Strong and Confined Acids Catalyze Asymmetric Intramolecular Hydroarylations of Unactivated Olefins with Indoles

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1. General information

Unless otherwise stated, all reactions were magnetically stirred and conducted in oven-dried (80 °C) or flame-dried glassware in anhydrous solvents under Ar, applying standard Schlenk techniques. Solvents and liquid reagents, as well as solutions of solid or liquid reagents were added via syringes, stainless steel or polyethylene cannulas through rubber septa or through a weak Ar counter-flow. Solid reagents were added through a weak Ar counter-flow. Cooling baths were prepared in Dewar vessels, filled with ice/water (0 °C), cooled acetone (> -78 °C) or dry ice/acetone (-78 °C). Heated oil baths were used for reactions requiring elevated temperatures. Solvents were removed under reduced pressure at 40 °C using a rotary evaporator, and unless otherwise stated, the remaining compound was dried in high vacuum (10^{-3} mbar) at ambient temperature. All given yields are isolated yields of chromatographically and NMR spectroscopically pure materials, unless otherwise stated.

Chemicals
Chemicals were purchased from commercial suppliers (including abcr, Acros, Alfa Aesar, Fluorochem, TCI and Sigma-Aldrich) and used without further purification unless otherwise stated.

Solvents
Solvents (CH_2Cl_2, $CHCl_3$, Et_2O, THF, toluene) were dried by distillation from an appropriate drying agent in the technical department of the Max-Planck-Institut für Kohlenforschung and received in Schlenk flasks under argon. In addition, more solvents (acetone, benzene, cyclohexane, methylcyclohexane, 1,4-dioxane, DMF, DMSO, EtOAc, EtOH, MeCN, MeOH, MTBE, *n*-hexane, *n*-heptane, *n*-pentane, methylene) were purchased from commercial suppliers and dried over molecular sieves.

Inert Gas
Dry argon was purchased from Air Liquide with > 99.5% purity.

Thin Layer chromatography
Thin-layer chromatography (TLC) was performed using silica gel pre-coated glass plates (SIL G-25, with fluorescent indicator UV254; Macherey-Nagel) and aluminium oxide pre-coated plastic sheets (Polygram AlOx N, 0.2 mm, with fluorescent indicator UV254; Macherey-Nagel), which were visualized by irradiation with UV light (λ = 254 or 366 nm), basic $KMnO_4$, and/or phosphomolybdic acid (PMA). Preparative thin-layer chromatography was performed on silica gel pre-coated glass plates SIL G-100, with fluorescent indicator UV254 (Macherey-Nagel).

Column Chromatography
Column chromatography (CC) was carried out using Merck silica gel (60 Å, 230−400 mesh, particle size 0.040−0.063 mm) using technical grade solvents. Elution was accelerated using compressed air. All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds.

Nuclear Magnetic Resonance Spectroscopy
^{1}H, ^{13}C, ^{19}F, ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-500, AV-400 spectrometer in a suitable deuterated solvent. The solvent employed and respective measuring frequency are indicated for each experiment. Chemical shifts are reported with

tetramethylsilane (TMS) serving as a universal reference of all nuclides and with two or one digits after the comma. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and bs (broad singlet). All spectra were recorded at 298 K unless otherwise noted, processed with program MestReNova 14.0, and coupling constants are reported as observed. The residual deuterated solvent signal relative to tetramethylsilane (TMS) was used as the internal reference in ^{1}H NMR spectra ($CDCl_3$ δ 7.26, CD_2Cl_2 δ 5.32, C_6D_6 δ 7.16, CD_3OD δ 3.31), and are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant *J* in Hz, number of protons). ^{13}C NMR spectra reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.2, CD_2Cl_2 δ 53.8, C_6D_6 δ 128.1, CD_3OD δ 49.0). All spectra are broadband decoupled unless otherwise noted.

Mass Spectrometry

Electron impact (EI) mass spectrometry (MS) was performed on a Finnigan MAT 8200 (70 eV) or MAT 8400 (70 eV) spectrometer. Electrospray ionization (ESI) mass spectrometry was conducted on a Bruker ESQ 3000 spectrometer. High resolution mass spectrometry (HRMS) was performed on a Finnigan MAT 95 (EI) or Bruker APEX III FTMS (7T magnet, ESI). The ionization method and mode of detection employed is indicated for the respective experiment and all masses are reported in atomic units per elementary charge (m/z) with an intensity normalized to the most intense peak.

High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AD liquid chromatograph (SIL-20AC auto sampler, CMB-20A communication bus module, DGU-20A5 degasser, CTO-20AC column oven, SPD-M20A diode array detector), Shimadzu LC-20AB liquid chromatograph (SIL-20ACHT auto sampler, DGU-20A5 degasser, CTO-20AC column oven, SPD-M20A diode array detector), or Shimadzu LC-20AB liquid chromatograph (reversed phase, SIL-20ACHT auto sampler, CTO-20AC column oven, SPD-M20A diode array detector) using Daicel columns with a chiral stationary phase. All solvents used were HPLC-grade solvents purchased from Sigma-Aldrich. The column employed and respective solvent mixture are indicated for each experiment.

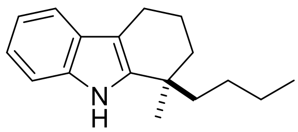
2. General procedure of the asymmetric hydroarylations

The initial screening conditions including concentration and solvents were originated from our recent paper in enantioselective hydroalkoxylations of unactived olefins.[1] Catalysts and temperature screenings were shown in the main text, **Table 1**.

Racemates were prepared by using 5 mol% of 3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-dinaphthyl-N,N'-bis-((trifluoromethyl)sulfonyl)phosphoramidimidate[2] (racemate) in toluene at 110 °C.

General procedure of the catalytic asymmetric hydroarylation: A Schlenk tube equipped with an aluminum foil was charged with IDPi **7e** (2 mol%) under argon, substrate **1** (0.1 mmol to 0.2 mmol) and cyclohexane (0.1 M) were added at room temperature. The resulting solution was heated at 60 °C for 2 days and the reaction was monitored by TLC. After full consumption of the starting material, the reaction mixture was diluted with pentane and purified by silica gel column chromatography (Pentane:Et_2O = 30:1 to 10:1) to afford the desired product.

(*R*)-1-butyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2a**)



0.15 mmol scale, s.m.(starting material, the same as following) 36 mg, obtain product 35 mg, 97% yield, colorless oil, e.r. 95:5.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.71 (bs, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.15 (td, *J* = 7.0, 1.3 Hz, 1H), 7.10 (td, *J* = 7.4, 1.2 Hz, 1H), 2.79–2.60 (m, 2H), 2.01–1.80 (m, 3H), 1.73–1.54 (m, 3H), 1.37–1.17 (m, 7H), 0.91 (t, *J* = 7.1 Hz, 3H).

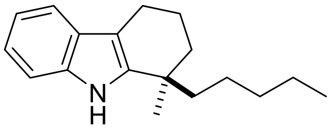
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 135.8, 127.8, 121.2, 119.1, 118.2, 110.5, 109.7, 41.9, 36.1, 34.7, 27.6, 26.9, 23.6, 21.5, 20.3, 14.3.

HRMS (ESI) (m/z): calculated for $C_{17}H_{23}N_1$ $[M]^+$: 241.1825; found 241.1831.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 7.2 min, t_{minor} = 9.9 min.

$[\alpha]_D^{25}$ = –15.0 (*c* 0.24, THF)

(*R*)-1-methyl-1-pentyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2b**)



0.15 mmol, s.m. 38 mg, obtain 37 mg, 97% yield, colorless oil, e.r. 95:5.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.70 (bs, 1H), 7.50 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.16 (td, *J* = 7.1, 1.4 Hz, 1H), 7.11 (td, *J* = 7.4, 1.2 Hz, 1H), 2.83–2.58 (m, 2H), 2.04–1.79 (m, 3H), 1.73–1.58 (m, 4H), 1.46–1.16 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 3H).

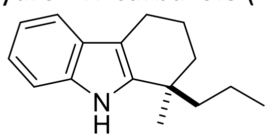
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 135.8, 127.8, 121.1, 119.1, 118.2, 110.5, 109.7, 42.2, 36.1, 34.7, 32.8, 27.6, 24.4, 22.8, 21.5, 20.3, 14.3.

HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M]^+$: 255.1982; found 255.1983.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 7.0 min, t_{minor} = 9.4 min.

$[\alpha]_D^{25}$ = – 18.9 (*c* 0.71, THF)

(*R*)-1-methyl-1-propyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2c**)



0.15 mmol, s.m. 34 mg, obtain 33 mg, 97% yield, colorless oil, e.r. 94:6.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.69 (bs, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.14 (td, *J* = 7.1, 1.3 Hz, 1H), 7.09 (td, *J* = 7.1, 1.1 Hz, 1H), 2.80–2.61 (m, 2H), 2.01–1.80 (m, 3H), 1.72–1.52 (m, 3H), 1.44–1.19 (m, 5H), 0.92 (t, *J* = 7.3 Hz, 3H).

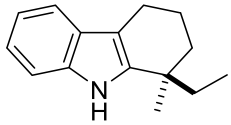
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 135.8, 127.8, 121.1, 119.1, 118.2, 110.5, 109.7, 44.6, 36.2, 34.8, 27.6, 21.5, 20.3, 18.0, 15.0.

HRMS (ESI) (m/z): calculated for $C_{16}H_{21}N_1$ $[M]^+$: 227.1668; found 227.1670.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 7.5 min, t_{minor} = 9.8 min.

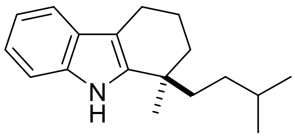
[α]$_D^{25}$ = – 16.7 (*c* 0.24, THF)

(*R*)-1-ethyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2d**)



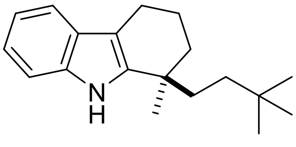
0.15 mmol, s.m. 32 mg, obtain 30 mg, 95% yield, colorless oil, e.r. 84:16.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.69 (bs, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.14–7.03 (m, 2H), 2.81–2.61 (m, 2H), 2.04–1.80 (m, 3H), 1.70 (q, *J* = 7.5 Hz, 2H), 1.63–1.55 (m, 1H), 1.29 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 135.8, 129.2, 128.4, 121.1, 119.1, 118.2, 110.5, 35.4, 34.9, 34.4, 27.1, 21.5, 20.2.
HRMS (ESI) (m/z): calculated for $C_{15}H_{19}N_1$ $[M]^+$: 213.1512; found 213.1512.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 7.8 min, t_{minor} = 9.4 min.
[α]$_D^{25}$ = – 10.7 (*c* 0.12, THF)

(*S*)-1-isopentyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2e**)



0.1 mmol, s.m. 26 mg, obtain 24.2 mg, 93% yield, colorless oil, e.r. 97:3.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.70 (bs, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.15 (td, *J* = 8.0, 1.1 Hz, 1H), 7.11 (td, *J* = 8.0, 1.1 Hz, 1H), 2.76–2.66 (m, 2H), 2.02–1.79 (m, 3H), 1.67–1.62 (m, 3H), 1.57–1.45 (m, 1H), 1.31 (s, 3H), 1.28–1.18 (m, 1H), 1.17–1.05 (m, 1H), 0.90 (t, *J* = 6.1 Hz, 6H) .
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 135.8, 127.8, 121.1, 119.1, 118.2, 110.6, 109.7, 39.8, 36.0, 34.6, 33.6, 28.9, 27.8, 22.8, 21.5, 20.3.
HRMS (ESI) (m/z): calculated for $C_{18}H_{26}N_1$ $[M+H]^+$: 256.2060; found 256.2057.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 6.6 min, t_{minor} = 9.3 min.
[α]$_D^{25}$ = – 31.2 (*c* 0.41, THF)

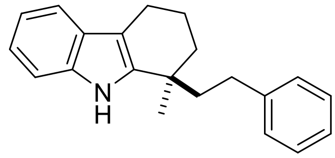
(*S*)-1-(3,3-dimethylbutyl)-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2f**)



0.1 mmol, s.m. 27 mg, obtain 26 mg, 97% yield, colorless oil, e.r. 98:2.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.69 (bs, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.32 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.13 (td, *J* = 7.1, 1.3 Hz, 1H), 7.09 (td, *J* = 7.1, 1.1 Hz, 1H), 2.79–2.55 (m, 2H), 1.99–1.79 (m, 3H), 1.68–1.56 (m, 3H), 1.34–1.18 (m, 4H), 1.13–1.05 (m, 1H), 0.88 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 135.8, 127.8, 121.1, 119.2, 118.2, 110.6, 109.7, 38.3, 36.4, 35.7, 34.5, 30.3, 29.5, 27.6, 21.5, 20.3.
HRMS (ESI) (m/z): calculated for $C_{19}H_{27}N_1$ $[M]^+$: 269.2138; found 269.2142.

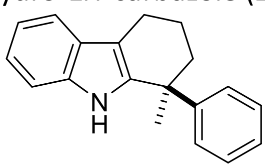
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 6.2 min, t_{minor} = 8.9 min.
[α]$_D^{25}$ = – 10.0 (*c* 0.5, THF)

(*S*)-1-methyl-1-phenethyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2g**)



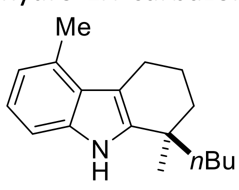
0.15 mmol, s.m. 43 mg, obtain 41 mg, 95% yield, white solid, e.r. 96:4.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.60 (bs, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.23–7.13 (m, 2H), 7.11–6.97 (m, 6H), 2.72–2.49 (m, 3H), 2.41 (ddd, *J* = 13.5, 11.7, 5.2 Hz, 1H), 1.97–1.74 (m, 5H), 1.68–1.56 (m, 1H), 1.28 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 140.7, 135.9, 128.5, 128.4, 127.8, 125.9, 121.3, 119.2, 118.3, 110.6, 110.2, 44.2, 36.0, 35.0, 31.3, 27.7, 21.5, 20.3.
HRMS (EI) (m/z): calculated for $C_{21}H_{23}N_1$ $[M]^+$: 289.1825; found 289.1825.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD-3 column: *n*Hept:*i*PrOH = 95 : 5, flow rate 0.7 mL/ min, t_{major} = 12.2 min, t_{minor} = 20.3 min.
[α]$_D^{25}$ = 7.2 (*c* 0.36, THF)

(*S*)-1-methyl-1-phenyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2h**)



0.15 mmol, s.m. 39.2 mg, obtain 35.4 mg, 88% yield, white solid, e.r. 95:5.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.54 (bs, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.20–7.18 (m, 3H), 7.14–7.09 (m, 1H), 7.08–7.04 (m, 4H), 2.79–2.62 (m, 2H), 2.02 (ddd, *J* = 13.1, 7.4, 2.8 Hz, 1H), 1.90 (ddd, *J* = 13.1, 10.2, 2.7 Hz, 1H), 1.79–1.73 (m, 1H), 1.68 (s, 3H), 1.63–1.57 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 139.4, 135.9, 128.2, 127.5, 127.1, 126.2, 121.5, 119.3, 118.4, 111.3, 110.8, 41.9, 40.4, 27.6, 21.3, 20.0.
HRMS (ESI) (m/z): calculated for $C_{19}H_{19}N_1$ $[M]^+$: 261.1514; found 261.1514.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD-3 column: *n*Hept:*i*PrOH = 97:3, flow rate 0.7 mL/ min, t_{major} = 8.7 min, t_{minor} = 9.7 min.
[α]$_D^{25}$ = 1.4 (*c* 0.14, THF)

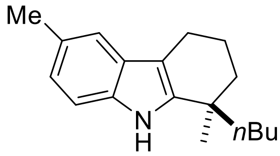
(*R*)-1-butyl-1,5-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2i**)



0.1 mmol, s.m. 22 mg, obtain 20.6 mg, 94% yield, colorless oil, e.r. 95:5.
^{1}H NMR (501 MHz, $CDCl_3$) δ ^{1}H NMR (501 MHz, $CDCl_3$)δ 7.66 (bs, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.1 Hz, 1H), 3.06–2.89 (m, 2H), 2.66 (s, 3H), 1.96–1.75 (m,

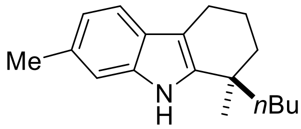
3H), 1.69–1.49 (m, 3H), 1.36–1.09 (m, 7H), 0.90–0.86 (t, J = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 135.8, 130.6, 126.6, 121.1, 120.5, 110.1, 108.4, 42.0, 35.5, 34.6, 27.7, 26.9, 24.2, 23.6, 20.6, 20.1, 14.3.
HRMS (ESI) (m/z): calculated for $C_{18}H_{24}N_1$ $[M-H]^-$: 254.1914; found 254.1917.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OJ-3 column: *n*Hept:*i*PrOH = 97:3, flow rate 0.7 mL/ min, t_{major} = 10.0 min, t_{minor} = 8.7 min.
$[\alpha]_D^{25}$ = – 19.0 (*c* 0.2, THF)

(*R*)-1-butyl-1,6-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2j**)



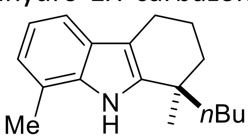
0.15 mmol, s.m. 38.5 mg, obtain 32.7 mg, 85% yield, colorless oil, e.r. 95:5.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.49 (bs, 1H), 7.16 (d, J = 3.5 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 2.65–2.46 (m, 2H), 2.36 (s, 3H), 1.91–1.68 (m, 3H), 1.60–1.41 (m, 3H), 1.26–1.03 (m, 7H), 0.79 (t, J = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 134.1, 128.3, 128.0, 122.5, 118.0, 110.2, 109.2, 41.9, 36.1, 34.8, 27.7, 26.9, 23.6, 21.6, 21.5, 20.3, 14.3.
HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M]^+$: 255.1981; found 255.1982.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OJ-3 column: *n*Hept:*i*PrOH = 97:3, flow rate 0.7 mL/ min, t_{major} = 12.0 min, t_{minor} = 14.9 min.
$[\alpha]_D^{25}$ = – 23.0 (*c* 0.2, THF)

(*R*)-1-butyl-1,7-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2k**)



0.1 mmol, s.m. 23 mg, obtain 21 mg, 91% yield, colorless oil, e.r. 96:4.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.56 (bs, 1H), 7.35 (d, J = 7.9 Hz, 1H), 7.10 (s, 1H), 6.91 (d, J = 7.9 Hz, 1H), 2.75–2.58 (m, 2H), 2.45 (s, 3H), 1.97–1.77 (m, 3H), 1.68–1.52 (m, 3H), 1.38–1.14 (m, 7H), 0.88 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 136.2, 130.8, 125.6, 120.7, 117.9, 110.6, 109.5, 41.9, 36.2, 34.7, 27.6, 27.0, 23.6, 21.9, 21.5, 20.3, 14.3.
HRMS (EI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M]^+$: 255.1981; found 255.1982.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OJ-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 11.4 min, t_{minor} = 14.0 min.
$[\alpha]_D^{25}$ = – 30.9 (*c* 0.22, THF)

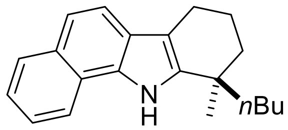
(*R*)-1-butyl-1,8-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2l**)



0.1 mmol, s.m. 25 mg, obtain 23.4 mg, 96% yield, colorless oil, e.r. 95:5.

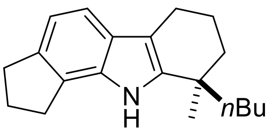
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.54 (bs, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.94 (dt, *J* = 7.1, 1.0 Hz, 1H), 2.79–2.58 (m, 2H), 2.49 (s, 3H), 2.00–1.77 (m, 3H), 1.71–1.58 (m, 3H), 1.39–1.15 (m, 7H), 0.90 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 135.2, 127.3, 121.9, 119.6, 119.4, 115.9, 110.2, 41.9, 36.1, 34.7, 27.6, 26.9, 23.6, 21.6, 20.3, 16.9, 14.2.
HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M]^+$: 255.1981; found 255.1984.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 5.9 min, t_{minor} = 6.9 min.
$[\alpha]_D^{25}$ = – 36.1 (*c* 0.36, THF)

(*R*)-10-butyl-10-methyl-8,9,10,11-tetrahydro-7*H*-benzo[*a*]carbazole (**2m**)



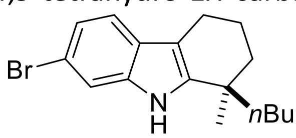
0.1 mmol, s.m. 29 mg, obtain 25.8 mg, 89% yield, colorless oil, e.r. 96:4.
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.39 (bs, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.53–7.47 (m, 2H), 7.38 (t, *J* = 8.1 Hz, 1H), 2.88–2.69 (m, 2H), 2.05–1.84 (m, 3H), 1.77–1.62 (m, 3H), 1.45–1.20 (m, 7H), 0.91 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 130.2, 129.9, 129.1, 125.2, 123.2, 121.7, 119.9, 119.3, 118.9, 111.5, 42.2, 36.2, 34.8, 27.9, 26.9, 23.6, 21.6, 20.4, 14.3.
HRMS (ESI) (m/z): calculated for $C_{21}H_{24}N_1$ $[M-H]^-$: 290.1914; found 290.1917.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 10.7 min, t_{minor} = 9.6 min.
$[\alpha]_D^{25}$ = – 77.4 (*c* 0.23, THF)

(*R*)-9-butyl-9-methyl-1,2,3,6,7,8,9,10-octahydrocyclopenta[*a*]carbazole (**2n**)



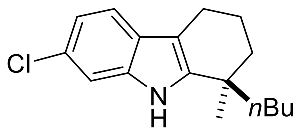
0.15 mmol, s.m. 42.5 mg, obtain 40 mg, 94% yield, colorless oil, e.r. 96:4.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.46 (bs, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 3.04 (t, *J* = 7.4 Hz, 4H), 2.77–2.58 (m, 2H), 2.22 (q, *J* = 7.3 Hz, 2H), 1.99–1.79 (m, 3H), 1.71–1.57 (m, 3H), 1.39–1.17 (m, 7H), 0.90 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 137.7, 132.8, 126.4, 124.9, 116.2, 116.0, 110.2, 41.9, 36.1, 34.7, 33.2, 30.1, 27.7, 26.9, 25.7, 23.6, 21.7, 20.3, 14.3.
HRMS (EI) (m/z): calculated for $C_{20}H_{27}N_1$ $[M]^+$: 281.2138; found 281.2140.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OJ-3 column: MeCN:H_2O = 90:10, flow rate 1.0 mL/ min, t_{major} = 10.6 min, t_{minor} = 8.2 min.
$[\alpha]_D^{25}$ = – 8.0 (*c* 0.1, THF)

(*R*)-7-bromo-1-butyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2o**)



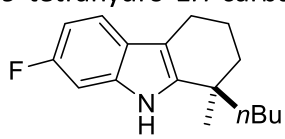
0.15 mmol, s.m. 48 mg, obtain 47 mg, 97% yield, colorless oil, e.r. 97:3.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.70 (bs, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.18 (dt, *J* = 8.3, 1.8 Hz, 1H), 2.73–2.54 (m, 2H), 1.98–1.76 (m, 3H), 1.66–1.57 (m, 3H), 1.35–1.12 (m, 7H), 0.90 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 136.6, 126.7, 122.3, 119.4, 114.4, 113.5, 109.9, 41.8, 35.9, 34.7, 27.5, 26.9, 23.6, 21.3, 20.1, 14.2.
HRMS (DE) (m/z): calculated for $C_{17}H_{22}N_1Br_1$ $[M]^+$: 319.0933; found 319.0936.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD-3 column: *n*Hept:*i*PrOH = 97:3, flow rate 0.7 mL/ min, t_{major} = 10.6 min, t_{minor} = 8.2 min.
$[\alpha]_D^{25}$ = – 35.8 (*c* 0.57, THF)

(*R*)-1-butyl-7-chloro-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2p**)



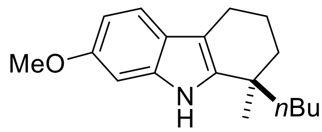
0.12 mmol, s.m. 31.7 mg, obtain 29 mg, 91% yield, colorless oil, e.r. 95:5.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.68 (bs, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.9 Hz, 1H), 2.72–2.54 (m, 2H), 1.96–1.80 (m, 3H), 1.65–1.56 (m, 3H), 1.37–1.10 (m, 7H), 0.88 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 136.1, 126.9, 126.4, 119.7, 119.0, 110.6, 109.8, 41.8, 35.9, 34.8, 27.5, 26.9, 23.6, 21.3, 20.1, 14.2.
HRMS (EI) (m/z): calculated for $C_{17}H_2N_1Cl$ $[M]^+$: 275.1435; found 275.1438.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD-3 column: *n*Hept:*i*PrOH = 97:3, flow rate 0.7 mL/ min, t_{major} = 9.1 min, t_{minor} = 7.3 min.
$[\alpha]_D^{25}$ = – 17.9 (*c* 0.48, THF)

(*R*)-1-butyl-7-fluoro-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2q**)



0.15 mmol, s.m. 40.3 mg, obtain 37.5 mg, 93% yield, colorless oil, e.r. 95:5.
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.68 (bs, 1H), 7.35 (dd, *J* = 8.6, 5.4 Hz, 1H), 6.99 (dd, *J* = 9.8, 2.3 Hz, 1H), 6.84 (ddd, *J* = 9.8, 8.6, 2.3 Hz, 1H), 2.75–2.56 (m, 2H), 1.99–1.77 (m, 3H), 1.73–1.52 (m, 3H), 1.37–1.14 (m, 7H), 0.89 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 141.8, 135.7, 124.4, 118.6, 109.6, 107.6, 107.4, 97.3, 97.1, 4195, 36.0, 34.7, 27.5, 26.9, 23.6, 21.4, 20.2, 14.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -122.6 (td, *J* = 9.8, 8.9, 5.2 Hz).
HRMS (ESI) (m/z): calculated for $C_{17}H_{21}N_1F_1$ $[M-H]^-$: 258.1663; found 258.1665.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel AD-3 column: *n*Hept:*i*PrOH = 97:3, flow rate 0.7 mL/ min, t_{major} = 7.6 min, t_{minor} = 6.6 min.
$[\alpha]_D^{25}$ = – 24.8 (*c* 0.46, THF)

(*R*)-1-butyl-7-methoxy-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2r**)



0.15 mmol, s.m. 40 mg, obtain 37 mg, 93% yield, colorless oil, e.r. 96:4.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.64 (bs, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.76 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.85 (s, 3H), 2.77–2.51 (m, 2H), 1.99–1.76 (m, 2H), 1.70–1.50 (m, 3H), 1.35–1.12 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H).

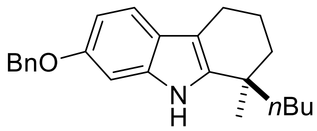
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 140.3, 136.5, 122.3, 118.6, 109.4, 108.4, 95.1, 56.0, 41.9, 36.1, 34.7, 27.6, 26.9, 23.6, 21.5, 20.3, 14.2.

HRMS (ESI) (m/z): calculated for $C_{18}H_{26}N_1O_1$ $[M+H]^+$: 272.2009; found 272.2009.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD-3 column: *n*Hept : *i*PrOH = 97:3, flow rate 0.7 mL/ min, t_{major} = 11.1 min, t_{minor} = 6.4 min.

$[\alpha]_D^{25}$ = – 41.3 (*c* 0.15, THF)

(*R*)-7-(benzyloxy)-1-butyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2s**)



0.15 mmol, s.m. 53.6 mg, obtain 51.1 mg, 95% yield, colorless oil, e.r. 96:4.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.60 (bs, 1H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.36–7.30 (m, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.13 (s, 2H), 2.75–2.54 (m, 2H), 2.02–1.75 (m, 3H), 1.68–1.59 (m, 3H), 1.37–1.15 (m, 7H), 0.90 (t, *J* = 7.1 Hz, 3H).

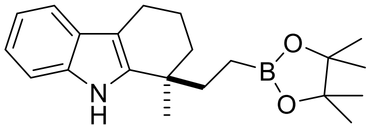
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 142.6, 138.1, 131.1, 128.6, 128.1, 127.8, 127.7, 111.6, 111.1, 109.6, 102.4, 71.3, 41.9, 36.1, 34.8, 27.6, 26.9, 23.6, 21.5, 20.2, 14.2.

HRMS (EI) (m/z): calculated for $C_{24}H_{29}N_1O_1$ $[M]^+$: 347.2243; found 347.2249.

The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IA-3 column: *n*Hept:*i*PrOH = 90:10, flow rate 0.7 mL/ min, t_{major} = 12.4 min, t_{minor} = 10.5 min.

$[\alpha]_D^{25}$ = – 9.4 (*c* 0.15, THF)

(*R*)-1-methyl-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2,3,4,9-tetrahydro-1*H*-carbazole (**2t**)



0.1 mmol, s.m. 34 mg, 3 mol % cat. 65 °C, 3d, obtain 23 mg, 67% yield, light yellow solid, e.r. 94:6.

^{1}H NMR (501 MHz, C_6D_6) δ 7.58 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.25 (td, *J* = 6.7, 1.6 Hz, 2H), 7.11 (d, *J* = 6.8 Hz, 1H), 7.04 (bs, 1H), 2.68–2.47 (m, 2H), 1.93–1.58 (m, 5H), 1.44–1.34 (m, 1H), 1.09–1.02 (m, 12H), 0.97–0.86 (m, 1H), 0.80–0.74 (ddd, *J* = 16.1, 11.2, 5.6 Hz, 1H).

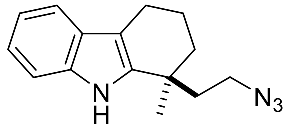
^{13}C NMR (126 MHz, C_6D_6) δ 140.9, 136.5, 128.5, 121.3, 119.4, 118.6, 111.0, 110.1, 83.0, 35.9, 35.6, 35.5, 27.0, 25.06, 25.0, 21.7, 20.5.

^{11}B NMR (161 MHz, C_6D_6) δ 34.3.

HRMS (DE) (m/z): calculated for $C_{21}H_{30}N_1O_2B_1$ $[M]^+$: 339.2370; found 339.2371.

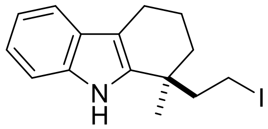
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 4.1 min, t_{minor} = 4.9 min.
[α]$_D^{25}$ = – 7.8 (*c* 0.36, THF)

(*S*)-1-(2-azidoethyl)-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2u**)



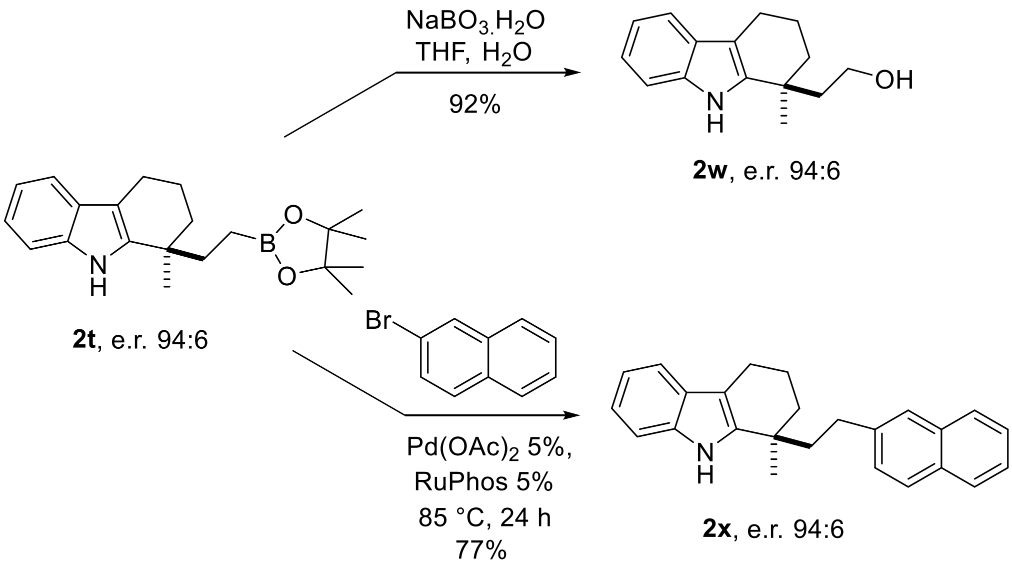
0.15 mmol, s.m. 38 mg, 4 mol % cat. 3d, obtain 30 mg, 79% yield, light yellow oil, e.r. 93:7.
^{1}H NMR (501 MHz, C_6D_6) δ 7.56 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.30–7.20 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.78 (bs, 1H), 2.70 (ddd, *J* = 12.3, 9.1, 6.9 Hz, 1H), 2.63–2.41 (m, 3H), 1.61–1.53 (m, 2H), 1.45 (ddd, *J* = 9.0, 6.6, 2.2 Hz, 2H), 1.41–1.31 (m, 1H), 1.26–1.17 (m, 1H), 0.89 (s, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 138.8, 136.5, 121.8, 119.7, 118.7, 111.0, 110.4, 47.9, 40.0, 36.3, 33.7, 27.5, 21.5, 20.4.
HRMS (ESI) (m/z): calculated for $C_{15}H_{17}N_4$ $[M-H]^-$: 253.1459; found 253.1460.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 8.1 min, t_{minor} = 10.5 min.
[α]$_D^{25}$ = – 17.0 (*c* 0.4, THF)

(*S*)-1-(2-iodoethyl)-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (**2v**)



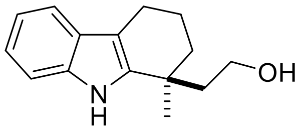
0.1 mmol, s.m. 34 mg, obtain 31.5 mg, 93% yield, colorless oil, e.r. 97:3.
^{1}H NMR (501 MHz, C_6D_6) δ 7.55 (d, *J* = 7.5 Hz, 1H), 7.28–7.22 (m, 2H), 7.13–7.10 (d, *J* = 7.5 Hz, 1H), 6.62 (bs, 1H), 2.70 (ddd, *J* = 12.8, 9.3, 5.0 Hz, 1H), 2.61–2.48 (m, 2H), 2.43 (ddd, *J* = 15.5, 7.4, 6.0 Hz, 1H), 1.94 (dtd, *J* = 39.6, 13.5, 4.9 Hz, 2H), 1.58–1.47 (m, 2H), 1.30 (ddd, *J* = 13.1, 8.1, 4.8 Hz, 1H), 1.12 (ddd, *J* = 13.3, 6.6, 4.1 Hz, 1H), 0.79 (s, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 138.4, 136.5, 121.8, 119.7, 118.7, 111.1, 110.6, 46.9, 37.2, 35.4, 26.9, 21.4, 20.3, 1.4.
HRMS (ESI) (m/z): calculated for $C_{15}H_{19}I_1N_1$ $[M+H]^+$: 340.0557; found 340.0556.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 7.5 min, t_{minor} = 11.4 min.
[α]$_D^{25}$ = 1.9 (*c* 0.22, THF)

3. Synthetic applications



Scheme **S1**. Synthetic application

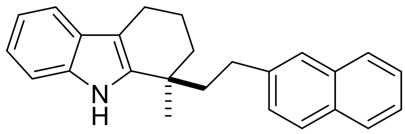
(*S*)-2-(1-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)ethan-1-ol (**2w**)



(*R*)-1-methyl-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2,3,4,9-tetrahydro-1H-carbazole **2t** (211 mg, 0.62 mmol, 1 equiv.) was dissolved in 15 mL THF, $NaBO_3 \cdot H_2O$ (310 mg, 3.1 mmol, 5 equiv.) and H_2O 15 mL were added. The resulting mixture was allowed to stir in an open flask at r.t. for 2 h. Then saturated NH_4Cl was added and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane : EtOAc = 1 : 1) to afford 131 mg product in 92% yield as oil.

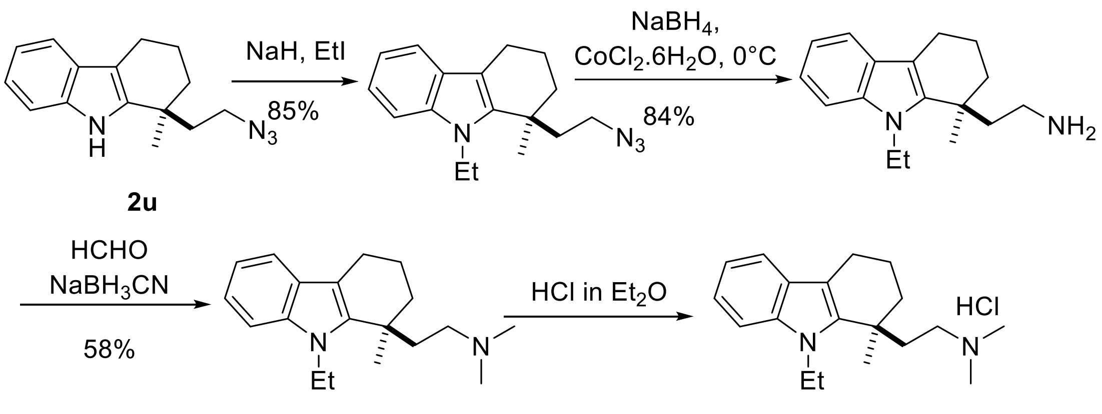
^{1}H NMR (501 MHz, C_6D_6) δ 8.20 (bs, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.32–7.19 (m, 3H), 3.36–3.32 (m, 1H), 3.19–3.16 (m, 1H), 2.80–2.53 (m, 2H), 1.79–1.66 (m, 2H), 1.63–1.53 (m, 2H), 1.49–1.31 (m, 2H), 1.11 (s, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 140.3, 136.5, 121.5, 119.4, 118.7, 111.0, 109.6, 59.8, 43.8, 38.7, 34.1, 27.3, 24.9, 21.7, 20.6.
HRMS (ESI) (m/z): calculated for $C_{15}H_{20}N_1O_1$ $[M+H]^+$: 230.1540; found 230.1540.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 90:10 , flow rate 0.7 mL/ min, t_{major} = 11.0 min, t_{minor} = 7.0 min.
$[\alpha]_D^{25}$ = – 13.5 (*c* 0.43, THF)

(*S*)-1-methyl-1-(2-(naphthalen-2-yl)ethyl)-2,3,4,9-tetrahydro-1*H*-carbazole (**2x**)



In a flame-dried Schlenk flask under Ar and equipped with a magnetic stir bar, (*R*)-1-methyl-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2,3,4,9-tetrahydro-1H-carbazole **2t** (34 mg, 0.1 mmol, 1 equiv.), 2-bromonaphthalene (23 mg, 0.11 mmol, 1.1 equiv.), cesium carbonate (130 mg, 0.4 mmol, 4 equiv.), $Pd(OAc)_2$ (1.2 mg, 0.005 mmol, 0.05 equiv.) and Ruphos (4.7 mg, 0.01 mmol, 0.1 equiv.) were dissolved in 1,4-dioxane (1 mL). After degassing with argon for 10 min, distilled water (0.1 mL) was sequentially added. Then the reaction mixture was heated at 85 °C. 15 h later, the mixture was cooled to r.t., it was quenched with saturated NH_4Cl and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1) to afford desired product 26 mg in 77 % yield.

^{1}H NMR (501 MHz, C_6D_6) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.64 (t, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.35–7.23 (m, 4H), 7.19 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.90 (bs, 1H), 2.78–2.49 (m, 3H), 2.40 (ddd, *J* = 13.4, 10.7, 6.0 Hz, 1H), 1.85–1.68 (m, 5H), 1.54–1.42 (m, 1H), 1.10 (s, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 140.6, 140.2, 136.56, 134.4, 132.67, 126.7, 126.3, 125.5, 121.6, 119.6, 118.7, 110.9, 110.3, 44.1, 36.1, 35.0, 31.6, 27.5, 21.7, 20.7.
HRMS (ESI) (m/z): calculated for $C_{25}H_{26}N_1$ $[M+H]^+$: 340.2060; found 340.2060.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OD-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.5 mL/ min, t_{major} = 23.5 min, t_{minor} = 27.4 min.
$[\alpha]_D^{25}$ = 3.2 (*c* 0.25, THF)

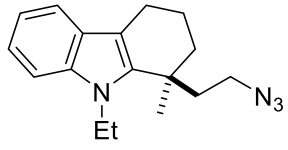


2u

8

Scheme **S2**. Synthesis of enantio-enriched potential anti-depressant

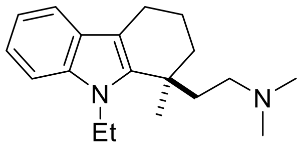
(*S*)-1-(2-azidoethyl)-9-ethyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole



A dried round flask equipped with a magnetic stirrer bar was charged with (*S*)-1-(2-azidoethyl)-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole **2u** (60 mg, 0.236 mmol, 1 equiv.) and DMF (4 mL) under Ar atmosphere. The reaction mixture was cooled down to 0 °C and NaH (60% in mineral oil, 14 mg, 0.283 mmol, 1.2 equiv.) was added and stirred for 10 min. Then ethyl iodide (40 µL, 0.283 mmol, 1.2 equiv.) was added and stirring was continued for 1h. Then isopropanol was drop wisely added at 0 °C till there is no more bubble. The reaction was quenched with ice-cold water and extracted with EtOAc 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1) to afford desired product 56 mg in 85% yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.19 (td, *J* = 6.9, 1.2 Hz, 1H), 7.10 (td, *J* = 7.0, 1.0 Hz, 1H), 4.39–4.19 (m, 2H), 3.32 (ddd, *J* = 12.3, 10.8, 5.8 Hz, 1H), 3.10 (ddd, *J* = 12.3, 10.7, 5.2 Hz, 1H), 2.80–2.72 (m, 1H), 2.66 (ddd, *J* = 15.3, 8.2, 5.4 Hz, 1H), 2.24 (ddd, *J* = 14.0, 10.8, 5.2 Hz, 1H), 2.04–1.76 (m, 4H), 1.73–1.61 (m, 1H), 1.47 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 136.6, 127.3, 121.4, 119.0, 118.4, 111.0, 109.3, 48.1, 39.8, 39.7, 39.3, 35.2, 27.7, 22.1, 20.3, 15.1.
HRMS (ESI) (m/z): calculated for $C_{17}H_{23}N_3$ $[M+H]^+$: 283.1917; found 283.1920.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IC-3 column: *n*Hept:*i*PrOH =99:1 , flow rate 0.7 mL/ min, t_{major} = 4.8 min, t_{minor} = 4.4 min.

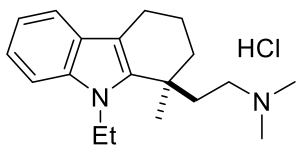
(*S*)-2-(9-ethyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)-*N*,*N*-dimethylethan-1-amine



To a mixture of (*S*)-1-(2-azidoethyl)-9-ethyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (35 mg, 0.124 mmol, 1 equiv.) and $CoCl_2·6H_2O$ (3 mg, 0.0124 mmol, 0.1 equiv.) in MeOH (4 mL) at 0 °C, $NaBH_4$ (9.4 mg, 0.248 mmol, 2 equiv.) was added. The resulting black mixture was stirred under Ar at 0 °C for 1 h and the reaction was monitored by TLC. After completion of the reaction, it was quenched with ice-cold water and extracted with DCM 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (DCM:MeOH = 5:1) to afford (*S*)-2-(9-ethyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)ethan-1-amine 26 mg in 84% yield.
A solution of (*S*)-2-(9-ethyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)ethan-1-amine (28 mg, 0.109 mmol, 1 equiv.) in MeOH (3 mL) was treated with formaldehyde (300 µL, 4 mmol, 37% solution in water) and sodium cyanoborohydride (13 mg, 2.218 mmol, 2 equiv.). The reaction was stirred for 3 h and then extracted water and DCM. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (DCM:MeOH = 10:1) to afford desired product 18 mg in 58% yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.37–4.27 (m, 2H), 2.75 (dt, *J* = 15.4, 4.9 Hz, 1H), 2.69–2.58 (m, 2H), 2.50 (s, 6H), 2.43–2.35 (m, 2H), 2.04 (td, *J* = 13.3, 4.2 Hz, 1H), 1.92–1.77 (m, 3H), 1.74–1.64 (m, 1H), 1.48 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 136.5, 127.3, 121.4, 119.0, 118.4, 111.1, 109.5, 55.3, 44.4, 39.9, 39.4, 36.9, 35.1, 27.7, 22.1, 20.3, 15.1.
HRMS (EI) (m/z): calculated for $C_{19}H_{23}N_2$ $[M]^+$: 284.2247; found 284.2247.

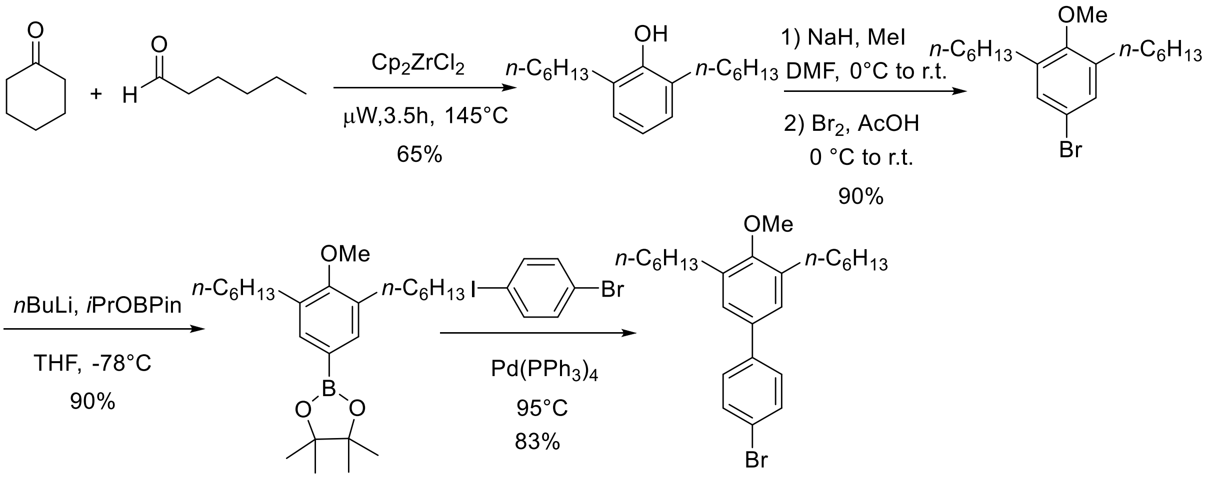
(*S*)-2-(9-ethyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)-*N*,*N*-dimethylethan-1-amine hydrochloride **(8)**



A solution of (*S*)-2-(9-ethyl-1-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl)-*N*,*N*-dimethylethan-1-amine (18 mg, 0.063 mmol, 1 equiv.) was added HCl solution (33 µL, 0.066 mmol, 1.05 equiv. 2.0 M in Et_2O) and stirred for 30 min. The volatiles were removed under reduced pressure to afford desired product **8** in quantitative yield.

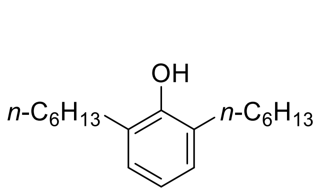
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.35–4.22 (m, 2H), 2.84 (t, *J* = 7.4 Hz, 1H), 2.74–2.38 (m, 10H), 2.15 (t, *J* = 11.6 Hz, 1H), 1.84–1.60 (m, 4H), 1.45 (s, 3H), 1.32 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 136.6, 127.2, 121.7, 119.2, 118.4, 111.6, 109.8, 55.1, 43.4, 43.2, 40.1, 39.5, 35.3, 35.0, 27.8, 22.0, 20.3, 15.1.
HRMS (EI) (m/z): calculated for $C_{19}H_{23}N_2$ $[M\text{-}Cl]^+$: 285.2324; found 285.2325.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OJ-3R column: Methanol : $(NH_4)HCO_3$ =85:15, pH 9.0, flow rate 1.0 mL/ min, t_{major} = 4.9 min, t_{minor} = 6.1 min.
$[\alpha]_D^{25}$ = – 6.2 (*c* 0.13, MeOH)

4. Synthesis of catalysts



Scheme S3: Synthesis of wing

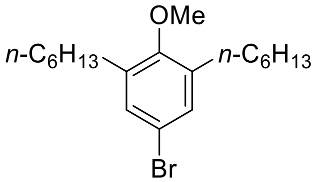
2,6-dihexylphenol



2,6-dihexylphenol was prepared following to the reported procedure,[3] the analytic data was identical to the reported value.
^{1}H NMR (501 MHz, $CDCl_3$) δ 6.98 (d, *J* = 7.5 Hz, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 4.64 (s, 1H), 2.65 – 2.49 (m, 4H), 1.69–1.50 (m, 4H), 1.45–1.23 (m, 12H), 0.95–0.84 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 128.1, 127.7, 120.4, 31.9, 30.3, 29.9, 29.5, 22.8, 14.3.

HRMS (ESI) (m/z): calculated for $C_{18}H_{29}O_1$ $[M]^+$: 261.2224; found 261.2227.

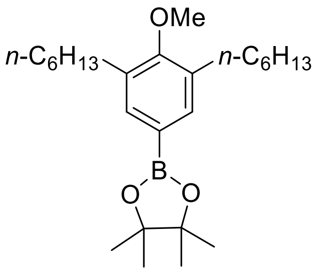
5-bromo-1,3-dihexyl-2-methoxybenzene



To the solution of 2,6-dihexylphenol (11.5g, 43.8 mmol, 1.0 equiv.) in DMF (50 mL) was added NaH (60% dispersion in mineral oil, 2.1 g, 52.6 mmol, 1.2 equiv.) at room temperature. After 10 min, to the suspension was added methyliodide (3.55 mL, 52.6 mmol, 1.2 equiv.) at room temperature and the mixture was stirred for 3 h. Then it was quenched with saturated NH_4Cl and extracted twice with MTBE. The combined organic layer was washed with brine, and then dried over Na_2SO_4, concentrated under reduced pressure and the crude product was used in the next step without further purification.
To the solution of the above-mentioned mixture in CH_3COOH (120 mL) was added Br_2 (2.34 mL, 1.05 equiv.) dropwise at 0 °C. The reaction was warmed up to r.t. and stirred for 30 min. The reaction was followed by GC-MS till all starting material was consumed. Then it was quenched with 2 M NaOH and extracted twice with Et_2O. The combined organic layers were washed with brine and then dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (pure hexane) to afford 13.9 g product as a colorless oil in 90% yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.07 (s, 2H), 3.63 (s, 3H), 2.54–2.45 (m, 4H), 1.55–1.48 (m, 4H), 1.31–1.18 (m, 12H), 0.84–0.77 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 138.2, 130.4, 116.9, 61.3, 31.8, 30.7, 29.8, 29.5, 22.7, 14.2.
HRMS (CI) (m/z): calculated for $C_{19}H_{31}O_1Br_1$ $[M]^+$: 354.1553; found 354.1559.

2-(3,5-dihexyl-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

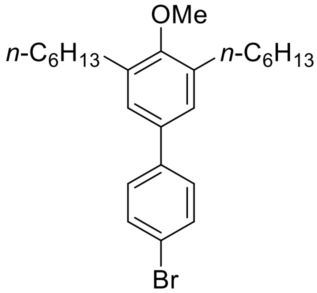


To a solution of 5-bromo-1,3-dihexyl-2-methoxybenzene (10.5 g, 29.5 mmol, 1 equiv.) in THF (60 mL) was slowly added *n*BuLi (2.5 M, 14.2 mL, 35.5 mmol, 1.2 equiv.) at –78 °C. After stirring at that temperature for 10 min, 2-isopropoxyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9 mL, 44.3 mmol, 1.5 equiv.) was added to the mixture then slowly warmed up to room temperature for 1 h. The reaction was quenched with cold saturated NH_4Cl and extracted by EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane : EtOAc = 50:1) to afford desired product 11.25 g as colorless oil in 90% yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.50 (s, 2H), 3.73 (s, 3H), 2.67–2.55 (m, 4H), 1.66–1.57 (m, 4H), 1.41–1.27 (m, 18H), 0.93–0.80 (m, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 135.4, 134.8, 83.8, 83.0, 61.3, 31.9, 31.2, 30.2, 29.8, 25.0,

25.0, 22.8, 14.3.
HRMS (ESI) (m/z): calculated for $C_{25}H_{43}B_1O_3$ [M+Na]$^+$: 425.3197; found 425.3203.

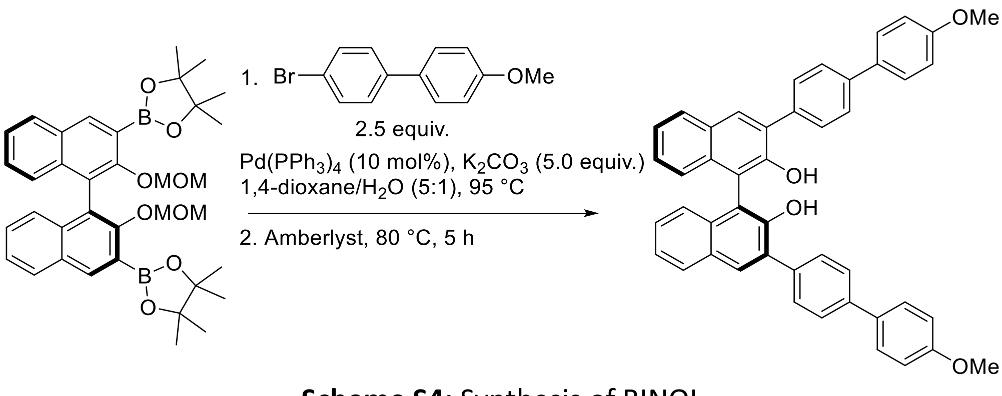
4'-bromo-3,5-dihexyl-4-methoxy-1,1'-biphenyl



In a flame-dried Schlenk flask under Ar and equipped with a magnetic stir bar, 2-(3,5-dihexyl-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (907 mg, 2.25 mmol, 1 equiv.), 1-bromo-3-iodobenzene (700 mg, 2.47 mmol, 1.1 equiv.), potassium carbonate (1.2 g, 9 mmol, 4 equiv.) and tetrakis(triphenylphosphine)palladium (130 mg, 0.11 mmol, 0.05 equiv.) were dissolved in 1,4-dioxane (15 mL). After degassing with argon for 10 min, distilled water (3 mL) was sequentially added. Then the reaction mixture was heated at 100 °C. 15 h later, the mixture was cooled to r.t., it was quenched with saturated NH_4Cl and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane : EtOAc = 50:1) to afford desired product 803 mg as oil in 83% yield.

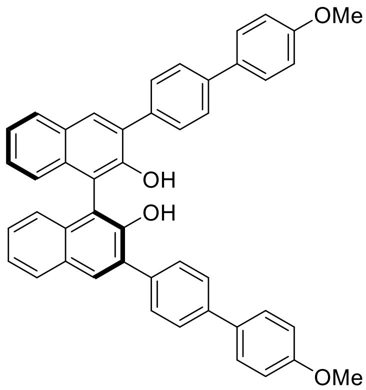
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.20 (s, 2H), 3.76 (s, 3H), 2.73–2.62 (m, 4H), 1.70–1.59 (m, 4H), 1.46–1.15 (m, 12H), 0.94–0.81 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 140.3, 136.4, 135.7, 131.8, 128.7, 126.4, 121.1, 61.4, 31.9, 31.1, 30.2, 29.7, 22.8, 14.3.
HRMS (APPI) (m/z): calculated for $C_{25}H_{35}Br_1O_1$ [M]$^+$: 430.1867; found 430.1867.

(*S*)-3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-diol and (*S*)-3,3'-di([1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol were prepared in a related procedure of 3,3'-substituted BINOL. The analytic data was identical to the reported value.[4]



Scheme S4: Synthesis of BINOL

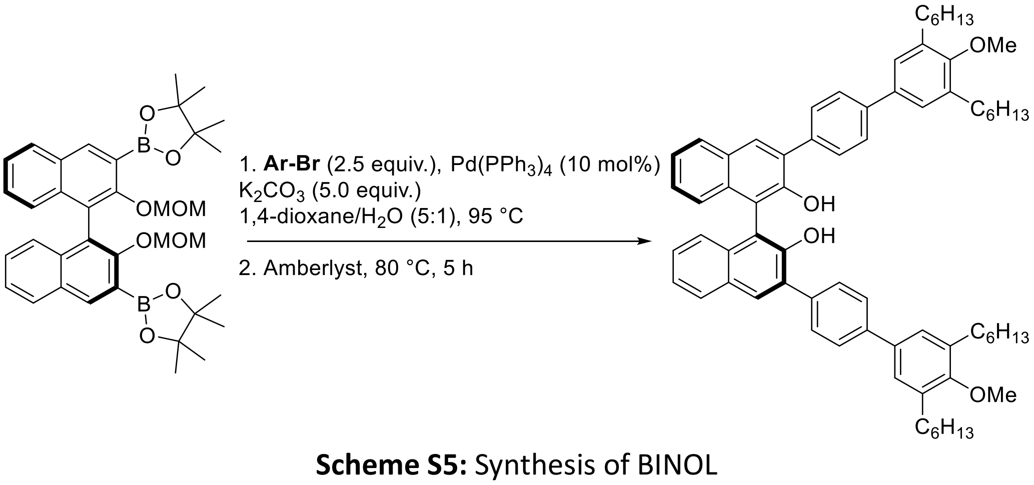
(S)-3,3'-bis(4'-methoxy-[1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol



In a flame-dried Schlenk flask under Ar and equipped with a magnetic stir bar, (S)-2,2'-(2,2'-bis(methoxymethoxy)-1, 1'binaphthyl-3, 3'-diyl)bis(4,4-5,5-tetramethyl-1,3,2-dioxaborolane) (665 mg, 1.06 mmol, 1 equiv.), 4-bromo-4'-methoxy-1,1'-biphenyl (582 mg, 2.55 mmol, 2.4 equiv.), potassium carbonate (880 mg, 24.24 mmol, 6 equiv.) and tetrakis(triphenylphosphine)palladium (122.7 mg, 0.1 mmol, 0.1 equiv.) were dissolved in 1,4-dioxane (10 mL). After degassing with argon for 10 min, distillated water (2 mL) was sequentially added. Then the reaction mixture was heated at 95 °C. 15 h later, the mixture was cooled to r.t., it was quenched with saturated NH_4Cl and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure.

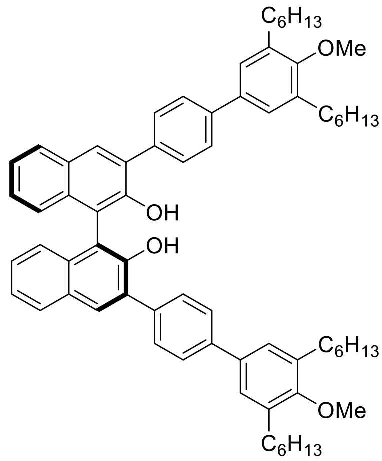
The suspension of the above-mentioned crude product and Amberlyst 15 (hydrogen form) in a mixture solvent of THF (15 mL) /MeOH (15 mL) was heated at 80 °C for 5 h. The cooled mixture was then filtered and purified by column chromatography (hexane/EtOAc = 5:1) afforded diol 552 mg (80 % yield) as a light yellow foam.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.83 (d, J = 8.3, 2H), 7.70 (d, J = 8.3, 4H), 7.57 (d, J = 7.3, 4H), 7.50 (m, J = 7.1, 4H), 7.29 (ddd, J = 8.1, 6.7, 1.3 Hz, 2H), 7.22 (ddd, J = 8.2, 6.8, 1.3 Hz, 2H), 7.15 (d, J = 8.6, 2H), 6.92–6.86 (m, 4H), 5.34 (s, 2H), 3.73 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 150.4, 140.3, 135.9, 133.4, 133.1, 131.4, 130.5, 130.1, 129.7, 128.6, 128.3, 127.5, 126.9, 124.5, 124.4, 114.4, 112.5, 55.5.
HRMS (ESI) (m/z): calculated for $C_{46}H_{33}O_4$ $[M-H]^+$: 649.2389; found 649.2384.
$[\alpha]_D^{25}$ = 84.8 (c 0.5, CH_2Cl_2)



Scheme S5: Synthesis of BINOL

(S)-3,3'-bis(3',5'-dihexyl-4'-methoxy-[1,1'-biphenyl]-4-yl)-[1,1'-binaphthalene]-2,2'-diol



In a flame-dried Schlenk flask under Ar and equipped with a magnetic stir bar, (*S*)-2,2'-(2,2'-bis(methoxymethoxy)-1, 1'binaphthyl-3, 3'-diyl)bis(4,4-5,5-tetramethyl-1,3,2-dioxaborolane) (238 mg, 0.38 mmol, 1 equiv.), 4'-bromo-3,5-dihexyl-4-methoxy-1,1'-biphenyl (410 mg, 0.95 mmol, 2.5 equiv.), potassium carbonate (210 mg, 1.52 mmol, 4 equiv.) and tetrakis(triphenylphosphine)palladium (44 mg, 0.04 mmol, 0.1 equiv.) were dissolved in 1,4-dioxane (6 mL). After degassing with argon for 10 min, distillated water (1 mL) was sequentially added. Then the reaction mixture was heated at 95 °C. 15 h later, the mixture was cooled to r.t., it was quenched with saturated NH_4Cl and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure.

The suspension of the above-mentioned crude product and Amberlyst 15 (hydrogen form) in a mixture solvent of THF (6 mL) /MeOH (6 mL) was heated at 80 °C for 5 h. The cooled mixture was then filtered and purified by column chromatography (hexane/EtOAc = 20:1) afforded diol 280 mg (75 % yield) as a white form.

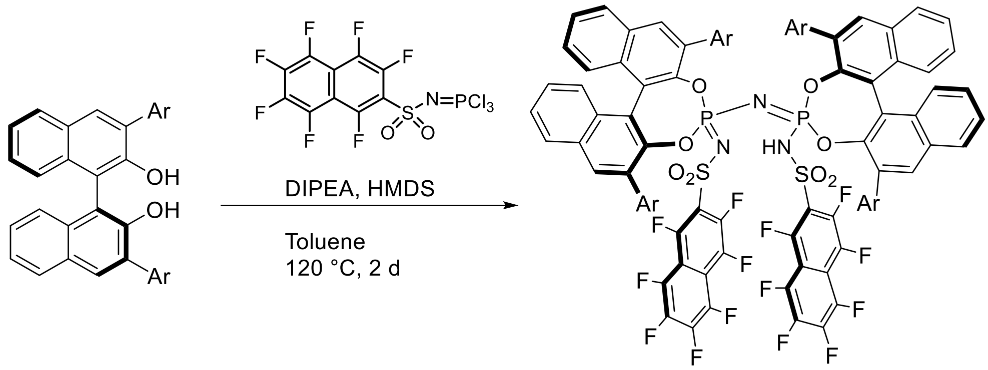
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.96 (d, *J* = 7.7, 2H), 7.87 – 7.78 (m, 4H), 7.76 – 7.65 (m, 4H), 7.42 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 2H), 7.38–7.34 (m, 6H), 7.28 (d, *J* = 7.7, 2H), 5.44 (s, 2H), 3.81 (s, 6H), 2.77–2.66 (m, 8H), 1.77–1.63 (m, 8H), 1.48–1.30 (m, 24H), 0.96–0.87 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 150.4, 140.9, 136.5, 136.3, 136.1, 133.1, 131.5, 130.5, 130.0, 129.7, 128.6, 127.5, 127.2, 126.6, 124.5, 124.5, 112.5, 61.5, 31.9, 31.1, 30.3, 29.7, 22.8, 14.3.

HRMS (ESI) (m/z): calculated for $C_{70}H_{81}O_4$ $[M-H]^+$: 985.6140; found 985.6142.

$[\alpha]_D^{25}$ = 50.7 (*c* 0.3, CH_2Cl_2)

General procedure of IDPi synthesis:

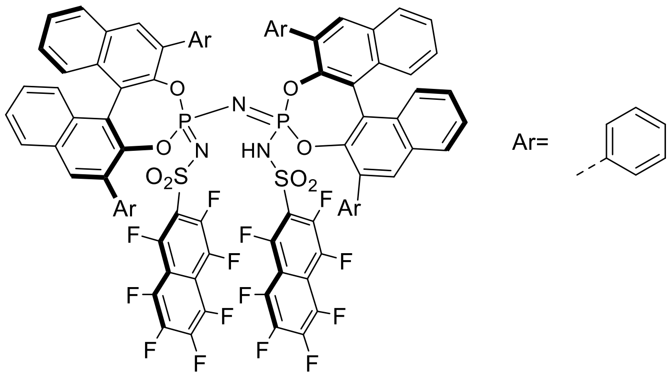


Scheme S6: General procedure of IDPi synthesis

((Perfluoronaphthalen-2-yl)sulfonyl)phosphorimidoyl trichloride was prepared following a reported procedure. [5]

In a flame dried pre-weighed Schlenk flask under Ar equipped with a magnetic stir bar, ((perfluoronaphthalen-2-yl)sulfonyl)phosphorimidoyl trichloride (2.04 equiv.) was added and weighed directly inside the Schlenk flask. 3, 3'-disubstituted BINOL (2.04 equiv.) was then added and the solids were evacuated and purged with Ar for 3 times. Then the solids were dissolved in toluene (2 mL) and *N, N*-diisopropylethylamine (16 equiv.) was added to form a heterogeneous mixture. The mixture was stirred at r.t. for 10 min and TLC showed diol was full consumed. Then hexamethyldisilazane (1 equiv.) was added and the mixture was heated to 120 °C for 2 d. The reaction mixture was cooled down to r.t., diluted with CH_2Cl_2 and quenching with 3 M HCl. Organic layer was separated and aqueous layer was washed with CH_2Cl_2. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (pentane:Et_2O = 20:1 to 1:1). The purified product was dissolved in CH_2Cl_2 and acidified with 3M HCl solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were collected and concentrated to afford colorless solid under high *vacuum*. (52 % to 65 % yield).

Imidodiphosphorimidate (IDPi **7b**)



^{1}H NMR (501 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.98 (s, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.64 (s, 2H), 7.49–7.37 (m, 8H), 7.33 (t, *J* = 7.7 Hz, 6H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.18–7.14 (m, 4H), 6.95 (t, *J* = 6.8 Hz, 2H), 6.74 – 6.63 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 142.4, 142.3, 134.5, 134.3, 133.2, 132.5, 131.2, 130.9, 130.4, 130.2, 129.9, 129.7, 128.7, 128.6, 127.7, 127.7, 127.0, 127.0, 126.5, 126.4, 126.1, 125.8, 125.7, 125.4, 125.3, 125.2, 124.6, 122.1, 121.5.

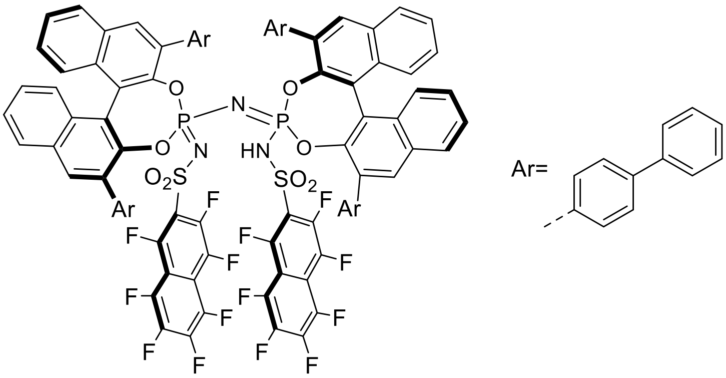
^{31}P NMR (203 MHz, $CDCl_3$) δ -10.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -111.4 (dd, *J* = 76.6, 18.9 Hz), -133.0 (d, *J* = 18.1 Hz), -140.7 (d, *J* = 76.7 Hz), -144.5 (dt, *J* = 58.8, 17.5 Hz), -146.4 (d, *J* = 58.5 Hz), -149.4, -154.2.

HRMS (ESI) (m/z): calculated for $C_{84}H_{40}N_3O_8S_2P_2F_{14}$ $[M-H]^-$: 1610.1514; found 1610.1510.

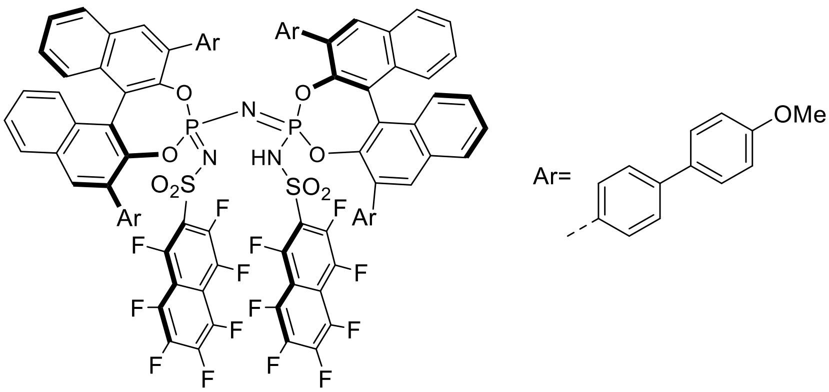
$[\alpha]_D^{25}$ = 82.7 (*c* 0.15, CH_2Cl_2)

Imidodiphosphorimidate (IDPi **7c**)



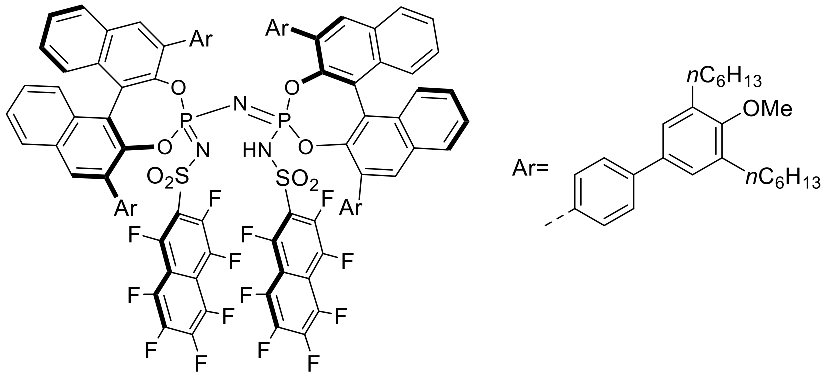
^{1}H NMR (501 MHz, CD_2Cl_2) δ 8.23 (d, *J* = 8.2 Hz, 2H), 8.04 (s, 2H), 7.93 (d, *J* = 6.2 Hz, 4H), 7.74 (ddd, *J* = 8.1, 6.7, 1.1 Hz, 2H), 7.48 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 4H), 7.39 (dd, *J* = 11.1, 5.6 Hz, 14H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.28–7.18 (m, 6H), 7.18–7.06 (m, 12H), 6.93 (d, *J* = 8.0 Hz, 4H), 6.88 (d, *J* = 8.1 Hz, 4H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.9, 140.7, 140.4, 140.3, 135.1, 134.5, 134.2, 133.7, 132.8, 132.3, 131.9, 131.6, 131.4, 131.0, 130.3, 129.4, 128.8, 128.7, 128.6, 127.7, 127.4, 127.4, 127.2, 127.17, 127.0, 126.9, 126.8, 126.8, 126.6, 123.5, 122.8.
^{19}F NMR (471 MHz, CD_2Cl_2) δ -112.7 (d, *J* = 95.0 Hz), -133.4 (d, *J* = 26.9 Hz), -140.4 – -143.4 (m), -144.8 – -146.4 (m), -146.4 – -148.1 (m), -150.1 (bs, 2F), -154.8 (bs, 2F).
$[\alpha]_D^{25}$ = 180.5 (*c* 0.5, $CHCl_3$)
HRMS (ESI) (m/z): calculated for $C_{108}H_{56}N_3O_8S_2P_2F_{14}$ $[M-H]^-$: 1914.2767; found 1914.2766.

Imidodiphosphorimidate (IDPi **7d**)



^{1}H NMR (501 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.98 (s, 2H), 7.86 (d, *J* = 9.3 Hz, 4H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.48–7.29 (m, 18H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 4H), 6.83 (s, 8H), 6.74 (d, *J* = 8.3 Hz, 4H), 6.63 (d, *J* = 8.2 Hz, 4H), 3.74 (s, 6H), 3.70 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 158.9, 139.9, 139.8, 134.2, 134.1, 134.0, 133.6, 133.4, 133.0, 132.4, 132.0, 131.6, 131.3, 131.3, 131.0, 130.7, 13017, 129.9, 128.9, 128.3, 128.1, 127.8, 127.2, 127.0, 126.9, 126.7, 126.3, 125.9, 125.7, 123.3, 122.4, 114.0, 113.8, 55.3, 55.3.
^{31}P NMR (203 MHz, $CDCl_3$) δ -10.7.
^{19}F NMR (471 MHz, $CDCl_3$) δ 112.3 (dd, *J* = 75.8, 18.9 Hz), -132.2 (d, *J* = 20.1 Hz), -141.0 (d, *J* = 77.6 Hz), -144.9 (dt, *J* = 58.2, 17.1 Hz), -146.6 (d, *J* = 57.6 Hz), -149.7 (bs), -154.5 (bs).
$[\alpha]_D^{25}$ = 216.0 (*c* 0.15, CH_2Cl_2)
HRMS (ESI) (m/z): calculated for $C_{112}H_{64}N_3O_{12}S_2P_2F_{14}$ $[M-H]^-$: 2034.3188; found 2034.3212.

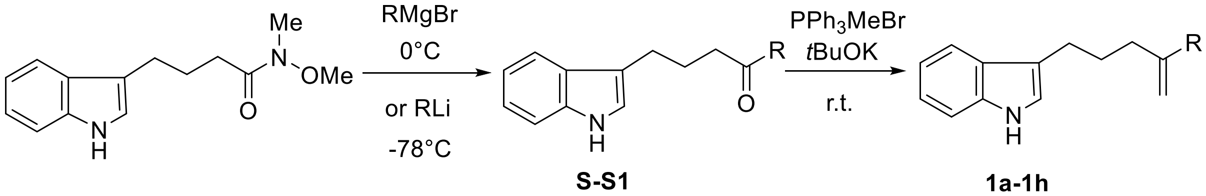
Imidodiphosphorimidate (IDPi **7e**)



^{1}H NMR (501 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 2H), 7.98 (s, 2H), 7.91 (s, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.46–7.39 (m, 8H), 7.35–7.28 (m, 8H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.09 (s, 4H), 6.86–6.77 (m, 8H), 6.73 (s, 4H), 3.67 (s, 6H), 3.56 (s, 6H), 2.57–2.43 (m, 8H), 2.38–2.34 (m, 4H), 2.21–2.16 (m, 4H), 1.51–1.45 (m, 8H), 1.36–1.02 (m, 56H), 0.83 (t, *J* = 7.2 Hz, 12H), 0.77 (t, *J* = 6.8 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 144.1, 143.8, 140.4, 136.3, 136.2, 135.8, 135.7, 134.5, 134.2, 133.8, 133.4, 132.5, 131.9, 131.6, 131.3, 130.9, 130.4, 129.8, 129.0, 128.1, 127.1, 127.0, 126.8, 126.7, 126.4, 126.3, 126.3, 123.4, 122.5, 61.3, 61.3, 31.8, 31.7, 31.1, 30.9, 30.0, 29.9, 29.8, 29.7, 22.8, 14.2, 14.1.
^{31}P NMR (203 MHz, $CDCl_3$) δ -9.4.
^{19}F NMR (471 MHz, $CDCl_3$) δ -112.2 (d, *J* = 78.6 Hz), -132.5 (d, *J* = 18.2 Hz), -139.7 – -141.4 (m), -143.9 – -145.6 (m), -146.3 (dd, *J* = 49.3, 29.6 Hz), -149.6 (d, *J* = 19.3 Hz), -154.2.
$[\alpha]_D^{25}$ = 203.3 (*c* 0.66, CH_2Cl_2)
HRMS (ESI) (m/z): calculated for $C_{160}H_{160}N_3O_{12}S_2P_2F_{14}$ $[M-H]^-$: 2707.0701; found 2707.0634.

5. Preparation of substrates

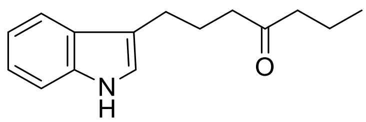
Route A



Scheme **S7:** Substrates synthesis of **1a-1h**

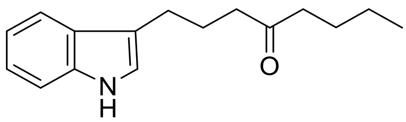
General synthetic procedure of S-S1: To a solution of 4-(1*H*-indol-3-yl)-*N*-methoxy-*N*-methylbutanamide in THF, which was prepared according to the literature,[6] freshly prepared Grignard reagent or lithium reagent (2.3 equiv.) was slowly added at 0 °C (-78 °C for lithium reagent). After stirring at that temperature for 1.5 h, the solution was slowly warmed up to room temperature and then quenched with cold saturated NH_4Cl. Then the mixture was extracted with Et_2O for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1) to afford product in 85 % to 93 % yield.

1-(1*H*-indol-3-yl)heptan-4-one



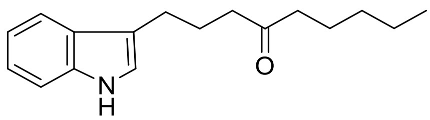
^{1}H NMR (501 MHz, C_6D_6) δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.17 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.00 (bs, 1H), 6.50 (dd, *J* = 2.3, 1.1 Hz, 1H), 2.70 (t, *J* = 7.3 Hz, 2H), 2.05 (t, *J* = 7.5 Hz, 2H), 2.03–1.94 (m, 2H), 1.86 (t, *J* = 7.2 Hz, 2H), 1.50–1.44 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 209.3, 136.9, 122.2, 121.5, 119.6, 119.3, 115.9, 111.5, 44.5, 42.1, 24.9, 24.7, 17.4, 13.9.
HRMS (EI) (m/z): calculated for $C_{15}H_{19}N_1O_1$ $[M]^+$: 229.1461; found 229.1462.

1-(1*H*-indol-3-yl)octan-4-one



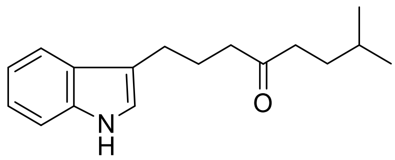
^{1}H NMR (501 MHz, C_6D_6) δ 7.69 (d, *J* = 7.7 Hz, 1H), 7.27–7.17 (m, 2H), 7.10 (dd, *J* = 8.0, 0.9 Hz, 1H), 6.87 (bs, 1H), 6.49 (d, *J* = 2.3 Hz, 1H), 2.71 (t, *J* = 8.1 Hz, 2H), 2.08 (t, *J* = 8.1 Hz, 2H), 1.99 (p, *J* = 7.2 Hz, 2H), 1.92 (t, *J* = 7.4 Hz, 2H), 1.48–1.42 (m, 2H), 1.20–1.06 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 209.2, 136.9, 122.2, 121.5, 119.6, 119.4, 116.0, 111.4, 42.4, 42.1, 26.2, 24.9, 24.7, 22.7, 14.1.
HRMS (ESI) (m/z): calculated for $C_{16}H_{20}N_1O_1$ $[M-H]^-$: 242.1550; found 242.1555.

1-(1*H*-indol-3-yl)nonan-4-one



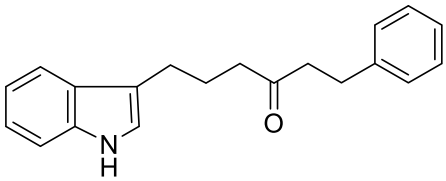
^{1}H NMR (501 MHz, C_6D_6) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.16 – 7.10 (m, 2H), 6.52 (d, *J* = 2.2 Hz, 1H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.08 (t, *J* = 7.5 Hz, 2H), 1.99 (p, *J* = 8.0 Hz, 2H), 1.92 (t, *J* = 7.4 Hz, 2H), 1.47 (p, *J* = 8.0 Hz, 2H), 1.26–1.14 (m, 2H), 1.14–1.05 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 209.6, 137.0, 122.2, 121.6, 119.6, 119.3, 115.9, 111.5, 42.7, 42.1, 31.8, 24.9, 24.7, 23.8, 22.9, 14.2.
HRMS (ESI) (m/z): calculated for $C_{17}H_{24}N_1O_1$ $[M]^+$: 258.1852; found 258.1856.

1-(1*H*-indol-3-yl)-7-methyloctan-4-one



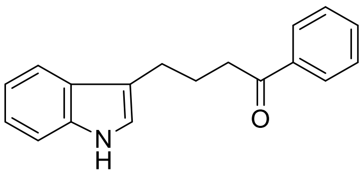
^{1}H NMR (501 MHz, C_6D_6) δ 7.69 (d, *J* = 8.1, 1H), 7.26 – 7.17 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.03 (bs, 1H), 6.52 (d, *J* = 2.2 Hz, 1H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.10 (t, *J* = 7.5 Hz, 2H), 2.06–1.88 (m, 4H), 1.45 – 1.29 (m, 3H), 0.77 (d, *J* = 6.4 Hz, 6H).
^{13}C NMR (126 MHz, C_6D_6) δ 209.5, 136.9, 122.2, 121.6, 119.6, 119.3, 115.9, 111.5, 42.1, 40.8, 32.9, 27.9, 24.9, 24.7, 22.5.
HRMS (ESI) (m/z): calculated for $C_{17}H_{23}N_1O_1$ $[M]^+$: 257.1774; found 257.1775.

6-(1*H*-indol-3-yl)-1-phenylhexan-3-one



^{1}H NMR (501 MHz, C_6D_6) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.26–7.17 (m, 2H), 7.15–7.09 (m, 3H), 7.05 (t, *J* = 7.4 Hz, 1H), 7.02–6.99 (m, 2H), 6.94 (bs, 1H), 6.46 (d, *J* = 2.2 Hz, 1H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.18 (t, *J* = 7.6 Hz, 2H), 2.02–1.88 (m, 4H).
^{13}C NMR (126 MHz, C_6D_6) δ 208.5, 141.8, 136.9, 128.7, 128.7, 126.3, 122.2, 121.6, 119.6, 119.3, 115.9, 111.4, 44.1, 42.2, 30.0, 24.8, 24.6.
HRMS (ESI) (m/z): calculated for $C_{20}H_{21}N_1O_1$ $[M]^+$: 291.1618; found 291.1618.

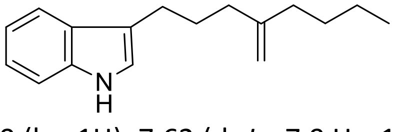
4-(1*H*-indol-3-yl)-1-phenylbutan-1-one



^{1}H NMR (501 MHz, $CDCl_3$) δ 8.11 (bs, 1H), 7.99–7.92 (m, 2H), 7.68 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.59–7.53 (m, 1H), 7.46 (t, *J* = 8.4 Hz, 2H), 7.37 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.23 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.16 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.98 (dd, *J* = 2.3, 1.1 Hz, 1H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.23 (p, *J* = 7.3 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 137.1, 136.5, 133.0, 128.6, 128.1, 127.6, 122.0, 121.6, 119.2, 119.0, 115.8, 111.2, 38.2, 24.7, 24.7.
HRMS (EI) (m/z): calculated for $C_{18}H_{17}N_1O_1$ $[M]^+$: 263.1305; found 263.1304.

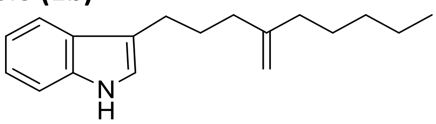
General synthetic procedure of 1a-1h : To a solution of 1M *t*BuOK in THF (3.0 equiv.) was added methyltriphenylphosphonium bromide (1.5 equiv.) at 0 °C and then the suspension was stirred at room temperature for 30 min. To the mixture was slowly added the solution of **S-S1** (1 equiv.) in THF at room temperature and then stirred for 15 h. Then the reaction mixture was quenched with saturated NH_4Cl and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1 to 5:1) to afford product in 85 % to 95 % yield.

3-(4-methyleneoctyl)-1*H*-indole **(1a)**



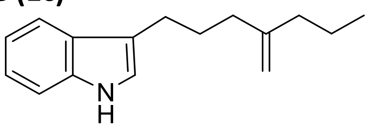
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.90 (bs, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.19 (td, *J* = 7.0, 1.2 Hz, 1H), 7.12 (td, *J* = 7.0, 1.0 Hz, 1H), 6.99 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.75 (s, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.13 (t, *J* = 7.7 Hz, 2H), 2.04 (t, *J* = 7.6 Hz, 2H), 1.92–1.77 (m, 2H), 1.46–1.37 (m, 2H), 1.37–1.25 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 136.5, 127.8, 122.0, 121.2, 119.2, 119.1, 117.0, 111.2, 108.8, 36.1, 36.0, 30.2, 28.4, 25.0, 22.7, 14.2.
HRMS (ESI) (m/z): calculated for $C_{17}H_{23}N_1$ $[M-H]^-$: 240.1758; found 240.1760.

3-(4-methylenenonyl)-1*H*-indole **(1b)**



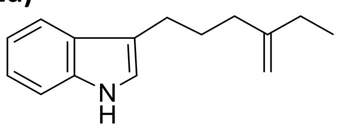
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.89 (bs, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 2.2 Hz, 1H), 4.75 (s, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.14 (t, *J* = 7.7 Hz, 2H), 2.04 (t, *J* = 7.7 Hz, 2H), 1.90–1.84 (m, 2H), 1.50–1.38 (m, 2H), 1.37–1.22 (m, 4H), 0.90 (t, *J* = 7.9Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 136.5, 127.8, 122.0, 121.2, 119.2, 119.1, 117.0, 111.2, 108.8, 36.3, 36.1, 31.8, 28.4, 27.7, 25.0, 22.7, 14.2.
HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M-H]^-$: 254.1914; found 254.1917.

3-(4-methyleneheptyl)-1*H*-indole **(1c)**



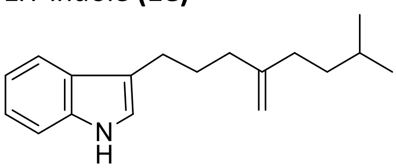
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.71 (bs, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.09 (t, *J* = 8.2 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 2.3 Hz, 1H), 4.66 (d, *J* = 6.6 Hz, 2H), 2.67 (t, *J* = 7.7 Hz, 2H), 2.03 (t, *J* = 7.7 Hz, 2H), 1.92 (t, *J* = 7.6 Hz, 2H), 1.83–1.72 (m, 2H), 1.39–1.34 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 136.5, 127.7, 121.9, 121.2, 119.2, 119.1, 116.9, 111.2, 109.0, 38.4, 36.1, 28.3, 25.0, 21.0, 14.0.
HRMS (ESI) (m/z): calculated for $C_{16}H_{20}N_1$ $[M-H]^-$: 226.1601; found 226.1604.

3-(4-methylenehexyl)-1*H*-indole**(1d)**[7]



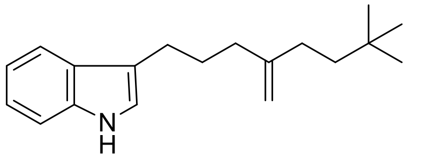
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.90 (bs, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.20 (td, *J* = 8.2, 1.2 Hz, 1H), 7.12 (td, *J* = 8.0, 1.0 Hz, 1H), 7.98 (s, 1H), 4.75 (s, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.16 (t, *J* = 7.7 Hz, 2H), 2.06 (q, *J* = 7.5 Hz, 2H), 1.89–1.85 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 136.5, 127.8, 122.0, 121.2, 119.2, 119.1, 117.0, 111.2, 107.8, 36.3, 28.9, 28.4, 25.0, 12.5.
HRMS (EI) (m/z): calculated for $C_{15}H_{19}N_1$ $[M]^+$: 213.1512; found 213.1511.

3-(7-methyl-4-methyleneoctyl)-1*H*-indole **(1e)**



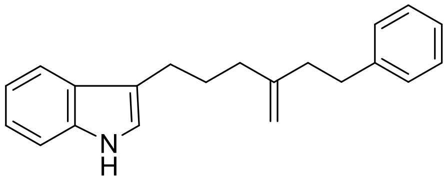
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.93 (bs, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.20 (td, *J* = 7.0, 1.2 Hz, 1H), 7.12 (td, *J* = 7.0, 1.1 Hz, 1H), 7.00 (dd, *J* = 2.3, 1.1 Hz, 1H), 4.74 (s, 2H), 2.77 (t, *J* = 7.1, 2H), 2.13 (t, *J* = 7.7 Hz, 2H), 2.06–1.98 (m, 2H), 1.89–1.83 (m, 2H), 1.57–1.50 (m, 1H), 1.36–1.23 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 136.3, 127.6, 121.9, 121.2, 119.2, 119.1, 116.9, 111.2, 108.6, 37.1, 36.1, 34.1, 28.2, 27.9, 25.0, 22.7.
HRMS (EI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M]^+$: 255.1981; found 255.1981.

3-(7,7-dimethyl-4-methyleneoctyl)-1*H*-indole (**1f**)[7]



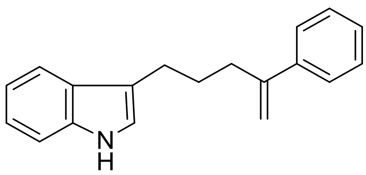
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.90 (bs, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.20 (td, *J* = 8.1, 1.2 Hz, 1H), 7.13 (td, *J* = 8.0, 1.1 Hz, 1H), 7.01–6.97 (m, 1H), 4.76 (d, *J* = 6.1 Hz, 2H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.17 (t, *J* = 7.7 Hz, 2H), 2.04–1.97 (m, 2H), 1.93–1.84 (m, 2H), 1.38–1.30 (m, 2H), 0.91 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 136.5, 127.7, 122.0, 121.2, 119.2, 119.1, 117.0, 111.2, 108.5, 42.5, 36.4, 31.3, 30.4, 29.5, 28.4, 25.0.
HRMS (EI) (m/z): calculated for $C_{19}H_{27}N_1$ $[M]^+$: 269.2138; found 269.2139.

3-(4-methylene-6-phenylhexyl)-1*H*-indole **(1g)**

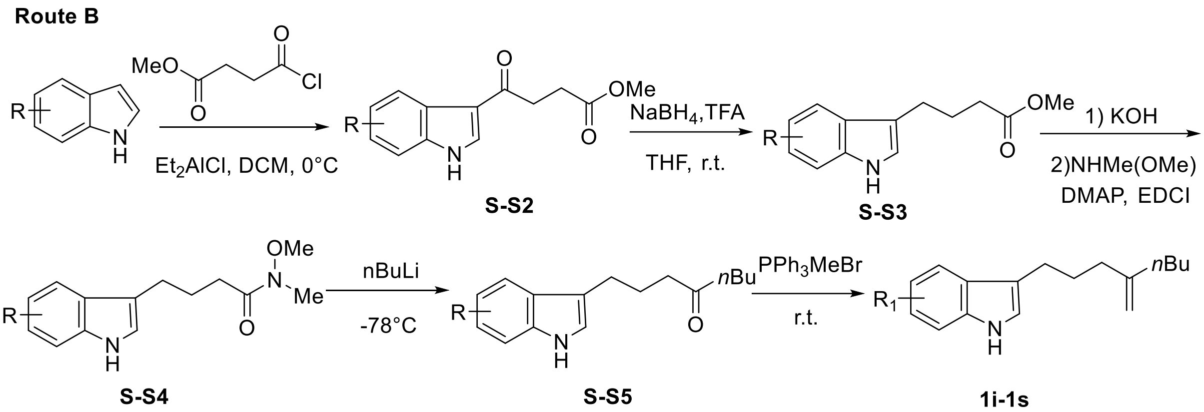


^{1}H NMR (501 MHz, $CDCl_3$) δ δ 7.81 (bs, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.22–7.15 (m, 2H), 7.12–7.09 (m, 4H), 7.07–7.00 (m, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 4.72 (d, *J* = 1.8 Hz, 2H), 2.71–2.66 (m, 4H), 2.26 (t, *J* = 7.7 Hz, 2H), 2.10 (t, *J* = 7.7 Hz, 2H), 1.82 (q, *J* = 7.9 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 142.4, 136.5, 128.5, 128.4, 127.7, 125.9, 122.0, 121.2, 119.3, 119.1, 116.9, 111.2, 109.5, 38.1, 36.3, 34.5, 28.3, 25.0.
HRMS (ESI) (m/z): calculated for $C_{21}H_{22}N_1$ $[M-H]^-$: 288.1758; found 288.1760.

3-(4-phenylpent-4-en-1-yl)-1*H*-indole **(1h)**



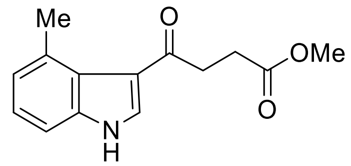
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.83 (bs, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.48–7.43 (m, 2H), 7.39–7.28 (m, 4H), 7.25–7.19 (m, 1H), 7.16–7.12 (m, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 5.35 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.14 (dd, *J* = 3.1, 1.6 Hz, 1H), 2.84 (t, *J* = 8.8 Hz, 2H), 2.66 (t, *J* = 8.8 Hz, 2H), 2.00–1.82 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 141.5, 136.5, 128.4, 127.7, 127.4, 126.3, 122.0, 121.3, 119.2, 119.1, 116.7, 112.5, 111.1, 35.3, 28.7, 24.8.
HRMS (EI) (m/z): calculated for $C_{19}H_{19}N_1$ $[M]^+$: 261.1512; found 261.1514.



Scheme S8: Substrates synthesis of **1i-1s**

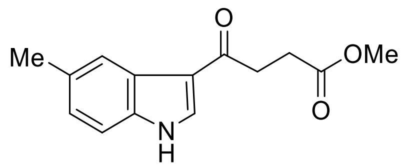
General synthetic procedure of S-S2: **S-S2** was prepared following to the reported procedure for similar compounds.[8] Substituted-indole derivative (1 equiv.) was dissolved in 30 mL anhydrous dichloromethane and cooled to 0 °C. Diethyl aluminum chloride (1.0 M in hexane) (1.2 equiv.) was then added to the solution, which was stirred for 30 min. Still at 0 °C, methyl-4-chloro-4-oxobutyrate (1.2 equiv.) was then slowly added to the flask and reaction proceeded for 2 hours, gradually warming to room temperature. The reaction mixture was slowly quenched with ice-cold saturated NH_4Cl solution, the organics were extracted in dichloromethane and washed with Rochelle's salt solution, dried over Na_2SO_4, and concentrated under reduced pressure to afford a crude solid. The crude product was purified by silica column chromatography (DCM:EtOAc = 15:1 then DCM:EtOAc = 10:1) or directly precipitation from hexane to afford desired product in 48 % to 65 % yield.

Methyl 4-(4-methyl-1*H*-indol-3-yl)-4-oxobutanoate



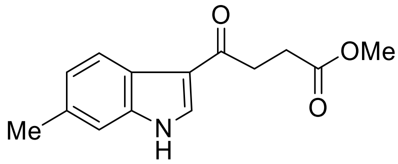
^{1}H NMR (501 MHz, $CDCl_3$) δ 9.00 (bs, 1H), 7.73 (d, *J* = 3.1 Hz, 1H), 7.18–7.13 (m 2H), 7.01 (d, *J* = 6.9 Hz, 1H), 3.71 (s, 3H), 3.15 (t, *J* = 6.7 Hz, 2H), 2.78–2.77 (m, 5H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 174.1, 137.3, 133.6, 131.9, 124.6, 124.3, 124.1, 119.8, 109.0, 51.9, 35.1, 28.7, 23.2.
HRMS (EI) (m/z): calculated for $C_{14}H_{15}N_1O_3$ $[M]^+$: 245.1046; found 245.1049.

Methyl 4-(5-methyl-1*H*-indol-3-yl)-4-oxobutanoate



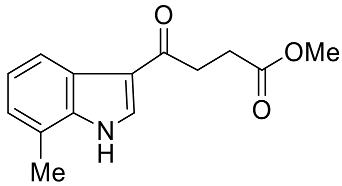
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.64 (bs, 1H), 8.18 (s, 1H), 7.87 (t, *J* = 3.1 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 3.71 (s, 3H), 3.22 (td, *J* = 6.9, 1.5 Hz, 2H), 2.80 (t, *J* = 6.9 Hz, 2H), 2.47 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 174.1, 134.7, 132.4, 131.4, 125.8, 125.3, 122.1, 117.3, 111.1, 52.0, 34.3, 28.4, 21.7.
HRMS (EI) (m/z): calculated for $C_{14}H_{16}N_1O_3$ $[M+H]^+$: 246.1125; found 246.1128.

Methyl 4-(6-methyl-1*H*-indol-3-yl)-4-oxobutanoate



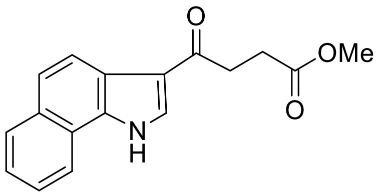
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.68 (bs, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 2.7 Hz, 1H), 7.10 (s, 1H), 7.03 (dd, *J* = 8.2, 1.4 Hz, 1H), 3.64 (s, 3H), 3.12 (t, *J* = 6.9 Hz, 2H), 2.72 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 174.0, 136.8, 133.9, 130.7, 124.6, 123.3, 122.1, 117.8, 111.4, 52.0, 34.3, 28.4, 21.8.
HRMS (EI) (m/z): calculated for $C_{14}H_{16}N_1O_3$ $[M+H]^+$: 246.1125; found 246.1124.

Methyl 4-(7-methyl-1*H*-indol-3-yl)-4-oxobutanoate



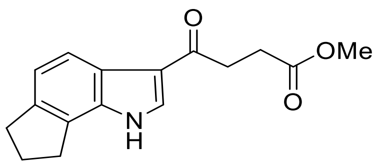
The analytic data was identical to the reported value.[9]

Methyl 4-(1*H*-benzo[*g*]indol-3-yl)-4-oxobutanoate



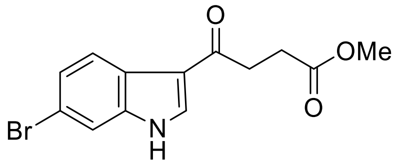
^{1}H NMR (501 MHz, DMSO-d_6) δ 12.79 (s, 1H), 8.44 (dd, *J* = 11.1, 5.6 Hz, 2H), 8.28 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 3.61 (s, 3H), 3.27 (t, *J* = 6.6 Hz, 2H), 2.69 (t, *J* = 6.5 Hz, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 193.7, 173.1, 131.4, 130.1, 128.4, 125.9, 124.5, 122.3, 121.7, 121.5, 120.8, 117.4, 51.3, 33.7, 27.8.
HRMS (ESI) (m/z): calculated for $C_{17}H_{14}N_1O_3$ $[M-H]^-$: 280.0979; found 280.0980.

Methyl 4-oxo-4-(1,6,7,8-tetrahydrocyclopenta[*g*]indol-3-yl)butanoate



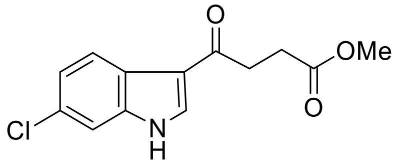
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.49 (bs, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 3.1 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 3.71 (s, 3H), 3.24 (t, *J* = 6.9 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 4H), 2.81 (t, *J* = 6.9 Hz, 2H), 2.23–2.19 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 174.1, 140.6, 133.6, 130.6, 125.8, 124.0, 120.4, 119.7, 118.4, 52.0, 34.4, 33.2, 29.9, 28.4, 25.5.
HRMS (EI) (m/z): calculated for $C_{16}H_{17}N_1O_1$ $[M]^+$: 271.1203; found 271.1206.

Methyl 4-(6-bromo-1*H*-indol-3-yl)-4-oxobutanoate



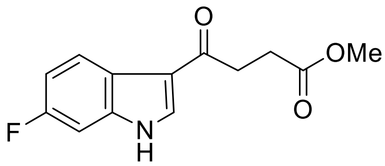
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.71 (bs, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 3.0 Hz, 1H), 7.56 (d, *J* = 1.8 Hz, 1H), 7.38 (dd, *J* = 8.6, 1.8 Hz, 1H), 3.72 (s, 3H), 3.21 (t, *J* = 7.1 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 174.0, 137.2, 131.6, 126.0, 124.4, 123.7, 117.6, 117.3, 114.6, 52.1, 34.2, 28.2.
HRMS (EI) (m/z): calculated for $C_{13}H_{12}N_1O_3Br_1$ $[M]^+$: 308.9995; found 308.9996.

Methyl 4-(6-chloro-1*H*-indol-3-yl)-4-oxobutanoate



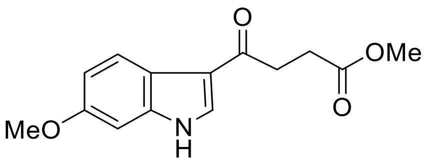
^{1}H NMR (501 MHz, $CDCl_3$) δ δ 8.73 (bs, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 2.9 Hz, 1H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.24 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.72 (s, 3H), 3.20 (t, *J* = 6.7 Hz, 2H), 2.80 (t, *J* = 6.7 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.5, 174.0, 136.8, 131.5, 129.8, 124.1, 123.6, 123.5, 117.8, 111.5, 52.1, 34.3, 28.2.
HRMS (EI) (m/z): calculated for $C_{13}H_{12}N_1O_3Cl_1$ $[M]^+$: 265.0500; found 265.0503.

Methyl 4-(6-fluoro-1*H*-indol-3-yl)-4-oxobutanoate



^{1}H NMR (501 MHz, DMSO-d_6) δ 11.70 (s, 1H), 8.11 (d, *J* = 3.0 Hz, 1H), 7.86 (dd, *J* = 8.7, 5.6 Hz, 1H), 6.99 (dd, *J* = 9.7, 2.4 Hz, 1H), 6.77 (td, *J* = 9.3, 2.4 Hz, 1H), 3.06 (s, 2H), 2.91 (t, *J* = 6.5 Hz, 2H), 2.38 (t, *J* = 6.5 Hz, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 193.1, 173.1, 160.1, 158.3, 136.6, 134.5, 122.4, 122.0, 115.8, 110.1, 109.9, 98.4, 98.2, 51.3, 33.3, 27.7.
^{19}F NMR (471 MHz, DMSO-d_6) δ -119.7 (d, *J* = 5.5 Hz).
HRMS (EI) (m/z): calculated for $C_{13}H_{12}N_1O_3F_1$ $[M]^+$: 249.0796; found 249.0798.

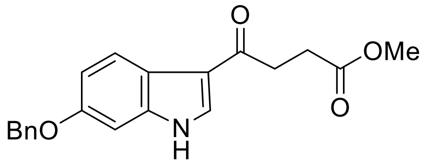
Methyl 4-(6-methoxy-1*H*-indol-3-yl)-4-oxobutanoate



^{1}H NMR (501 MHz, DMSO-d_6) δ 11.73 (s, 1H), 8.22 (d, *J* = 3.0 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.78 (s, 3H), 3.60 (s, 3H), 3.15 (t, *J* = 6.6 Hz, 2H), 2.63 (t, *J* = 6.5 Hz, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 192.9, 173.1, 156.3, 137.4, 132.7, 121.8, 119.3, 115.9, 111.5, 95.1, 55.2, 51.3, 33.2, 27.8.

HRMS (EI) (m/z): calculated for $C_{14}H_{15}N_1O_4$ $[M]^+$: 261.0996; found 261.0997.

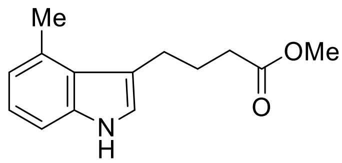
Methyl 4-(6-(benzyloxy)-1*H*-indol-3-yl)-4-oxobutanoate



¹H NMR (501 MHz, $CDCl_3$) δ 8.61 (bs, 1H), 7.99 (d, *J* = 2.5 Hz, 1H), 7.84 (d, *J* = 3.2 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.43–7.35 (m, 2H), 7.34–7.31 (m, 1H), 7.29 (d, *J* = 8.8 Hz, 1H), 7.00 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.12 (s, 2H), 3.72 (s, 3H), 3.21 (t, *J* = 6.8 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 193.7, 174.0, 155.8, 137.5, 131.4, 128.7, 128.0, 127.8, 126.4, 117.7, 115.2, 112.3, 105.0, 70.7, 52.0, 34.2, 28.3.
HRMS (EI) (m/z): calculated for $C_{20}H_{19}N_1O_4$ $[M+H]^+$: 337.1309; found 337.1309.

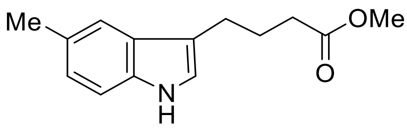
General synthetic procedure of S-S3: In a two-neck round-bottomed flask fitted with a magnetic stirring bar, $NaBH_4$ (2 equiv.) was added to a stirred solution of **S-S2** (1 equiv.) in THF (20 mL). Trifluoroacetic acid (1 equiv.) was then added dropwise. The reaction was stirred at room temperature and monitored by TLC and GC-MS upon full conversion of the starting material (generally 2h). Then the reaction was carefully quenched with cold 1M NaOH solution and extracted with EtOAc for 3 times. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 3:1) to afford product in 40 % to 55 % yield.

Methyl 4-(4-methyl-1*H*-indol-3-yl)butanoate



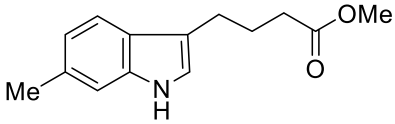
¹H NMR (501 MHz, $CDCl_3$) δ 7.94 (bs, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.95 (s, 1H), 6.84 (d, *J* = 7.1 Hz, 1H), 3.67 (s, 3H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.70 (s, 3H), 2.44 (t, *J* = 7.5 Hz, 2H), 2.03 (p, *J* = 7.5 Hz, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 174.3, 137.0, 131.0, 126.0, 122.1, 121.8, 121.1, 116.7, 109.1, 51.6, 33.8, 26.7, 26.7, 20.4
HRMS (ESI) (m/z): calculated for $C_{14}H_{16}N_1O_2$ $[M-H]^-$: 230.1187; found 230.1187.

Methyl 4-(5-methyl-1*H*-indol-3-yl)butanoate



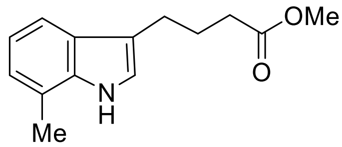
¹H NMR (501 MHz, $CDCl_3$) δ 8.17 (bs, 1H), 7.57 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.18 (dd, *J* = 8.4, 1.5 Hz, 1H), 6.98 (d, *J* = 2.3 Hz, 1H), 3.83 (s, 3H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.65 (s, 3H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.21 (p, *J* = 7.5 Hz, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 174.5, 134.6, 128.1, 127.5, 123.3, 121.8, 118.4, 114.5, 110.9, 51.5, 33.6, 25.3, 24.4, 21.5.
HRMS (EI) (m/z): calculated for $C_{14}H_{17}N_1O_2$ $[M]^+$: 231.1254; found 231.1254.

Methyl 4-(6-methyl-1*H*-indol-3-yl)butanoate



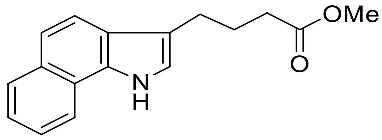
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 1.6 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.90 (dd, *J* = 2.2, 1.1 Hz, 1H), 3.68 (s, 3H), 2.80 (t, *J* = 7.4 Hz, 2H), 2.48 (s, 3H), 2.40 (t, *J* = 7.5 Hz, 2H), 2.06 (p, *J* = 7.5 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 137.0, 131.8, 125.4, 121.1, 118.7, 115.5, 111.2, 51.6, 33.8, 25.5, 24.7, 21.8.
HRMS (EI) (m/z): calculated for $C_{14}H_{17}N_1O_2$ $[M]^+$: 231.1256; found 231.1254.

Methyl 4-(7-methyl-1*H*-indol-3-yl)butanoate



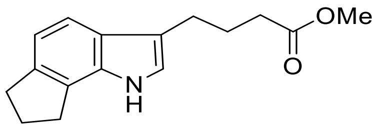
The analytic data was identical to the reported value.[9]

Methyl 4-(1*H*-benzo[*g*]indol-3-yl)butanoate



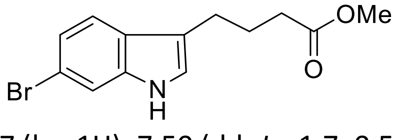
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.72 (bs, 1H), 7.95 (dd, *J* = 24.6, 8.2 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 3.67 (s, 3H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 2.10 (p, *J* = 7.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) 174.4, 131.0, 130.6, 129.0, 125.5, 124.0, 123.3, 121.9, 120.3, 119.8, 119.5, 119.1, 117.6, 51.6, 33.8, 25.9, 24.7.
HRMS (ESI) (m/z): calculated for $C_{17}H_{18}N_1O_2$ $[M+H]^+$: 268.1332; found 268.1333.

Methyl 4-(1,6,7,8-tetrahydrocyclopenta[*g*]indol-3-yl)butanoate



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.78 (bs, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.93 (s, 1H), 3.67 (s, 3H), 3.07-3.04 (m, 4H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.22 (p, *J* = 7.4 Hz, 2H), 2.06 (p, *J* = 7.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 138.6, 133.7, 126.2, 125.6, 120.8, 117.1, 116.3, 51.6, 33.8, 33.2, 30.0, 25.6, 25.5, 24.8.
HRMS (EI) (m/z): calculated for $C_{16}H_{19}N_1O_2$ $[M]^+$: 257.1410; found 257.1413.

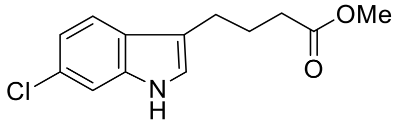
Methyl 4-(6-bromo-1*H*-indol-3-yl)butanoate



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.97 (bs, 1H), 7.50 (dd, *J* = 1.7, 0.5 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.21 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.96 (d, *J* = 2.1 Hz, 1H), 3.66 (s, 3H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.38

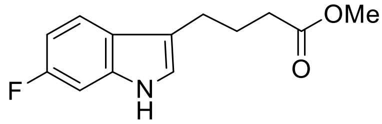
(t, J = 7.4 Hz, 2H), 2.02 (p, J = 7.5 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 137.3, 126.5, 122.7, 122.1, 120.3, 116.0, 115.7, 114.1, 51.7, 33.7, 25.4, 24.5.
HRMS (EI) (m/z): calculated for $C_{13}H_{14}N_1O_2Br_1$ $[M]^+$: 295.0203; found 295.0203.

Methyl 4-(6-chloro-1*H*-indol-3-yl)butanoate



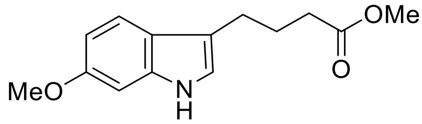
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.00 (bs, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.33 (dd, J = 1.8, 0.6 Hz, 1H), 7.08 (dd, J = 8.5, 1.8 Hz, 1H), 6.97 (dd, J = 2.2, 1.1 Hz, 1H), 3.66 (s, 3H), 2.77 (t, J = 7.5 Hz, 2H), 2.38 (t, J = 7.4 Hz, 2H), 2.03 (p, J = 7.5 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 136.8, 128.0, 126.2, 122.2, 120.1, 119.9, 115.9, 111.1, 51.7, 33.7, 25.4, 24.5.
HRMS (EI) (m/z): calculated for $C_{13}H_{14}N_1O_2Cl_1$ $[M]^+$: 251.0708; found 251.0711.

Methyl 4-(6-fluoro-1*H*-indol-3-yl)butanoate



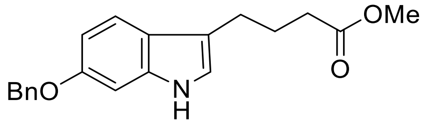
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.98 (bs, 1H), 7.50 (dd, J = 8.7, 5.3 Hz, 1H), 7.03 (dd, J = 9.7, 2.3 Hz, 1H), 6.96 (dd, J = 2.1, 1.0 Hz, 1H), 6.88 (ddd, J = 9.6, 8.7, 2.2 Hz, 1H), 3.67 (s, 3H), 2.78 (t, J = 7.5 Hz, 2H), 2.39 (t, J = 7.4 Hz, 2H), 2.11–1.97 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 161.1, 136.4, 124.2, 121.8, 119.7, 115.9, 108.00, 97.4, 51.6, 33.8, 25.4, 24.6.
HRMS (EI) (m/z): calculated for $C_{13}H_{14}N_1O_2F_1$ $[M]^+$: 235.1003; found 235.1006.

Methyl 4-(6-methoxy-1*H*-indol-3-yl)butanoate



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.94 (bs, 1H), 7.48 (d, J = 8.5 Hz, 1H), 6.86 (d, J = 2.2 Hz, 1H), 6.84–6.78 (m, 2H), 3.84 (s, 3H), 3.68 (s, 3H), 2.78 (t, J = 7.5 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2H), 2.05 (p, J = 7.5 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 156.5, 137.2, 122.0, 120.4, 119.5, 115.5, 109.2, 94.8, 55.8, 51.6, 33.8, 25.4, 24.7.
HRMS (EI) (m/z): calculated for $C_{14}H_{17}N_1O_3$ $[M]^+$: 247.1203; found 247.1208.

Methyl 4-(6-(benzyloxy)-1*H*-indol-3-yl)butanoate

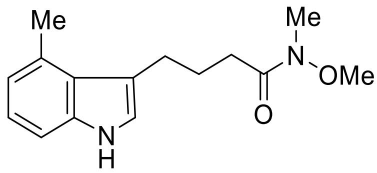


^{1}H NMR (501 MHz, $CDCl_3$)) δ 7.90 (bs, 1H), 7.54–7.48 (m, 2H), 7.43–7.38 (m, 2H), 7.36–7.31 (m, 1H), 7.24 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 6.95 (dd, J = 8.9, 2.4 Hz, 2H), 5.13 (s, 2H), 3.68 (s, 3H), 2.77 (t, J = 7.3 Hz, 2H), 2.40 (t, J = 7.4 Hz, 2H), 2.04 (p, J = 7.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 153.2, 137.8, 131.9, 128.6, 127.9, 127.9, 127.8, 122.5, 115.4, 112.9, 111.9, 102.7, 71.2, 51.6, 33.8, 25.3, 24.6.

HRMS (EI) (m/z): calculated for $C_{20}H_{21}N_1O_3$ $[M]^+$: 323.1516; found 323.1518.

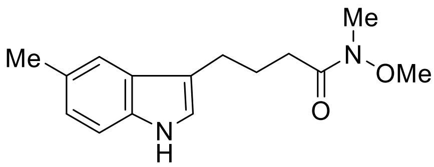
General synthetic procedure of S-S4: To a solution of **S-S3** (1 equiv.) in MeOH:H_2O = 1:1 was added KOH (3 quiv.), the solution mixture was stirred at 80 °C with a condenser for 2 hours. Then the mixture was extracted by DCM and saturated NH_4Cl. The organic layer was separated and dried over Na_2SO_4, and concentrated under reduced pressure. To a solution of the crude residue in DCM were added *N,O*-dimethylhydroxylamine hydrochloride (1.2 equiv.), DMAP (1.2 equiv.) and EDCI (1.2 equiv.) sequentially at room temperature. The mixture was stirred for 4 h then followed by extraction with DCM and washed with saturated NH_4Cl. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 1:2) to afford product in 85 % to 90 % yield.

N-methoxy-*N*-methyl-4-(4-methyl-1*H*-indol-3-yl)butanamide



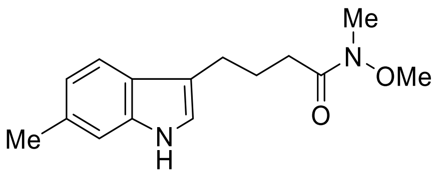
¹H NMR (501 MHz, $CDCl_3$) δ 7.97 (bs, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 1.1, 1H), 6.83 (d, *J* = 7.1 Hz, 1H), 3.66 (s, 3H), 3.19 (s, 3H), 2.99 (t, *J* = 7.7 Hz, 2H), 2.71 (s, 3H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.05 (t, *J* = 7.6 Hz, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 174.8, 137.0, 131.1, 126.1, 122.1, 121.7, 121.0, 117.2, 109.1, 61.3, 31.8, 27.0, 26.2, 20.4.
HRMS (ESI) (m/z): calculated for $C_{15}H_{19}N_2O_2$ $[M-H]^-$: 259.1452; found 259.1455.

N-methoxy-*N*-methyl-4-(5-methyl-1*H*-indol-3-yl)butanamide



¹H NMR (501 MHz, $CDCl_3$) δ 7.85 (bs, 1H), 7.40 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.97 (s, 1H), 3.61 (s, 3H), 3.18 (s, 3H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 2.06 (p, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 174.9, 134.8, 128.5, 127.9, 123.6, 121.6, 118.8, 115.7, 110.8, 61.3, 31.7, 25.0, 24.9, 21.7.
HRMS (EI) (m/z): calculated for $C_{15}H_{20}N_2O_2$ $[M]^+$: 260.1519; found 260.1523.

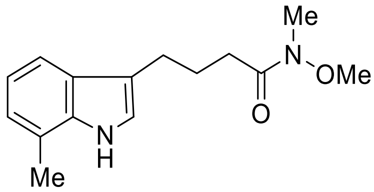
N-methoxy-*N*-methyl-4-(6-methyl-1*H*-indol-3-yl)butanamide



¹H NMR (501 MHz, $CDCl_3$) δ 7.89 (bs, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.14 (s, 1H), 6.97 – 6.87 (m, 2H), 3.61 (s, 3H), 3.18 (s, 3H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.51 (t, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 2.07 (p, *J* = 7.5 Hz, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 174.8, 137.0, 131.7, 125.6, 121.0, 120.8, 118.8, 116.0, 111.1, 61.3,

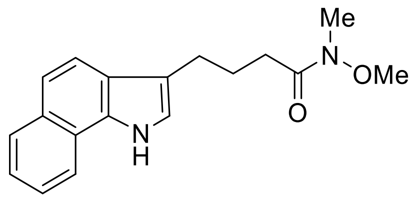
32.4, 31.7, 25.0, 24.9, 21.8.
HRMS (EI) (m/z): calculated for $C_{15}H_{20}N_2O_2$ $[M]^+$: 260.1519; found 260.1522.

N-methoxy-*N*-methyl-4-(7-methyl-1*H*-indol-3-yl)butanamide



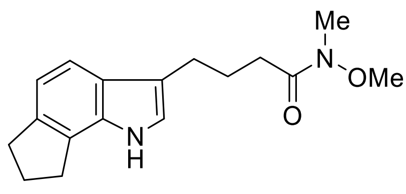
¹H NMR (501 MHz, $CDCl_3$) δ 7.94 (bs, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.12–6.94 (m, 3H), 3.62 (s, 3H), 3.18 (s, 3H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.51 (t, *J* = 6.4 Hz, 2H), 2.48 (s, 3H), 2.15–2.01 (m, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 173.9, 135.1, 126.2, 121.5, 120.2, 119.3, 118.5, 115.9, 115.7, 60.3, 30.7, 28.9, 24.1, 24.0, 15.7.
HRMS (ESI) (m/z): calculated for $C_{15}H_{20}N_2O_2$ $[M]^+$: 260.1519; found 260.1521.

4-(1*H*-benzo[*g*]indol-3-yl)-*N*-methoxy-*N*-methylbutanamide



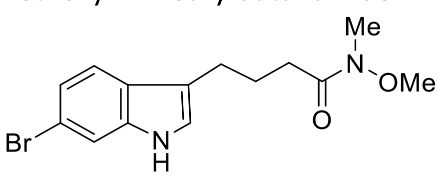
¹H NMR (501 MHz, $CDCl_3$) δ 8.90 (bs, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.50 (dd, *J* = 8.4, 4.1 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 3.61 (s, 3H), 3.19 (s, 3H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.12 (p, *J* = 7.6 Hz, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 175.0, 131.0, 130.6, 129.0, 125.4, 123.9, 123.4, 122.0, 120.1, 119.8, 119.6, 119.3, 117.9, 61.3, 31.6, 29.9, 25.4, 24.9.
HRMS (ESI) (m/z): calculated for $C_{18}H_{21}N_2O_2$ $[M+H]^+$: 297.1598; found 297.1595.

N-methoxy-*N*-methyl-4-(1,6,7,8-tetrahydrocyclopenta[*g*]indol-3-yl)butanamide



¹H NMR (501 MHz, $CDCl_3$) δ 7.99 (bs, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 3.64 (s, 3H), 3.20 (s, 3H), 3.04 (dt, *J* = 14.1, 7.3 Hz, 4H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.21 (p, *J* = 7.4 Hz, 2H), 2.10 (p, *J* = 7.5 Hz, 2H).
¹³C NMR (126 MHz, $CDCl_3$) δ 174.9, 138.4, 133.7, 126.3, 125.5, 120.7, 117.1, 116.6, 116.1, 61.3, 33.2, 32.2, 31.7, 29.9, 25.5, 25.1, 25.0.
HRMS (ESI) (m/z): calculated for $C_{17}H_{21}N_2O_3$ $[M-H]^-$: 285.1609; found 285.1611.

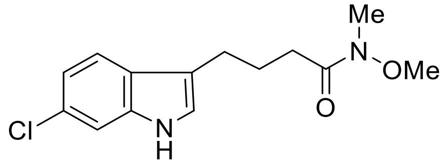
4-(6-bromo-1*H*-indol-3-yl)-*N*-methoxy-*N*-methylbutanamide



¹H NMR (501 MHz, $CDCl_3$) δ 8.06 (bs, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.20 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.97 (dd, *J* = 2.2, 1.1 Hz, 1H), 3.61 (s, 3H), 3.18 (s, 3H), 2.79 (t, *J* = 7.4

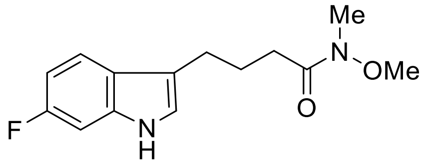
Hz, 2H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.04 (p, *J* = 7.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 137.3, 126.6, 122.5, 122.1, 120.4, 116.4, 115.6, 114.1, 61.3, 31.6, 29.8, 25.0, 24.7.
HRMS (EI) (m/z): calculated for $C_{14}H_{17}N_2O_2Br_1$ $[M]^+$: 324.0468; found 324.0471.

4-(6-chloro-1*H*-indol-3-yl)-*N*-methoxy-*N*-methylbutanamide



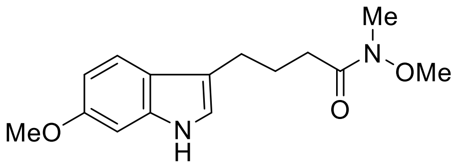
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.33 (bs, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.06 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.98–6.87 (m, 1H), 3.62 (s, 3H), 3.19 (s, 3H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.04 (p, *J* = 7.6 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 136.8, 127.8, 126.3, 122.2, 119.9, 119.9, 116.2, 111.1, 61.3, 32.4, 31.6, 25.0, 24.7.
HRMS (EI) (m/z): calculated for $C_{14}H_{17}N_2O_2Cl_1$ $[M]^+$: 280.0973; found 280.0978.

4-(6-fluoro-1*H*-indol-3-yl)-*N*-methoxy-*N*-methylbutanamide



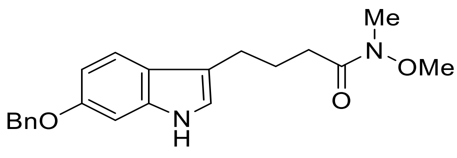
^{1}H NMR (501 MHz, $CDCl_3$) δ 8.37 (bs, 1H), 7.50 (dd, *J* = 8.6, 5.3 Hz, 1H), 7.01 (dd, *J* = 9.7, 2.3 Hz, 1H), 6.93 (dd, *J* = 2.2, 1.1 Hz, 1H), 6.86 (ddd, *J* = 9.6, 8.6, 2.3 Hz, 1H), 3.62 (s, 3H), 3.19 (s, 3H), 2.79 (t, *J* = 8.3 Hz, 2H), 2.52 (t, *J* = 7.7 Hz, 2H), 2.05 (p, *J* = 7.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 160.9, 159.1, 136.3, 124.3, 121.8, 119.6, 116.0, 107.9, 107.7, 97.6, 97.3, 61.3, 32.3, 31.6, 25.0, 24.8.
HRMS (EI) (m/z): calculated for $C_{14}H_{17}N_2O_2F_1$ $[M]^+$: 264.1269; found 264.1271.

N-methoxy-4-(6-methoxy-1*H*-indol-3-yl)-*N*-methylbutanamide



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.85 (bs, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 6.89 (d, *J* = 1.0 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.84 (s, 3H), 3.61 (s, 3H), 3.18 (s, 3H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.05 (p, *J* = 7.6 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 156.6, 137.2, 122.2, 120.2, 119.7, 116.0, 109.2, 94.8, 61.3, 55.8, 31.8, 25.0, 24.9.
HRMS (EI) (m/z): calculated for $C_{15}H_{20}N_2O_3$ $[M]^+$: 276.1468; found 276.1470.

4-(6-(benzyloxy)-1*H*-indol-3-yl)-*N*-methoxy-*N*-methylbutanamide

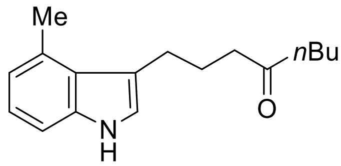


^{1}H NMR (501 MHz, $CDCl_3$) δ 7.98 (bs, 1H), 7.52–7.46 (m, 2H), 7.42–7.35 (m, 2H), 7.35–7.29 (m,

1H), 7.24 (d, J = 8.7 Hz, 1H), 7.16 (d, J = 2.4 Hz, 1H), 6.97 (d, J = 2.1 Hz, 1H), 6.93 (dd, J = 8.7, 2.4 Hz, 1H), 5.12 (s, 2H), 3.61 (s, 3H), 3.19 (s, 3H), 2.78 (t, J = 7.1 Hz, 2H), 2.52 (t, J = 7.5 Hz, 2H), 2.06 (p, J = 7.5 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 153.1, 137.9, 131.9, 128.6, 128.1, 127.9, 127.8, 122.4, 115.9, 112.8, 111.8, 102.7, 71.2, 61.3, 31.7, 2497, 24.8.
HRMS (EI) (m/z): calculated for $C_{21}H_{24}N_2O_3$ $[M]^+$: 352.1781; found 352.1785.

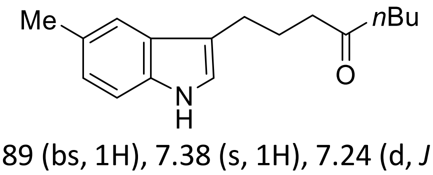
General synthetic procedure of S-S5: To a solution of **S-S4** in THF was slowly added *n*BuLi (2.3 equiv.) at -78 °C. After stirring at that temperature for 1.5 h, the solution was slowly warmed up to room temperature and then quenched with cold saturated NH_4Cl. Then the mixture was extracted by DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1) to afford product in 90 % to 95 % yield.

1-(4-methyl-1*H*-indol-3-yl)octan-4-one



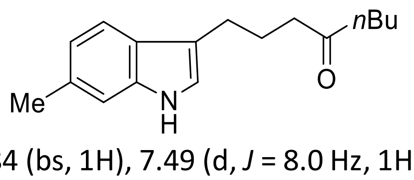
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.93 (bs, 1H), 7.18 (dt, J = 8.2, 0.8 Hz, 1H), 7.05 (dd, J = 8.1, 7.1 Hz, 1H), 6.94 (dd, J = 2.3, 1.1 Hz, 1H), 6.83 (dt, J = 7.1, 1.0 Hz, 1H), 2.92 (t, J = 7.6 Hz, 2H), 2.70 (s, 3H), 2.52 (t, J = 7.3 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2H), 1.98 (p, J = 7.5 Hz, 2H), 1.63–1.52 (m, 2H), 1.38–1.25 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.6, 137.0, 131.0, 126.0, 122.1, 121.7, 121.1, 117.0, 109.1, 42.8, 42.5, 26.8, 26.1, 25.5, 22.5, 20.4, 14.0.
HRMS (EI) (m/z): calculated for $C_{17}H_{23}N_1O_1$ $[M]^+$: 257.1774; found 257.1776.

1-(5-methyl-1*H*-indol-3-yl)octan-4-one



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.89 (bs, 1H), 7.38 (s, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.02 (dd, J = 8.2, 1.6 Hz, 1H), 6.93 (d, J = 2.3 Hz, 1H), 2.75 (t, J = 7.5 Hz, 2H), 2.47 (s, 5H), 2.37 (t, J = 7.5 Hz, 2H), 2.08–1.89 (m, 2H), 1.59–1.49 (m, 2H), 1.36–1.23 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.8, 134.8, 128.5, 127.8, 123.7, 121.7, 118.7, 115.5, 110.9, 42.7, 42.5, 26.1, 24.6, 24.3, 22.5, 21.6, 14.0.
HRMS (ESI) (m/z): calculated for $C_{17}H_{22}N_1O_1$ $[M-H]^-$: 256.1707; found 256.1710.

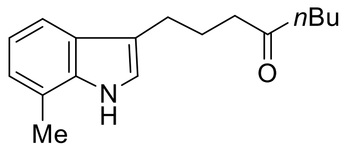
1-(6-methyl-1*H*-indol-3-yl)octan-4-one



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.14 (s, 1H), 6.95 (dd, J = 8.1, 1.4 Hz, 1H), 6.89 (d, J = 2.2 Hz, 1H), 2.75 (td, J = 7.5, 0.9 Hz, 2H), 2.47–2.45 (m, 5H), 2.37 (t, J = 7.5 Hz, 2H), 2.00 (p, J = 7.3 Hz, 2H), 1.57–1.51 (m, 2H), 1.34–1.25 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H).

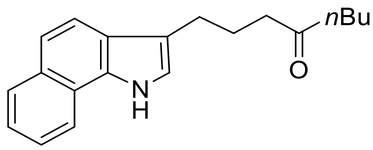
^{13}C NMR (126 MHz, $CDCl_3$) δ 215.9, 137.0, 133.6, 128.9, 126.1, 121.1, 119.5, 118.3, 110.6, 29.7, 26.0, 24.1, 23.2, 22.0, 21.6, 14.0.
HRMS (EI) (m/z): calculated for $C_{17}H_{23}N_1O_1$ $[M]^+$: 257.1774; found 257.1776.

1-(7-methyl-1*H*-indol-3-yl)octan-4-one



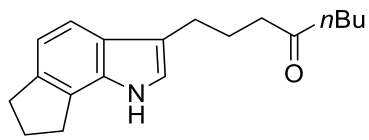
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.87 (bs, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 7.01–6.97 (m, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.50–2.43 (m, 5H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.00 (p, *J* = 7.4 Hz, 2H), 1.56–1.47 (m, 2H), 1.32–1.22 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.0, 135.9, 133.9, 128.9, 127.8, 123.2, 119.9, 119.6, 116.4, 29.7, 26.1, 24.2, 23.2, 21.7, 16.9, 14.1.
HRMS (EI) (m/z): calculated for $C_{17}H_{25}N_1O_1$ $[M]^+$: 257.1774; found 257.1776.

1-(1*H*-benzo[*g*]indol-3-yl)octan-4-one



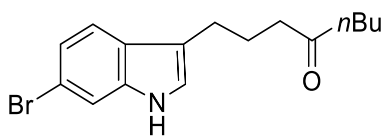
^{1}H NMR (501 MHz, THF-d_8) δ 10.84 (bs, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.46–7.34 (m, 2H), 7.31 (td, *J* = 8.1, 1.2 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.4 Hz, 2H), 1.97 (p, *J* = 7.3 Hz, 2H), 1.50 (p, *J* = 7.5 Hz, 2H), 1.36–1.22 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, THF-d_8) δ 209.6, 132.5, 131.6, 129.4, 125.7, 124.5, 124.0, 123.7, 121.1, 121.0, 120.1, 112.0, 117.9, 42.9, 42.7, 30.8, 26.9, 23.4, 14.4.
HRMS (ESI) (m/z): calculated for $C_{20}H_{23}N_1O_1$ $[M-H]^-$: 290.1914; found 290.1917.

1-(1,6,7,8-tetrahydrocyclopenta[*g*]indol-3-yl)octan-4-one



^{1}H NMR (501 MHz, C_6D_6) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 2.12 (t, *J* = 6.7 Hz, 2H), 2.07–2.00 (m, 4H), 1.93 (t, *J* = 7.4 Hz, 2H), 1.46 (p, *J* = 7.4 Hz, 2H), 1.14 (p, *J* = 7.4 Hz, 2H), 0.79 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 209.2, 138.3, 134.1, 127.1, 125.4, 120.7, 117.6, 116.6, 42.4, 42.2, 33.5, 30.1, 26.2, 25.9, 25.2, 24.81 22.7, 14.1.
HRMS (EI) (m/z): calculated for $C_{19}H_{25}N_1O_1$ $[M]^+$: 283.1930; found 283.1932.

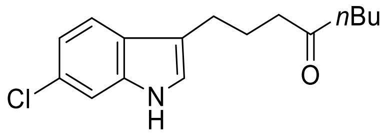
1-(6-bromo-1*H*-indol-3-yl)octan-4-one



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.97 (bs, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.20 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.46 (t, *J* = 7.3 Hz, 2H),

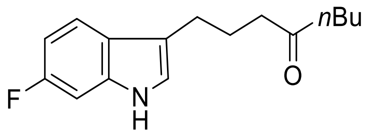
2.37 (t, J = 7.5 Hz, 2H), 1.97 (p, J = 7.4 Hz, 2H), 1.57–1.47 (m, 2H), 1.35–1.21 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.5, 137.3, 126.6, 122.7, 122.0, 120.3, 116.4, 115.7, 114.1, 42.8, 42.3, 26.1, 24.5, 24.2, 22.5, 14.0.
HRMS (EI) (m/z): calculated for $C_{16}H_{20}N_1O_1Br_1$ $[M]^+$: 321.0723; found 321.0723.

1-(6-chloro-1*H*-indol-3-yl)octan-4-one



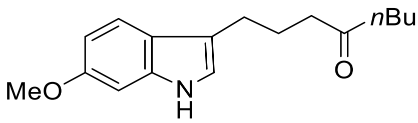
^{1}H NMR (501 MHz, C_6D_6) δ 7.37 (d, J = 8.4 Hz, 1H), 7.18 (dd, J = 8.4, 1.8 Hz, 1H), 7.11 (d, J = 1.8 Hz, 1H), 6.68 (bs, 1H), 6.38 (d, J = 2.3 Hz, 1H), 2.57 (t, J = 7.5 Hz, 2H), 2.03 (t, J = 7.1 Hz, 2H), 1.94–1.87 (m, 4H), 1.45 (p, J = 7.4 Hz, 2H), 1.14 (p, J = 7.5 Hz, 2H), 0.80 (t, J = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 209.1, 137.1, 126.7, 122.2, 120.2, 116.2, 111.4, 42.4, 42.0, 26.2, 24.6, 24.5, 22.7, 14.1.
HRMS (EI) (m/z): calculated for $C_{16}H_{20}N_1O_1Cl_1$ $[M]^+$: 277.1228; found 277.1229.

1-(6-fluoro-1*H*-indol-3-yl)octan-4-one



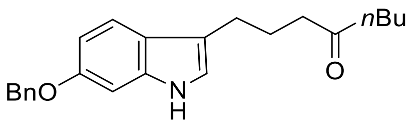
^{1}H NMR (501 MHz, C_6D_6) δ 7.40 (dd, J = 8.7, 5.4 Hz, 1H), 6.95 (ddd, J = 9.6, 8.6, 2.3 Hz, 1H), 6.81 (dd, J = 9.7, 2.3 Hz, 1H), 6.76 (bs, 1H), 6.42 (dd, J = 2.2, 1.1 Hz, 1H), 2.61 (t, J = 7.4 Hz, 2H), 2.05 (t, J = 7.1 Hz, 2H), 1.98–1.84 (m, 4H), 1.46 (p, J = 8.9 Hz, 2H), 1.21–1.08 (m, 2H), 0.80 (t, J = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, C_6D_6) δ 209.2, 161.6, 159.7, 136.8, 124.7, 121.8, 120.1, 120.0, 116.1, 108.3, 108.1, 97.8, 97.6, 42.4, 42.0, 26.2, 24.8, 24.5, 22.7, 14.1.
^{19}F NMR (471 MHz, C_6D_6) δ -121.66 (q, J = 4.6, 4.0 Hz).
HRMS (EI) (m/z): calculated for $C_{16}H_{20}N_1O_1F_1$ $[M]^+$: 261.1523; found 261.1525.

1-(6-methoxy-1*H*-indol-3-yl)octan-4-one



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.46 (d, J = 8.7 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.78 (dd, J = 8.6, 2.3 Hz, 1H), 3.84 (s, 3H), 2.73 (t, J = 7.4 Hz, 2H), 2.46 (t, J = 7.3 Hz, 2H), 2.36 (t, J = 7.5 Hz, 2H), 1.98 (p, J = 7.4 Hz, 2H), 1.57–1.47 (m, 2H), 1.36–1.22 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.6, 156.9, 137.4, 133.3, 128.8, 122.8, 119.2, 113.3, 108.7, 94.8, 55.9, 29.6, 26.0, 24.1, 23.3, 21.6, 14.0.
HRMS (EI) (m/z): calculated for $C_{17}H_{23}N_1O_2$ $[M]^+$: 273.1723; found 273.1725.

1-(6-(benzyloxy)-1*H*-indol-3-yl)octan-4-one

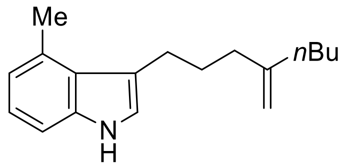


^{1}H NMR (501 MHz, $CDCl_3$) δ 7.91 (bs, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.44–7.39 (m, 2H), 7.37–7.31

(m, 1H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 6.99–6.94 (m, 2H), 5.14 (s, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.00 (p, *J* = 7.4 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.38–1.27 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.7, 153.2, 137.9, 131.9, 128.6, 128.0, 127.8, 127.7, 122.4, 120.2, 115.8, 112.9, 111.9, 111.2, 102.7, 71.2, 42.7, 42.4, 26.1, 24.7, 24.2, 22.5, 14.0.
HRMS (ESI) (m/z): calculated for $C_{23}H_{28}N_1O_2$ $[M+H]^+$: 350.2115; found 350.2118.

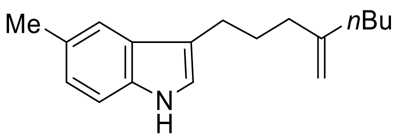
General synthetic procedure of 1i-1s: To a solution of 1M *t*BuOK in THF (3.0 equiv.) was added methyltriphenylphosphonium bromide (1.5 equiv.) at 0 °C and then the suspension was stirred at room temperature for 30 min. To the mixture was slowly added the solution of **S-S5** (1 equiv.) in THF at room temperature and then stirred for 15 h. Then the reaction mixture was quenched with saturated NH_4Cl and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1 to 5:1) to afford product in 85 % to 95 % yield.

4-methyl-3-(4-methyleneoctyl)-1*H*-indole (**1i**)



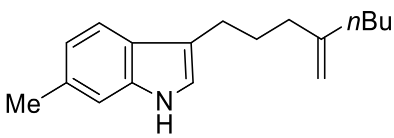
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.86 (bs, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 7.0 Hz, 1H), 4.80 (d, *J* = 5.0 Hz, 2H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.74 (s, 3H), 2.20 (t, *J* = 7.7 Hz, 2H), 2.08 (t, *J* = 7.7 Hz, 2H), 1.95–1.78 (m, 2H), 1.48–1.43 (m, 2H), 1.41–1.30 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 136.9, 131.1, 126.1, 122.0, 121.4, 121.0, 118.0, 109.1, 108.9, 36.1, 36.0, 30.2, 29.7, 27.2, 22.7, 20.4, 14.2.
HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M-H]^-$: 254.1914; found 254.1917.

5-methyl-3-(4-methyleneoctyl)-1*H*-indole (**1j**)



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.66 (bs, 1H), 7.30 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 4.66 (s, 2H), 2.64 (t, , *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 2.04 (t, *J* = 7.7 Hz, 2H), 1.95 (t, *J* = 7.7 Hz, 2H), 1.79–1.74 (m, 2H), 1.36–1.30 (m, 2H), 1.27–1.21 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 134.8, 128.4, 128.0, 123.6, 121.4, 118.8, 116.5, 110.8, 108.8, 36.1, 36.0, 30.2, 28.3, 25.0, 22.7, 21.7, 14.2.
HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M-H]^-$: 254.1914; found 254.1917.

6-methyl-3-(4-methyleneoctyl)-1*H*-indole (**1k**)

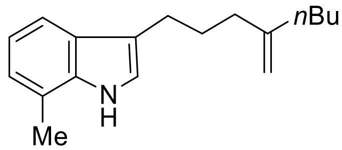


^{1}H NMR (501 MHz, $CDCl_3$) δ 7.73 (bs, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.15 (s, 1H), 6.98 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 4.78 (s, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.50 (s, 3H), 2.16 (t, *J* = 7.7 Hz, 2H), 2.07 (t, *J* = 7.7 Hz, 2H), 1.91-1.86 (m, 2H), 1.50–1.40 (m, 2H), 1.40–1.28 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 137.0, 131.7, 125.6, 121.0, 120.6, 118.8, 116.8, 111.1, 108.8, 36.1, 36.0, 30.2, 28.4, 25.1, 22.7, 21.8, 14.2.

HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M-H]^-$: 254.1914; found 254.1917.

7-methyl-3-(4-methyleneoctyl)-1*H*-indole (**1l**)

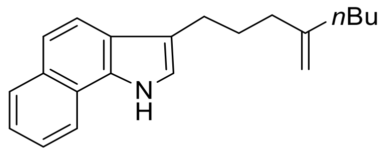


^{1}H NMR (501 MHz, $CDCl_3$) δ 7.82 (bs, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.05 – 6.99 (m, 2H), 4.78 (s, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.50 (s, 3H), 2.16 (t, *J* = 7.7 Hz, 2H), 2.07 (t, *J* = 7.5 Hz, 2H), 1.92-1.86 (m, 2H), 1.47–1.42 (m, 2H), 1.38–1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 136.0, 127.2, 122.4, 120.8, 120.2, 119.4, 117.4, 116.8, 108.7, 36.0, 35.9, 30.1, 28.3, 25.1, 22.6, 16.6, 14.1.

HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M-H]^-$: 254.1914; found 254.1917.

3-(4-methyleneoctyl)-1*H*-benzo[*g*]indole (**1m**)

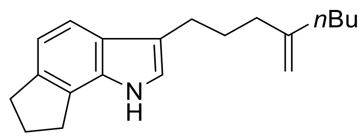


^{1}H NMR (501 MHz, $CDCl_3$) δ 8.61 (bs, 1H), 7.95 (dd, *J* = 11.5, 8.0 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.52 (t, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 8.3 Hz, 1H), 7.05 (s, 1H), 4.77 (s, 2H), 2.85 (t, *J* = 7.7 Hz, 2H), 2.17 (t, *J* = 7.7 Hz, 2H), 2.06 (t, *J* = 7.6 Hz, 2H), 2.00–1.82 (m, 2H), 1.46–1.40 (m, 2H), 1.38–1.24 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 130.9, 130.6, 129.0, 125.5, 123.9, 123.5, 122.0, 120.1, 119.5, 119.3, 118.8, 108.9, 36.1, 36.0, 30.2, 28.8, 25.1, 22.7, 14.2.

HRMS (ESI) (m/z): calculated for $C_{21}H_{25}N_1$ $[M-H]^-$: 290.1914; found 290.1917.

3-(4-methyleneoctyl)-1,6,7,8-tetrahydrocyclopenta[*g*]indole (**1n**)

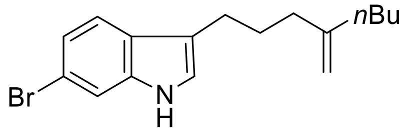


^{1}H NMR (501 MHz, $CDCl_3$) δ 7.70 (bs, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 4.76 (s, 2H), 3.06 (dt, *J* = 15.5, 7.4 Hz, 4H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.25-2.21 (m, 2H), 2.15 (t, *J* = 7.7 Hz, 2H), 2.05 (t, *J* = 7.7 Hz, 2H), 1.90–1.85 (m, 2H), 1.44 (tt, *J* = 7.6, 5.8 Hz, 2H), 1.37–1.29 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 138.5, 133.7, 126.4, 125.5, 120.4, 117.6, 117.2, 116.2, 108.8, 36.1, 36.0, 33.2, 30.2, 29.9, 28.4, 25.6, 25.3, 22.7, 14.2.

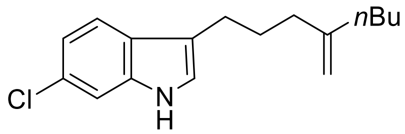
HRMS (ESI) (m/z): calculated for $C_{20}H_{27}N_1$ $[M-H]^-$: 281.2138; found 281.2139.

6-bromo-3-(4-methyleneoctyl)-1H-indole (**1o**)



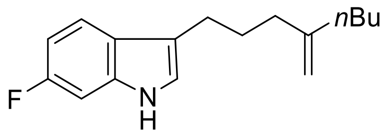
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.87 (bs, 1H), 7.49 (d, J = 1.7 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.22 (dd, J = 8.4, 1.7 Hz, 1H), 6.95 (dd, J = 2.3, 1.0 Hz, 1H), 4.75 (s, 2H), 2.73 (t, J = 7.6 Hz, 2H), 2.12 (t, J = 7.6 Hz, 2H), 2.04 (t, J = 7.6 Hz, 2H), 1.84 (p, J = 7.7 Hz, 2H), 1.47–1.38 (m, 2H), 1.37–1.25 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 137.2, 126.7, 122.5, 121.8, 120.4, 117.2, 115.6, 114.1, 108.9, 36.0, 36.0, 30.2, 28.3, 24.8, 22.6, 14.2.
HRMS (EI) (m/z): calculated for $C_{17}H_{22}N_1Br_1$ $[M]^+$: 319.0928; found 319.0930.

6-chloro-3-(4-methyleneoctyl)-1H-indole (**1p**)



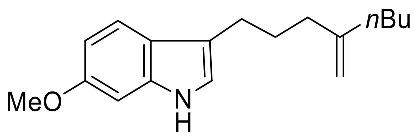
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.89 (bs, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 1.8 Hz, 1H), 7.09 (dd, J = 8.5, 1.8 Hz, 1H), 6.97 (d, J = 2.1 Hz, 1H), 4.75 (s, 2H), 2.74 (t, J = 7.8 Hz, 2H), 2.12 (t, J = 7.6 Hz, 2H), 2.04 (t, J = 7.6 Hz, 2H), 1.89–1.79 (m, 2H), 1.48–1.37 (m, 2H), 1.35–1.29 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 136.8, 127.9, 126.4, 121.9, 120.0, 120.0, 117.2, 111.1, 109.0, 36.0, 35.9, 30.2, 28.3, 24.8, 22.6, 14.2.
HRMS (ESI) (m/z): calculated for $C_{17}H_{22}N_1Cl_1$ $[M-H]^-$: 274.1373; found 274.1368.

6-fluoro-3-(4-methyleneoctyl)-1H-indole (**1q**)



^{1}H NMR (501 MHz, $CDCl_3$) δ 7.89 (bs, 1H), 7.50 (dd, J = 8.7, 5.3 Hz, 1H), 7.03 (dd, J = 9.7, 2.3 Hz, 1H), 6.95 (dq, J = 2.9, 1.9, 1.5 Hz, 1H), 6.90 – 6.84 (m, 1H), 4.74 (t, J = 1.1 Hz, 2H), 2.73 (td, J = 7.6, 1.0 Hz, 2H), 2.12 (t, J = 7.6 Hz, 2H), 2.03 (t, J = 7.6 Hz, 2H), 1.89–1.77 (m, 2H), 1.45–1.36 (m, 2H), 1.36–1.23 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 159.2, 150.0, 124.4, 121.4, 119.8, 119.7, 117.1, 108.9, 108.0, 107.8, 97.5, 97.3, 36.0, 36.0, 30.2, 28.3, 24.9, 22.7, 14.2.
^{19}F NMR (471 MHz, $CDCl_3$) δ -121.61 – -121.70 (m).
HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1O_1$ $[M-H]^-$: 270.1863; found 270.1867.

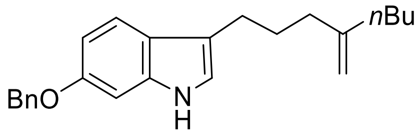
6-methoxy-3-(4-methyleneoctyl)-1H-indole (**1r**)



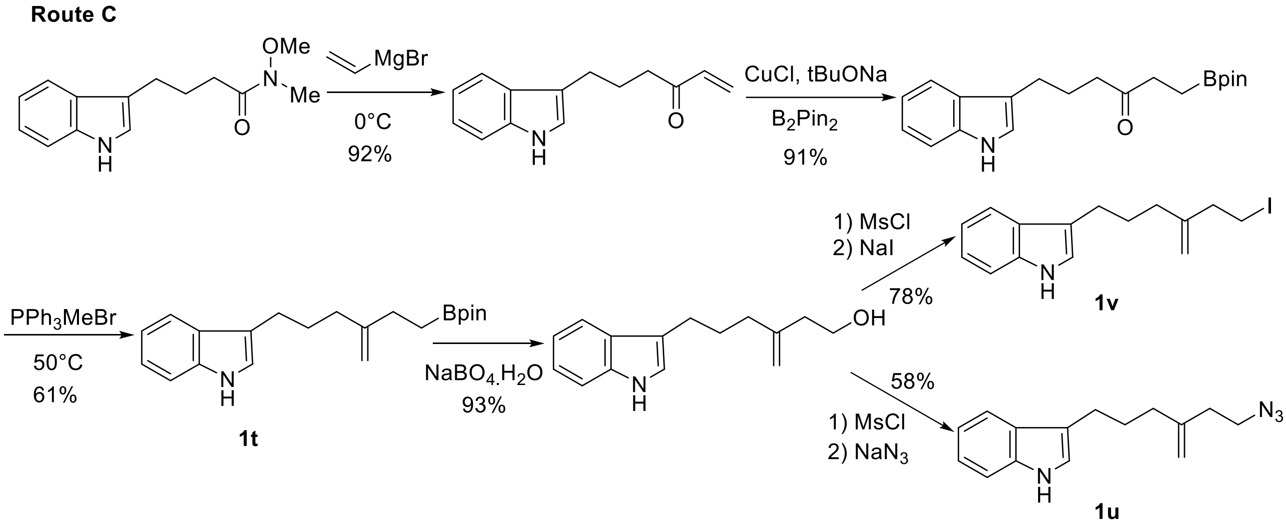
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.77 (bs, 1H), 7.48 (d, J = 8.6 Hz, 1H), 6.89–6.83 (m, 2H), 6.80 (dd, J = 8.6, 2.3 Hz, 1H), 4.75 (s, 2H), 3.85 (s, 3H), 2.73 (t, J = 7.7 Hz, 2H), 2.13 (t, J = 7.7 Hz, 2H), 2.04 (t, J = 7.6 Hz, 2H), 1.88-1.82 (m, 2H), 1.47–1.37 (m, 2H), 1.36–1.25 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 150.2, 137.2, 122.2, 112.0, 119.7, 117.0, 109.2, 108.8, 94.8,

55.9, 36.1, 36.0, 30.2, 28.4, 25.1, 22.7, 14.2.
HRMS (ESI) (m/z): calculated for $C_{18}H_{25}N_1O_1$ $[M-H]^-$: 270.1863; found 270.1867.

6-(benzyloxy)-3-(4-methyleneoctyl)-1*H*-indole (**1s**)

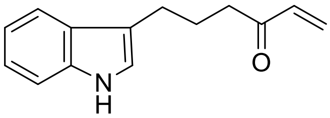


^{1}H NMR (501 MHz, $CDCl_3$) δ 7.69 (bs, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 7.05 (s, 1H), 6.84 (dt, *J* = 4.7, 2.8 Hz, 2H), 5.03 (s, 2H), 4.66 (s, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.03 (t, *J* = 7.7 Hz, 2H), 1.95 (t, *J* = 7.7 Hz, 2H), 1.82–1.66 (m, 2H), 1.35–1.31 (m, 2H), 1.26–1.18 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 150.1, 137.9, 131.9, 128.6, 128.1, 127.9, 127.8, 122.2, 116.7, 112.8, 111.8, 108.8, 102.9, 71.2, 36.1, 36.0, 30.2, 28.2, 25.0, 22.7, 14.2.
HRMS (EI) (m/z): calculated for $C_{24}H_{29}N_1O_1$ $[M]^+$: 347.2243; found 347.2244.



Scheme S9: Substrates synthesis of **1t-1v**

6-(1*H*-indol-3-yl)hex-1-en-3-one

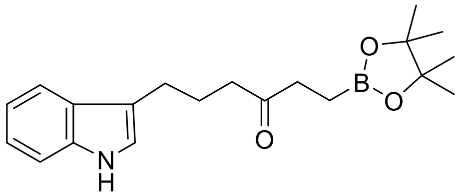


To a solution of 4-(1*H*-indol-3-yl)-*N*-methoxy-*N*-methylbutanamide (1.5 g, 6.09 mmol) in THF (15 mL), vinylmagnesium bromide solution (2 M, 7 mL, 2.3 equiv.) was slowly added at 0 °C. After stirring at that temperature for 1.5 h, the solution was slowly warmed up to room temperature and then quenched with cold saturated NH_4Cl. Then the mixture was extracted by EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 5:1) to afford product 1.2 g in 92% yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.08 (bs, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.35 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.20 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.13 (dt, *J* = 7.1, 1.1 Hz, 1H), 6.97 (dd, *J* = 2.3, 1.1 Hz, 1H), 6.35 (dd, *J* = 17.7, 10.6 Hz, 1H), 6.19 (dd, *J* = 17.7, 1.1 Hz, 1H), 5.80 (dd, *J* = 10.6, 1.1 Hz, 1H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.13–2.00 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.2, 136.6, 136.5, 128.1, 127.6, 122.0, 121.6, 119.3, 119.0, 115.8, 111.2, 39.3, 24.6, 24.4.
HRMS (ESI) (m/z): calculated for $C_{14}H_{14}N_1O_1Na_1$ $[M-H]^-$: 212.1081; found 212.1083.

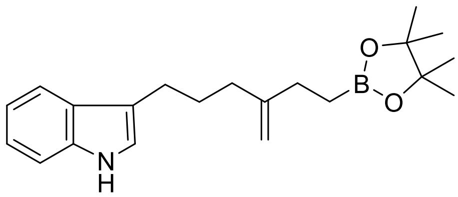
6-(1*H*-indol-3-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-one



A mixture of copper(I) chloride (65 mg, 0.66 mmol, 20 mol%) and *t*BuONa (63 mg, 0.66 mmol, 20 mol%) in THF (10 mL) was stirred at r.t. for 10 min, then bis(pinacolato)diboron (875 mg, 3.45 mmol, 1.05 equiv.) was added and the resulting black solution was stirred for 10 min before addition of 6-(1*H*-indol-3-yl)hex-1-en-3-one (700 mg, 3.28 mmol, 1 equiv.) and methanol (1 mL). The mixture was allowed to stir at r.t. for 2 h and quenched with saturated NH_4Cl. Then the mixture was extracted by EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 3:1) to afford 1 g product in 91% yield.

^{1}H NMR (501 MHz, C_6D_6) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.27–7.17 (m, 2H), 7.08 (dt, *J* = 8.2, 0.9 Hz, 1H), 6.71 (bs, 1H), 6.48 (dd, *J* = 2.3, 1.0 Hz, 1H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.29 (t, *J* = 6.8 Hz, 2H), 2.07 (t, *J* = 6.8 Hz, 2H), 2.01–1.92 (m, 2H), 1.13 (s, 12H).
^{13}C NMR (126 MHz, C_6D_6) δ 209.9, 136.9, 128.4, 122.2, 121.5, 119.6, 119.5, 116.1, 111.4, 83.0, 41.5, 37.8, 25.0, 24.9, 24.8, 24.7.
HRMS (ESI) (m/z): calculated for $C_{20}H_{28}B_1N_1O_3Na_1$ $[M+Na]^+$: 364.2054; found 364.2053.

3-(4-methylene-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1*H*-indole (**1t**)

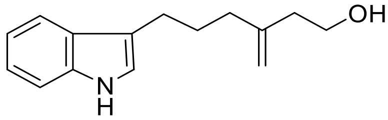


A suspension of *t*BuOK (210 mg, 1.88 mmol, 2 equiv.) and methyltriphenylphosphonium bromide (502 mg, 1.4 mmol, 1.5 equiv.) in THF (10 mL) was stirred at 50 °C for 1h. The solution of 6-(1*H*-indol-3-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-one (320 mg, 0.94 mmol, 1 equiv.) in THF (5 mL) was added into above mentioned mixture and stirred at 50 °C for 24h. Then the reaction mixture was quenched with saturated NH_4Cl and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 3:1) to afford 195 mg product in 61% yield.

^{1}H NMR (501 MHz, C_6D_6) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.25–7.18 (m, 2H), 7.08 (d, *J* = 8.0Hz, 1H), 6.70 (bs, 1H), 6.47 (d, *J* = 2.3Hz, 1H), 4.91 (d, *J* = 49 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.36 (t, *J* = 7.8 Hz, 2H), 2.16 (t, *J* = 7.6 Hz, 2H), 1.89 (dq, *J* = 8.7, 7.6 Hz, 2H), 1.21–1.11 (m, 2H), 1.06 (s, 12H).
^{13}C NMR (126 MHz, C_6D_6) δ 151.7, 136.9, 122.0, 121.2, 119.4, 116.8, 111.3, 108.2, 82.9, 36.7, 30.6, 28.8, 25.3, 25.0.

HRMS (ESI) (m/z): calculated for $C_{21}H_{30}B_{1}N_{1}O_{2}Na_{1}$ $[M+Na]^+$: 362.2262; found 362.2261.

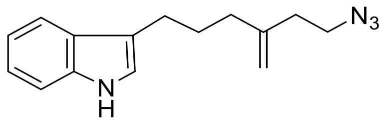
6-(1*H*-indol-3-yl)-3-methylenehexan-1-ol



To a solution of the boronate ester **1t** (105 mg, 0.31 mmol, 1 equiv.) in THF/H_2O (3 mL/3 mL) at room temperature open to air was added $NaBO_3{\cdot}H_2O$ (154 mg, 1.55 mmol, 5 equiv.), and the mixture was stirred for 2 h. Then saturated NH_4Cl was added and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 1:1) to afford 66 mg product in 93% yield.

^{1}H NMR (501 MHz, C_6D_6) δ 7.67 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.28–7.18 (m, 2H), 7.08 (dt, *J* = 8.2, 1.0 Hz, 1H), 6.67 (bs, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 4.80 (dd, *J* = 28.0, 1.6 Hz 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.07 (t, *J* = 6.6 Hz, 2H), 1.99 (t, *J* = 7.7 Hz, 2H), 1.90–1.75 (m, 2H).
^{13}C NMR (126 MHz, C_6D_6) δ 146.6, 136.9, 122.2, 121.2, 119.5, 119.4, 116.5, 111.4, 60.8, 39.7, 36.1, 28.7, 25.2.
HRMS (ESI) (m/z): calculated for $C_{15}H_{18}N_{1}O_{1}$ $[M-H]^-$: 228.1394; found 228.1394.

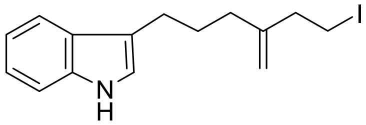
3-(6-azido-4-methylenehexyl)-1*H*-indole (**1u**)



To a mixture of 6-(1*H*-indol-3-yl)-3-methylenehexan-1-ol (144 mg, 0.63 mmol, 1 equiv.) and DMAP (15 mg, 0.126 mmol, 0.2 equiv.) in 5 mL THF were added dropwise MsCl (75 µL, 0.95 mmol, 1.5 equiv.) and Et_3N (127 µL, 0.95 mmol, 1.5 equiv.) at r.t. The resulting mixture was stirred for 3 h and the reaction was monitored by TLC. After the starting material was all consumed, reaction mixture was quenched with saturated NH_4Cl and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The mixture of the above-mentioned crude product and NaN_3 (204 mg, 3.15 mmol, 5 equiv.) in 5 mL DMF was stirred at 80 °C overnight. The reaction mixture was washed with water and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 4:1) to afford 93 mg product in 58% yield.

^{1}H NMR (501 MHz, C_6D_6) δ 7.66 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.28 – 7.17 (m, 2H), 7.08 (dt, *J* = 8.3, 0.9 Hz, 2H), 6.62 (bs, 1H), 6.46 (d, *J* = 2.2 Hz, 1H), 4.75 (d, *J* = 52.0 Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.2 Hz, 2H), 2.01–1.84 (m, 4H), 1.79–1.61 (m, 2H).
^{13}C NMR (126 MHz, C_6D_6) δ 145.9, 136.9, 122.2, 121.2, 119.6, 119.3, 116.3, 111.5, 111.4, 49.5, 35.9, 35.2, 28.5, 25.1.
HRMS (ESI) (m/z): calculated for $C_{15}H_{17}N_4$ $[M-H]^-$: 253.1459; found 253.1463.

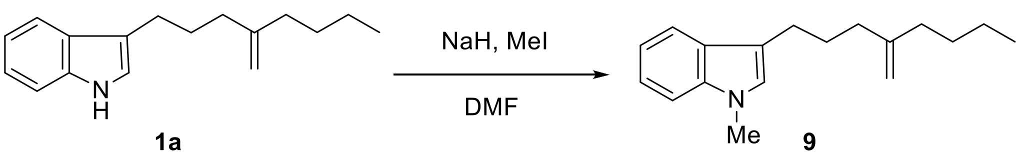
3-(6-iodo-4-methylenehexyl)-1*H*-indole (**1v**)



To a mixture of 6-(1*H*-indol-3-yl)-3-methylenehexan-1-ol (33 mg, 0.14 mmol, 1 equiv.) and DMAP (4 mg, 0.03 mmol, 0.2 equiv.) in 3 mL THF were added MsCl (18 µL, 0.22 mmol, 1.5 equiv.) and Et_3N (29 µL, 0.22 mmol, 1.5 equiv.) at r.t. The resulting mixture was stirred for 3 h and the reaction was monitored by TLC. After the starting material was all consumed, reaction mixture was quenched with saturated NH_4Cl and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The mixture of the above-mentioned crude product and NaI (107 mg, 0.72 mmol, 5 equiv.) in 5 mL acetone was stirred at r.t. overnight. The reaction mixture was washed with water and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 5:1) to afford 38 mg product in 78% yield.

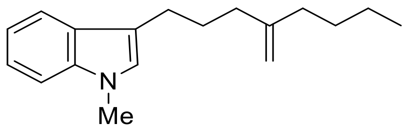
^{1}H NMR (501 MHz, C_6D_6) δ 7.65 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.27–7.18 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.59 (bs, 1H), 6.43 (d, *J* = 2.3 Hz, 1H), 4.71 (dd, *J* = 77.2, 1.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.27 (td, *J* = 7.7, 1.1 Hz, 2H), 1.85 (t, *J* = 7.6 Hz, 2H), 1.73–1.68 (m, 2H).
^{13}C NMR (126 MHz, C_6D_6) δ 148.0, 136.9, 122.2, 121.2, 119.6, 119.3, 116.3, 111.4, 111.3, 40.6, 35.3, 28.4, 25.1, 3.5.
HRMS (ESI) (m/z): calculated for $C_{15}H_{19}N_1I_1$ $[M+H]^+$: 340.0557; found 340.0557.

Route D



Scheme S10: Substrates synthesis of **9**

1-methyl-3-(4-methyleneoctyl)-1*H*-indole (**9**)

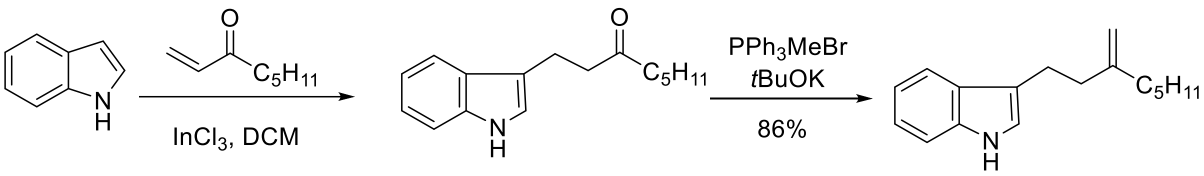


To the solution of **1a** (71.6 mg, 0.30 mmol, 1.0 equiv.) in THF (3 mL) was added NaH (60% dispersion in mineral oil, 24 mg, 0.6 mmol, 2.0 equiv.) at room temperature. After 10 min, to the suspension was added methyliodide (28 µL, 0.45 mmol, 1.5 equiv.) at room temperature and the mixture was stirred for 4.5 h. Then it was quenched with saturated NH_4Cl and extracted twice with Et_2O. The combined organic layer was washed with brine, and then dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:Et_2O = 20:1) to afford 70 mg product as a yellow oil in 92% yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 4.74 (s, 2H), 3.75 (s, 3H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.13 (t, *J* = 7.7 Hz, 2H), 2.03 (t, *J* = 7.6 Hz, 2H), 1.91–1.76 (m, 2H), 1.46–1.36 (m, 2H), 1.36–1.26 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 137.2, 128.1, 126.2, 121.5, 119.2, 118.6, 115.5, 109.2, 108.8, 36.2, 36.0, 32.7, 30.2, 28.6, 25.0, 22.7, 14.2.
HRMS (EI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M]^+$: 255.1981; found 255.1987.

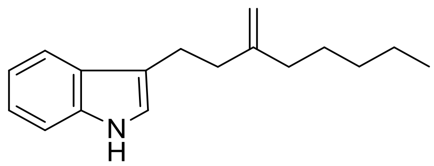
Route E



11

Scheme S11: Substrates synthesis of **11**

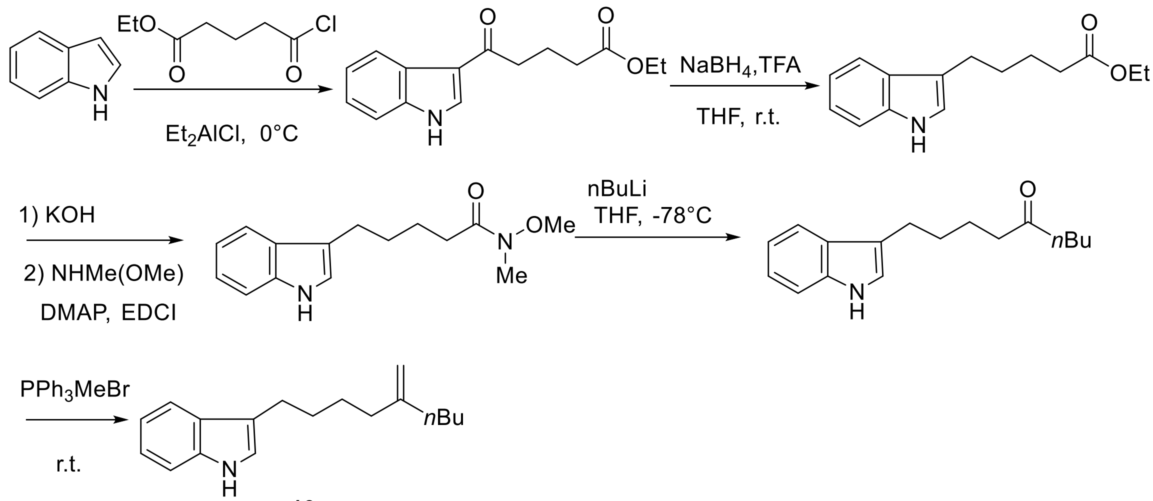
3-(3-methyleneoctyl)-1*H*-indole(**11**)



1-(1*H*-indol-3-yl)octan-3-one was prepared following to the reported procedure for similar compounds.[10] The analytic data was identical to the reported value.[11]
To a solution of *t*BuOK (770 mg, 6.9 mmol, 3.2 equiv.) in THF (10 mL) was added methyltriphenylphosphonium bromide (1.19 g, 3.3 mmol, 1.6 equiv.) at 0 °C and then the suspension was stirred at room temperature for 1 h. To the mixture was slowly added 1-(1*H*-indol-3-yl)octan-3-one (522 mg, 2.1 mmol, 1.0 equiv.) as a solid at room temperature. After 18 h, the reaction mixture was quenched with saturated NH_4Cl and extracted with EtOAc for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography using 5-20 % Et_2O in hexane as eluent to afford the desired product as a red oil (444 mg, 86 %).

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 4.87 (d, *J* = 5.6 Hz, 2H), 2.95 (t, *J* = 5.5 Hz, 2H), 2.49 (t, *J* = 6.2 Hz, 2H), 2.15 (t, *J* = 7.6 Hz, 2H), 1.54–1.52 (m, 2H), 1.44–1.28 (m, 4H), 0.96 (t, *J* = 9.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 136.4, 127.6, 122.0, 121.1, 119.3, 119.0, 116.8, 111.2, 108.9, 36.6, 36.4, 31.8, 27.7, 23.9, 22.7, 14.2.
HRMS (EI) (m/z): calculated for $C_{17}H_{22}N_1$ $[M-H]^-$: 240.1758; found 240.1759.

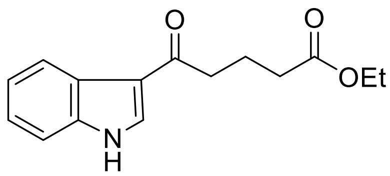
Route F



13

Scheme S12: Substrates synthesis of **13**

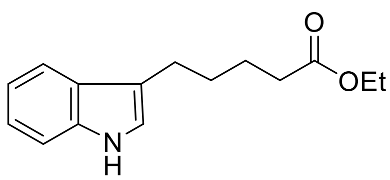
Ethyl 5-(1*H*-indol-3-yl)-5-oxopentanoate



Indole (2 g, 1 equiv.) was dissolved in 30 mL anhydrous dichloromethane and cooled to 0 °C. Diethyl aluminum chloride (1.0 M in hexane) (20 mL, 1.2 equiv.) was then added to the solution, which was stirred for 30 min. Still at 0 °C, ethyl glutaryl chloride (1.2 equiv.) was then slowly added to the flask, the mixture turned to red and reaction proceeded for 2 hours, gradually warming to room temperature. The reaction mixture was slowly quenched with cold 2M HCl solution, the organics were extracted in EtOAc and washed with Rochelle's salt solution, dried over Na_2SO_4, and concentrated under reduced pressure to afford a crude solid. The crude product dissolved in small amount of MeOH and then the precipitation was slowly came out by adding pentane to afford 1.3 g pure product in 40% yield.

^{1}H NMR (501 MHz, DMSO-*d*$_6$) δ 11.91 (s, 1H), 8.29 (d, *J* = 3.1 Hz, 1H), 8.18 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.52 – 7.37 (m, 1H), 7.28 – 7.08 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.37 (t, *J* = 7.5 Hz, 3H), 1.89 (p, *J* = 7.4 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 194.7, 172.7, 136.6, 133.8, 125.3, 122.7, 121.6, 121.3, 116.2, 112.1, 59.7, 37.7, 33.0, 20.2, 14.1.
HRMS (ESI) (m/z): calculated for $C_{15}H_{18}N_1O_3$ $[M+H]^+$: 260.1281; found 260.1282.

Ethyl 5-(1*H*-indol-3-yl)pentanoate

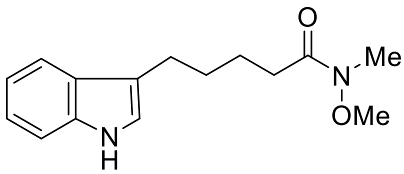


In a two-neck round-bottomed flask fitted with a magnetic stirring bar, $NaBH_4$ (3 equiv.) was added to a stirred solution of Ethyl 5-(1*H*-indol-3-yl)-5-oxopentanoate (1 equiv.) in THF (20 mL). Trifluoroacetic acid (0.5 equiv.) was then drop wisely added. 30 min later, another 0.5 equiv.

of trifluoroacetic acid was again drop wisely. The reaction was stirred at room temperature and followed on TLC upon full conversion of the starting material (2h). Then the reaction was carefully quenched with cold 1M NaOH solution and extracted with EtOAc for 3 times. The combined organic layer were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (Hexane:EtOAc = 3:1) to afford product in 60 % yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.35 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.19 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.85–1.65 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.5, 127.6, 122.0, 121.3, 119.2, 119.0, 116.5, 111.2, 60.4, 34.4, 29.7, 25.0, 14.4.
HRMS (CI) (m/z): calculated for $C_{15}H_{20}N_1O_2$ $[M+H]^+$: 246.1489; found 246.1490.

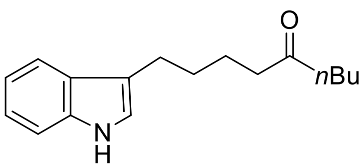
5-(1*H*-indol-3-yl)-*N*-methoxy-*N*-methylpentanamide



To a solution of Ethyl 5-(1*H*-indol-3-yl)pentanoate (156 mg, 0.636 mmol, 1 equiv.) in MeOH:H_2O = 1:1 (5 mL:5 mL) was added KOH (107 mg, 2 equiv.), the mixture solution was stirred at 80 °C with a condenser for 2 hours. Then the mixture was extracted by DCM and saturated NH_4Cl. The organic layer was separated and dried over Na_2SO_4, and concentrated under reduced pressure. To a solution of the crude residue in DCM were added *N*,*O*-dimethylhydroxylamine hydrochloride (74 mg, 0.763 mmol, 1.2 equiv.), DMAP (93 mg, 0.763 mmol, 1.2 equiv.) and EDCI (146 mg, 0.763 mmol, 1.2 equiv.) sequentially at room temperature. The mixture was stirred for 4 h then worked up by addition of water, followed by extraction with DCM and washed by saturated NH_4Cl. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 1:2) to afford 158 mg product in 96 % yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.04 (bs, 1H), 7.61 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.18 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.11 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.98 (s, 1H), 3.65 (s, 3H), 3.18 (s, 3H), 2.80 (t, *J* = 6.5 Hz, 2H), 2.48 (t, *J* = 7.1 Hz, 2H), 1.81 -1.75 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 174.8, 136.5, 127.7, 121.9, 121.4, 119.1, 119.0, 116.5, 111.2, 61.3, 31.9, 30.0, 25.1, 24.7.
HRMS (EI) (m/z): calculated for $C_{15}H_{20}N_2O_2$ $[M]^+$: 260.1520; found 260.1521.

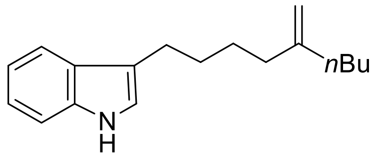
1-(1*H*-indol-3-yl)nonan-5-one



To a solution of 5-(1*H*-indol-3-yl)-*N*-methoxy-*N*-methylpentanamide (150 mg, 0.57 mmol, 1 equiv.) in THF (10 mL) was slowly added *n*BuLi (2.5 M, 530 µL, 2.3 equiv.) at -78°C. After stirring at that temperature for 1.5 h, the solution was slowly warmed up to room temperature and then quenched with cold saturated NH_4Cl. The mixture was extracted by DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 5:1) to afford desired product in 68% yield (100 mg).

^{1}H NMR (501 MHz, $CDCl_3$) δ 8.08 (bs, 1H), 7.63 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.35 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.95 (dd, *J* = 2.3, 1.1 Hz, 1H), 2.80 (t, *J* = 7.1 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.79–1.66 (m, 4H), 1.58 (p, *J* = 7.5 Hz, 2H), 1.42–1.25 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 211.9, 136.5, 127.6, 121.8, 121.4, 119.1, 118.9, 116.3, 111.2, 42.7, 42.6, 29.8, 26.1, 25.1, 23.9, 22.4, 13.9.
HRMS (ESI) (m/z): calculated for $C_{17}H_{24}N_1O_1$ $[M+H]^+$: 258,1852; found 258.1853.

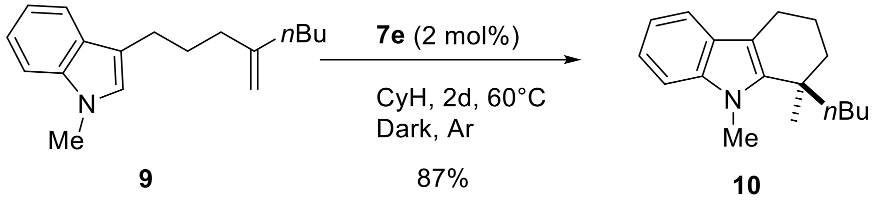
3-(5-methylenenonyl)-1*H*-indole(**13**)



To a solution of 1M *t*BuOK (2.7 mL, 2.68 mmol, 3.0 equiv.) in 10 mL THF was added methyltriphenylphosphonium bromide (480 mg, 1.34 mmol, 1.5 equiv.) then the suspension was stirred at room temperature for 30 min. To the mixture, the solution of 1-(1*H*-indol-3-yl)nonan-5-one (230 mg, 0.89 mmol, 1 equiv.) in 5 mL THF was slowly added at room temperature and then stirred for 15 h. The reaction mixture was quenched with saturated NH_4Cl and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1) to afford product 190 mg in 83 % yield.

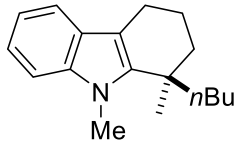
^{1}H NMR (501 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.64 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.36 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.98 (dd, *J* = 2.2, 1.1 Hz, 1H), 4.73 (s, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.09 (t, *J* = 7.6 Hz, 2H), 2.03 (t, *J* = 7.6 Hz, 2H), 1.84–1.70 (m, 2H), 1.64–1.53 (m, 2H), 1.49–1.39 (m, 2H), 1.37–1.27 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 136.5, 127.74, 122.0, 121.1, 119.2, 119.1, 117.2, 111.1, 108.7, 36.1, 35.9, 30.2, 30.0, 27.9, 25.2, 22.7, 14.2.
HRMS (ESI) (m/z): calculated for $C_{18}H_{24}N_1$ $[M-H]^-$: 254.1914; found 254.1914.

6. Control experiments



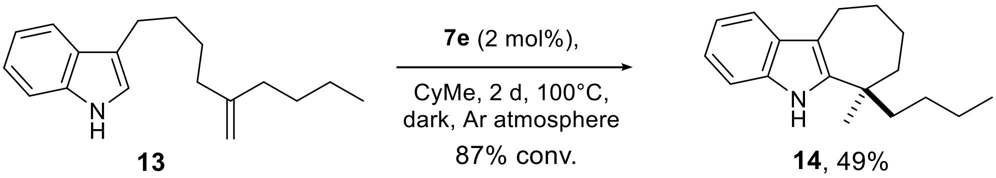
Scheme **S13**. Hydroarylation of olefin with methylated indole **9**

1-butyl-1,9-dimethyl-2,3,4,9-tetrahydro-1*H*-carbazole (**10**)



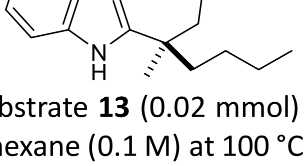
A Schlenk tube equipped with an aluminum foil was charged with IDPi **7e** (2 mol%) under Argon, substrate **9** (0.15 mmol) and cyclohexane (0.1 M) were added at room temperature. The resulting solution was heated at 60 °C for 2 days and the reaction was monitored by TLC. After full consumption of the starting material, the reaction mixture was diluted with pentane and directly purified by silica gel column chromatography (Pentane:Et_2O = 10:1) to afford the desired product in 87% yield.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.49 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.19 (td, *J* = 7.0, 1.2 Hz, 1H), 7.09 (td, *J* = 7.0, 1.0 Hz, 1H), 3.80 (s, 3H), 2.84–2.73 (m, 1H), 2.66 (ddd, *J* = 15.1, 9.2, 5.4 Hz, 1H), 2.09–1.74 (m, 4H), 1.66–1.54 (m, 2H), 1.39 (s, 3H), 1.36–1.24 (m, 3H), 1.10–0.96 (m, 1H), 0.89 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 137.5, 127.0, 120.9, 118.7, 118.1, 110.5, 108.5, 40.9, 38.7, 36.0, 31.8, 27.4, 26.9, 23.6, 22.2, 20.5, 14.2.
HRMS (EI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M]^+$: 255.1981; found 255.1987.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel OJ-3 column: *n*Hept:*i*PrOH = 99:1, flow rate 0.7 mL/ min, t_{major} = 4.2 min, t_{minor} = 5.6 min. e.r. = 71:29



Scheme **S14**. Hydroarylation of substrate **13**

(*R*)-6-butyl-6-methyl-5,6,7,8,9,10-hexahydrocyclohepta[*b*]indole (**14**)



Reactions were performed with substrate **13** (0.02 mmol) in the presence of with IDPi **7e** (2 mol%) under Argon in methylcyclohexane (0.1 M) at 100 °C for 2 days. Conversions, yields and regioisomeric ratios were determined by ^{1}H NMR analysis with mesitylene as an internal standard. Some amount of isomerization of the 1,1-disubstituted olefin leading to the trisubstituted olefins was observed (a mixture of regioisomers, NMR signals were represented as *isom. in the following figure), which remain unreactive under the reaction conditions. The moderate yield is presumely due to the isomerization.

^{1}H NMR (501 MHz, $CDCl_3$) δ 7.84 (bs, 1H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.14–7.04 (m, 2H), 3.02–2.93 (m, 1H), 2.73–2.71 (m, 1H), 1.99–1.81 (m, 4H), 1.79–1.51 (m, 4H), 1.37 (s, 3H), 1.33–1.20 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 133.9, 129.2, 120.7, 119.0, 117.8, 112.5, 110.3, 39.8, 39.7, 38.9, 28.6, 26.7, 26.3, 26.0, 24.1, 23.6, 14.2.
HRMS (EI) (m/z): calculated for $C_{18}H_{25}N_1$ $[M]^+$: 255.1981; found 255.1984.
The enantiomeric ratio was measured by HPLC analysis using following parameters: Daicel Chiralcel IB-3 column: *n*Hept:*i*PrOH = 95:5, flow rate 0.7 mL/ min, t_{major} = 6.6 min, t_{minor} = 7.6 min. e.r. = 76:24.

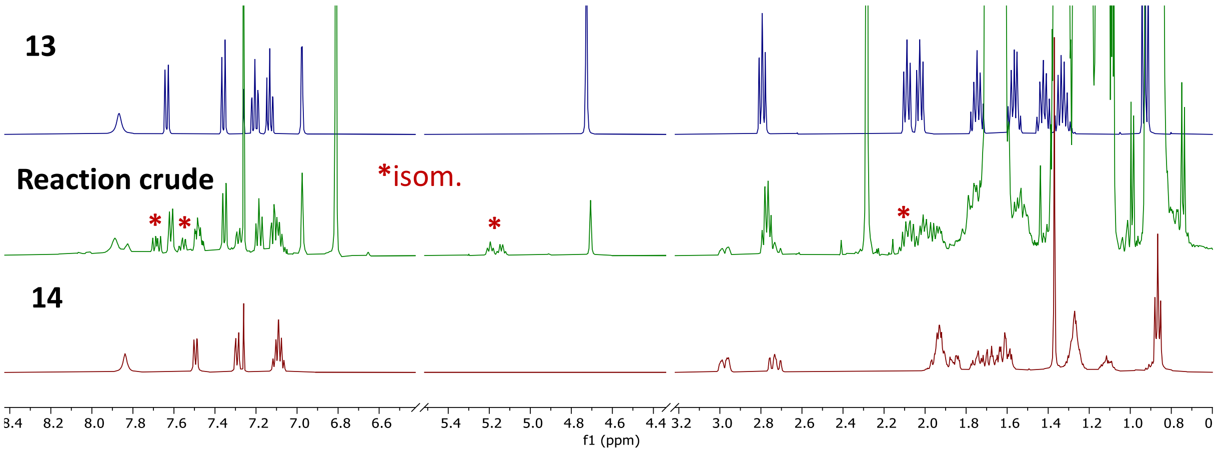
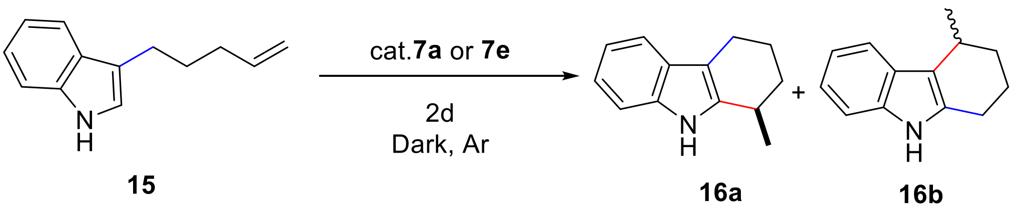


Figure **S1**. Stacked ^{1}H NMR of the formation of 7-membered ring **14** ($CDCl_3$, 501 MHz)



catalyst	loading	T (°C)	conv.	yield	r.r	e.r.$_{16a}$
7a	4 mol%	100	95%	70%	6.7:1	51:49
7a	4 mol%	60	<10%	trace	nd	nd
7e	2 mol%	60	Full	72%	>20:1	69:31

Scheme **S15**. Hydroarylation of monosubstituted terminal olefin **15**

A Schlenk tube equipped with an aluminum foil was charged with IDPi (2 mol %) under Argon, substrate **15** (0.02 mmol) and cyclohexane or methylcyclohexane (0.1 M) were added at room temperature. The resulting solution was heated at 60 °C or 100 °C for 2 days and the reaction was monitored by TLC. Conversions, yields and and regioisomeric ratios (r.r.) were obtained by ^{1}H NMR analysis with mesitylene as an internal standard. Chiralcel IB-3 column: *n*Hept:*i*PrOH

= 95:5, flow rate 0.7 mL/ min, t_{major} = 7.7 min, t_{minor} = 8.2 min. e.r. = 69:31. Here, the protonation of **15** will lead to a secondary rather than a tertiary cation as in all other cases. The lower enantiomeric ratio was presumely due to the more challenging enantidifferentiation of this highly reactive and sterically unbiased cation.

15 was prepared following to the reported procedure.[12]

The analytic data of **16a** was identical to the reported value.[13]

The analytic data of **16b** was identical to the reported value.[14] *Represents NMR signal of **16b** in the following Figure.

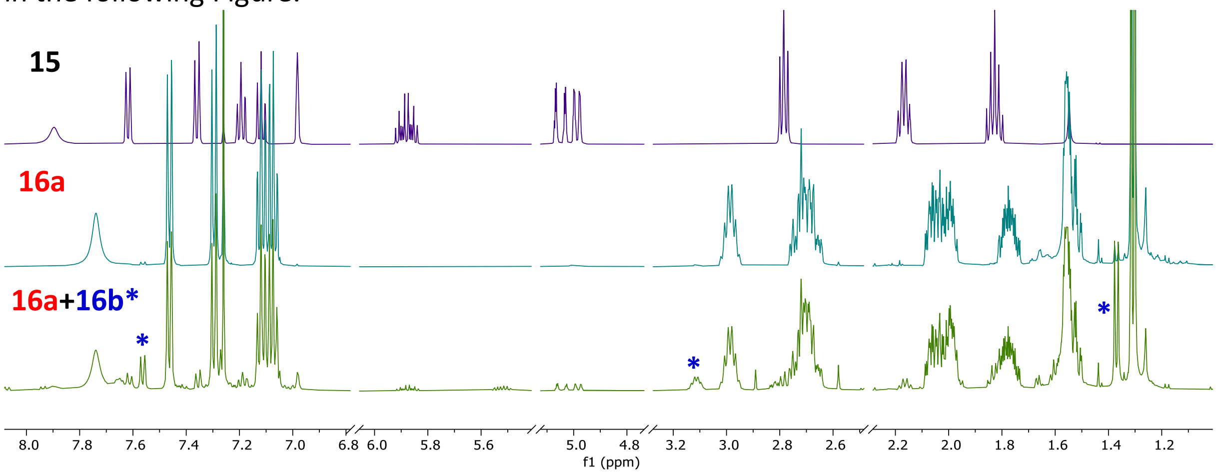
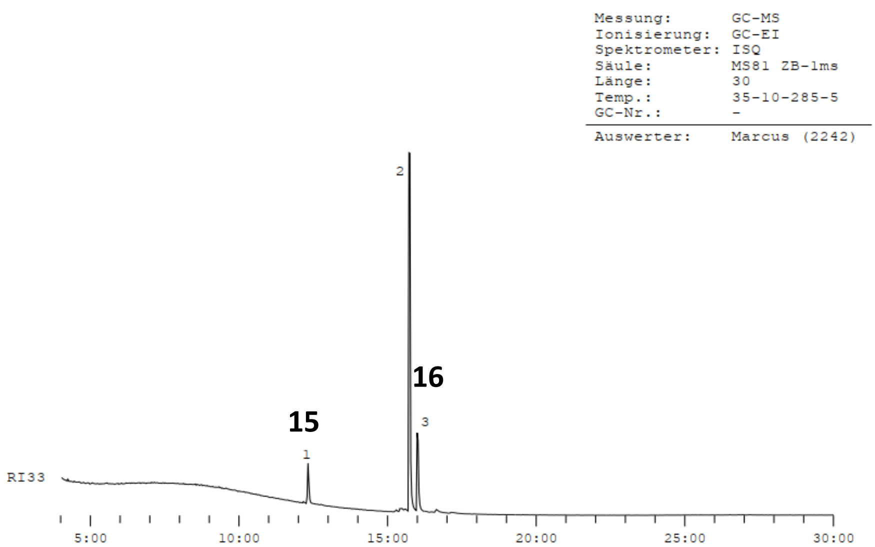
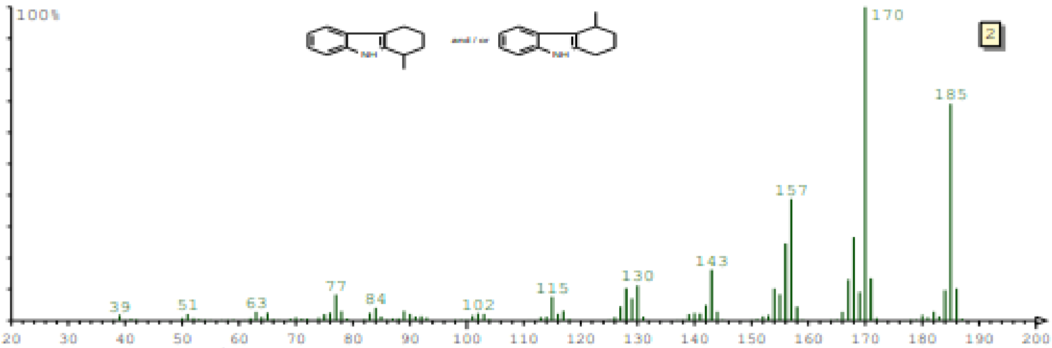


Figure **S2**. Stacked ^{1}H NMR of regioisomers of **16** ($CDCl_3$, 501 MHz)

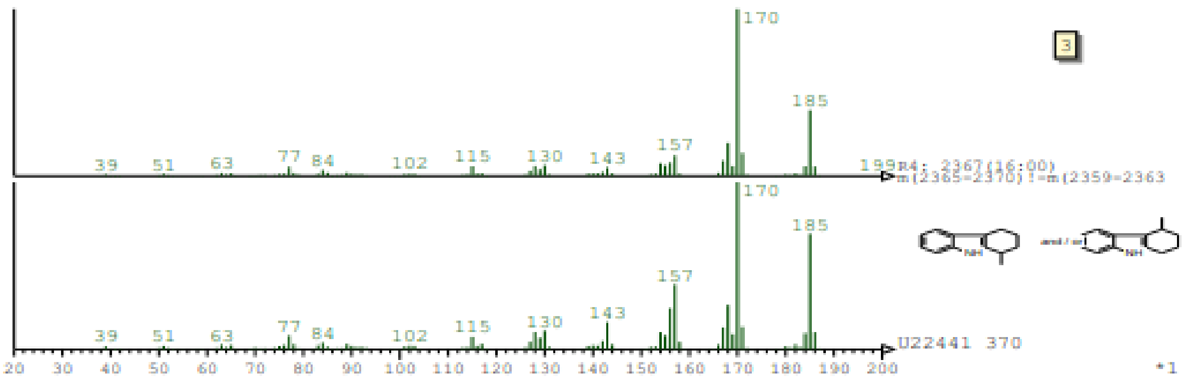




U22441 20% MW:370/370.54 C26H30N2 148465a-00 ZHP-ZB-261-03

37	0.04	60	0.01	82	0.40	105	0.04	129	7.06	155	8.45	181	1.08
38	0.24	61	0.11	83	2.42	106	0.05	130	11.20	156	24.70	182	2.84
39	1.80	62	0.79	84	4.10	109	0.01	131	1.31	157	38.79	183	1.43
40	0.20	63	2.78	85	1.39	110	0.05	132	0.08	158	4.51	184	9.64
41	0.61	64	1.20	86	0.35	111	0.09	135	0.01	159	0.25	185	69.14
42	0.42	65	2.50	87	0.75	112	0.07	137	0.13	163	0.03	186	10.20
43	0.02	66	0.43	88	0.77	113	1.06	138	0.19	164	0.19	187	0.66
45	0.01	67	0.20	89	3.09	114	1.31	139	2.02	165	0.31	188	0.03
47	0.01	68	0.06	90	2.09	115	7.61	140	2.39	166	2.78		
48	0.01	69	0.61	91	1.40	116	2.12	141	2.21	167	13.11		
49	0.04	70	1.07	92	1.47	117	3.12	142	5.02	168	26.64		
50	0.86	71	0.65	93	1.00	118	0.54	143	16.25	169	9.11		
51	2.07	72	0.71	94	0.01	119	0.02	144	2.83	170	100.00		
52	0.83	74	0.97	97	0.01	121	0.01	145	0.24	171	13.42		
53	0.47	75	1.98	98	0.24	122	0.01	146	0.02	172	0.87		
54	0.24	76	2.51	99	0.26	123	0.01	149	0.02	173	0.06		
55	0.17	77	8.34	100	0.29	124	0.02	150	0.17	176	0.02		
56	0.06	78	3.00	101	1.64	125	0.19	151	0.48	177	0.07		
57	0.17	79	0.70	102	2.28	126	1.13	152	1.44	178	0.29		
58	0.23	80	0.04	103	2.10	127	4.59	153	1.71	179	0.26		
59	0.33	81	0.02	104	0.52	128	10.29	154	10.18	180	1.76		

U224410% MW:185/185.27 C13H15N1 148465a-00 ZHP-ZB-261-03

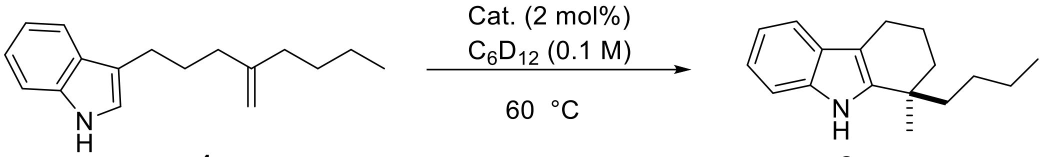


35	0.03	61	0.07	84	3.72	109	0.01	131	0.85	154	7.62	175	0.01
37	0.00	62	0.60	85	2.02	110	0.04	132	0.07	155	6.41	176	0.02
38	0.18	63	1.91	86	0.37	111	0.04	134	0.00	156	8.19	177	0.05
39	0.99	64	0.98	87	0.54	112	0.08	135	0.03	157	12.47	178	0.20
40	0.27	65	1.64	88	0.70	113	0.74	136	0.01	158	1.40	179	0.12
41	0.38	66	0.33	89	2.11	114	1.04	137	0.05	159	0.09	180	0.99
42	0.36	67	0.07	90	1.27	115	5.92	138	0.08	160	0.01	181	0.74
43	0.01	68	0.06	91	0.98	116	1.48	139	1.45	161	0.00	182	1.74
44	0.02	69	0.40	92	1.08	117	1.64	140	1.54	162	0.01	183	0.83
46	0.02	70	0.40	93	0.50	118	0.37	141	1.68	163	0.02	184	5.91
48	0.00	71	0.63	96	0.00	119	0.01	142	2.43	164	0.10	185	39.44
50	0.50	72	0.66	98	0.17	121	0.01	143	5.23	165	0.18	186	5.79
51	1.21	74	0.61	99	0.17	122	0.01	144	1.50	166	1.95	187	0.43
52	0.52	75	1.11	100	0.18	123	0.02	145	0.12	167	9.29	188	0.01
53	0.26	76	1.33	101	1.06	124	0.00	146	0.07	168	19.91	191	0.01
54	0.10	77	5.58	102	1.37	125	0.14	148	0.00	169	6.02	195	0.02
55	0.09	78	1.91	103	1.27	126	0.83	149	0.02	170	100.00	197	0.01
56	0.03	79	0.85	104	0.34	127	3.22	150	0.11	171	13.80	198	0.00
57	0.12	80	0.03	105	0.03	128	6.06	151	0.23	172	0.88	199	0.04
58	0.14	82	0.24	106	0.03	129	4.22	152	1.03	173	0.05	200	0.01
59	0.26	83	1.27	108	0.00	130	6.44	153	1.45	174	0.00		

R4:2367(16:00) m(2365-2370) 148465a-00! -m(2359-2363 2378-2382) 455 29% 148465a-00 * ZHP-Z

Figure **S3**. GC-MS of regioisomers of **16**

7. NMR study



1a **2a**

Scheme **S15**. NMR study

A solution of **1a** (7.23 mg, 0.03 mmol, 1 equiv.) and catalyst **7e** (1.62 mg, 2 mol %) in 300 µL C_6D_{12} was transferred in a 3 mm J-Young NMR tube. The sample was placed inside to a preheated to 60 °C NMR machine. ^{1}H NMR was recorded every 15 min for 48h, only signals attributed to **1a** and **2a** were observed. Select spectra were stacked and presented in the following. SM (starting material) **1a**, pro (product): **2a**.

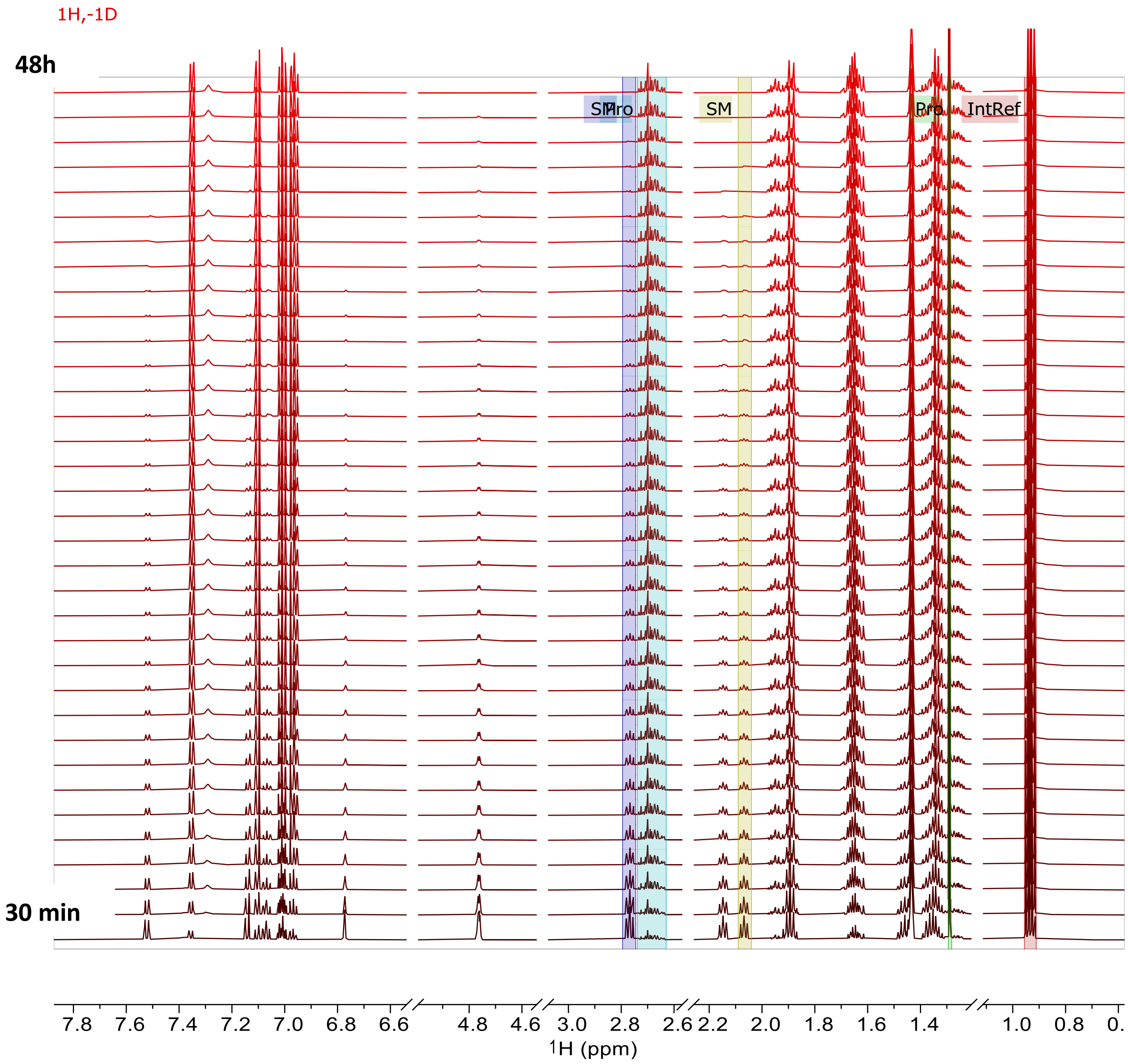


Figure **S4**. Stacked ^{1}H NMR, C_6D_{12}, 60°C, SM **1a**, Pro **2a.**

8. X-Ray analysis

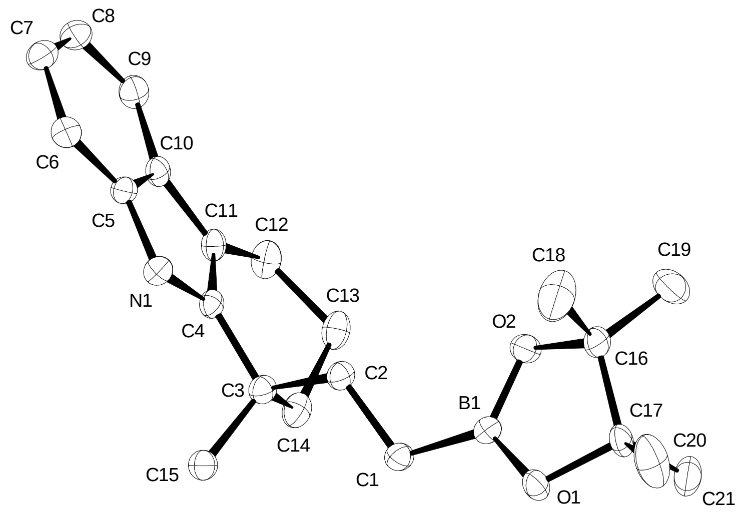


Figure **S5**. Single-crystal X-ray diffraction of **2t**

Table S1. Crystal data and structure refinement.

Identification code	13531	
Empirical formula	$C_{21} H_{30} B N O_2$	
Color	colourless	
Formula weight	339.27 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	ORTHORHOMBIC	
Space group	**$P2_12_12_1$, (no. 19)**	
Unit cell dimensions	a = 8.0048(3) Å	α= 90°.
	b = 9.3168(3) Å	β= 90°.
	c = 25.9145(9) Å	γ = 90°.
Volume	1932.68(12) $Å^3$	
Z	4	
Density (calculated)	1.166 $Mg \cdot m^{-3}$	
Absorption coefficient	0.565 mm^{-1}	
F(000)	736 e	
Crystal size	0.296 x 0.256 x 0.070 mm^3	
θ range for data collection	3.411 to 71.761°.	
Index ranges	$-9 \le h \le 9, -11 \le k \le 10, -31 \le l \le 31$	
Reflections collected	69388	
Independent reflections	3718 [R_{int} = 0.0413]	
Reflections with $I>2\sigma(I)$	3338	
Completeness to θ = 67.679°	99.6 %	
Absorption correction	Gaussian	

Max. and min. transmission	0.96 and 0.90	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3718 / 0 / 235	
Goodness-of-fit on F^2	1.167	
Final R indices [I>2σ(I)]	R_1 = 0.0349	wR^2 = 0.0856
R indices (all data)	R_1 = 0.0615	wR^2 = 0.1012
Absolute structure parameter	0.05(3)	
Largest diff. peak and hole	0.3 and -0.3 e · $Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°].

_

O(1)-C(17)	1.473(3)	O(1)-B(1)	1.375(3)
O(2)-C(16)	1.461(3)	O(2)-B(1)	1.364(3)
N(1)-H(1)	0.90(3)	N(1)-C(4)	1.390(3)
N(1)-C(5)	1.378(3)	C(1)-C(2)	1.541(3)
C(1)-B(1)	1.561(3)	C(2)-C(3)	1.547(3)
C(3)-C(4)	1.507(3)	C(3)-C(14)	1.547(3)
C(3)-C(15)	1.533(3)	C(4)-C(11)	1.369(3)
C(5)-C(6)	1.397(3)	C(5)-C(10)	1.412(3)
C(6)-C(7)	1.385(3)	C(7)-C(8)	1.401(3)
C(8)-C(9)	1.382(3)	C(9)-C(10)	1.404(3)
C(10)-C(11)	1.438(3)	C(11)-C(12)	1.497(3)
C(12)-C(13)	1.521(3)	C(13)-C(14)	1.528(3)
C(16)-C(17)	1.549(3)	C(16)-C(18)	1.507(4)
C(16)-C(19)	1.521(4)	C(17)-C(20)	1.514(3)
C(17)-C(21)	1.510(3)		
B(1)-O(1)-C(17)	107.32(17)	B(1)-O(2)-C(16)	
107.42(17)	C(4)-N(1)-H(1)	127.9(19)	C(5)-
N(1)-H(1)	122.8(19)	C(5)-N(1)-C(4)	
108.69(18)	C(2)-C(1)-B(1)	112.04(18)	C(1)-
C(2)-C(3)	117.19(18)	C(4)-C(3)-C(2)	
108.41(17)	C(4)-C(3)-C(14)	106.17(17)	C(4)-
C(3)-C(15)	111.18(19)	C(14)-C(3)-C(2)	
111.11(18)	C(15)-C(3)-C(2)	110.10(18)	C(15)-
C(3)-C(14)	109.81(19)	N(1)-C(4)-C(3)	
123.65(19)	C(11)-C(4)-N(1)	109.44(18)	C(11)-
C(4)-C(3)	126.81(19)	N(1)-C(5)-C(6)	130.3(2)
N(1)-C(5)-C(10)	107.95(18)	C(6)-C(5)-C(10)	121.8(2)
C(7)-C(6)-C(5)	117.7(2)	C(6)-C(7)-C(8)	121.2(2)
C(9)-C(8)-C(7)	121.2(2)	C(8)-C(9)-C(10)	118.8(2)
C(5)-C(10)-C(11)	106.72(18)	C(9)-C(10)-C(5)	119.2(2)
C(9)-C(10)-C(11)	134.0(2)	C(4)-C(11)-C(10)	
107.19(18)	C(4)-C(11)-C(12)	123.5(2)	C(10)-
C(11)-C(12)	129.3(2)	C(11)-C(12)-C(13)	
109.45(18)	C(12)-C(13)-C(14)	111.37(19)	C(13)-
C(14)-C(3)	114.03(18)	O(2)-C(16)-C(17)	

102.48(17)	O(2)-C(16)-C(18)	105.6(2)	O(2)-
C(16)-C(19)	108.1(2)	C(18)-C(16)-C(17)	114.5(2)
C(18)-C(16)-C(19)	110.5(2)	C(19)-C(16)-C(17)	114.7(2)
O(1)-C(17)-C(16)	101.59(16)	O(1)-C(17)-C(20)	
109.69(19)	O(1)-C(17)-C(21)	107.13(19)	C(20)-
C(17)-C(16)	114.5(2)	C(21)-C(17)-C(16)	113.2(2)
C(21)-C(17)-C(20)	110.1(2)	O(1)-B(1)-C(1)	124.8(2)
O(2)-B(1)-O(1)	112.4(2)	O(2)-B(1)-C(1)	
122.80(19)			

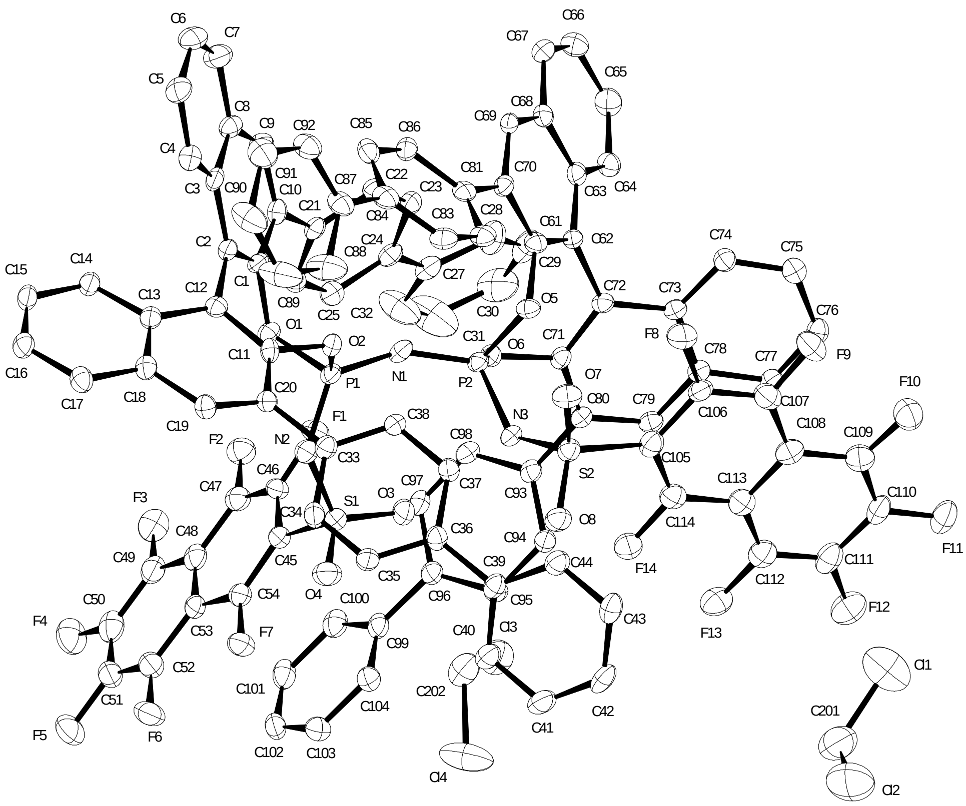


Figure **S6**. Single-crystal X-ray diffraction of **7c**

Table S3. Crystal data and structure refinement.

Identification code	13247	
Empirical formula	C_{110} H_{61} Cl_4 F_{14} N_3 O_8 P_2 S_2	
Color	colourless	
Formula weight	2086.47 g·mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$, (No. 19)	
Unit cell dimensions	a = 14.3036(7) Å	α= 90°.
	b = 23.2545(12) Å	β= 90°.
	c = 28.5467(15) Å	γ = 90°.
Volume	9495.3(8) Å^3	
Z	4	
Density (calculated)	1.460 Mg·m^{-3}	
Absorption coefficient	0.292 mm^{-1}	
F(000)	4248 e	
Crystal size	0.060 x 0.051 x 0.043 mm^3	
θ range for data collection	1.427 to 30.998°.	

Index ranges	$-20 \le h \le 20$, $-33 \le k \le 31$, $-41 \le l \le 41$	
Reflections collected	323711	
Independent reflections	30283 [R_{int} = 0.0859]	
Reflections with I>2σ(I)	23128	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99053 and 0.98690	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	30283 / 0 / 1292	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2σ(I)]	R_1 = 0.0523	wR^2 = 0.1210
R indices (all data)	R_1 = 0.0786	wR^2 = 0.1329
Absolute structure parameter	0.009(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.823 and -0.817 e·Å^{-3}	

Table S4. Bond lengths [Å] and angles [°].

Cl(1)-C(201)	1.726(6)	Cl(2)-C(201)	1.766(7)
C(201)-H(20A)	0.9900	C(201)-H(20B)	0.9900
Cl(3)-C(202)	1.754(5)	Cl(4)-C(202)	1.757(5)
C(202)-H(20C)	0.9900	C(202)-H(20D)	0.9900
S(1)-O(3)	1.449(3)	S(1)-O(4)	1.419(3)
S(1)-N(2)	1.546(3)	S(1)-C(45)	1.795(4)
S(2)-O(7)	1.425(3)	S(2)-O(8)	1.412(3)
S(2)-N(3)	1.653(3)	S(2)-C(105)	1.784(4)
P(1)-O(1)	1.584(2)	P(1)-O(2)	1.588(2)
P(1)-N(1)	1.555(3)	P(1)-N(2)	1.582(3)
P(2)-O(5)	1.571(2)	P(2)-O(6)	1.579(2)
P(2)-N(1)	1.530(3)	P(2)-N(3)	1.658(3)
F(1)-C(46)	1.338(4)	F(2)-C(47)	1.351(4)
F(3)-C(49)	1.339(5)	F(4)-C(50)	1.342(5)
F(5)-C(51)	1.328(4)	F(6)-C(52)	1.345(5)
F(7)-C(54)	1.341(4)	F(8)-C(106)	1.300(4)
F(9)-C(107)	1.335(4)	F(10)-C(109)	1.321(5)
F(11)-C(110)	1.337(4)	F(12)-C(111)	1.329(5)
F(13)-C(112)	1.367(5)	F(14)-C(114)	1.334(4)
O(1)-C(1)	1.412(4)	O(2)-C(11)	1.403(4)
O(5)-C(61)	1.413(4)	O(6)-C(71)	1.420(4)
N(3)-H(3)	1.01(4)	C(1)-C(2)	1.385(5)
C(1)-C(10)	1.406(5)	C(2)-C(3)	1.436(5)
C(2)-C(12)	1.488(5)	C(3)-C(4)	1.431(5)
C(3)-C(8)	1.416(5)	C(4)-H(4)	0.9500
C(4)-C(5)	1.362(5)	C(5)-H(5)	0.9500
C(5)-C(6)	1.416(6)	C(6)-H(6)	0.9500
C(6)-C(7)	1.363(5)	C(7)-H(7)	0.9500
C(7)-C(8)	1.421(5)	C(8)-C(9)	1.418(5)
C(9)-H(9)	0.9500	C(9)-C(10)	1.376(5)
C(10)-C(21)	1.488(5)	C(11)-C(12)	1.375(5)
C(11)-C(20)	1.429(5)	C(12)-C(13)	1.434(4)
C(13)-C(14)	1.413(5)	C(13)-C(18)	1.416(5)
C(14)-H(14)	0.9500	C(14)-C(15)	1.373(5)
C(15)-H(15)	0.9500	C(15)-C(16)	1.400(6)
C(16)-H(16)	0.9500	C(16)-C(17)	1.368(5)

C(17)-H(17)	0.9500	C(17)-C(18)	1.424(5)
C(18)-C(19)	1.426(5)	C(19)-H(19)	0.9500
C(19)-C(20)	1.363(5)	C(20)-C(33)	1.487(5)
C(21)-C(22)	1.411(5)	C(21)-C(26)	1.383(5)
C(22)-H(22)	0.9500	C(22)-C(23)	1.396(5)
C(23)-H(23)	0.9500	C(23)-C(24)	1.391(5)
C(24)-C(25)	1.398(5)	C(24)-C(27)	1.488(5)
C(25)-H(25)	0.9500	C(25)-C(26)	1.388(5)
C(26)-H(26)	0.9500	C(27)-C(28)	1.396(5)
C(27)-C(32)	1.388(6)	C(28)-H(28)	0.9500
C(28)-C(29)	1.390(6)	C(29)-H(29)	0.9500
C(29)-C(30)	1.362(7)	C(30)-H(30)	0.9500
C(30)-C(31)	1.407(8)	C(31)-H(31)	0.9500
C(31)-C(32)	1.386(7)	C(32)-H(32)	0.9500
C(33)-C(34)	1.384(5)	C(33)-C(38)	1.400(5)
C(34)-H(34)	0.9500	C(34)-C(35)	1.377(5)
C(35)-H(35)	0.9500	C(35)-C(36)	1.402(5)
C(36)-C(37)	1.387(5)	C(36)-C(39)	1.480(5)
C(37)-H(37)	0.9500	C(37)-C(38)	1.403(5)
C(38)-H(38)	0.9500	C(39)-C(40)	1.397(5)
C(39)-C(44)	1.392(5)	C(40)-H(40)	0.9500
C(40)-C(41)	1.386(5)	C(41)-H(41)	0.9500
C(41)-C(42)	1.379(6)	C(42)-H(42)	0.9500
C(42)-C(43)	1.398(6)	C(43)-H(43)	0.9500
C(43)-C(44)	1.384(5)	C(44)-H(44)	0.9500
C(45)-C(46)	1.412(5)	C(45)-C(54)	1.358(5)
C(46)-C(47)	1.354(5)	C(47)-C(48)	1.407(5)
C(48)-C(49)	1.413(5)	C(48)-C(53)	1.411(6)
C(49)-C(50)	1.367(6)	C(50)-C(51)	1.385(7)
C(51)-C(52)	1.370(6)	C(52)-C(53)	1.419(5)
C(53)-C(54)	1.433(5)	C(61)-C(62)	1.363(4)
C(61)-C(70)	1.424(4)	C(62)-C(63)	1.433(5)
C(62)-C(72)	1.499(4)	C(63)-C(64)	1.418(5)
C(63)-C(68)	1.424(5)	C(64)-H(64)	0.9500
C(64)-C(65)	1.361(5)	C(65)-H(65)	0.9500
C(65)-C(66)	1.415(6)	C(66)-H(66)	0.9500
C(66)-C(67)	1.372(5)	C(67)-H(67)	0.9500
C(67)-C(68)	1.420(5)	C(68)-C(69)	1.422(5)
C(69)-H(69)	0.9500	C(69)-C(70)	1.371(5)

C(70)-C(81)	1.486(5)	C(71)-C(72)	1.372(4)
C(71)-C(80)	1.413(4)	C(72)-C(73)	1.427(4)
C(73)-C(74)	1.417(5)	C(73)-C(78)	1.428(4)
C(74)-H(74)	0.9500	C(74)-C(75)	1.370(5)
C(75)-H(75)	0.9500	C(75)-C(76)	1.401(5)
C(76)-H(76)	0.9500	C(76)-C(77)	1.375(5)
C(77)-H(77)	0.9500	C(77)-C(78)	1.430(4)
C(78)-C(79)	1.414(5)	C(79)-H(79)	0.9500
C(79)-C(80)	1.379(4)	C(80)-C(93)	1.482(5)
C(81)-C(82)	1.390(5)	C(81)-C(86)	1.398(5)
C(82)-H(82)	0.9500	C(82)-C(83)	1.396(5)
C(83)-H(83)	0.9500	C(83)-C(84)	1.389(5)
C(84)-C(85)	1.393(6)	C(84)-C(87)	1.489(5)
C(85)-H(85)	0.9500	C(85)-C(86)	1.390(5)
C(86)-H(86)	0.9500	C(87)-C(88)	1.391(6)
C(87)-C(92)	1.391(5)	C(88)-H(88)	0.9500
C(88)-C(89)	1.380(6)	C(89)-H(89)	0.9500
C(89)-C(90)	1.365(6)	C(90)-H(90)	0.9500
C(90)-C(91)	1.383(6)	C(91)-H(91)	0.9500
C(91)-C(92)	1.392(5)	C(92)-H(92)	0.9500
C(93)-C(94)	1.389(5)	C(93)-C(98)	1.408(5)
C(94)-H(94)	0.9500	C(94)-C(95)	1.396(5)
C(95)-H(95)	0.9500	C(95)-C(96)	1.391(5)
C(96)-C(97)	1.402(5)	C(96)-C(99)	1.479(5)
C(97)-H(97)	0.9500	C(97)-C(98)	1.393(5)
C(98)-H(98)	0.9500	C(99)-C(100)	1.399(5)
C(99)-C(104)	1.390(5)	C(100)-H(100)	0.9500
C(100)-C(101)	1.400(5)	C(101)-H(101)	0.9500
C(101)-C(102)	1.375(6)	C(102)-H(102)	0.9500
C(102)-C(103)	1.397(6)	C(103)-H(103)	0.9500
C(103)-C(104)	1.391(5)	C(104)-H(104)	0.9500
C(105)-C(106)	1.446(5)	C(105)-C(114)	1.359(5)
C(106)-C(107)	1.372(5)	C(107)-C(108)	1.399(6)
C(108)-C(109)	1.439(5)	C(108)-C(113)	1.417(5)
C(109)-C(110)	1.357(6)	C(110)-C(111)	1.409(6)
C(111)-C(112)	1.360(6)	C(112)-C(113)	1.388(5)
C(113)-C(114)	1.436(5)		

Cl(1)-C(201)-Cl(2)	111.6(3)	Cl(1)-C(201)-H(20A)	109.3

Cl(1)-C(201)-H(20B)	109.3	Cl(2)-C(201)-H(20A)	109.3
Cl(2)-C(201)-H(20B)	109.3	H(20A)-C(201)-H(20B)	108.0
Cl(3)-C(202)-Cl(4)	111.9(3)	Cl(3)-C(202)-H(20C)	109.2
Cl(3)-C(202)-H(20D)	109.2	Cl(4)-C(202)-H(20C)	109.2
Cl(4)-C(202)-H(20D)	109.2	H(20C)-C(202)-H(20D)	107.9
O(3)-S(1)-N(2)	114.03(16)	O(3)-S(1)-C(45)	
104.22(16)	O(4)-S(1)-O(3)	116.81(17)	O(4)-
S(1)-N(2)	109.87(17)	O(4)-S(1)-C(45)	
106.94(17)	N(2)-S(1)-C(45)	103.67(17)	O(7)-
S(2)-N(3)	110.22(16)	O(7)-S(2)-C(105)	
106.03(17)	O(8)-S(2)-O(7)	120.75(17)	O(8)-
S(2)-N(3)	104.84(15)	O(8)-S(2)-C(105)	
108.31(17)	N(3)-S(2)-C(105)	105.83(16)	O(1)-
P(1)-O(2)	102.96(12)	N(1)-P(1)-O(1)	
110.07(14)	N(1)-P(1)-O(2)	105.52(14)	N(1)-
P(1)-N(2)	122.24(16)	N(2)-P(1)-O(1)	
104.67(15)	N(2)-P(1)-O(2)	109.82(15)	O(5)-
P(2)-O(6)	105.58(13)	O(5)-P(2)-N(3)	
100.90(14)	O(6)-P(2)-N(3)	109.40(14)	N(1)-
P(2)-O(5)	116.65(15)	N(1)-P(2)-O(6)	
106.62(15)	N(1)-P(2)-N(3)	117.05(16)	C(1)-
O(1)-P(1)	119.5(2)	C(11)-O(2)-P(1)	116.5(2)
C(61)-O(5)-P(2)	118.5(2)	C(71)-O(6)-P(2)	116.7(2)
P(2)-N(1)-P(1)	150.3(2)	S(1)-N(2)-P(1)	
134.48(19)	S(2)-N(3)-P(2)	130.16(18)	S(2)-
N(3)-H(3)	114(2)	P(2)-N(3)-H(3)	115(2)
C(2)-C(1)-O(1)	117.2(3)	C(2)-C(1)-C(10)	124.6(3)
C(10)-C(1)-O(1)	118.2(3)	C(1)-C(2)-C(3)	117.5(3)
C(1)-C(2)-C(12)	120.8(3)	C(3)-C(2)-C(12)	121.4(3)
C(4)-C(3)-C(2)	123.3(3)	C(8)-C(3)-C(2)	119.0(3)
C(8)-C(3)-C(4)	117.6(3)	C(3)-C(4)-H(4)	119.3
C(5)-C(4)-C(3)	121.4(3)	C(5)-C(4)-H(4)	119.3
C(4)-C(5)-H(5)	119.8	C(4)-C(5)-C(6)	120.4(3)
C(6)-C(5)-H(5)	119.8	C(5)-C(6)-H(6)	120.0
C(7)-C(6)-C(5)	120.0(3)	C(7)-C(6)-H(6)	120.0
C(6)-C(7)-H(7)	119.6	C(6)-C(7)-C(8)	120.8(4)
C(8)-C(7)-H(7)	119.6	C(3)-C(8)-C(7)	119.8(3)
C(3)-C(8)-C(9)	119.9(3)	C(9)-C(8)-C(7)	120.2(3)
C(8)-C(9)-H(9)	119.1	C(10)-C(9)-C(8)	121.8(3)

C(10)-C(9)-H(9)	119.1
C(9)-C(10)-C(1)	117.0(3)
O(2)-C(11)-C(20)	117.3(3)
C(12)-C(11)-C(20)	124.3(3)
C(11)-C(12)-C(13)	118.0(3)
C(14)-C(13)-C(12)	122.8(3)
C(18)-C(13)-C(12)	118.6(3)
C(15)-C(14)-C(13)	120.8(3)
C(14)-C(15)-H(15)	119.7
C(16)-C(15)-H(15)	119.7
C(17)-C(16)-C(15)	120.6(3)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(13)-C(18)-C(19)	119.8(3)
C(18)-C(19)-H(19)	118.8
C(20)-C(19)-H(19)	118.8
C(19)-C(20)-C(11)	116.4(3)
C(22)-C(21)-C(10)	118.7(3)
C(26)-C(21)-C(22)	117.9(3)
C(23)-C(22)-C(21)	120.6(3)
C(22)-C(23)-H(23)	119.2
C(24)-C(23)-H(23)	119.2
C(23)-C(24)-C(27)	121.4(3)
C(24)-C(25)-H(25)	118.9
C(26)-C(25)-H(25)	118.9
C(21)-C(26)-H(26)	119.6
C(28)-C(27)-C(24)	121.0(4)
C(32)-C(27)-C(28)	117.3(4)
C(29)-C(28)-C(27)	121.0(4)
C(28)-C(29)-H(29)	119.4
C(30)-C(29)-H(29)	119.4
C(29)-C(30)-C(31)	118.8(4)
C(30)-C(31)-H(31)	120.2
C(32)-C(31)-H(31)	120.2
C(31)-C(32)-C(27)	121.9(5)
C(34)-C(33)-C(20)	120.1(3)
C(38)-C(33)-C(20)	122.4(3)
C(35)-C(34)-C(33)	122.3(3)
C(34)-C(35)-H(35)	119.5
C(1)-C(10)-C(21)	122.1(3)
C(9)-C(10)-C(21)	120.8(3)
C(12)-C(11)-O(2)	118.4(3)
C(11)-C(12)-C(2)	119.8(3)
C(13)-C(12)-C(2)	122.2(3)
C(14)-C(13)-C(18)	118.4(3)
C(13)-C(14)-H(14)	119.6
C(15)-C(14)-H(14)	119.6
C(14)-C(15)-C(16)	120.5(3)
C(15)-C(16)-H(16)	119.7
C(17)-C(16)-H(16)	119.7
C(16)-C(17)-C(18)	120.0(3)
C(13)-C(18)-C(17)	119.6(3)
C(17)-C(18)-C(19)	120.6(3)
C(20)-C(19)-C(18)	122.3(3)
C(11)-C(20)-C(33)	122.6(3)
C(19)-C(20)-C(33)	120.9(3)
C(26)-C(21)-C(10)	123.4(3)
C(21)-C(22)-H(22)	119.7
C(23)-C(22)-H(22)	119.7
C(24)-C(23)-C(22)	121.5(3)
C(23)-C(24)-C(25)	116.9(3)
C(25)-C(24)-C(27)	121.7(3)
C(26)-C(25)-C(24)	122.2(3)
C(21)-C(26)-C(25)	120.9(3)
C(25)-C(26)-H(26)	119.6
C(32)-C(27)-C(24)	121.6(4)
C(27)-C(28)-H(28)	119.5
C(29)-C(28)-H(28)	119.5
C(30)-C(29)-C(28)	121.3(4)
C(29)-C(30)-H(30)	120.6
C(31)-C(30)-H(30)	120.6
C(32)-C(31)-C(30)	119.7(5)
C(27)-C(32)-H(32)	119.1
C(31)-C(32)-H(32)	119.1
C(34)-C(33)-C(38)	117.4(3)
C(33)-C(34)-H(34)	118.9
C(35)-C(34)-H(34)	118.9
C(34)-C(35)-C(36)	120.9(3)

C(36)-C(35)-H(35)	119.5	C(35)-C(36)-C(39)	121.8(3)
C(37)-C(36)-C(35)	117.4(3)	C(37)-C(36)-C(39)	120.7(3)
C(36)-C(37)-H(37)	119.3	C(36)-C(37)-C(38)	121.5(3)
C(38)-C(37)-H(37)	119.3	C(33)-C(38)-C(37)	120.5(3)
C(33)-C(38)-H(38)	119.8	C(37)-C(38)-H(38)	119.8
C(40)-C(39)-C(36)	120.7(3)	C(44)-C(39)-C(36)	121.7(3)
C(44)-C(39)-C(40)	117.7(3)	C(39)-C(40)-H(40)	119.3
C(41)-C(40)-C(39)	121.4(4)	C(41)-C(40)-H(40)	119.3
C(40)-C(41)-H(41)	119.8	C(42)-C(41)-C(40)	120.4(4)
C(42)-C(41)-H(41)	119.8	C(41)-C(42)-H(42)	120.5
C(41)-C(42)-C(43)	119.0(3)	C(43)-C(42)-H(42)	120.5
C(42)-C(43)-H(43)	119.8	C(44)-C(43)-C(42)	120.3(4)
C(44)-C(43)-H(43)	119.8	C(39)-C(44)-H(44)	119.4
C(43)-C(44)-C(39)	121.2(3)	C(43)-C(44)-H(44)	119.4
C(46)-C(45)-S(1)	117.9(2)	C(54)-C(45)-S(1)	124.9(3)
C(54)-C(45)-C(46)	117.2(3)	F(1)-C(46)-C(45)	119.3(3)
F(1)-C(46)-C(47)	118.5(3)	C(47)-C(46)-C(45)	122.2(3)
F(2)-C(47)-C(46)	118.2(3)	F(2)-C(47)-C(48)	120.6(3)
C(46)-C(47)-C(48)	121.2(3)	C(47)-C(48)-C(49)	123.2(4)
C(47)-C(48)-C(53)	118.4(3)	C(53)-C(48)-C(49)	118.4(3)
F(3)-C(49)-C(48)	120.2(3)	F(3)-C(49)-C(50)	118.6(4)
C(50)-C(49)-C(48)	121.2(4)	F(4)-C(50)-C(49)	119.6(4)
F(4)-C(50)-C(51)	119.8(4)	C(49)-C(50)-C(51)	120.6(4)
F(5)-C(51)-C(50)	119.7(4)	F(5)-C(51)-C(52)	120.3(4)
C(52)-C(51)-C(50)	120.0(4)	F(6)-C(52)-C(51)	117.9(3)
F(6)-C(52)-C(53)	121.1(3)	C(51)-C(52)-C(53)	121.0(4)
C(48)-C(53)-C(52)	118.7(3)	C(48)-C(53)-C(54)	118.1(3)
C(52)-C(53)-C(54)	123.1(4)	F(7)-C(54)-C(45)	120.8(3)
F(7)-C(54)-C(53)	116.4(3)	C(45)-C(54)-C(53)	122.8(3)
O(5)-C(61)-C(70)	117.4(3)	C(62)-C(61)-O(5)	117.4(3)
C(62)-C(61)-C(70)	125.2(3)	C(61)-C(62)-C(63)	118.3(3)
C(61)-C(62)-C(72)	120.5(3)	C(63)-C(62)-C(72)	120.9(3)
C(64)-C(63)-C(62)	123.6(3)	C(64)-C(63)-C(68)	117.9(3)
C(68)-C(63)-C(62)	118.4(3)	C(63)-C(64)-H(64)	119.3
C(65)-C(64)-C(63)	121.4(3)	C(65)-C(64)-H(64)	119.3
C(64)-C(65)-H(65)	119.8	C(64)-C(65)-C(66)	120.5(3)
C(66)-C(65)-H(65)	119.8	C(65)-C(66)-H(66)	119.9
C(67)-C(66)-C(65)	120.3(3)	C(67)-C(66)-H(66)	119.9
C(66)-C(67)-H(67)	120.0	C(66)-C(67)-C(68)	120.0(3)

C(68)-C(67)-H(67)	120.0	C(67)-C(68)-C(63)	119.9(3)
C(67)-C(68)-C(69)	120.4(3)	C(69)-C(68)-C(63)	119.6(3)
C(68)-C(69)-H(69)	118.7	C(70)-C(69)-C(68)	122.6(3)
C(70)-C(69)-H(69)	118.7	C(61)-C(70)-C(81)	123.9(3)
C(69)-C(70)-C(61)	115.7(3)	C(69)-C(70)-C(81)	120.3(3)
C(72)-C(71)-O(6)	118.4(3)	C(72)-C(71)-C(80)	124.9(3)
C(80)-C(71)-O(6)	116.7(3)	C(71)-C(72)-C(62)	119.8(3)
C(71)-C(72)-C(73)	118.1(3)	C(73)-C(72)-C(62)	122.1(3)
C(72)-C(73)-C(78)	118.3(3)	C(74)-C(73)-C(72)	123.2(3)
C(74)-C(73)-C(78)	118.5(3)	C(73)-C(74)-H(74)	119.5
C(75)-C(74)-C(73)	120.9(3)	C(75)-C(74)-H(74)	119.5
C(74)-C(75)-H(75)	119.6	C(74)-C(75)-C(76)	120.9(3)
C(76)-C(75)-H(75)	119.6	C(75)-C(76)-H(76)	119.8
C(77)-C(76)-C(75)	120.5(3)	C(77)-C(76)-H(76)	119.8
C(76)-C(77)-H(77)	120.0	C(76)-C(77)-C(78)	120.1(3)
C(78)-C(77)-H(77)	120.0	C(73)-C(78)-C(77)	119.2(3)
C(79)-C(78)-C(73)	120.0(3)	C(79)-C(78)-C(77)	120.8(3)
C(78)-C(79)-H(79)	119.0	C(80)-C(79)-C(78)	122.0(3)
C(80)-C(79)-H(79)	119.0	C(71)-C(80)-C(93)	121.6(3)
C(79)-C(80)-C(71)	116.2(3)	C(79)-C(80)-C(93)	122.2(3)
C(82)-C(81)-C(70)	123.2(3)	C(82)-C(81)-C(86)	118.2(3)
C(86)-C(81)-C(70)	118.7(3)	C(81)-C(82)-H(82)	119.9
C(81)-C(82)-C(83)	120.3(3)	C(83)-C(82)-H(82)	119.9
C(82)-C(83)-H(83)	119.2	C(84)-C(83)-C(82)	121.6(4)
C(84)-C(83)-H(83)	119.2	C(83)-C(84)-C(85)	118.1(3)
C(83)-C(84)-C(87)	121.8(3)	C(85)-C(84)-C(87)	120.1(3)
C(84)-C(85)-H(85)	119.7	C(86)-C(85)-C(84)	120.6(3)
C(86)-C(85)-H(85)	119.7	C(81)-C(86)-H(86)	119.4
C(85)-C(86)-C(81)	121.3(3)	C(85)-C(86)-H(86)	119.4
C(88)-C(87)-C(84)	120.7(3)	C(92)-C(87)-C(84)	121.7(3)
C(92)-C(87)-C(88)	117.4(3)	C(87)-C(88)-H(88)	119.6
C(89)-C(88)-C(87)	120.8(4)	C(89)-C(88)-H(88)	119.6
C(88)-C(89)-H(89)	119.2	C(90)-C(89)-C(88)	121.7(4)
C(90)-C(89)-H(89)	119.2	C(89)-C(90)-H(90)	120.7
C(89)-C(90)-C(91)	118.6(4)	C(91)-C(90)-H(90)	120.7
C(90)-C(91)-H(91)	119.9	C(90)-C(91)-C(92)	120.2(4)
C(92)-C(91)-H(91)	119.9	C(87)-C(92)-C(91)	121.2(4)
C(87)-C(92)-H(92)	119.4	C(91)-C(92)-H(92)	119.4
C(94)-C(93)-C(80)	121.5(3)	C(94)-C(93)-C(98)	118.3(3)

C(98)-C(93)-C(80)	120.2(3)	C(93)-C(94)-H(94)	119.4
C(93)-C(94)-C(95)	121.1(3)	C(95)-C(94)-H(94)	119.4
C(94)-C(95)-H(95)	119.7	C(96)-C(95)-C(94)	120.6(3)
C(96)-C(95)-H(95)	119.7	C(95)-C(96)-C(97)	118.6(3)
C(95)-C(96)-C(99)	120.4(3)	C(97)-C(96)-C(99)	121.0(3)
C(96)-C(97)-H(97)	119.7	C(98)-C(97)-C(96)	120.6(3)
C(98)-C(97)-H(97)	119.7	C(93)-C(98)-H(98)	119.7
C(97)-C(98)-C(93)	120.5(3)	C(97)-C(98)-H(98)	119.7
C(100)-C(99)-C(96)	121.3(3)	C(104)-C(99)-C(96)	120.2(3)
C(104)-C(99)-C(100)	118.5(3)	C(99)-C(100)-H(100)	120.1
C(99)-C(100)-C(101)	119.9(4)	C(101)-C(100)-H(100)	120.1
C(100)-C(101)-H(101)	119.5	C(102)-C(101)-C(100)	121.0(4)
C(102)-C(101)-H(101)	119.5	C(101)-C(102)-H(102)	120.2
C(101)-C(102)-C(103)	119.7(3)	C(103)-C(102)-H(102)	120.2
C(102)-C(103)-H(103)	120.3	C(104)-C(103)-C(102)	119.4(4)
C(104)-C(103)-H(103)	120.3	C(99)-C(104)-C(103)	121.6(4)
C(99)-C(104)-H(104)	119.2	C(103)-C(104)-H(104)	119.2
C(106)-C(105)-S(2)	122.3(3)	C(114)-C(105)-S(2)	119.0(3)
C(114)-C(105)-C(106)	118.2(3)	F(8)-C(106)-C(105)	121.2(3)
F(8)-C(106)-C(107)	119.9(3)	C(107)-C(106)-C(105)	118.8(3)
F(9)-C(107)-C(106)	116.8(3)	F(9)-C(107)-C(108)	120.6(3)
C(106)-C(107)-C(108)	122.6(3)	C(107)-C(108)-C(109)	122.5(4)
C(107)-C(108)-C(113)	120.0(3)	C(113)-C(108)-C(109)	117.3(3)
F(10)-C(109)-C(108)	121.0(4)	F(10)-C(109)-C(110)	117.9(4)
C(110)-C(109)-C(108)	121.1(4)	F(11)-C(110)-C(109)	122.0(4)
F(11)-C(110)-C(111)	118.0(4)	C(109)-C(110)-C(111)	120.0(3)
F(12)-C(111)-C(110)	119.0(3)	F(12)-C(111)-C(112)	120.8(4)
C(112)-C(111)-C(110)	120.2(4)	F(13)-C(112)-C(113)	120.7(3)
C(111)-C(112)-F(13)	117.9(4)	C(111)-C(112)-C(113)	121.5(4)
C(108)-C(113)-C(114)	116.0(3)	C(112)-C(113)-C(108)	119.9(4)
C(112)-C(113)-C(114)	124.1(3)	F(14)-C(114)-C(105)	119.1(3)
F(14)-C(114)-C(113)	116.8(3)	C(105)-C(114)-C(113)	124.1(3)

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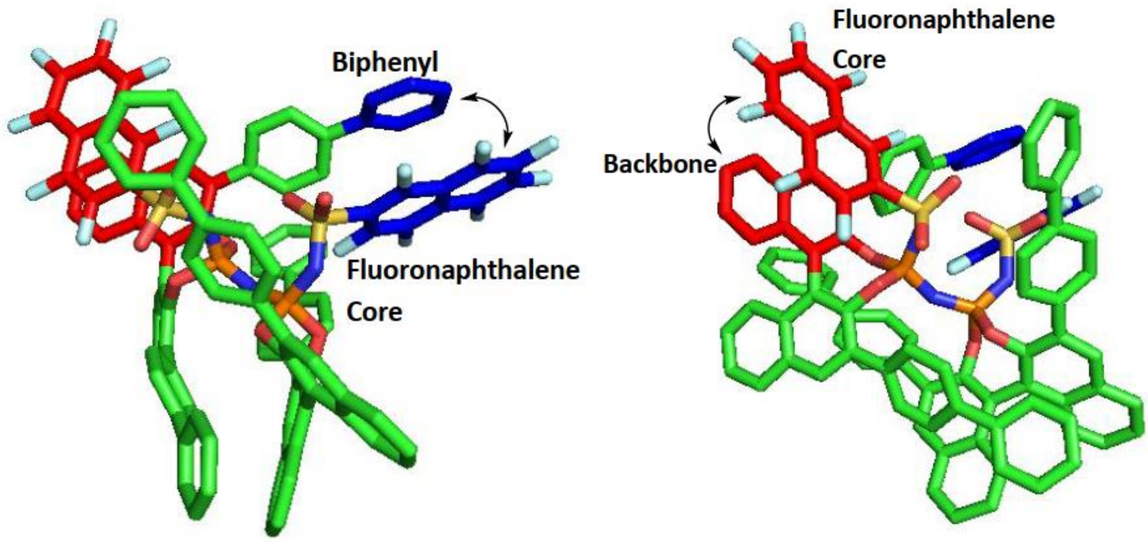
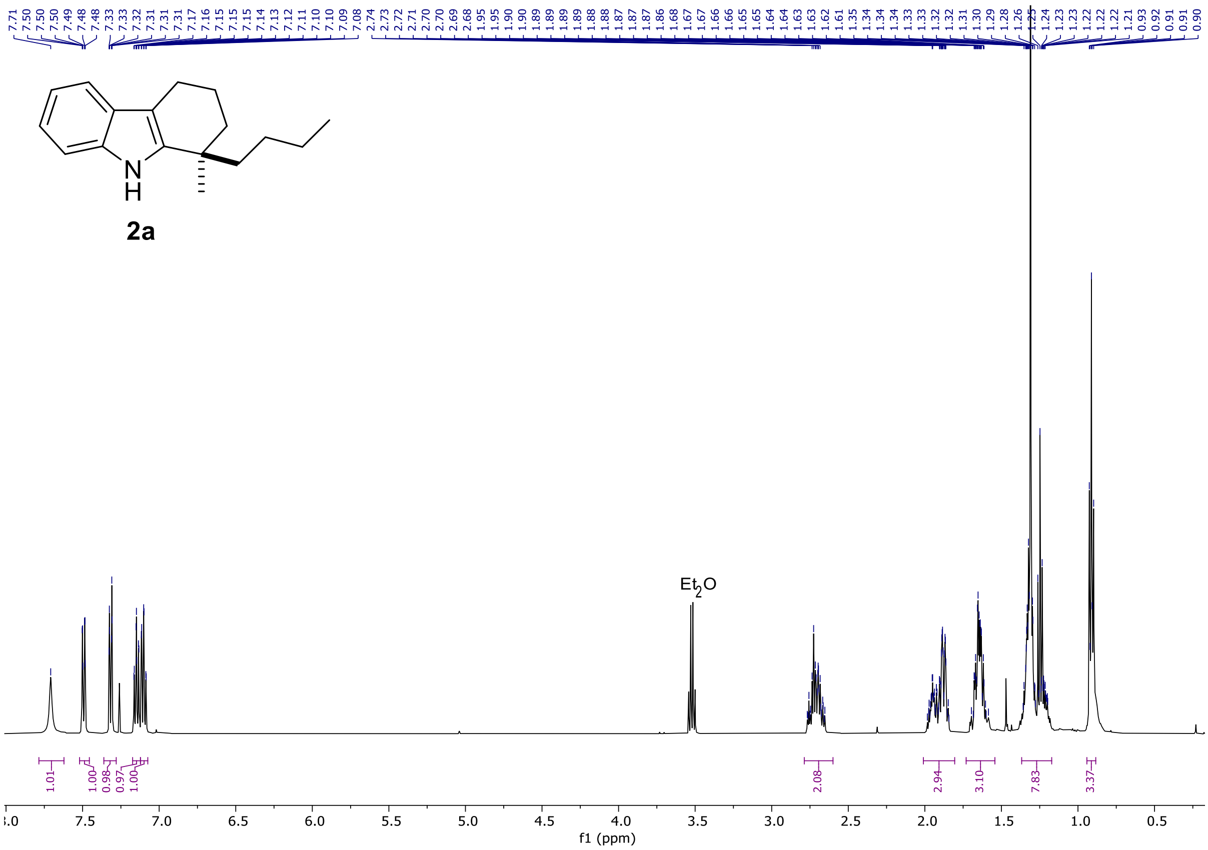


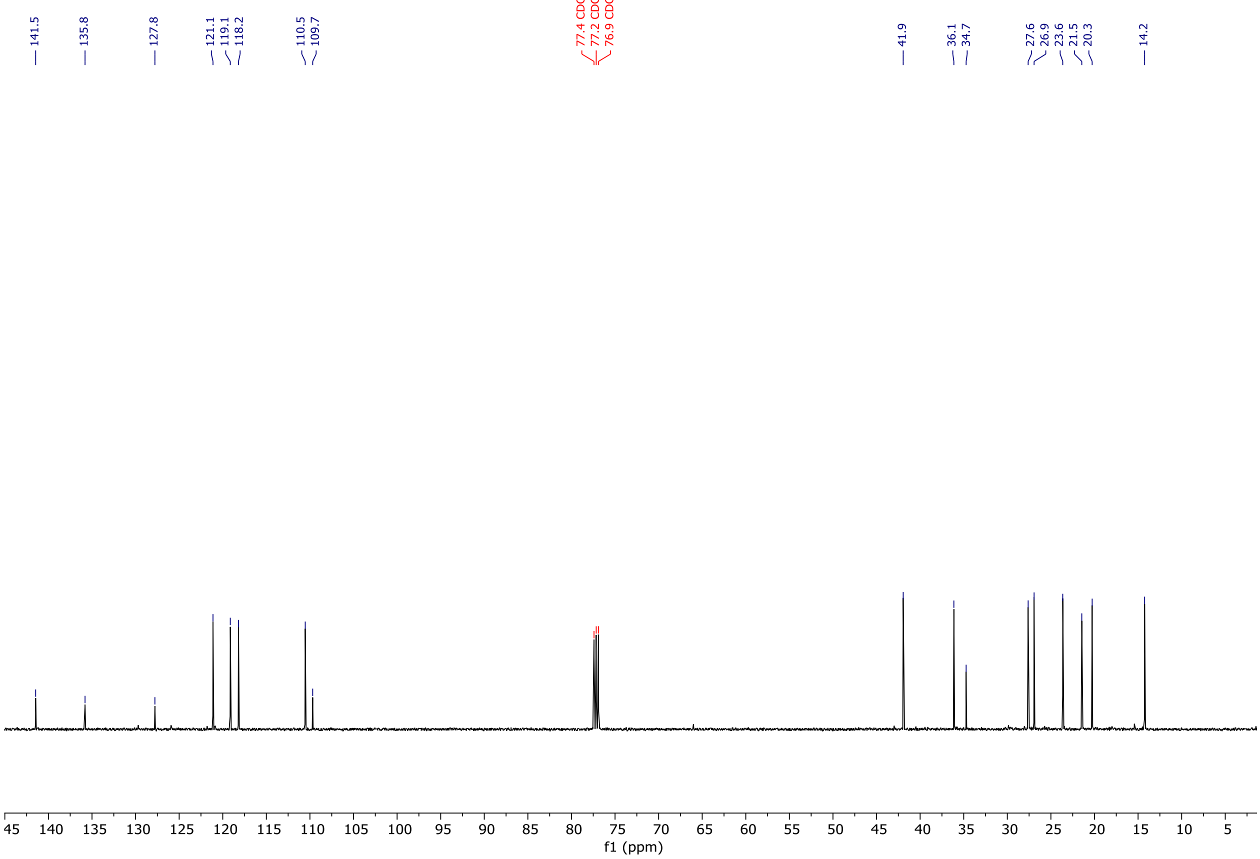
Figure S7. Schematic representation (Pymol, Schrödinger) of π-π stackings between core & backbone / core & biphenyl of **7c** based on single-crystal X-ray diffraction. For clarity, solvents and hydrogens are omitted.

9. NMR spectra

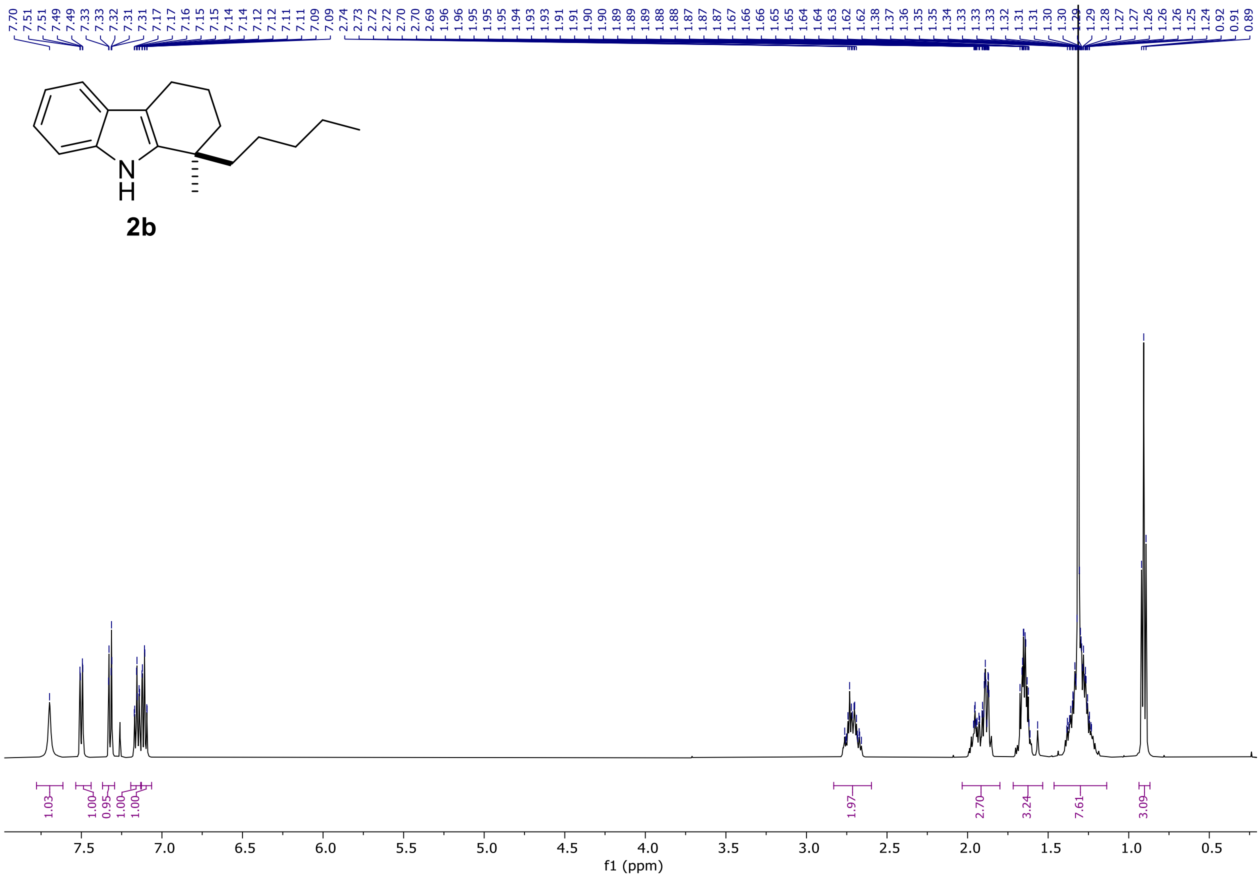


2a

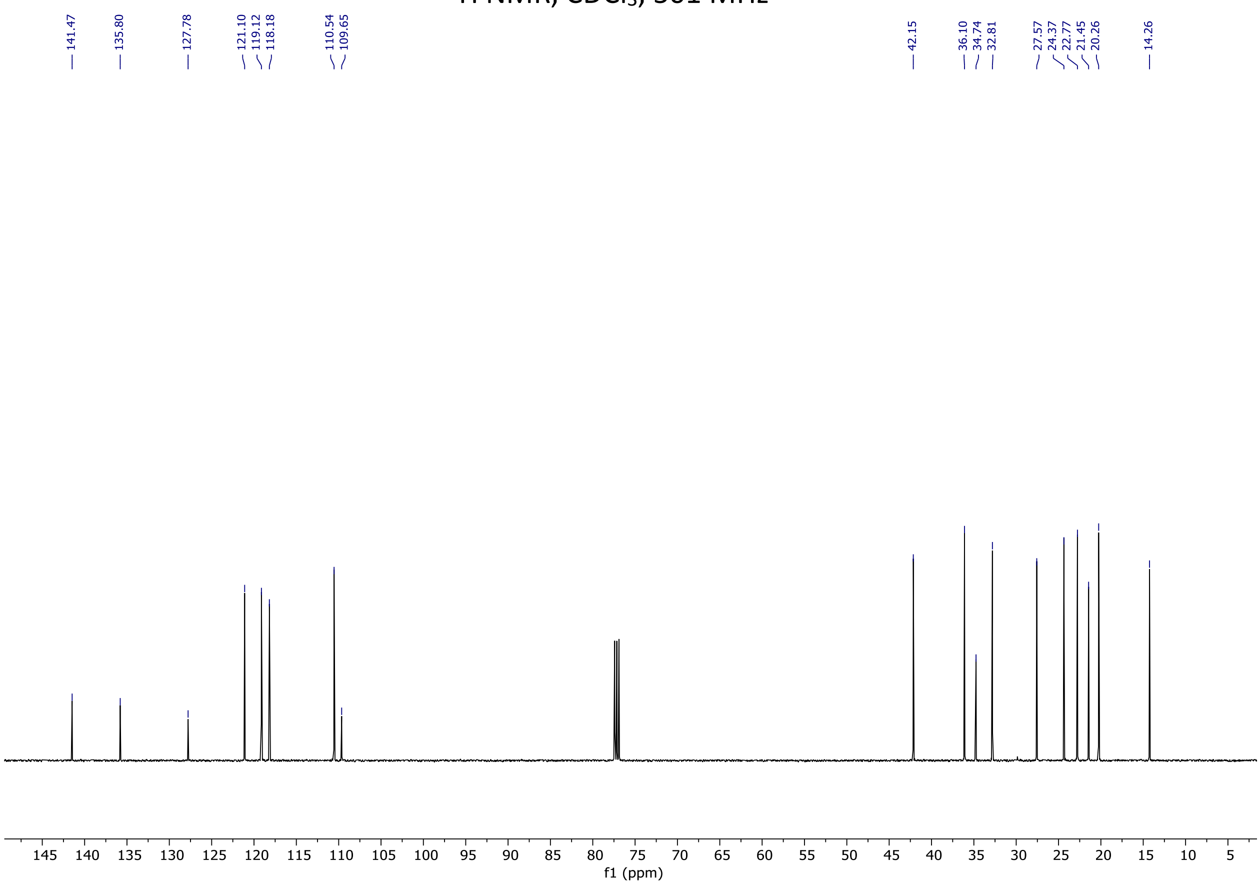
^{1}H NMR, $CDCl_3$, 501 MHz



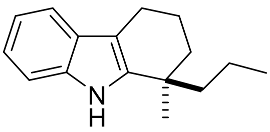
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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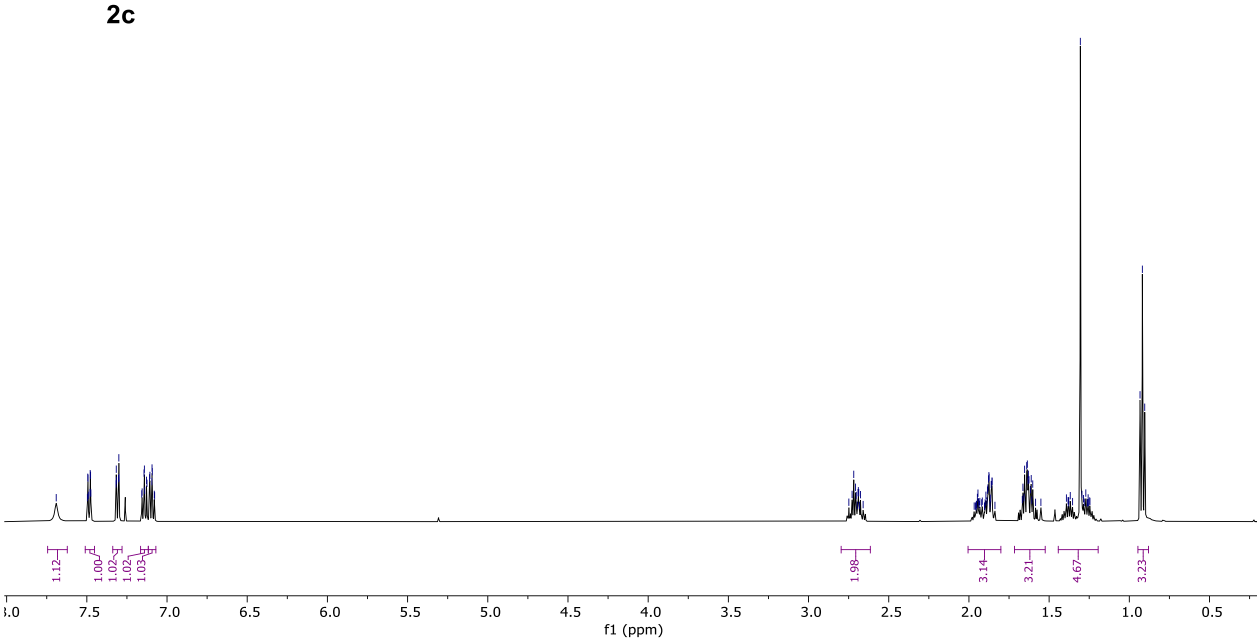
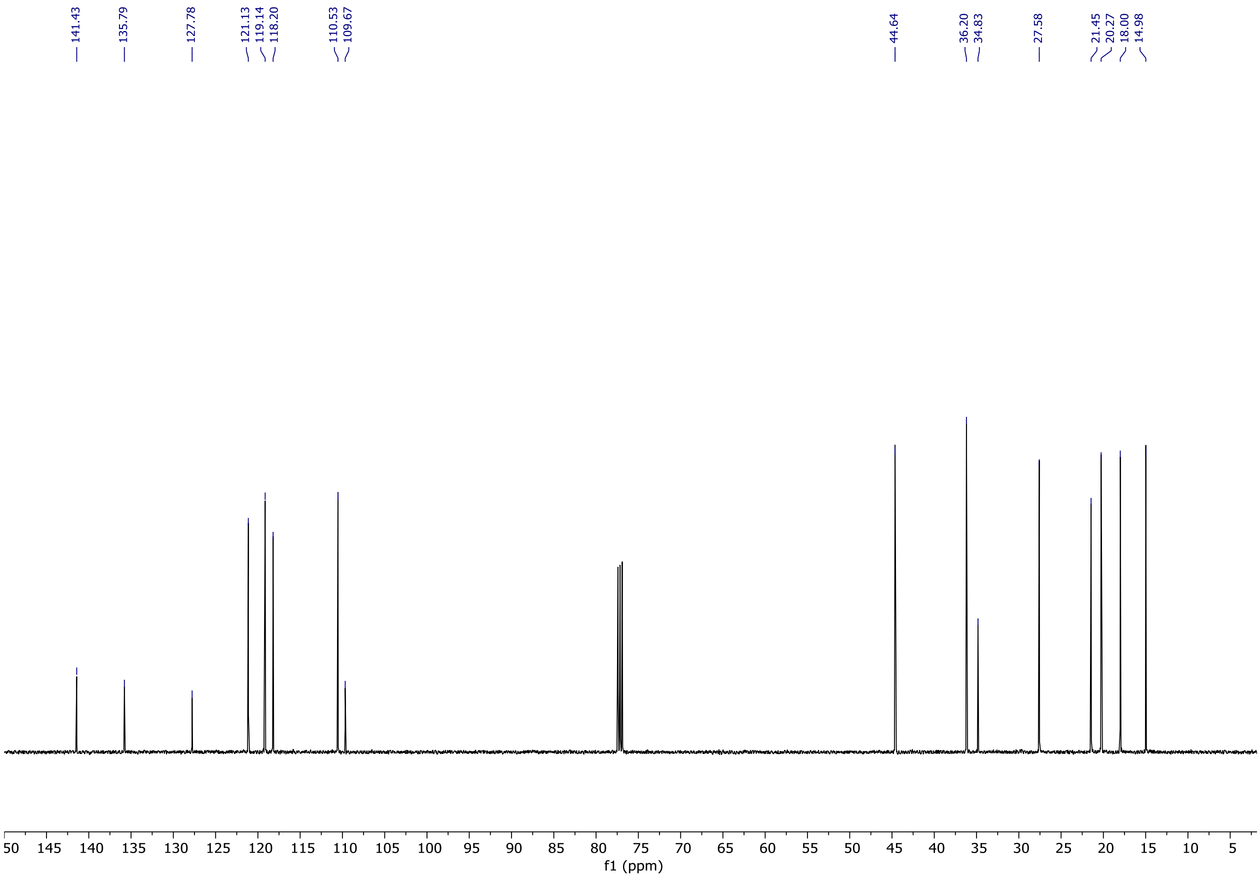
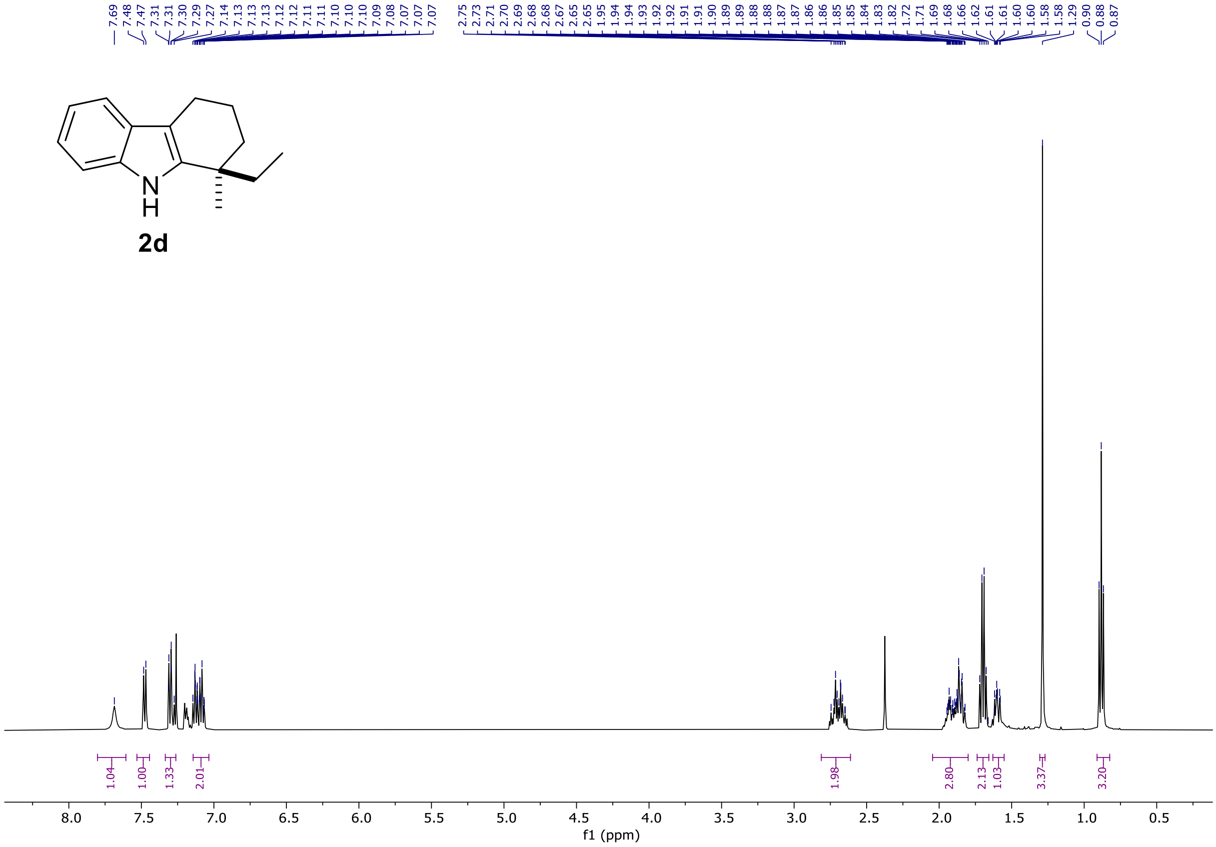


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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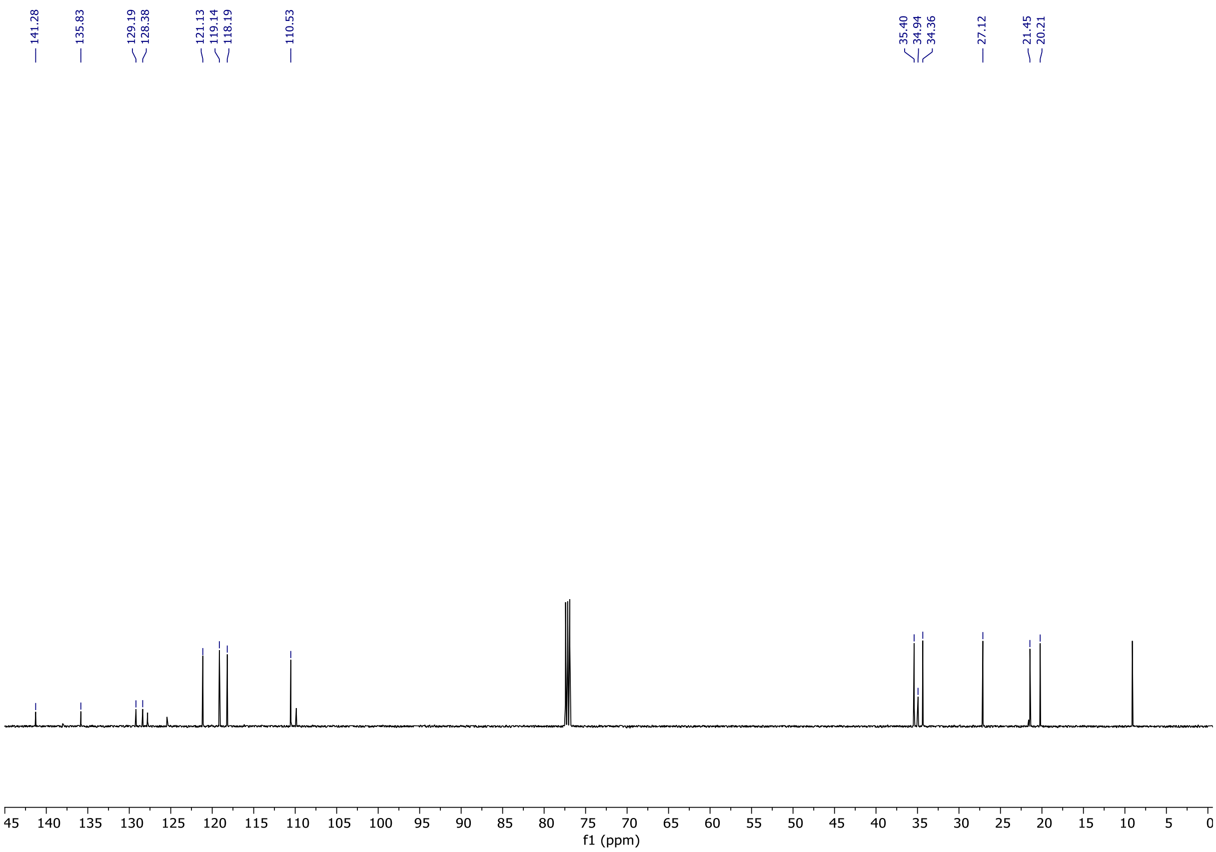
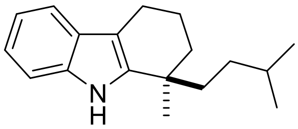
^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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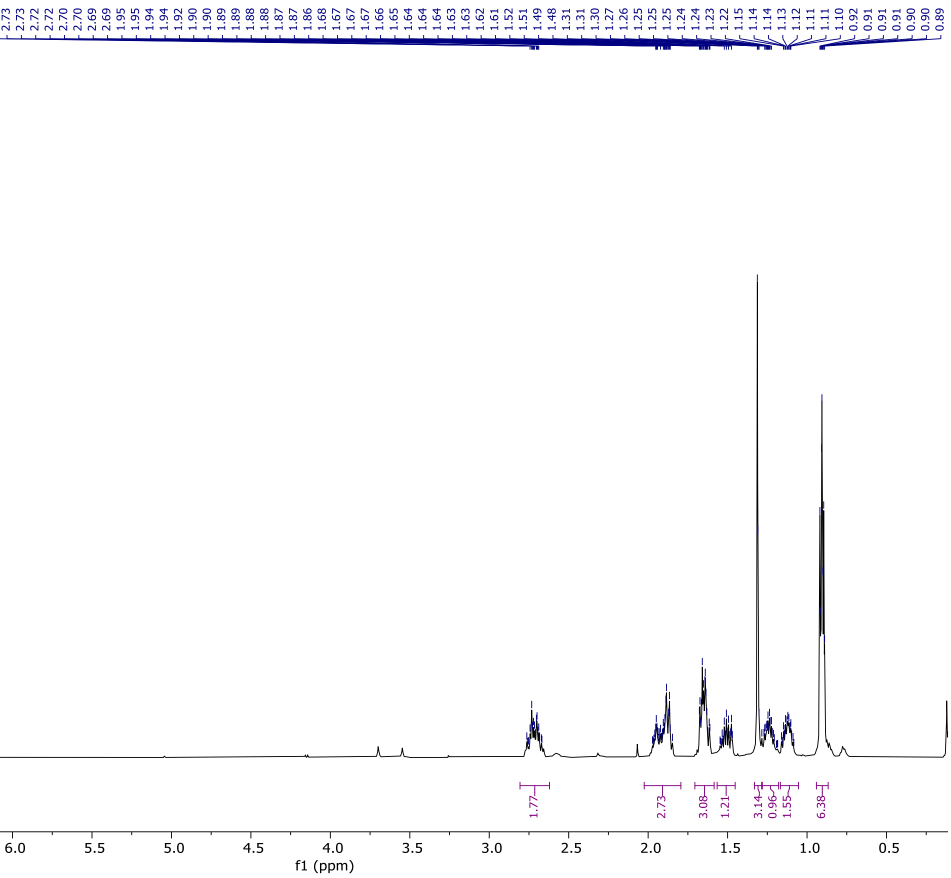
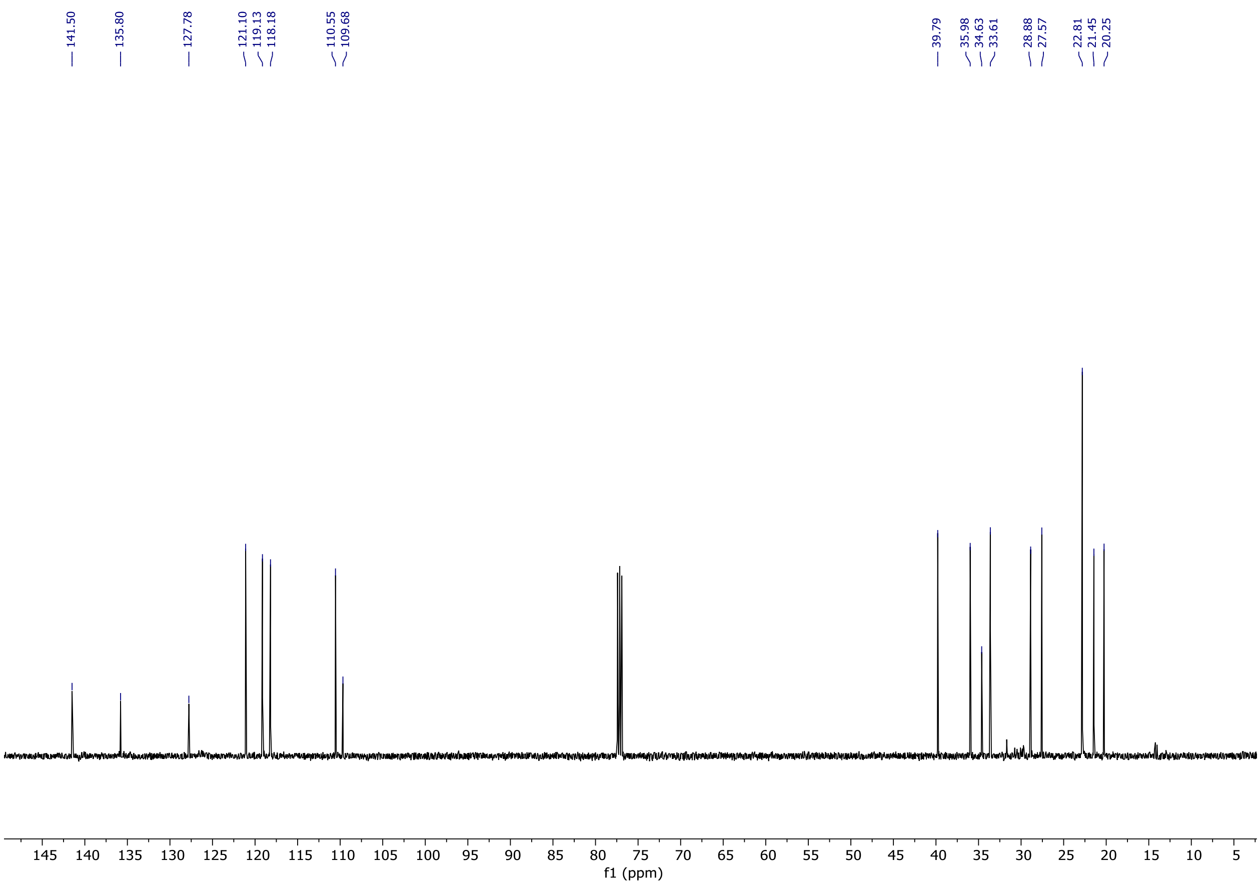


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

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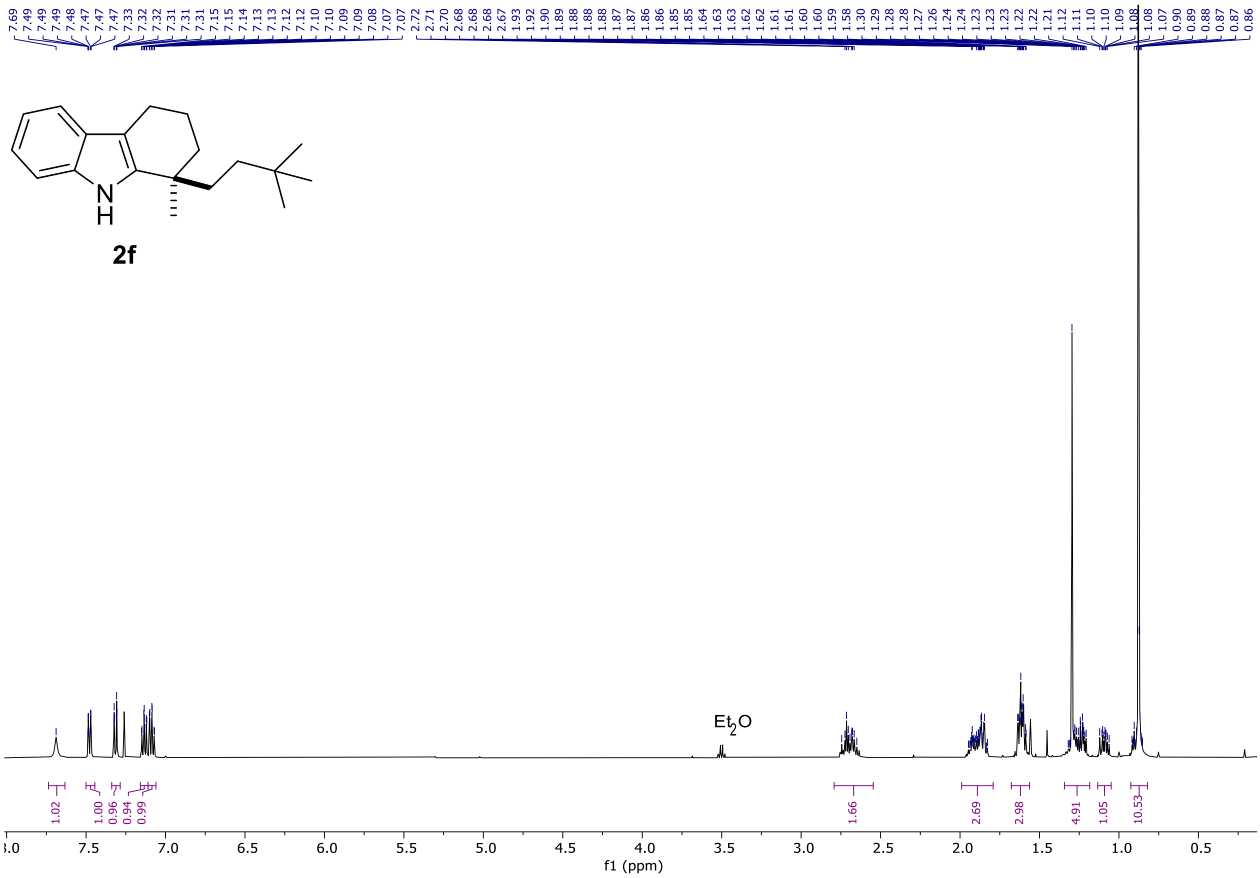
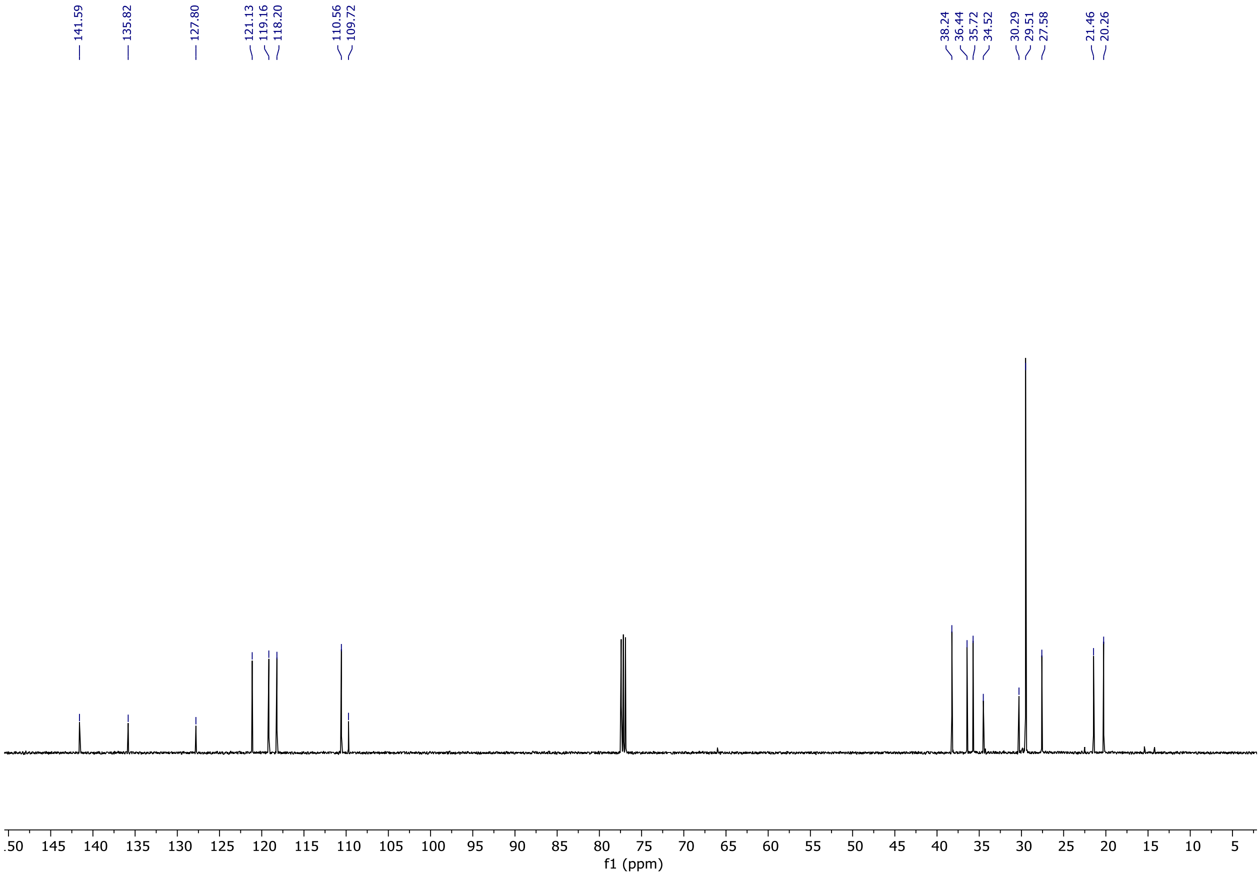
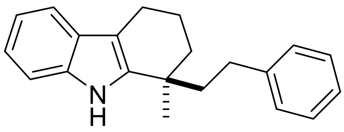


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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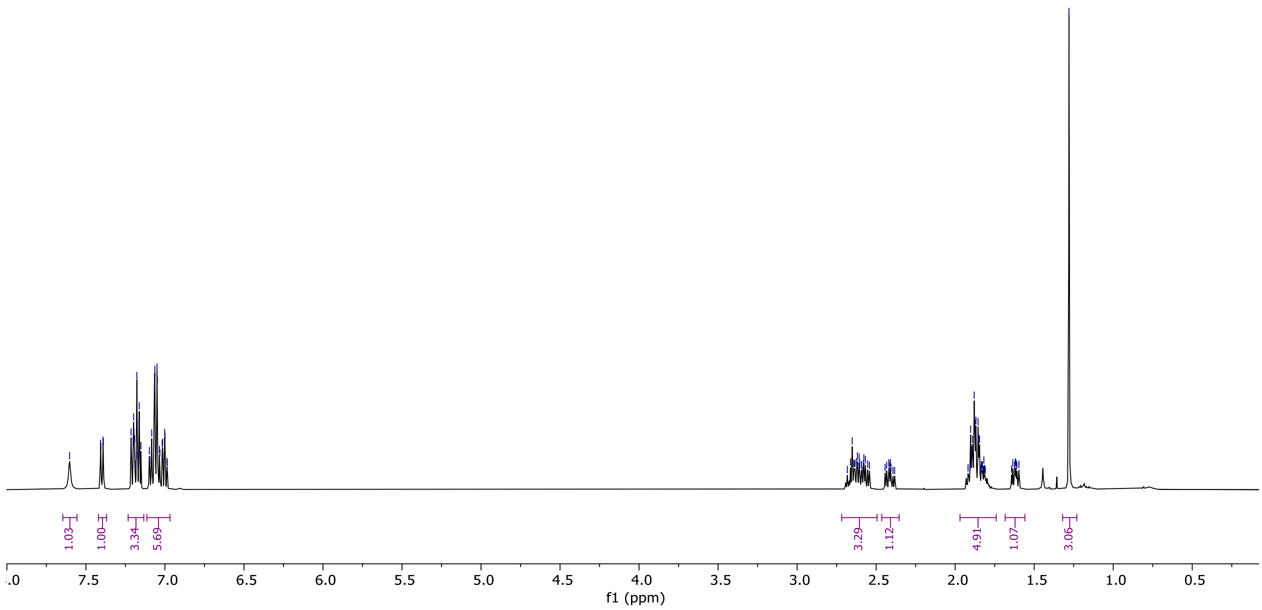
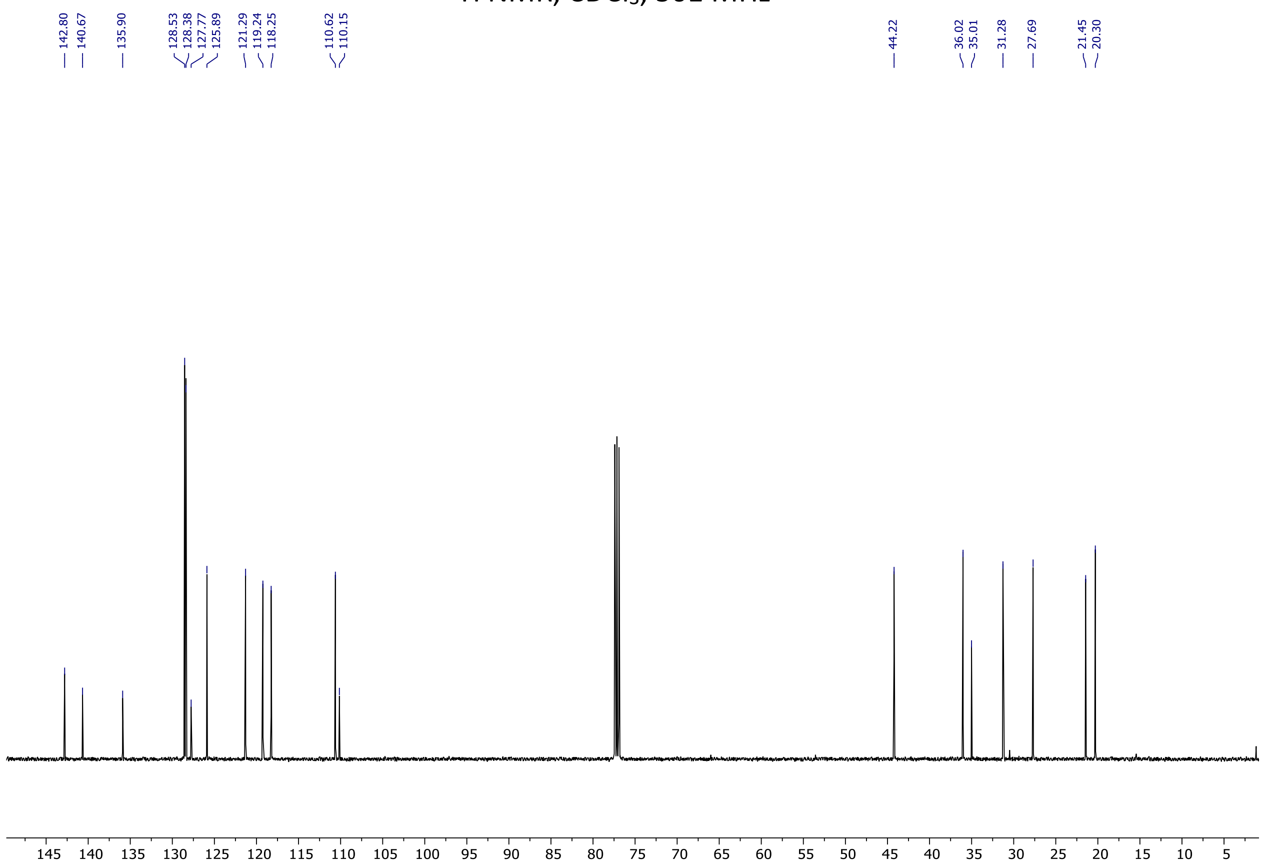
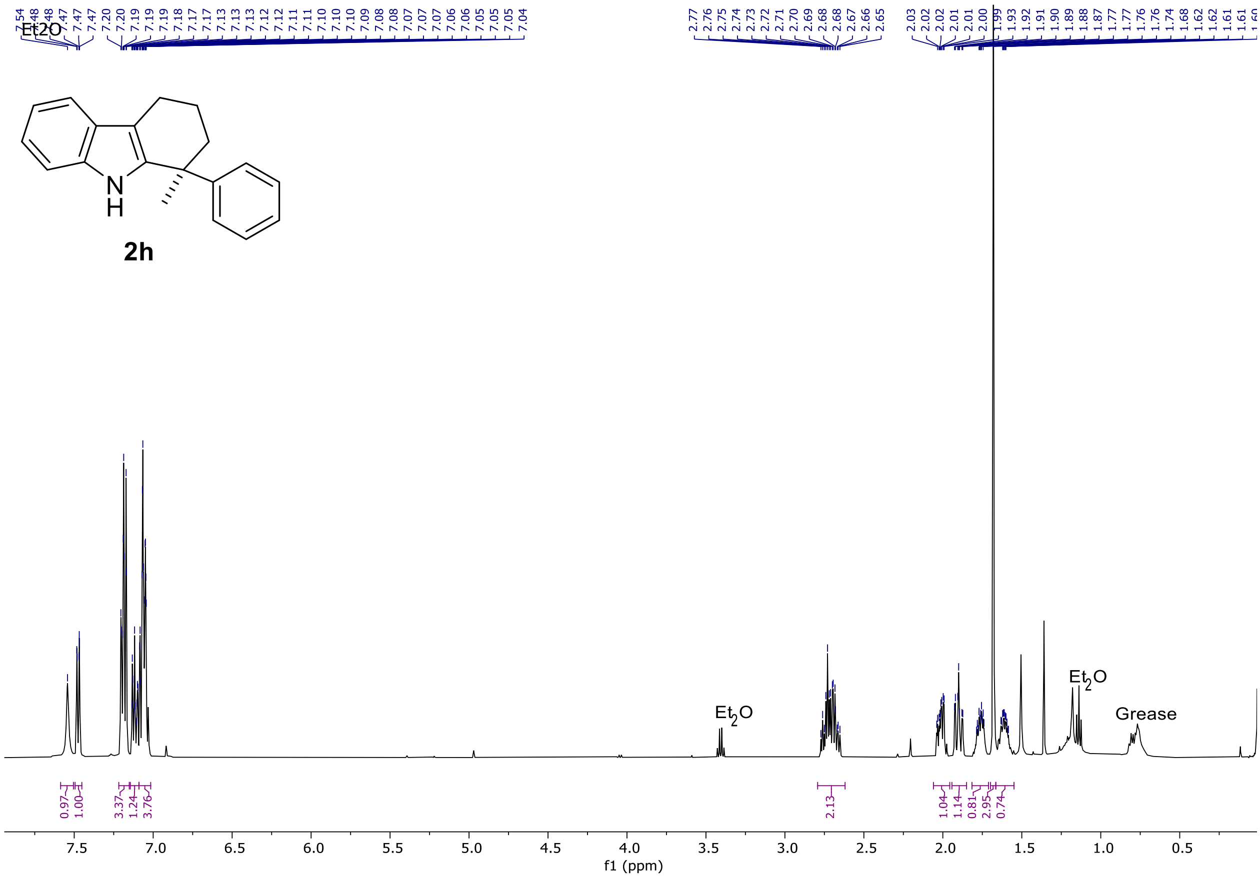


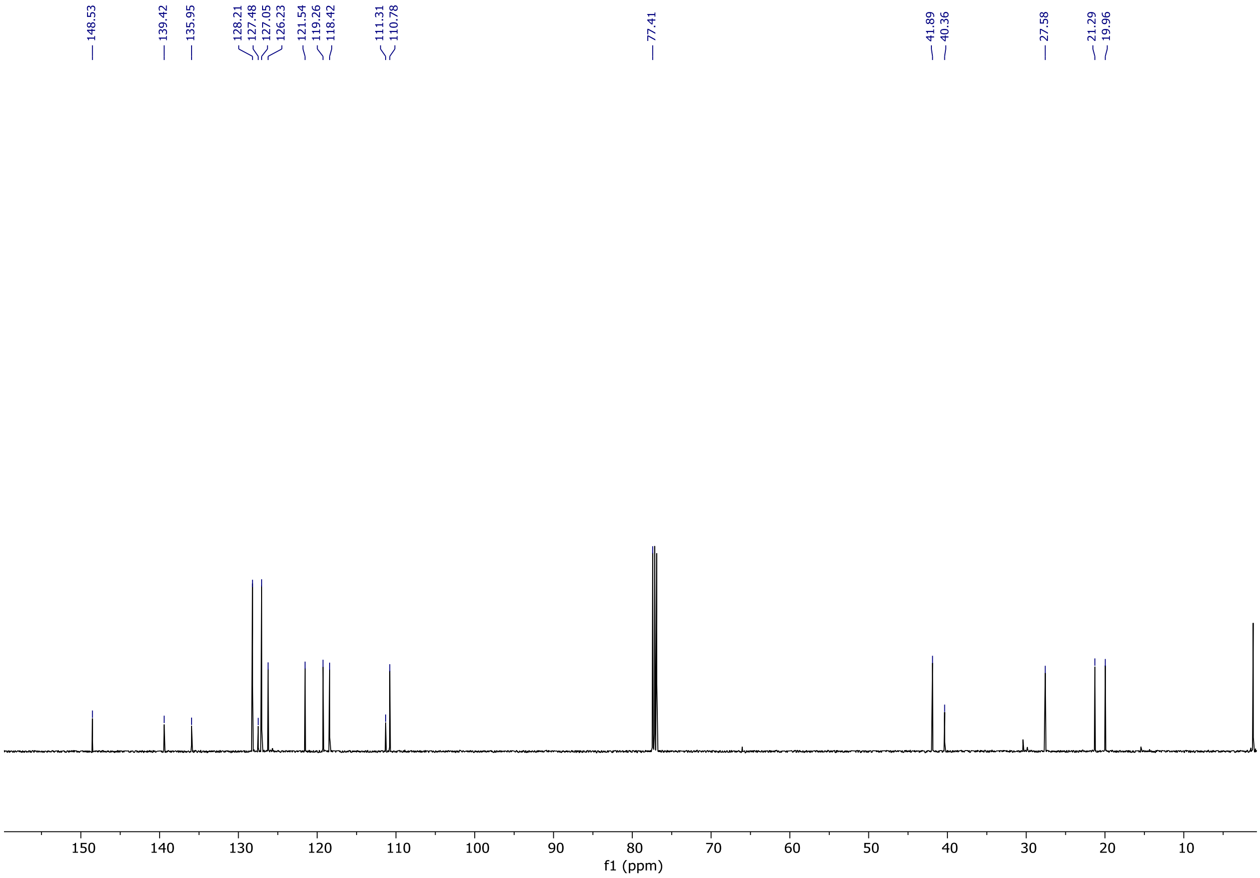
^{1}H NMR, $CDCl_3$, 501 MHz



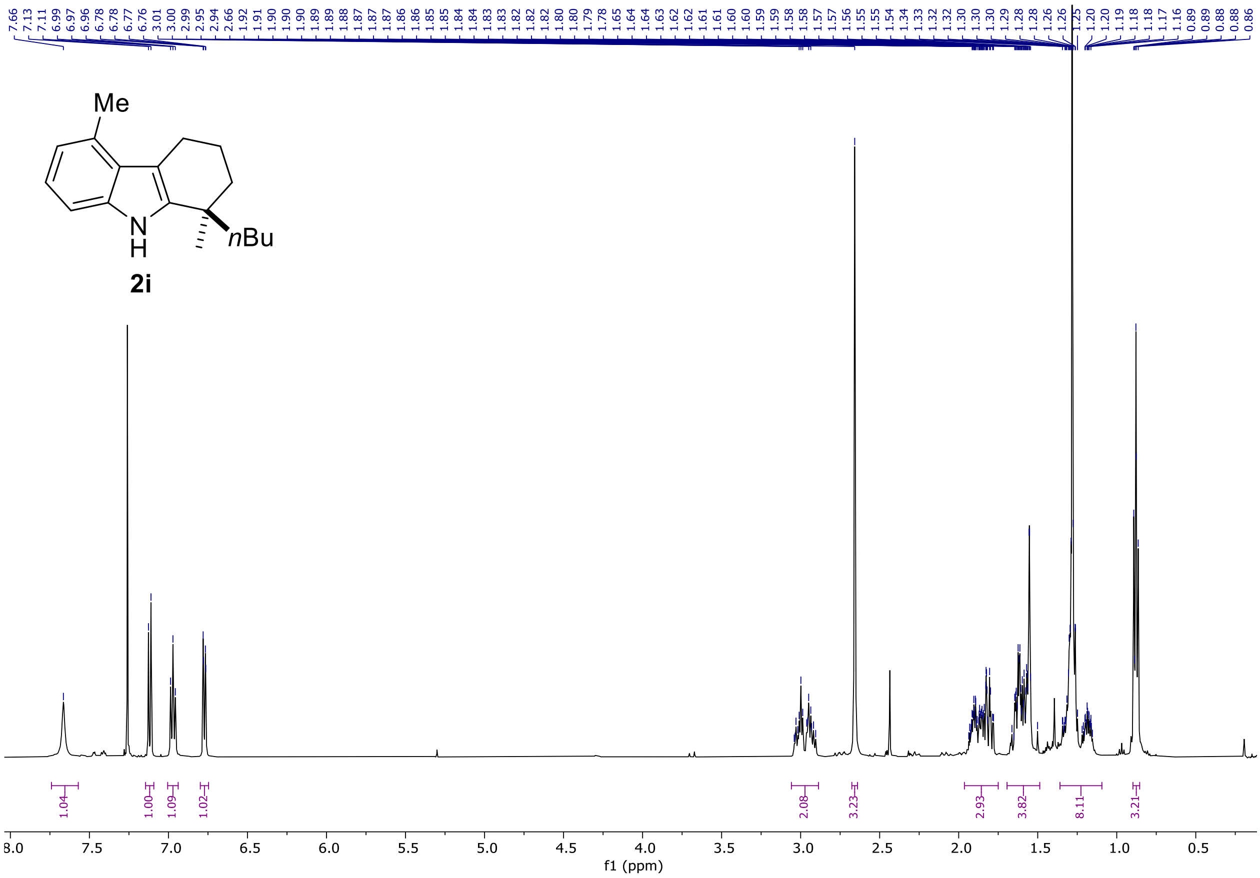
^{13}C NMR, $CDCl_3$, 126 MHz



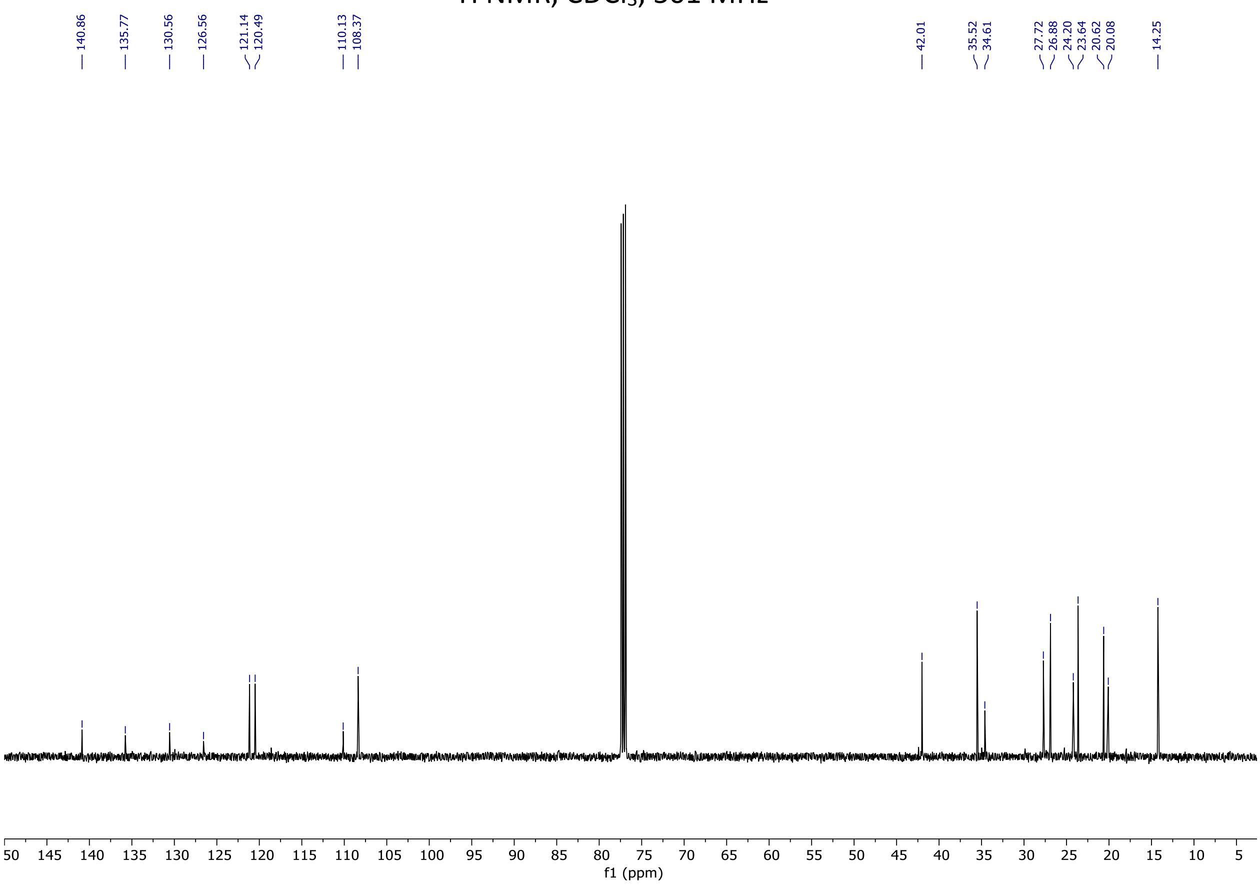
^{1}H NMR, $CDCl_3$, 501 MHz



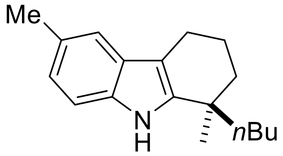
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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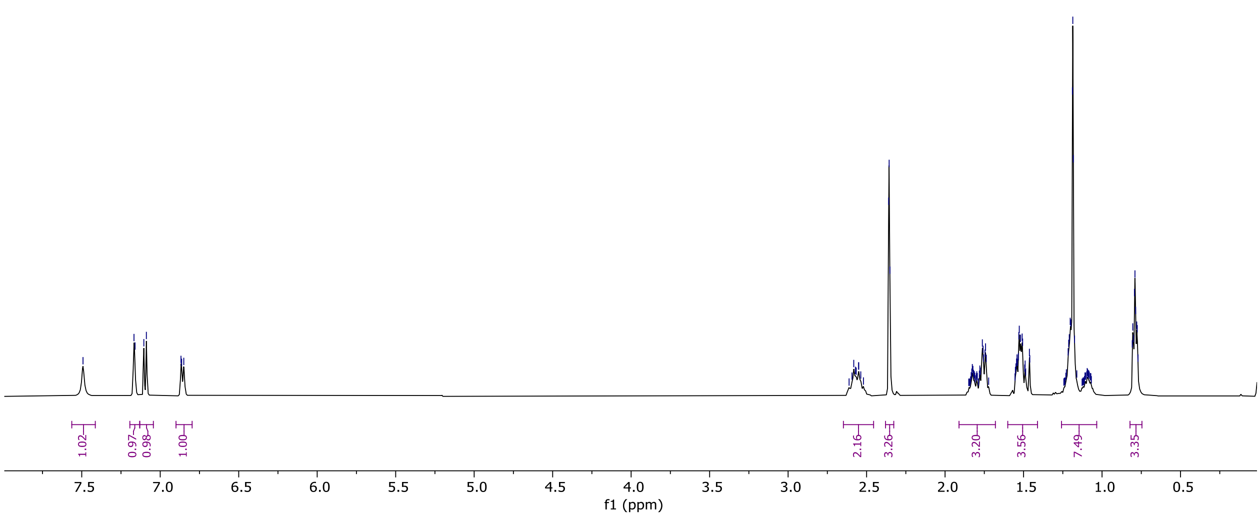
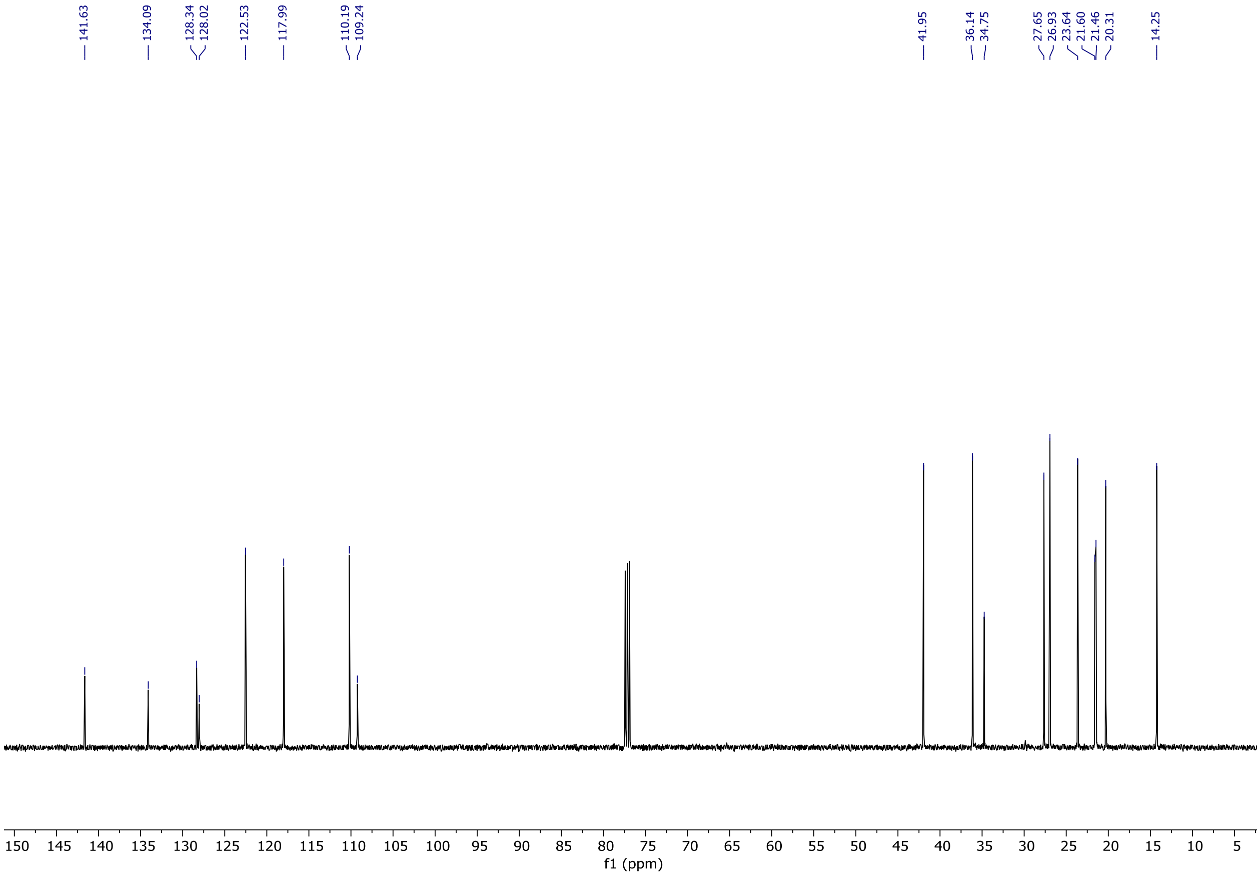
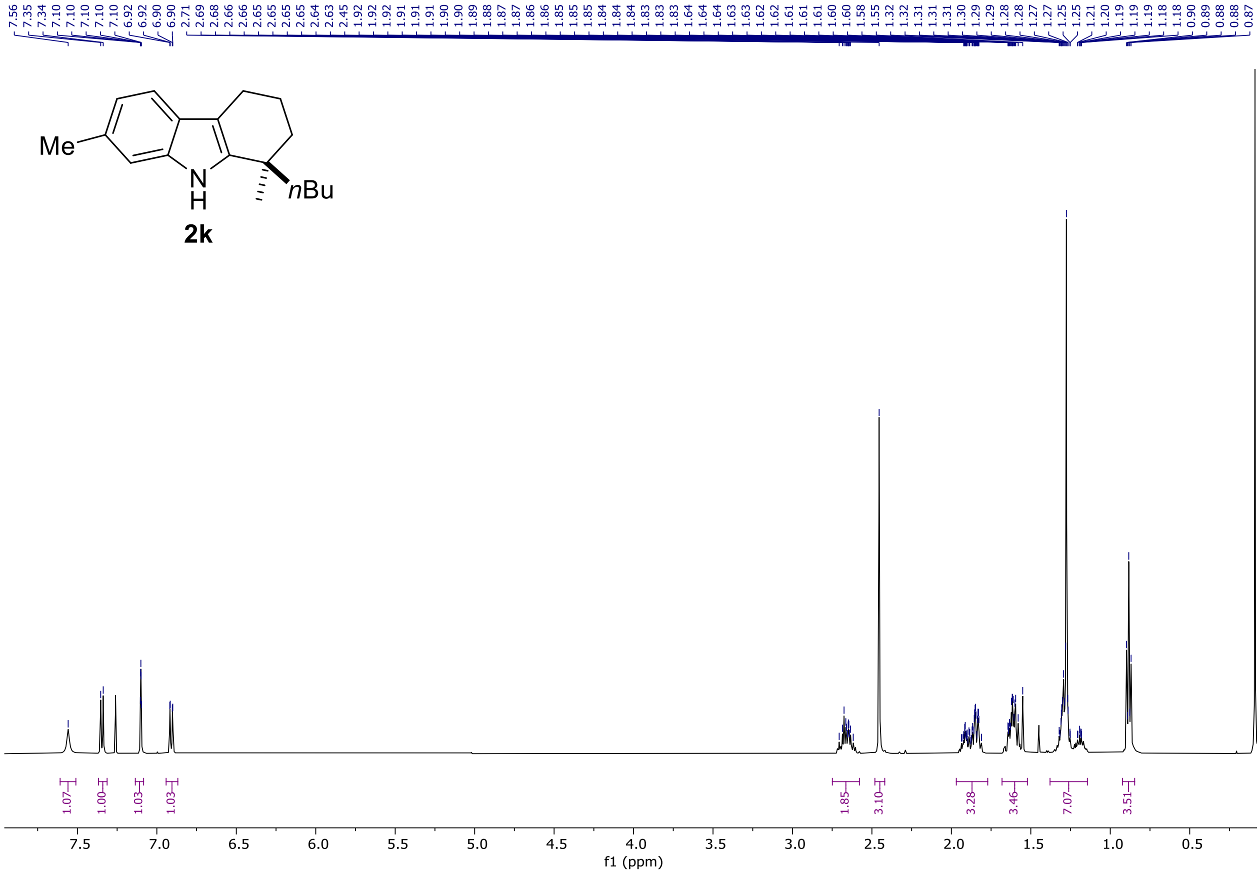


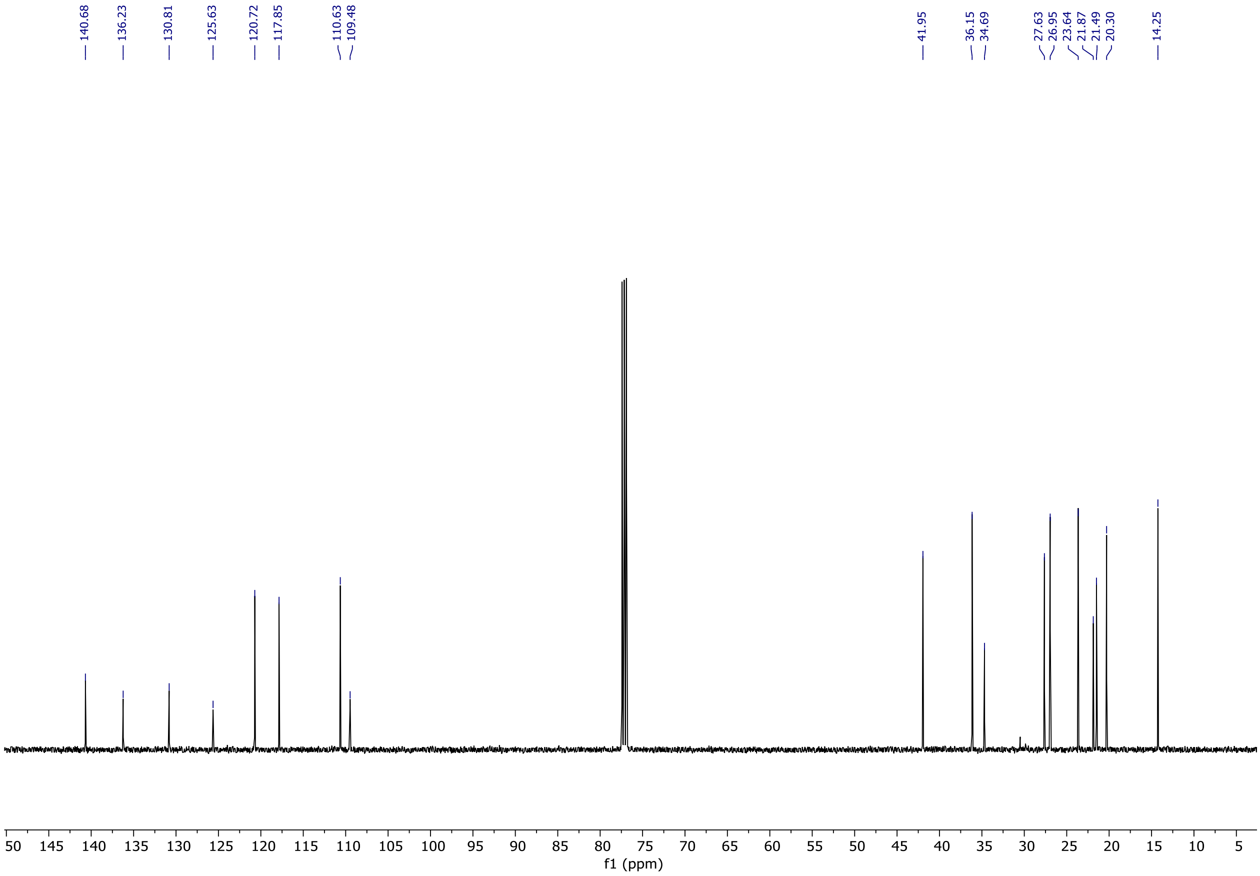
^{1}H NMR, $CDCl_3$, 501 MHz



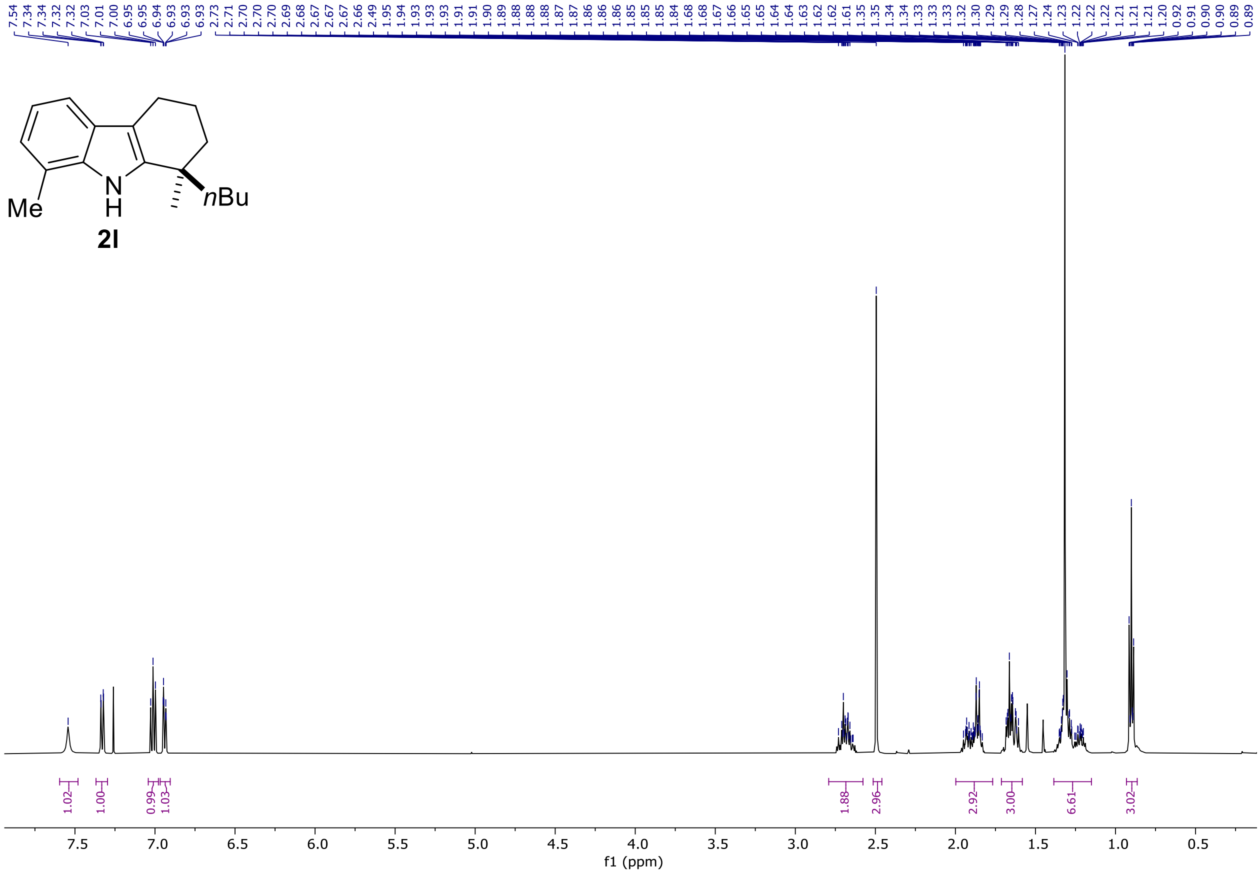
^{13}C NMR, $CDCl_3$, 126 MHz



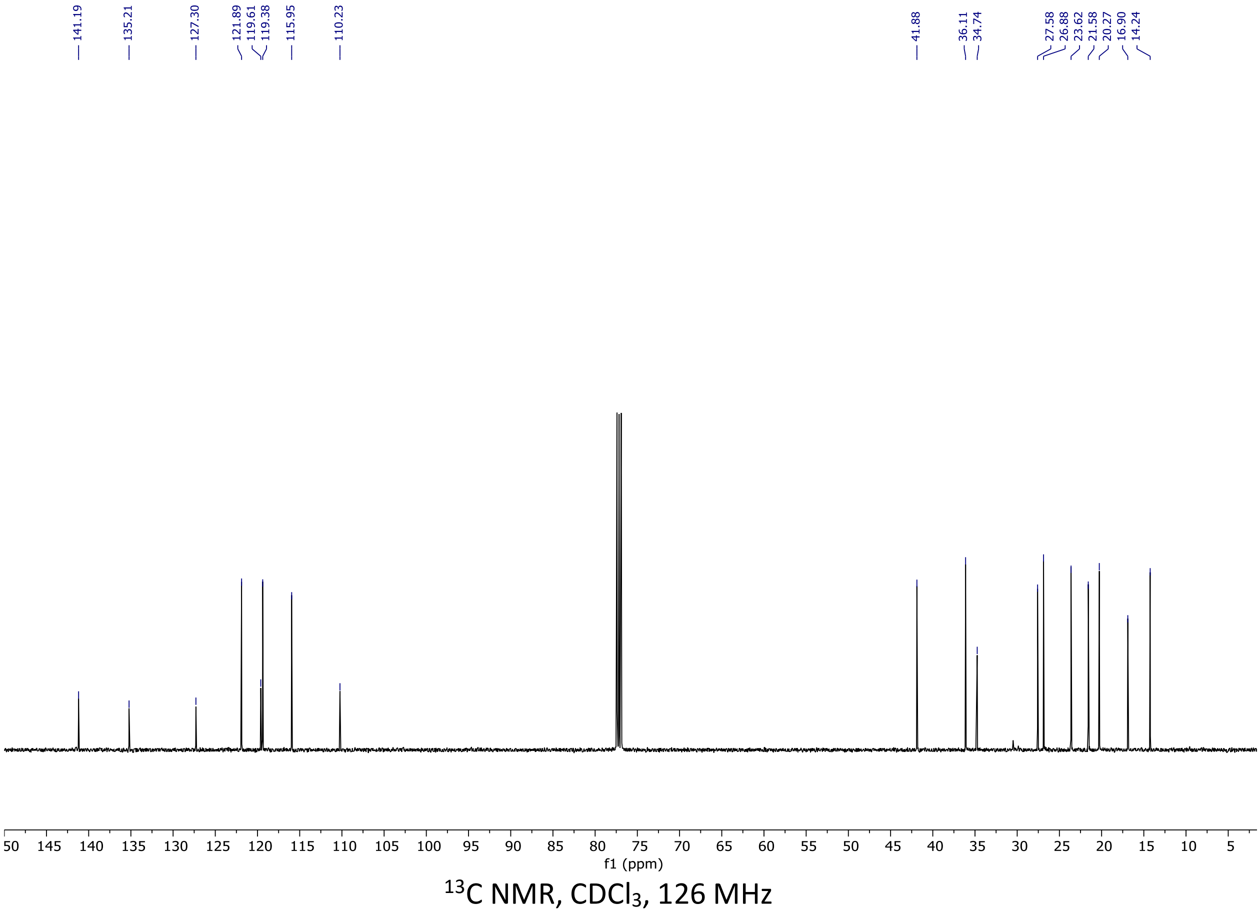
^{1}H NMR, $CDCl_3$, 501 MHz



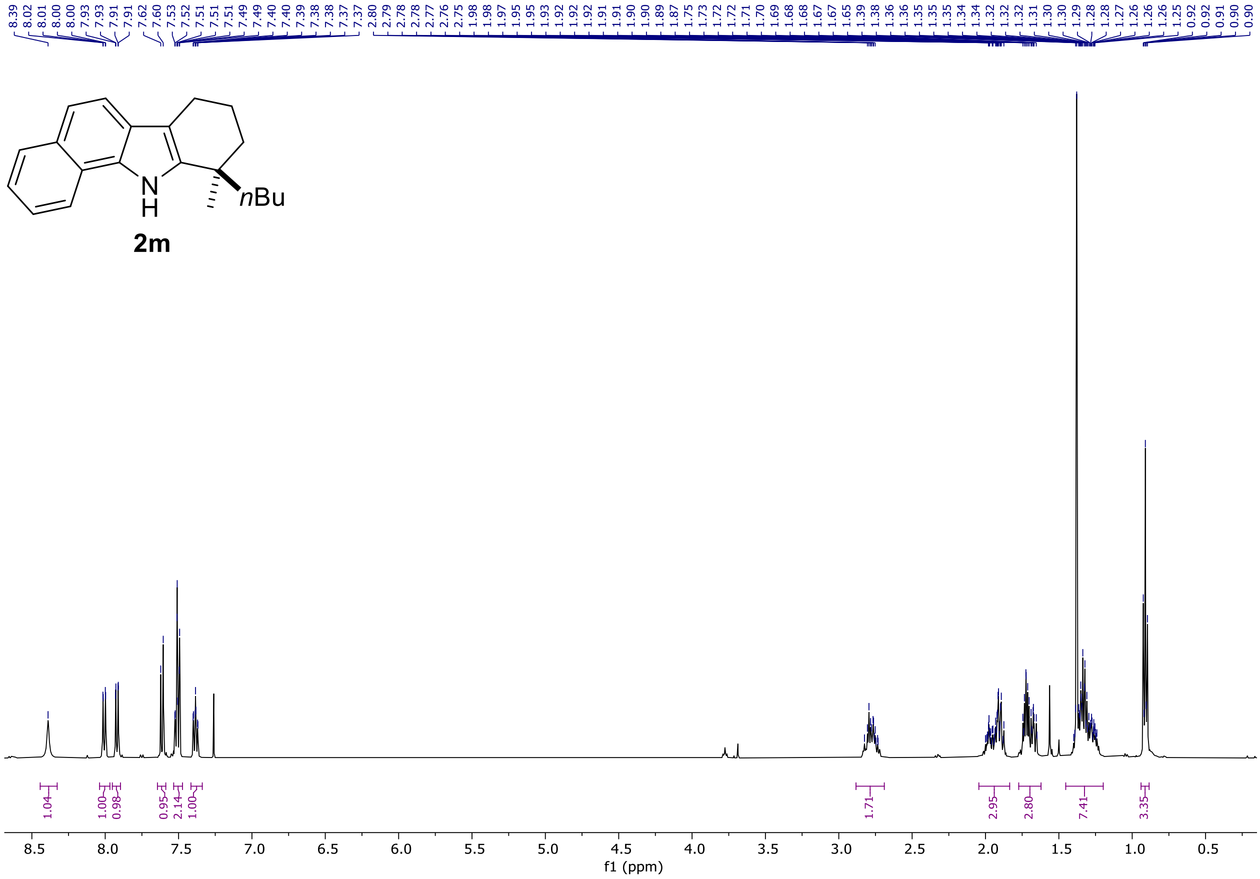
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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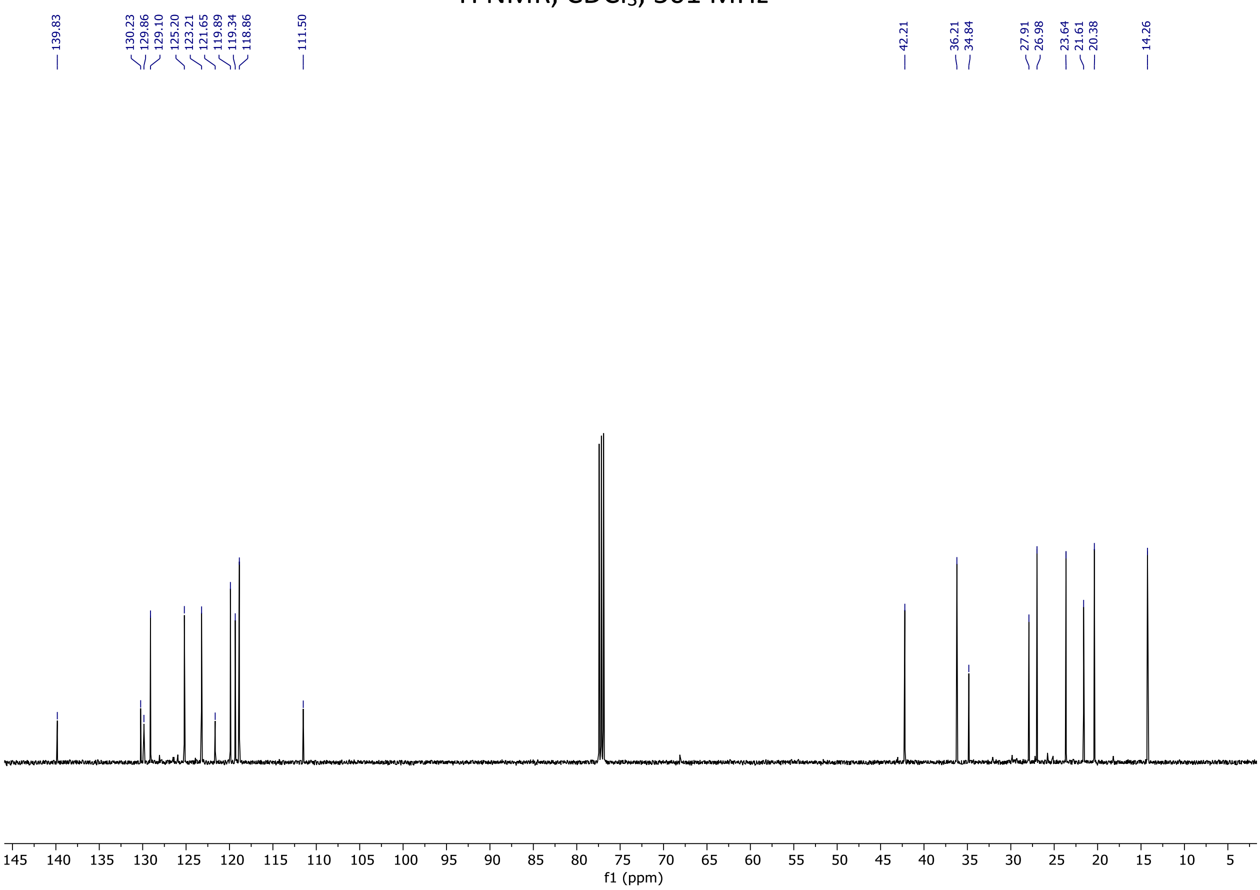
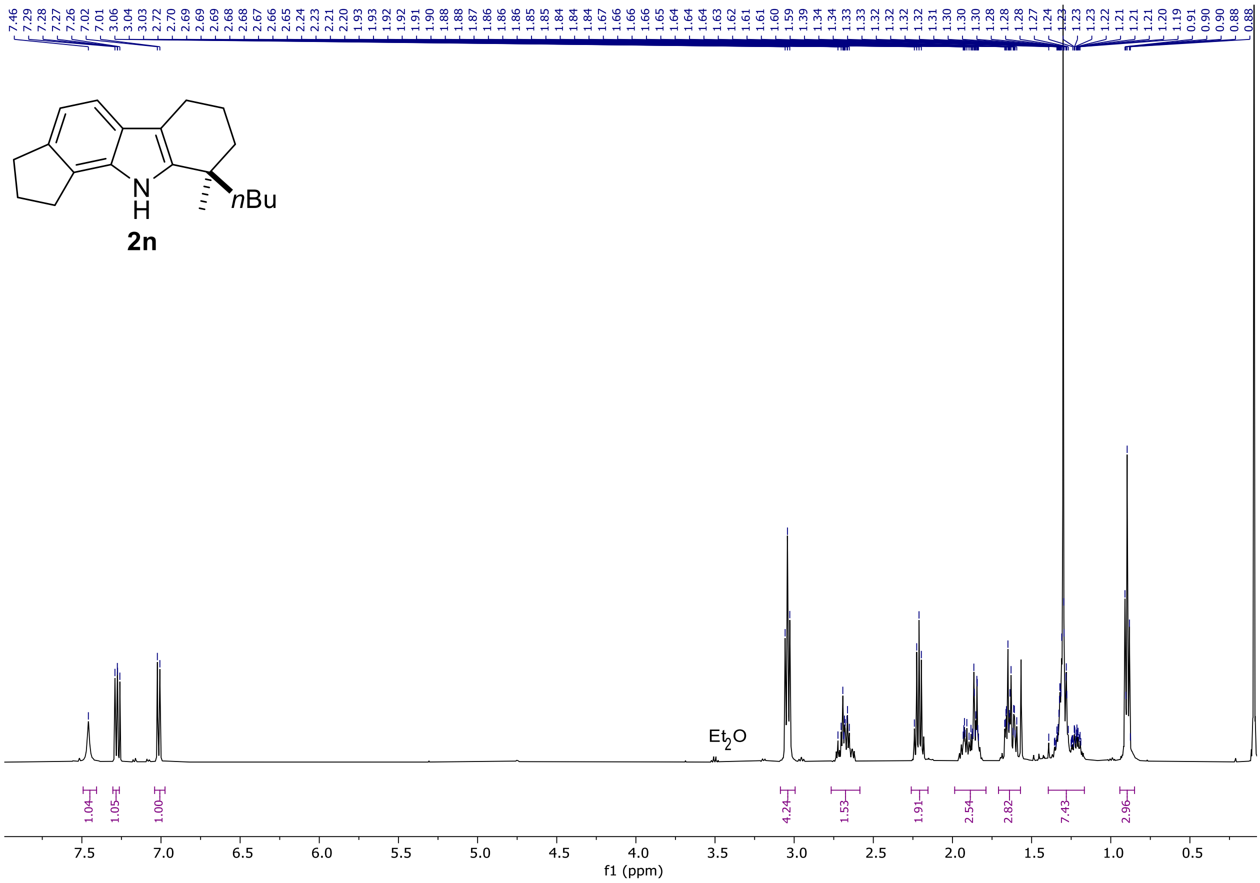
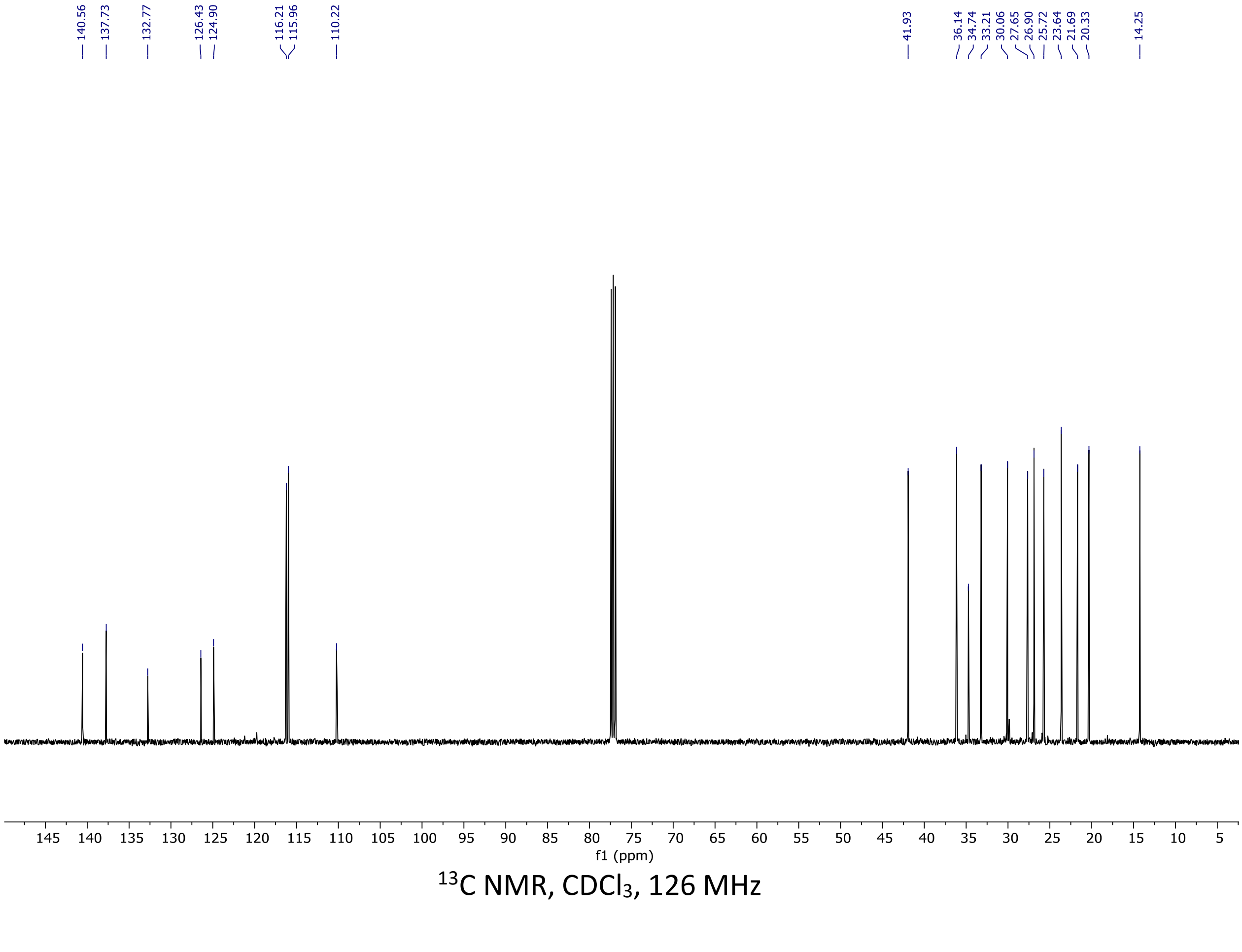
^{1}H NMR, $CDCl_3$, 501 MHz



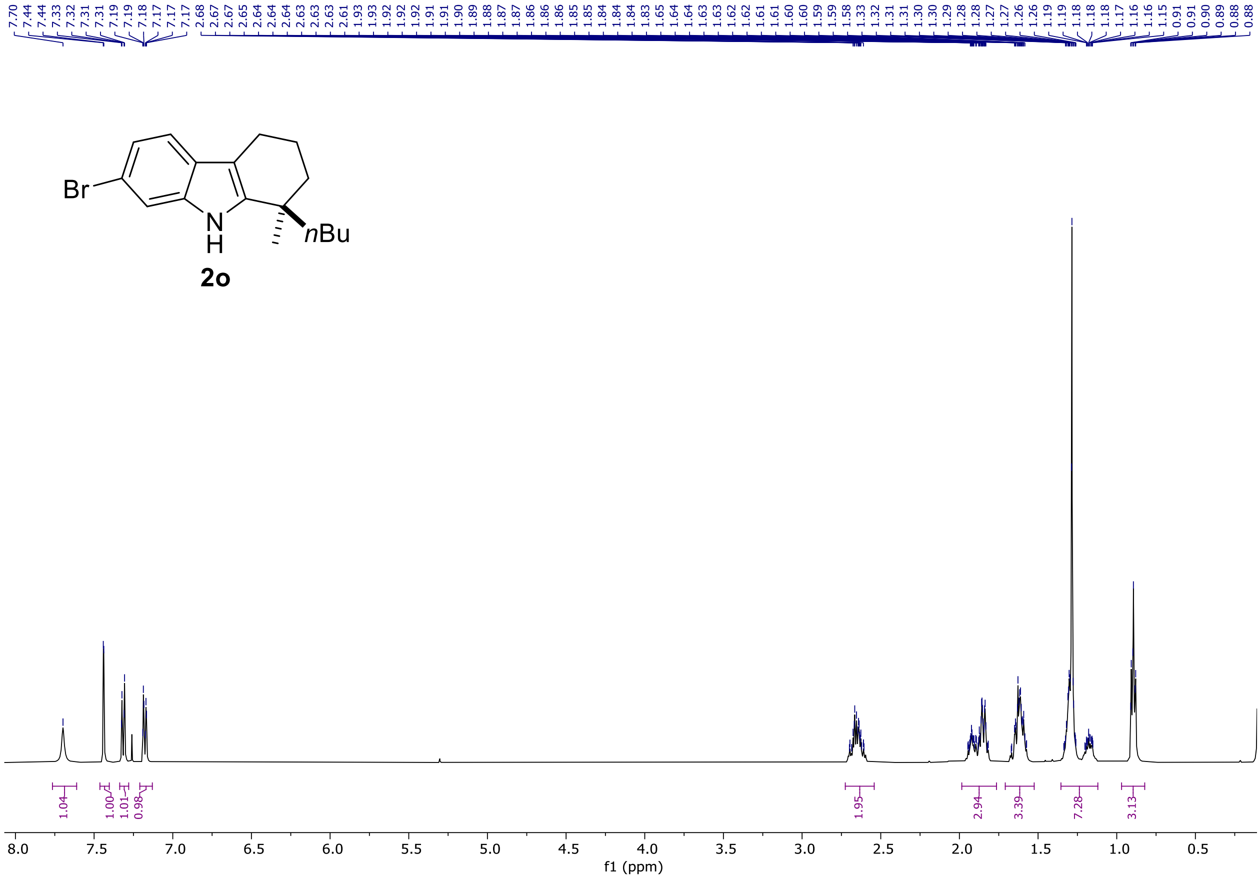
^{13}C NMR, $CDCl_3$, 126 MHz



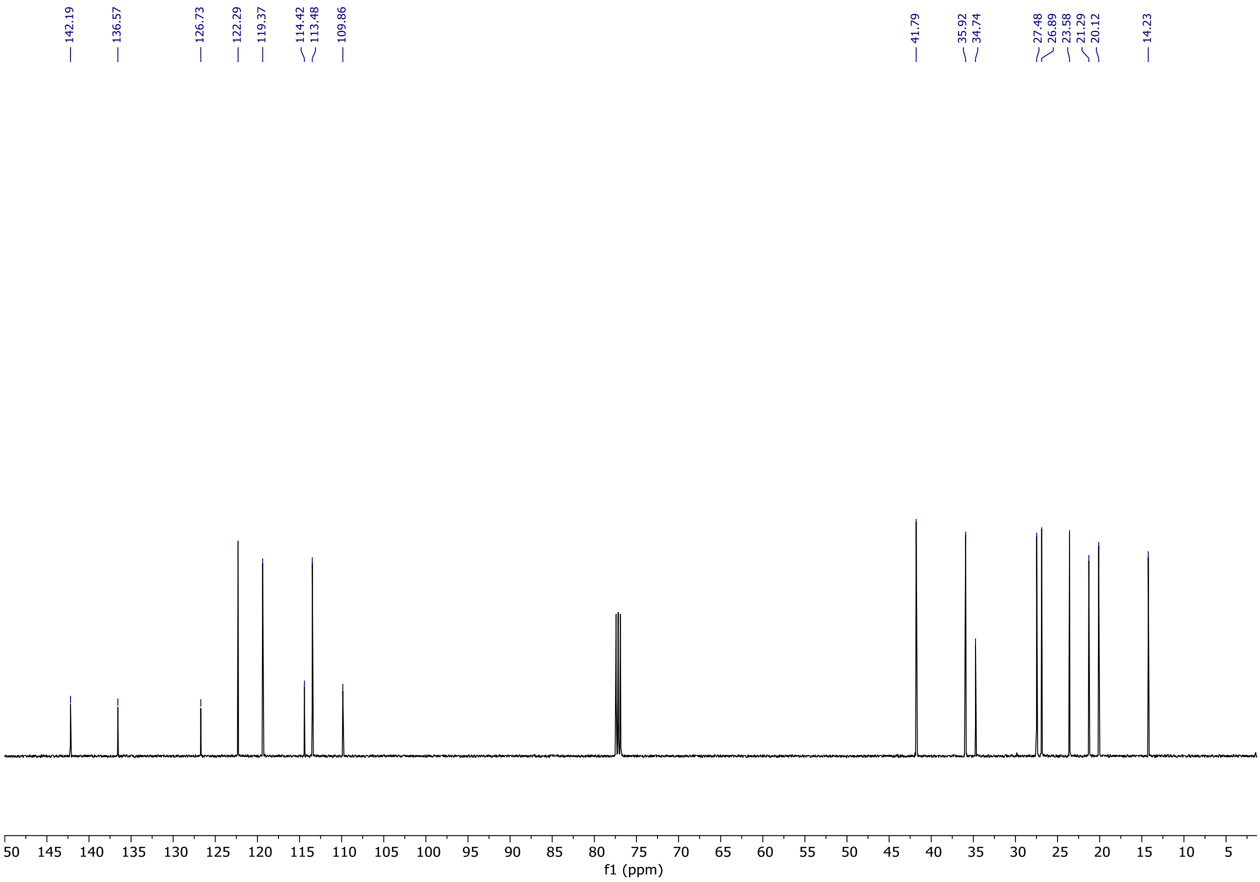
^{1}H NMR, $CDCl_3$, 501 MHz



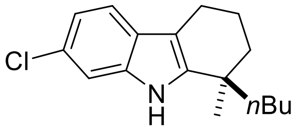
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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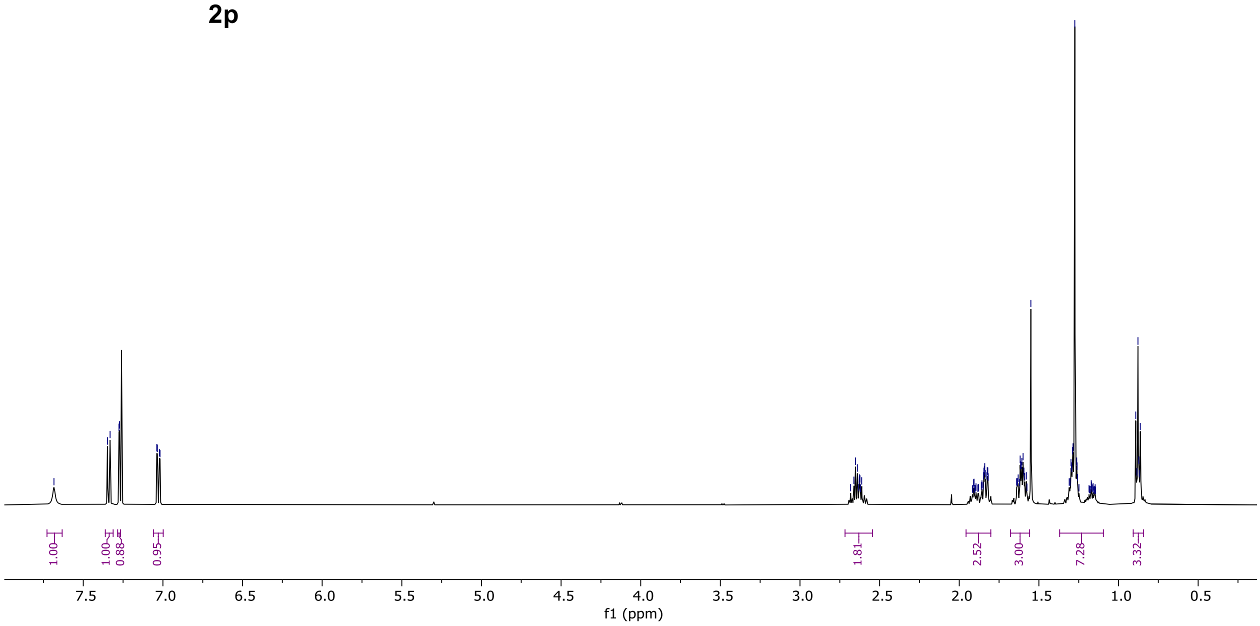
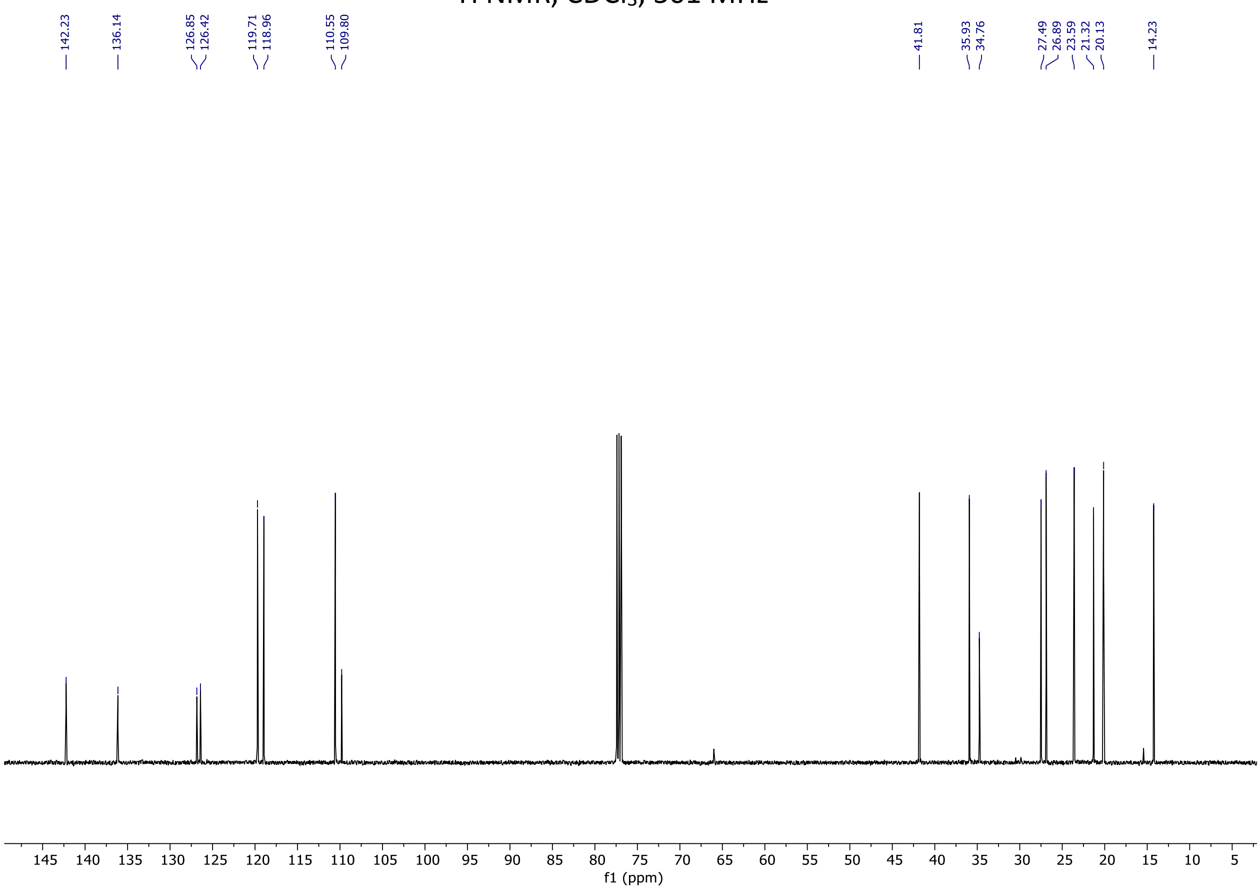
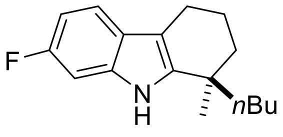


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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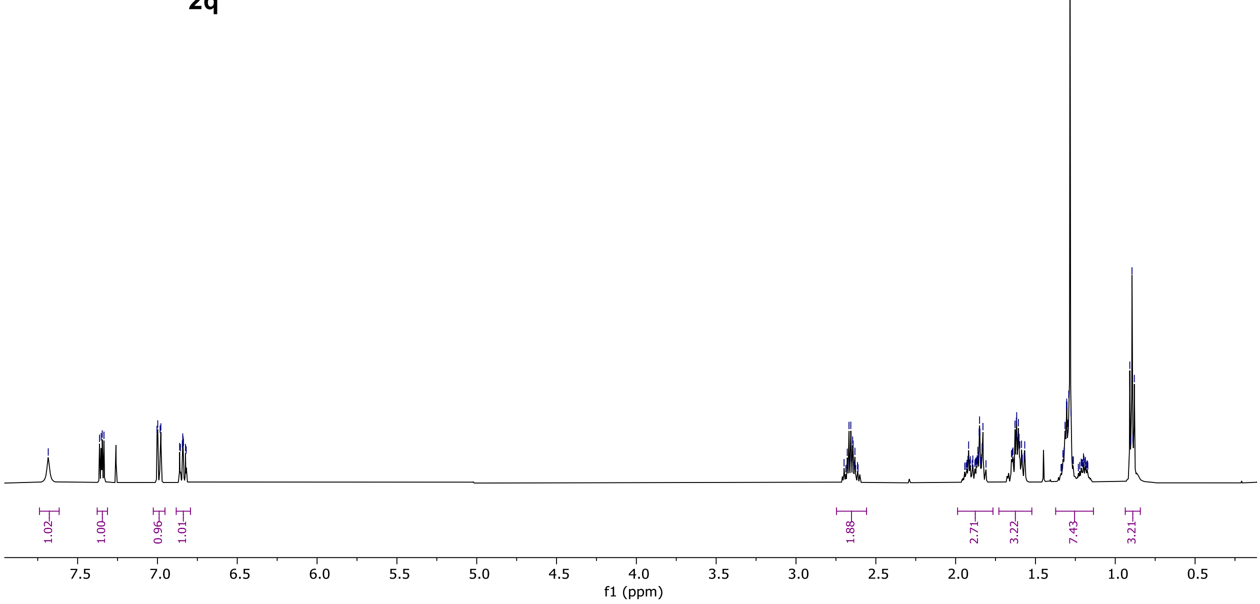
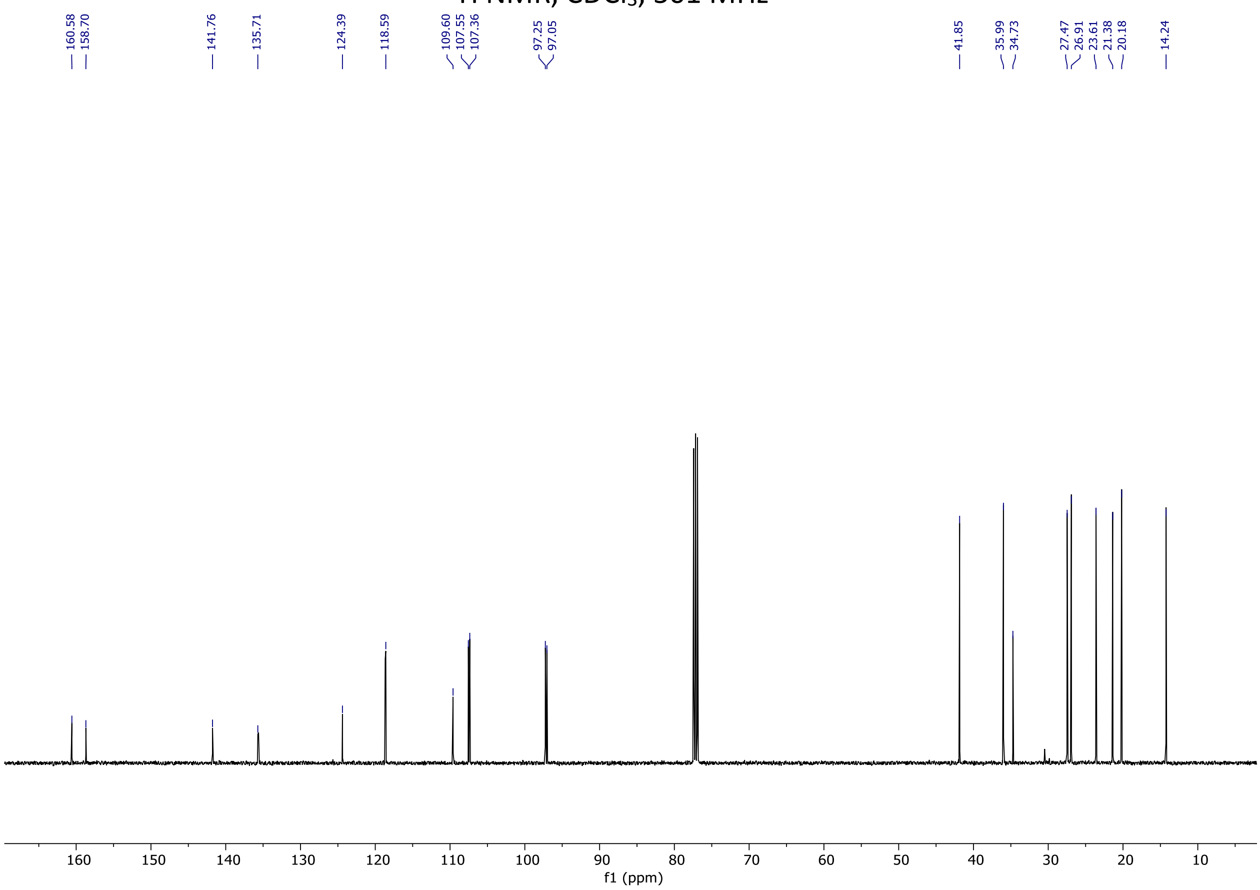
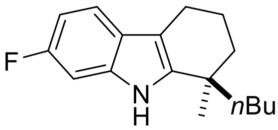


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

^{19}F



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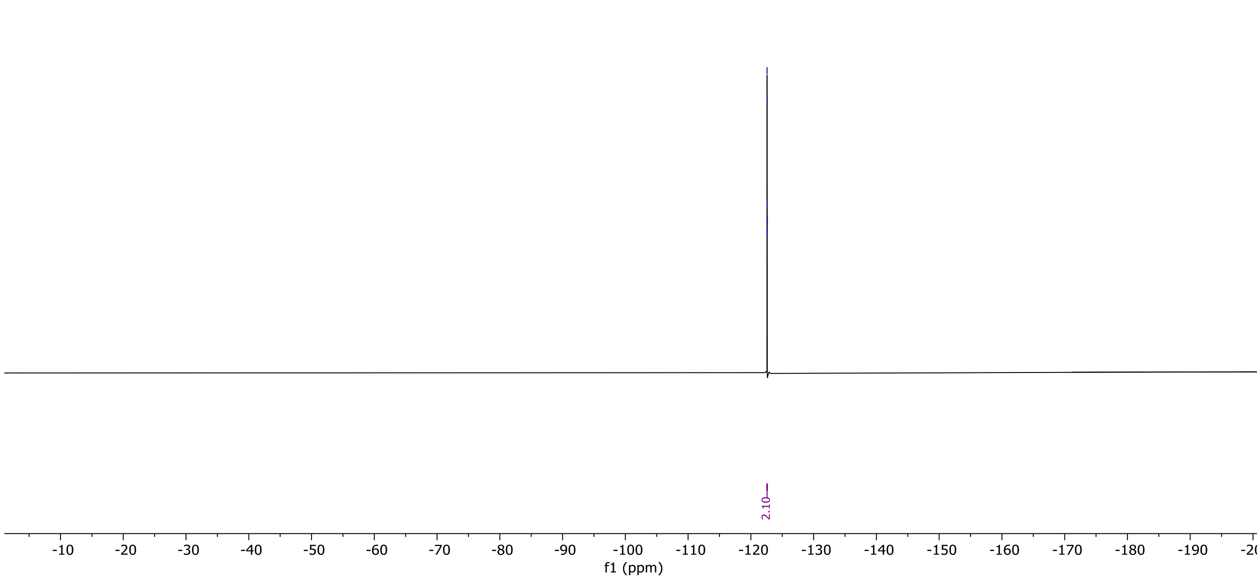
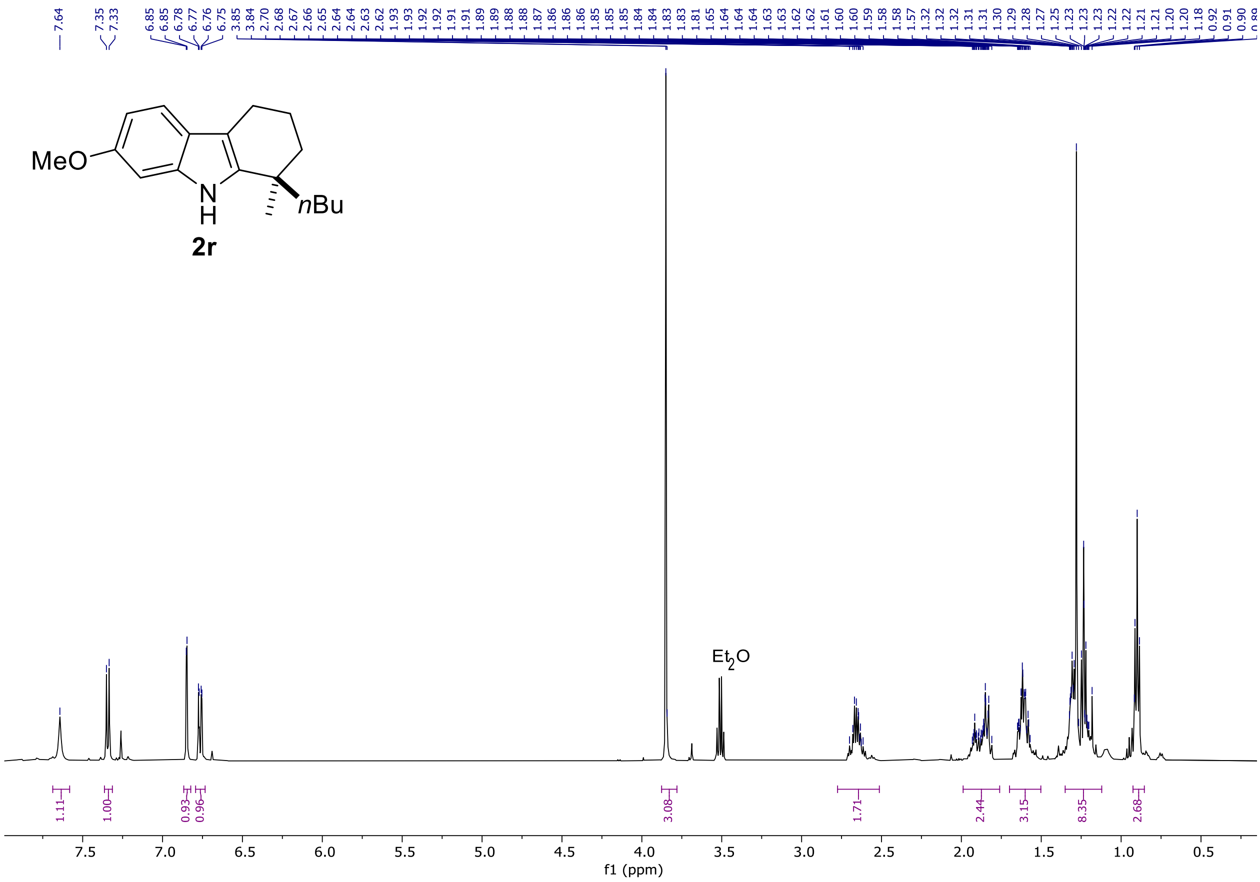
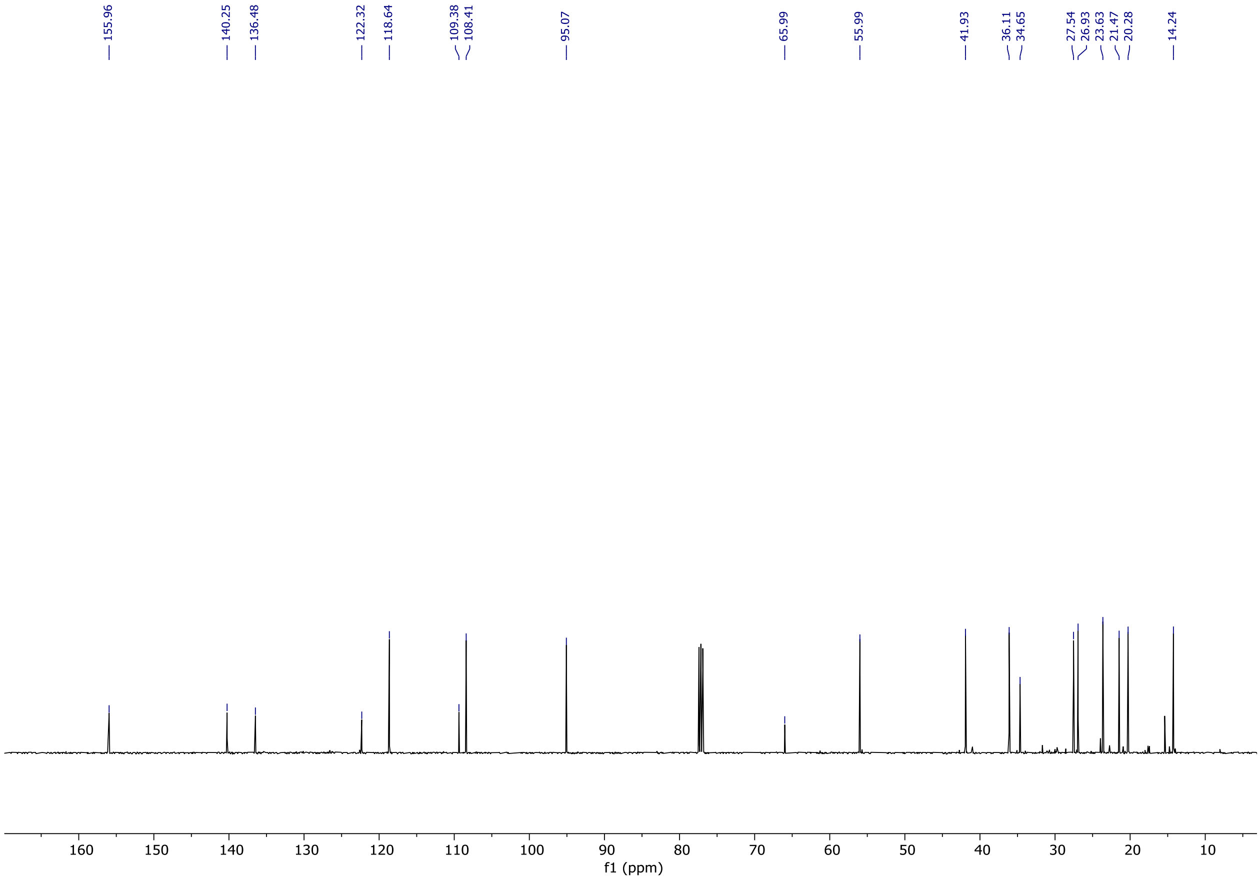


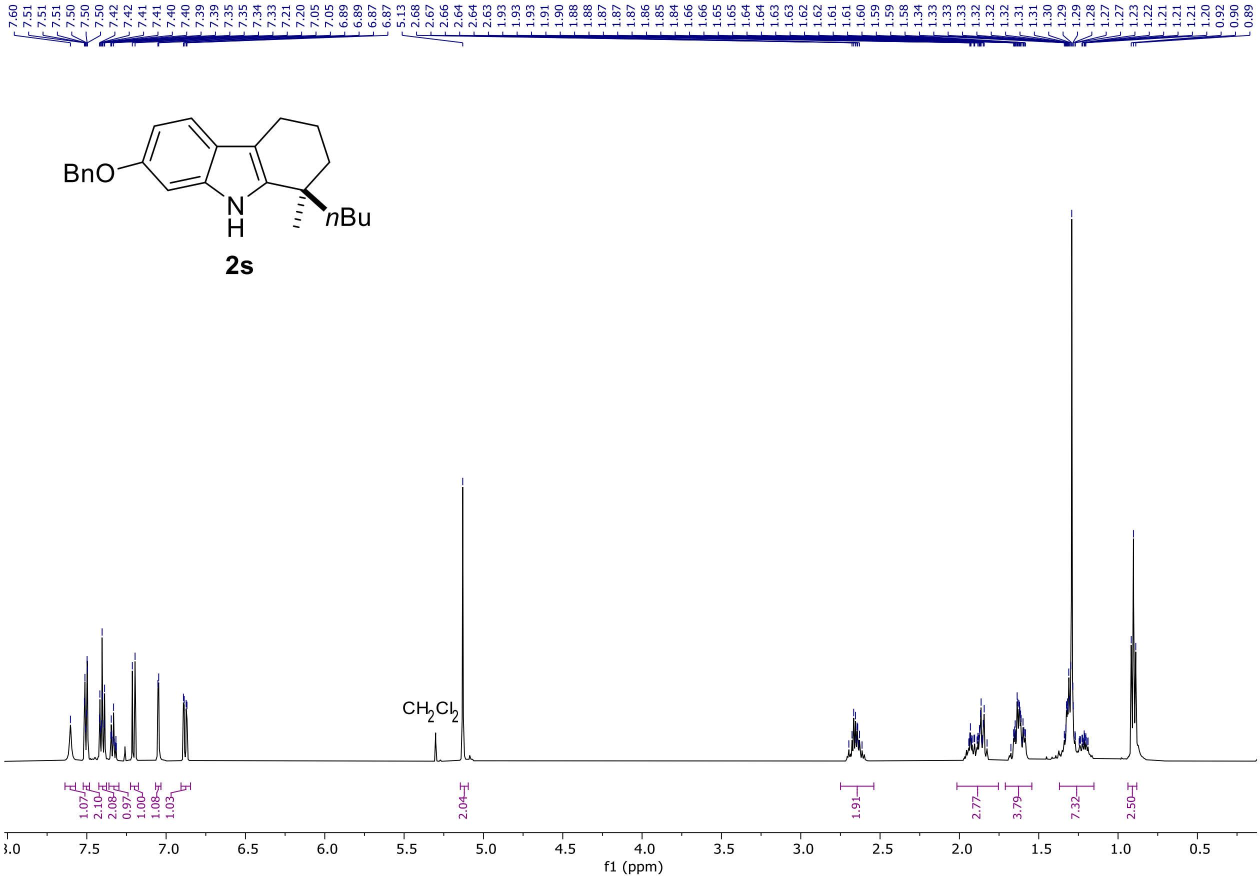
^{19}F NMR, $CDCl_3$, 471 MHz



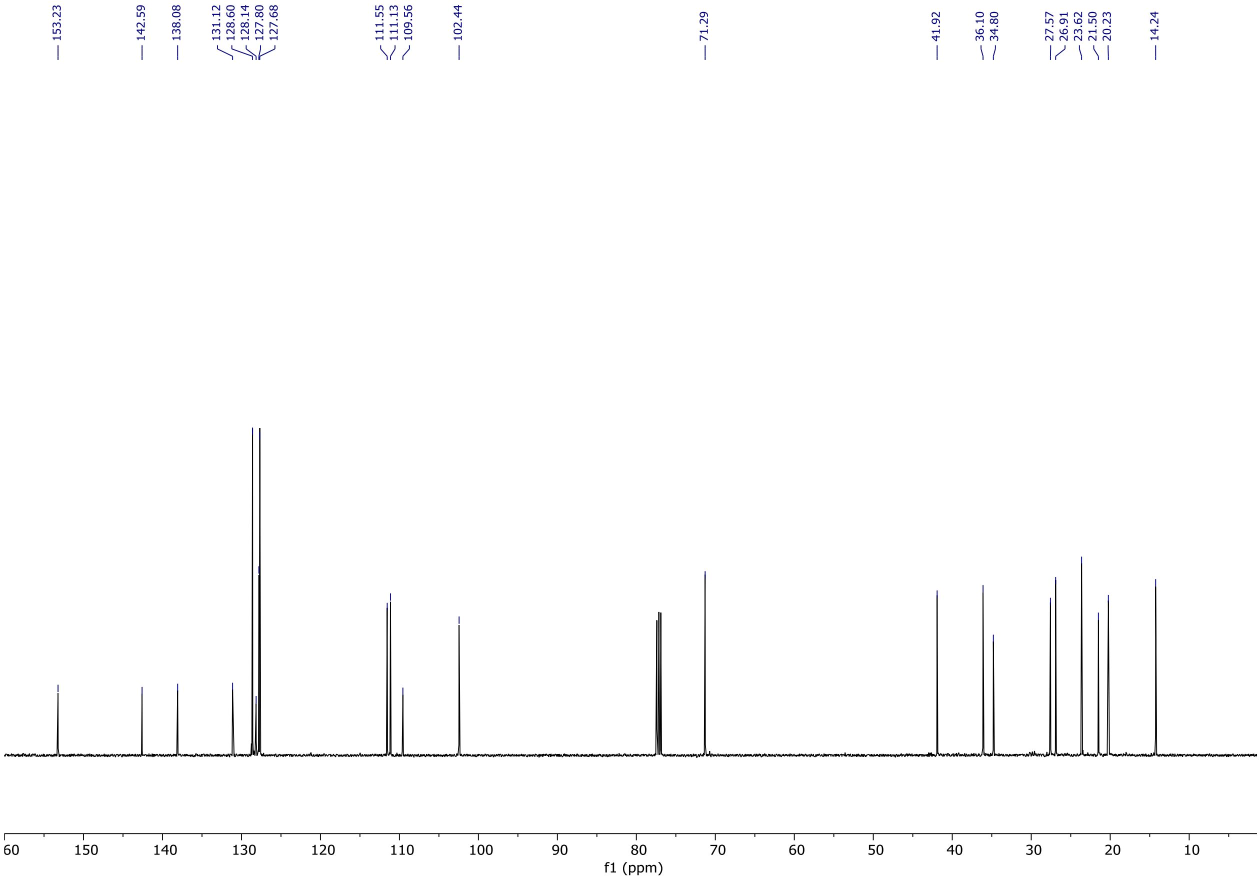
^{1}H NMR, $CDCl_3$, 501 MHz



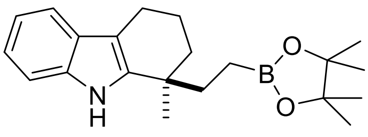
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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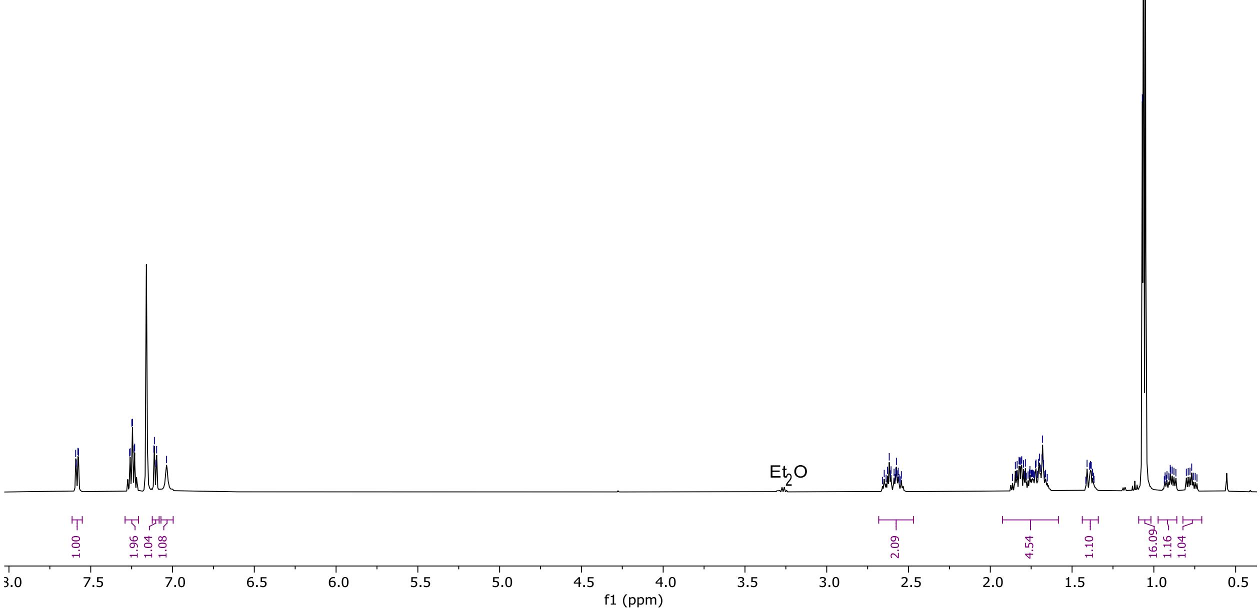
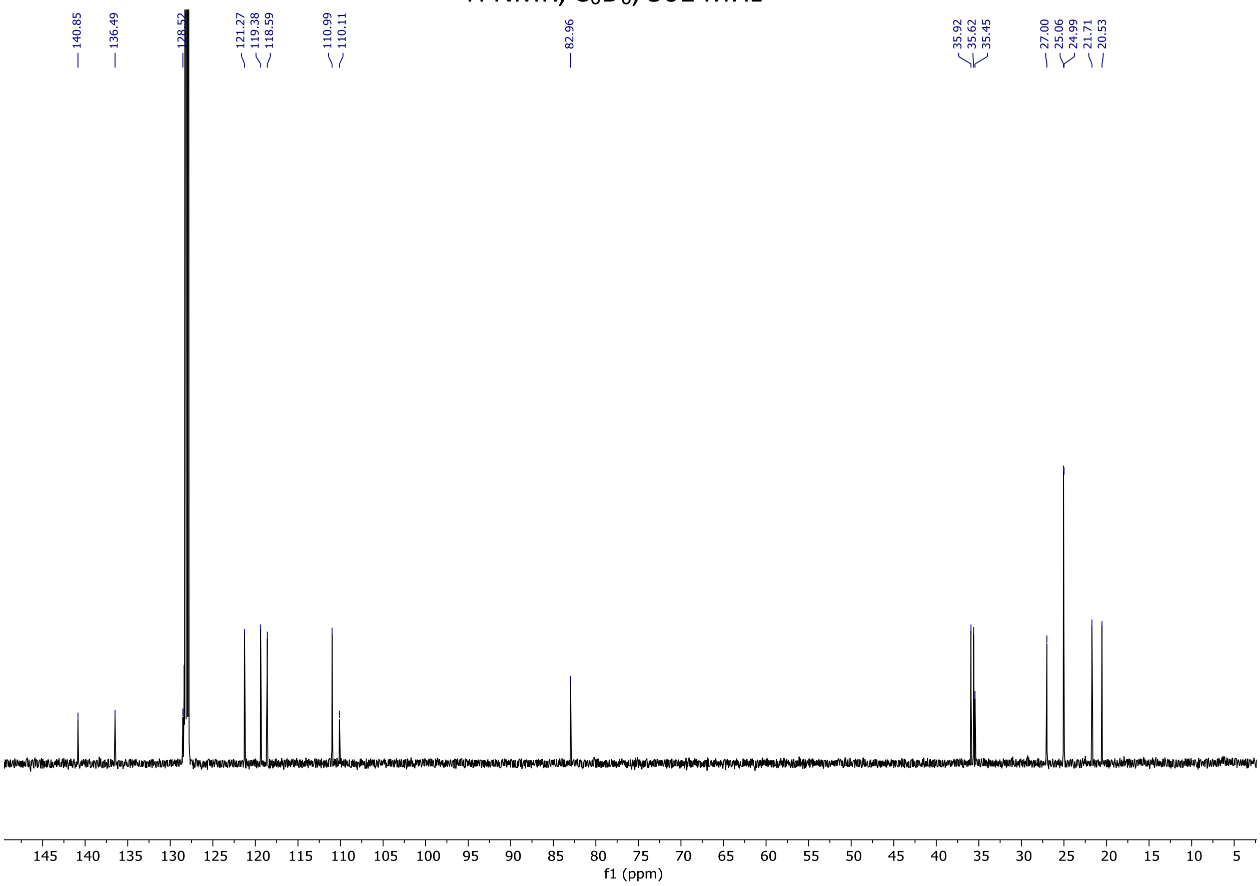
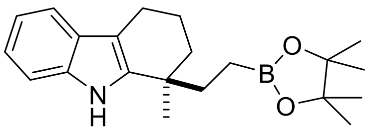


^{1}H NMR, C_6D_6, 501 MHz



^{13}C NMR, C_6D_6, 126 MHz

^{11}B



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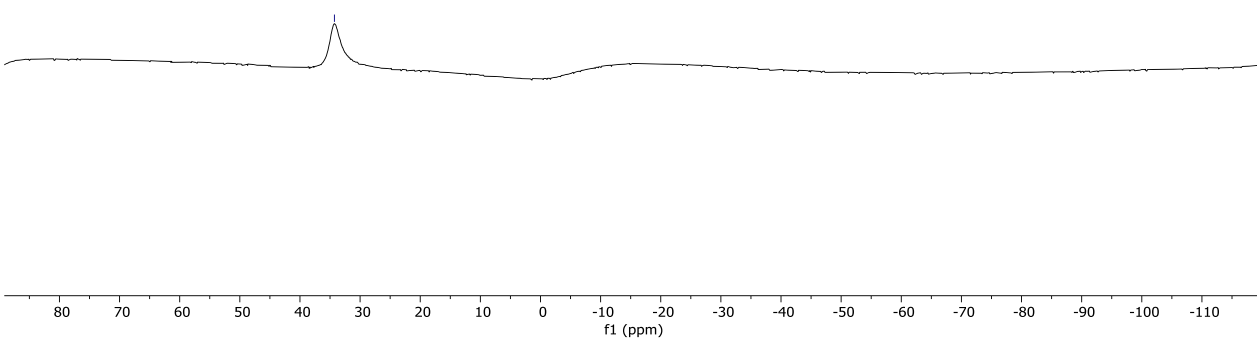
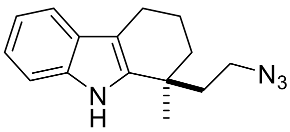


^{11}B NMR, C_6D_6, 161 MHz



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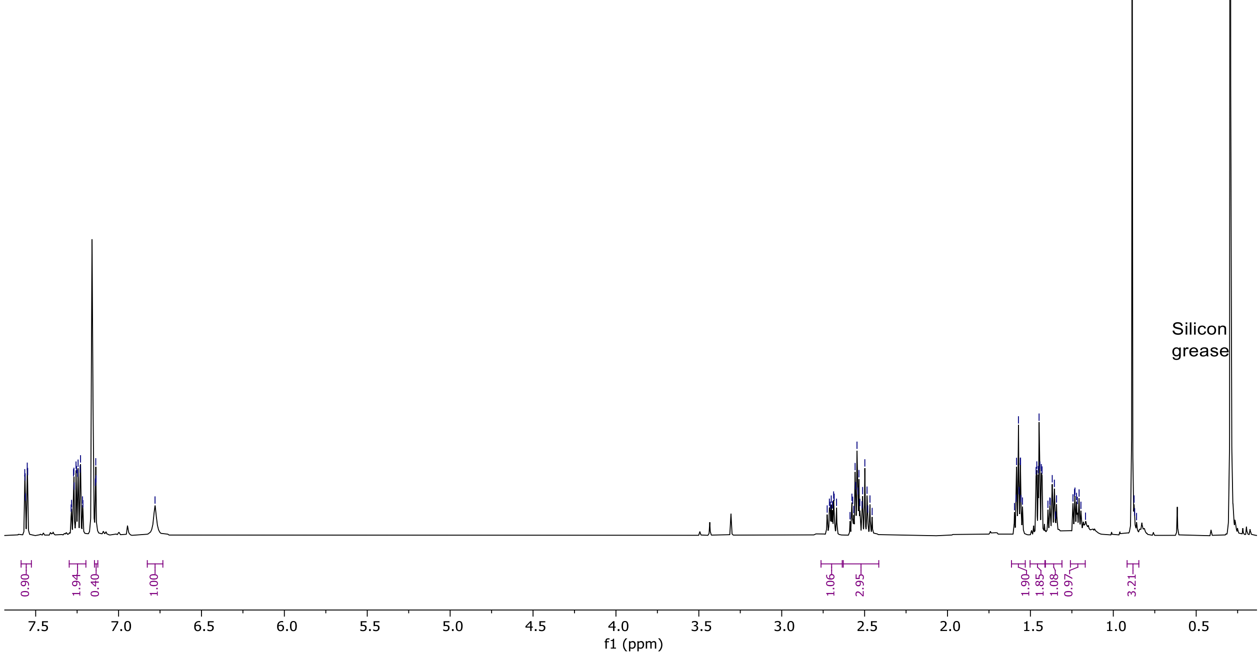
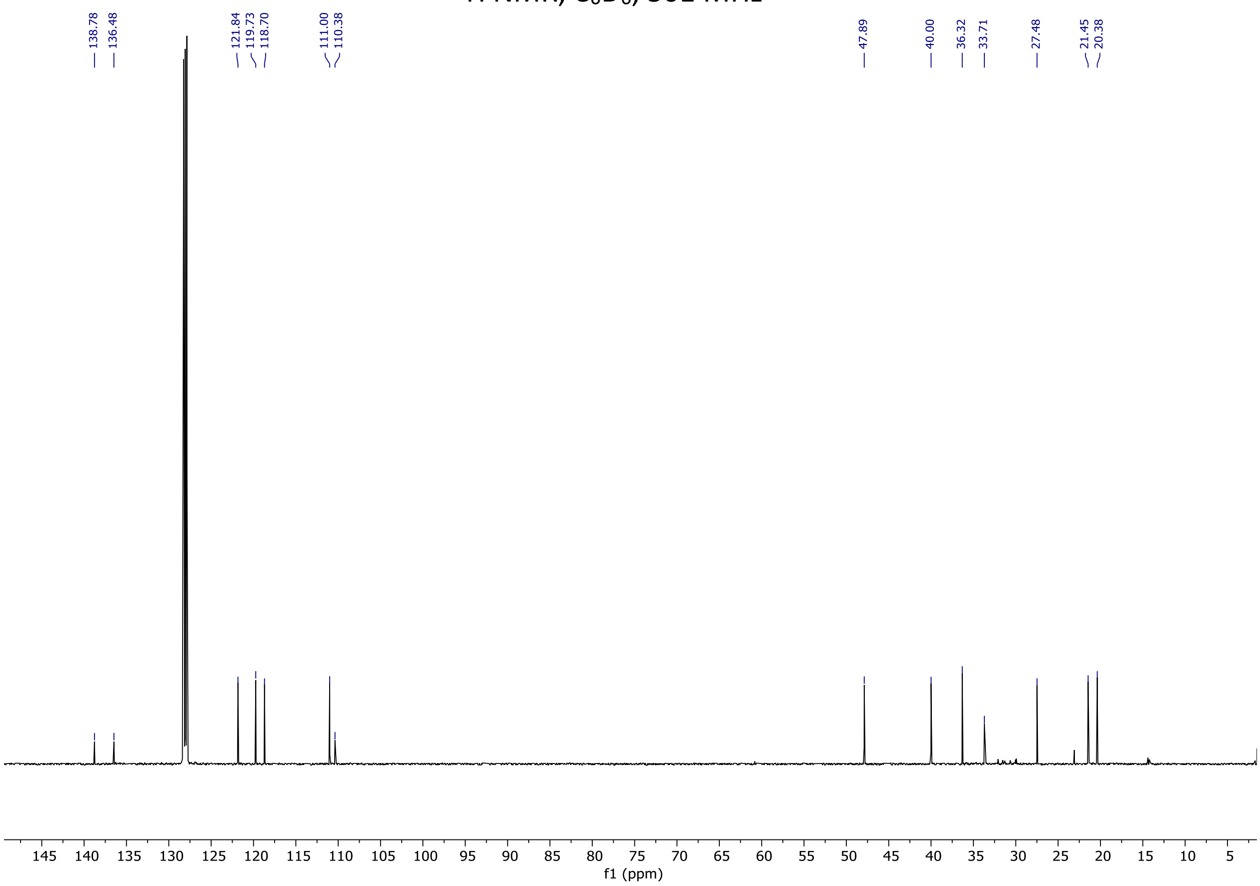
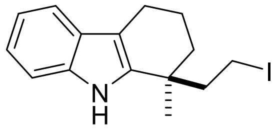


^{1}H NMR, C_6D_6, 501 MHz



^{13}C NMR, C_6D_6, 126 MHz



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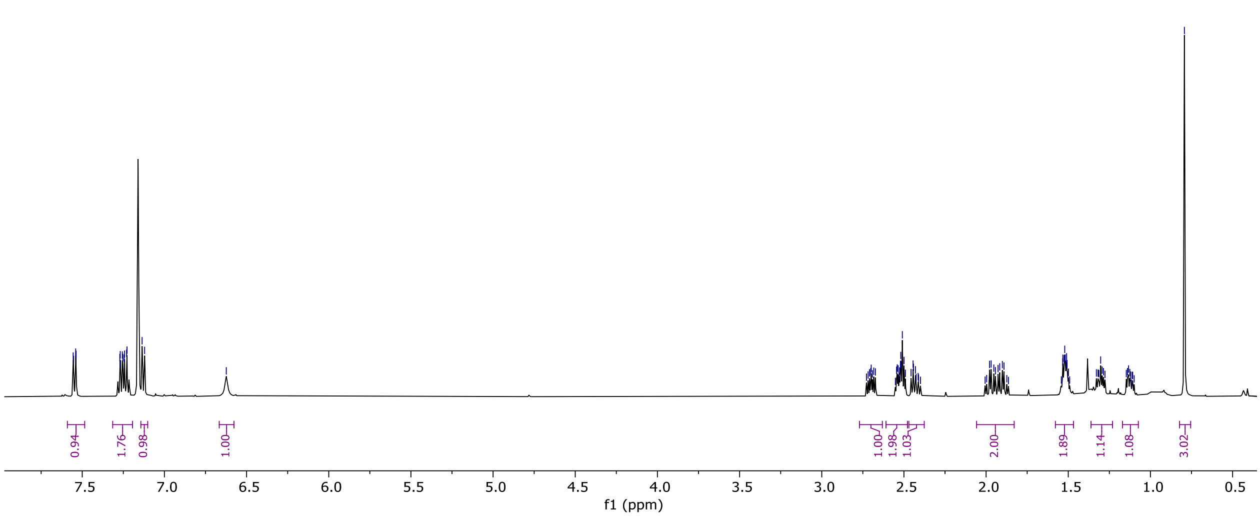
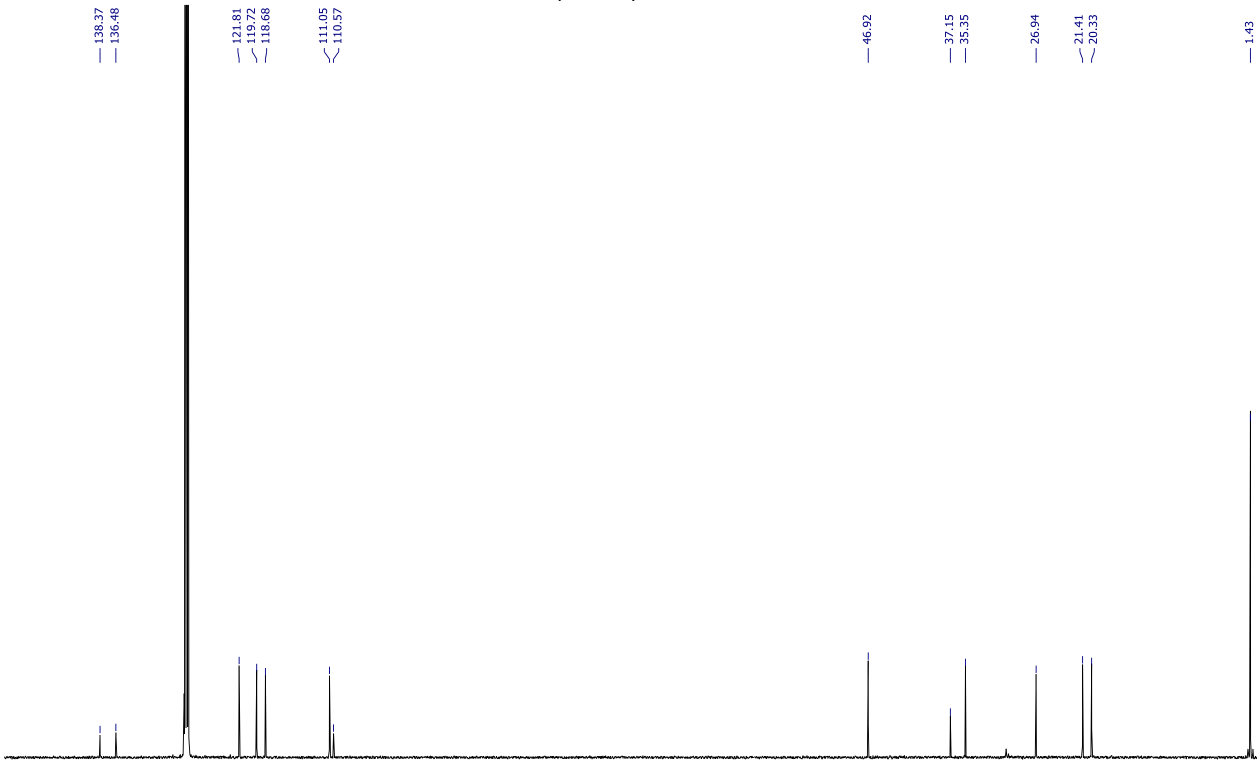
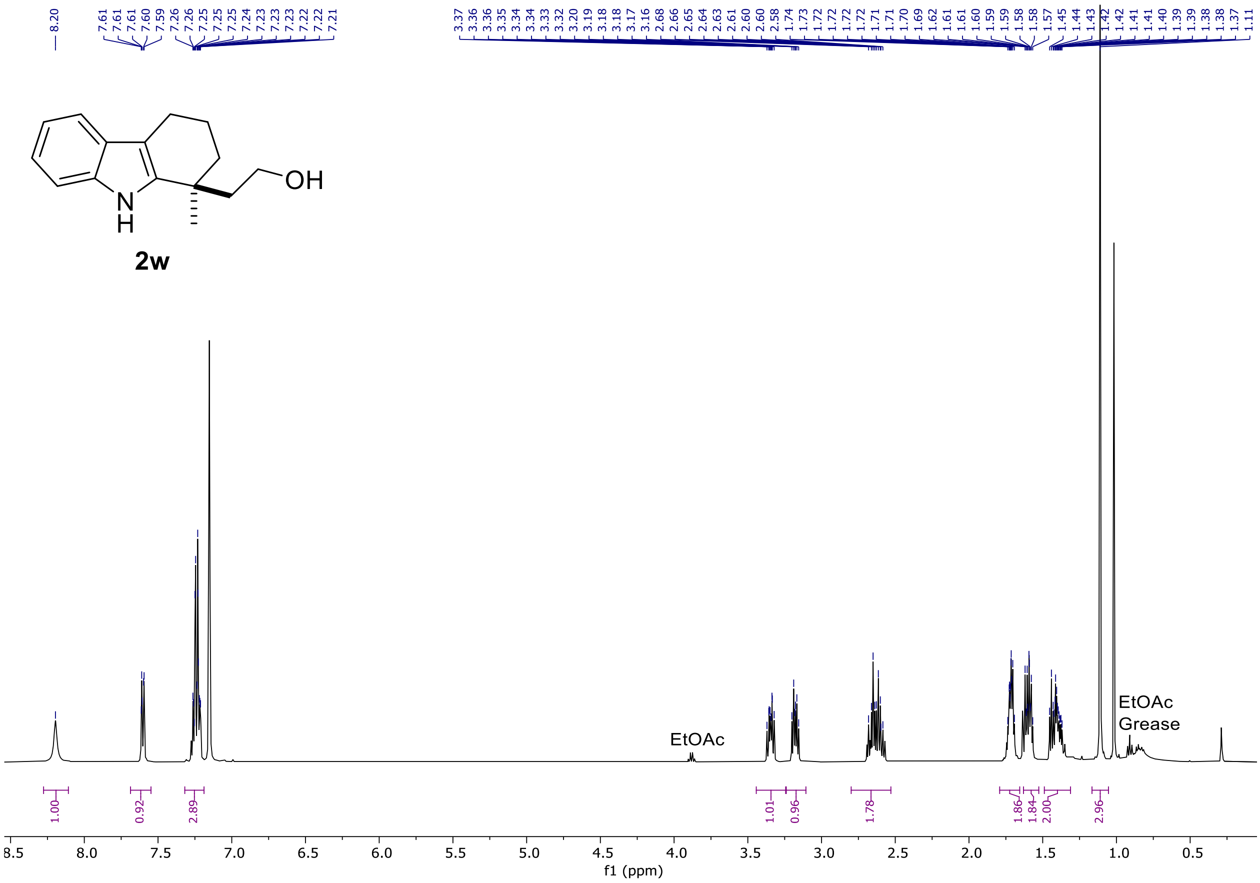


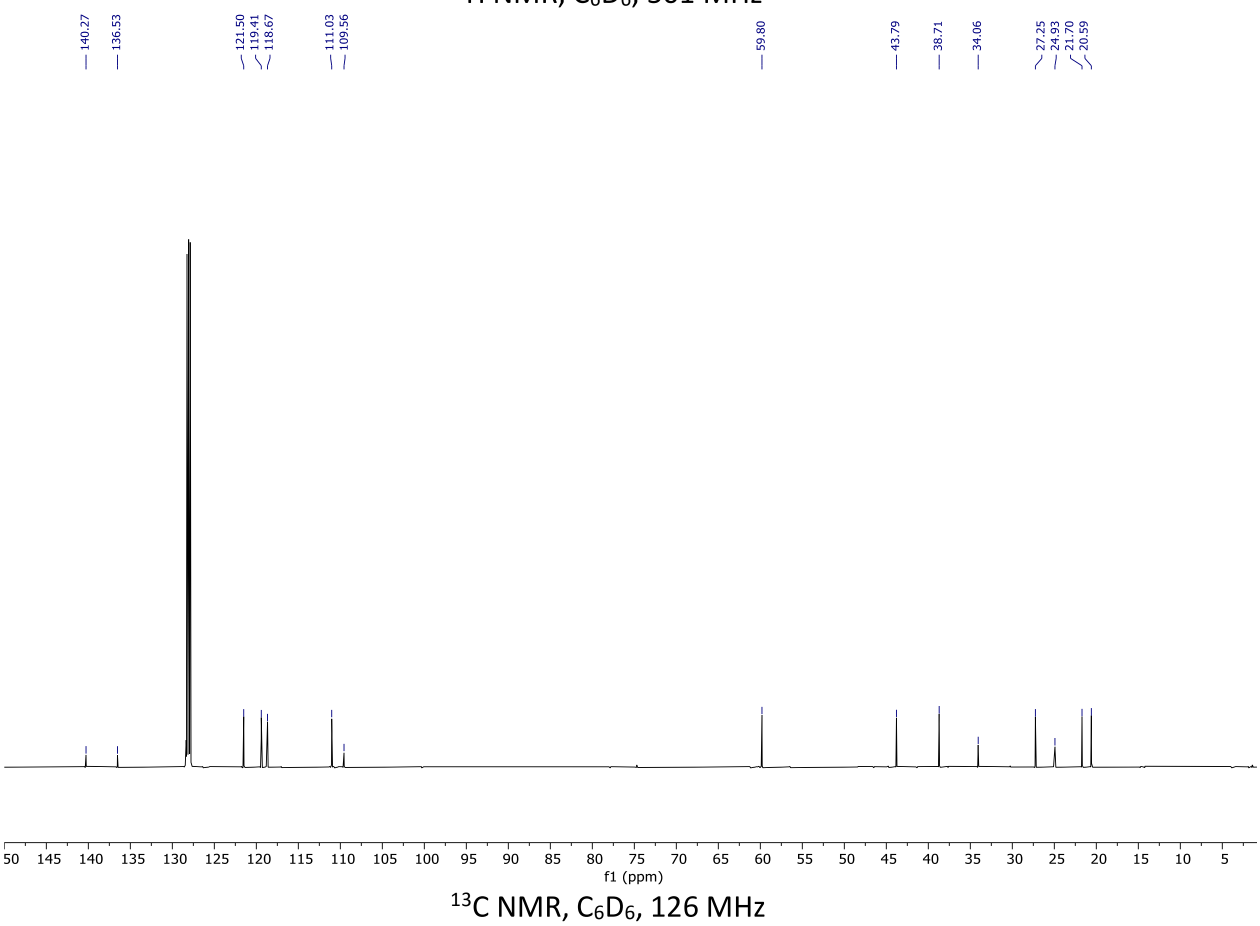
^{1}H NMR, C_6D_6, 501 MHz



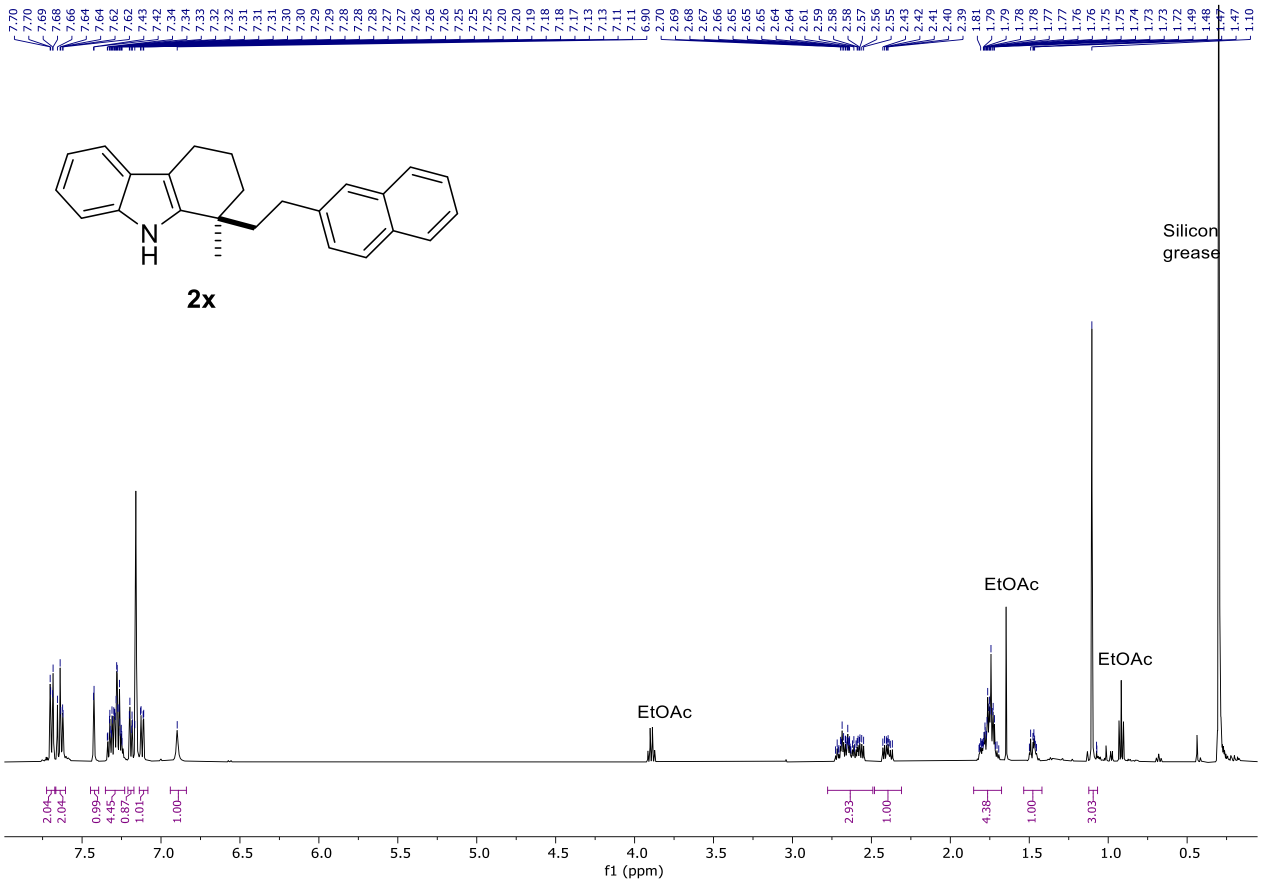
^{13}C NMR, C_6D_6, 126 MHz



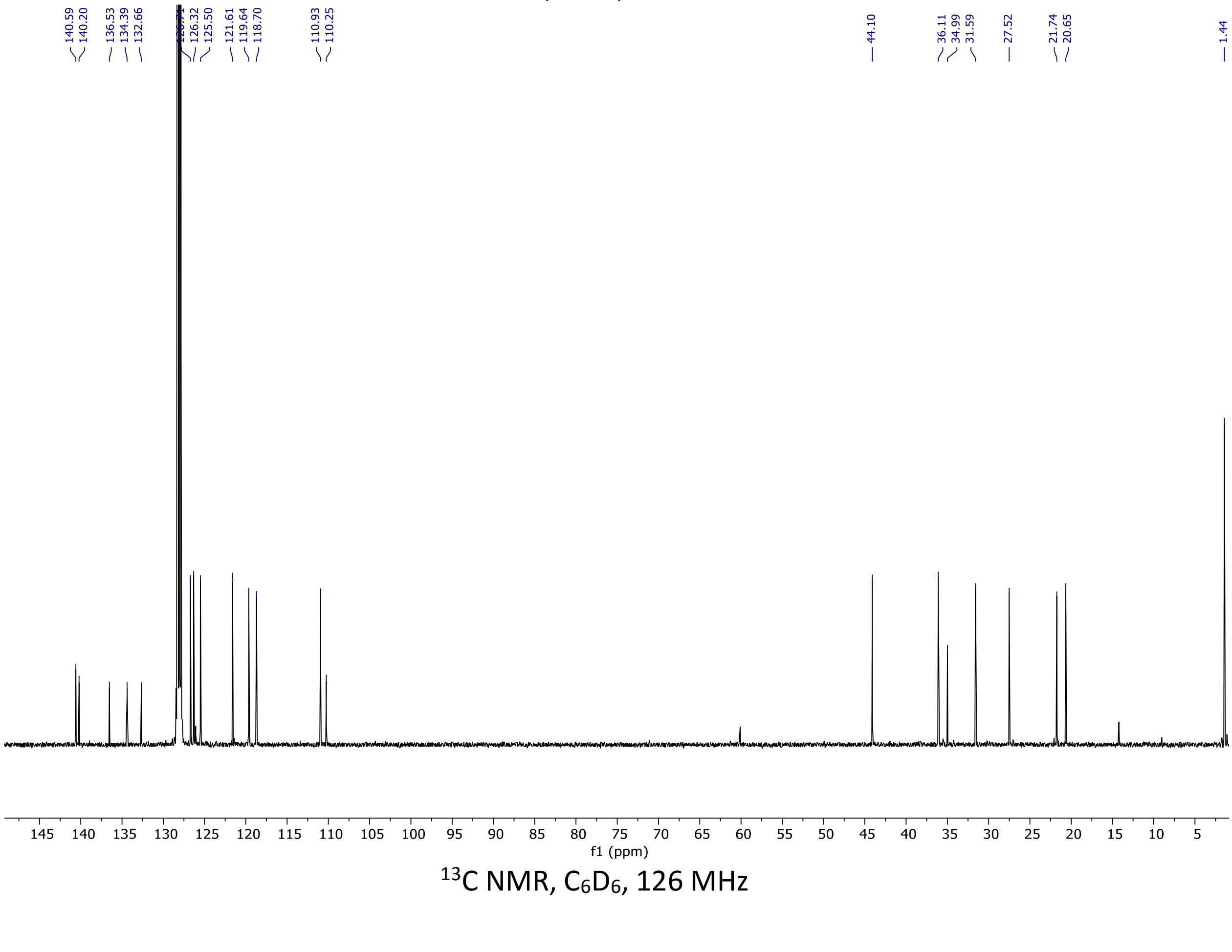
^{1}H NMR, C_6D_6, 501 MHz



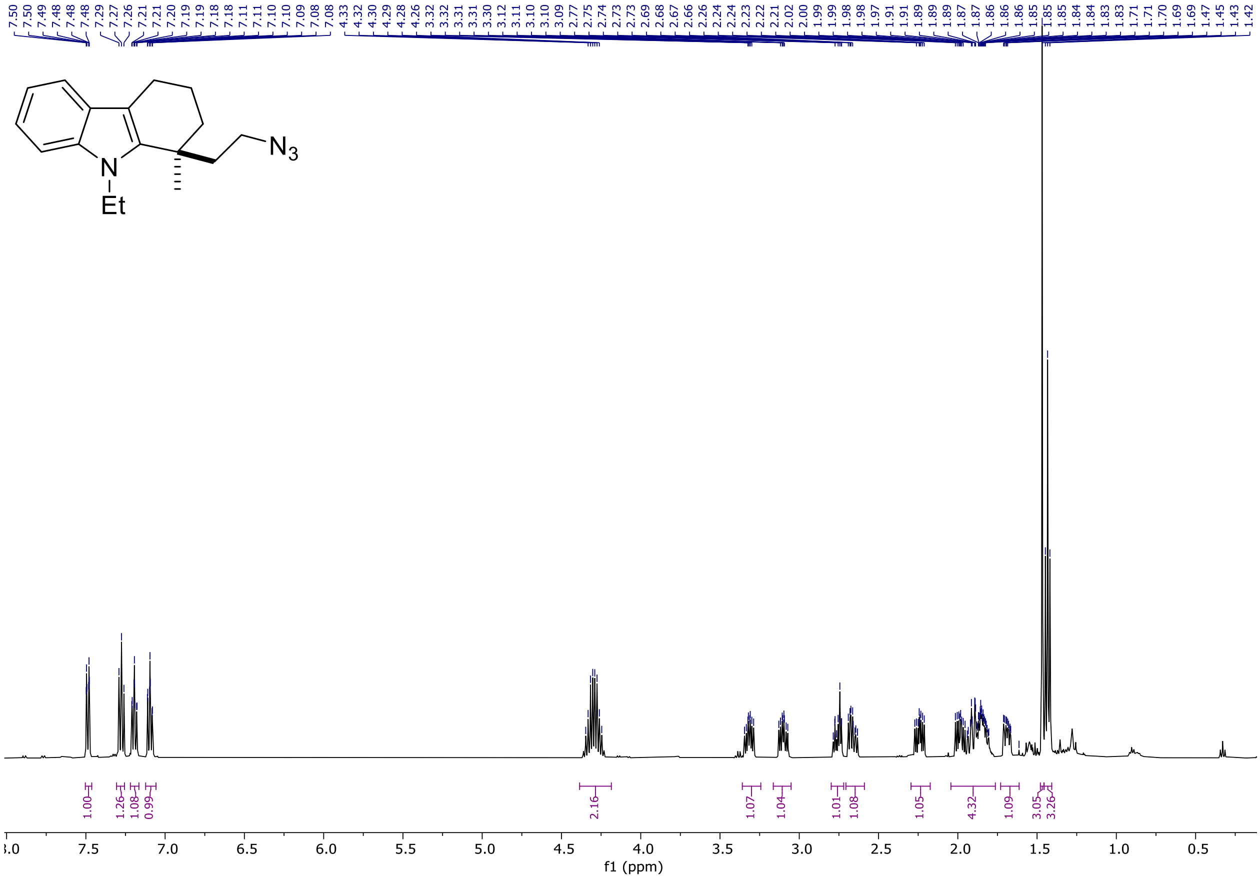
^{13}C NMR, C_6D_6, 126 MHz



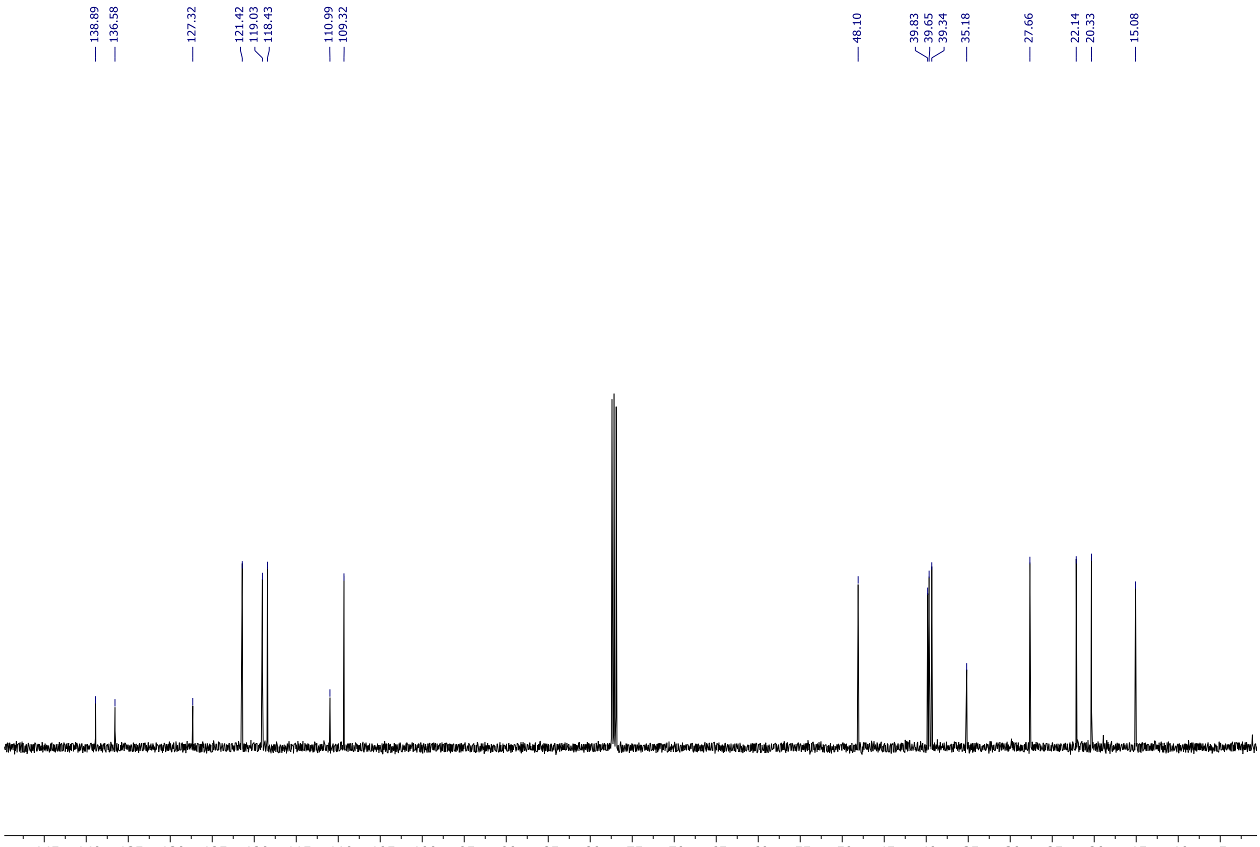
^{1}H NMR, C_6D_6, 501 MHz



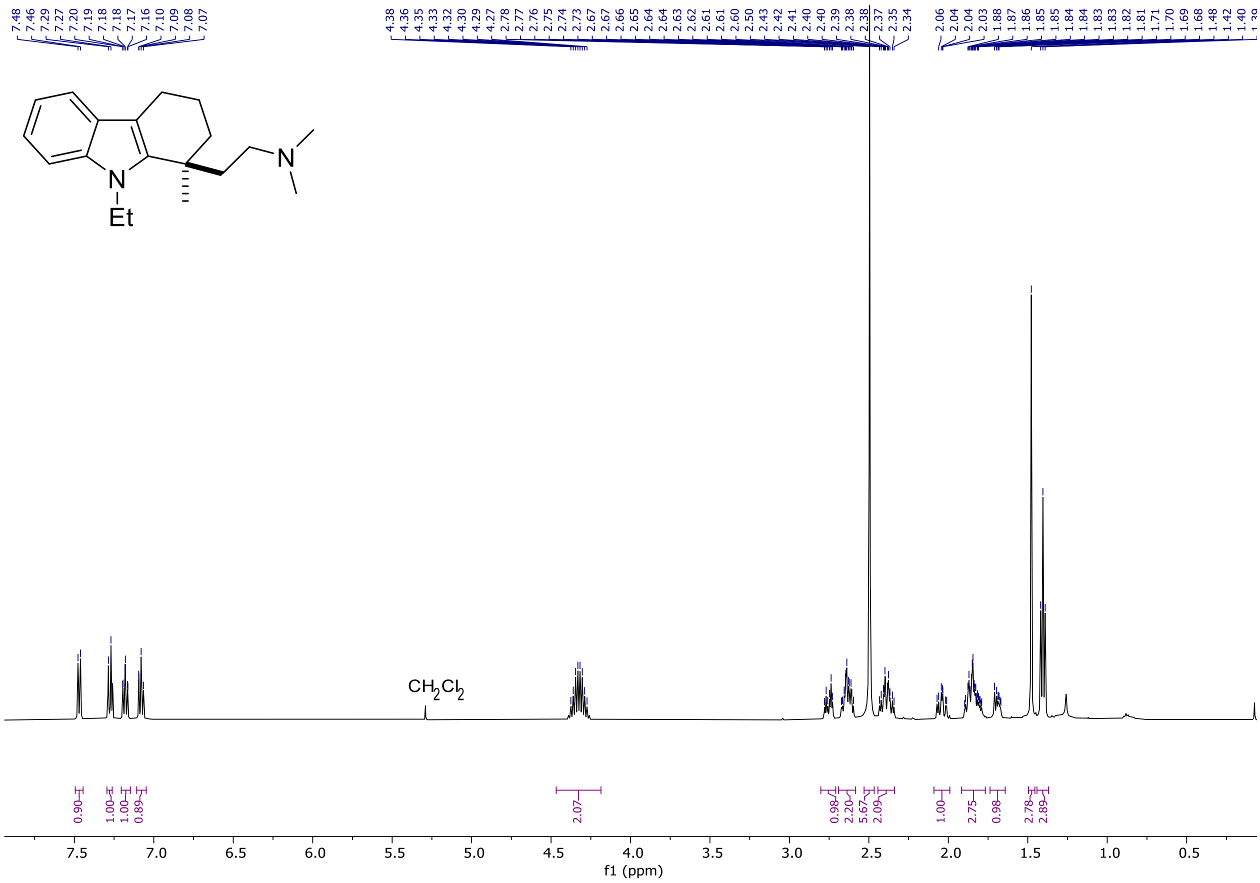
^{13}C NMR, C_6D_6, 126 MHz



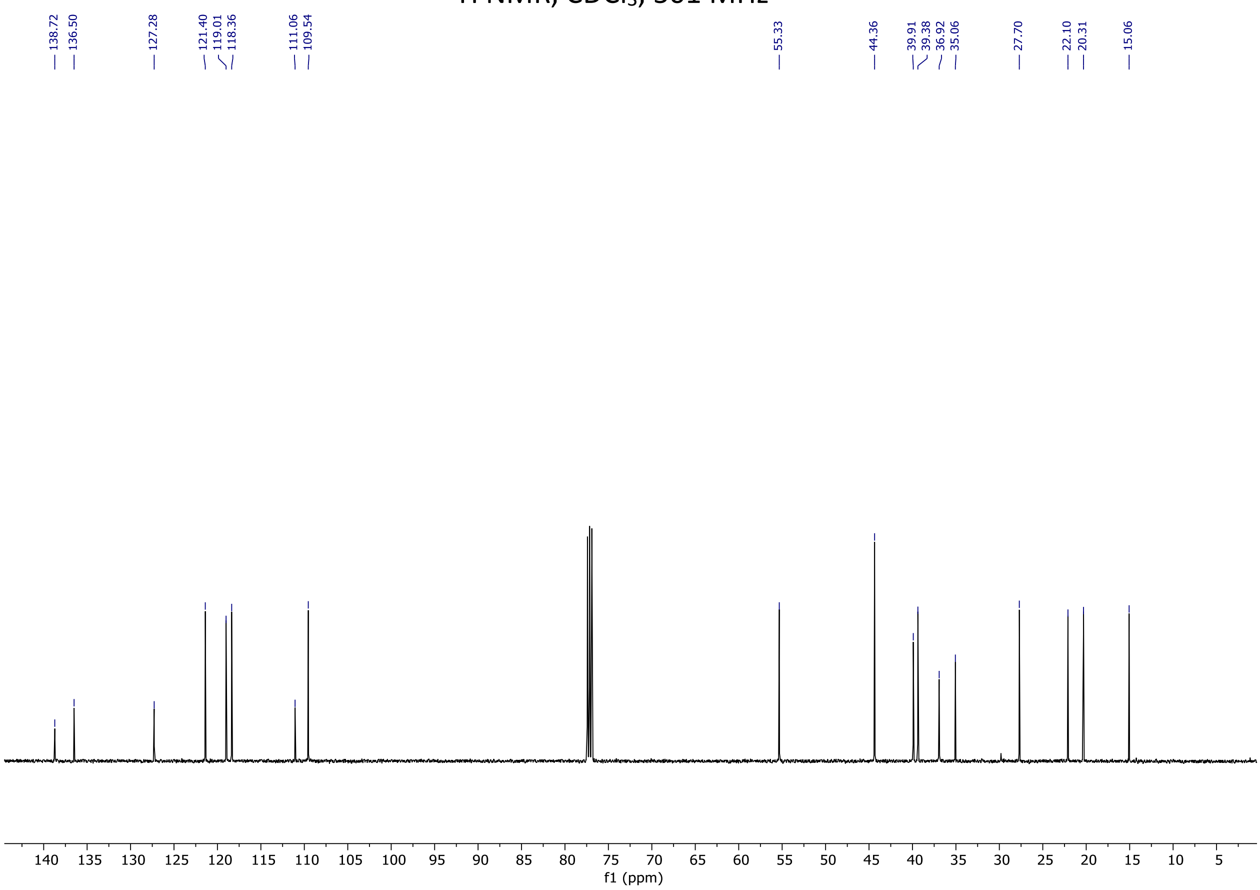
^{1}H NMR, $CDCl_3$, 501 MHz



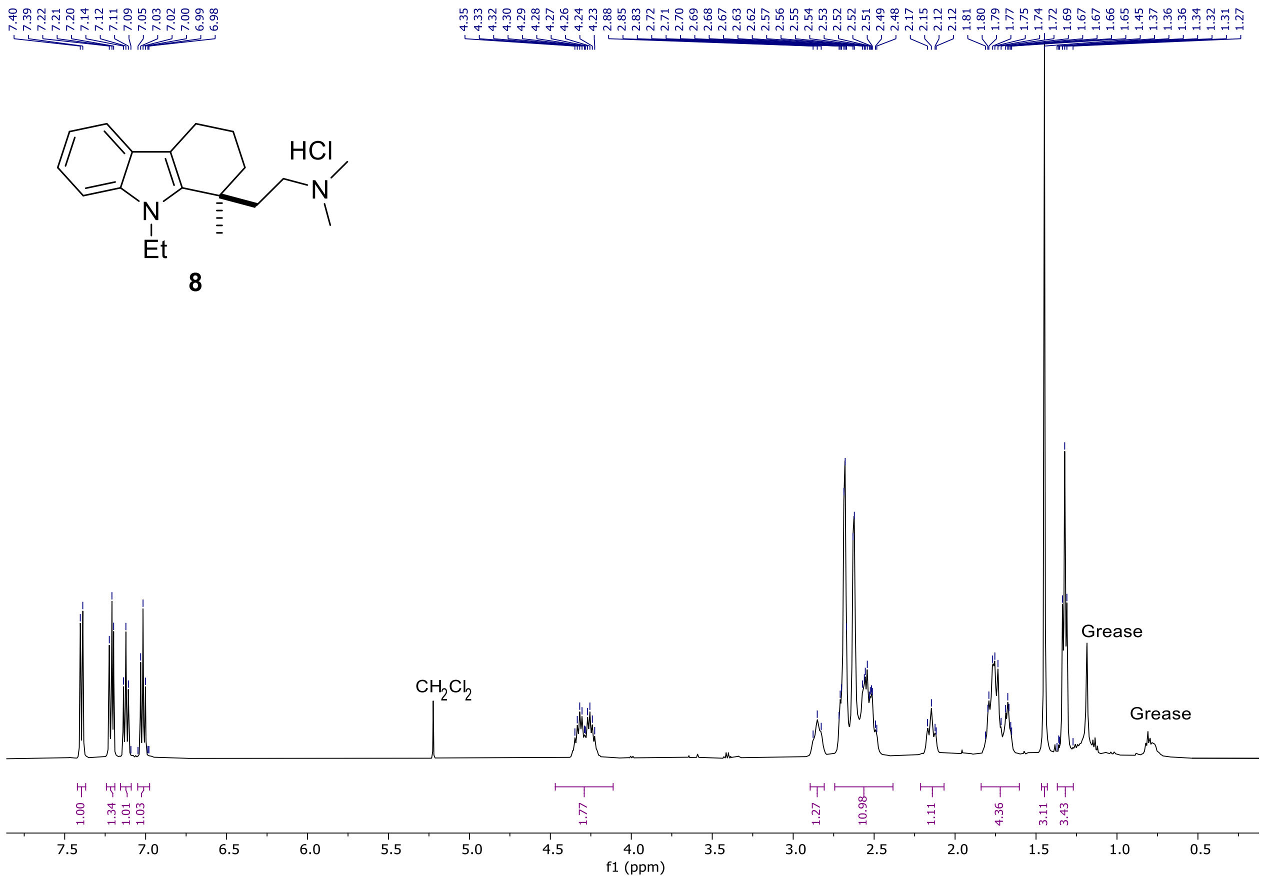
^{13}C NMR, $CDCl_3$, 126 MHz



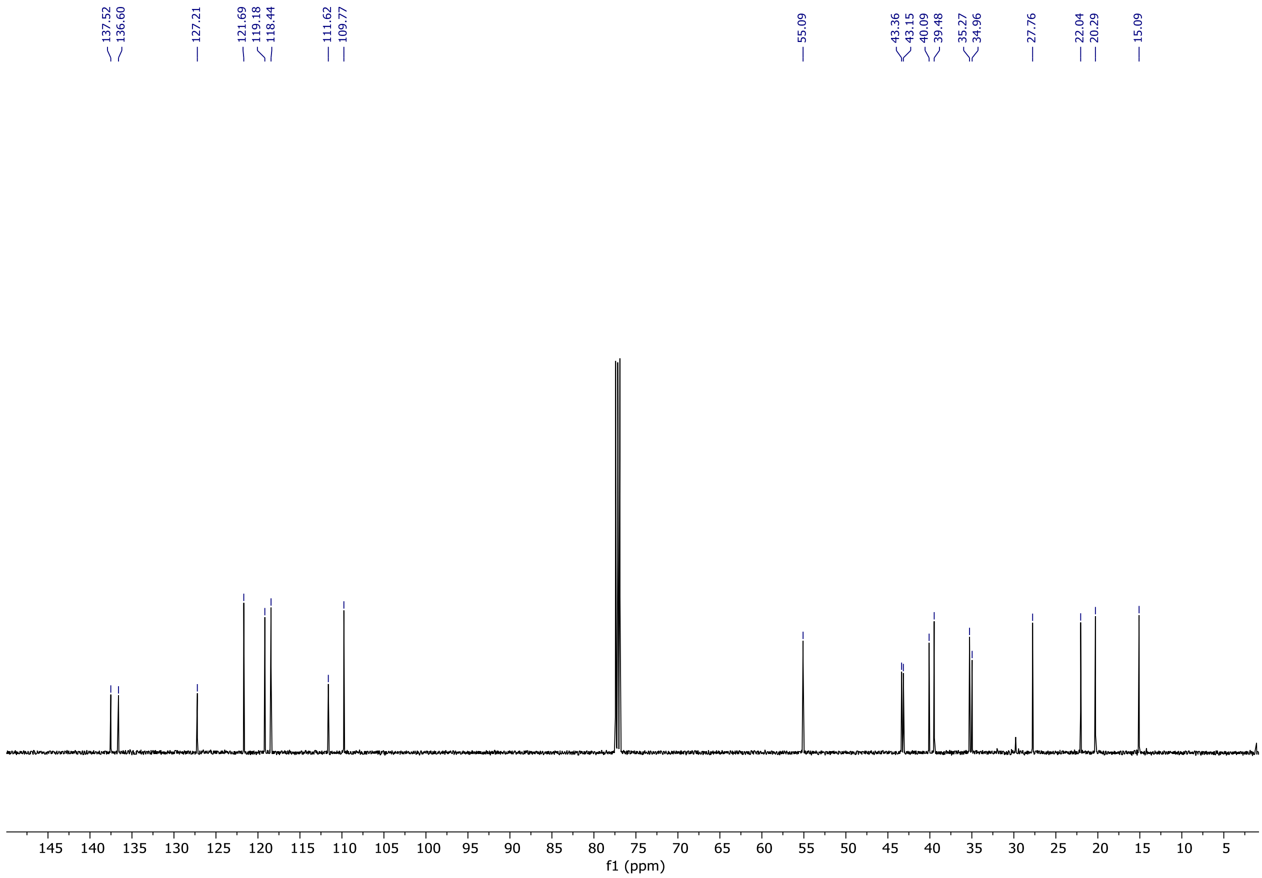
^{1}H NMR, $CDCl_3$, 501 MHz



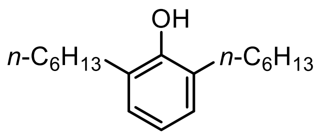
^{13}C NMR, $CDCl_3$, 126 MHz

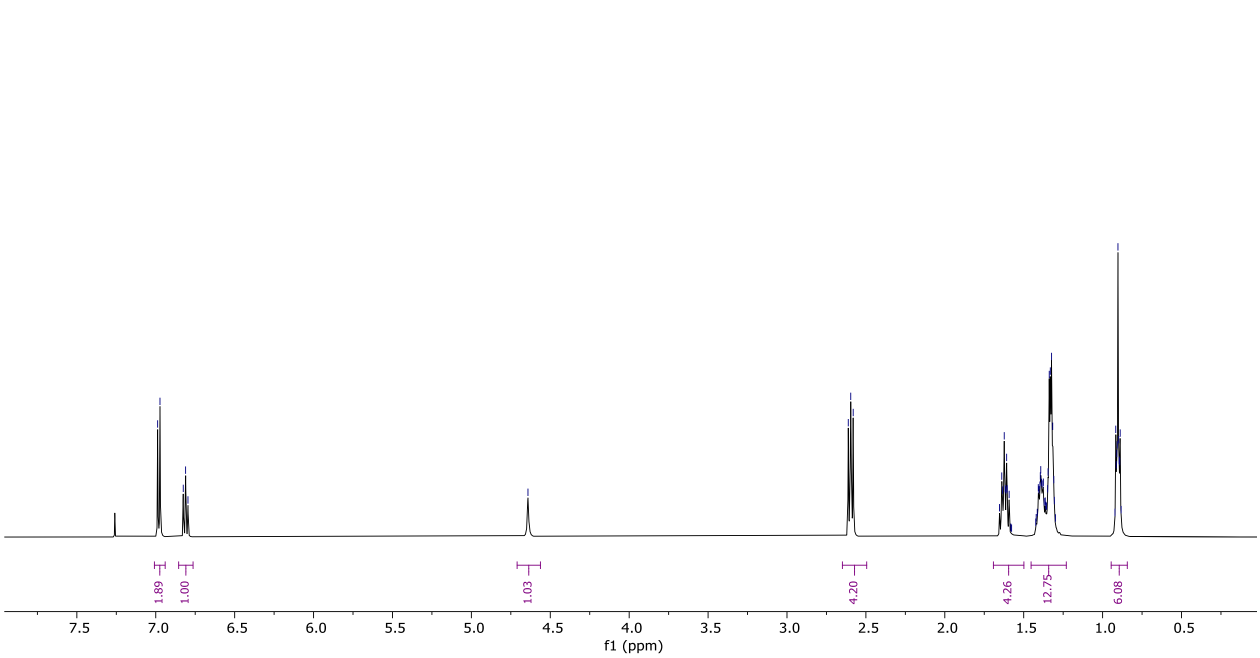


^{1}H NMR, $CDCl_3$, 501 MHz

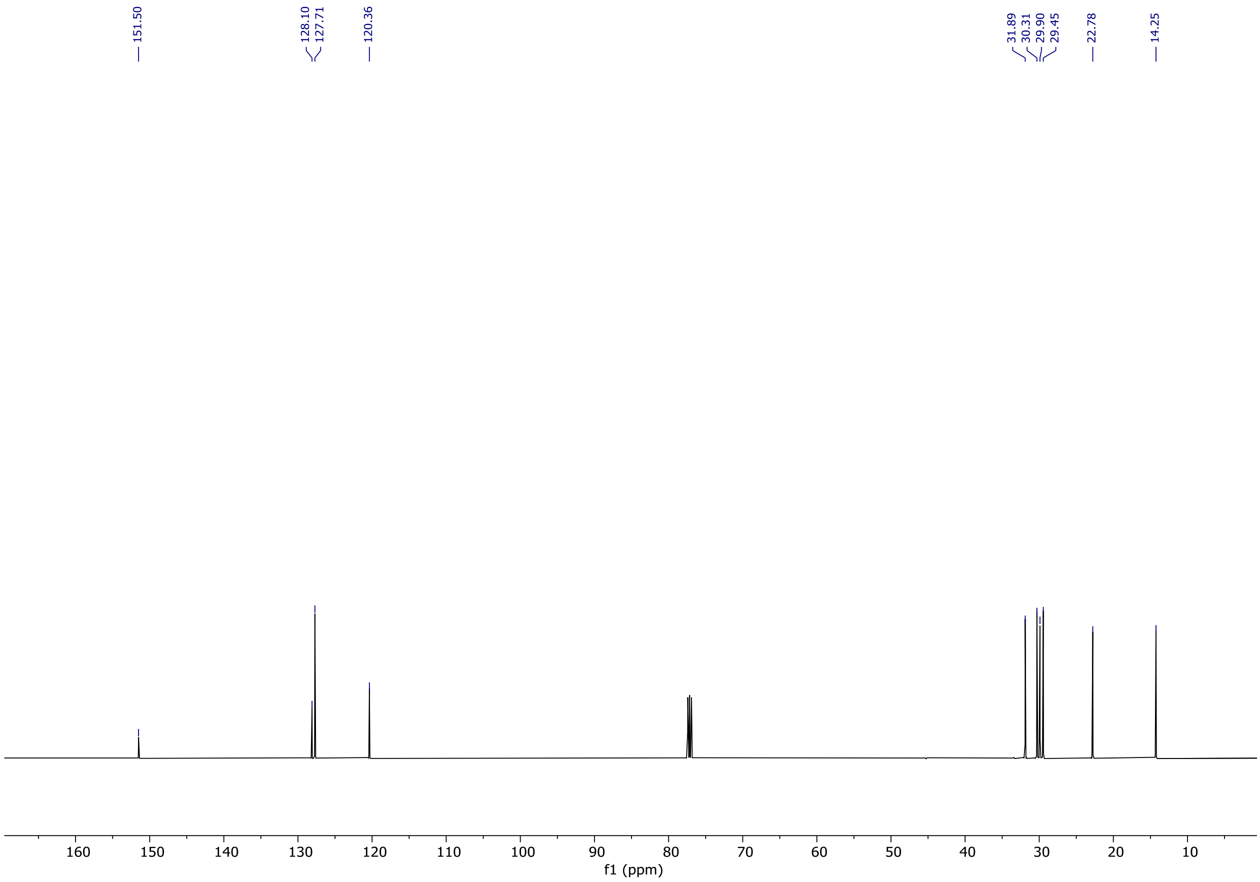


^{13}C NMR, $CDCl_3$, 126 MHz

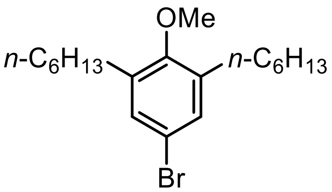


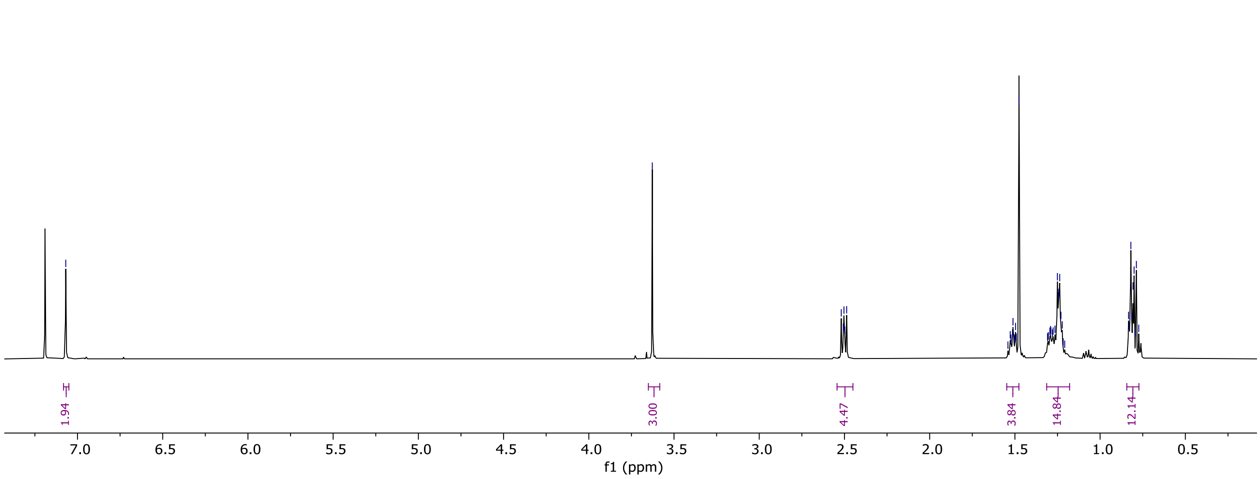


^{1}H NMR, $CDCl_3$, 501 MHz

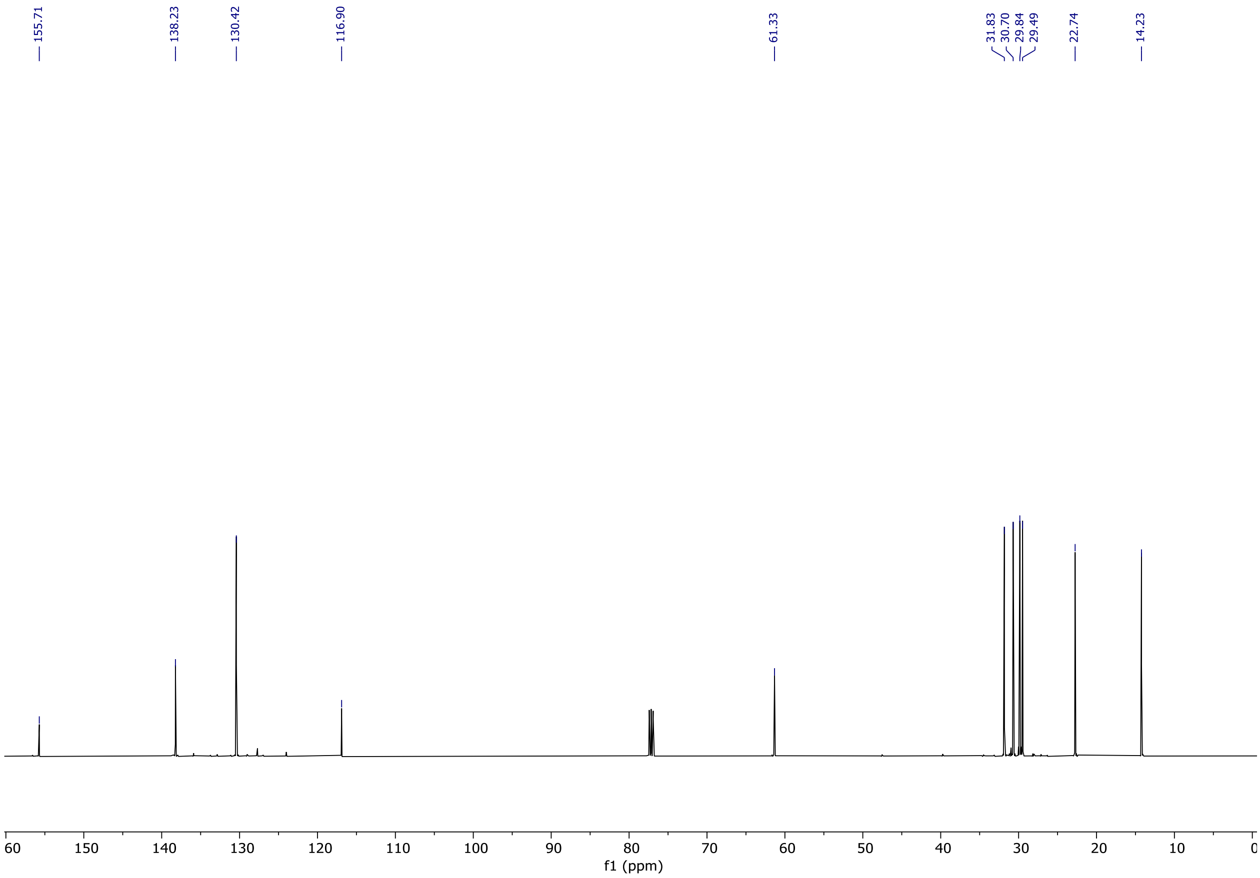


^{13}C NMR, $CDCl_3$, 126 MHz

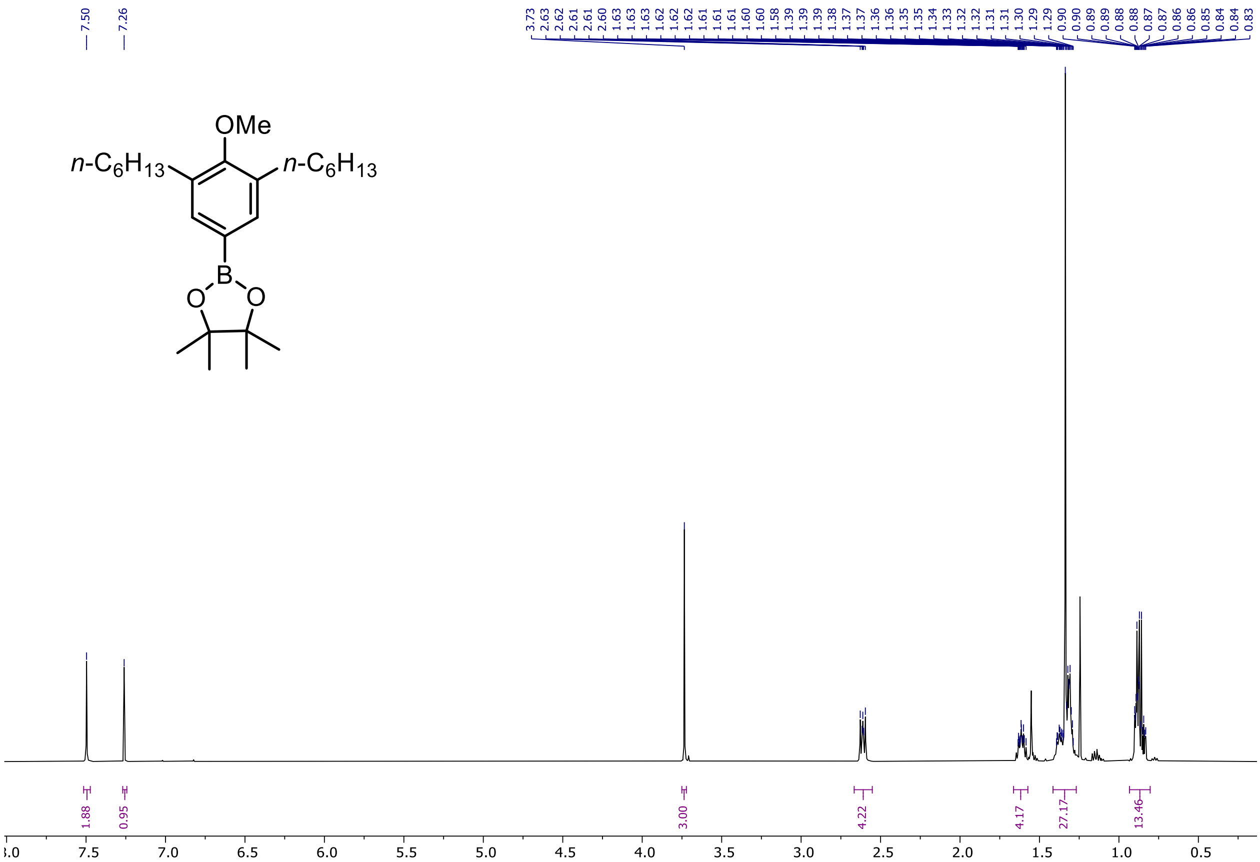




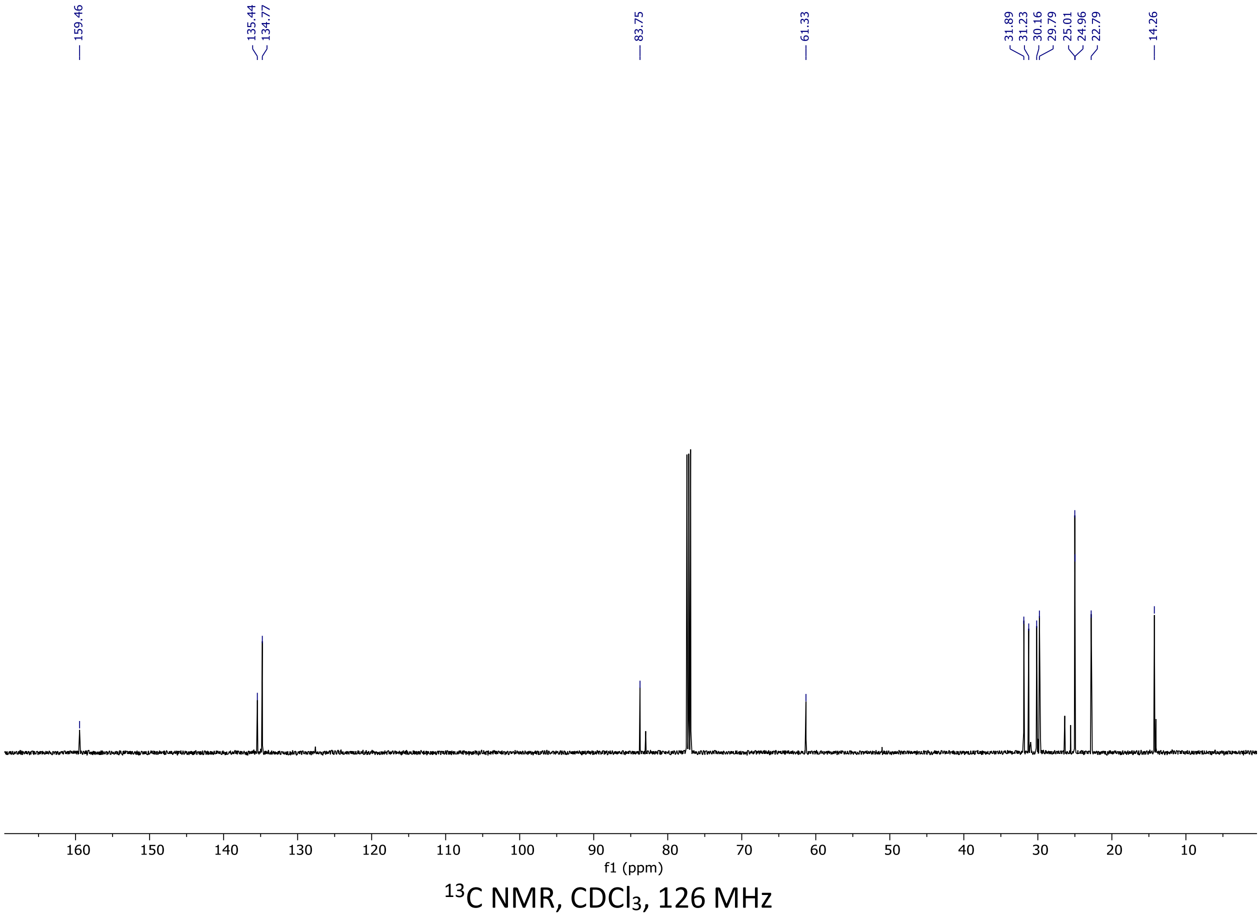
^1H NMR, $CDCl_3$, 501 MHz



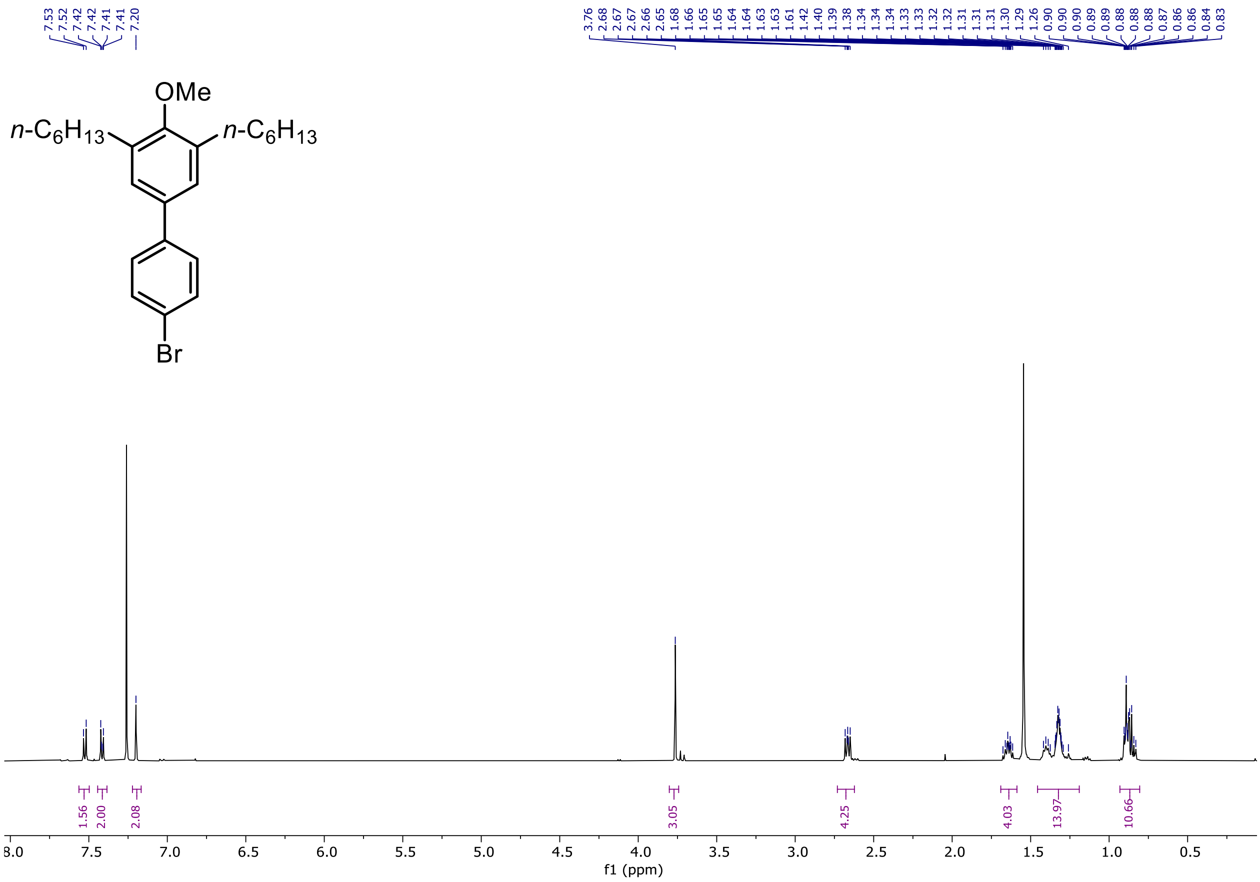
^{13}C NMR, $CDCl_3$, 126 MHz



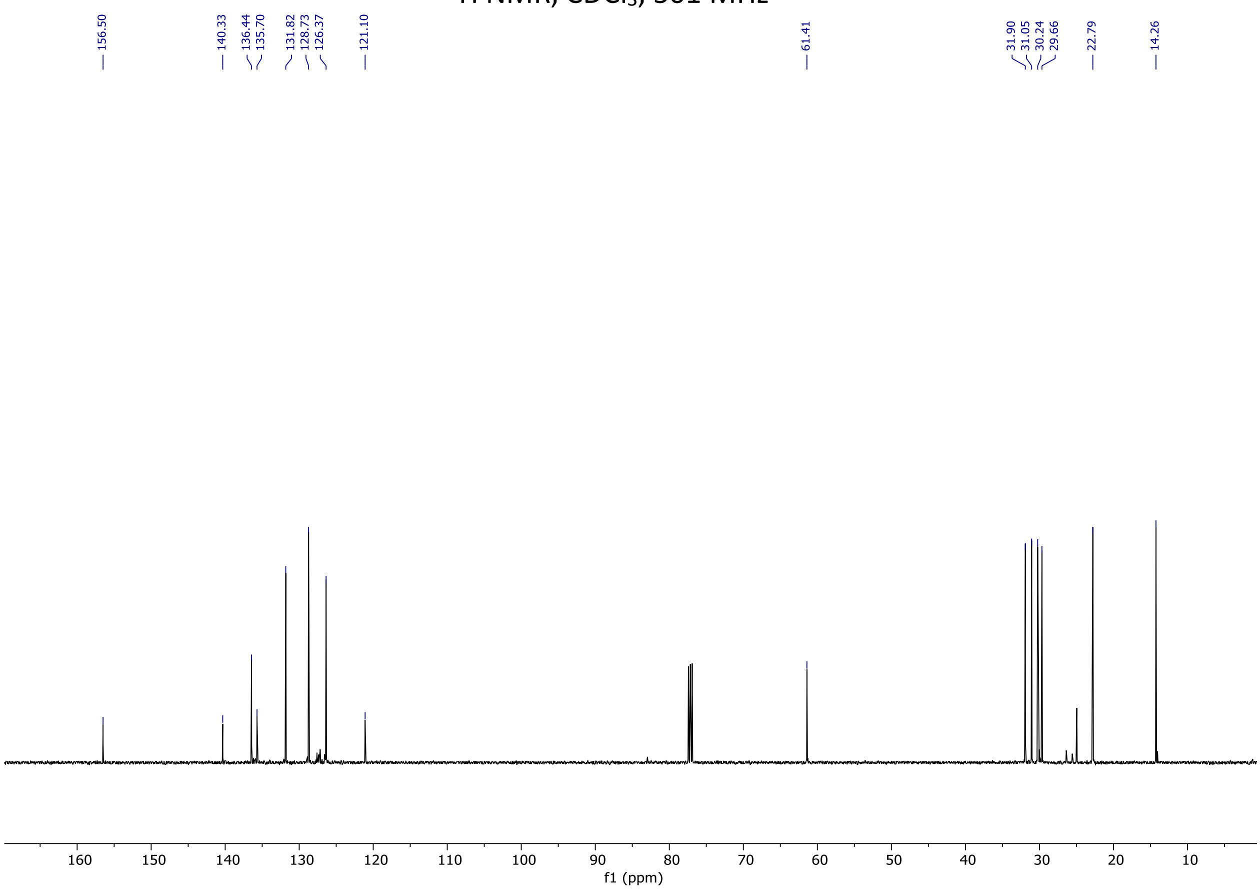
^{1}H NMR, CDCl$_3$, 501 MHz



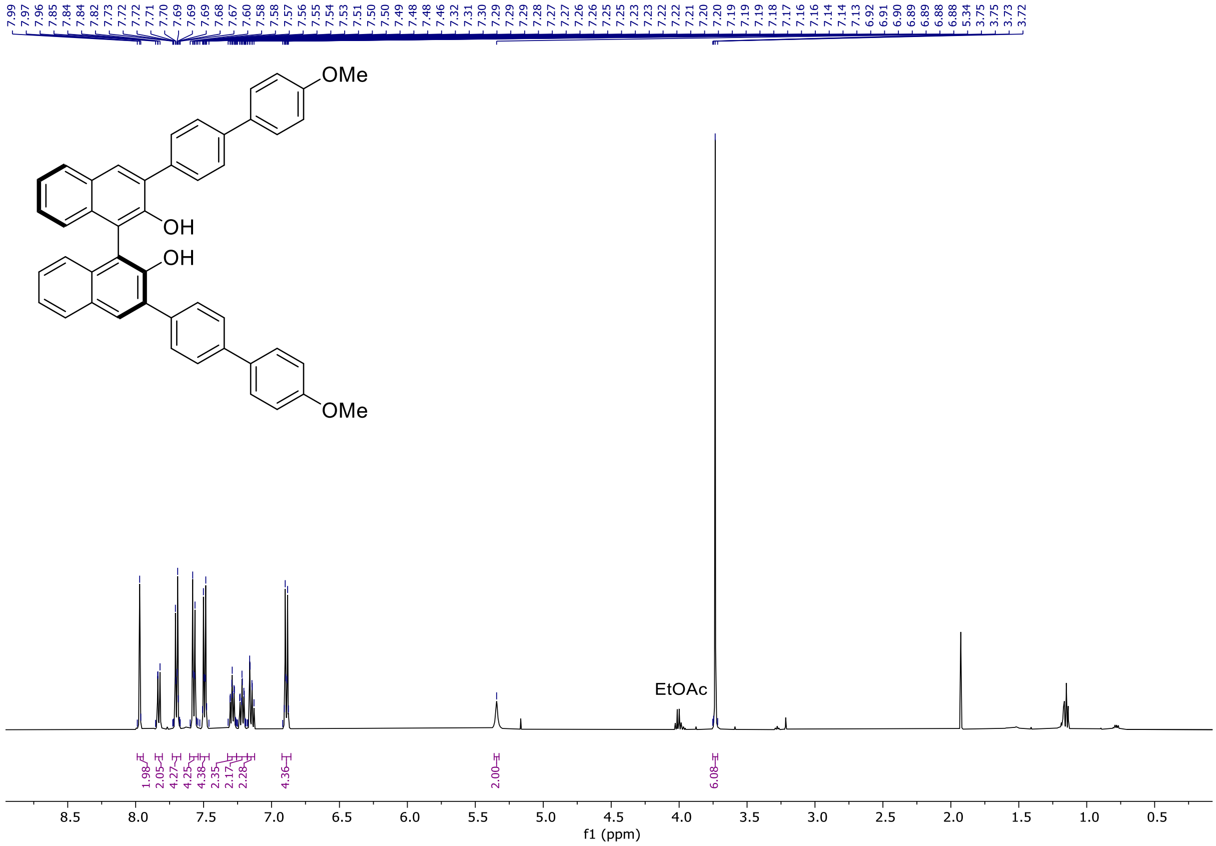
^{13}C NMR, CDCl$_3$, 126 MHz



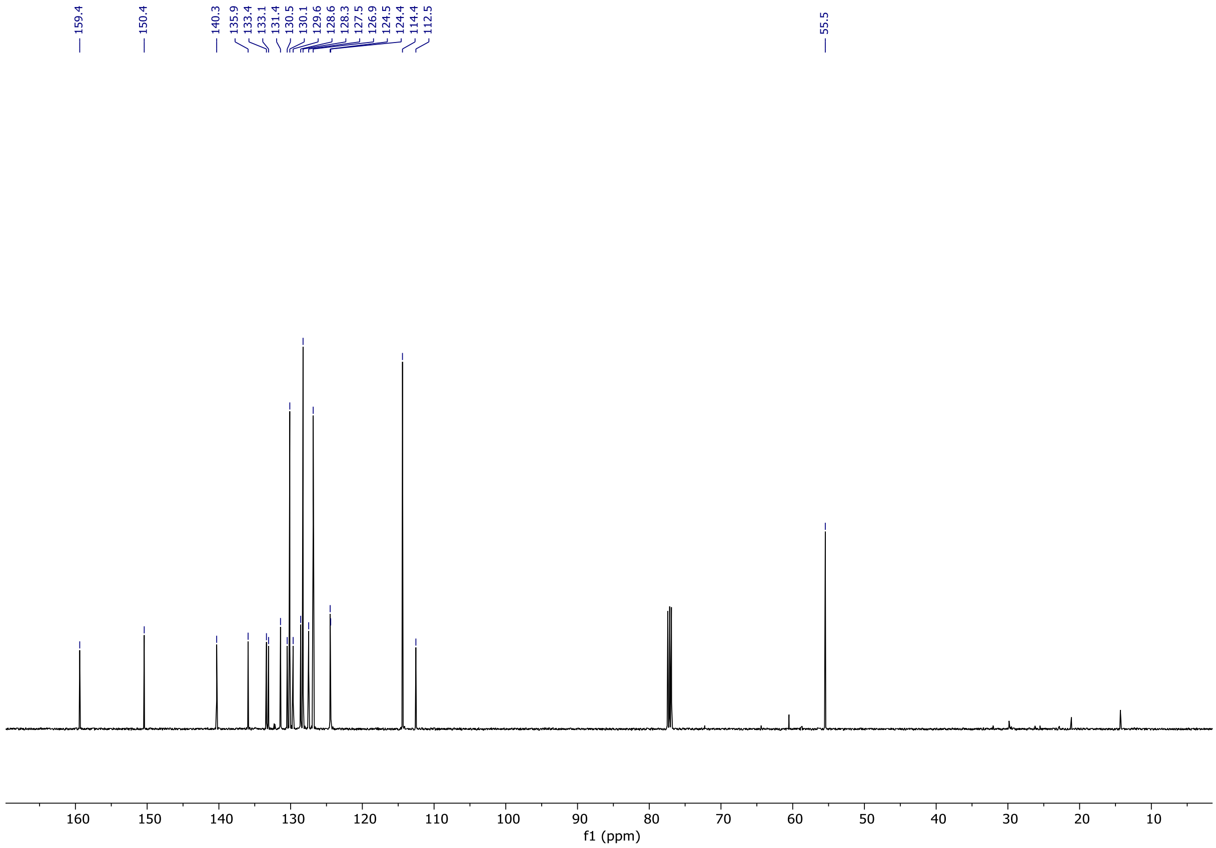
^{1}H NMR, $CDCl_3$, 501 MHz



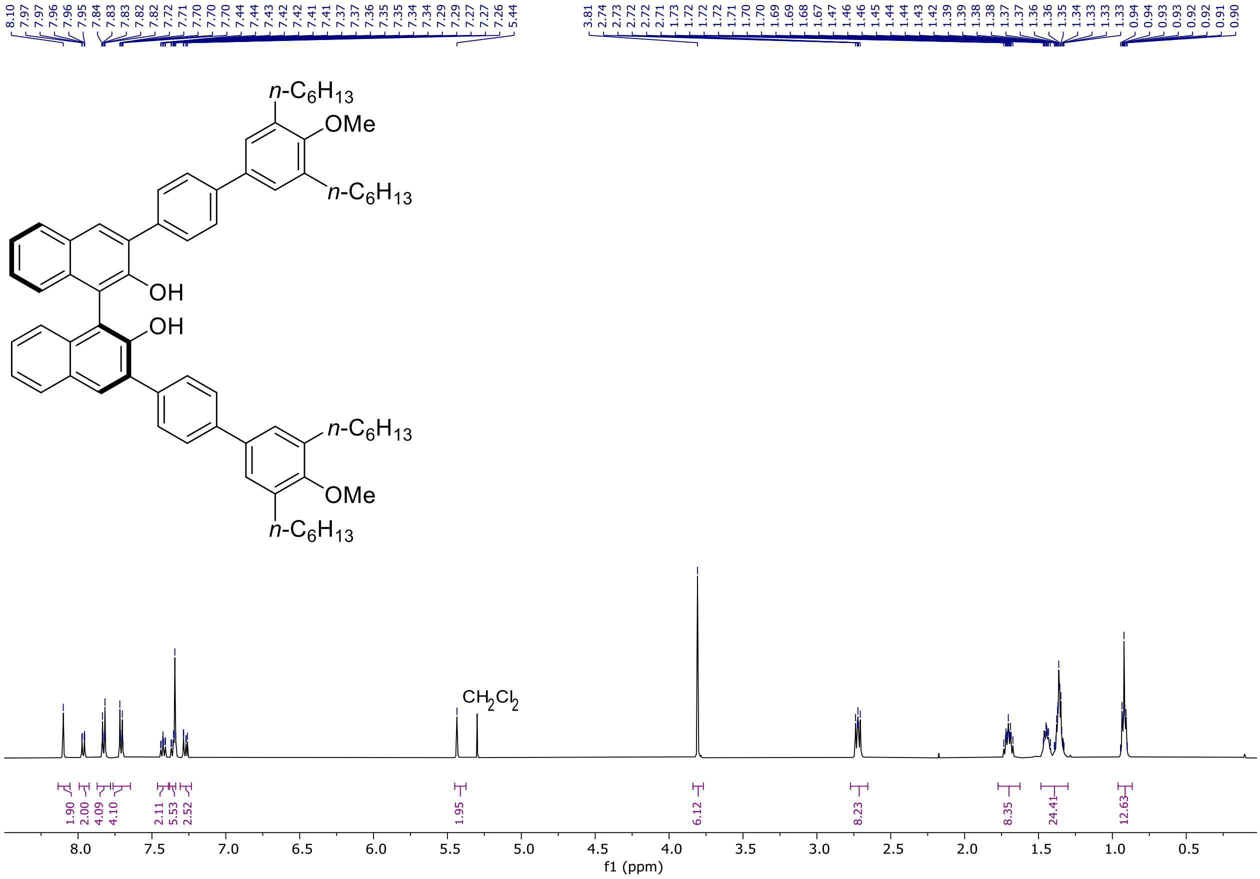
^{13}C NMR, $CDCl_3$, 126 MHz



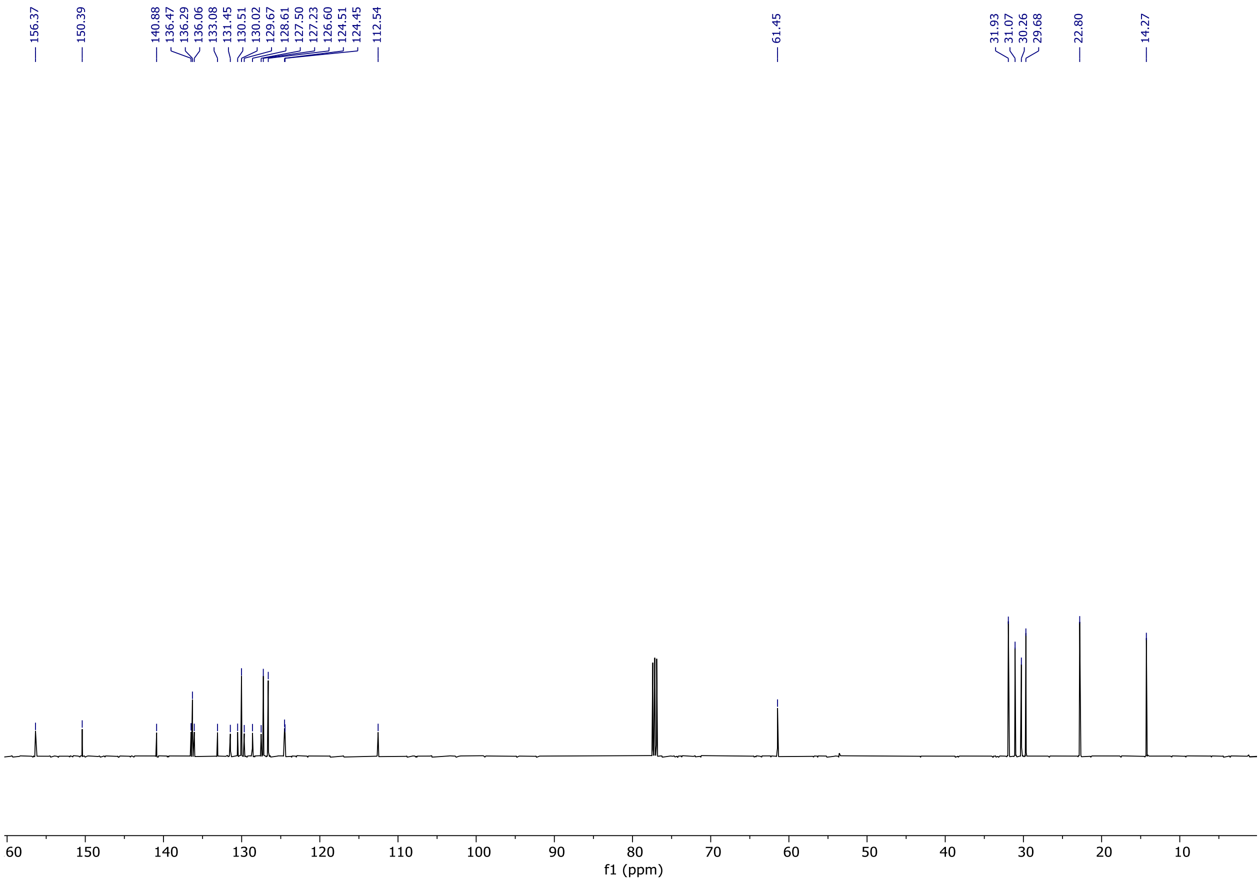
^{1}H NMR, $CDCl_3$, 501 MHz



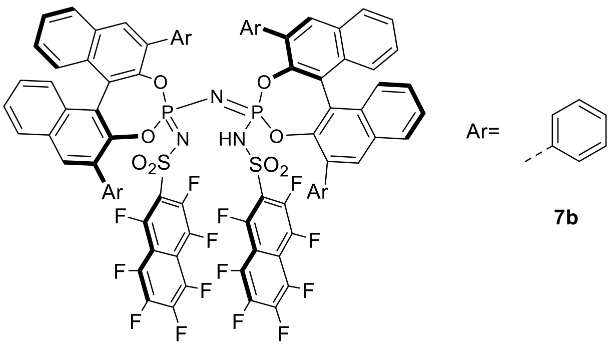
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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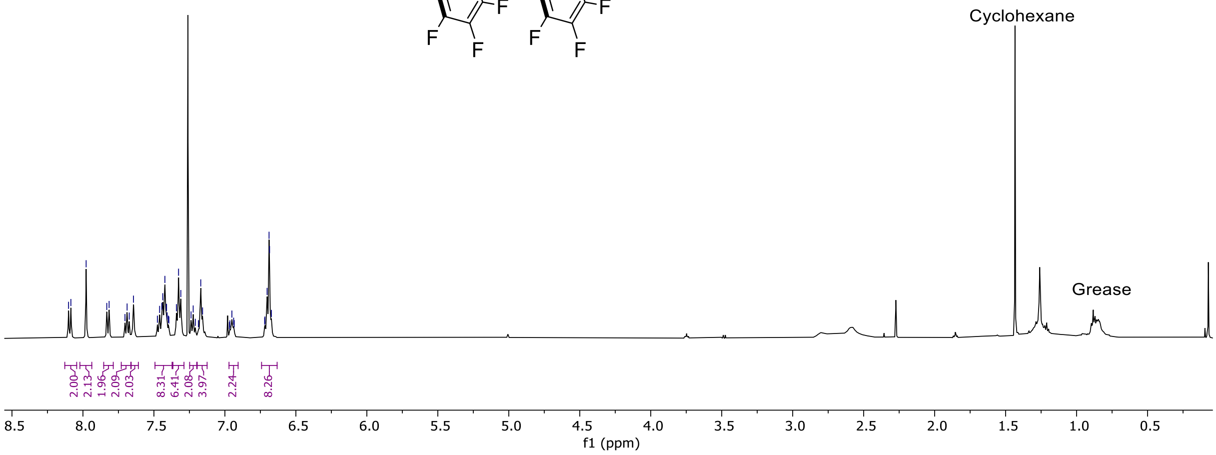
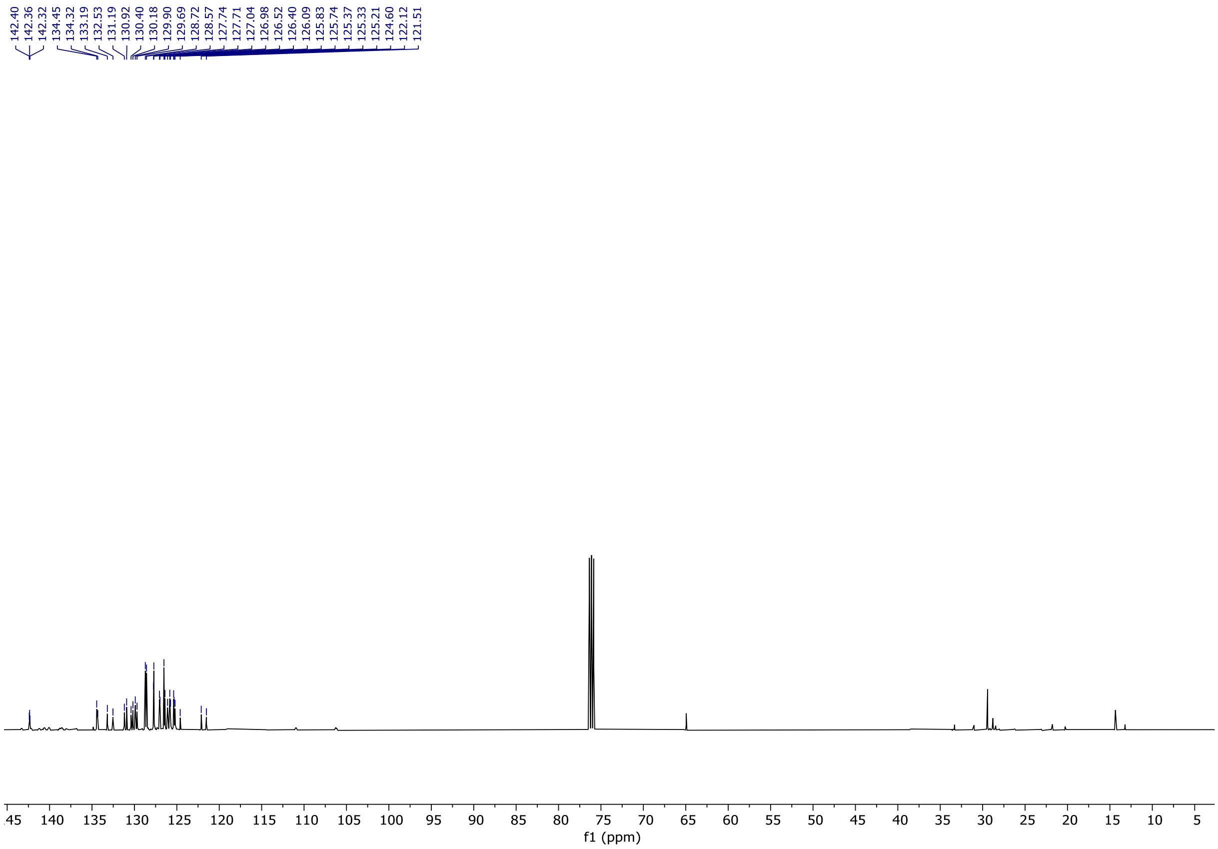
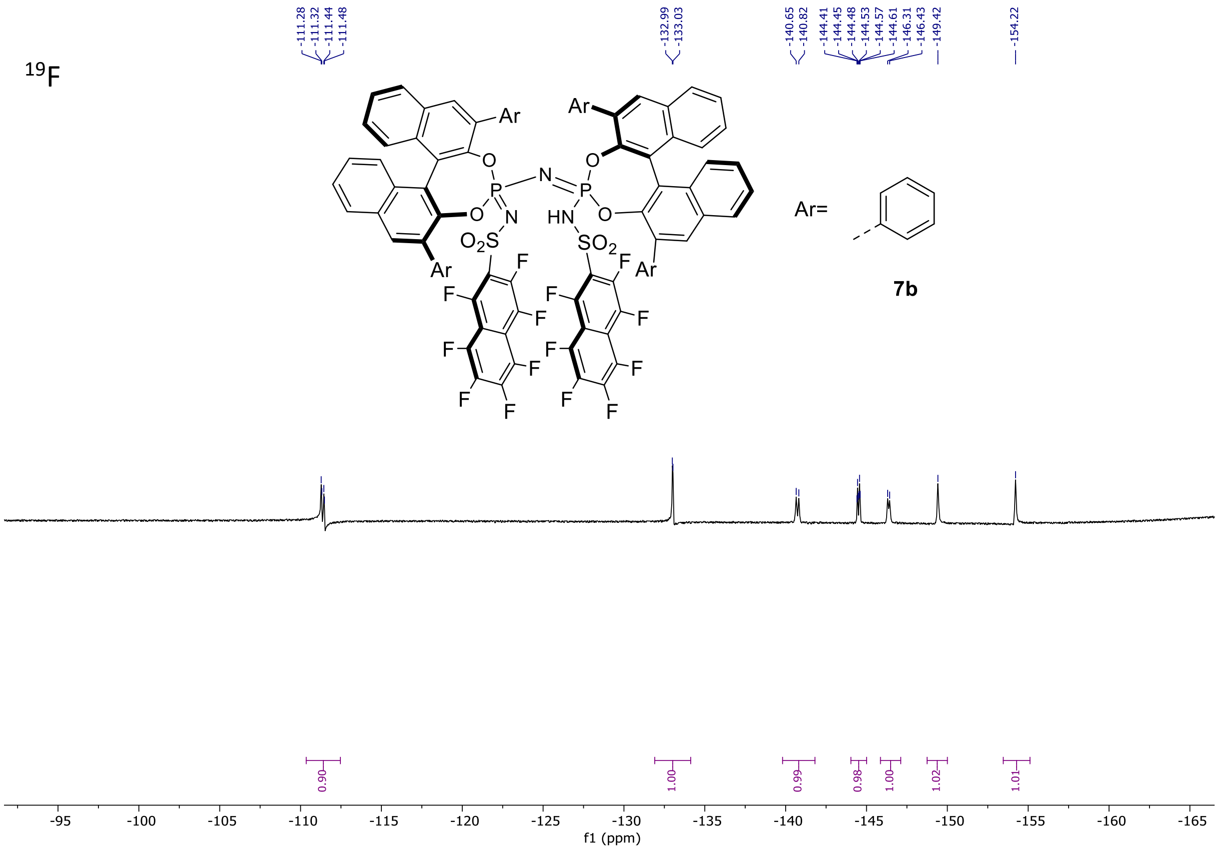


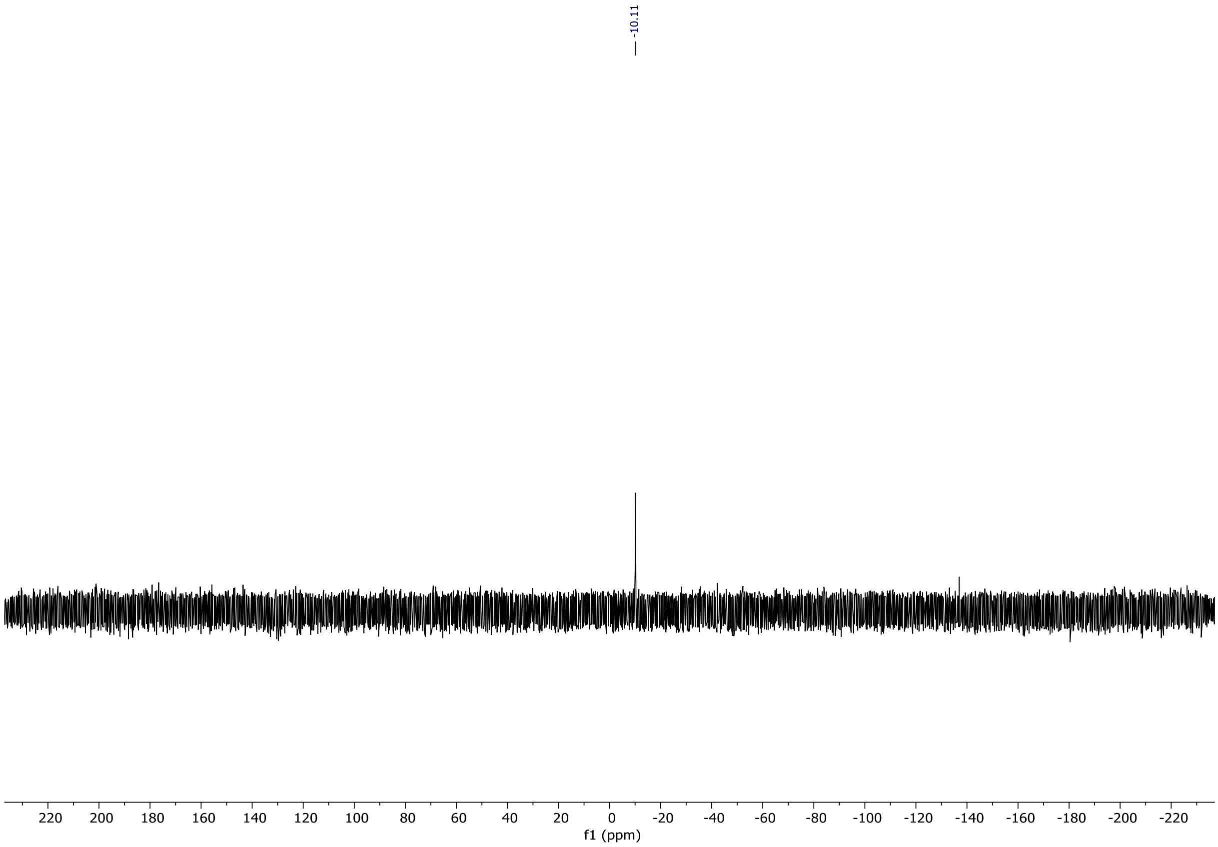
^{1}H NMR, $CDCl_3$, 501 MHz



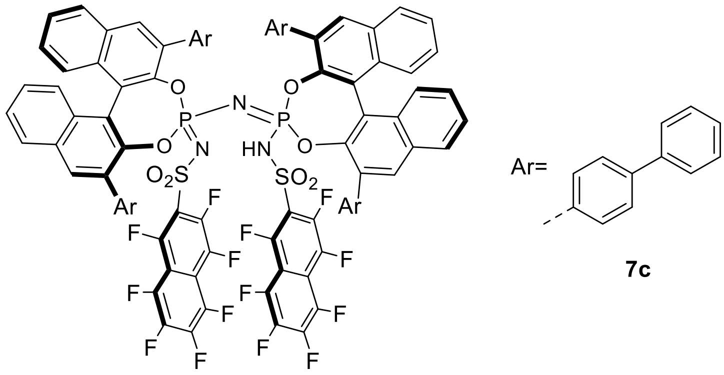
^{13}C NMR, $CDCl_3$, 126 MHz



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



^{31}P NMR, $CDCl_3$, 203 MHz



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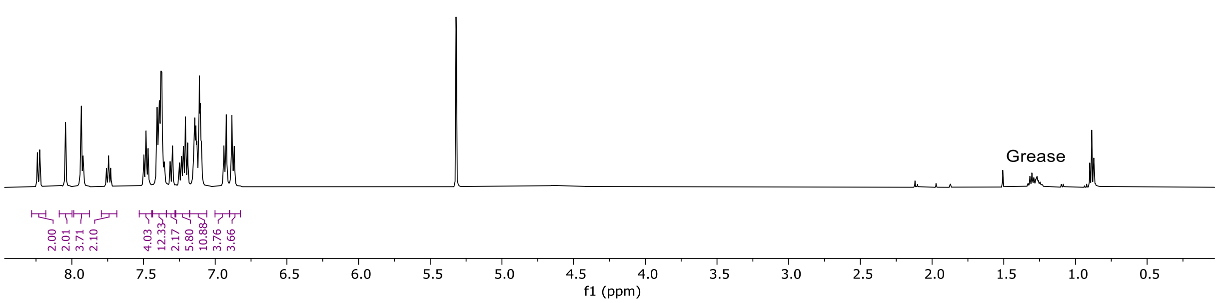
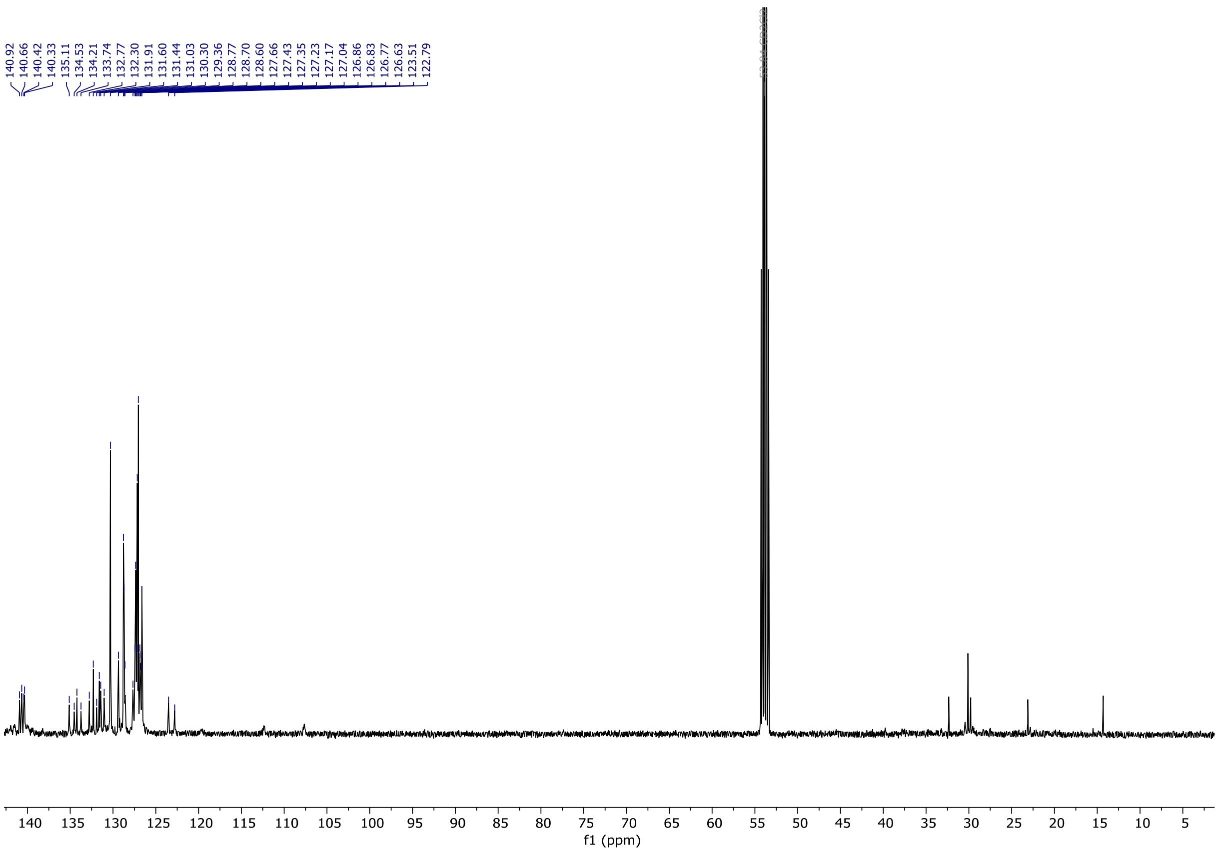
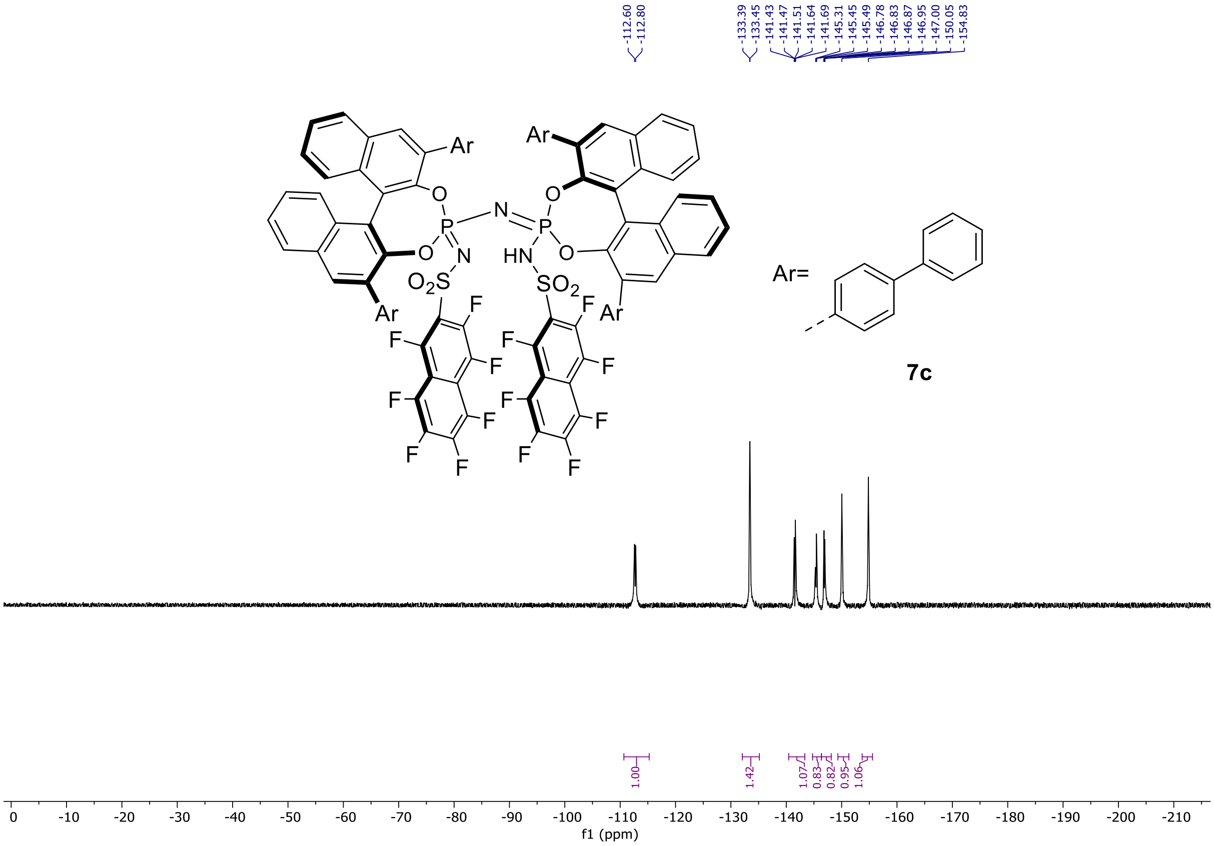


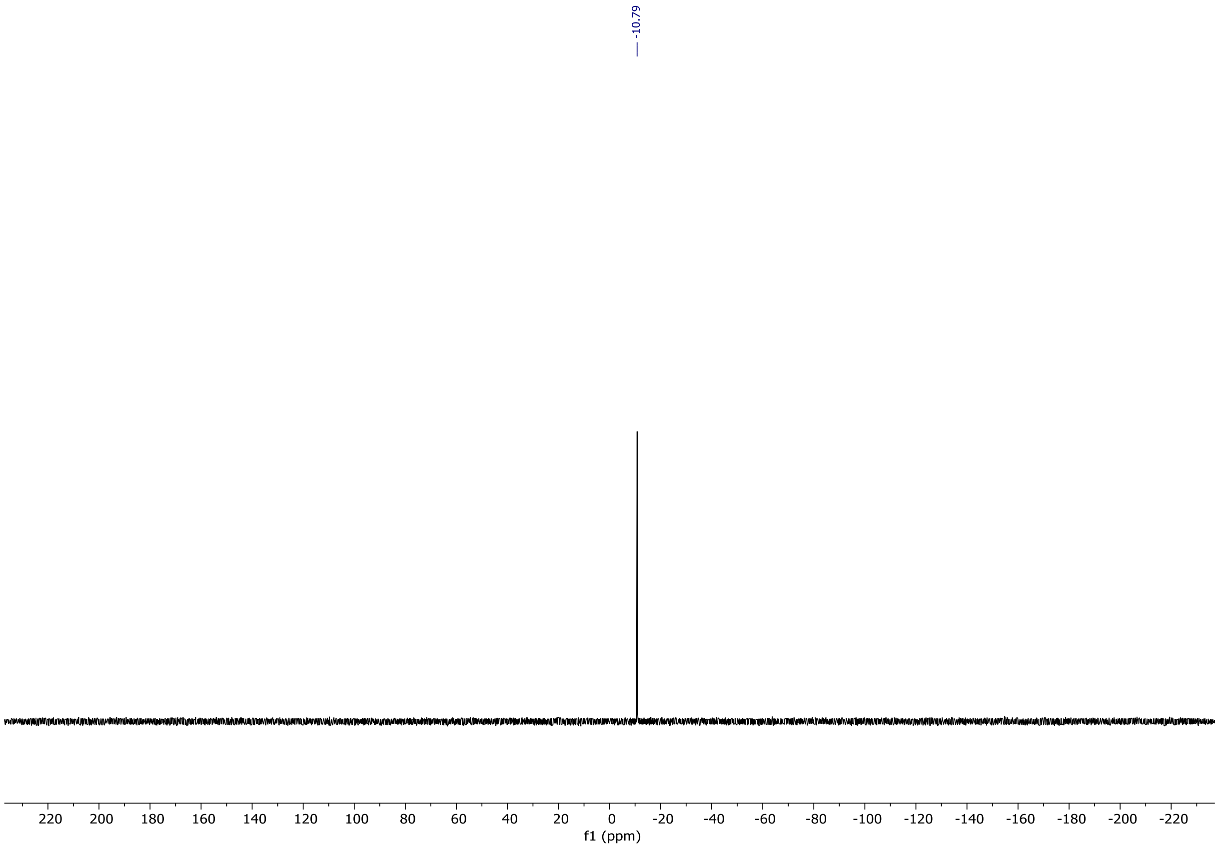
^{1}H NMR, CD_2Cl_2, 501 MHz



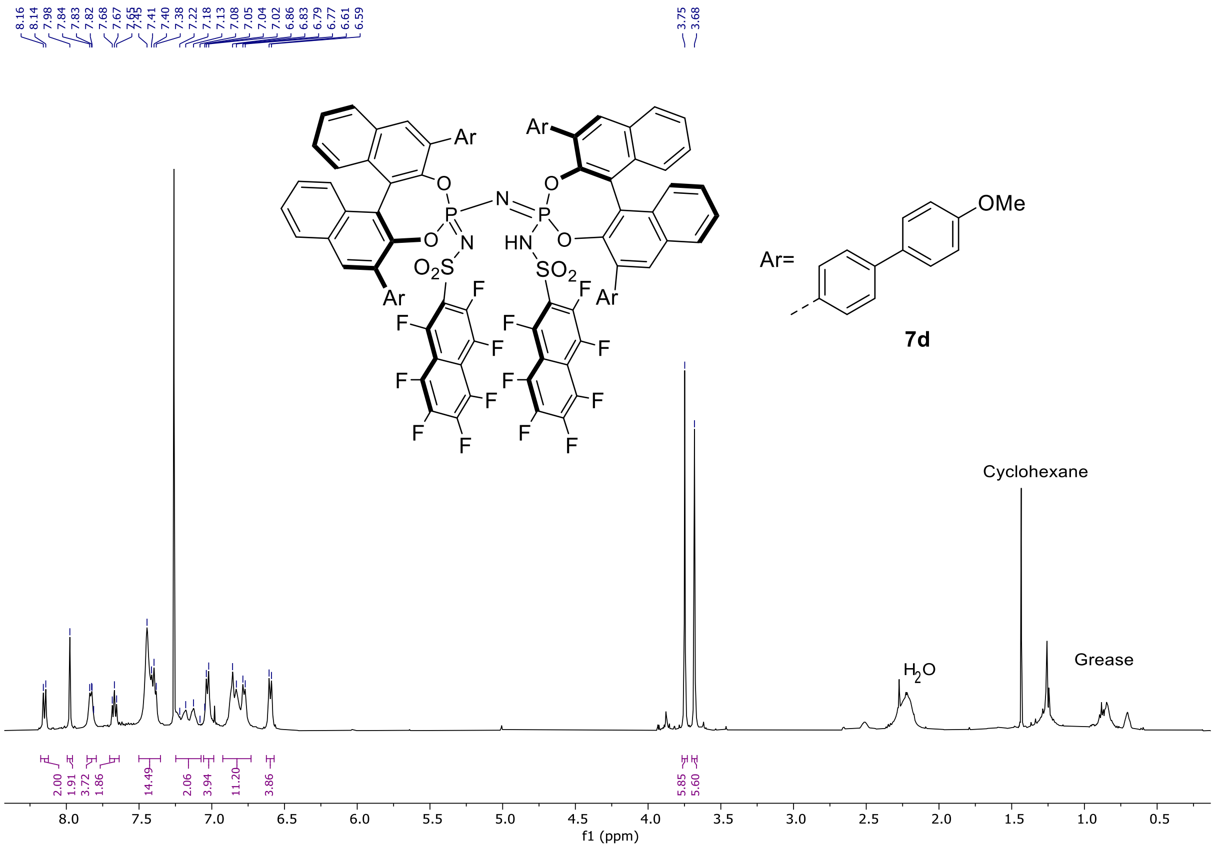
^{13}C NMR, CD_2Cl_2, 126 MHz



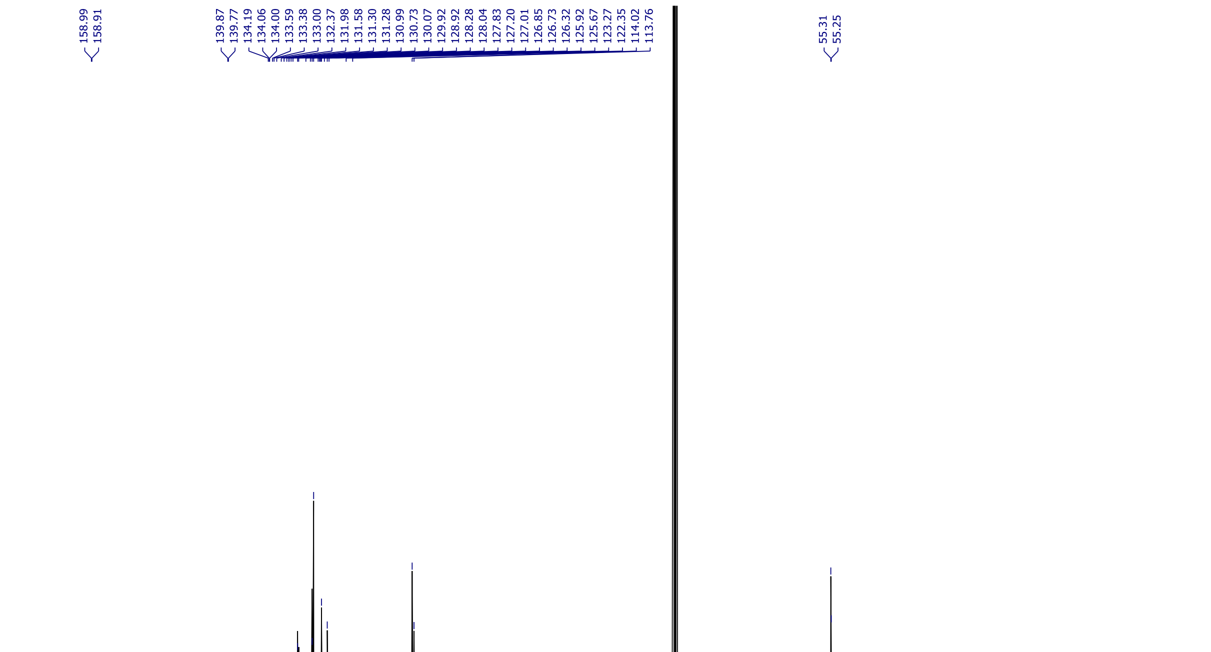
^{19}F NMR, CD_2Cl_2, 471 MHz



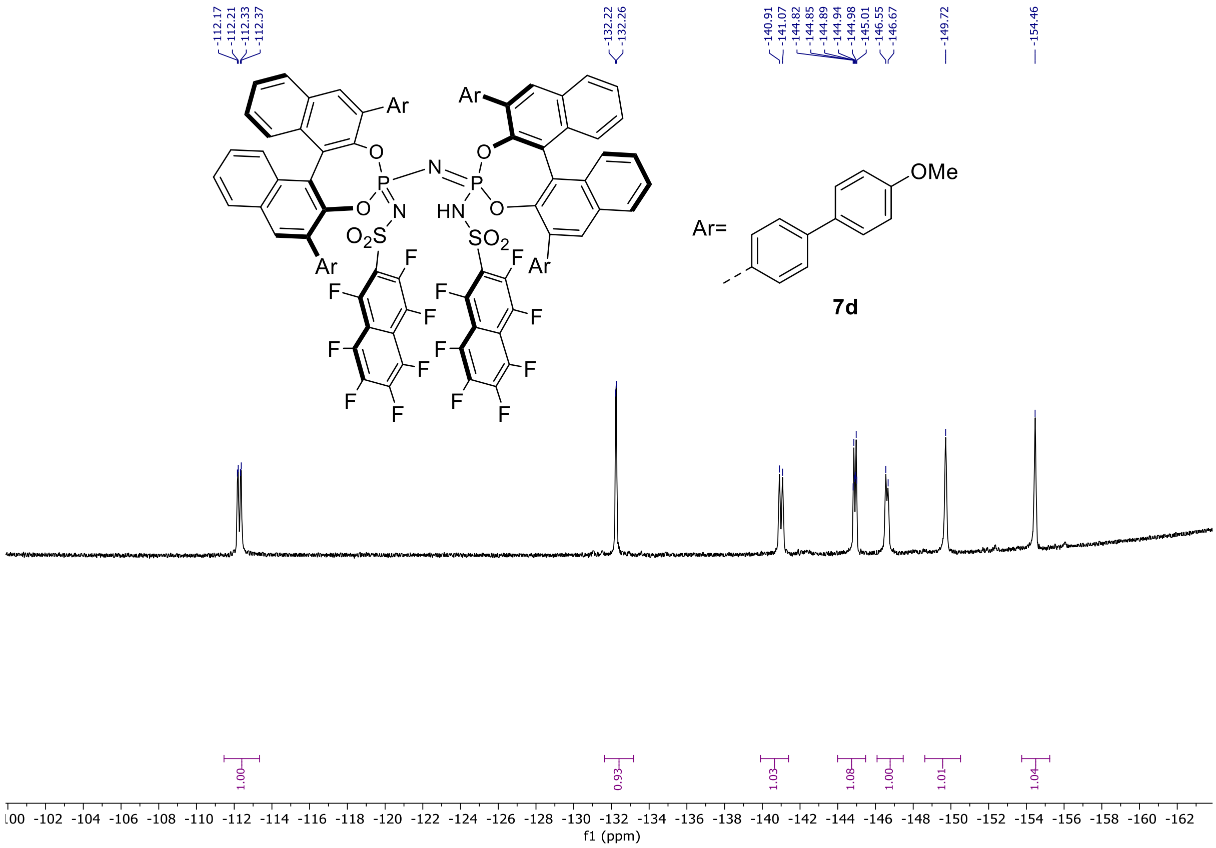
^{31}P NMR, CD_2Cl_2, 203 MHz



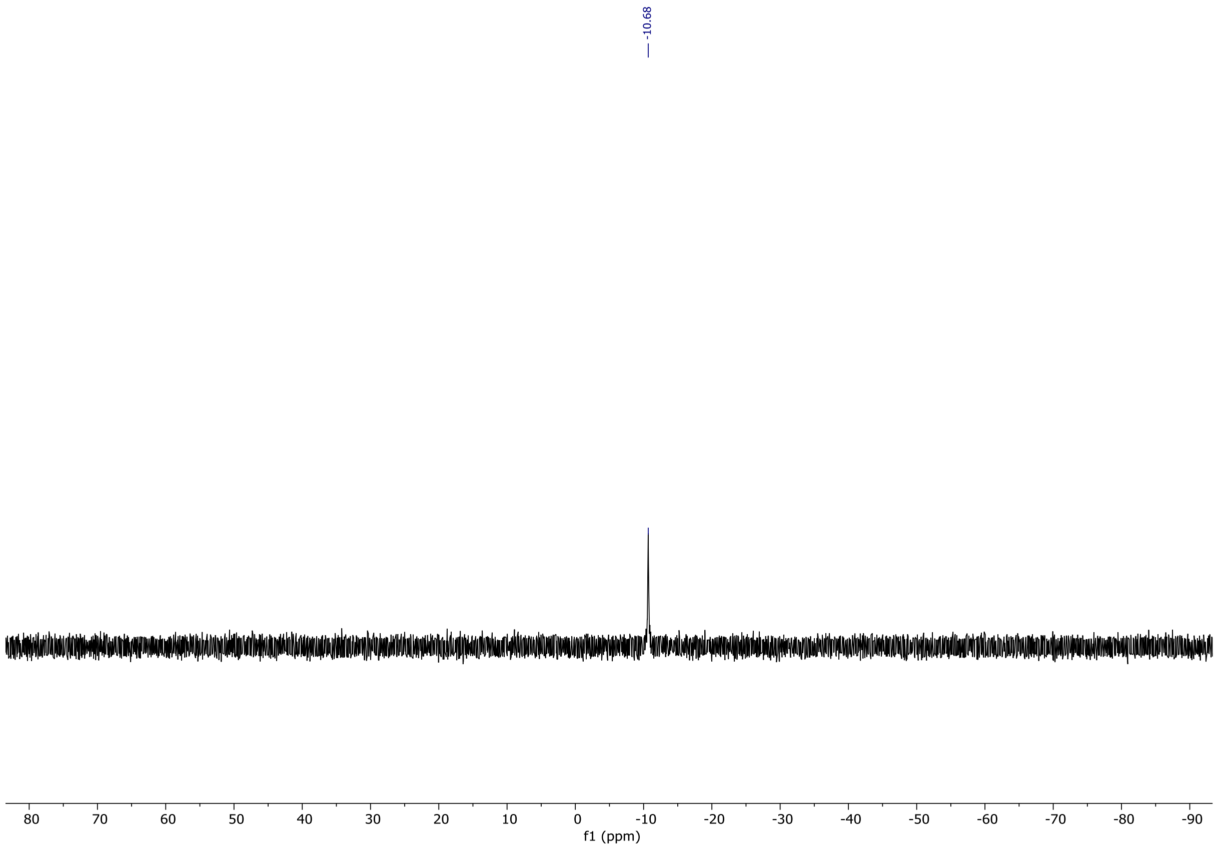
^{1}H NMR, $CDCl_3$, 501 MHz



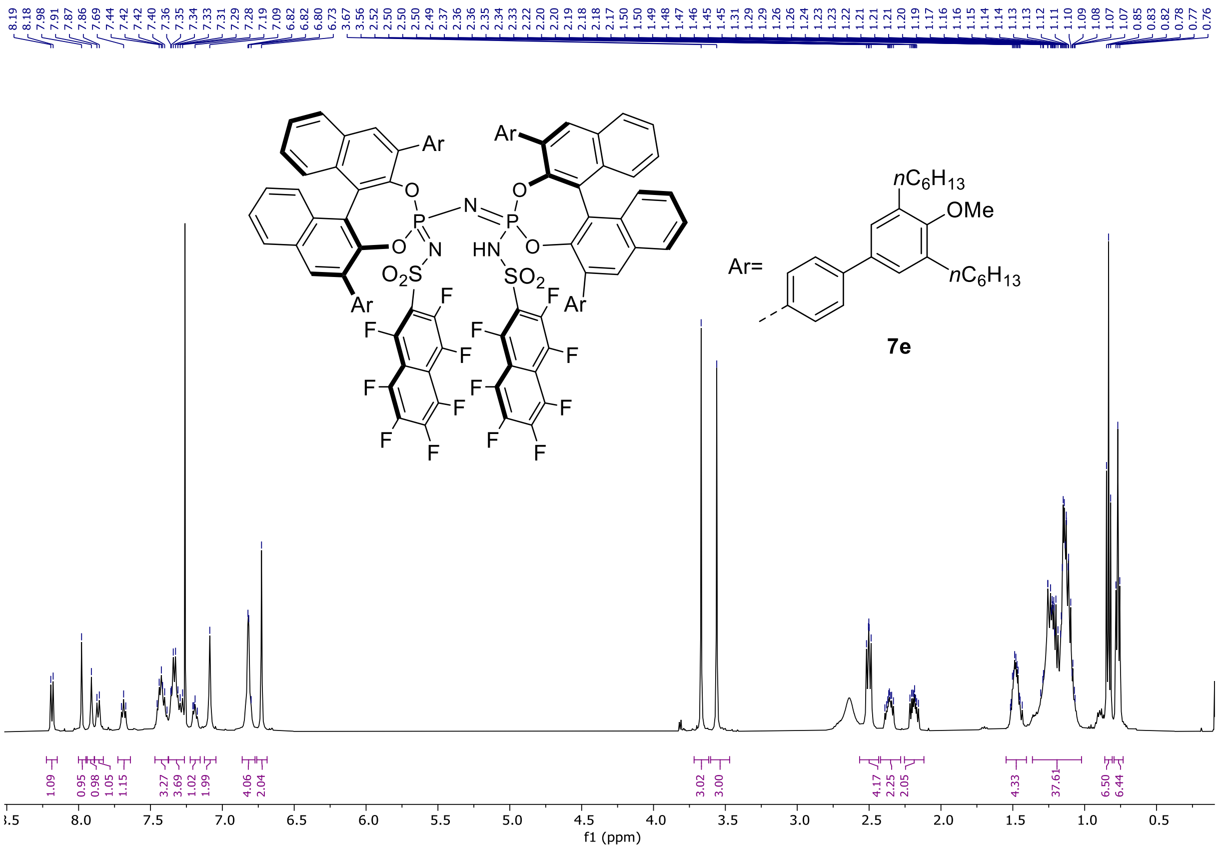
^{13}C NMR, $CDCl_3$, 126 MHz



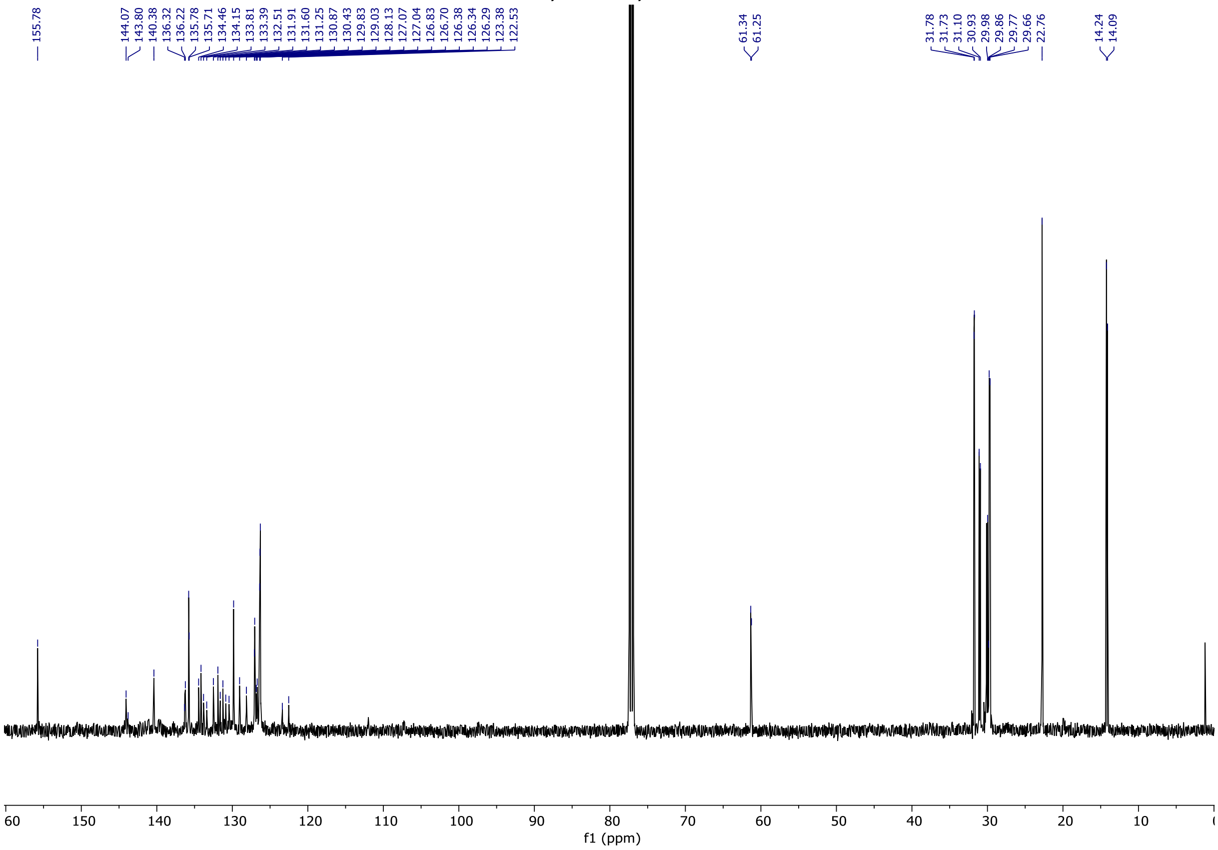
^{19}F NMR, $CDCl_3$, 471 MHz



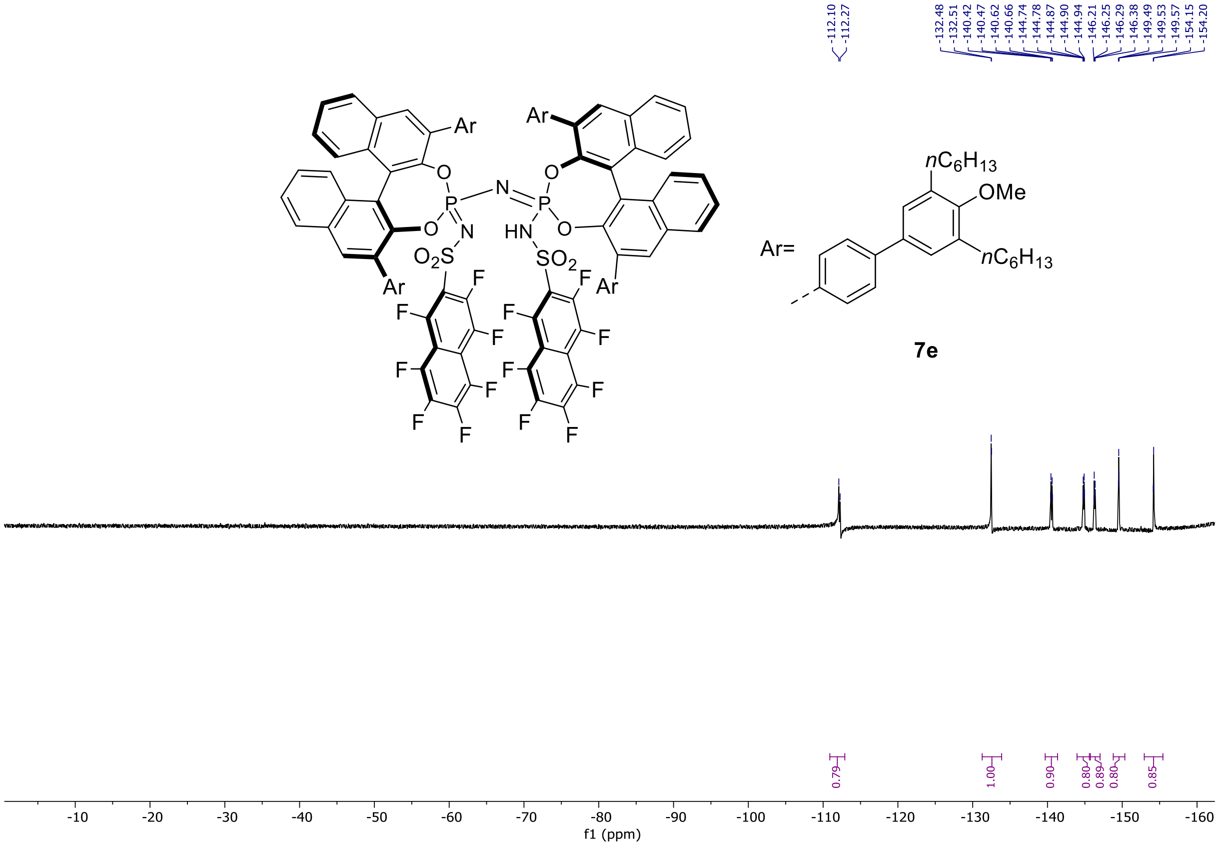
^{31}P NMR, $CDCl_3$, 206 MHz



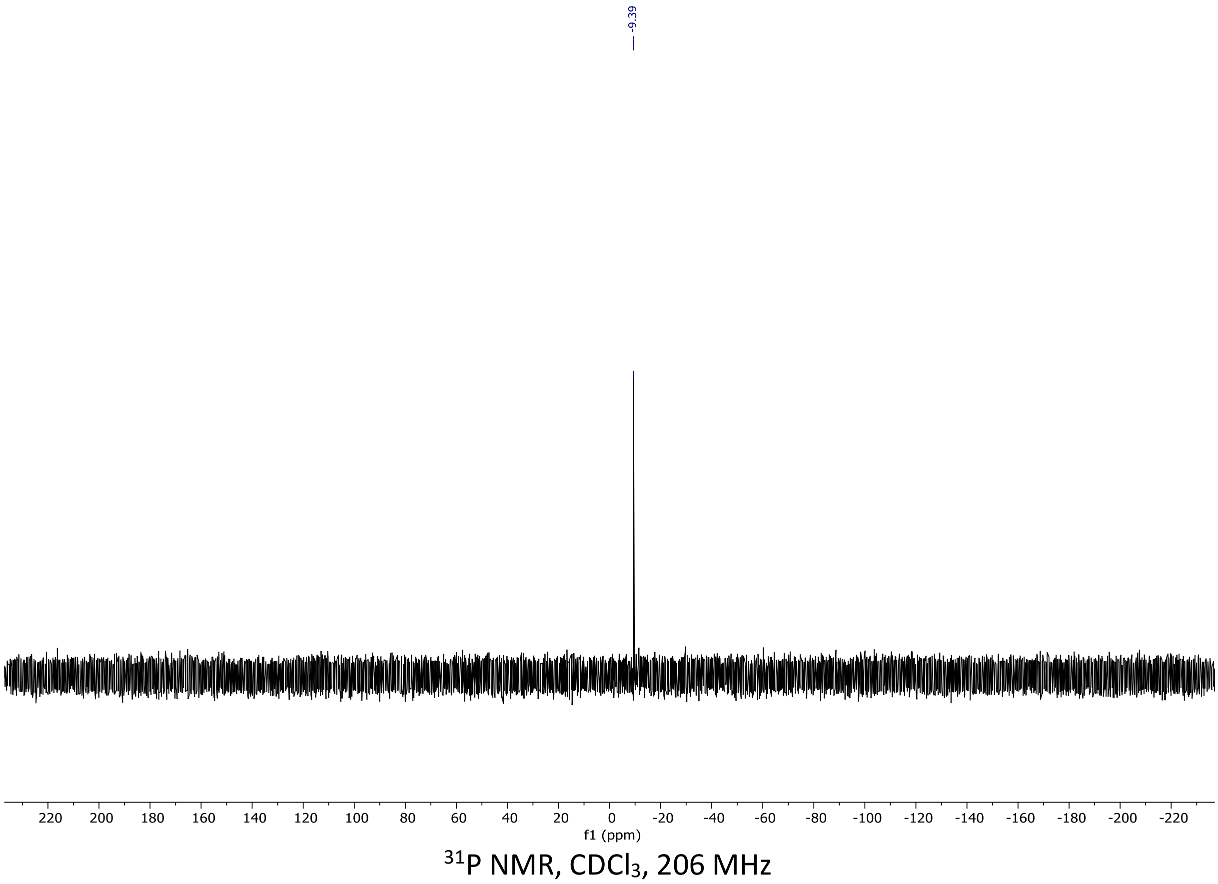
^{1}H NMR, $CDCl_3$, 501 MHz



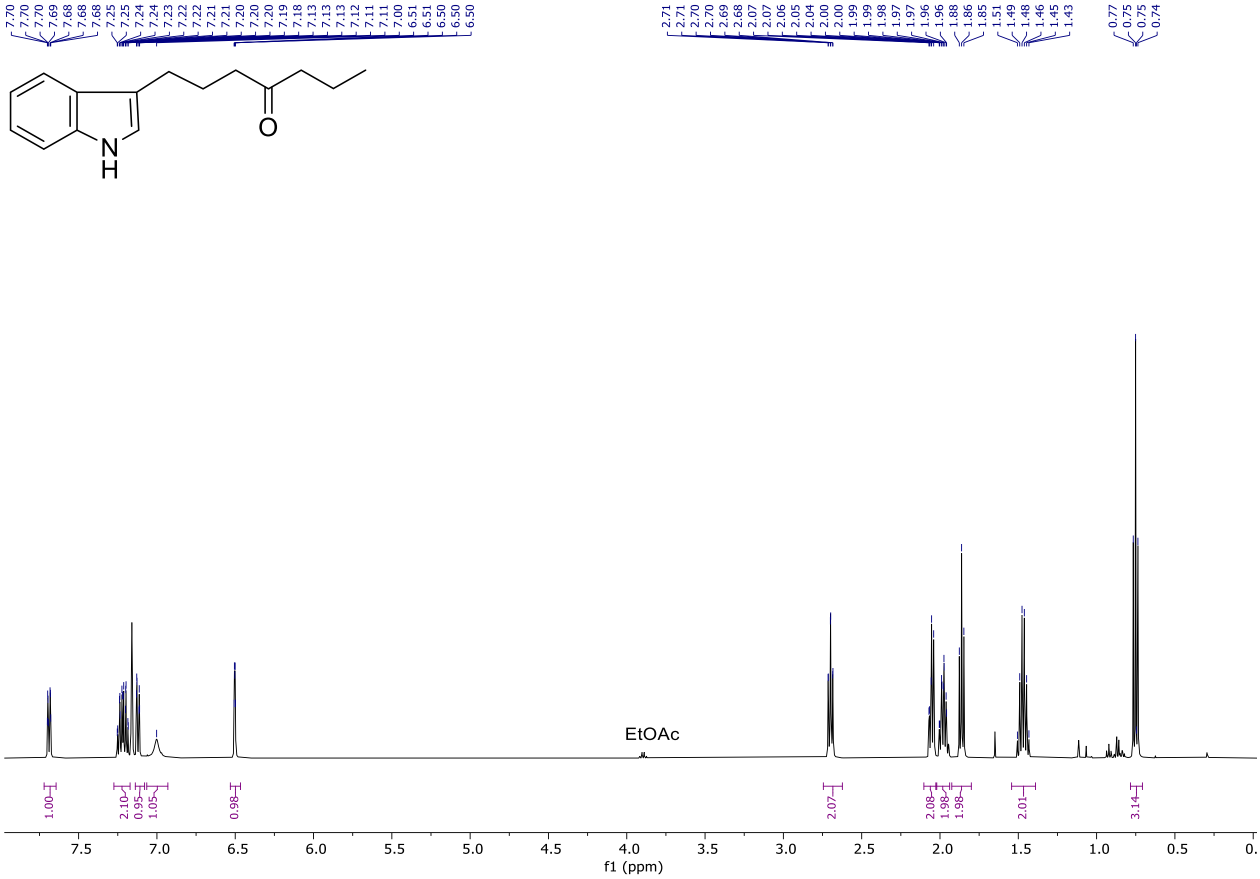
^{13}C NMR, $CDCl_3$, 126 MHz



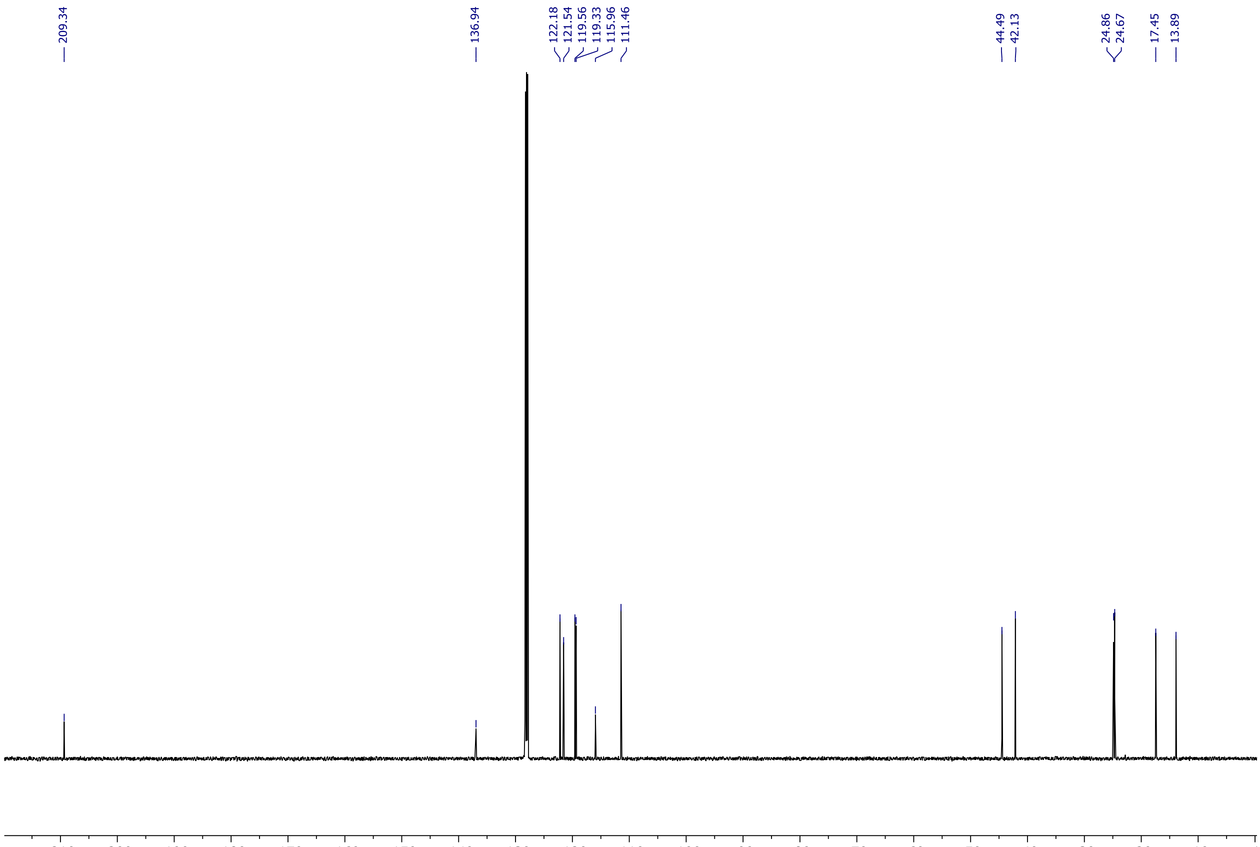
^{19}F NMR, $CDCl_3$, 471 MHz



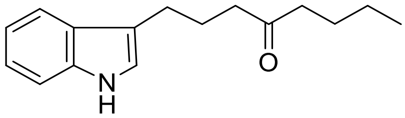
^{31}P NMR, $CDCl_3$, 206 MHz

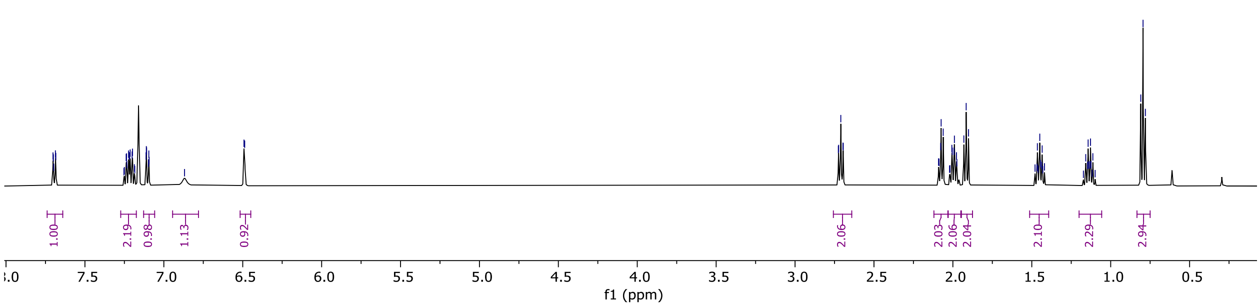


^{1}H NMR, C_6D_6, 501 MHz

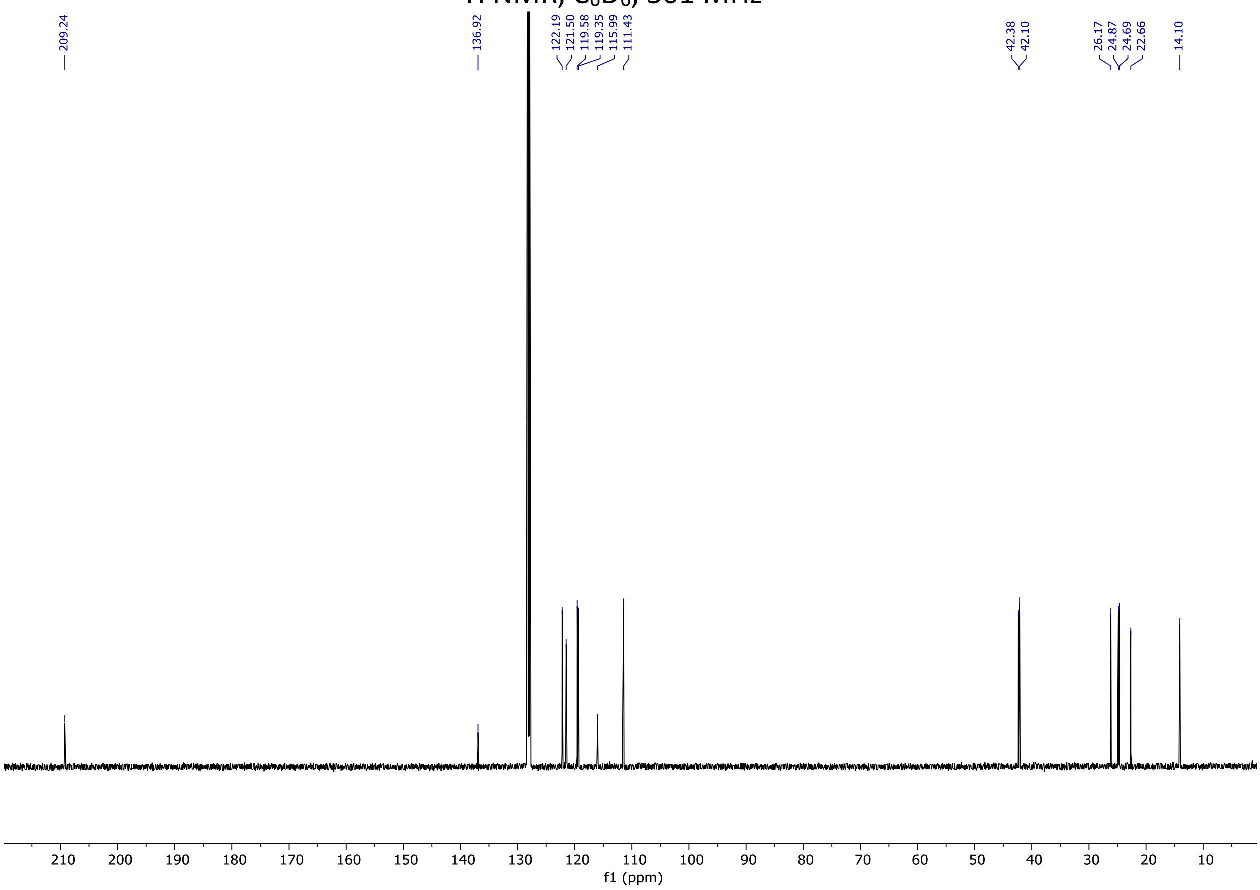


^{13}C NMR, C_6D_6, 126 MHz

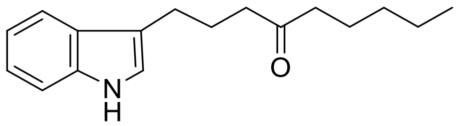


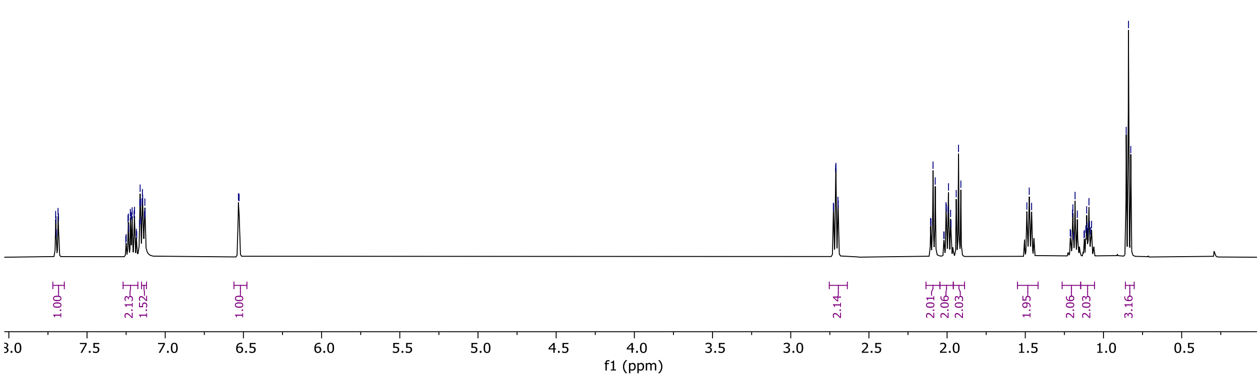


^{1}H NMR, C_6D_6, 501 MHz

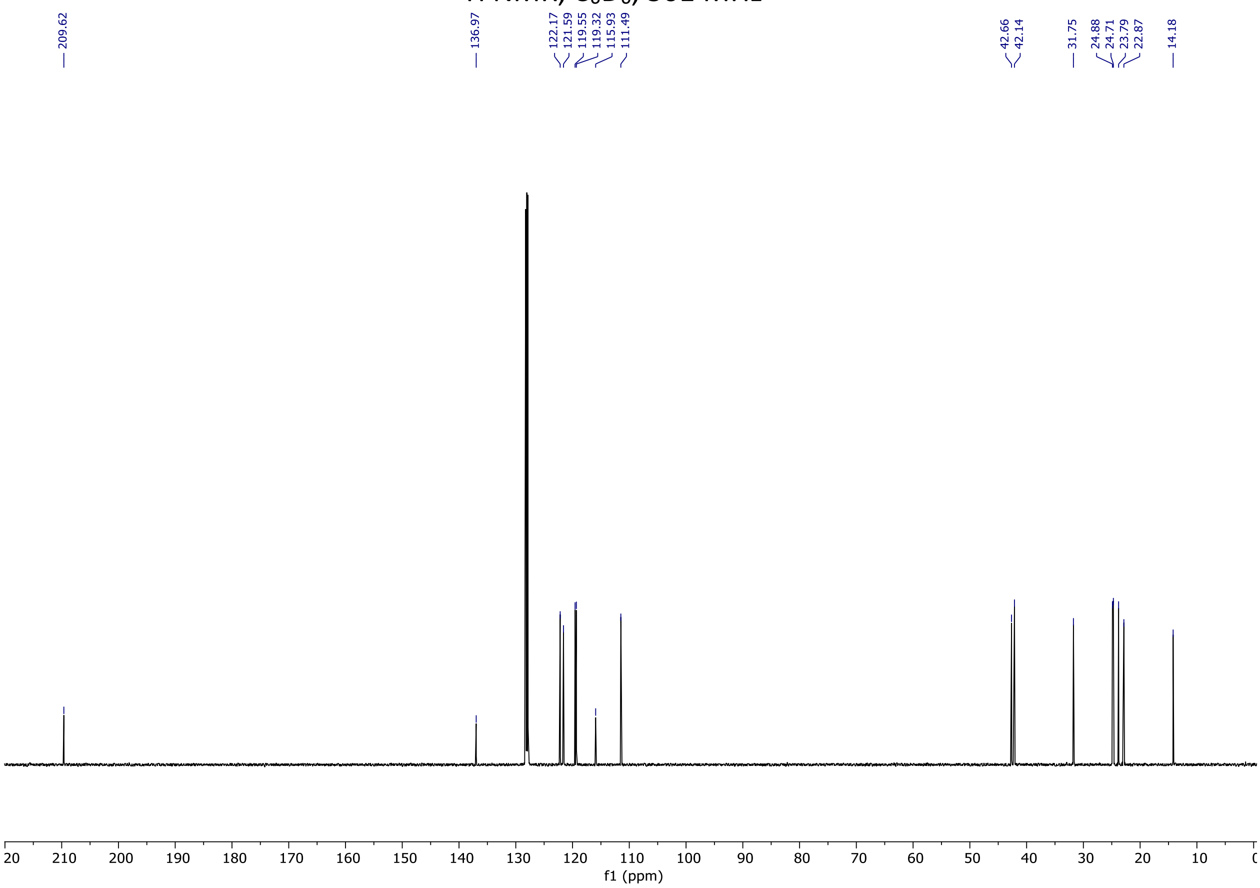


^{13}C NMR, C_6D_6, 126 MHz

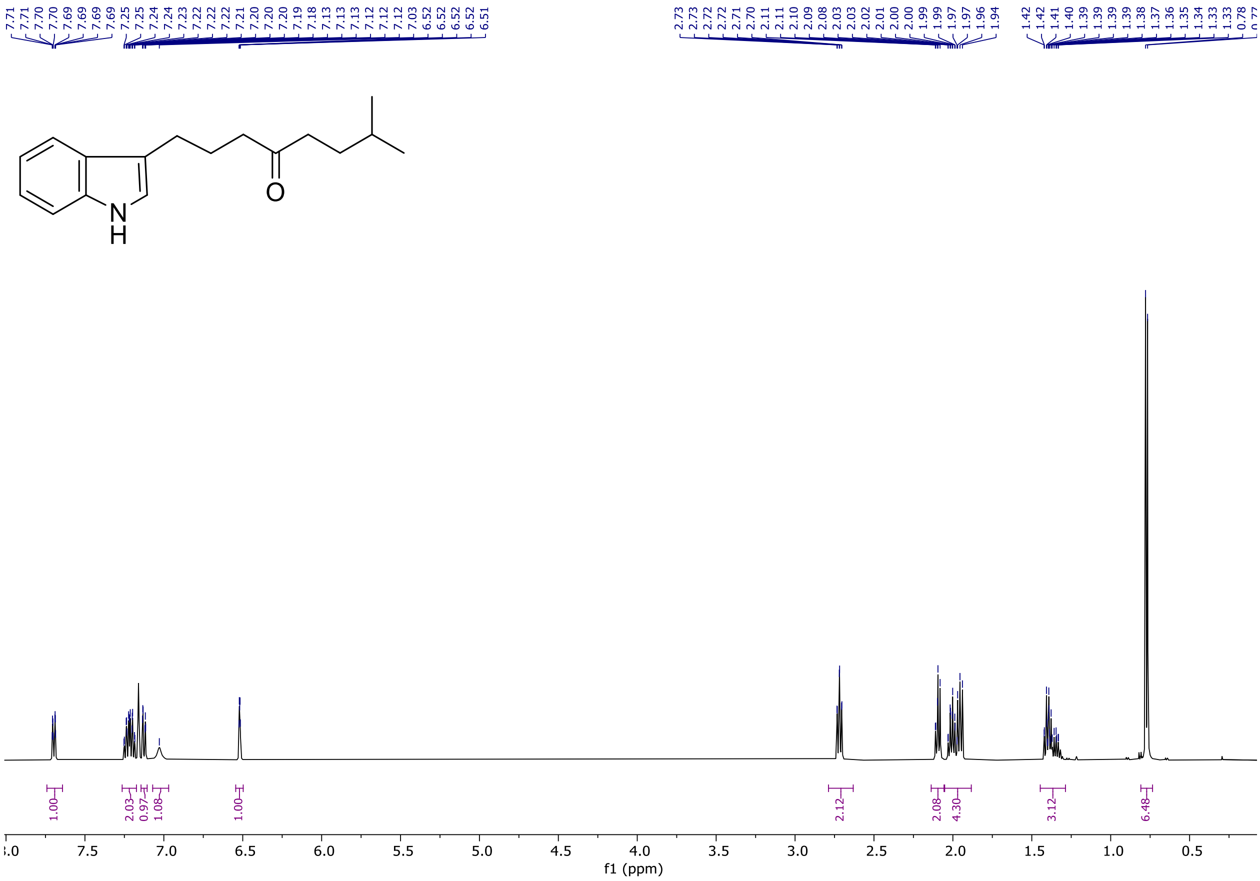




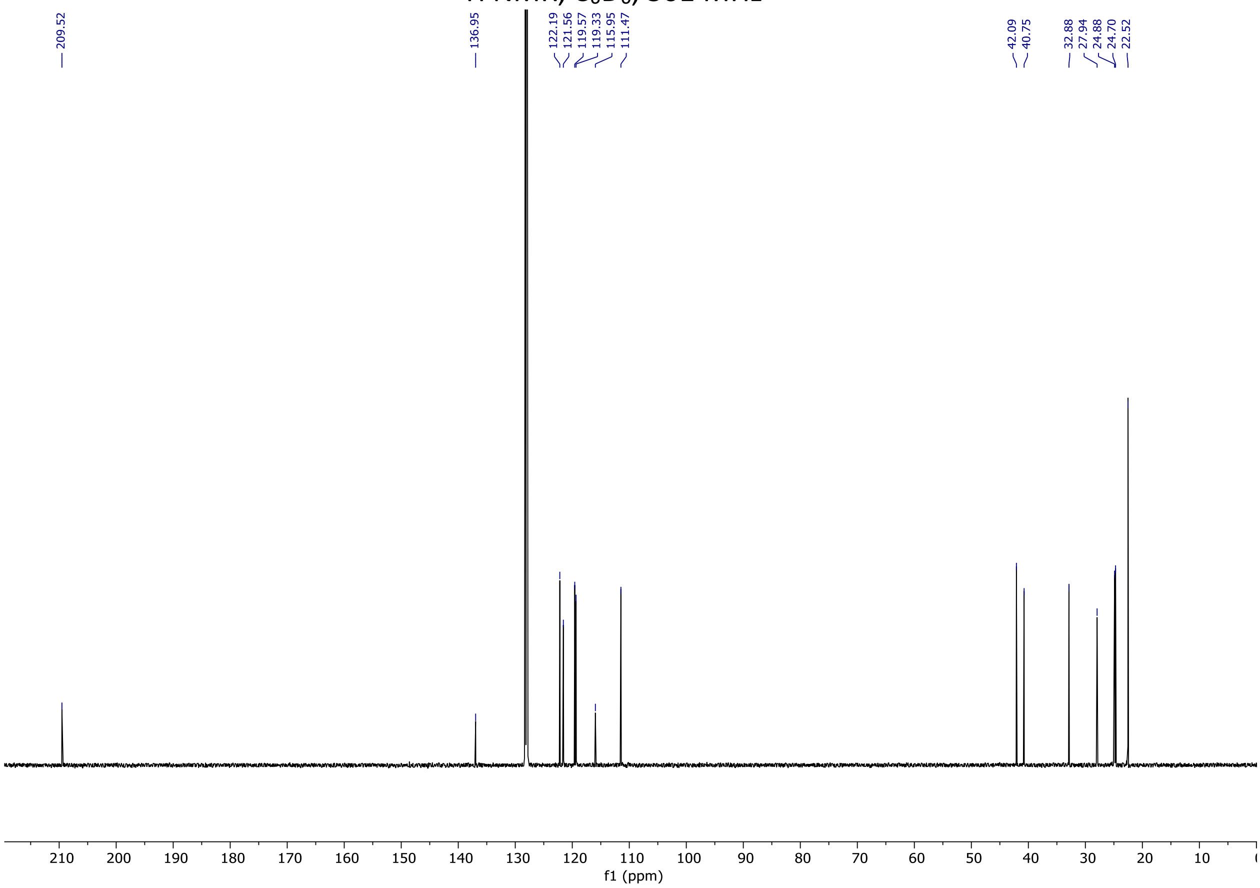
^{1}H NMR, C_6D_6, 501 MHz



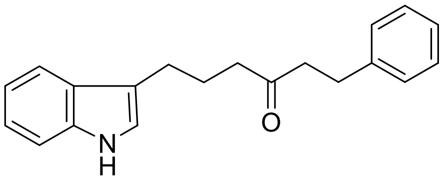
^{13}C NMR, C_6D_6, 126 MHz

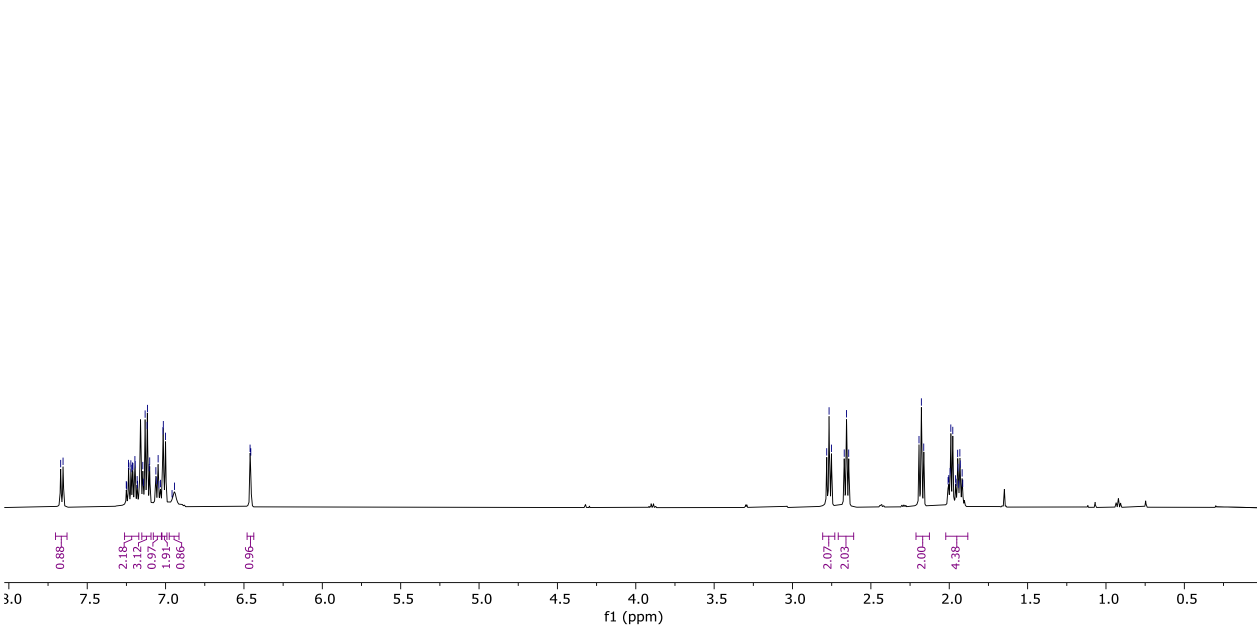


^{1}H NMR, C_6D_6, 501 MHz

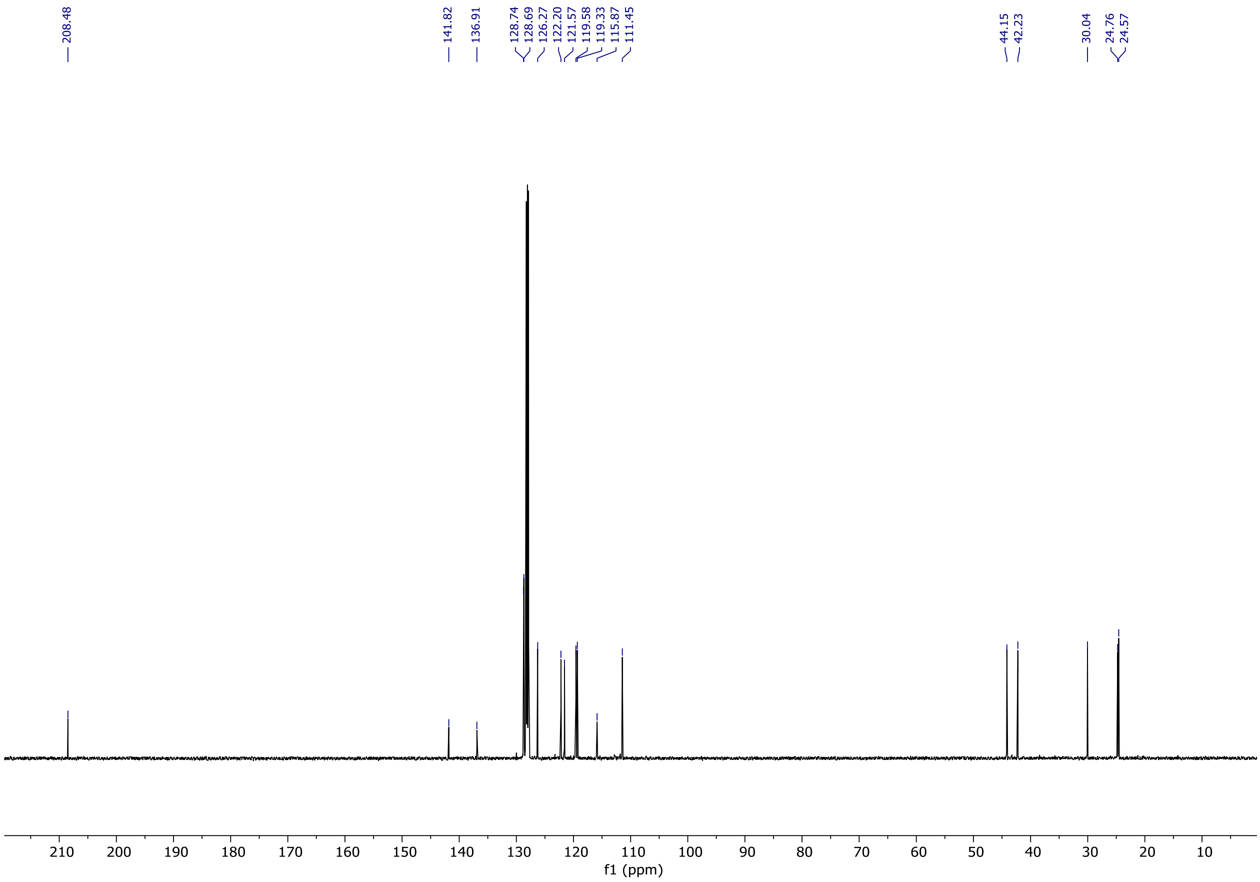


^{13}C NMR, C_6D_6, 126 MHz

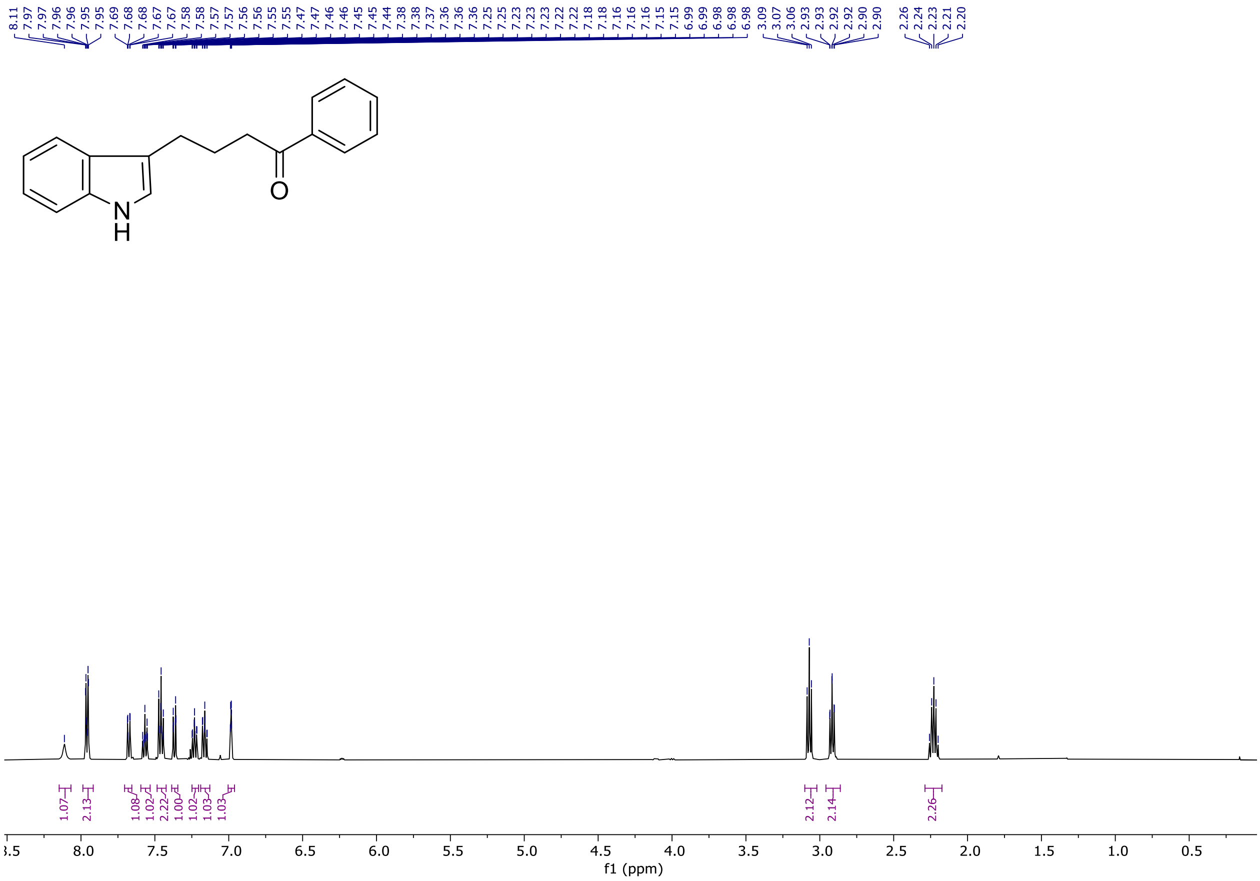




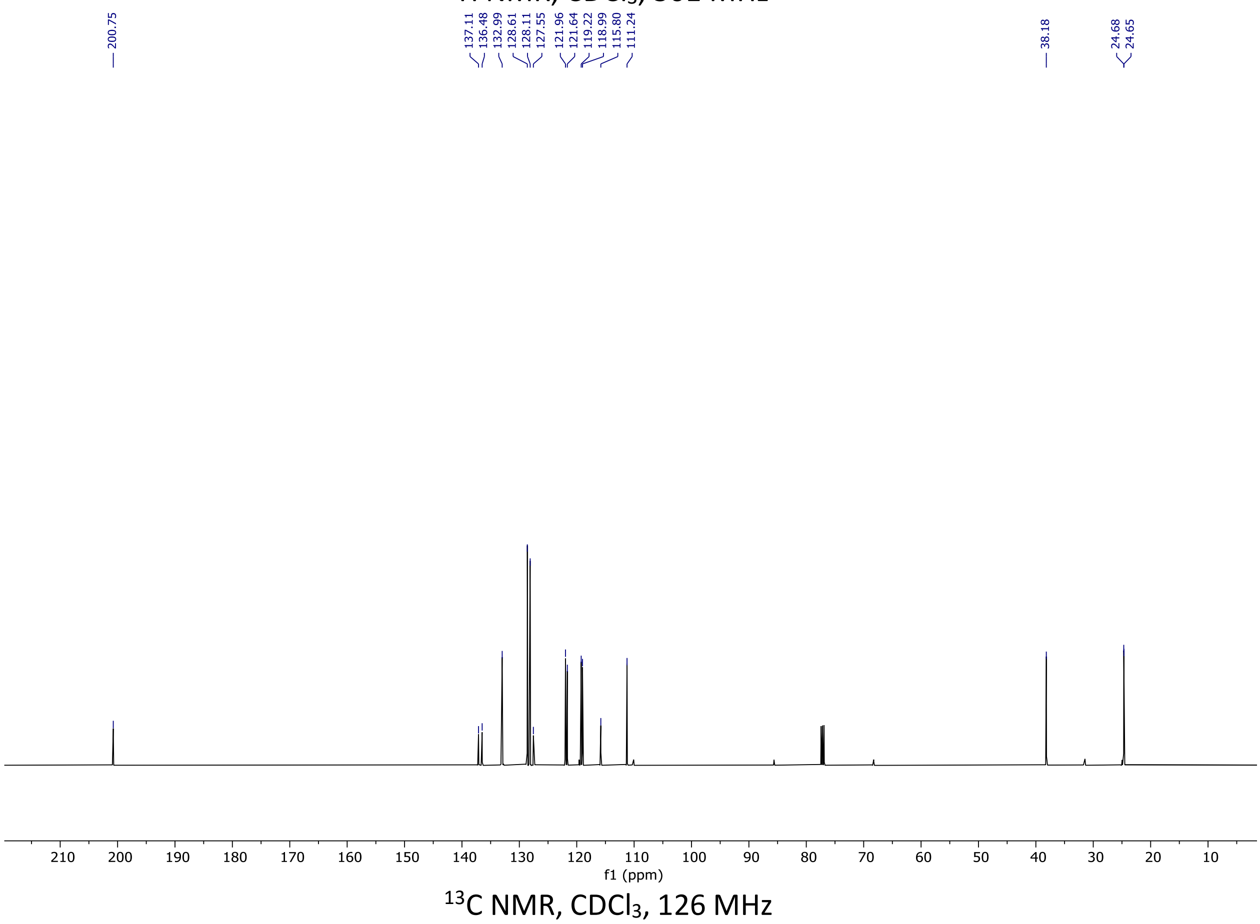
^{1}H NMR, C_6D_6, 501 MHz



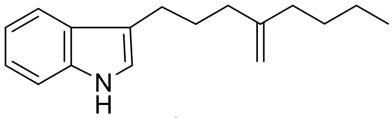
^{13}C NMR, C_6D_6, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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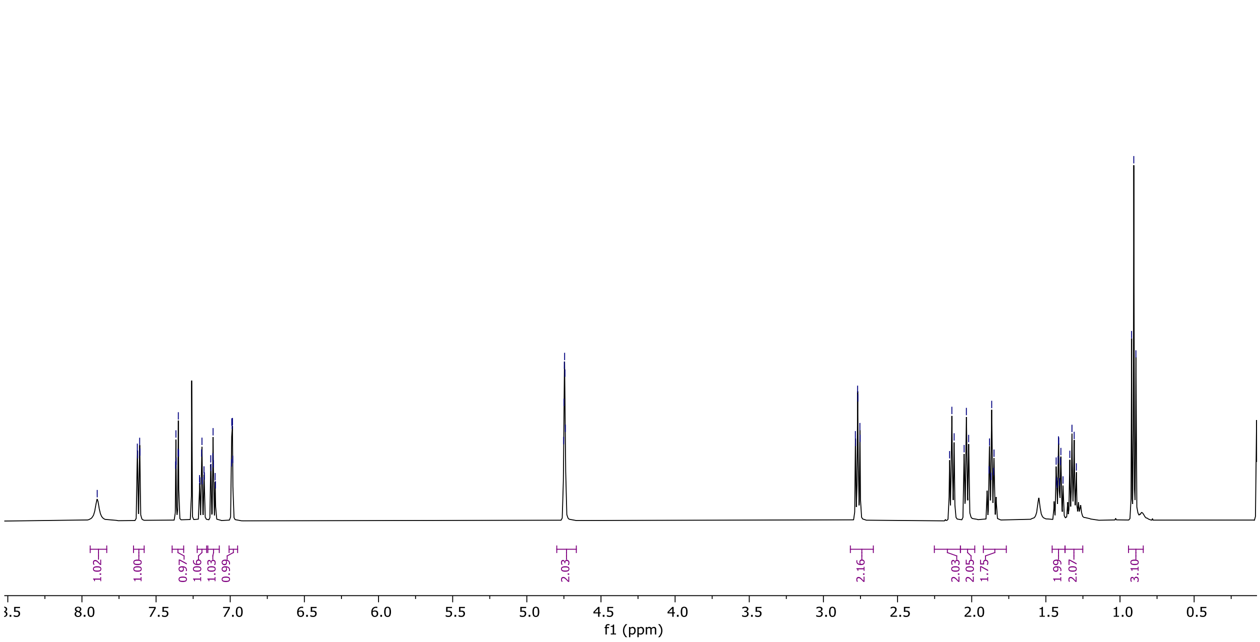
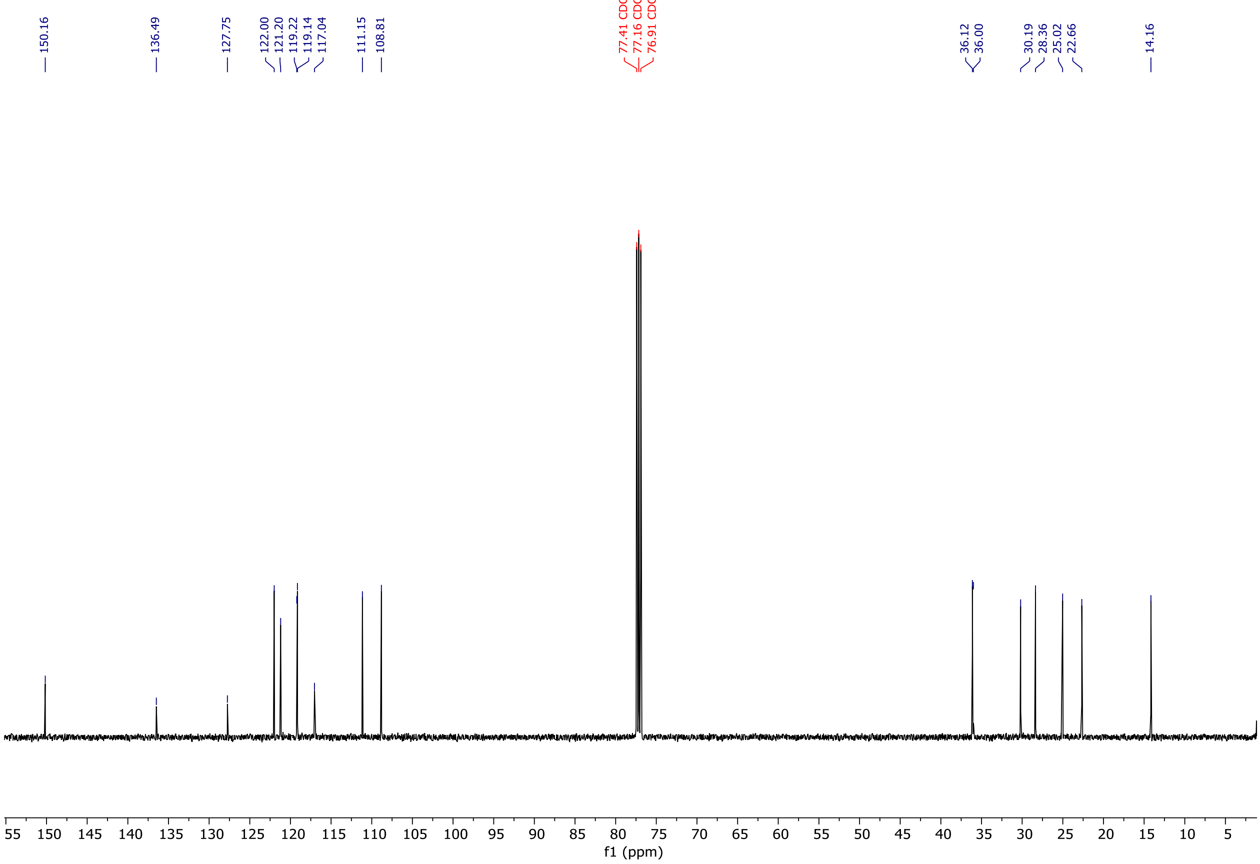
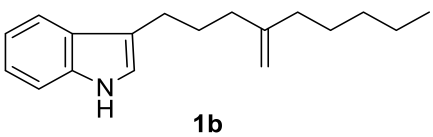


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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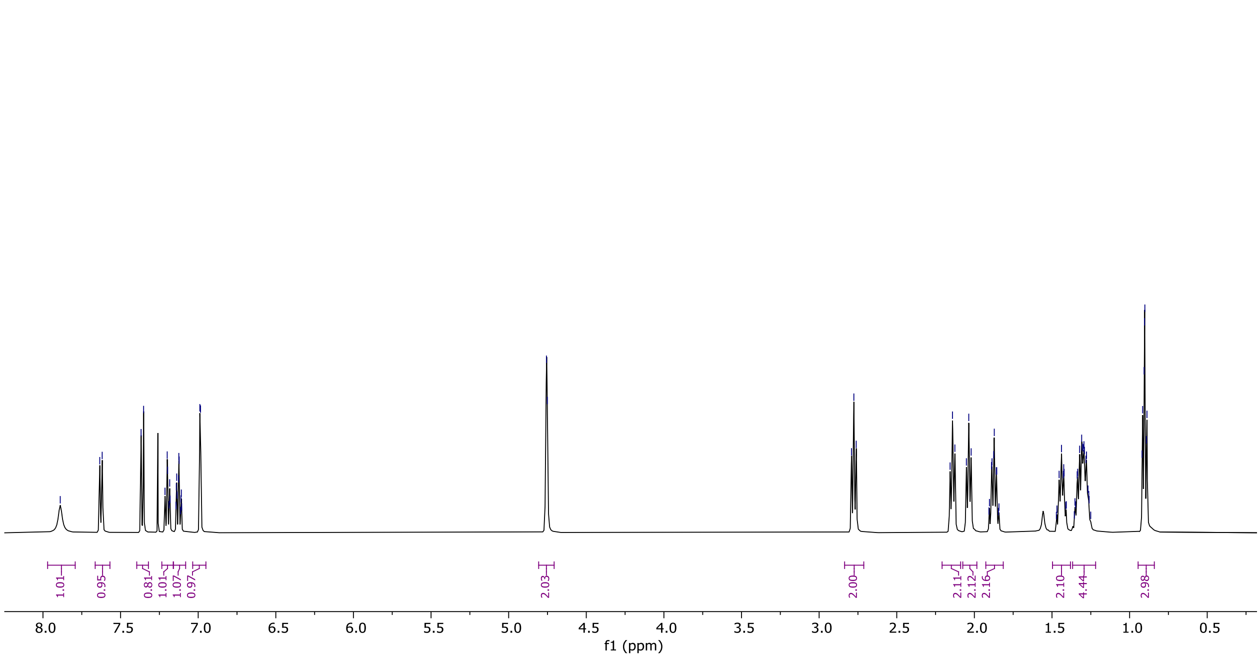
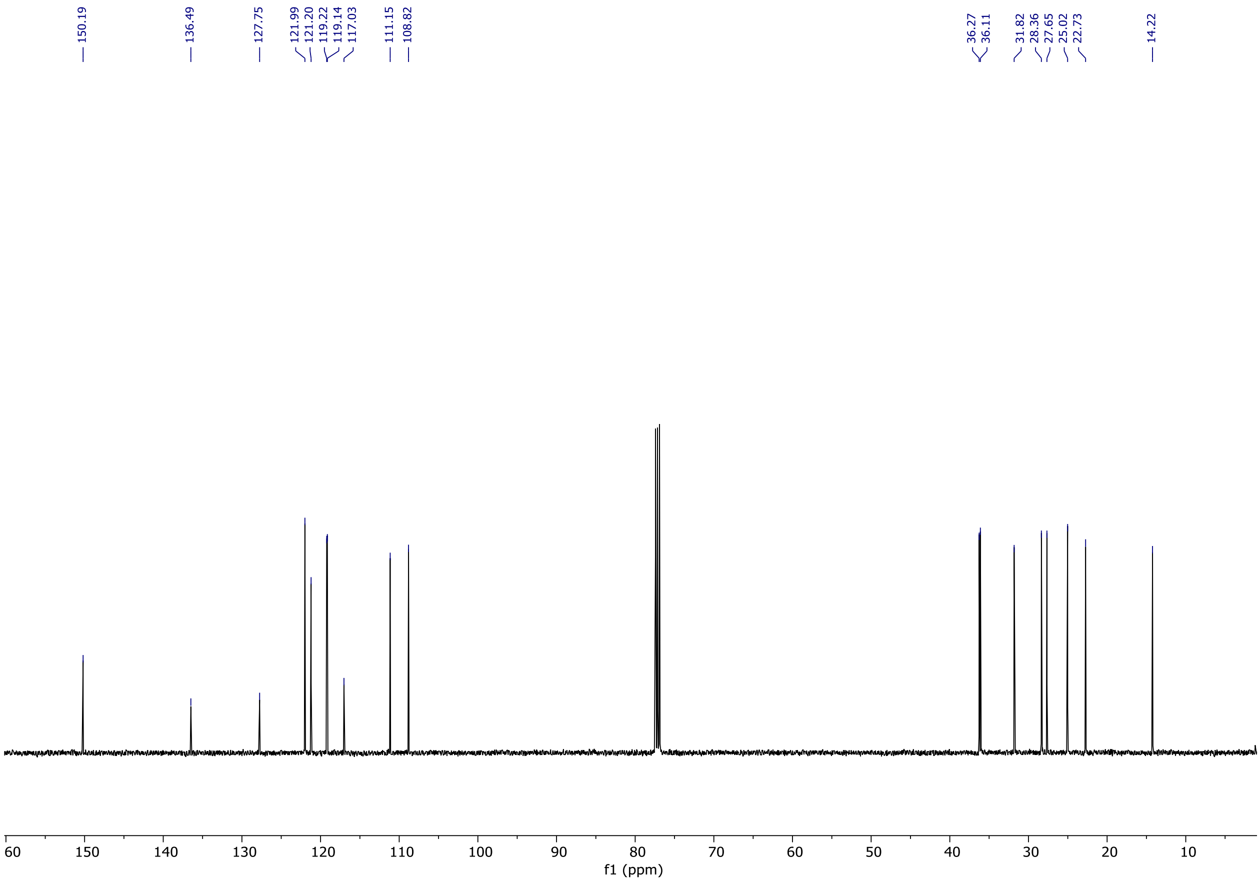
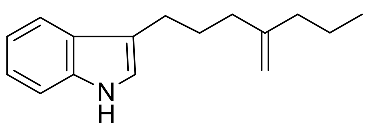


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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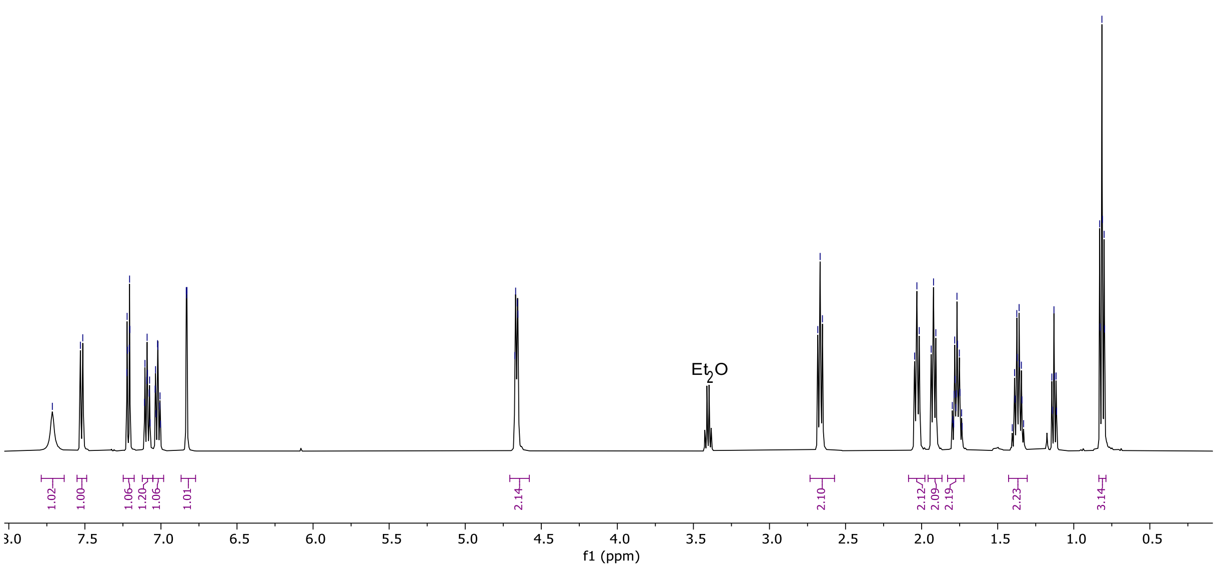
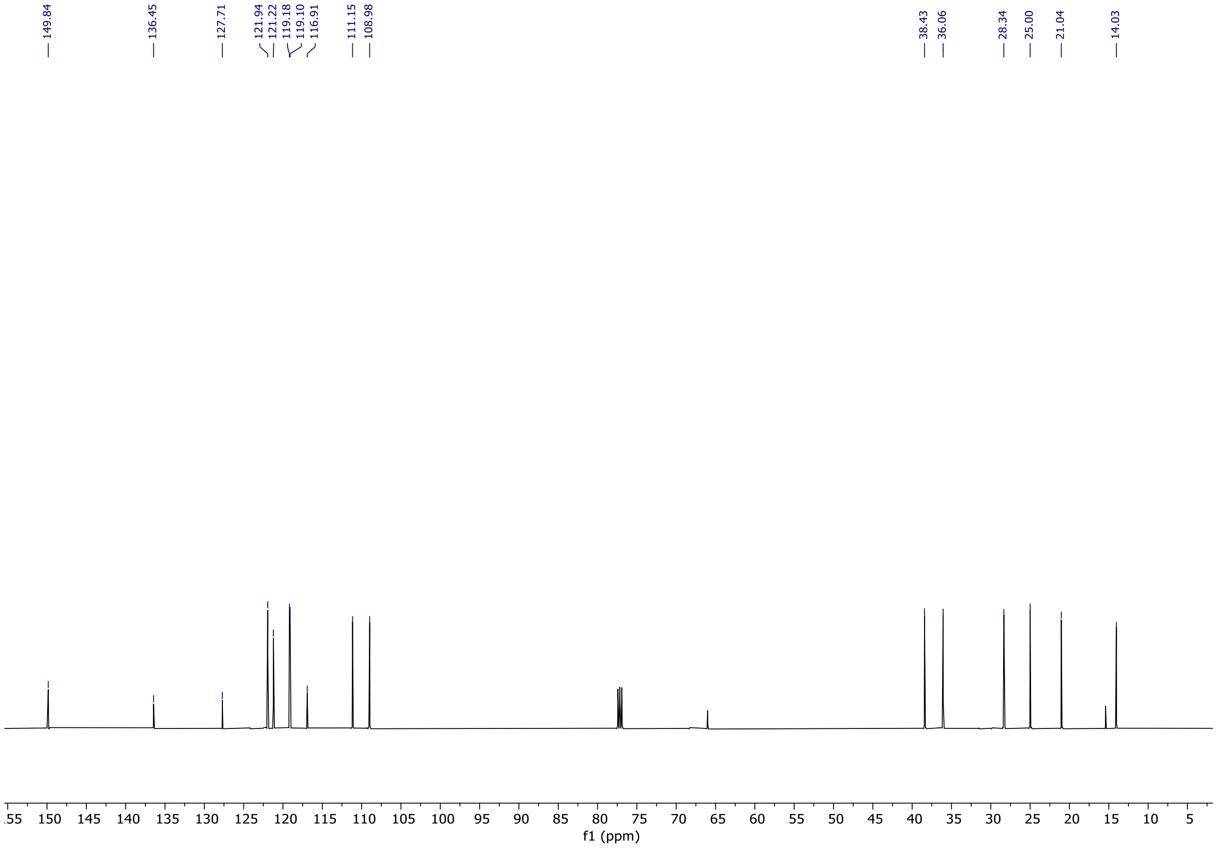
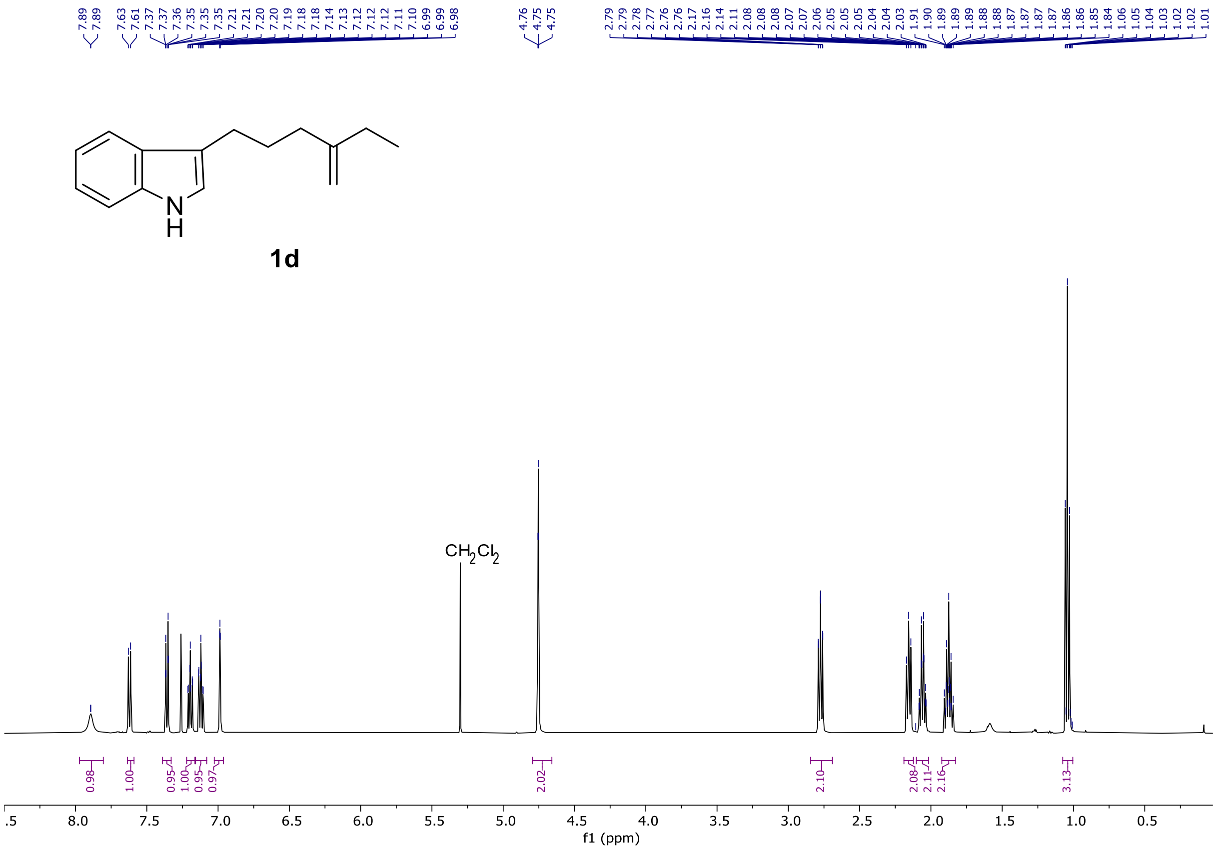


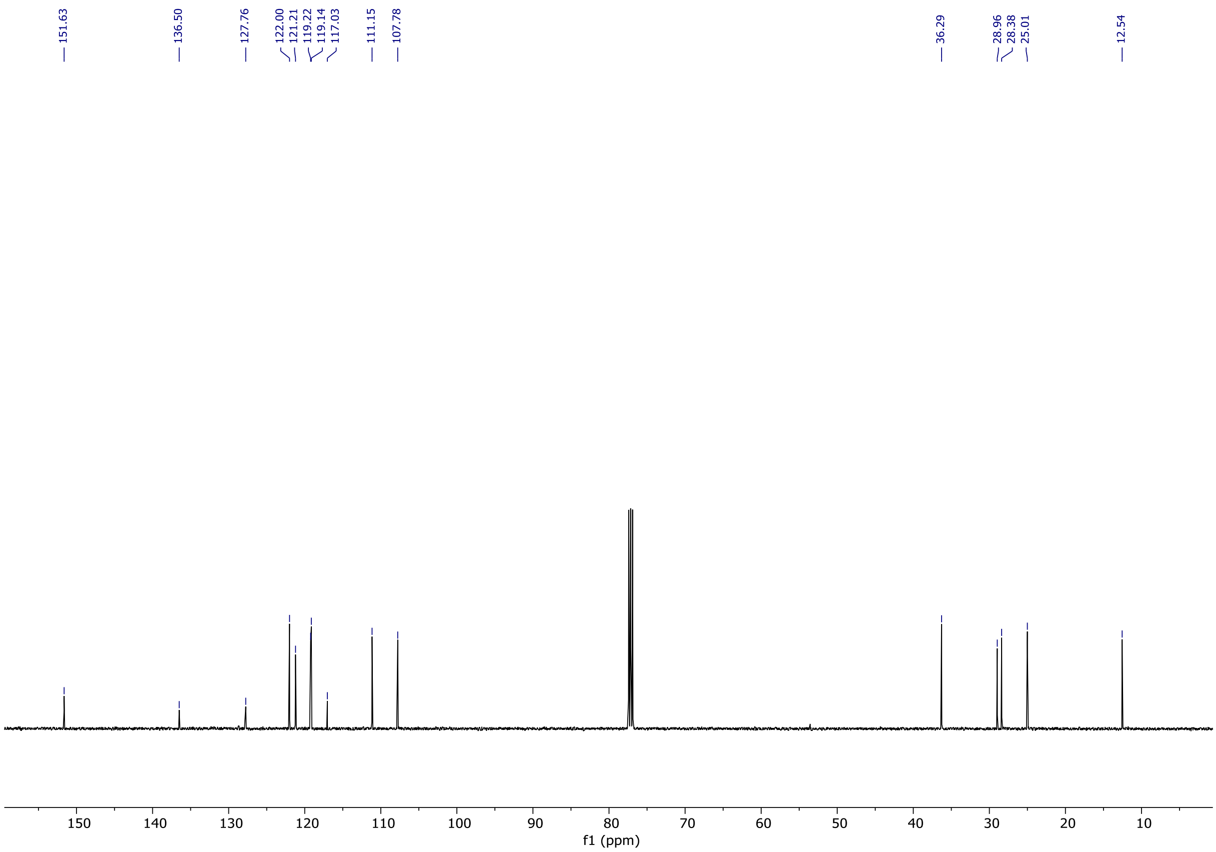
^{1}H NMR, $CDCl_3$, 501 MHz



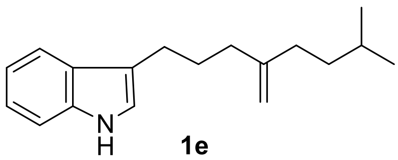
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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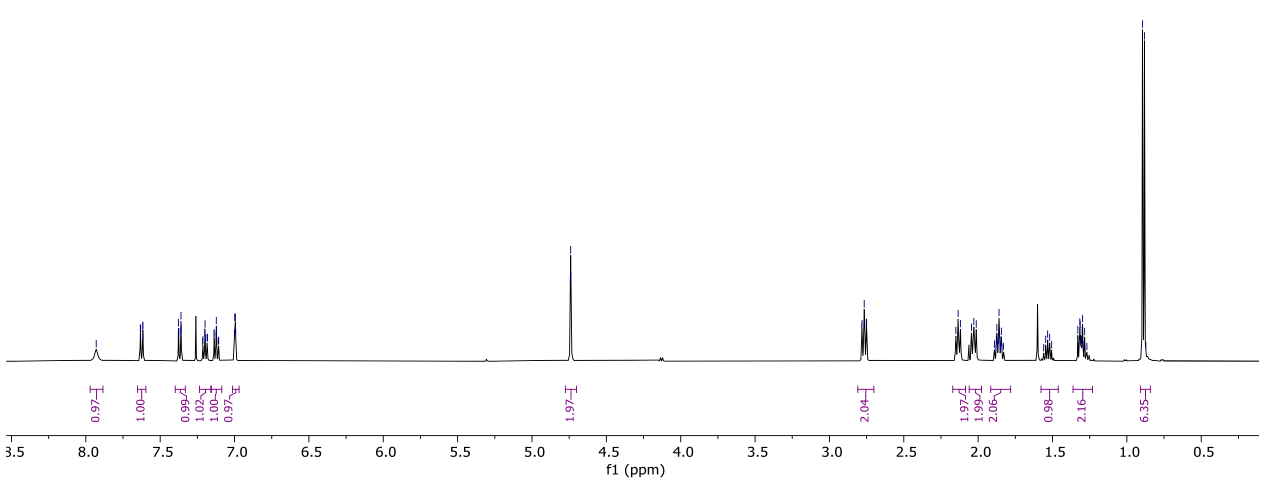
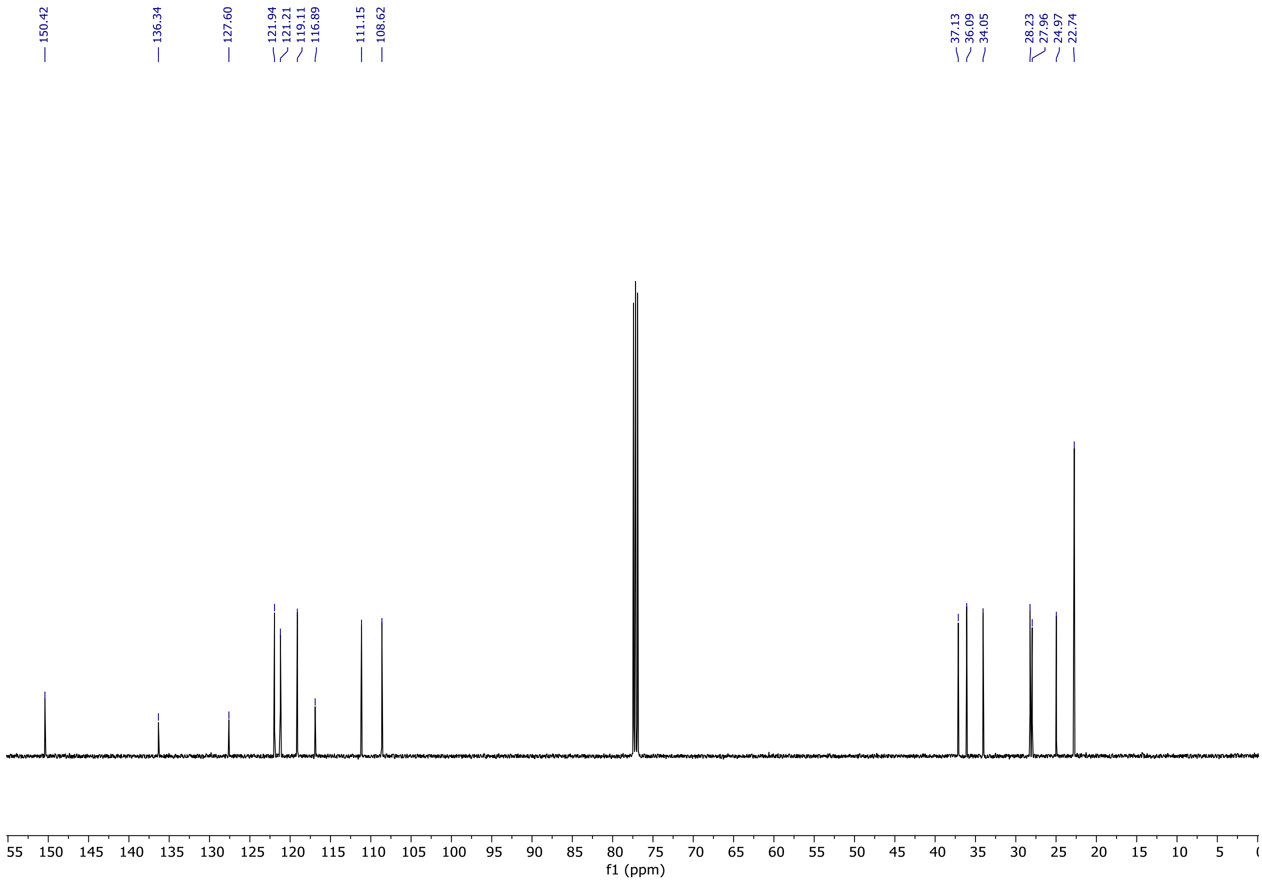
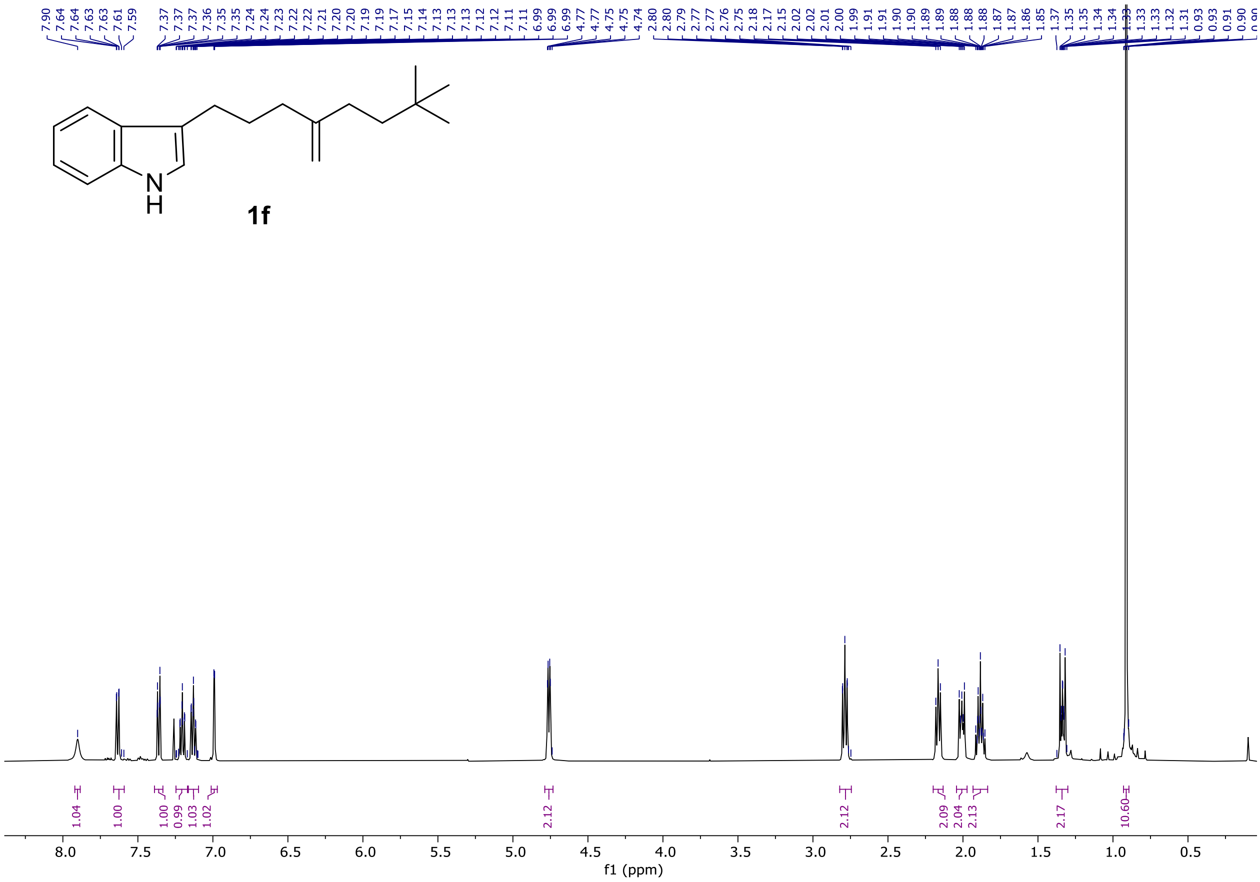


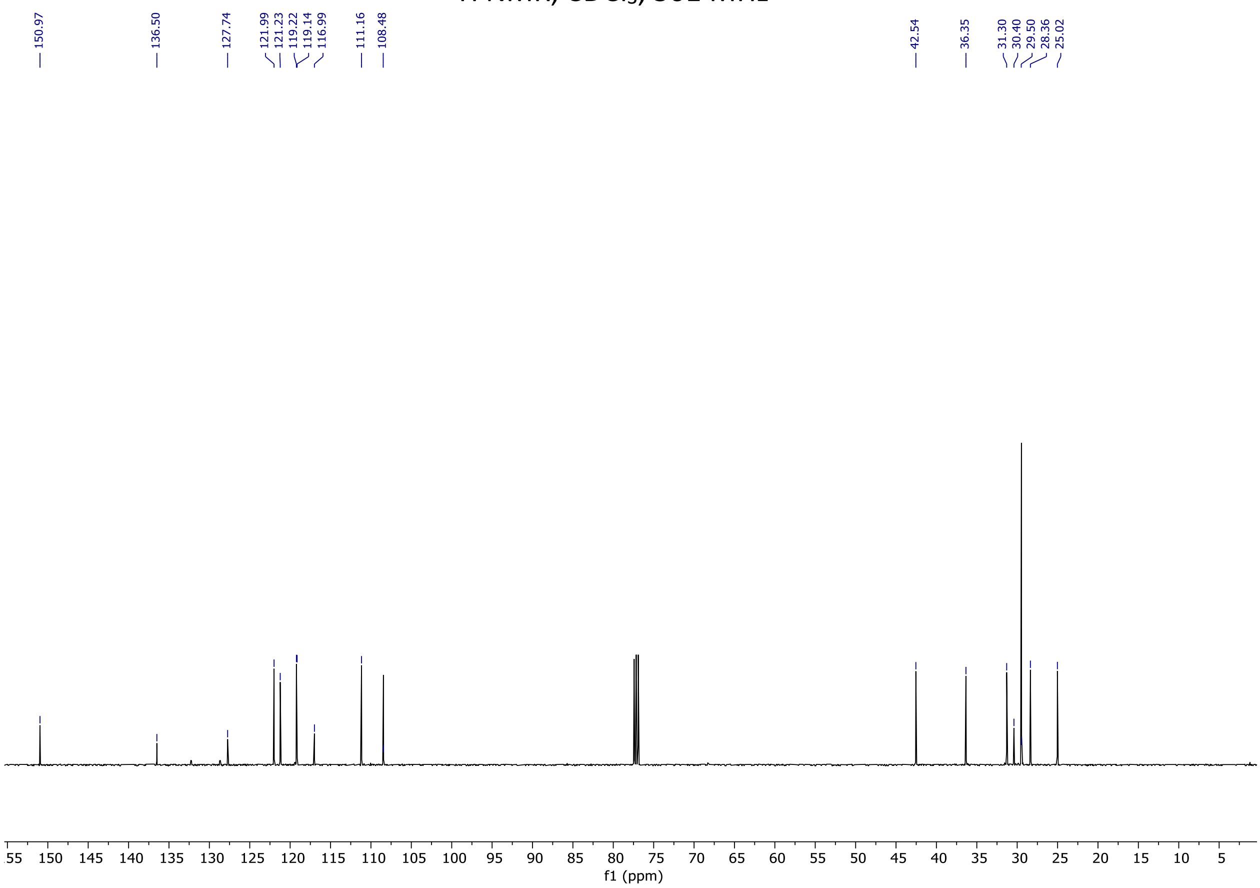
^{1}H NMR, $CDCl_3$, 501 MHz



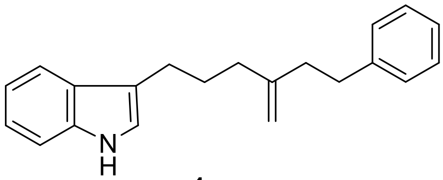
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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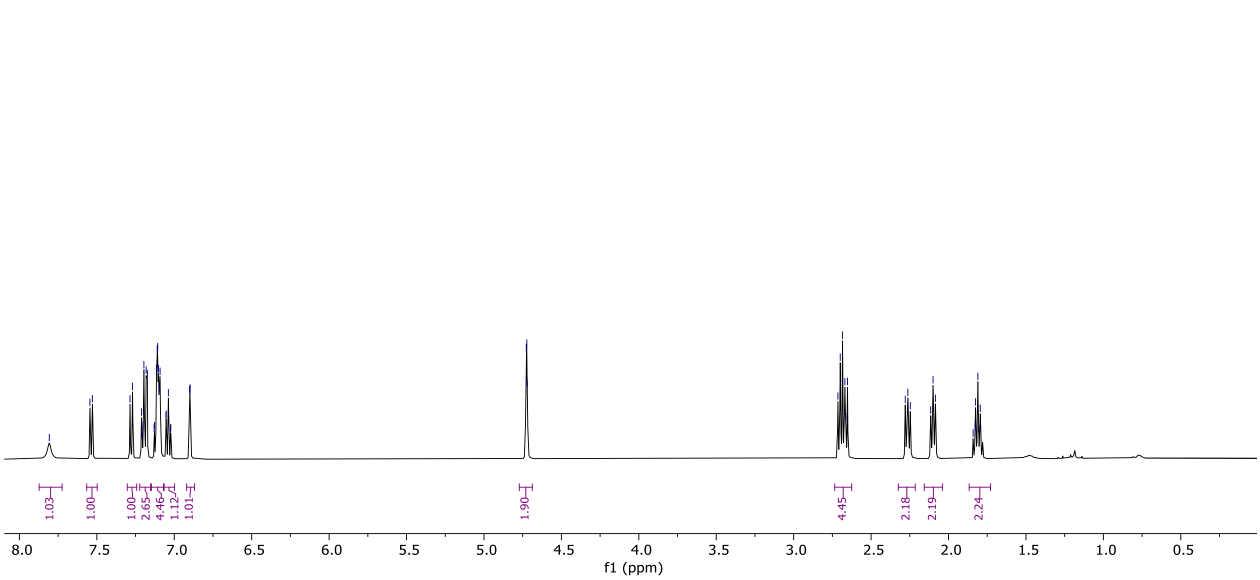
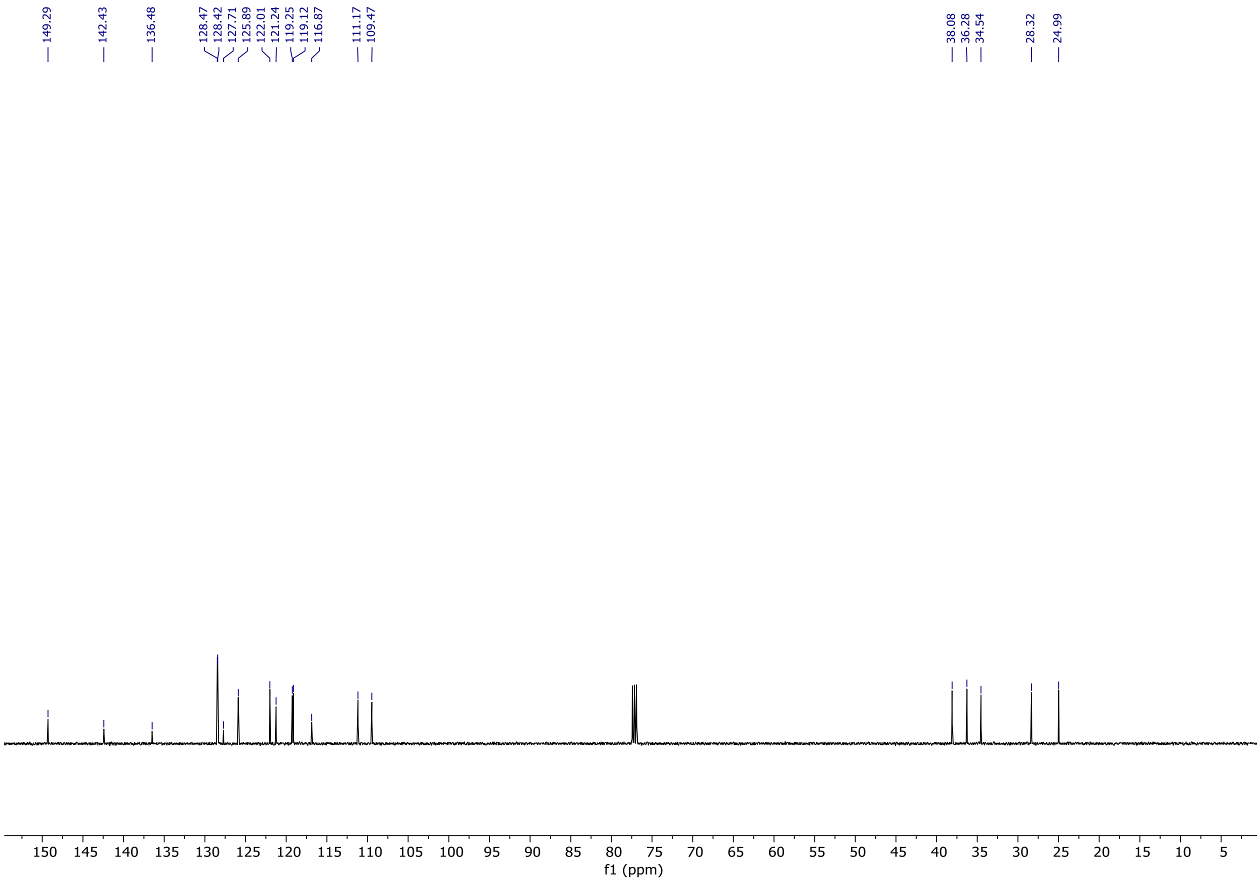
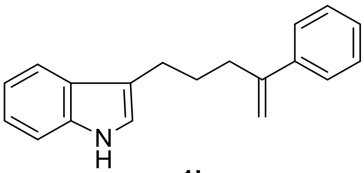


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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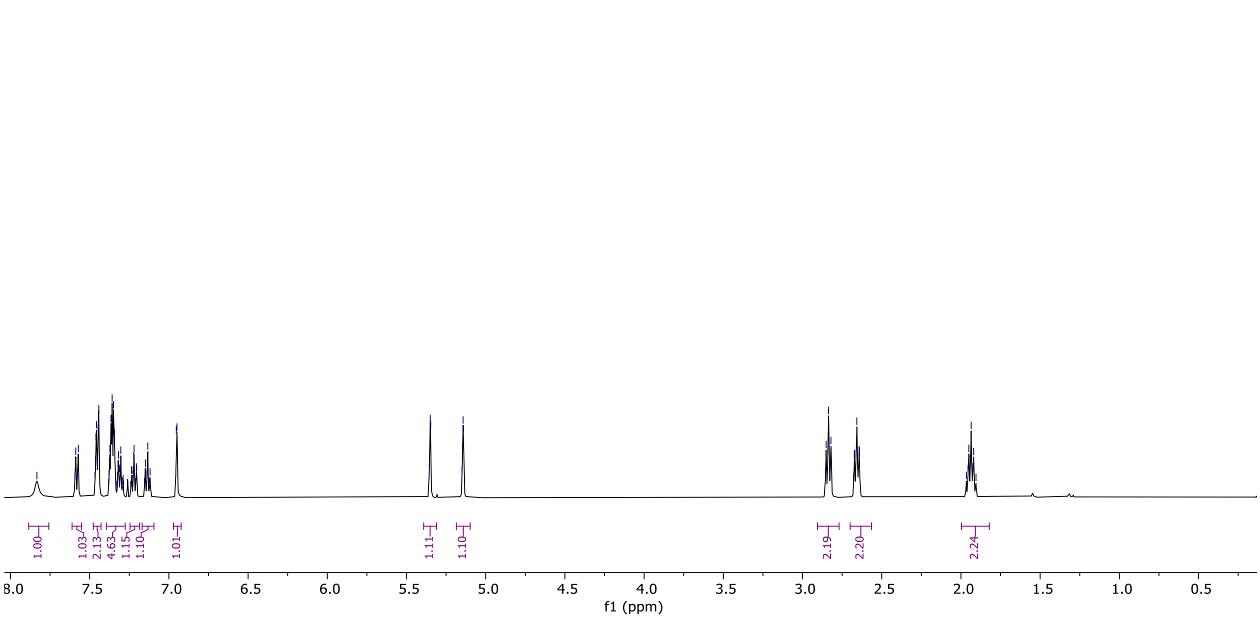
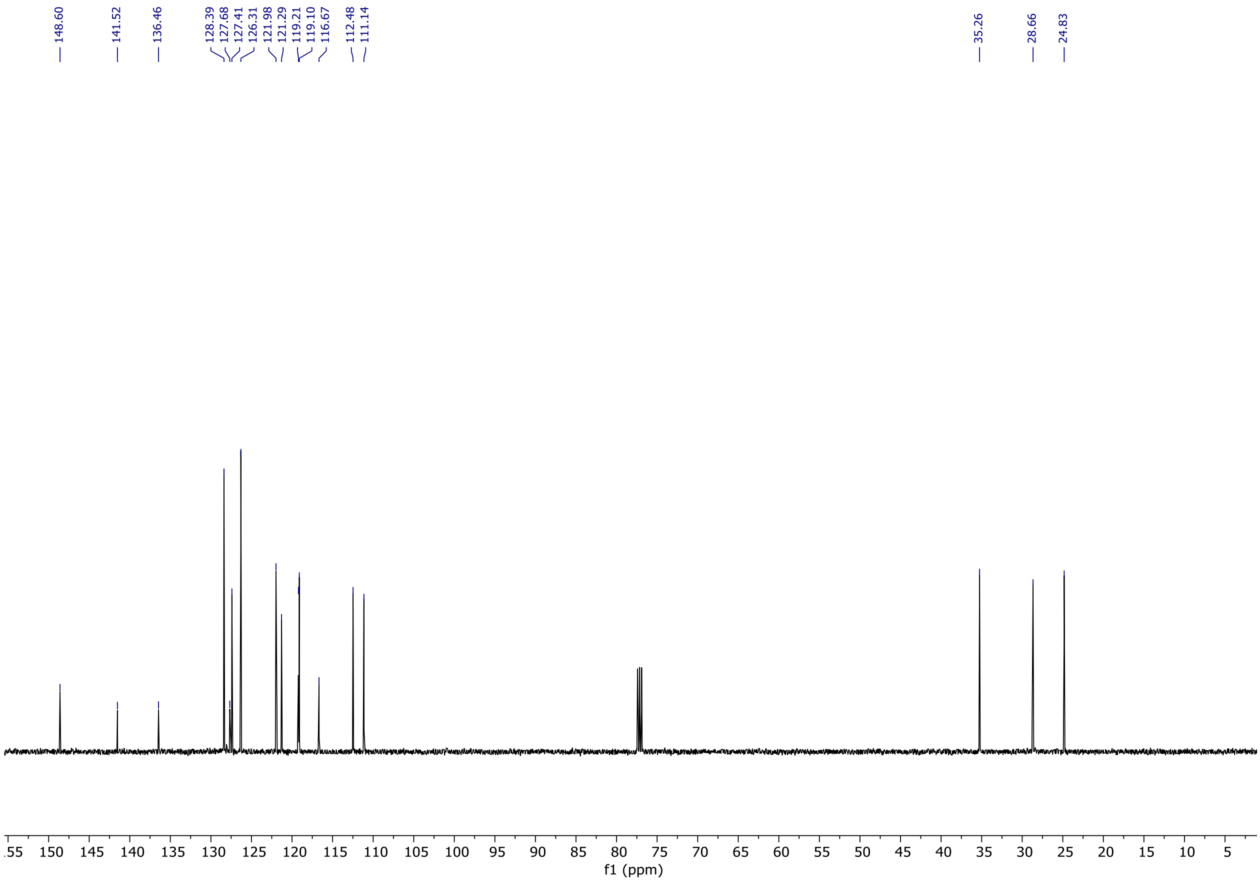
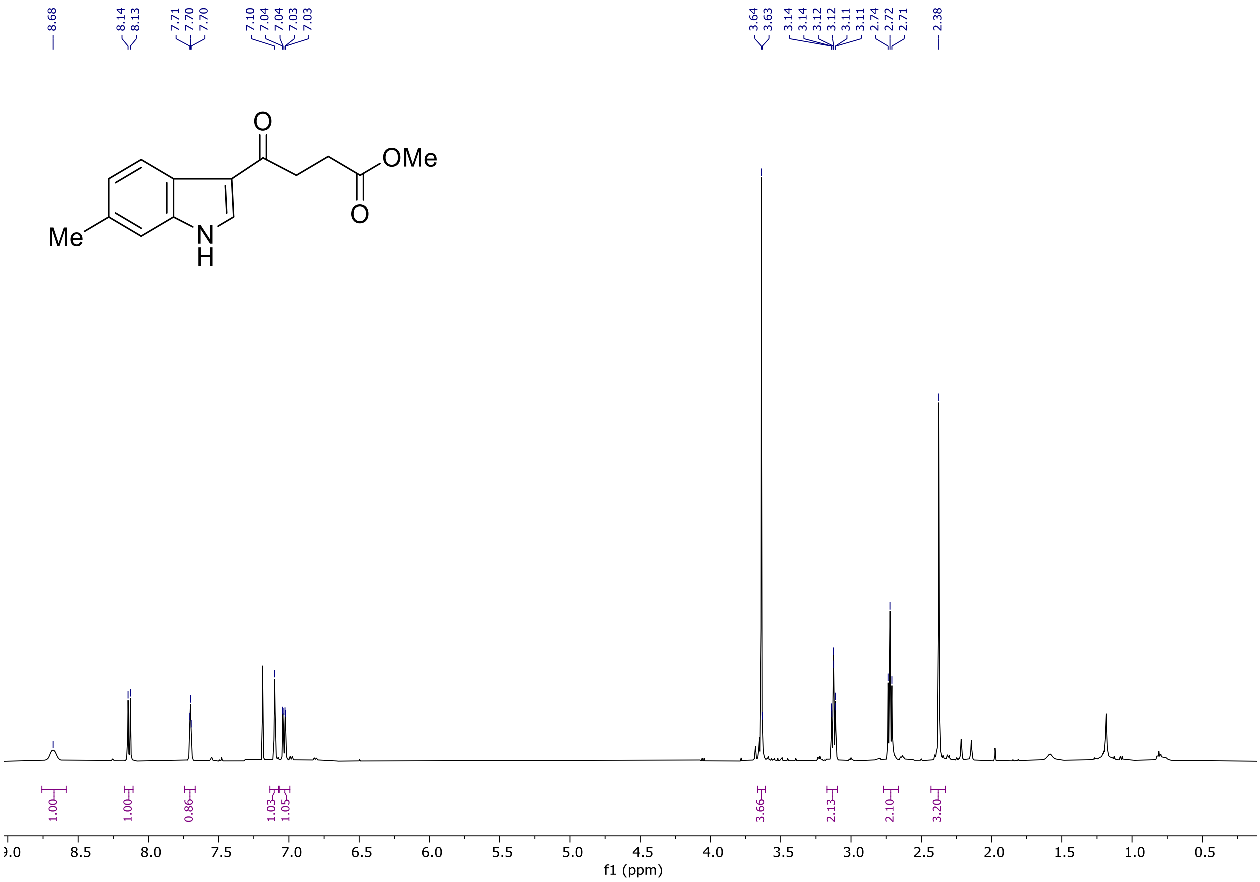


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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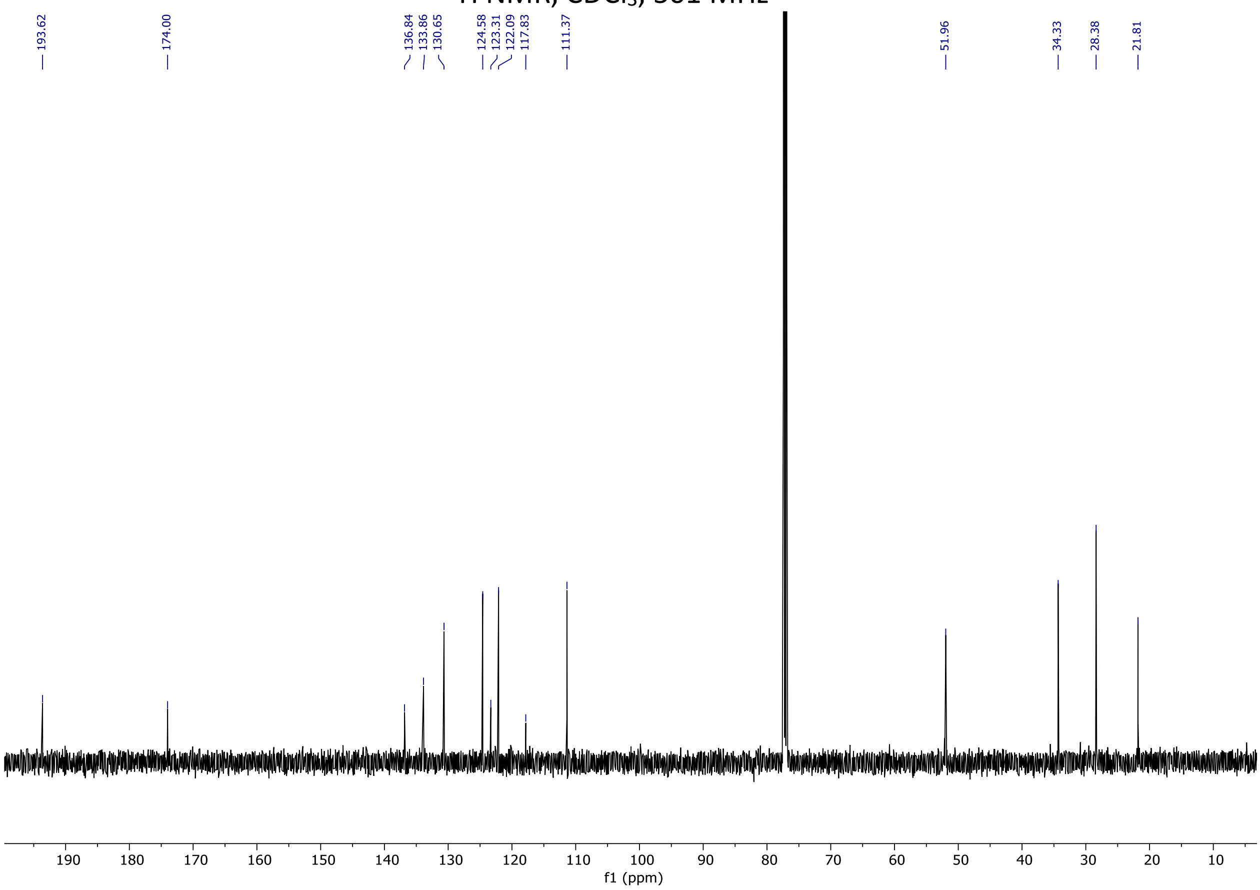
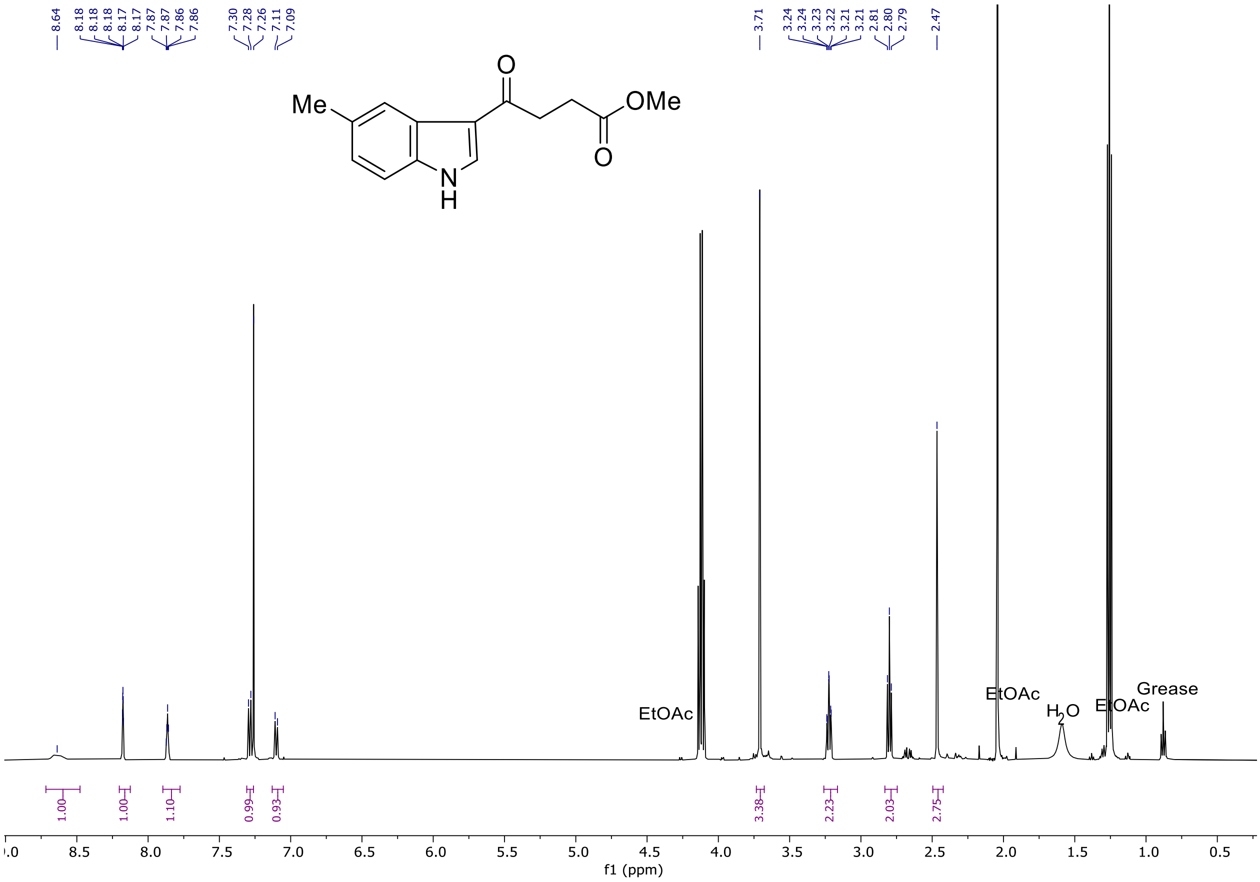
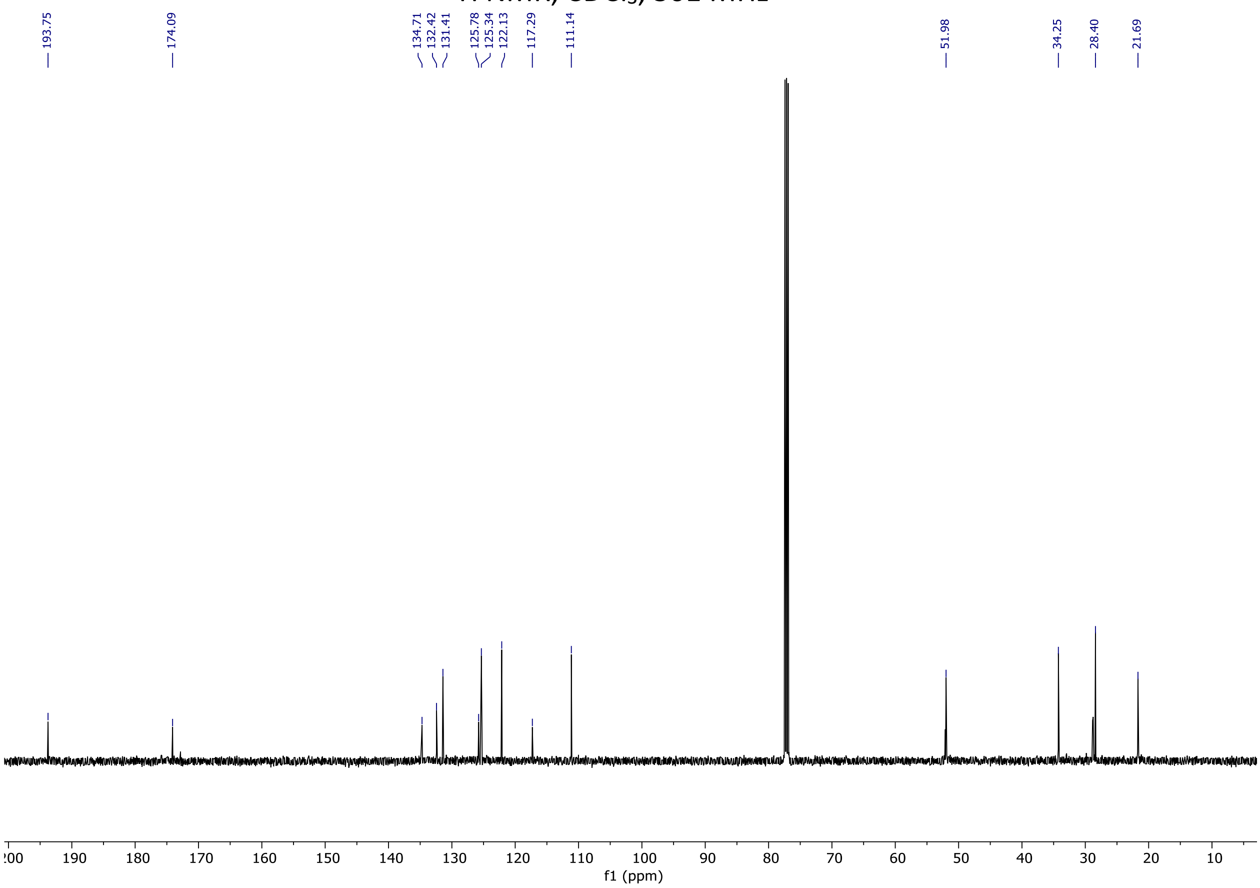


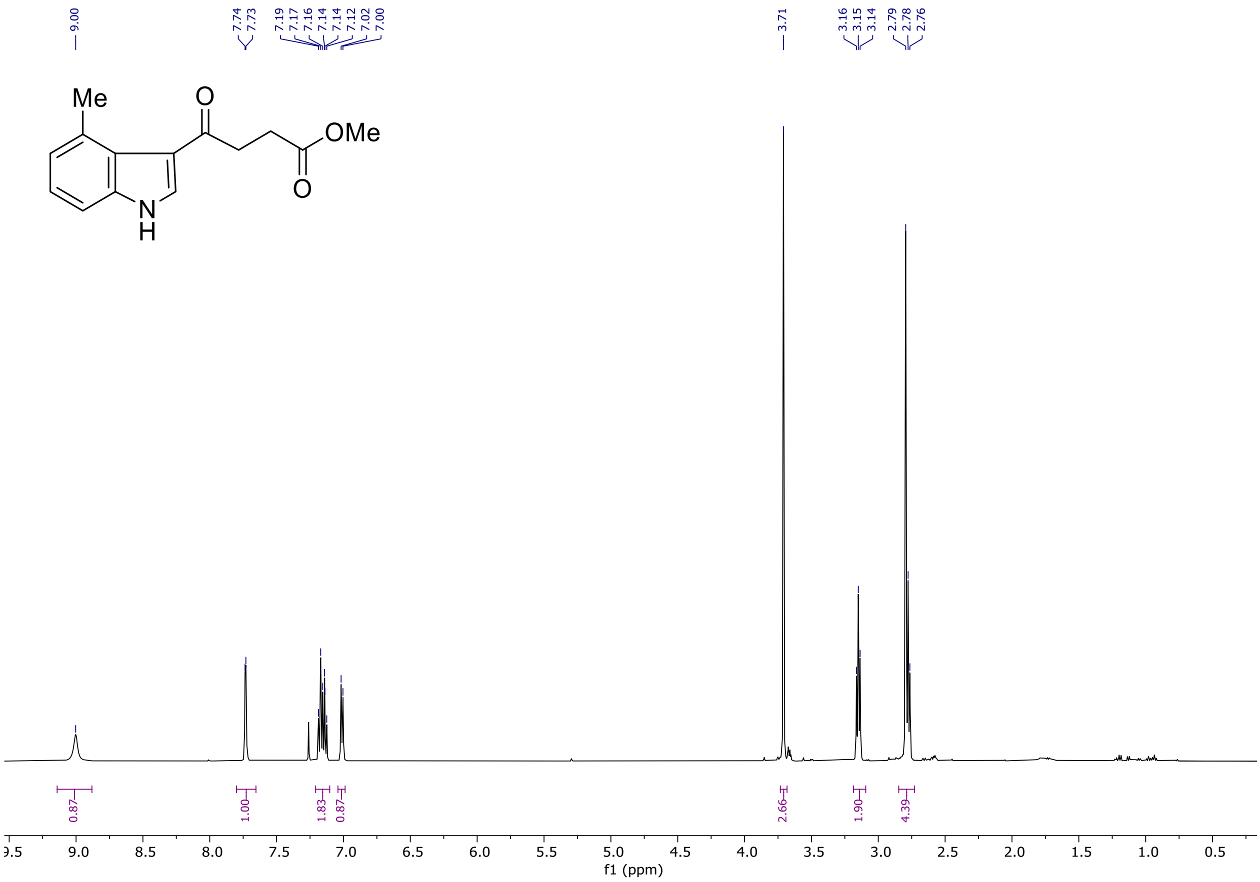
^{13}C NMR, $CDCl_3$, 126 MHz



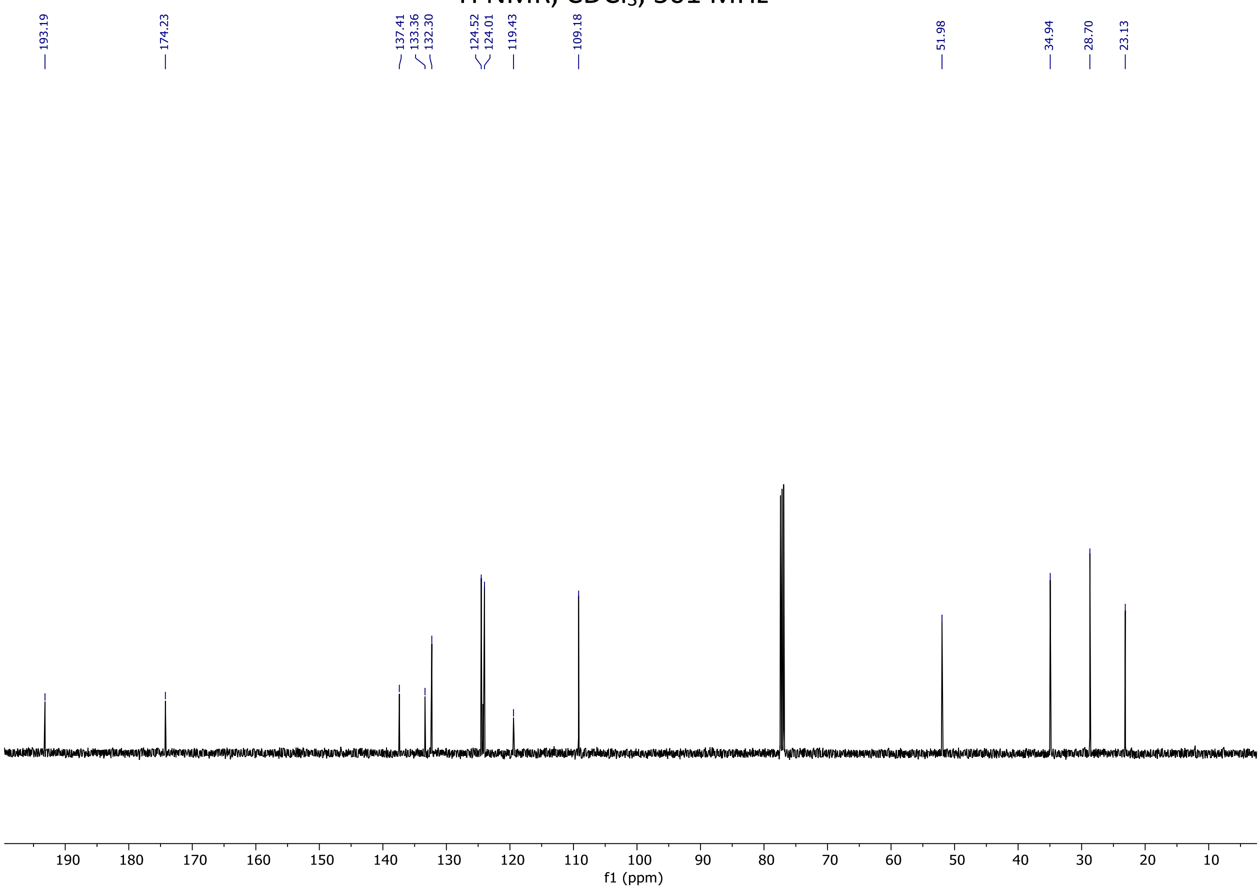
^{1}H NMR, $CDCl_3$, 501 MHz



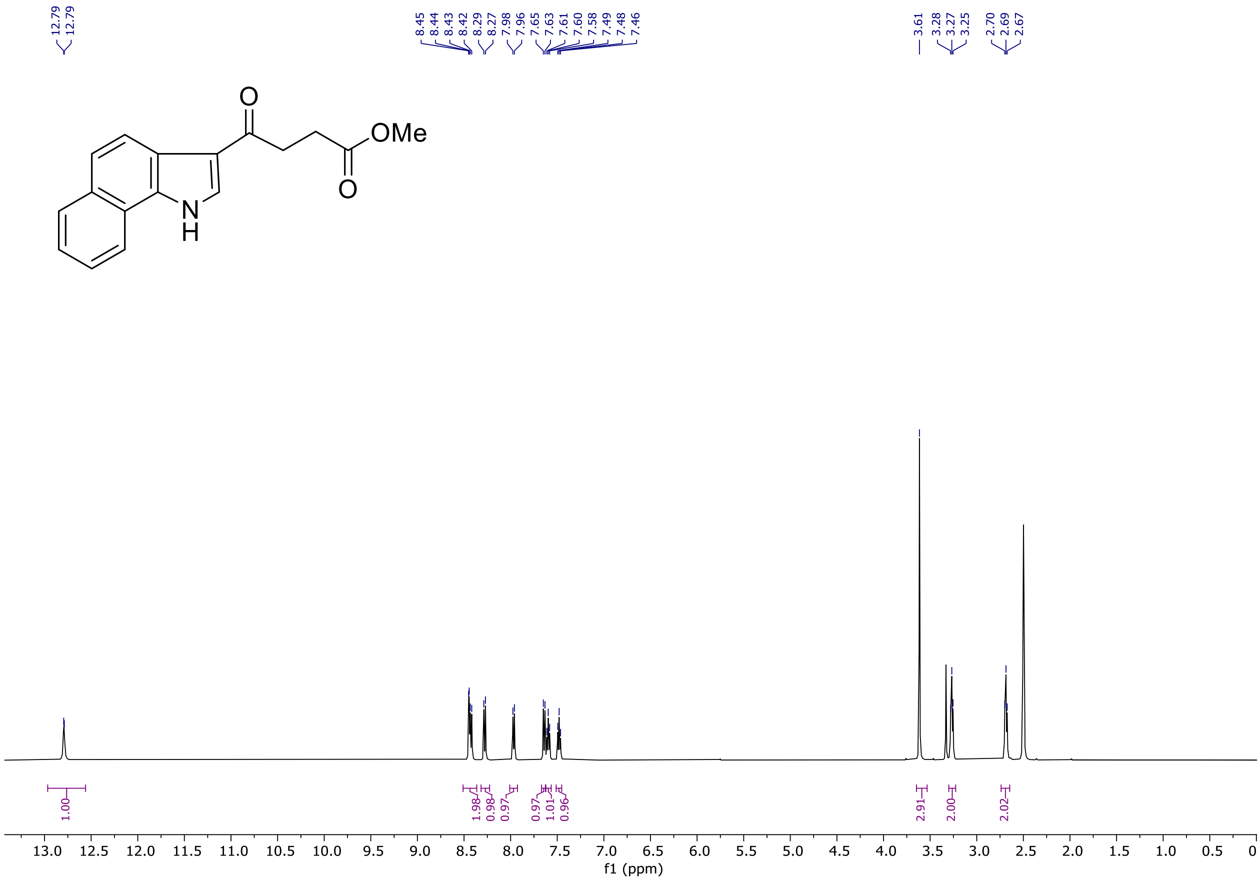
^{13}C NMR, $CDCl_3$, 126 MHz



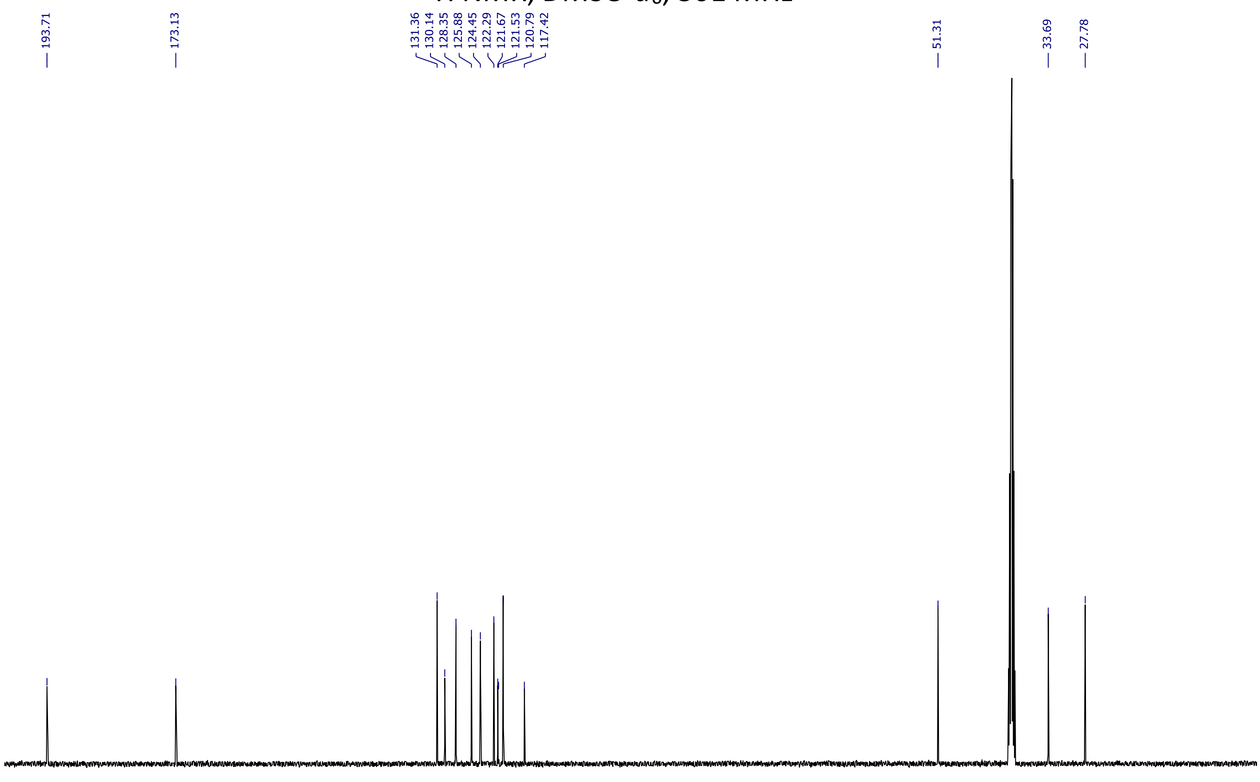
^{1}H NMR, $CDCl_3$, 501 MHz



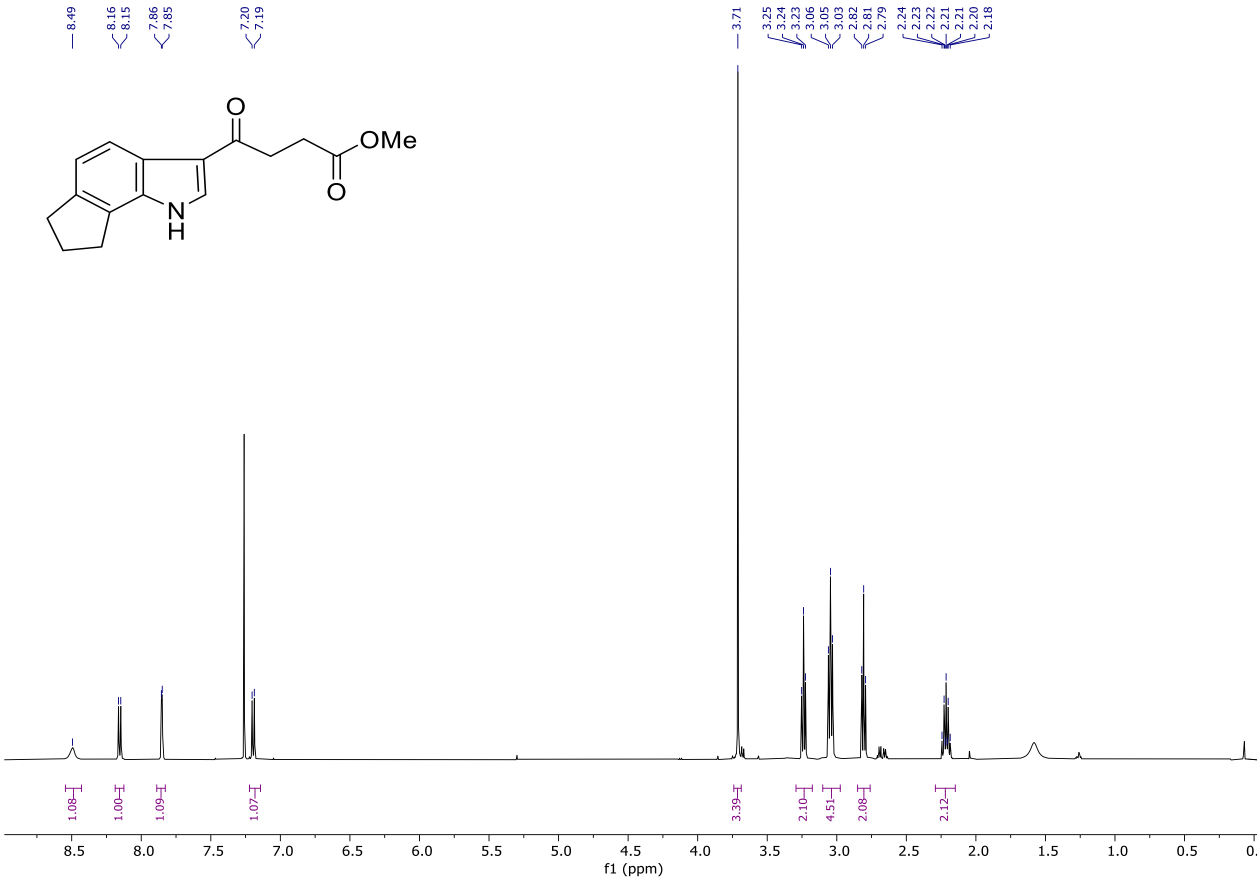
^{13}C NMR, $CDCl_3$, 126 MHz



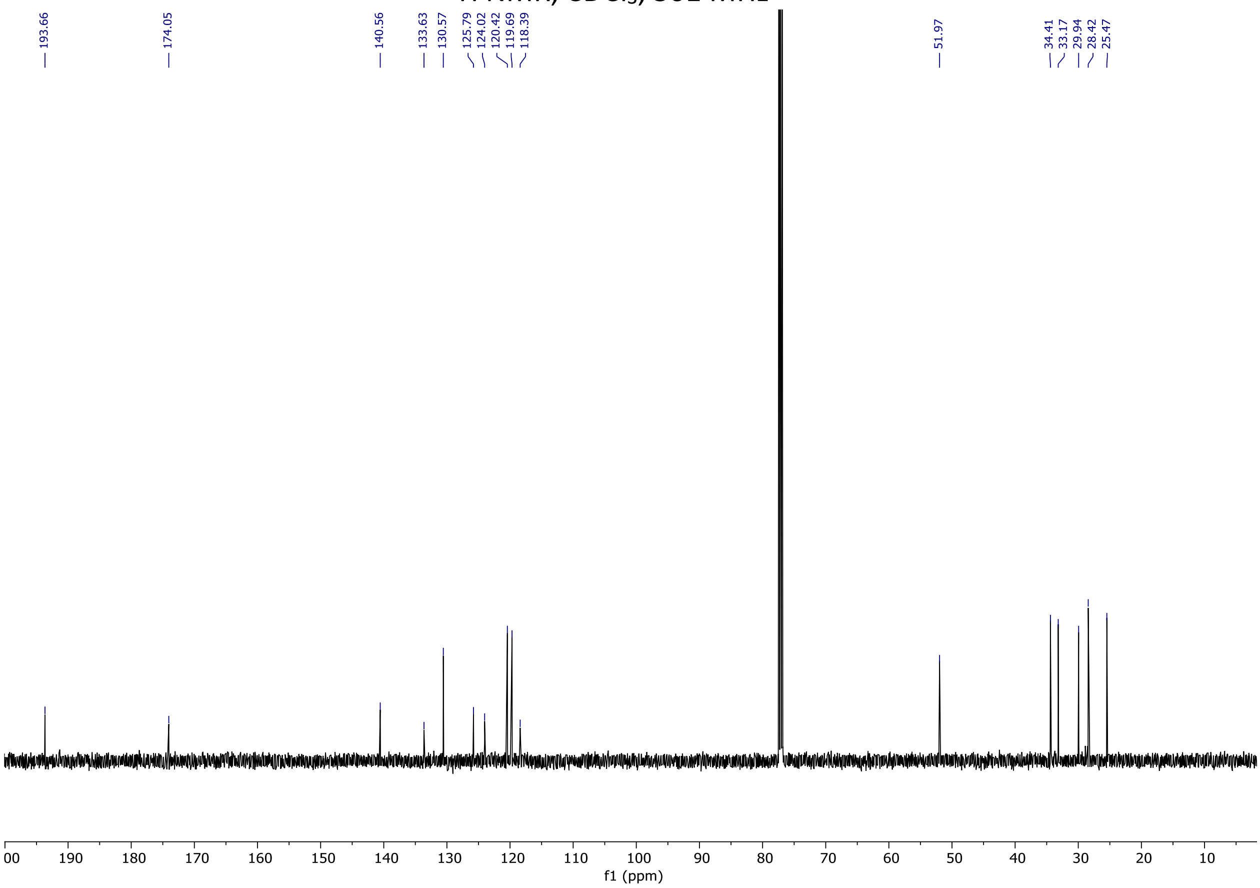
^{1}H NMR, DMSO-d_6, 501 MHz



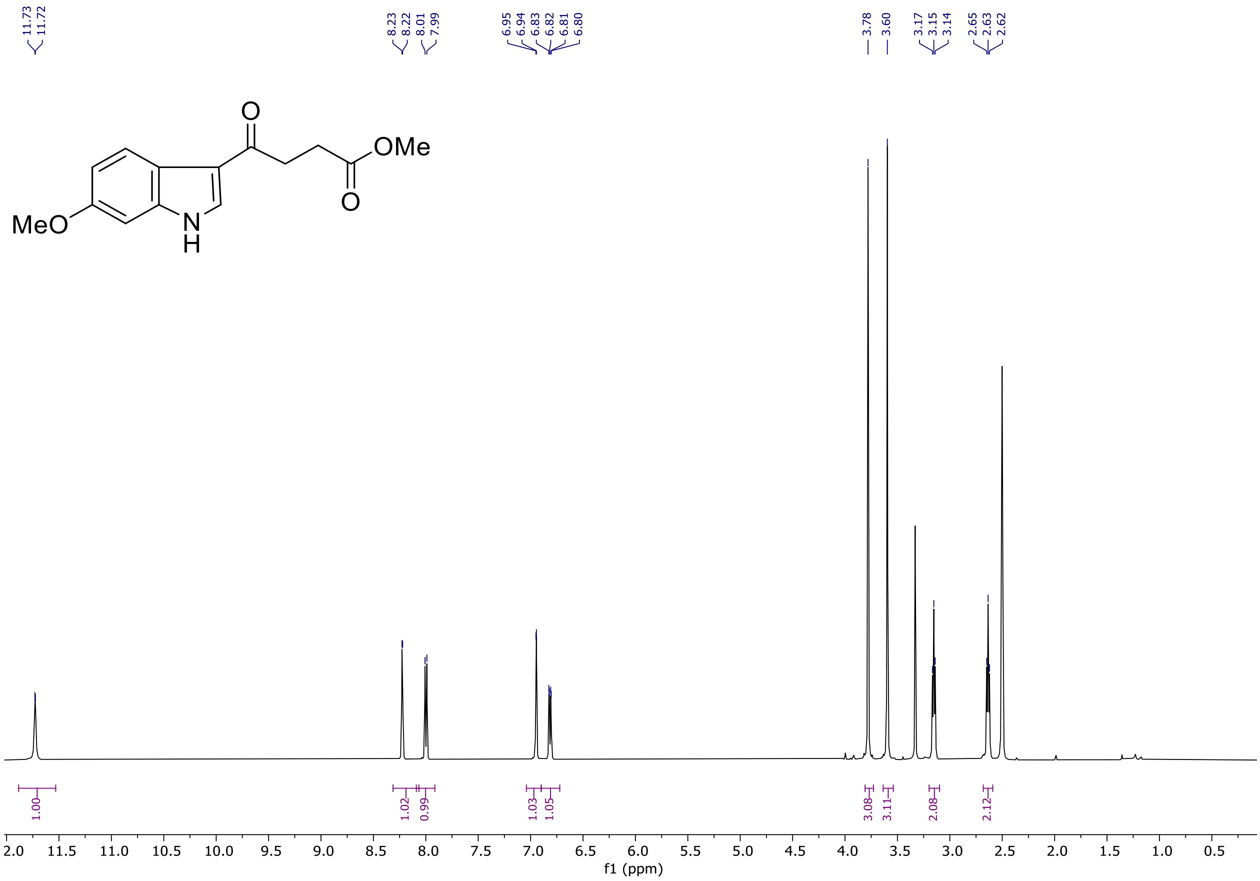
^{13}C NMR, DMSO-d_6, 126 MHz



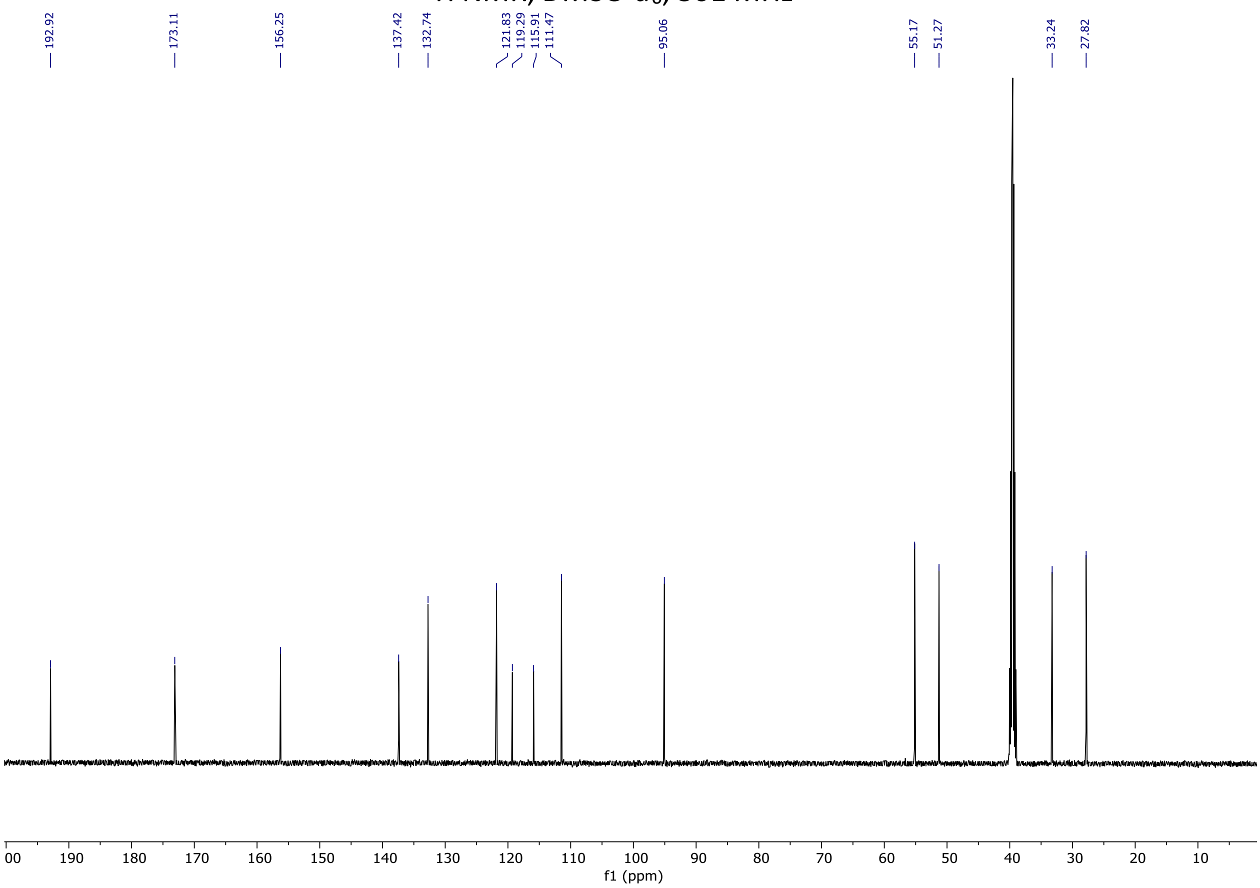
^{1}H NMR, $CDCl_3$, 501 MHz



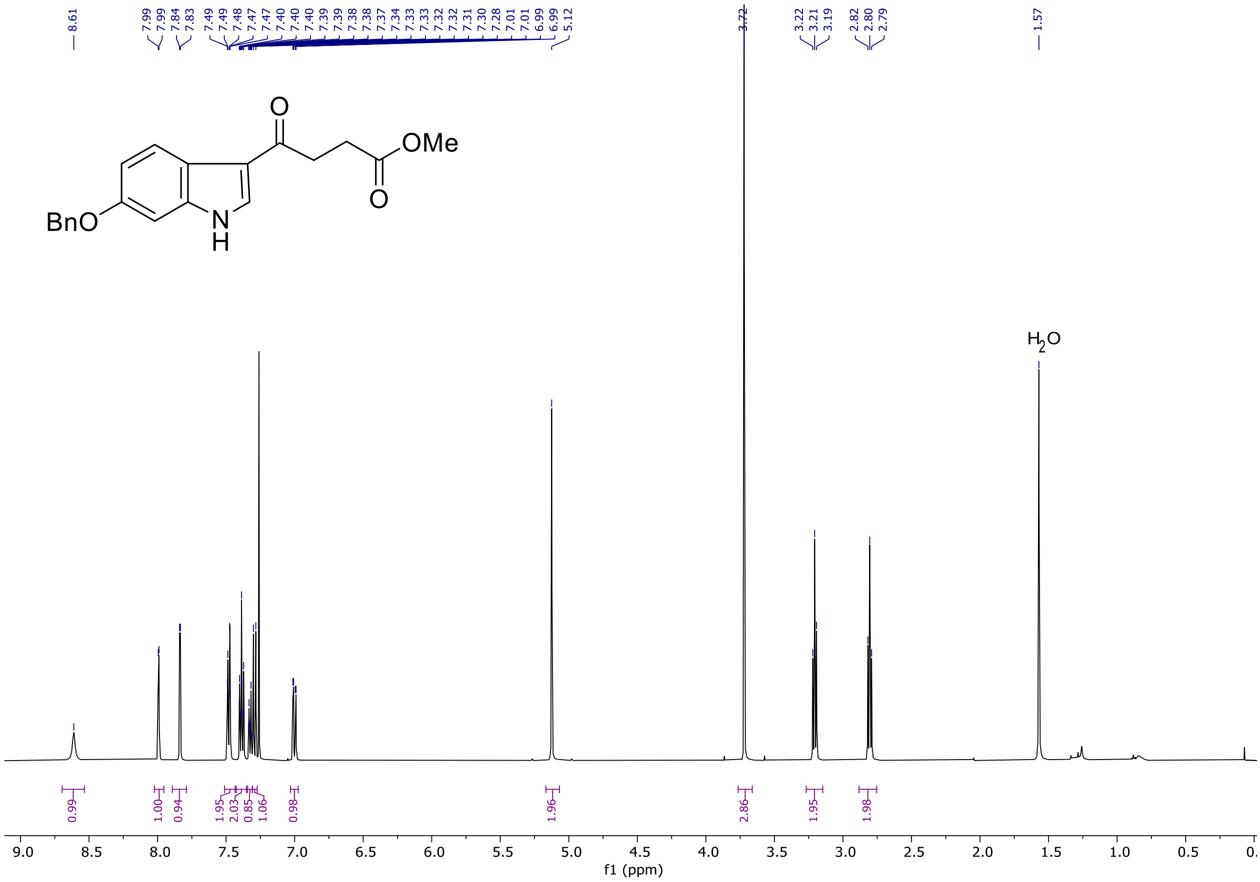
^{13}C NMR, $CDCl_3$, 126 MHz



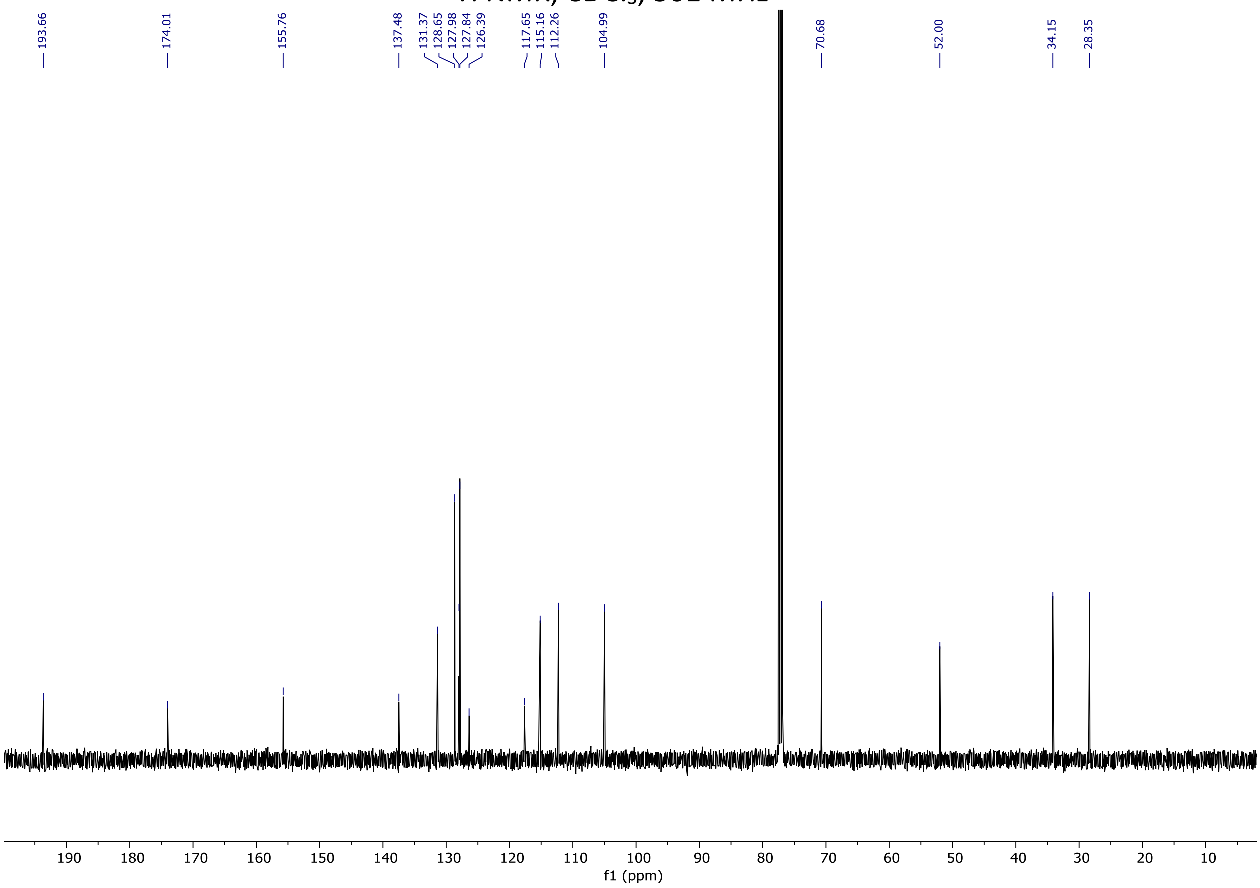
^{1}H NMR, DMSO-d_6, 501 MHz



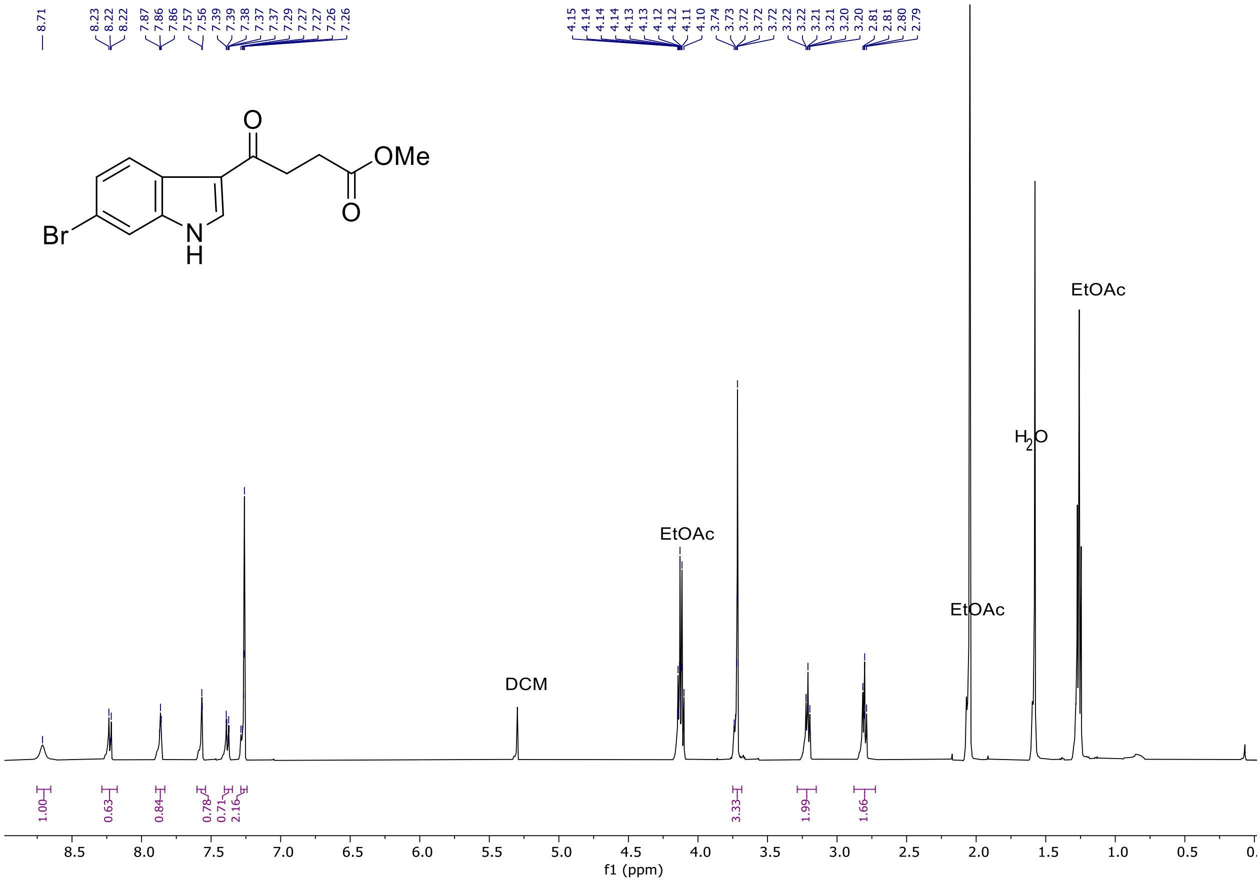
^{13}C NMR, DMSO-d_6, 126 MHz



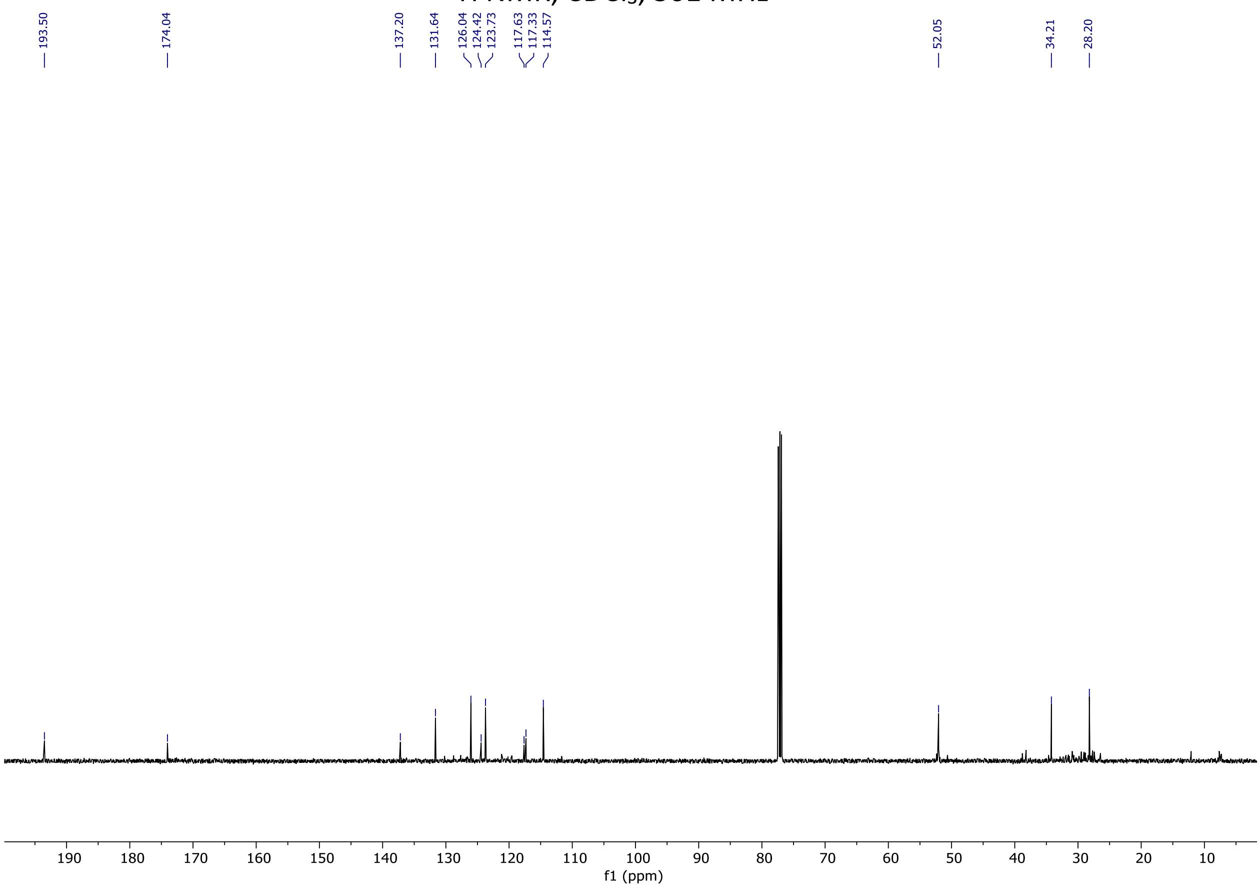
^{1}H NMR, $CDCl_3$, 501 MHz



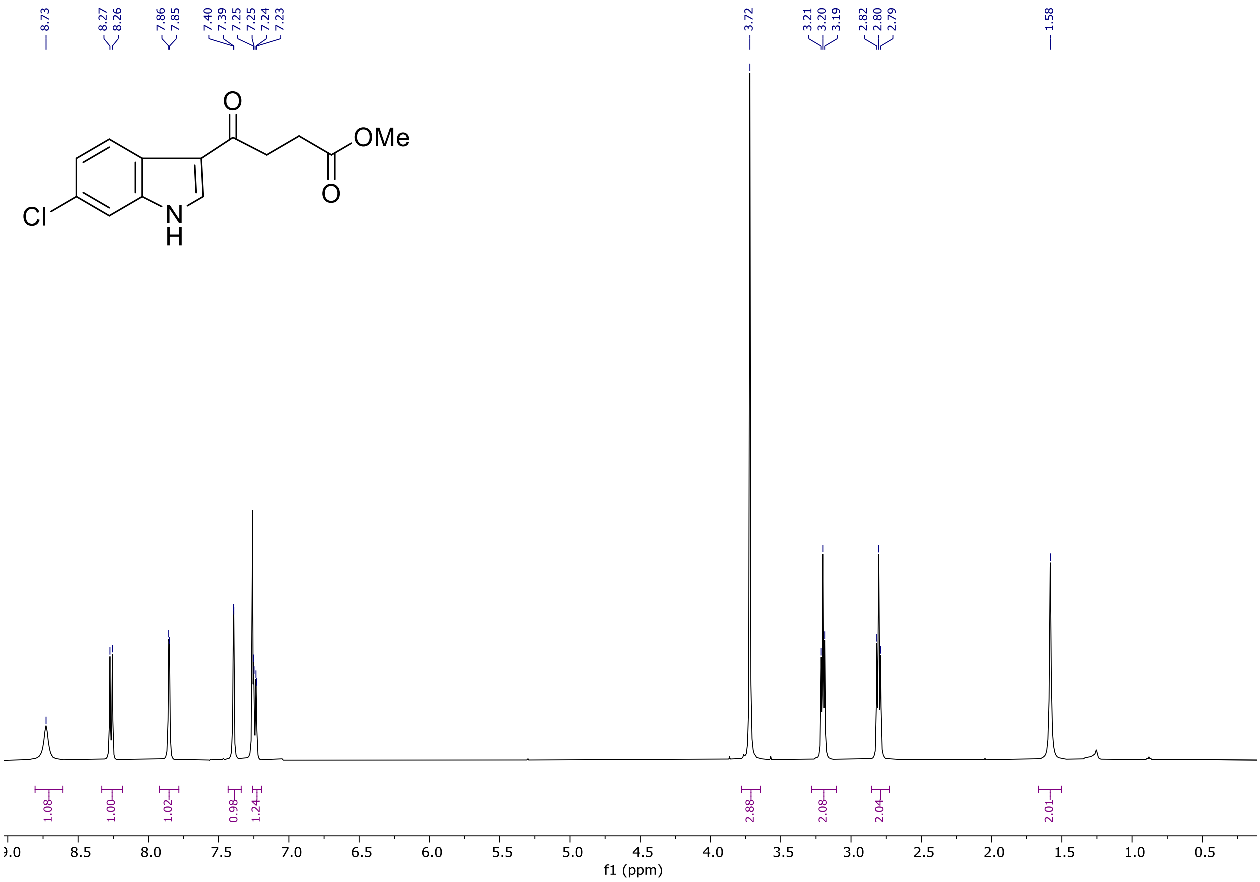
^{13}C NMR, $CDCl_3$, 126 MHz



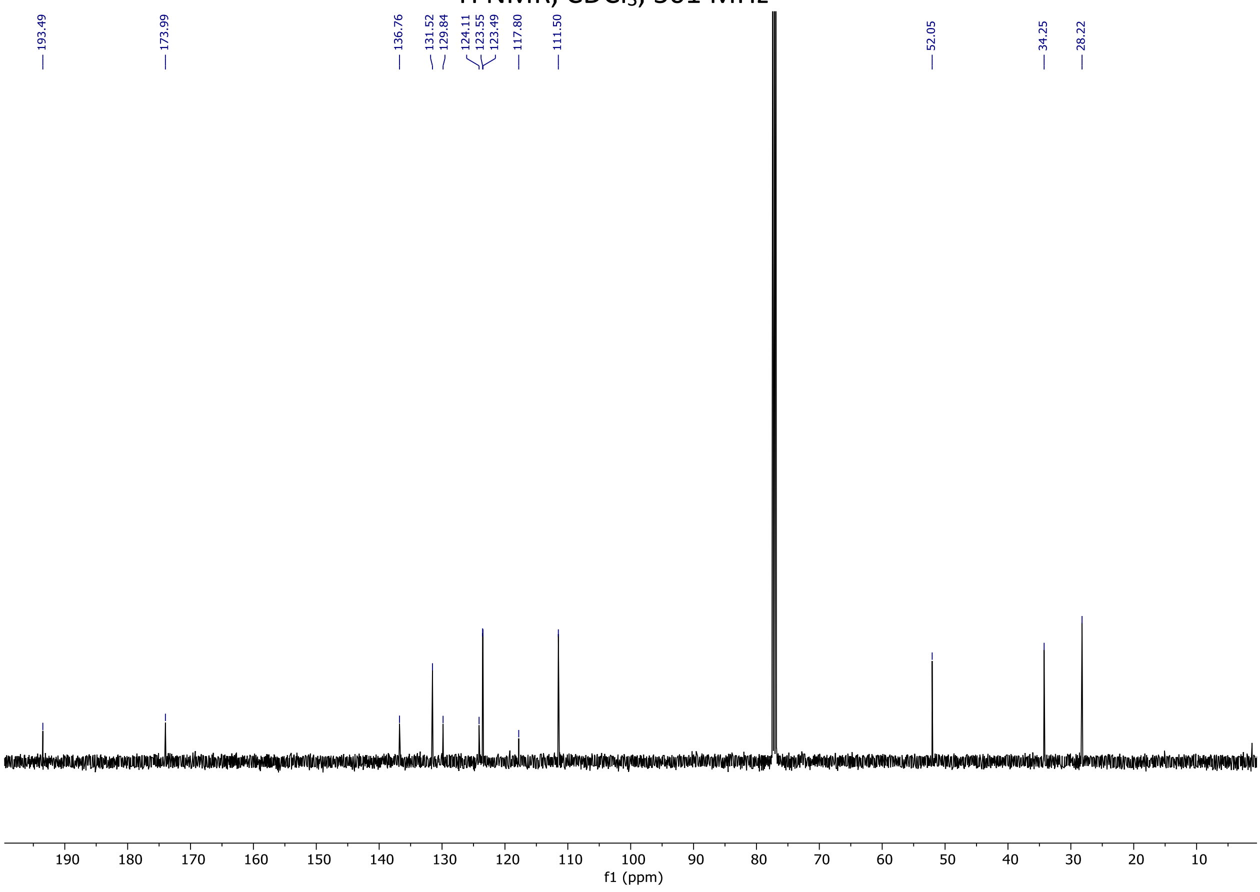
[1]H NMR, $CDCl_3$, 501 MHz



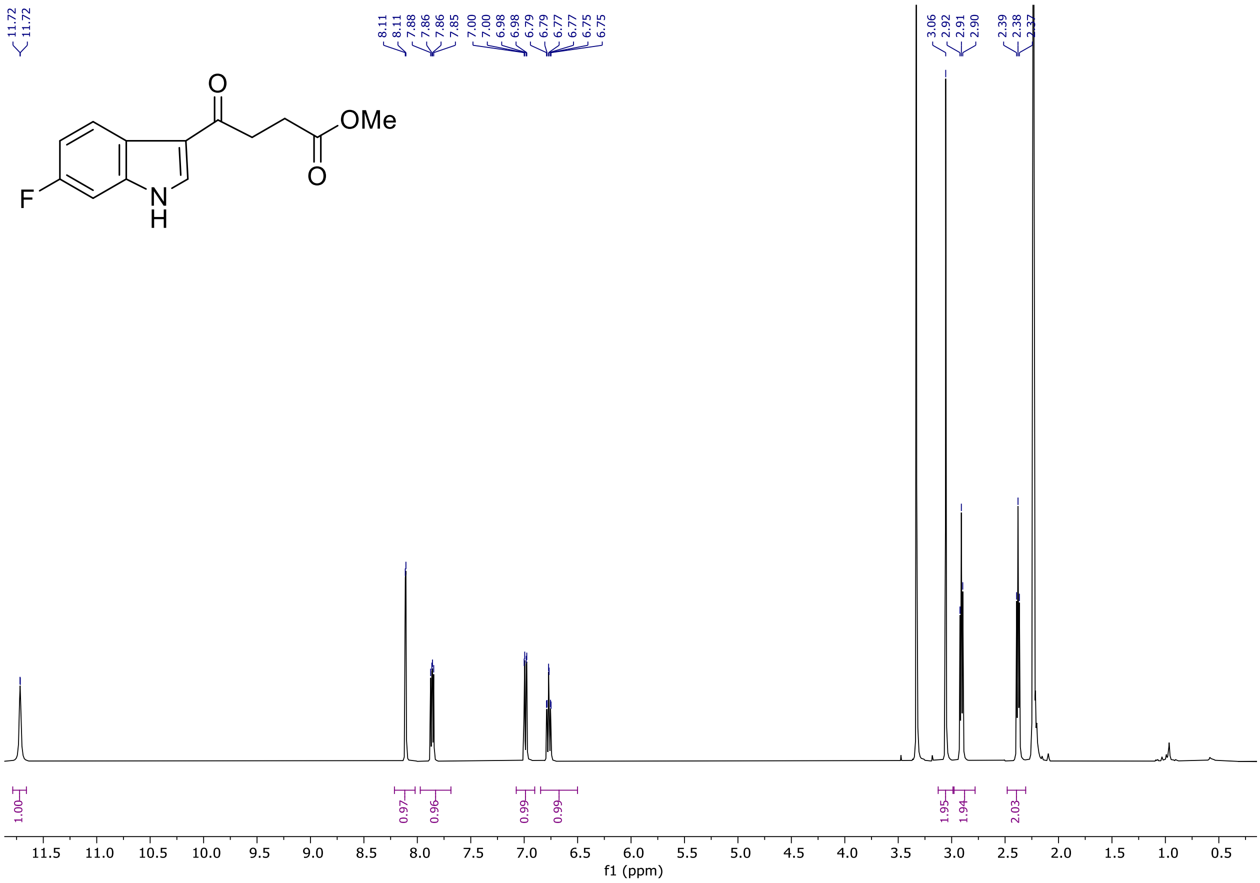
[13]C NMR, $CDCl_3$, 126 MHz



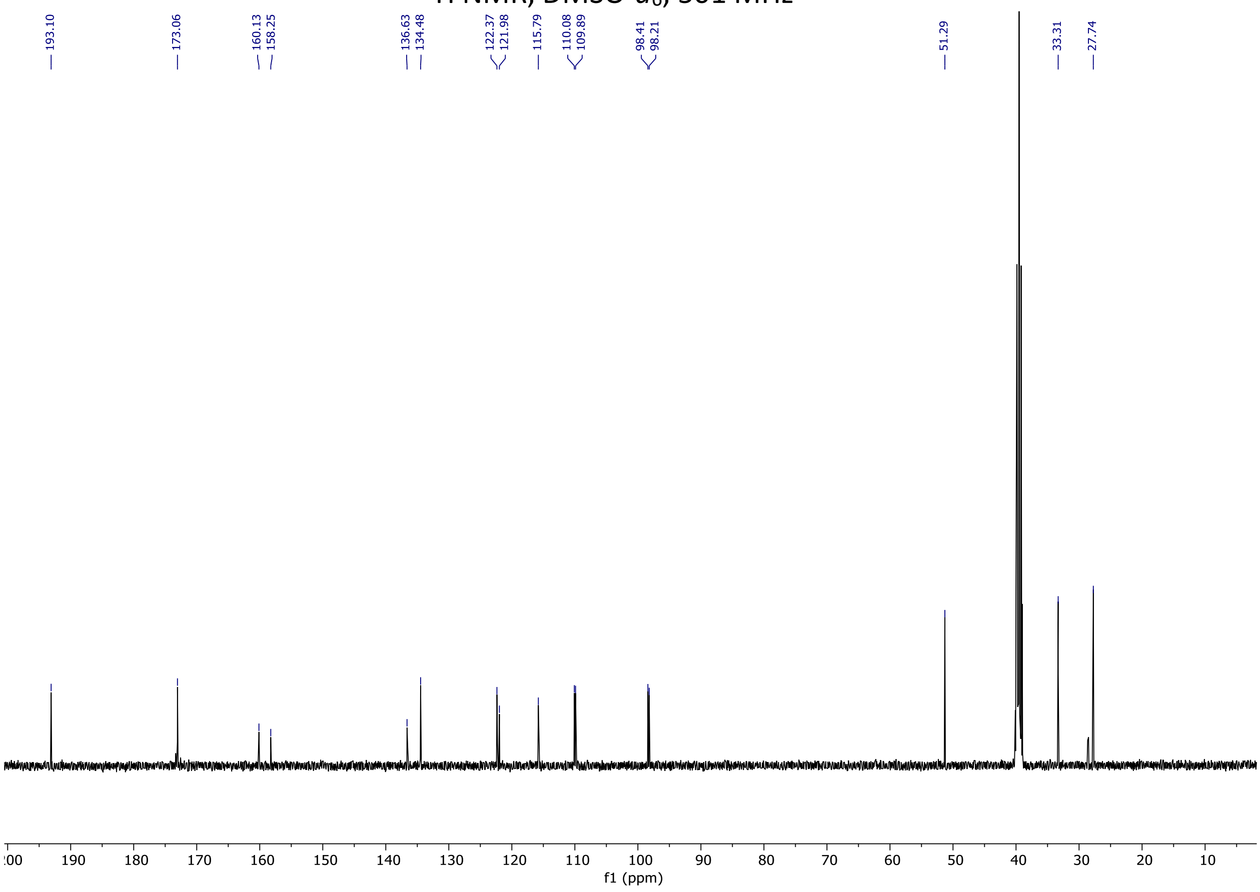
^{1}H NMR, $CDCl_3$, 501 MHz



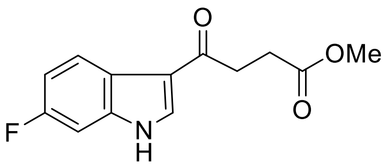
^{13}C NMR, $CDCl_3$, 126 MHz

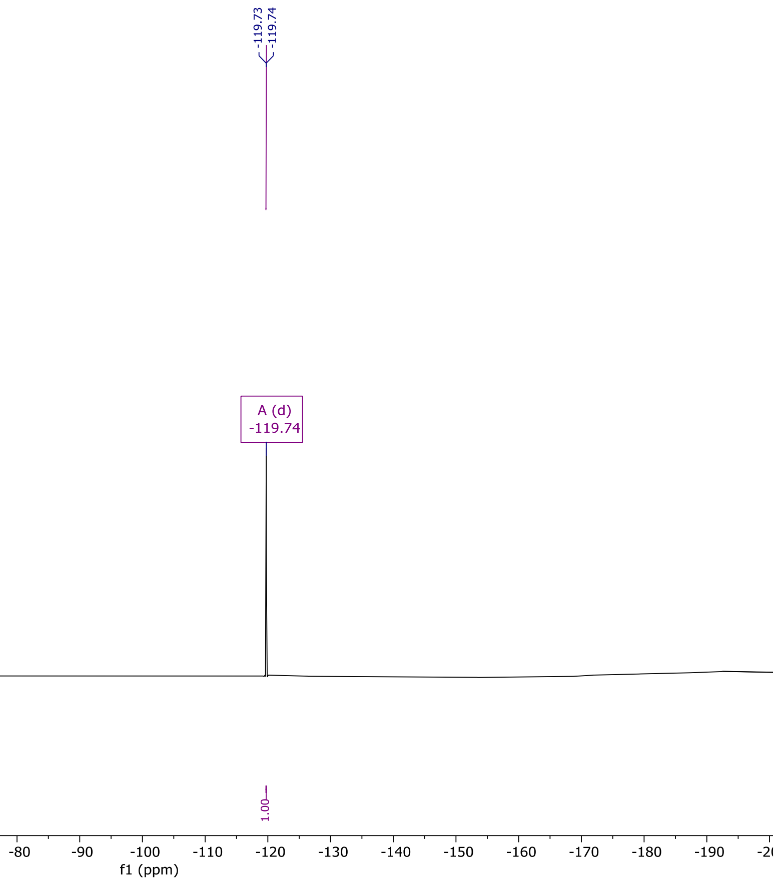


^{1}H NMR, DMSO-d_6, 501 MHz

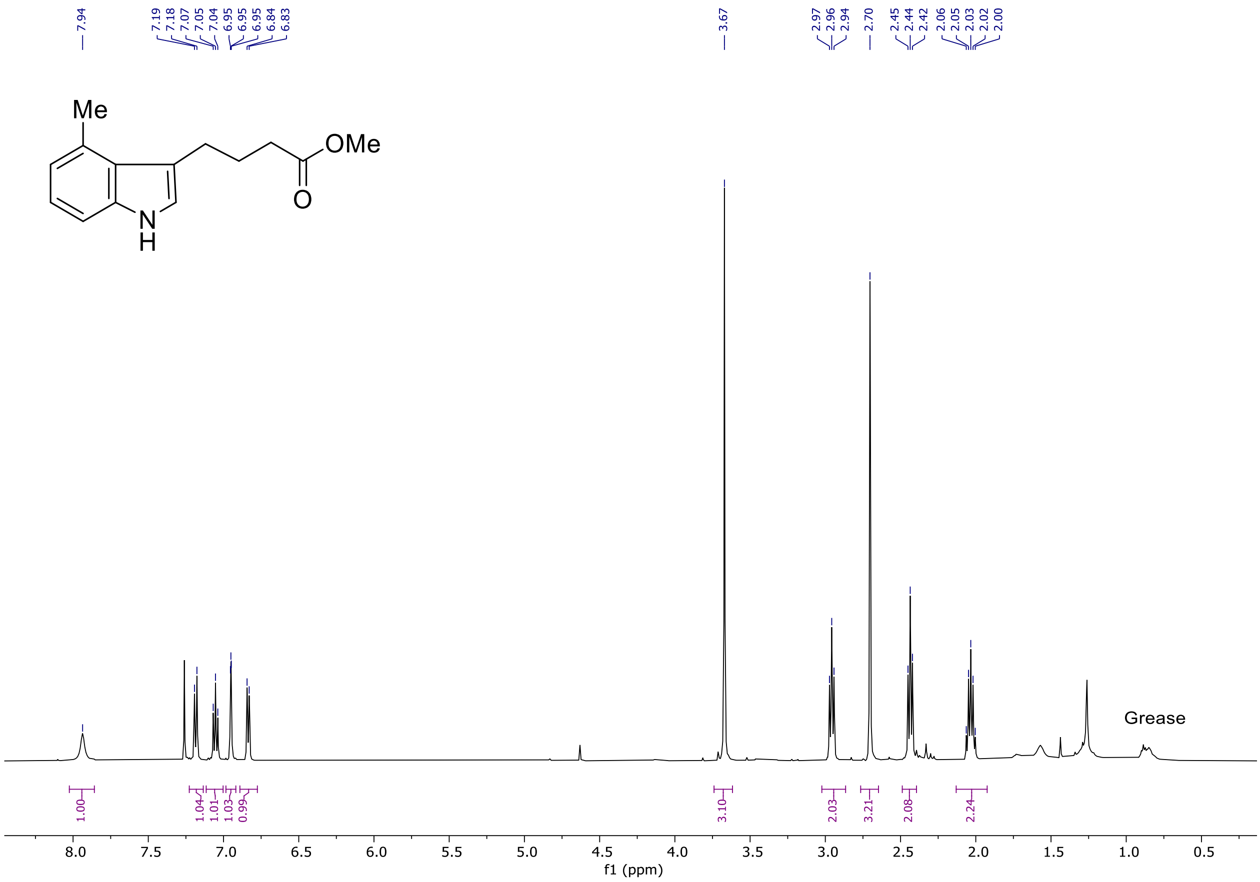


^{13}C NMR, DMSO-d_6, 126 MHz

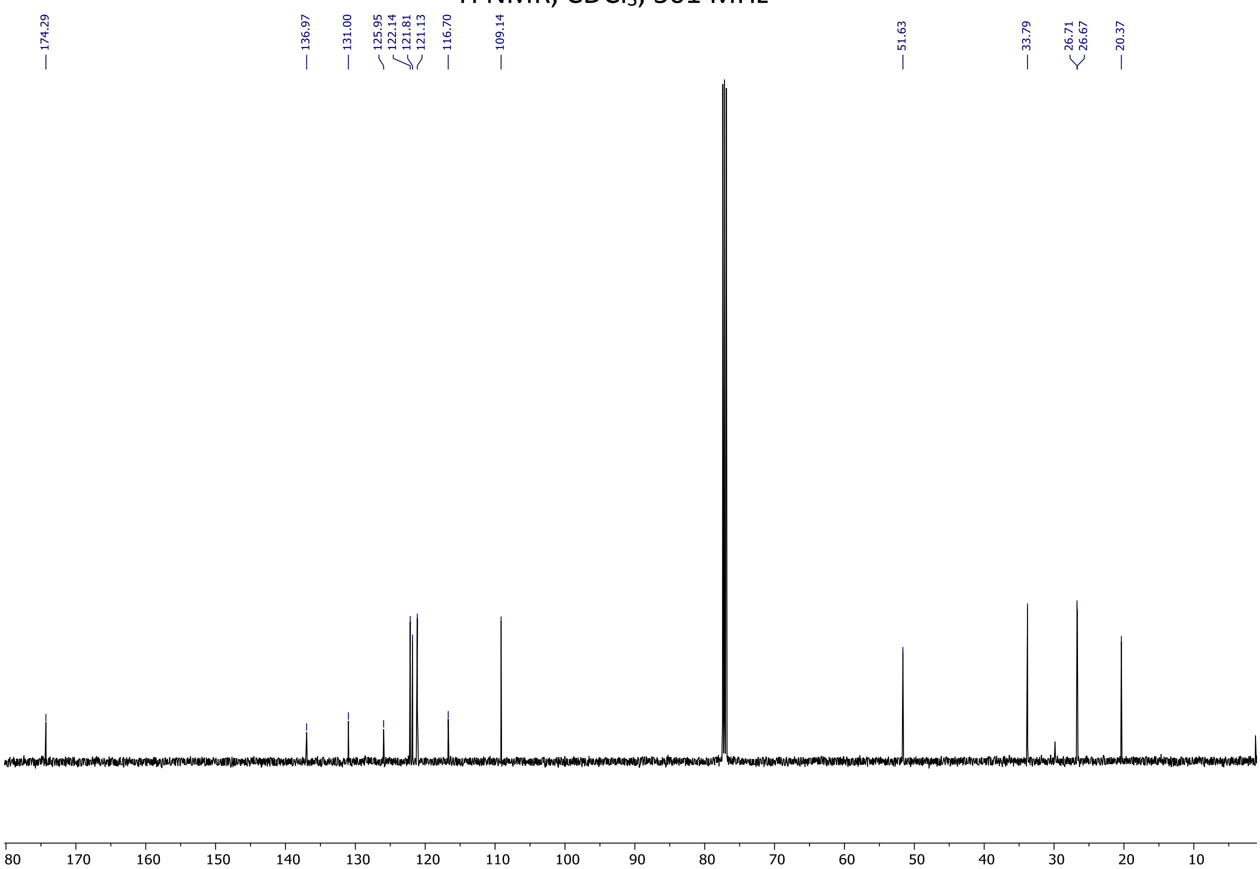




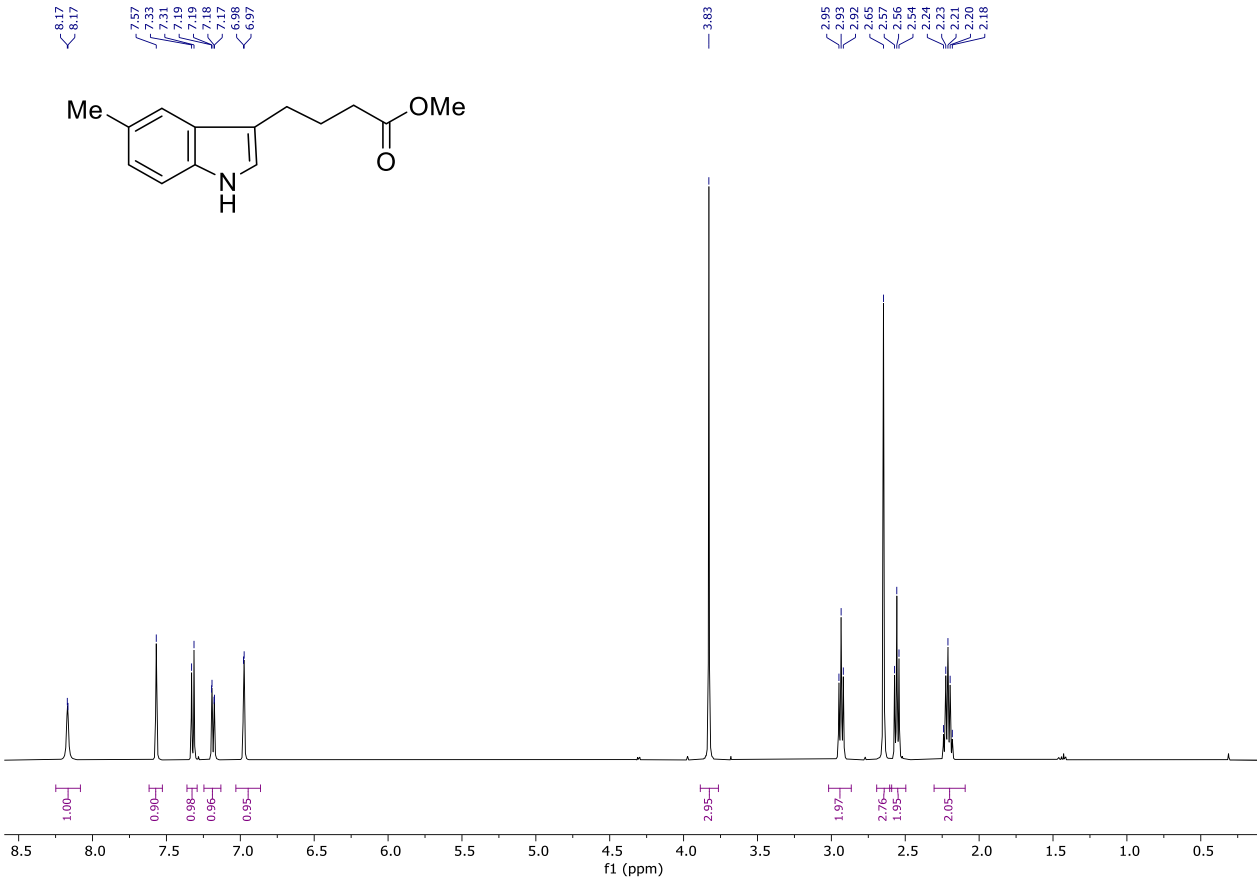
^{19}F NMR, DMSO-d_6, 471 MHz



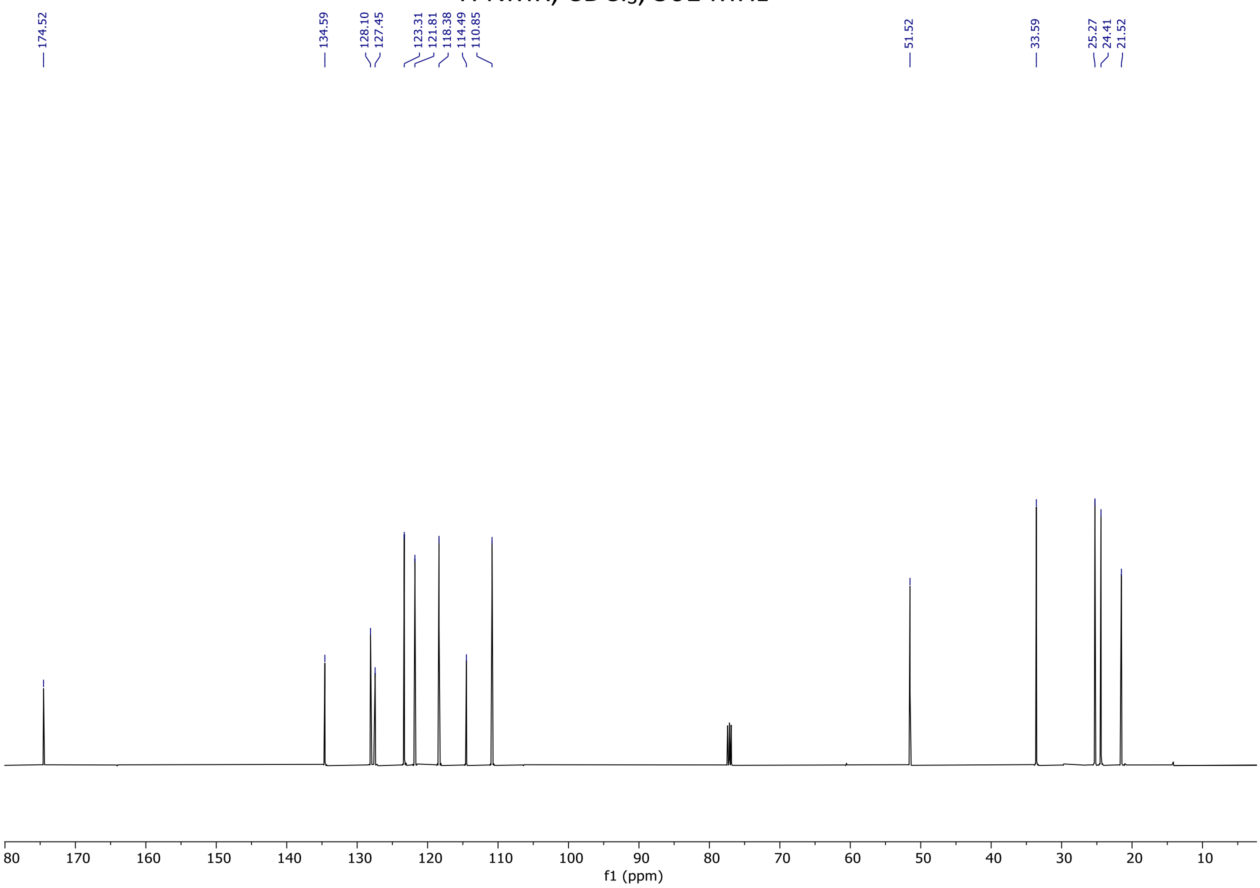
^{1}H NMR, $CDCl_3$, 501 MHz



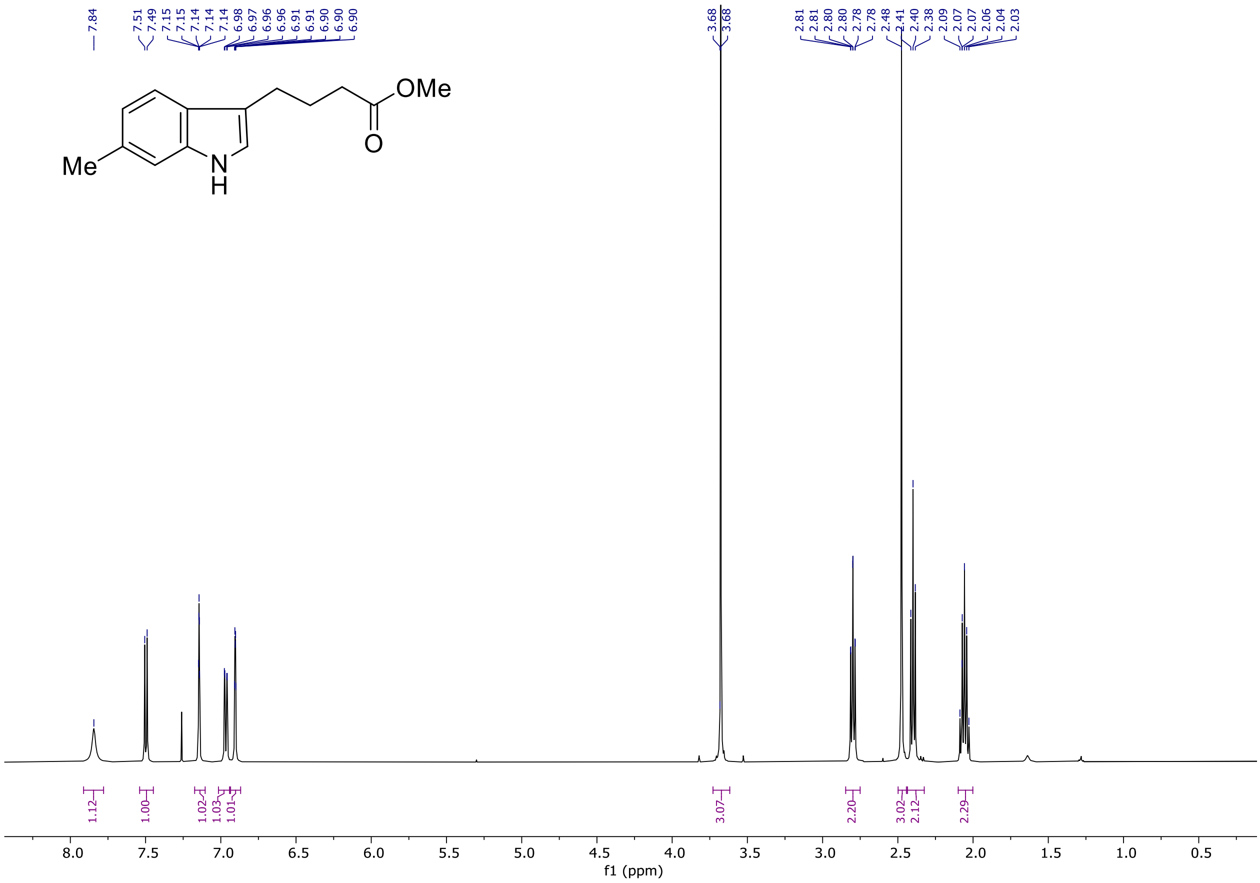
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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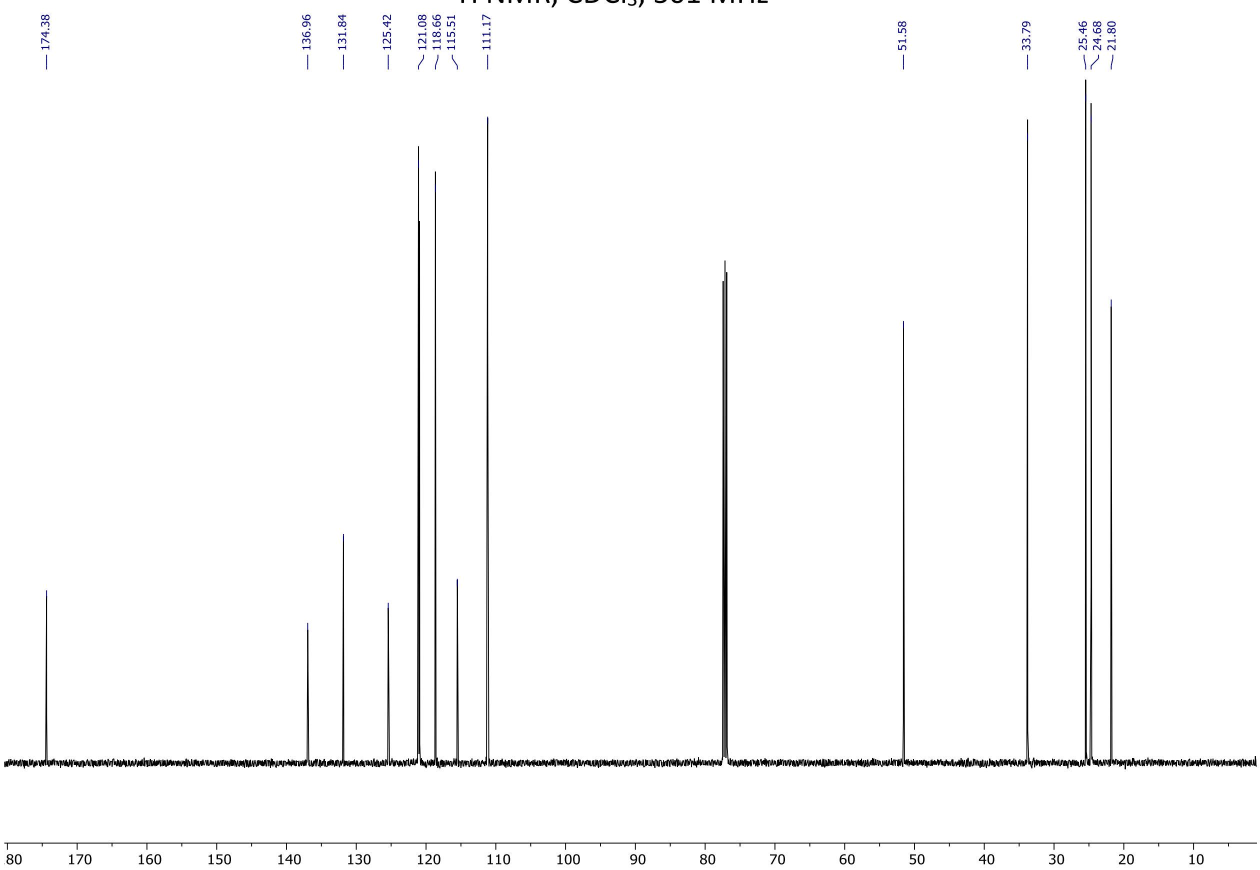

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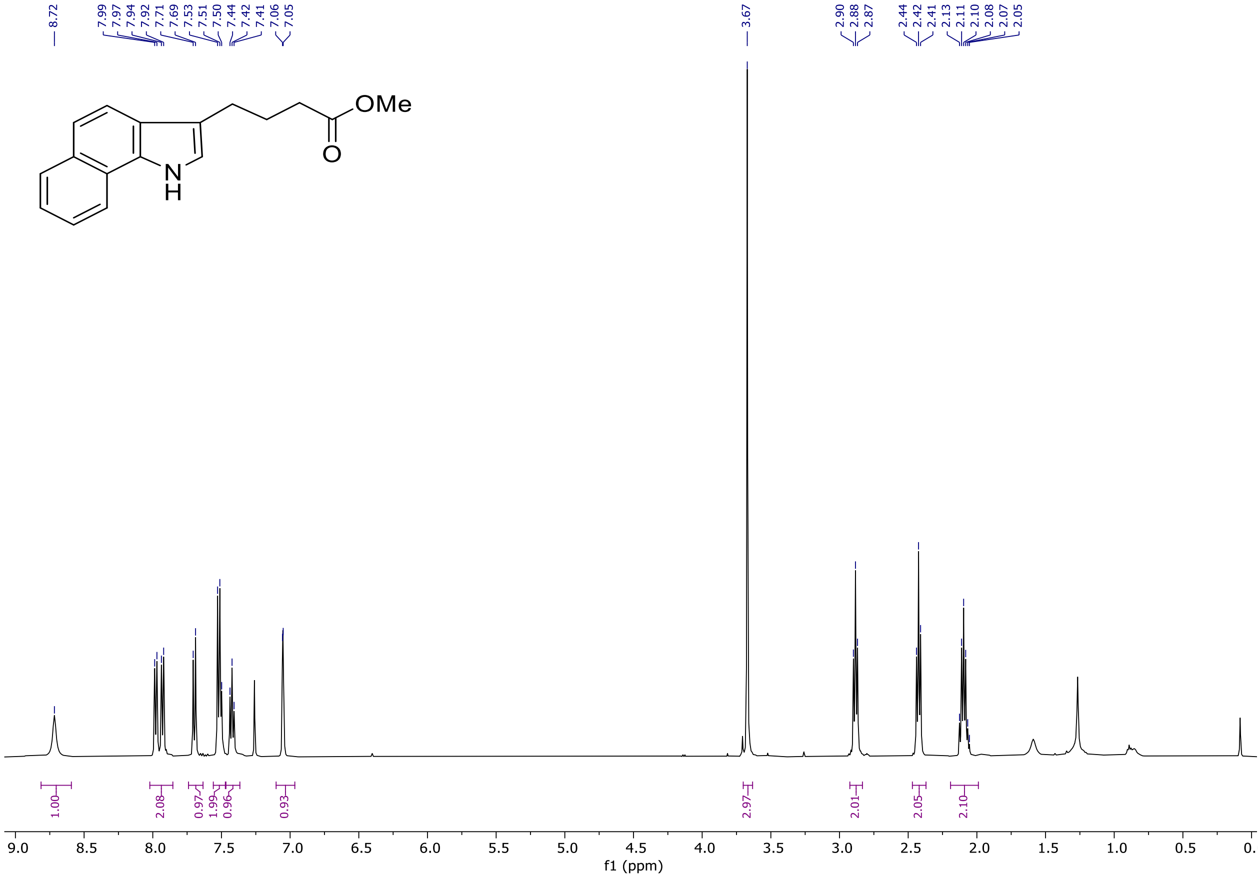

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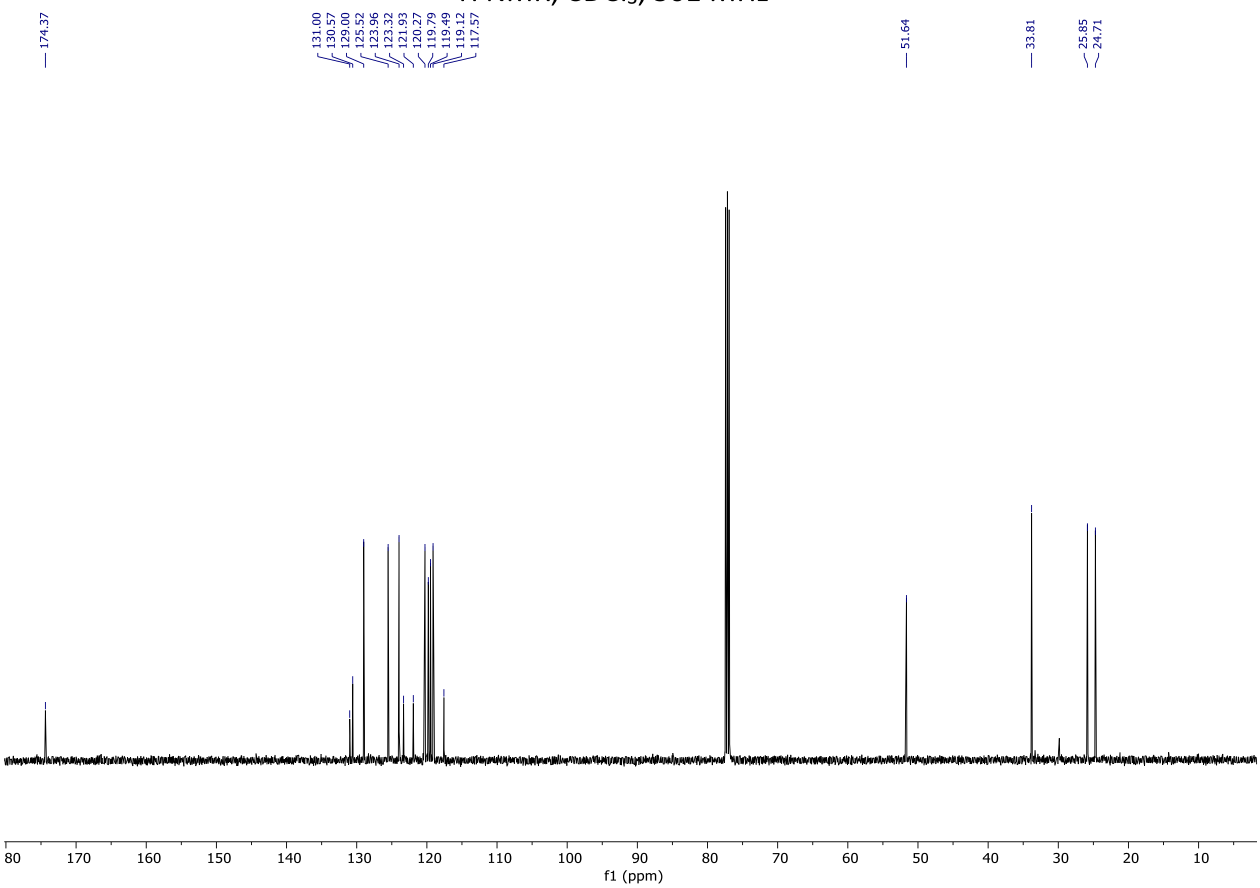
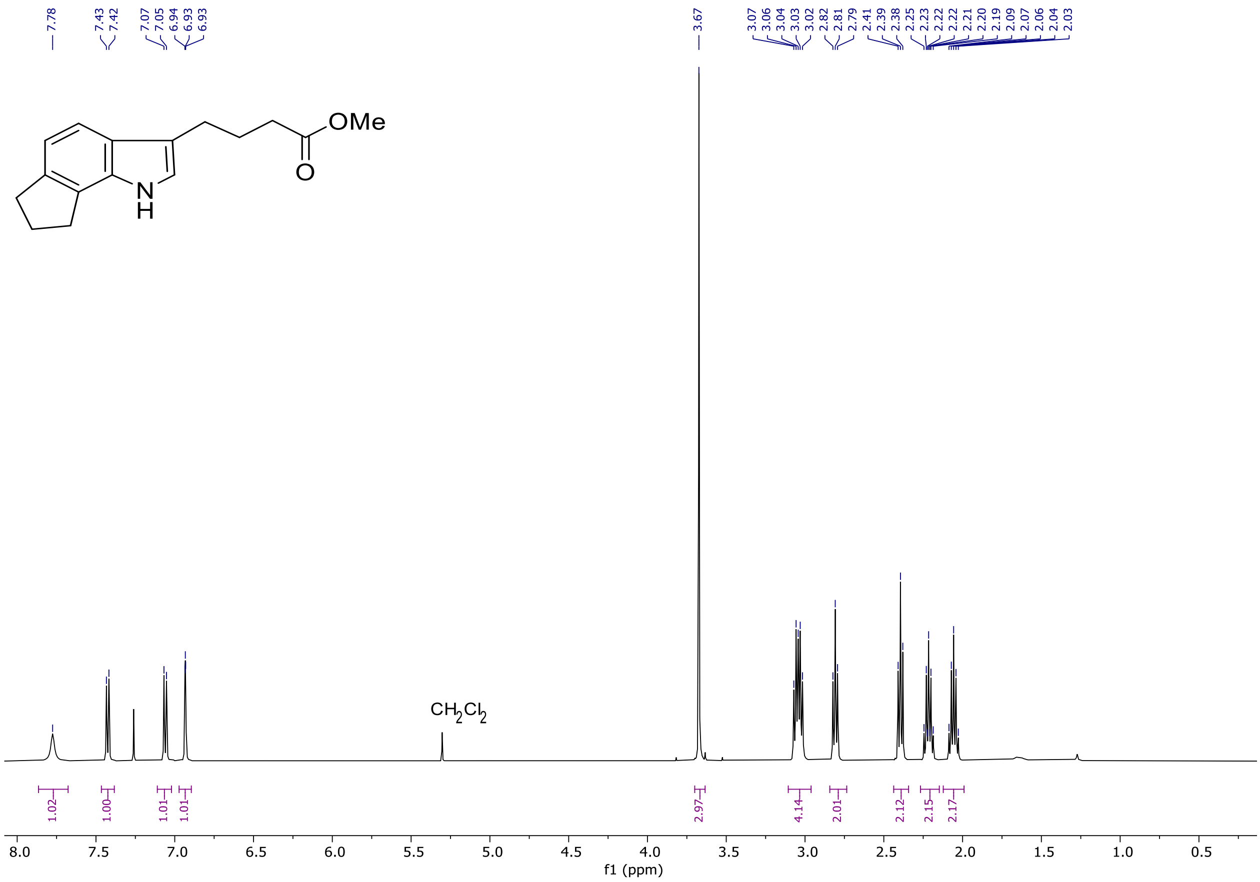
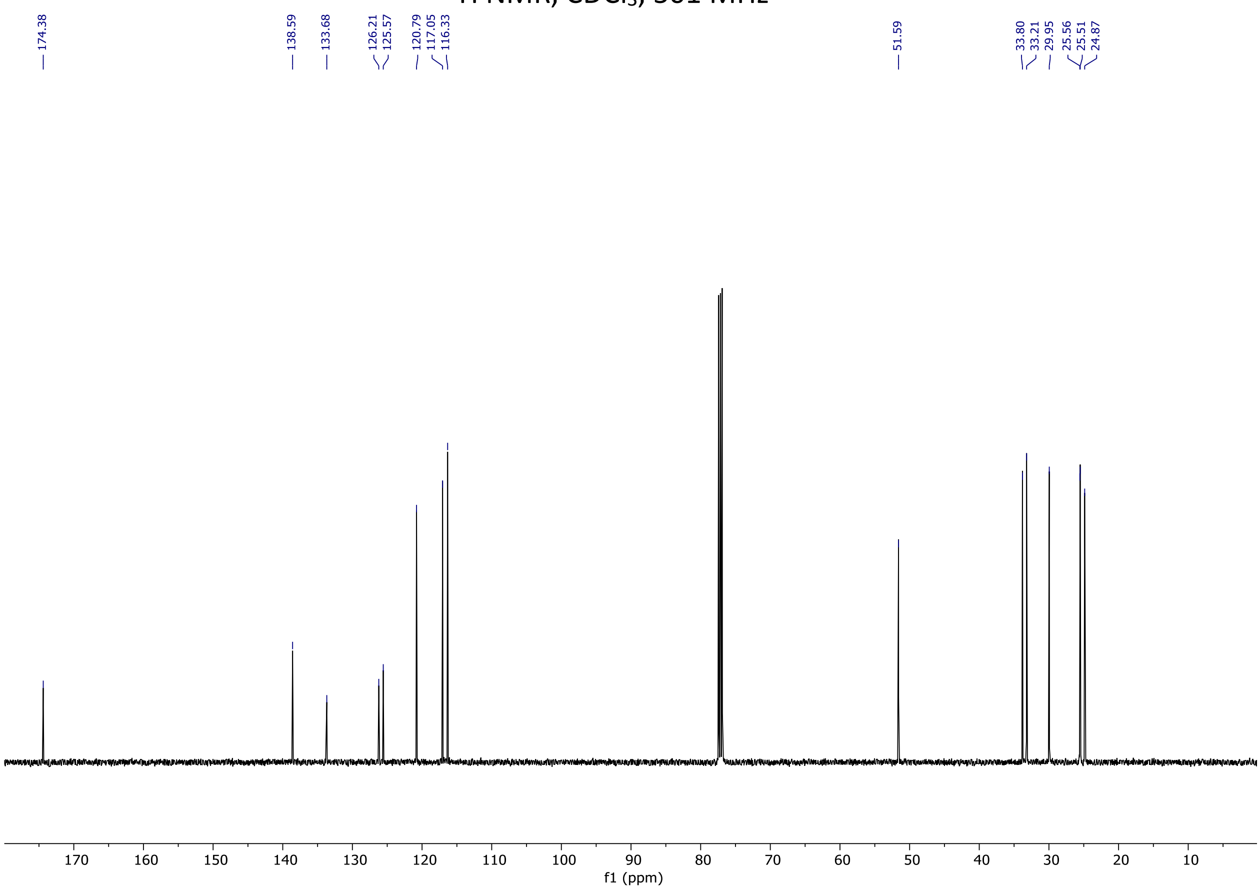


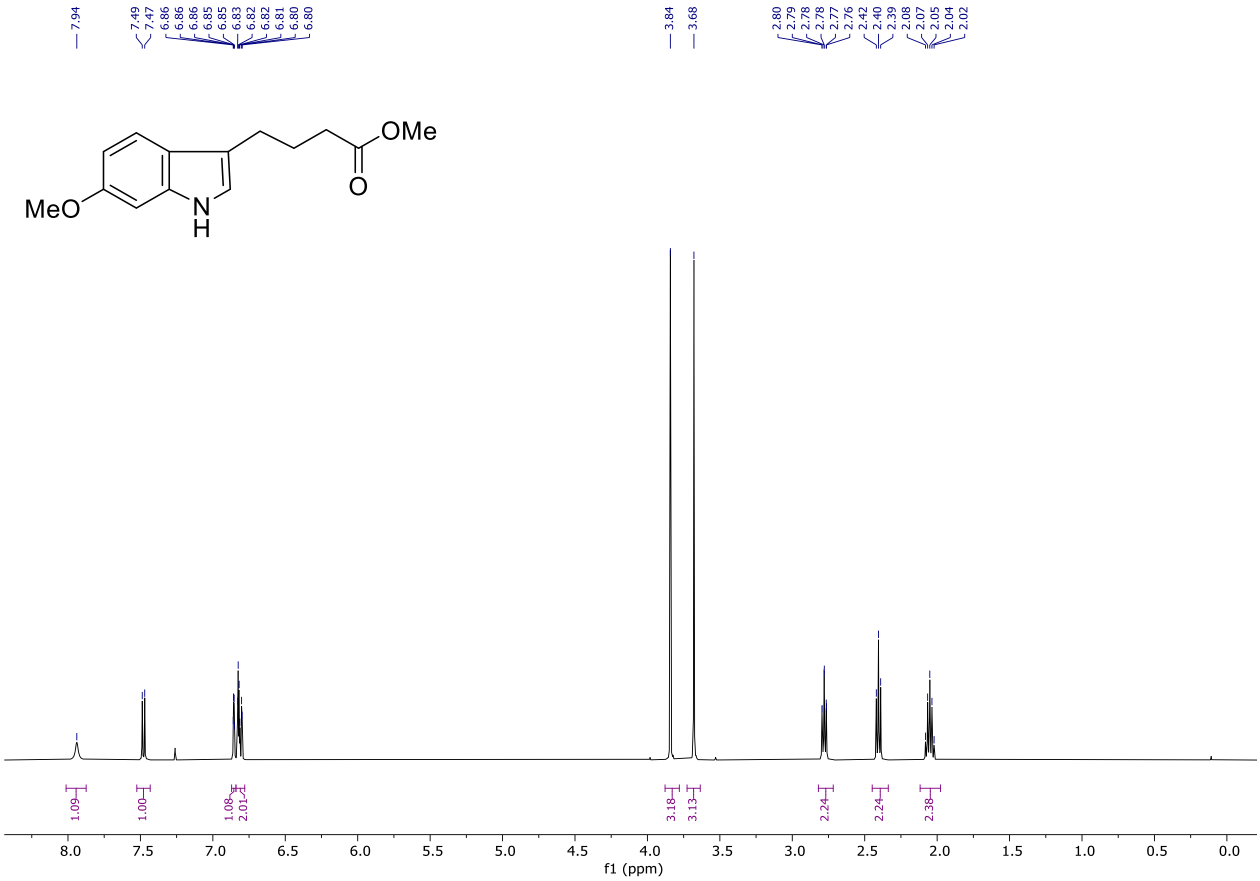
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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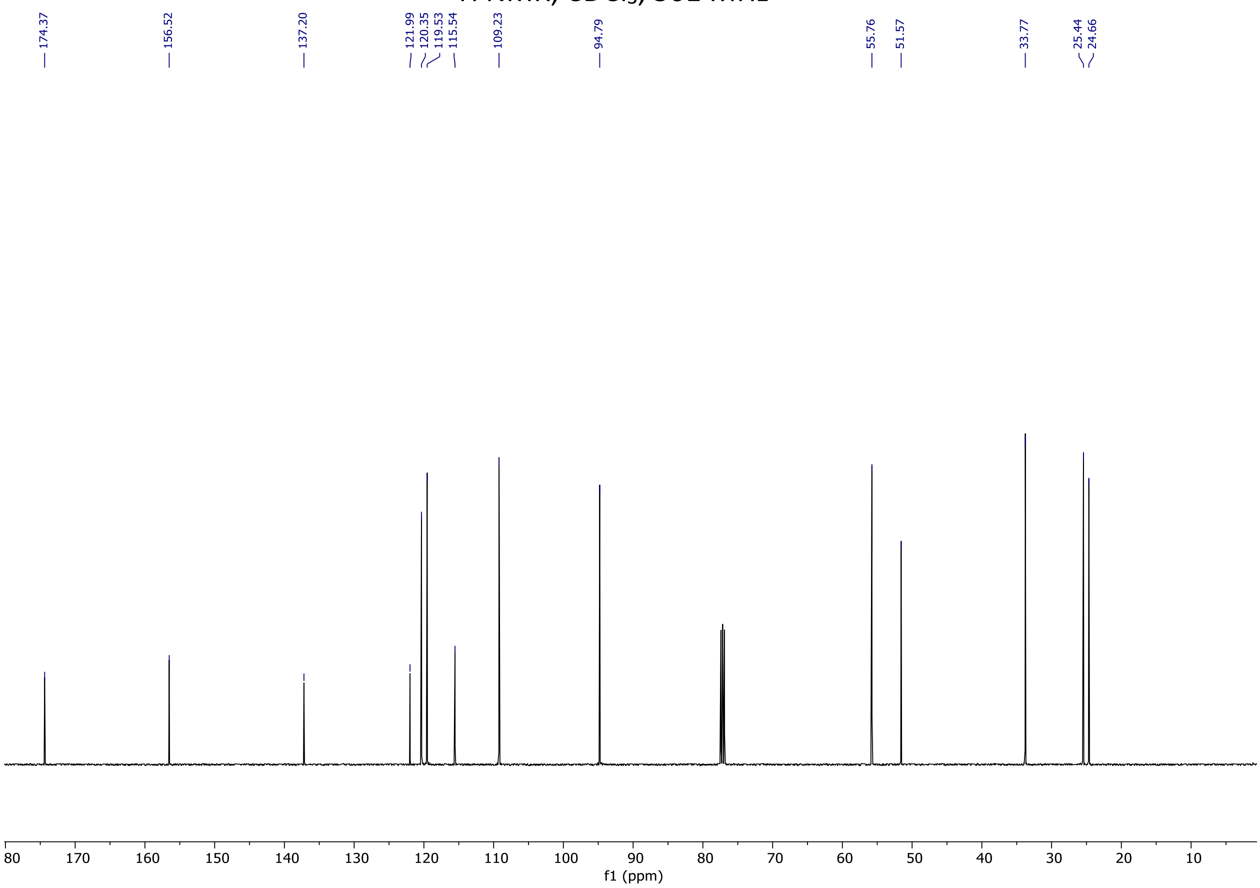
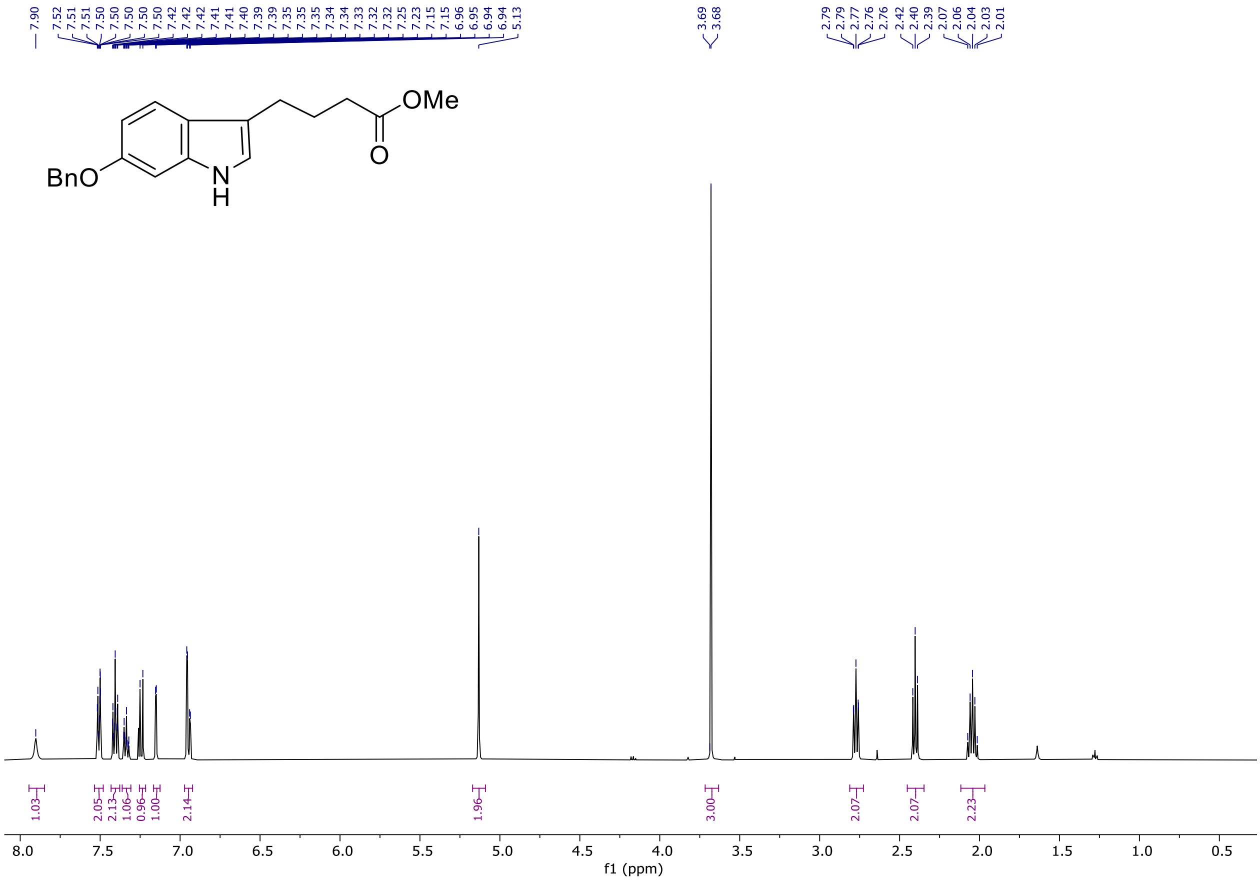
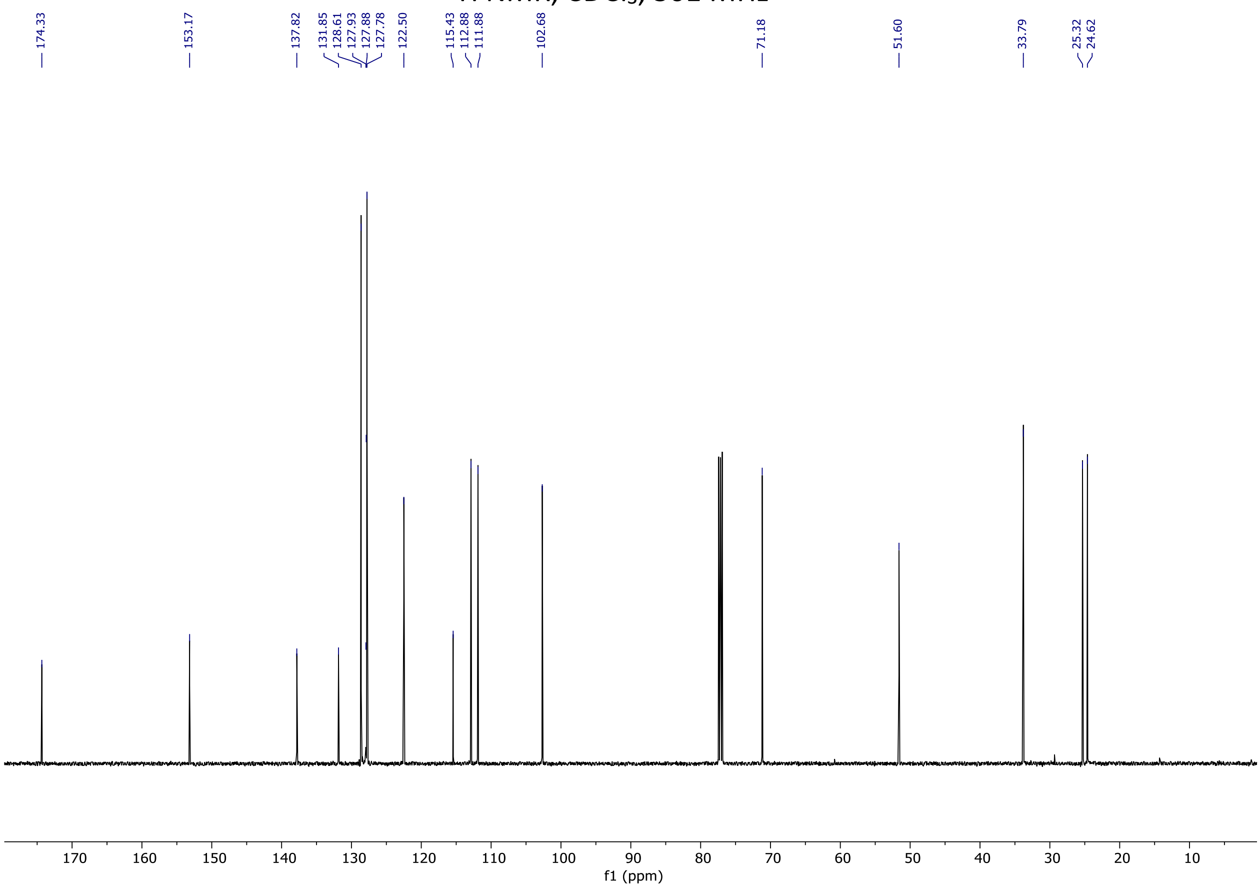


^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



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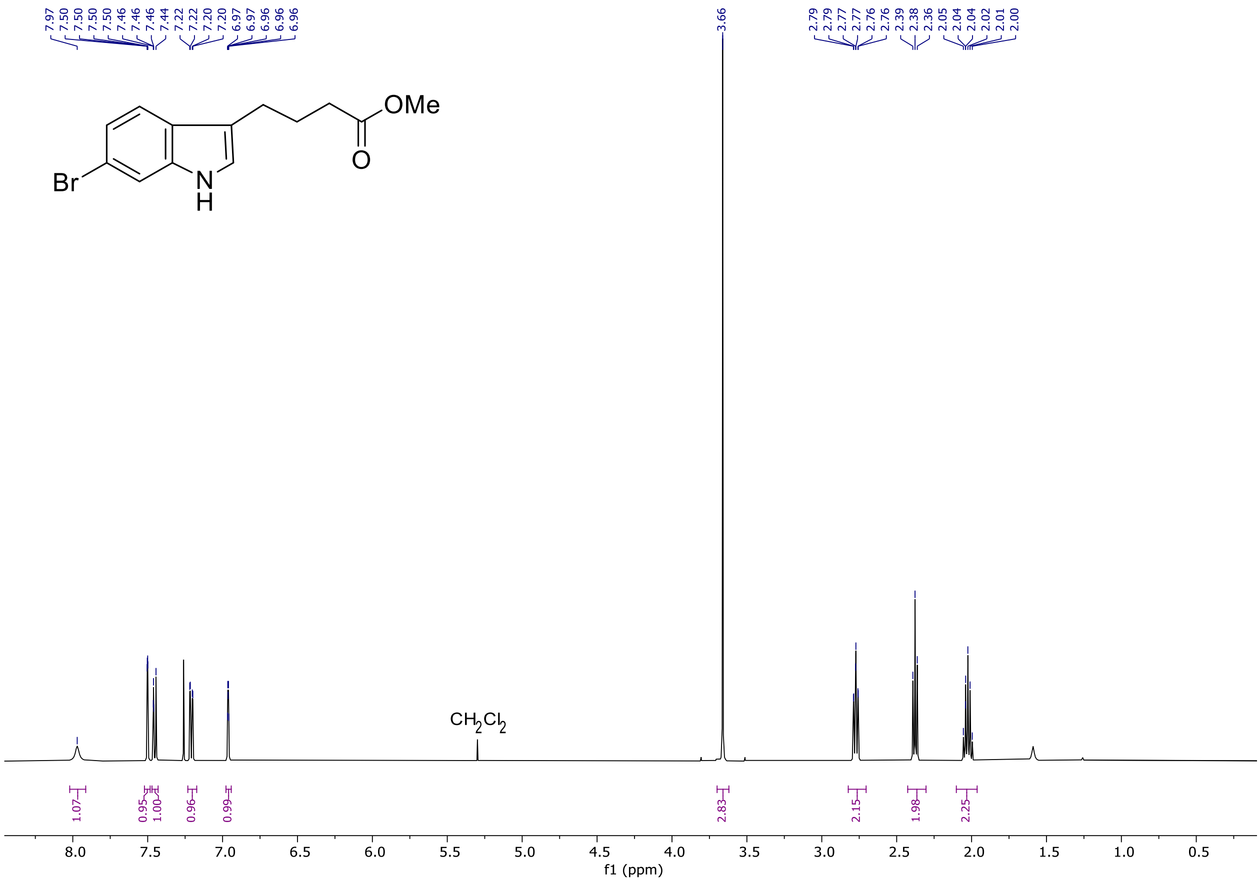

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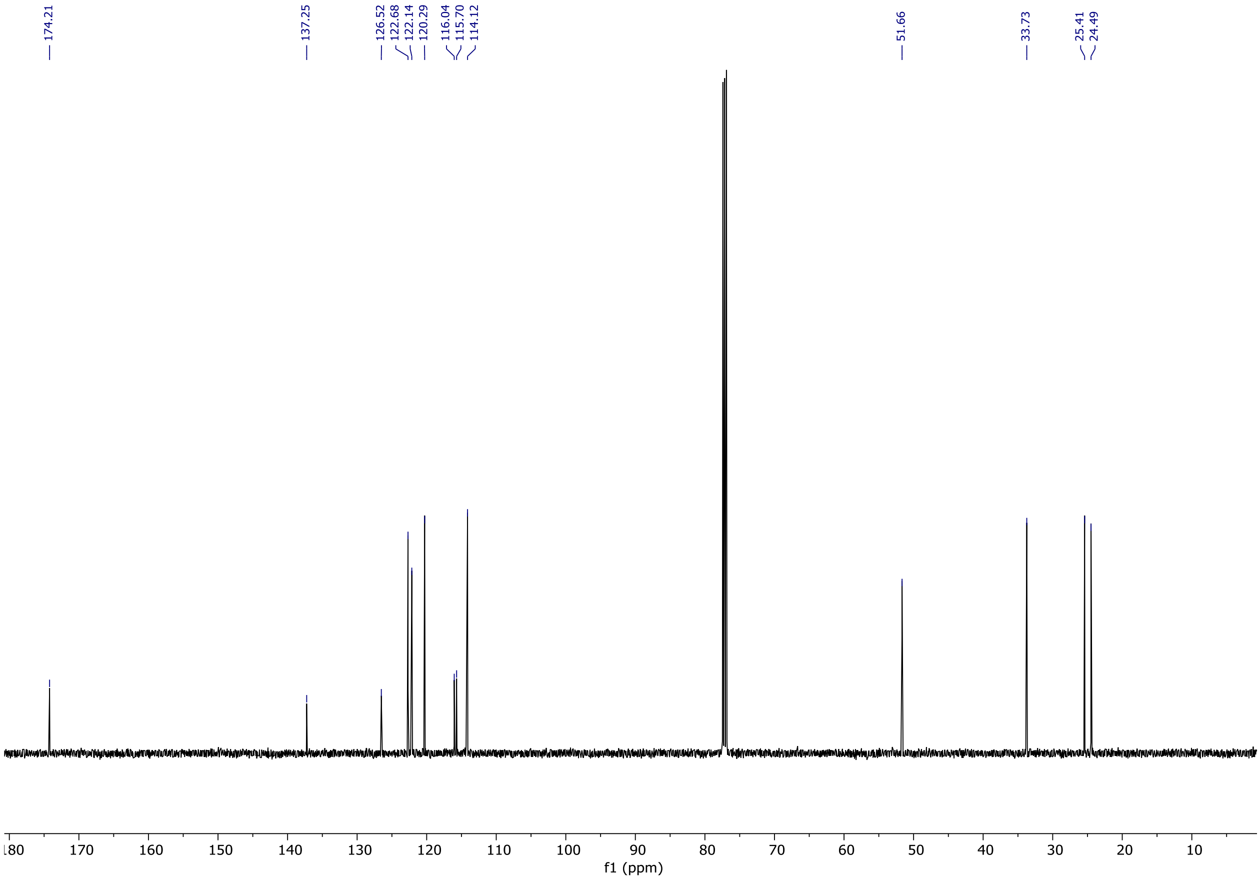

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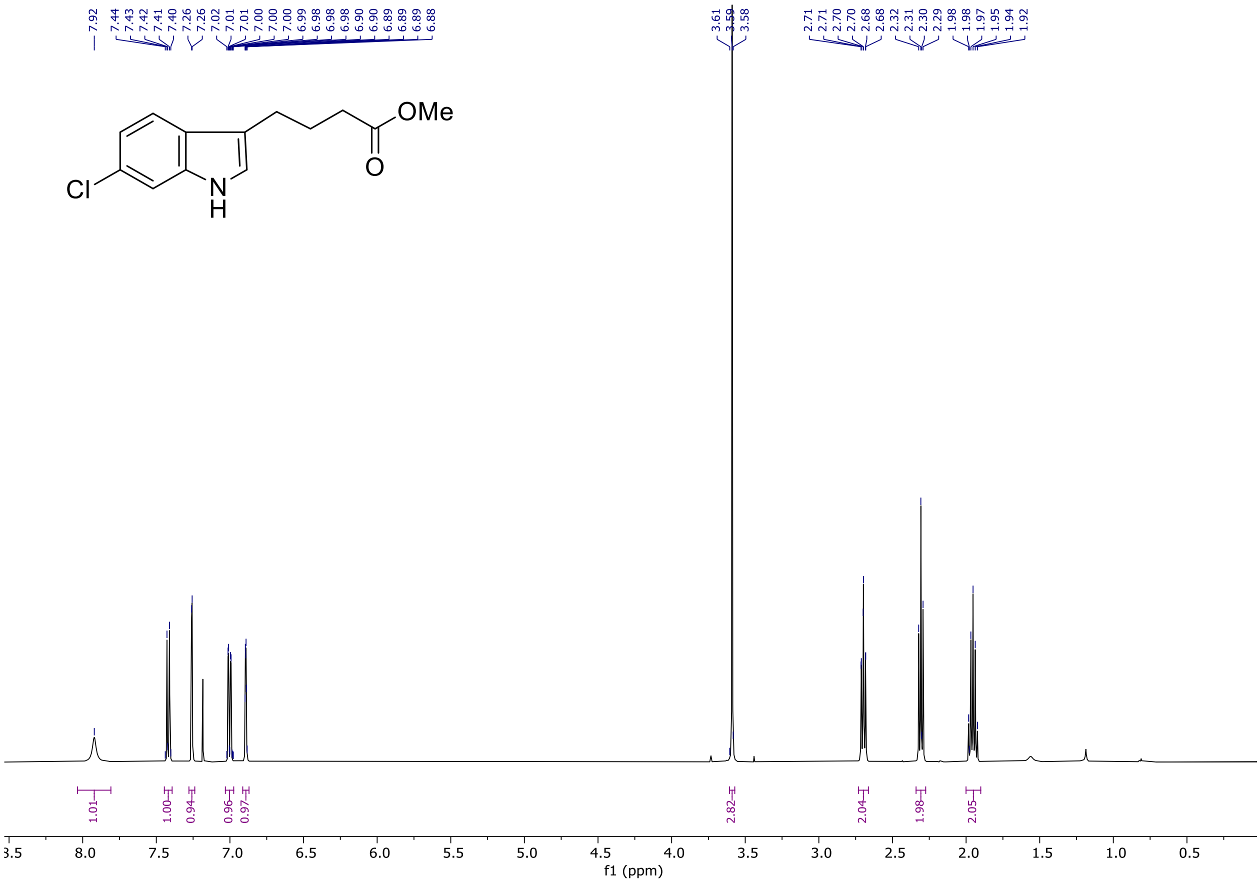

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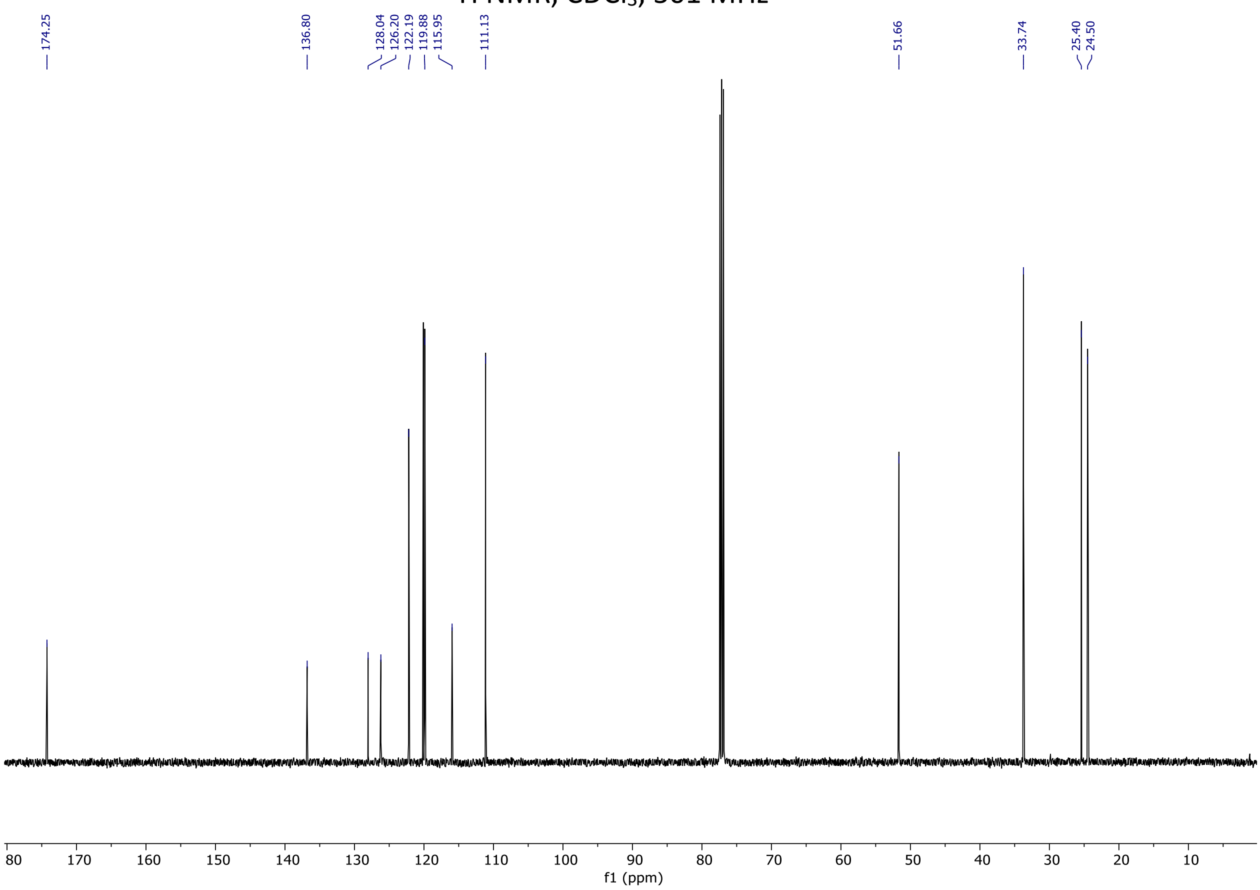

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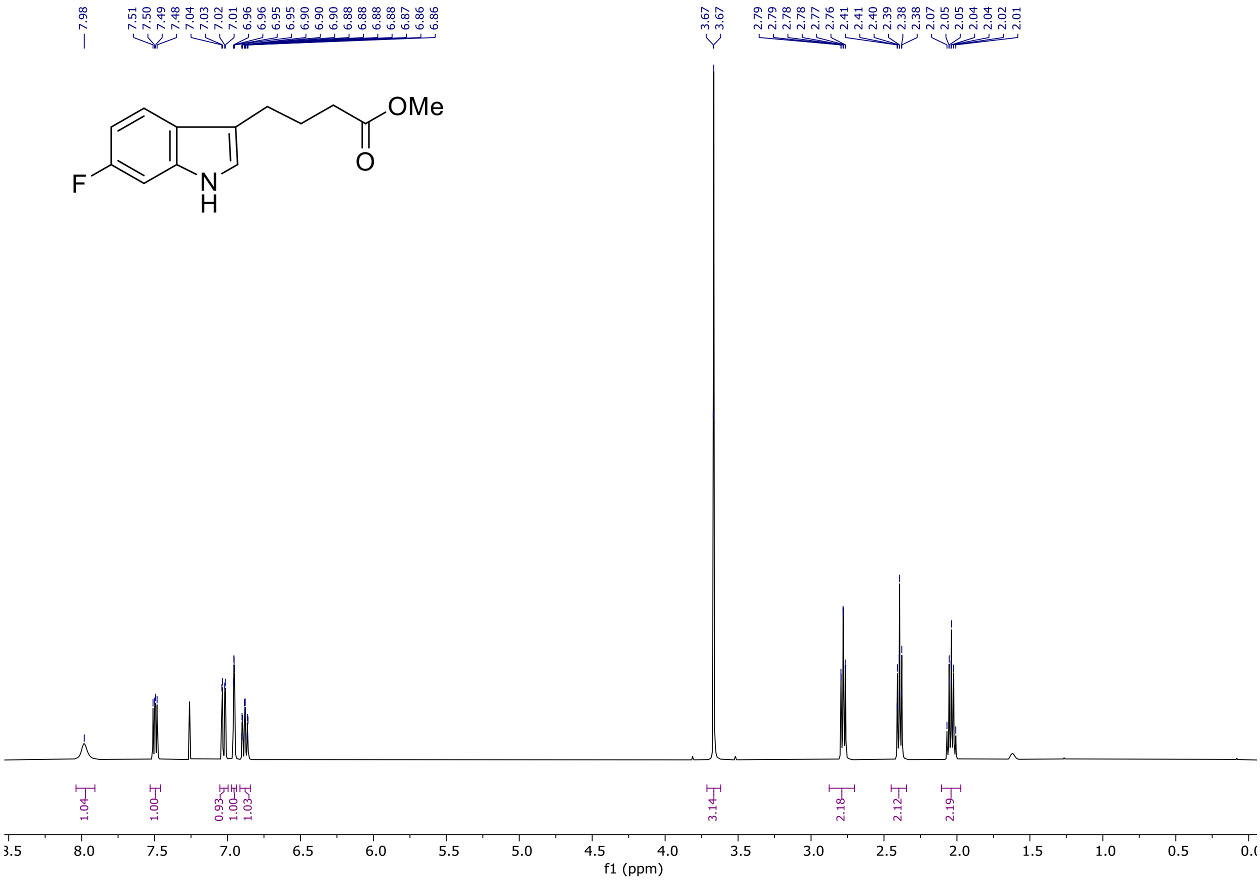

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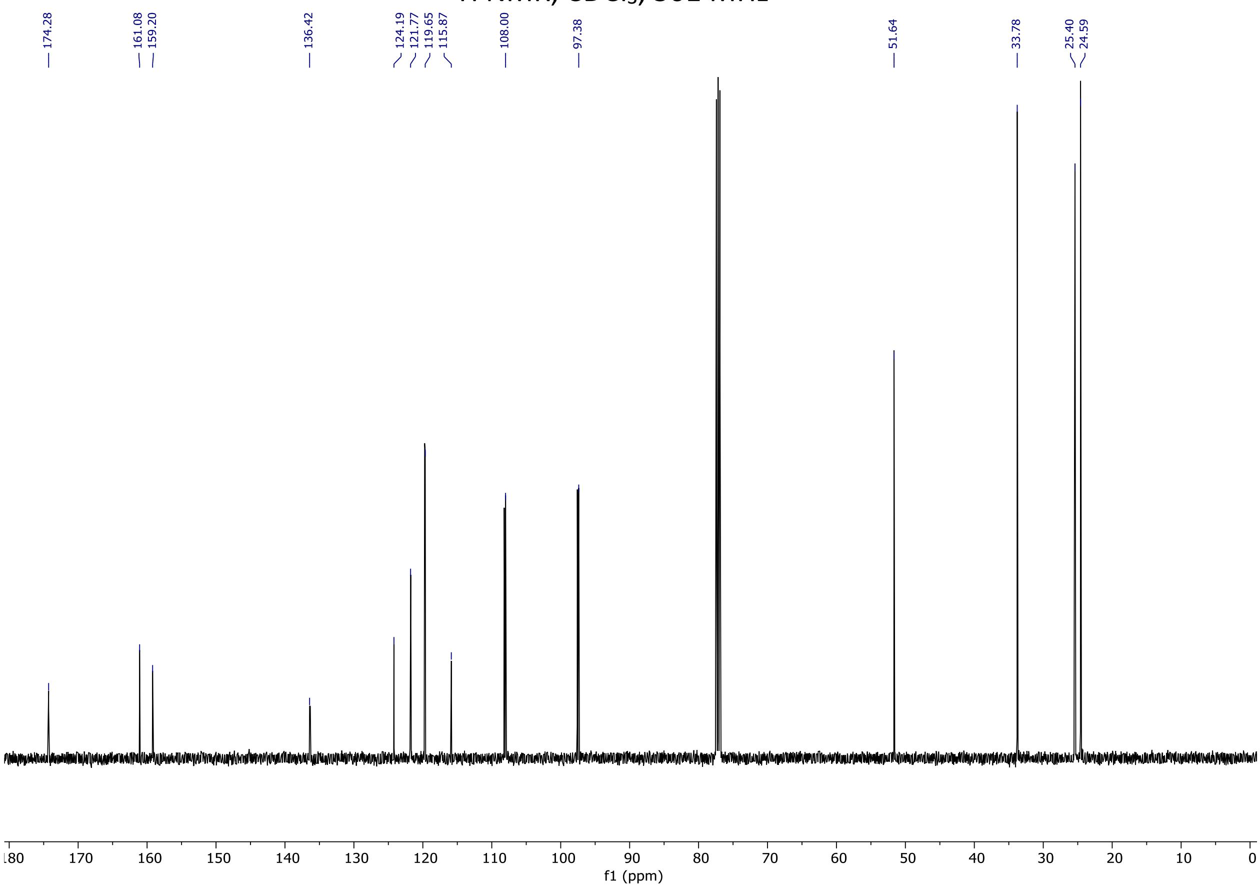

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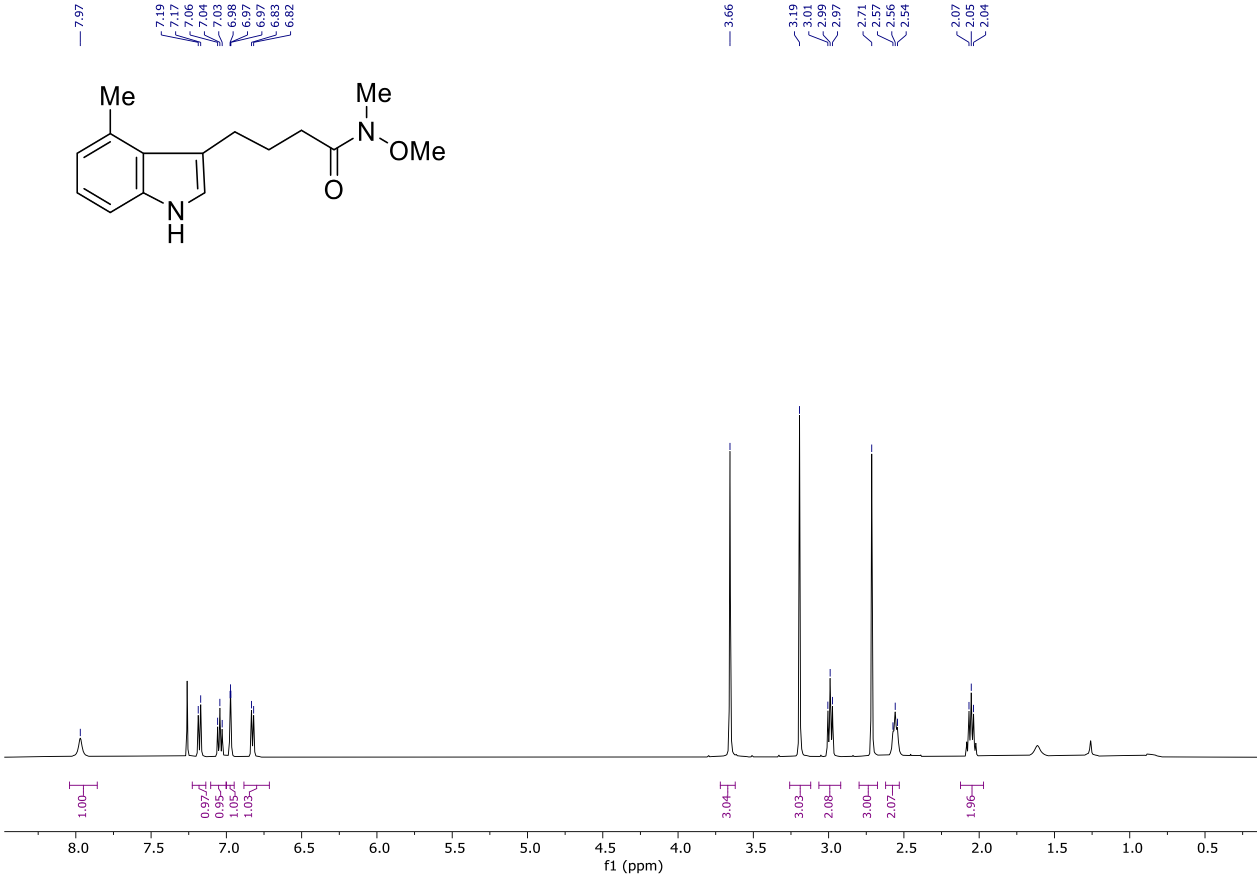

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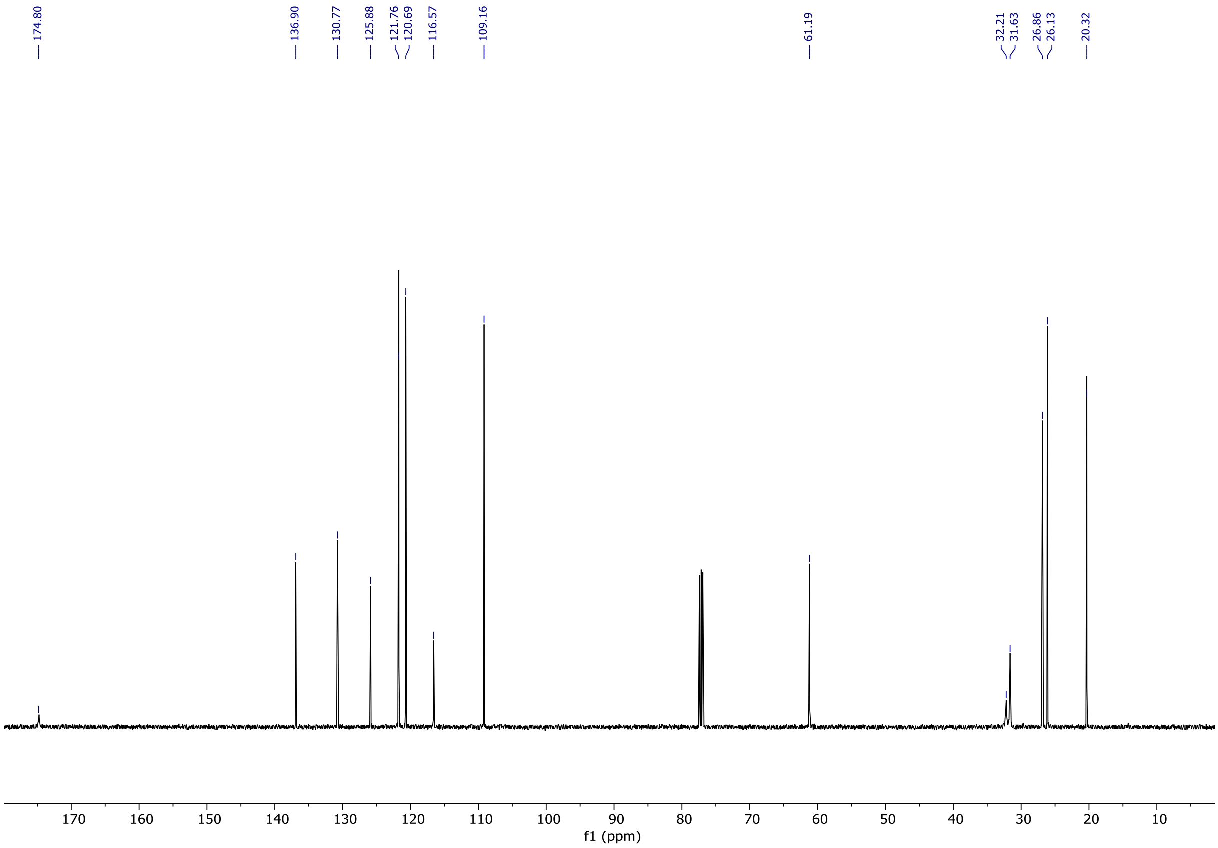

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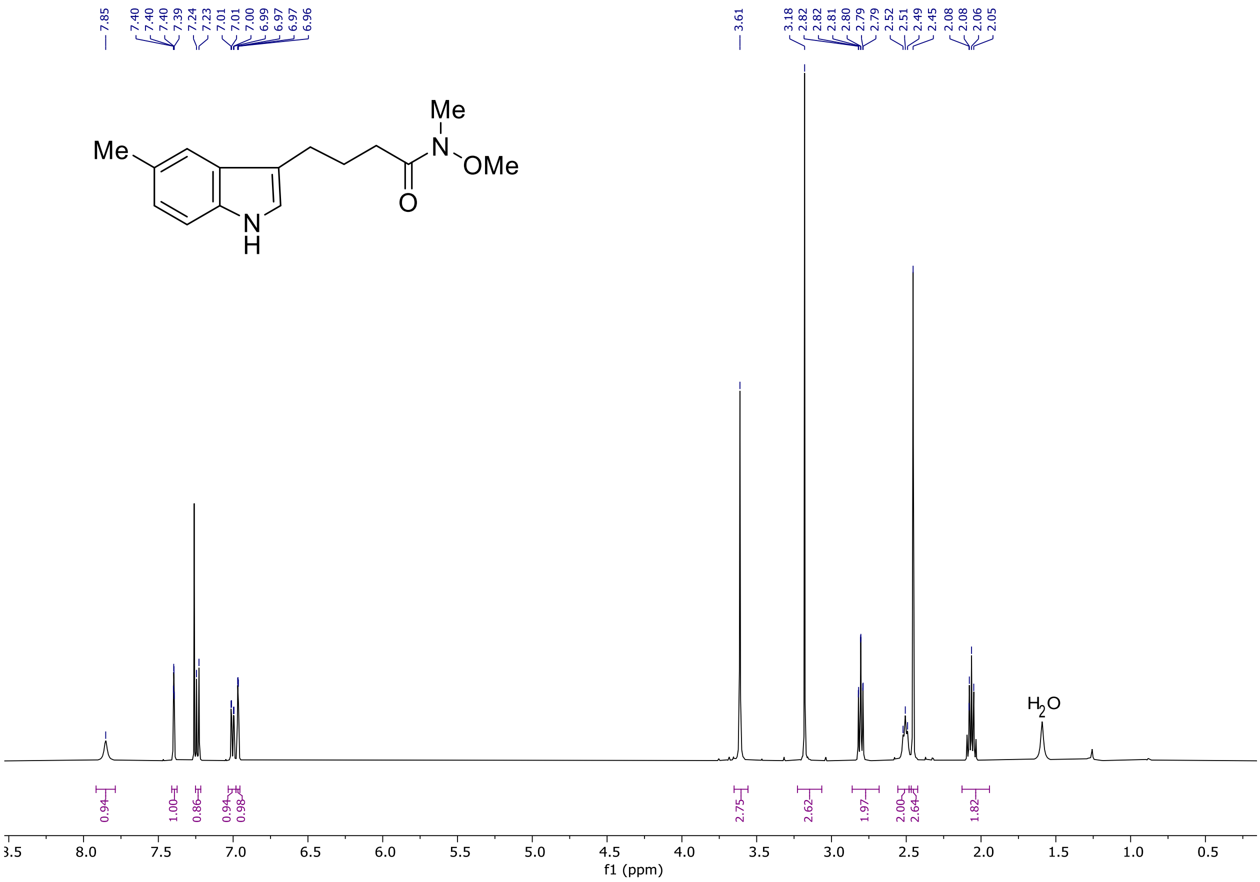

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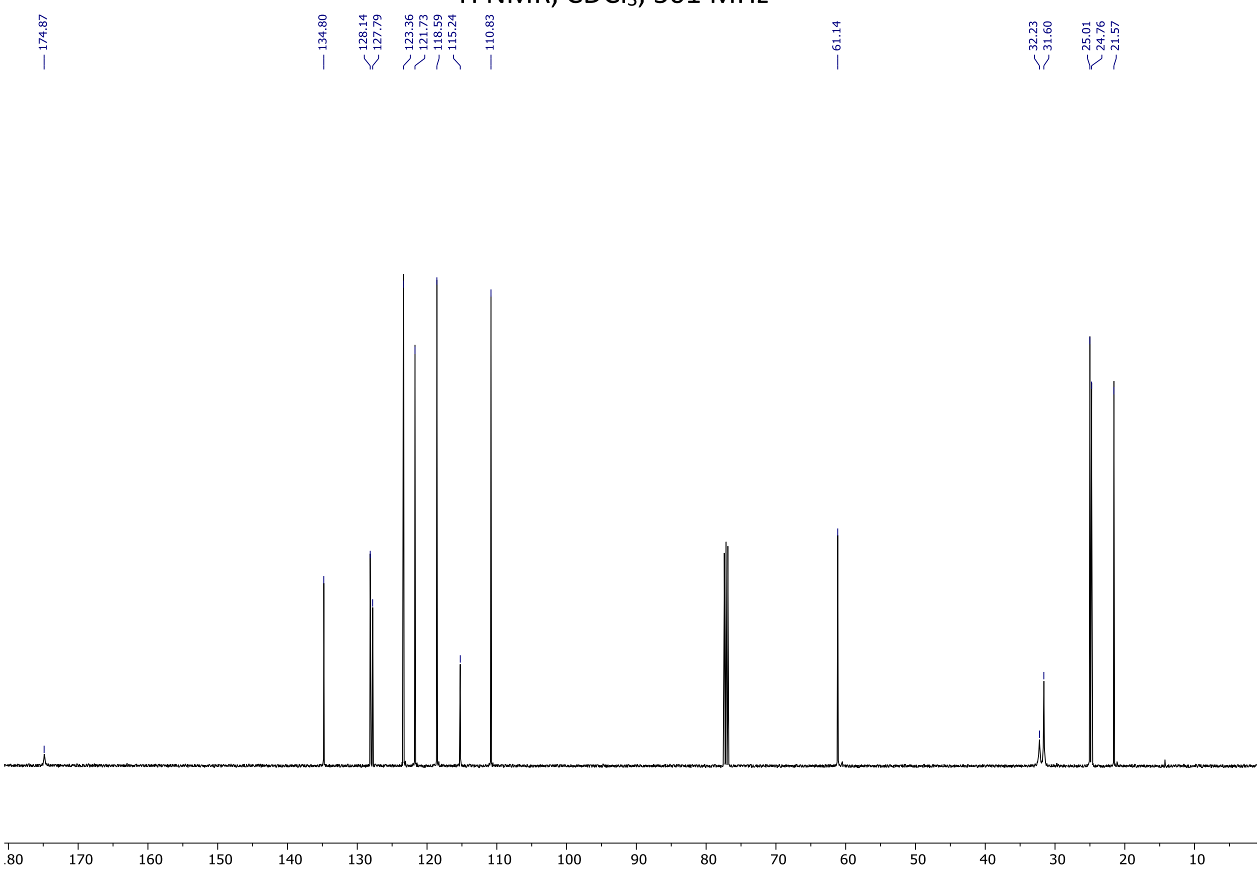

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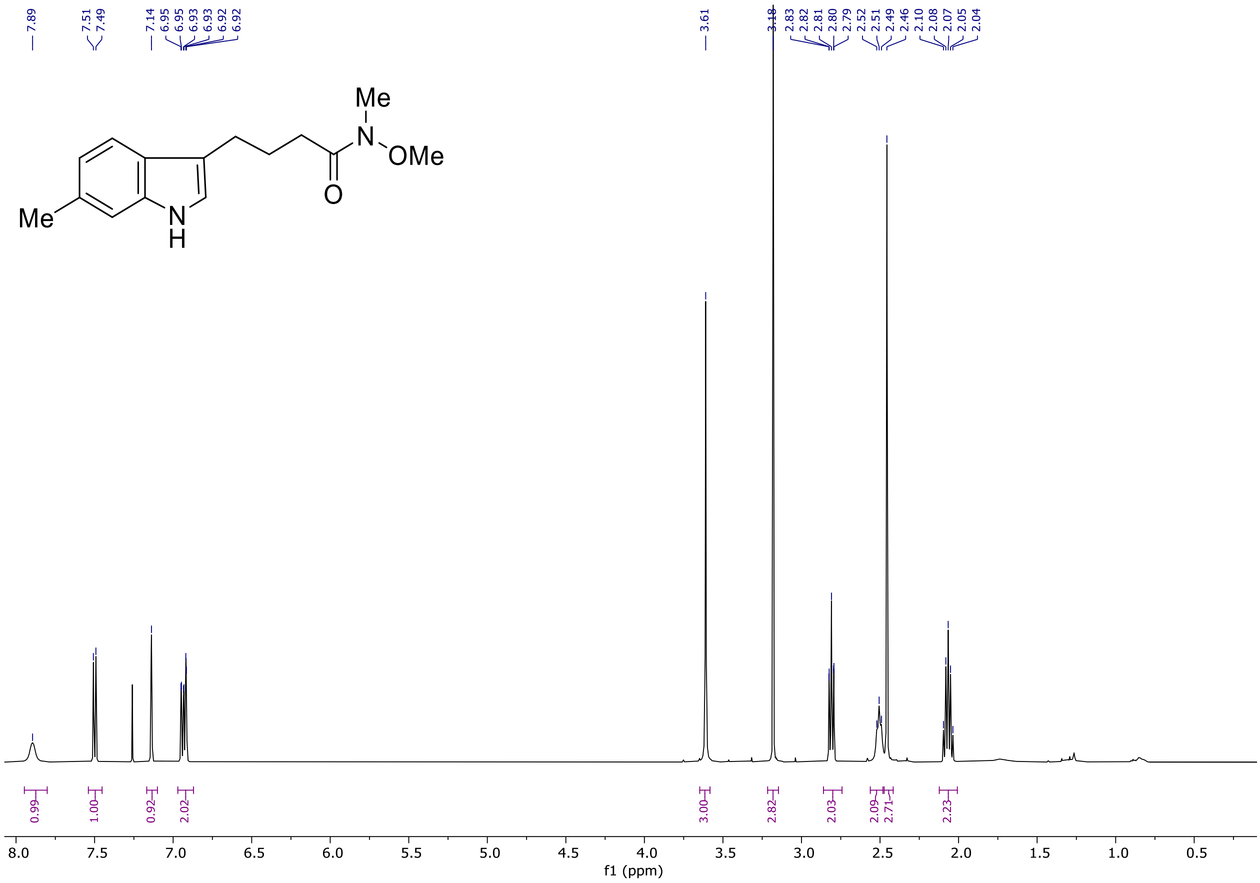

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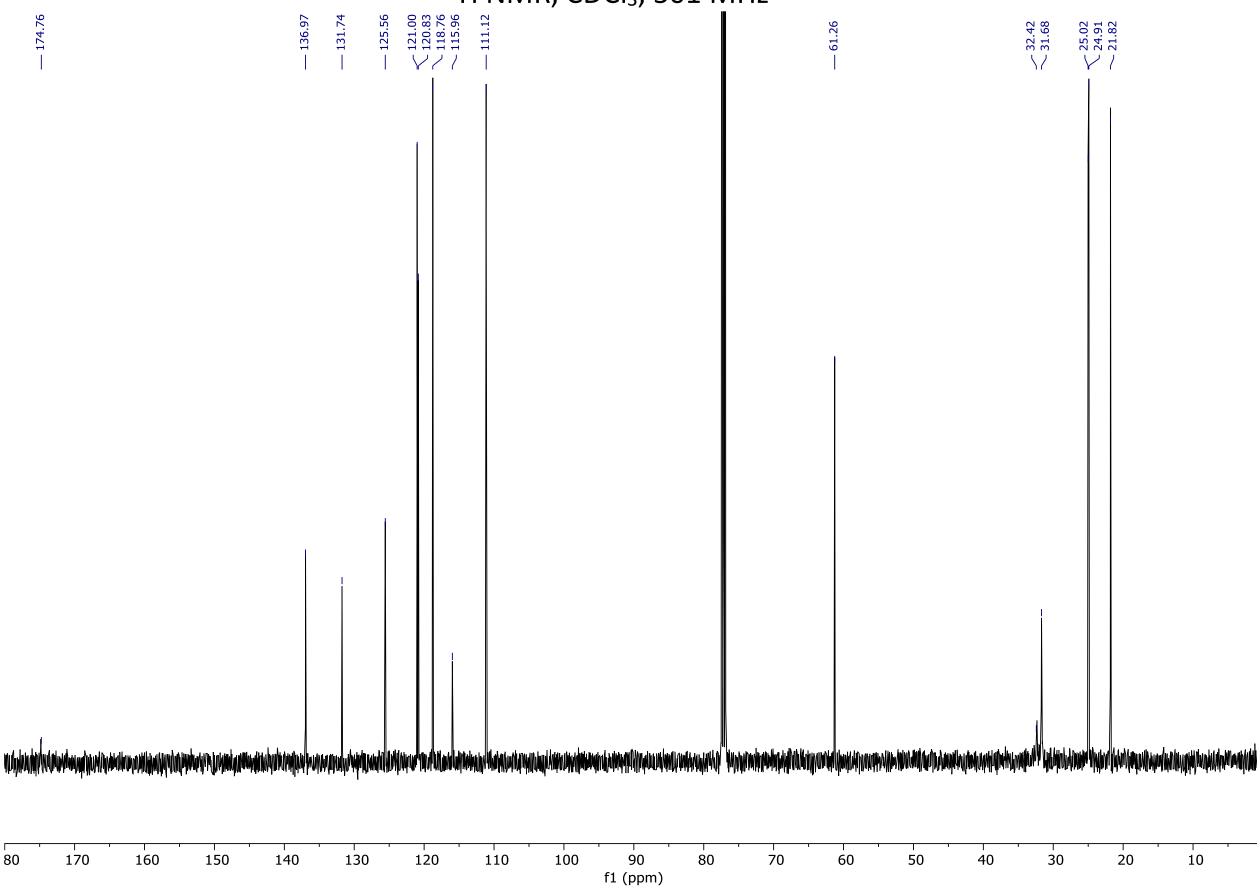

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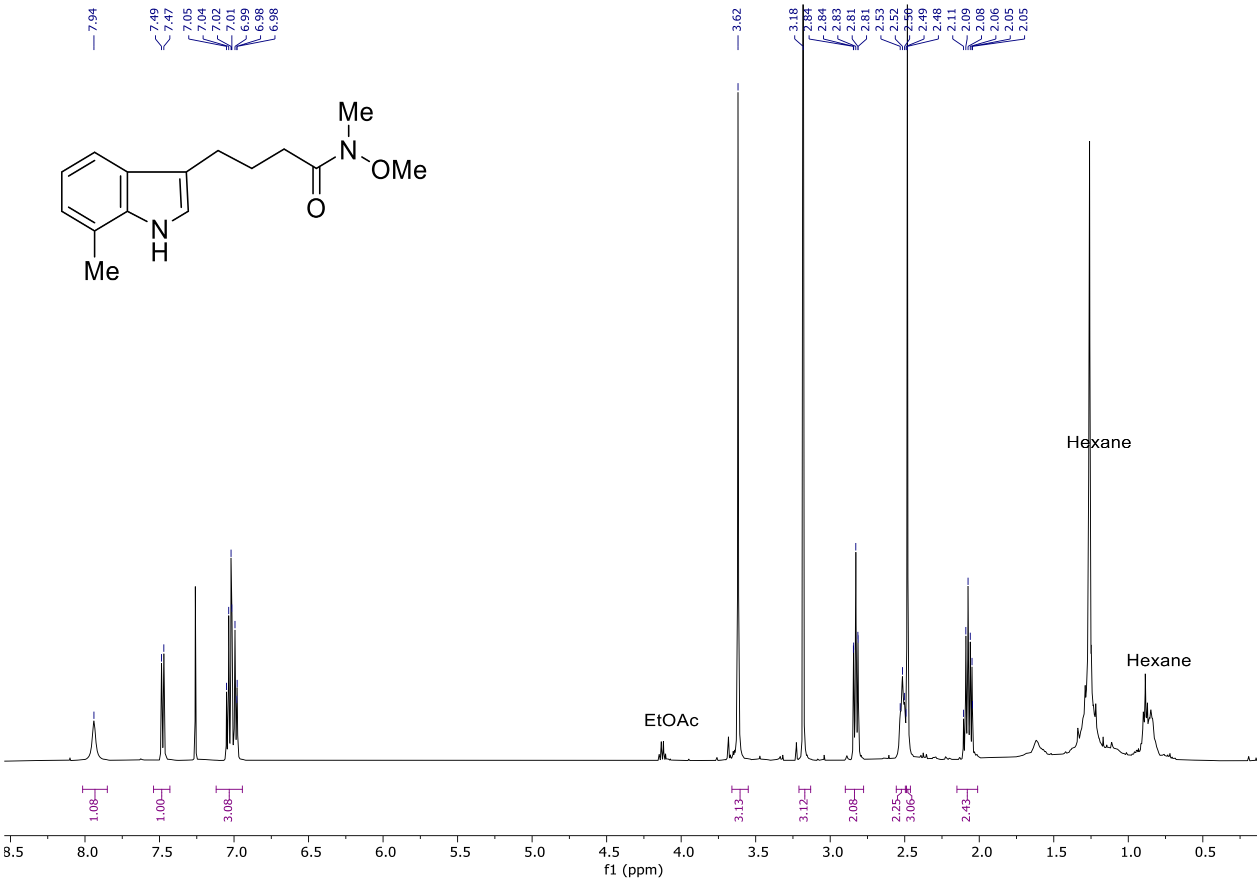

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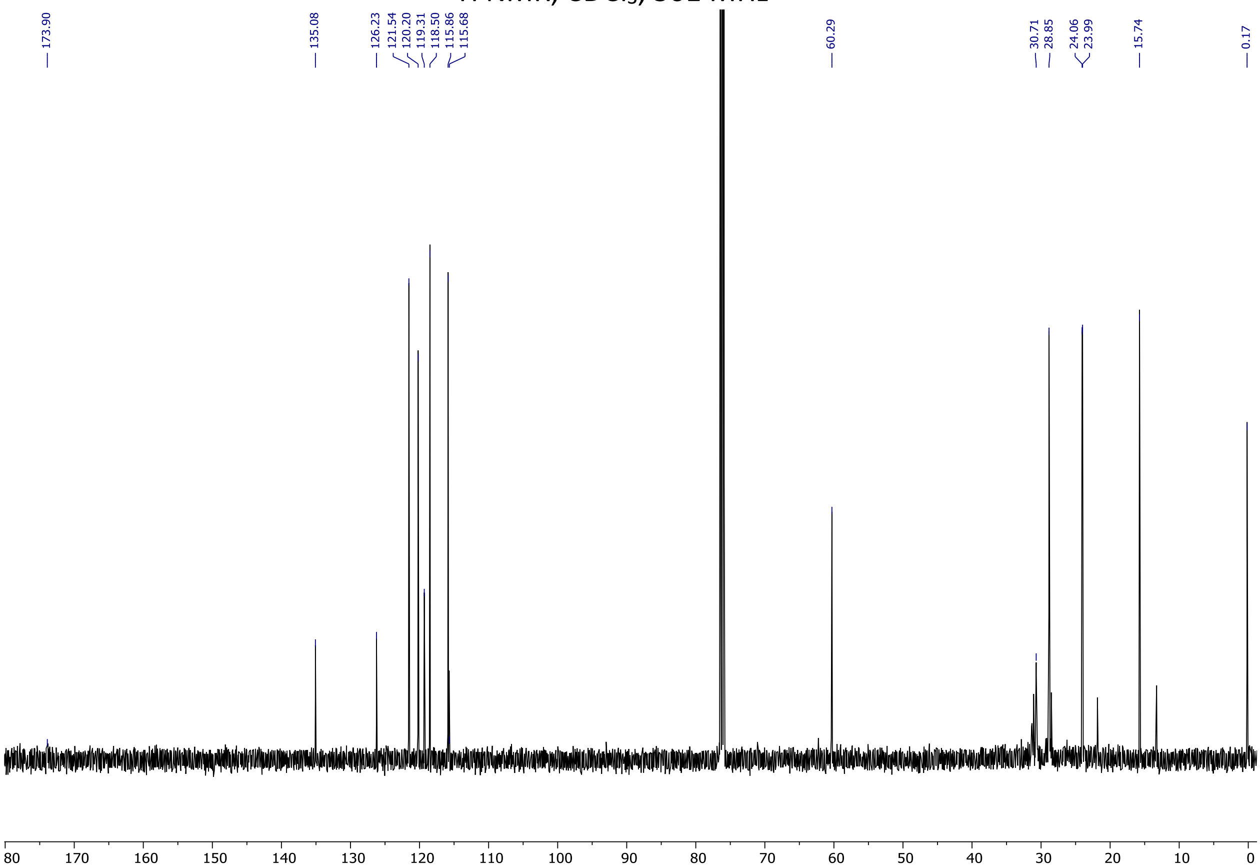

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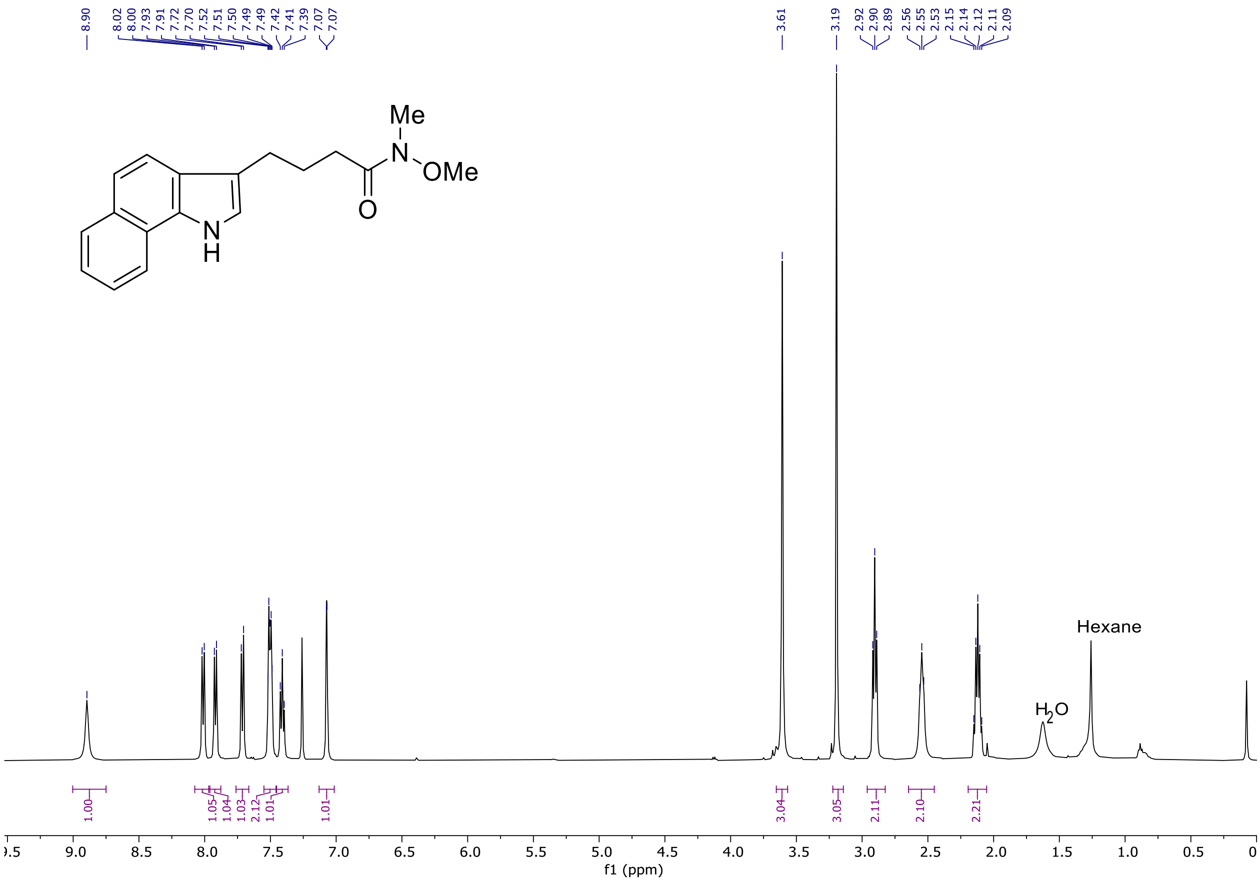

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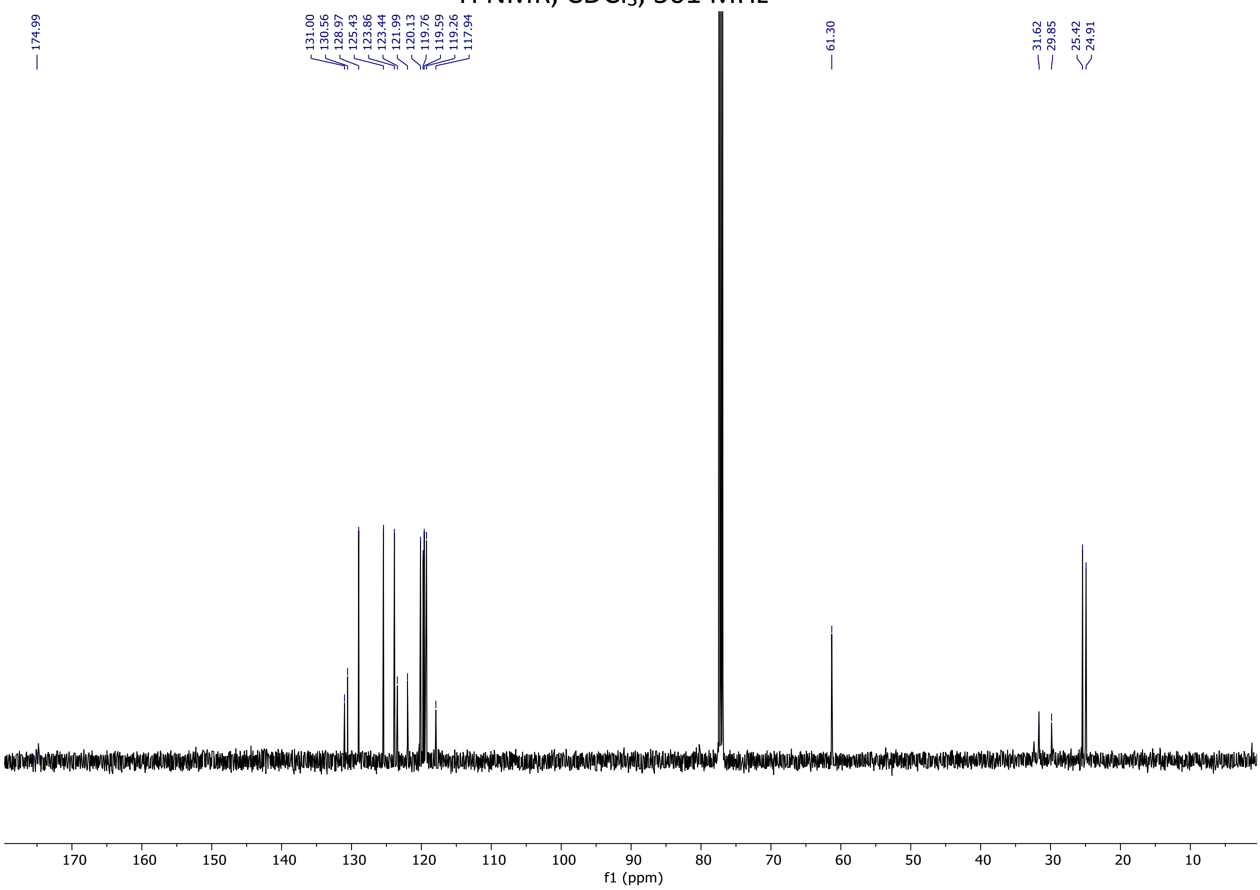

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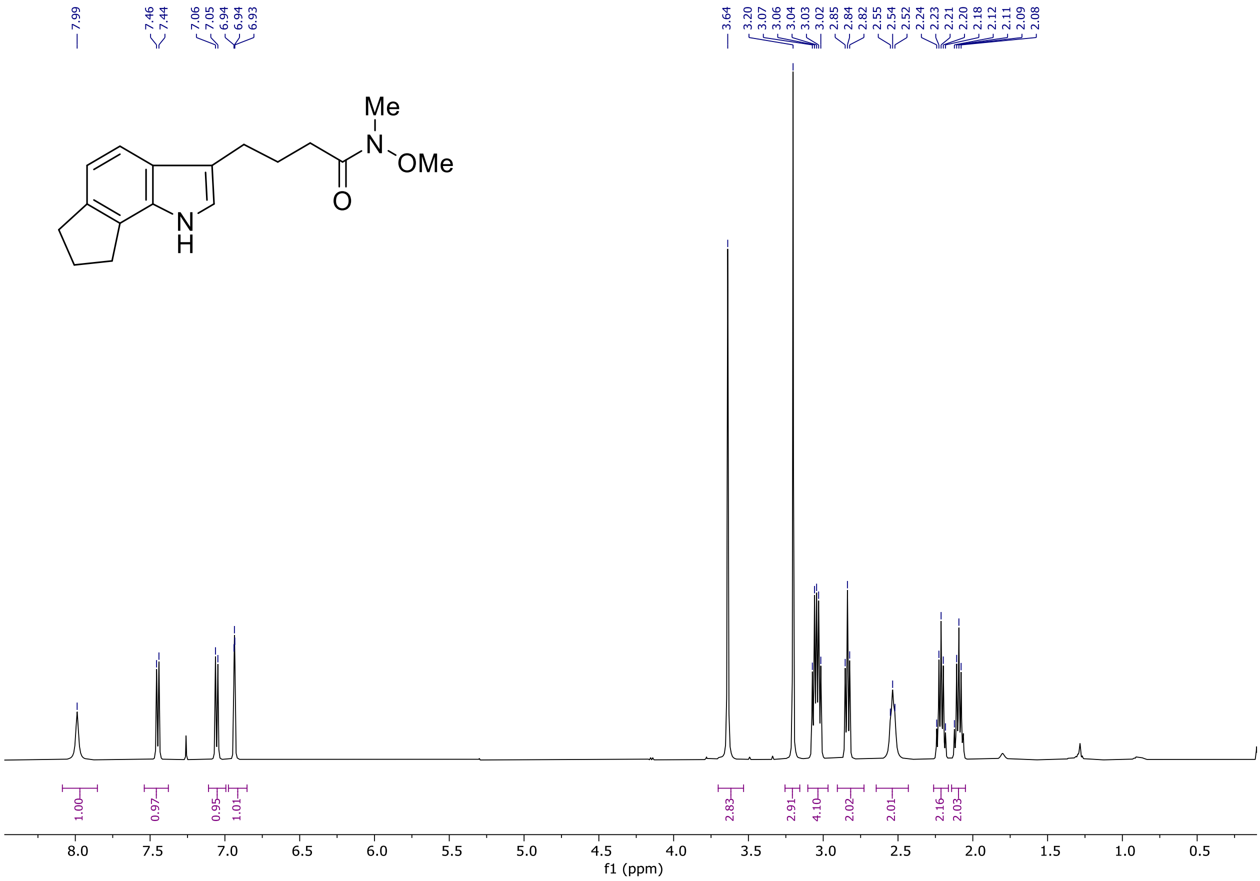

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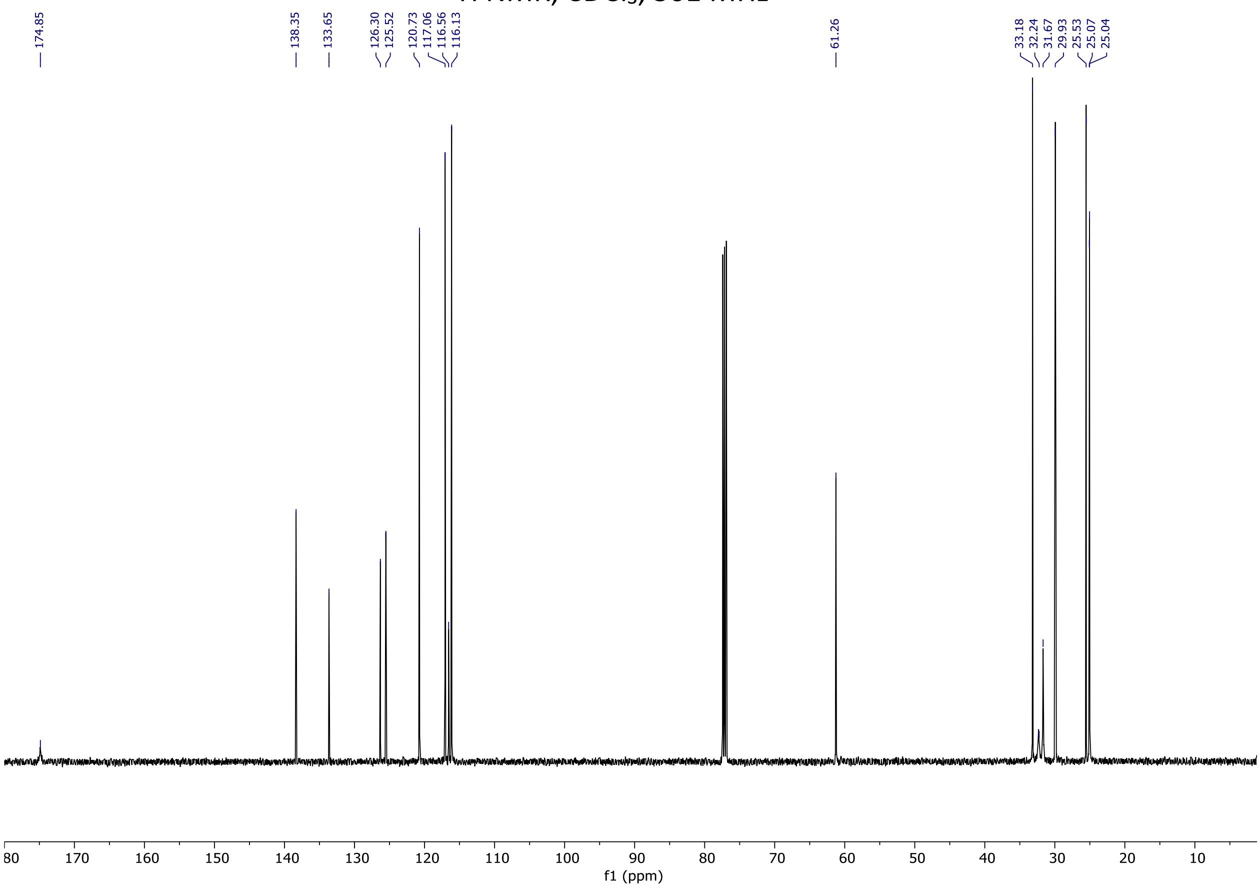

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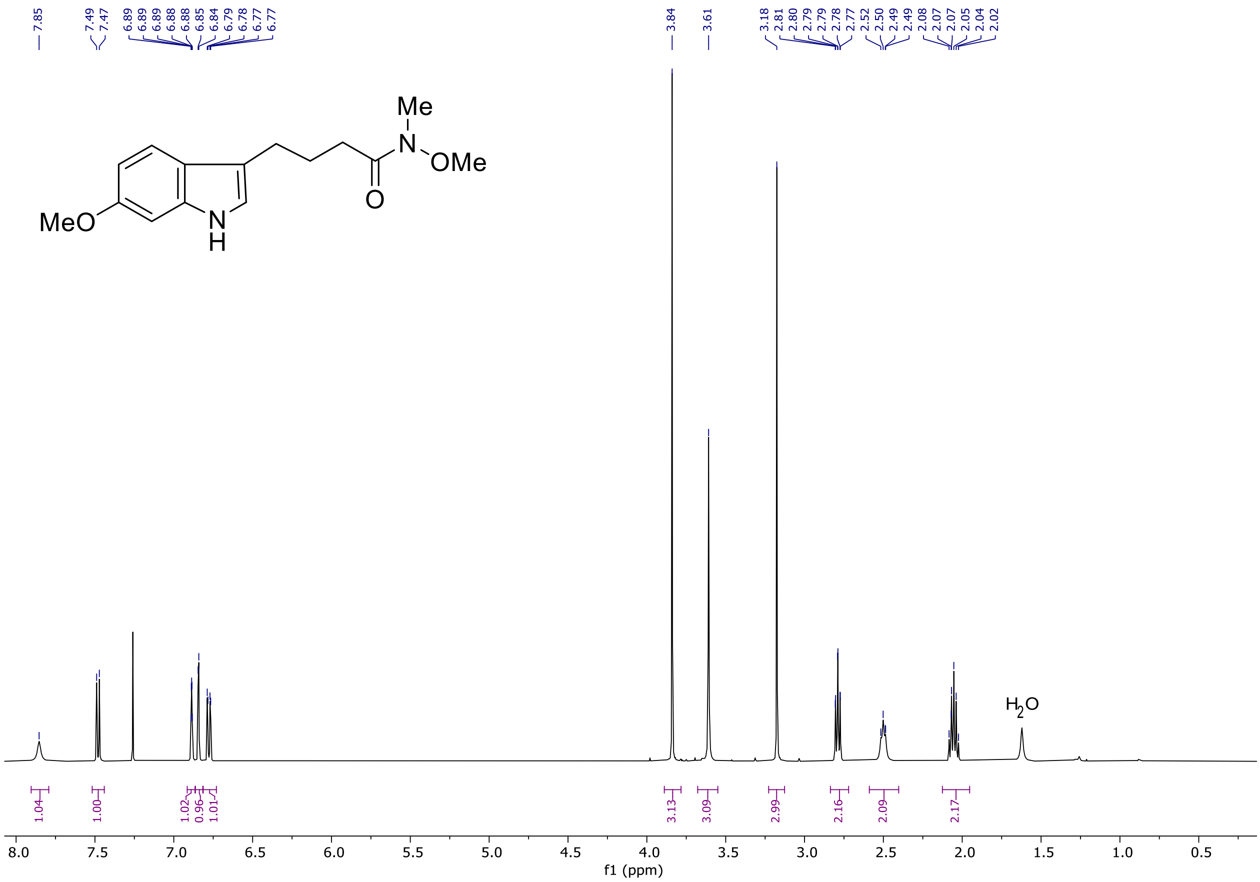

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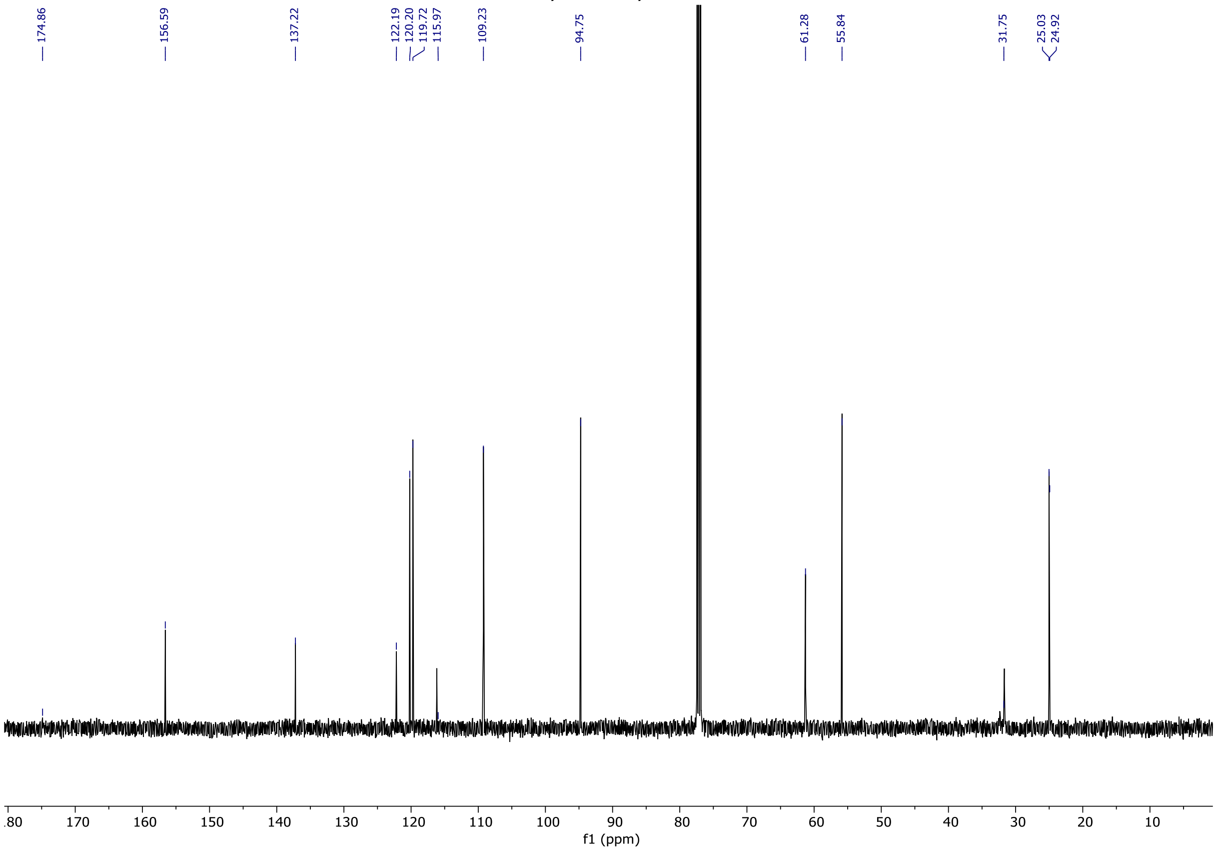

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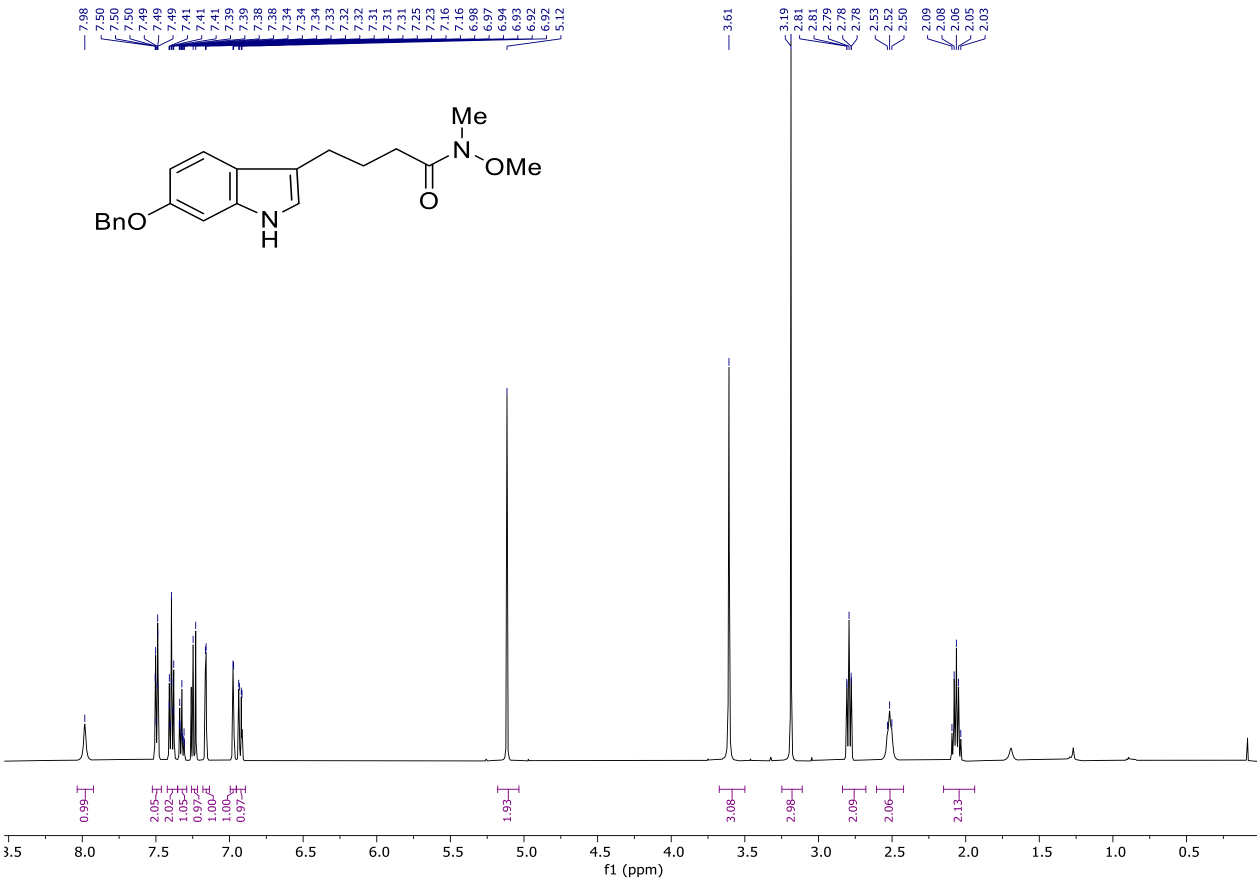

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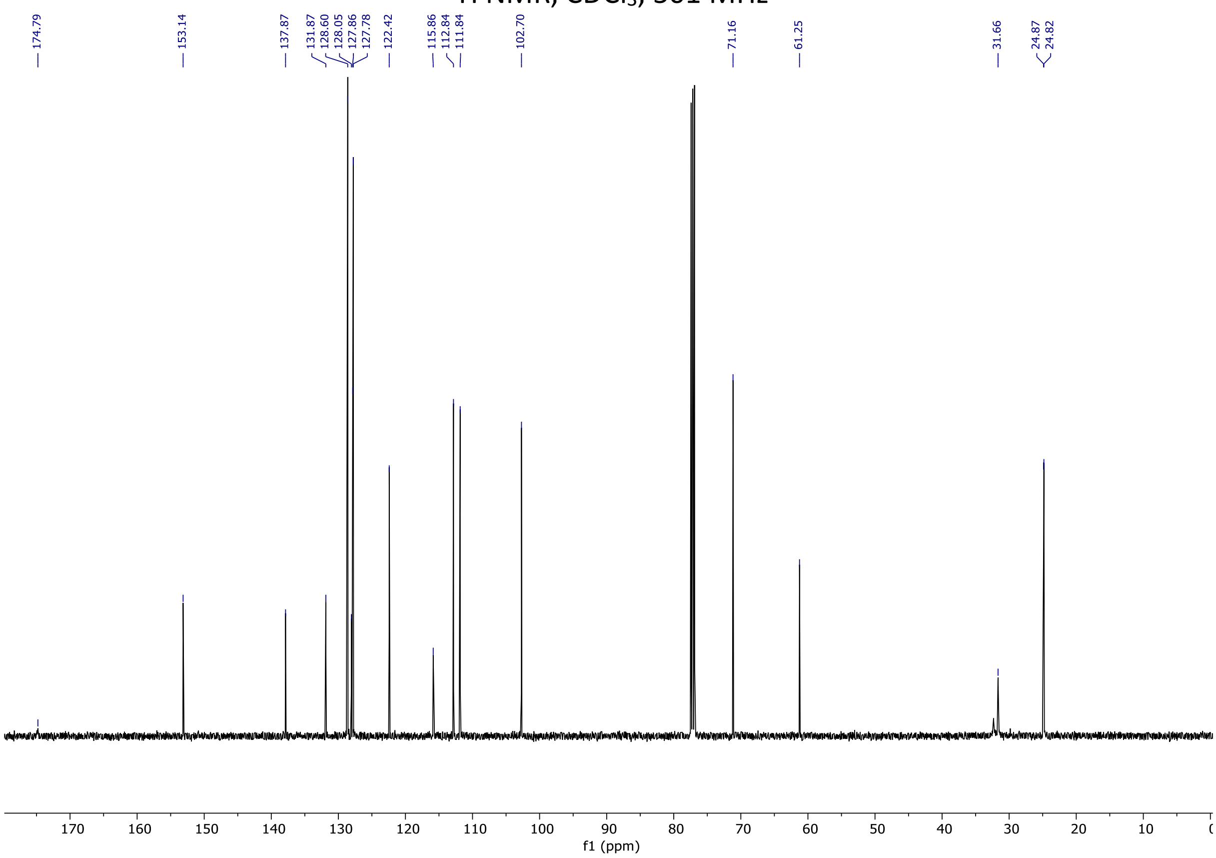

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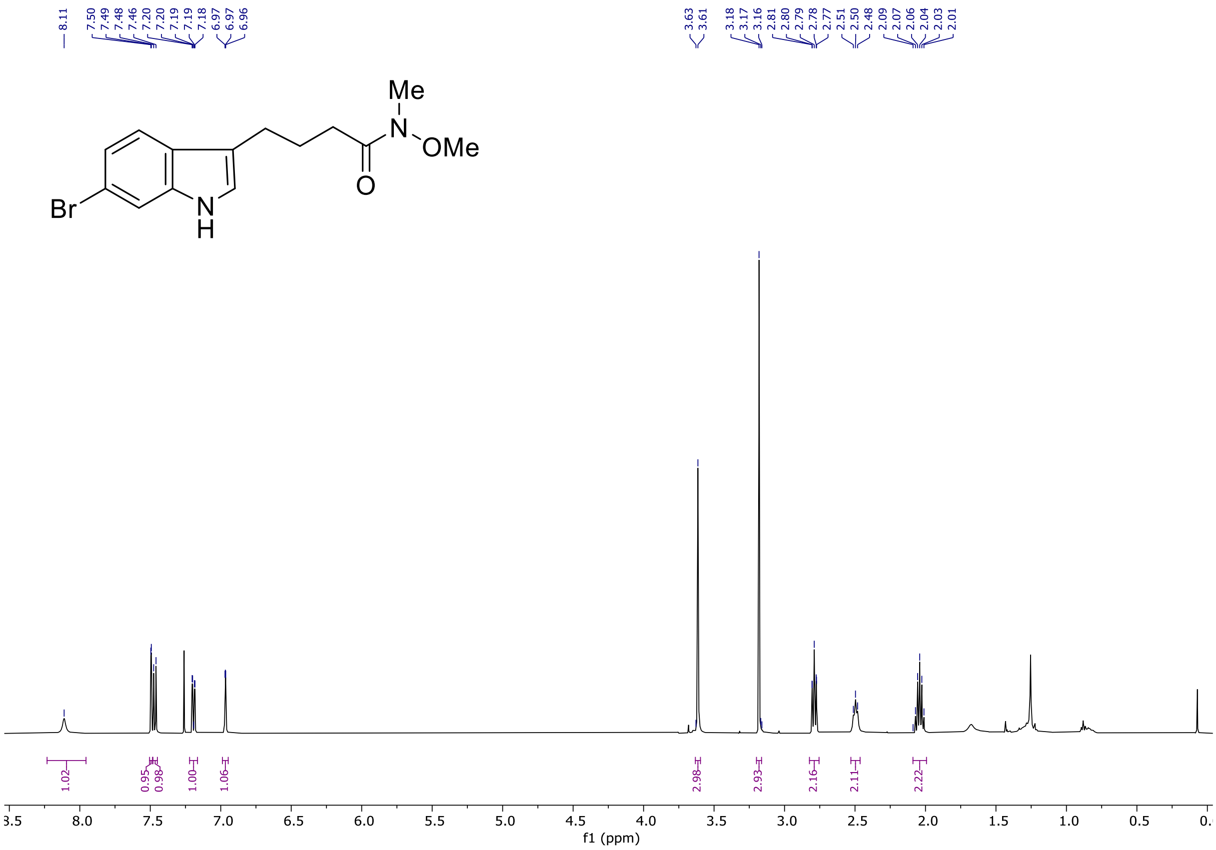

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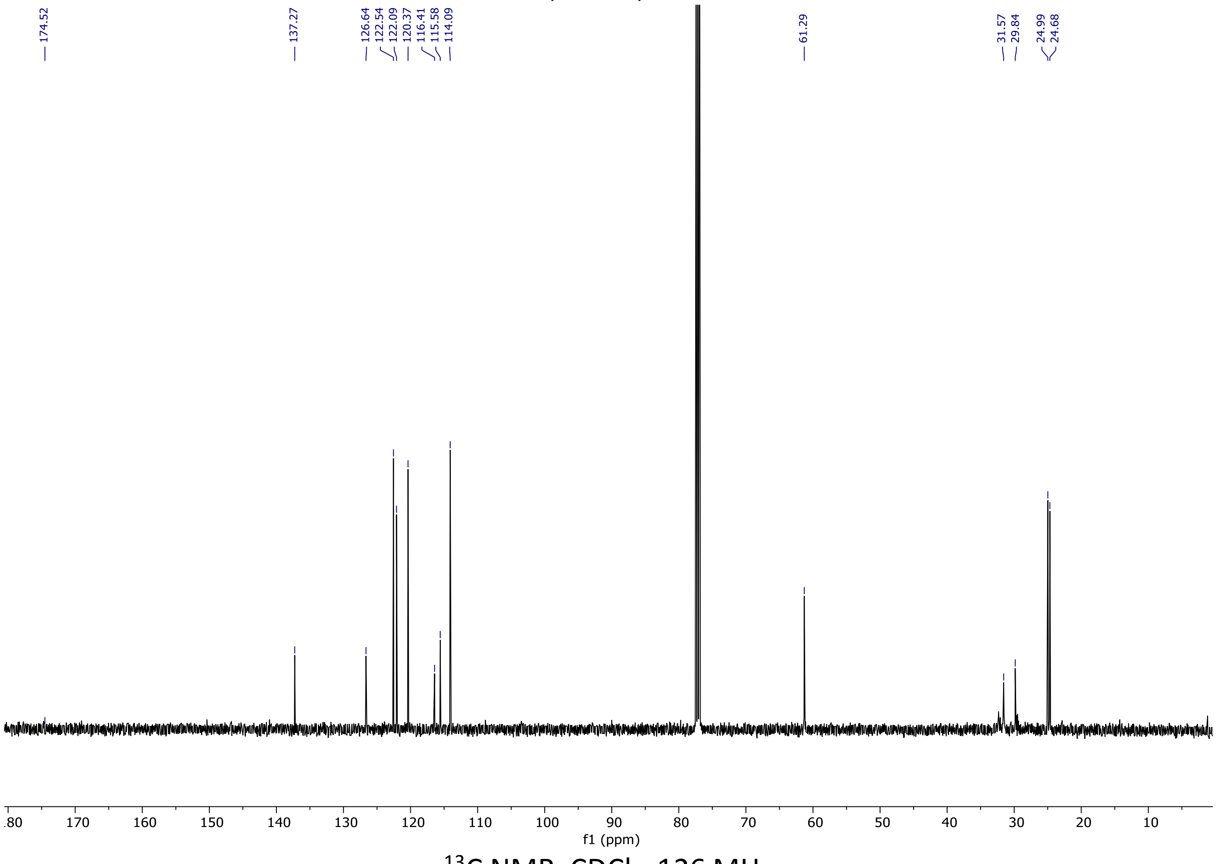

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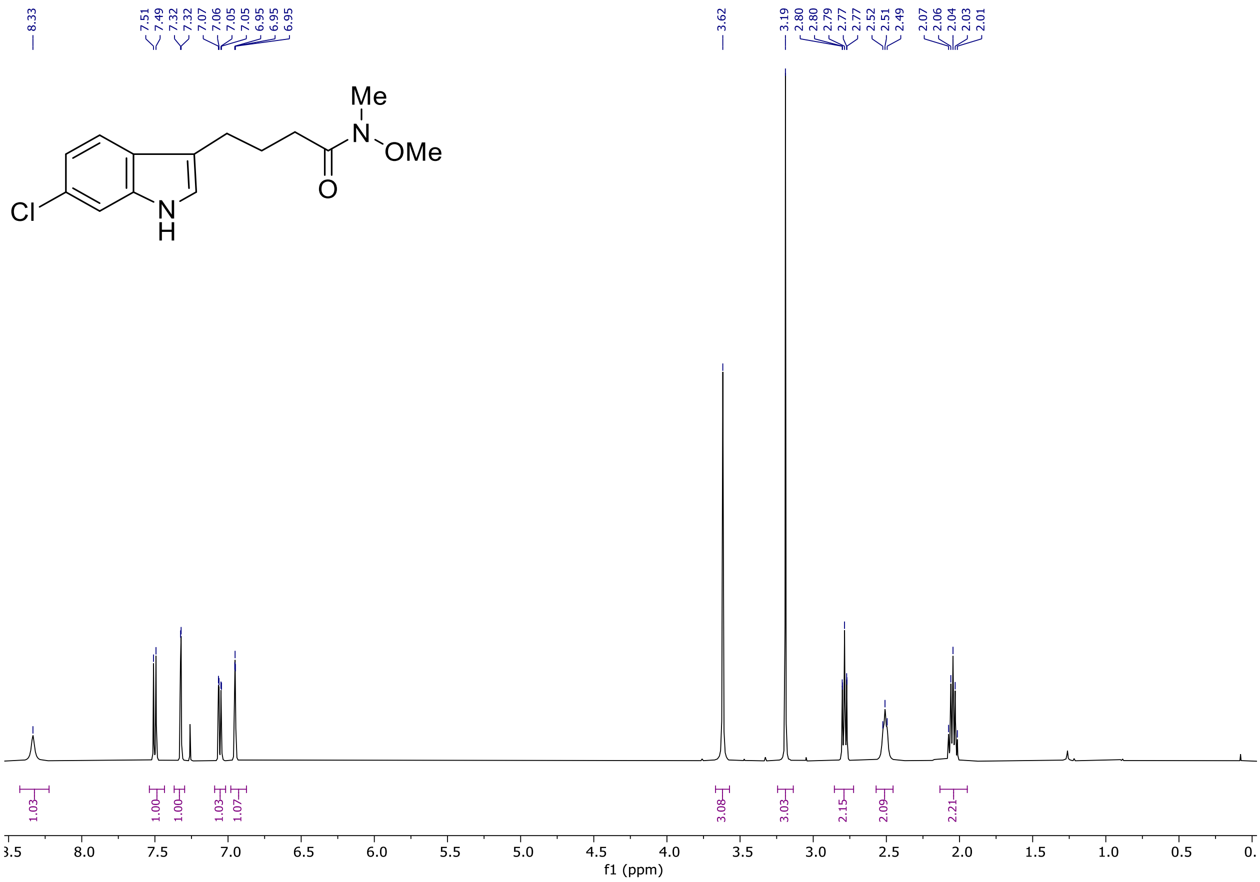

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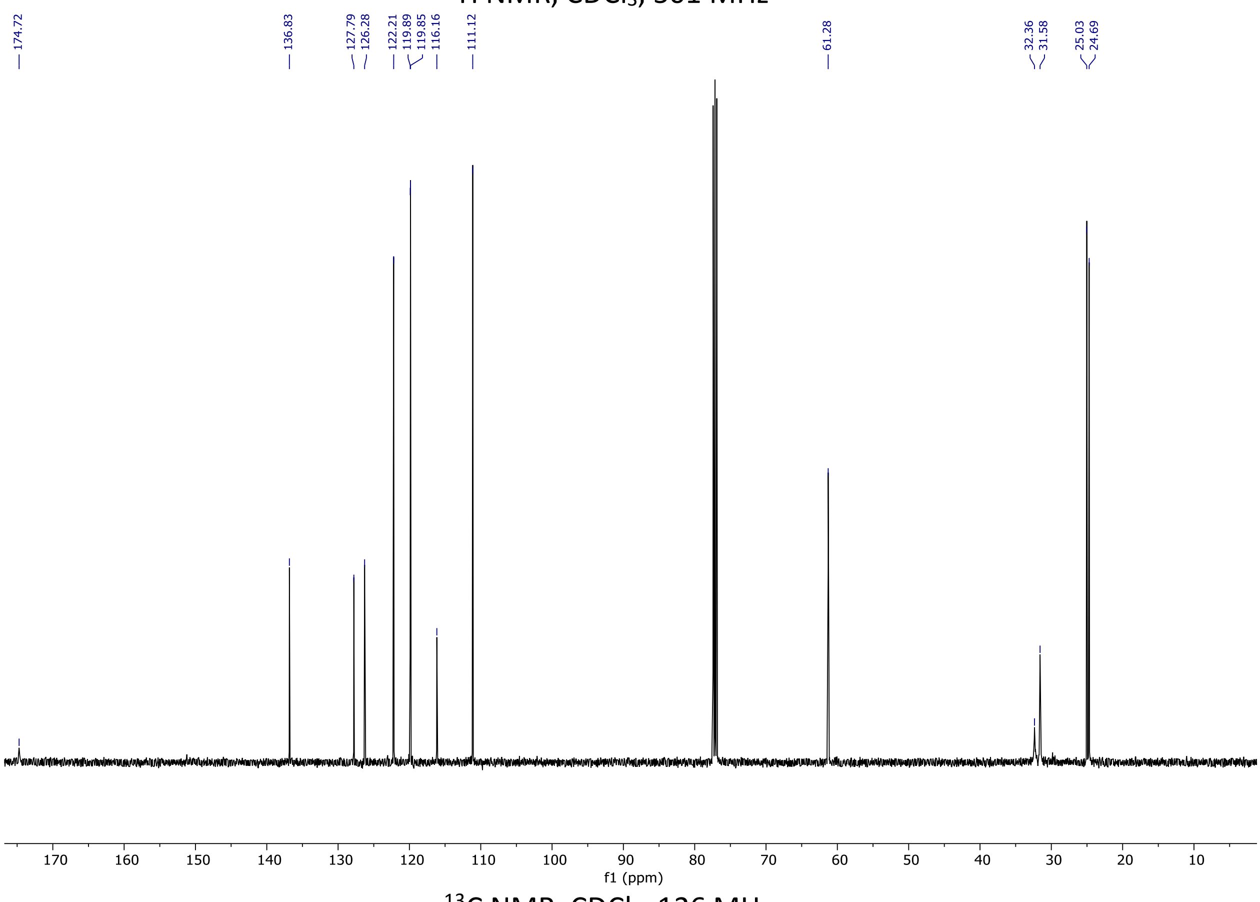

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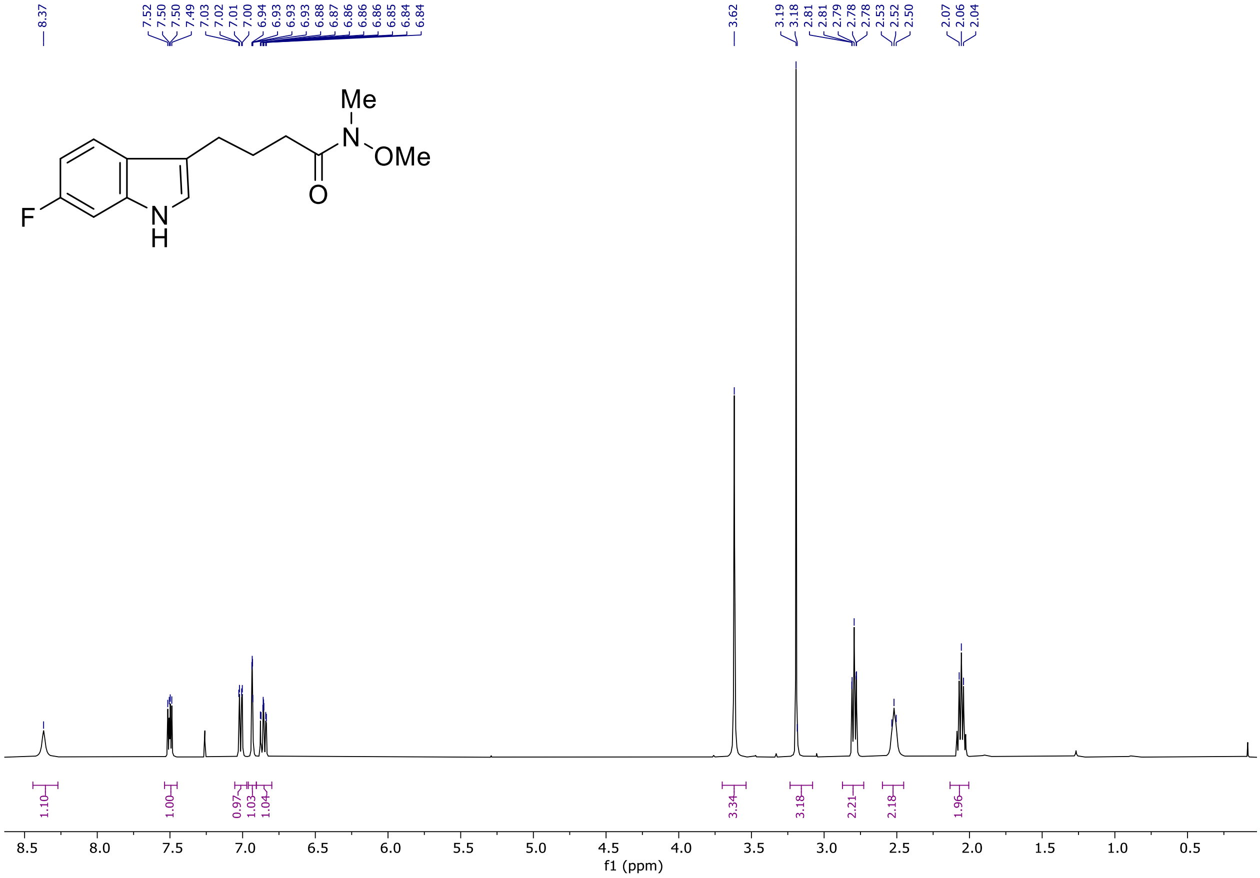

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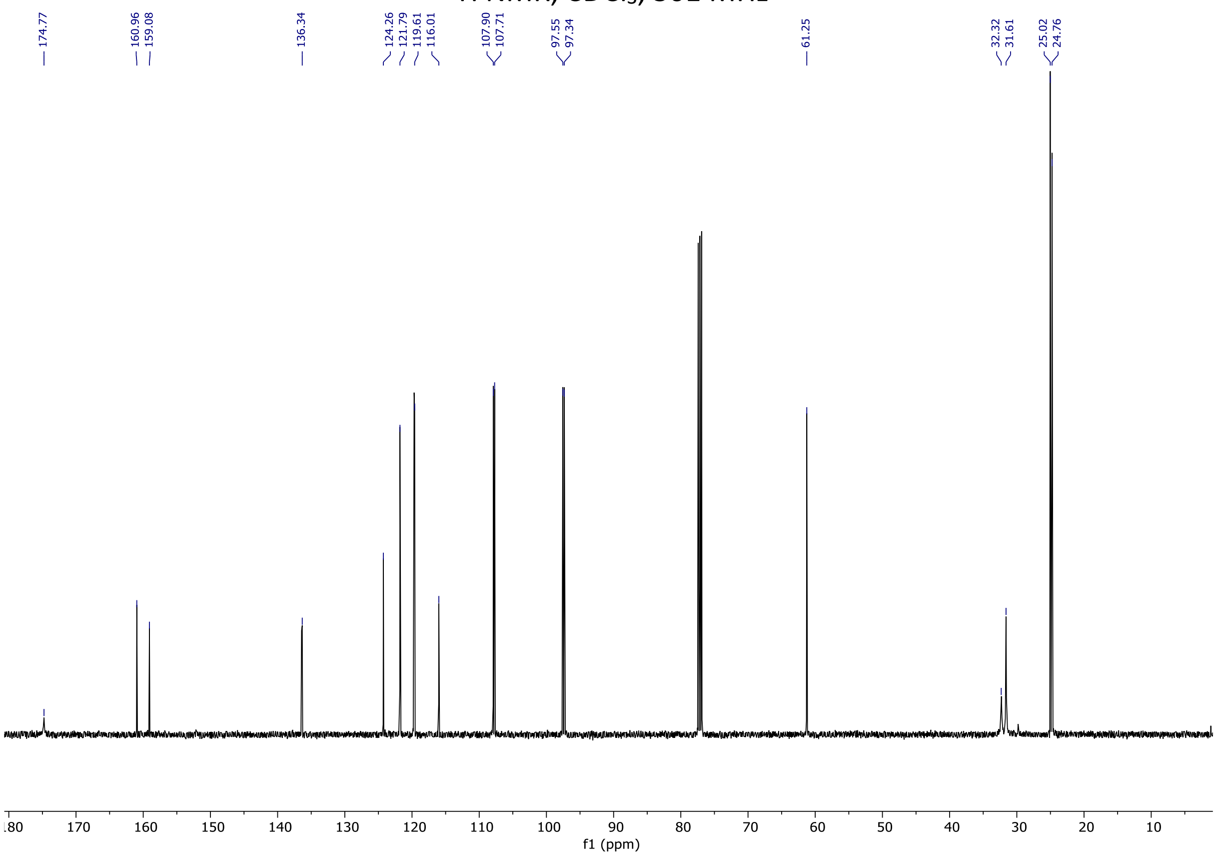
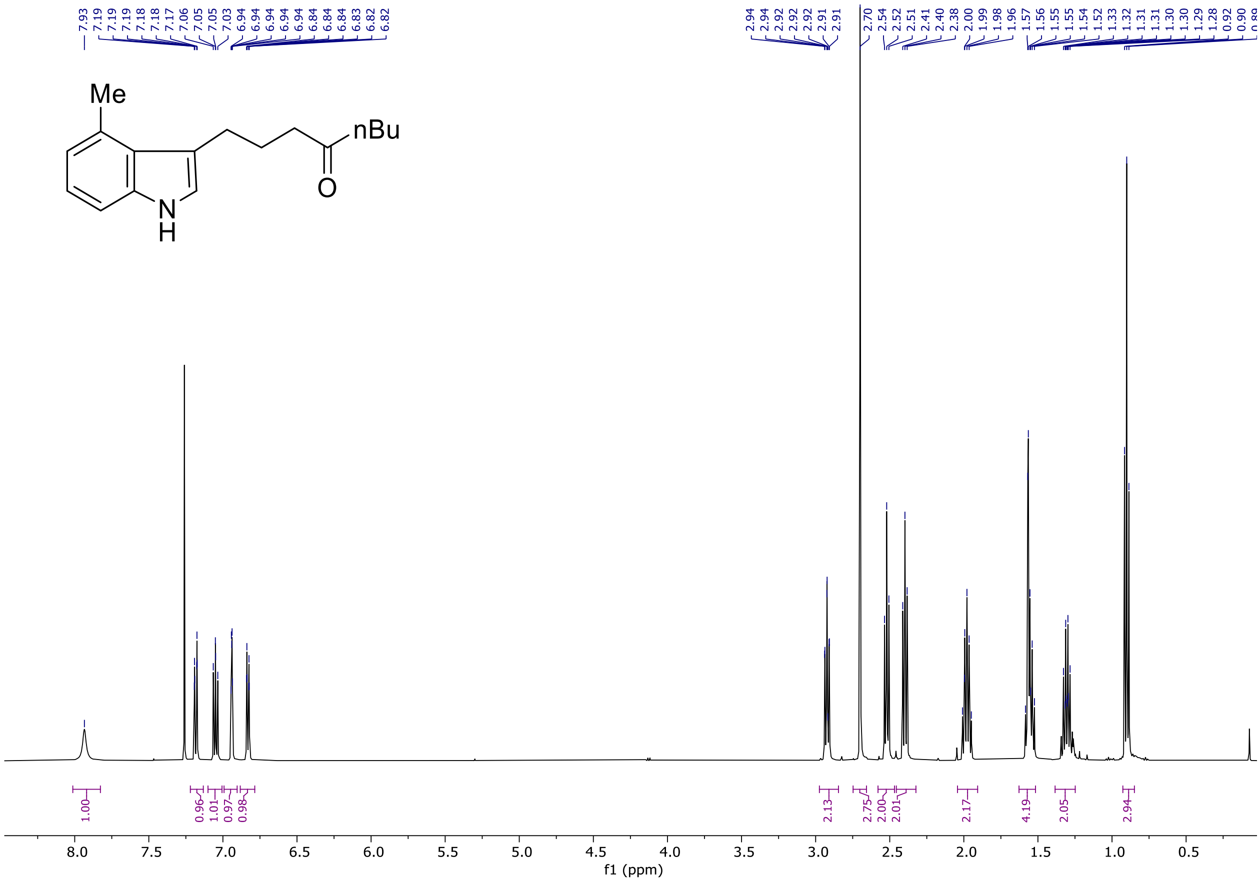


^{13}C NMR, $CDCl_3$, 126 MHz



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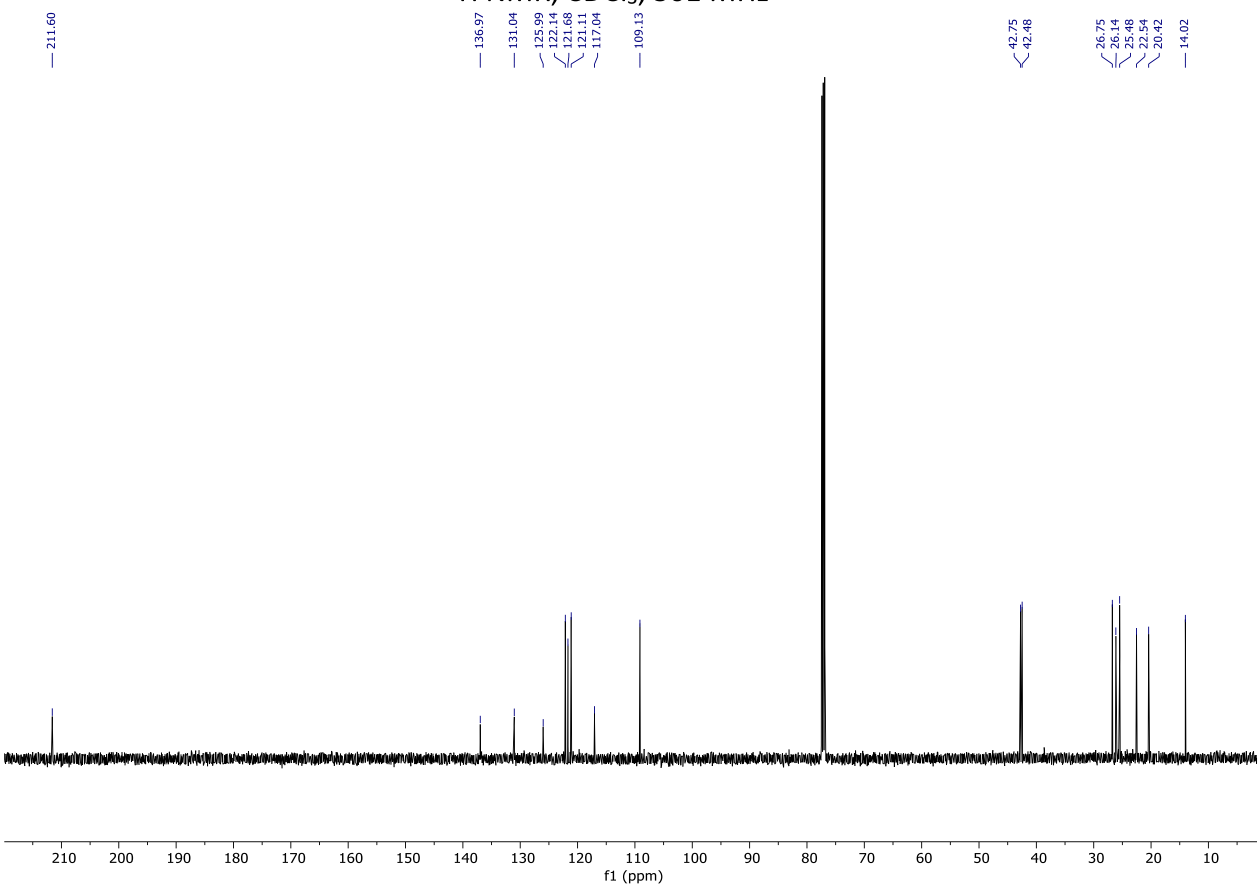

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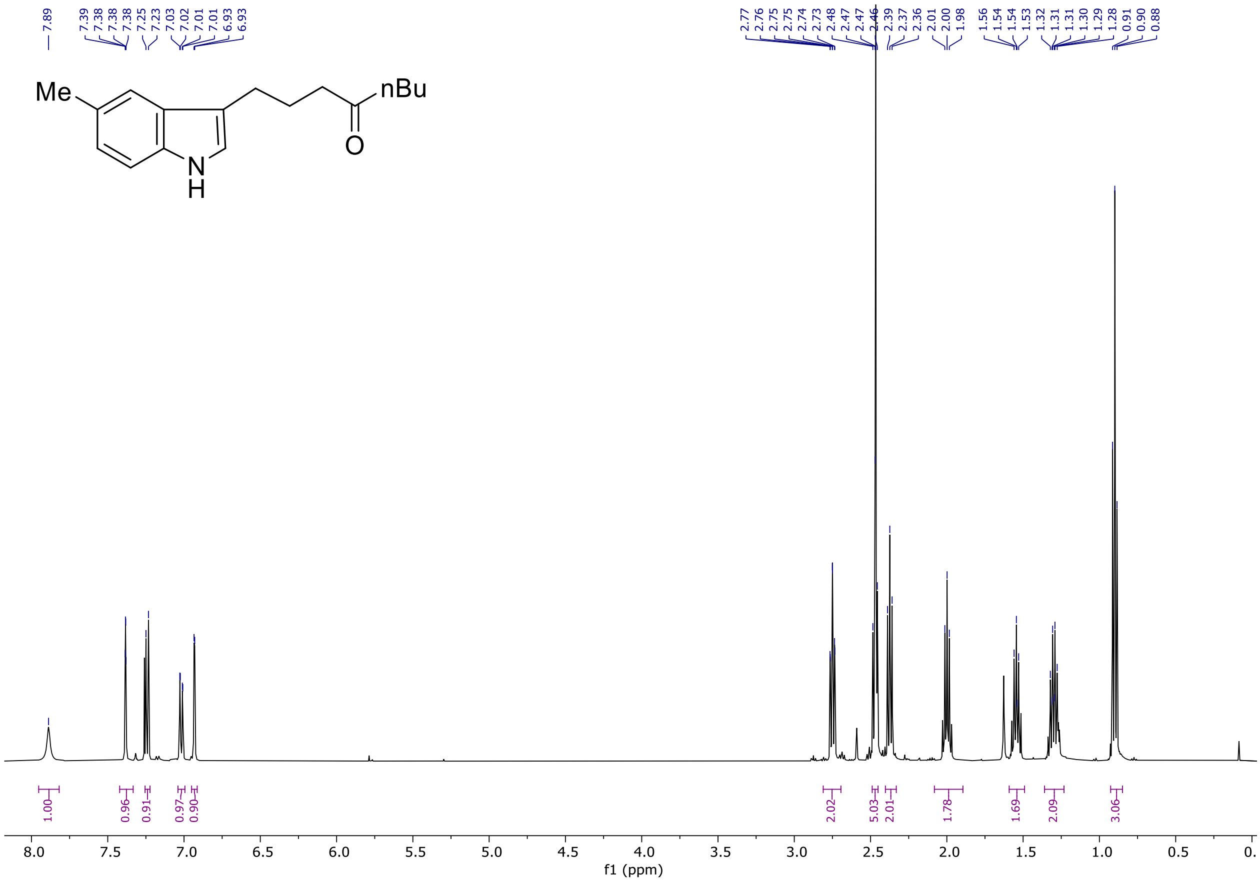

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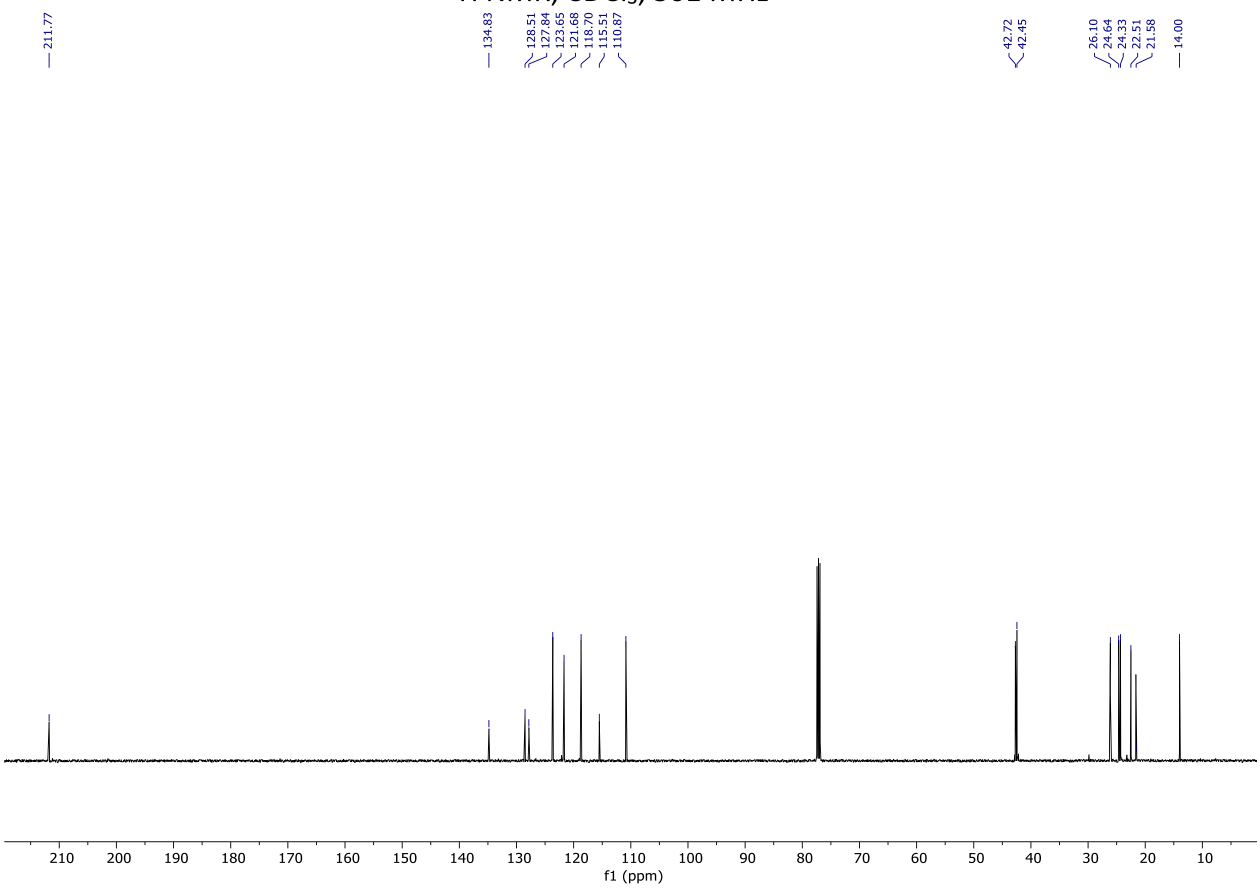

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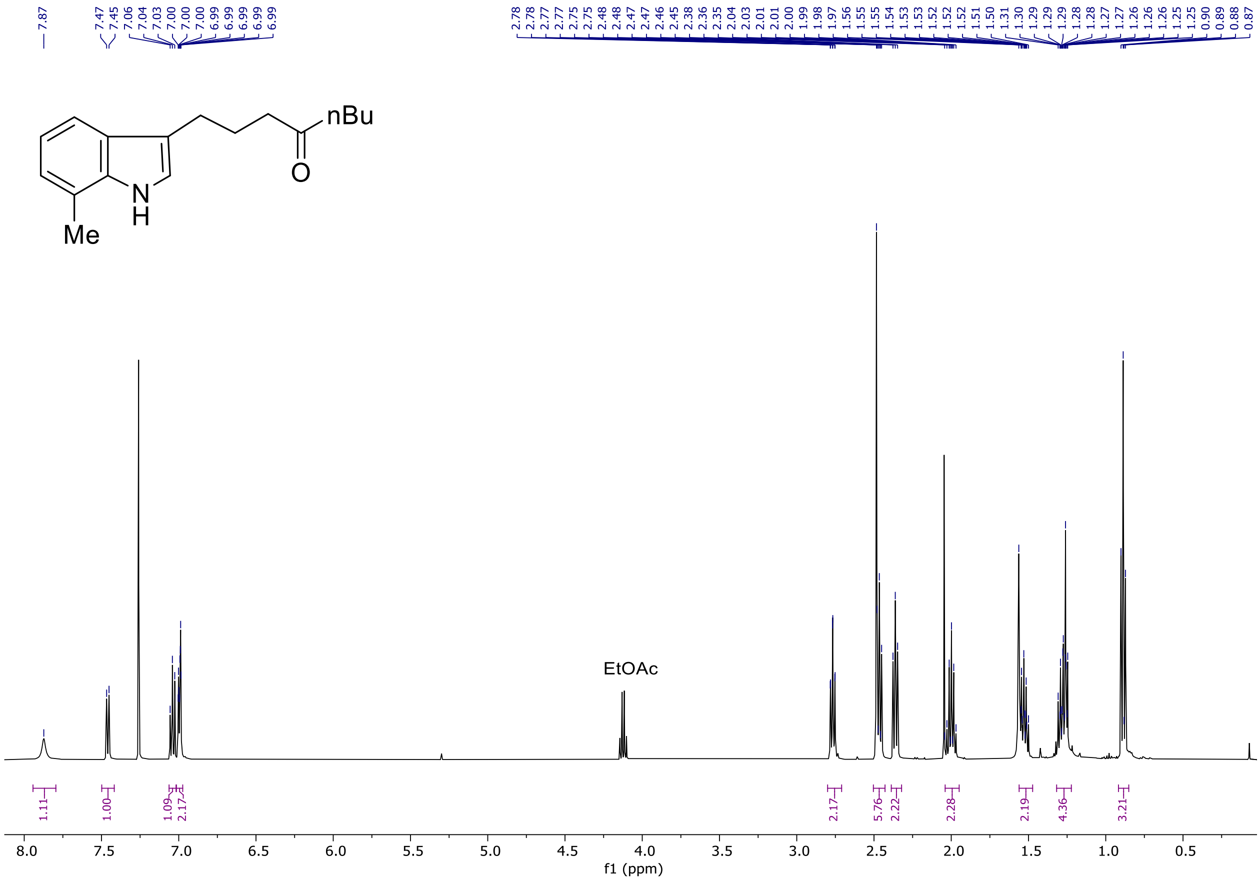

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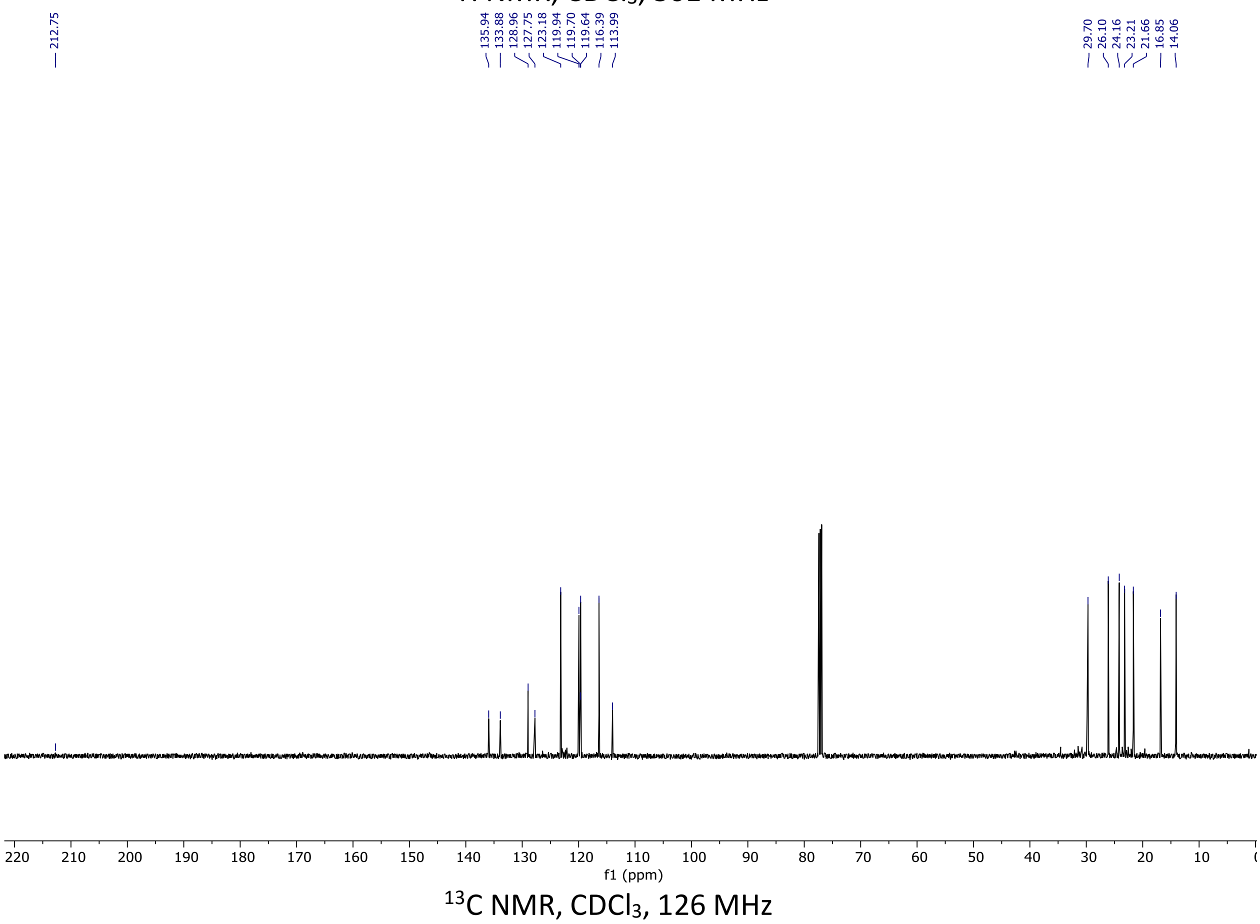
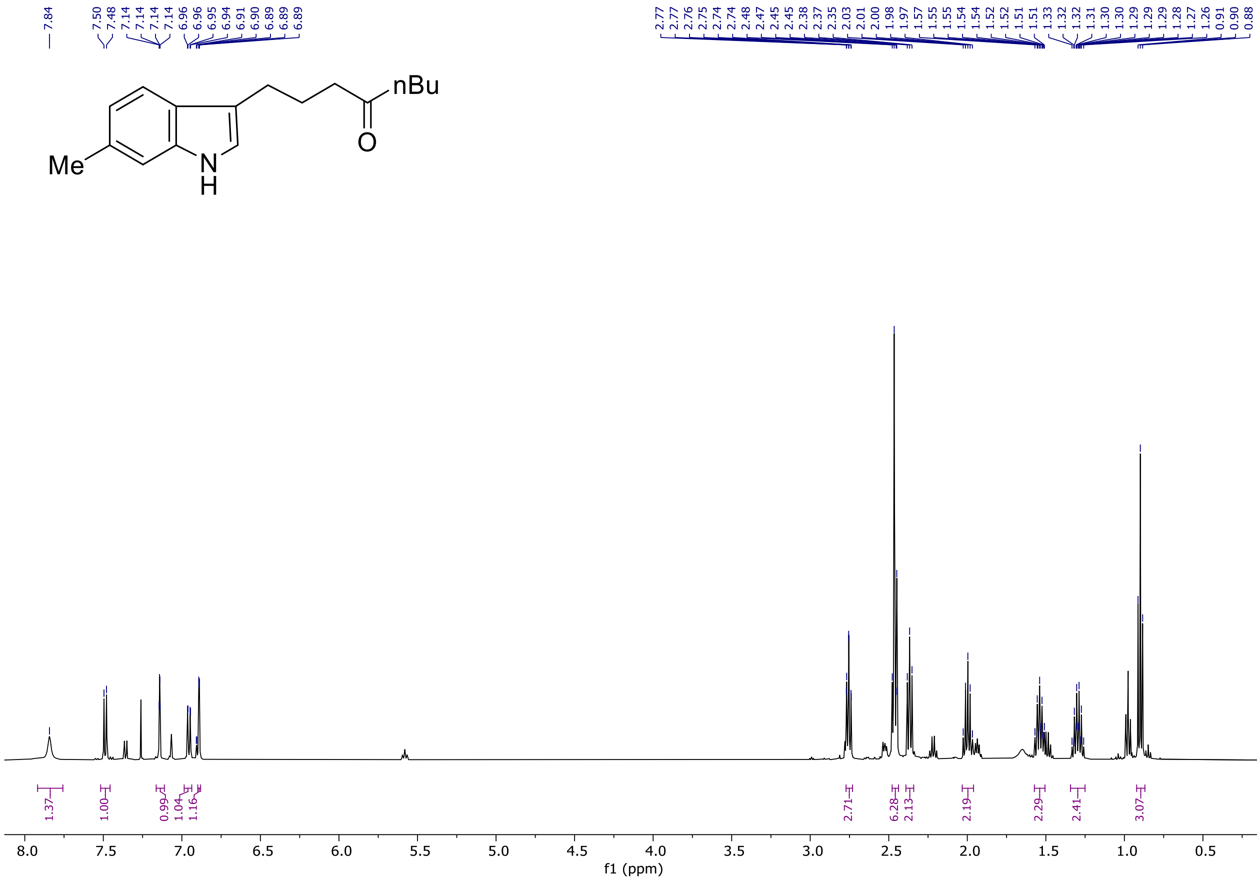
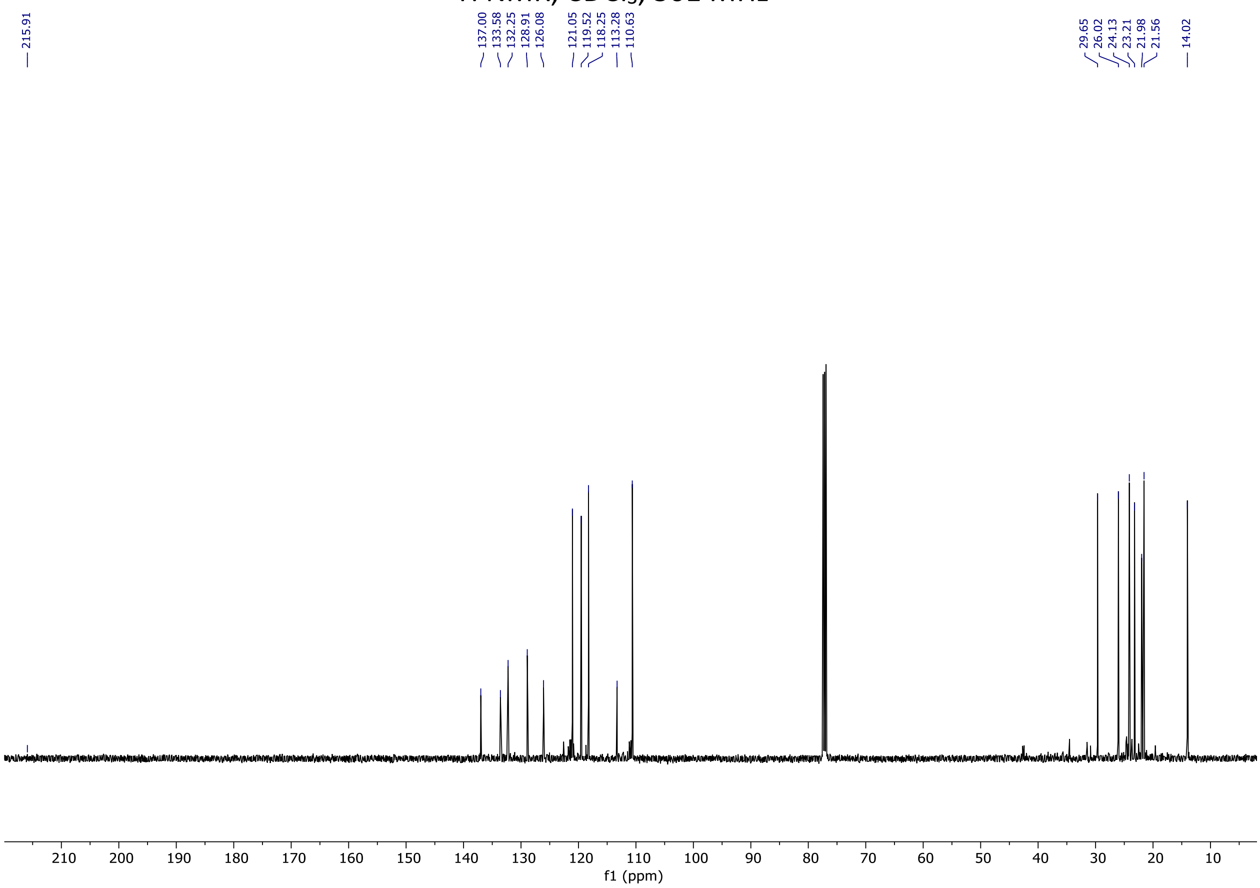


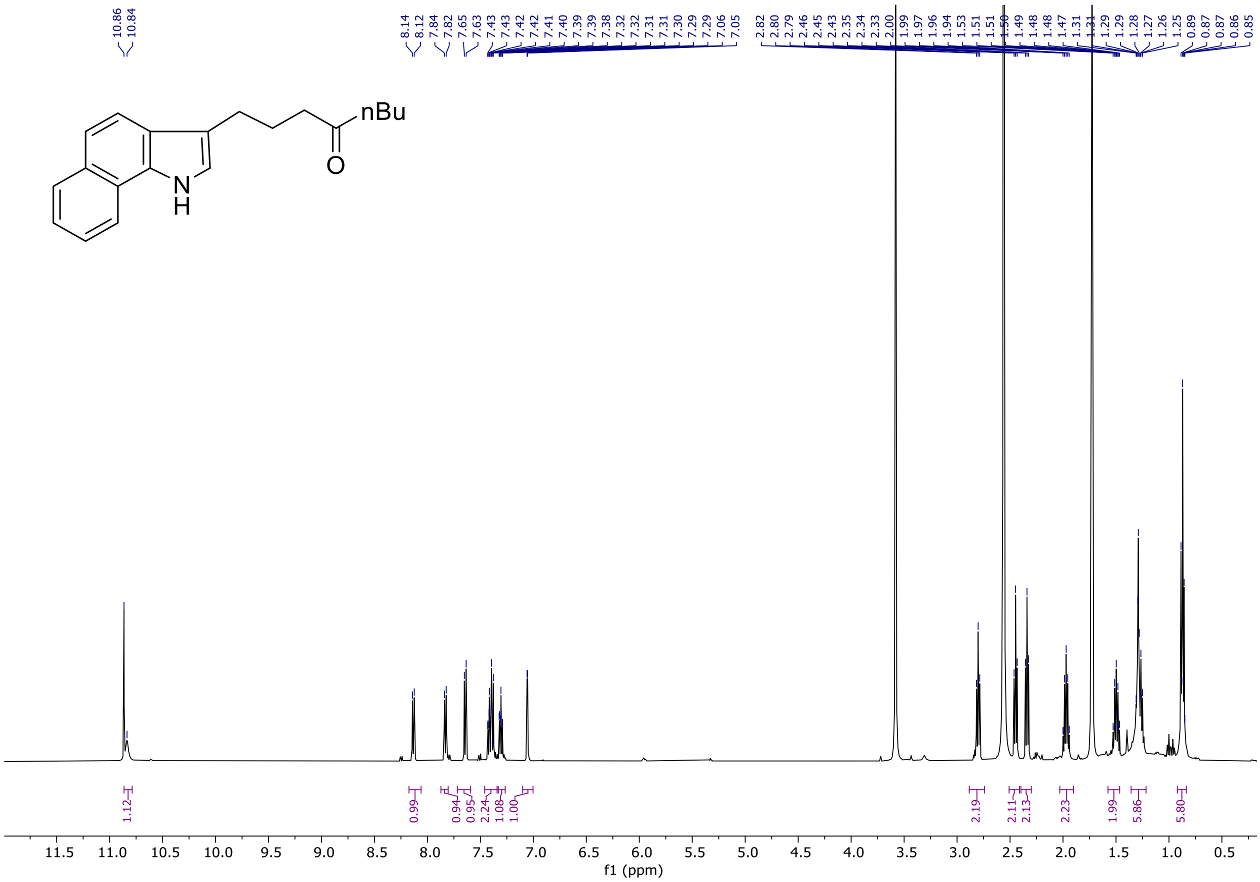
^{13}C NMR, $CDCl_3$, 126 MHz



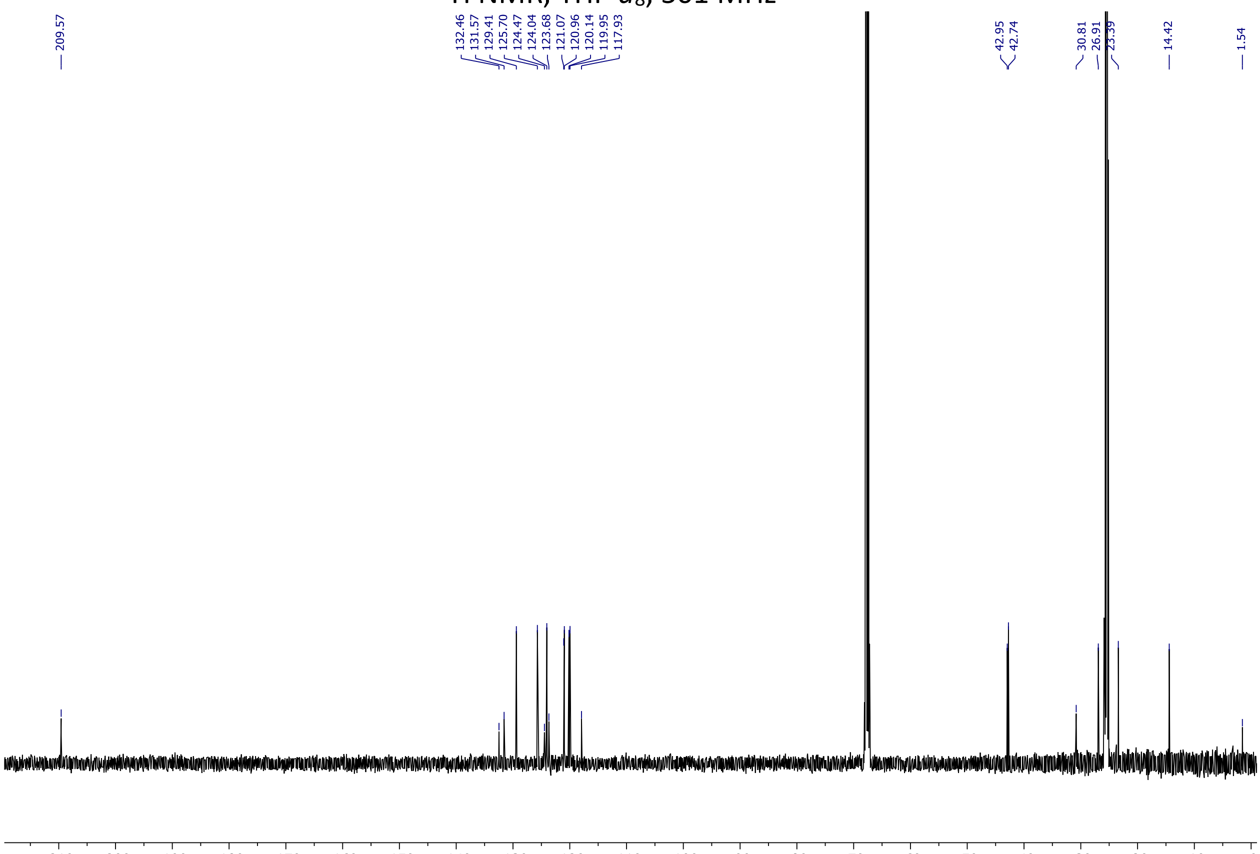
^{1}H NMR, $CDCl_3$, 501 MHz



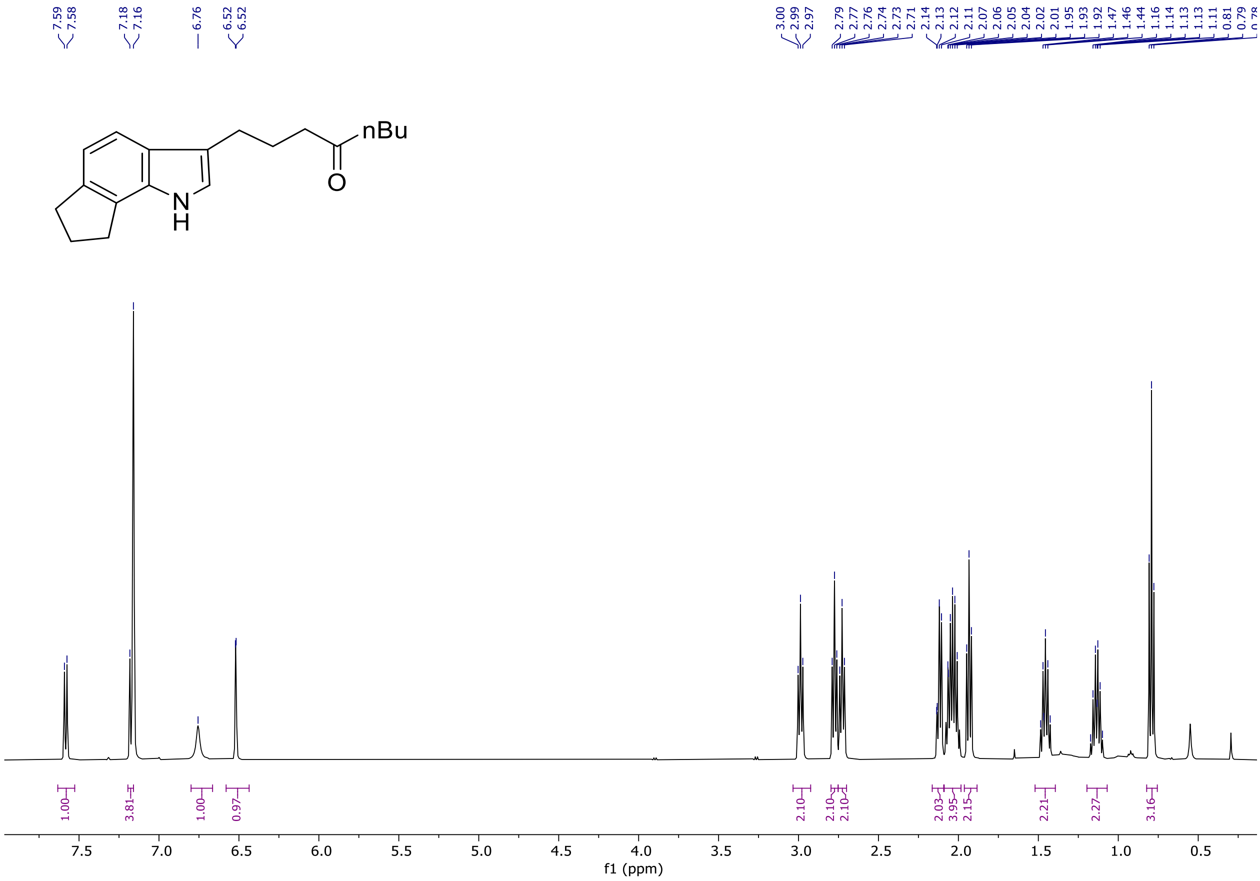
^{13}C NMR, $CDCl_3$, 126 MHz



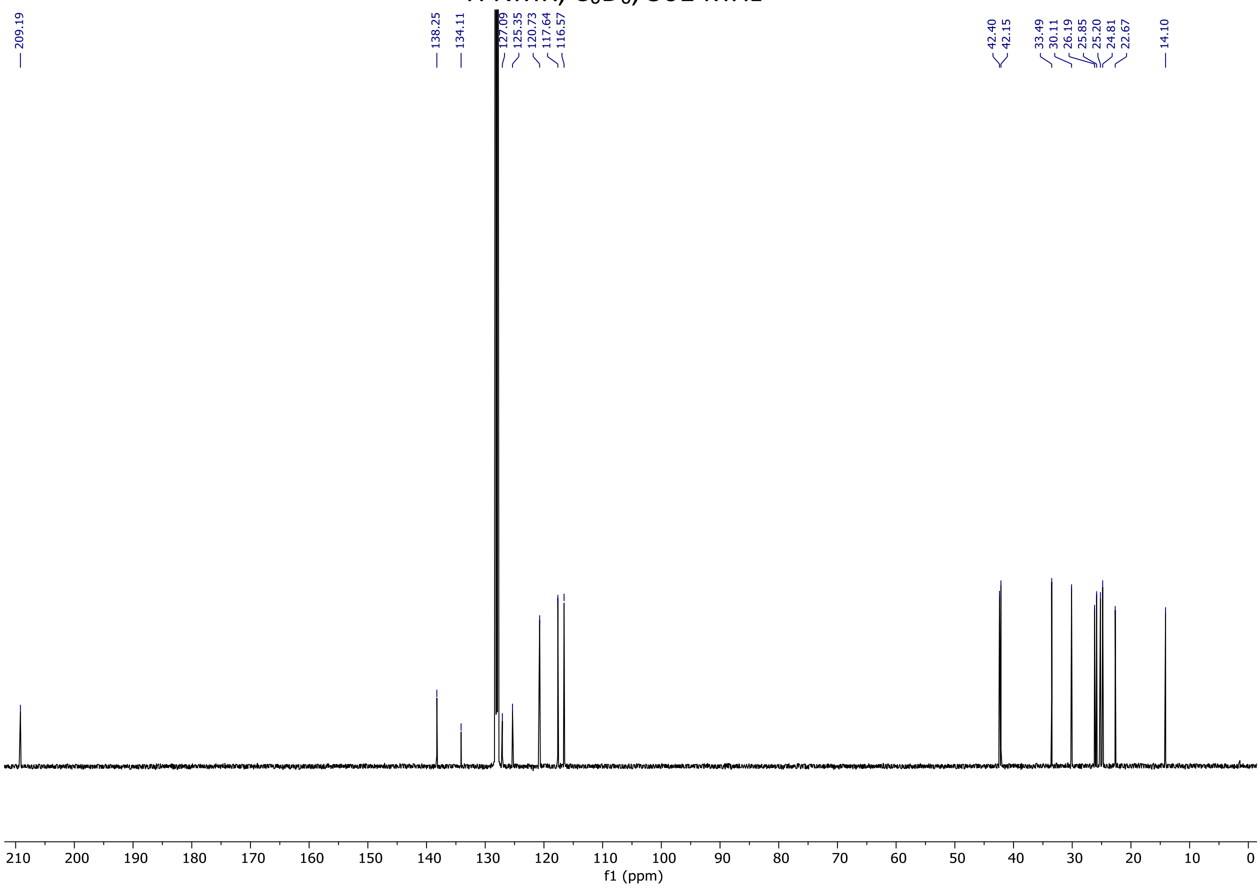
^{1}H NMR, THF-d_8, 501 MHz



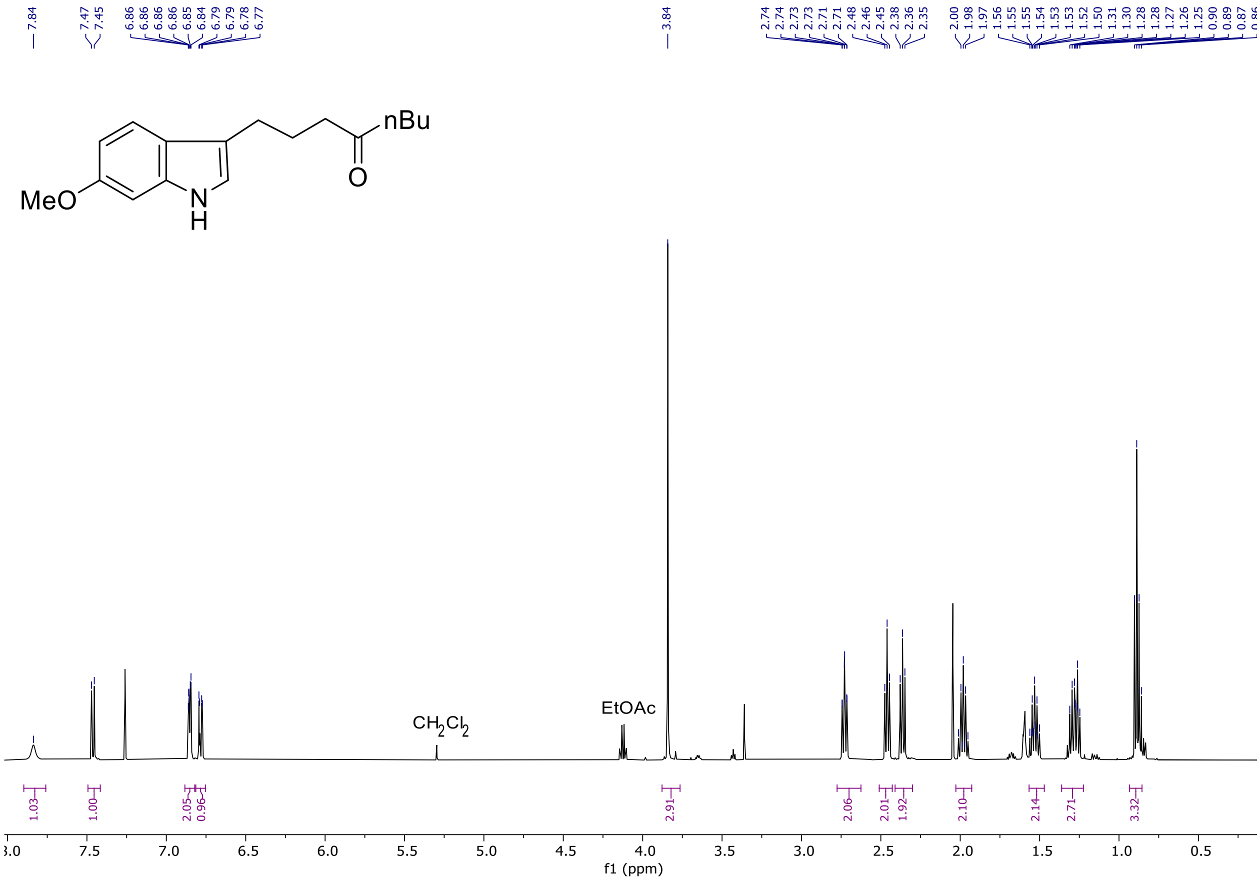
^{13}C NMR, THF-d_8, 126 MHz



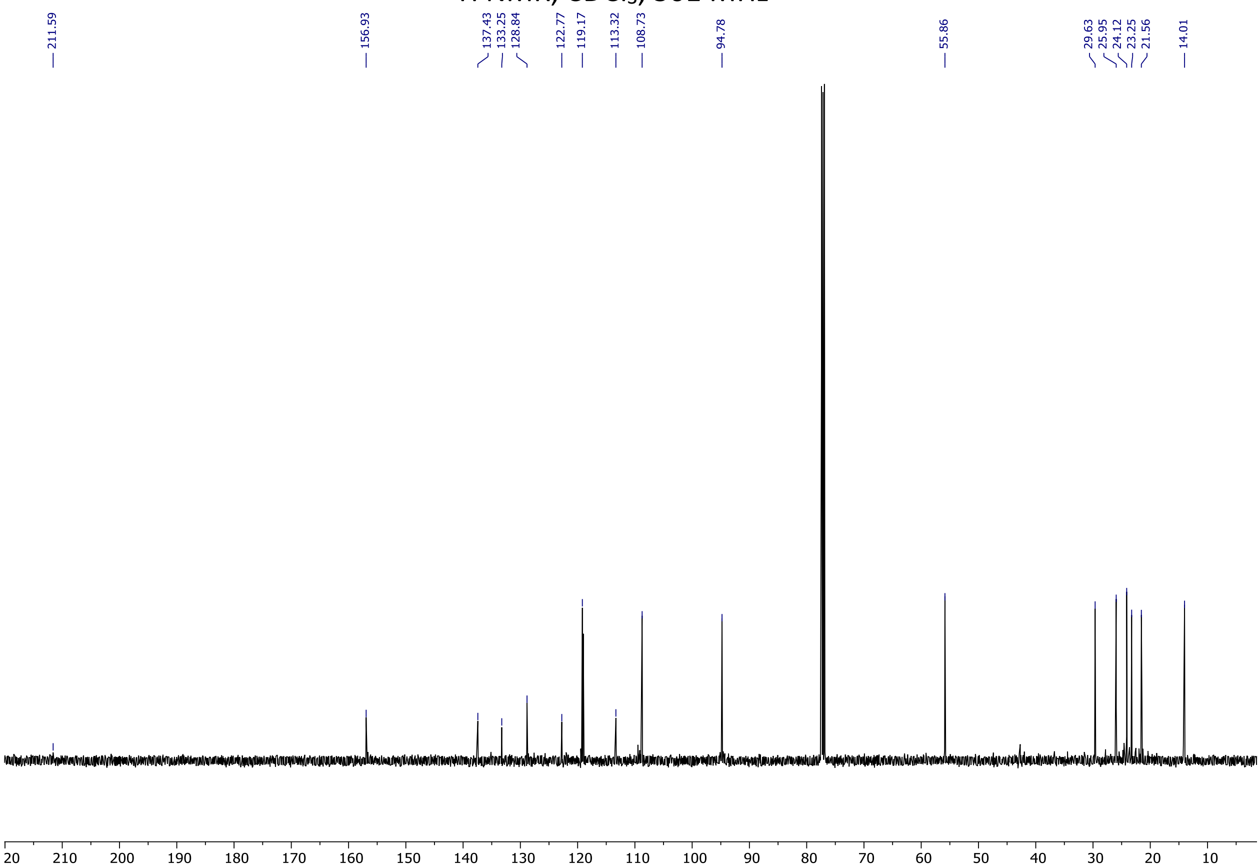
^{1}H NMR, C_6D_6, 501 MHz



^{13}C NMR, C_6D_6, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



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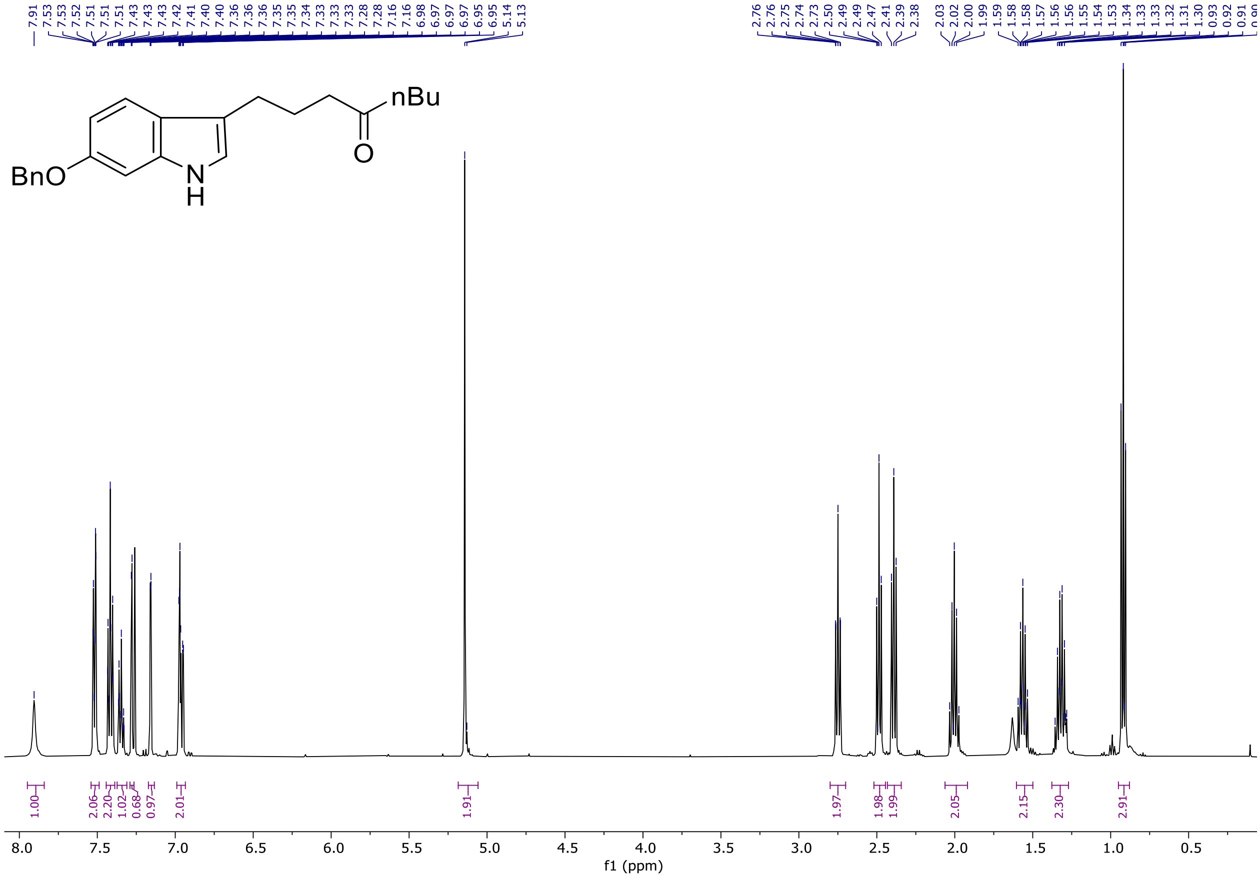
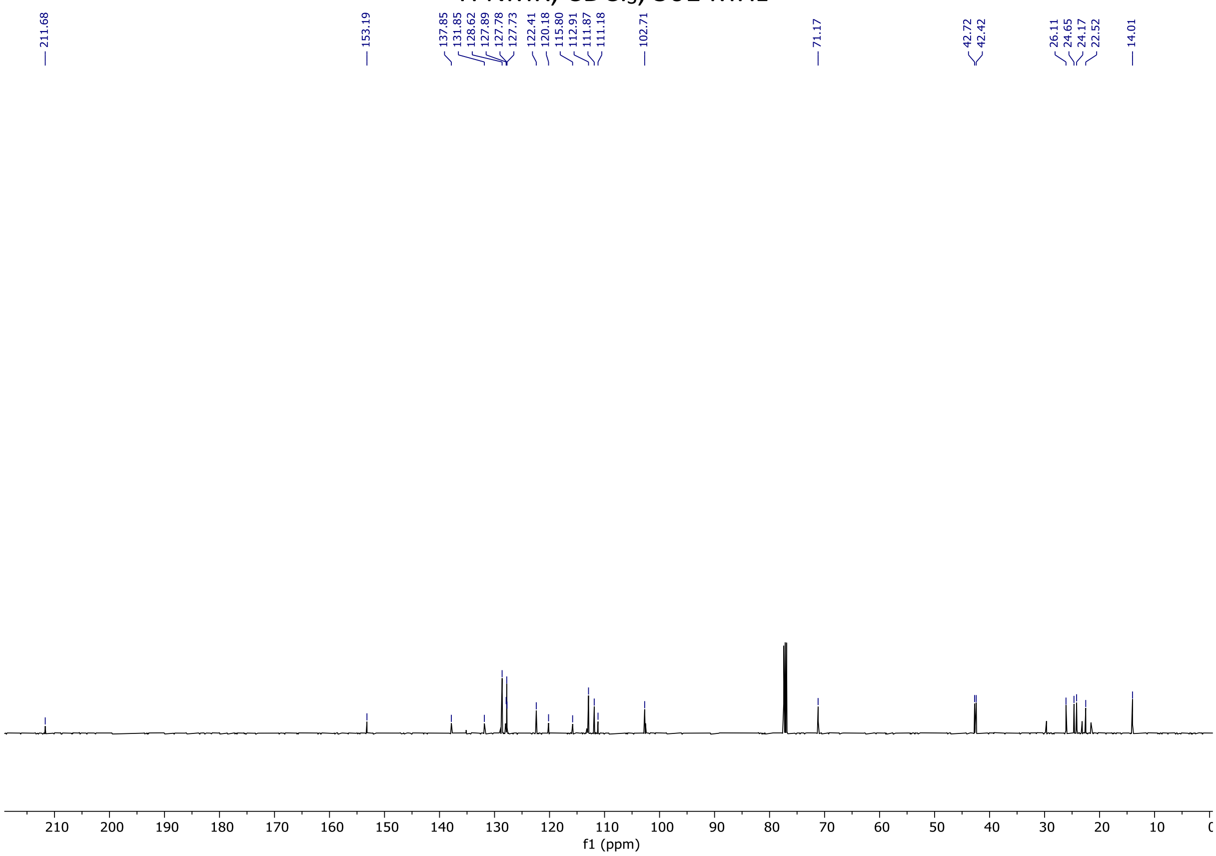
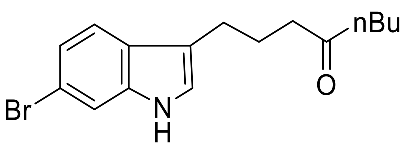
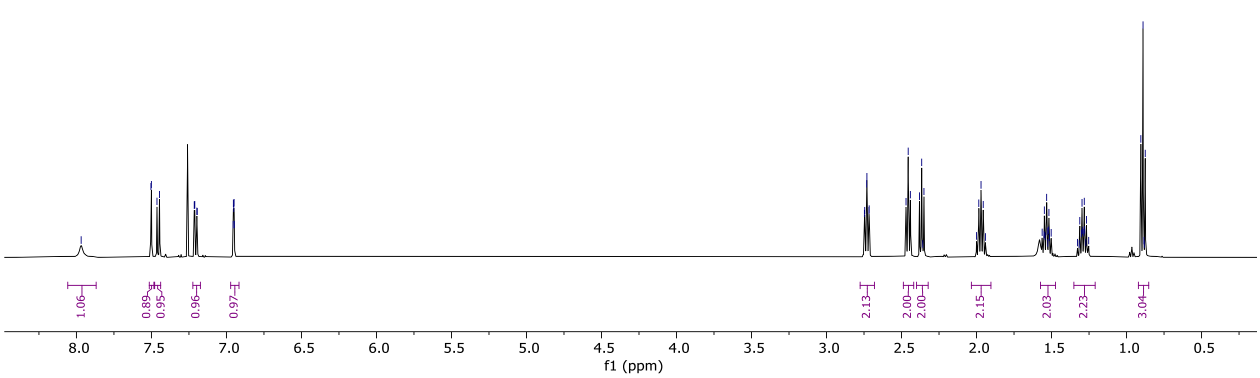


^{1}H NMR, $CDCl_3$, 501 MHz

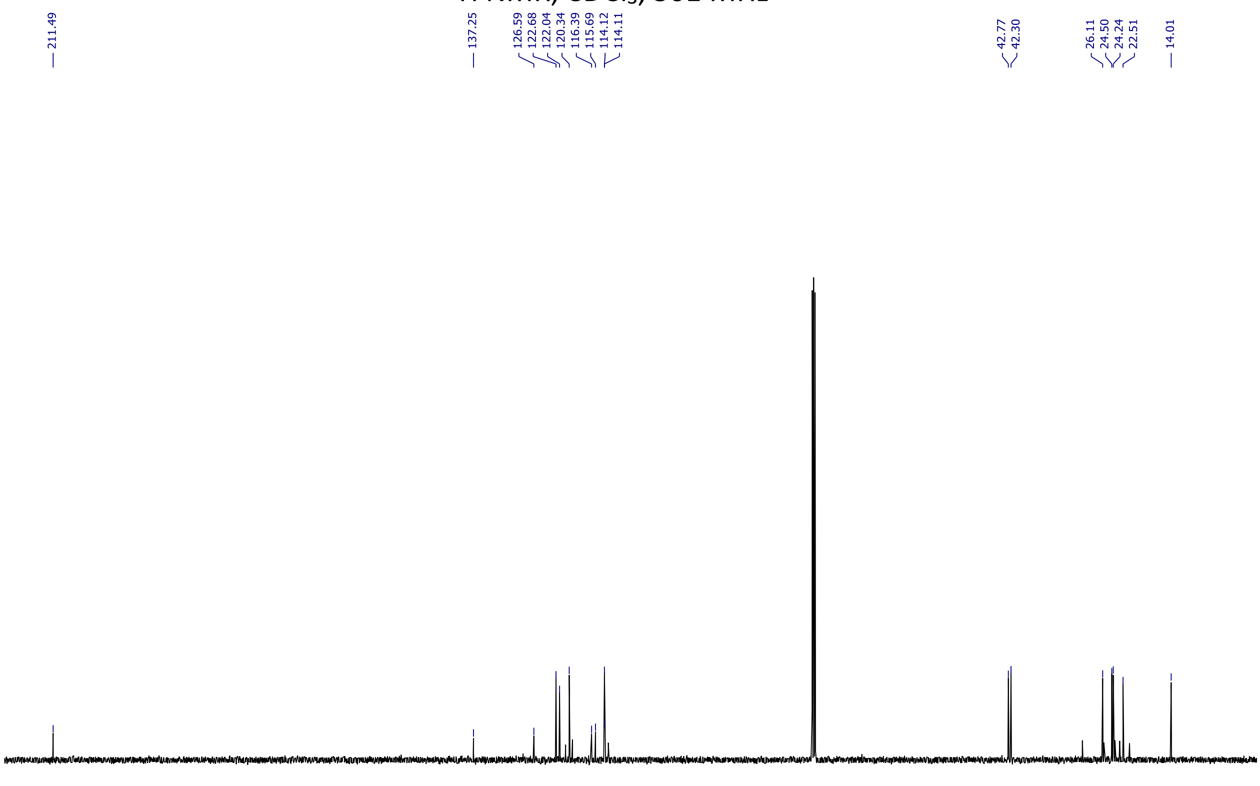


^{13}C NMR, $CDCl_3$, 126 MHz

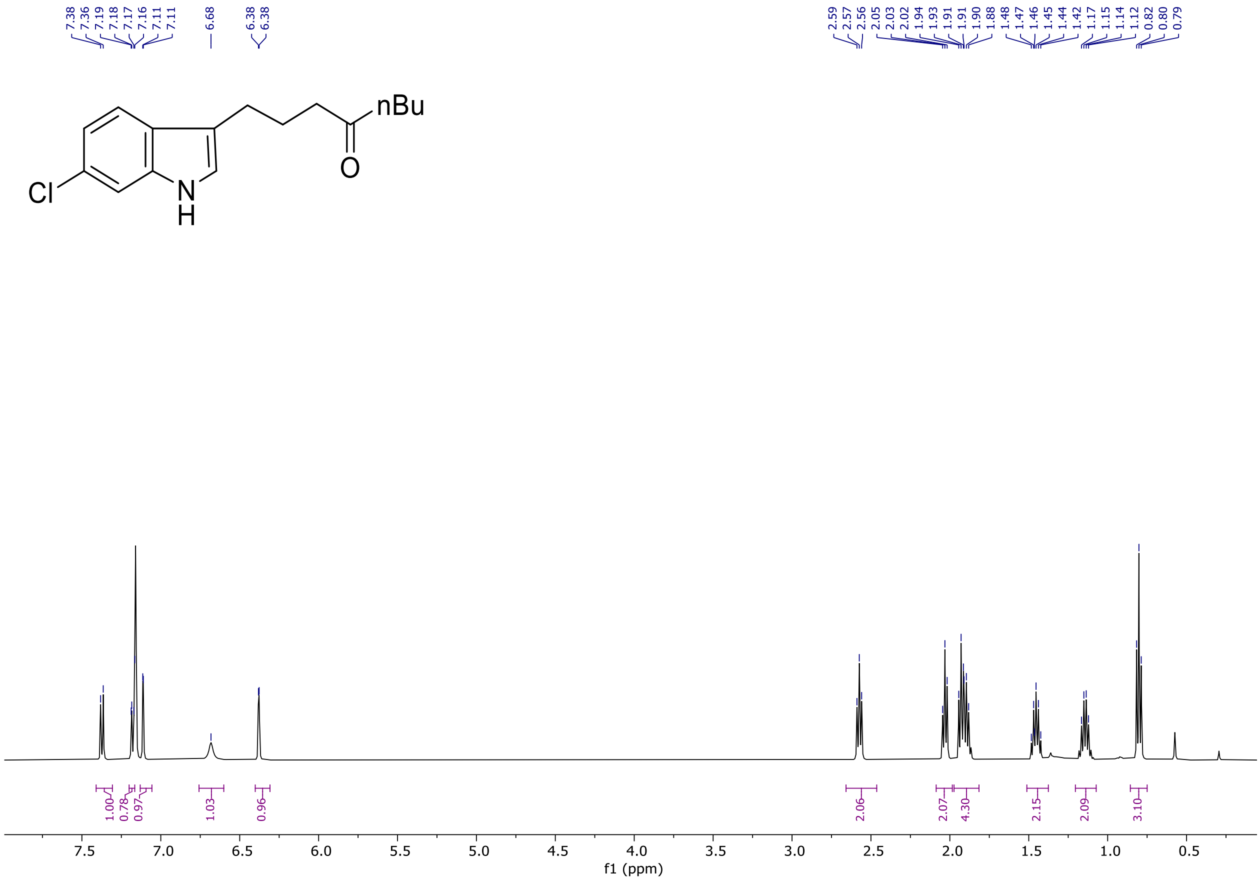




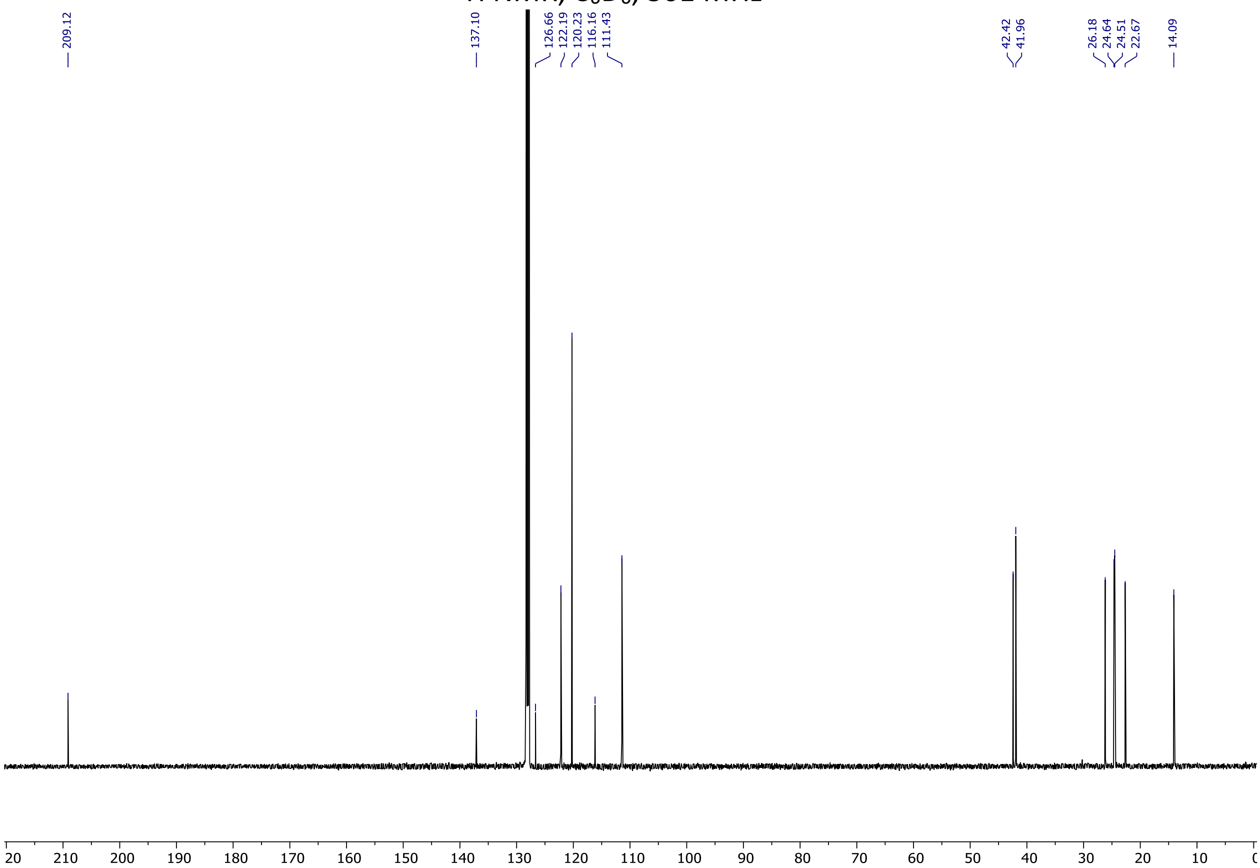
^{1}H NMR, $CDCl_3$, 501 MHz



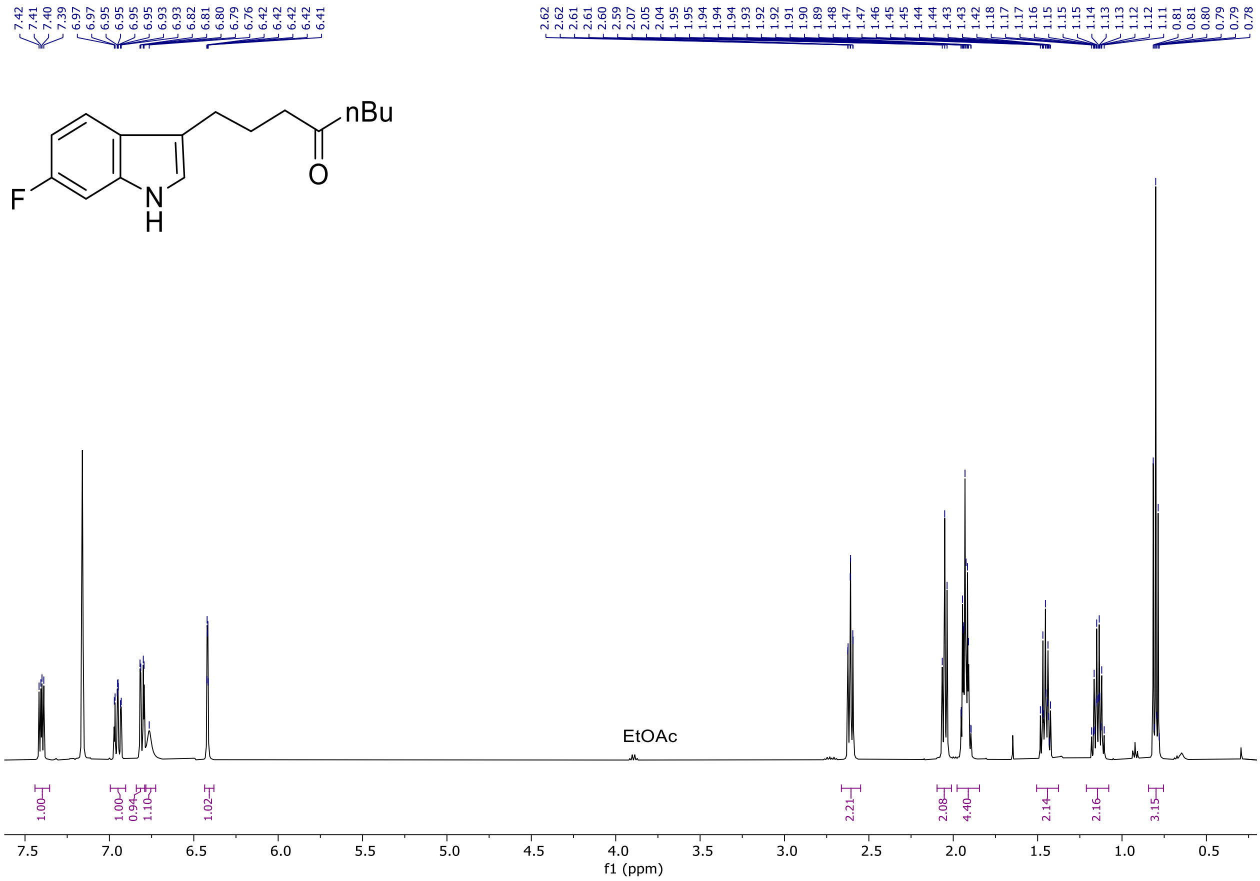
^{13}C NMR, $CDCl_3$, 126 MHz



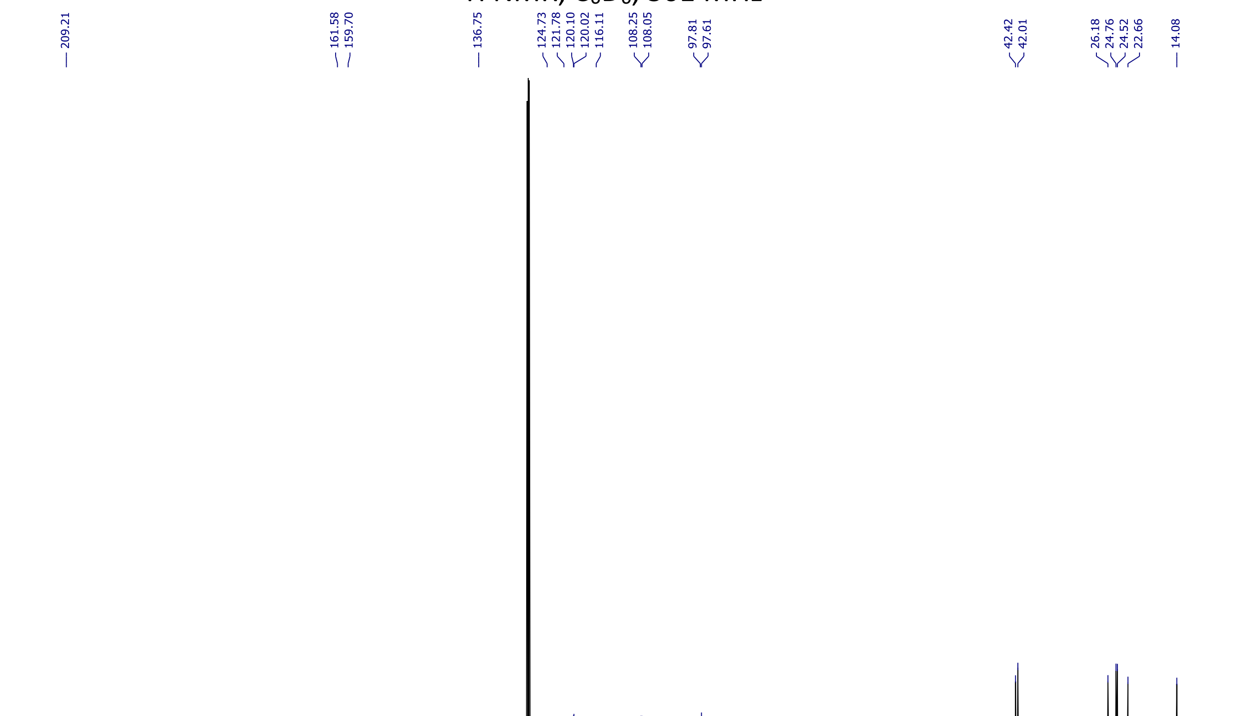
^{1}H NMR, C_6D_6, 501 MHz



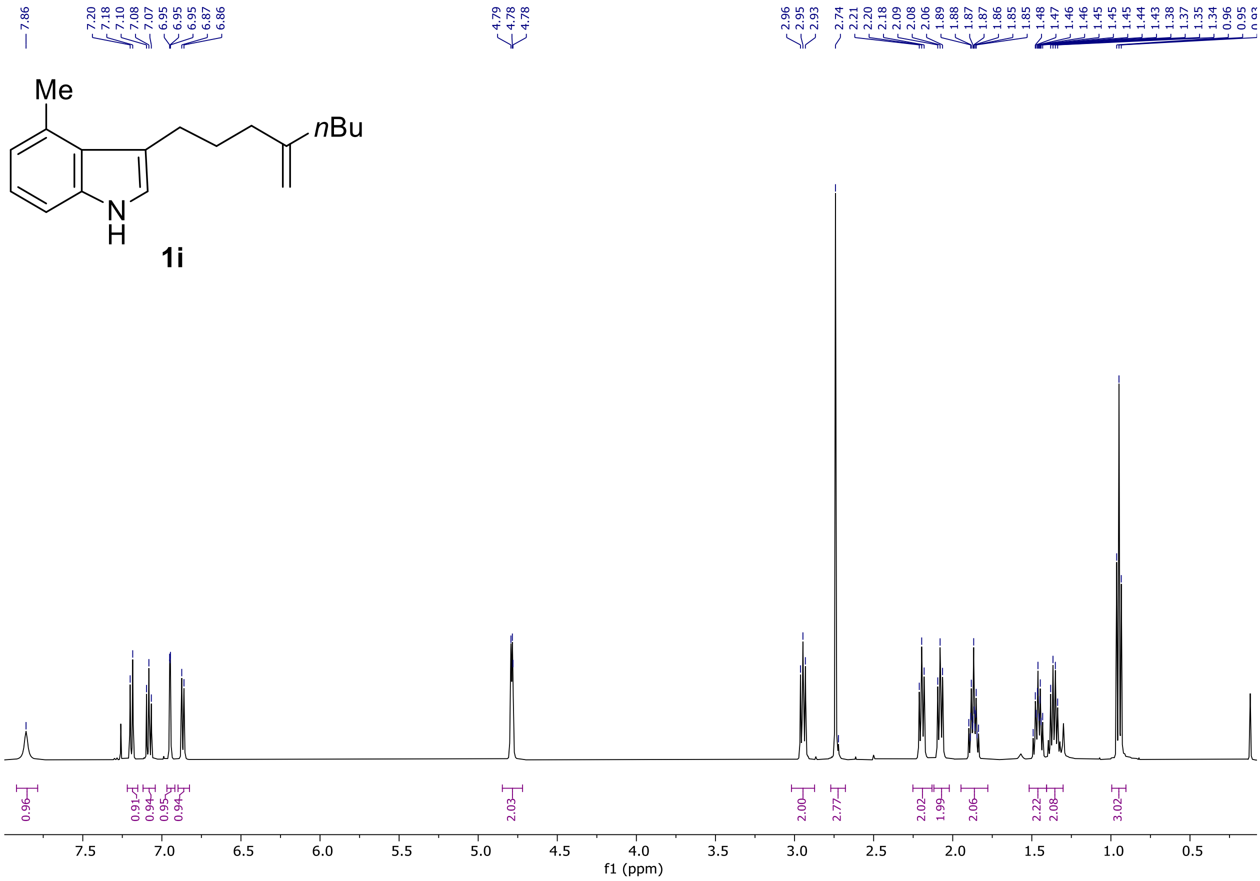
^{13}C NMR, C_6D_6, 126 MHz



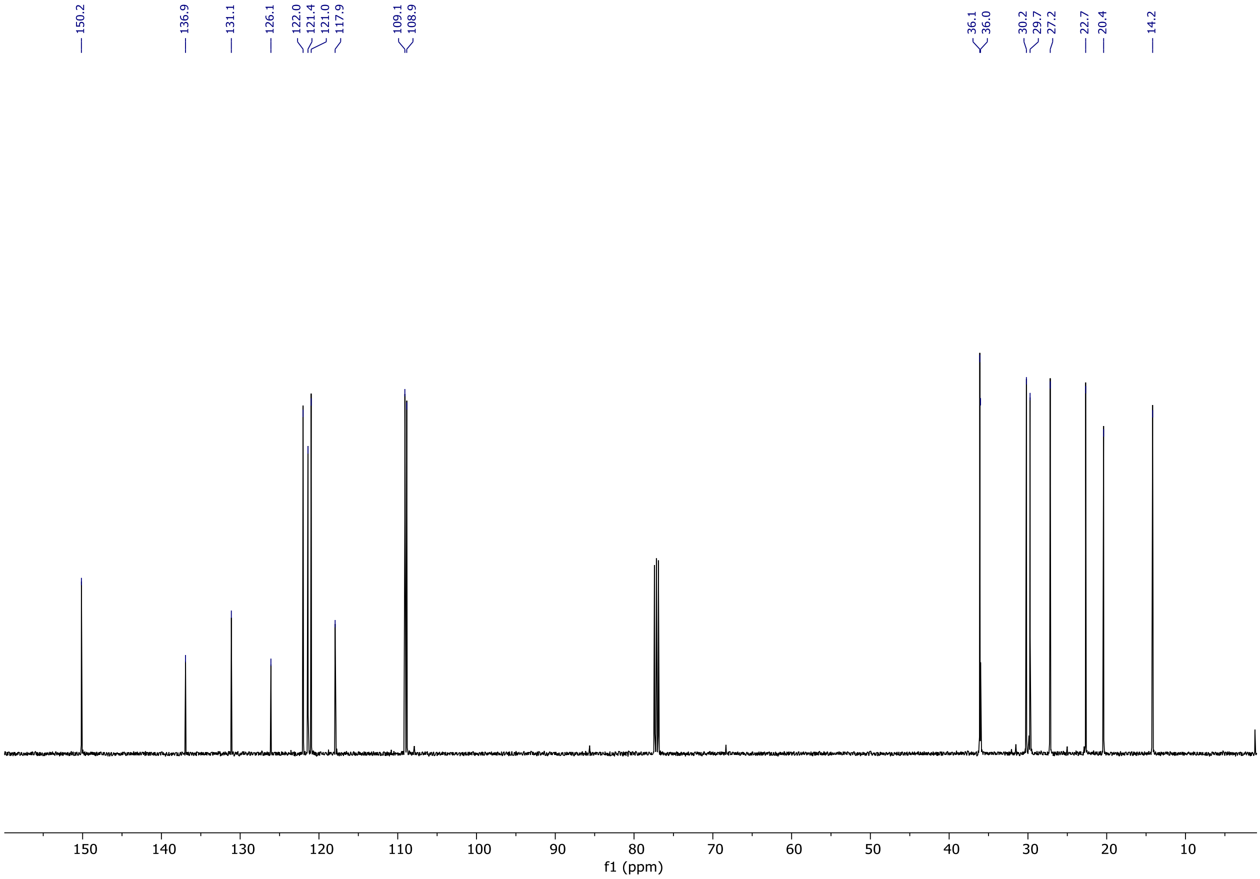
^{1}H NMR, C_6D_6, 501 MHz



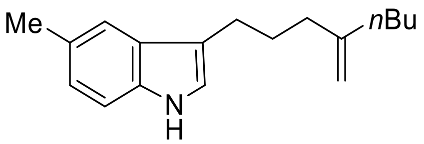
^{13}C NMR, C_6D_6, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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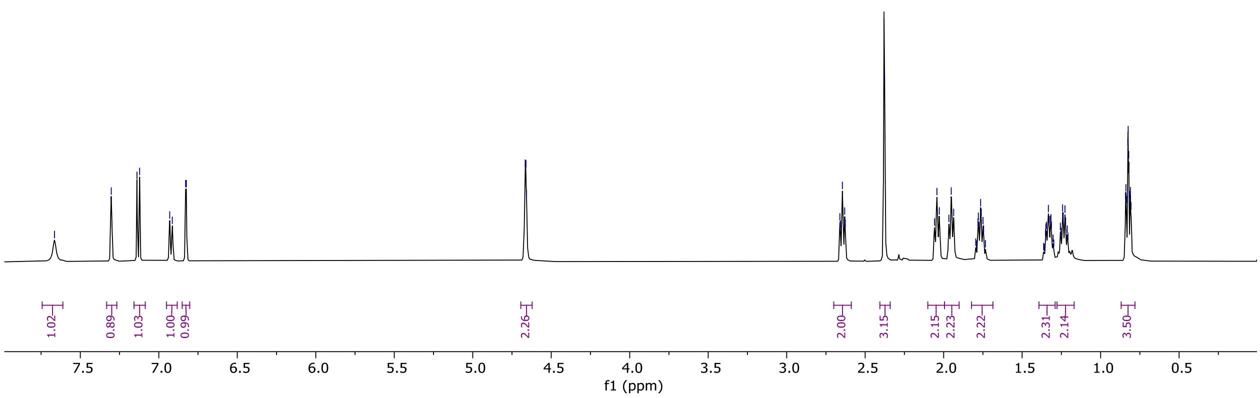
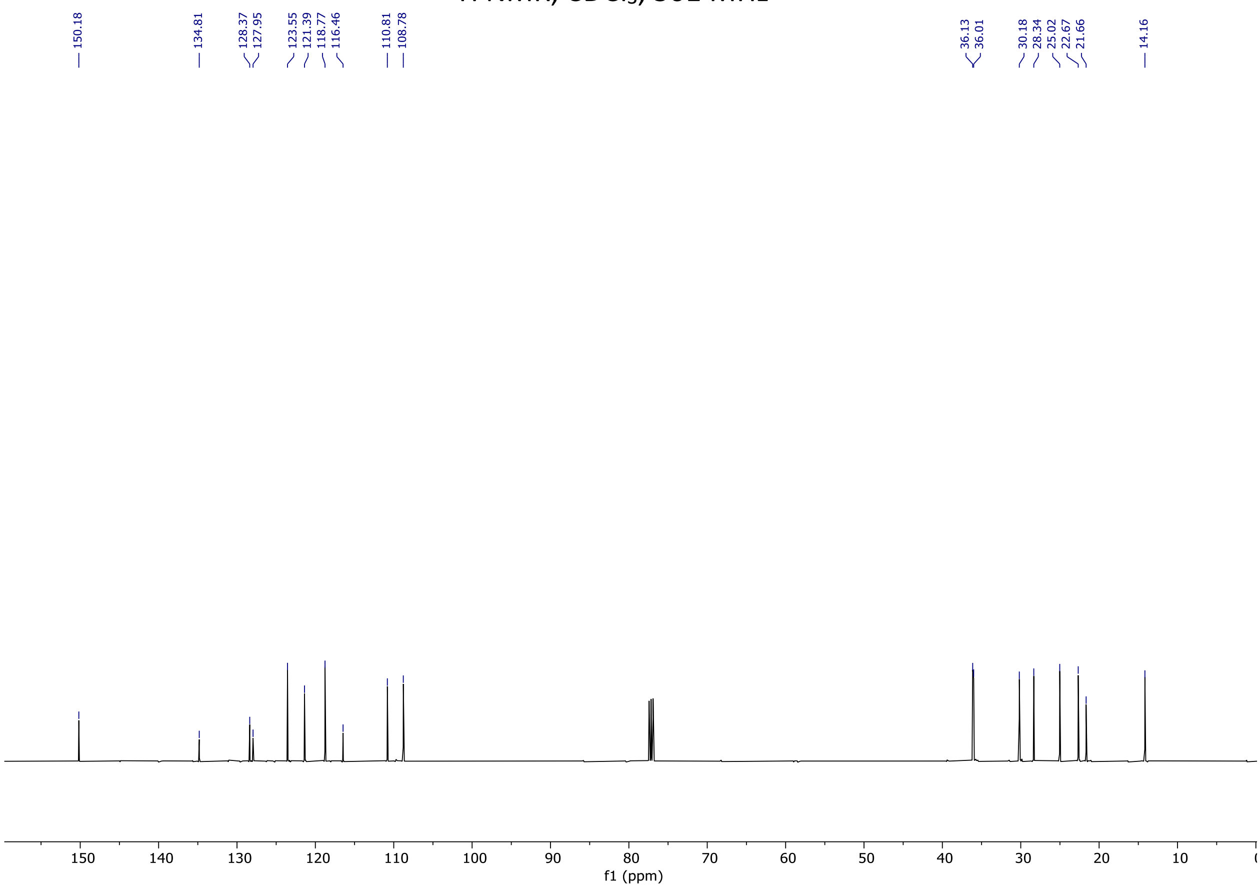
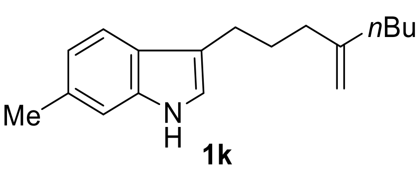


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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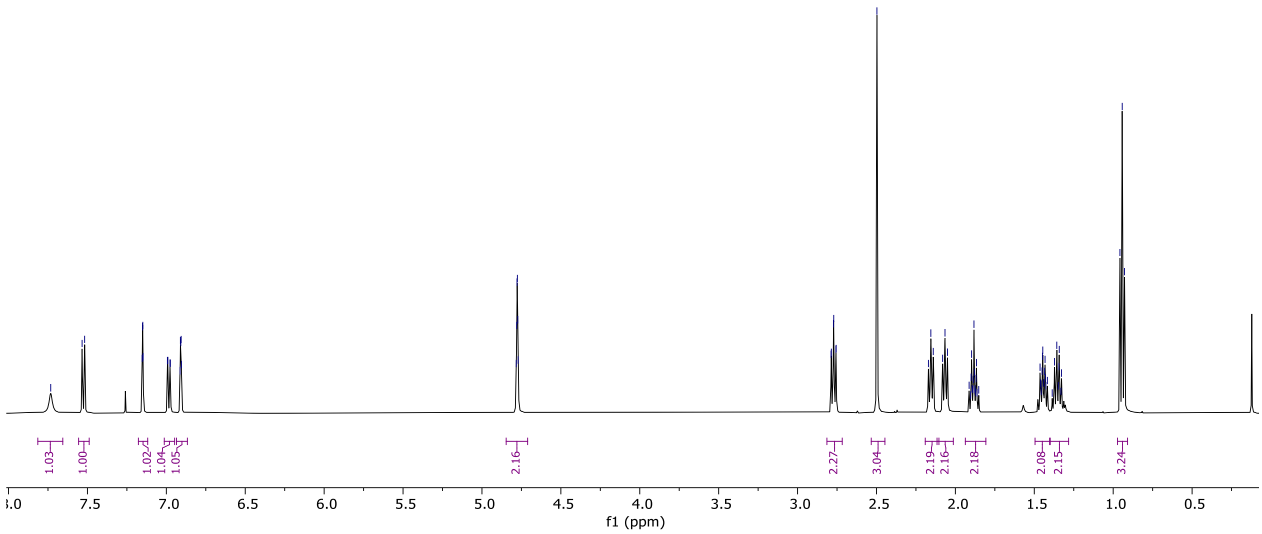
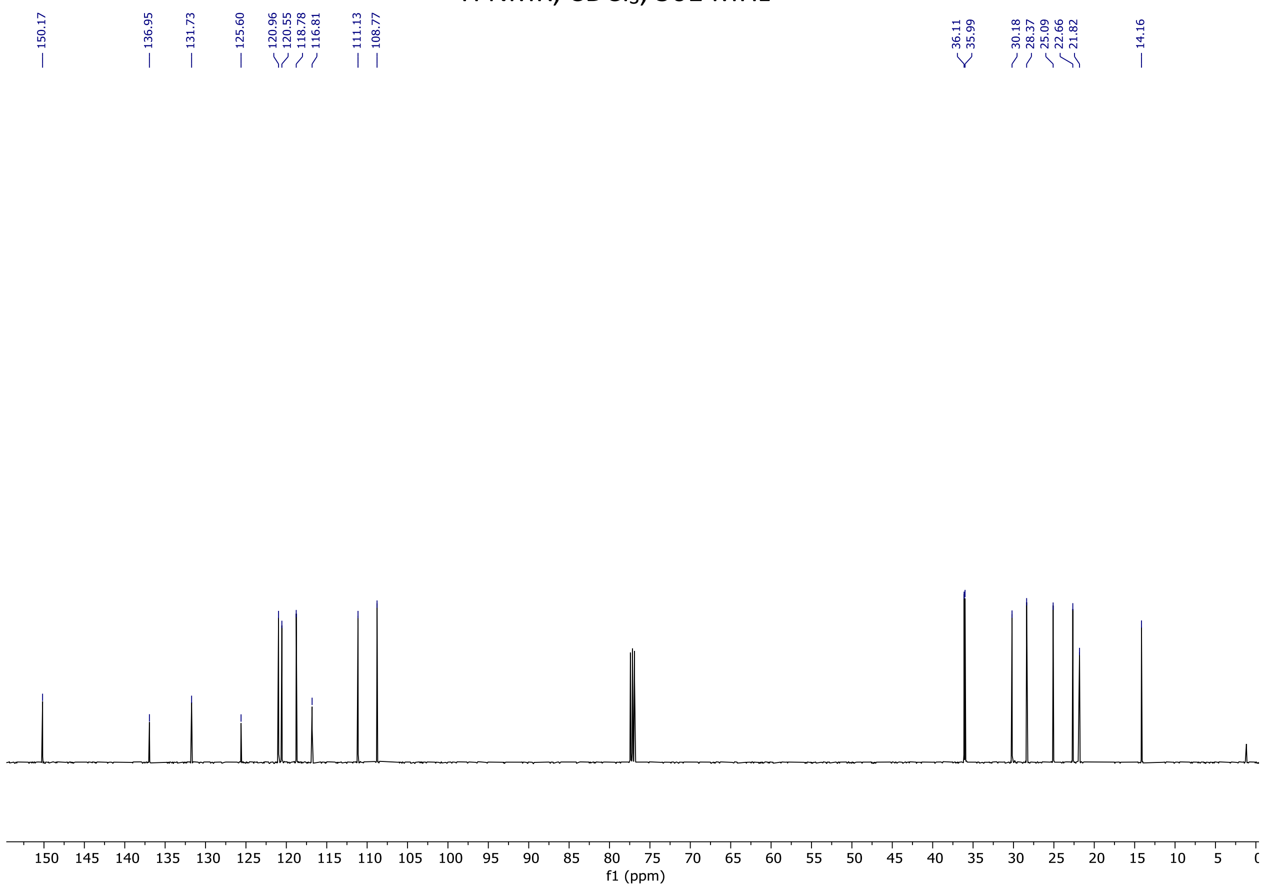
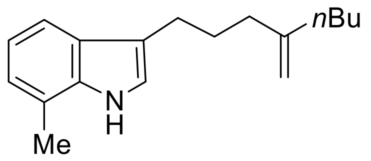


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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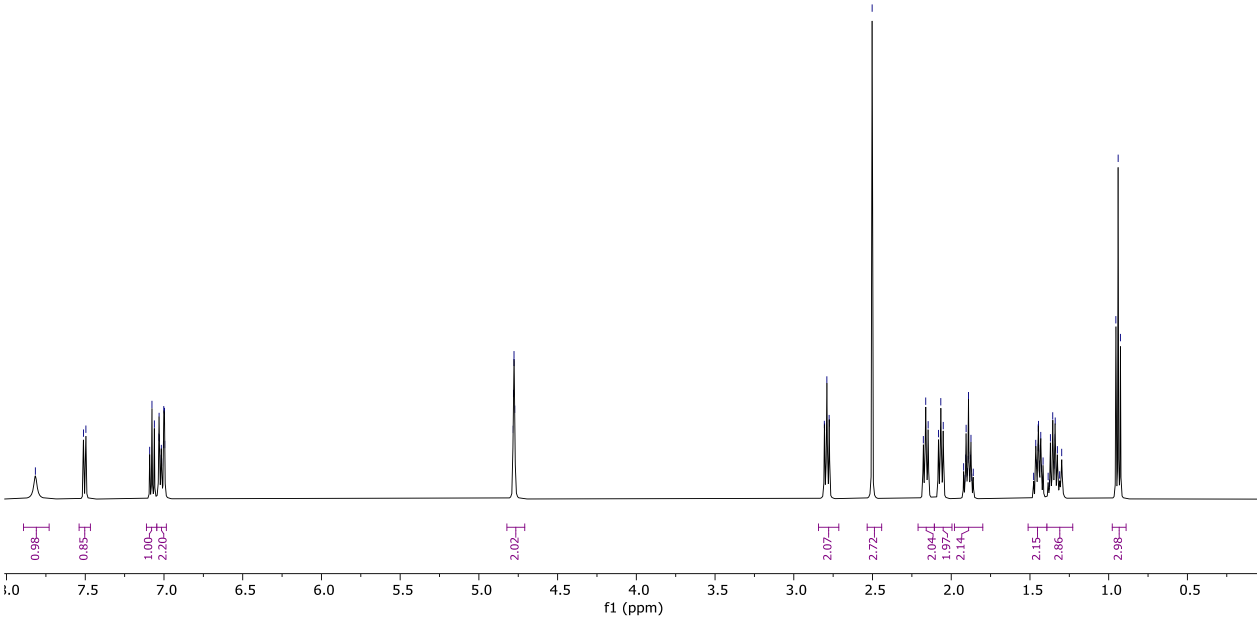
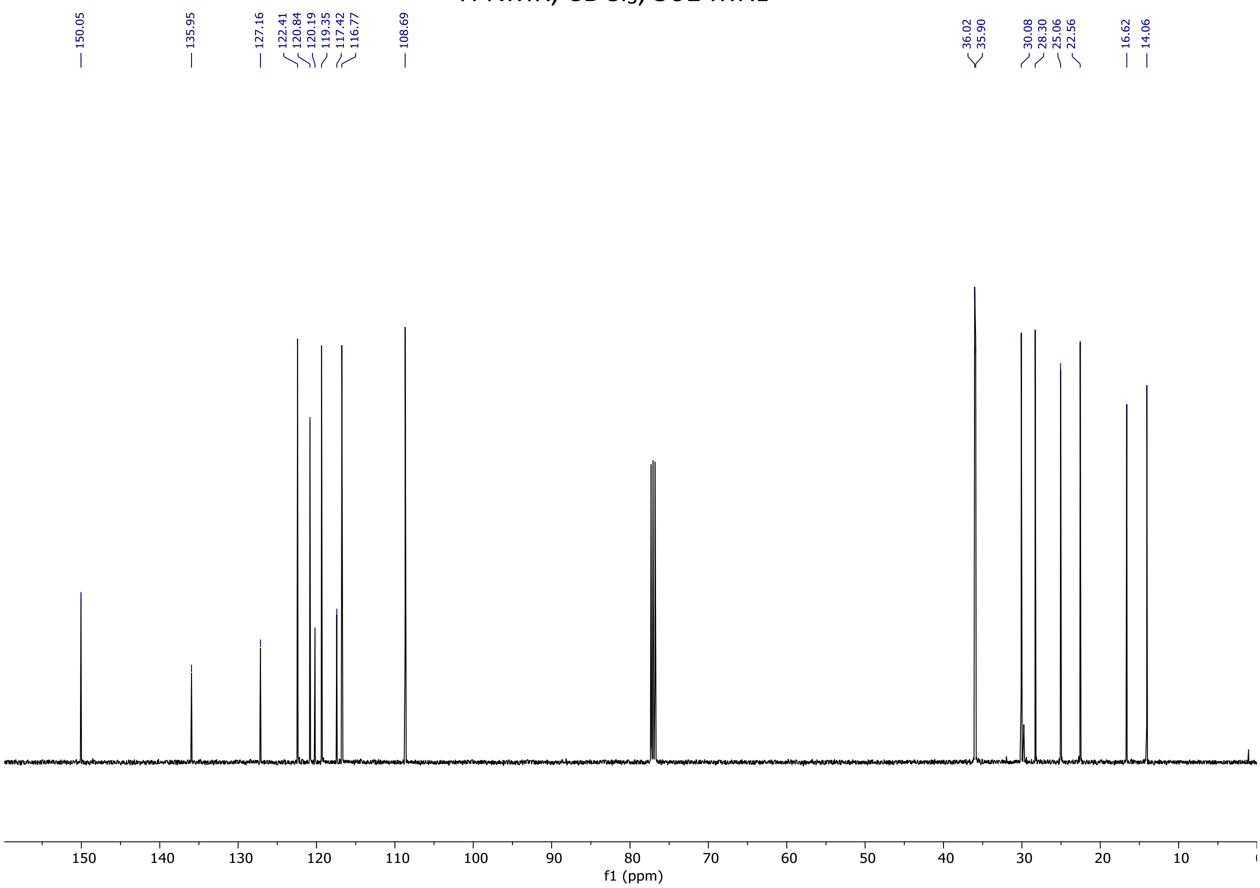
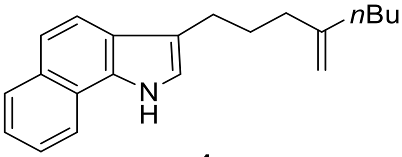


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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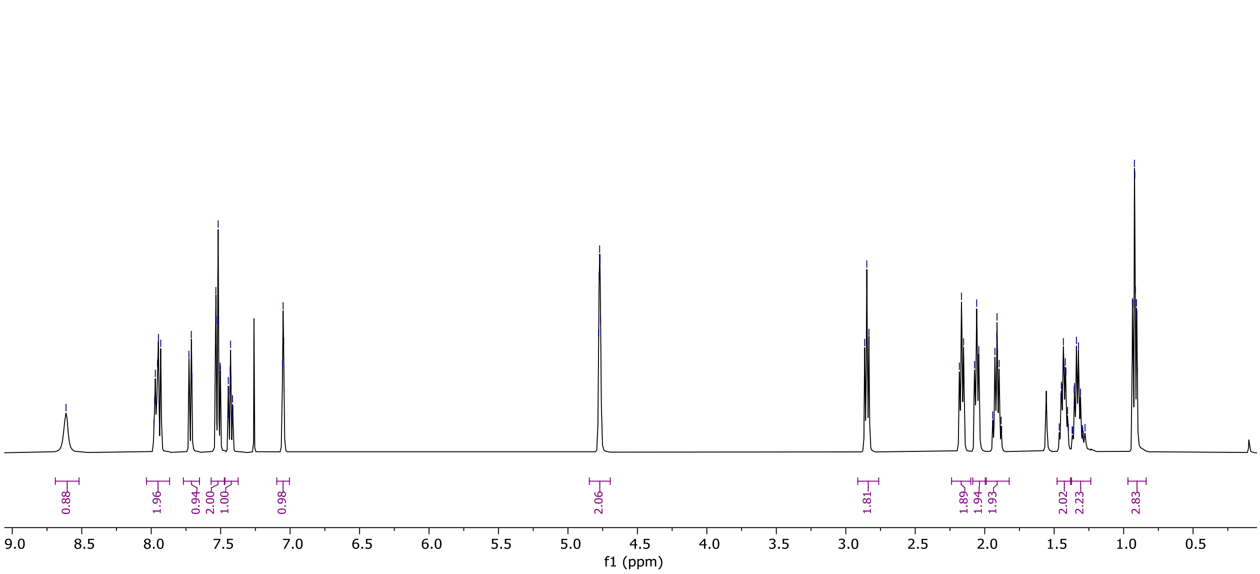
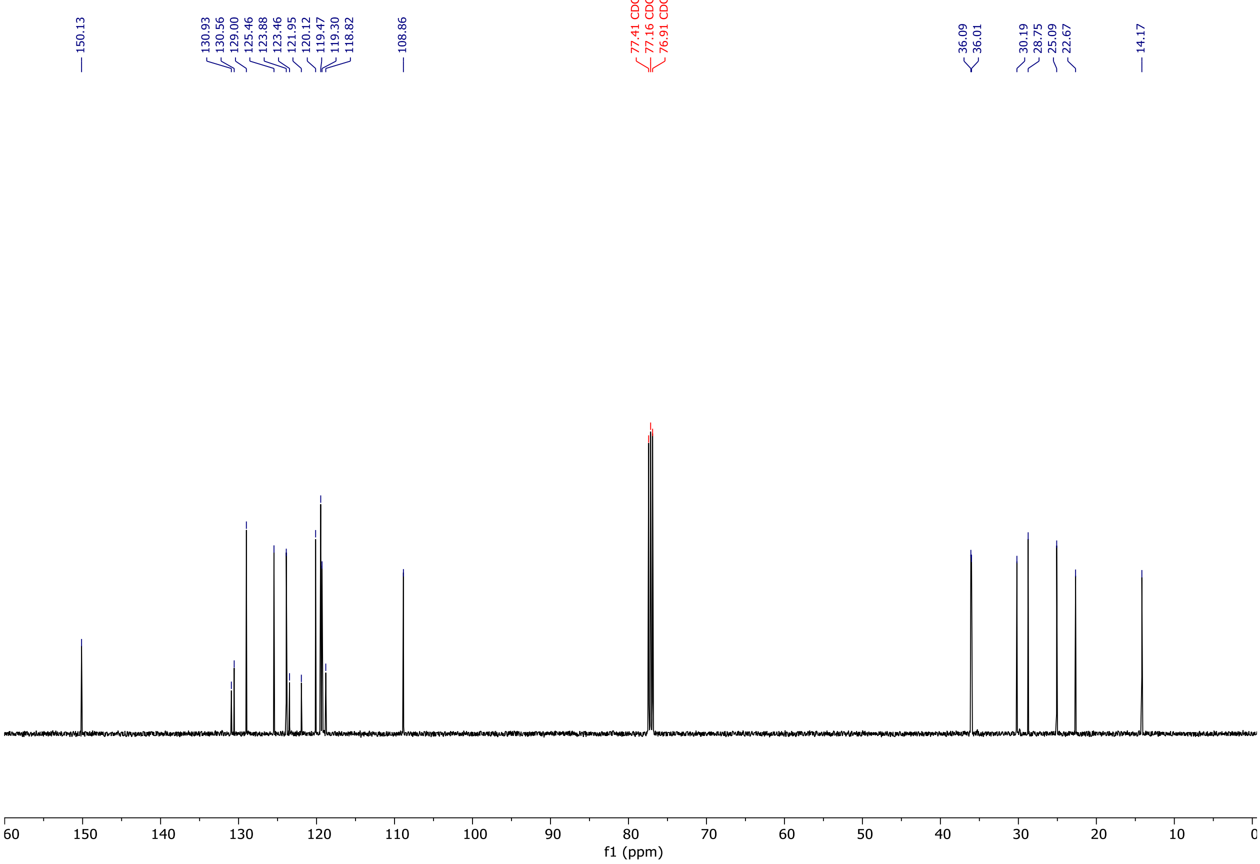
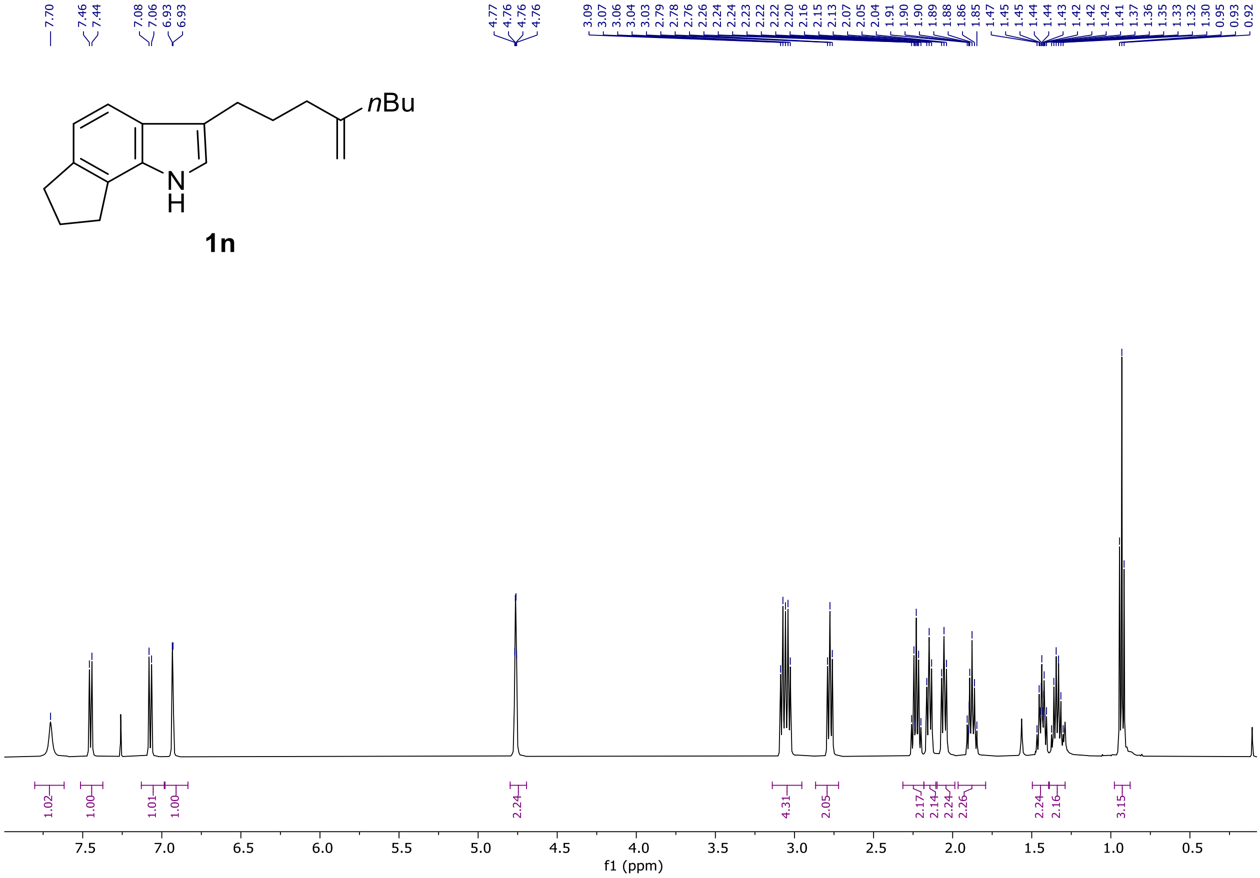


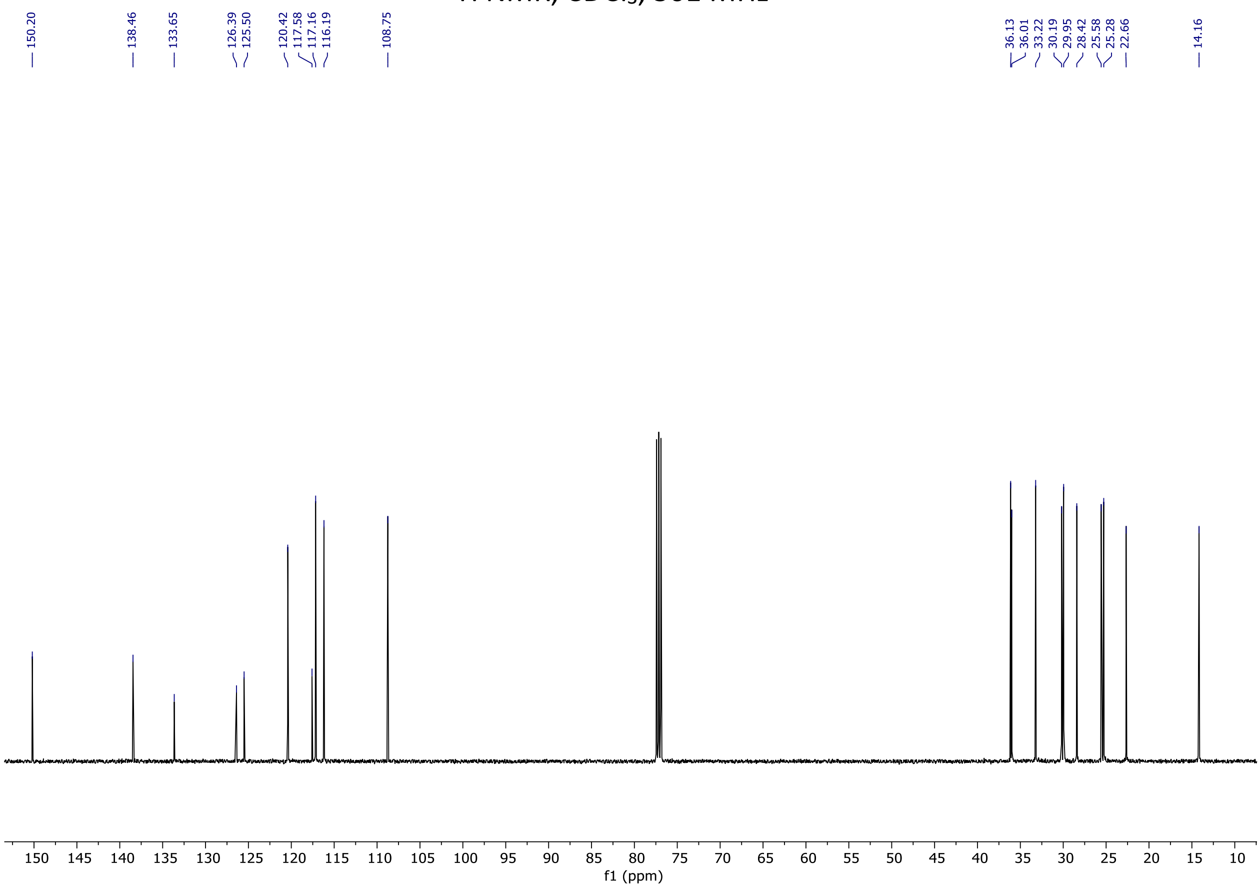
^1H NMR, $CDCl_3$, 501 MHz



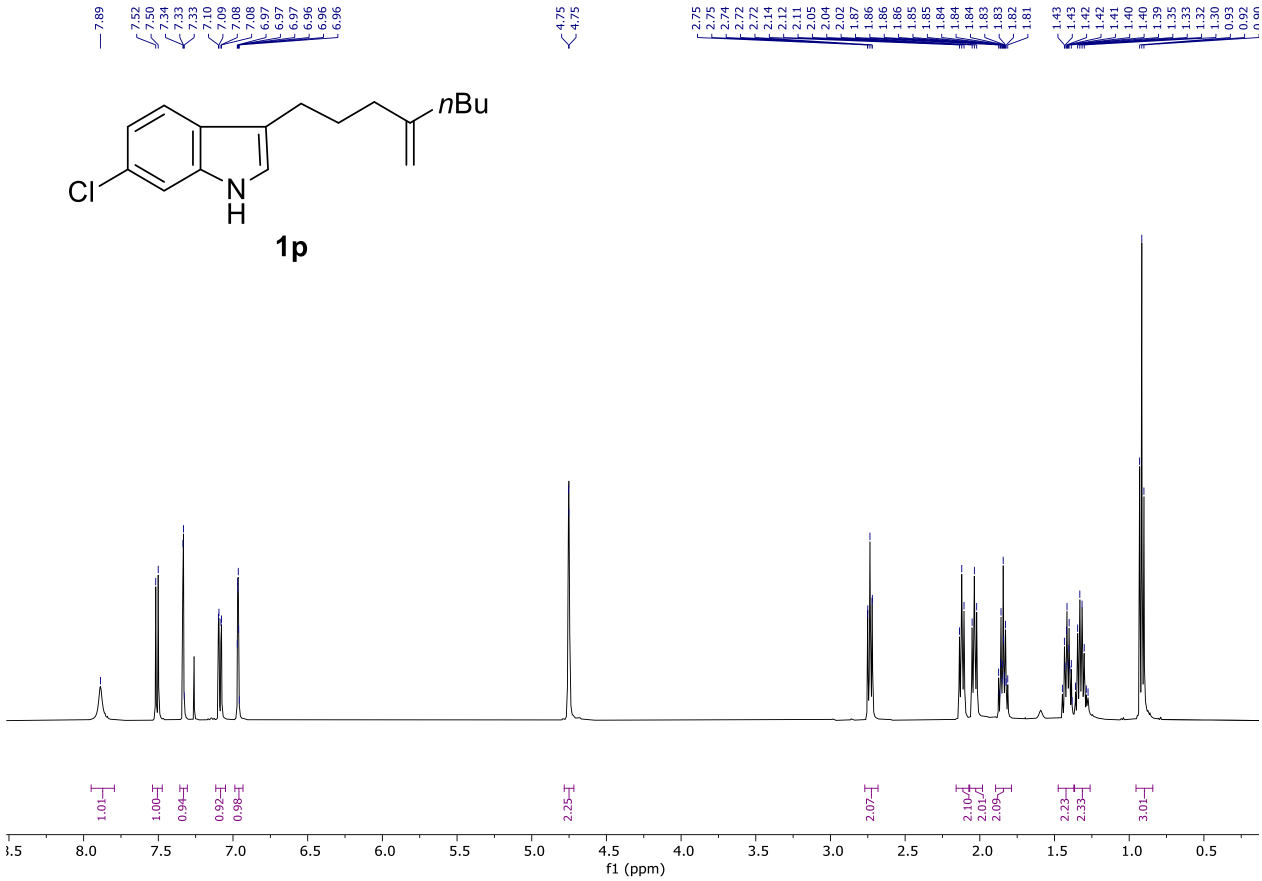
^{13}C NMR, $CDCl_3$, 126 MHz



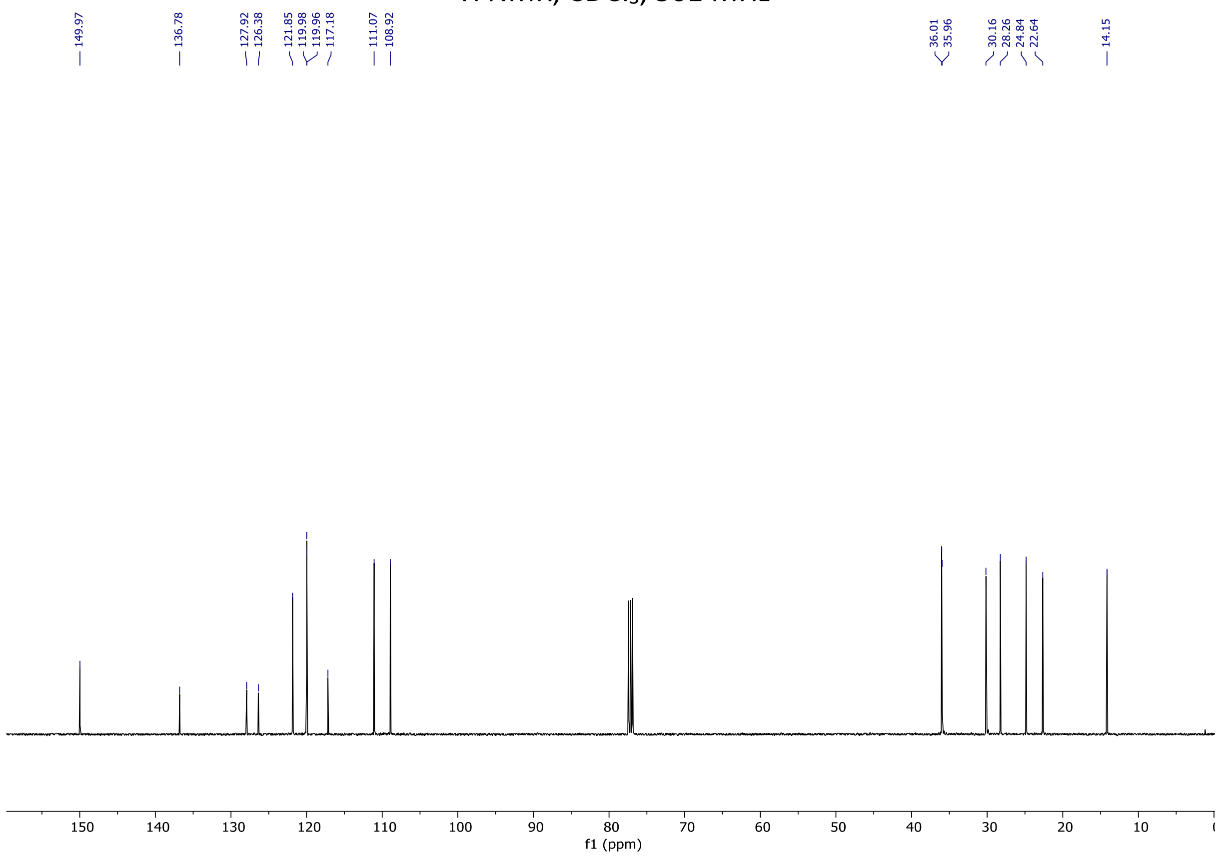
^{1}H NMR, $CDCl_3$, 501 MHz



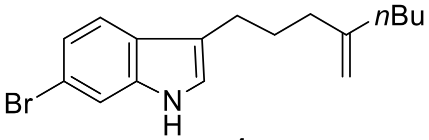
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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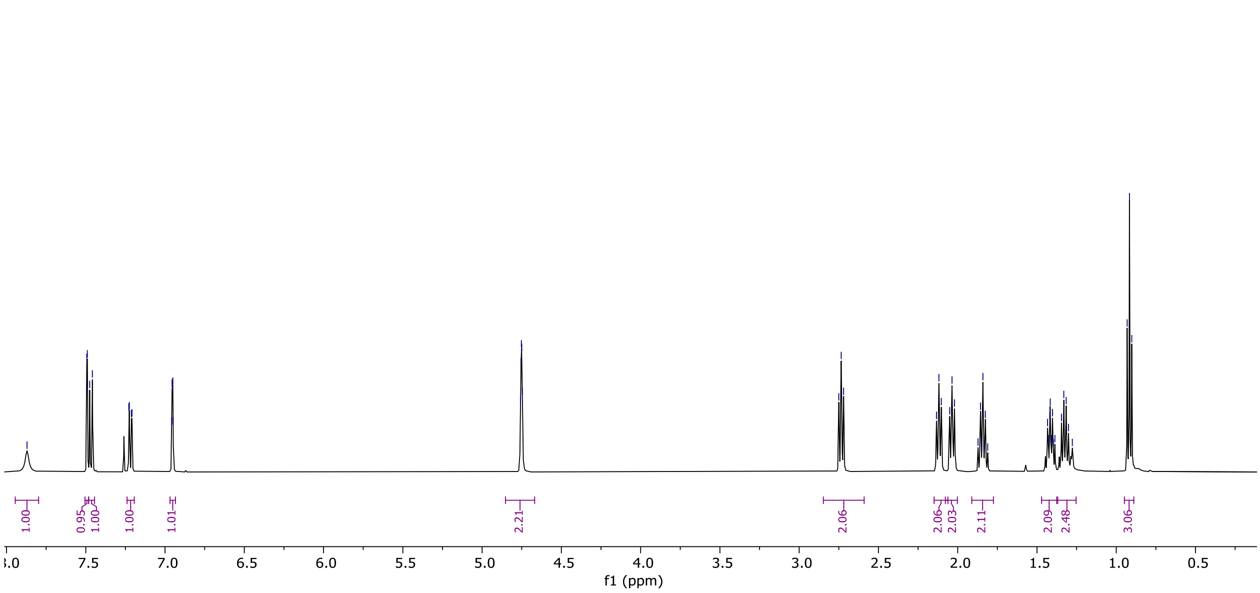
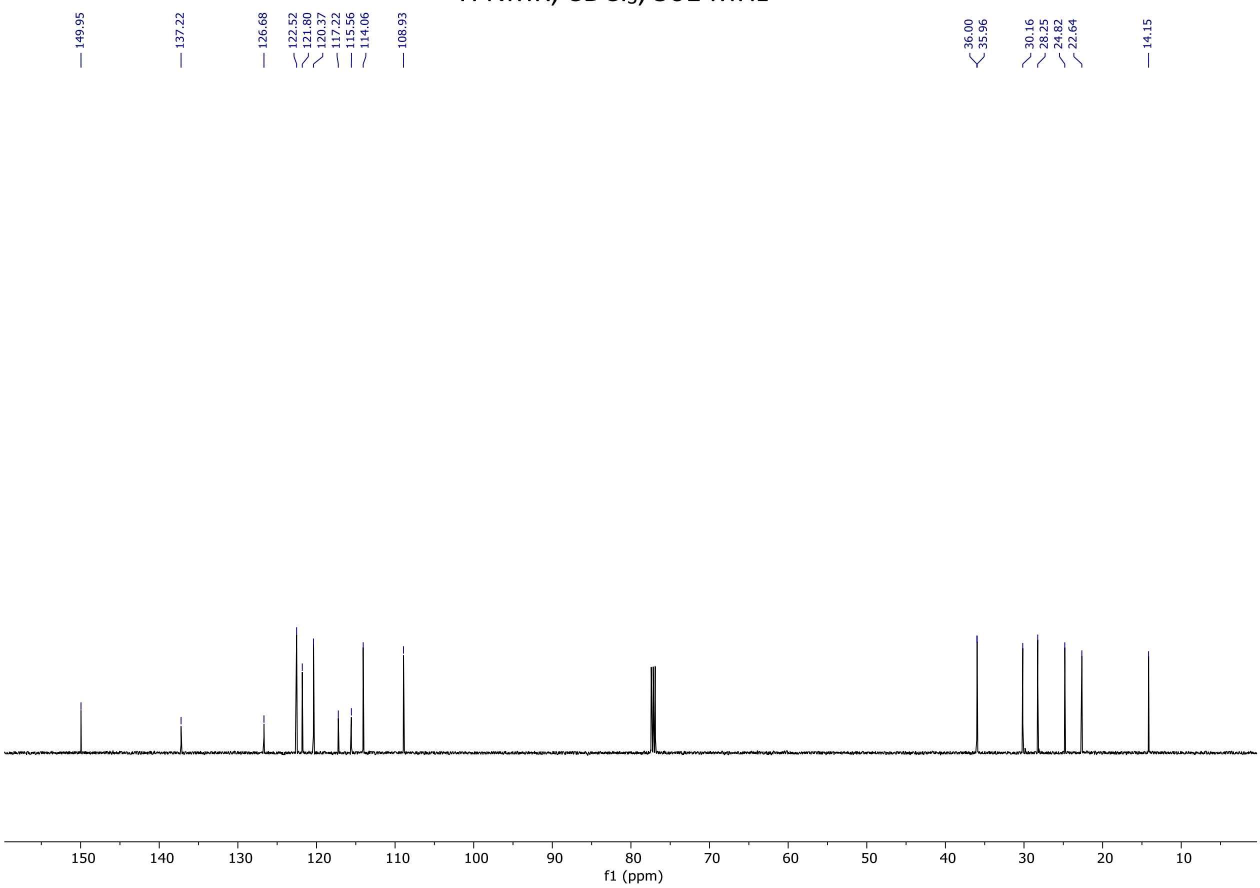
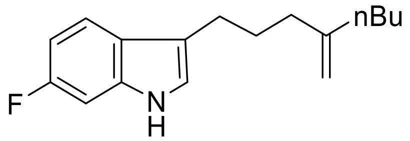


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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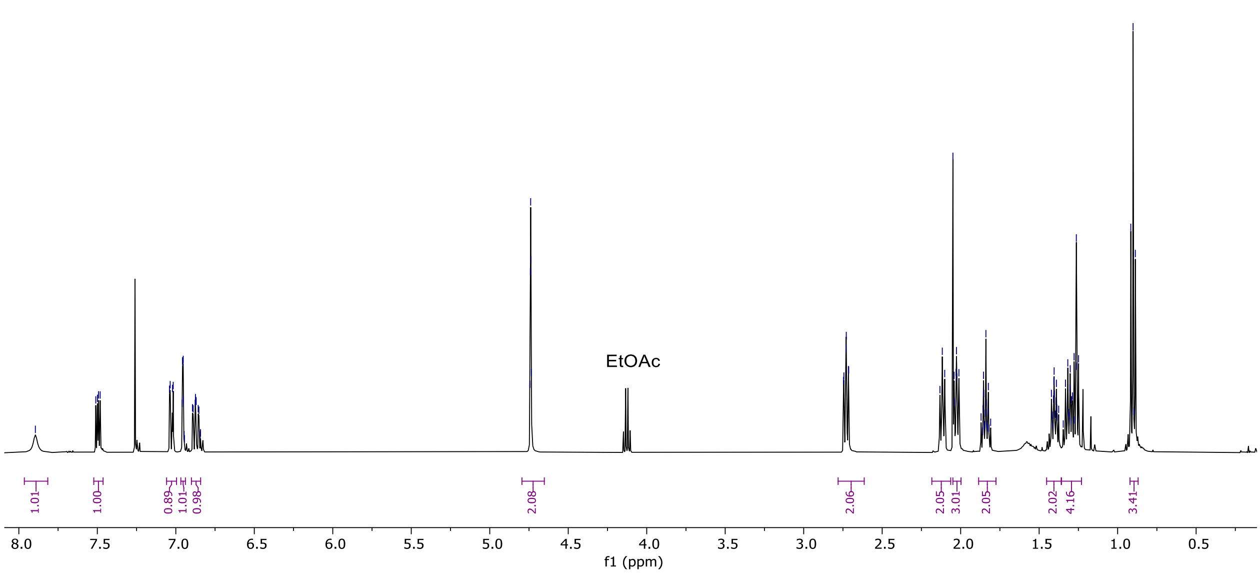
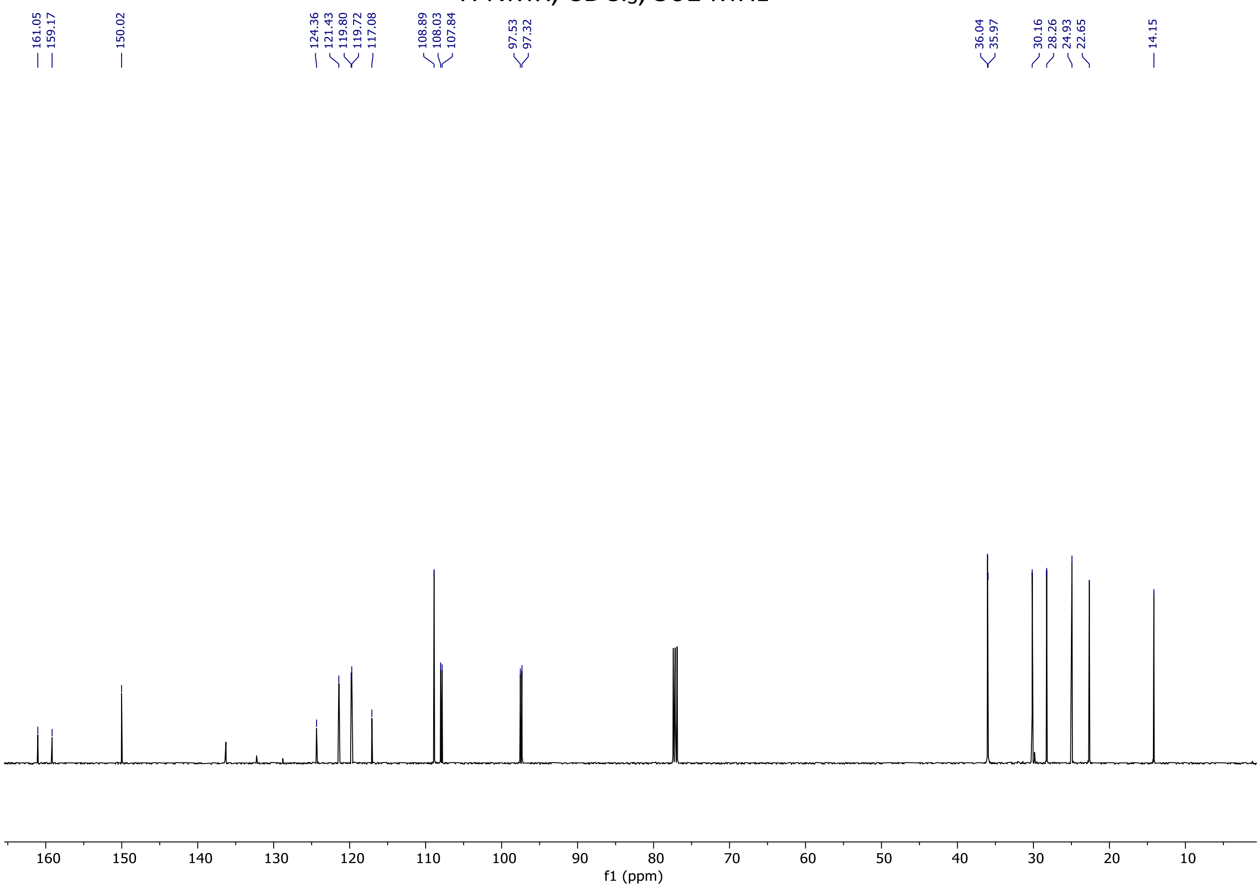
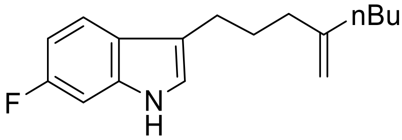


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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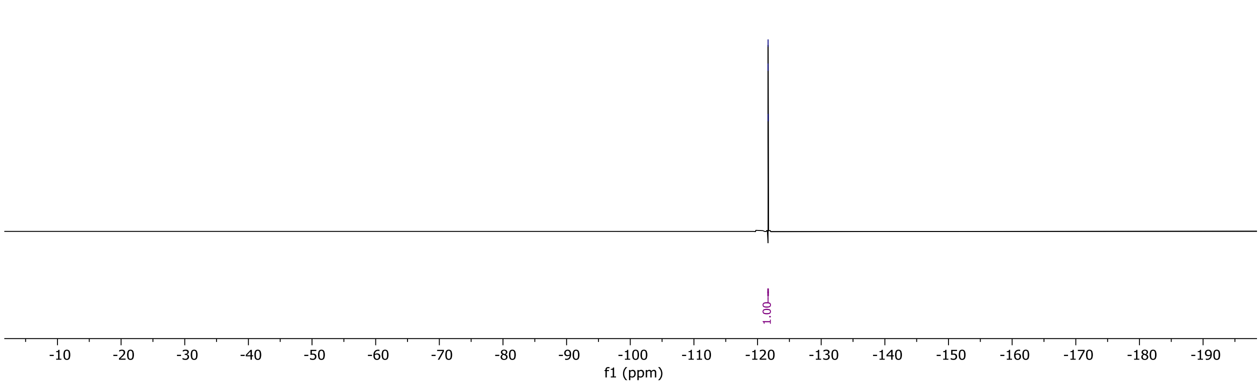
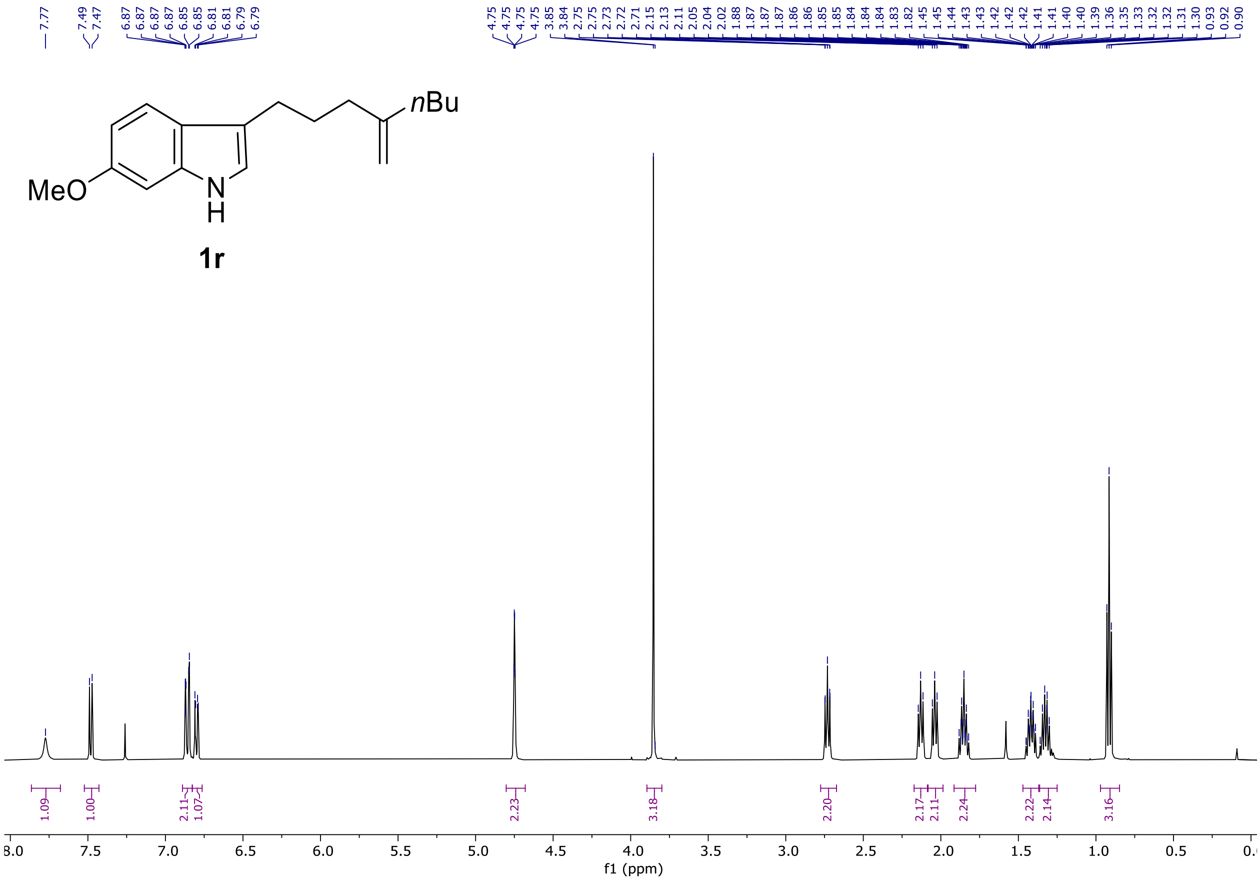
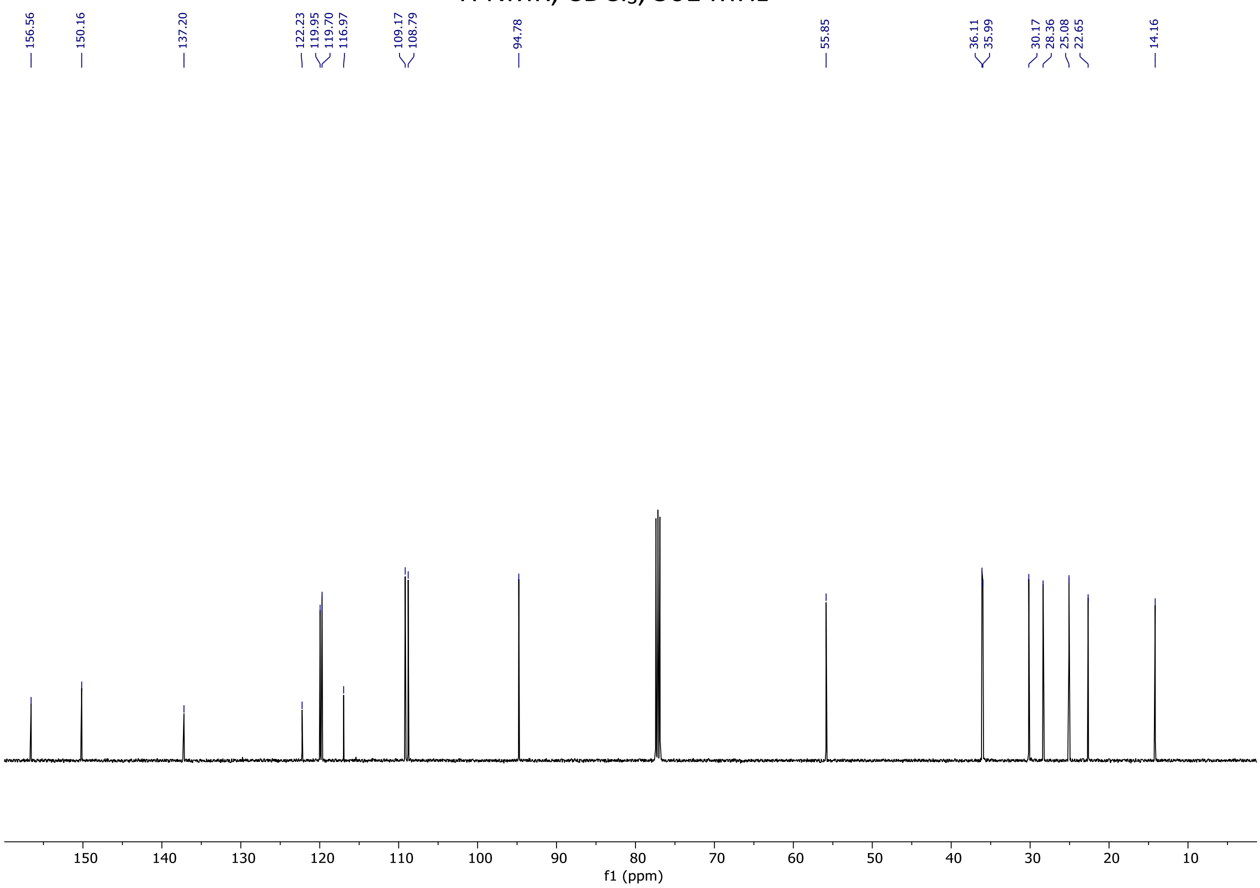


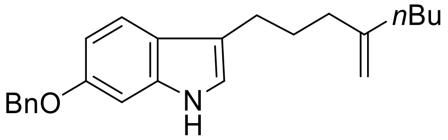
^{19}F NMR, $CDCl_3$, 471 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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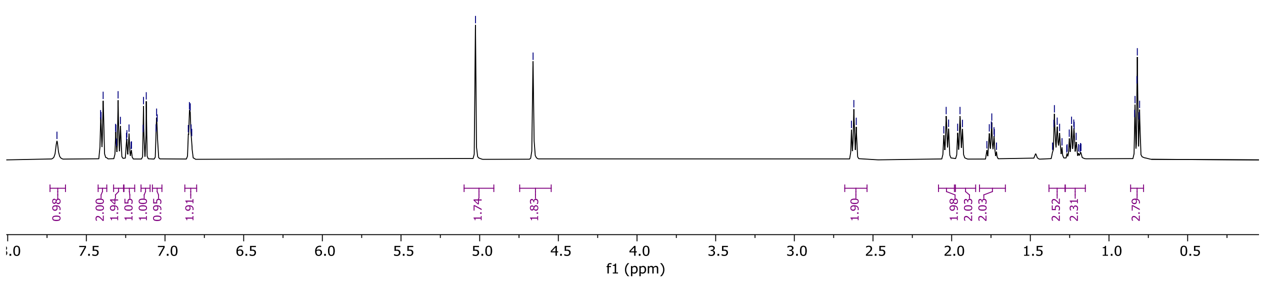
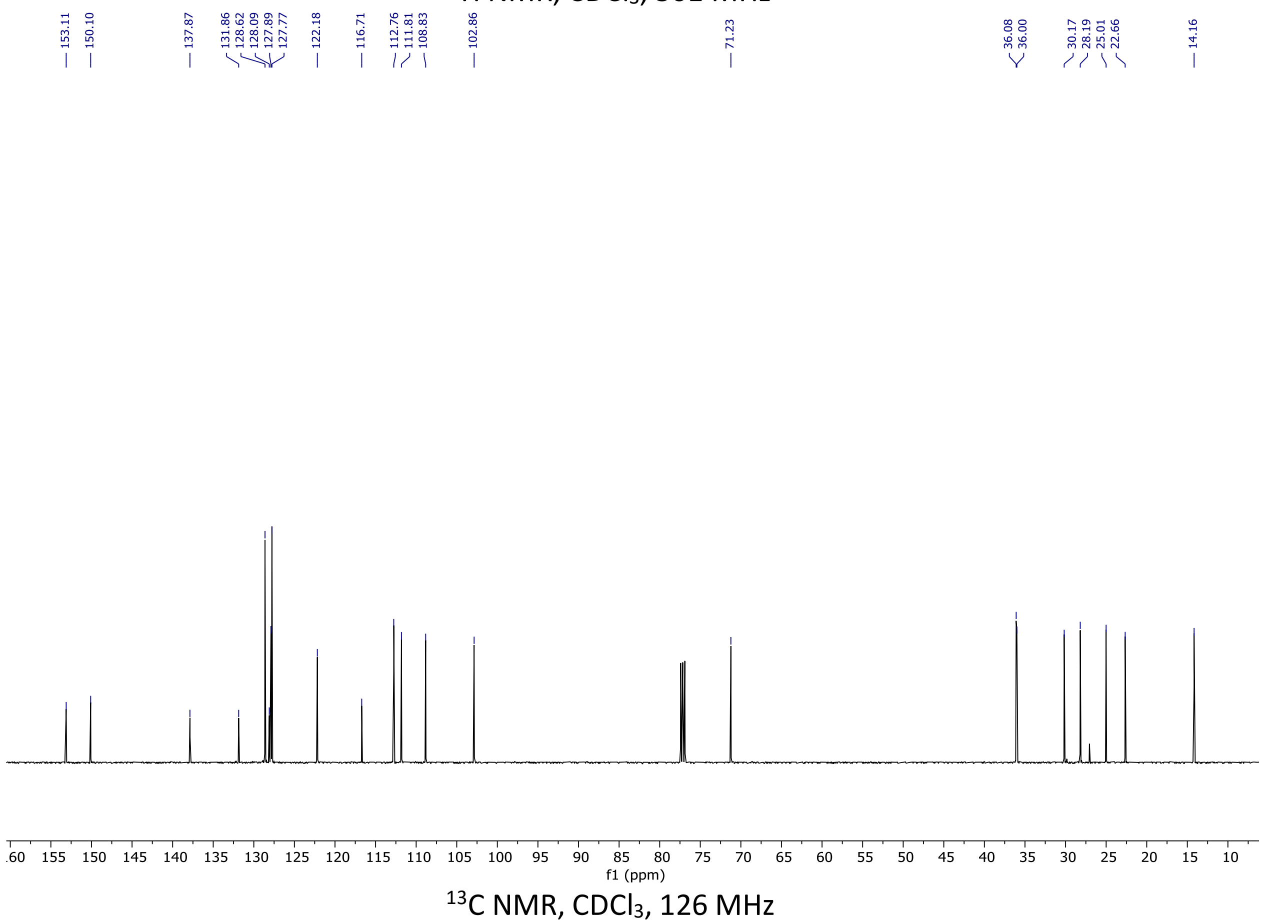
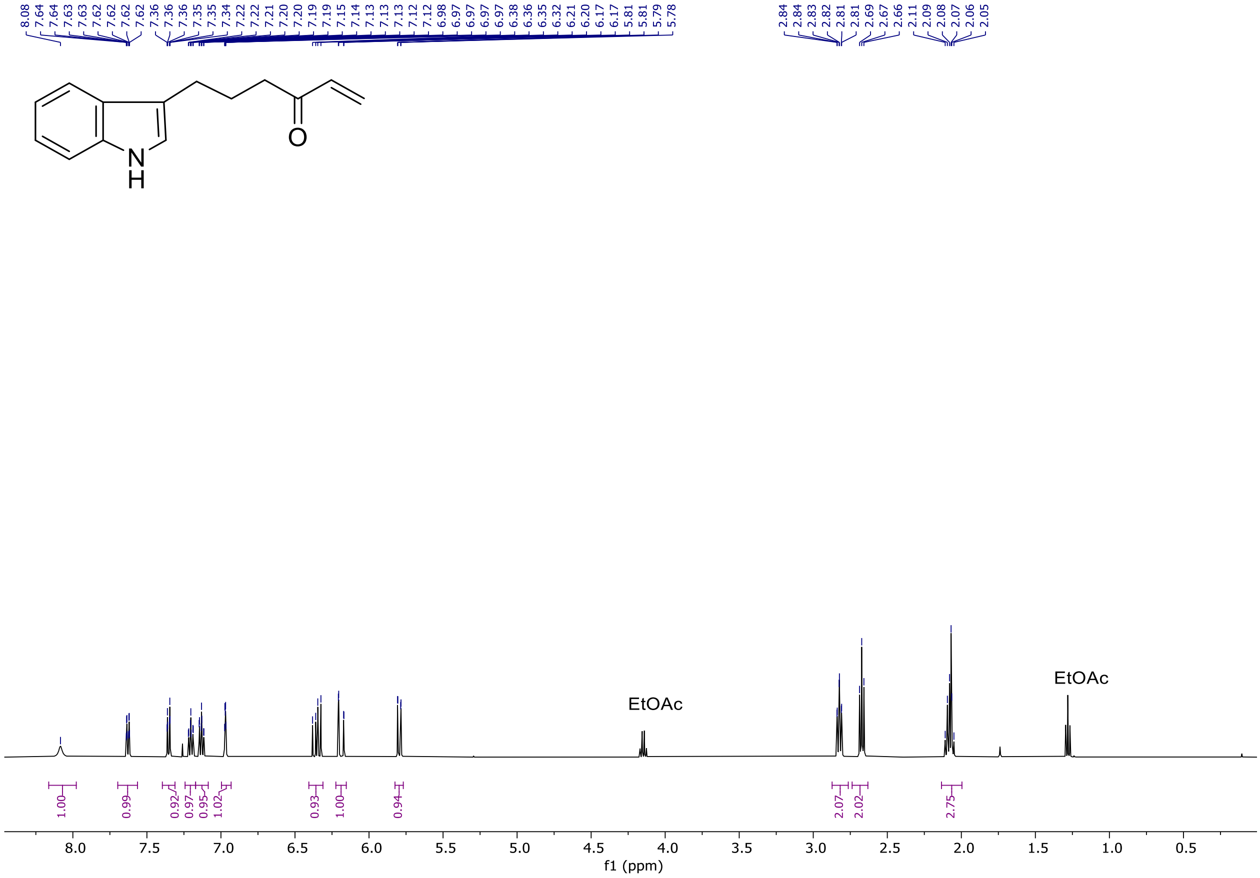


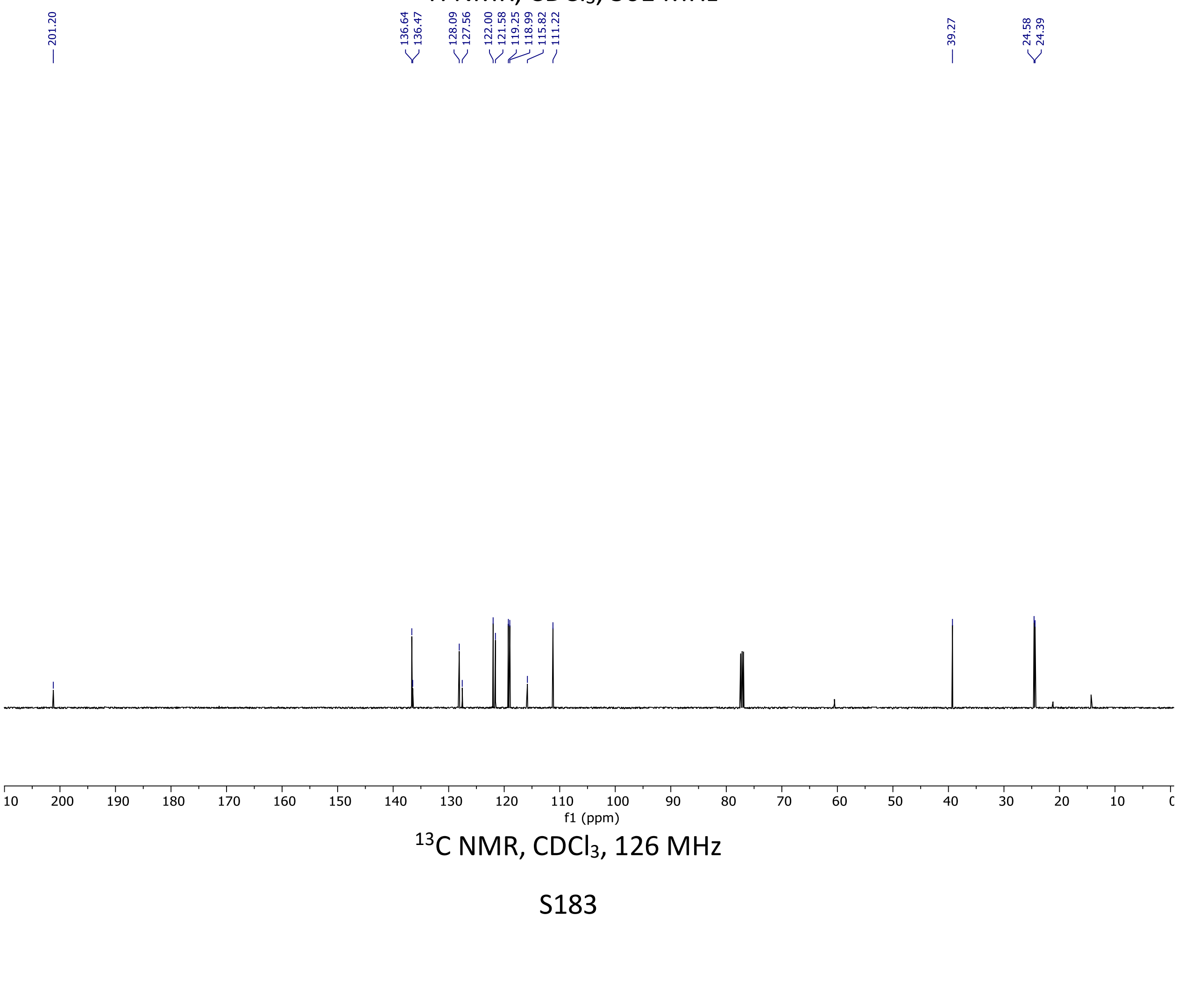
^{1}H NMR, $CDCl_3$, 501 MHz



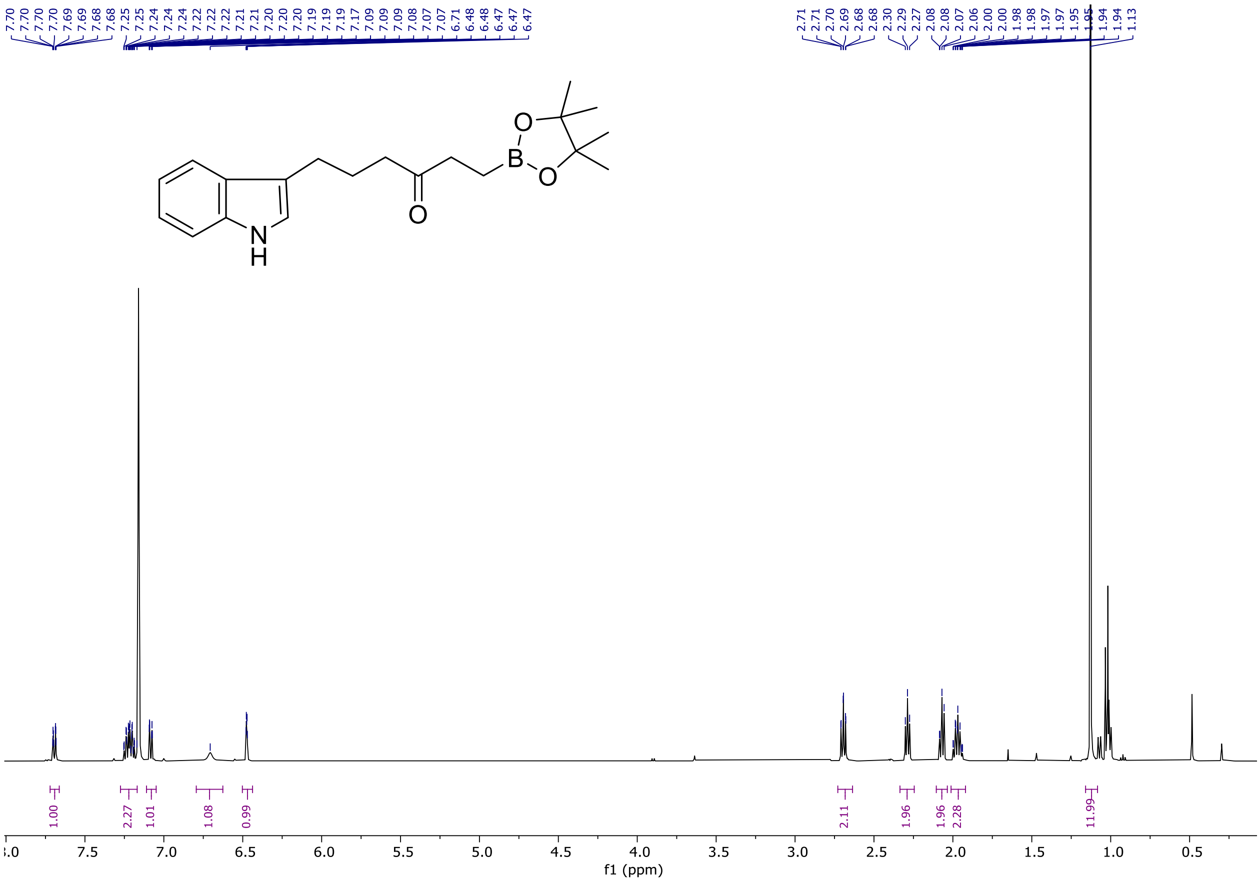
^{13}C NMR, $CDCl_3$, 126 MHz



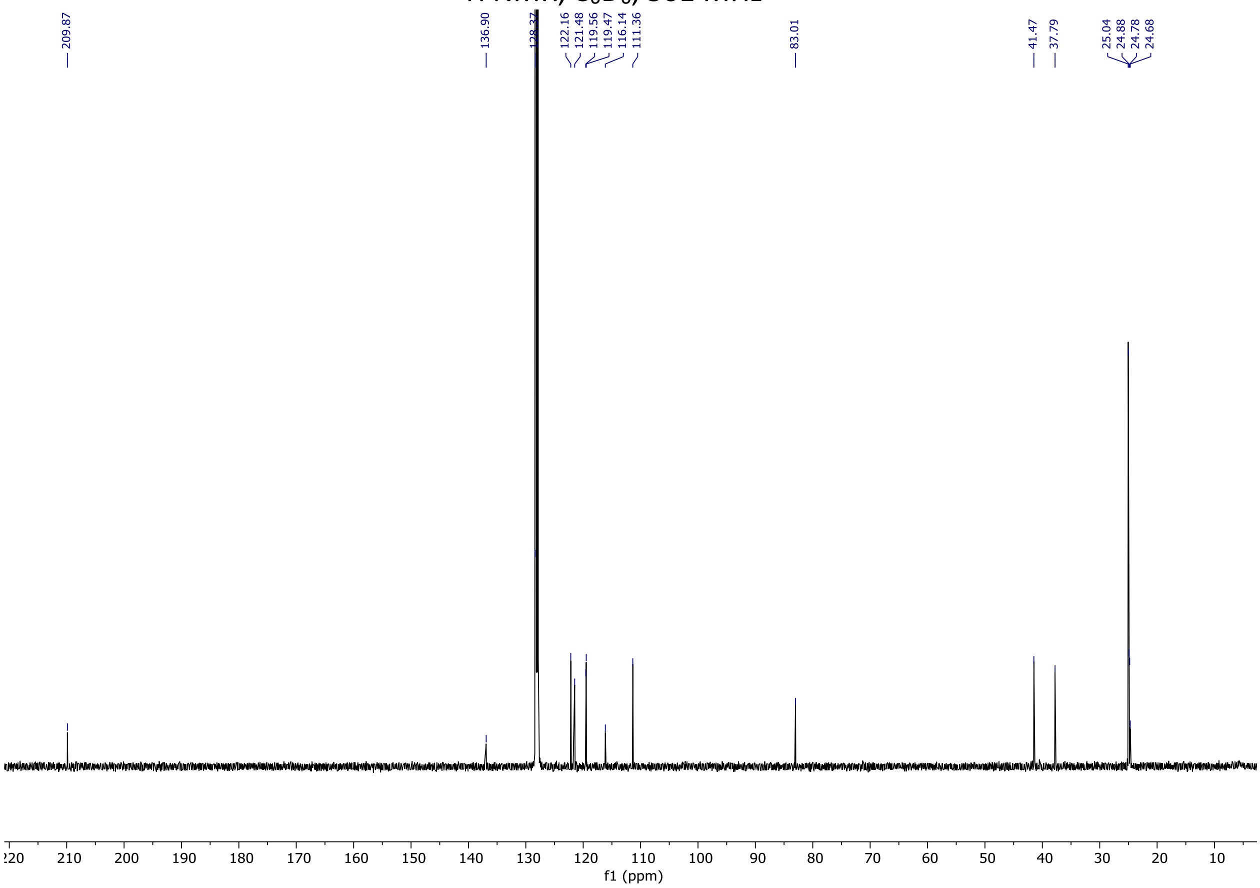
^{1}H NMR, $CDCl_3$, 501 MHz



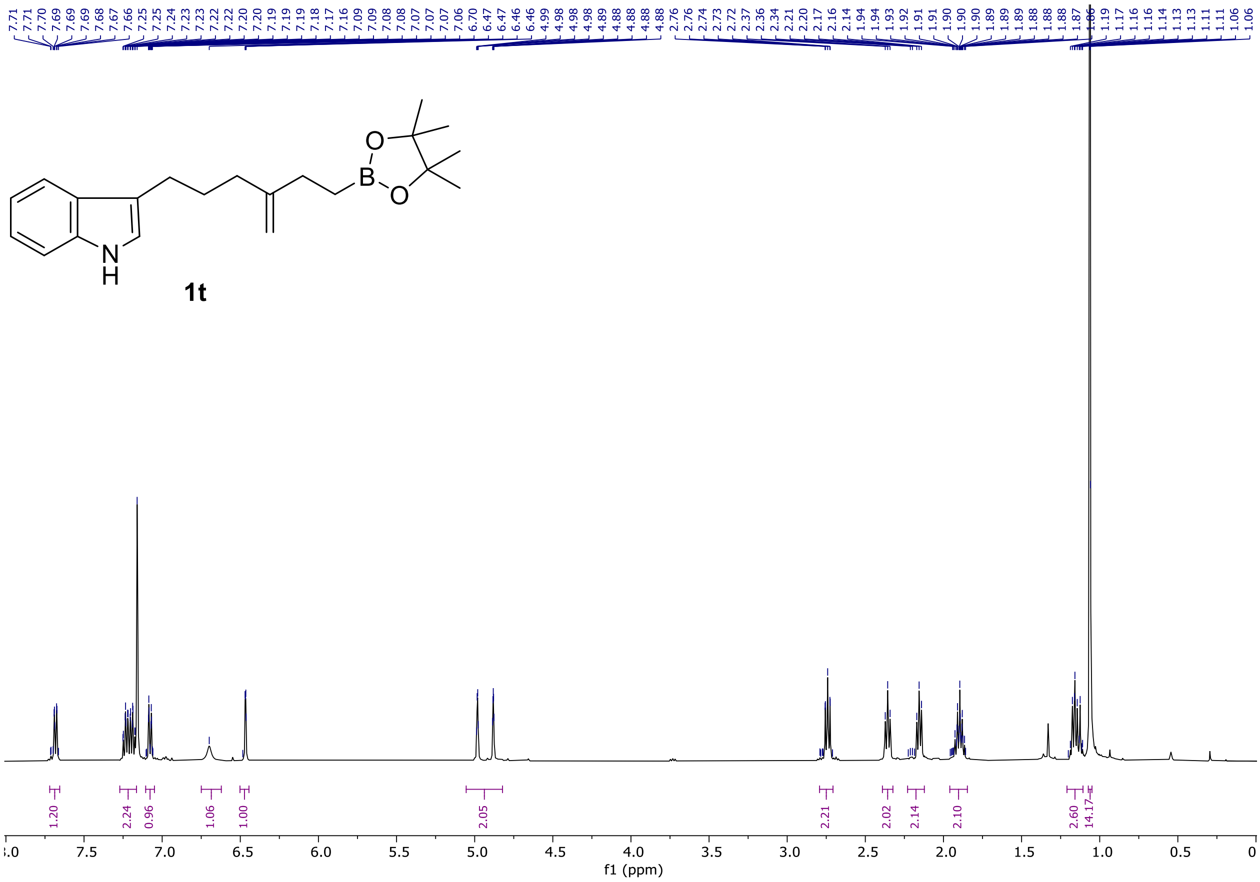
^{13}C NMR, $CDCl_3$, 126 MHz



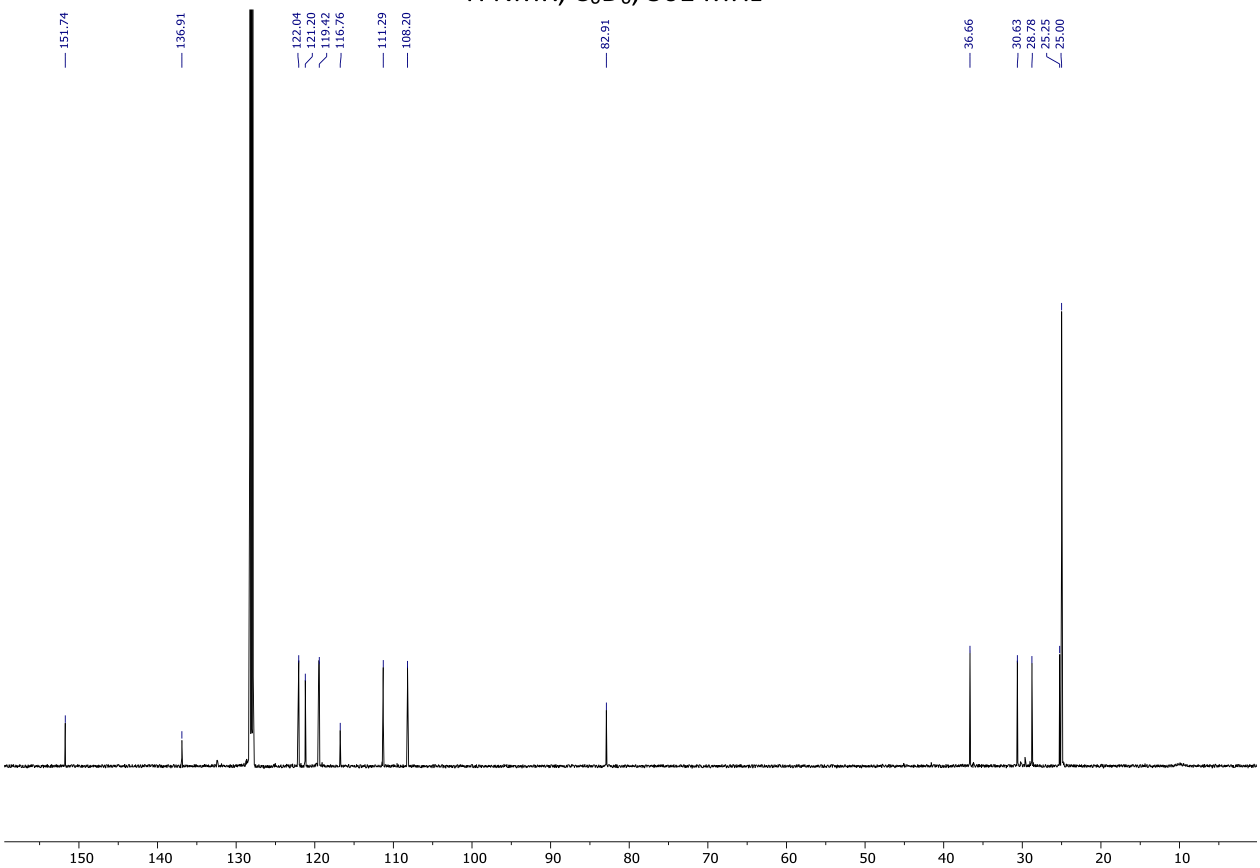
^{1}H NMR, C_6D_6, 501 MHz



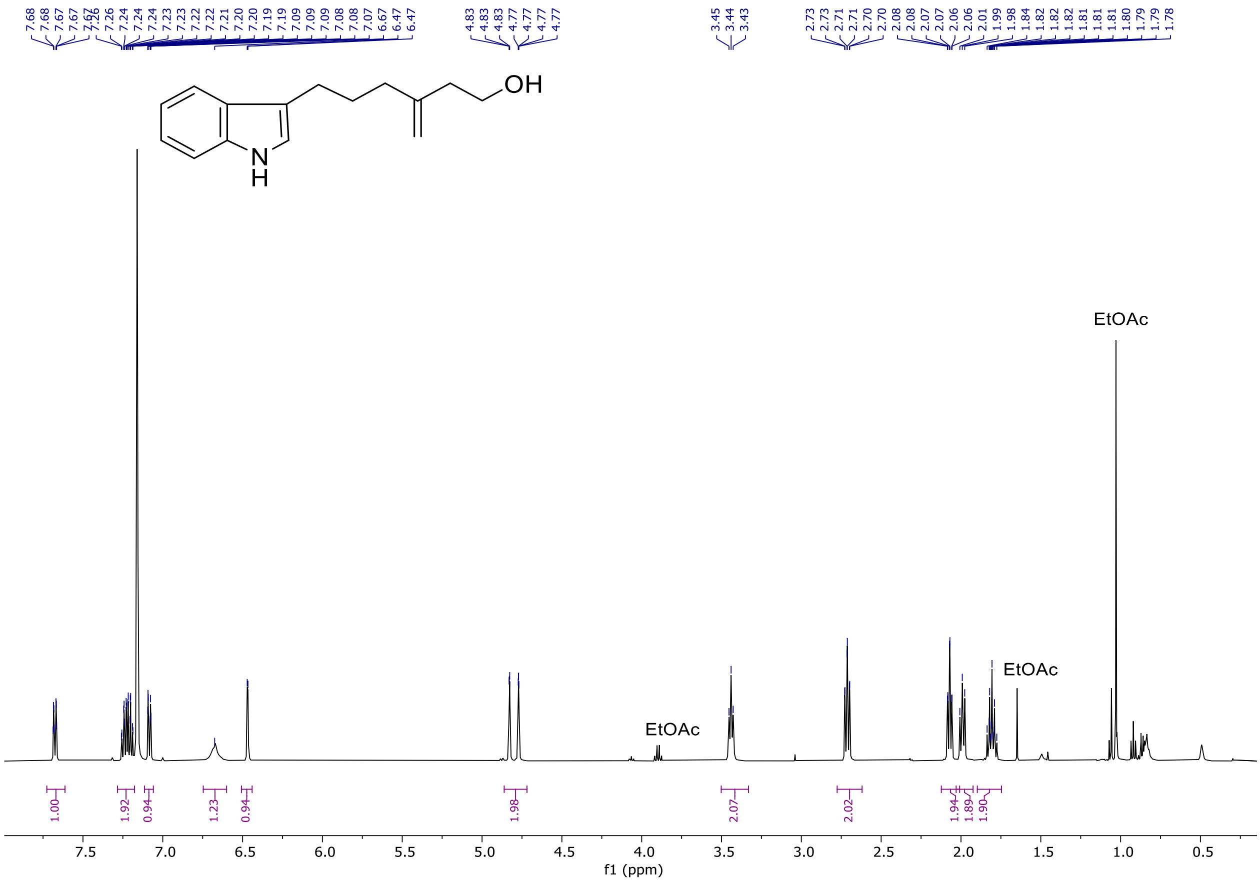
^{13}C NMR, C_6D_6, 126 MHz



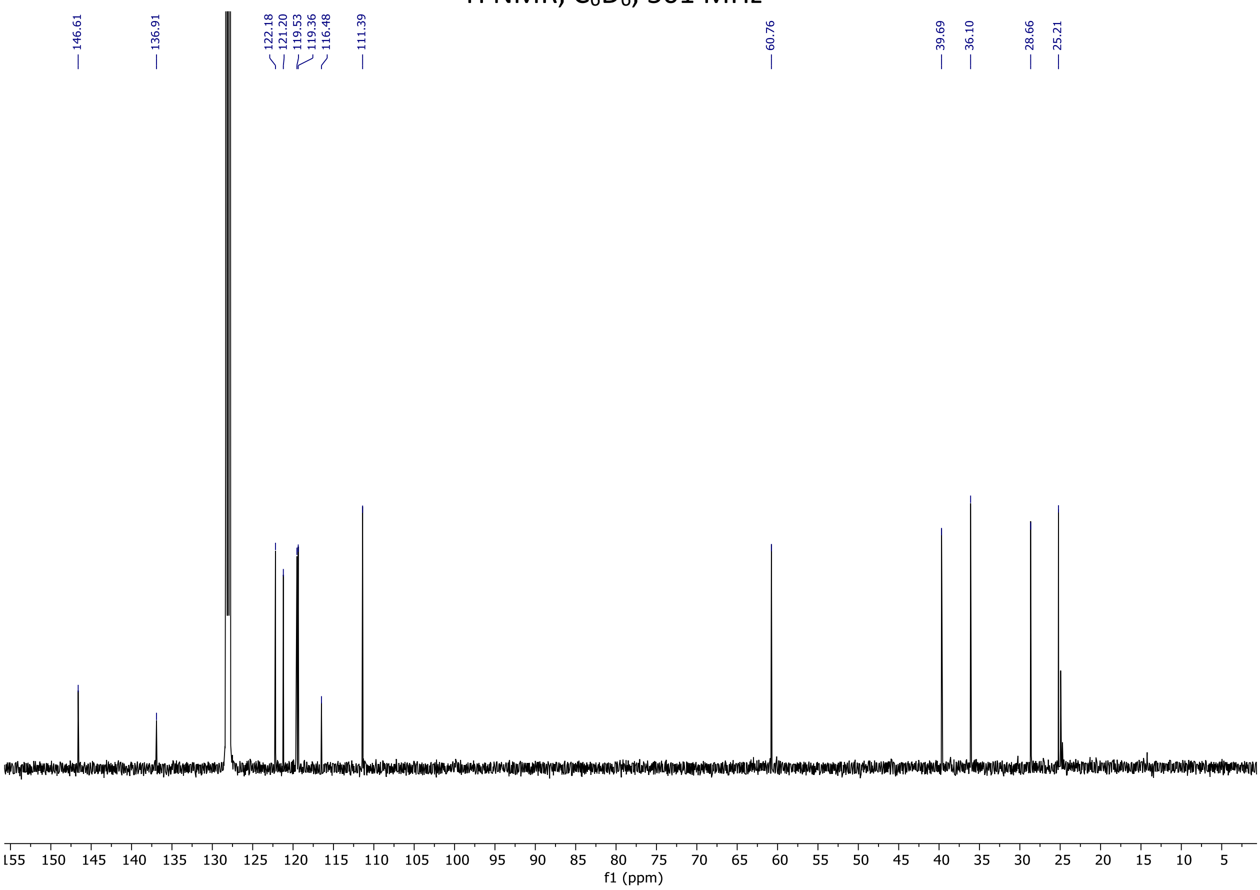
^{1}H NMR, C_6D_6, 501 MHz



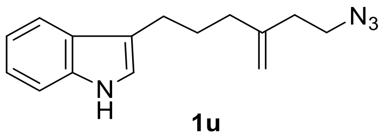
^{13}C NMR, C_6D_6, 126 MHz



^{1}H NMR, C_6D_6, 501 MHz



^{13}C NMR, C_6D_6, 126 MHz



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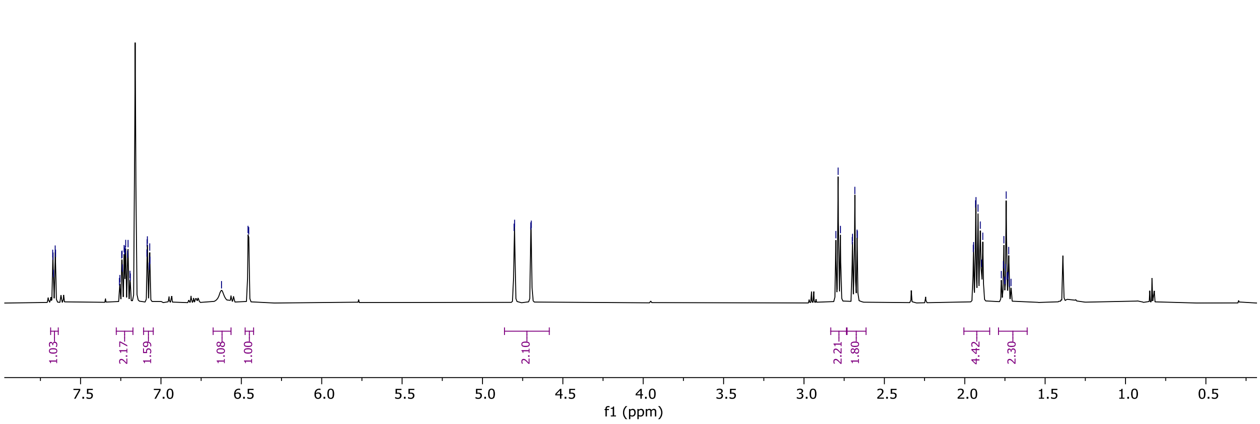
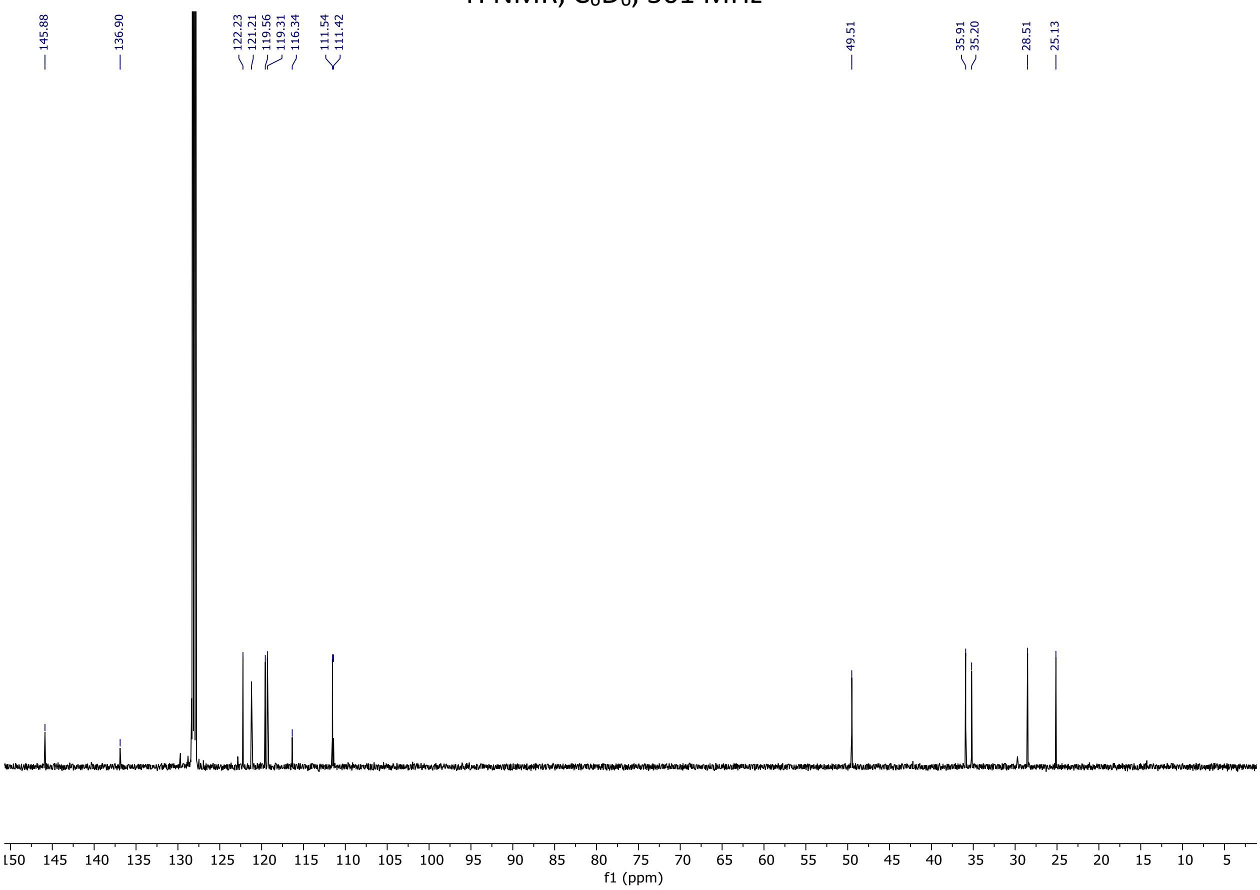
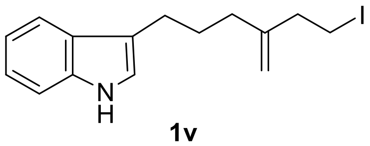


^{1}H NMR, C_6D_6, 501 MHz



^{13}C NMR, C_6D_6, 126 MHz



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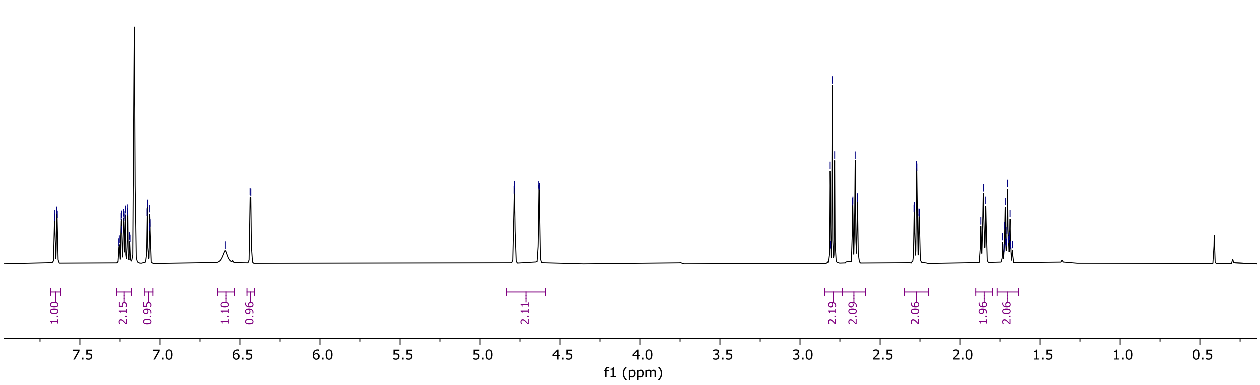
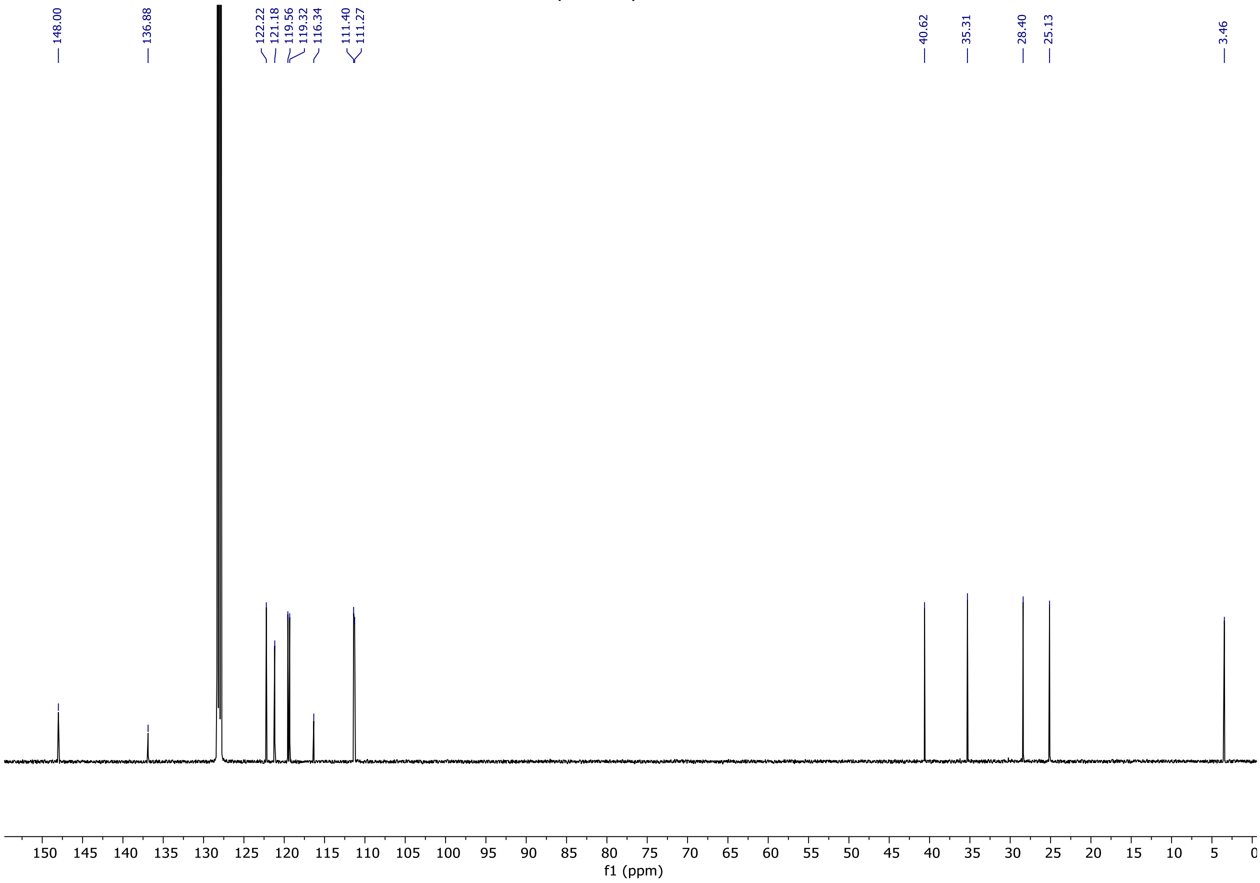
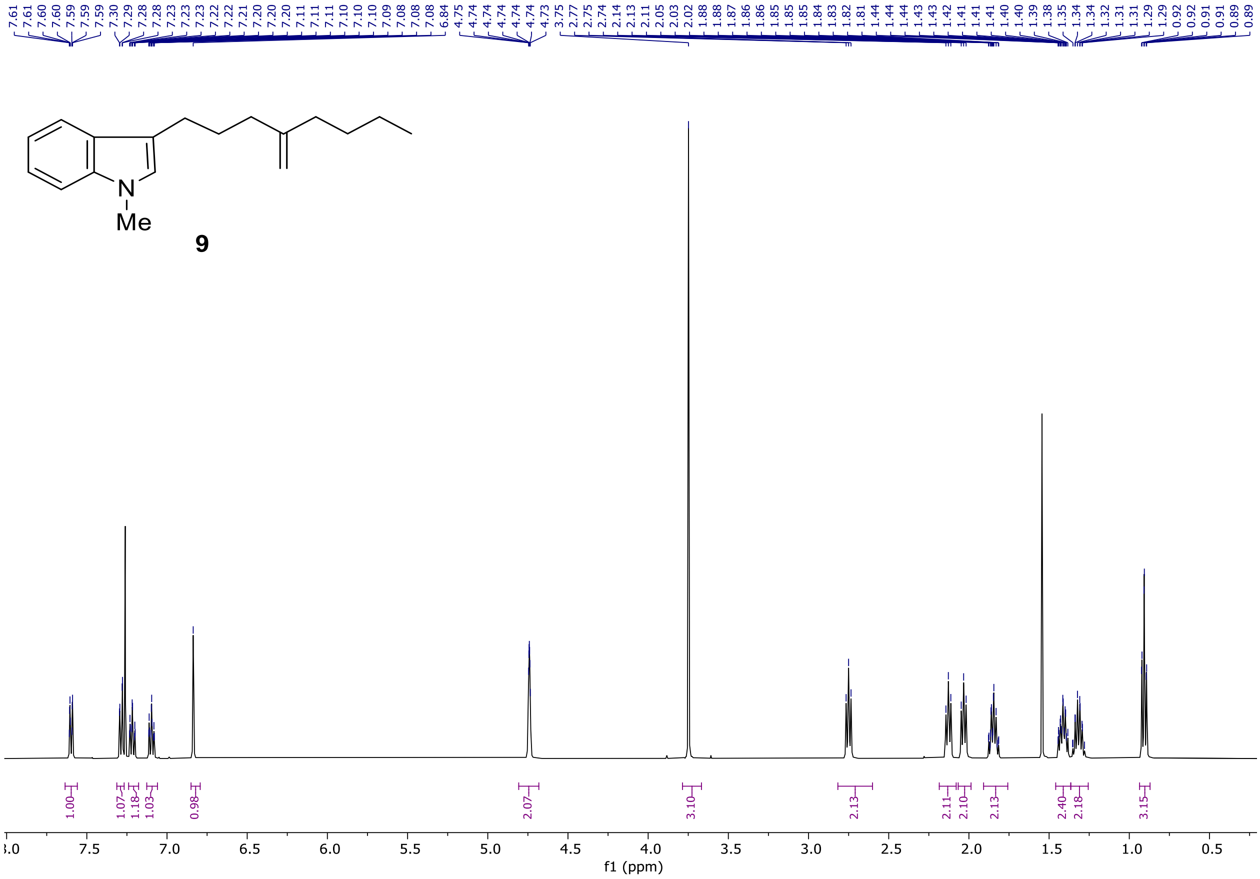


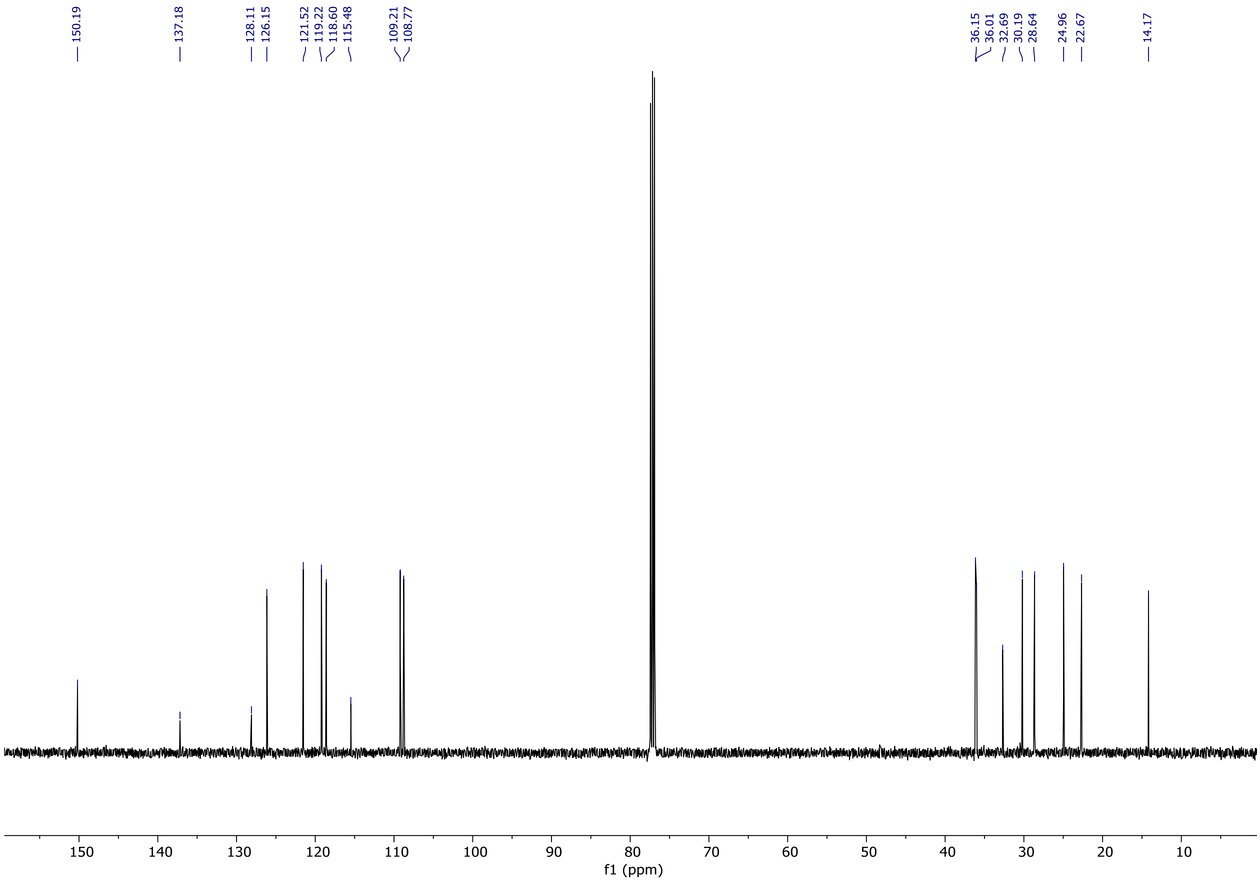
^{1}H NMR, C_6D_6, 501 MHz



^{13}C NMR, C_6D_6, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

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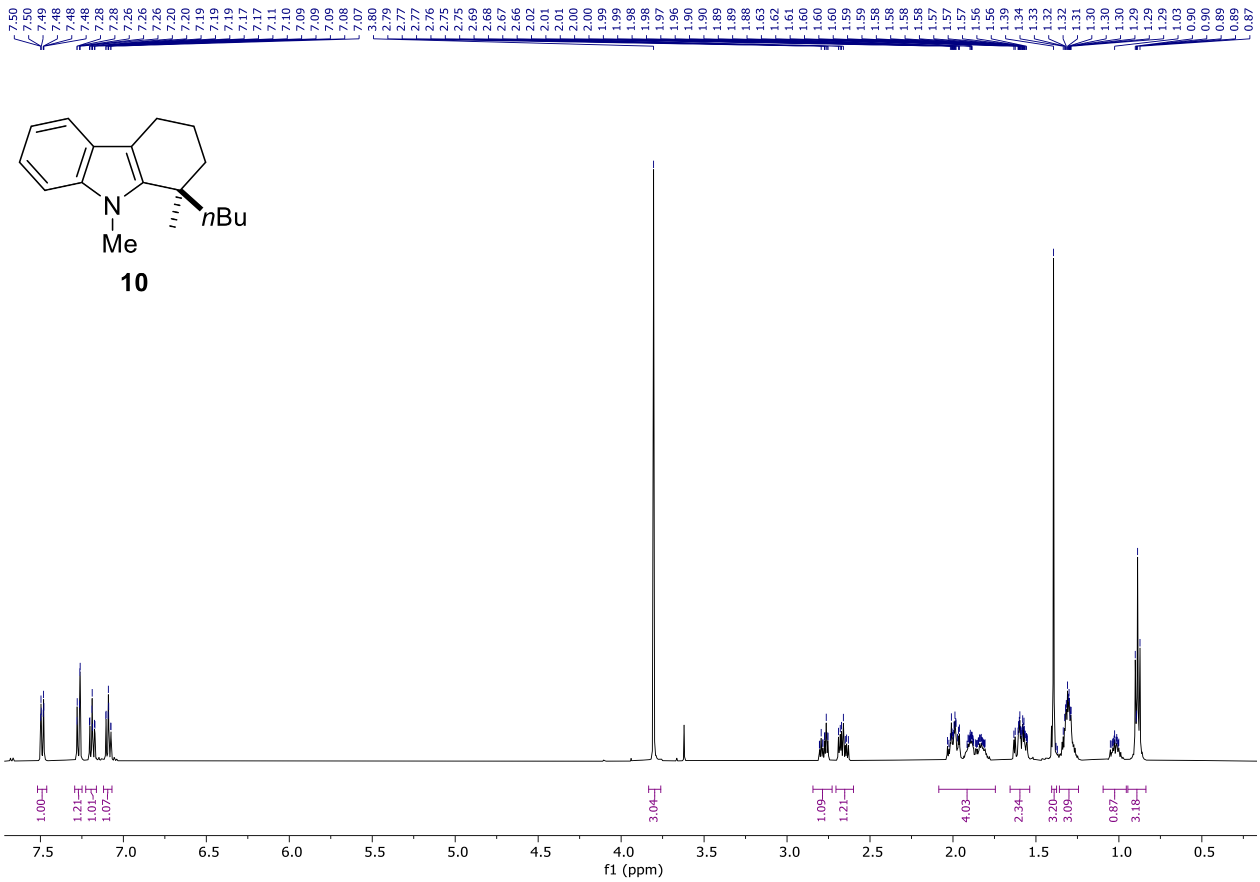
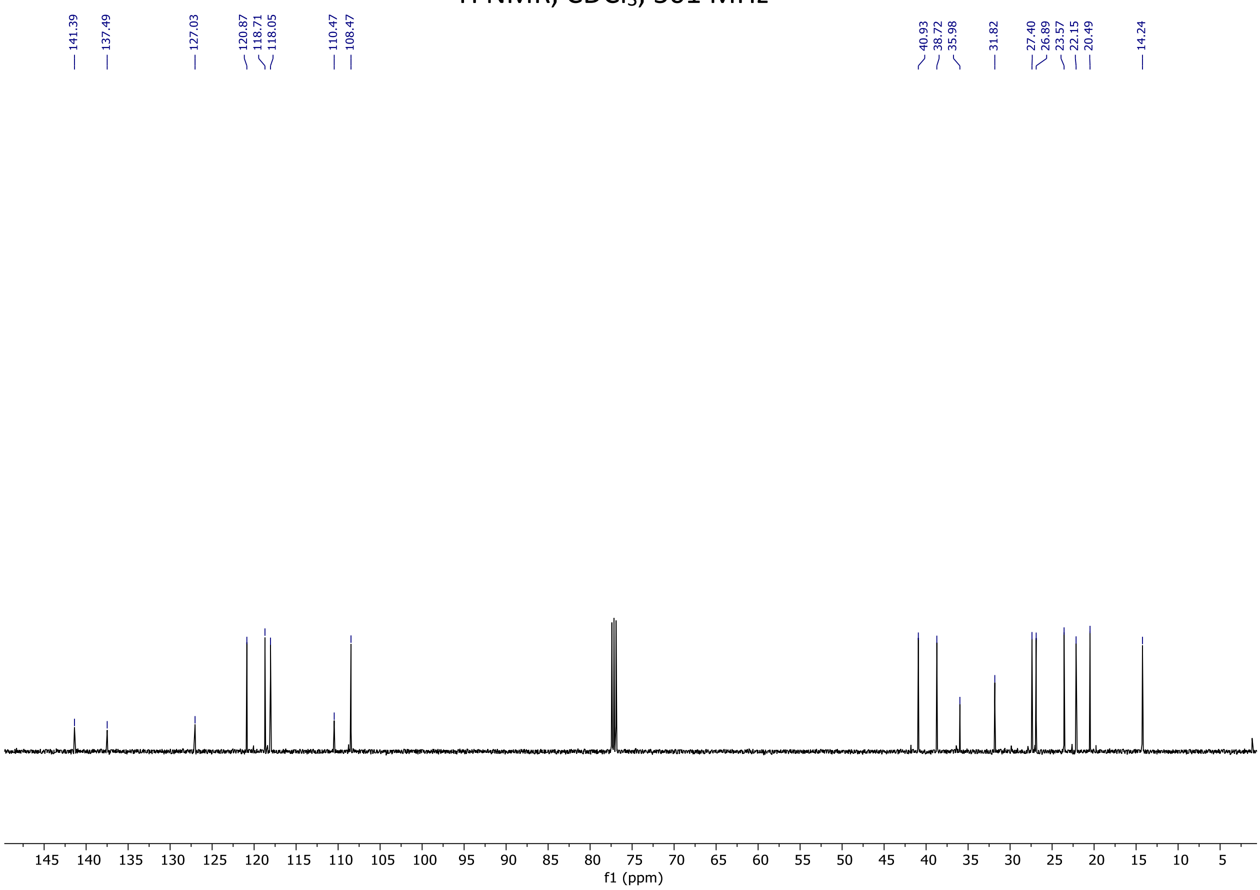
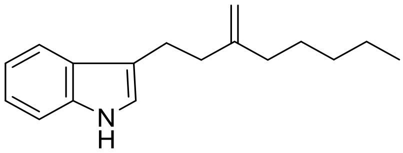


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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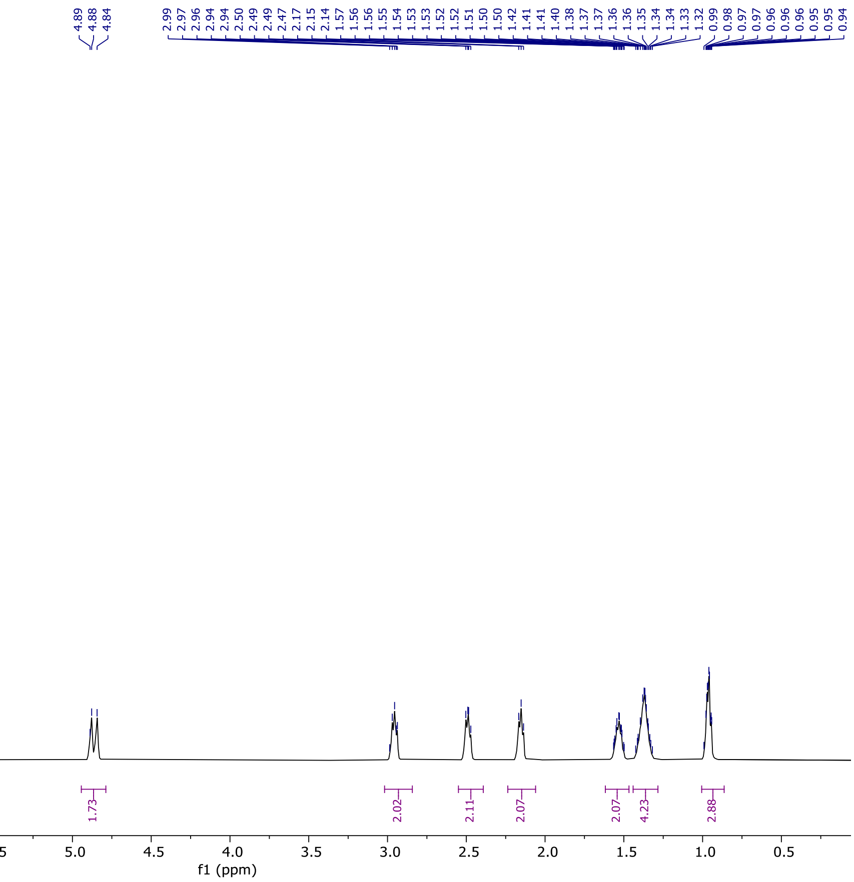
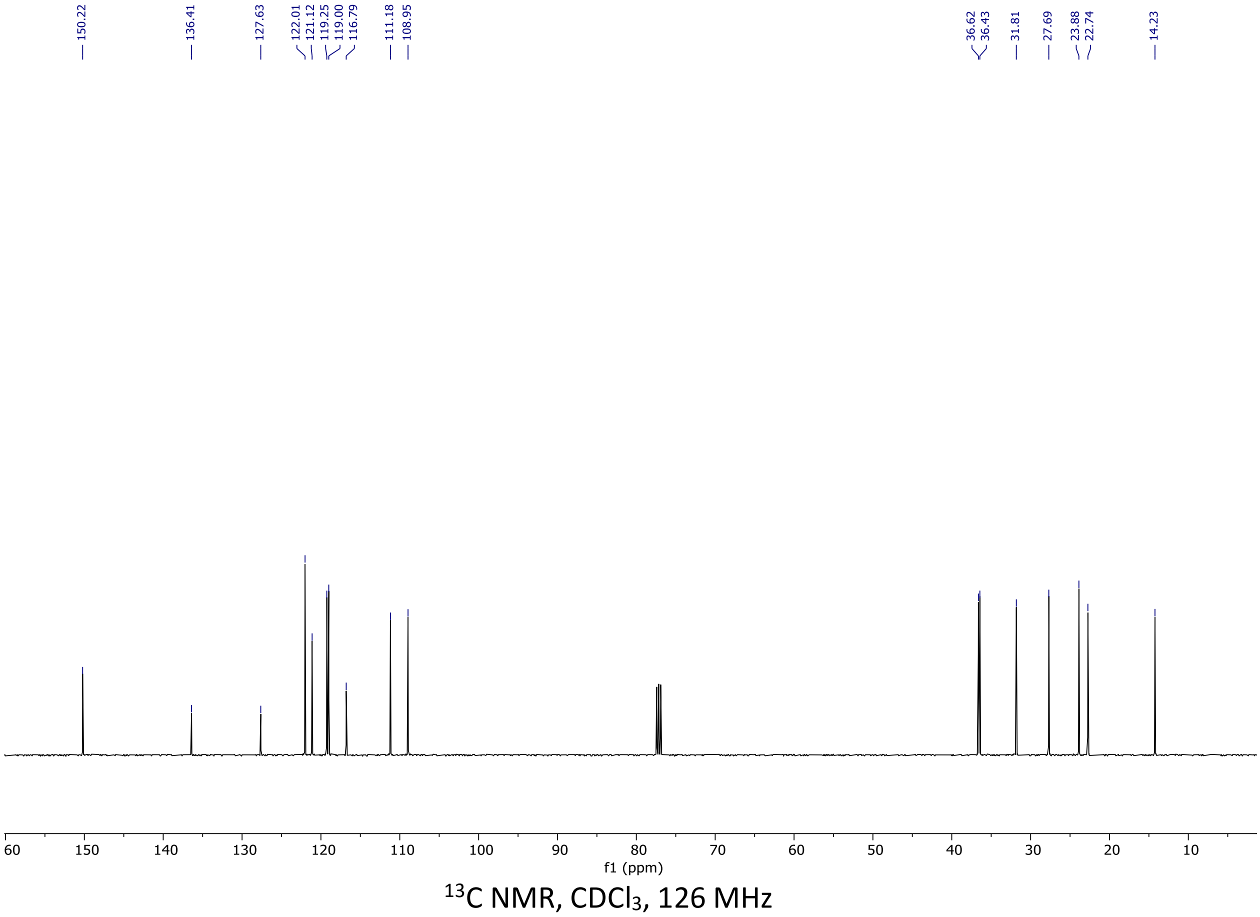
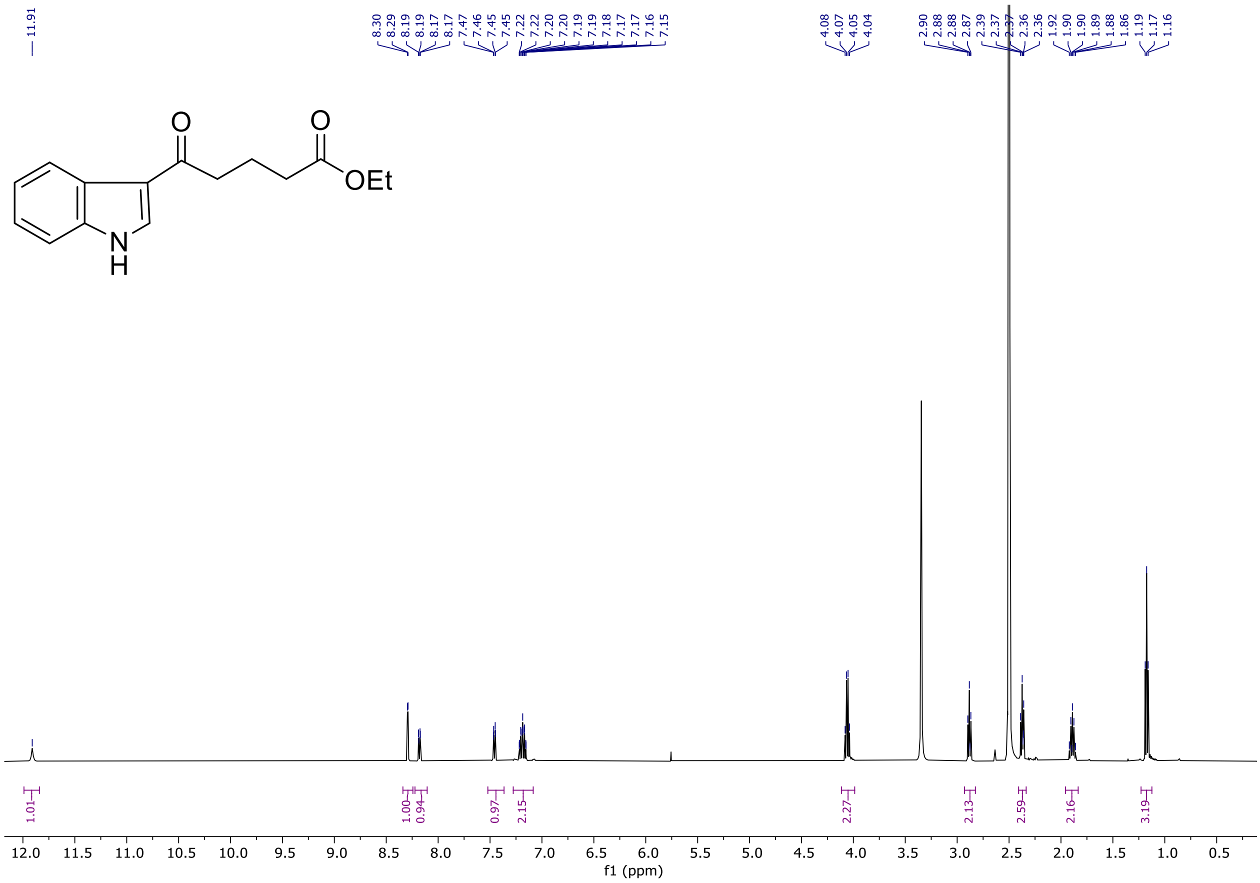


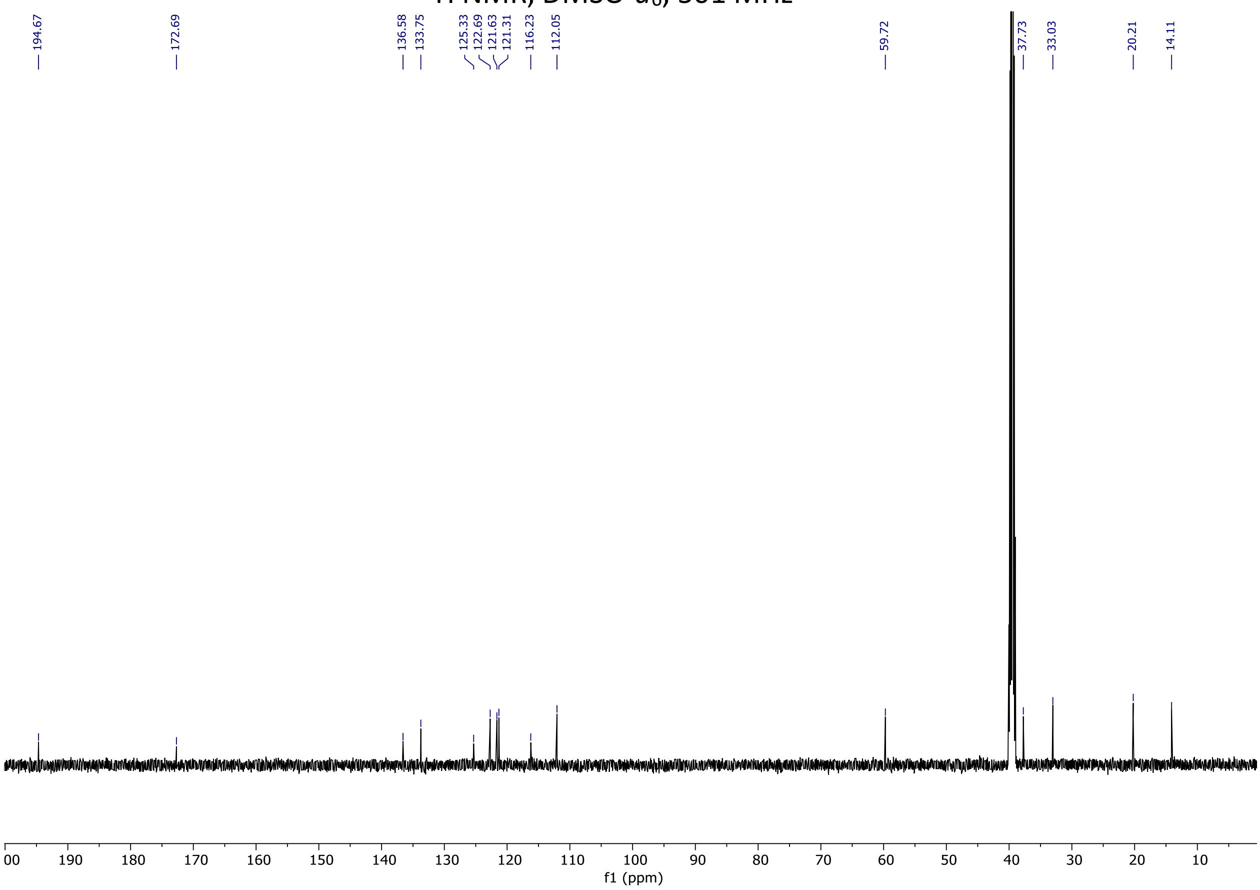
^{1}H NMR, $CDCl_3$, 501 MHz



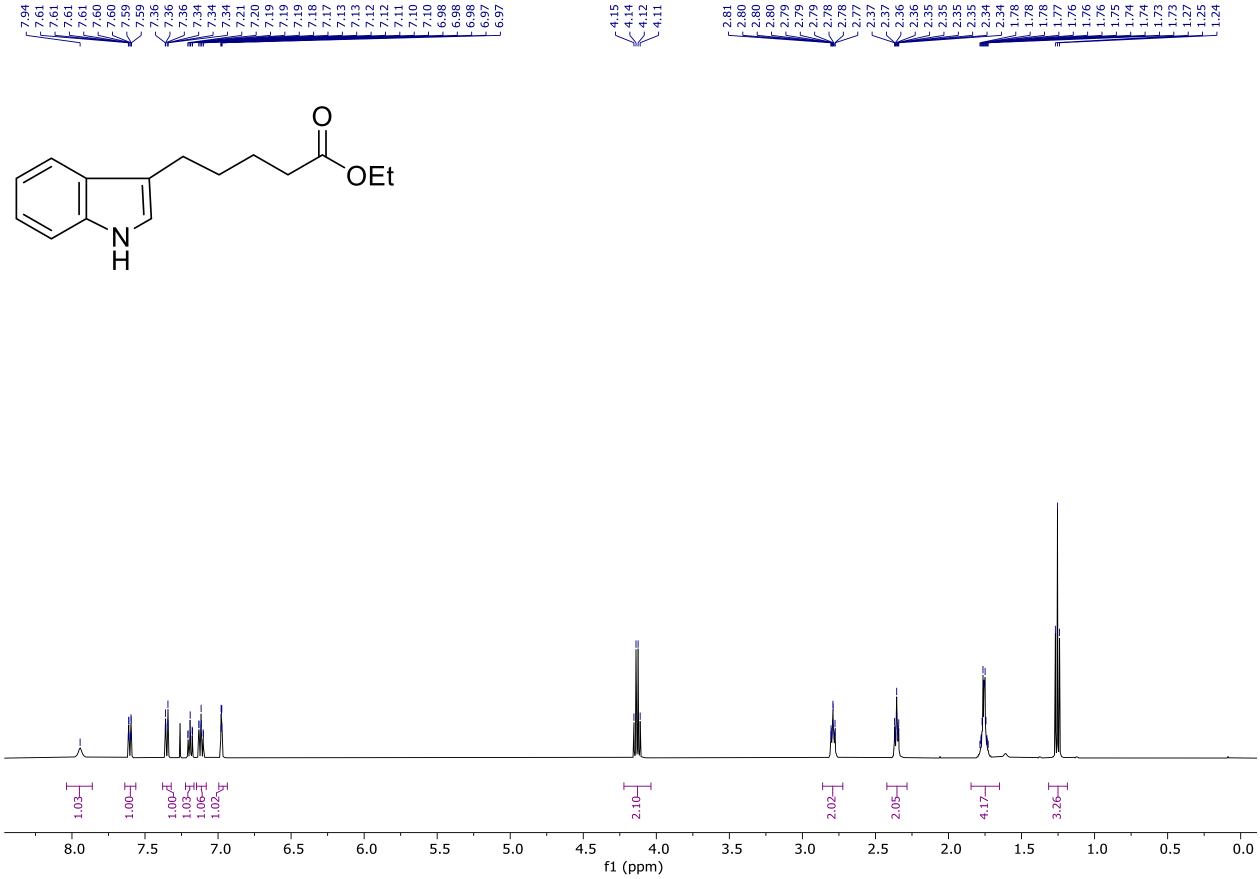
^{13}C NMR, $CDCl_3$, 126 MHz



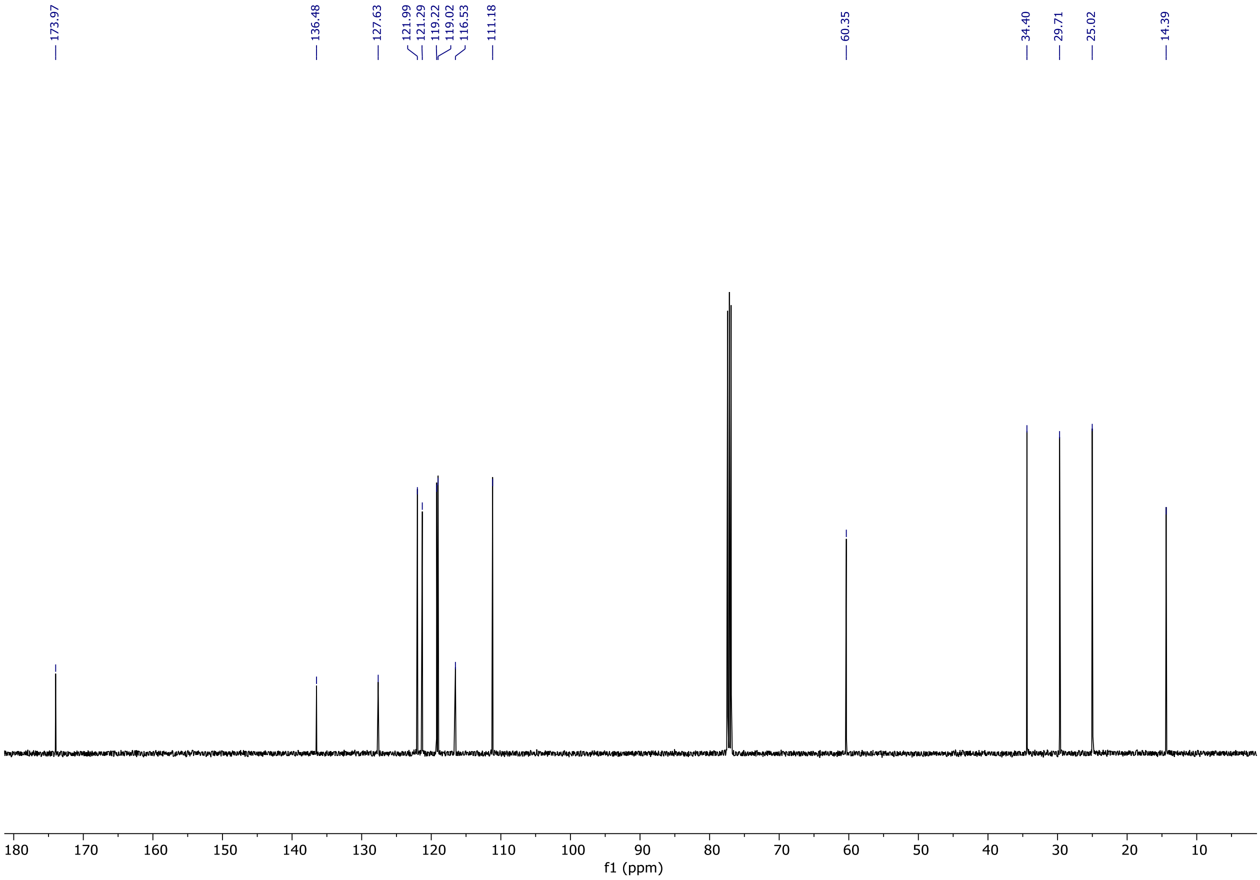
^{1}H NMR, DMSO-d_6, 501 MHz



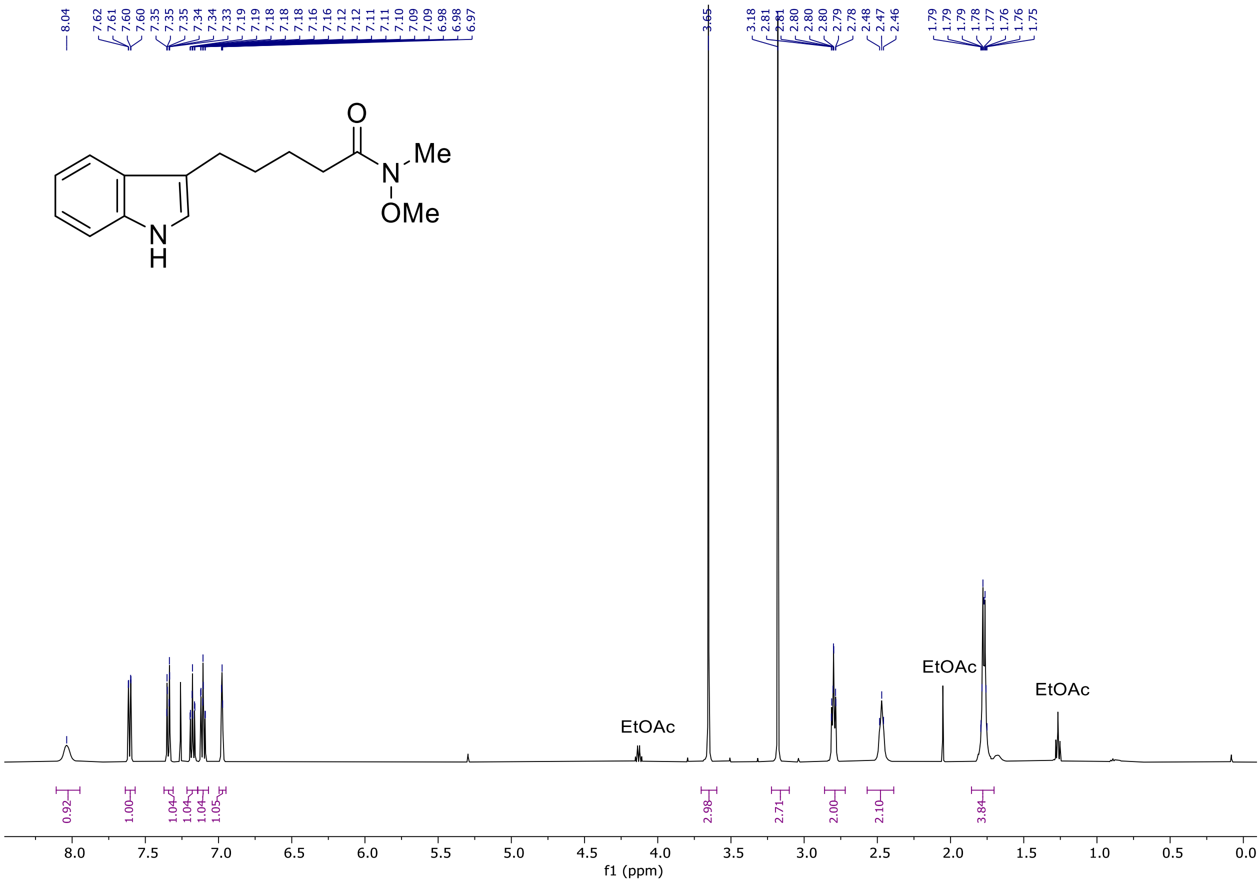
^{13}C NMR, DMSO-d_6, 126 MHz



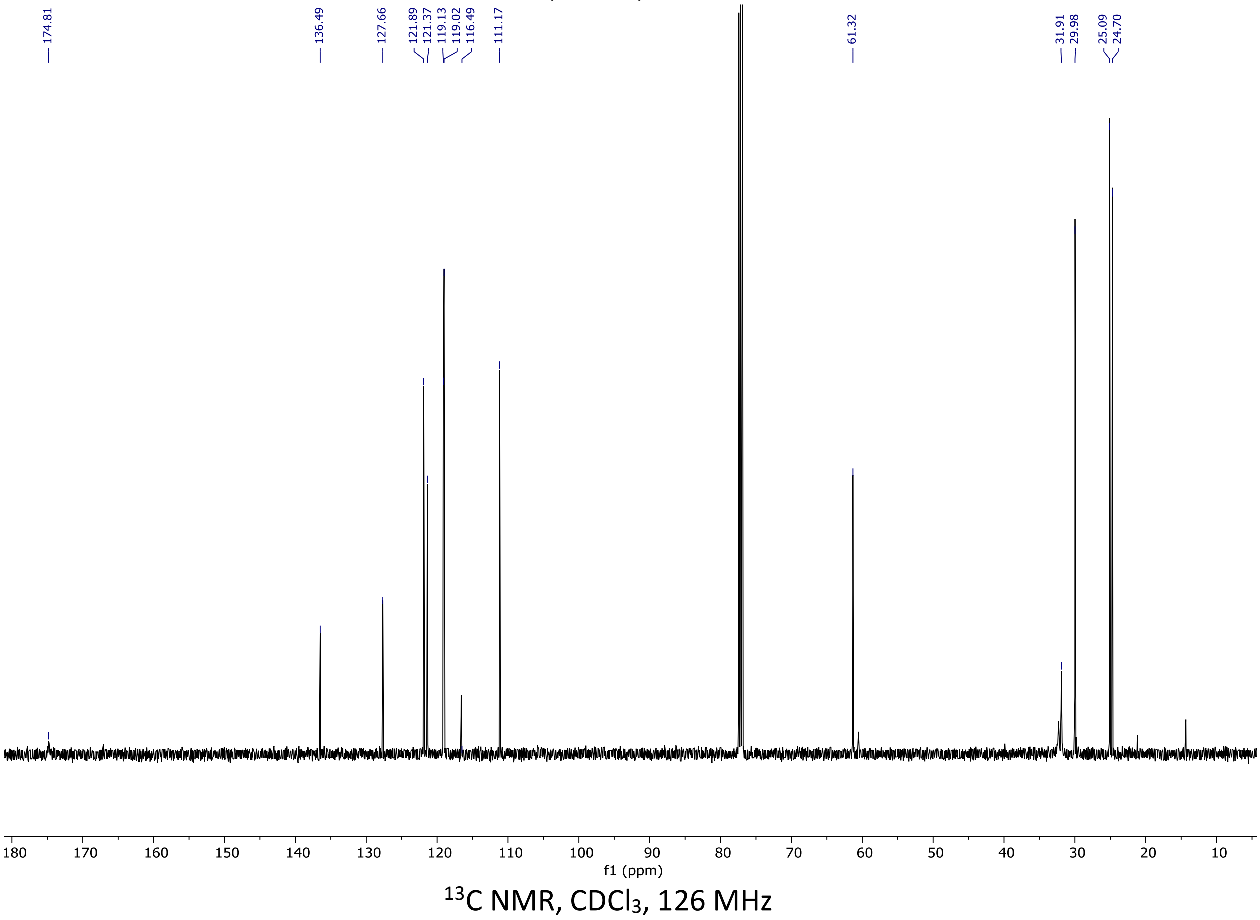
^{1}H NMR, $CDCl_3$, 501 MHz



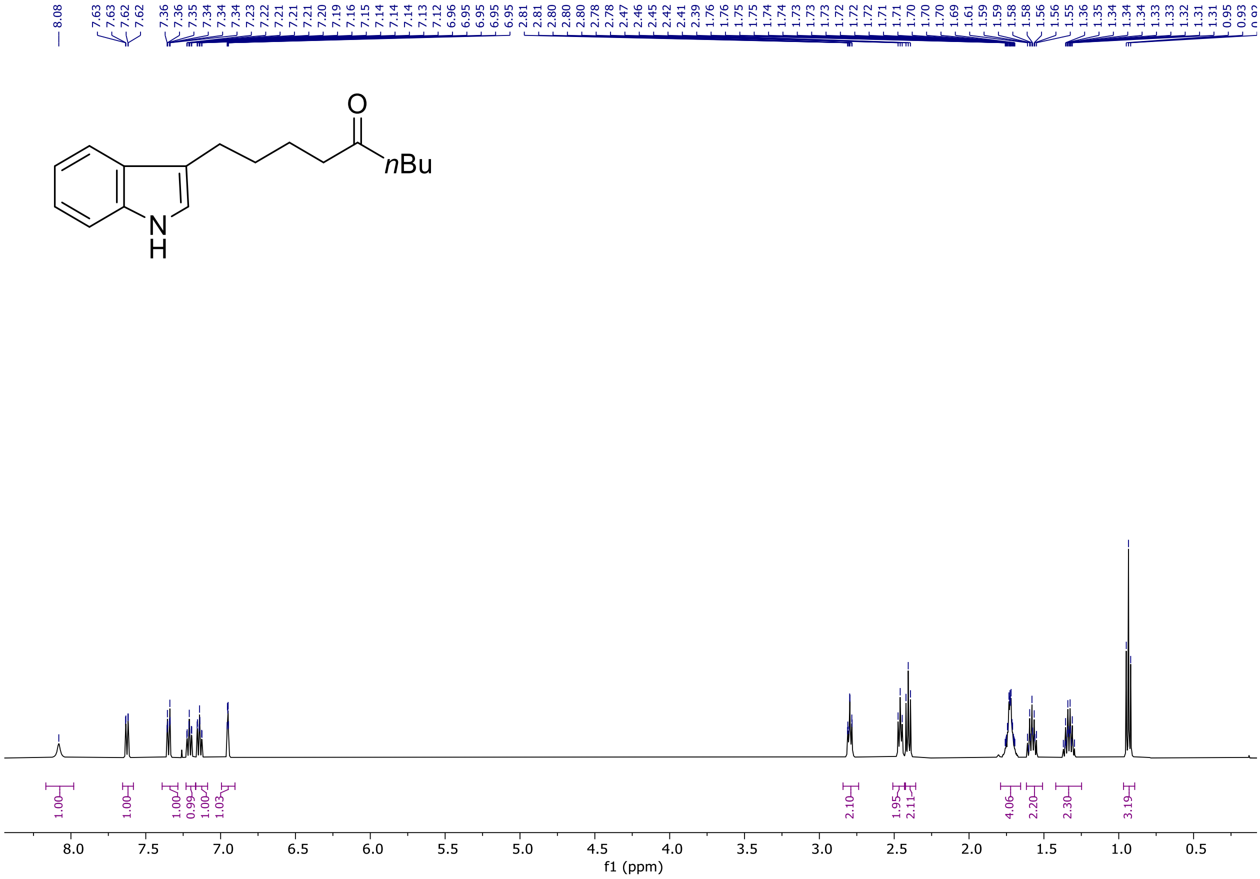
^{13}C NMR, $CDCl_3$, 126 MHz



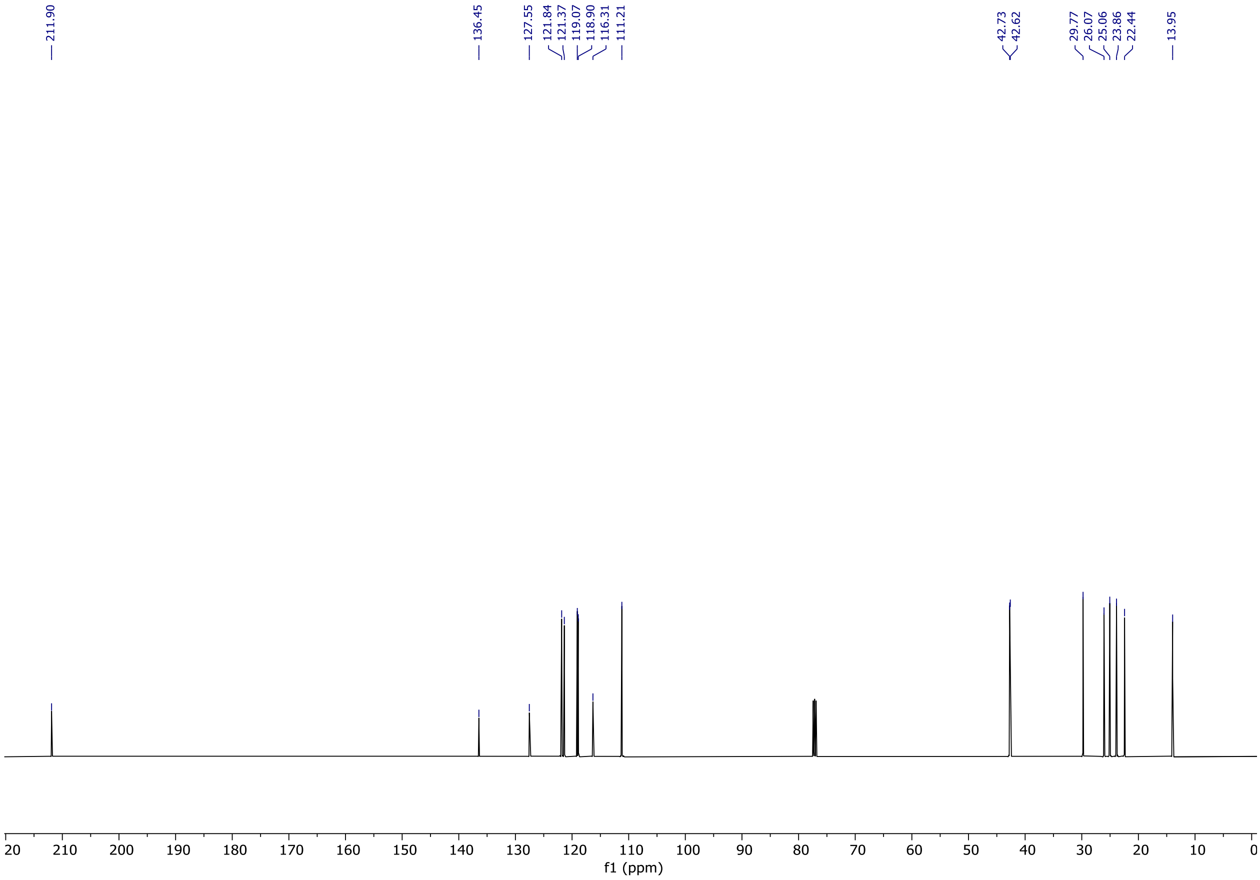
^{1}H NMR, $CDCl_3$, 501 MHz



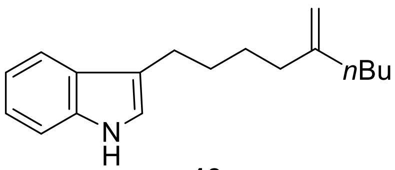
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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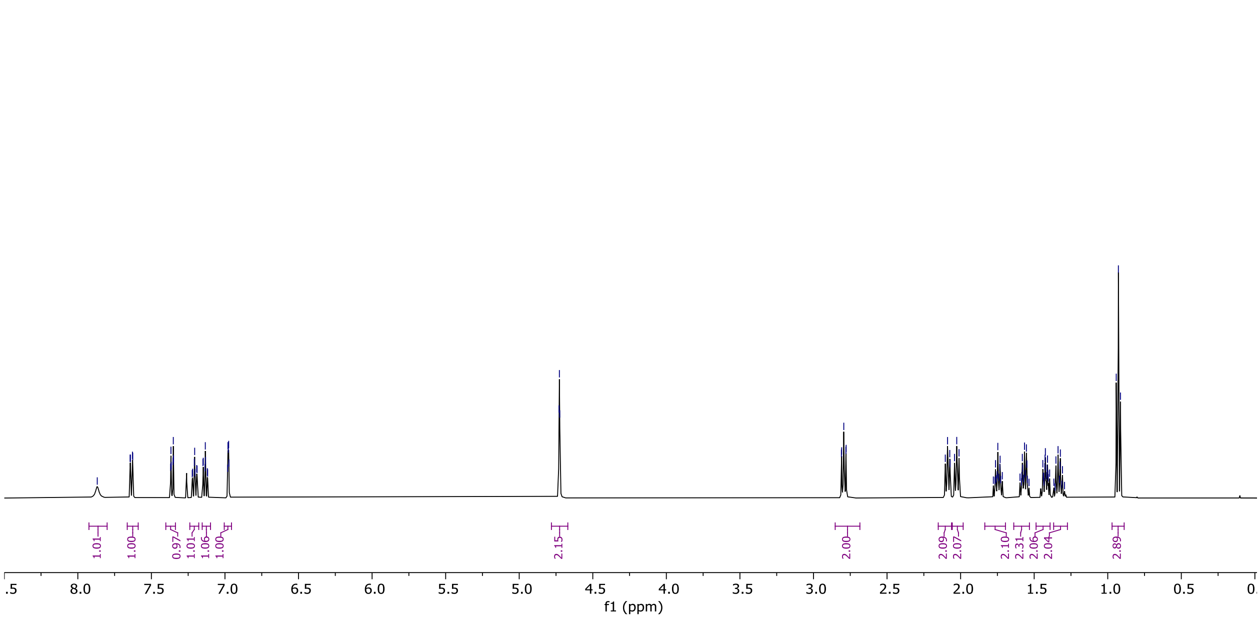
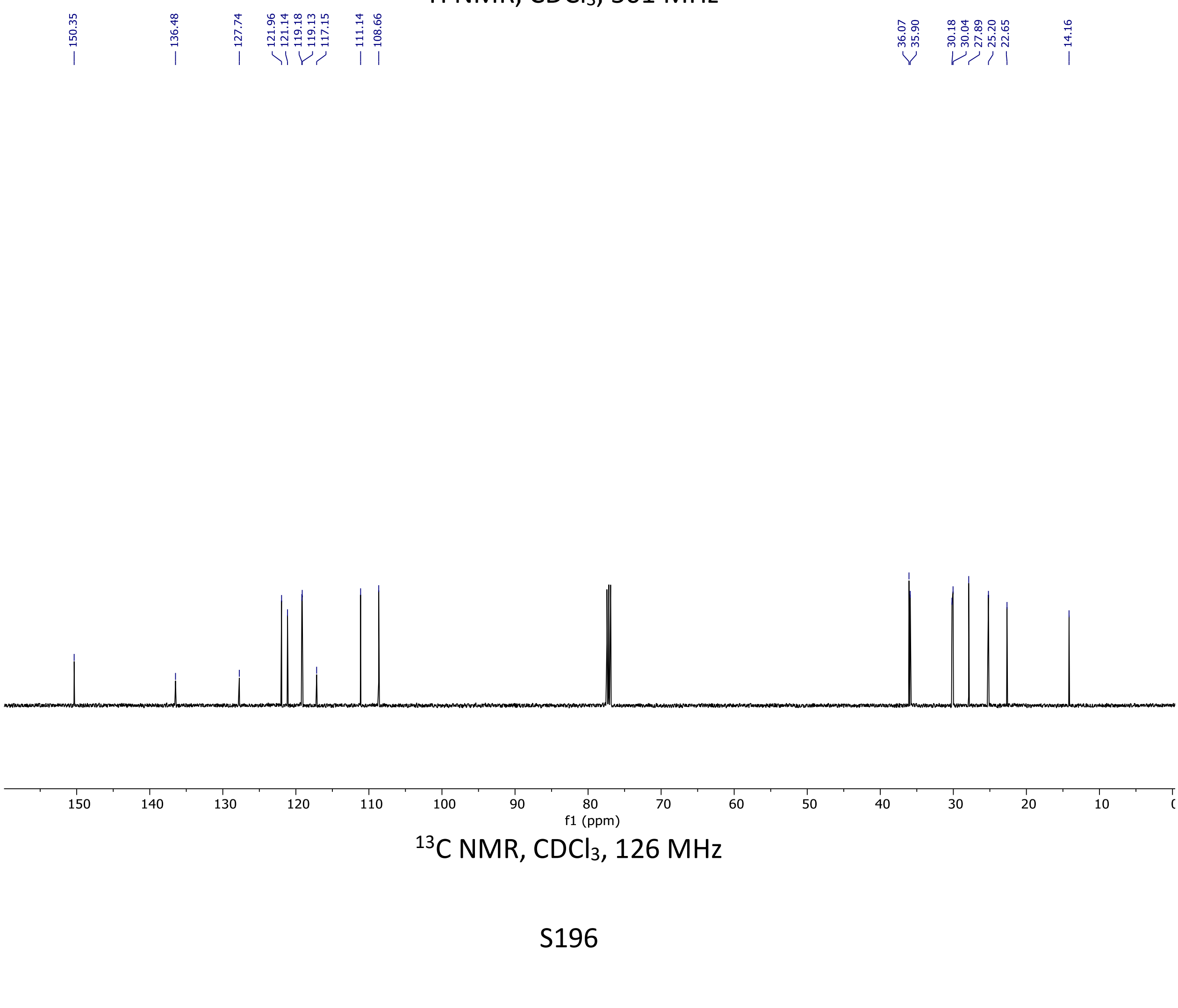
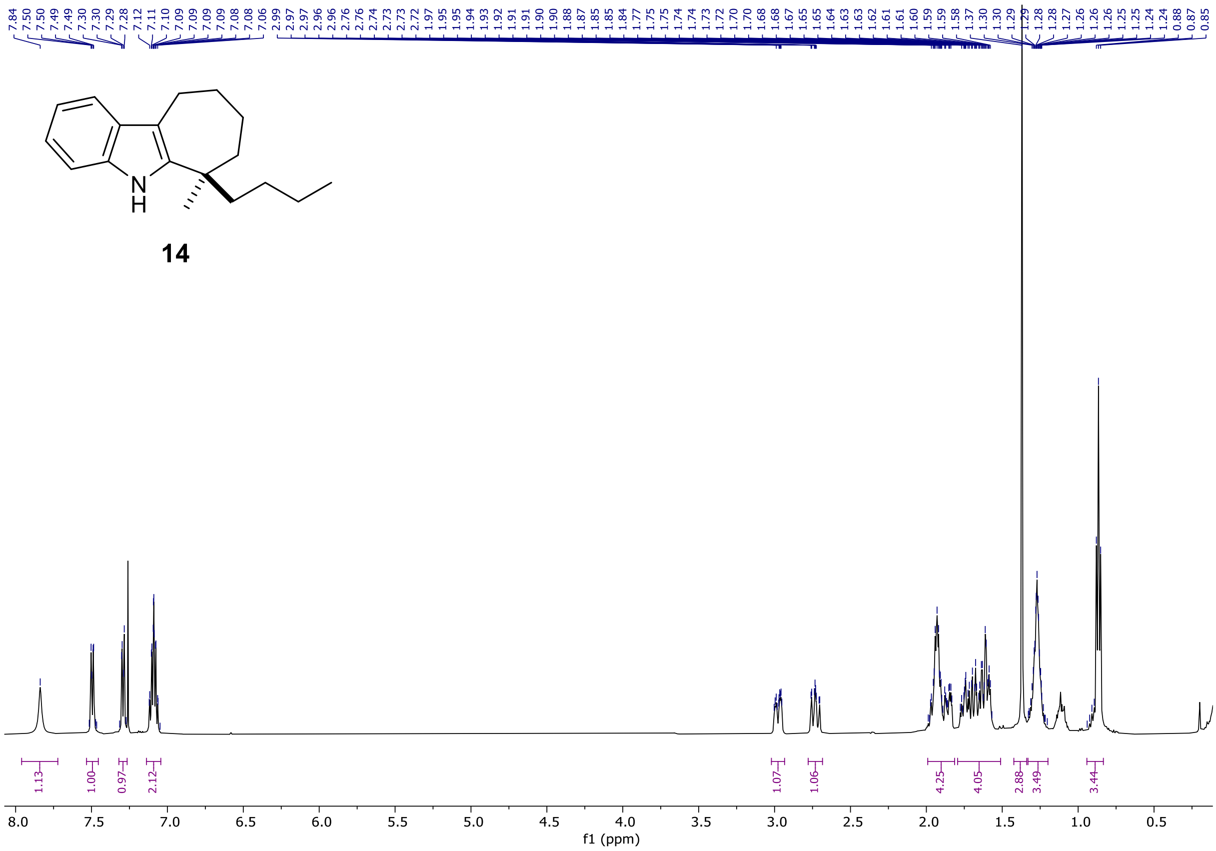


^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



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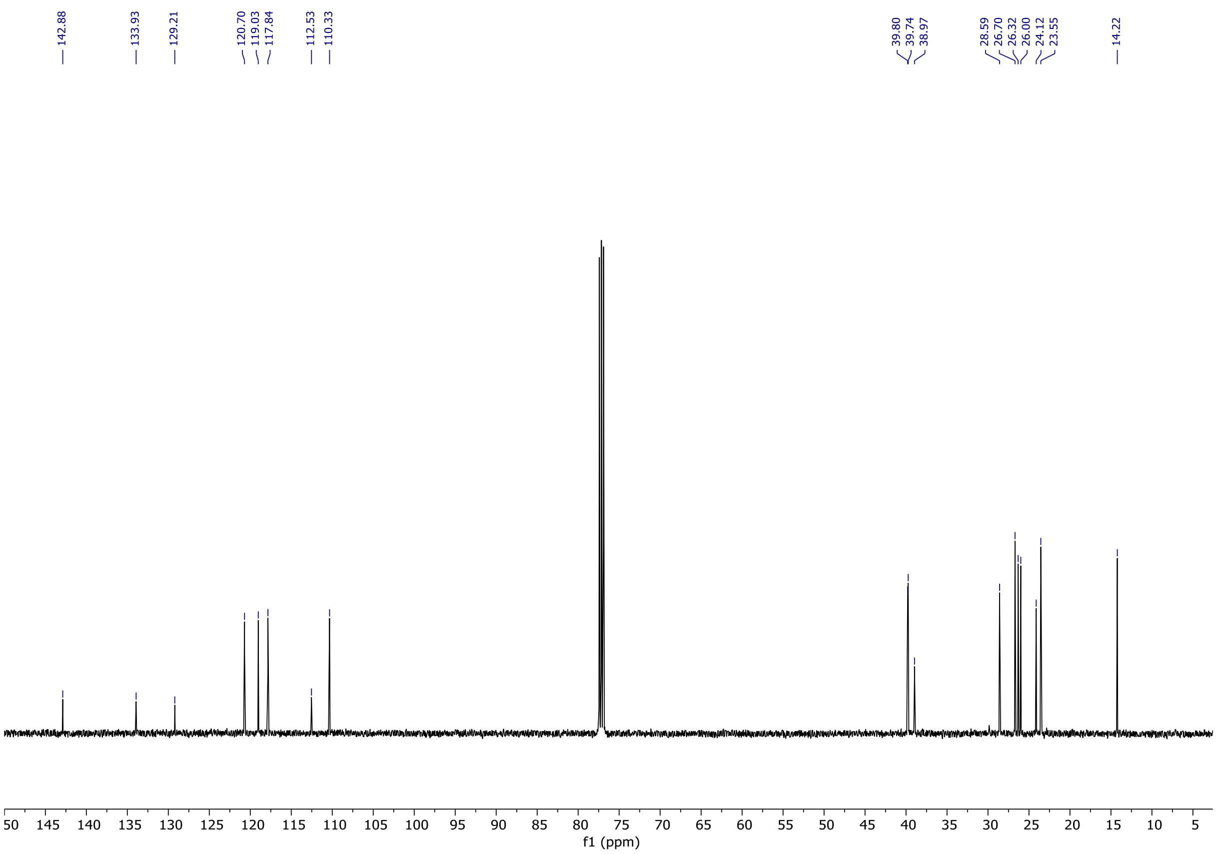
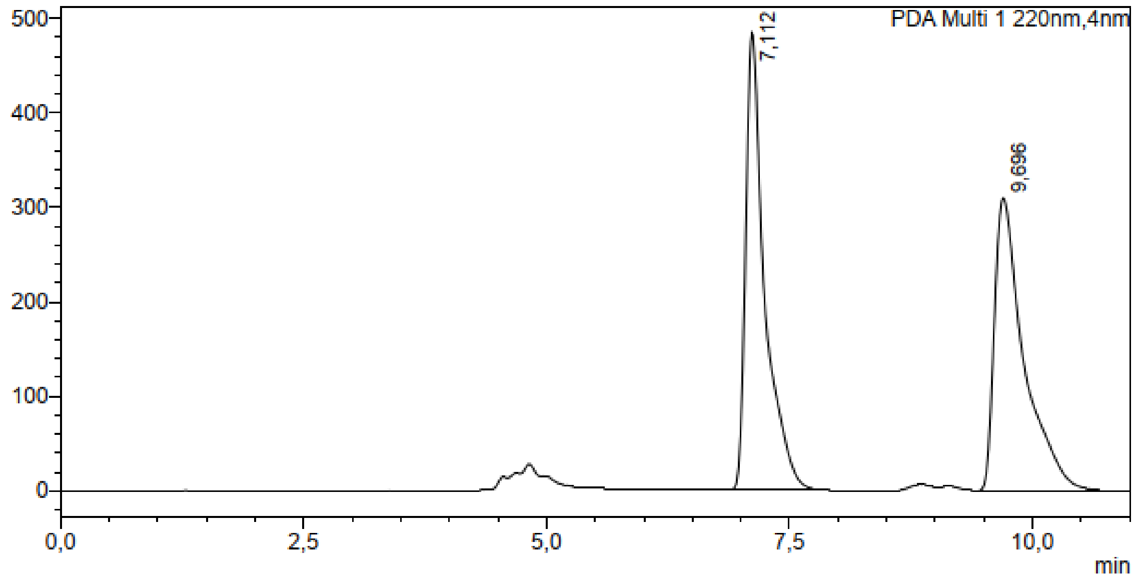
^{1}H NMR, $CDCl_3$, 501 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

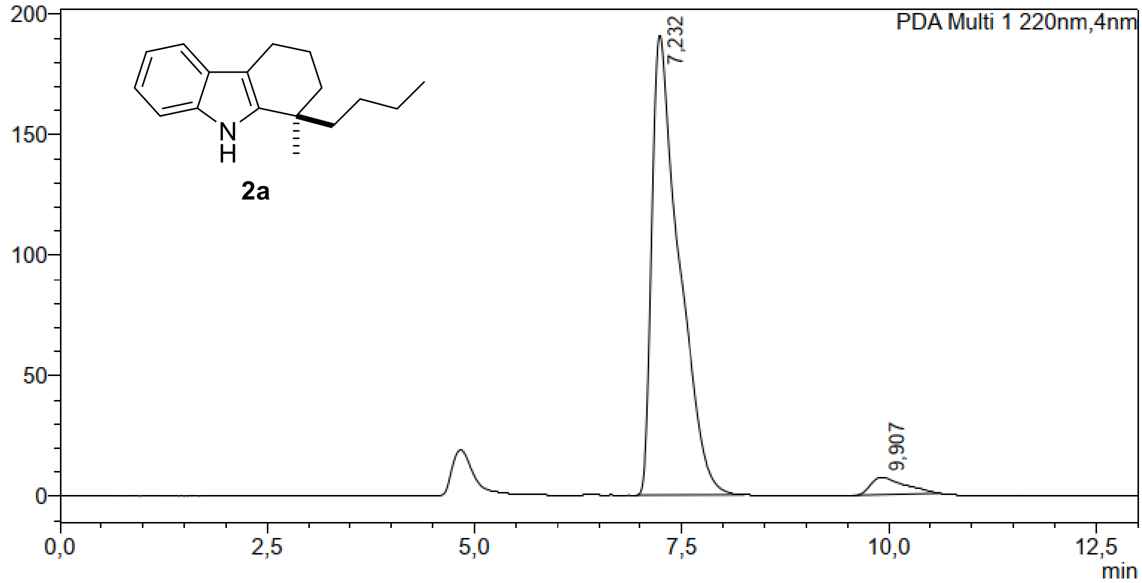
10. HPLC traces



<Peak Table>

PDA Ch1 220nm

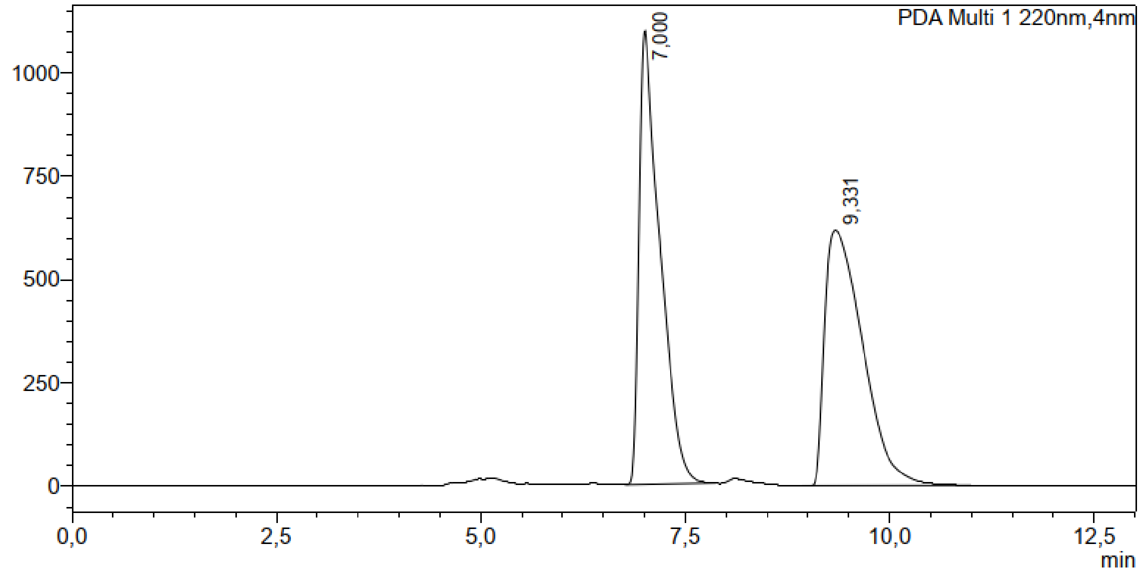
Peak#	Ret. Time	Area	Area%	Height	Name
1	7,112	6555072	49,795	483335	
2	9,696	6609106	50,205	310010	
Total		13164177	100,000	793345	



<Peak Table>

PDA Ch1 220nm

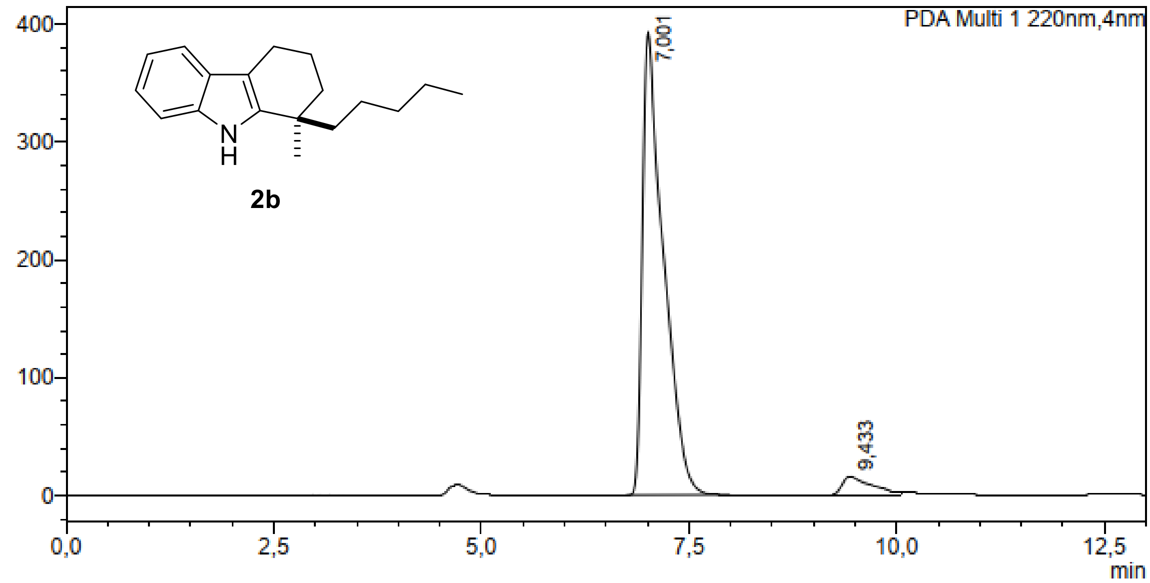
Peak#	Ret. Time	Area	Area%	Height	Name
1	7,232	4330774	95,434	190668	
2	9,907	207213	4,566	7211	
Total		4537987	100,000	197879	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7,000	19512771	49,350	1096976	
2	9,331	20026729	50,650	618493	
Total		39539500	100,000	1715469	



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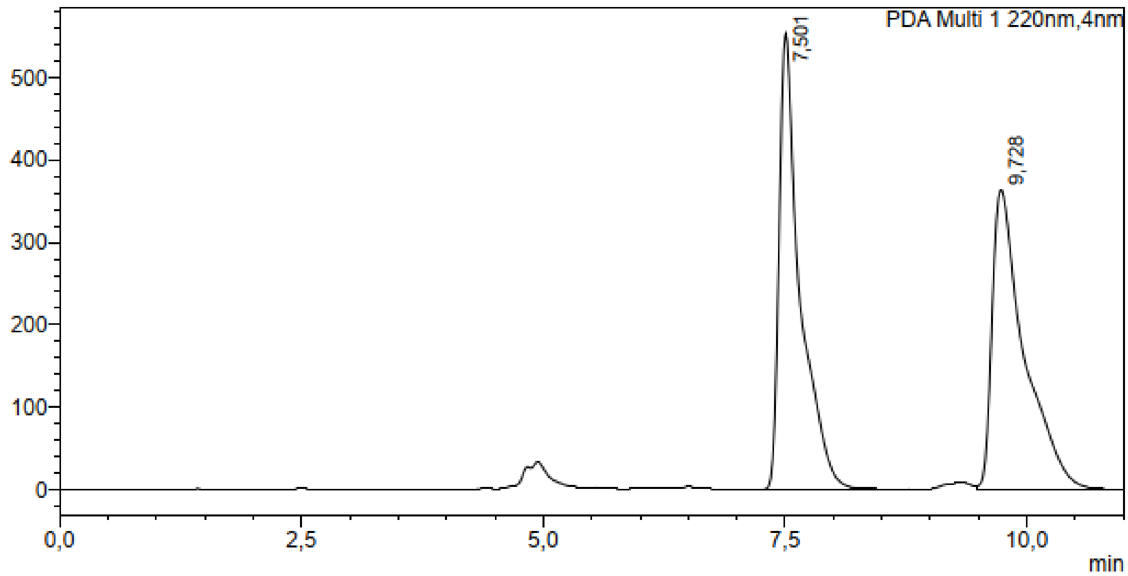
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7,001	6944002	94,714	391758	
2	9,433	387571	5,286	15752	
Total		7331573	100,000	407510	



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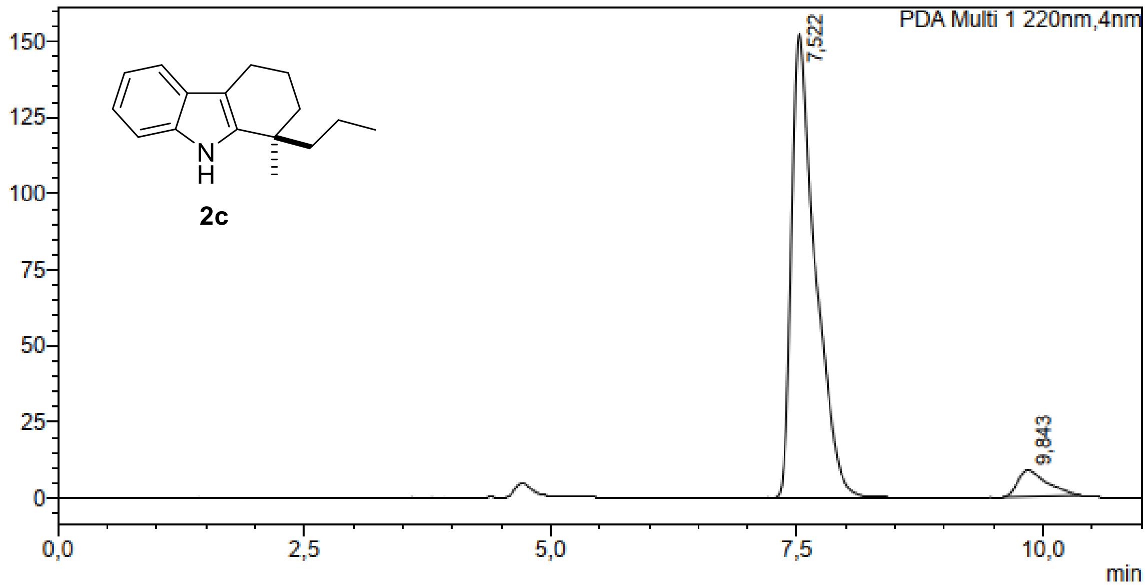
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7,501	8359157	50,026	552864	
2	9,728	8350557	49,974	362939	
Total		16709713	100,000	915803	



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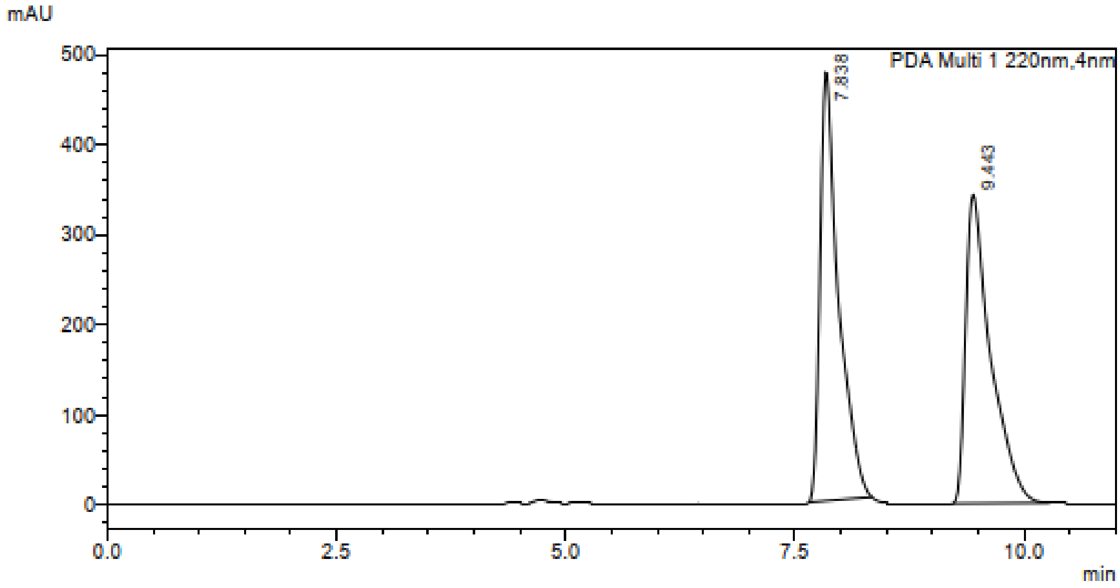
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7,522	2564434	93,502	152164	
2	9,843	178207	6,498	8689	
Total		2742641	100,000	160853	



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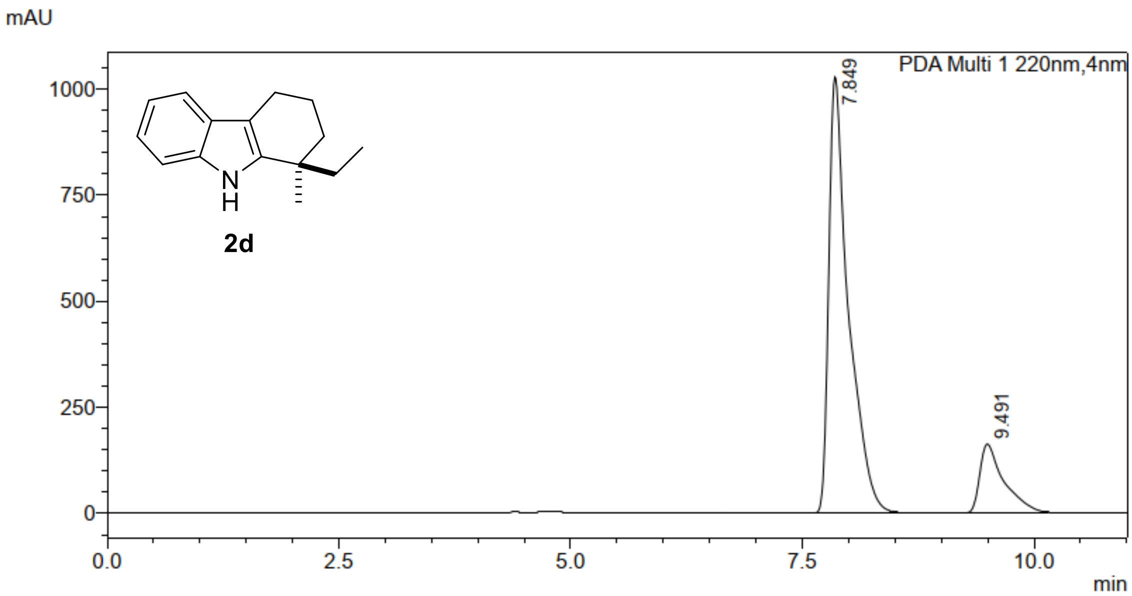
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7.838	6715221	50.766	475700	
2	9.443	6512648	49.234	342501	
Total		13227869	100.000	818201	



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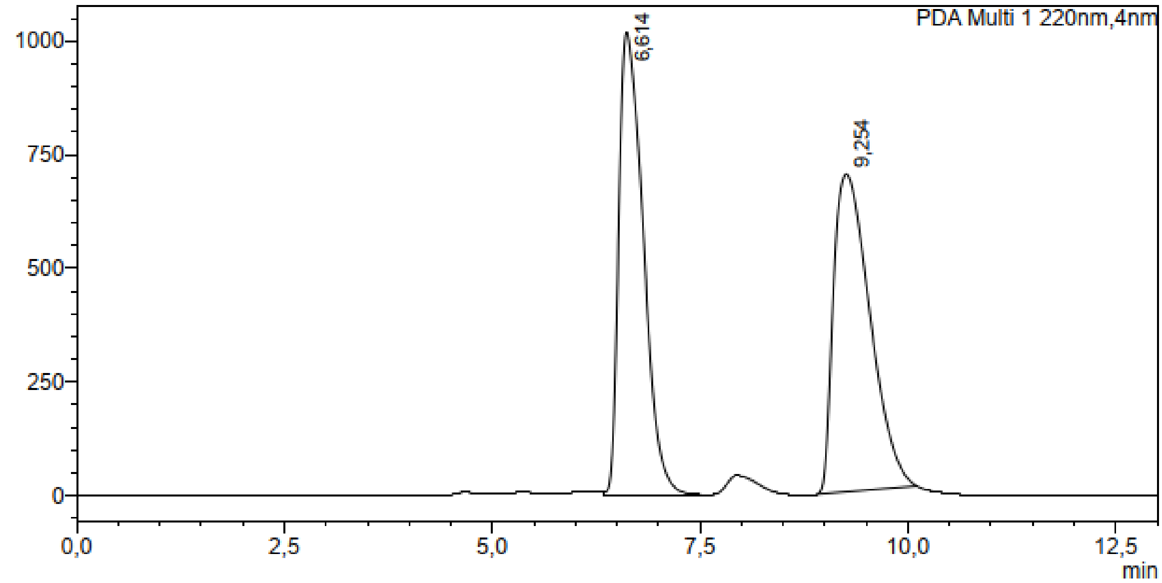
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7.849	15264071	83.703	1028036	
2	9.491	2971977	16.297	162700	
Total		18236048	100.000	1190736	



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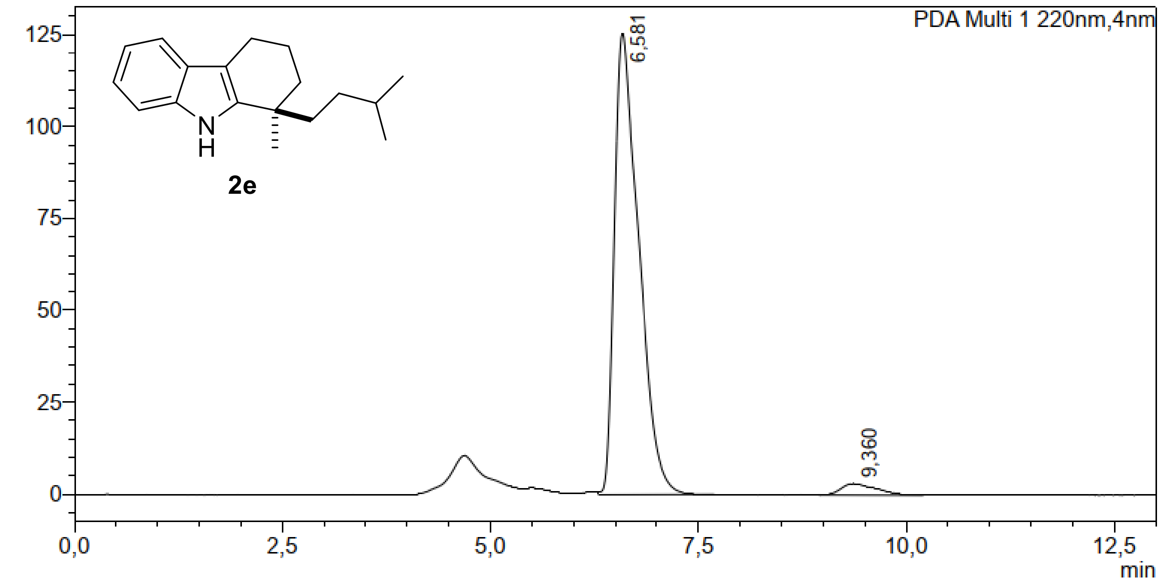
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	6,614	20922165	49,446	1019391	
2	9,254	21391080	50,554	700006	
Total		42313245	100,000	1719397	



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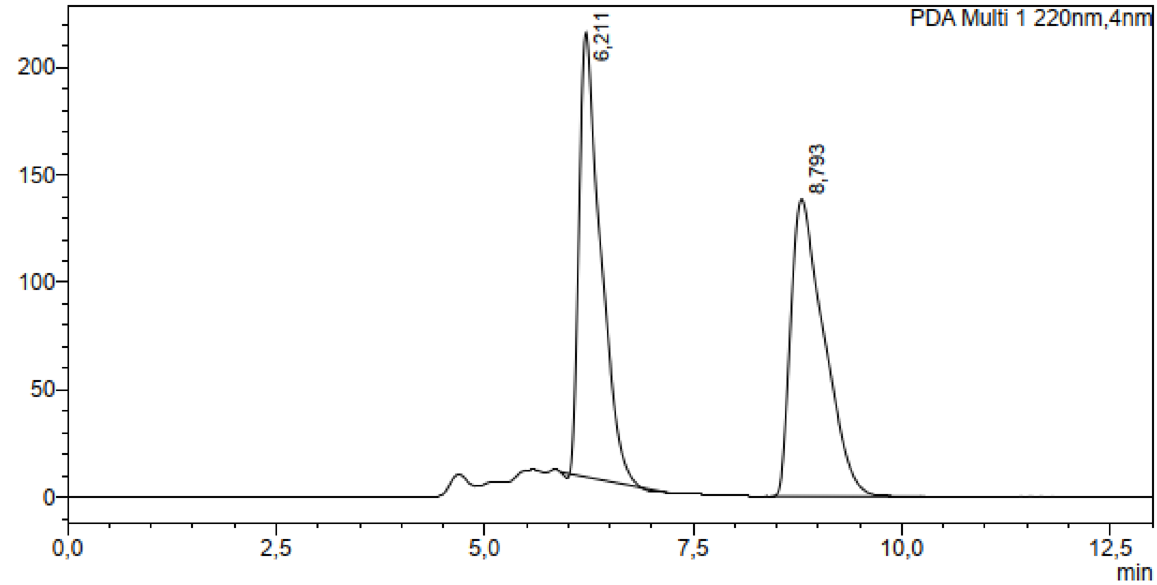
PDA Ch1 220nm

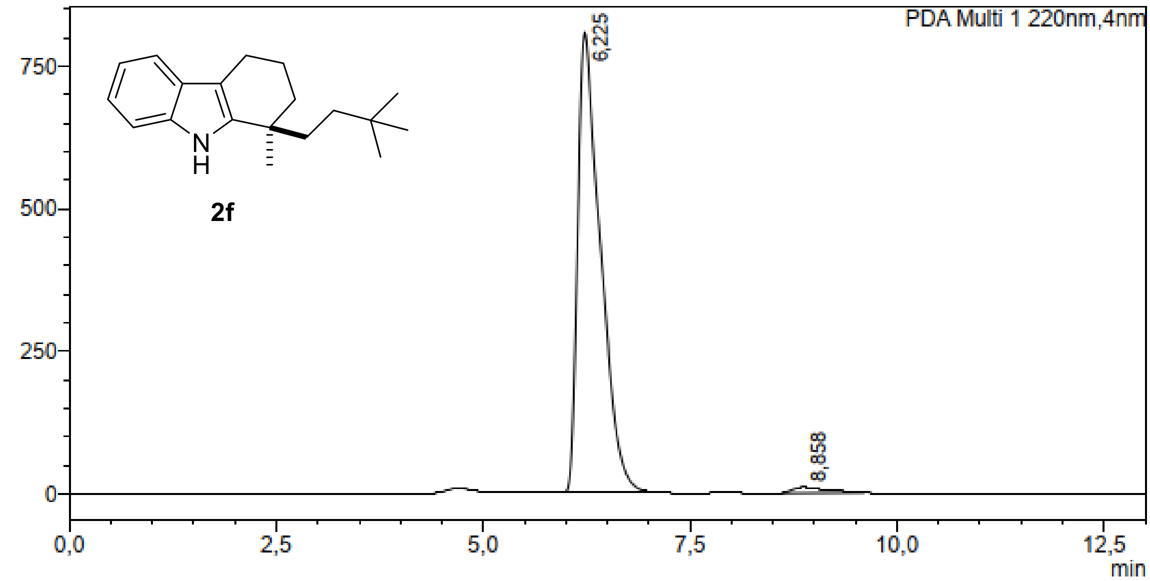
Peak#	Ret. Time	Area	Area%	Height	Name
1	6,581	2564232	96,601	125597	
2	9,360	90226	3,399	3129	
Total		2654459	100,000	128725	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	6,211	3702578	49,090	206907	
2	8,793	3839873	50,910	138327	
Total		7542451	100,000	345233	



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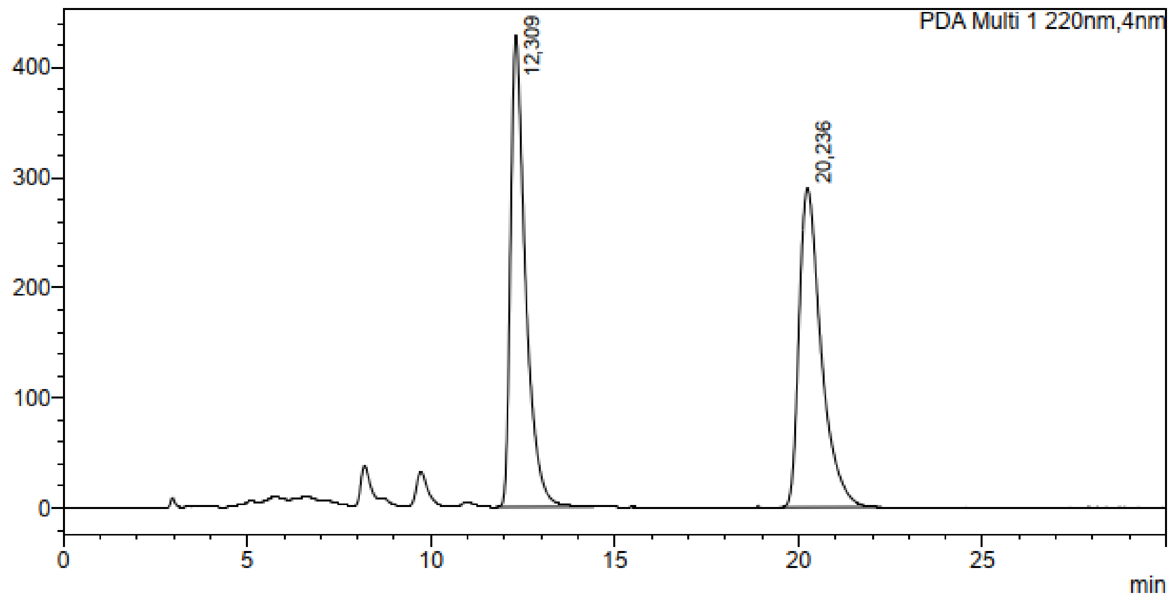
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	6,225	15428327	98,186	806205	
2	8,858	285118	1,814	9948	
Total		15713445	100,000	816152	



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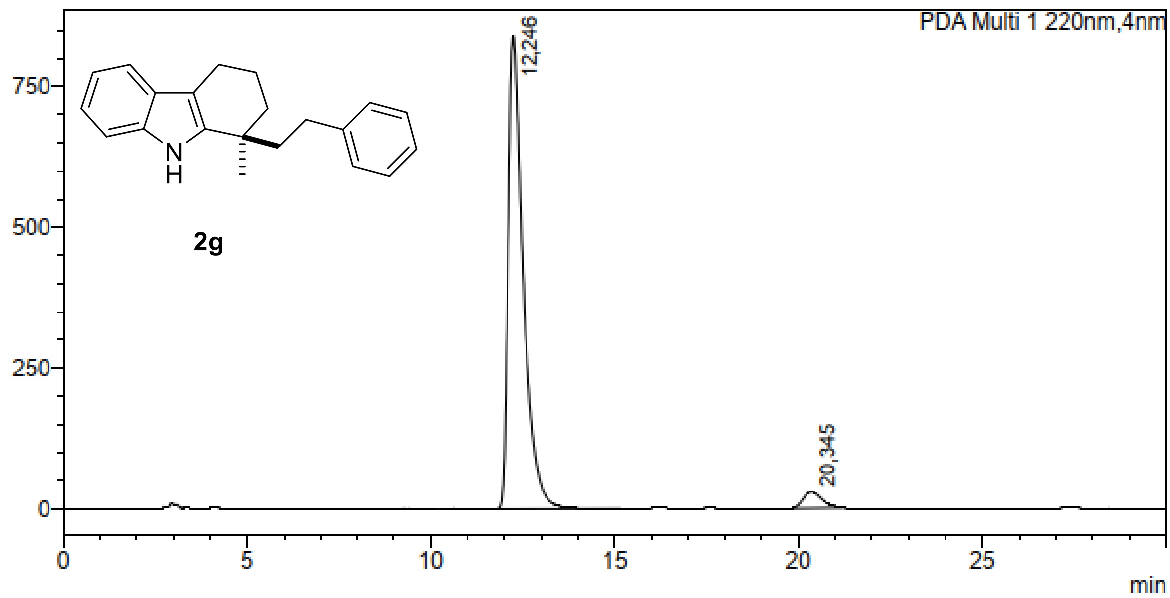
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	12,309	12136096	49,966	427897	
2	20,236	12152710	50,034	289520	
Total		24288806	100,000	717417	



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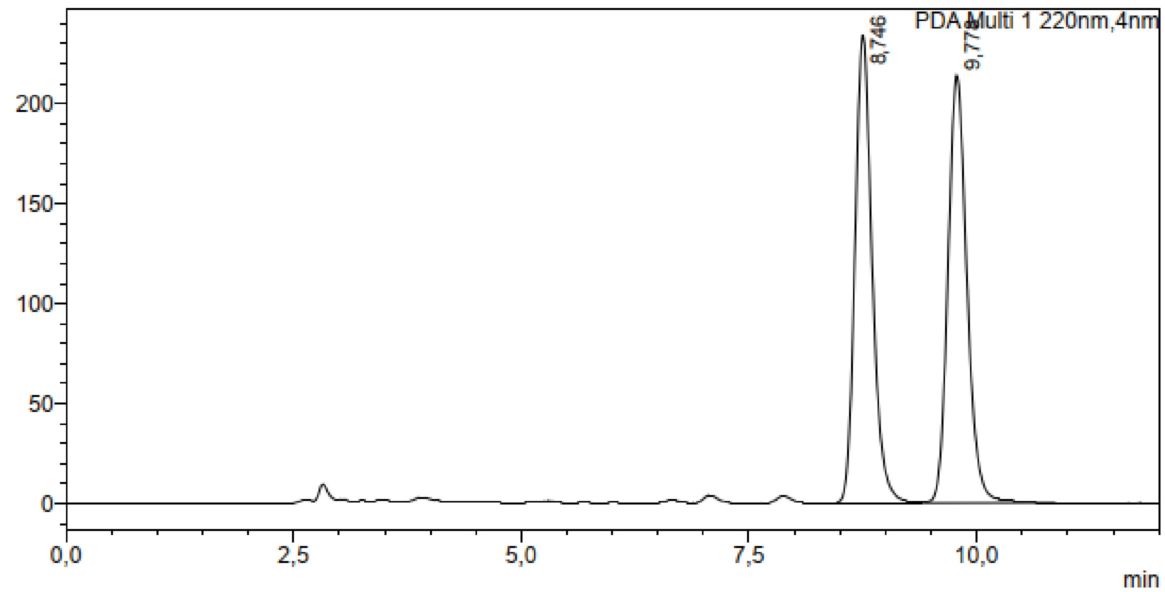
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	12,246	23972452	96,011	838683	
2	20,345	995988	3,989	28360	
Total		24968440	100,000	867043	



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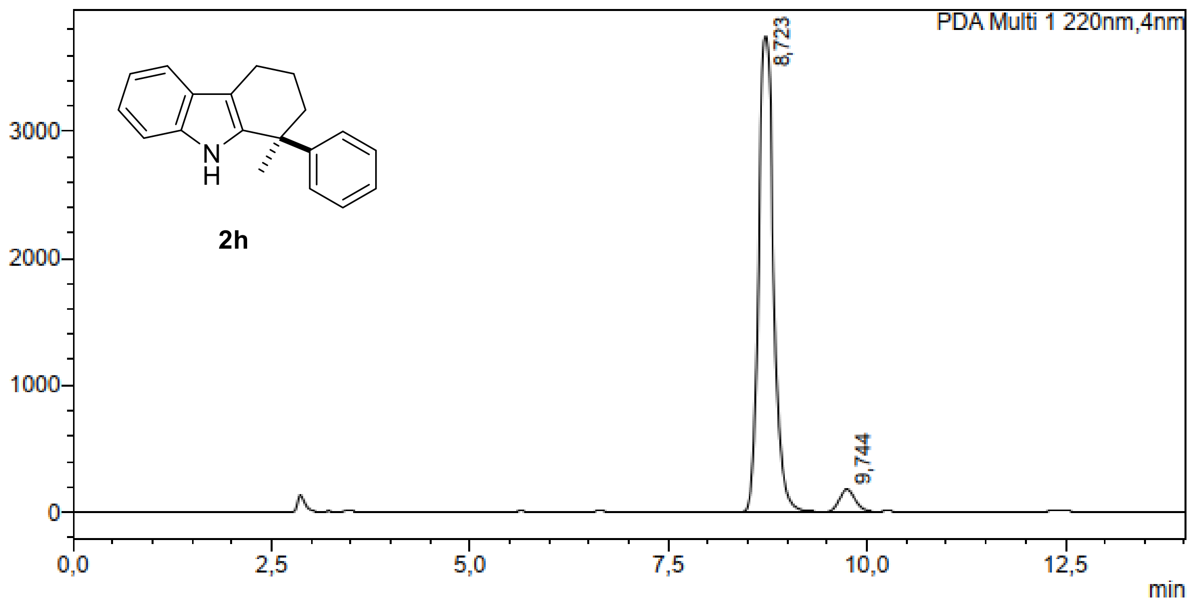
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	8,746	3079010	49,826	233869	
2	9,778	3100570	50,174	213586	
Total		6179580	100,000	447455	



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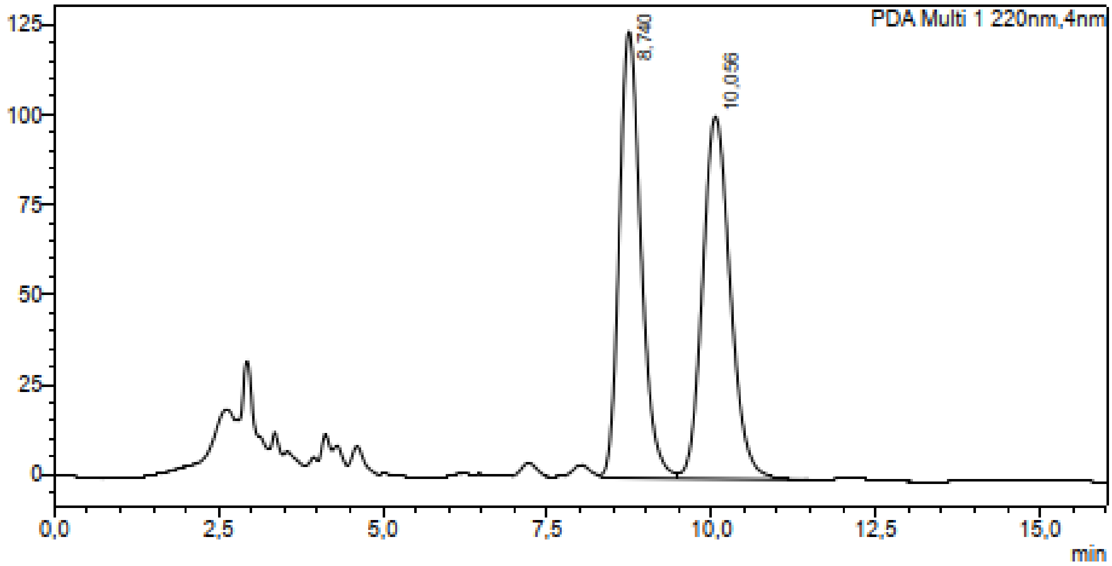
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	8,723	49297650	94,942	3741856	
2	9,744	2626386	5,058	179021	
Total		51924036	100,000	3920877	



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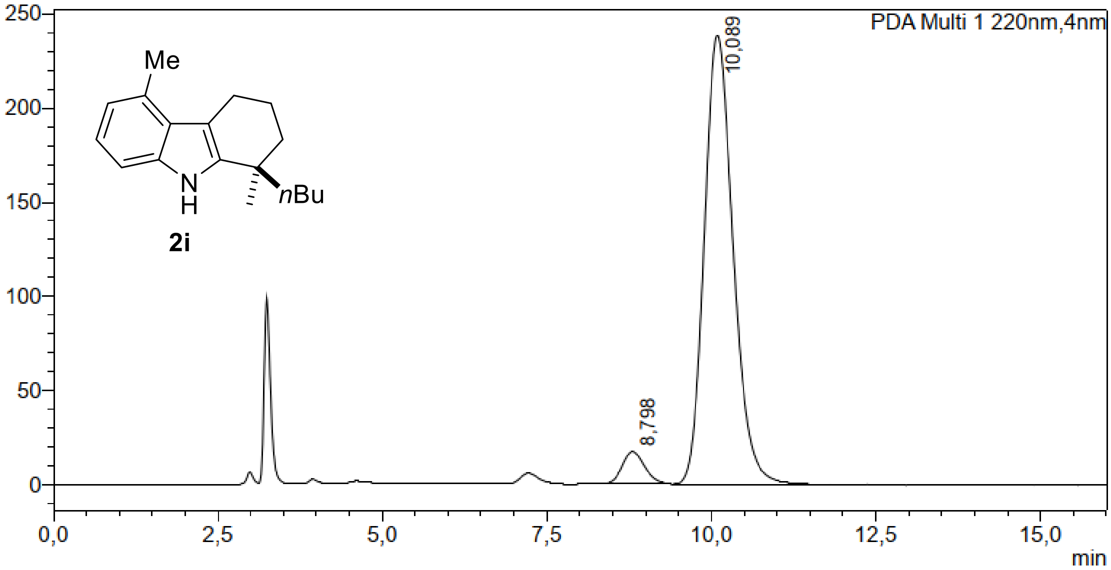
PDA Ch1 220nm

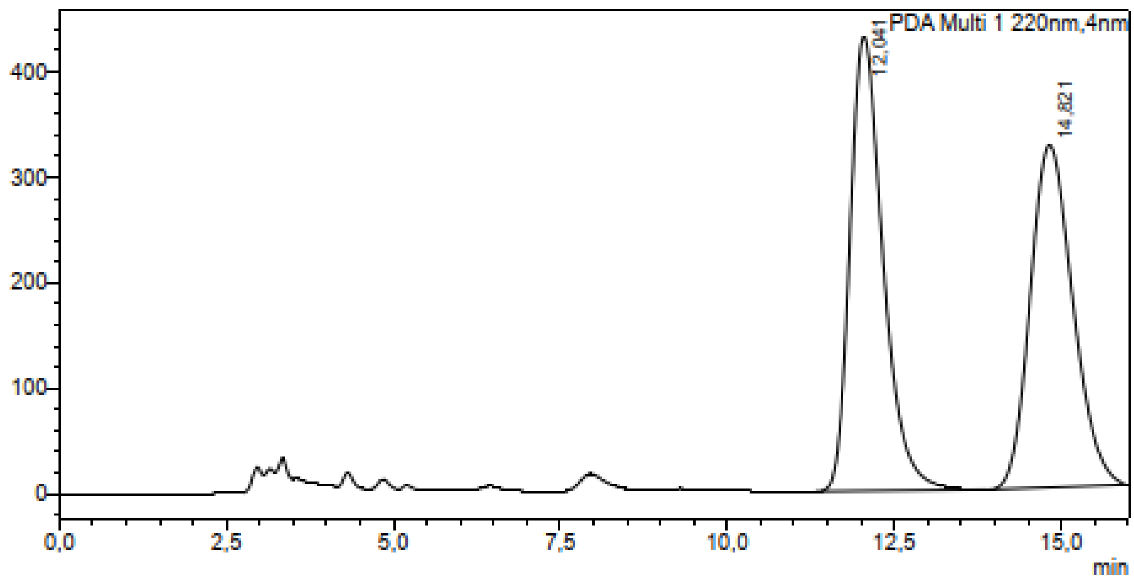
Peak#	Ret. Time	Area	Area%	Height	Name
1	8,740	2841866	49,075	123895	
2	10,056	2949010	50,925	100602	
Total		5790876	100,000	224497	



<Peak Table>

PDA Ch1 220nm

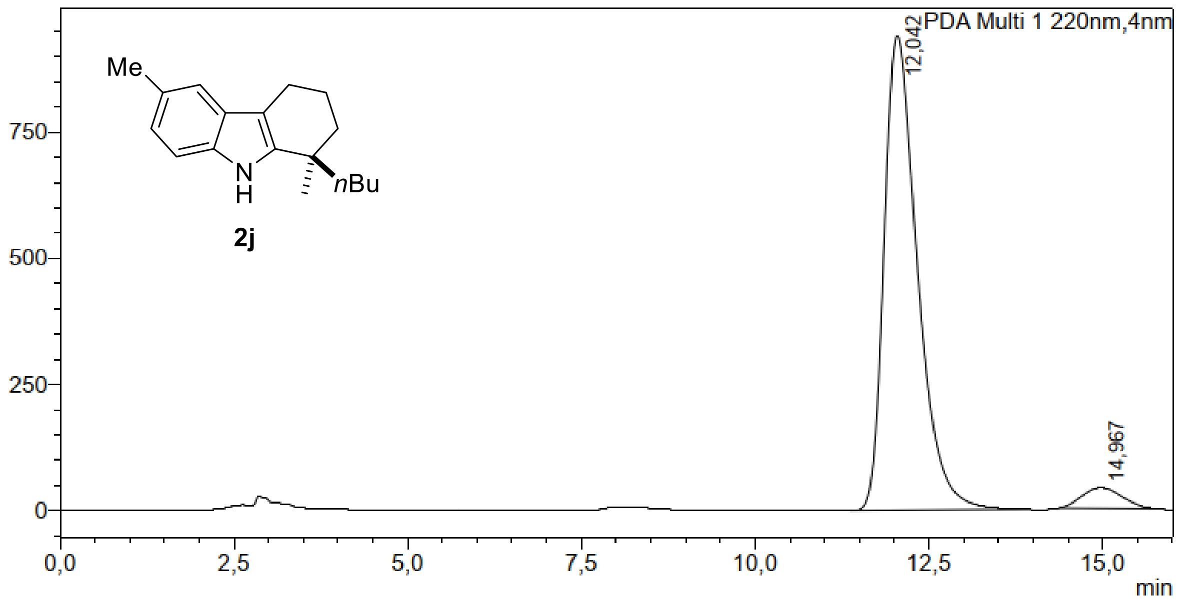
Peak#	Ret. Time	Area	Area%	Height	Name
1	8,798	375426	4,928	16631	
2	10,089	7242353	95,072	238074	
Total		7617779	100,000	254705	



<Peak Table>

PDA Ch1 220nm

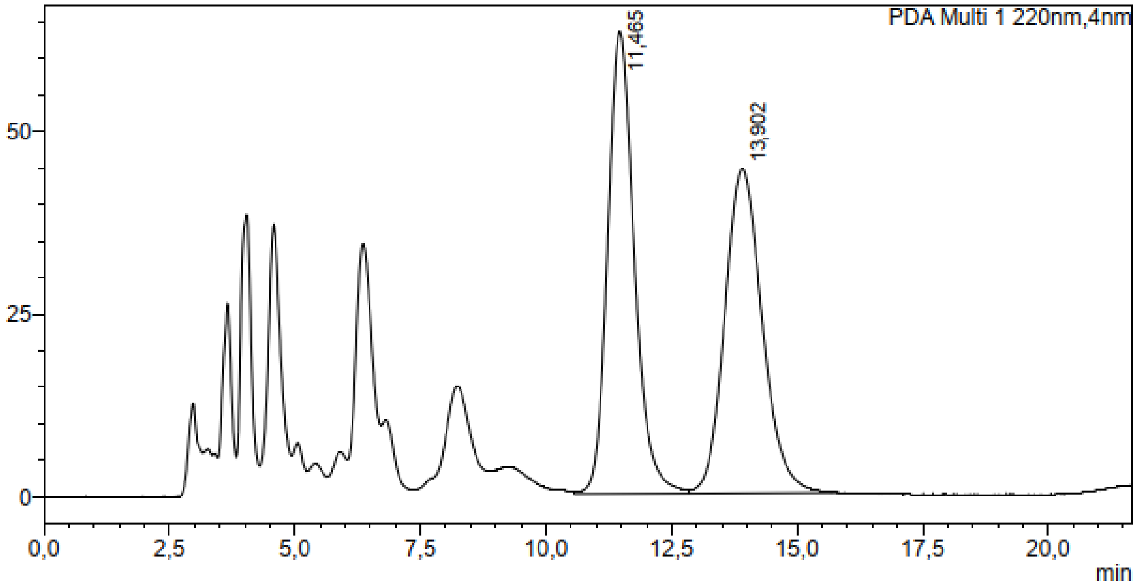
Peak#	Ret. Time	Area	Area%	Height	Name
1	12,041	14895339	50,883	430846	
2	14,821	14378121	49,117	324266	
Total		29273460	100,000	755111	



<Peak Table>

PDA Ch1 220nm

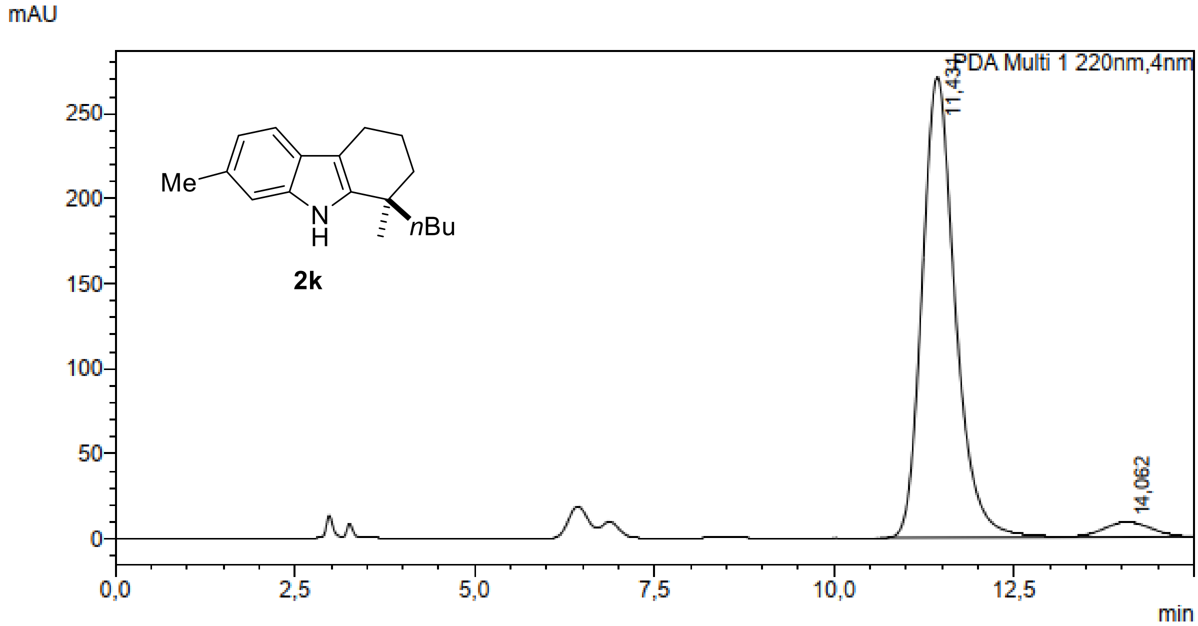
Peak#	Ret. Time	Area	Area%	Height	Name
1	12,042	31329201	95,014	941062	
2	14,967	1643938	4,986	41069	
Total		32973139	100,000	982131	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	11,465	2342081	50,406	63161	
2	13,902	2304356	49,594	44382	
Total		4646437	100,000	107543	



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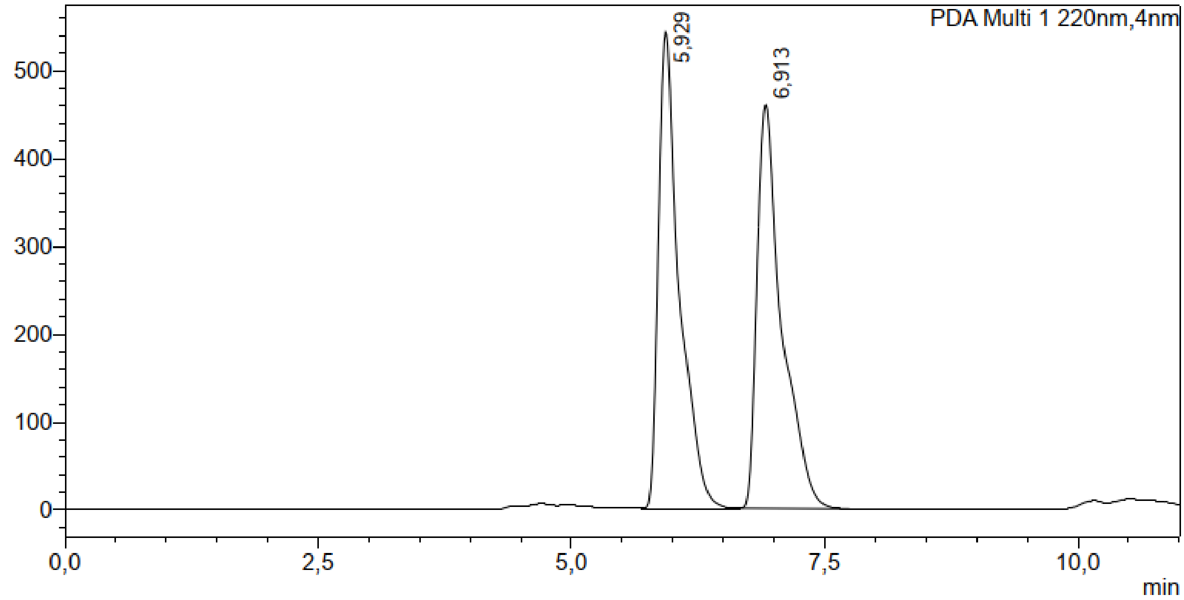
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	11,431	8687713	95,502	270802	
2	14,062	409186	4,498	8818	
Total		9096899	100,000	279621	



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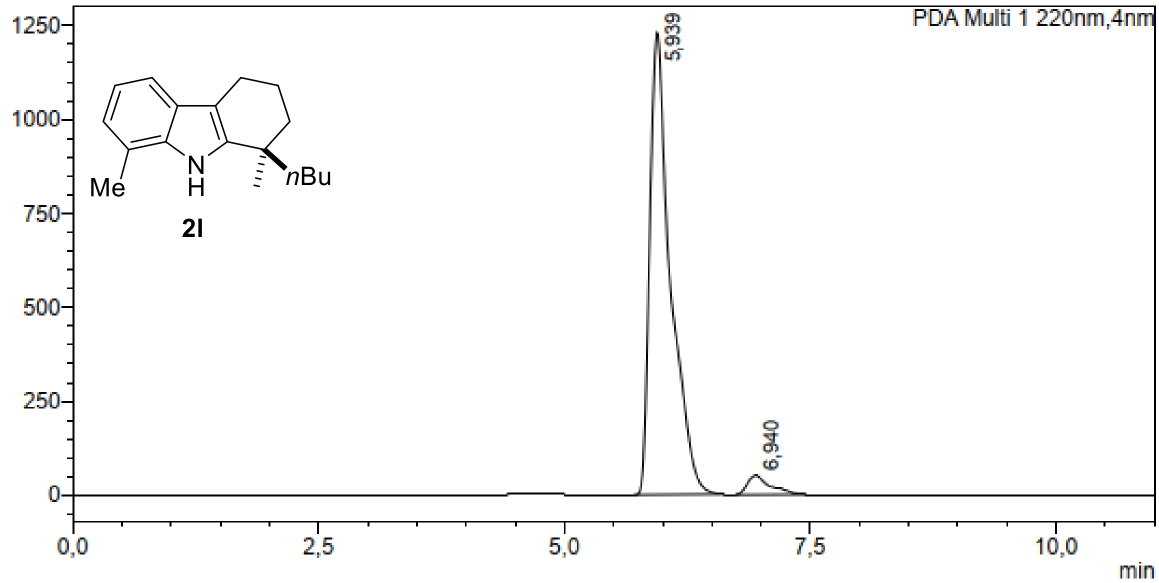
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	5,929	7878754	50,187	543785	
2	6,913	7820119	49,813	459484	
Total		15698873	100,000	1003269	



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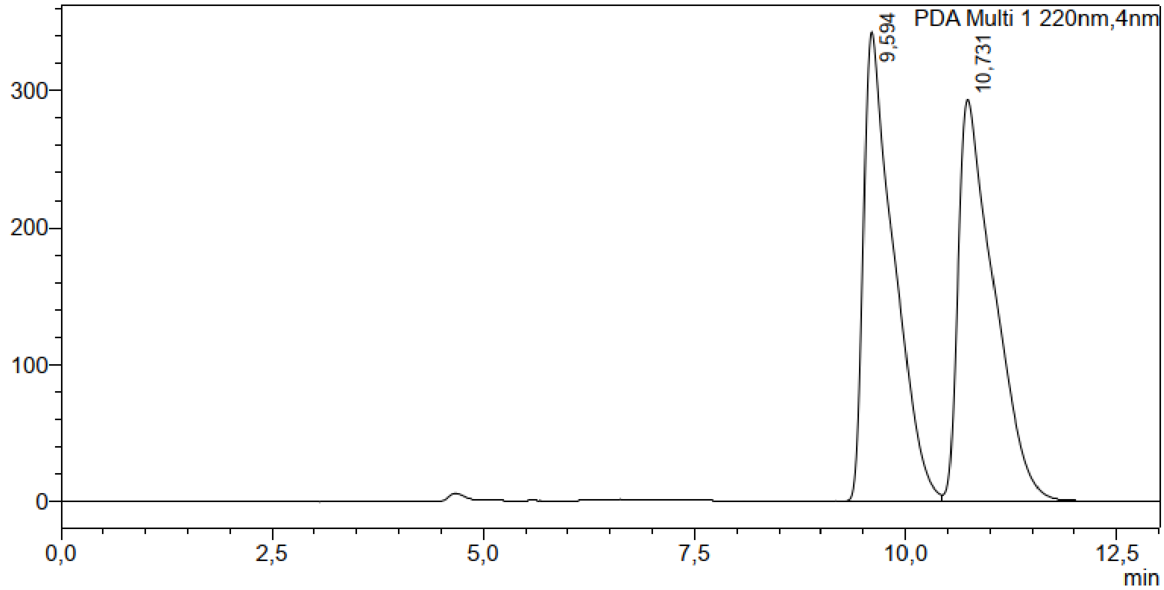
PDA Ch1 220nm

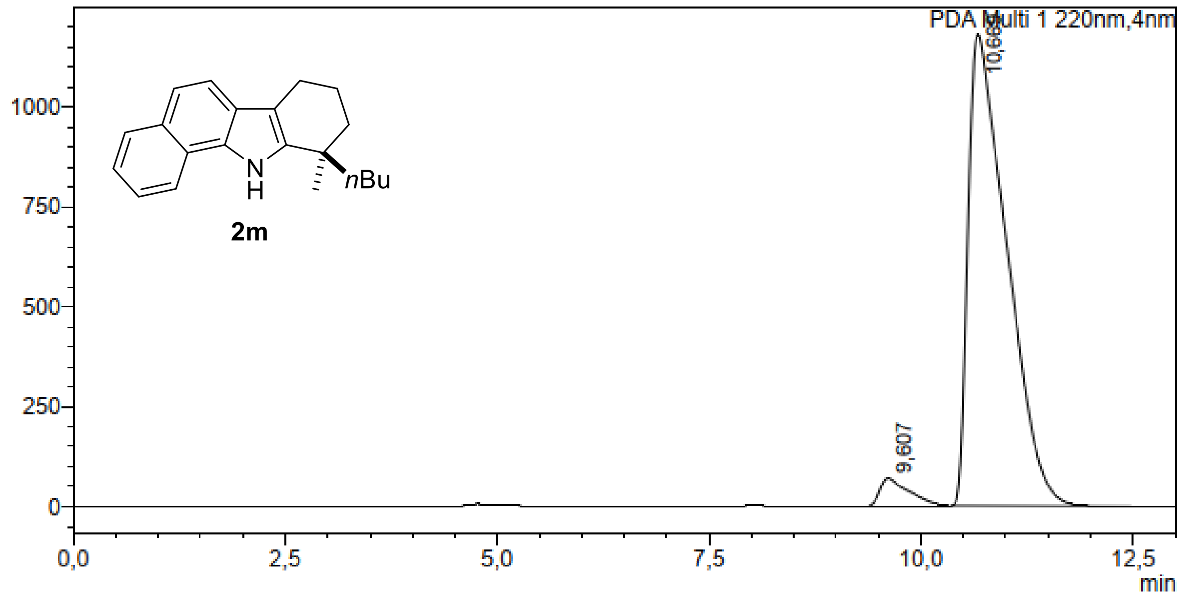
Peak#	Ret. Time	Area	Area%	Height	Name
1	5,939	18015707	95,574	1230517	
2	6,940	834319	4,426	51171	
Total		18850026	100,000	1281688	



<Peak Table>

PDA Ch1 220nm

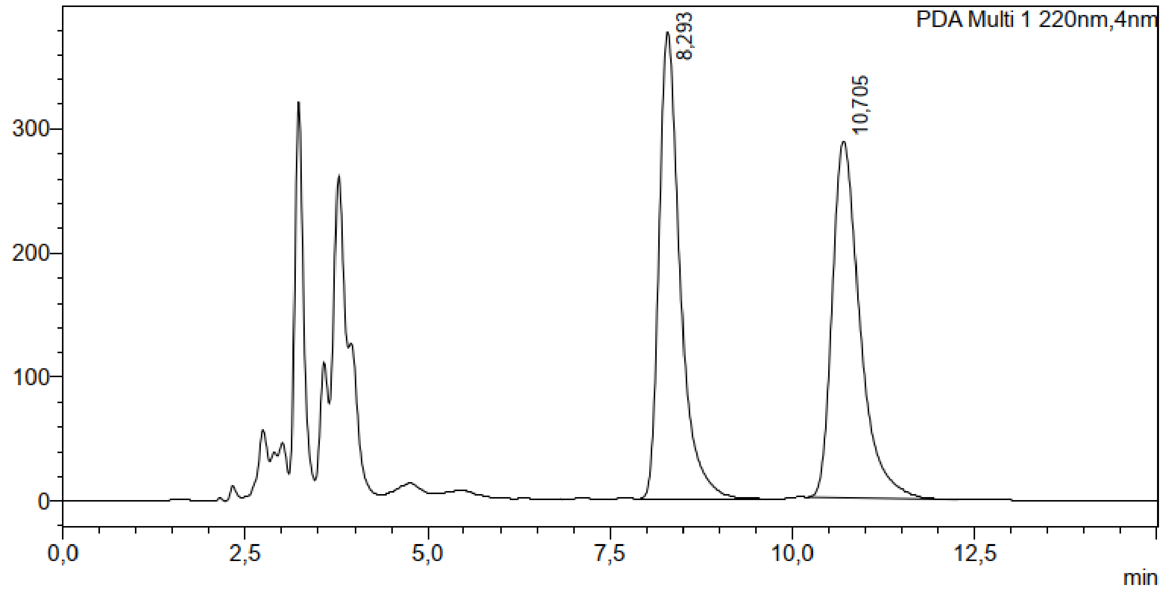
Peak#	Ret. Time	Area	Area%	Height	Name
1	9,594	8569120	49,782	342203	
2	10,731	8644182	50,218	292624	
Total		17213302	100,000	634827	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	9,607	1739927	4,435	70747	
2	10,669	37488515	95,565	1179652	
Total		39228442	100,000	1250399	



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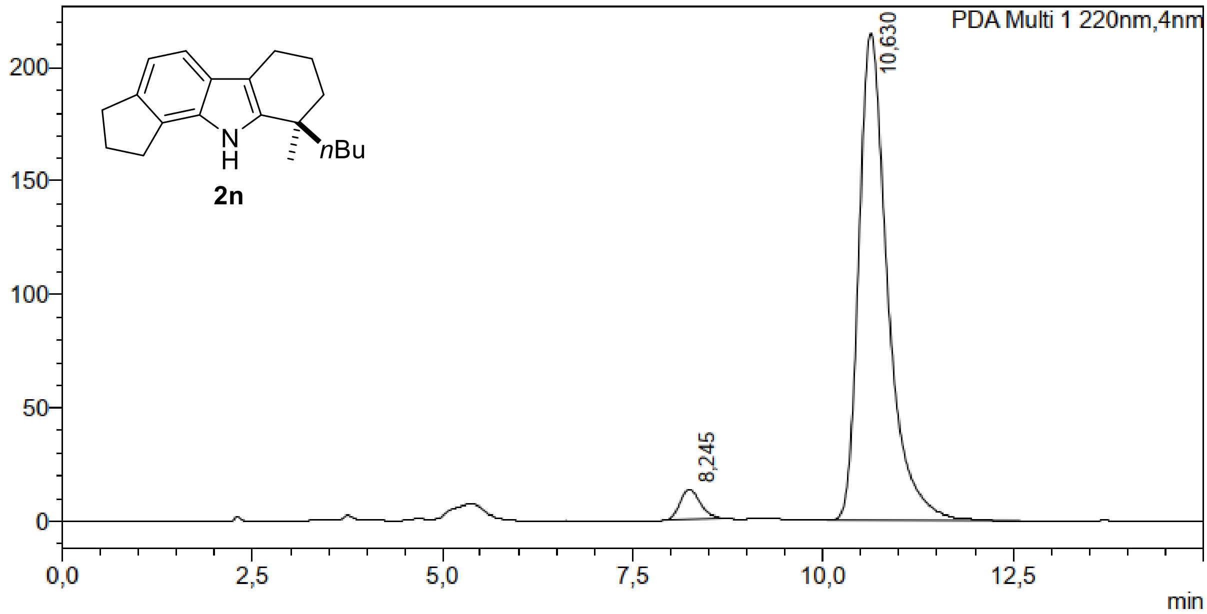
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	8,293	7606953	50,035	375958	
2	10,705	7596282	49,965	287486	
Total		15203234	100,000	663444	



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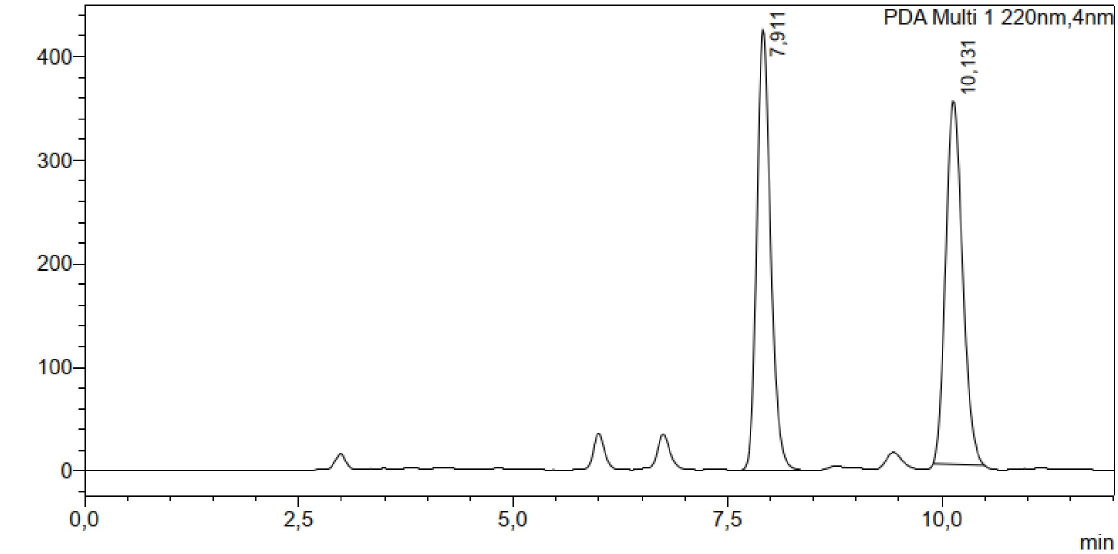
PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	8,245	246908	4,173	13367	
2	10,630	5669500	95,827	214534	
Total		5916409	100,000	227900	



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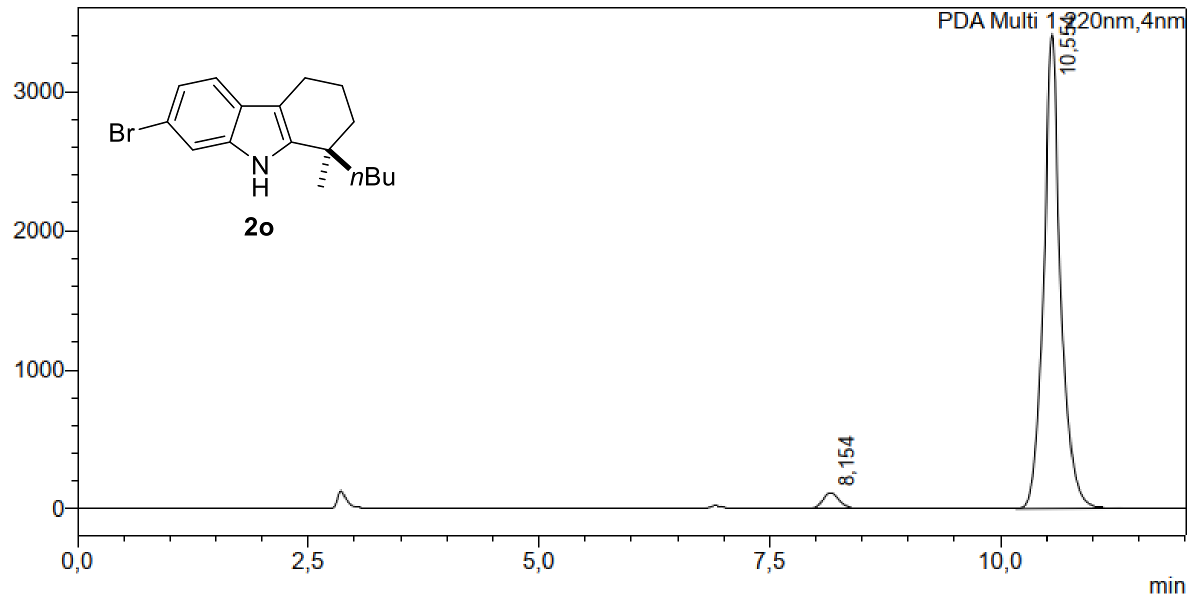
PDA Ch1 220nm

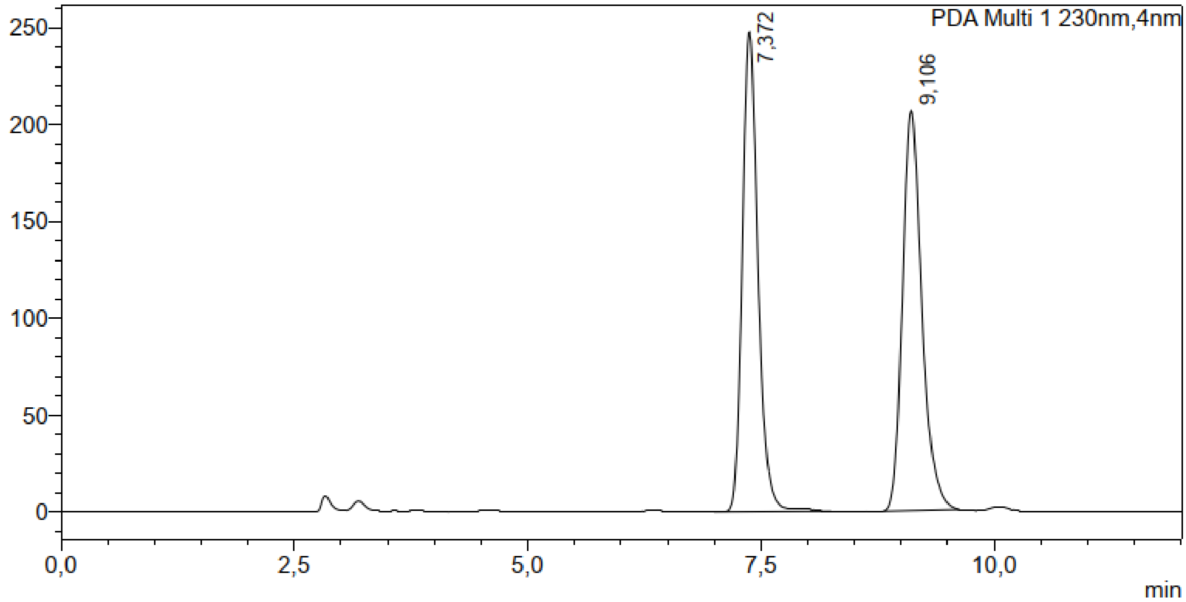
Peak#	Ret. Time	Area	Area%	Height	Name
1	7,911	4774281	49,770	424466	
2	10,131	4818341	50,230	350540	
Total		9592622	100,000	775007	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	8,154	1546750	3,427	120182	
2	10,554	43592129	96,573	3405550	
Total		45138879	100,000	3525733	



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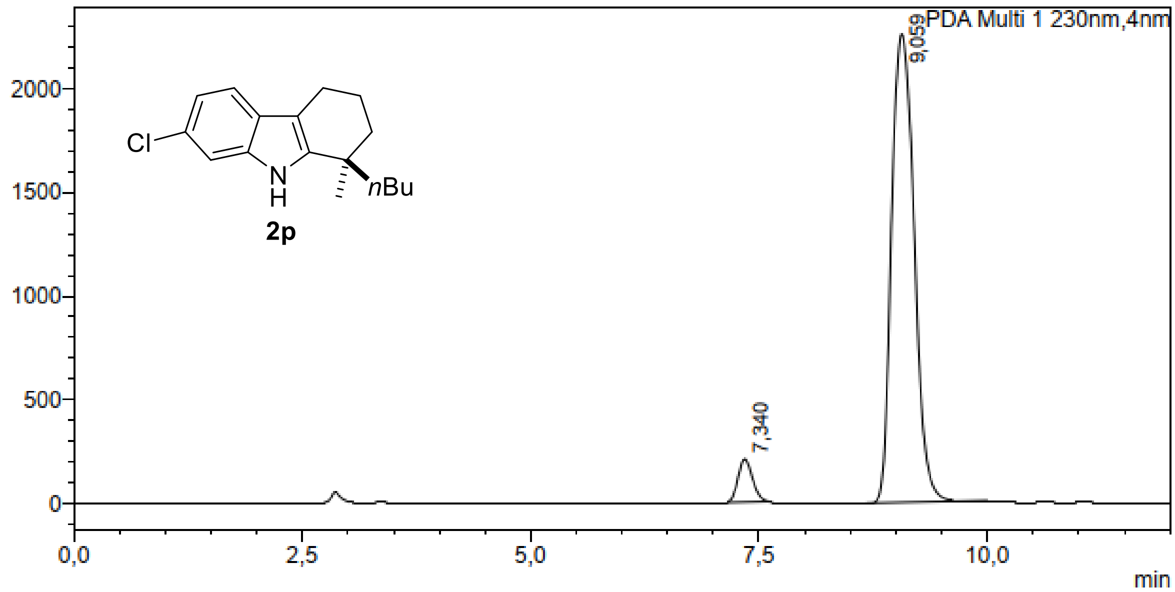
PDA Ch1 230nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7,372	2905287	49,339	247493	
2	9,106	2983156	50,661	206308	
Total		5888442	100,000	453801	



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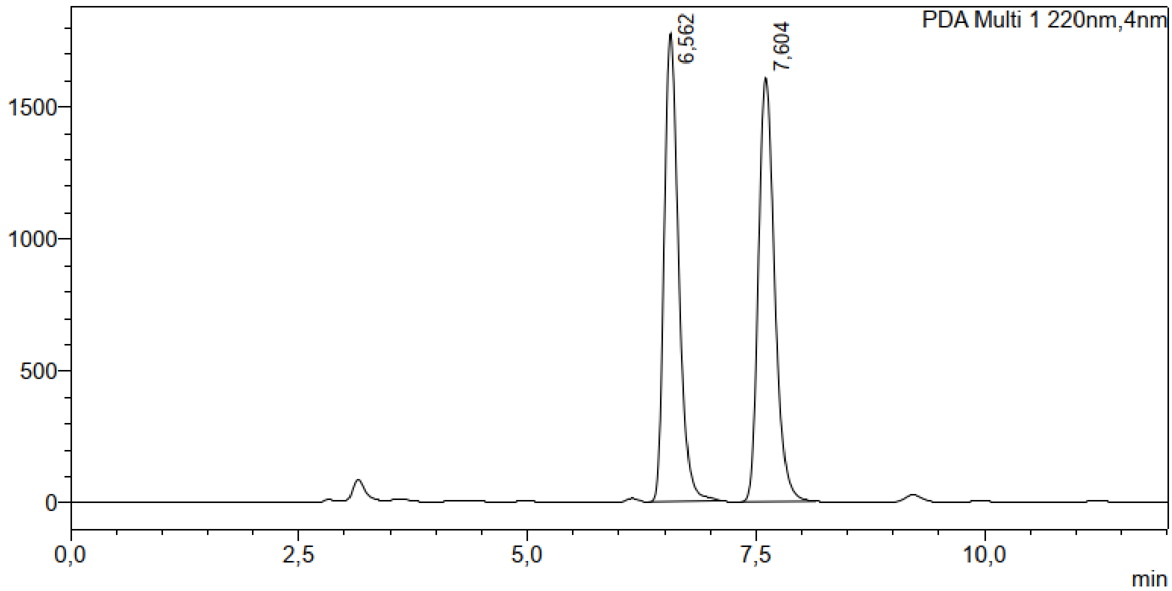
PDA Ch1 230nm

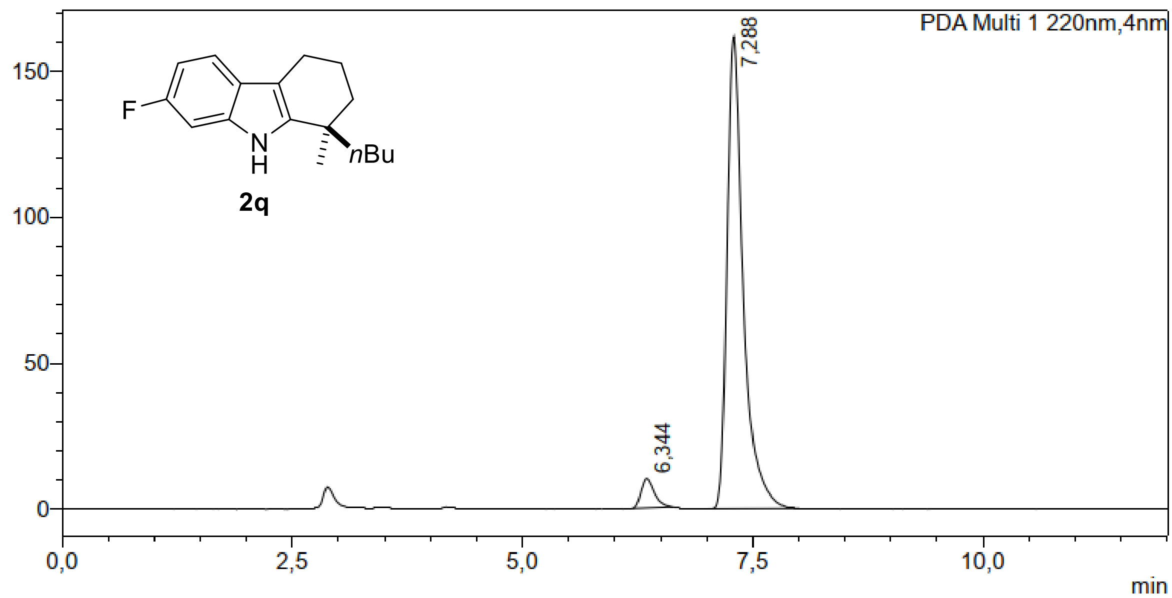
Peak#	Ret. Time	Area	Area%	Height	Name
1	7,340	2283562	5,553	207902	
2	9,059	38842440	94,447	2258741	
Total		41126003	100,000	2466643	



<Peak Table>

PDA Ch1 220nm

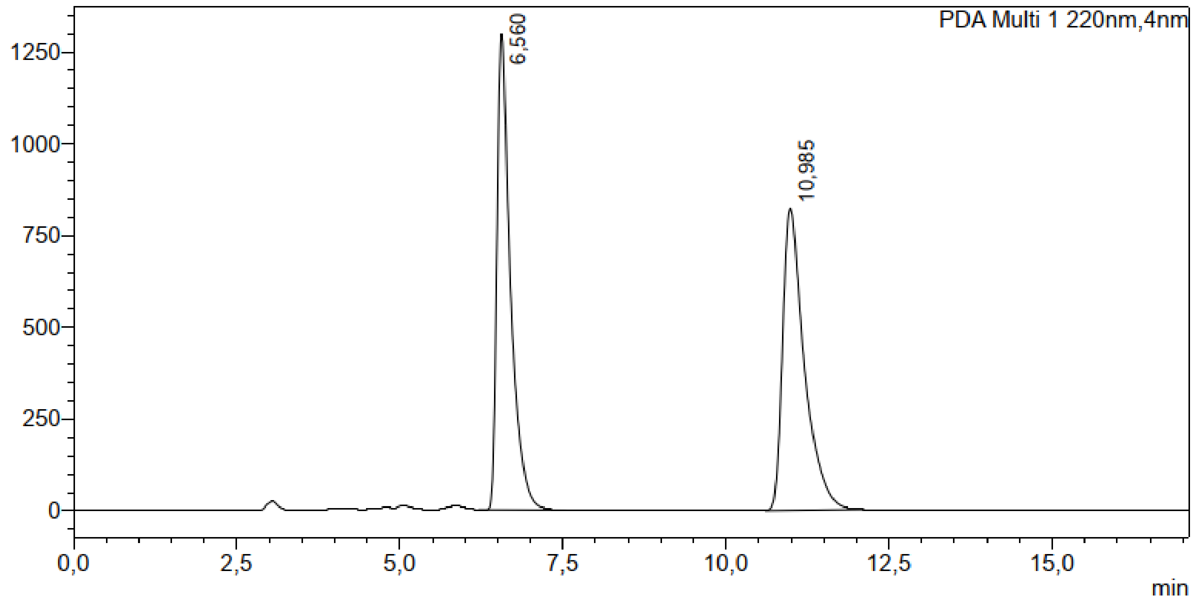
Peak#	Ret. Time	Area	Area%	Height	Name
1	6,562	19690920	49,607	1774505	
2	7,604	20003040	50,393	1607242	
Total		39693959	100,000	3381748	



<Peak Table>

PDA Ch1 220nm

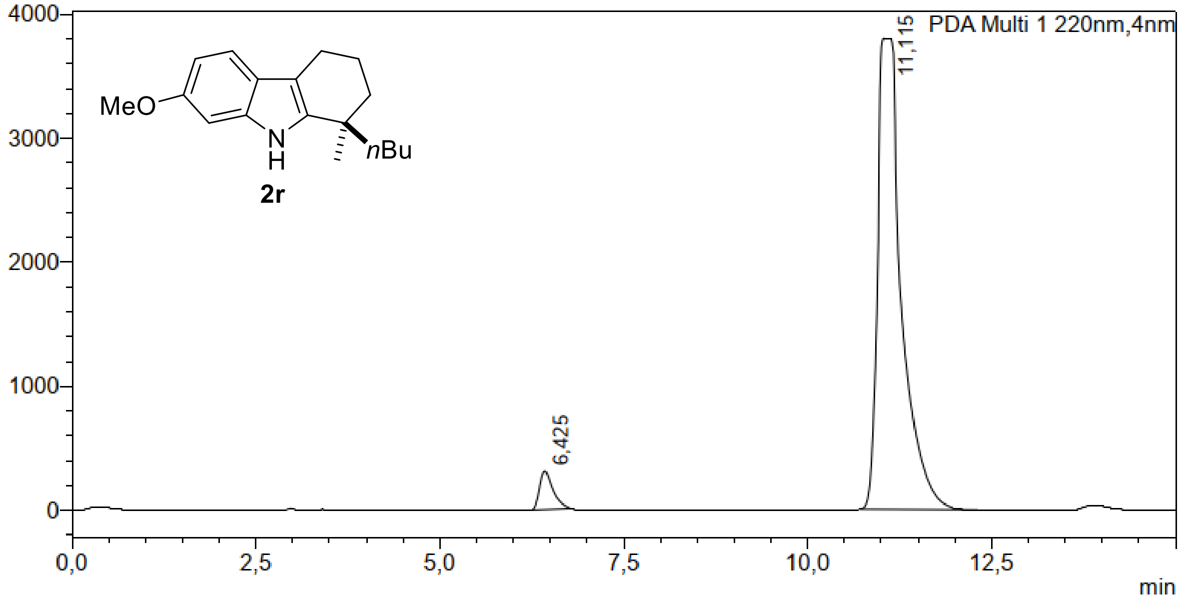
Peak#	Ret. Time	Area	Area%	Height	Name
1	6,344	101443	4,849	10051	
2	7,288	1990808	95,151	161546	
Total		2092251	100,000	171597	



<Peak Table>

PDA Ch1 220nm

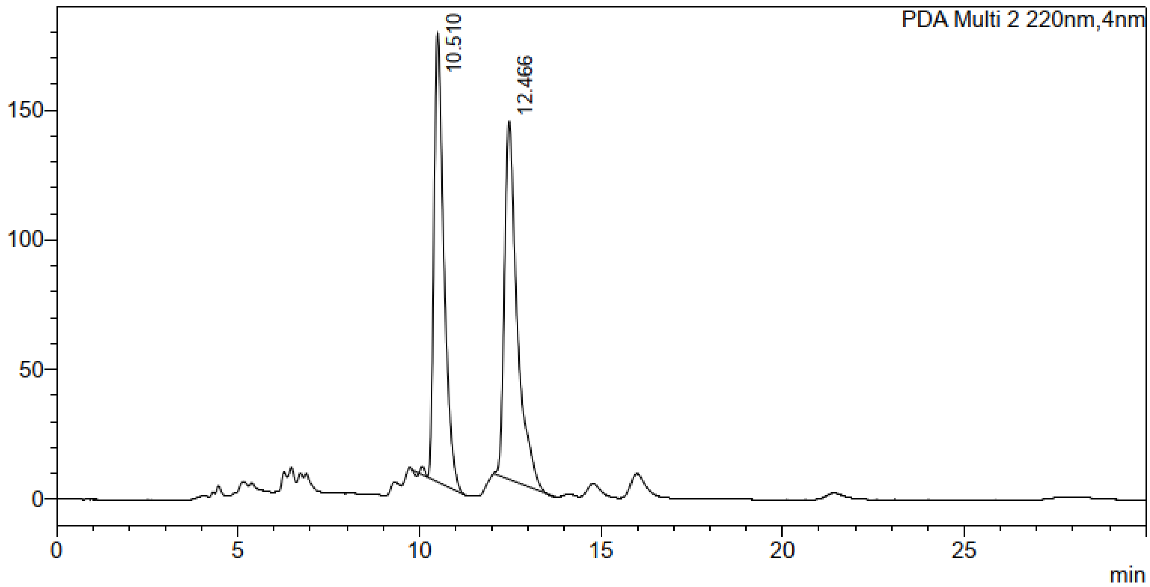
Peak#	Ret. Time	Area	Area%	Height	Name
1	6,560	18737260	49,510	1298200	
2	10,985	19108510	50,490	822725	
Total		37845770	100,000	2120925	



<Peak Table>

PDA Ch1 220nm

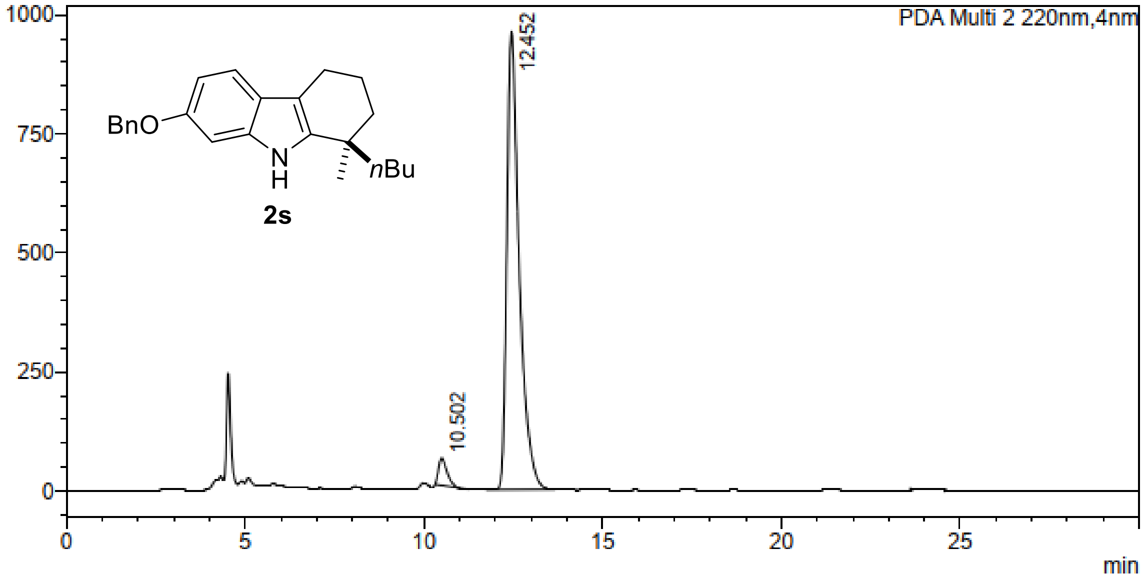
Peak#	Ret. Time	Area	Area%	Height	Name
1	6,425	3922393	4,389	309181	
2	11,115	85443278	95,611	3801258	
Total		89365671	100,000	4110439	



<Peak Table>

PDA Ch2 220nm

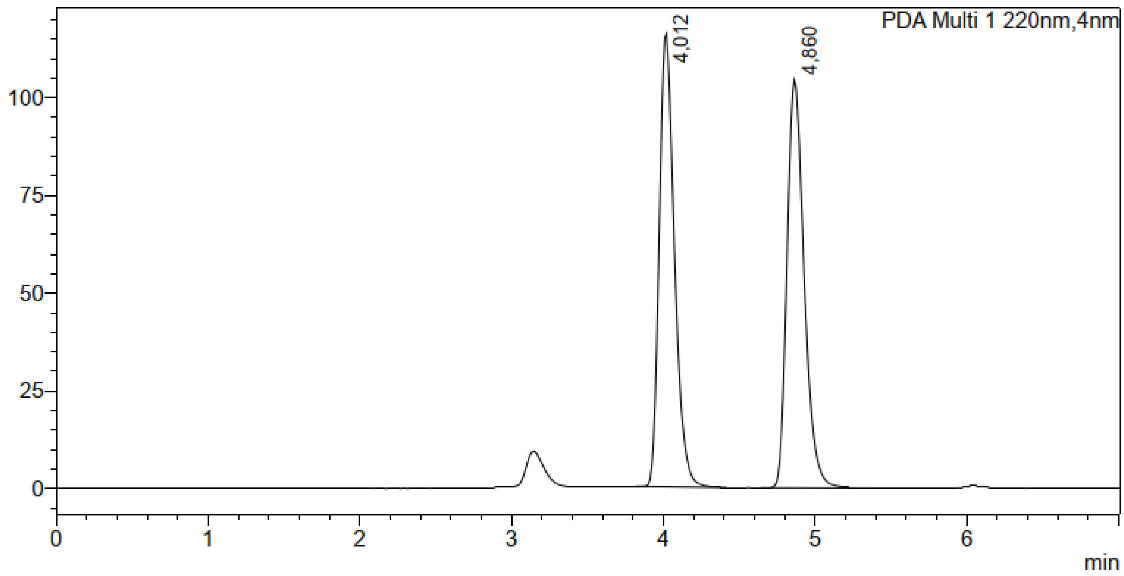
Peak#	Ret. Time	Area	Area%	Height	Name
1	10.510	3312486	49.515	172791	
2	12.466	3377320	50.485	137783	
Total		6689807	100.000	310574	



<Peak Table>

PDA Ch2 220nm

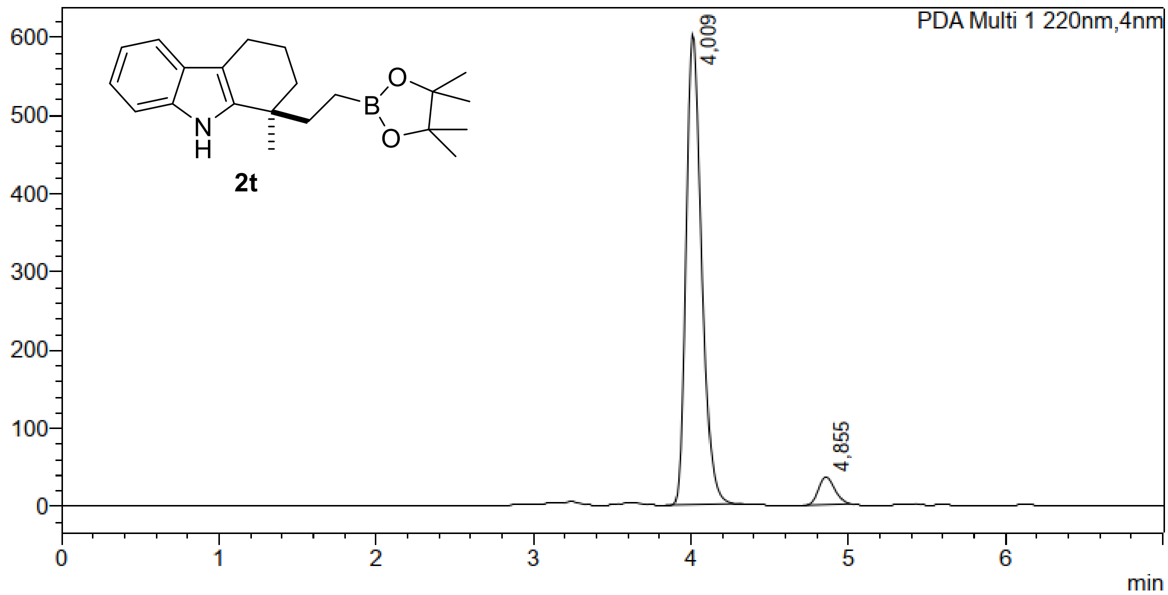
Peak#	Ret. Time	Area	Area%	Height	Name
1	10.502	928395	3.863	56355	
2	12.452	23105518	96.137	960388	
Total		24033913	100.000	1016743	



<Peak Table>

PDA Ch1 220nm

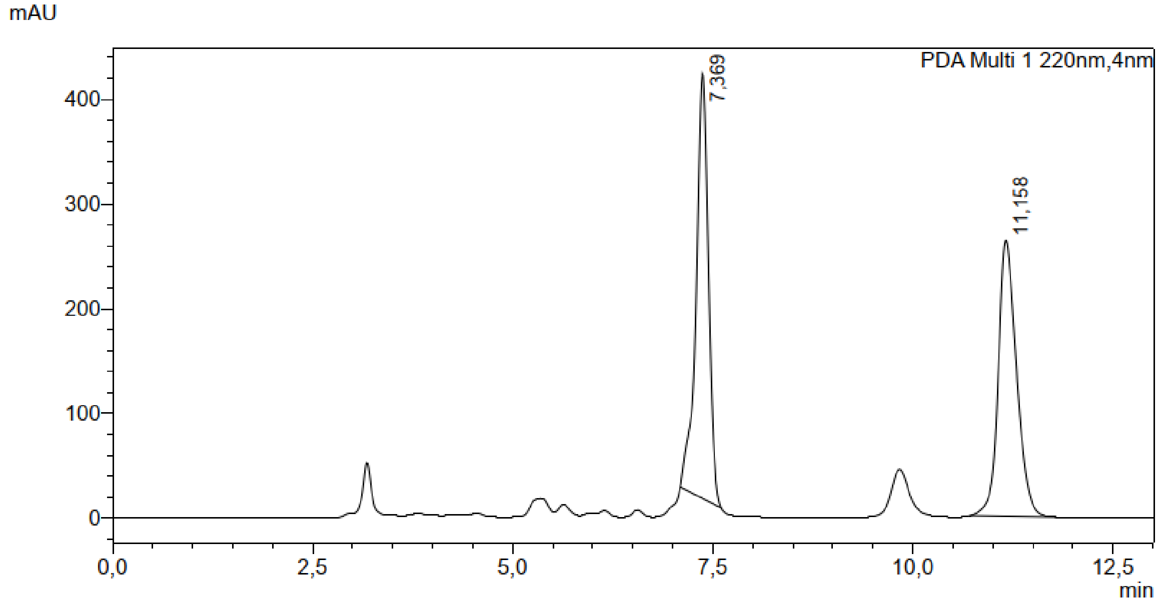
Peak#	Ret. Time	Area	Area%	Height	Name
1	4,012	813969	49,965	115962	
2	4,860	815110	50,035	104302	
Total		1629079	100,000	220264	



<Peak Table>

PDA Ch1 220nm

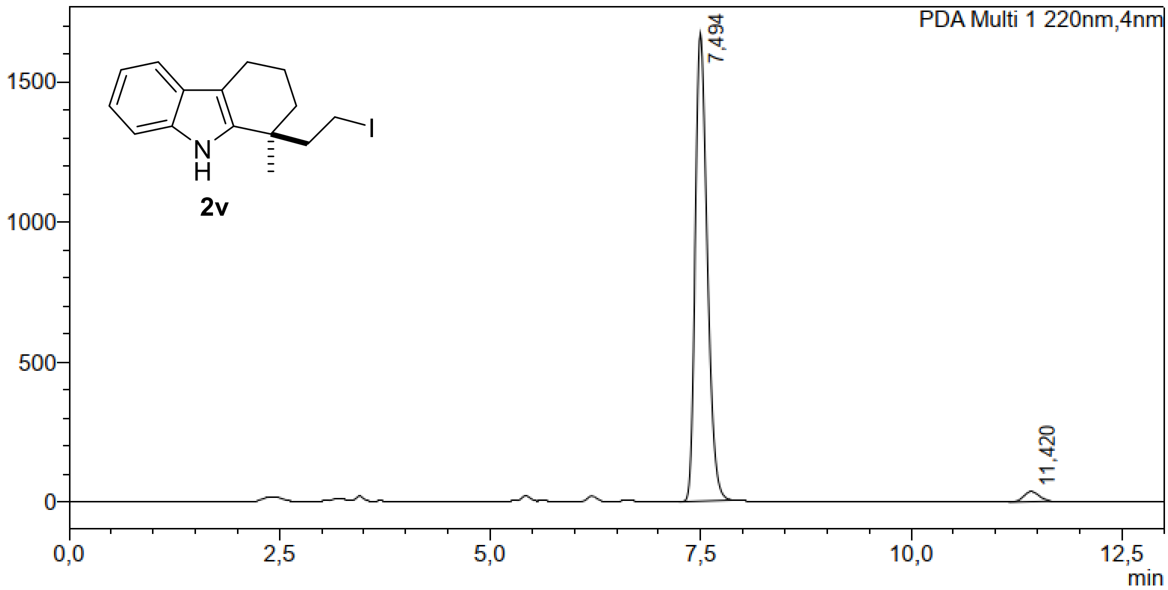
Peak#	Ret. Time	Area	Area%	Height	Name
1	4,009	4162256	94,125	601331	
2	4,855	259817	5,875	35785	
Total		4422073	100,000	637116	



<Peak Table>

PDA Ch1 220nm

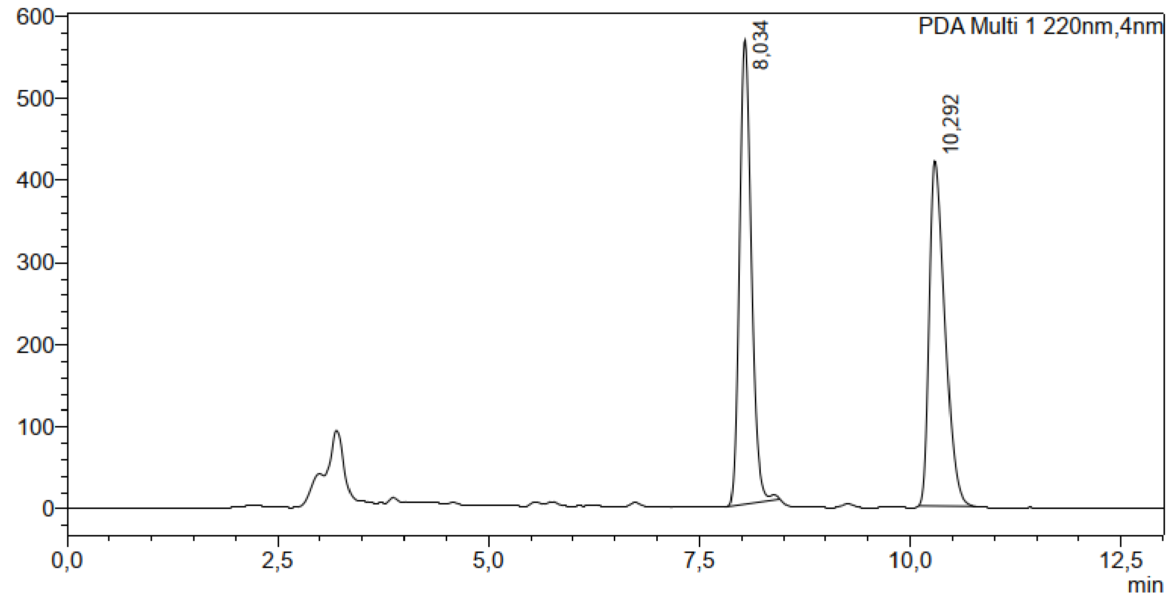
Peak#	Ret. Time	Area	Area%	Height	Name
1	7,369	4334297	50,822	405738	
2	11,158	4194088	49,178	263174	
Total		8528385	100,000	668912	



<Peak Table>

PDA Ch1 220nm

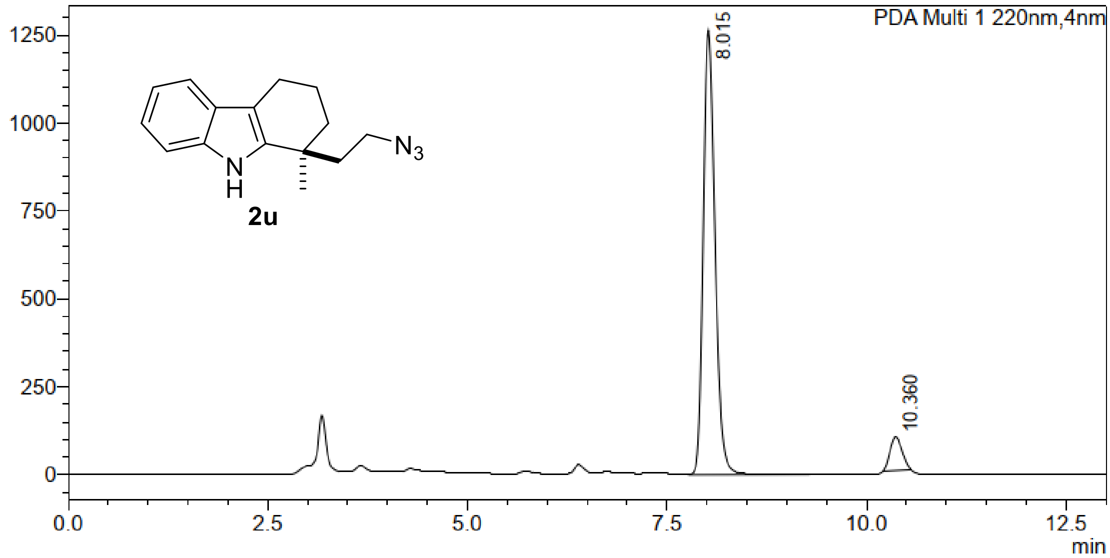
Peak#	Ret. Time	Area	Area%	Height	Name
1	7,494	16744702	97,319	1670506	
2	11,420	461232	2,681	35841	
Total		17205934	100,000	1706347	



<Peak Table>

PDA Ch1 220nm

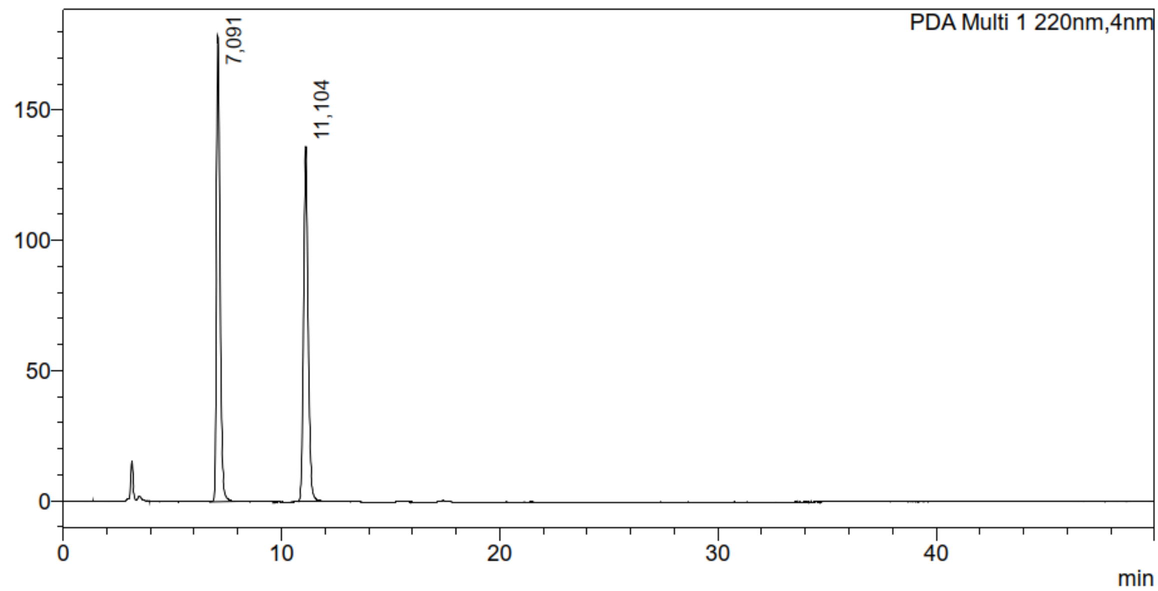
Peak#	Ret. Time	Area	Area%	Height	Name
1	8,034	5559367	50,314	565582	
2	10,292	5489953	49,686	420178	
Total		11049319	100,000	985761	



<Peak Table>

PDA Ch1 220nm

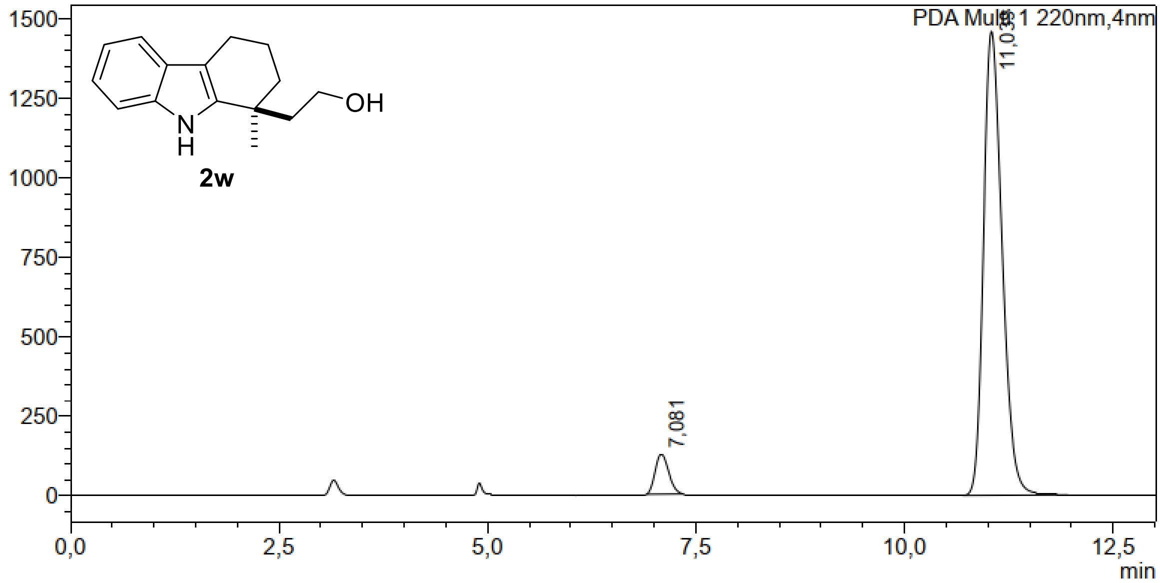
Peak#	Ret. Time	Area	Area%	Height	Name
1	8.015	12921517	92.725	1262075	
2	10.360	1013859	7.275	94736	
Total		13935376	100.000	1356810	



<Peak Table>

PDA Ch1 220nm

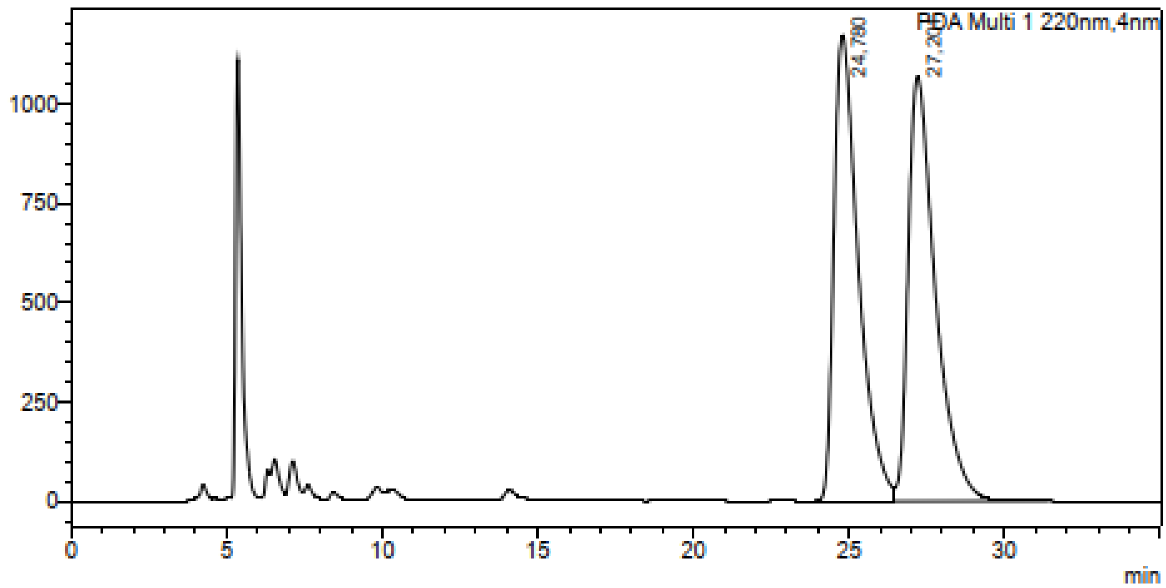
Peak#	Ret. Time	Area	Area%	Height	Name
1	7,091	1985369	49,882	178897	
2	11,104	1994798	50,118	136250	
Total		3980167	100,000	315147	



<Peak Table>

PDA Ch1 220nm

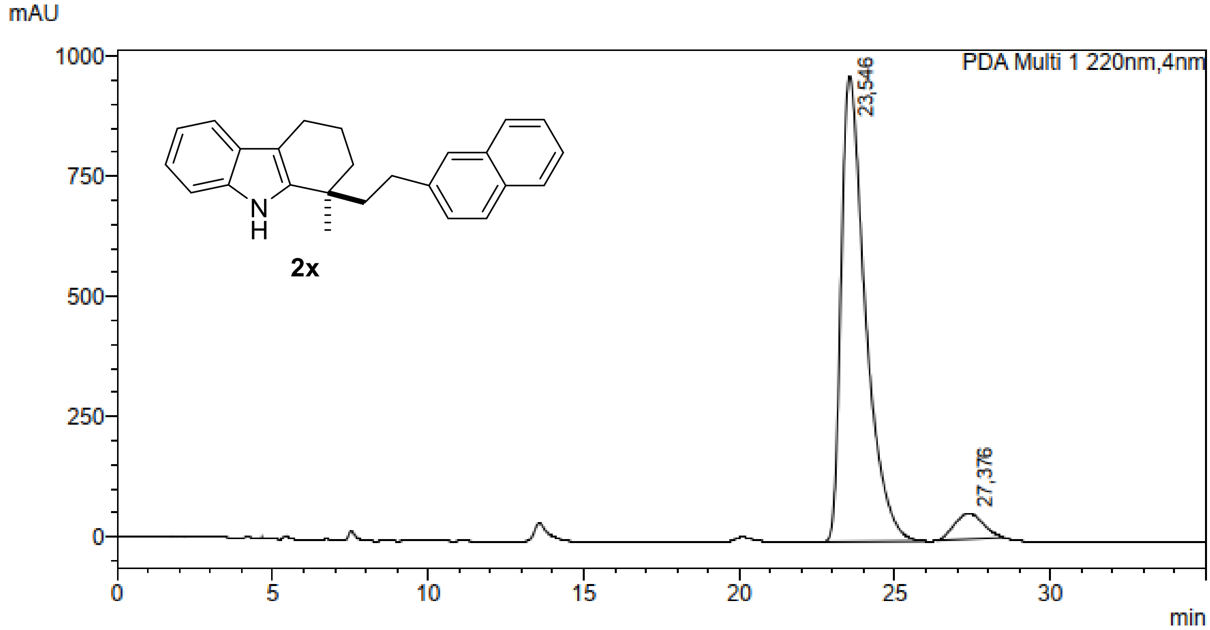
Peak#	Ret. Time	Area	Area%	Height	Name
1	7,081	1415777	5,888	126313	
2	11,039	22628864	94,112	1457819	
Total		24044642	100,000	1584132	



<Peak Table>

PDA Ch1 220nm

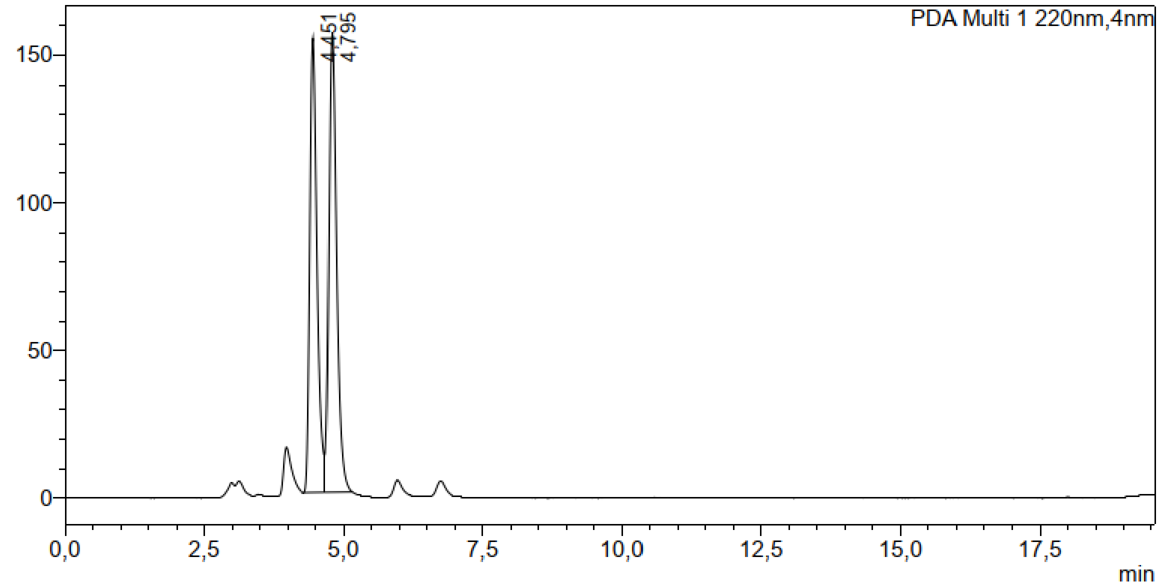
Peak#	Ret. Time	Area	Area%	Height	Name
1	24,780	64547963	49,661	1172403	
2	27,201	65428664	50,339	1067687	
Total		129976627	100,000	2240091	



<Peak Table>

PDA Ch1 220nm

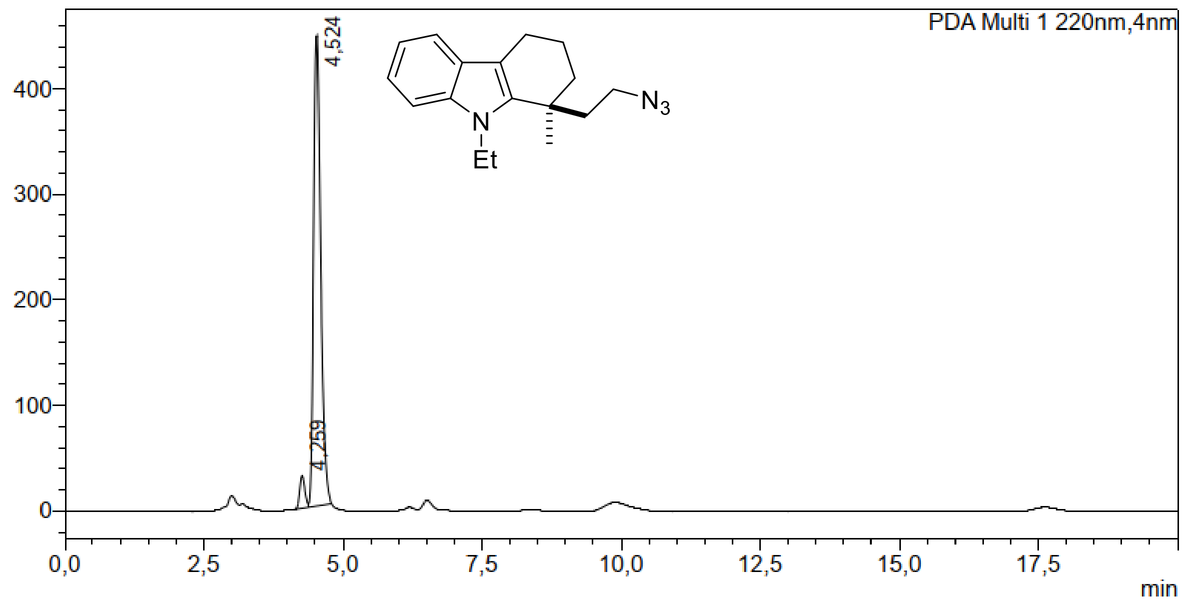
Peak#	Ret. Time	Area	Area%	Height	Name
1	23,546	52538878	93,838	968883	
2	27,376	3450098	6,162	53451	
Total		55988976	100,000	1022334	



<Peak Table>

PDA Ch1 220nm

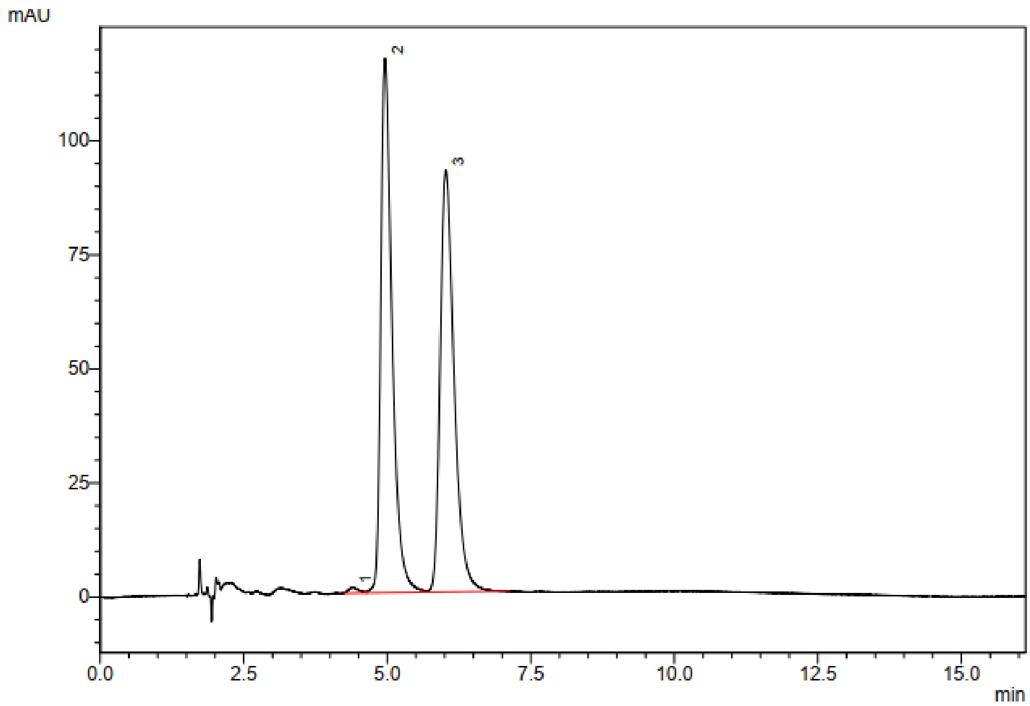
Peak#	Ret. Time	Area	Area%	Height	Name
1	4,451	1380860	48,452	153628	
2	4,795	1469089	51,548	155791	
Total		2849949	100,000	309418	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	4,259	201437	5,000	30640	
2	4,524	3826934	95,000	445381	
Total		4028371	100,000	476021	

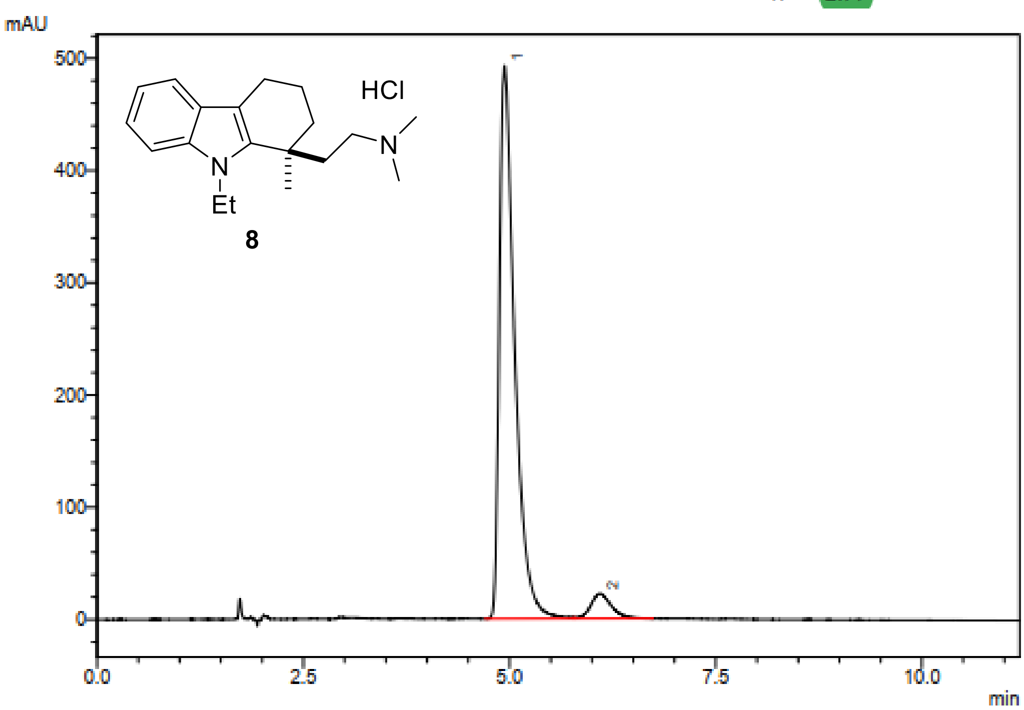


1 220nm,4nm

PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name	Width at 50% Height	Separation Factor
1	4.40	0.48		0.192	--
2	4.96	50.35	1. Enantiomer	0.200	1.21
3	6.02	49.17	2. Enantiomer	0.251	1.33
Total		100.00			

R = 2.77

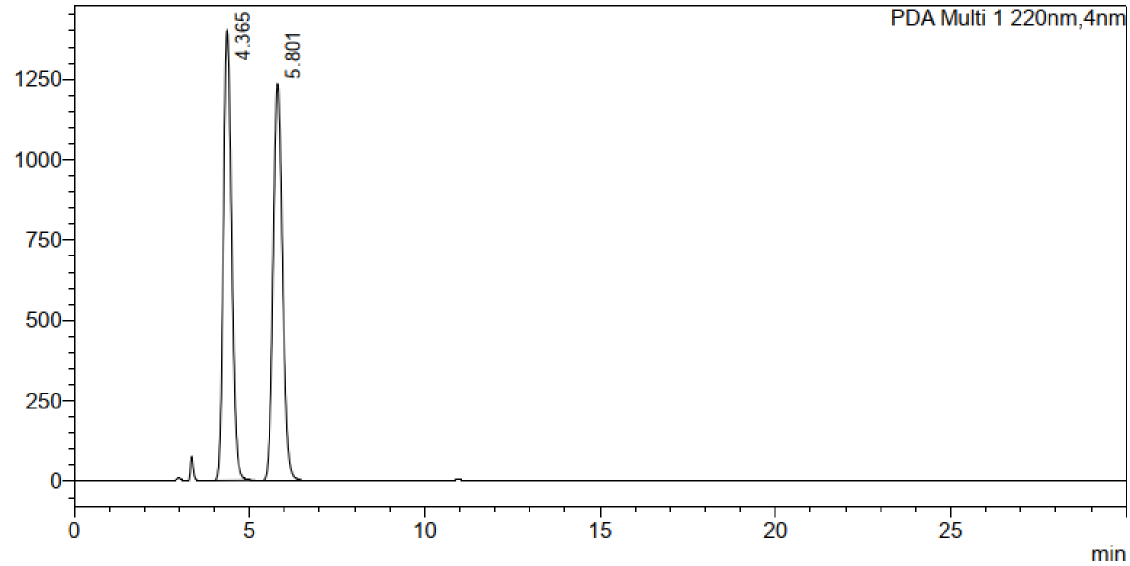


1 220nm,4nm

PDA Ch1 220nm

Peak #	Ret. Time	Area %	Name
1	4.94	94.26	1. Enantiomer
2	6.10	5.74	2. Enantiomer
Total		100.00	

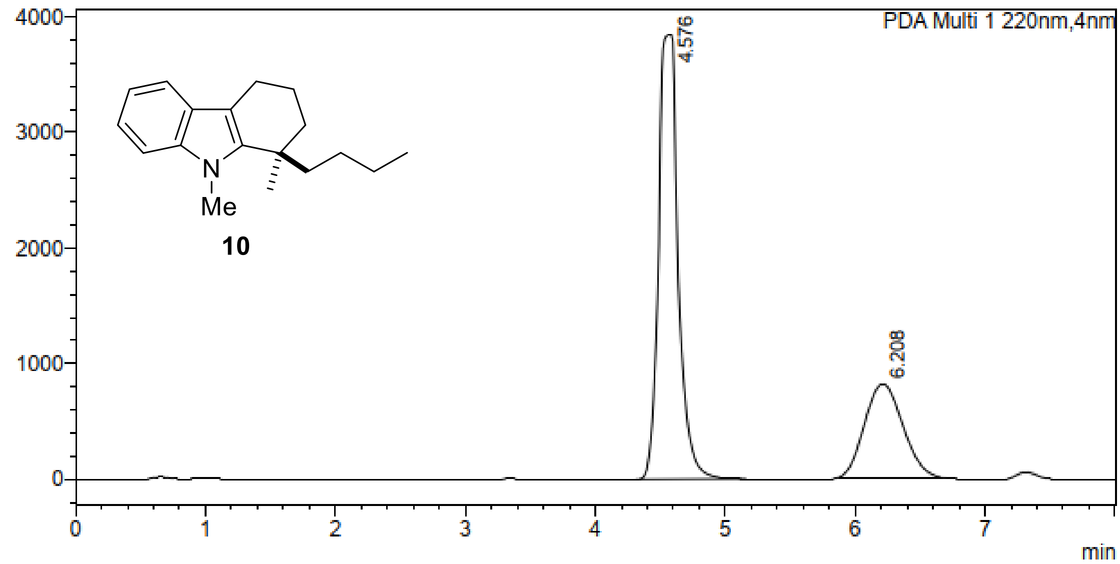
ee = 88.5%



<Peak Table>

PDA Ch1 220nm

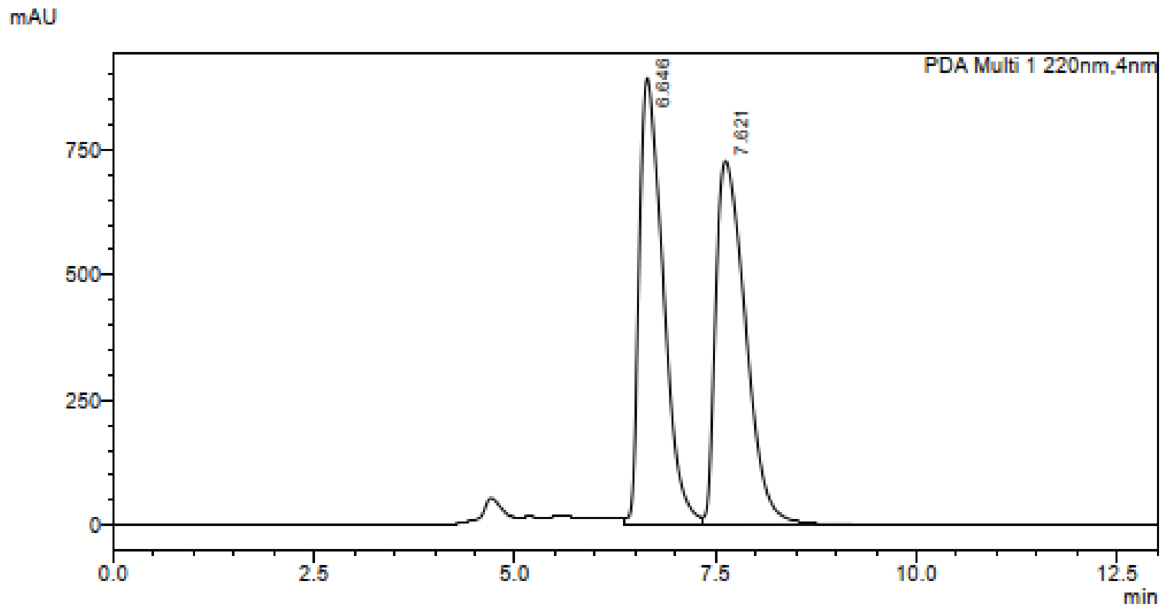
Peak#	Ret. Time	Area	Area%	Height	Name
1	4.365	22838271	50.058	1397256	
2	5.801	22785297	49.942	1232723	
Total		45623568	100.000	2629979	



<Peak Table>

PDA Ch1 220nm

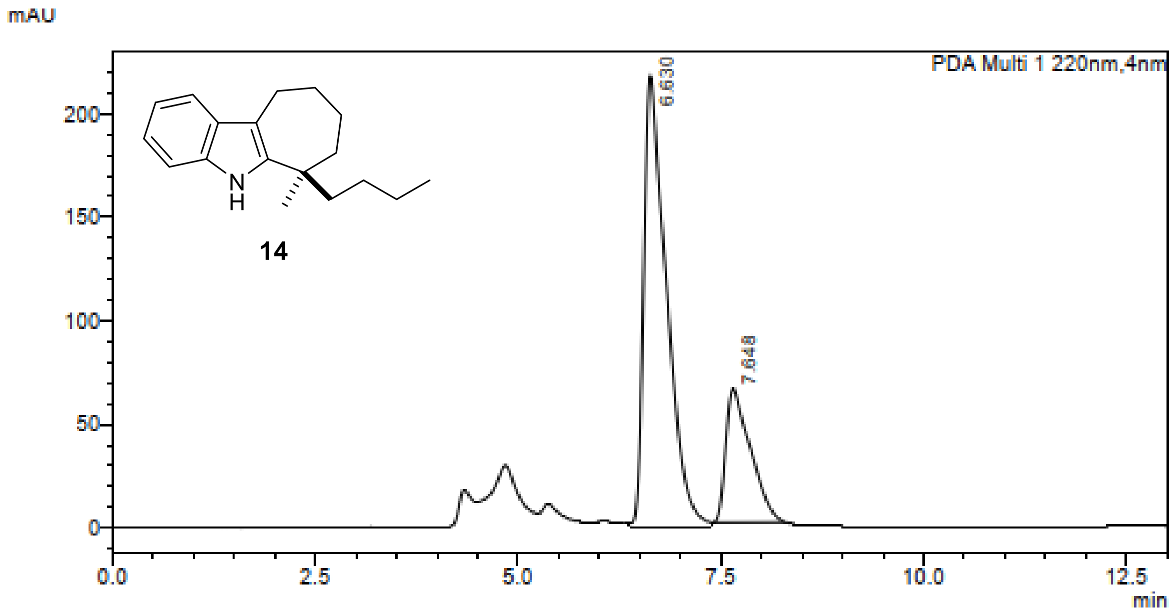
Peak#	Ret. Time	Area	Area%	Height	Name
1	4.576	40369654	71.225	3841556	
2	6.208	16309110	28.775	806288	
Total		56678764	100.000	4647844	



<Peak Table>

PDA Ch1 220nm

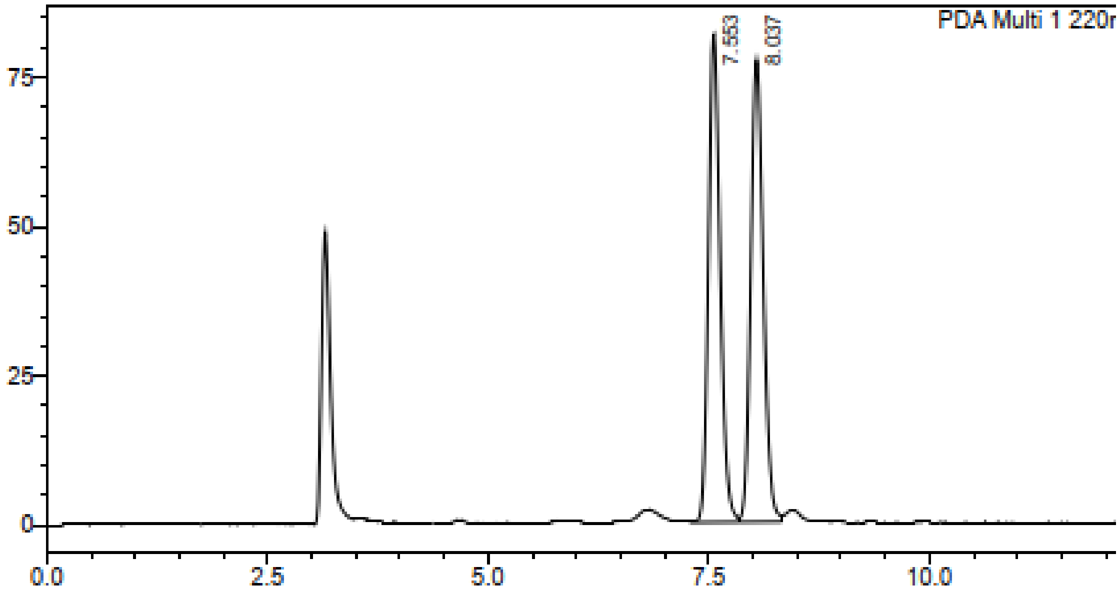
Peak#	Ret. Time	Area	Area%	Height	Name
1	6.646	18530780	49.566	892571	
2	7.621	18855284	50.434	727128	
Total		37386064	100.000	1619699	



<Peak Table>

PDA Ch1 220nm

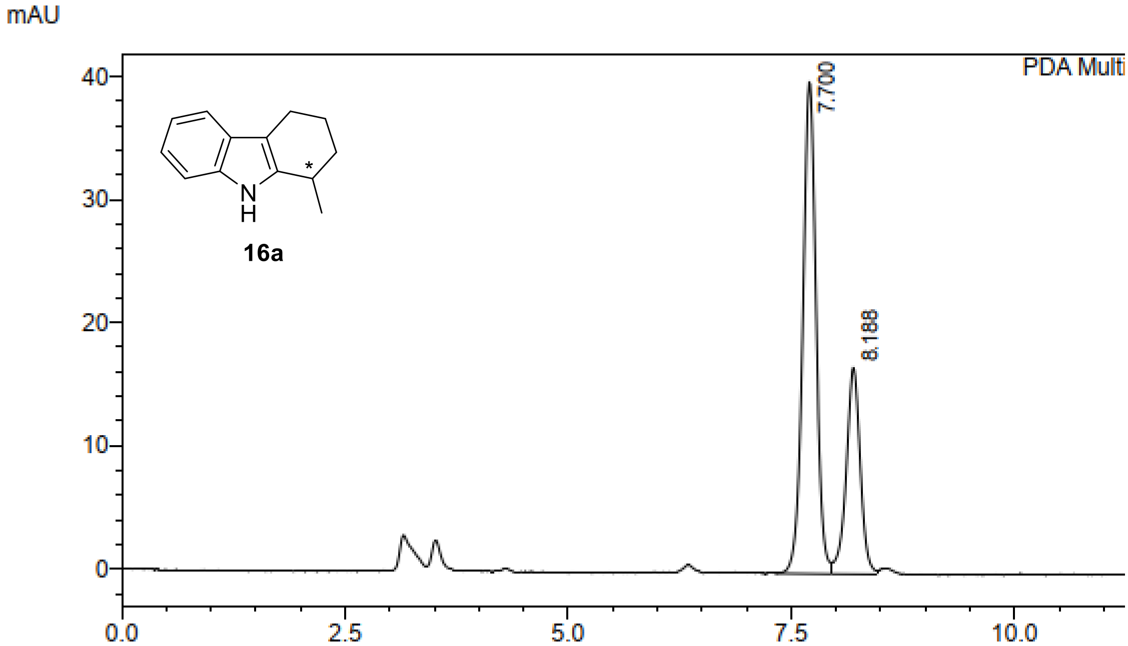
Peak#	Ret. Time	Area	Area%	Height	Name
1	6.630	4222569	75.539	217476	
2	7.648	1367346	24.461	64303	
Total		5589914	100.000	281779	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7.553	764757	50.163	81697	
2	8.037	759787	49.837	77175	
Total		1524543	100.000	158872	



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Area%	Height	Name
1	7.700	411384	68.966	39890	
2	8.188	185122	31.034	16704	
Total		596505	100.000	56594	

11. Reference and notes

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