Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

[Au(Np$^{\#}$)Cl]: Highly Reactive and Broadly Applicable Au(I)–NHC Catalysts for Alkyne π-Activation Reactions

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List of Known Compounds/General Methods

All starting materials reported in the manuscript have been previously described in literature and prepared by the method reported previously unless stated otherwise. All experiments were performed using standard Schlenk techniques under nitrogen or argon unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 500 (^{1}H NMR) and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.26 and 77.36 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet.GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (split less mode of injection, total run time of 22.0 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument. All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glassplates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm UV lamp or aqueous potassium permanganate.^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental for characterization purposes. ^{1}H NMR,^{13}C NMR, and HRMS data are given for all new compounds. All products have been previously reported, unless stated otherwise.

Experimental Procedures and Characterization Data

The ligands, **IPr$^{\#}$·HCl**,[1] **NP$^{\#}$·HCl**[1] and **BIAN-IPr$^{\#}$·HCl**[1] are commercially available and previously reported in the literature. The compounds **1**,[1] **4**,[2] **5**,[3] **8a**,[4] **8b**,[4] **8d**,[5] **8e**,[4] **8h**,[4] **8n**,[6] **10a**,[8] **10b**,[7,11] **10c**,[9] **10d**,[10] **10e**,[12] **10f**,[7] **10g**,[13] **10h**,[11,14] **10i**,[7,11] **10j**,[11] **10k**,[11] **10l**,[7] **10m**,[11] **10n**,[14] **10o**,[13] **11a**,[16] **11b**,[15,16,17] **11c**,[15,16,17] **11d**,[15] **11e**,[16] **11f**,[16,17] **11g**,[18] **11h**[17] and **11i**[15,16] have been previously reported in the literature. Spectroscopic properties matched literature data.

A. General Procedure for the Synthesis of [Au(NHC)Cl] Complexes. An oven-dried pressure tube equipped with a stir bar was charged with NHC·HCl salt (0.11 mmol, 1.1 equiv), [Au(Me$_2$S)Cl] (0.1 mmol, 1.0 equiv) and K_2CO_3 (0.5 mmol, 5.0 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Acetone or THF (2.0 mL, 0.05 M) was added, and the reaction mixture was stirred at 60 °C for 15 h. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and filtered. The solution was collected and concentrated. The title product was obtained by trituration from hexanes as a solid.

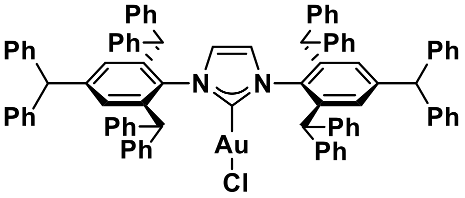
B. [Au(NHC)Cl] Catalyzed Hydrocarboxylation of Alkynes: An oven-dried pressure tube equipped with a stir bar was charged with an alkyne substrate (0.2 mmol, 1.0 equiv), a carboxylic acid derivative (0.25 mmol, 1.25 equiv), [Au-NHC] complex (2.0 mol%) and NaBAr$^F_4$ (4.0 mol%). Toluene (0.2 mL, 1.0 M) was added, and the pressure tube was sealed under air atmosphere and placed in a pre-heated oil bath at 80 °C. After 25 h, the solvent was removed under reduced pressure. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. The product was purified by flash column using natural silica as stationary phase and EtOAc/Hexane (1/30 v/v) as eluent.

C. [Au(NHC)Cl] Catalyzed Hydroamination of Alkynes: An oven-dried pressure tube equipped with a stir bar was charged with an alkyne substrate (0.5 mmol, 1.0 equiv), a aniline derivative (0.6 mmol, 1.2 equiv), [Au-NHC] complex (1.5 mol%) and NaBAr$^F_4$ (3.0 mol%). The pressure tube was sealed under air atmosphere and placed in a pre-heated oil bath at 50 °C for 15 hours. After the indicated time, the reaction mixture was cooled to room temperature. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. The crude product was dissolved in THF/MeOH (10 mL / 5 mL) and placed on ice bath. $NaBH_4$ (3.0 mmol, 6.0 equiv) was added slowly to the mixture with continuous stirring. After 2 hours, the solvent was removed, and saturate $NaHCO_3$ solution (10 mL) was added. The product was extracted by EtOAc (3 x 10 mL), and the combined organic layer was dried and concentrated. The product was purified by flash column using natural silica as stationary phase and EtOAc/Hexane (1/15 v/v) as eluent.

D. [Au(NHC)Cl] Catalyzed Addition Hydration of Alkynes: An oven-dried pressure tube equipped with a stir bar was charged with an alkyne substrate (0.5 mmol) [Au-NHC] complex (50.0 ppm), $AgSbF_6$ (spatula top) and methanol (1.0 mL, 0.5 M). the pressure tube was sealed under air atmosphere and stirred for 1 min. Water (0.2 mL) was added, and the pressure tube was placed in a pre-heated oil bath at 80 °C. After 15 hours, water (5.0 mL) was added, and the product was extracted by ethyl ether or *n*-pentane (3 x 10 mL), and the combined organic layer was dried and concentrated. The sample was analyzed by ^{1}H NMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, selectivity and yield using internal standard and comparison with authentic samples. Majorities of products did not require further purification. For very few substrates, the product was purified by flash column using natural silica as stationary phase and EtOAc (or ethyl ether)/Hexane (1/100 v/v) as eluent.

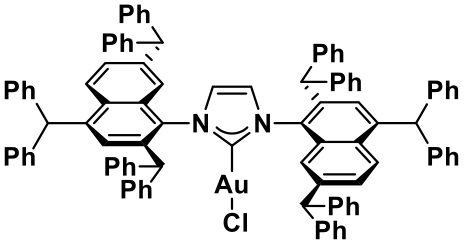
E. [Au(NHC)Cl] Catalyzed Hydroamination of Alkynes on Gram Scale: An oven-dried pressure tube equipped with a stir bar was charged with phenylacetylene (1.02 g, 10.0 mmol, 1.0 equiv), aniline (1.12 g, 12.0 mmol, 1.2 equiv), [Au(Np$^{\#}$)Cl] complex (15.5 mg, 0.1 mol%) and Na[BAr^F]$_4$ (18.0 mg, 0.2 mol%). The pressure tube was sealed under air atmosphere and placed in a pre-heated oil bath at 50 °C for 15 hours. After the indicated time, the reaction mixture was cooled to room temperature. The reaction mixture was dissolved in THF (100 mL) and placed on ice bath. $NaBH_4$ (1.52 g, 40.0 mmol, 4.0 equiv) was added slowly to the mixture with continuous stirring. Finally, MeOH (50 mL) was added to the system slowly over 10 min with continuous stirring. After 5 hours, the solvent was removed, and saturate $NaHCO_3$ solution was added to quince the reduction reaction. The organic layer was extracted by EtOAc (3 x 50 mL), and the combined organic layer was dried and concentrated. The crude product was purified by flash column using natural silica as stationary phase and EtOAc/Hexane (1/15 v/v) as eluent to offer pure product as oil (1.76 g, 89%).

F. Characterization Data of [Au(NHC)Cl] Complexes.



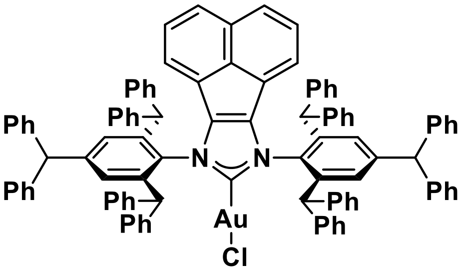
1: [Au(IPr$^{\#}$)Cl]

[Au(IPr$^{\#}$)Cl] **1**: White Solid. Yield 90% (131.0 mg). Decomposed at >200 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.3 Hz, 8H), 7.16 – 7.10 (m, 16H), 7.09 – 7.04 (m, 12H), 6.98 – 6.93 (m, 16H), 6.79 (d, *J* = 4.2 Hz, 4H), 6.77 (d, *J* = 6.6 Hz, 8H), 5.89 (s, 2H), 5.39 (s, 2H), 5.25 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.34 (C-Au), 145.98 (C_{Ar}), 143.10 (C_{Ar}), 142.93 (C_{Ar}), 142.16 (C_{Ar}), 141.03 (C_{Ar}), 134.30 (C_{Ar}), 130.95 (C_{Ar}), 129.55 (C_{Ar}), 129.38 (C_{Ar}), 129.36 (C_{Ar}), 128.53 (C_{Ar}), 128.50 (C_{Ar}), 128.44 (C_{Ar}), 126.73 (C_{Ar}), 126.64 (C_{Ar}), 126.48 (C_{Ar}), 123.22 (C_{imi}), 56.28 (Ph_2CH), 51.39 (Ph_2CH).



2: [Au(NP$^{\#}$)Cl]

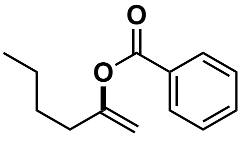
[Au(Np$^{\#}$)Cl] **2**: White Solid. Yield 75% (116.0 mg). Decomposed at >200 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 9.3, 7.2 Hz, 2H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.19 – 7.12 (m, 8H), 7.10 – 6.89 (m, 34H), 6.89 – 6.74 (m, 16H), 6.72 (s, 1H), 6.69 – 6.66 (m, 1H), 6.63 (s, 1H), 6.56 – 6.52 (m, 2H), 6.49 (s, 1H), 6.30 (s, 1H), 6.08 (d, *J* = 3.6 Hz, 2H), 5.53 – 5.30 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.13 (C-Au), 176.01 (C-Au), 143.29 (C_{Ar}), 143.23 (C_{Ar}), 143.20 (C_{Ar}), 143.08 (C_{Ar}), 142.98 (C_{Ar}), 142.82 (C_{Ar}), 142.72 (C_{Ar}), 142.52 (C_{Ar}), 142.45 (C_{Ar}), 142.37 (C_{Ar}), 142.27 (C_{Ar}), 142.23 (C_{Ar}), 141.84 (C_{Ar}), 141.81 (C_{Ar}), 141.76 (C_{Ar}), 138.82 (C_{Ar}), 138.18 (C_{Ar}), 131.40 (C_{Ar}), 131.37 (C_{Ar}), 130.80 (C_{Ar}), 130.75 (C_{Ar}), 130.32 (C_{Ar}), 129.99 (C_{Ar}), 129.44 (C_{Ar}), 129.36 (C_{Ar}), 129.30 (C_{Ar}), 129.22 (C_{Ar}), 128.90 (C_{Ar}), 128.58 (C_{Ar}), 128.47 (C_{Ar}), 128.42 (C_{Ar}), 128.35 (C_{Ar}), 128.28 (C_{Ar}), 126.66 (C_{Ar}), 126.63 (C_{Ar}), 126.58 (C_{Ar}), 126.53 (C_{Ar}), 126.47 (C_{Ar}), 126.43 (C_{Ar}), 126.34 (C_{Ar}), 125.27 (C_{Ar}), 125.16 (C_{Ar}), 123.87 (C_{Ar}), 123.71 (C_{Ar}), 122.89 (C_{imi}), 122.79 (C_{imi}), 57.40 (Ph_2CH), 57.22 (Ph_2CH), 53.47 (Ph_2CH), 53.31 (Ph_2CH), 51.73 (Ph_2CH), 51.30 (Ph_2CH). HRMS (ESI) m/z: $[M - Cl]^+$ Calcd for $C_{101}H_{76}N_2Au$ 1513.5669; Found 1513.5698.



3: [Au(BIAN-IPr#)Cl]

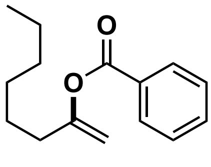
[Au(BIAN-IPr#)Cl] **3**: Yellow Solid. Yield 78% (123.0 mg). Decomposed at >200 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 8H), 7.18 (t, *J* = 7.3 Hz, 4H), 7.03 – 6.91 (m, 34H), 6.74 (t, *J* = 7.2 Hz, 4H), 6.68 (t, *J* = 7.3 Hz, 8H), 6.61 (d, *J* = 7.2 Hz, 8H), 6.08 (d, *J* = 6.9 Hz, 2H), 5.48 (s, 2H), 5.42 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.71 (C-Au), 145.91 (C_{Ar}), 143.22 (C_{Ar}), 142.01 (C_{Ar}), 141.78 (C_{Ar}), 141.67 (C_{Ar}), 138.30 (C_{Ar}), 133.52 (C_{Ar}), 131.07 (C_{Ar}), 129.63 (C_{Ar}), 129.45 (C_{Ar}), 129.43 (C_{Ar}), 128.51 (C_{Ar}), 128.38 (C_{Ar}), 128.03 (C_{Ar}), 127.41 (C_{Ar}), 126.53 (C_{Ar}), 126.50 (C_{Ar}), 126.36 (C_{Ar}), 124.12 (C_{Ar}), 121.76 (C_{Ar}), 56.37 (Ph_2CH), 51.58 (Ph_2CH). HRMS (ESI) m/z: $[M - Cl]^+$ Calcd for $C_{103}H_{76}N_2Au$ 1537.5669; Found 1537.5139.

G. Characterization Data of Carboxylic Acid Addition Products:



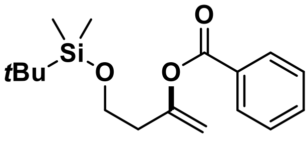
8a

Compound 8a: According to the general procedure the addition of benzoic acid (30.5 mg, 0.25 mmol) to 1-hexyne (16.5 mg, 0.20 mmol) afforded the title product (36.0 mg, 88%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.01 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.86 (d, *J* = 1.2 Hz, 1H), 4.84 (d, *J* = 1.1 Hz, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.56 – 1.49 (m, 2H), 1.43 – 1.35 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.92 (CO), 156.96 (=C(O)–), 133.40 (C_{Ar}), 130.06 (C_{Ar}), 128.59 (C_{Ar}), 101.44 ($=CH_2$), 33.29 (CH_2), 28.81 (CH_2), 22.26 (CH_2), 13.98 (CH_3).



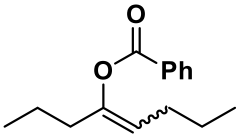
8b

Compound 8b: According to the general procedure, the addition of benzoic acid (30.5 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (40.0 mg, 86%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.18 – 7.95 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.86 (s, 1H), 4.83 (d, *J* = 0.9 Hz, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.53 (dt, *J* = 15.2, 7.4 Hz, 2H), 1.36 (dt, *J* = 14.6, 7.2 Hz, 2H), 1.32 – 1.25 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.91 (CO), 156.98 (=C(O)–), 133.39 (C$_{Ar}$), 130.06 (C$_{Ar}$), 128.58 (C$_{Ar}$), 101.44 (=CH$_2$), 33.58 (CH$_2$), 31.72 (CH$_2$), 28.82 (CH$_2$), 26.65 (CH$_2$), 22.69 (CH$_2$), 14.18 (CH$_3$).



8c

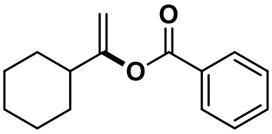
Compound 8c: According to the general procedure, the addition of benzoic acid (30.5 mg, 0.25 mmol) to 1-OTBS-butyne (36.9 mg, 0.20 mmol) afforded the title product (55.0 mg, 90%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.16 – 7.97 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.94 (d, *J* = 1.4 Hz, 1H), 4.90 (s, 1H), 3.81 (t, *J* = 6.6 Hz, 2H), 2.57 (t, *J* = 6.6 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.87 (CO), 153.92 (=C(O)–), 133.45 (C$_{Ar}$), 130.08 (C$_{Ar}$), 129.94 (C$_{Ar}$), 128.59 (C$_{Ar}$), 103.33 (=CH$_2$), 60.51(OCH$_2$), 37.40 (CH$_2$), 26.01 (CH$_3$), 18.43 (SiC$_{tBu}$), -5.22 (SiCH$_3$). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{17}H_{27}O_3Si$ 307.1724; Found 307.1690.



8d

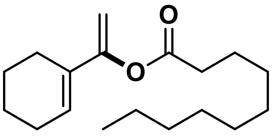
Compound 8d: According to the general procedure, the addition of benzoic acid (30.5 mg, 0.25 mmol) to 4-octyne (22.1 mg, 0.20 mmol) afforded the title product (31.0 mg, 67%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.11 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.11 (t, *J* = 7.3 Hz, 1H), 2.28 (t, *J* = 7.2 Hz, 2H), 1.96 (q, *J* = 7.3 Hz, 2H), 1.56 –

1.48 (m, 2H), 1.43 – 1.34 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.60 (CO), 148.64 (=C(O)–), 133.31 (C_{Ar}), 130.07 (C_{Ar}), 128.60 (C_{Ar}), 116.69 (=CH), 35.68 (CH_2), 27.59 (CH_2), 22.48 (CH_2), 20.14 (CH_2), 13.90(CH_3), 13.70 (CH_3).



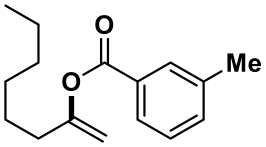
8e

Compound 8e: According to the general procedure, the addition of benzoic acid (30.5 mg, 0.25 mmol) to cyclohexylacetylene (21.6 mg, 0.20 mmol) afforded the title product (37.0 mg, 80%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.01 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.90 – 4.83 (m, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 2.25 (td, *J* = 10.8, 3.1 Hz, 1H), 1.99 (dd, *J* = 10.9, 10.0 Hz, 2H), 1.77 (dt, *J* = 14.2, 7.3 Hz, 2H), 1.69 (dd, *J* = 7.2, 5.8 Hz, 1H), 1.31 – 1.16 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.04 (CO), 160.87 (=C(O)–), 133.38 (C_{Ar}), 130.14 (C_{Ar}), 130.08 (C_{Ar}), 128.60 (C_{Ar}), 99.82 (=CH_2), 41.99 (CH_2), 30.80 (CH_2), 26.23 (CH_2), 26.12 (CH_{Cy}).



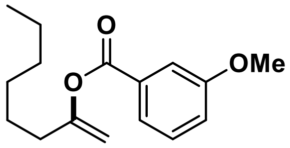
8f

Compound 8f: According to the general procedure, the addition of *n*-decanoic acid (43.1 mg, 0.25 mmol) to 1-ethynylcyclohexene (21.2 mg, 0.20 mmol) afforded the title product (44.0 mg, 79%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 (d, *J* = 1.2 Hz, 1H), 4.65 (d, *J* = 1.5 Hz, 1H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.08 (tt, *J* = 11.0, 2.6 Hz, 1H), 1.88 (d, *J* = 12.0 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.67 – 1.63 (m, 3H), 1.34 – 1.23 (m, 13H), 1.19 – 1.14 (m, 2H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.39 (CO), 160.84 (=C(O)–), 132.65 (=$C_{q(cy)}$), 120.11 (=CH–), 99.50 (=CH_2), 41.99 (CH_2), 34.71 (CH_2), 33.16 (CH_2), 32.10 (CH_2), 30.85 (CH_2), 29.67 (CH_2), 29.49 (CH_2), 29.35 (CH_2), 26.34 (CH_2), 26.22 (CH_2), 25.25 (CH_2), 22.90 (CH_2), 14.33 (CH_3). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{31}O_2$ 279.2319; Found 279.2280.



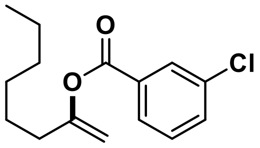
8g

Compound 8g: According to the general procedure, the addition of 3-methylbenzoic acid (34.0 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (35.0 mg, 71%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95 – 7.82 (m, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 4.84 (d, *J* = 1.1 Hz, 1H), 4.83 (d, *J* = 1.0 Hz, 1H), 2.42 (s, 3H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.53 (dt, *J* = 15.2, 7.4 Hz, 2H), 1.36 (dt, *J* = 20.6, 7.0 Hz, 2H), 1.28 (ddd, *J* = 9.8, 8.6, 5.1 Hz, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.10 (CO), 157.05 (=C(O)–), 138.42 (C$_{Ar}$), 134.17 (C$_{Ar}$), 130.58 (C$_{Ar}$), 129.98 (C$_{Ar}$), 128.49 (C$_{Ar}$), 127.22 (C$_{Ar}$), 101.40 (=CH$_2$), 33.58 (CH$_2$), 31.73 (CH$_2$), 28.84 (CH$_2$), 26.65 (CH$_2$), 22.70 (CH$_2$), 21.41 (CH$_{3(Ar)}$), 14.19 (CH$_3$). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{23}O_2$ 247.1693; Found 247.1625.



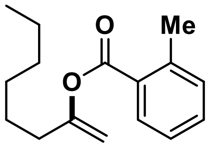
8h

Compound 8h: According to the general procedure, the addition of 3-methoxybenzoic acid (38.0 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (38.0 mg, 73%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.18 – 7.08 (m, 1H), 4.85 (d, *J* = 1.1 Hz, 1H), 4.83 (d, *J* = 0.8 Hz, 1H), 3.86 (s, 3H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.53 (dt, *J* = 15.3, 7.5 Hz, 2H), 1.39 – 1.25 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.79 (CO), 159.76 (=C(O)–), 157.00 (C$_{Ar}$), 131.36 (C$_{Ar}$), 129.61 (C$_{Ar}$), 122.47 (C$_{Ar}$), 119.97 (C$_{Ar}$), 114.42 (C$_{Ar}$), 101.45 (=CH$_2$), 55.61 (OCH$_3$), 33.55 (CH$_2$), 31.72 (CH$_2$), 28.83 (CH$_2$), 26.64 (CH$_2$), 22.70 (CH$_2$), 14.19 (CH$_3$).



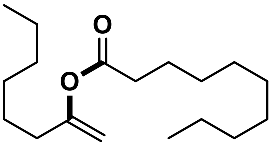
8i

Compound 8i: According to the general procedure, the addition of 3-chlorobenzoic acid (39.1 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (41.0 mg, 77%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (t, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.56 (ddd, *J* = 7.9, 2.0, 0.9 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 4.86 (d, *J* = 1.4 Hz, 1H), 4.84 (s, 1H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.55 – 1.49 (m, 2H), 1.39 – 1.24 (m, 7H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.70 (CO), 156.84 (=C(O)–), 134.78 (C_{Ar}), 133.43 (C_{Ar}), 131.82 (C_{Ar}), 130.10 (C_{Ar}), 129.92 (C_{Ar}), 128.18 (C_{Ar}), 101.66 (=CH_2), 33.48 (CH_2), 31.70 (CH_2), 28.80 (CH_2), 26.62 (CH_2), 22.69 (CH_2), 14.18 (CH_3). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{20}ClO_2$ 267.1146; Found 267.1102.



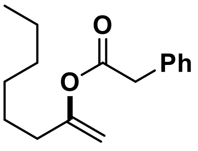
8j

Compound 8j: According to the general procedure, the addition of 2-methylbenzoic acid (34.0 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (41.0 mg, 83%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.28 (dd, *J* = 7.4, 3.8 Hz, 2H), 4.83 (d, *J* = 3.5 Hz, 2H), 2.63 (s, 3H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.54 (dt, *J* = 15.3, 7.4 Hz, 2H), 1.37 (dt, *J* = 14.5, 7.1 Hz, 2H), 1.33 – 1.26 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.68 (CO), 157.00 (=C(O)–), 140.99 (C_{Ar}), 132.49 (C_{Ar}), 131.97 (C_{Ar}), 131.05 (C_{Ar}), 129.19 (C_{Ar}), 125.93 (C_{Ar}), 101.41 (CH_2), 33.62 (CH_2), 31.74 (CH_2), 28.84 (CH_2), 26.67 (CH_2), 22.70 (CH_2), 21.97 (CH_3), 14.19 (CH_3). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{23}O_2$ 247.1693; Found 247.1649.



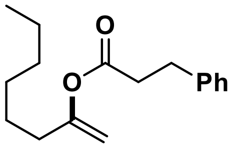
8k

Compound 8k: According to the general procedure, the addition of decanoic acid (43.1 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (50.0 mg, 88%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.70 (d, *J* = 1.0 Hz, 1H), 4.68 (d, *J* = 1.0 Hz, 1H), 2.37 (t, *J* = 7.5 Hz, 2H), 2.19 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.49 – 1.40 (m, 2H), 1.34 – 1.24 (m, 18H), 0.90 – 0.85 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.14 (CO), 156.80 (=C(O)–), 101.01 (=CH$_2$), 34.57 (CH$_2$), 33.51 (CH$_2$), 32.00 (CH$_2$), 31.73 (CH$_2$), 29.56 (CH$_2$), 29.39 (CH$_2$), 29.23 (CH$_2$), 28.81 (CH$_2$), 26.57 (CH$_2$), 25.12 (CH$_2$), 22.80 (CH$_2$), 22.69 (CH$_2$), 14.22 (CH$_3$), 14.18 (CH$_3$). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{18}H_{35}O_2$ 283.2632; Found 283.2593.



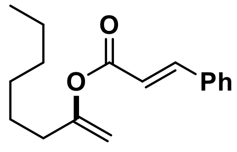
8l

Compound 8l: According to the general procedure, the addition of phenylacetic acid (34.0 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (42.0 mg, 85%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 – 7.19 (m, 5H), 4.71 (s, 2H), 3.70 (s, 2H), 2.23 – 2.13 (m, 2H), 1.41 – 1.32 (m, 2H), 1.31 – 1.18 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 169.81 (CO), 156.77 (=C(O)–), 133.84 (C$_{Ar}$), 129.37 (C$_{Ar}$), 128.76 (C$_{Ar}$), 127.34 (C$_{Ar}$), 101.23 (=CH$_2$), 41.65 (CH$_2$), 33.33 (CH$_2$), 31.67 (CH$_2$), 28.70 (CH$_2$), 26.40 (CH$_2$), 22.64 (CH$_2$), 14.18 (CH$_3$). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{23}O_2$ 247.1693; Found 247.1654.



8m

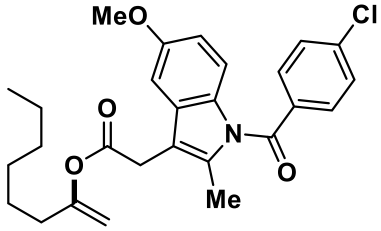
Compound 8m: According to the general procedure, the addition of 3-phenylpropanoic acid (37.5 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (46.0 mg, 88%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.26 (m, 2H), 7.26 – 7.14 (m, 3H), 4.70 (d, J = 1.0 Hz, 1H), 4.66 (d, J = 1.1 Hz, 1H), 3.00 (t, J = 7.8 Hz, 2H), 2.72 (t, J = 7.8 Hz, 2H), 2.15 (t, J = 7.6 Hz, 2H), 1.44 – 1.36 (m, 2H), 1.33 – 1.23 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 171.19 (CO), 156.75 (=C(O)–), 140.35 (C$_{Ar}$), 128.65 (C$_{Ar}$), 128.46 (C$_{Ar}$), 126.48 (C$_{Ar}$), 101.13 (=CH$_2$), 36.08 (CH$_2$), 33.45 (CH$_2$), 31.69 (CH$_2$), 31.09 (CH$_2$), 28.77 (CH$_2$), 26.50 (CH$_2$), 22.68 (CH$_3$), 14.19 (CH$_3$). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{17}H_{25}O_2$ 261.1849; Found 261.1809.



8n

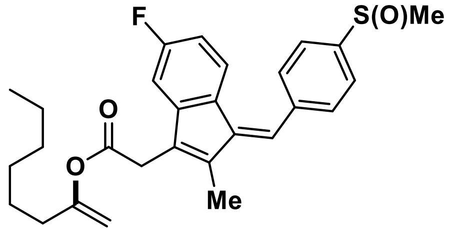
Compound 8n: According to the general procedure, the addition of cinnamic acid (37.0 mg, 0.25 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (41.0 mg, 80%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 16.0 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.47 – 7.31 (m, 3H), 6.49 (d, *J* = 16.0 Hz, 1H), 4.81 (d, *J* = 1.2 Hz, 1H), 4.78 (d, *J* = 1.0 Hz, 1H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.56 – 1.44 (m, 2H), 1.39 – 1.26 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.20 (CO), 156.82 (=C(O)–), 145.97 (=CH$_{CO}$), 134.38 (C$_{Ar}$), 130.64 (C$_{Ar}$), 129.07 (C$_{Ar}$), 128.32 (C$_{Ar}$), 117.80 (=CH$_{Ar}$), 101.22 (=CH$_2$), 33.57 (CH$_2$), 31.72 (CH$_2$), 28.82 (CH$_2$), 26.60 (CH$_2$), 22.69 (CH$_2$), 14.19 (CH$_3$).

H. Characterization Data of Derivatization of Pharmaceuticals Products:



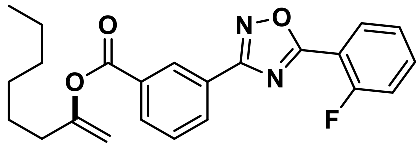
8o: from *Indomethacin*

Compound 8o: According to the general procedure, the addition of *Indomethacin* (35.8 mg, 0.10 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (38.0 mg, 81%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.74 – 7.57 (m, 2H), 7.54 – 7.38 (m, 2H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.71 (s, 2H), 3.83 (s, 3H), 3.74 (s, 2H), 2.41 (s, 3H), 2.16 (t, *J* = 7.5 Hz, 2H), 1.38 – 1.30 (m, 2H), 1.28 – 1.14 (m, 6H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 169.07 (CO), 168.38 (CO), 156.67 (=C(O)–), 156.20 (C$_{Ar}$), 139.41 (C$_{Ar}$), 136.12 (C$_{Ar}$), 134.00 (C$_{Ar}$), 131.29 (C$_{Ar}$), 130.92 (C$_{Ar}$), 130.63 (C$_{Ar}$), 129.24 (C$_{Ar}$), 115.08 (C$_{Ar}$), 112.41 (C$_{Ar}$), 111.90 (C$_{Ar}$), 101.31 (C$_{Ar}$), 101.28 (=CH$_2$), 55.78 (OCH$_3$), 33.39(CH$_2$), 31.64 (CH$_2$), 30.66 (CH$_2$), 28.70 (CH$_2$), 26.42 (CH$_2$), 22.62 (CH$_2$), 14.16 (CH$_3$), 13.48 (CH$_3$). HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{27}$H$_{31}$ClO$_4$N 468.1936; Found 468.1931.



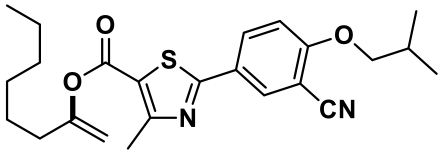
8p: from *Sulindac*

Compound 8p: According to the general procedure, the addition of *Sulindac* (35.6 mg, 0.10 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (35.0 mg, 75%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.15 (s, 1H), 6.92 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.59 (td, *J* = 9.0, 2.4 Hz, 1H), 4.71 (d, *J* = 4.8 Hz, 2H), 3.63 (s, 2H), 2.55 (s, 3H), 2.23 (s, 3H), 2.16 (t, *J* = 7.5 Hz, 2H), 1.35 (dd, *J* = 14.6, 7.2 Hz, 2H), 1.27 – 1.17 (m, 6H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 168.63 (CO), 163.26 (d, *J* = 245.7 Hz), 156.73 (=C(O)–), 146.48 (d, *J* = 8.7 Hz) (C$_{Ar}$), 140.22 (CH), 139.31 (C$_{Ar}$), 138.76 (C$_{Ar}$), 133.08 (C$_{Ar}$), 130.59 (d, *J* = 2.5 Hz) (C$_{Ar}$), 130.11 (d, *J* = 1.4 Hz) (C$_{Ar}$), 130.05 (C$_{Ar}$), 129.91 (d, *J* = 2.7 Hz) (C$_{Ar}$), 126.07 (C$_{Ar}$), 123.83 (d, *J* = 8.9 Hz) (C$_{Ar}$), 110.73 (d, *J* = 22.6 Hz) (C$_{Ar}$), 105.88 (d, *J* = 23.8 Hz) (C$_{Ar}$), 101.34 (=CH$_2$), 33.41 (CH$_2$), 32.15 (CH$_2$), 31.68 (CH$_2$), 28.73 (CH$_2$), 26.46 (CH$_2$), 22.64 (CH$_2$), 15.56 (CH$_3$), 14.19 (CH$_3$), 10.76 (CH$_3$). ^{19}F NMR (471 MHz, CDCl$_3$) δ -113.80 (s). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{28}H_{32}FO_3S$ 467.2051; Found 467.2043.



8q: from *PTC-124*

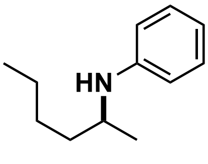
Compound 8q: According to the general procedure, the addition of *PTC-124* (28.4 mg, 0.10 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (25.0 mg, 63%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.89 (t, *J* = 1.5 Hz, 1H), 8.47 – 8.36 (m, 1H), 8.30 – 8.19 (m, 2H), 7.66 – 7.60 (m, 2H), 7.36 (td, *J* = 7.8, 0.9 Hz, 1H), 7.33 – 7.28 (m, 1H), 4.90 (d, *J* = 1.4 Hz, 1H), 4.87 (d, *J* = 1.0 Hz, 1H), 2.37 (t, *J* = 7.6 Hz, 2H), 1.57 (dd, *J* = 15.2, 7.3 Hz, 2H), 1.38 (dt, *J* = 14.1, 6.9 Hz, 2H), 1.33 – 1.28 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 173.26 (d, *J* = 4.3 Hz) (C$_{Ar}$), 168.17 (CO), 164.23 (=C(O)–), 160.97 (d, *J* = 260.9 Hz) (C$_{Ar}$), 156.97 (C$_{Ar}$), 134.92 (d, *J* = 8.6 Hz) (C$_{Ar}$), 132.70 (C$_{Ar}$), 132.25 (C$_{Ar}$), 131.14 (C$_{Ar}$), 130.98 (C$_{Ar}$), 129.24 (d, *J* = 18.6 Hz) (C$_{Ar}$), 127.51 (C$_{Ar}$), 124.90 (d, *J* = 3.7 Hz) (C$_{Ar}$), 117.35 (d, *J* = 20.8 Hz) (C$_{Ar}$), 115.63 (C$_{Ar}$), 112.85 (d, *J* = 11.4 Hz) (C$_{Ar}$), 101.66 (=CH$_2$), 33.54 (CH$_2$), 31.73 (CH_2), 28.85 (CH_2), 26.65 (CH_2), 22.71 (CH_2), 14.20 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.14 (s). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}FO_3N_2$ 395.1765; Found 395.1752.



8r: from *Febuxostat*

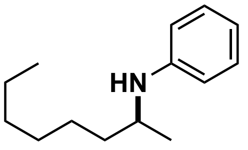
Compound 8r: According to the general procedure, the addition of *Febuxostat* (31.6 mg, 0.10 mmol) to 1-octyne (22.1 mg, 0.20 mmol) afforded the title product (35.0 mg, 82%) as oil. ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.2 Hz, 1H), 8.10 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 4.95 – 4.74 (m, 2H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.78 (s, 3H), 2.31 (t, *J* = 7.6 Hz, 2H), 2.21 (tt, *J* = 13.3, 6.7 Hz, 1H), 1.52 (dt, *J* = 15.2, 7.4 Hz, 2H), 1.38 – 1.27 (m, 6H), 1.09 (d, *J* = 6.7 Hz, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.86 (CO), 162.74 (C_{Ar}), 162.43 (C_{Ar}), 160.18 (=C(O)–), 156.37 (C_{Ar}), 132.74 (C_{Ar}), 132.31 (C_{Ar}), 126.07 (C_{Ar}), 121.28 (C_{Ar}), 115.50 (C_{Ar}), 112.78 (C_{Ar}), 103.19 (CN), 101.90 (=CH_2), 75.86 (OCH_2), 33.58 (CH), 31.71 (CH_2), 28.77 (CH_2), 28.30 (CH_2), 26.60 (CH_2), 22.70 (CH_2), 19.19 (CH_3), 17.70 (CH_3), 14.20 (CH_3). $[M + H]^+$ Calcd for $C_{24}H_{31}SO_3N_2$ 427.2050; Found 427.2040.

I. Characterization Data of Hydroamination Products:



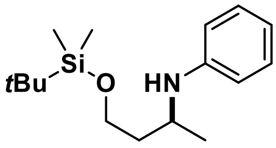
10a

Compound 10a: According to the general procedure, the addition of aniline (55.9 mg, 0.60 mmol) to 1-hexyne (41.1 mg, 0.50 mmol) afforded the title product (81.0 mg, 91%) as oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 2H), 3.49 (td, *J* = 12.5, 6.3 Hz, 2H), 1.65 – 1.57 (m, 1H), 1.50 – 1.34 (m, 5H), 1.21 (d, *J* = 6.3 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.84 (C_{Ar}), 129.38 (C_{Ar}), 116.84 (C_{Ar}), 113.17 (C_{Ar}), 48.54 (HCN), 37.06 (CH_2), 28.49 (CH_2), 22.89 (CH_2), 20.91 (CH_3), 14.22 (CH_3).



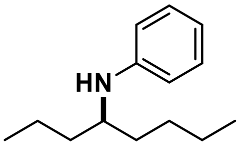
10b

Compound 10b: According to the general procedure, the addition of aniline (55.9 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (84.0 mg, 82%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.19 (dd, J = 8.4, 7.4 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.7 Hz, 2H), 3.52 – 3.39 (m, 2H), 1.64 – 1.56 (m, 1H), 1.49 – 1.38 (m, 3H), 1.37 – 1.29 (m, 6H), 1.20 (d, J = 6.2 Hz, 3H), 0.92 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.86 (C$_{Ar}$), 129.38 (C$_{Ar}$), 116.84 (C$_{Ar}$), 113.18 (C$_{Ar}$), 48.58 (HCN), 37.38 (CH$_2$), 31.98 (CH$_2$), 29.50 (CH$_2$), 26.26 (CH$_2$), 22.76 (CH$_2$), 20.91 (CH$_3$), 14.22 (CH$_3$).



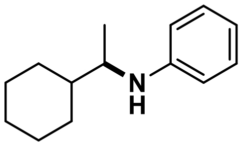
10c

Compound 10c: According to the general procedure, the addition of aniline (55.9 mg, 0.60 mmol) to 1-OTBS-butyne (92.2 mg, 0.50 mmol) afforded the title product (105.0 mg, 75%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.19 (dd, J = 8.3, 7.5 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.8 Hz, 2H), 3.83 (ddd, J = 12.0, 7.0, 5.2 Hz, 2H), 3.78 – 3.67 (m, 2H), 1.82 (ddd, J = 18.5, 11.7, 6.4 Hz, 1H), 1.77 – 1.66 (m, 1H), 1.24 (d, J = 6.3 Hz, 3H), 0.96 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 147.87 (C$_{Ar}$), 129.33 (C$_{Ar}$), 116.84 (C$_{Ar}$), 113.24 (C$_{Ar}$), 60.62 (HCN), 46.32 (CH$_2$), 39.74 (CH$_2$), 26.08 (CH$_{3(tBu)}$), 20.76 (CH$_3$), 18.38 (SiC$_q$), -5.28 (d, J = 1.7 Hz) (SiCH$_3$).



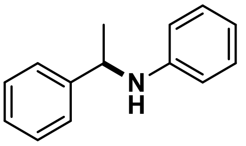
10d

Compound 10d: According to the general procedure, the addition of aniline (55.9 mg, 0.60 mmol) to 4-octyne (55.1 mg, 0.50 mmol) afforded the title product (85.0 mg, 83%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.16 (dd, J = 8.4, 7.4 Hz, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 7.7 Hz, 2H), 3.39 (s, 1H), 3.38 – 3.32 (m, 1H), 1.57 – 1.30 (m, 10H), 0.92 (dt, J = 11.0, 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.36 (C_{Ar}), 129.39 (C_{Ar}), 116.56 (C_{Ar}), 112.92 (C_{Ar}), 52.70 (HCN), 37.41 (CH_2), 34.82 (CH_2), 28.26 (CH_2), 23.01 (CH_2), 19.27 (CH_2), 14.37 (CH_3), 14.24 (CH_3).



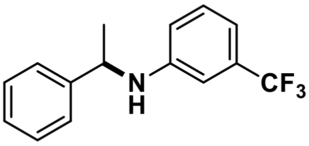
10e

Compound 10e: According to the general procedure, the addition of aniline (55.9 mg, 0.60 mmol) to cyclohexylacetylene (54.1 mg, 0.50 mmol) afforded the title product (81.0 mg, 80%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (dd, J = 8.4, 7.4 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 7.7 Hz, 2H), 3.49 (s, 1H), 3.39 – 3.29 (m, 1H), 1.87 – 1.66 (m, 5H), 1.51 – 1.42 (m, 1H), 1.29 – 1.03 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.09 (C_{Ar}), 129.39 (C_{Ar}), 116.63 (C_{Ar}), 113.07 (C_{Ar}), 53.10 (HCN), 43.10 ($CH_{(Cy)}$), 29.92 (CH_2), 28.54 (CH_2), 26.78 (CH_2), 26.63 (CH_2), 26.48 (CH_2), 17.55 (CH_3).



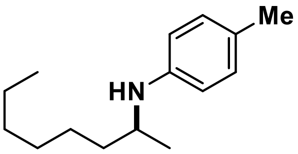
10f

Compound 10f: According to the general procedure, the addition of aniline (55.9 mg, 0.60 mmol) to phenylacetylene (51.1 mg, 0.50 mmol) afforded the title product (91.0 mg, 92%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.17 (dd, J = 8.5, 7.4 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.59 (d, J = 7.7 Hz, 2H), 4.56 (q, J = 6.7 Hz, 1H), 4.09 (s, 1H), 1.58 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.38 (C_{Ar}), 145.33 (C_{Ar}), 129.20 (C_{Ar}), 128.73 (C_{Ar}), 126.96 (C_{Ar}), 125.94 (C_{Ar}), 117.33 (C_{Ar}), 113.39 (C_{Ar}), 53.54 (HCN), 25.11 (CH_3).



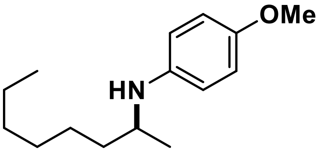
10g

Compound 10g: According to the general procedure, the addition of 3-trifluoromethyl aniline (96.7 mg, 0.60 mmol) to phenylacetylene (51.1 mg, 0.50 mmol) in presence of 0.05 mol% of catalyst loading afforded the title product (118.0 mg, 89%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.76 (s, 1H), 6.61 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.51 (q, *J* = 6.6 Hz, 1H), 4.23 (s, 1H), 1.54 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.47 (C_{Ar}), 144.47 (C_{Ar}), 131.47 (q, *J* = 31.7 Hz) (C_{Ar}), 129.67 (C_{Ar}), 128.92 (C_{Ar}), 127.30 (C_{Ar}), 125.89 (C_{Ar}), 124.43 (q, *J* = 272.3 Hz) (CF_3), 116.05 (C_{Ar}), 113.75 (q, *J* = 3.9 Hz) (C_{Ar}), 109.91 (q, *J* = 3.9 Hz) (C_{Ar}), 53.54 (HCN), 24.93 (CH_3). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.88 (s).



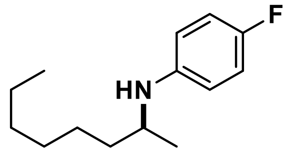
10h

Compound 10h: According to the general procedure, the addition of *p*-toluidine (64.3 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (93.0 mg, 85%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 8.4 Hz, 2H), 3.49 – 3.39 (m, 1H), 3.30 (s, 1H), 2.25 (s, 3H), 1.62 – 1.53 (m, 1H), 1.45 – 1.26 (m, 9H), 1.17 (d, *J* = 6.3 Hz, 3H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.60 (C_{Ar}), 129.88 (C_{Ar}), 126.08 (C_{Ar}), 113.47 (C_{Ar}), 48.92 (HCN), 37.40 (CH_2), 31.99 (CH_2), 29.52 (CH_2), 26.28 (CH_2), 22.77 (CH_2), 20.94 (CH_3), 20.47 (CH_3), 14.22 (CH_3).



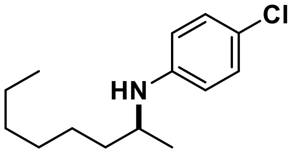
10i

Compound 10i: According to the general procedure, the addition of *p*-anisidine (73.9 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (90.0 mg, 76%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 – 6.65 (m, 2H), 6.64 – 6.51 (m, 2H), 3.75 (s, 3H), 3.42 – 3.32 (m, 1H), 3.15 (s, 1H), 1.62 – 1.52 (m, 1H), 1.45 – 1.35 (m, 3H), 1.34 – 1.25 (m, 6H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.90 (C_{Ar}), 142.12 (C_{Ar}), 115.07 (C_{Ar}), 114.78 (C_{Ar}), 55.94 (OCH_3), 49.63 (HCN), 37.40 (CH_2), 31.98 (CH_2), 29.52 (CH_2), 26.27 (CH_2), 22.75 (CH_2), 20.93 (CH_3), 14.21 (CH_3).



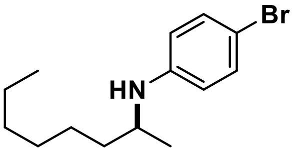
10j

Compound 10j: According to the general procedure, the addition of 4-fluoroaniline (66.7 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (98.0 mg, 88%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.98 – 6.75 (m, 2H), 6.58 – 6.44 (m, 2H), 3.41 – 3.34 (m, 1H), 3.28 (s, 1H), 1.59 – 1.52 (m, 1H), 1.44 – 1.27 (m, 9H), 1.16 (d, J = 6.3 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 155.61 (d, J = 234.3 Hz) (C$_{Ar}$), 144.22 (d, J = 1.7 Hz) (C$_{Ar}$), 115.77 (d, J = 22.2 Hz) (C$_{Ar}$), 114.10 (d, J = 7.3 Hz) (C$_{Ar}$), 49.40 (HCN), 37.31 (CH$_2$), 31.97 (CH$_2$), 29.50 (CH$_2$), 26.24 (CH$_2$), 22.76 (CH$_2$), 20.83 (CH$_3$), 14.22 (CH$_3$). ^{19}F NMR (471 MHz, CDCl$_3$) δ -128.82 (s).



10k

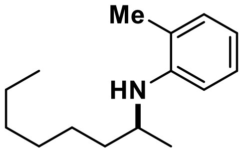
Compound 10k: According to the general procedure, the addition of 4-chloroaniline (76.5 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (107.0 mg, 89%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.11 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 3.44 – 3.38 (m, 2H), 1.59 – 1.51 (m, 1H), 1.46 – 1.27 (m, 9H), 1.17 (d, J = 6.2 Hz, 3H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.41 (C$_{Ar}$), 129.17 (C$_{Ar}$), 121.26 (C$_{Ar}$), 114.21 (C$_{Ar}$), 48.81 (HCN), 37.21 (CH$_2$), 31.95 (CH$_2$), 29.45 (CH$_2$), 26.19 (CH$_2$), 22.74 (CH$_2$), 20.75 (CH$_3$), 14.20 (CH$_3$).



10l

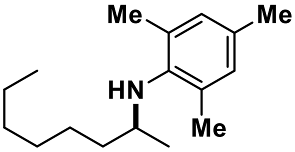
Compound 10l: According to the general procedure, the addition of 4-bromoaniline (103.2 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (122.0 mg, 86%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.17 (m, 2H), 6.55 – 6.33 (m, 2H), 3.46 (s, 1H), 3.40 (dq, J = 12.6, 6.3 Hz, 1H), 1.55 (ddd, J = 9.8, 9.2, 5.5 Hz, 1H), 1.45 – 1.26 (m, 9H), 1.16

(d, *J* = 6.2 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.81 (C$_{Ar}$), 132.05 (C$_{Ar}$), 114.72 (C$_{Ar}$), 108.23 (C$_{Ar}$), 48.73 (HCN), 37.19 (CH$_2$), 31.95 (CH$_2$), 29.45 (CH$_2$), 26.19 (CH$_2$), 22.75 (CH$_2$), 20.74 (CH$_3$), 14.21 (CH$_3$).



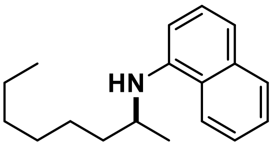
10m

Compound 10m: According to the general procedure, the addition of *o*-toluidine (64.3 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (98.0 mg, 89%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.15 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.1 Hz, 1H), 6.65 (t, *J* = 8.0 Hz, 2H), 3.62 – 3.49 (m, 1H), 3.33 (s, 1H), 2.16 (s, 3H), 1.66 (tt, *J* = 9.1, 5.0 Hz, 1H), 1.54 – 1.41 (m, 3H), 1.39 – 1.31 (m, 6H), 1.25 (d, *J* = 6.3 Hz, 3H), 0.94 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 145.69 (C$_{Ar}$), 130.33 (C$_{Ar}$), 127.22 (C$_{Ar}$), 121.70 (C$_{Ar}$), 116.28 (C$_{Ar}$), 110.13 (C$_{Ar}$), 48.42 (HCN), 37.46 (CH$_2$), 31.98 (CH$_2$), 29.52 (CH$_2$), 26.29 (CH$_2$), 22.77 (CH$_2$), 21.13 (CH$_3$), 17.71 (CH$_3$), 14.22 (CH$_3$).



10n

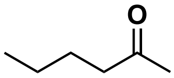
Compound 10n: According to the general procedure, the addition of 2,4,6-trimethylaniline (81.1 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (97.0 mg, 78%) as oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.83 (s, 2H), 3.29 – 3.15 (m, 1H), 2.70 (s, 1H), 2.26 (s, 9H), 1.62 – 1.55 (m, 1H), 1.46 – 1.37 (m, 3H), 1.37 – 1.29 (m, 6H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.93 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 142.69 (C$_{Ar}$), 130.41 (C$_{Ar}$), 129.57 (C$_{Ar}$), 129.22 (C$_{Ar}$), 52.79 (HCN), 38.56 (CH$_2$), 32.02 (CH$_2$), 29.66 (CH$_2$), 26.62 (CH$_2$), 22.77 (CH$_2$), 21.39 (CH$_3$), 20.65 (CH$_3$), 19.07 (CH$_3$), 14.22 (CH$_3$).



10o

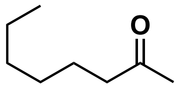
Compound 10o: According to the general procedure, the addition of 1-aminonaphthalene (85.9 mg, 0.60 mmol) to 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (95.0 mg, 74%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.25 (dd, *J* = 10.0, 5.8 Hz, 1H), 7.10 (t, *J* = 7.0 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 4.09 (s, 1H), 3.60 – 3.50 (m, 1H), 1.67 – 1.58 (m, 1H), 1.50 – 1.42 (m, 1H), 1.39 – 1.30 (m, 2H), 1.28 – 1.17 (m, 9H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.78 (C_{Ar}), 134.67 (C_{Ar}), 128.84 (C_{Ar}), 126.82 (C_{Ar}), 125.69 (C_{Ar}), 124.56 (C_{Ar}), 123.48 (C_{Ar}), 119.89 (C_{Ar}), 116.63 (C_{Ar}), 104.57 (C_{Ar}), 48.64 (HCN), 37.28 (CH_2), 31.99 (CH_2), 29.54 (CH_2), 26.35 (CH_2), 22.78 (CH_2), 20.76 (CH_3), 14.24 (CH_3).

J. Characterization Data of Hydration Products:



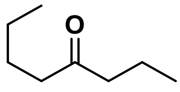
11a

Compound 11a: According to the general procedure, the hydration of 1-Hexyne (41.1 mg, 0.50 mmol) afforded the title product (48.0 mg, 96%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (t, *J* = 7.5 Hz, 2H), 2.12 (s, 3H), 1.54 (dt, *J* = 20.8, 7.5 Hz, 2H), 1.30 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.48 (CO), 43.63 (CH_2), 29.96 (CH_2), 26.08 (CH_2), 22.41 (CH_3), 13.96 (CH_3).



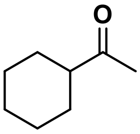
11b

Compound 11b: According to the general procedure, the hydration of 1-octyne (55.1 mg, 0.50 mmol) afforded the title product (61.0 mg, 95%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (t, *J* = 7.5 Hz, 2H), 2.07 (s, 3H), 1.55 – 1.46 (m, 2H), 1.27 – 1.19 (m, 6H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.28 (CO), 43.81 (CH_2), 31.63 (CH_2), 29.82 (CH_2), 28.88 (CH_2), 23.86 (CH_2), 22.52 (CH_3), 14.03 (CH_3).



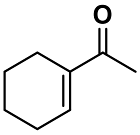
11c

Compound 11c: According to the general procedure, the hydration of 4-octyne (55.1 mg, 0.50 mmol) afforded the title product (60.0 mg, 94%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36 (dd, *J* = 14.2, 7.0 Hz, 4H), 1.62 – 1.49 (m, 4H), 1.29 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.89 (ddd, *J* = 11.2, 7.2, 3.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.66 (CO), 44.82 (CH_2), 42.66 (CH_2), 26.08 (CH_2), 22.50 (CH_2), 17.43 (CH_2), 13.97 (CH_3), 13.88 (CH_3).



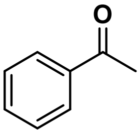
11d

Compound 11d: According to the general procedure, the hydration of cyclohexylacetylene (54.1 mg, 0.50 mmol) afforded the title product (53.0 mg, 84%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.29 (ddd, *J* = 11.0, 7.2, 3.4 Hz, 1H), 2.10 (s, 3H), 1.88 – 1.81 (m, 2H), 1.75 (dt, *J* = 5.8, 2.7 Hz, 2H), 1.66 – 1.61 (m, 1H), 1.33 – 1.16 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.40 (CO), 51.54 (CH_{Cy}), 28.52 (CH_2), 27.96 (CH_2), 25.95 (CH_2), 25.72 (CH_3).



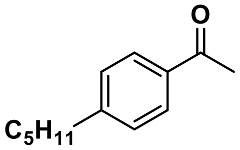
11e

Compound 11e: According to the general procedure, the hydration of 1-ethynylcyclohexene (53.1 mg, 0.50 mmol) afforded the title product (57.0 mg, 92%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 – 6.86 (m, 1H), 2.26 (s, 3H), 2.25 – 2.18 (m, 4H), 1.64 – 1.56 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.48 (CO), 141.01 (C_q), 139.80 (=CH–), 26.22 (CH_2), 25.28 (CH_2), 23.06 (CH_2), 22.03 (CH_2), 21.63 (CH_3).



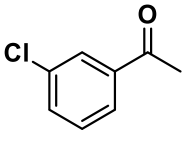
11f

Compound 11f: According to the general procedure, the hydration of phenylacetylene (51.1 mg, 0.50 mmol) afforded the title product (55.0 mg, 92%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 8.1, 1.0 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.46 (dd, J = 10.7, 4.7 Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.37 (CO), 137.35 (C_{Ar}), 133.32 (C_{Ar}), 128.79 (C_{Ar}), 128.53 (C_{Ar}), 26.83 (CH_3).



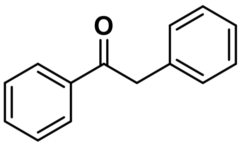
11g

Compound 11g: According to the general procedure, the hydration of 1-ethynyl-4-pentylbenzene (86.1 mg, 0.50 mmol) afforded the title product (79.0 mg, 83%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 2.67 – 2.62 (m, 2H), 2.57 (s, 3H), 1.62 (dt, J = 15.0, 7.6 Hz, 2H), 1.36 – 1.28 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.91, 148.91 (C_{Ar}), 135.02 (C_{Ar}), 128.69 (C_{Ar}), 128.56 (C_{Ar}), 36.05 (CH_2), 31.52 (CH_2), 30.89 (CH_2), 26.61 (CH_2), 22.59 (CH_3), 14.08 (CH_3).



11h

Compound 11h: According to the general procedure, the hydration of 3-chlorophenylacetylene (68.3 mg, 0.50 mmol) afforded the title product (60.0 mg, 78%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (t, J = 1.8 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.53 (ddd, J = 7.9, 2.0, 0.9 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.94 (CO), 138.84 (C_{Ar}), 135.16 (C_{Ar}), 133.27 (C_{Ar}), 130.17 (C_{Ar}), 128.66 (C_{Ar}), 126.64 (C_{Ar}), 26.88 (CH_3).



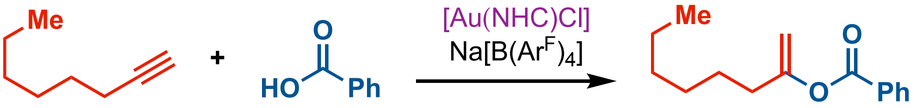
11i

Compound 11i: According to the general procedure, the hydration of diphenylacetylene (89.1 mg, 0.50 mmol) afforded the title product (79.0 mg, 80%) as oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 5.2, 3.3 Hz, 2H), 7.53 – 7.46 (m, 1H), 7.40 (dd, J = 10.6, 4.8 Hz, 2H), 7.32 –

7.24 (m, 2H), 7.24 – 7.13 (m, 3H), 4.23 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.73 (CO), 136.73 (C_{Ar}), 134.66 (C_{Ar}), 133.28 (C_{Ar}), 129.59 (C_{Ar}), 128.79 (C_{Ar}), 128.76 (C_{Ar}), 128.73 (C_{Ar}), 127.01 (C_{Ar}), 45.62 (CH_3).

K. Additional Studies

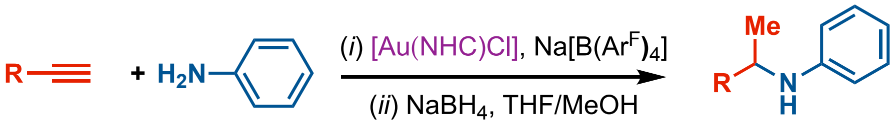
Chart S1. Hydrocarboxylation of Alkynes using [Au(NHC)Cl] Complexes[a]



Entry	Au(I)–NHC Catalyst	Yield (%) [Au] (1 mol%)	Yield (%) [Au] (2 mol%)
1	**1**: [Au(IPr#)Cl]	32	58
2	**2**: [Au(Np#)Cl]	58	75
3	**3**: [Au(BIAN-IPr#)Cl]	25	47
4	**4**: [Au(IPr*)Cl]	16	63
5	**5**: [Au(IPr)Cl]	25	38

[a] Conditions: 1-Octyne (1.0 equiv), benzoic acid (1.2 equiv), [Au(NHC)Cl] (**1–5**) (1-2.0 mol%), NaBAr$^F_4$ (4.0 mol%), toluene (1.0 M), 80 °C, 15 h.

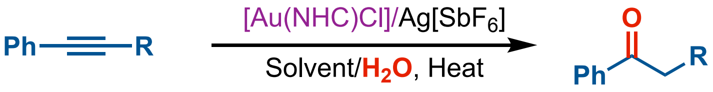
Chart S2. Hydroamination of Alkynes using [Au(NHC)Cl] Complexes[a]



Entry	Au(I)–NHC Catalyst	Yield (%) R = Ph	Yield (%) R = C_6H_{13}
1	**1**: [Au(IPr#)Cl]	89	85
2	**2**: [Au(Np#)Cl]	93	87
3	**3**: [Au(BIAN-IPr#)Cl]	90	81
4	**4**: [Au(IPr*)Cl]	89	83
5	**5**: [Au(IPr)Cl]	91	75

[a] Conditions: Alkyne (1.0 equiv), aniline (1.2 equiv), [Au(NHC)Cl] (**1–5**) (x mol%), NaBAr$^F_4$ (2 x mol%), 50 °C, 15 h. R = Ph, [Au] = 0.01 mol%; R = C_6H_{13}, [Au] = 1.5 mol%.

Chart S3. Hydration of Alkynes using [Au(NHC)Cl] Complexes[a]



Entry	Au(I)–NHC Catalyst	Yield (%) R = Ph
1	**1**: [Au(IPr$^{\#}$)Cl]	22
2	**2**: [Au(Np$^{\#}$)Cl]	59
3	**3**: [Au(BIAN-IPr$^{\#}$)Cl]	16
4	**4**: [Au(IPr*)Cl]	30
5	**5**: [Au(IPr)Cl]	42

[a]Conditions: Alkyne (1.0 equiv), [Au(NHC)Cl] (**1**–**5**) (x mol%), $AgSbF_4$. [Au] = 0.01 mol%, dioxane/water, 110 °C, 65 h.

L. Details of Crystal Structure Analysis

Crystallographic information for all the compounds is given in Table S1 in the Supporting Information. All compounds were colorless single crystals. Full datasets were collected using graphite-monochromated CuKα radiation (λ = 1.54178 Å) on a Bruker SMART APEX2 single crystal diffractometer. X-rays were provided by a fine-focus sealed X-ray tube operated at 48kV and 30mA. Lattice constants were all determined using the Bruker SAINT software package using all available reflections (after data collection, ORTEP files, see Figures S1-S3).

All data were corrected for absorption by measuring the faces of each crystal and doing a numerical absorption correction. The Bruker software package SHELXTL-2014 was used to solve all the structures using the direct methods technique and difference electron density maps. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the same software package. The final structural model for each compound was refined using anisotropic thermal parameters for all non-hydrogen atoms; all the H atoms were located in difference maps but were placed in geometrically idealized positions and allowed to “ride” on their parent C, O or N atoms, with bond lengths of 0.95, 1.00, 0.99, 0.98, and 0.84 Å for aromatic, methine, methylene, methyl, and hydroxyl, respectively. The isotropic thermal parameters for these H atoms were fixed to be 1.2 times the U_{iso} for C or N and 1.5 times the U_{iso} for O.

Details for all the structures are given in Table S1. Also included in this table is the largest shifts/s.u. for the final cycle of refinement and the largest maxima and minima in any of the final difference maps.

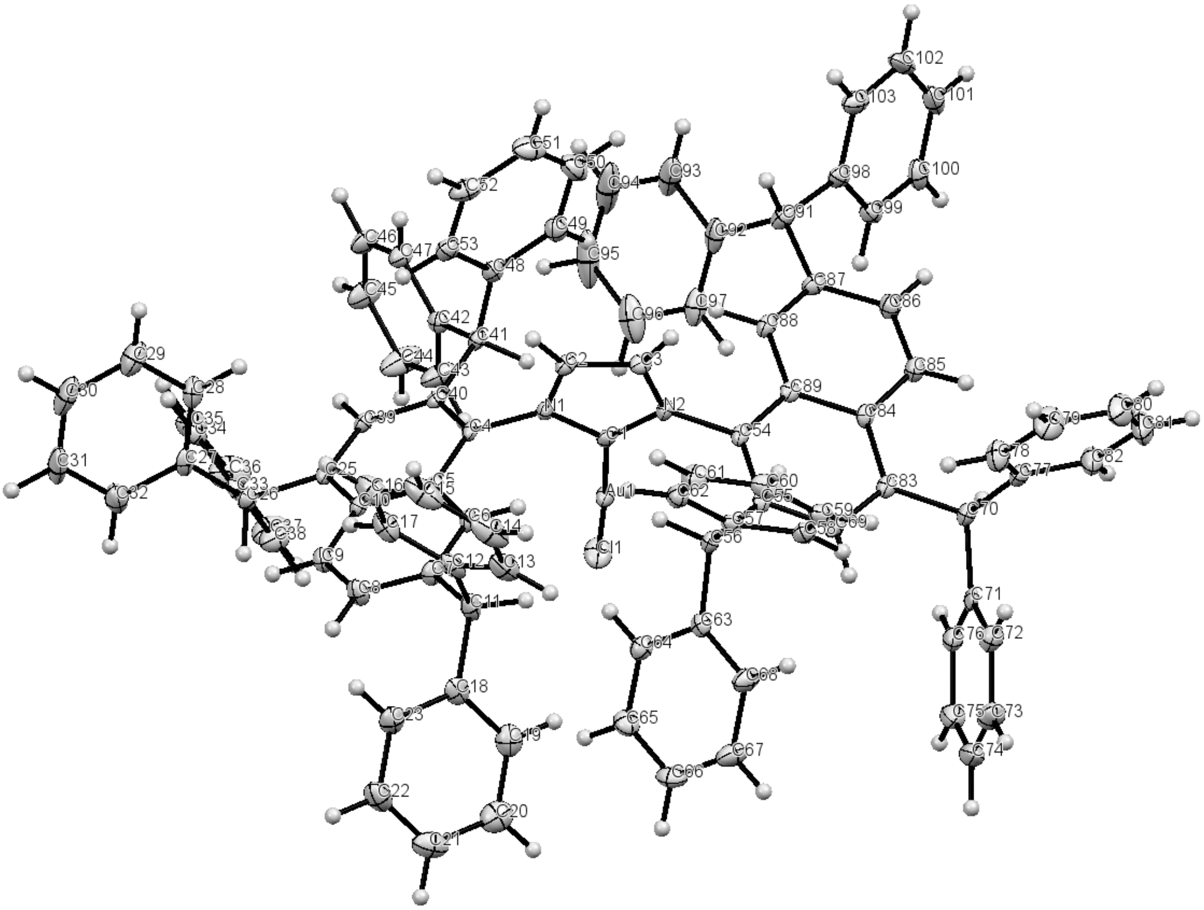
Table S1. Crystal Data and Structure Refinement Summaries for **[Au(Np$^{\#}$)Cl]** (**2**).

Compound	**2**
Chemical formula	$C_{101}H_{76}AuClN_2 \cdot CH_2Cl_2$
M_r	1634.98
Crystal system, space group	Triclinic, *P*1
Temperature (K)	100
a, *b*, *c* (Å)	9.8807 (2), 19.9006 (4), 20.5724 (4)
α, β, γ (°)	91.843 (1), 101.967 (1), 101.976 (1)
V (Å^3)	3859.18 (13)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	4.93
Crystal size (mm)	0.33 × 0.27 × 0.14
Data collection	
Diffractometer	Bruker *SMART* CCD Apex-II area-detector
Absorption correction	Numerical *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.334, 0.632
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	43421, 12981, 12738
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.053, 1.06
No. of reflections	12981
No. of parameters	974
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.57, −0.57

Computer programs: *APEX* 2 (Bruker, 2006), *APEX* 2, *SAINT* (Bruker, 2005), *SHELXL2016*/6 (Sheldrick, 2016), *SHELXTL*.

Figure S1. ORTEP Structure of **[Au(Np$^{\#}$)Cl]** (**2**) (50% ellipsoids). (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2260430).

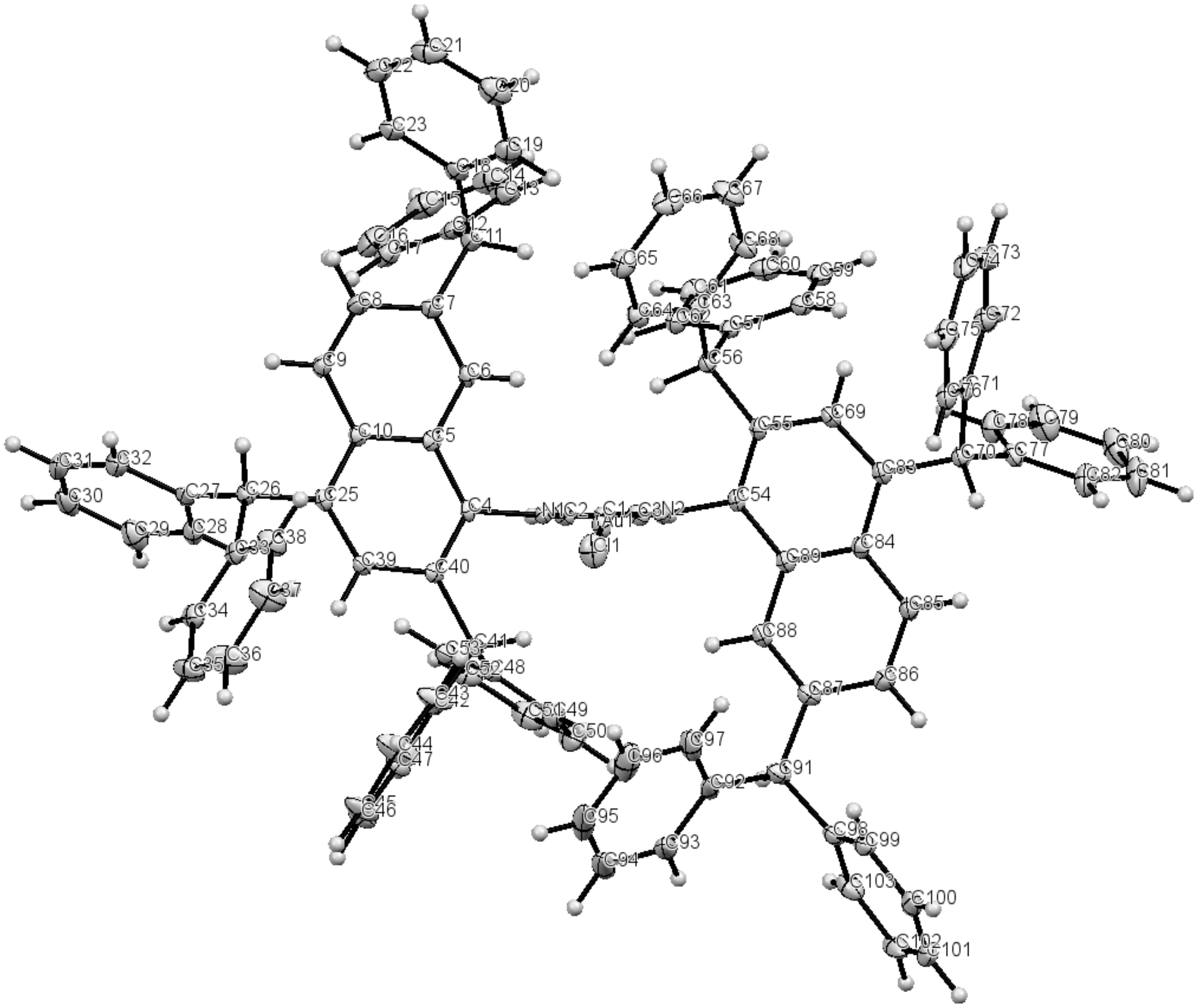
Front View:



Selected bond lengths [Å], bond angle [°] and dihedral angles [°] (**2**): Au1–Cl1, 2.2823(7); Au1–C1, 1.983(2); C1–N1, 1.358(3); C1–N2, 1.353(2); N1–C4, 1.443(2); N2–C54, 1.440(3); Cl1–Au1–C1, 174.31(6); Au1–C1–N1, 125.3(1); Au1–C1–N2, 129.5(1); Au1–C1–N1–C4, 11.4(3); Au1–C1–N2–C54, 19.0(3); C89–C54–N2–C1, 101.9(2); C55–C54–N2–C1, 78.2(3); C40–C4–N1–C1, 79.0(3); C5–C4–N1–C1, 100.3(2); C54–N2–N1–C4, 16.9(7).

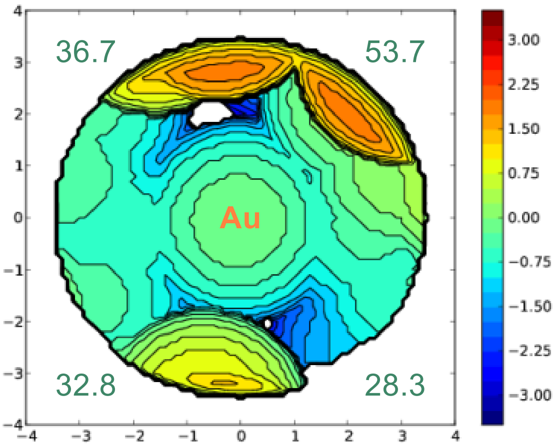
Figure S2. ORTEP Structure of **[Au(NP$^{\#}$)Cl]** (**2**) (50% ellipsoids). (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2260430).

<u>Side View:</u>



Selected bond lengths [Å], bond angle [°] and dihedral angles [°] (**2**): Au1–Cl1, 2.2823(7); Au1–C1, 1.983(2); C1–N1, 1.358(3); C1–N2, 1.353(2); N2–C54, 1.440(3); N1–C4, 1.443(2); Cl1–Au1–C1, 174.31(6); Au1–C1–N1, 125.3(1); Au1–C1–N2, 129.5(1); Au1–C1–N1–C4, 11.4(3); Au1–C1–N2–C54, 19.0(3); C89–C54–N2–C1, 101.9(2); C55–C54–N2–C1, 78.2(3); C40–C4–N1–C1, 79.0(3); C5–C4–N1–C1, 100.3(2); C54–N2–N1–C4, 16.9(7).

Figure S3. Topographical steric map of complex **[Au(Np$^{\#}$)Cl]** (**2**). X-ray single crystal structure, showing %V$_{bur}$ per quadrant.



[Au(**NP$^{\#}$**)Cl]

%V$_{bur}$ = 46.2

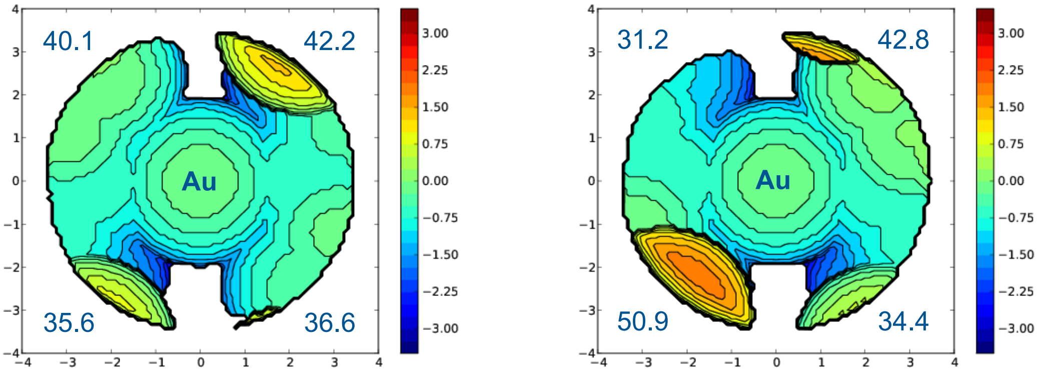
Computational Methods

Computational Methods. All the calculations were performed using Gaussian 09 suite of programs. All of the geometry optimizations were performed at the B3LYP level of theory in the gas phase with the QZVP basis set for gold and the 6-311++G(d,p) basis set for the other atoms. For geometry optimizations, we employed the X-ray structures of [(Np#)AuCl], [(IPr*)AuCl] and [(IPr)AuCl] as the starting geometry and performed full optimization. The absence of imaginary frequencies was used to characterize the structures as minima on the potential energy surface. All of the optimized geometries were verified as minima (no imaginary frequencies). NBO calculations were performed at the DFT/B3LYP level using NBO program implemented in Gaussian software package. Energetic parameters were calculated under standard conditions (298.15 K and 1 atm). Structural representations were generated using CYLview software (Legault, C. Y. CYL view version 1.0 BETA, University of Sherbrooke). All other representations were generated using Gauss View (GaussView, version 5, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission, KS, 2009) or ChemCraft software (Andrienko, G. L. ChemCraft version b562a, https://www.chemcraftprog.com).

Full Reference for Gaussian 09

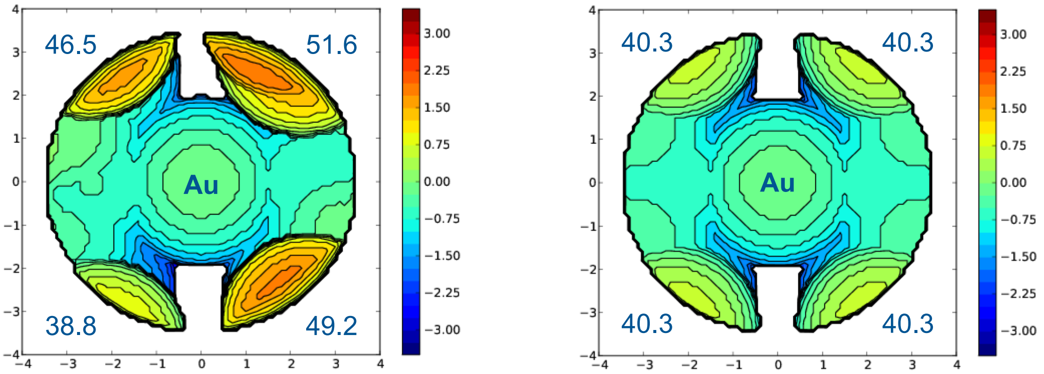
Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Figure S4. Topographical steric maps of complexes [Au(Np$^\#$)Cl] (*anti*) (**2**), [Au(Np$^\#$)Cl] (*syn*) (**2**), [Au(IPr*)Cl] (**4**) and [Au(IPr)Cl] (**5**) at the B3LYP 6-311++g(d,p) level.



2: [Au(NP$^\#$)Cl] (*anti*)
(%V_{bur} = 38.6)

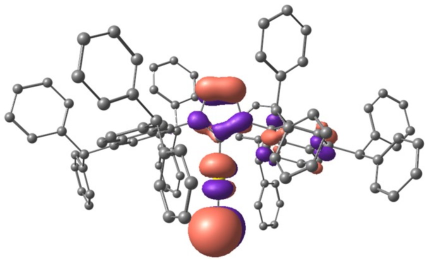
2: [Au(NP$^\#$)Cl] (*syn*)
(%V_{bur} = 39.8)



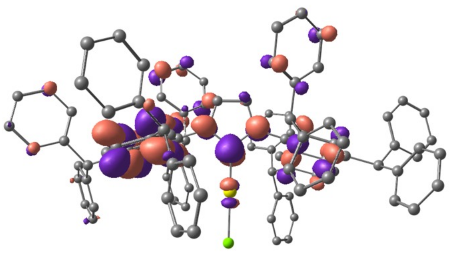
4: [Au(IPr*)Cl]
(%V_{bur} = 46.5)

5: [Au(IPr)Cl] (*syn*)
(%V_{bur} = 40.3)

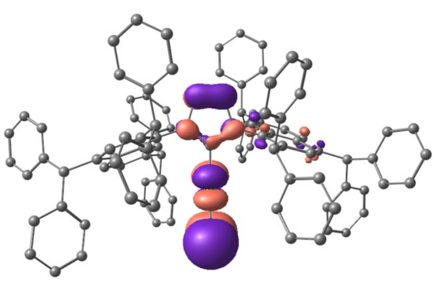
Figure S5. Graphical Representation of Frontier Orbitals of Complexes [Au(Np$^{\#}$)Cl] (*anti*) (**2**), [Au(Np$^{\#}$)Cl] (*syn*) (**2**), [Au(IPr*)Cl] (**4**) and [Au(IPr)Cl] (**5**) at the B3LYP 6-311++g(d,p) Level.



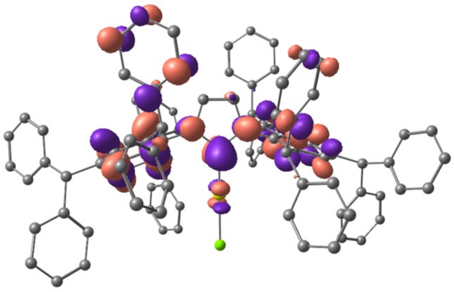
2: [Au(NP$^{\#}$)Cl] (*anti*)
HOMO (-6.20 eV)



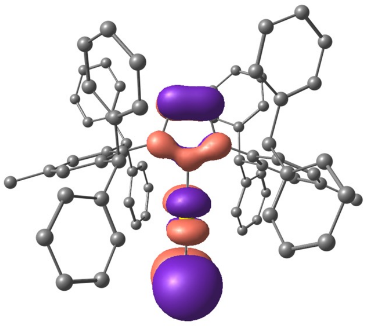
2: [Au(NP$^{\#}$)Cl] (*anti*)
LUMO+2 (-1.17 eV)



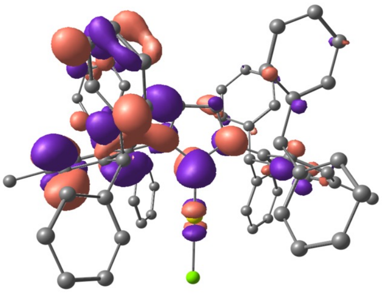
2: [Au(NP$^{\#}$)Cl] (*syn*)
HOMO-2 (-6.31 eV)



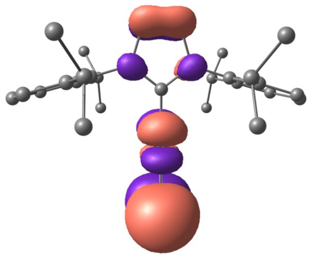
2: [Au(NP$^{\#}$)Cl] (*syn*)
LUMO+2 (-1.17 eV)



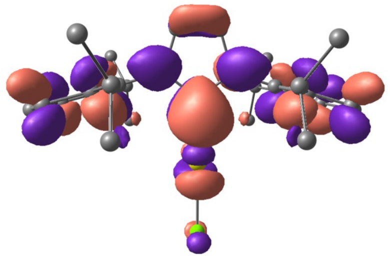
4: [Au(IPr*)Cl]
HOMO (-6.32 eV)



4: [Au(IPr*)Cl]
LUMO (-1.22 eV)



5: [Au(IPr)Cl]
HOMO-2 (-6.11 eV)



5: [Au(IPr)Cl]
LUMO+2 (-1.04 eV)

Table S2. HOMO and LUMO Energy Levels Calculated at the B3LYP 6-311++g(d,p) Level

entry	compound	orbital	E [au]	E [eV]	ΔE[a] [eV]
1	[Au(Np$^{\#}$)Cl] (**2**)	HOMO	-0.2279	-6.20	5.03[b]
2[d]	(*anti*)	LUMO+2	-0.0431	-1.17	
3[e]	[Au(Np$^{\#}$)Cl] (**2**)	HOMO-2	-0.2320	-6.31	5.14[c]
4[d]	(*syn*)	LUMO+2	-0.0429	-1.17	
5	[Au(IPr*)Cl] (**4**)	HOMO	-0.2321	-6.32	5.10
6		LUMO	-0.0447	-1.22	
7	[Au(IPr)Cl] (**5**)	HOMO	-0.2284	-6.21	5.17
8		LUMO	-0.0382	-1.04	

[a] $\Delta E = E_{LUMO} - E_{HOMO}$. [b] $\Delta E = E_{LUMO+2} - E_{HOMO}$. [c] $\Delta E = E_{LUMO+2} - E_{HOMO-2}$. [d] LUMO+2 and [e] HOMO-2 due to required symmetry.

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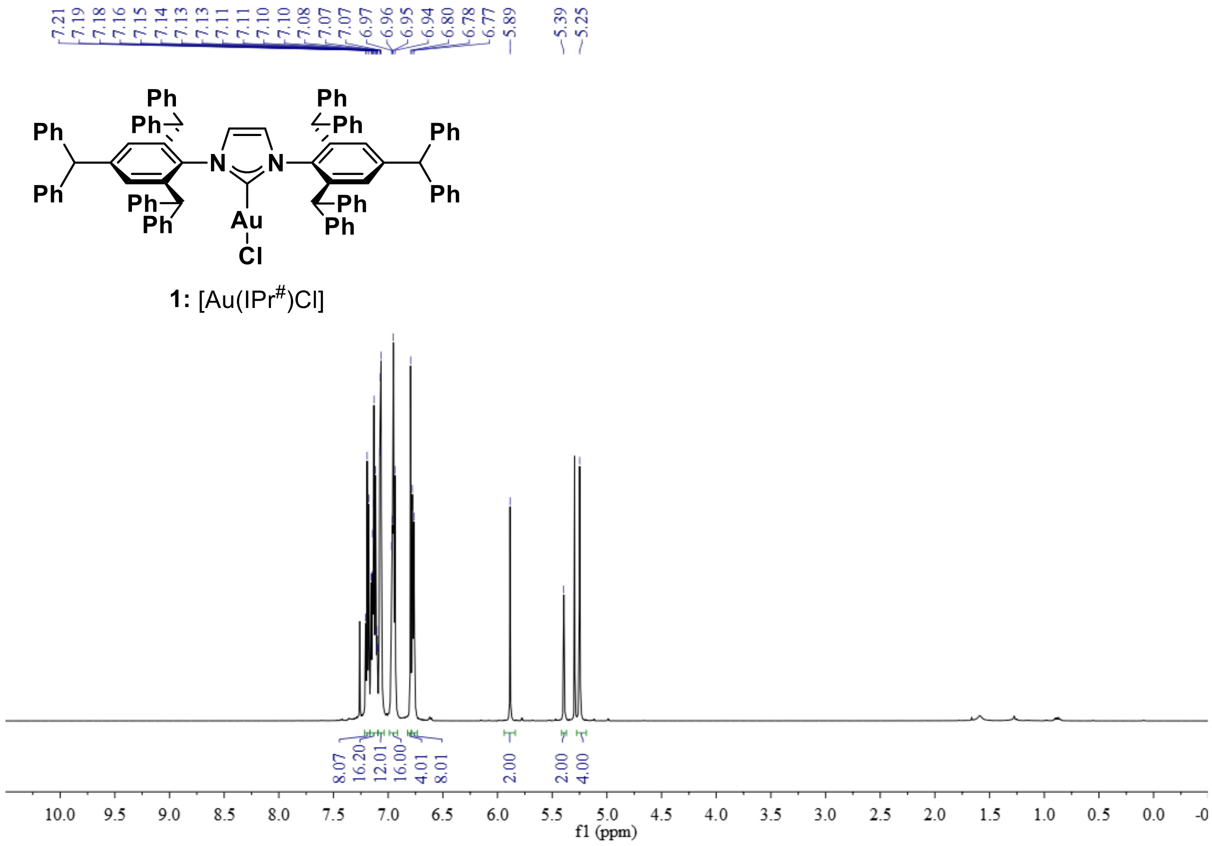
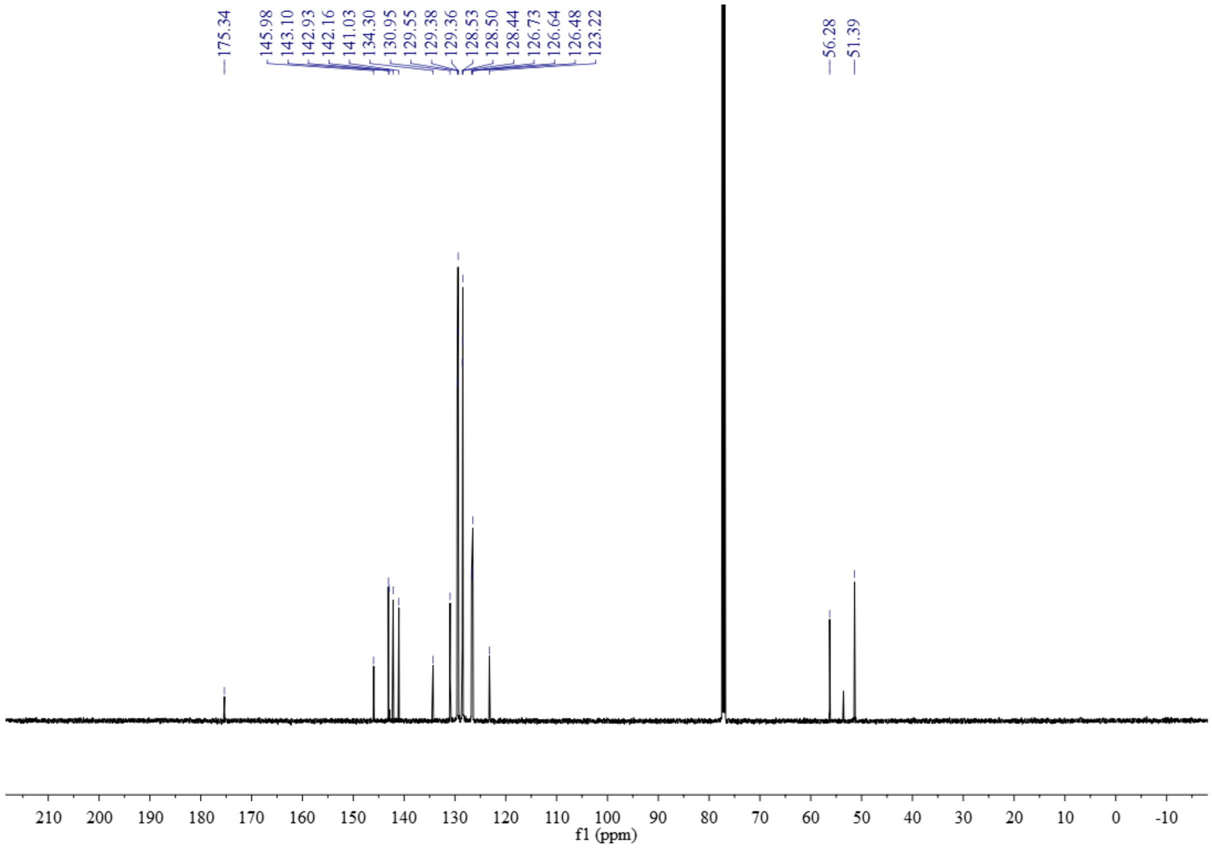
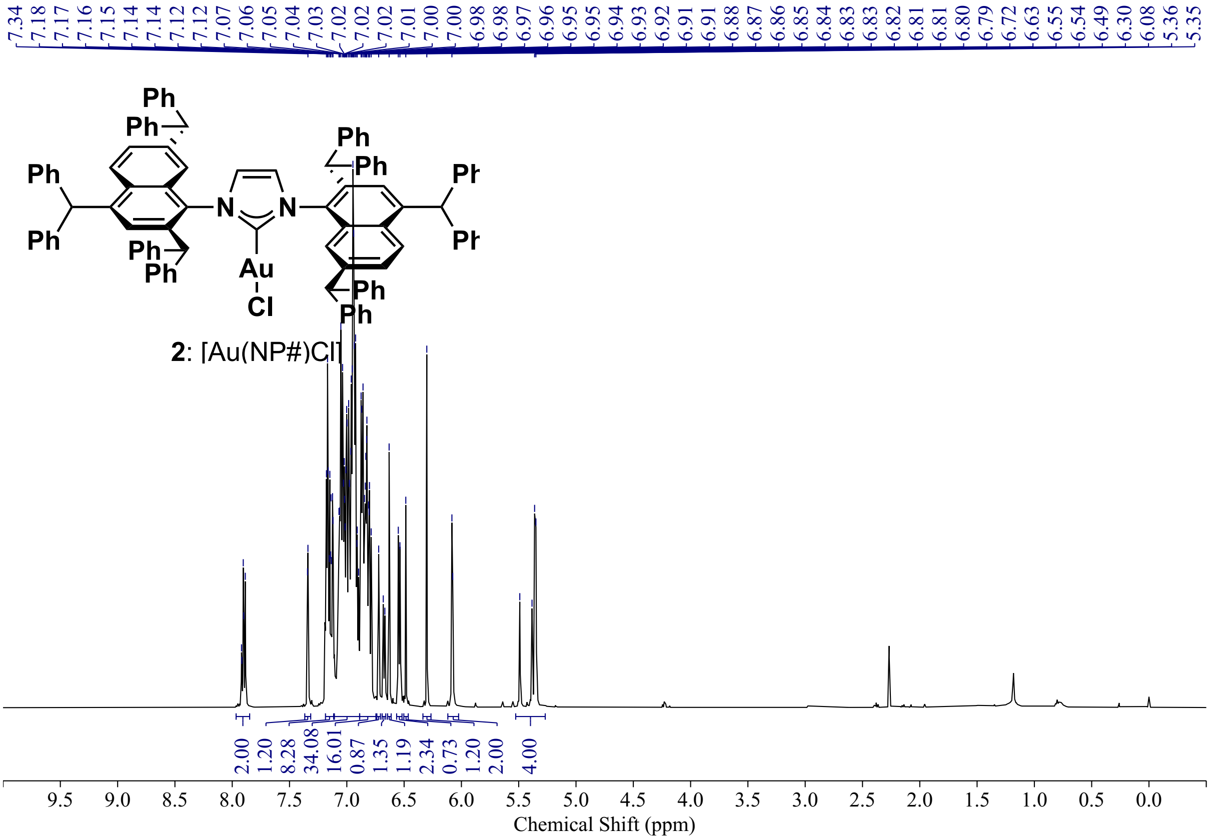


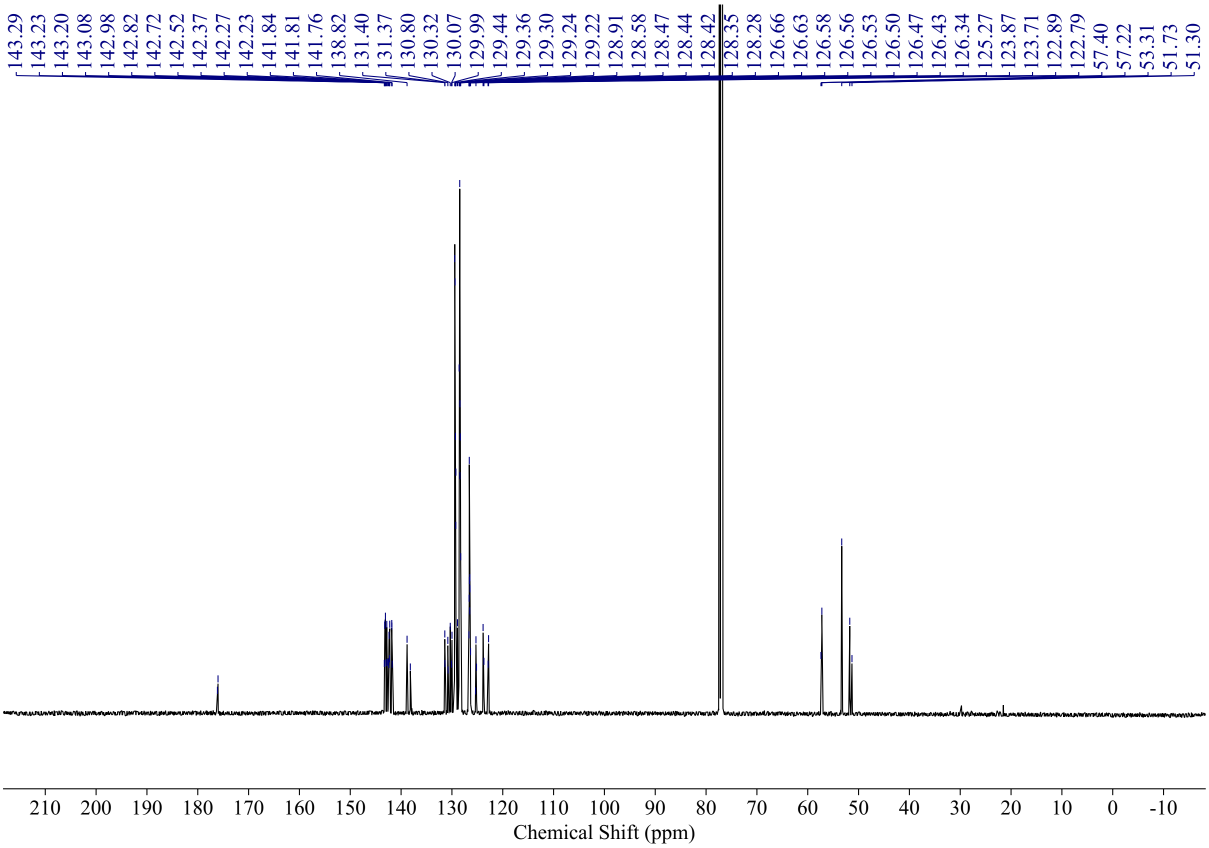
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of [Au(IPr$^{\#}$)Cl] (**1**).



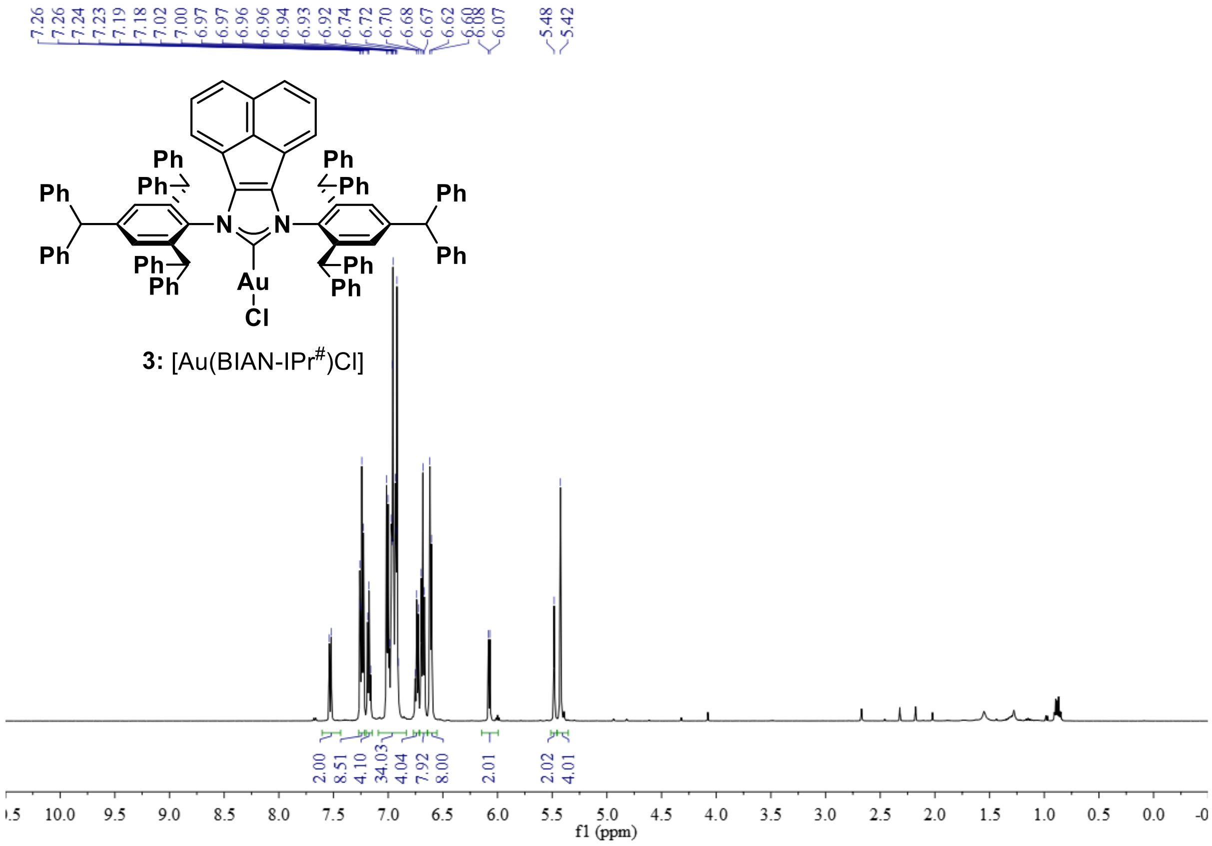
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of [Au(IPr$^{\#}$)Cl] (**1**).



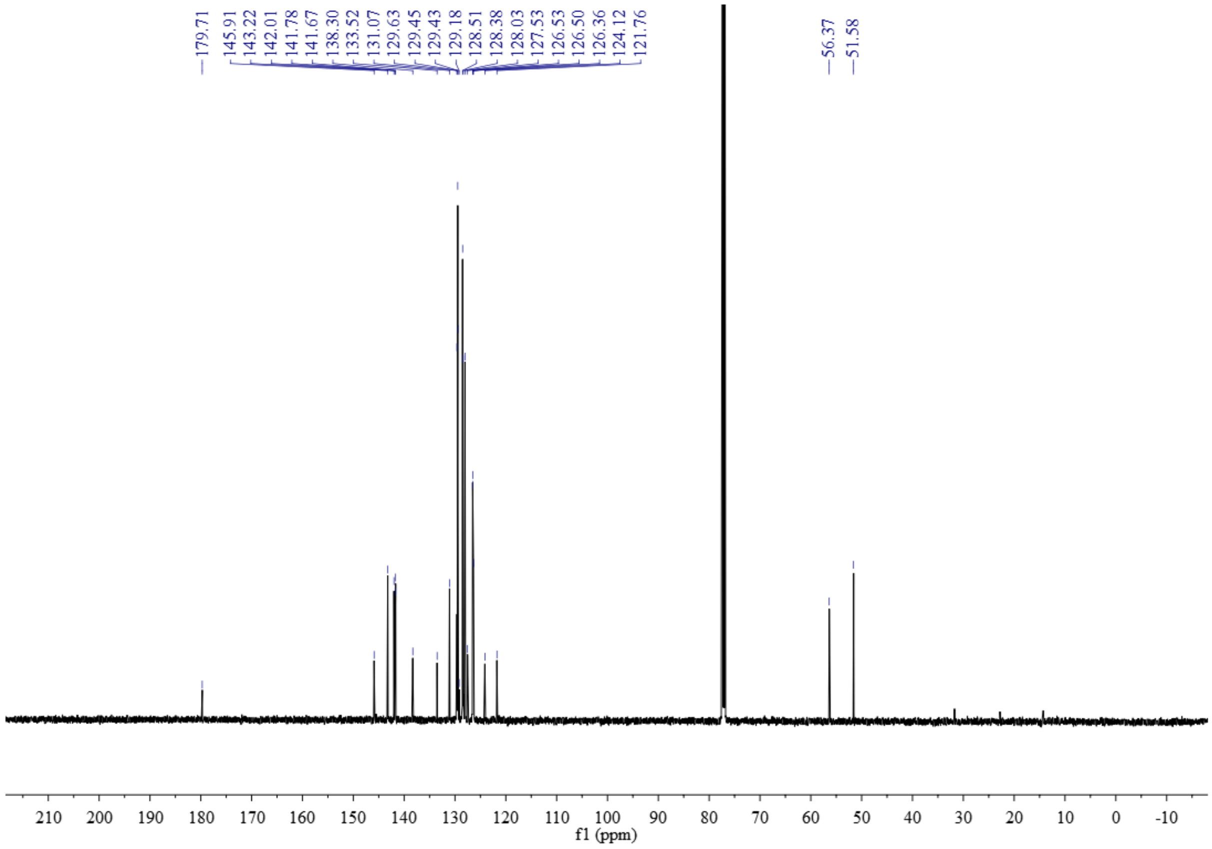
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of [Au(NP$^{\#}$)Cl] (**2**).



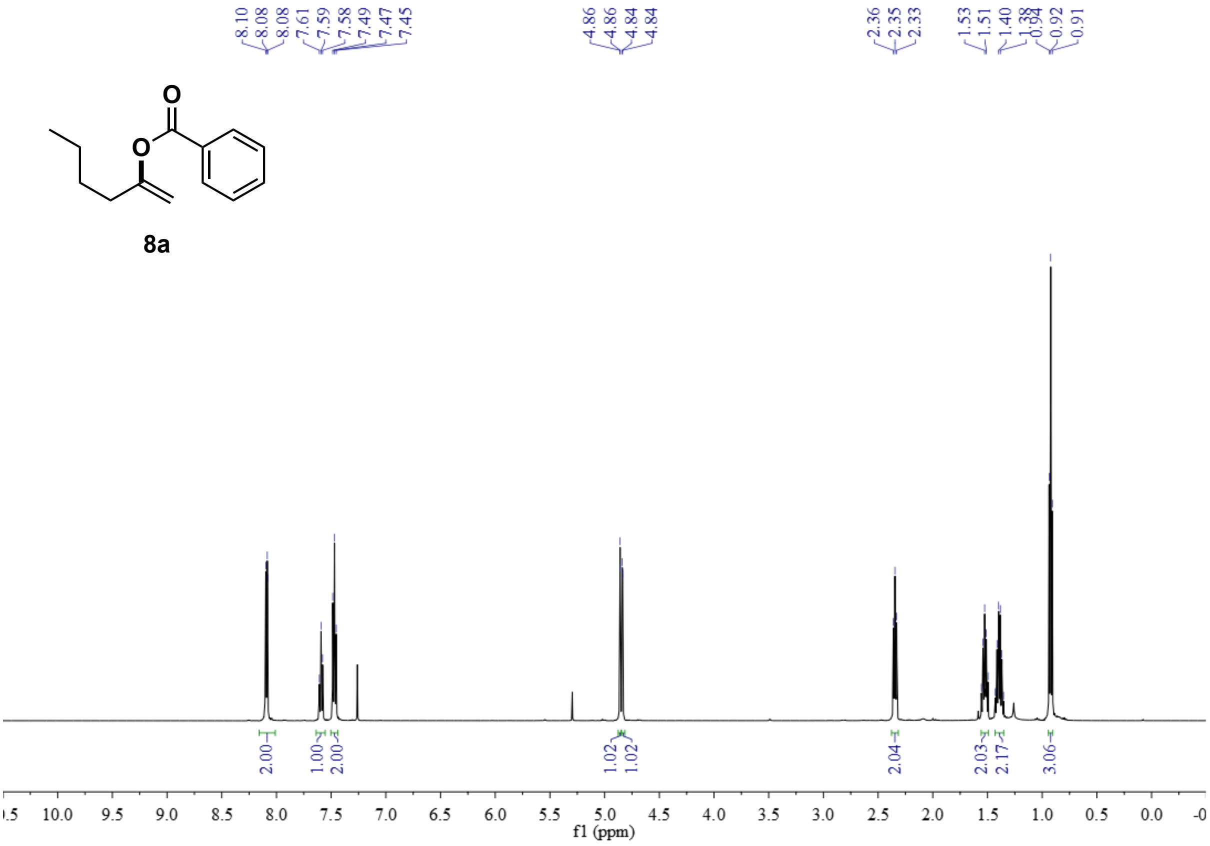
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of [Au(NP$^{\#}$)Cl] (**2**).



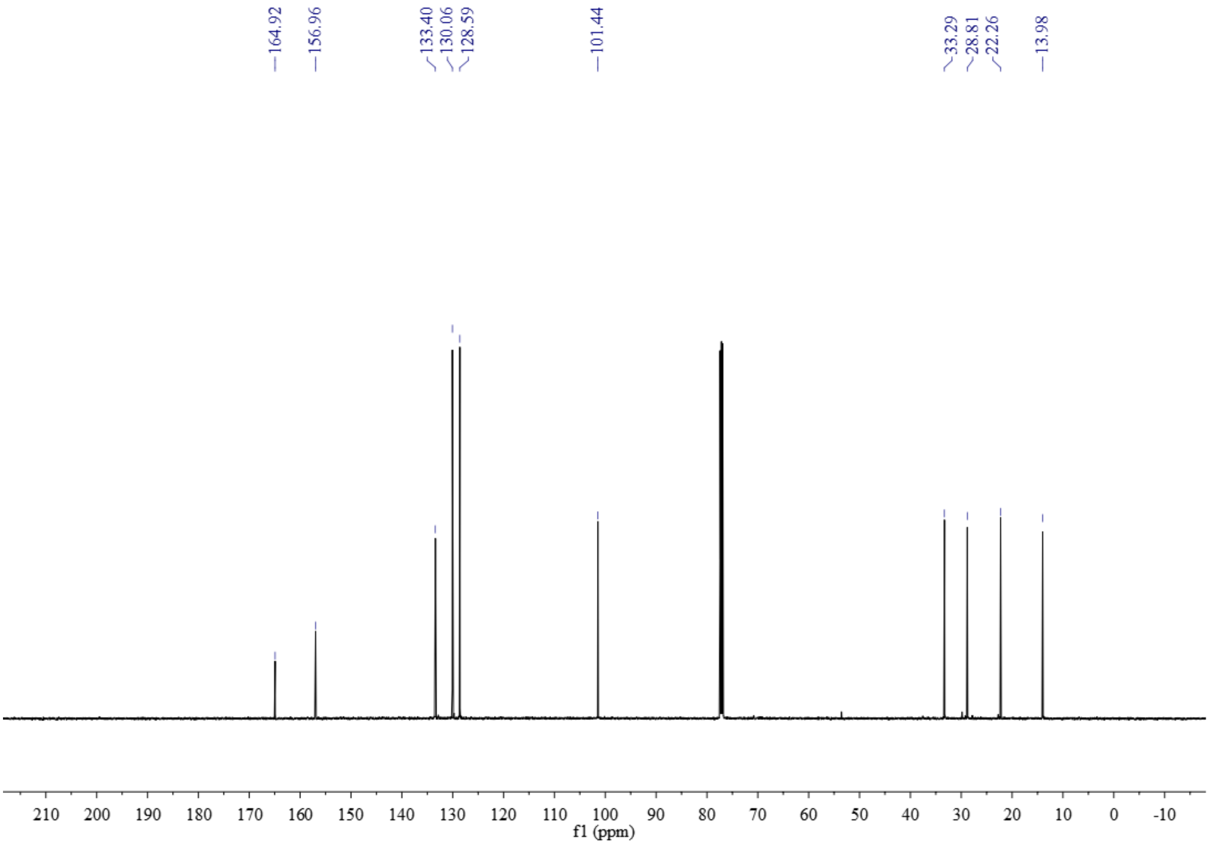
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of [Au(BIAN-IPr$^{\#}$)Cl] (**3**).



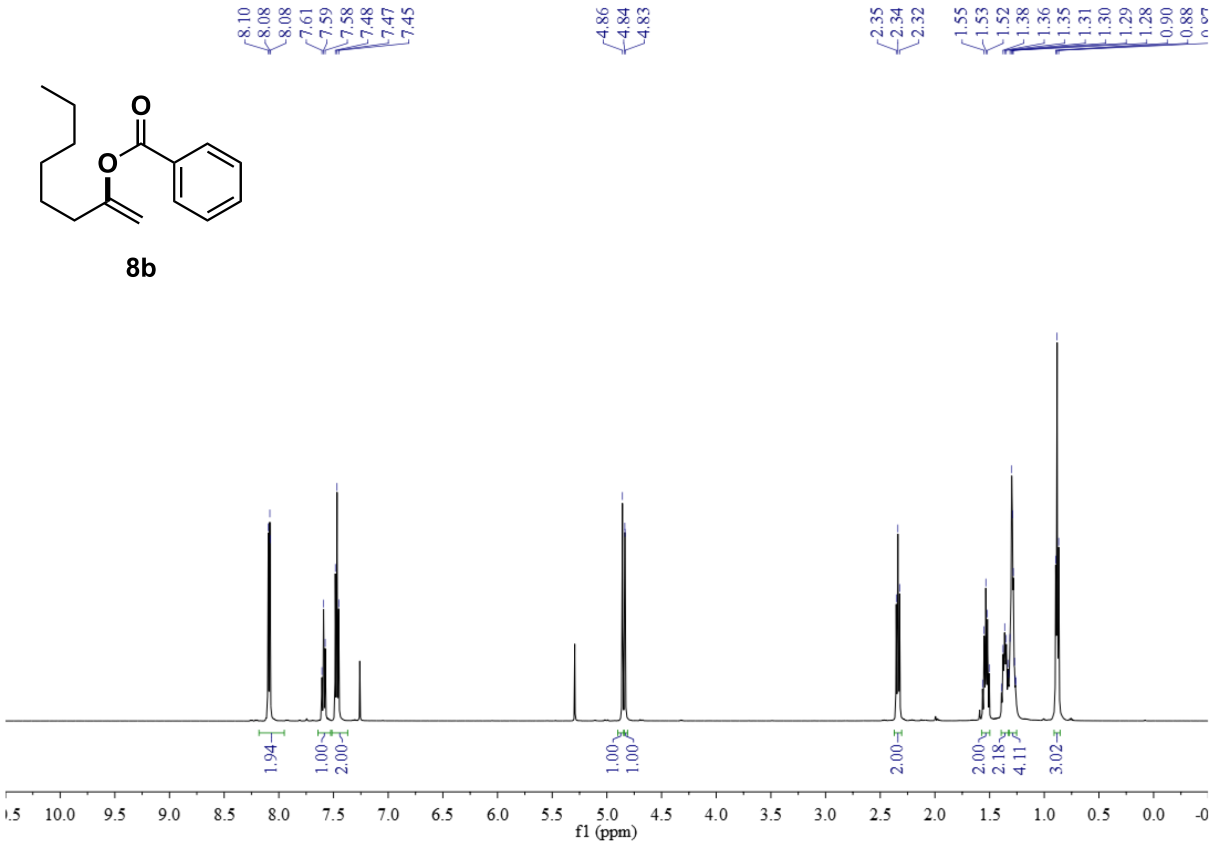
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of [Au(BIAN-IPr$^{\#}$)Cl] (**3**).



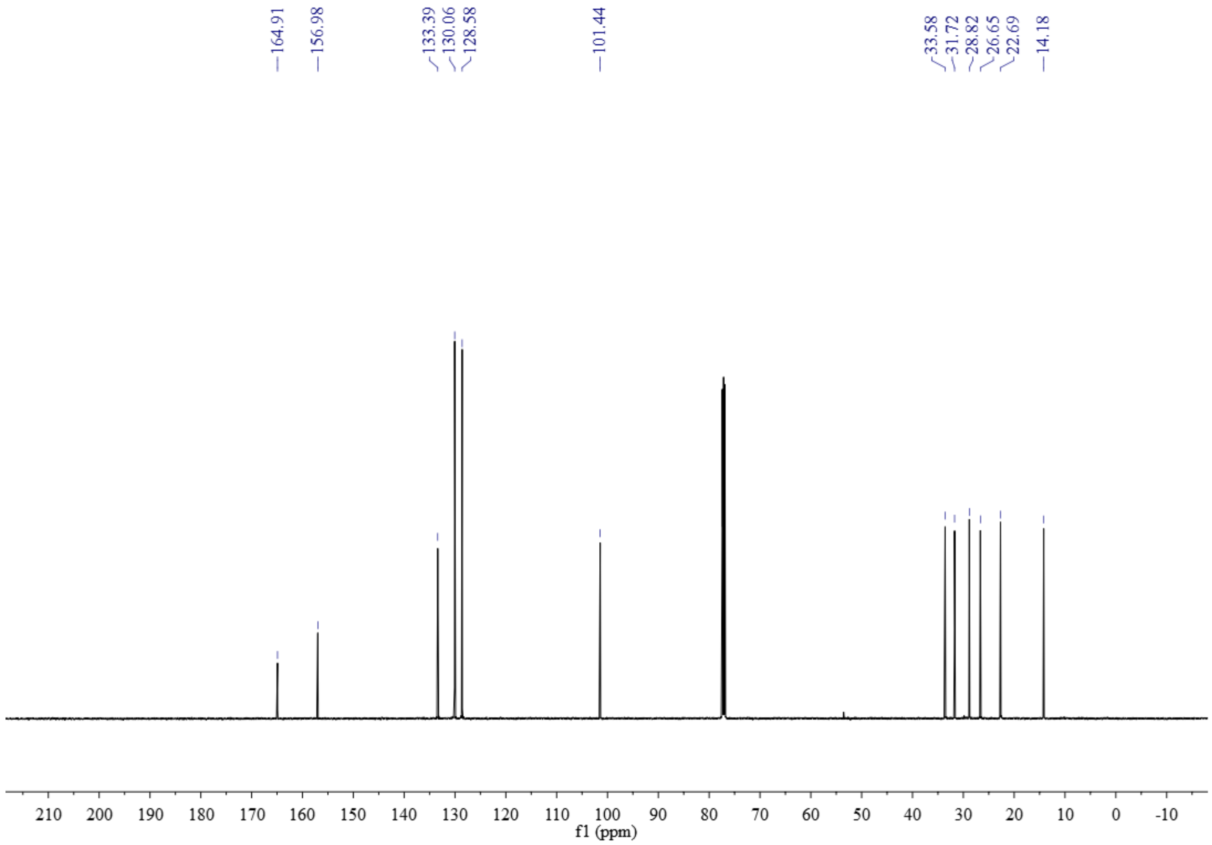
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **8a**.



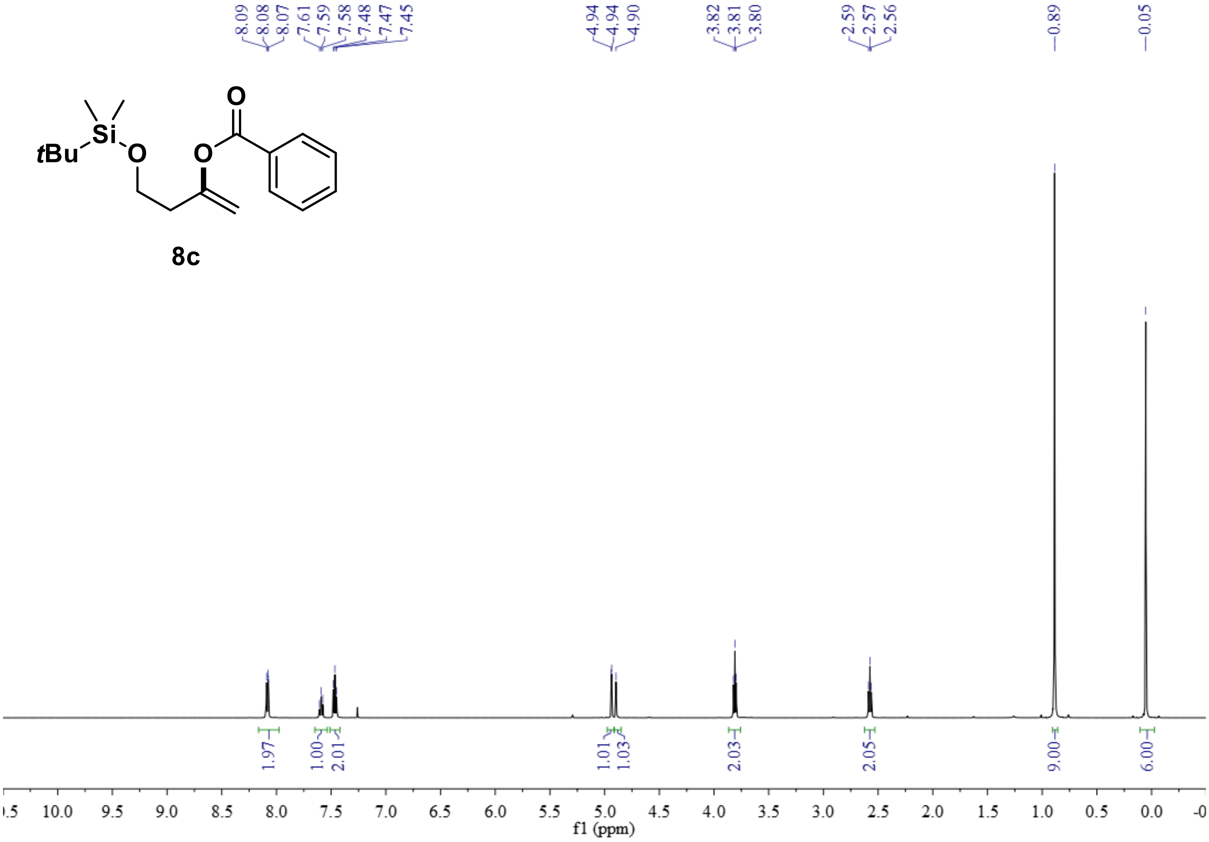
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **8a**.



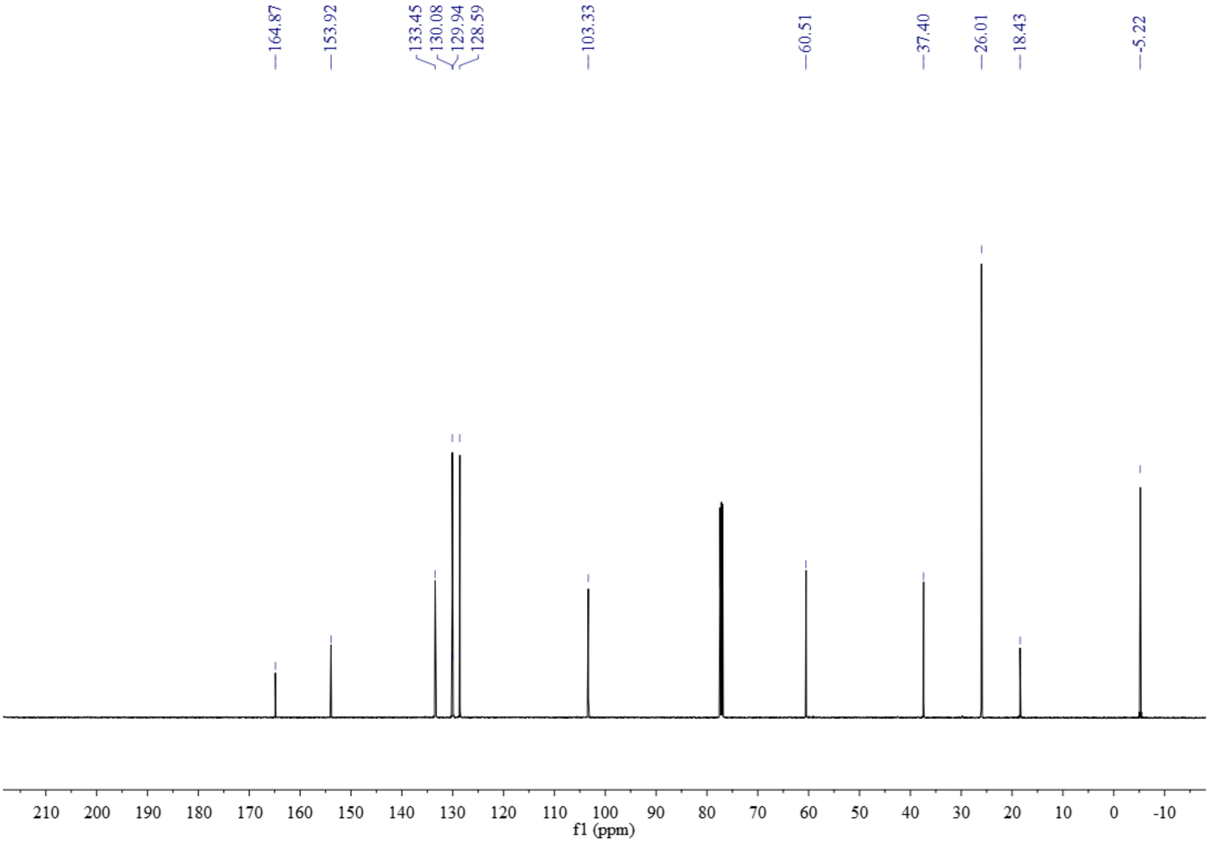
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **8b**.



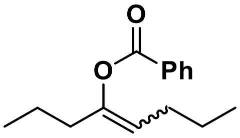
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **8b**.



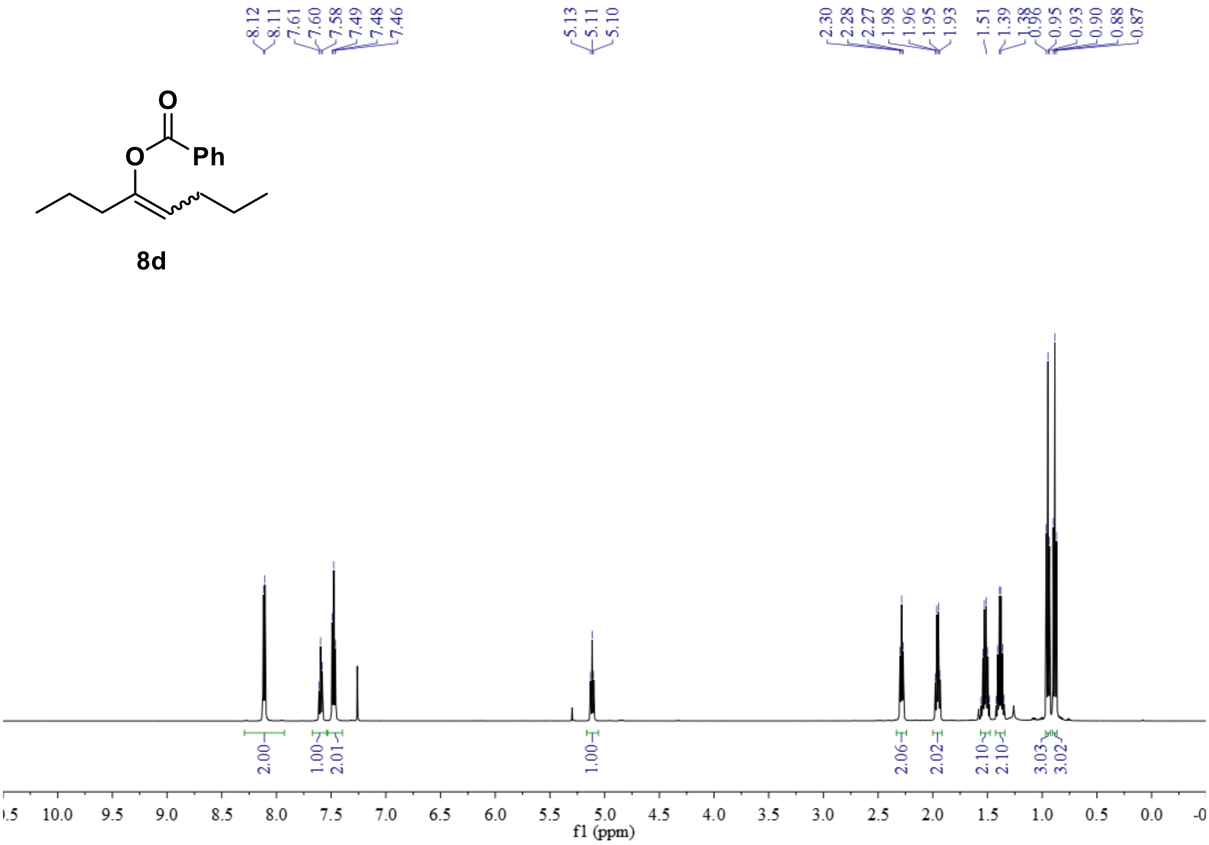
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8c**.



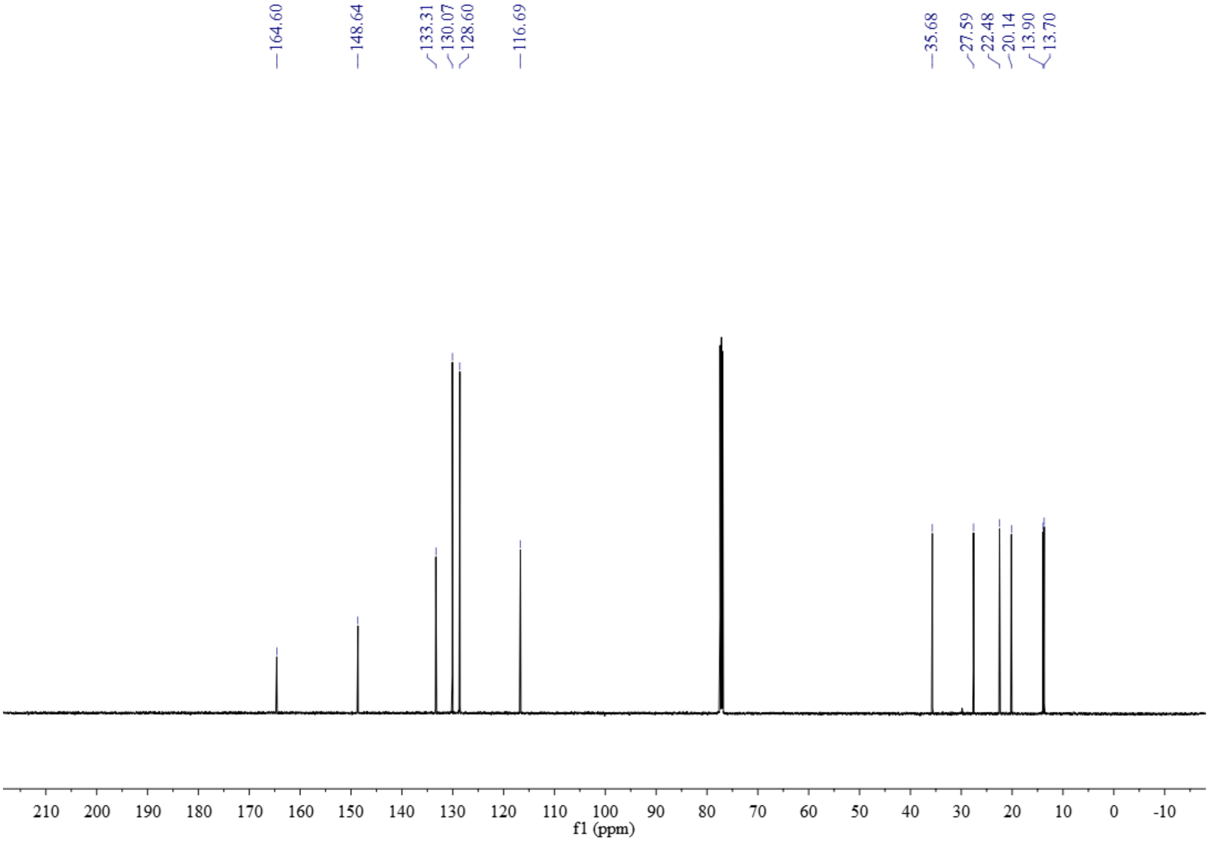
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8c**.



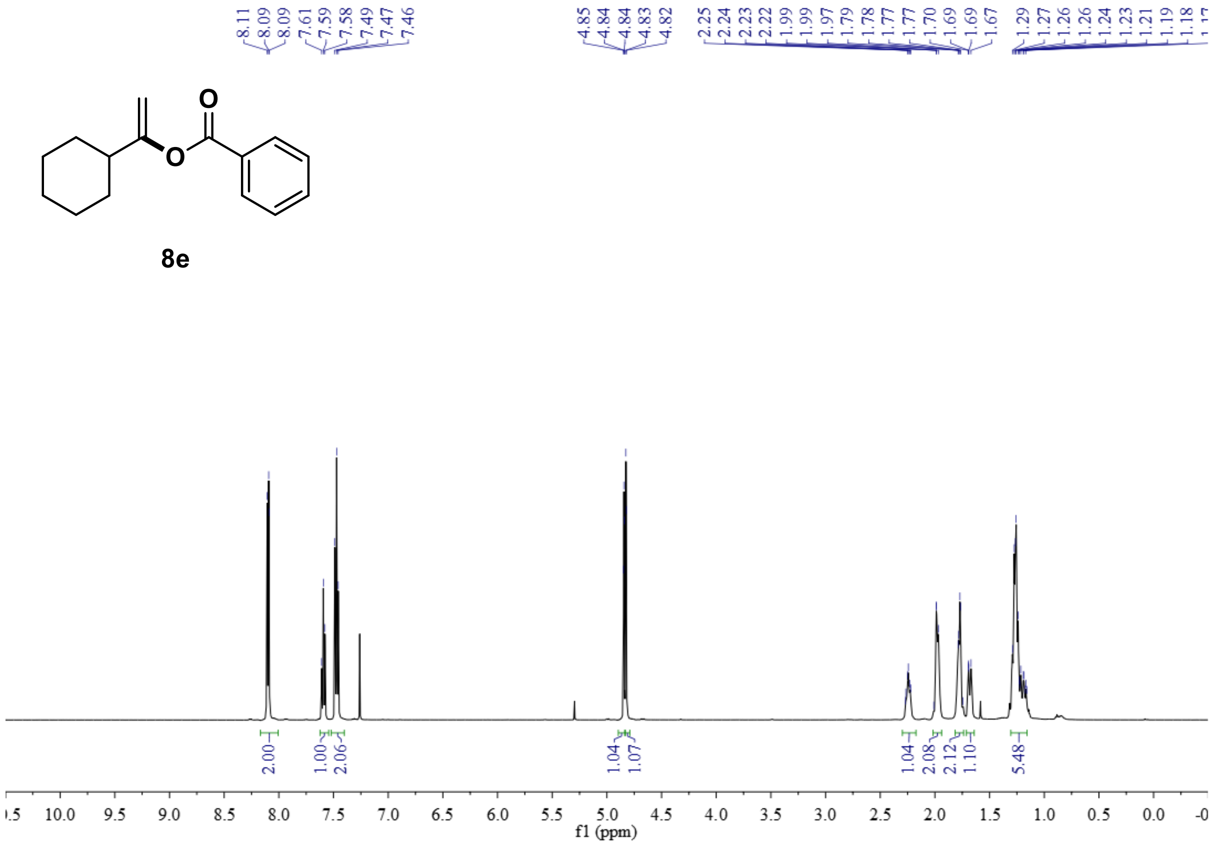
8d



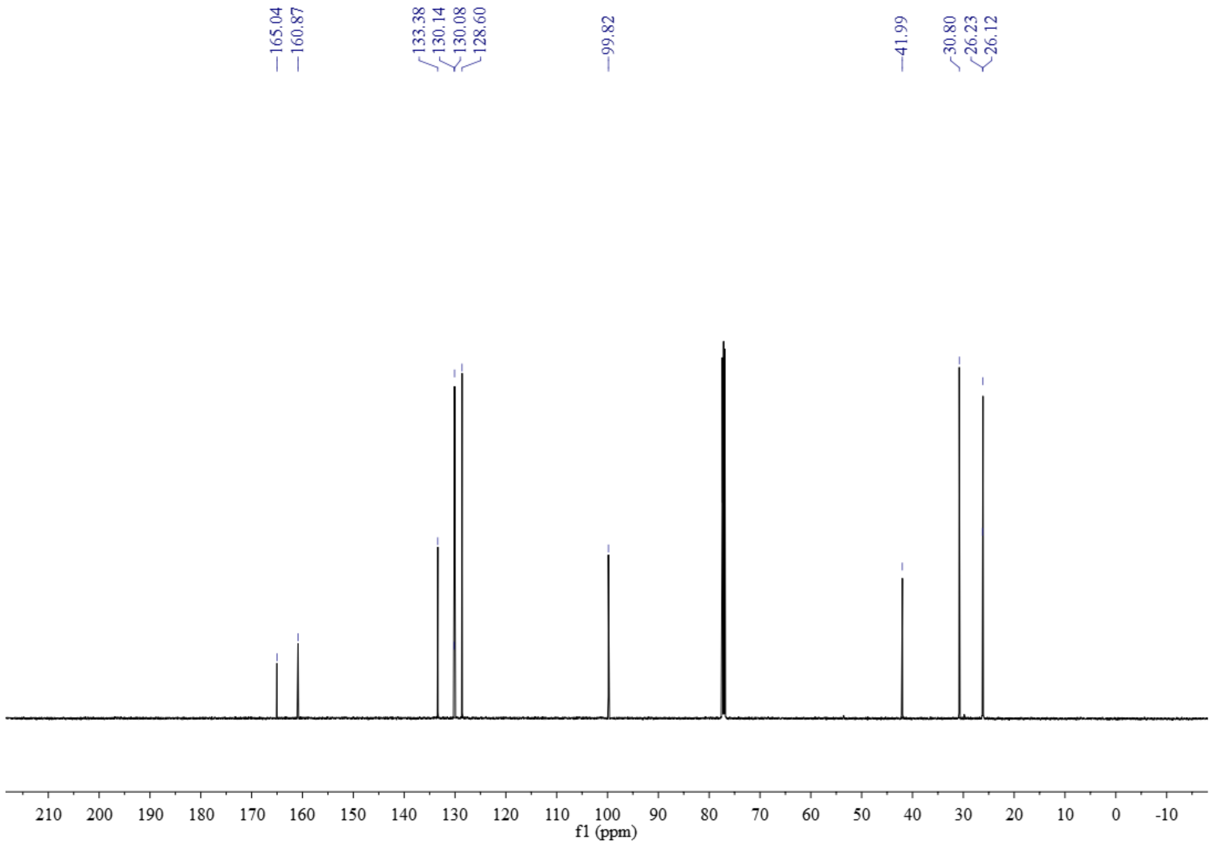
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **8d**.



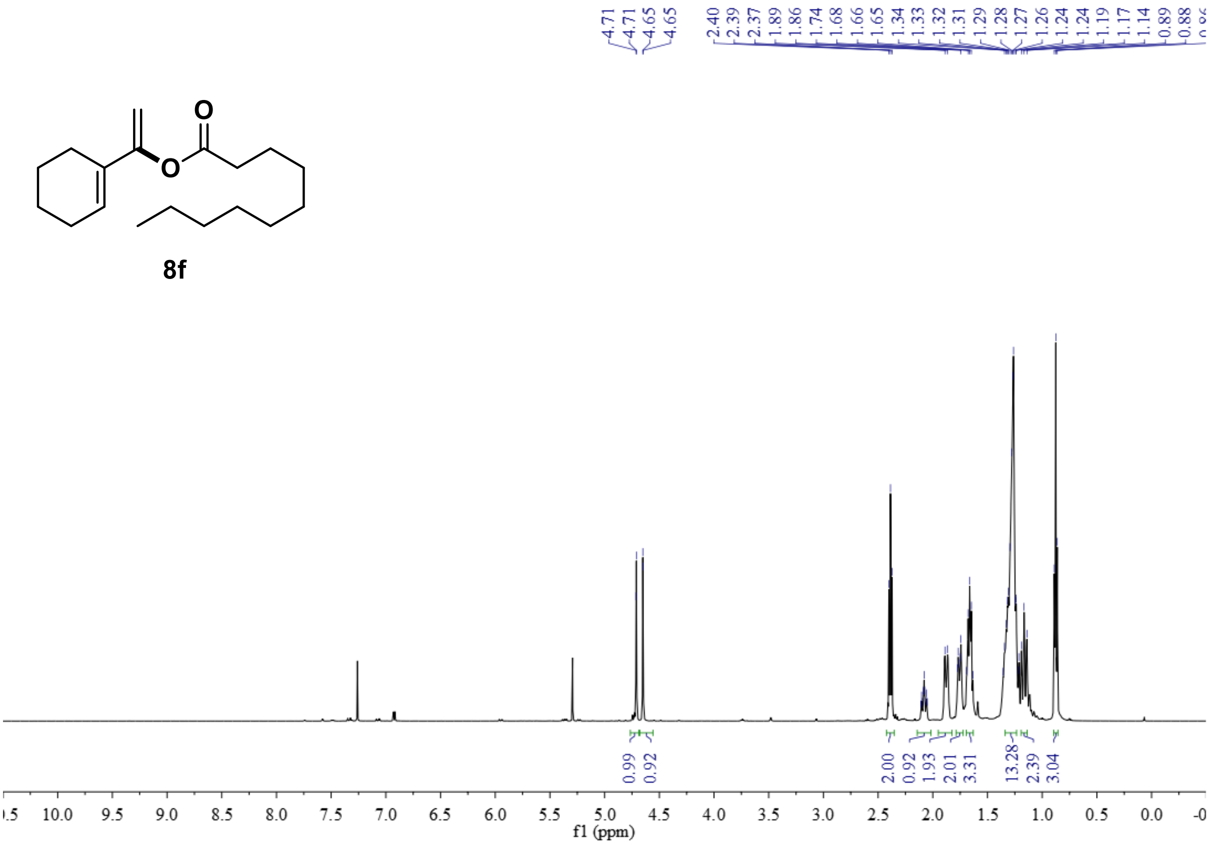
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **8d**.



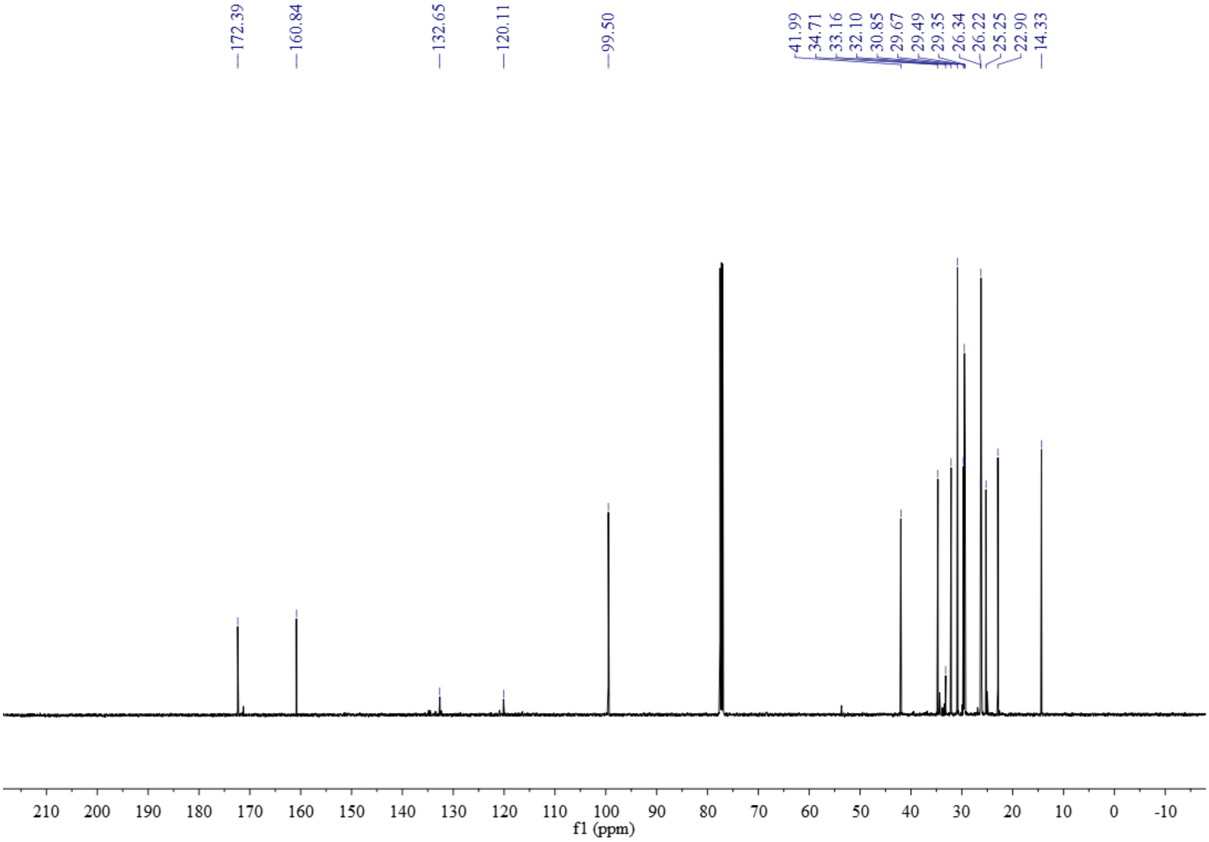
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8e**.



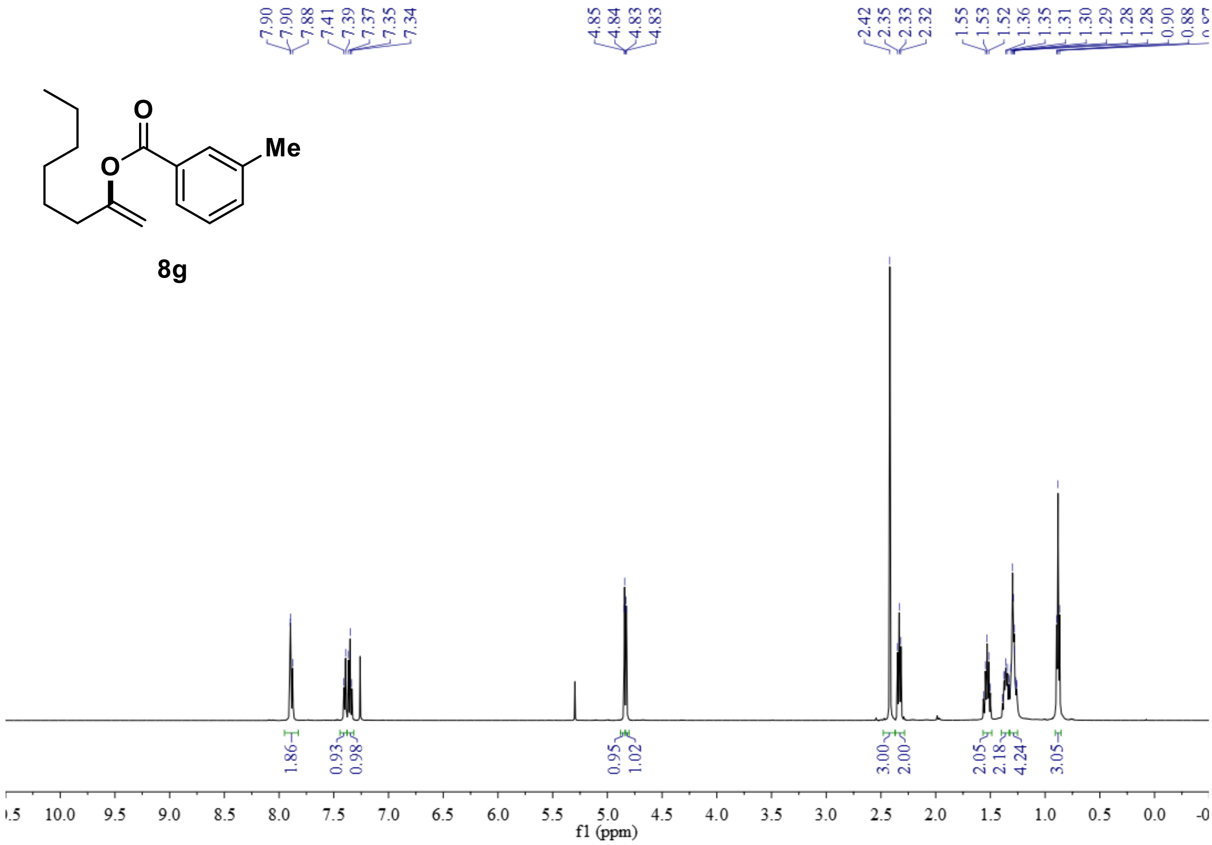
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8e**.



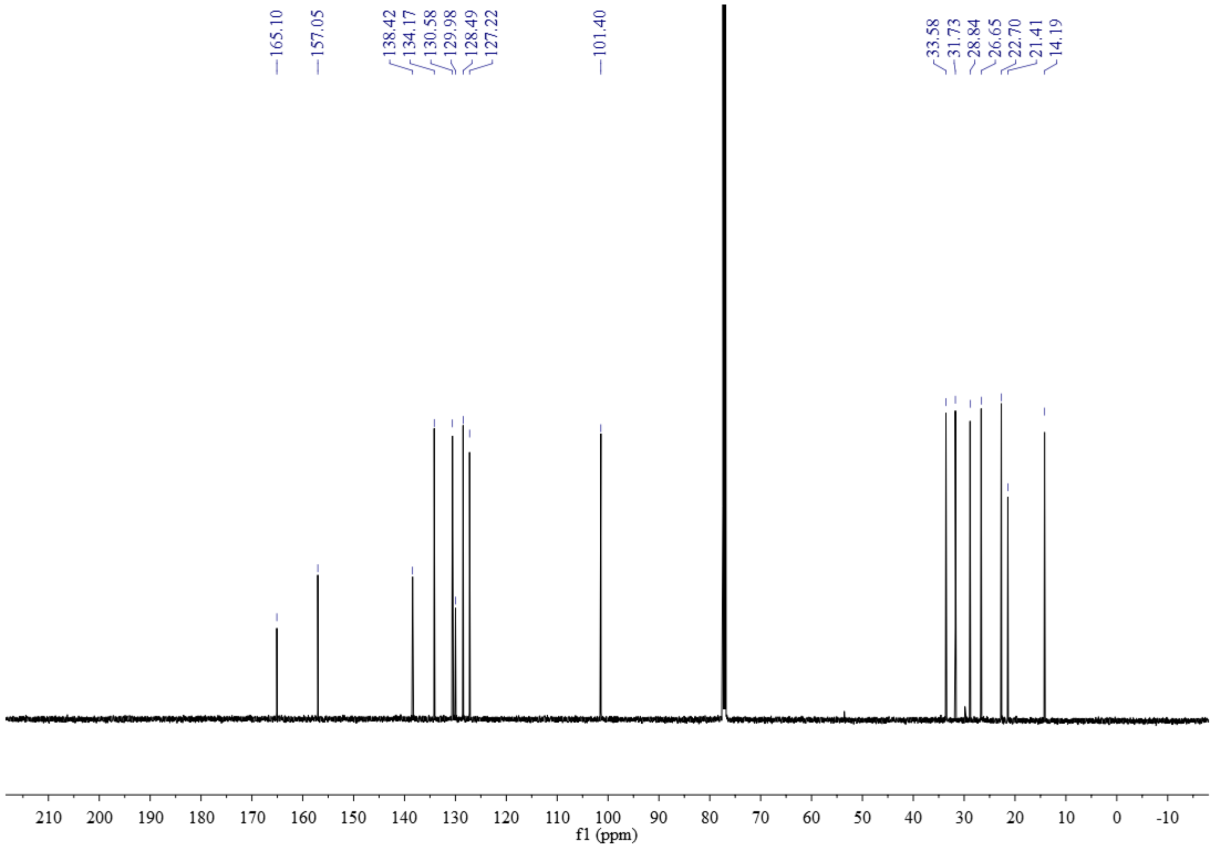
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8f**.



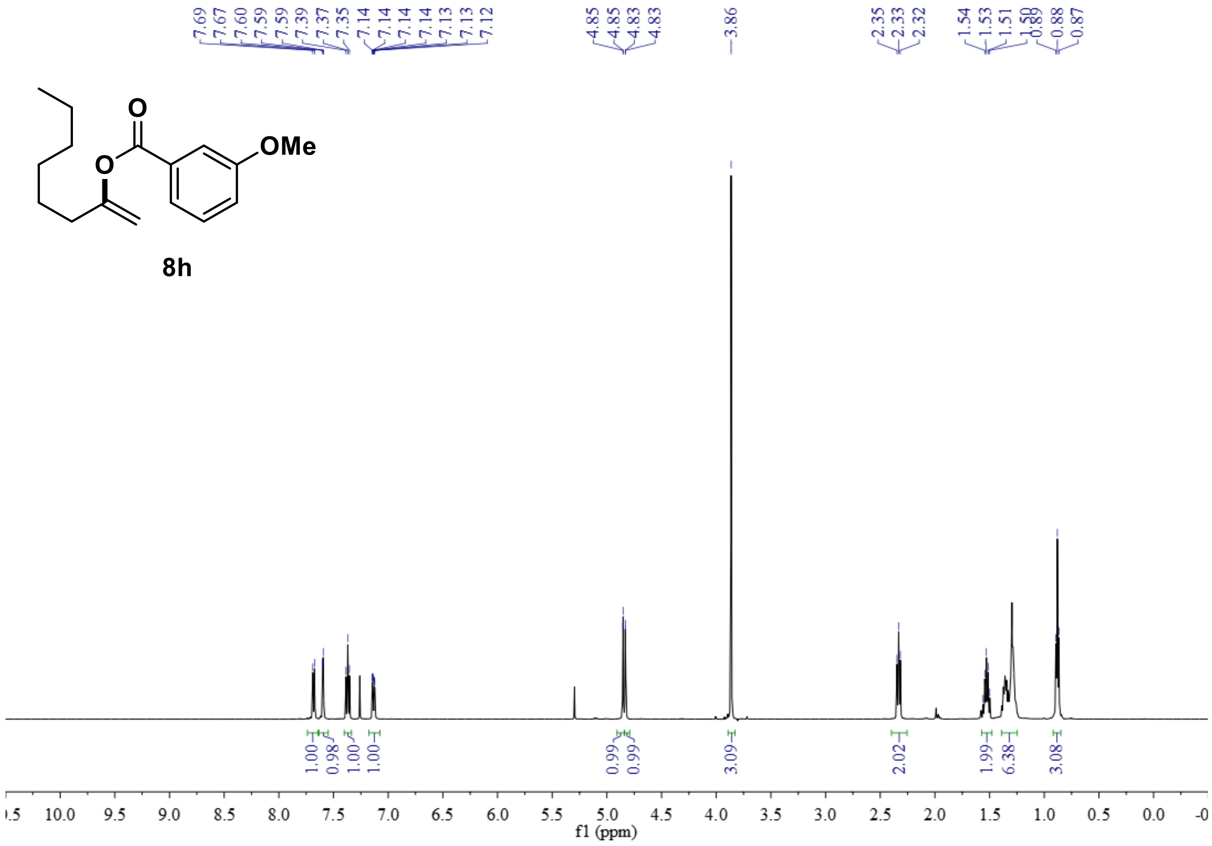
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8f**.



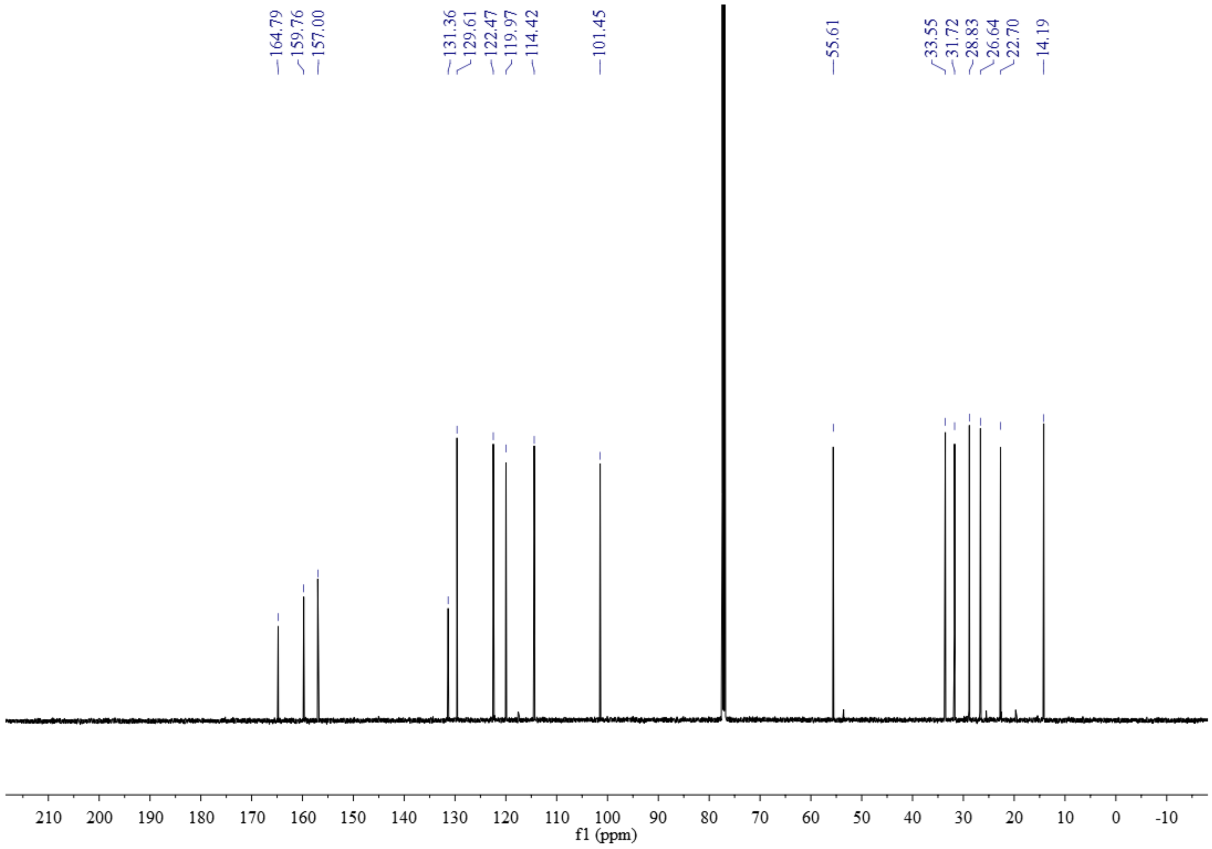
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8g**.



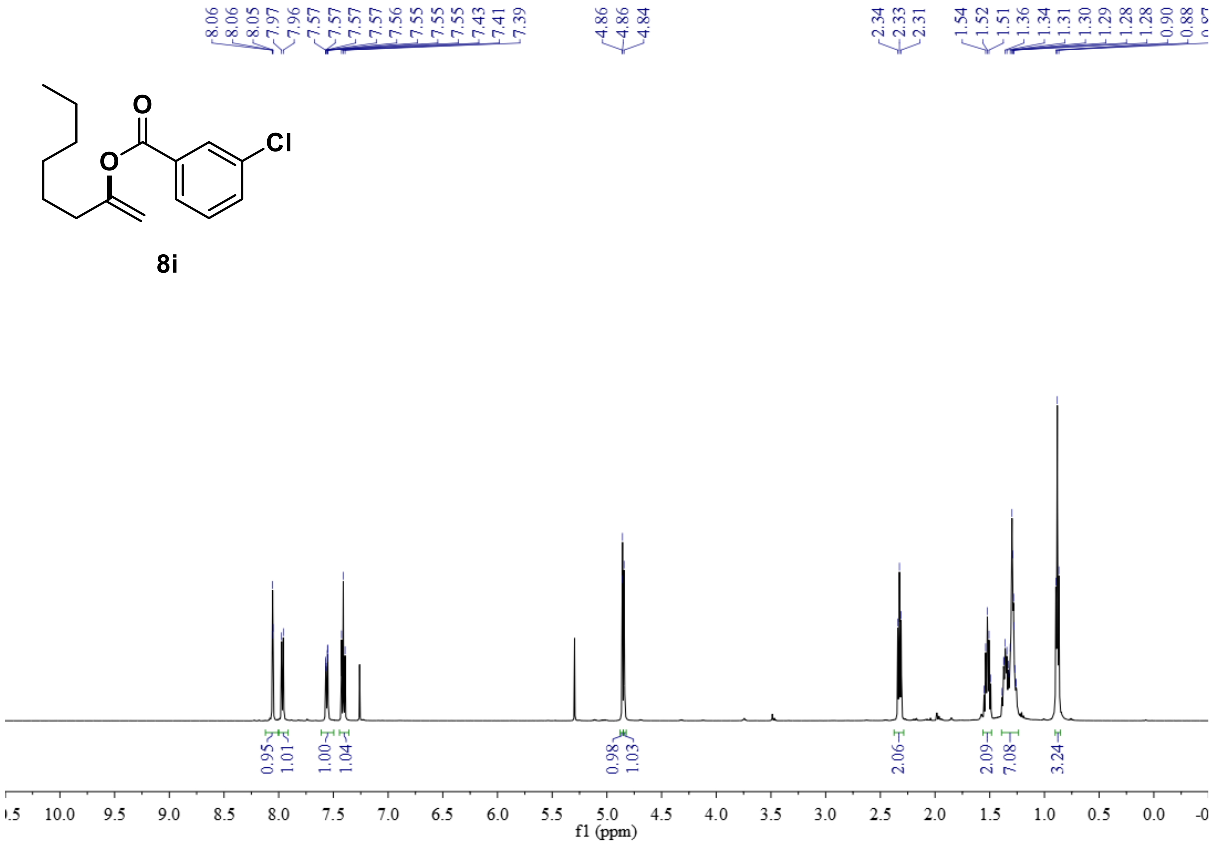
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8g**.



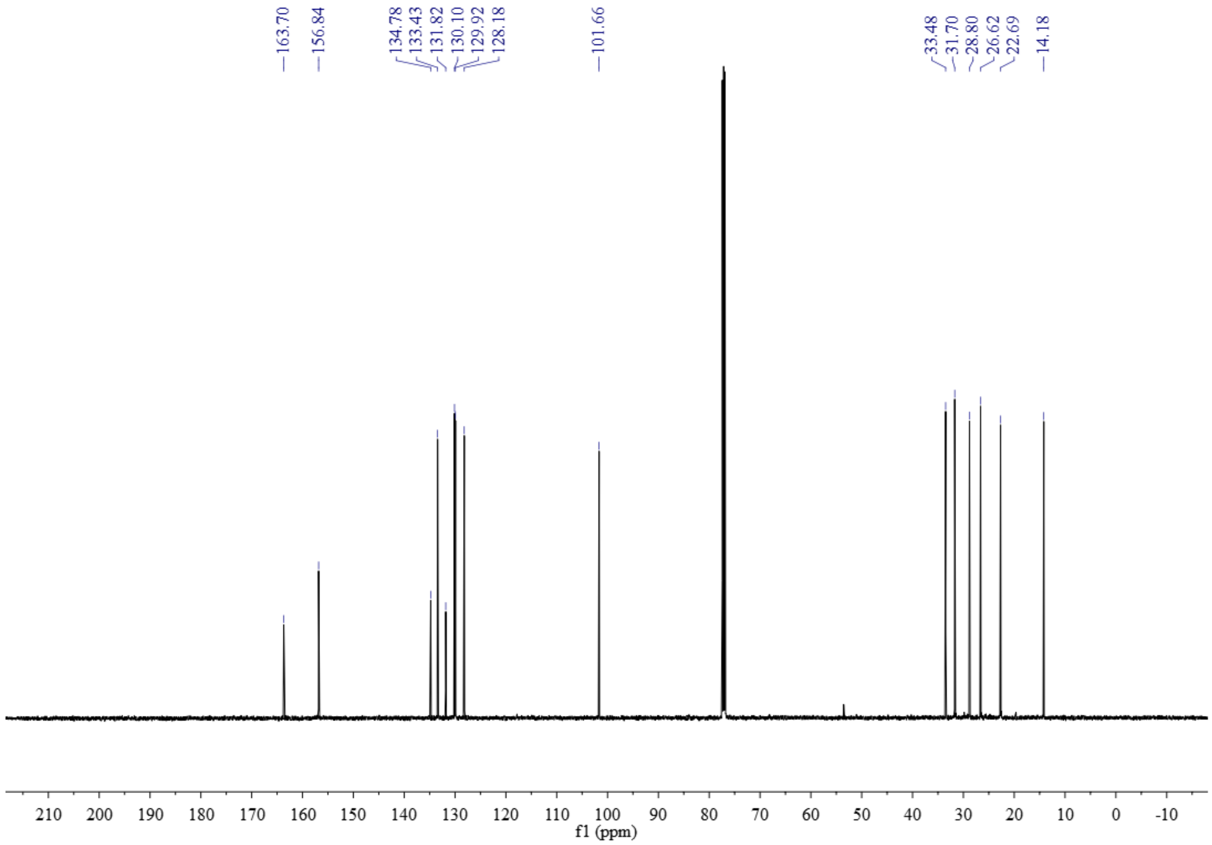
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8h**.



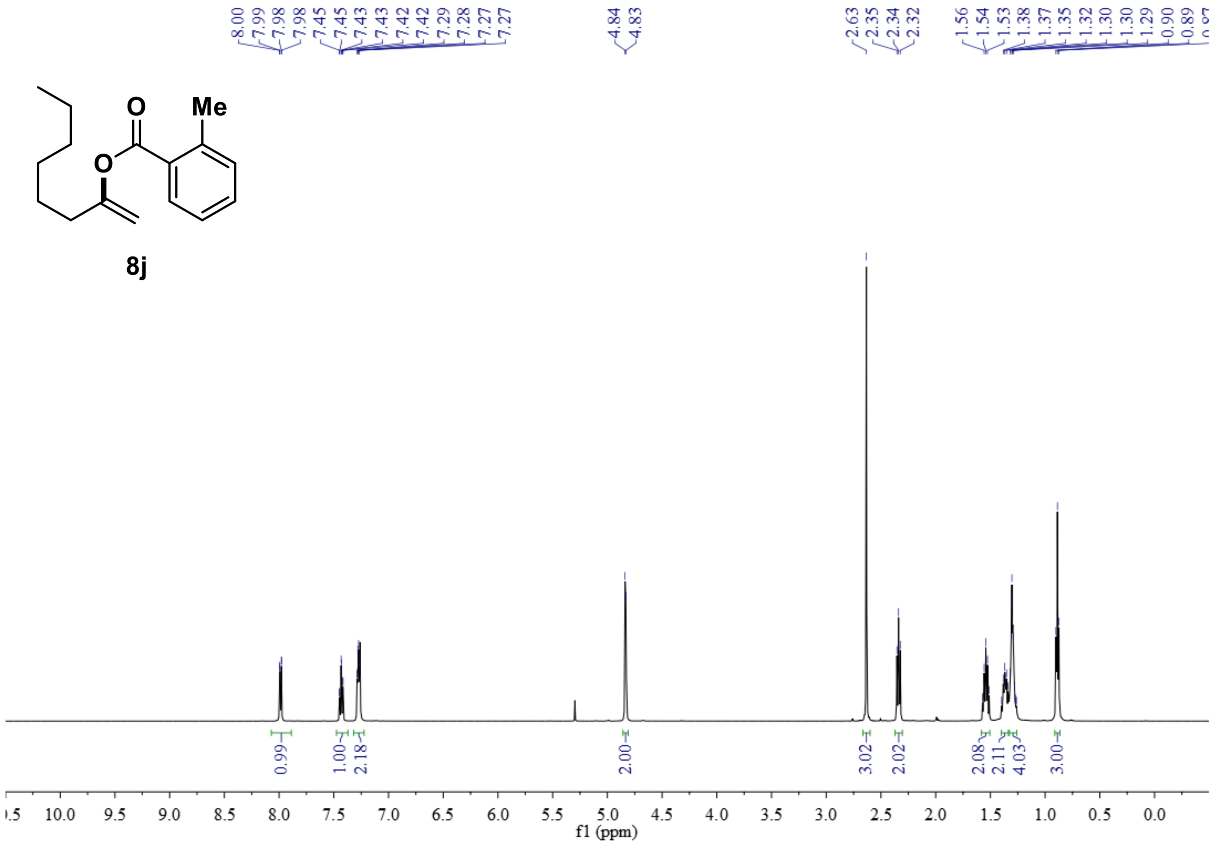
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8h**.



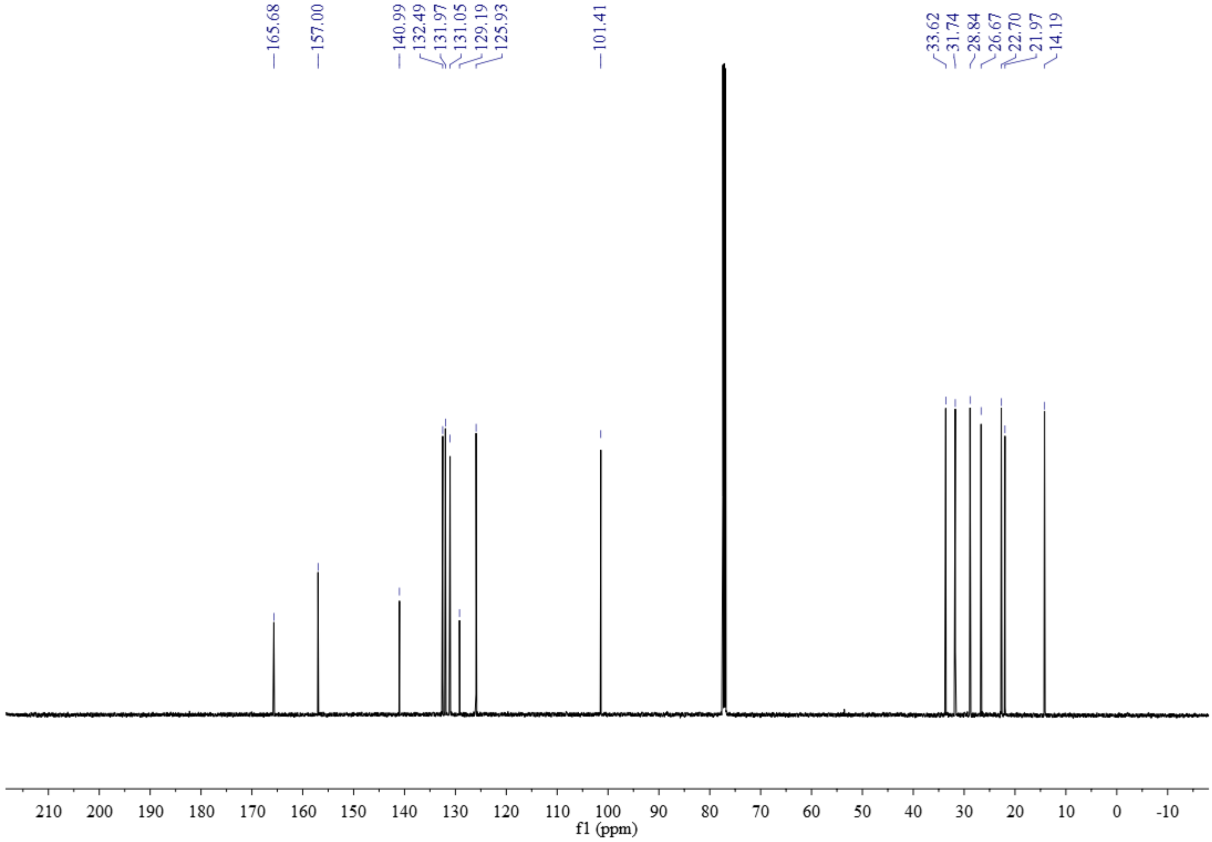
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8i**.



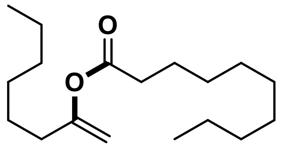
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8i**.



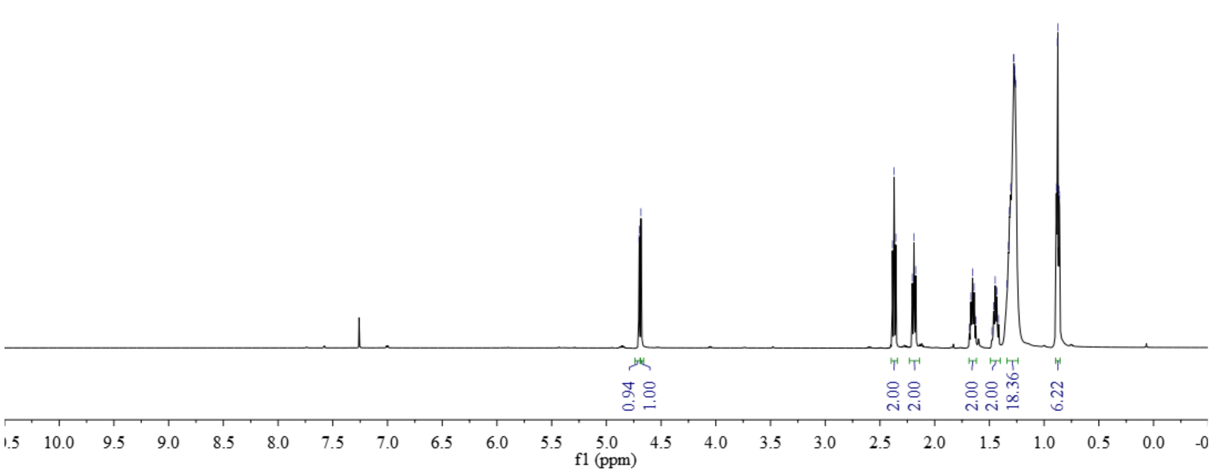
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **8j**.



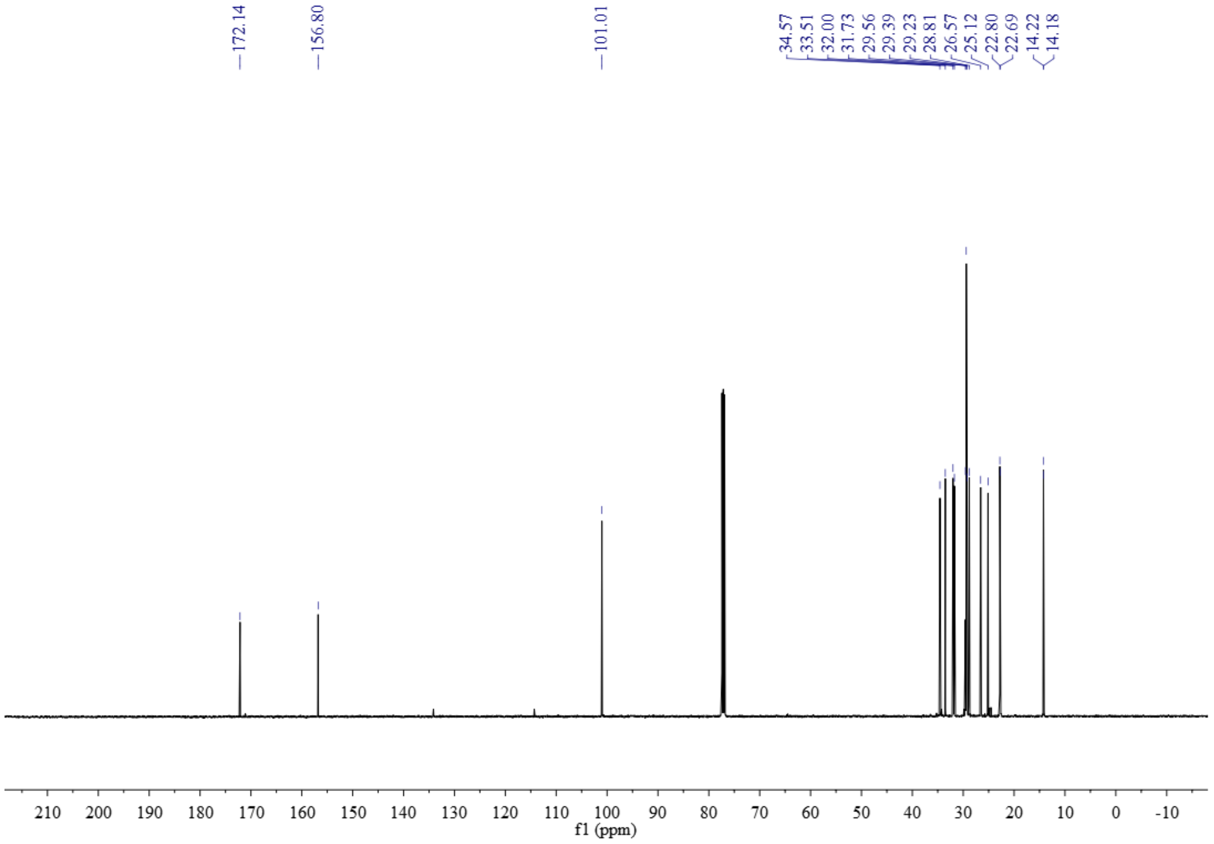
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **8j**.



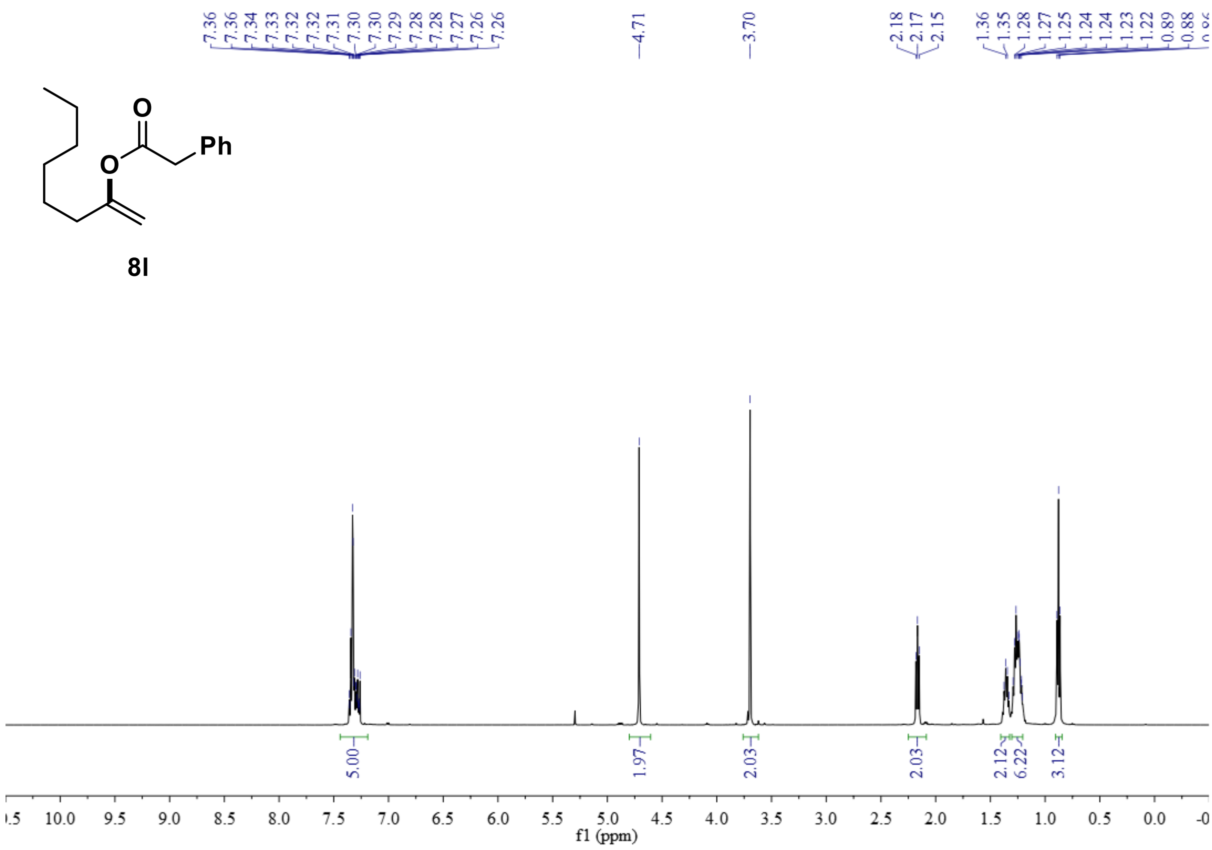
8k



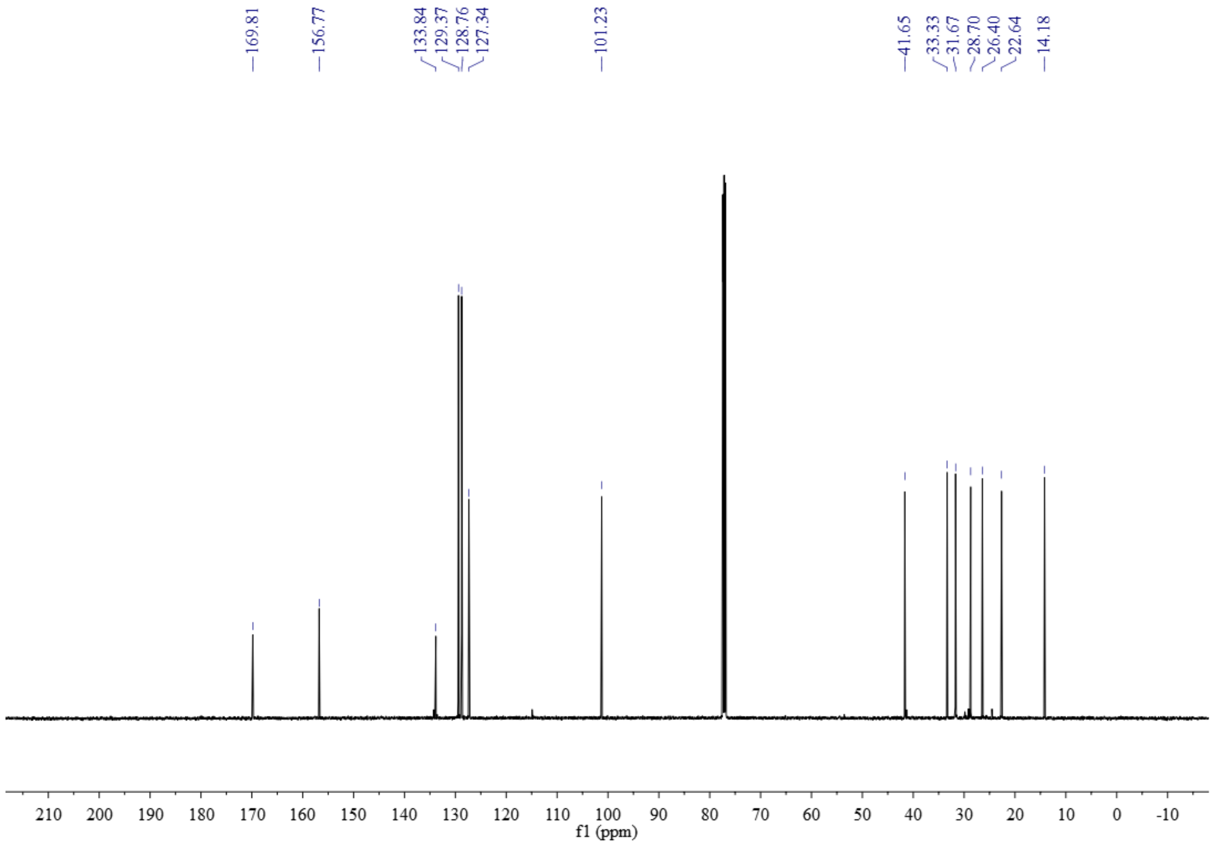
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8k**.



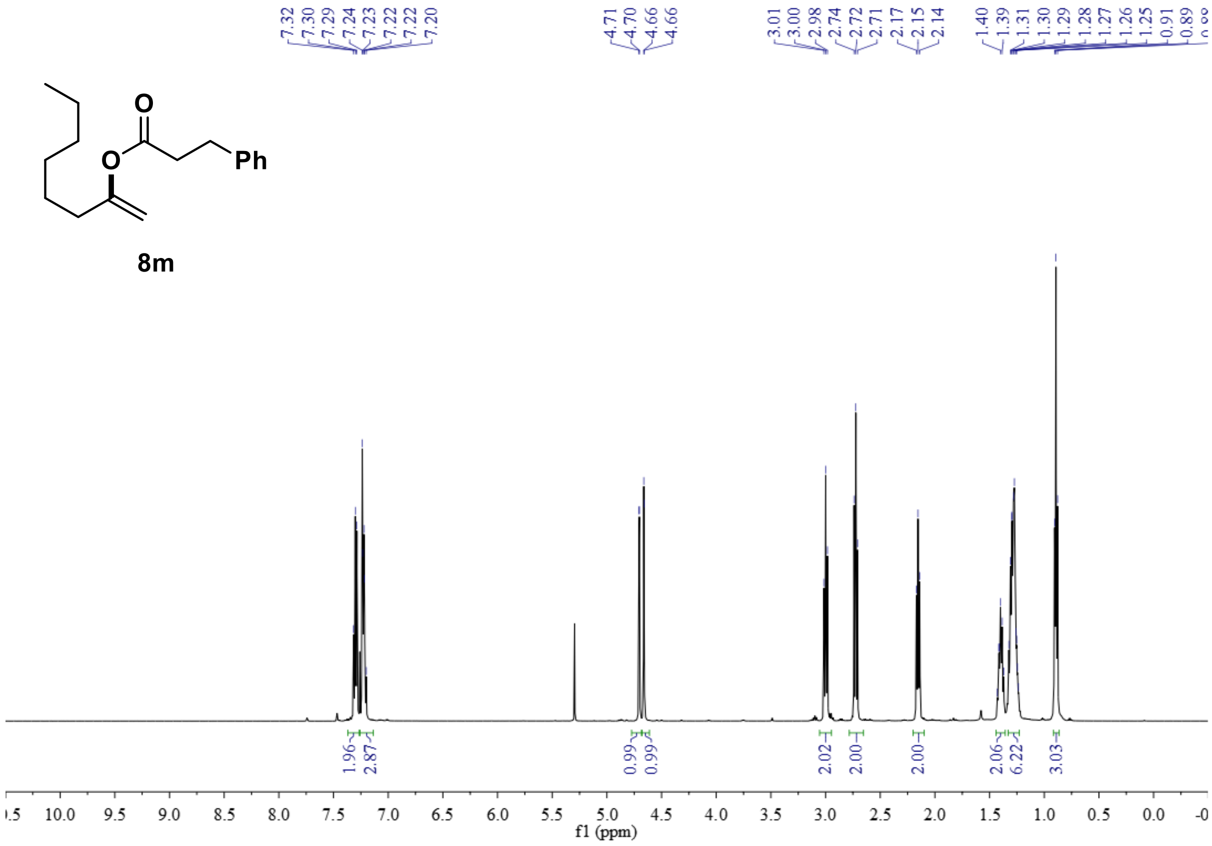
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8k**.



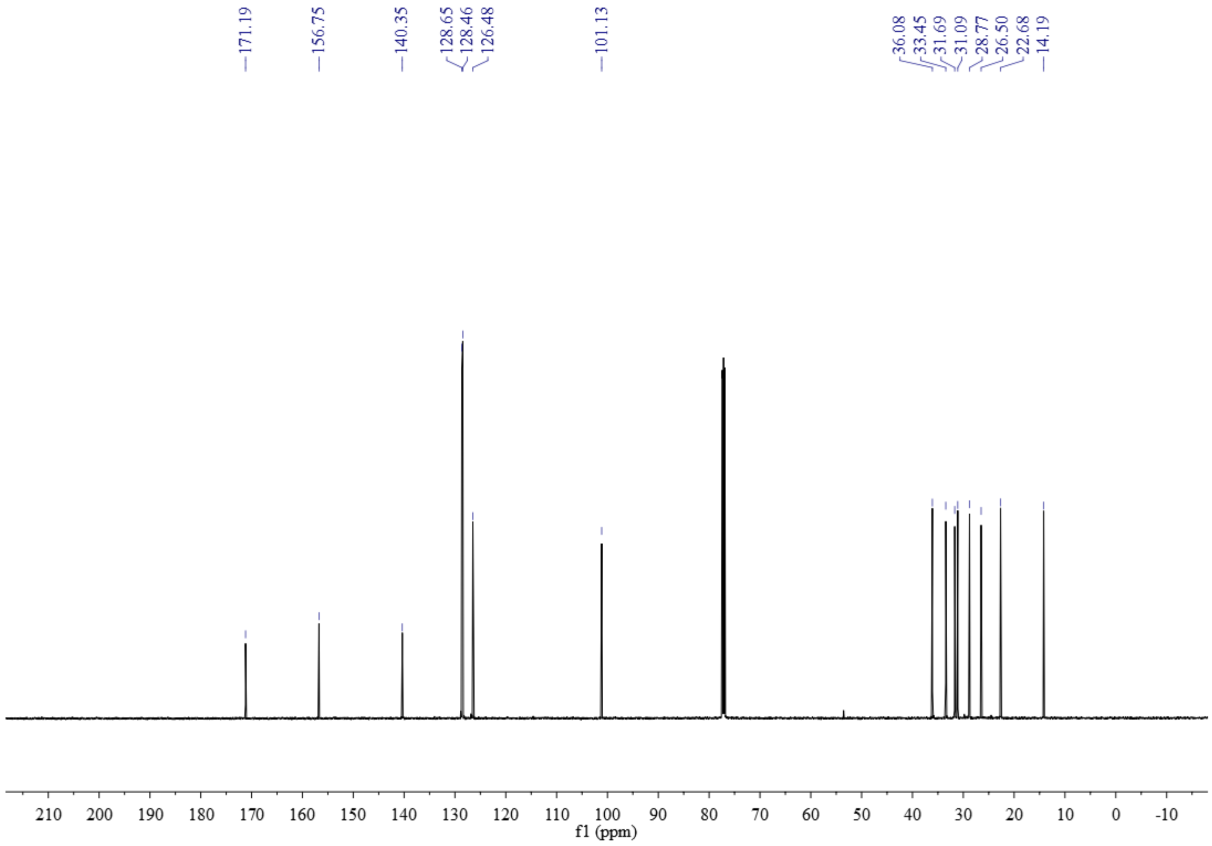
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8l**.



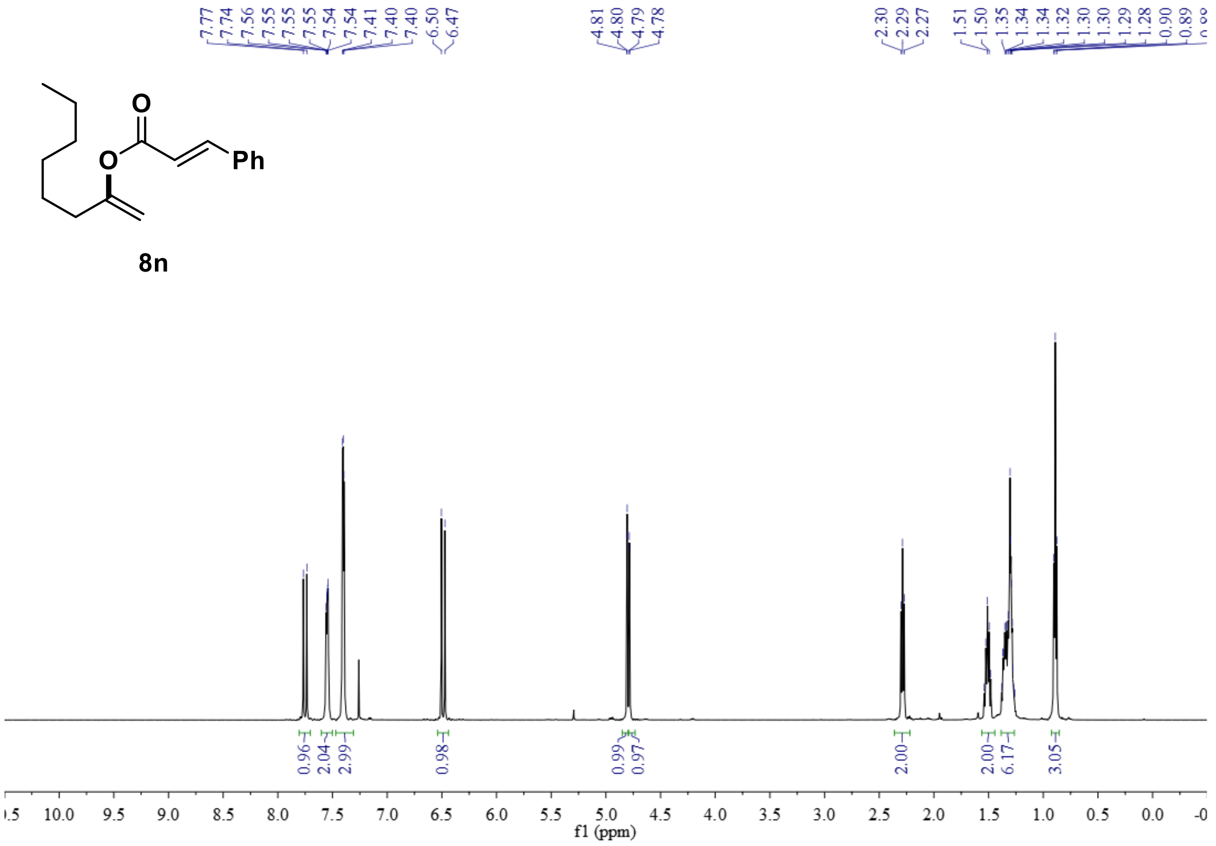
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8l**.



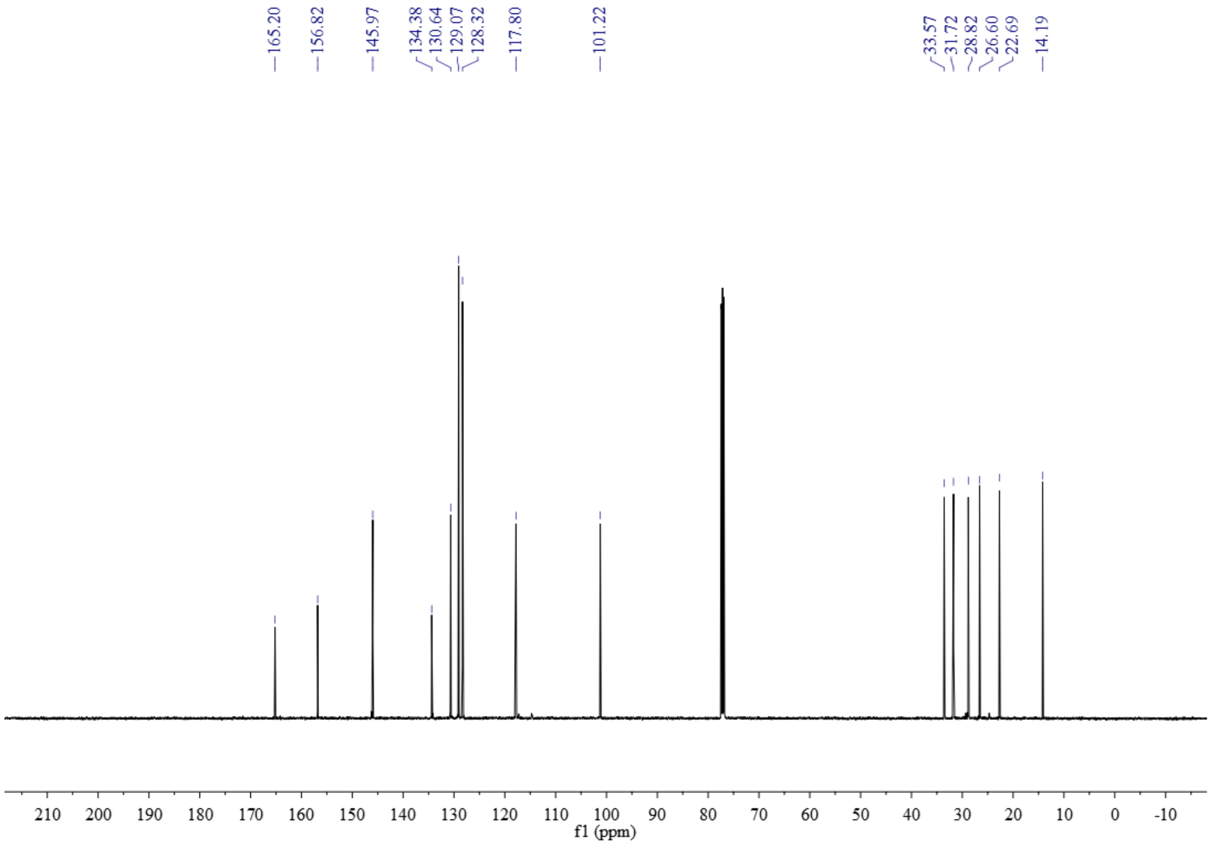
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8m**.



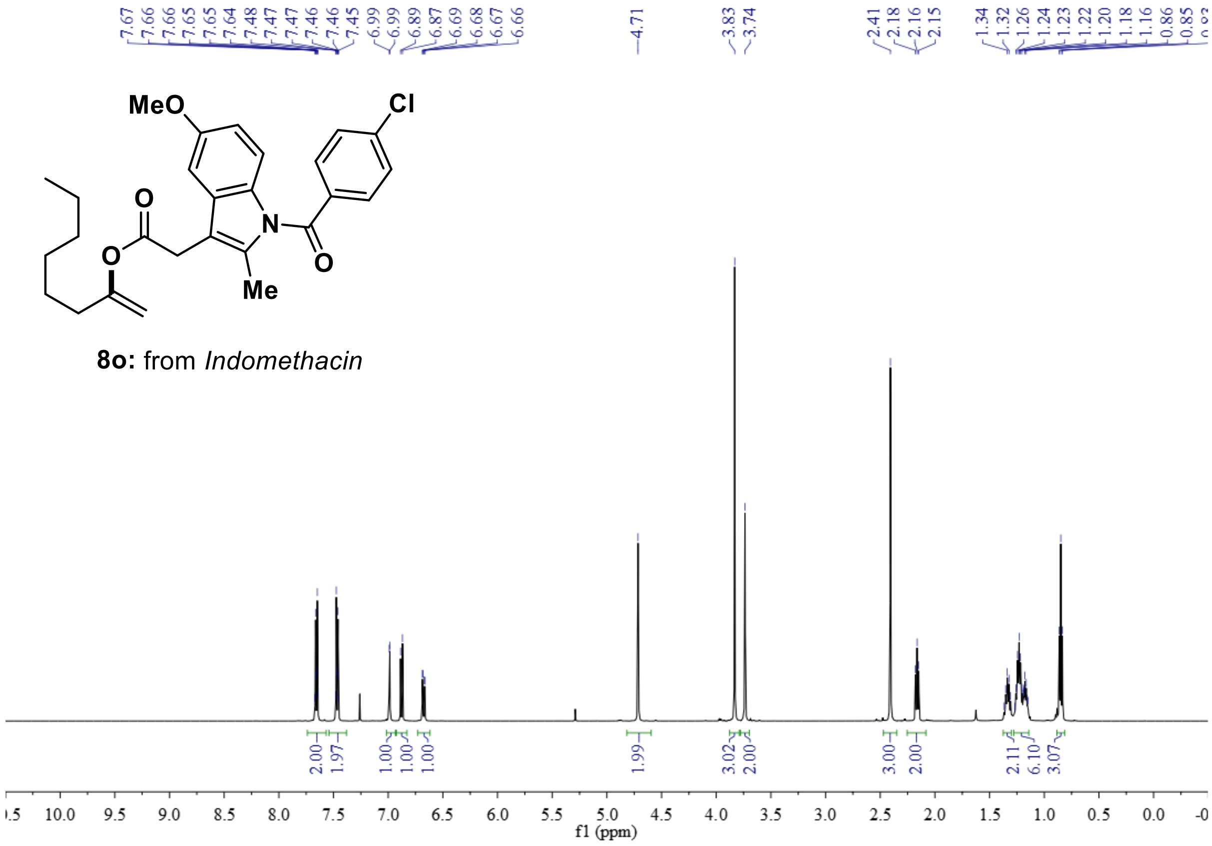
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8m**.



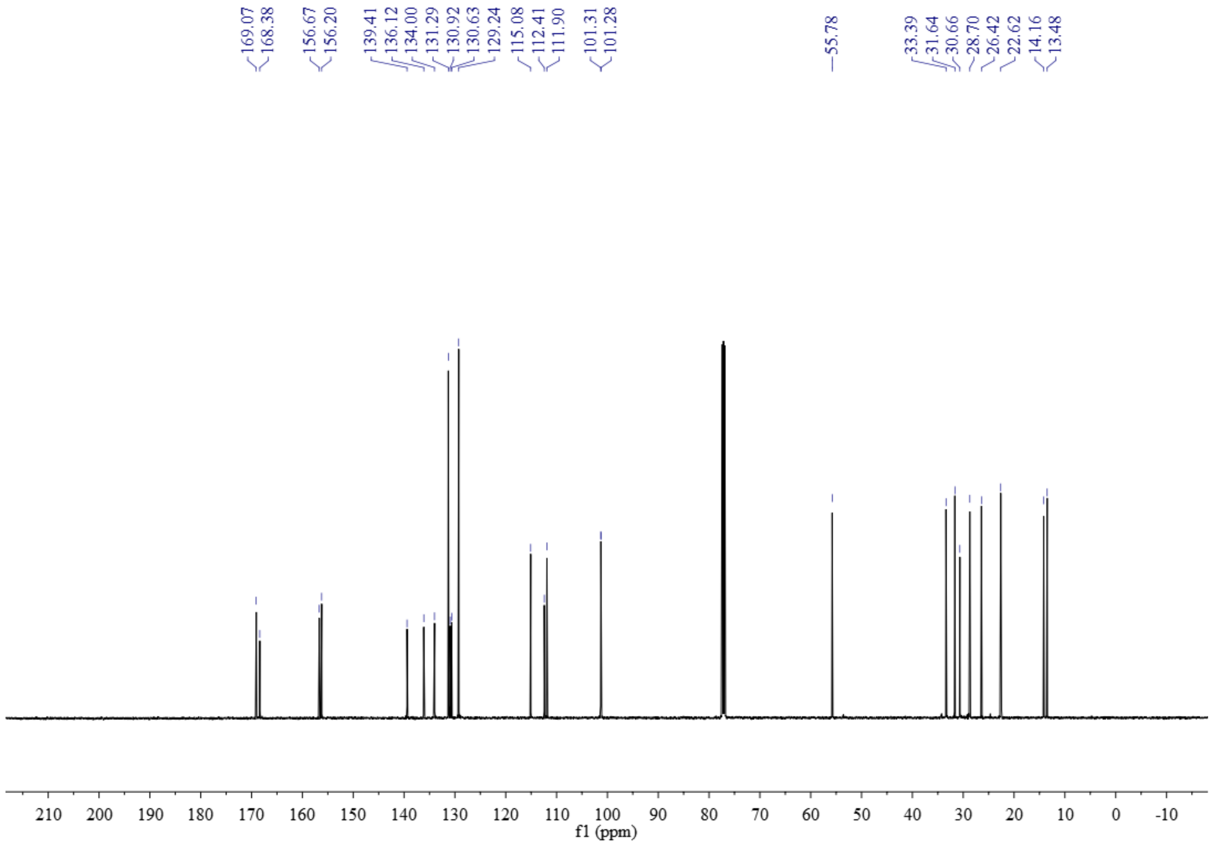
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8n**.



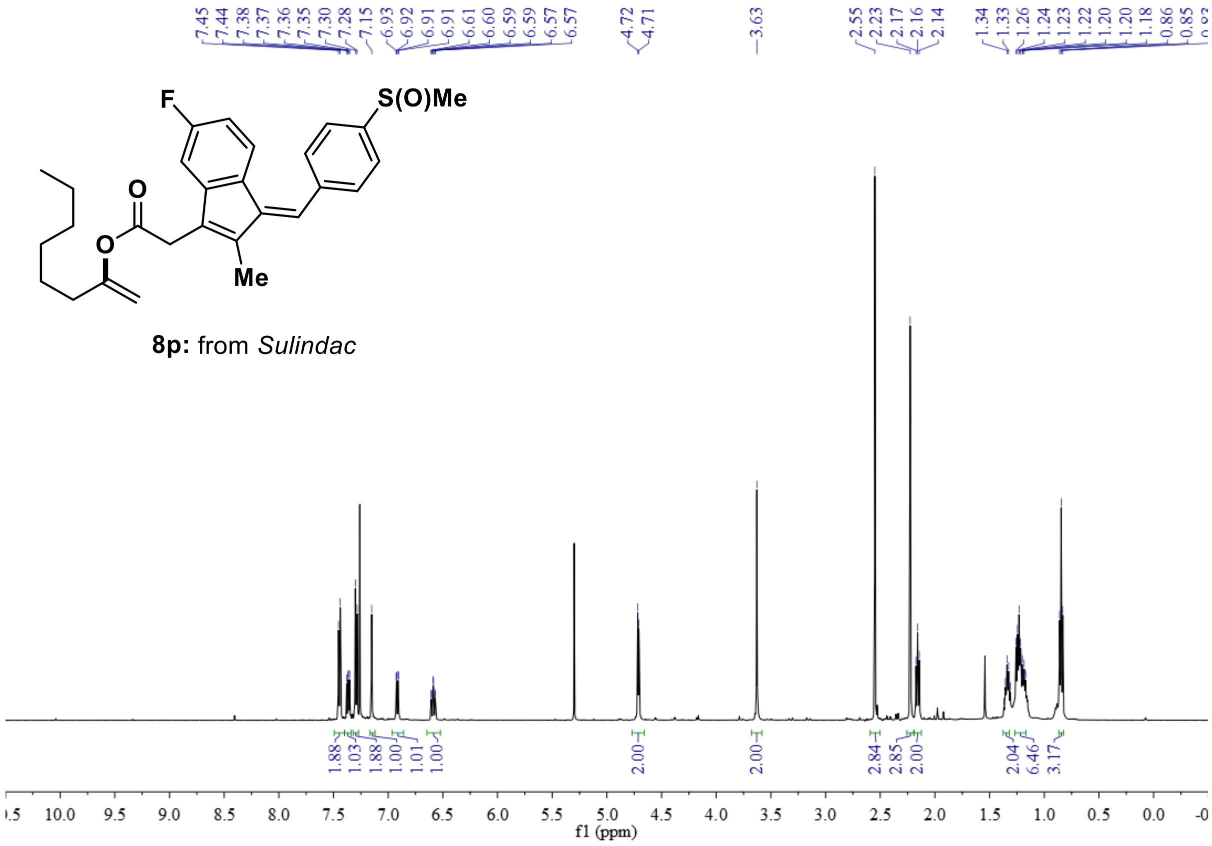
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8n**.



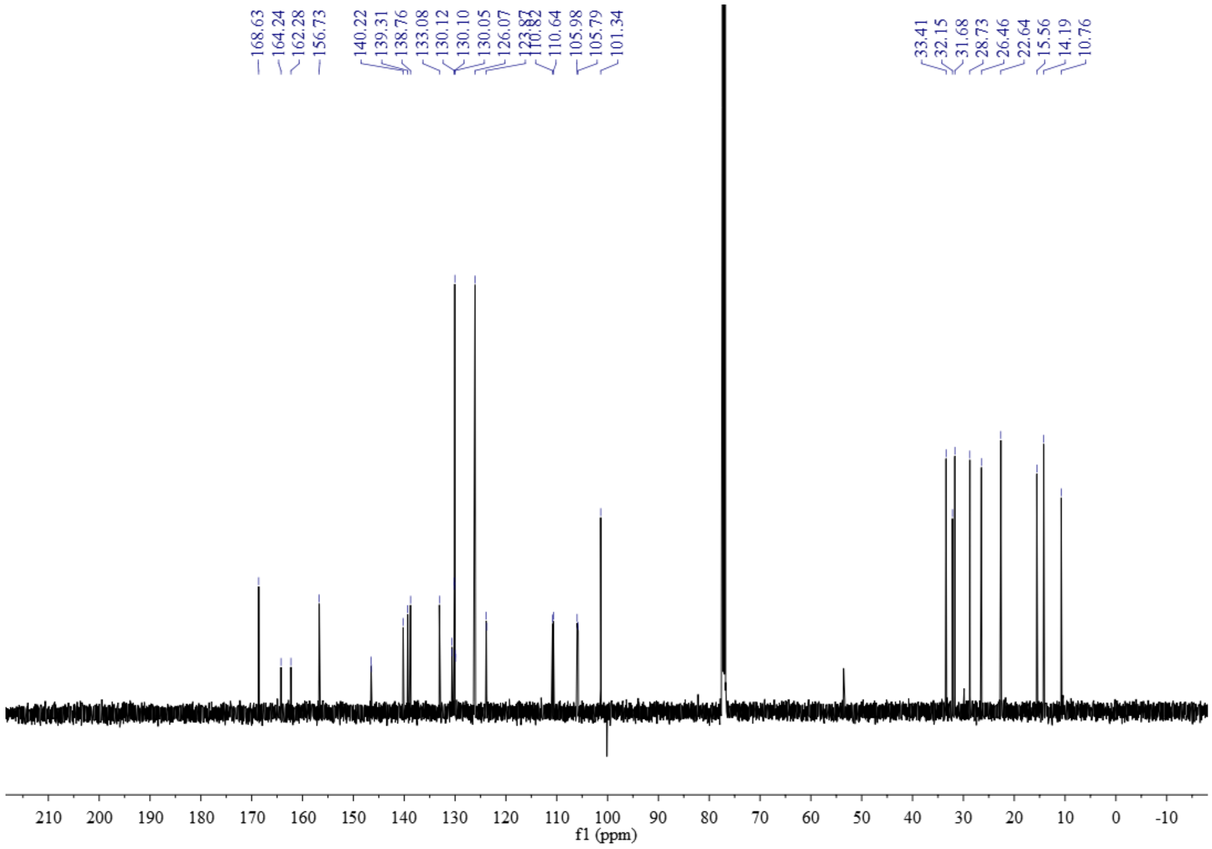
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8o**.



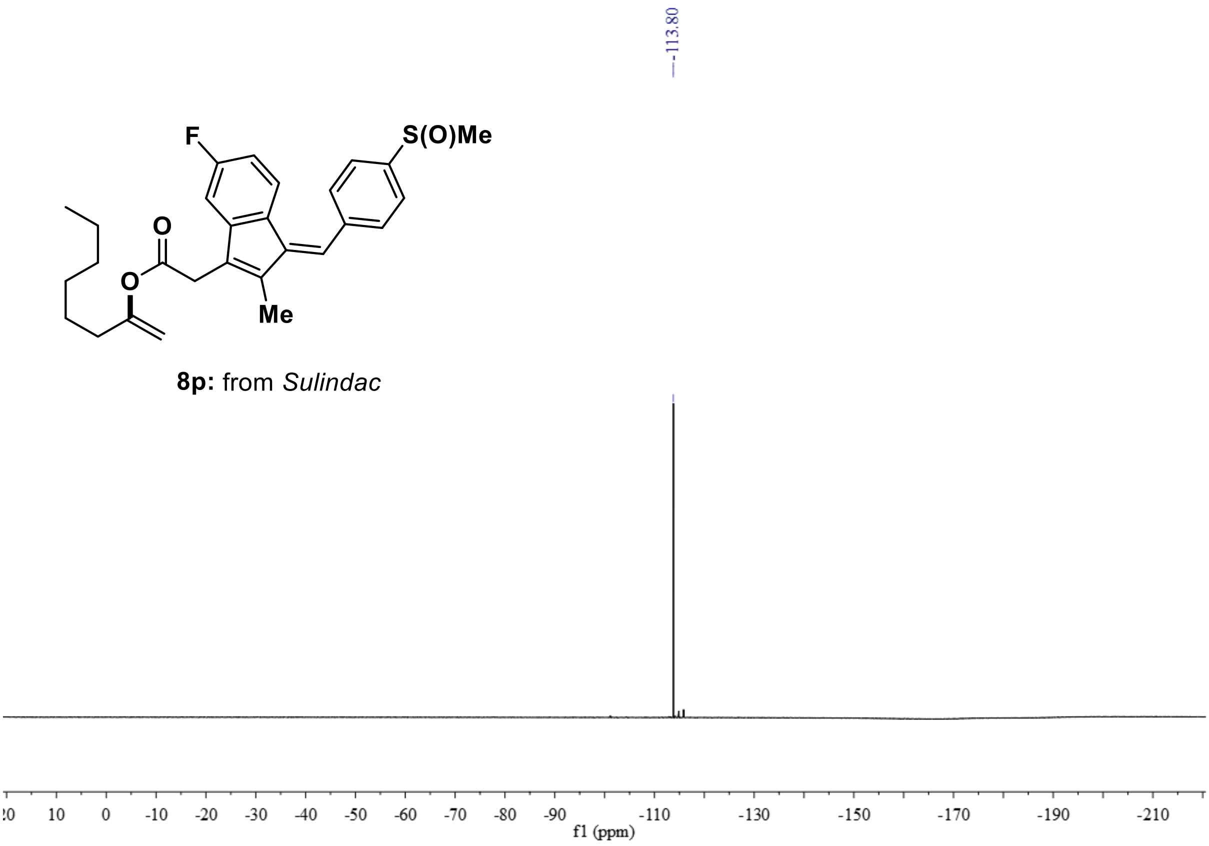
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8o**.



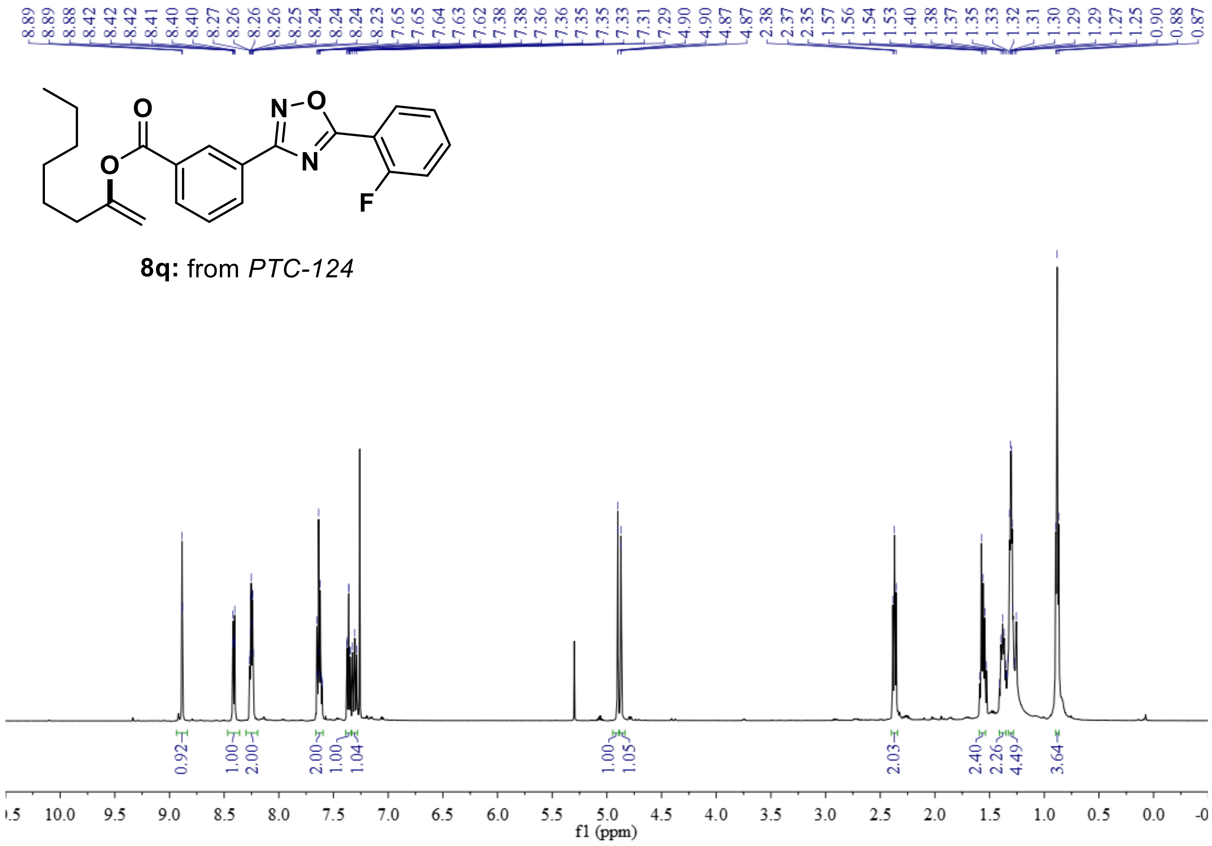
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **8p**.



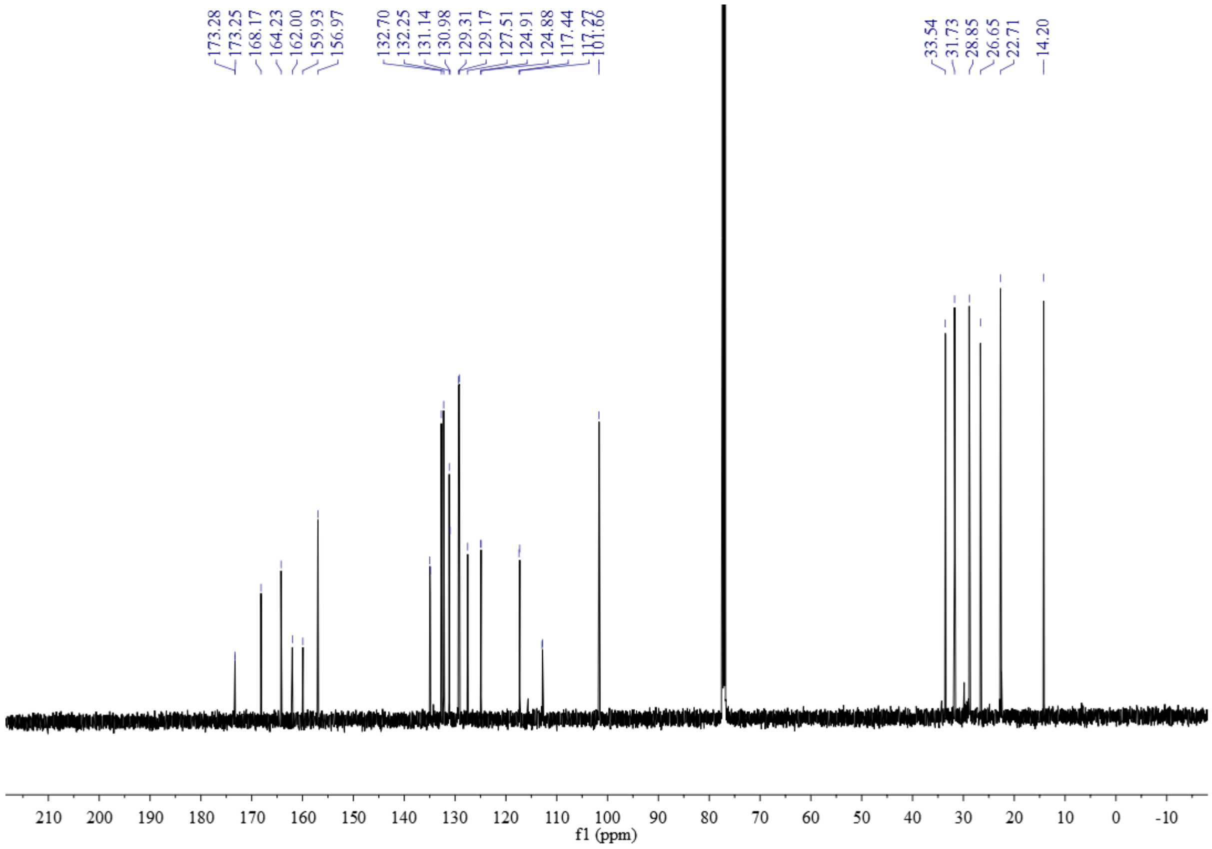
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **8p**.



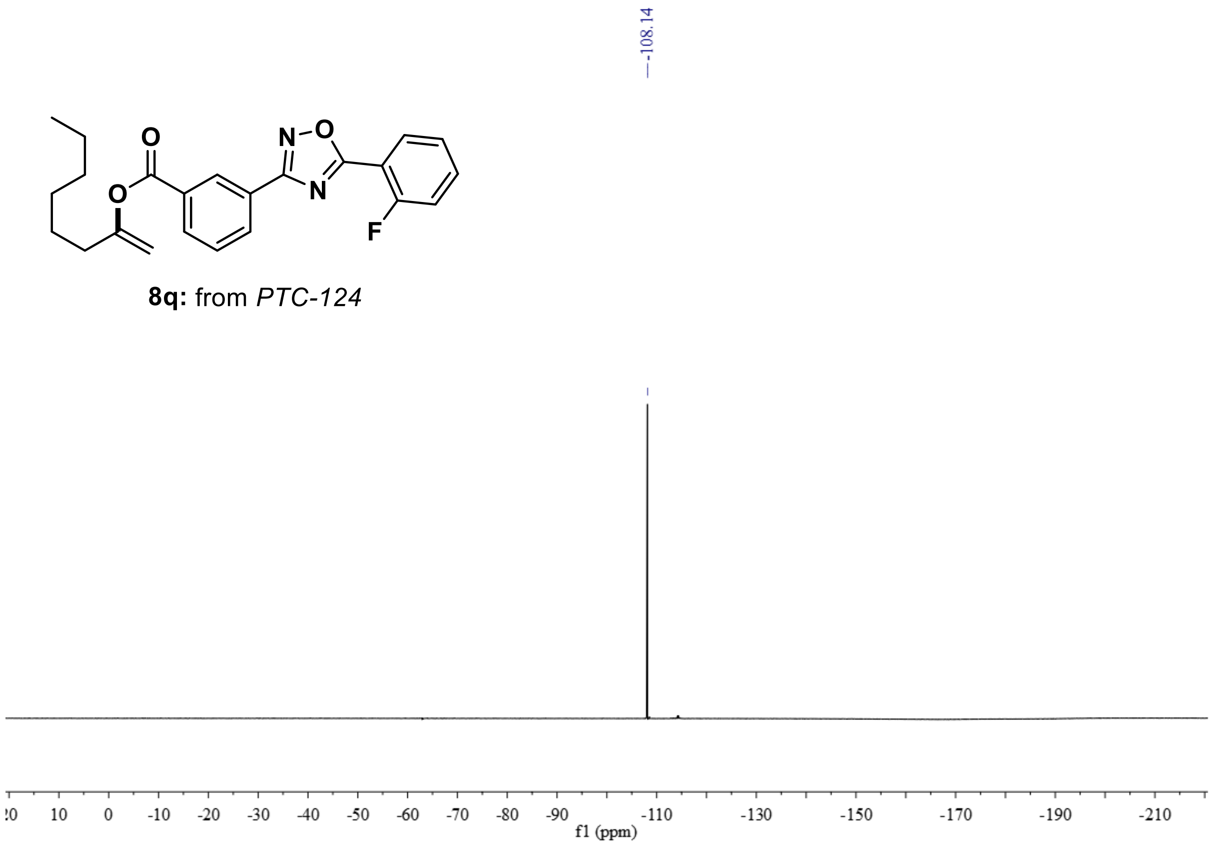
^{19}F NMR (471 MHz, CDCl$_3$) Spectrum of Compound **8p**.



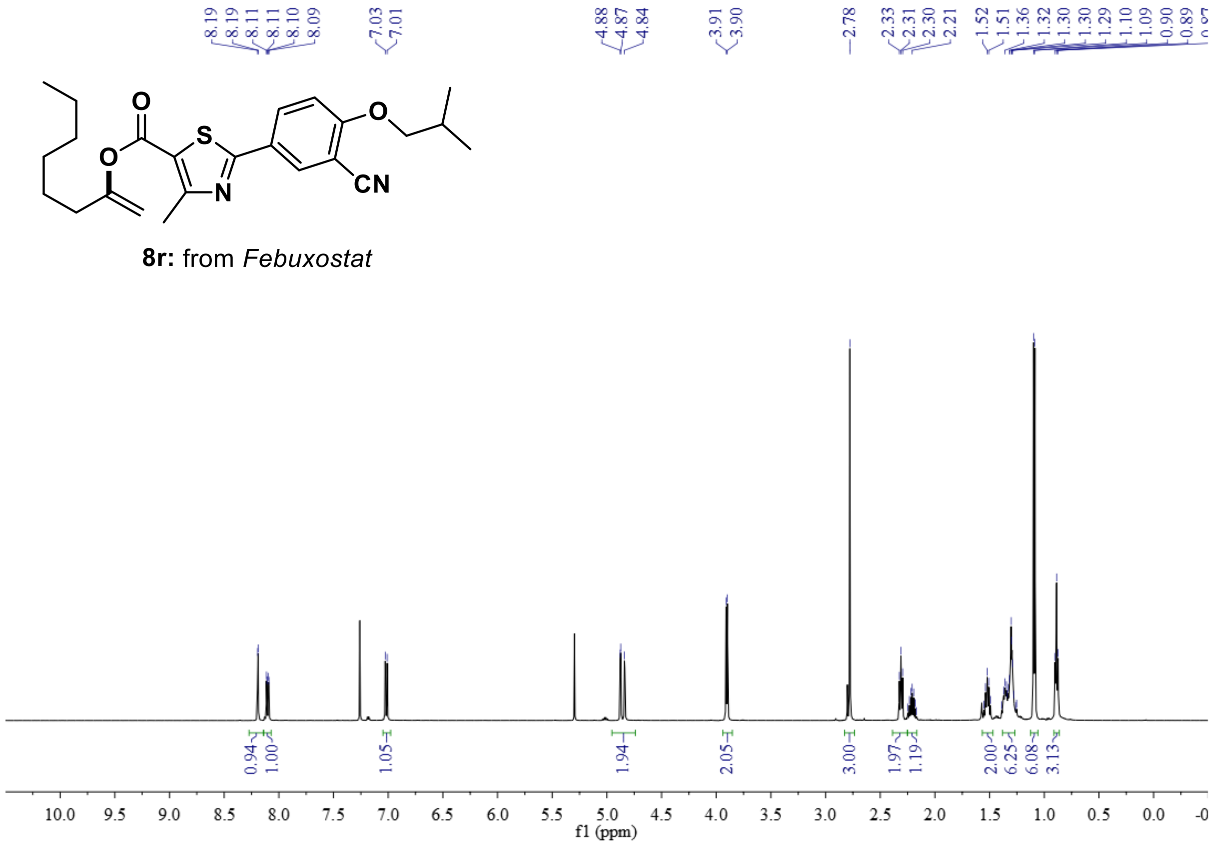
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **8q**.



^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **8q**.

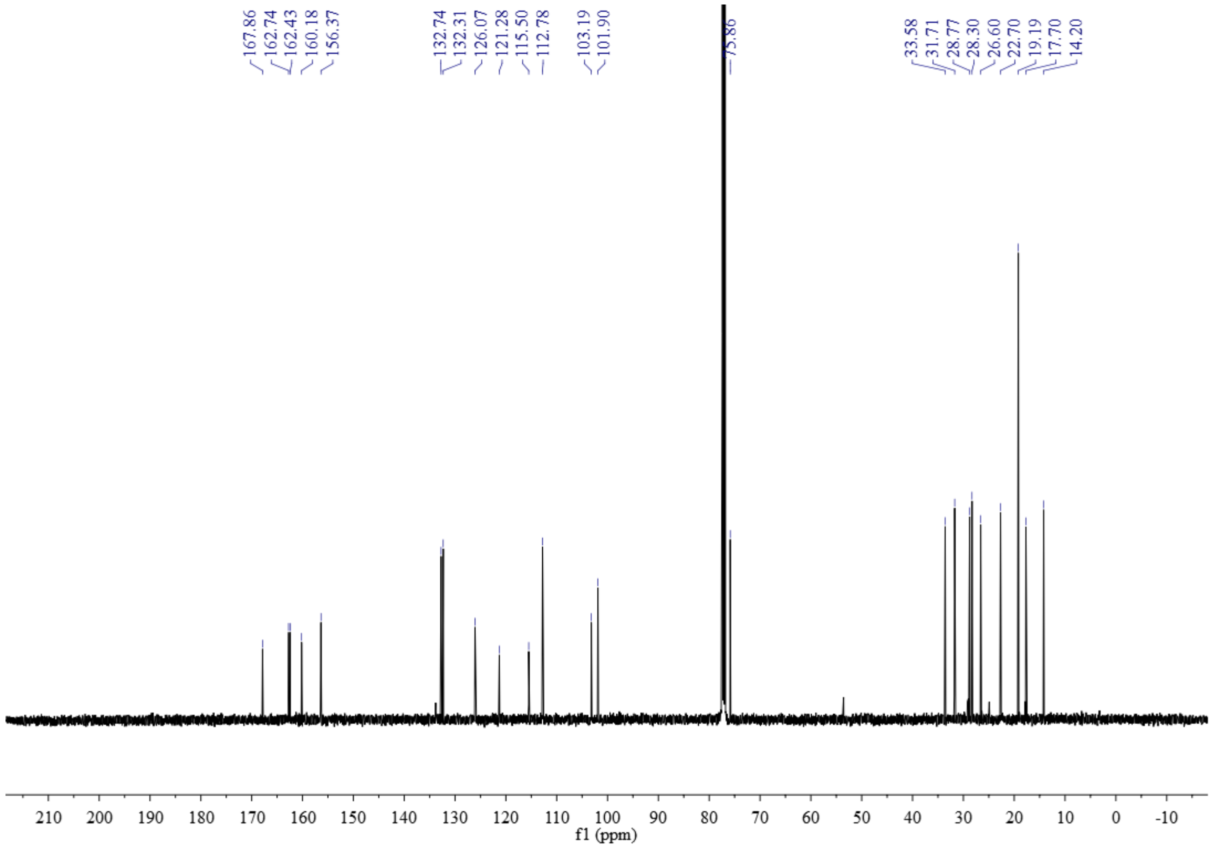


^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **8q**.

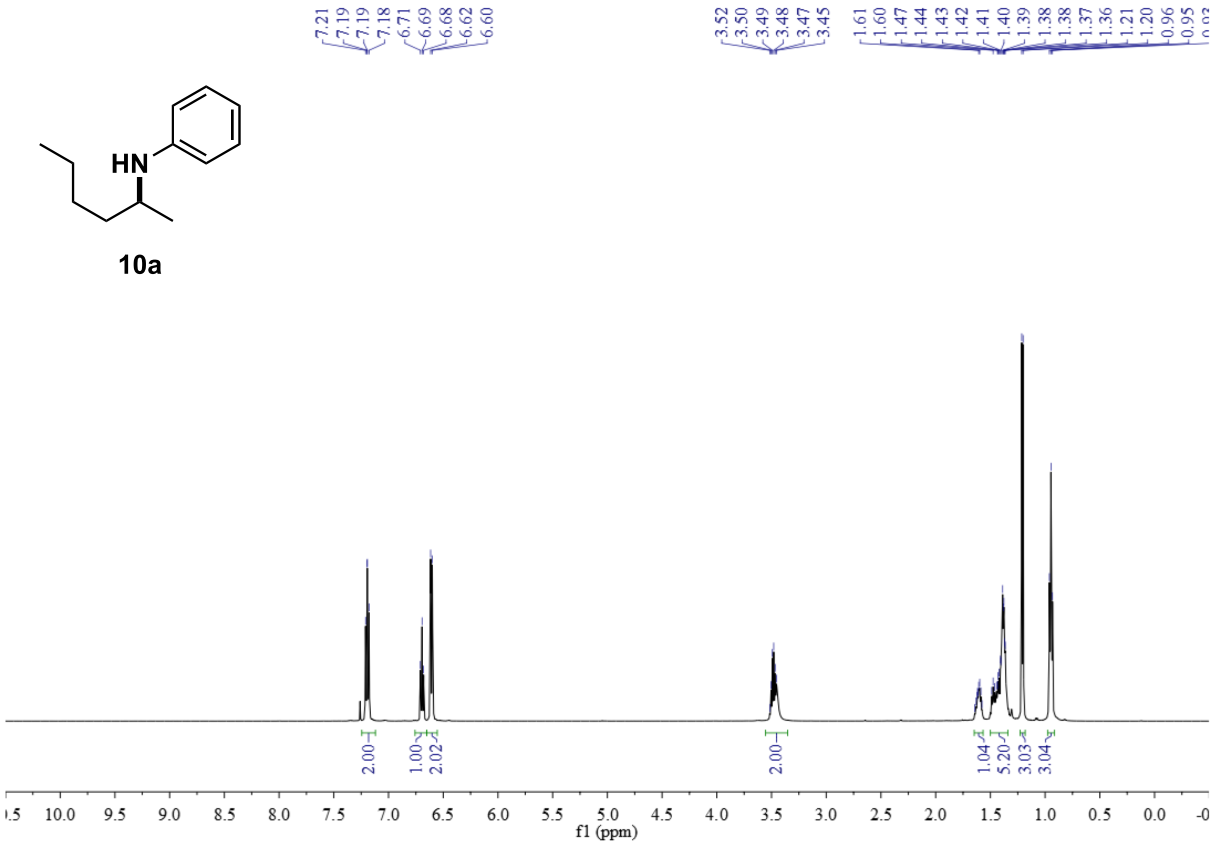


8r: from *Febuxostat*

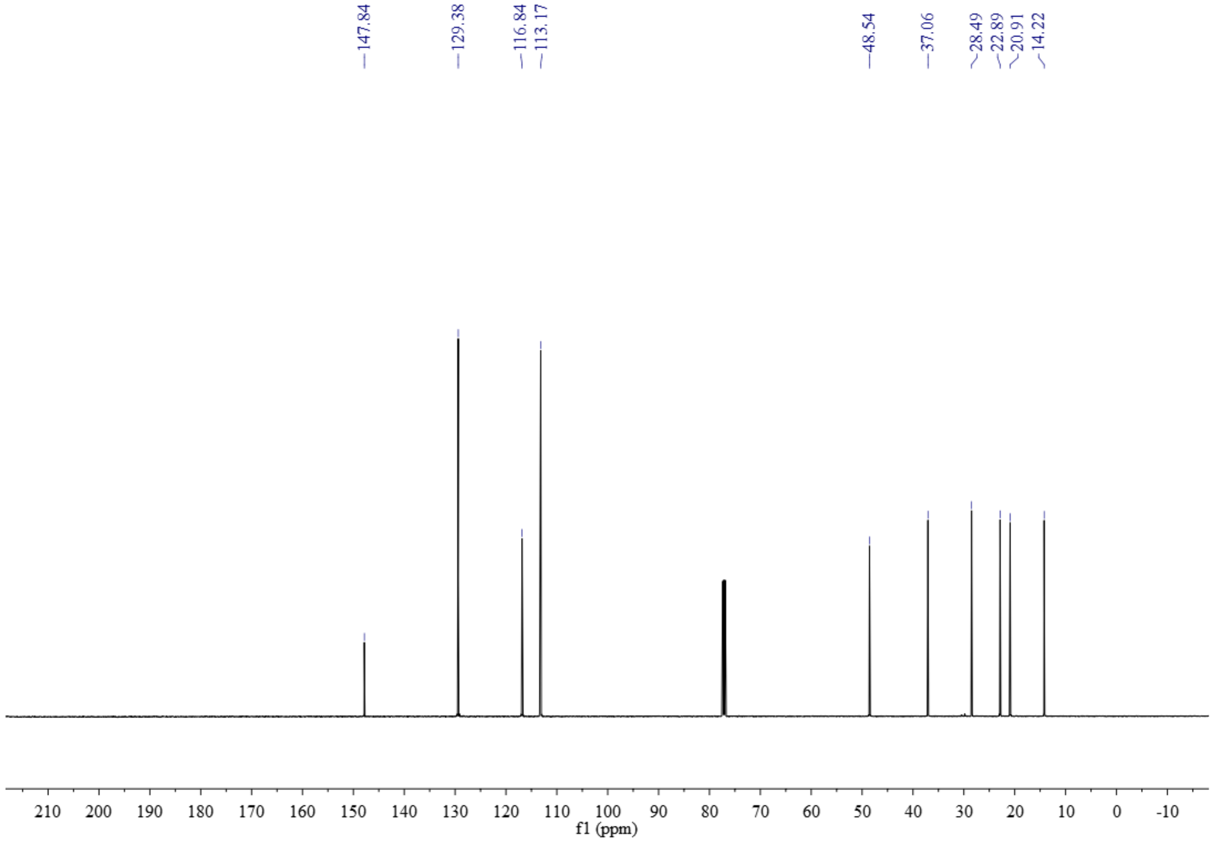
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **8r**.



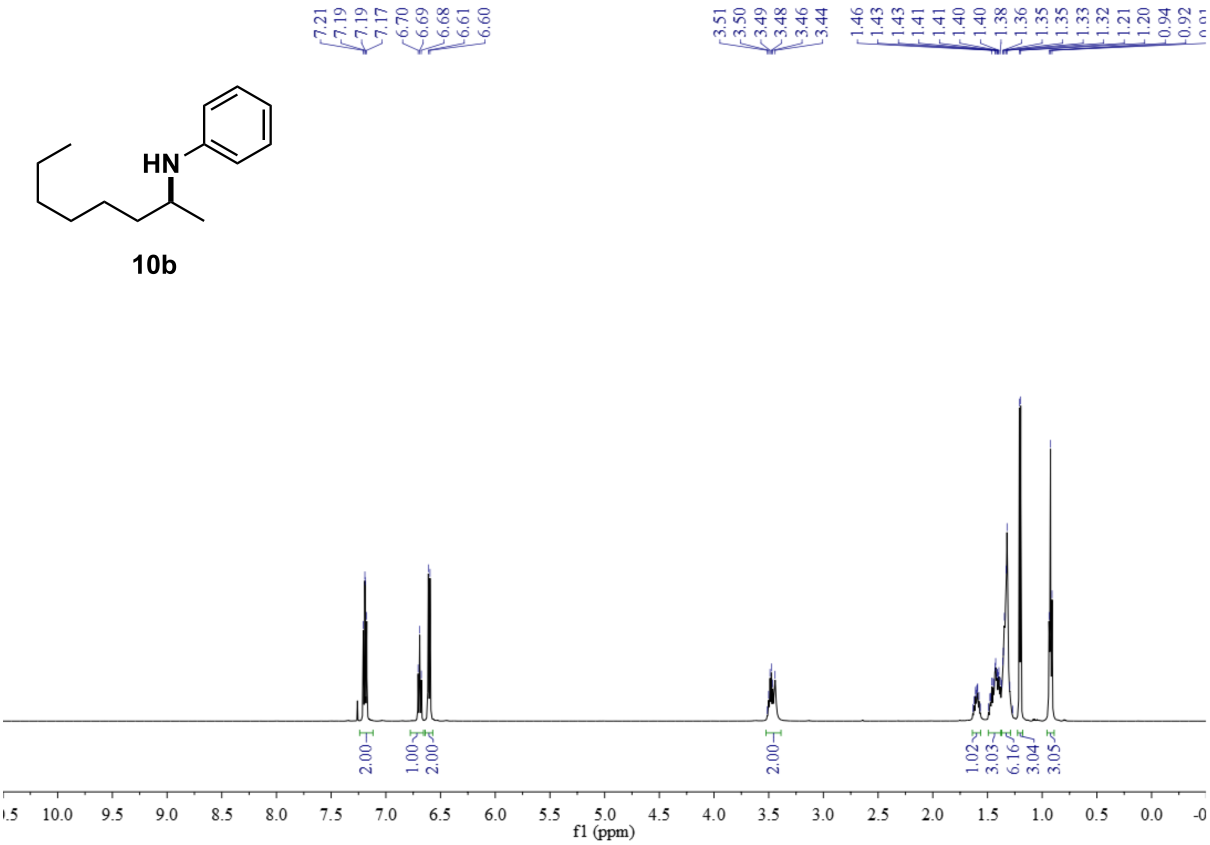
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **8r**.



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **10a**.

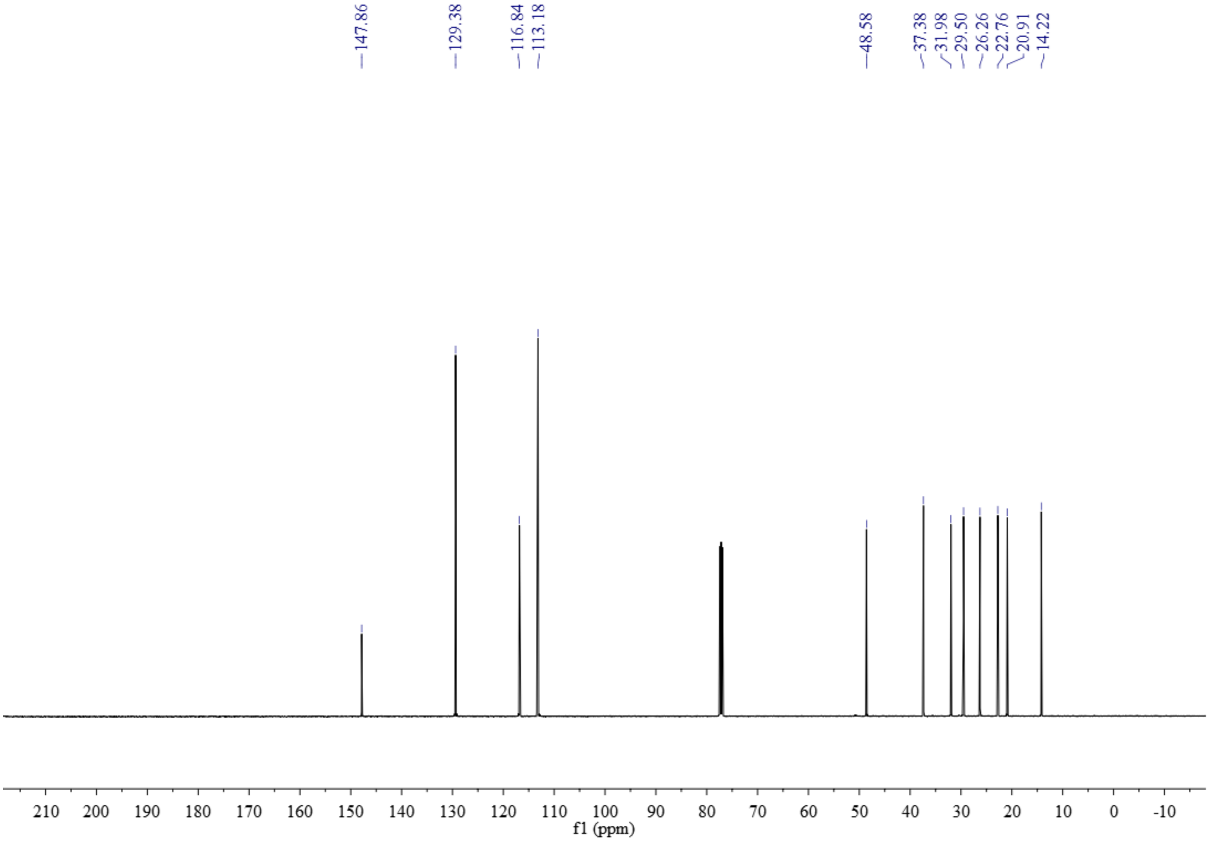


^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **10a**.

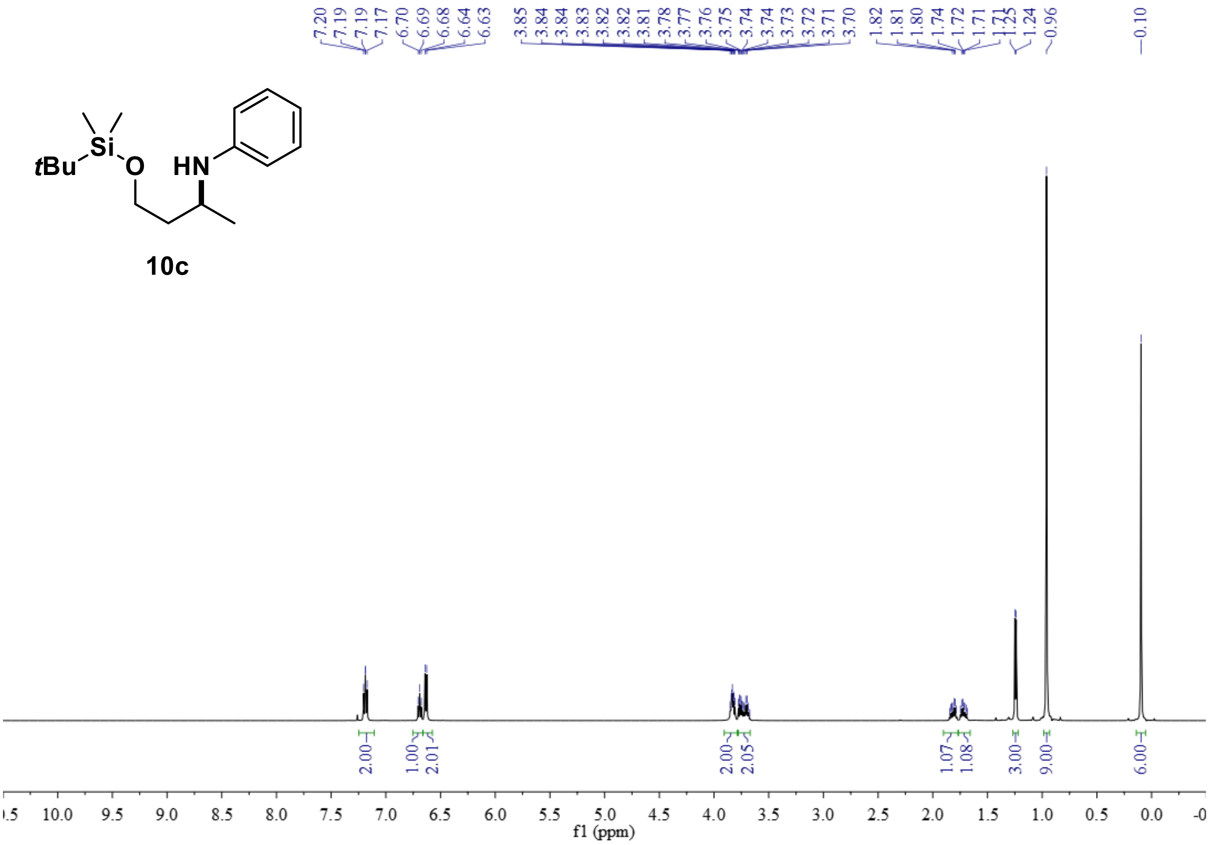


10b

^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **10b**.

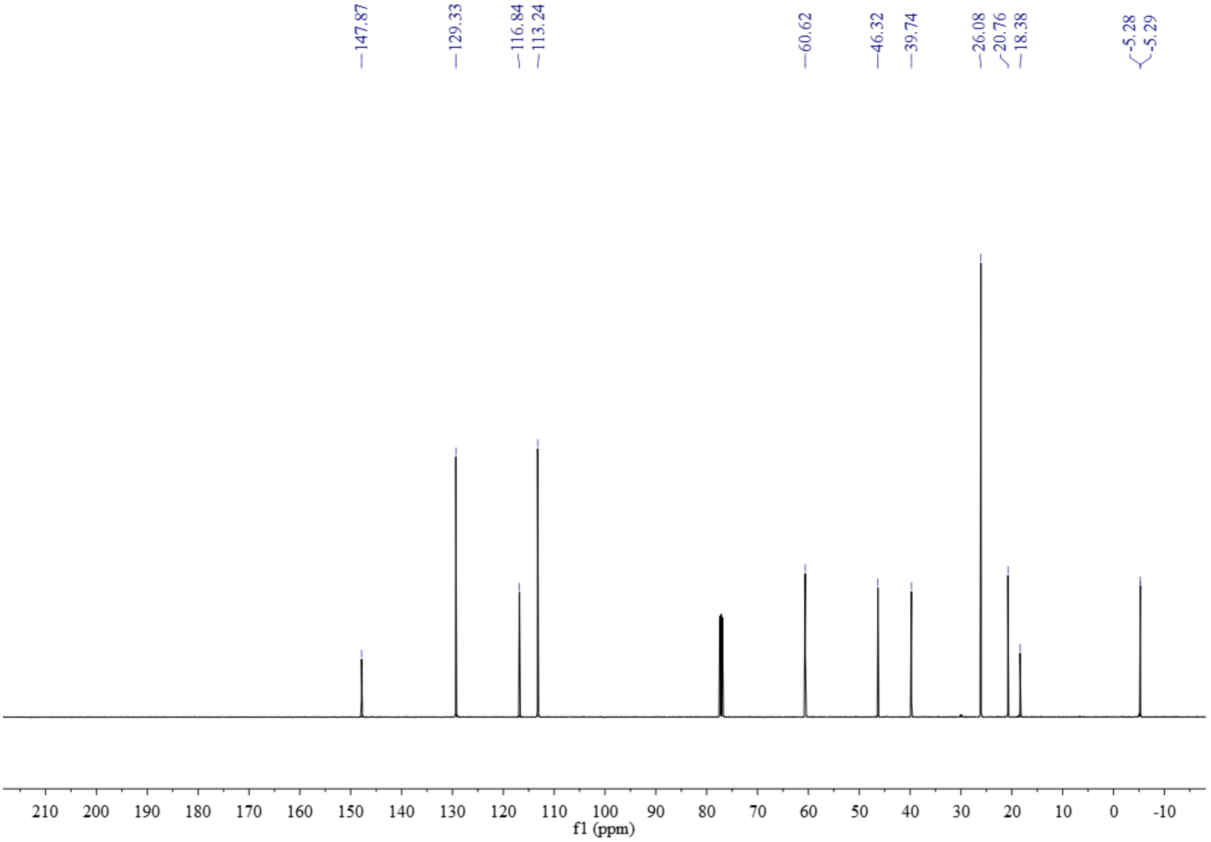


^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **10b**.

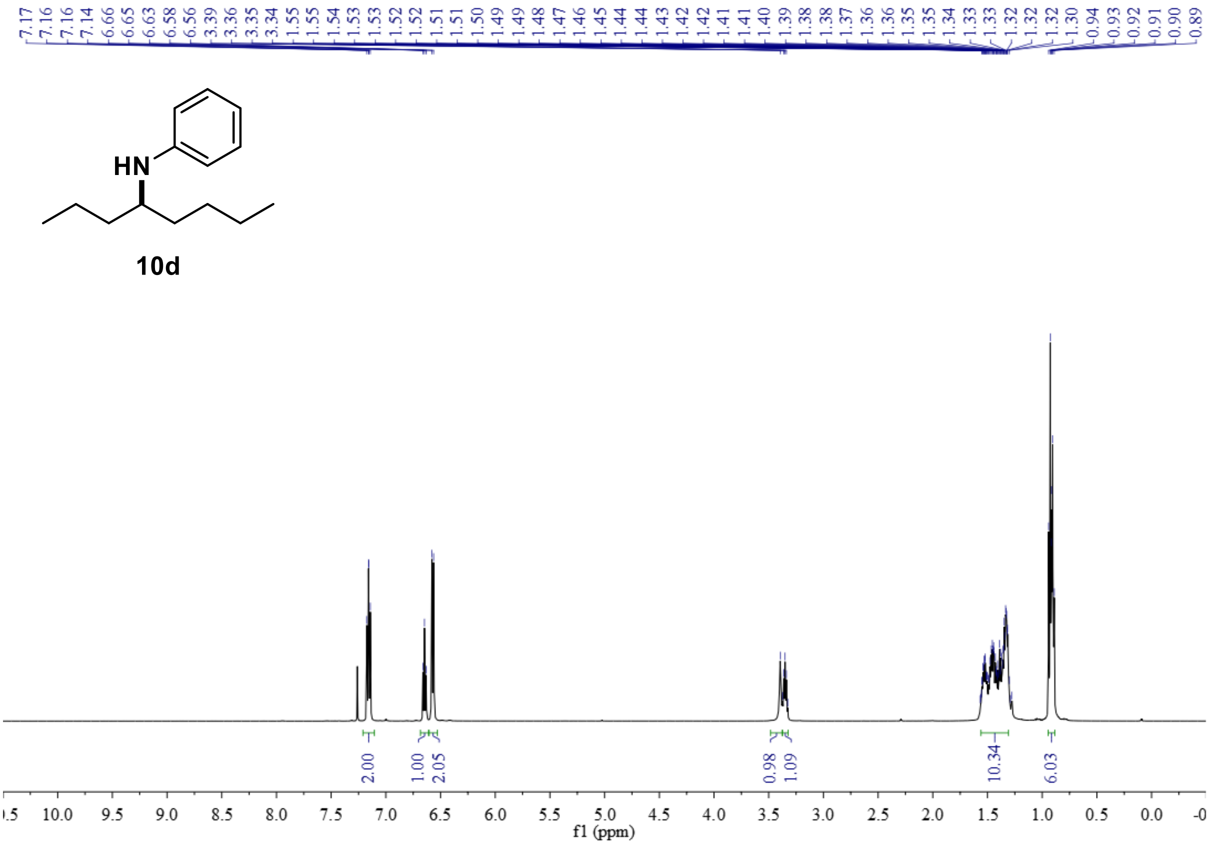


10c

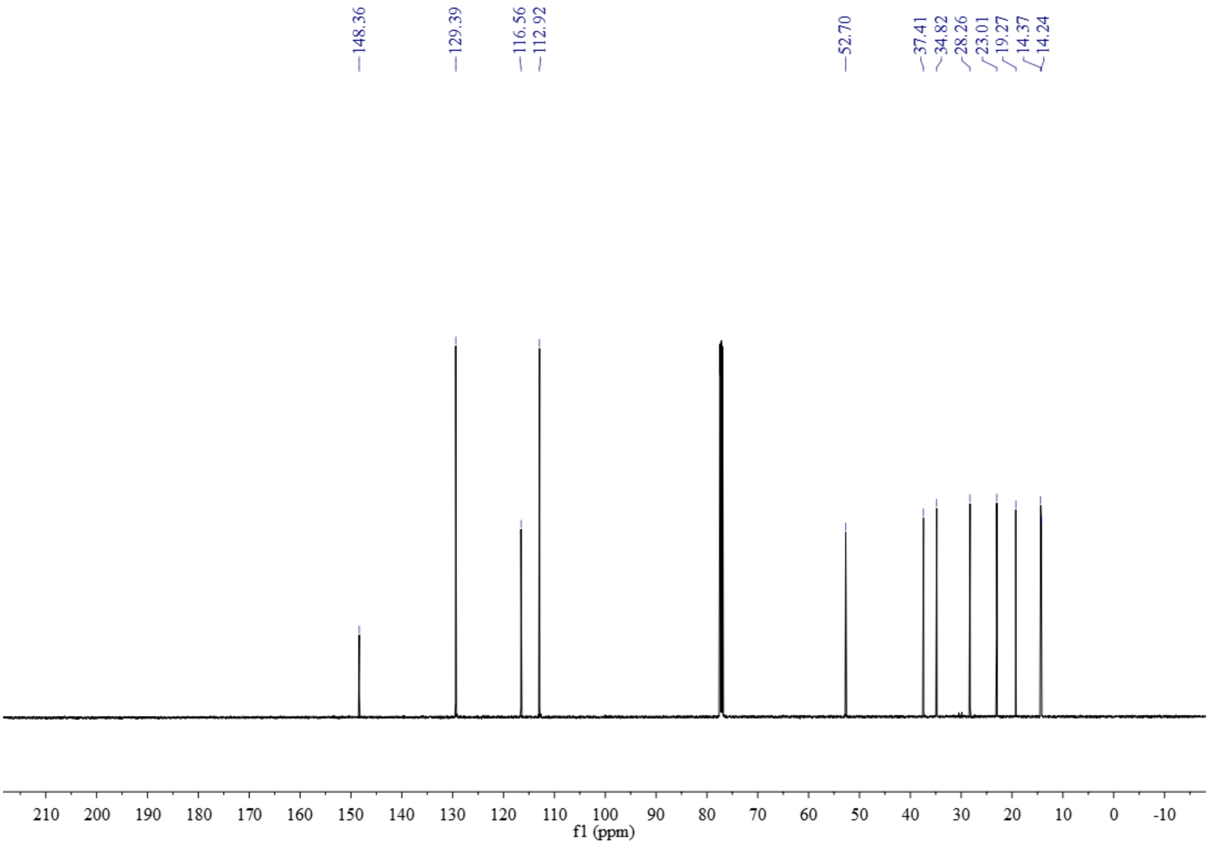
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **10c**.



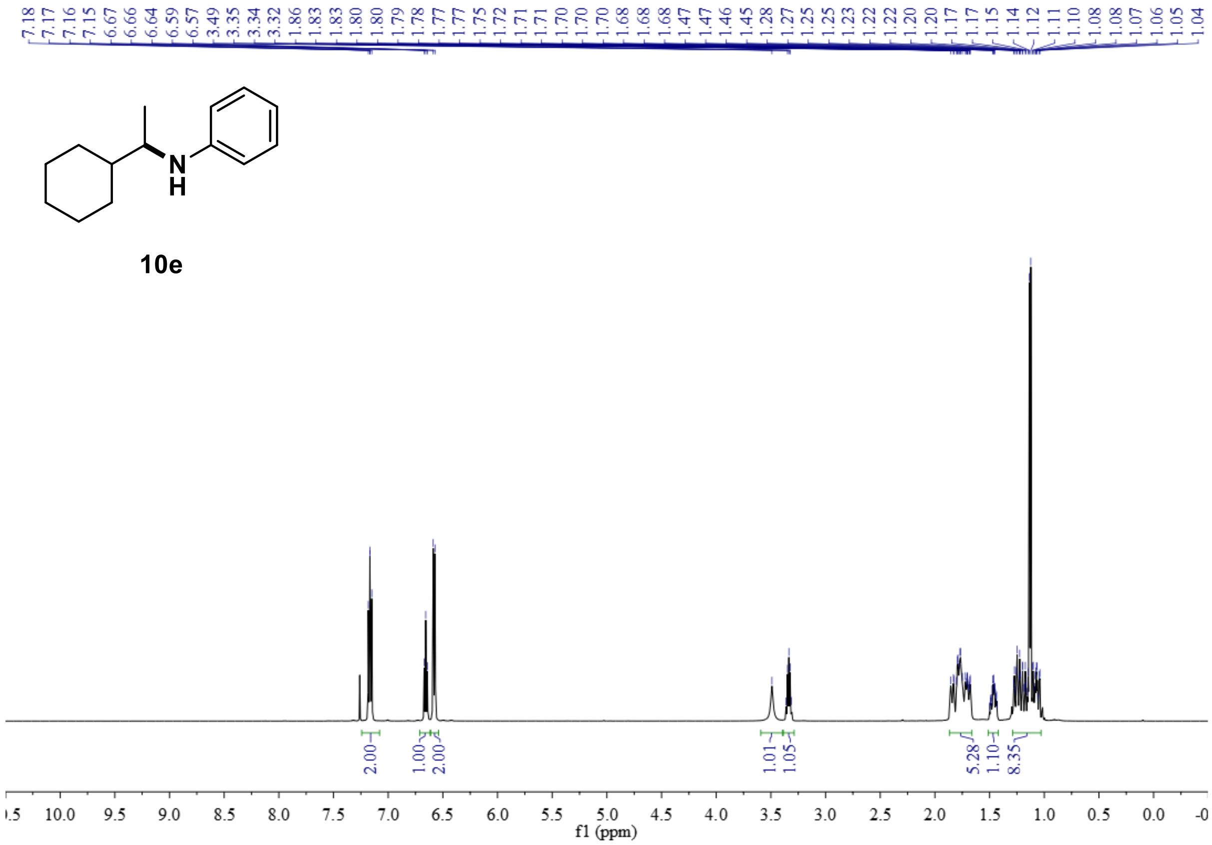
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **10c**.



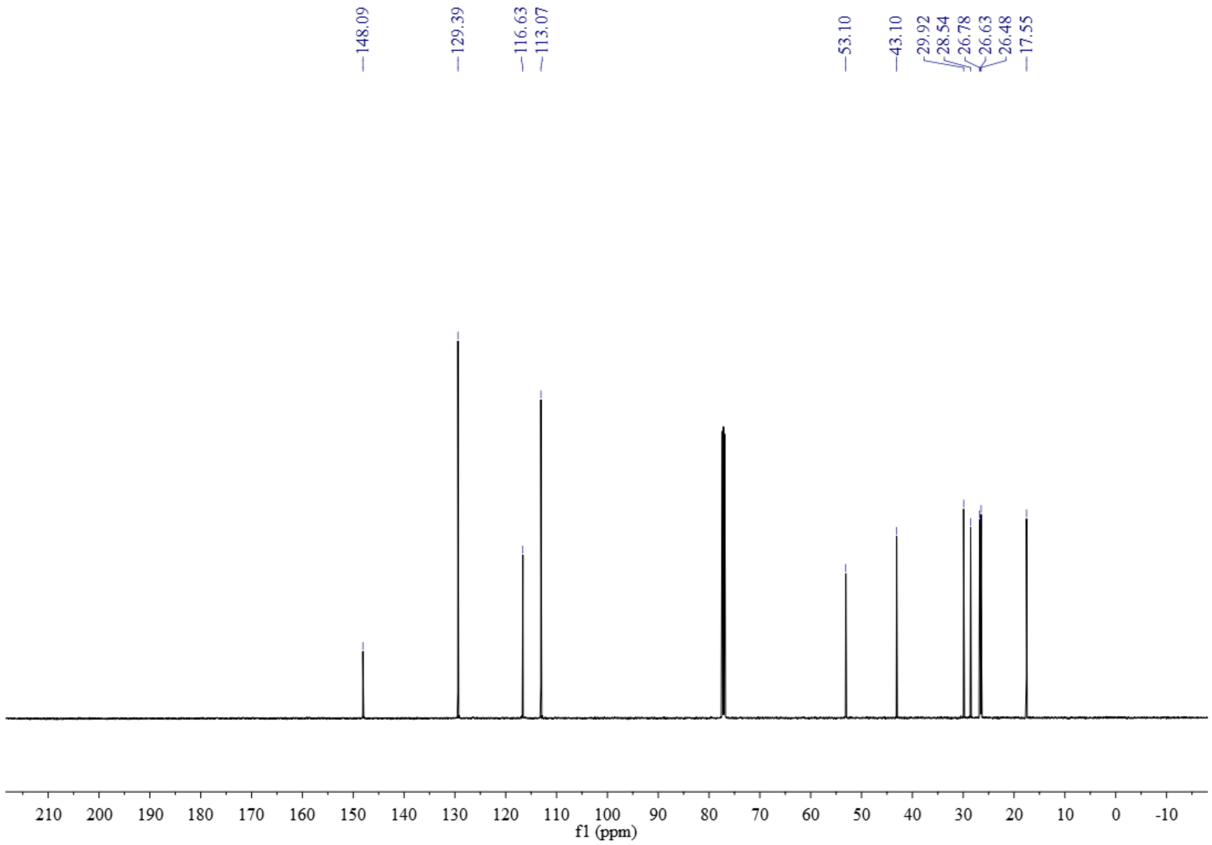
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **10d**.



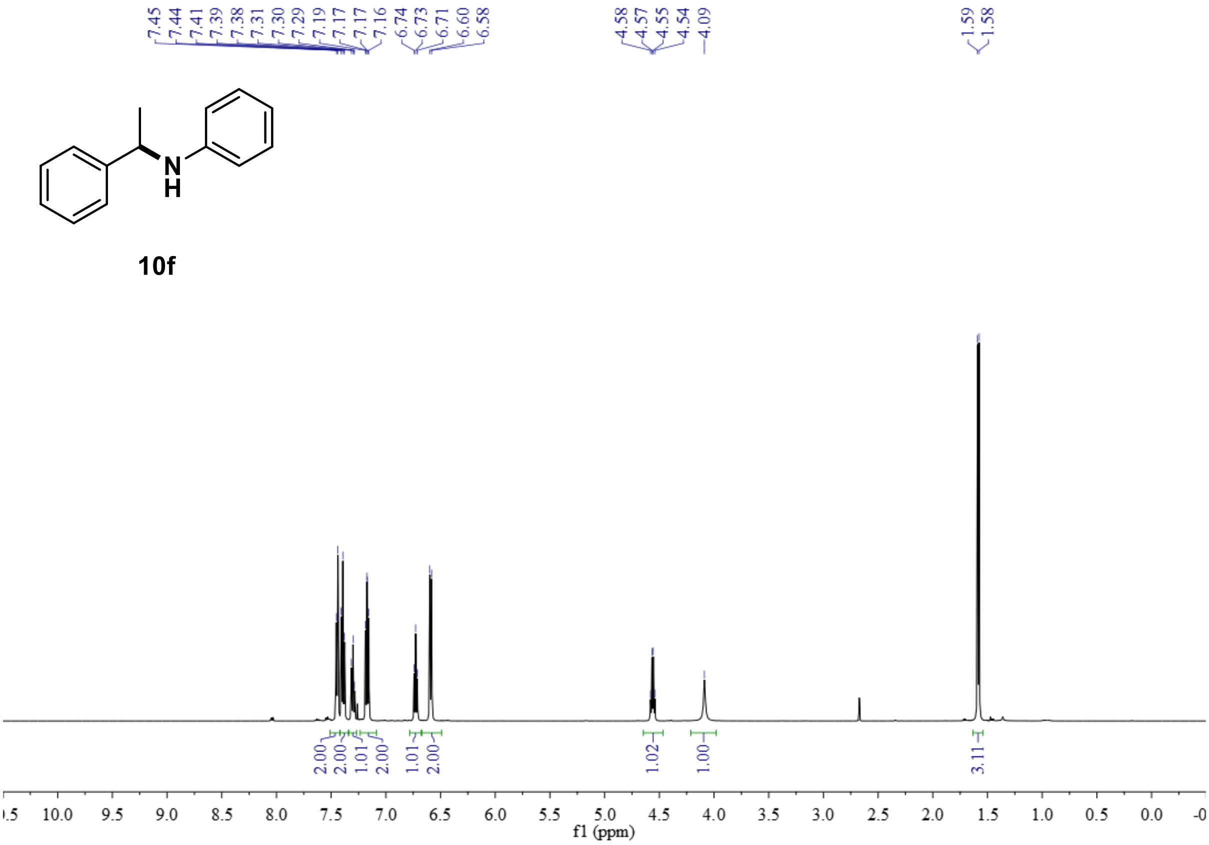
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **10d**.



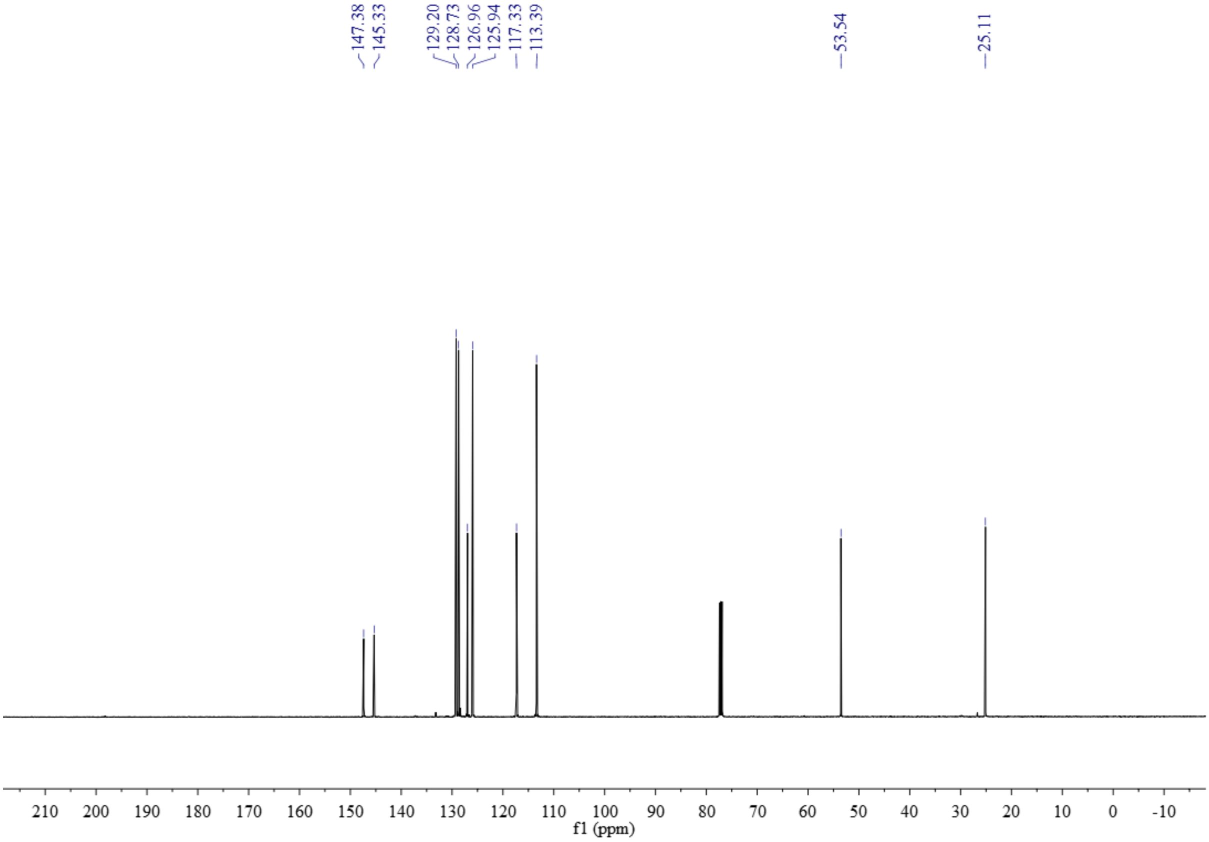
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **10e**.



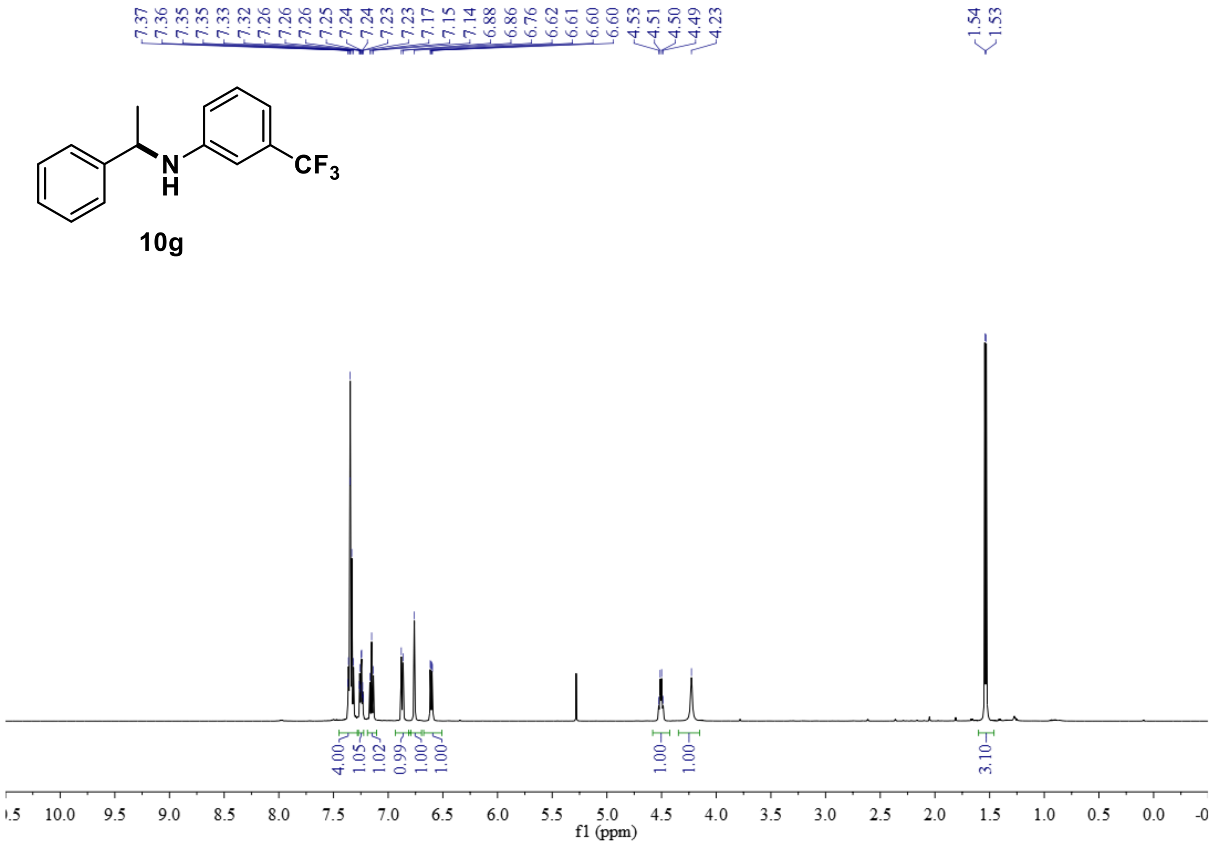
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **10e**.



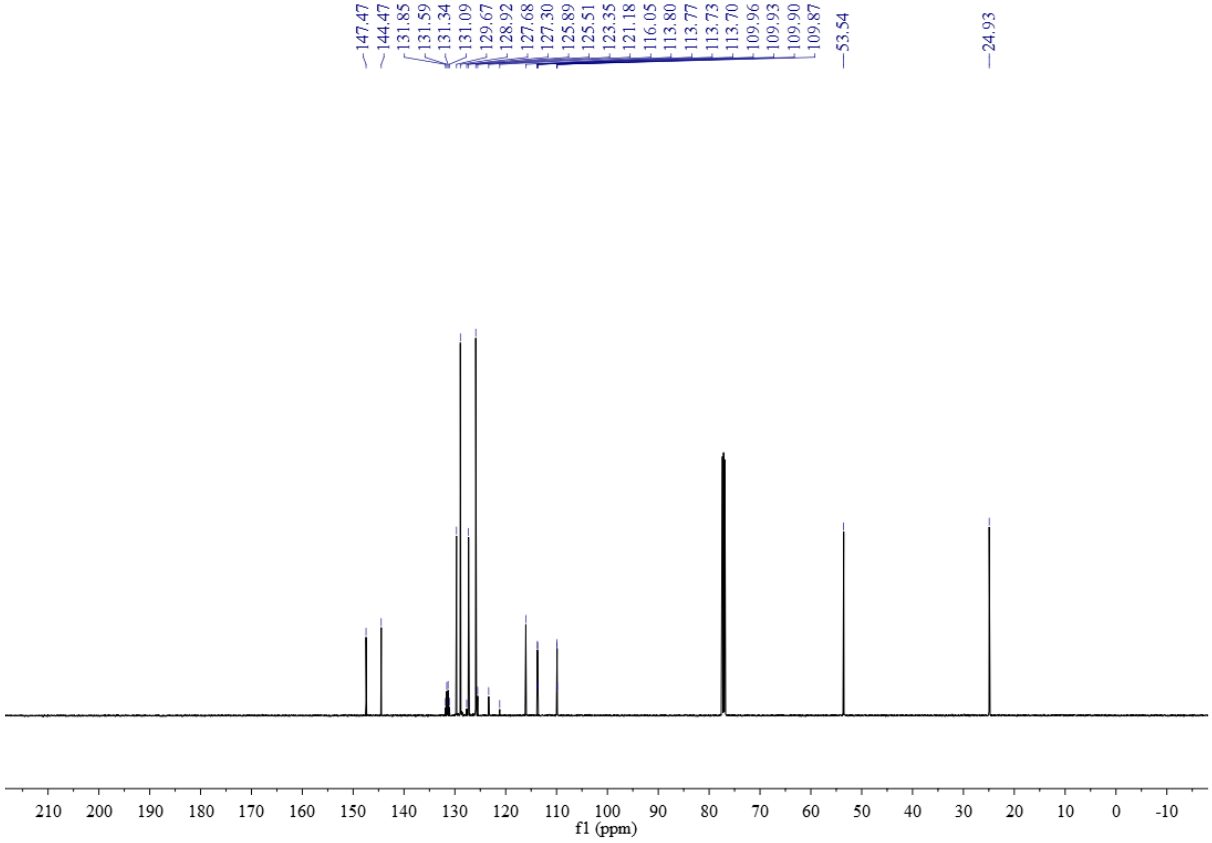
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **10f**.



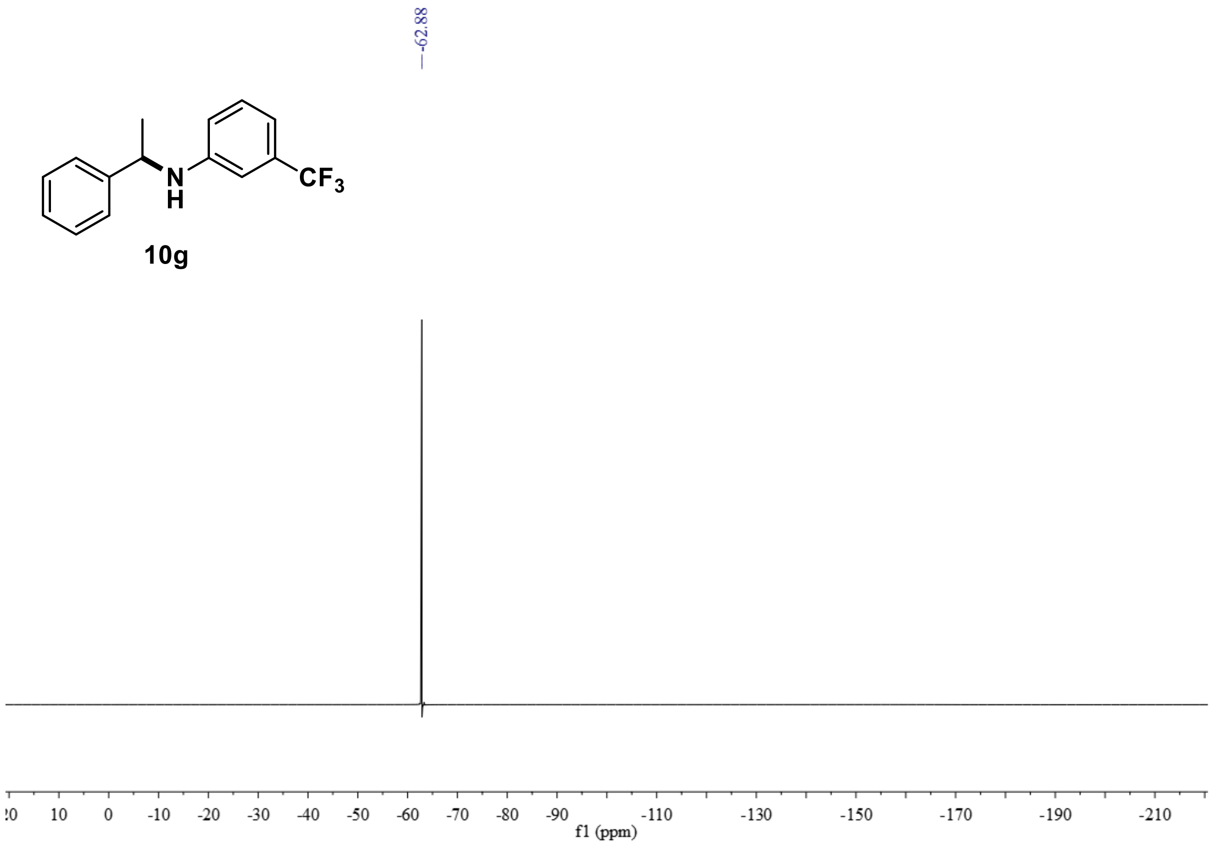
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **10f**.



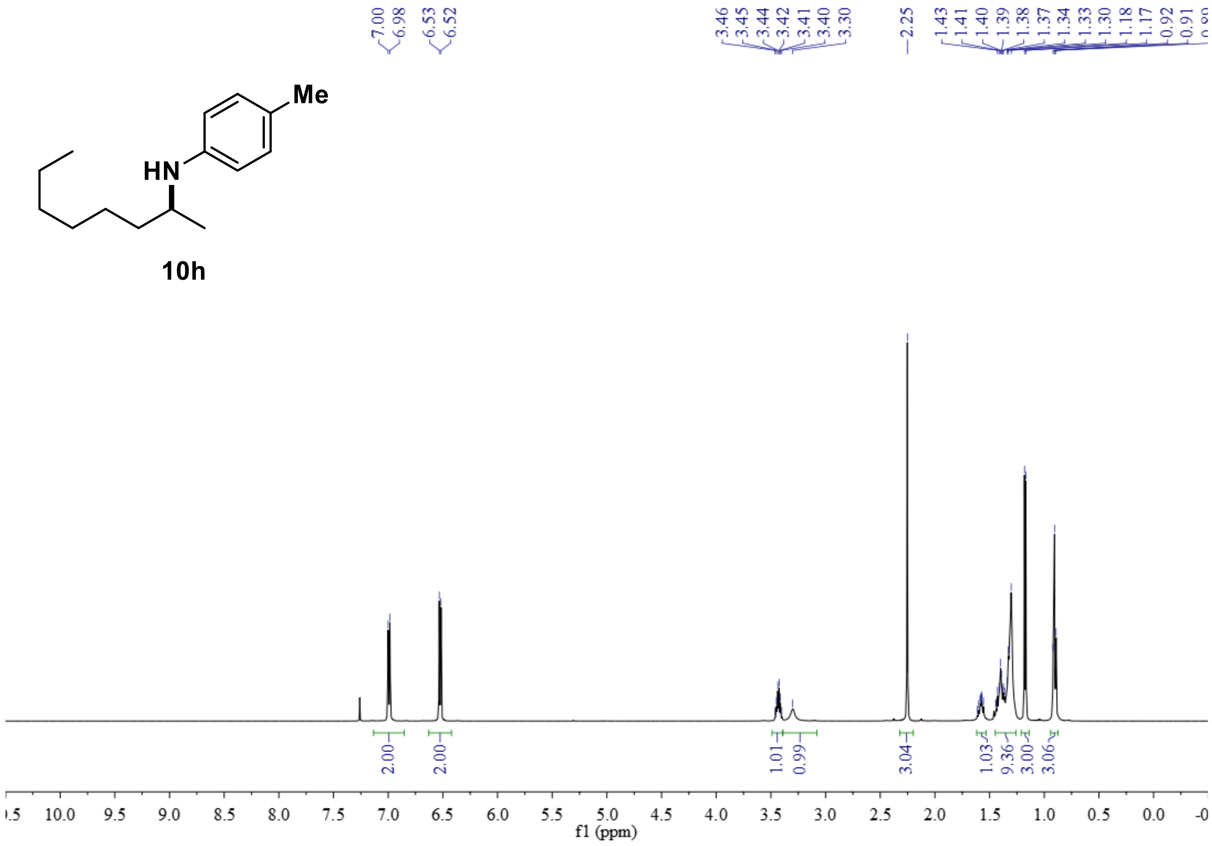
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **10g**.



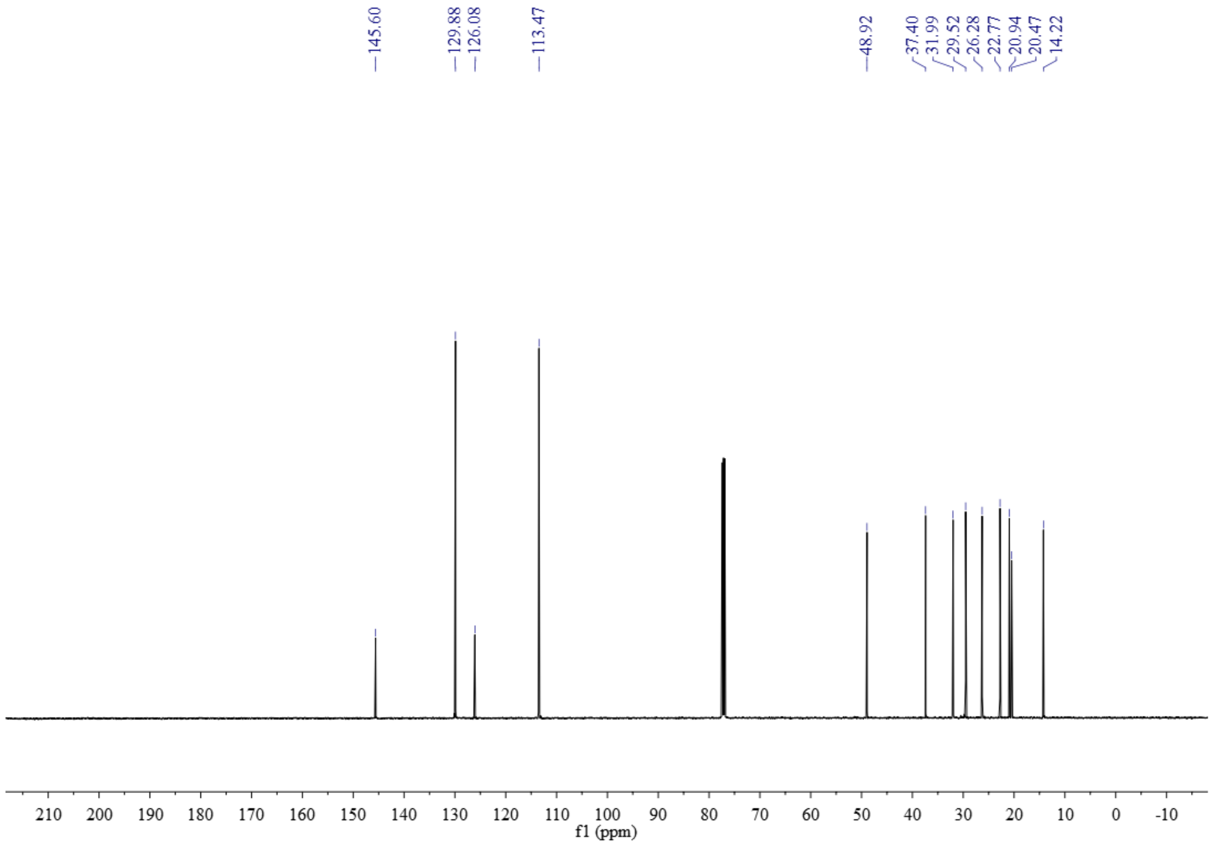
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **10g**.



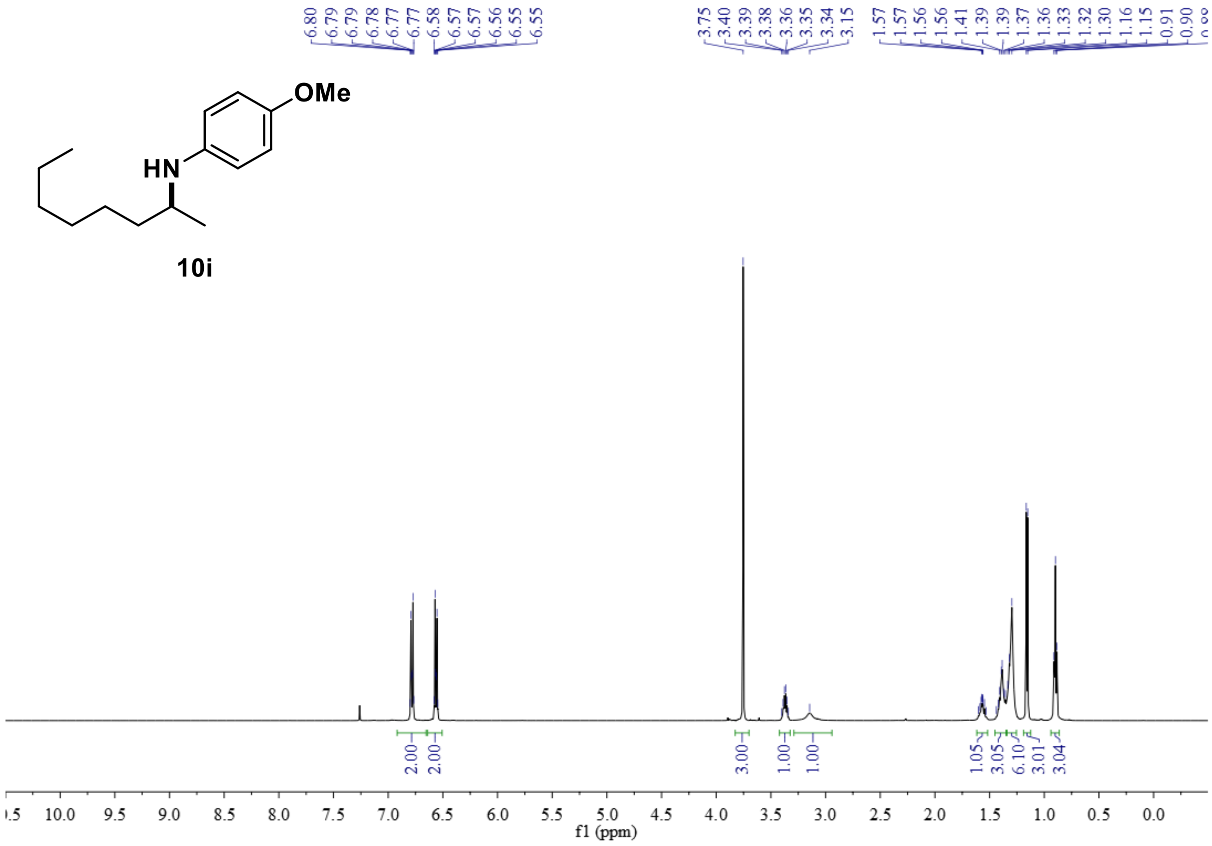
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **10g**.



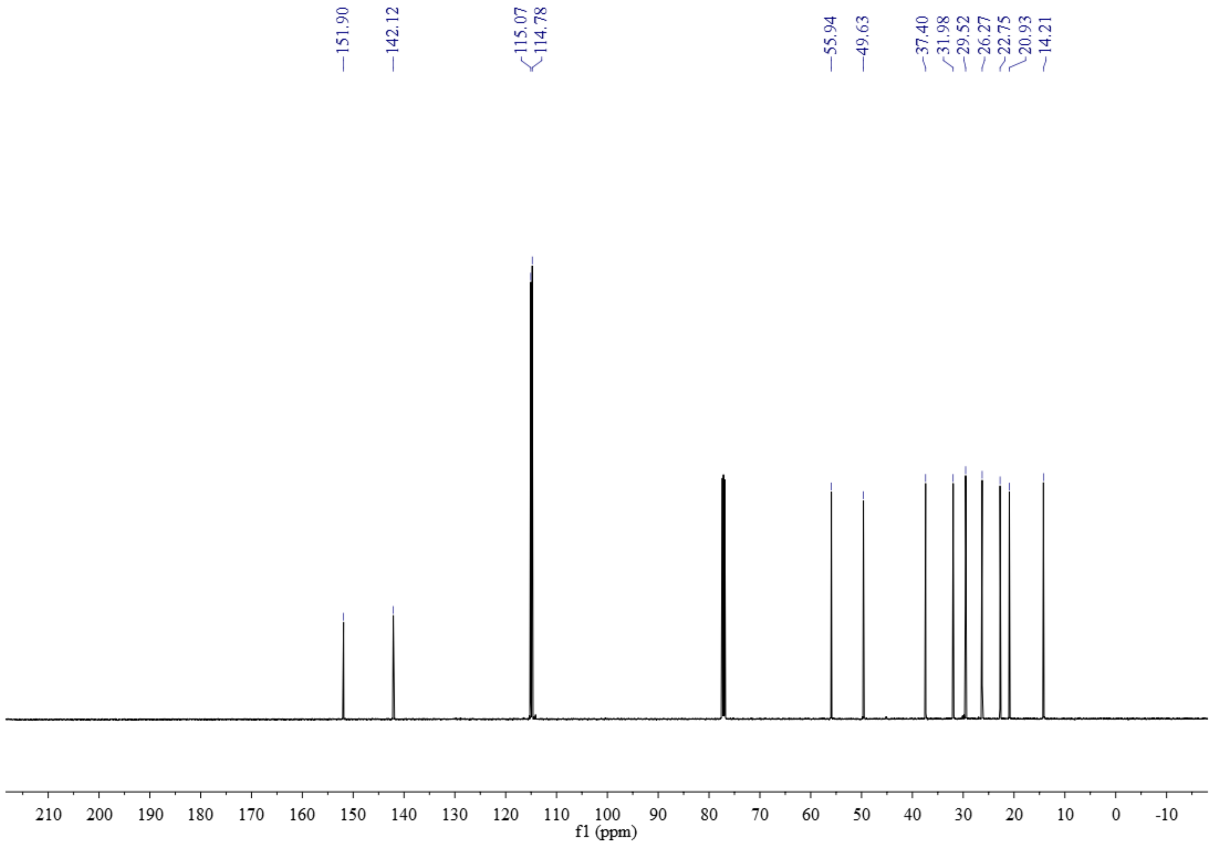
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **10h**.



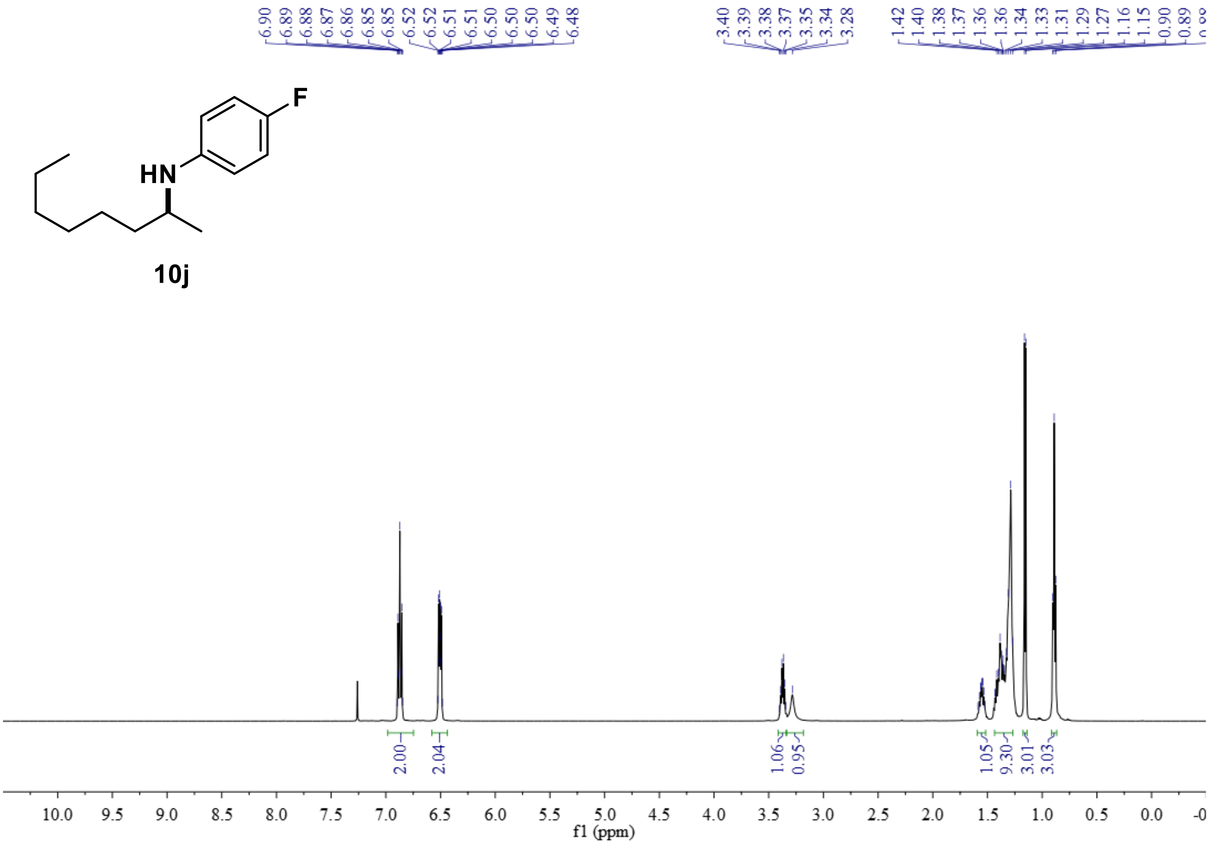
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **10h**.



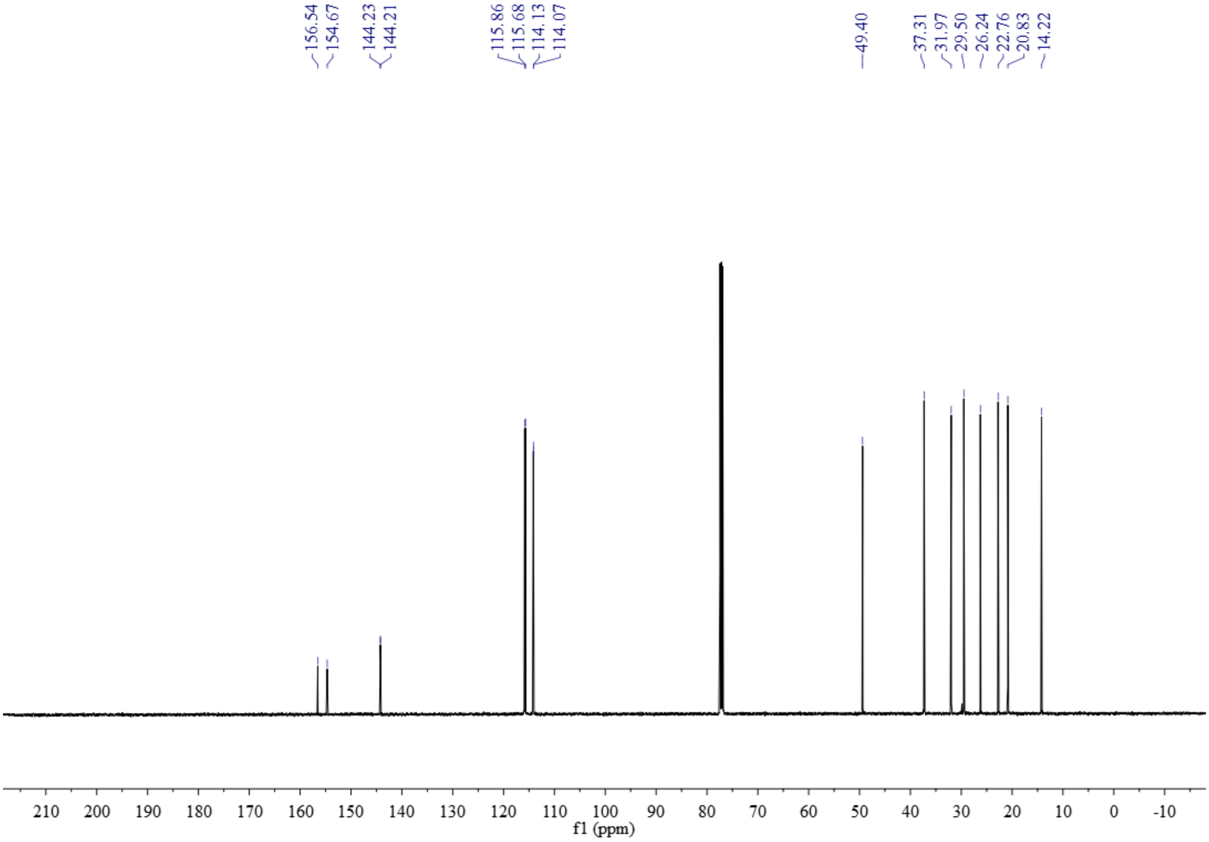
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **10i**.



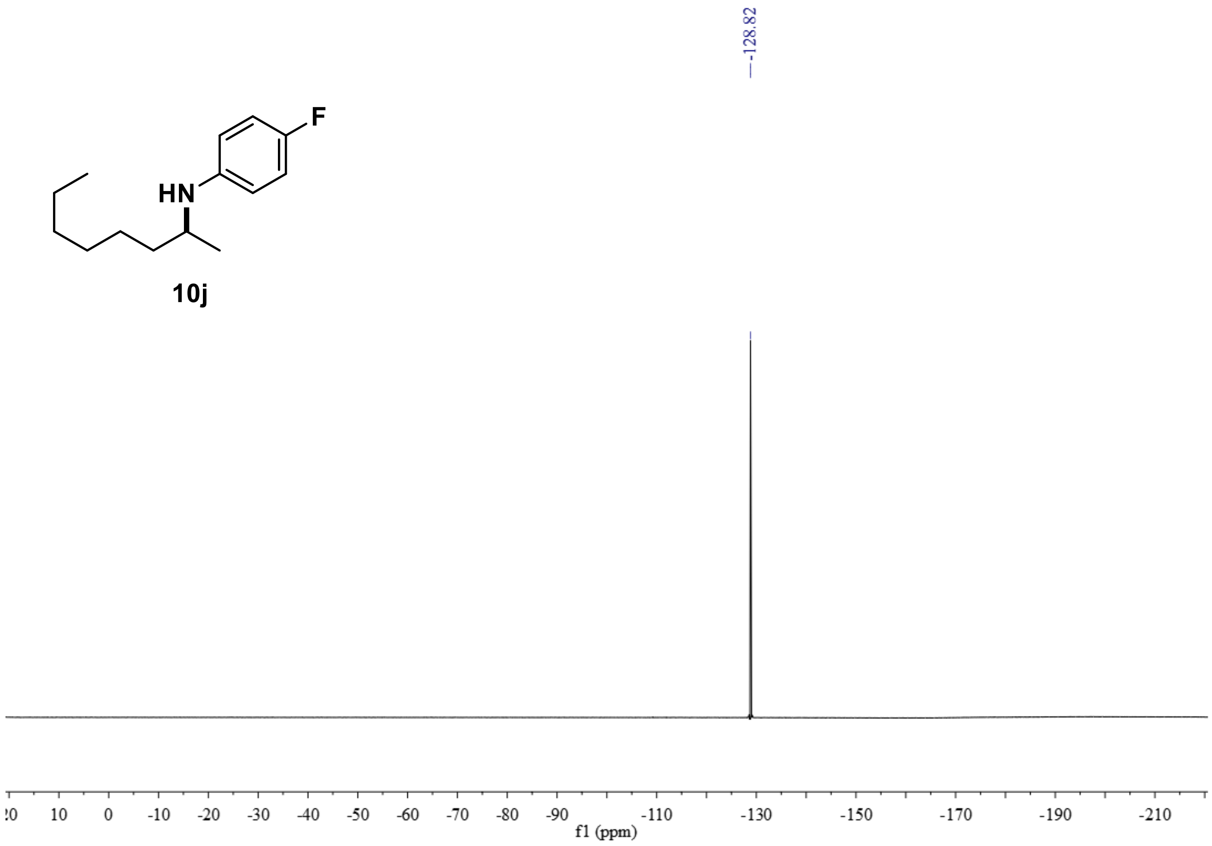
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **10i**.


10j

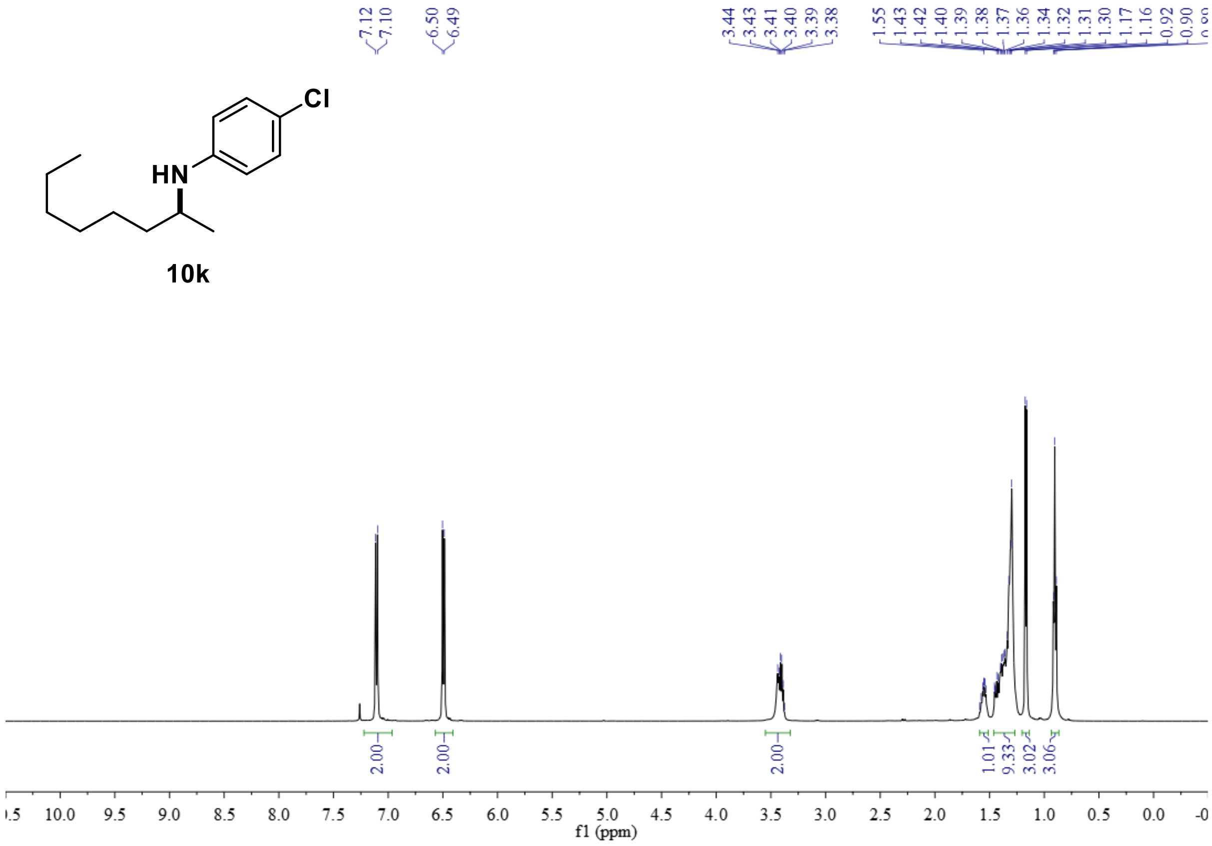
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **10j**.



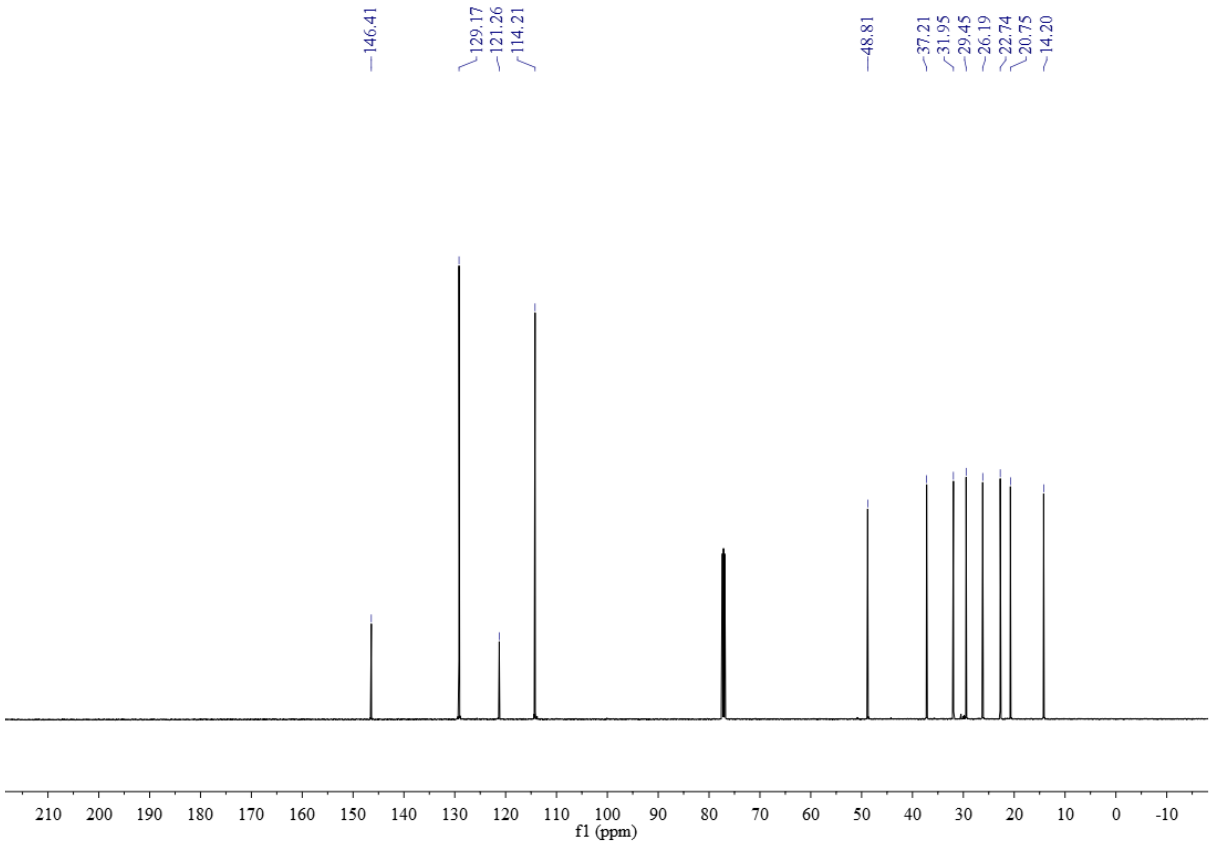
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **10j**.



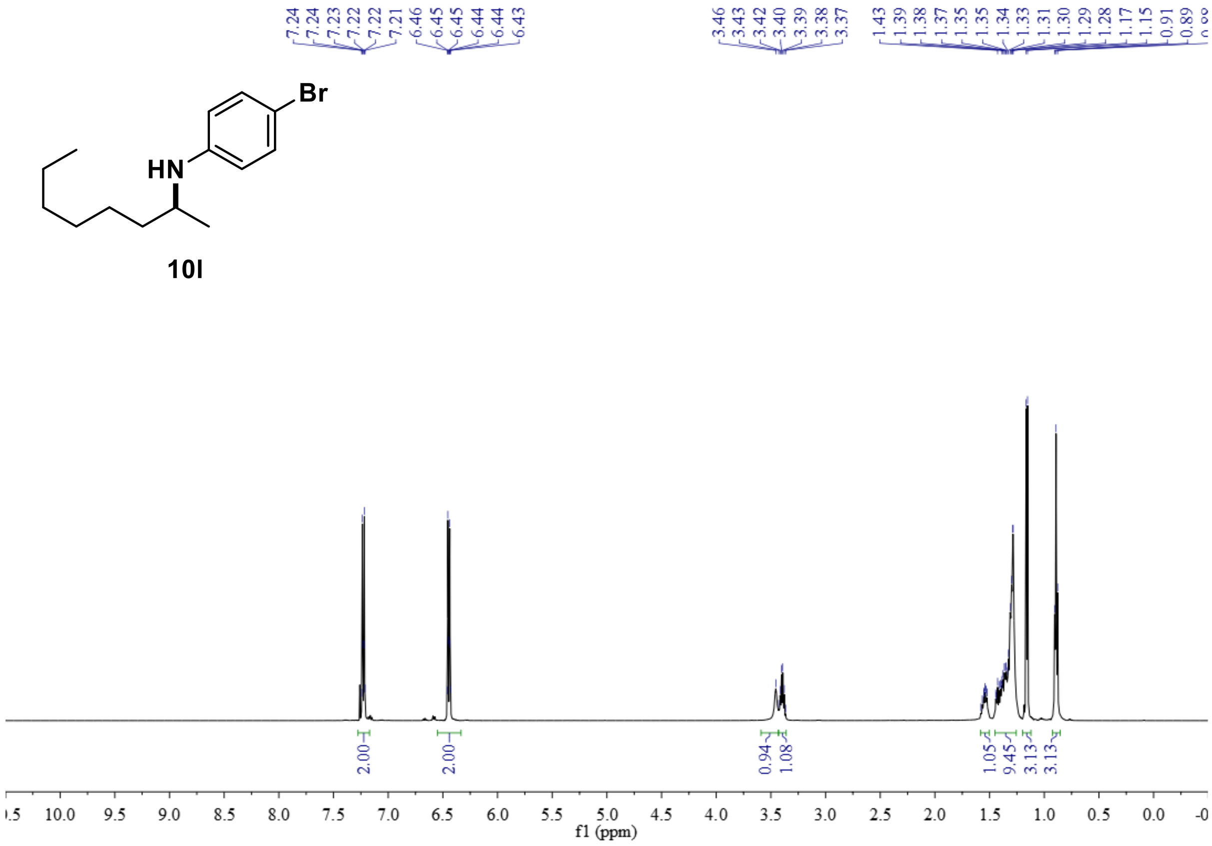
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **10j**.



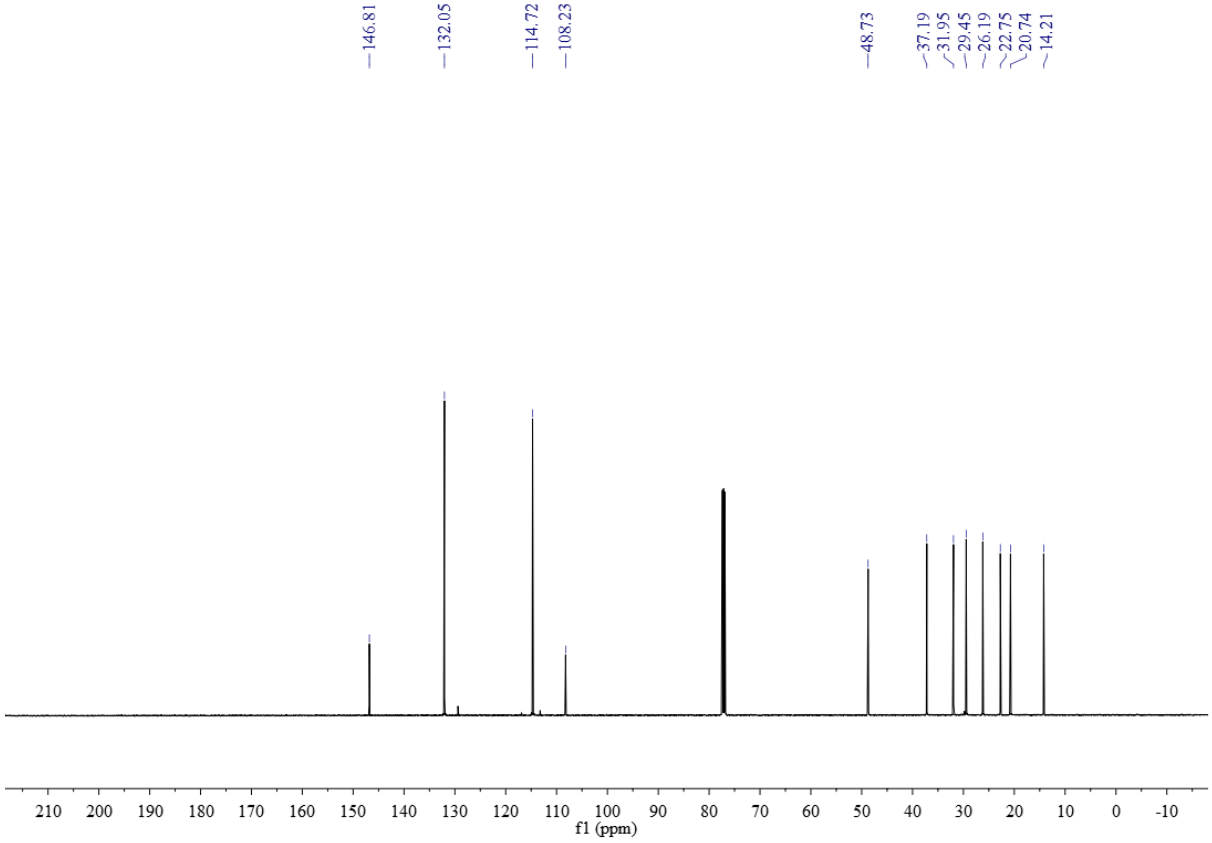
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **10k**.



^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **10k**.

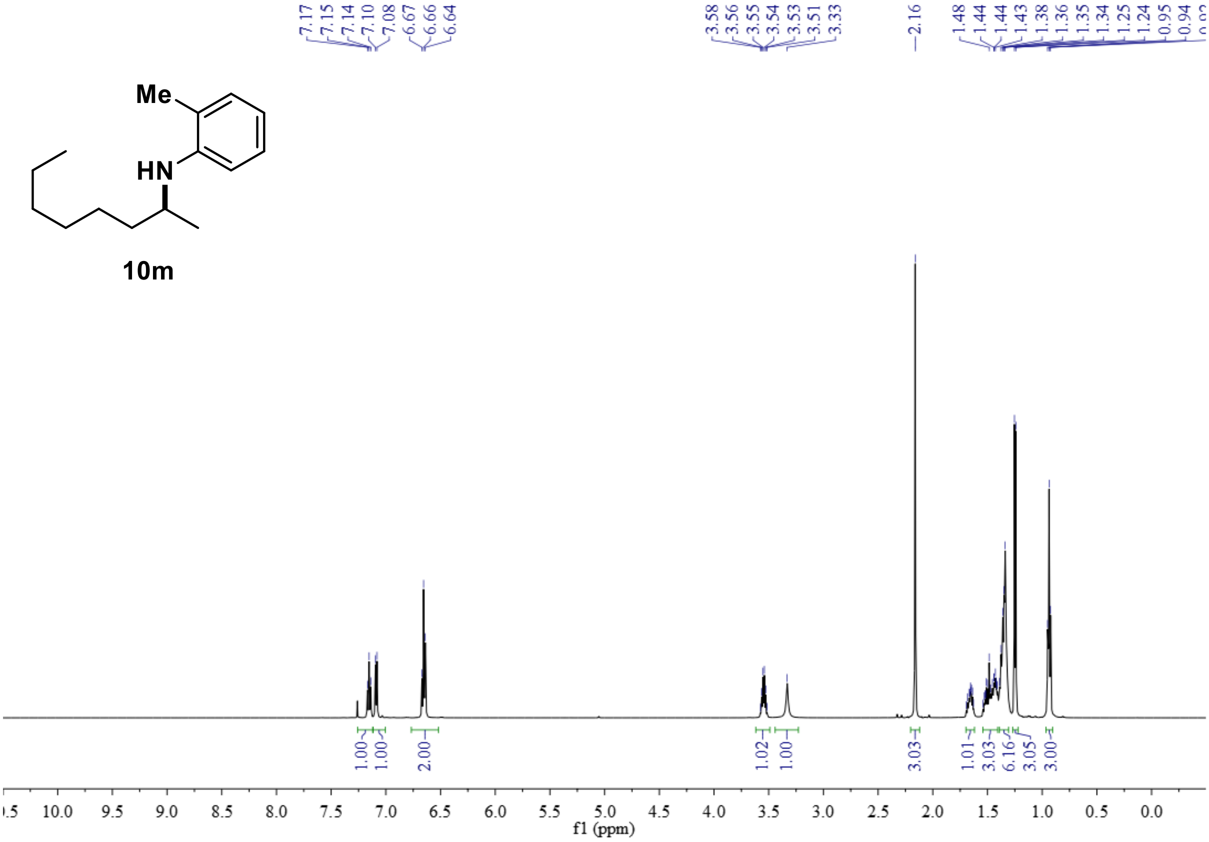


^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **10l**.

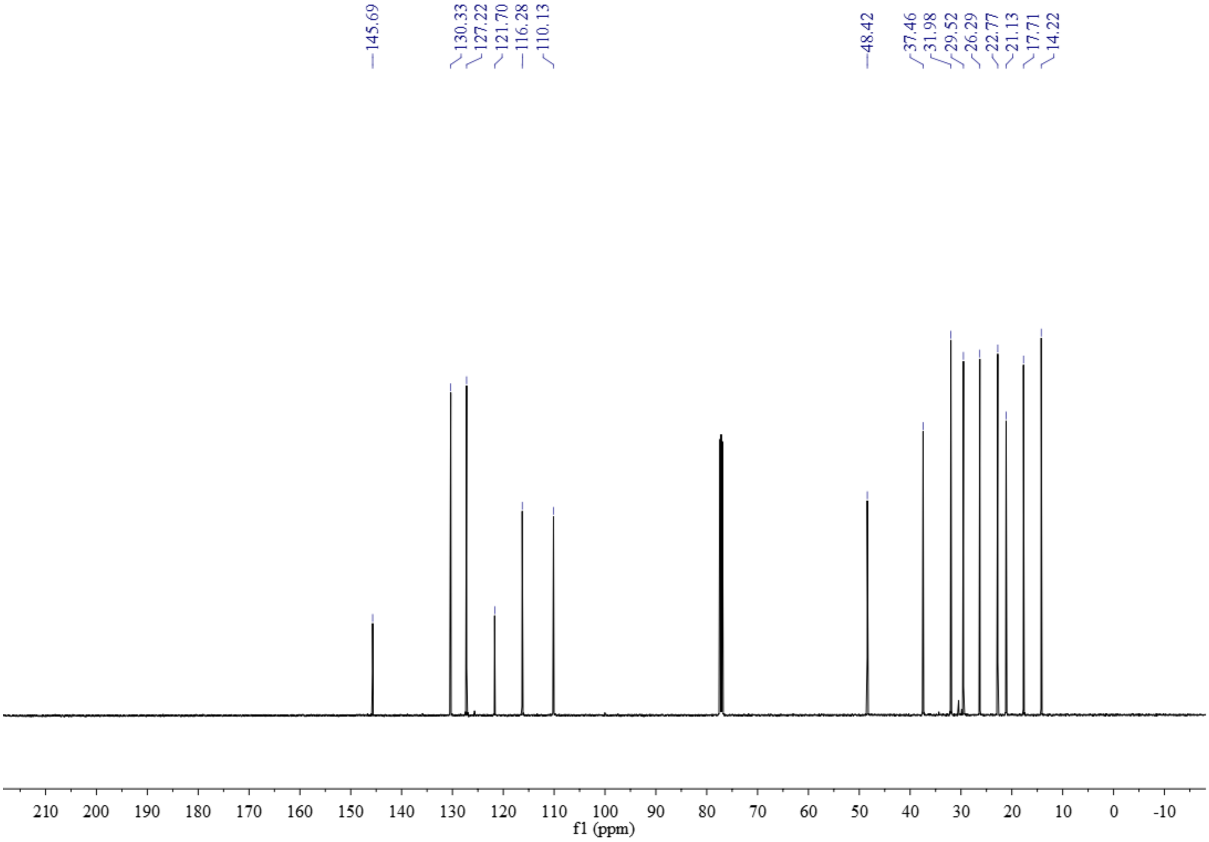


^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **10l**.

10m

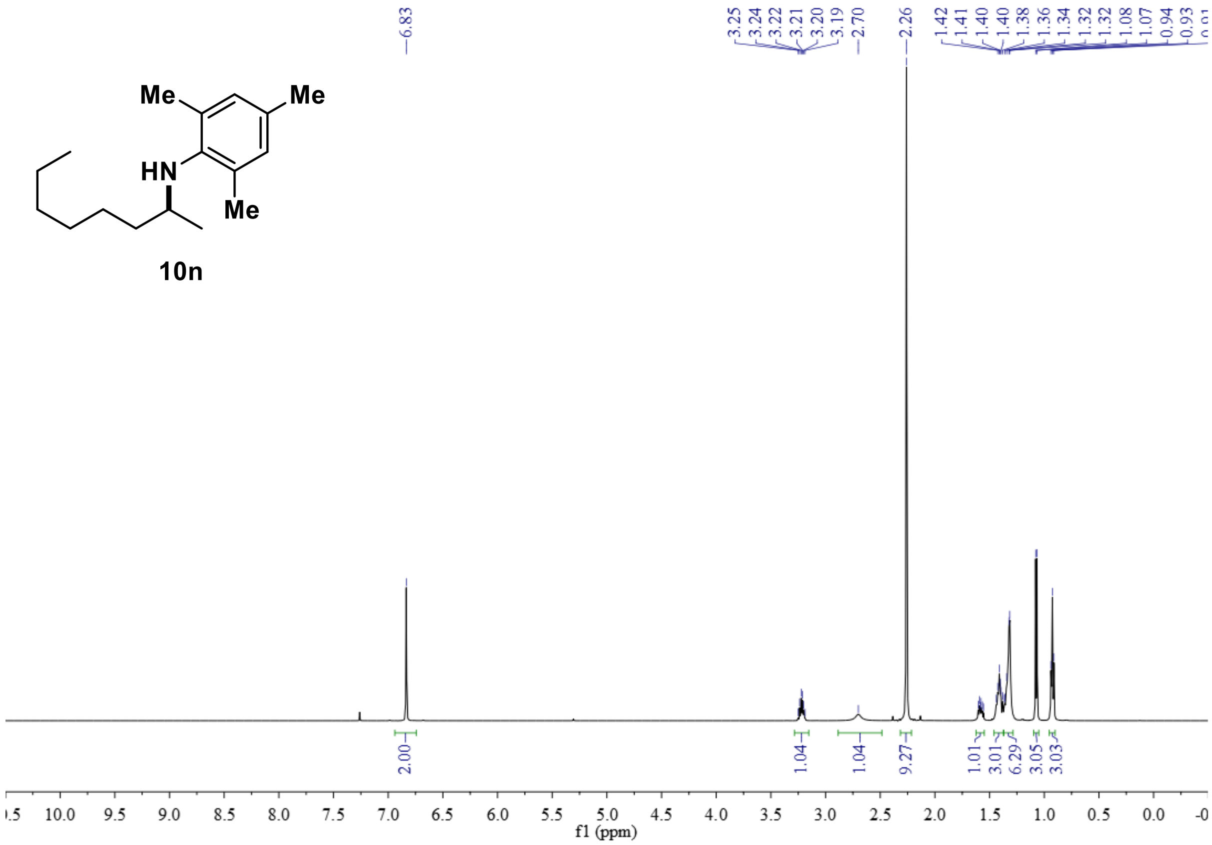


^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **10m**.

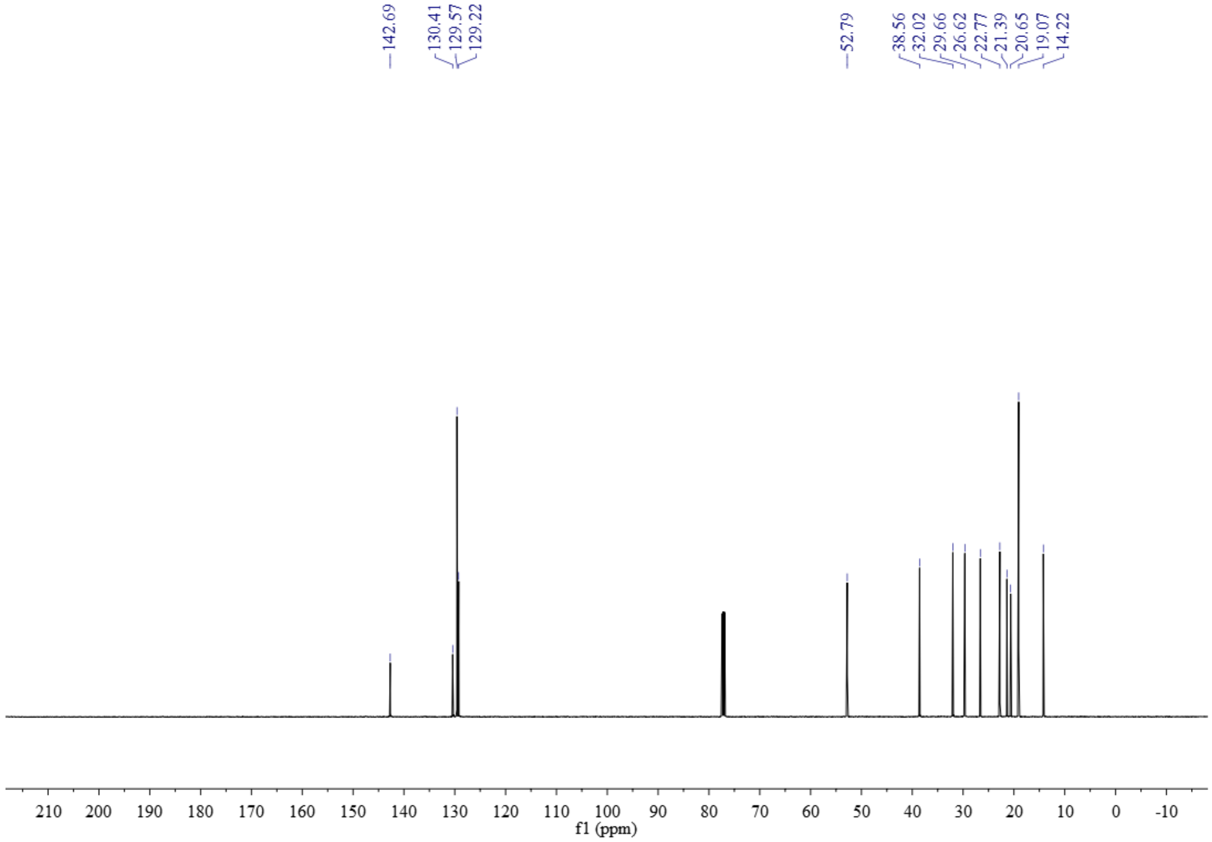


^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **10m**.

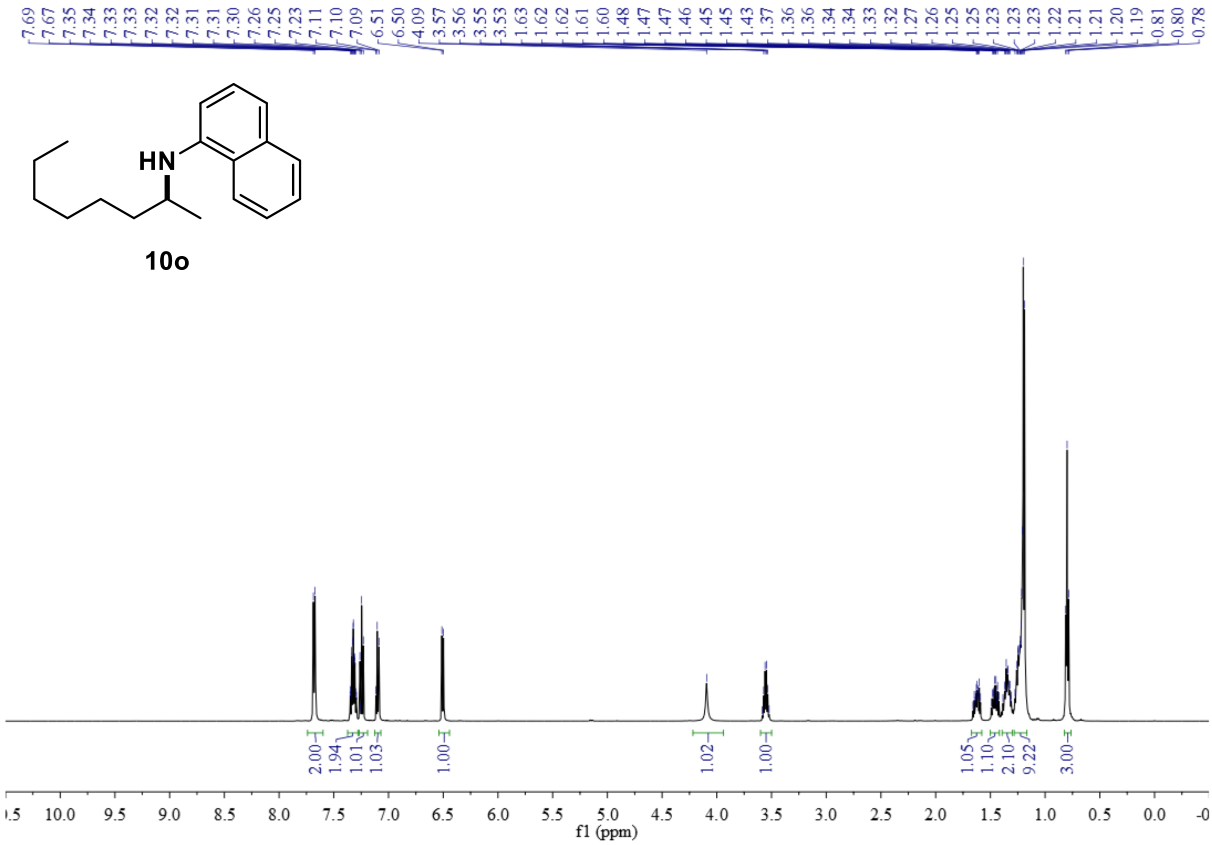
10n



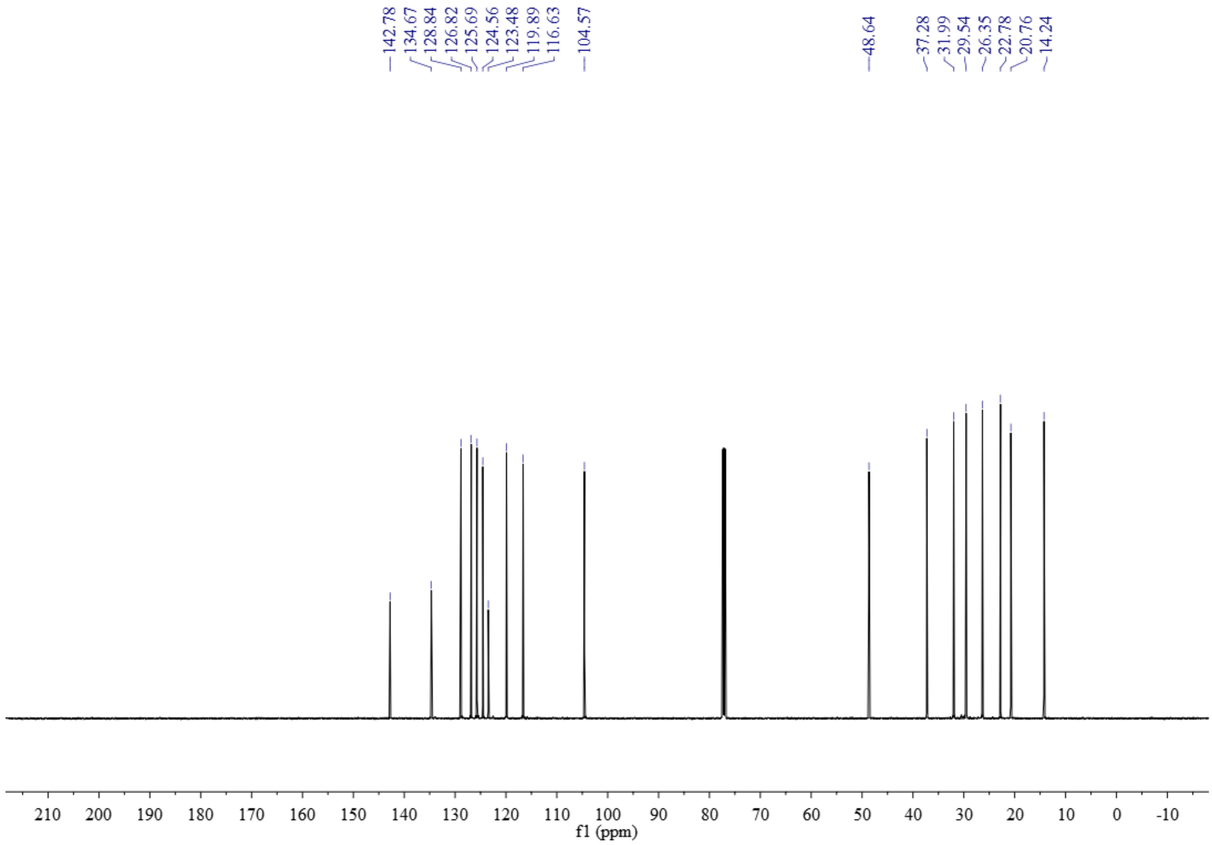
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **10n**.



^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **10n**.

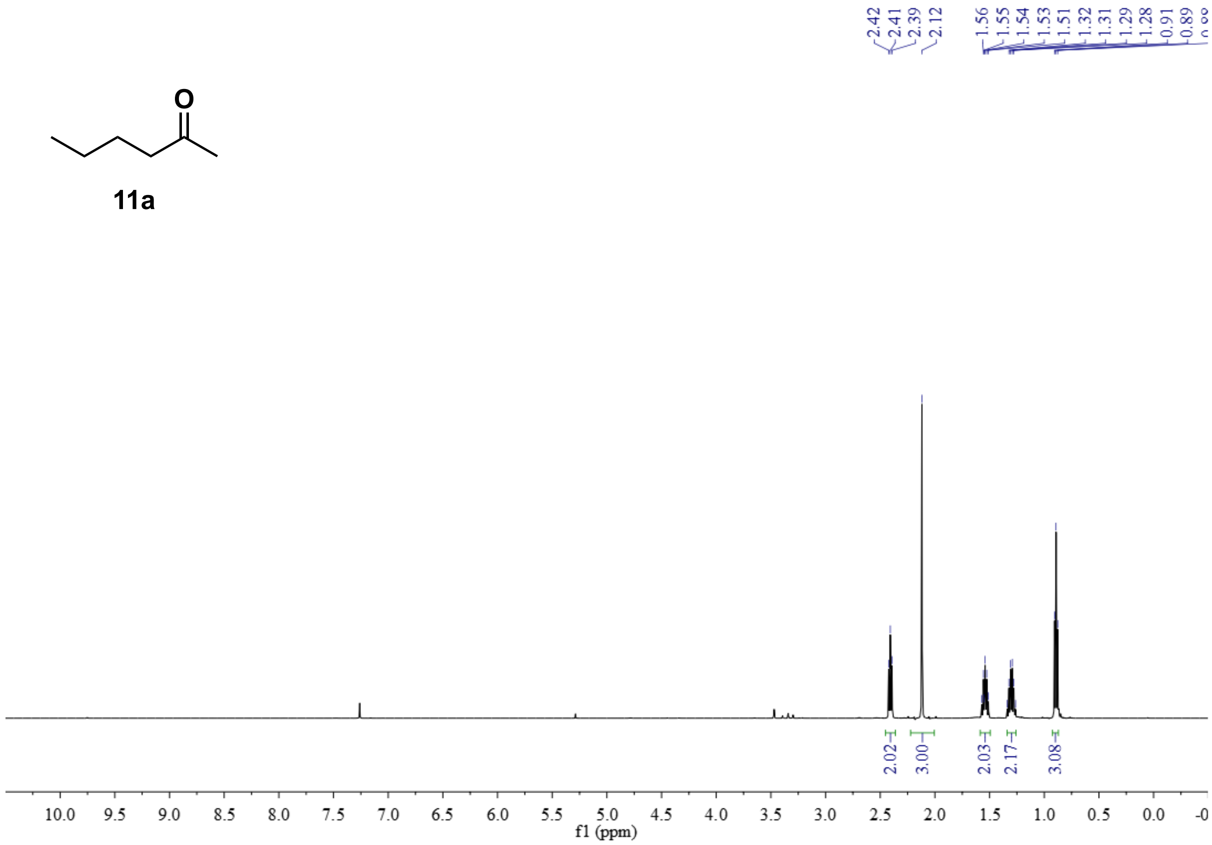


^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **10o**.

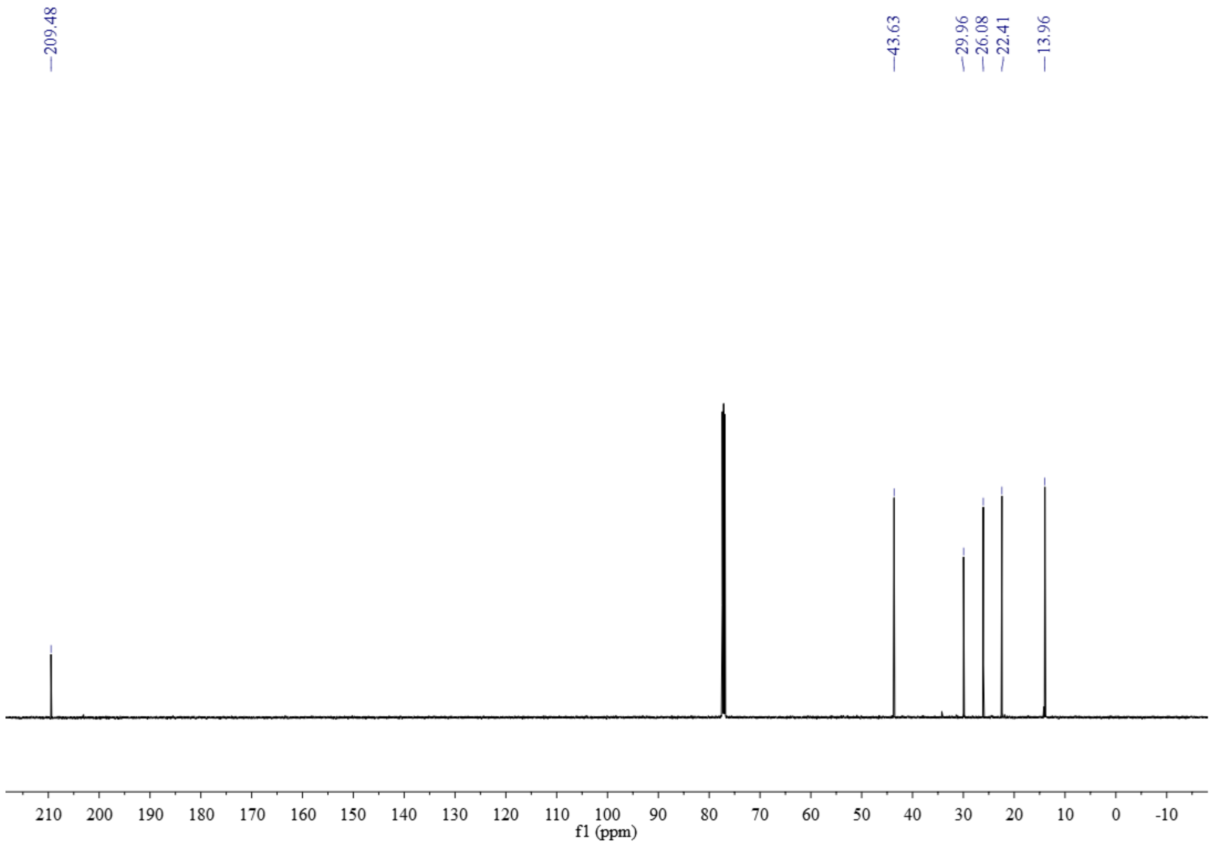


^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **10o**.

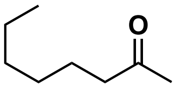
11a



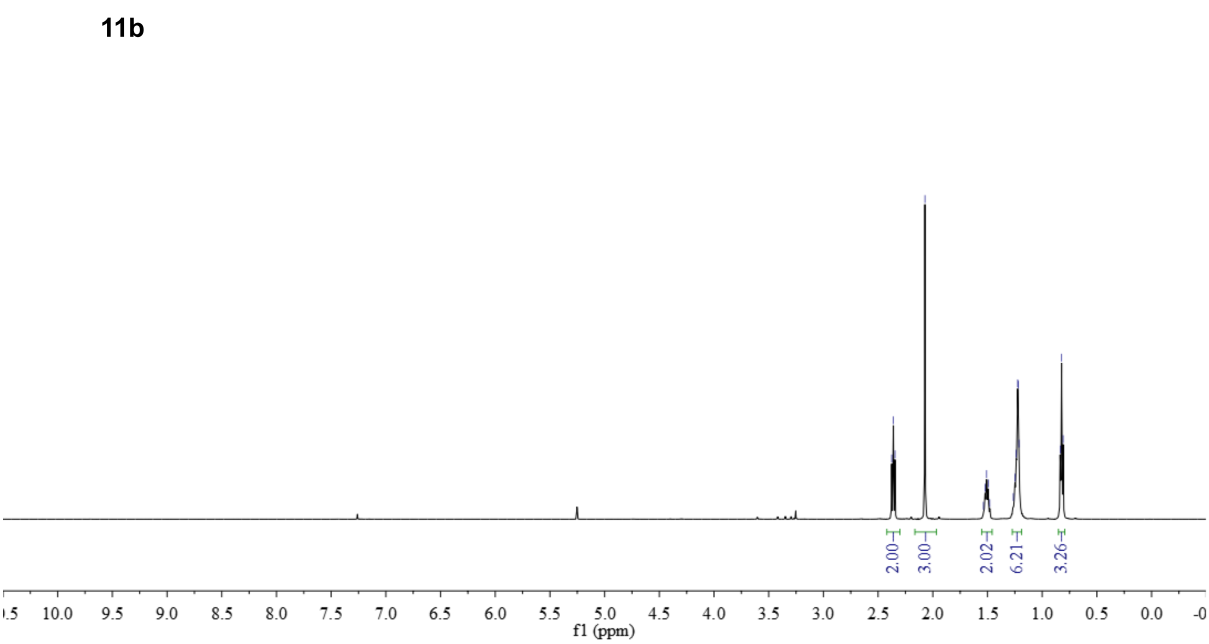
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **11a**.



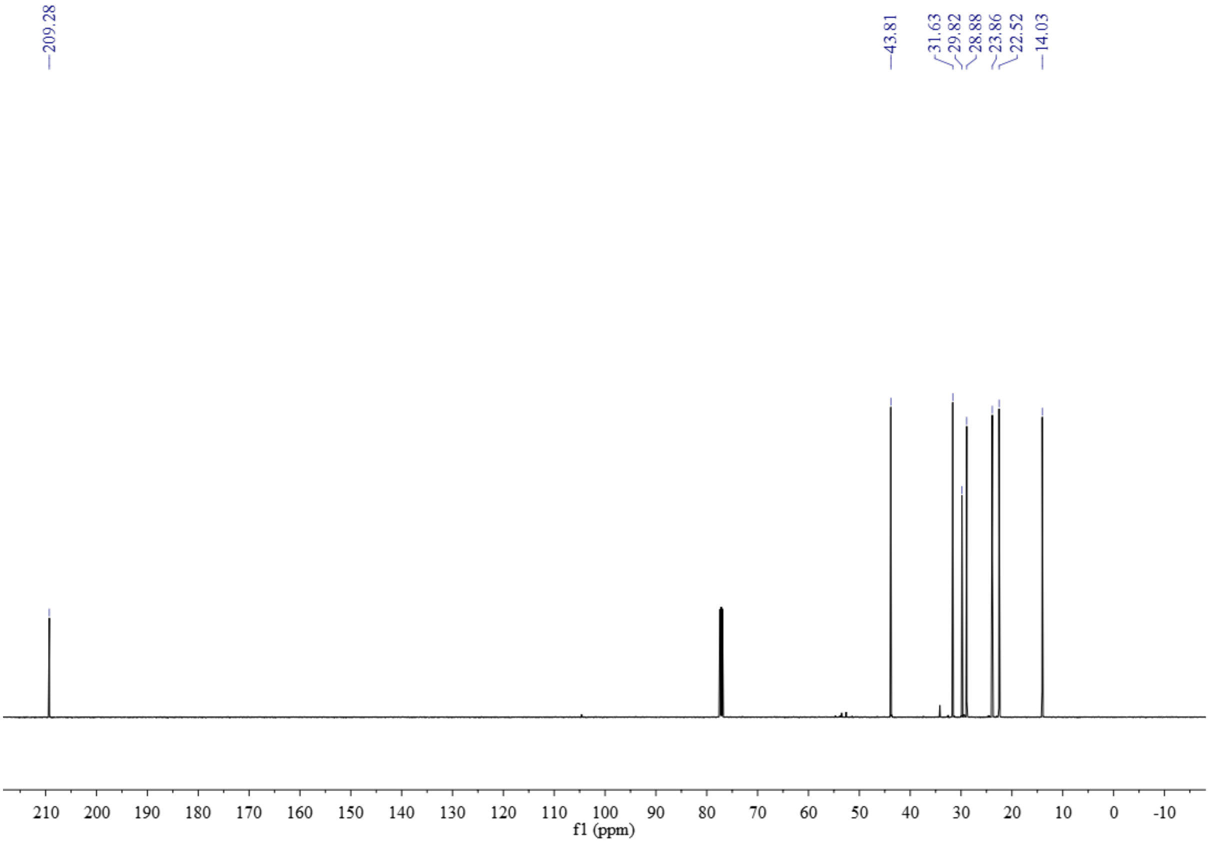
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **11a**.



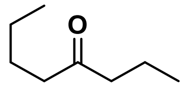
11b



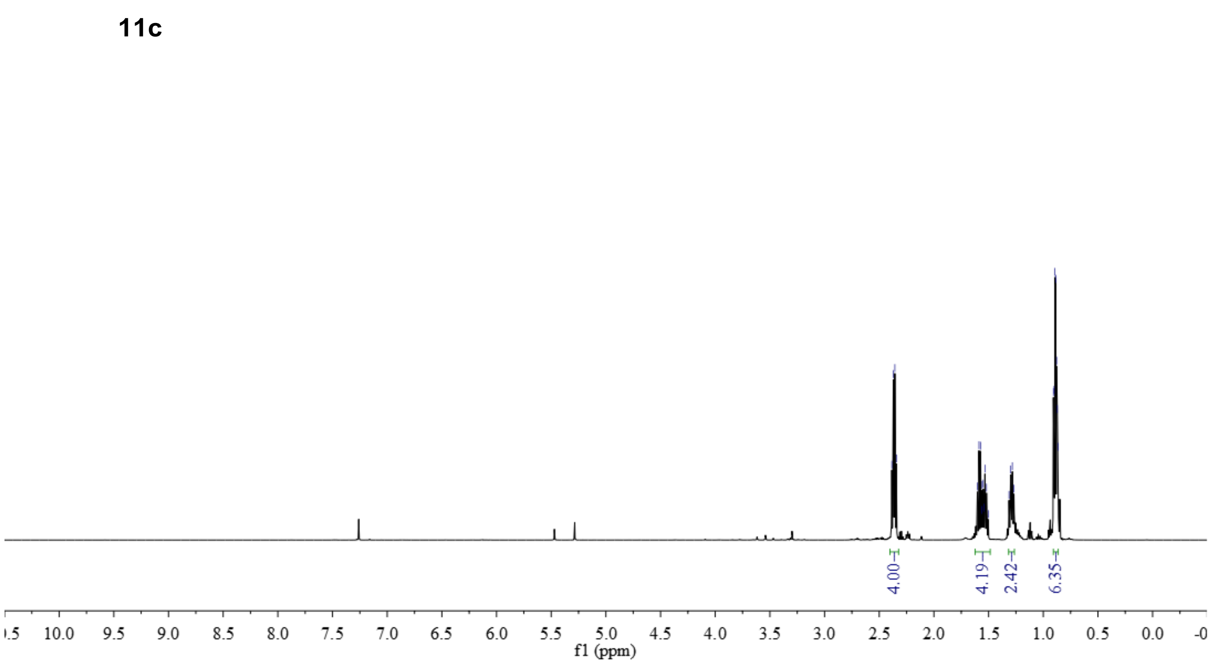
^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **11b**.



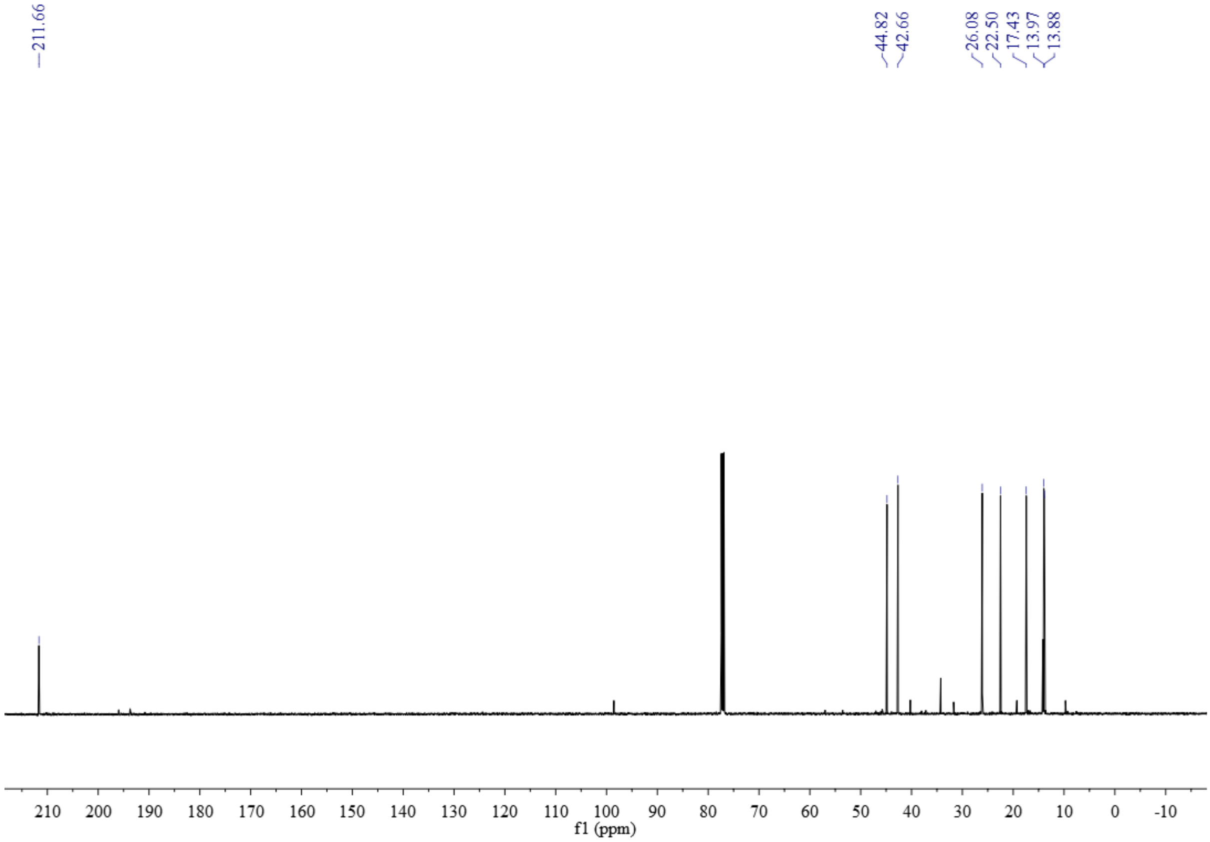
^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **11b**.



11c

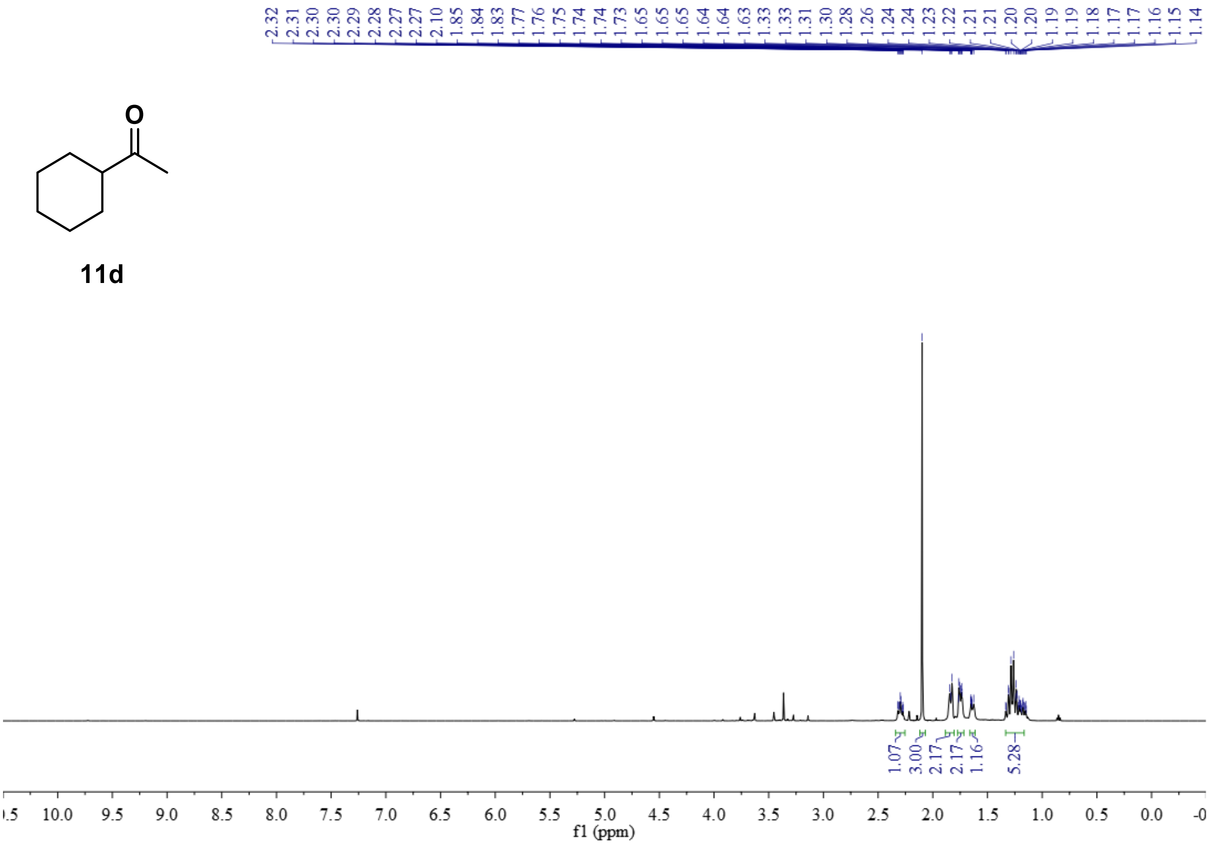


^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **11c**.

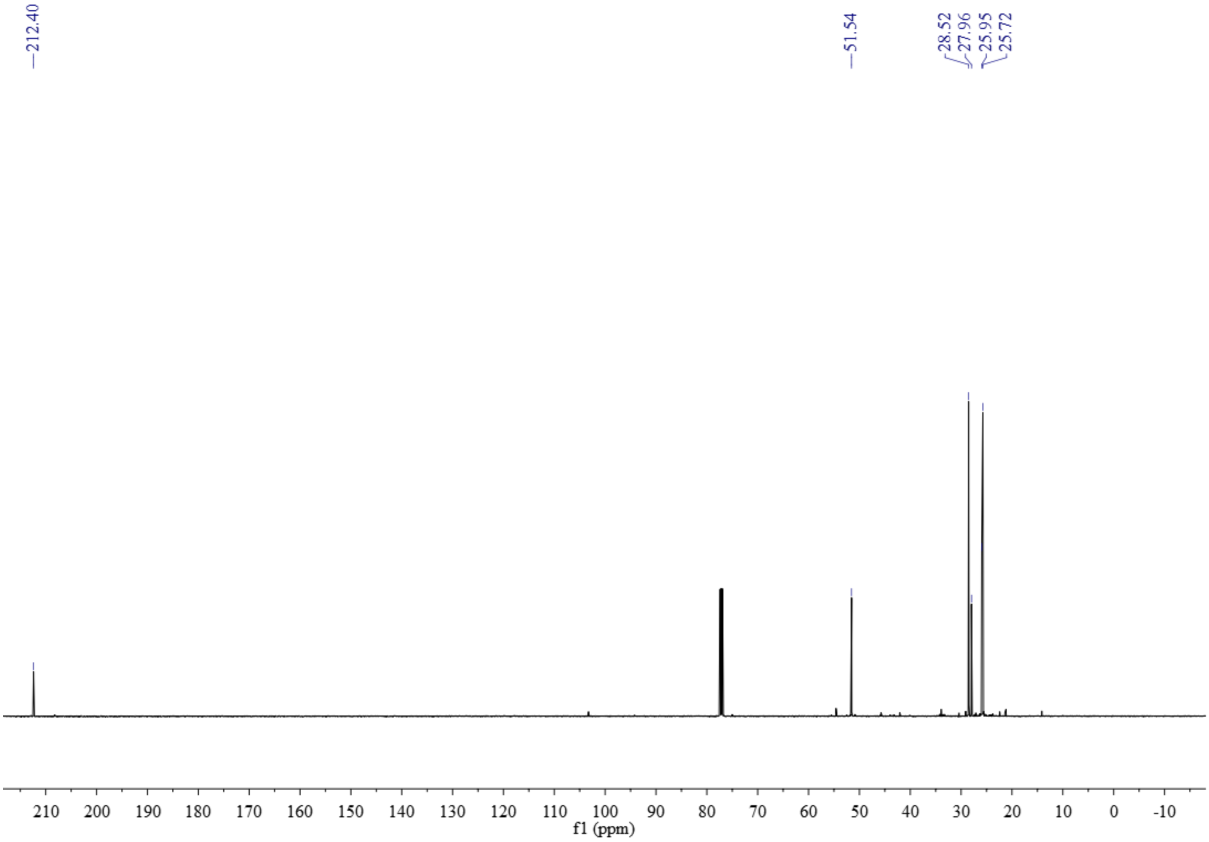


^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **11c**.

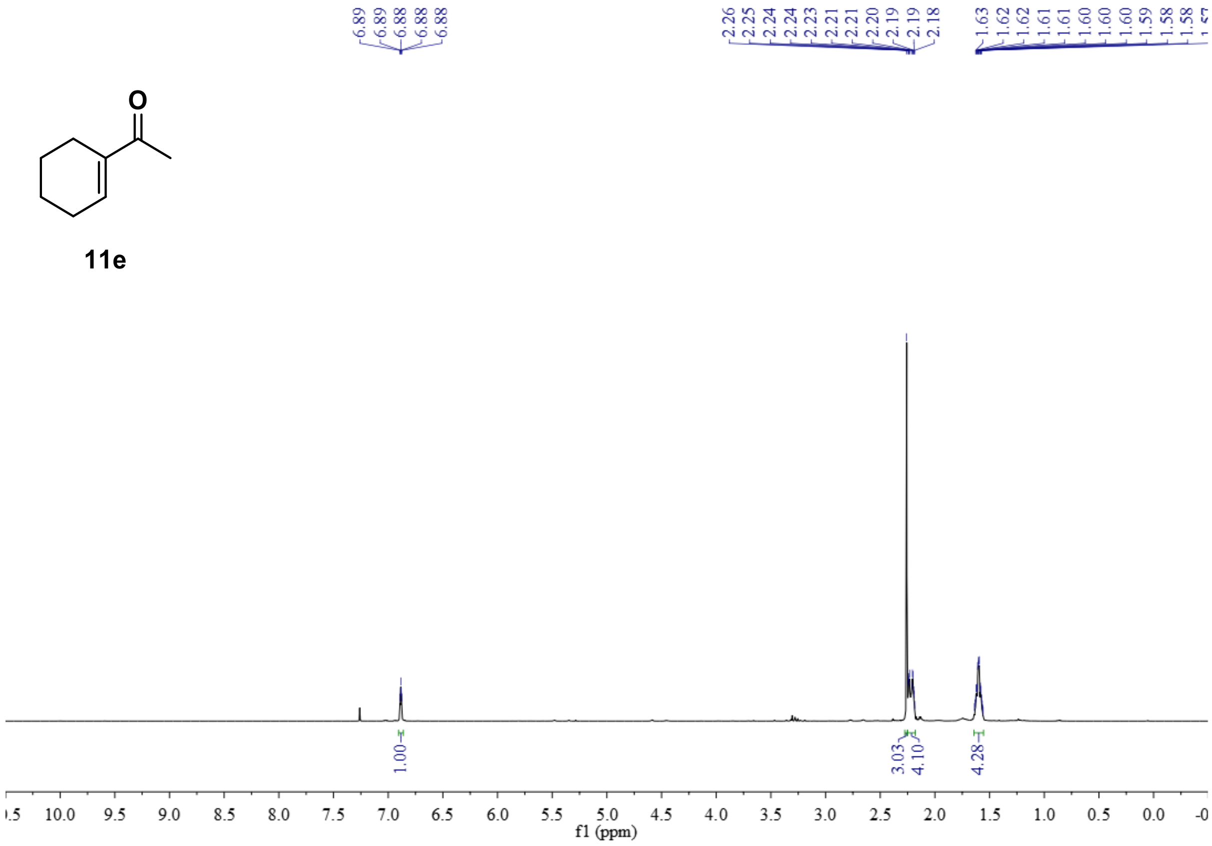
11d



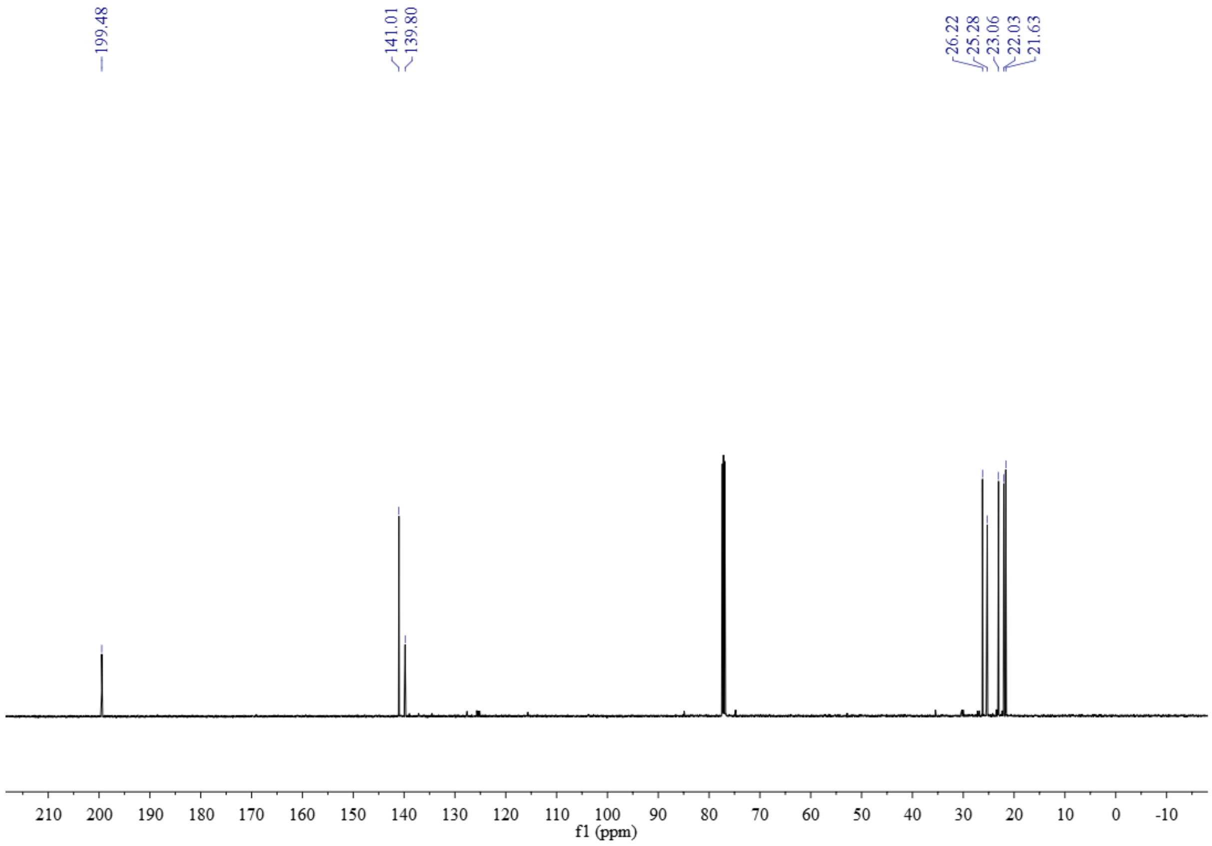
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **11d**.



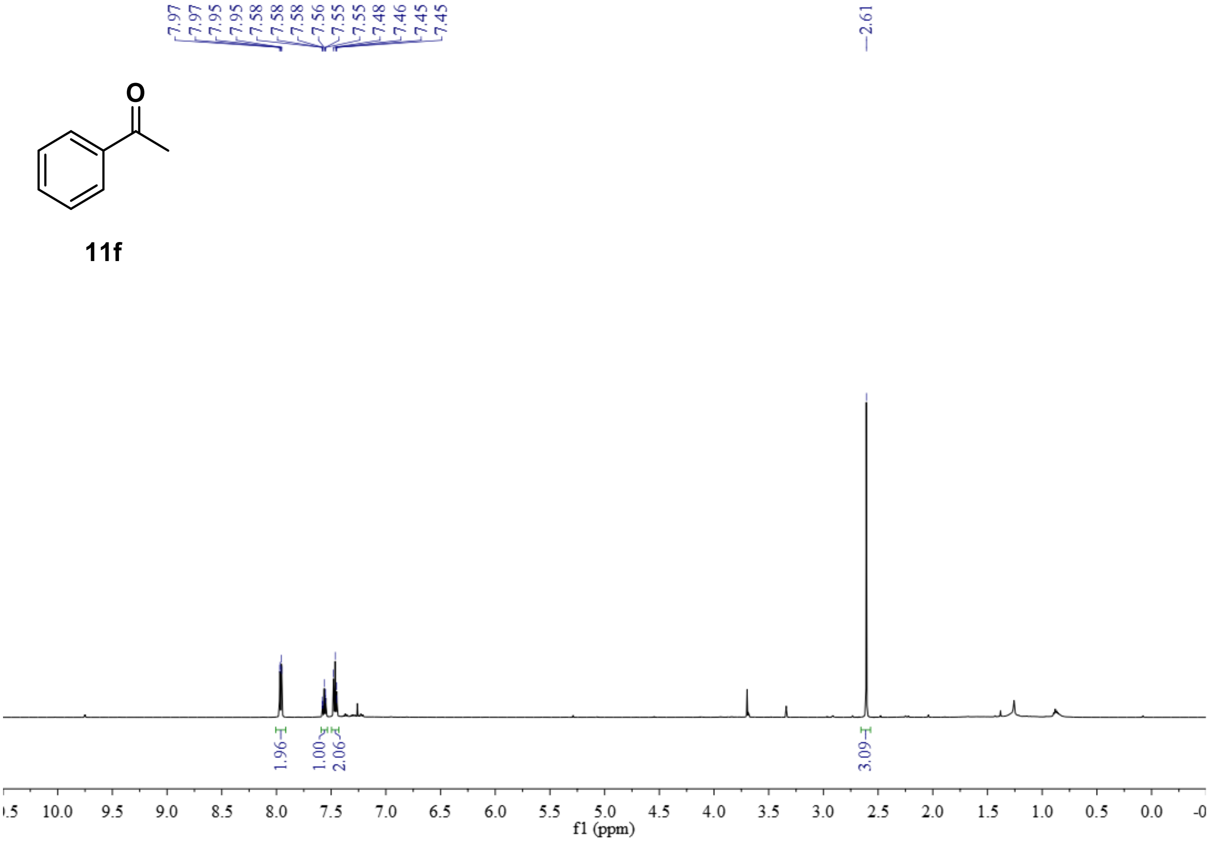
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **11d**.



^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **11e**.

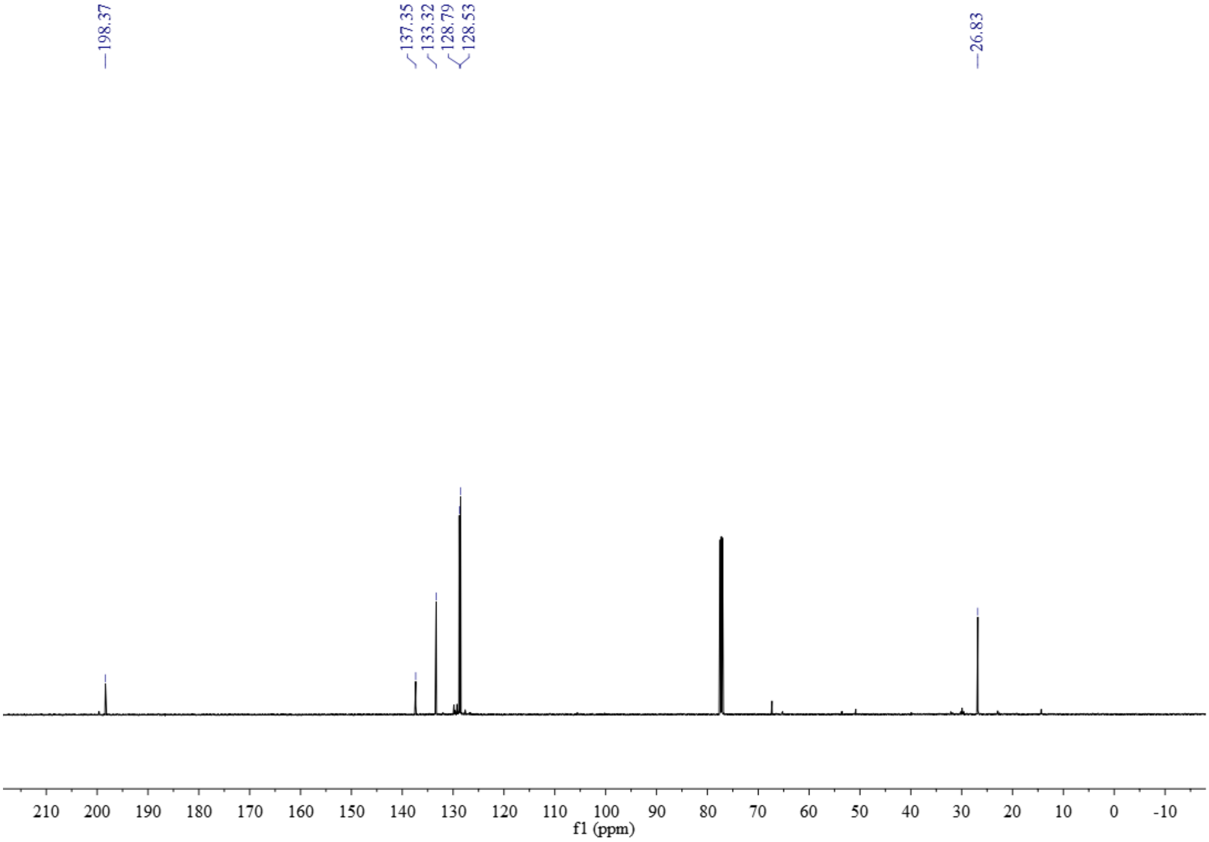


^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **11e**.

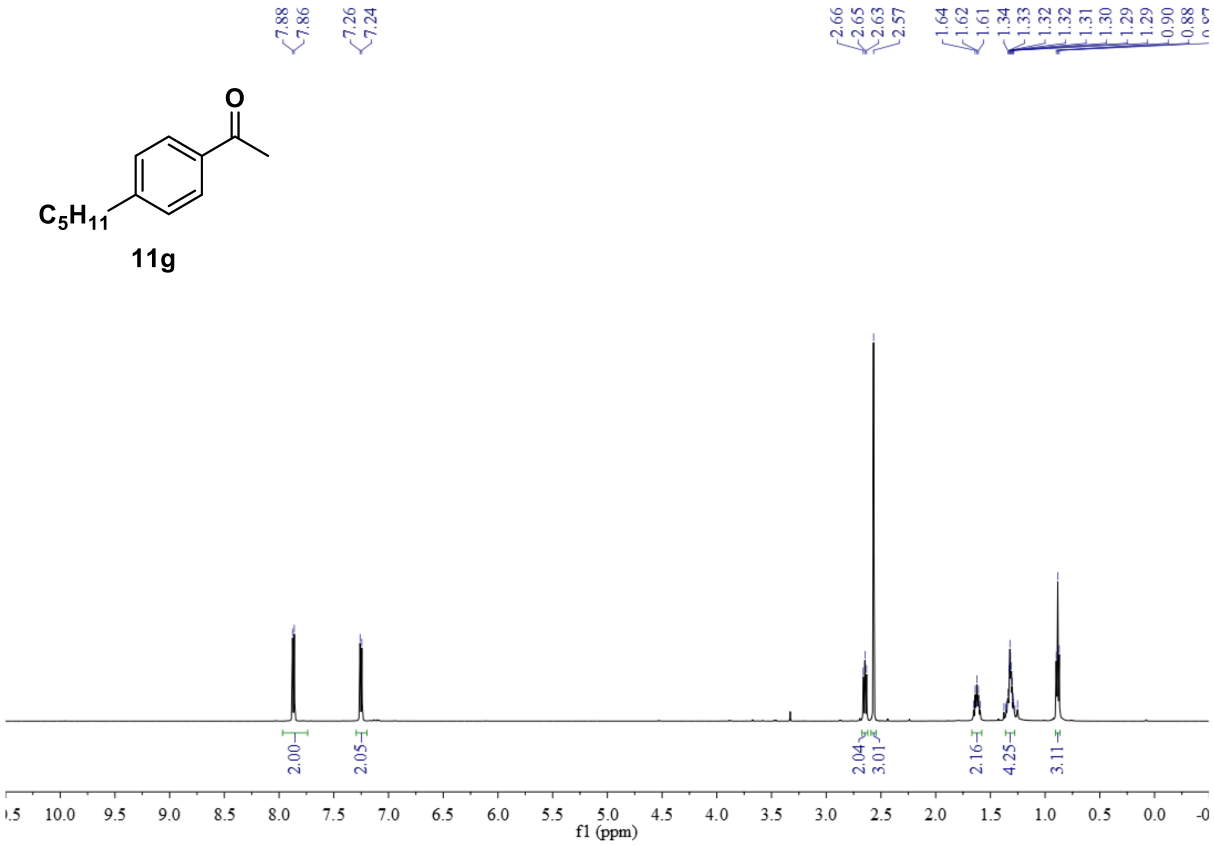


11f

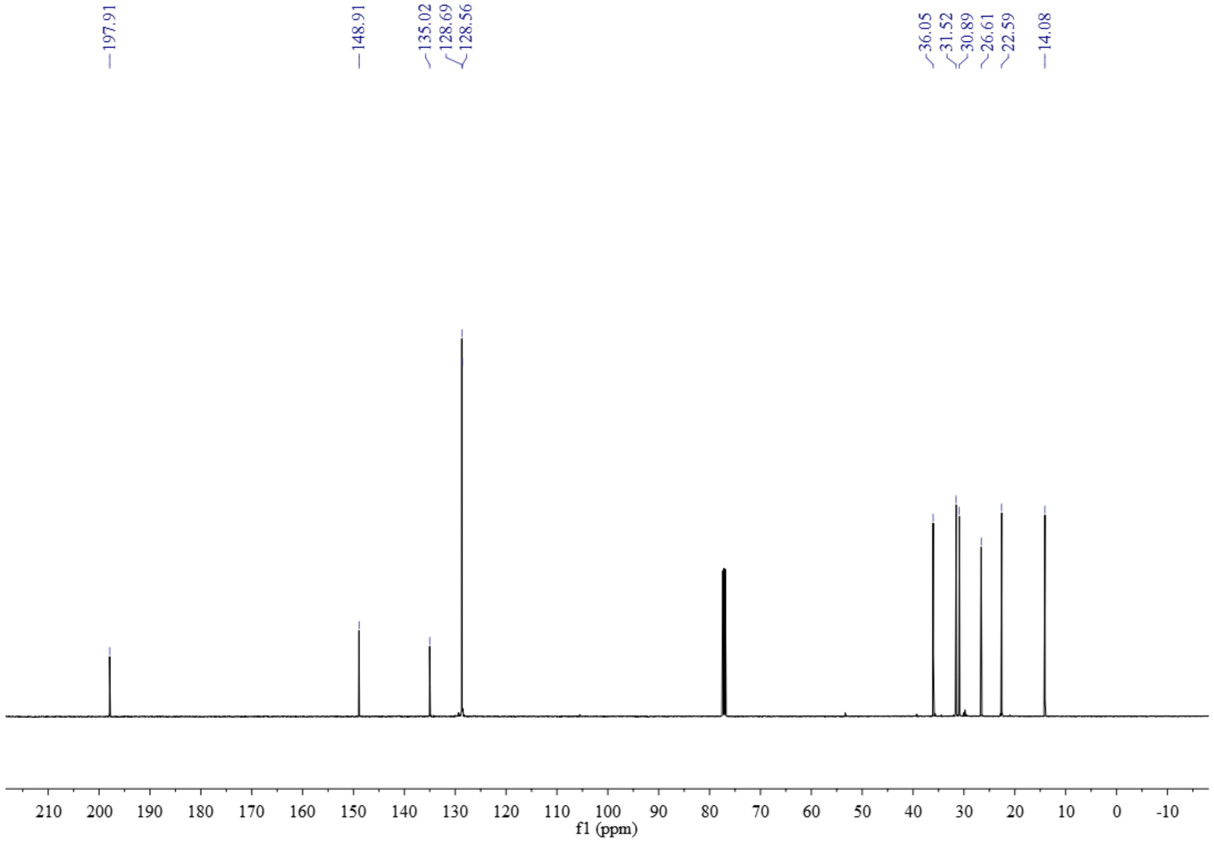
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **11f**.



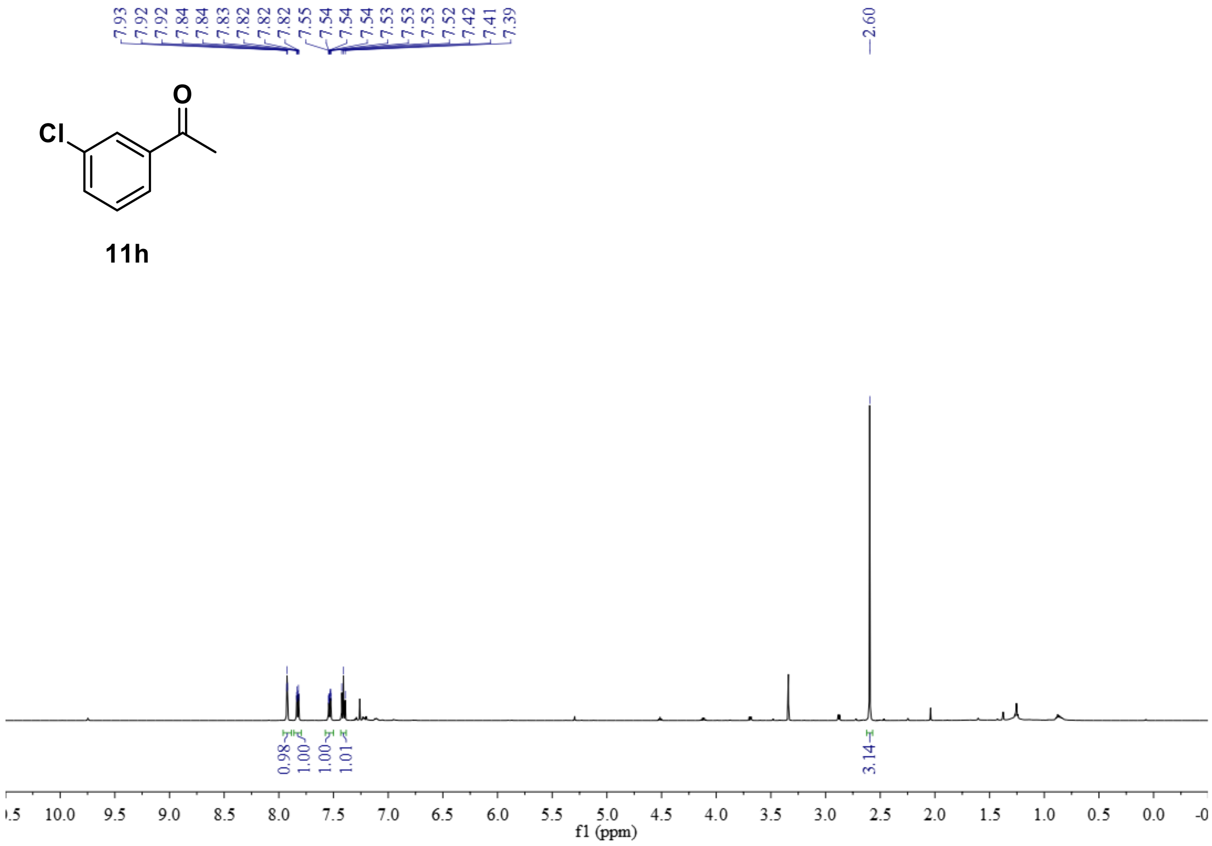
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **11f**.



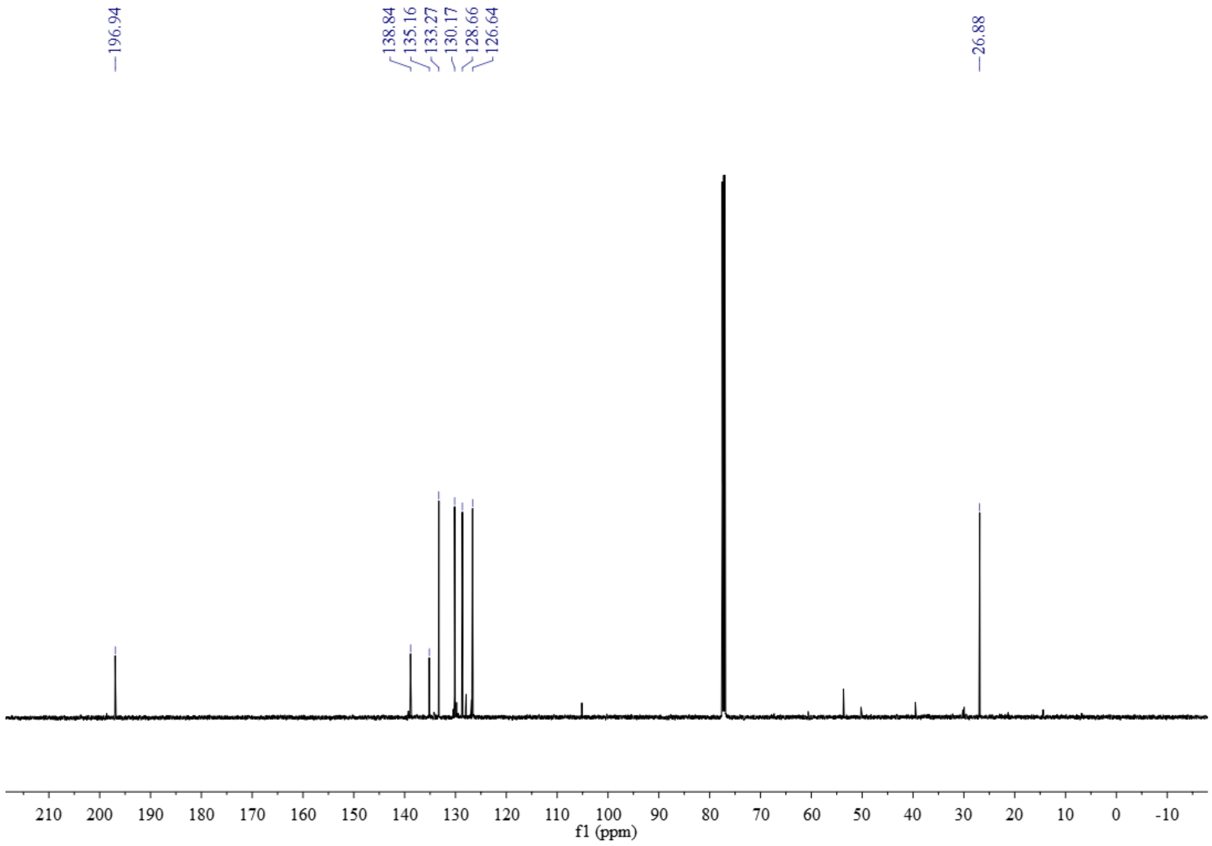
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **11g**.



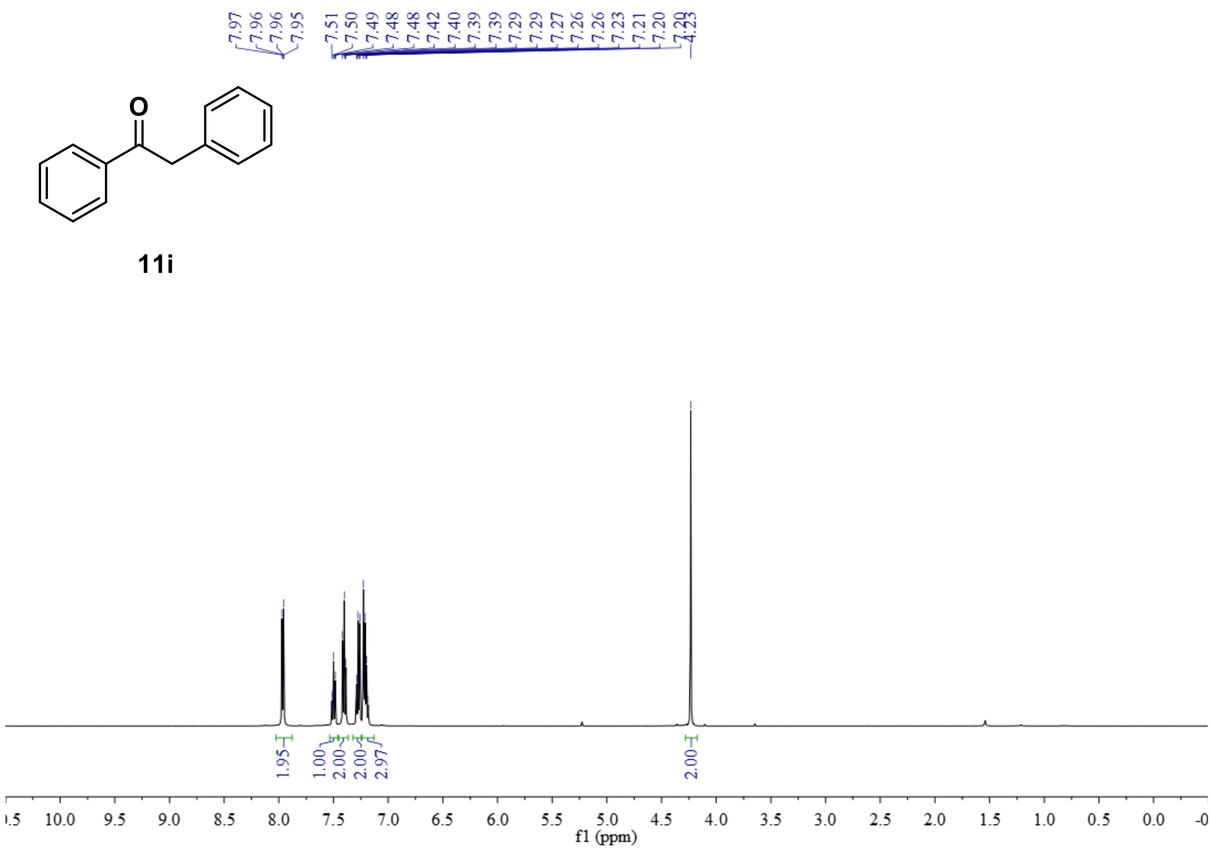
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **11g**.



^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of Compound **11h**.

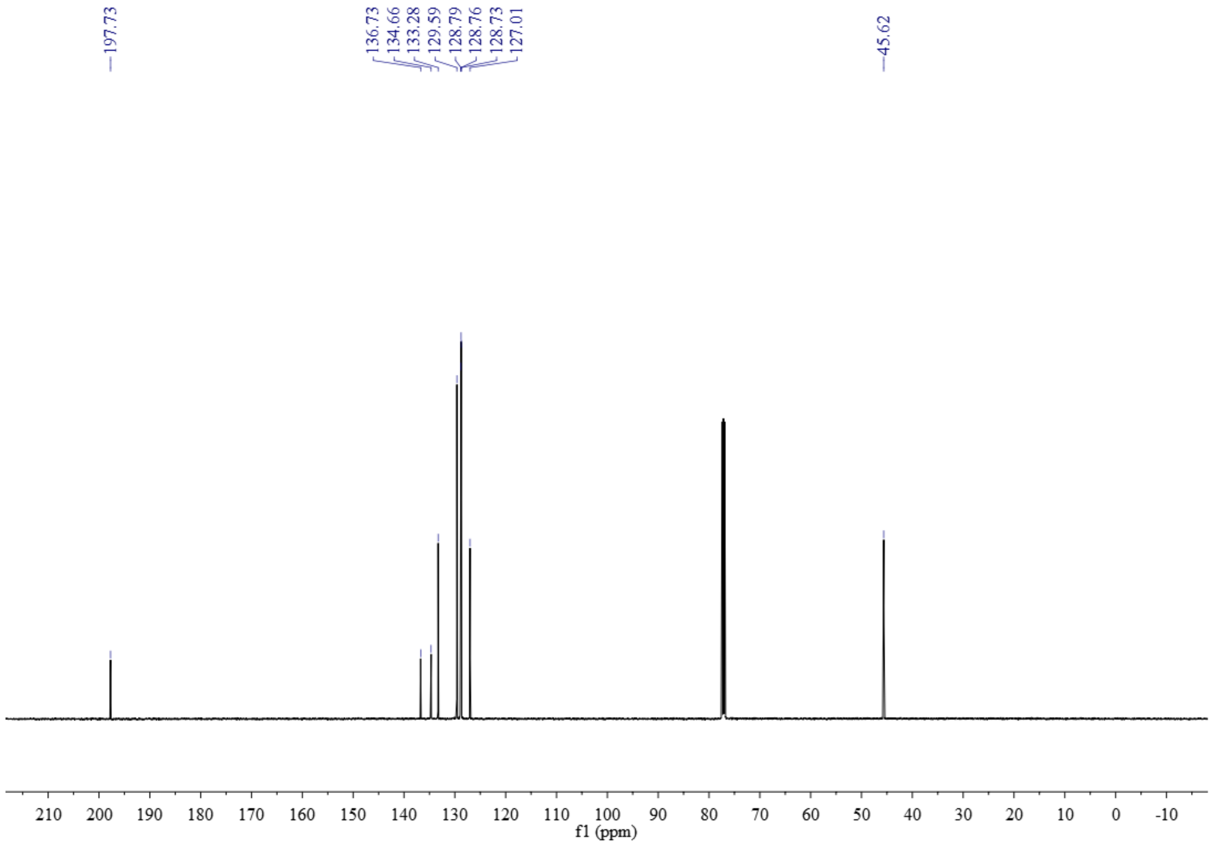


^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of Compound **11h**.



11i

^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **11i**.



^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **11i**.

[Au(Np#)Cl] anti

Energy: -4601.127345 au

Sum of electronic and thermal Energies: -4599.577268 au

Geometry:

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C	-0.00624100	0.07347600	0.17903700
C	-0.66342300	0.19323300	2.34960800
H	-1.36319500	0.28511800	3.16123900
C	0.68292100	0.07414900	2.34340400
H	1.39413200	0.02216100	3.14869500
C	-2.45714200	0.28569300	0.60934700
C	-3.13603200	-0.91513100	0.23805000
C	-2.48182900	-2.17247300	0.19558500
H	-1.43418100	-2.22476600	0.46141300
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C	-4.49370100	-3.23977000	-0.55592600
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C	-5.16477400	-2.04220300	-0.50886600
H	-6.21234800	-2.02468700	-0.77628900
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H	-0.47216400	-7.71984600	2.70094600
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H	-2.33490900	-7.52669000	4.33754400
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C	2.44093700	4.65300900	-2.57400700
H	2.91745700	3.68107200	-2.56198100
C	3.54059300	5.78818000	0.79547500
C	4.45742600	6.65583000	0.19334800
H	4.53386700	6.69057900	-0.88734600
C	5.26060400	7.49387300	0.96610700
H	5.96455300	8.16000100	0.47930600
C	5.15607900	7.48398300	2.35536600
H	5.77699000	8.13975500	2.95526400
C	4.24124100	6.62820300	2.96702100
H	4.14599500	6.61578400	4.04731800
C	3.44442000	5.78916600	2.19169100
H	2.73909200	5.12160200	2.67720000
Cl	0.00108300	-0.19693100	-4.12555300
Au	-0.00915200	-0.02886300	-1.82254900

[Au(Np#)Cl] syn

Energy: -4601.125764 au

Sum of electronic and thermal Energies: -4599.575343 au

Geometry:

N	1.15209500	-0.62068600	1.19950600
C	5.18522000	-0.12426700	-0.09989400
C	4.41416800	1.02269600	0.27796600
C	6.62818600	0.04838100	-0.58589700
H	7.08464000	0.80195100	0.06364400
C	3.79782300	-3.23894100	2.75206500
H	4.40990500	-2.36686400	2.55531700
C	3.26052100	-1.57944200	0.37957700
C	3.93996600	-3.91253700	3.96762900
H	4.65713000	-3.55328500	4.69767400
C	7.69585100	-2.13633300	-1.41921400
H	7.25671800	-1.97132500	-2.39587800
C	3.22203700	-3.86219600	-0.73495600
C	0.77923900	-0.59347300	2.54076600
H	1.50470000	-0.52063600	3.33161800
C	3.06124600	0.84450000	0.70985300
C	6.70980800	0.60792700	-2.01048700
C	7.48538100	-1.20645900	-0.39745100
C	4.60026100	-1.36638800	-0.03618800
H	5.17947500	-2.23416300	-0.32107500
C	2.88581600	-3.68128200	1.79099200
C	2.70272100	-3.00410400	0.42862500
H	1.62458300	-2.92349800	0.27257400
C	4.22341700	-4.82368000	-0.57297600
H	4.65058200	-5.00087500	0.40698600
C	1.98373700	4.43691000	1.54009700
H	0.94559700	4.17262700	1.31223600

C	2.51479800	-0.47530100	0.74004700
C	2.27087900	5.71898500	0.74839600
C	2.03819600	4.62310800	3.05791300
C	5.71666700	0.38013100	-2.96643200
H	4.83078200	-0.18616300	-2.70429600
C	3.20351000	4.40958600	3.80138900
H	4.10659700	4.07366100	3.30515300
C	3.17331700	-5.04128500	4.24003600
H	3.28753200	-5.56700000	5.18141300
C	2.11680700	-4.81786500	2.07916800
H	1.41298600	-5.18595100	1.33926200
C	8.47431500	-3.27272000	-1.19884600
H	8.62376300	-3.98258500	-2.00480100
C	0.88466200	5.03841200	3.73371600
H	-0.03030000	5.20839900	3.17522600
C	7.83426600	1.35607800	-2.38071100
H	8.61776900	1.53932900	-1.65148800
C	8.86313600	-2.57039100	1.07031300
H	9.32111500	-2.72748700	2.04082200
C	9.06062800	-3.49458600	0.04480500
H	9.67063700	-4.37506500	0.21295800
C	2.25850200	-5.49317300	3.28738100
H	1.65839200	-6.37503200	3.48409300
C	2.86013000	6.85063900	1.31616000
H	3.12440800	6.85133900	2.36661700
C	2.68322100	-3.66476700	-2.01251500
H	1.90731800	-2.92091000	-2.16361600
C	2.06403400	5.03030200	5.84207400
H	2.07439200	5.18500500	6.91520800
C	2.16791500	6.89215200	-1.37967600
H	1.89129000	6.89924900	-2.42806500

C	1.92799900	5.75788500	-0.61056600
H	1.47618700	4.88623900	-1.07365700
C	3.21779800	4.61403600	5.18094800
H	4.13197700	4.44294900	5.73901200
C	4.67658700	-5.56908500	-1.66205100
H	5.45392800	-6.31110000	-1.51578100
C	0.89504200	5.24041700	5.11228200
H	-0.01159300	5.55877800	5.61500100
C	8.08277600	-1.43882000	0.84758100
H	7.93645400	-0.72282700	1.65087900
C	7.96470700	1.86198700	-3.67096300
H	8.84211400	2.44157800	-3.93642500
C	0.05649700	-0.71716000	0.39339600
C	2.76107500	8.01574900	-0.80217400
H	2.94911300	8.90138900	-1.39863300
C	3.10552800	7.98972300	0.54586700
H	3.56401400	8.85798400	1.00663100
C	5.84499100	0.88458100	-4.26127700
H	5.05987900	0.69960700	-4.98579600
C	6.96793500	1.62634800	-4.61809400
H	7.06484500	2.02220200	-5.62278100
C	4.13318500	-5.36570800	-2.92800200
H	4.48254100	-5.94870200	-3.77302100
C	3.13323600	-4.40863100	-3.09989000
H	2.69771400	-4.23869200	-4.07812000
N	-1.00210300	-0.76315900	1.25486900
C	-5.04910400	-1.28320400	-0.00247000
C	-4.31960000	-2.30665500	0.56141000
H	-4.77708800	-3.28562100	0.64738100
C	-6.47275500	-1.62251700	-0.46462000
H	-6.70125600	-2.56255600	0.04945600

C	-3.84856300	4.74640900	1.39644900
H	-4.49729700	3.88286200	1.31763300
C	-3.08001400	0.18010600	0.30562800
C	-4.11197700	5.70896600	2.37390300
H	-4.96409800	5.58155300	3.03273600
C	-8.49894400	-0.05504000	-0.79744400
H	-8.47154200	-0.24999300	-1.86251500
C	-2.59622500	4.41301300	-1.98610000
C	-0.56933000	-0.67984000	2.57550800
H	-1.25594000	-0.70853200	3.40288600
C	-2.98106900	-2.17002900	0.99990400
C	-6.57447500	-1.97125700	-1.95386300
C	-7.55349400	-0.64982300	0.04193300
C	-4.43114100	0.00128300	-0.13997600
C	-2.76035500	4.88402900	0.53124200
C	-2.41981400	3.86644600	-0.56251900
H	-1.35003400	3.65665200	-0.45317200
C	-3.45076900	5.47622200	-2.28836500
H	-3.99184400	5.97645100	-1.49368500
C	-2.25763700	-3.36882100	1.61493800
H	-1.18699400	-3.18940400	1.49187300
C	-2.37912800	-0.93570100	0.85317300
C	-2.54670500	-4.66267200	0.83994400
C	-2.48674300	-3.49278200	3.12525100
C	-5.70187200	-1.47884000	-2.92773600
H	-4.89234600	-0.81540300	-2.65366600
C	-3.67031600	-3.09279800	3.75334000
H	-4.46949900	-2.65148300	3.17046300
C	-3.28864200	6.82303300	2.50510800
H	-3.49394800	7.57025200	3.26357900
C	-1.93490000	6.00844600	0.67799800

H	-1.08424400	6.13776700	0.01667400
C	-9.48108200	0.79235700	-0.28135000
H	-10.20184700	1.24556700	-0.95318700
C	-1.47075100	-4.04333500	3.91677200
H	-0.53931500	-4.34982900	3.45308600
C	-7.58350200	-2.85754500	-2.35660500
H	-8.26372700	-3.26321700	-1.61387700
C	-8.60598300	0.45925800	1.93351400
H	-8.64171500	0.65072600	3.00051000
C	-9.53928700	1.05427600	1.08428800
H	-10.30324800	1.71113800	1.48466500
C	-2.19354500	6.96810600	1.65187700
H	-1.53945100	7.82807500	1.74466700
C	-3.27725400	-5.72505900	1.37631300
H	-3.65818800	-5.66288900	2.38863200
C	-1.89974600	3.79486900	-3.03295900
H	-1.24291200	2.95657100	-2.82269200
C	-2.82044500	-3.79855800	5.90516600
H	-2.94879000	-3.91401900	6.97551400
C	-2.28974800	-5.92688200	-1.21870800
H	-1.90036400	-5.99569400	-2.22815400
C	-2.05480700	-4.77988700	-0.46744900
H	-1.49244300	-3.96113600	-0.90576900
C	-3.83708000	-3.24574300	5.13077300
H	-4.76376000	-2.92851800	5.59645700
C	-3.60690300	5.91124100	-3.60552900
H	-4.27411000	6.73890400	-3.82066800
C	-1.63286700	-4.19592200	5.29115200
H	-0.82889600	-4.62003900	5.88253000
C	-7.62677000	-0.38282000	1.41553800
H	-6.90358400	-0.83537700	2.08621600

C	-7.72896400	-3.22609600	-3.69061700
H	-8.51623800	-3.91530500	-3.97596400
C	-3.02395300	-6.98173900	-0.67496300
H	-3.20835100	-7.87634600	-1.25903200
C	-3.51577000	-6.87644500	0.62260600
H	-4.08521100	-7.69128400	1.05634900
C	-5.84251100	-1.84900100	-4.26635800
H	-5.14628900	-1.46009600	-5.00078100
C	-6.85724900	-2.71882700	-4.65419800
H	-6.96225600	-3.00857000	-5.69366500
C	-2.90819100	5.29109200	-4.63795700
H	-3.02825600	5.63089200	-5.66062100
C	-2.05194100	4.22878800	-4.34659600
H	-1.50420100	3.73356000	-5.14046900
C	4.92471500	2.34611700	0.23832700
C	4.16535100	3.42549900	0.62082900
C	2.83363600	3.25651600	1.06627400
C	2.30586500	1.98317200	1.09032400
H	5.93005000	2.52036500	-0.12031200
H	4.58601700	4.42237600	0.56197000
H	1.28355200	1.84816900	1.42151500
C	-2.47195100	1.45586900	0.16722900
C	-3.12605400	2.52220900	-0.40690700
C	-4.45076300	2.33015400	-0.86851300
C	-5.07987700	1.11931900	-0.72996500
H	-1.45274900	1.58625000	0.50709100
H	-4.97161900	3.14865900	-1.35128300
H	-6.09203700	1.01362500	-1.08991900
Cl	-0.02303900	-0.78659500	-3.92221700
Au	0.01152100	-0.75483000	-1.61124900