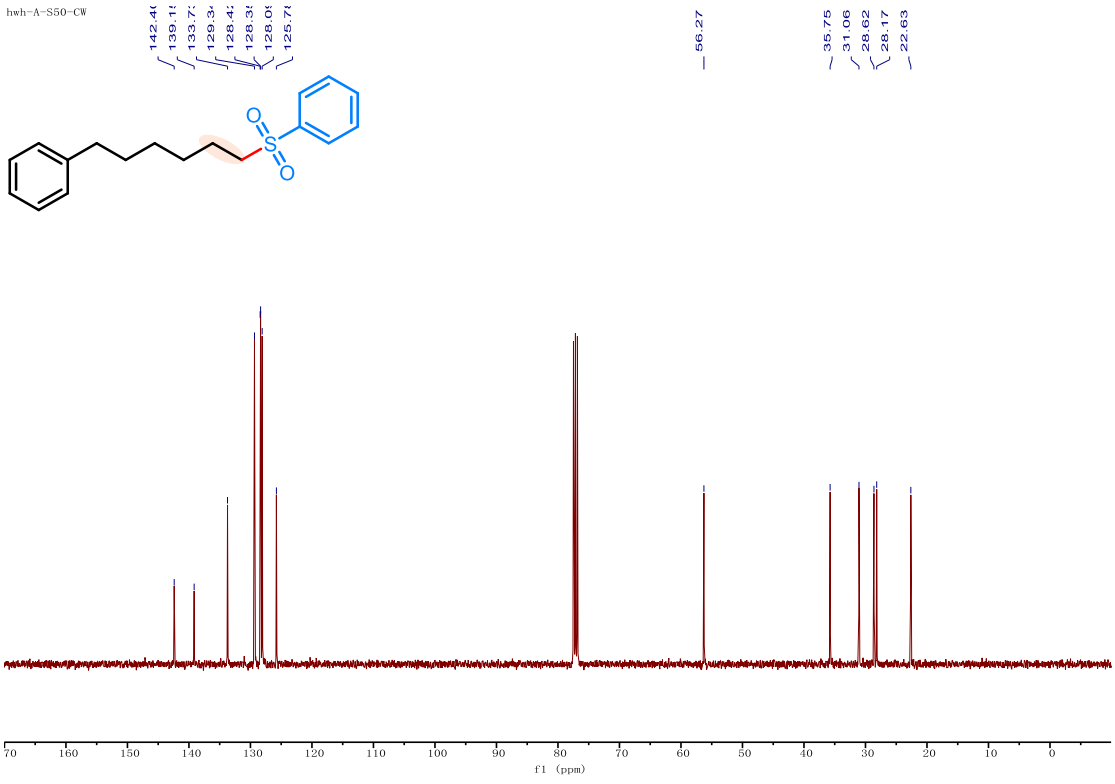
^{13}C {^{1}H} NMR Spectrum of 9 ($CDCl_3$ as solvent, 101 MHz)



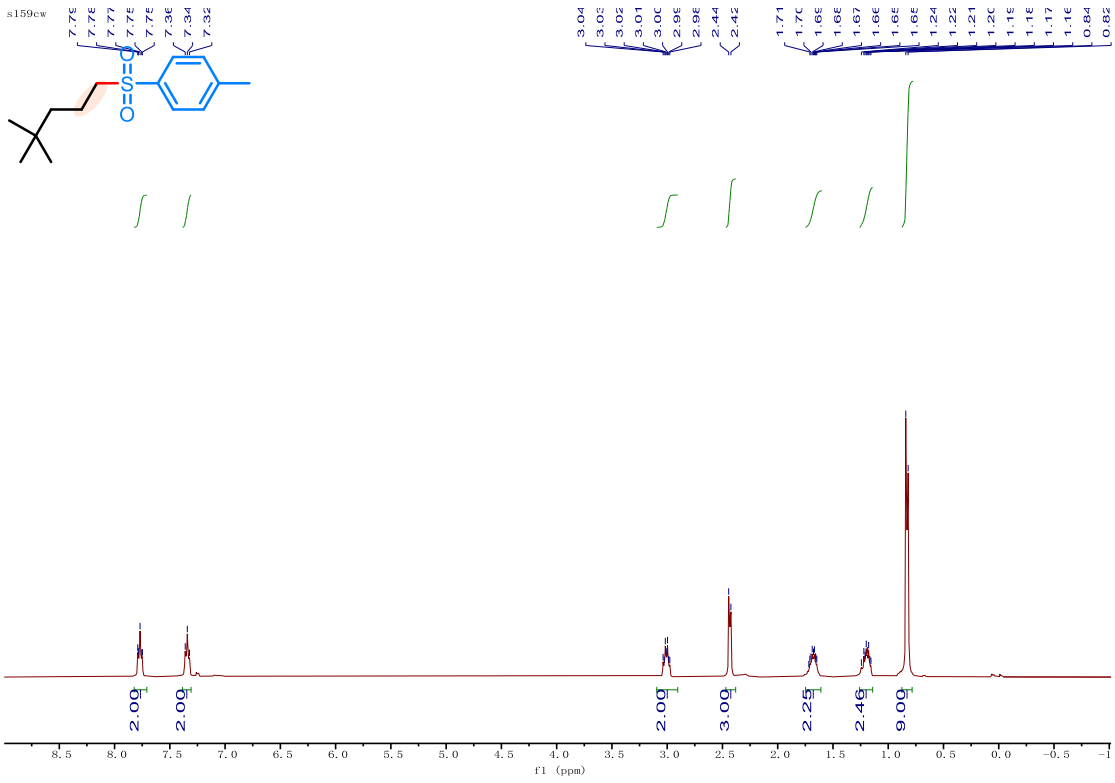
^{1}H NMR Spectrum of 10 ($CDCl_3$ as solvent, 400 MHz)



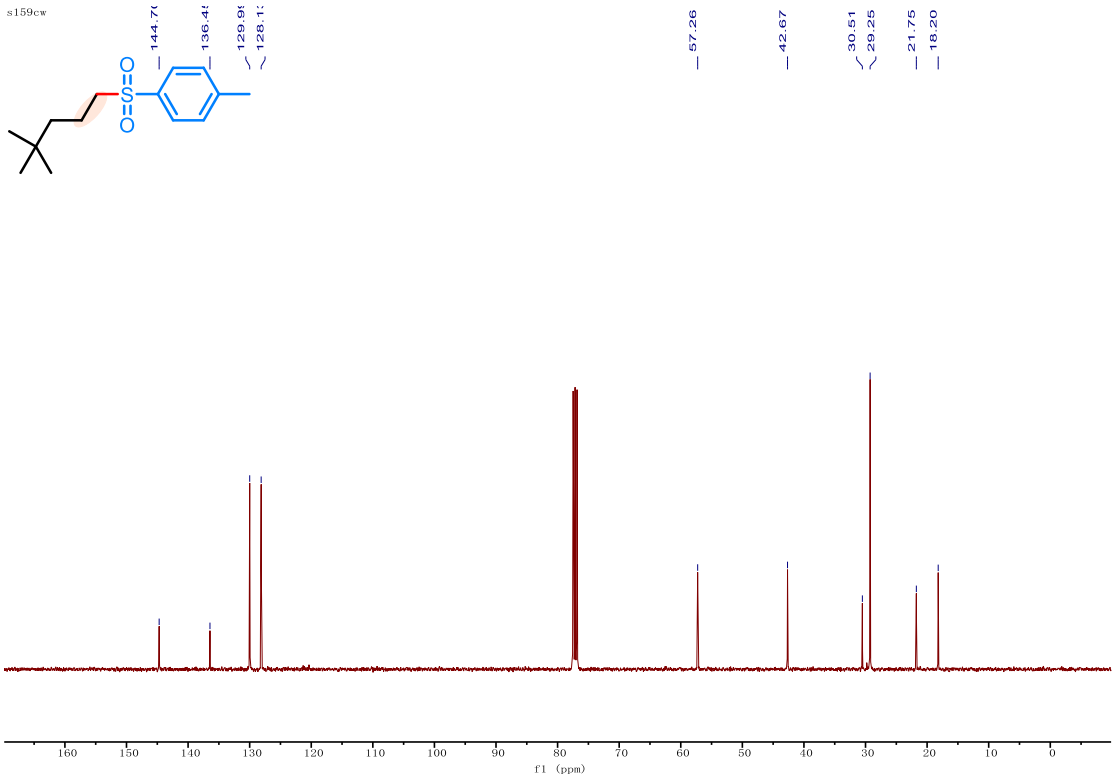
^{13}C {^{1}H} NMR Spectrum of 10 ($CDCl_3$ as solvent, 101 MHz)



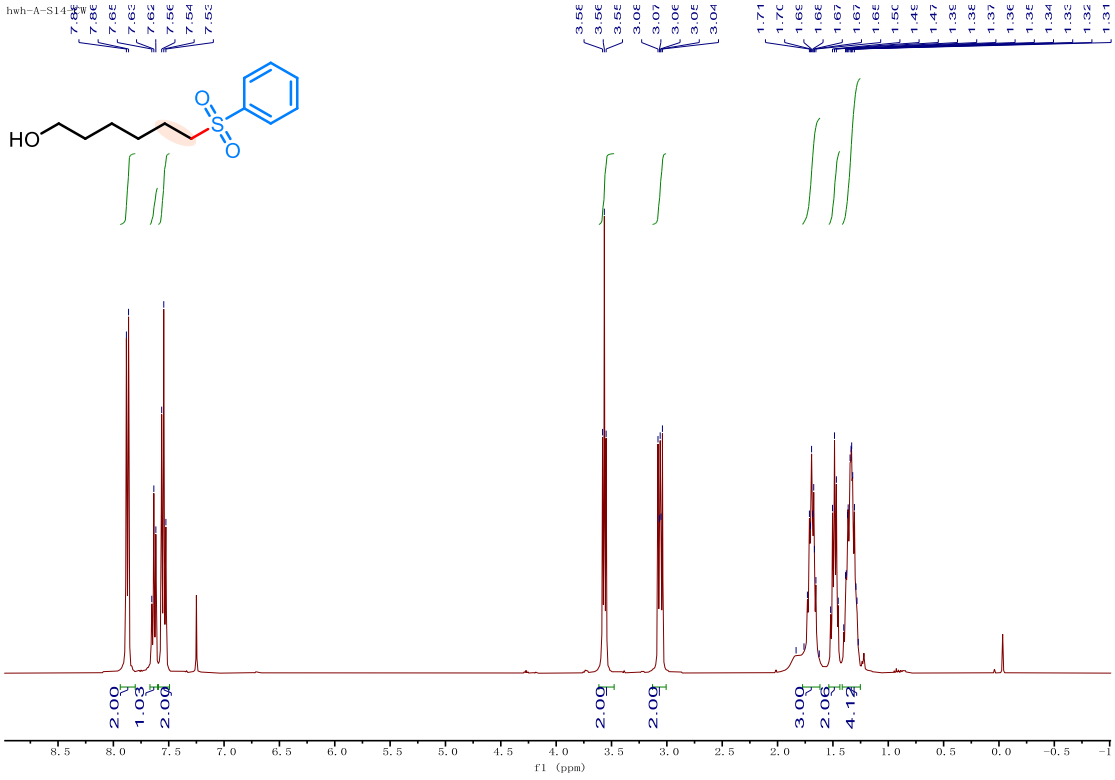
^{1}H NMR Spectrum of 11 ($CDCl_3$ as solvent, 400 MHz)



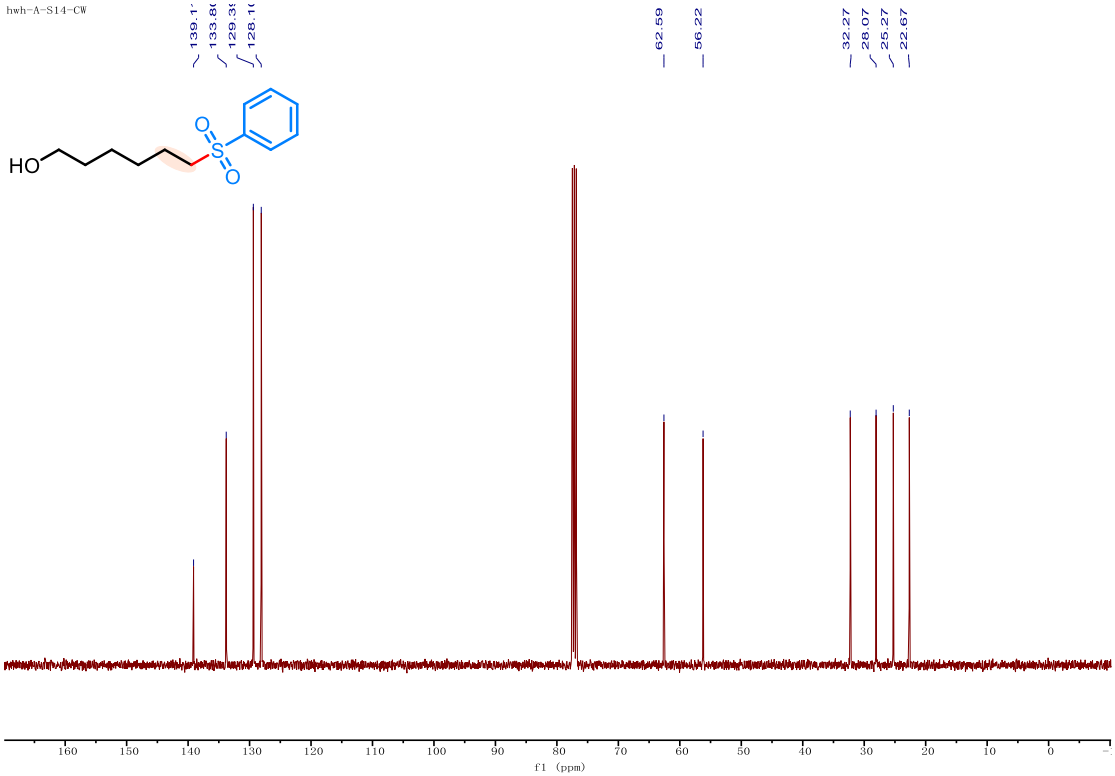
^{13}C {^{1}H} NMR Spectrum of 11 ($CDCl_3$ as solvent, 101 MHz)



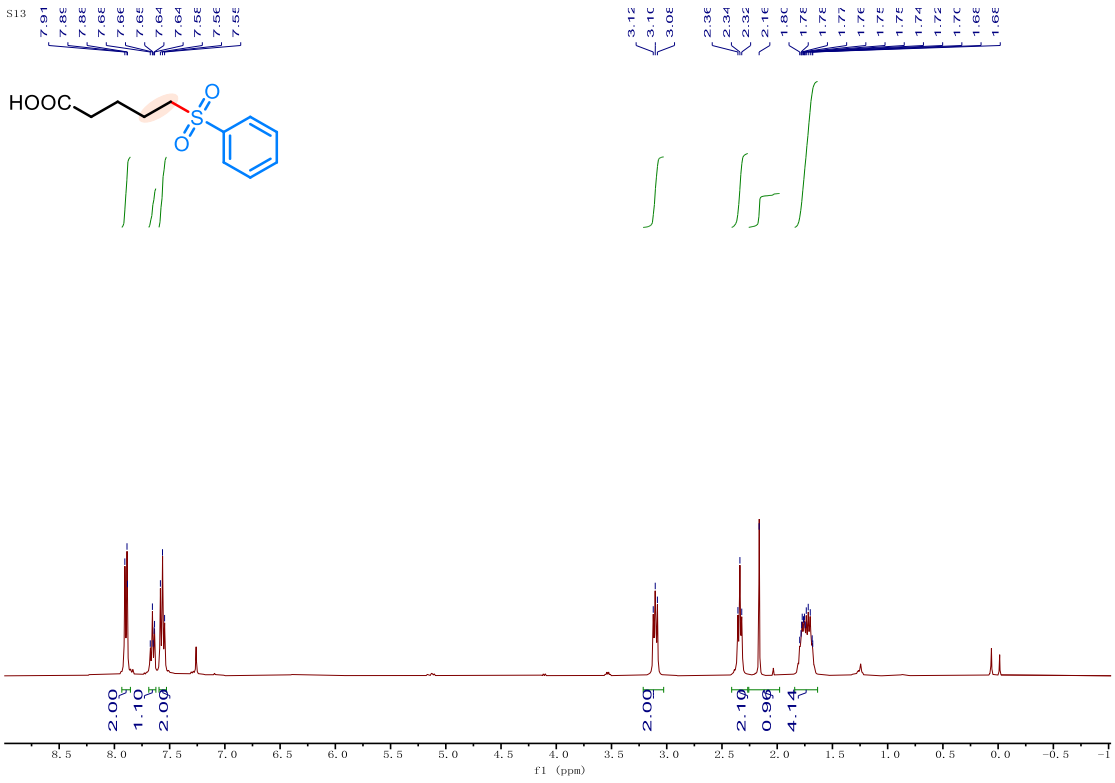
^{1}H NMR Spectrum of 12 ($CDCl_3$ as solvent, 400 MHz)



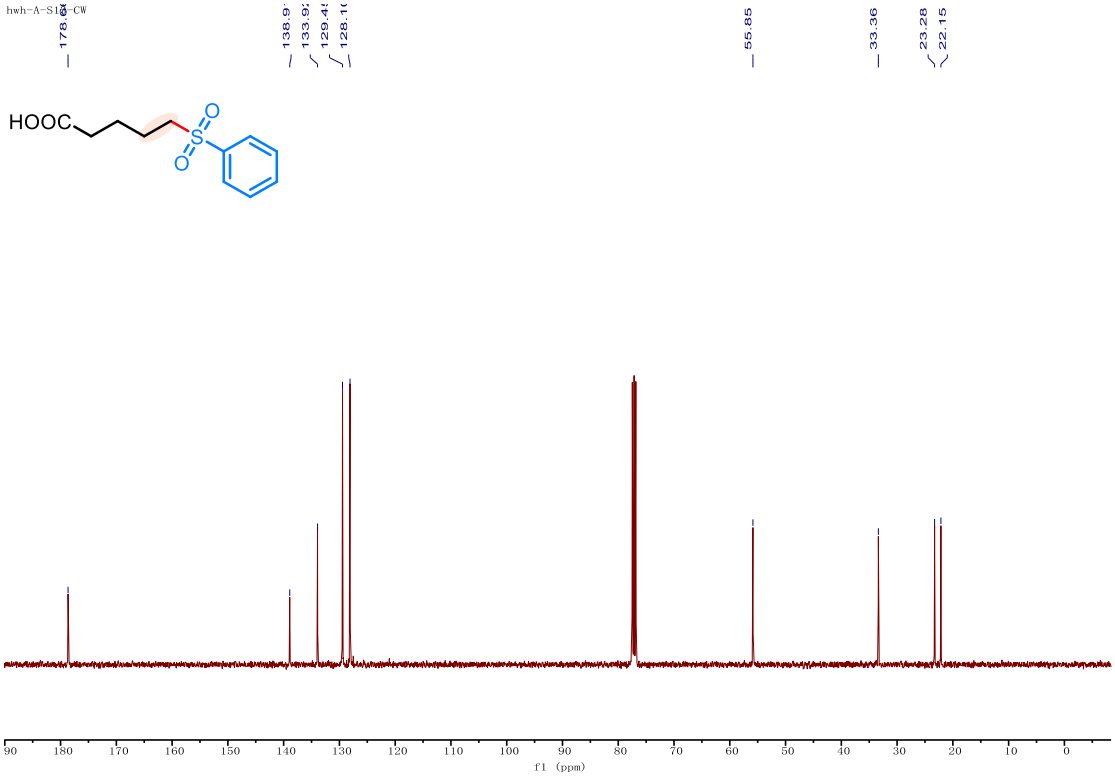
^{13}C {^{1}H} NMR Spectrum of 12 ($CDCl_3$ as solvent, 151 MHz)



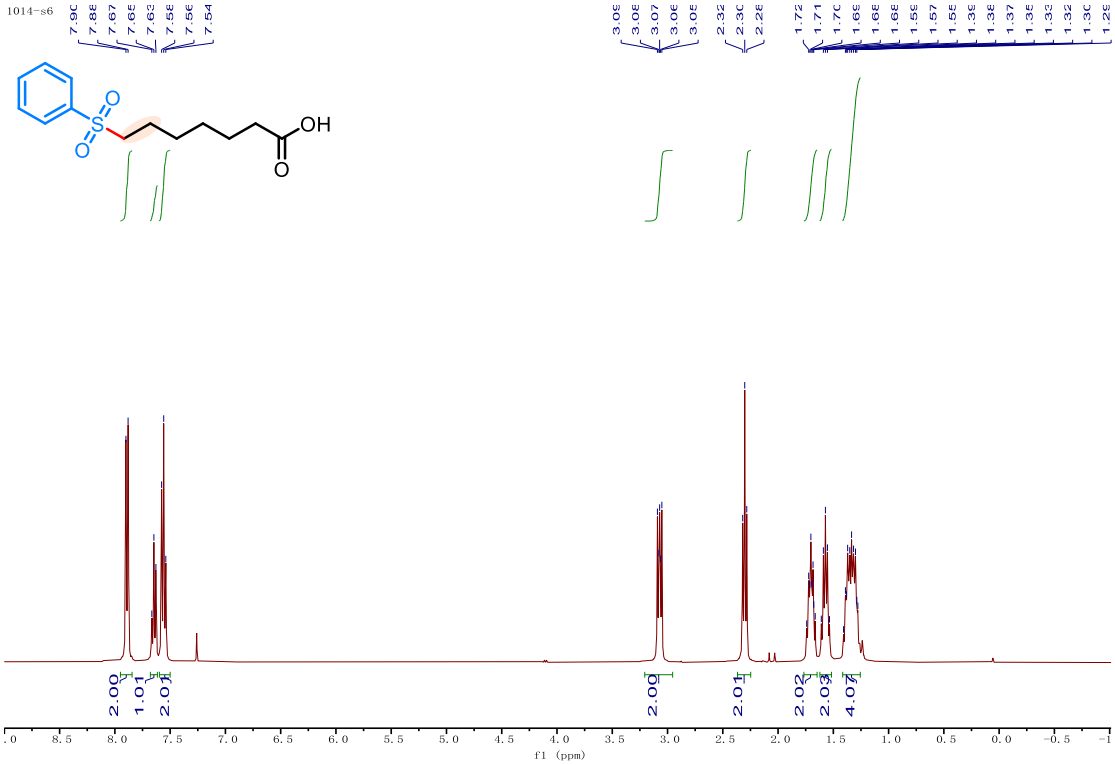
^{1}H NMR Spectrum of 13 ($CDCl_3$ as solvent, 400 MHz)



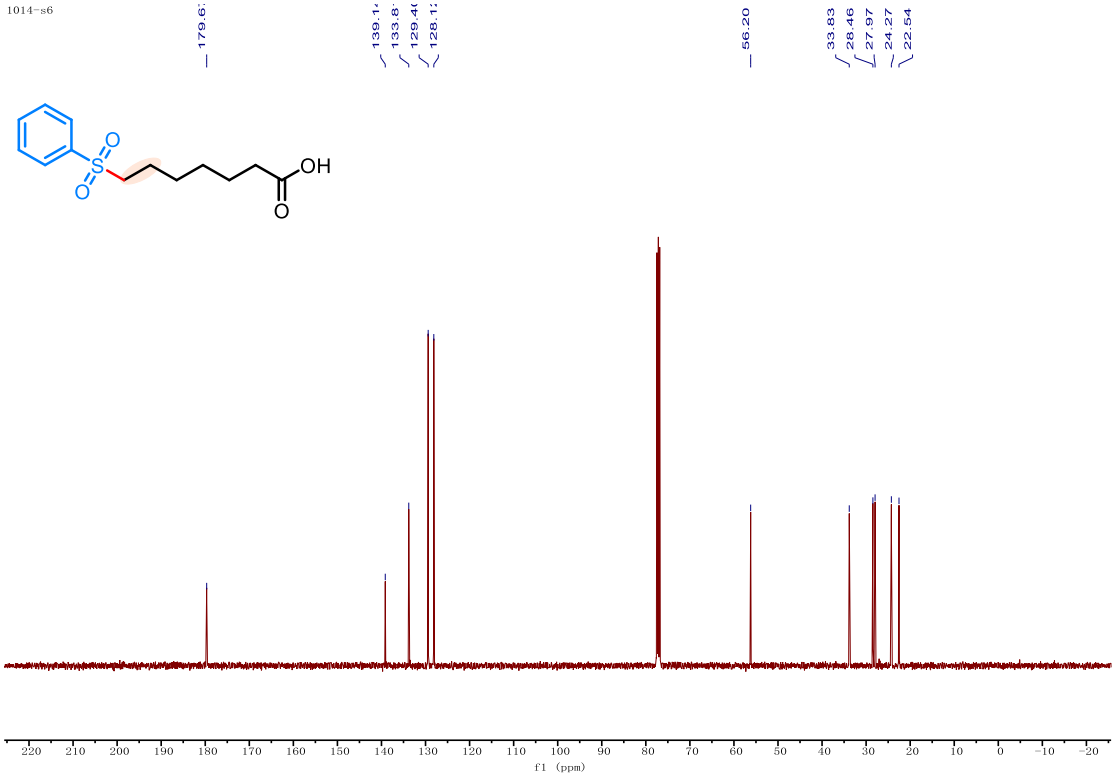
^{13}C {^{1}H} NMR Spectrum of 13 ($CDCl_3$ as solvent, 101 MHz)



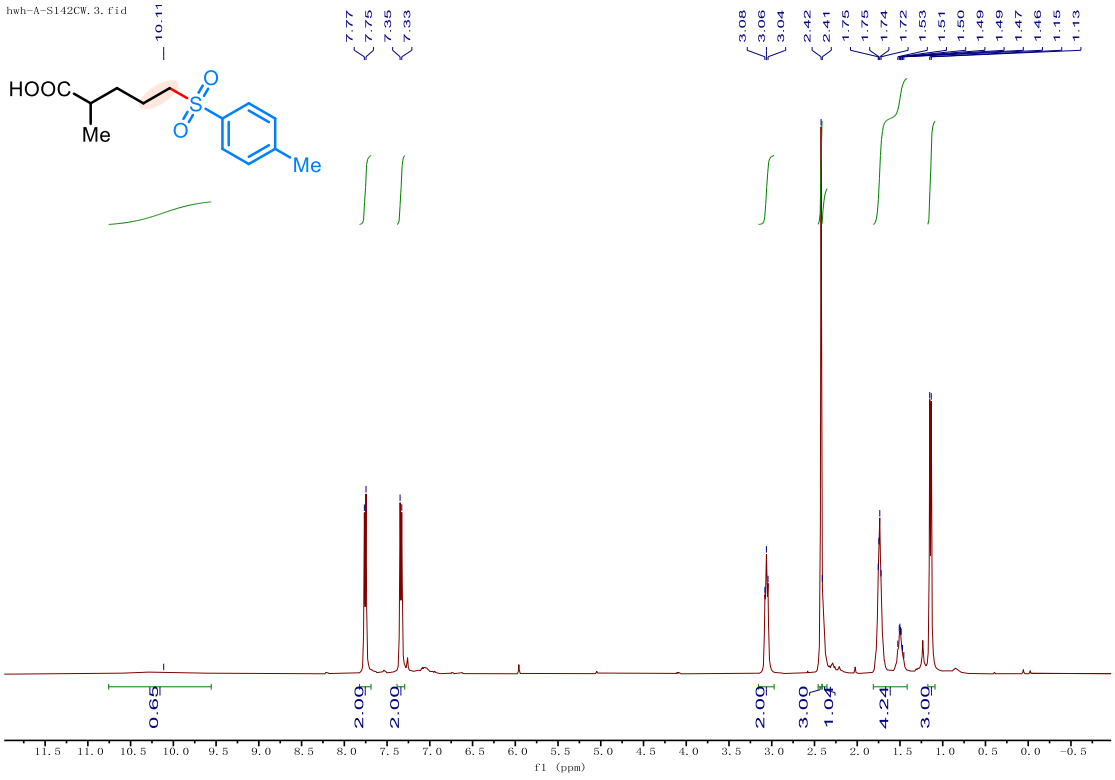
^{1}H NMR Spectrum of 14 ($CDCl_3$ as solvent, 400 MHz)



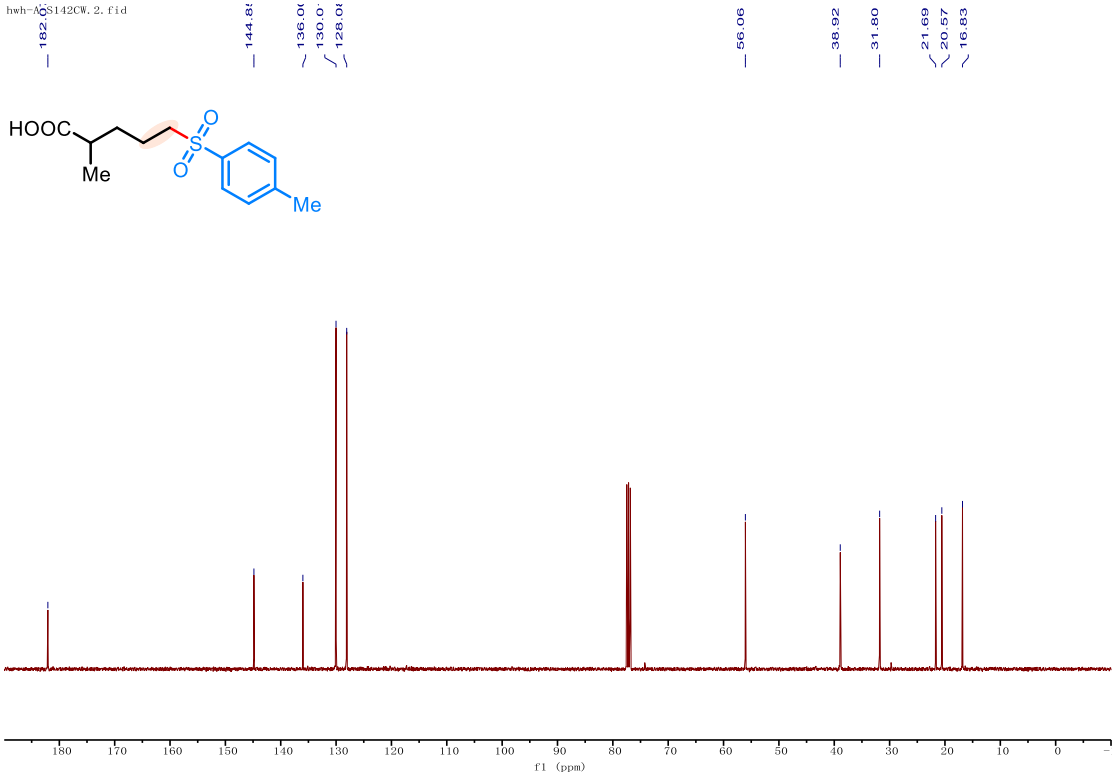
^{13}C {^{1}H} NMR Spectrum of 14 ($CDCl_3$ as solvent, 101 MHz)



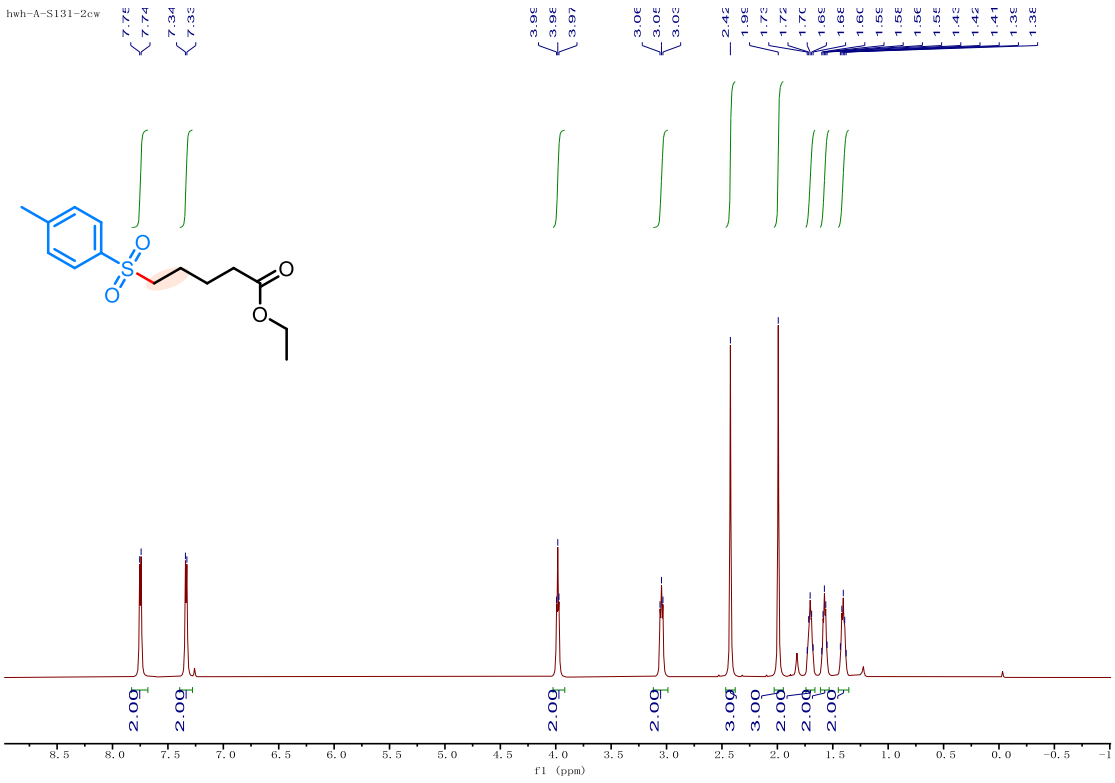
^{1}H NMR Spectrum of 15 ($CDCl_3$ as solvent, 400 MHz)



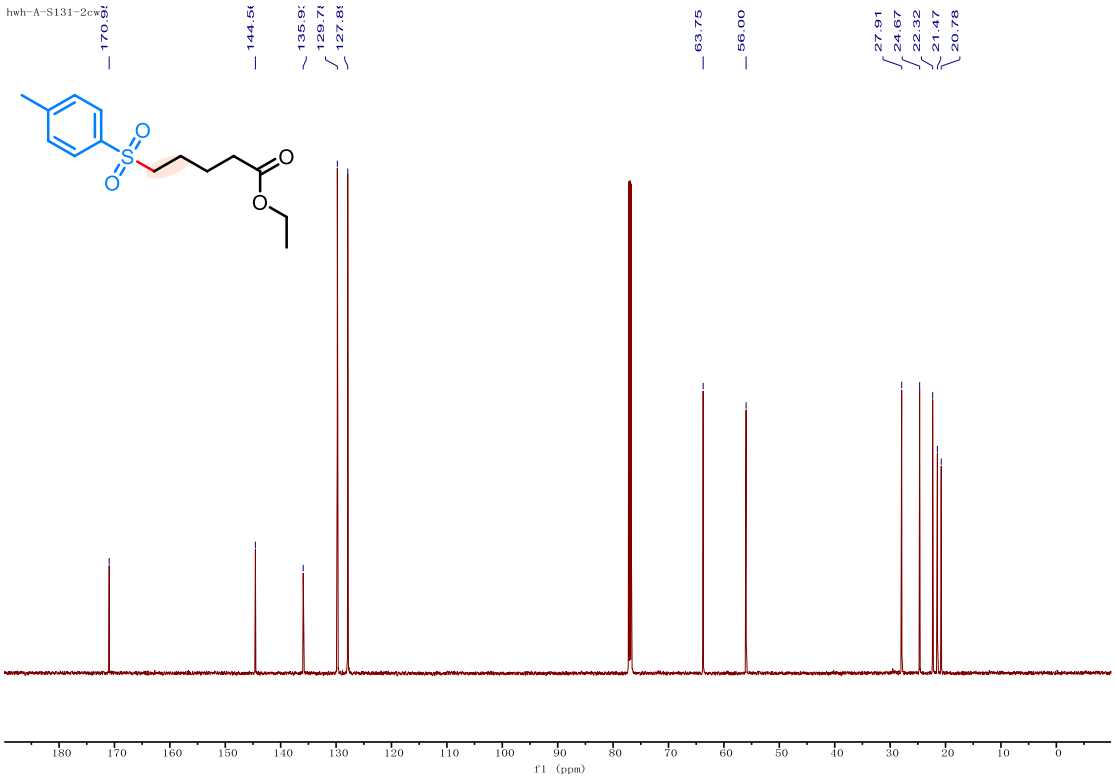
^{13}C {^{1}H} NMR Spectrum of 15 ($CDCl_3$ as solvent, 101 MHz)



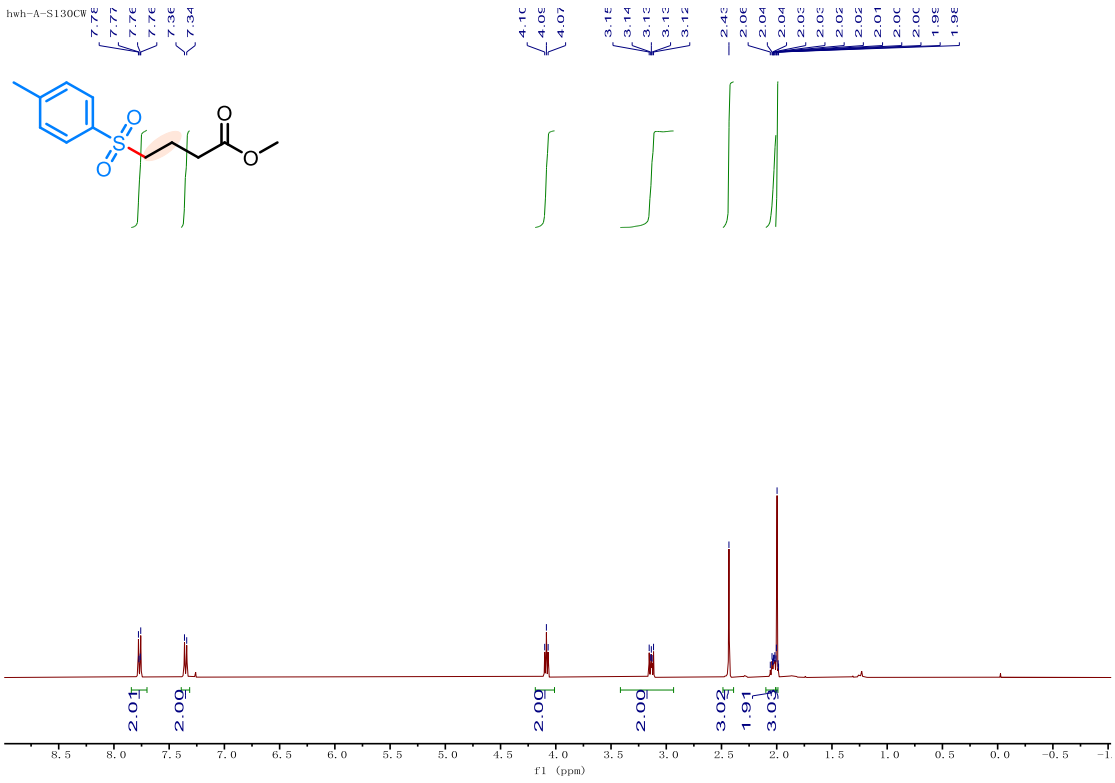
^{1}H NMR Spectrum of 16 ($CDCl_3$ as solvent, 600 MHz)



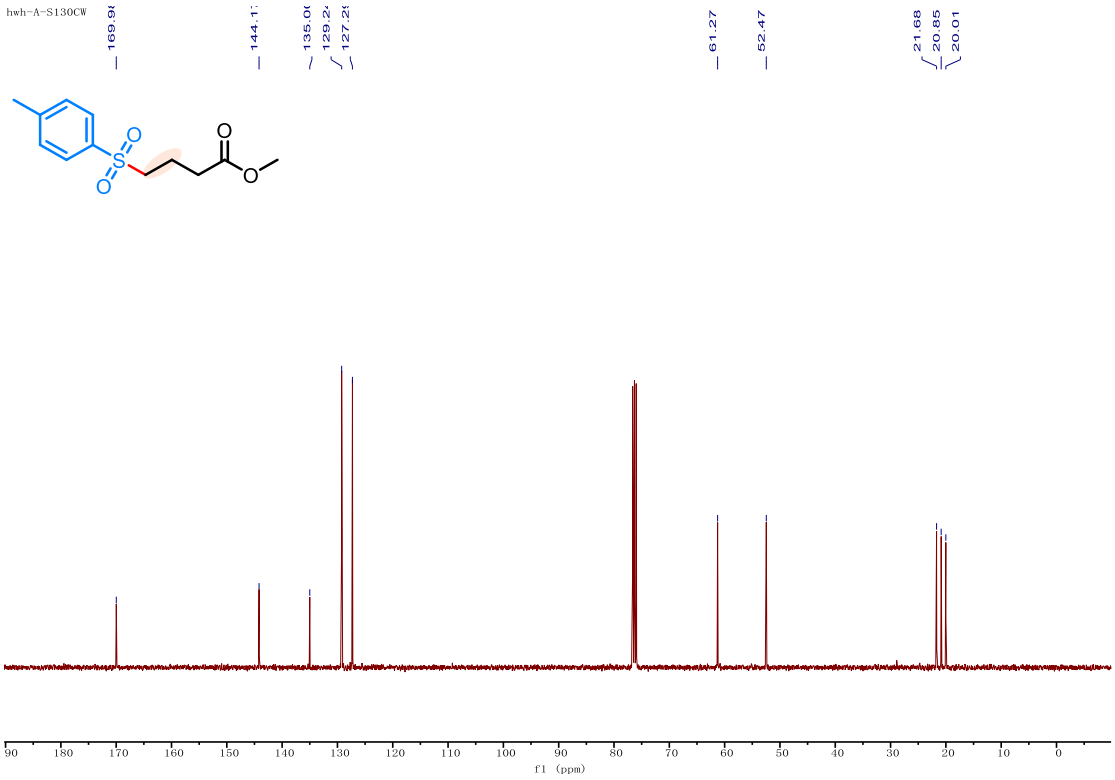
^{13}C {^{1}H} NMR Spectrum of 16 ($CDCl_3$ as solvent, 151 MHz)



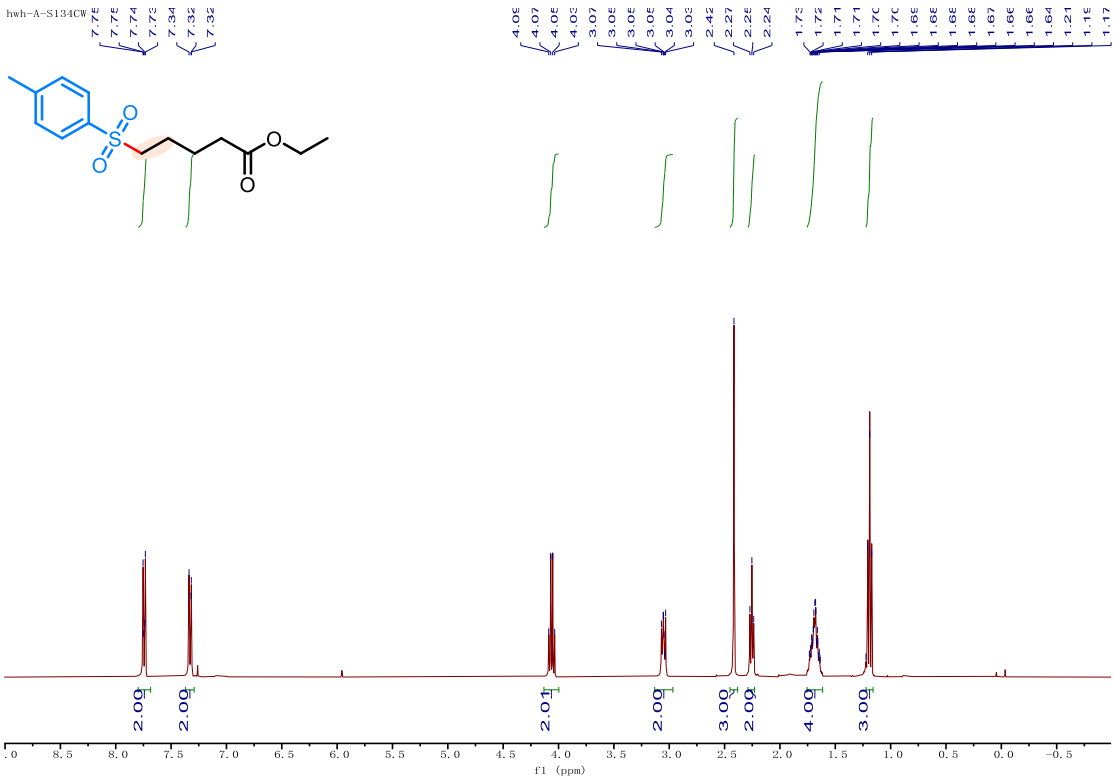
^{1}H NMR Spectrum of 17 ($CDCl_3$ as solvent, 400 MHz)



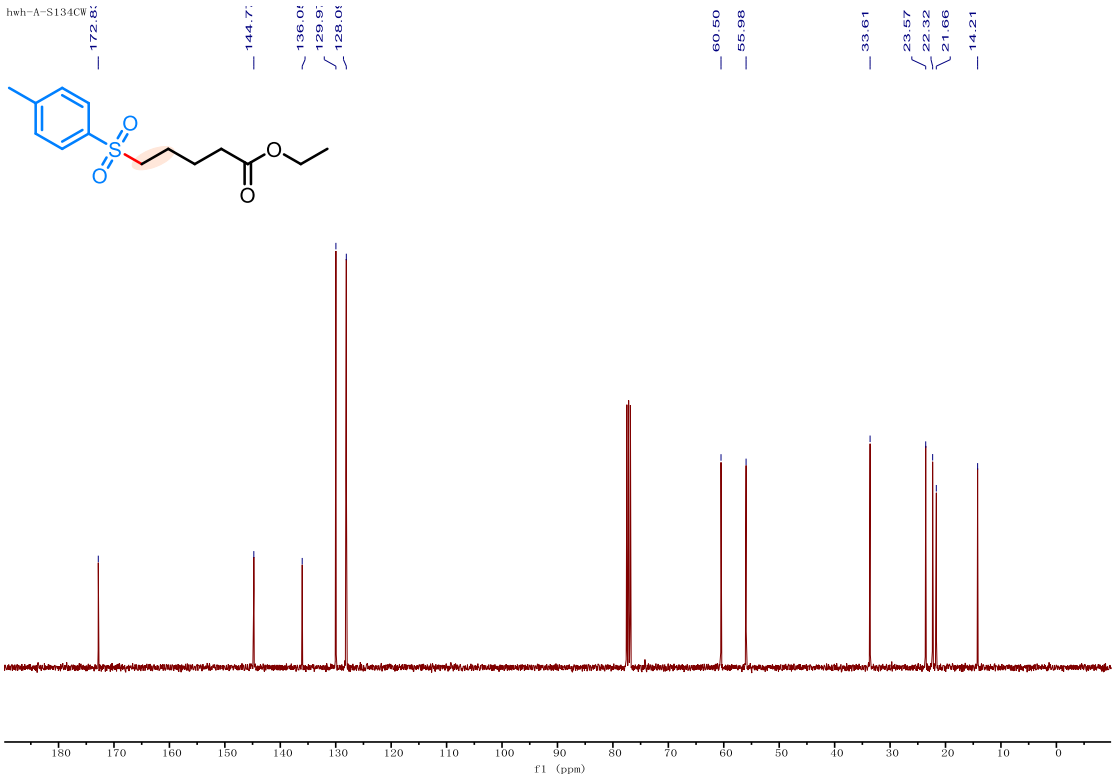
^{13}C {^{1}H} NMR Spectrum of 17 ($CDCl_3$ as solvent, 101 MHz)



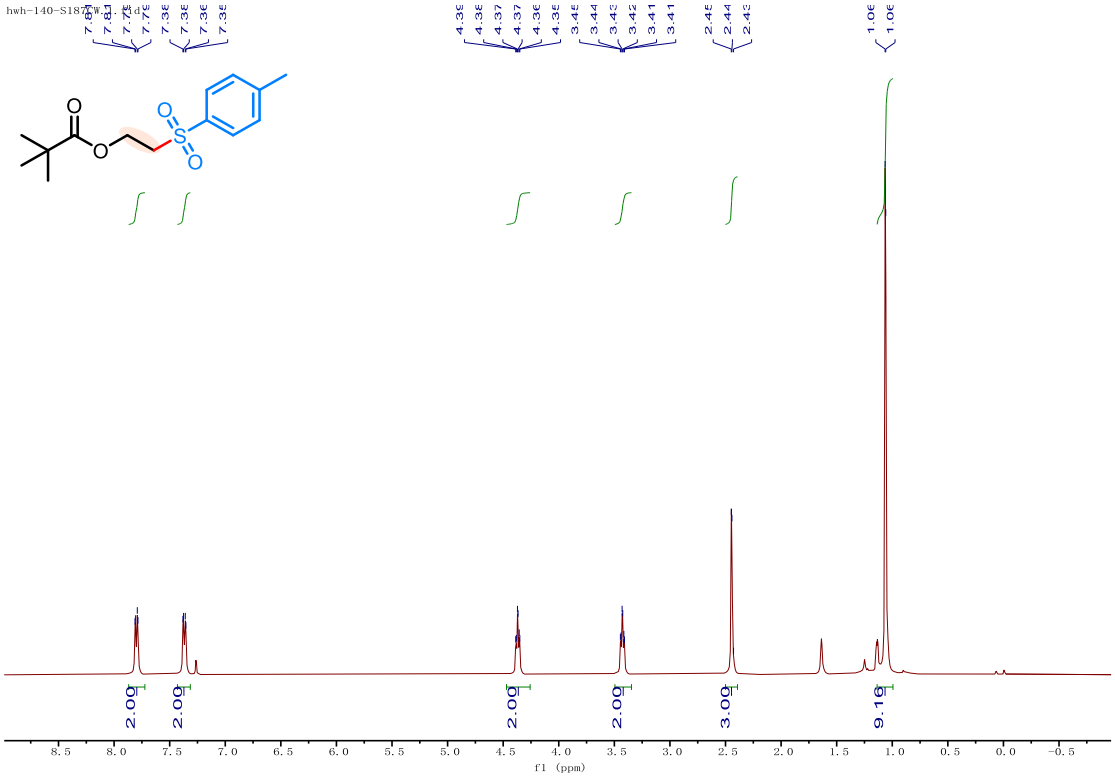
^{1}H NMR Spectrum of 18 ($CDCl_3$ as solvent, 400 MHz)



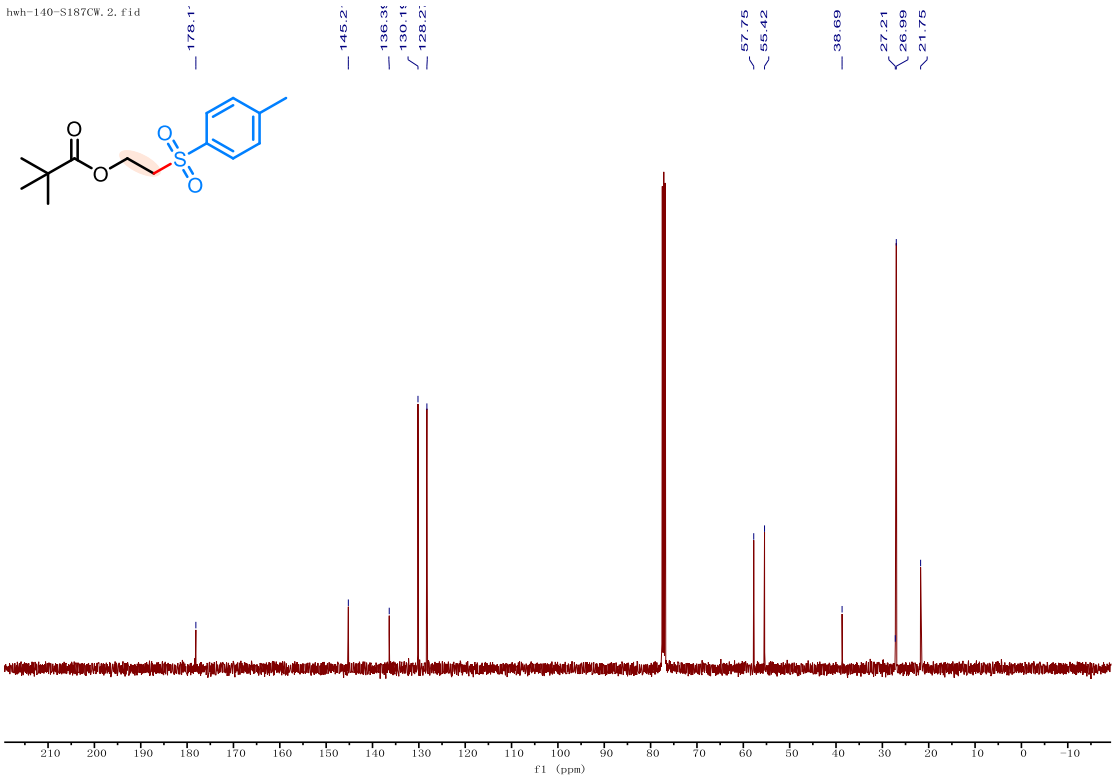
^{13}C {^{1}H} NMR Spectrum of 18 ($CDCl_3$ as solvent, 101 MHz)



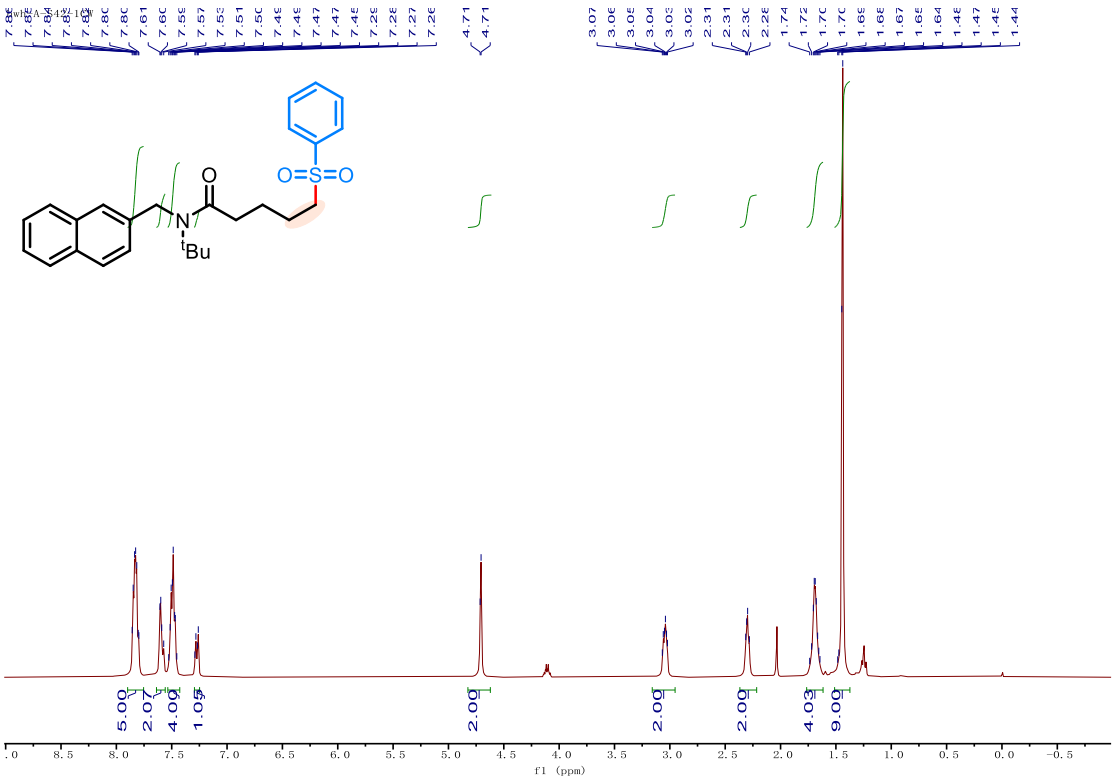
^{1}H NMR Spectrum of 19 ($CDCl_3$ as solvent, 400 MHz)



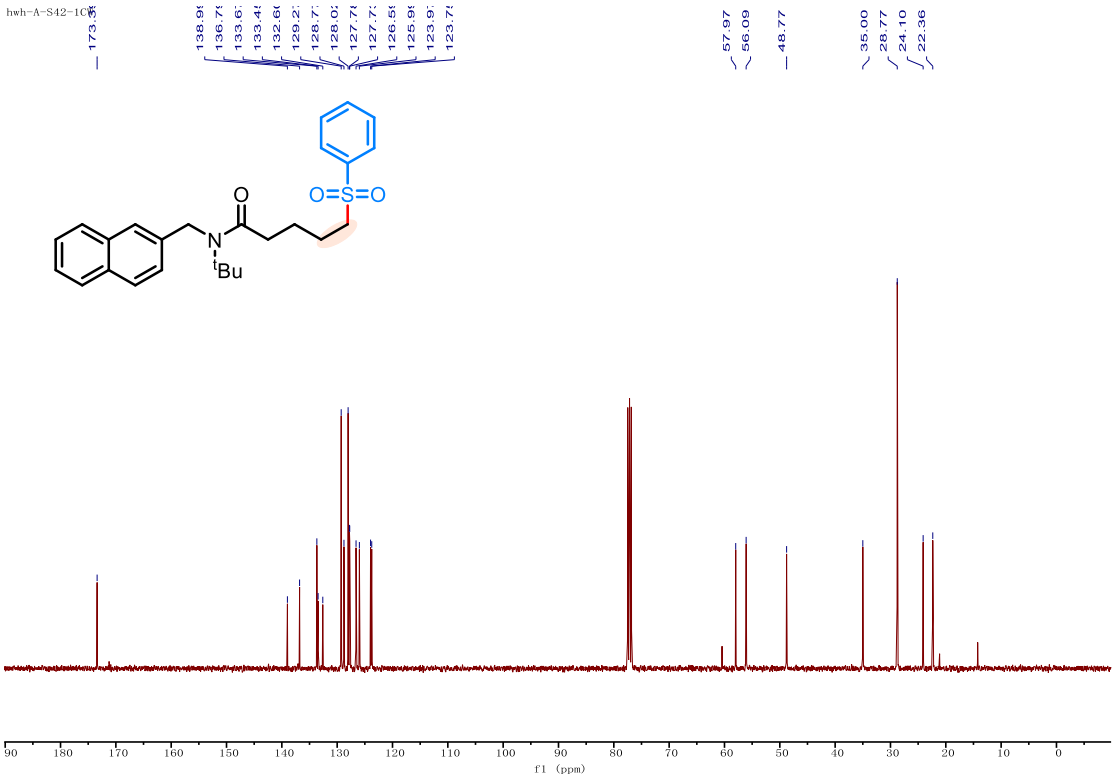
^{13}C {^{1}H} NMR Spectrum of 19 ($CDCl_3$ as solvent, 101 MHz)



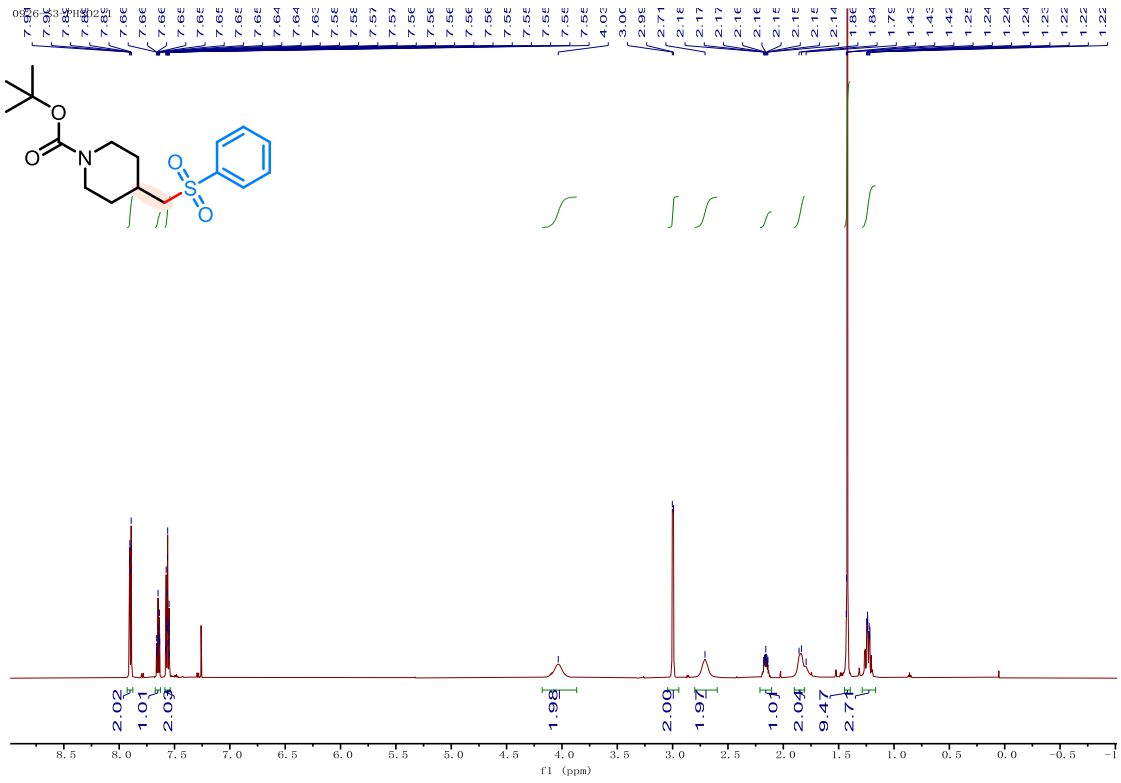
^{1}H NMR Spectrum of 20 ($CDCl_3$ as solvent, 400 MHz)



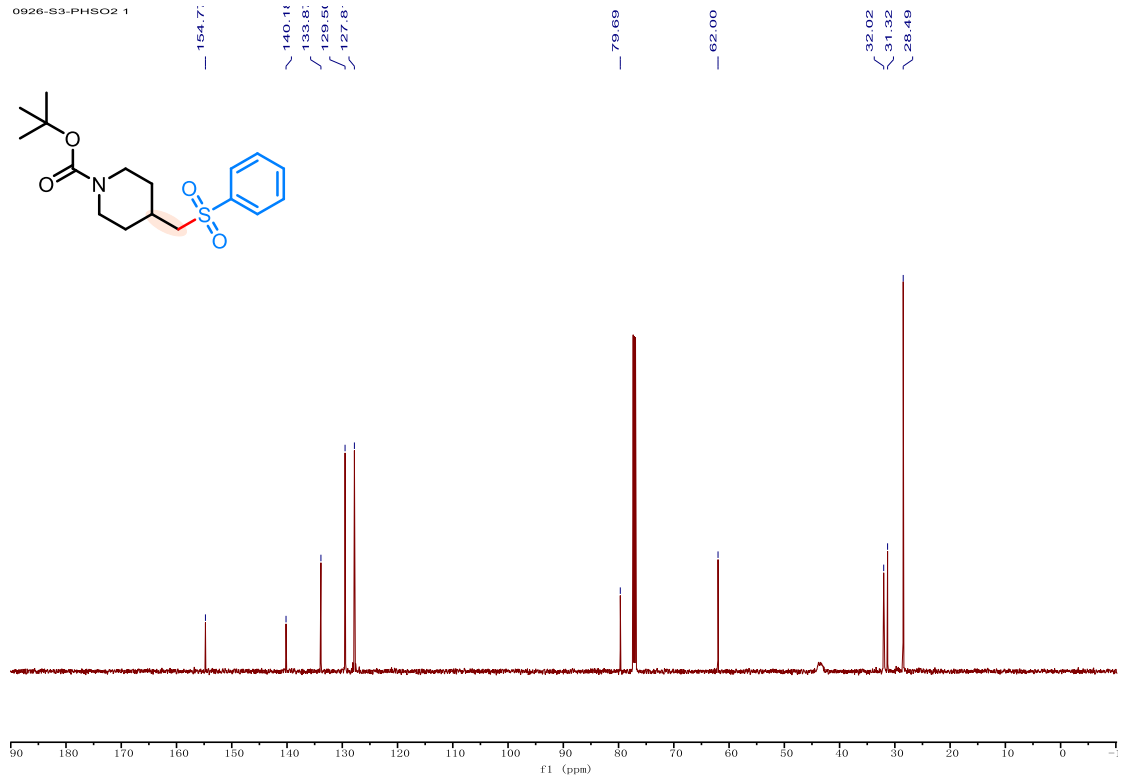
^{13}C {^{1}H} NMR Spectrum of 20 ($CDCl_3$ as solvent, 101 MHz)



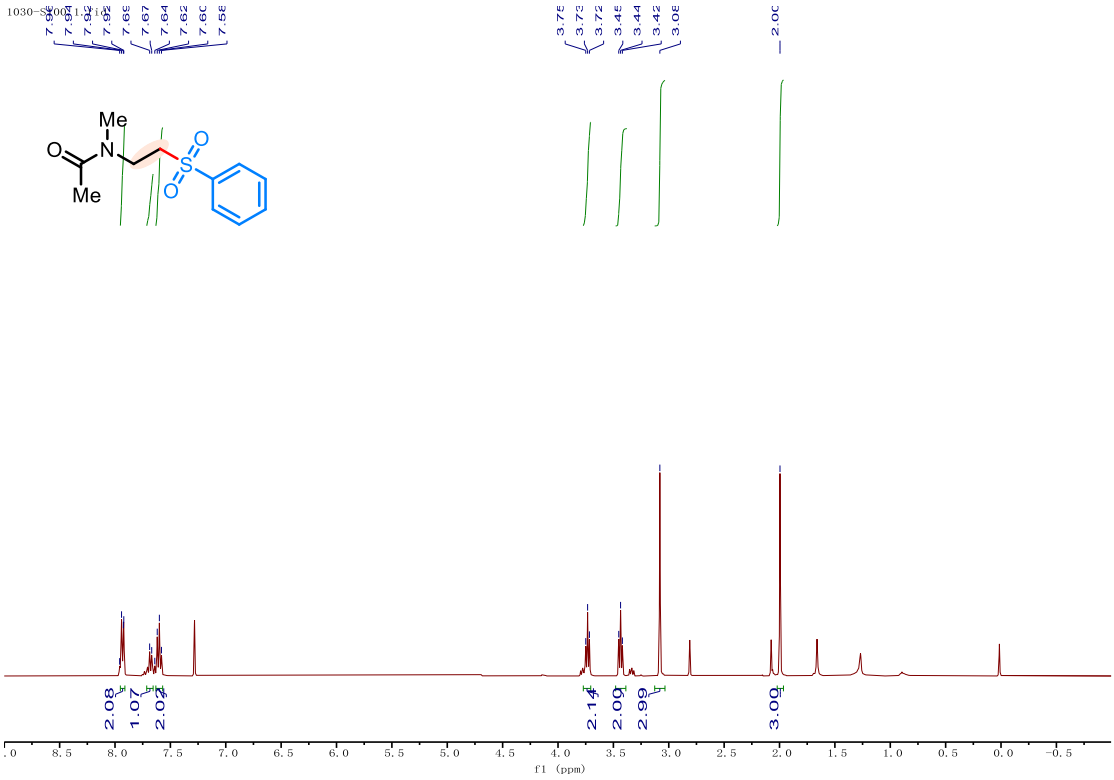
^{1}H NMR Spectrum of 21 ($CDCl_3$ as solvent, 600 MHz)



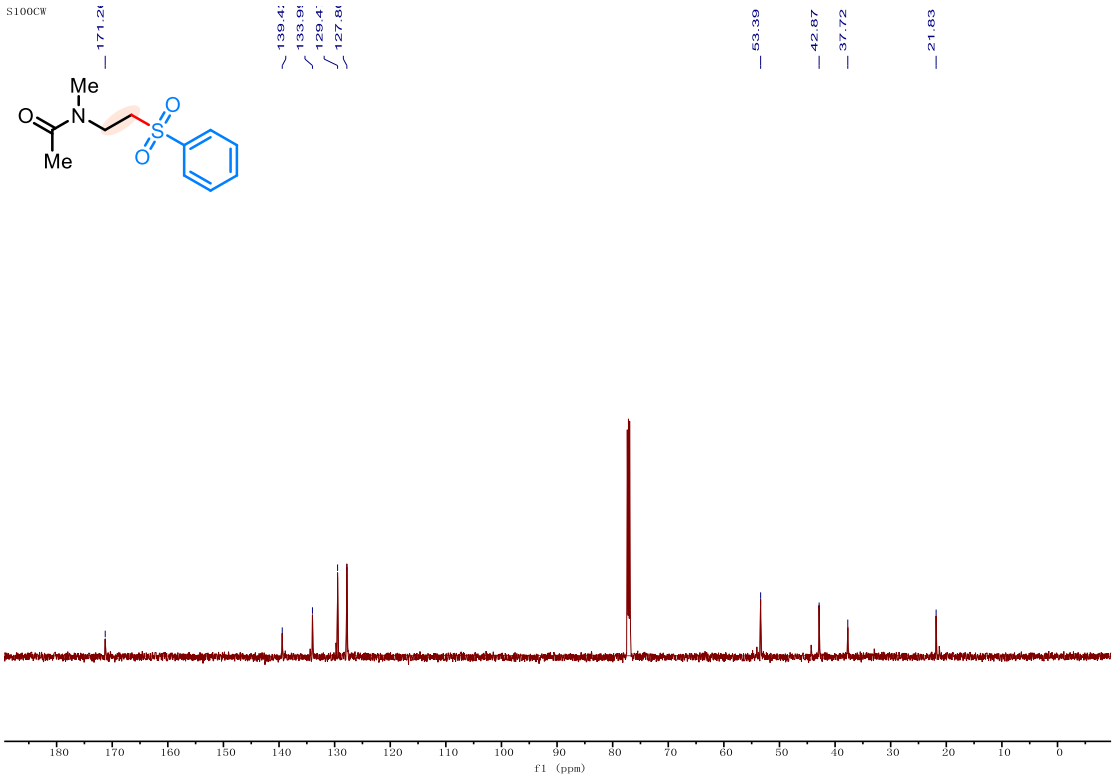
^{13}C {^{1}H} NMR Spectrum of 21 ($CDCl_3$ as solvent, 151 MHz)



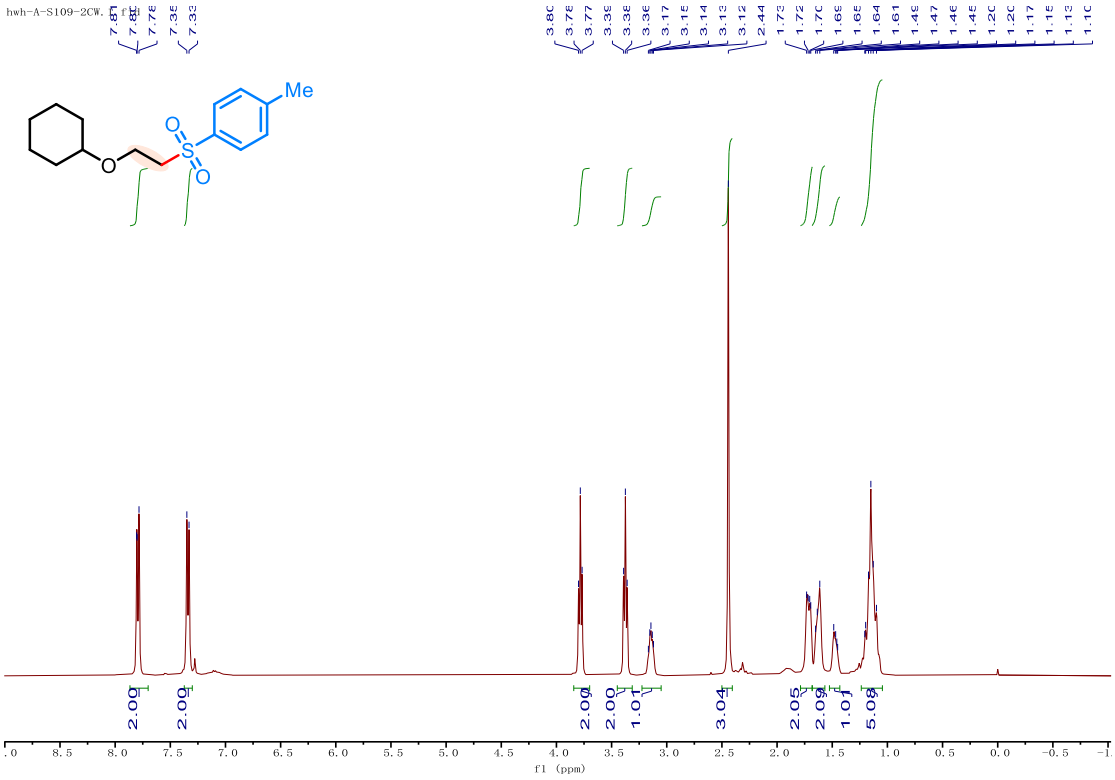
^{1}H NMR Spectrum of 22 ($CDCl_3$ as solvent, 600 MHz)



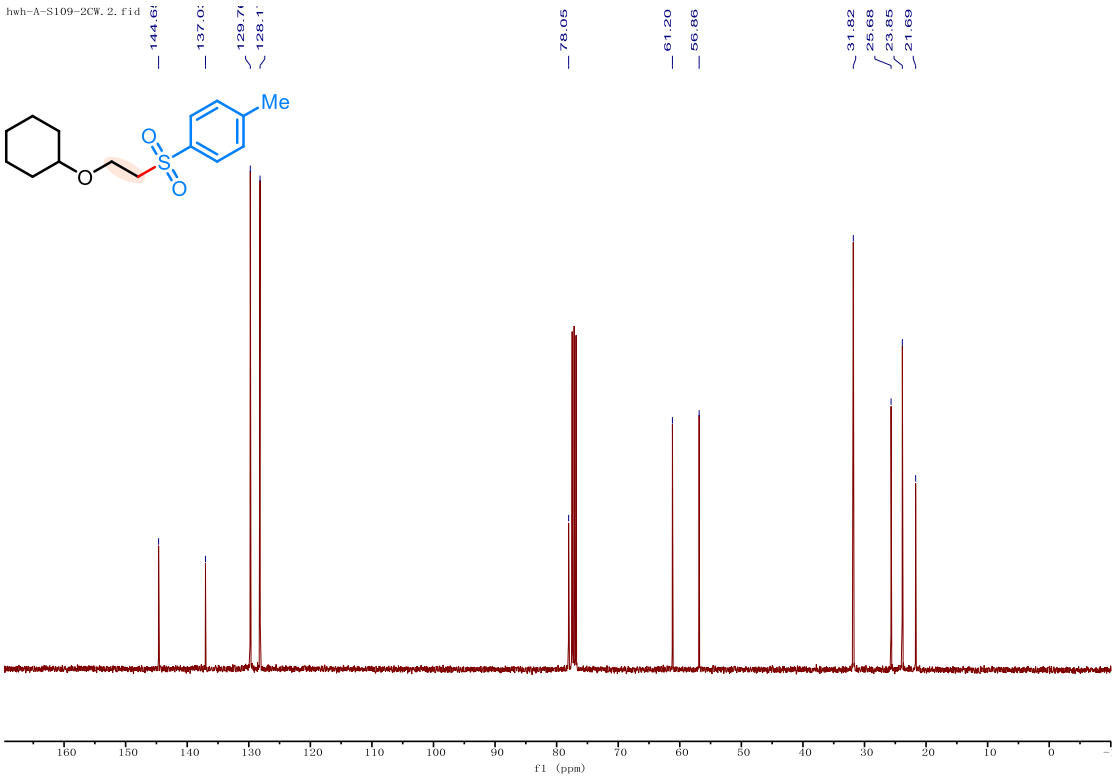
^{13}C {^{1}H} NMR Spectrum of 22 ($CDCl_3$ as solvent, 151 MHz)



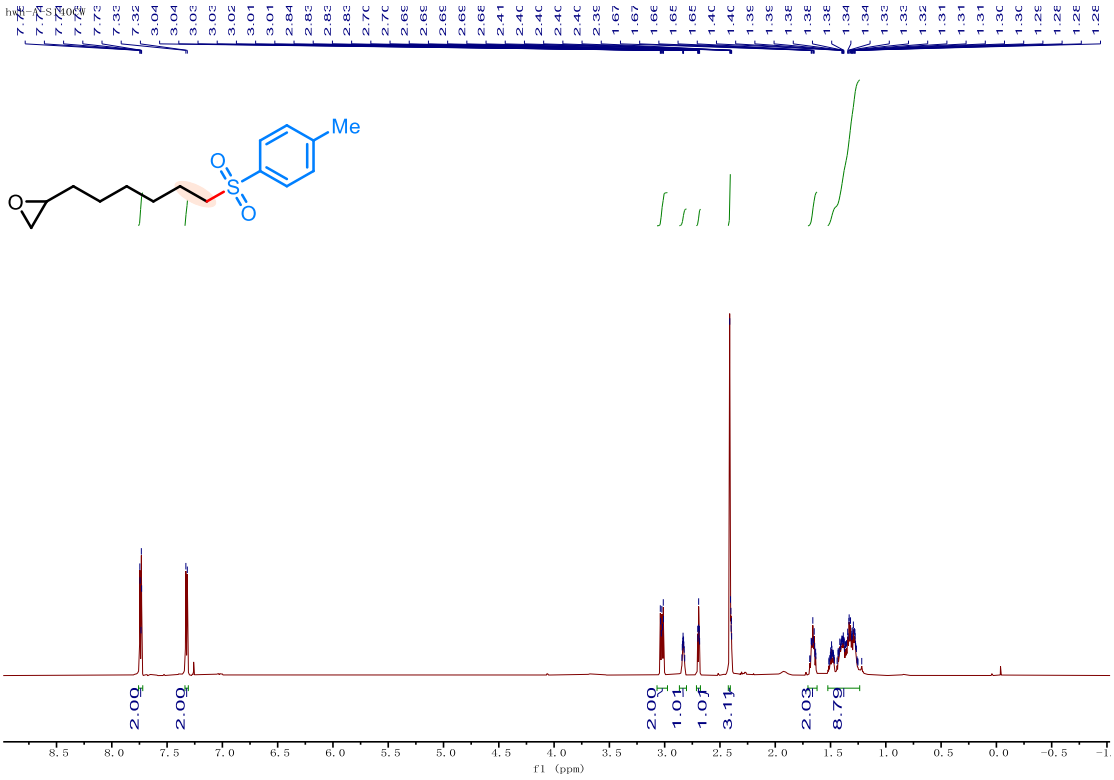
^{1}H NMR Spectrum of 23 ($CDCl_3$ as solvent, 400 MHz)



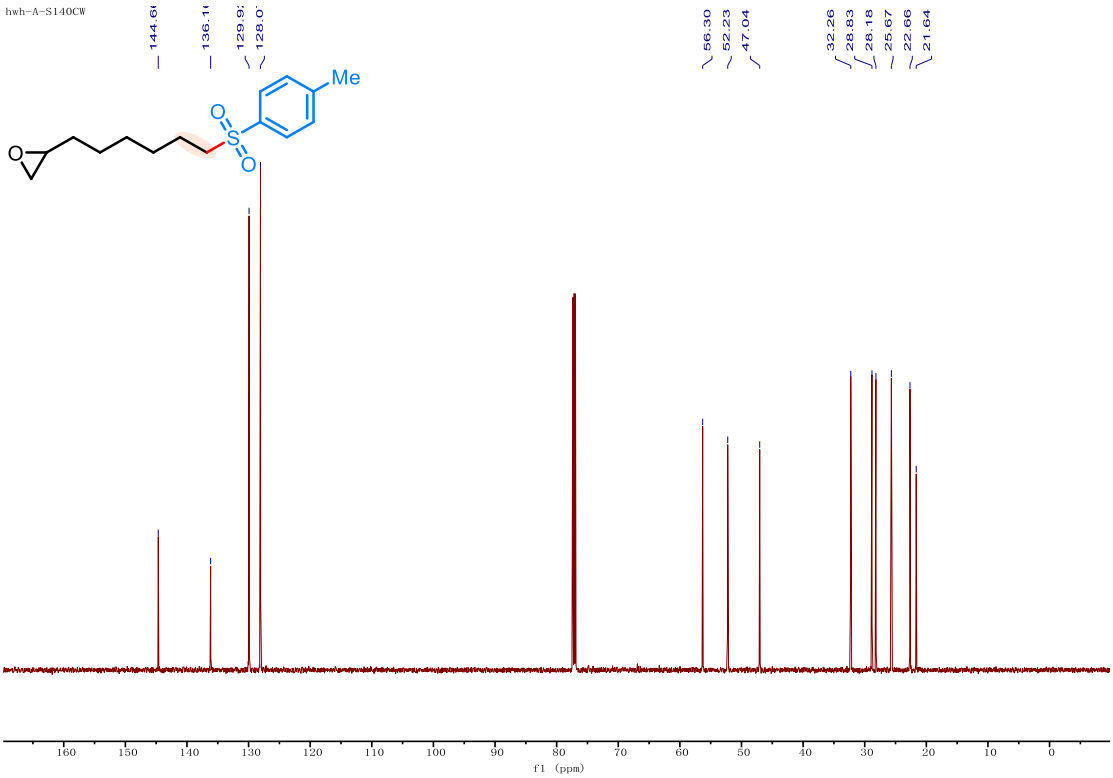
^{13}C {^{1}H} NMR Spectrum of 23 ($CDCl_3$ as solvent, 101 MHz)



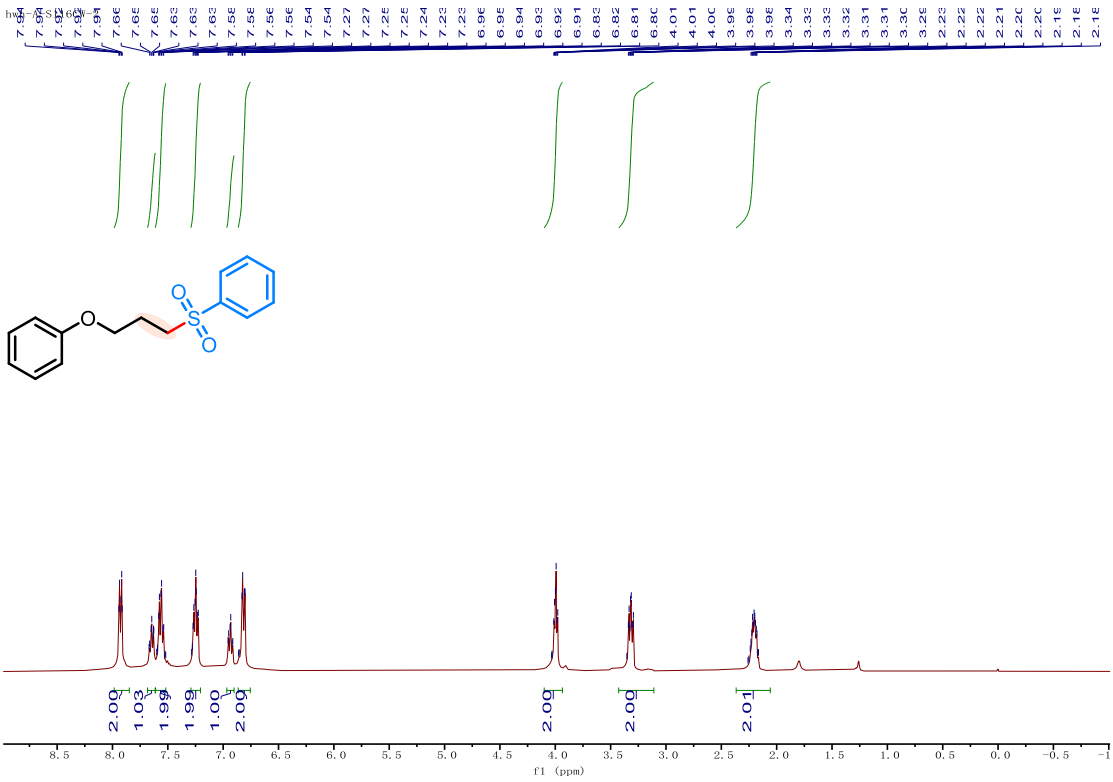
^{1}H NMR Spectrum of 24 ($CDCl_3$ as solvent, 600 MHz)



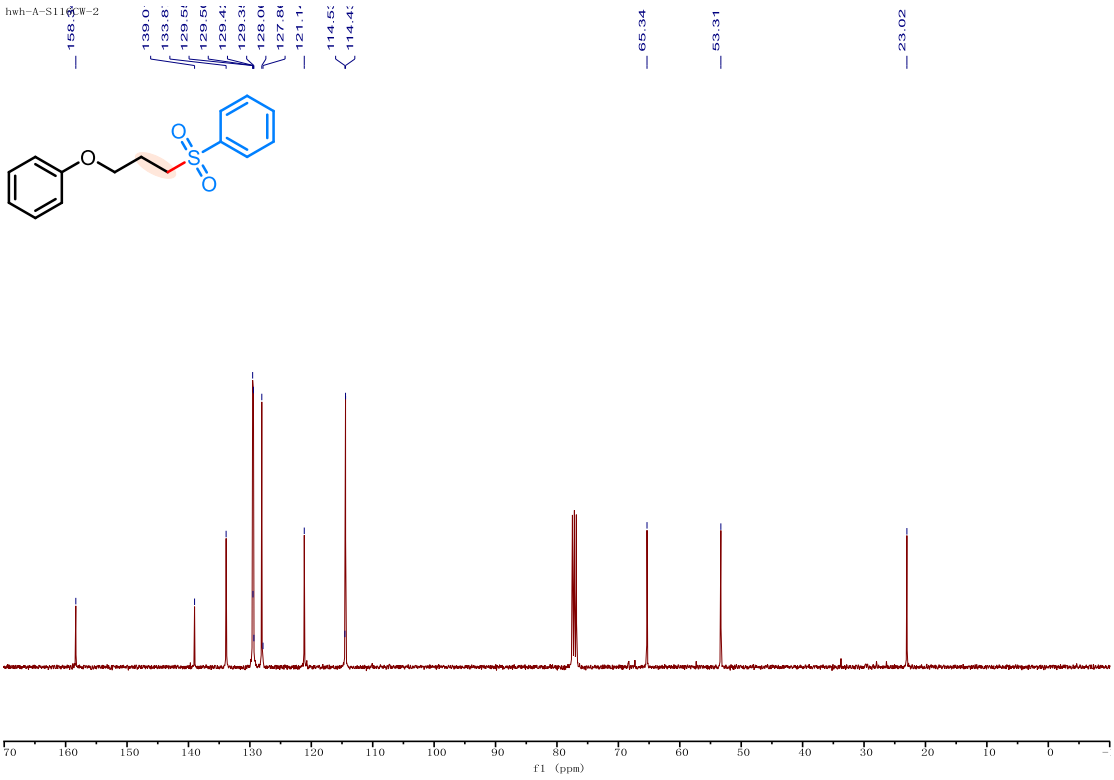
^{13}C {^{1}H} NMR Spectrum of 24 ($CDCl_3$ as solvent, 151 MHz)



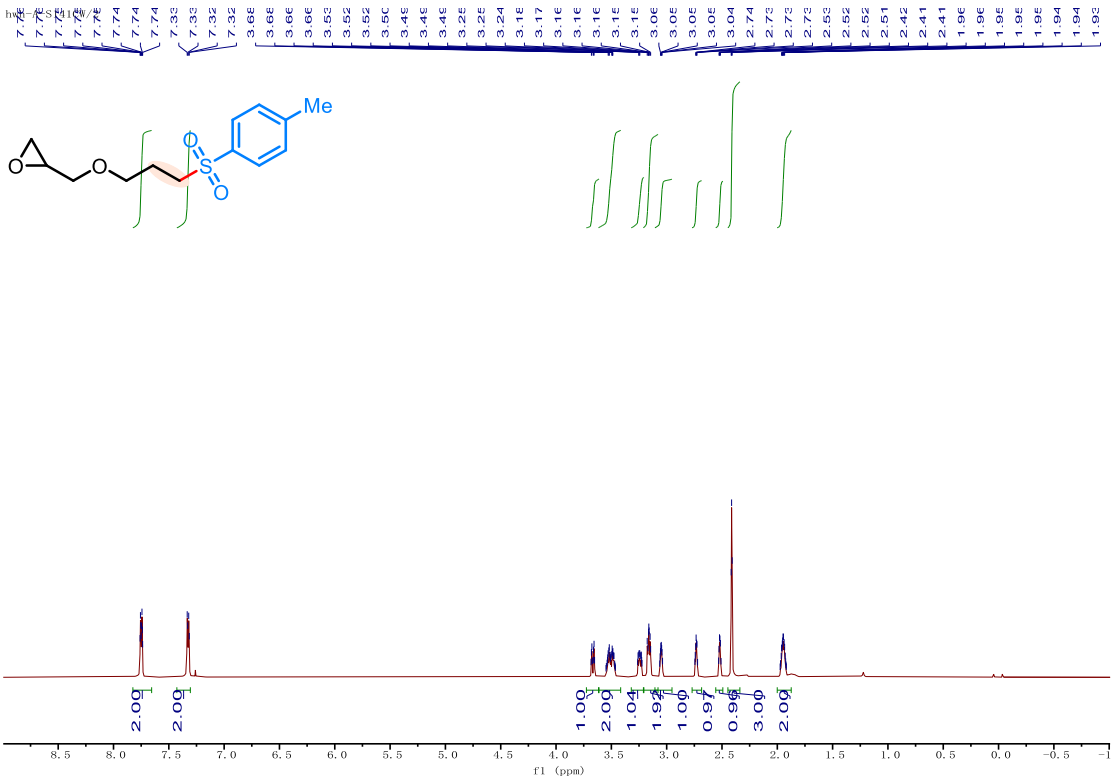
^{1}H NMR Spectrum of 25 ($CDCl_3$ as solvent, 400 MHz)



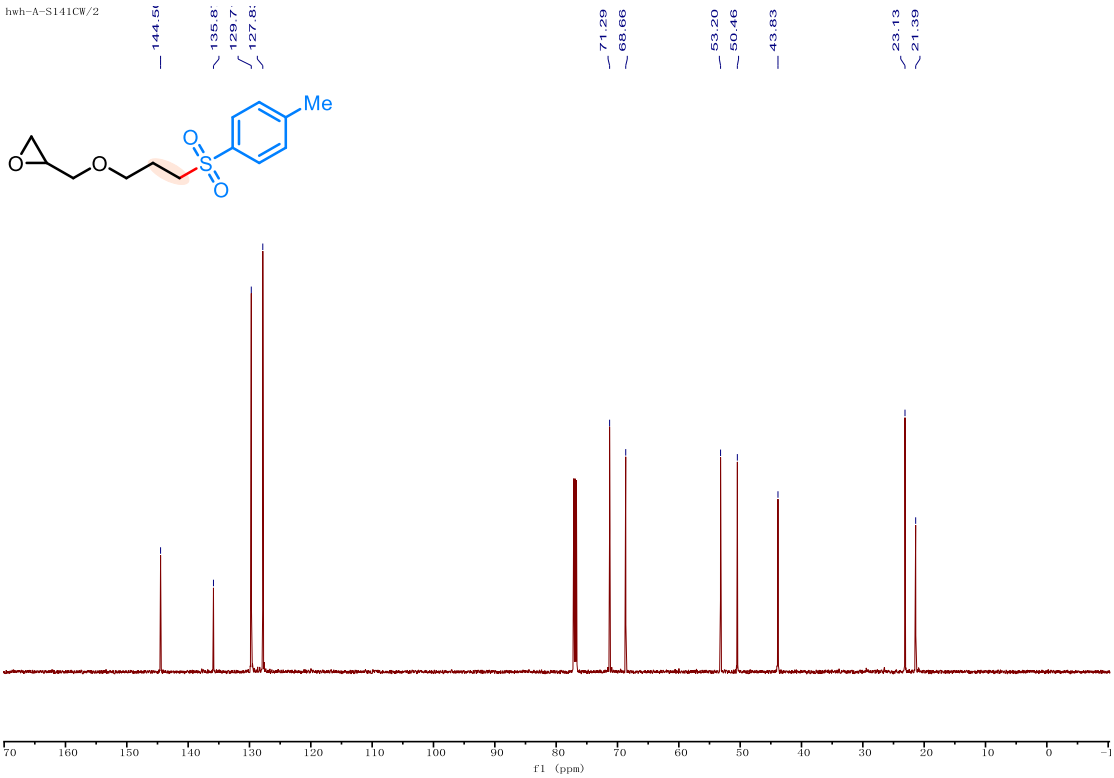
^{13}C {^{1}H} NMR Spectrum of 25 ($CDCl_3$ as solvent, 101 MHz)



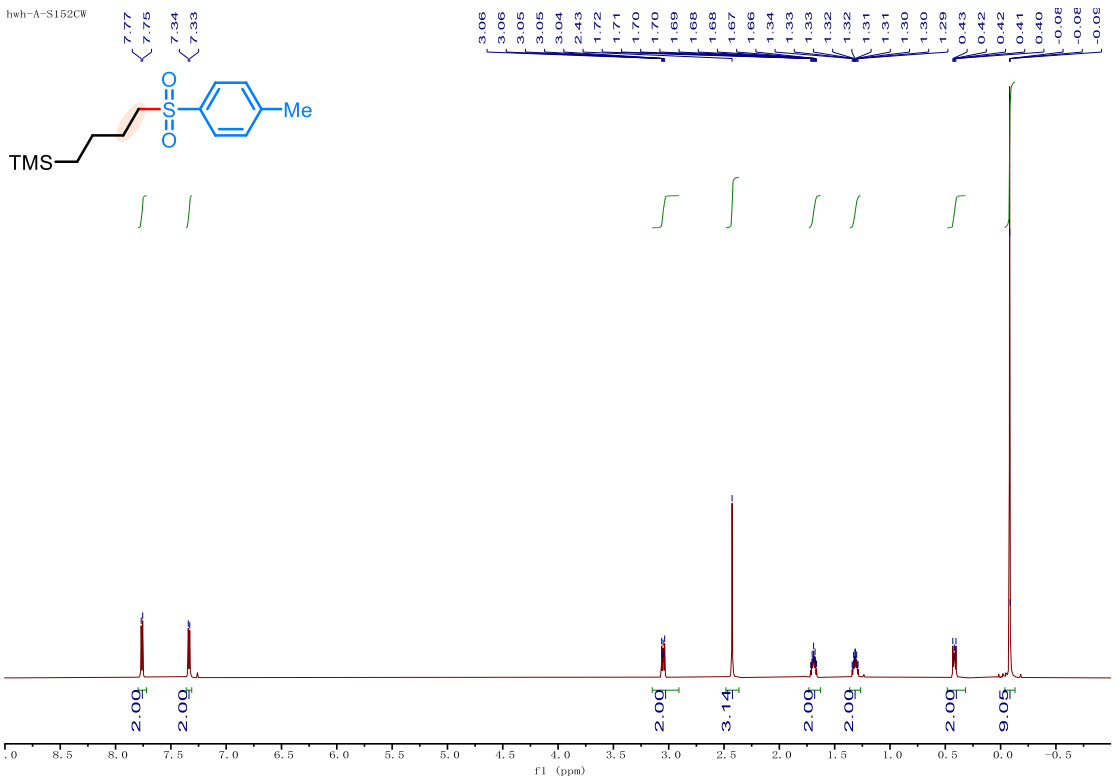
^{1}H NMR Spectrum of 26 ($CDCl_3$ as solvent, 600 MHz)



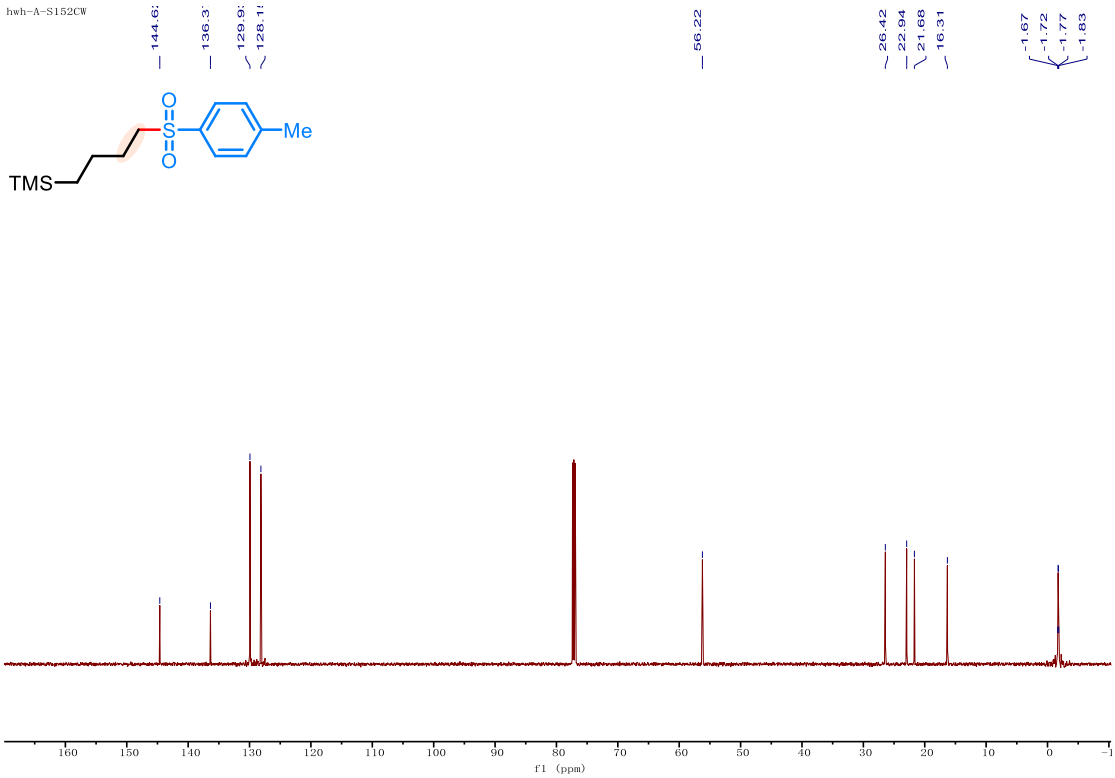
^{13}C {^{1}H} NMR Spectrum of 26 ($CDCl_3$ as solvent, 151 MHz)



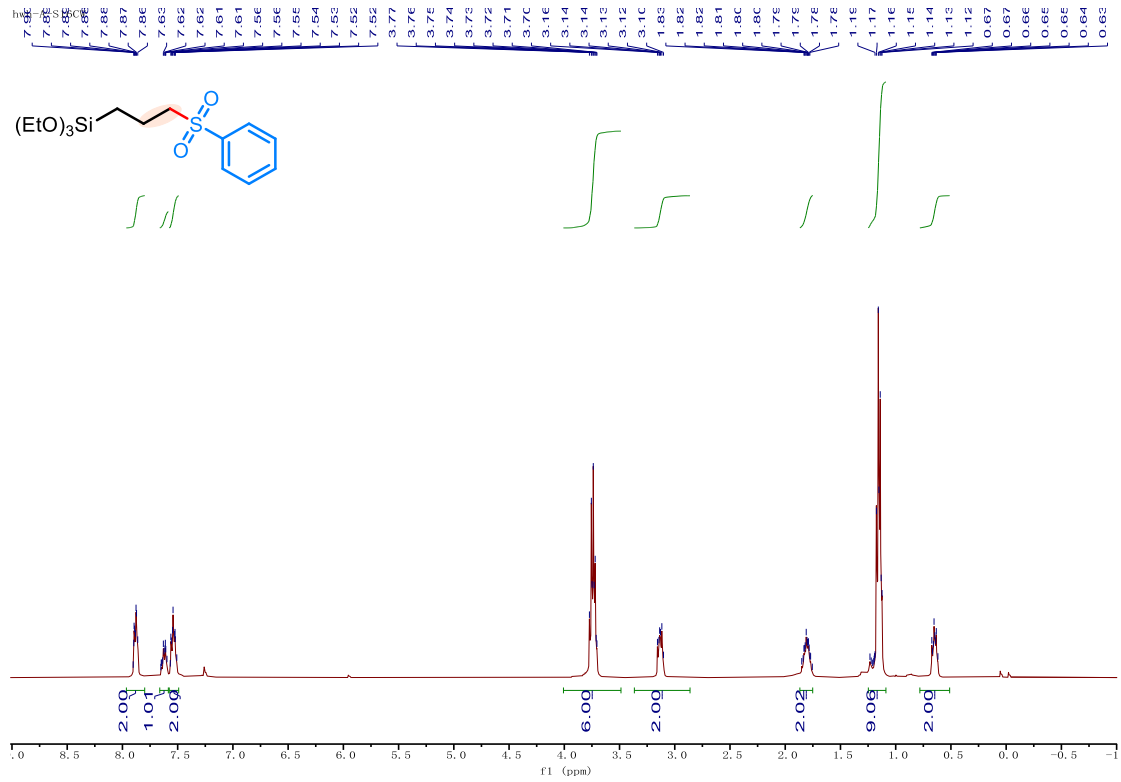
^{1}H NMR Spectrum of 27 ($CDCl_3$ as solvent, 600 MHz)



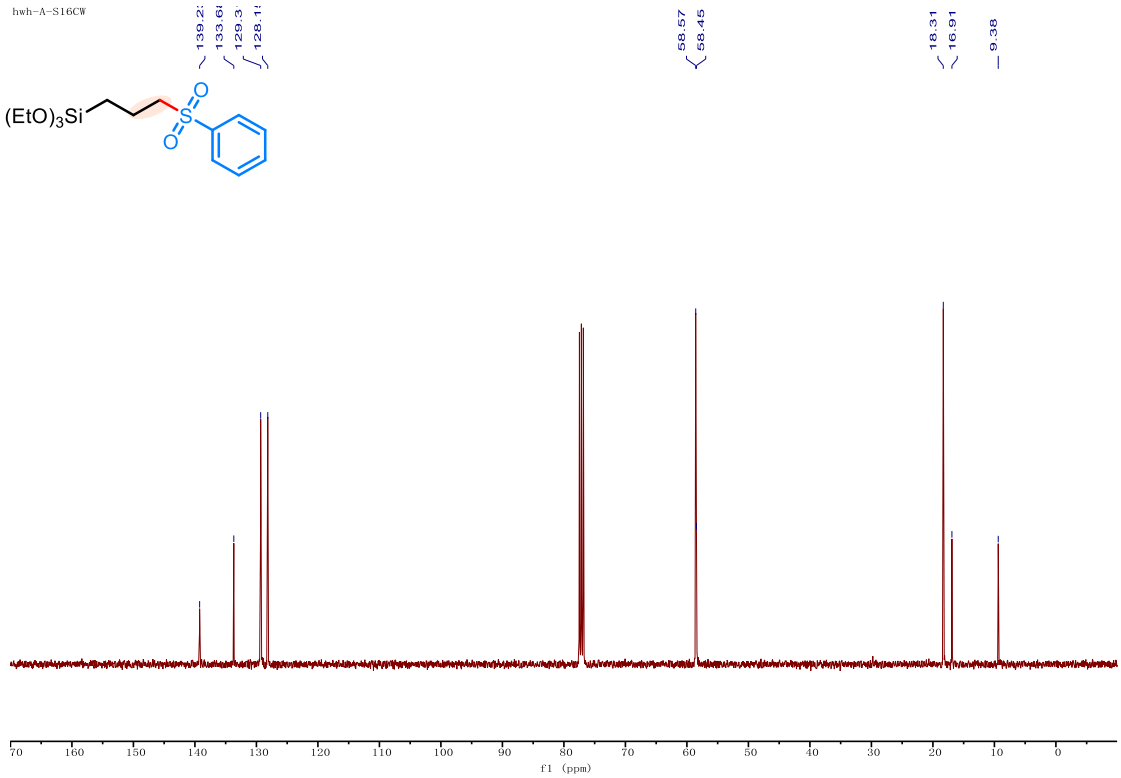
^{13}C {^{1}H} NMR Spectrum of 27 ($CDCl_3$ as solvent, 105 MHz)



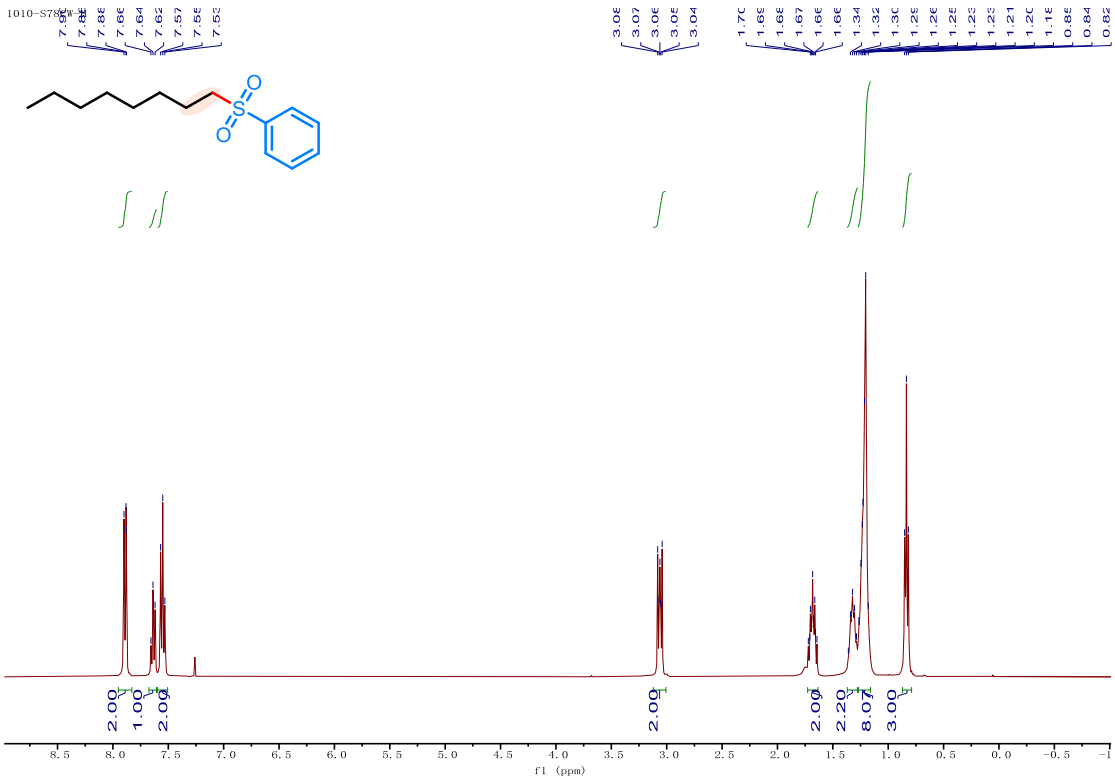
^{1}H NMR Spectrum of 28 ($CDCl_3$ as solvent, 400 MHz)



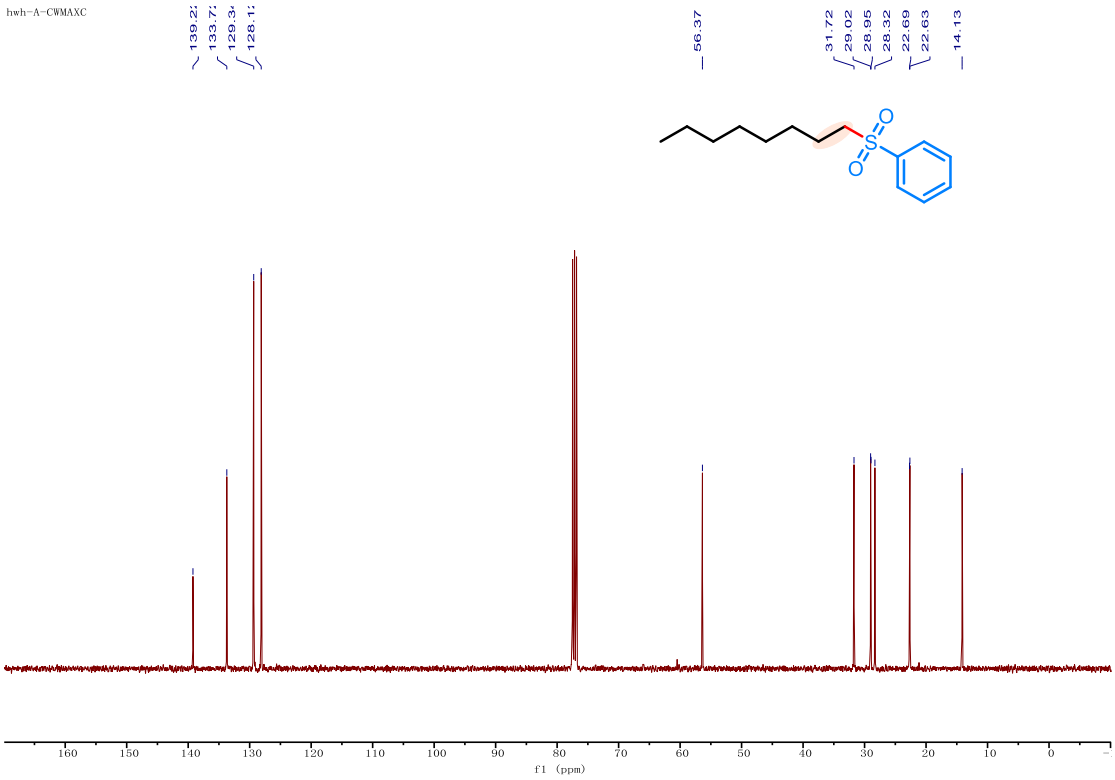
^{13}C {^{1}H} NMR Spectrum of 28 ($CDCl_3$ as solvent, 101 MHz)



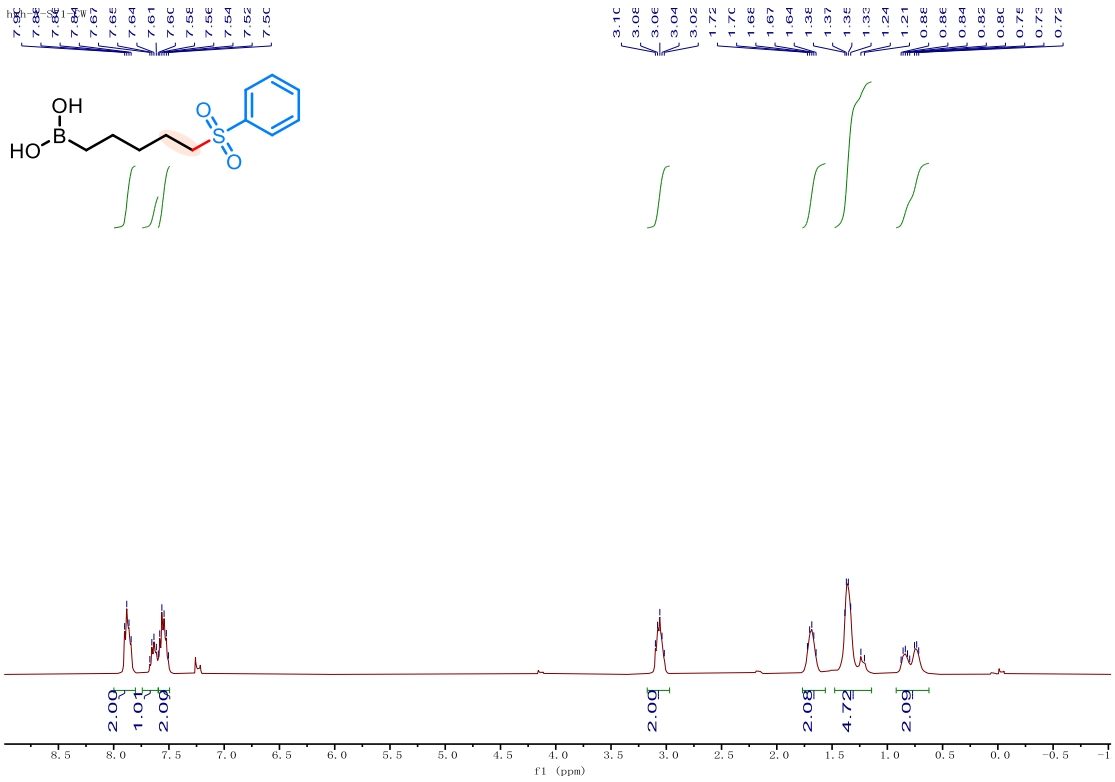
^{1}H NMR Spectrum of 29 ($CDCl_3$ as solvent, 400 MHz)



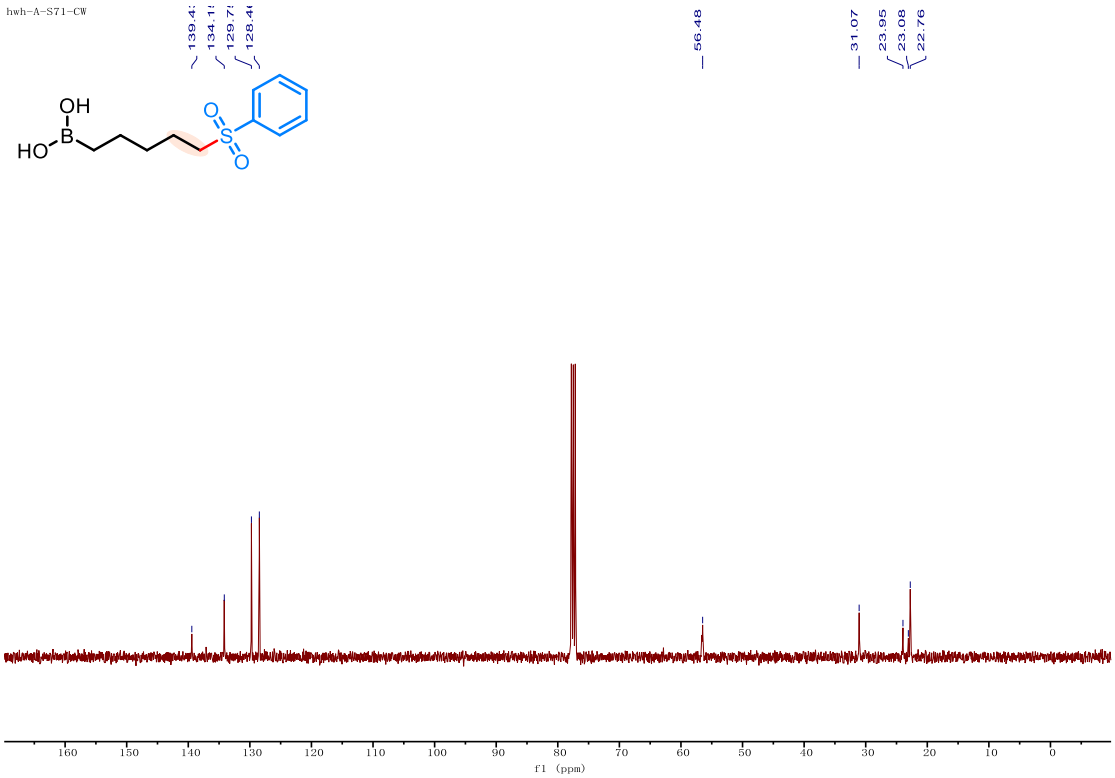
^{13}C {^{1}H} NMR Spectrum of 29 ($CDCl_3$ as solvent, 101 MHz)



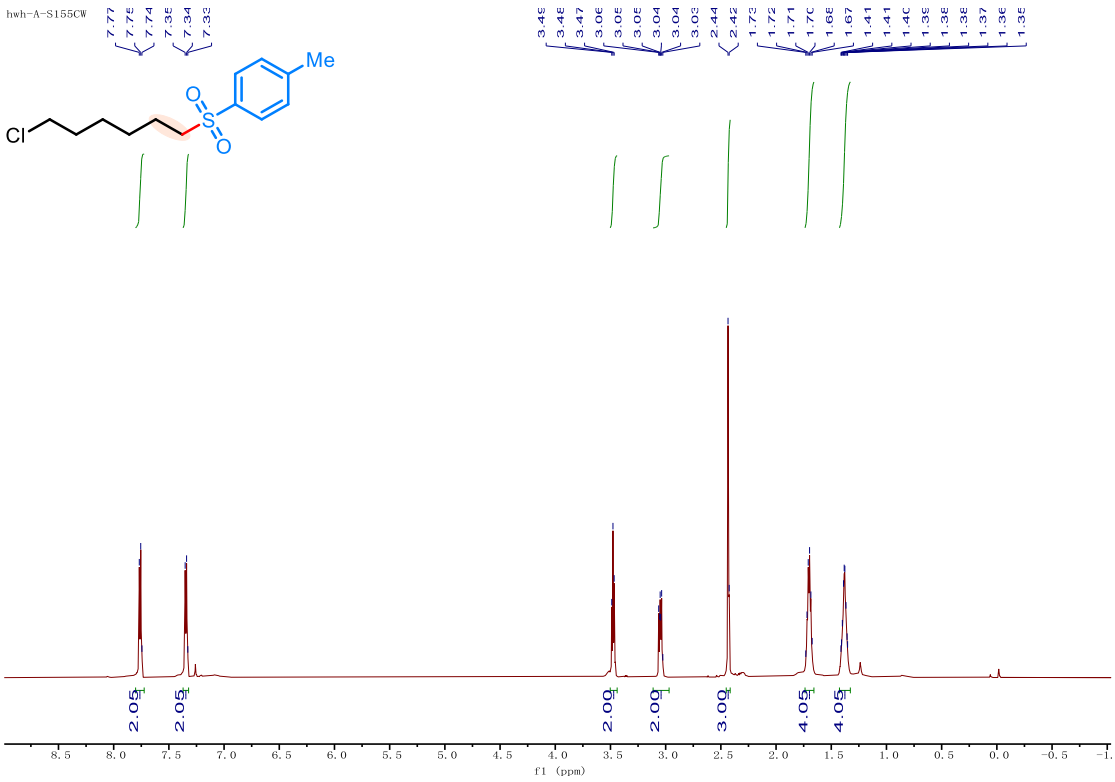
^{1}H NMR Spectrum of 30 ($CDCl_3$ as solvent, 400 MHz)



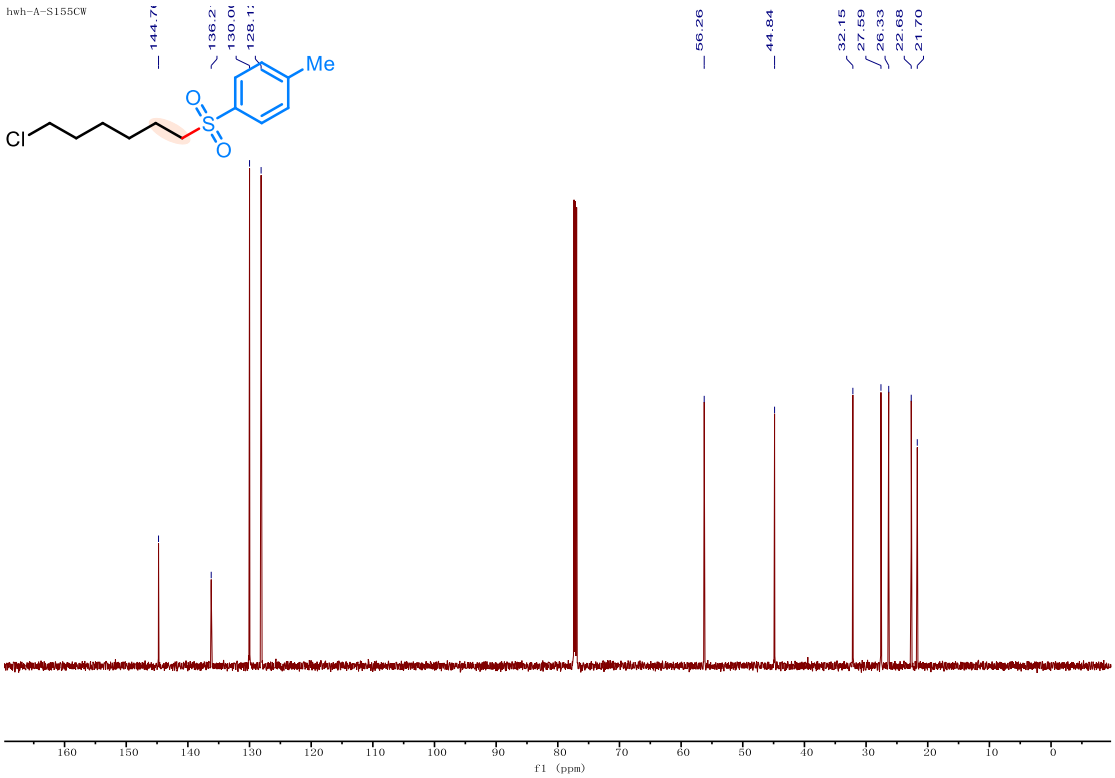
^{13}C {^{1}H} NMR Spectrum of 30 ($CDCl_3$ as solvent, 101 MHz)



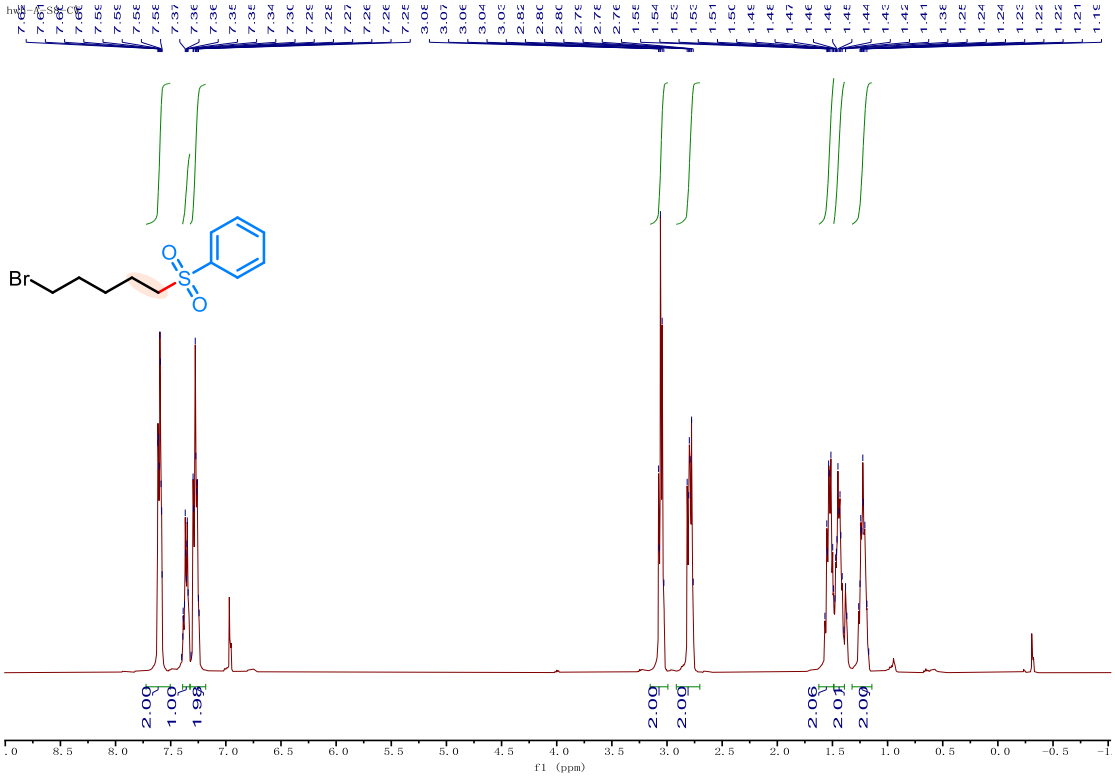
^{1}H NMR Spectrum of 31 ($CDCl_3$ as solvent, 600 MHz)



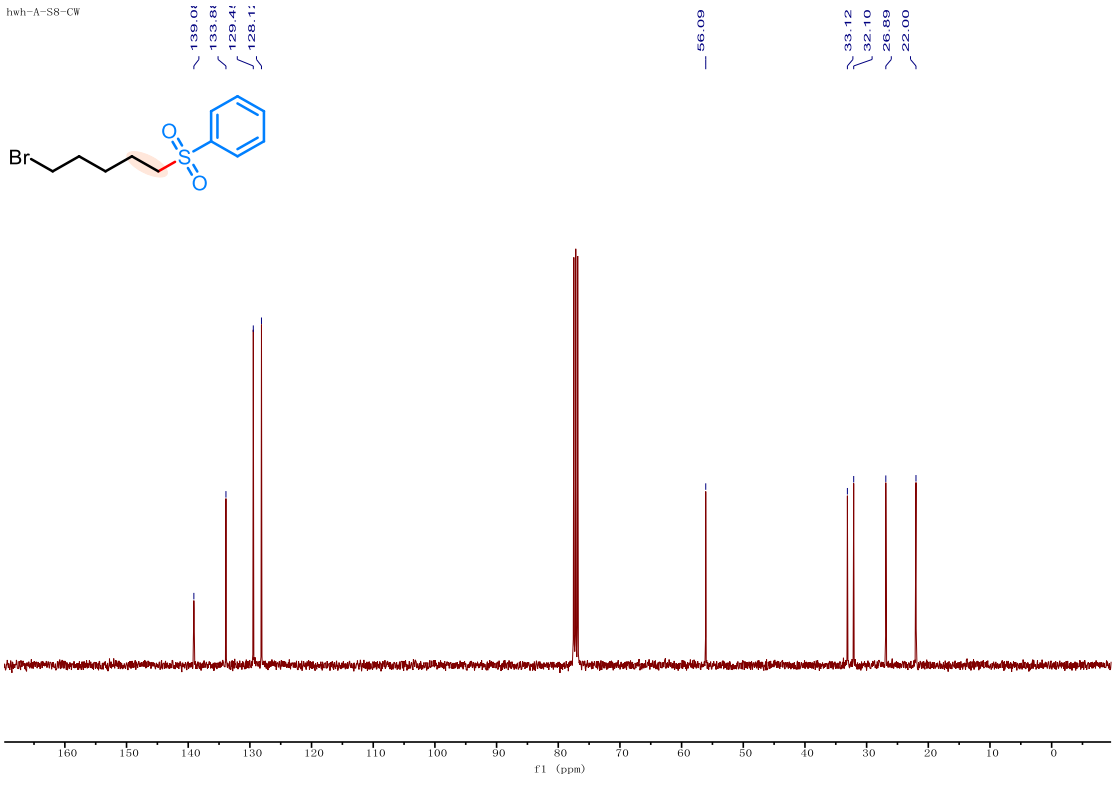
^{13}C {^{1}H} NMR Spectrum of 31 ($CDCl_3$ as solvent, 151 MHz)



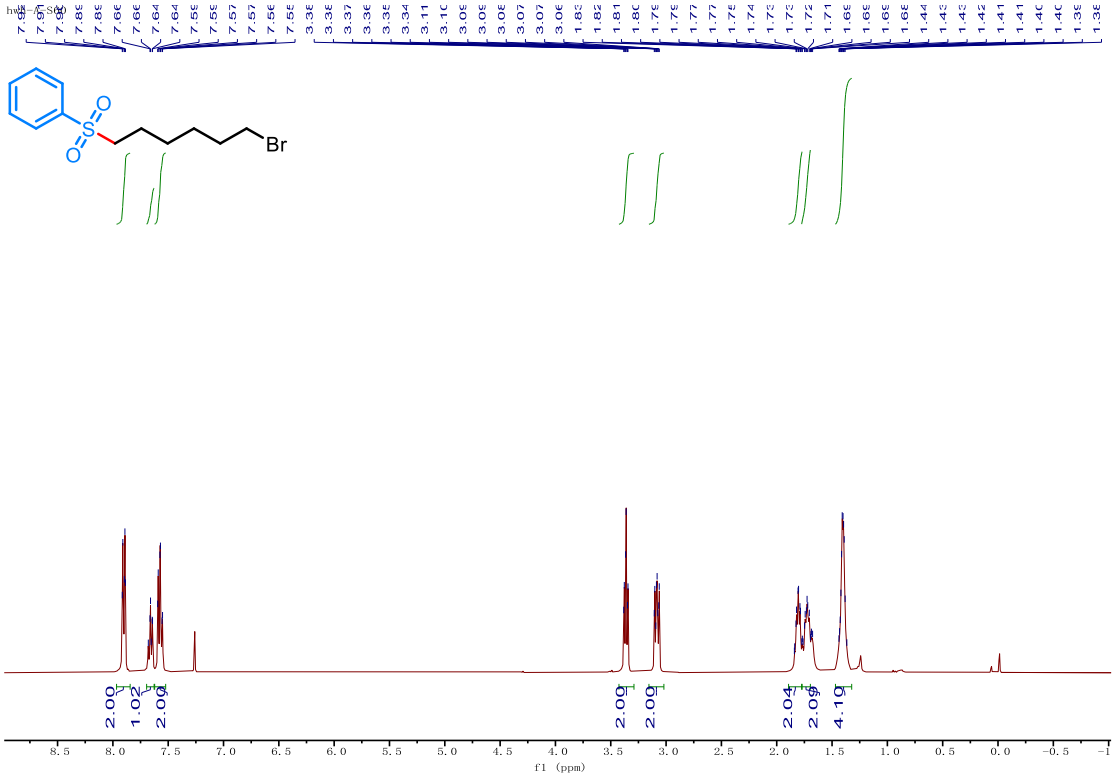
^{1}H NMR Spectrum of 32 ($CDCl_3$ as solvent, 400 MHz)



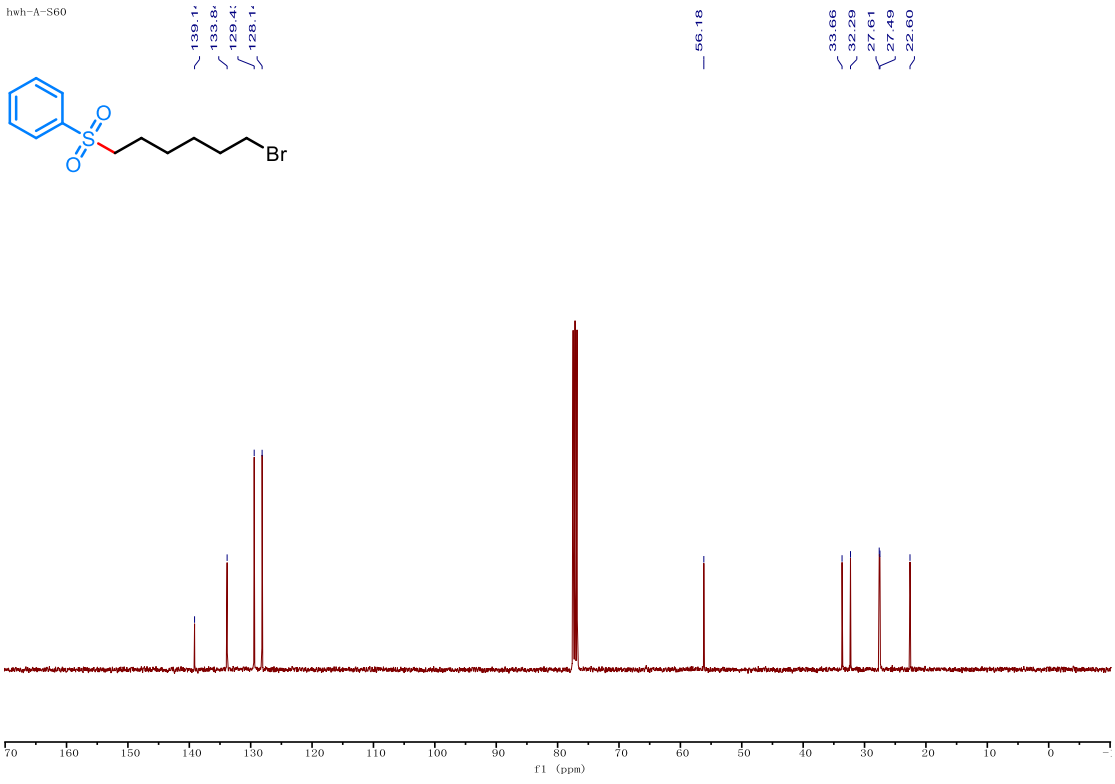
^{13}C {^{1}H} NMR Spectrum of 32 ($CDCl_3$ as solvent, 101 MHz)



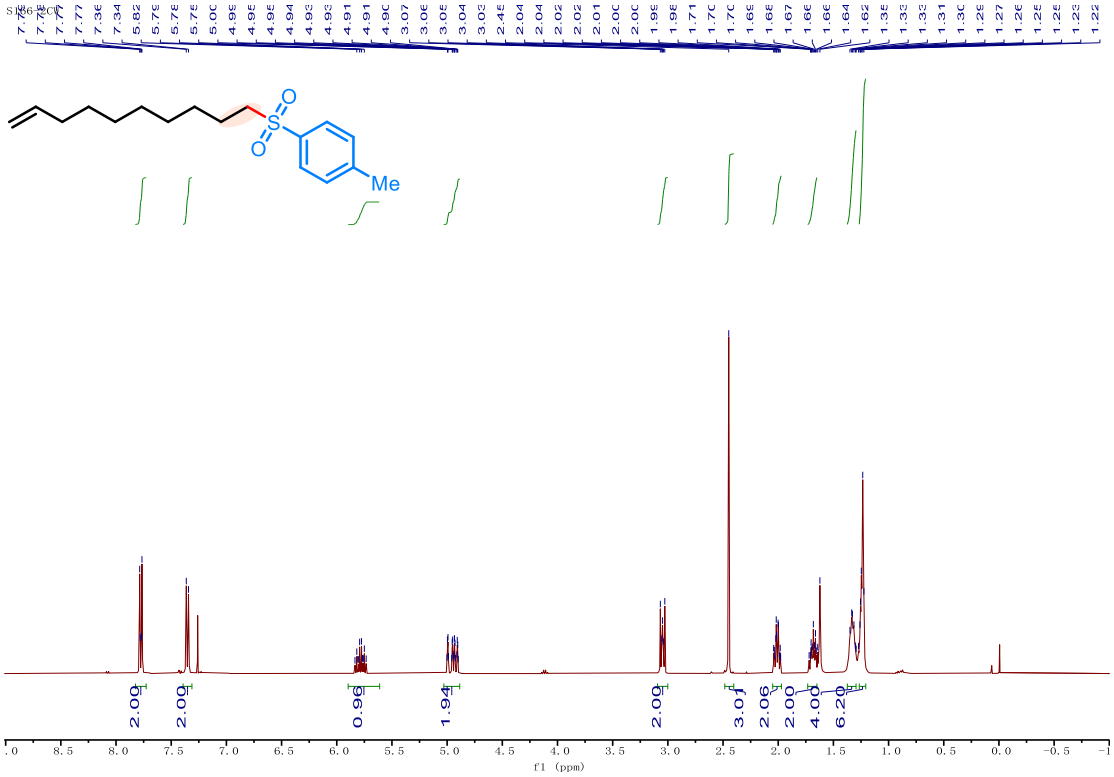
^{1}H NMR Spectrum of 33 ($CDCl_3$ as solvent, 400 MHz)



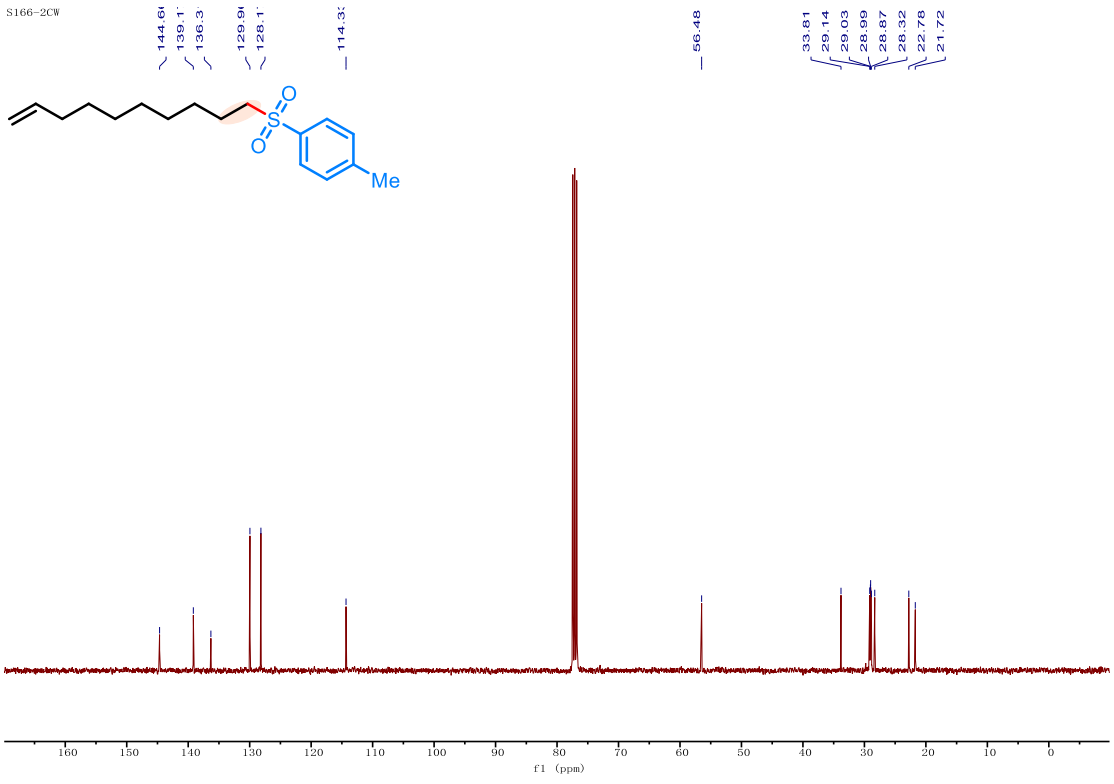
^{13}C {^{1}H} NMR Spectrum of 33 ($CDCl_3$ as solvent, 101 MHz)



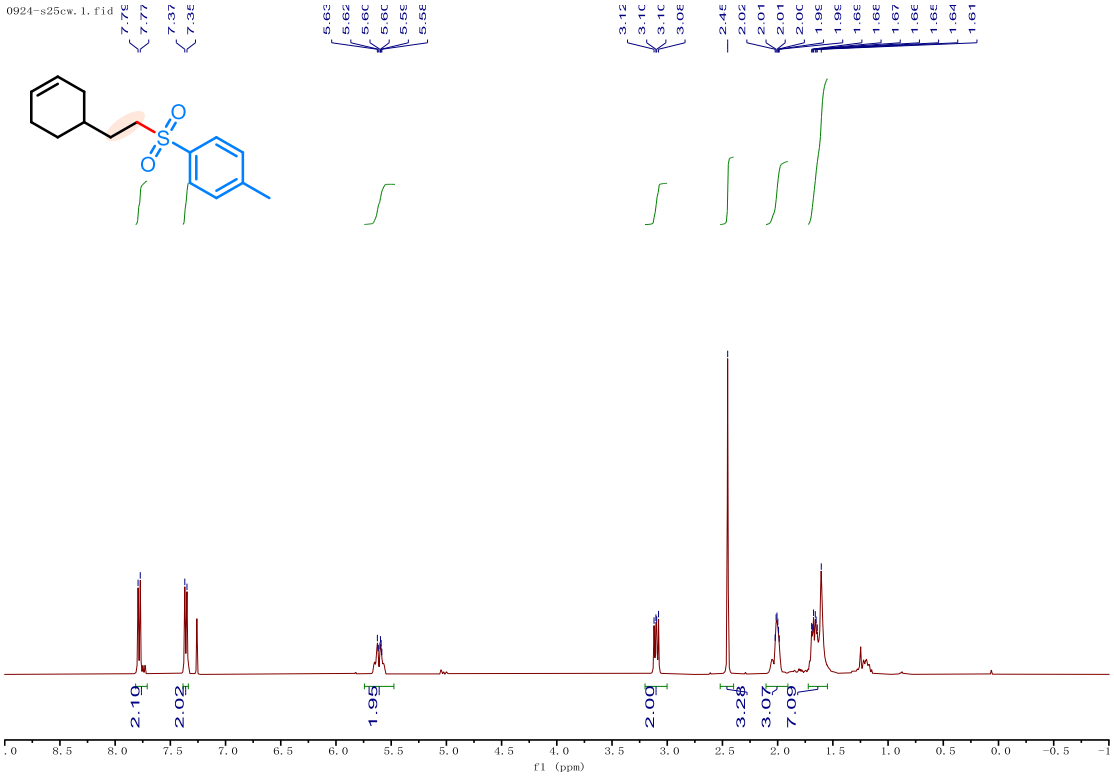
^{1}H NMR Spectrum of 34 ($CDCl_3$ as solvent, 400 MHz)



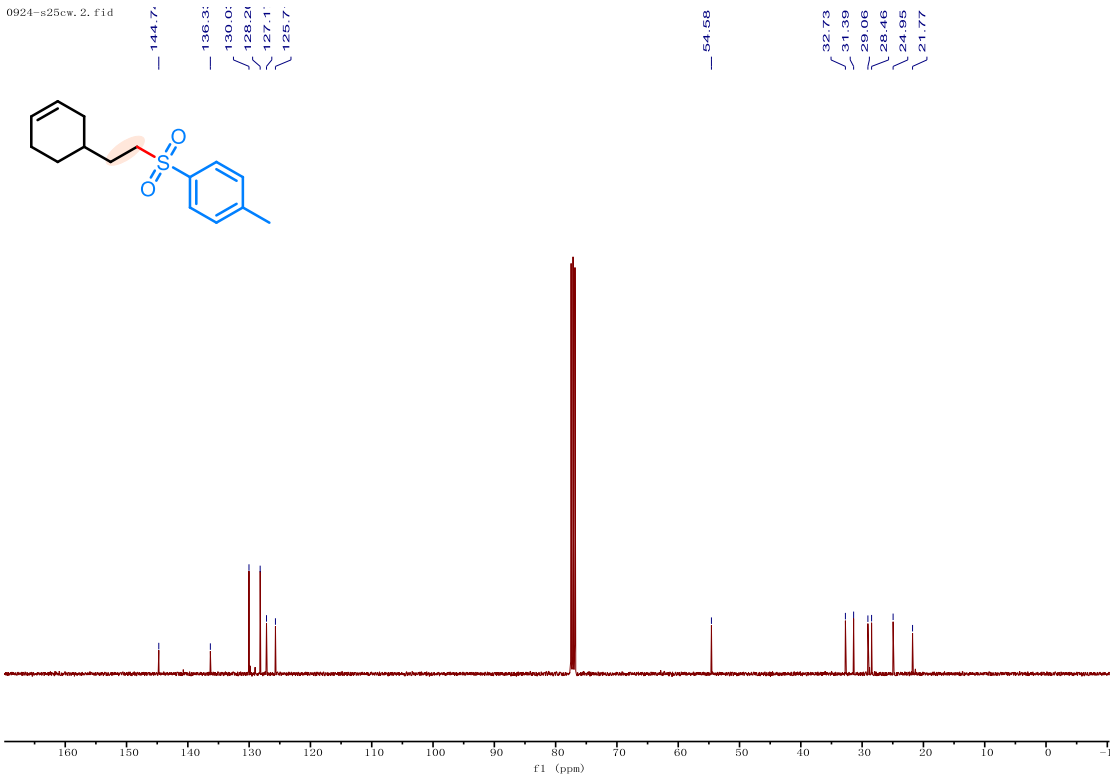
^{13}C {^{1}H} NMR Spectrum of 34 ($CDCl_3$ as solvent, 101 MHz)



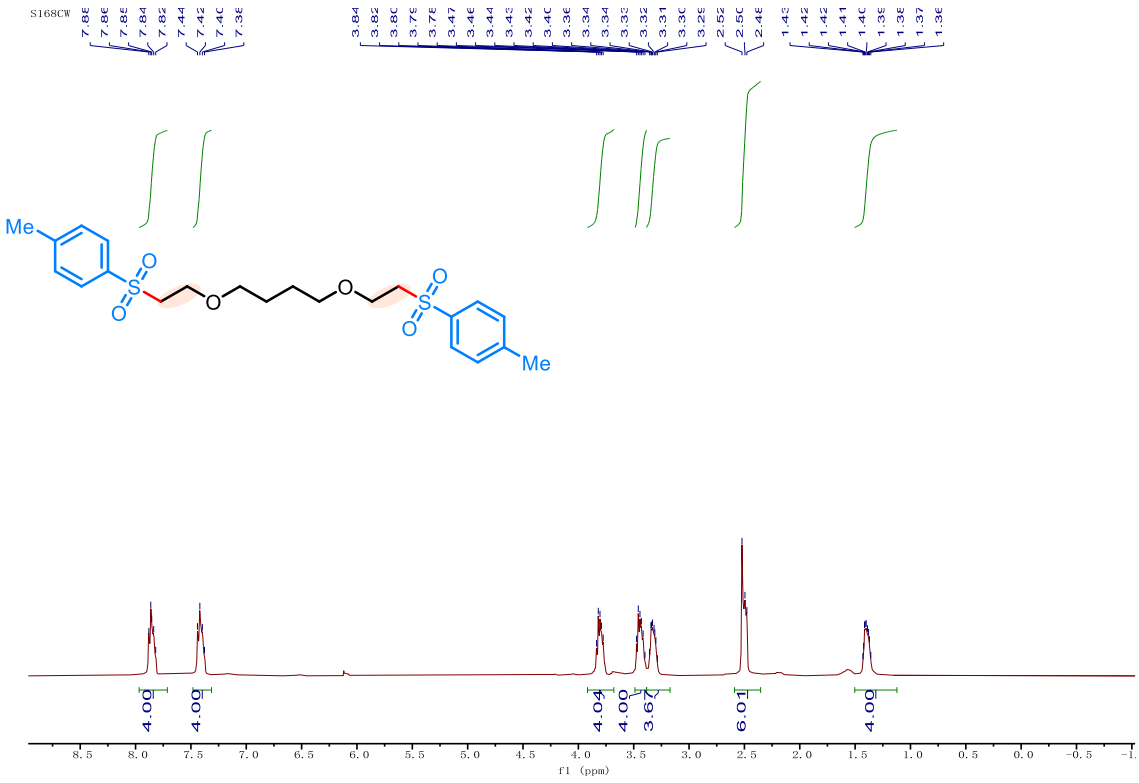
^{1}H NMR Spectrum of 35 ($CDCl_3$ as solvent, 400 MHz)



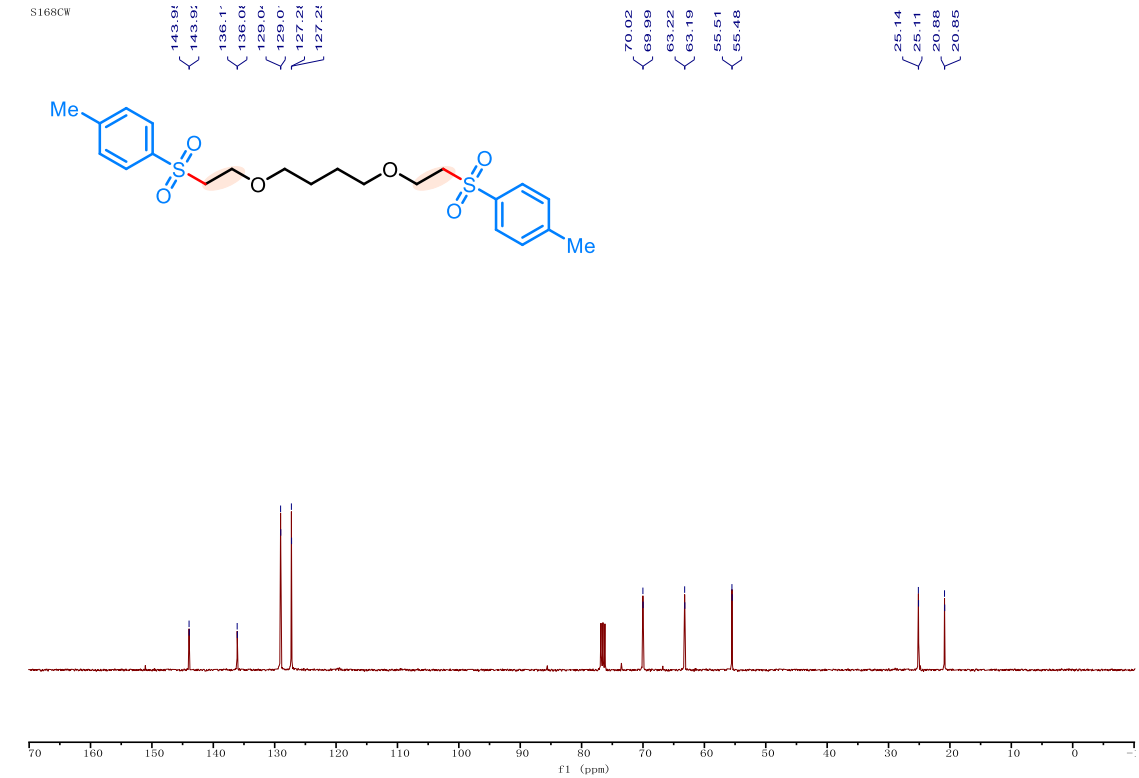
^{13}C {^{1}H} NMR Spectrum of 35 ($CDCl_3$ as solvent, 101 MHz)



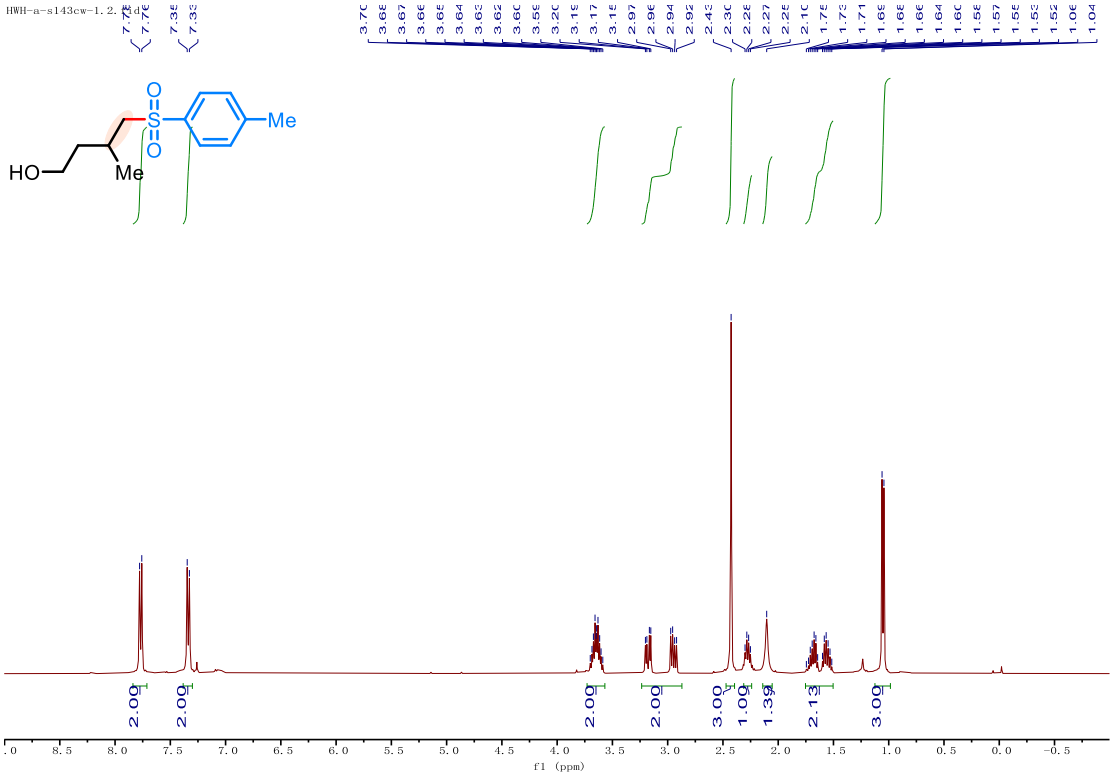
^{1}H NMR Spectrum of 36 ($CDCl_3$ as solvent, 400 MHz)



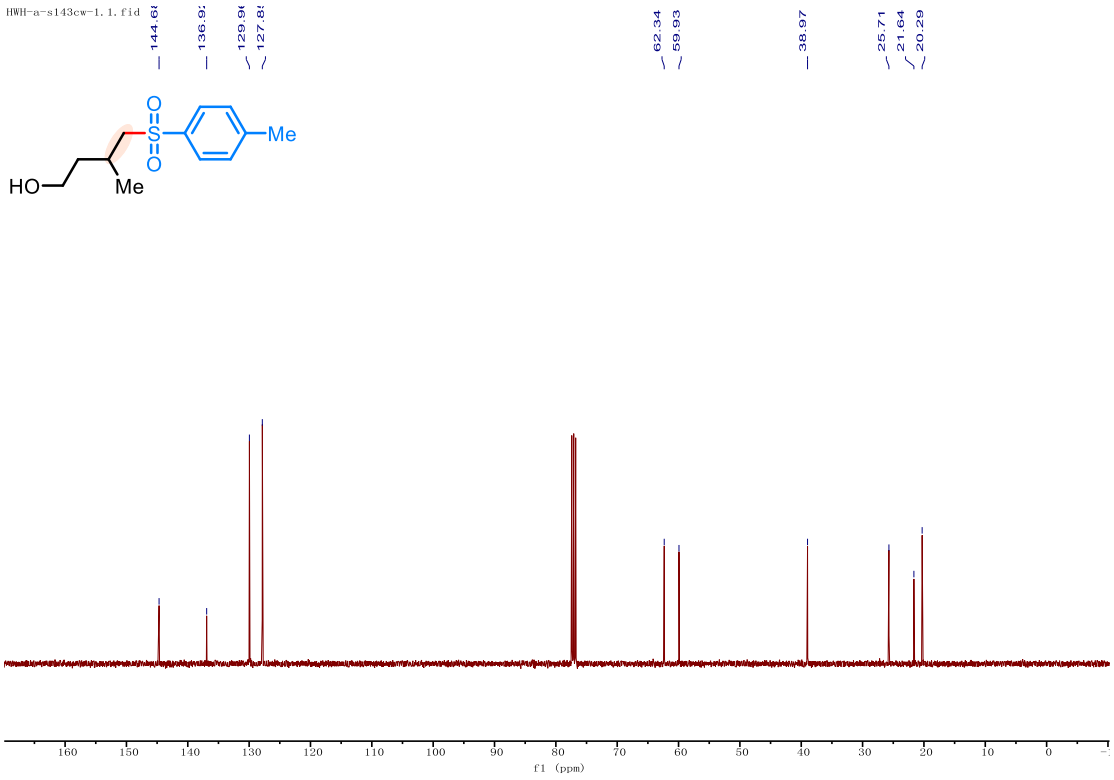
^{13}C {^{1}H} NMR Spectrum of 36 ($CDCl_3$ as solvent, 101 MHz)



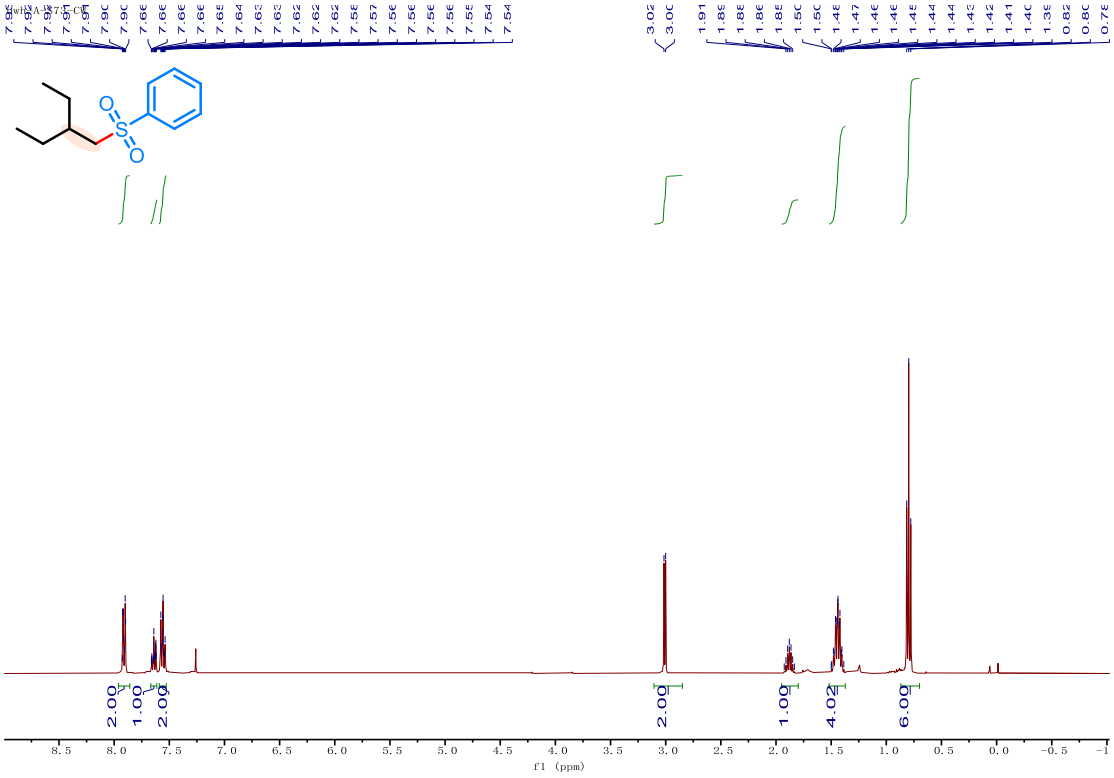
^{1}H NMR Spectrum of 37 ($CDCl_3$ as solvent, 400 MHz)



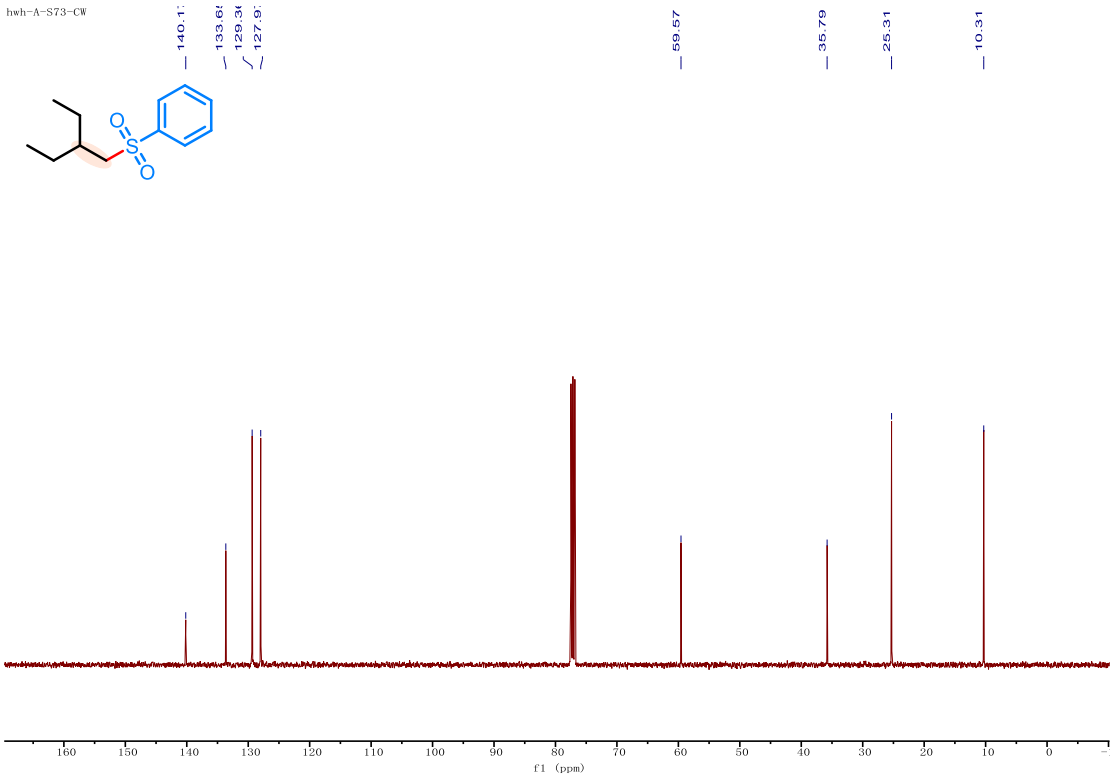
^{13}C {^{1}H} NMR Spectrum of 37 ($CDCl_3$ as solvent, 101 MHz)



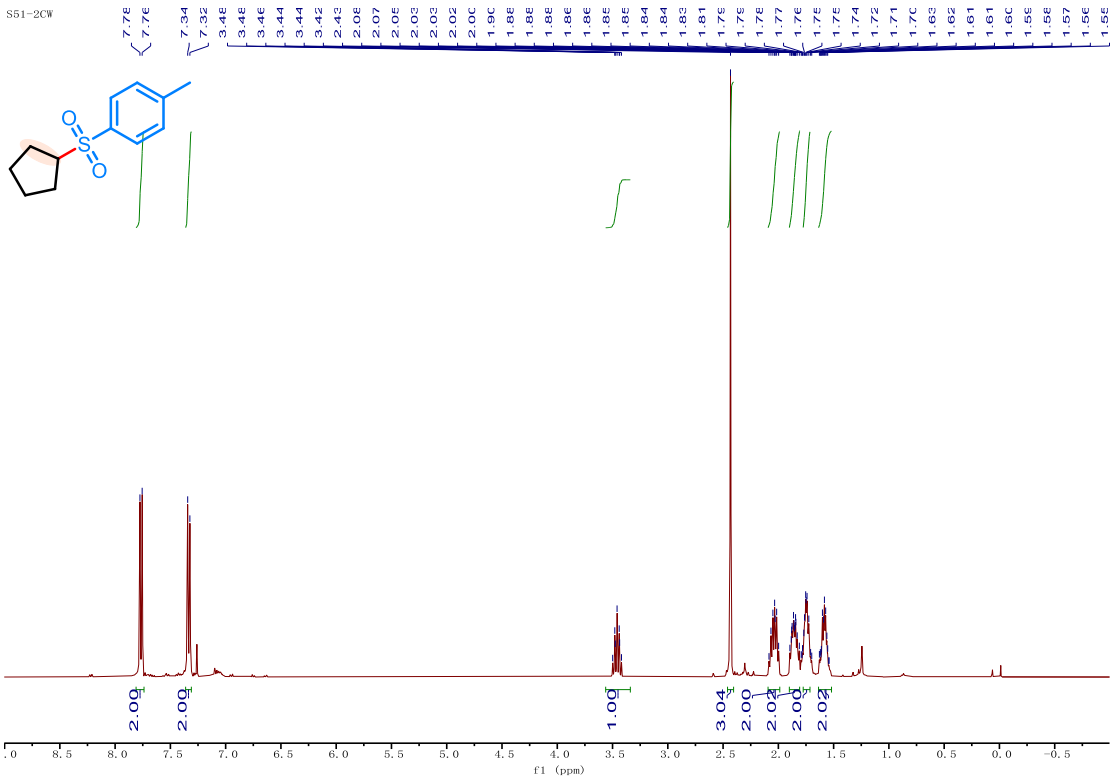
^{1}H NMR Spectrum of 38 ($CDCl_3$ as solvent, 400 MHz)



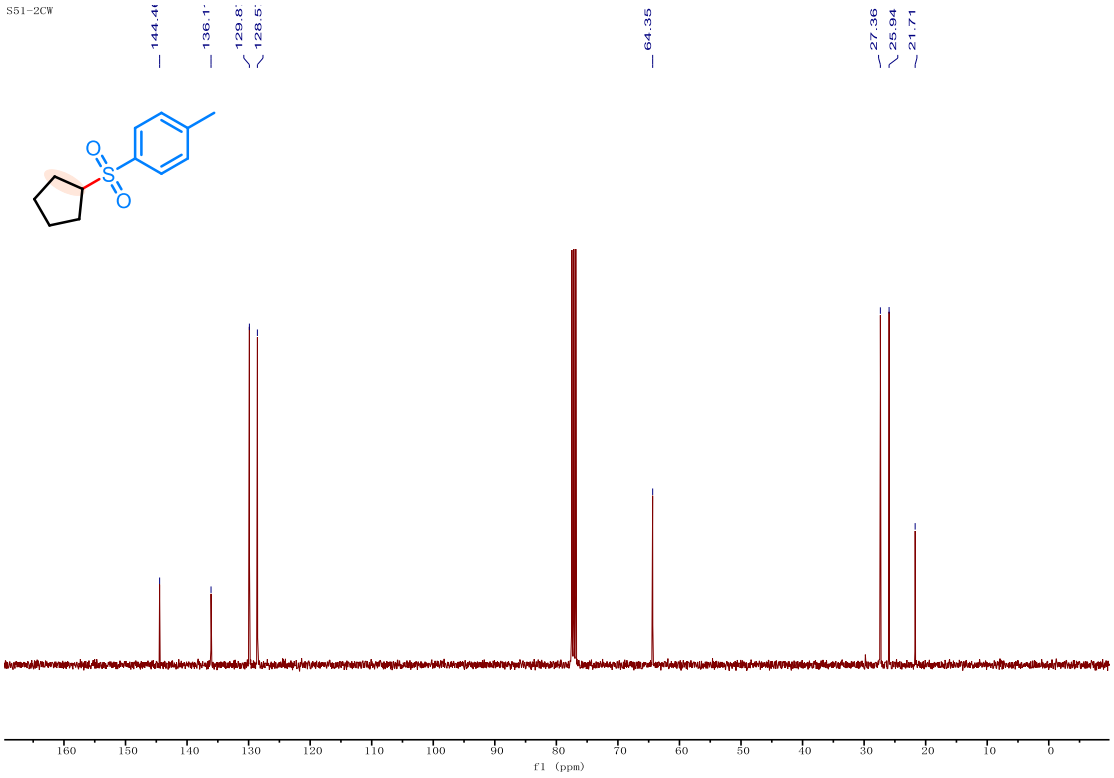
^{13}C {^{1}H} NMR Spectrum of 38 ($CDCl_3$ as solvent, 101 MHz)



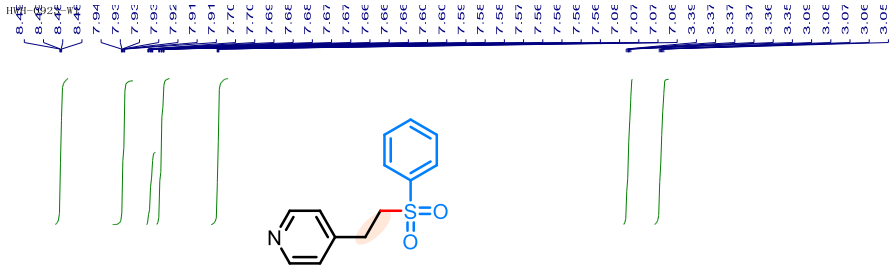
^{1}H NMR Spectrum of 39 ($CDCl_3$ as solvent, 400 MHz)

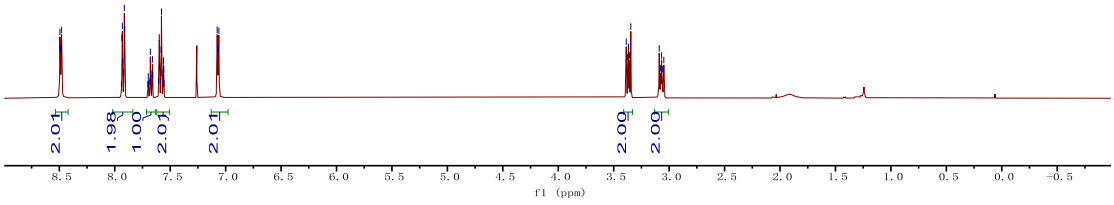


^{13}C {^{1}H} NMR Spectrum of 39 ($CDCl_3$ as solvent, 101 MHz)

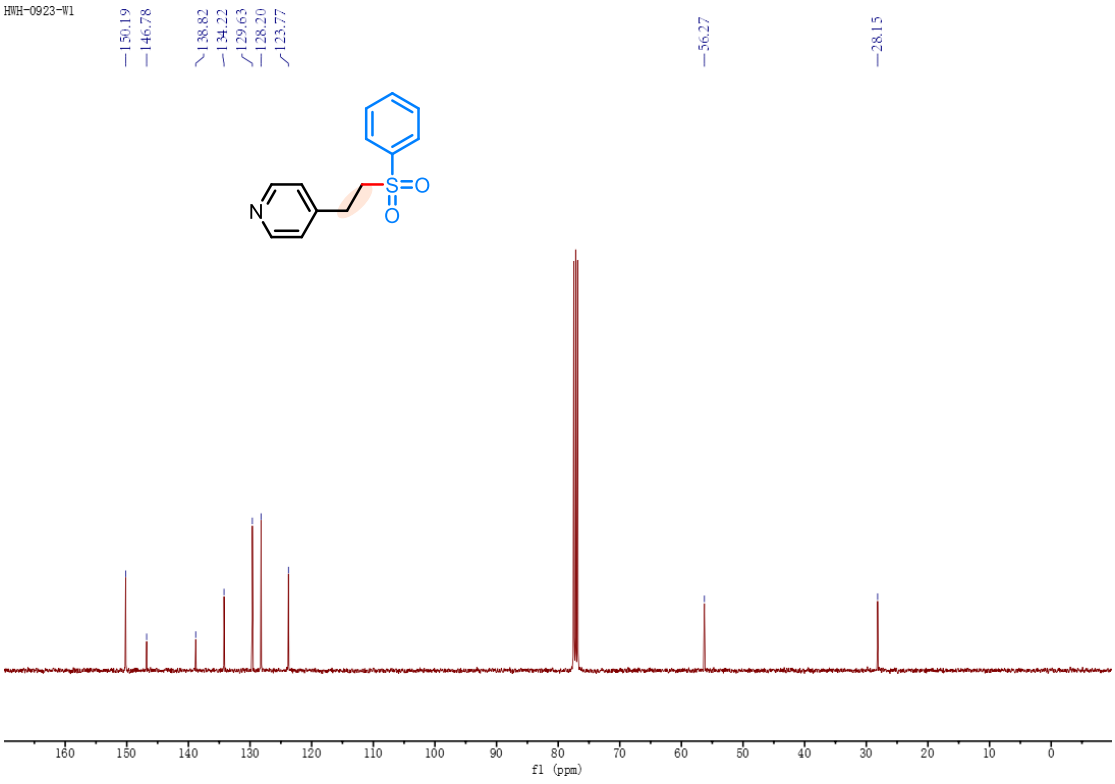


^{1}H NMR Spectrum of 41 ($CDCl_3$ as solvent, 400 MHz)

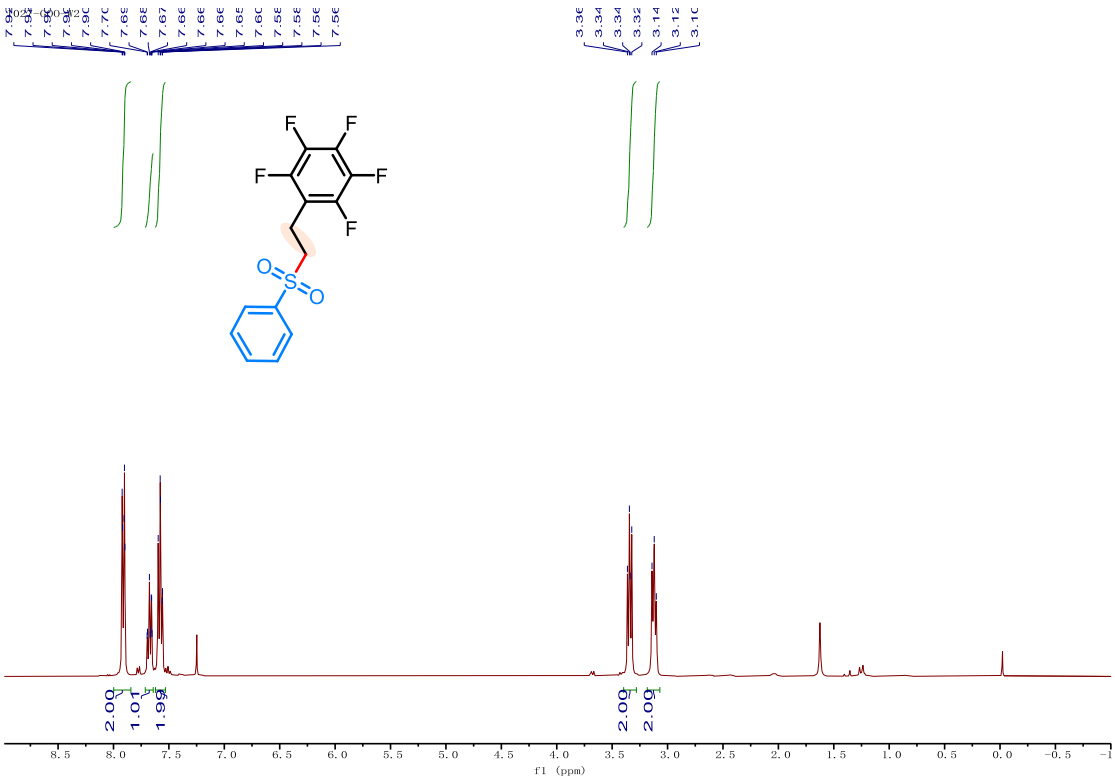




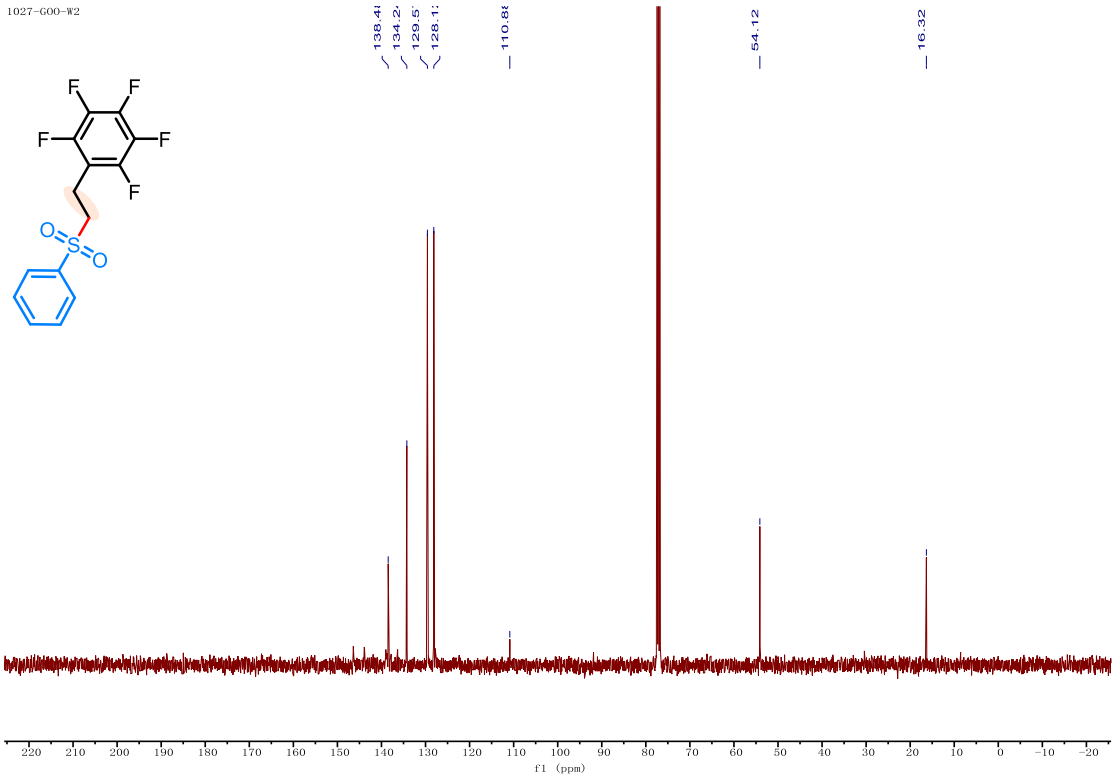
^{13}C {^{1}H} NMR Spectrum of 41 ($CDCl_3$ as solvent, 101 MHz)



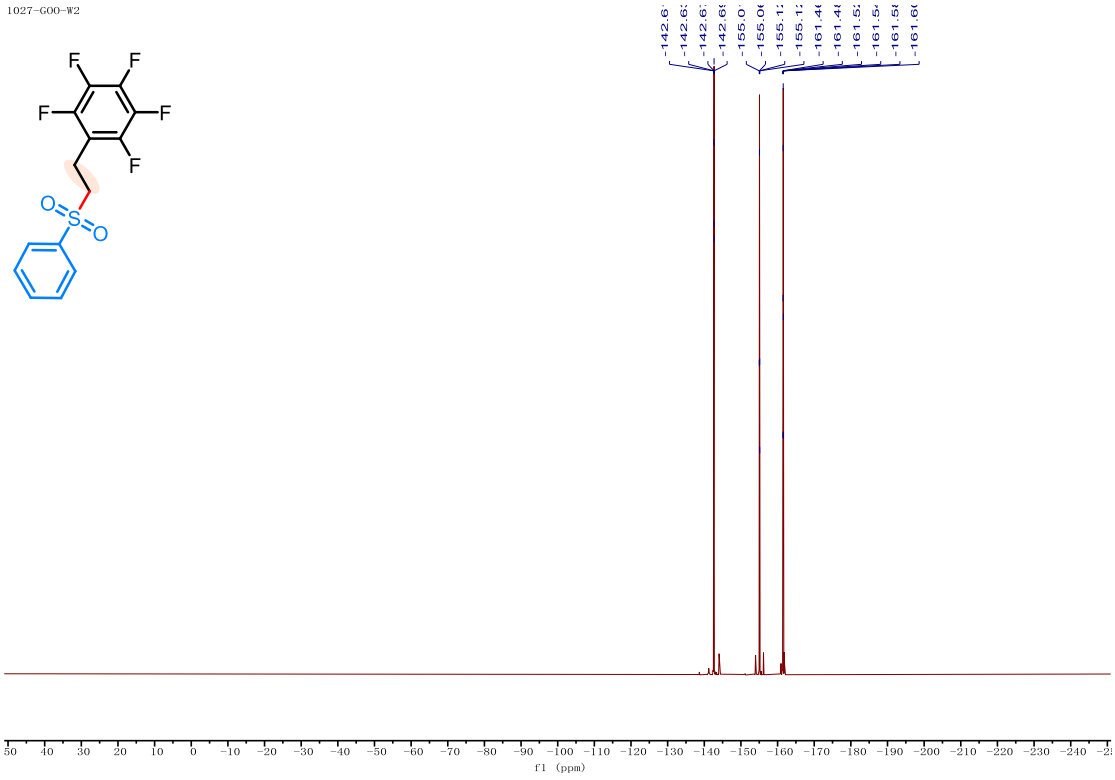
^{1}H NMR Spectrum of 42 ($CDCl_3$ as solvent, 400 MHz)



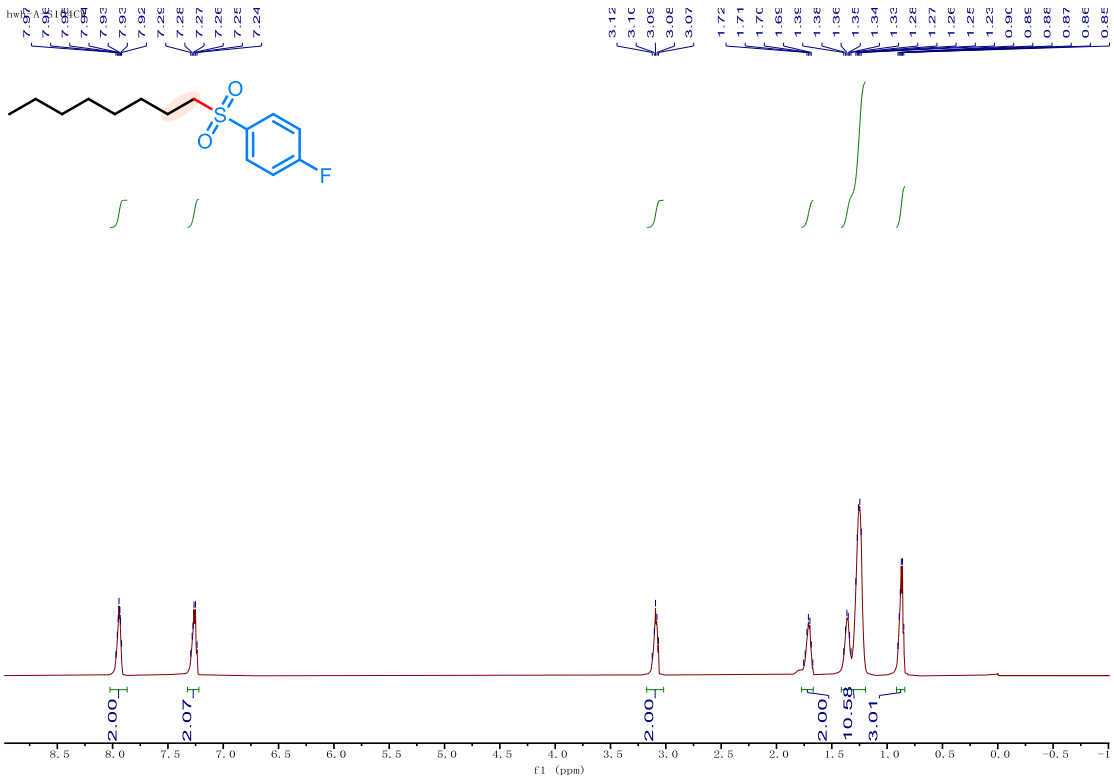
^{13}C {^{1}H} NMR Spectrum of 42 ($CDCl_3$ as solvent, 101 MHz)



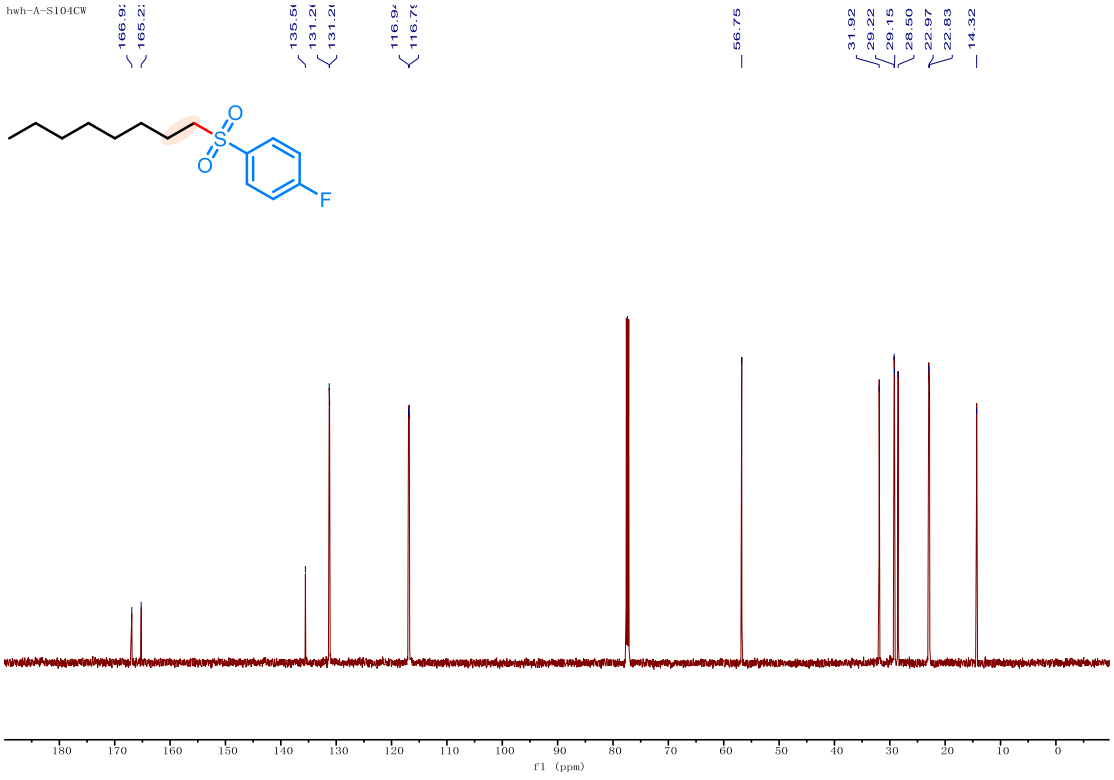
^{19}F {^{1}H} NMR Spectrum of 42 ($CDCl_3$ as solvent, 101 MHz)



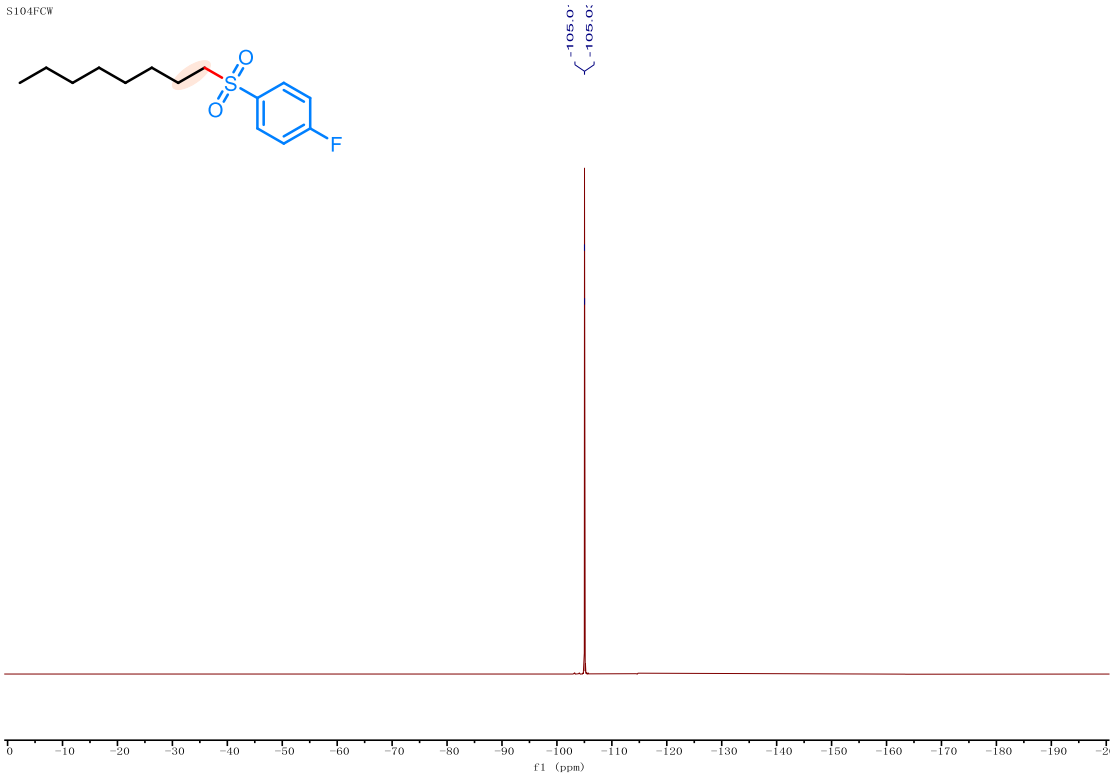
^{1}H NMR Spectrum of 43 ($CDCl_3$ as solvent, 600 MHz)



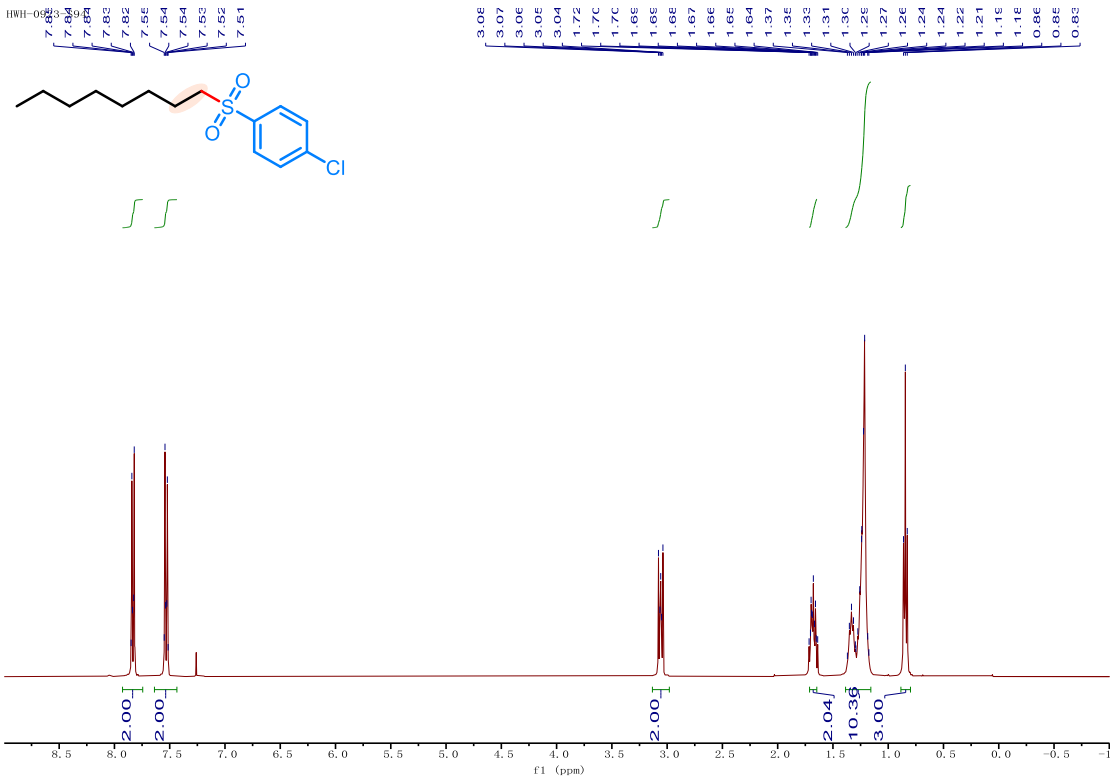
^{13}C {^{1}H} NMR Spectrum of 43 ($CDCl_3$ as solvent, 151 MHz)



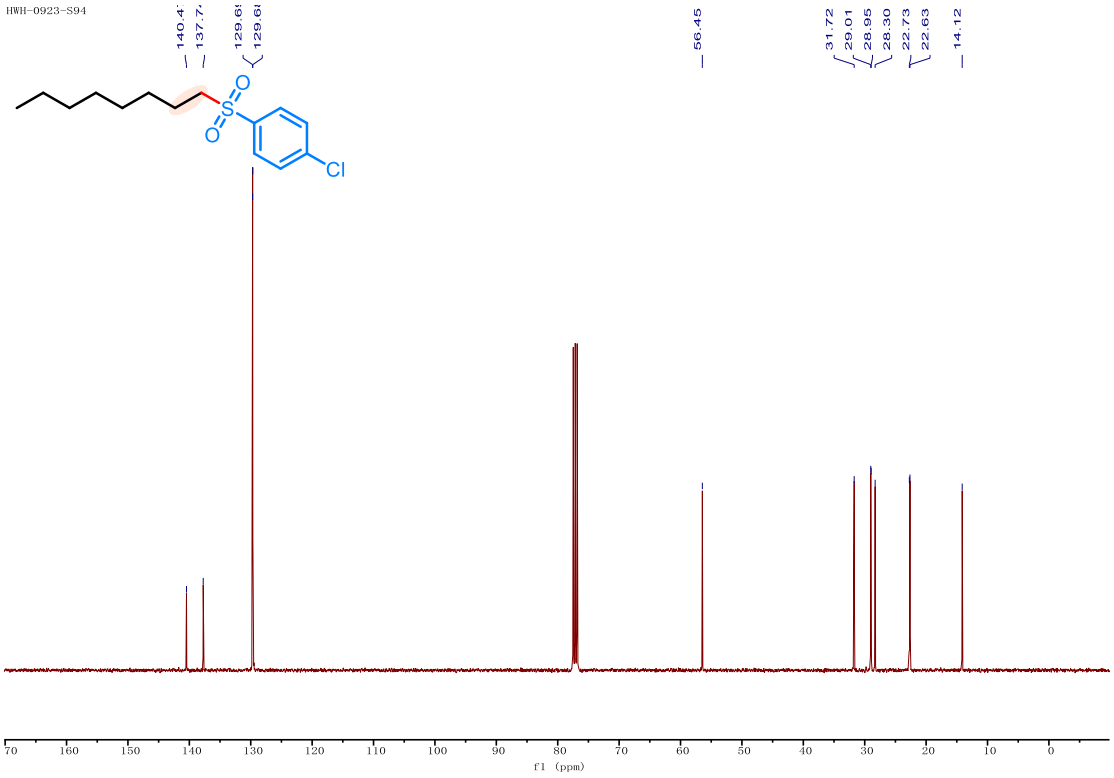
^{19}F {^{1}H} NMR Spectrum of 43 ($CDCl_3$ as solvent, 151 MHz)



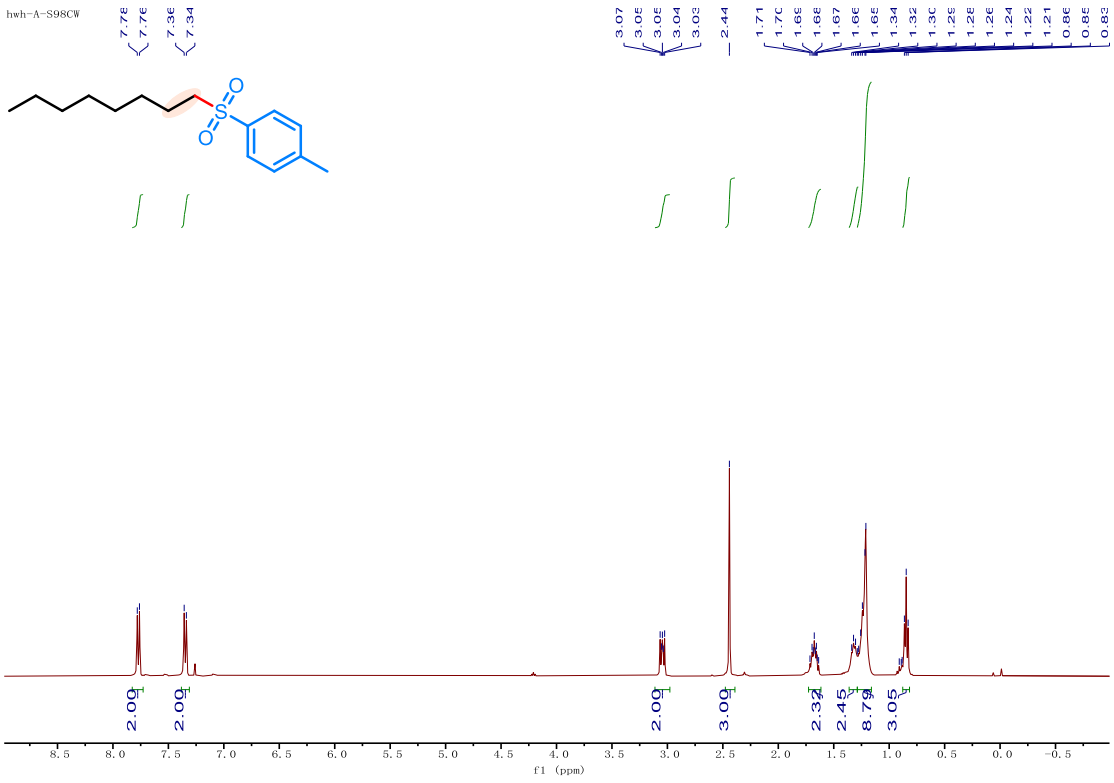
^{1}H NMR Spectrum of 44 ($CDCl_3$ as solvent, 400 MHz)



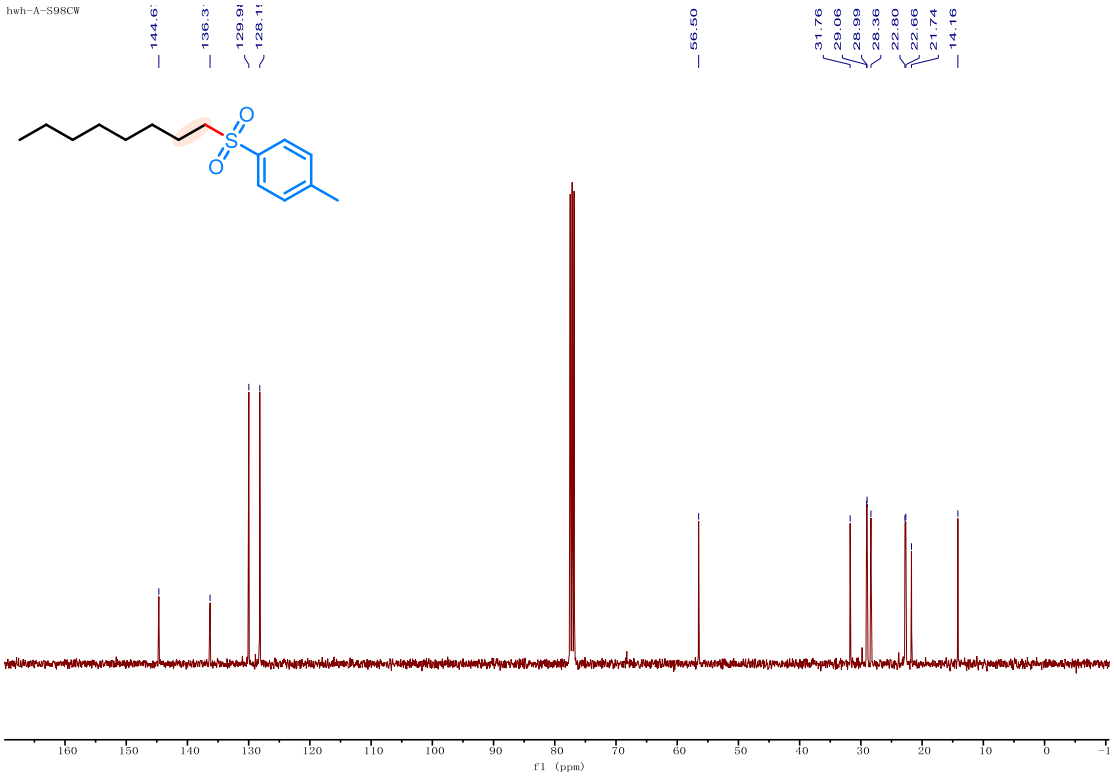
^{13}C {^{1}H} NMR Spectrum of 44 ($CDCl_3$ as solvent, 101 MHz)



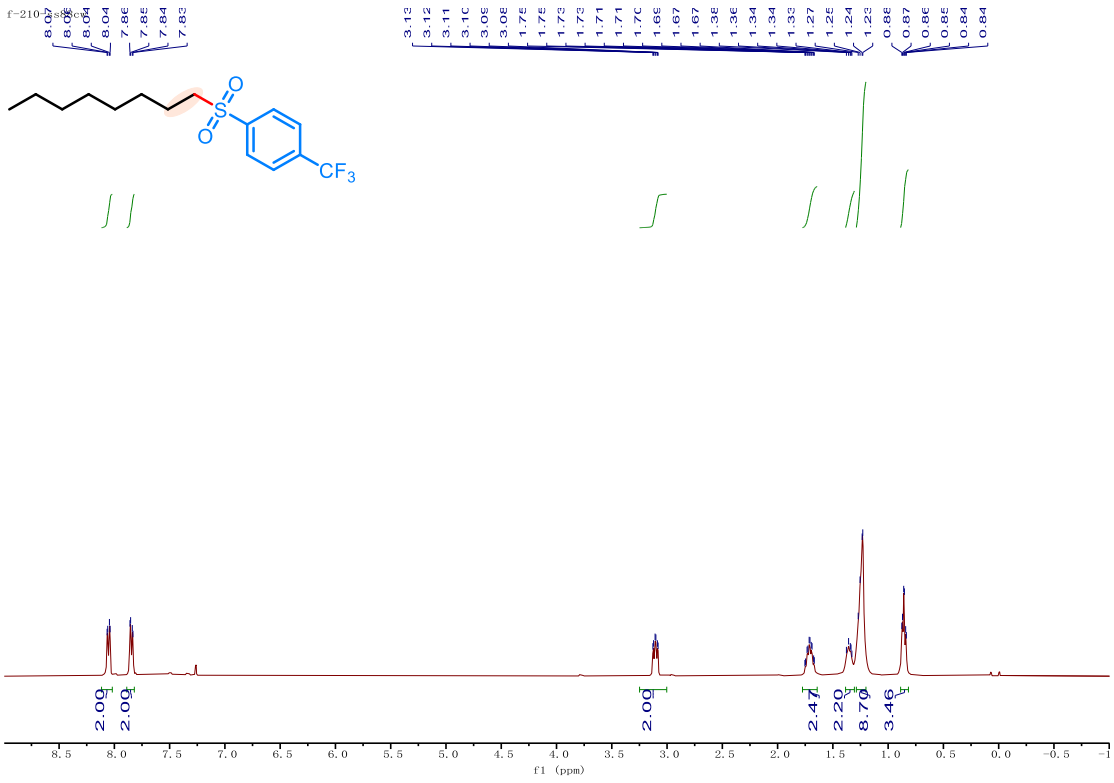
^{1}H NMR Spectrum of 45 ($CDCl_3$ as solvent, 400 MHz)



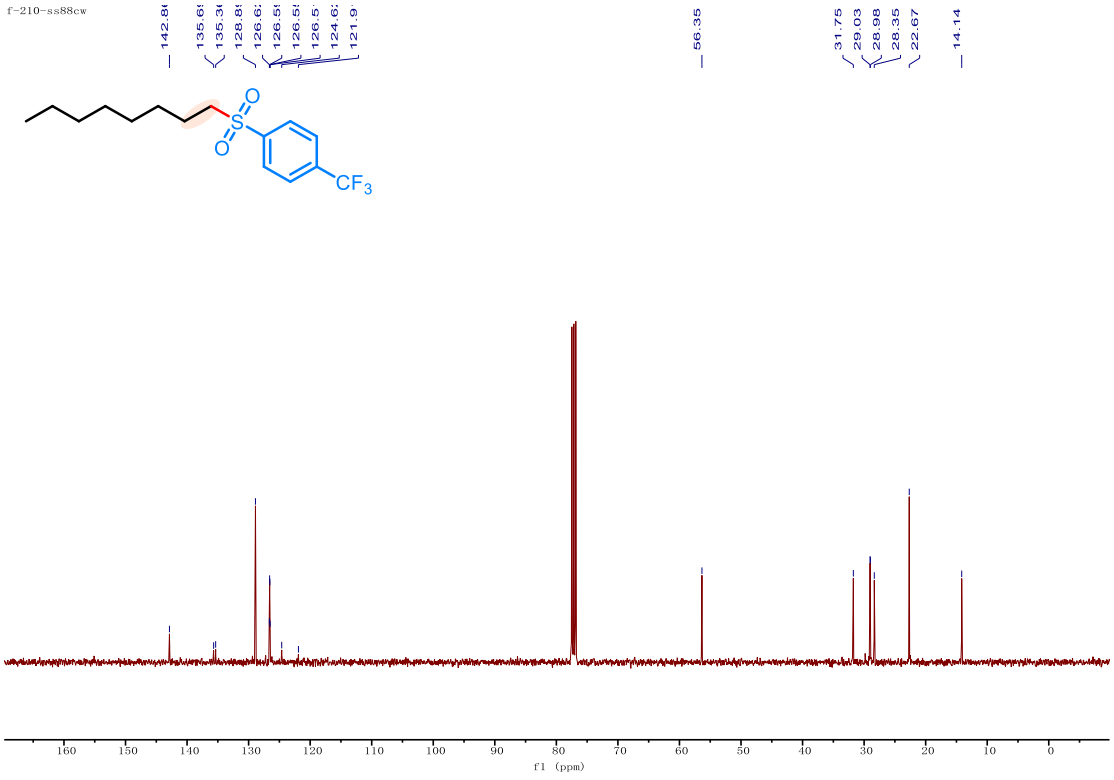
^{13}C {^{1}H} NMR Spectrum of 45 ($CDCl_3$ as solvent, 151 MHz)



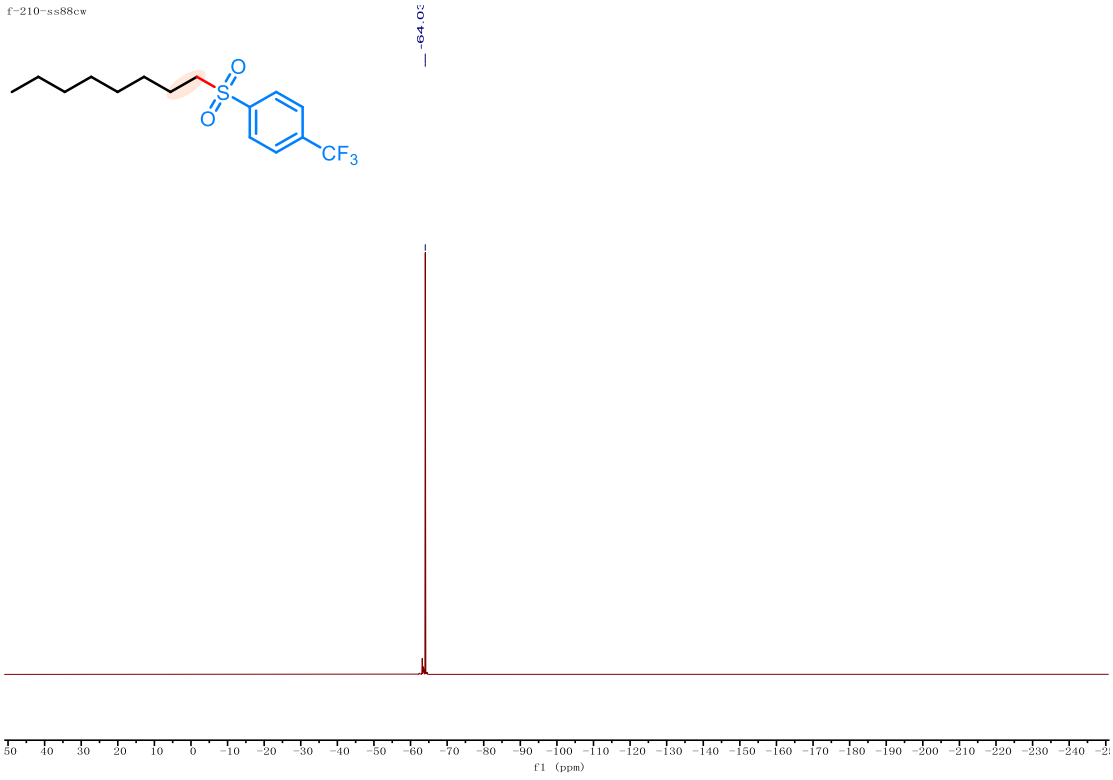
^{1}H NMR Spectrum of 46 ($CDCl_3$ as solvent, 400 MHz)



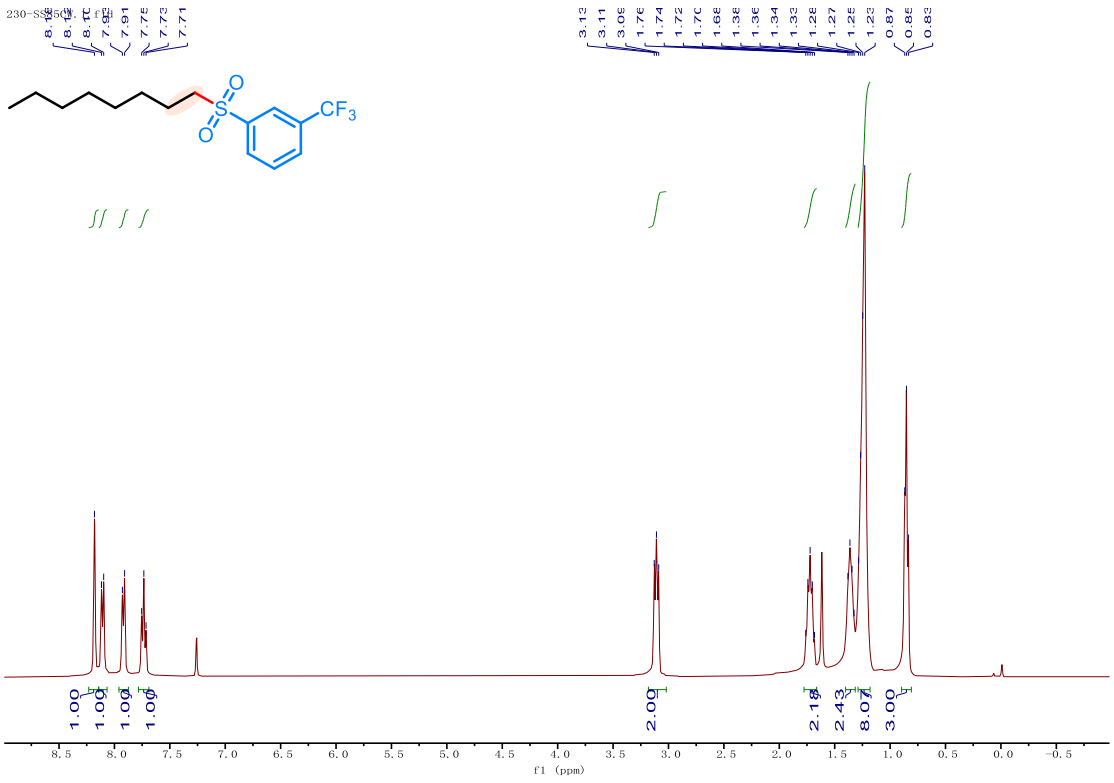
^{13}C {^{1}H} NMR Spectrum of 46 ($CDCl_3$ as solvent, 101 MHz)



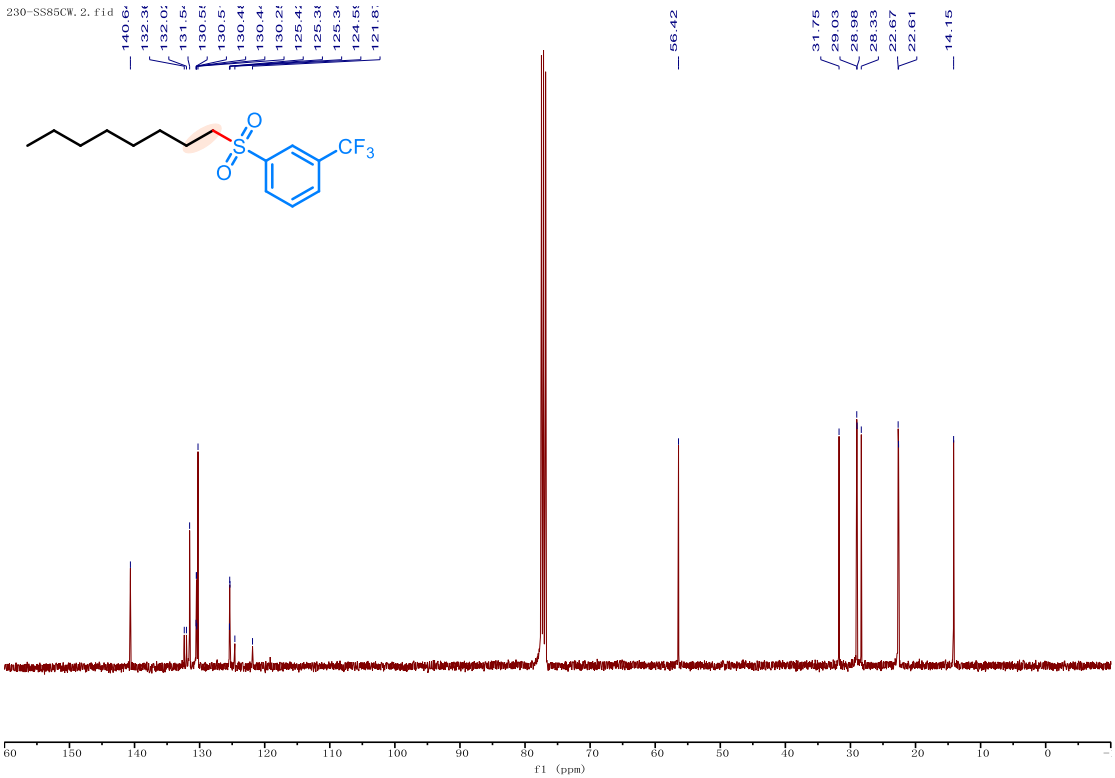
^{19}F {^{1}H} NMR Spectrum of 46 ($CDCl_3$ as solvent, 151 MHz)



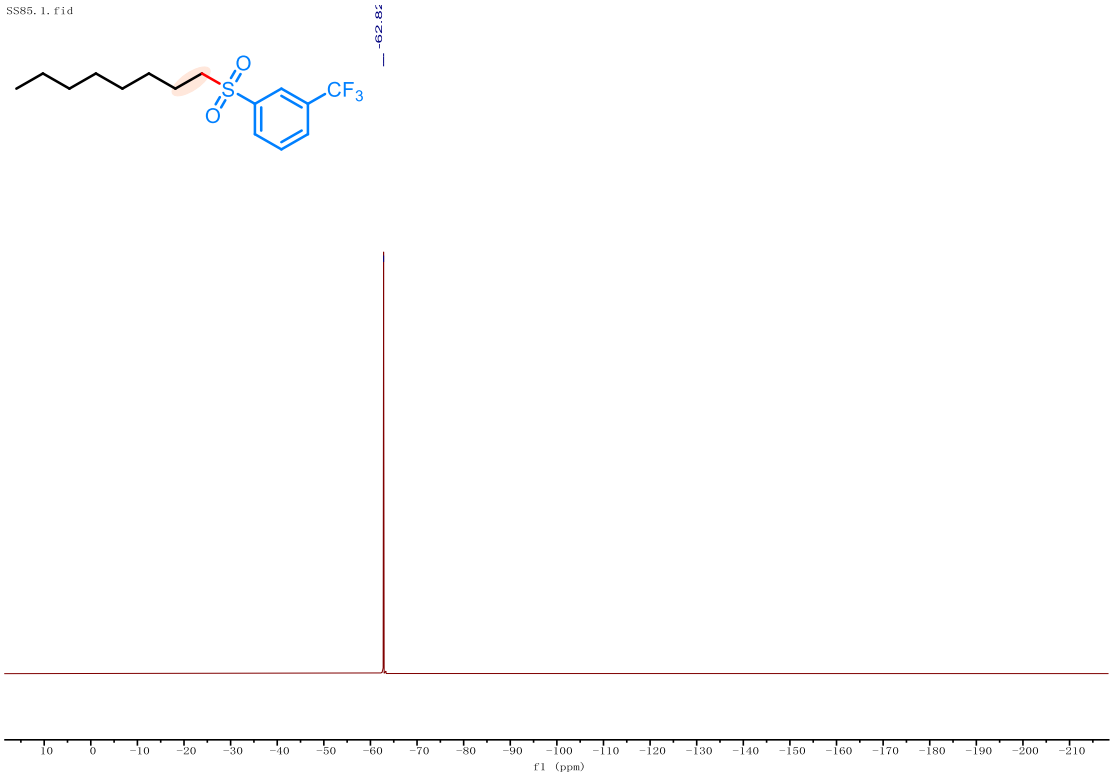
^{1}H NMR Spectrum of 47 ($CDCl_3$ as solvent, 400 MHz)



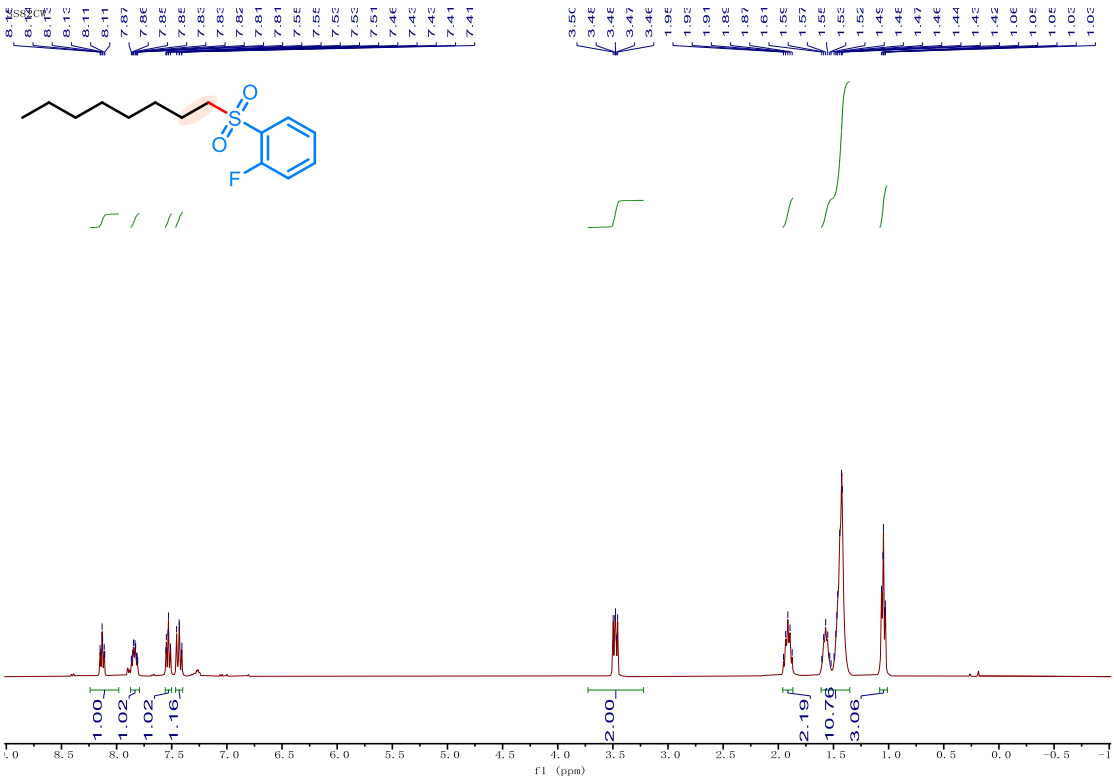
^{13}C {^{1}H} NMR Spectrum of 47 ($CDCl_3$ as solvent, 101 MHz)



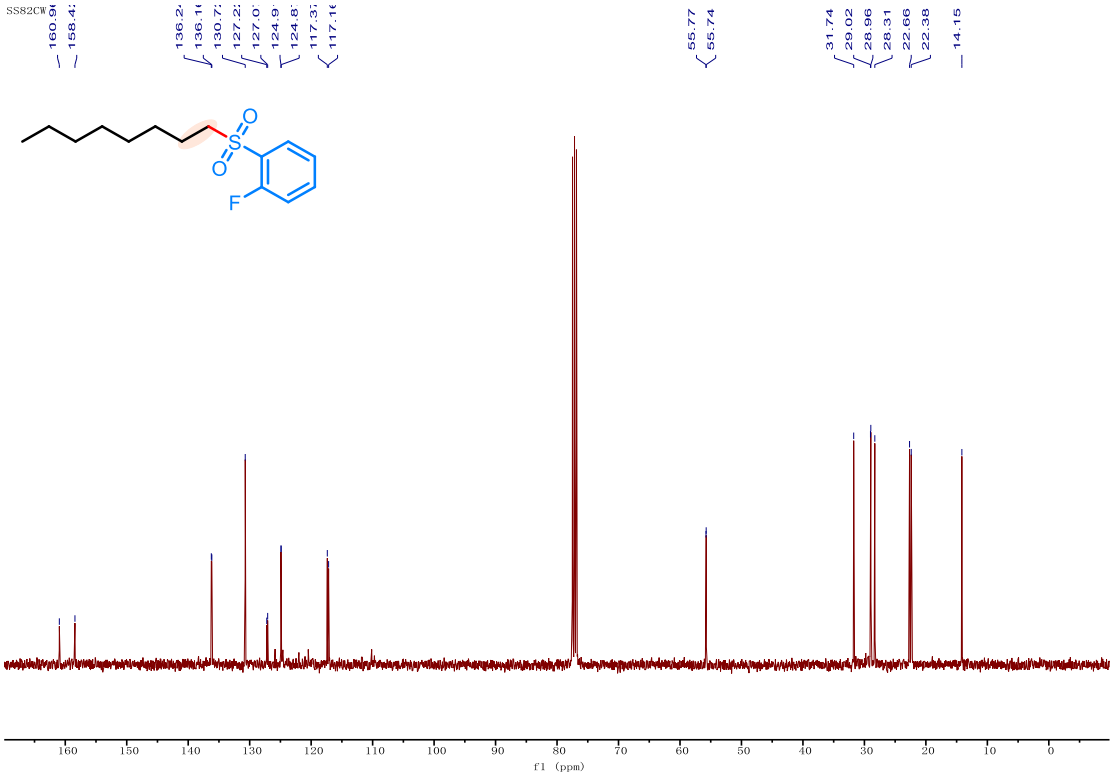
^{19}F {^{1}H} NMR Spectrum of 47 ($CDCl_3$ as solvent, 101 MHz)



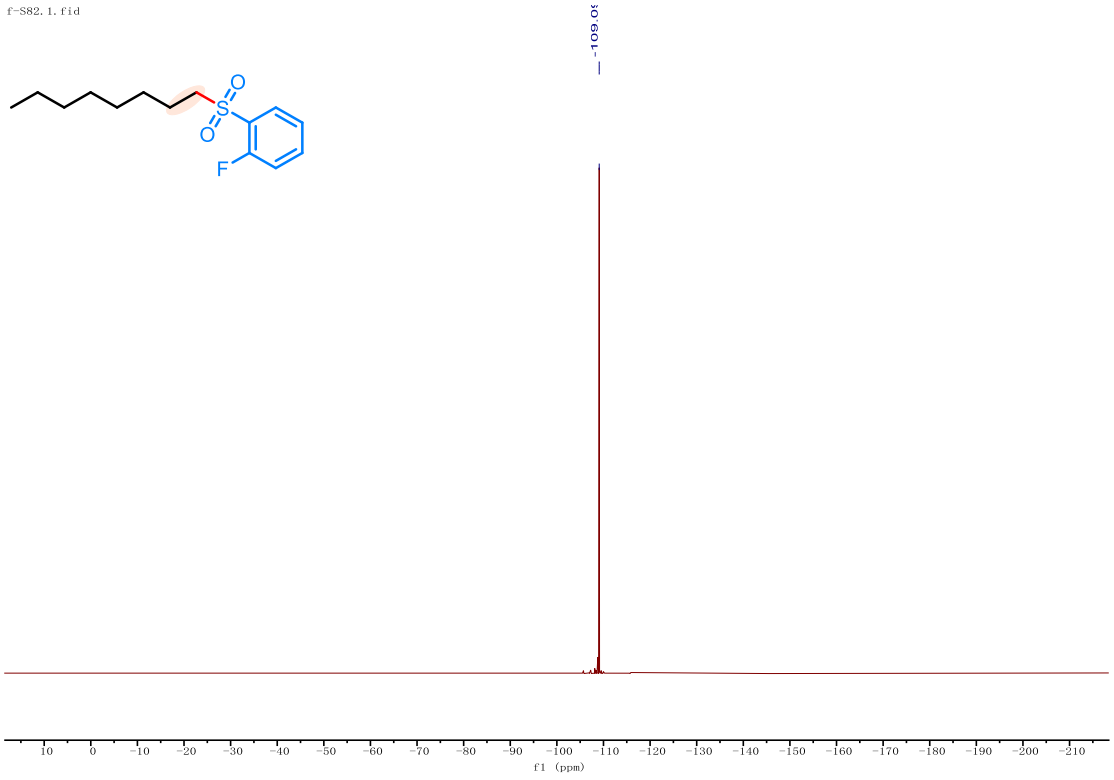
^{1}H NMR Spectrum of 48 ($CDCl_3$ as solvent, 400 MHz)



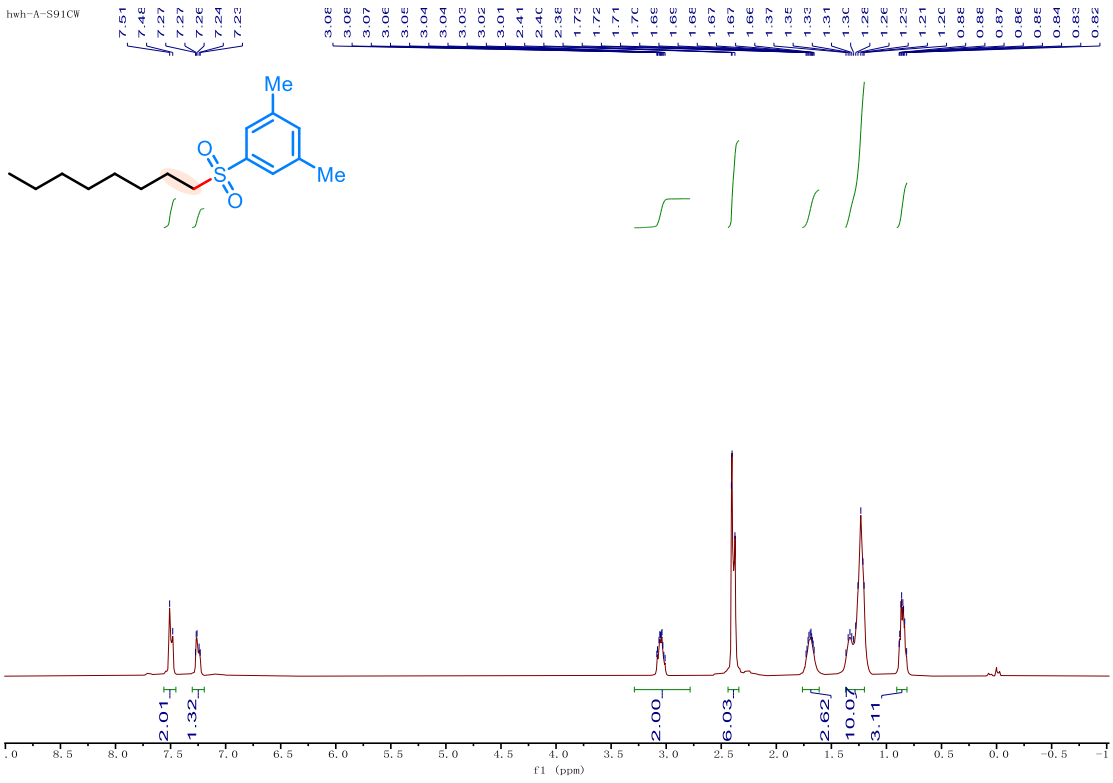
^{13}C {^{1}H} NMR Spectrum of 48 ($CDCl_3$ as solvent, 101 MHz)



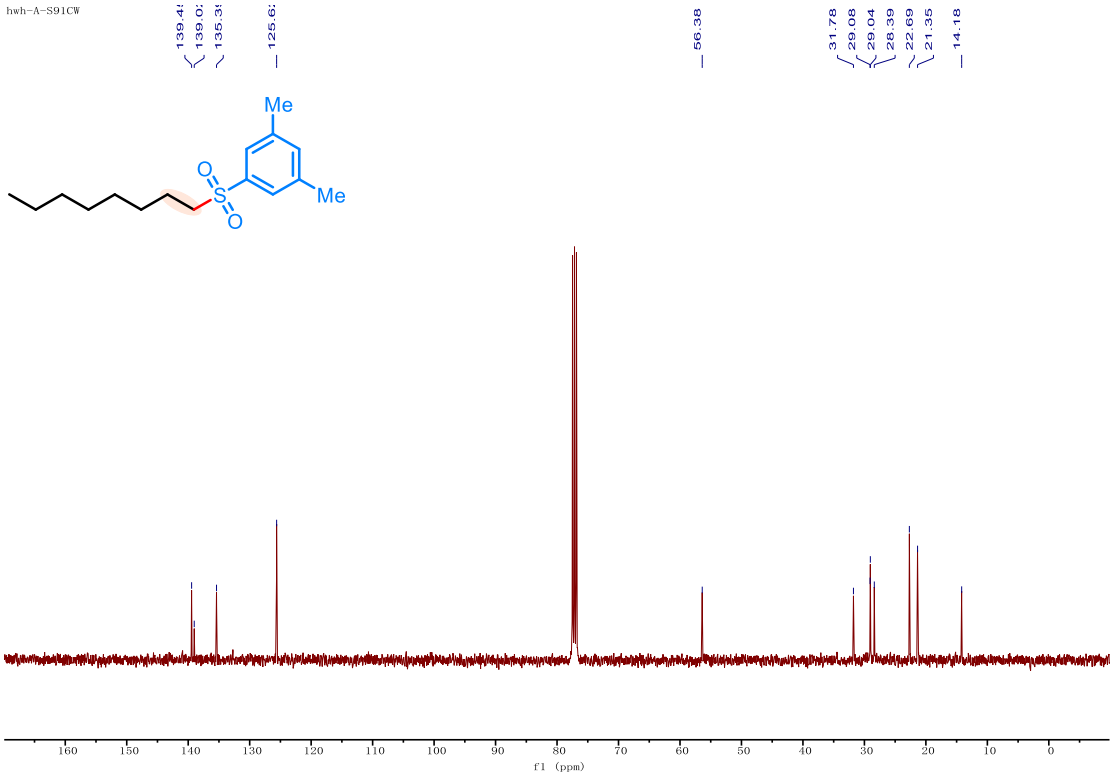
^{19}F {^{1}H} NMR Spectrum of 48 ($CDCl_3$ as solvent, 101 MHz)



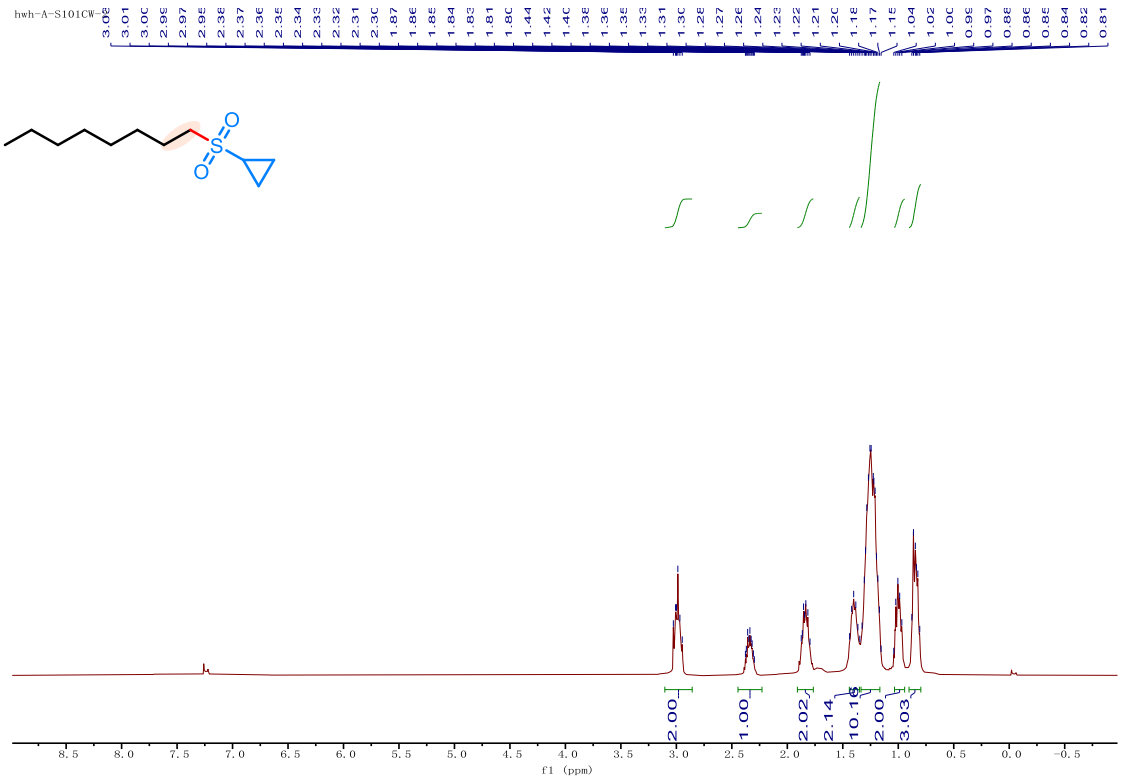
^{1}H NMR Spectrum of 49 ($CDCl_3$ as solvent, 400 MHz)



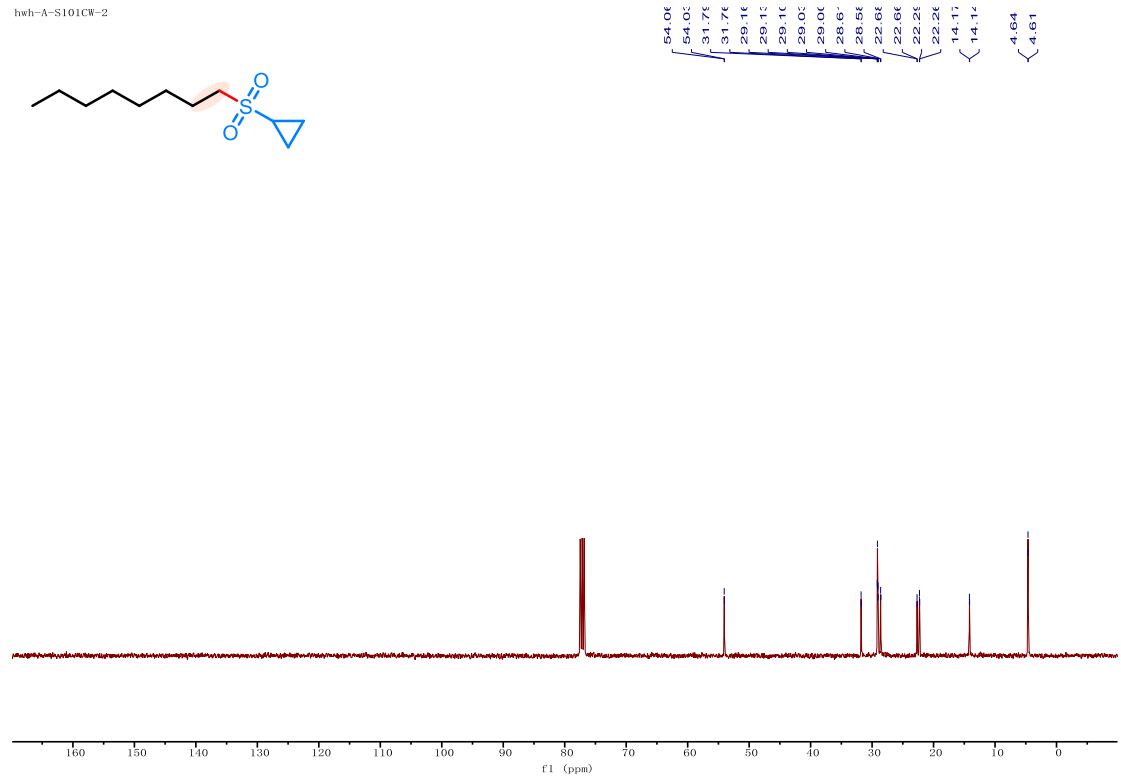
^{13}C {^{1}H} NMR Spectrum of 49 ($CDCl_3$ as solvent, 101 MHz)



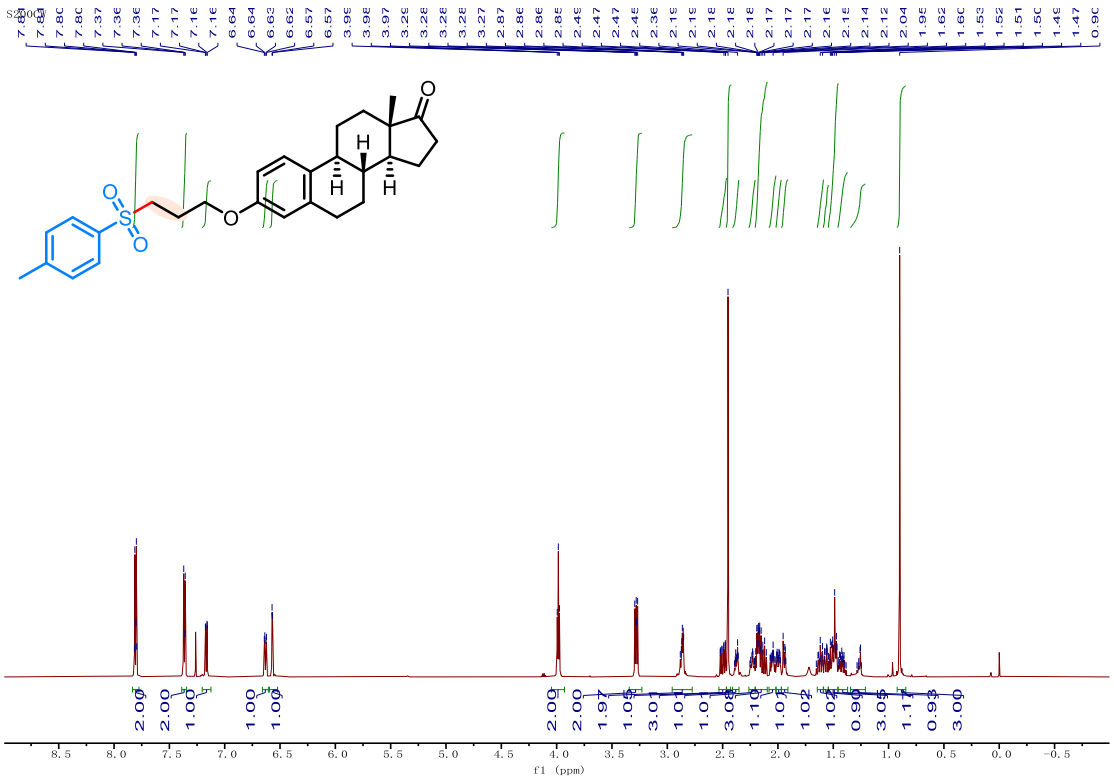
^{1}H NMR Spectrum of 50 ($CDCl_3$ as solvent, 400 MHz)



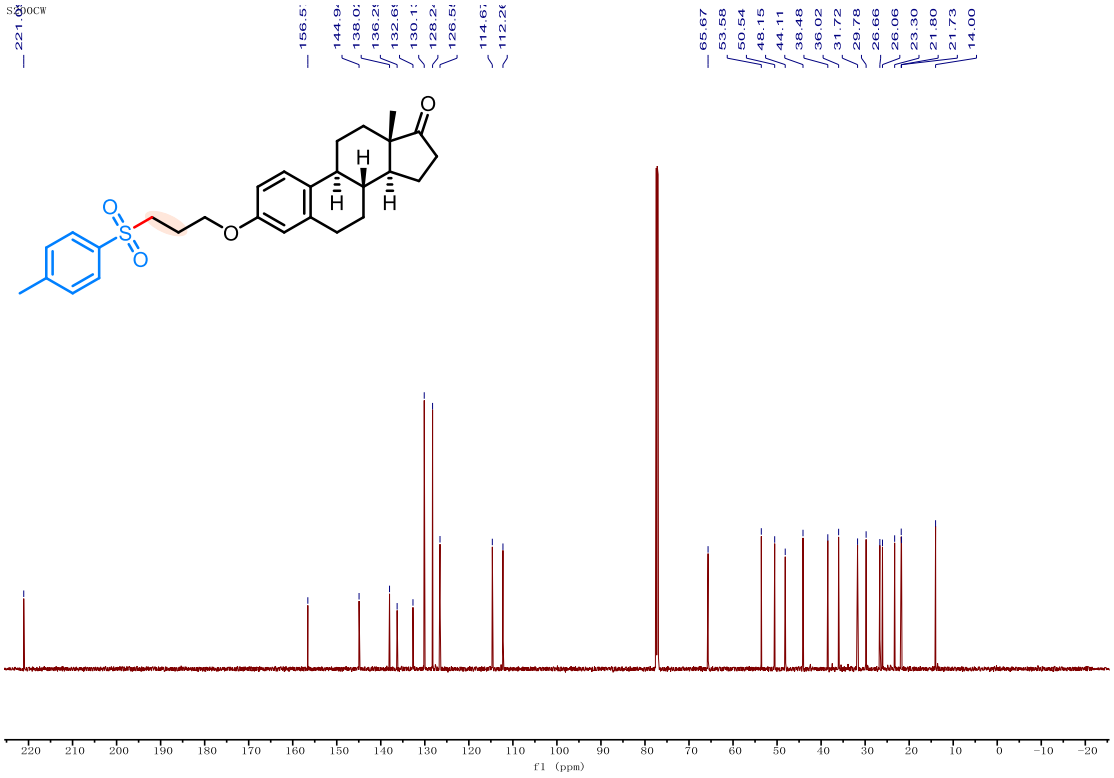
^{13}C {^{1}H} NMR Spectrum of 50 ($CDCl_3$ as solvent, 101 MHz)



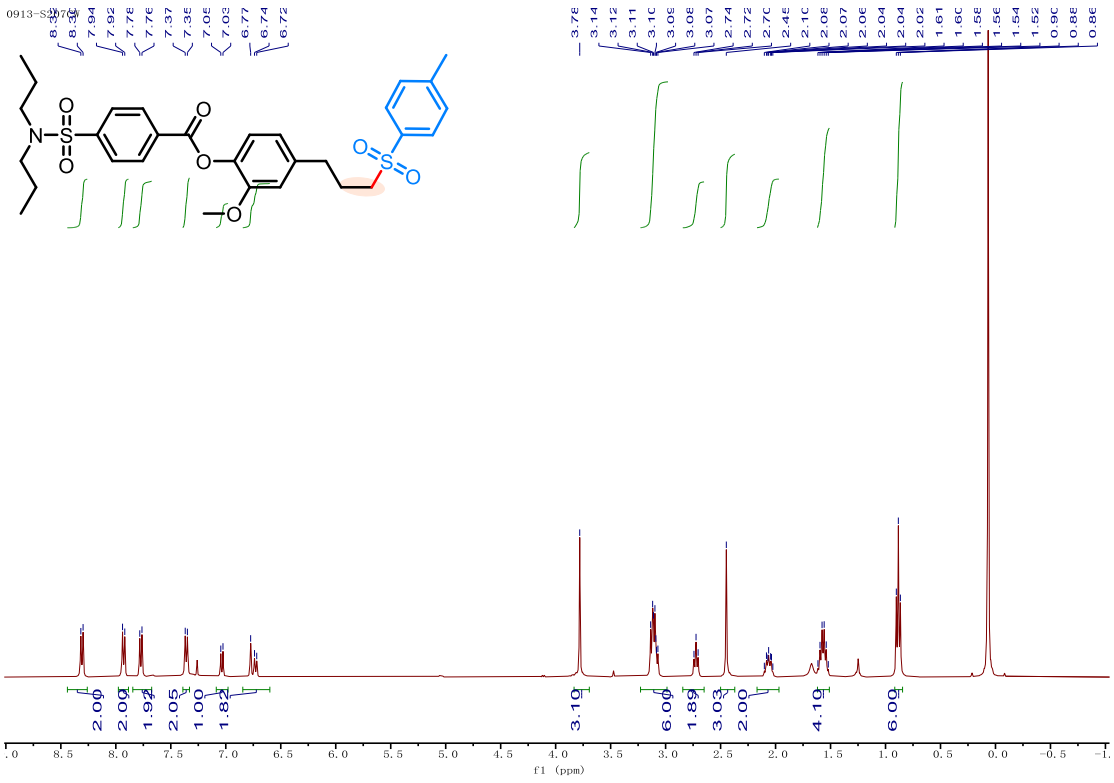
^{1}H NMR Spectrum of 51 ($CDCl_3$ as solvent, 600 MHz)



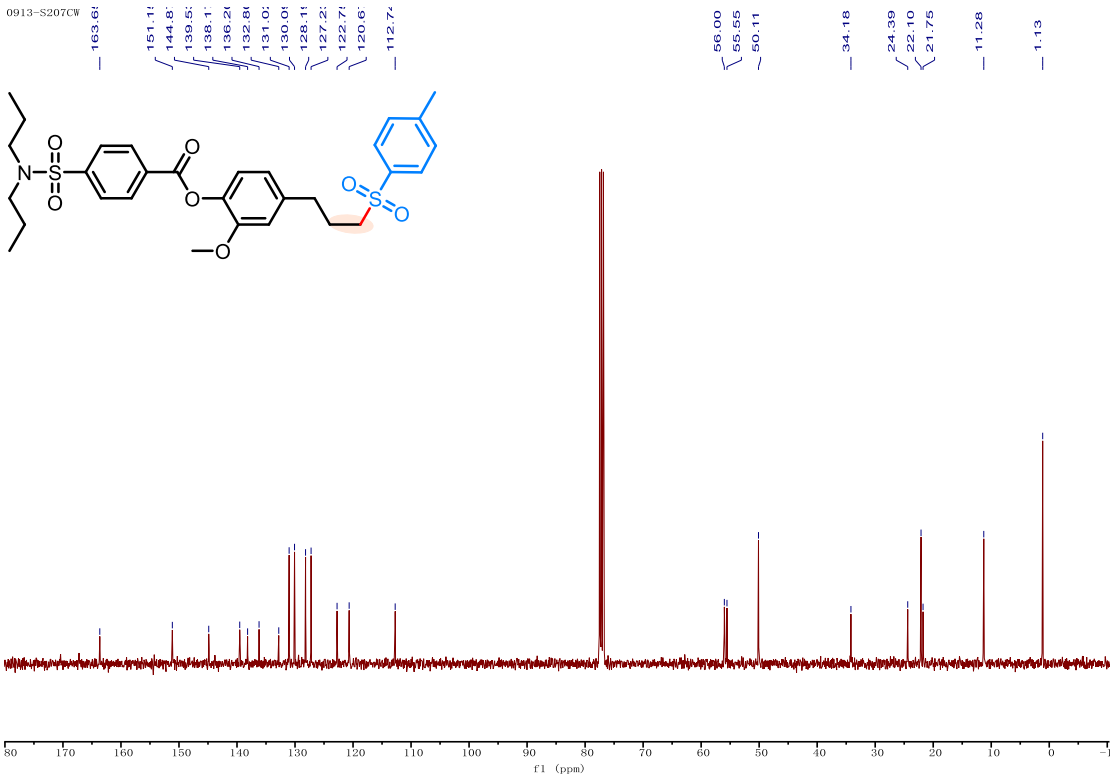
^{13}C {^{1}H} NMR Spectrum of 51 ($CDCl_3$ as solvent, 101 MHz)



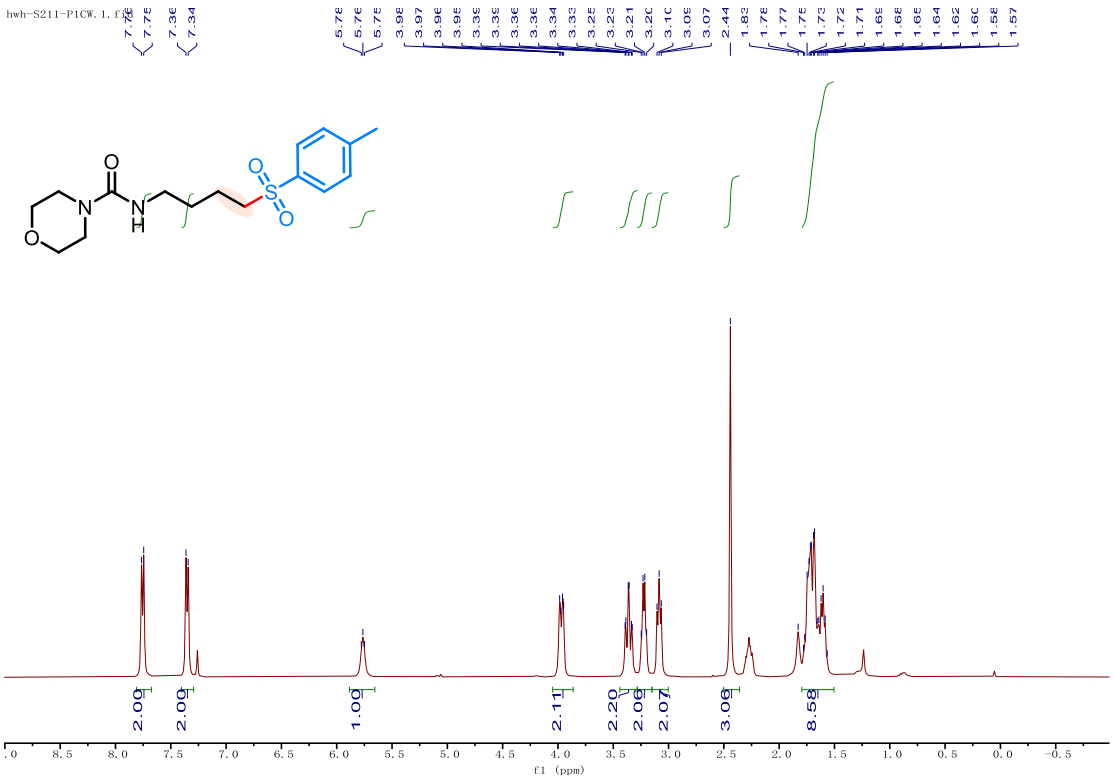
^{1}H NMR Spectrum of 52 ($CDCl_3$ as solvent, 400 MHz)



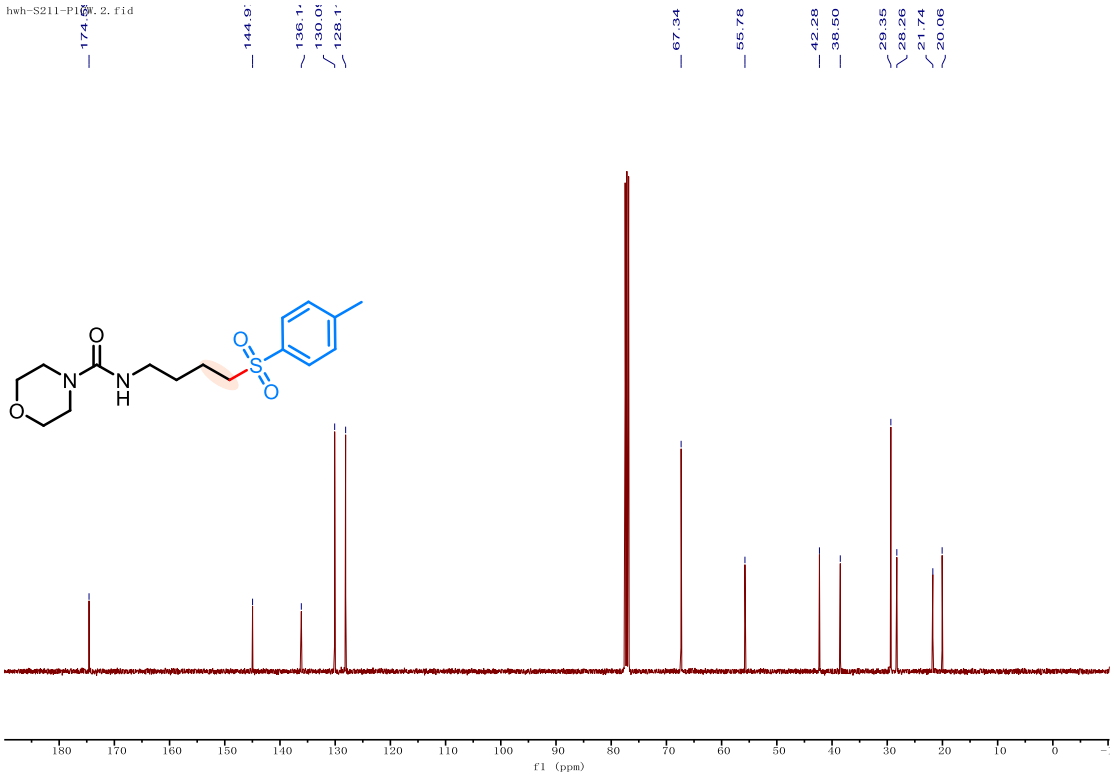
^{13}C {^{1}H} NMR Spectrum of 52 ($CDCl_3$ as solvent, 101 MHz)



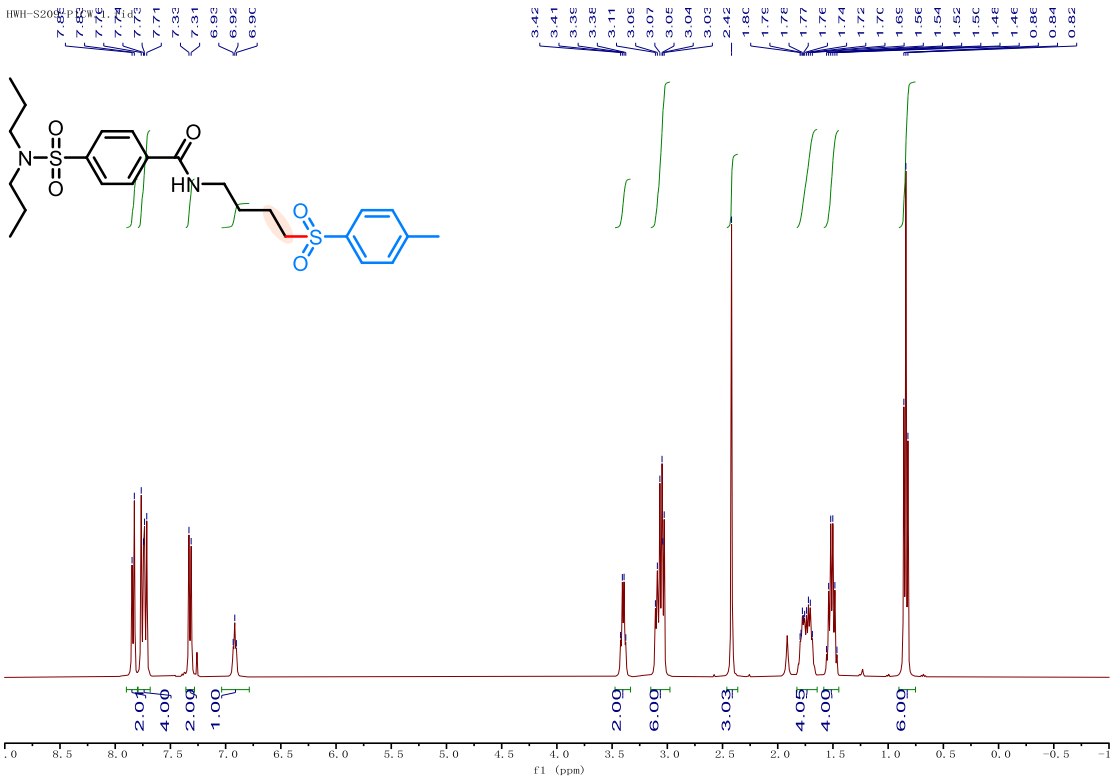
^{1}H NMR Spectrum of 53 ($CDCl_3$ as solvent, 400 MHz)



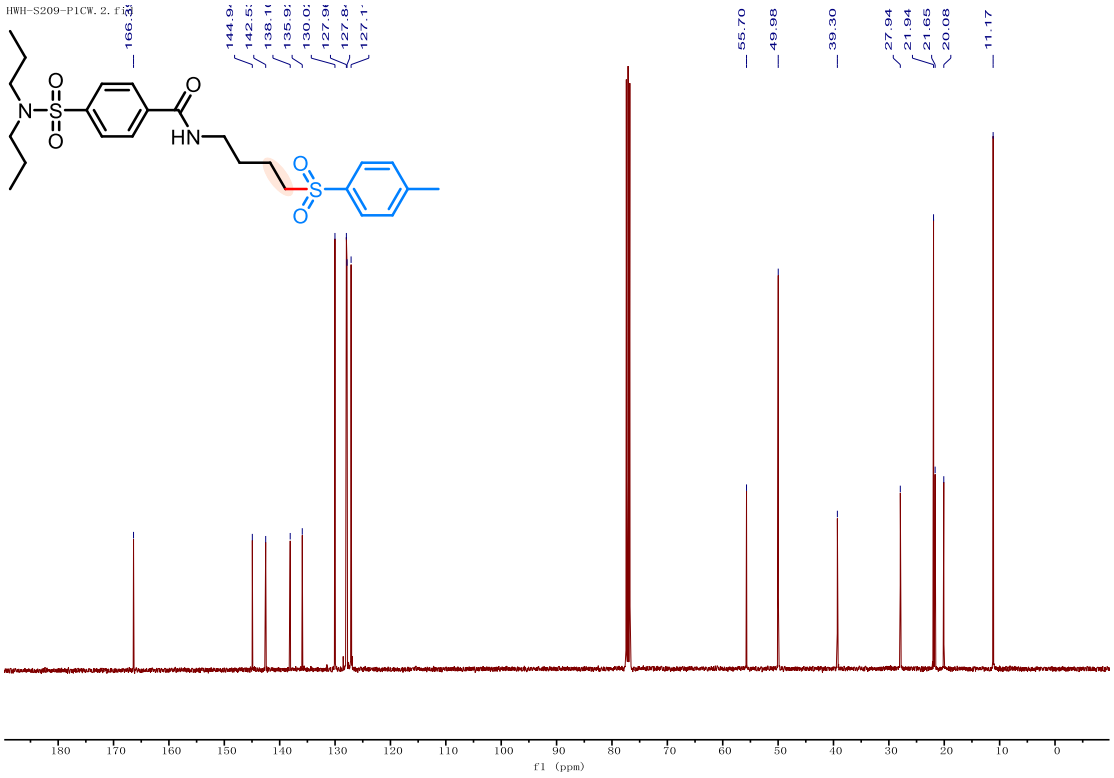
^{13}C {^{1}H} NMR Spectrum of 53 ($CDCl_3$ as solvent, 101 MHz)



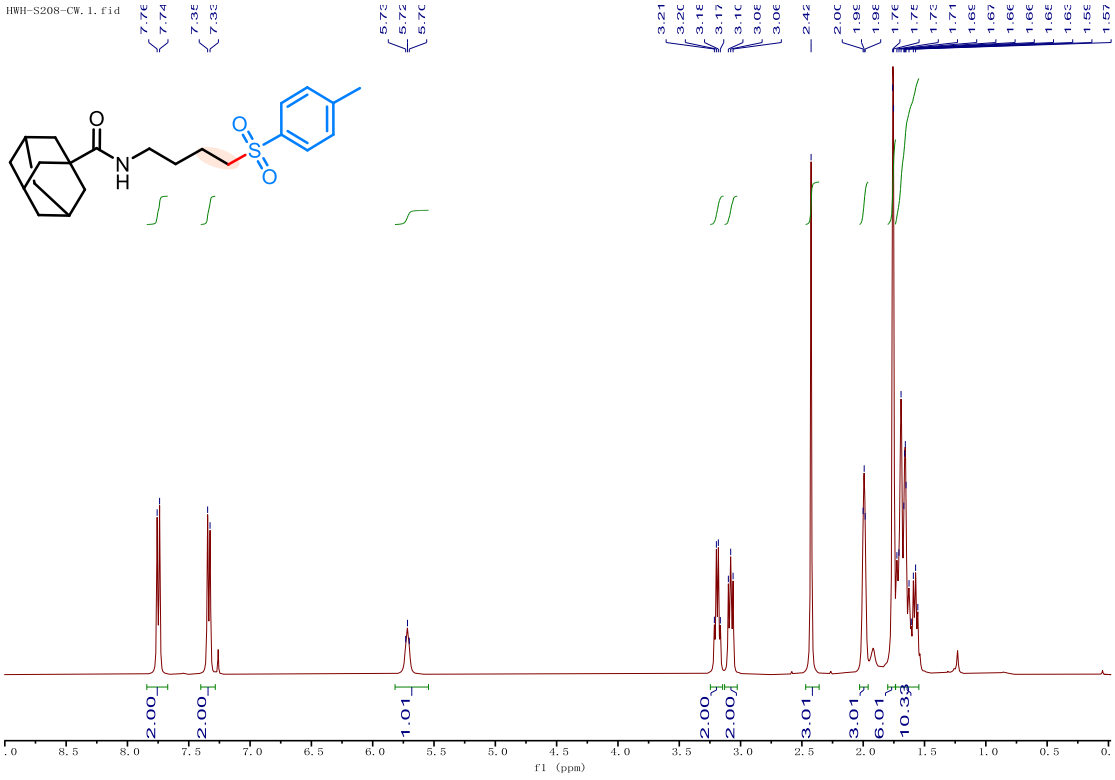
^{1}H NMR Spectrum of 54 ($CDCl_3$ as solvent, 400 MHz)



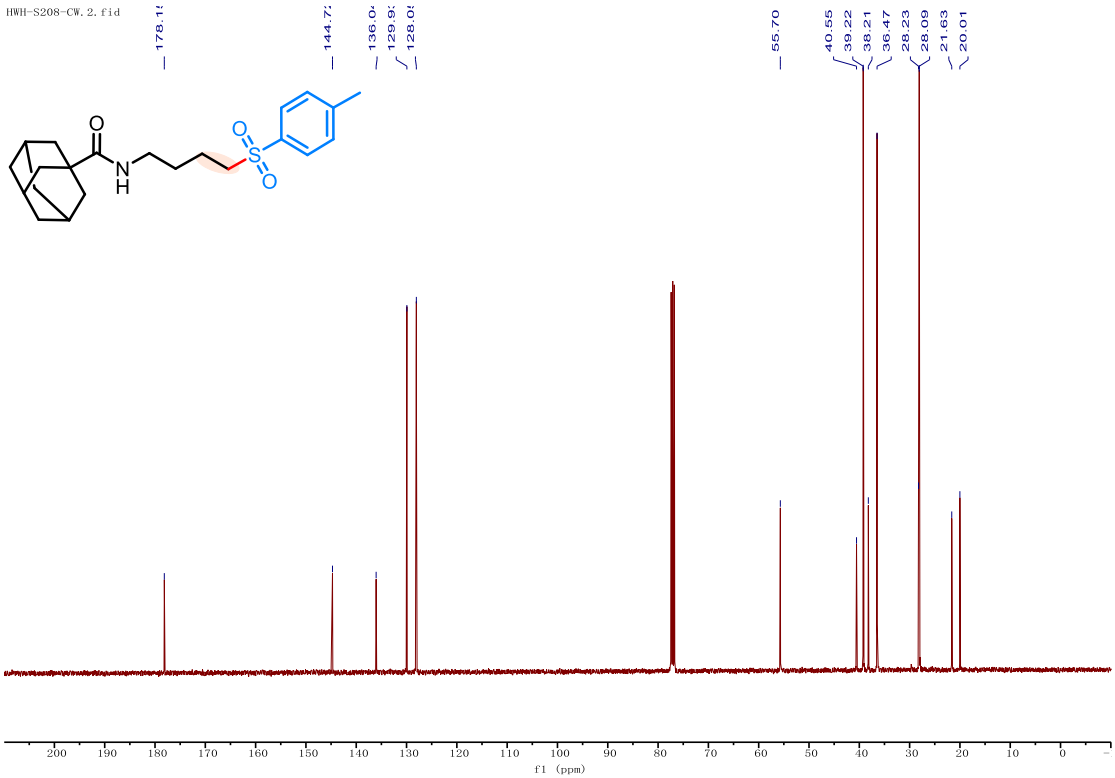
^{13}C {^{1}H} NMR Spectrum of 54 ($CDCl_3$ as solvent, 101 MHz)



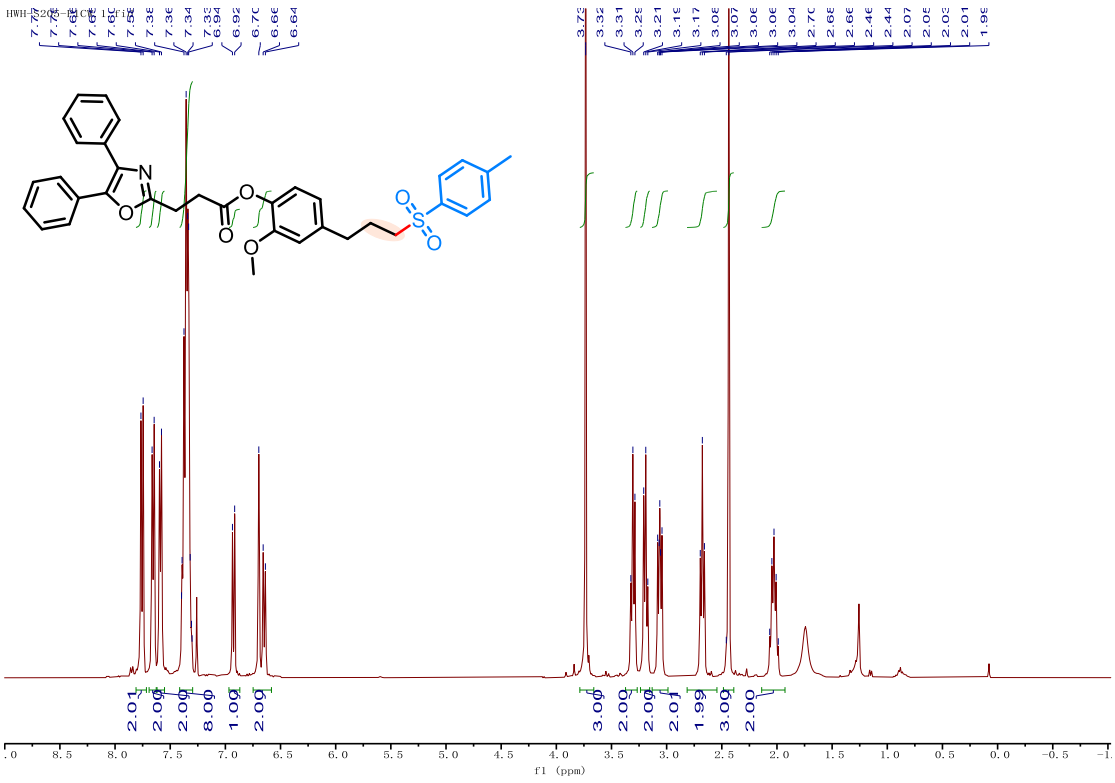
^{1}H NMR Spectrum of 55 ($CDCl_3$ as solvent, 400 MHz)



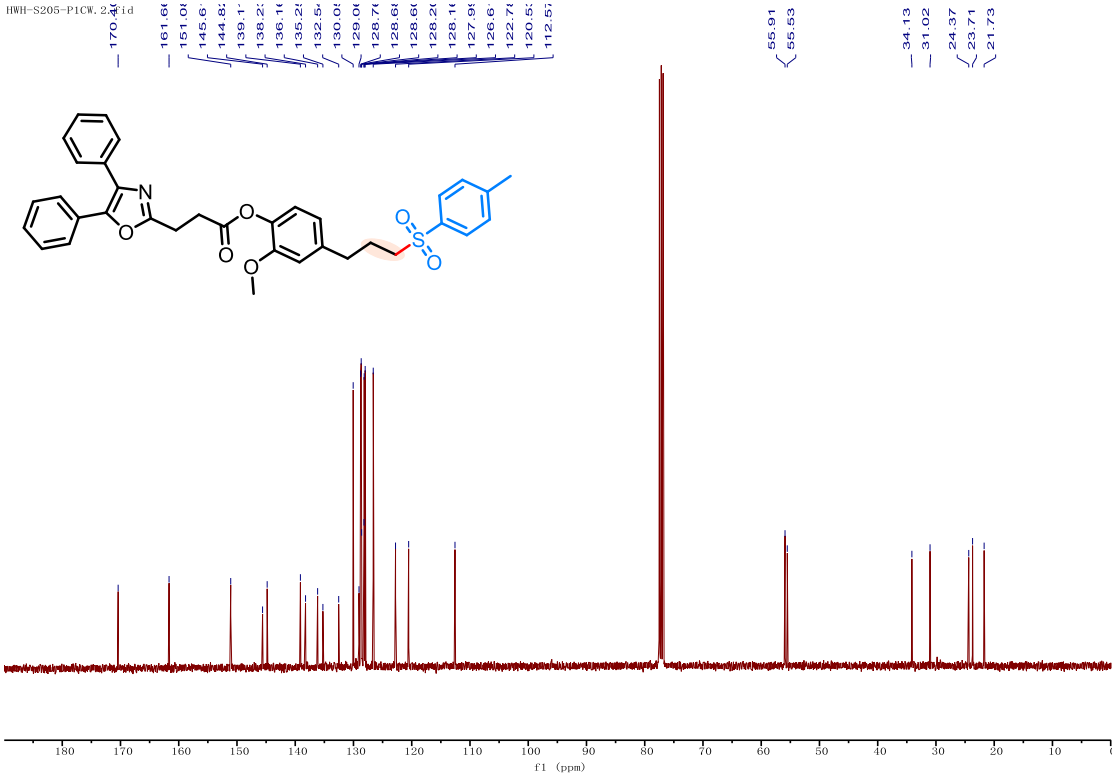
^{13}C {^{1}H} NMR Spectrum of 55 ($CDCl_3$ as solvent, 101 MHz)



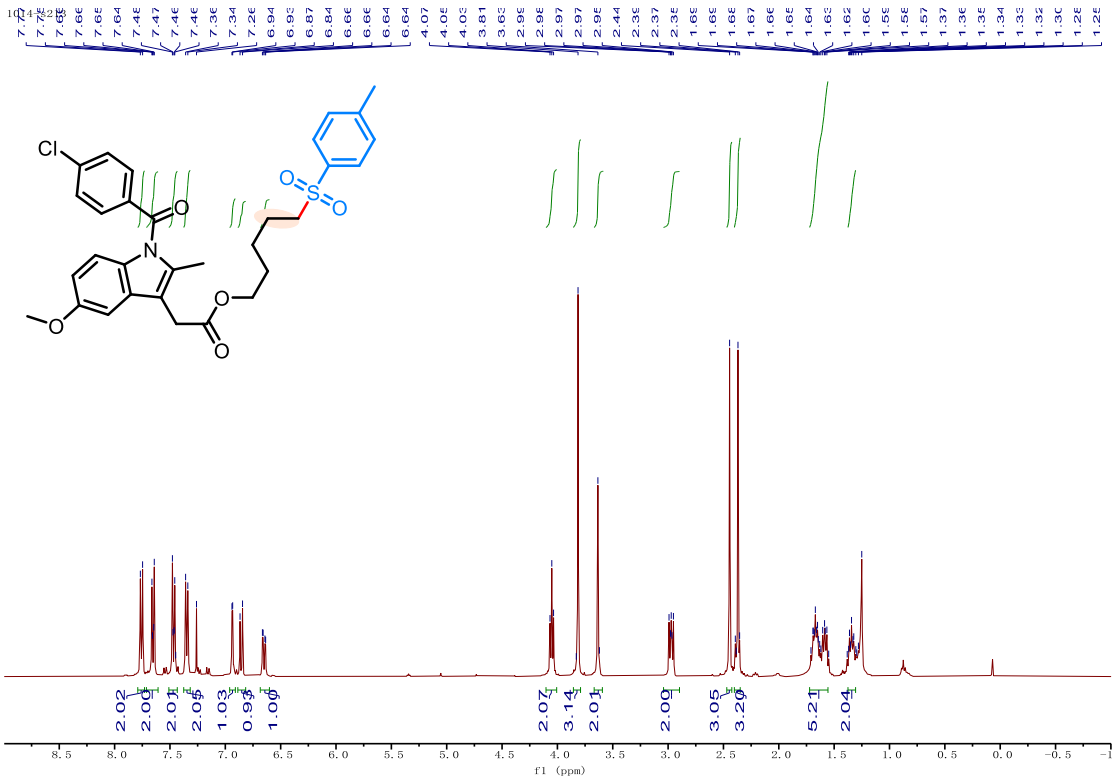
^{1}H NMR Spectrum of 56 ($CDCl_3$ as solvent, 600 MHz)



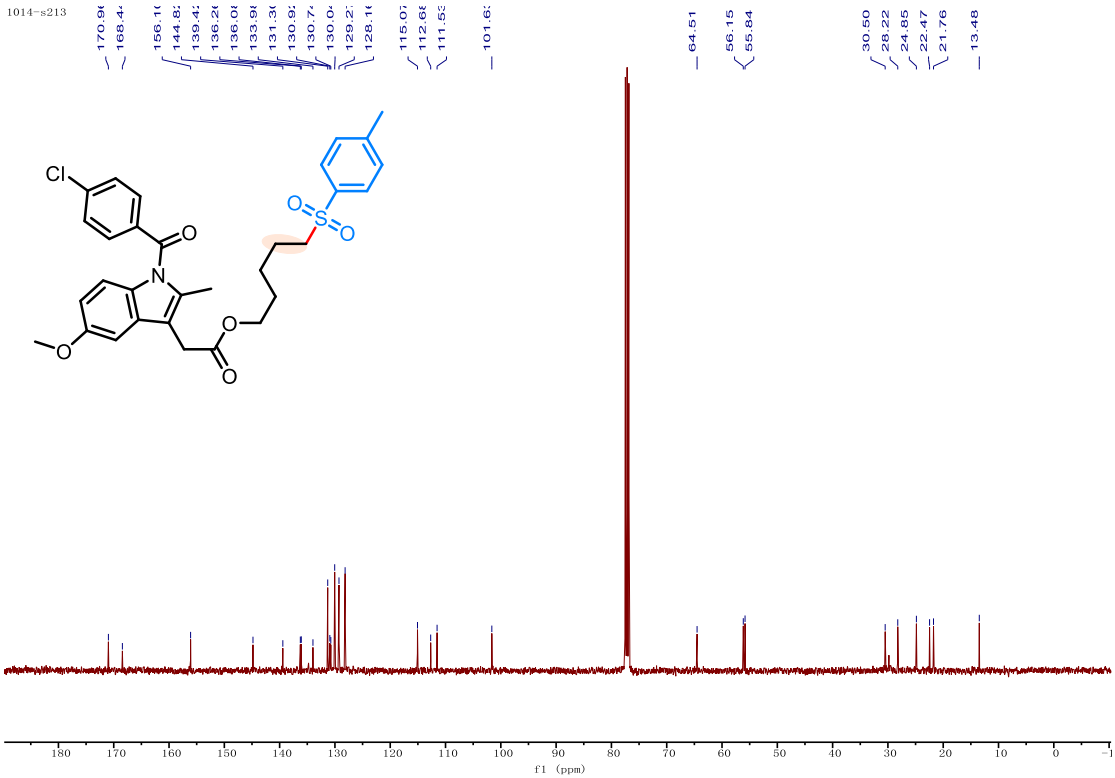
^{13}C {^{1}H} NMR Spectrum of 56 ($CDCl_3$ as solvent, 101 MHz)



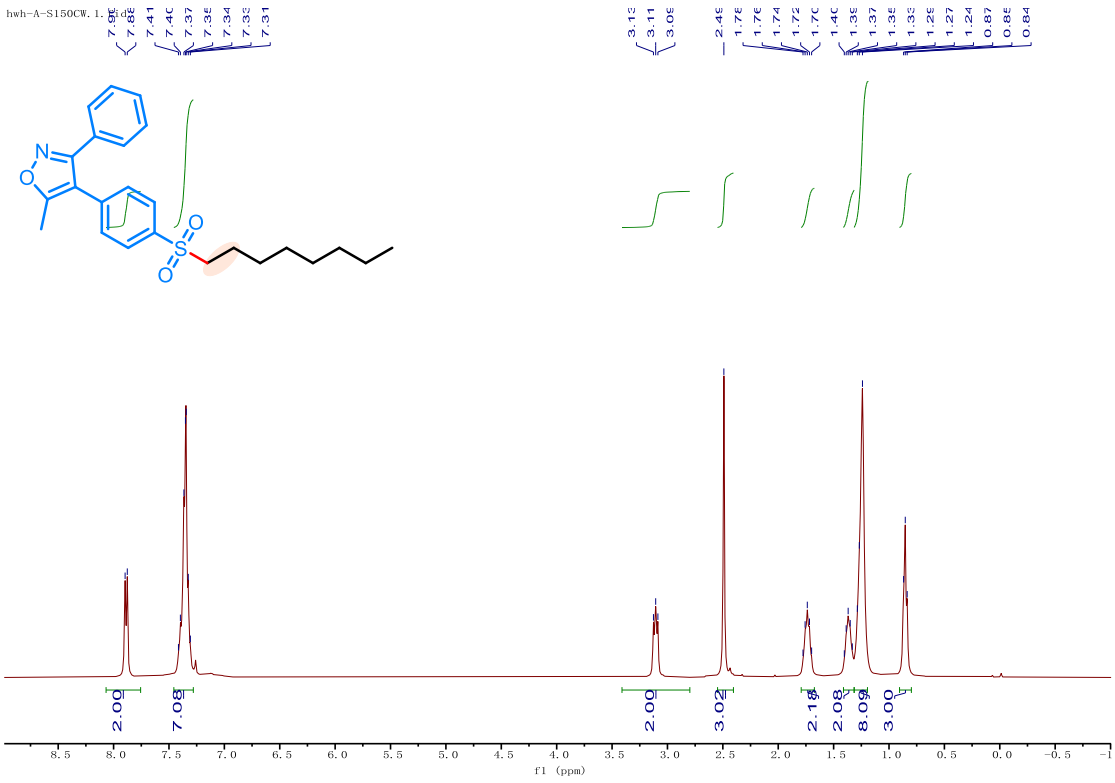
^{1}H NMR Spectrum of 57 ($CDCl_3$ as solvent, 400 MHz)



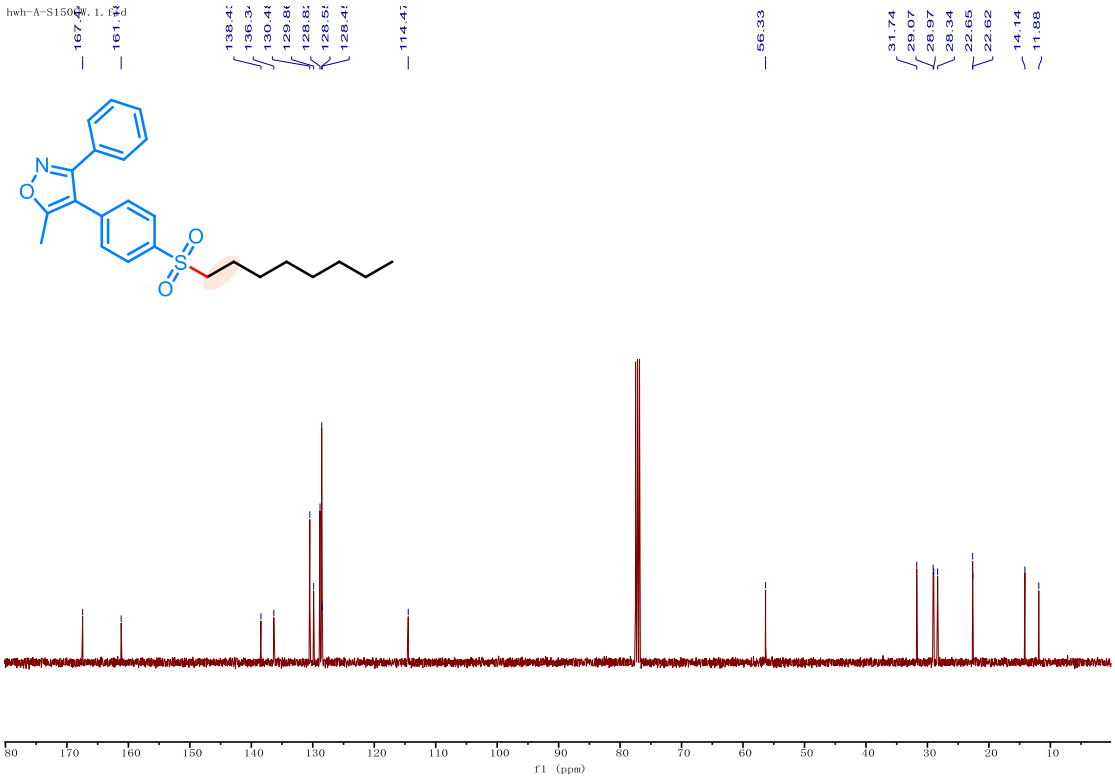
^{13}C {^{1}H} NMR Spectrum of 57 ($CDCl_3$ as solvent, 101 MHz)



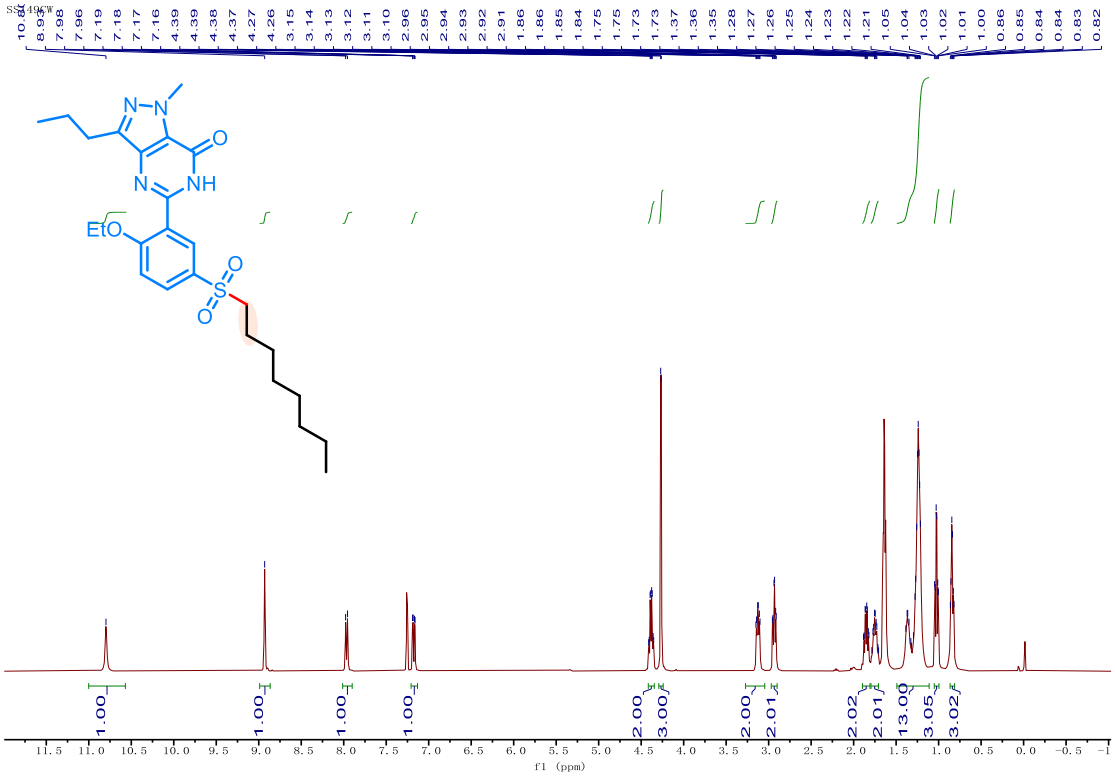
^{1}H NMR Spectrum of 58 ($CDCl_3$ as solvent, 400 MHz)



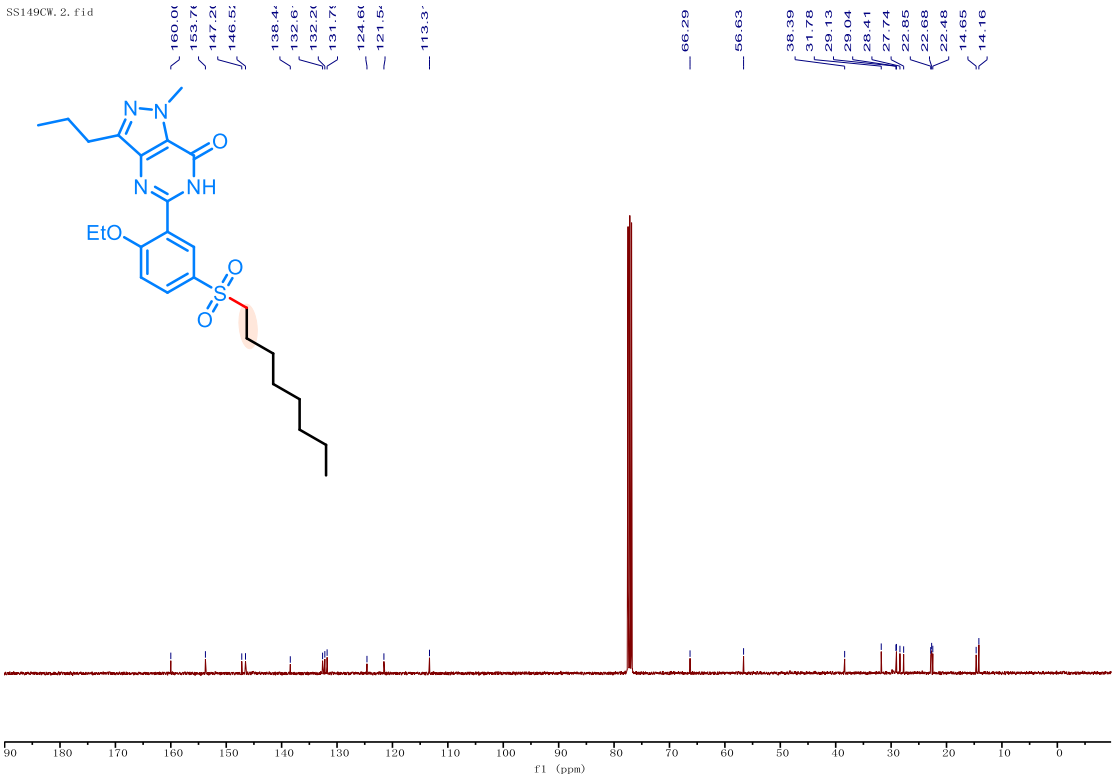
^{13}C {^{1}H} NMR Spectrum of 58 ($CDCl_3$ as solvent, 101 MHz)



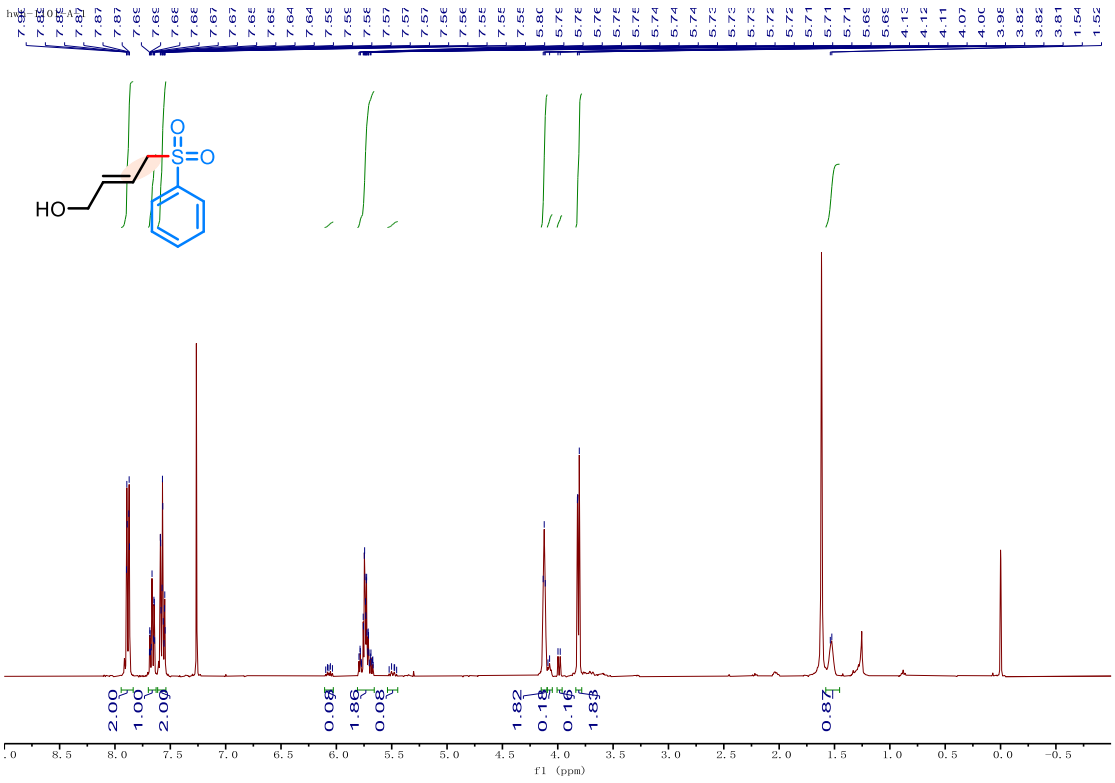
^{1}H NMR Spectrum of 59 ($CDCl_3$ as solvent, 400 MHz)



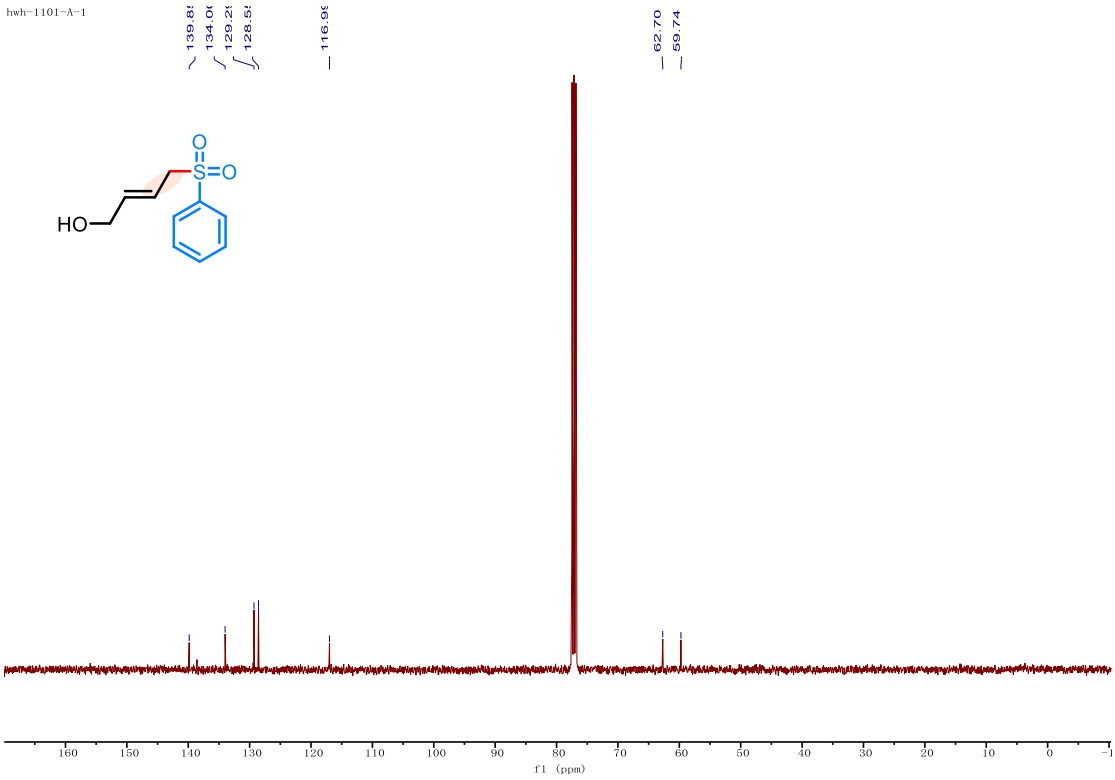
^{13}C {^{1}H} NMR Spectrum of 59 ($CDCl_3$ as solvent, 101 MHz)



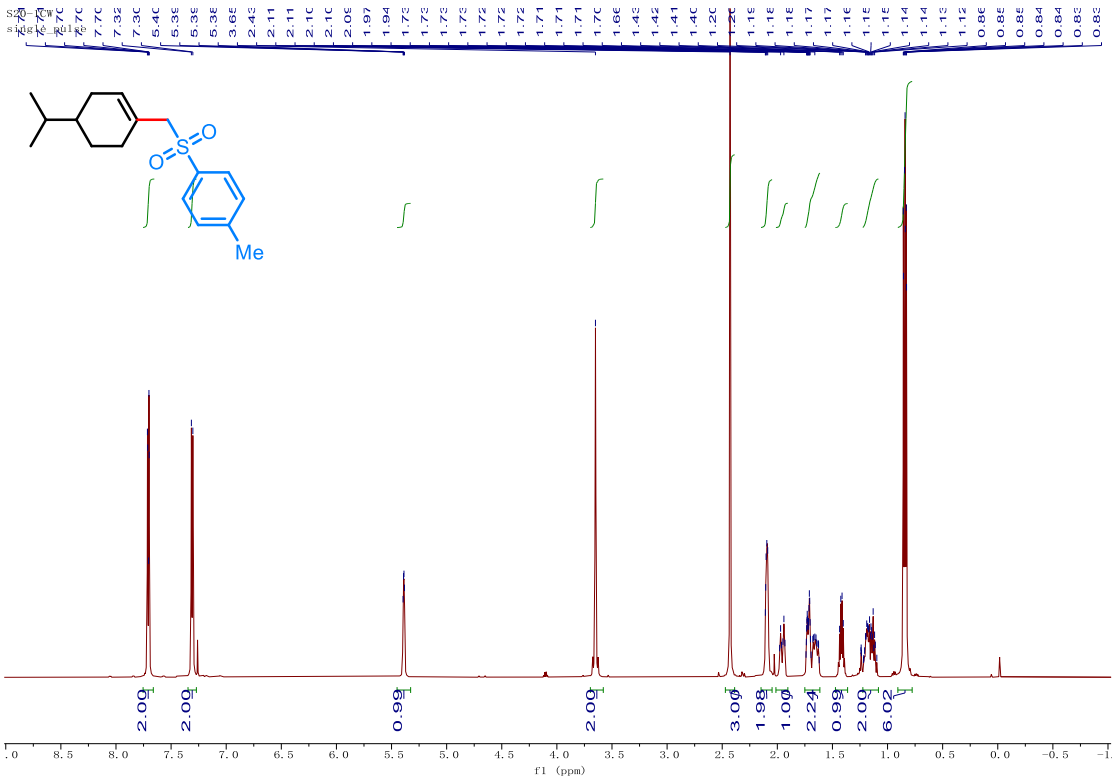
^{1}H NMR Spectrum of 61 ($CDCl_3$ as solvent, 400 MHz)



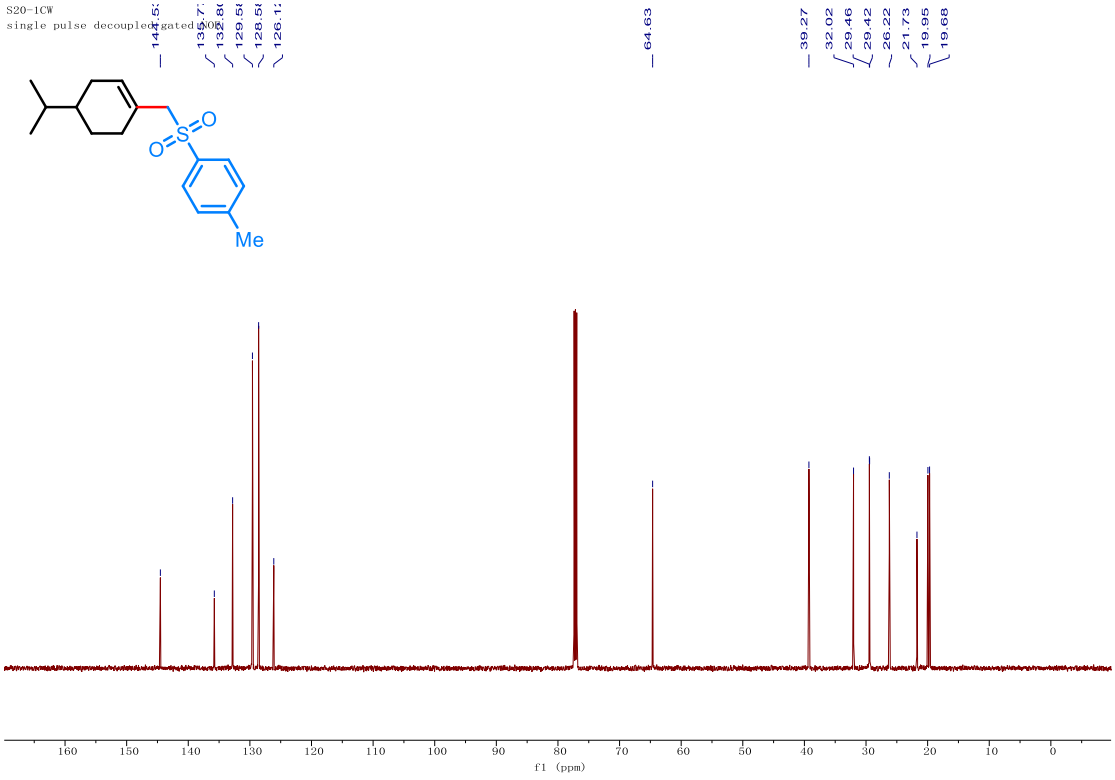
^{13}C {^{1}H} NMR Spectrum of 61 ($CDCl_3$ as solvent, 101 MHz)



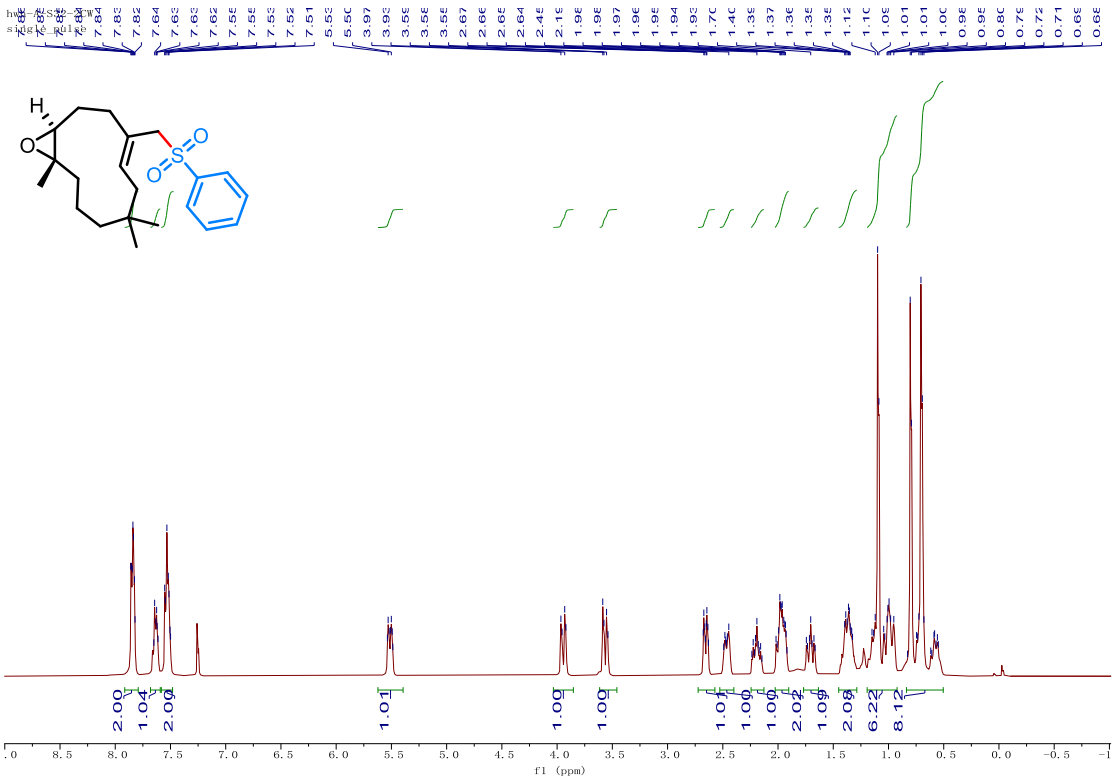
^{1}H NMR Spectrum of 62 ($CDCl_3$ as solvent, 600 MHz)



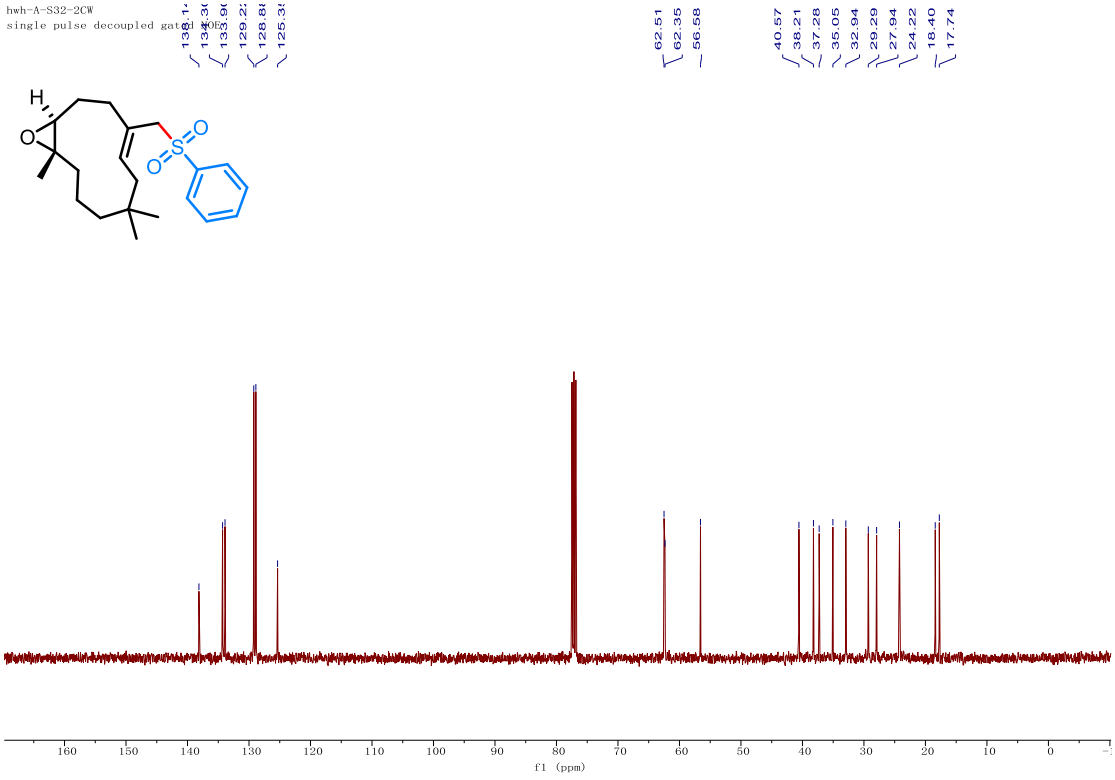
^{13}C {^{1}H} NMR Spectrum of 62 ($CDCl_3$ as solvent, 151 MHz)



^{1}H NMR Spectrum of 63 ($CDCl_3$ as solvent, 400 MHz)

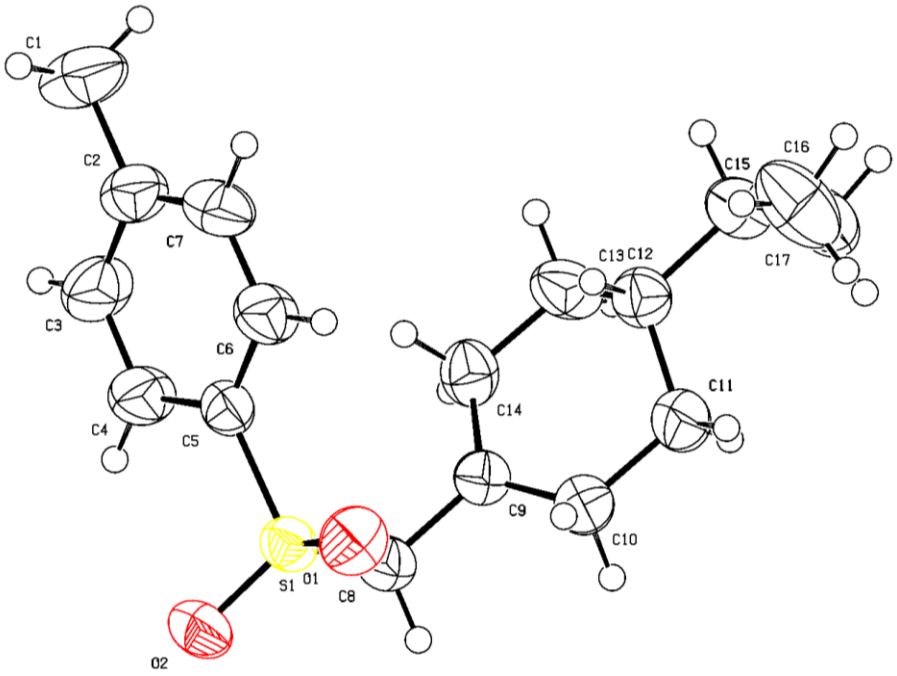


^{13}C {^{1}H} NMR Spectrum of 63 ($CDCl_3$ as solvent, 101 MHz)



5. Crystal data of Products

Qualified crystal of **62** suitable for the X-ray crystallographic study were readily obtained by slow diffusion of n-haxane into methylbenzene solution of **62**. Crystal data Crystallographic data for compound **62** has been deposited with the Cambridge Crystallographic Data Centre.

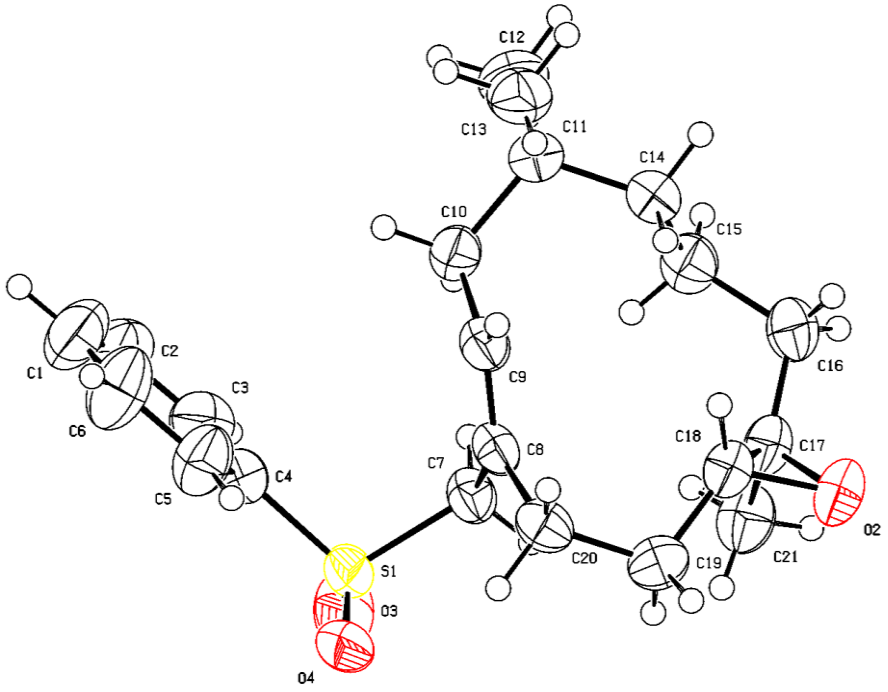


Supplementary Figure 5. X-ray structure of **62**(CCDC 2367386). Hydrogen atoms have been omitted for clarity. The ellipsoid contour percent probability level is 50%

Identification code	**s20-1_auto**	
Empirical formula	$C_{17}H_{25}O_2S$	
Formula weight	293.43	
Temperature	293K	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.1654(2)	=86.315(2) °
	b = 10.1994(3)	=76.450(3) °
	c = 11.9077(4)	=73.545(3) °
Volume	811.37(5)Å3	
Z	2	
Density	1.201 g/cm^3	
Absorption coefficient	1.756mm^{-1}	
F(000)	318	
Crystal size	0.3 x 0.15 x 0.09 mm^3	
Completeness to theta = 78.801 °	94.1 %	
Theta range for data collection	7.636 to 157.602 °	
Index ranges	$-9 \le h \le 9, -11 \le k \le 12, -15 \le l \le 14$	

Reflections collected	9076
Independent reflections	3293 [R(int) = 0.0311]
Data/restraints/parameters	3293 / 0 / 184
Goodness-of-fit on F^2	1.188
Final R indexes [I>=2σ (I)]	R_1 = 0.0615, wR_2 = 0.1689
Final R indexes (all data)	R_1 = 0.0653, wR_2 = 0.1712
Largest diff. peak and hole	0.28 and -0.36 e Å^{-3}

Qualified crystal of **63** suitable for the X-ray crystallographic study were readily obtained by slow diffusion of n-haxane into methylbenzene solution of 63. Crystal data Crystallographic data for compound **63** has been deposited with the Cambridge Crystallographic Data Centre.



Supplementary Figure 6. X-ray structure of **63** (CCDC 2367416). Hydrogen atoms have been omitted for clarity. The ellipsoid contour percent probability level is 50%

Identification code	SZX_auto	
Empirical formula	$C_{21}H_{30}O_3S$	
Formula weight	362.51	
Temperature	293K	
Wavelength	1.54184 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.30717(15)	= 90 °
	b = 12.2319(2)	= 90 °
	c = 20.0460(3)	= 90 °

Volume/Å^3	2036.93(7)
Z	4
Density(calculated)	1.182Mg/m^3
Absorption coefficient	0.091mm^{-1}
F(000)	784
Crystal size	0.2x 0.16x 0.18mm^3
Completeness to theta = 78.637	1.55 / 0.89
Theta range for data collection	8.468 to 157.274 °.
Index ranges	$-10 \leq h \leq 10$, $-9 \leq k \leq 15$, $-24 \leq l \leq 25$
Reflections collected	7844
Independent reflections	3905 [R(int) = 0.0269]
Data/restraints/parameters	3905 / 0 / 229
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0909
Final R indexes [all data]	R_1 = 0.0372, wR_2 = 0.0928
Largest diff. peak and hole	0.16 and -0.33 e Å^{-3}

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