Catalytic Three-Component Carboamination of Unactivated Alkenes with Primary Sulfonamides

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SUPPORTING INFORMATION

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1. General Experimental

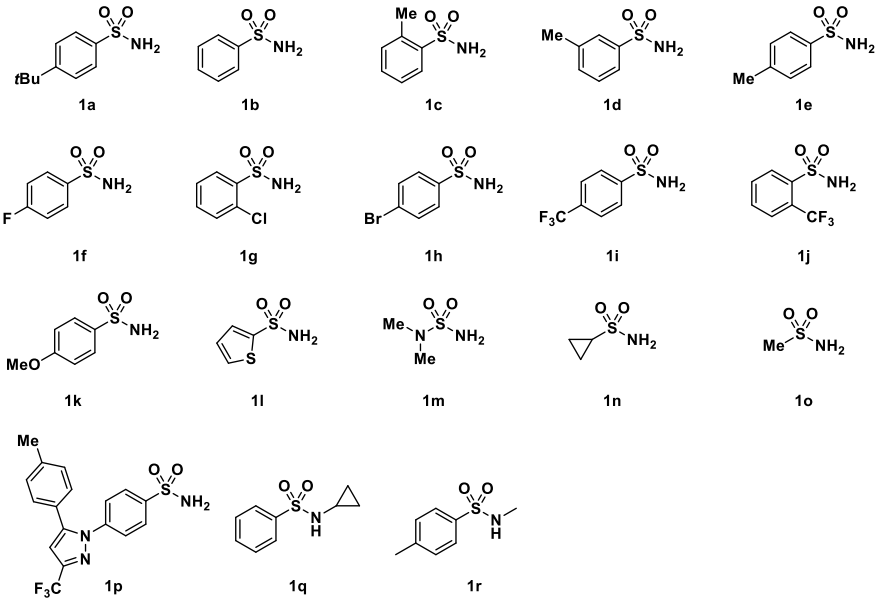
All experiments were performed in oven-dried glassware under nitrogen unless otherwise stated. All reagents were purchased from Alfa Aesar, Adamas-beta®, Accela, Bidepharm, Energy chemical, J&K chemical, Macklin, TCI and used without further purification, unless otherwise stated. Dry solvents were purchased from J&k chemical (Extra Dry, H_2O < 10 ppm) in J&KSeal® bottles, stored under molecular sieves and used as received or obtained from commercial sources. Dichloromethane, toluene, diethyl ether, THF were purified by passage through an activated alumina column under argon. Thin-layer chromatography (TLC) analysis of reaction mixtures were performed using Huanghai silica gel HSGF254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or potassium permanganate.

1.1 Analysis

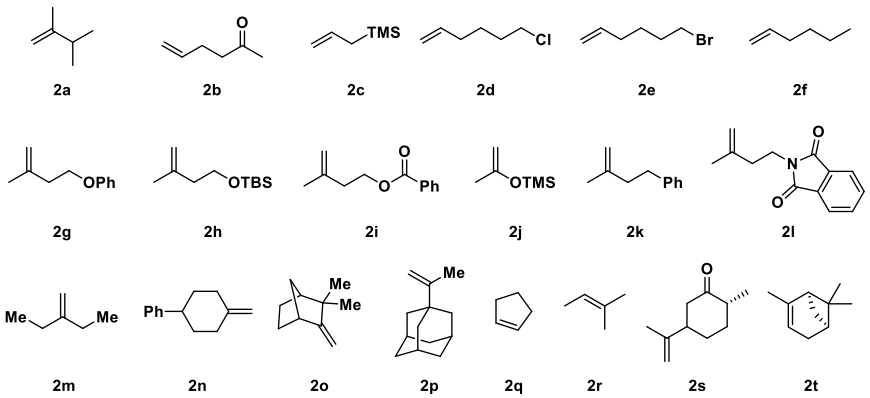
Nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance III HD spectrometer (FT, 400 MHz or 500 MHz for ^1H, 101 MHz or 126 MHz for ^{13}C). All spectral data were acquired at 295 K. Chemicals shifts (δ) are quoted in parts per million (ppm) against tetramethylsilane (TMS, δ = 0.00 ppm). The following residual solvent signals were used as references for ^1H and ^{13}C NMR spectra: $CDCl_3$, δ_H 7.26 ppm, δ_C 77.16 ppm; CD_2Cl_2, δ_H 5.32 ppm, δ_C 54.00 ppm; DMSO-d_6, δ_H 2.50 ppm, δ_C 39.52 ppm; C_6D_6, δ_H 7.16 ppm, δ_C 128.06 ppm; D_2O, δ_H 4.79 ppm, δ_C calibrated using absolute referencing to the ^1H spectrum). ^{19}F NMR spectra were calibrated using absolute referencing to the ^1H NMR spectrum, as suggested by IUPAC. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used (or combinations thereof) are: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet. High-resolution mass spectra (HRMS) were obtained from the Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI^+)/atmospheric pressure chemical ionization (APCI) mode. Ultraviolet-visible (UV-vis) absorption spectra were recorded by an AgilentCary 3000 UV-vis spectrophotometer at 25 °C. Stern-Volmer luminescence quenching analyses were conducted using an Edinburgh Instruments FS5 spectrometer.

2. Preparation of Starting Materials

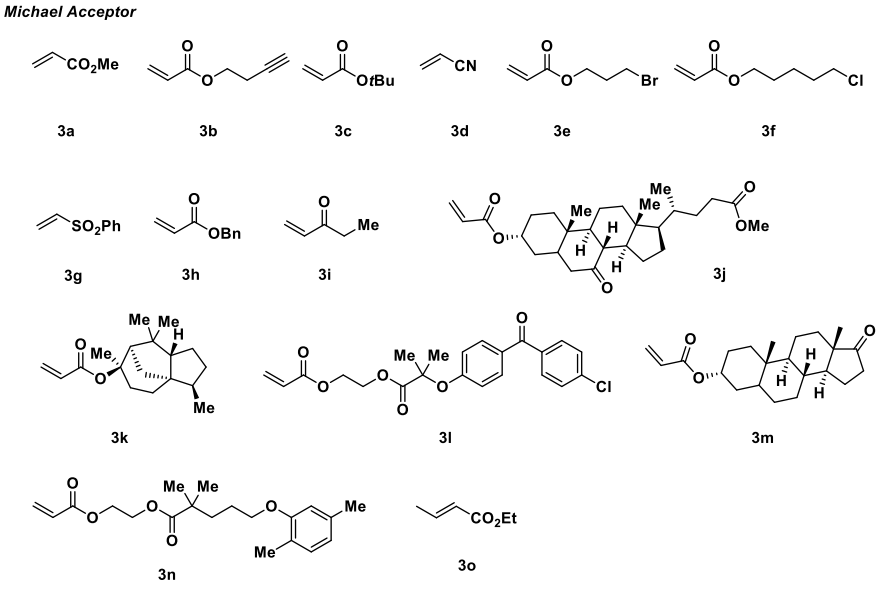
Sulfonamide Scope



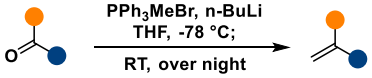
Olefin Scope



Alkene **2g**, **2h**, **2i**, **2k**, **2l**, **2n**, **2p**, Michael Acceptor **3b**, **3e**, **3f, 3j, 3k, 3l, 3m, 3n** were prepared following literature procedures[1–5]. Other reagents were purchased from Alfa Aesar, Adamas-beta®, Accela, Bidepharm, Energy chemical, J&K chemical, Macklin, TCI and used directly without further purification.

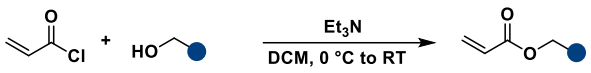


2.1 General Procedure A: Preparation of substituted alkenes



To an oven-dried Schlenk tube equipped with a stir bar was added PPh_3MeBr (1.60 equiv.). The flask was evacuated and back filled with N_2(g) and dry THF (0.1 M) was added. The resultant mixture was cooled to -78 °C to which a solution of *n*BuLi in hexanes (2.5 M, 1.55 equiv.) was added. The solution was allowed to warm to RT and stirred for 30 mins before ketone substrate was added (1.0 equiv.). The reaction was allowed to stir at RT for 18 h before being diluted with hexane and quenched with H_2O. The aqueous layer was separated and washed with PE. The organic layers were combined, dried (Na_2SO_4), filtered and concentrated in vacuo. The resultant crude alkenes were purified via column chromatography.

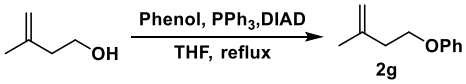
2.2 General Procedure B: Preparation of Michael Acceptor



To a stirred solution of alcohol substrate (1 equiv.) and triethylamine (1.2 equiv.) in 30 mL of dry DCM a solution of acryloyl chloride (1.2 equiv.) was added dropwise at 0°C. After complete addition, the mixture was allowed to warm to RT and stirred overnight. The mixture was washed with water, dilute hydrochloric acid, saturated aqueous

sodium bicarbonate solution and brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The resultant crude Michael acceptor were purified via column chromatography.

2.3 Synthesis Procedure and Characterization of The Starting Materials



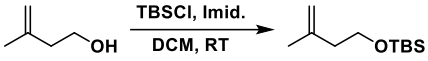
2g

((3-Methylbut-3-en-1-yl)oxy)benzene (2g): A solution of phenol (2.6 mL, 30 mmol, 3 equiv.), 3-methyl-3-buten-1-ol (1 mL, 10 mmol, 1 equiv.), triphenylphosphine (3.4 g, 13 mmol, 1.3 equiv.), diisopropyl azo-dicarboxylate (2.6 mL, 13 mmol) in THF (50 mL) for 1.5 hours at reflux. After concentrated in vacuo, the residue was purified by column chromatography (PE: DCM = 4: 1) to give **2g** (848.8 mg, 52%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 2H), 6.99 – 6.91 (m, 3H), 4.85 (d, *J* = 16.3 Hz, 2H), 4.10 (t, *J* = 6.9 Hz, 2H), 2.53 (t, *J* = 6.9 Hz, 2H), 1.84 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 142.3, 129.5 (2×C), 120.7, 114.6 (2×C), 112.0, 66.4, 37.3, 22.9 ppm;

HRMS (ESI) calcd. for $C_{11}H_{15}O^+$ ($M+H^+$): 163.1117. Found: 163.1121.



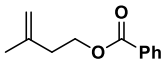
2h

***Tert*-butyldimethyl((3-methylbut-3-en-1-yl)oxy)silane (2h):** To a solution of 3-methylbut-3-en-1-ol (1.8 mL, 17.4 mmol, 1 equiv.) and imidazole (2.37g, 34.8 mmol, 2.0 equiv.) in dry DCM (35 mL) was added TBSCl (3.28g, 21.75 mmol, 1.25 equiv.) and the resulting mixture was stirred at RT for 18 h. The resultant mixture was diluted with DCM (30 mL) and H_2O (30 mL) was added. The mixture was extracted with DCM (3×50 mL) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The resultant oil was purified via column chromatography (PE: EA = 4: 1) to yield the **2h** as a colorless oil (1.82 g, 52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.72 – 4.62 (m, 2H), 3.66 (t, *J* = 7.1 Hz, 2H), 2.19 (td, *J* = 7.1, 1.2 Hz, 2H), 1.68 (t, *J* = 1.2 Hz, 3H), 0.84 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.1, 111.5, 62.2, 41.1, 26.0 (3×C), 22.9, 18.3, -5.3 (2×C) ppm;

HRMS (ESI) calcd. for $C_{11}H_{25}OSi^+$ ($M+H^+$): 201.1669. Found: 201.1670.



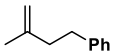
2i

3-Methylbut-3-en-1-yl benzoate (2i): **2i** was synthesized following **General procedure B** and purified by column chromatography on silica gel (PE: EA = 95: 5) to give **2i** (915.7 mg, 48%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 – 8.00 (m, 2H), 7.57 – 7.51 (m, 1H), 7.43 (dd, *J* = 8.4, 7.0 Hz, 2H), 4.87 – 4.79 (m, 2H), 4.44 (t, *J* = 6.8 Hz, 2H), 2.48 (td, *J* = 6.8, 1.2 Hz, 2H), 1.81 (d, *J* = 1.2 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 141.7, 132.9, 130.4, 129.6 (2×C), 128.4 (2×C), 112.5, 63.2, 36.8, 22.6 ppm;

HRMS (ESI) calcd. for $C_{12}H_{15}O_2^+$ ($M+H^+$): 191.1067. Found: 191.1064.



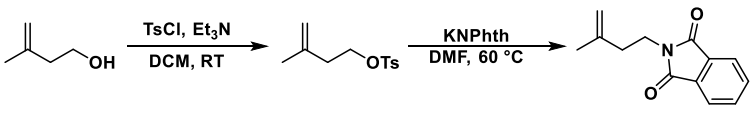
2k

(3-Methylbut-3-en-1-yl)benzene (2k): 2k was synthesized following **General procedure A** and purified by column chromatography on silica gel (PE) to give **2k** as a colorless oil (856.7 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 4.78 – 4.69 (m, 2H), 2.77 (tdd, *J* = 8.3, 5.0, 2.9 Hz, 2H), 2.33 (tt, *J* = 8.0, 3.8 Hz, 2H), 1.78 (t, *J* = 3.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.4, 142.3, 128.4 (2×C), 128.3 (2×C), 125.8, 110.2, 39.7, 34.3, 22.7 ppm;

HRMS (ESI) calcd. for $C_{11}H_{15}^+$ ($M+H^+$): 147.1168. Found: 147.1164.



2l

2-(3-Methylbut-3-en-1-yl) isoindoline-1,3-dione (2l): To a solution of 3-methylbut-3-en-1-ol (1 mL, 10 mmol, 1 equiv.), Et_3N (1.7 mL, 12 mmol, 1.2 equiv.) in dry DCM (20 mL) was added TsCl (2.1 g, 11 mmol, 1.10 equiv.) and the resulting mixture stirred at RT for 18 h. The reaction mixture was quenched with saturated $NaHCO_3$ (30 mL) and extracted with DCM

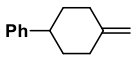
(3×30 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated in vacuo to yield a colorless oil which was purified via column chromatography (PE: EA = 9: 1) to yield 3-methylbut-3-en1-yl 4-methylbenzene-sulfonate as a colorless oil.

A 100 mL round bottom flask was charged with 3-methylbut-3-en1-yl 4-methylbenzenesulfonate (1 equiv.), potassium 1,3-dioxoiso-indolin-2-ide (1.1 equiv.) and dry DMF (60 mL). The resulting reaction mixture was heated to 60 ℃ for 24 h and then quenched with H_2O. The organic layer was separated and washed with H_2O and brine before being dried over Na_2SO_4, filtered and then concentrated in vacuo. The resultant oil was purified via column chromatography (PE: EA = 9: 1) to yield **2l** as white solid (1.5 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.71 (ddd, *J* = 25.9, 2.7, 1.4 Hz, 2H), 3.83 (t, *J* = 7.2 Hz, 2H), 2.45 – 2.36 (m, 2H), 1.82 (d, *J* = 1.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 142.2, 133.9 (2×C), 132.1, 123.2 (2×C), 112.8, 36.5, 36.4, 22.1 ppm;

HRMS (ESI) calcd. for $C_{13}H_{14}NO_2^+$ ($M+H^+$): 216.1019. Found: 216.1014.



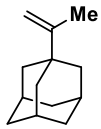
2n

(4-Methylenecyclohexyl)benzene (2n): **2n** was synthesized following **General procedure A** and purified by column chromatography on silica gel (PE: EA= 9: 1) to give **2n** as a colorless oil (826 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 4.68 (q, *J* = 1.7 Hz, 2H), 2.66 (ddt, *J* = 15.6, 12.1, 3.3 Hz, 1H), 2.42 (ddd, *J* = 13.3, 4.0, 2.0 Hz, 2H), 2.24 – 2.12 (m, 2H), 2.03 – 1.93 (m, 2H), 1.63 – 1.46 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.9, 146.9, 128.4 (2×C), 126.9 (2×C), 126.1, 107.5, 44.2, 35.6, 35.2 ppm;

HRMS (ESI) calcd. for $C_{13}H_{17}^+$ ($M+H^+$): 173.1325. Found: 173.1320.



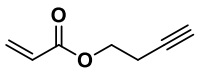
2p

1-(Prop-1-en-2-yl)adamantine (2p): **2p** was synthesized following **General procedure A** and purified by column chromatography on silica gel (PE: EA = 9: 1) to give **2p** as a colorless oil (939.1 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.67 (dt, *J* = 3.4, 1.8 Hz, 2H), 2.03 – 1.97 (m, 3H), 1.75 – 1.63 (m, 15H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 107.4, 41.0 (3×C), 37.4, 37.0 (3×C), 28.7 (3×C), 18.5 ppm;

HRMS (ESI) calcd. for $C_{13}H_{21}^+$ ($M+H^+$): 177.1638. Found: 177.1633.



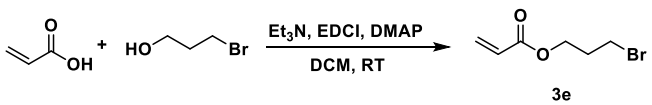
3b

But-3-yn-1-yl acrylate (3b): **3b** was synthesized following **General procedure B** and purified by column chromatography on silica gel (PE: EA = 25: 1) to give **3b** as a colorless oil (566.3 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (dt, *J* = 17.4, 1.3 Hz, 1H), 6.15 (ddd, *J* = 17.3, 10.4, 1.1 Hz, 1H), 5.87 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.28 (td, *J* = 6.8, 1.2 Hz, 2H), 2.58 (tdd, *J* = 6.8, 2.6, 1.1 Hz, 2H), 2.03 (d, *J* = 5.4 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.3, 128.1, 80.0, 70.0, 62.2, 18.9 ppm;

HRMS (ESI) calcd. for $C_7H_9O_2^+$ ($M+H^+$): 125.0597. Found: 125.0593.



3e

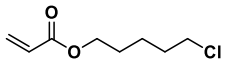
3-Bromopropyl acrylate (3e): To a solution of acrylic acid (685.6 µL, 10 mmol, 1 equiv.), hydroxyl substrate (1.35 mL, 15 mmol, 1.5 equiv.), DMAP (122.17 mg, 1 mmol, 0.1 equiv.), 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDCI, 2.88 g, 15 mmol, 1.5 equiv.) and Et_3N (4.17 mL, 30 mmol, 3 equiv.) in DCM (20 mL). The reaction mixture was

stirred at RT over night. Then the reaction was quenched with H_2O (10 mL) and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated and purified by flash chromatography (PE: EA = 25: 1) to afford the desired product **3e** (609.6 mg, 32%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42 (dt, *J* = 17.4, 1.4 Hz, 1H), 6.13 (ddd, *J* = 17.4, 10.4, 1.2 Hz, 1H), 5.86 (dt, *J* = 10.4, 1.3 Hz, 1H), 4.31 (td, *J* = 6.0, 1.3 Hz, 2H), 3.49 (td, *J* = 6.5, 1.1 Hz, 2H), 2.23 (pd, *J* = 6.3, 1.2 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 131.1, 128.2, 62.2, 31.7, 29.4 ppm;

HRMS (ESI) calcd. for $C_6H_{10}BrO_2^+$ ($M+H^+$): 192.9859. Found: 192.9855.



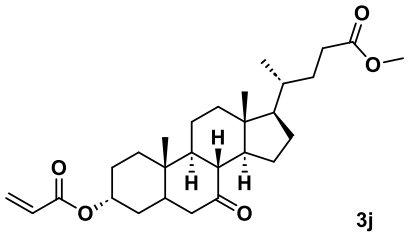
3f

5-Chloropentyl acrylate (3f): **3f** was synthesized following **General procedure B** and purified by column chromatography on silica gel (PE: EA = 25: 1) to give **3f** as a colorless oil (661.9 mg, 37%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.41 (dq, *J* = 17.4, 1.2 Hz, 1H), 6.12 (ddd, *J* = 17.3, 10.5, 1.4 Hz, 1H), 5.83 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.17 (td, *J* = 6.6, 1.5 Hz, 2H), 3.55 (td, *J* = 6.6, 1.5 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.76 – 1.67 (m, 2H), 1.59 – 1.50 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 130.7, 128.5, 64.3, 44.8, 32.1, 27.9, 23.4 ppm;

HRMS (ESI) calcd. for $C_8H_{14}ClO_2^+$ ($M+H^+$): 177.0677. Found: 177.0673.



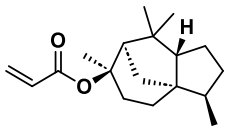
3j

Methyl (4*R*)-4-((3*R*, 8*R*, 9*S*, 10*S*, 13*R*, 14*S*, 17*R*)-3-(acryloyloxy)-10,13-dimethyl-7-oxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl) pentanoate (3j): **3j** was synthesized following **General procedure B** in the scale of 3 mmol and purified by column chromatography on silica gel (PE/EA = 50:1) to give **3j** as a colorless oil (421.9 mg, 31%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.03 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.78 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.75 (tt, *J* = 11.3, 4.8 Hz, 1H), 3.64 (s, 3H), 2.85 (dd, *J* = 12.6, 6.1 Hz, 1H), 2.43 – 2.30 (m, 2H), 2.19 (ddt, *J* = 13.2, 9.7, 6.8 Hz, 2H), 2.01 – 1.85 (m, 5H), 1.84 – 1.72 (m, 5H), 1.49 – 1.31 (m, 7H), 1.30 – 1.23 (m, 2H), 1.20 (s, 3H), 1.17 – 1.04 (m, 2H), 0.90 (d, *J* = 6.3 Hz, 3H), 0.63 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 211.9, 174.7, 165.6, 130.6, 128.8, 73.1, 54.8, 51.5, 49.5, 48.9, 45.9, 45.3, 42.8, 42.6, 38.9, 35.2, 35.2, 33.8, 33.1, 31.0, 31.0, 28.3, 26.0, 24.8, 23.0, 21.7, 18.4, 12.1 ppm;

HRMS (ESI) calcd. for $C_{28}H_{43}O_5^+$ ($M+H^+$): 459.3105. Found: 459.3100.



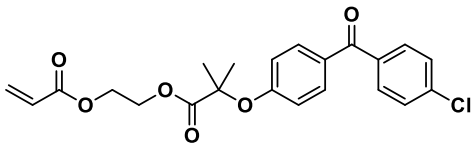
3k

(3*R*, 3a*S*, 6*R*, 7*R*, 8a*S*)-3, 6, 8, 8-Tetramethyloctahydro-1*H*-3a, 7-methanoazulen-6-yl acrylate (3k): **3k** was synthesized following **General procedure B** in the scale of 20 mmol and purified by column chromatography on silica gel (PE/EA = 100:1) to give **3k** as a colorless oil (2.29 g, 41%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.22 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.96 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.65 (dd, *J* = 10.4, 1.6 Hz, 1H), 2.43 – 2.34 (m, 1H), 2.06 – 1.87 (m, 2H), 1.87 – 1.69 (m, 2H), 1.60 (ddd, *J* = 12.6, 6.4, 4.2 Hz, 2H), 1.52 (d, *J* = 1.0 Hz, 3H), 1.45 (ddd, *J* = 12.1, 8.6, 6.1 Hz, 1H), 1.41 – 1.37 (m, 1H), 1.35 – 1.28 (m, 2H), 1.26 – 1.17 (m, 2H), 1.07 (s, 3H), 0.91 (s, 3H), 0.77 (d, *J* = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 130.6, 129.3, 86.7, 56.8, 56.7, 54.0, 43.4, 41.3, 41.0, 37.0, 33.2, 31.2, 28.5, 27.1, 25.9, 25.3, 15.5 ppm;

HRMS (ESI) calcd. for $C_{18}H_{29}O_2^+$ ($M+H^+$): 277.2162. Found: 277.2160.

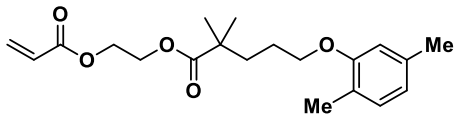


3l

2-((2-(4-(4-Chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)ethyl acrylate (3l): 3l was synthesized following **General procedure B** in the scale of 2 mmol and purified by column chromatography on silica gel (PE/EA = 5:1) to give **3l** as a colorless oil (323.3 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (t, J = 8.5 Hz, 4H), 7.42 – 7.35 (m, 2H), 6.83 – 6.76 (m, 2H), 6.25 (dd, J = 17.3, 1.4 Hz, 1H), 5.93 (dd, J = 17.3, 10.4 Hz, 1H), 5.72 (dd, J = 10.4, 1.4 Hz, 1H), 4.40 – 4.33 (m, 2H), 4.27 (dd, J = 5.8, 3.4 Hz, 2H), 1.61 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.2, 173.5, 165.7, 159.5, 138.4, 136.3, 132.1 (2×C), 131.6, 131.2 (2×C), 130.4, 128.6 (2×C), 127.7, 117.3 (2×C), 79.3, 63.2, 61.9, 25.4 (2×C) ppm;



3o

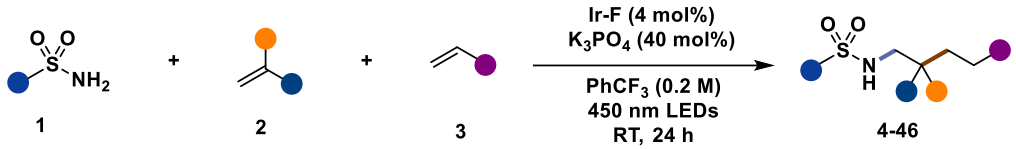
2-((2-(4-(4-Chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)ethyl acrylate (3o): **3o** was synthesized following **General procedure B** in the scale of 20 mmol and purified by column chromatography on silica gel (PE/EA = 100:1) to give **3o** as a colorless oil (2.29 g, 41%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, *J* = 7.4 Hz, 1H), 6.66 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.62 – 6.59 (m, 1H), 6.41 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.11 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.42 – 4.36 (m, 2H), 4.35 – 4.29 (m, 2H), 3.95 – 3.87 (m, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 1.76 – 1.70 (m, 4H), 1.23 (s, 6H).

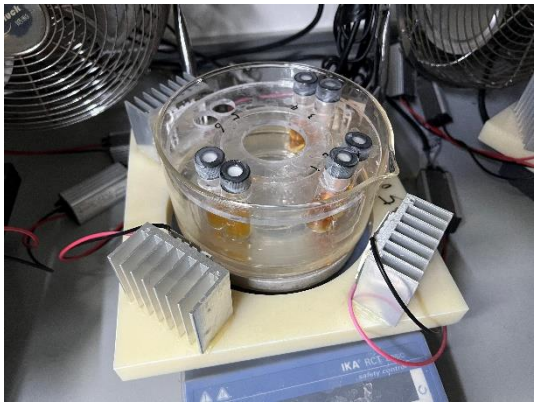
^{13}C NMR (101 MHz, $CDCl_3$): δ 177.6, 165.9, 156.9, 136.5, 131.4, 130.3, 128.0, 123.5, 120.7, 111.9, 67.9, 62.2, 62.0, 42.2, 37.0, 25.2 (2×C), 21.4, 15.8 ppm.

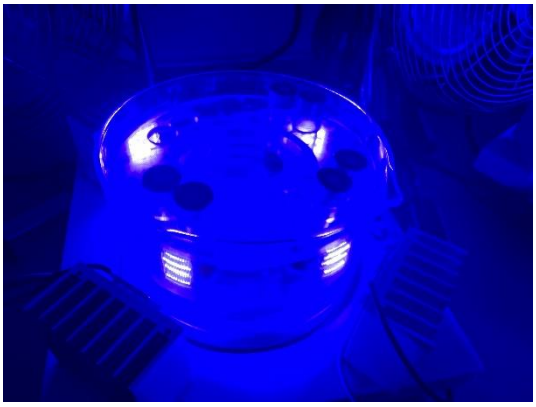
3. Catalytic Intermolecular Three-Component Carboamination of Unactivated Alkenes with Primary Sulfonamides

3.1 General Procedure C

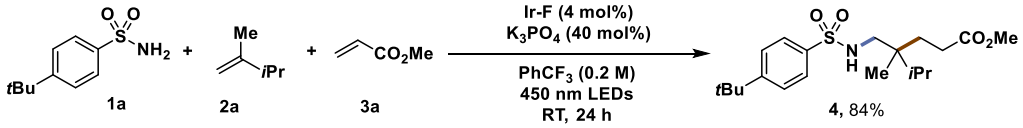


An 8-mL vial was charged with a Teflon® septum, sulfonamide (0.2 mmol, 1.0 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.), then the vial was sealed with a poly-tetrafluoroethylene-lined cap. After the vial was vacuumed and refilled with N_2 for three times, $PhCF_3$ (1 ml), olefin (0.4 mmol, 2 equiv.) and Michael acceptor (0.4 mmol, 2 equiv.) was added, then irradiated with a 30 W blue LED lamp (450 nm, at approximately 3 cm away from the light source) at room temperature. After 24 h, the reaction mixture was transferred to a 100mL round-bottom bottle and concentrated *in vacuo*. Purification by column chromatography on silica gel (PE: EA = 5:1) provided the desired product.





3.2 Characterization of The Products



1a 2a 3a 4, 84%

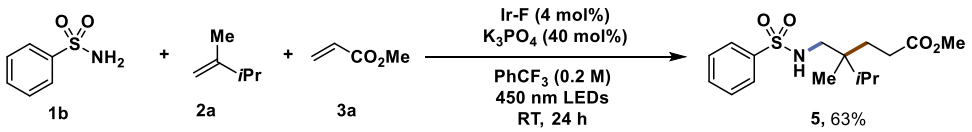
Methyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (4):

According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a**(0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f= 0.4) as a yellow oil (68.2 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.73 (m, 2H), 7.56 – 7.47 (m, 3H), 4.79 (t, *J* = 7.0 Hz, 1H), 3.59 (s, 3H), 2.74 – 2.62 (m, 2H), 2.19 (t, *J* = 7.9 Hz, 2H), 1.71 – 1.66 (m, 1H), 1.63 – 1.54 (m, 2H), 1.34 (s, 9H), 0.80 (t, *J* = 6.4 Hz, 6H), 0.73 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 156.3, 136.7, 126.9 (2×C), 126.1 (2×C), 51.8, 48.3, 38.1, 35.1, 32.0, 31.1 (3×C), 29.6, 28.2, 18.2, 16.99, 16.95 ppm;

HRMS (ESI) calcd. for $C_{20}H_{34}NO_4S^+$ ($M+H^+$):384.2203. Found: 384.2191.

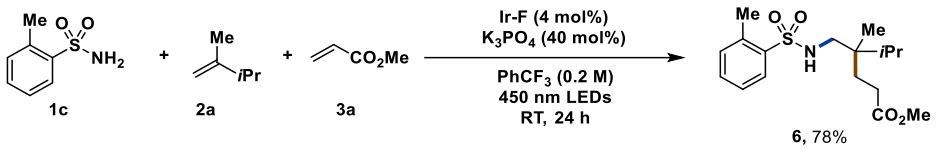


Methyl 4,5-dimethyl-4-(phenylsulfonamidomethyl)hexanoate (5): According to the General procedure C, benzenesulfonamide **1b** (0.2 mmol, 31.4 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a**(0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.21) as a yellow oil (41.5 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.85 (m, 2H), 7.62 – 7.48 (m, 3H), 5.10 (t, *J* = 6.9 Hz, 1H), 3.61 (s, 3H), 2.75 – 2.62 (m, 2H), 2.20 (t, *J* = 7.9 Hz, 2H), 1.72 – 1.53 (m, 3H), 0.83 – 0.77 (m, 6H), 0.73 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 139.7, 132.6, 129.1 (2×C), 127.1 (2×C), 51.8, 48.4, 38.1, 32.0, 29.6, 28.2, 18.2, 17.0, 16.9 ppm;

HRMS (ESI) calcd. for $C_{16}H_{26}NO_4S^+$ ($M+H^+$):328.1577. Found: 328.1581.

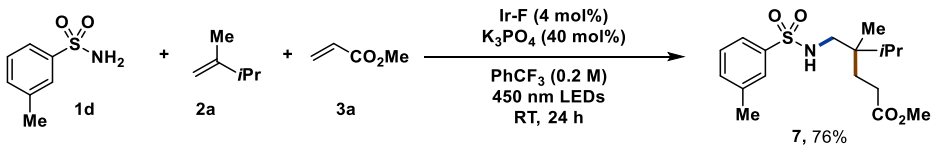


Methyl 4,5-dimethyl-4-(((2-methylphenyl)sulfonamido)methyl)hexanoate (6): According to the General procedure C, 2-methylbenzenesulfonamide **1c** (0.2 mmol, 34.2 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.20) as a yellow oil (57.4 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.45 (td, *J* = 7.4, 1.4 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 4.91 (t, *J* = 7.0 Hz, 1H), 3.64 (s, 3H), 2.77 – 2.60 (m, 5H), 2.15 (t, *J* = 7.9 Hz, 2H), 1.65 (dt, *J* = 14.4, 7.9 Hz, 1H), 1.59 – 1.49 (m, 2H), 0.78 (dd, *J* = 12.0, 6.8 Hz, 6H), 0.70 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 137.6, 137.1, 132.7, 132.6, 129.5, 126.1, 51.8, 48.2, 38.1, 31.9, 29.5, 28.1, 20.3, 18.1, 16.94, 16.91 ppm;

HRMS (ESI) calcd. for $C_{17}H_{28}NO_4S^+$ ($M+H^+$):342.1734. Found: 342.1726.

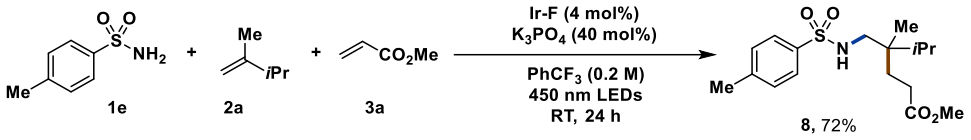


Methyl 4,5-dimethyl-4-(((2-methylphenyl)sulfonamido)methyl)hexanoate (7): According to the General procedure C, 3-methylbenzenesulfonamide **1d** (0.2 mmol, 34.2 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.20) as a yellow oil (55.9 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.60 (m, 2H), 7.42 – 7.32 (m, 2H), 5.10 (t, *J* = 6.8 Hz, 1H), 3.59 (s, 3H), 2.71 – 2.59 (m, 2H), 2.40 (s, 3H), 2.17 (t, *J* = 8.0 Hz, 2H), 1.64 (dt, *J* = 14.5, 8.0 Hz, 1H), 1.60 – 1.50 (m, 2H), 0.78 (t, *J* = 7.2 Hz, 6H), 0.71 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 139.6, 139.3, 133.4, 129.0, 127.4, 124.2, 51.8, 48.4, 38.1, 32.0, 29.6, 28.3, 21.4, 18.2, 17.02, 16.98 ppm;

HRMS (ESI) calcd. for $C_{17}H_{28}NO_4S^+$ ($M+H^+$):342.1734. Found: 342.1731.

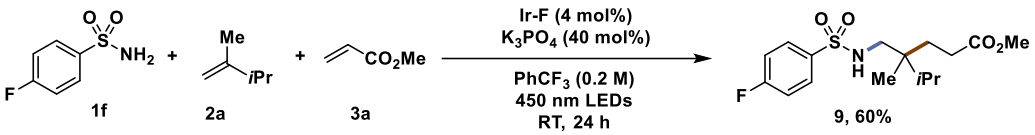


Methyl 4,5-dimethyl-4-(((4-methylphenyl)sulfonamido)methyl)hexanoate (8): According to the General procedure C, 4-methylbenzenesulfonamide **1e** (0.2 mmol, 34.2 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.20) as a yellow oil (49 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.68 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.12 – 5.01 (m, 1H), 3.62 (s, 3H), 2.73 – 2.59 (m, 2H), 2.43 (s, 3H), 2.19 (t, *J* = 8.0 Hz, 2H), 1.71 – 1.52 (m, 3H), 0.80 (dd, *J* = 8.6, 6.8 Hz, 6H), 0.72 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 143.3, 136.7, 129.7 (2×C), 127.1 (2×C), 51.8, 48.3, 38.0, 32.0, 29.6, 28.2, 21.5, 18.2, 17.0, 16.9 ppm;

HRMS (ESI) calcd. for $C_{17}H_{28}NO_4S^+$ ($M+H^+$): 342.1734. Found: 342.1726.



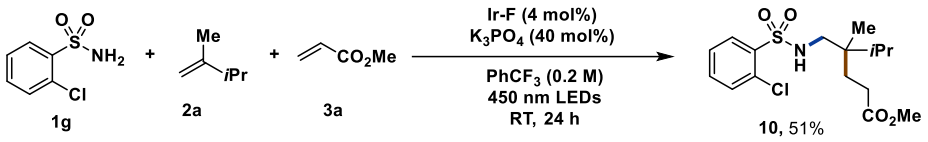
Methyl 4-(((4-fluorophenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (9): According to the General procedure C, 4-fluorobenzenesulfonamide **1f** (0.2 mmol, 35.0 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.30) as a yellow oil (42 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 – 7.85 (m, 2H), 7.21 – 7.15 (m, 2H), 5.16 (t, *J* = 6.9 Hz, 1H), 3.60 (s, 3H), 2.70 – 2.61 (m, 2H), 2.17 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 2H), 1.69 – 1.60 (m, 1H), 1.60 – 1.51 (m, 2H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.71 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.8, 164.98 (d, *J* = 254.4 Hz), 135.9, 129.80 (d, *J* = 9.1 Hz, 2×C), 116.31 (d, *J* = 22.5 Hz, 2×C), 51.8, 48.3, 38.1, 31.9, 29.5, 28.1, 18.1, 16.94, 16.92 ppm;

^{19}F NMR (471 MHz, $CDCl_3$): δ -105.5 ppm;

HRMS (ESI) calcd. for $C_{16}H_{25}FNO_4S^+$ ($M+H^+$): 346.1483. Found: 346.1478.

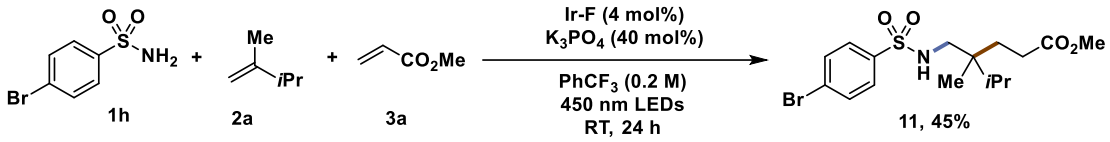


Methyl 4-(((2-chlorophenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (10): According to the General procedure C, 2-chlorobenzenesulfonamide **1g** (0.2 mmol, 38.3 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.28) as a white solid (37.1 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.68 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.12 – 5.01 (m, 1H), 3.62 (s, 3H), 2.73 – 2.59 (m, 2H), 2.43 (s, 3H), 2.19 (t, *J* = 8.0 Hz, 2H), 1.71 – 1.52 (m, 3H), 0.80 (dd, *J* = 8.6, 6.8 Hz, 6H), 0.72 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 136.9, 133.8, 131.6, 131.4, 131.2, 127.3, 51.8, 48.5, 38.1, 32.1, 29.8, 28.3, 18.3, 17.0, 16.9 ppm;

HRMS (ESI) calcd. for $C_{16}H_{25}ClNO_4S^+$ ($M+H^+$): 362.1187. Found: 362.1193.

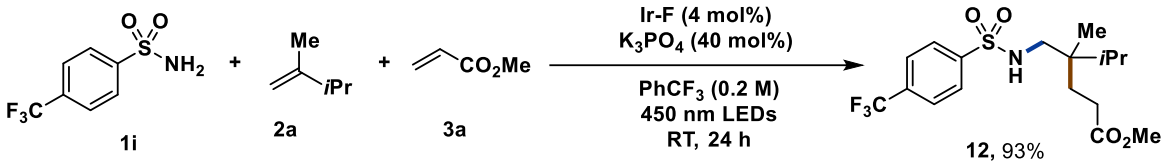


Methyl 4-(((4-bromophenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (11): According to the General procedure C, 4-bromobenzenesulfonamide **1h** (0.2 mmol, 47.2 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.30) as a white solid (36.9 mg, 45%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.70 (m, 2H), 7.67 – 7.62 (m, 2H), 5.16 (t, *J* = 6.9 Hz, 1H), 3.61 (s, 3H), 2.70 – 2.61 (m, 2H), 2.18 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 2H), 1.68 – 1.60 (m, 1H), 1.55 (dt, *J* = 15.5, 7.8 Hz, 2H), 0.80 (dd, *J* = 8.2, 6.9 Hz, 6H), 0.72 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.9, 138.9, 132.4 (2×C), 128.7 (2×C), 127.5, 51.9, 48.4, 38.2, 31.9, 29.5, 28.1, 18.1, 17.0, 16.9 ppm;

HRMS (ESI) calcd. for $C_{16}H_{25}BrNO_4S^+$ ($M+H^+$): 406.0682. Found: 406.0679



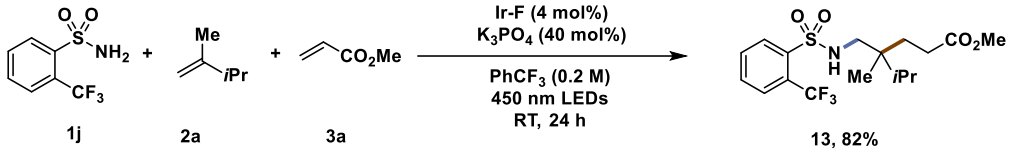
Methyl 4,5-dimethyl-4-(((4-(trifluoromethyl)phenyl)sulfonamido)methyl) hexanoate (12): According to the General procedure C, 4-(trifluoromethyl)benzene-sulfonamide **1i** (0.2 mmol, 45.0 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.28) as a white solid (73.5 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 5.42 (dt, *J* = 9.6, 4.3 Hz, 1H), 3.58 (s, 3H), 2.74 – 2.62 (m, 2H), 2.19 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 2H), 1.70 – 1.60 (m, 1H), 1.60 – 1.51 (m, 2H), 0.79 (dd, *J* = 6.9, 5.4 Hz, 6H), 0.72 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.0, 143.6, 134.30 (q, *J* = 33.0 Hz), 127.7 (2×C), 126.35 (q, *J* = 3.7 Hz, 2×C), 122.00 (q, *J* = 270.6 Hz), 51.9, 48.5, 38.3, 32.0, 29.5, 28.2, 18.2, 17.02, 16.99 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.1 ppm;

HRMS (ESI) calcd. for $C_{17}H_{25}F_3NO_4S^+$ ($M+H^+$): 396.1451. Found: 396.1449.



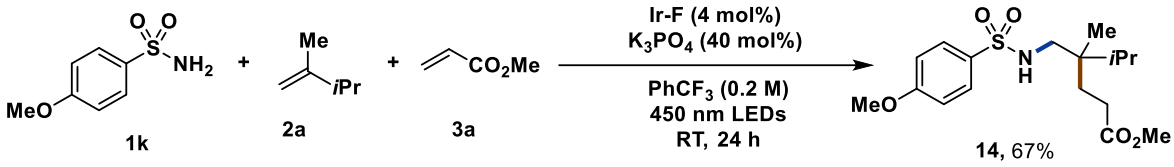
Methyl 4,5-dimethyl-4-(((2-(trifluoromethyl)phenyl)sulfonamido)methyl) hexanoate (13): According to the General procedure C, 2-(trifluoromethyl)benzene-sulfonamide **1j** (0.2 mmol, 45.0 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.28) as a white solid (64.6 mg, 82%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 7.0, 2.3 Hz, 1H), 7.88 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.75 – 7.67 (m, 2H), 4.92 (t, *J* = 6.8 Hz, 1H), 3.63 (s, 3H), 2.78 (dd, *J* = 12.8, 7.1 Hz, 1H), 2.68 (dd, *J* = 12.8, 6.3 Hz, 1H), 2.19 (t, *J* = 8.1 Hz, 2H), 1.66 (dt, *J* = 14.4, 8.0 Hz, 1H), 1.61 – 1.49 (m, 2H), 0.80 (d, *J* = 6.9 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H), 0.72 (s, 3H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 138.4, 132.7, 132.4, 131.7, 128.50 (q, *J* = 6.0 Hz), 127.44 (q, *J* = 32.9 Hz), 123.00 (q, *J* = 273.8 Hz), 51.8, 48.6, 38.1, 32.0, 29.6, 28.2, 18.3, 16.9 ppm;

^{19}F NMR (471 MHz, $CDCl_3$): δ -58.1 ppm;

HRMS (ESI) calcd. for $C_{17}H_{25}F_3NO_4S^+$ ($M+H^+$): 396.1451. Found: 396.1445.



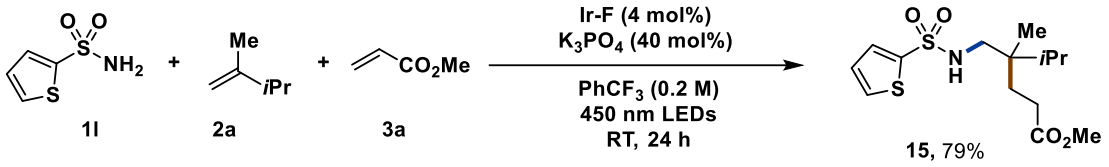
Methyl 4-(((4-methoxyphenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (14):

According to the General procedure C, 4-methoxybenzenesulfonamide **1k** (0.2 mmol, 37.4 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.28) as a white solid (48.3 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.70 (m, 2H), 7.02 – 6.90 (m, 2H), 4.86 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.61 (s, 3H), 2.65 (h, *J* = 6.6 Hz, 2H), 2.17 (t, *J* = 8.0 Hz, 2H), 1.64 (dt, *J* = 16.0, 8.1 Hz, 1H), 1.59 – 1.48 (m, 2H), 0.83 – 0.74 (m, 6H), 0.71 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 162.9, 131.4, 129.3 (2×C), 114.3 (2×C), 55.7, 51.9, 48.4, 38.1, 32.1, 29.7, 28.3, 18.3, 17.1, 17.0 ppm;

HRMS (ESI) calcd. for $C_{17}H_{28}NO_5S^+$ ($M+H^+$): 358.1683. Found: 358.1679.

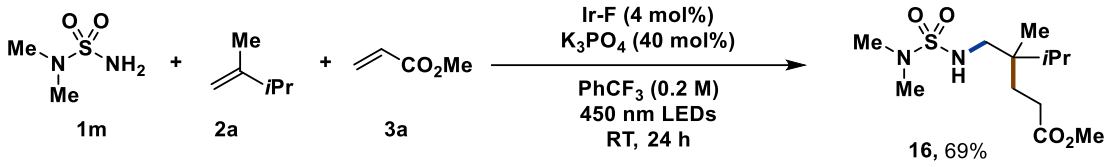


Methyl 4,5-dimethyl-4-((thiophene-2-sulfonamido)methyl)hexanoate (15): According to the General procedure C, thiophene-2-sulfonamide **1l** (0.2 mmol, 32.6 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.17) as a yellow oil (52.7 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ7.60 (ddd, *J* = 8.9, 4.4, 1.4 Hz, 2H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.15 (t, *J* = 6.8 Hz, 1H), 3.63 (s, 3H), 2.85 – 2.72 (m, 2H), 2.23 (t, *J* = 7.9 Hz, 2H), 1.75 – 1.54 (m, 3H), 0.83 (t, *J* = 6.5 Hz, 6H), 0.76 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 140.7, 132.0, 131.7, 127.4, 51.8, 48.7, 38.1, 32.0, 29.6, 28.2, 18.2, 17.0, 16.9 ppm;

HRMS (ESI) calcd. for $C_{14}H_{24}NO_4S_2^+$ ($M+H^+$): 334.1141. Found: 334.1143.

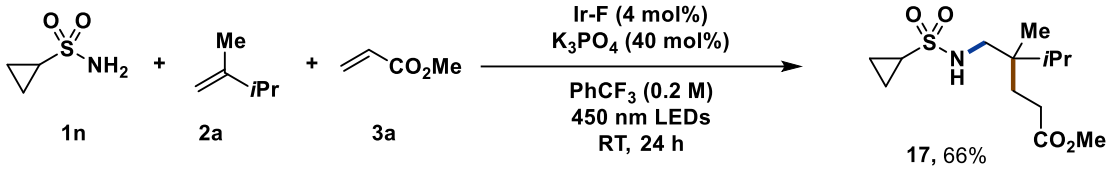


Methyl 4-(((N,N-dimethylsulfamoyl)amino)methyl)-4,5-dimethylhexanoate (16): According to the General procedure C, N,N-Dimethylsulfamide **1m** (0.2 mmol, 32.6 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.17) as a yellow oil (52.7 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.61 (t, *J* = 6.8 Hz, 1H), 3.68 (s, 3H), 2.93 – 2.82 (m, 2H), 2.81 (s, 6H), 2.29 (t, *J* = 8.1 Hz, 2H), 1.76 – 1.56 (m, 3H), 0.90 – 0.86 (m, 6H), 0.80 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ174.7, 51.8, 48.6, 38.1 (3×C), 32.0, 29.7, 28.4, 18.4, 17.04, 16.96 ppm;

HRMS (ESI) calcd. for $C_{12}H_{27}N_2O_4S^+$ ($M+H^+$): 295.1686. Found: 295.1691.

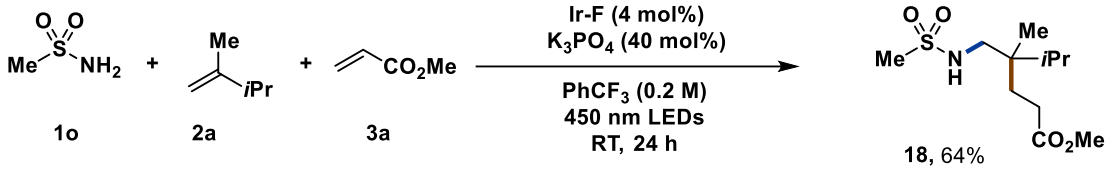


Methyl 4-(cyclopropanesulfonamidomethyl)-4,5-dimethylhexanoate (17): According to the General procedure C, cyclopropanesulfonamide **1n** (0.2 mmol, 24.2 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.16) as a yellow oil (38.7 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.66 (t, *J* = 6.9 Hz, 1H), 3.68 (s, 3H), 3.03 – 2.90 (m, 2H), 2.42 (tt, *J* = 8.0, 4.8 Hz, 1H), 2.31 (t, *J* = 8.0 Hz, 2H), 1.79 – 1.58 (m, 3H), 1.18 (dt, *J* = 6.9, 4.5 Hz, 2H), 1.03 – 0.96 (m, 2H), 0.88 (d, *J* = 6.9 Hz, 6H), 0.82 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ174.8, 51.8, 48.5, 38.2, 32.0, 29.7, 29.6, 28.3, 18.3, 17.04, 17.00, 5.3, 5.2 ppm;

HRMS (ESI) calcd. for $C_{13}H_{26}NO_4S^+$ ($M+H^+$): 292.1577. Found: 292.1580.

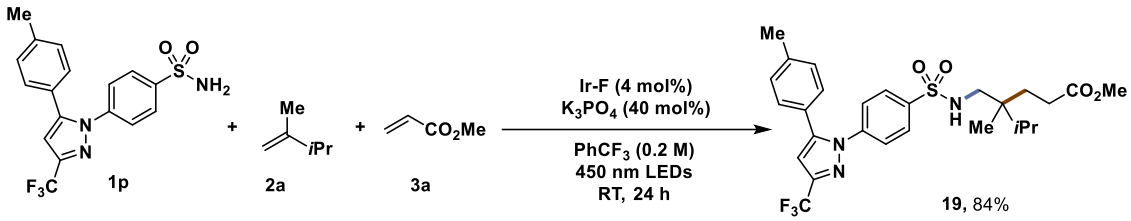


Methyl 4,5-dimethyl-4-(methylsulfonamidomethyl)hexanoate (18): According to the General procedure C, methanesulfonamide **1o** (0.2 mmol, 19 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 2:1, R_f = 0.3) as a yellow oil (34 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.87 (t, *J* = 6.9 Hz, 1H), 3.66 (s, 3H), 2.93 (s, 3H), 2.92 – 2.85 (m, 2H), 2.28 (t, *J* = 8.0 Hz, 2H), 1.74 – 1.55 (m, 3H), 0.86 (d, *J* = 6.9 Hz, 6H), 0.79 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.8, 51.9, 48.5, 39.7, 38.2, 31.9, 29.6, 28.3, 18.3, 17.03, 17.00 ppm;

HRMS (ESI) calcd. for $C_{11}H_{24}NO_4S^+$ ($M+H^+$): 266.1421. Found: 266.1413.

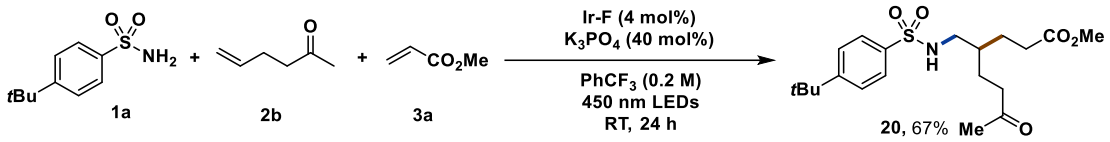


Methyl 4,5-dimethyl-4-(((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl) sulfonamido)methyl)hexanoate (19): According to the General procedure C, 4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide **1p** (0.2 mmol, 76.3 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.3) as a yellow oil (92.7 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.12 – 7.05 (m, 2H), 6.74 (s, 1H), 5.24 (t, *J* = 6.9 Hz, 1H), 3.59 (s, 3H), 2.71 – 2.58 (m, 2H), 2.36 (s, 3H), 2.20 (t, *J* = 7.7 Hz, 2H), 1.65 (dt, *J* = 15.1, 7.7 Hz, 1H), 1.56 (dtd, *J* = 14.9, 7.6, 4.9 Hz, 2H), 0.79 (dd, *J* = 9.3, 6.8 Hz, 6H), 0.72 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.0, 145.3, 143.92 (q, *J* = 38.5 Hz), 142.5, 139.9, 139.4, 129.8 (2×C), 128.8 (2×C), 128.2 (2×C), 125.71, 125.68 (2×C), 121.14 (q, *J* = 269.0 Hz), 106.3, 52.0, 48.5, 38.2, 32.0, 29.5, 28.1, 21.4, 18.2, 17.0 (2×C) ppm;

HRMS (ESI) calcd. for $C_{27}H_{33}F_3N_3O_4S^+$ ($M+H^+$): 552.2138. Found: 552.2140.



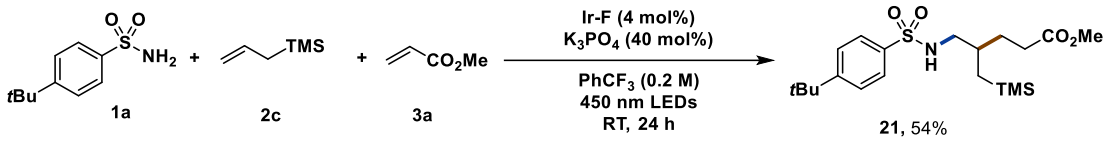
Methyl-4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-7-oxooctanoate (20):

According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), hex-5-en-2-one **2b** (0.4 mmol, 46.4 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.2) as a yellow oil (53.3 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.75 (m, 2H), 7.55 – 7.49 (m, 2H), 5.27 (t, *J* = 6.6 Hz, 1H), 3.63 (s, 3H), 2.79 (t, *J* = 5.9 Hz, 2H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.29 (td, *J* = 7.4, 1.4 Hz, 2H), 2.11 (s, 3H), 1.56 (dddd, *J* = 25.9, 24.4, 11.3, 6.3 Hz, 6H), 1.34 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 208.9, 174.1, 156.3, 136.7, 126.9 (2×C), 126.1 (2×C), 51.7, 45.1, 40.4, 37.1, 35.1, 31.1, 31.0 (3×C), 30.0, 26.3, 24.7 ppm;

HRMS (ESI) calcd. for $C_{20}H_{32}NO_5S^+$ ($M+H^+$): 398.1996. Found: 398.2005.

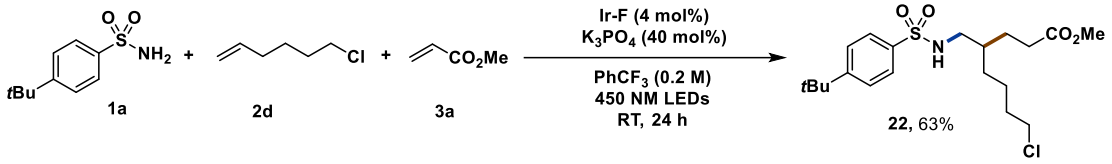


Methyl-5-((4-(*tert*-butyl)phenyl)sulfonamido)-4-((trimethylsilyl)methyl)pentanoate (21): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), allyltrimethylsilane **2c** (0.4 mmol, 63.6 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.3) as a yellow oil (44.9 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 – 7.83 (m, 2H), 7.60 – 7.55 (m, 2H), 5.10 (t, *J* = 6.4 Hz, 1H), 3.69 (s, 3H), 2.91 (ddd, *J* = 11.5, 6.7, 4.2 Hz, 1H), 2.79 (dt, *J* = 12.4, 6.0 Hz, 1H), 2.31 (td, *J* = 6.9, 3.4 Hz, 2H), 1.74 – 1.64 (m, 3H), 1.40 (s, 9H), 0.55 – 0.49 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.1, 157.2, 137.8, 127.8 (2×C), 127.0 (2×C), 52.6, 48.9, 36.0, 34.9, 32.0 (3×C), 31.5, 29.6, 20.3, -0.0 (3×C) ppm;

HRMS (ESI) calcd. for $C_{20}H_{36}NO_4SSi^+$ ($M+H^+$): 414.2129. Found: 414.2137.



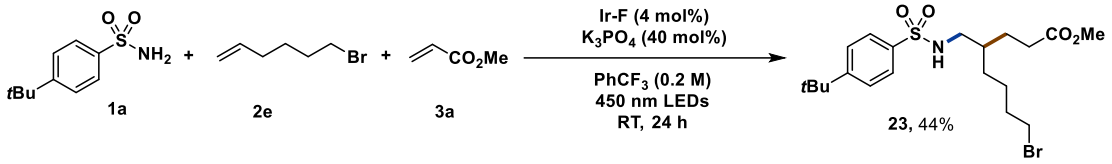
Methyl-4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-8-chlorooctanoate (22):

According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 1-(vinyloxy)butane **2d** (0.4 mmol, 52.9 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.25) as a yellow oil (53 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.77 (m, 2H), 7.55 – 7.51 (m, 2H), 5.15 (t, *J* = 6.5 Hz, 1H), 3.63 (s, 3H), 3.49 (t, *J* = 6.6 Hz, 2H), 2.84 (t, *J* = 6.1 Hz, 2H), 2.27 (td, *J* = 7.4, 2.2 Hz, 2H), 1.65 (dq, *J* = 26.5, 7.2 Hz, 4H), 1.53 – 1.46 (m, 1H), 1.35 (s, 9H), 1.31 – 1.24 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.2, 156.4, 136.8, 126.9 (2×C), 126.1 (2×C), 77.4, 77.1, 76.8, 51.7, 45.4, 44.9, 37.4, 35.1, 32.5, 31.1 (3×C), 31.0, 30.5, 26.1, 23.7 ppm;

HRMS (ESI) calcd. for $C_{20}H_{33}ClNO_4S^+$ ($M+H^+$): 418.1813. Found: 418.1802.



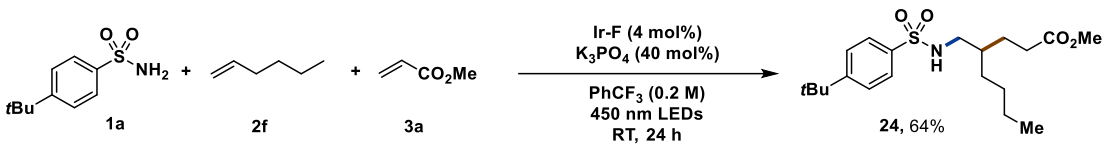
Methyl-8-bromo-4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)octanoate (23):

According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 1-(vinyloxy)butane **2e** (0.4 mmol, 53.5 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.25) as a yellow oil (41 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.76 (m, 2H), 7.56 – 7.50 (m, 2H), 5.01 (t, *J* = 6.5 Hz, 1H), 3.63 (s, 3H), 3.36 (t, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 6.1 Hz, 2H), 2.27 (td, *J* = 7.4, 3.4 Hz, 2H), 1.82 – 1.74 (m, 3H), 1.61 (q, *J* = 7.0 Hz, 2H), 1.54 – 1.46 (m, 1H), 1.41 – 1.36 (m, 2H), 1.35 (s, 9H), 1.32 – 1.25 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.1, 156.4, 136.8, 126.9 (2×C), 126.1 (2×C), 51.7, 45.4, 37.4, 35.2, 33.7, 32.6, 31.1 (3×C), 31.0, 30.4, 26.1, 25.0 ppm;

HRMS (ESI) calcd. for $C_{20}H_{33}BrNO_4S^+$ ($M+H^+$):462.1308. Found: 462.1302.

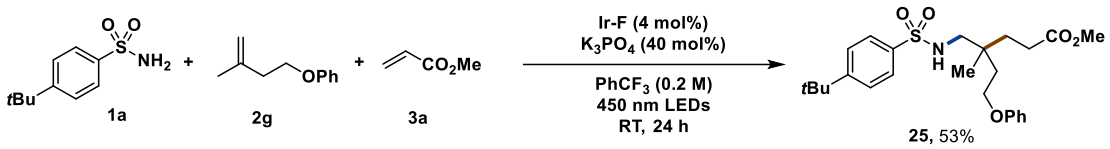


Methyl-4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)octanoate (21): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), hex-1-ene **2f** (0.4 mmol, 49.7 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.22) as a yellow oil (32.8 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.77 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 5.09 – 4.96 (m, 1H), 3.63 (d, *J* = 1.2 Hz, 3H), 2.84 (dq, *J* = 16.5, 6.5 Hz, 2H), 2.26 (td, *J* = 7.5, 2.4 Hz, 2H), 1.65 – 1.56 (m, 2H), 1.46 (td, *J* = 10.8, 4.8 Hz, 1H), 1.34 (d, *J* = 1.1 Hz, 9H), 1.22 (dt, *J* = 18.7, 4.6 Hz, 6H), 0.87 – 0.81 (m, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.2, 156.3, 136.8, 126.9 (2×C), 126.1 (2×C), 51.7, 45.7, 37.4, 35.1, 31.1 (3×C), 31.04, 31.00, 28.6, 26.2, 22.8, 14.0 ppm;

HRMS (ESI) calcd. for $C_{20}H_{34}NO_4S^+$ ($M+H^+$): 384.2203. Found: 384.2204.

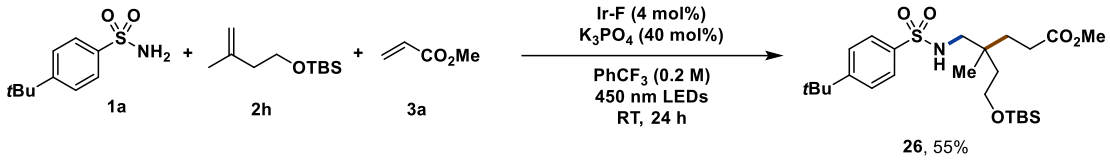


Methyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4-methyl-6-phenoxy-hexanoate (25): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), ((3-methylbut-3-en-1-yl)oxy)benzene **2g** (0.4 mmol, 64.5 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.23) as a yellow oil (41.6 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.73 (m, 2H), 7.51 – 7.46 (m, 2H), 7.28 – 7.19 (m, 2H), 6.94 (td, *J* = 7.3, 1.1 Hz, 1H), 6.78 – 6.72 (m, 2H), 5.35 – 5.28 (m, 1H), 3.97 (t, *J* = 5.8 Hz, 2H), 3.64 (s, 3H), 2.83 – 2.70 (m, 2H), 2.41 – 2.23 (m, 2H), 1.79 – 1.64 (m, 4H), 1.32 (s, 9H), 0.94 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 158.2, 156.3, 137.0, 129.5 (2×C), 126.8 (2×C), 126.1 (2×C), 121.1, 114.3 (2×C), 64.0, 51.8, 50.3, 36.1, 35.9, 35.1, 32.4, 31.1 (3×C), 28.4, 22.7 ppm;

HRMS (ESI) calcd. for $C_{25}H_{36}NO_5S^+$ ($M+H^+$):462.2309. Found: 462.2296.

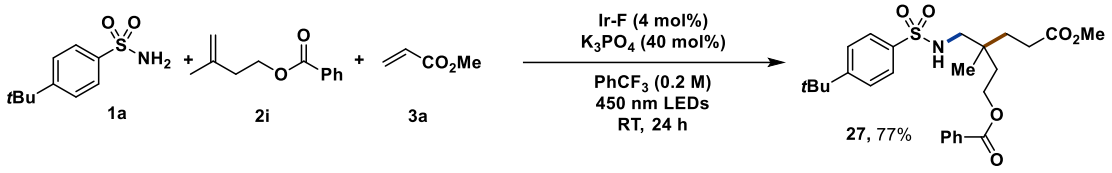


Methyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-6-((*tert*-butyldimethylsilyl)oxy)-4-methylhexanoate (26): According to the General procedure C, 4-*tert*-butylbenzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), *tert*-butyldimethyl((3-methylbut-3-en-1-yl)oxy)silane **2h** (0.4 mmol, 95 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.32) as a yellow solid (55.4 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.70 (m, 2H), 7.51 – 7.44 (m, 2H), 5.53 (t, *J* = 7.1 Hz, 1H), 3.63 (s, 3H), 2.75 (qd, *J* = 12.8, 7.2 Hz, 2H), 2.37 – 2.17 (m, 2H), 1.73 – 1.55 (m, 2H), 1.46 (q, *J* = 5.6 Hz, 2H), 1.32 (s, 9H), 0.87 (s, 3H), 0.80 (s, 9H), -0.00 (d, *J* = 1.2 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 156.0, 137.5, 126.8 (2×C), 126.0 (2×C), 59.3, 51.7, 50.5, 40.0, 35.8, 35.1, 32.6 (3×C), 31.1, 28.5, 26.0 (3×C), 22.9, 18.3, -5.47, -5.51 ppm;

HRMS (ESI) calcd. for $C_{25}H_{46}NO_5SSi^+$ ($M+H^+$):500.2860. Found: 500.2844.

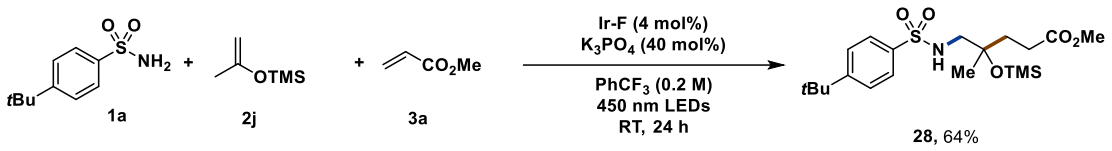


3-(((4-(*Tert*-butyl)phenyl)sulfonamido)methyl)-6-methoxy-3-methyl-6-oxohexyl benzoate (27): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 3-methylbut-3-en-1-yl benzoate **2i** (0.4 mmol, 70.5 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.2) as a yellow oil (75.6 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.97 (m, 2H), 7.77 – 7.72 (m, 2H), 7.60 – 7.54 (m, 1H), 7.49 – 7.40 (m, 4H), 5.44 (t, *J* = 7.2 Hz, 1H), 4.33 (t, *J* = 7.1 Hz, 2H), 3.60 (s, 3H), 2.75 (d, *J* = 7.2 Hz, 2H), 2.31 (dd, *J* = 9.0, 6.9 Hz, 2H), 2.02 (d, *J* = 15.2 Hz, 1H), 1.75 (t, *J* = 7.0 Hz, 2H), 1.69 (dd, *J* = 8.9, 7.0 Hz, 2H), 1.32 (s, 9H), 0.96 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.3, 166.7, 156.3, 136.8, 133.1, 130.0, 129.6 (2×C), 128.5 (2×C), 126.8 (2×C), 126.1 (2×C), 61.3, 51.8, 50.2, 35.8, 35.3, 35.1, 31.8, 31.1 (3×C), 28.3, 22.6 ppm;

HRMS (ESI) calcd. for $C_{26}H_{36}NO_6S^+$ ($M+H^+$):490.2258. Found: 490.2245.

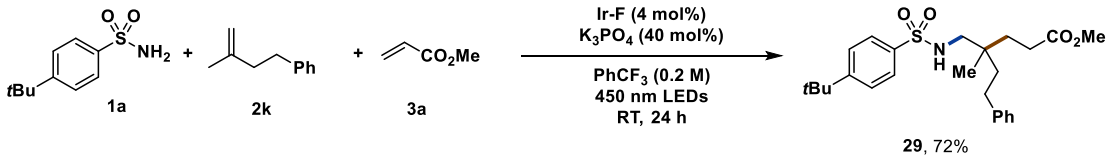


Methyl 5-((4-(*tert*-butyl)phenyl)sulfonamido)-4-methyl-4-((trimethylsilyl)oxy) pentanoate (28): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), trimethyl(prop-1-en-2-yloxy)silane **2j** (0.4 mmol, 66.8 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.3) as a yellow oil (55.3 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.68 (m, 2H), 7.51 – 7.45 (m, 2H), 4.78 (td, *J* = 7.6, 5.3 Hz, 1H), 3.59 (s, 3H), 2.80 (dd, *J* = 12.0, 7.4 Hz, 1H), 2.66 (dd, *J* = 11.9, 5.3 Hz, 1H), 2.25 (t, *J* = 7.8 Hz, 2H), 1.86 (dt, *J* = 14.1, 7.8 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.29 (s, 9H), 1.19 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.8, 154.1, 134.3, 124.6 (2×C), 123.8 (2×C), 72.3, 49.7, 49.4, 32.8, 32.4, 28.8 (3×C), 26.4, 23.1, 0.0 (3×C) ppm;

HRMS (ESI) calcd. for $C_{20}H_{36}NO_5SSi^+$ ($M+H^+$):430.2078. Found: 430.2069.

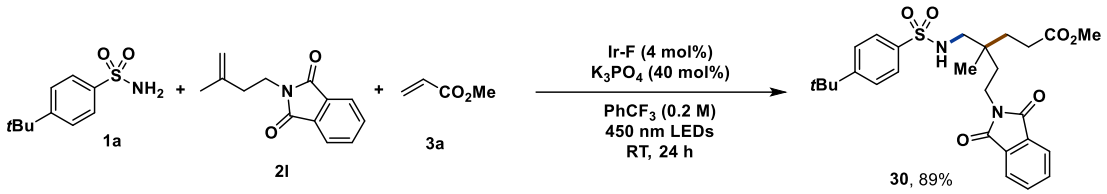


Methyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4-methyl-6-phenyl-hexanoate (29): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), (3-methylbut-3-en-1-yl)benzene **2k** (0.4 mmol, 61 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.25) as a yellow oil (63.8 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.75 (m, 2H), 7.52 – 7.48 (m, 2H), 7.24 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.14 (dd, *J* = 6.9, 5.2 Hz, 3H), 5.10 (t, *J* = 7.0 Hz, 1H), 3.61 (s, 3H), 2.70 (dd, *J* = 7.1, 2.2 Hz, 2H), 2.49 (td, *J* = 7.3, 2.7 Hz, 2H), 2.30 – 2.21 (m, 2H), 1.68 – 1.60 (m, 2H), 1.51 (dd, *J* = 11.4, 6.3 Hz, 2H), 1.33 (s, 9H), 0.91 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.5, 156.3, 142.3, 136.8, 128.4 (2×C), 128.3 (2×C), 126.9 (2×C), 126.1 (2×C), 125.8, 51.8, 50.0, 39.3, 36.2, 35.1, 31.5, 31.1 (3×C), 29.7, 28.4, 22.5 ppm;

HRMS (ESI) calcd. for $C_{25}H_{36}NO_4S^+$ ($M+H^+$):446.2360. Found: 446.2350.

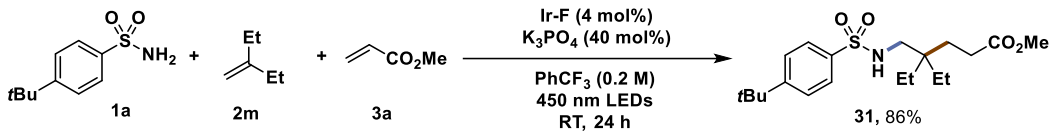


Methyl 4-(((4-(*Tert*-butyl)phenyl)sulfonamido)methyl)-6-(1,3-dioxoisoindolin-2-yl)-4-methylhexanoate (30): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), (3-methylbut-3-en-1-yl)benzene **2l** (0.4 mmol, 86.1 mg, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.21) as a yellow oil (90.6 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.81 (m, 4H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.55 – 7.50 (m, 2H), 5.57 (t, *J* = 7.2 Hz, 1H), 3.63 (s, 3H), 3.61 – 3.54 (m, 2H), 2.84 – 2.71 (m, 2H), 2.34 (td, *J* = 7.3, 2.1 Hz, 2H), 1.67 (t, *J* = 8.0 Hz, 2H), 1.59 (ddd, *J* = 10.6, 6.9, 2.3 Hz, 2H), 1.34 (s, 9H), 0.97 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.2, 168.3 (2×C), 156.2, 136.9, 134.1 (2×C), 132.0 (2×C), 126.9 (2×C), 126.1 (2×C), 123.4 (2×C), 51.8, 49.7, 35.8, 35.1, 34.9, 33.0, 31.6, 31.1 (3×C), 28.2, 22.3 ppm;

HRMS (ESI) calcd. for $C_{27}H_{35}N_2O_6S^+$ ($M+H^+$):515.2210. Found: 515.2201.

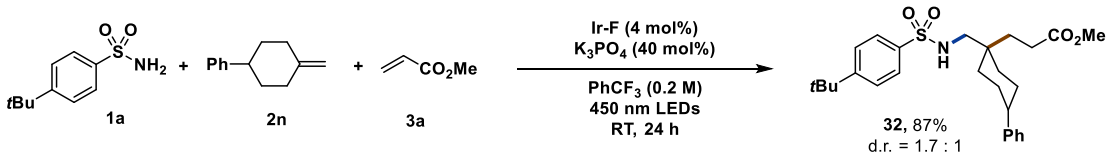


Methyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4-ethylhexanoate (31): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 3-methylenepentane **2m** (0.4 mmol, 49 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.4) as a white solid (66 mg, 86%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 – 7.75 (m, 2H), 7.52 – 7.47 (m, 2H), 5.07 (t, *J* = 6.9 Hz, 1H), 3.57 (s, 3H), 2.58 (d, *J* = 7.0 Hz, 2H), 2.18 – 2.10 (m, 2H), 1.53 – 1.46 (m, 2H), 1.32 (s, 9H), 1.18 (ddt, *J* = 16.6, 14.4, 7.2 Hz, 4H), 0.69 (t, *J* = 7.5 Hz, 6H) ppm;

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.6, 156.2, 136.7, 126.9 (2×C), 126.1 (2×C), 51.7, 46.7, 38.3, 35.1, 31.1, 28.0, 27.8, 25.7, 7.1 ppm;

HRMS (ESI) calcd. for $C_{20}H_{34}NO_4S^+$ ($M+H^+$):384.2203. Found: 384.2198.

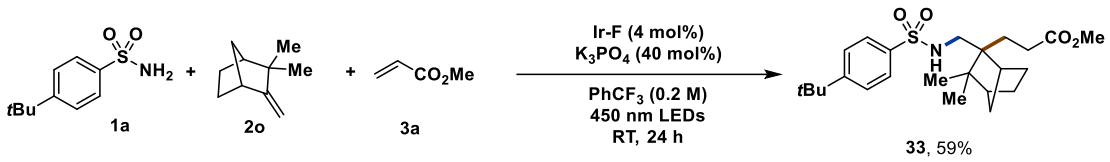


Methyl 3-(1-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4-phenylcyclohexyl) propanoate (32): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), (4-methylenecyclohexyl)benzene **2n** (0.4 mmol, 73.3 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.25) as a yellow oil (82.1 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.70 (m, 2H), 7.48 – 7.40 (m, 2H), 7.23 – 7.14 (m, 3H), 7.09 (d, *J* = 7.5 Hz, 2H), 5.30 (td, *J* = 6.4, 2.3 Hz, 1H), 3.54 (s, 3H), 2.69 (dd, *J* = 94.1, 7.0 Hz, 2H), 2.30 (tq, *J* = 11.7, 3.9 Hz, 1H), 2.16 (dt, *J* = 11.2, 7.8 Hz, 2H), 1.79 – 1.55 (m, 4H), 1.55 – 1.45 (m, 4H), 1.24 (d, *J* = 14.7 Hz, 9H), 1.19 – 1.16 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.7, 156.3, 149.8, 146.8, 137.0, 128.4 (2×C), 126.9 (2×C), 126.8 (2×C), 126.1 (2×C), 60.5, 51.8, 44.1, 35.1, 34.3, 33.4, 31.1 (3×C), 31.1, 28.7, 27.9, 25.4, 21.1 ppm;

HRMS (ESI) calcd. for $C_{27}H_{38}NO_4S^+$ ($M+H^+$):472.2516. Found: 472.2508.

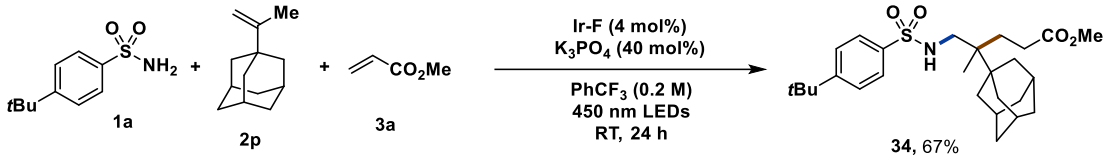


Methyl 3-(-2-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-3,3-dimethylbicyclo [2.2.1] heptan-2-yl)propanoate (33): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane **2n** (0.4 mmol, 64.1 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.24) as a white solid (51.4 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.77 (m, 2H), 7.56 – 7.50 (m, 2H), 4.86 (t, *J* = 6.3 Hz, 1H), 3.61 (s, 3H), 2.81 (qd, *J* = 12.3, 6.4 Hz, 2H), 2.25 – 2.11 (m, 2H), 1.92 – 1.86 (m, 2H), 1.75 – 1.60 (m, 2H), 1.51 – 1.41 (m, 1H), 1.35 (s, 9H), 1.30 – 1.20 (m, 2H), 1.08 – 1.02 (m, 1H), 0.98 (s, 3H), 0.88 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.6, 156.4, 136.1, 127.0 (2×C), 126.1 (2×C), 51.8, 51.7, 46.5, 45.7, 44.5, 42.5, 35.2, 34.9, 31.1 (3×C), 30.2, 28.1, 27.4, 23.4, 22.8, 22.4 ppm;

HRMS (ESI) calcd. for $C_{24}H_{38}NO_4S^+$ ($M+H^+$):436.2516. Found: 436.2510.

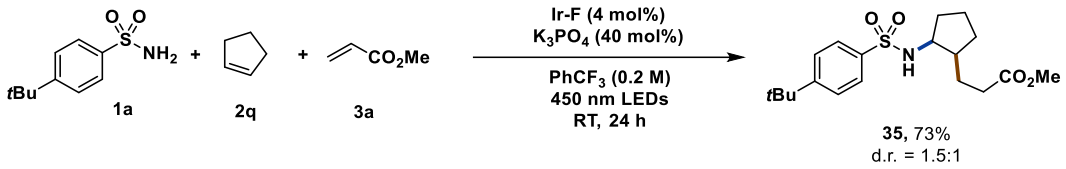


Methyl 4-(adamantan-1-yl)-5-((4-(*tert*-butyl)phenyl)sulfonamido)-4-methyl-pentanoate (34): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 1-(prop-1-en-2-yl)adamantane **2p** (0.4 mmol, 72 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.26) as a yellow oil (64.2 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.73 (m, 2H), 7.56 – 7.48 (m, 2H), 4.79 – 4.71 (m, 1H), 3.63 (s, 3H), 2.87 (dd, *J* = 13.0, 7.6 Hz, 1H), 2.68 (dd, *J* = 13.0, 6.0 Hz, 1H), 2.25 (td, *J* = 7.7, 3.9 Hz, 2H), 1.95 – 1.90 (m, 3H), 1.70 – 1.60 (m, 6H), 1.54 (d, *J* = 11.0 Hz, 8H), 1.35 (s, 9H), 0.71 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.9, 156.3, 136.6, 127.0 (2×C), 126.1 (2×C), 51.7, 46.8, 40.2, 37.9, 37.0 (3×C), 36.7 (3×C), 35.1, 31.1 (3×C), 29.6, 28.6 (3×C), 27.0, 17.3 ppm;

HRMS (ESI) calcd. for $C_{27}H_{42}NO_4S^+$ ($M+H^+$):476.2829. Found: 476.2817.

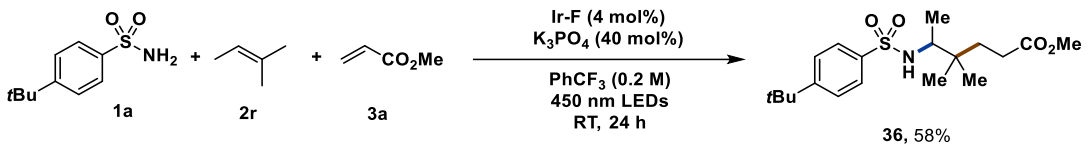


Methyl 3-(-2-((4-(*tert*-butyl)phenyl)sulfonamido)cyclopentyl)propanoate (35): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), cyclopentene **2q** (0.4 mmol, 35.3 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.34) as a yellow oil (57.4 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.76 (m, 2H), 7.54 – 7.48 (m, 2H), 4.59 (d, *J* = 7.6 Hz, 1H, major), 3.65 (s, *J* = 1.6 Hz, 3H), 3.16 (p, *J* = 7.5 Hz, 1H), 2.26 – 2.17 (m, 2H), 1.84 – 1.72 (m, 3H), 1.67 – 1.49 (m, 6H), 1.34 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.9, 155.3, 136.7, 125.90 (2×C, major), 125.86 (2×C, minor), 125.02 (2×C, minor), 125.0 (2×C, major), 59.0 (major), 55.8 (minor), 50.6 (major), 50.5 (minor), 44.8 (major), 41.8 (minor), 34.1 (major), 32.1 (minor), 31.43 (major), 31.36 (minor), 30.1 (3×C), 28.7 (minor), 28.5 (major), 27.7 (minor), 27.4 (major), 23.4, 20.9 (major), 19.8 (minor) ppm;

HRMS (ESI) calcd. for $C_{19}H_{29}NNaO_4S^+$ ($M+Na^+$): 390.1710. Found: 390.1706.

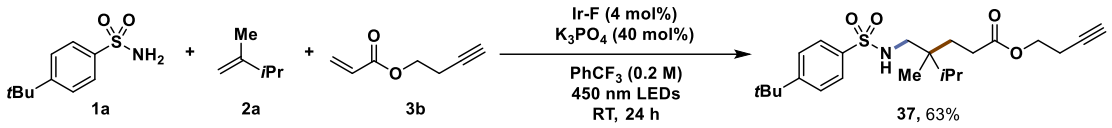


Methyl 5-((4-(*tert*-butyl)phenyl)sulfonamido)-4,4-dimethylhexanoate (36): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2-methylbut-2-ene **2r** (0.4 mmol, 42.4 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.28) as a yellow oil (42.5 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.75 (m, 2H), 7.53 – 7.48 (m, 2H), 4.50 (d, *J* = 9.8 Hz, 1H), 3.64 (s, 3H), 3.11 (dq, *J* = 9.7, 6.7 Hz, 1H), 2.23 (dqt, *J* = 26.2, 10.3, 5.3 Hz, 2H), 1.63 – 1.48 (m, 2H), 1.33 (s, 9H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.80 (d, *J* = 7.8 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 156.4, 138.0, 126.9 (2×C), 126.0 (2×C), 56.8, 51.7, 36.7, 35.1, 33.4, 31.1 (3×C), 28.9, 23.1, 22.8, 16.2 ppm;

HRMS (ESI) calcd. for $C_{19}H_{32}NO_4S^+$ ($M+H^+$): 370.2047. Found: 370.2045.

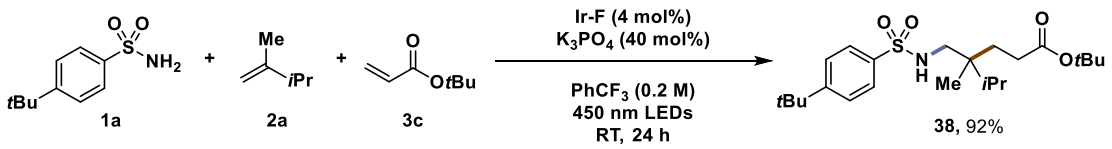


But-3-yn-1-yl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (37): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a**(0.4 mmol, 50 μL, 2 equiv.), but-3-yn-1-yl acrylate **3b** (0.4 mmol, 49.7 mg, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.4) as a yellow oil (57.9 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.75 (m, 2H), 7.56 – 7.48 (m, 2H), 5.04 (t, *J* = 6.9 Hz, 1H), 4.12 (td, *J* = 6.9, 2.3 Hz, 2H), 2.69 (qd, *J* = 12.7, 6.9 Hz, 2H), 2.49 (td, *J* = 6.8, 2.7 Hz, 2H), 2.23 (t, *J* = 7.9 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.75 – 1.52 (m, 3H), 1.35 (s, 9H), 0.80 (t, *J* = 6.9 Hz, 6H), 0.74 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.0, 156.2, 136.7, 126.9 (2×C), 126.1 (2×C), 80.0, 70.1, 62.2, 48.4, 38.1, 35.1, 31.9, 31.1 (3×C), 29.5, 28.3, 18.9, 18.2, 17.0, 16.9 ppm;

HRMS (ESI) calcd. for $C_{23}H_{36}NO_4S^+$ ($M+H^+$): 422.2360. Found: 422.2350.

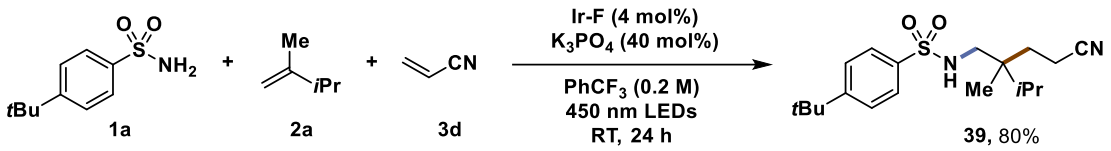


***Tert*-butyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (38):** According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), *tert*-butyl acrylate **3c** (0.4 mmol, 58.6 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.34) as a yellow oil (78.2 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.72 (m, 2H), 7.51 – 7.44 (m, 2H), 5.27 – 5.18 (m, 1H), 2.70 (dd, *J* = 12.7, 7.2 Hz, 1H), 2.61 (dd, *J* = 12.7, 6.7 Hz, 1H), 2.09 (t, *J* = 7.6 Hz, 2H), 1.64 – 1.54 (m, 2H), 1.53 – 1.43 (m, 2H), 1.37 (s, 9H), 1.31 (s, 9H), 0.77 (dd, *J* = 6.8, 3.7 Hz, 6H), 0.71 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.9, 156.1, 136.9, 126.8 (2×C), 126.0 (2×C), 80.6, 77.4, 77.1, 76.8, 48.4, 38.2, 35.1, 31.8, 31.1 (3×C), 29.5, 29.3 (3×C), 28.0, 18.2, 17.01, 16.96 ppm;

HRMS (ESI) calcd. for $C_{23}H_{40}NO_4S^+$ ($M+H^+$): 426.2673. Found: 426.2660.



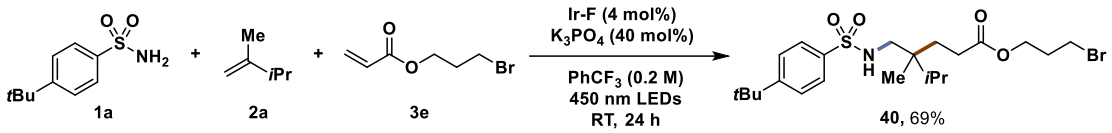
4-(*Tert*-butyl)-N-(4-cyano-2-isopropyl-2-methylbutyl)benzenesulfonamide (39):

According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), acrylonitrile **3d** (0.4 mmol, 26.3 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.23) as a yellow oil (55.8 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 – 7.68 (m, 2H), 7.52 – 7.45 (m, 2H), 4.98 (t, *J* = 7.1 Hz, 1H), 2.65 (d, *J* = 7.0 Hz, 2H), 2.25 – 2.13 (m, 2H), 1.74 – 1.59 (m, 3H), 1.48 (p, *J* = 6.9 Hz, 1H), 1.28 (s, 9H), 0.73 (dd, *J* = 17.6, 6.9 Hz, 6H), 0.69 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.7, 136.4, 126.8 (2×C), 126.4 (2×C), 120.3, 47.9, 38.4, 35.2, 31.9, 31.09 (3×C), 31.06, 17.9, 16.94, 16.91, 11.8 ppm;

HRMS (ESI) calcd. for $C_{19}H_{31}N_2O_2S^+$ ($M+H^+$): 351.2101. Found: 351.2096.

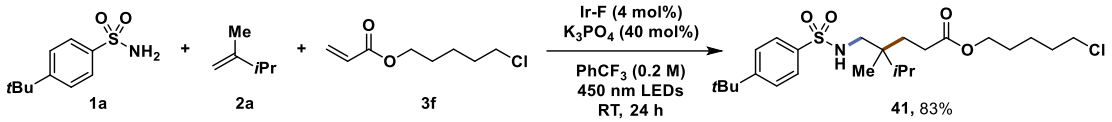


3-Bromopropyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (40): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), 3-bromopropyl acrylate **3e** (0.4 mmol, 77.2 mg, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.38) as a yellow oil (67.3 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.75 (m, 2H), 7.56 – 7.50 (m, 2H), 5.06 (t, *J* = 7.0 Hz, 1H), 4.16 (td, *J* = 6.2, 1.2 Hz, 2H), 3.45 (t, *J* = 6.5 Hz, 2H), 2.70 (qd, *J* = 12.7, 6.9 Hz, 2H), 2.28 – 2.11 (m, 4H), 1.73 – 1.54 (m, 3H), 1.35 (s, 9H), 0.80 (dd, *J* = 9.4, 6.8 Hz, 6H), 0.74 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.1, 156.3, 136.7, 126.9 (2×C), 126.1 (2×C), 77.4, 77.1, 76.8, 62.3, 48.4, 41.3, 38.1, 35.1, 32.0, 31.6, 31.1 (3×C), 29.6, 28.4, 18.2, 17.00, 16.96 ppm;

HRMS (ESI) calcd. for $C_{22}H_{37}BrNO_4S^+$ ($M+H^+$): 490.1621. Found: 490.1609.

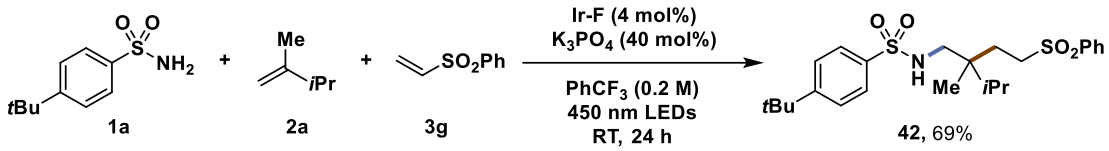


5-Chloropentyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethyl-hexanoate (41): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), 5-chloropentyl acrylate **3f** (0.4 mmol, 70.7 mg, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.4) as a yellow oil (78.4 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.75 (m, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 5.06 (t, *J* = 6.9 Hz, 1H), 4.03 (td, *J* = 6.5, 1.3 Hz, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.70 (qd, *J* = 12.7, 6.9 Hz, 2H), 2.21 (t, *J* = 7.9 Hz, 2H), 1.80 (p, *J* = 6.8 Hz, 2H), 1.72 – 1.54 (m, 6H), 1.51 (qd, *J* = 7.4, 2.5 Hz, 3H), 1.35 (s, 9H), 0.80 (dd, *J* = 8.8, 6.8 Hz, 6H), 0.74 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.3, 156.2, 136.8, 126.9 (2×C), 126.1 (2×C), 64.3, 48.4, 44.8, 38.1, 35.1, 32.1, 31.9, 31.1 (3×C), 29.6, 28.5, 27.9, 23.3, 18.3, 16.99, 16.95 ppm;

HRMS (ESI) calcd. for $C_{24}H_{41}ClNO_4S^+$ ($M+H^+$): 474.2439. Found: 474.2430.

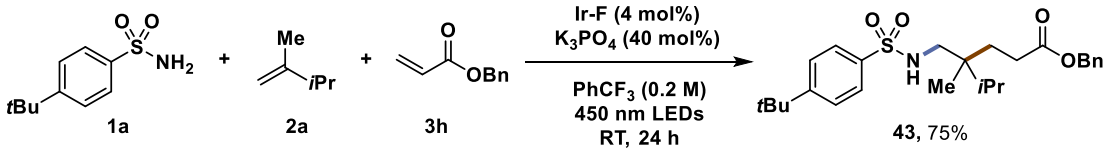


4-(*tert*-butyl)-N-(2-isopropyl-2-methyl-4-(phenylsulfonyl)butyl)benzenesulfonamide (42): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), (vinylsulfonyl)benzene **3g** (0.4 mmol, 67.3 mg, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.3) as a yellow oil (64.6 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.89 (m, 2H), 7.76 – 7.72 (m, 2H), 7.66 – 7.61 (m, 1H), 7.56 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.54 – 7.48 (m, 2H), 5.07 (t, *J* = 7.1 Hz, 1H), 3.09 (tq, *J* = 13.6, 6.7 Hz, 2H), 2.73 – 2.58 (m, 2H), 1.77 – 1.62 (m, 2H), 1.47 (p, *J* = 6.8 Hz, 1H), 1.33 (d, *J* = 2.6 Hz, 9H), 0.71 (dd, *J* = 9.5, 6.8 Hz, 6H), 0.69 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.5, 138.9, 136.6, 133.8, 129.3 (2×C), 128.1 (2×C), 126.8 (2×C), 126.3 (2×C), 51.2, 48.5, 38.3, 35.2, 32.0, 31.1 (3×C), 27.6, 18.3, 17.0, 16.8 ppm;

HRMS (ESI) calcd. for $C_{24}H_{36}NO_4S_2^+$ ($M+H^+$): 466.2080. Found: 466.2070.

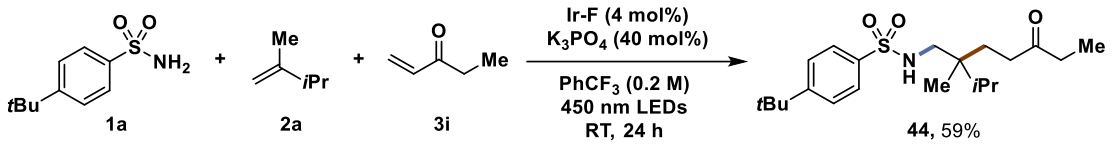


Benzyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (43): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), benzyl acrylate **3h** (0.4 mmol, 61.6 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.25) as a yellow oil (68.8 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.67 (m, 2H), 7.45 – 7.40 (m, 2H), 7.32 – 7.22 (m, 5H), 4.96 (d, *J* = 2.6 Hz, 2H), 4.89 (t, *J* = 6.9 Hz, 1H), 2.70 – 2.54 (m, 2H), 2.17 (t, *J* = 7.9 Hz, 2H), 1.67 – 1.46 (m, 3H), 1.25 (s, 9H), 0.72 (dd, *J* = 6.9, 5.6 Hz, 6H), 0.66 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.1, 156.3, 136.8, 135.8, 128.6 (2×C), 128.3 (3×C), 126.9 (2×C), 126.1 (2×C), 66.5, 48.4, 38.1, 35.1, 32.0, 31.1 (3×C), 29.5, 28.5, 18.3, 17.01, 16.97 ppm;

HRMS (ESI) calcd. for $C_{26}H_{38}NO_4S^+$ ($M+H^+$): 460.2516. Found: 460.2506.



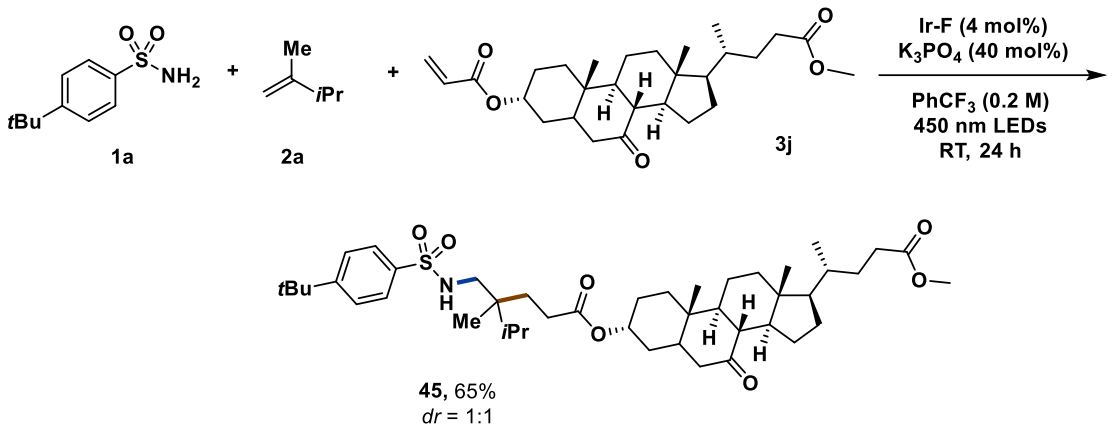
4-(*Tert*-butyl)-N-(2-isopropyl-2-methyl-5-oxoheptyl)benzenesulfonamide (44):

According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), pent-1-en-3-one **3i** (0.4 mmol, 49.5 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.35) as a yellow oil (45.2 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.75 (m, 2H), 7.53 – 7.49 (m, 2H), 5.05 (t, *J* = 6.9 Hz, 1H), 2.63 (d, *J* = 6.9 Hz, 2H), 2.40 – 2.27 (m, 4H), 1.63 – 1.49 (m, 3H), 1.34 (s, 9H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.80 (t, *J* = 6.4 Hz, 6H), 0.71 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 216.1, 212.2, 156.2, 136.7, 126.9 (2×C), 126.0 (2×C), 48.4, 38.0, 36.3, 36.0, 32.0, 31.1 (3×C), 28.3, 18.0, 17.02, 16.99, 7.9 ppm;

HRMS (ESI) calcd. for $C_{21}H_{36}NO_3S^+$ ($M+H^+$): 382.2410. Found: 382.2400.

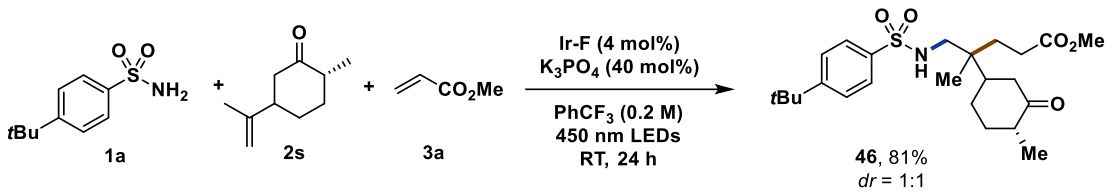


(3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-methoxy-5-oxopentan-2-yl)-10,13-dimethyl-7-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (45): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.1 mmol, 21.3 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.2 mmol, 25 μL, 2 equiv.), methyl (4*R*)-4-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*) -3-(acryloyloxy)-10,13-dimethyl-7-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl) pentanoate **3j** (0.4 mmol, 183.4 mg, 4 equiv.), Ir-F (0.004 mmol, 4.5 mg, 0.04 equiv.) and K_3PO_4 (0.04 mmol, 8.5 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.34) as a yellow oil (49.1 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 4.91 (t, *J* = 6.9 Hz, 1H), 4.64 (tt, *J* = 11.0, 4.9 Hz, 1H), 3.64 (s, 3H), 2.84 (dd, *J* = 12.7, 6.1 Hz, 1H), 2.68 (ddt, *J* = 23.6, 13.1, 6.7 Hz, 2H), 2.42 – 2.33 (m, 2H), 2.31 (dd, *J* = 10.1, 5.0 Hz, 1H), 2.24 – 2.17 (m, 2H), 2.11 (t, *J* = 7.8 Hz, 2H), 1.96 – 1.84 (m, 6H), 1.78 (dd, *J* = 13.3, 9.0 Hz, 4H), 1.72 – 1.63 (m, 3H), 1.63 – 1.51 (m, 4H), 1.48 – 1.41 (m, 4H), 1.32 (s, 9H), 1.19 (s, 3H), 1.09 (t, *J* = 9.6 Hz, 2H), 0.89 (d, *J* = 6.3 Hz, 3H), 0.76 (dd, *J* = 9.3, 6.8 Hz, 6H), 0.70 (d, *J* = 5.0 Hz, 3H), 0.63 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$):δ 211.8, 174.7, 173.7, 156.2, 136.8, 126.9 (2×C), 126.1 (2×C), 73.1, 54.8, 51.5, 49.5, 48.9, 48.5, 48.3, 45.8, 45.3, 42.7, 42.6, 38.9, 38.1, 35.22, 35.15, 33.8, 33.1, 31.1 (3×C), 31.04, 30.98, 29.6, 28.7, 28.3, 26.0, 24.8, 23.0, 21.7, 18.38, 18.37, 18.27, 17.01, 16.98, 12.1 ppm;

HRMS (APCI) calcd. for $C_{44}H_{70}NO_7S^+$ ($M+H^+$): 756.4868. Found: 756.4850.

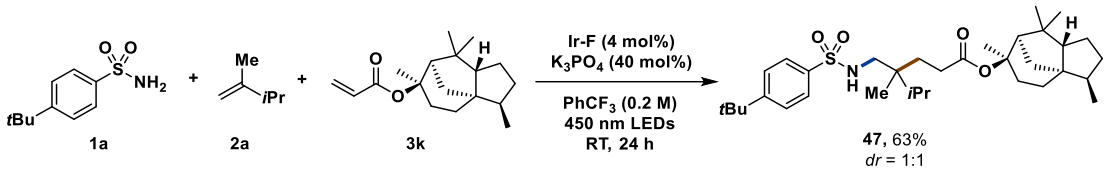


Methyl 5-((4-(*tert*-butyl)phenyl)sulfonamido)-4-methyl-4-((4*R*)-4-methyl-3-oxo-cyclohexyl)pentanoate (46): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), (2*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one **2s** (0.4 mmol, 65.6 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.34) as a yellow oil (73.2 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 8.5, 3.2 Hz, 2H), 7.56 – 7.48 (m, 2H), 5.50 (t, *J* = 7.1 Hz, 1H), 3.60 (d, *J* = 9.5 Hz, 3H), 2.81 – 2.59 (m, 2H), 2.32 – 2.27 (m, 1H), 2.26 – 2.18 (m, 2H), 2.18 – 2.07 (m, 2H), 1.81 (dq, *J* = 13.1, 3.3 Hz, 1H), 1.75 – 1.64 (m, 2H), 1.63 – 1.46 (m, 2H), 1.35 (t, *J* = 1.9 Hz, 10H), 1.28 – 1.17 (m, 2H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.83 (d, *J* = 8.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.9, 174.4, 174.3, 156.4, 136.7, 126.8 (2×C), 126.1 (2×C), 51.8, 48.0, 44.8, 44.6, 42.5, 38.3, 35.1, 31.1 (3×C), 29.5, 28.0, 25.8, 19.0, 14.3 ppm;

HRMS (ESI) calcd. for $C_{24}H_{38}NO_5S^+$ ($M+H^+$): 452.2465. Found: 452.2454.



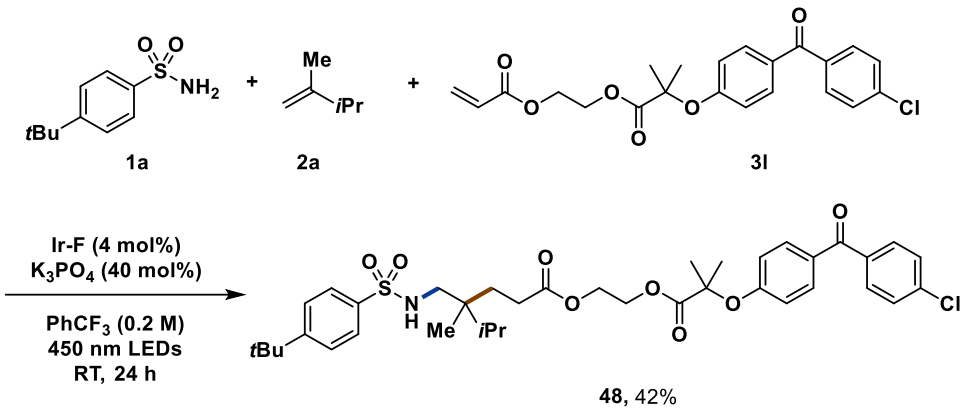
(3*R*,3a*S*,6*R*,7*R*,8a*S*)-3,6,8,8-tetramethyloctahydro-1*H*-3*a*,7-methanoazulen-6-yl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (47):

According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.1 mmol, 21.3 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.2 mmol, 25 μL, 2 equiv.), (3*R*,3a*S*,6*R*,7*R*,8a*S*)-3,6,8,8-tetramethyloctahydro-1*H*-3*a*,7-methanoazulen-6-yl acrylate **3k** (0.4 mmol, 110.6 mg, 4 equiv.), Ir-F (0.004 mmol, 4.5 mg, 0.04 equiv.) and K_3PO_4 (0.04 mmol, 8.5 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.3) as a yellow oil (35.4 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 5.13 (td, J = 7.0, 3.4 Hz, 1H), 2.75 (major, dd, J = 12.7, 7.6 Hz, 1H), 2.69 – 2.64 (m, 1H), 2.57 (minor, dd, J = 12.7, 6.3 Hz, 1H), 2.32 (s, 1H), 2.10 (t, J = 7.5 Hz, 2H), 2.05 – 2.00 (m, 1H), 1.87 (dq, J = 11.9, 7.7 Hz, 3H), 1.77 (t, J = 8.0 Hz, 2H), 1.66 – 1.62 (m, 2H), 1.54 – 1.50 (m, 2H), 1.44 (d, J = 2.4 Hz, 3H), 1.33 (s, 9H), 1.10 (s, 3H), 0.97 (s, 1H), 0.94 (d, J = 7.4 Hz, 3H), 0.85 – 0.77 (m, 12H), 0.73 (d, J = 7.9 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 156.0, 137.0, 126.9 (2×C), 126.0 (2×C), 86.8, 57.05(minor), 57.00 (major), 56.6, 53.9, 48.5 (minor), 48.4 (major), 43.4, 41.3, 41.0, 38.2, 37.0, 35.1, 33.1, 31.9, 31.7, 31.3, 31.1 (3×C), 29.6, 29.15 (major), 29.09 (minor), 28.5, 27.2, 25.8 (major), 25.7 (minor), 25.3, 18.3 (minor), 18.2 (major), 17.03 (major), 16.99 (minor), 15.5 ppm;

HRMS (ESI) calcd. for $C_{34}H_{55}NNaO_4S^+$ ($M+H^+$): 596.3744. Found: 596.3733.

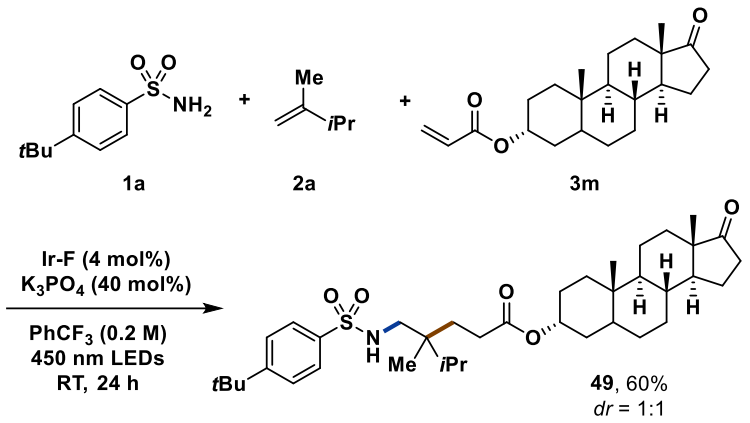


2-((2-(4-(4-Chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)ethyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (48): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.1 mmol, 21.3 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.2 mmol, 25 μL, 2 equiv.), 2-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)ethyl acrylate **3l** (0.4 mmol, 166.4 mg, 4 equiv.), Ir-F (0.004 mmol, 4.5 mg, 0.04 equiv.) and K_3PO_4 (0.04 mmol, 8.5 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 3:1, R_f = 0.3) as a yellow oil (30.3 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.75 (m, 2H), 7.72 (t, J = 8.5 Hz, 4H), 7.53 – 7.49 (m, 2H), 7.47 – 7.43 (m, 2H), 6.89 – 6.84 (m, 2H), 4.86 (t, J = 6.9 Hz, 1H), 4.37 (dd, J = 6.1, 3.3 Hz, 2H), 4.24 – 4.18 (m, 2H), 2.69 (qd, J = 12.8, 7.0 Hz, 2H), 2.15 (t, J = 8.0 Hz, 2H), 1.69 (s, 6H), 1.58 – 1.51 (m, 2H), 1.34 (s, 9H), 1.30 – 1.22 (m, 2H), 0.76 (dd, J = 9.7, 6.8 Hz, 6H), 0.69 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.4, 173.8, 173.6, 159.5, 156.3, 138.5, 136.8, 136.2, 132.1 (2×C), 131.3 (2×C), 130.5, 128.6 (2×C), 126.9 (2×C), 126.1 (2×C), 117.4 (2×C), 79.3, 63.2, 62.0, 48.4, 38.1, 35.1, 32.0, 31.1 (3×C), 29.6, 28.2, 25.5, 25.4, 18.2, 17.0, 16.9 ppm;

HRMS (APCI) calcd. for $C_{38}H_{49}ClNO_8S^+$ ($M+H^+$): 714.2862. Found: 714.2847.

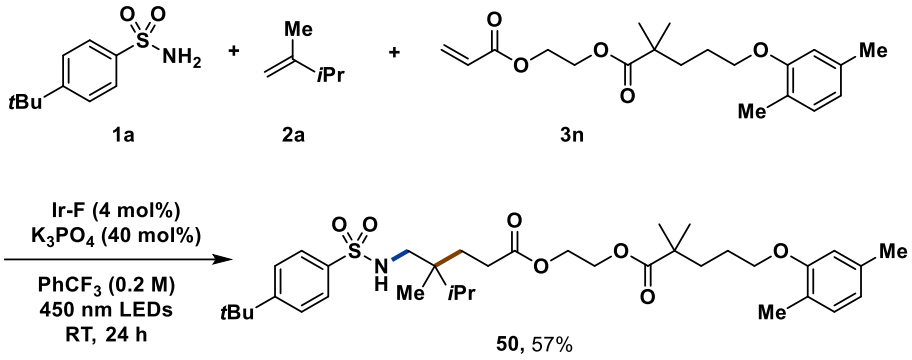


(3*R*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]-phenanthren-3-yl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethyl-hexanoate (49): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), (3R,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[*a*]phenanth-ren-3-yl acrylate **3m** (0.4 mmol, 137.8 mg, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.34) as a yellow oil (76.5 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.73 (m, 2H), 7.53 – 7.47 (m, 2H), 4.96 (s, 1H), 4.84 (td, *J* = 6.9, 4.7 Hz, 1H), 2.77 – 2.60 (m, 2H), 2.44 (dd, *J* = 19.2, 8.7 Hz, 1H), 2.21 (t, *J* = 7.7 Hz, 2H), 2.12 – 2.01 (m, 2H), 1.93 (td, *J* = 10.2, 5.7 Hz, 1H), 1.83 – 1.76 (m, 2H), 1.72 – 1.62 (m, 4H), 1.57 (dt, *J* = 13.8, 5.9 Hz, 4H), 1.50 – 1.41 (m, 5H), 1.34 (s, 9H), 1.31 – 1.19 (m, 7H), 0.86 (s, 3H), 0.81 (d, *J* = 5.9 Hz, 6H), 0.80 – 0.77 (m, 3H), 0.74 (d, *J* = 1.7 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.1, 174.0, 156.2, 136.9, 126.9 (2×C), 126.1 (2×C), 70.3, 54.2, 51.5, 48.4, 47.8, 40.1, 38.2, 36.0, 35.9, 35.1, 35.0, 32.84, 32.80, 31.9, 31.5, 31.1 (3×C), 30.7, 29.5, 28.8, 28.0, 26.0, 21.8, 20.1, 18.2, 17.0 (2×C), 13.8, 11.4 ppm;

HRMS (ESI) calcd. for $C_{38}H_{60}NO_5S^+$ ($M+H^+$):642.4187. Found: 642.4191.



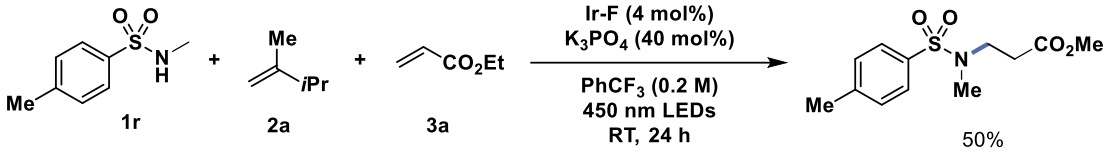
2-((5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)ethyl 4-(((4-(*tert*-butyl)phenyl)sulfonamido)methyl)-4,5-dimethylhexanoate (50): According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.1 mmol, 21.3 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a**(0.2 mmol, 25 μL, 2 equiv.), 2-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)ethyl acrylate **3n** (0.4 mmol, 166.4 mg, 4 equiv.), Ir-F (0.004 mmol, 4.5 mg, 0.04 equiv.) and K_3PO_4 (0.04 mmol, 8.5 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product was isolated by column chromatography on silica gel (PE: EA = 2:1, R_f = 0.3) as a yellow oil (36.8 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 7.4 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 6.60 (s, 1H), 4.83 (t, J = 7.0 Hz, 1H), 4.27 – 4.21 (m, 4H), 3.90 (d, J = 5.5 Hz, 2H), 2.68 (qd, J = 12.8, 7.0 Hz, 2H), 2.29 (s, 3H), 2.21 (t, J = 7.9 Hz, 2H), 2.16 (s, 3H), 1.73 (s, 4H), 1.67 – 1.61 (m, 1H), 1.56 (dt, J = 11.3, 7.3 Hz, 2H), 1.34 (s, 9H), 1.22 (s, 6H), 0.80 – 0.75 (m, 6H), 0.70 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ 177.5, 174.0, 156.9, 156.3, 136.8, 136.5, 130.3, 126.9 (2×C), 126.1 (2×C), 123.5, 120.7, 111.9, 67.9, 62.4, 62.0, 48.4, 42.1, 38.1, 37.0, 35.1, 32.0, 31.1 (3×C), 29.5, 28.3, 25.2 (3×C), 21.4, 18.2, 17.0, 16.9, 15.8 ppm;

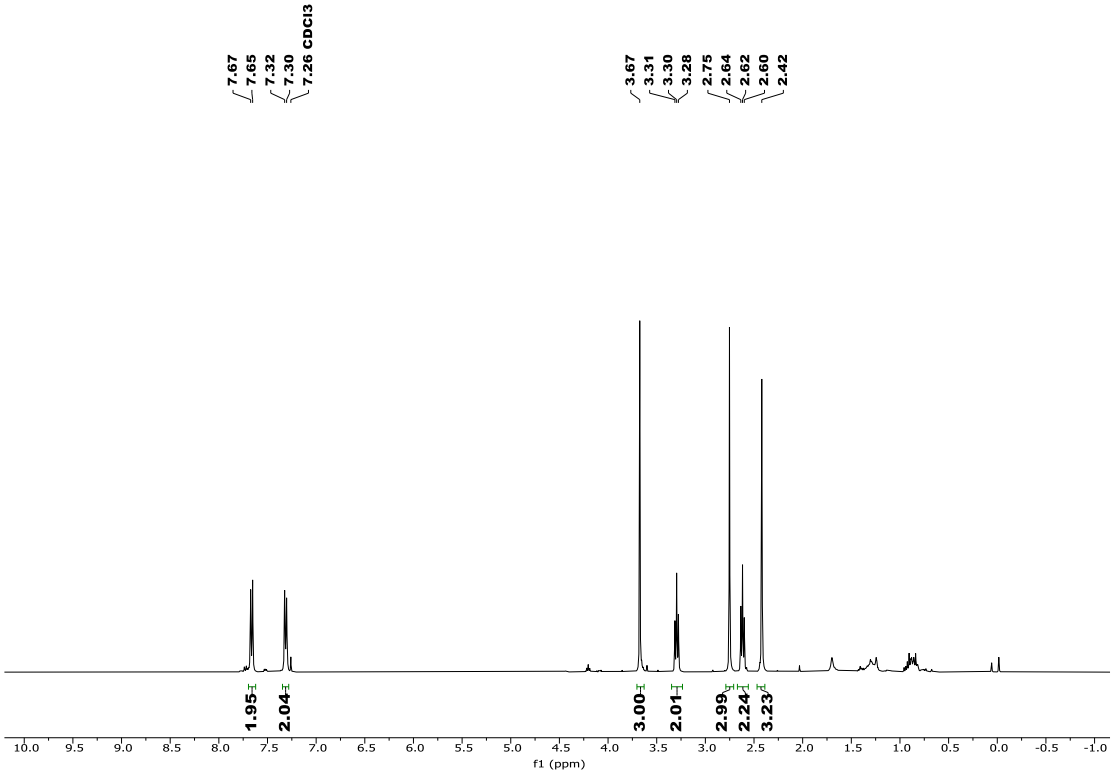
HRMS (APCI) calcd. for $C_{36}H_{56}NO_7S^+$ ($M+H^+$): 646.3772. Found: 646.3759.

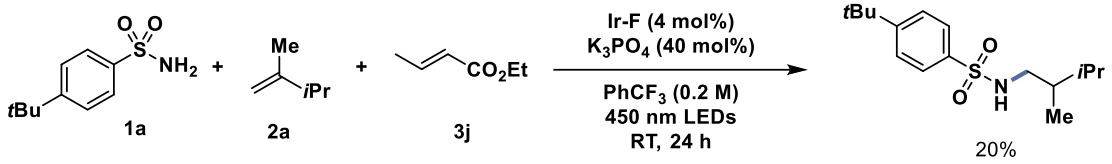
Failure examples



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.67 (s, 3H), 3.30 (t, *J* = 7.2 Hz, 2H), 2.75 (s, 3H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H) ppm.

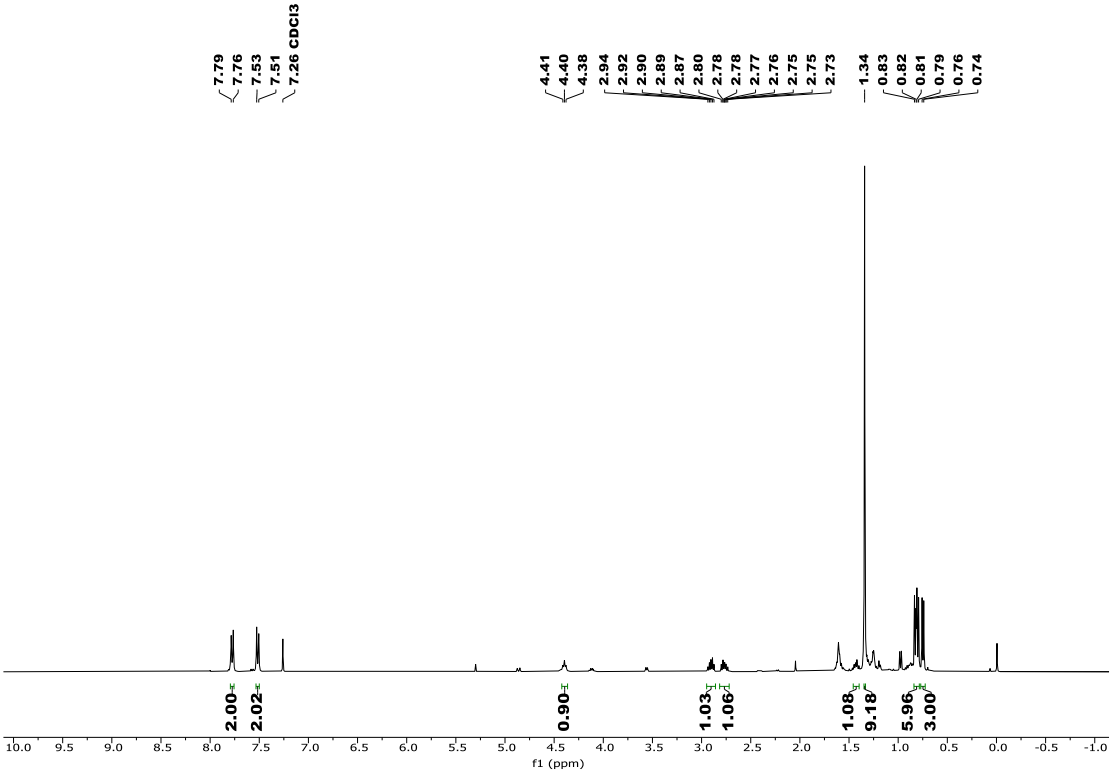
^{1}H NMR (400 MHz, $CDCl_3$)





^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 4.40 (t, *J* = 6.4 Hz, 1H), 2.90 (dt, *J* = 12.4, 6.2 Hz, 1H), 2.82 – 2.72 (m, 1H), 1.43 (q, *J* = 7.1 Hz, 1H), 1.34 (s, 9H), 0.81 (dd, *J* = 9.9, 6.9 Hz, 6H), 0.75 (d, *J* = 6.8 Hz, 3H) ppm.

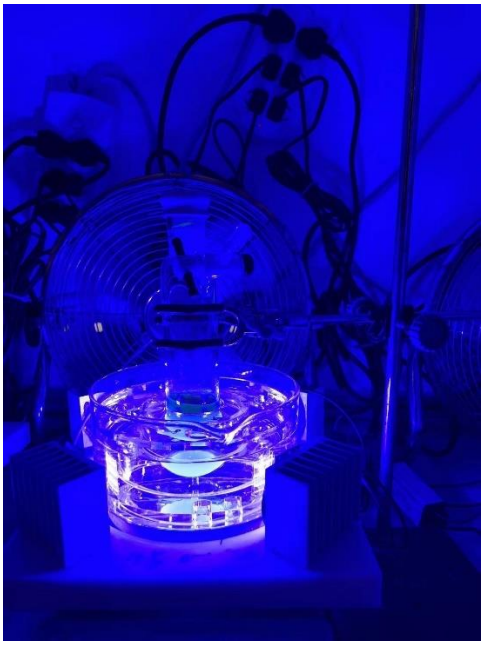
^{1}H NMR (400 MHz, $CDCl_3$)



4. Gram-scale Experiment

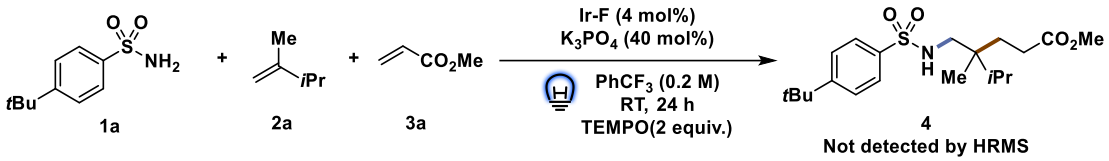
A 100 mL Schlenk tube was charged with a stir bar, **1a** (6.0 mmol, 1.28 g, 1.0 equiv.), Ir-F (0.24 mmol, 269.0 mg, 0.04 equiv.) and K_3PO_4 (2.4 mmol, 509.5 mg, 0.4 equiv.). After the flask was evacuated and back filled with N_2(g), $PhCF_3$ (30 ml), **2a** (12 mmol, 1.5 mL, 2 equiv.) and **3a** (12 mmol, 1.1 mL, 2 equiv.) was added, then irradiated with a 30 W blue LED lamp (450 nm, at approximately 3 cm away from the light source) at room temperature. After 24 h, the reaction mixture was transferred to a 100mL round-bottom bottle and concentrated *in vacuo*. Purification by column chromatography on silica gel (PE: EA=5:1) provided the desired product **4** (1.44g, 63%).

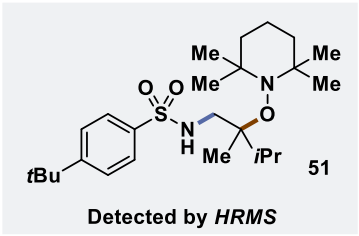
Also, to improve the method's sustainability and scalability, we decreased our photocatalyst loading. A 100 mL Schlenk tube was charged with a stir bar, **1a** (5.0 mmol, 1.07 g, 1.0 equiv.), Ir-F (0.1 mmol, 112 mg, 0.02 equiv.) and K_3PO_4 (2.0 mmol, 425 mg, 0.4 equiv.). After the flask was evacuated and back filled with N_2(g), $PhCF_3$ (25 ml), **2a** (10 mmol, 1.2 mL, 2 equiv.) and **3a** (10 mmol, 0.9 mL, 2 equiv.) was added, then irradiated with a 30 W blue LED lamp (450 nm, at approximately 3 cm away from the light source) at room temperature. After 24 h, the reaction mixture was transferred to a 100mL round-bottom bottle and concentrated *in vacuo*. Purification by column chromatography on silica gel (PE: EA=5:1) provided the desired product **4** (1.18g, 53%).



5. Mechanistic Studies

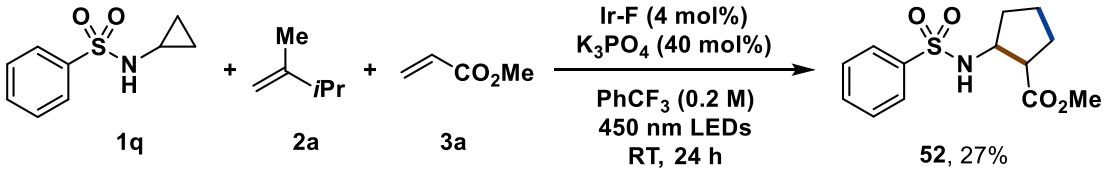
5.1 Radical-trapping Experiment with TEMPO





According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.), K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) and TEMPO (0.4 mmol, 62.5 mg, 2 equiv.) in $PhCF_3$ were used. The reaction was carried out under an atmosphere of nitrogen and was stirred under 450nm LED irradiation for 24 hours. HRMS analysis of the reaction mixture showed that no desired product formed and **47** could be detected.

5.2 Radical Probing Experiment

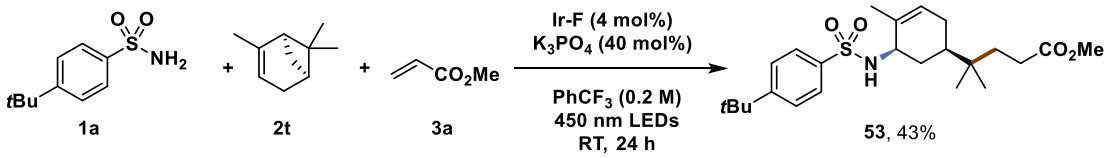


According to the General procedure C, N-cyclopropylbenzenesulfonamide **1q** (0.2 mmol, 39.5 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product **52** was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.25) as a yellow oil (15.3 mg, 27%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.86 (m, 2H), 7.61 – 7.56 (m, 1H), 7.56 – 7.50 (m, 2H), 5.20 (dd, *J* = 7.1, 3.5 Hz, 1H), 3.76 (p, *J* = 7.3 Hz, 1H), 3.57 (s, 3H), 2.66 (dt, *J* = 9.3, 7.6 Hz,

1H), 1.98 (dqd, *J* = 9.3, 7.3, 5.6 Hz, 2H), 1.70 – 1.58 (m, 2H), 1.48 (dq, *J* = 12.0, 7.5 Hz, 1H) ppm;

^{13}C NMR (101 MHz, CDCl$_3$): δ 174.6, 140.1, 132.7, 129.5, 129.1, 128.2, 127.2, 57.8, 52.0, 50.7, 33.6, 28.1, 22.8 ppm.

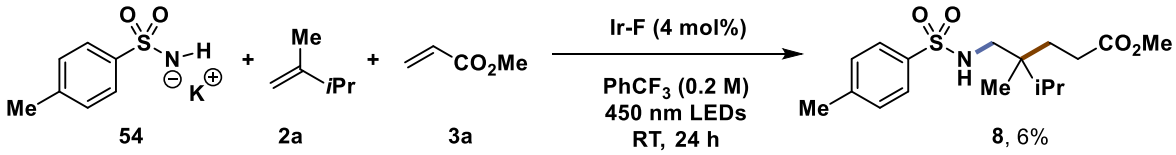


According to the General procedure C, 4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), (*1S*) - (-) -alpha-Pinene **2t** (0.4 mmol, 62.3 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.) and K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were used. After 24 h, the product **53** was isolated by column chromatography on silica gel (PE: EA = 5:1, R_f = 0.28) as a yellow oil (37.4 mg, 43%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.84 – 7.77 (m, 2H), 7.53 – 7.45 (m, 2H), 5.50 (dt, *J* = 5.4, 1.7 Hz, 1H), 4.65 (d, *J* = 8.3 Hz, 1H), 3.65 (s, 3H), 2.25 – 2.12 (m, 2H), 1.95 – 1.86 (m, 1H), 1.71 – 1.64 (m, 1H), 1.63 – 1.57 (m, 1H), 1.50 – 1.48 (m, 3H), 1.48 – 1.35 (m, 2H), 1.32 (s, 9H), 1.30 – 1.21 (m, 2H), 1.17 (dd, *J* = 12.9, 4.1 Hz, 1H), 0.66 (s, 3H), 0.63 (s, 3H) ppm;

^{13}C NMR (101 MHz, CDCl$_3$): δ 174.7, 156.3, 138.3, 131.6, 127.1, 126.9, 126.1, 52.9, 51.6, 36.0, 35.1, 34.4, 33.8, 31.1, 30.2, 29.0, 26.2, 24.3, 23.6, 20.2 ppm.

5.3 Sulfonamide anion as coupling partner

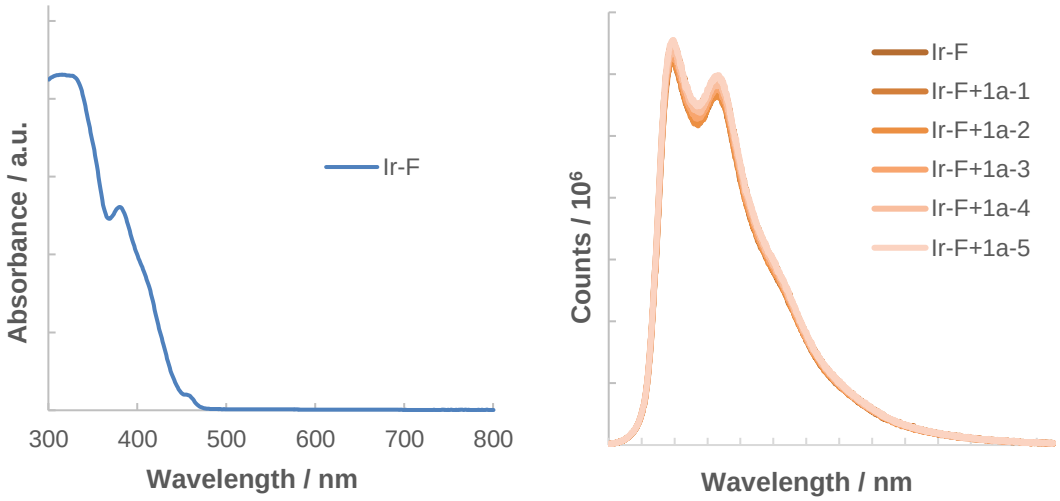


According to the General procedure C, potassium tosylamide **54** (0.2 mmol, 41.9 mg, 1.0 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.), K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) and TEMPO (0.4 mmol, 62.5 mg, 2 equiv.) in $PhCF_3$ were used. After 24 h, the yield of **8** was measured 6% by ^{1}H NMR with CH_2Br_2(0.2 mmol, 14 μL) as internal standard.

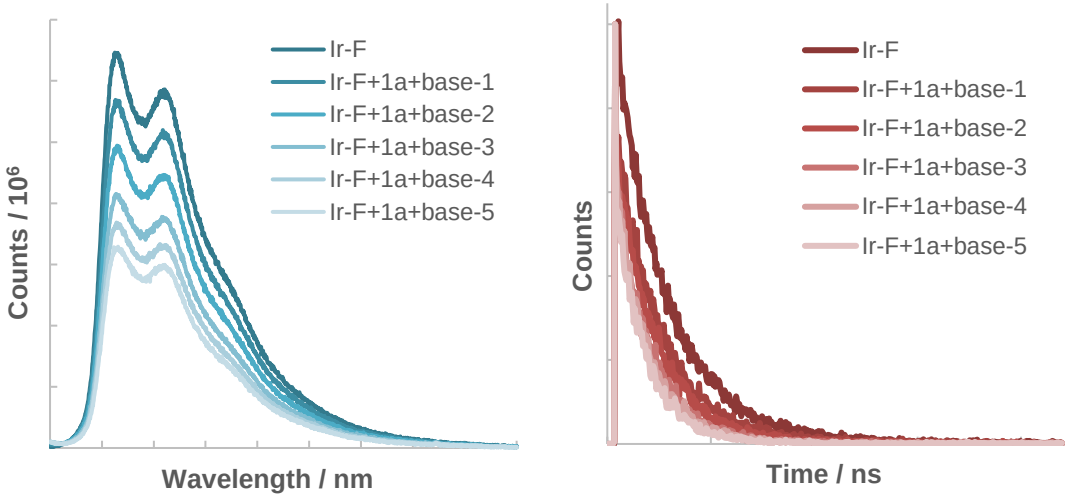
5.4 Stern-Volmer Luminescence Quenching Analyses

Emission intensities were recorded using a Fluorolog-3 luminescence spectrometer. Solutions of different complex were prepared and introduced to a 1 cm path length quartz cuvette in glovebox. All the solution was excited at 420 nm and the emission intensity was collected at 538 nm. In a typical experiment, to a 0.002 M solution of Ir-F in $PhCF_3$ was added the appropriate amount of **1a** solution in $PhCF_3$ or **1a** and K_3PO_4 solution in $PhCF_3$ in a screw-top quartz cuvette in glovebox and the emission of the sample was collected.

The solution of Ir-F (0.002M, 10 mL), 1a (0.04M, 10mL) and 1a + K_3PO_4 (0.004M, 10mL) were prepared in glovebox. Add 100 μ L Ir-F solution and 100 μL, 200 μL, 300 μL, 400 μL, 500 μL 1a solution respectively in the quartz cuvette, then diluted the solution to 2 mL. (Figure S.b)



(a) (b)



(c) (d)

Figure S1. (a) UV-Vis Absorption Spectra. UV-visible spectra were recoded with Ir-F (0.002 M) in degassed $PhCF_3$. (b) Stern-Volmer quenching experiments of PC and **1a**. (c) Stern-Volmer quenching experiments of PC, **1a** and K_3PO_4. (d) Transient Absorption Spectroscopy experiments of PC, **1a** and K_3PO_4. The decay data was collected at 430nm upon 420nm excitation.

The solution of Ir-F in $PhCF_3$ (0.002M, 10 mL), 1a in $PhCF_3$ (0.04M, 10mL) and 1a + K_3PO_4 in $PhCF_3$ (0.004M, 10mL) were prepared in glovebox. Add 100 μL Ir-F solution and 100 μL, 200 μL, 300 μL, 400 μL, 500 μL 1a + K_3PO_4 solution respectively in the quartz cuvette, then diluted the solution to 2 mL. Because K_3PO_4 is insoluble in $PhCF_3$, transient absorption spectroscopy experiments were illustrated to explain the quenching phenomenon with photocatalyst, 1a and K_3PO_4 as a PCET process (Figure S1.c and d), which would not be influenced by scattering.

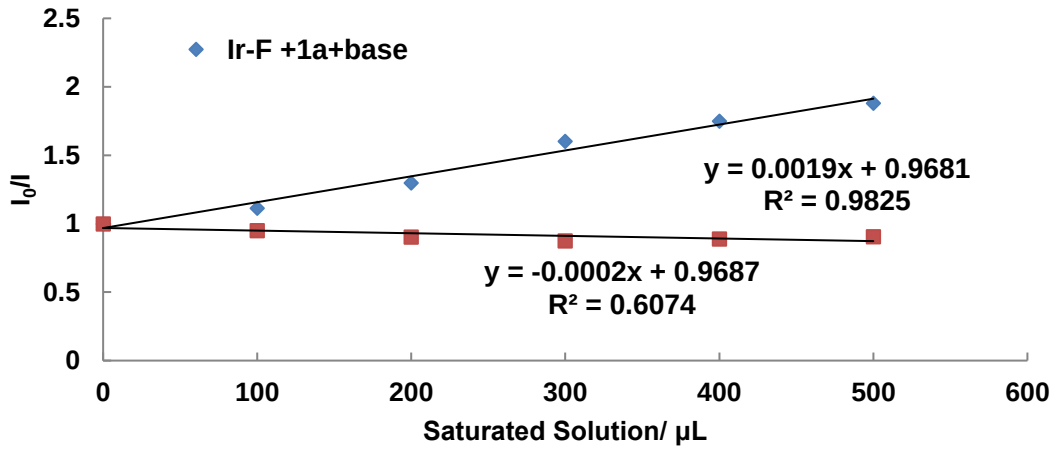
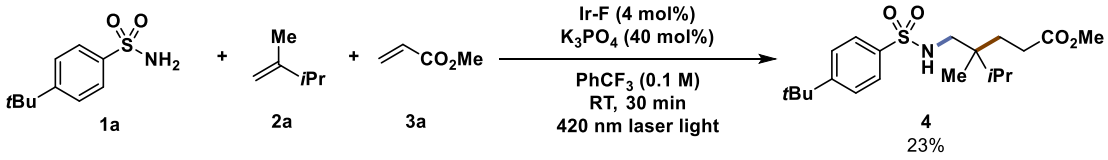


Figure S2. Stern-Volmer Luminescence Quenching Analysis

5.5 Quantum Yield Experiment



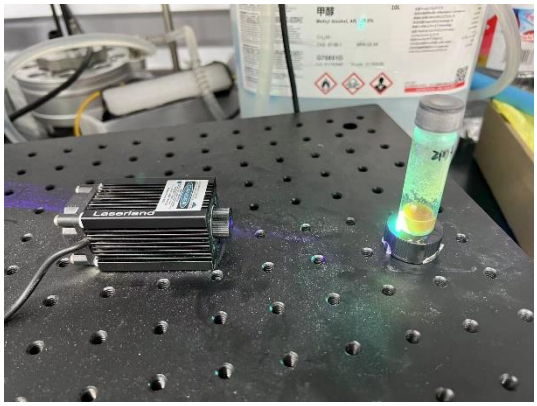
4-*tert*-butyl-benzenesulfonamide **1a** (0.2 mmol, 42.7 mg, 1 equiv.), 2,3-dimethylbut-1-ene **2a** (0.4 mmol, 50 μL, 2 equiv.), methyl acrylate **3a** (0.4 mmol, 36 μL, 2 equiv.), Ir-F (0.008 mmol, 9.0 mg, 0.04 equiv.), K_3PO_4 (0.08 mmol, 16.9 mg, 0.4 equiv.) in $PhCF_3$ were were prepared and introduced to a 1 cm path length quartz cuvette equipped with a Teflon® septum in glovebox. The reaction was carried out under an atmosphere of nitrogen and was stirred under 420nm Laser light irradiation for 30 minutes.

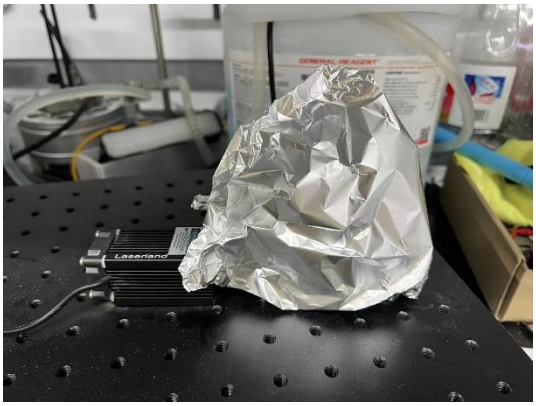
To determine the photon flux of the LED, optical power meter was used. The measured value is 244.7 mW.

The yield was measured through ^{1}H NMR by adding 11 μL CH_3NO_3 as internal standard. The measured yield is 23% after stirred for 30 minutes, which indicated that the quantum yield was 0.028 using the ***Equivalent 1*** below.

***Equivalent 1*:**

$$\Phi = \frac{Ne}{Np} \times 100\% = \frac{1.2 \times 10^8 \times (\upsilon \times \mathrm{K})}{(I \times A \times \lambda)}$$


甲醇
Laserland


Laserland

6. Cyclic voltammetry

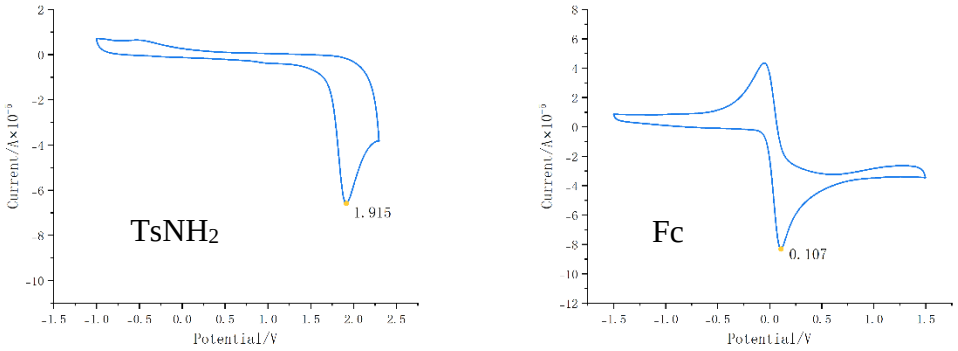


Figure S3 Cyclic voltammetry of **1e** ($E_{p/2}^{ox}$ + 1.81 V vs Fc/Fc^+). CV conditions: MeCN (0.2M), $LiClO_4$ electrolyte, Glassy Carbon Electrode working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode, 0.05 V/s.

$E_{p/2}^{ox}$ = +1.915V - 0.107V = +1.81 V vs Fc/Fc^+

The calculated potential was converted to SCE using the formula $E_{p/2}$ (Fc/Fc^+) = +0.40 V vs SCE. A value of +2.21 V vs SCE was obtained for comparison purposes against literature.

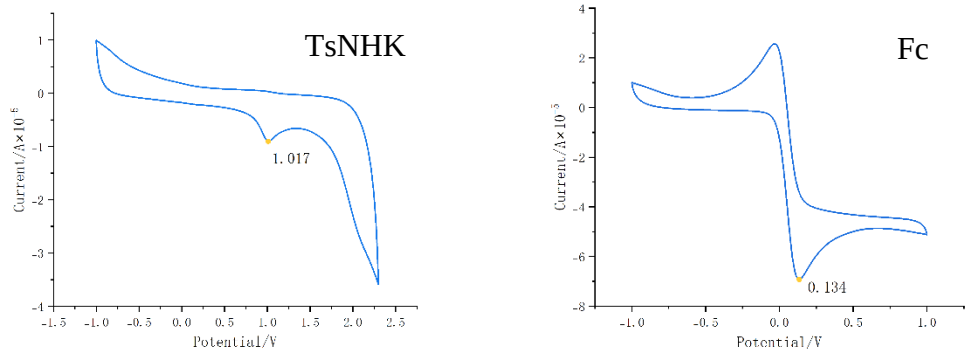


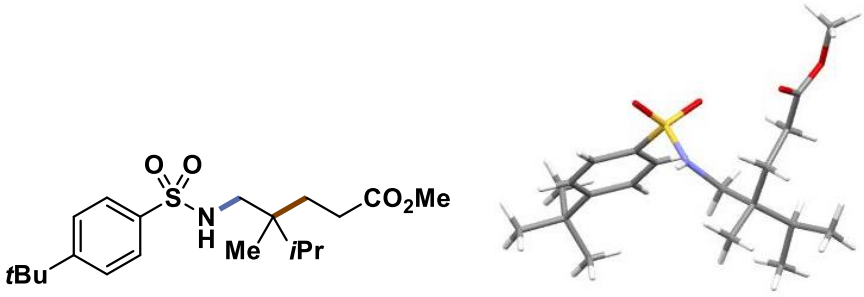
Figure S4 Cyclic voltammetry of **50** ($E_{p/2}^{ox}$ + 0.88 V vs Fc/Fc^+). CV conditions: MeCN (saturated at 25 °C), $LiClO_4$ electrolyte, Glassy Carbon Electrode working electrode, Pt counter electrode, $Ag/AgNO_3$ reference electrode, 0.05 V/s.

$E_{p/2}^{ox}$ = +1.017V - 0.134V = + 0.88 V vs Fc/Fc^+

The calculated potential was converted to SCE using the formula $E_{p/2}$ (Fc/Fc^+) = +0.40 V vs SCE. A value of +1.28 V vs SCE was obtained for comparison purposes against literature.

7. X-ray Structure of 4

CCDC 2335224



4

Deposition number 2335224

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Bond precision:   C-C = 0.0043 A          Wavelength=1.34138

Cell:             a=13.1602(6)     b=9.3426(4)         c=17.4352(8)
                  alpha=90         beta=94.511(2)      gamma=90
Temperature:      150 K

                  Calculated                Reported
Volume            2137.03(17)               2137.03(17)
Space group       P 21/n                    P 1 21/n 1
Hall group        -P 2yn                    -P 2yn
Moiety formula    C20 H33 N O4 S            C20 H33 N O4 S
Sum formula       C20 H33 N O4 S            C20 H33 N O4 S
Mr                383.53                    383.53
Dx,g cm-3         1.192                     1.192
Z                 4                         4
Mu (mm-1)         0.999                     0.999
F000              832.0                     832.0
F000'             834.89
h,k,lmax          16,11,21                  16,11,21
Nref              4390                      4376
Tmin,Tmax                                   0.612,0.751
Tmin'

Correction method= # Reported T Limits: Tmin=0.612 Tmax=0.751
AbsCorr = NONE

Data completeness= 0.997          Theta(max)= 57.053

R(reflections)= 0.0642( 3443)                wR2(reflections)=
                                             0.1829( 4376)
S = 1.051                 Npar= 243
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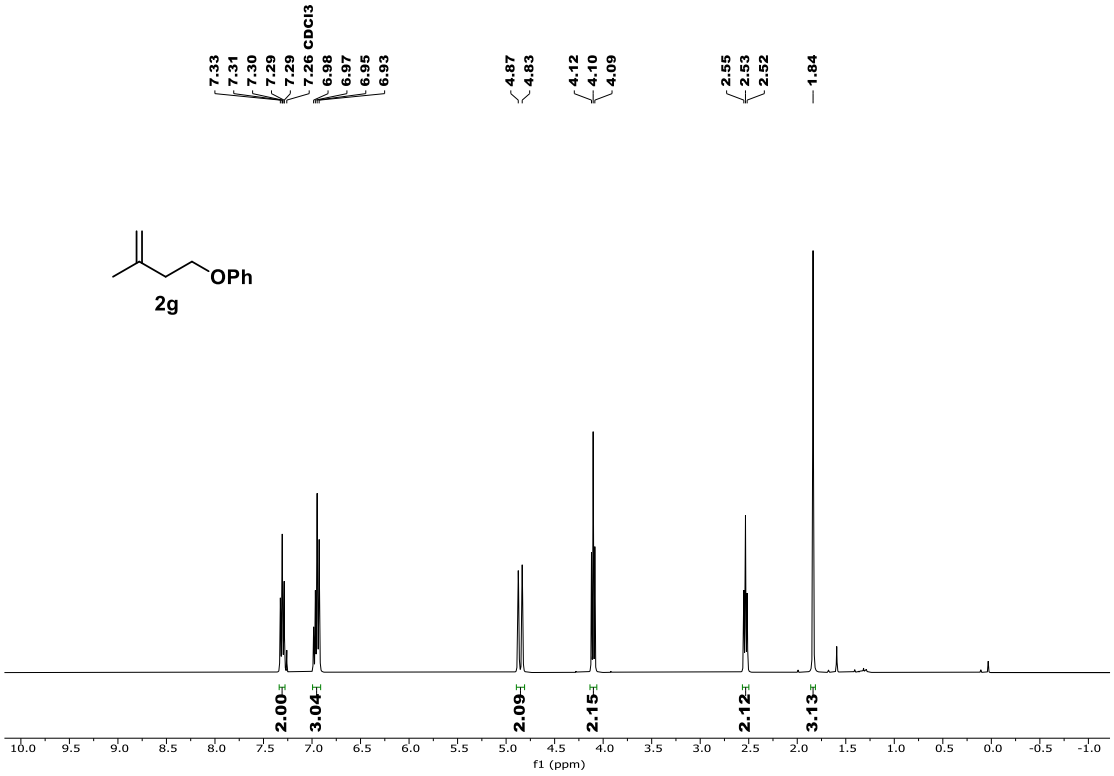
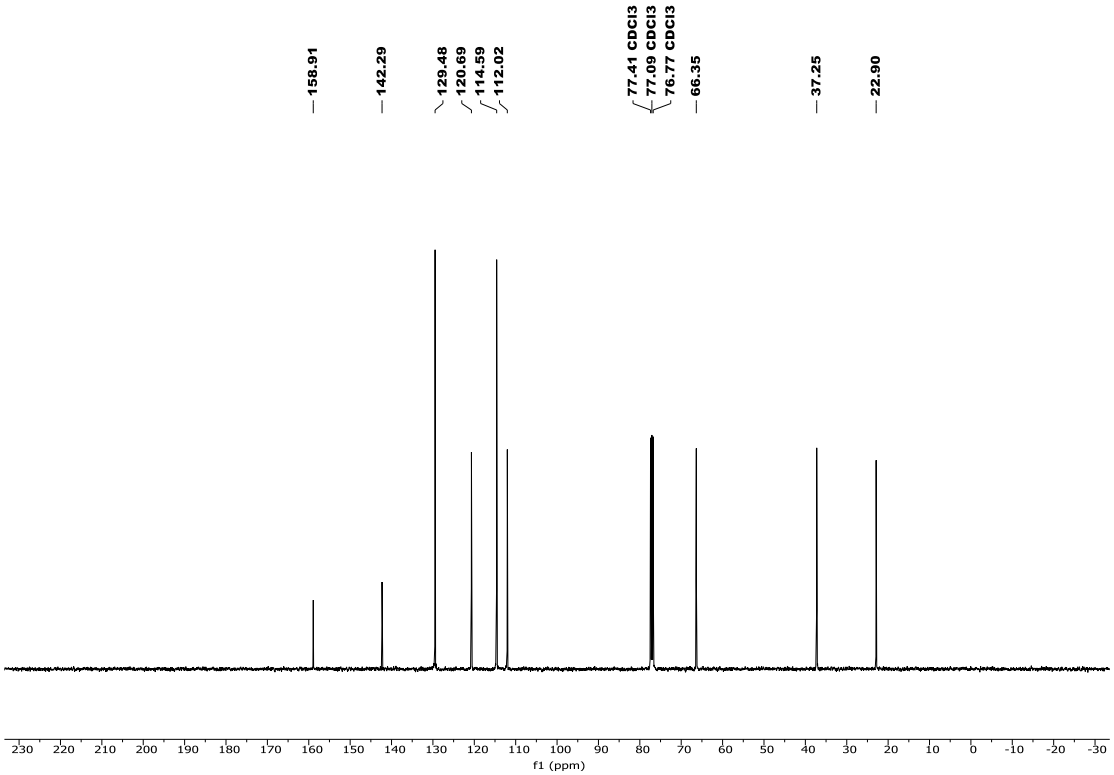
8. ^{1}H and ^{13}C NMR Spectra of Compounds

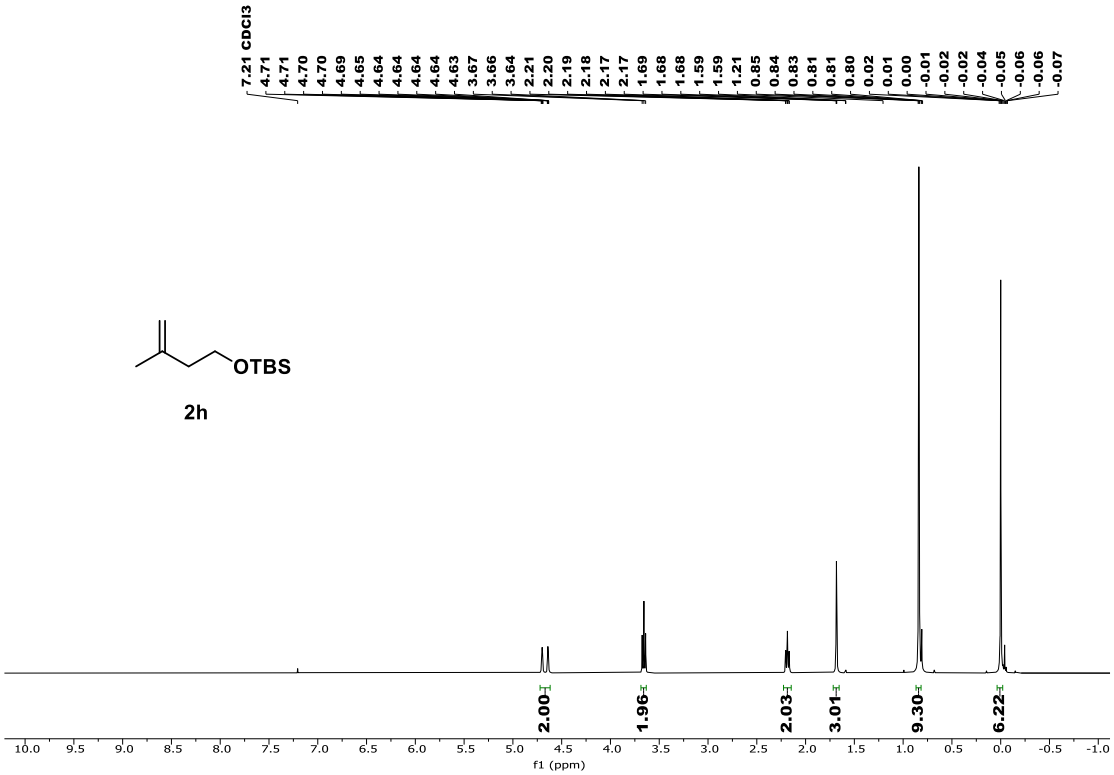
^{1}H NMR (400 MHz, $CDCl_3$):



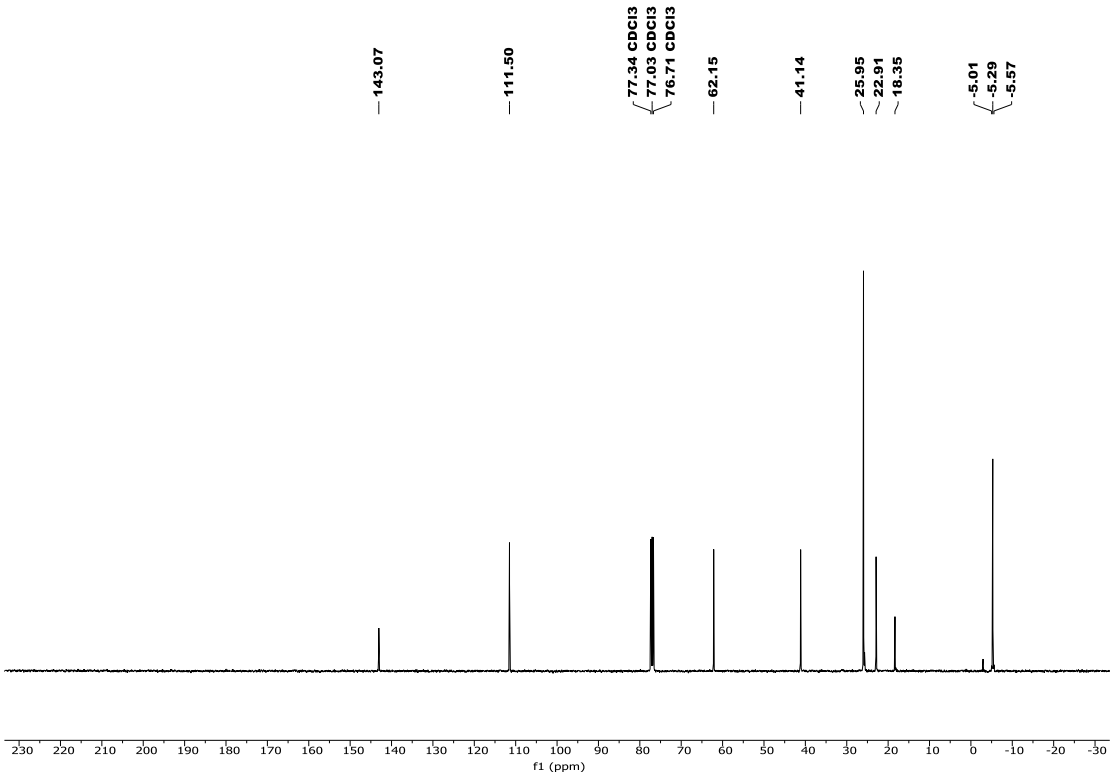
^{13}C NMR (101 MHz, $CDCl_3$):



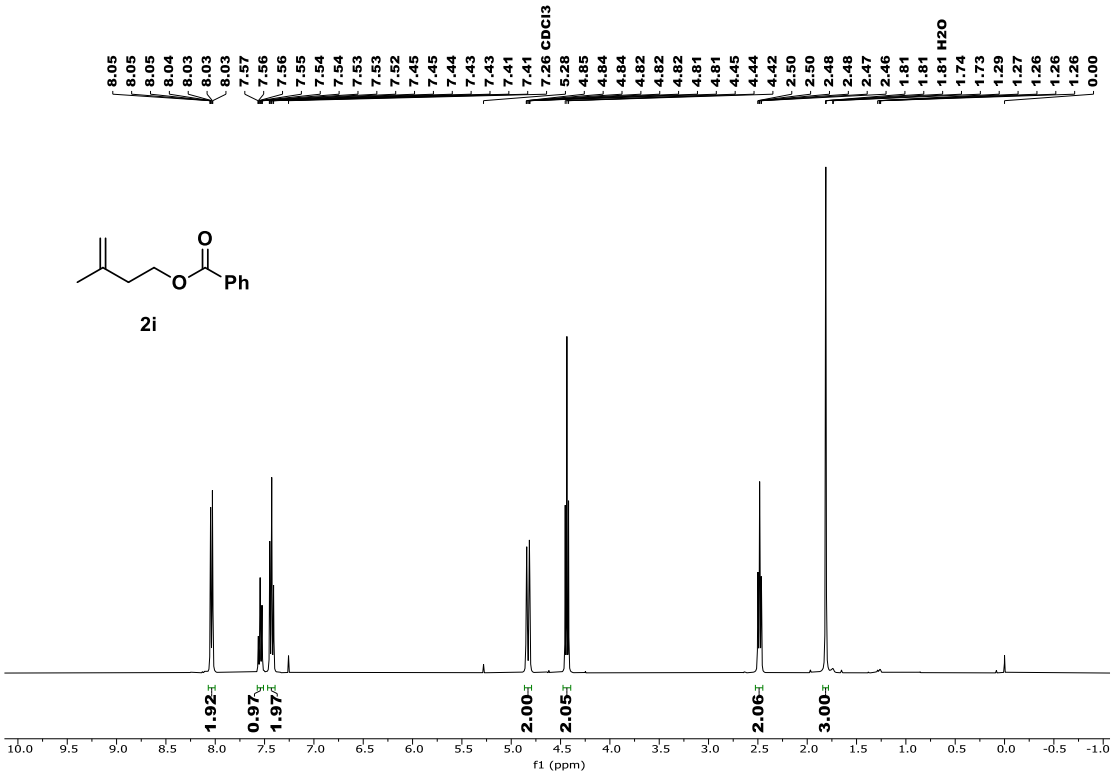
^{1}H NMR (400 MHz, $CDCl_3$):



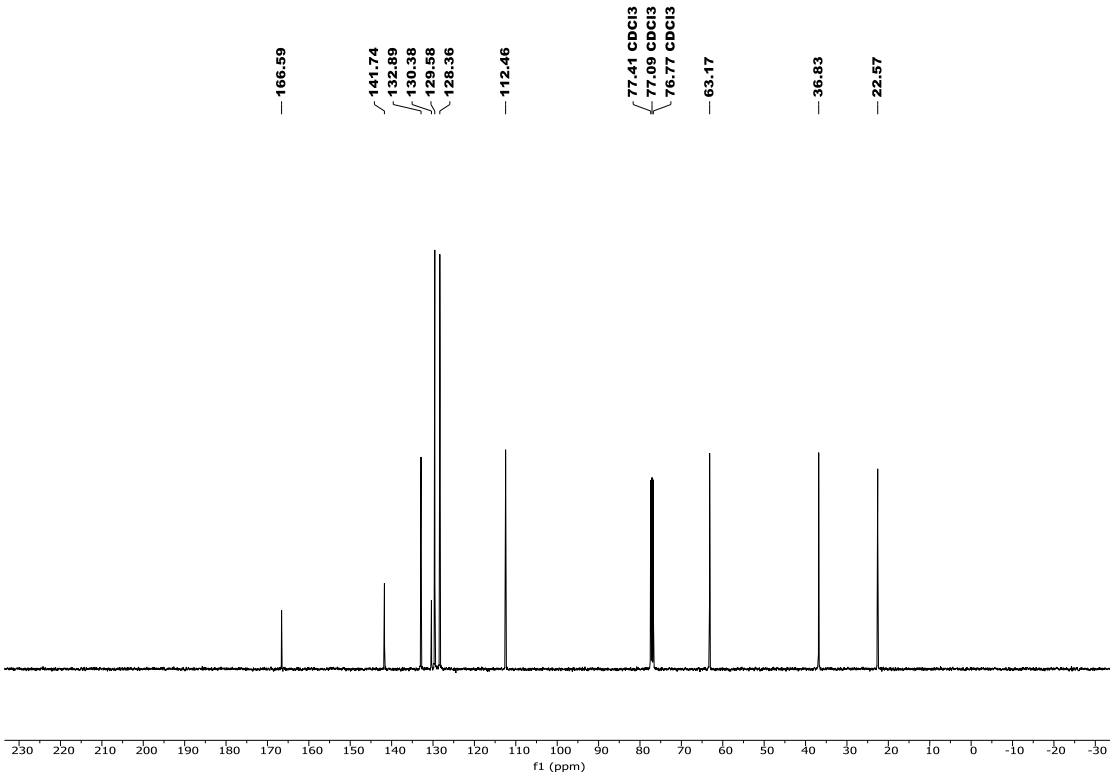
^{13}C NMR (101 MHz, $CDCl_3$):



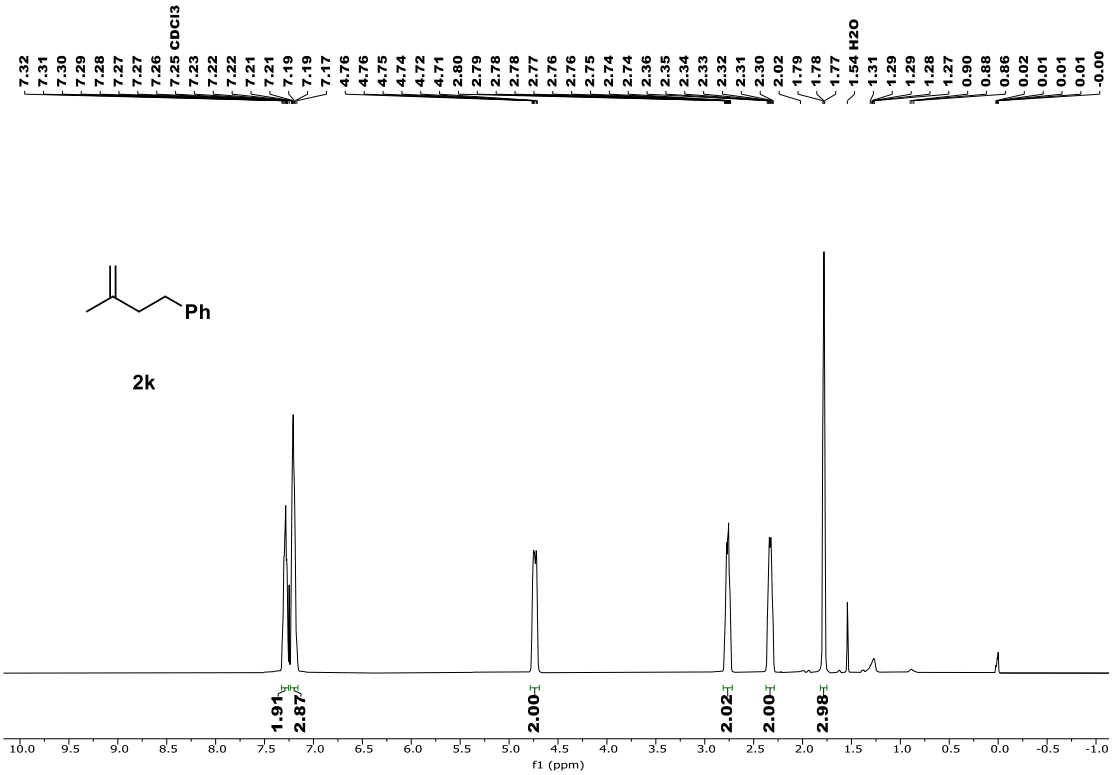
^{1}H NMR (400 MHz, $CDCl_3$):



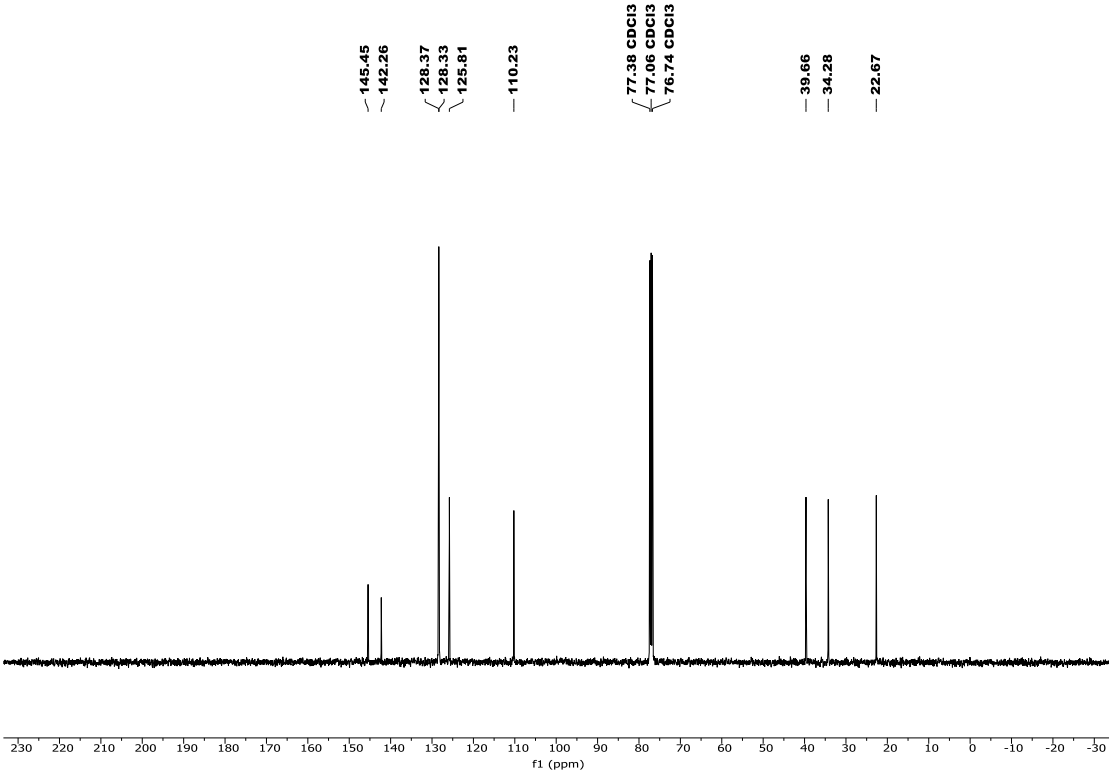
^{13}C NMR (101 MHz, $CDCl_3$):



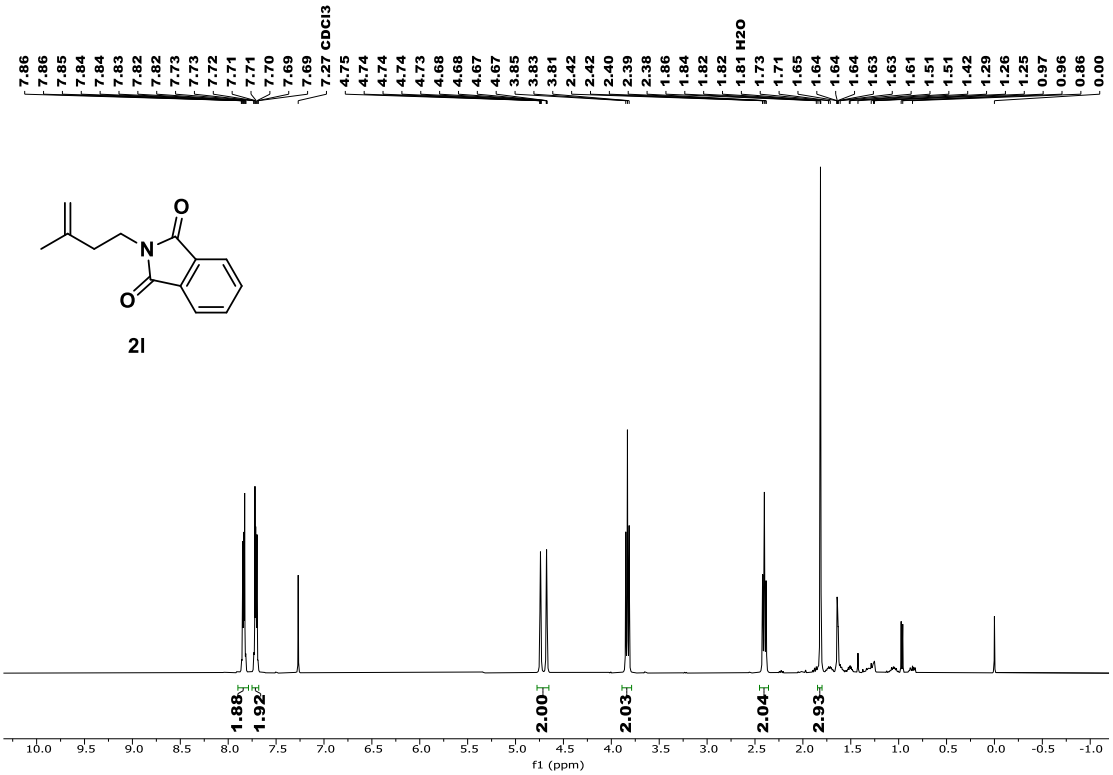
^{1}H NMR (400 MHz, $CDCl_3$):



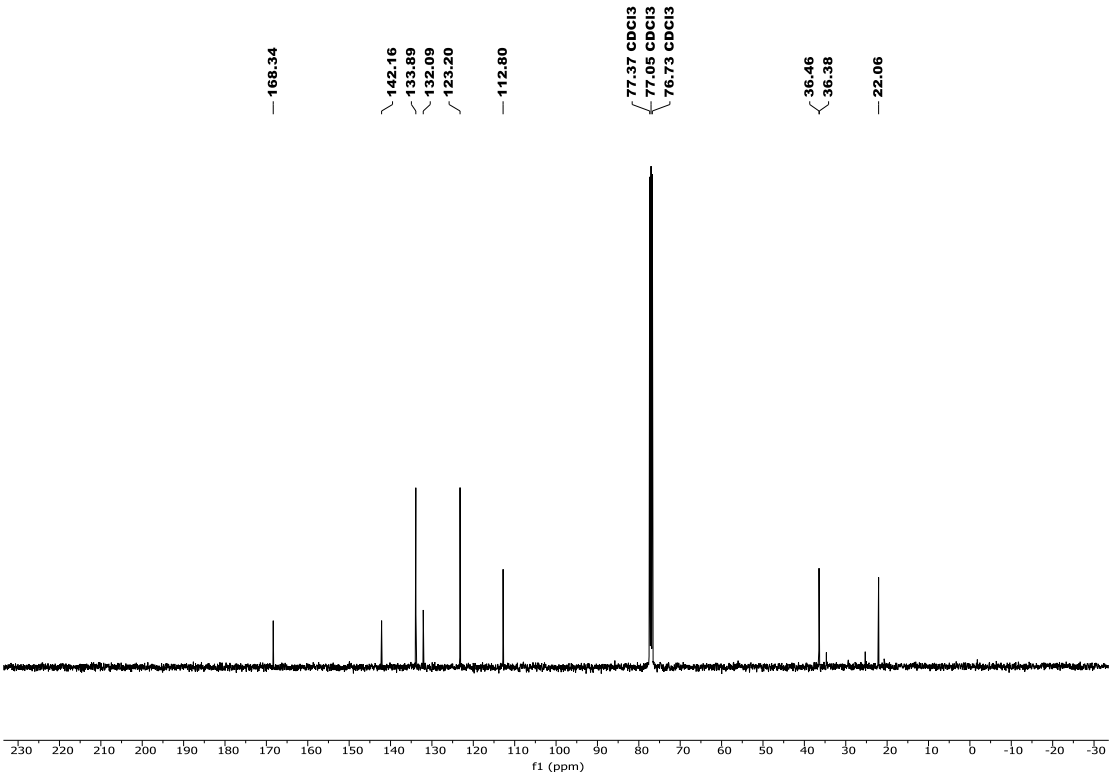
^{13}C NMR (101 MHz, $CDCl_3$):



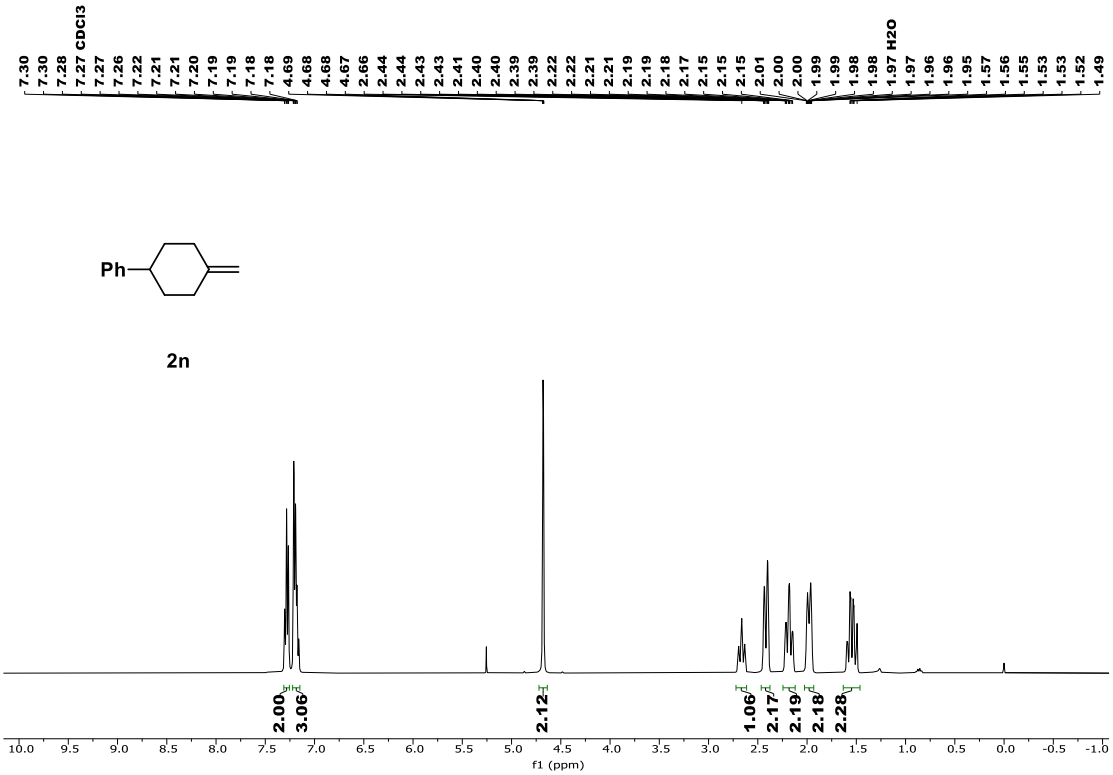
^{1}H NMR (400 MHz, $CDCl_3$):



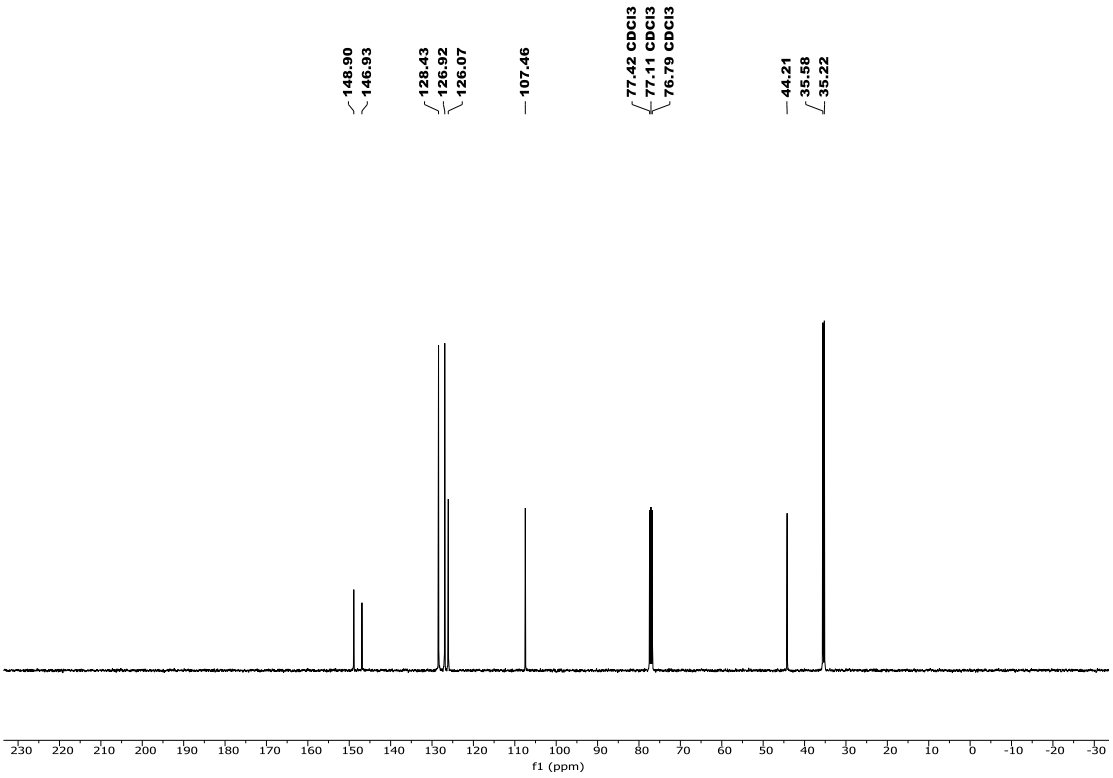
^{13}C NMR (101 MHz, $CDCl_3$):



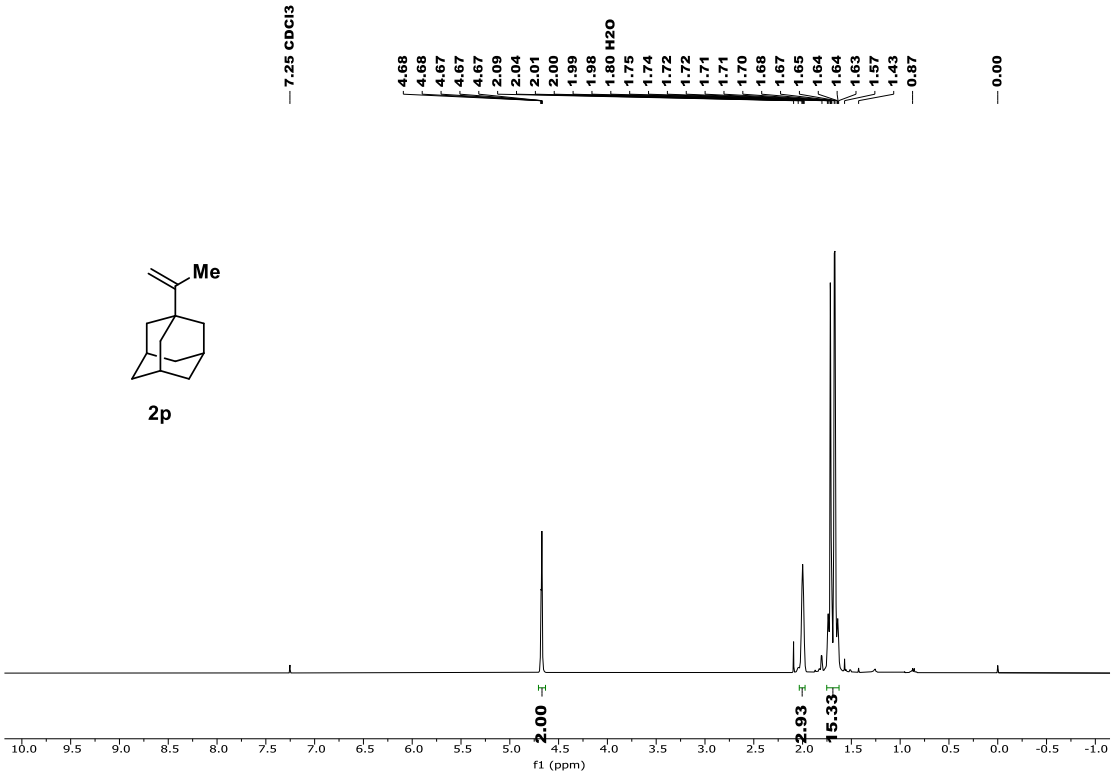
^{1}H NMR (400 MHz, $CDCl_3$):



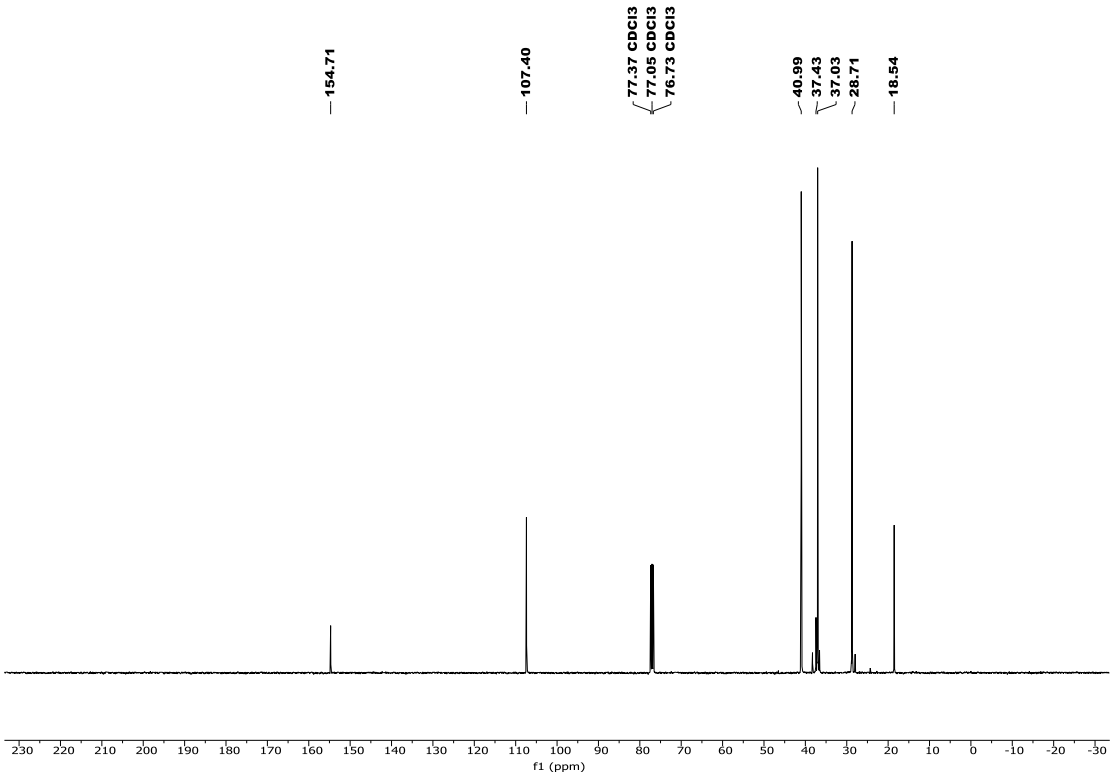
^{13}C NMR (101 MHz, $CDCl_3$):



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



^{13}C NMR (101 MHz, $CDCl_3$):



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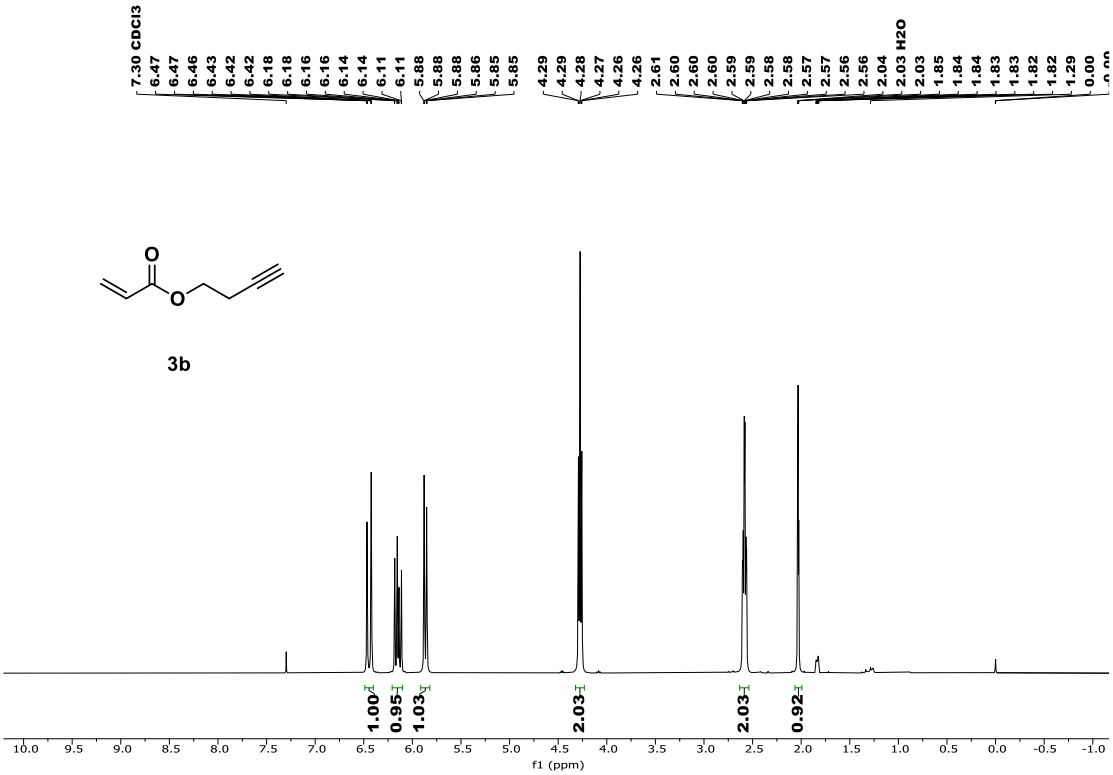
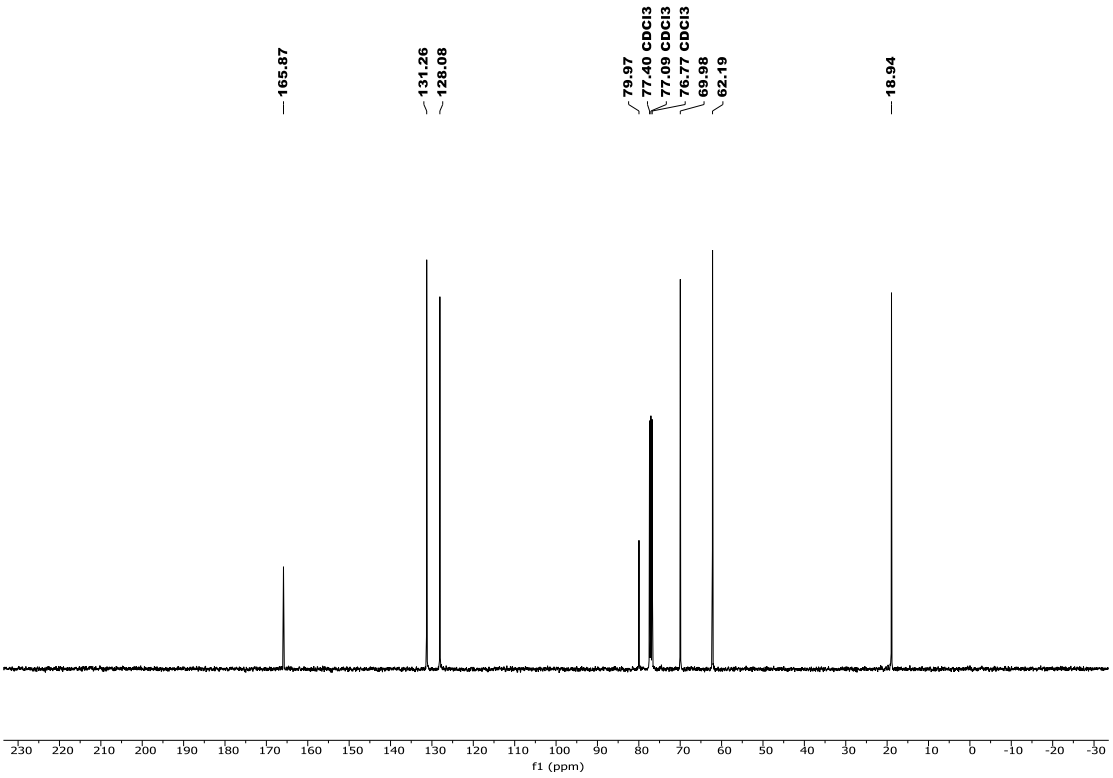


^{13}C NMR (101 MHz, $CDCl_3$):



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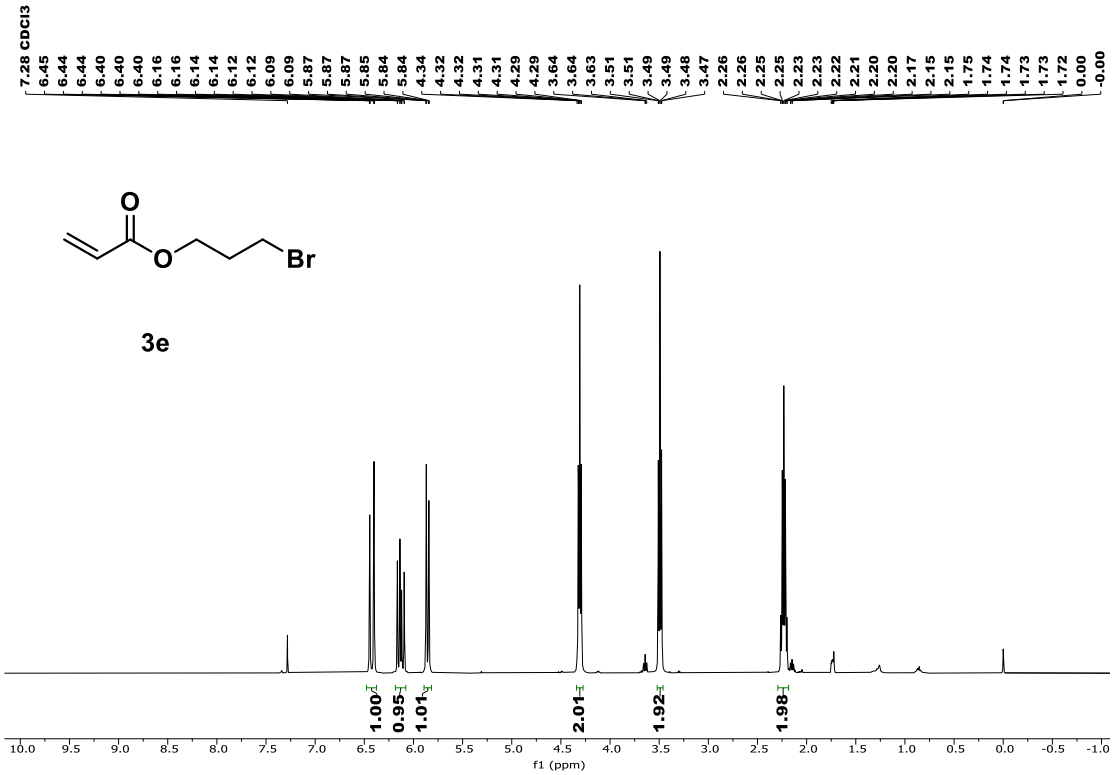
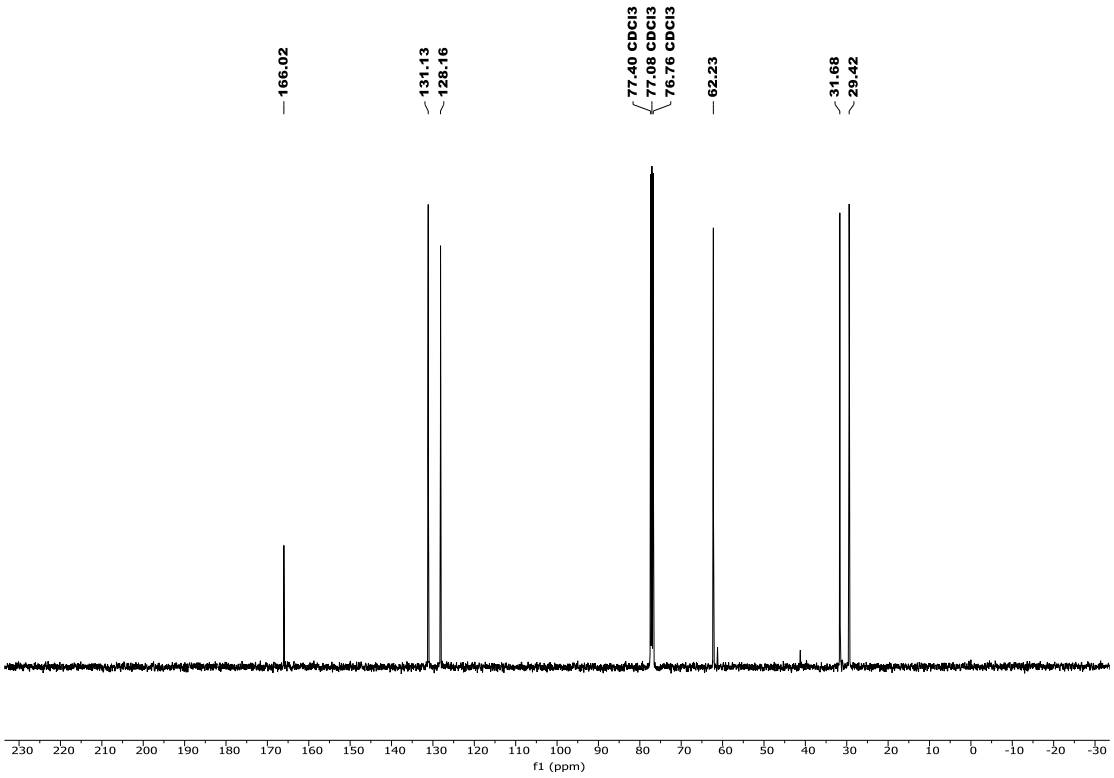


^{13}C NMR (101 MHz, $CDCl_3$):



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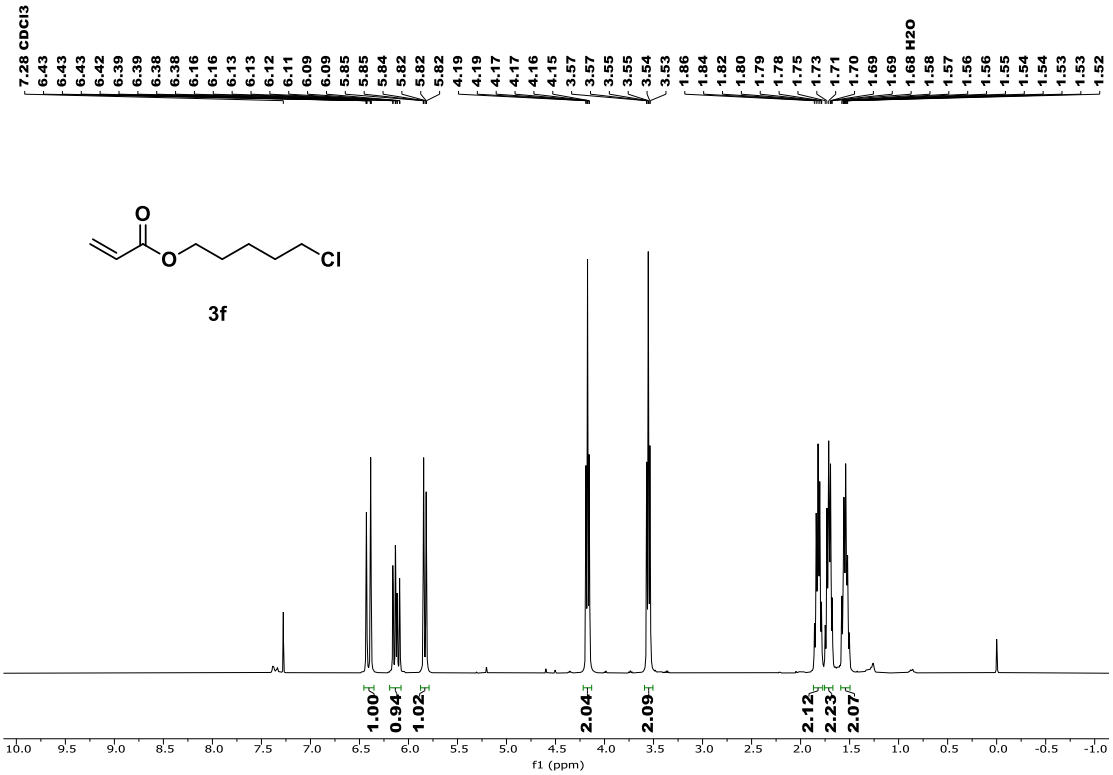
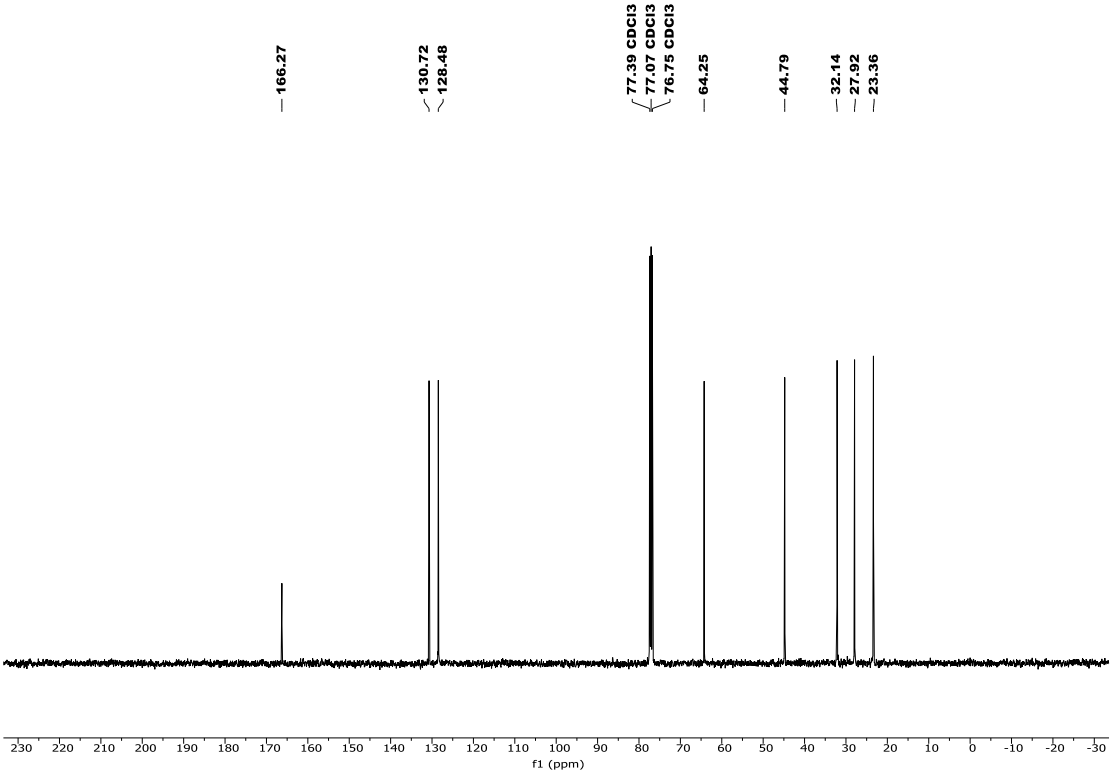
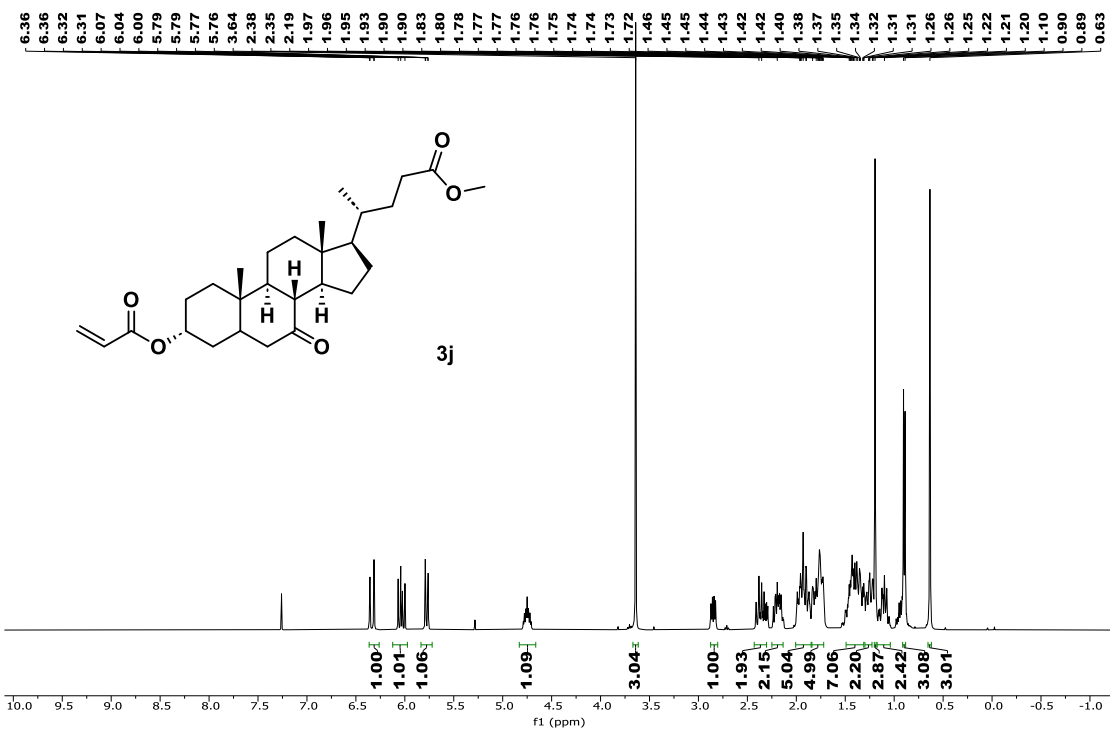


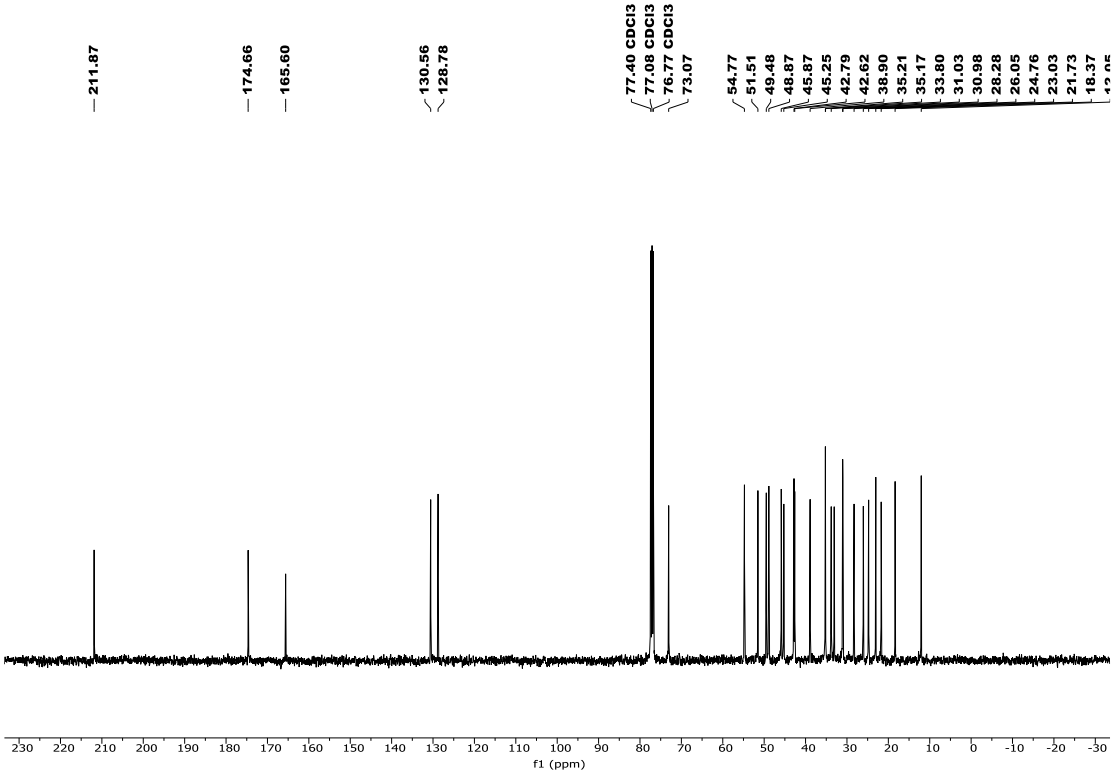
^{13}C NMR (101 MHz, $CDCl_3$):



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



^{13}C NMR (101 MHz, $CDCl_3$):



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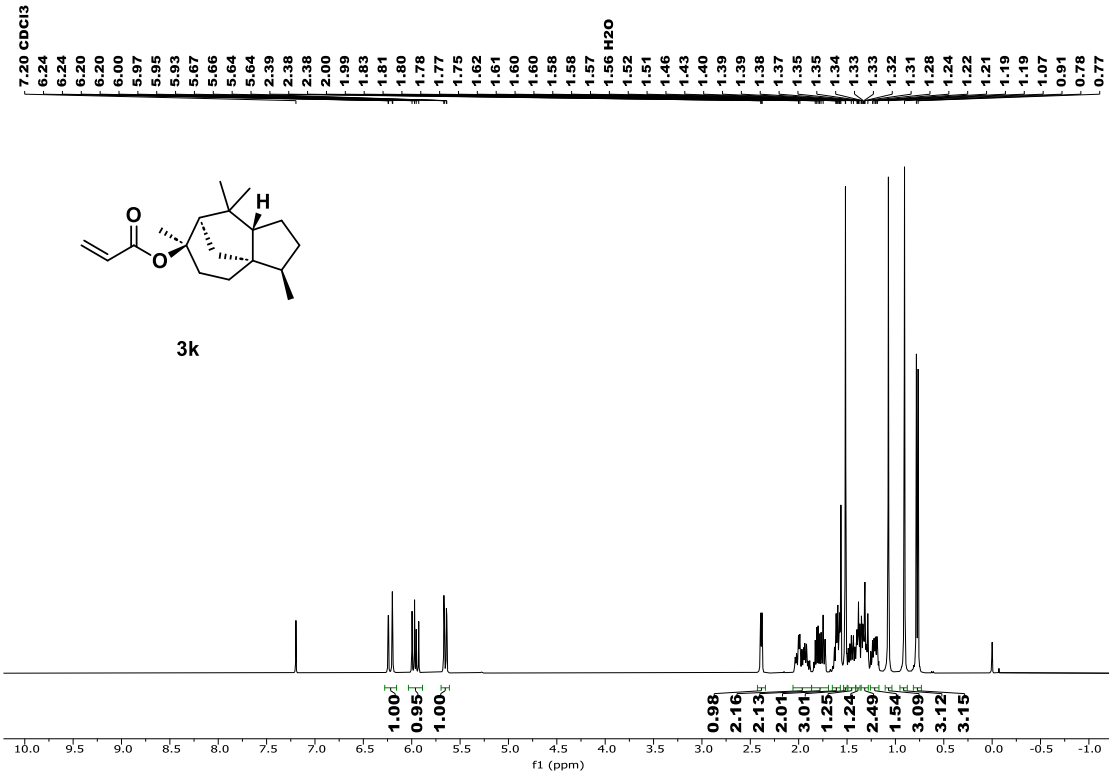

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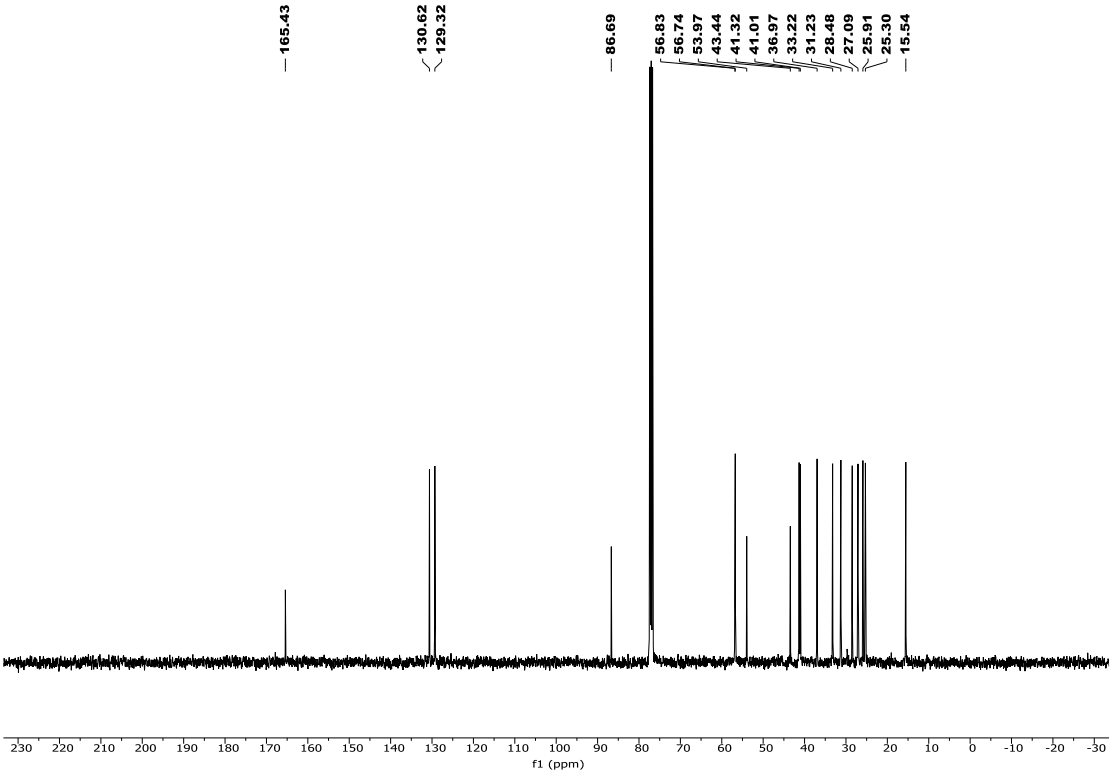
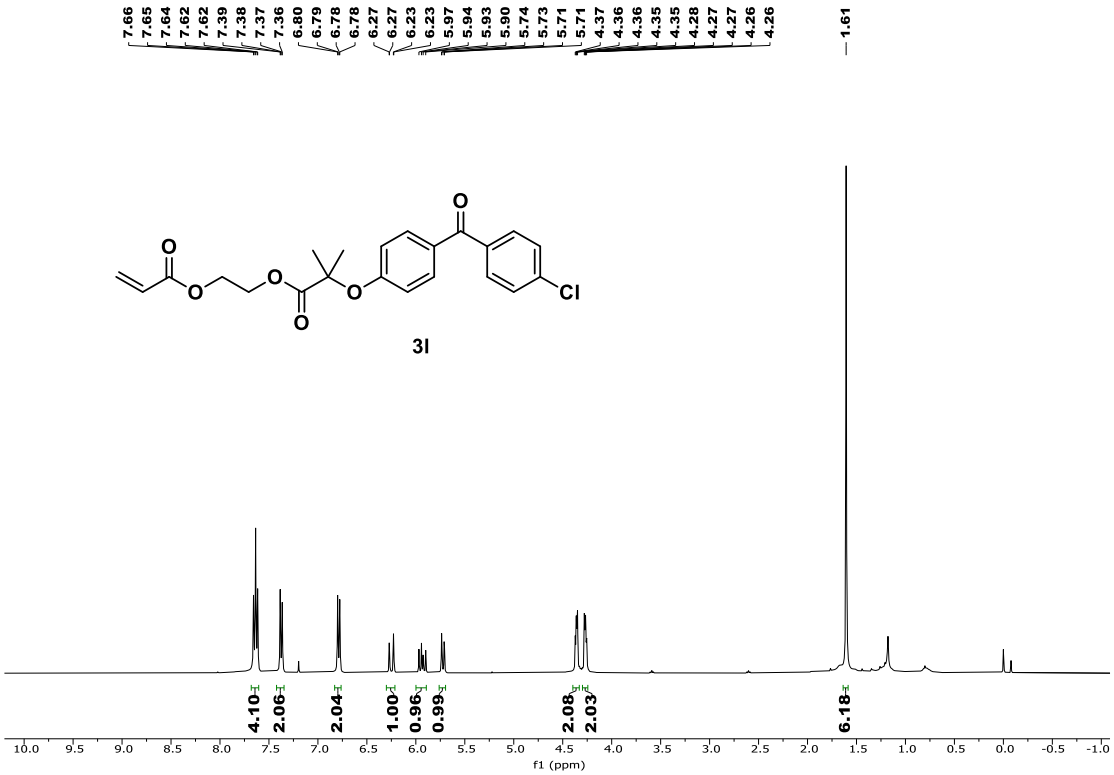
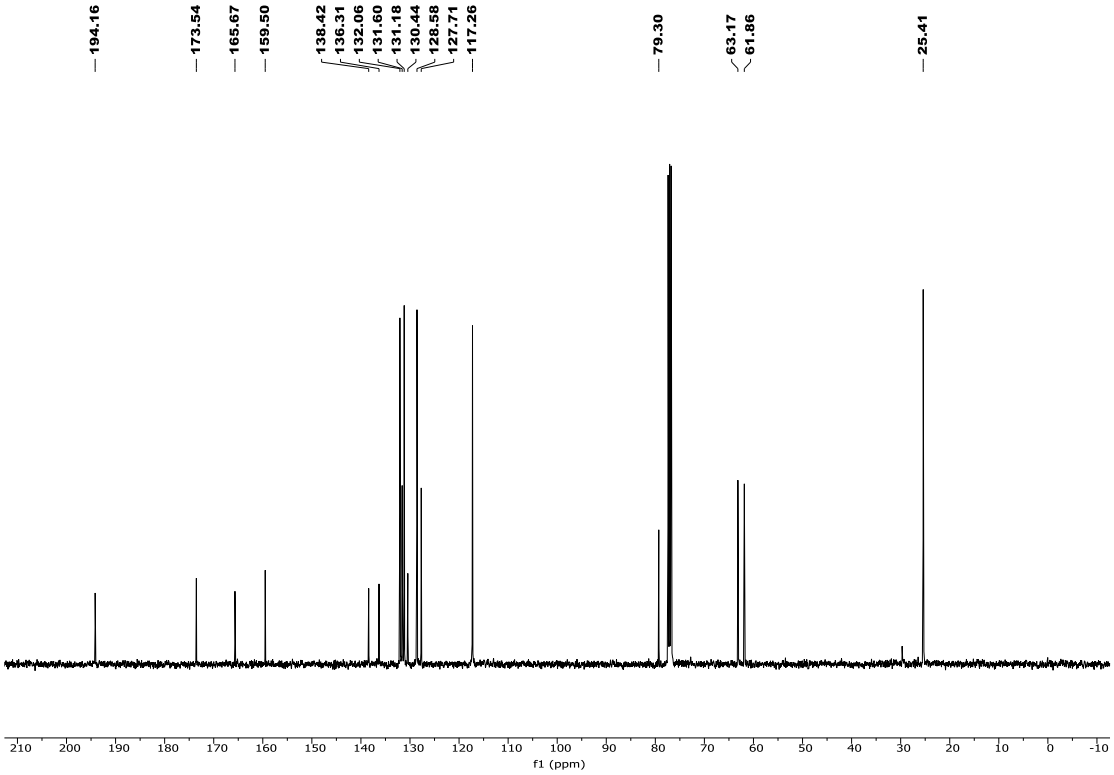


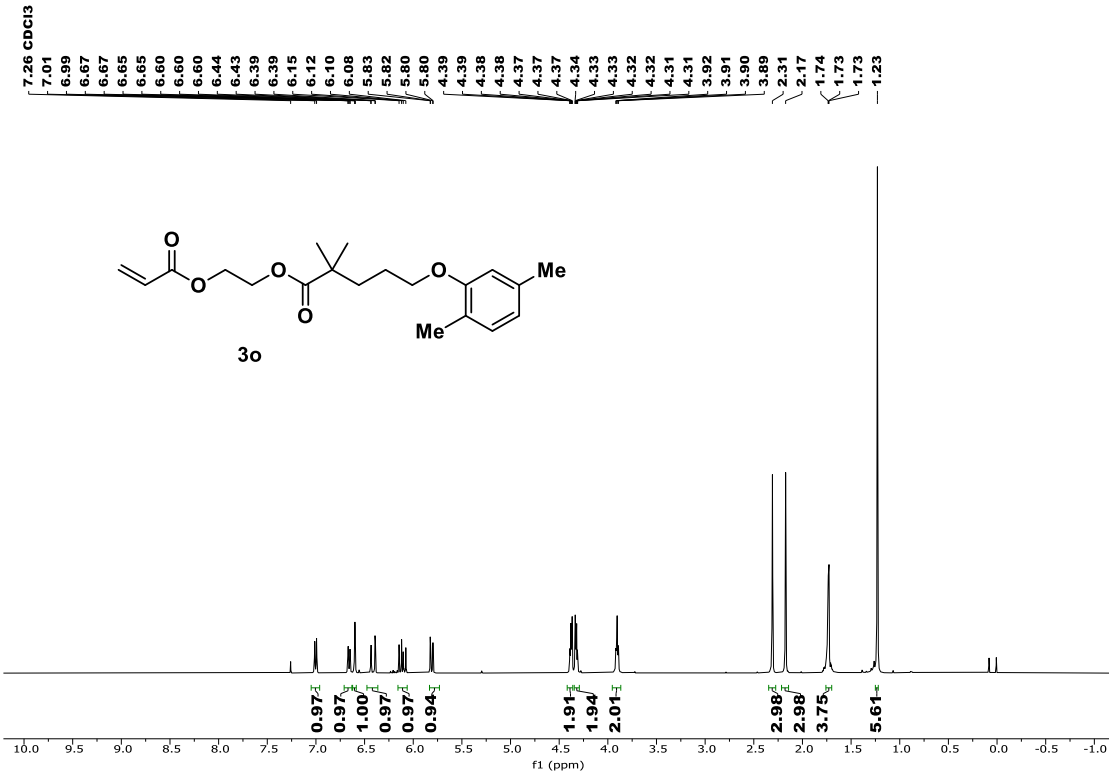
^{1}H NMR (400 MHz, $CDCl_3$)



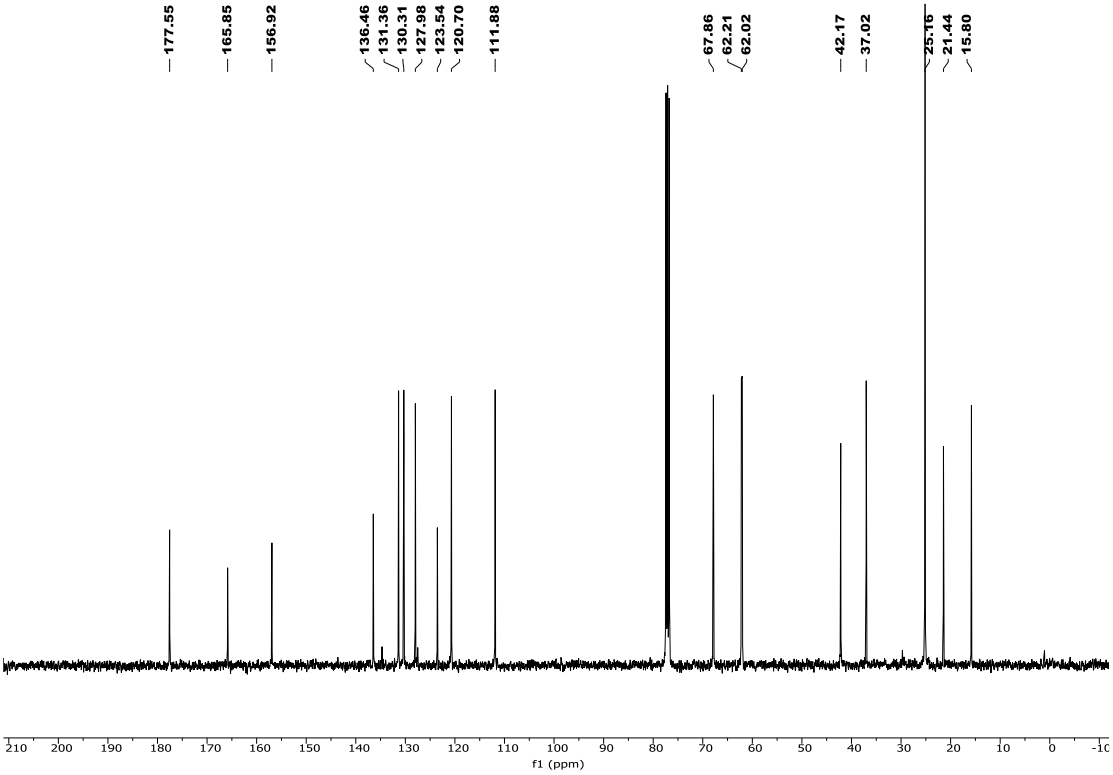
^{13}C NMR (101 MHz, $CDCl_3$)



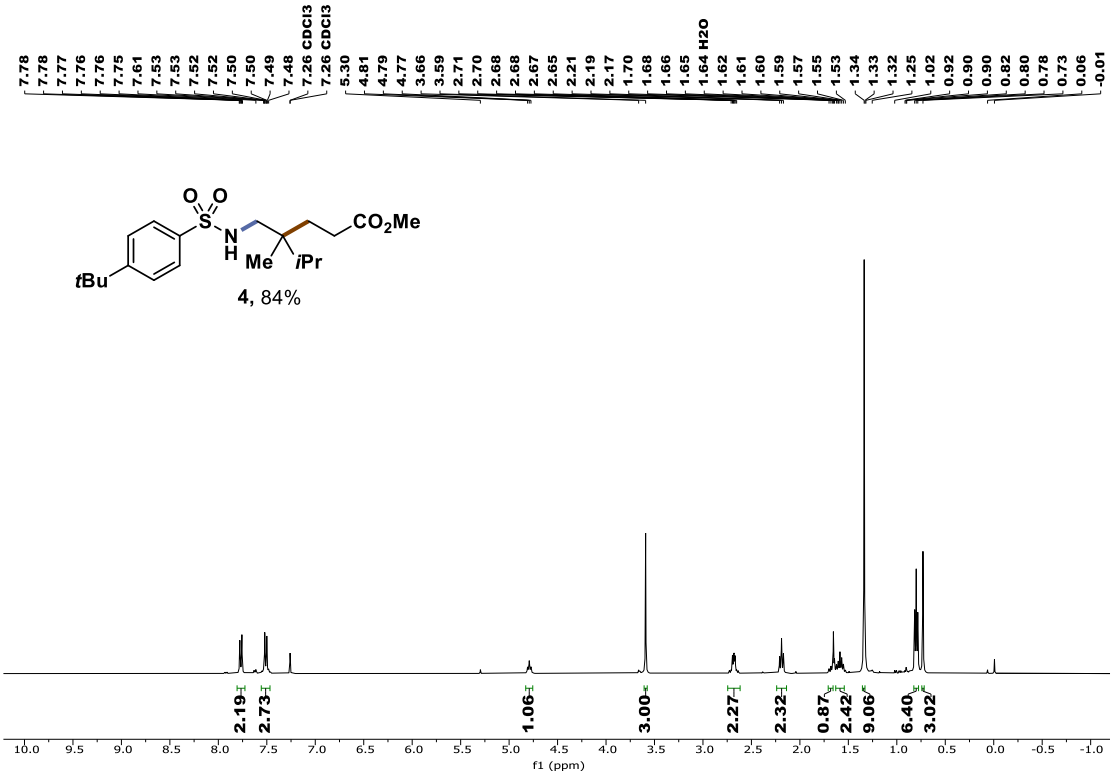
^{1}H NMR (400 MHz, $CDCl_3$)



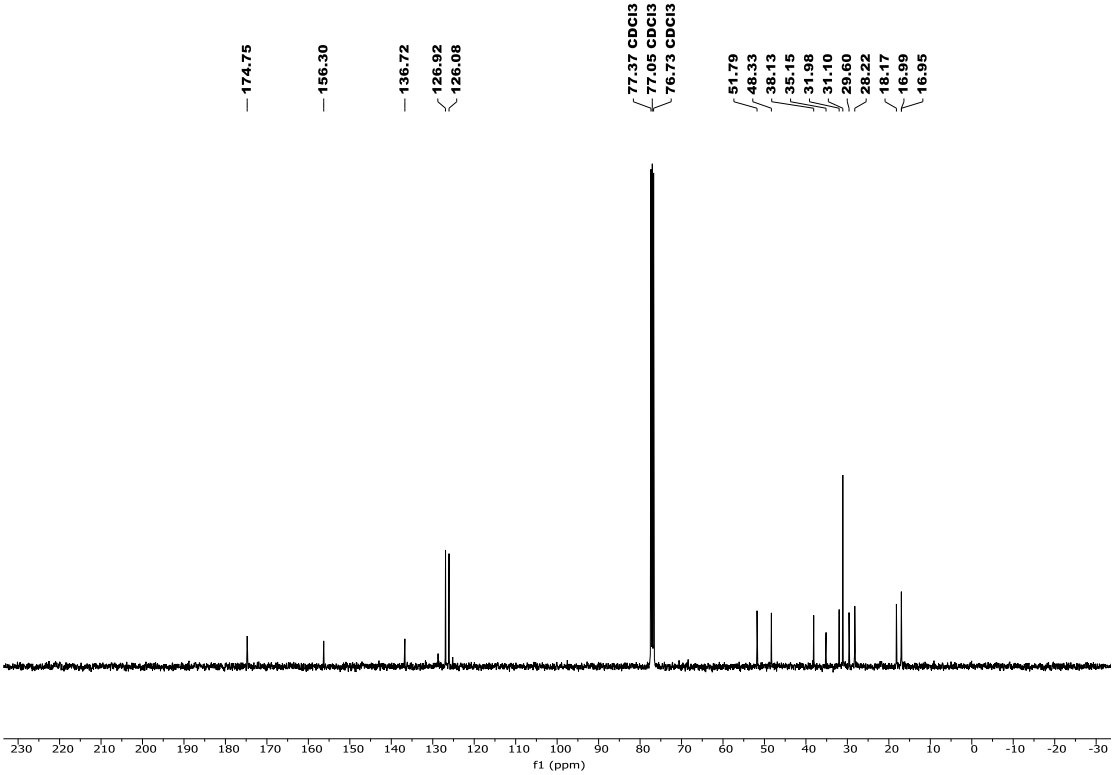
^{13}C NMR (101 MHz, $CDCl_3$)



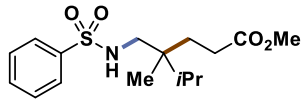
^{1}H NMR (400 MHz, $CDCl_3$):



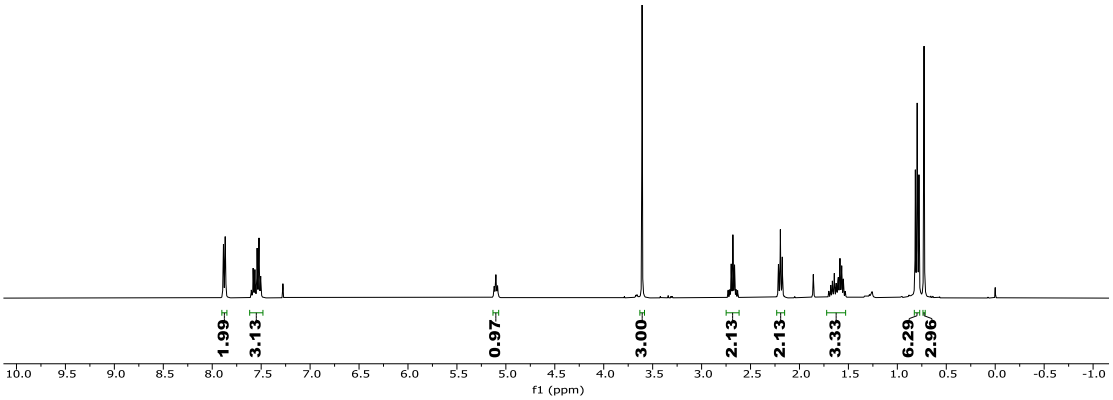
^{13}C NMR (101 MHz, $CDCl_3$):



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



5, 63%



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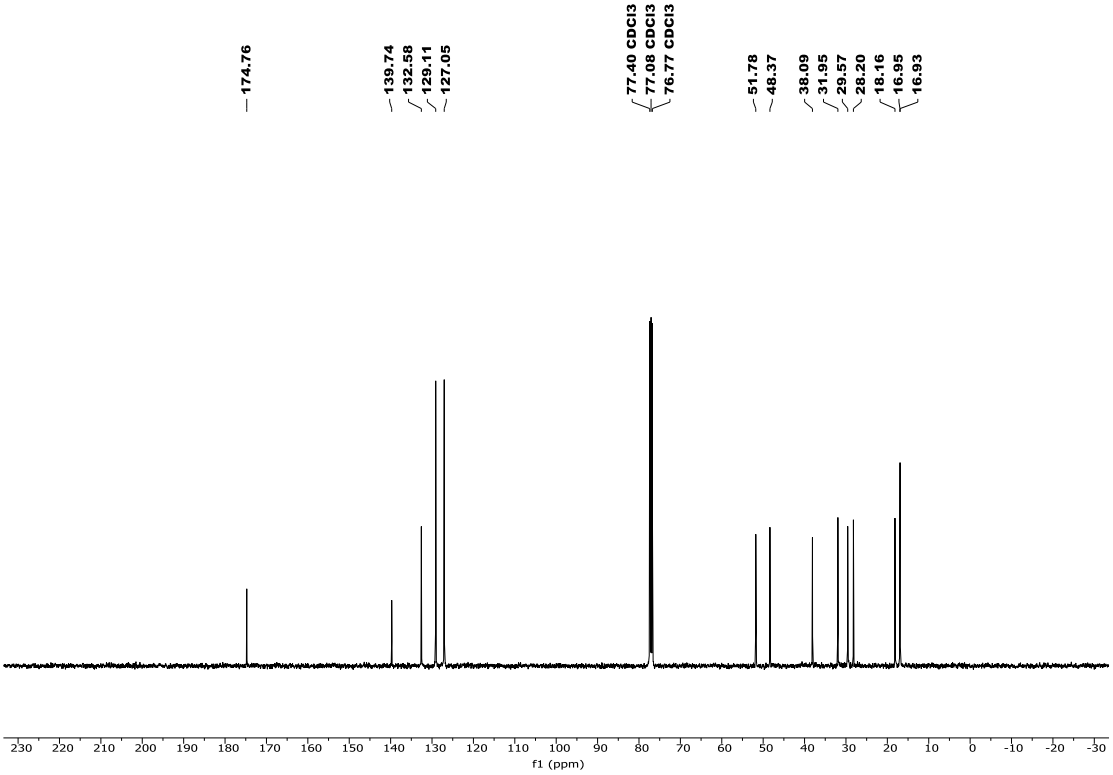
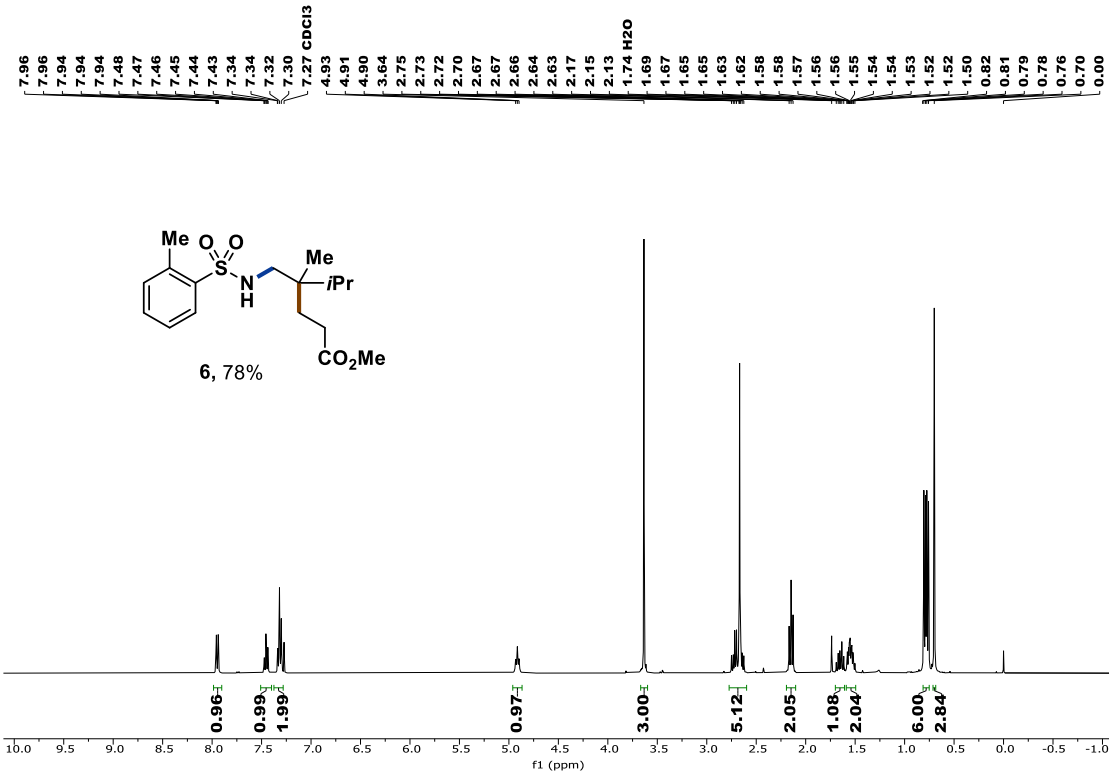
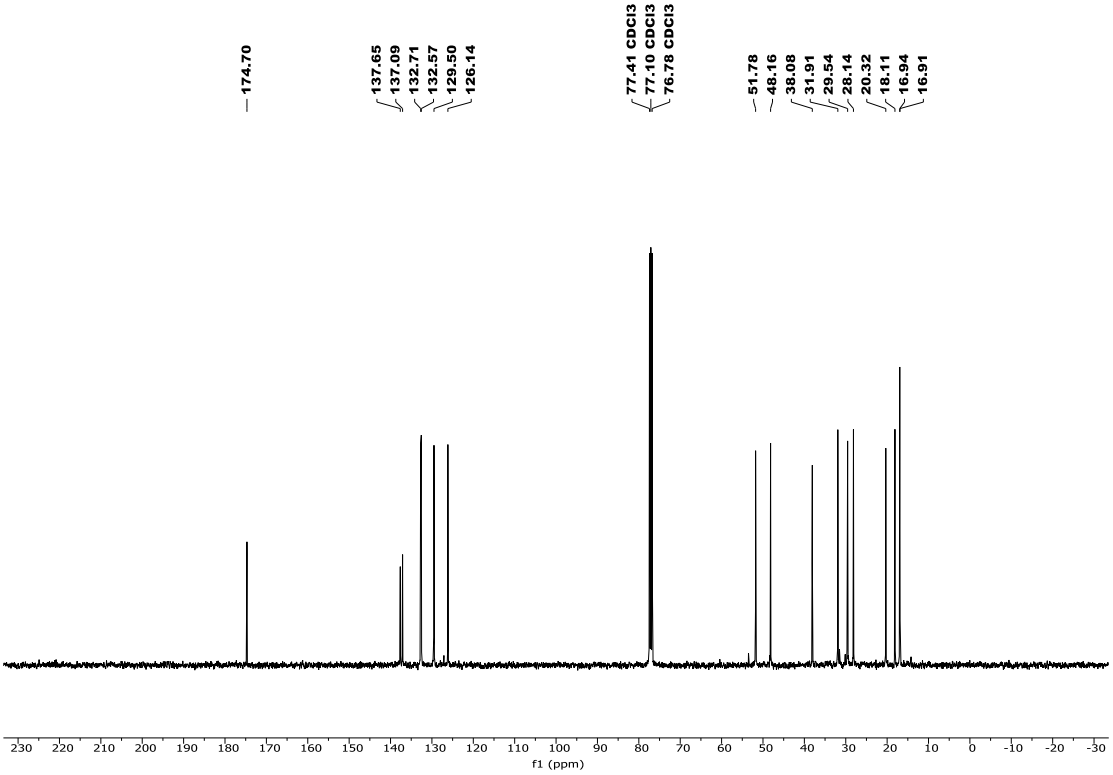


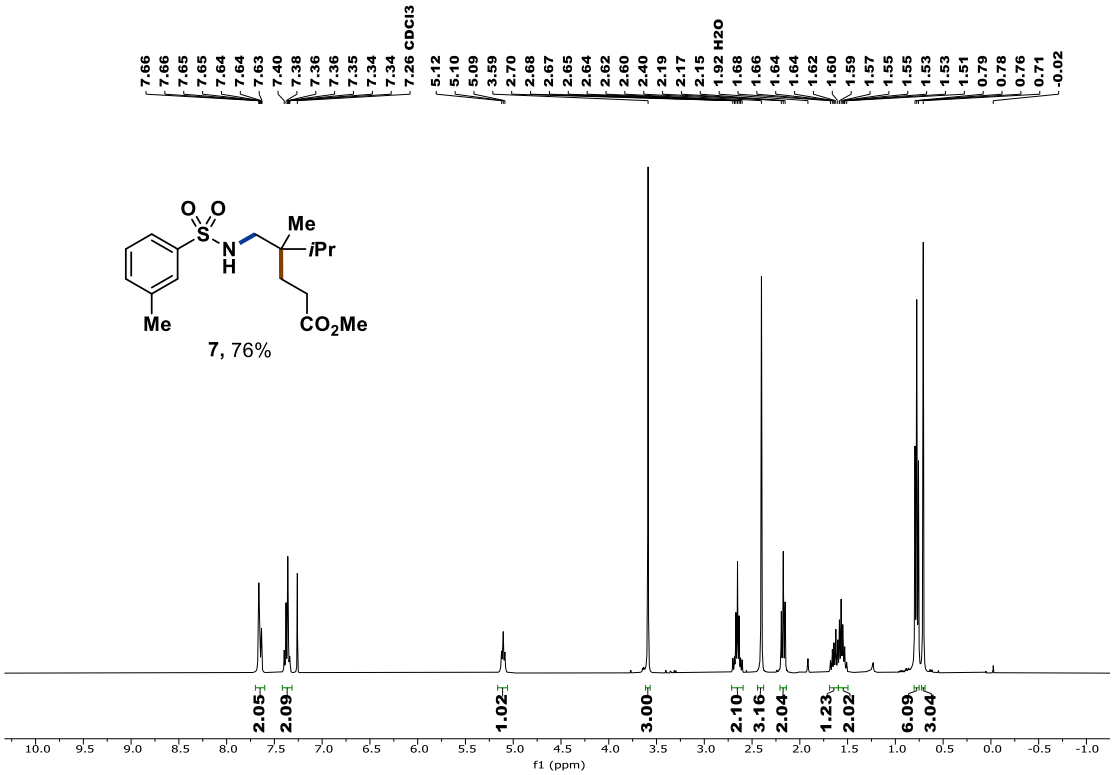
^{1}H NMR (400 MHz, $CDCl_3$):



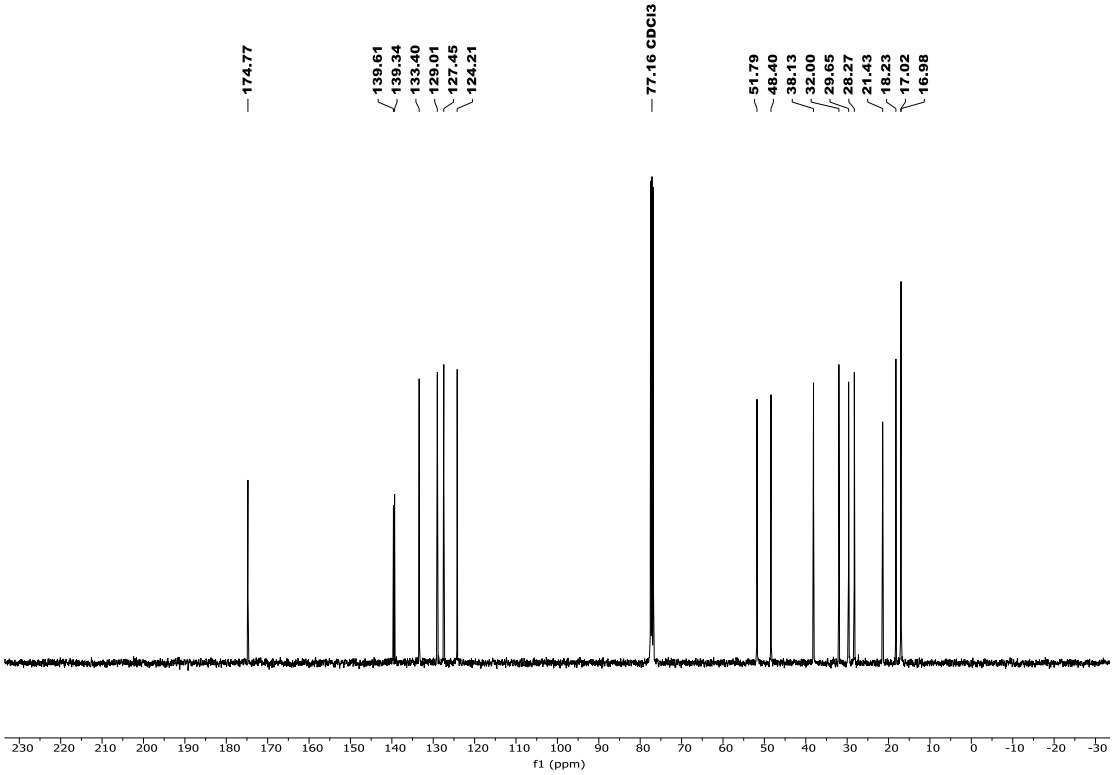
^{13}C NMR (101 MHz, $CDCl_3$):



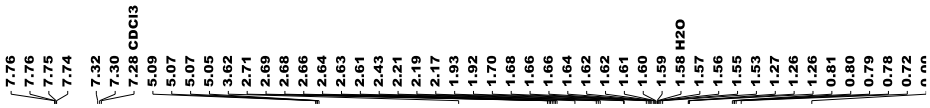
^{1}H NMR (400 MHz, $CDCl_3$):

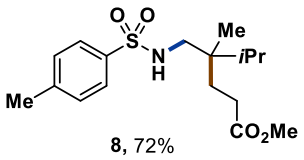


^{13}C NMR (101 MHz, $CDCl_3$):

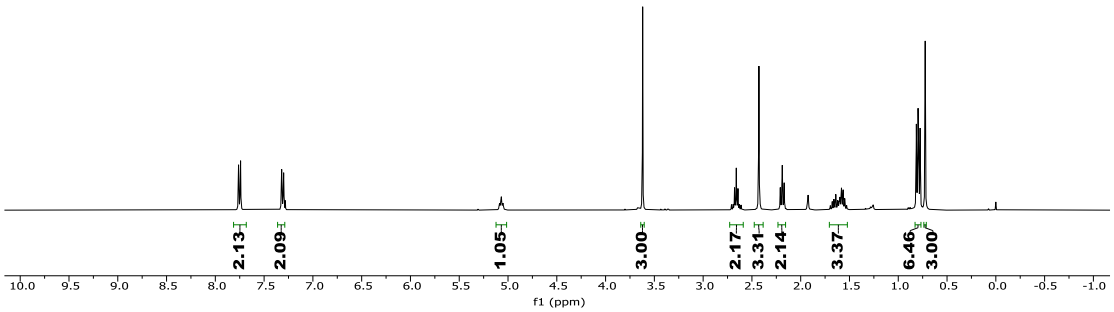


^{1}H NMR (400 MHz, $CDCl_3$):

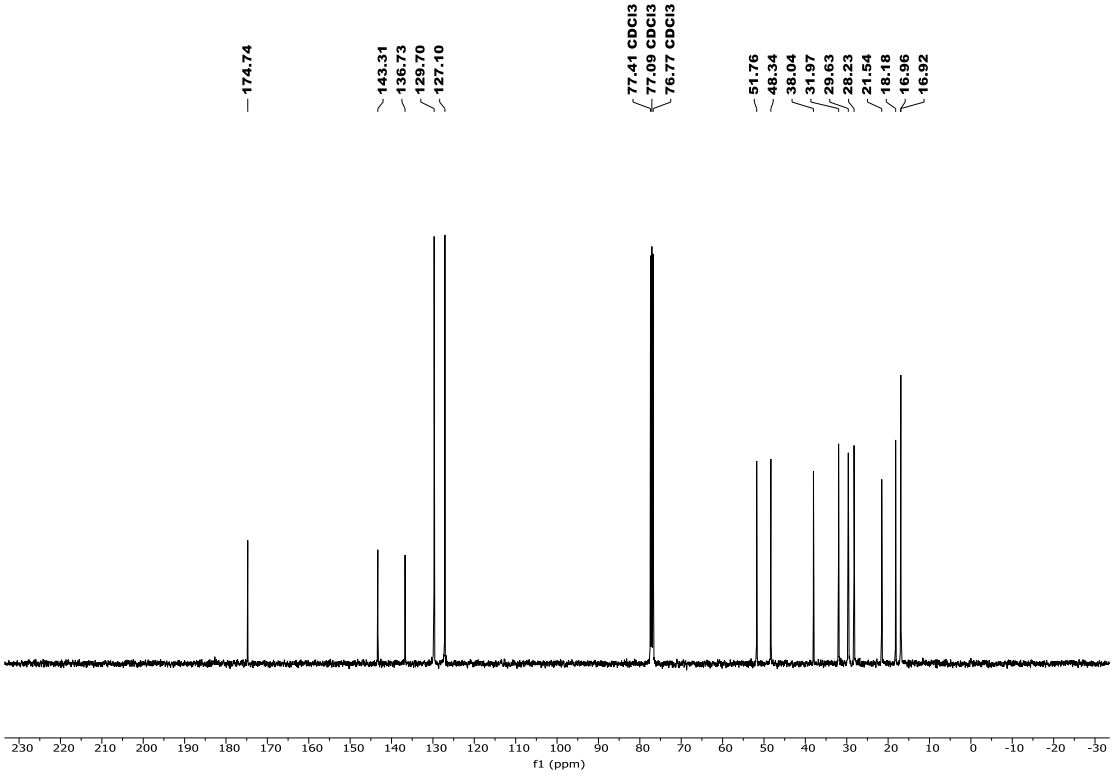




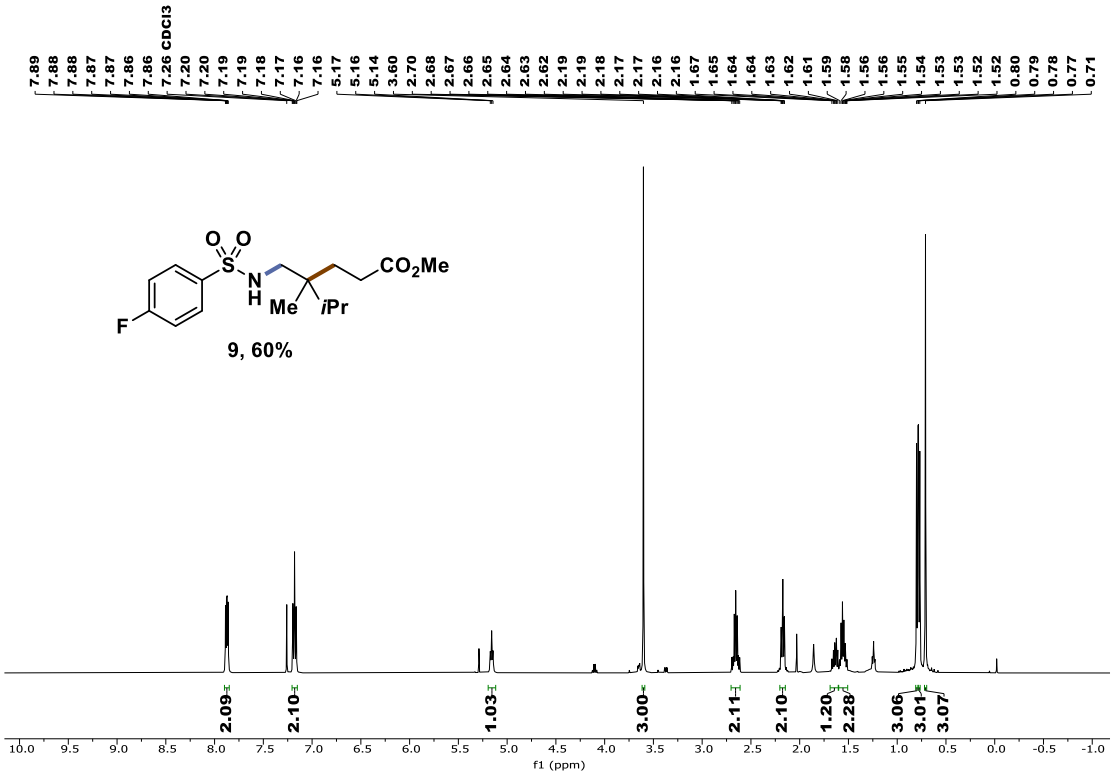
8, 72%



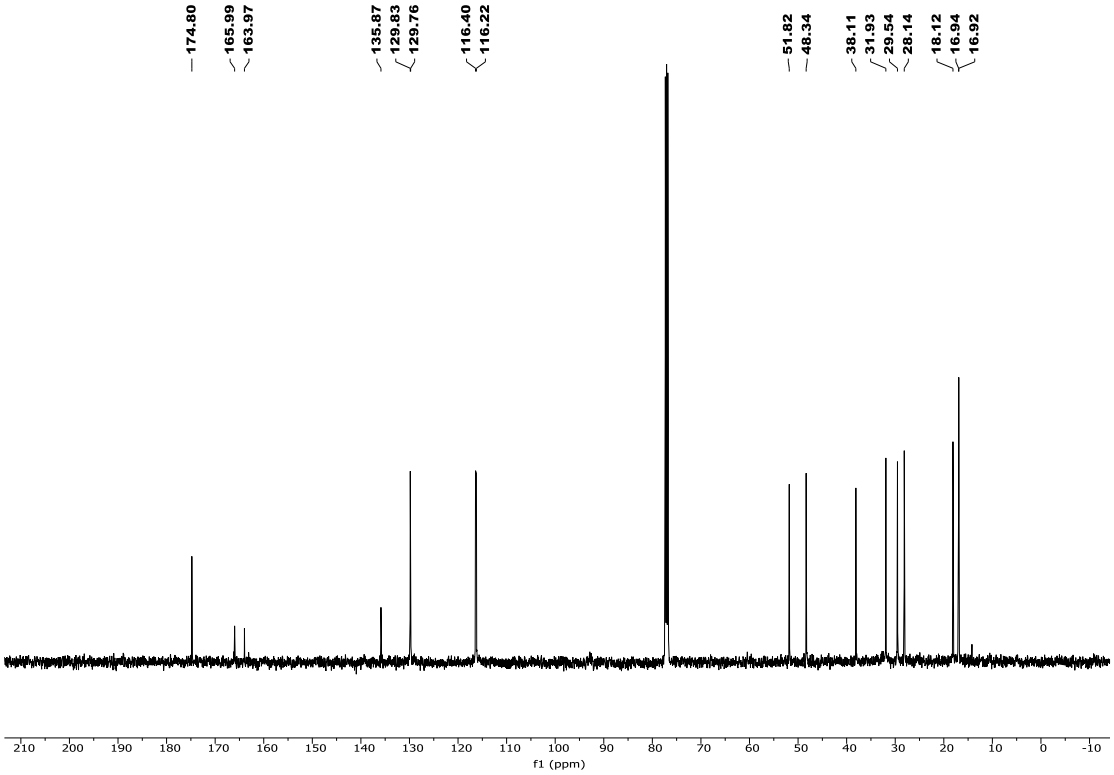
^{13}C NMR (101 MHz, $CDCl_3$):



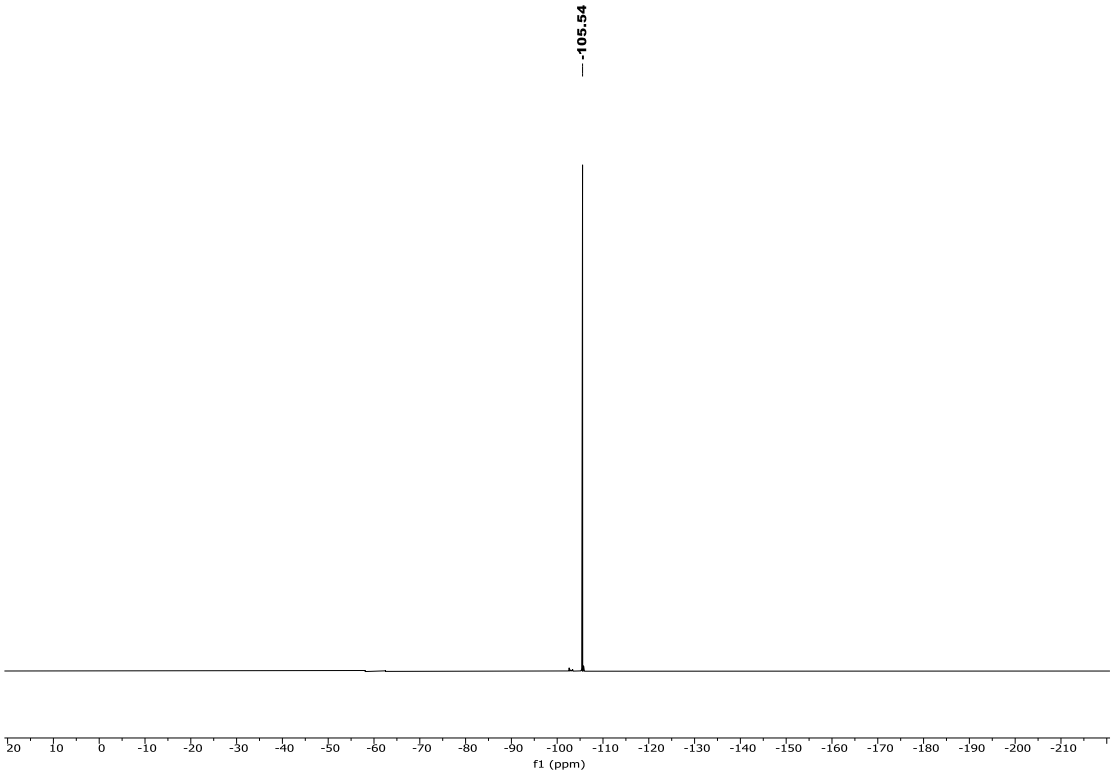
^{1}H NMR (500 MHz, $CDCl_3$):



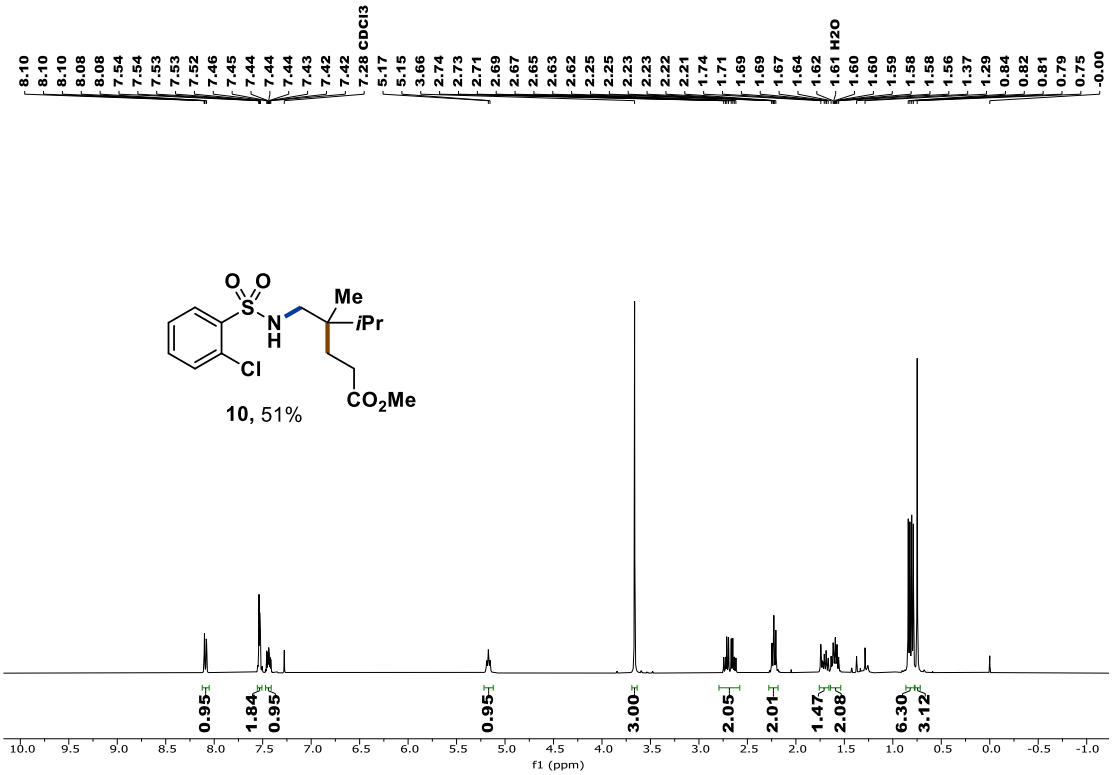
^{13}C NMR (126 MHz, $CDCl_3$):



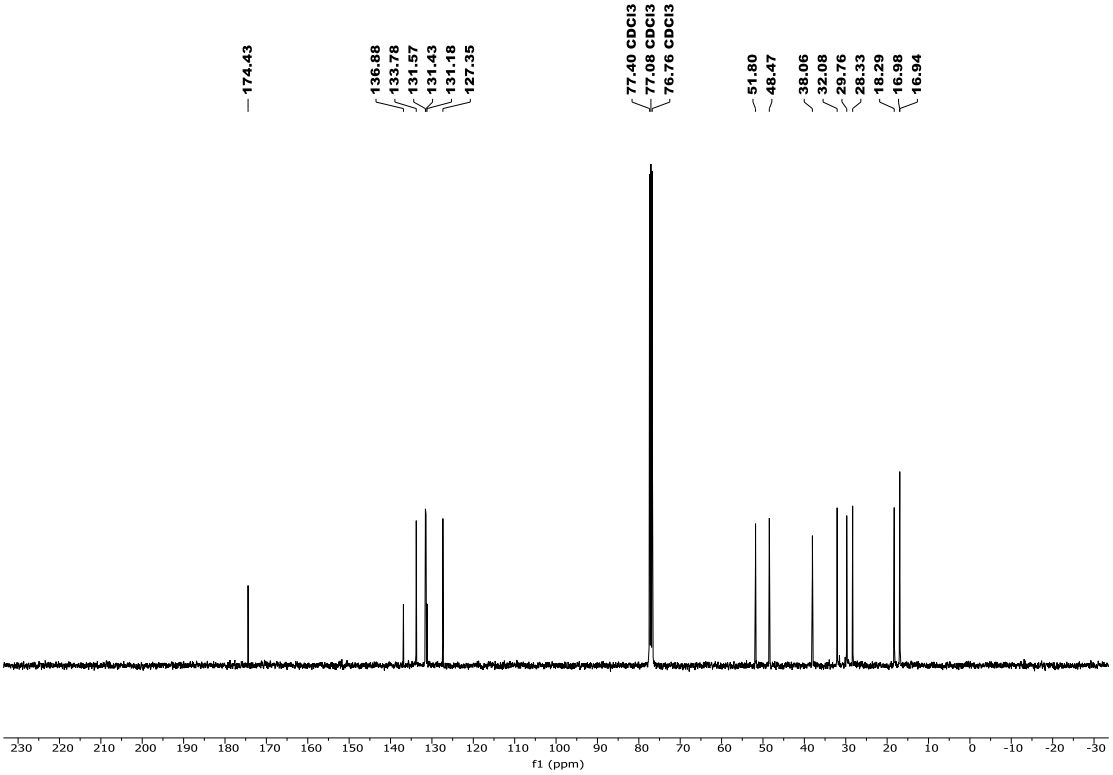
^{19}F NMR (471 MHz, $CDCl_3$)



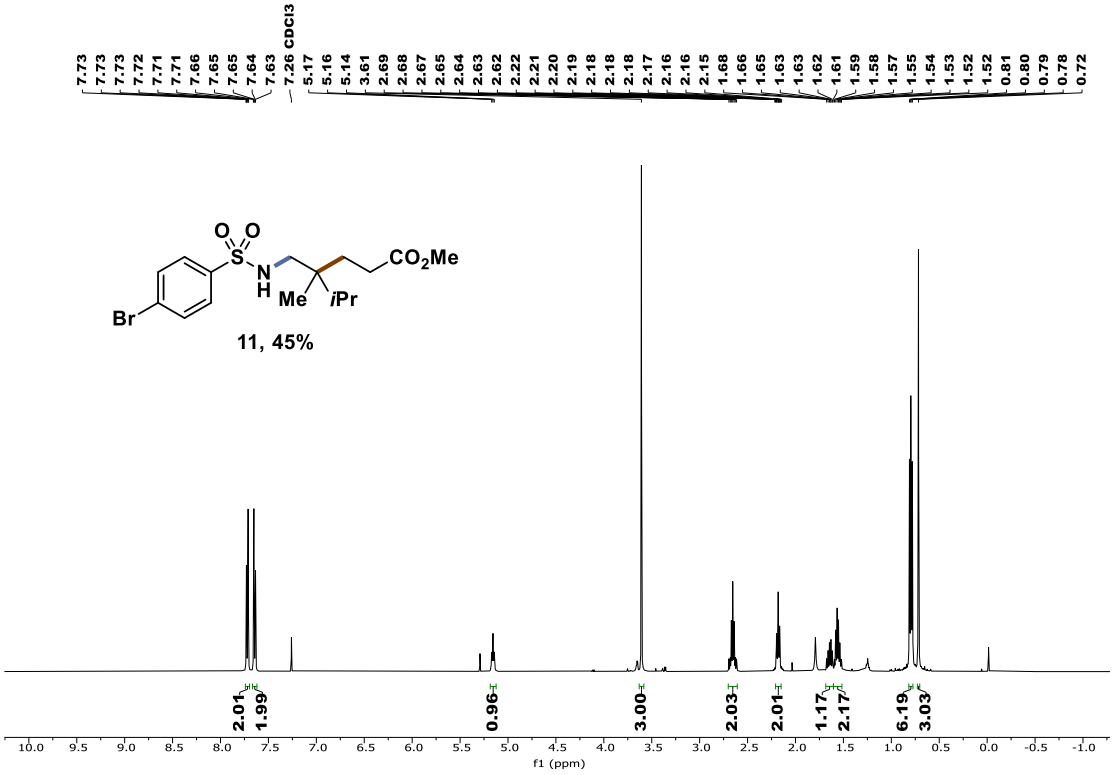
^{1}H NMR (400 MHz, $CDCl_3$):



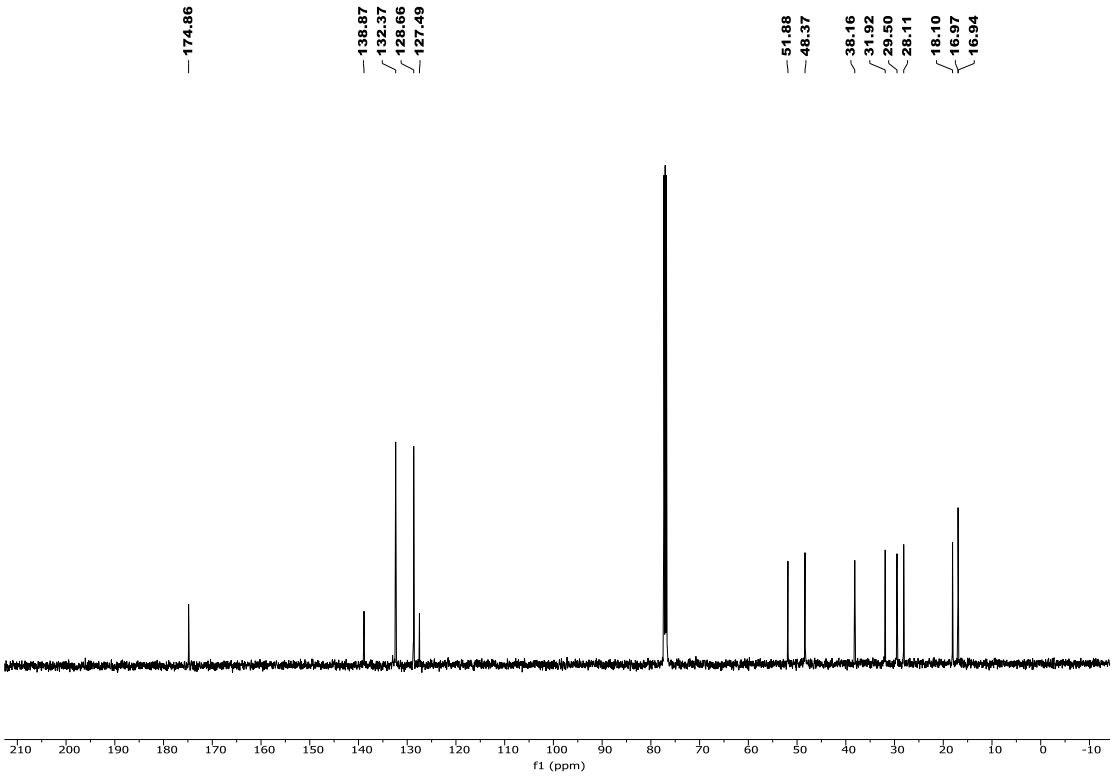
^{13}C NMR (101 MHz, $CDCl_3$):



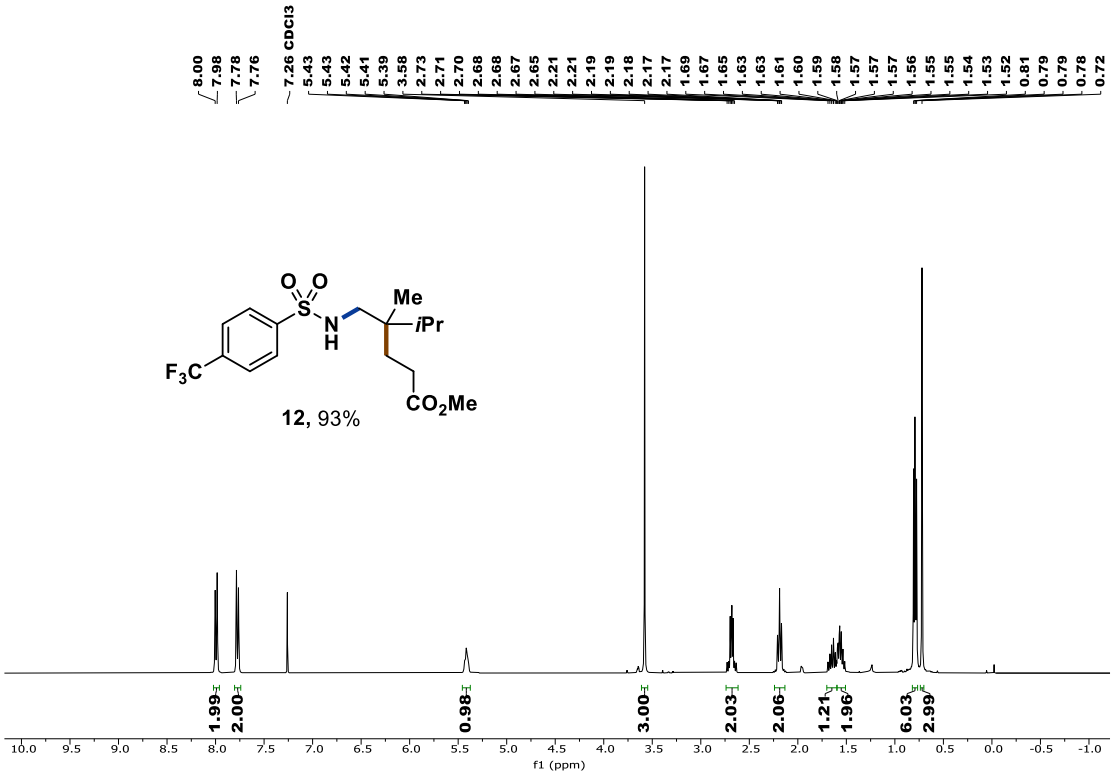
^{1}H NMR (400 MHz, $CDCl_3$):



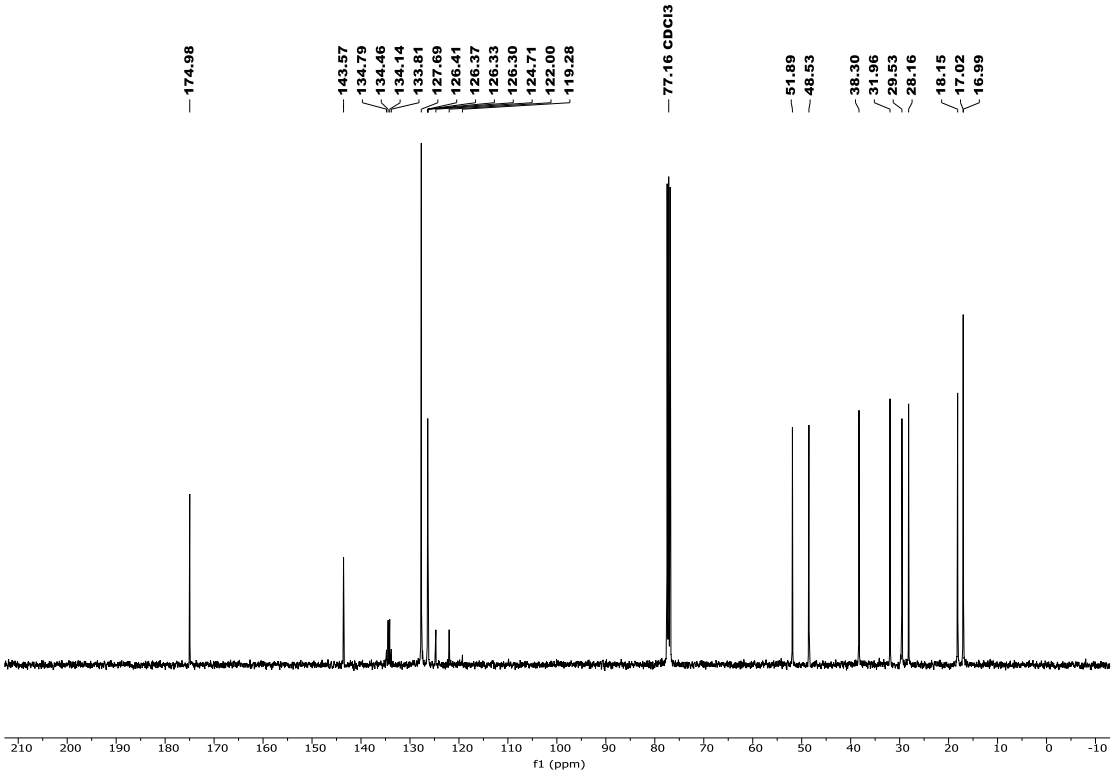
^{13}C NMR (101 MHz, $CDCl_3$):

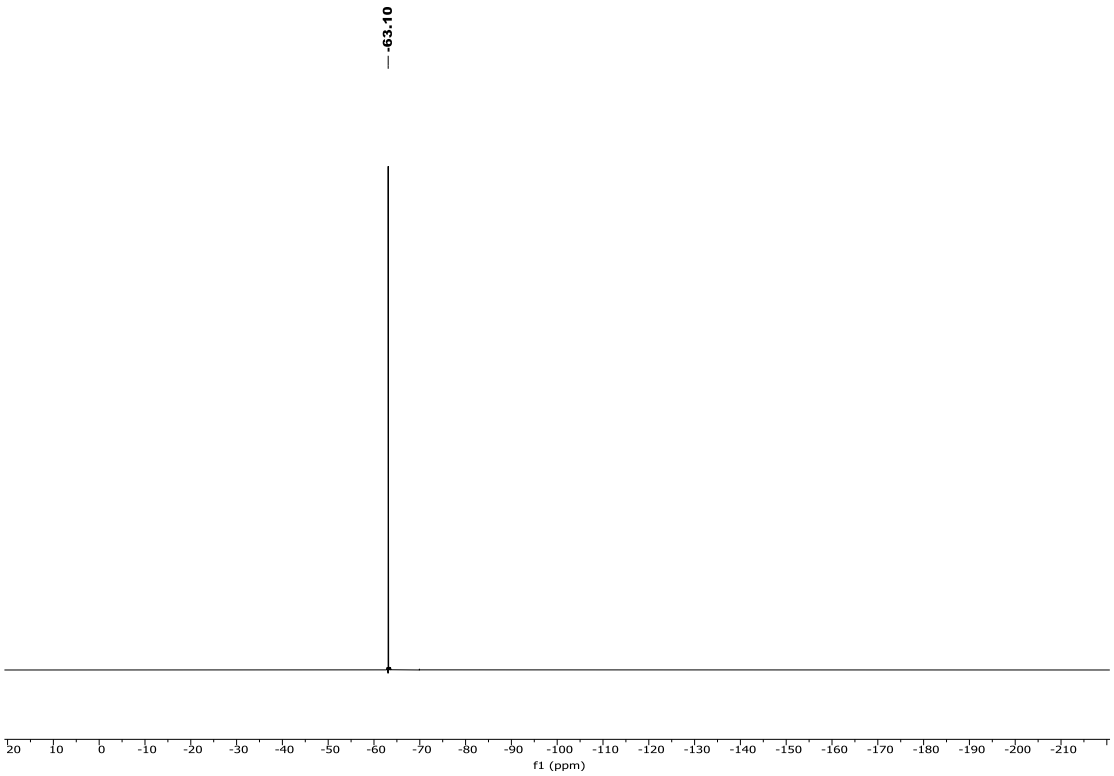


^{1}H NMR (400 MHz, $CDCl_3$):

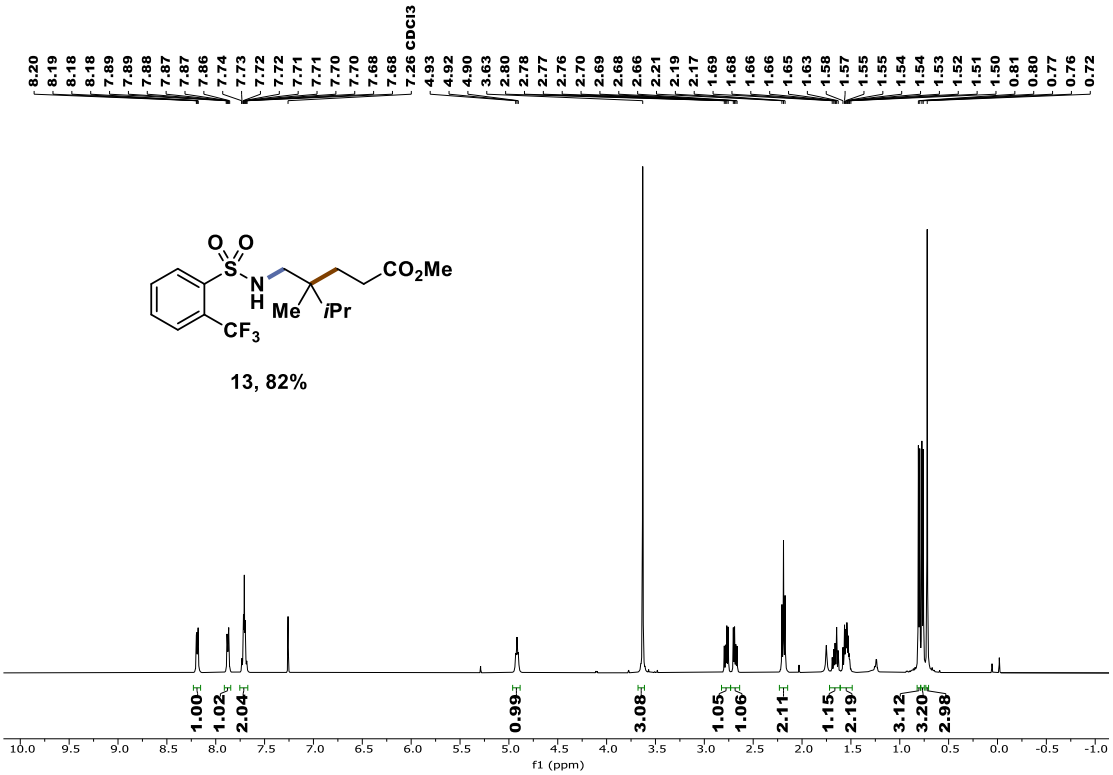


^{13}C NMR (101 MHz, $CDCl_3$):

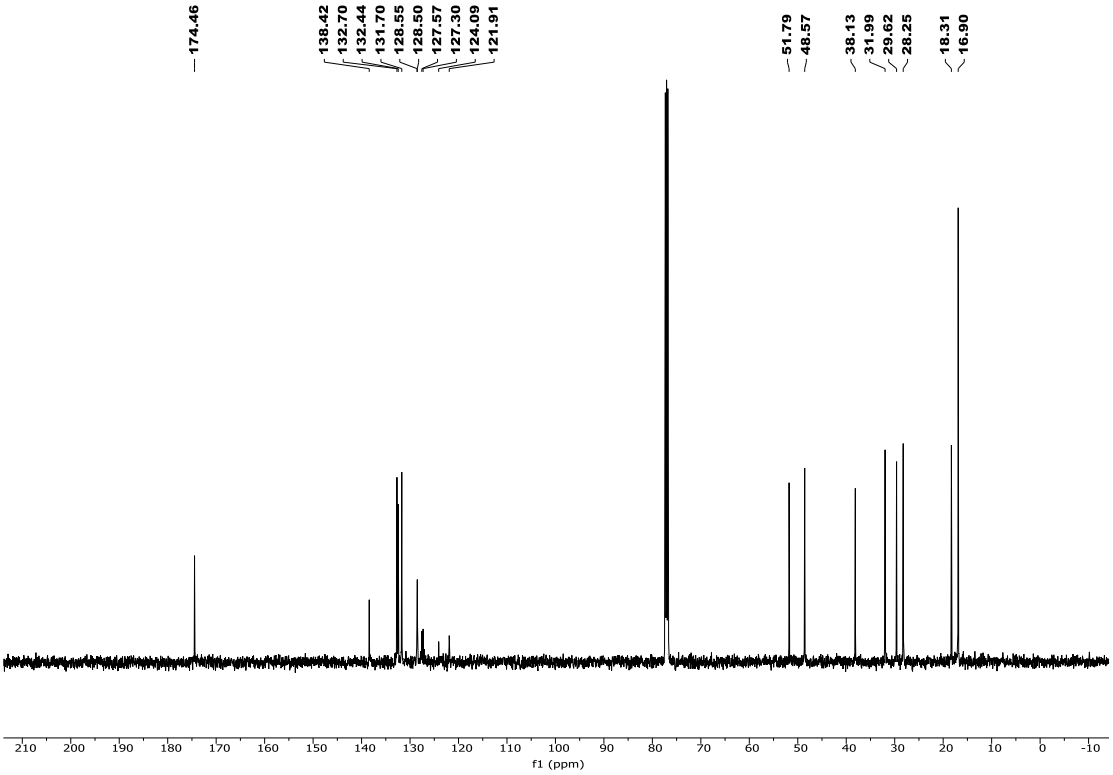



-63.10
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

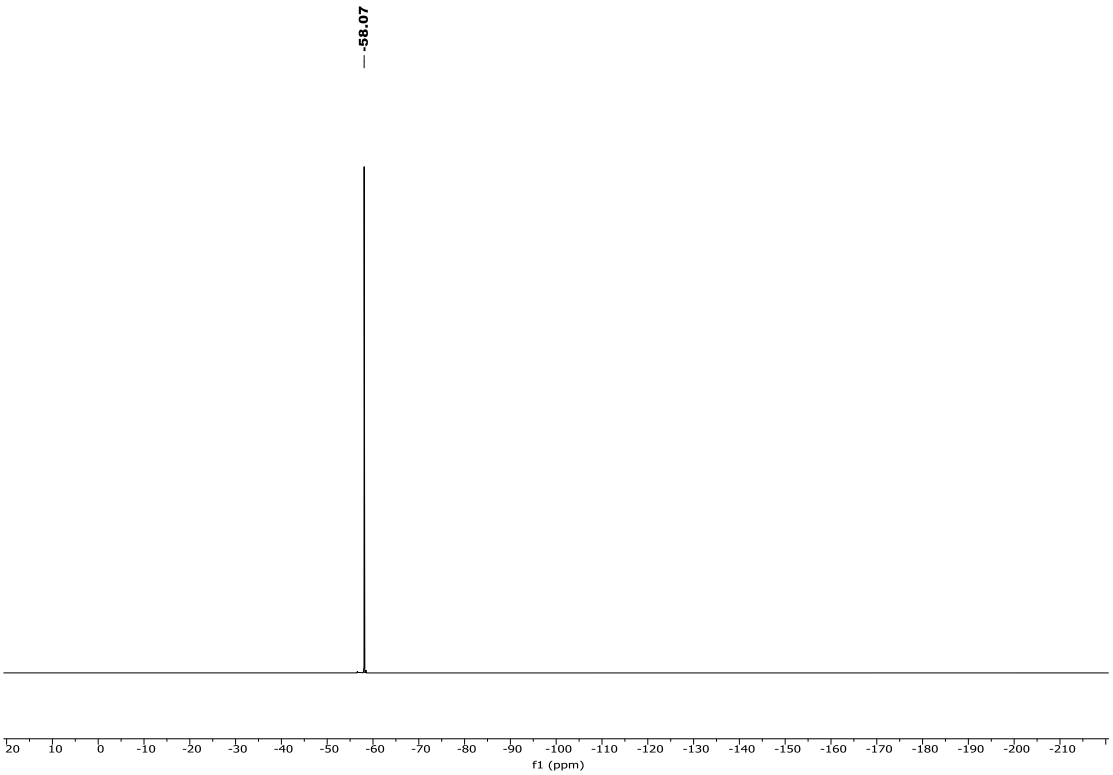
^{1}H NMR (500 MHz, $CDCl_3$):



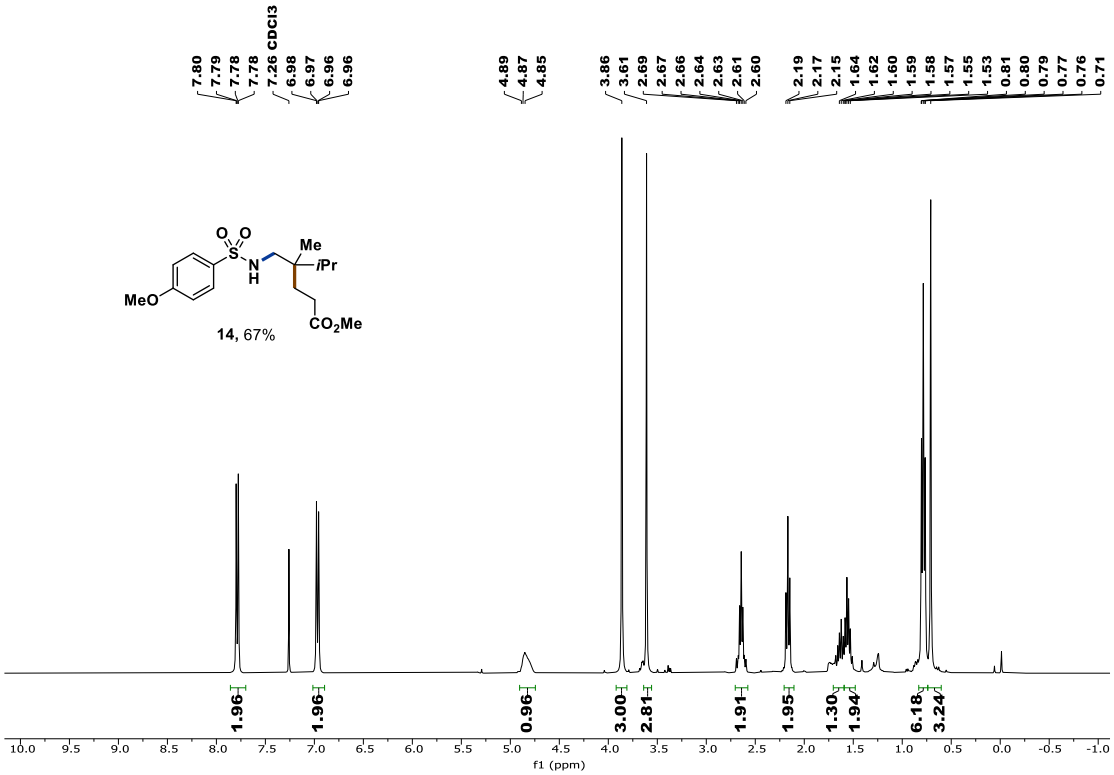
^{13}C NMR (126 MHz, $CDCl_3$):



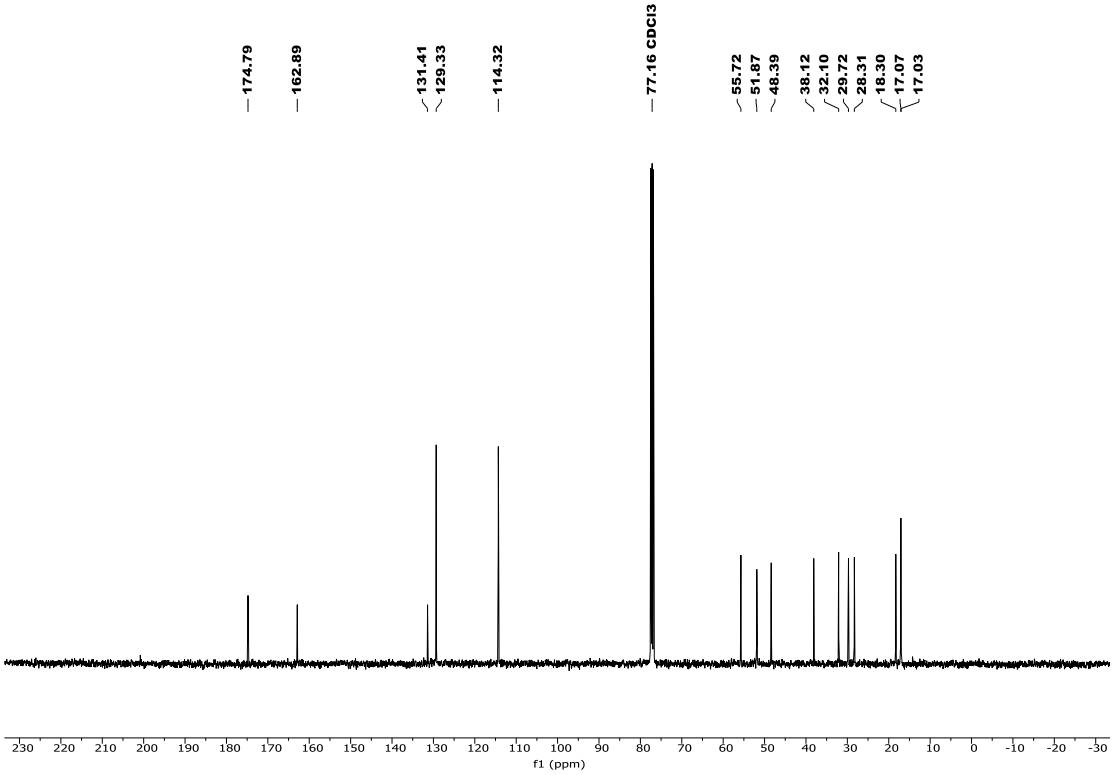
^{19}F NMR (471 MHz, $CDCl_3$)



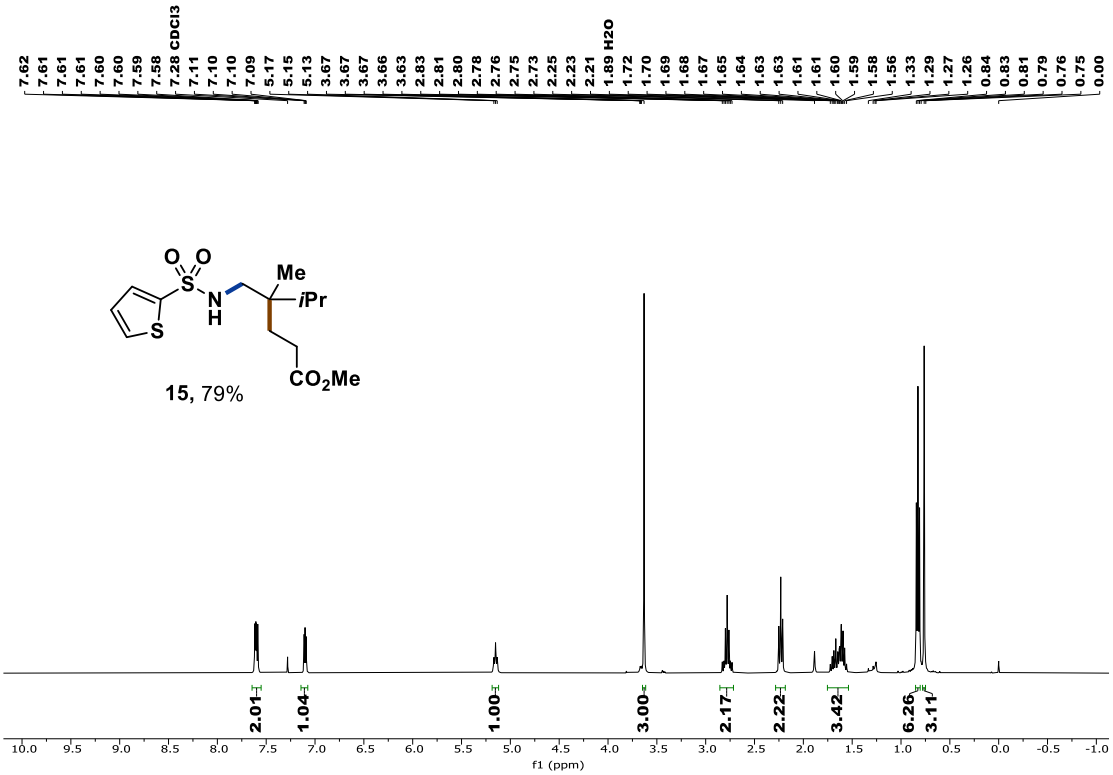
^{1}H NMR (400 MHz, $CDCl_3$):



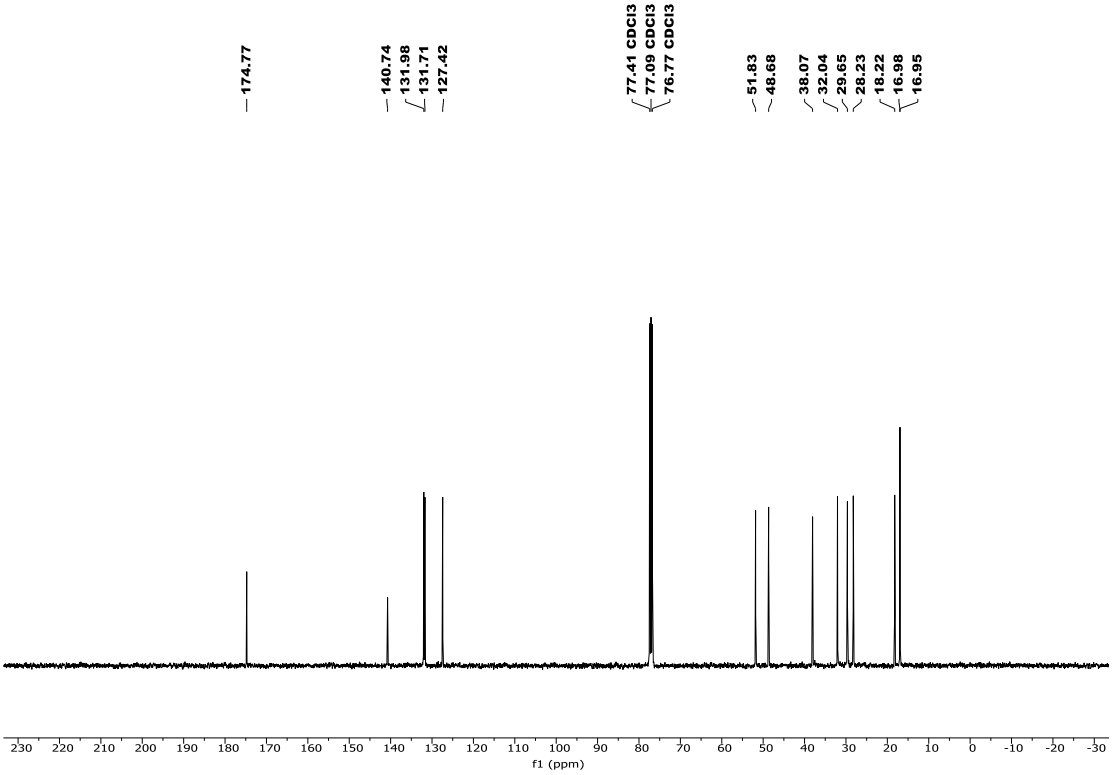
^{13}C NMR (101 MHz, $CDCl_3$):



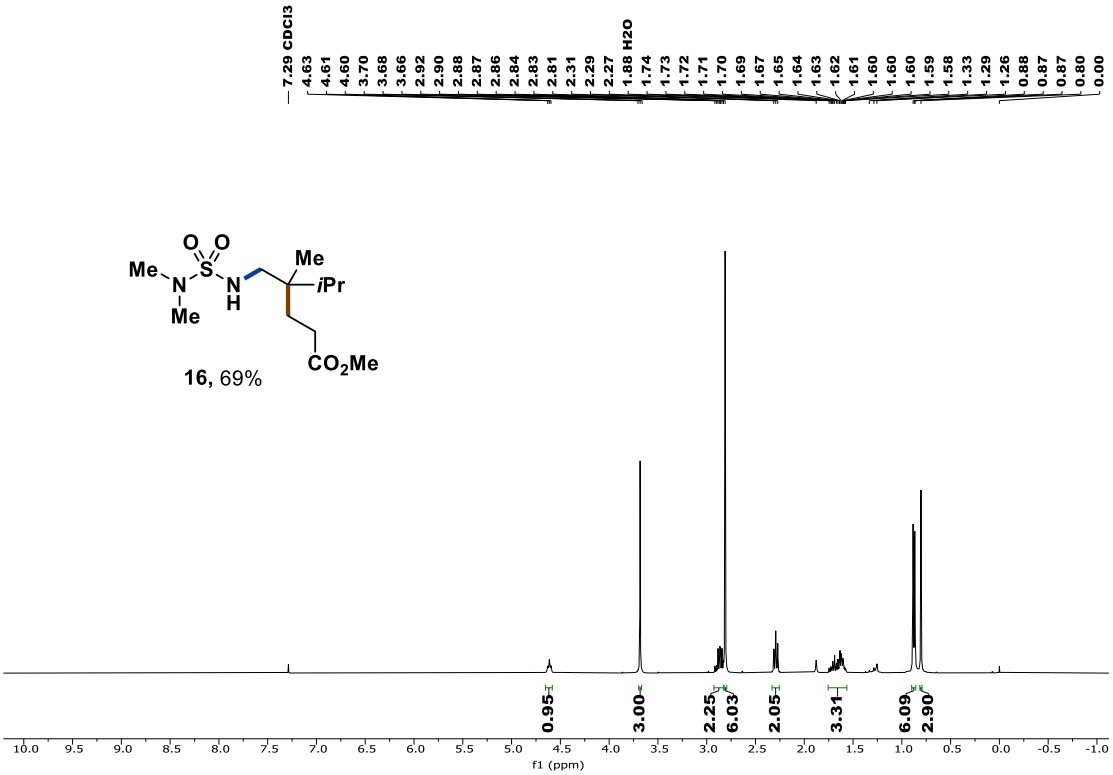
^{1}H NMR (400 MHz, $CDCl_3$):



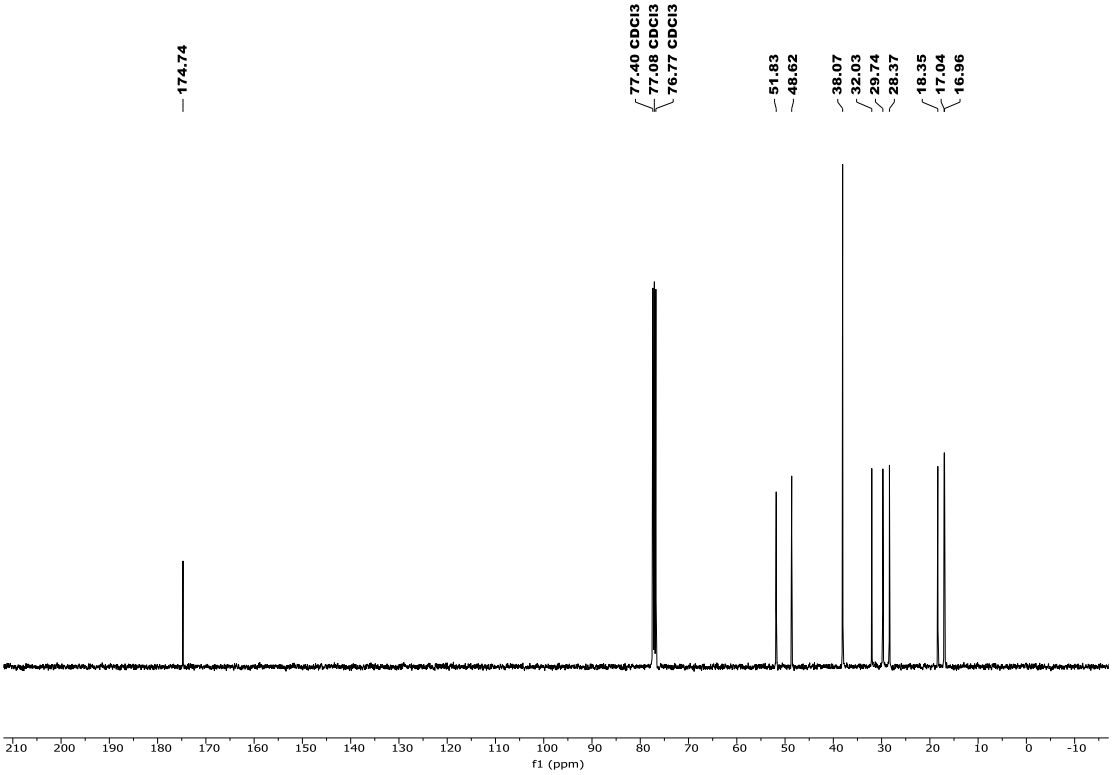
^{13}C NMR (101 MHz, $CDCl_3$):



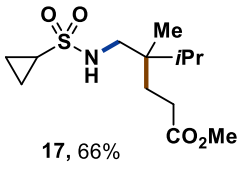
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):

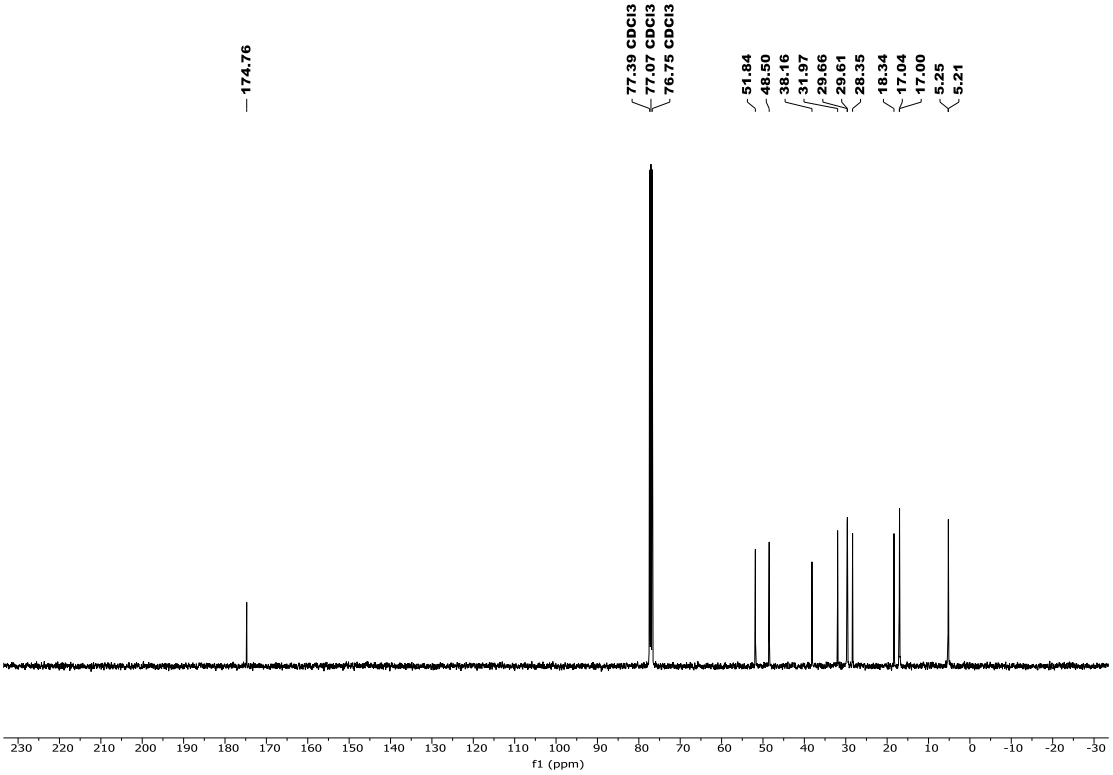


^{1}H NMR (400 MHz, $CDCl_3$):

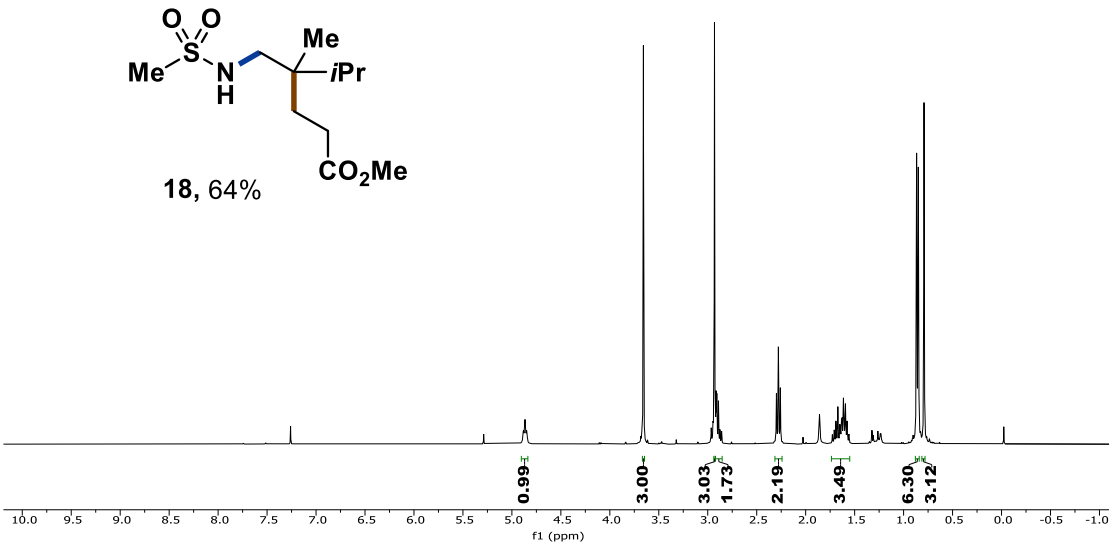


17, 66%

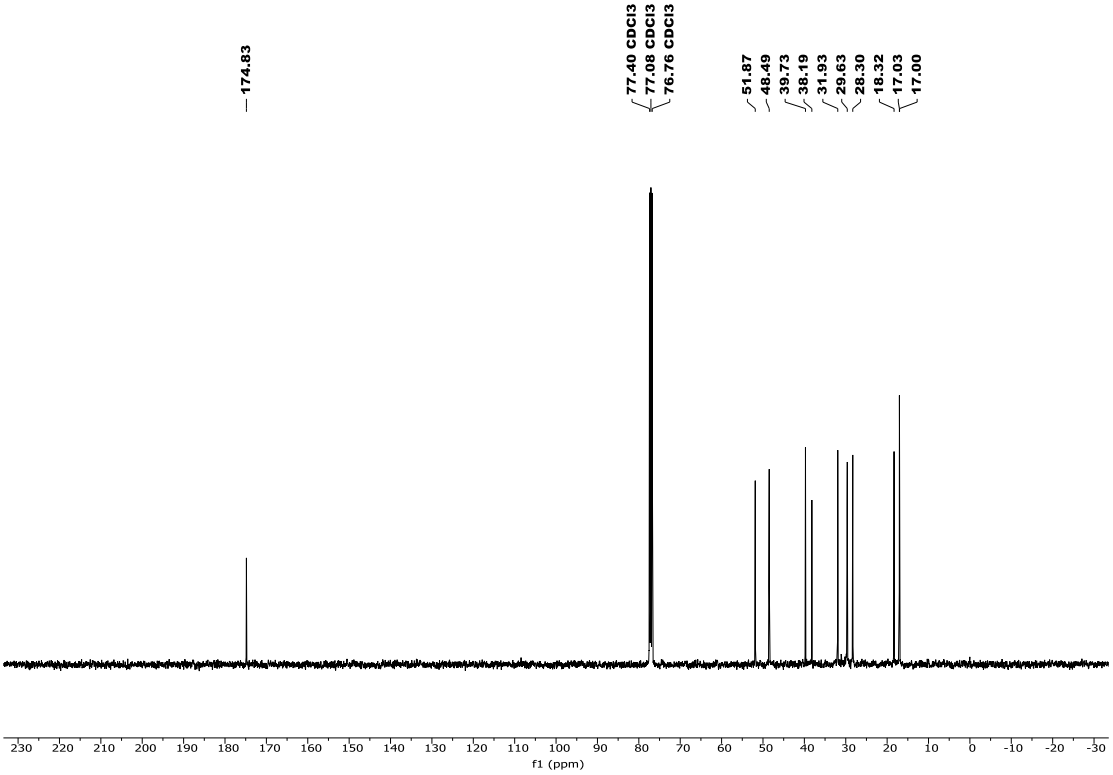
^{13}C NMR (101 MHz, $CDCl_3$):



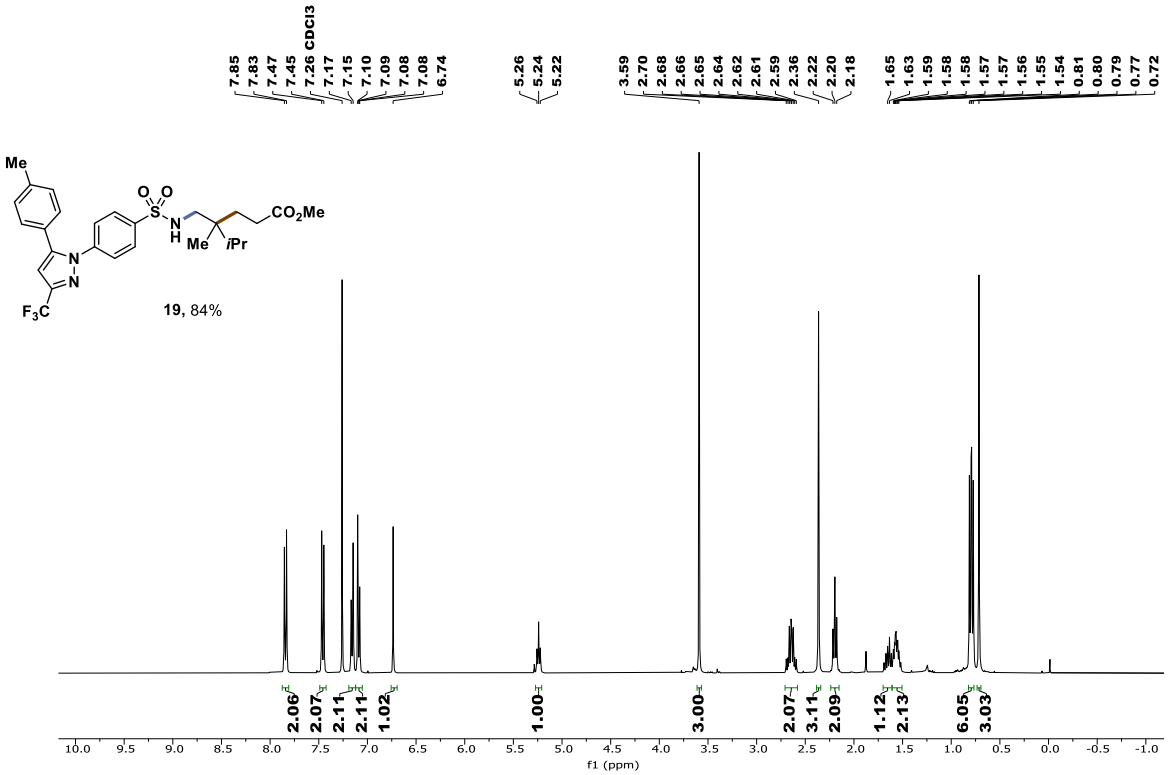
^{1}H NMR (400 MHz, $CDCl_3$):



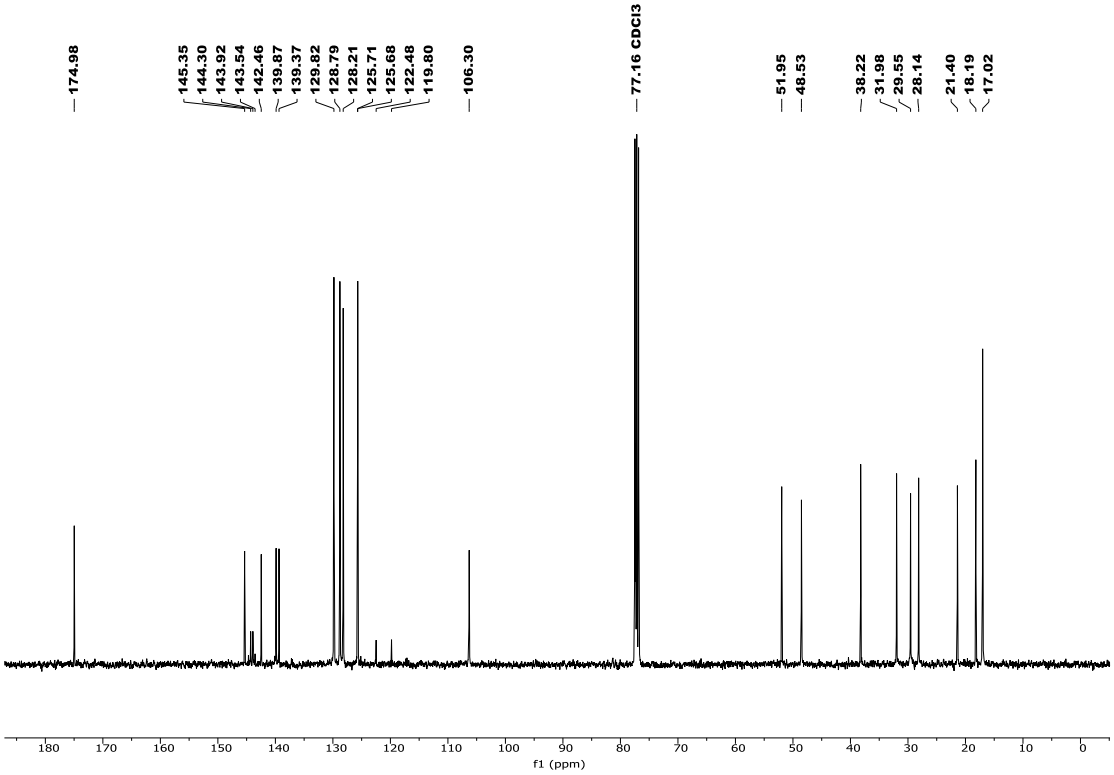
^{13}C NMR (101 MHz, $CDCl_3$):



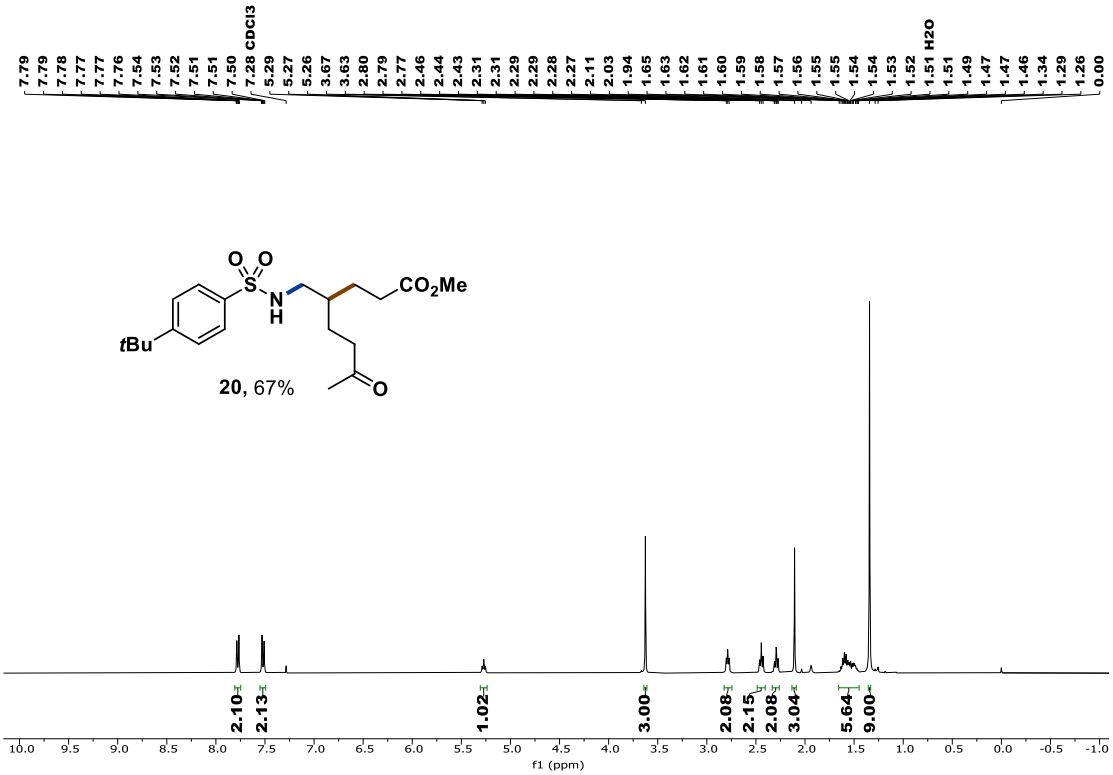
^{1}H NMR (400 MHz, $CDCl_3$):



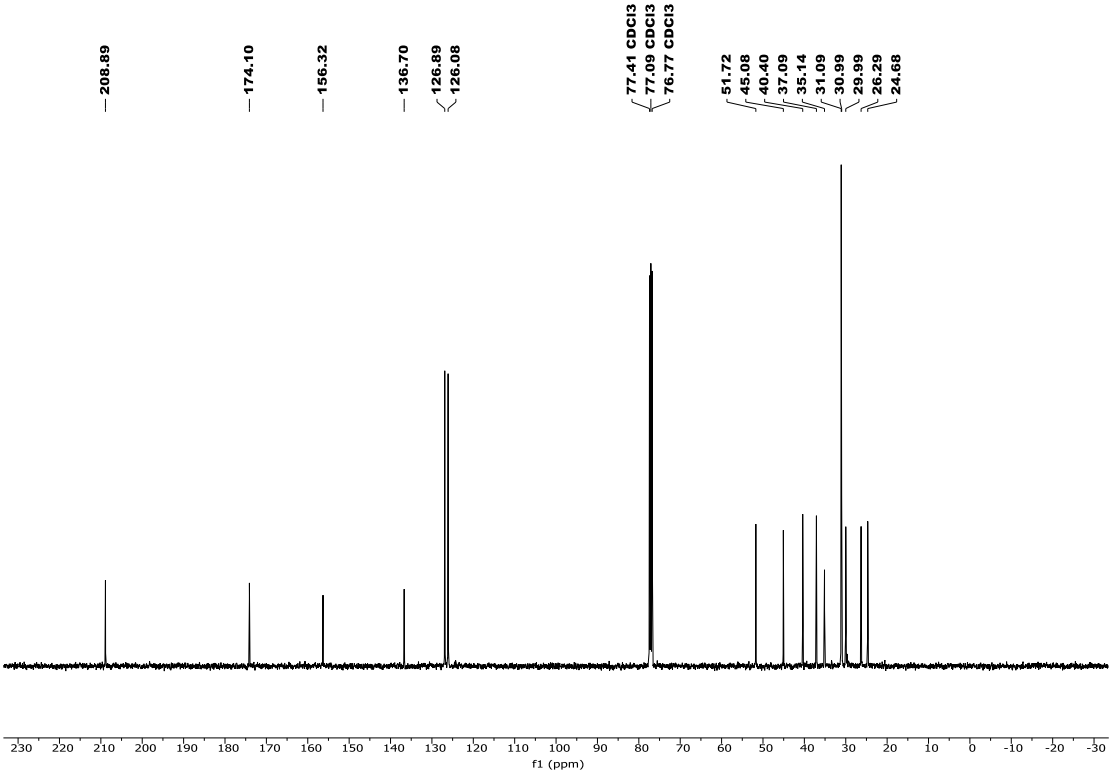
^{13}C NMR (101 MHz, $CDCl_3$):



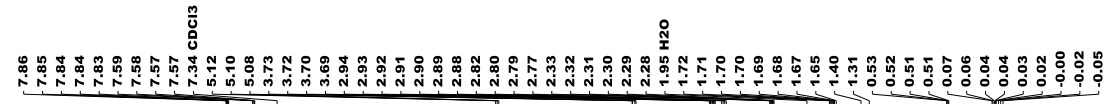
^{1}H NMR (400 MHz, $CDCl_3$):

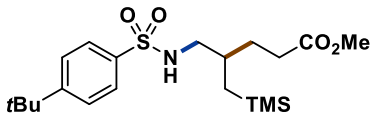


^{13}C NMR (101 MHz, $CDCl_3$):

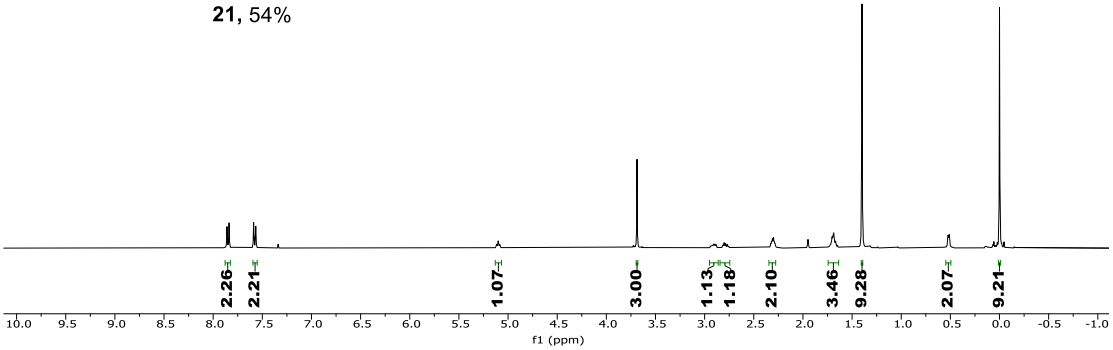


^{1}H NMR (400 MHz, $CDCl_3$):

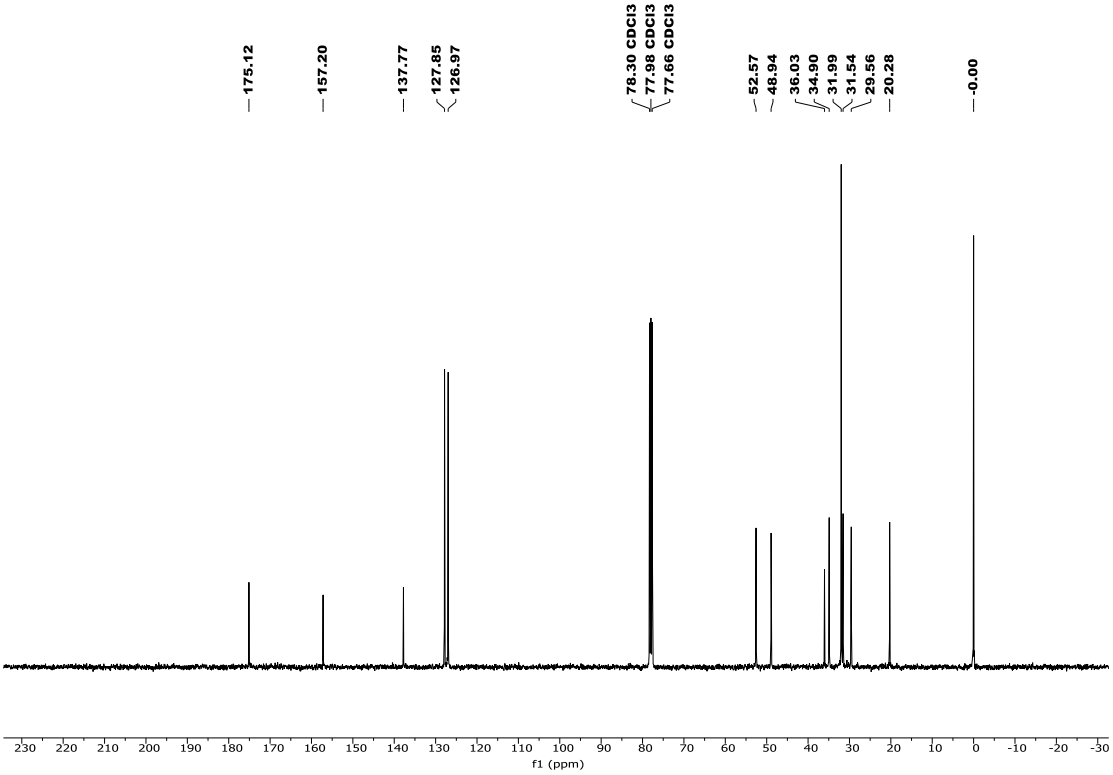




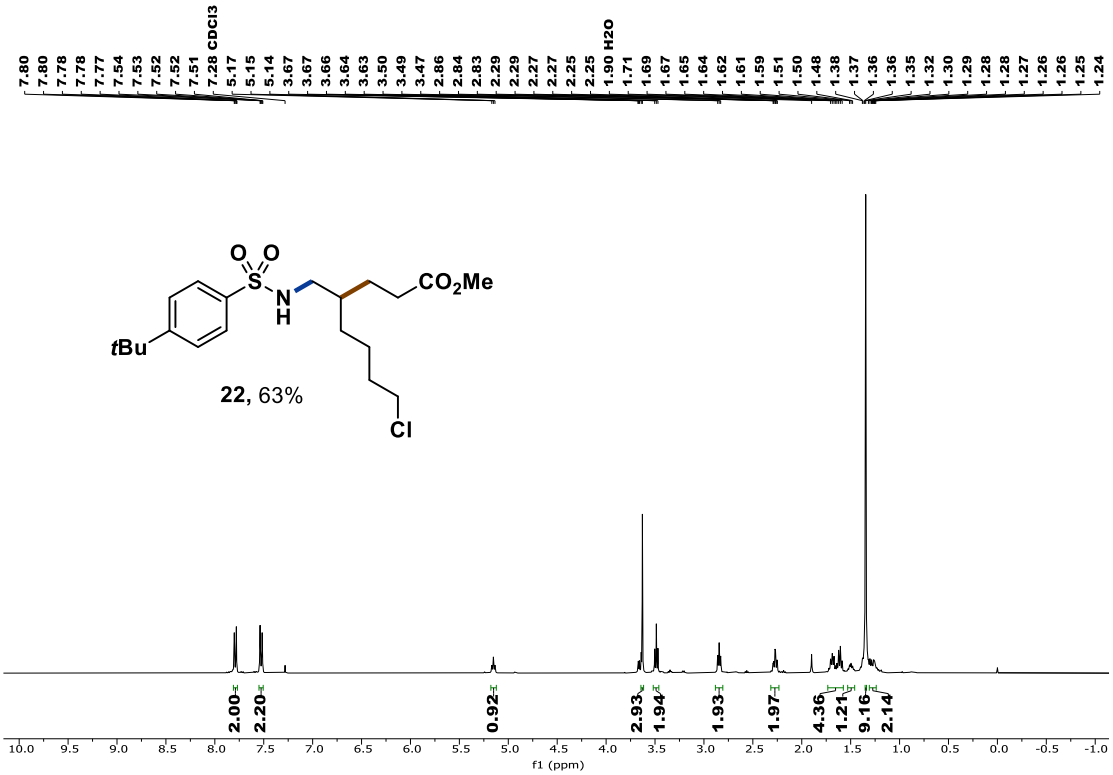
21, 54%



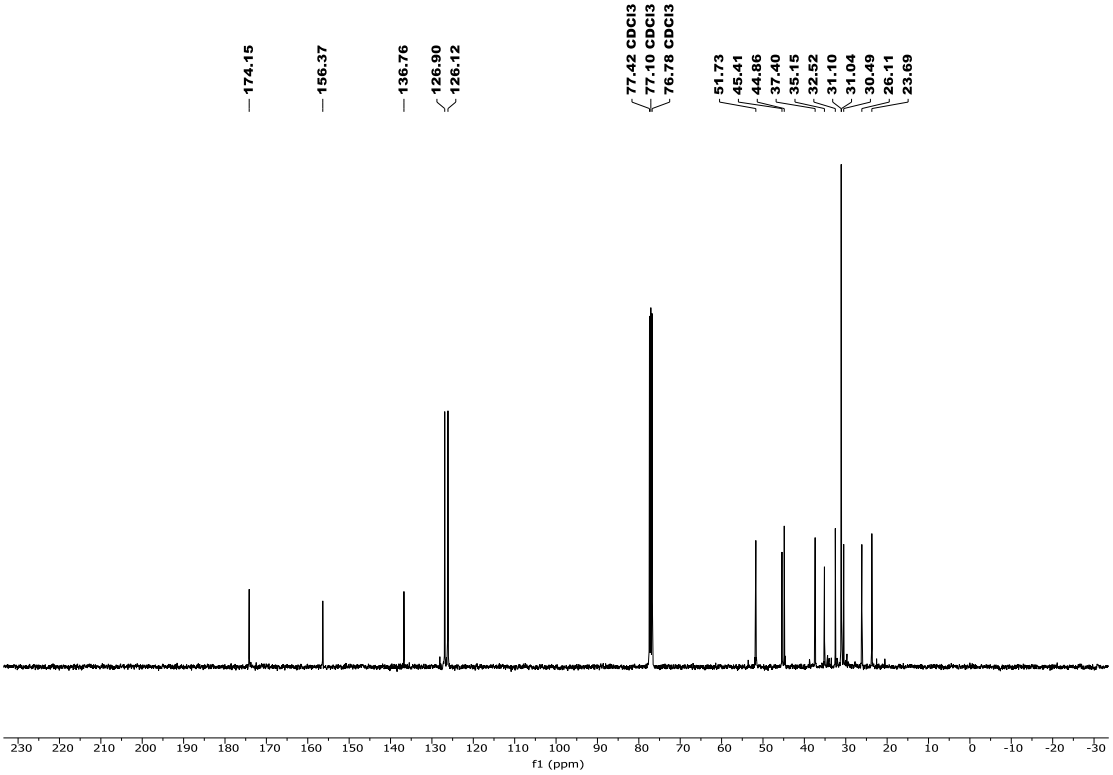
^{13}C NMR (101 MHz, $CDCl_3$):



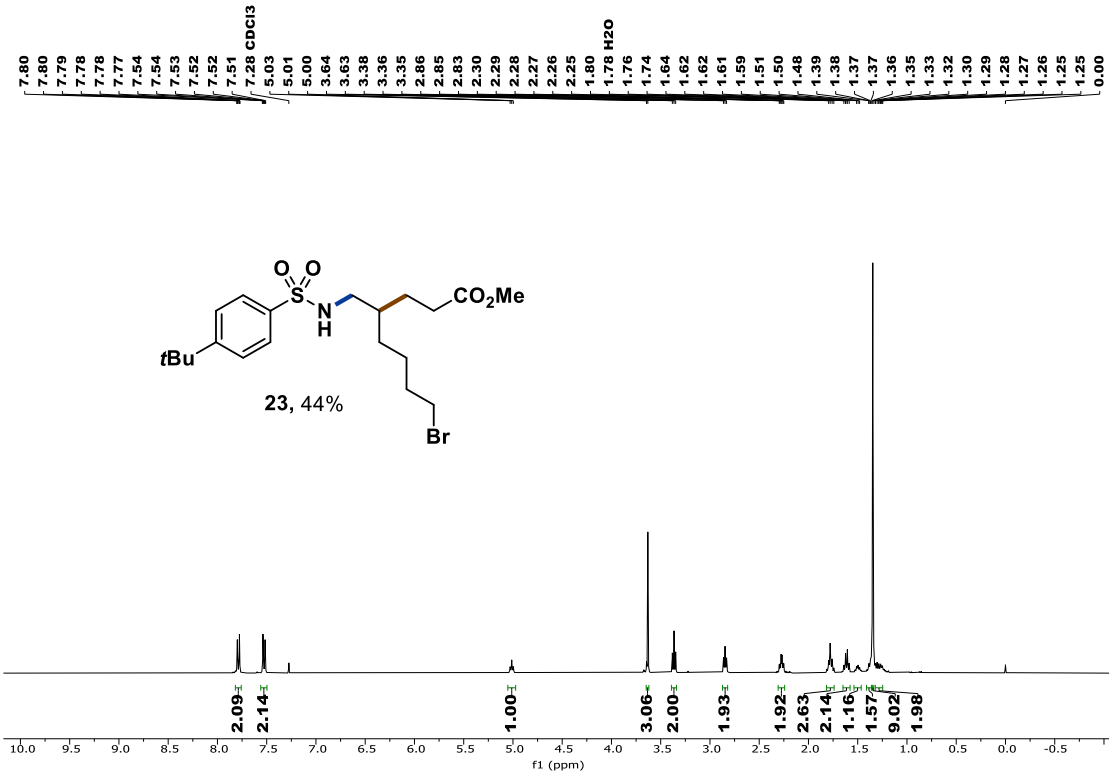
^{1}H NMR (400 MHz, $CDCl_3$):



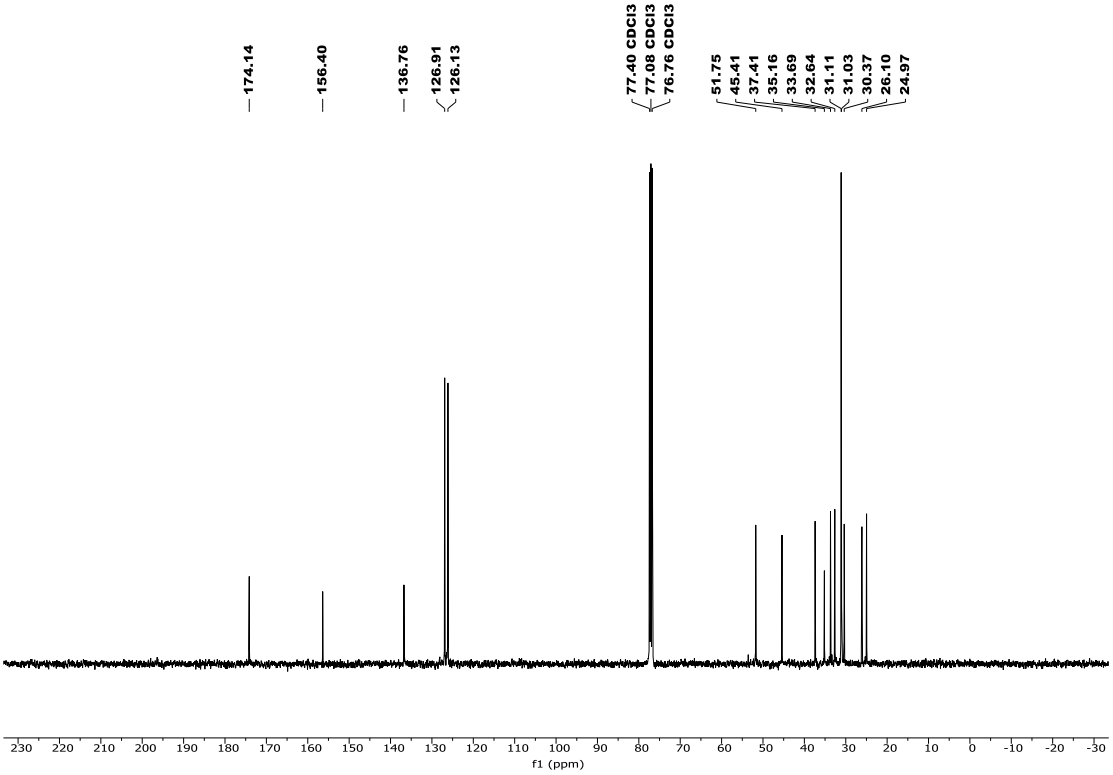
^{13}C NMR (101 MHz, $CDCl_3$):



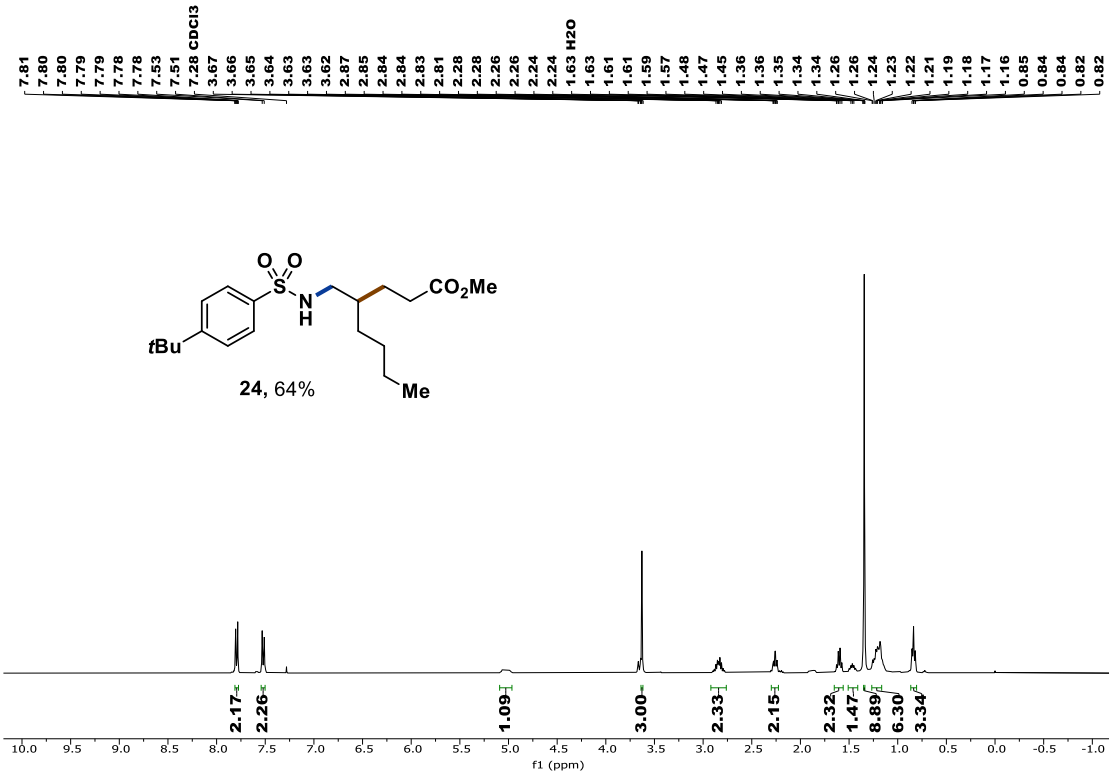
^{1}H NMR (400 MHz, $CDCl_3$):



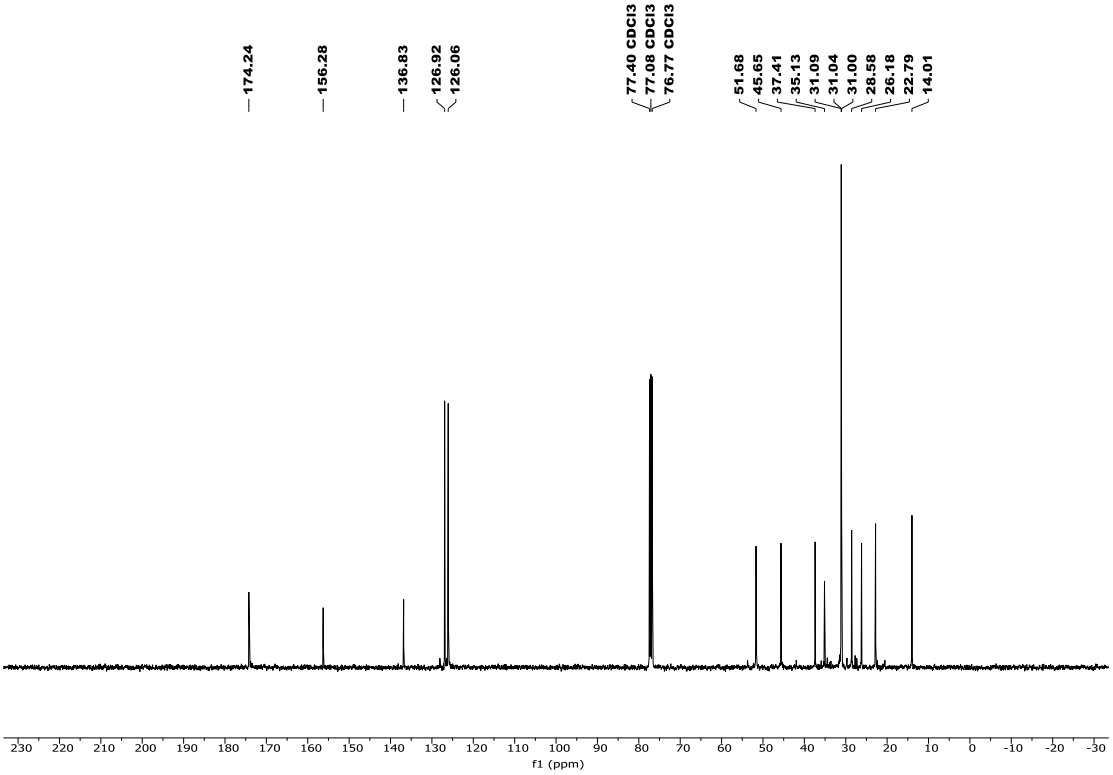
^{13}C NMR (101 MHz, $CDCl_3$):



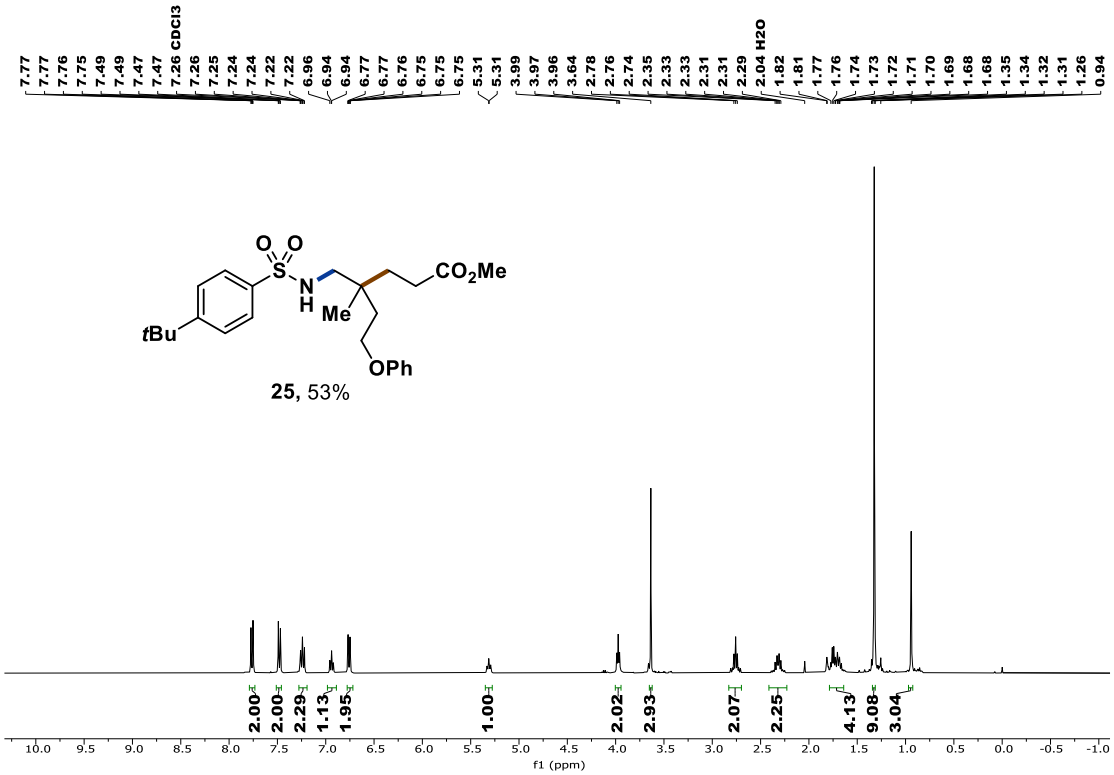
^{1}H NMR (400 MHz, $CDCl_3$):



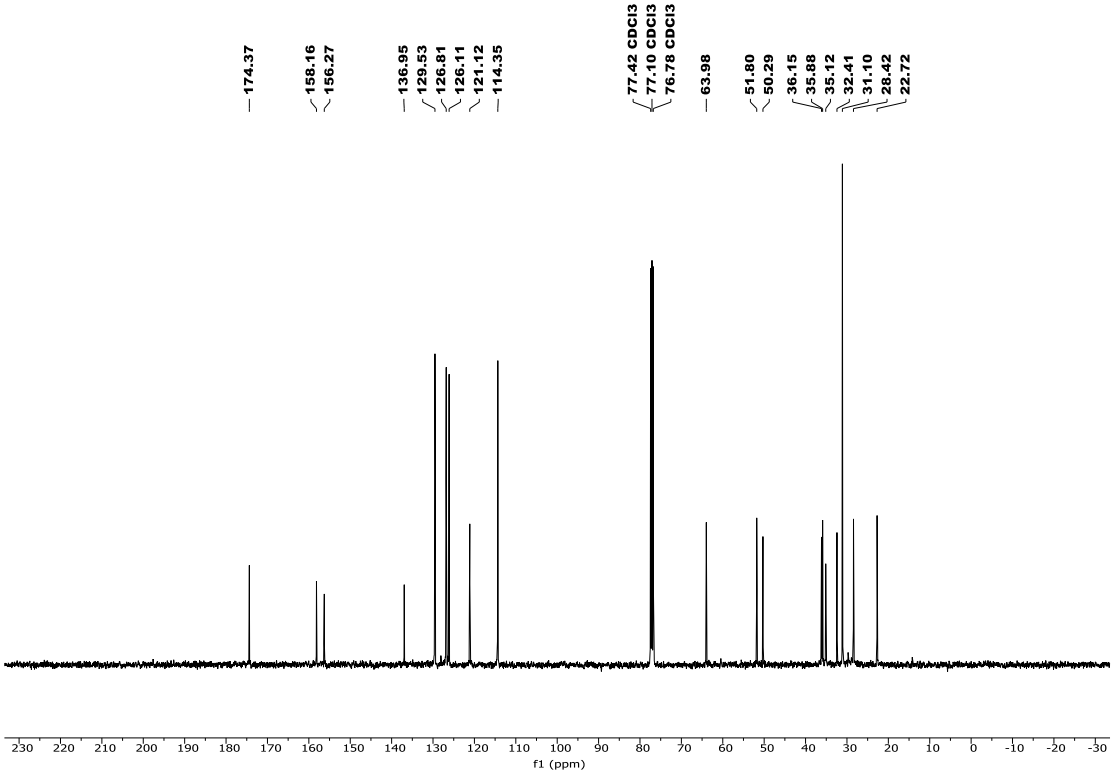
^{13}C NMR (101 MHz, $CDCl_3$):



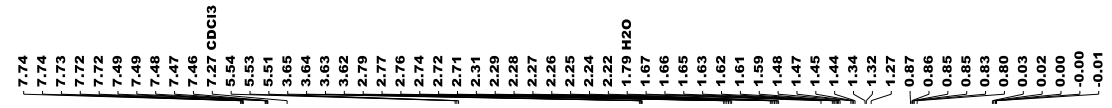
^{1}H NMR (400 MHz, $CDCl_3$):

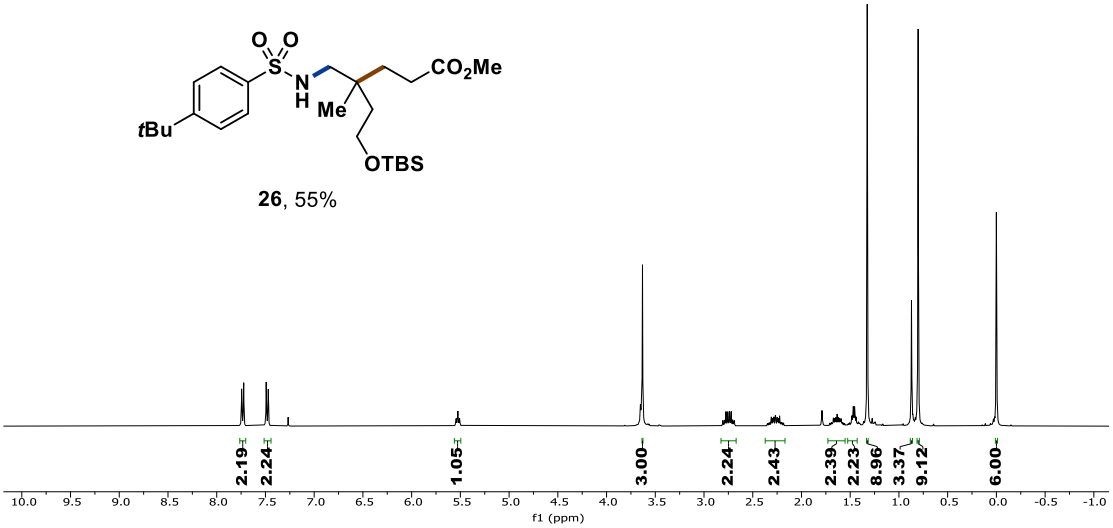


^{13}C NMR (101 MHz, $CDCl_3$):



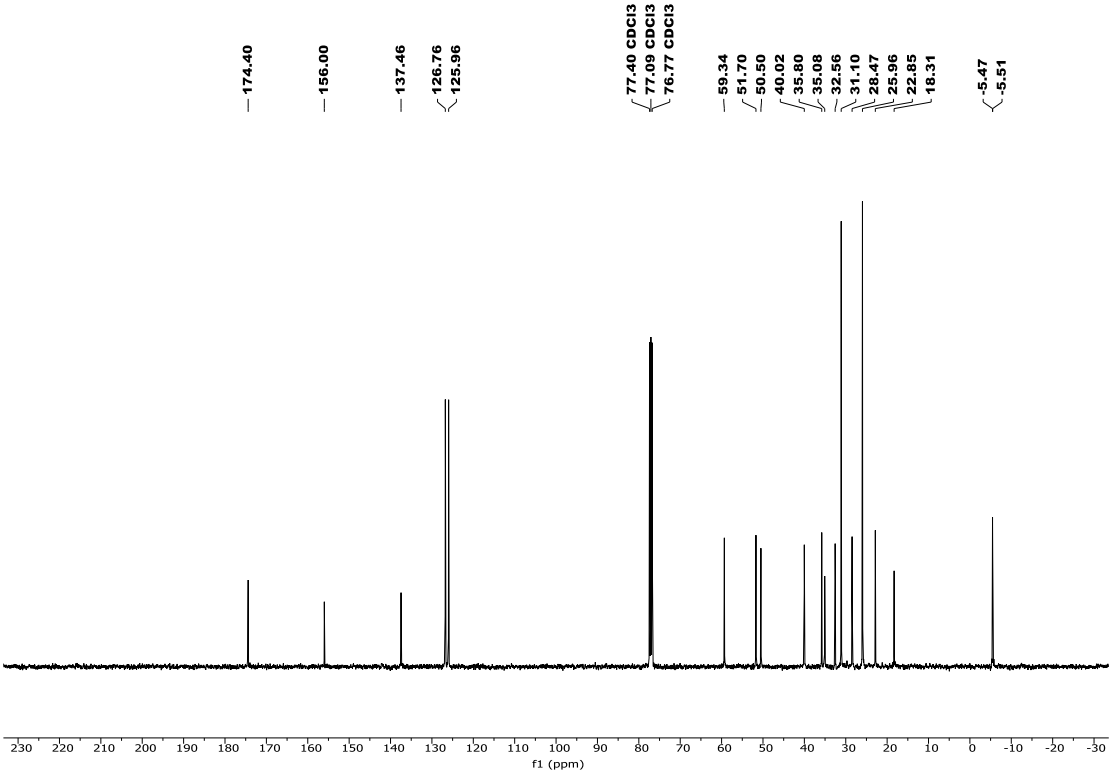
^{1}H NMR (400 MHz, $CDCl_3$):



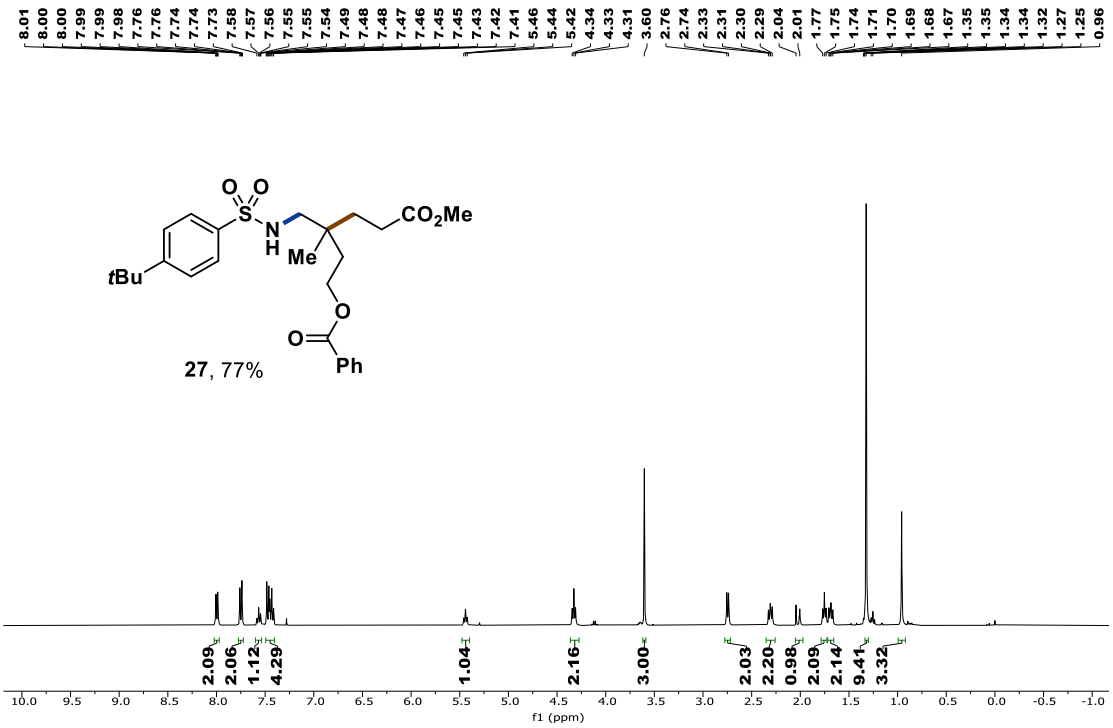


26, 55%

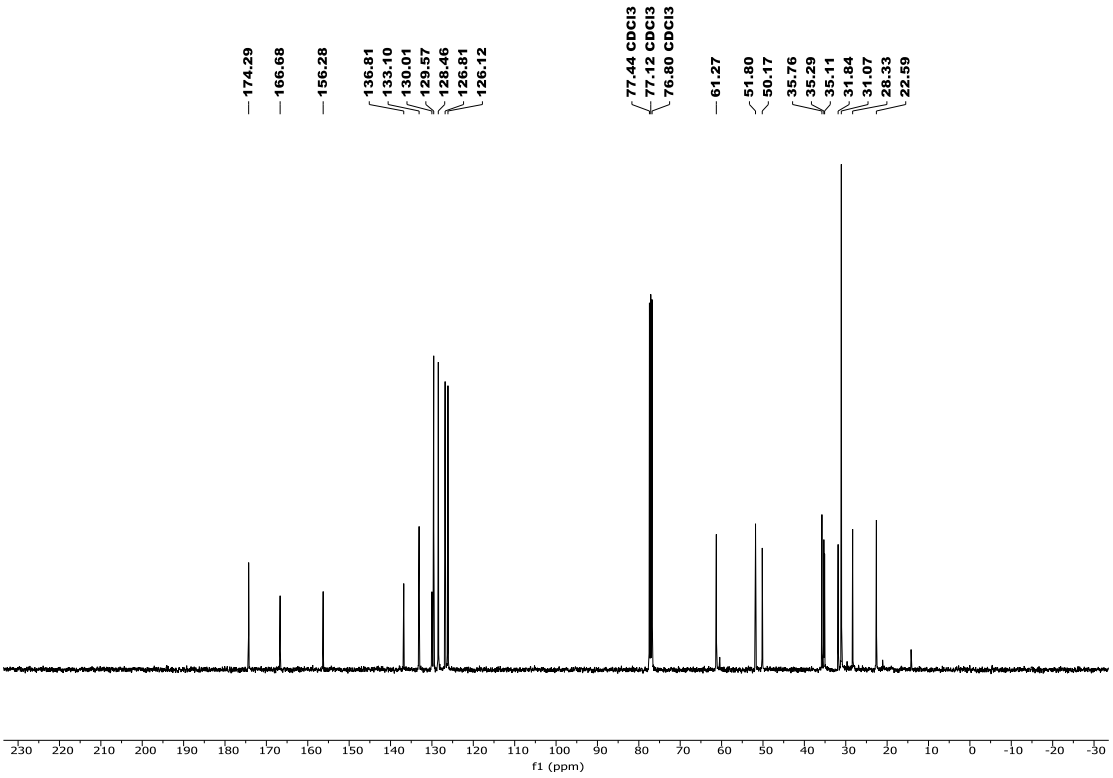
^{13}C NMR (101 MHz, $CDCl_3$):



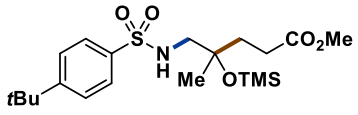
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):

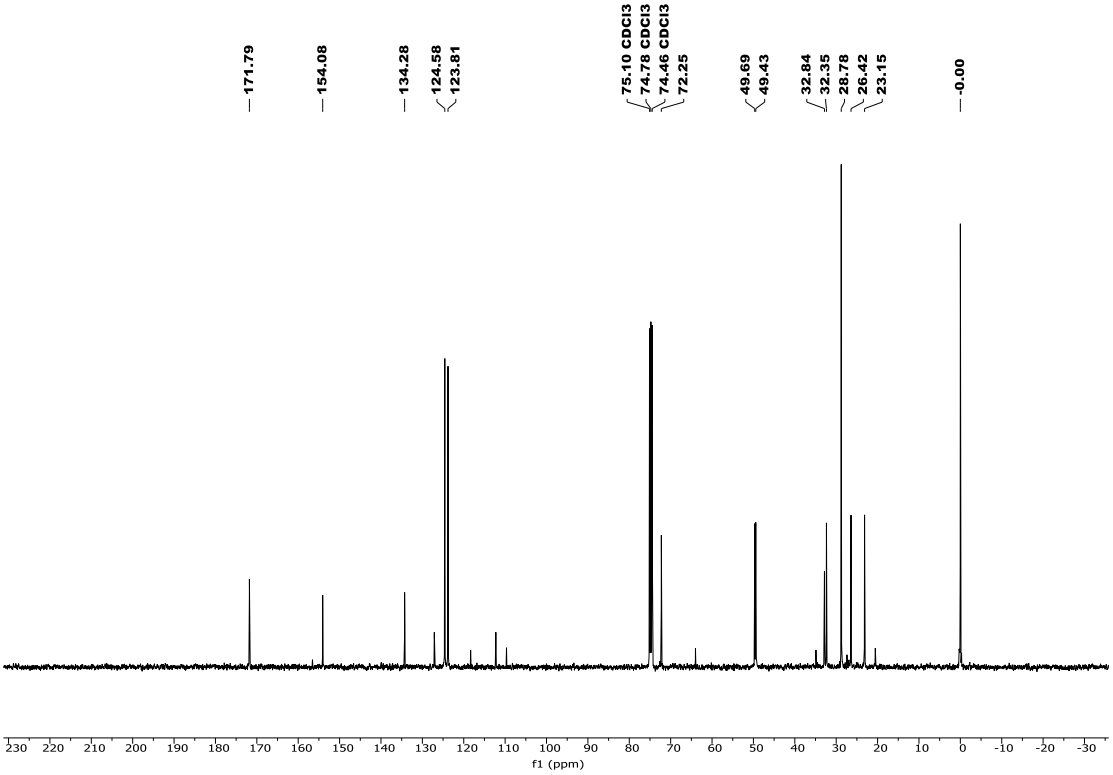


^{1}H NMR (400 MHz, $CDCl_3$):

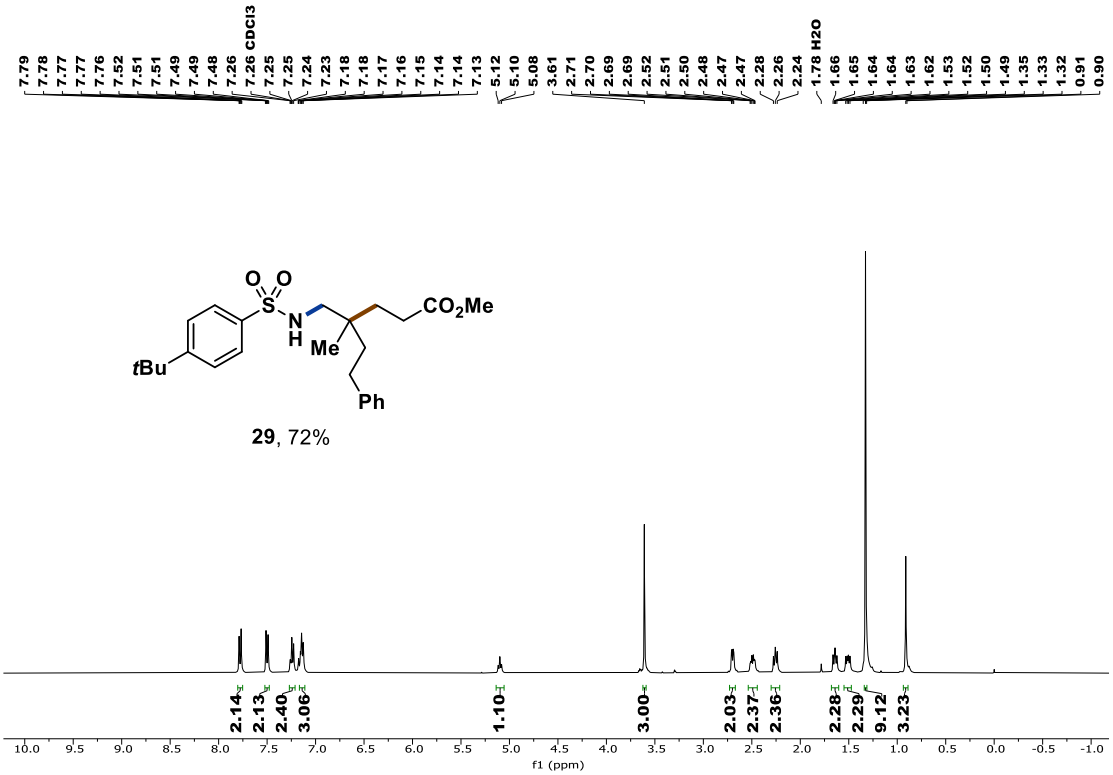


28, 64%

^{13}C NMR (101 MHz, $CDCl_3$):

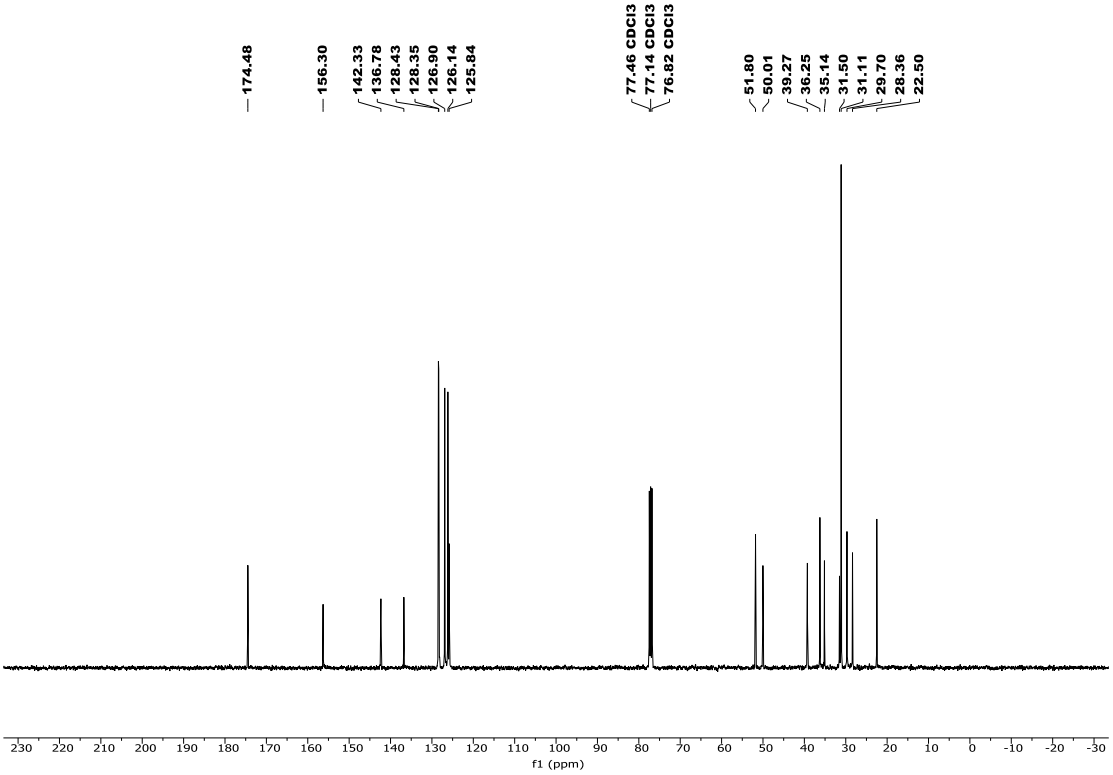


^{1}H NMR (400 MHz, $CDCl_3$):

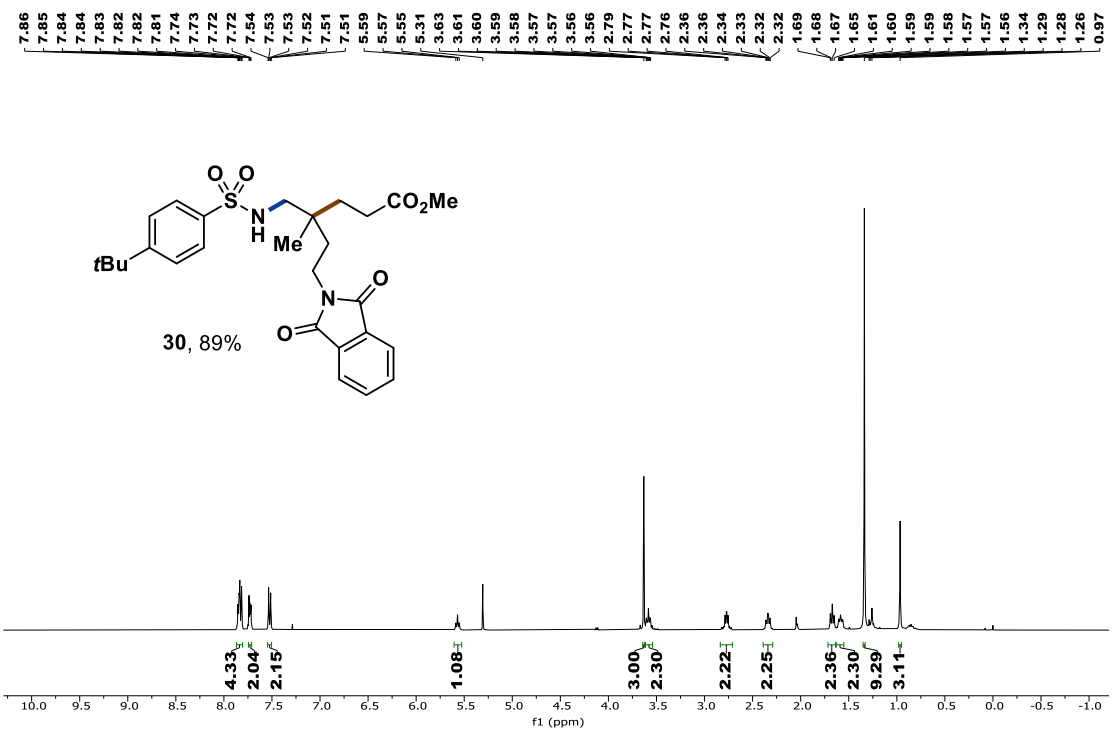


29, 72%

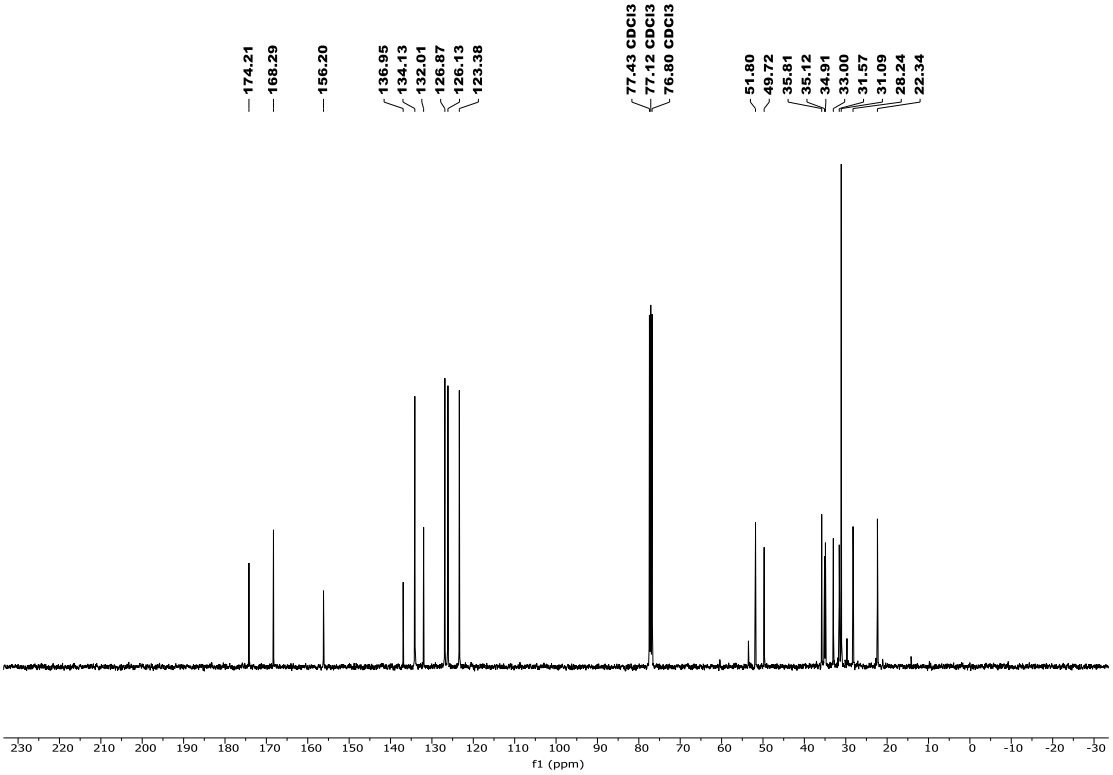
^{13}C NMR (101 MHz, $CDCl_3$):



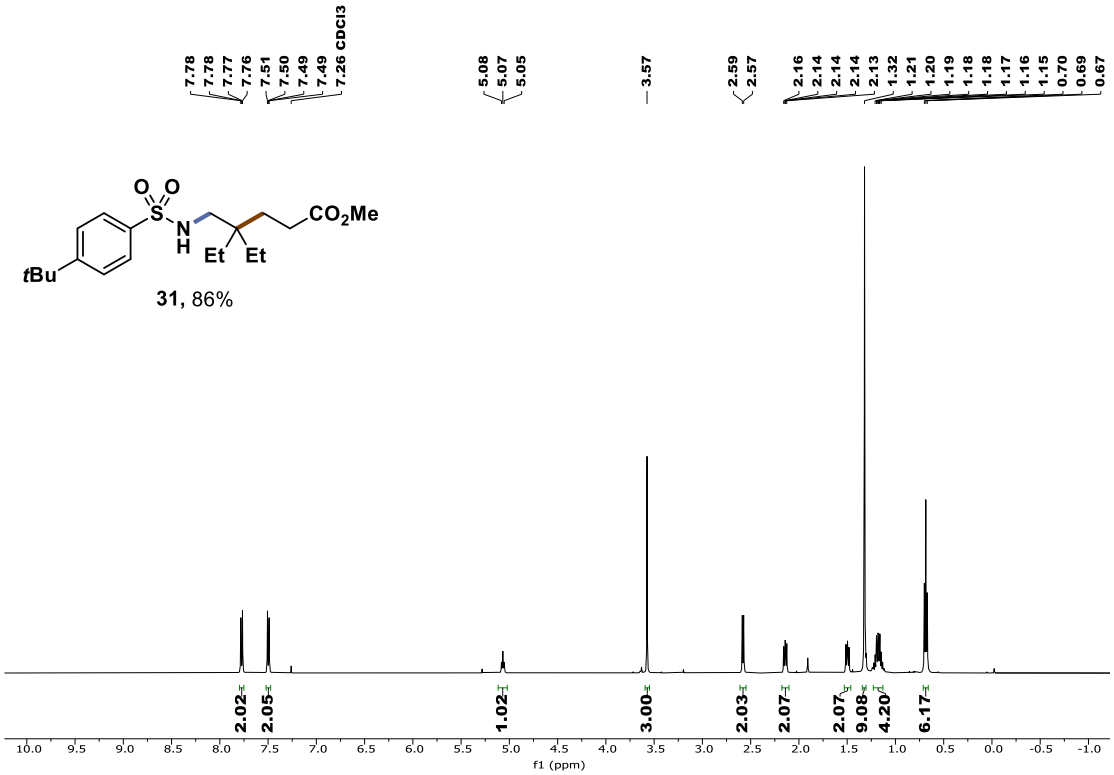
^{1}H NMR (400 MHz, $CDCl_3$):



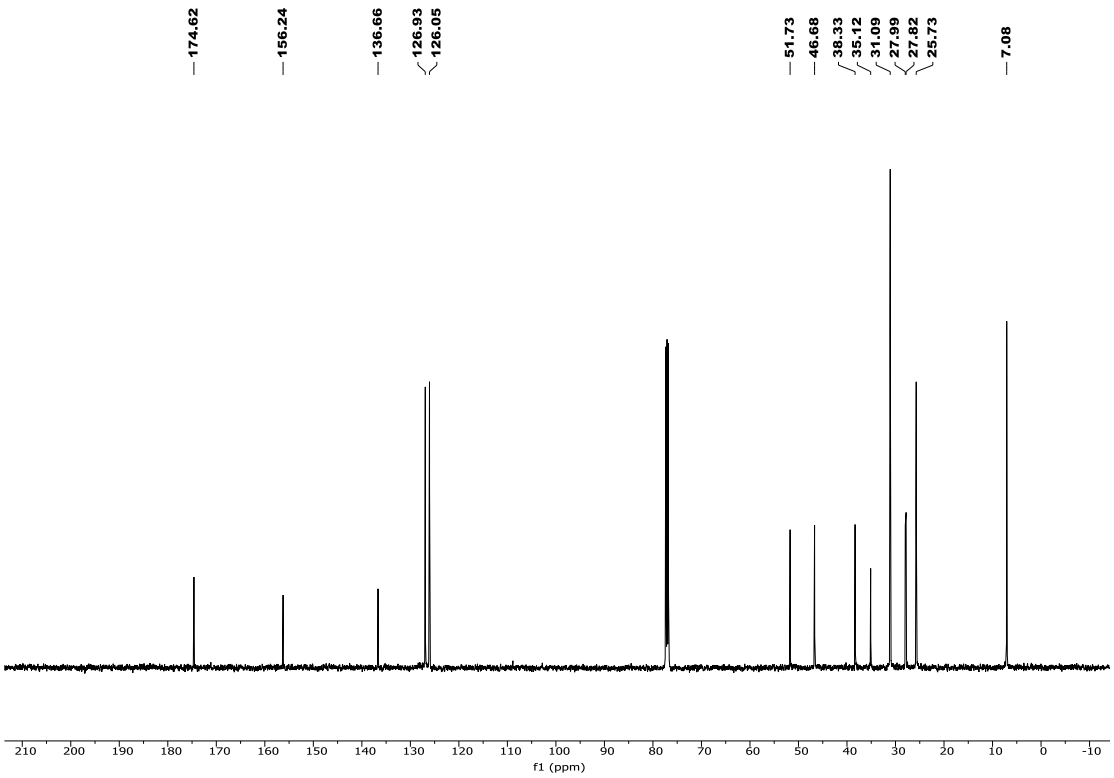
^{13}C NMR (101 MHz, $CDCl_3$):



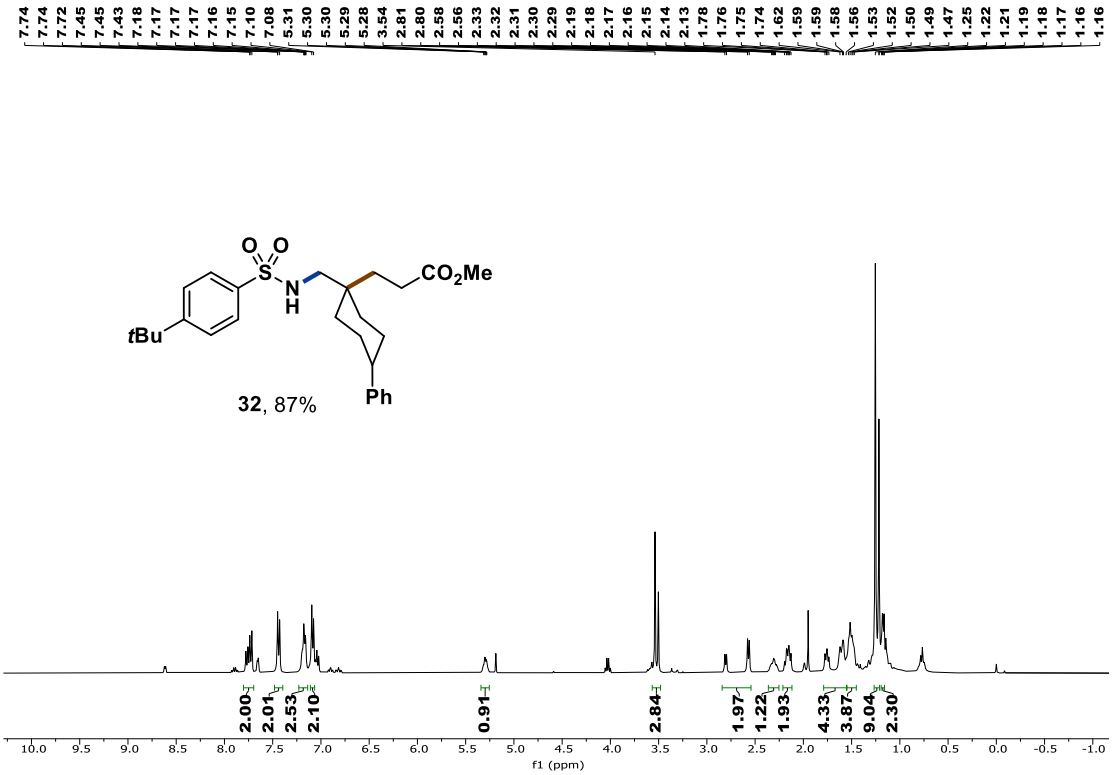
^{1}H NMR (500 MHz, $CDCl_3$):



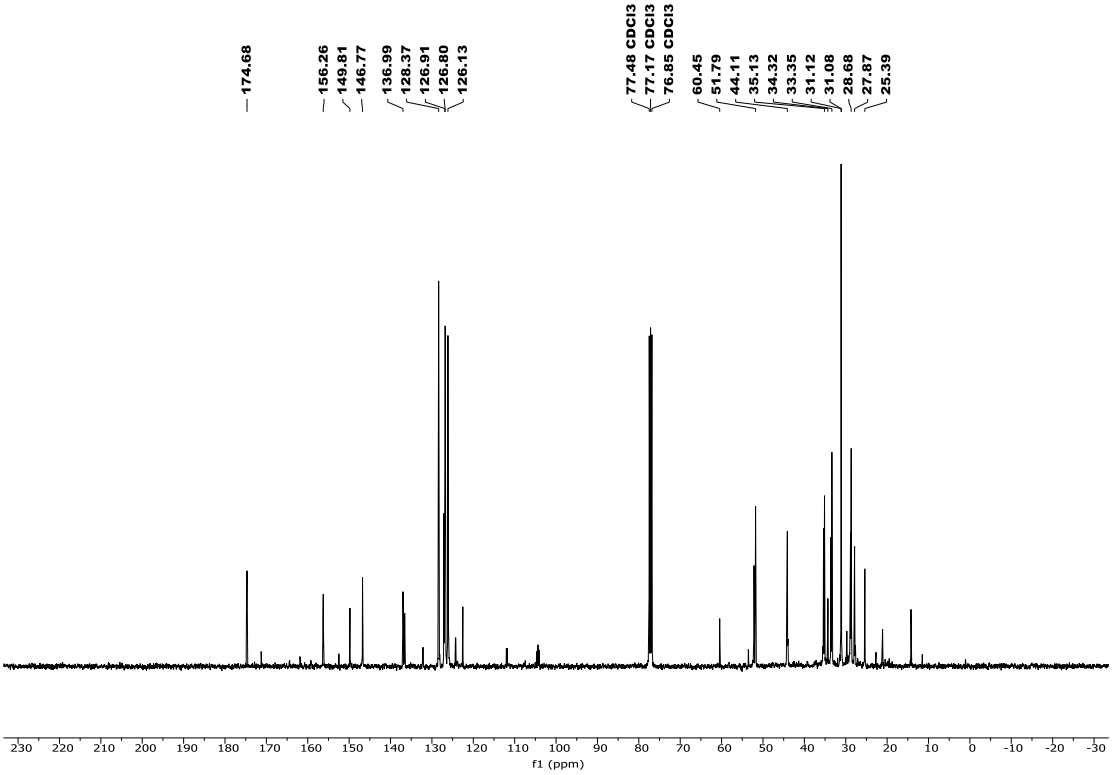
^{13}C NMR (126 MHz, $CDCl_3$):



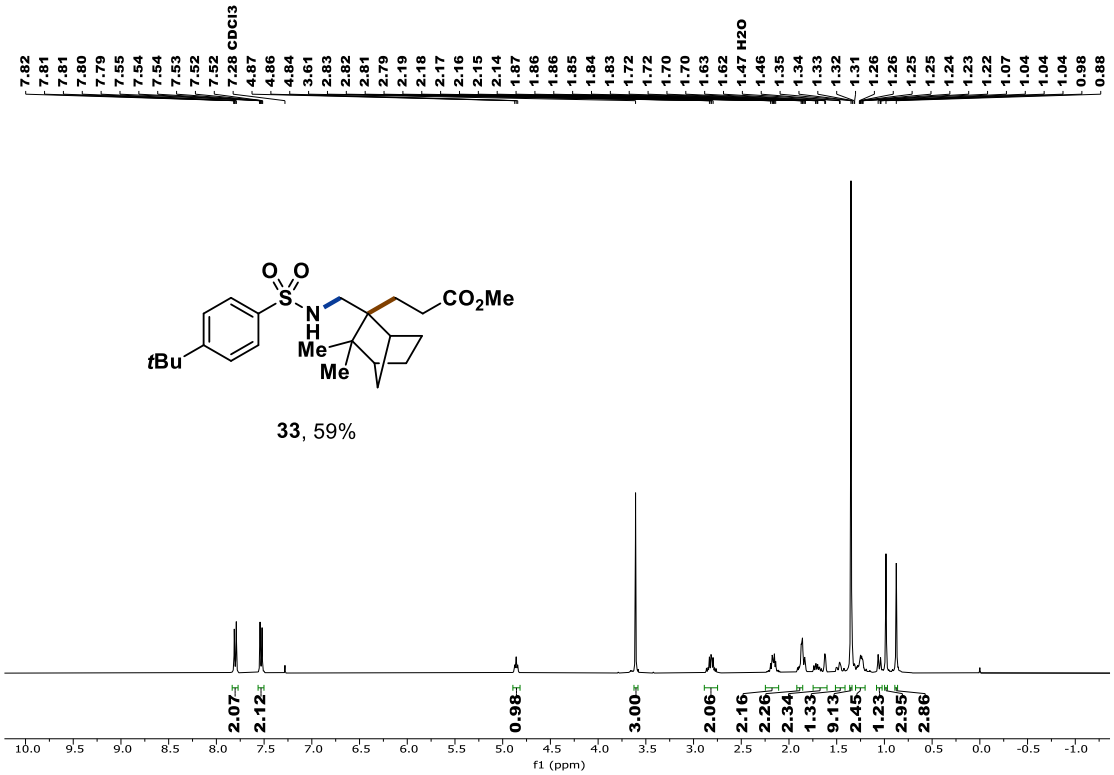
^{1}H NMR (400 MHz, $CDCl_3$):



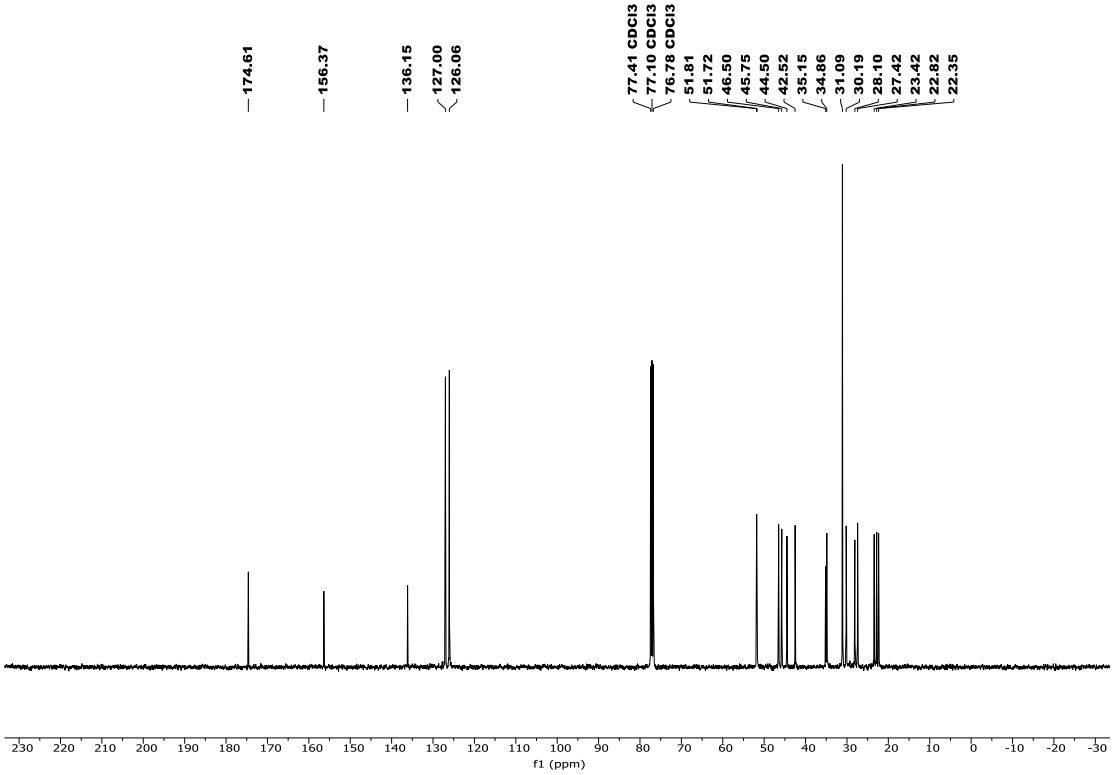
^{13}C NMR (101 MHz, $CDCl_3$):



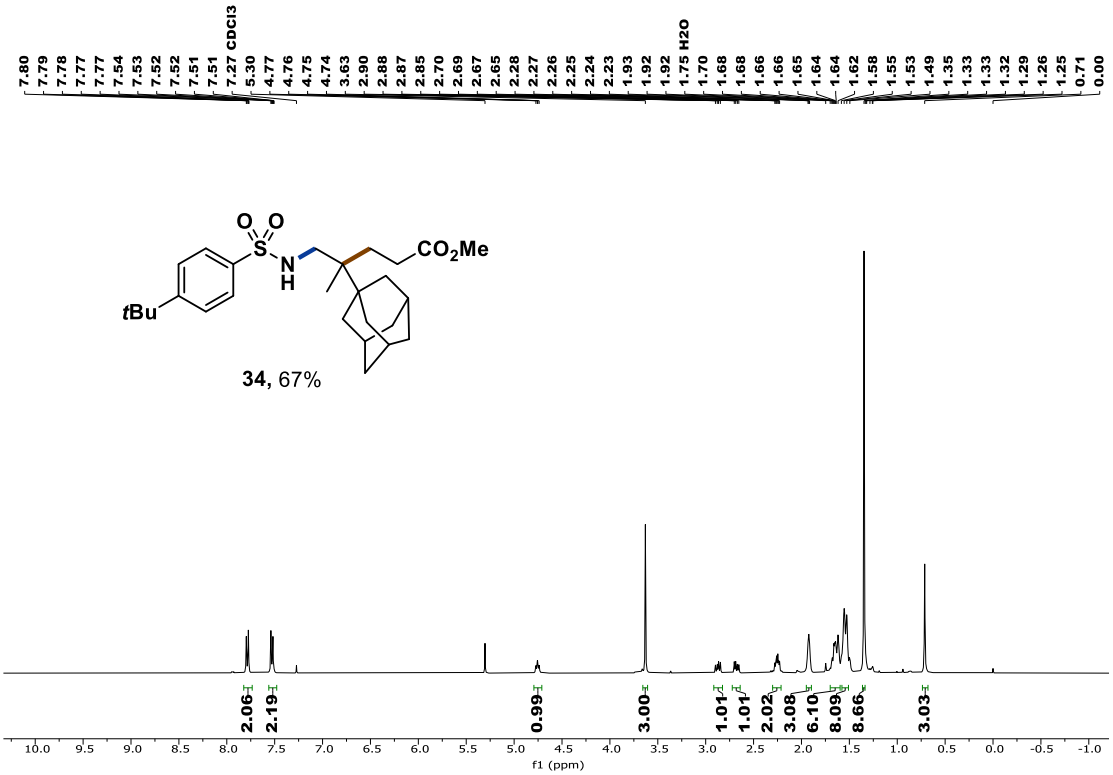
^{1}H NMR (400 MHz, $CDCl_3$):



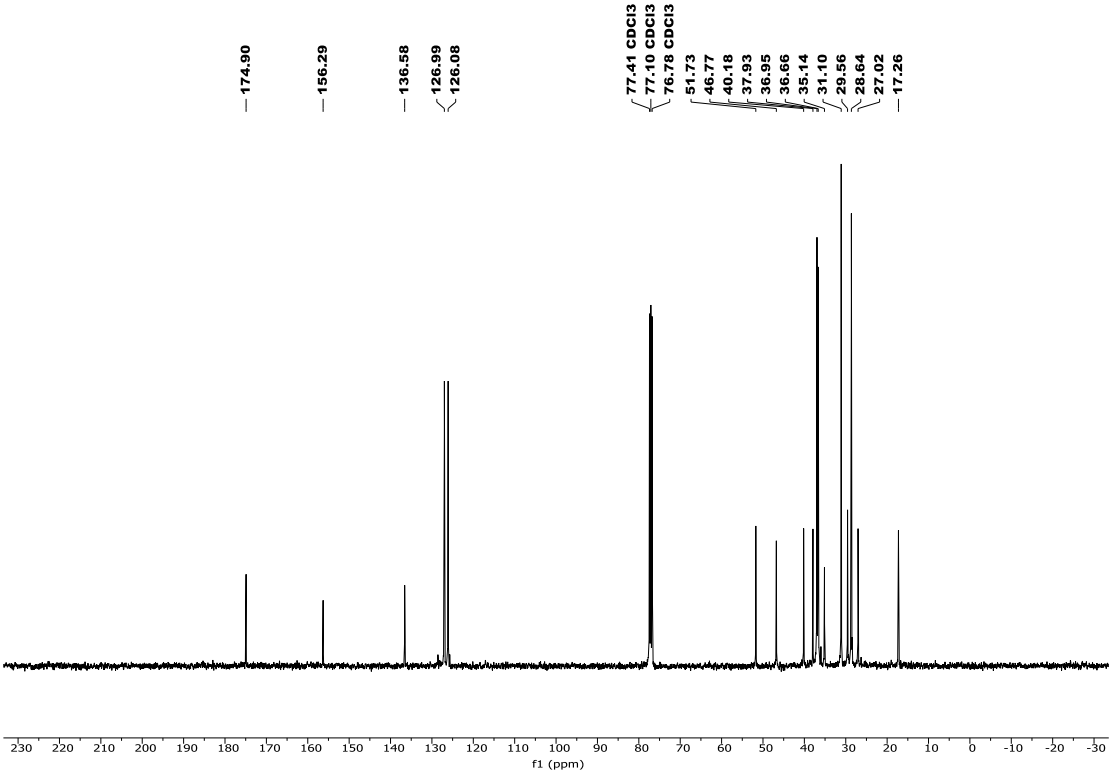
^{13}C NMR (101 MHz, $CDCl_3$):



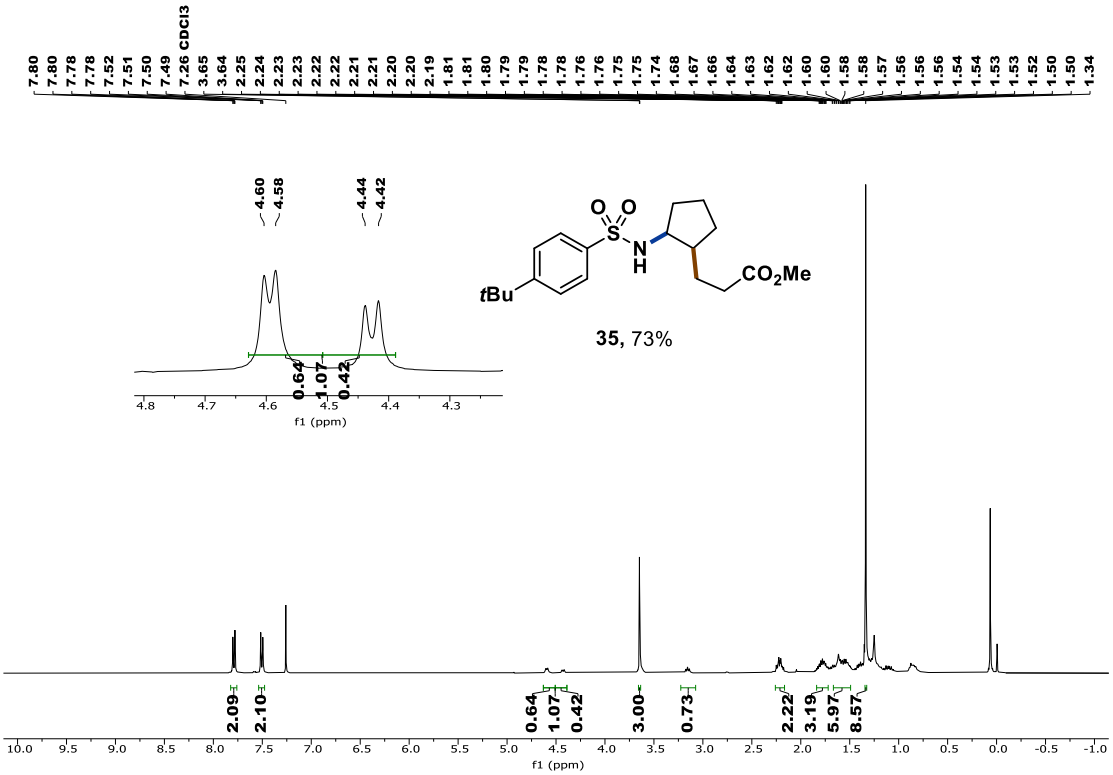
^{1}H NMR (400 MHz, $CDCl_3$):



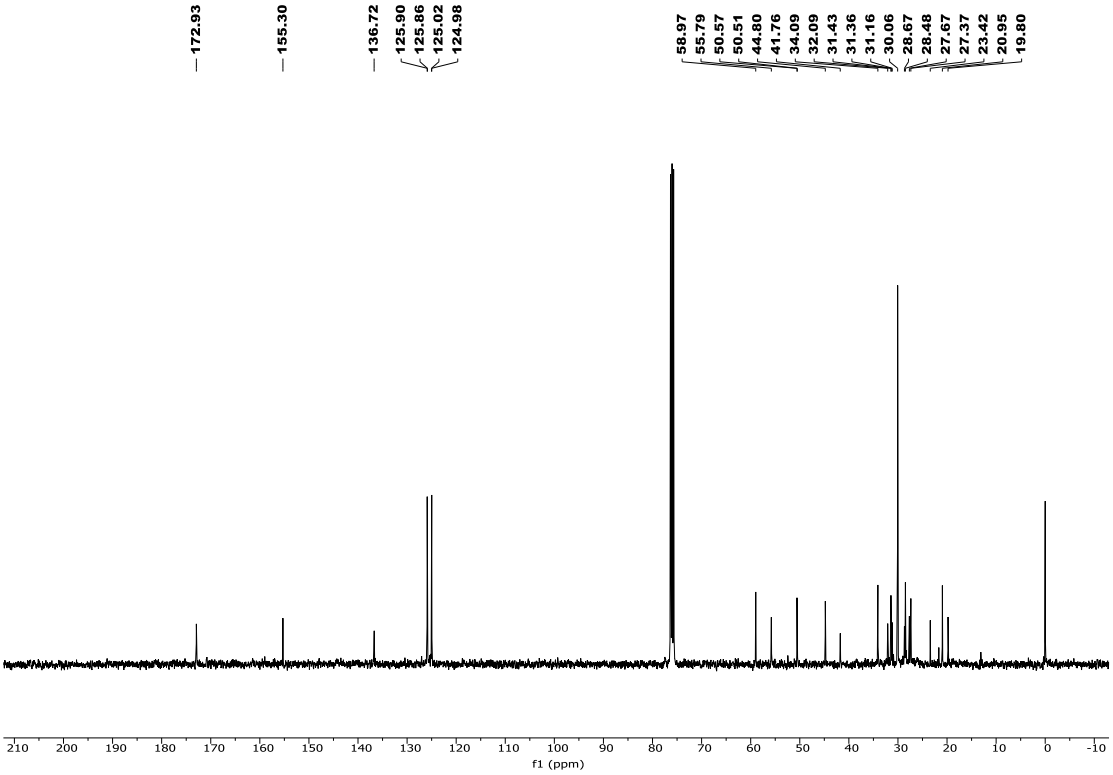
^{13}C NMR (101 MHz, $CDCl_3$):



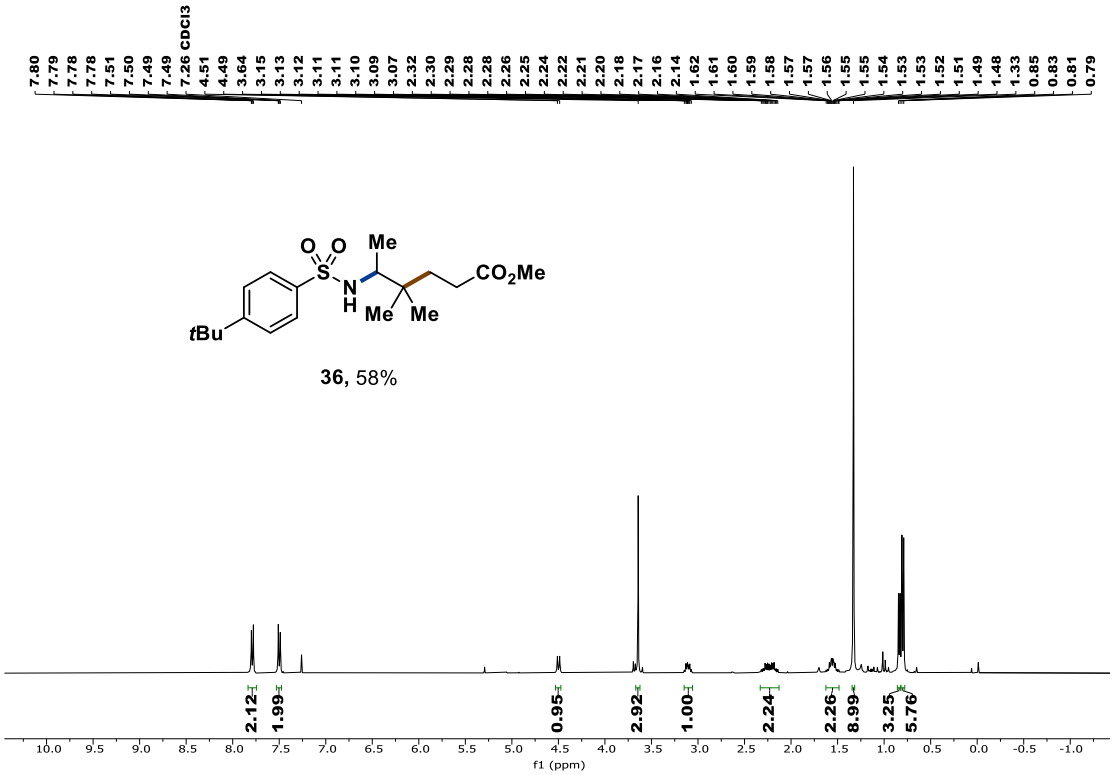
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):

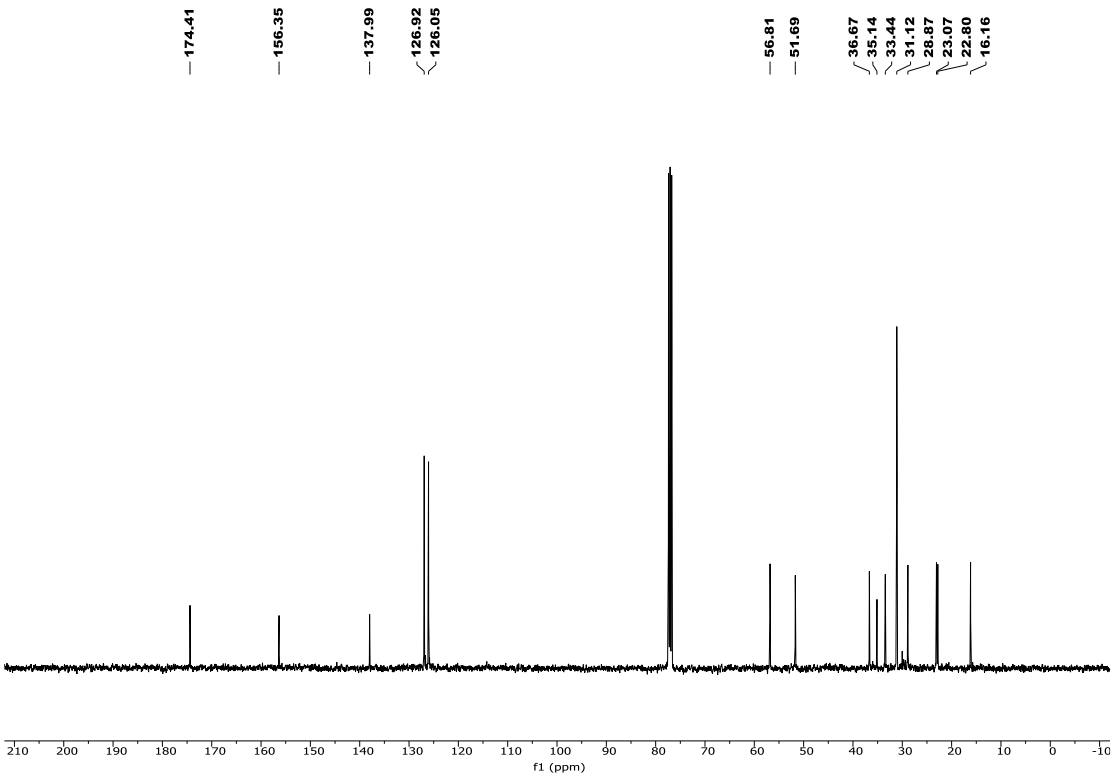


^{1}H NMR (400 MHz, $CDCl_3$):

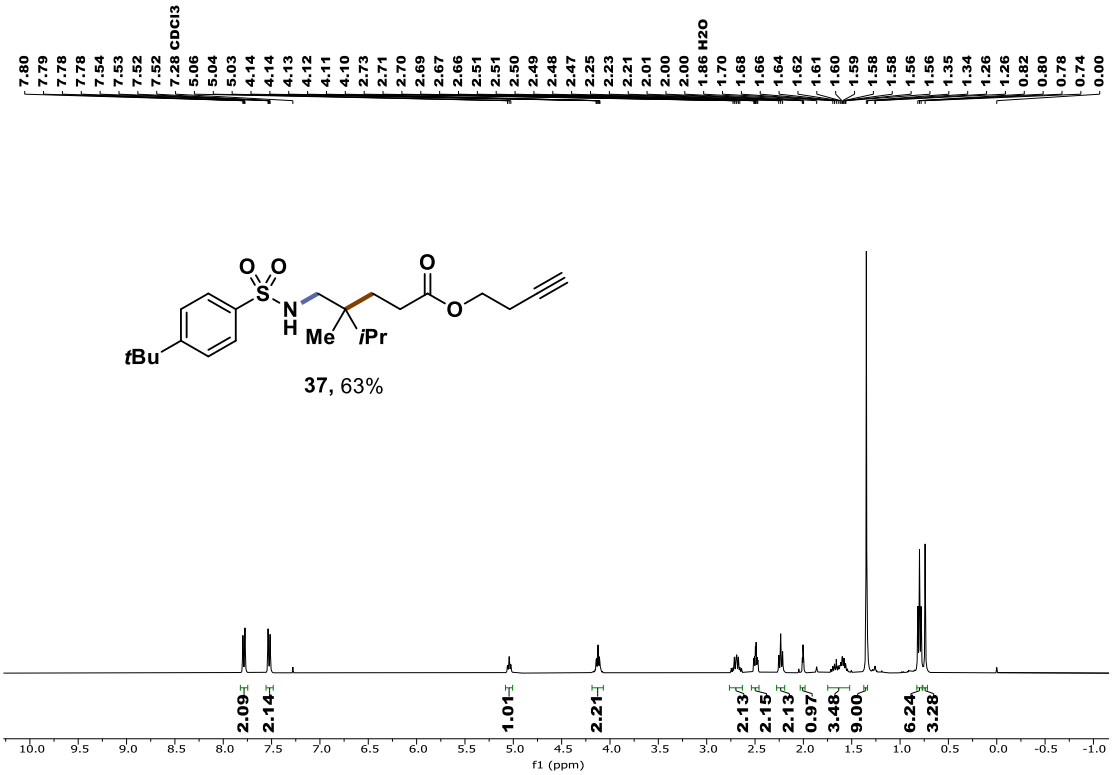


36, 58%

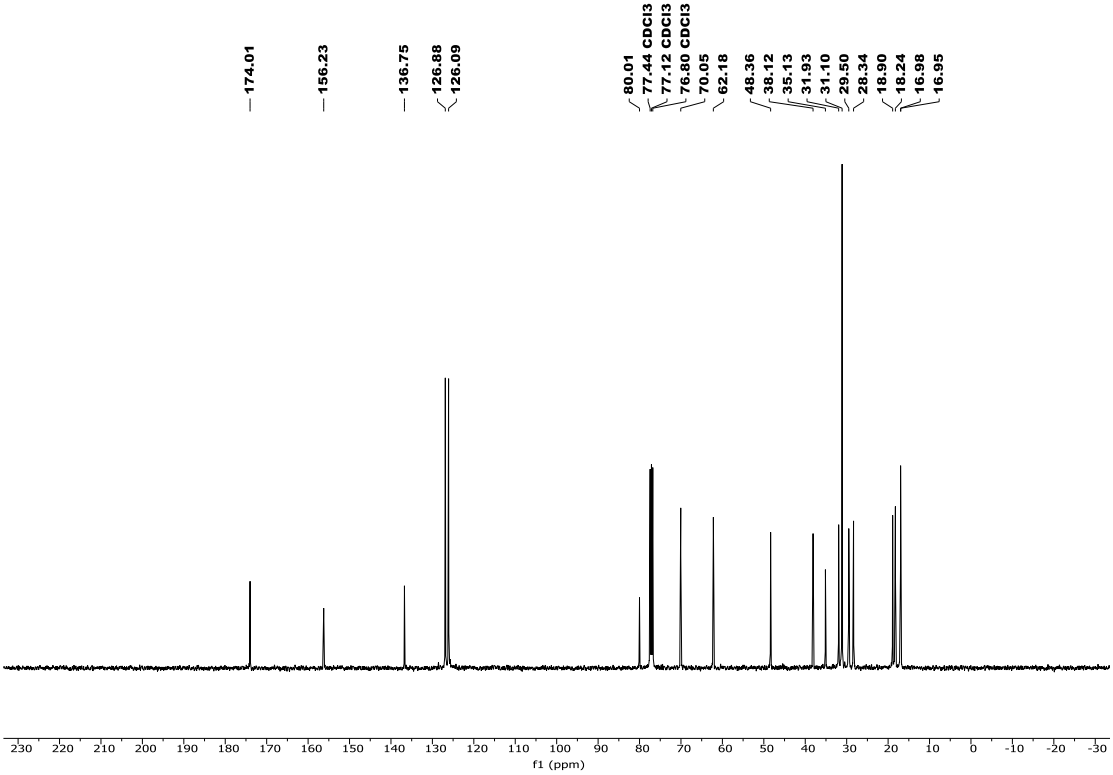
^{13}C NMR (101 MHz, $CDCl_3$):



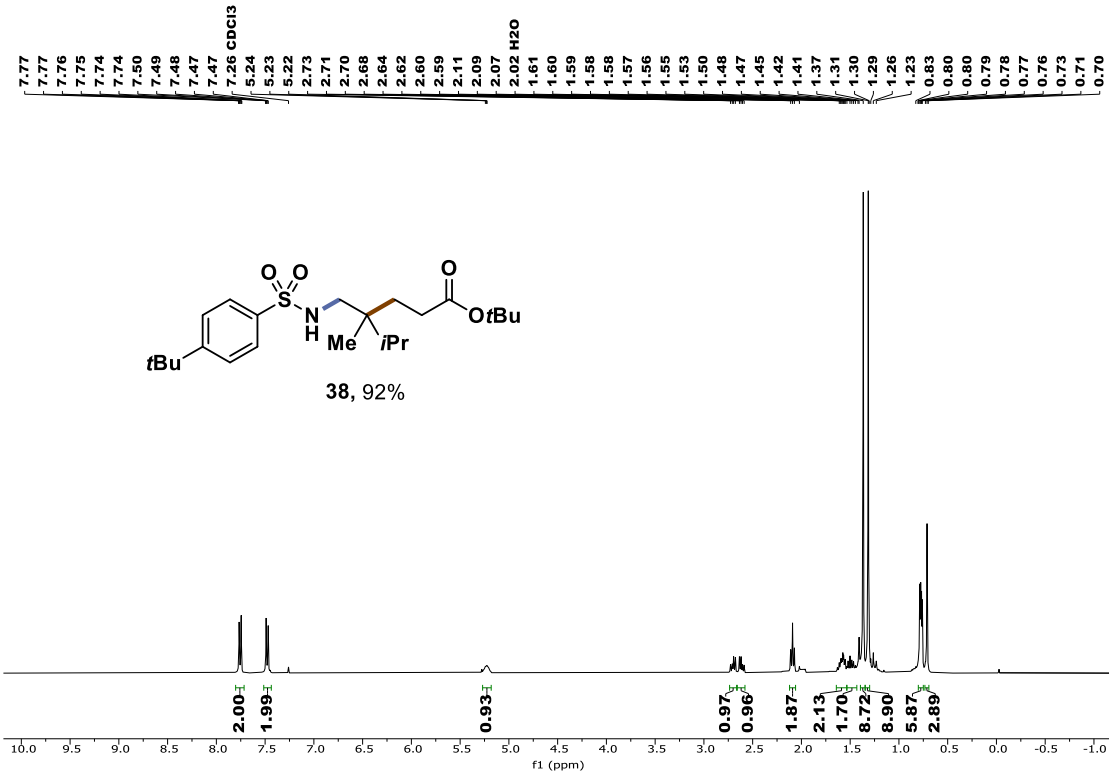
^{1}H NMR (400 MHz, $CDCl_3$):



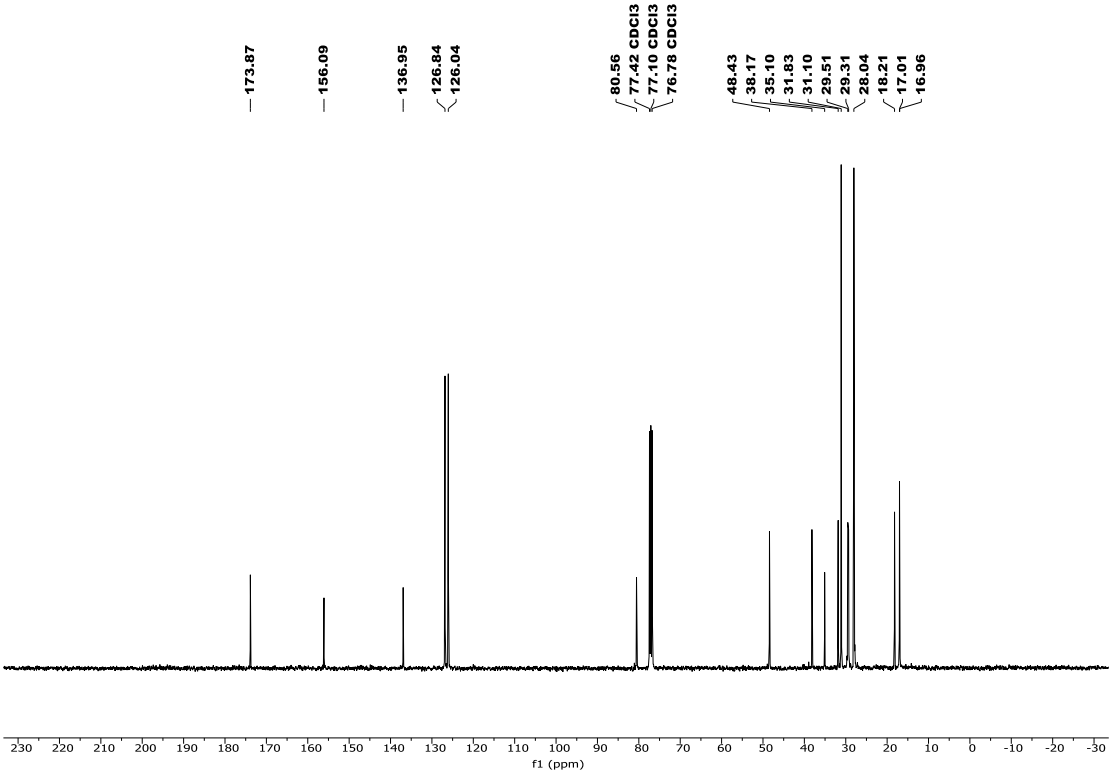
^{13}C NMR (101 MHz, $CDCl_3$):



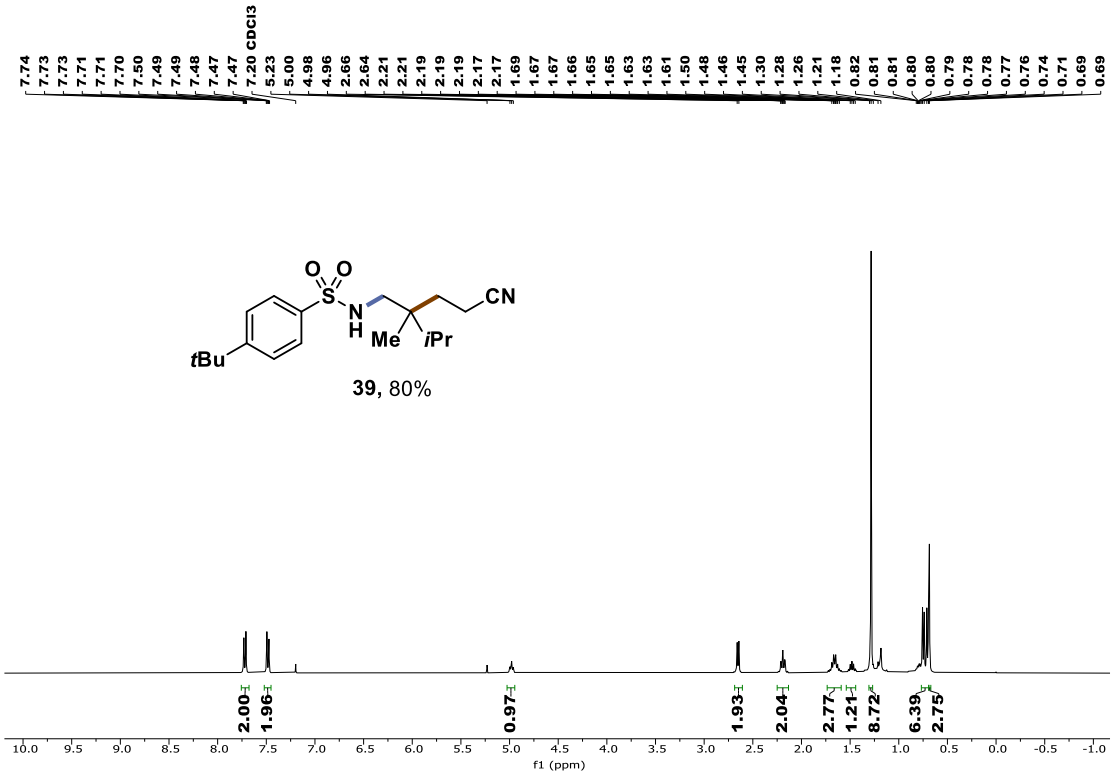
^{1}H NMR (400 MHz, $CDCl_3$):



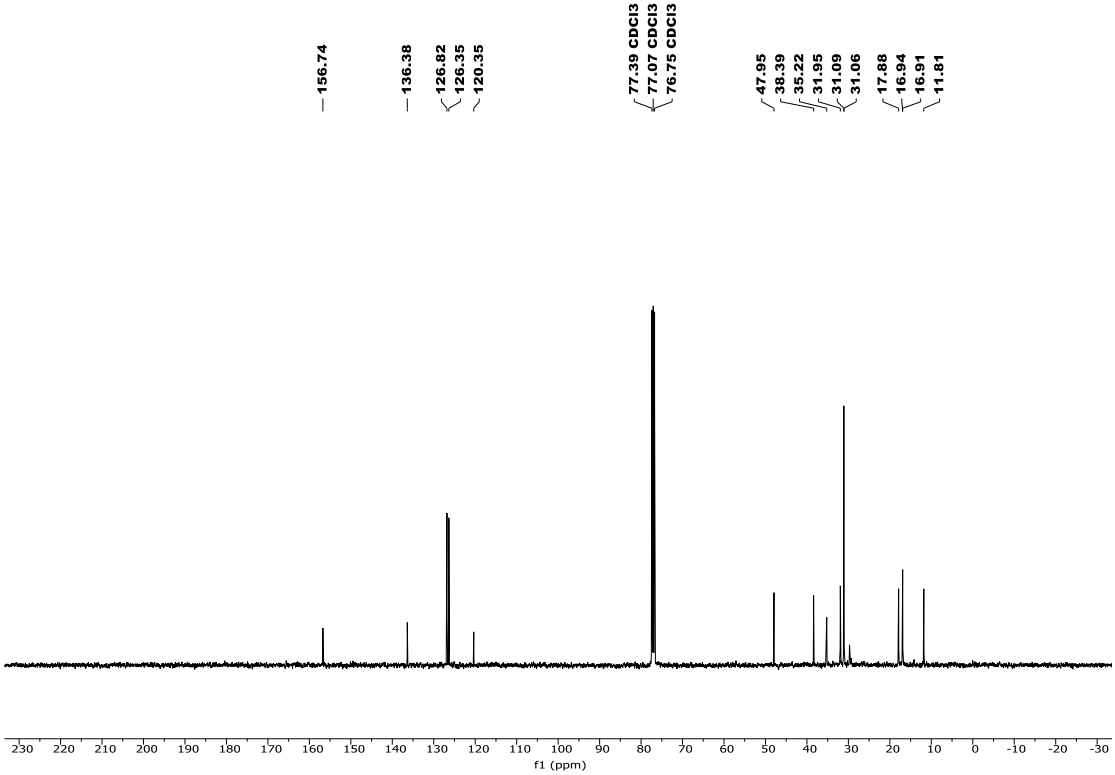
^{13}C NMR (101 MHz, $CDCl_3$):



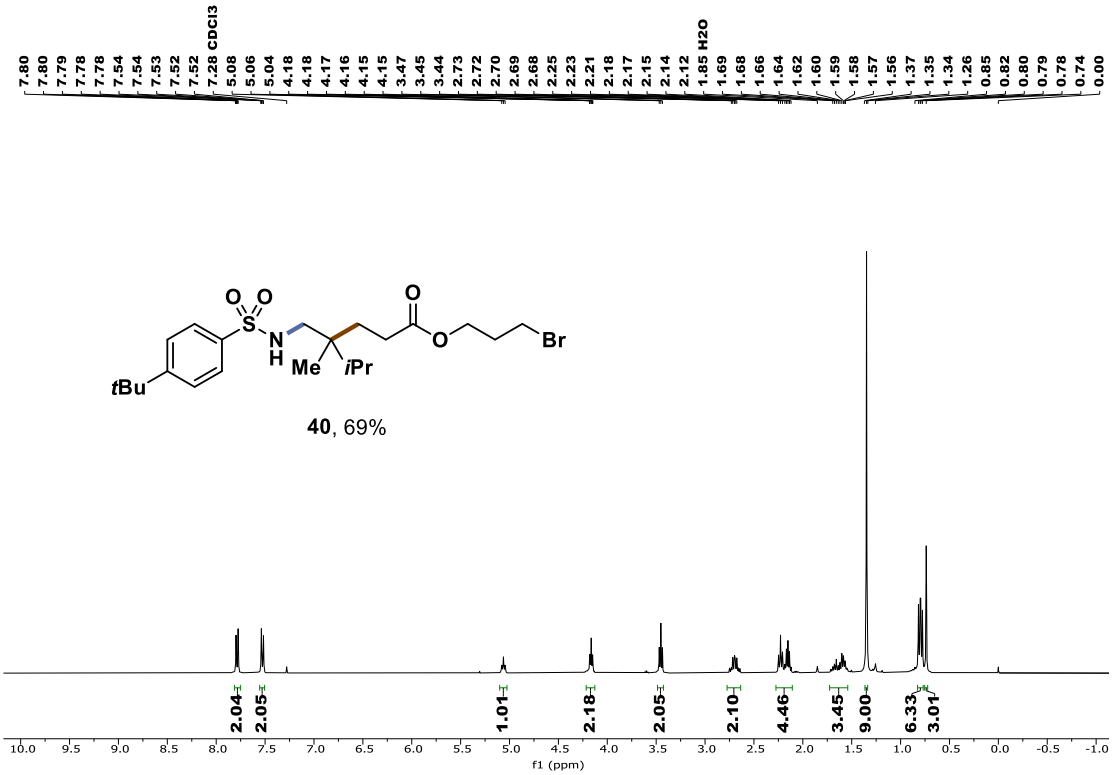
^{1}H NMR (400 MHz, $CDCl_3$):



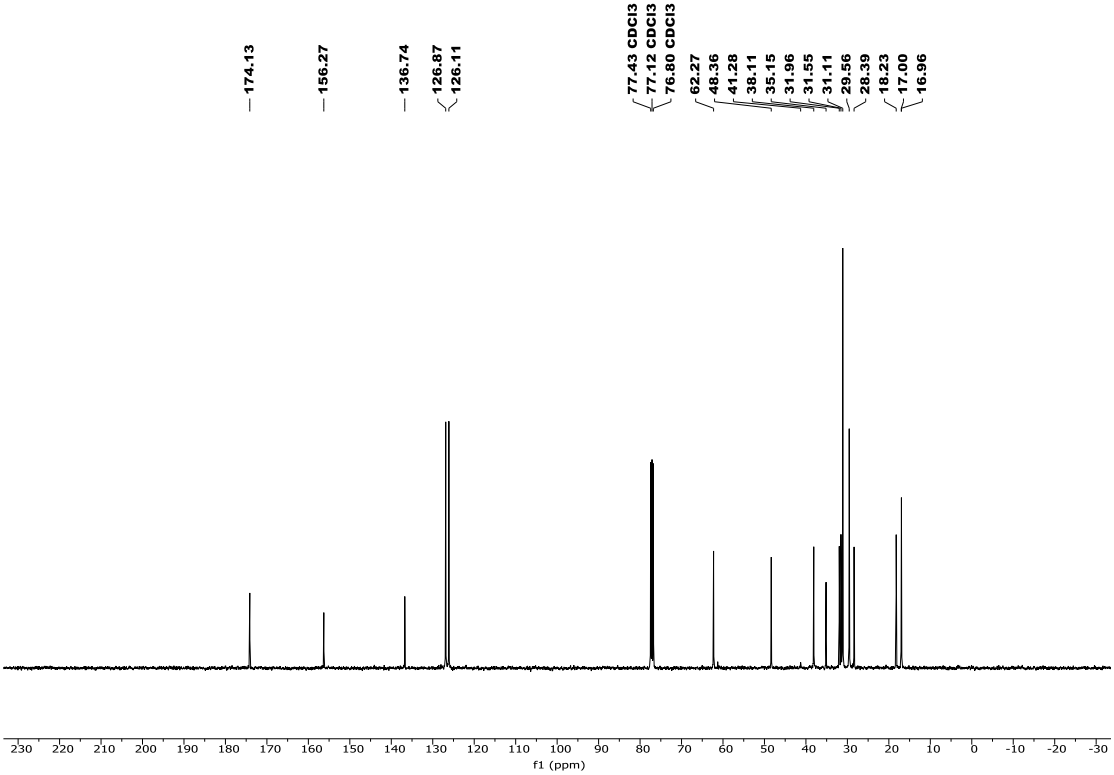
^{13}C NMR (101 MHz, $CDCl_3$):



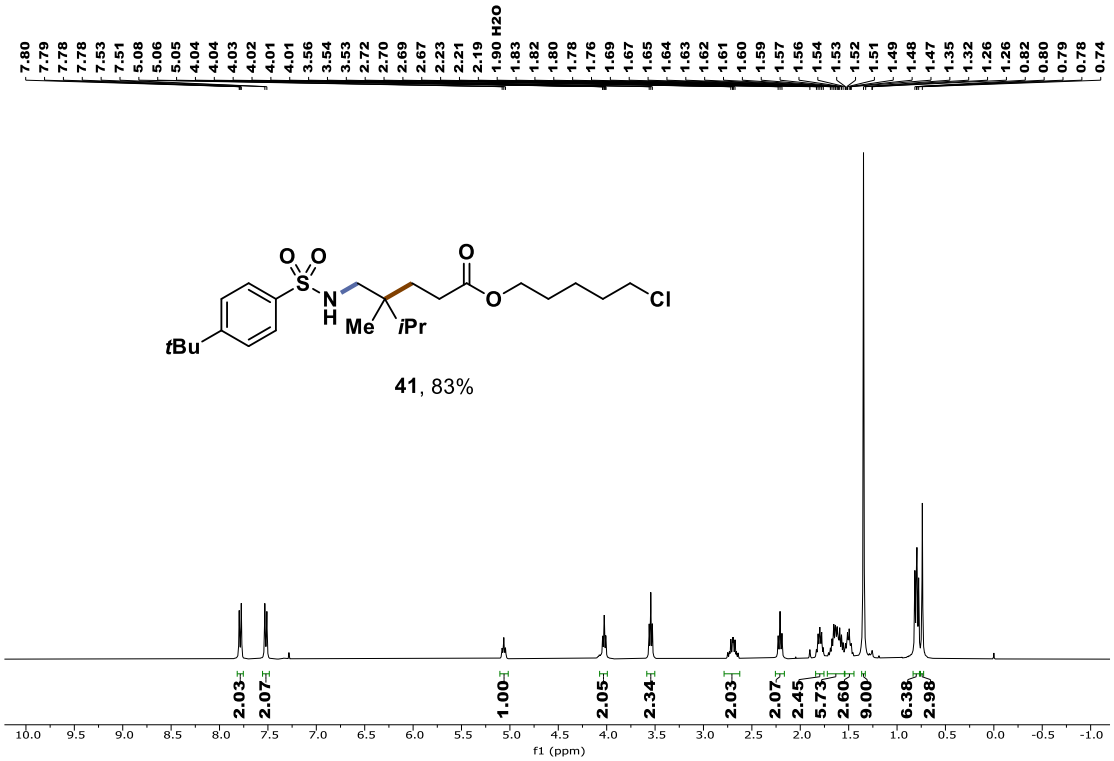
^{1}H NMR (400 MHz, $CDCl_3$):



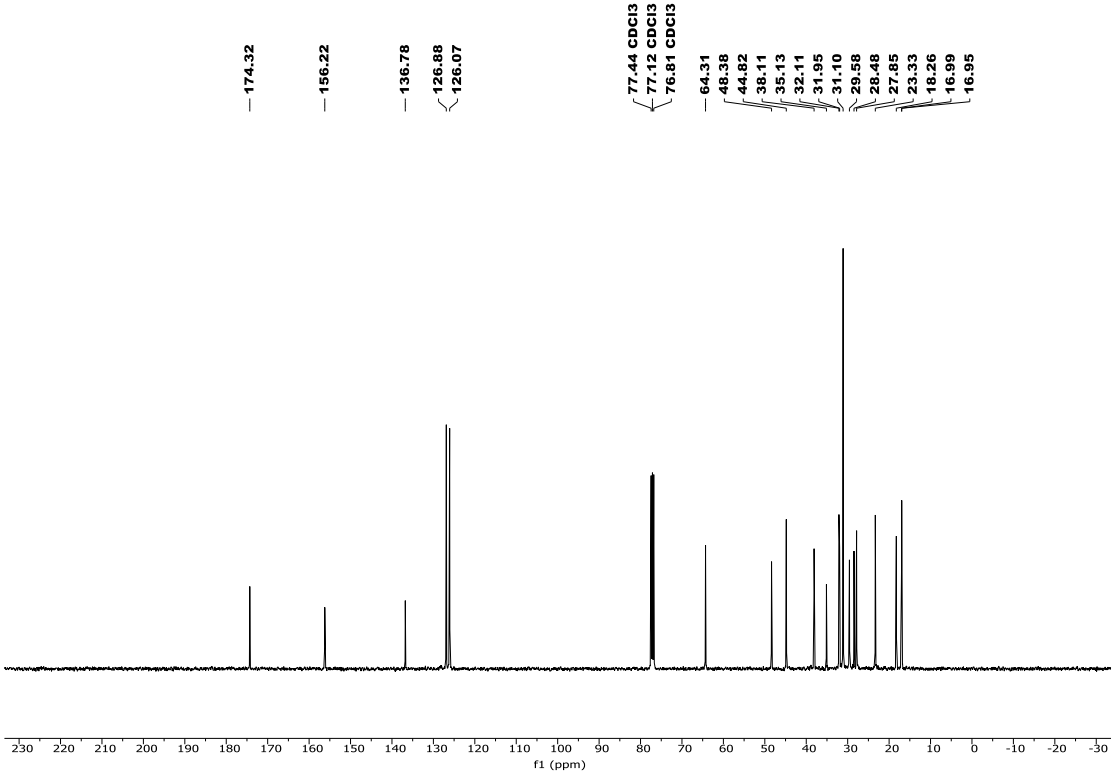
^{13}C NMR (101 MHz, $CDCl_3$):



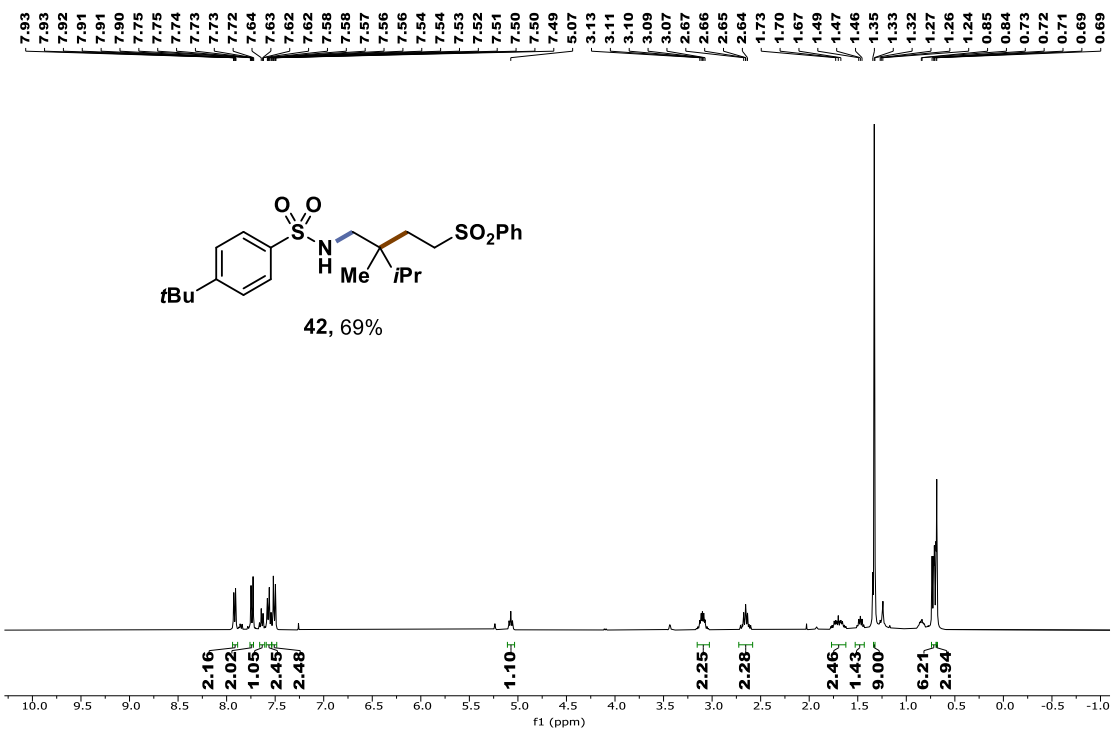
^{1}H NMR (400 MHz, $CDCl_3$):



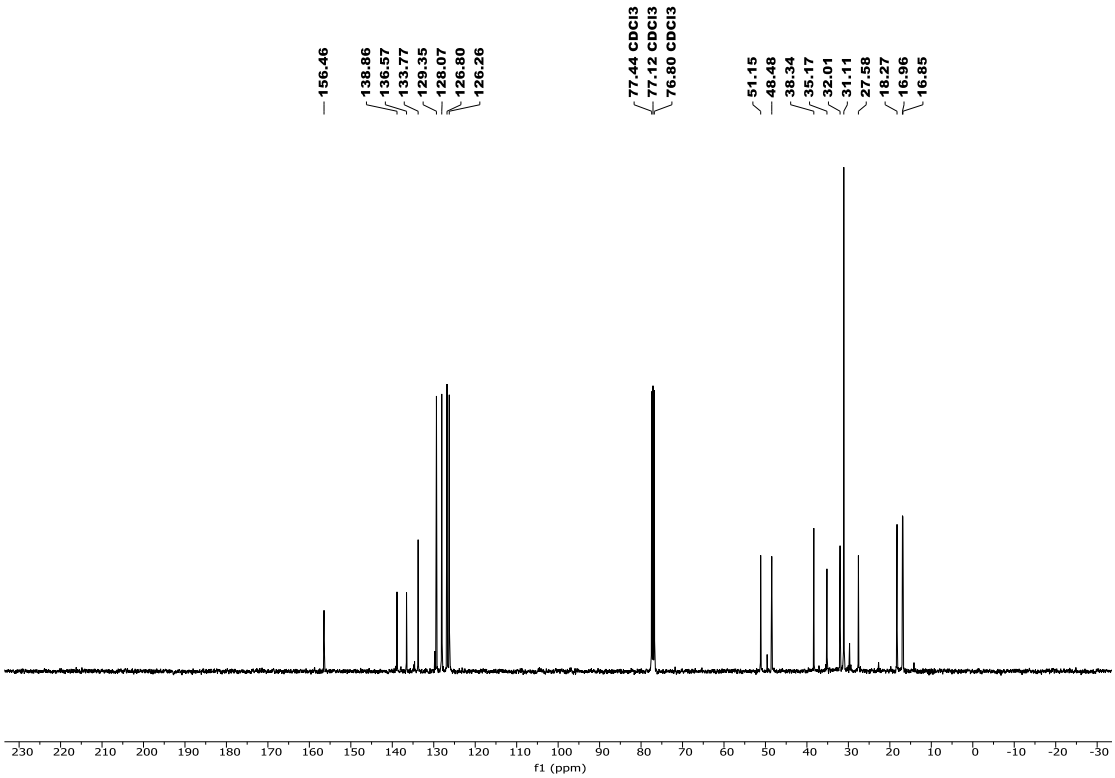
^{13}C NMR (101 MHz, $CDCl_3$):



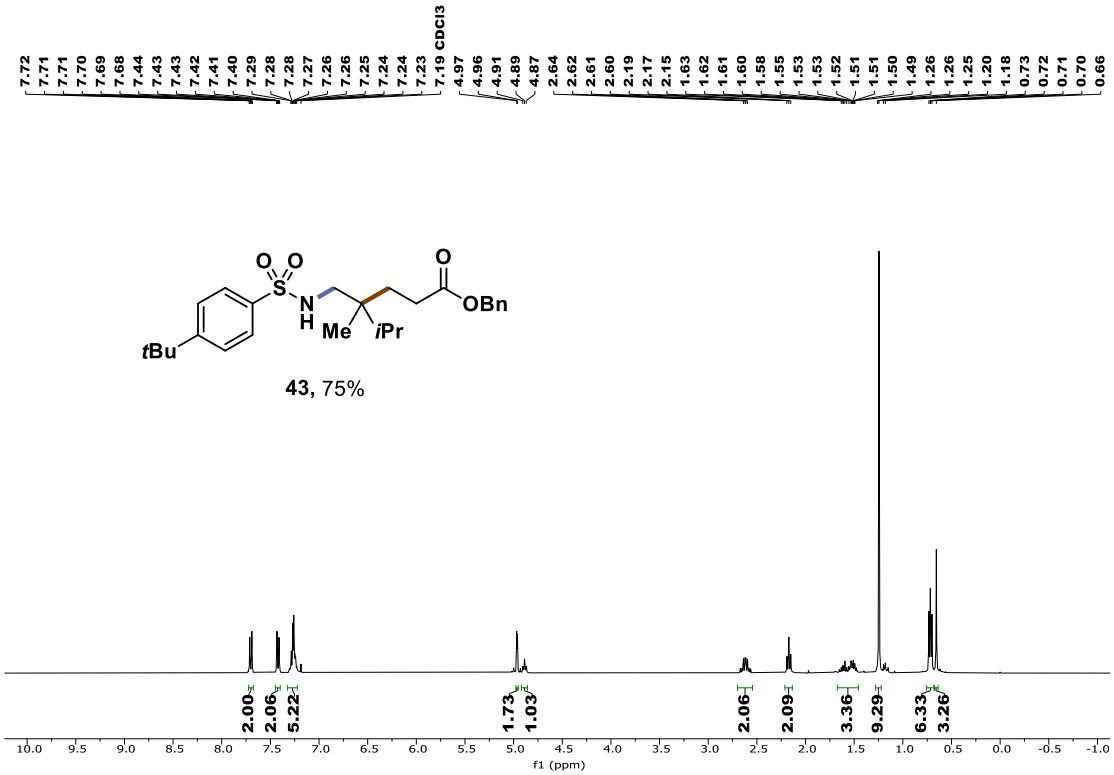
^{1}H NMR (400 MHz, $CDCl_3$):



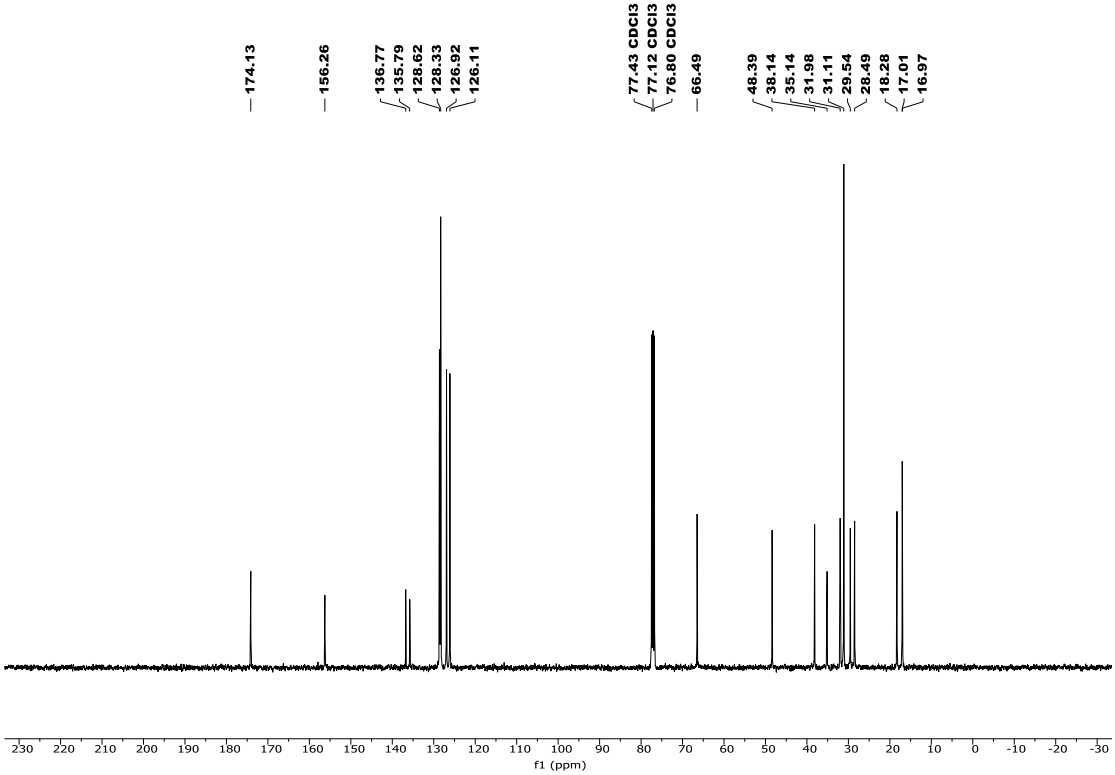
^{13}C NMR (101 MHz, $CDCl_3$):



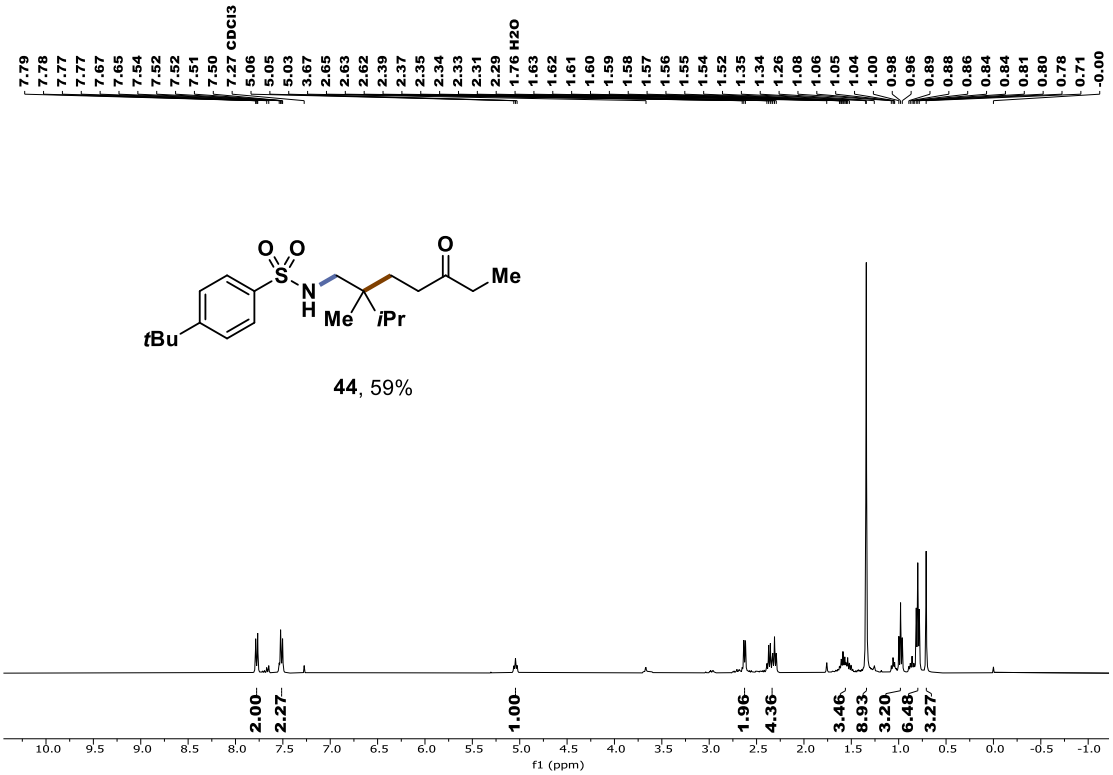
^{1}H NMR (400 MHz, $CDCl_3$):



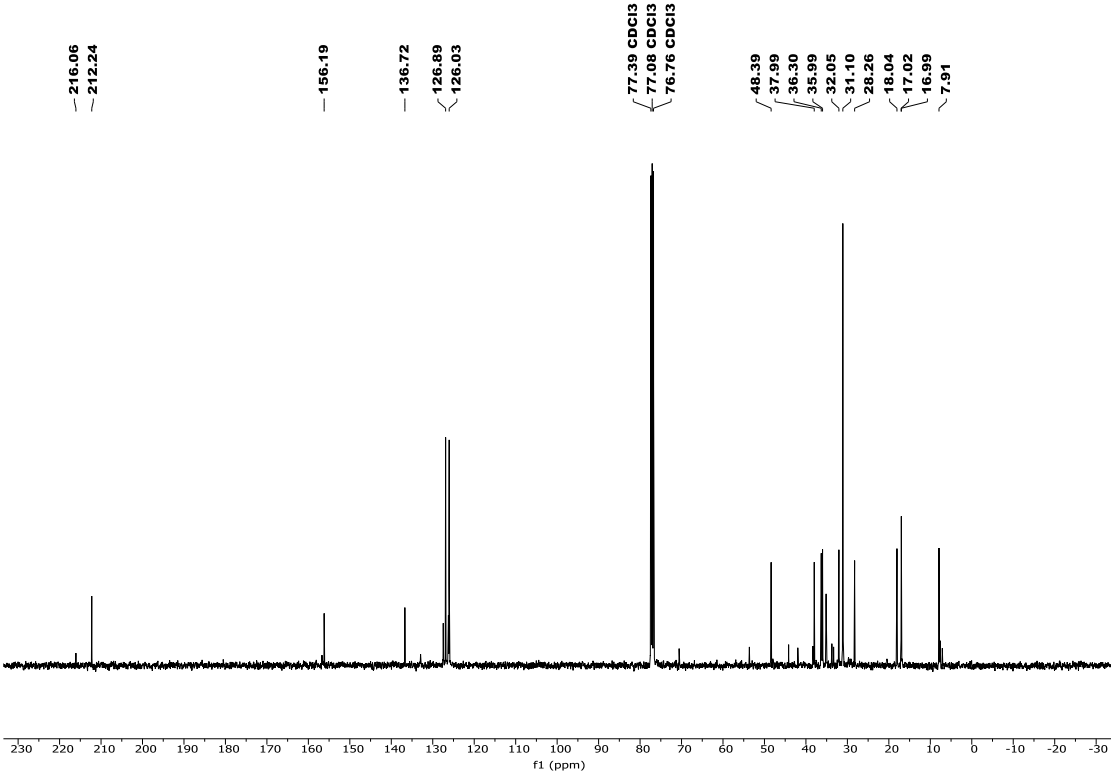
^{13}C NMR (101 MHz, $CDCl_3$):



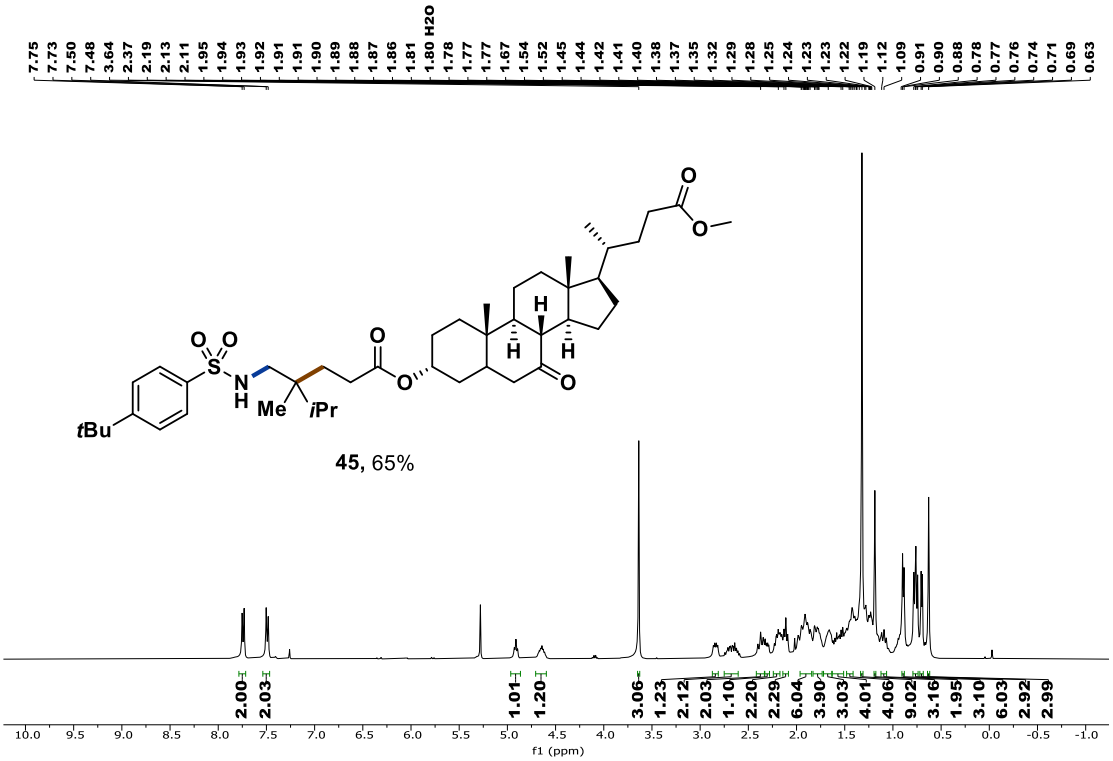
^{1}H NMR (400 MHz, $CDCl_3$):



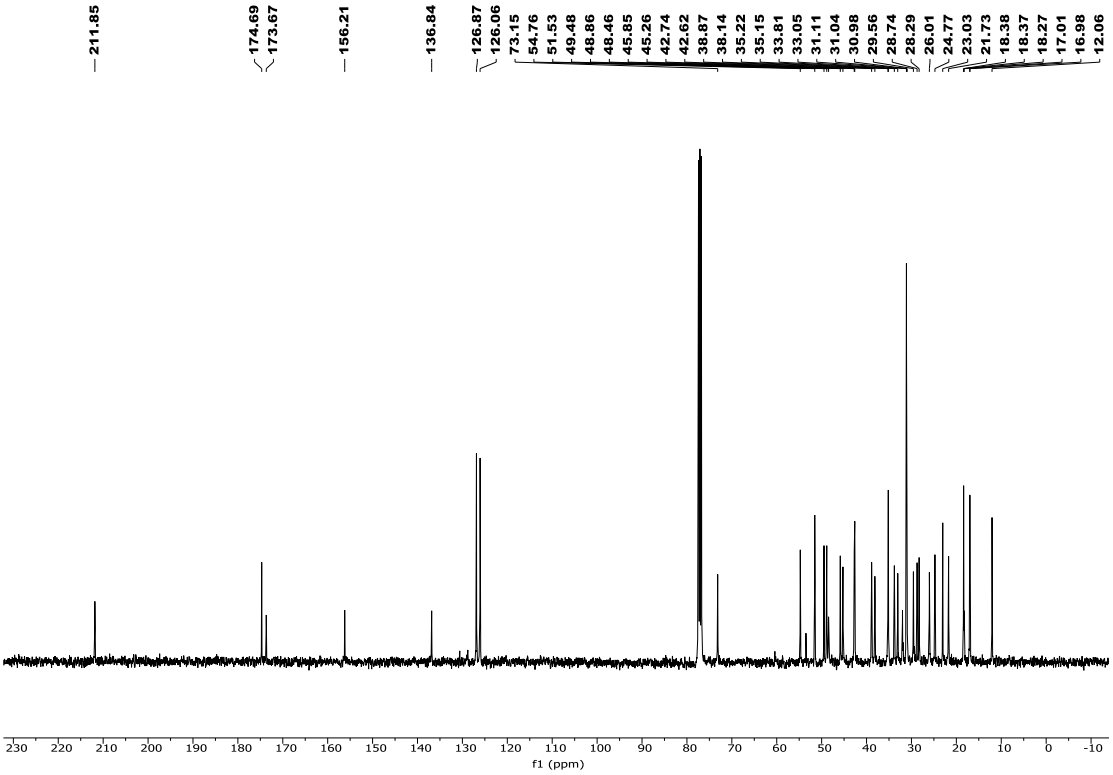
^{13}C NMR (101 MHz, $CDCl_3$):



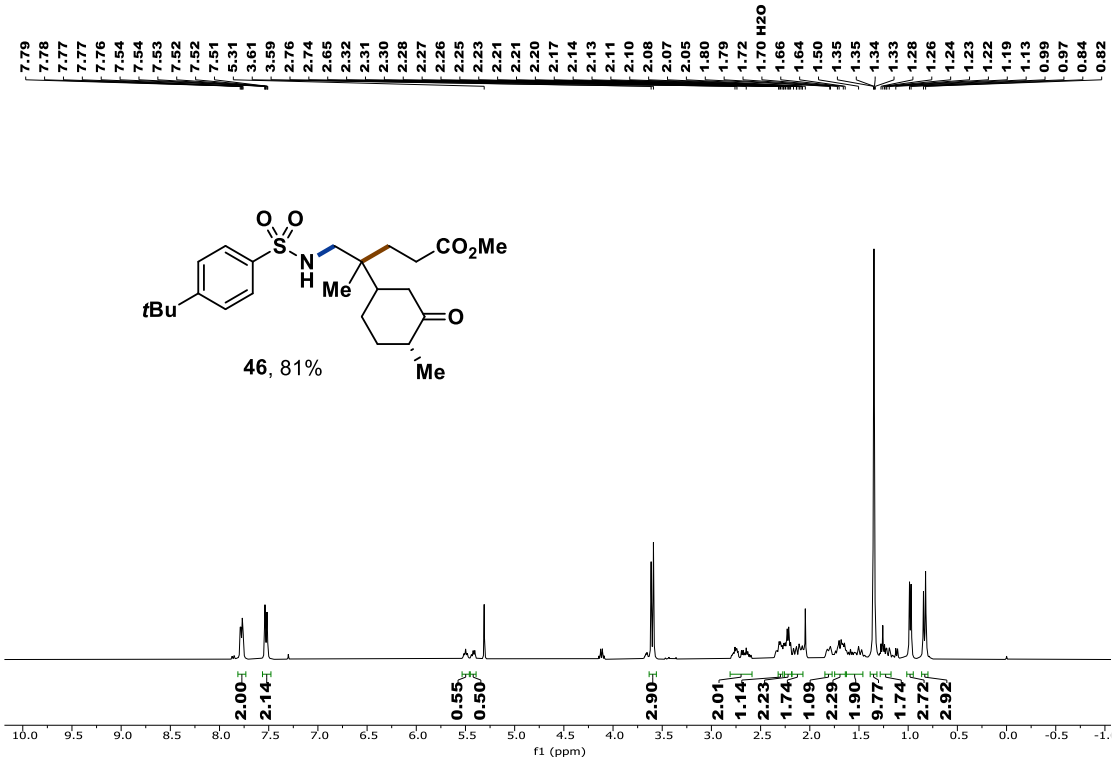
^{1}H NMR (400 MHz, $CDCl_3$):



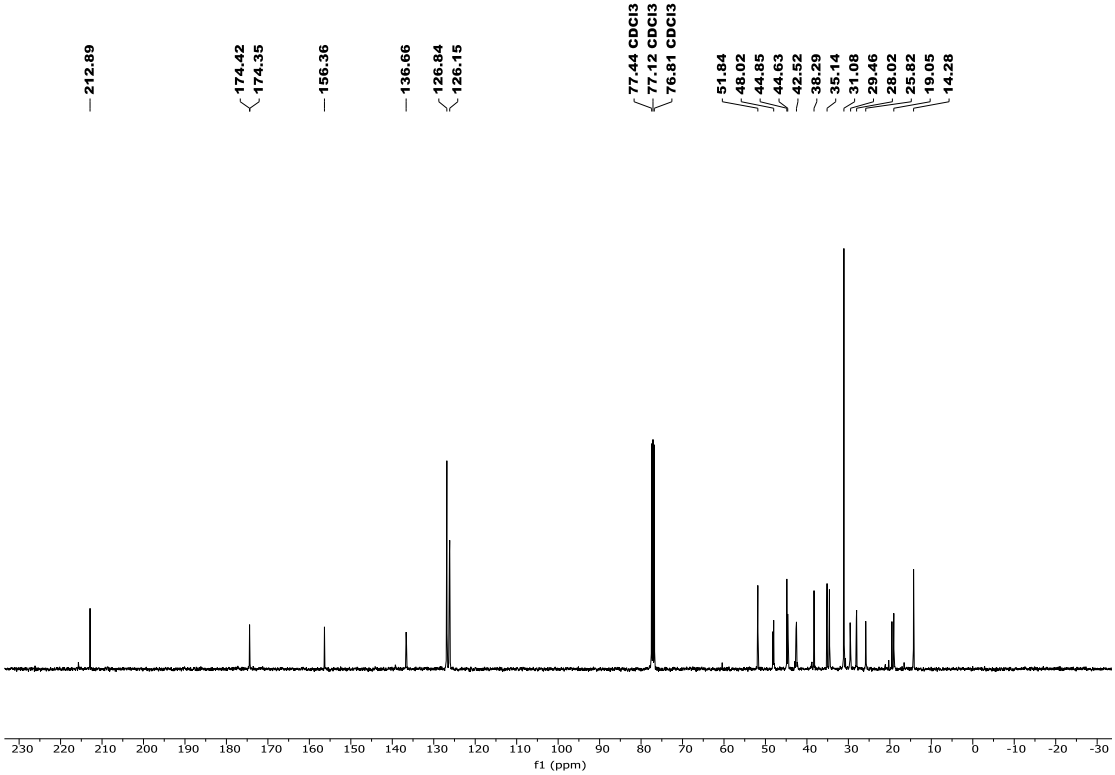
^{13}C NMR (101 MHz, $CDCl_3$):



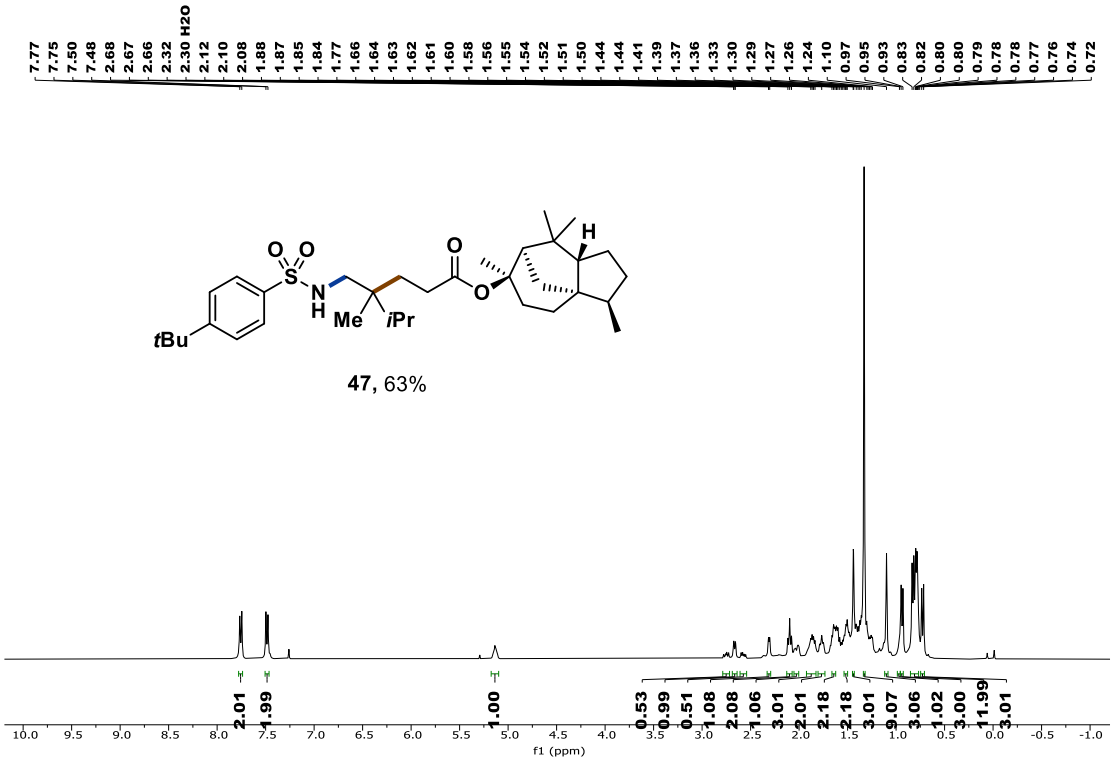
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):

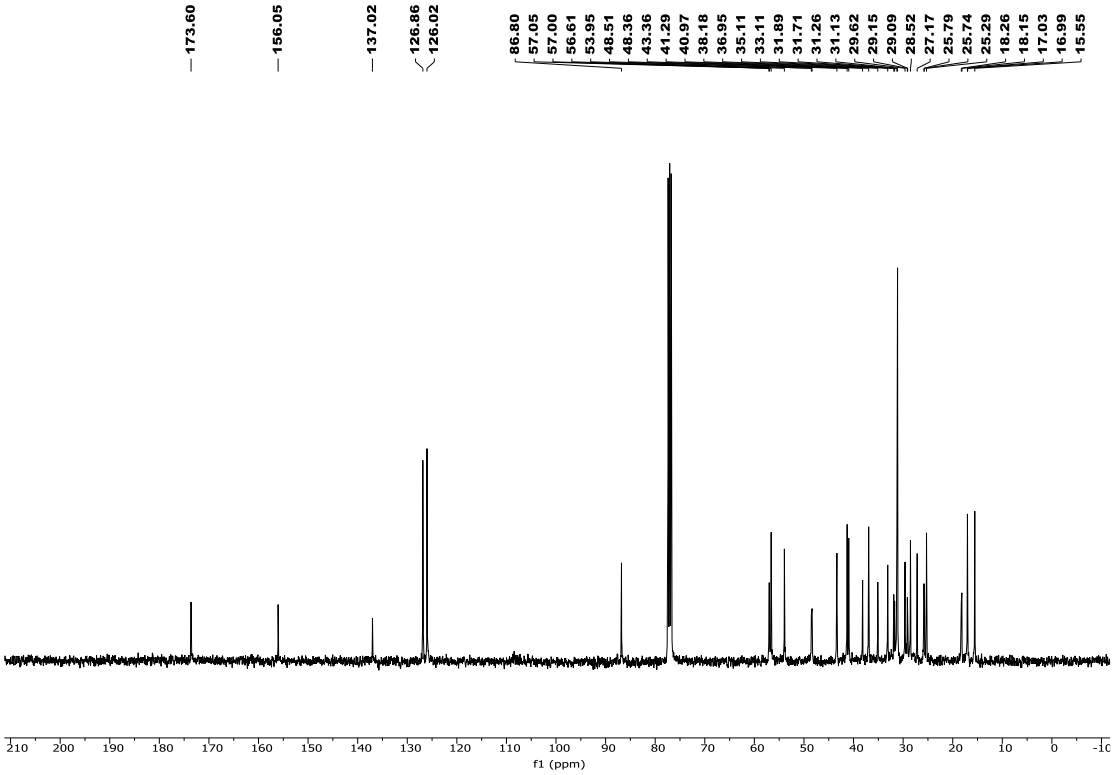


^{1}H NMR (400 MHz, $CDCl_3$):

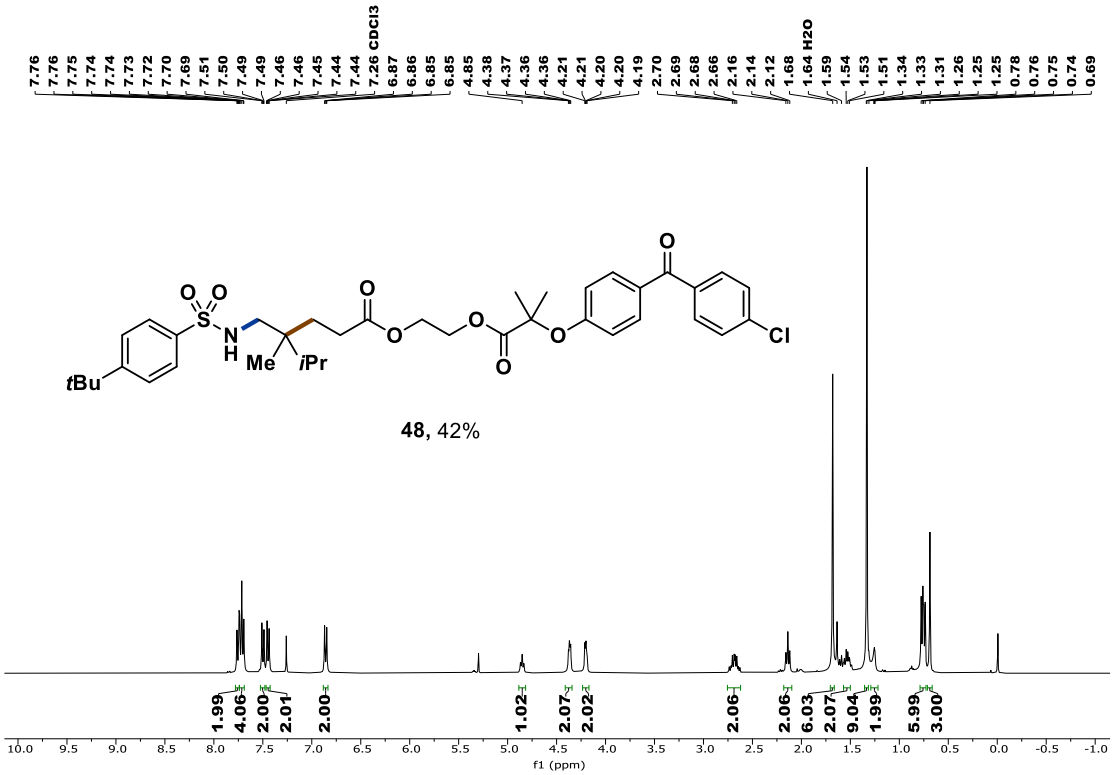


47, 63%

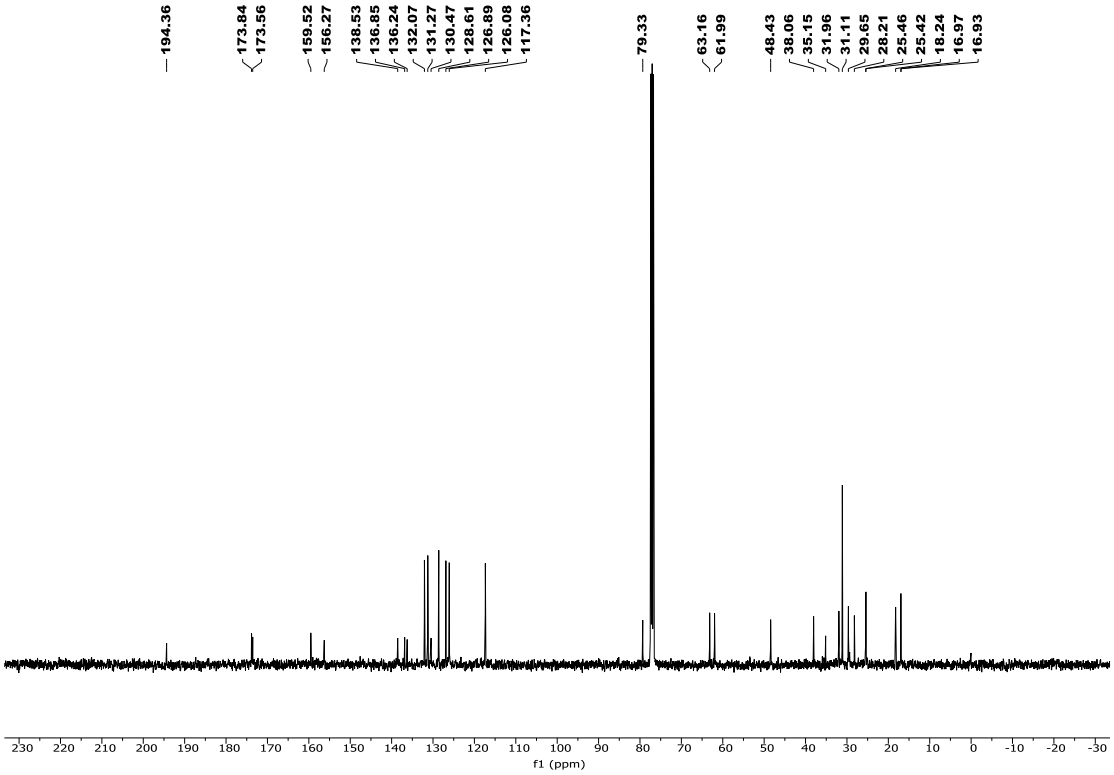
^{13}C NMR (101 MHz, $CDCl_3$):



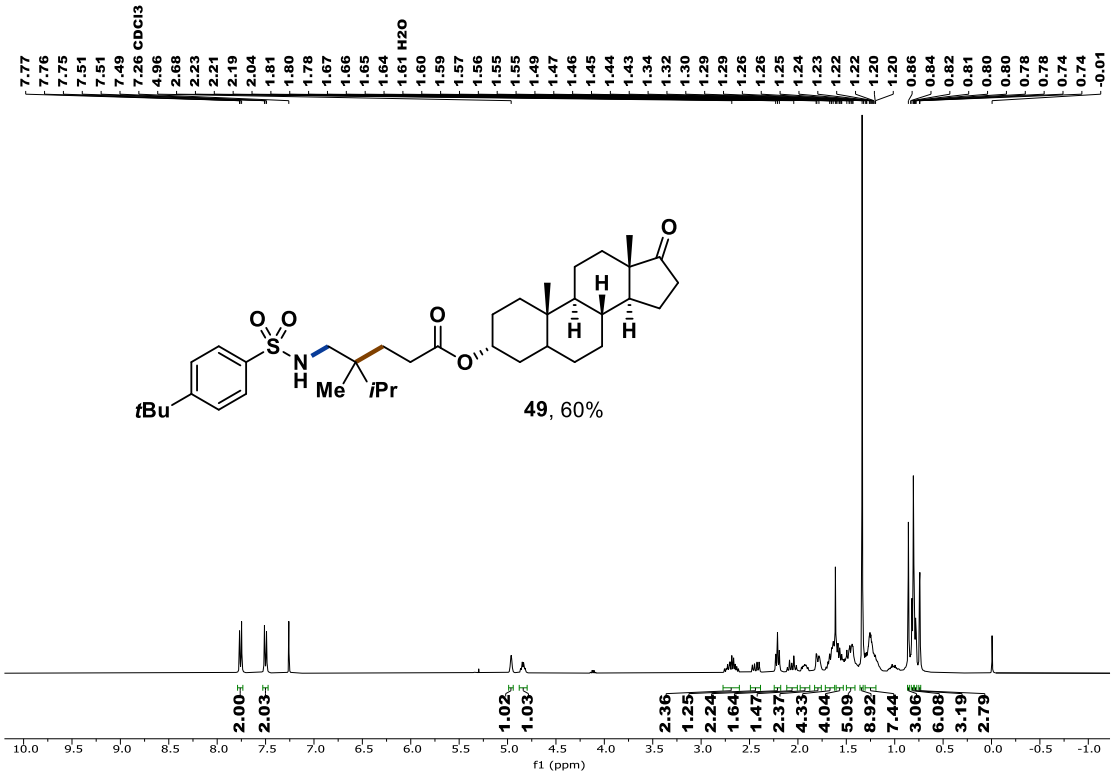
^{1}H NMR (400 MHz, $CDCl_3$):



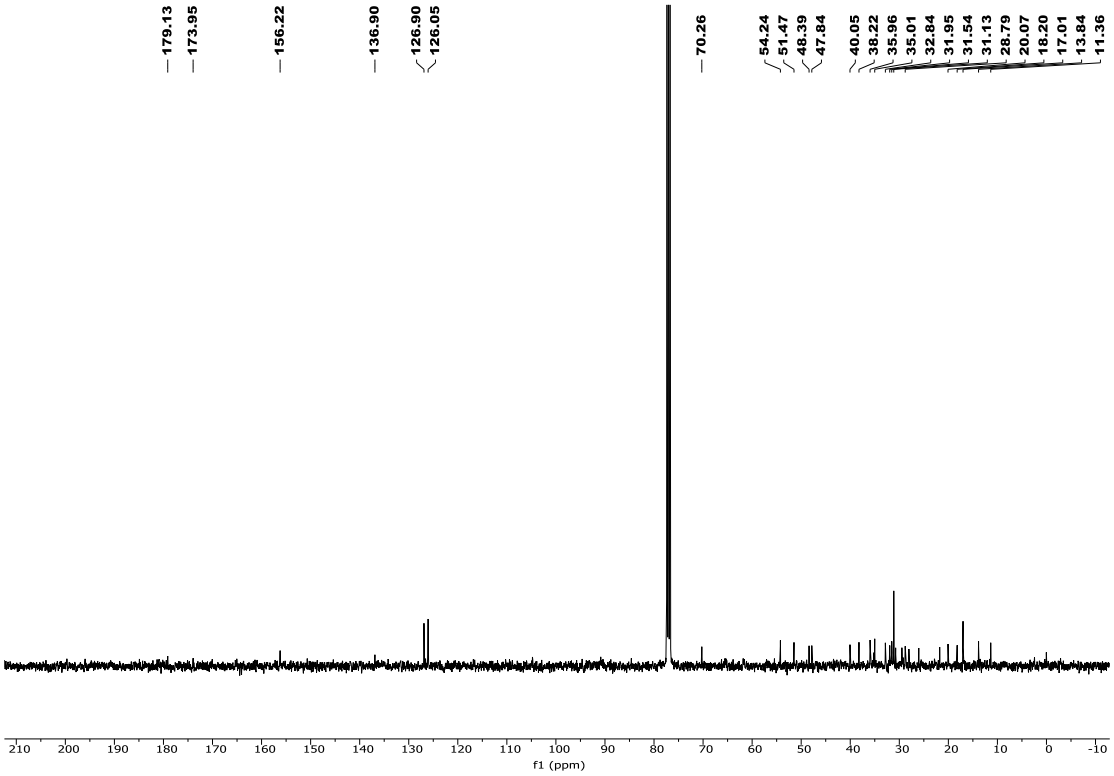
^{13}C NMR (101 MHz, $CDCl_3$):



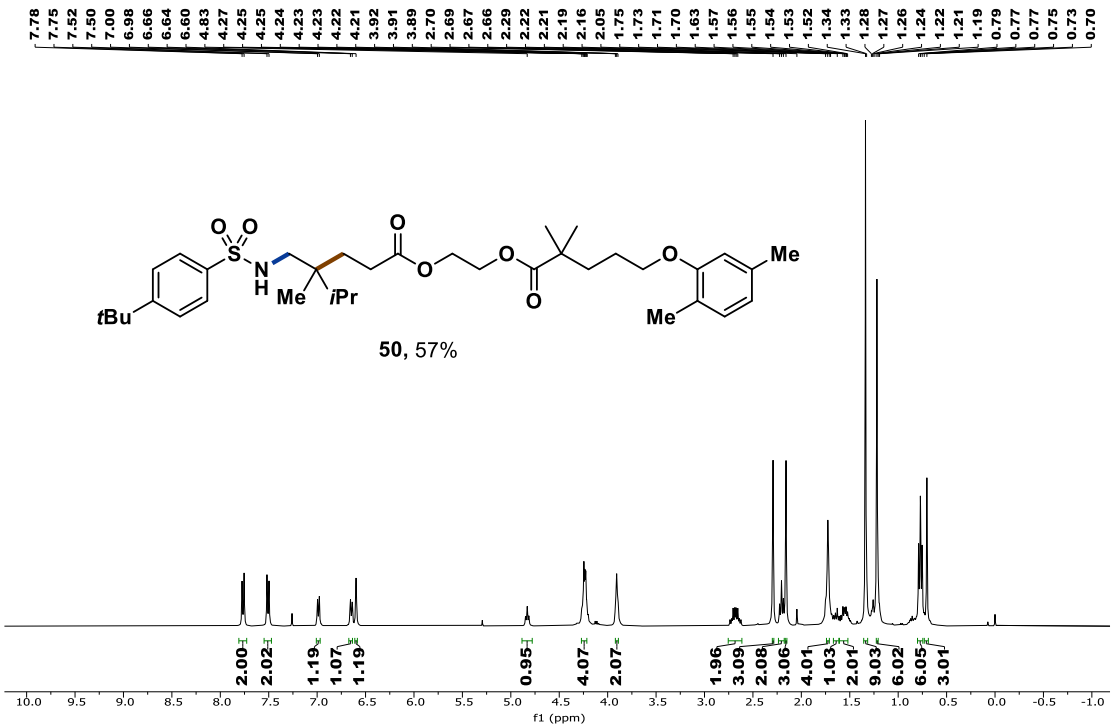
^{1}H NMR (400 MHz, $CDCl_3$):



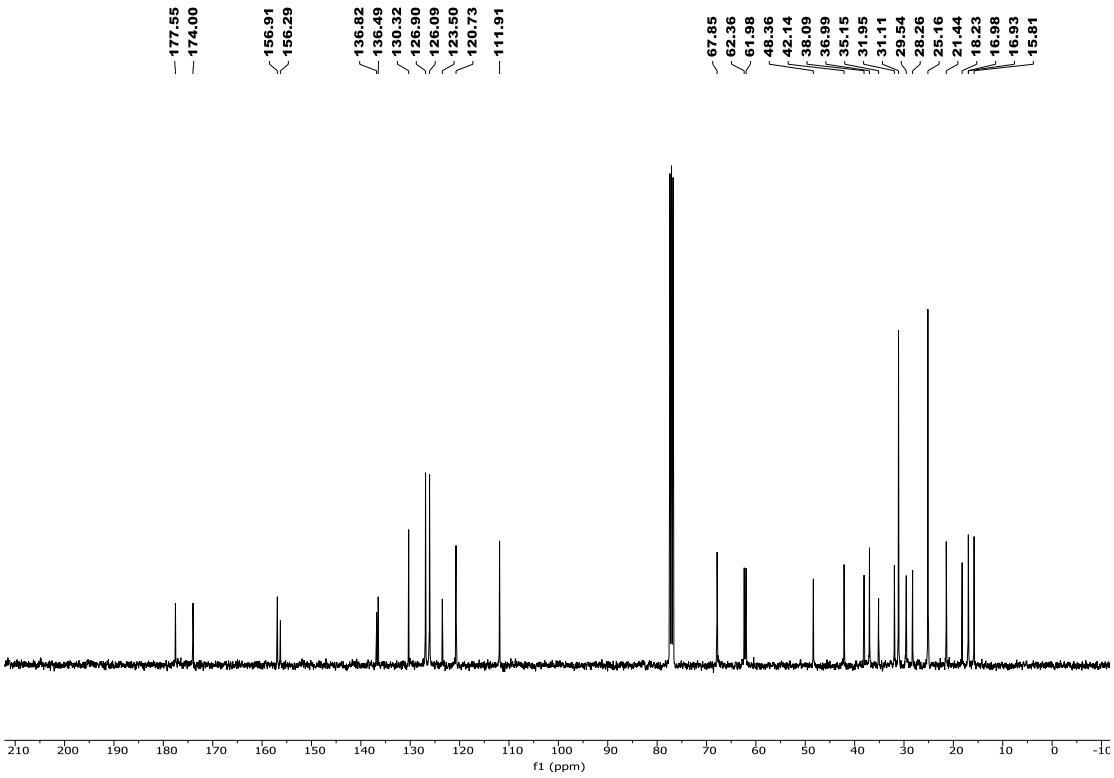
^{13}C NMR (101 MHz, $CDCl_3$):



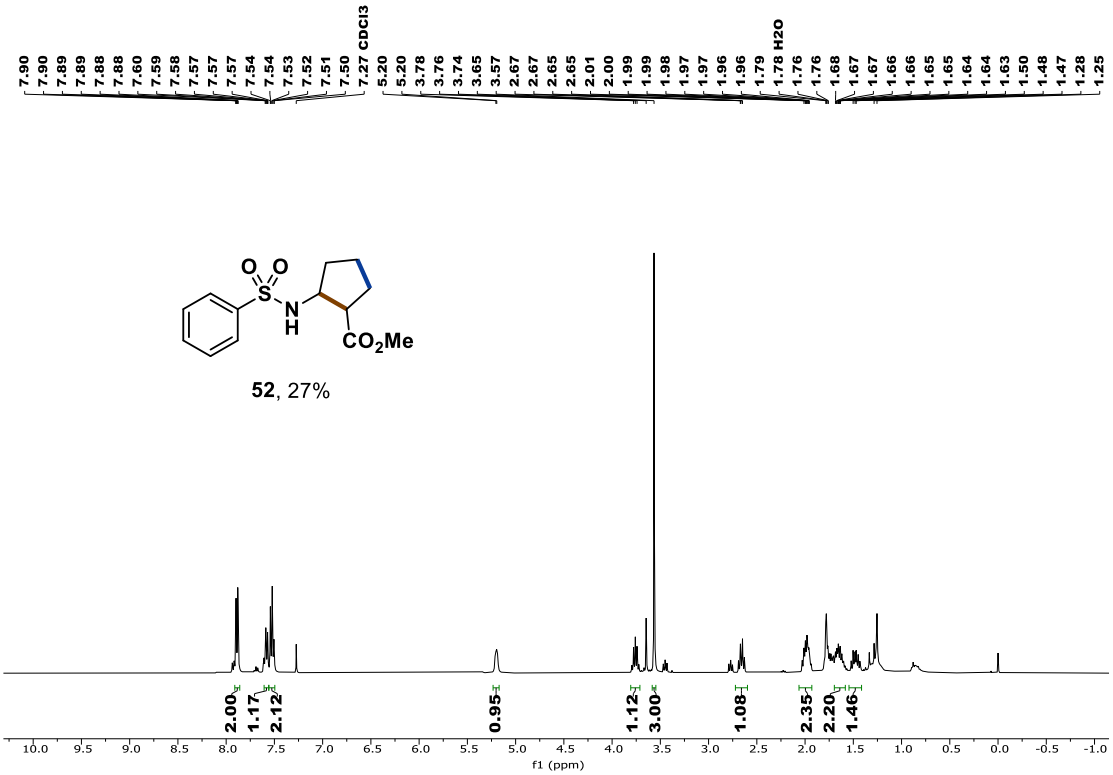
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (101 MHz, $CDCl_3$):

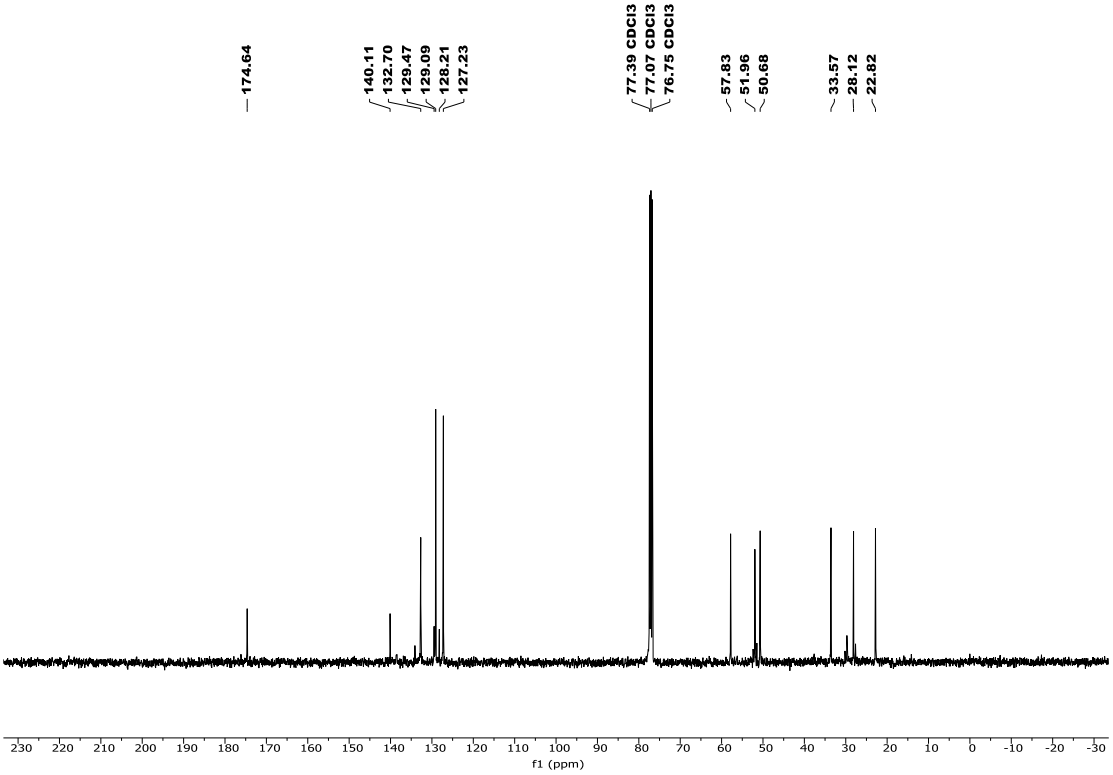


^{1}H NMR (400 MHz, $CDCl_3$):

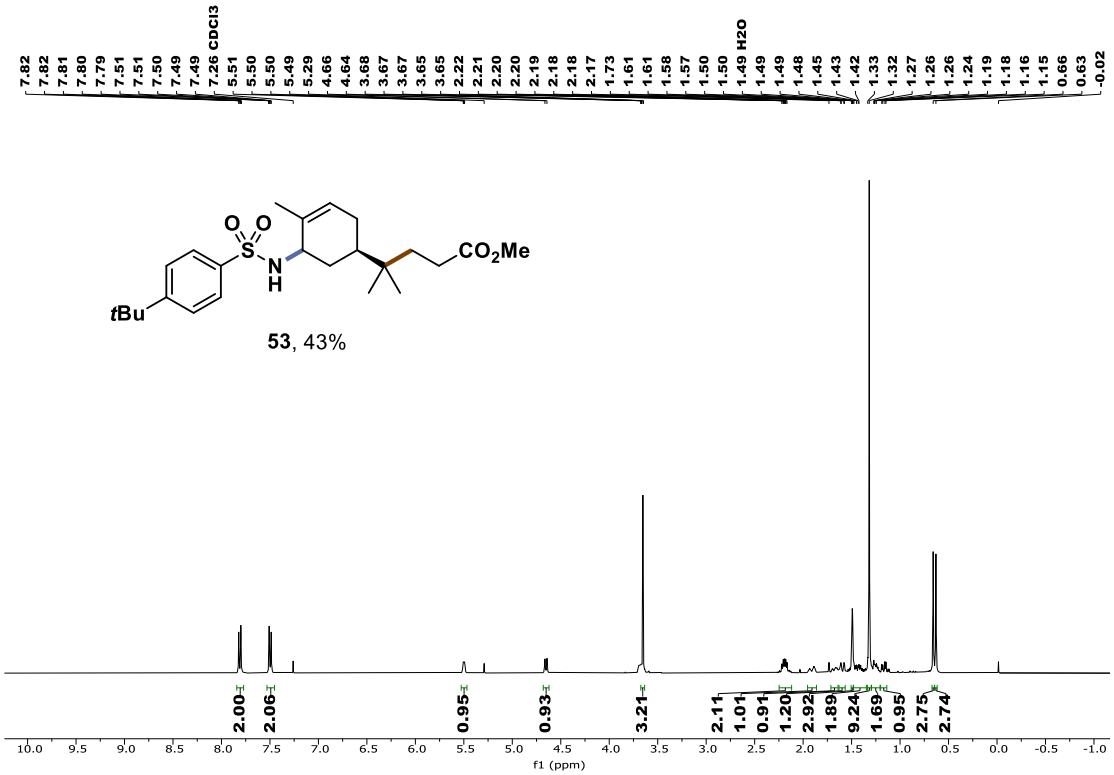


52, 27%

^{13}C NMR (101 MHz, $CDCl_3$)

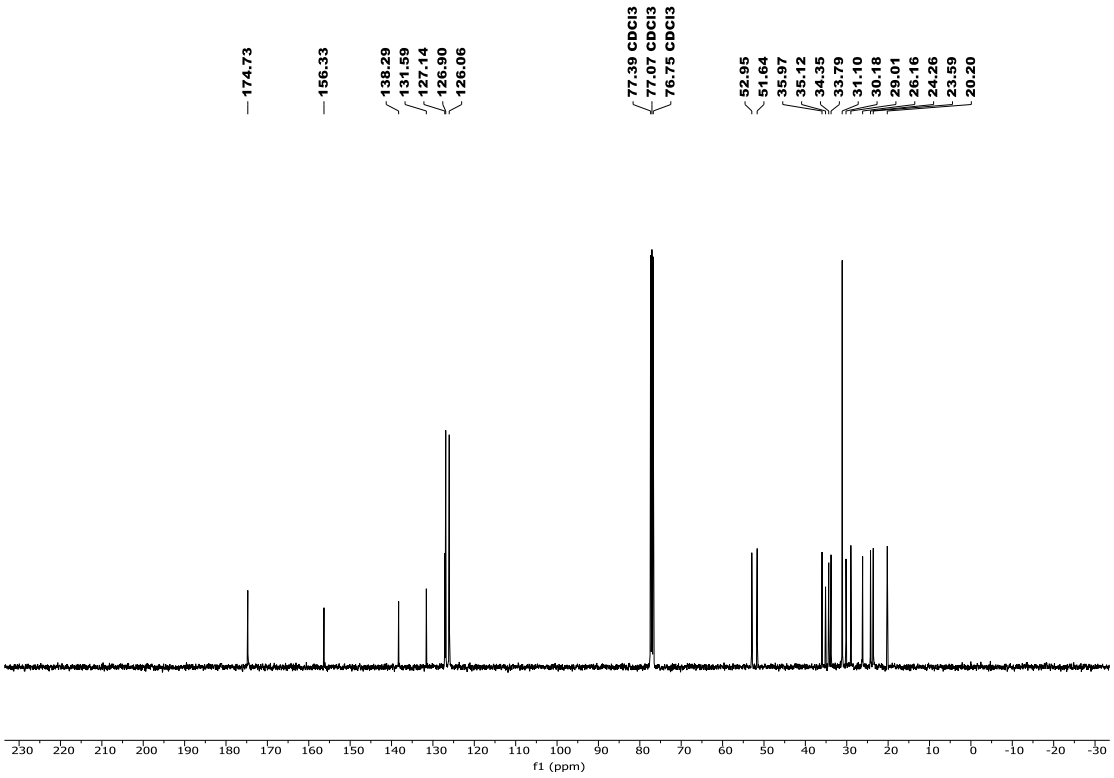


^{1}H NMR (400 MHz, $CDCl_3$):



53, 43%

^{13}C NMR (101 MHz, $CDCl_3$):



9. References

[1] X. Du, J. S. Zhen, X. H. Xu, H. Yuan, Y. H. Li, Y. Zheng, C. Xue, Y. Luo, *Org. Lett.* **2022**, *24*, 3944–3949.

[2] T. Friedberger, P. Wucher, S. Mecking, *J. Am. Chem. Soc.* **2012**, *134*, 1010–1018.

[3] H. Shigehisa, T. Ano, H. Honma, K. Ebisawa, K. Hiroya, *Org. Lett.* **2016**, *18*, 3622–3625.

[4] J. C. Siu, J. B. Parry, S. Lin, *J. Am. Chem. Soc.* **2019**, *141*, 2825–2831.

[5] A. Nasrallah, G. Grelier, M. I. Lapuh, F. J. Duran, B. Darses, P. Dauban, *Eur. J. Org. Chem.* **2018**, *2018*, 5836–5842.