Supporting Information

Direct Deoxygenative Sulfonylation of Free Alcohols Enabled by Triphenylphosphine EDA Complexes

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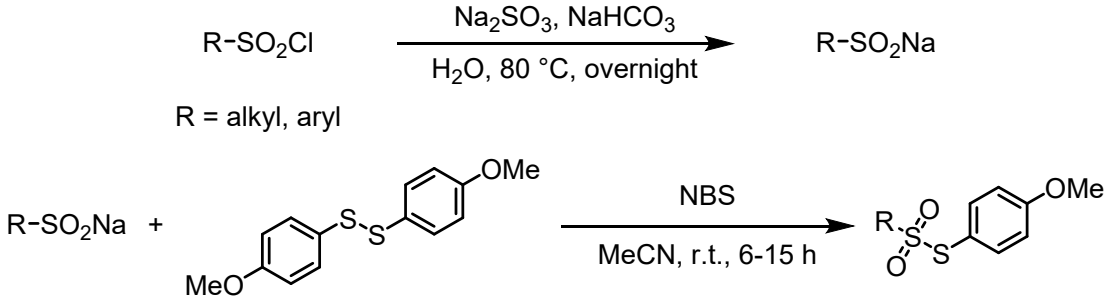
1. General Information

All manipulations were carried out by standard Schlenk techniques. Unless otherwise stated, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in dichloromethane (bp. 39.8 ºC). Gradient flash chromatography was conducted and eluted with a continuous gradient from petroleum to ethyl acetate. All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR. The ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. The chemical shifts (δ) were given in part per million relative to Chloroform-d (7.26 ppm for ^{1}H NMR), Chloroform-d (77.16 ppm for ^{13}C NMR), DMSO (2.50 ppm for ^{1}H NMR), DMSO (40.0 ppm for ^{13}C NMR). High resolution mass spectra (HRMS) were measured with a AB SCIEX Triple TOF 5600^{+}. Premier. Electrolysis experiments were performed using a dual display potentiostat (DJS-292B) or galvanostat (made in China). Cyclic voltammograms (CV) were obtained on a CHI 660E potentiostat. UV-Vis spectra was collected on PerkinElmer Lambda 365 spectrophotometer.

2. Experimental Section

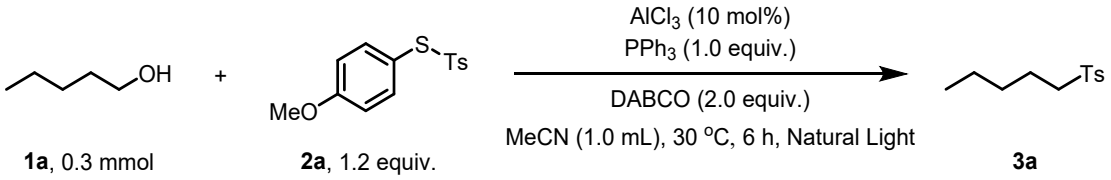
General procedure for the synthesis of unsymmetrical thiosulfonates.



Synthesis of sodium sulfinate salts: To a oven dried 100 mL round-bottom flask, equipped with a magnetic stirrer, was charged with sulfonyl chloride (5 mmol), Na_2SO_3 (2.0 equiv.) followed by $NaHCO_3$ (2.0 equiv.) in water (5 mL). The round-bottom flask was sealed with a rubber septa and the resulting mixture was stirred at 80 ℃ for 10 h. Later, the reaction was cooled to room temperature and the water was removed in a vacuum. The residue was extracted in ethanol and recrystallization from ethanol furnished the sodium sulfinates as a white or light yellow solid.

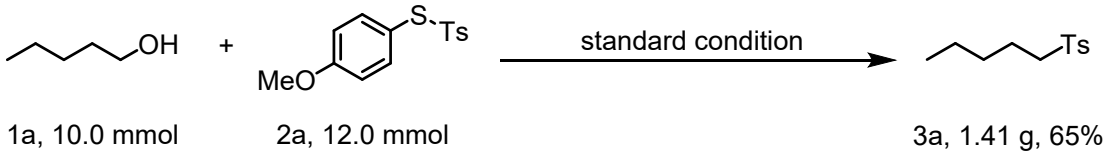
Synthesis of thiosulfonates: To a solution of sodium sulfinate (8 mmol) and disulfide (2 mmol) in CH_3CN (10.0 ml) was added NBS (4 mmol) while mixing. the reaction mixture was washed with water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel (200-300 mesh) with hexane/EtOAc as eluent to afford the desired products.

General procedure for the synthesis of Sulfonylation

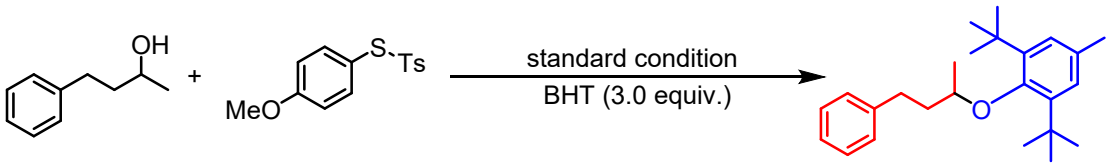


An oven-dried glass vial (10 mL) was equipped with a magnetic stir bar and charged with alcohol (0.3 mmol), 2a (0.36 mmol, 1.2 equiv.), Triphenylphosphine (0.3 mmol, 1.0 equiv.), DABCO (0.6 mmol, 2.0 equiv.). The flask was evacuated and backfilled with argon and then MeCN (1.0 mL) was added. The reaction mixture was irradiated with natural light at 30 °C for 6 h. After the reaction, the residue was diluted with water (5 mL) and extracted with EtOAc (10 mL × 3). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography with hexane/EtOAc as eluent to afford the desired products.

Procedure for the gram-scale synthesis of Sulfonylation



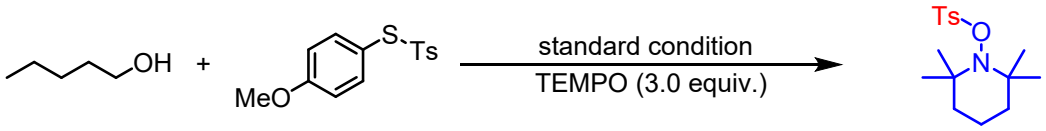
The mixture of 1-Pentanol (10.0 mmol), 2a (12 mmol, 1.2 equiv.), Triphenylphosphine (10 mmol, 1.0 equiv.), DABCO (20.0 mmol, 2.0 equiv.) and MeCN (30 mL) were sequentially added in a 100 mL round bottom flask. Then the reaction system was carried out under natural light at 30 ℃ under an Ar atmosphere for 8 h. Once completed, the mixture was diluted with water (30 mL) and extracted with EtOAc (30 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel chromatography using hexane/EtOAc (10:1, v/v) as eluent to afford the desired product 3a (1.41 g, 65%).



Detected by HRMS
Mass + H^+: 352.2766

General procedure for radical inhibition experiment

In an oven-dried undivided Schlenk tube (10 mL) equipped with a stir bar. A solution of alcohol (0.3 mmol), S-(4-methoxyphenyl)-4-methylbenzenesulfonothioate (0.36 mmol, 1.2 equiv.), Triphenylphosphine (0.3 mmol, 1.0 equiv.), DABCO (0.6 mmol, 2.0 equiv.), BHT (0.9 mmol, 3.0 equiv.) in MeCN (1.0 mL) stirring under nitrogen atmosphere. The reaction mixture was irradiated with natural light at 30 °C for 6 h. After completion of the reaction, it was quenched by 2.0 M HCl. The aqueous solution was extracted with EtOAc (3 × 10 mL) and the combined extracts were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The reaction solution uses HRMS to detect free radical trapping products. No target product was found in TLC spot plate test of reaction solution. The reaction solution uses HRMS to detect free radical inhibition products, HRMS (ESI, m/z) calcd for $C_{25}H_{36}O^+$ $(M+H)^+$: 352.2766; Found: 352.2766.



Detected by HRMS
Mass + H^+: 311.1550

General procedure for radical capture experiment

In an oven-dried undivided Schlenk tube (10 mL) equipped with a stir bar. A solution of alcohol (0.3 mmol), S-(4-methoxyphenyl)-4-methylbenzenesulfonothioate (0.36 mmol, 1.2 equiv.), Triphenylphosphine (0.3 mmol, 1.0 equiv.), DABCO (0.6 mmol, 2.0 equiv.), Tempo (0.9 mmol, 3.0 equiv.) in MeCN (1.0 mL) stirring under nitrogen atmosphere. The reaction mixture was irradiated with natural light at 30 °C for 6 h. After completion of the reaction, it was quenched by 2.0 M HCl. The aqueous solution was extracted with EtOAc (3 × 10 mL) and the combined extracts were dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The reaction solution uses HRMS to detect free radical trapping products. No target product was found in TLC spot plate test of reaction solution.. No target product was found in TLC spot plate test of reaction solution. The reaction

solution uses HRMS to detect free radical trapping products, HRMS (ESI, m/z) calcd for $C_{16}H_{25}NO_3S^+$ $(M+H)^+$: 311.1555; Found: 311.1550.

General procedure for UV-Vis experiment (Supplementary Figures S1)

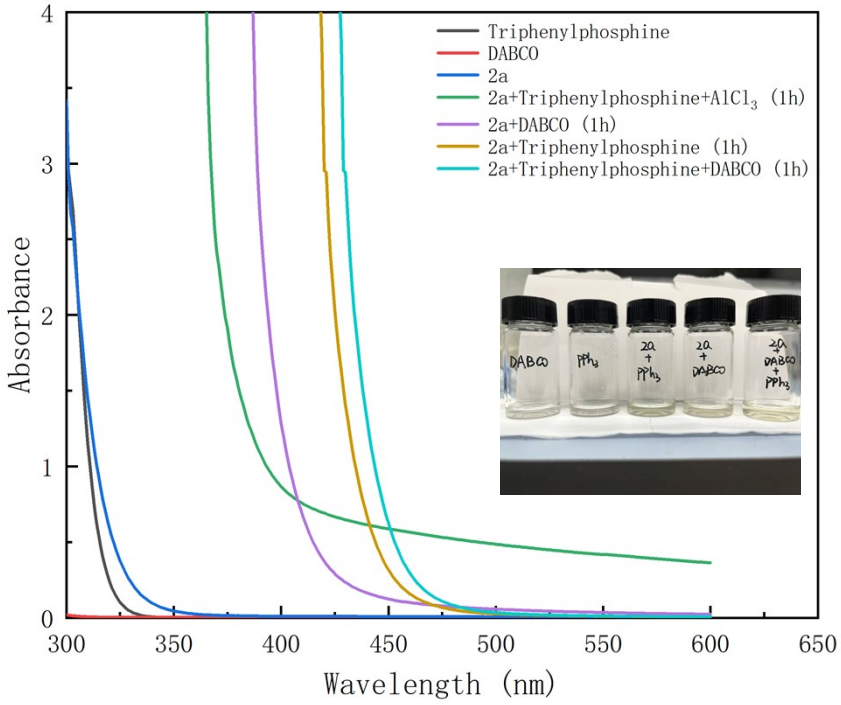


Figure S1 UV-Vis experiment

In-situ UV-Vis absorption data was acquired on an PerkinElmer Lambda 365 spectrophotometer. In order to identify light-absorbing species in this transformation, absorption spectra of the series of solutions were recorded. The results indicate, that none of the reaction components (Triphenylphosphine, 2a and DABCO) can individually absorb visible light. The mixture of 2a and triphenylphosphine showed a significant red shift (brown curve). Moreover, both the mixture of 2a and DABCO (purple curve) and the ternary mixture of all three components (blue curve) also displayed pronounced red shifts, with absorption observed in the visible range of 425-500 nm. When aluminum chloride is added to the mixture of triphenylphosphine and 2a (green curve), the absorption intensity in the visible light range significantly increases. The coloration of the prepared solutions additionally supports the formation of the EDA-complex. Individually, the components of the reaction remain clear even upon prolonged standing. In contrast, mixing 2a, Triphenylphosphine in MeCN, rapidly develops the yellow color of the solution.

General procedure for NMR titration experiments (^{31}P-NMR titration experiment)

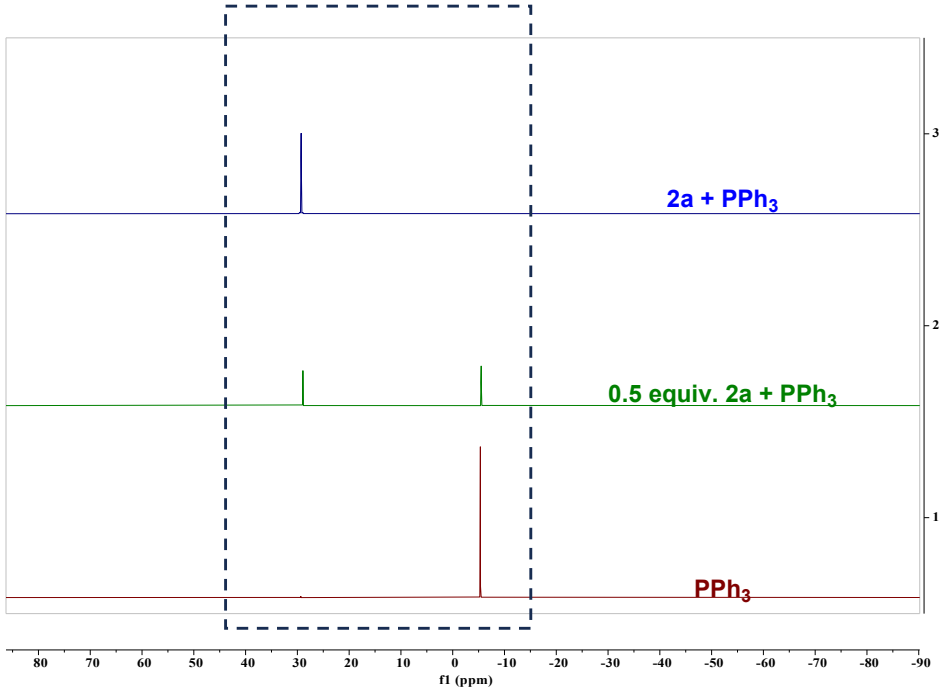


Figure S2 ^{31}P-NMR titration experiments of EDA complex

(Supplementary Figures S2)

^{31}P-NMR spectra of mixtures of 2a and in Triphenylphosphine were recorded at 300 K. In an NMR tube, the total volume of the mixture was 0.6 mL, the concentration of Triphenylphosphine (0.3 mmol) was kept constant at 0.5 M, and that of 2a was varied from 0 to 0.6 M. The molar ratios of 2a: Triphenylphosphine were 0:1, 0.5:1, 1:1, in Chloroform-d. The ^{31}P NMR signal of Triphenylphosphine shifted with increasing the amount of 2a, indicating the formation of EDA-complex between 2a with Triphenylphosphine. To clarify the specific roles of triphenylphosphine (PPh_3) and DABCO in the reaction, we conducted a nuclear magnetic resonance (NMR) titration experiment (Scheme 4d). As substrate 2a was gradually added to the triphenylphosphine solution, the original signal intensity of triphenylphosphine in the ^{31}P NMR spectrum decreased progressively, while a new phosphine signal peak emerged, indicating an interaction between the two.

General procedure for NMR titration experiments (^{1}H-NMR titration experiment) (Supplementary Figures S3)

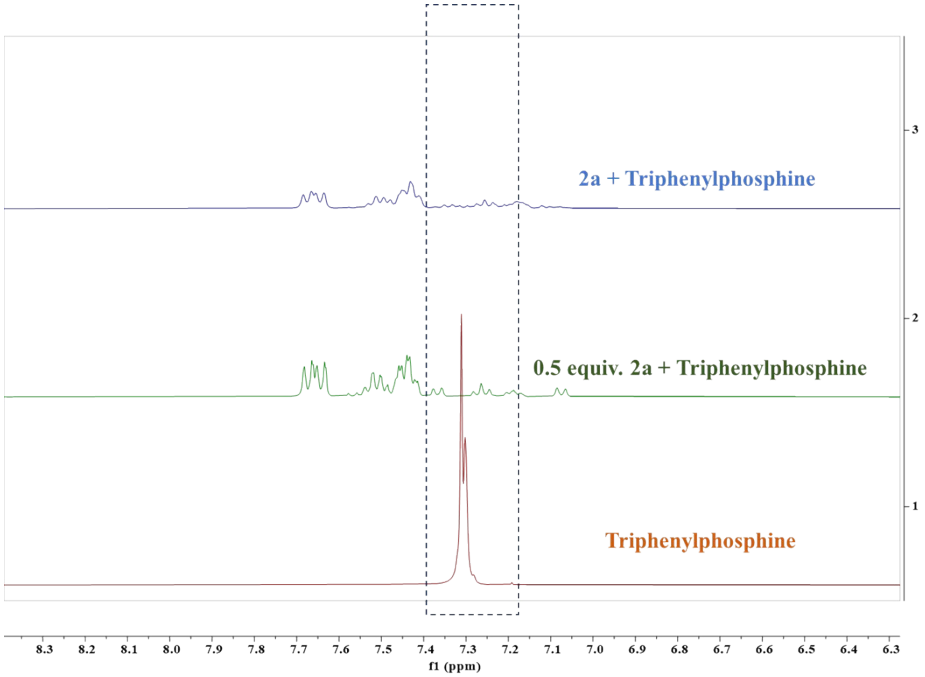


Figure S3 ^{1}H-NMR titration experiments of EDA complex

^{1}H-NMR spectra of mixtures of 2a and in Triphenylphosphine were recorded at 300 K. In an NMR tube, the total volume of the mixture was 0.6 mL, the concentration of Triphenylphosphine (0.3 mmol) was kept constant at 0.5 M, and that of 2a was varied from 0 to 0.6 M. The molar ratios of 2a: Triphenylphosphine were 0:1, 0.5:1, 1:1, in Chloroform-d. The ^{1}H NMR signal of Triphenylphosphine shifted with increasing the amount of 2a, indicating the formation of EDA-complex between 2a with Triphenylphosphine. To clarify the specific roles of triphenylphosphine (PPh_3) and DABCO in the reaction, we conducted a nuclear magnetic resonance (NMR) titration experiment. As substrate 2a was gradually added to the triphenylphosphine solution, the original signal intensity of triphenylphosphine in the ^{1}H NMR spectrum decreased progressively, indicating an interaction between the two.

General procedure for NMR titration experiments (^{1}H-and ^{31}P-NMR titration experiments) (Supplementary Figures S4)

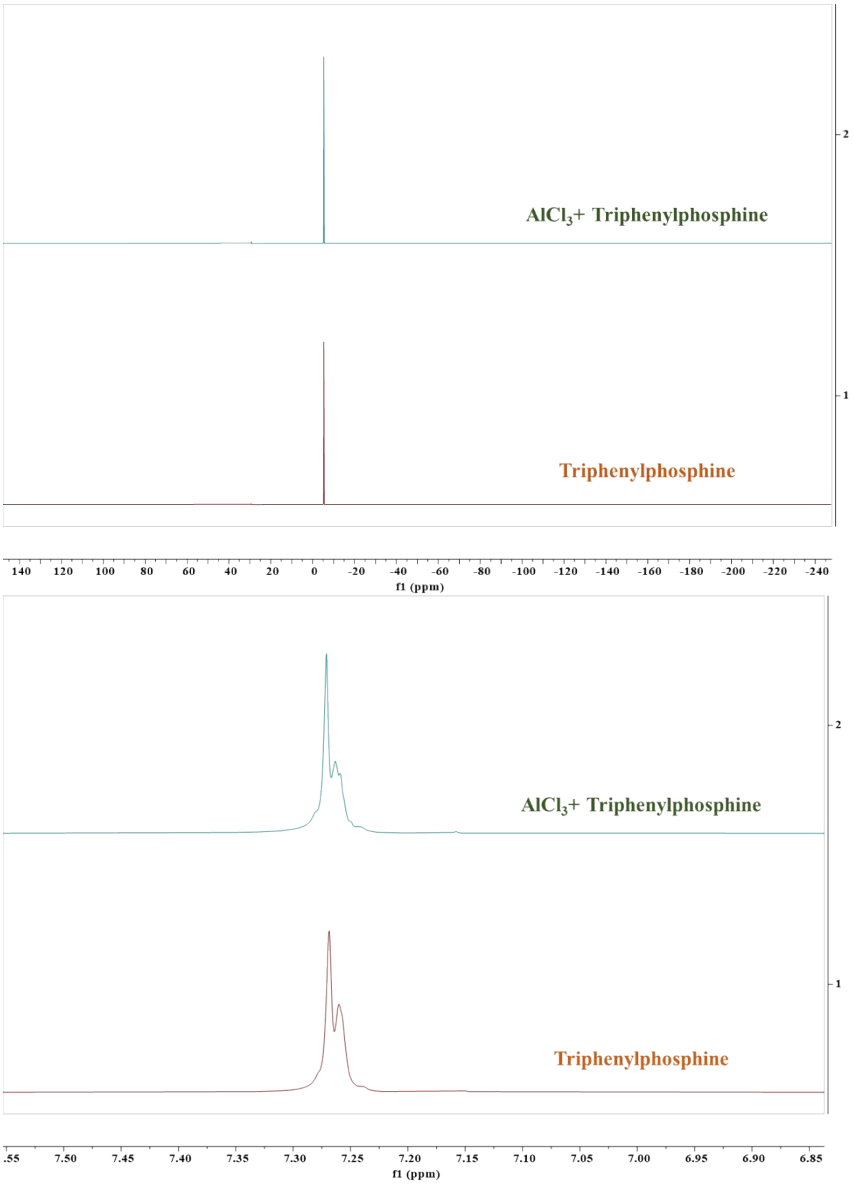


Figure S4 ^{1}H-and ^{31}P-NMR titration experiments of $AlCl_3$ and PPh_3

^{1}H-NMR and ^{31}P-NMR spectra of mixtures of Triphenylphosphine and $AlCl_3$ in Triphenylphosphine were recorded at 300 K. In an NMR tube, the total volume of the mixture was 0.6 mL, the concentration of Triphenylphosphine (0.3 mmol) was kept constant at 0.5 M, and that of AlCl3 (0.03 mmol) was kept constant at 0.05M. When $AlCl_3$ was added to the triphenylphosphine solution, the original signal intensity of triphenylphosphine in the ^{1}H-NMR and ^{31}P-NMR spectrum did not show any significant change, indicating that there was not an interaction between the two.

General procedure for NMR titration experiments (^{1}H-NMR titration experiments) (Supplementary Figures S5)

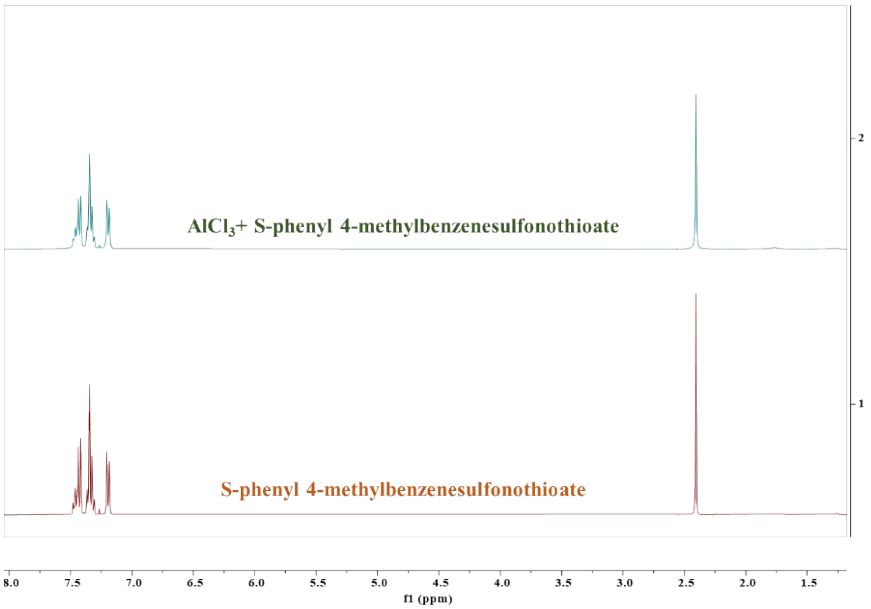


Figure S5 ^{1}H-NMR titration experiments of $AlCl_3$ and 2a

^{1}H-NMR spectra of mixtures of S-phenyl 4-methylbenzenesulfonothioate and $AlCl_3$ in S-phenyl 4-methylbenzenesulfonothioate were recorded at 300 K. In an NMR tube, the total volume of the mixture was 0.6 mL, the concentration of S-phenyl 4-methylbenzenesulfonothioate (0.36 mmol) was kept constant at 0.6 M, and that of $AlCl_3$ (0.03 mmol) was kept constant at 0.05M. When $AlCl_3$ was added to the triphenylphosphine solution, the original signal intensity of triphenylphosphine in the ^{1}H-NMR spectrum did not show any significant change, indicating that there was not an interaction between the two.

General procedure for NMR titration experiments (^{1}H-NMR titration experiments) (Supplementary Figures S6)

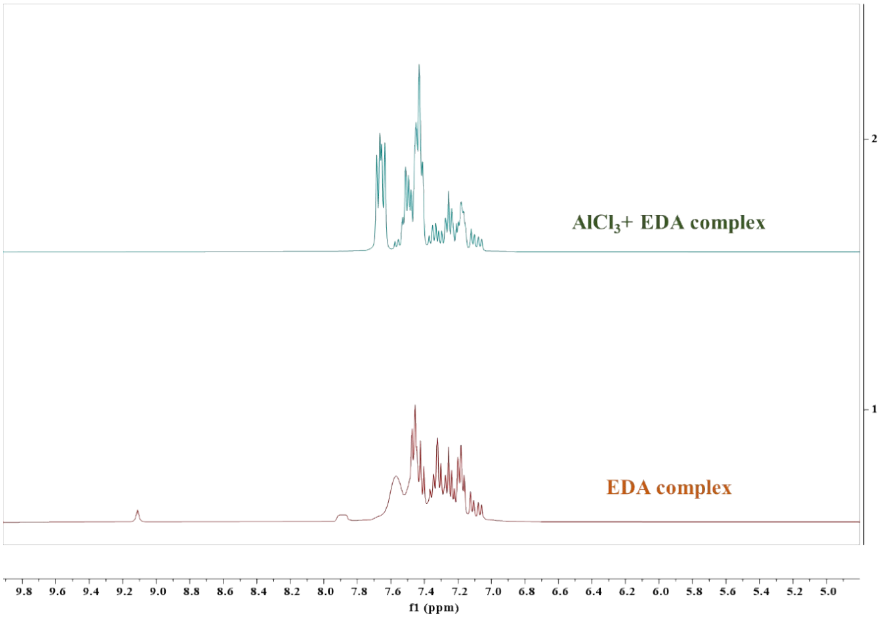


Figure S6 ^{1}H-NMR titration experiments of $AlCl_3$ and EDA complex

^{1}H-NMR spectra of mixtures of EDA complex and $AlCl_3$ in EDA complex were recorded at 300 K. In an NMR tube, the total volume of the mixture was 0.6 mL, the concentration of $AlCl_3$ (0.03 mmol) was kept constant at 0.05M. When $AlCl_3$ was added to the EDA complex solution, the original signal intensity of EDA complex in the ^{1}H-NMR spectrum did show any significant change, indicating that there was an interaction between the two.

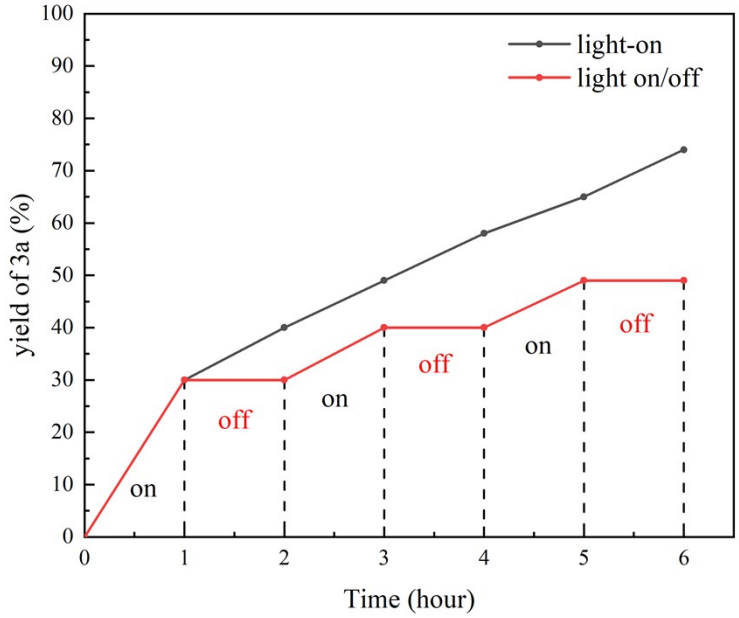


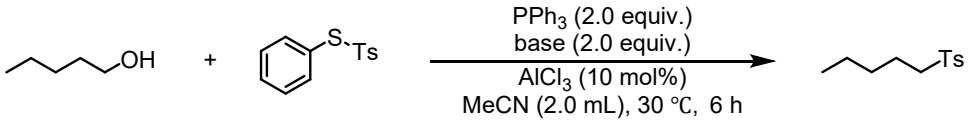
Figure S7 Light-on/off experiments

General procedure for Light-on/off experiments (Supplementary Figures S7)

Six standard reaction mixtures were prepared in 10 mL vials, each containing 1a (0.3 mmol), 2a (0.36 mmol, 1.2 equiv.), Triphenylphosphine (0.3 mmol, 1.0 equiv.), and DABCO (0.6 mmol, 2.0 equiv.) in MeCN (1.0 mL). The vials were purged with argon for 10 minutes. The reactions were then stirred and irradiated under natural light at 30 °C. After 1 hour of irradiation, the natural light were turned off, and one vial was removed for analysis. The remaining five vials were stirred in the dark for an additional 1 hour. At this point, another vial was removed for analysis, and the natural light were turned back on to irradiate the remaining four reaction mixtures. After another 1 hour of irradiation, the natural light were turned off again, and a third vial was removed for analysis. The remaining three vials were stirred in the dark for an additional 1 hour. Then, one more vial was removed for analysis, and the natural light were turned on once more for 1 hours of irradiation. After this final period of light exposure, one vial was removed for analysis, leaving the last vial to be stirred in the dark for an additional 1 hour before analysis. The red line represents the yield of the reaction during intervals of light exposure and darkness. The black line represents the yield of the reaction continuously irradiated with visible light.

3. Conditional optimization

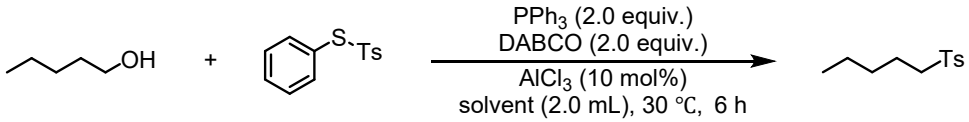
Table S1. The influence of base



1a, 0.3 mmol 2a, 2.0 equiv. 3a

Entry	Condition	Yield of 3a
1	base = Cs_2CO_3	n.d.
2	base = K_2CO_3	23%
3	base = DBU	43%
4	base = Et_3N	trace

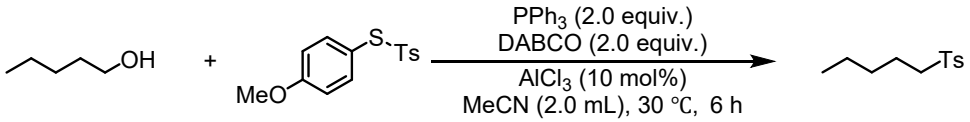
Table S2. The influence of solvent



1a, 0.3 mmol 2a, 2.0 equiv. 3a

Entry	Condition	Yield of 3a
1	solvent = MeCN	45%
2	solvent = DMAc	trace
3	solvent = DCE	37%
4	solvent = EA	33%

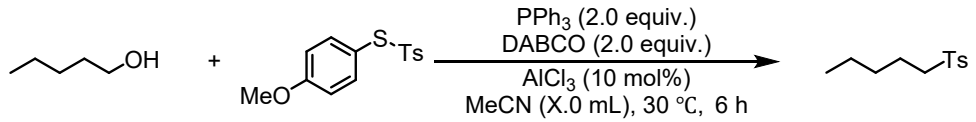
Table S3. The influence of Temperature



1a, 0.3 mmol 2a, 2.0 equiv. 3a

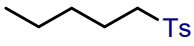
Entry	Condition	Yield of 3a
1	none	63%
2	50 °C instead of 30 °C	60%
3	80 °C instead of 30 °C	62%
4	0 °C instead of 30 °C	50%

Table S4. The influence of Concentration



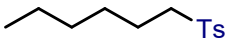
1a, 0.3 mmol 2a, 2.0 equiv. 3a

Entry	Condition	Yield of 3a
1	MeCN = 1 mL	72%
2	MeCN = 3 mL	trace
3	MeCN = 4 mL	trace
4	MeCN = 5 mL	trace
5	MeCN = 6 mL	trace



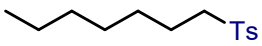
4. Characterization of Products

1-methyl-4-(pentylsulfonyl)benzene (3a), yield:73%, 49 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 4.04 - 3.98 (m, 1H), 3.63 - 3.57 (m, 1H), 2.42 (s, 3H), 1.65 – 1.59 (m, 2H), 1.31 - 1.25 (m, 4H), 0.88 - 0.85 (m, 3H). **^{13}C NMR** (101 MHz,



Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.8, 64.8, 29.5, 28.0, 22.3, 21.6, 14.0.

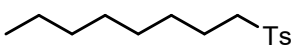
1-(hexylsulfonyl)-4-methylbenzene (3b), yield:63%, 45 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 4.04 - 3.98 (m, 1H), 3.63 - 3.57 (m, 1H), 2.42 (s, 3H), 1.65 – 1.59 (m, 3H), 1.33 - 1.22 (m, 5H), 0.88 - 0.85 (m, 3H). **^{13}C NMR** (101 MHz,



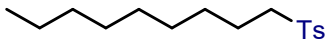
Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.8, 64.8, 29.5, 28.0, 22.3, 21.6, 14.0.

1-(heptylsulfonyl)-4-methylbenzene (3c), yield:60%, 46 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.04 - 3.98 (m, 1H), 3.62 - 3.57 (m, 1H), 2.42 (s, 3H), 1.64-1.57 (m, 2H), 1.32 - 1.23 (m, 8H), 0.87 - 0.84 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.8, 142.7, 129.9, 128.0, 66.9, 31.8, 29.8, 28.9, 25.8, 22.7, 21.7, 14.8.

1-methyl-4-(octylsulfonyl)benzene (3d), yield:60%, 49 mg, colorless oil. **^{1}H NMR** (400 MHz,



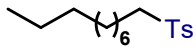
Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.04 - 3.98 (m, 1H), 3.63 - 3.57



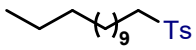
(m, 1H), 2.42 (s, 3H), 1.61-1.58 (m, 2H), 1.33 - 1.23 (m, 10H), 0.89 - 0.80 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.4, 64.8, 32.0, 29.8, 29.6, 29.3, 25.9, 22.8, 21.6, 14.3.

1-methyl-4-(nonylsulfonyl)benzene (3e), yield:59%, 50 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.04 - 3.98 (m, 1H), 3.63 - 3.57 (m, 1H), 2.42 (s, 3H), 1.61-1.58 (m, 2H), 1.25 - 1.23 (m, 12H), 0.89 - 0.80 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.4, 64.8, 32.0, 29.8, 29.6, 29.3, 29.3, 25.9, 22.8, 21.6, 14.3.

1-(decylsulfonyl)-4-methylbenzene (3f), yield:59%, 53 mg, colorless oil. **^{1}H NMR** (400 MHz,



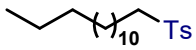
Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.04 - 3.98 (m, 1H), 3.63 - 3.57 (m, 1H), 2.42 (s, 3H), 1.65-1.58 (m, 4H), 1.25 - 1.23 (m, 12H), 0.89 - 0.83 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.4, 64.8, 32.0, 29.8, 29.6, 29.6, 29.4, 29.3, 25.9,



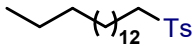
22.8, 21.6, 14.3.

1-methyl-4-(tridecylsulfonyl)benzene (3g), yield:56%, 57 mg, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 4.05 - 3.98 (m, 1H), 3.63 - 3.57 (m, 1H), 2.42 (s, 3H), 1.66 - 1.57 (m, 3H), 1.31 - 1.25 (m, 19H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.4, 64.8, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 25.9, 22.8, 21.6, 14.3.

1-methyl-4-(tetradecylsulfonyl)benzene (3h), yield:53%, 56 mg, white solid. **^{1}H NMR** (400 MHz,



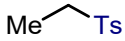
Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.04 - 3.98 (m, 1H), 3.63 - 3.57 (m, 1H), 2.42 (s, 3H), 1.64 - 1.58 (m, 4H), 1.33 - 1.25 (m, 20H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.4, 64.8, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 25.9, 22.8, 21.6, 14.3.



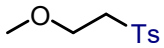
1-(hexadecylsulfonyl)-4-methylbenzene (3i), yield:52%, 59 mg, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.05 - 3.98 (m, 1H), 3.63 - 3.57 (m, 1H), 2.42 (s, 3H), 1.64 - 1.61 (m, 3H), 1.33 - 1.25 (m, 25H), 0.88 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.4, 64.8, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 25.9, 22.8, 21.6, 14.3

MeTs

1-methyl-4-(methylsulfonyl)benzene (3j), yield:32%, 16 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 3.00 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.7, 137.7, 130.0, 127.4, 44.6, 21.6.

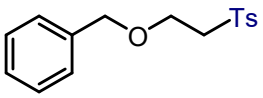


1-(ethylsulfonyl)-4-methylbenzene (3k), yield:30%, 17 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 4.14 - 4.06 (m, 1H), 3.76 - 3.68 (m, 1H), 2.43 (s, 3H), 1.27 (t, *J* = 7.2Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 141.9,

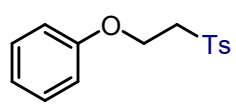


129.9, 127.9, 21.7, 14.8.

1-((2-methoxyethyl)sulfonyl)-4-methylbenzene (3l), yield:58%, 37 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 9.3 Hz, 2H), 7.40 (d, *J* = 9.4Hz, 2H), 3.72 (t, *J* = 7.8 Hz, 2H), 3.50 (t, *J* = 7.8 Hz, 2H), 3.39 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 141.8, 130.4, 127.2, 73.8, 61.8, 59.0, 21.9.

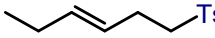


1-((2-(benzyloxy)ethyl)sulfonyl)-4-methylbenzene (3m), yield:53%, 46 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.2, 2H), 7.36 - 7.28 (m, 7H), 4.57 - 4.49 (m, 2H), 4.21 - 4.16 (m, 1H), 3.79 - 3.73 (m, 1H), 3.66 - 3.60 (m, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz,



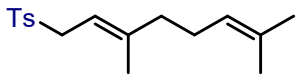
Chloroform-*d*) δ 143.0, 141.8, 138.0, 129.9, 128.6, 127.9, 125.5, 73.3, 68.8, 63.4, 21.7.

1-methyl-4-((2-phenoxyethyl)sulfonyl)benzene (3n), yield:51%, 42 mg, colorless oil. **^{1}H NMR**

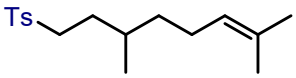


(400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.38 - 4.32 (m, 2H), 4.19 - 4.10 (m, 1H), 3.98 - 3.92 (m, 1H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 158.4, 143.1, 141.7, 129.9, 129.7, 125.5, 121.4, 114.8, 66.7, 62.6, 21.7.

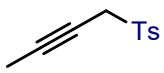
(E)-1-(hex-3-en-1-ylsulfonyl)-4-methylbenzene (3o), yield:56%, 40 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.49 - 5.46 (m, 1H), 5.27 - 5.23 (m, 1H), 4.03 - 3.97 (m, 1H), 3.63 - 3.57 (m, 1H), 2.42 (s, 3H), 2.36 (q, *J* = 7.2 Hz, 2H), 2.03 - 1.95 (m, 2H), 0.92 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.8, 142.0, 135.5, 129.8, 125.4, 123.8, 64.4, 33.2, 25.7, 21.7, 13.8.



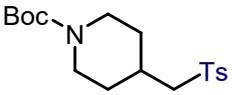
(E)-1-((3,7-dimethylocta-2,6-dien-1-yl)sulfonyl)-4-methylbenzene (3p), yield:30%, 26 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 5.30 (t, *J* = 7.5 Hz, 1H), 5.05 (t, *J* = 7.5 Hz, 1H), 4.54 (dd, *J* = 11.5, 7.4 Hz, 1H), 4.14 (dd, *J* = 11.5, 7.3 Hz, 1H), 2.42 (s, 3H), 2.07 - 1.99 (m, 4H), 1.67 (s, 3H), 1.61 (s, 3H), 1.58 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.8, 142.0, 131.5, 129.8, 125.4, 124.7, 63.0, 37.0, 36.7, 29.3, 25.9, 25.5, 21.7, 19.4, 17.8.



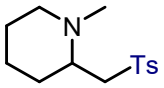
1-((3,7-dimethyloct-6-en-1-yl)sulfonyl)-4-methylbenzene (3q), yield:42%, 37 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.08 - 5.02 (m, 1H), 4.10 - 4.01 (m, 1H), 3.69 - 3.60 (m, 1H), 2.42 (s, 3H), 2.00 - 1.88 (dq, *J* = 15.2, 7.4 Hz, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.55 - 1.38 (m, 4H), 1.16 - 1.06 (m, 1H), 0.84 (dd, *J* = 17.7, 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 142.8, 142.0, 131.5, 129.8, 125.4, 124.7, 63.0, 37.0, 36.7, 29.3, 25.8, 25.4, 21.7, 19.4, 17.8.



1-(but-2-yn-1-ylsulfonyl)-4-methylbenzene (3r), yield:40%, 25 mg, yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 9.3 Hz, 2H), 7.40 (d, *J* = 9.1 Hz, 2H), 4.21 (d, *J* = 2.0 Hz, 2H), 2.48 (s, 3H), 1.84 (t, *J* = 2.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 141.8, 130.4, 127.2, 51.5, 21.9, 3.7.



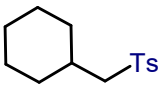
Tert-butyl 4-(tosylmethyl)piperidine-1-carboxylate (3s), yield:42%, 44 mg, white solid. **^{1}H**



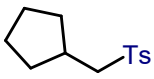
NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 4.06 (d, *J* = 12.0 Hz, 2H), 3.84 (dd, *J* = 9.8, 6.8 Hz, 1H), 3.37 (dd, *J* = 9.8, 6.8 Hz, 1H), 2.65 (t, *J* = 12.9 Hz, 2H), 2.42 (s, 3H), 1.65 (m, 2H), 1.43 (s, 9H), 1.16 - 1.02 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.9, 142.9, 141.7, 129.9, 125.4, 79.6, 68.1, 36.6, 28.6, 21.7.

1-methyl-2-(tosylmethyl)piperidine (3t), yield:47%, 37 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 9.3 Hz, 2H), 7.30 (d, *J* = 9.3Hz, 2H), 4.07 – 4.02 (m, 1H), 3.87 - 3.75 (m, 4H), 3.60 - 3.54 (m, 2H), 3.10 (t, *J* = 12.4 Hz, 1H), 2.43 (s, 3H), 1.93 - 1.79 (m, 4H), 1.50 - 1.45 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.3, 138.3, 129.8, 127.0, 62.5, 60.5, 58.8, 54.7, 44.8, 41.4, 24.9, 24.7, 24.2, 22.2, 22.1, 21.6, 19.1. HRMS (ESI, m/z) calcd for $C_{14}H_{22}NO_2S^+$ $(M+H)^+$: 268.1366; Found:293.1367.

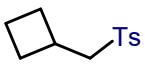
1-((cyclohexylmethyl)sulfonyl)-4-methylbenzene (3u), yield:55%, 42 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.82 (dd, *J* = 9.6, 6.4



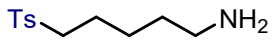
Hz, 1H), 3.37 (dd, *J* = 9.6, 6.4 Hz, 1H), 2.42 (s, 3H), 1.73 - 1.55 (m, 7H), 1.20 - 1.09 (m, 2H), 0.94 - 0.83 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.1, 129.8, 125.4, 69.6, 38.0, 29.7, 29.4, 25.8, 21.6, 14.3.



1-((cyclopentylmethyl)sulfonyl)-4-methylbenzene (3v), yield:55%, 39 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.90 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.44 (dd, *J* = 9.6, 6.9 Hz, 1H), 2.42 (s, 3H), 2.23 - 2.12 (m, 1H), 1.77 - 1.46 (m, 8H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.4, 68.4, 58.6, 39.5, 29.4, 25.4, 21.6, 18.6.



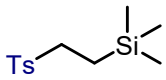
1-((cyclobutylmethyl)sulfonyl)-4-methylbenzene (3w), yield:49%, 33 mg, colorless oil. **^{1}H NMR**



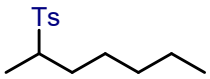
(400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.90 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.44 (dd, *J* = 9.6, 6.9 Hz, 1H), 2.42 (s, 3H), 2.23 - 2.12 (m, 1H), 1.77 - 1.46 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.0, 129.8, 125.4, 68.4, 58.6, 39.5, 29.4, 25.3, 21.6, 18.6.

5-tosylpentan-1-amine (3x), yield:37%, 26 mg, colorless oil **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.59 (t, *J* = 10.1 Hz, 2H), 2.93 (q, *J* = 6.6 Hz 2H), 2.42 (s, 3H), 1.54 - 1.46 (m, 4H), 1.40 - 1.33 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.5, 137.1, 130.4, 127.2, 62.6, 43.2, 32.1, 29.4, 22.8, 21.6.

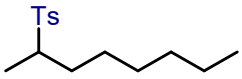
Trimethyl(2-tosylethyl)silane (3y), yield:30%, 23 mg, colorless oil. **^{1}H NMR** (400 MHz,



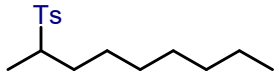
Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 4.17 - 4.10 (m, 1H), 3.83 - 3.76 (m, 1H), 2.42 (s, 3H), 1.10 - 0.93 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.2, 129.8, 125.3, 63.6, 21.6, 19.0, -1.4.

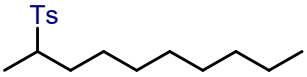


1-(heptan-2-ylsulfonyl)-4-methylbenzene (3z), yield:66%, 50 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 4.48 - 4.38 (m, 1H), 2.41 (s, 3H), 1.73 - 1.43 (m, 3H), 1.37 (d, *J* = 6.2 Hz, 2H), 1.24 - 1.19 (m, 6H), 0.90 - 0.83 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0, 142.6, 129.7, 125.2, 37.4, 31.8, 29.1, 25.2, 22.7, 22.0, 21.6, 14.2.



1-methyl-4-(octan-2-ylsulfonyl)benzene (3aa), yield:62%, 50 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 4.48 - 4.38 (m, 1H), 2.41 (s, 3H), 1.73 - 1.43 (m, 3H), 1.37 (d, *J* = 6.2 Hz, 2H), 1.24 - 1.19 (m, 8H), 0.90 - 0.83 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0, 142.6, 129.7, 125.2, 37.4, 31.8, 29.1, 25.2, 22.7, 22.0, 21.6, 14.2.

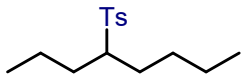




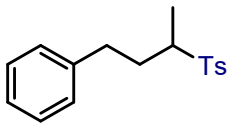
1-methyl-4-(nonan-2-ylsulfonyl)benzene (3ab), yield:60%, 51 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 4.48 - 4.38 (m, 1H), 2.41 (s, 3H), 1.70 - 1.36 (m, 3H), 1.37 (d, *J* = 6.2 Hz, 2H), 1.28 - 1.19 (m, 10H), 0.90 - 0.85 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0, 142.6, 129.7, 125.0, 37.4, 32.0, 29.5, 29.4, 25.3, 22.8, 22.1, 21.6, 14.2.

1-(decan-2-ylsulfonyl)-4-methylbenzene (3ac), yield:57%, 51 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 4.49 - 4.39 (m, 1H), 2.42 (s, 3H), 1.70 - 1.41 (m, 3H), 1.37 (d, *J* = 6.3 Hz, 2H), 1.29 - 1.20 (m, 12H), 0.90 - 0.84 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0, 142.6, 129.7, 125.0, 37.4, 32.0, 29.5, 29.4, 25.3, 22.8, 22.1, 21.6, 14.2. HRMS (ESI, m/z) calcd for $C_{17}H_{29}O_2S^+$ $(M+H)^+$: 297.1883; Found:297.1880.

1-methyl-4-(octan-4-ylsulfonyl)benzene (3ad), yield:50%, 40 mg, colorless oil. **^{1}H**

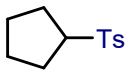


NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 4.48 - 4.38 (m, 1H), 2.41 (s, 3H), 1.73 - 1.43 (m, 3H), 1.37 (d, *J* = 6.2 Hz, 2H), 1.24 - 1.19 (m, 8H), 0.90 - 0.83 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0, 142.6, 129.7, 125.2, 37.4, 31.8, 29.1, 25.2, 22.7, 22.0, 21.6, 14.2. HRMS (ESI, m/z) calcd for $C_{15}H_{25}O_2S^+$ $(M+H)^+$: 269.1570; Found:269.1575.

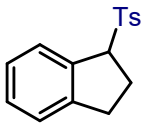


1-methyl-4-((4-phenylbutan-2-yl)sulfonyl)benzene (3ae), yield:45%, 39 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 - 7.60 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.19 (dt, *J* = 7.4, 5.7 Hz, 2H), 7.13 (d, *J* = 6.8 Hz, 2H), 4.55 - 4.43 (m, 1H), 3.85 - 3.74 (m, 1H), 2.80 - 2.59 (m, 2H), 2.43 (s, 3H), 2.07 - 1.77 (m, 3H), 1.43 (d, *J* = 6.2 Hz, 1H), 1.28 (d, *J* = 6.6

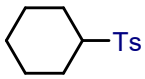
Hz, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0, 142.7, 141.5, 129.8, 128.6, 128.5, 126.1, 125.1, 39.0, 31.5, 29.8, 22.2, 21.7.



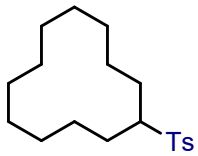
1-(cyclopentylsulfonyl)-4-methylbenzene (3af), yield:59%, 40 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.83 - 4.80 (m, 1H), 2.42 (s, 3H), 1.93 - 1.86 (m, 2H), 1.77 - 1.66 (m, 4H), 1.58 - 1.50 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.9, 142.6, 129.8, 125.3, 34.3, 33.9, 23.4, 21.6.



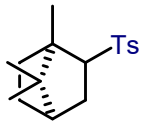
1-tosyl-2,3-dihydro-1H-indene (3ag), yield:50%, 41 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 9.1 Hz, 2H), 7.49 - 7.37 (m, 3H), 7.29 - 7.18 (m, 3H), 5.27 - 5.17 (m, 1H), 3.14 - 3.03 (m, 1H), 2.87 - 2.79 (m, 1H), 2.49 (s, 3H), 2.48 - 2.43 (m, 1H), 2.18 - 1.91 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 141.8, 130.4, 128.4, 127.2, 126.8, 125.0, 124.3, 76.6, 36.1, 29.9, 21.9.



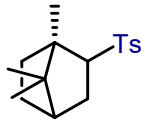
1-(cyclohexylsulfonyl)-4-methylbenzene (3ah), yield:60%, 43 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 4.37 - 4.29 (m, 1H), 2.42 (s, 3H), 2.04 - 1.97 (m, 2H), 1.82 - 1.68 (m, 3H), 1.58 - 1.17 (m, 7H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.1, 142.5, 129.7, 125.2, 33.9, 33.8, 25.3, 24.0, 21.7.



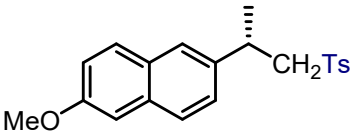
Tosylcyclododecane (3ai), yield:49%, 47 mg, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.7 H z, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 4.51 - 4.45 (m, 1H), 2.41 (s, 3H), 1.88 - 1.79 (m, 1H), 1.75 - 1.64 (m, 2H), 1.53 - 1.19 (m, 19H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.1, 142.6, 129.7, 125.1, 31.0 (d, *J* = 10.5 Hz), 24.4, 24.2, 24.0, 23.5, 23.3, 21.6, 21.0.



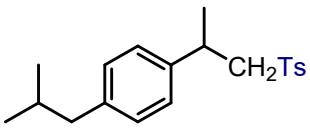
(1R,4R)-1,7,7-trimethyl-2-tosylbicyclo[2.2.1]heptane (3aj), yield:60%, 53 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 4.58 - 4.42 (m, 1H), 2.42 (s, 3H), 1.93 - 1.87 (m, 1H), 1.73 - 1.57 (m, 4H), 1.31 - 1.19 (m, 2H), 0.83 (d, *J* = 9.7 Hz, 6H), 0.82 (d, *J* = 71.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.0, 142.5, 129.7, 125.4, 84.6, 83.6, 49.9, 49.7, 48.0, 47.9, 45.2, 45.1, 37.7, 37.2, 28.2, 28.1, 26.9, 26.8, 21.7, 19.9, 19.9, 18.9, 13.5, 13.1. HRMS (ESI, m/z) calcd for $C_{17}H_{25}O_2S^+$ $(M+H)^+$: 293.1570; Found:293.1571.



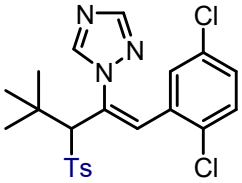
(1R)-1,7,7-trimethyl-2-tosylbicyclo[2.2.1]heptane (3ak), yield:56%, 49 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 4.58 - 4.42 (m, 1H), 2.42 (s, 3H), 1.93 - 1.87 (m, 1H), 1.73 - 1.57 (m, 4H), 1.31 - 1.19 (m, 2H), 0.83 (d, *J* = 9.7 Hz, 6H), 0.82 (d, *J* = 71.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ143.0, 142.5, 129.7, 125.4, 84.6, 83.6, 49.9, 49.7, 48.0, 47.9, 45.2, 45.1, 37.7, 37.2, 28.2, 28.1, 26.9, 26.8, 21.7, 19.9, 19.9, 18.9, 13.5, 13.1. HRMS (ESI, m/z) calcd for $C_{17}H_{25}O_2S^+$ $(M+H)^+$: 293.1570; Found:293.1573.



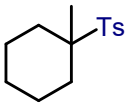
(S)-2-methoxy-6-(1-tosylpropan-2-yl)naphthalene (3al), yield:25%, 27 mg, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 - 7.76 (m, 1H), 7.70 - 7.63 (m, 1H), 7.55 - 7.46 (m, 1H), 7.44 - 7.39 (m, 2H), 7.29 - 7.10 (m, 5H), 4.24 - 4.07 (m, 1H), 3.93 (d, *J* = 14.4 Hz, 3H), 3.73 - 3.66 (m, 1H), 3.18 (p, *J* = 6.7 Hz, 1H), 2.54 (d, *J* = 127.1 Hz, 3H), 1.37 - 1.26 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 142.7, 141.8, 141.5, 138.1, 138.0, 137.4, 133.7, 132.8, 131.3, 130.2, 129.7, 129.7, 129.3, 129.1, 128.0, 127.2, 127.1, 127.1, 126.5, 126.4, 126.0, 125.7, 125.4, 125.3, 124.8, 105.9, 105.7, 69.7, 68.6, 55.6, 55.5, 40.0, 39.9, 26.7, 21.6, 18.2, 18.0. HRMS (ESI, m/z) calcd for $C_{21}H_{23}O_3S^+$ $(M+H)^+$: 355.1362; Found:355.1367.



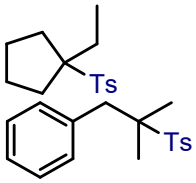
1-isobutyl-4-(1-tosylpropan-2-yl)benzene (3am), yield:50%, 49 mg, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 - 7.44 (m, 2H), 7.29 - 7.26 (m, 2H), 7.07 - 7.01 (m, 4H), 4.16 - 3.98 (m, 1H), 3.65 - 3.59 (m, 1H), 3.05 - 2.98 (m, 1H), 2.44 (dd, *J* = 7.2, 2.9 Hz, 2H), 2.41 (s, 3H), 1.88 - 1.80 (m, 1H), 1.27 (dd, *J* = 6.9, 2.0 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.7, 140.1, 129.8, 129.4, 127.3, 127.2, 125.5, 125.4, 68.9, 45.2, 39.6, 30.4, 22.5, 21.7, 18.1. HRMS (ESI, m/z) calcd for $C_{20}H_{27}O_2S^+$ $(M+H)^+$: 311.1726; Found:311.1726.



(Z)-1-(1-(2,5-dichlorophenyl)-4,4-dimethyl-3-tosylpent-1-en-2-yl)-1H-1,2,4-triazole (3an), yield:26%, 36 mg, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, J = 11.0 Hz, 1H), 7.72 (dd, *J* = 30, 8.3 Hz, 1H), 7.68 (d, J = 7.8 Hz, 2H), 7.51 (t, J = 2.8 Hz, 1H), 7.38 (t, J = 6.8 Hz, 3H), 7.29 (s, 1H), 7.18 - 7.09 (m, 1H), 5.07 (d, J = 41.7 Hz, 1H), 2.46 (s, 3H), 0.72 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.7, 146.9, 143.3, 141.7, 137.9, 135.1, 134.7, 131.5, 131.1, 130.3, 129.7, 127.6, 127.1, 125.0, 76.2, 36.2, 26.0, 21.9. HRMS (ESI, m/z) calcd for $C_{22}H_{24}Cl_2N_3O_2S^+$ $(M+H)^+$: 464.0961; Found:464.0960.



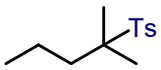
1-methyl-4-((1-methylcyclohexyl)sulfonyl)benzene (3ao), yield:30%, 23 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 2.48 (s, 3H), 1.64 - 1.58 (m, 2H), 1.54 - 1.40 (m, 8H), 1.19 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.8, 141.7, 130.2, 127.1, 70.0, 39.4, 29.5, 25.6, 22.7, 21.8.



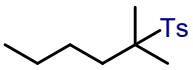
1-((1-ethylcyclopentyl)sulfonyl)-4-methylbenzene (3ap), yield:27%, 20 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 6.3 Hz, 2H), 2.41 (s, 3H), 2.05 - 1.61 (m, 10H), 1.02 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.2, 142.1, 129.8, 124.9, 41.9, 23.7, 23.6, 23.1, 21.6, 9.1. HRMS (ESI, m/z) calcd for $C_{14}H_{21}O_2S^+$ $(M+H)^+$: 253.1257; Found:253.1257.

1-methyl-4-((2-methyl-1-phenylpropan-2-yl)sulfonyl)benzene (3aq), yield:30%, 26 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.29 - 7.26 (m, 2H), 7.23 - 7.20 (m, 1H), 7.19 - 7.16 (m, 2H), 2.73 (s, 2H), 2.45 (s, 3H), 1.19 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 141.8, 137.9, 130.6, 130.3, 128.3, 127.2, 126.6, 70.9, 49.8, 29.3, 21.9.

1-methyl-4-((2-methylpentan-2-yl)sulfonyl)benzene (3ar), yield:29%, 23 mg, colorless oil. **^{1}H**



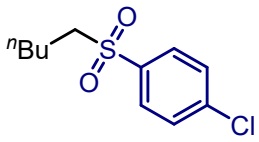
NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.76 - 1.70 (m, 2H), 1.53 (s, 6H), 1.48 - 1.28 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz,



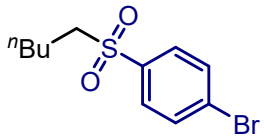
Chloroform-*d*) δ 129.7, 125.0, 45.3, 28.1, 27.8, 21.6, 17.5, 14.5.

1-methyl-4-((2-methylhexan-2-yl)sulfonyl)benzene (3as), yield:32%, 24 mg, colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.76 - 1.70 (m, 2H), 1.53 (s, 6H), 1.48 - 1.28 (m, 6H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.0, 142.1, 129.7, 125.0, 42.7, 28.0, 27.8, 26.4, 23.1, 21.6, 14.2. HRMS (ESI, m/z) calcd for $C_{14}H_{23}O_2S^+$ $(M+H)^+$: 255.1413; Found:255.1413.

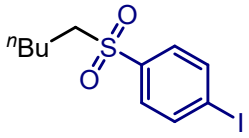
1-chloro-4-(pentylsulfonyl)benzene (3at), yield:52%, 38 mg, colorless oil. **^{1}H NMR** (600 MHz,



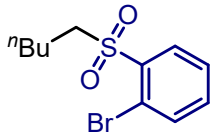
Chloroform-*d*) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 3.08 - 3.05 (m, 2H), 1.72 - 1.67 (m, 2H), 1.36 - 1.26 (m, 5H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.5, 137.8, 129.7, 56.5, 30.4, 22.5, 22.2, 13.8.



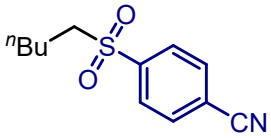
1-bromo-4-(pentylsulfonyl)benzene (3au), yield:54%, 47 mg, white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 3.11 - 2.84 (m, 2H), 1.67 - 1.59 (m, 2H), 1.37 - 1.17 (m, 5H), 0.80 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.4, 137.7, 129.6, 56.4, 30.3, 22.4, 22.1, 13.7.



1-iodo-4-(pentylsulfonyl)benzene (3av), yield:56%, 57 mg, colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 3.11 - 2.84 (m, 2H), 1.67 - 1.59 (m, 2H), 1.37 - 1.17 (m, 5H), 0.80 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.4, 137.7, 129.6, 56.4, 30.3, 22.4, 22.1, 13.7.

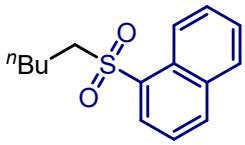


1-bromo-2-(pentylsulfonyl)benzene (3aw), yield:46%, 40 mg, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.76 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54 - 7.45 (m, 2H), 3.45 - 3.41 (m, 2H), 1.72 - 1.68 (m, 2H), 1.39 - 1.26 (m, 5H), 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz,

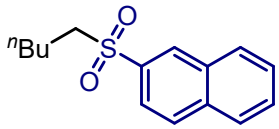


Chloroform-*d*) δ 138.6, 135.6, 134.8, 132.2, 128.1, 121.0, 53.9, 30.5, 22.2, 13.8.

4-(pentylsulfonyl)benzonitrile (3ax), yield:54%, 38 mg, white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (s, 2H), 7.57 (d, *J* = 10.9 Hz, 3H), 4.10 - 4.05 (m, 1H), 3.67 - 3.61 (m, 1H), 1.62 - 1.56 (m, 1H), 1.67 - 1.62 (m, 2H), 1.53 - 1.26 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.7, 142.2, 132.9, 126.3, 66.2, 29.5, 27.9, 22.3, 14.0.

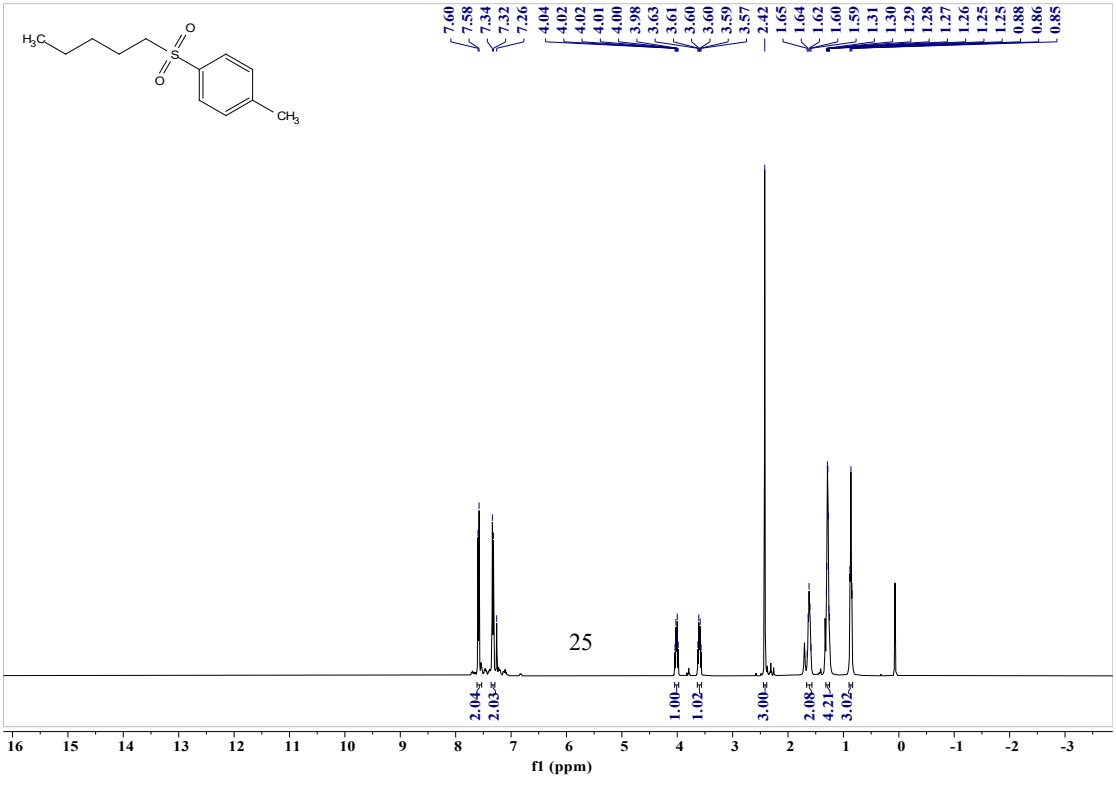


1-(pentylsulfonyl)naphthalene (3az), yield:29%, 23 mg, white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.74 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.13 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.97 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.90 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.72 - 7.69 (m, 1H), 7.64 - 7.59 (m, 2H), 3.29 - 3.26 (m, 2H), 1.73 - 1.68 (m, 2H), 1.33 - 1.22 (m, 5H), 0.81 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 135.2, 134.3, 130.8, 129.4, 129.1, 128.8, 127.1, 124.5, 124.2, 56.0, 30.4, 22.4, 22.2, 13.8.

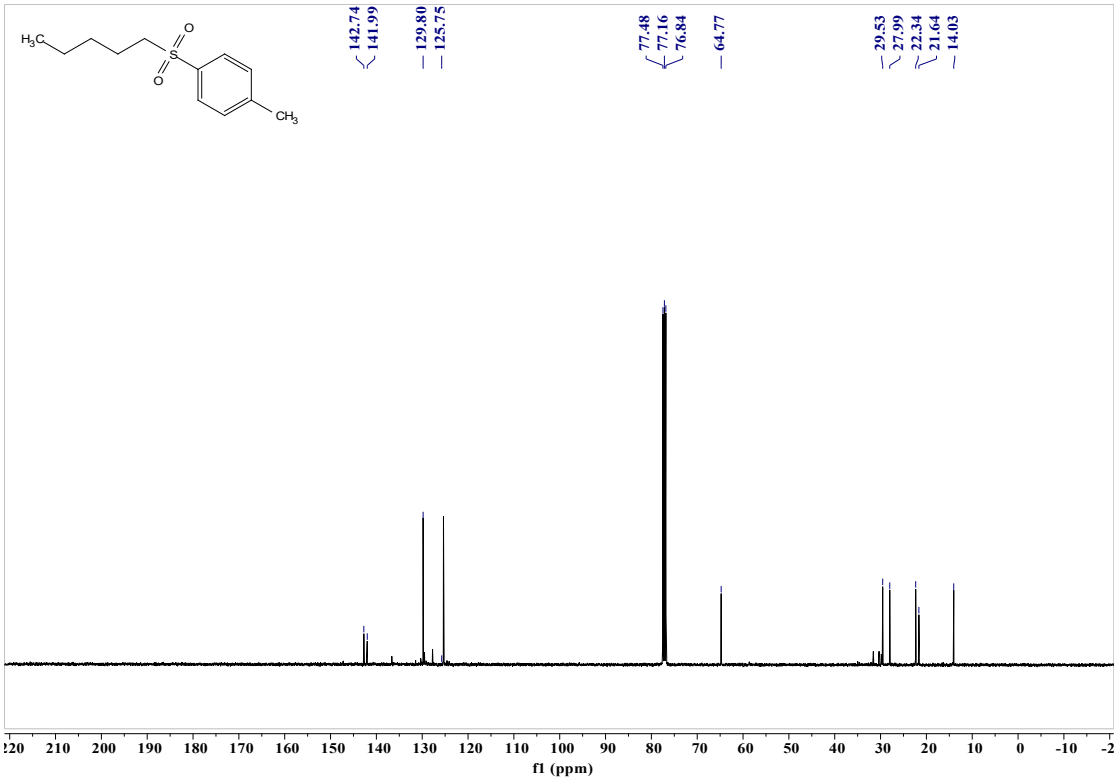


2-(pentylsulfonyl)naphthalene (3ba), yield:29%, 23 mg, white solid. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 1.9 Hz, 1H), 8.01 (dd, *J* = 8.4, 5.3 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.69 - 7.64 (m, 2H), 3.17 - 3.14 (m, 2H), 1.77 - 1.72 (m, 2H), 1.37 - 1.24 (m, 5H), 0.84 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 136.2, 135.4, 132.3, 130.0, 129.7, 129.5, 129.4, 128.1, 127.8, 122.9, 56.5, 30.5, 22.6, 22.2, 13.8.

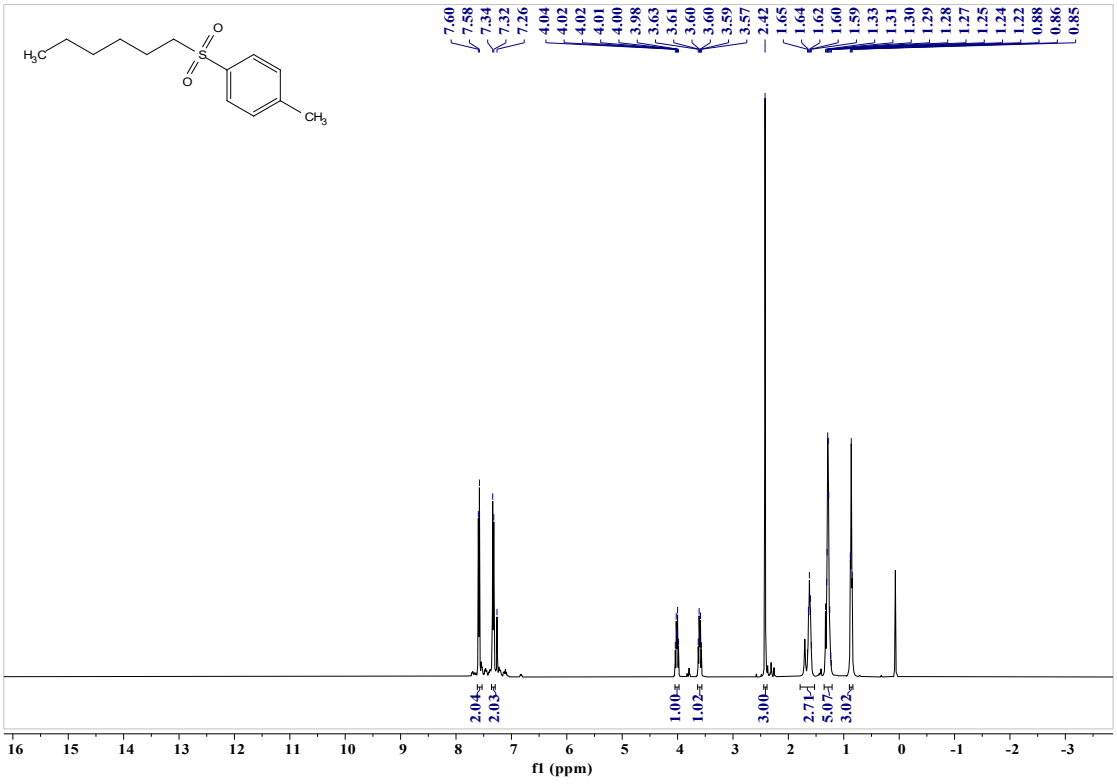
Compound 3a, ^{1}H NMR (400 MHz, Chloroform-d)



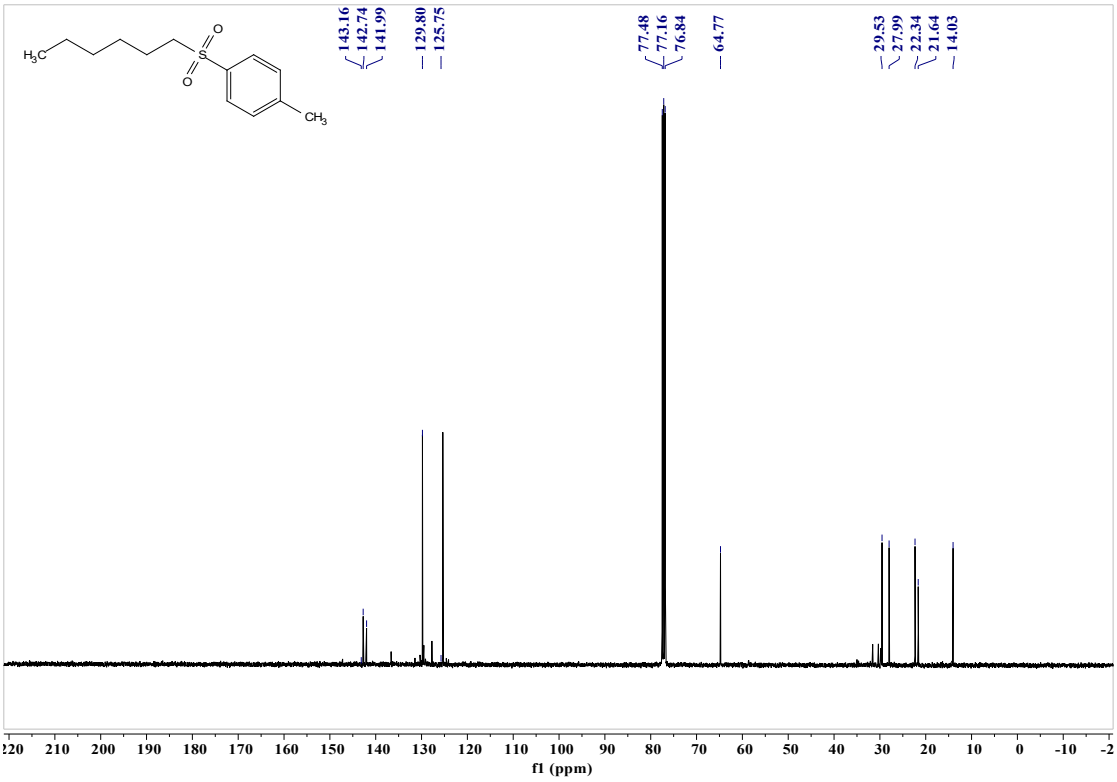
Compound 3a, ^{13}C NMR (101 MHz, Chloroform-d)



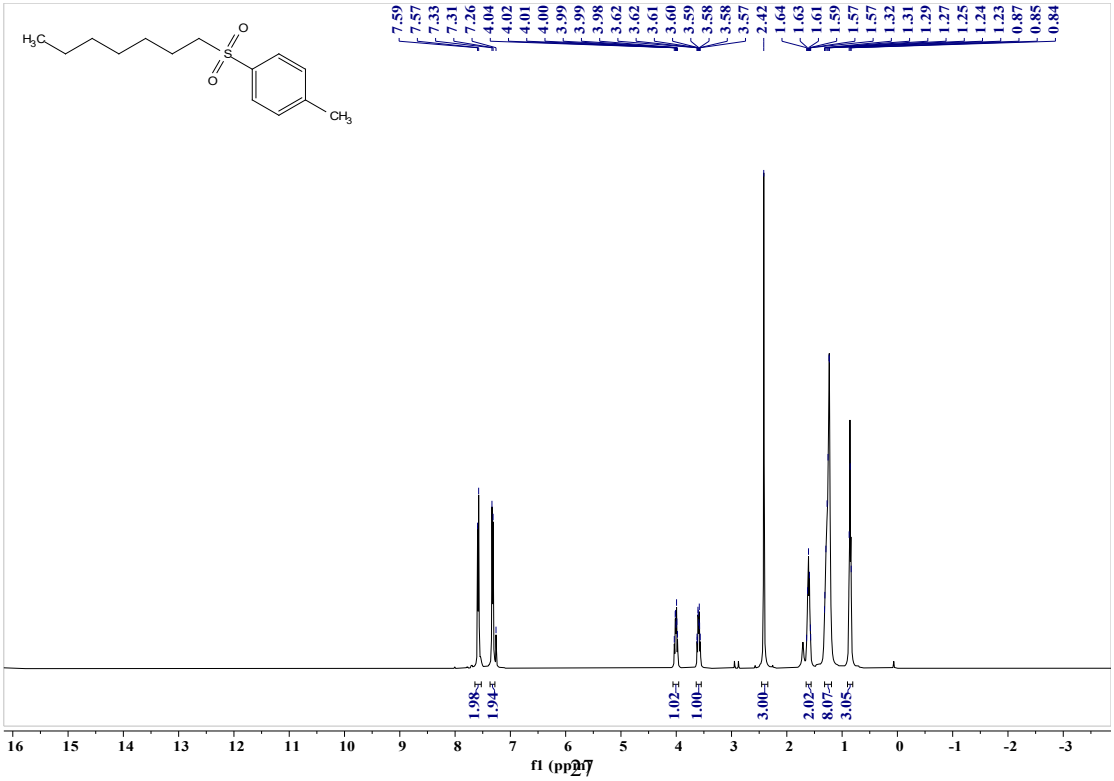
Compound 3b, ^{1}H NMR (400 MHz, Chloroform-d)



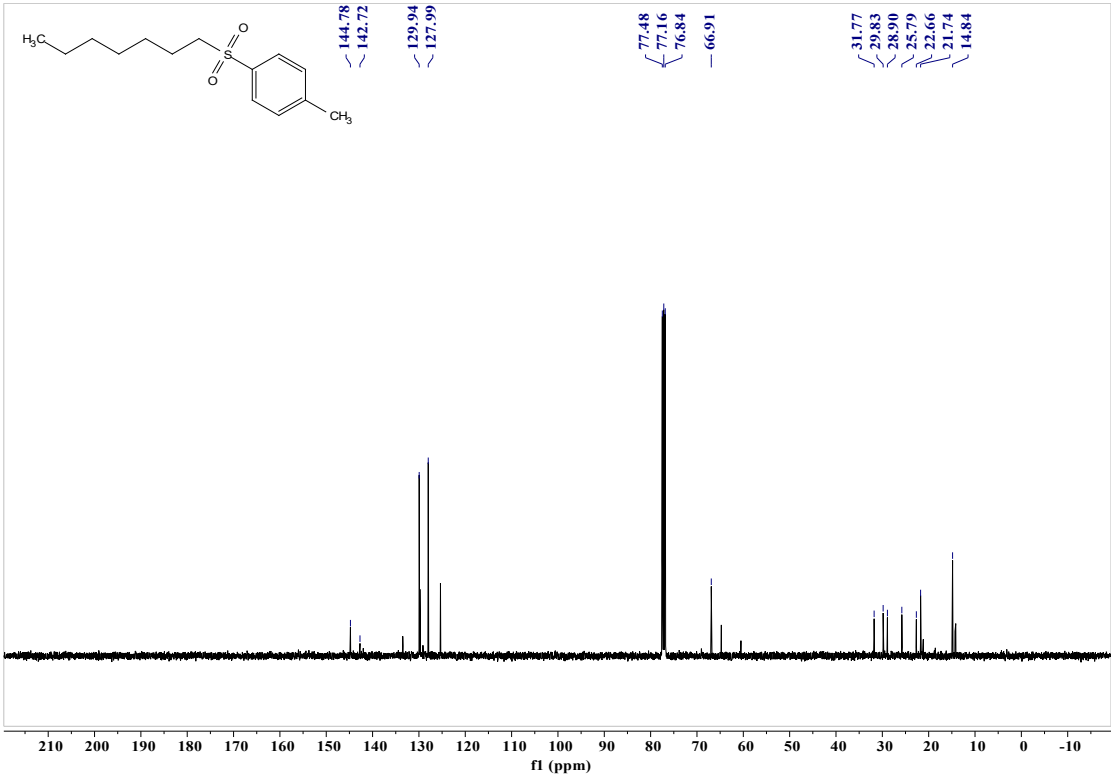
Compound 3b, ^{13}C NMR (101 MHz, Chloroform-d)



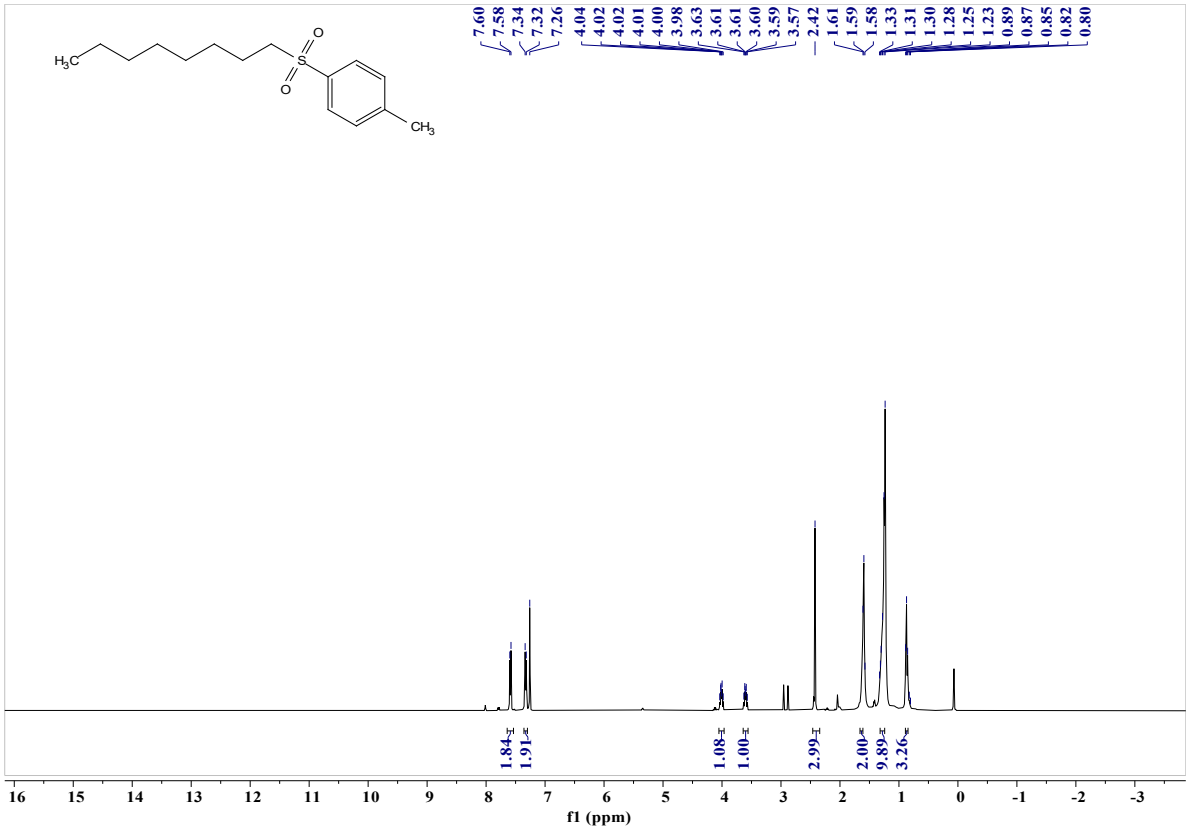
Compound 3c, ^{1}H NMR (400 MHz, Chloroform-d)



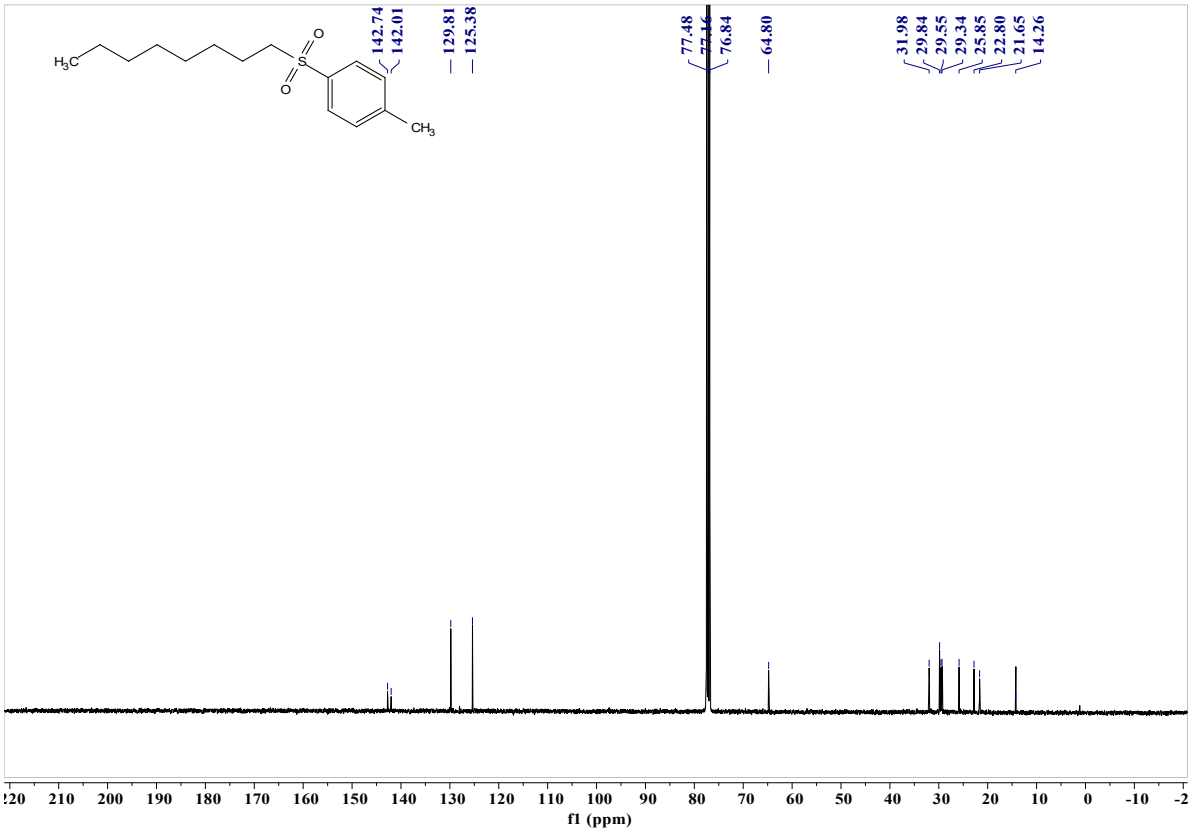
Compound 3c, ^{13}C NMR (101 MHz, Chloroform-d)



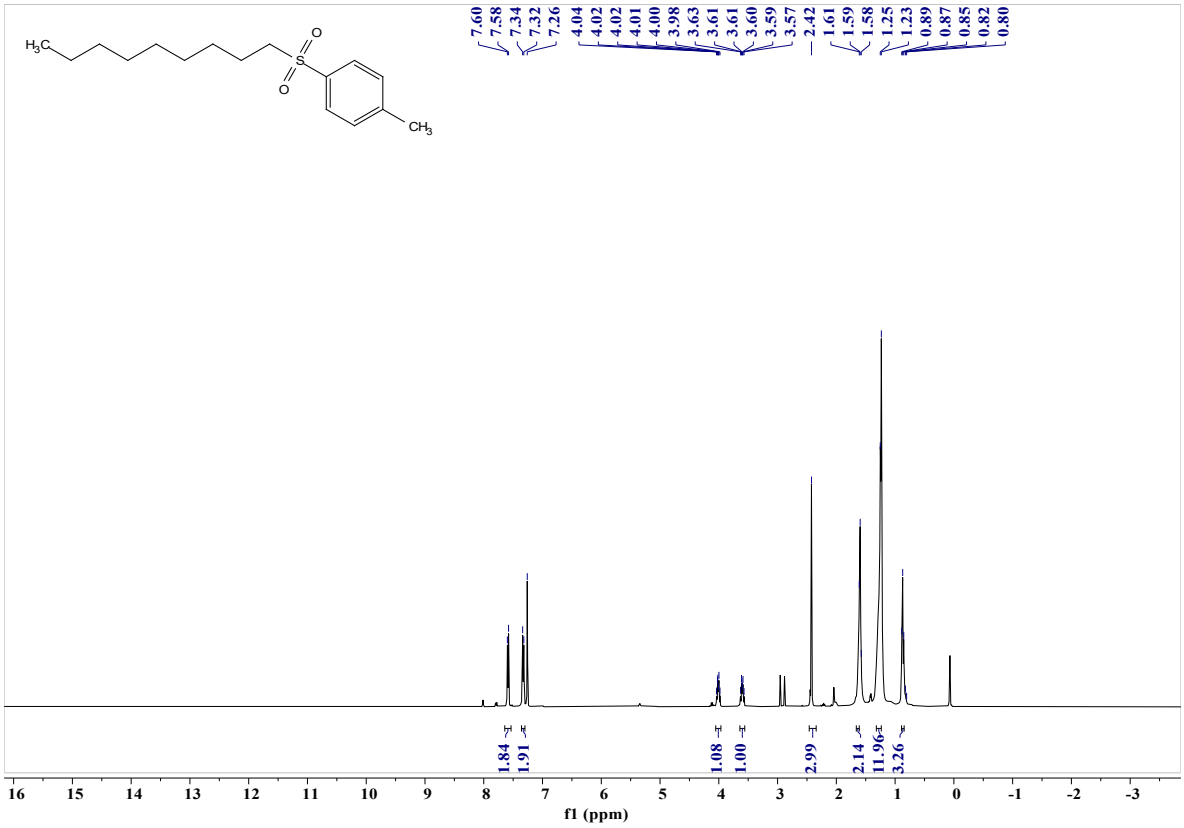
Compound 3d, ^{1}H NMR (400 MHz, Chloroform-d)



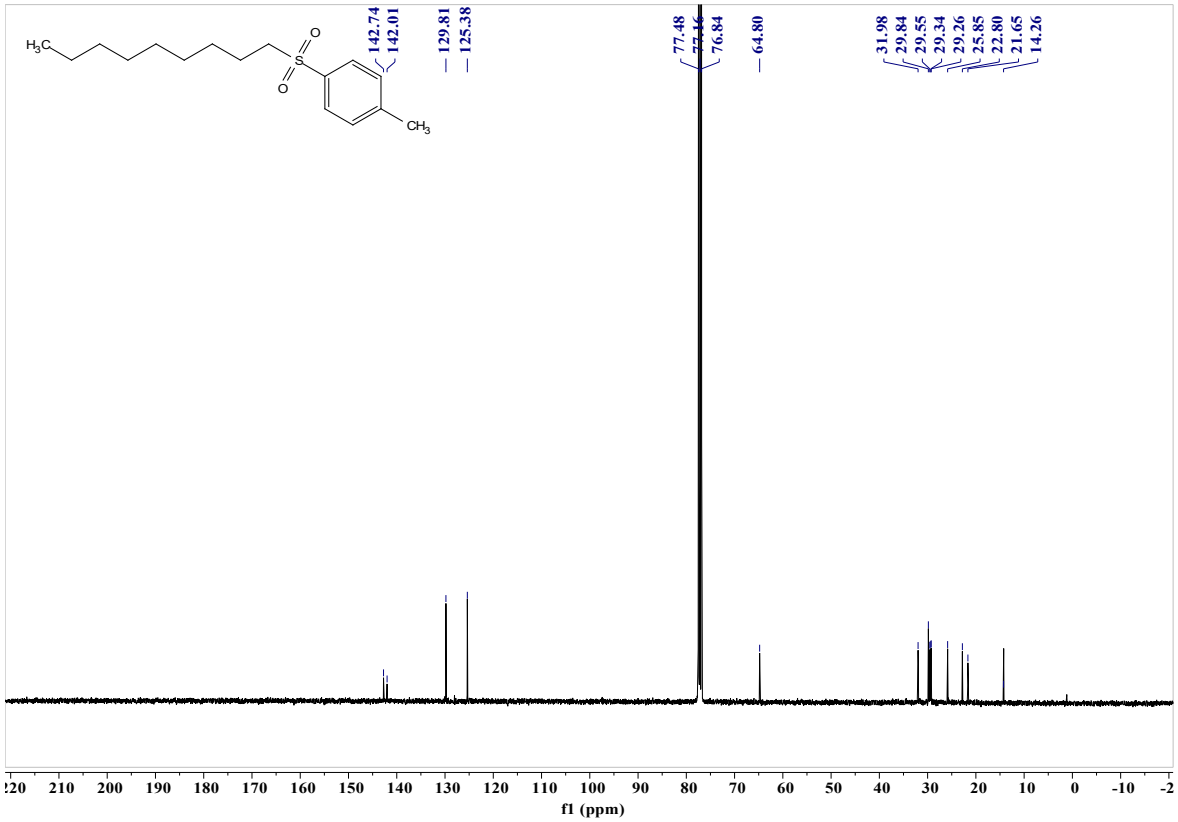
Compound 3d, ^{13}C NMR (101 MHz, Chloroform-d)



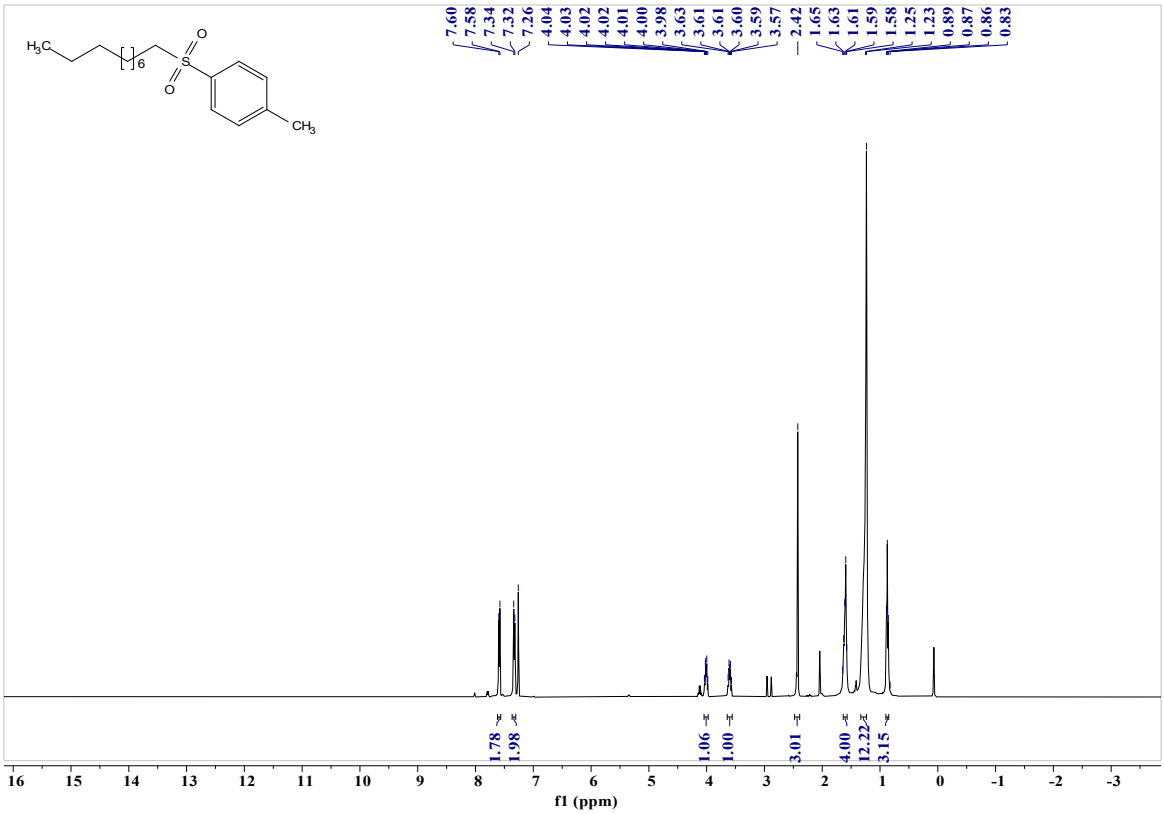
Compound 3e, ^{1}H NMR (400 MHz, Chloroform-d)



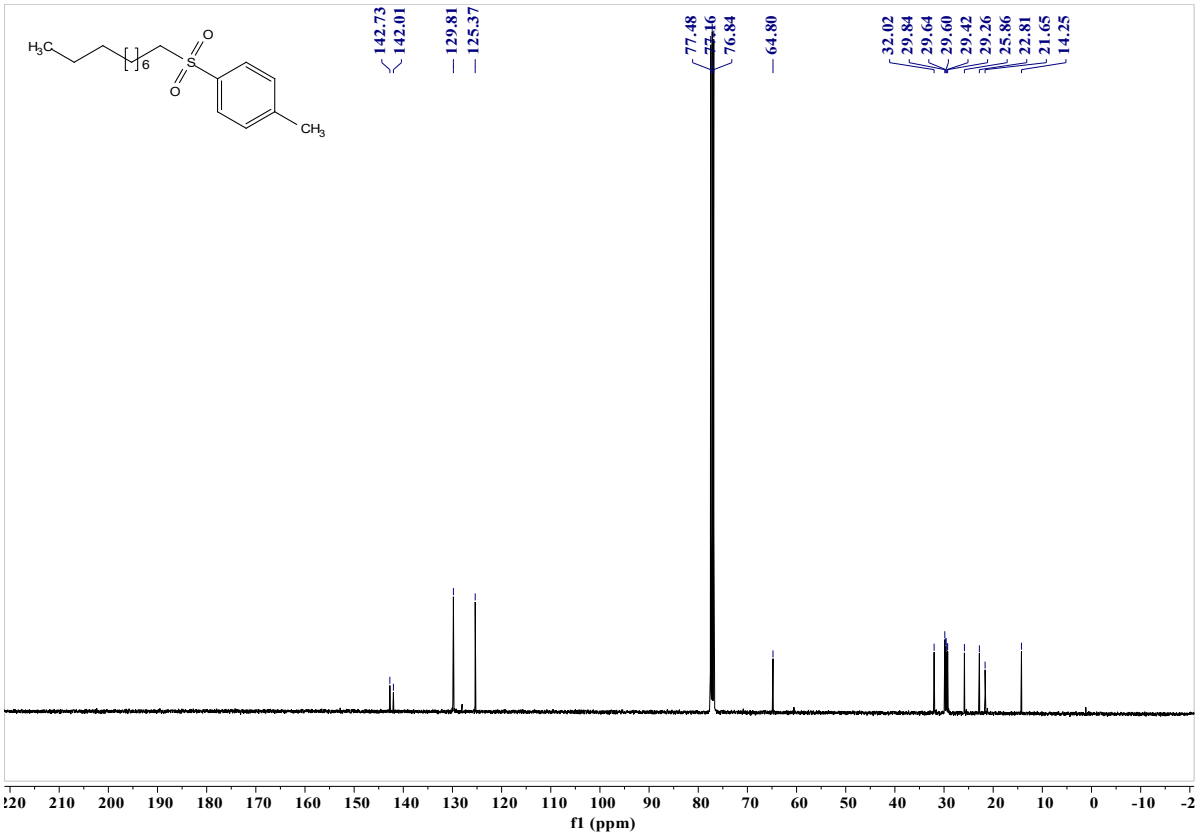
Compound 3e, ^{13}C NMR (101 MHz, Chloroform-d)



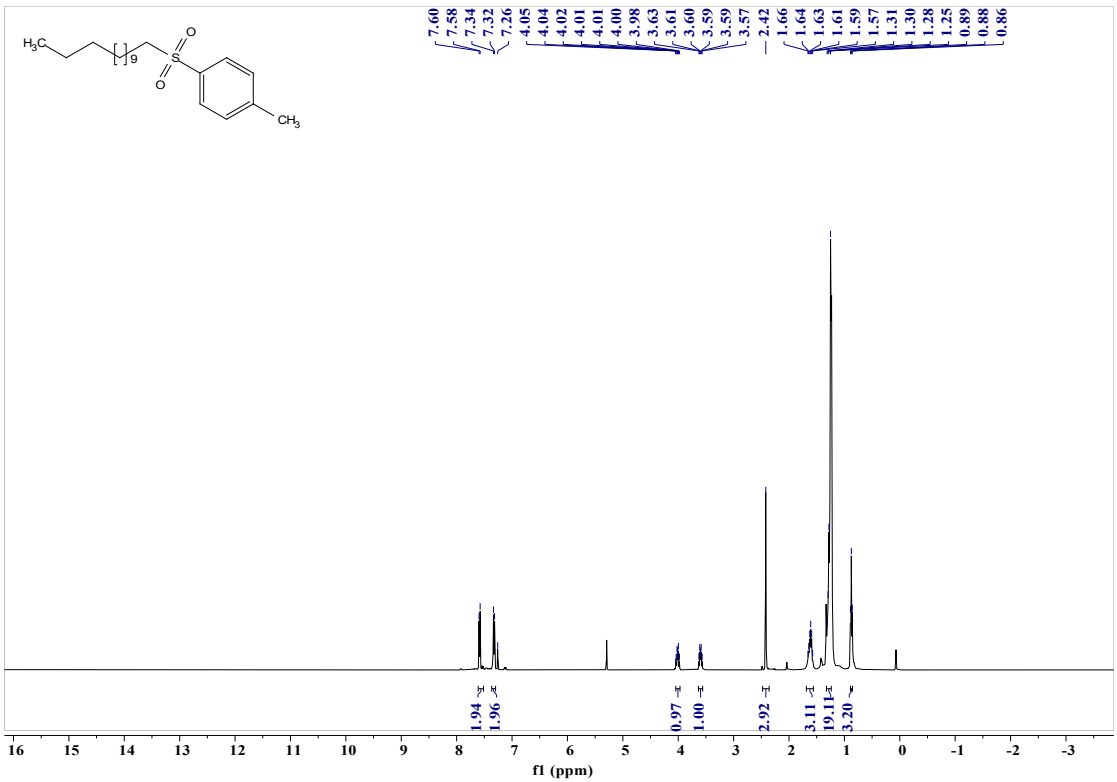
Compound 3f, ^{1}H NMR (400 MHz, Chloroform-d)



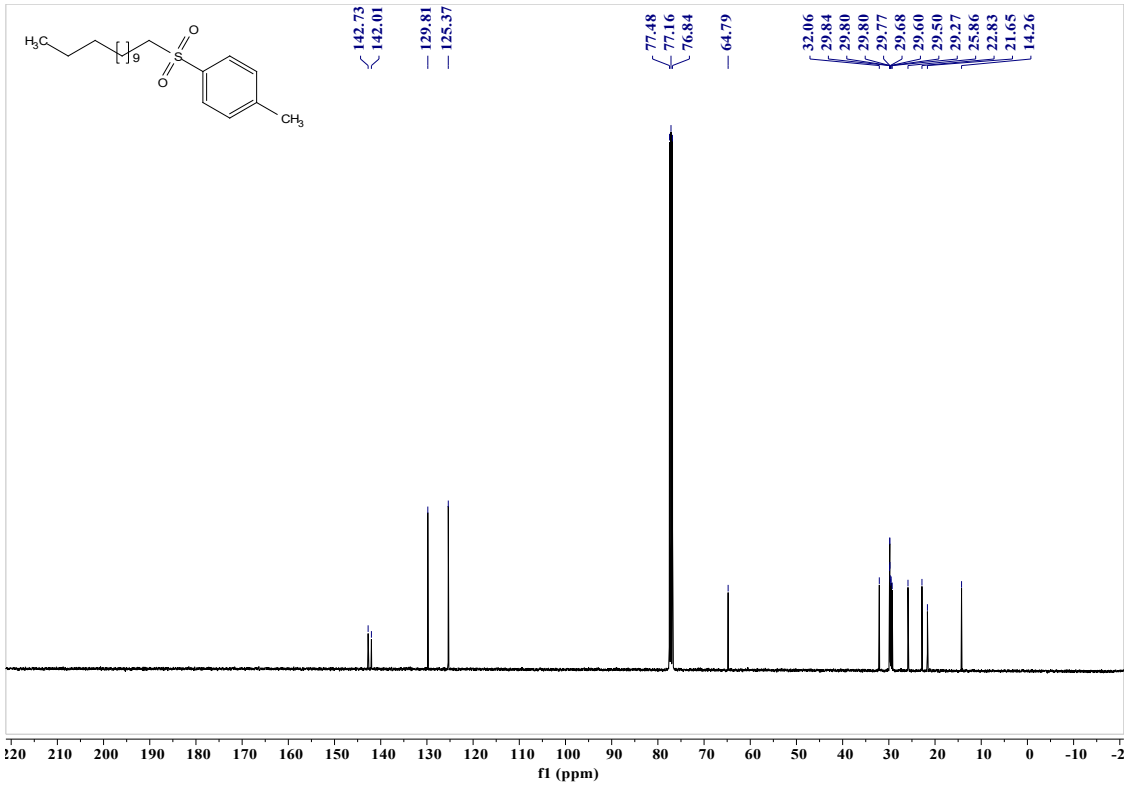
Compound 3f, ^{13}C NMR (101 MHz, Chloroform-d)



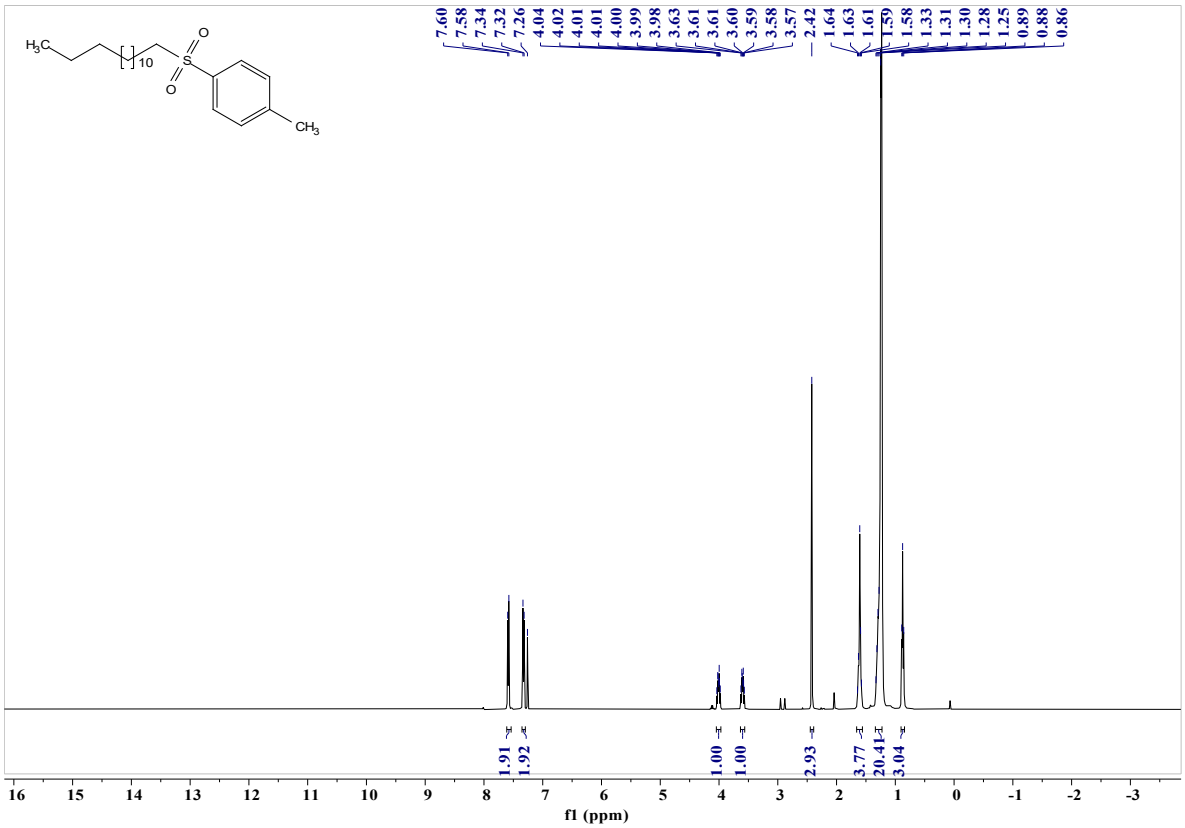
Compound 3g, ^{1}H NMR (400 MHz, Chloroform-d)



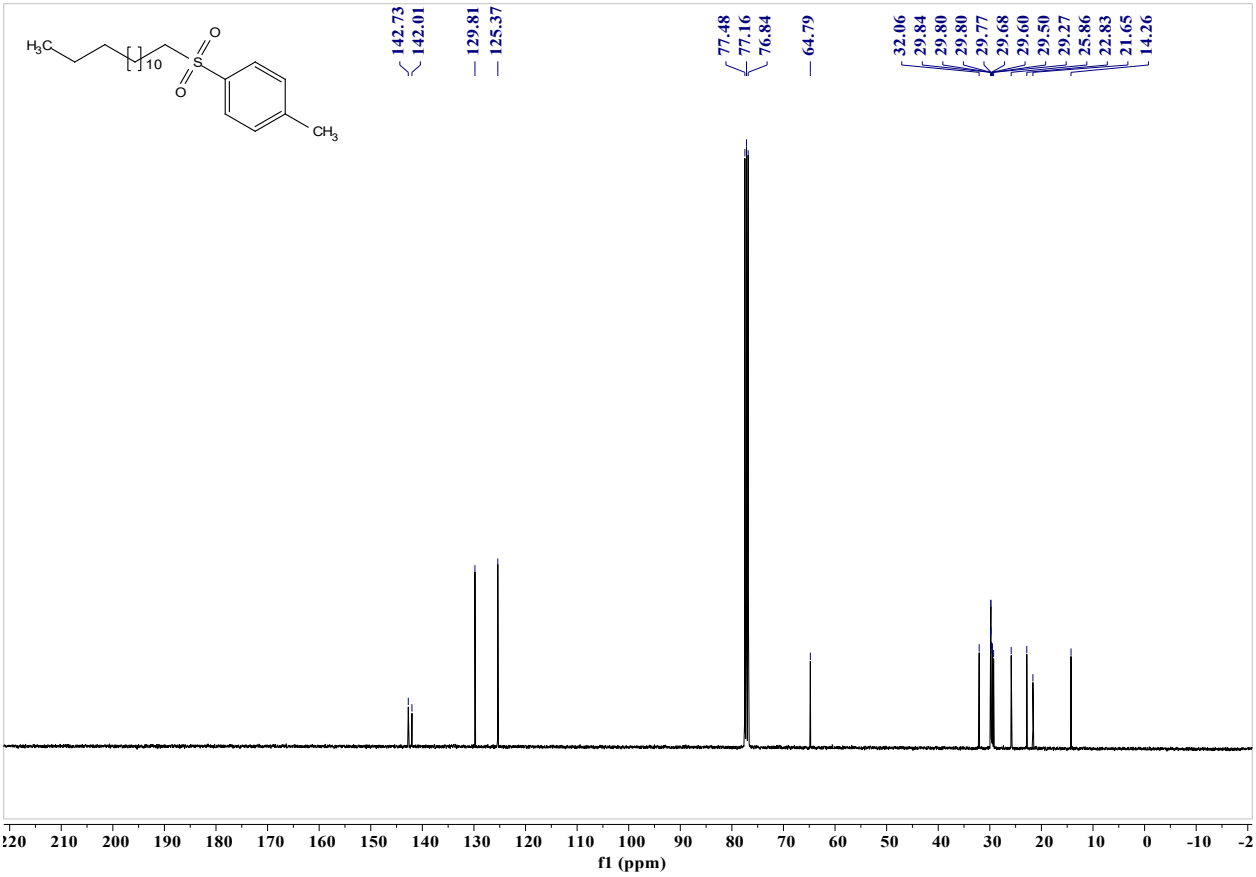
Compound 3g, ^{13}C NMR (101 MHz, Chloroform-d)



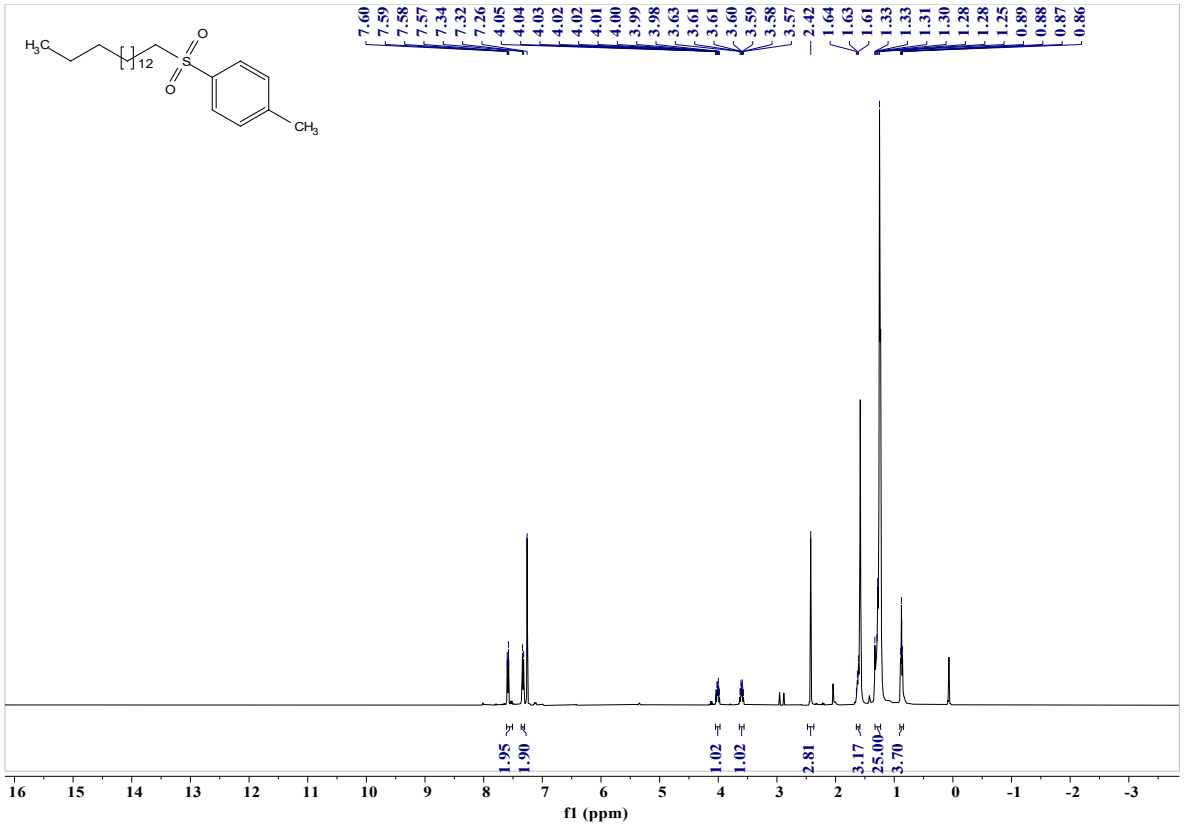
Compound 3h, ^{1}H NMR (400 MHz, Chloroform-d)



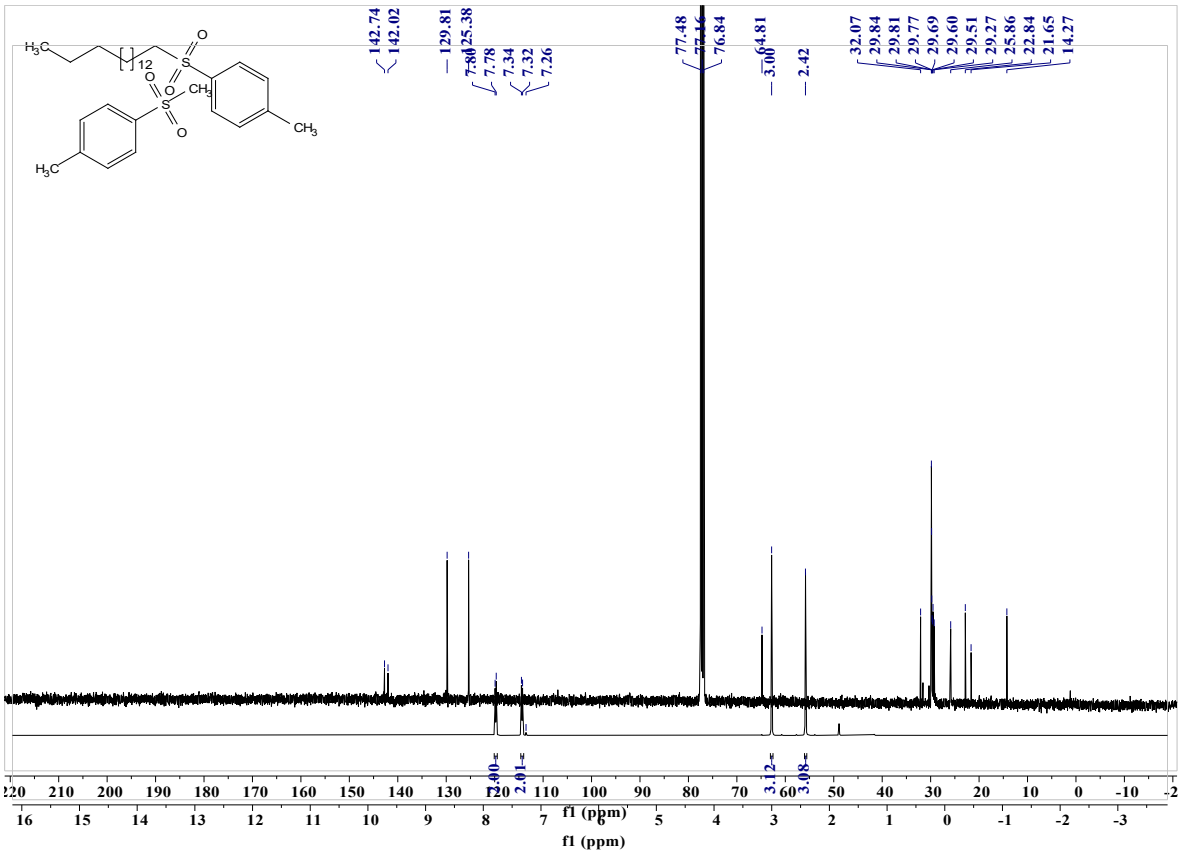
Compound 3h, ^{13}C NMR (101 MHz, Chloroform-d)



Compound 3i, ^{1}H NMR (400 MHz, Chloroform-d)

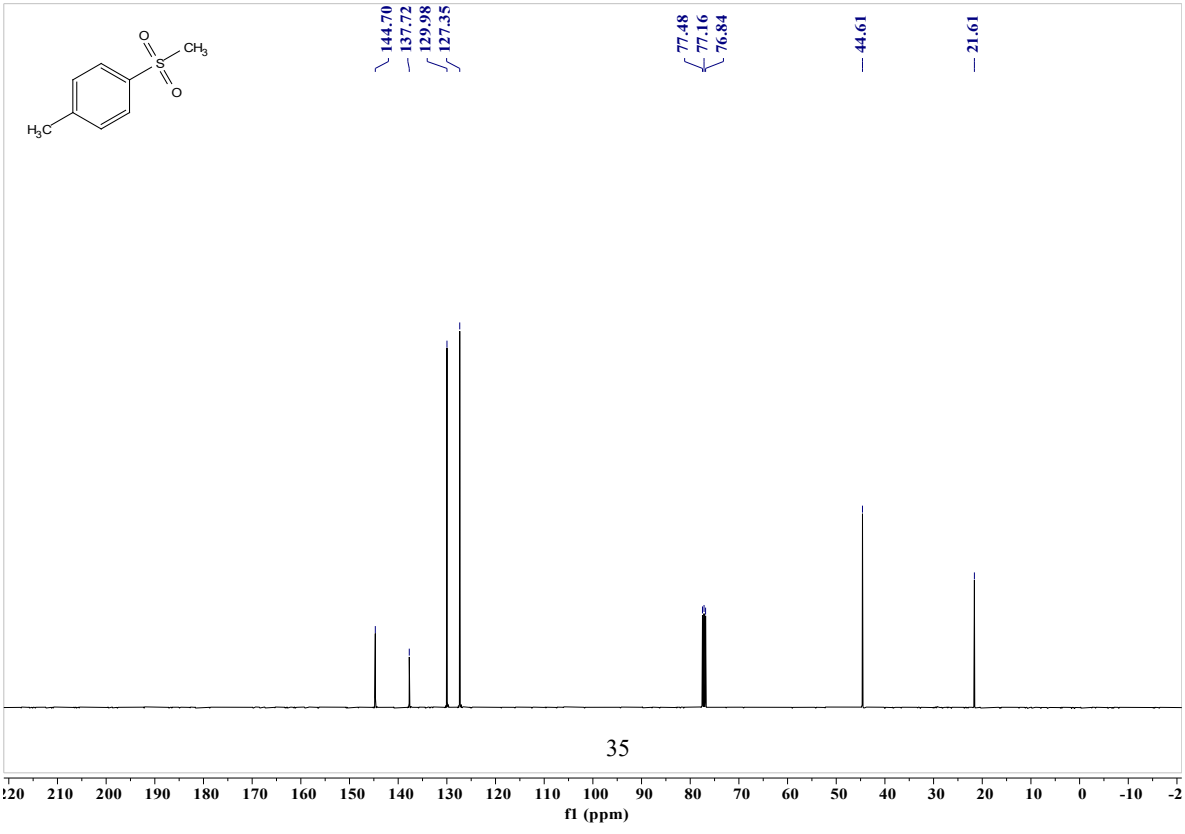


Compound 3i, ^{13}C NMR (101 MHz, Chloroform-d)

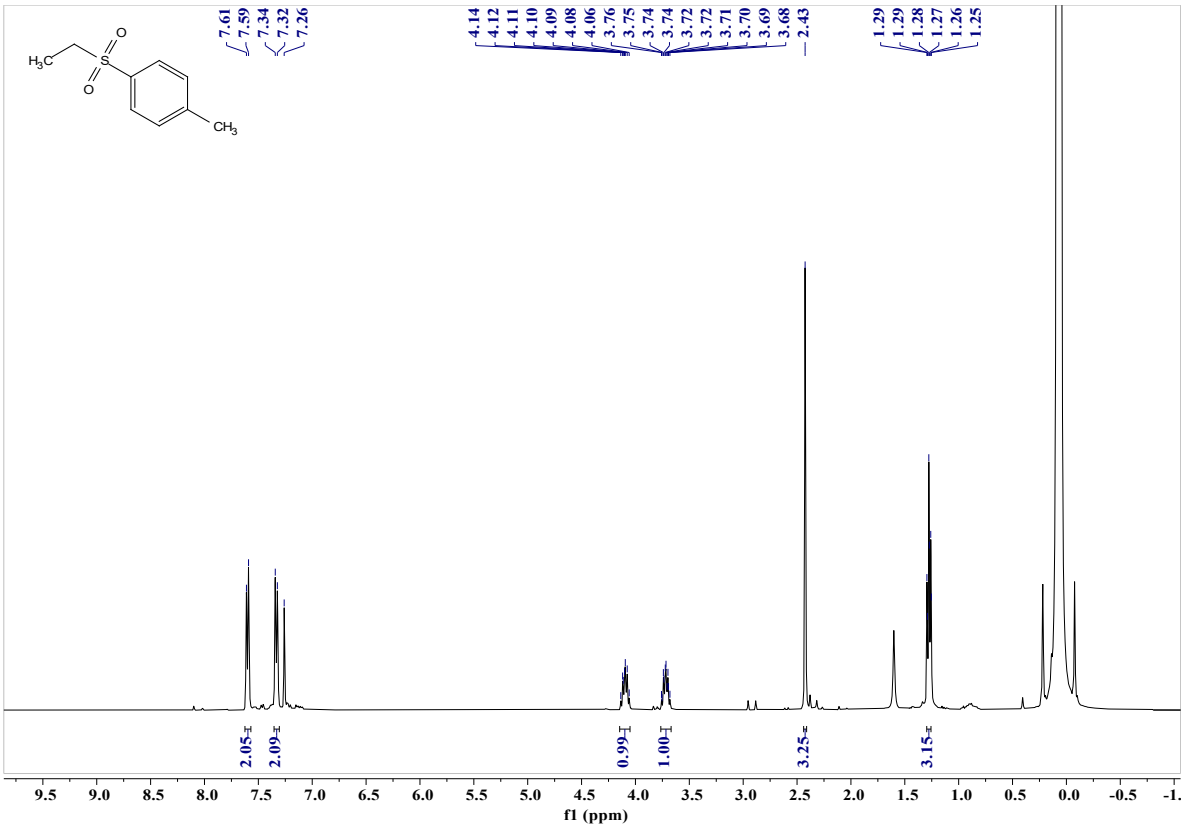


Compound 3j, ^{1}H NMR (400 MHz, Chloroform-d)

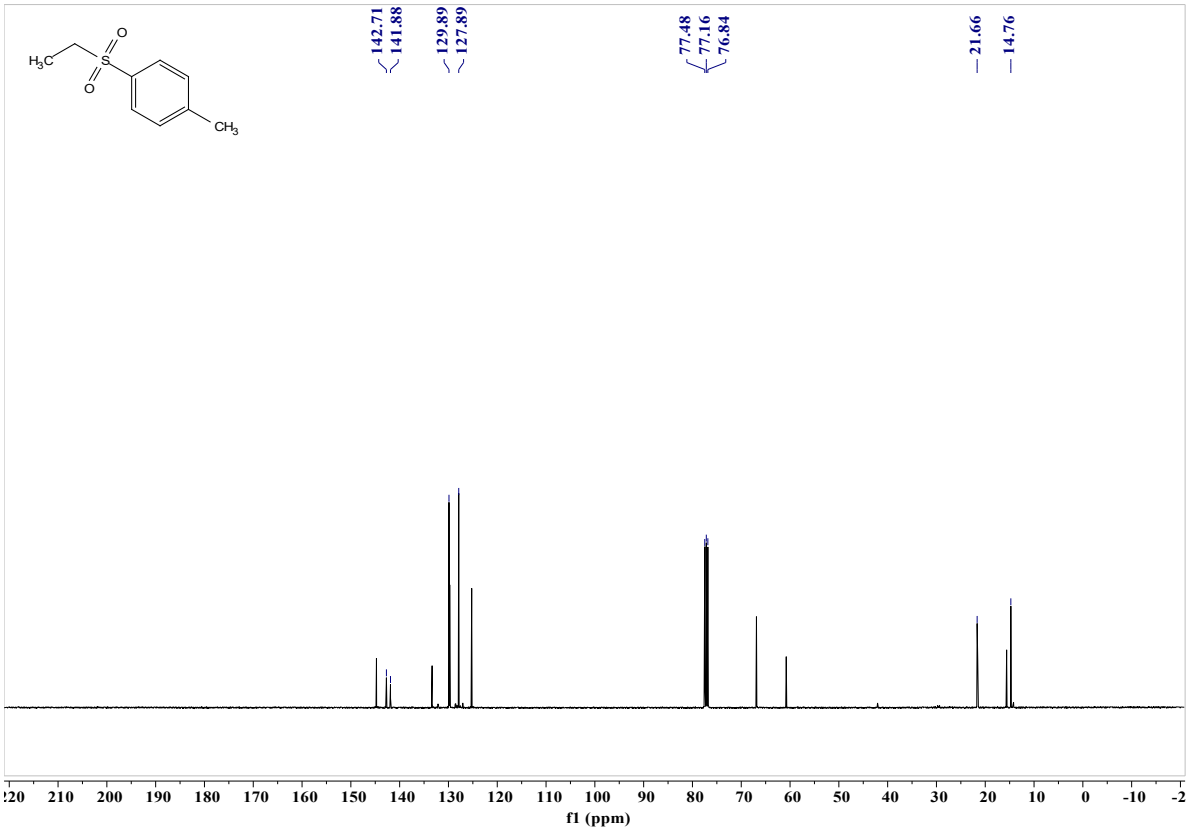
Compound 3j, ^{13}C NMR (101 MHz, Chloroform-d)



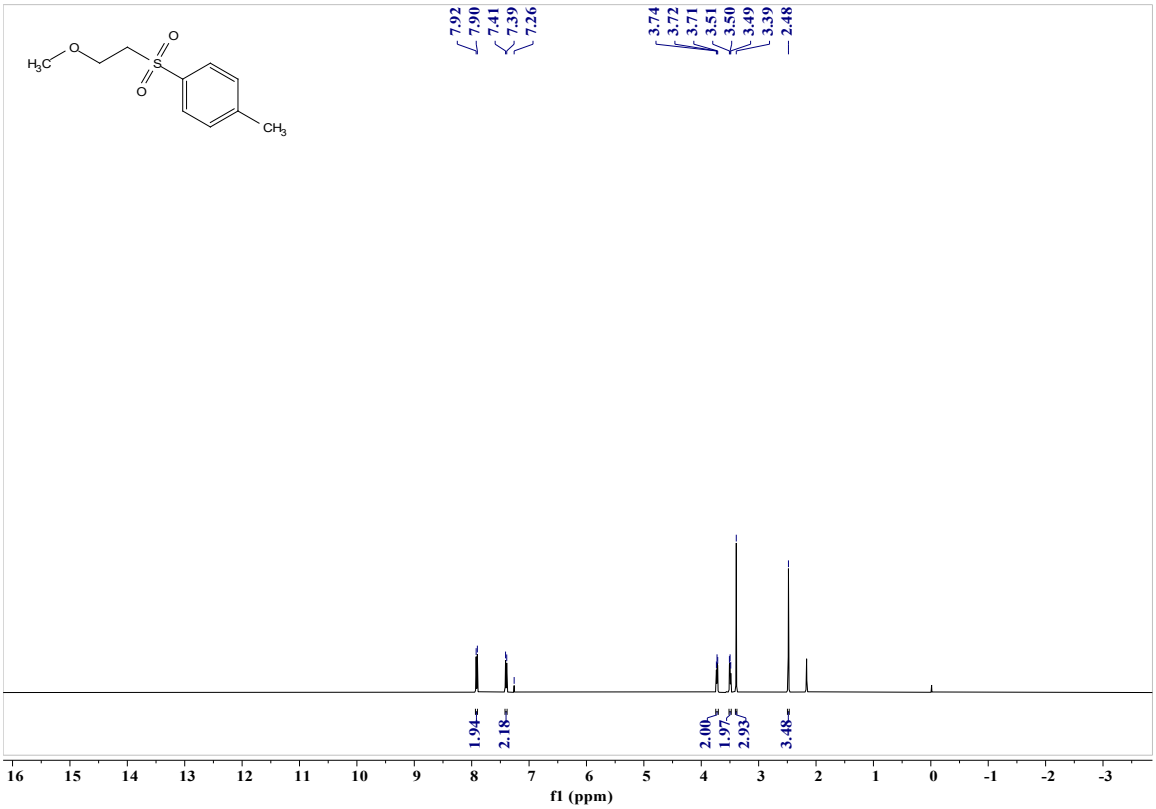
Compound 3k, ^{1}H NMR (400 MHz, Chloroform-d)



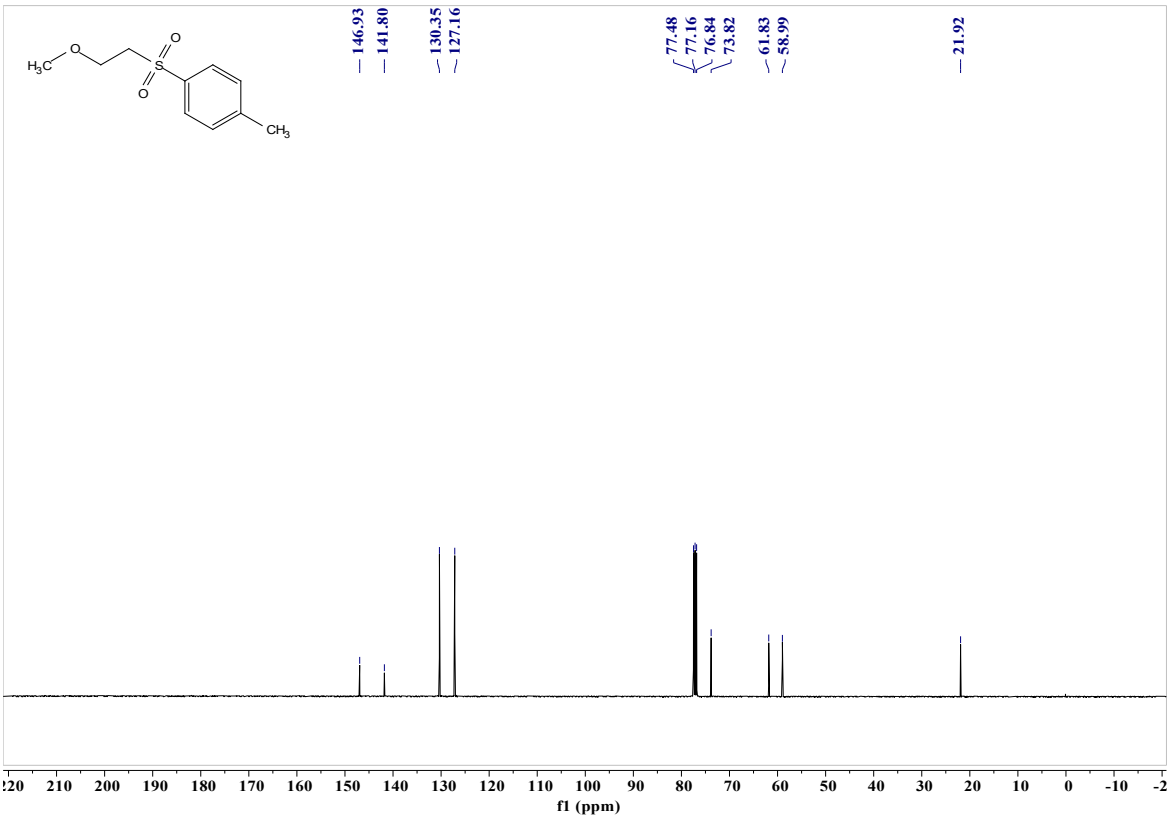
Compound 3k, ^{13}C NMR (101 MHz, Chloroform-d)



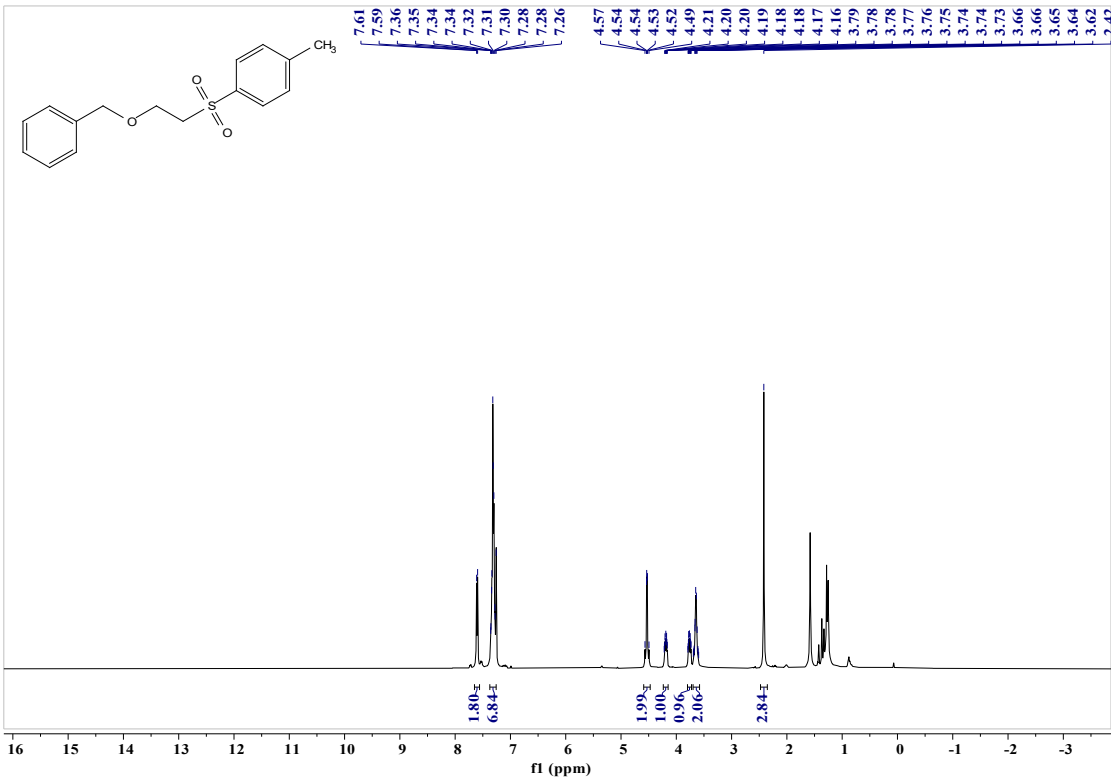
Compound 3l, ^{1}H NMR (400 MHz, Chloroform-d)



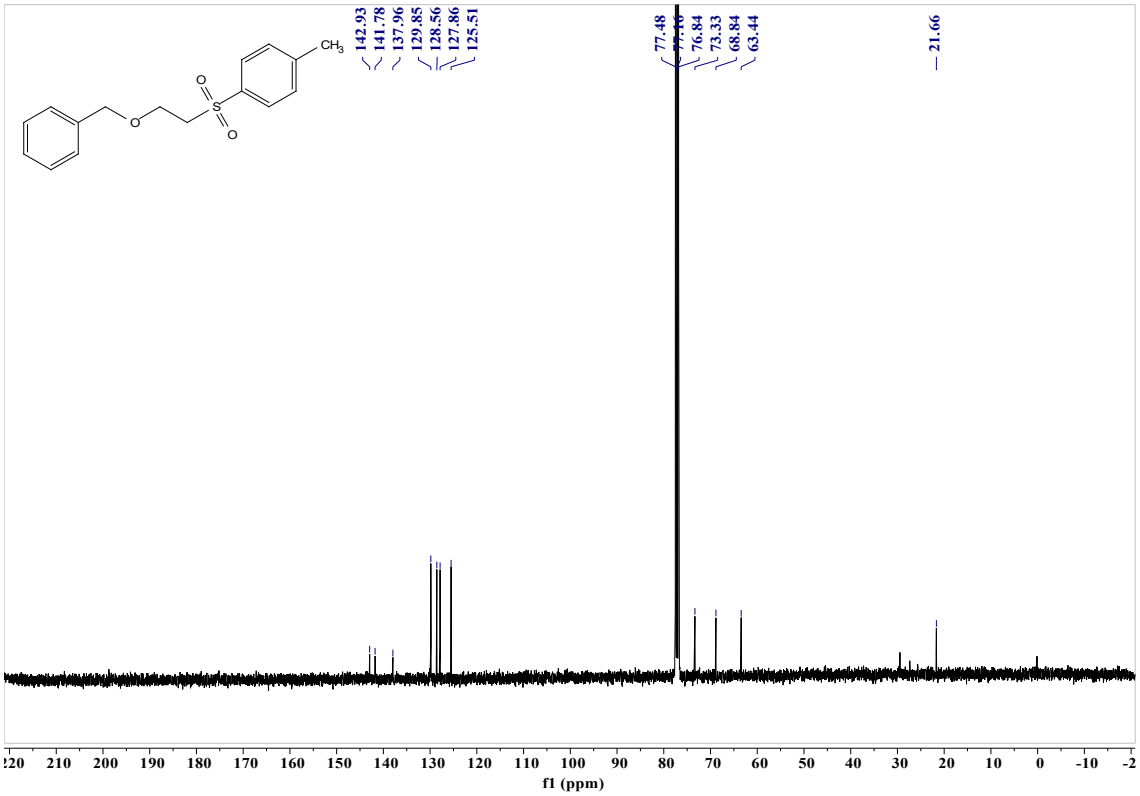
Compound 3l, ^{13}C NMR (101 MHz, Chloroform-d)

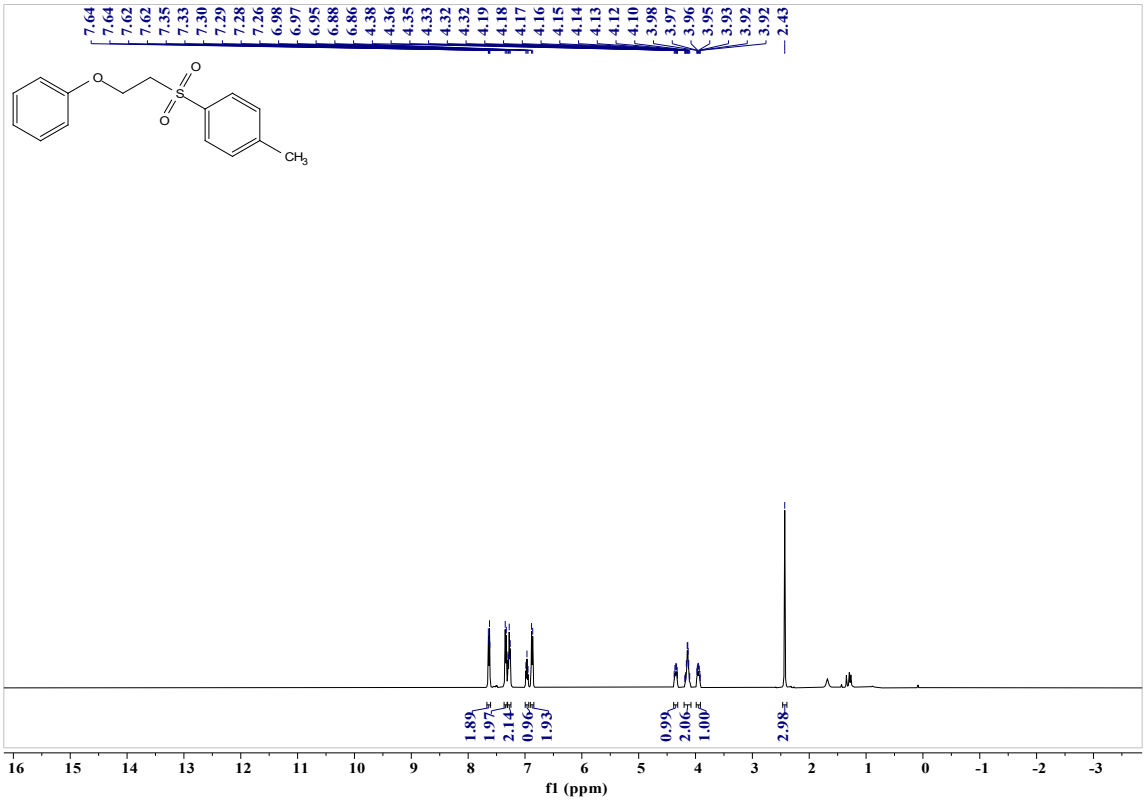


Compound 3m, ^{1}H NMR (400 MHz, Chloroform-d)



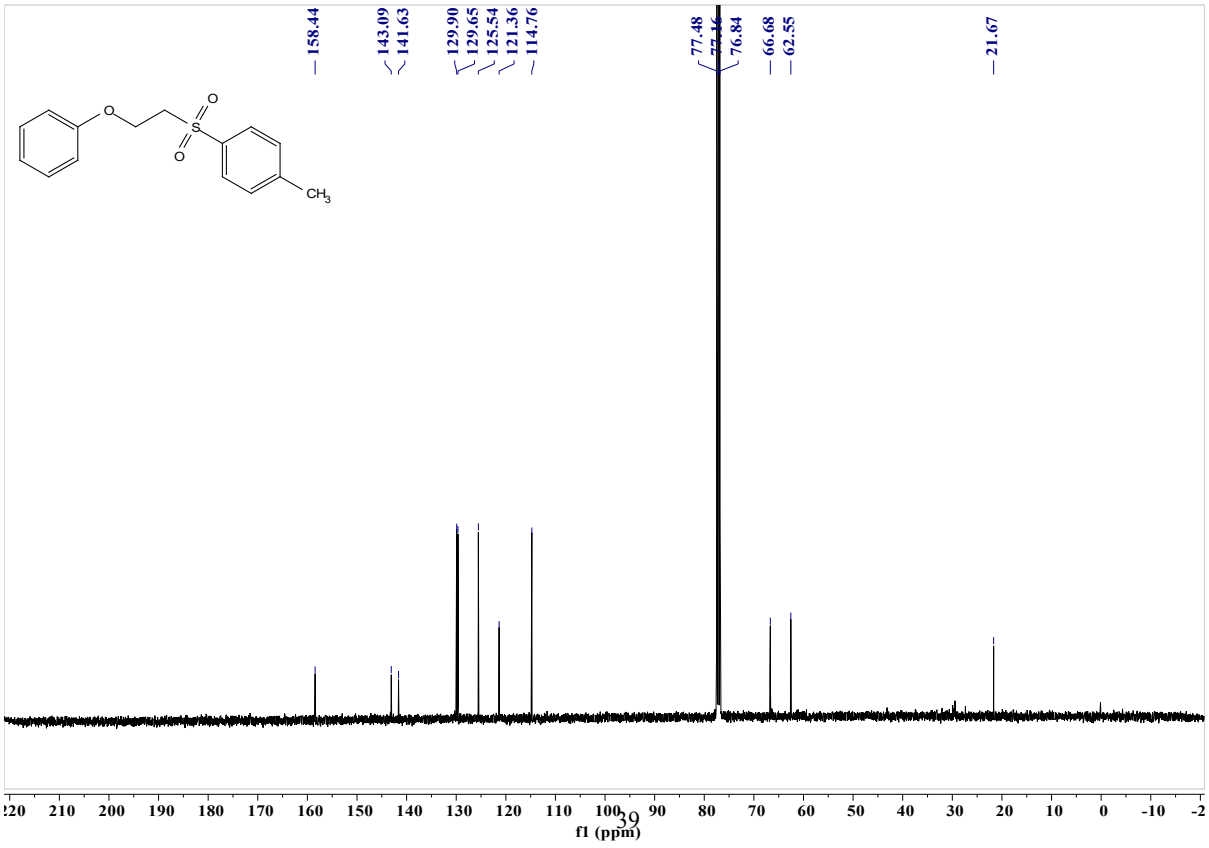
Compound 3m, ^{13}C NMR (101 MHz, Chloroform-d)



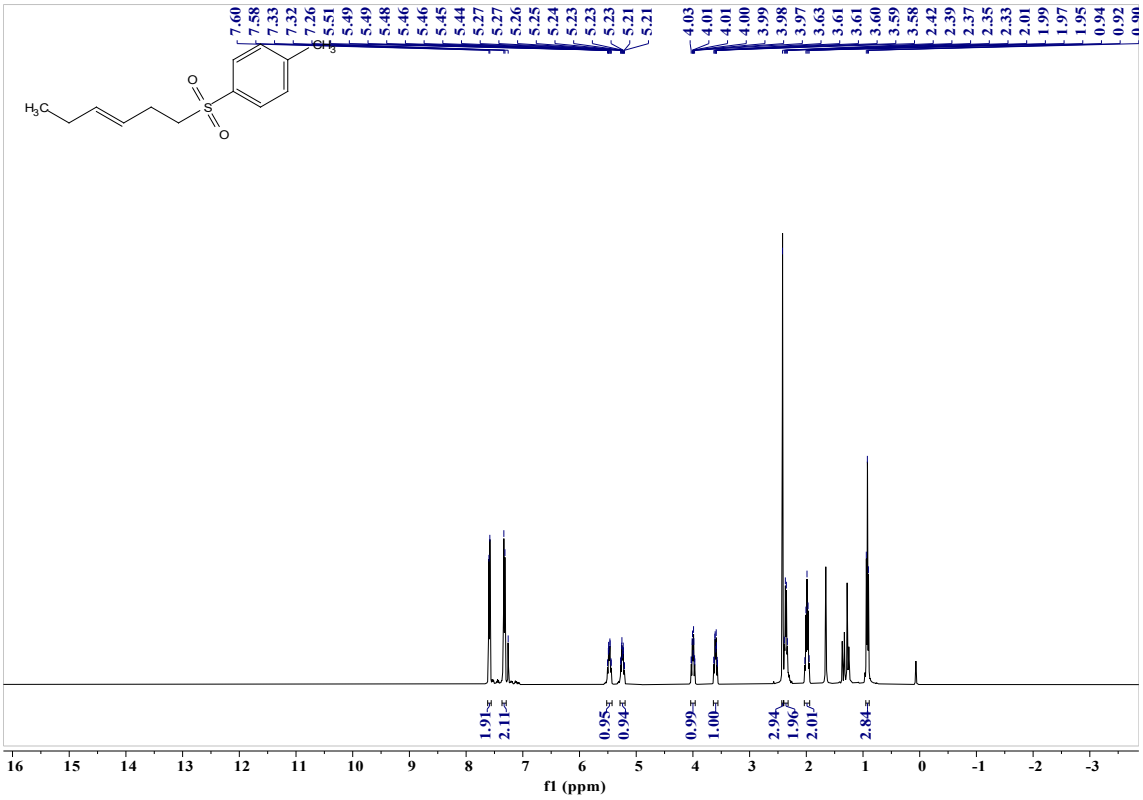


Compound 3n, ^{1}H NMR (400 MHz, Chloroform-d)

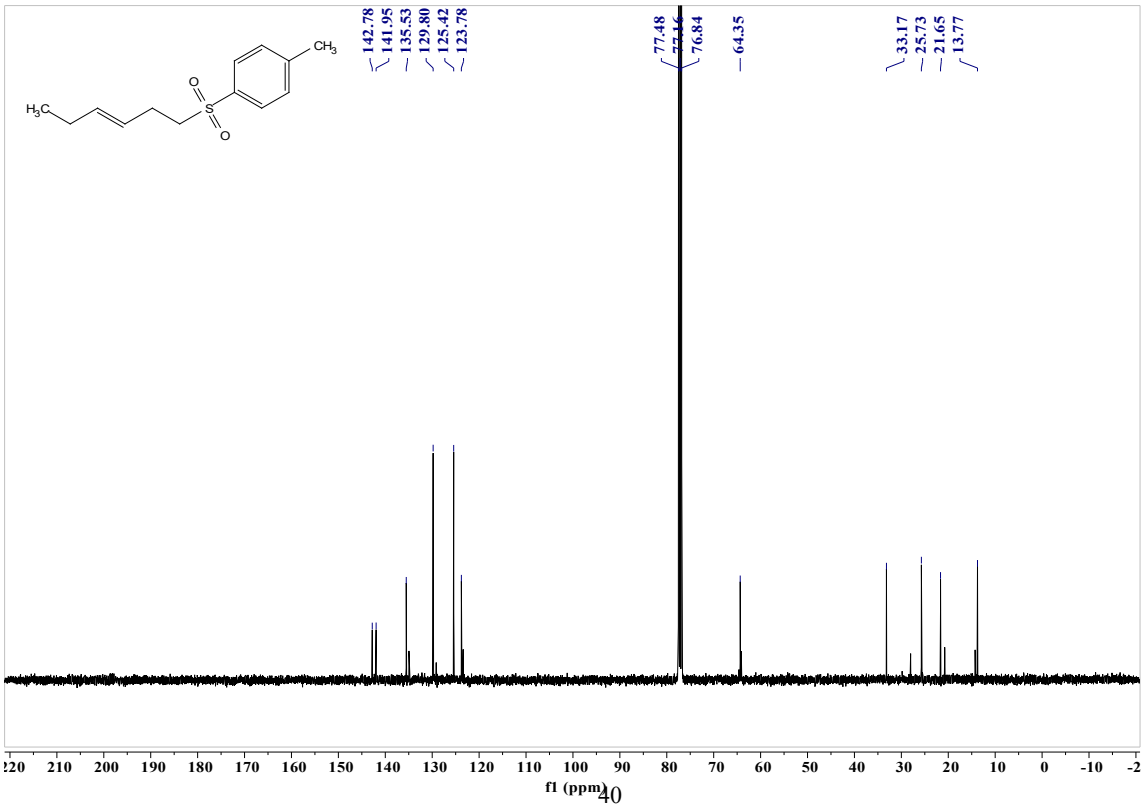
Compound 3n, ^{13}C NMR (101 MHz, Chloroform-d)



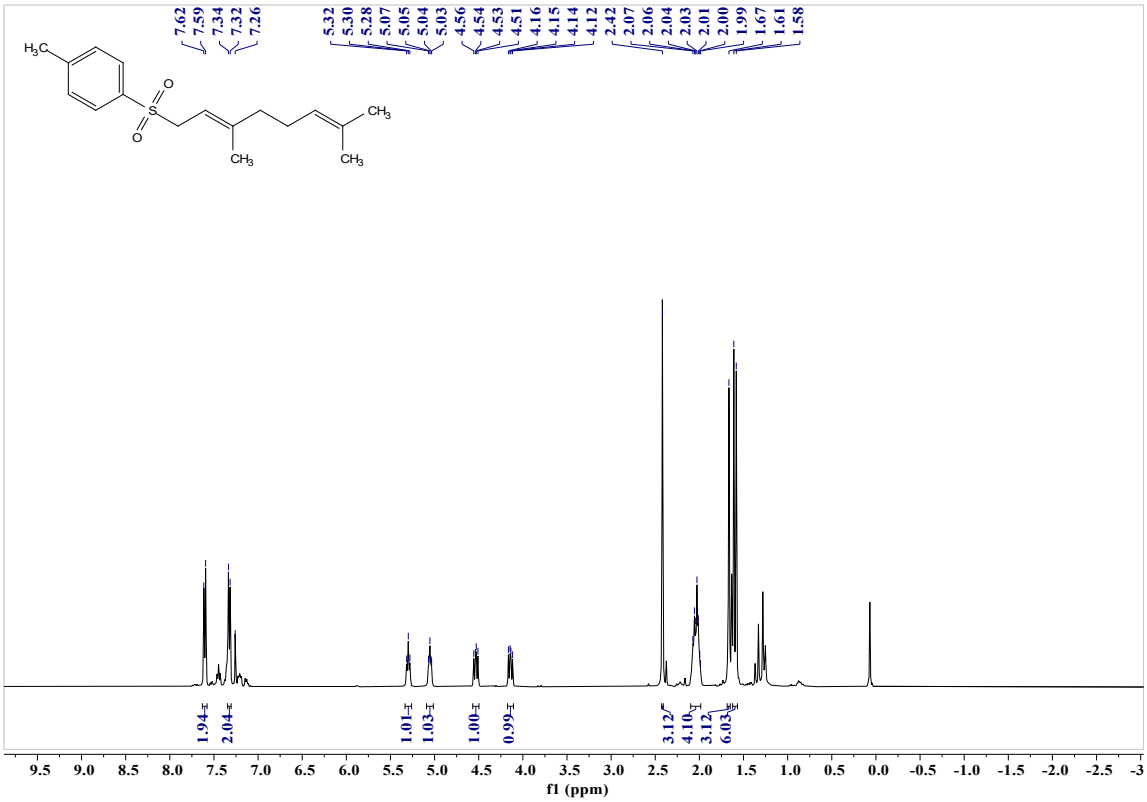
Compound 3o, ^{1}H NMR (400 MHz, Chloroform-d)



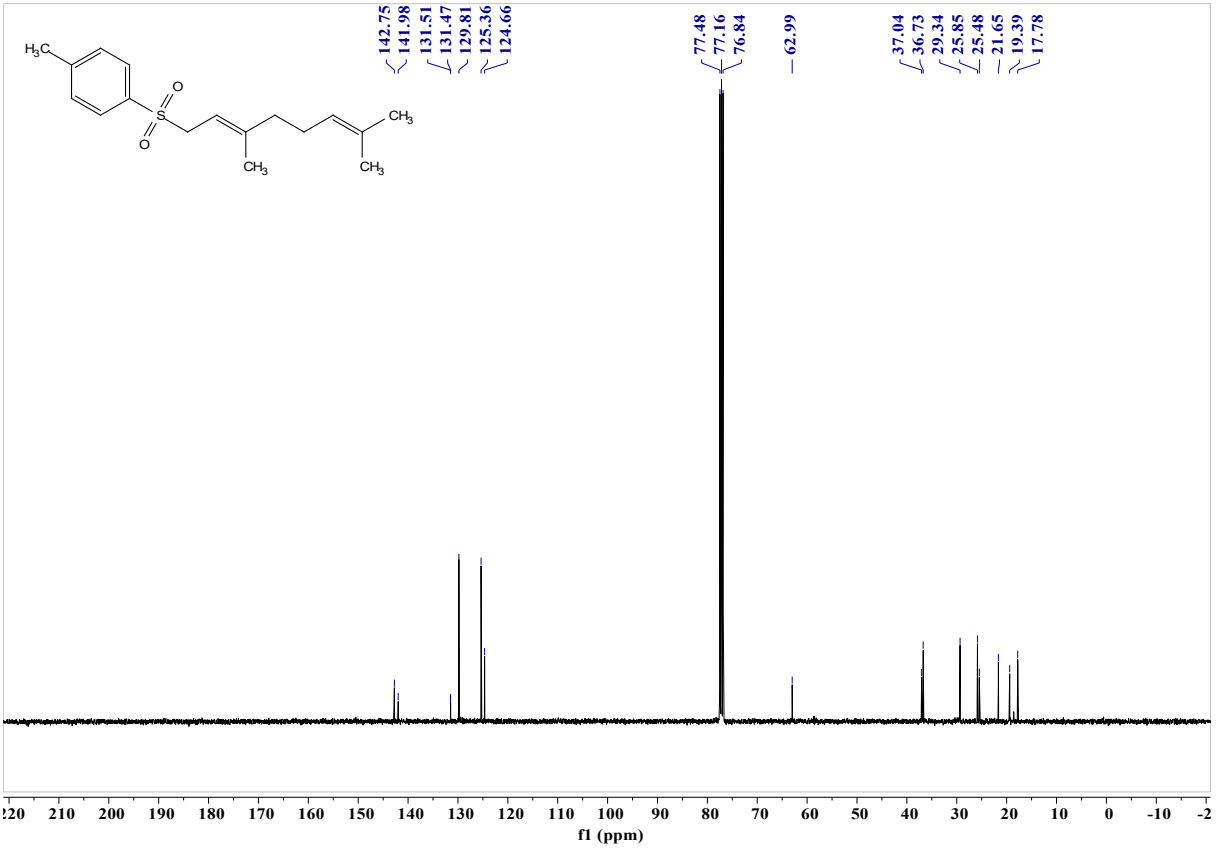
Compound 3o, ^{13}C NMR (101 MHz, Chloroform-d)



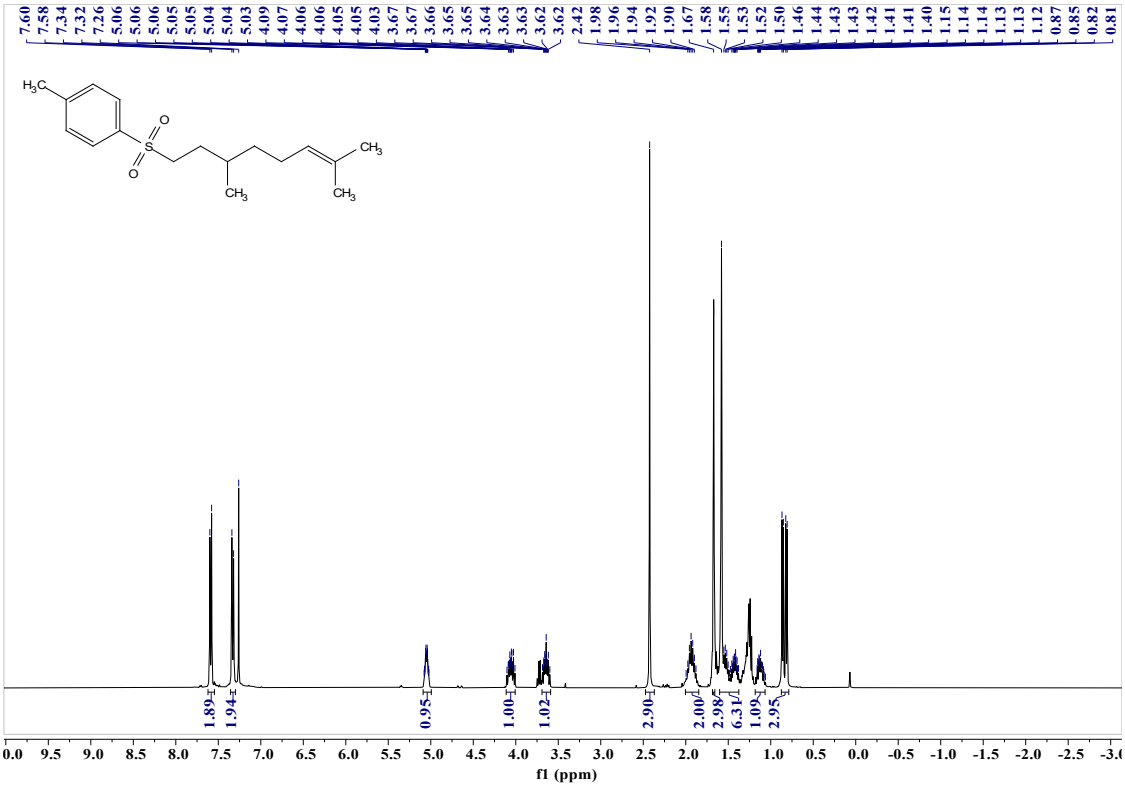
Compound 3p, ^{1}H NMR (400 MHz, Chloroform-d)



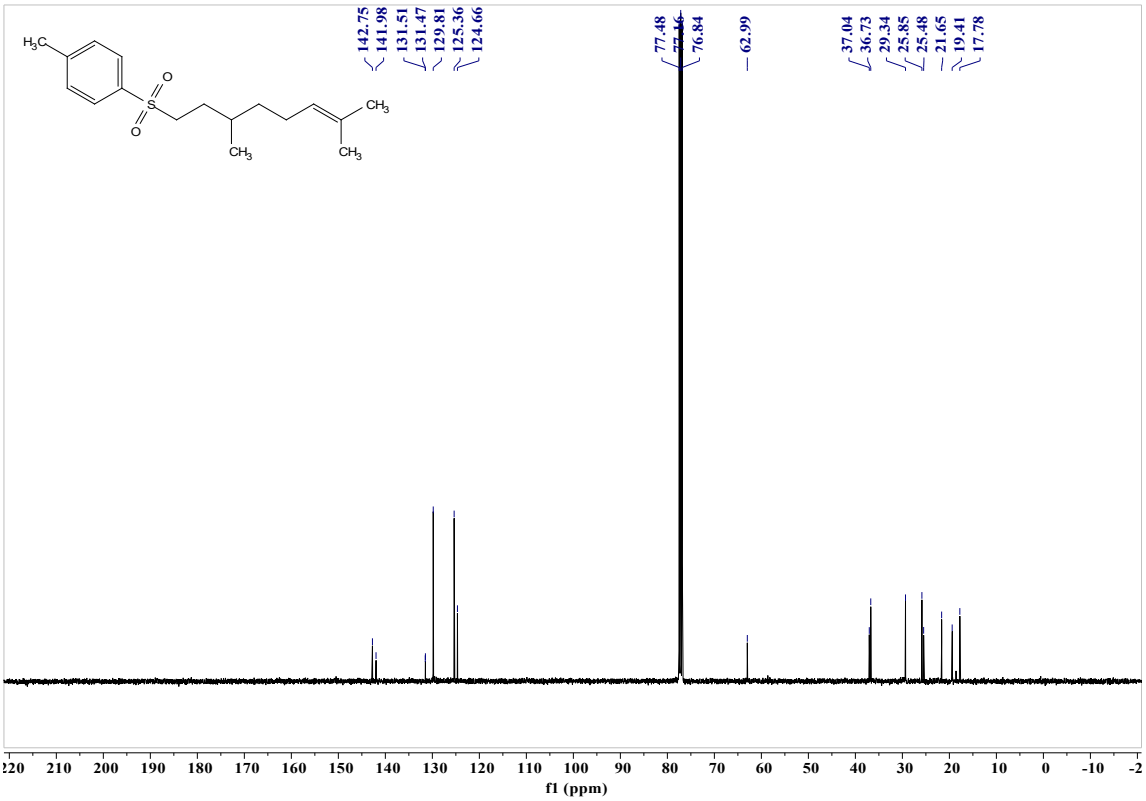
Compound 3p, ^{13}C NMR (101 MHz, Chloroform-d)



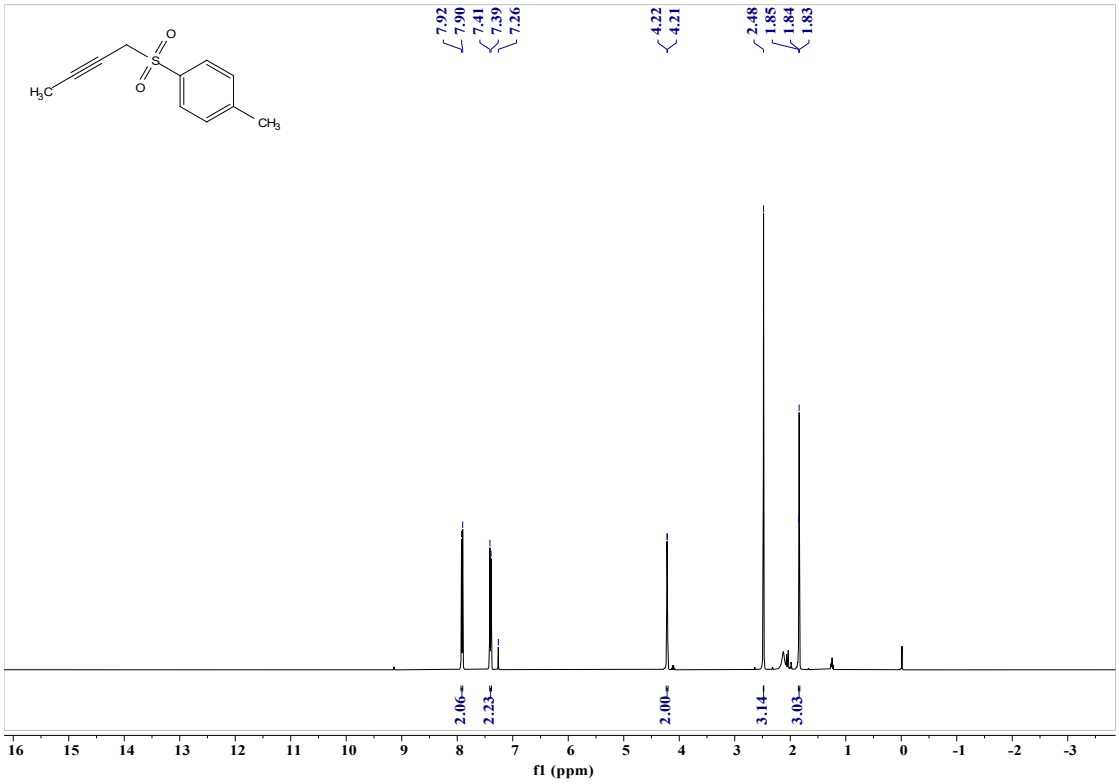
Compound 3q, ^{1}H NMR (400 MHz, Chloroform-d)



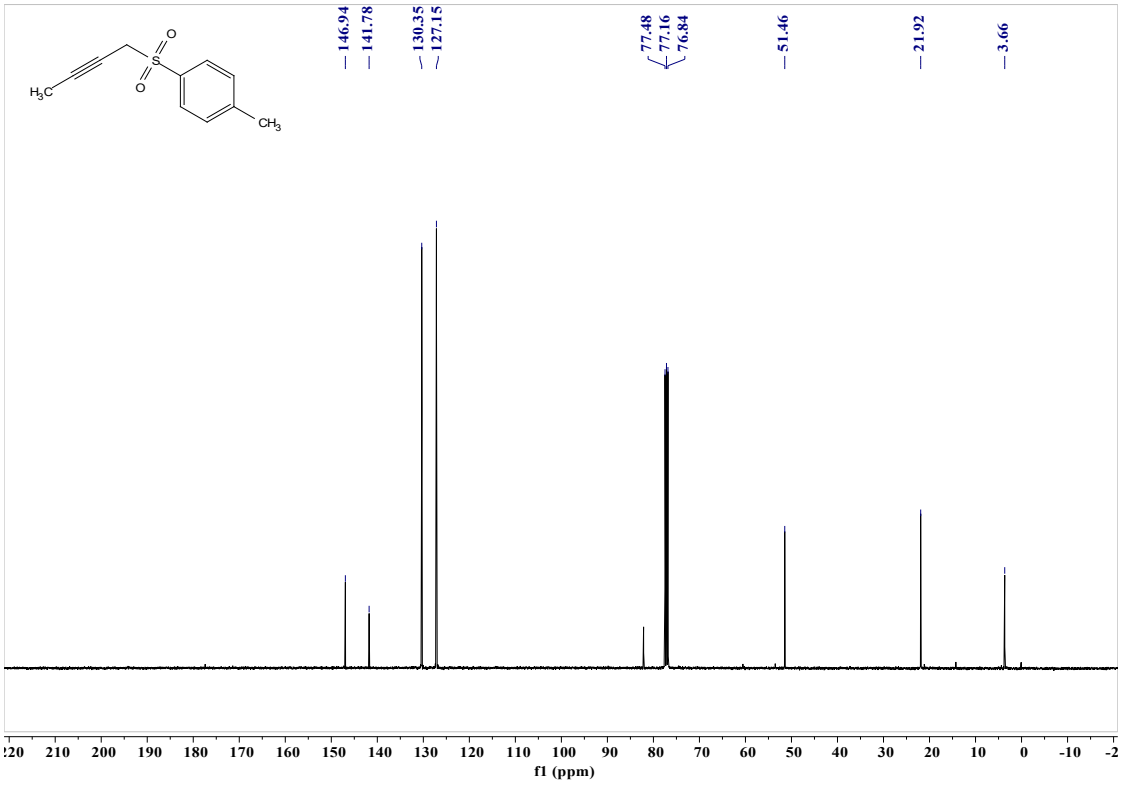
Compound 3q, ^{13}C NMR (101 MHz, Chloroform-d)



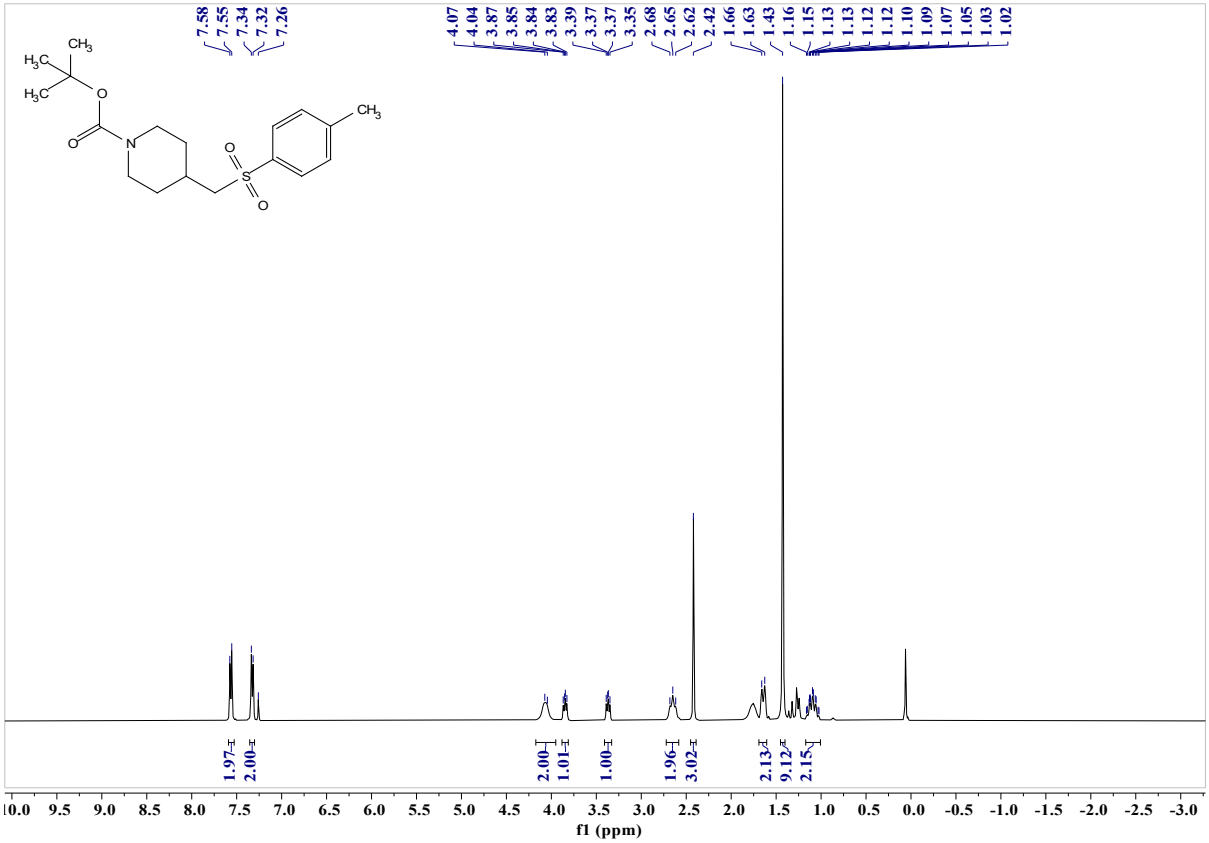
Compound 3r, ^{1}H NMR (400 MHz, Chloroform-d)



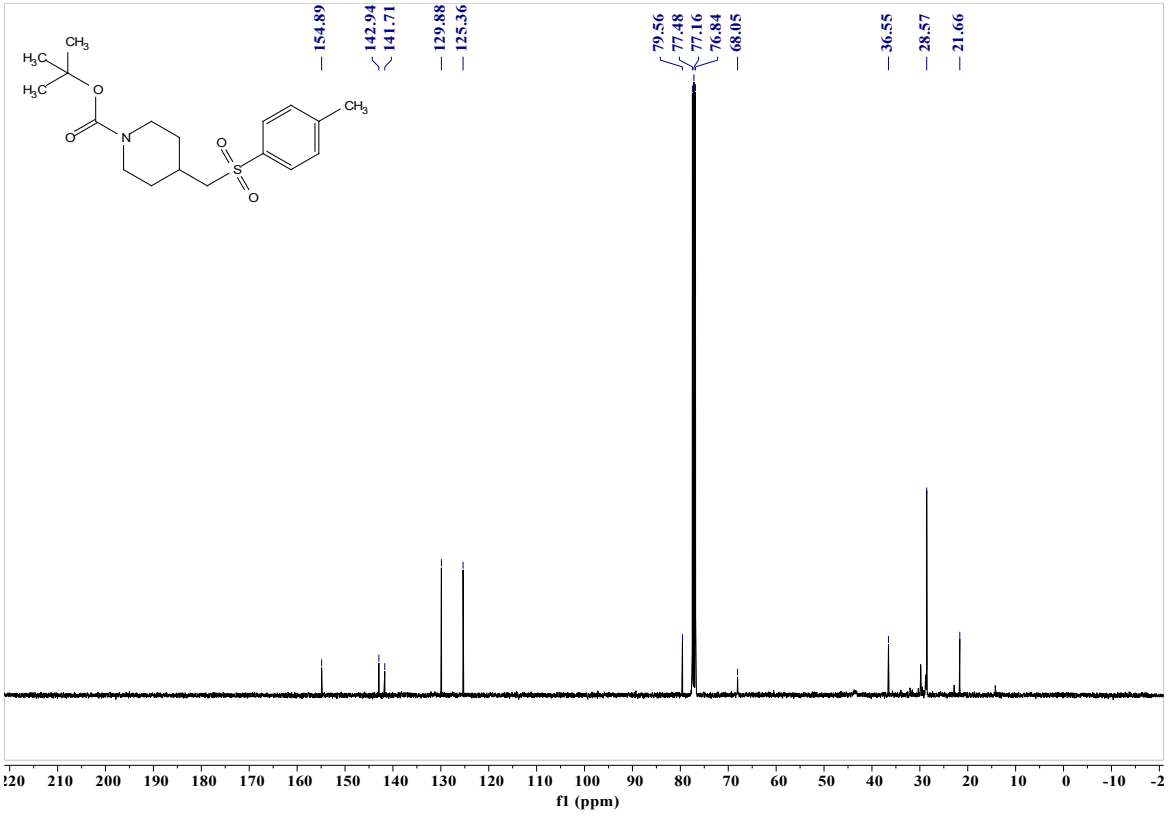
Compound 3r, ^{13}C NMR (101 MHz, Chloroform-d)



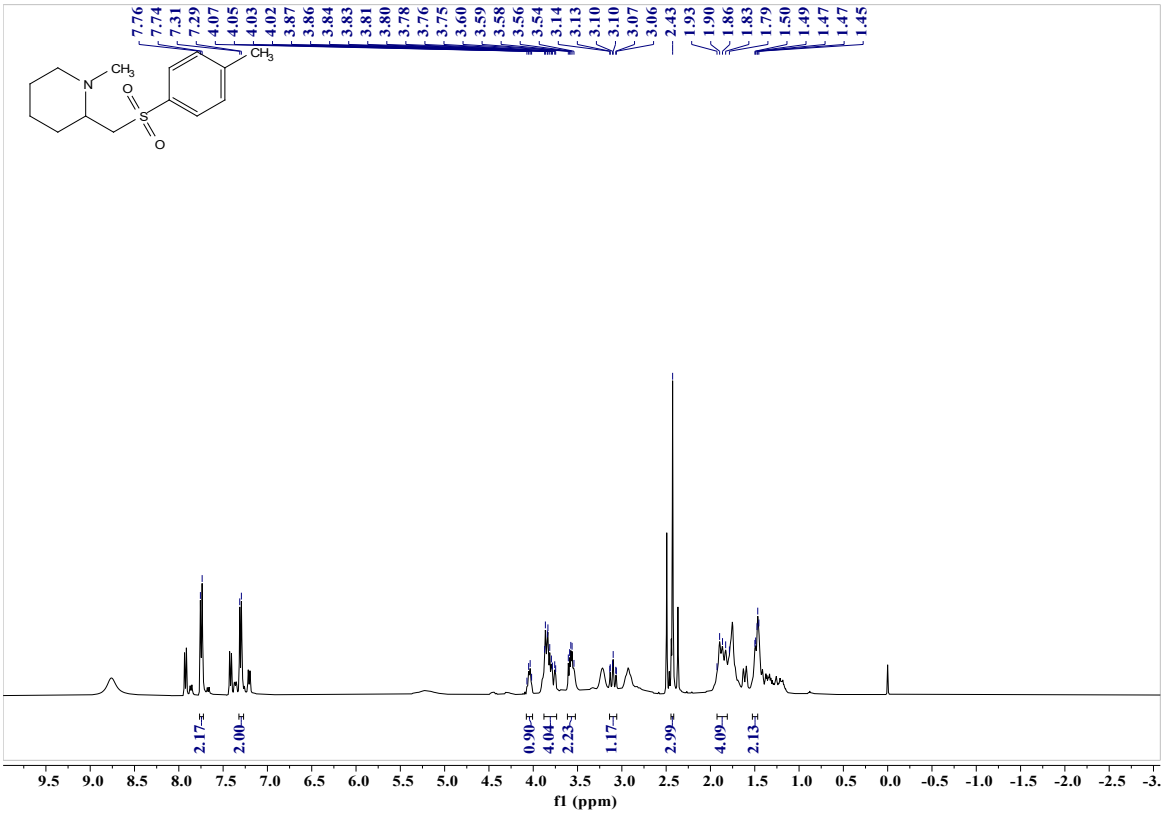
Compound 3s, ^{1}H NMR (400 MHz, Chloroform-d)



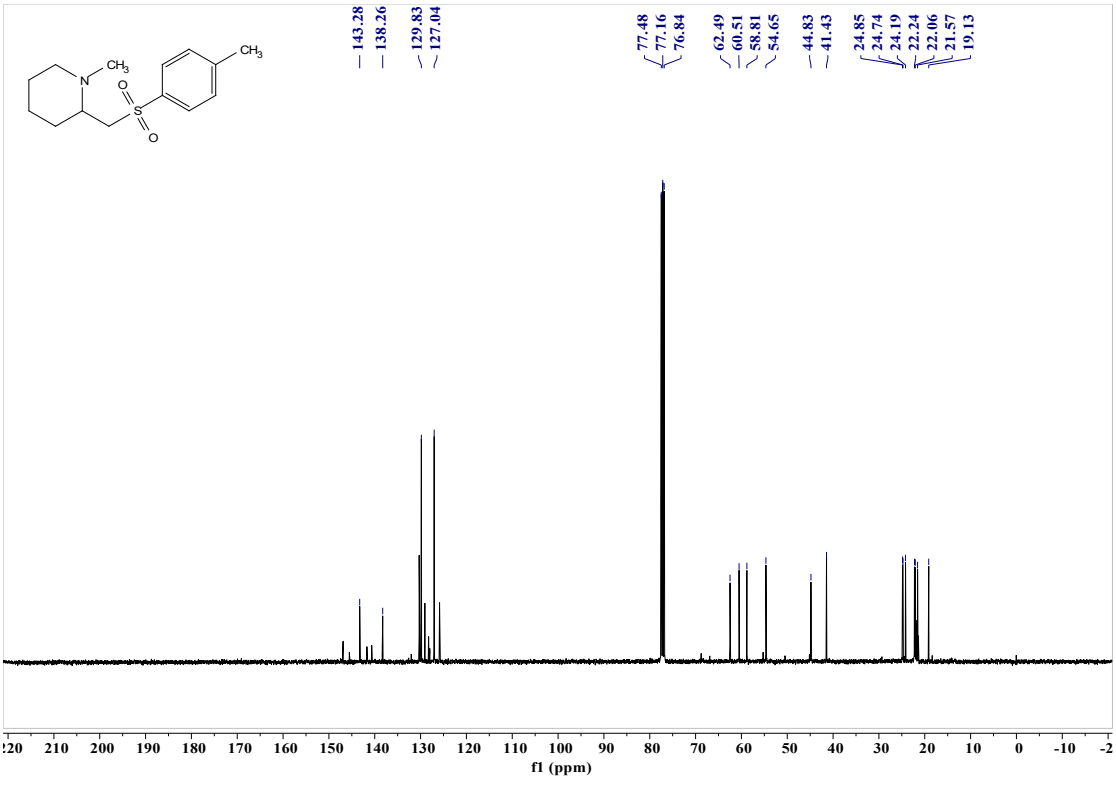
Compound 3s, ^{13}C NMR (101 MHz, Chloroform-d)



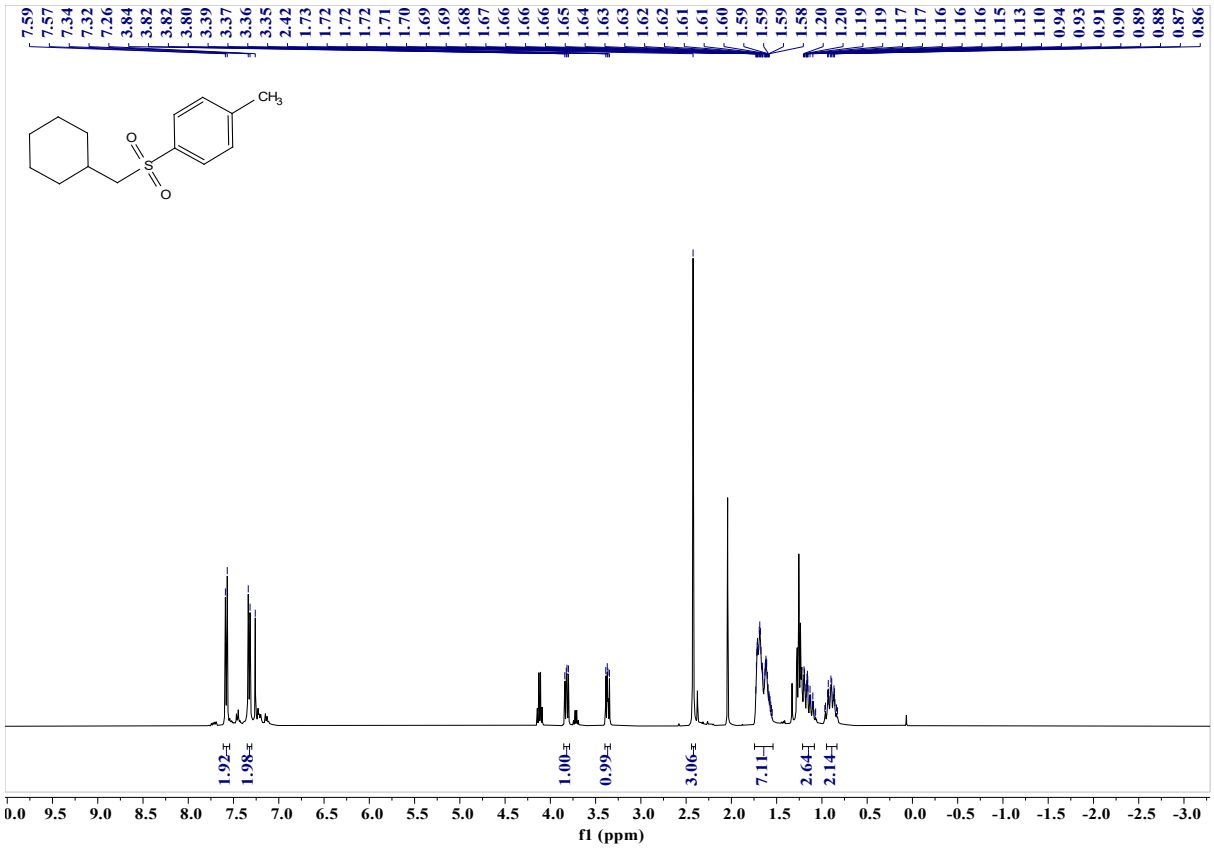
Compound 3t, ^{1}H NMR (400 MHz, Chloroform-d)



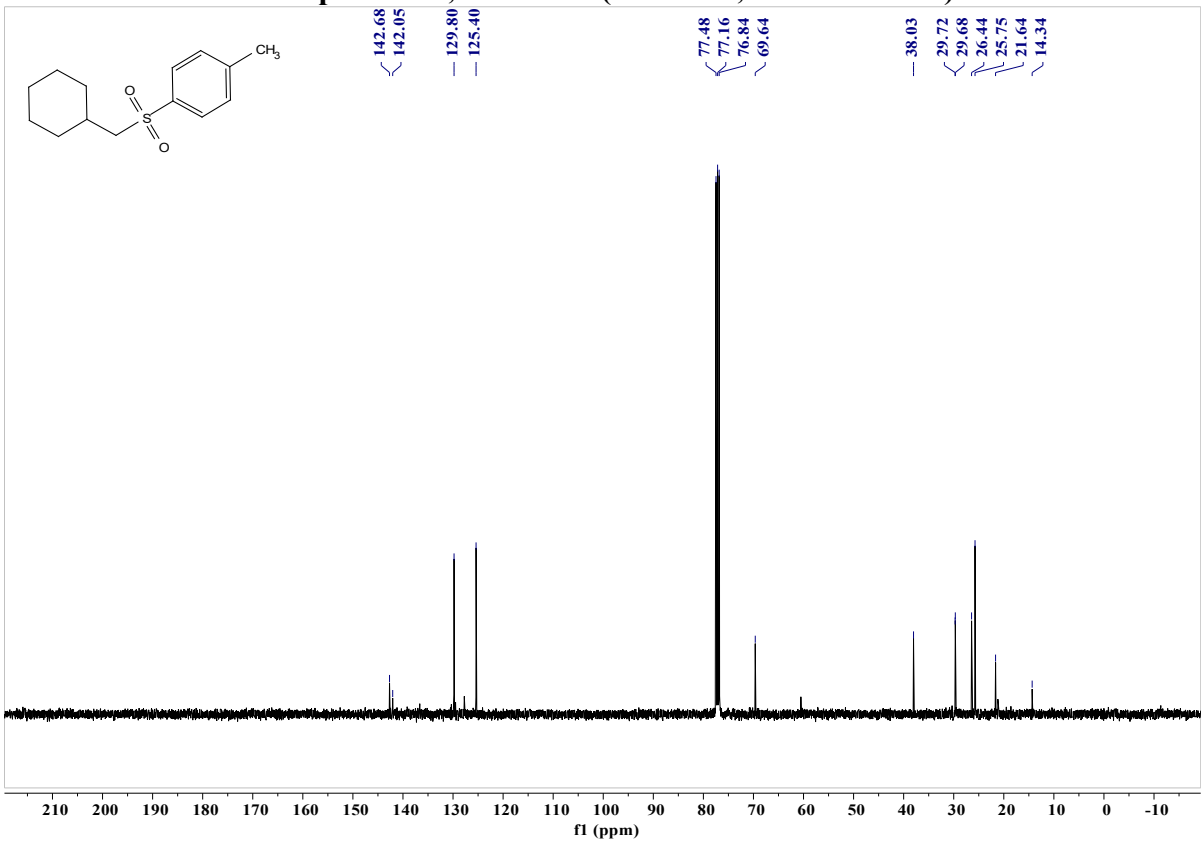
Compound 3t, ^{13}C NMR (101 MHz, Chloroform-d)



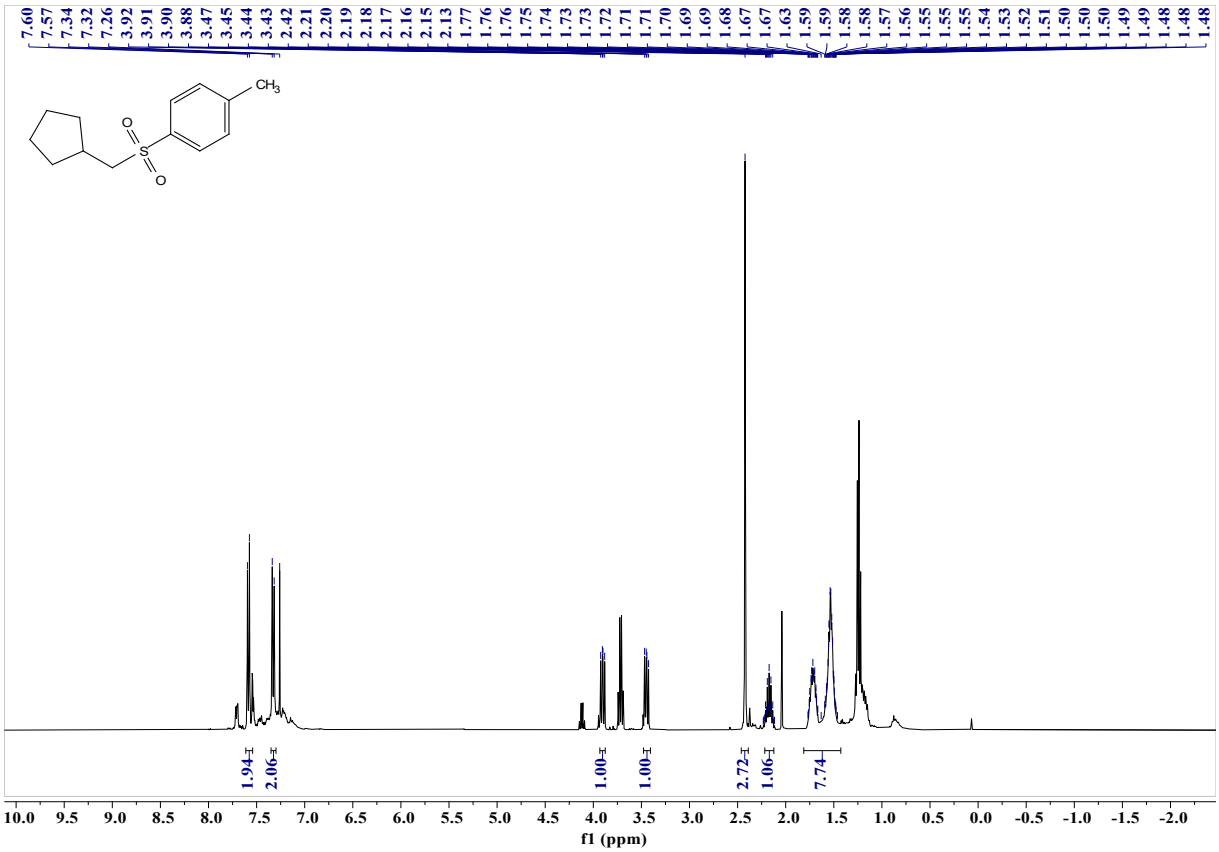
Compound 3u, ^{1}H NMR (400 MHz, Chloroform-d)



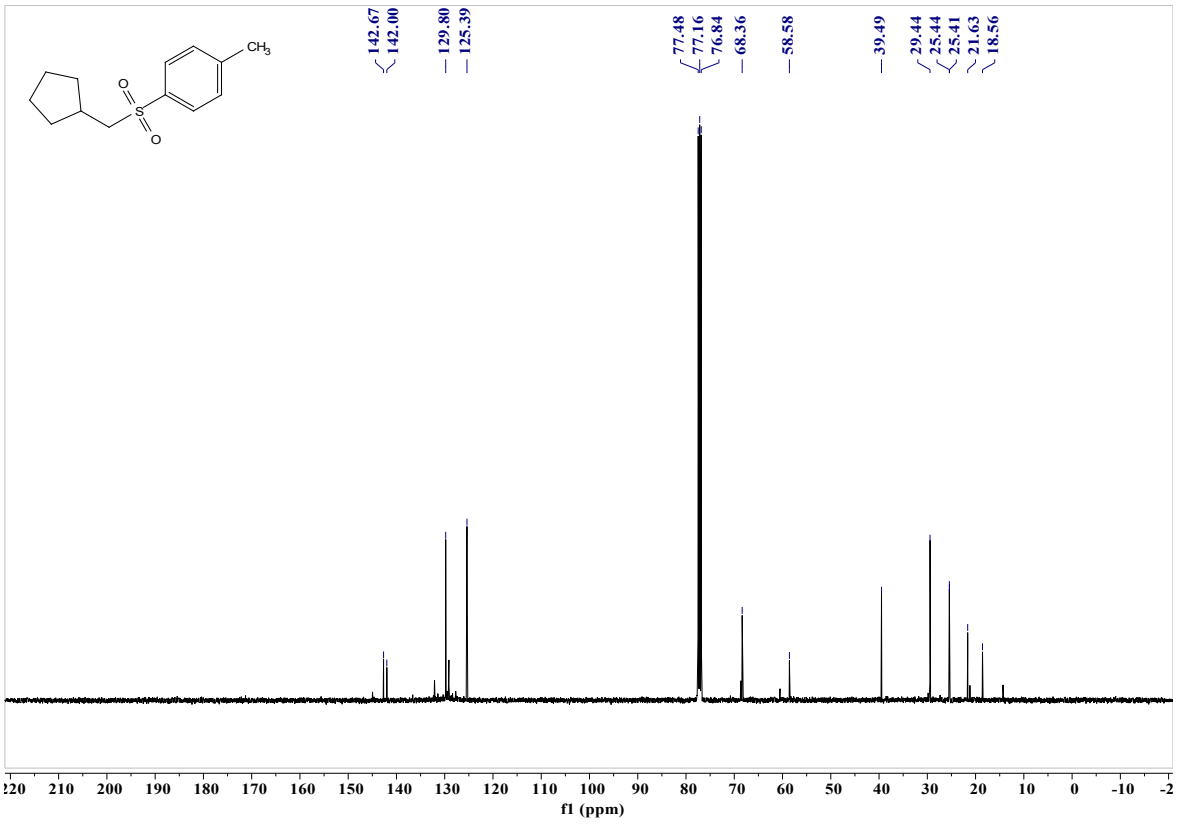
Compound 3u, ^{13}C NMR (101 MHz, Chloroform-d)



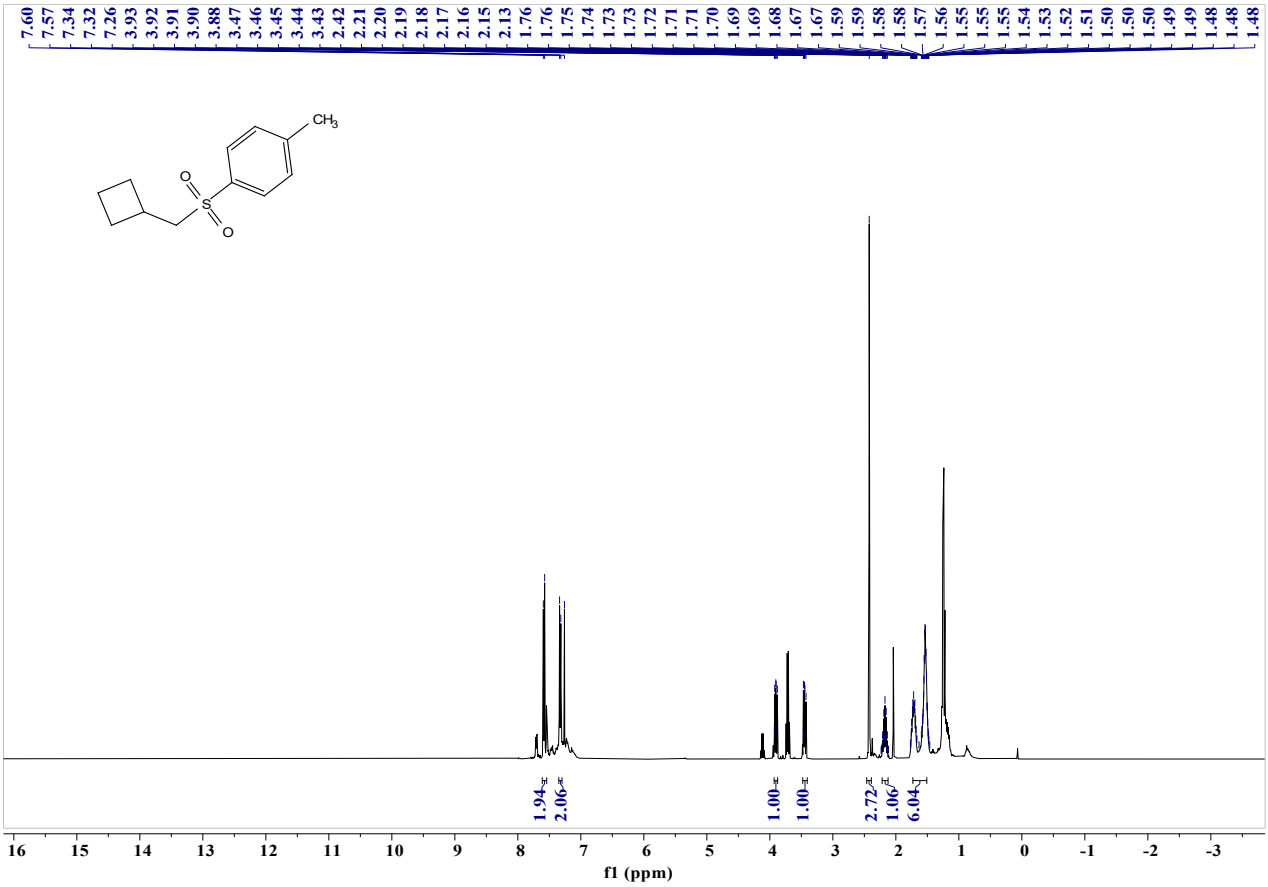
Compound 3v, ^{1}H NMR (400 MHz, Chloroform-d)



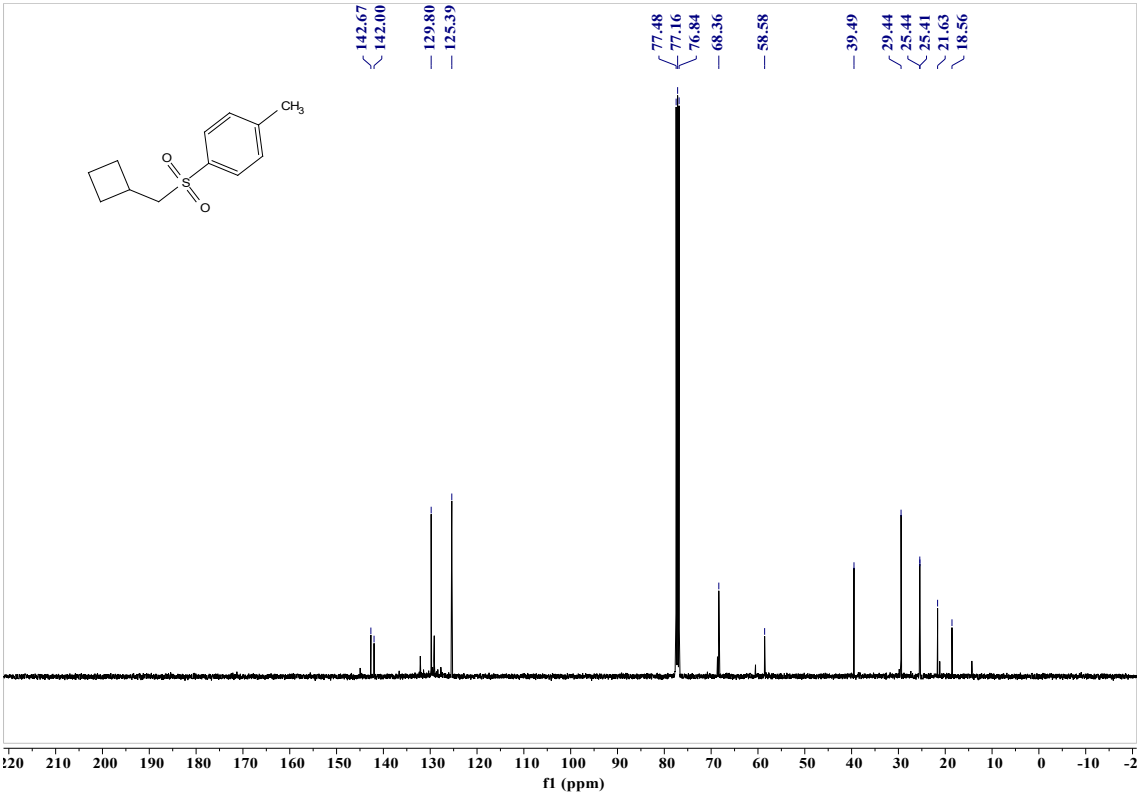
Compound 3v, ^{13}C NMR (101 MHz, Chloroform-d)

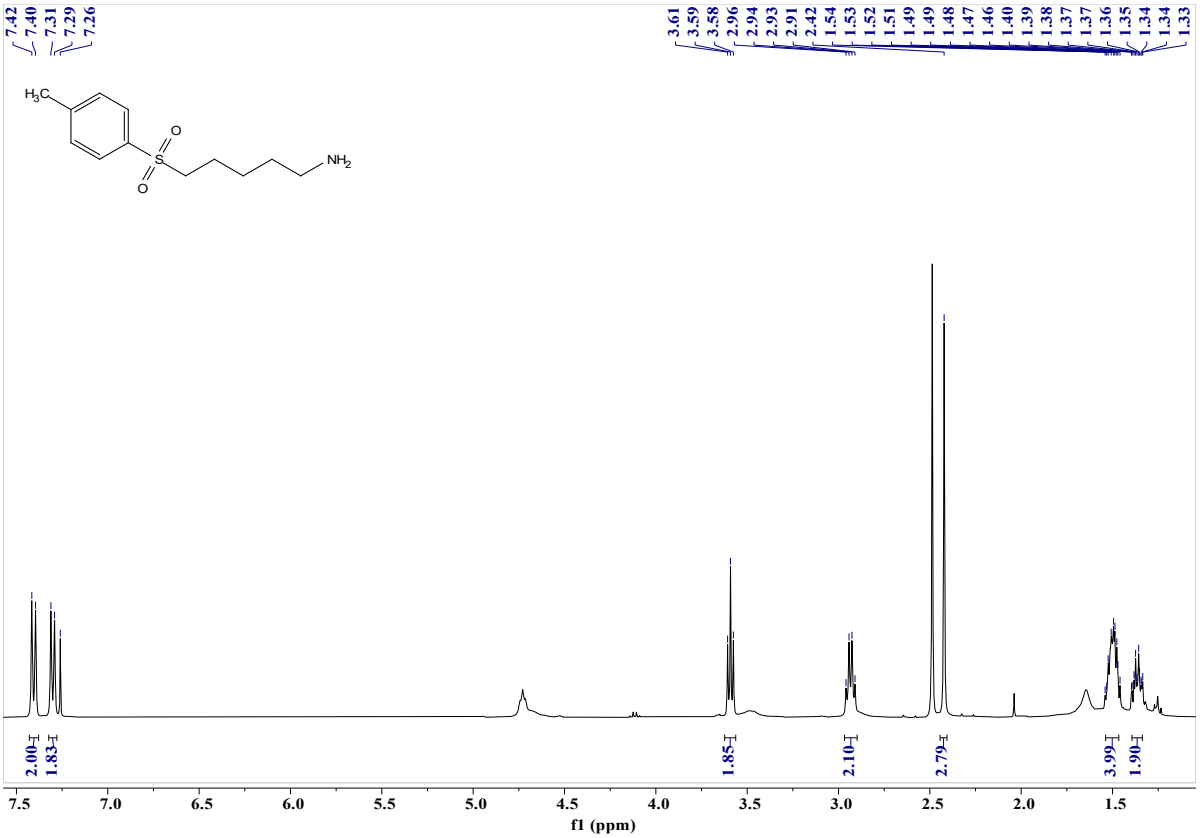


Compound 3w, ^{1}H NMR (400 MHz, Chloroform-d)



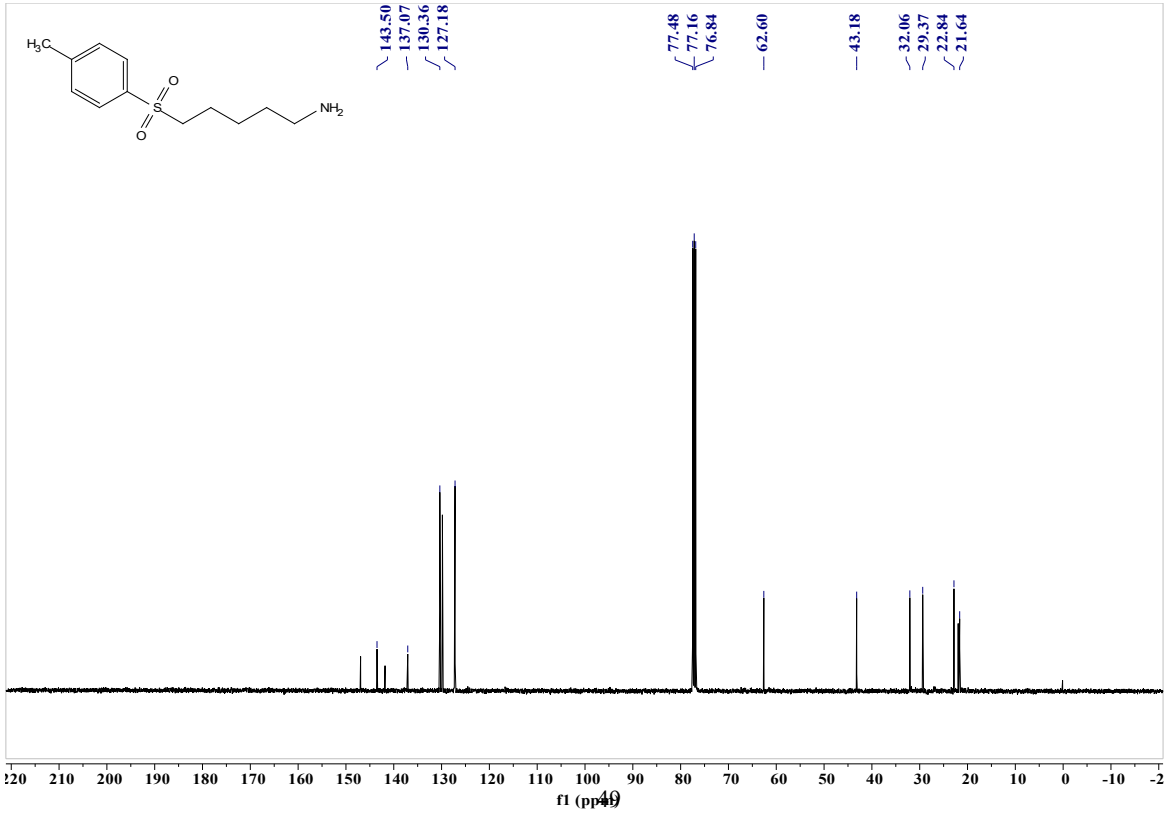
Compound 3w, ^{13}C NMR (101 MHz, Chloroform-d)

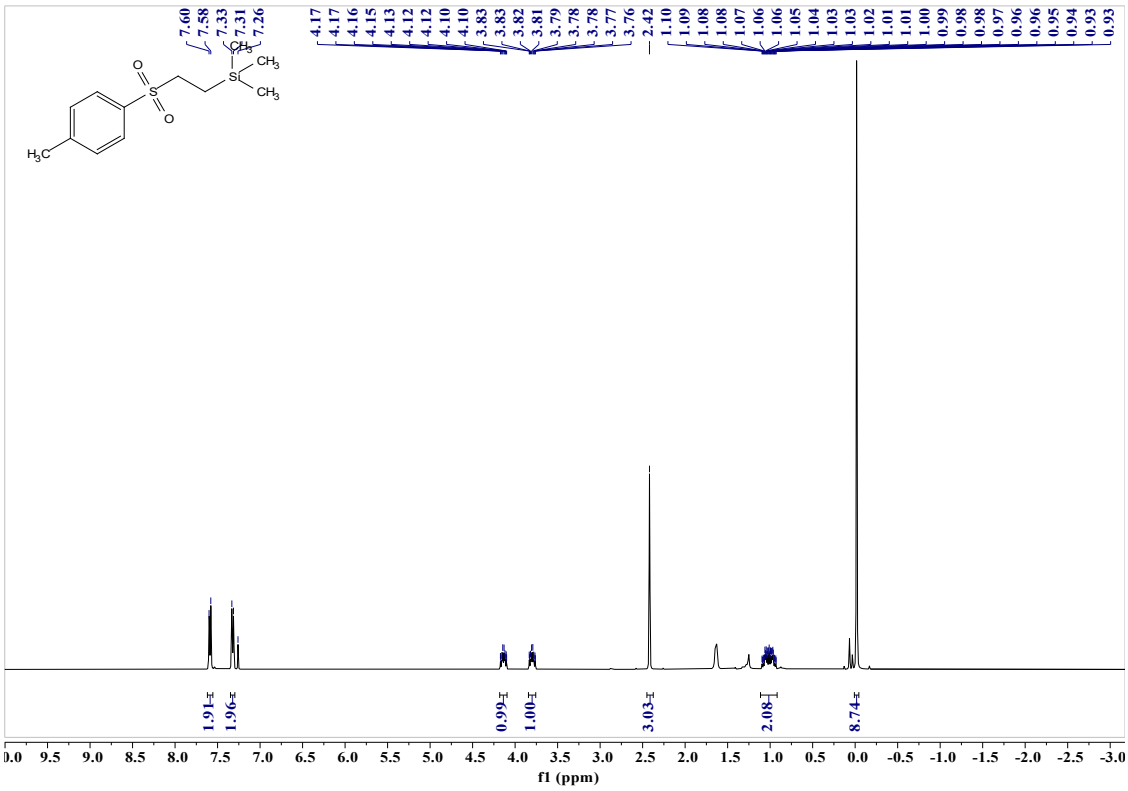




Compound 3x, ^{1}H NMR (400 MHz, Chloroform-d)

Compound 3x, ^{13}C NMR (101 MHz, Chloroform-d)

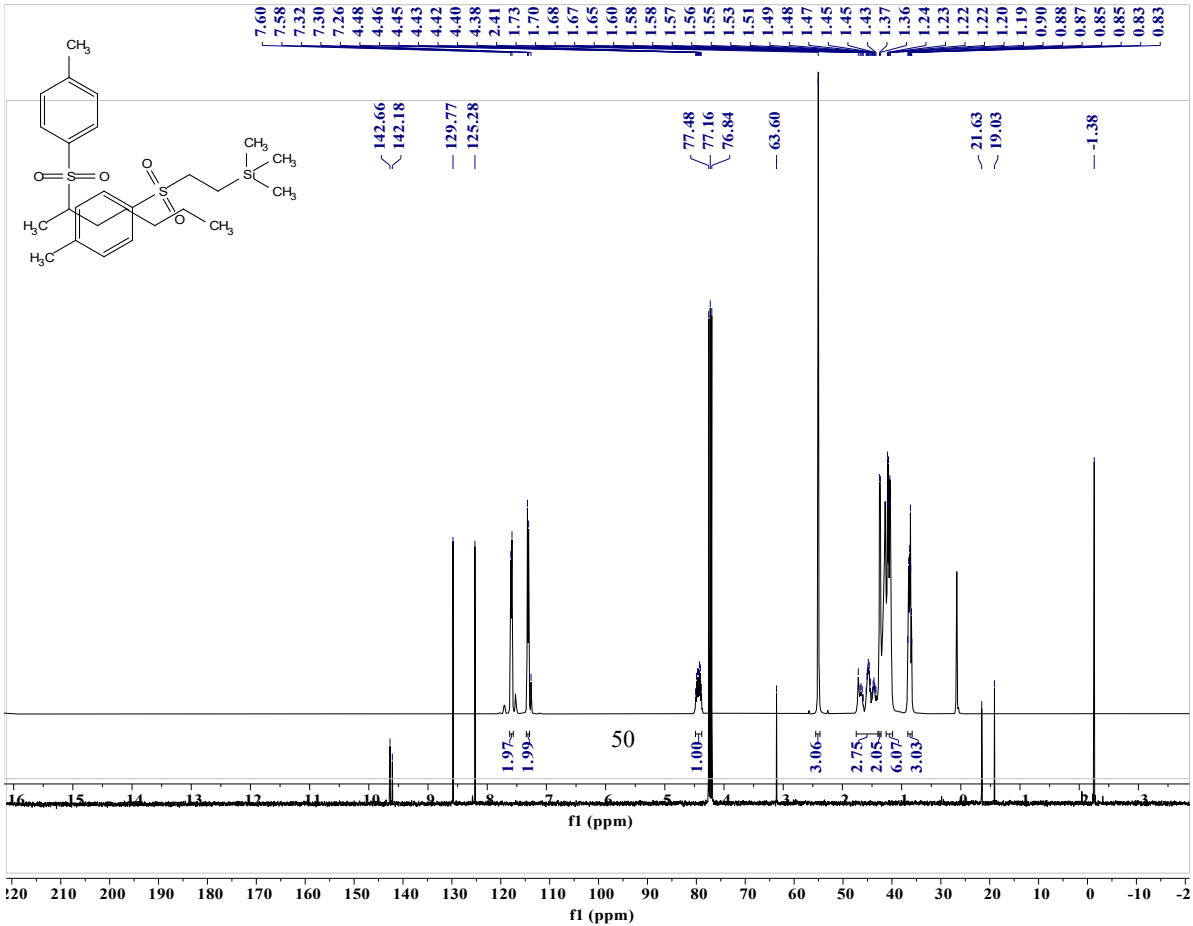




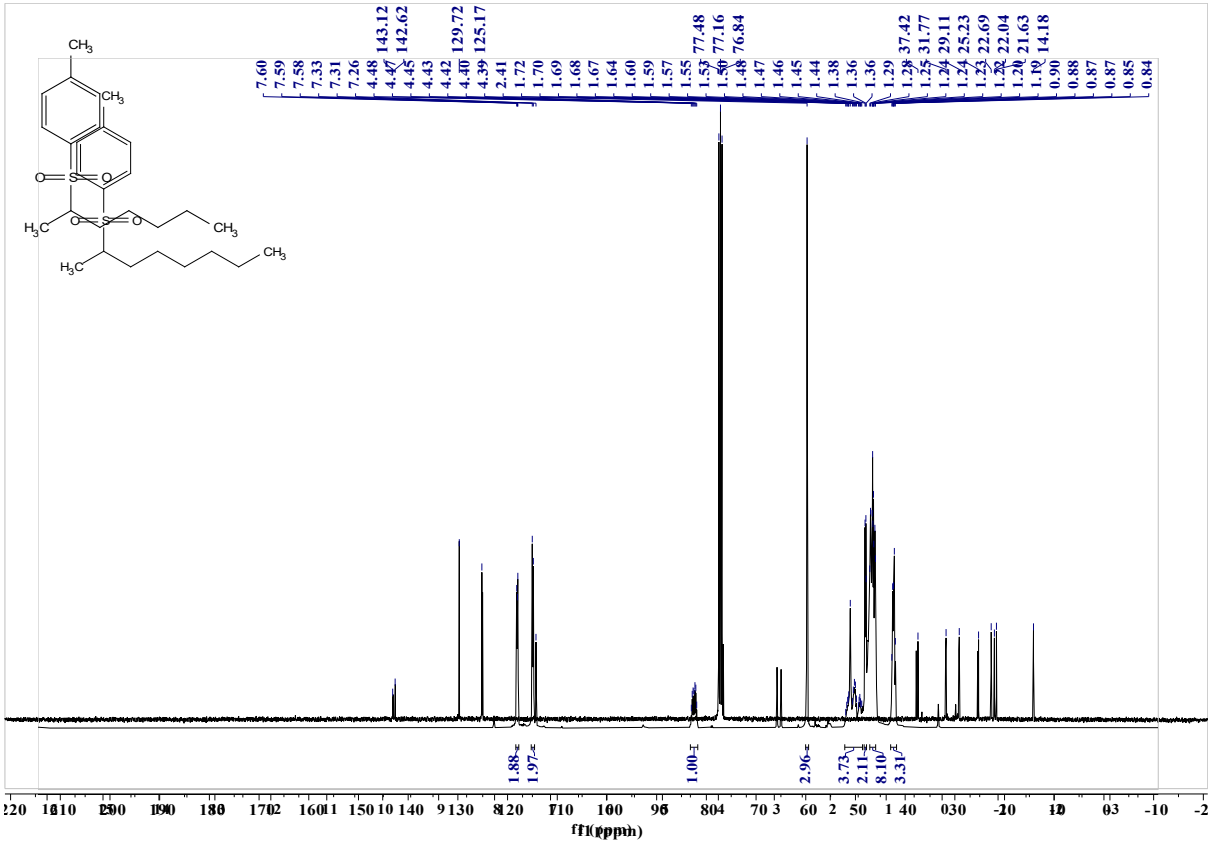
Compound 3y, ^{1}H NMR (400 MHz, Chloroform-d)

Compound 3y, ^{13}C NMR (101 MHz, Chloroform-d)

Compound 3z, ^{1}H NMR (400 MHz, Chloroform-d)

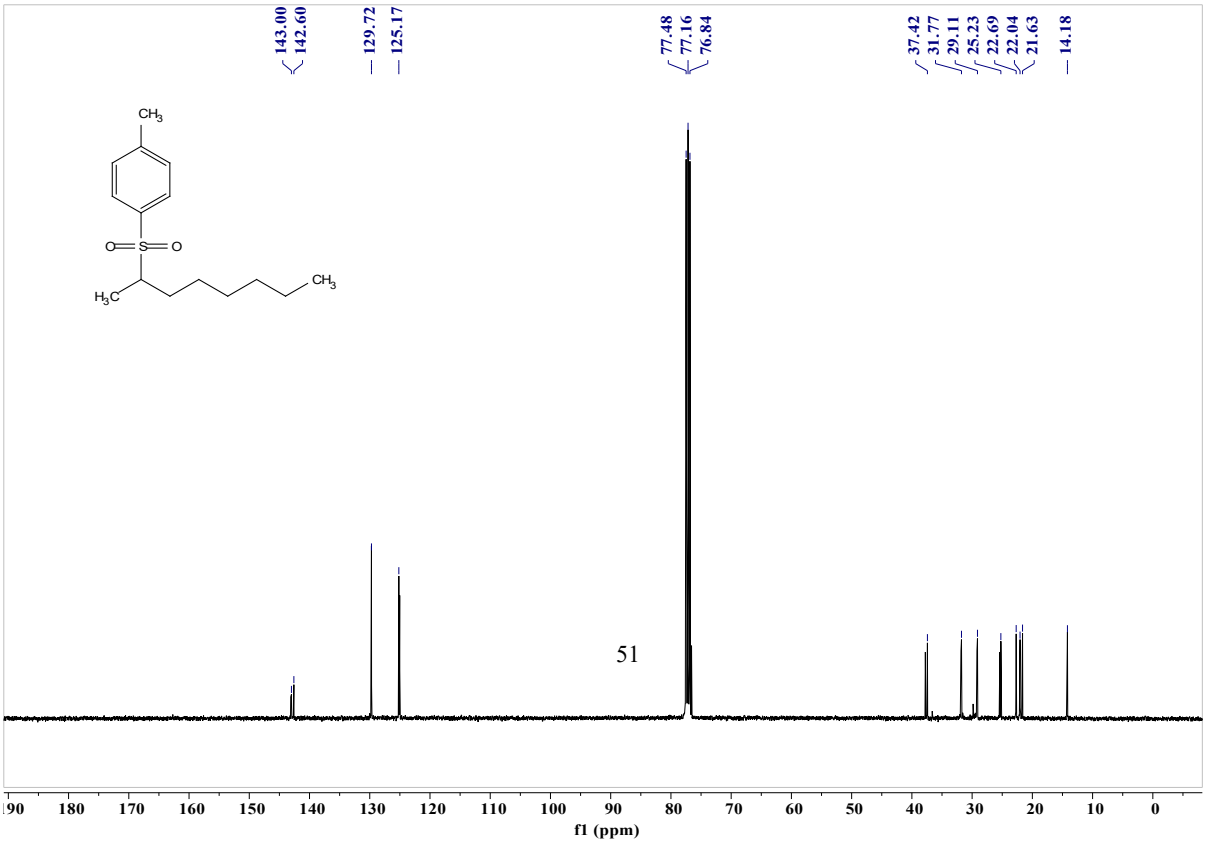


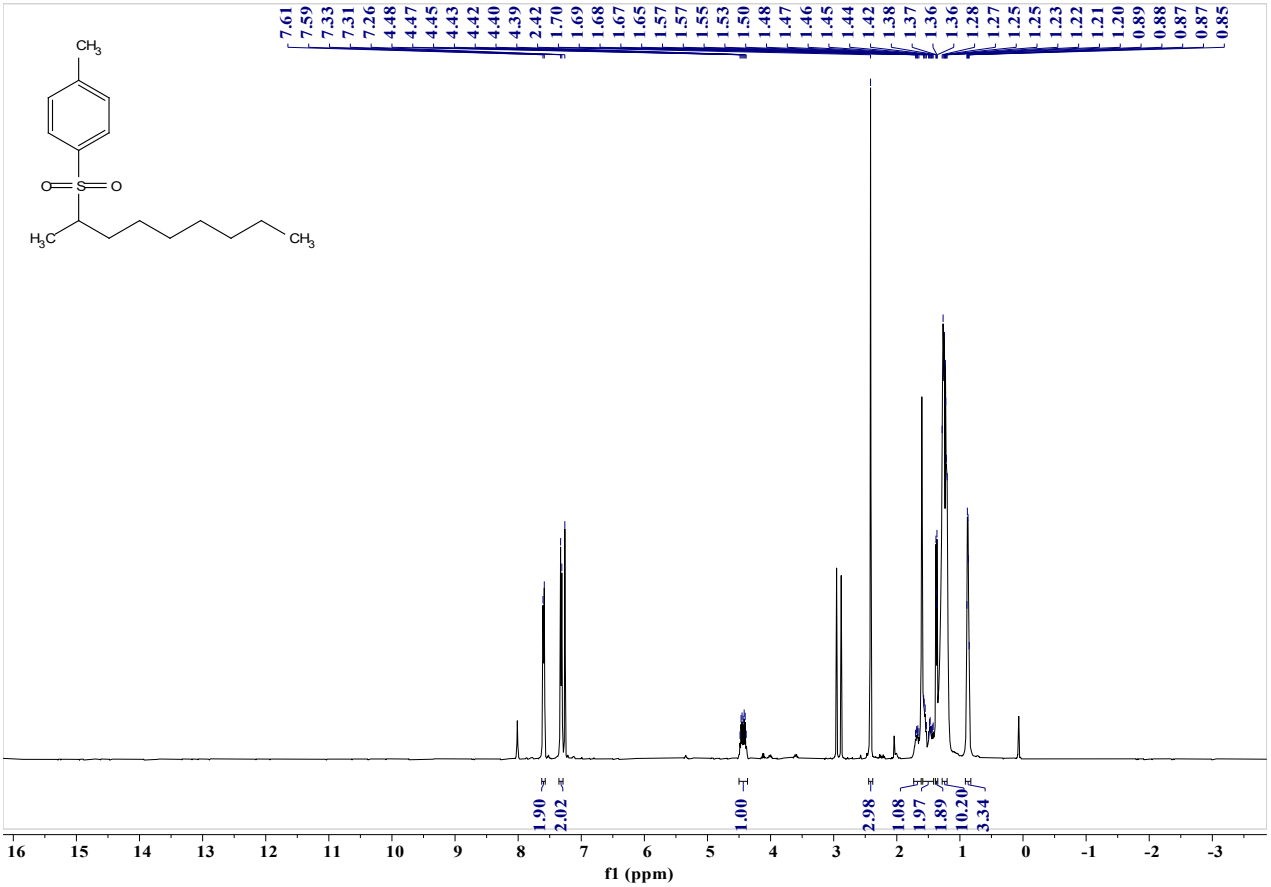
Compound 3z, ^{13}C NMR (101 MHz, Chloroform-d)



Compound 3aa, ^{1}H NMR (400 MHz, Chloroform-d)

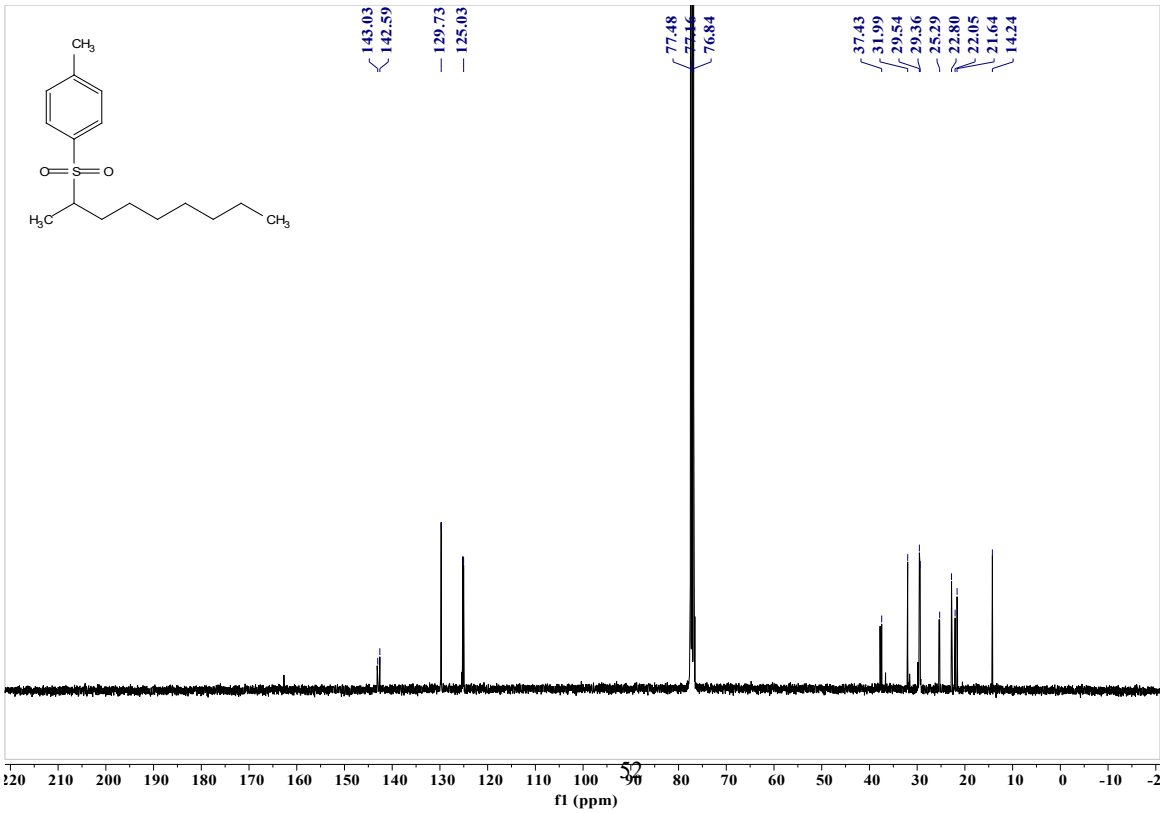
Compound 3aa, ^{13}C NMR (101 MHz, Chloroform-d)



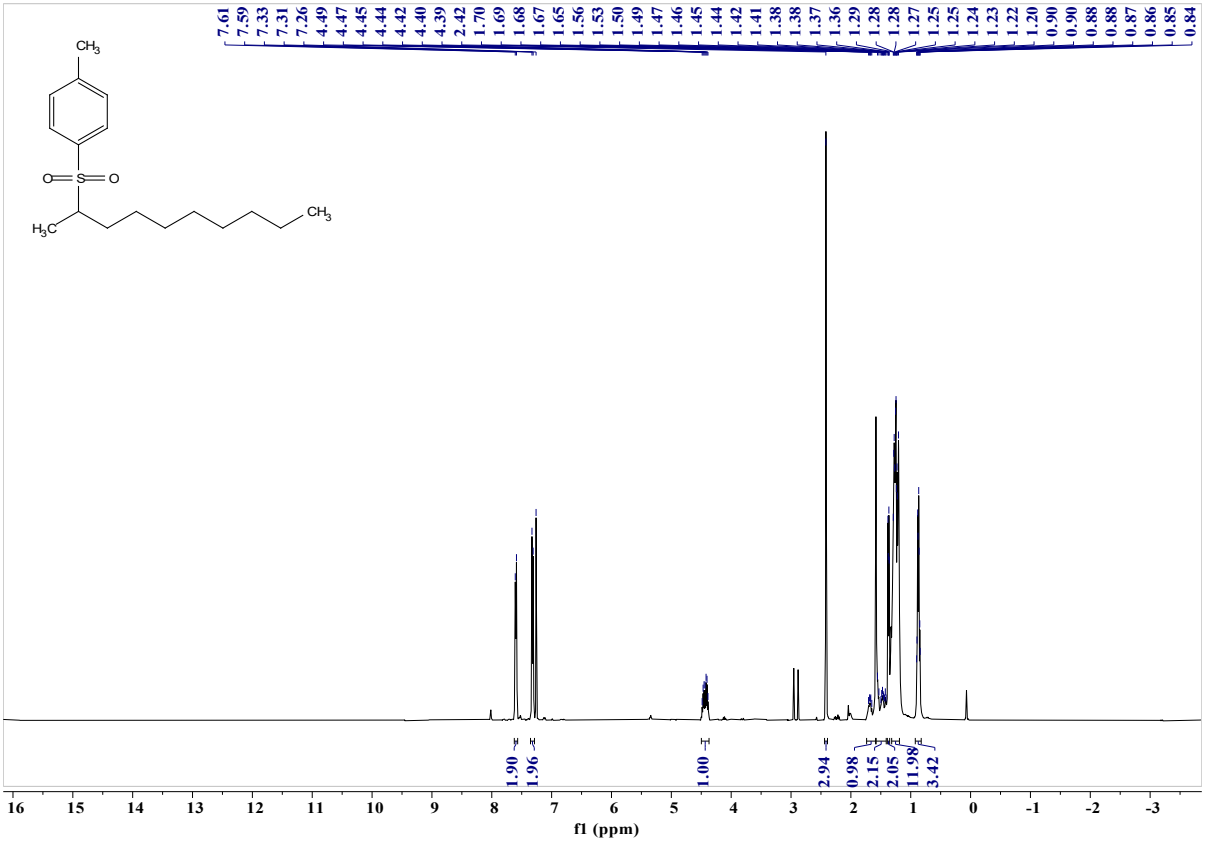


Compound 3ab, ^{1}H NMR (400 MHz, Chloroform-d)

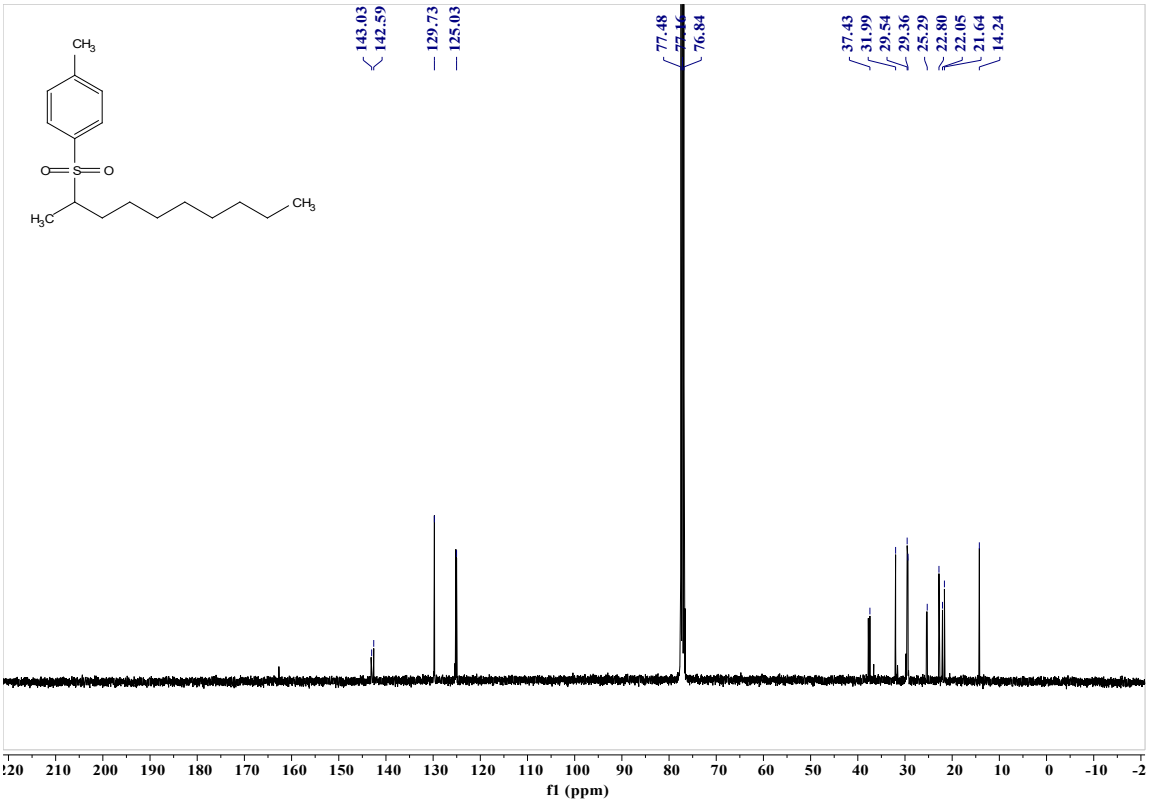
Compound 3ab, ^{13}C NMR (101 MHz, Chloroform-d)



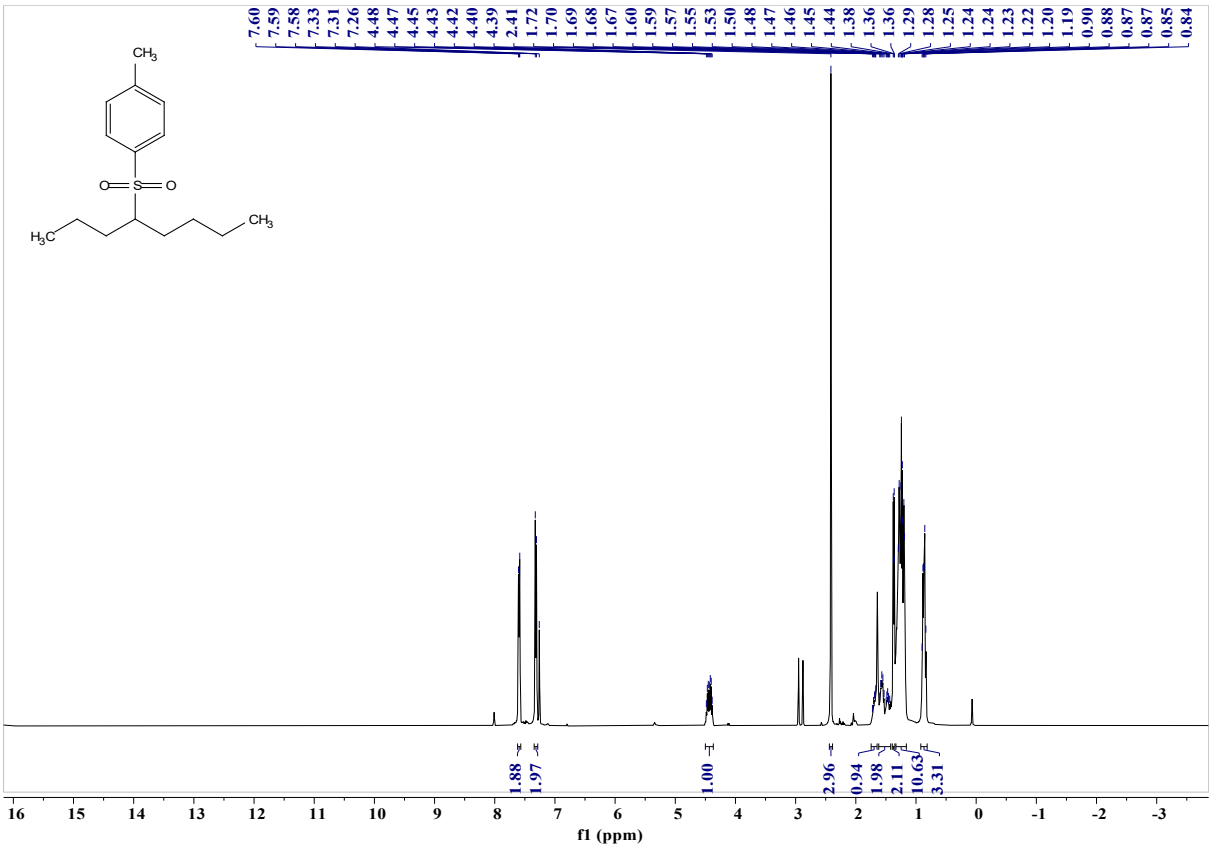
Compound 3ac, ^{1}H NMR (400 MHz, Chloroform-d)



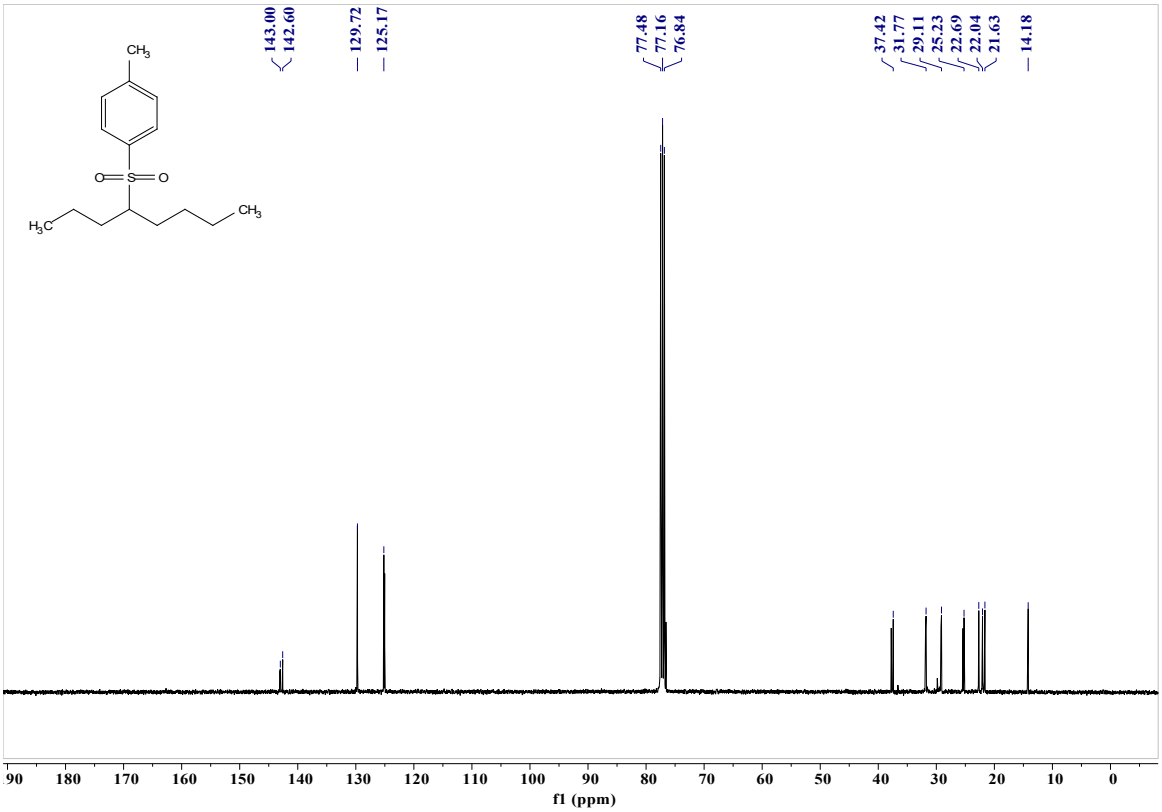
Compound 3ac, ^{13}C NMR (101 MHz, Chloroform-d)



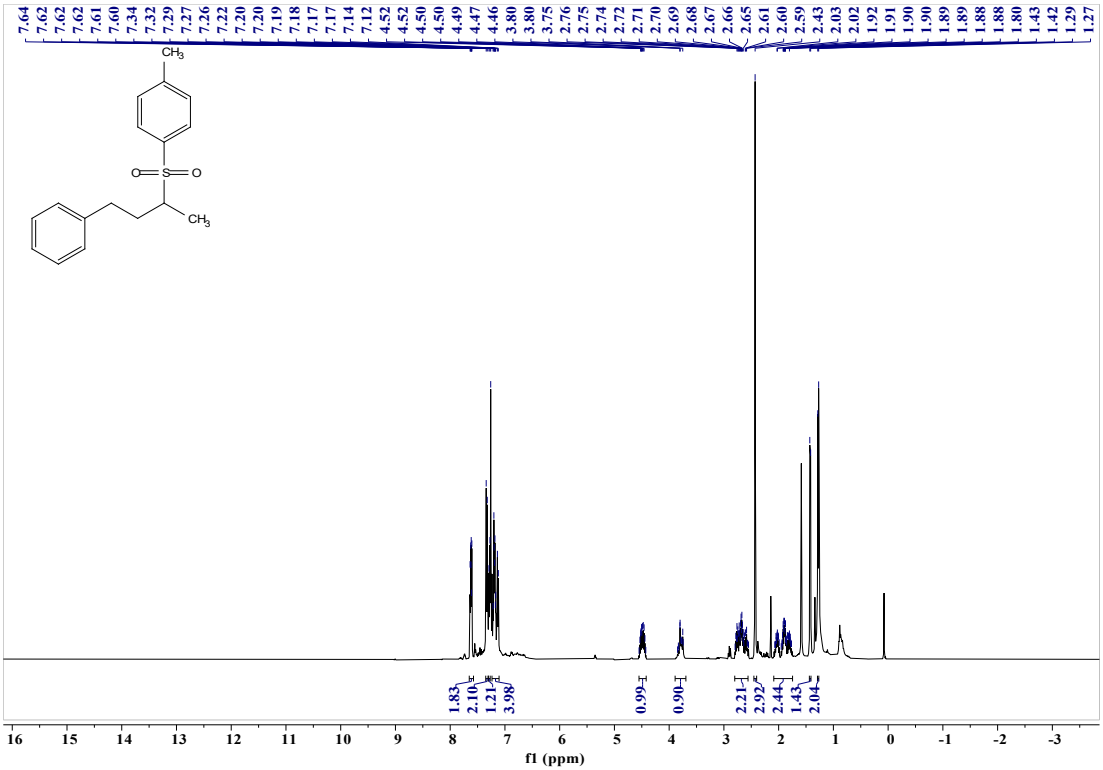
Compound 3ad, ^{1}H NMR (400 MHz, Chloroform-d)



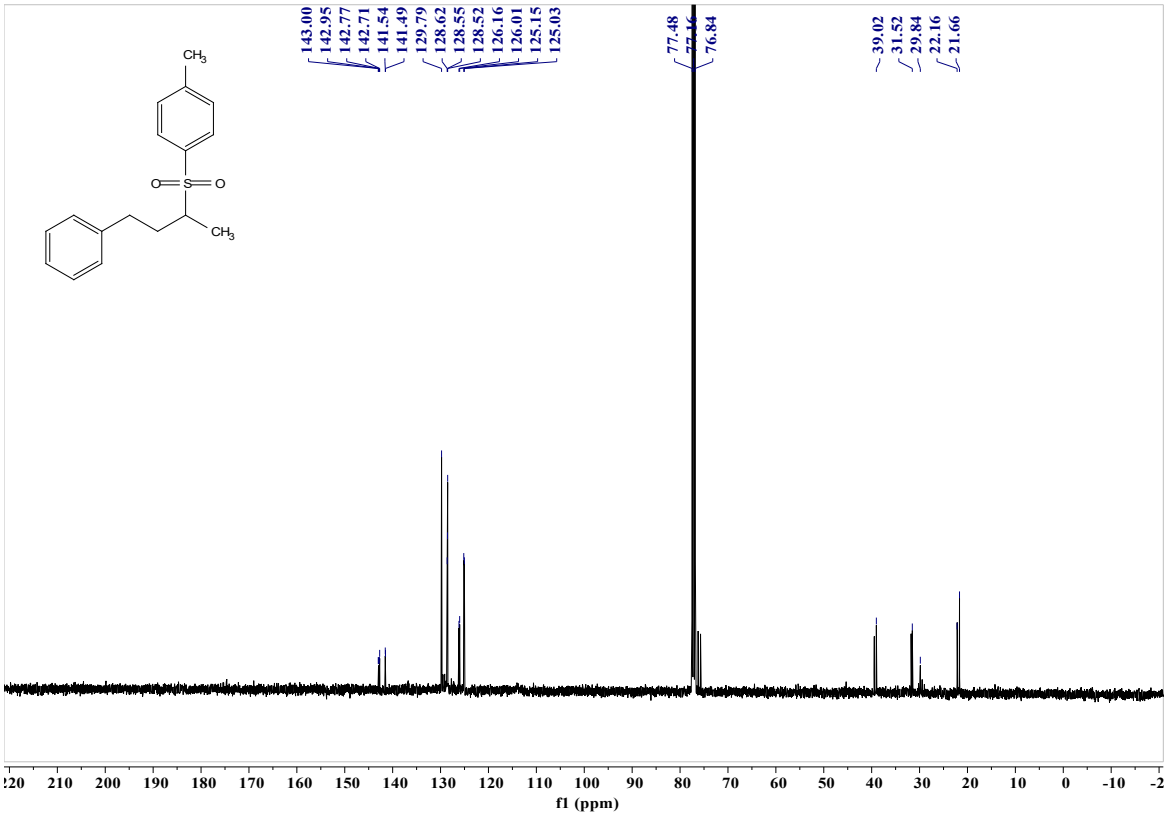
Compound 3ad, ^{13}C NMR (101 MHz, Chloroform-d)



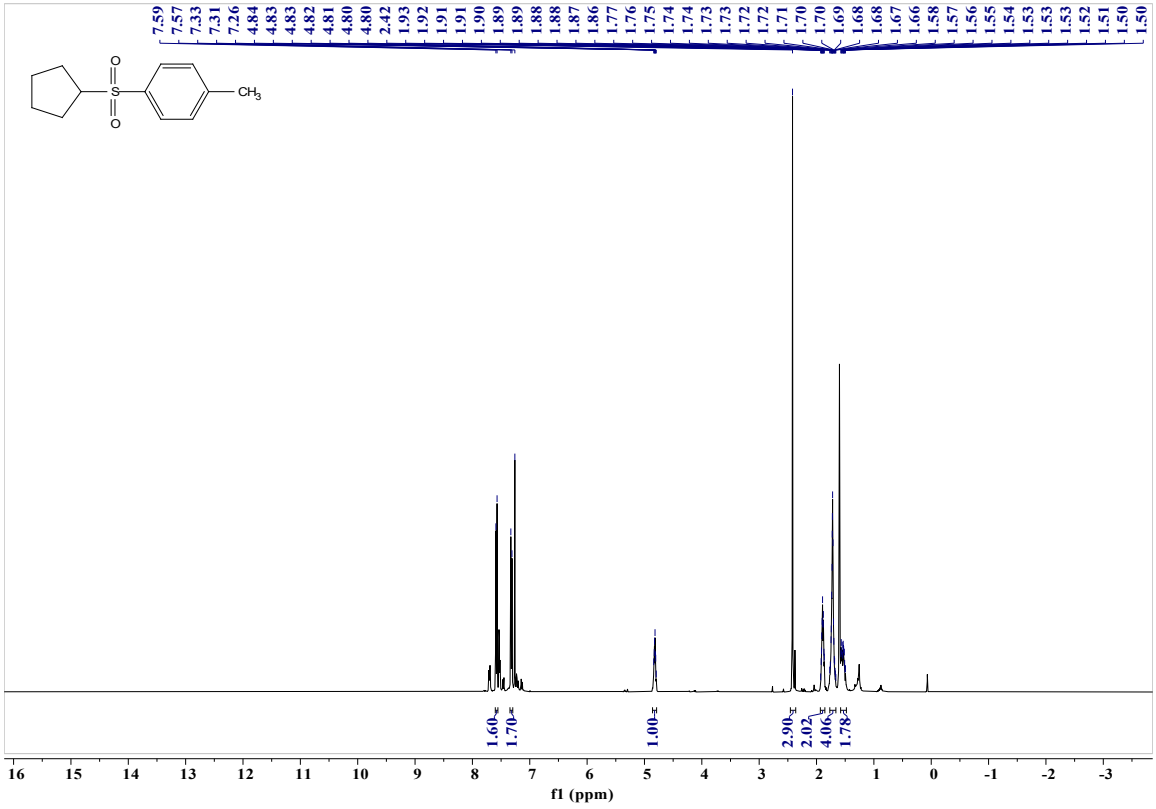
Compound 3ae, ^{1}H NMR (400 MHz, Chloroform-d)



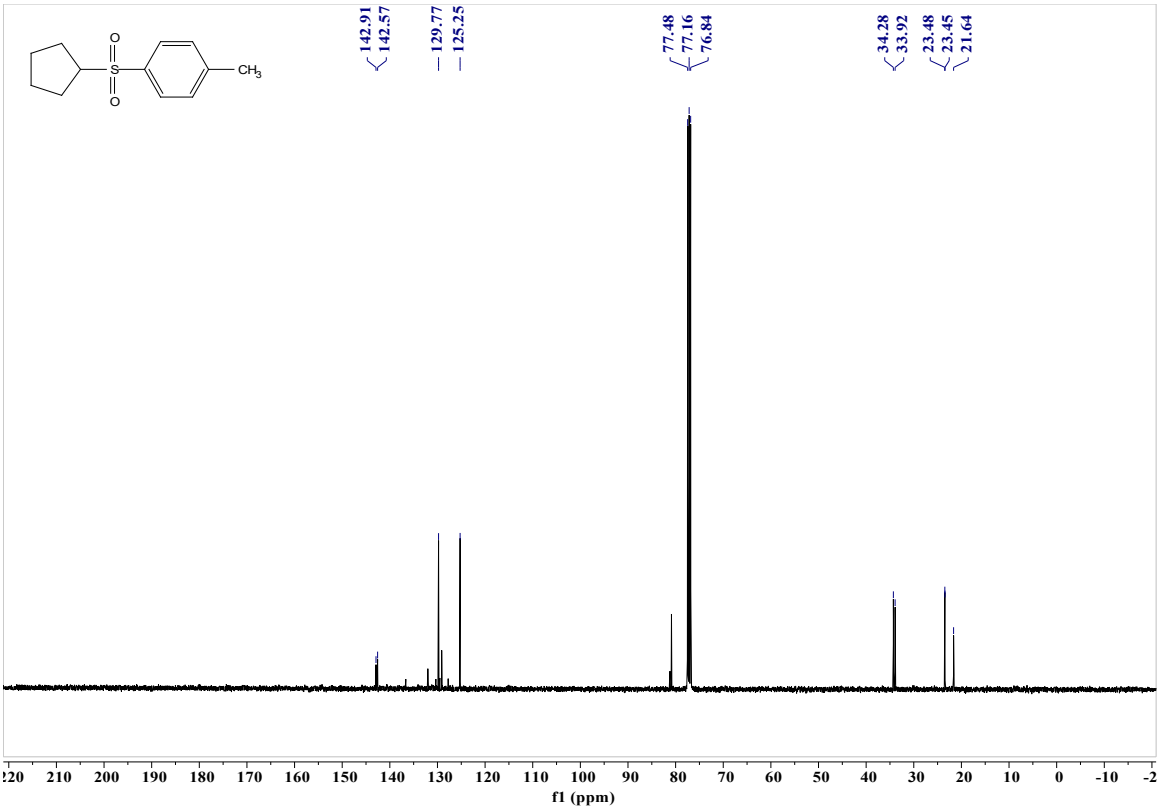
Compound 3ae, ^{13}C NMR (101 MHz, Chloroform-d)



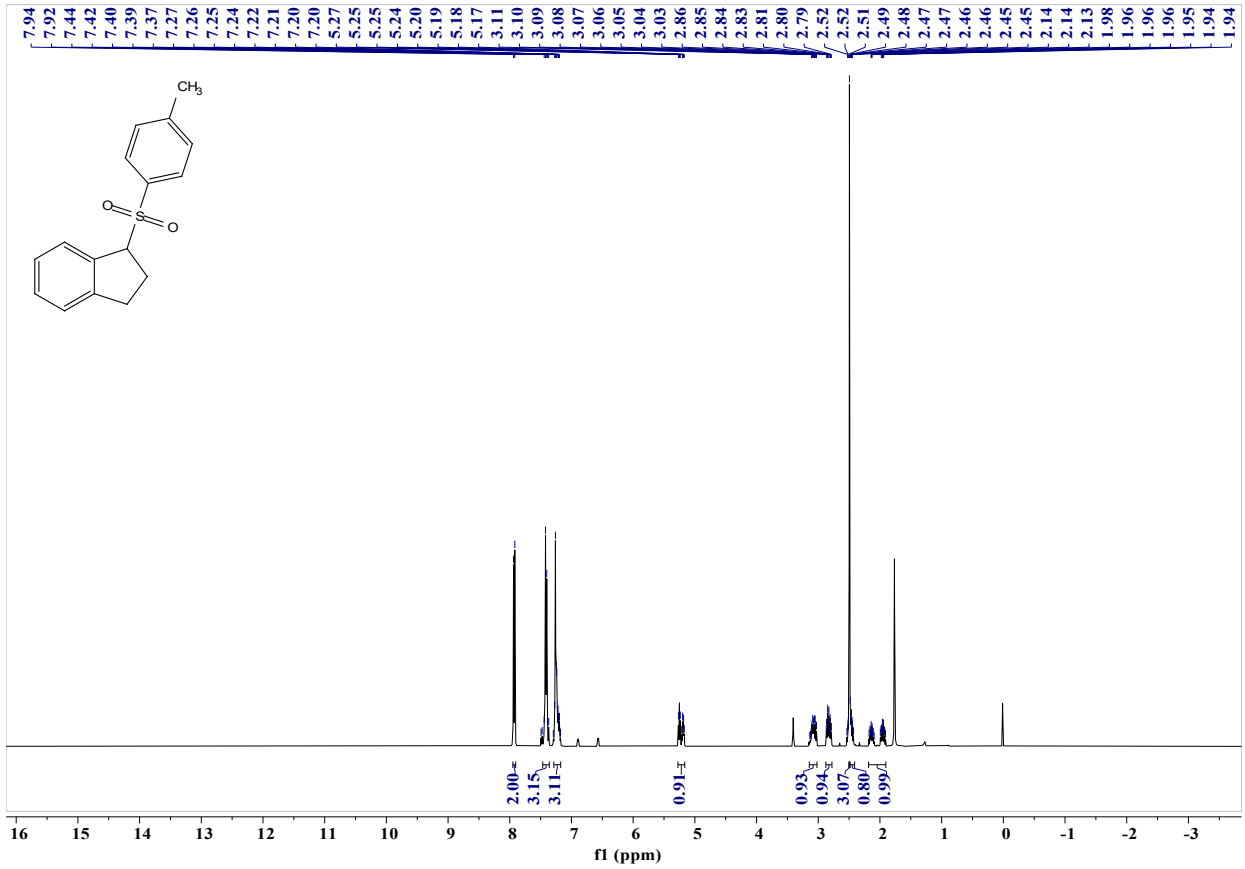
Compound 3af, ^{1}H NMR (400 MHz, Chloroform-d)



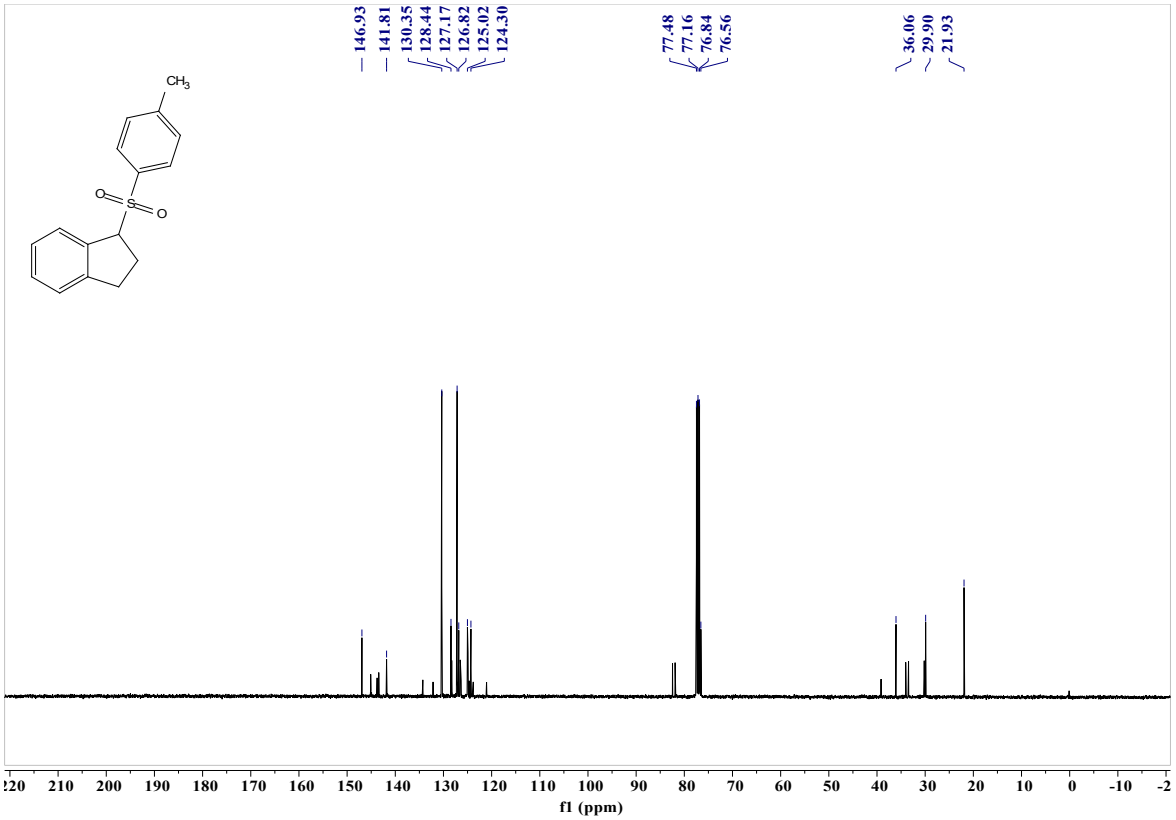
Compound 3af, ^{13}C NMR (101 MHz, Chloroform-d)



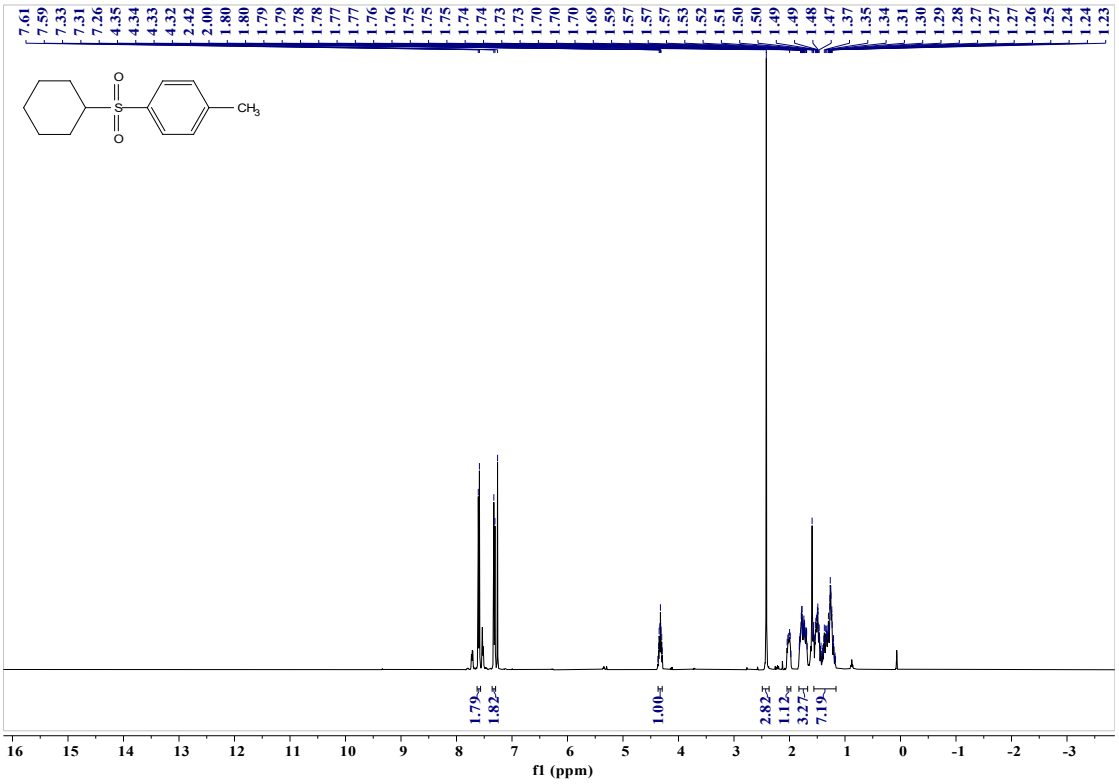
Compound 3ag, ^{1}H NMR (400 MHz, Chloroform-d)



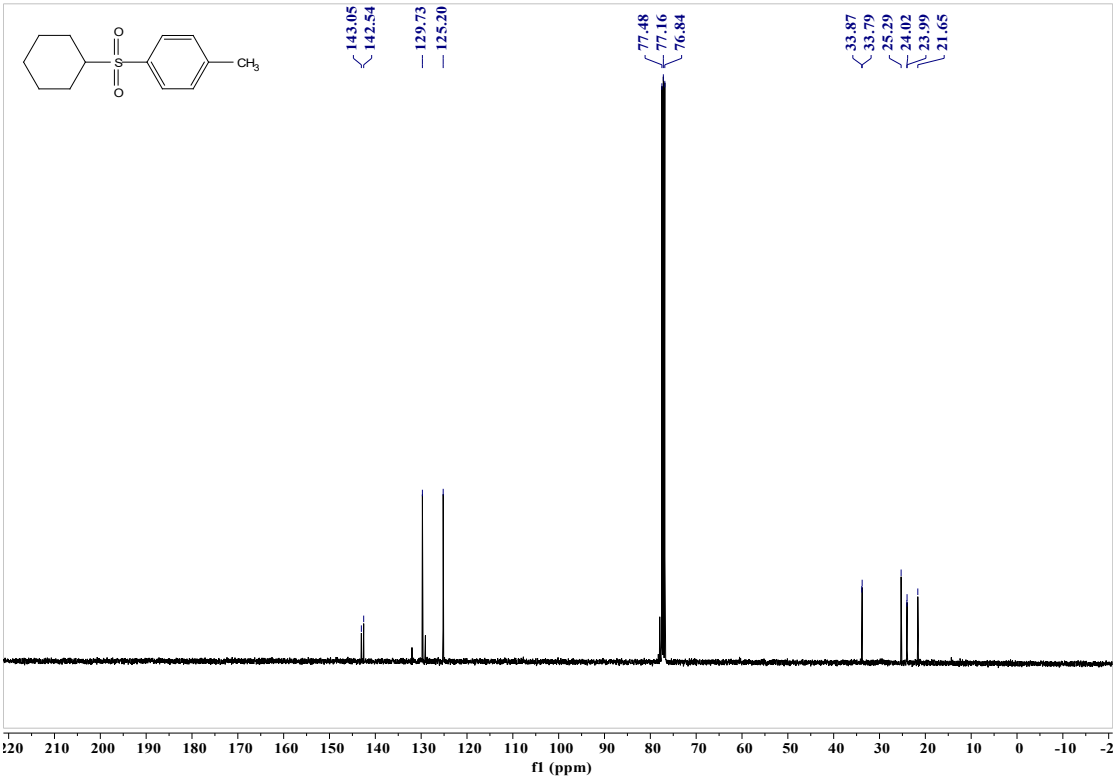
Compound 3ag, ^{13}C NMR (101 MHz, Chloroform-d)



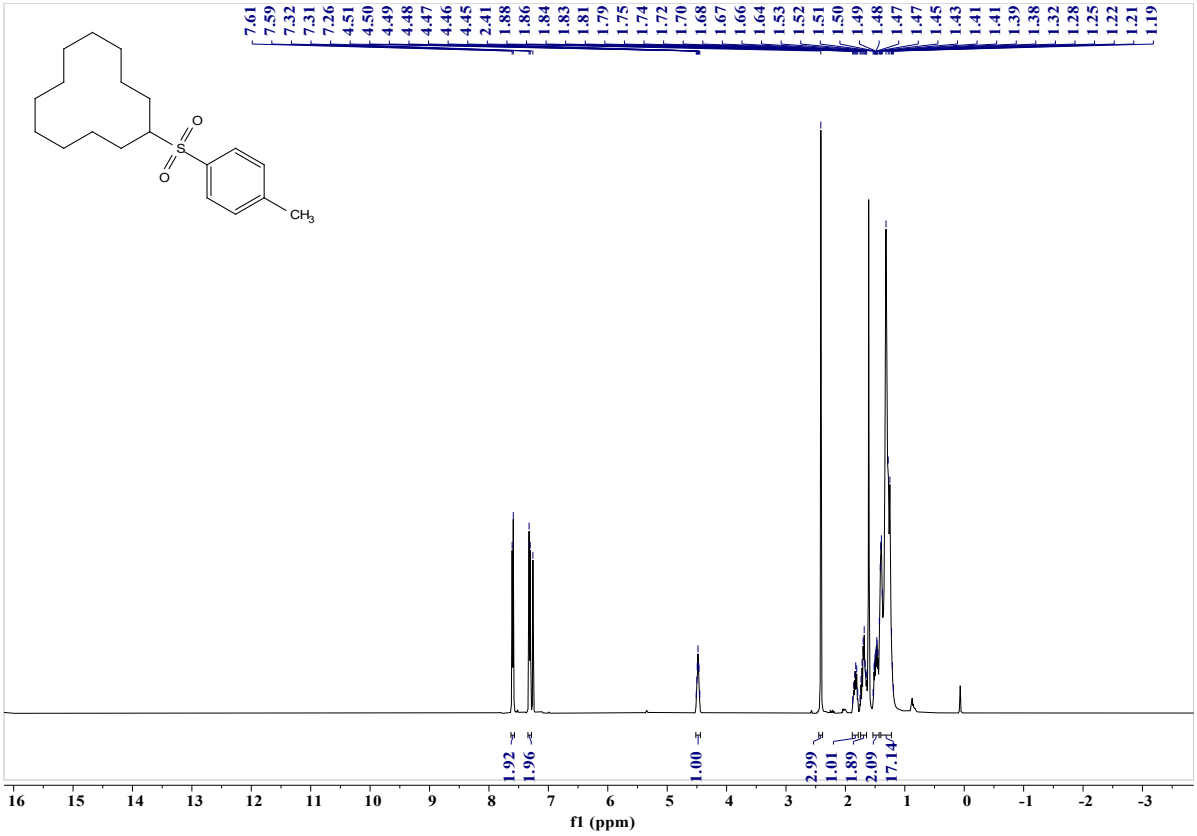
Compound 3ah, ^{1}H NMR (400 MHz, Chloroform-d)



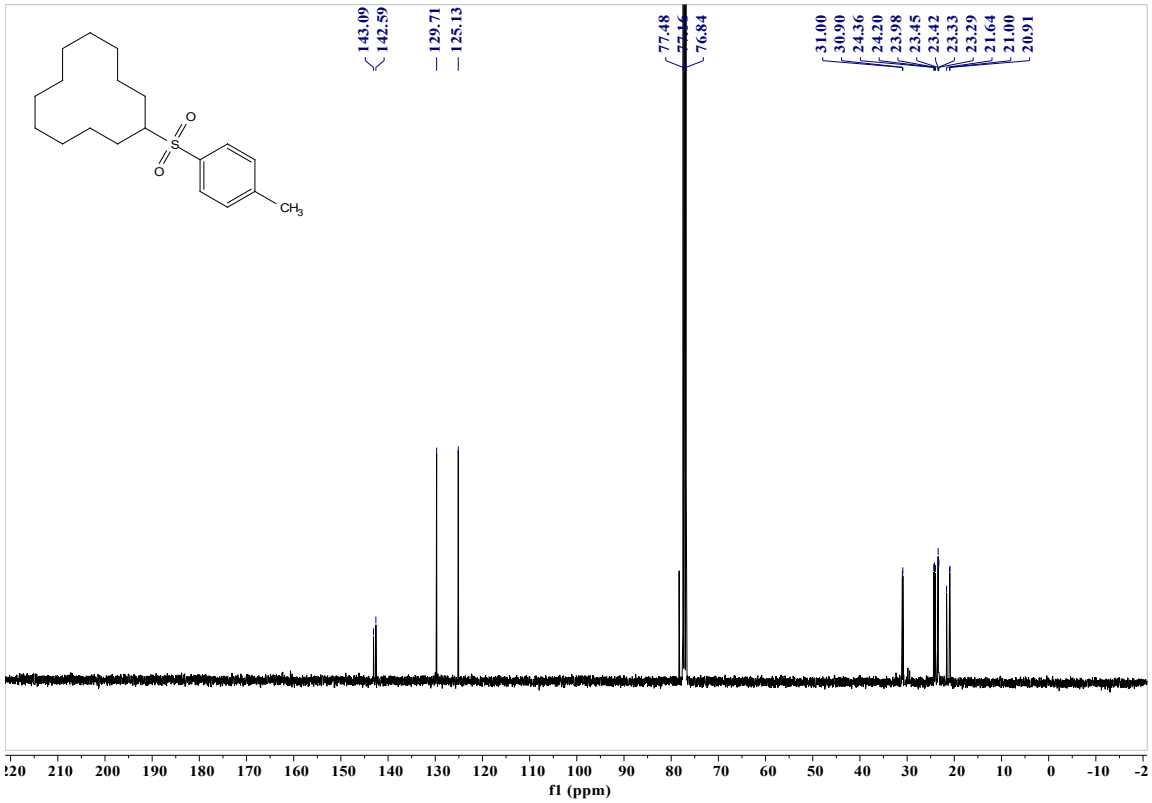
Compound 3ah, ^{13}C NMR (101 MHz, Chloroform-d)

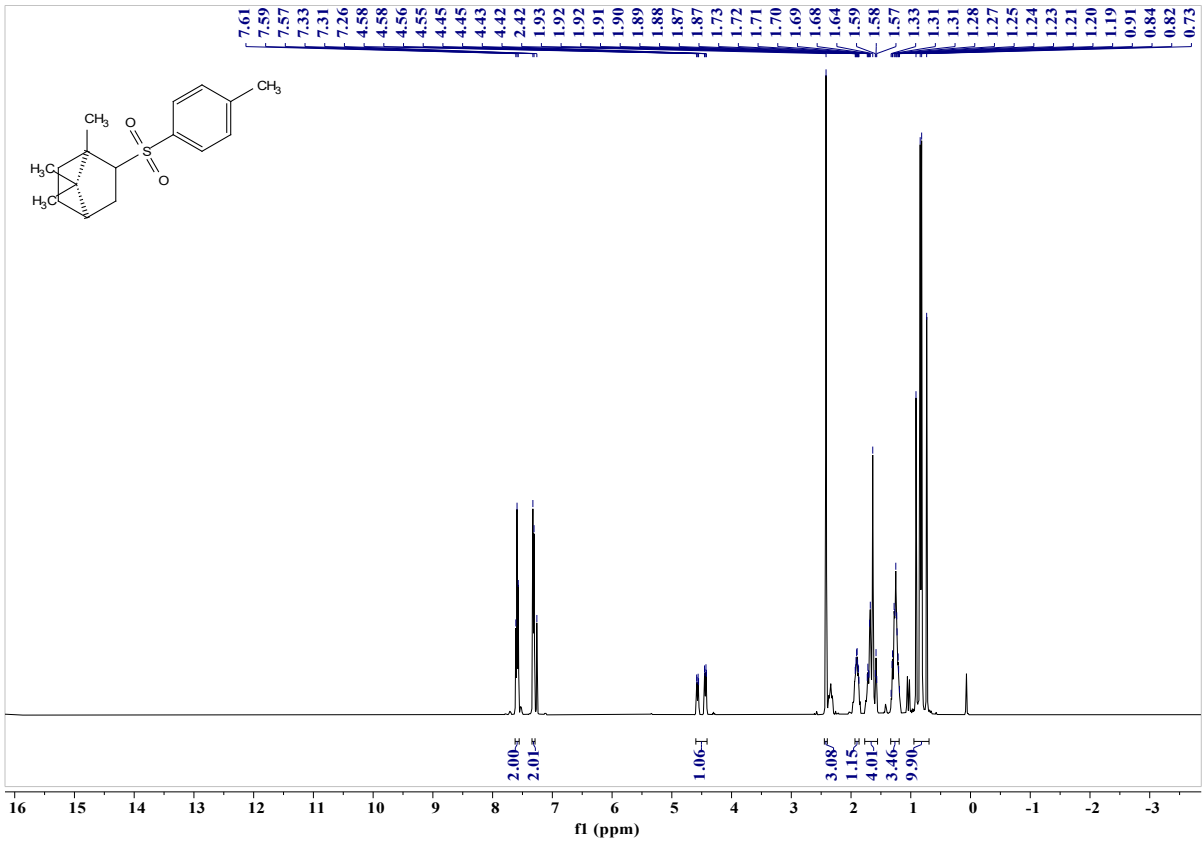


Compound 3ai, ^{1}H NMR (400 MHz, Chloroform-d)



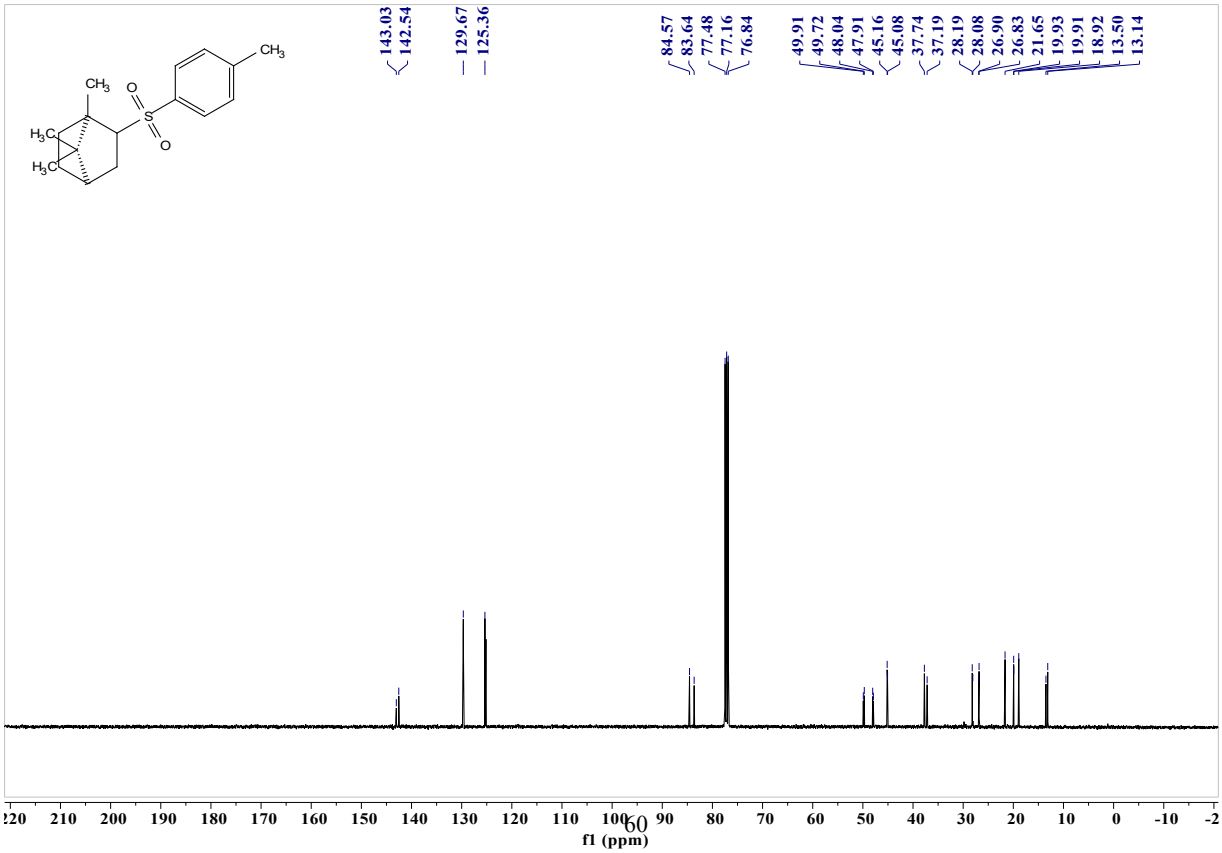
Compound 3ai, ^{13}C NMR (101 MHz, Chloroform-d)

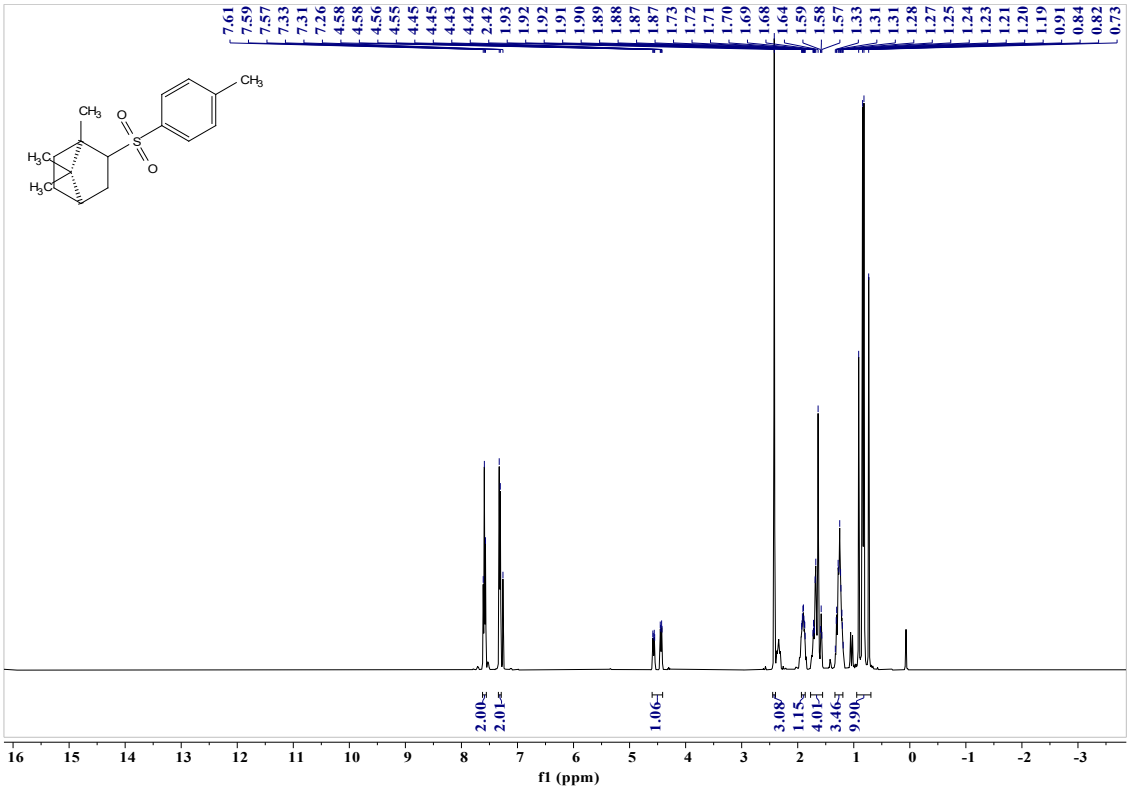




Compound 3aj, ^{1}H NMR (400 MHz, Chloroform-d)

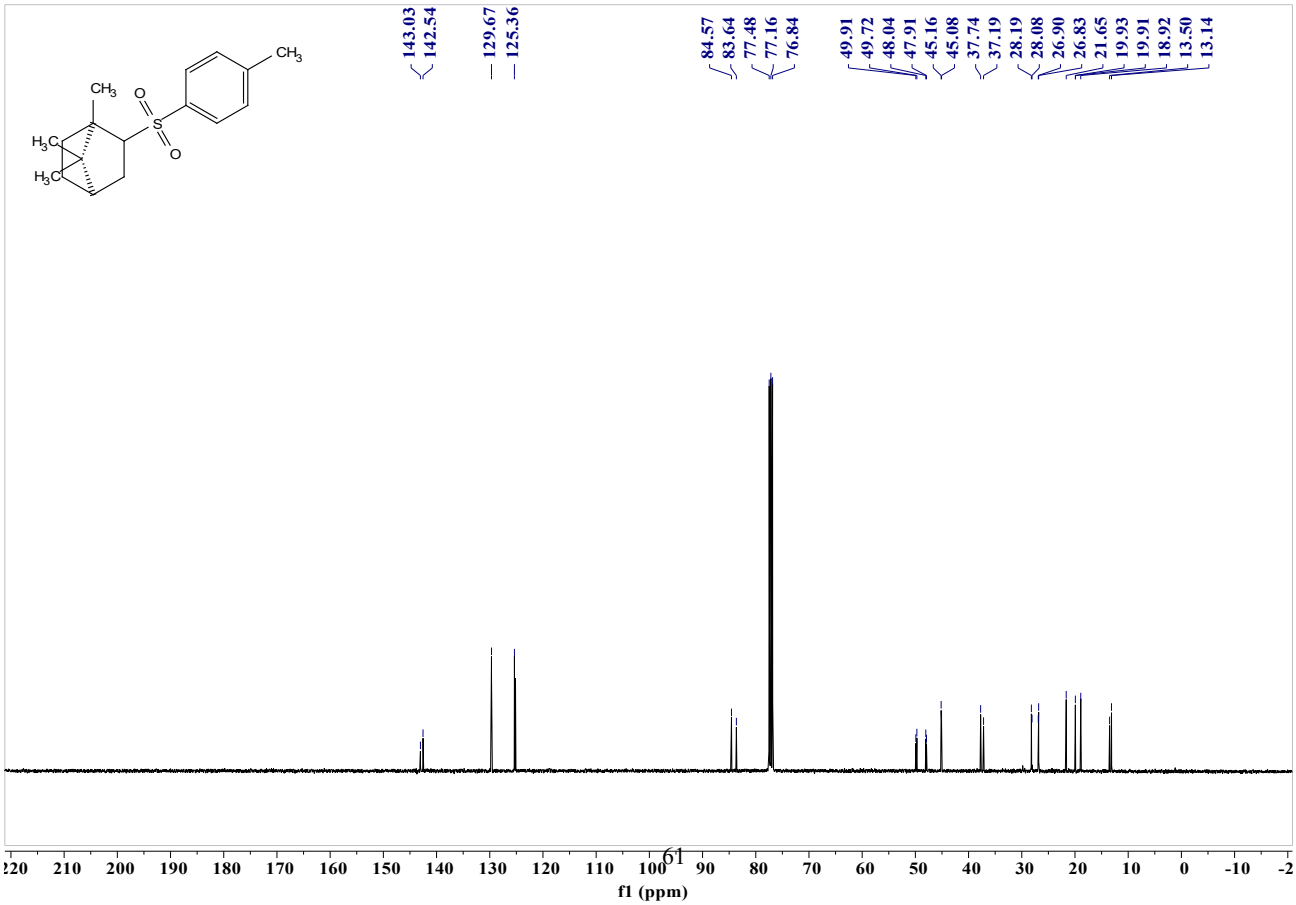
Compound 3aj, ^{13}C NMR (101 MHz, Chloroform-d)



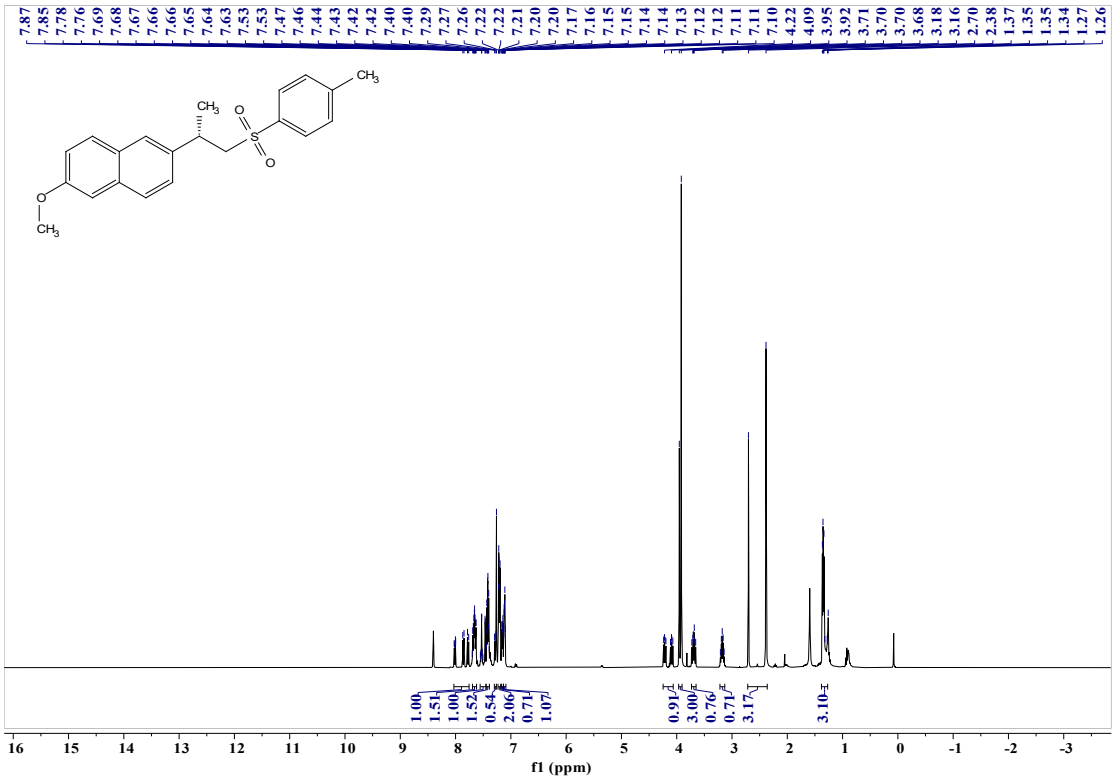


Compound 3ak, ^{1}H NMR (400 MHz, Chloroform-d)

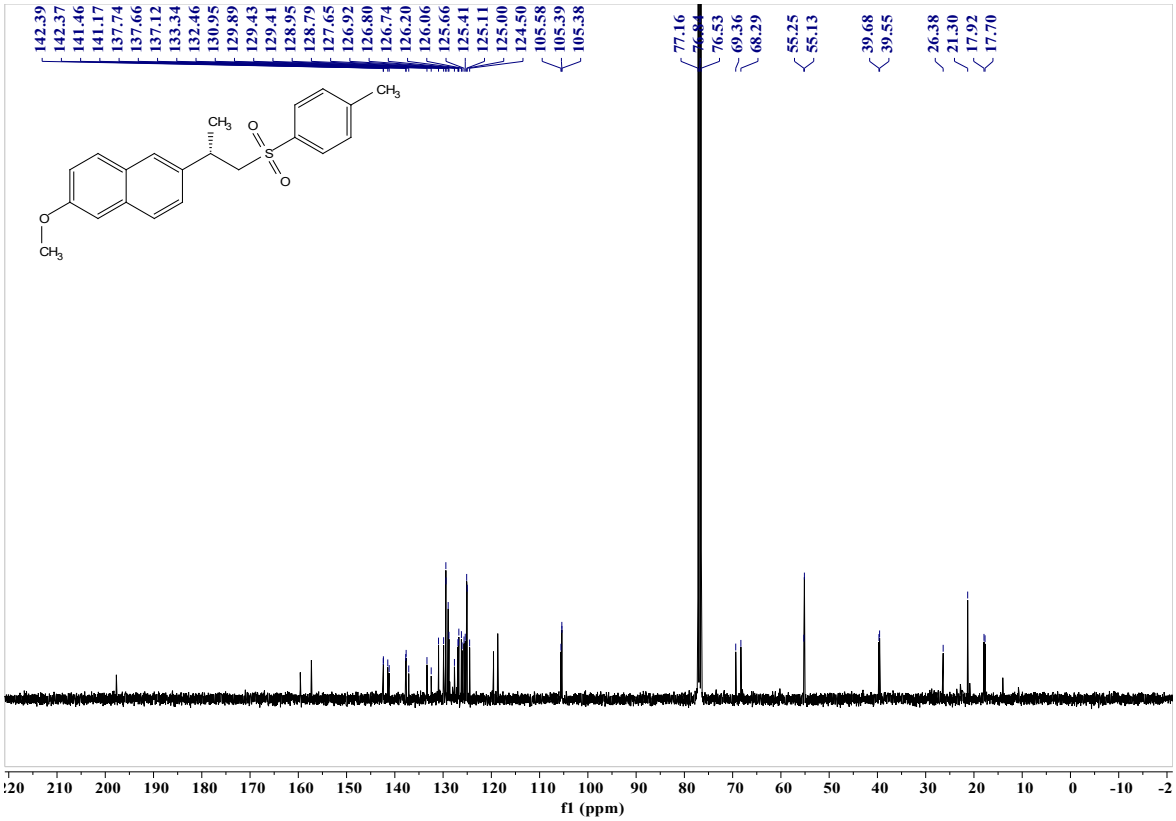
Compound 3ak, ^{13}C NMR (101 MHz, Chloroform-d)

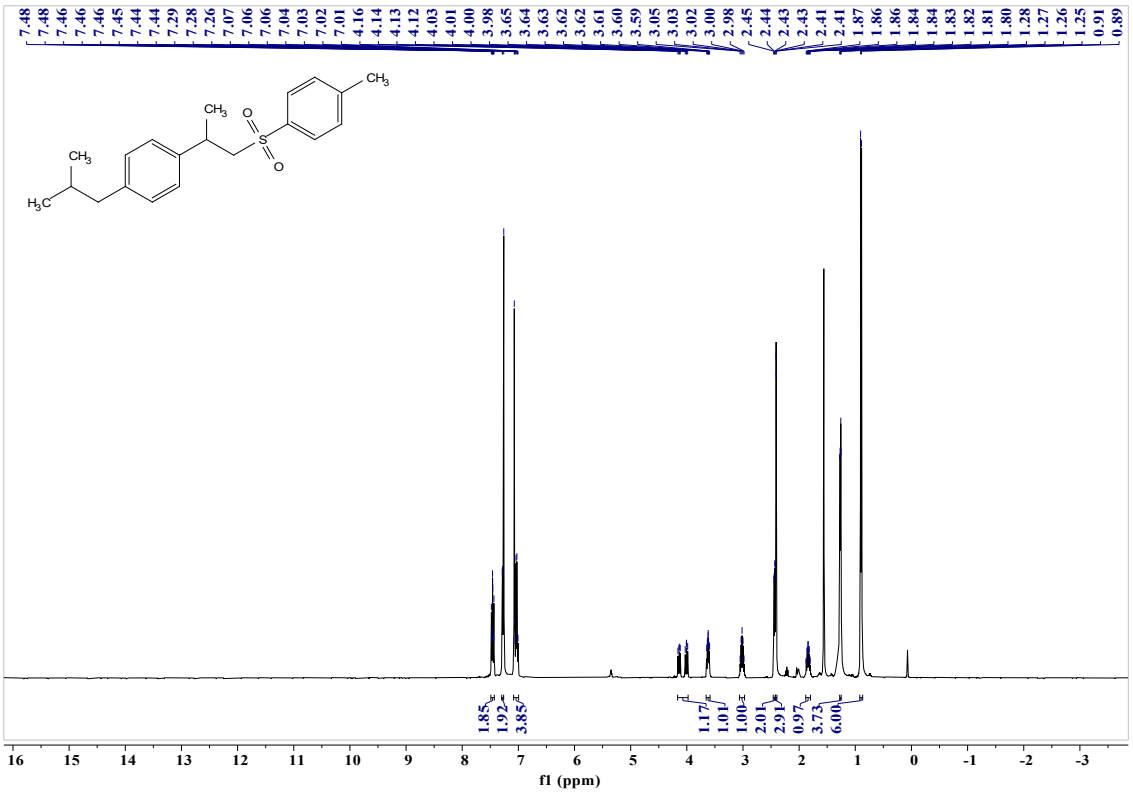


Compound 3al, ^{1}H NMR (400 MHz, Chloroform-d)



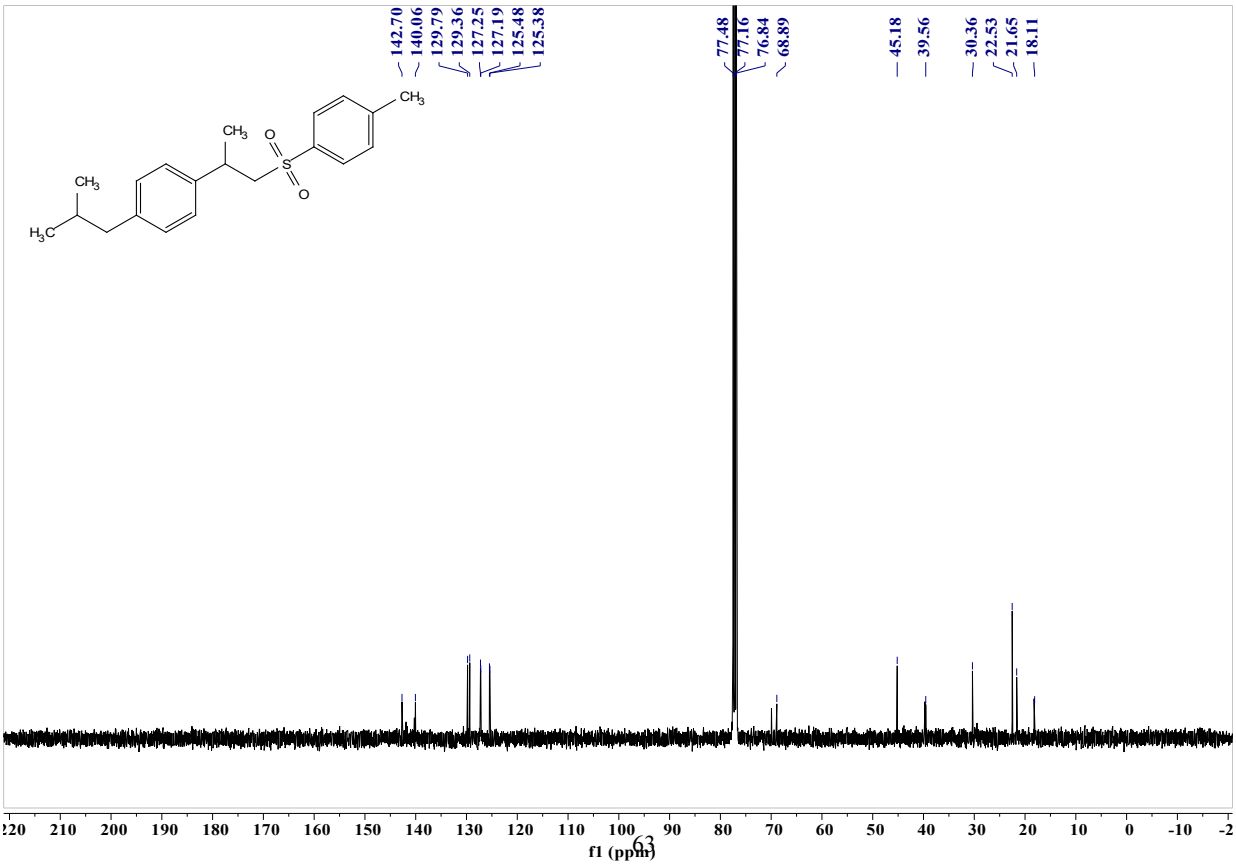
Compound 3al, ^{13}C NMR (101 MHz, Chloroform-d)



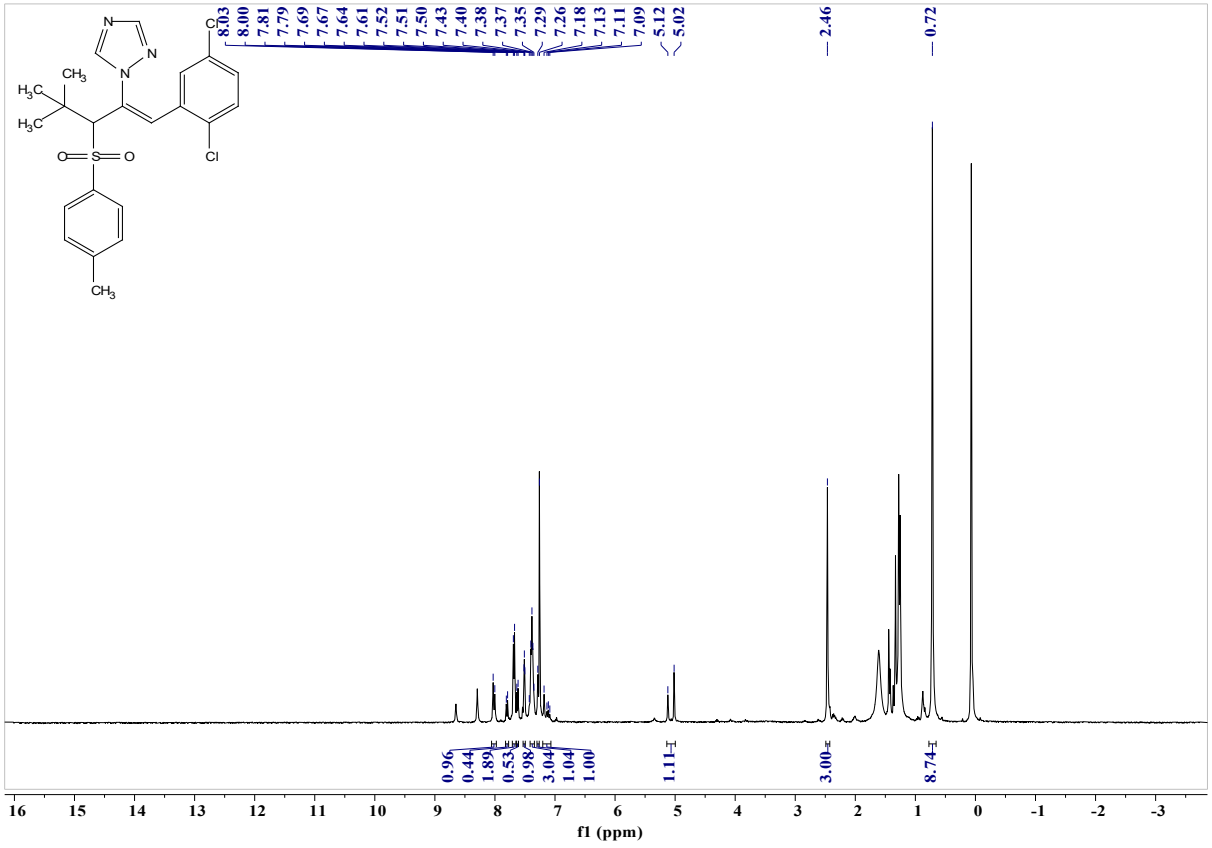


Compound 3am, ^{1}H NMR (400 MHz, Chloroform-d)

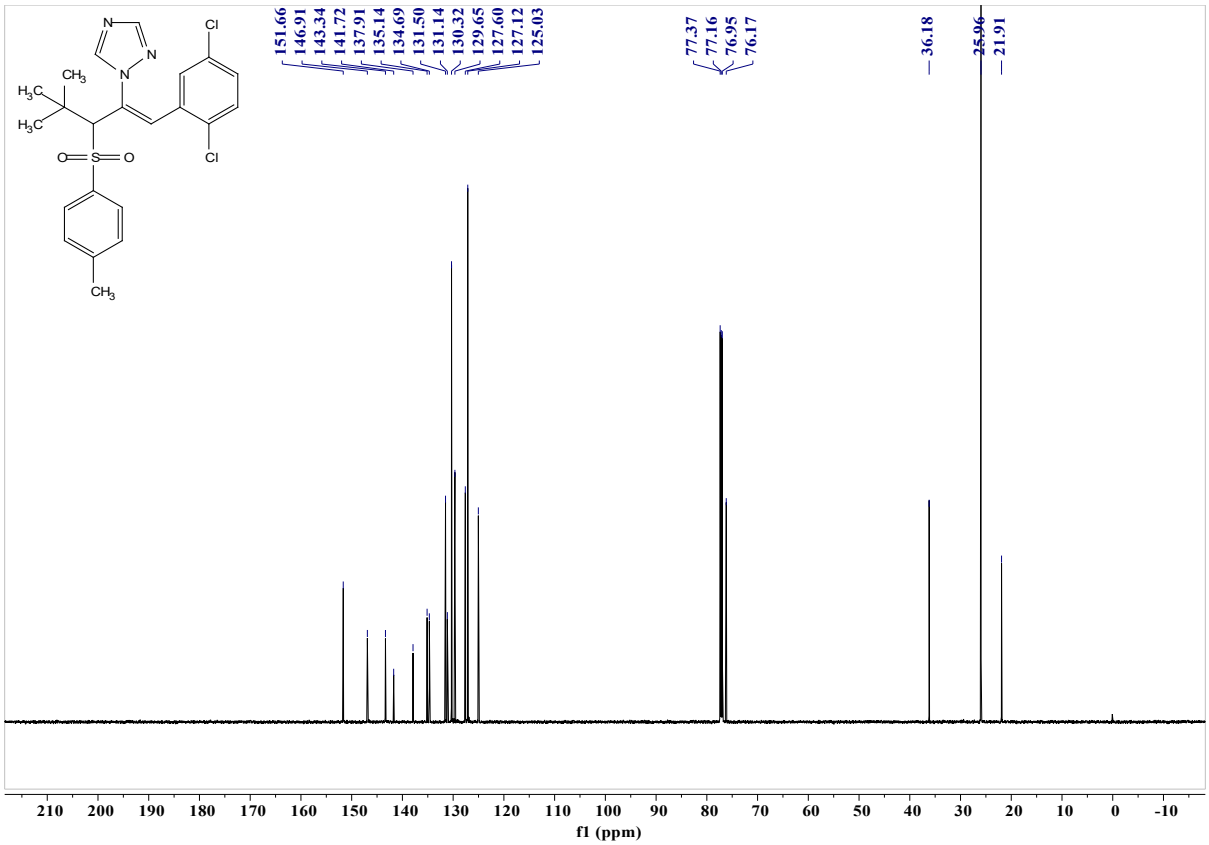
Compound 3am, ^{13}C NMR (101 MHz, Chloroform-d)



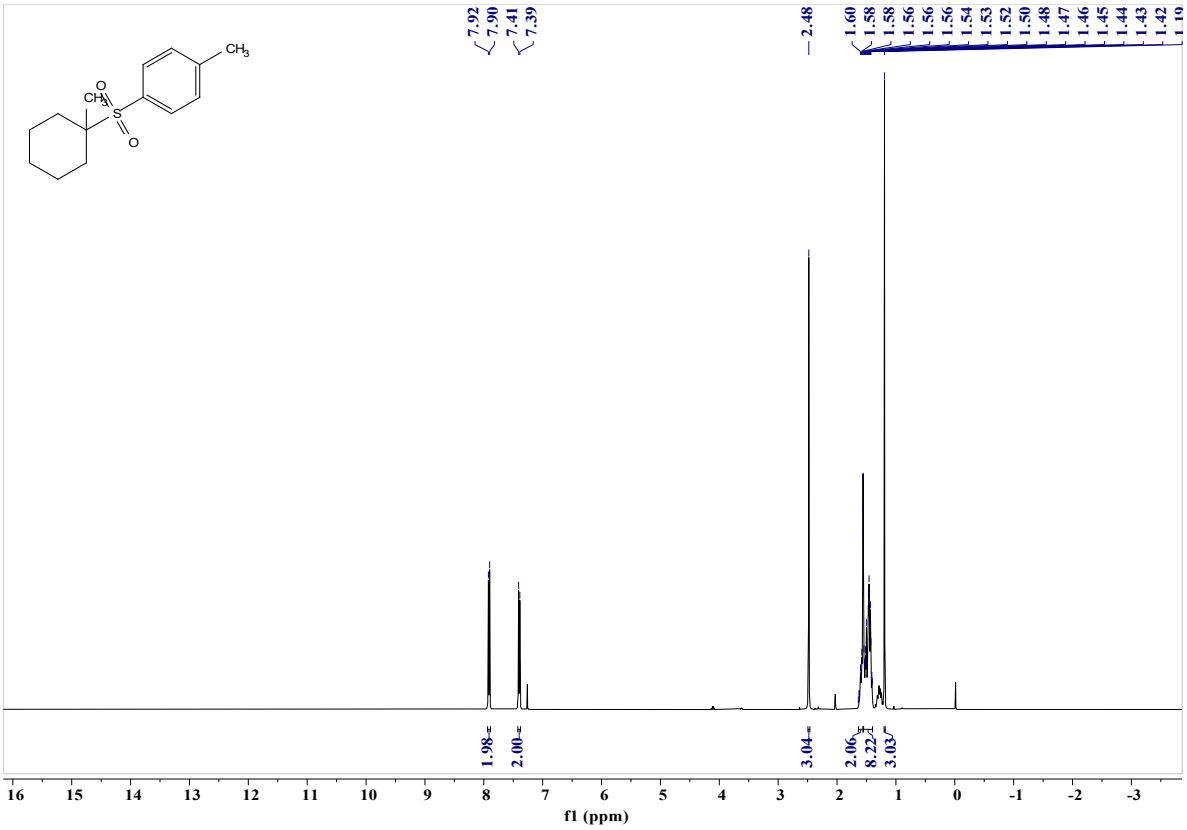
Compound 3an, ^{1}H NMR (400 MHz, Chloroform-d)



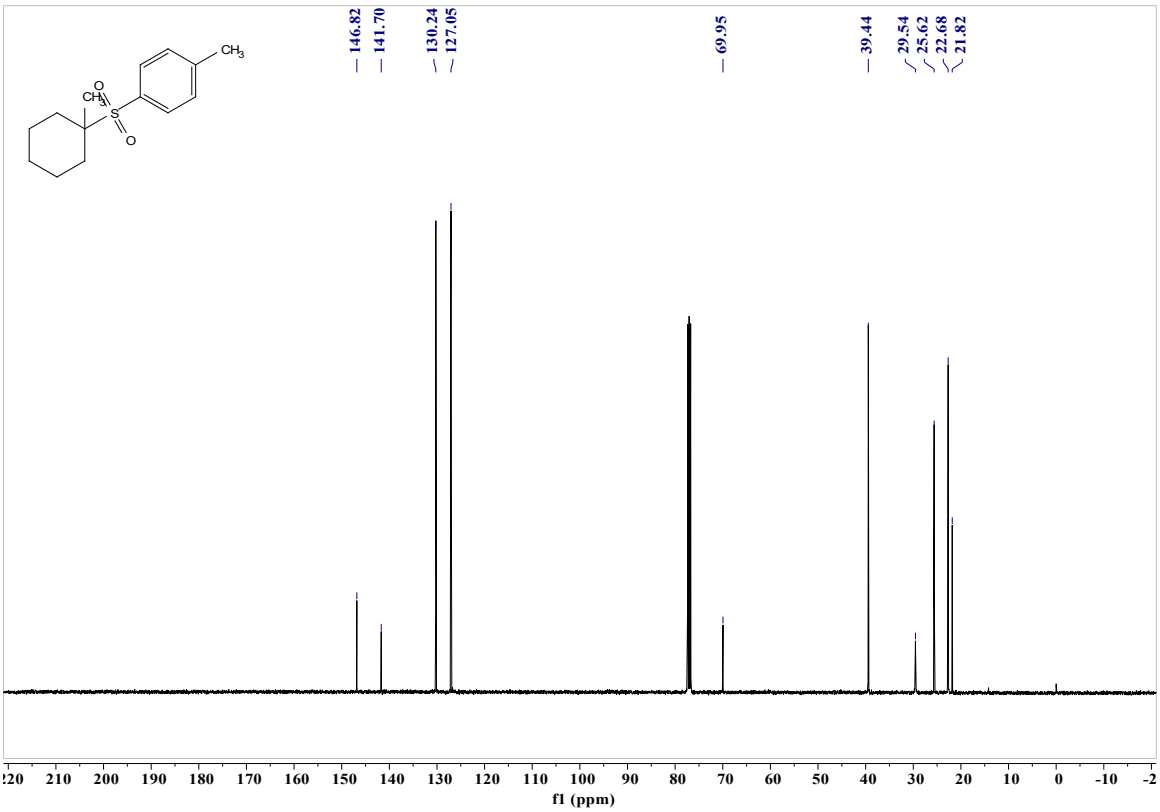
Compound 3an, ^{13}C NMR (101 MHz, Chloroform-d)



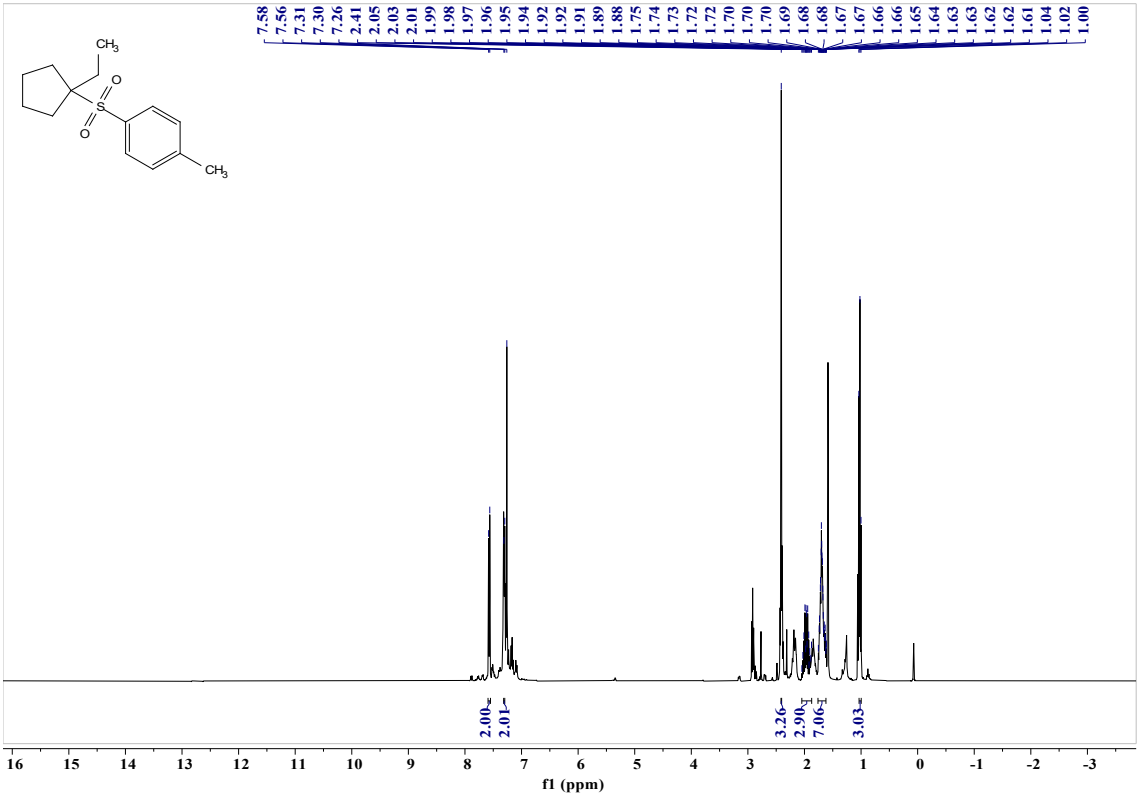
Compound 3ao, ^{1}H NMR (400 MHz, Chloroform-d)



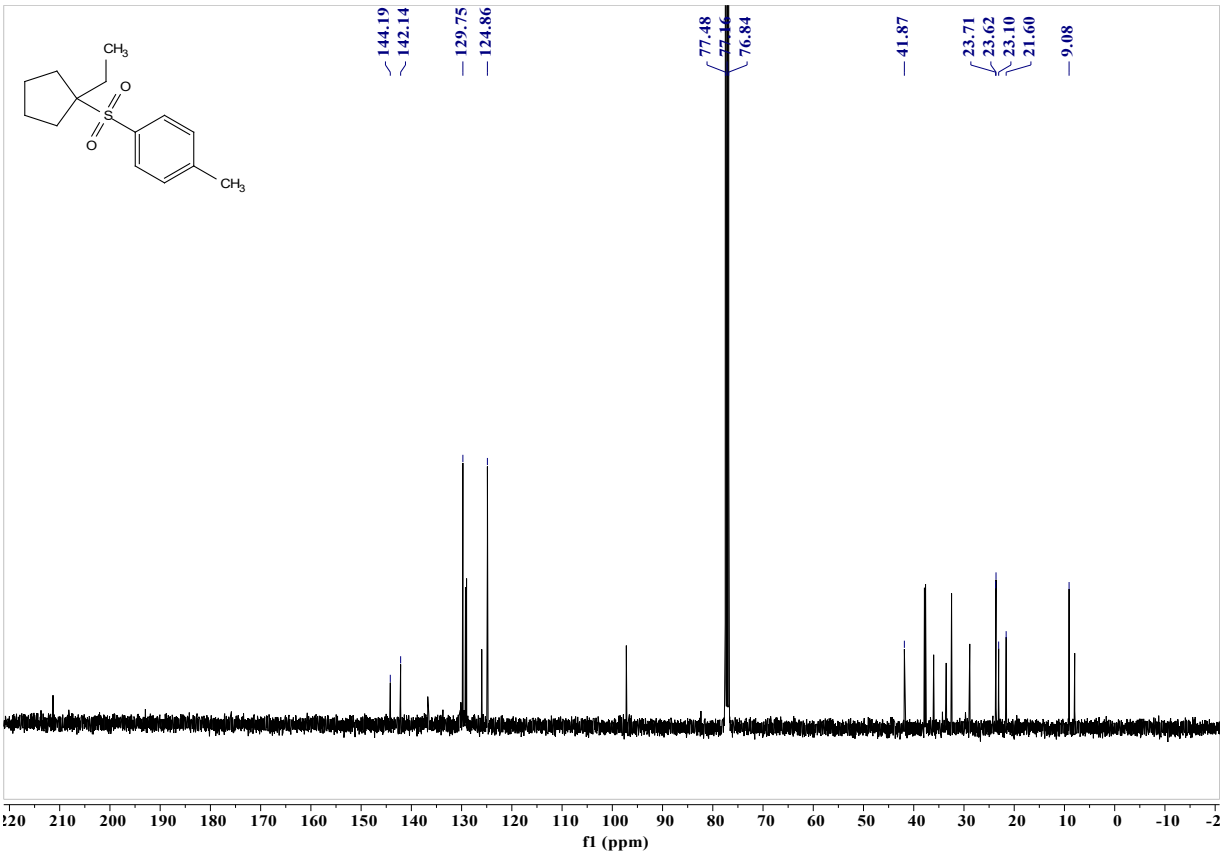
Compound 3ao, ^{13}C NMR (101 MHz, Chloroform-d)

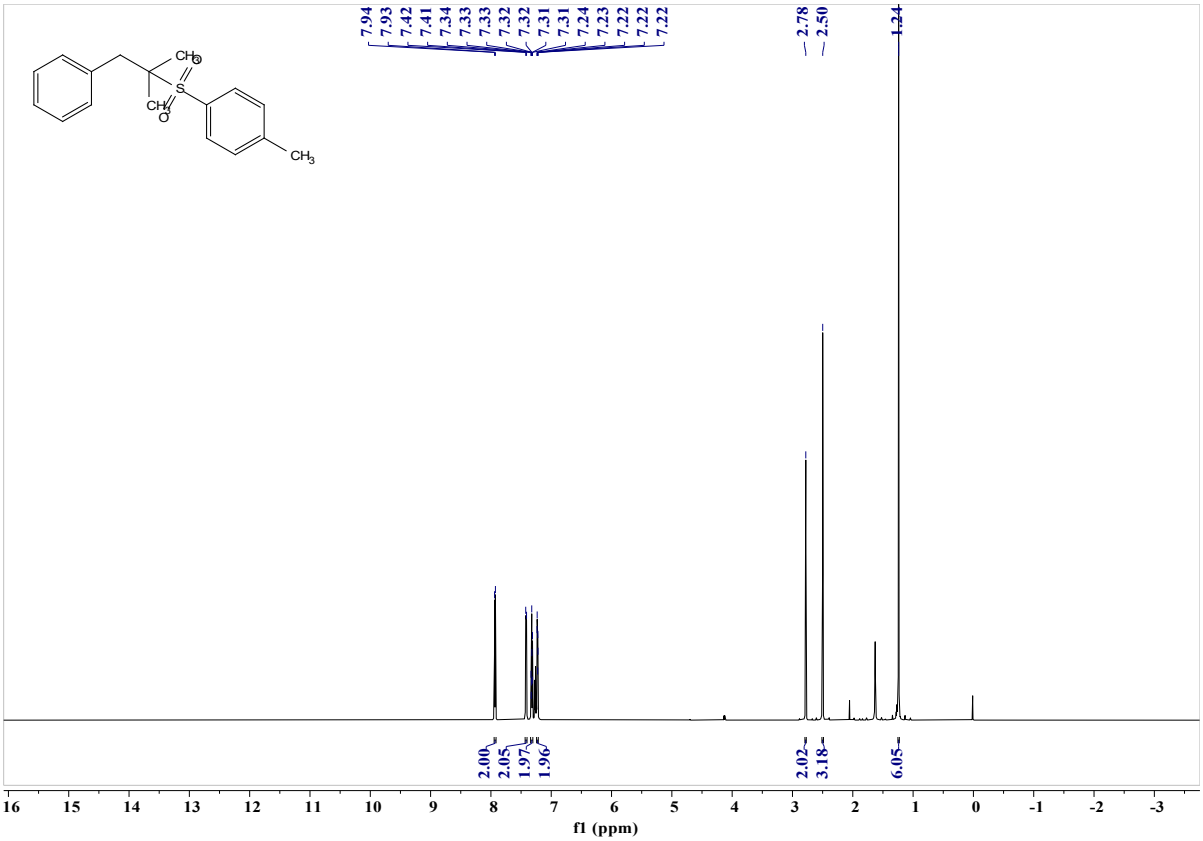


Compound 3ap, ^{1}H NMR (400 MHz, Chloroform-d)



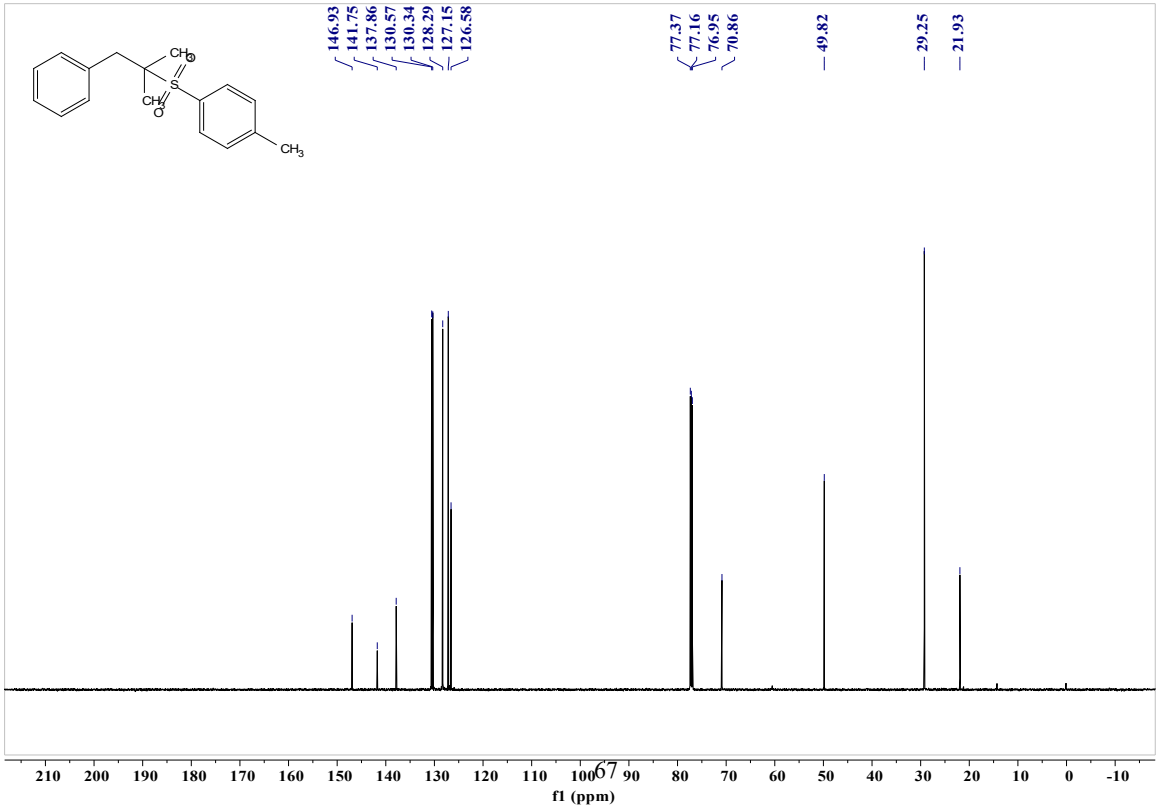
Compound 3ap, ^{13}C NMR (101 MHz, Chloroform-d)



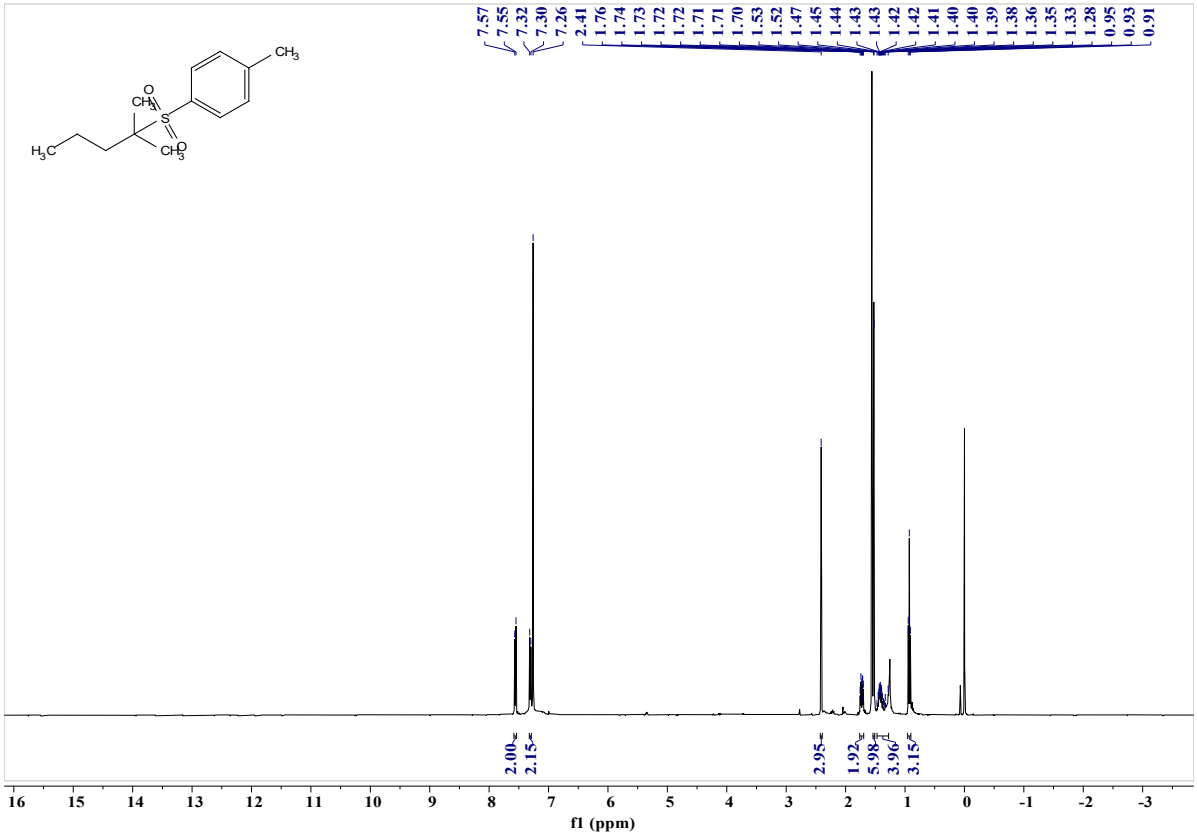


Compound 3aq, ^{1}H NMR (400 MHz, Chloroform-d)

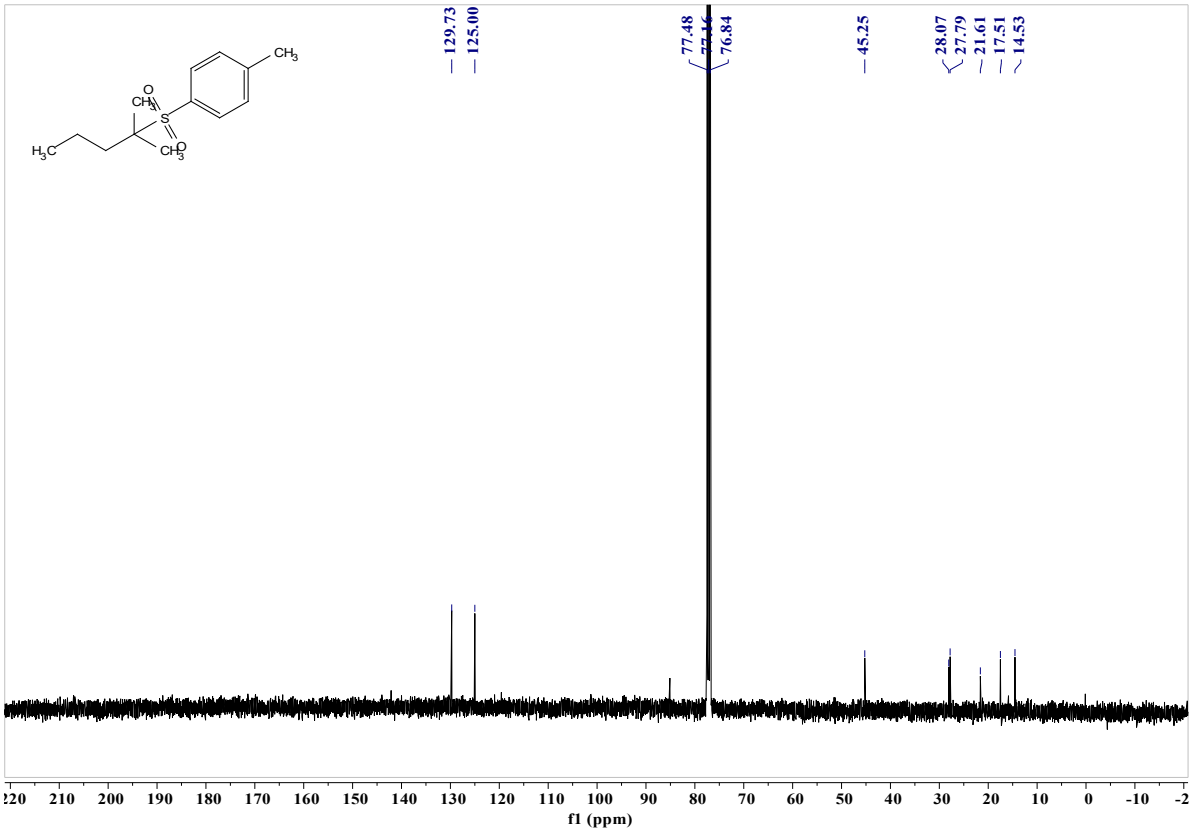
Compound 3aq, ^{13}C NMR (101 MHz, Chloroform-d)



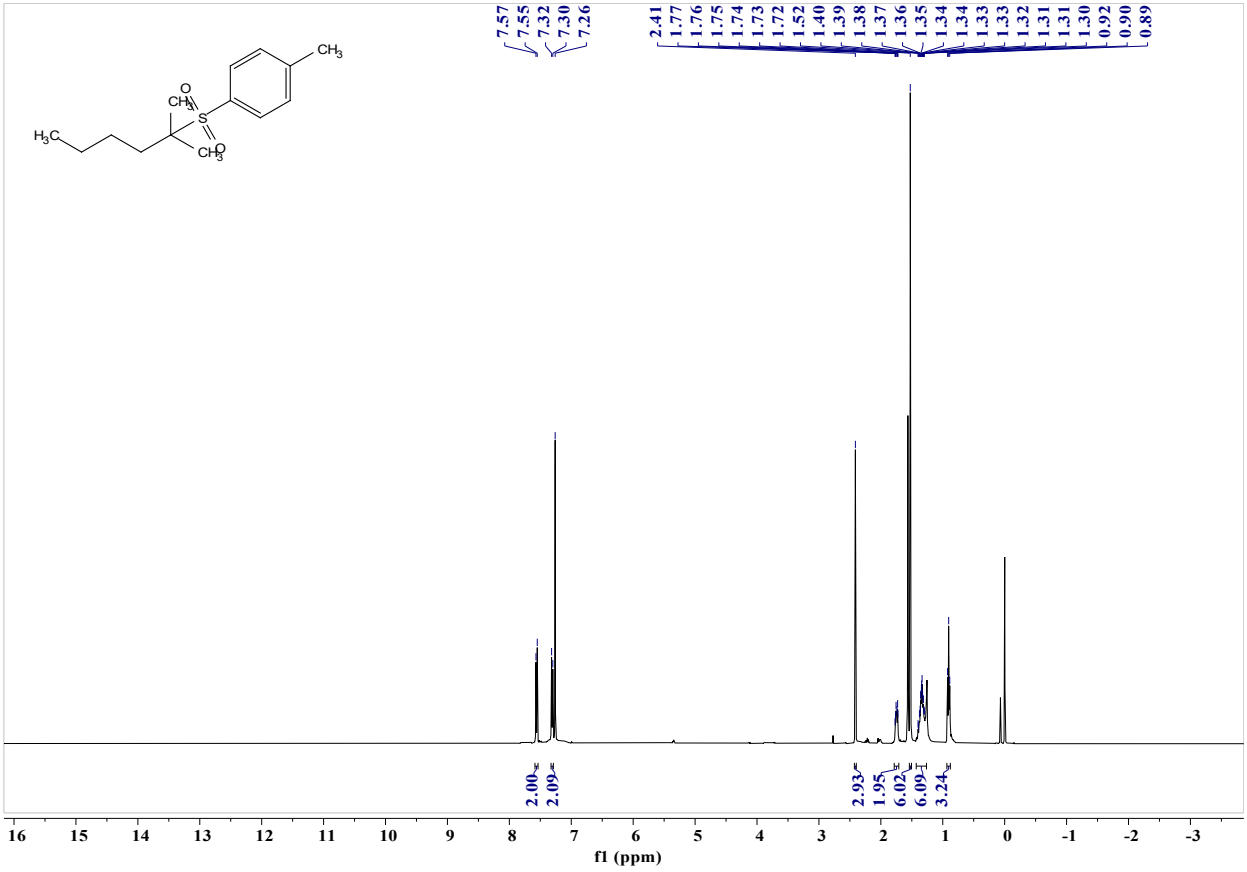
Compound 3ar, ^{1}H NMR (400 MHz, Chloroform-d)



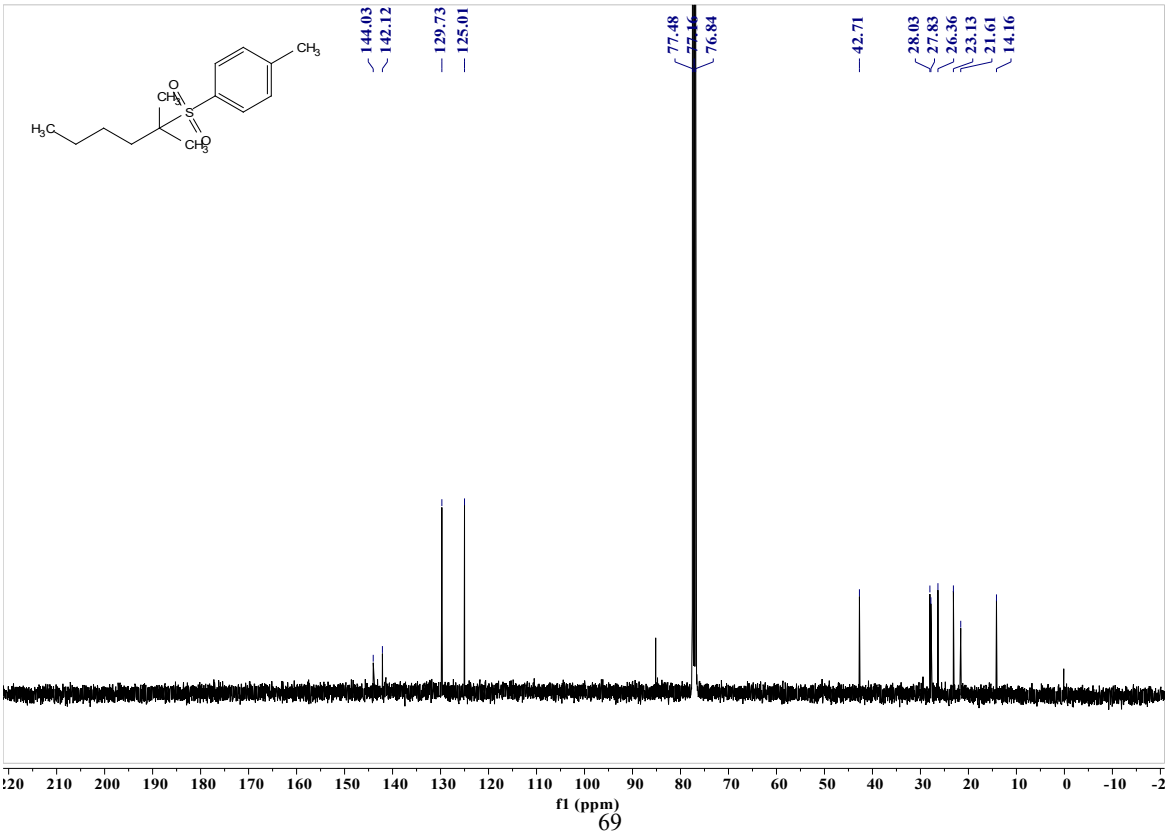
Compound 3ar, ^{13}C NMR (101 MHz, Chloroform-d)



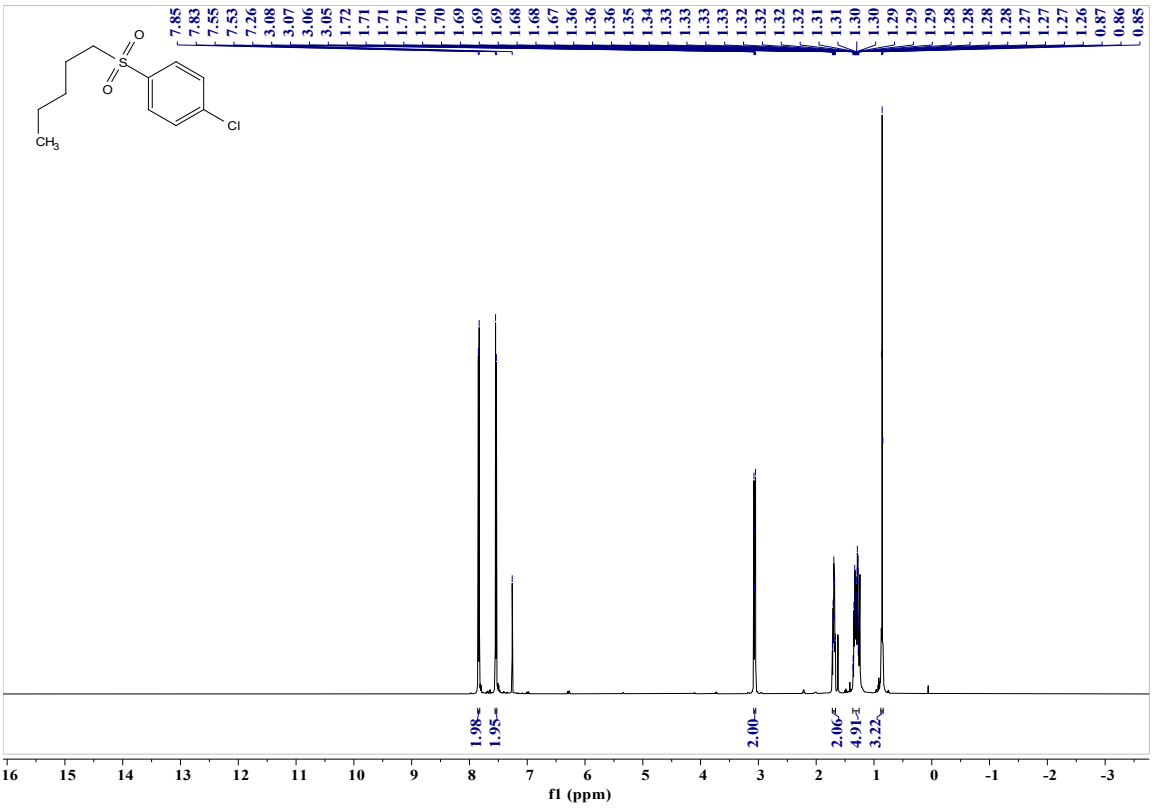
Compound 3as, ^{1}H NMR (400 MHz, Chloroform-d)



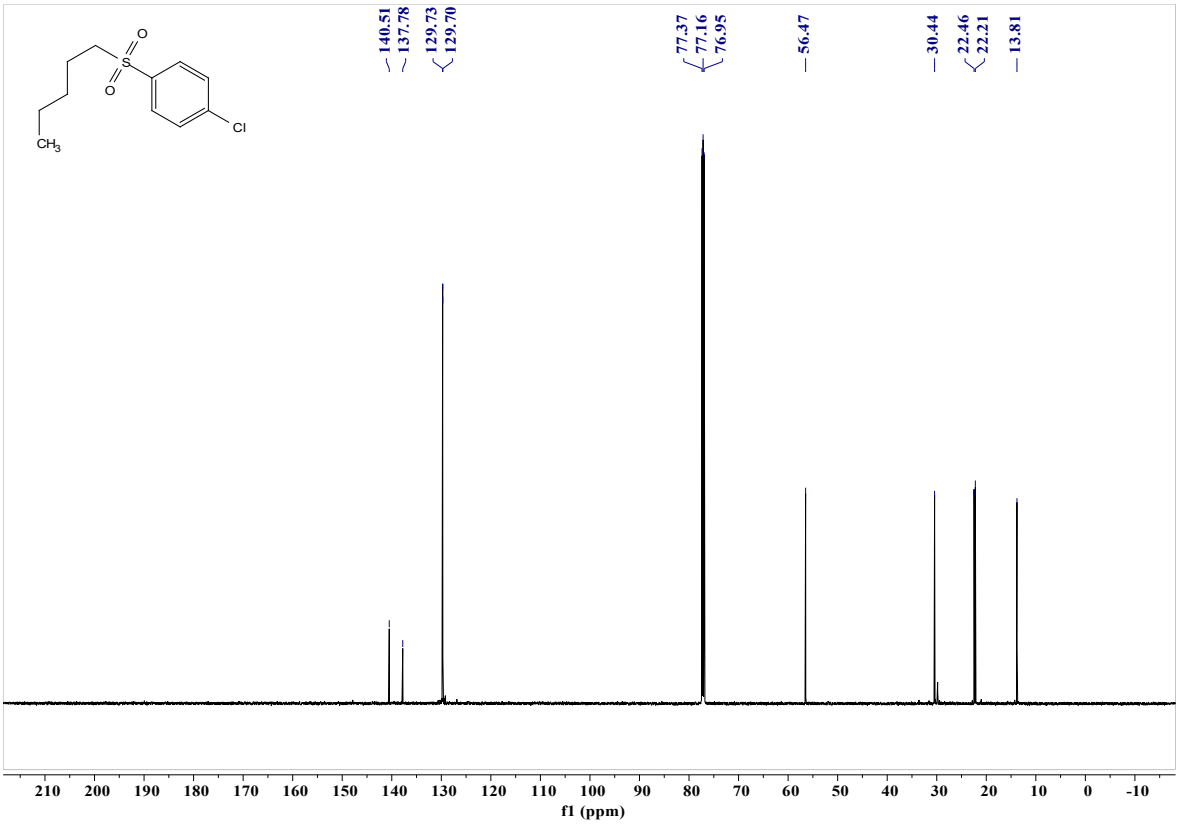
Compound 3as, ^{13}C NMR (101 MHz, Chloroform-d)



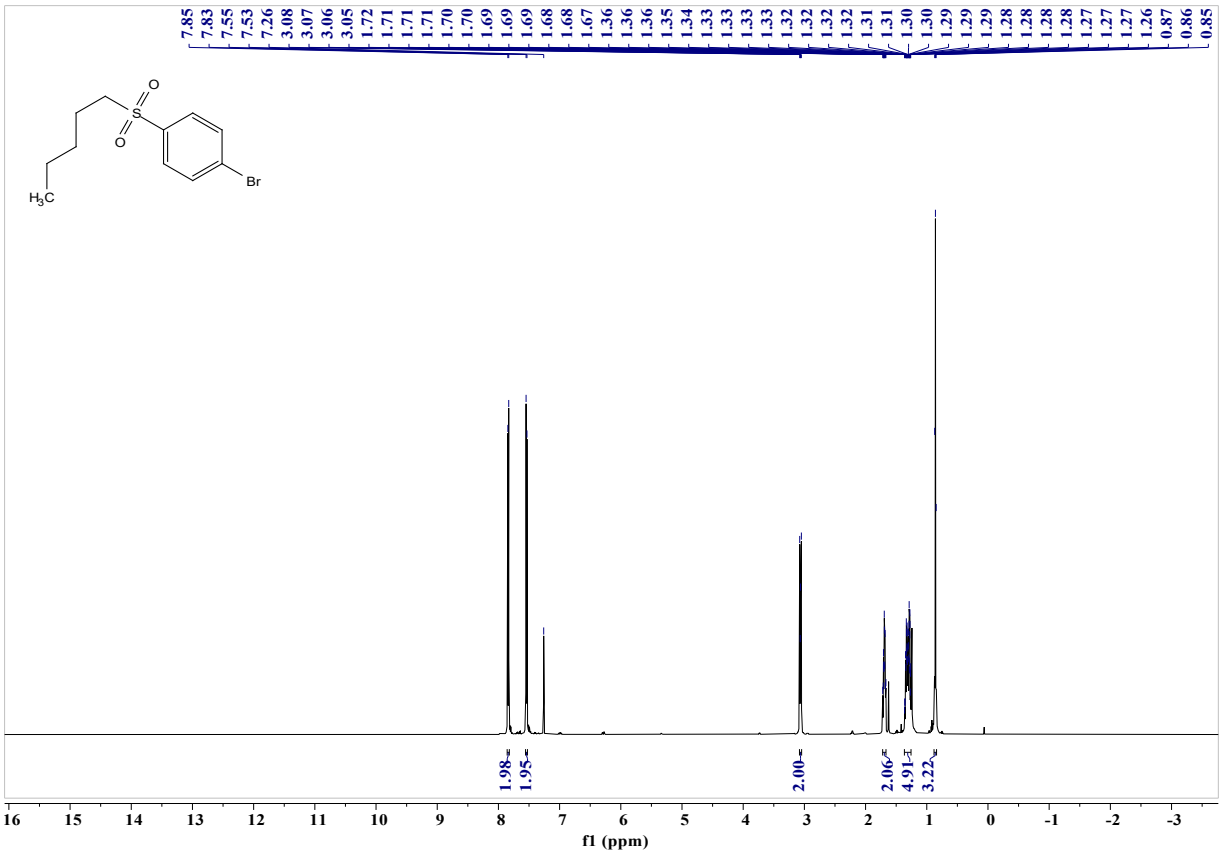
Compound 3at, ^{1}H NMR (600 MHz, Chloroform-d)



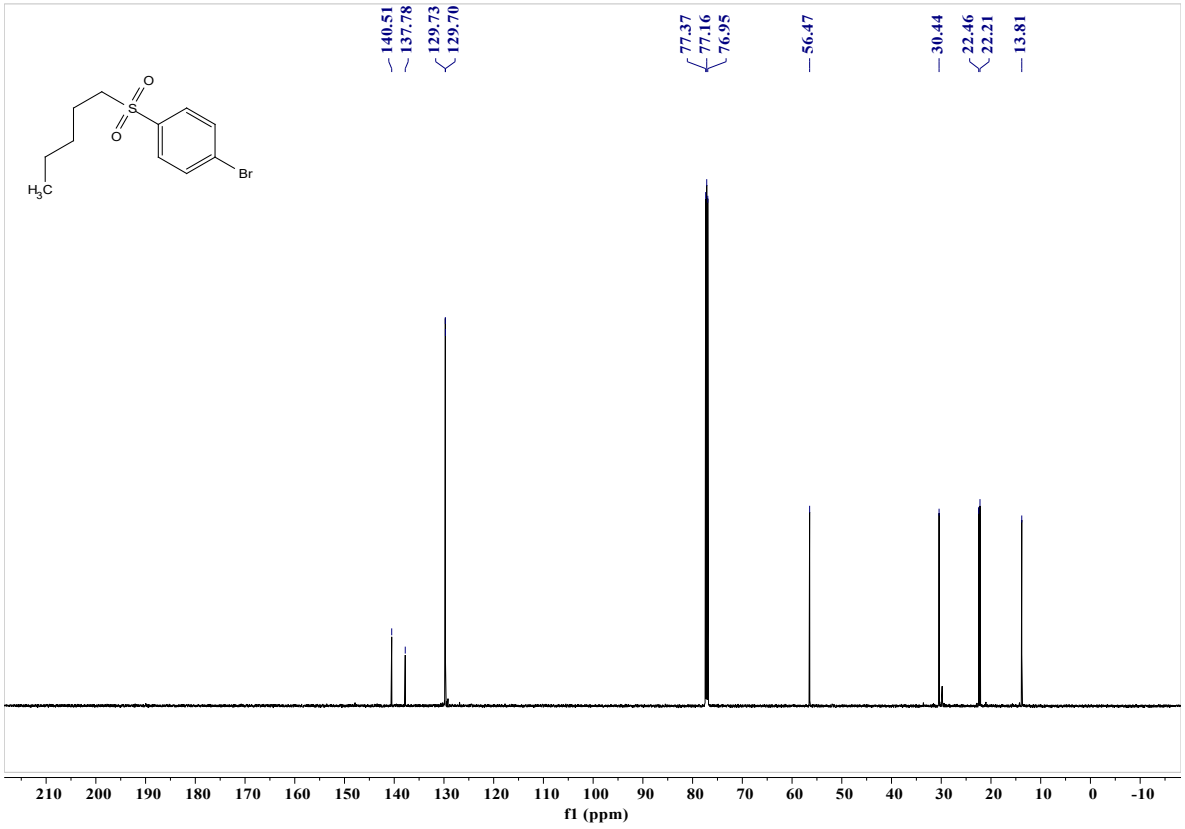
Compound 3at, ^{13}C NMR (151 MHz, Chloroform-d)



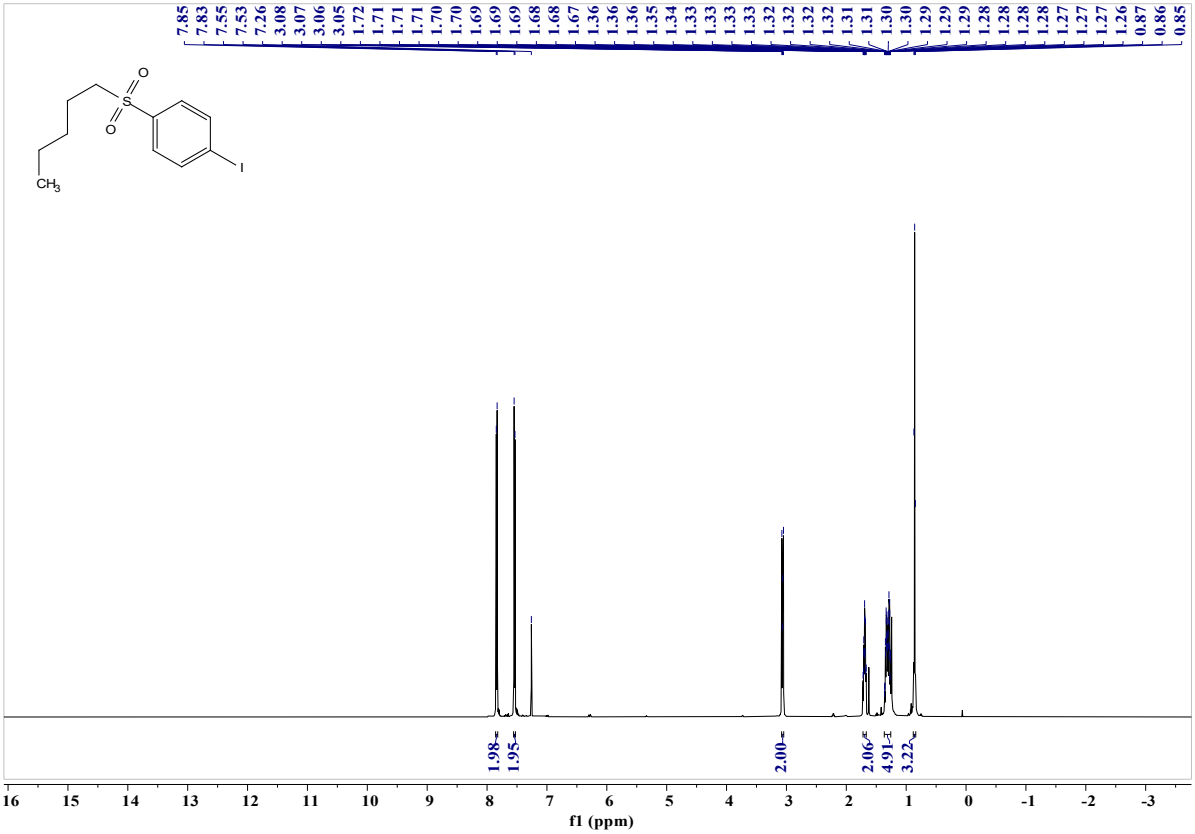
Compound 3au, ^{1}H NMR (60 MHz, Chloroform-d)



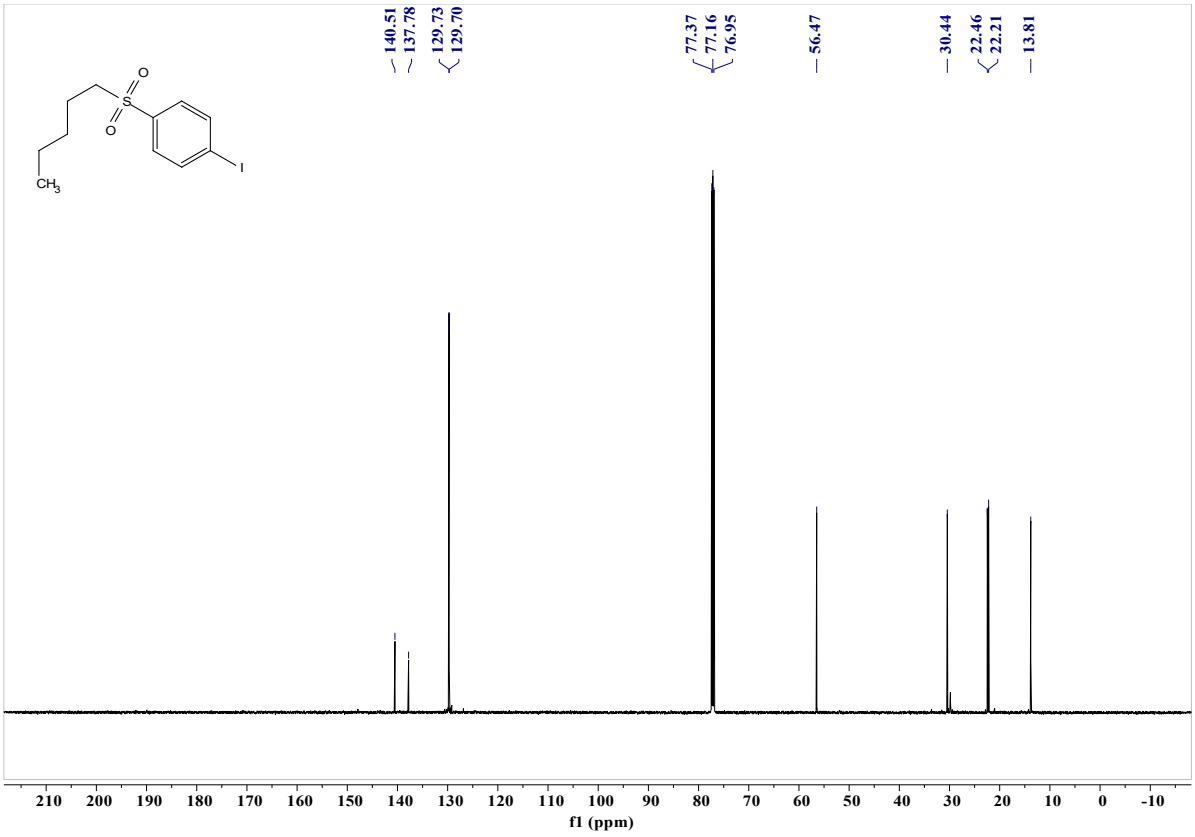
Compound 3au, ^{13}C NMR (151 MHz, Chloroform-d)

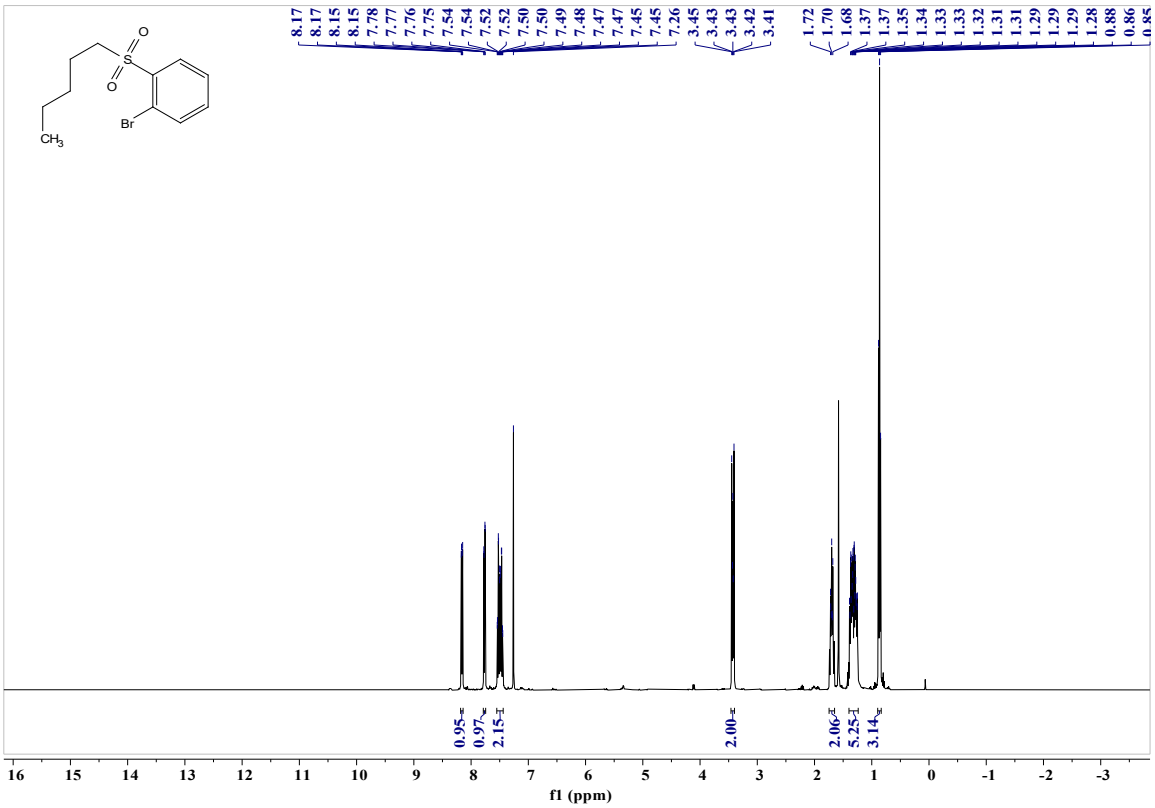


Compound 3av, ^{1}H NMR (600 MHz, Chloroform-d)



Compound 3av, ^{13}C NMR (151 MHz, Chloroform-d)

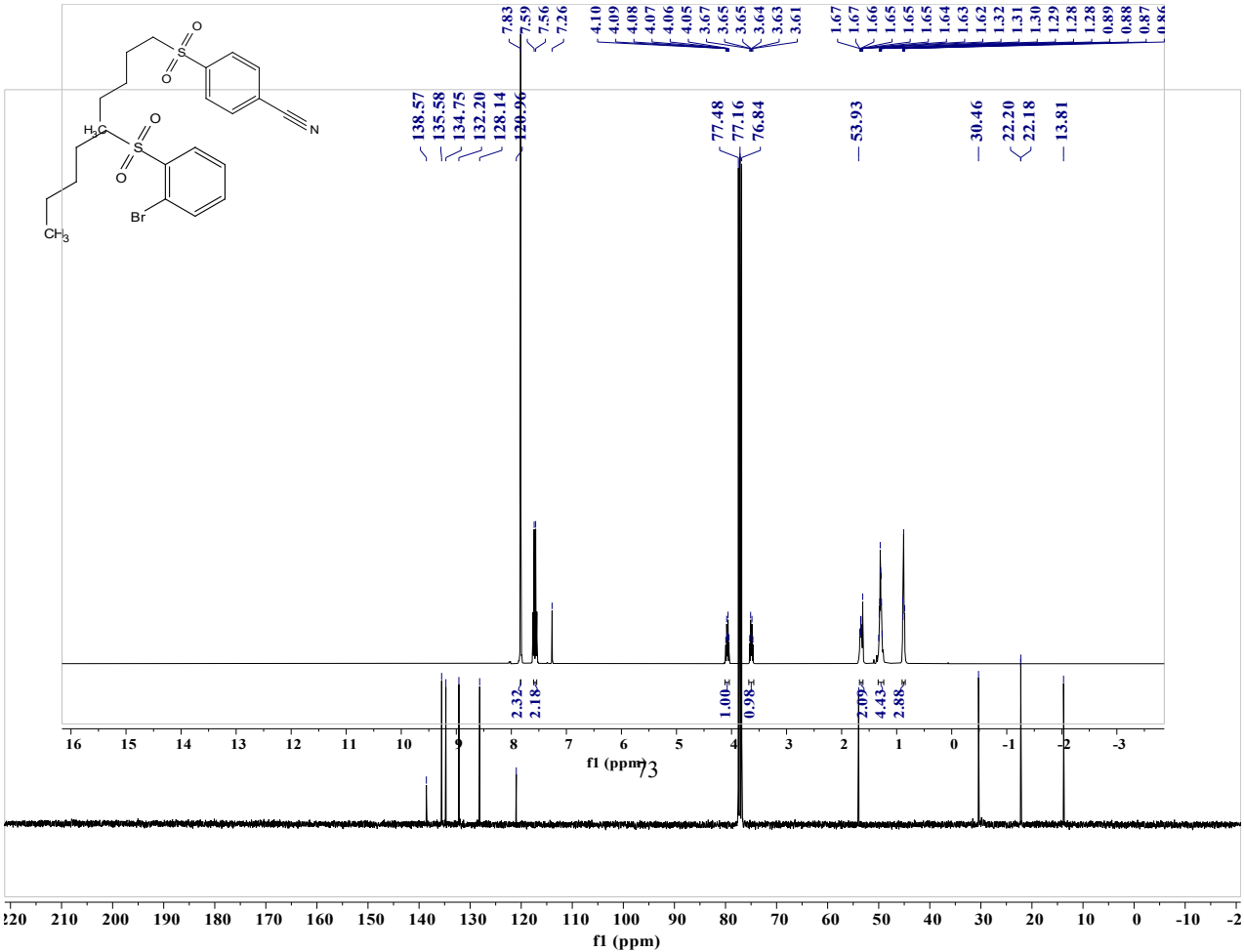




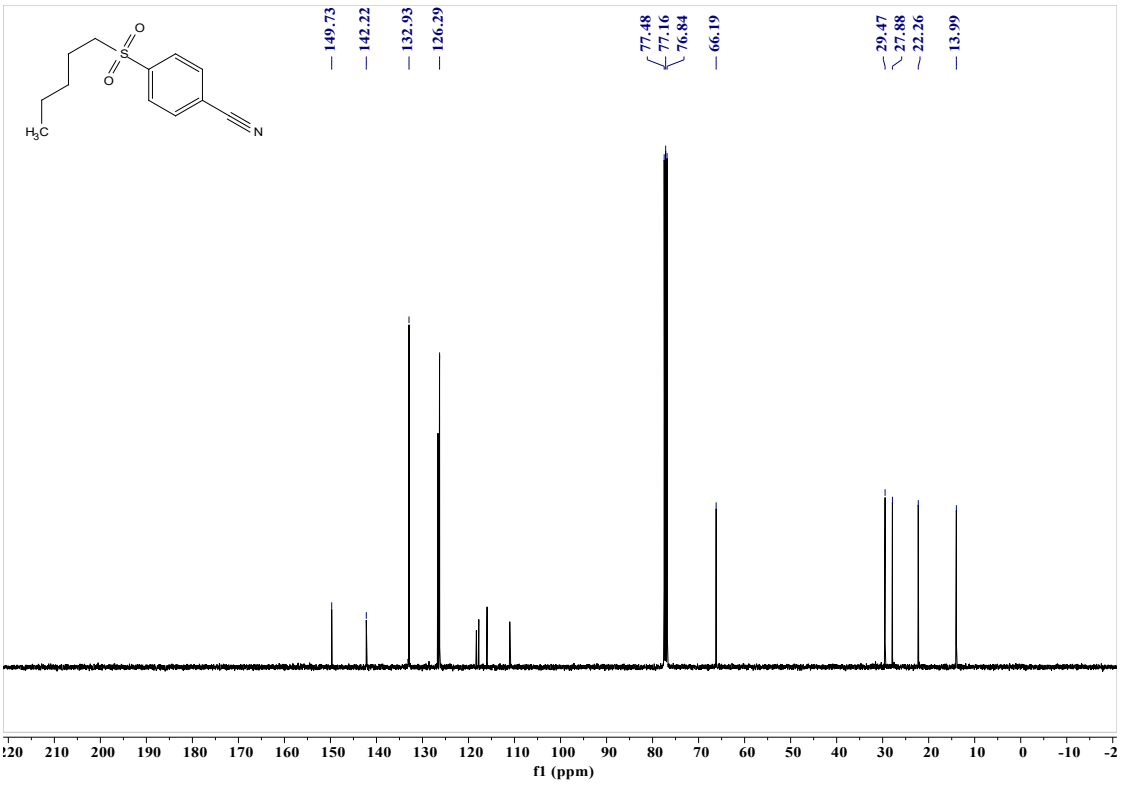
Compound 3aw, ^{1}H NMR (400 MHz, Chloroform-d)

Compound 3aw, ^{13}C NMR (101 MHz, Chloroform-d)

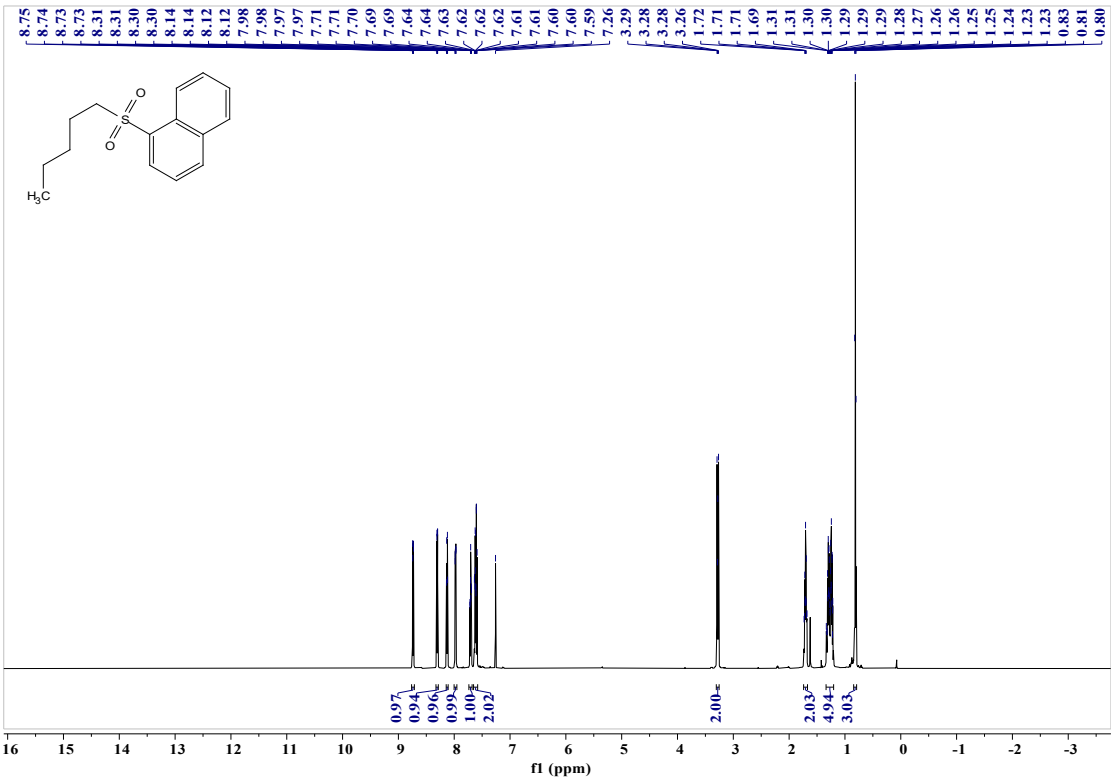
Compound 3ax, ^{1}H NMR (400 MHz, Chloroform-d)



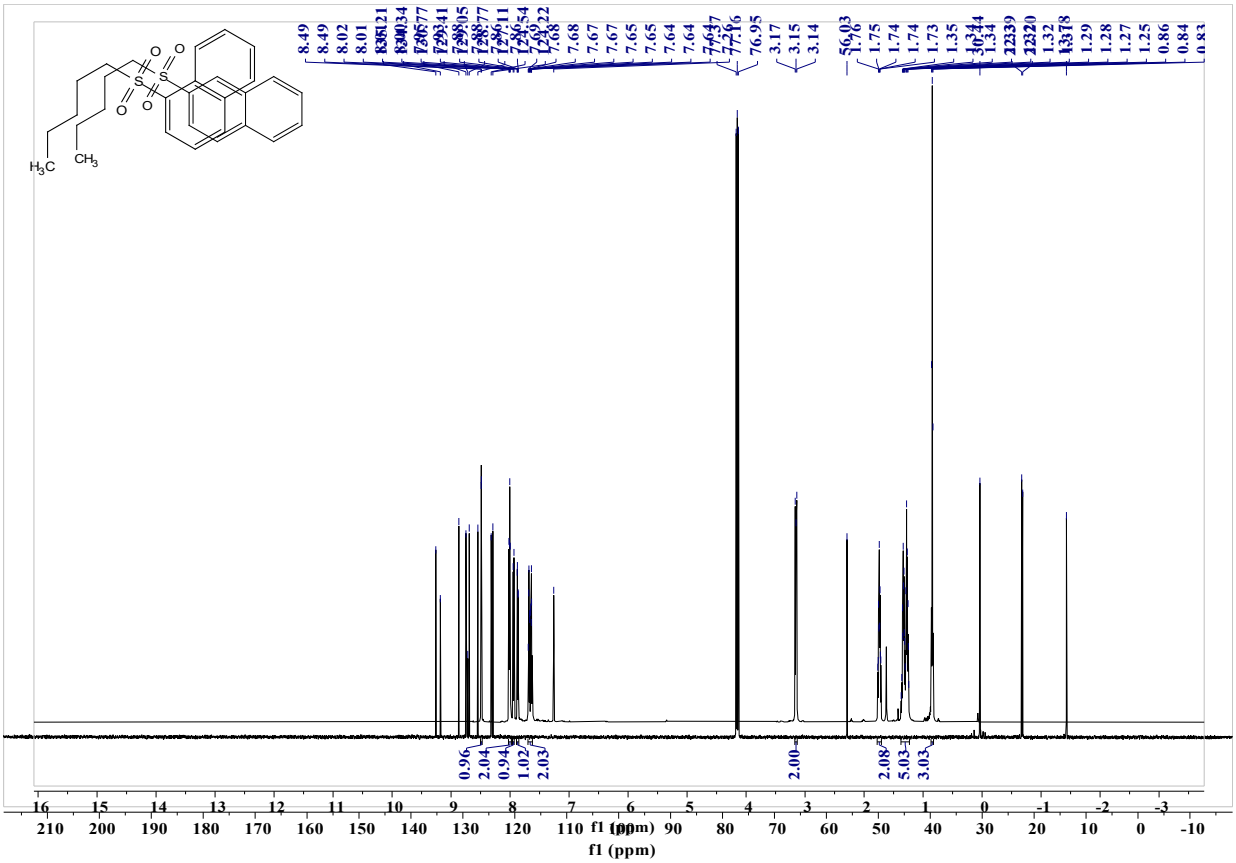
Compound 3ax, ^{13}C NMR (101 MHz, Chloroform-d)



Compound 3az, ^{1}H NMR (600 MHz, Chloroform-d)



Compound 3az, ^{13}C NMR (151 MHz, Chloroform-d)



Compound 3ba, ^{1}H NMR (600 MHz, Chloroform-d)

Compound 3ba, ^{13}C NMR (151 MHz, Chloroform-d)