Supporting Information

Homologative Electrochemical Installation of Unprotected Functionalities Across Alkenes

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1 General information

Starting materials and reagents were purchased from commercial suppliers (Sigma Aldrich, TCI, Alfa Aesar, Acros, BLD Pharma, Thermo Fischer Scientific, and Fluka) and were used without further purification. Solvents were used as p.a. grade whereas high purity water was obtained by circulating deionized water through a Milli-Q® water purification system. Reactions were monitored by GC-FID, GC-MS and UPLC-MS. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm and 356 nm) and/or were dipped into a solution of $KMnO_4$ stain. The $KMnO_4$ stain is particularly useful for primary alcohol and amines. The stain mentioned was prepared with $KMnO_4$ (1.5 g), K_2CO_3 (10.0 g) and KOH (1.5 mL of 10% solution) in H_2O (200 mL).

Power supply

Galvanostat Rohde & Schwarz - HMP4040 was used as a DC power supply in all the electrochemical reactions. The experiments were performed under galvanostatic conditions using a simple two-electrode reaction setup.

Electrodes

- Leaded Bronze (all types) was purchased from the company Metallwerk Langenau GmbH, Germany.* In batch-type screening cells, 3.0 mm thick electrodes were used.
- Nickel foam was purchased from the company Recemat BV, Netherlands. The foam was cut to the desired dimensions with a regular disc-shaped rotating blade saw.
- Nickel plate electrode was obtained from IKA Werke GmbH & Co. KG, Germany.
- Stainless-steel electrode was obtained from Montanstahl GmbH, Oelde, Germany.
- Iridium oxide coated titanium dimensionally stable anodes (DSA) were obtained from DeNora, Italy with 12 g Ir/m^2 on titanium as support.
- Zinc electrodes were obtained from Grillo-Werke AG, Duisburg, Germany*
- Glassy carbons were obtained from HTW, Thierhaupten, Germany
- Carbon graphite electrode (Highly isostatic, V2100) was obtained from SGL Carbon, Bonn, Germany.*

*The larger pieces were obtained and machined to the necessary dimension with the help of in-house mechanical workshop

Cation exchange membrane

Sulfonic acid-based cation exchange membrane Nafion™ N324 membrane was obtained from Ion Power GmbH, Munich, Germany. Prior to use it was conditioned in ca. 5% aq. H_2SO_4.

NMR spectroscopy

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded at 25 °C on a Bruker AVANCE III HD 400 MHz NMR spectrometer with a Bruker Prodigy probe (Bruker BioSpin GmbH, Rheinstetten, Germany). Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals purchased form Deutero GmbH (Kastellaun, Germany) were used as references for ^{1}H and ^{13}C NMR spectra (relative to Tetramethylsilane at 0.0 ppm, $CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm, CD_2Cl_2: δH = 5.32 ppm, δC = 54.00 ppm). Chemical shifts (*δ*) are reported in parts per million (ppm). ^{19}F NMR chemical shifts are reported in ppm relative to $CFCl_3$ (δ = 0.0 ppm) using the IUPAC-recommended Ξ value for indirect referencing. All chemical shifts are reported in *δ*-scale as parts per million [ppm] (multiplicity, coupling constant *J*, number of protons), relative to the solvent residual peaks as the internal standard. Coupling constants *J* are given in Hertz [Hz]. Abbreviations used for signal multiplicity: ^{1}H NMR: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. All the NMRs were processed using Mestrenova 14 applying standard phase and baseline corrections. Coupling constants (*J*) are quoted in Hz.

Ultra-performance liquid chromatography – mass spectrometry (UPLC-MS)

Ultra-performance liquid chromatography – mass spectrometry (UPLC-MS) was performed on a Waters™ ACQUITY™ UPLC™ H-Class PLUS System (Waters Corporation, Milford, USA) using a quaternary solvent manager (ACQ H-CLASS QSM PLUS), a sample manager with flow-through needle (ACQ H-Class FTN-H PLUS) design, a column heater (ACQUITY UPLC CM-A) and an ACQUITY UPLC® BEH C18 1.7 µm 2.1 x 50 mm column. Mass spectra were measured using a single quadrupole mass detection (ACQUITY QDa Detector) employing ESI+. Acetonitrile (HPLC-MS grade) and water (Milli-Q®) were used as eluents, eluent with 0.1% (v/v) formic acid was added directly before mass detection using a second isocratic solvent manager (Waters™ ACQ Isoc Solvent Mgr).

Gas chromatography (GC-FID and GC-MS)

GC measurements were performed on a GCMS QP2010SE (Shimadzu, Kyoto, Japan) equipped with either flame ionization detector (FID) or an electron ionization (EI) source and a quadrupole mass analyzer. A quartz capillary column Zebron ZB-5PLUS (Avantor VWR, Radnor, USA) with the following specification was used: length 30 m, int. diam 0.25 mm, film 0.25 µm as dimensions. Helium was used as carrier gas (1.2 mL/ min, constant flow). The GC temperature ramp started at 50 °C (holding for 1 min) and heated to

300 °C (holding for 4.71 min) with a temperature ramp of 17.5 °C/min (total program time: 20.0 min). Measurements were performed at an injector temperature of 270 °C and a temperature of the EI source of 250 °C.

Cyclic voltammetry (CV)

Cyclic voltammetry was conducted using a three-electrode setup consisting of a nickel disc working electrode 'WE' (r = 2 mm, Parafilm® wrapped Ni rod with exposed tip), Ag/AgCl reference electrode 'RE' (eDAQ) and a glassy carbon rod counter-electrode 'CE'. Before use and between measurements, the working electrode was mechanically cleaned by polishing with diamond polishing suspension (Buehler Metadi, 1 Micron particle size) followed by rinsing with MeOH and distilled water. Supporting electrolyte NBu_4BF_4 was used as obtained commercially from TCI (98%+). Unless otherwise stated, all analytes were prepared as 10 mM solution in 0.1 M NEt_4BF_4 in 10 mL MeOH. The solutions were purged with Ar for 15 min prior to measurement. Electrochemical measurements were carried out using an Autolab PGSTAT204 potentiostat at room temperature (ca. 298 K). The scanning rate was 100 mV/sec and each measurement was performed in 2 scans starting in a reductive direction, unless otherwise stated. Data acquisition and processing were performed with Metrohm Autolab Nova 42.1.10.4.1.11.

Mass spectrometry

High resolution Mass Spectrometry (HRMS) experiments were performed on a Thermo Scientific™ Q Exactive Plus or a Thermo Scientific™ Q Exactive GC Orbitrap device.

Electrolysers

Batch-type screening experiments were conducted in divided Teflon™ electrolysis cells, which are commercially available as IKA Screening S8 system package (IKA®-Werke GmbH & Co. KG, Germany). Further information is provided in the previous report.[1] Nafion™ N324 membrane (Ion Power GmbH, Munich, Germany) was used as a separator material between the two compartments. The membrane was conditioned in 5% aq. H_2SO_4 for at least 4 hours, washed with fresh H_2O and wiped before being installed in the electrochemical cell. Each cell compartment was equipped with a magnetic stirring bar. Both electrodes, each with exposed geometric surface of 3 cm^2 (submerged part of the electrode in a typical experiment) were arranged at 20 mm distance relative to each other. The reactions were typically performed at room temperature and constant stirring rate of 500 rpm.

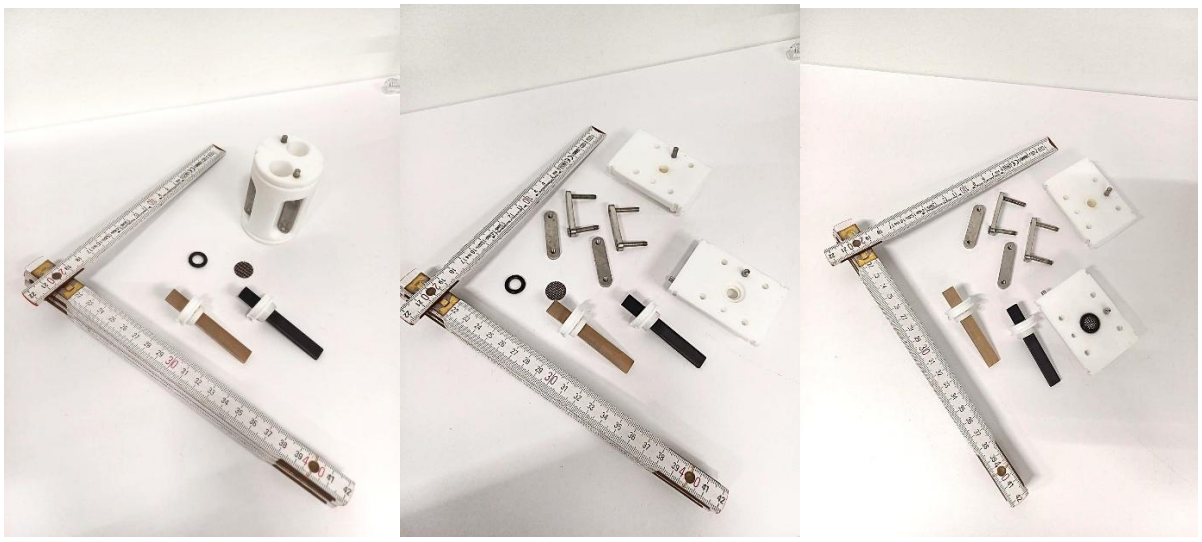


Figure S1: Batch-type cells-divided. Ruler scale in centimeters.

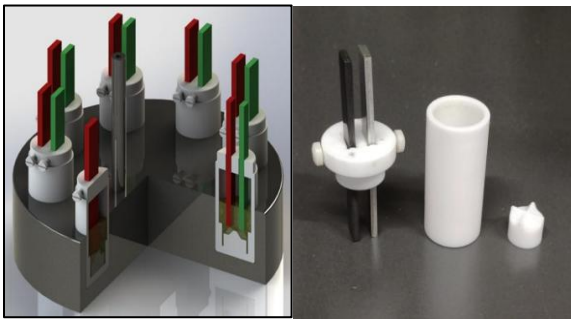
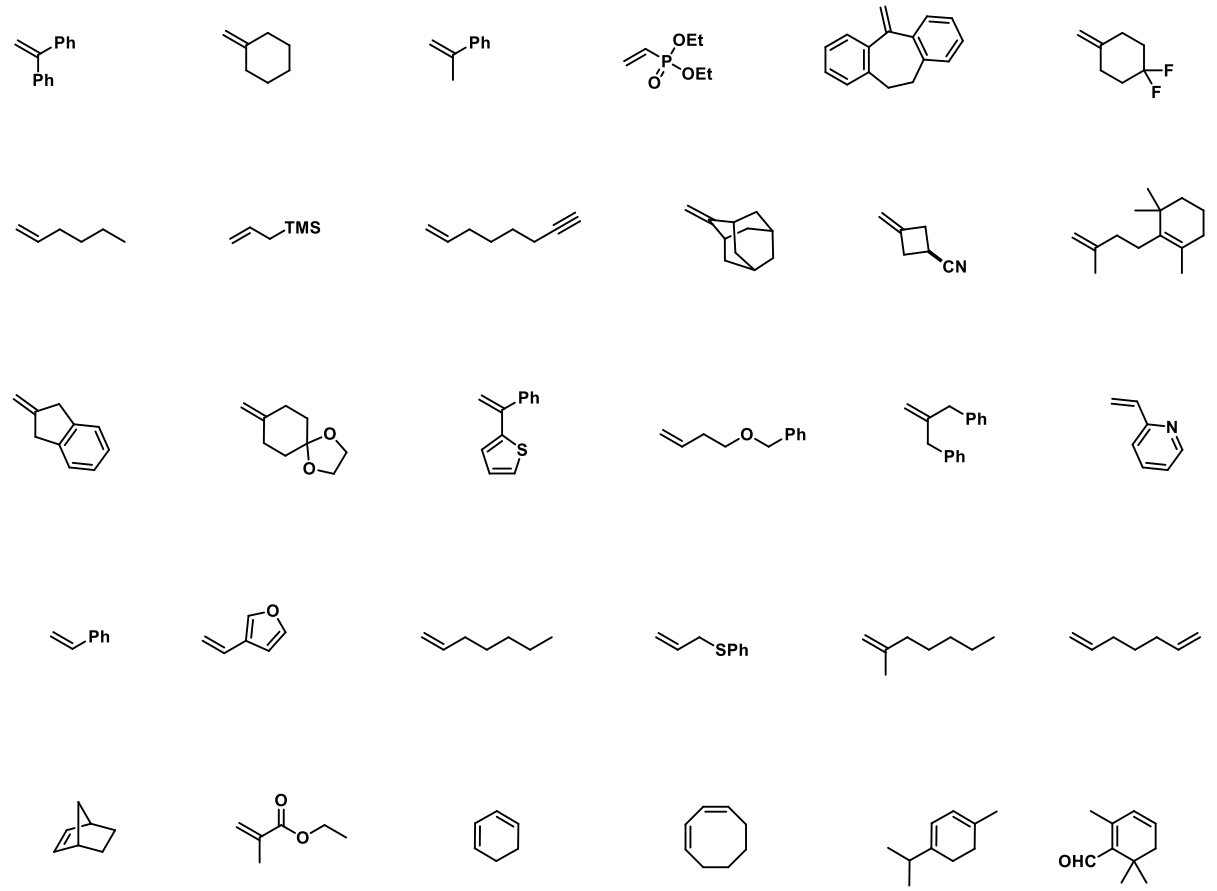


Figure S2: Batch-type cells- undivided.

2 General experimental procedures and characterization data

2.1 Commercially available alkenes

Alkenes used in the scope



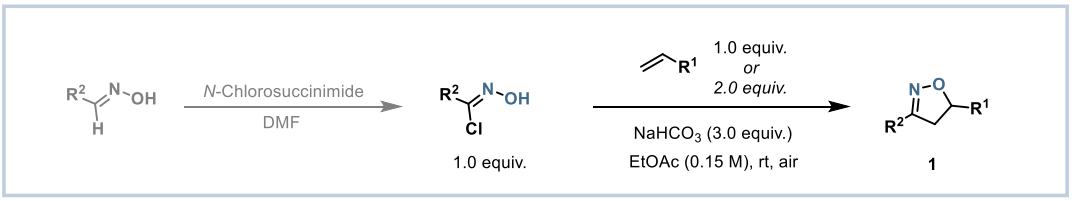
2.2 Starting material synthesis

2.2.1 Synthesis of substituted isoxazolines

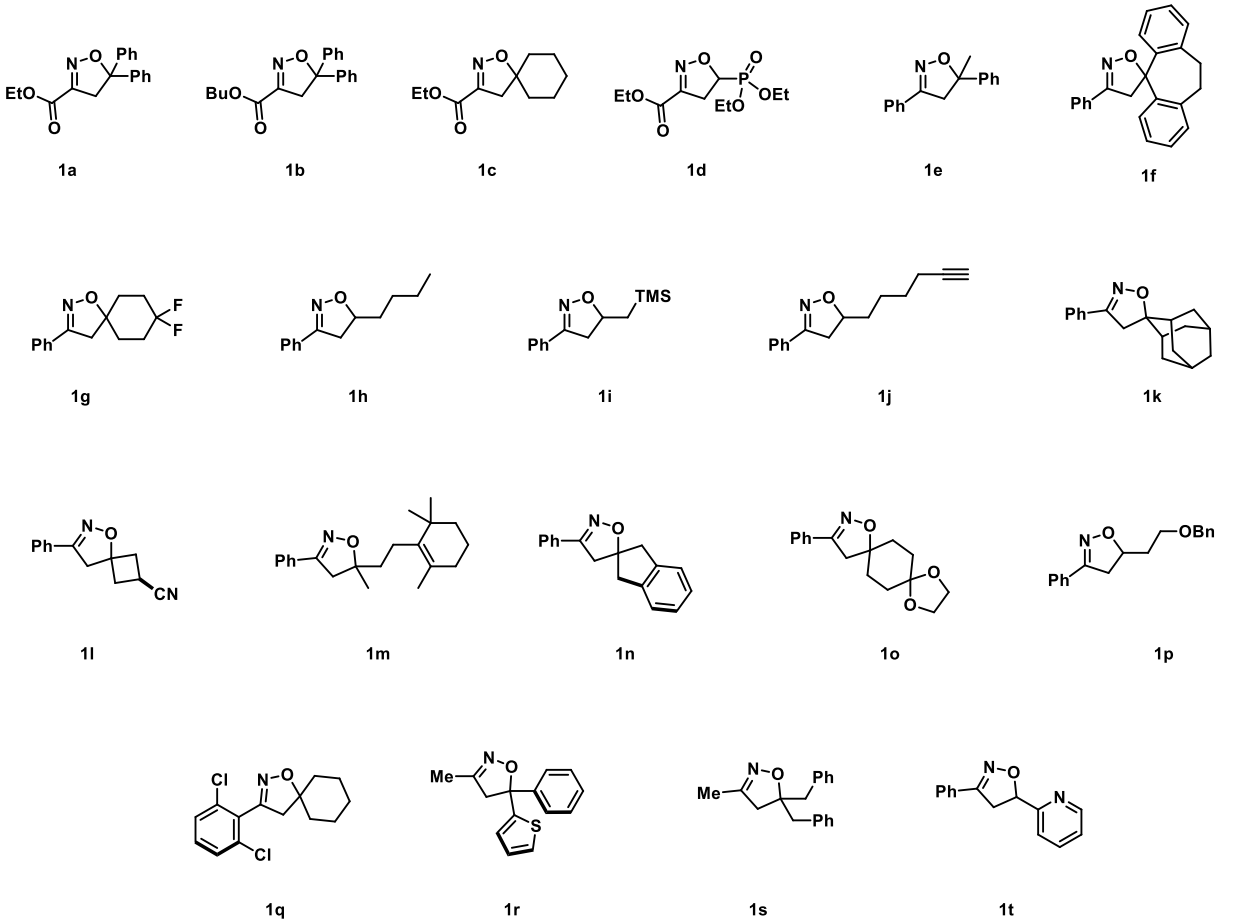
The chlorohydroxylimine reagent was synthesized starting from corresponding aldoxime following a reported literature.[2] The crude was used directly in the next step.

General procedure I (GP-1): In an oven-dried 250 mL round bottom flask containing PTFE stirrer, (*Z*)-*N*-hydroxyalkylimidoyl chloride (1.0 equiv.), alkene (1.0 equiv for activated alkene; 2.0 equiv. for unactivated alkene), and EtOAc (0.15 M) was added. Under vigorous stirring, $NaHCO_3$ (3.0 equiv.) was added and allowed it to stir overnight. The reaction mixture was filtered, and volatiles were removed under

high vacuum. The crude mixture was then purified using column chromatography with below-mentioned solvent gradients (pentane: diethyl ether).

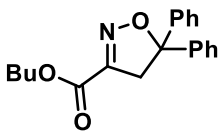


Dihydroisoxazole derived from alkene



*Compound **1a** is commercially available.*

Butyl 5,5-diphenylisoxazoline-3-carboxylate (1b)



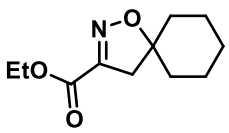
The title compound was synthesized using GP-1 on 5.0 mmol scale. *The analytical data match with the literature precedence.*[3]

R_f: 0.7 (80:20 pentane:diethyl ether)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.49 – 7.29 (m, 10H), 4.31 – 4.25 (m, 2H), 3.92 – 3.85 (m, 2H), 1.77 – 1.69 (m, 2H), 1.51 – 1.40 (m, 2H), 1.01 – 0.93 (m, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.8, 151.8, 143.6, 128.9, 128.4, 126.2, 95.0, 66.2, 47.1, 30.8, 19.5, 13.9.

Ethyl 5-spirocyclohexylisoxazoline-3-carboxylate (1c)



The title compound was synthesized using GP-1 on 5.0 mmol scale. *The analytical data match with the literature precedence.* [4]

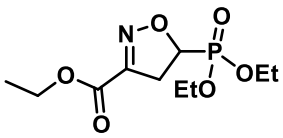
R_f: 0.4 (80:20 pentane:diethyl ether)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.31 (2H, q, *J* = 7.1), 2.89 (2H, s), 1.40–1.90 (10H, m), 1.37 (3H, t, *J* = 7.1).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.7, 150.6, 90.5, 61.2, 43.0, 35.9, 24.5, 23.0, 13.8

GCMS (EI) calc'd for [$C_{11}H_{17}NO_3$] 211.1203, found 211.1202.

Ethyl 5-(diethoxyphosphoryl)isoxazoline-3-carboxylate (1d)



The title compound was synthesized using GP-1 on 5.0 mmol scale. *The analytical data match with the literature precedence.*[5]

R_f: 0.4 (60:40 pentane:diethyl ether)

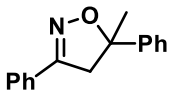
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 – 4.80 (m, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.26 – 4.14 (m, 4H), 3.46 (dd, J = 24.0, 11.4 Hz, 2H), 1.39 – 1.22 (m, 9H).;

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 151.5 (d, *J* = 6.3 Hz), 77.3 (d, *J* = 169.7 Hz), 63.7 (d, *J* = 7.0 Hz), 62.4, 36.4, 16.5 (dd, *J* = 5.5, 1.1 Hz), 14.1.

^{31}P NMR (101 MHz, CD_2Cl_2); 16.8

HRMS (ESI+) calc'd for $[C_{10}H_{18}NO_6P+Na]^+$ 302.0764, found 302.0765.

3,5-Diphenyl-5-methylisoxazoline (1e)



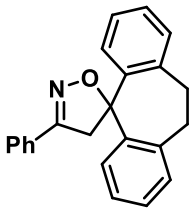
The title compound was synthesized using GP-1 on 5.0 mmol scale. *The analytical data match with the literature precedence.*[6]

R_f: 0.4 (80:20 pentane:diethyl ether)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.63-7.67 (2H, m), 7.48-7.50 (2H, m), 7.35-7.39 (5H, m), 7.25-7.29 (1H, m), 3.53 (1H, d, J = 16.4 Hz), 3.46 (1H, d, J = 16.4 Hz), 1.81 (3H, s);

^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.1, 145.5, 129.9, 128.6, 128.5, 127.2, 126.4, 124.7, 88.1, 48.5, 28.2.

3-Phenyl-5-spirofluorenylisoxazoline (1f)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

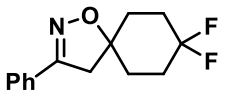
R_f: 0.4 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.61 – 7.47 (m, 2H), 7.25 (s, 3H), 7.17 – 7.01 (m, 6H), 3.81 (s, 2H), 3.46 – 3.30 (m, 2H), 2.99 – 2.86 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 142.2, 136.7, 130.4, 129.9, 129.2, 128.5, 127.6, 126.4, 126.3, 125.3, 90.1, 52.6, 32.9.

GCMS (EI) calc'd for [$C_{23}H_{19}NO$] 325.1461, found 325.1459.

3-Phenyl-5-spiro(4,4-difluorocyclohexyl)isoxazoline (1g)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

R_f: 0.4 (90:10 pentane:diethyl ether)

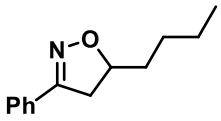
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7 – 7.6 (m, 2H), 7.5 – 7.3 (m, 3H), 3.1 (s, 2H), 2.3 – 2.2 (m, 2H), 2.1 – 2.0 (m, 4H), 2.0 – 1.8 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 130.3, 129.8, 128.9, 126.6, 122.9 (dd, *J* = 243.1, 238.9 Hz), 84.2 (d, *J* = 1.6 Hz), 45.4, 32.8 (dd, *J* = 8.9, 1.6 Hz), 31.0 – 30.3 (m).

^{19}F NMR (376 MHz, CDCl3) δ -98.8 (dd, J = 3463.9, 237.4 Hz).

GCMS (EI) calc'd for [$C_{14}H_{15}F_2NO$] 251.1116, found 251.1117.

5-Butyl-3-phenylisoxazoline (1h)



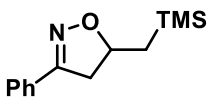
The title compound was synthesized using GP-1 on 5.0 mmol scale. *The analytical data match with the literature precedence.*[7]

R_f: 0.6 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.64 (m, 2H), 7.44–7.37 (m, 3H), 4.78–4.71 (m, 1H), 3.40 (dd, *J* = 15.0, 10.0 Hz, 1H), 2.98 (dd, *J* = 15.0, 10.0 Hz, 1H), 1.84–1.77 (m, 1H), 1.69–1.62 (m, 1H), 1.54–1.45 (m, 1H), 1.43–1.36 (m, 3H), 0.94 (t, *J* = 10.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 129.89, 129.8, 128.6, 126.5, 81.4, 39.8, 35.0, 27.6, 22.5, 13.9.

3-Phenyl-5-(2-trimethylsilylethyl)isoxazoline (1i)



The title compound was synthesized with **1d** using GP-1 on 5.0 mmol scale.

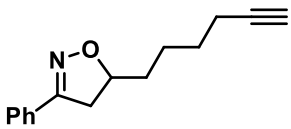
R_f: 0.6 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 2H), 7.39 (pd, *J* = 3.6, 2.0 Hz, 3H), 4.93 – 4.76 (m, 1H), 3.38 (ddt, *J* = 16.1, 9.7, 1.0 Hz, 1H), 2.89 (ddd, *J* = 16.2, 9.3, 1.2 Hz, 1H), 1.30 (ddd, *J* = 14.2, 6.2, 1.2 Hz, 1H), 1.07 (dd, *J* = 14.2, 8.4 Hz, 1H), 0.11 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 130.2, 129.9, 128.7, 126.6, 80.3, 42.3, 24.4, 0.9;

GCMS (EI) calc'd for [$C_{13}H_{19}NOSi$] 233.1230, found 233.1229.

3-Phenyl-5-(5-hexynyl)isoxazoline (1j)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

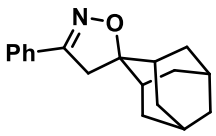
R_f: 0.6 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (ddt, *J* = 5.6, 3.1, 1.6 Hz, 2H), 7.46 – 7.33 (m, 3H), 4.79 – 4.68 (m, 1H), 3.40 (dd, *J* = 16.4, 10.3 Hz, 1H), 2.97 (dd, *J* = 16.4, 8.1 Hz, 1H), 2.23 (tt, *J* = 6.5, 3.6 Hz, 2H), 1.95 (t, *J* = 2.7 Hz, 1H), 1.63 (s, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 130.0, 130.0, 128.8, 126.7, 84.3, 81.3, 68.6, 40.1, 34.9, 28.3, 24.8, 18.4;

HRMS (ESI+) calc'd for $[C_{15}H_{17}NO+Na]^+$ 250.1202, found 250.1201.

4'*H*-3'-Phenyl-spiro[adamantane-2,5'-isoxazole] (1k)



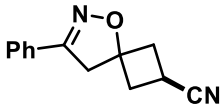
The title compound was synthesized using GP-1 on 5.0 mmol scale. *The analytical data match with the literature precedence* [6].

R_f: 0.6 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.67 (m, 2H), 7.40 – 7.38 (m, 3H), 3.16 (s, 2H), 2.34 – 2.31 (m, 2H), 1.98 – 1.93 (m, 2H), 1.90 – 1.87 (m, 4H), 1.79 – 1.78 (m, 4H), 1.67 – 1.63 (m, 2H);

^{13}C NMR (101MHz, $CDCl_3$): δ 156.0, 130.3, 129.6, 128.5, 91.4, 43.7, 37.3, 37.0, 35.6, 33.2, 26.9, 26.6.

3-Phenylspiro[isoxazoline-5,1′-cyclobutane]-3′-carbonitrile (1l)



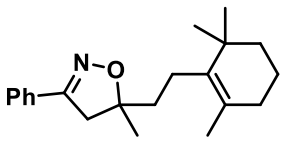
The title compound was synthesized using GP-1 on 5.0 mmol scale. *The analytical data match with the literature precedence.* [8]

R_f: 0.3 (85:15 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.56 (m, 2H), 7.47 – 7.35 (m, 3H), 3.55 (s, 2H), 3.22 – 3.10 (m, 1H), 3.03 – 2.96 (m, 2H), 2.71 – 2.62 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 130.4, 129.0, 128.8, 126.6, 122.2, 84.2, 46.1, 40.8, 15.2.

3-Phenyl-5-[2-(2,6,6-trimethylcyclohex-1-enyl)ethyl]-5-methylisoxazoline (1m)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

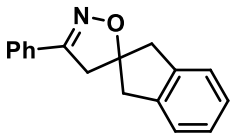
R_f: 0.4 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.59 (m, 2H), 7.46 – 7.32 (m, 3H), 3.20 (d, *J* = 16.5 Hz, 1H), 3.04 (d, *J* = 16.5 Hz, 1H), 2.14 (dd, *J* = 10.7, 6.8 Hz, 2H), 1.91 (t, *J* = 6.3 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.63 (s, 3H), 1.61 – 1.54 (m, 2H), 1.47 (s, 3H), 1.46 – 1.38 (m, 2H), 1.02 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 136.2, 130.4, 129.7, 128.6, 127.4, 126.4, 87.4, 44.8, 40.3, 39.8, 35.1, 32.8, 28.7, 25.6, 23.0, 19.8, 19.5.

HRMS (ESI+) calc'd for $[C_{21}H_{29}NO+H]^+$ 312.2322, found 312.2321.

3-Phenyl-5-spiro(indan-1,5′-isoxazoline) (1n)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

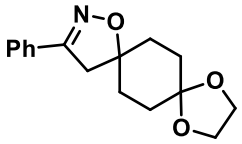
R_f: 0.4 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (ddd, *J* = 6.6, 2.8, 1.5 Hz, 2H), 7.30 (q, *J* = 3.6 Hz, 3H), 7.17 – 7.03 (m, 4H), 3.36 (d, *J* = 16.3 Hz, 2H), 3.30 (s, 2H), 3.08 (d, *J* = 16.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 140.3, 129.8, 129.7, 128.5, 126.7, 126.3, 124.4, 93.7, 45.5, 45.2.

GCMS (EI) calc'd for $[C_{17}H_{15}NO]$ 249.1148, found 249.1148.

3-Phenyl-5-spiro(1,3-dioxolane-2,5′-isoxazoline) (1o)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

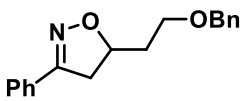
R_f: 0.4 (80:20 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.56 (m, 2H), 7.38 (ddt, *J* = 5.7, 3.9, 2.1 Hz, 3H), 4.06 – 3.89 (m, *J* = 3.6 Hz, 4H), 3.09 (s, 2H), 2.03 (dddt, *J* = 13.0, 11.1, 8.1, 2.8 Hz, 4H), 1.95 – 1.82 (m, 2H), 1.70 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 130.2, 130.0, 128.8, 126.5, 108.0, 85.5, 64.5, 64.4, 45.2, 34.0, 31.6.

HRMS (ESI+) calc'd for $[C_{16}H_{19}NO_3+Na]^+$ 296.1257, found 296.1258.

3-Phenyl-5-(2-benzyloxyethyl)isoxazoline (1p)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

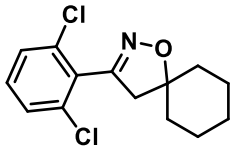
R_f: 0.4 (80:20 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.19 (s, 8H), 4.77 (m, 1H), 4.43 – 4.31 (m, 2H), 3.58 – 3.47 (m, 2H), 3.23 (dd, *J* = 16.5, 10.4 Hz, 1H), 2.91 (dd, *J* = 16.5, 7.8 Hz, 1H), 1.98 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 138.2, 129.9, 129.8, 128.6, 128.3, 127.6, 127.6, 126.6, 78.7, 73.1, 66.7, 40.1, 35.4.

HRMS (ESI+) calc'd for $[C_{18}H_{19}NO_2+Na]+$ 304.1308, found 304.1308.

3-(2,6-Dichlorophenyl)-5-spirocyclohexylisoxazoline (1q)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

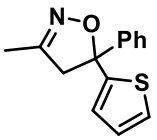
R_f: 0.4 (80:20 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.45 (m, 3H), 3.20 (s, 2H), 2.18 – 1.90 (m, 6H), 1.68 (q, *J* = 4.9 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 135.2, 130.9, 129.6, 128.1, 87.9, 47.4, 36.6, 25.2, 23.6;

GCMS (EI) calc'd for ^{35}Cl isotope $[C_{14}H_{15}Cl_2NO]$ 283.0525, found 283.0524.

3-Methyl-5-thienyl-5-phenylisoxazoline (1r)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

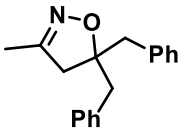
R_f: 0.4 (80:20 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.26 (s, 3H), 7.15 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.82 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.77 (dd, *J* = 3.7, 1.2 Hz, 1H), 3.62 – 3.35 (m, 2H), 1.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 149.0, 144.3, 128.8, 128.3, 127.0, 126.2, 126.0, 89.0, 53.8, 13.8.

GCMS (EI) calc'd for $[C_{14}H_{13}NOS]$ 243.0712, found 243.0710.

3-Methyl-5,5-dibenzylisoxazoline (1s)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

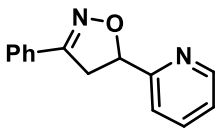
R_f: 0.4 (80:20 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 10H), 3.04 (d, *J* = 14.0 Hz, 2H), 2.90 (d, *J* = 13.9 Hz, 2H), 2.73 – 2.59 (m, 2H), 1.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 136.7, 130.6, 128.2, 126.7, 88.7, 45.2, 44.8, 13.2.

HRMS (ESI+) calc'd for $[C_{18}H_{19}NO+Na]^+$ 288.1359, found 288.1357.

3-Phenyl-5-(pyridin-2-yl)isoxazoline (1t)



The title compound was synthesized using GP-1 on 5.0 mmol scale. *The analytical data match with the literature precedence [6].*

R_f: 0.3 (100% diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (t, 1H, *J* = 2.0 Hz), 7.77 – 7.67 (m, 3H), 7.60 (d, 1H, *J* = 8.0 Hz), 7.45 – 7.37 (m, 3H), 7.22 (t, 1H, *J* = 6.0 Hz), 5.88 – 5.84 (m, 1H), 3.88 – 3.81 (m, 1H), 3.74 – 3.69 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 156.4, 149.3, 137.0, 130.3, 129.2, 128.6, 126.9, 122.9, 120.4, 82.3, 41.5.

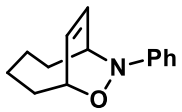
GCMS (EI) calc'd for [$C_{14}H_{12}N_2O$] 211.1203, found 211.1202.

2.2.2 Synthesis of bicyclic system containing N–O bonds

General procedure III (GP-3): The procedure was adapted and modified using published report.[12] In an oven-dried 100 mL round bottom flask with PTFE stirrer, 1,3-diene (2.0 equiv.) was added to a solution of nitrosobenzene (1.0 equiv.) in CH_2Cl_2 (0.1 M) at 0 °C. The reaction mixture was allowed to stir at 0 °C, with a change in colour from green to pale brown. The completion of the reaction was tracked with TLC. The volatiles were removed under high vacuum. The crude mixture was then purified using column chromatography with below-mentioned solvent gradients (pentane: diethyl ether).

*The analytical data of **5a** match with the literature precedence.*[12]

8-Phenyl-7-oxa-8-azabicyclo[4.2.2]dec-9-ene (3b)



The title compound was synthesized using GP-3 on 5.0 mmol scale.

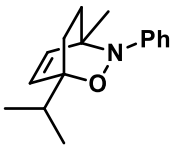
R_f: 0.7 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 2H), 7.04 – 6.95 (m, 2H), 6.94 – 6.86 (m, 1H), 6.15 (dd, *J* = 10.1, 6.8 Hz, 1H), 5.82 (dd, *J* = 10.1, 4.5 Hz, 1H), 5.00 – 4.92 (m, 1H), 4.39 – 4.31 (m, 1H), 2.35 – 2.26 (m, 1H), 2.23 – 2.06 (m, 2H), 1.92 – 1.81 (m, 1H), 1.80 – 1.61 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 129.6, 128.9, 126.8, 121.3, 115.9, 73.1, 58.5, 34.8, 32.8, 26.4, 22.5.

GCMS (EI) calc'd for [$C_{14}H_{17}NO$] 215.1305, found 215.1306.

1-Isopropyl-4-methyl-3-phenyl-2-oxa-3-azabicyclo[2.2.2]oct-5-ene (3c)



The title compound was synthesized using GP-3 on 5.0 mmol scale.

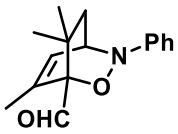
R_f: 0.7 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 2H), 7.13 – 7.02 (m, 3H), 6.62 (d, *J* = 8.5 Hz, 1H), 5.87 (d, *J* = 8.5 Hz, 1H), 2.15 – 1.99 (m, 3H), 1.56 – 1.37 (m, 2H), 1.27 (s, 3H), 1.11 (dd, *J* = 18.5, 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 133.8, 133.0, 127.2, 125.0, 124.3, 78.3, 58.5, 33.1, 31.7, 28.3, 23.7, 17.6, 17.6.

HRMS (ESI+) calc'd for $[C_{16}H_{21}NO+H]^+$ 244.1696, found 244.1698.

6,7,7-Trimethyl-3-phenyl-2-oxa-3-azabicyclo[2.2.2]oct-5-ene-1-carbaldehyde (3d)



The title compound was synthesized using GP-3 on 5.0 mmol scale.

R_f: 0.7 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 2H), 7.13 – 7.02 (m, 3H), 6.62 (d, *J* = 8.5 Hz, 1H), 5.87 (d, *J* = 8.5 Hz, 1H), 2.15 – 1.99 (m, 3H), 1.56 – 1.37 (m, 2H), 1.27 (s, 3H), 1.11 (dd, *J* = 18.5, 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 133.8, 133.0, 127.2, 125.0, 124.3, 78.3, 58.5, 33.1, 31.7, 28.3, 23.7, 17.6, 17.6.

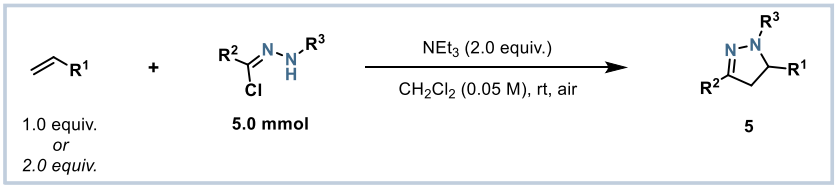
GCMS (EI) calc'd for $[C_{16}H_{19}NO_2]$ 257.1410, found 257.1407.

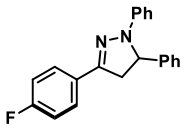
2.2.3 Synthesis of substituted pyrazolines

The chlorohydrozone reagent was synthesized starting from corresponding hydrazone following a reported literature.[9] A modified report was used for the synthesis of phenylacetohydrazonoyl chloride.[10] The crudes were used directly in the next step**.**

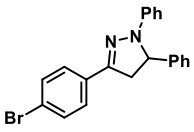
General procedure II (GP-2): The procedure was adapted and modified using published report. In an oven-dried 150 mL Schlenk flask containing PTFE stirrer, alkene (1.0 equiv for activated alkene; 2.0 equiv. for unactivated alkene), NEt_3 (2.0 equiv.), and CH_2Cl_2 (0.05 M) were added. Then (*Z*)-*N*-

phenylalkylhydrazonoyl chloride (1.0 equiv.) was added dropwise to the stirring reaction mixture at room temperature. The reaction mixture was filtered, and volatiles were removed under high vacuum. The crude mixture was then purified using column chromatography with below-mentioned solvent gradients (pentane: diethyl ether).

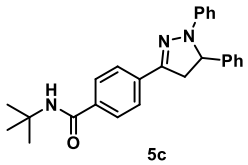




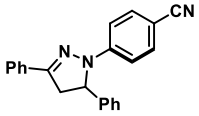
5a



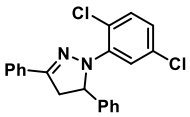
5b



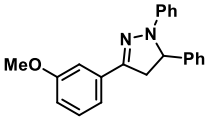
5c



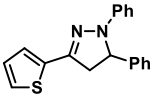
5d



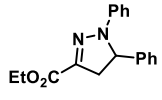
5e



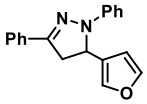
5f



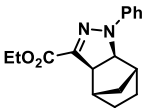
5g



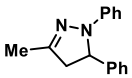
5h



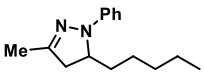
5i



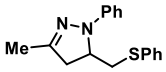
5j



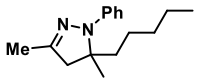
5k



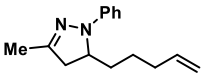
5l



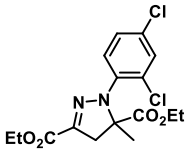
5m



5n



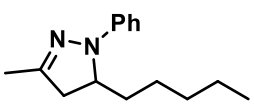
5o



5p

*The analytical data (**5a-5k, 5p**) match with the literature precedence.*[11]

3-Methyl-5-pentyl-1-phenylpyrazoline (5l)



The title compound was synthesized using GP-1 on 5.0 mmol scale.

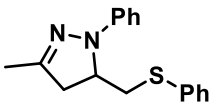
R_f: 0.5 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 2H), 6.94 – 6.86 (m, 2H), 6.66 (tt, *J* = 7.3, 1.1 Hz, 1H), 3.97 (m, 1H), 2.91 (m, 1H), 2.42 (m, 1H), 1.93 (t, *J* = 1.2 Hz, 3H), 1.75 – 1.64 (m, 1H), 1.42 – 1.30 (m, 1H), 1.20 (dt, *J* = 8.1, 3.0 Hz, 6H), 0.84 – 0.72 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 145.8, 129.1, 118.4, 113.2, 60.2, 42.8, 32.9, 31.8, 25.0, 22.8, 16.2, 14.1.

GCMS (EI) calc'd for [$C_{15}H_{22}N_2$] 230.1777, found 230.1777.

3-Methyl-1-phenyl-5-((phenylthio)methyl)pyrazoline (5m)



The title compound was synthesized using GP-2 on 5.0 mmol scale.

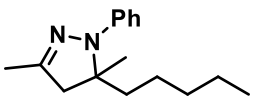
R_f: 0.55 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.37 – 7.18 (m, 5H), 6.94 – 6.86 (m, 2H), 6.80 (tt, *J* = 7.3, 1.1 Hz, 1H), 4.26 (tdd, *J* = 10.3, 4.7, 2.8 Hz, 1H), 3.37 (dd, *J* = 13.2, 2.8 Hz, 1H), 3.07 (ddq, *J* = 17.7, 10.6, 1.5 Hz, 1H), 2.84 (ddq, *J* = 17.6, 4.7, 1.0 Hz, 1H), 2.76 (dd, *J* = 13.2, 10.2 Hz, 1H), 2.07 (t, *J* = 1.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 144.9, 135.0, 130.8, 129.3, 129.2, 127.1, 119.1, 113.3, 59.4, 42.6, 36.3, 16.2.

GCMS (EI) calc'd for [$C_{17}H_{18}N_2S$] 282.1185, found 282.1182.

3,5-Dimethyl-5-pentyl-1-phenylpyrazoline (5n)



The title compound was synthesized using GP-2 on 5.0 mmol scale.

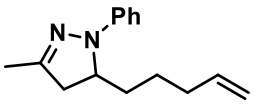
R_f: 0.55 (90:10 pentane:diethyl ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.03 (m, 4H), 6.76 (tt, *J* = 7.1, 1.4 Hz, 1H), 2.75 (dq, *J* = 17.1, 1.3 Hz, 1H), 2.47 (dq, *J* = 17.0, 1.1 Hz, 1H), 1.91 (t, *J* = 1.2 Hz, 3H), 1.79 (s, 1H), 1.62 – 1.49 (m, 1H), 1.26 – 1.10 (m, 9H), 0.82 – 0.71 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 145.6, 128.7, 120.4, 117.4, 68.8, 50.7, 39.7, 32.2, 24.9, 24.3, 22.6, 16.3, 14.1.

GCMS (EI) calc'd for [$C_{16}H_{24}N_2$] 244.1934, found 244.1934.

3-Methyl-5-(pent-4-enyl)-1-phenylpyrazoline (5o)



The title compound was synthesized using GP-2 on 5.0 mmol scale.

R_f: 0.55 (90:10 pentane:diethyl ether)

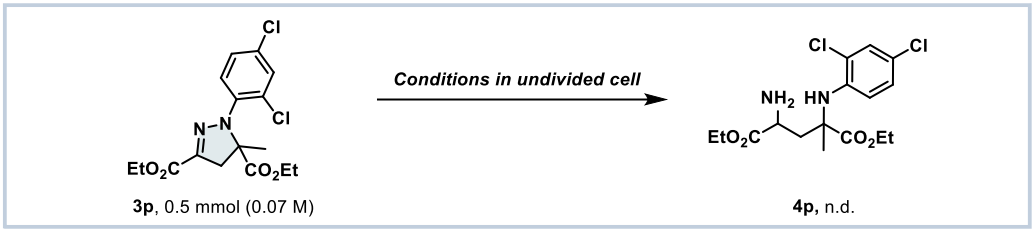
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.06 (m, 2H), 6.95 – 6.87 (m, 2H), 6.67 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.67 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 4.96 – 4.80 (m, 2H), 4.04 – 3.94 (m, 1H), 2.92 (ddq, *J* = 17.2, 10.9, 1.3 Hz, 1H), 2.42 (ddt, *J* = 17.2, 5.9, 1.1 Hz, 1H), 1.93 (s, 5H), 1.79 – 1.65 (m, 1H), 1.47 – 1.23 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 145.7, 138.4, 129.2, 118.6, 115.0, 113.3 (d, *J* = 3.1 Hz), 60.1, 42.8, 33.7, 32.4, 24.6, 16.2.

HRMS (ESI+) calc'd for $[C_{15}H_{20}N_2+H]^+$ 228.1621, found 228.1622.

2.3 Screening and optimization in batch-type cells

- **Undivided batch-type cells**



3p, 0.5 mmol (0.07 M) | **4p**, n.d.

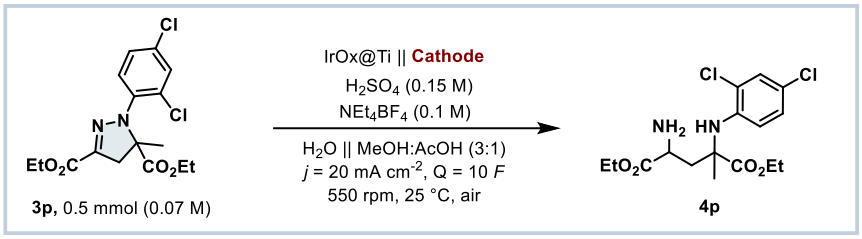
GC | Zn	C_{Gr} | StSt	GC | BDD	DSA | GC
AcOH (5.0 eq.)	KOAc (0.5 eq.)	H_2SO_4 (0.5 M)	NEt_4BF_4 (0.1 M)
NEt_4BF_4 (0.1 M)	MeOH (0.1 M)	HFIP:MeOH (0.1 M)	MeOH:H_2O (0.1 M)
MeOH (0.1 M)	*j* = 20 mA cm^{-2}, Q = 10 *F*, rt	*j* = 20 mA cm^{-2}, Q = 10 *F*, rt	*j* = 20 mA cm^{-2}, Q = 10 *F*, rt
j = 20 mA cm^{-2}, Q = 10 *F*, rt			

GC = Glassy carbon, C_{Gr} = Graphite; StSt = Stainless steel; BDD = Boron-doped diamond; DSA = Dimensionally-stable anode

<u>*Result and Conclusion*</u>: Neither of the reaction conditions worked for the selective reduction of **3p** to **4p**. This stems from the anodic degradation of the amine product. This prompted us to try divided cells.

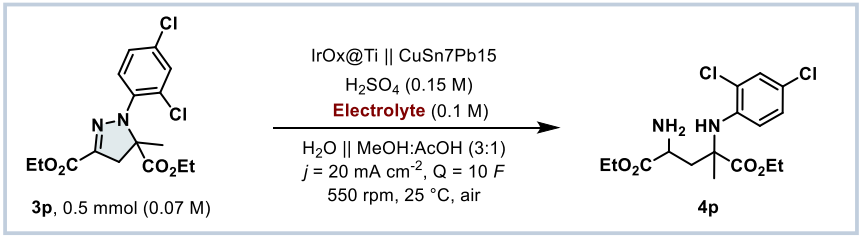
- **Divided batch-type cells**

1) Cathode screening (N–N cleavage)



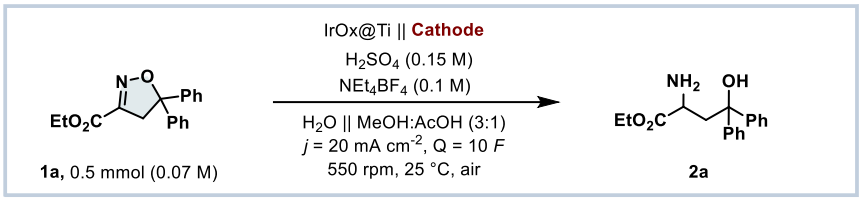
Entry	Cathode	% Yield 4p
1	Ni plate	n.d.
2	Stainless steel	n.d.
3	Sn	22
4	Pb	67
5	Bronze	61
6	Cu	n.d.
7	CuSn7Pb15	72
8	CuSn7Zn4Pb7	27
9	CuZn40Pb2	60
10	CuSn10Pb10	27
11	CuSn5Pb20	41

2) Electrolyte screening (N–N cleavage)



Entry	Electrolyte	% Yield 4p
1	NH_4BF_4	24
2	$LiBF_4$	50
3	NEt_4BF_4	72
4	NBu_4BF_4	43
5	0.3 M H_2SO_4	51

3) Cathode screening (N–O cleavage)

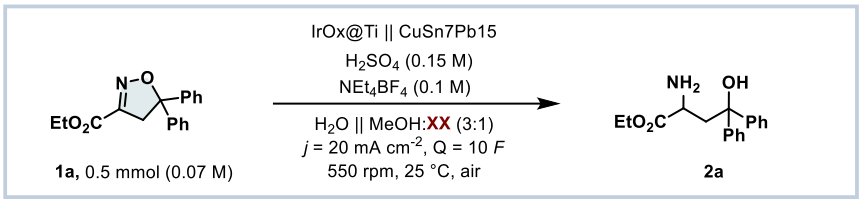


1a, 0.5 mmol (0.07 M)

2a

Entry	Cathode	% Yield 2a
1	Ni plate	n.d.
2	Stainless steel	n.d.
3	GC	n.d.
4	Cu	n.d.
5	Bronze	61
6	Zn	64
7	CuSn7Pb15	69
8	CuSn7Zn4Pb7	43
9	CuZn40Pb2	60
10	CuSn10Pb10	18
11	CuSn5Pb20	45

4) Acid and co-solvent screening (N–O cleavage)

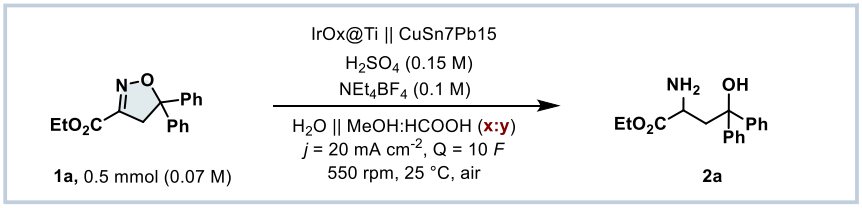


1a, 0.5 mmol (0.07 M)

2a

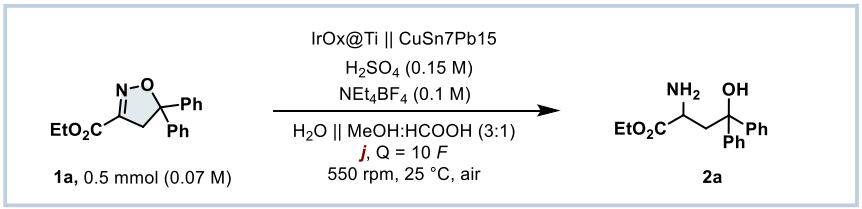
Entry	XX	% Yield 2a
1	HCOOH	81
2	AcOH + $MeSO_3H$ (2.0 equiv.)	62
3	CF_3COOH	62
4	HFIP	<5

5) Solvent ratio (N–O cleavage)



Entry	x:y	% Yield 2a
1	3:1	81
2	1:1	42
3	1:3	36
4	0:100	16

6) Current density (N–O cleavage)



Entry	*j* (mA cm^{-2})	% Yield 2a
1	10	72
2	20	80
3	30	60
4[a]	50	46
5[a]	70	44

[a]***Note**: Due to poor conductivity/high terminal voltage of the cell, additional 2.0 equiv. H_2SO_4 was added.*

2.4 Parameter-based sensitivity assessment

To check the reproducibility of the presented transformation, a series of sensitivity tests were conducted. These experiments were conducted with **1a** under *condition A*.

Entry	Modification	Execution	Deviation (%)
1	High concentration (*c*)	0.14 M instead of 0.07 M	−3
2	Low concentration (*c*)	0.035 M instead of 0.07 M	−4
3	High current density (*j*)	30 mA cm^{-2}	−9
4	Low current density (*j*)	10 mA cm^{-2}	−11
5	High stirring rate (*rpm*)	800 rpm	−9
6	Low stirring rate (*rpm*)	200 rpm	−40
7	High S.E. concentration	0.2 M	−7
8	Low S.E. concentration	0.05 M	−50
9	Large scale	5.0 mmol (×10 times)	−12

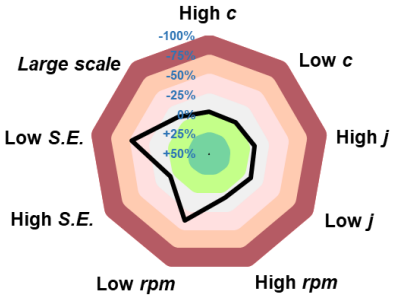
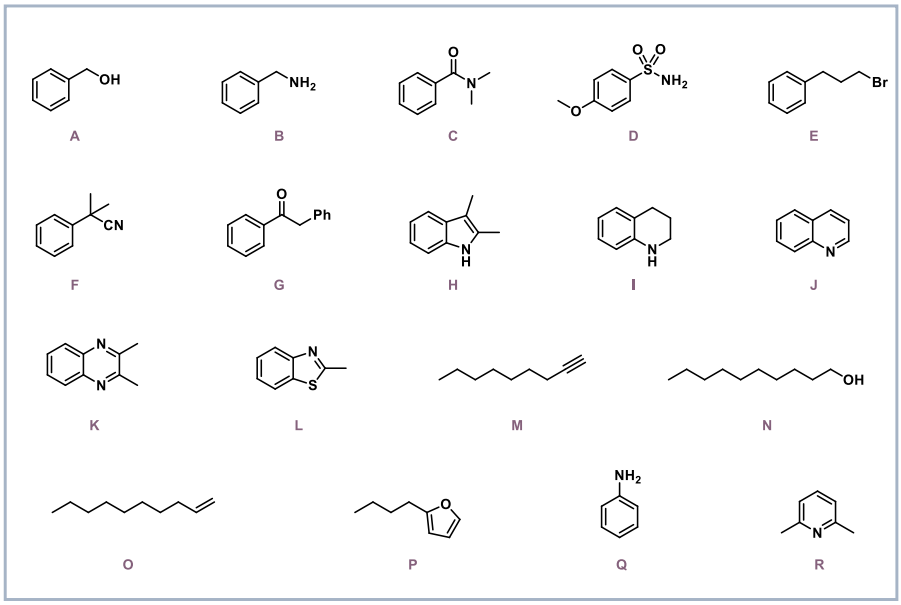


Figure S3: Graphical depiction of sensitivity assessment.

2.5 Additive-based robustness screen

The robustness screening includes a series of additives containing various functional groups and heterocycles. The screening provides a data on the stability of these reaction additives and the tolerance of functional groups of our methodology. The electrochemical setup was prepared according to **GP-4** with substrate **1a,** and one additive (1.0 equiv) added to each one of the set-ups. Once the reaction was complete, the work-up was done accordingly. Mesitylene as internal standard was added to each and every organic extract. The reaction yield and the remaining additive were analyzed by GC-FID. One reaction was performed without any additive under same reaction condition as a control reaction.



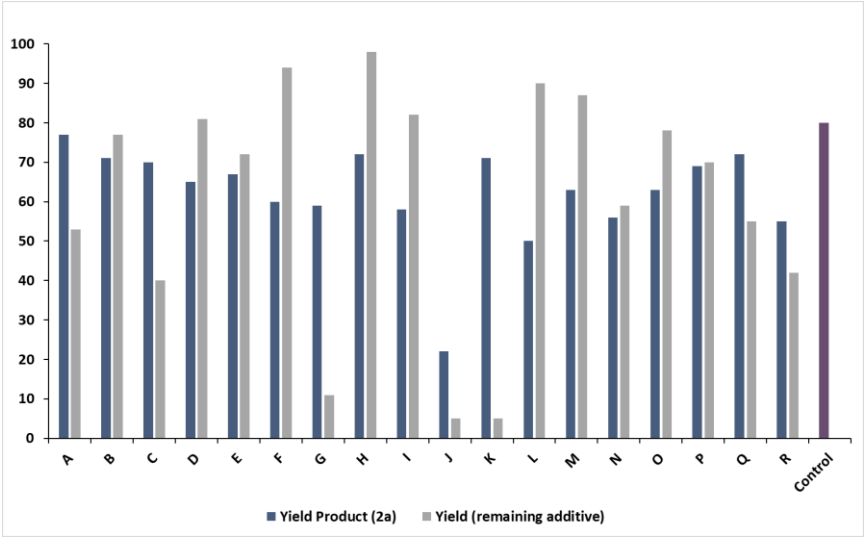


Figure S4: Graphical depiction of additive-based robustness screening

3 Scope

General protocol for preparative electrolysis in batch-type divided cell used in synthetic scope investigations on 0.5 mmol scale.

We used the reaction setup as described and shown in **Figure S1**. The anodic compartment was filled with 7 mL H_2O and the cathodic compartment was filled with:

A) 7 mL 3:1 MeOH/HCOOH mixture (***GP-4***)
B) 7 mL 3:1 MeOH/AcOH mixture (***GP-5***)

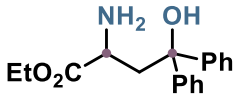
Then H_2SO_4 (55 µL, 1.0 mmol, 2.0 equiv.) was added to each compartment. In the catholyte, NEt_4BF_4 (152 mg, 0.7 mmol, 0.1 M) and substrate (0.5 mmol) was added. The reaction mixture was allowed to stir at elevated stirring rate for 2 mins for complete homogenization. The electrolysis started using DSA (IrO_x on Ti) as anode and leaded bronze (CuSn7Pb15) as cathode. The current density was set to 20 mA/cm^2 with an amount of applied charge to 482 C (10 *F*). The reaction was performed at room temperature and constant stirring rate of 400 rpm. After electrolysis, the catholyte was transferred into a 50 mL centrifuge tube. The catholyte was rinsed with ethyl acetate twice. Then, adequate amount of $NaHCO_3$ was added to neutralize the protonated amines by increasing the pH around 9-10. The basified reaction mixture was extracted two times with EtOAc. A second phase of extraction was performed using CH_2Cl_2 to make sure all the organic materials are collected. Combined organic fractions were dried over Na_2SO_4 and concentrated under vacuum. The crude was purified using column chromatography.

Note I*: Changes in the reaction condition are mentioned alongside the scope characterization data.*

Note II*: All diastereomeric ratios were obtained from crude ^1H NMR analysis.*

3.1 Synthesis of 1,3-Amino alcohols

Butyl 2-amino-4-hydroxy-4,4-diphenylbutanoate (2a)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.4 (70:30 pentane:diethyl ether)

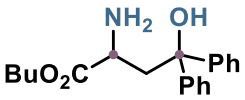
Yield: 118 mg, 79% (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 – 7.61 (m, 2H), 7.53 – 7.37 (m, 4H), 7.37 – 7.26 (m, 3H), 7.26 – 7.18 (m, 1H), 4.20 (q, *J* = 7.1, 2H), 3.52 (dd, *J* = 11.8, 2.4 Hz, 1H), 2.97 (dd, *J* = 14.3, 2.4 Hz, 1H), 2.16 (dd, *J* = 14.3, 11.8 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 175.4, 148.8, 147.2, 128.6, 128.4, 126.9, 126.9, 126.8, 125.9, 78.5, 61.7, 52.8, 43.1, 14.4.

HRMS (ESI+) calc'd for $[C_{15}H_{16}NO + H]^+$ 300.1594, found 300.1593.

Butyl 2-amino-4-hydroxy-4,4-diphenylbutanoate (2b)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.4 (70:30 pentane:diethyl ether)

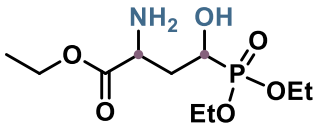
Yield: 81 mg, 50% (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.60 (dt, *J* = 8.2, 1.4 Hz, 2H), 7.47 – 7.35 (m, 4H), 7.34 – 7.09 (m, 4H), 4.12 (tt, *J* = 6.7, 1.5 Hz, 2H), 3.52 – 3.46 (m, 1H), 2.93 (ddd, *J* = 14.3, 2.2, 1.2 Hz, 1H), 2.12 (ddd, *J* = 14.2, 11.7, 1.3 Hz, 1H), 1.71 – 1.59 (m, 2H), 1.47 – 1.29 (m, 2H), 0.97 (td, *J* = 7.3, 1.3 Hz, 3H).

^{13}C NMR (101 MHz, CD2Cl2) δ 175.5, 148.9, 147.2, 128.6, 128.4, 127.0, 126.9, 126.8, 125.8, 78.5, 65.6, 52.8, 43.2, 31.0, 19.5, 13.9.

HRMS (ESI+) calc'd for $[C_{20}H_{25}NO_3 + H]^+$ 328.1907, found 328.1910.

Ethyl 2-amino-4-(diethoxyphosphoryl)-4-hydroxybutanoate (2c)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.3 (95:5 CH_2Cl_2:MeOH)

Yield: 100 mg, 70%, *d.r.* = 1:1, (appearance: yellow solid)

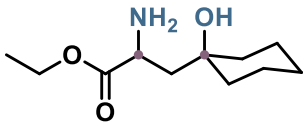
^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 4.24 – 4.07 (m, 7H), 3.96 – 3.63 (m, 1H), 3.17 (s, 3H), 2.12 (s, 1H), 1.91 – 1.75 (m, 1H), 1.39 – 1.21 (m, 9H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 175.2, 174.4, 67.9 (d, *J* = 170.0 Hz), 65.2 (d, *J* = 165.4 Hz), 62.7 (d, *J* = 7.4 Hz), 62.6 (d, *J* = 7.4 Hz), 62.4 (d, *J* = 2.0 Hz), 62.4 (d, *J* = 1.7 Hz), 61.3, 61.2, 54.5 (d, *J* = 17.4 Hz), 51.3 (d, *J* = 11.9 Hz), 34.4, 34.1, 16.3, 16.3, 16.3, 16.3, 13.9, 13.9.

^{31}P NMR (162 MHz, CD_2Cl_2) δ 23.71 (d, *J* = 265.0 Hz).

HRMS (ESI+) calc'd for $[C_{10}H_{22}NO_6P + H]^+$ 284.1258, found 284.1257.

Ethyl 2-amino-3-(1-hydroxycyclohexyl)propanoate (2d)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.3 (95:5 CH_2Cl_2:MeOH)

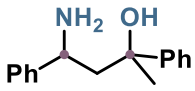
Yield: 73 mg, 50% (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 4.14 (q, *J* = 7.1 Hz, 2H), 3.70 (dd, *J* = 11.9, 2.9 Hz, 1H), 2.86 (s, 3H), 1.88 (dd, *J* = 14.3, 2.9 Hz, 1H), 1.70 – 1.59 (m, 3H), 1.51 (dd, *J* = 11.3, 5.6 Hz, 6H), 1.33 – 1.23 (m, 5H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 176.3, 71.0, 61.5, 51.7, 43.4, 40.4, 36.7, 26.5, 22.7, 22.4, 14.4.

HRMS (ESI+) calc'd for $[C_{11}H_{21}NO_3 + H]^+$ 216.1600, found 216.1602.

4-Amino-2,4-diphenylbutan-2-ol (2e)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.3 (95:5 CH_2Cl_2:MeOH)

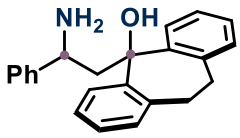
Yield: 85 mg, 70%, *d.r.* = 1:1, (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.56 – 7.18 (m, 9H), 7.13 – 7.08 (m, 1H), 4.73 (s, 3H), 4.08 (dd, *J* = 11.4, 2.3 Hz, 1H), 2.39 – 1.97 (m, 2H), 1.58 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 149.6, 147.4, 143.5, 142.7, 129.4, 129.3, 128.8, 128.6, 128.5, 128.2, 127.1, 127.0, 126.7, 126.2, 125.4, 124.7, 75.9, 74.9, 54.3, 54.1, 48.5, 48.4, 32.7, 28.1.

HRMS (ESI+) calc'd for $[C_{16}H_{19}NO + H]^+$ 242.1539, found 242.1539.

5-(2-Amino-2-phenylethyl)-10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ol (2f)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

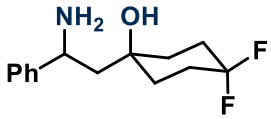
Yield: 113 mg, 69%, (appearance: colorless solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.11 (ddd, *J* = 7.4, 5.7, 1.5 Hz, 2H), 7.31 – 7.02 (m, 11H), 3.67 (s, 3H), 3.56 – 3.42 (m, 2H), 3.30 (dt, *J* = 16.9, 5.0 Hz, 1H), 3.09 – 2.86 (m, 3H), 2.16 (dd, *J* = 14.9, 11.8 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 146.9, 145.7, 145.5, 138.9, 137.1, 131.5, 130.2, 129.1, 127.7, 127.7, 127.5, 127.2, 127.1, 126.6, 126.3, 125.8, 78.7, 54.1, 50.4, 34.6, 33.9.

HRMS (ESI+) calc'd for $[C_{23}H_{23}NO + H]^+$ 330.1860, found 330.1861.

1-(2-Amino-2-phenylethyl)-4,4-difluorocyclohexan-1-ol (2g)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 112 mg, 88%, (appearance: yellow solid)

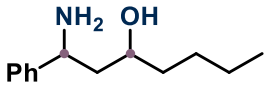
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.42 – 7.25 (m, 5H), 4.35 – 4.10 (m, 1H), 3.74 (s, 3H), 2.30 – 1.83 (m, 6H), 1.75 – 1.49 (m, 4H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 146.6, 129.2, 127.7, 125.9, 124.7 (dd, *J* = 241.7, 238.5 Hz), 69.7 (d, *J* = 1.6 Hz), 53.6 (d, *J* = 2.0 Hz), 47.5, 36.8 (d, *J* = 9.0 Hz), 32.9 (d, *J* = 9.3 Hz), 30.4 – 29.9 (dd, *J* = 25.0, 23.2 Hz), 30.1 – 29.4 (dd, *J* = 25.0, 23.2 Hz).

^{19}F NMR (376 MHz, CD_2Cl_2) δ -98.1 (dd, *J* = 4502.2, 233.4 Hz).

HRMS (ESI+) calc'd for $[C_{14}H_{19}F_2NO + H]^+$ 256.1508, found 256.1507.

1-Amino-1-phenylheptan-3-ol (2h)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

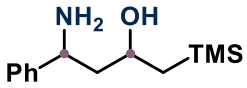
Yield: 66 mg, 64%, *d.r.* = 1.2:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.42 – 7.18 (m, 5H), 4.87 – 4.60 (m, 3H), 4.45 – 4.06 (m, 1H), 3.84 – 3.58 (m, 1H), 1.98 – 1.70 (m, 2H), 1.51 – 1.18 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 143.8, 129.2, 129.0, 127.8, 127.8, 126.6, 126.4, 72.7, 68.8, 53.6, 43.6, 38.3, 37.5, 28.3, 28.1, 23.2, 14.3.

HRMS (ESI+) calc'd for $[C_{13}H_{21}NO + H]^+$ 208.1696, found 208.1697.

4-Amino-4-phenyl-1-(trimethylsilyl)butan-2-ol (2i)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

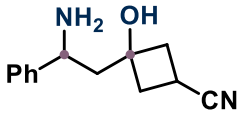
Yield: 93 mg, 80%, *d.r.* = 1.2:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.40 (m, 5H), 5.66 (s, 4H), 4.60 (dd, *J* = 10.7, 2.8 Hz, 1H), 4.00 – 3.84 (m, 1H), 2.16 (m, 1H), 1.86 (m, 1H), 0.99 – 0.69 (m, 2H), -0.08 (s, 9H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 137.4, 136.7, 129.8, 129.8, 129.7, 129.5, 127.4, 127.0, 71.2, 68.0, 57.1, 54.0, 42.4, 40.9, 28.1, 25.7, -1.0, -1.3.

HRMS (ESI+) calc'd for $[C_{13}H_{23}NOSi + H]^+$ 238.1622, found 238.1621.

3-(2-Amino-2-phenylethyl)-3-hydroxycyclobutane-1-carbonitrile (2j)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

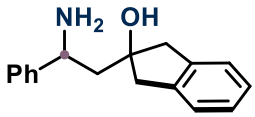
Yield: 66 mg, 61%, *d.r.* = 1.4:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *major diasteromer*) 7.44 – 7.24 (m, 5H), 4.05 (dd, *J* = 11.1, 2.6 Hz, 1H), 3.20 – 3.09 (m, 1H), 2.59 – 2.40 (m, 3H), 2.26 (m, 1H), 2.14 – 1.94 (m, 2H);

^{13}C NMR (101 MHz, CD_2Cl_2, *major diasteromer*) δ 146.6, 129.3, 127.7, 125.7, 123.8, 74.8, 53.7, 47.0, 41.5, 40.8, 15.3.

HRMS (ESI+) calc'd for $[C_{13}H_{16}N_2O + H]^+$ 217.1335, found 217.1336.

1*H*-2-(2-Amino-2-phenylethyl)-2,3-dihydroinden-2-ol (2k)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

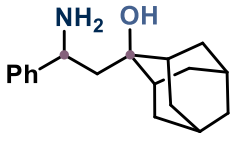
Yield: 93 mg, 74%, (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) 7.39 – 7.11 (m, 9H), 4.36 – 4.18 (m, 4H), 3.11 (d, *J* = 2.6 Hz, 2H), 2.92 (d, *J* = 6.7 Hz, 2H), 2.26 (dd, *J* = 14.6, 11.5 Hz, 1H), 1.92 (dd, *J* = 14.5, 2.4 Hz, 1H).;

^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.4, 141.9, 141.8, 129.3, 128.2, 126.9, 126.8, 126.3, 125.3, 125.1, 82.9, 55.1, 48.9, 46.1, 45.7.

HRMS (ESI+) calc'd for $[C_{17}H_{19}NO + H]^+$ 254.1539, found 254.1536.

2-(2-Amino-2-phenylethyl)adamantan-2-ol (2l)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

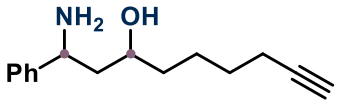
Yield: 56 mg, 41%, (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) 7.40 – 7.18 (m, 5H), 4.09 (dd, *J* = 12.0, 2.3 Hz, 1H), 3.00 (s, 3H), 2.35 (m, 3H), 2.08 (m, 1H), 1.77 (m, 13H);

^{13}C NMR (101 MHz, CD_2Cl_2) δ 148.4, 129.1, 127.3, 125.8, 74.8, 52.7, 44.6, 40.6, 38.9, 36.3, 34.9, 34.9, 33.5, 33.0, 28.3, 28.1.

HRMS (ESI+) calc'd for $[C_{18}H_{25}NO + H]^+$ 272.2009, found 272.2008.

1-Amino-1-phenylnon-8-yn-3-ol (2m)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

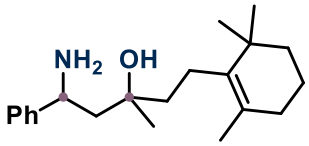
Yield: 88 mg, 77%, *d.r.* = 1.2:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.47 – 7.31 (m, 5H), 5.45 (s, 3H), 4.59 (ddd, *J* = 50.3, 9.4, 2.9 Hz, 1H), 3.84 – 3.61 (m, 1H), 2.29 – 1.80 (m, 5H), 1.49 – 1.16 (m, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 137.4, 136.9, 129.9, 129.8, 129.7, 129.5, 127.4, 126.9, 84.7, 84.6, 72.9, 69.4, 68.7, 68.7, 57.2, 54.1, 39.9, 39.0, 37.7, 36.0, 28.6, 28.5, 24.9, 24.7, 18.5, 18.5.

HRMS (ESI+) calc'd for $[C_{15}H_{21}NO + H]^+$ 232.1696, found 232.1697.

1-Amino-3-methyl-1-phenyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pentan-3-ol (2n)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

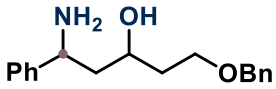
Yield: 126 mg, 81%, *d.r.* = 1:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromer*) 7.5 – 7.2 (m, 5H), 4.2 (dd, *J* = 11.8, 2.5 Hz, 1H), 3.8 (s, 3H), 2.1 – 1.7 (m, 7H), 1.7 – 1.5 (m, 6H), 1.5 – 1.4 (m, 2H), 1.3 (s, 3H), 1.0 (s, 6H).;

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromer*) δ 146.5, 146.4, 137.3, 137.3, 129.2, 129.2, 127.7, 127.3, 127.2, 126.1, 126.0, 73.2, 73.0, 53.9, 53.8, 47.2, 46.8, 45.1, 41.0, 40.3, 35.4, 35.4, 33.2, 33.1, 29.0, 28.9, 28.9, 28.4, 26.0, 24.0, 22.9, 20.1, 20.0, 20.0.

HRMS (ESI+) calc'd for $[C_{21}H_{33}NO + H]^+$ 312.2322, found 312.2321.

1-Amino-5-(benzyloxy)-1-phenylpentan-3-ol (2o)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

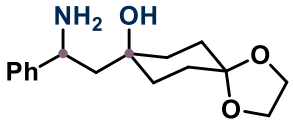
Yield: 115 mg, 68%, *d.r.* = 1:1 (appearance: yellow oil)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromer*) δ 7.40 – 7.22 (m, 10H), 4.56 – 4.45 (m, 2H), 4.35 – 3.88 (m, 2H), 3.68 – 3.55 (m, 2H), 3.23 (s, 3H), 1.85 – 1.67 (m, 4H);

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromer*) δ 146.9, 145.7, 139.2, 139.0, 129.1, 128.9, 128.7, 128.7, 128.0, 128.0, 127.9, 127.8, 127.5, 127.4, 126.5, 126.2, 73.3, 73.3, 70.4, 68.6, 68.0, 67.4, 57.0, 53.4, 44.8, 44.8, 38.3, 37.5.

HRMS (ESI+) calc'd for $[C_{18}H_{23}NO_2 + H]^+$ 286.1800, found 286.1799.

8-(2-Amino-2-phenylethyl)-1,4-dioxaspiro[4.5]decan-8-ol (2p)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale, without H_2SO_4. To maintain the conductivity, 0.2 M NEt_4BF_4 was used.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

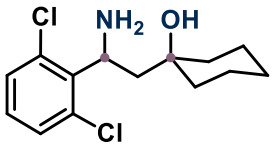
Yield: 96 mg, 70%, (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) 7.4 – 7.3 (m, 5H), 4.8 (s, 3H), 4.4 – 4.3 (m, 1H), 4.0 – 3.8 (m, 4H), 2.1 – 1.5 (m, 10H);

^{13}C NMR (101 MHz, CD_2Cl_2) δ 142.4, 129.5, 128.6, 126.6, 108.9, 71.3, 64.6, 64.6, 46.0, 37.7, 33.2, 30.9, 30.6.

HRMS (ESI+) calc'd for $[C_{16}H_{23}NO_3 + Na]^+$ 278.1751, found 278.1750.

1-(2-Amino-2-(2,6-dichlorophenyl)ethyl)cyclohexan-1-ol (2q)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

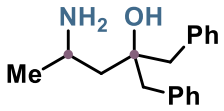
Yield: 136 mg, 94%, (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 5.12 (dd, *J* = 12.2, 2.6 Hz, 1H), 3.33 (s, 3H), 2.25 (dd, *J* = 14.4, 12.2 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.77 – 1.23 (m, 10H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 140.1, 134.6, 130.8, 129.2, 128.8, 71.6, 50.6, 42.7, 40.9, 36.9, 26.6, 23.0, 22.6.

HRMS (ESI+) calc'd for ^{35}Cl isotope $[C_{14}H_{19}Cl_2NO + Na]^+$ 310.0744, found 310.0740.

4-Amino-2-benzyl-1-phenylpentan-2-ol (2r)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale. The amount of applied charge was 20 *F*.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

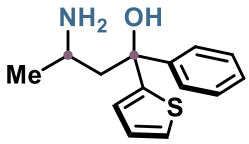
Yield: 73 mg, 54%, (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.41 – 7.16 (m, 10H), 4.84 (s, 3H), 3.58 (dq, *J* = 13.1, 6.8 Hz, 1H), 3.04 – 2.69 (m, 4H), 1.87 – 1.54 (m, 2H), 1.22 (d, *J* = 6.6 Hz, 3H).;

^{13}C NMR (101 MHz, CD_2Cl_2) δ 136.7, 136.3, 131.2, 130.9, 129.1, 128.8, 127.5, 127.3, 75.8, 47.7, 46.7, 45.5, 41.9, 20.8.;

HRMS (ESI+) calc'd for $[C_{18}H_{23}NO + H]^+$ 270.1852, found 270.1852.

2-(3-Amino-1-hydroxy-1-phenylbutyl)thiophene (2s)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale, without NEt_4BF_4. The amount of applied charge was 20 *F*.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 67 mg, 54%, *d.r.* = 1:1 (appearance: yellow solid)

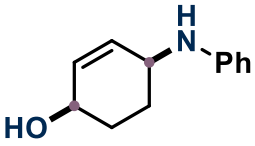
^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromer*) δ 7.69 – 6.74 (m, 8H), 3.74 (s, 3H), 3.19 – 2.75 (m, 1H), 2.47 (dd, *J* = 14.4, 2.2 Hz, 1H), 1.97 (dd, *J* = 14.4, 11.3 Hz, 1H), 1.14 (d, *J* = 6.4 Hz, 3H);

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromer*) δ 155.8, 155.2, 149.2, 147.6, 128.4, 128.3, 127.2, 126.9, 126.5, 126.3, 125.2, 124.3, 123.0, 122.5, 78.1, 77.7, 49.2, 49.1, 46.1, 45.8, 27.5, 27.4;

HRMS (ESI+) calc'd for $[C_{14}H_{17}NOS + H]^+$ 248.1104, found 248.1103.

3.2 Synthesis of 1,4-Amino alcohols

***cis*-4-(Phenylamino)cyclohex-2-en-1-ol (4a)**



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

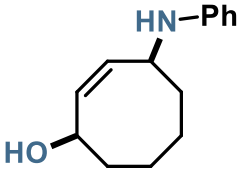
R_f: 0.5 (70:30 Pentane:diethyl ether)

Yield: 77 mg, 81%, (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26 – 7.11 (m, 2H), 6.76 – 6.62 (m, 3H), 5.94 – 5.85 (m, 2H), 4.24 – 4.17 (m, 1H), 3.99 – 3.92 (m, 1H), 3.66 – 3.33 (m, 2H), 1.93 – 1.68 (m, 4H);

^{13}C NMR (101 MHz, CD_2Cl_2) δ 147.2, 132.9, 131.1, 129.7, 118.0, 113.9, 65.4, 48.4, 29.2, 25.1;

***cis*-4-(Phenylamino)cyclooct-2-en-1-ol (4b)**



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (70:30 Pentane:diethyl ether)

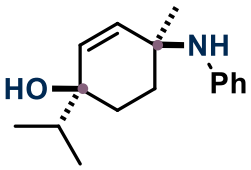
Yield: 100 mg, 92%, (appearance: yellow solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.14 (m, 2H), 6.74 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.69 – 6.59 (m, 2H), 5.70 (ddd, *J* = 10.9, 6.9, 1.5 Hz, 1H), 5.35 (ddd, *J* = 10.9, 8.2, 1.8 Hz, 1H), 4.77 – 4.65 (m, 1H), 4.17 – 4.06 (m, 1H), 3.54 – 3.18 (s, 2H), 2.05 – 1.90 (m, 2H), 1.80 – 1.41 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 135.1, 132.9, 129.2, 117.8, 113.5, 69.8, 51.5, 38.9, 36.6, 24.0, 23.6;

GCMS (EI) calc'd for [$C_{14}H_{19}NO$] 217.1461, found 217.1462.

***cis*-1-Isopropyl-4-methyl-4-(phenylamino)cyclohex-2-en-1-ol (4c)**



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (70:30 Pentane:diethyl ether)

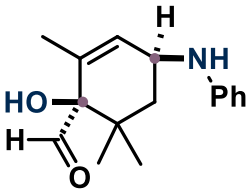
Yield: 109 mg, 89%, (appearance: yellow solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.06 (m, 2H), 6.84 – 6.76 (m, 2H), 6.72 – 6.63 (m, 1H), 5.85 (dd, *J* = 10.2, 1.7 Hz, 1H), 5.63 (dd, *J* = 10.2, 1.8 Hz, 1H), 2.53 (td, *J* = 13.7, 3.9 Hz, 1H), 1.90 – 1.62 (m, 3H), 1.45 (dtd, *J* = 13.2, 3.7, 1.7 Hz, 1H), 1.29 (s, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H).;

^{13}C NMR (101 MHz, CD_2Cl_2) δ 147.0, 139.4, 131.8, 129.2, 117.8, 115.9, 71.4, 38.3, 29.8, 28.6, 27.9, 17.6, 16.5;

GCMS (EI) calc'd for [$C_{16}H_{23}NO$] 245.1774, found 245.1774.

***cis*-1-Hydroxy-2,6,6-trimethyl-4-(phenylamino)cyclohex-2-ene-1-carbaldehyde (4d)**



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (70:30 Pentane:diethyl ether)

Yield: 102 mg, 79%, (appearance: yellow solid)

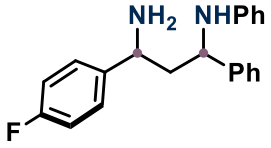
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.27 – 7.13 (m, 2H), 6.75 – 6.60 (m, 3H), 5.95 – 5.89 (m, 1H), 4.22 – 4.12 (m, 1H), 3.72 (s, 2H), 1.96 – 1.83 (m, 1H), 1.73 (dd, *J* = 13.7, 6.9 Hz, 1H), 1.60 (t, *J* = 1.8 Hz, 3H), 1.11 (s, 3H), 0.98 (s, 3H);

^{13}C NMR (101 MHz, CD_2Cl_2) δ 203.6, 147.5, 133.2, 129.8, 129.7, 117.8, 113.6, 83.0, 47.4, 39.8, 37.4, 24.6, 23.9, 18.5.

GCMS (EI) calc'd for [$C_{16}H_{21}NO_2$] 259.1567, found 259.1566.

3.3 Synthesis of 1,3-Diamines

3-(4-Fluorophenyl)-*N*[1],1-diphenylpropane-1,3-diamine (6a)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R$_f$: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 124 mg, 78%, *d.r.* = 1.2:1 (appearance: yellow solid)

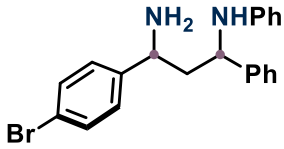
^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.35 – 7.20 (m, 7H), 7.09 – 6.98 (m, 4H), 6.64 – 6.43 (m, 3H), 4.48 – 4.33 (m, 1H), 4.21 – 3.96 (m, 1H), 3.06 (s, 3H), 2.19 – 1.95 (m, 2H).;

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 162.4 (d, *J* = 245.0 Hz), 162.3 (d, *J* = 244.5 Hz), 147.8, 147.7, 144.5, 144.2, 142.0, 129.4, 129.0, 129.0, 128.3 (d, *J* = 6.8 Hz), 128.2 (d, *J* = 6.8 Hz), 127.4, 127.4, 126.9, 126.5, 117.8, 117.5, 115.9, 115.8, 115.7, 115.6, 114.2, 113.7, 57.7, 56.0, 53.1, 47.5;

^{19}F NMR (376 MHz, CD_2Cl_2, *mix diasteromers*) δ -115.9, -116.4.

GCMS (EI) calc'd for [$C_{21}H_{21}FN_2$] 320.1683, found 320.1679.

3-(4-Bromophenyl)-*N*[1],1-diphenylpropane-1,3-diamine (6b)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R$_f$: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 97 mg, 51%, *d.r.* = 1.2:1 (appearance: yellow solid)

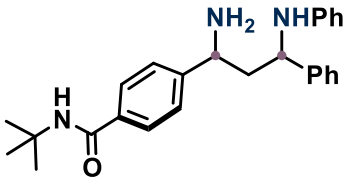
^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.32 (m, 4H), 7.32 – 7.14 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.71 – 6.46 (m, 3H), 5.33 (s, 0.5H), 5.15 (s, 0.5H), 4.53 (s, 1H), 2.11 (s, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 147.7, 144.3, 131.9, 131.9, 129.4, 129.3, 129.0, 128.9, 128.7, 128.6, 127.4, 127.3, 126.8, 126.6, 121.4, 121.0, 117.6, 117.4, 114.1, 113.6, 57.5, 55.9, 54.2, 47.9;

Note: The ^{13}C signal of the carbon para to Br is not visible even after extensive scans.

HRMS (ESI+) calc'd for ^{79}Br isotope $[C_{21}H_{21}BrN_2 + H]^+$ 381.0961, found 381.0960.

4-(1-Amino-3-phenyl-3-(phenylamino)propyl)-*N*-(*tert*-butyl)benzamide (6c)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 190 mg, 95%, *d.r.* = 1.1:1 (appearance: yellow solid)

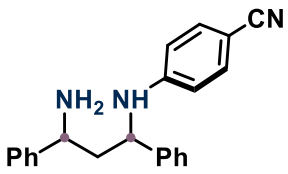
^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.84 (s, 1H), 7.39 – 7.01 (m, 11H), 6.69 – 6.45 (m, 3H), 5.62 (s, 3H), 4.56 – 3.94 (m, 2H), 2.48 – 2.06 (m, 2H), 1.30 (s, 9H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 178.6, 178.5, 147.1, 147.0, 143.2, 142.8, 138.7, 138.3, 135.6, 134.0, 129.4, 129.1, 129.0, 128.2, 128.0, 127.8, 127.6, 126.9, 126.4, 122.5, 122.5, 118.8, 118.3, 115.2, 114.4, 56.6, 55.4, 55.2, 43.4, 42.9, 39.8, 27.6, 27.6;

Note: Some diasteromeric ^{13}C signals are merged into one peak.

HRMS (ESI+) calc'd for $[C_{26}H_{31}N_3O + H]^+$ 402.2540, found 402.2544.

4-((3-Amino-1,3-diphenylpropyl)amino)benzonitrile (6d)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

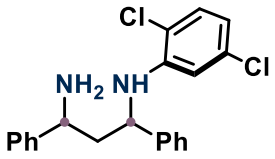
Yield: 116 mg, 71%, *d.r.* = 1.5:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.56 – 7.07 (m, 12H), 6.80 – 5.92 (m, 3H), 4.84 – 3.33 (m, 4H), 2.28 (m, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 151.3, 151.0, 144.2, 143.9, 143.0, 142.4, 133.7, 129.5, 129.3, 129.2, 128.8, 128.2, 127.8, 127.8, 126.8, 126.6, 126.3, 120.8, 113.5, 113.2, 98.6, 98.3, 55.9, 55.7, 45.6;

HRMS (ESI+) calc'd for $[C_{22}H_{21}N_3 + H]^+$ 328.1808, found 328.1811.

N^1-(2,5-Dichlorophenyl)-1,3-diphenylpropane-1,3-diamine (6e)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R$_f$: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 142 mg, 77%, *d.r.* = 1.2:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.42 – 7.23 (m, 10H), 7.19 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.56 (ddd, *J* = 8.4, 7.6, 2.4 Hz, 1H), 6.33 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.61 – 4.36 (m, 1H), 4.17 – 3.91 (m, 1H), 2.55 (s, 2H), 2.34 – 2.11 (m, 2H).

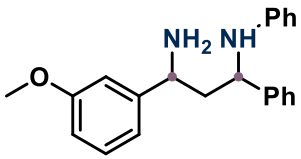
^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 146.2, 144.8, 144.7, 143.3, 142.6, 133.6, 133.5, 130.1, 129.3, 129.2, 129.2, 129.2, 127.9, 127.8, 127.7, 127.6, 126.8, 126.4, 126.4, 126.3, 118.1, 117.8, 117.2, 116.8, 112.7, 112.1, 57.4, 56.2, 54.8, 53.3, 47.5, 46.4;

HRMS (ESI+) calc'd for ^{35}Cl isotopes $[C_{21}H_{20}Cl_2N_2 + H]^+$ 371.1076, found 371.1078.

Note I: ^{1}H signal from N-H proton is not visible due to faster exchange with CD_2Cl_2.

Note II: Some diasteromeric ^{13}C signals are merging into one peak.

3-(3-Methoxyphenyl)-*N*^{1},1-diphenylpropane-1,3-diamine (6f)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R$_f$: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 76 mg, 46%, *d.r.* = 1.2:1 (appearance: yellow solid)

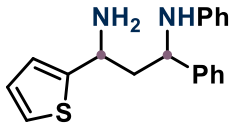
^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.36 – 7.18 (m, 6H), 7.09 – 6.98 (m, 2H), 6.93 – 6.75 (m, 3H), 6.69 – 6.45 (m, 3H), 5.40 (s, 3H), 4.45 – 3.77 (m, 2H), 3.71 (s, 3H), 2.45 – 2.05 (m, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 160.6, 147.3, 147.1, 143.6, 143.5, 143.0, 142.15, 140.9, 130.7, 130.6, 129.4, 129.1, 129.0, 127.7, 127.6, 126.9, 126.5, 119.2, 119.0, 118.4, 118.4, 115.0, 114.8, 114.5, 114.3, 112.6, 112.5, 56.5, 55.6, 55.6, 54.0, 44.2;

HRMS (ESI+) calc'd for $[C_{22}H_{24}N_2O + H]^+$ 333.1961, found 333.1960.

Note: Acetone remains strongly retained due to strong H-bonding interactions with the substrate and could not be completely removed despite repeated exposure to high vacuum.

2-[1-Amino-3-(phenylamino)-3-phenylpropyl]thiophene (6g)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

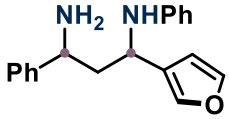
Yield: 106 mg, 69%, *d.r.* = 1.5:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.43 – 7.33 (m, 4H), 7.31 – 7.23 (m, 2H), 7.09 (tt, *J* = 7.4, 0.7 Hz, 2H), 7.02 – 6.89 (m, 2H), 6.64 (m, 1H), 6.53 (m, 2H), 4.56 (dd, *J* = 8.0, 5.6 Hz, 1H), 4.39 – 4.30 (m, 1H), 2.30 – 2.15 (m, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 152.3, 151.9, 148.0, 147.8, 144.7, 144.3, 129.4, 129.3, 129.0, 129.0, 127.4, 127.4, 127.1, 127.1, 126.9, 126.6, 124.0, 123.2, 123.2, 117.5, 117.4, 113.9, 113.6, 57.5, 55.9, 50.9, 49.5, 48.9, 48.3;

GCMS (EI) calc'd for $[C_{19}H_{20}N_2S]$ 308.1342, found 308.1342.

3-[*N*^{1},3-Diphenylpropane-1,3-diamine]furan (6h)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 92 mg, 63%, *d.r.* = 1.1:1 (appearance: yellow solid)

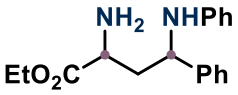
^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.40 – 7.18 (m, 6H), 7.16 – 7.03 (m, 2H), 6.76 – 6.66 (m, 1H), 6.66 – 6.49 (m, 2H), 6.28 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.14 (d, *J* = 3.2 Hz, 1H), 4.54 – 4.31 (m, 4H), 4.19 – 3.92 (m, 1H), 2.38 – 2.16 (m, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 156.0, 155.8, 147.4, 147.3, 143.6, 142.1, 142.0, 129.5, 129.4, 129.3, 128.6, 128.2, 127.0, 126.7, 118.8, 118.5, 114.6, 114.2, 110.5, 110.5, 106.9, 106.4, 54.6, 53.67, 50.7, 49.9, 42.6, 42.4;

HRMS (ESI+) calc'd for $[C_{19}H_{20}N_2O + H]^+$ 293.1648, found 293.1647.

Note: Acetone remains strongly retained due to strong H-bonding interactions with the substrate and could not be completely removed despite repeated exposure to high vacuum.

Ethyl 2-amino-4-phenyl-4-(phenylamino)butanoate (6i)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

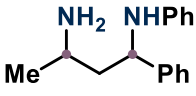
Yield: 120 mg, 80%, *d.r.* = 1:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.47 – 7.34 (m, 4H), 7.30 – 7.24 (m, 1H), 7.13 – 7.03 (m, 2H), 6.67 – 6.51 (m, 3H), 4.69 (dd, *J* = 8.8, 4.7 Hz, 1H), 4.16 (q, *J* = 7.1, 2H), 3.54 (dd, *J* = 9.2, 3.5 Hz, 1H), 2.17 (s, 1H), 2.04 – 1.90 (m, 1H), 1.27 (td, *J* = 7.1, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 176.1, 176.0, 148.2, 147.8, 144.6, 144.0, 129.5, 129.4, 129.3, 129.0, 128.9, 127.5, 127.3, 126.8, 126.7, 117.4, 117.3, 113.8, 113.5, 61.5, 61.4, 57.9, 55.5, 53.8, 52.4, 42.9, 42.9, 14.4;

HRMS (ESI+) calc'd for $[C_{18}H_{22}N_2O_2 + H]^+$ 299.1754, found 299.1751.

***N*^{1},1-Diphenylbutane-1,3-diamine (6j)**



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

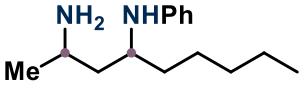
Yield: 71 mg, 59%, *d.r.* = 1.2:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.35 – 7.16 (m, 5H), 7.13 – 7.00 (m, 2H), 6.77 – 6.66 (m, 3H), 5.65 (s, 3H), 4.60 (dd, *J* = 10.7, 3.7 Hz, 1H), 3.75 – 3.53 (m, 1H), 2.24 – 2.10 (m, 1H), 2.04 – 1.85 (m, 1H), 1.36 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 146.6, 146.5, 142.6, 142.0, 129.6, 129.5, 129.3, 129.2, 128.0, 127.9, 126.6, 126.4, 120.0, 119.9, 116.4, 116.1, 58.1, 54.9, 50.1, 48.0, 41.9, 40.4, 19.4, 17.9.

HRMS (ESI+) calc'd for $[C_{16}H_{20}N_2 + H]^+$ 241.1699, found 241.1699.

N^4-Phenylnonane-2,4-diamine (6k)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

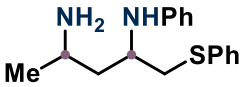
Yield: 65 mg, 55%, *d.r.* = 1.1:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.21 – 7.10 (m, 2H), 6.81 – 6.66 (m, 3H), 6.27 (s, 3H), 3.64 – 3.54 (m, 1H), 3.55 – 3.39 (m, 1H), 1.96 – 1.70 (m, 2H), 1.57 – 1.19 (m, 11H), 0.93 – 0.77 (m, 3H);

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 147.4, 147.4, 129.7, 129.7, 119.4, 119.3, 115.9, 115.4, 54.2, 51.2, 49.6, 47.4, 38.6, 37.3, 35.6, 34.9, 32.1, 32.1, 25.8, 25.6, 22.9, 19.6, 18.6, 14.1, 14.1.

GCMS (EI) calc'd for $[C_{15}H_{26}N_2]$ 234.2090, found 234.2089.

N^2-Phenyl-1-(phenylthio)pentane-2,4-diamine (6l)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

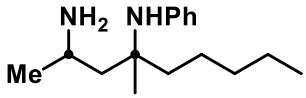
Yield: 112 mg, 79%, *d.r.* = 1.1:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.42 – 7.20 (m, 5H), 7.18 – 7.03 (m, 2H), 6.83 – 6.72 (m, 1H), 6.63 – 6.48 (m, 2H), 6.06 (s, 3H), 3.72 – 3.60 (m, 1H), 3.59 – 3.45 (m, 1H), 3.12 (dd, *J* = 12.1, 3.1 Hz, 1H), 2.73 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.12 (s, 1H), 1.98 – 1.72 (m, 1H), 1.25 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 146.0, 145.9, 135.4, 135.2, 131.2, 131.0, 129.7, 129.7, 129.5, 129.5, 127.4, 127.2, 120.5, 120.4, 116.4, 116.3, 54.0, 50.6, 50.0, 48.1, 38.6, 38.5, 37.0, 35.2, 19.4, 17.7.

HRMS (ESI+) calc'd for $[C_{17}H_{22}N_2S + H]^+$ 287.1577, found 287.1574.

4-Methyl-N^4-phenylnonane-2,4-diamine (6m)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

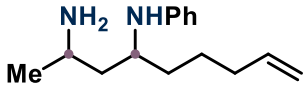
Yield: 89 mg, 72%, *d.r.* = 1.1:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.27 – 7.17 (m, 2H), 7.00 (m, 1H), 6.96 – 6.83 (m, 2H), 5.90 (s, 3H), 3.78 – 3.54 (m, 1H), 1.95 (dd, *J* = 11.8, 3.6 Hz, 1H), 1.71 – 1.60 (m, 1H), 1.57 – 1.06 (m, 14H), 0.86 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 143.6, 143.6, 129.4, 129.3, 123.5, 123.5, 123.2, 58.5, 58.3, 47.3, 47.1, 43.0, 42.4, 40.6, 39.2, 32.5, 32.4, 25.3, 24.6, 24.1, 23.3, 23.0, 22.8, 20.3, 20.3, 14.2, 14.1.

HRMS (ESI+) calc'd for $[C_{16}H_{28}N_2 + H]^+$ 249.2325, found 249.2325.

N^4-Phenylnon-8-ene-2,4-diamine (6n)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

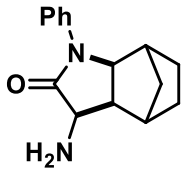
Yield: 78 mg, 67%, *d.r.* = 1.4:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromers*) δ 7.17 (m, 2H), 6.87 – 6.67 (m, 3H), 5.75 (m, 4H), 5.03 – 4.88 (m, 2H), 3.71 – 3.45 (m, 2H), 2.07 – 1.96 (m, 2H), 1.90 – 1.71 (m, 2H), 1.61 – 1.27 (m, 7H);

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromers*) δ 147.1, 147.1, 138.8, 129.8, 129.7, 120.0, 119.8, 116.5, 115.9, 115.0, 114.9, 54.8, 51.3, 50.4, 47.9, 38.0, 36.5, 35.1, 34.5, 33.9, 33.8, 25.3, 25.1, 19.7, 18.2.

HRMS (ESI+) calc'd for $[C_{15}H_{24}N_2 + H]^+$ 233.2012, found 233.2012.

2*H*-3-Amino-1-phenyloctahydro-4,7-methanoindol-2-one (6o)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

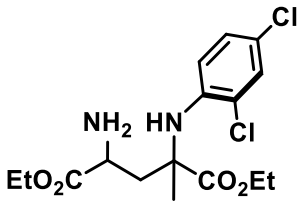
Yield: 81 mg, 67%, *d.r.* = 1.4:1 (appearance: yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *single diasteromer*) δ 7.53 – 7.50 (m, 2H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.26 – 7.15 (m, 1H), 4.03 (d, *J* = 7.6 Hz, 1H), 3.28 (d, *J* = 4.1 Hz, 1H), 2.33 – 2.21 (m, 2H), 2.03 – 1.97 (m, 1H), 1.86 (s, 2H), 1.61 – 1.52 (m, 2H), 1.37 – 1.26 (m, 2H), 1.22 – 1.14 (m, 2H);

^{13}C NMR (101 MHz, CD_2Cl_2, *single diasteromer*) δ 176.3, 138.9, 129.2, 125.7, 123.1, 66.0, 59.3, 48.5, 41.9, 39.1, 32.6, 28.5, 25.6.

HRMS (ESI+) calc'd for $[C_{15}H_{18}N_2O + H]^+$ 243.1492, found 243.1492.

Diethyl 4-amino-2-((2,4-dichlorophenyl)amino)-2-methylpentanedioate (6p)



The title compound was synthesized using GP-5 (condition B) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 127 mg, 68%, *d.r.* = 1:1 (appearance: colorless solid)

^{1}H NMR (400 MHz, CD_2Cl_2, *mix diasteromer*) δ 7.27 (d, *J* = 2.5 Hz, 1H), 7.17 – 6.67 (m, 2H), 6.44 (d, *J* = 8.8 Hz, 1H), 4.27 – 4.07 (m, 4H), 3.60 (dd, *J* = 10.6, 2.7 Hz, 1H), 2.34 (dd, *J* = 14.4, 2.7 Hz, 1H), 2.15 – 1.91 (m, 1H), 1.76 (d, *J* = 10.5 Hz, 1H), 1.60 (s, 3H), 1.30 – 1.17 (m, 6H);

^{13}C NMR (101 MHz, CD_2Cl_2, *mix diasteromer*) δ 175.9, 175.6, 175.4, 174.5, 141.5, 141.1, 129.4, 129.3, 127.5, 127.3, 121.3, 121.2, 121.1, 120.9, 114.1, 113.9, 62.2, 61.9, 61.6, 60.8, 60.3, 51.8, 51.6, 44.0, 42.5, 24.1, 21.8, 14.4, 14.3, 14.3, 14.2.

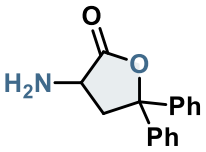
HRMS (ESI+) calc'd for ^{35}Cl isotope $[C_{16}H_{22}Cl_2N_2O_4 + H]^+$ 377.1033, found 377.1037.

Note I: ^{1}H signal from N-H proton is not visible due to intramolecular hydrogen bonding.

4 Product diversifications

The versatility of this protocol has been demonstrated through the modification of 1,3-amino alcohol and 1,3-diamines.

3-Amino-5,5-diphenyloxolan-2-one (7a)



Procedure: A solution of **2a** (60 mg, 0.2 mmol) and *p*-TsOH (52 mg, 0.3 mmol, 1.5 equiv.) in CH_2Cl_2 (3 mL) was refluxed overnight. Once the starting material was consumed, the reaction was cooled back to room temperature. The reaction mixture was basified with aq. saturated $NaHCO_3$ solution and extracted thrice with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporated in *vacuo*. The crude was purified with column chromatography.

R_f: 0.4 (50:50 *n*-Pentane:diethyl ether)

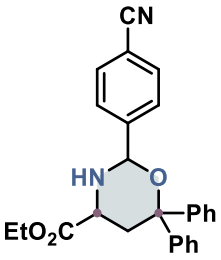
Yield: 31 mg, 61%, (appearance: colorless solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.53 – 7.24 (m, 10H), 3.67 (ddd, *J* = 11.9, 7.7, 1.2 Hz, 1H), 3.40 (ddd, *J* = 12.6, 7.7, 1.2 Hz, 1H), 2.63 – 2.48 (m, 1H), 1.67 (s, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.01, 144.18, 142.80, i129.08, 128.94, 128.32, 128.29, 125.60, 125.57, 86.43, 51.98, 44.84.

HRMS (ESI+) calc'd for $[C_{16}H_{15}NO_2 + H]^+$ 254.1176, found 254.1174.

Ethyl 2-(4-cyanophenyl)-6,6-diphenyl-1,3-oxazinane-4-carboxylate (7b)



Procedure: A solution of **2a** (104 mg, 0.35 mmol), 4-formylbenzonitrile 2.0 equiv.), and AcOH (2-3 drops) in EtOH (3 mL) was refluxed overnight. Once the starting material was consumed, the reaction was cooled back to room temperature. All the volatiles were removed. The reaction mixture was basified with aq. saturated $NaHCO_3$ solution and extracted thrice with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporated in *vacuo*. The crude was purified with column chromatography.

R_f: 0.4 (30:70 *n*-Pentane:diethyl ether)

Yield: 83 mg, 58%, (appearance: colorless solid)

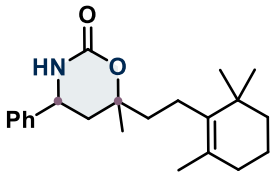
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.76 – 7.66 (m, 2H), 7.59 – 7.12 (m, 12H), 5.31 (s, 1H), 4.32 – 4.17 (m, 2H), 4.09 (d, *J* = 12.3 Hz, 1H), 3.04 (dd, *J* = 14.0, 2.8 Hz, 1H), 2.10 – 1.86 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 147.9, 145.3, 141.5, 132.3, 129.4, 128.4, 127.9, 127.5, 127.2, 127.2, 125.0, 119.0, 112.2, 81.2, 80.7, 61.6, 54.7, 38.9, 14.4.

HRMS (ESI+) calc'd for $[C_{26}H_{24}N_2O_3 + H]^+$ 413.1860, found 413.1860.

Note: Trace amount of diethyl ether remains strongly retained with the product and could not be completely removed despite repeated exposure to high vacuum.

6-Methyl-4-phenyl-6-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl)-1,3-oxazinan-2-one (7c)



Procedure: An oven-dried Schlenk tube was charged with a solution of **2m** (63 mg, 0.2 mmol), CDI (65 mg, 0.4 mmol, 1.5 equiv.) in anhydrous THF (4 mL) under inert condition. The reaction mixture was sealed for reflux at 70 °C overnight. The reaction mixture was washed with NH_4Cl and extracted with EtOAc. The organic phases were collected and washed with Na_2SO_4 followed by evaporating in *vacuo*. The crude was purified with column chromatography.

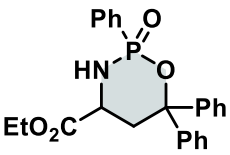
R_f: 0.3 (30:70 *n*-Pentane:diethyl ether)**; Yield**: 55 mg, 54% (appearance: off colorless solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.49 – 7.27 (m, 5H), 5.39 (s, 1H), 4.63 (dd, *J* = 11.9, 4.7 Hz, 1H), 2.21 – 2.08 (m, 3H), 1.97 – 1.88 (m, 3H), 1.84 – 1.74 (m, 2H), 1.65 (s, 3H), 1.63 – 1.56 (m, 3H), 1.49 – 1.44 (m, 2H), 1.42 (s, 3H), 1.04 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 153.6, 141.8, 136.3, 129.4, 128.7, 128.2, 126.6, 81.2, 53.3, 41.1, 40.2, 38.2, 35.4, 33.2, 28.9, 28.7, 26.2, 22.9, 20.0, 19.9.

HRMS (ESI+) calc'd for $[C_{22}H_{31}NO_2 + Na]^+$ 364.2247, found 364.2247.

Ethyl 2,6,6-triphenyl-1,3,2-oxazaphosphinane-4-carboxylate 2-oxide (7d)



Procedure: To a solution of **2a** (104 mg, 0.35 mmol), NEt_3 (2.0 equiv) in THF (5 mL) was added a solution of phenylphosphonic dichloride in THF (1.5 equiv). Once the starting material was consumed, the reaction was quenched with water. The reaction mixture was extracted three times by CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporated in *vacuo*. The crude was purified with column chromatography.

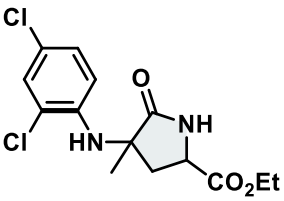
Yield: 46 mg, 54%, (appearance: pale yellow solid)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 2H), 7.75 – 7.64 (m, 2H), 7.51 – 7.38 (m, 5H), 7.35 – 7.27 (m, 5H), 7.25 – 7.21 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.09 (dtt, *J* = 12.2, 4.1, 2.4 Hz, 1H), 3.58 (d, *J* = 8.5 Hz, 1H), 3.22 (dd, *J* = 14.6, 3.8 Hz, 1H), 2.51 (dd, *J* = 14.6, 12.2 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7 (d, *J* = 7.8 Hz), 144.6 (d, *J* = 6.7 Hz), 141.4, 133.9 (d, *J* = 183.7 Hz), 131.8 (d, *J* = 3.2 Hz), 131.4 (d, *J* = 10.9 Hz), 128.9, 128.6, 128.5, 128.1, 128.0, 126.3, 125.4, 87.5 (d, *J* = 9.0 Hz), 62.2, 51.4, 37.8 (d, *J* = 7.7 Hz), 14.3.

HRMS (ESI+) calc'd for $[C_{24}H_{24}NO_4P + Na]^+$ 444.1338, found 444.1335.

Ethyl 4-amino-1-(2,4-dichlorophenyl)-2-methyl-5-oxopyrrolidine-2-carboxylate (7e)



Procedure: A solution of **6p** (76 mg, 0.2 mmol) and trifluoroacetic acid (60 mg, 1.0 mmol, 5.0 equiv.) in CH_2Cl_2 (1 mL) was refluxed overnight. Once the starting material was consumed, the reaction was cooled back to room temperature. The reaction mixture was basified with aq. saturated $NaHCO_3$ solution and extracted thrice with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporated in *vacuo*. The crude was purified with column chromatography.

R_f: 0.4 (100% diethyl ether)

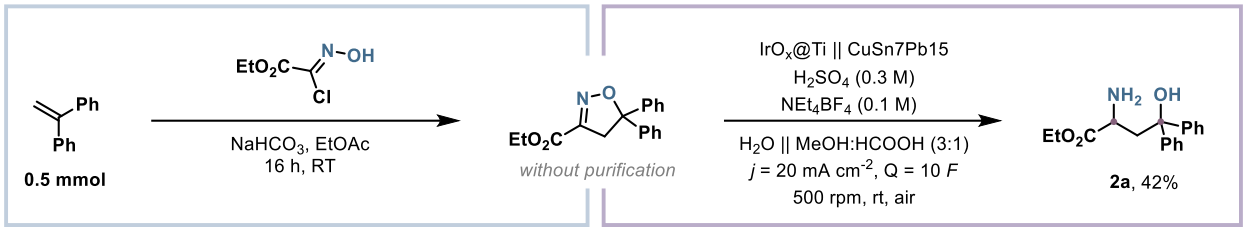
Yield: 48 mg, 74%, (appearance: pale yellow solid)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.29 (d, *J* = 2.5 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.88 (s, 1H), 6.63 (d, *J* = 8.8 Hz, 1H), 4.87 (s, 1H), 4.29 – 4.17 (m, 3H), 2.65 (dd, *J* = 12.9, 7.5 Hz, 1H), 2.47 (dd, *J* = 12.9, 9.1 Hz, 1H), 1.50 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 4H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 177.5, 171.3, 140.1, 129.5, 127.8, 122.4, 121.1, 114.3, 62.3, 59.0, 52.2, 38.1, 22.8, 14.3.

HRMS (ESI+) calc'd for ^{35}Cl isotope $[C_{14}H_{16}Cl_2N_2O_3 + H]^+$ 331.0615, found 331.0612.

5 One-pot synthesis



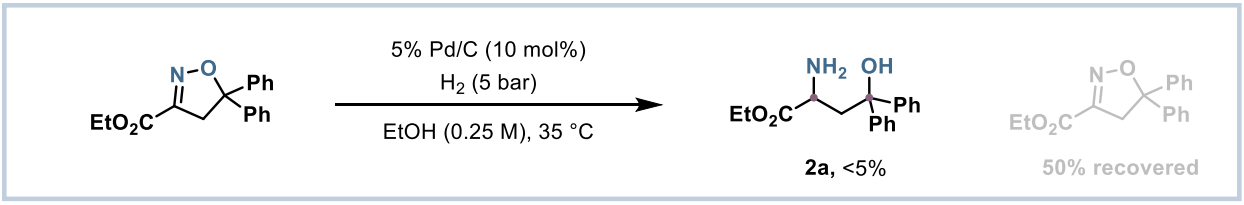
In an oven-dried 10 mL round bottom flask containing PTFE stirrer, ethene-1,1-diyldibenzene (90 mg, 0.5 mmol) and EtOAc (0.15 M) was added. To this mixture, ethyl (*Z*)-2-chloro-2-(hydroxyimino)acetate (151 mg, 2.0 equiv.) and $NaHCO_3$ (126 mg, 3.0 equiv.) were added. The reaction mixture was allowed to stir overnight at room temperature. The reaction mixture was filtered through Celite™ and volatiles were removed under high vacuum. The crude mixture was used in the next step without purification.

The electrochemical cell was set up according to general procedure **GP-1** with the impure mixture in the catholyte, keeping the remaining parameters as it is. After the described workup procedure in **GP-1**, the crude was analyzed using GC-FID. Result: 42% GC yield.

6 Method comparison

To validate and highlight the advantages of the electrochemical approach, comparative experiments were performed using conventional reduction methods.

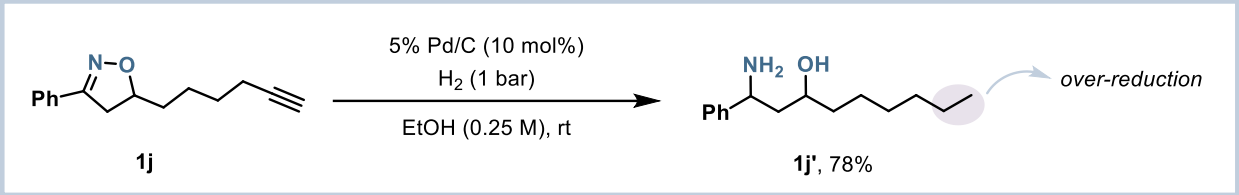
a) Classical hydrogenation (H_2/Pd)



To a 7 ml dram vial equipped with a PTFE-coated stir bar was added **1a** (74.0 mg, 0.25 mmol, 1.0 equiv.) and 10% Pd/C (26.0 mg, 10 mol%), and EtOH (1 mL) was added. The glass vial was placed in a 50 mL stainless-steel autoclave. The autoclave was sealed, pressurized, and depressurized with hydrogen gas three times before the 5 bar pressure was set. The reaction mixture was stirred at 35 °C for overnight. After the

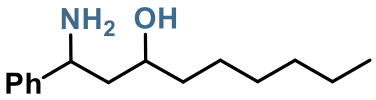
careful depressurization of autoclave, the reaction mixture was filtered through a pad of Celite™. Then, mesitylene (0.25 mmol) was added as GC internal standard and the reaction mixture was analyzed.

Inference and Conclusion: Even with low pressure and temperature, half of the starting material is decomposed, with poor yield. This makes our electrochemical pathway way more productive with better safety and sustainable checkpoints. Additionally, lower conversion might also arise from the two bulky Ph units, causing a hindered approach towards the catalyst surface.



Similarly, another compound **1j'** (0.25 mmol) was used under the classical hydrogenation protocol described before. The desired cleavage was observed, however, the alkyne moiety also got hydrogenated, overall leading to over-reduced product.

1-Amino-1-phenylnonan-3-ol (1j')



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

R_f: 0.5 (95:5 CH_2Cl_2:MeOH)

Yield: 46 mg, 78%, (appearance: yellow oil)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.40 – 7.23 (m, 5H), 4.37 (dd, *J* = 8.4, 3.5 Hz, 0.5H), 4.23 (s, 3H), 4.10 (dd, *J* = 8.8, 5.2 Hz, 0.5H), 3.81 – 3.64 (m, 1H), 1.95 – 1.70 (m, 2H), 1.50 – 1.19 (m, 10H), 0.92 – 0.80 (m, 3H).

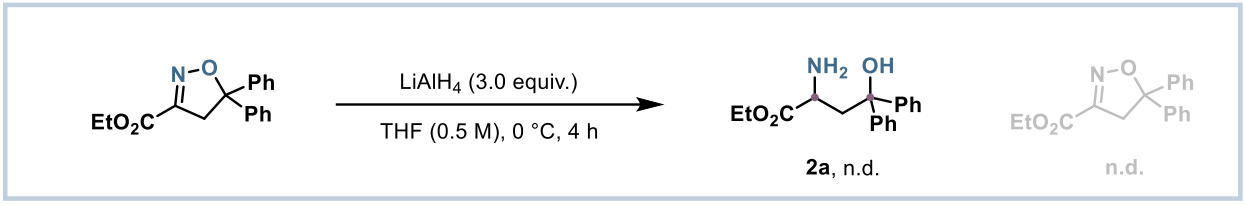
^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.5, 142.8, 128.8, 128.6, 127.5, 127.5, 126.3, 126.0, 72.1, 68.2, 56.6, 53.0, 43.3, 43.0, 38.3, 37.4, 31.9, 31.8, 29.4, 25.7, 25.5, 22.6, 22.6, 13.8.

HRMS (ESI+) calc'd for $[C_{15}H_{25}NO + H]^+$ 236.2009, found 236.2008.

Inference and Conclusion: Thereby, our electrochemical methods provide a controlled and chemoselective reduction platform, where **1j'** was selectively reduced to its amino-alcohol core, with alkyne group intact.

b) Reduction by $LiAlH_4$

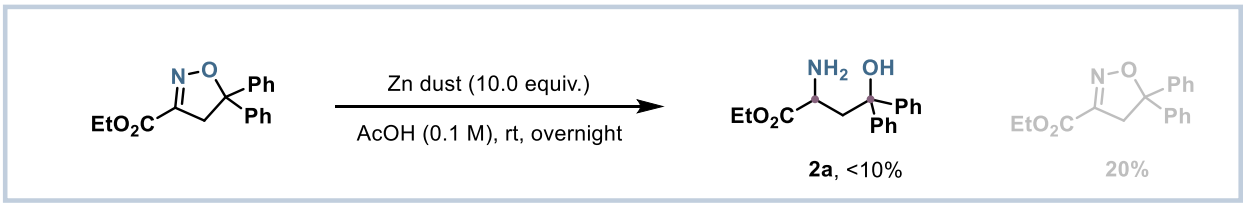
To a 10 mL Schlenk tube equipped with a PTFE-coated stir bar was added **1a** (147 mg, 0.5 mmol, 1.0 equiv.) and THF (5 mL). The solution was cooled to 0 °C and $LiAlH_4$ (57 mg, 1.5 mmol, 3.0 equiv.) was added portion-wise. After stirring for 4 hours at 0 °C, the reaction was quenched with H_2O and diluted with CH_2Cl_2 (5 mL), the fractions were separated and the organic fraction was collected. The aq. fraction was further extracted with CH_2Cl_2 (3 x 3 mL). The combined org. fractions were dried over $MgSO_4$, and filtered. Then, mesitylene (0.5 mmol) was added as GC internal standard and the reaction mixture was analyzed.



Inference and Conclusion: No desired amino alcohol was detected, and the starting material was completely consumed, suggesting the formation of unidentified byproducts or decomposition. The electrochemical pathway is selective towards reducing C=N and N–O bonds.

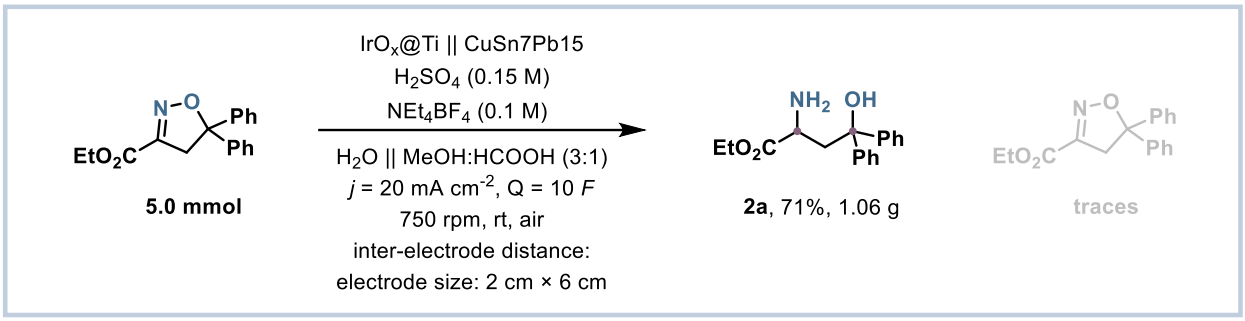
c) Reduction by Zn/AcOH

To a 10 mL Schlenk tube equipped with a PTFE-coated stir bar was added **1a** (147 mg, 0.5 mmol, 1.0 equiv.) and AcOH (5 mL). Then, Zn dust (325 mg, 5 mmol, 10 equiv.) was added portion-wise. The mixture was allowed to stir overnight under room temperature. The reaction was basified to pH 9-10 with $NaHCO_3$, followed by extraction with EtOAc and CH_2Cl_2 consecutively. The combined org. fractions were dried over $MgSO_4$, and filtered. Then, mesitylene (0.5 mmol) was added as GC internal standard and the reaction mixture was analyzed.



Inference and Conclusion: The desired product was obtained in poor yield (<10% GC yield) with surprisingly 80% conversion. This suggests the decomposition of starting material (or intermediate and product) under this condition. The electrochemical condition provides unarguably a better platform for the same transformation.

7 Scale-up in batch



We used the reaction setup as described and shown in **Figure S1**. The anodic compartment was filled with 70 mL H_2O and the cathodic compartment was filled with 70 mL 3:1 MeOH/HCOOH mixture. Then H_2SO_4 (550 µL, 1.0 mmol, 2.0 equiv.) was added to each compartment. In the catholyte, NEt_4BF_4 (1.52 g, 7 mmol, 0.1 M) and substrate (1.47g, 5 mmol) were added. The reaction mixture was allowed to stir at elevated stirring rate (>1000 rpm) for 2 mins for complete homogenization, and then back to 750 rpm for the electrolysis. The electrolysis started using DSA (IrO_x on Ti) as anode and leaded bronze (CuSn7Pb15) as cathode (electrode sizes: 2 cm × 6 cm × 0.3 cm). The current density was set to 20 mA/cm^2 with an amount of applied charge to 4820 C (10 *F*). The reaction was performed at room temperature and constant stirring rate of 750 rpm. After electrolysis, the catholyte was transferred into a separating flask. The catholyte was rinsed with ethyl acetate twice. Then, adequate amount of $NaHCO_3$ was added to neutralize the protonated amines by increasing the pH around 9-10. The basified reaction mixture was extracted two times with EtOAc. A second phase of extraction was performed using CH_2Cl_2 to make sure all the organic materials are collected. Combined organic fractions were dried over Na_2SO_4 and concentrated under vacuum. The crude was purified using column chromatography. Result: 1.06 g isolated yield (71%).

8 Crystal Structures

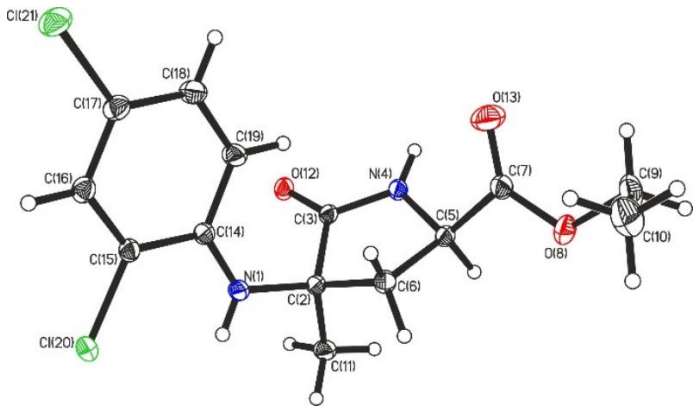


Figure S6. Crystal data and structure refinement for CCDC **2562161**.

CCDC Number	**2562161**	
Empirical formula	**C14 H16 Cl2 N2 O3**	
Formula weight	**331.19**	
Temperature	**100(2) K**	
Wavelength	**0.71073 Å**	
Crystal system	**Monoclinic**	
Space group	**$P2_1/c$; No. 14**	
Unit cell dimensions	**a = 13.1949(15) Å**	**α= 90°.**
	b = 12.6702(14) Å	**β= 99.610(5)°.**
	c = 9.8792(11) Å	**γ = 90°.**
Volume	**1628.4(3) $Å^3$**	
Z	**4**	
Density (calculated)	**1.351 Mg/m^3**	
Absorption coefficient	**0.409 mm^{-1}**	
F(000)	**688**	
Crystal size	**0.275 x 0.200 x 0.050 mm^3**	
Theta range for data collection	**2.24 to 45.41°.**	
Index ranges	**-26<=h<=26, -25<=k<=25, -19<=l<=19**	
Reflections collected	**198068**	
Independent reflections	**13680 [R(int) = 0.0532]**	
Completeness to theta = 25.24°	**99.6 %**	
Absorption correction	**Numerical**	
Max. and min. transmission	**0.98 and 0.90**	

Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**13680 / 14 / 210**
Goodness-of-fit on F^2	**1.015**
Final R indices [I>2sigma(I)]	**R1 = 0.0332, wR2 = 0.0904**
R indices (all data)	**R1 = 0.0463, wR2 = 0.0998**
Largest diff. peak and hole	**0.743 and -0.493 e.Å^{-3}**

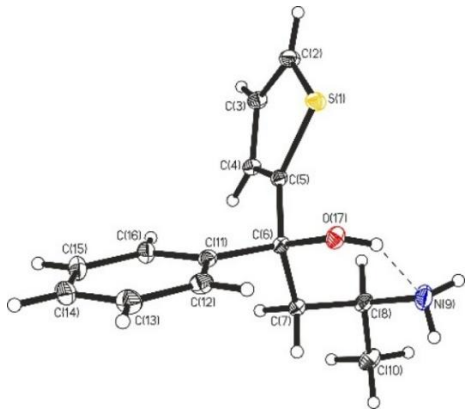


Figure S7. Crystal data and structure refinement for CCDC **2564054**.

CCDC	**2564054**	
Empirical formula	**C14 H17 N O S**	
Formula weight	**247.34**	
Temperature	**85(2) K**	
Wavelength	**0.71073 Å**	
Crystal system	**Orthorhombic**	
Space group	**$Pca2_1$; No. 29**	
Unit cell dimensions	**a = 14.6094(4) Å**	**α= 90°.**
	b = 5.9626(2) Å	**β= 90°.**
	c = 28.8704(8) Å	**γ = 90°.**
Volume	**2514.90(13) Å^3**	
Z	**8**	
Density (calculated)	**1.307 Mg/m^3**	
Absorption coefficient	**0.240 mm^{-1}**	
F(000)	**1056**	
Crystal size	**0.139 x 0.093 x 0.083 mm^3**	
Theta range for data collection	**2.79 to 36.37°.**	

Index ranges	**-24<=h<=24, -9<=k<=9, -48<=l<=48**
Reflections collected	**257002**
Independent reflections	**12223 [R(int) = 0.0477]**
Completeness to theta = 25.24°	**100.0 %**
Absorption correction	**Semi-empirical from equivalents**
Max. and min. transmission	**0.98 and 0.91**
Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**12223 / 7 / 324**
Goodness-of-fit on F^2	**1.152**
Final R indices [I>2sigma(I)]	**R1 = 0.0421, wR2 = 0.1137**
R indices (all data)	**R1 = 0.0427, wR2 = 0.1141**
Absolute structure parameter	**0.69(5)**
Largest diff. peak and hole	**1.627 and -0.336 e.Å^{-3}**

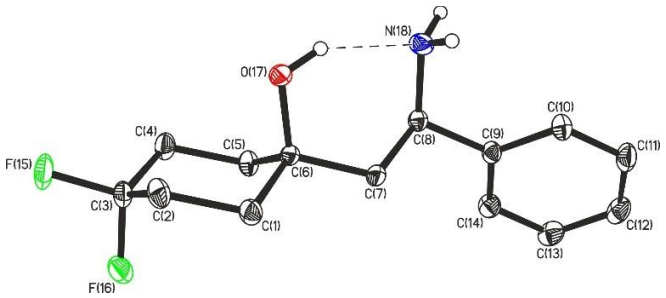
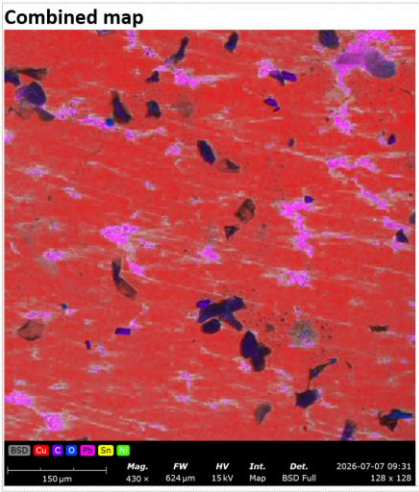


Figure S8. Crystal data and structure refinement for CCDC **2562162**.

CCDC	**2562162**	
Empirical formula	**C14 H19 F2 N O**	
Formula weight	**255.30**	
Temperature	**100(2) K**	
Wavelength	**0.71073 Å**	
Crystal system	**Monoclinic**	
Space group	**$P2_1/c$; No. 14**	
Unit cell dimensions	**a = 7.0917(15) Å**	**α= 90°.**
	b = 20.475(4) Å	**β= 102.129(7)°.**
	c = 9.212(2) Å	**γ = 90°.**
Volume	**1307.7(5) Å^3**	
Z	**4**	
Density (calculated)	**1.297 Mg/m^3**	
Absorption coefficient	**0.100 mm^{-1}**	

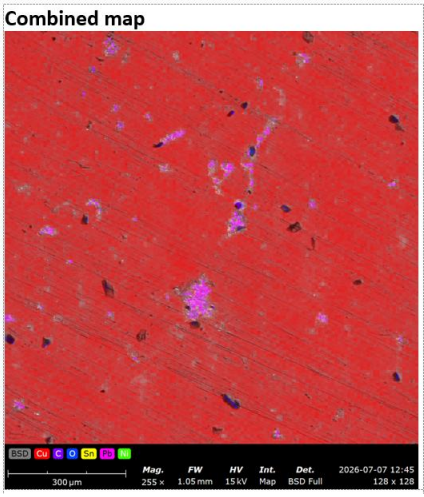
F(000)	**544**
Crystal size	**0.247 x 0.118 x 0.090 mm^3**
Theta range for data collection	**1.99 to 45.42°.**
Index ranges	**-14<=h<=14, -40<=k<=40, -18<=l<=18**
Reflections collected	**109077**
Independent reflections	**10962 [R(int) = 0.0428]**
Completeness to theta = 25.24°	**99.4 %**
Absorption correction	**Numerical**
Max. and min. transmission	**0.99 and 0.94**
Refinement method	**Full-matrix least-squares on F^2**
Data / restraints / parameters	**10962 / 1 / 172**
Goodness-of-fit on F^2	**1.037**
Final R indices [I>2sigma(I)]	**R1 = 0.0395, wR2 = 0.1146**
R indices (all data)	**R1 = 0.0514, wR2 = 0.1248**
Largest diff. peak and hole	**0.621 and -0.298 e.$Å^{-3}$**

9 Surface analysis



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
29	Cu	Copper	40.22	57.67
6	C	Carbon	34.79	9.43
8	O	Oxygen	17.77	6.41
82	Pb	Lead	4.10	19.15
50	Sn	Tin	2.36	6.33
28	Ni	Nickel	0.76	1.01

Figure S9. CuSn7Pb15 electrode as received (*closest to the bulk alloy*)



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
29	Cu	Copper	43.43	68.01
6	C	Carbon	39.31	11.64
8	O	Oxygen	12.38	4.88
50	Sn	Tin	2.62	7.66
82	Pb	Lead	1.24	6.34
28	Ni	Nickel	1.02	1.47

Figure S10. CuSn7Pb15 electrode after 7 consecutive electrolysis

Conclusion: EDS elemental mapping revealed that the Cu-rich matrix and the distribution of Sn remained largely unchanged after 7 consecutive electrolysis runs. Pb-rich inclusions were still observed after electrolysis, indicating that the heterogeneous microstructure of the CuSn7Pb15 alloy was largely preserved. Quantitative EDS of the mapped region showed an apparent lower Pb content after electrolysis. Because Pb is distributed as discrete segregated inclusions in leaded bronze, this decrease may partly arise from local sampling of different microstructural regions. Nevertheless, partial surface depletion of Pb during electrolysis cannot be excluded.[13]

10 Mechanistic studies

10.1 Cyclic voltammetry

In the first part, we investigated the behavior of CuSn7Pb15 as working electrode (with methanol and NBu_4BF_4). We used Ag/AgCl reference electrode and glassy carbon rod counter electrode.

1. First, the blank runs were conducted with both glassy carbon and CuSn7Pb15 as working electrode. A reversible wave was observed in the case of CuSn7Pb15 around -0.34 V (*vs* Ag/AgCl).

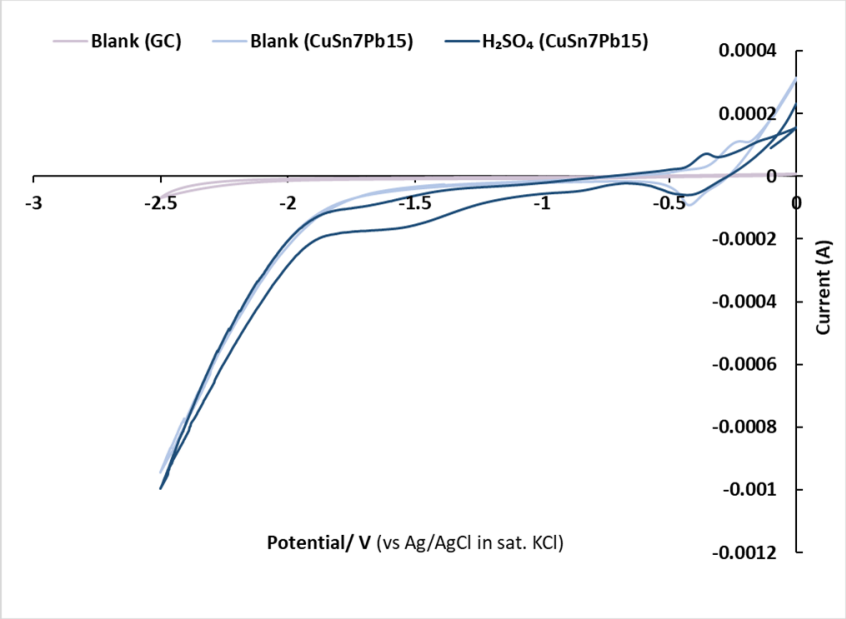


Figure S11. Blank run with GC and CuSn7Pb15 electrodes.

2. Next, different substrates with varied α-substitutions were tested with glassy carbon as working electrode. This cyclic voltammogram further supports the low productivity observed in the case of **A,** where no reduction wave was observed under the applied voltage regime. When the Me group was replaced by either ester or Ph substituents (**B**, **C**, and **D**), reduction waves were observed. The amino alcohol precursors (**B** and **C**) show lower reduction potential than diamine precursor **D**. This is also experimentally observed where a slightly higher amount of applied charge was used for diamine synthesis.

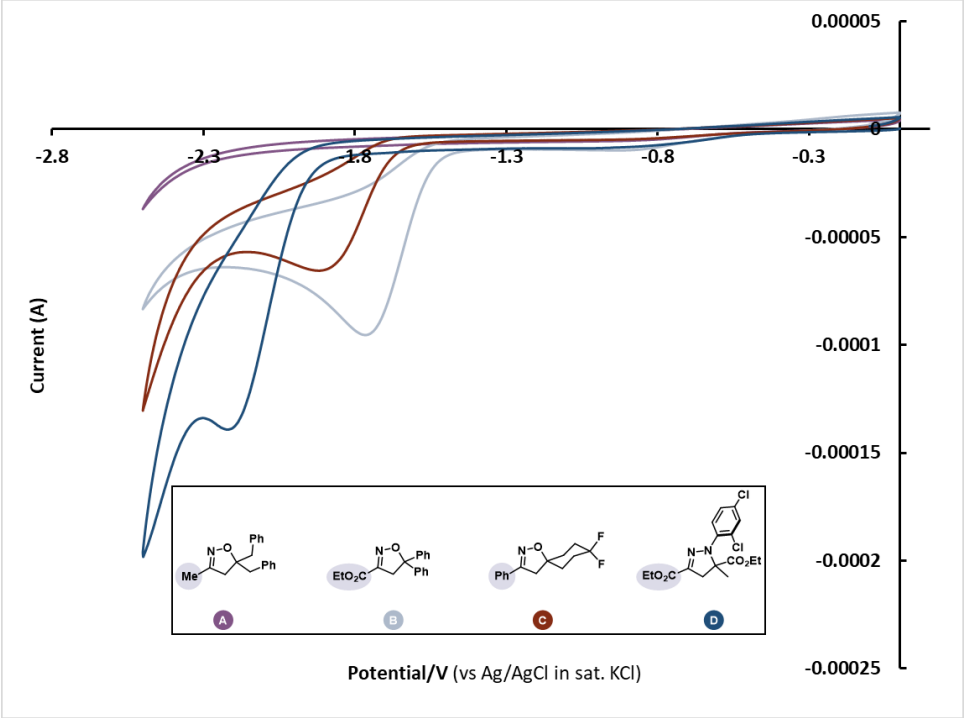


Figure S12. Cyclic voltammetry for various substrates under reductive condition.

3. The role of H_2SO_4 was also checked with **B**. The onset of reduction wave shifted to the right side upon the addition of H_2SO_4 (–1.3 V *vs* Ag/AgCl), owing the protonation of imine N. In absence of acid, the reduction potential was measured to be –1.5 V *vs* Ag/AgCl.

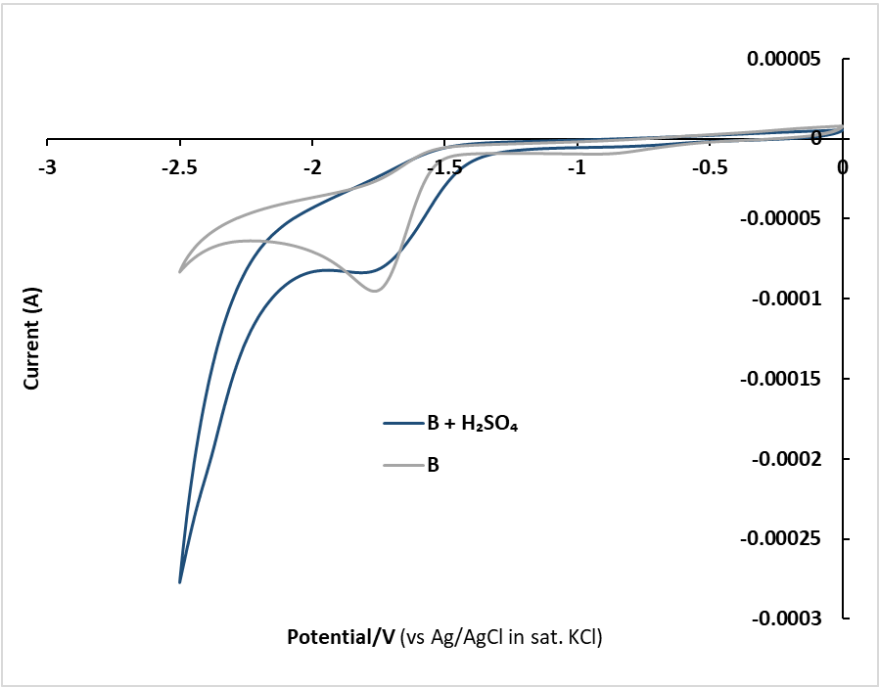
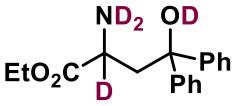


Figure S13. Influence of acid on reductive waves.

10.2 Deuteration studies

Ethyl 2-(amino-*d*2)-4-(hydroxy-*d*)-4,4-diphenylbutanoate-2-*d* (8)



The title compound was synthesized with **1c** using GP-4 (condition A) on 0.5 mmol scale. All the H sources were replaced by D source in the protocol (MeOD, D_2SO_4, D_2O, DCOOD)

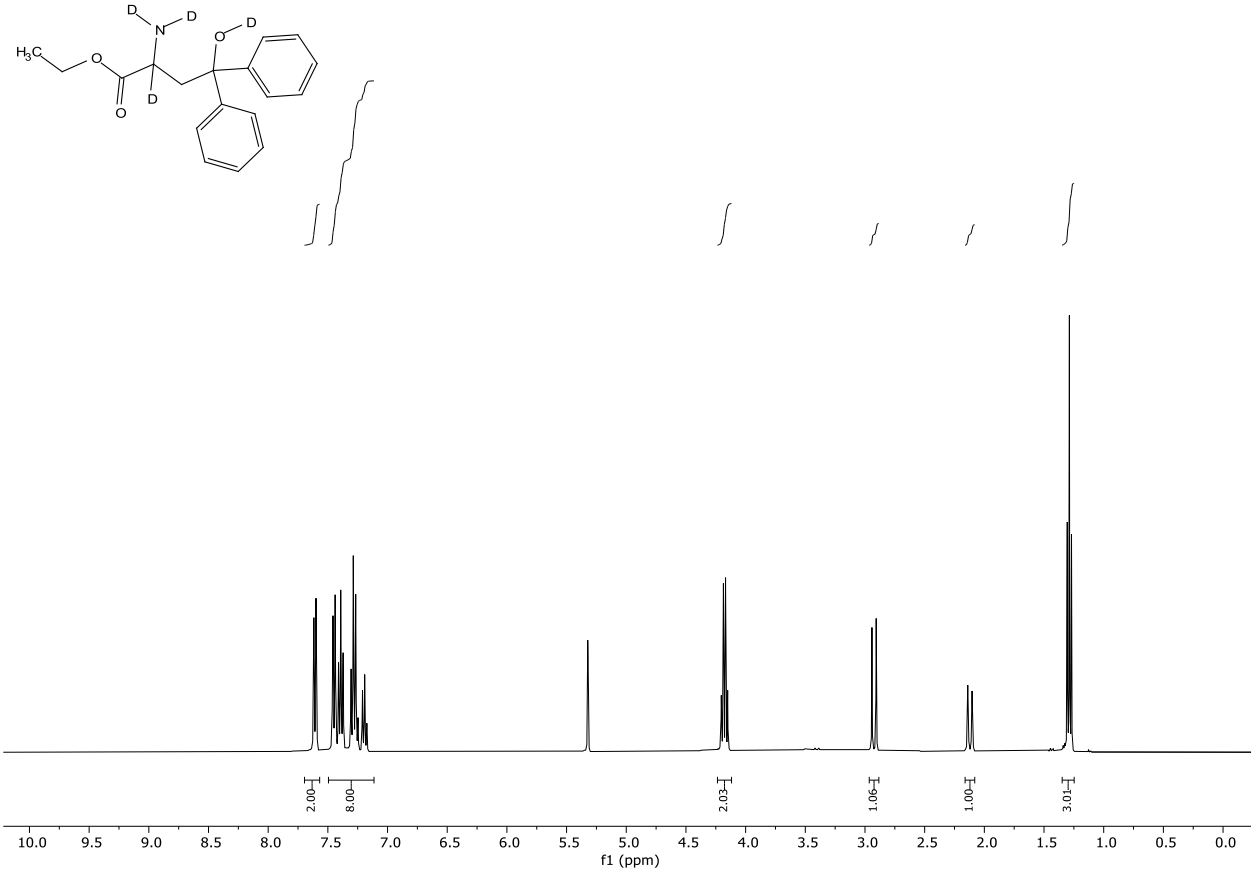
R_f: 0.8 (80:20 pentane:diethyl ether)

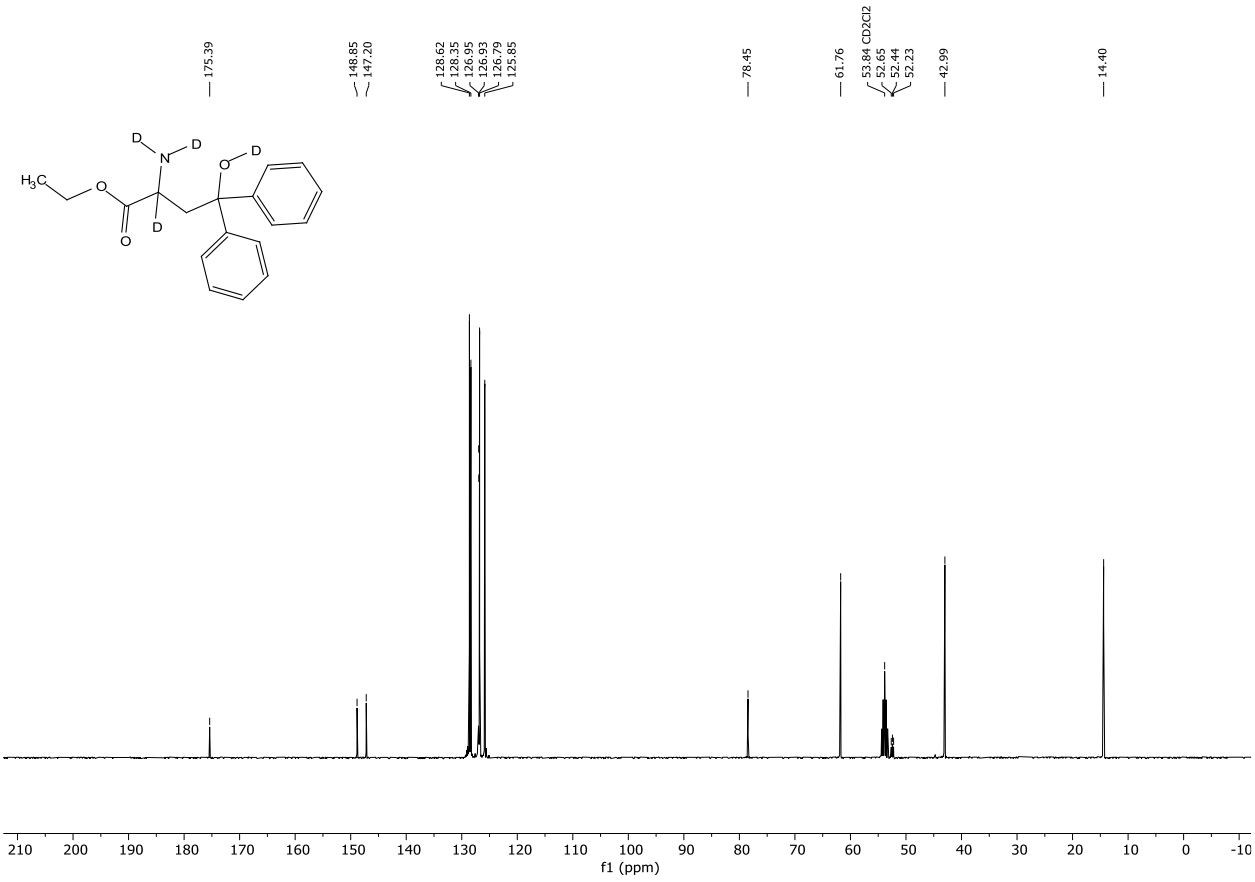
Yield: 107 mg, 71%

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 – 7.57 (m, 2H), 7.49 – 7.11 (m, 8H), 4.24 – 4.12 (m, 2H), 2.92 (d, *J* = 14.2 Hz, 1H), 2.12 (d, *J* = 14.3 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

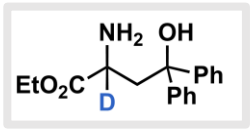
^{13}C NMR (101 MHz, CD_2Cl_2) δ 175.4, 148.9, 147.2, 128.6, 128.4, 126.9, 126.9, 126.8, 125.9, 78.4, 61.8, 52.4 (t, *J* = 21.0 Hz), 43.0, 14.4.

GCMS(EI) m/z: calc'd for $C_9H_8ND_3$ 136.1074; found 136.1075.





Furthermore, the source of protons was investigated by introducing one deuterated parameter at a time and keeping every other as normal H-source. For this, the incorporation was calculated for the proton *α* to the N.

	Source	Incorporation (%)
	D_2O *in anolyte*	20
	D_2SO_4 *in both compartments*	10
	CD_3OD *in catholyte*	66
	DCOOD *in catholyte*	28

10.3 Kinetic study

We used the reaction setup as described and shown in **Figure S1**. Respective anolyte and catholyte stock solutions were prepared.

***Anolyte stock solution**:* 825 µL of H_2SO_4 was dissolved in 105 mL of H_2O. This gives 0.15 M concentration.

***Catholyte stock solution**:* 2.21 g of **1a'** and 2.28 g NEt_4BF_4 was dissolved in 105 mL 3:1 MeOH/HCOOH mixture. 825 µL of H_2SO_4 was added subsequently. The mixture was vigorously stirred for proper homogenization.

10 divided electrochemical cell set-ups were prepared according to **GP-1**. 10 reactions were simultaneously placed with 1*F*, 2*F*, 3*F*, 4*F*, 5*F*, 6*F*, 7*F*, 8*F*, 10*F*, and 12*F* amount of applied charge respectively. After the workup process, each reaction mixture was subjected to GC-FID analysis.

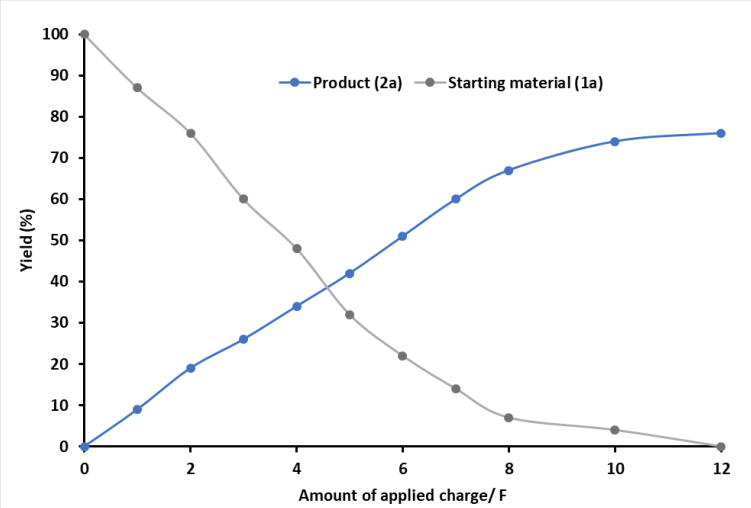
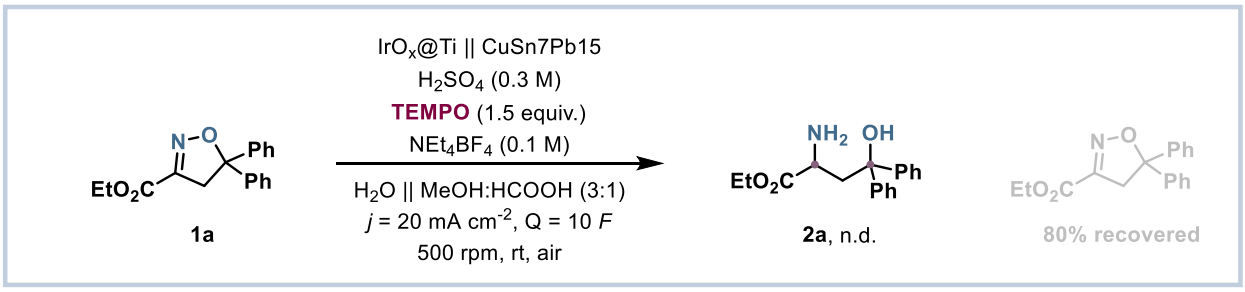


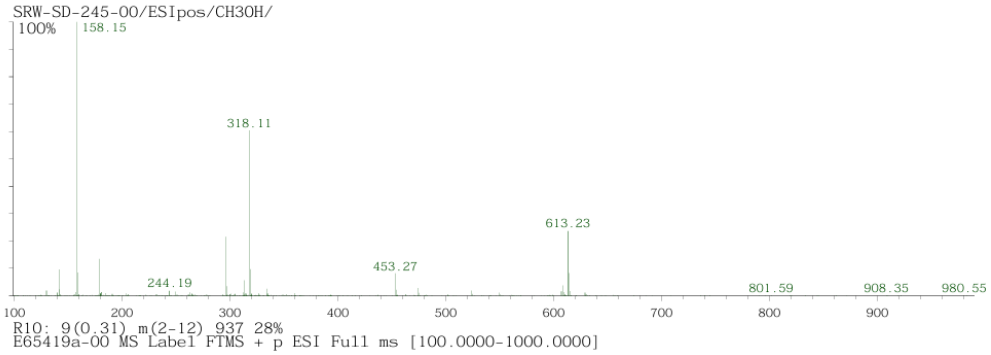
Figure S14. Reaction kinetics of **1a**.

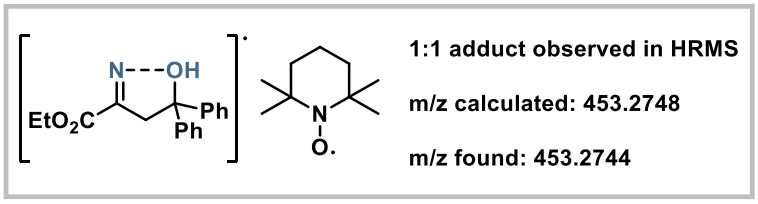
10.4 TEMPO-trapping experiment

We used the reaction setup as described and shown in **Figure S1**. The anodic compartment was filled with 7 mL H_2O and the cathodic compartment was filled with 7 mL 3:1 MeOH/HCOOH mixture (*condition A*). Then H_2SO_4 (55 µL, 1.0 mmol, 2.0 equiv.) was added to each compartment. In the catholyte, NEt_4BF_4 (0.7 mmol, 0.1 M), **1a** (0.5 mmol), and TEMPO (117 mg, 1.5 equiv.) were added. The reaction mixture was allowed to stir at elevated stirring rate for 2 mins for complete homogenization. The electrolysis was started using DSA (IrO_x on Ti) as anode and CuSn7Pb15 as cathode. The current density was set to 20 mA/cm^2 with an amount of applied charge to 482 C (10 *F*). After electrolysis, the catholyte was transferred into a 50 mL centrifuge tube. The catholyte was rinsed with ethyl acetate twice. Then, adequate amount of $NaHCO_3$ was added to neutralize the protonated amines by increasing the pH around 9-10. The basified reaction mixture was extracted two times with EtOAc. A second phase of extraction was performed using CH_2Cl_2 to make sure all the organic materials are collected. The combined organics were analyzed using GC-MS and HRMS.

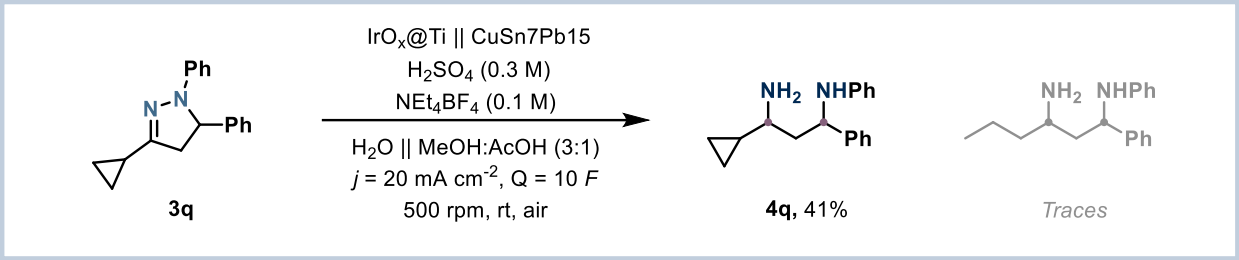


Results: TEMPO-adduct observed with partially reduced **1a'**.



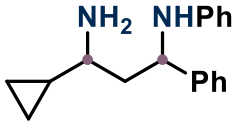


10.5 Radical clock experiment



We used the reaction setup as described and shown in **Figure S1**. The anodic compartment was filled with 7 mL H_2O and the cathodic compartment was filled with 7 mL 3:1 MeOH/AcOH mixture (*condition B*). Then H_2SO_4 (55 µL, 1.0 mmol, 2.0 equiv.) was added to each compartment. In the catholyte, NEt_4BF_4 (0.7 mmol, 0.1 M), and **3q** (0.5 mmol). The reaction mixture was allowed to stir at elevated stirring rate for 2 mins for complete homogenization. The electrolysis was started using DSA (IrO_x on Ti) as anode and CuSn7Pb15 as cathode. The current density was set to 20 mA/cm^2 with an amount of applied charge to 482 C (10 *F*). After electrolysis, the catholyte was transferred into a 50 mL centrifuge tube. The catholyte was rinsed with ethyl acetate twice. Then, adequate amount of $NaHCO_3$ was added neutralize the protonated amines by increasing the pH around 9-10. The basified reaction mixture was extracted two times with EtOAc. A second phase of extraction was performed using CH_2Cl_2 to make sure all the organic materials are collected.

3-Cyclopropyl-*N*^{1},1-diphenylpropane-1,3-diamine (4q)



The title compound was synthesized using GP-4 (condition A) on 0.5 mmol scale.

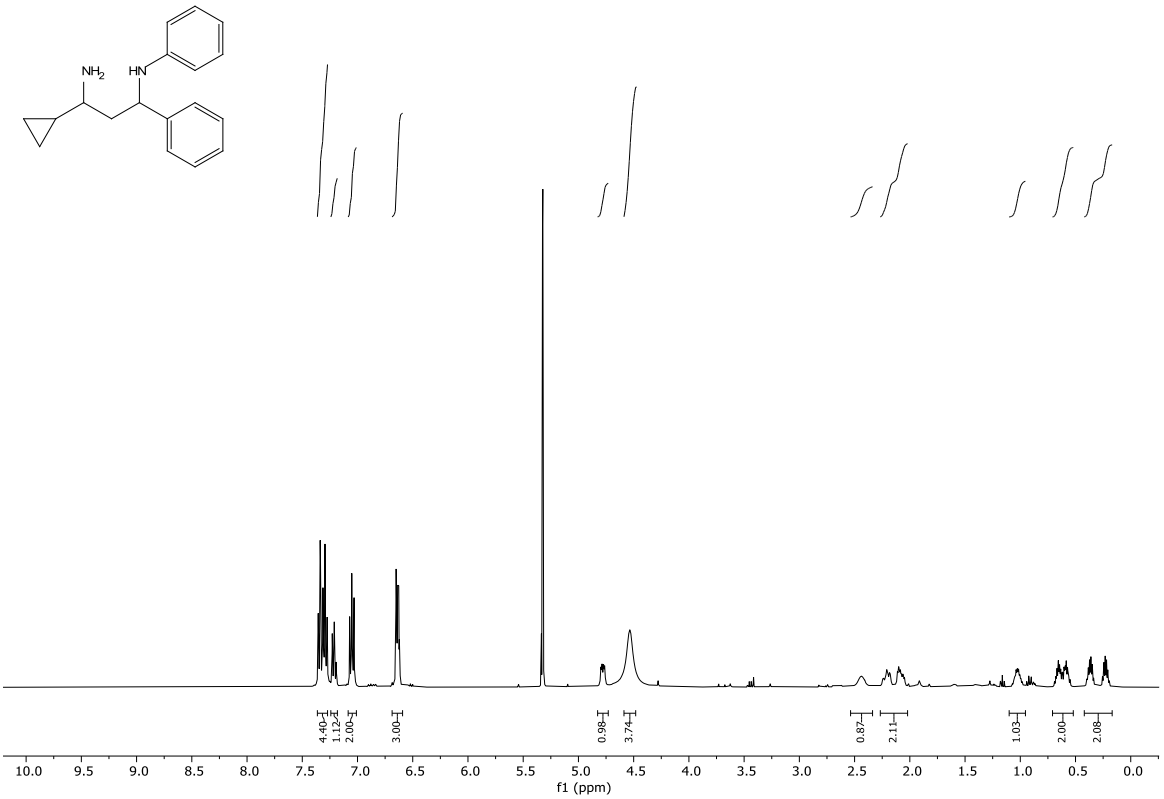
R$_f$: 0.5 (95:5 CH_2Cl_2:MeOH)

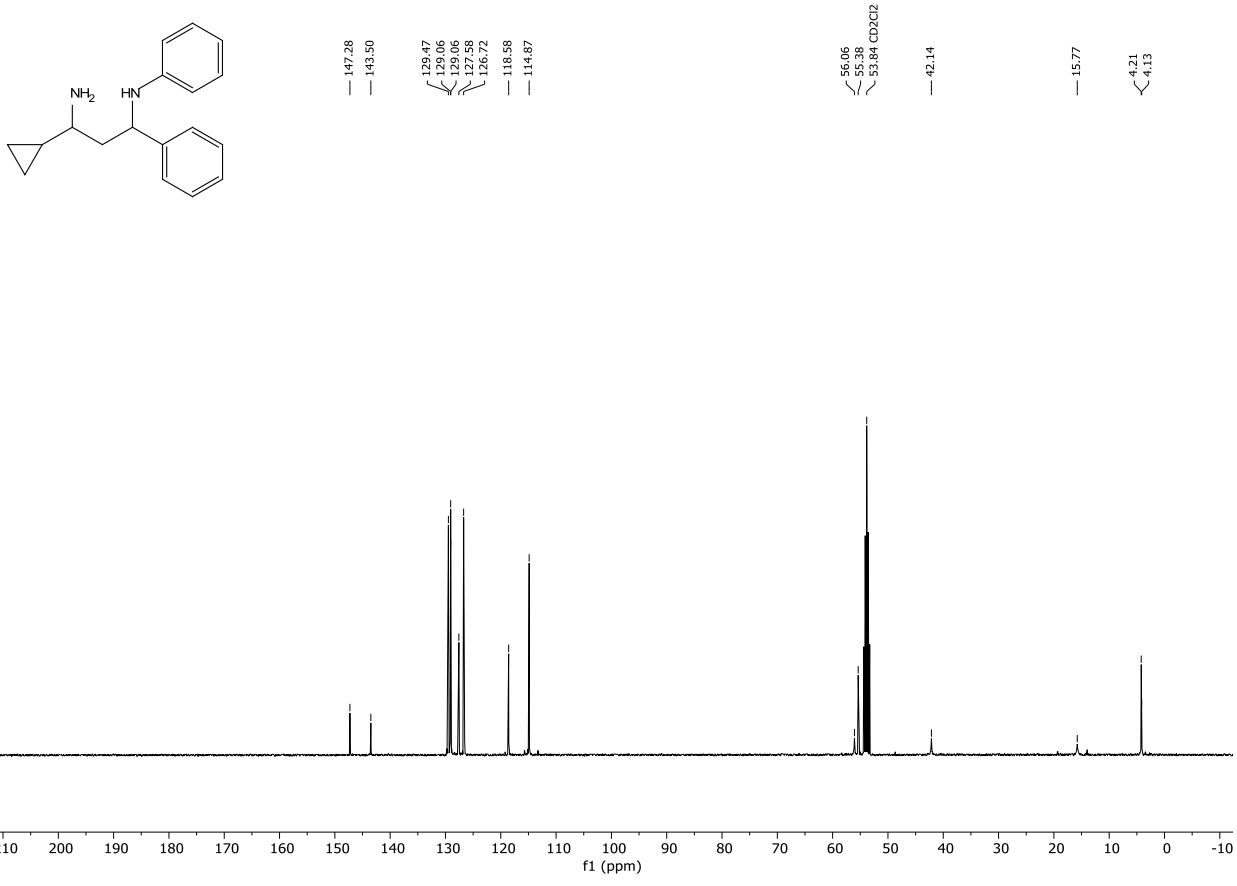
Yield: 53 mg, 41%, (appearance: yellow oil)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.27 (m, 4H), 7.24 – 7.18 (m, 1H), 7.08 – 7.01 (m, 2H), 6.69 – 6.59 (m, 3H), 4.78 (dd, *J* = 9.7, 4.2 Hz, 1H), 4.54 (s, 4H), 2.44 (s, 1H), 2.27 – 2.02 (m, 2H), 1.10 – 0.95 (m, 1H), 0.71 – 0.52 (m, 2H), 0.42 – 0.17 (m, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 147.3, 143.5, 129.5, 129.2 – 129.0 (m), 127.6, 126.7, 118.6, 114.9, 56.1, 55.4, 42.1, 15.8, 4.2, 4.1.

HRMS (ESI+) calc'd for $[C_{18}H_{22}N_2 + H]^+$ 267.1856, found 276.1856.


NH2
HN
4.40
1.12
2.00
3.00
0.98
3.74
0.87
2.11
1.03
2.00
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


NH2
HN
147.28
143.50
129.47
129.06
129.06
127.58
126.72
118.58
114.87
56.06
55.38
53.84 CD2Cl2
42.14
15.77
4.21
4.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

10.6 Reusability and reproducibility study

***Anolyte stock solution**:* 412 µL of H_2SO_4 was dissolved in 52 mL of H_2O. This gives 0.15 M concentration.

***Catholyte stock solution**:* 1.105 g of **1a'** and 1.14 g NEt_4BF_4 was dissolved in 52 mL 3:1 MeOH/HCOOH mixture. 412 µL of H_2SO_4 was added subsequently. The mixture was vigorously stirred for proper homogenization.

To evaluate the reusability of the components, reactions with **1a** were carried out consecutively 7 times using one set of electrode pair. The electrolyses were performed sequentially without opening the batch-type cell. However, after 4th cycle, yield started dropping and required surface polishing. As per observation, the following cycles (5th onwards) showed enhanced yields.

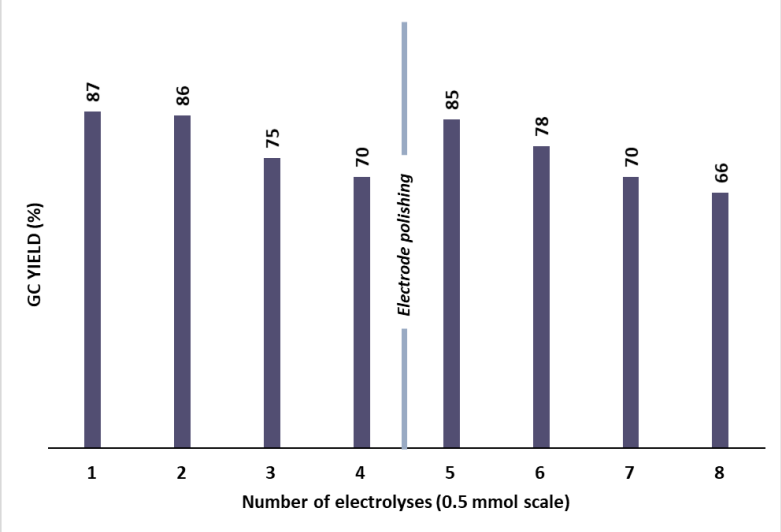


Figure S15: Reusability and reproducibility study of the reaction of **1a** in batch cell setup.

The results demonstrate that all components of the electrolyzer can be reused over multiple reaction cycles. If a noticeable decline in yield is observed, simple polishing of the electrode surface with sandpaper or light milling readily restores its performance.

10.7 DFT Studies

Computational Details

All quantum-chemical calculations were performed using ORCA version 6.1.1.[14] Geometry optimizations and vibrational frequency calculations were carried out at the B3LYP-D3(BJ)/cc-pVTZ level of theory. Tight self-consistent-field convergence criteria were applied throughout. All investigated species were optimized independently in their respective charge and spin states at the same level of theory.

Solvent effects were treated using a cluster–continuum approach. Three methanol molecules were included explicitly in each molecular model, while the remaining bulk solvent environment was represented by the SMD implicit solvation model for methanol, as implemented through the CPCM framework in ORCA.

Generation of Micro-solvated Structures and Conformational Sampling

Initial micro-solvated structures were generated using the SOLVATOR module implemented in ORCA 6.1.1. Three explicit methanol molecules were automatically placed around each solute at the GFN2-xTB/ALPB(MeOH) level of theory.

The resulting micro-solvated clusters were subsequently subjected to conformational sampling using the Global Optimization Algorithm (GOAT) at the GFN2-xTB/ALPB(MeOH) level of theory.[15] The GOAT conformer energy window was set to 10.0 kcal mol^{-1} relative to the lowest-energy structure. An automatic ellipsoidal wall potential was applied during the conformational search to prevent dissociation of the micro-solvated clusters and to retain the explicit methanol molecules in the vicinity of the solute.

The GFN2-xTB/ALPB (MeOH) energies obtained during the SOLVATOR and GOAT calculations were used exclusively for conformational prescreening. All energies entering the final Gibbs free-energy profile were obtained from the subsequent DFT calculations.

Vibrational Frequency Calculations and Thermochemistry

For each investigated species, the lowest-energy structure identified in the corresponding GOAT ensemble was selected for subsequent DFT refinement. The selected clusters were fully reoptimized and characterized by vibrational frequency calculations at the B3LYP-D3(BJ)/cc-pVTZ/SMD (MeOH) level of theory.[16] The three explicit methanol molecules were retained during the final geometry optimizations and frequency calculations. All structures were checked for imaginary frequencies to assign them as real minima. Thermochemical quantities were evaluated at 298.15 K and 1 atm. Low-frequency vibrational modes were treated using the quasi-rigid-rotor harmonic-oscillator treatment implemented in ORCA.

The Gibbs free energy of each microsolvated cluster was taken from the calculation output "Final Gibbs free energy".

For the balanced proton-transfer reactions considered herein, the number of independently treated molecular species was identical on both sides of the reaction. Therefore, the proton transfer couple H_2SO_4/HSO_4^- was calculated at the same level of theory and used to take the proton transfer in account.

Calculation of Reduction Potentials

Reduction potentials were calculated from the Gibbs free-energy differences between the independently optimized oxidized and reduced states. Division by the Faraday constant results in the potential of the reduction that is then referenced against the standard hydrogen electrode (SHE) which is referenced against Ag/AgCl ($E_{1/2}^{0,SHE} = 4.281\ V;\ E_{1/2}^{0,Ag/AgCl} = 0.197\ V$).[17] Therefore, the values can be compared with the data acquired by cyclic voltammetry measurements.

$$E_{red}^{0} = \frac{\Delta G_{reduced\ species} - \Delta G_{oxidized\ species}}{-96.485 \frac{kJ}{mol \cdot V}} - E_{1/2}^{0,SHE} + E_{1/2}^{0,Ag/AgCl}$$

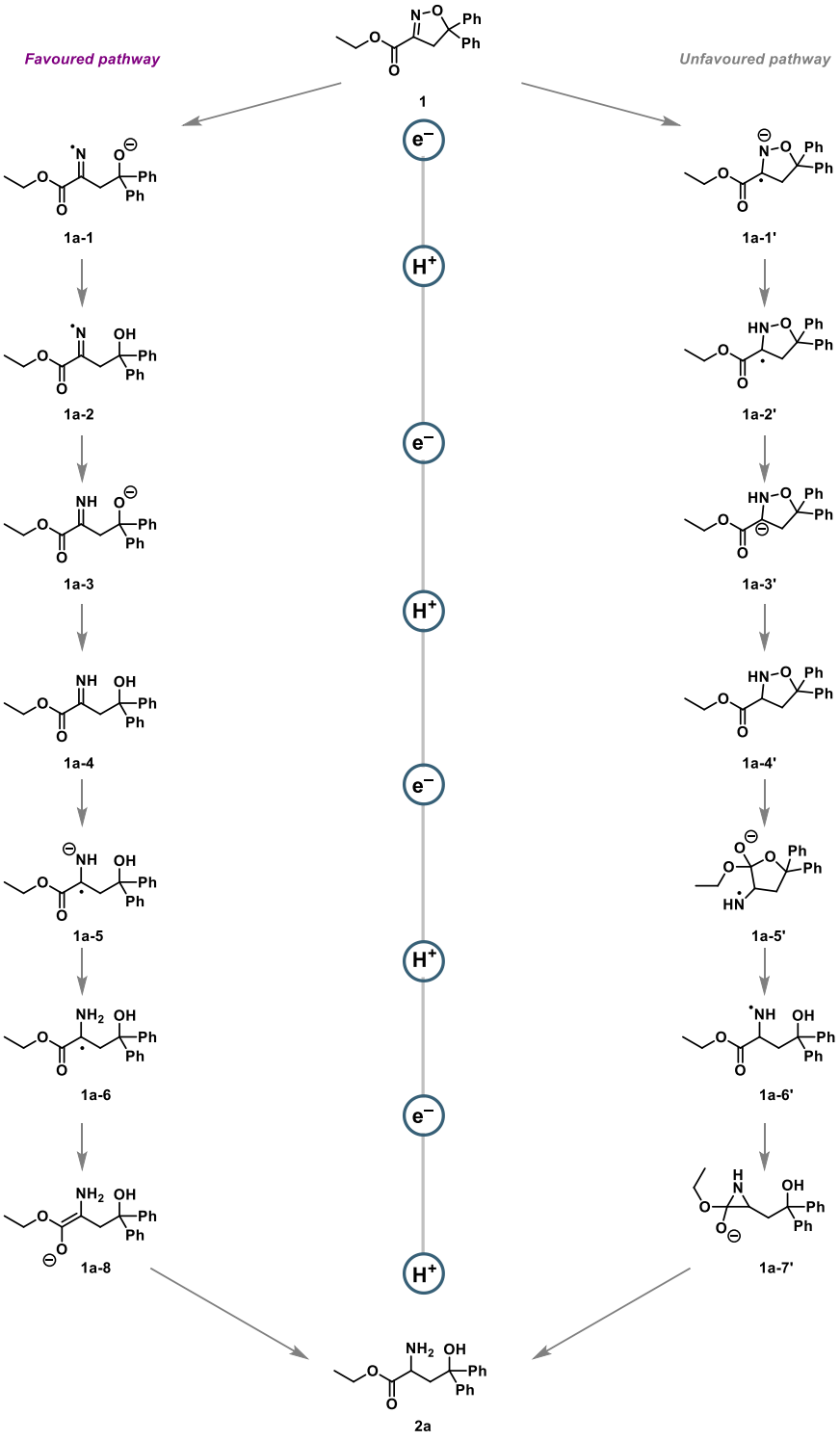
Applied Electrode Potential and Electron-Transfer Free Energies

For construction of the potential-dependent Gibbs free-energy profile, an electrode potential of $U_{applied}$ = -1.70 V vs. Ag/AgCl was selected based on the cathodic halve wave potential observed by cyclic voltammetry.

For a one-electron reduction with a calculated reduction potential, the potential-dependent Gibbs free-energy contribution was calculated according to:

$$\Delta G_{ET} = -96.485 \frac{kJ}{mol \cdot V} \cdot (U_{applied} - E_{red}^{0})$$

Overview of the calculated molecules



Calculated ΔG values

Name	Final Gibbs free energy [Eh]	$\Delta\Delta G_{\text{without electrode potential}}$ [kJ/mol]	$\Delta\Delta G_{\text{at -1.7 V}}$ [kJ/mol]
1	-1323.1745	0	0
1a-1'	-1323.2852	-290.5903663	-60.67
1a-2'	-1323.7394	-322.1414986	-92.22
1a-3'	-1323.8670	-657.2523633	-197.35
1a-4'	-1324.3642	-801.5861277	-341.69
1a-5'	-1324.4774	-1098.959552	-409.09
1a-6'	-1324.9541	-1189.593912	-499.72
1a-7'	-1325.0859	-1535.512438	-615.67
2a	-1325.6092	-1748.57683	-828.73
1a-1	-1323.2952	-316.7914647	-86.82
1a-2	-1323.7722	-408.2049948	-178.23
1a-3	-1323.9369	-840.7425197	-380.78
1a-4	-1324.4183	-943.6696811	-483.71
1a-5	-1324.5233	-1219.22121	-529.29
1a-6	-1324.9976	-1303.799434	-613.87
1a-7	-1325.1099	-1598.469959	-678.57
H_2SO_4	-1047.3013	-	-
HSO_4^-	-1046.8592	-	-

Calculated reduction potentials

Reduction process	Calculated reduction potential vs. Ag/AgCl [V]
1 to 1a-1'	-1.07
1 to 1a-1	-0.80
1a-2' to 1a-3'	-0.61
1a-2 to 1a-3	0.40
1a-4' to 1a-5'	-1.00
1a-4 to 1a-5	-1.23
1a-6' to 1a-7'	-0.50
1a-6 to 1a-7	-1.03

Cartesian Coordinates for all calculated structures

All coordinates include three explicit calculated methanol molecules.

1a

Charge: 0; Multiplicity: 1

Atom	X	Y	Z
O	-2.4856014	-0.4267799	-0.1314614
C	-1.3574673	0.01943935	-0.0082286
O	-0.5697635	0.3676091	-1.0094205
C	-1.113018	0.30336915	-2.3652958
C	-1.9014379	1.5514849	-2.6871374
C	-0.7381014	0.22357223	1.31852143
N	0.34908781	0.8829541	1.43931212
O	0.68212098	1.00040126	2.76680632
C	-0.190623	0.11826095	3.5798052
C	0.59804596	-1.1382871	3.94109532
C	1.9736188	-1.2200466	3.74676416

C	2.668094	-2.3676686	4.11983354
C	1.99669718	-3.4396804	4.69326611
C	0.62109835	-3.3598998	4.89172617
C	-0.0731421	-2.2170698	4.51928796
C	-0.56193	0.88330554	4.83483622
C	0.36915284	1.73465006	5.43079538
C	0.05380381	2.40872534	6.60368968
C	-1.1884396	2.22795971	7.20369535
C	-2.1120547	1.36845711	6.62128978
C	-1.8025249	0.69933722	5.44164524
C	-1.3521964	-0.1783284	2.6160643
H	-1.7113764	-0.6001375	-2.4552467
H	-0.2280858	0.21344435	-2.9891037
H	-2.7868665	1.63692909	-2.0578721
H	-2.225787	1.50491559	-3.7282839
H	-1.2856298	2.44150758	-2.5578148
H	2.50558231	-0.3933598	3.30059068
H	3.7369157	-2.4195013	3.95839091
H	2.53795244	-4.3307729	4.98255621
H	0.08671712	-4.1891956	5.33623421
H	-1.1422706	-2.1680274	4.67860859
H	1.34070959	1.87530088	4.97874994
H	0.78144939	3.07352813	7.05037996
H	-1.4324496	2.75151549	8.11859341
H	-3.0796641	1.21679521	7.08147922
H	-2.5305392	0.02799733	5.00870512
H	-2.2250666	0.44399846	2.80949461
H	-1.6674674	-1.2164448	2.62859593
C	-5.0129636	0.74648237	1.78347453
O	-4.5995741	-0.6183145	1.67862328
H	-5.8736933	0.7800929	2.44945982
H	-4.2220971	1.37617316	2.19876634
H	-5.3041863	1.14223912	0.80751881
H	-3.8264167	-0.6479868	1.08679193
C	-1.0815318	3.68737327	0.54634703
O	0.14668294	3.39276642	-0.1195416
H	-1.4048358	4.67362	0.21497663
H	-1.8645528	2.96510575	0.29805639
H	-0.9546278	3.70748474	1.63249296
H	0.46749156	2.54711808	0.22954445
C	-5.2447782	-2.3294423	4.49901221
O	-4.0289584	-1.6807261	4.13617752
H	-5.1072709	-2.7762633	5.4836407
H	-6.079336	-1.6230352	4.55212286
H	-5.5047453	-3.1232639	3.79146464
H	-4.1606378	-1.2865566	3.24783966

1a-1’

Charge: -1; Multiplicity: 2

Atom	X	Y	Z
O	-0.486353	0.135438	1.555308
C	-0.681253	0.77356	0.477984
C	-1.784364	0.604892	-0.365705
C	-2.933875	-0.313491	-0.071384
C	-3.479975	-0.520228	-1.488847
C	-2.756042	-1.669655	-2.197861
C	-2.803749	-2.954236	-1.654434
C	-2.159943	-4.012783	-2.280356
C	-1.457617	-3.802536	-3.463854
C	-1.411119	-2.527389	-4.0128
C	-2.058316	-1.466787	-3.384386
C	-4.978055	-0.712577	-1.603538
C	-5.630651	-0.371535	-2.789669
C	-6.99711	-0.578484	-2.928001
C	-7.729128	-1.143207	-1.887484
C	-7.083485	-1.495611	-0.708503
C	-5.715982	-1.279701	-0.56674
O	-3.149513	0.741707	-2.127934
N	-1.928528	1.23211	-1.548819
O	0.229632	1.712031	0.04711
C	1.459482	1.811594	0.787746
C	2.316515	2.864192	0.124238
H	-3.678772	0.175943	0.561971
H	-2.63067	-1.23761	0.410279
H	-3.345752	-3.130821	-0.734927
H	-2.202554	-5.001304	-1.841844
H	-0.951057	-4.625666	-3.950509
H	-0.866047	-2.351755	-4.931198
H	-2.007812	-0.477324	-3.81219
H	-5.067574	0.057176	-3.606979
H	-7.490481	-0.302159	-3.850839
H	-8.79301	-1.307975	-1.996719
H	-7.642404	-1.937165	0.10629
H	-5.228262	-1.559595	0.35639
H	1.95831	0.840707	0.78982
H	1.240161	2.079113	1.822516
H	3.263224	2.948646	0.661082
H	1.827606	3.839022	0.14202
H	2.532873	2.603139	-0.911769
C	-0.325741	4.588765	-2.181382
O	0.810313	4.043041	-2.845363
H	-0.49104	4.128818	-1.203162

H	-0.149461	5.654996	-2.035073
H	-1.237344	4.468372	-2.775731
H	0.612401	3.100361	-3.037868
C	1.120068	0.497683	-3.029746
O	0.105036	1.449958	-3.345218
H	2.005421	0.746255	-3.615603
H	1.383388	0.52521	-1.97175
H	0.806561	-0.516383	-3.289745
H	-0.639797	1.362056	-2.687214
C	0.592268	-2.296332	-0.476328
O	-0.128012	-2.466219	0.743359
H	-0.003851	-1.779883	-1.230816
H	1.520797	-1.73902	-0.318904
H	0.84852	-3.28604	-0.854287
H	-0.300295	-1.57156	1.105681

1a-2'

Charge: 0; Multiplicity: 2

Atom	X	Y	Z
O	1.78565785	-1.0884296	-0.6833286
C	1.89711413	0.1144109	-0.4048419
O	1.06992687	0.76340266	0.44231633
C	0.04504913	-0.0131379	1.11750753
C	0.59878298	-0.7290269	2.32996101
C	2.90316159	0.95749237	-0.9383109
C	3.95186298	0.60955296	-1.9322794
C	4.92859576	1.79003449	-1.7728255
C	5.95299583	1.56182071	-0.6621039
C	6.71535663	0.39413785	-0.6506818
C	7.68370989	0.19483437	0.32447281
C	7.90035916	1.16010303	1.30292449
C	7.1472551	2.32750423	1.29151946
C	6.18243831	2.53066366	0.31062749
C	5.62472948	2.23144711	-3.0414176
C	6.02009274	3.56057442	-3.1921286
C	6.67571574	3.96968179	-4.3459735
C	6.96101743	3.052209	-5.3520505
C	6.58519148	1.72326709	-5.1966337
C	5.91657906	1.31440305	-4.0477857
O	4.02347393	2.87866037	-1.3899446
N	3.07669019	2.25546688	-0.5310719
H	-0.3998039	-0.7056262	0.40556977
H	-0.6985381	0.72805785	1.40096265
H	1.32445572	-1.4902743	2.04609571
H	-0.2210067	-1.2183525	2.85970508
H	1.07490111	-0.0230246	3.01106844
H	3.52037602	0.60632692	-2.9366394
H	4.40896428	-0.3579299	-1.7542677
H	6.56131439	-0.3637069	-1.4063594
H	8.26489569	-0.7178211	0.3223769
H	8.64959214	1.00180169	2.06729741
H	7.30522448	3.08349039	2.04935232
H	5.60124326	3.44060891	0.31079341
H	5.80945921	4.27872734	-2.4123058
H	6.96530056	5.00616901	-4.4579245
H	7.47392728	3.37113866	-6.2497208
H	6.8051629	1.00158575	-5.9721523
H	5.62553155	0.27867924	-3.9436397
H	2.27983087	2.87315943	-0.4047901
C	2.9043102	3.59360224	-4.9707117
O	2.2895915	3.29454835	-3.7165451
H	2.11843472	3.59142201	-5.7257137
H	3.37664623	4.5793042	-4.9639495
H	3.65137564	2.84454856	-5.2437363
H	2.97006962	3.31866752	-3.0284572
C	4.20181485	0.23604228	2.37242311
O	3.74440392	1.58818128	2.45972198
H	4.27539774	-0.1451589	3.39041705
H	3.50118763	-0.3866537	1.81787046
H	5.18326958	0.17077008	1.89937455
H	3.64472718	1.92602564	1.55831873
C	4.22896196	-3.1964155	0.98766976
O	4.28761005	-2.3017981	-0.120405
H	5.22771997	-3.6070839	1.13390819
H	3.92650493	-2.6885153	1.9080678
H	3.53675566	-4.0230654	0.80131223
H	3.39157727	-1.968586	-0.3012003

1a-3'

Charge: -1; Multiplicity: 0

Atom	X	Y	Z
O	2.41068715	0.43417537	1.33256359
C	1.62031382	0.04794468	0.38603036
C	0.79649266	0.81557426	-0.3681701
C	0.80132273	2.28964934	-0.504729
C	1.00699034	2.42414709	-2.042769
C	0.40633433	3.68020452	-2.6493796
C	0.24461362	4.84433941	-1.9008927

C	-0.2654397	5.99971822	-2.486191
C	-0.6243777	6.00428654	-3.8283781
C	-0.4645392	4.84618866	-4.5839435
C	0.05175838	3.69660456	-3.999754
C	2.49091065	2.30910823	-2.3890363
C	3.04300927	1.08043267	-2.7455147
C	4.40455229	0.96210113	-3.0102776
C	5.23534806	2.07133932	-2.9196433
C	4.69317066	3.30248804	-2.5625918
C	3.33431488	3.41915927	-2.3013028
O	0.2806146	1.29547646	-2.5800688
N	0.01174303	0.31295353	-1.4560768
O	1.50463429	-1.326788	0.15197939
C	2.64627763	-2.140582	0.47200479
C	3.76717202	-1.9866453	-0.5372961
H	1.58560625	2.77287883	0.06588116
H	-0.1580746	2.74375509	-0.2443486
H	0.52115455	4.85988426	-0.8565332
H	-0.3819002	6.8949116	-1.8891357
H	-1.02365	6.9012937	-4.283357
H	-0.7391793	4.83921852	-5.6308659
H	0.18087607	2.80422029	-4.5964388
H	2.40761734	0.21143921	-2.8246662
H	4.81375815	-0.0017452	-3.2837614
H	6.29414553	1.97961867	-3.122922
H	5.32974548	4.1743519	-2.4845435
H	2.93076038	4.38308665	-2.0243493
H	0.44157861	-0.5470456	-1.795781
H	2.26251514	-3.1602966	0.4690162
H	2.99235733	-1.9095829	1.47905546
H	3.41841849	-2.2229916	-1.5438889
H	4.58031347	-2.6728078	-0.2888742
H	4.16813907	-0.973868	-0.5327138
C	0.3886797	2.59307647	3.03569882
O	1.79621052	2.36592373	3.00999893
H	0.15358261	3.16496677	3.93365746
H	0.0528164	3.16220385	2.16498791
H	-0.1612809	1.64929006	3.07042258
H	1.99552324	1.66209332	2.33558721
C	3.2533226	4.85000947	1.10762099
O	3.21840335	4.6366602	2.51678746
H	3.92593399	5.6854693	0.90911299
H	3.62695384	3.97368935	0.57459009
H	2.26427384	5.10540017	0.71534183
H	2.69568993	3.82140703	2.68410754
C	5.44567572	1.72207673	1.77104929
O	4.73876947	1.49100005	0.55783509
H	6.44626162	2.07486846	1.51827256
H	4.95903744	2.4829583	2.38862022
H	5.54340486	0.80498045	2.36156705
H	3.857828	1.11217388	0.79686887

1a-4’

Charge: 0; Multiplicity: 0

Atom	X	Y	Z
O	0.94697275	-3.1005825	0.90718933
C	1.54088956	-2.2872809	0.22632335
O	1.39732666	-2.1509433	-1.0815463
C	0.42488054	-3.0014053	-1.7584597
C	-0.9620811	-2.4074603	-1.6694912
C	2.52764143	-1.3124326	0.84790115
C	1.81771069	-0.3289962	1.78650187
C	1.44615389	0.8417537	0.84920628
C	-0.0063939	0.85190509	0.37720519
C	-1.052306	0.39656961	1.17643541
C	-2.3662452	0.44350784	0.7195372
C	-2.6534558	0.95232186	-0.5403541
C	-1.6158573	1.42667912	-1.336871
C	-0.3061065	1.38097087	-0.8800367
C	1.79013509	2.19421838	1.46235888
C	2.5418439	3.13657083	0.76634103
C	2.85582897	4.3599005	1.35189742
C	2.41081972	4.65953337	2.63354051
C	1.64411747	3.72746222	3.32690496
C	1.33589918	2.50494025	2.74466505
O	2.26511904	0.61863421	-0.3449449
N	3.20538896	-0.4428838	-0.1034355
H	0.47512815	-3.9976749	-1.3251153
H	0.77937968	-3.0375329	-2.7848528
H	-1.309017	-2.3599232	-0.6380446
H	-1.6534393	-3.0354488	-2.2346461
H	-0.9816132	-1.4058005	-2.0964445
H	3.27081719	-1.9055209	1.37896073
H	2.5237574	0.00522206	2.54052544
H	0.96607152	-0.7727625	2.28736183
H	-0.8587516	0.00300606	2.16358169
H	-3.1630502	0.07617669	1.35296679
H	-3.6743266	0.98247035	-0.897454
H	-1.8250574	1.83083894	-2.3186629
H	0.48802247	1.75533336	-1.5073311

H	2.8962558	2.91038234	-0.2281229
H	3.45116214	5.07713352	0.80207302
H	2.65699679	5.60967124	3.08885224
H	1.29046384	3.94949797	4.3253402
H	0.74309725	1.7873505	3.29656976
H	3.9860025	0.00525945	0.38871116
C	5.16735896	1.38663101	2.65714629
O	5.27255345	1.24753642	1.23575429
H	5.37995236	0.41128986	3.09155769
H	5.89594022	2.10865932	3.03462666
H	4.16641551	1.69988682	2.95691306
H	4.99825383	2.08027764	0.83375098
C	4.2212476	-2.44075	-2.9088275
O	3.84439241	-1.0756083	-2.7370794
H	4.52051872	-2.5781397	-3.9475297
H	5.06680047	-2.6996124	-2.2655684
H	3.39361237	-3.1207488	-2.6904319
H	3.64088995	-0.9229935	-1.7808204
C	1.62902888	1.07648966	-4.0671781
O	1.40179401	-0.2769274	-3.6877295
H	0.66785003	1.5218649	-4.3238562
H	2.07436596	1.65837821	-3.254684
H	2.28544248	1.14646169	-4.9412247
H	2.26304603	-0.6428848	-3.3925986

1a-5’

Charge: -1; Multiplicity: 2

Atom	X	Y	Z
O	0.27784639	3.98765931	-1.9782576
C	0.66953467	2.80485289	-2.2220365
C	1.5295277	2.06820201	-0.970689
N	0.70347231	1.45901377	-0.037328
C	2.45956475	1.16669971	-1.7714394
C	2.87707813	2.03391059	-2.9609294
C	3.95640512	3.04266391	-2.5497268
C	5.20868409	2.57638473	-2.1435645
C	6.20979903	3.46252278	-1.7702658
C	5.97668161	4.83524642	-1.8027247
C	4.73552318	5.30610183	-2.2109745
C	3.73128757	4.41520341	-2.5827651
C	3.36843893	1.26510149	-4.1811178
C	3.61760484	-0.1034746	-4.1546536
C	4.07843823	-0.7620398	-5.2926686
C	4.28797879	-0.0592707	-6.4713873
C	4.04589237	1.31218428	-6.5044772
C	3.60032446	1.96749747	-5.3664065
O	1.66429267	2.71758383	-3.3277657
O	-0.329291	1.86803462	-2.6543026
C	-1.6055445	2.02415157	-2.0307511
C	-2.4665793	0.8429365	-2.4187632
H	2.06099135	2.91026634	-0.5266071
H	0.38989094	0.56006037	-0.4066472
H	1.89274931	0.30353478	-2.1207695
H	3.30748382	0.81627975	-1.1871207
H	5.40460756	1.51198694	-2.124798
H	7.17345706	3.08253453	-1.4563548
H	6.756237	5.52774794	-1.5133202
H	4.54178852	6.37069595	-2.2406507
H	2.76712875	4.78940108	-2.8905066
H	3.46083013	-0.6700983	-3.2485532
H	4.26882981	-1.8266863	-5.2534079
H	4.64029734	-0.571686	-7.3569925
H	4.20806643	1.87034656	-7.4173622
H	3.4247596	3.03433611	-5.3971195
H	-2.0639722	2.96150107	-2.352593
H	-1.4823791	2.07395319	-0.9445839
H	-2.6082083	0.80153711	-3.4996657
H	-3.4489791	0.93166895	-1.95097
H	-2.0163224	-0.0957856	-2.0907301
C	0.30094656	0.67332597	-5.8723396
O	0.33920705	2.09205896	-5.7061795
H	-0.451736	0.44817112	-6.627407
H	1.26487611	0.2905091	-6.2140982
H	0.02740068	0.17000742	-4.9427826
H	0.82501293	2.2927527	-4.8802968
C	-1.9936311	4.47125767	-5.0034048
O	-2.1780636	3.0893175	-5.2979174
H	-2.9542198	4.88087232	-4.6896652
H	-1.2728227	4.62176301	-4.1951221
H	-1.6513897	5.02831409	-5.8825563
H	-1.290451	2.70964636	-5.4717004
C	-0.1680624	4.22371101	1.73415491
O	-0.6973125	2.90524399	1.81851063
H	-0.7225473	4.85995565	2.42561535
H	0.89055638	4.25651676	2.01506332
H	-0.2693859	4.63897172	0.72678344
H	-0.1842488	2.33879627	1.18265392

1a-6’

Charge: 0; Multiplicity: 2

Atom	X	Y	Z
O	-0.7120218	1.41208423	-3.3229162
C	-0.4634342	0.66704807	-2.3890489
C	0.93304174	0.55086771	-1.7964391
N	0.98639778	0.04740104	-0.4532612
C	1.81319786	-0.3820945	-2.6878255
C	2.46302109	0.2920075	-3.911455
C	3.3049746	1.49495535	-3.4764885
C	4.37789477	1.30170173	-2.603237
C	5.15594599	2.37328884	-2.1884465
C	4.87607423	3.65948976	-2.6428755
C	3.81375419	3.85857878	-3.5144287
C	3.03239944	2.78229887	-3.9284324
C	3.35312303	-0.6857109	-4.6843459
C	3.85365515	-0.2718417	-5.921539
C	4.65095304	-1.1125121	-6.6836425
C	4.97101399	-2.3848345	-6.2167772
C	4.485486	-2.8004356	-4.9849421
C	3.6799315	-1.9568228	-4.2225462
O	1.4537817	0.68697474	-4.8582564
O	-1.353652	-0.1140709	-1.8060489
C	-2.715529	-0.128492	-2.3424572
C	-2.8231719	-1.0701496	-3.5181484
H	1.35994215	1.55389932	-1.8204171
H	0.3213425	-0.7283563	-0.3865515
H	1.22221182	-1.236434	-3.0120042
H	2.60175397	-0.755587	-2.0404268
H	4.61393442	0.3063942	-2.2506482
H	5.98370851	2.20466315	-1.5119659
H	5.48325116	4.49527058	-2.3209452
H	3.58700217	4.8528776	-3.8768438
H	2.2108216	2.9517778	-4.6084429
H	3.61187013	0.71500965	-6.2912349
H	5.02454131	-0.7750361	-7.6415869
H	5.59338587	-3.0429879	-6.80862
H	4.72635611	-3.7865149	-4.6099658
H	3.31402617	-2.3128775	-3.2722353
H	0.75071594	1.18564729	-4.4022831
H	-2.9896196	0.89091062	-2.6032473
H	-3.3181571	-0.460251	-1.5013764
H	-2.1916546	-0.7496296	-4.3459521
H	-3.8587614	-1.0832448	-3.8633729
H	-2.5446606	-2.0841254	-3.2331994
C	0.87158649	-2.1139446	-6.8992261
O	0.12570523	-1.5301922	-5.8273861
H	0.24951344	-2.8859877	-7.3503119
H	1.11085258	-1.3691727	-7.6612648
H	1.79772952	-2.5702929	-6.5441548
H	0.6112732	-0.7467128	-5.4938244
C	0.68921112	-4.4613134	-4.0800705
O	-0.1187342	-3.3311565	-3.7638286
H	0.56606207	-5.1956396	-3.2843026
H	0.38362847	-4.9217715	-5.0248556
H	1.74768708	-4.1968621	-4.1465853
H	-0.0272278	-2.6761108	-4.4878497
C	0.73986283	-3.5679043	-0.3546685
O	1.97188963	-3.443066	-1.0694348
H	-0.0333236	-3.089222	-0.9519631
H	0.46754951	-4.6168741	-0.2082448
H	0.79194842	-3.0769617	0.6206787
H	2.66558208	-3.8596561	-0.5465939

1a-7’

Charge: -1; Multiplicity: 1

Atom	X	Y	Z
O	-2.2743335	-2.3509595	3.63325357
C	-1.59902	-1.4901238	2.90131273
C	-0.1196312	-1.5191477	2.78970686
N	-0.9792573	-1.9095071	1.61418461
C	0.76123427	-0.3035096	2.73835025
C	1.46143806	-0.0266838	4.08981053
C	2.44672075	-1.1219565	4.51264046
C	3.00292786	-2.029748	3.61361639
C	3.90646998	-2.99721	4.04489329
C	4.27191797	-3.0692816	5.38310421
C	3.73112336	-2.1594066	6.2866711
C	2.830486	-1.1966395	5.85264194
C	2.19144114	1.31269398	3.98935681
C	1.62725226	2.4815129	4.49625879
C	2.2964862	3.69690207	4.3894547
C	3.53403122	3.76478547	3.76260115
C	4.09527531	2.60564026	3.23542243
C	3.43017961	1.39179526	3.35056084
O	0.45331626	0.11136476	5.0993225
O	-2.1901507	-0.1827704	2.72455986
C	-3.2702123	0.18897981	3.58274211
C	-2.8260713	0.77745018	4.91053068
H	0.35312511	-2.3891281	3.2275399

H	-1.016904	-1.1095585	0.9864909
H	0.16553435	0.57693195	2.49896519
H	1.51607798	-0.3992199	1.95459075
H	2.73640654	-1.9962326	2.56786821
H	4.32030985	-3.696321	3.3297522
H	4.97079603	-3.8240809	5.71896884
H	4.00992017	-2.1991374	7.33175814
H	2.41909149	-0.4966858	6.56263512
H	0.66664583	2.44869024	4.98581059
H	1.8482349	4.58960071	4.80553818
H	4.05702965	4.70891634	3.68492705
H	5.05785223	2.64377553	2.74201901
H	3.88837143	0.49789019	2.95063113
H	0.01442378	-0.7581431	5.27825817
H	-3.9256231	-0.6664954	3.74478499
H	-3.829412	0.93610665	3.01619325
H	-2.3195266	0.03810073	5.52872871
H	-3.7008011	1.13695309	5.45899225
H	-2.1523851	1.62202816	4.75727623
C	-0.1366893	-3.3051129	6.01967878
O	-0.8964329	-2.1224666	5.80126065
H	0.45607118	-3.1747334	6.92475957
H	-0.790605	-4.1715543	6.15746613
H	0.54324639	-3.5144383	5.18890511
H	-1.4922134	-2.2608836	4.9867992
C	0.35117769	0.20856545	8.49987029
O	0.54542029	1.25458829	7.5482633
H	0.26277303	0.66687166	9.48419109
H	-0.5634938	-0.35114	8.28960144
H	1.19408251	-0.4877276	8.51352197
H	0.5489014	0.86195942	6.64707874
C	3.96162458	2.03745625	7.32060726
O	2.82712037	2.76056415	7.78879207
H	4.82599159	2.69988357	7.37751529
H	4.16321582	1.15614338	7.93811644
H	3.84243472	1.71596587	6.28352992
H	2.03742358	2.18433623	7.71032697

2a

Charge: 0; Multiplicity: 1

Atom	X	Y	Z
O	6.92039392	0.39640278	-2.0803594
C	6.12456226	0.00897222	-1.2306782
O	6.29998975	-1.0969892	-0.5277467
C	7.53299543	-1.8571291	-0.7095988
C	8.66818404	-1.2398206	0.07435765
C	4.78993259	0.68650855	-0.9588814
N	3.70230289	-0.1171539	-1.5315217
C	4.53555975	0.9254657	0.52932424
C	5.34644149	2.07880965	1.15200549
C	4.93171394	3.47057136	0.66195205
C	3.76104148	3.71327991	-0.0519313
C	3.42917099	5.00502856	-0.4548075
C	4.26138512	6.07236462	-0.1467805
C	5.43067216	5.84078958	0.57301073
C	5.75828829	4.55394975	0.97370648
C	5.16209706	2.01808124	2.67003026
C	6.22107967	1.7171001	3.52203527
C	6.02391782	1.64787951	4.89926433
C	4.76600529	1.8764014	5.44157451
C	3.70232054	2.17789973	4.59516843
C	3.9004939	2.24901419	3.22299868
O	6.73610536	1.87140554	0.86303813
H	7.75117411	-1.9202686	-1.772942
H	7.28046721	-2.8467876	-0.3382541
H	8.92203133	-0.2508519	-0.3044342
H	9.54933817	-1.8776781	-0.0155819
H	8.41050955	-1.1582996	1.13060295
H	4.82273542	1.63276247	-1.4941033
H	3.66123617	-1.0157422	-1.0607044
H	3.88949501	-0.3003217	-2.5163466
H	4.77109676	0.01717923	1.08334146
H	3.47088797	1.10320299	0.66487954
H	3.09248325	2.90487528	-0.3076416
H	2.51667529	5.17028988	-1.0127076
H	4.00350944	7.07497684	-0.4615981
H	6.08645901	6.66433184	0.82395949
H	6.66737243	4.38459108	1.53442909
H	7.20321763	1.53942833	3.11164678
H	6.85949797	1.41434499	5.54663612
H	4.61391941	1.82338847	6.51162715
H	2.71743053	2.36195629	5.00449473
H	3.06757552	2.49535607	2.57796265
H	6.96830019	2.3526277	0.04191969
C	8.92739131	3.19148548	-1.4704297
O	7.50561713	3.04639548	-1.5361623
H	9.13740224	4.09437354	-0.8991211
H	9.39358943	2.33954043	-0.9693286
H	9.3577986	3.29621406	-2.4693753
H	7.30389192	2.20166149	-1.9758368

C	7.81161977	-0.376257	-5.4717759
O	7.05549213	-1.0573482	-4.4646746
H	7.5316303	-0.7994902	-6.4352042
H	7.59513957	0.69416875	-5.4795496
H	8.88412402	-0.5216772	-5.319854
H	7.18814727	-0.5948857	-3.6196711
C	4.47443175	1.12934932	-4.7667613
O	4.39729421	-0.2786453	-4.5457548
H	3.49046126	1.553277	-4.5662108
H	5.19823419	1.60604146	-4.1014159
H	4.74565142	1.35666778	-5.8022254
H	5.31045812	-0.6306439	-4.5627585

1a-1

Charge: -1; Multiplicity: 2

Atom	X	Y	Z
O	2.175711	-0.429238	-4.055205
C	1.95453	0.1913	-3.042437
C	2.671154	-0.131975	-1.724566
C	4.17846	-0.23962	-1.830086
C	5.020598	0.025701	-0.551804
C	4.876758	1.471949	-0.053171
C	5.623893	1.850798	1.067456
C	5.602398	3.153274	1.541816
C	4.831094	4.119706	0.898231
C	4.092903	3.761809	-0.22032
C	4.117848	2.449134	-0.690597
C	4.58125	-0.985647	0.525745
C	5.025608	-2.30539	0.418032
C	4.638257	-3.269185	1.34006
C	3.799213	-2.929669	2.398645
C	3.350544	-1.620583	2.517686
C	3.736226	-0.659643	1.586664
O	6.356739	-0.183206	-0.894846
N	1.940186	-0.33046	-0.741474
O	1.102712	1.187072	-2.893934
C	0.256528	1.549436	-4.032158
C	-0.997562	0.708436	-4.027222
H	4.511764	0.42771	-2.623555
H	4.39288	-1.255805	-2.165162
H	6.234096	1.11115	1.568242
H	6.188543	3.418352	2.41258
H	4.811546	5.137662	1.26504
H	3.493735	4.500978	-0.736353
H	3.535715	2.216947	-1.569277
H	5.683373	-2.576673	-0.396054
H	4.994373	-4.28627	1.235381
H	3.501742	-3.677987	3.121787
H	2.698283	-1.341595	3.335418
H	3.374386	0.351838	1.695433
H	0.834716	1.434596	-4.945681
H	0.041791	2.601703	-3.868267
H	-0.767326	-0.344522	-4.190716
H	-1.658018	1.044224	-4.828547
H	-1.523664	0.813225	-3.077819
C	6.952991	1.942054	-3.336685
O	7.558803	1.799792	-2.062153
H	5.924707	2.315808	-3.264966
H	7.530813	2.664072	-3.917506
H	6.93445	0.998131	-3.891986
H	7.094851	1.042178	-1.583348
C	8.491034	-1.775008	-2.679638
O	7.079006	-1.746594	-2.826758
H	8.91126	-2.422908	-3.451112
H	8.935723	-0.779375	-2.79062
H	8.790171	-2.171526	-1.702217
H	6.721794	-1.159767	-2.088496
C	0.322193	2.512141	0.21827
O	-0.359605	1.274659	0.01181
H	-0.418982	3.244651	0.537822
H	1.084462	2.427883	0.997483
H	0.793217	2.873592	-0.699283
H	0.311362	0.609421	-0.215481

1a-2

Charge: 0; Multiplicity: 2

Atom	X	Y	Z
O	3.329546	3.894275	-1.466098
C	3.609765	3.235803	-0.486466
O	4.472727	2.247371	-0.442532
C	5.12778	1.868914	-1.699728
C	5.957802	0.645228	-1.419044
C	3.008514	3.490591	0.895463
C	2.140998	2.431	1.541411
C	0.752179	2.268324	0.864728
C	0.850816	1.748341	-0.578344
C	1.723081	0.710401	-0.910649
C	1.786223	0.224005	-2.210327

C	0.97143	0.760678	-3.200996
C	0.087837	1.782689	-2.875033
C	0.025116	2.268749	-1.573817
C	-0.084595	1.260069	1.664166
C	-1.458318	1.459368	1.804008
C	-2.24662	0.529983	2.473467
C	-1.675437	-0.616681	3.013296
C	-0.307945	-0.824005	2.875709
C	0.480952	0.104532	2.206016
O	0.073243	3.512537	0.924077
N	3.29724	4.568217	1.443958
H	5.730148	2.716282	-2.022556
H	4.347376	1.682143	-2.434452
H	6.702528	0.844352	-0.648345
H	6.479237	0.356975	-2.33313
H	5.333101	-0.189164	-1.103026
H	1.971739	2.723535	2.575149
H	2.706406	1.501908	1.53304
H	2.365685	0.277528	-0.160919
H	2.474999	-0.575563	-2.449417
H	1.023418	0.384505	-4.214193
H	-0.556845	2.206561	-3.63403
H	-0.667539	3.061531	-1.337013
H	-1.914611	2.34513	1.389429
H	-3.310183	0.705406	2.571691
H	-2.288467	-1.340008	3.534788
H	0.152297	-1.711541	3.289801
H	1.538197	-0.091887	2.109924
H	0.44321	4.14644	0.269902
C	1.208894	6.628649	-0.442593
O	0.942407	5.32348	-0.96415
H	0.255721	7.060988	-0.142264
H	1.868982	6.583671	0.426262
H	1.662948	7.267958	-1.203534
H	1.783894	4.924003	-1.247974
C	5.332793	-0.714686	2.03133
O	4.023542	-0.449534	1.538291
H	5.720466	0.207716	2.463919
H	5.321057	-1.485067	2.80945
H	6.010477	-1.034864	1.235508
H	3.724104	-1.212858	1.004041
C	1.73196	-2.840409	0.224039
O	3.100681	-2.50468	-0.045601
H	1.665758	-3.086754	1.28151
H	1.066358	-2.004147	0.008146
H	1.424171	-3.708123	-0.363622
H	3.171567	-2.224183	-0.965401

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Charge: -1; Multiplicity: 0

Atom	X	Y	Z
O	-2.893765	0.397205	4.247485
C	-1.680064	0.288077	4.225961
C	-0.81414	0.863943	3.120614
C	-1.415424	1.999273	2.334828
C	-0.967955	2.076845	0.846909
C	-1.415333	0.835935	0.047996
C	-2.319388	-0.110301	0.525871
C	-2.689643	-1.207236	-0.250203
C	-2.166216	-1.372749	-1.52511
C	-1.269108	-0.428084	-2.018686
C	-0.900453	0.660098	-1.239855
C	-1.695512	3.304519	0.252826
C	-0.989746	4.465137	-0.051385
C	-1.642848	5.585337	-0.560775
C	-3.015977	5.562113	-0.771071
C	-3.732361	4.407639	-0.465193
C	-3.076931	3.29244	0.040453
O	0.416461	2.204322	0.783219
N	0.327672	0.342738	2.935766
O	-0.981016	-0.347737	5.151984
C	-1.713813	-0.99917	6.232408
C	-2.190937	-2.369839	5.810938
H	-1.091841	2.929079	2.810805
H	-2.496471	1.978814	2.419678
H	-2.75632	-0.007546	1.507295
H	-3.39064	-1.929614	0.148373
H	-2.452794	-2.223749	-2.129227
H	-0.856921	-0.539819	-3.013638
H	-0.205293	1.387034	-1.635497
H	0.075725	4.494662	0.118995
H	-1.073825	6.476931	-0.792692
H	-3.524093	6.431182	-1.168467
H	-4.802925	4.374938	-0.623466
H	-3.648189	2.401842	0.265062
H	0.755364	0.824097	2.133449
H	-2.535051	-0.353015	6.534754
H	-0.98681	-1.057995	7.038177
H	-2.920949	-2.307223	5.004179
H	-2.664381	-2.860119	6.663548

H	-1.353404	-2.986594	5.48309
C	2.934411	3.576195	2.26854
O	1.547582	3.798817	2.470545
H	3.494202	4.179568	2.98612
H	3.208829	2.526557	2.425976
H	3.253852	3.866632	1.261087
H	1.053133	3.200868	1.823168
C	-5.695182	0.937678	1.986153
O	-5.029575	1.763224	2.940236
H	-6.531613	1.508781	1.584062
H	-5.037131	0.65757	1.159933
H	-6.084554	0.025227	2.447515
H	-4.311922	1.248487	3.342623
C	2.801129	1.788525	-1.334297
O	1.869571	2.855358	-1.248839
H	3.479077	1.981357	-2.167942
H	3.40244	1.692722	-0.422712
H	2.306718	0.826686	-1.513323
H	1.233256	2.630727	-0.499973

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Charge: 0; Multiplicity: 0

Atom	X	Y	Z
O	2.729514	3.924472	-3.053772
C	2.873467	2.821922	-2.568833
C	4.089219	2.467006	-1.724687
C	4.224957	1.067454	-1.200011
C	5.187132	0.928895	-0.007305
C	4.644309	1.686231	1.212807
C	5.404959	2.646704	1.872943
C	4.899266	3.307007	2.989559
C	3.626082	3.014443	3.461228
C	2.861824	2.050545	2.809742
C	3.368559	1.391295	1.69786
C	5.412998	-0.528873	0.38975
C	6.467609	-0.820601	1.257991
C	6.723073	-2.125756	1.651701
C	5.920032	-3.165461	1.19026
C	4.862833	-2.882714	0.336183
C	4.610041	-1.571897	-0.061694
O	6.479011	1.435983	-0.388222
N	4.965105	3.358238	-1.513317
O	2.010611	1.824484	-2.665236
C	0.797371	2.039746	-3.44936
C	1.046727	1.800858	-4.920415
H	4.579465	0.446543	-2.025243
H	3.240238	0.693955	-0.936998
H	6.395736	2.884928	1.516268
H	5.505186	4.052714	3.487828
H	3.232644	3.5287	4.328129
H	1.870222	1.80898	3.169856
H	2.766442	0.634516	1.213223
H	7.097771	-0.020445	1.619999
H	7.549687	-2.332916	2.318763
H	6.117782	-4.184507	1.495587
H	4.230781	-3.681202	-0.029855
H	3.784003	-1.383126	-0.730063
H	6.307163	2.328393	-0.76002
H	4.711372	4.238821	-1.963561
H	0.436774	3.046722	-3.251802
H	0.095677	1.318499	-3.039225
H	1.439696	0.798175	-5.090423
H	1.744225	2.528558	-5.332213
H	0.099412	1.892336	-5.455115
C	8.096156	-1.335882	-1.845967
O	7.619152	-0.093511	-2.370537
H	8.837993	-1.169247	-1.062128
H	7.283062	-1.942906	-1.444572
H	8.567704	-1.876834	-2.665481
H	7.216411	0.433396	-1.646636
C	5.131419	-1.761874	-3.984603
O	5.861261	-0.588938	-4.346256
H	5.780677	-2.641588	-3.97642
H	4.664278	-1.659925	-3.002864
H	4.349909	-1.911125	-4.729052
H	6.502511	-0.384861	-3.624888
C	5.595303	2.683501	-4.778959
O	4.526405	1.762903	-4.596902
H	6.285102	2.680069	-3.92927
H	6.16464	2.460714	-5.687367
H	5.169227	3.681789	-4.875699
H	4.926425	0.870313	-4.502513

1a-5

Charge: -1; Multiplicity: 2

Atom	X	Y	Z
O	2.537132	2.21947	2.749097
C	3.174877	1.341715	3.392103

C	3.509386	0.045355	2.927175
N	4.176489	-0.875118	3.645249
C	3.001928	-0.395575	1.584142
C	1.832014	-1.405938	1.734099
C	0.662483	-0.691941	2.422572
C	-0.100132	0.241269	1.718267
C	-1.111367	0.954257	2.34802
C	-1.378358	0.745521	3.698464
C	-0.625629	-0.182928	4.406617
C	0.388216	-0.8961	3.771748
C	1.377141	-1.989838	0.399037
C	0.498673	-3.076373	0.416142
C	0.065022	-3.662311	-0.764356
C	0.496477	-3.164245	-1.991339
C	1.360066	-2.077779	-2.019091
C	1.79807	-1.49527	-0.831475
O	2.279046	-2.517701	2.522689
O	3.612213	1.597788	4.672943
C	3.450304	2.937541	5.176632
C	4.541081	3.866339	4.681247
H	4.418007	-0.515541	4.563231
H	3.801965	-0.891692	1.033962
H	2.666535	0.459679	1.006535
H	0.1018	0.417604	0.669987
H	-1.69071	1.674905	1.785403
H	-2.165661	1.301199	4.190948
H	-0.822659	-0.353612	5.457334
H	0.971171	-1.613027	4.330902
H	0.157468	-3.469525	1.364244
H	-0.610587	-4.507215	-0.728707
H	0.160248	-3.61919	-2.913879
H	1.702243	-1.679754	-2.965625
H	2.47467	-0.655822	-0.882915
H	2.951639	-2.165807	3.149959
H	3.498173	2.827081	6.25894
H	2.462162	3.309562	4.909303
H	5.526886	3.466155	4.924216
H	4.440221	4.839661	5.166578
H	4.478927	4.015913	3.603927
C	5.524096	-3.938271	3.203204
O	5.718747	-2.736524	2.464225
H	5.815999	-3.809602	4.250205
H	4.482784	-4.272323	3.173184
H	6.149185	-4.716804	2.765167
H	5.158374	-2.018169	2.899493
C	4.100613	-4.319083	-0.147242
O	4.88241	-3.127809	-0.1166
H	3.629259	-4.38796	-1.128035
H	4.720102	-5.210754	-0.00076
H	3.31585	-4.312507	0.611348
H	5.190361	-2.986516	0.805695
C	5.344232	2.44568	0.869224
O	4.191887	3.284999	0.856172
H	6.103203	2.911555	0.239593
H	5.754321	2.334897	1.877435
H	5.128417	1.450216	0.4703
H	3.548088	2.916401	1.497

1a-6

Charge: 0; Multiplicity: 2

Atom	X	Y	Z
O	-1.052754	1.684032	0.229696
C	-0.059503	1.843304	0.960702
C	0.310811	0.96107	2.017289
N	1.403137	1.229532	2.767048
C	-0.462651	-0.285043	2.267648
C	0.152612	-1.596652	1.684095
C	0.330072	-1.401984	0.17811
C	1.369976	-0.620748	-0.334462
C	1.465326	-0.366248	-1.696406
C	0.52485	-0.891811	-2.576681
C	-0.512168	-1.669011	-2.077906
C	-0.60949	-1.915776	-0.711885
C	1.433105	-2.034475	2.410887
C	1.476582	-2.002615	3.808756
C	2.580688	-2.477799	4.504373
C	3.664137	-3.015647	3.8168
C	3.622889	-3.078039	2.430344
C	2.518923	-2.591226	1.737418
O	-0.849098	-2.580956	1.964178
O	0.802945	2.882479	0.814453
C	0.542572	3.843911	-0.235578
C	-0.474549	4.879724	0.191158
H	1.989277	2.018186	2.549903
H	1.733687	0.565772	3.447248
H	-1.444093	-0.186237	1.811151
H	-0.61193	-0.422122	3.338209
H	2.115439	-0.205718	0.32799
H	2.277765	0.243689	-2.069438
H	0.600126	-0.694641	-3.637773

H	-1.253153	-2.083052	-2.749291
H	-1.428289	-2.509091	-0.335132
H	0.638484	-1.614765	4.369906
H	2.590481	-2.4334	5.585674
H	4.524368	-3.388087	4.357377
H	4.448418	-3.509225	1.879038
H	2.510751	-2.657853	0.66245
H	-0.526828	-3.451796	1.637645
H	0.229699	3.31411	-1.132541
H	1.512071	4.301358	-0.421825
H	-1.441419	4.425997	0.405354
H	-0.609247	5.606117	-0.612621
H	-0.132429	5.412431	1.079792
C	-0.938429	-5.533685	0.088317
O	0.028411	-4.986971	0.987836
H	-1.890033	-5.589226	0.615249
H	-1.064203	-4.905979	-0.796964
H	-0.653056	-6.540235	-0.228029
H	0.890391	-4.971216	0.520032
C	-1.850294	1.969953	-2.992105
O	-2.308335	2.818925	-1.94291
H	-2.299104	2.316453	-3.923418
H	-0.761974	2.006592	-3.098878
H	-2.148025	0.93018	-2.828716
H	-1.887283	2.505594	-1.120652
C	2.095332	-4.328482	-1.758181
O	2.31497	-5.052605	-0.537575
H	1.970259	-3.282766	-1.492857
H	2.955297	-4.426469	-2.423923
H	1.199352	-4.680586	-2.272099
H	2.444953	-5.983356	-0.754598

1a-7

Charge: -1; Multiplicity: 1

Atom	X	Y	Z
O	1.39815	-0.433048	0.002156
C	2.467493	-0.45789	-0.73923
C	3.097597	-1.530708	-1.273167
N	4.162798	-1.366604	-2.229841
C	2.522804	-2.910554	-1.161242
C	3.296651	-4.007831	-0.375049
C	4.736835	-4.102754	-0.87649
C	5.772879	-3.422116	-0.23399
C	7.065349	-3.44583	-0.745684
C	7.345127	-4.155695	-1.908395
C	6.320713	-4.840326	-2.553084
C	5.02803	-4.811383	-2.041944
C	3.258488	-3.873079	1.147305
C	2.605749	-2.837687	1.808984
C	2.585974	-2.786981	3.202446
C	3.210413	-3.773236	3.953204
C	3.862988	-4.816521	3.301188
C	3.891182	-4.858075	1.91499
O	2.568253	-5.210425	-0.730403
O	2.994637	0.800922	-1.114311
C	3.200444	1.74292	-0.043766
C	4.247363	1.26114	0.93961
H	4.428737	-0.391711	-2.276716
H	4.987822	-1.89042	-1.964385
H	2.426805	-3.325094	-2.170282
H	1.519945	-2.858802	-0.73999
H	5.571166	-2.859923	0.666555
H	7.853002	-2.907825	-0.234392
H	8.351192	-4.17691	-2.306262
H	6.52619	-5.397204	-3.458186
H	4.238229	-5.342436	-2.553187
H	2.109879	-2.059874	1.249685
H	2.084123	-1.965203	3.695174
H	3.193218	-3.731687	5.034543
H	4.356856	-5.591869	3.872594
H	4.422597	-5.664704	1.425397
H	2.978537	-5.961807	-0.285304
H	2.253688	1.943717	0.456852
H	3.521517	2.658238	-0.539544
H	3.941342	0.330293	1.418243
H	4.39193	2.010179	1.720741
H	5.203636	1.093848	0.440819
C	1.698675	0.180683	-4.198822
O	2.238522	1.408373	-3.709659
H	1.336306	0.359158	-5.211598
H	2.457847	-0.605154	-4.229405
H	0.860352	-0.165454	-3.587899
H	2.51521	1.263376	-2.784912
C	-0.808746	1.571949	-1.660688
O	-0.341278	1.552023	-0.317677
H	-1.635611	2.281276	-1.724401
H	-0.029702	1.892022	-2.358806
H	-1.178619	0.59077	-1.976016
H	0.322223	0.8187	-0.236735
C	-0.067044	-0.0236	2.892446

O	1.255919	0.369149	2.545826
H	-0.21585	0.179334	3.953774
H	-0.817824	0.536395	2.325247
H	-0.233468	-1.092061	2.721128
H	1.404169	0.093039	1.607567

H_2SO_4

Charge: 0; Multiplicity: 1

Atom	X	Y	Z
O	0.699686	0.150803	-0.173953
S	2.065744	-0.072425	-1.005975
O	2.111398	0.958761	-2.041107
O	3.17143	0.115588	-0.010642
O	1.955879	-1.45217	-1.474092
H	0.657967	1.108234	0.159454
H	3.151974	-0.702752	1.223952
C	1.601868	2.712787	1.822007
O	0.667425	2.572886	0.735248
H	2.623661	2.542911	1.483262
H	1.519931	3.706738	2.263477
H	1.332933	1.966385	2.565251
H	0.917972	3.17875	0.026665
C	3.53547	-0.488947	3.246101
O	3.057853	-1.251638	2.099384
H	4.585037	-0.272474	3.073218
H	2.961025	0.428936	3.342989
H	3.414993	-1.118747	4.122029
H	2.033082	-1.457905	2.173653
C	0.209668	-2.935217	1.612434
O	0.585369	-1.61573	2.056857
H	0.521135	-3.63476	2.384438
H	-0.871417	-2.988637	1.485759
H	0.704716	-3.181334	0.672334
H	0.390352	-0.98278	1.340344

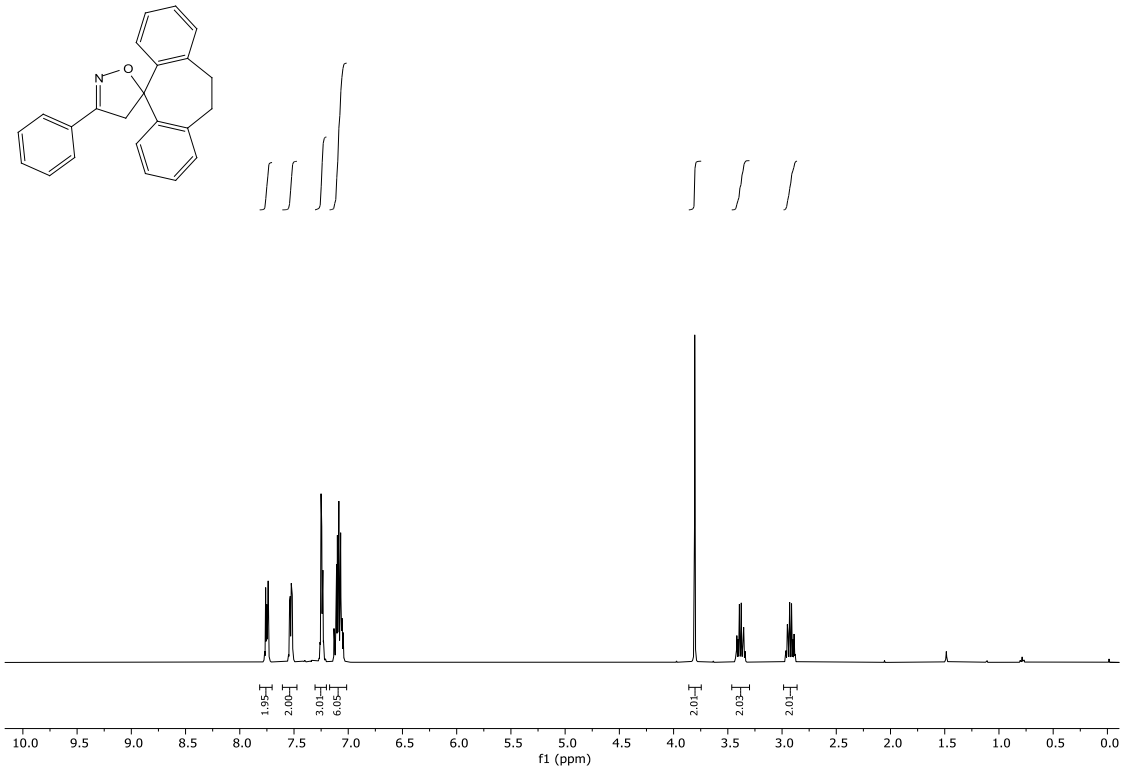
HSO_4^-

Charge: -1; Multiplicity: 1

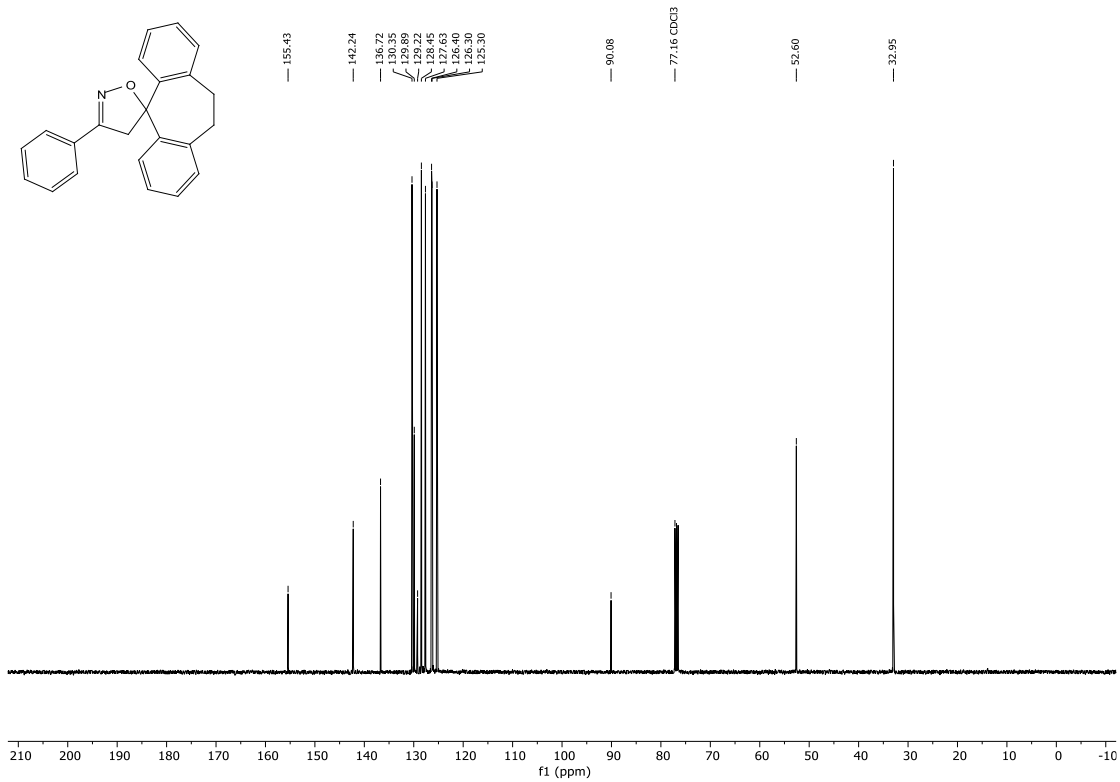
Atom	X	Y	Z
O	2.09577	-0.44338	-0.61548
S	3.501934	-0.148048	-0.941759
O	4.354793	-1.335693	-0.987679
O	3.498328	0.500767	-2.434163
O	4.063501	0.969162	-0.153721
H	3.12857	-0.136701	-3.066677
C	1.127302	2.910189	-0.694366
O	0.319701	1.73769	-0.593105
H	0.457477	3.764705	-0.79278
H	1.746135	3.056189	0.194832
H	1.777171	2.877994	-1.57346
H	0.914422	0.966833	-0.594483
C	1.892766	0.754917	2.619381
O	2.920648	1.700663	2.32578
H	1.572843	0.925442	3.647418
H	1.029583	0.879262	1.96061
H	2.253005	-0.273944	2.535155
H	3.288115	1.480208	1.453203
C	5.657212	-0.604584	2.427901
O	6.279375	0.201756	1.429443
H	6.447777	-1.065746	3.020437
H	5.02702	-0.009874	3.0952
H	5.050961	-1.401127	1.986797
H	5.579204	0.529642	0.84081

11 NMR spectra

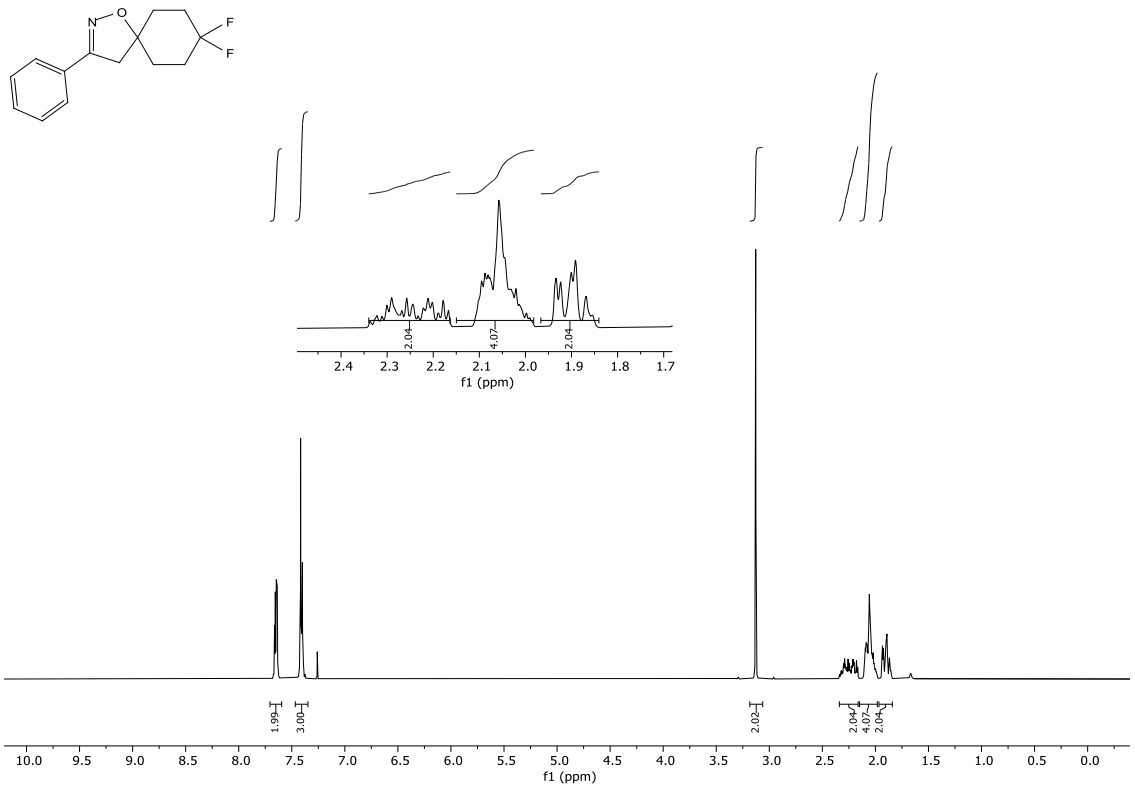
^{1}H NMR spectrum for **1f**



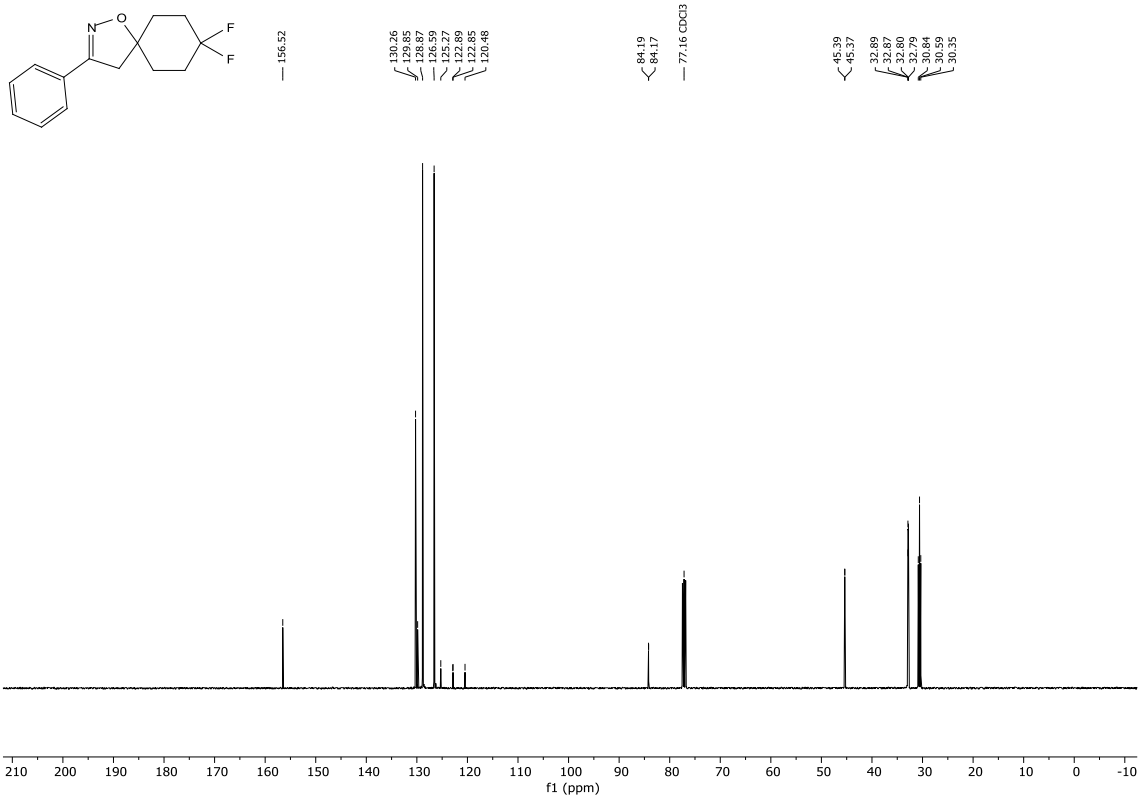
^{13}C NMR spectrum for **1f**



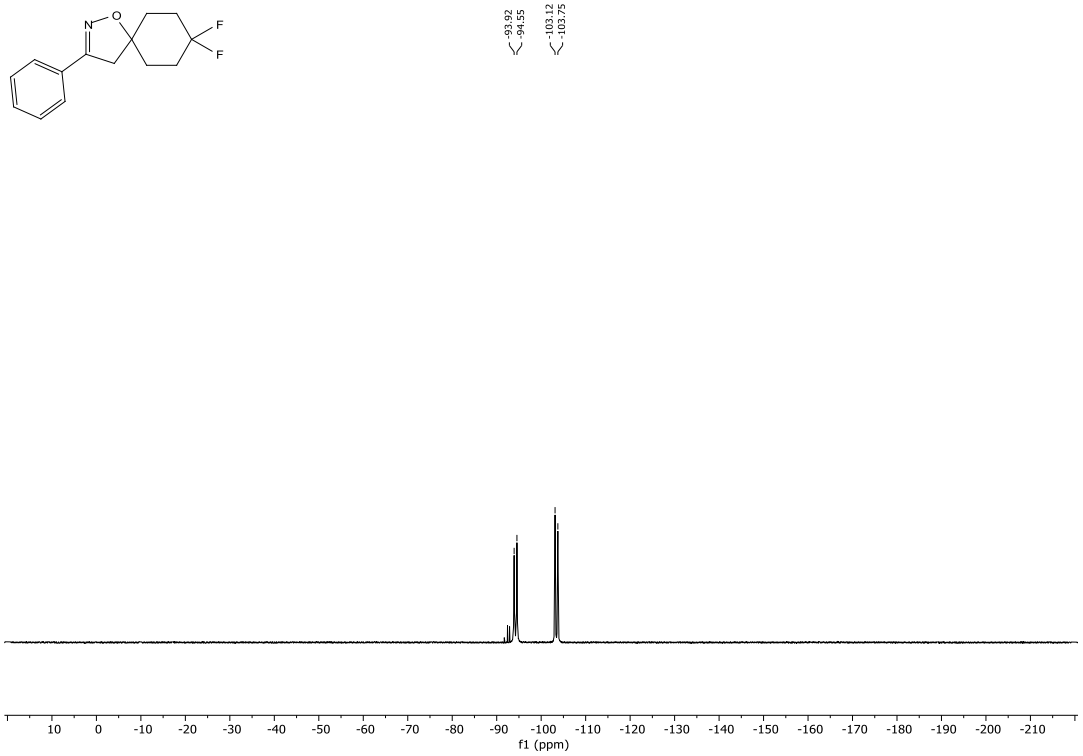
^{1}H NMR spectrum for **1g**



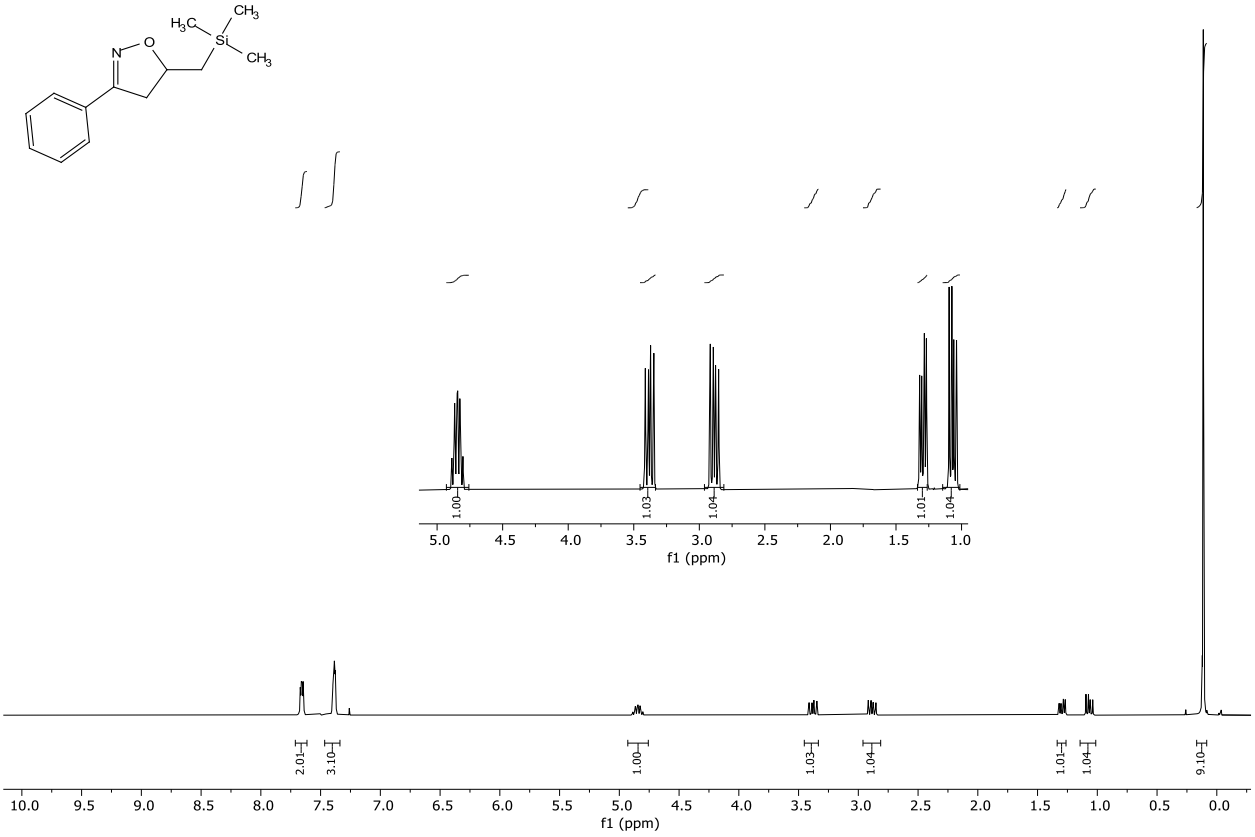
^{13}C NMR spectrum for **1g**



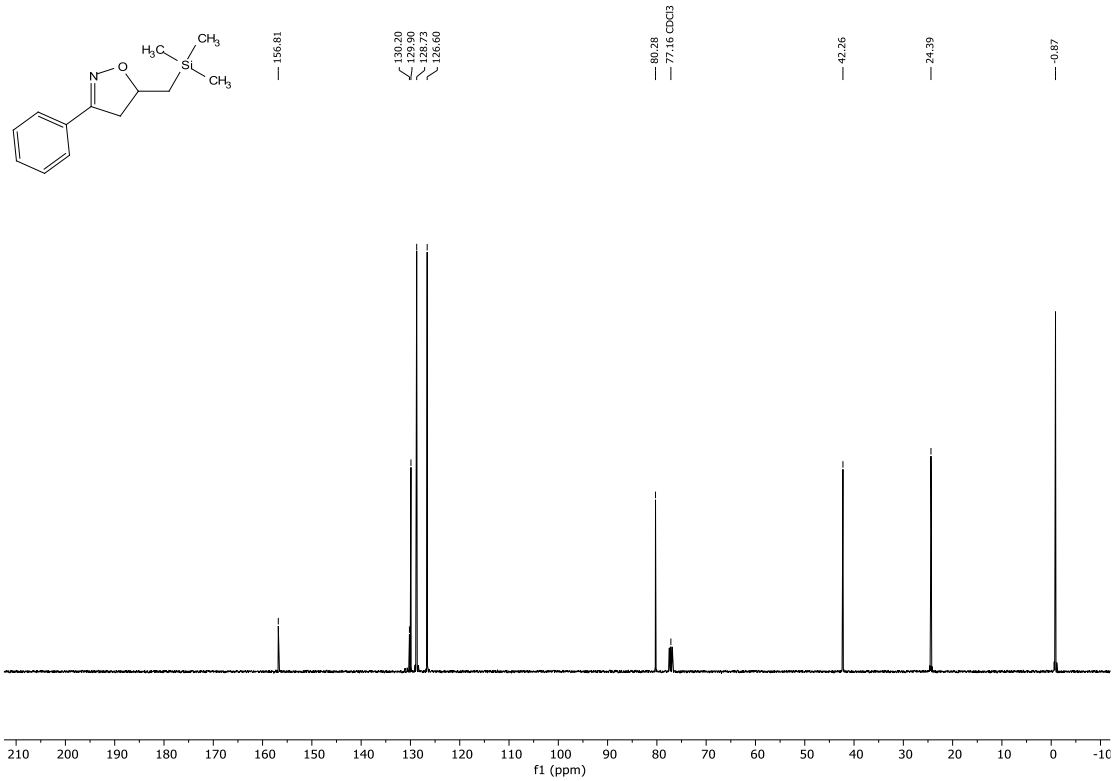
^{19}F NMR spectrum for **1g**



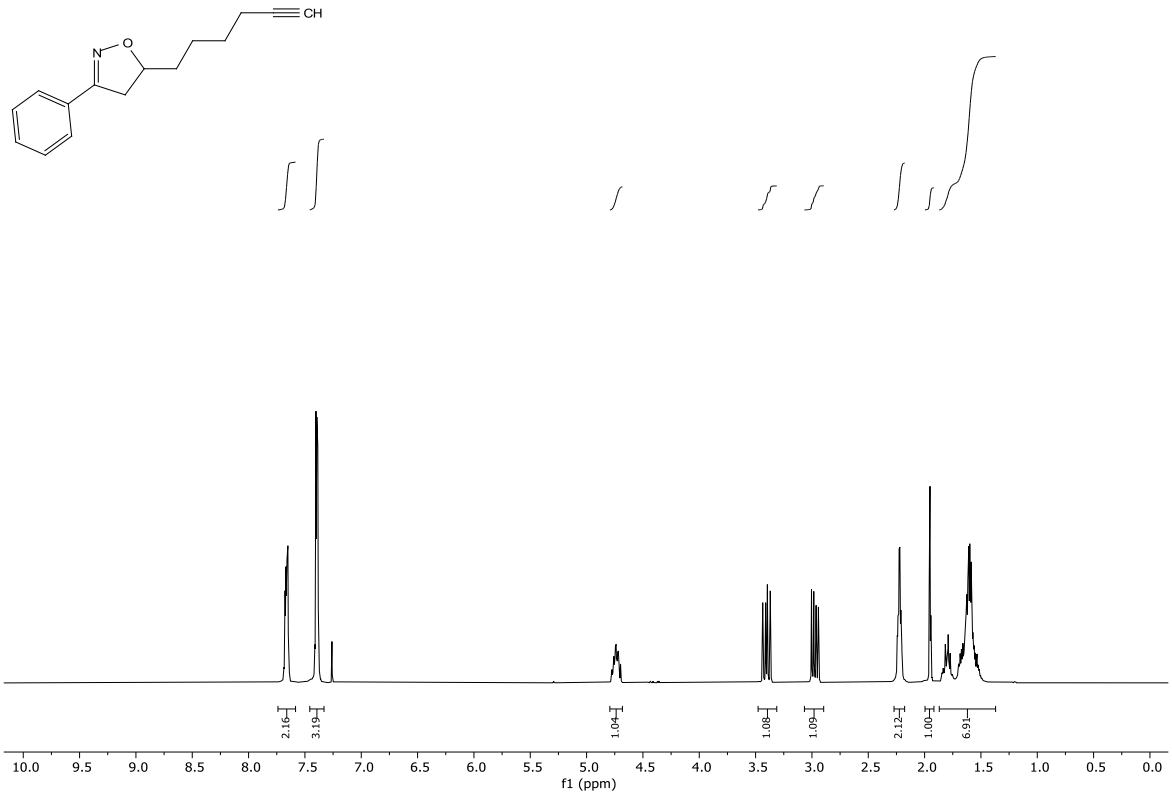
^{1}H NMR spectrum for **1i**



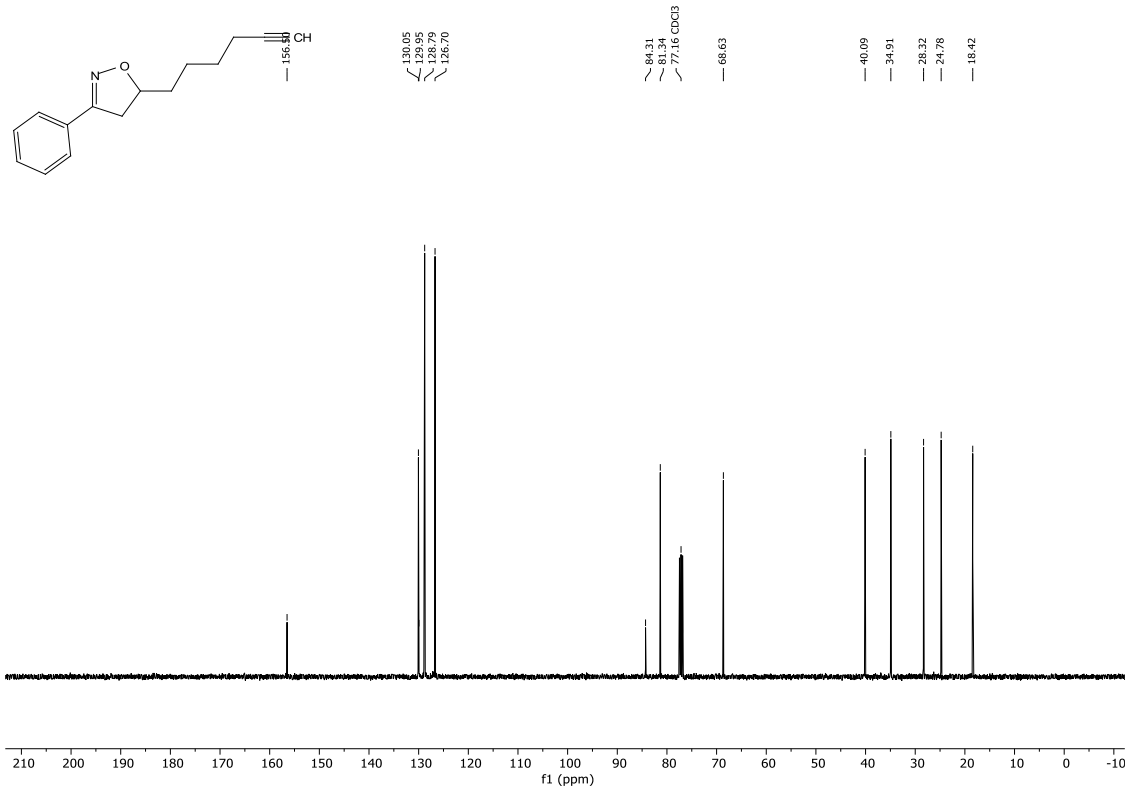
^{13}C NMR spectrum for **1i**



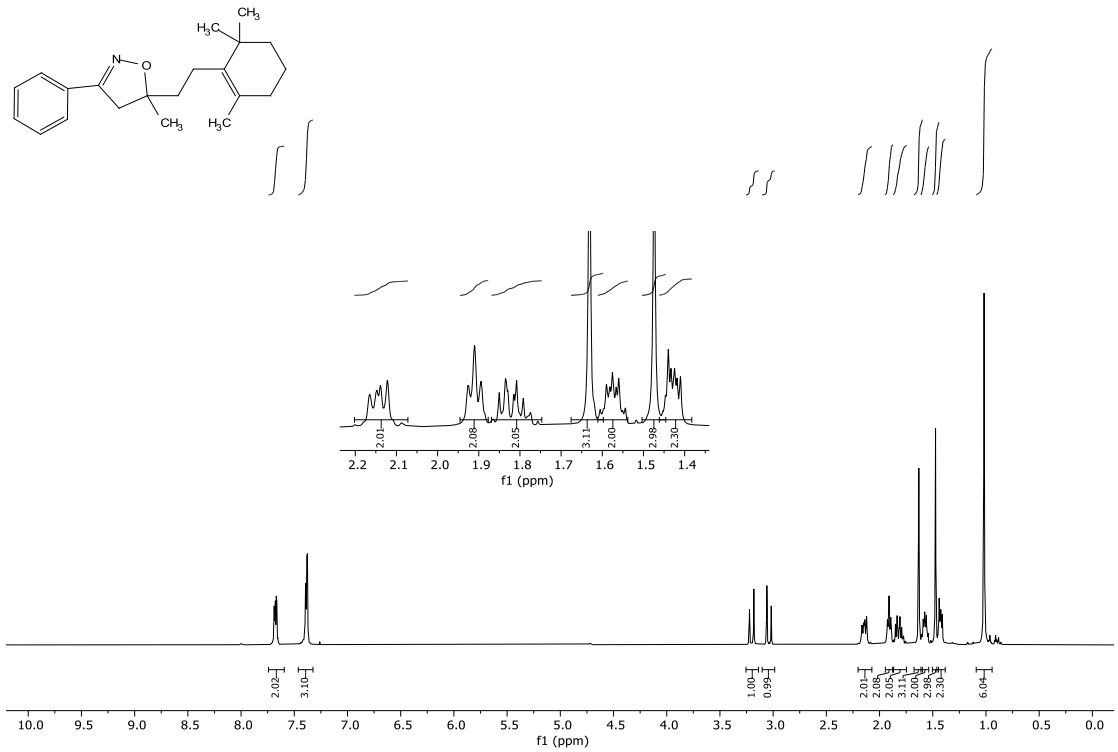
^{1}H NMR spectrum for **1j**



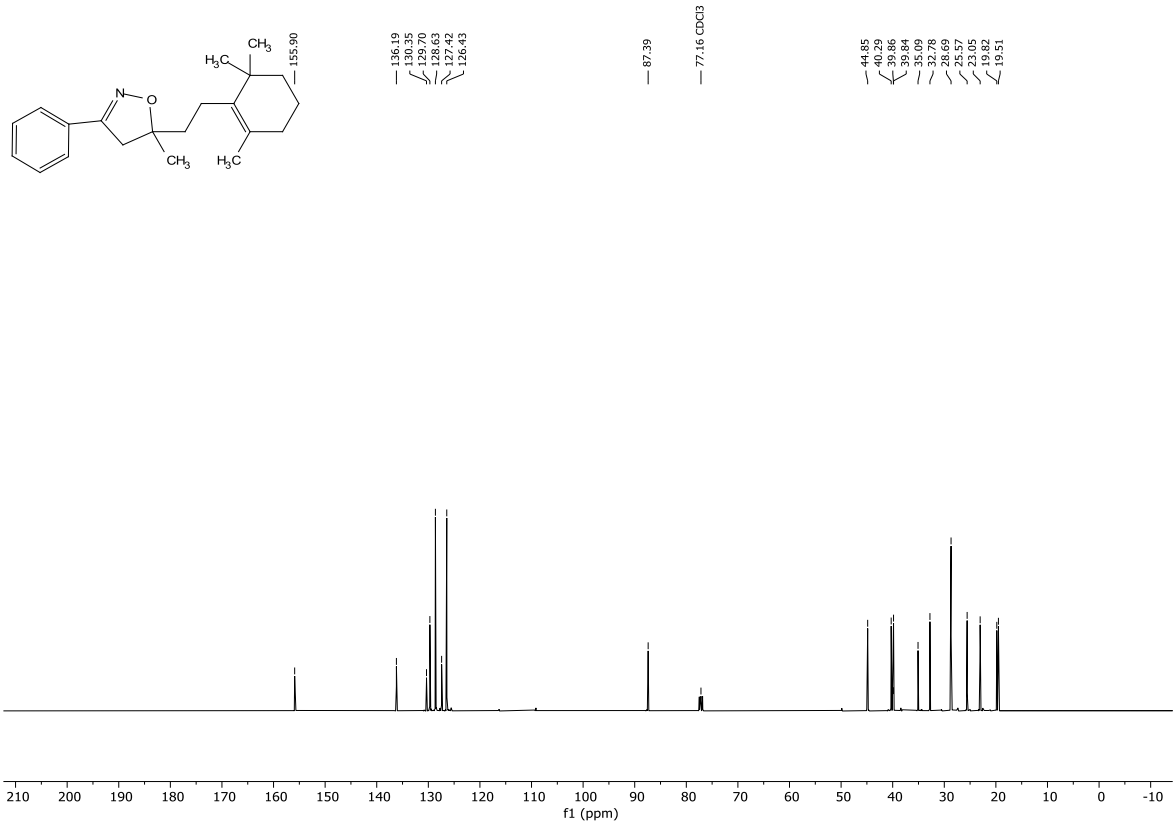
^{13}C NMR spectrum for **1j**



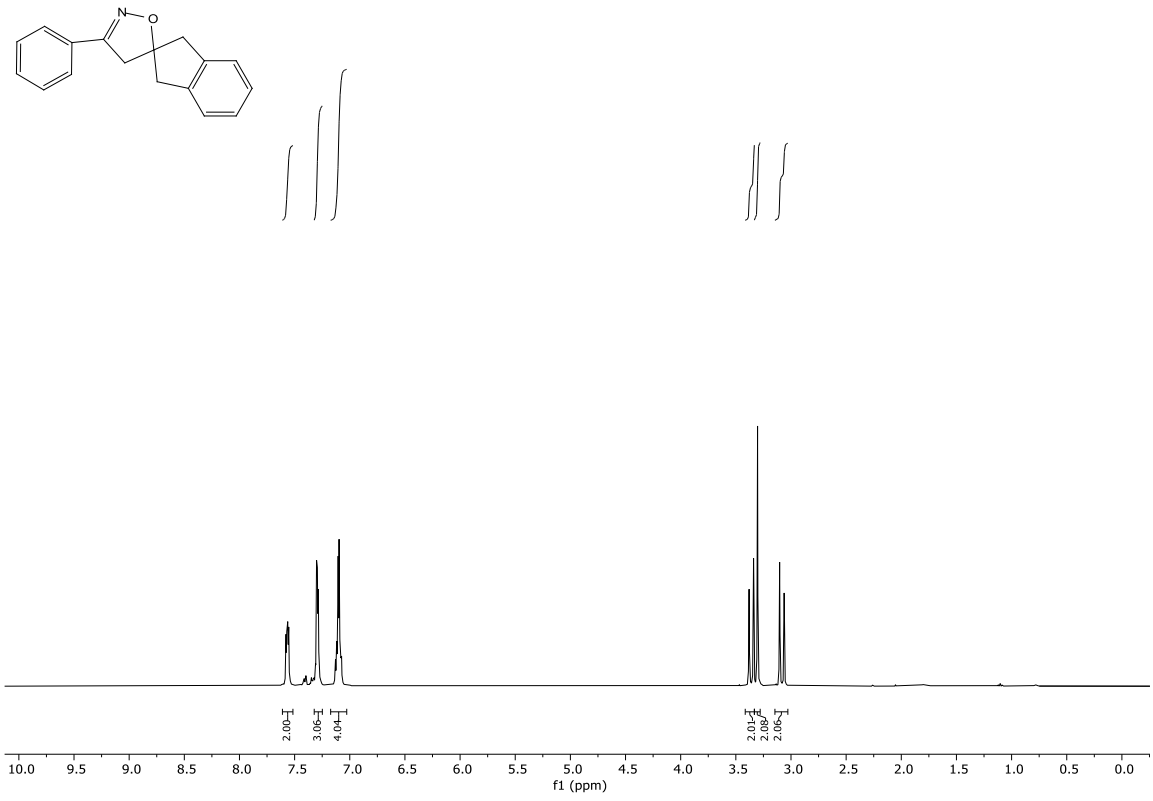
^{1}H NMR spectrum for **1m**



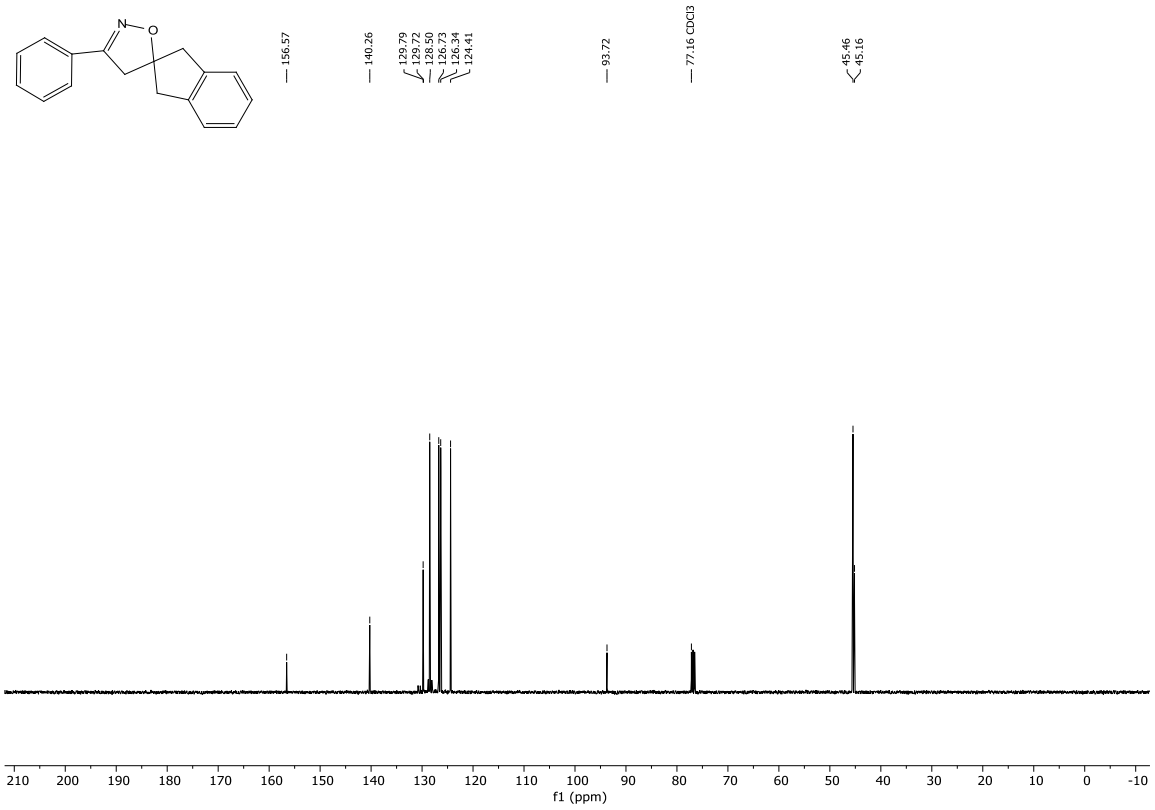
^{13}C NMR spectrum for **1m**



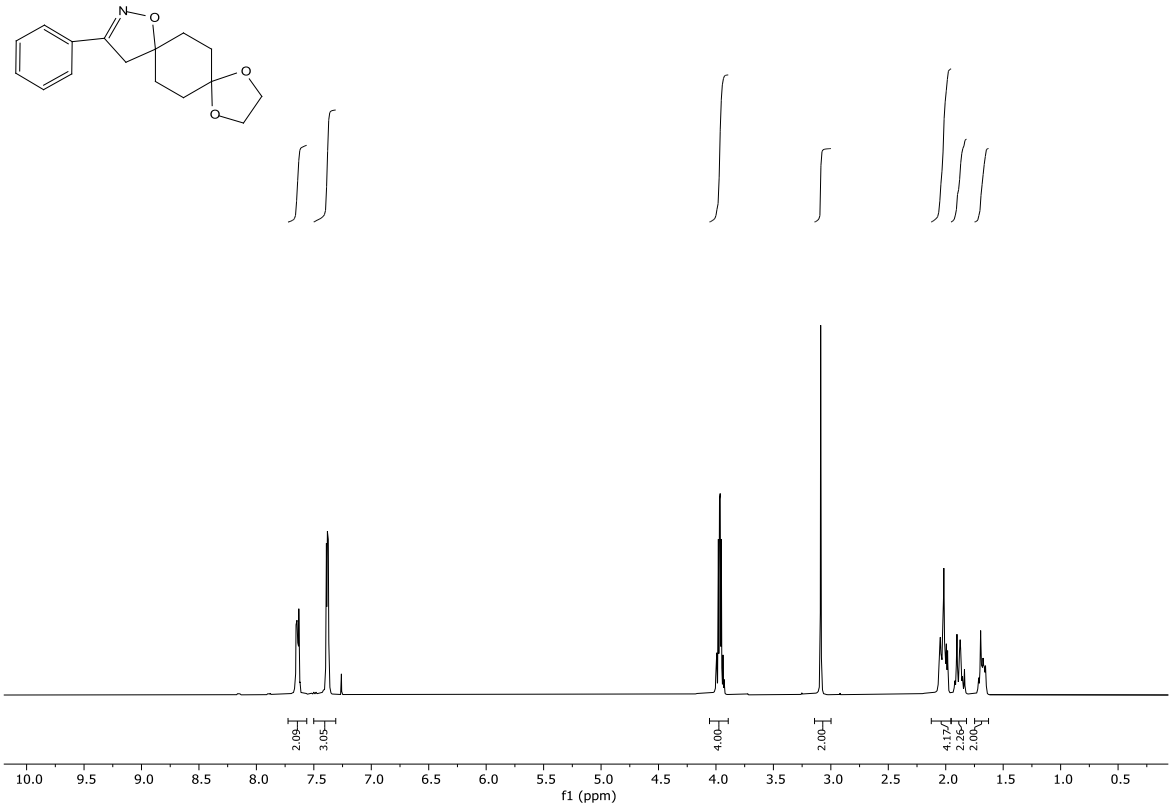
^{1}H NMR spectrum for **1n**



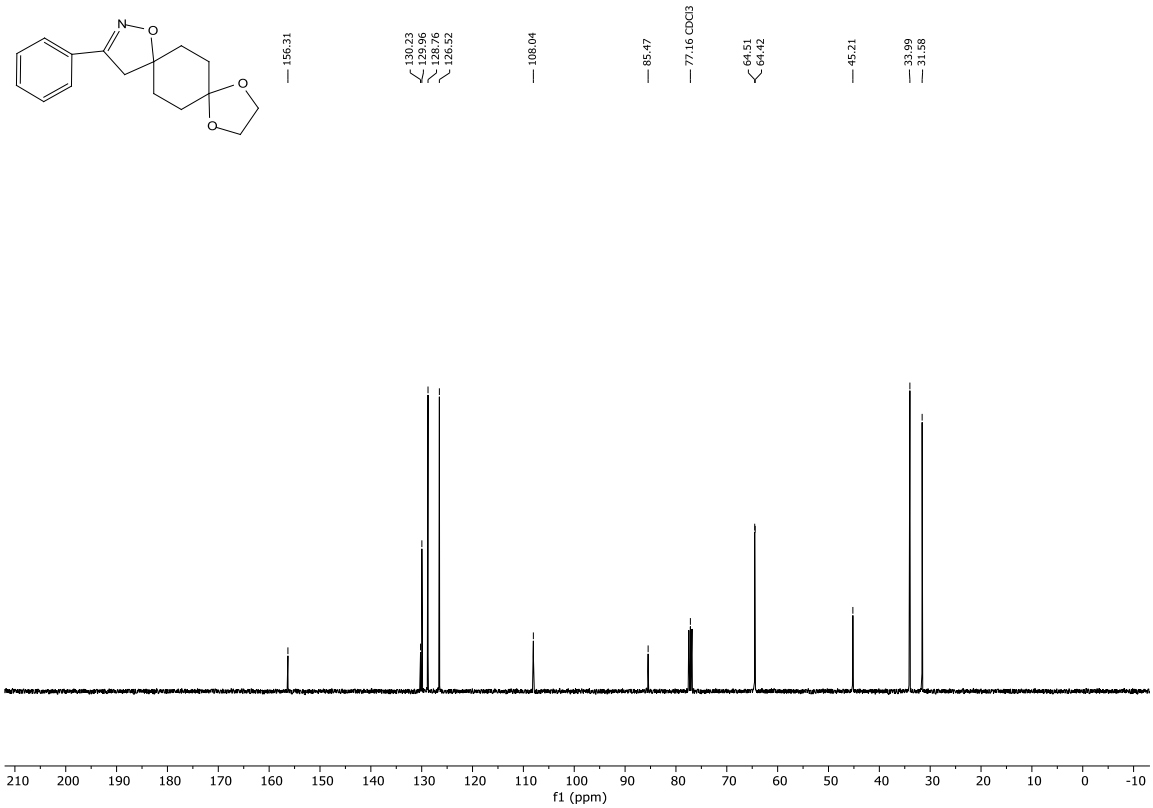
^{13}C NMR spectrum for **1n**



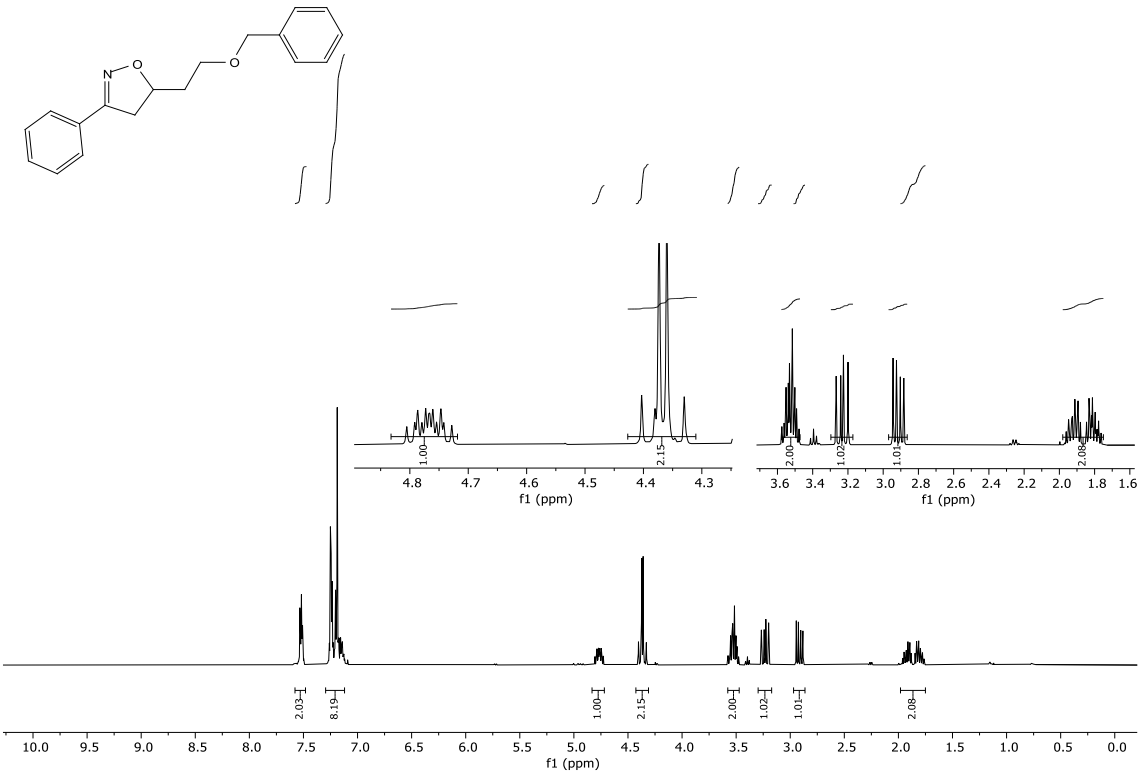
^{1}H NMR spectrum for **1o**



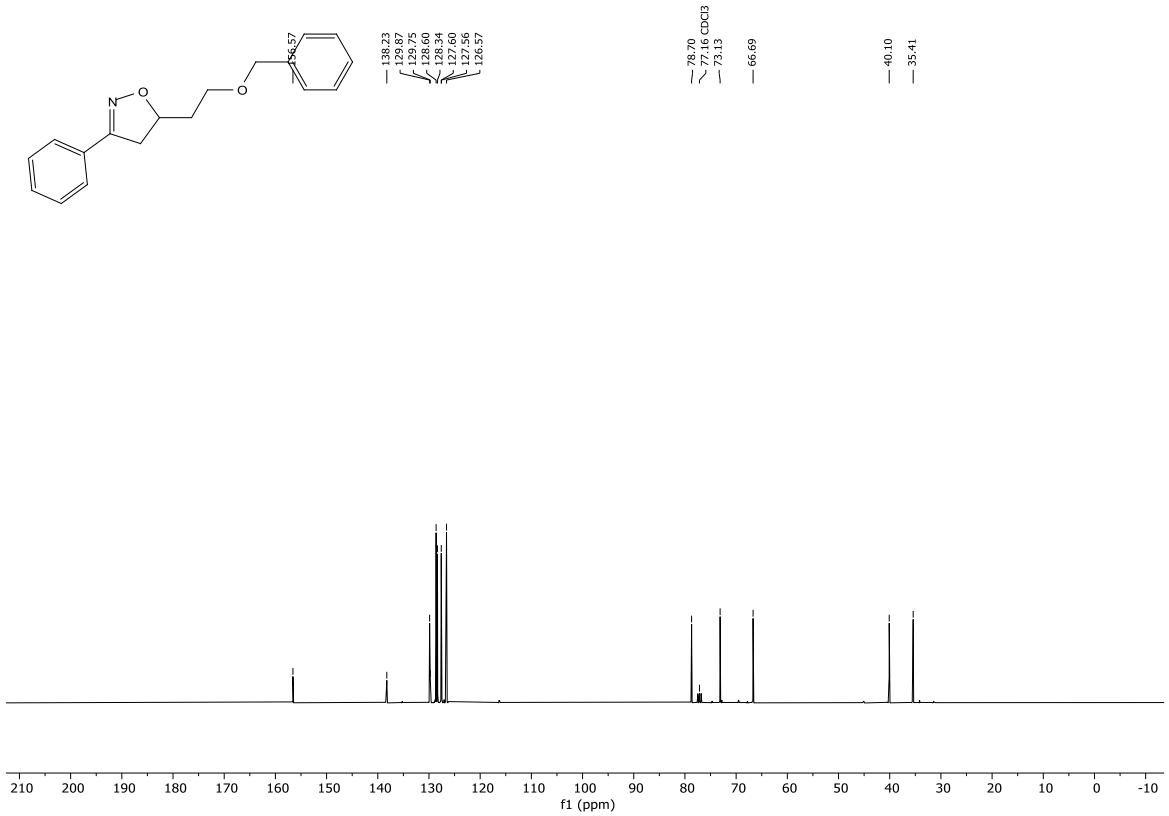
^{13}C NMR spectrum for **1o**



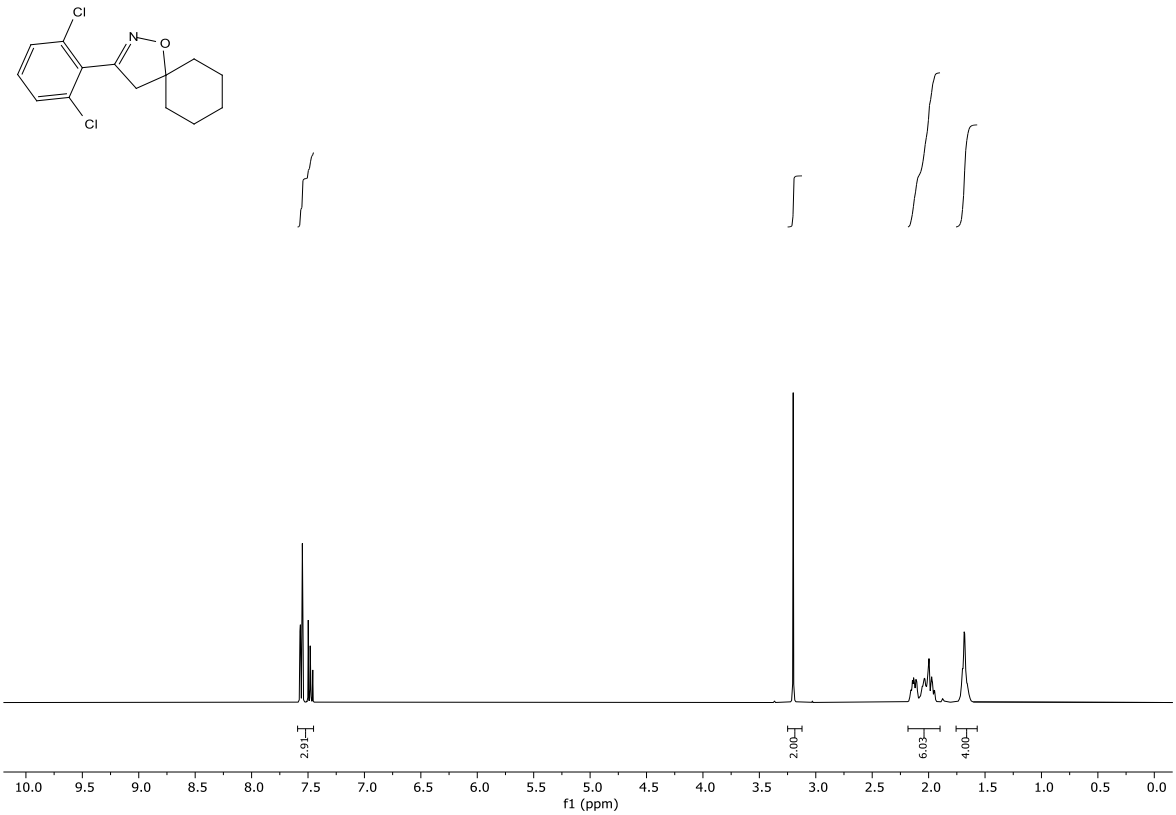
^{1}H NMR spectrum for **1p**



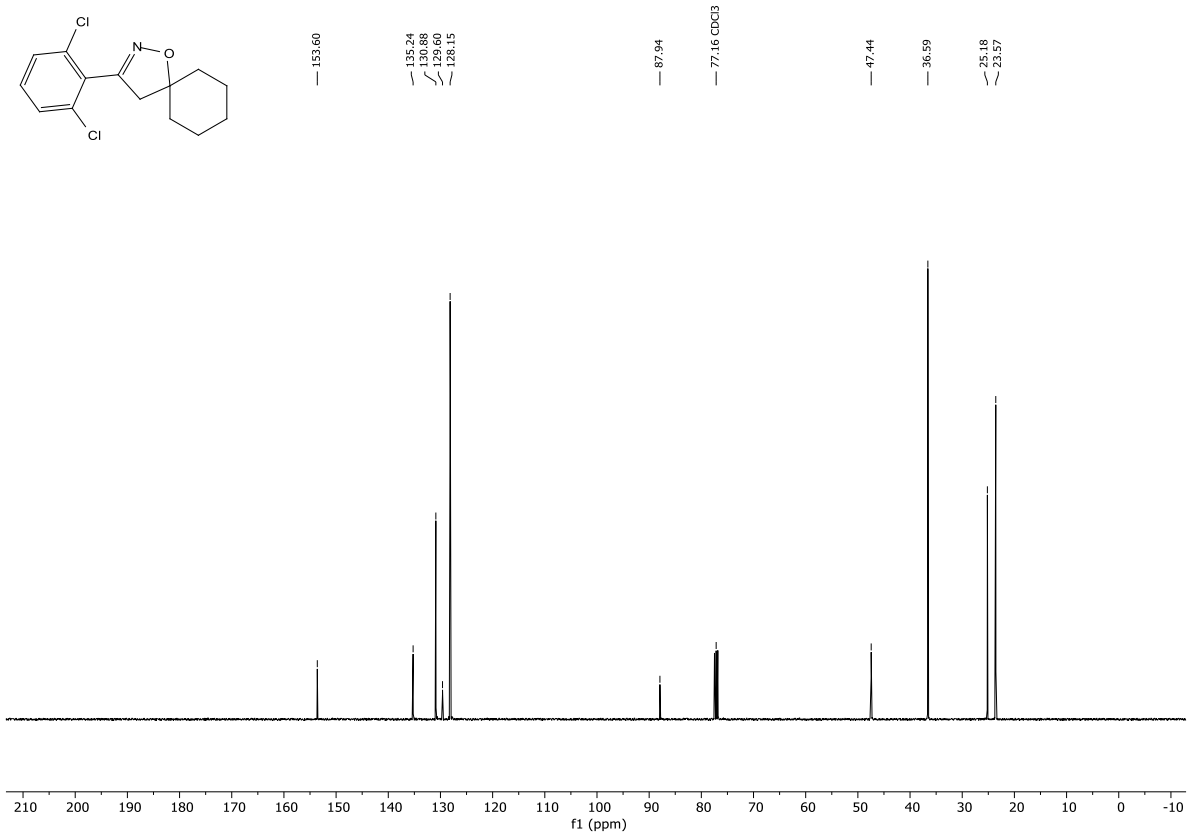
^{13}C NMR spectrum for **1p**



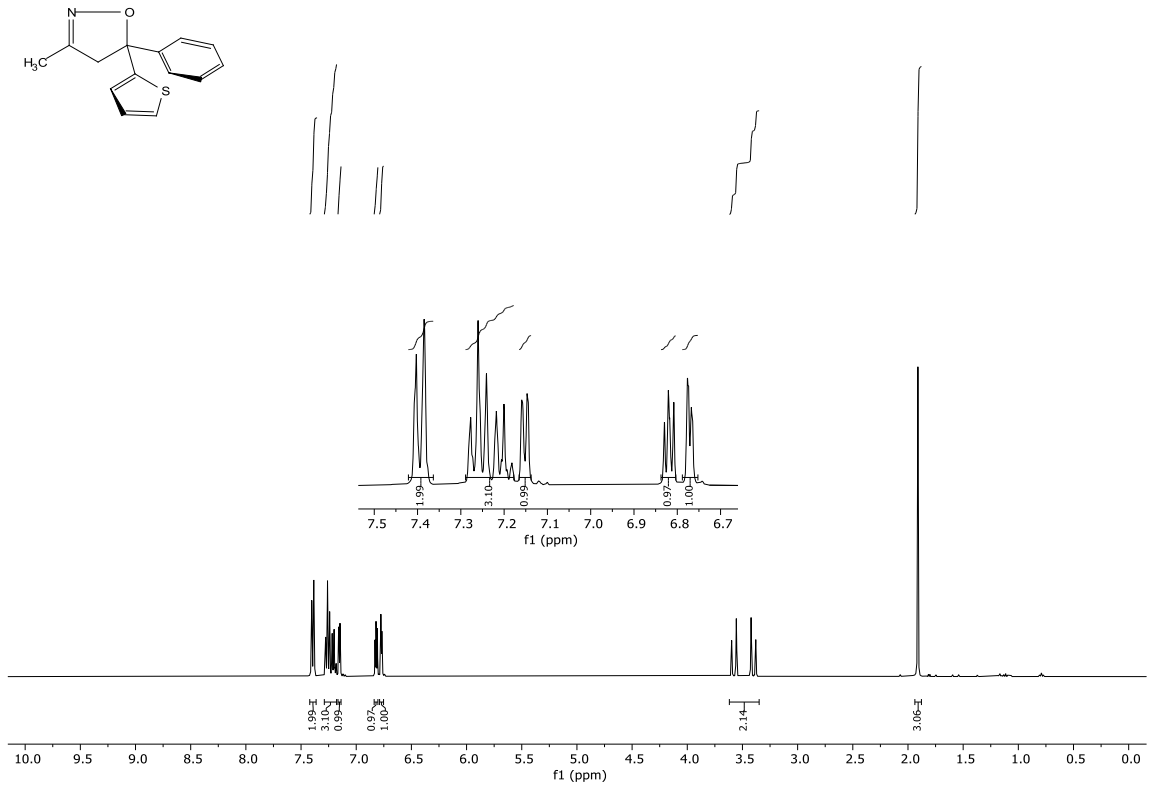
^{1}H NMR spectrum for **1q**



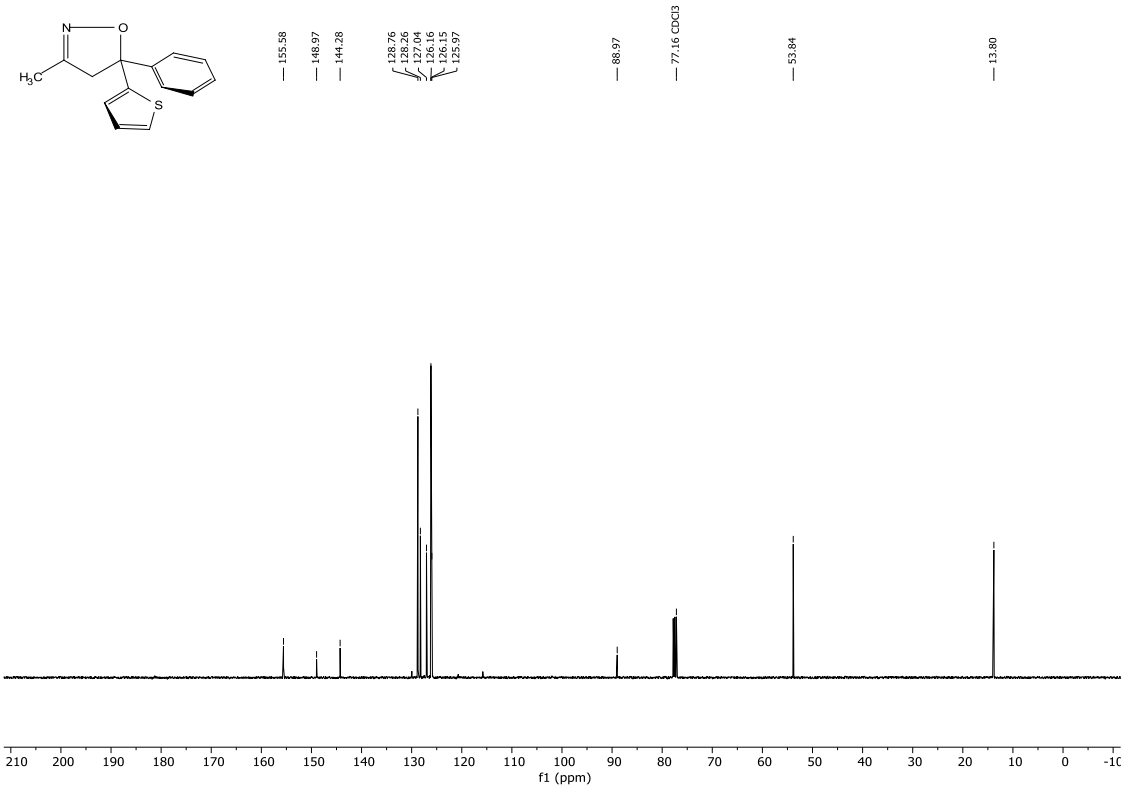
^{13}C NMR spectrum for **1q**



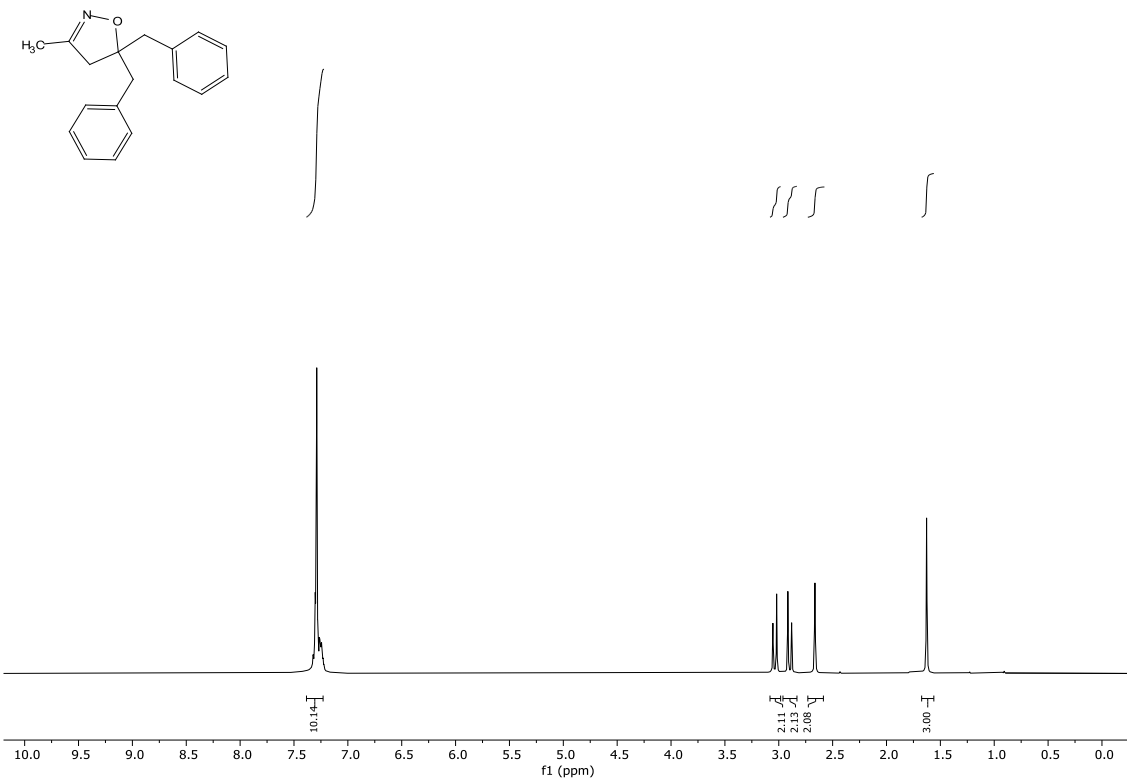
^{1}H NMR spectrum for **1r**



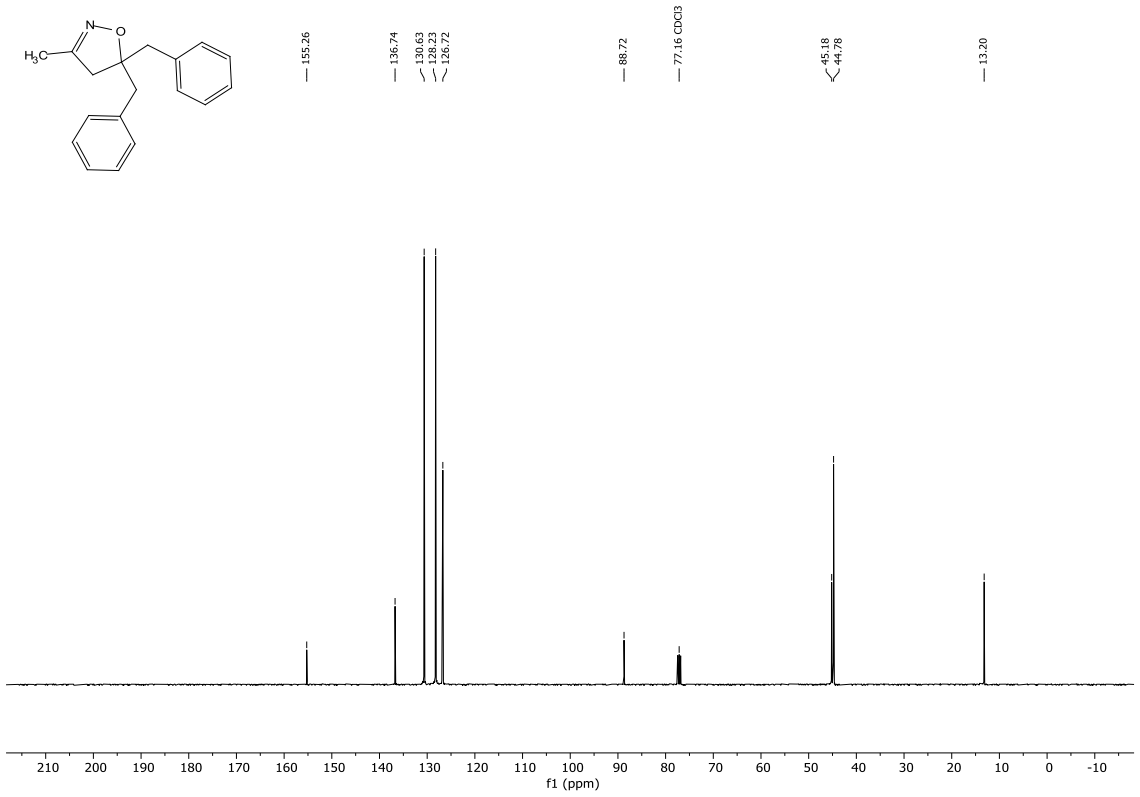
^{13}C NMR spectrum for **1r**



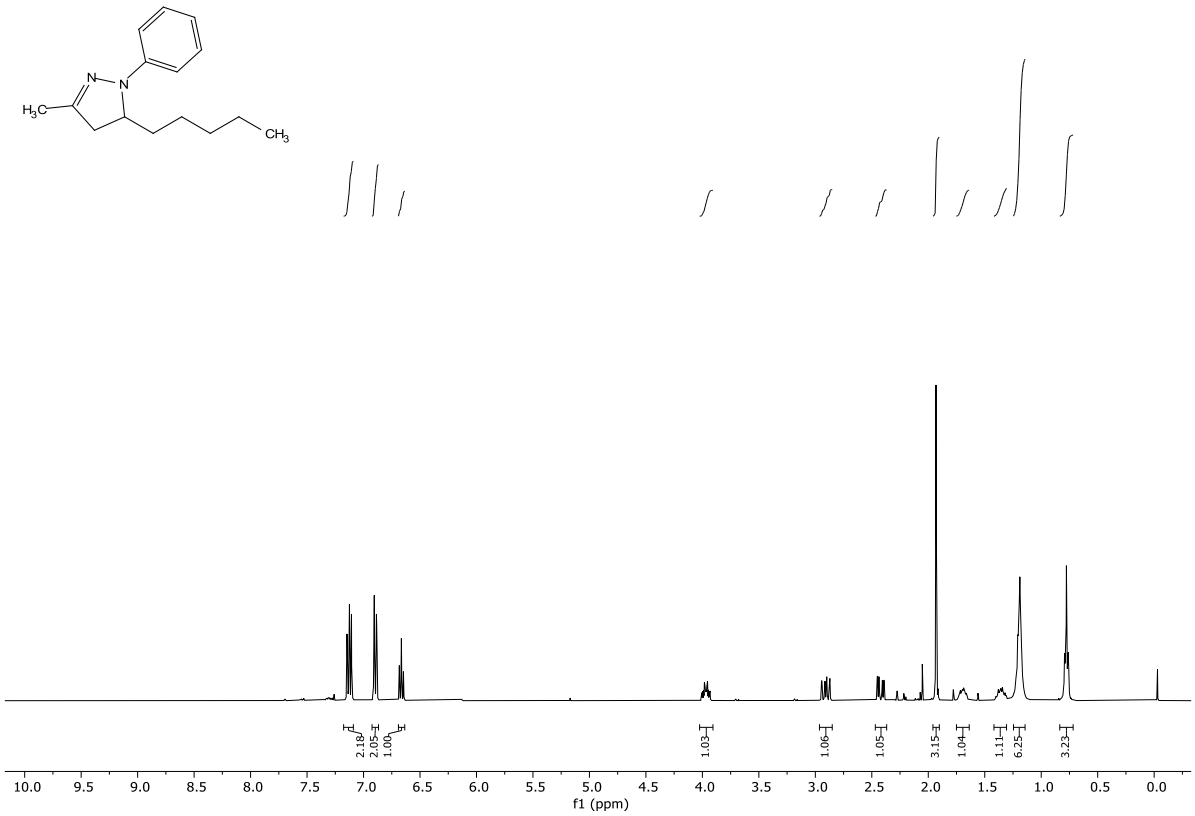
^{1}H NMR spectrum for **1s**



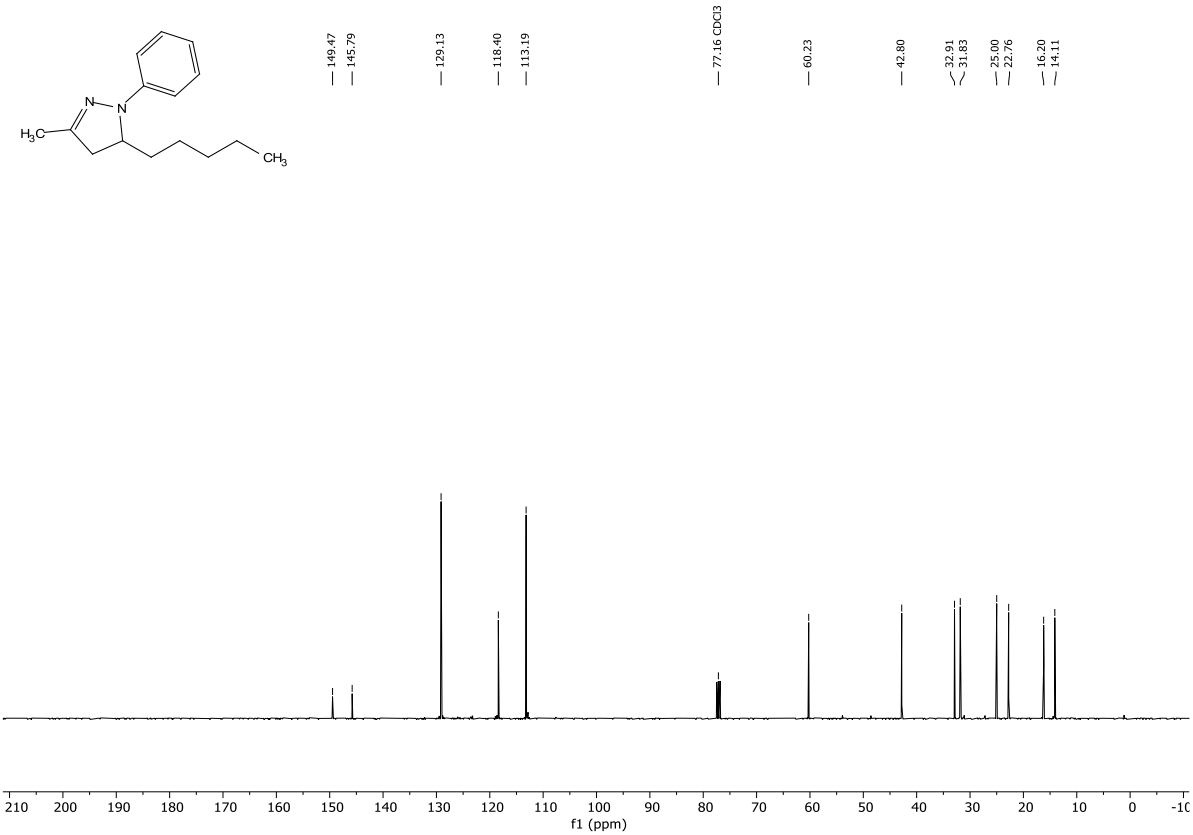
^{13}C NMR spectrum for **1s**



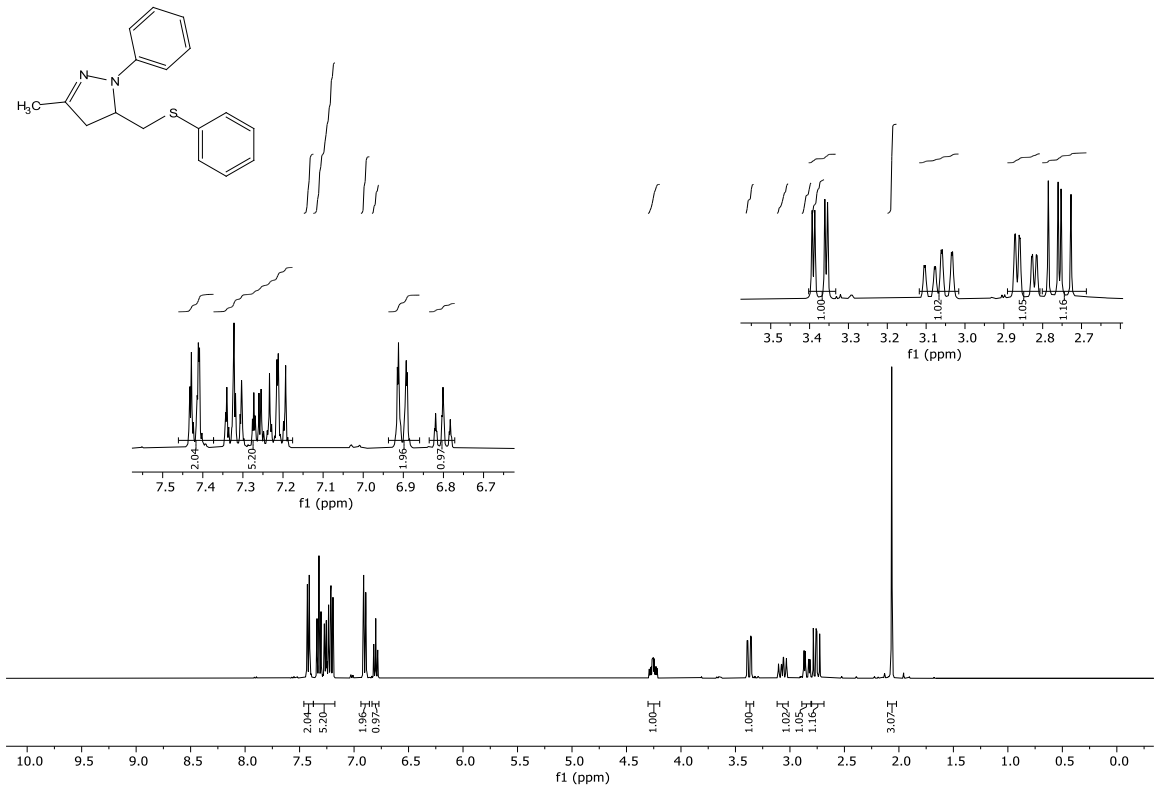
^{1}H NMR spectrum for **3l**



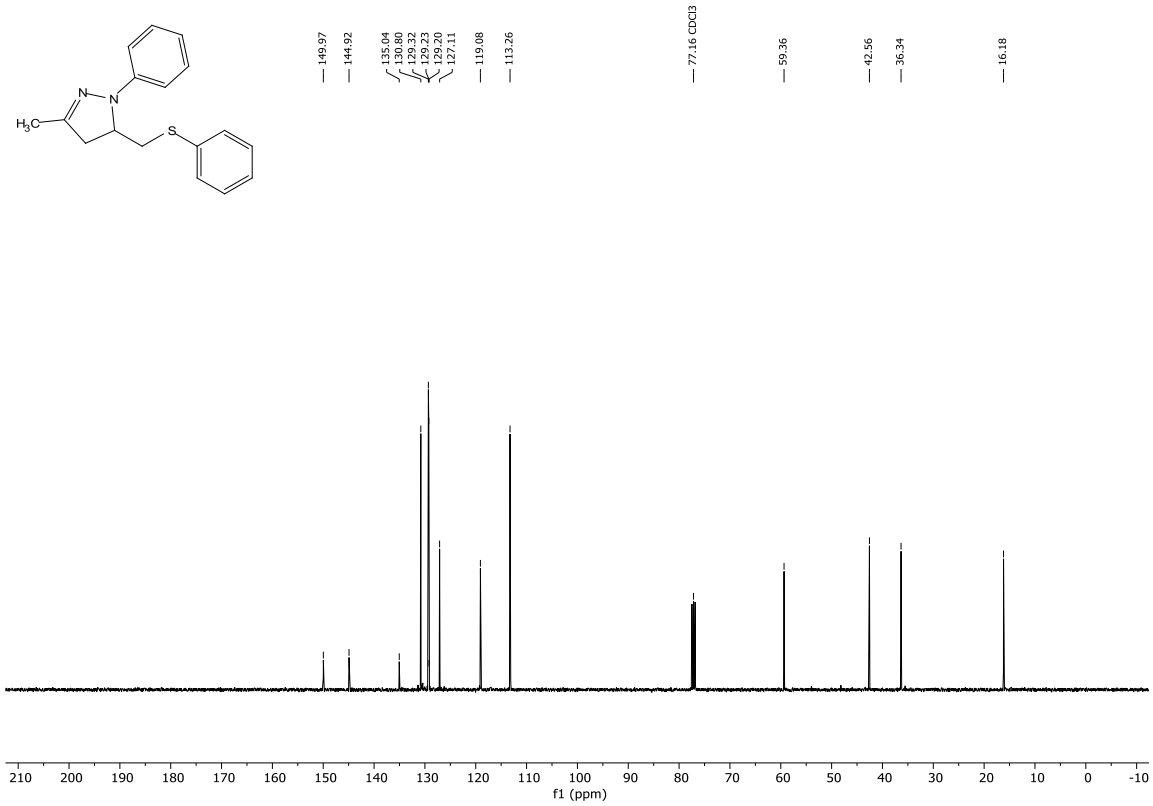
^{13}C NMR spectrum for **3l**



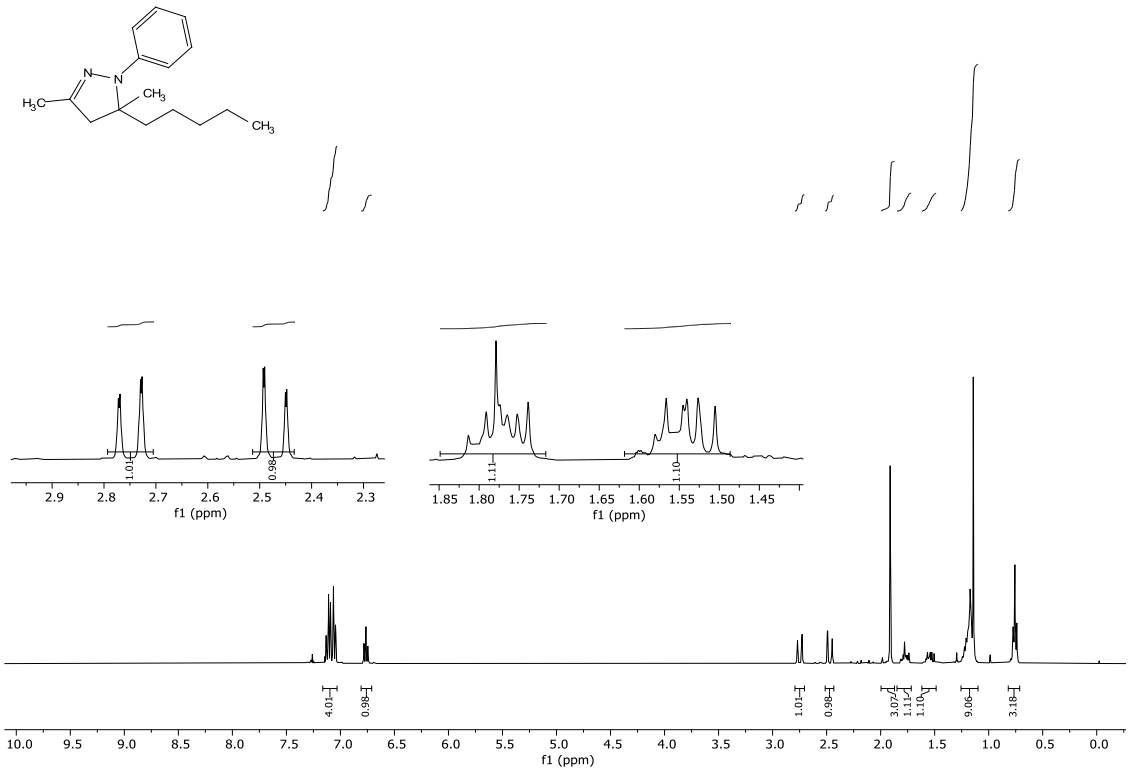
^{1}H NMR spectrum for **3m**



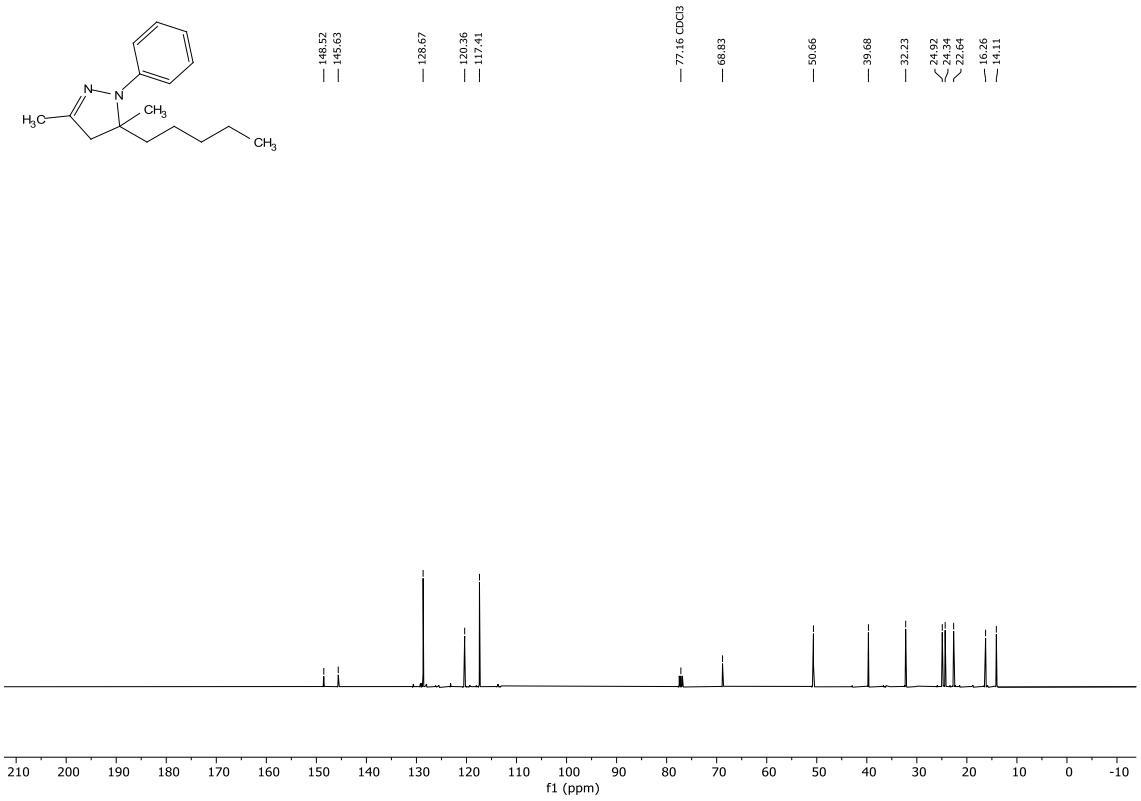
^{13}C NMR spectrum for **3m**



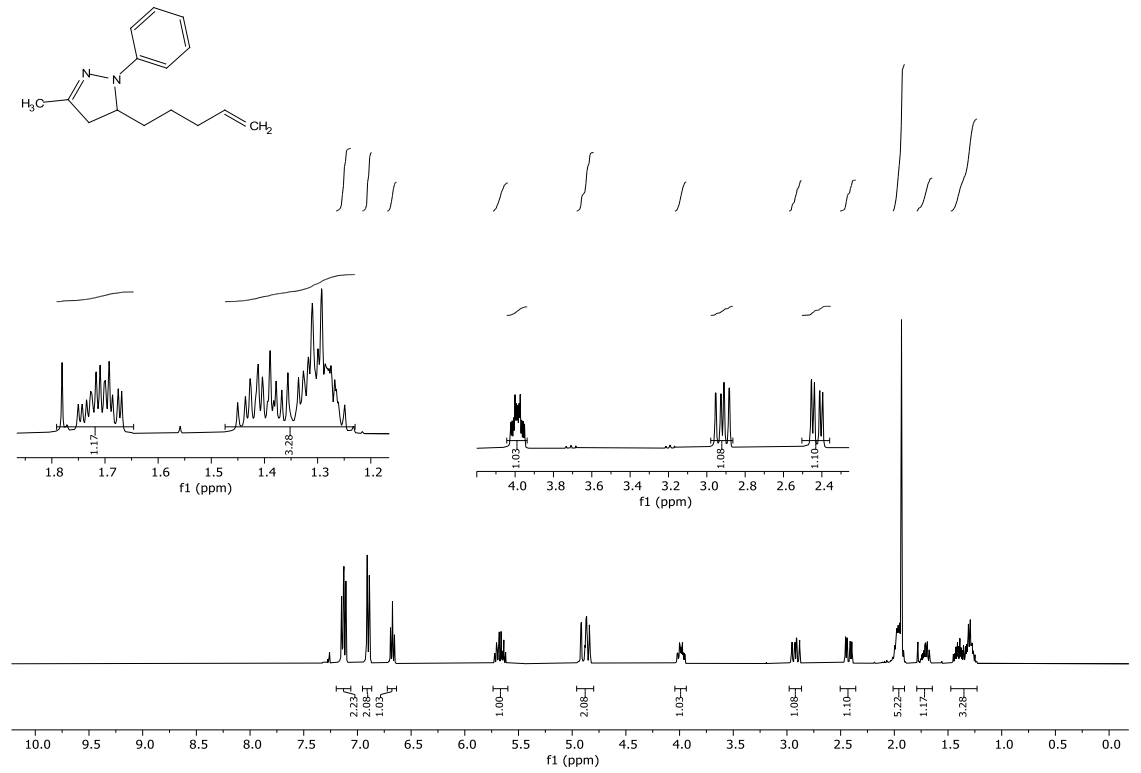
^{1}H NMR spectrum for **3n**



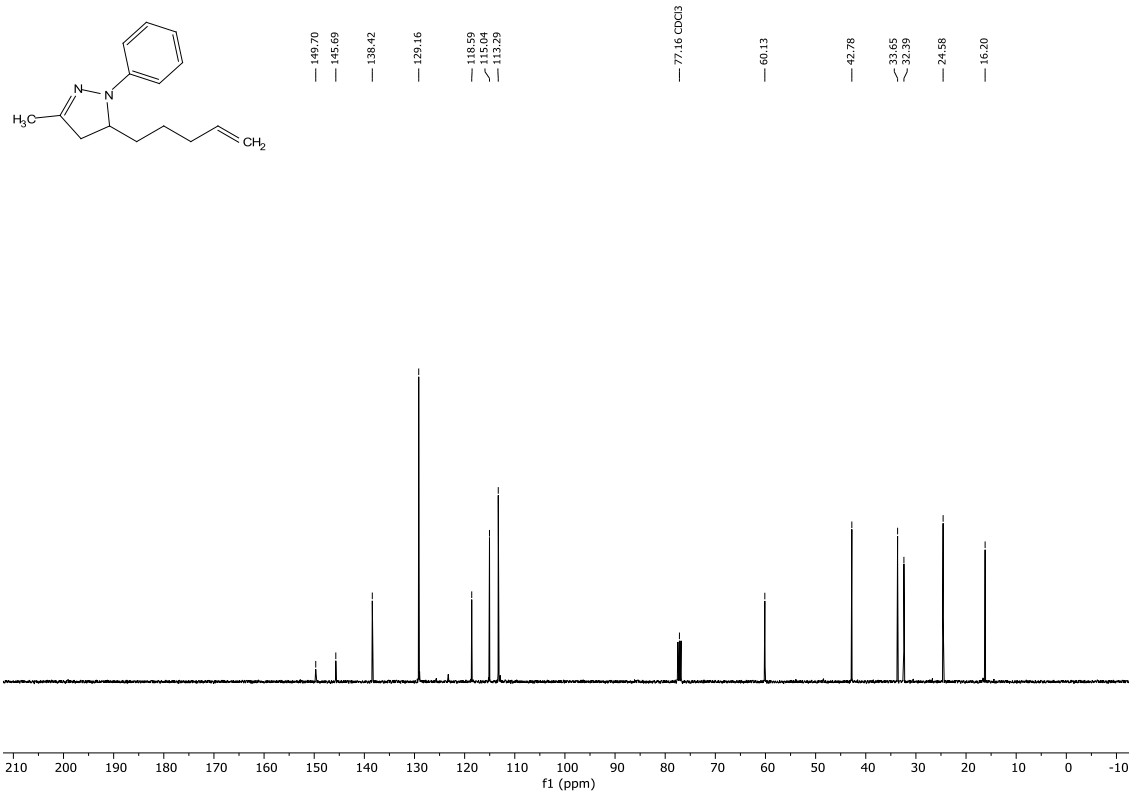
^{13}C NMR spectrum for **3n**



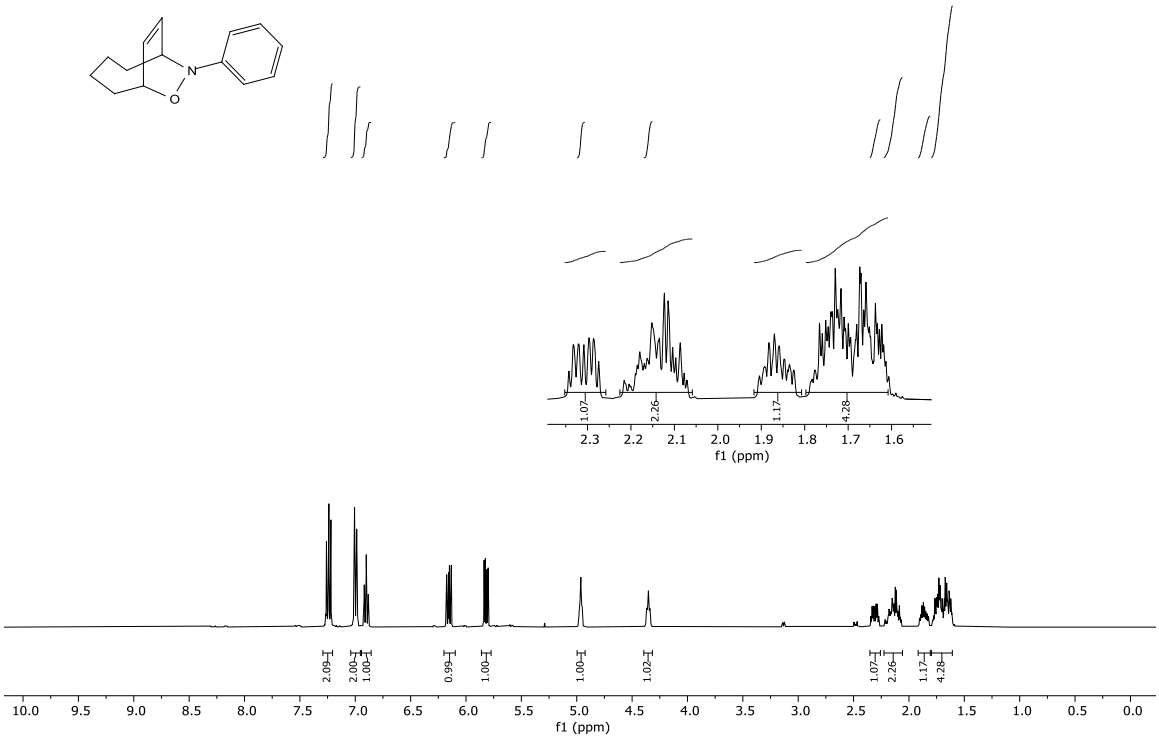
^{1}H NMR spectrum for **3o**



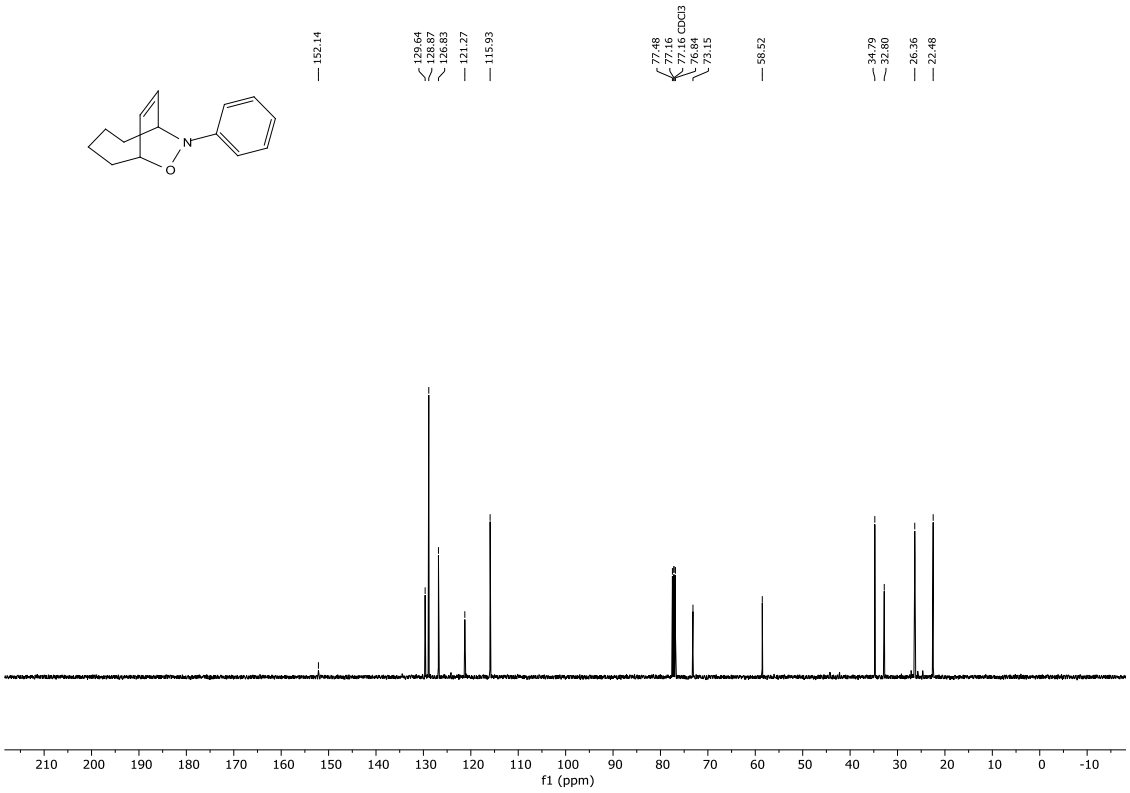
^{13}C NMR spectrum for **3o**



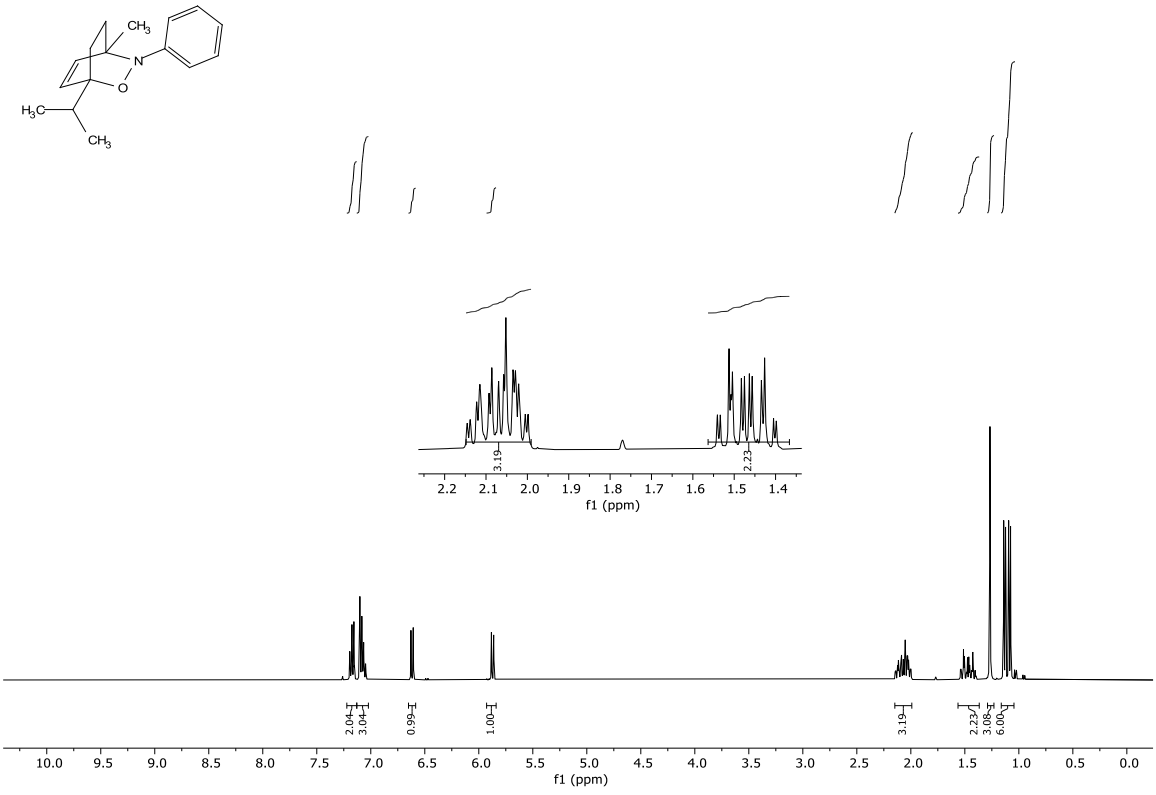
^{1}H NMR spectrum for **5b**



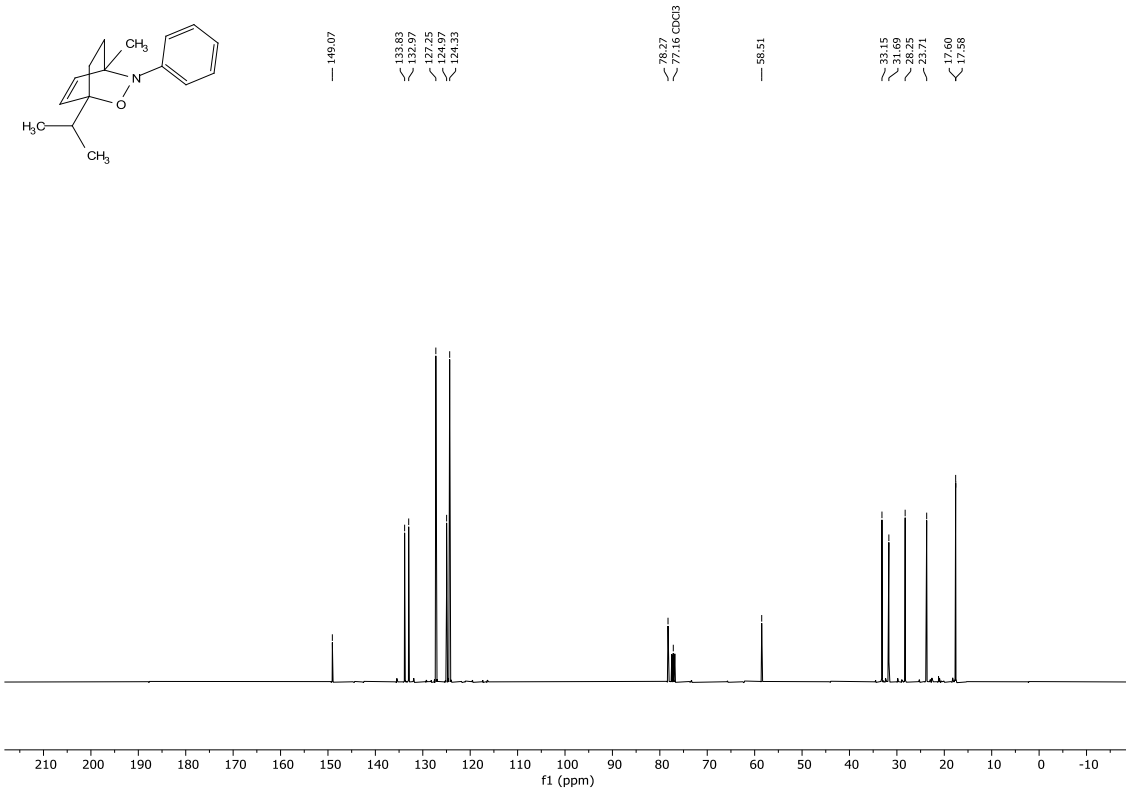
^{13}C NMR spectrum for **5b**



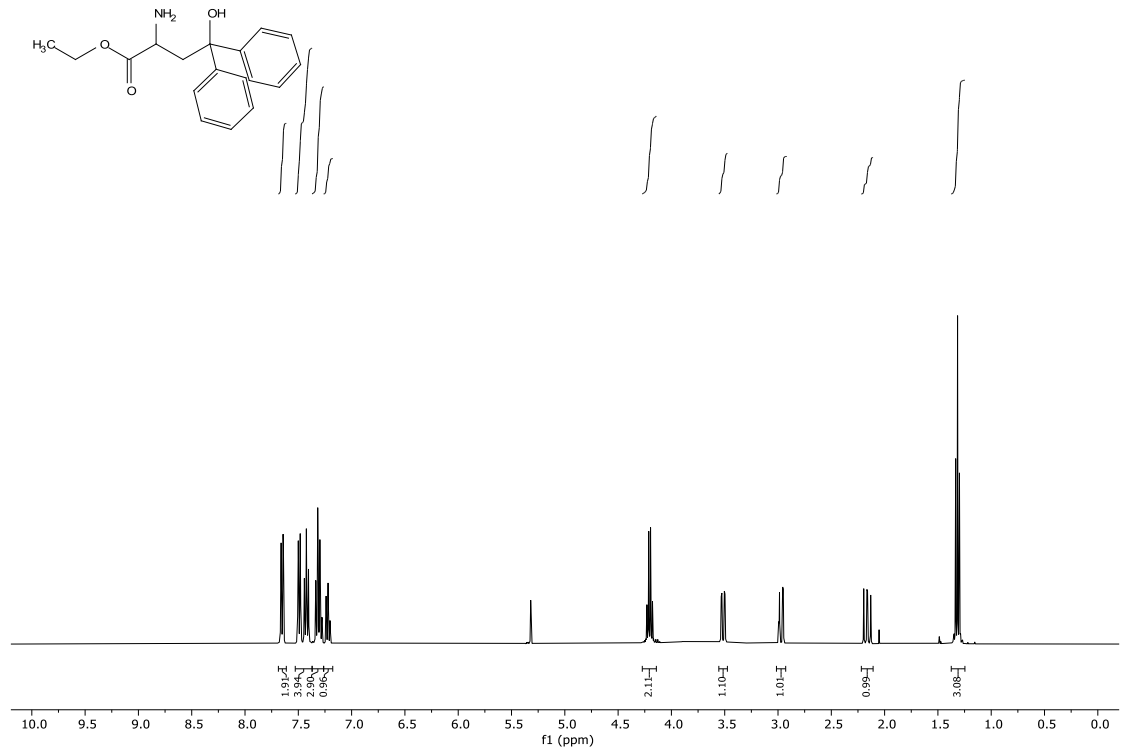
^{1}H NMR spectrum for **5c**



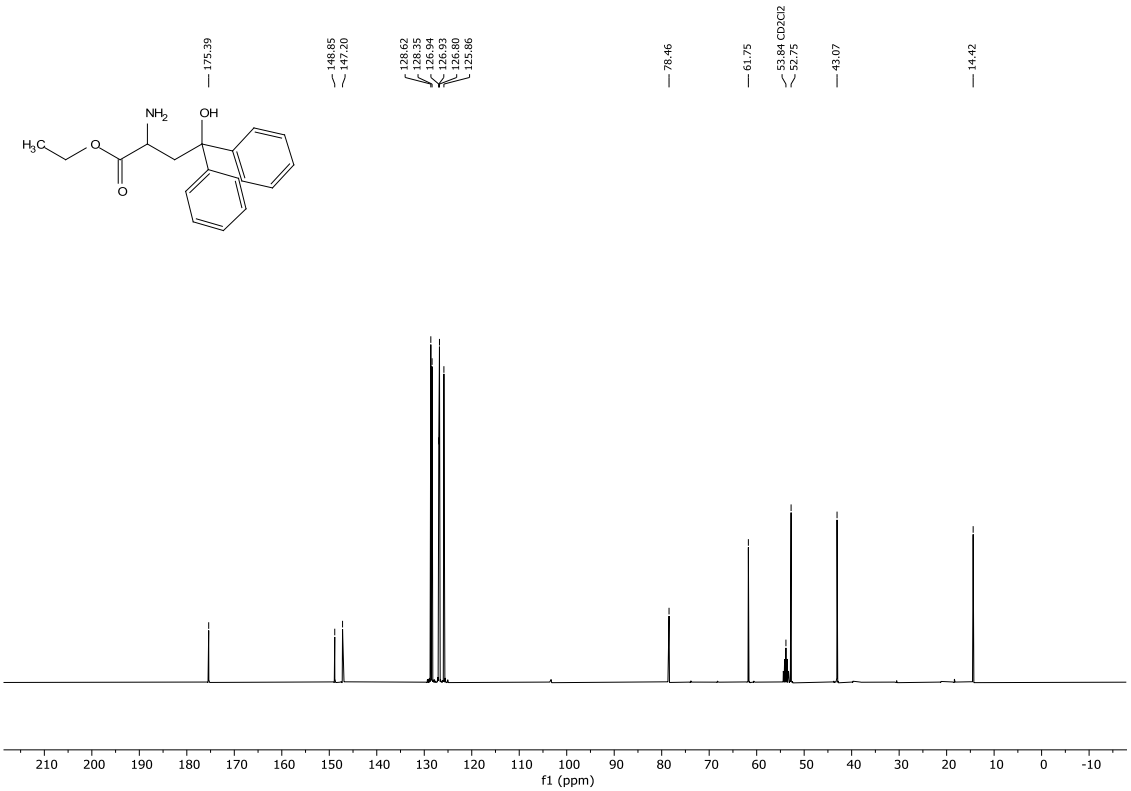
^{13}C NMR spectrum for **5c**



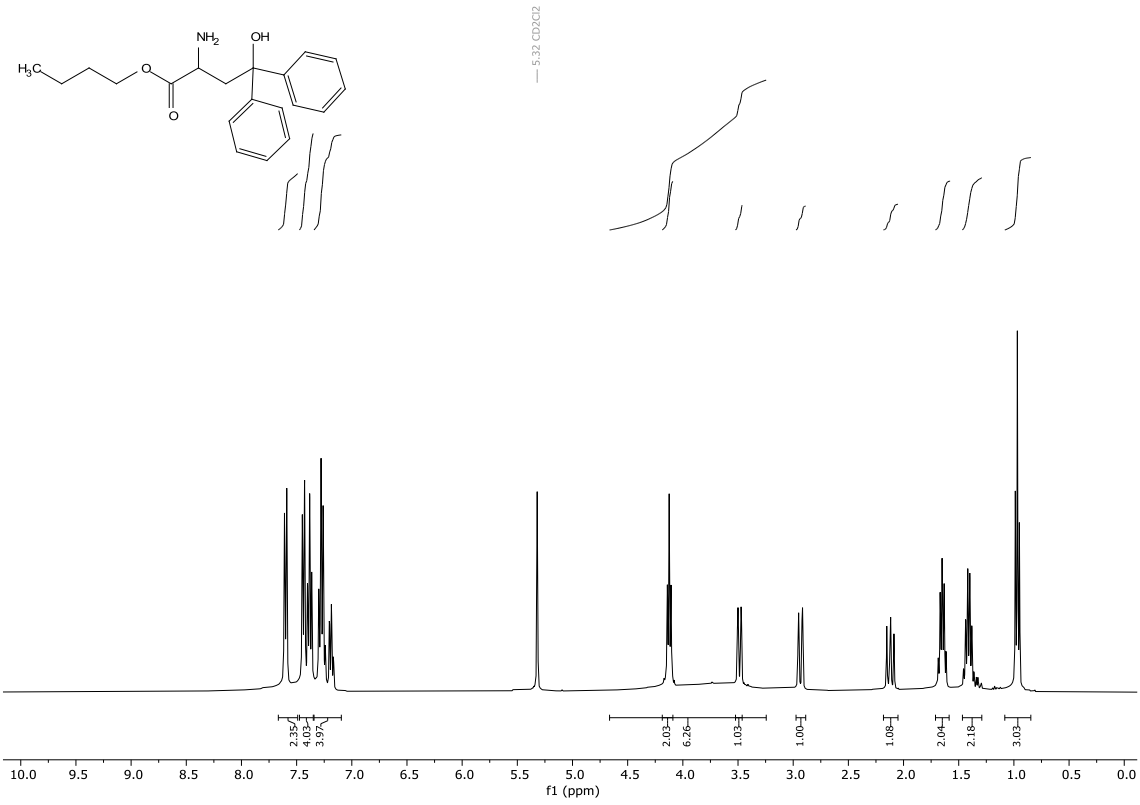
^{1}H NMR spectrum for **2a**



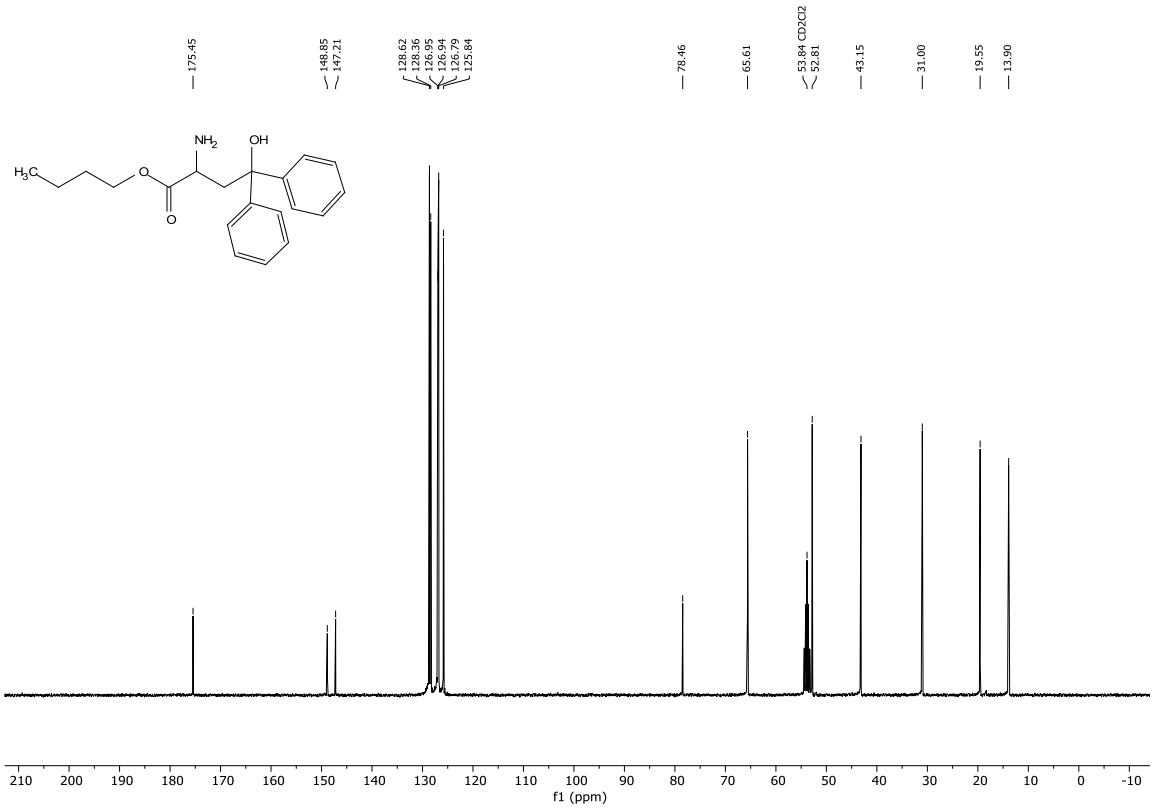
^{13}C NMR spectrum for **2a**



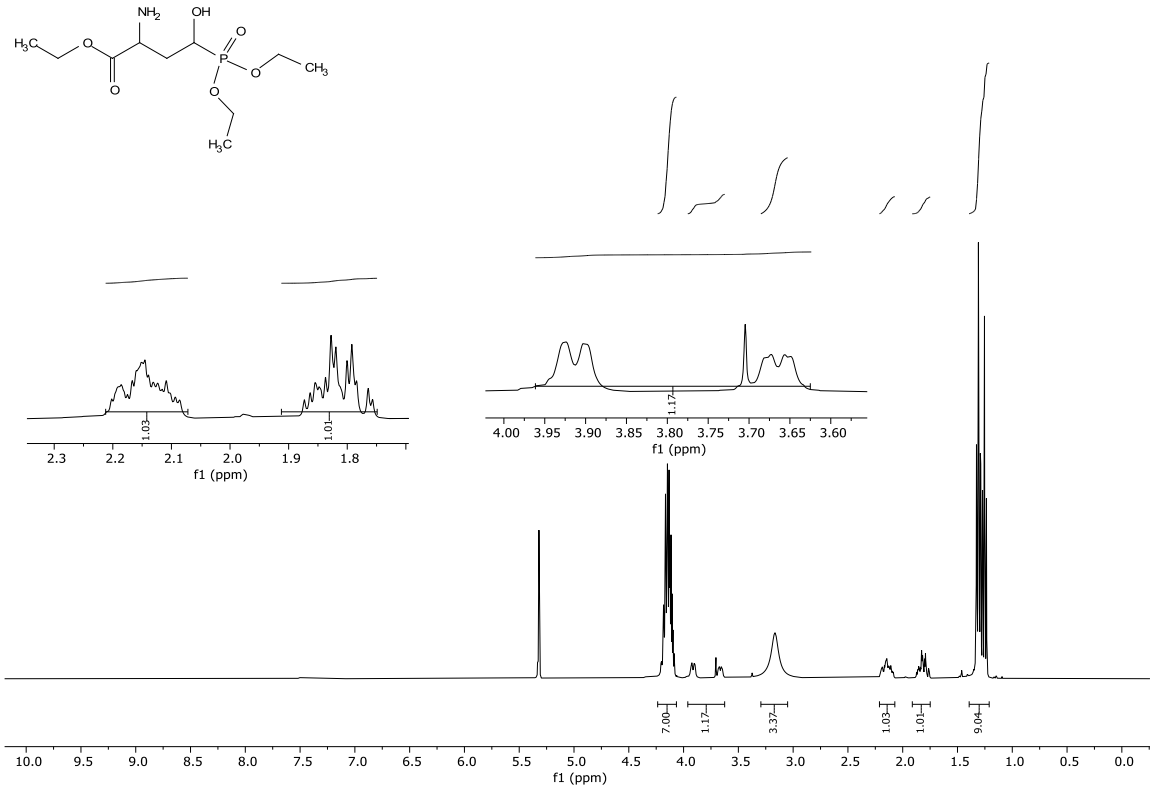
^{1}H NMR spectrum for **2b**



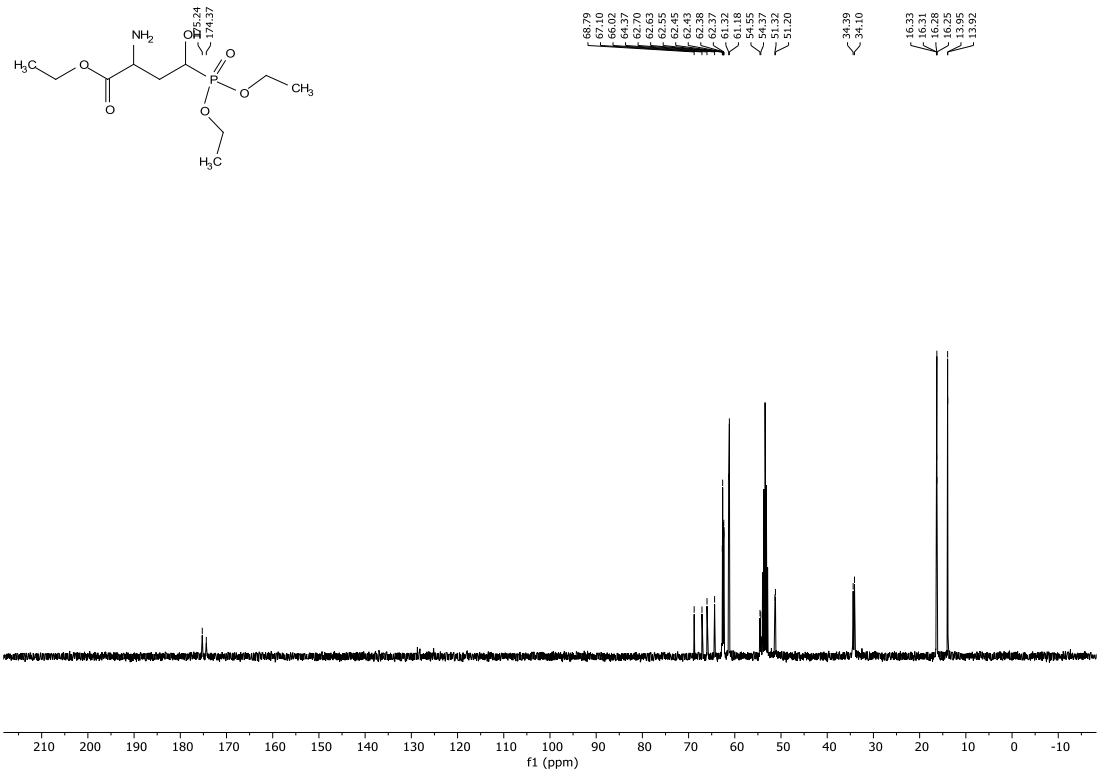
^{13}C NMR spectrum for **2b**



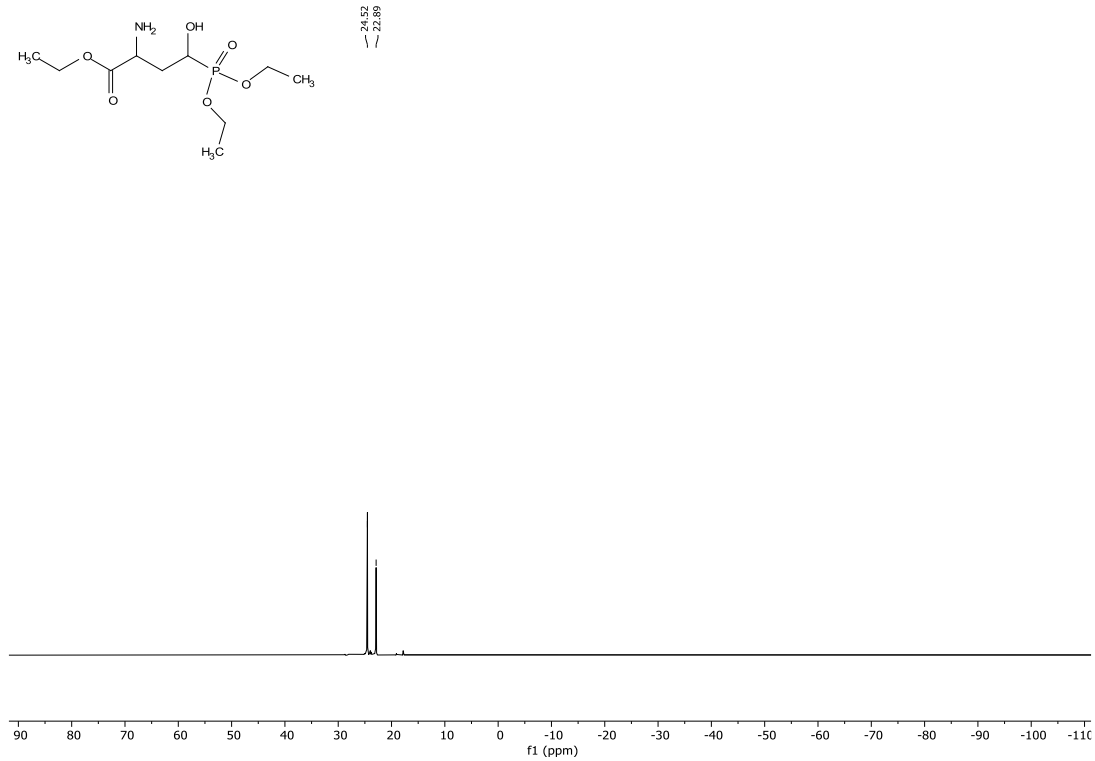
^{1}H NMR spectrum for **2c**



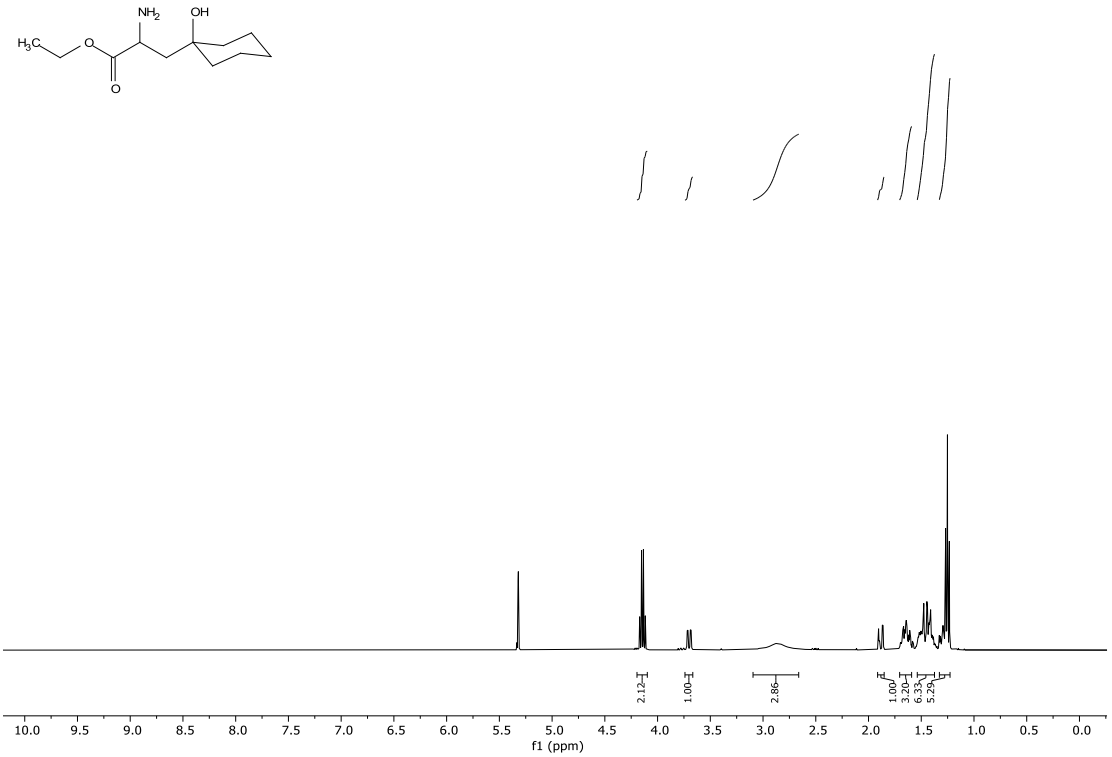
^{13}C NMR spectrum for **2c**



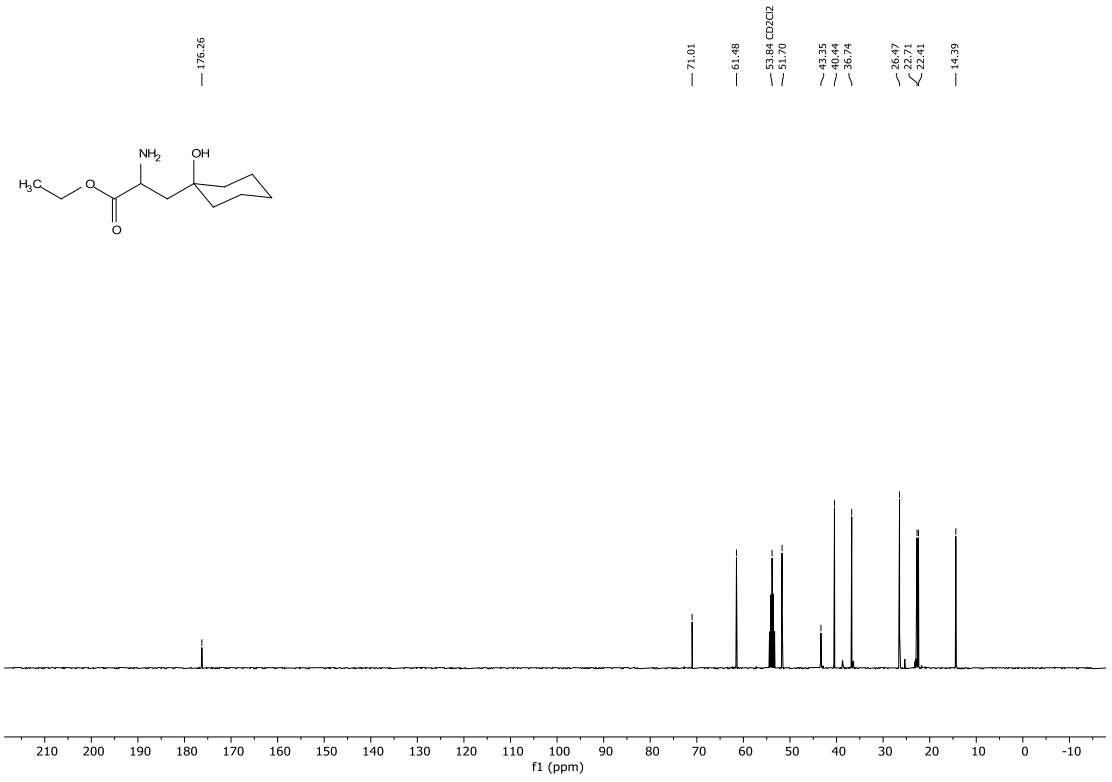
^{31}P NMR spectrum for **2c**



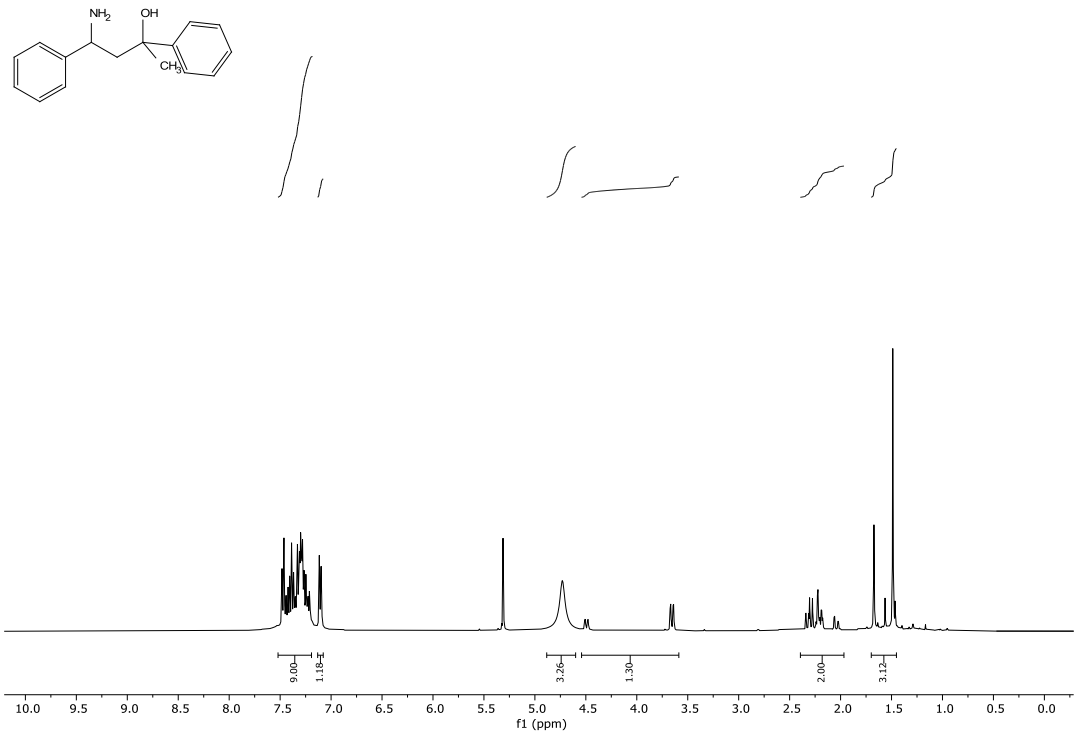
^{1}H NMR spectrum for **2d**



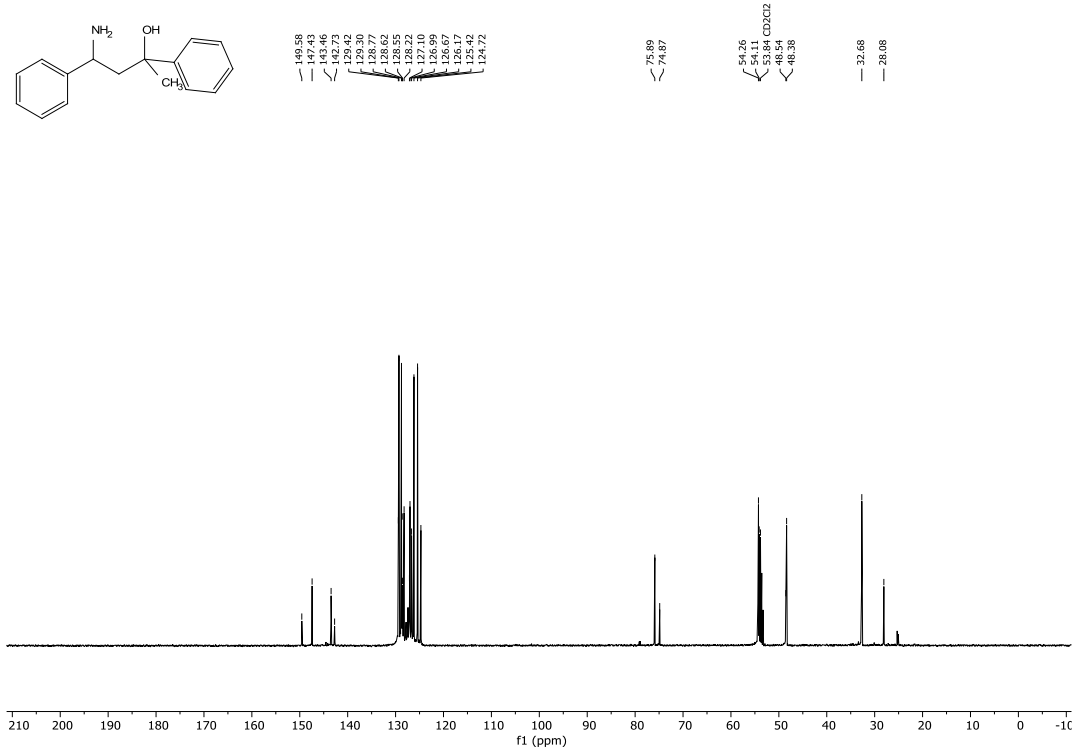
^{13}C NMR spectrum for **2d**



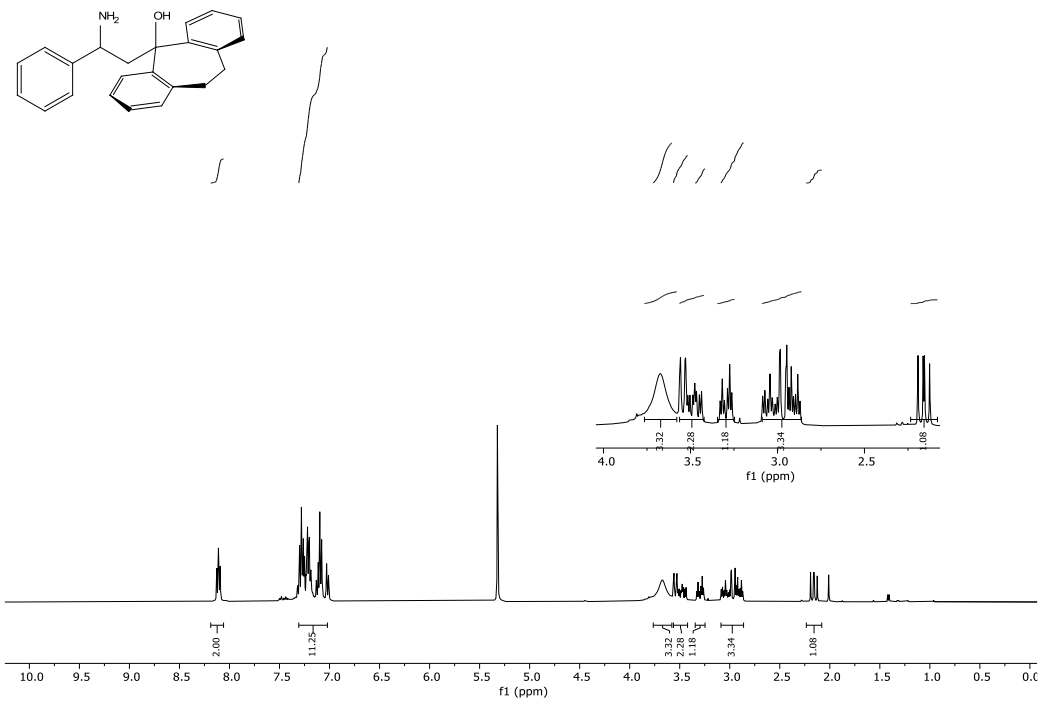
^{1}H NMR spectrum for **2e**



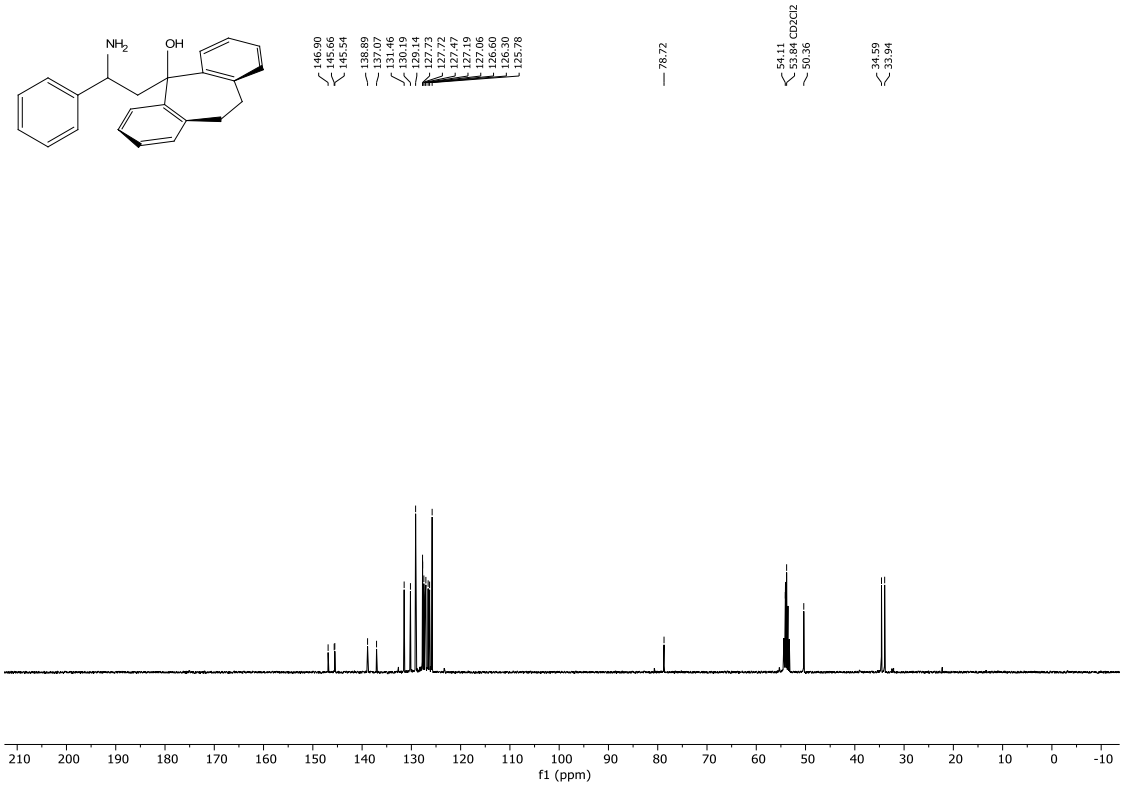
^{13}C NMR spectrum for **2e**



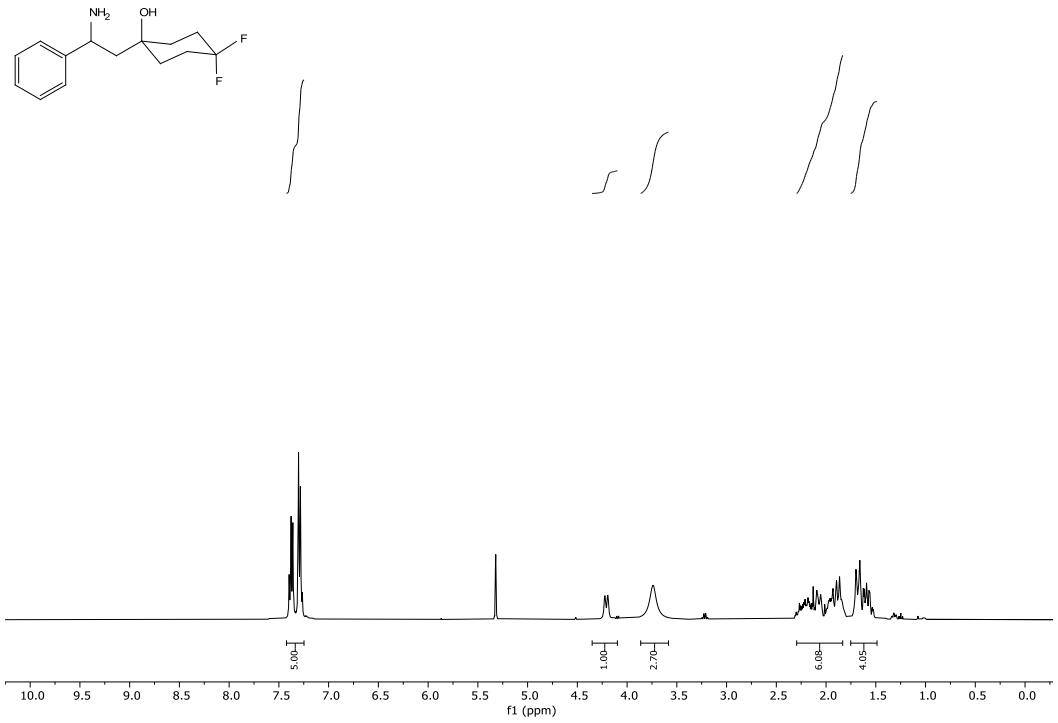
^{1}H NMR spectrum for **2f**



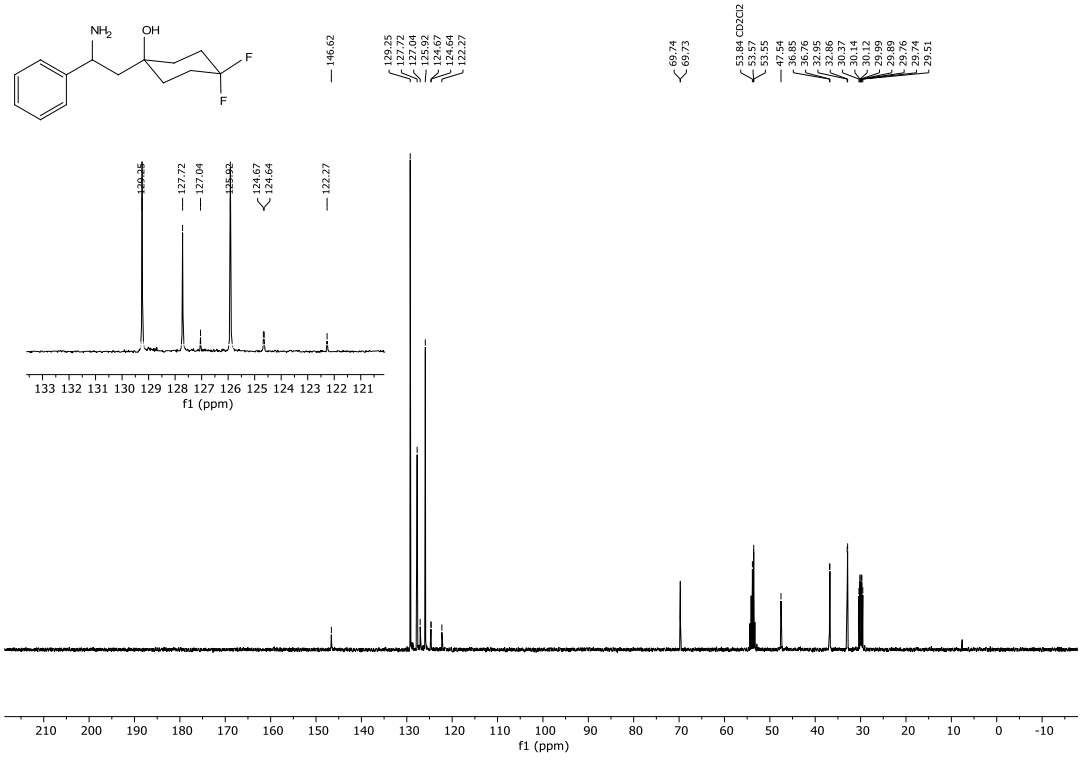
^{13}C NMR spectrum for **2f**



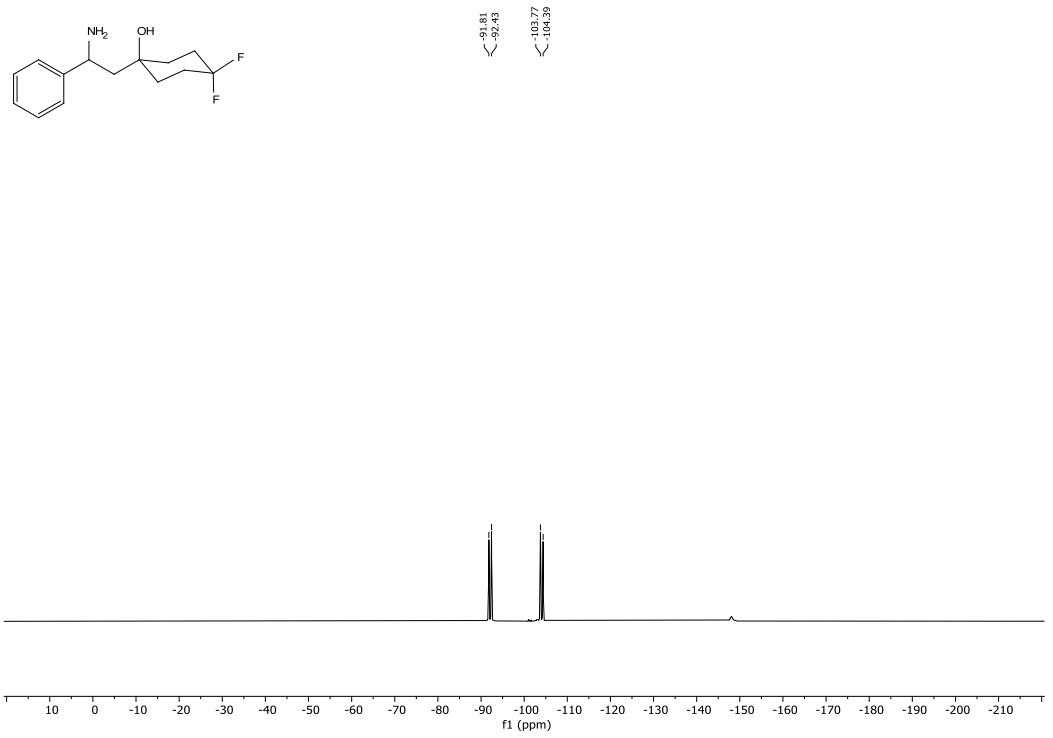
^{1}H NMR spectrum for **2g**



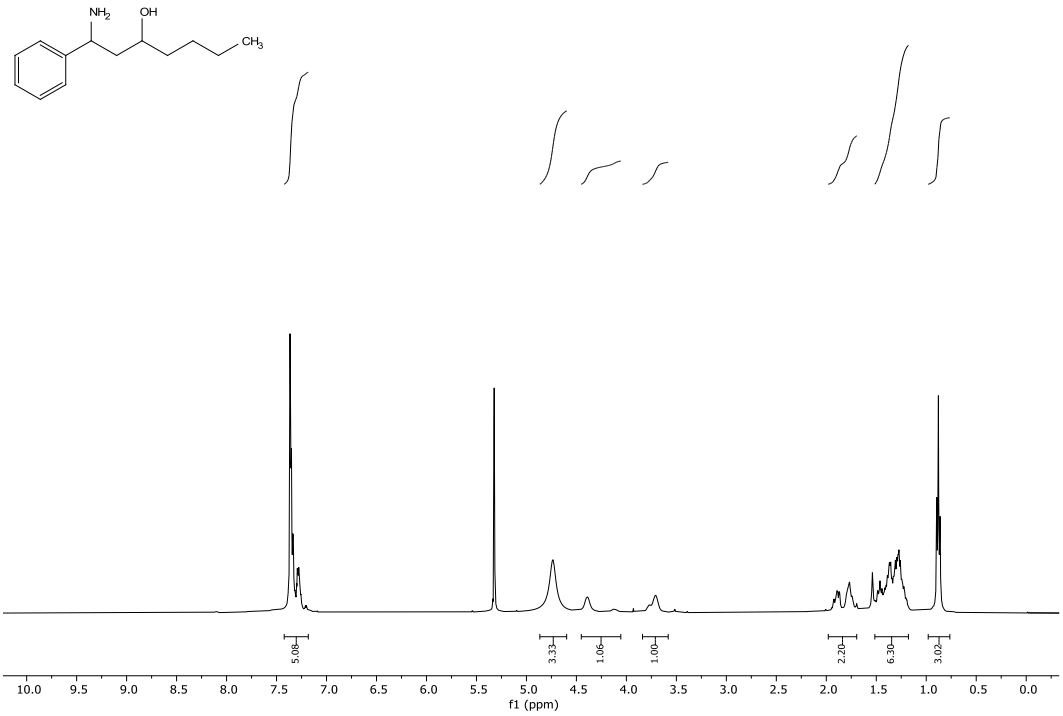
^{13}C NMR spectrum for **2g**



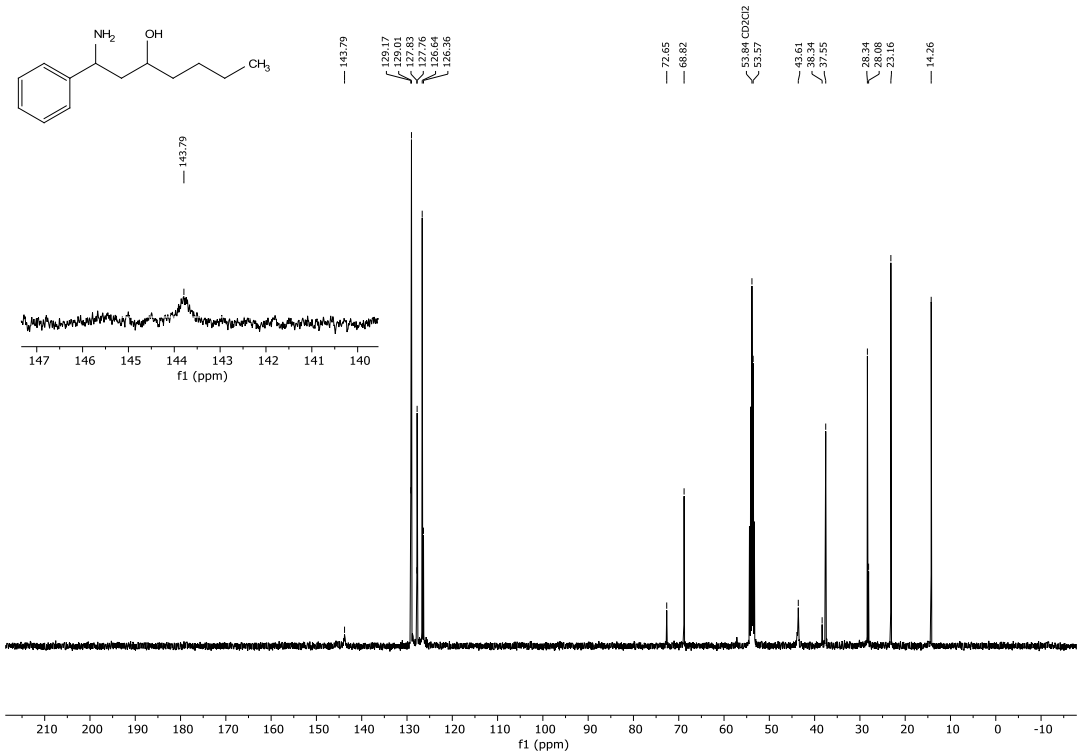
^{19}F NMR spectrum for **2g**



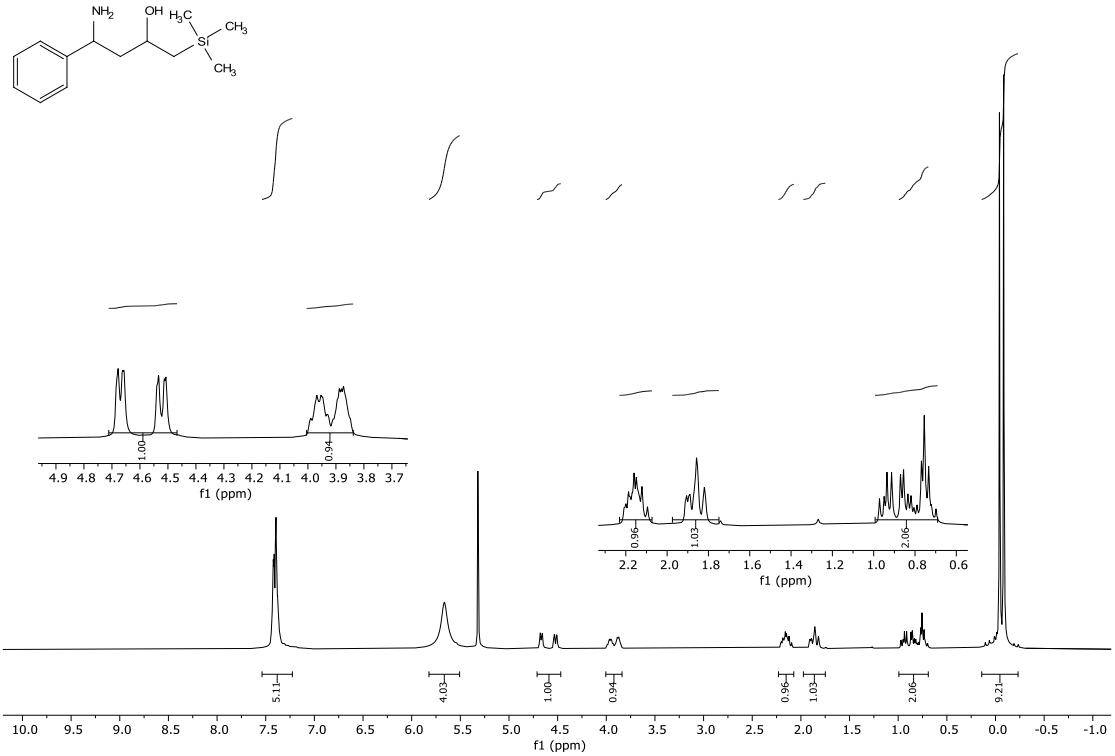
^{1}H NMR spectrum for **2h**



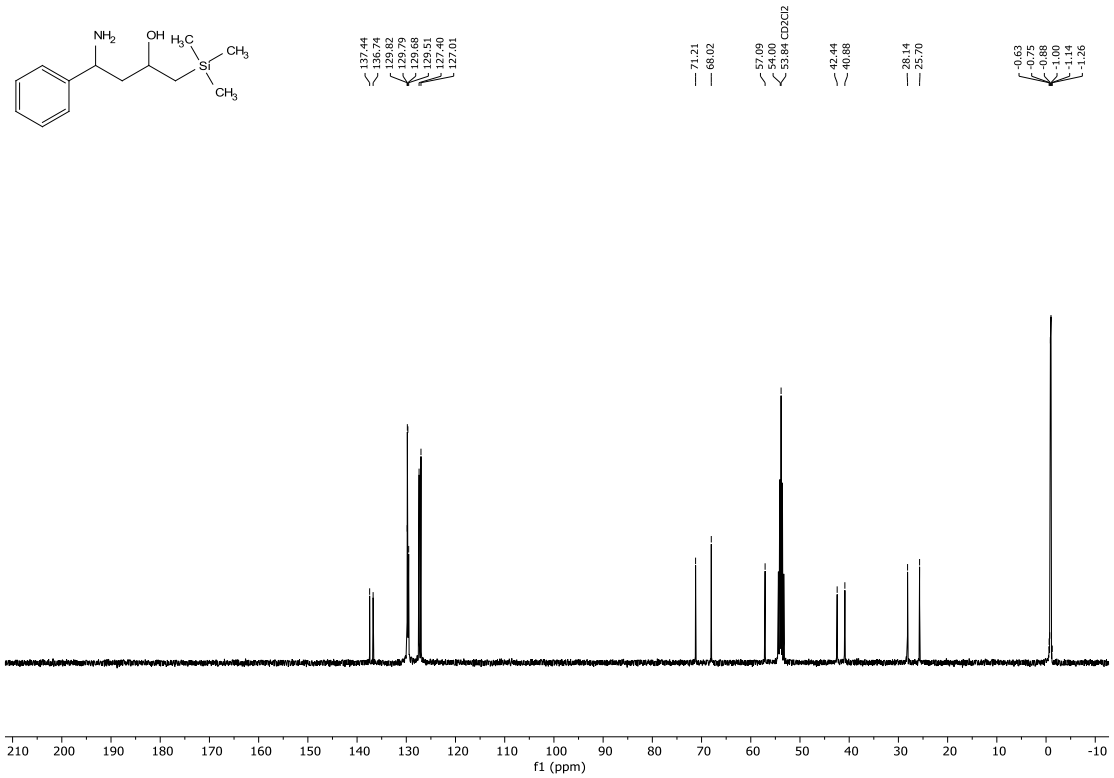
^{13}C NMR spectrum for **2h**



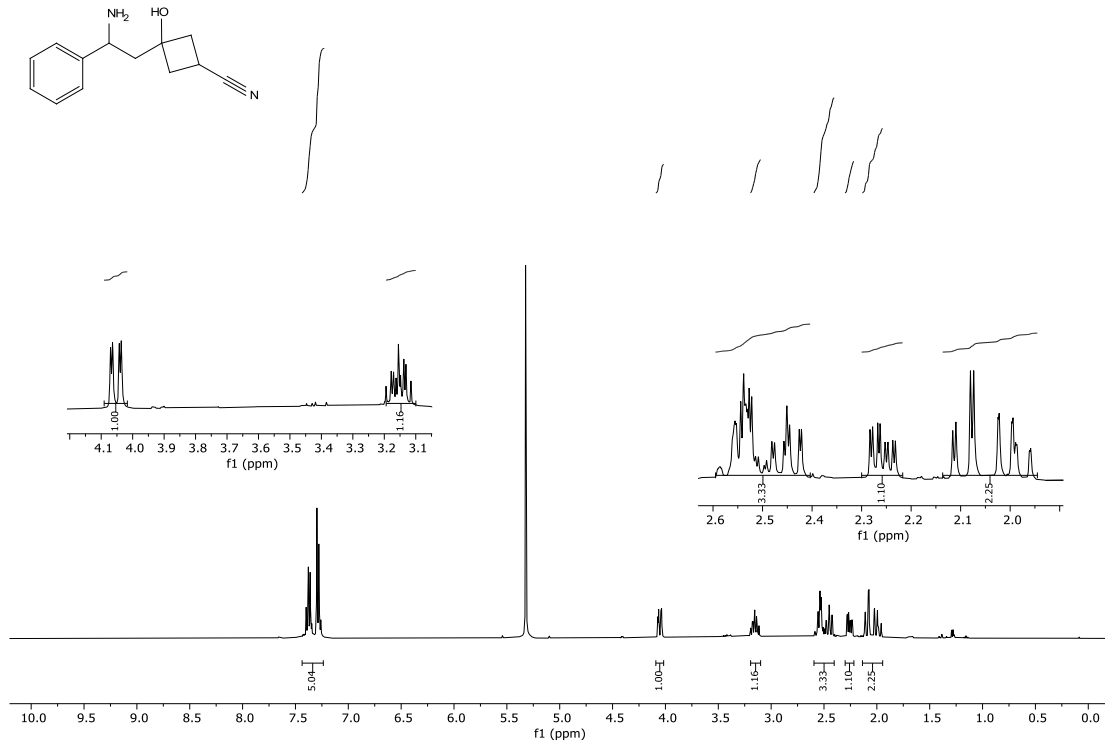
^{1}H NMR spectrum for **2i**



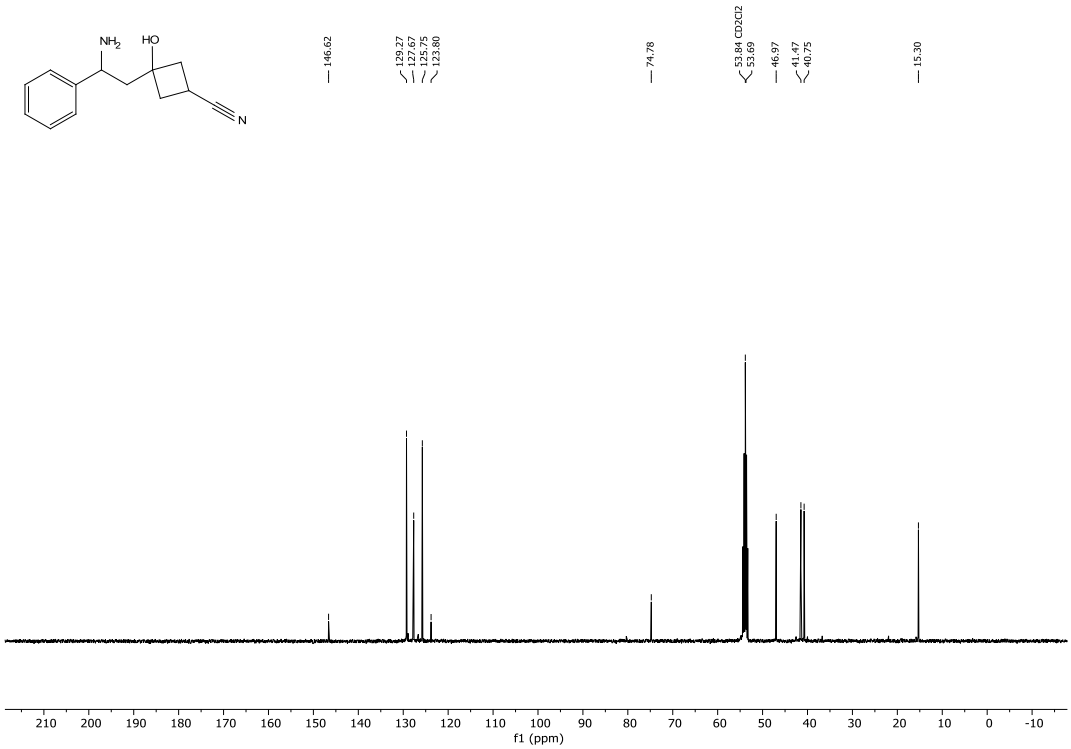
^{13}C NMR spectrum for **2i**



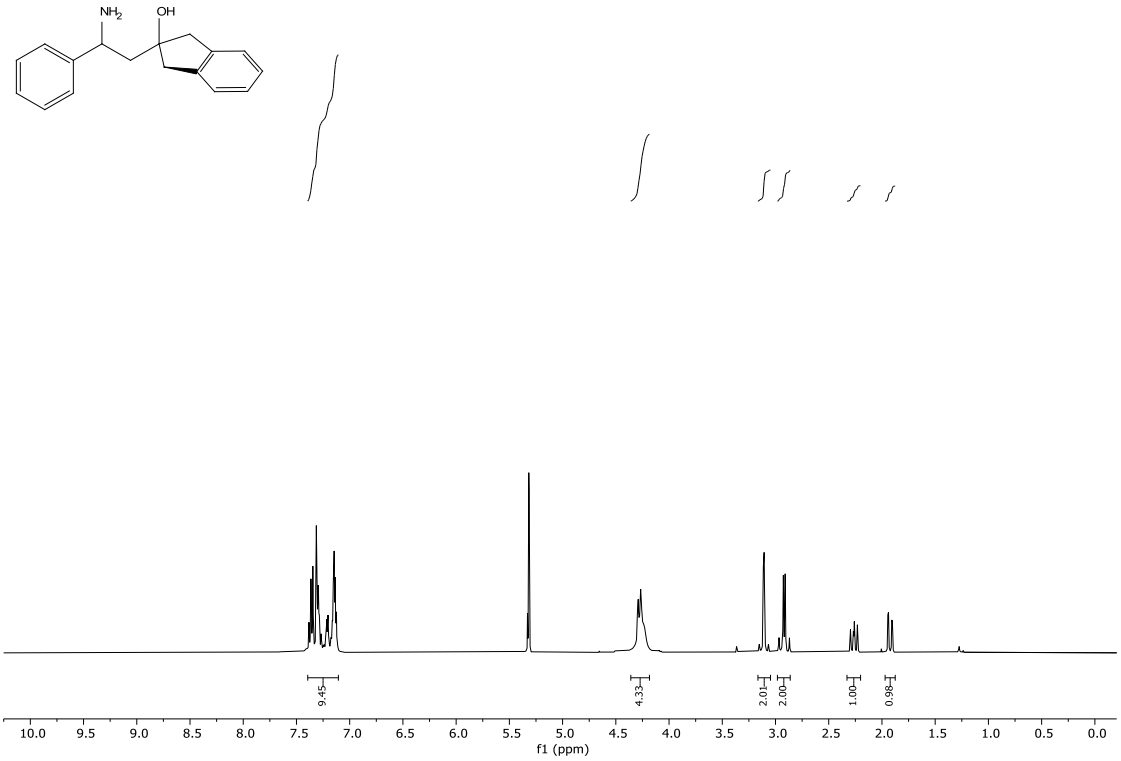
^{1}H NMR spectrum for **2j**



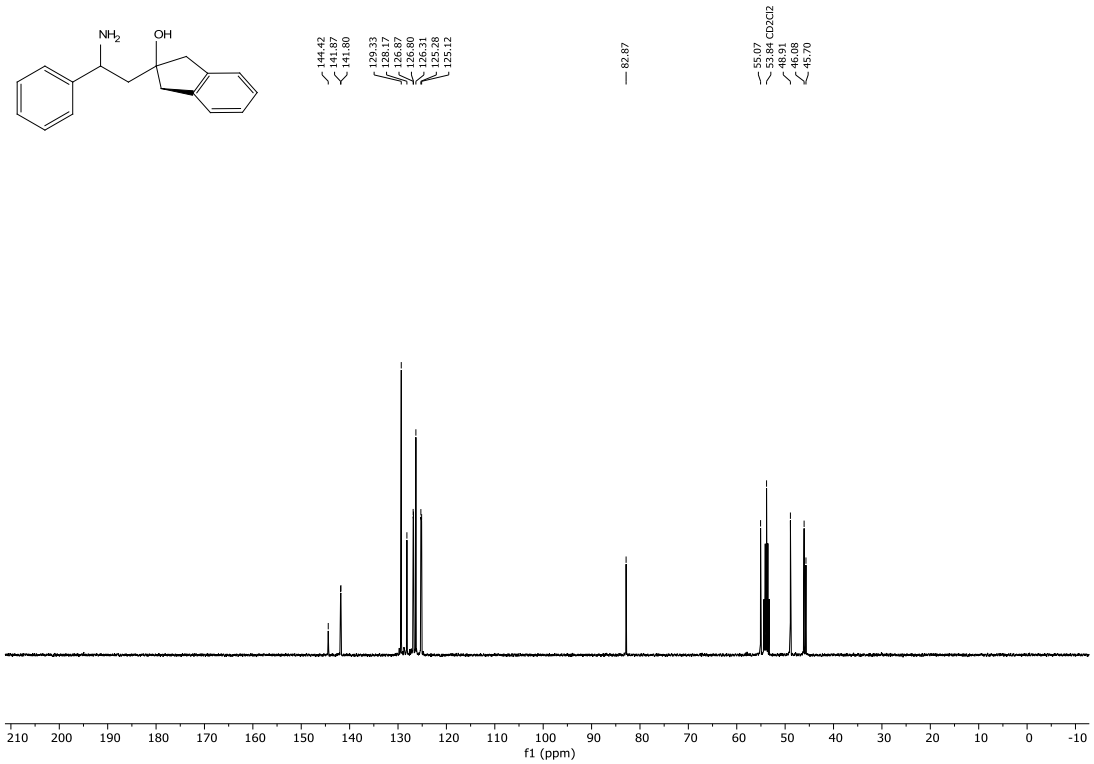
^{13}C NMR spectrum for **2j**



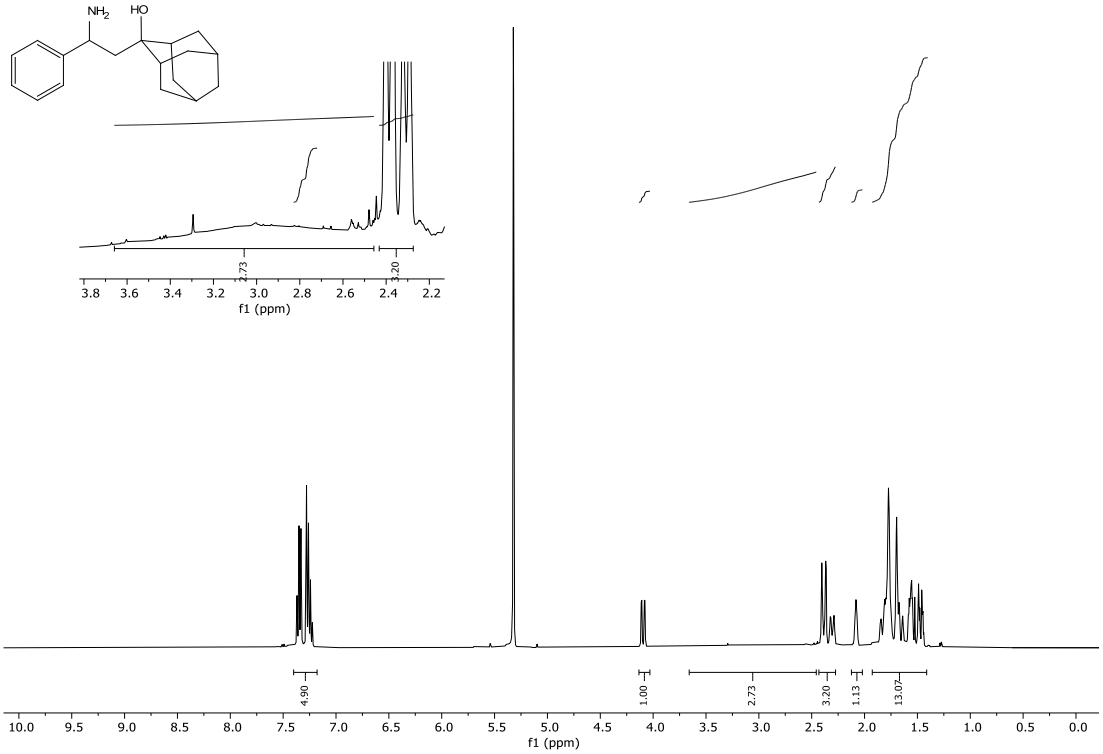
^{1}H NMR spectrum for **2k**



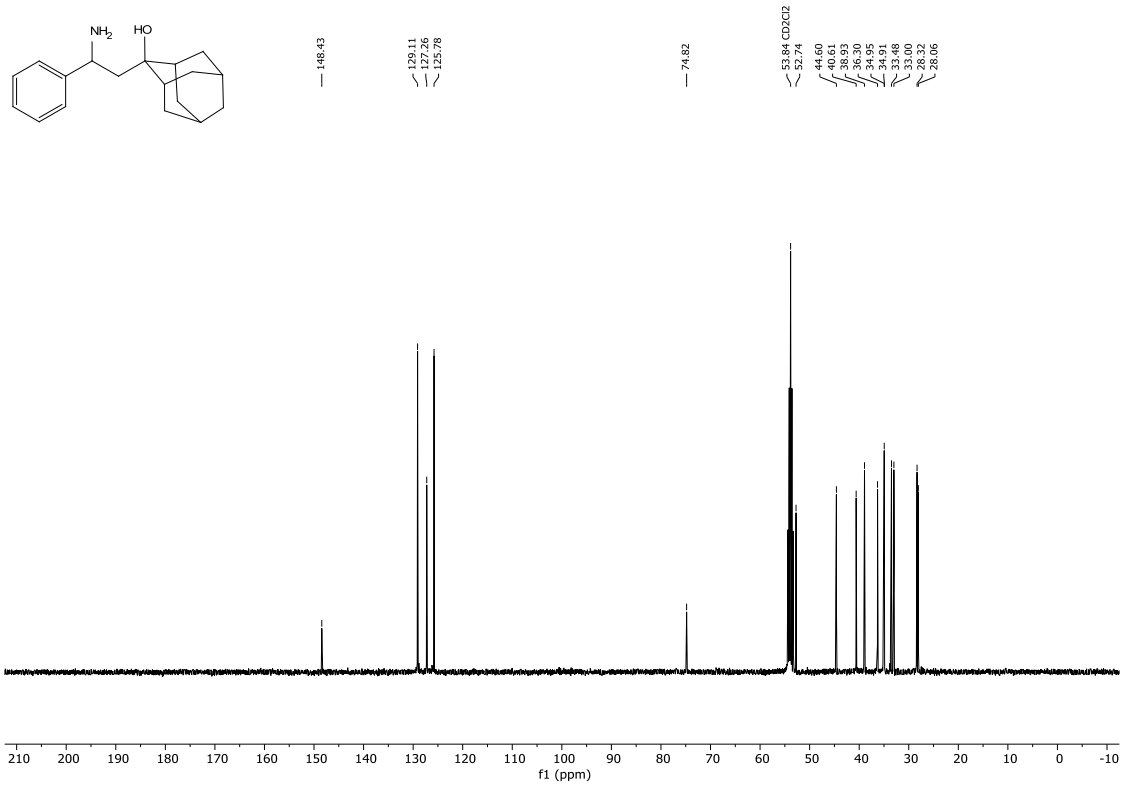
^{13}C NMR spectrum for **2k**



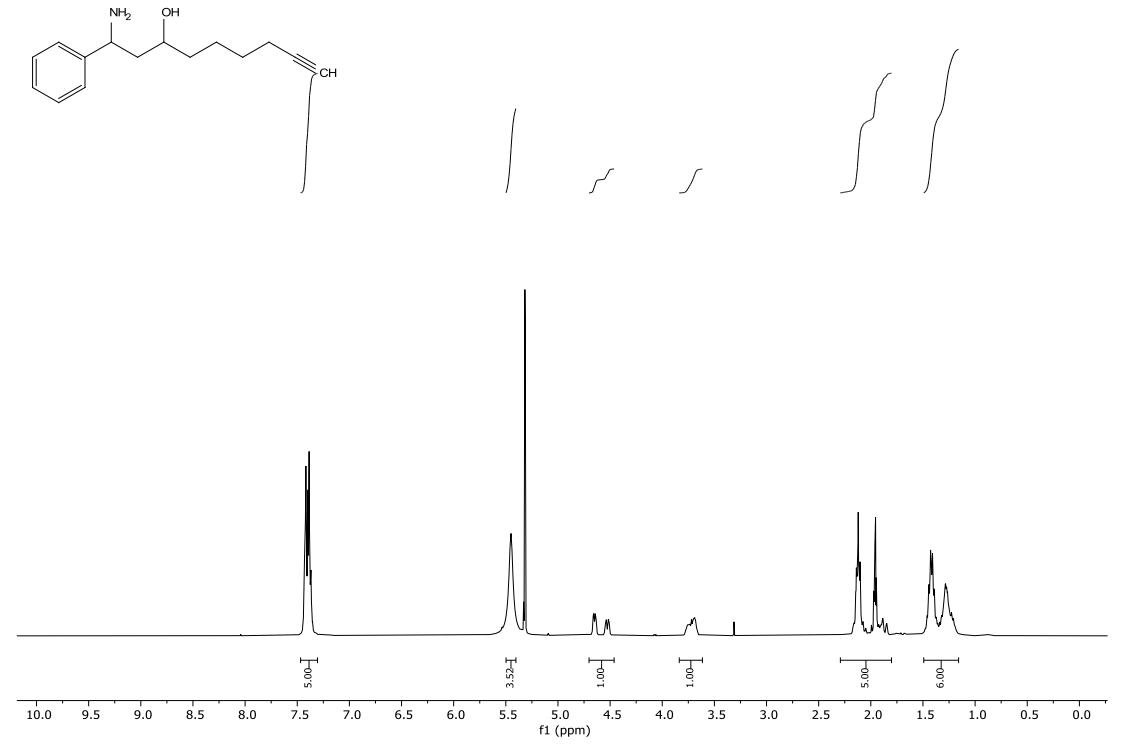
^{1}H NMR spectrum for **2l**



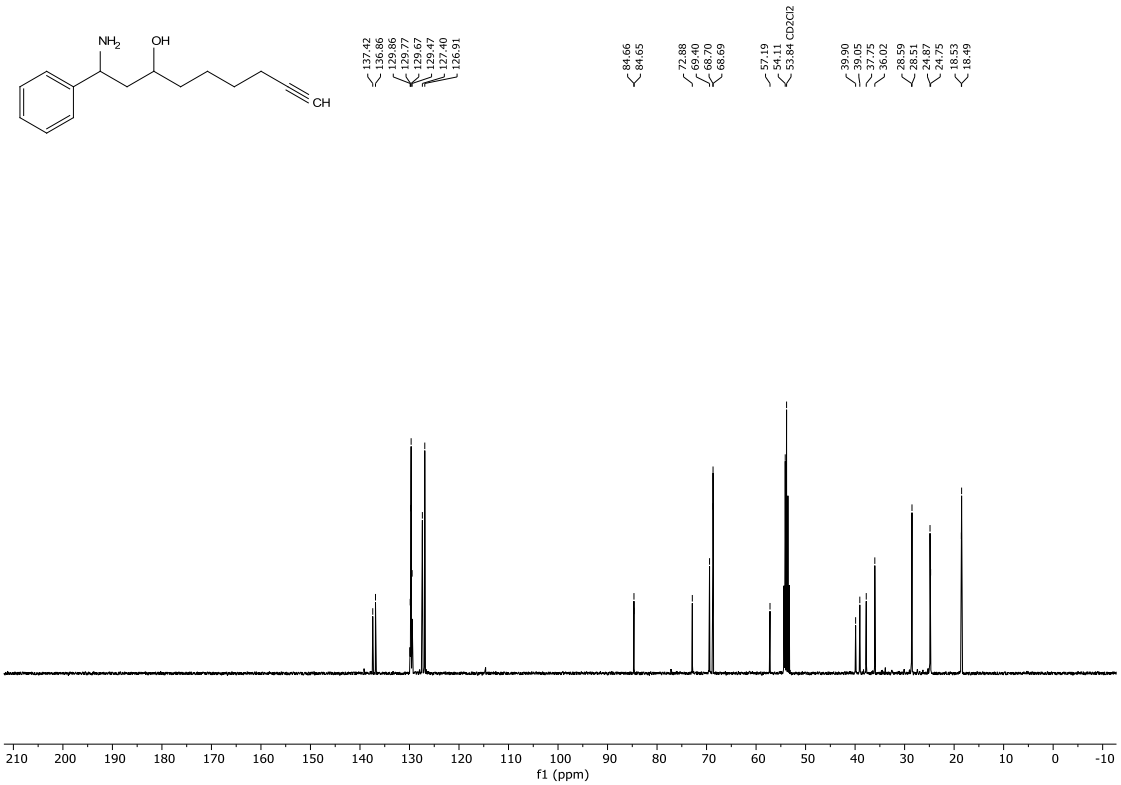
^{13}C NMR spectrum for **2l**



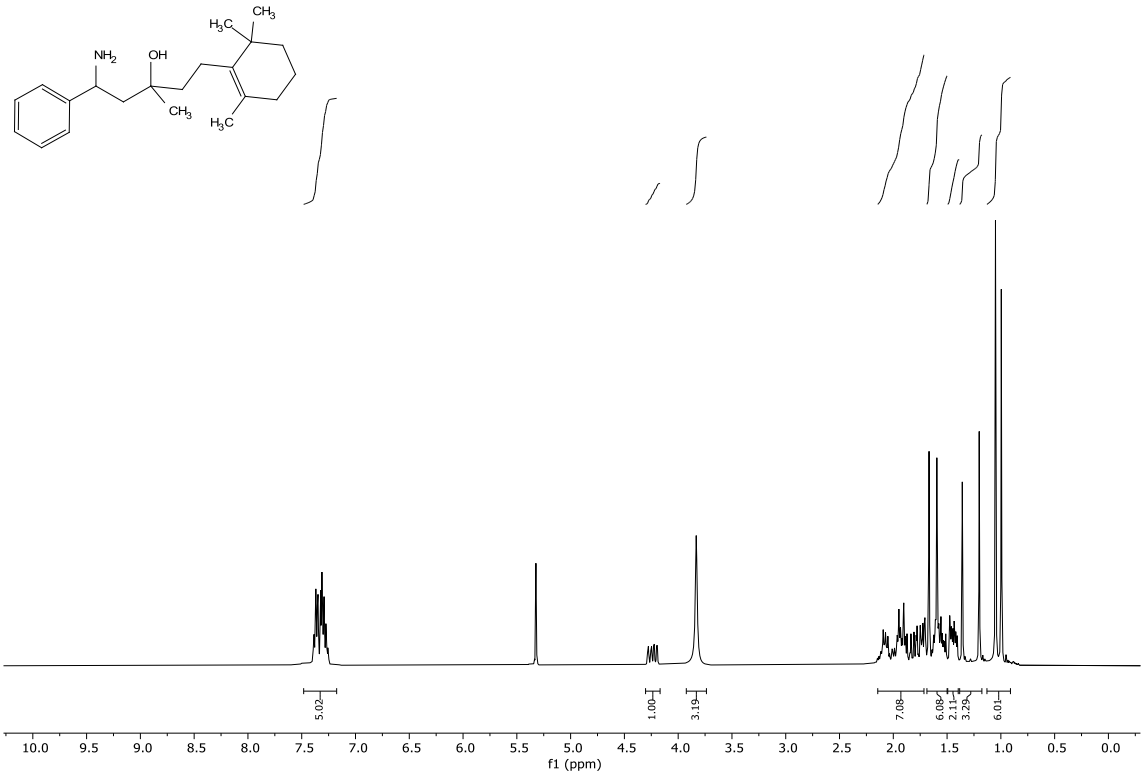
^{1}H NMR spectrum for **2m**



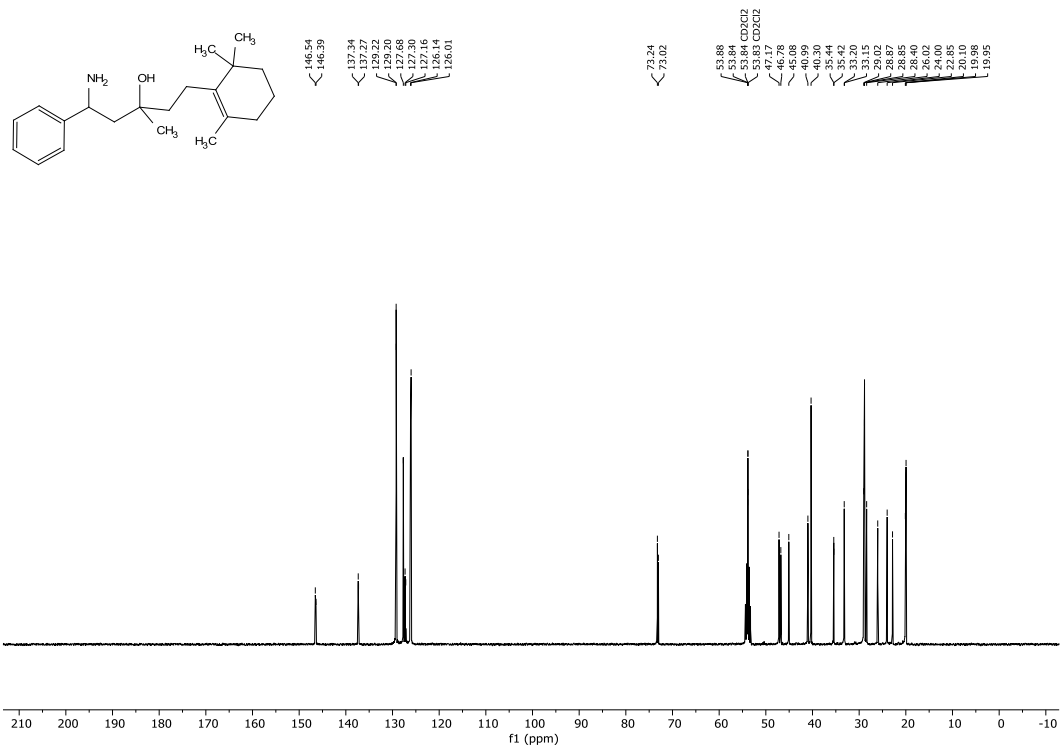
^{13}C NMR spectrum for **2m**



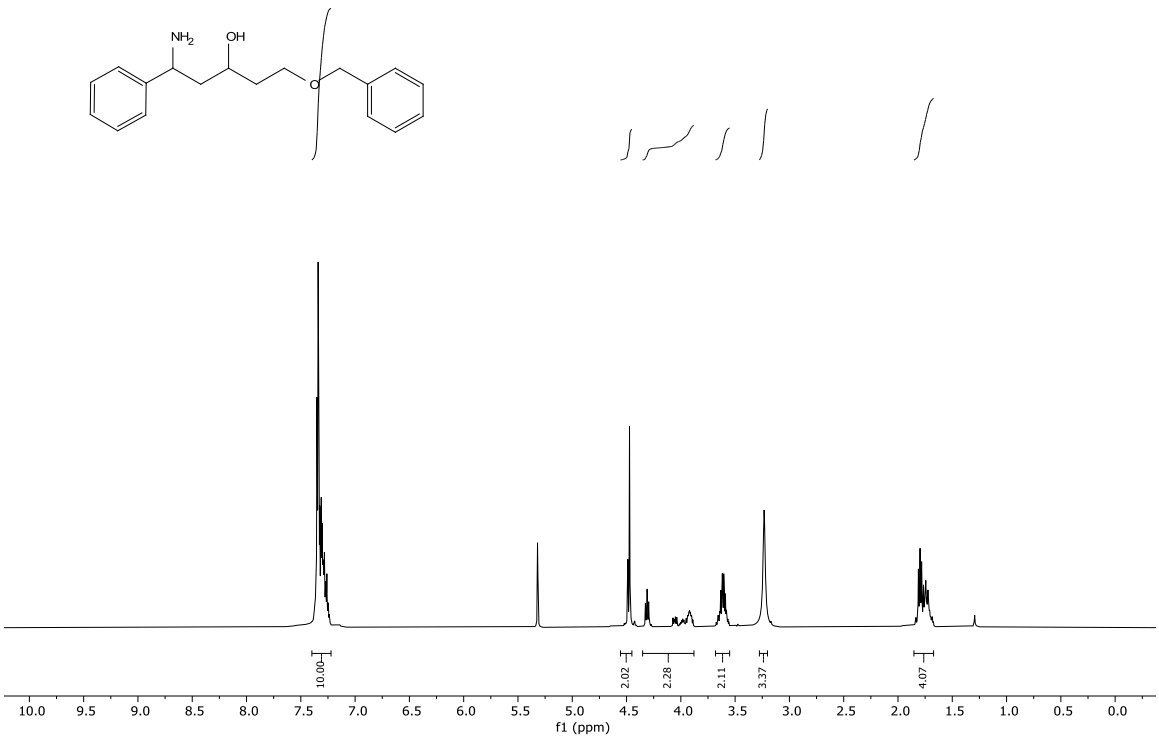
^{1}H NMR spectrum for **2n**



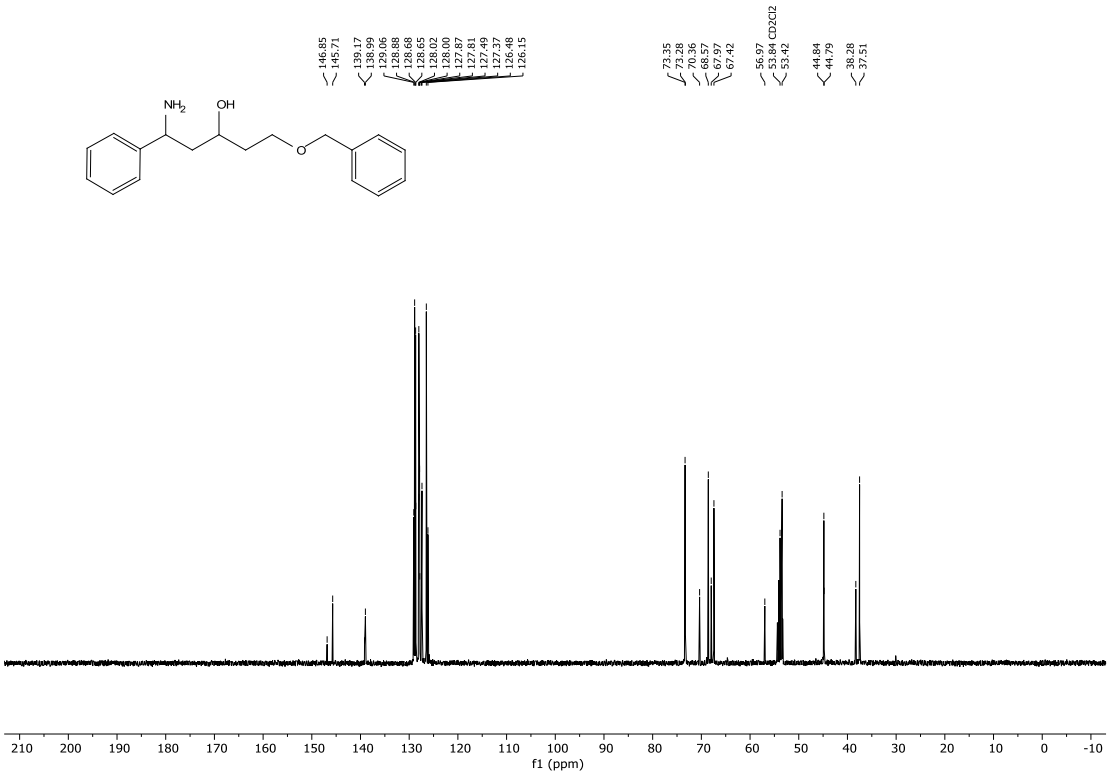
^{13}C NMR spectrum for **2n**



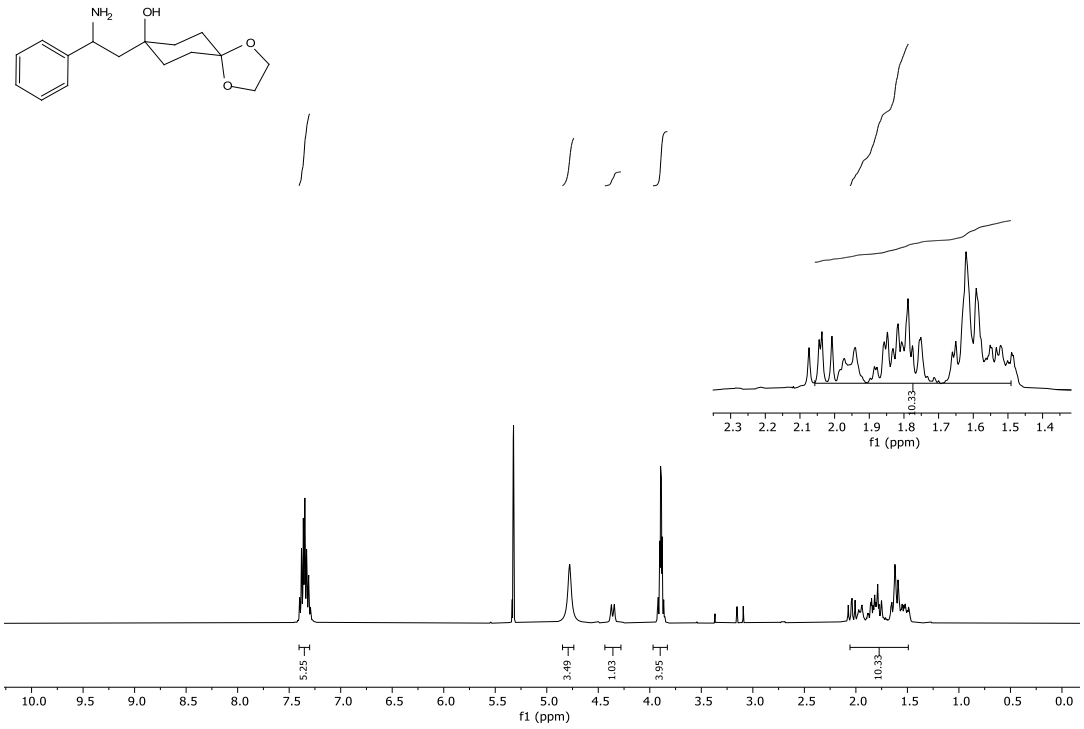
^{1}H NMR spectrum for **2o**



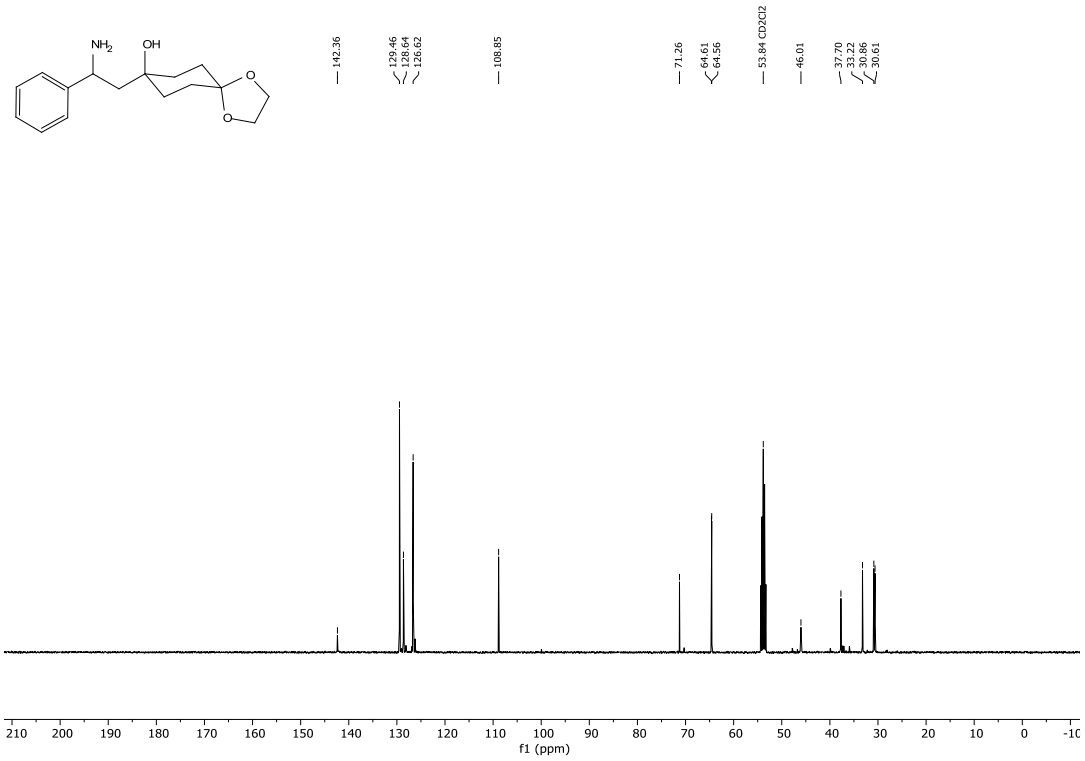
^{13}C NMR spectrum for **2o**



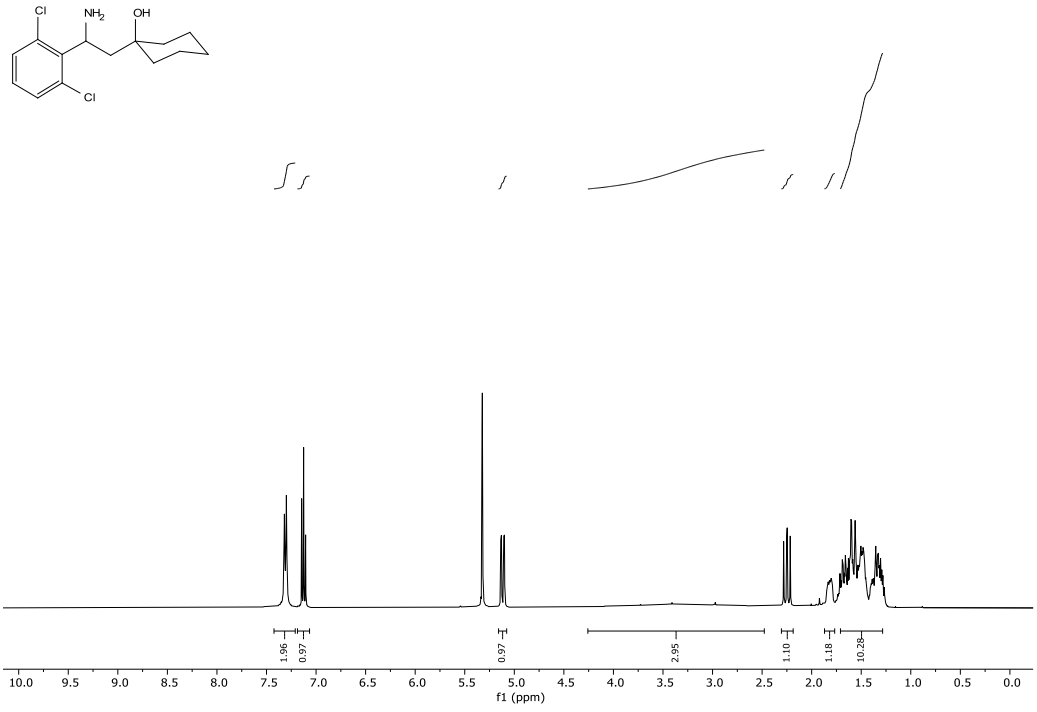
^{1}H NMR spectrum for **2p**



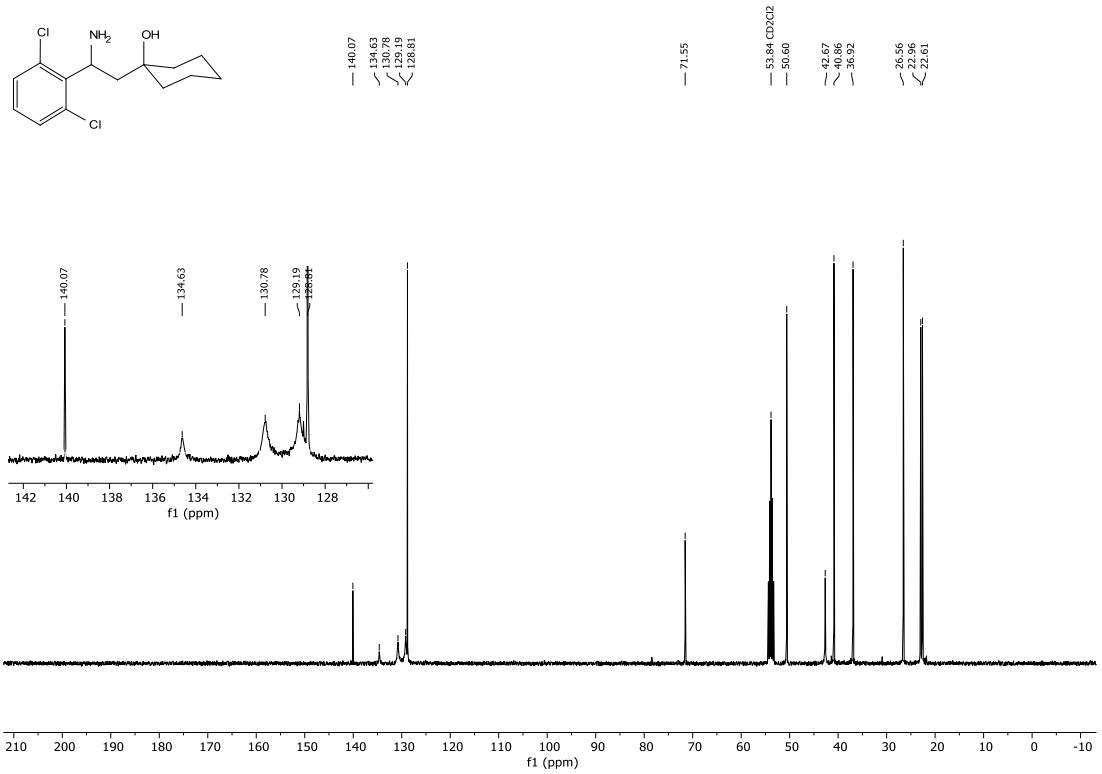
^{13}C NMR spectrum for **2p**



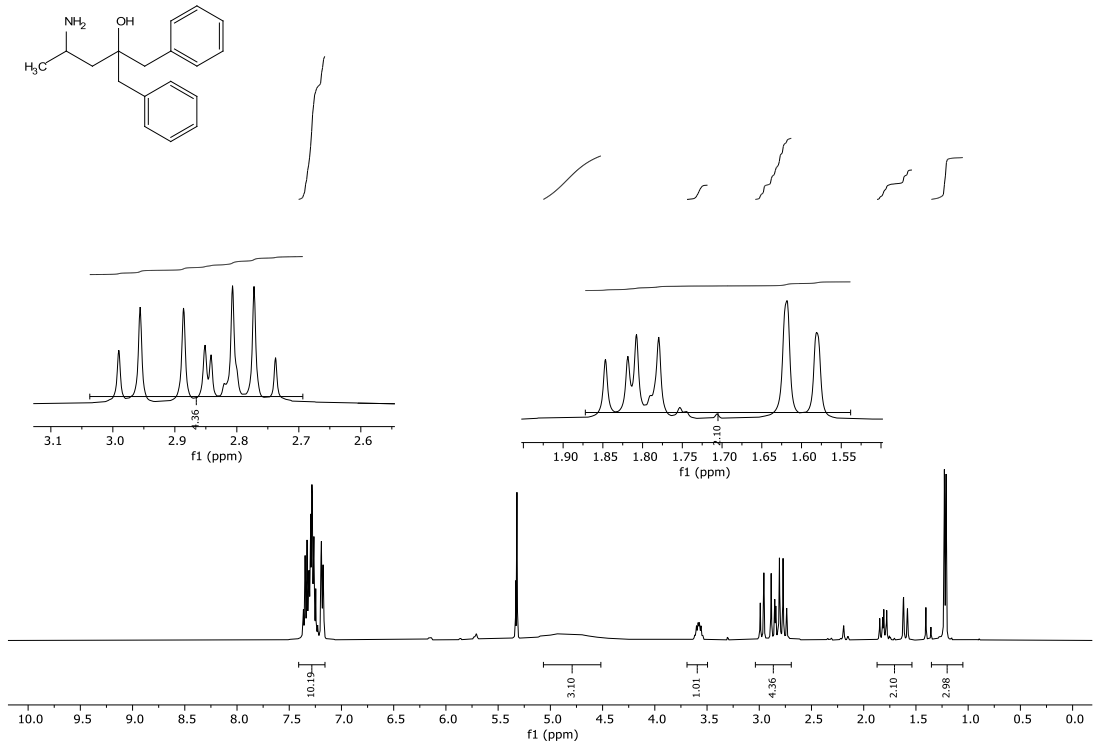
^{1}H NMR spectrum for **2q**



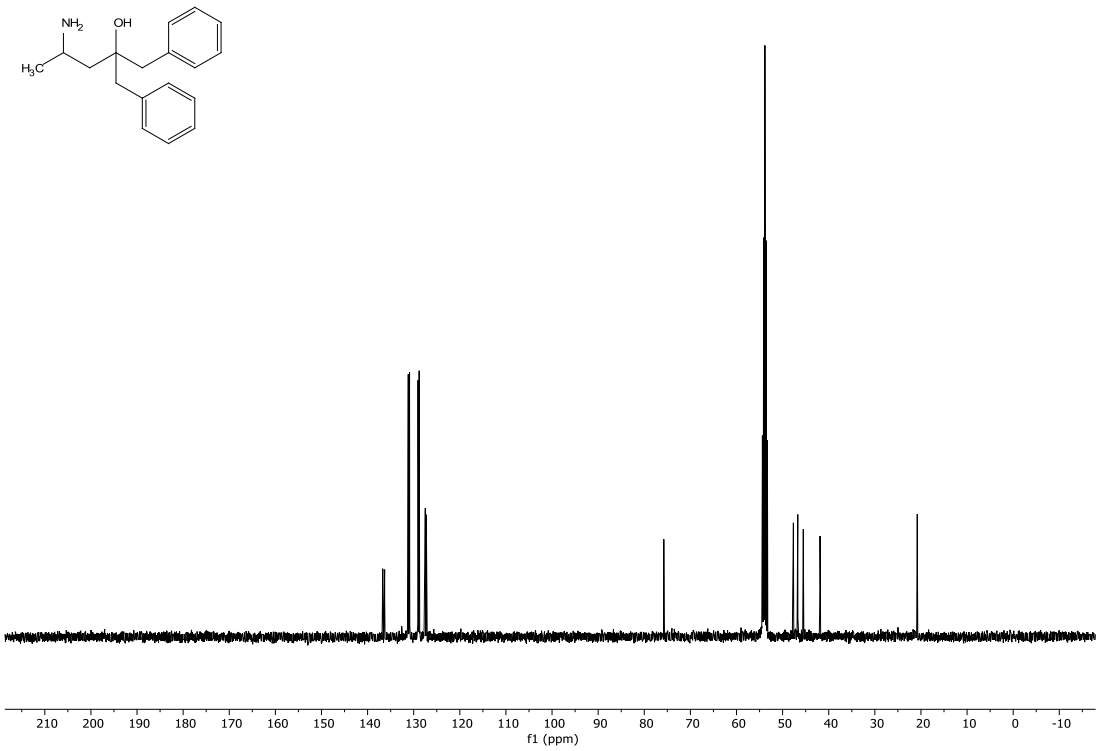
^{13}C NMR spectrum for **2q**



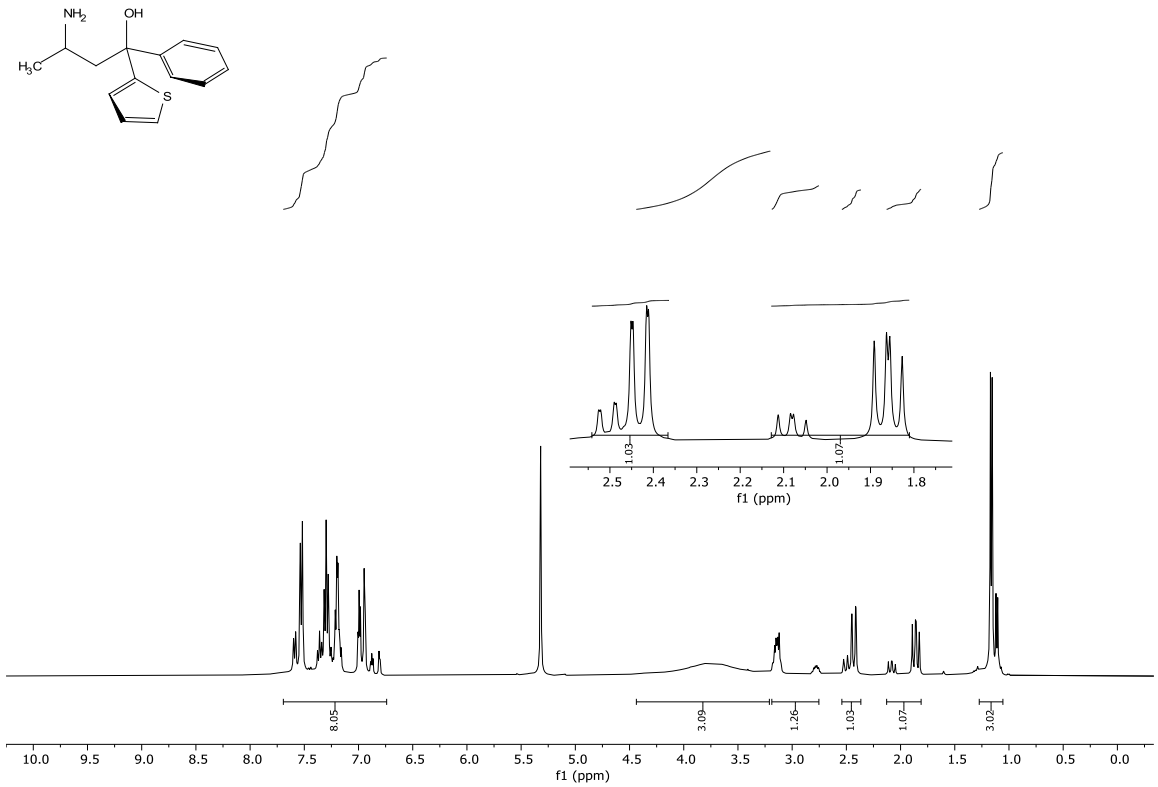
^{1}H NMR spectrum for **2r**



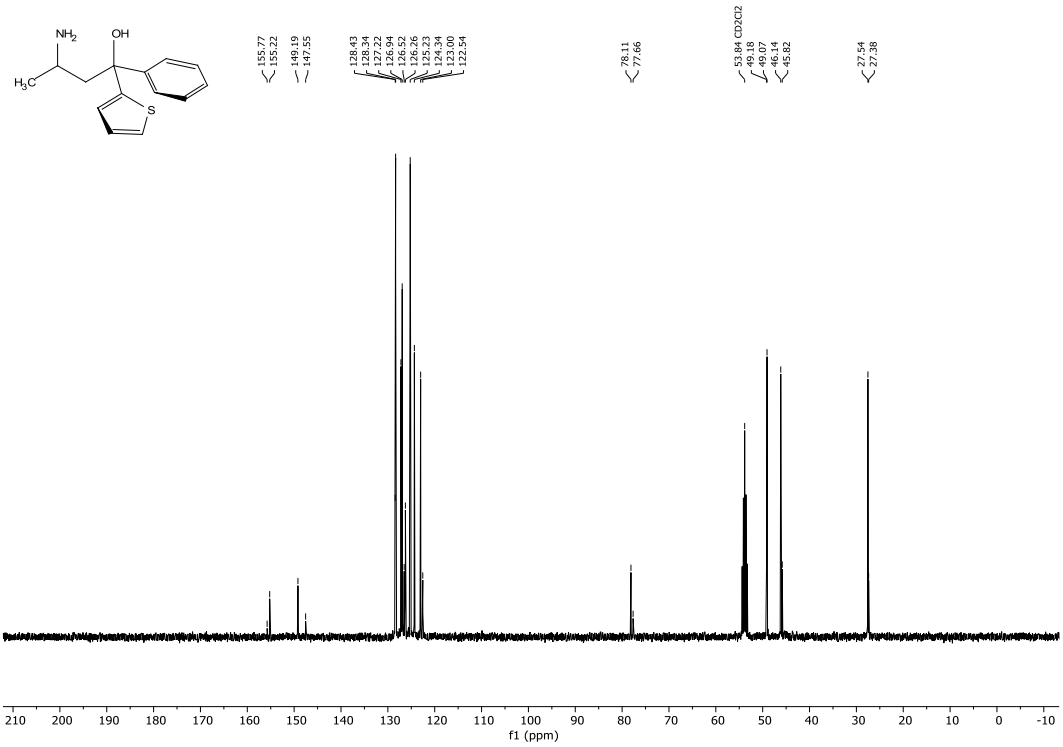
^{13}C NMR spectrum for **2r**



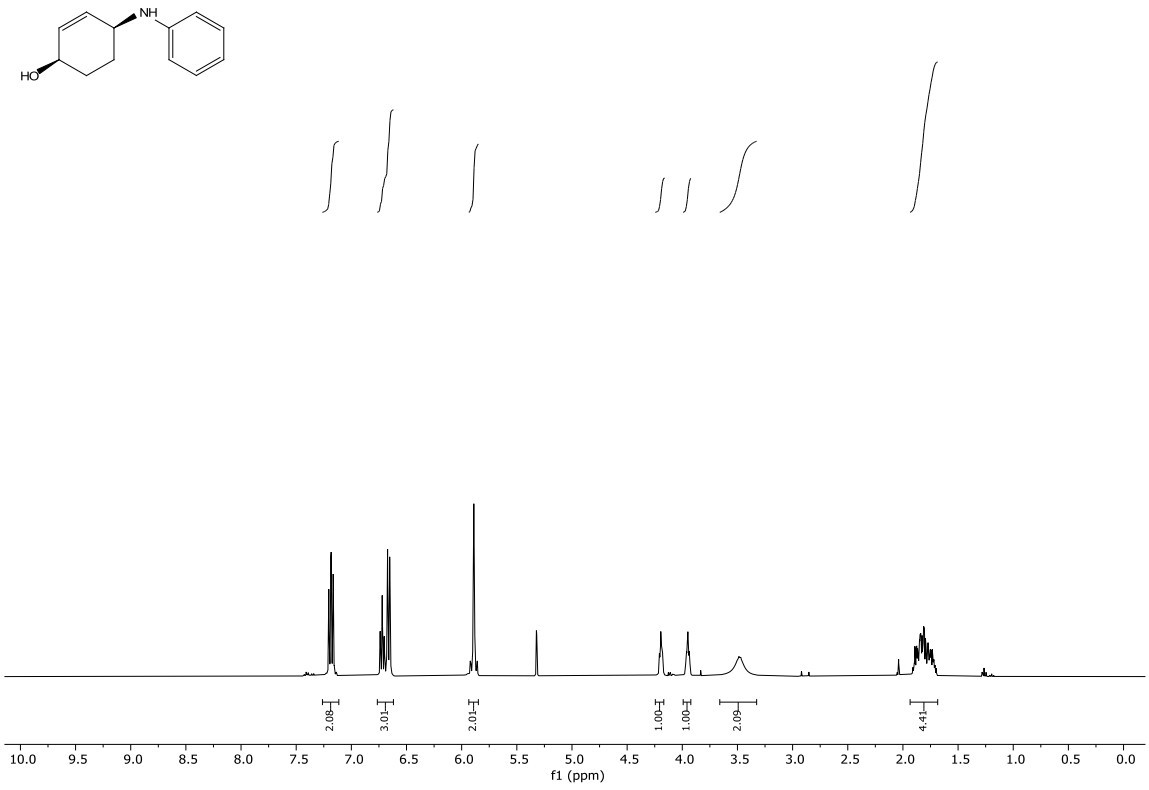
^{1}H NMR spectrum for **2s**



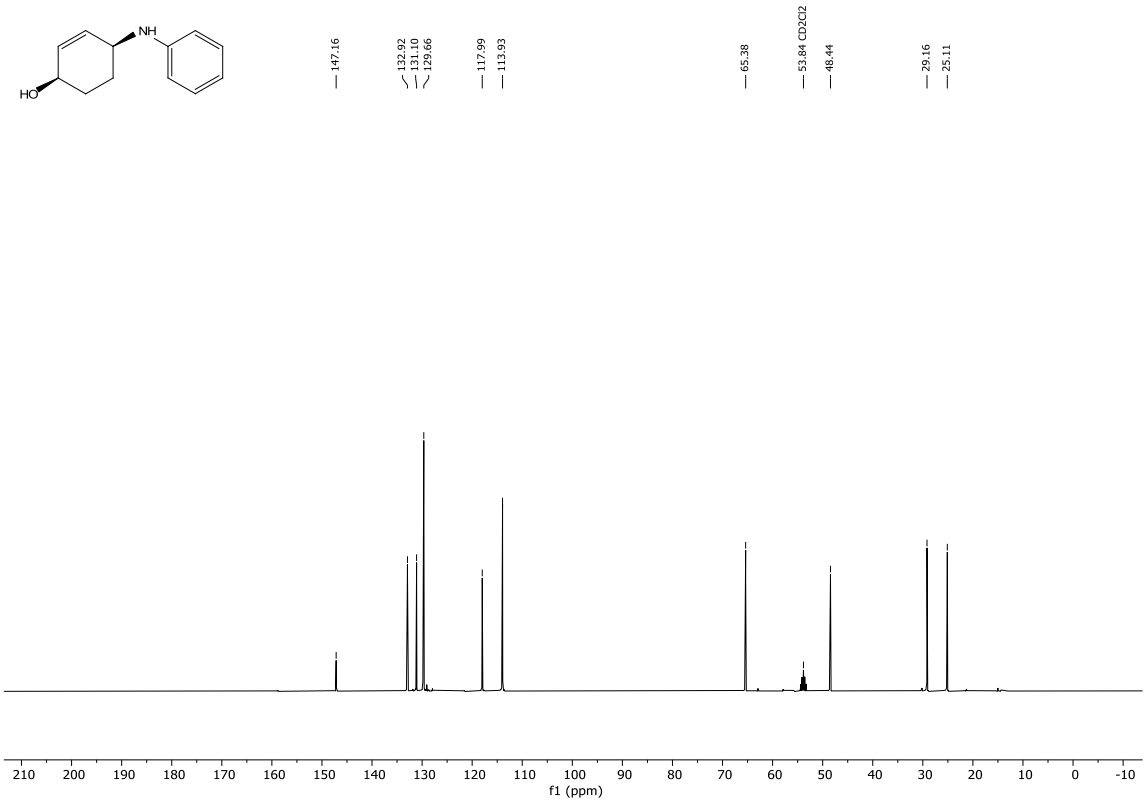
^{13}C NMR spectrum for **2s**



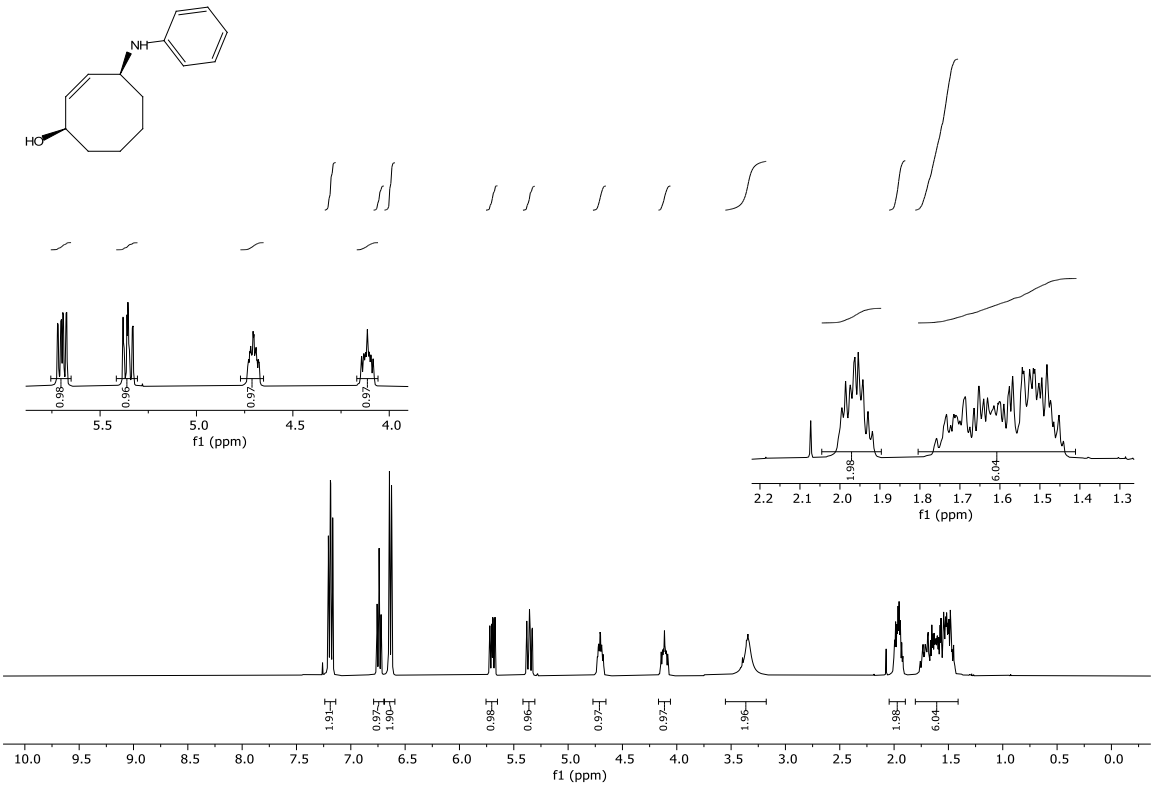
^{1}H NMR spectrum for **4a**



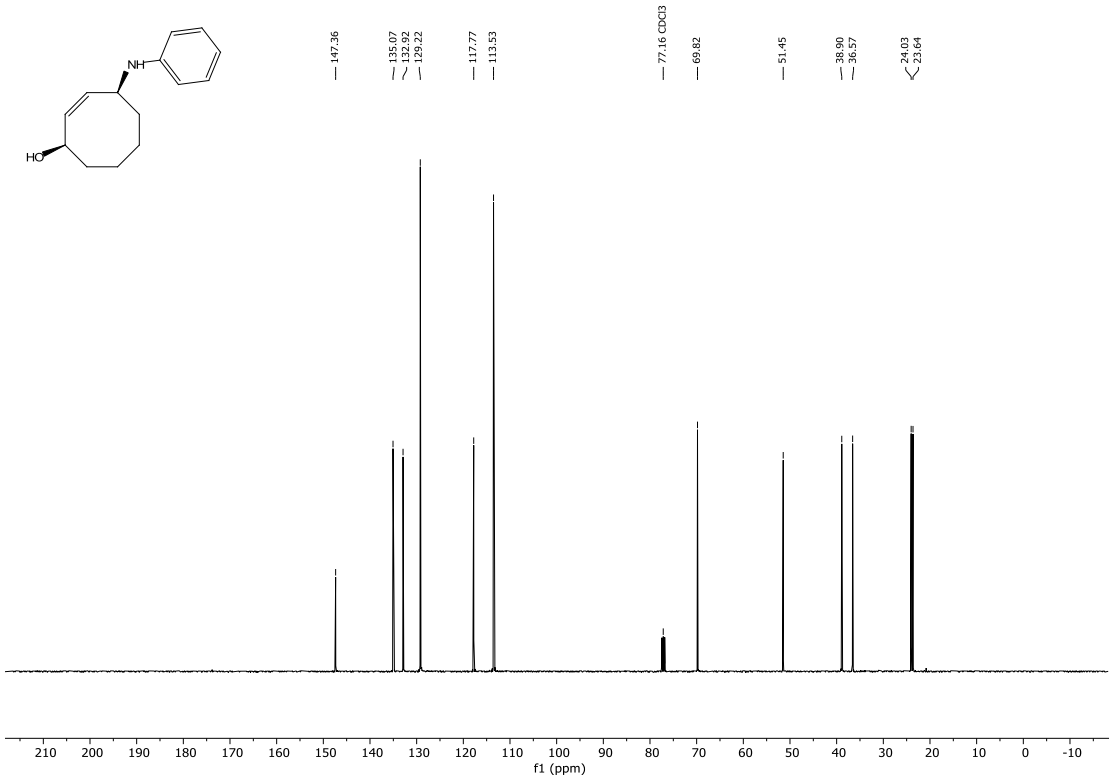
^{13}C NMR spectrum for **4a**



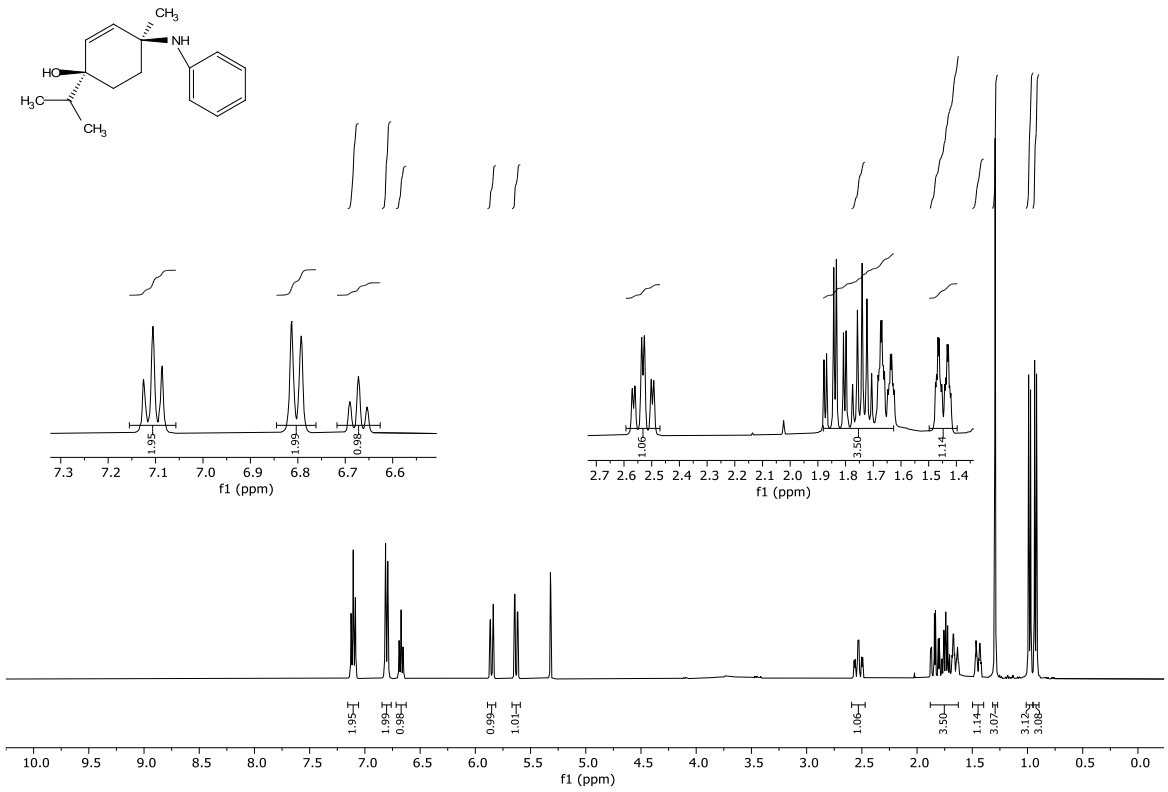
^{1}H NMR spectrum for **4b**



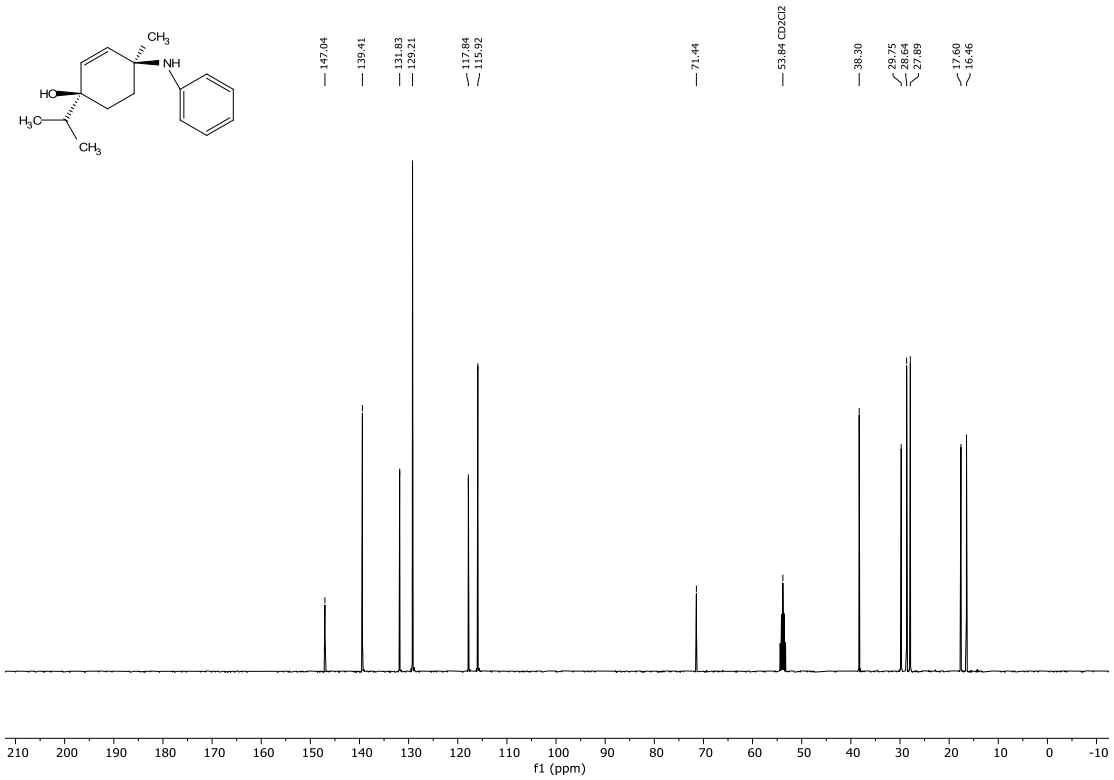
^{13}C NMR spectrum for **4b**



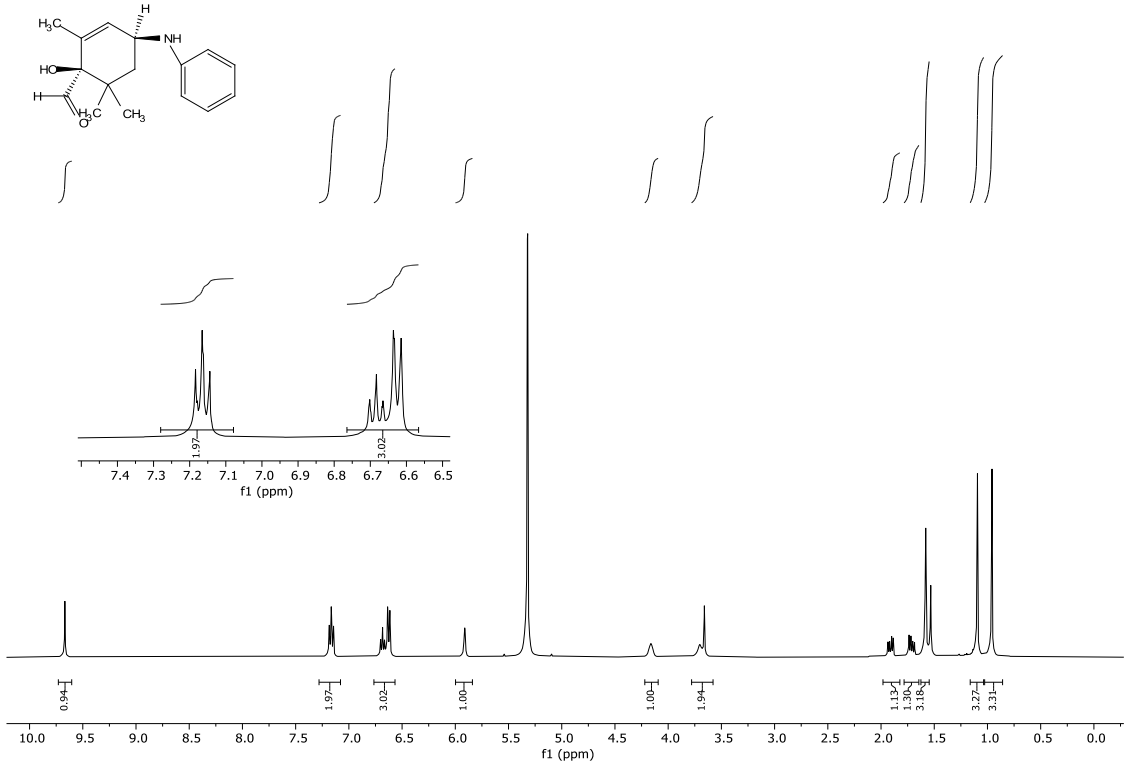
^{1}H NMR spectrum for **4c**



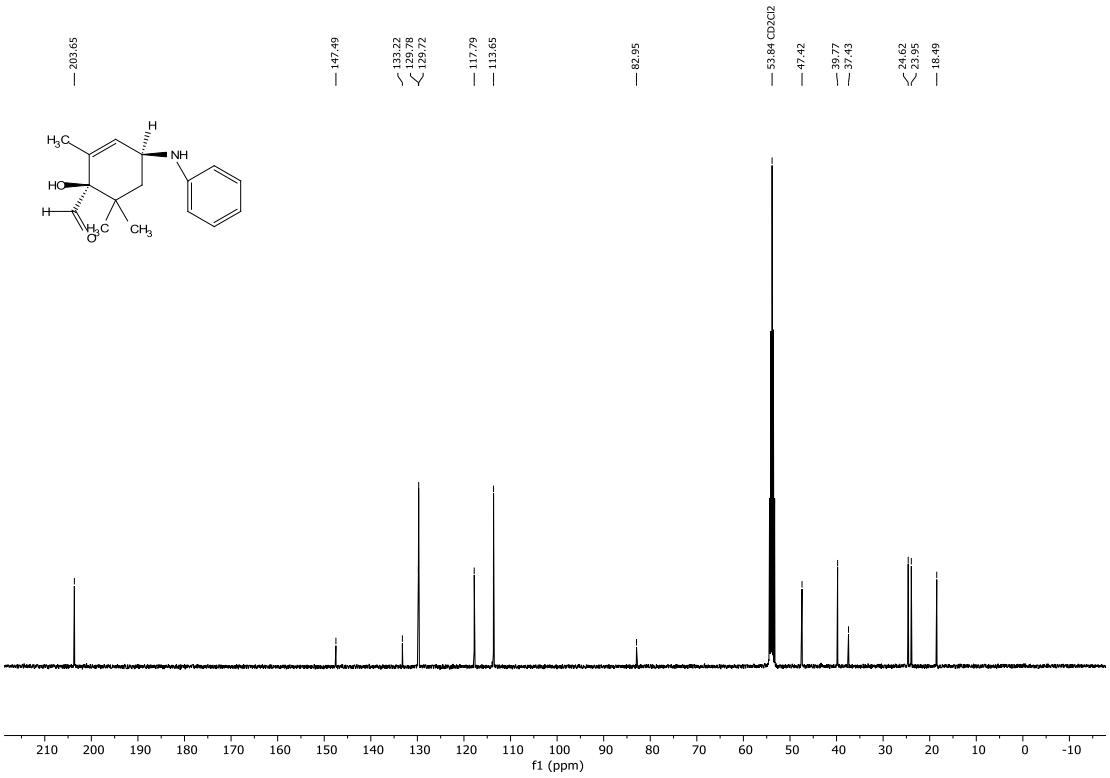
^{13}C NMR spectrum for **4c**



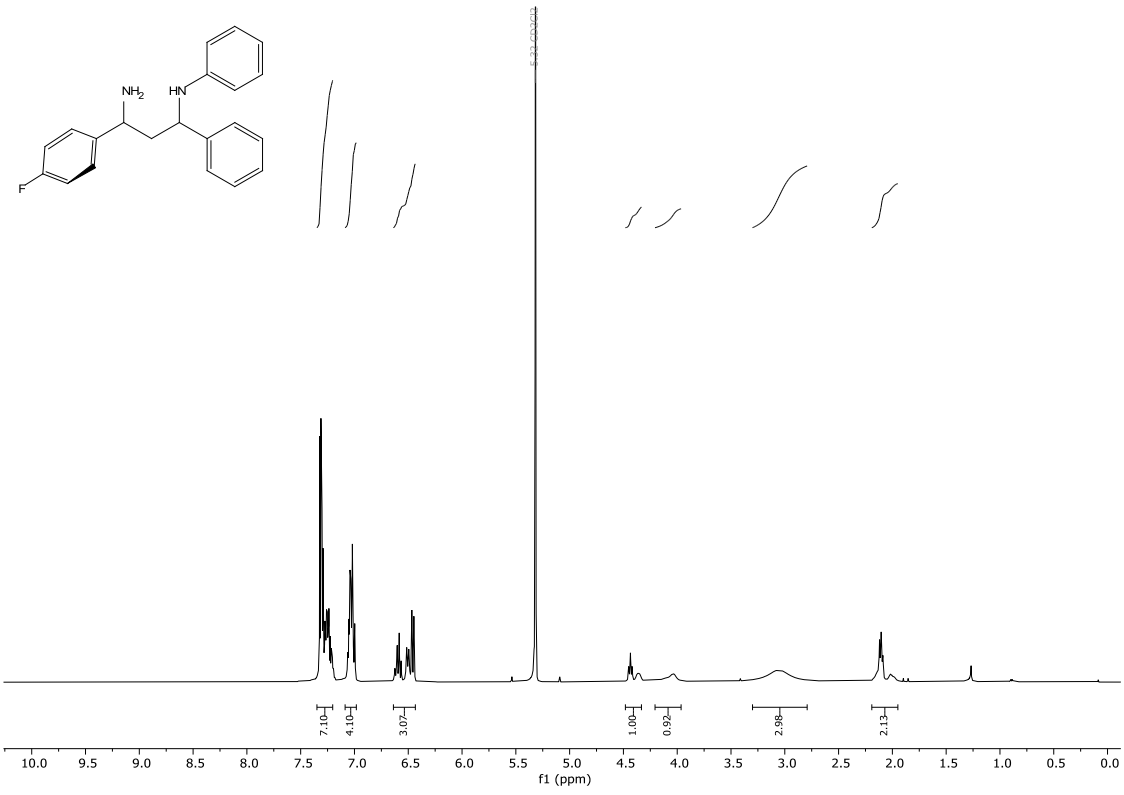
^{1}H NMR spectrum for **4d**



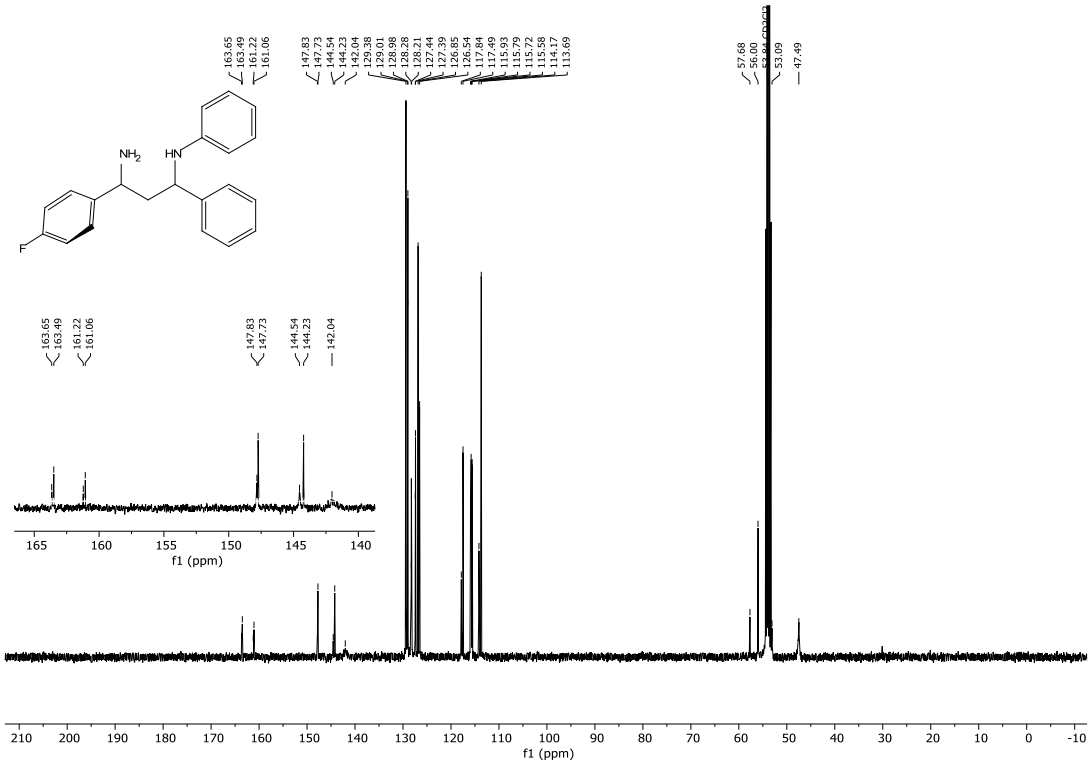
^{13}C NMR spectrum for **4d**



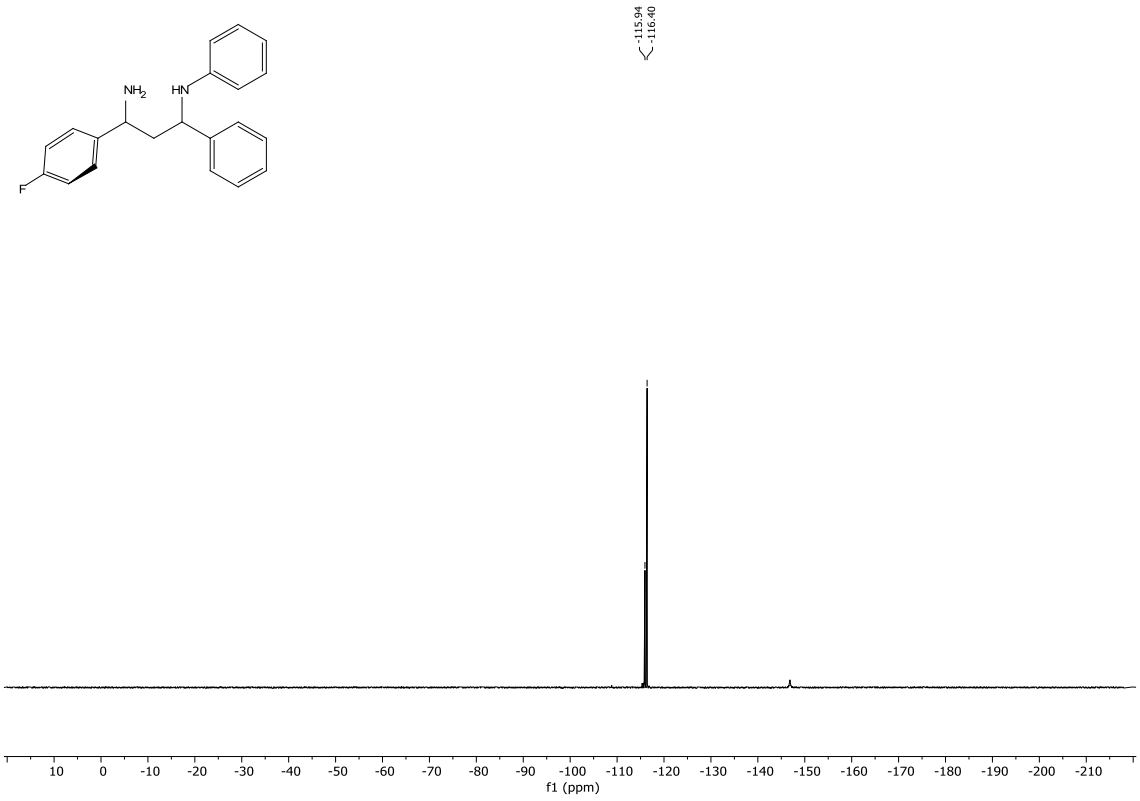
^{1}H NMR spectrum for **6a**



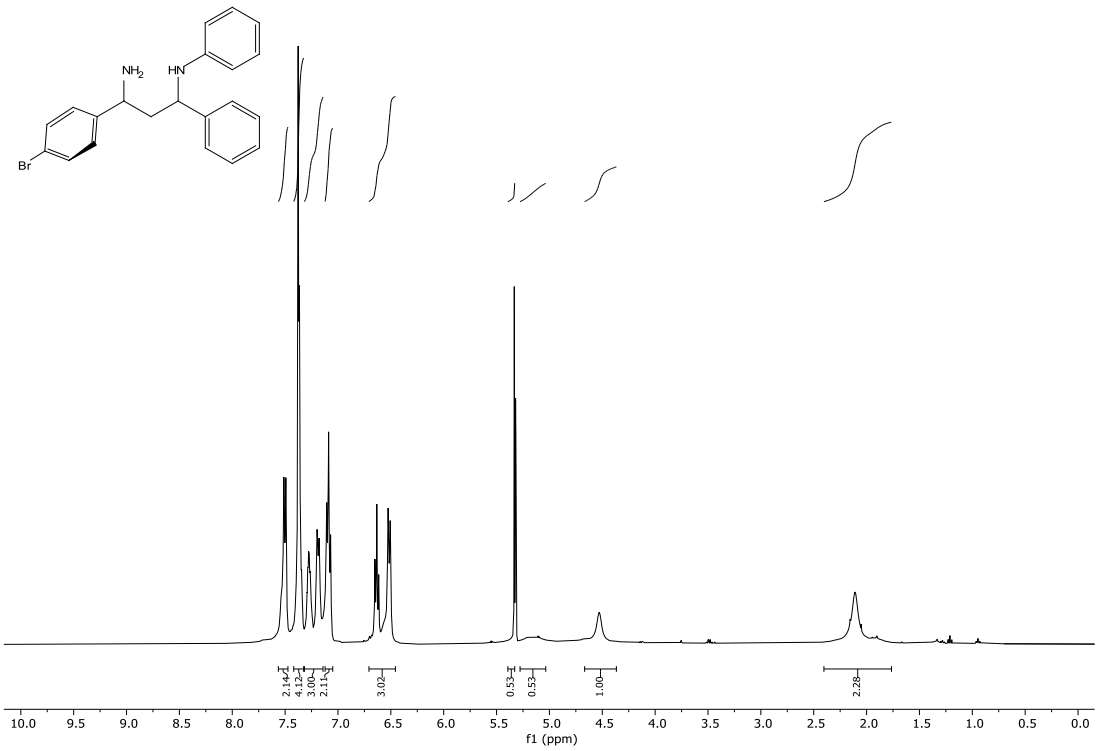
^{13}C NMR spectrum for **6a**



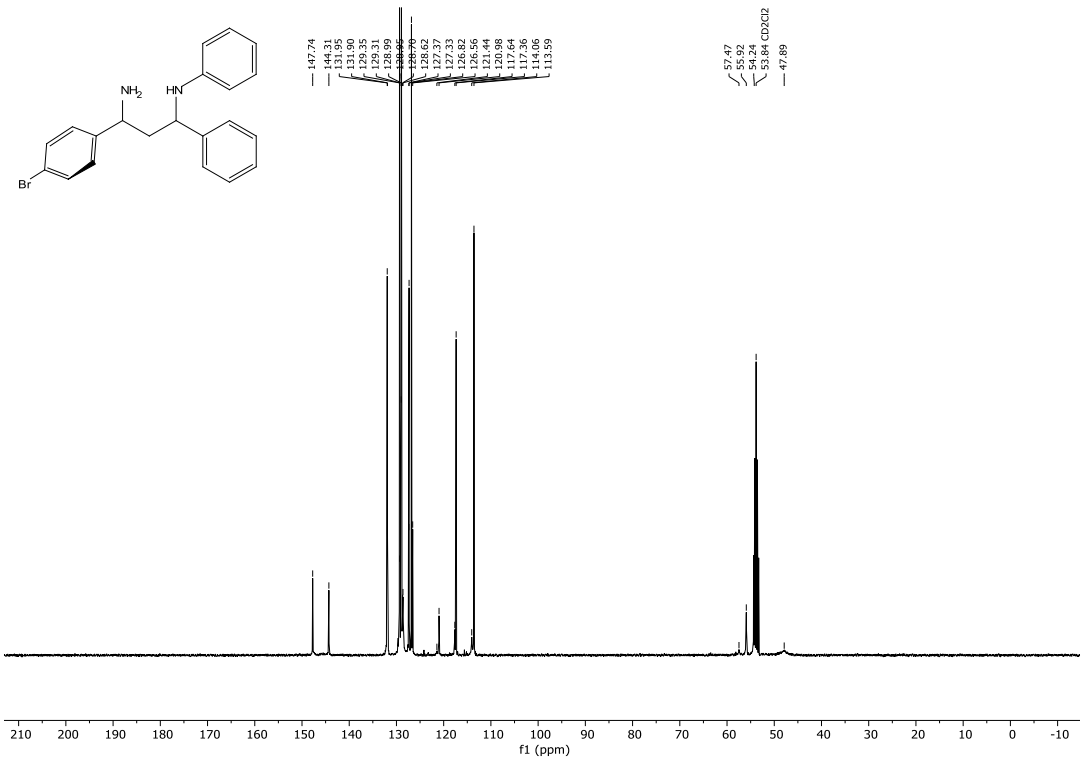
^{19}F NMR spectrum for **6a**



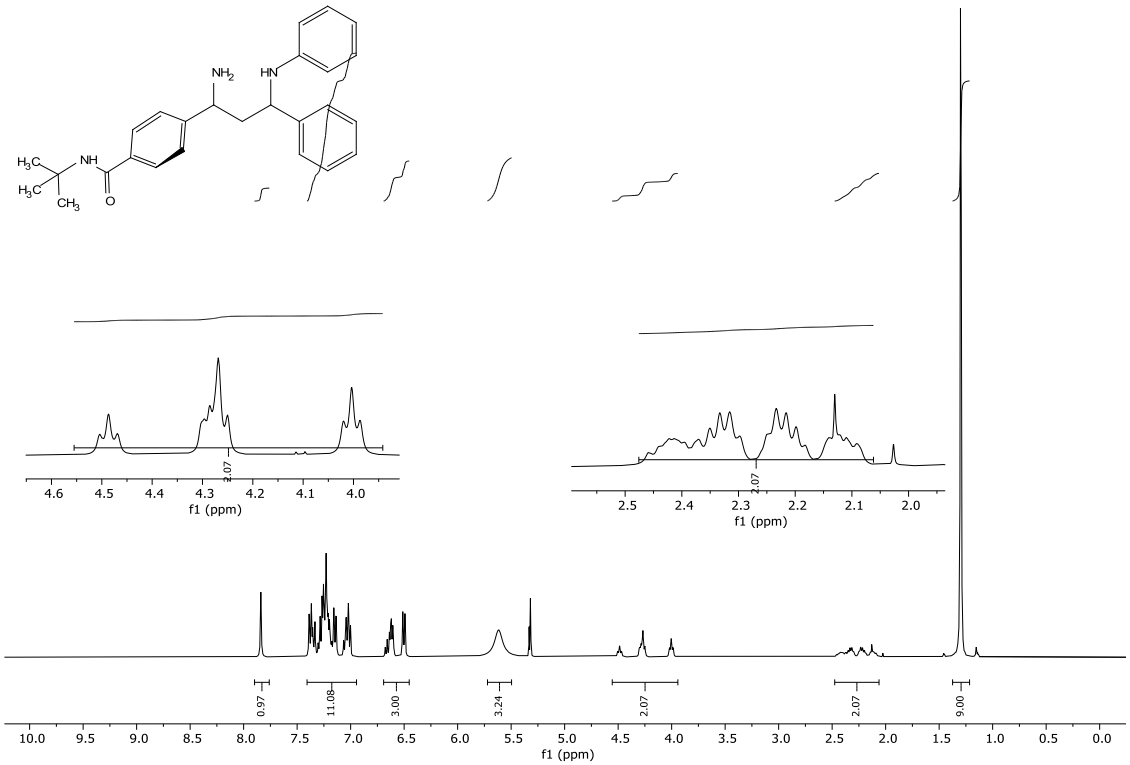
^{1}H NMR spectrum for **6b**



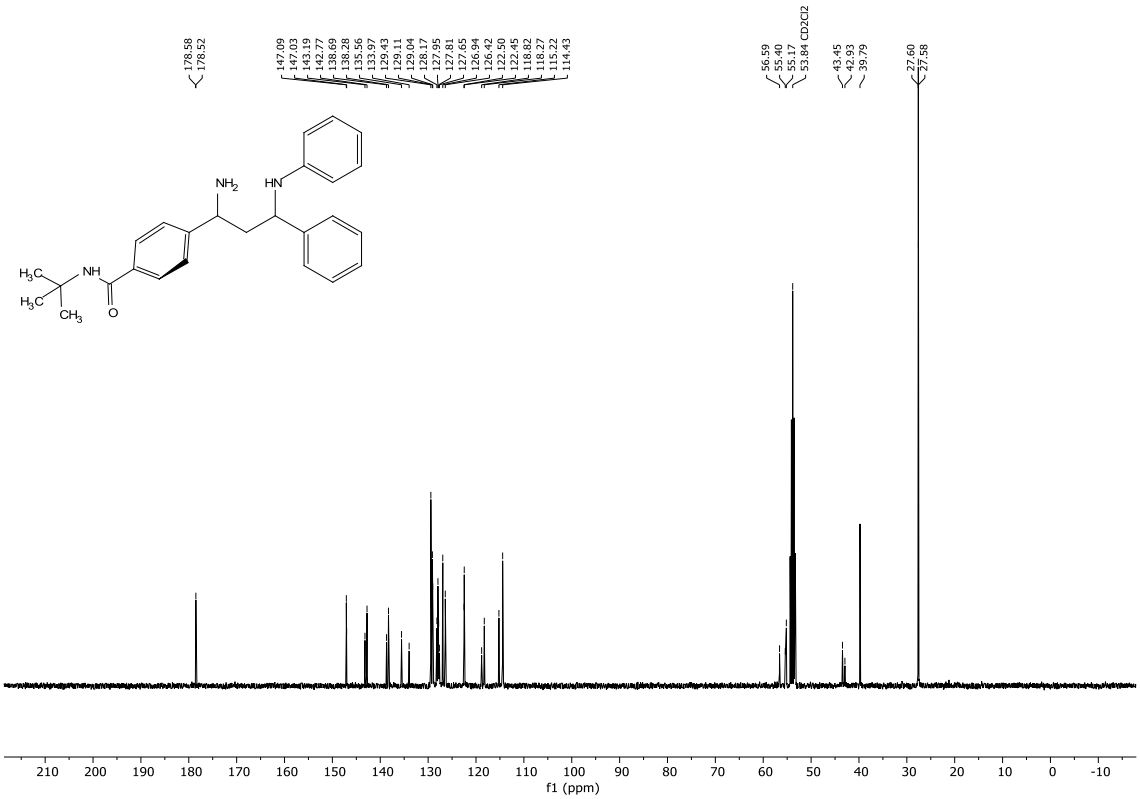
^{13}C NMR spectrum for **6b**



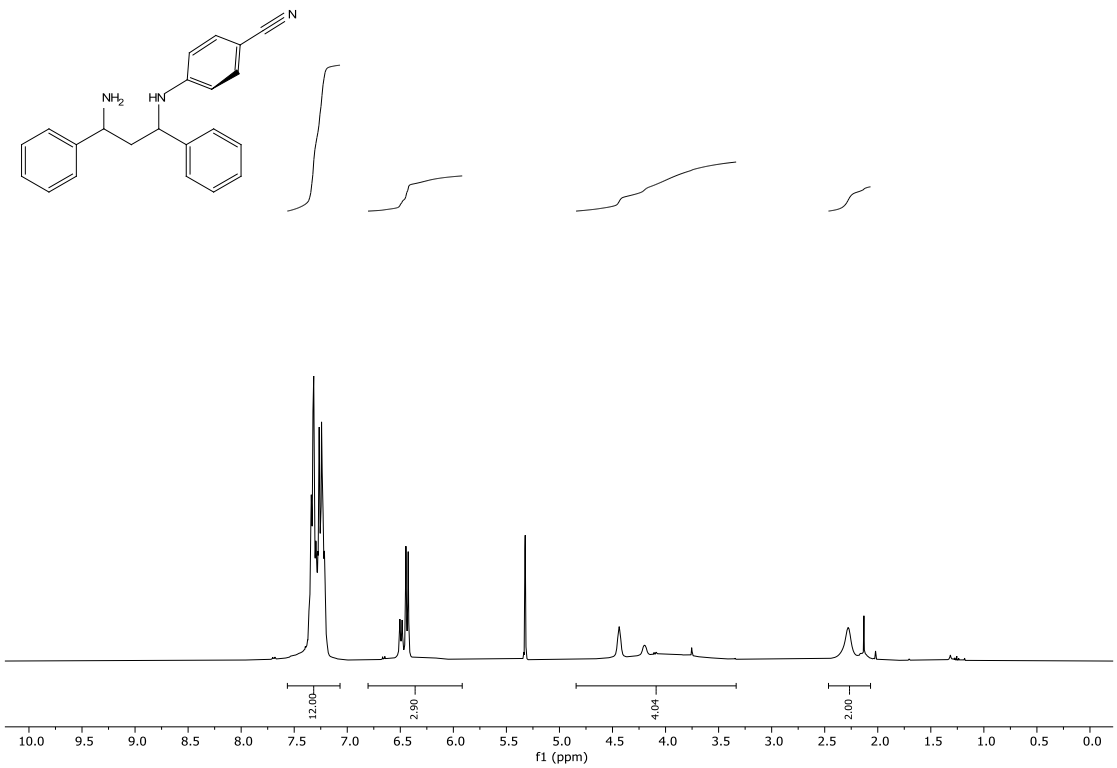
^{1}H NMR spectrum for **6c**



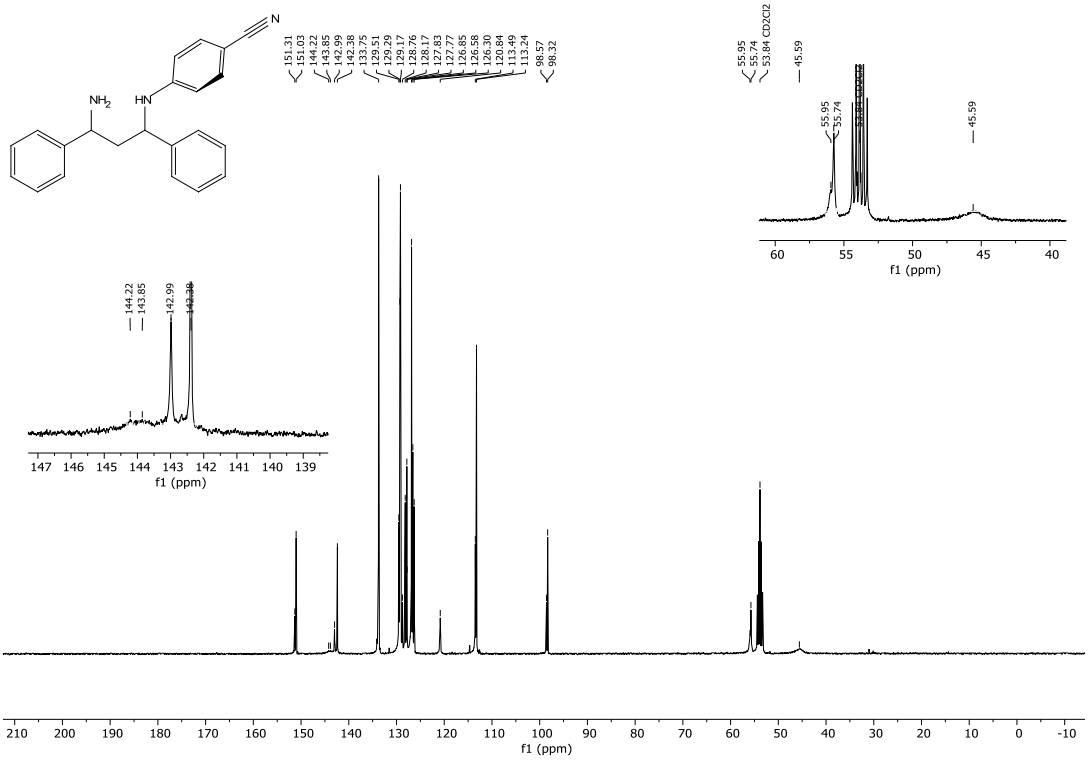
^{13}C NMR spectrum for **6c**



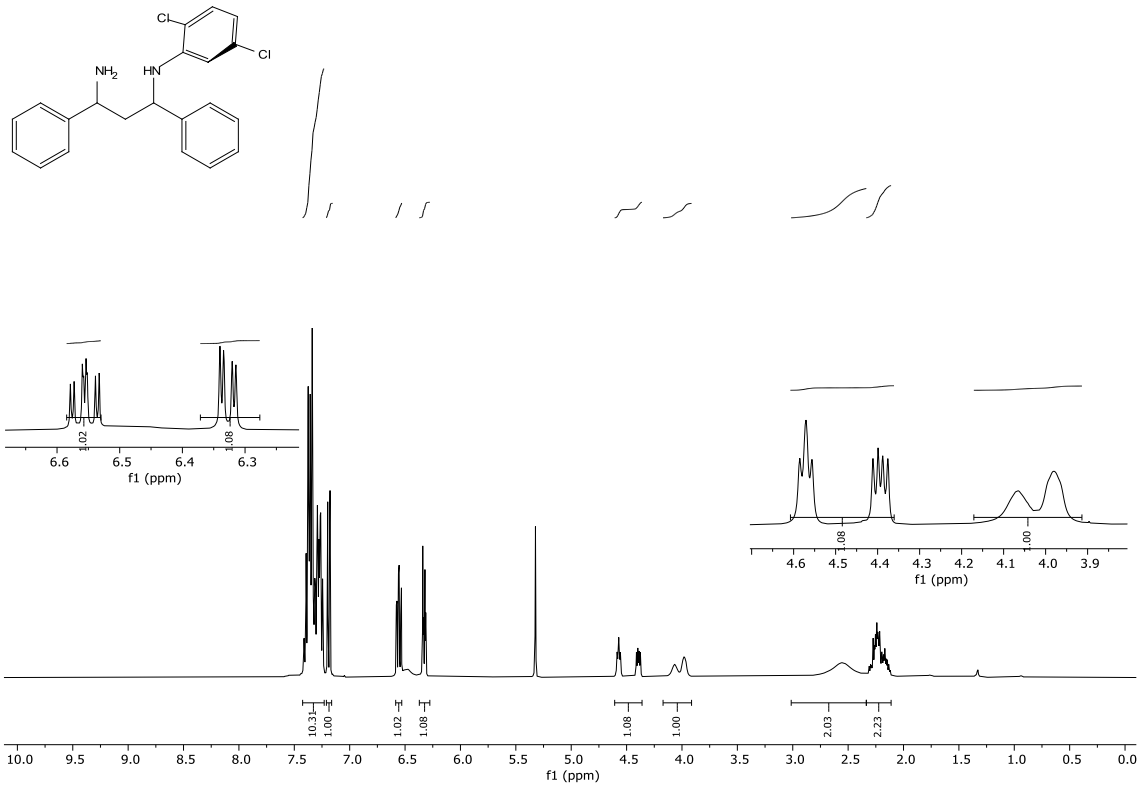
^{1}H NMR spectrum for **6d**



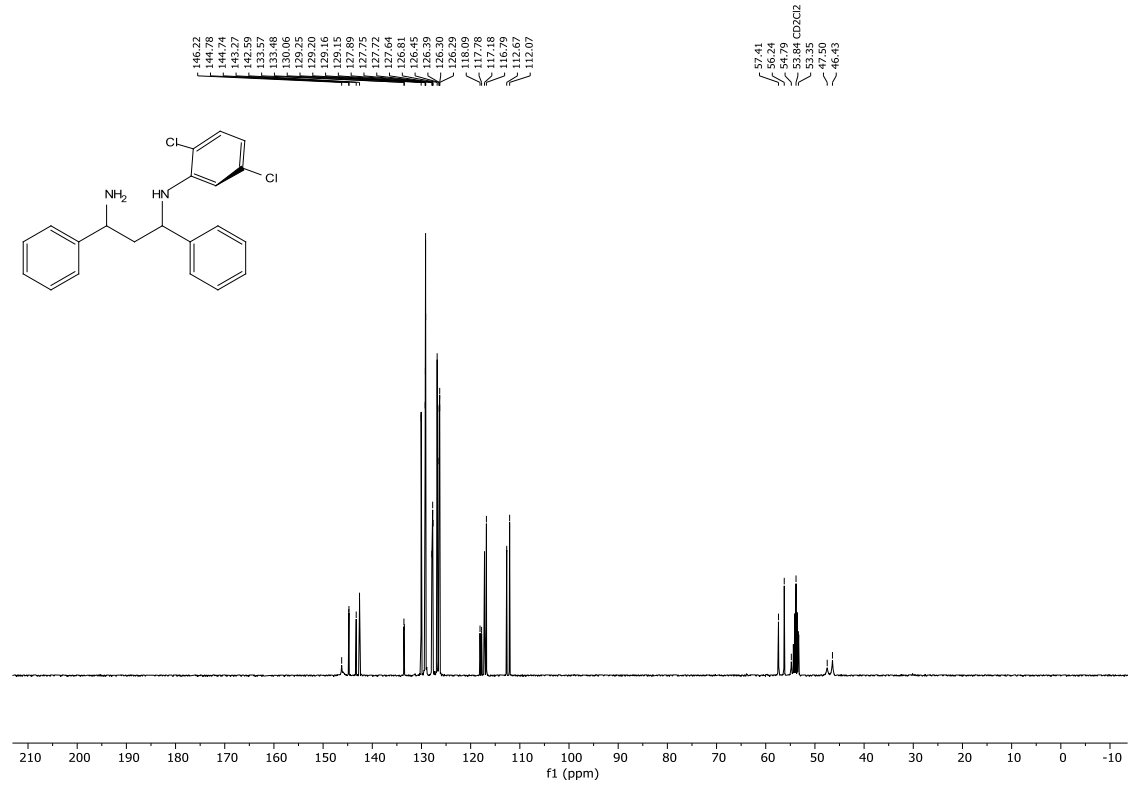
^{13}C NMR spectrum for **6d**



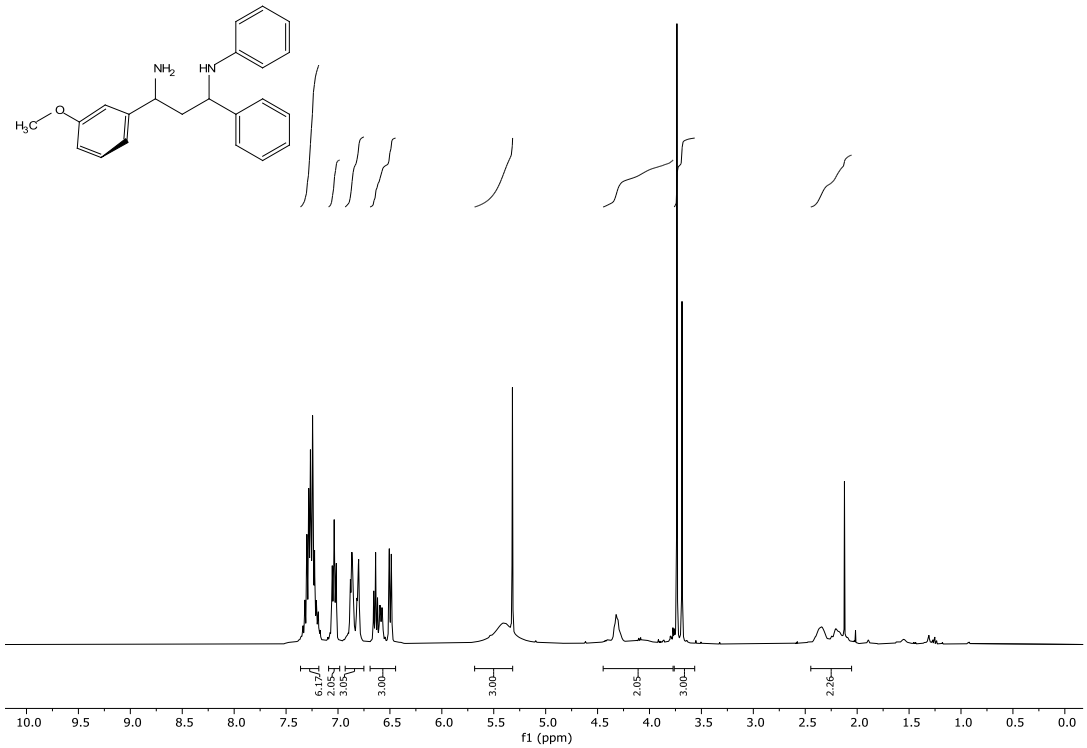
^{1}H NMR spectrum for **6e**



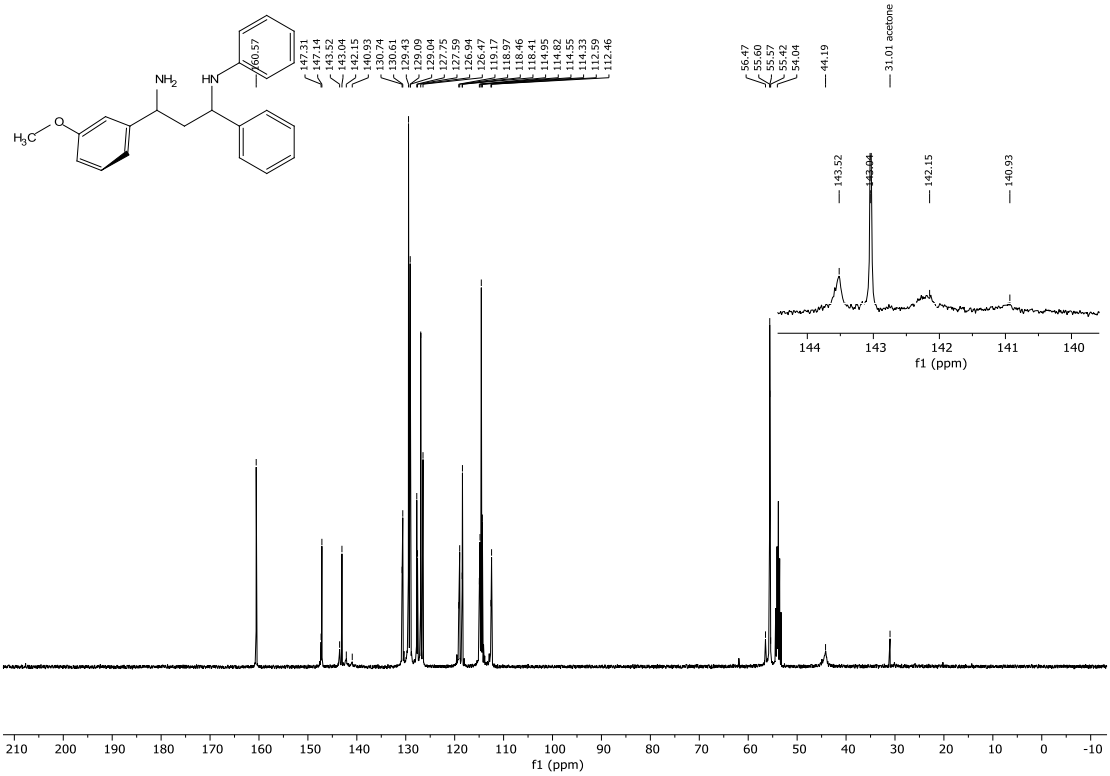
^{13}C NMR spectrum for **6e**



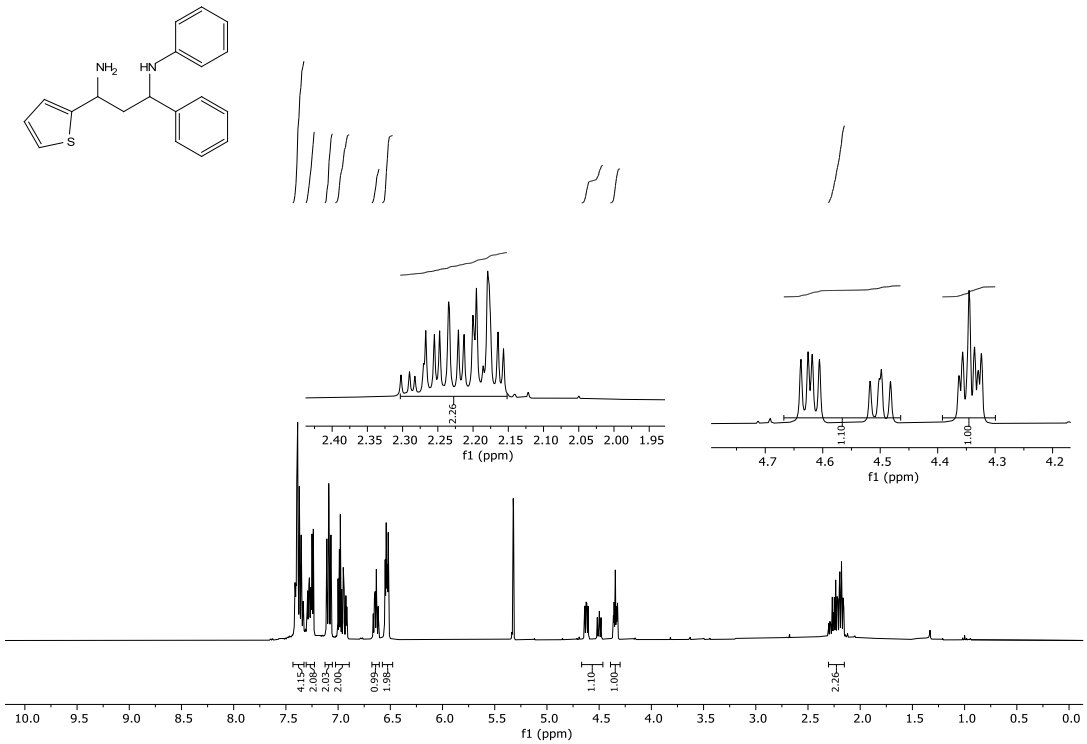
^{13}C NMR spectrum for **6f**



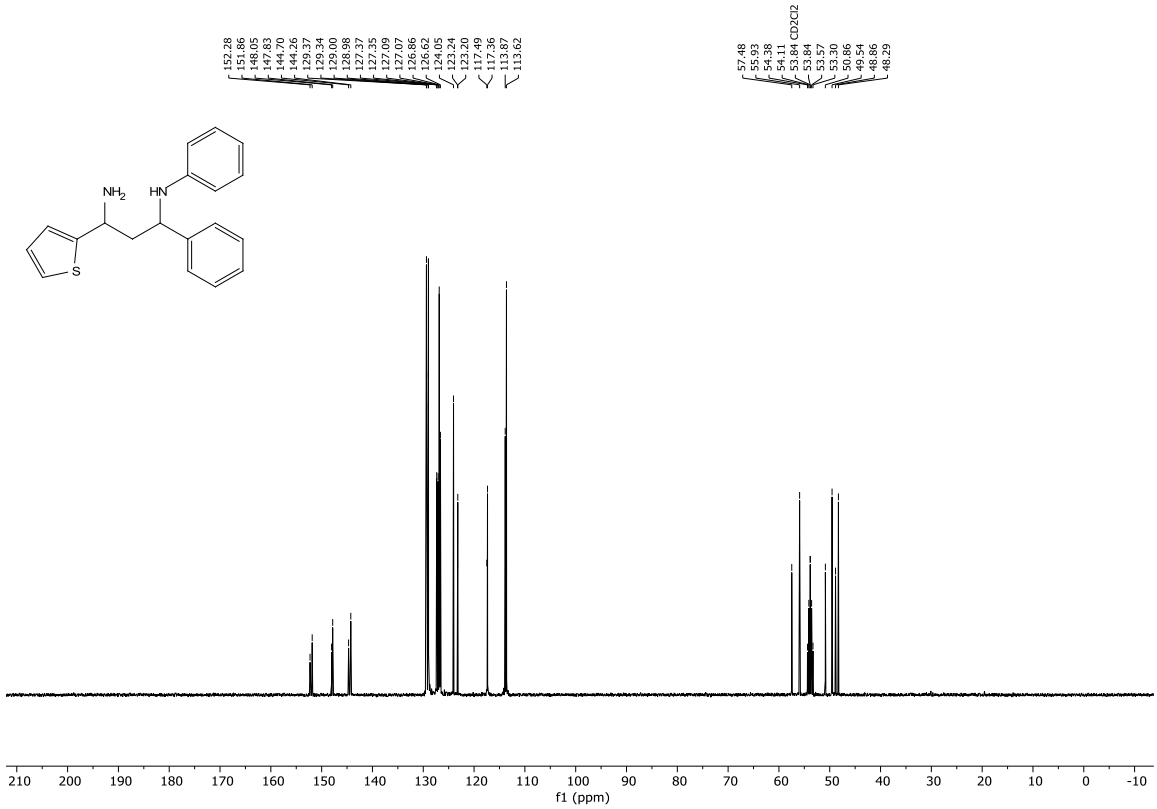
^{13}C NMR spectrum for **6f**



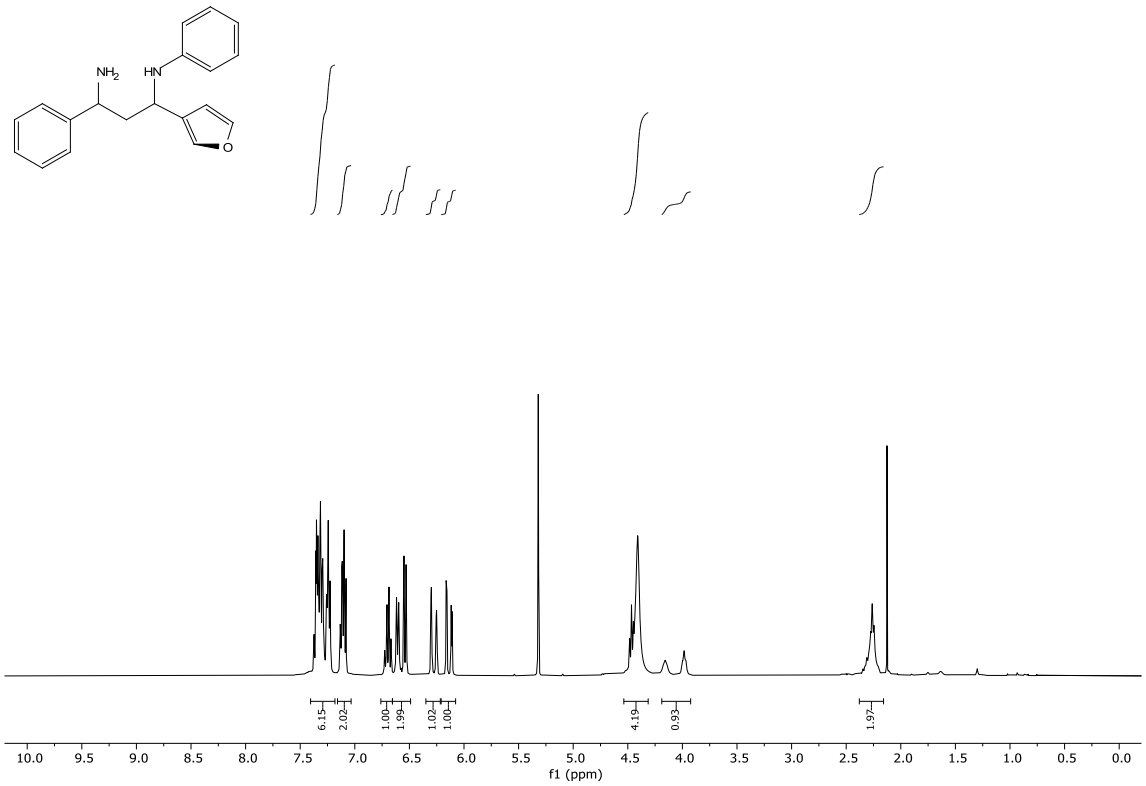
^{1}H NMR spectrum for **6g**



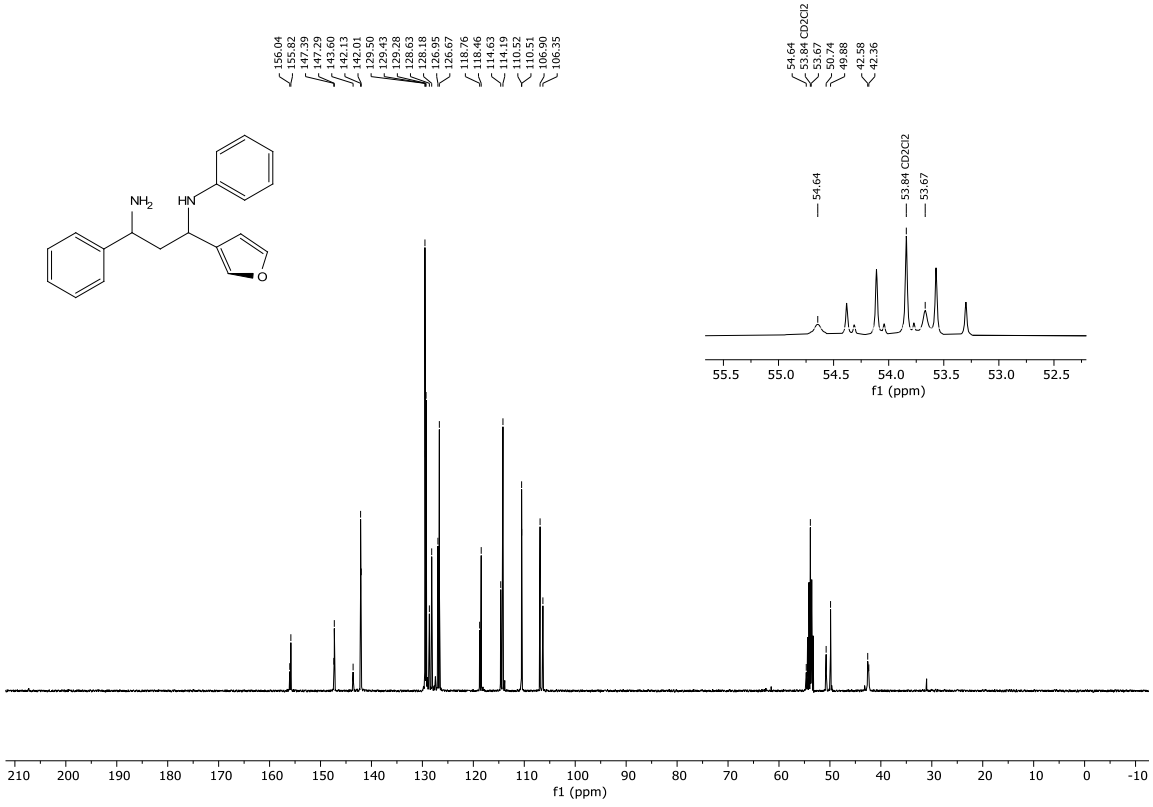
^{13}C NMR spectrum for **6g**



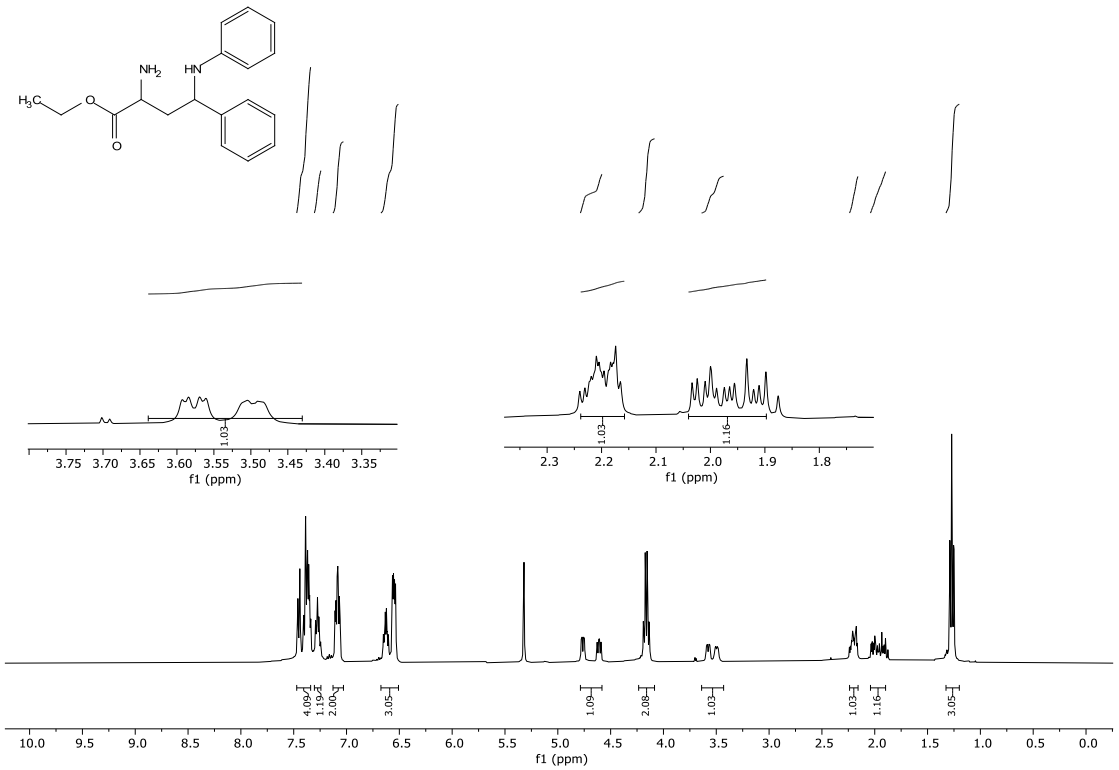
^{1}H NMR spectrum for **6h**



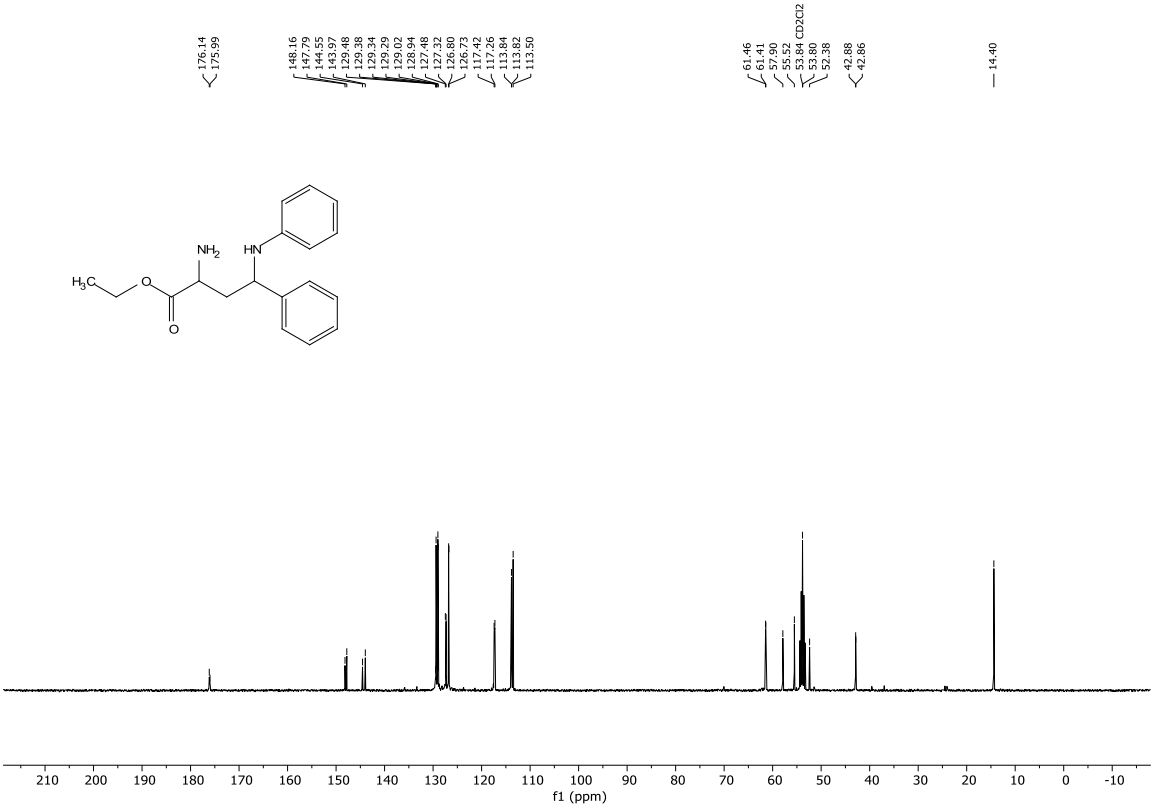
^{13}C NMR spectrum for **6h**



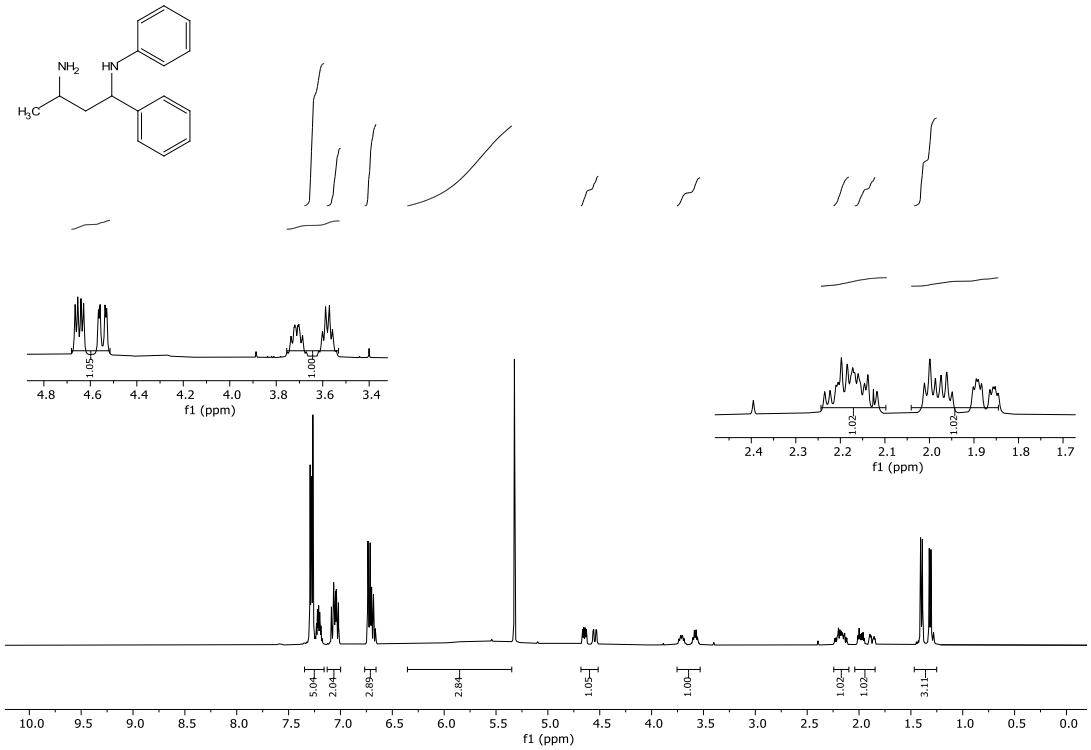
^{1}H NMR spectrum for **6i**



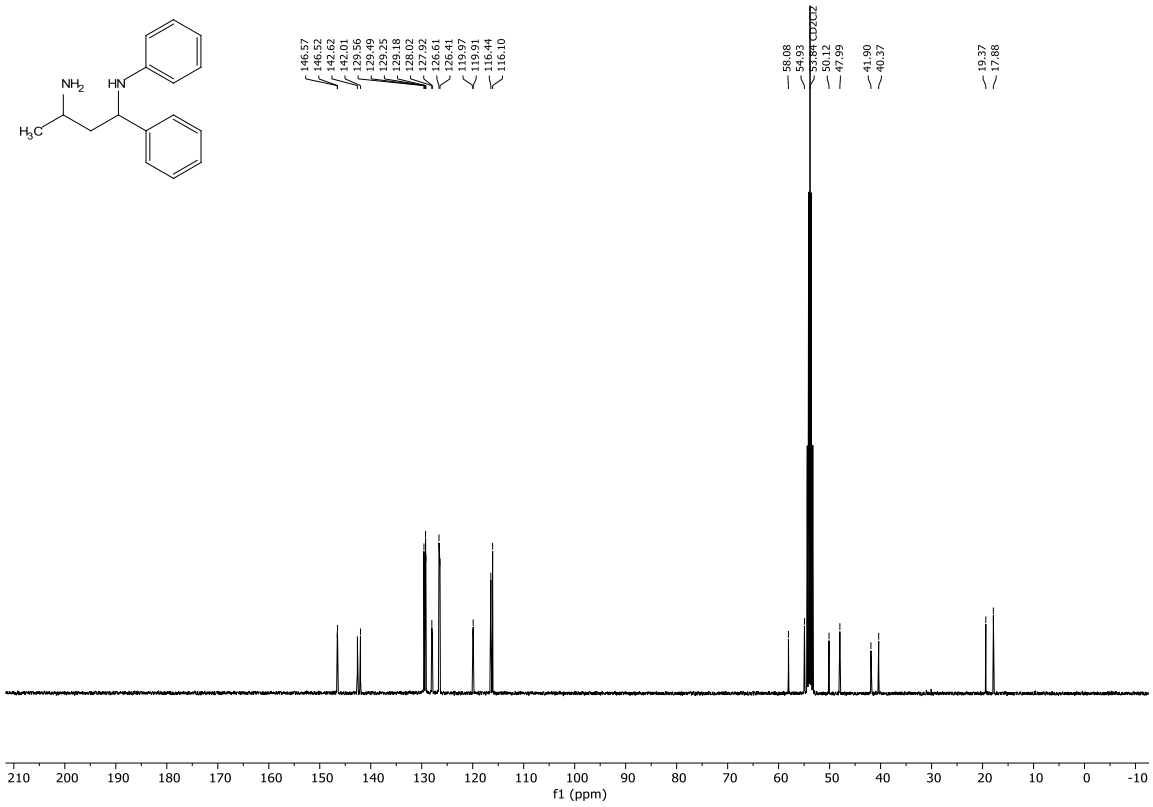
^{13}C NMR spectrum for **6i**



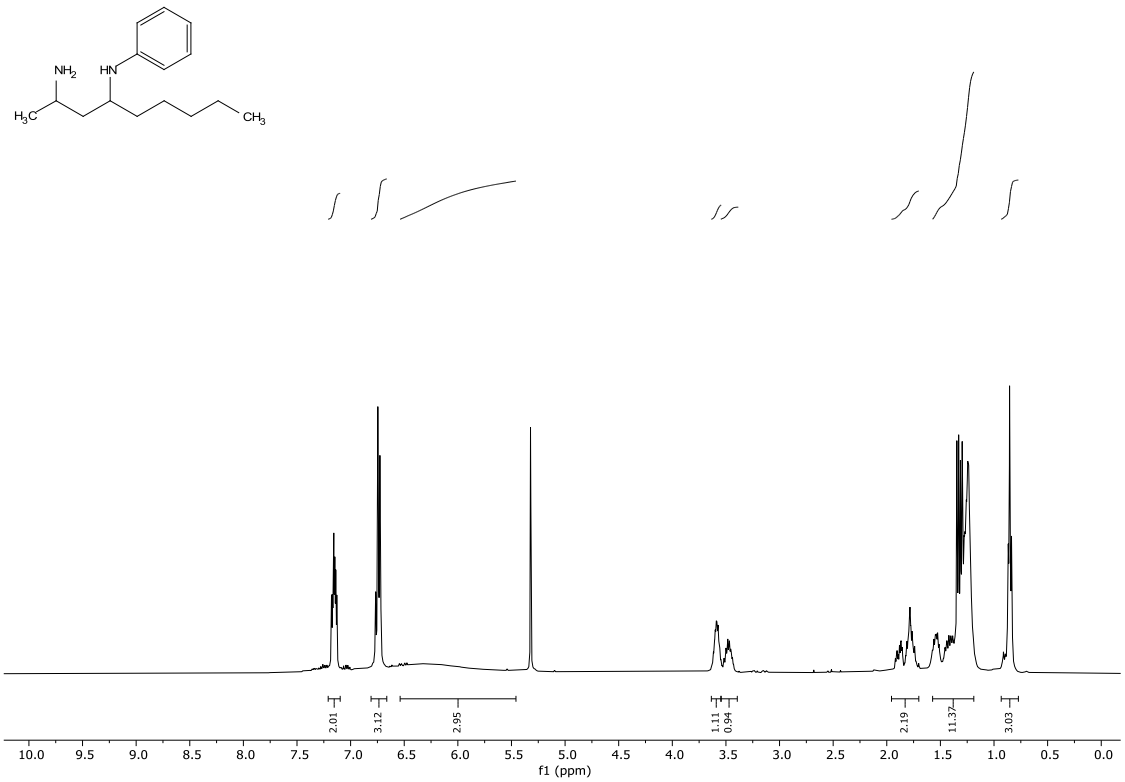
^{1}H NMR spectrum for **6j**



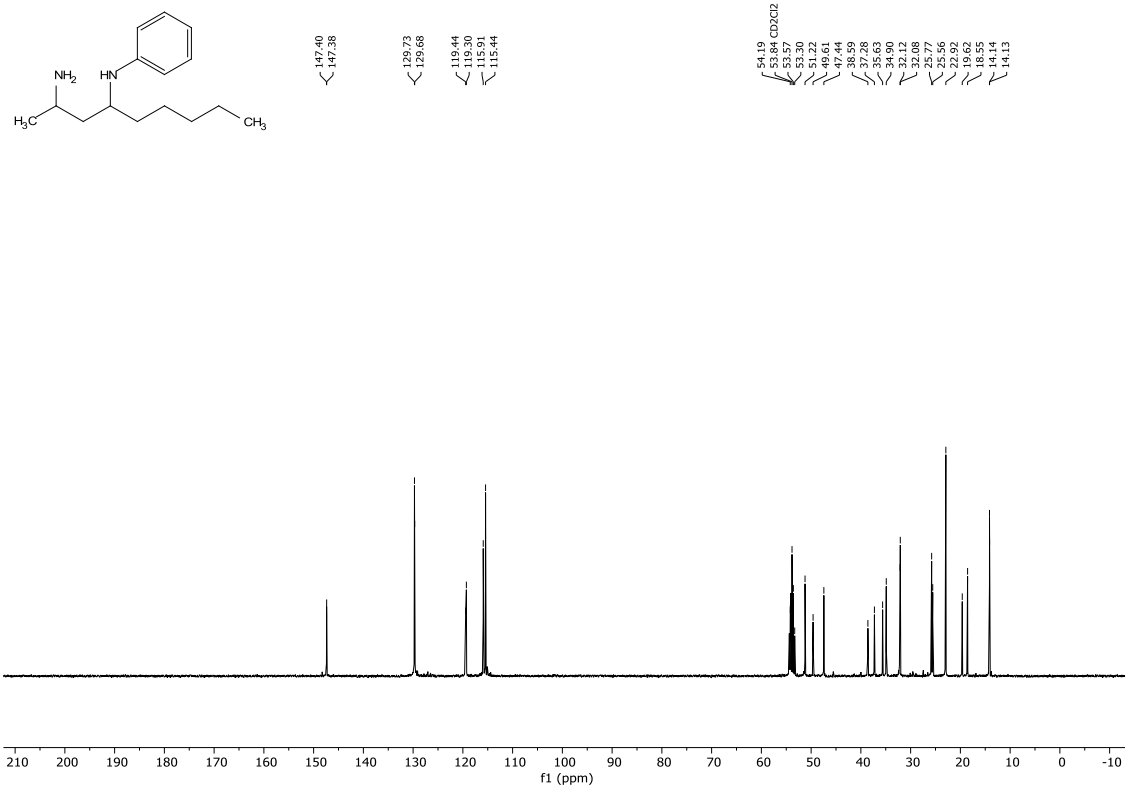
^{13}C NMR spectrum for **6j**



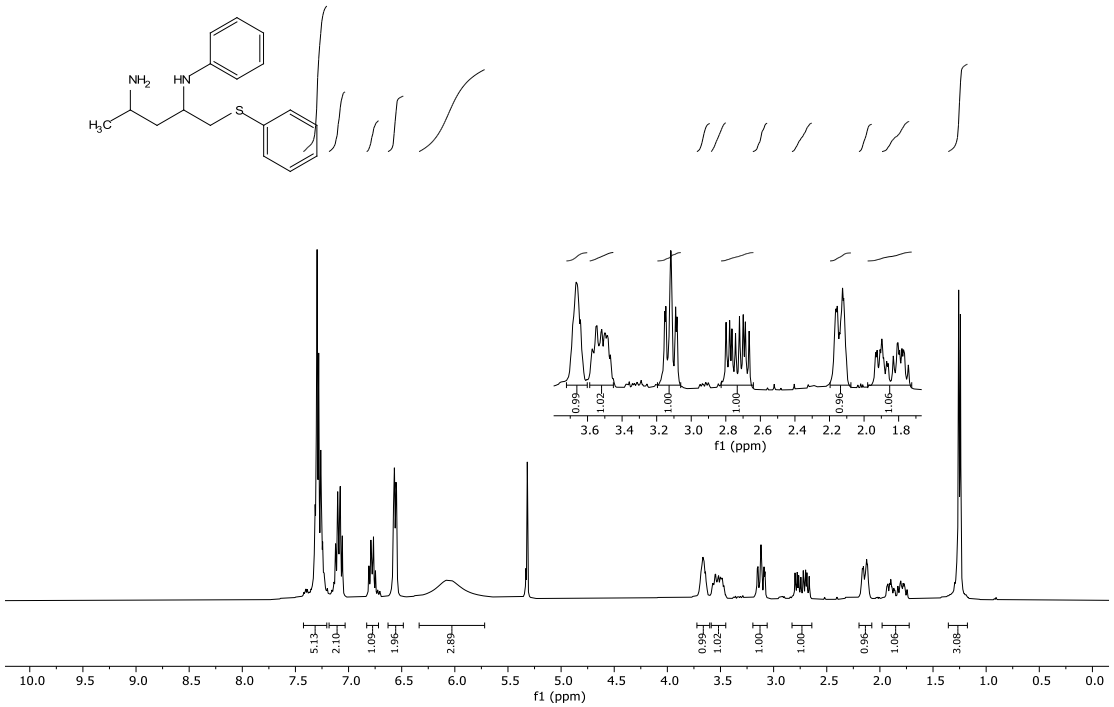
^{1}H NMR spectrum for **6k**



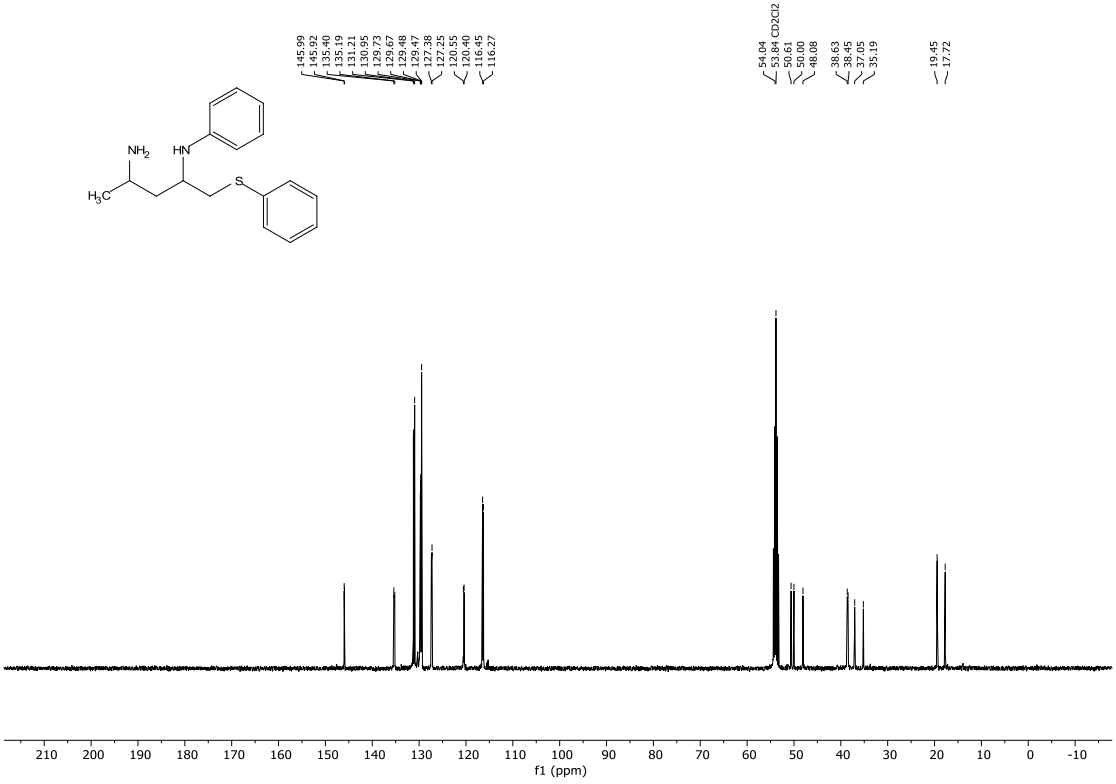
^{13}C NMR spectrum for **6k**



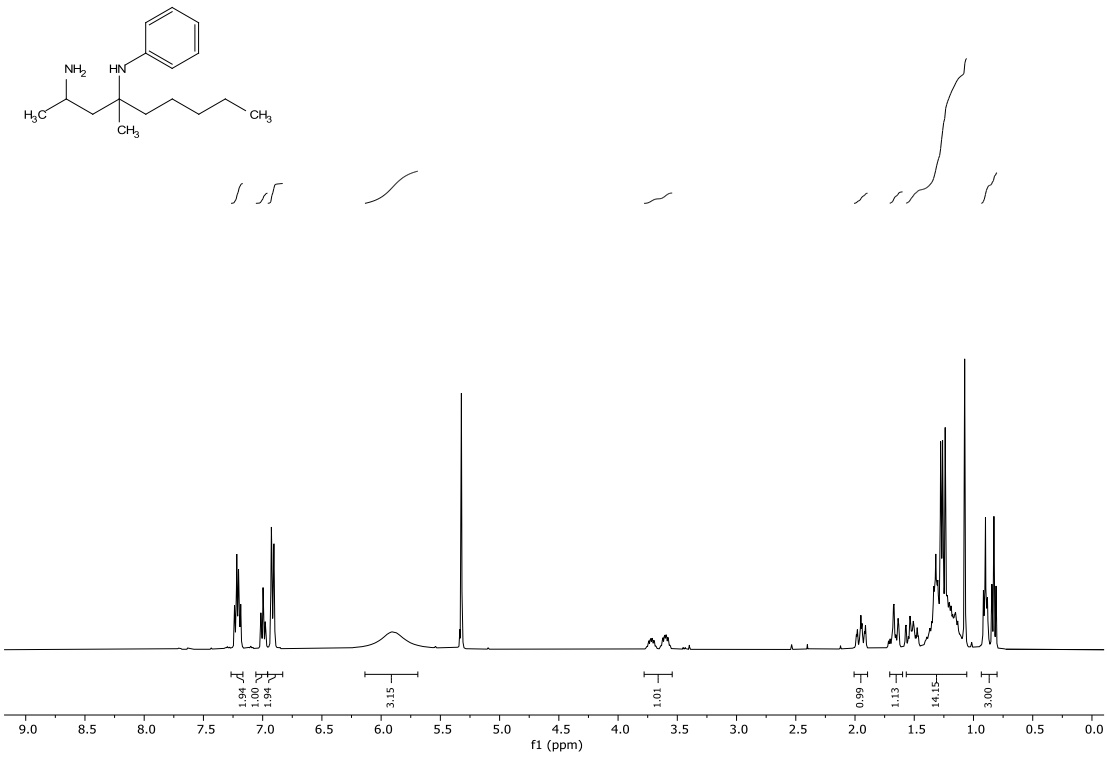
^{1}H NMR spectrum for **6l**



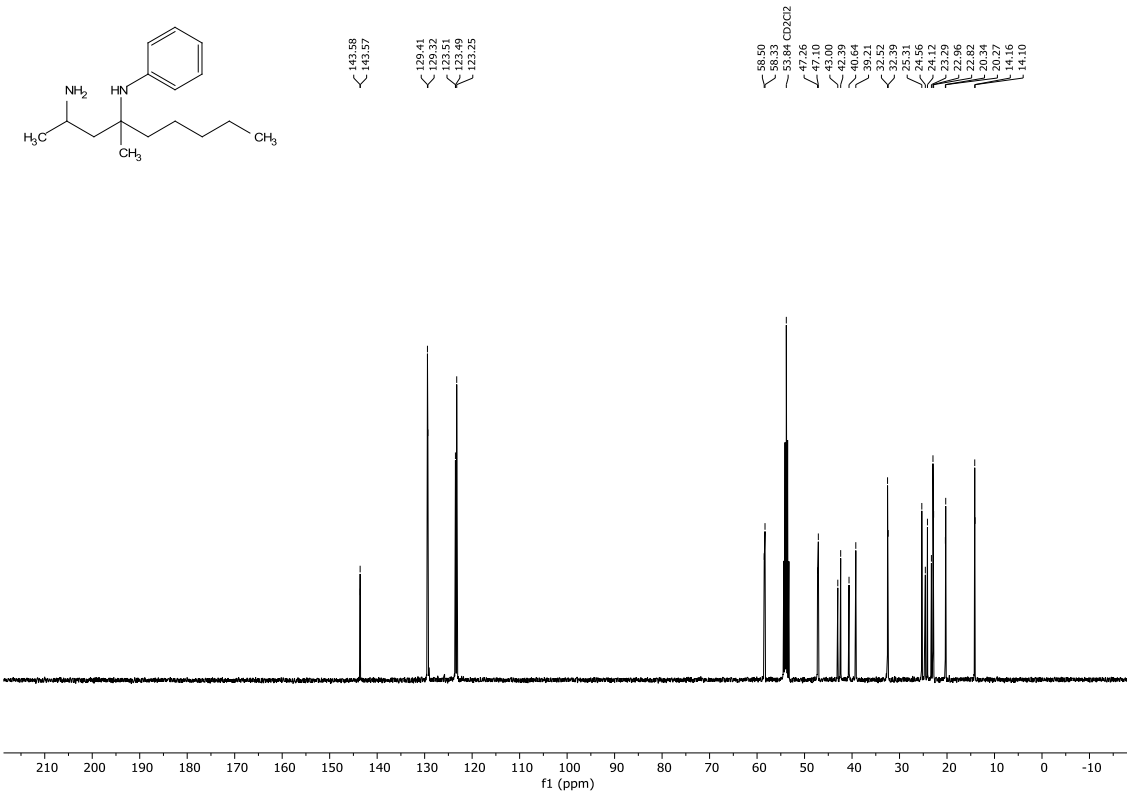
^{13}C NMR spectrum for **6l**



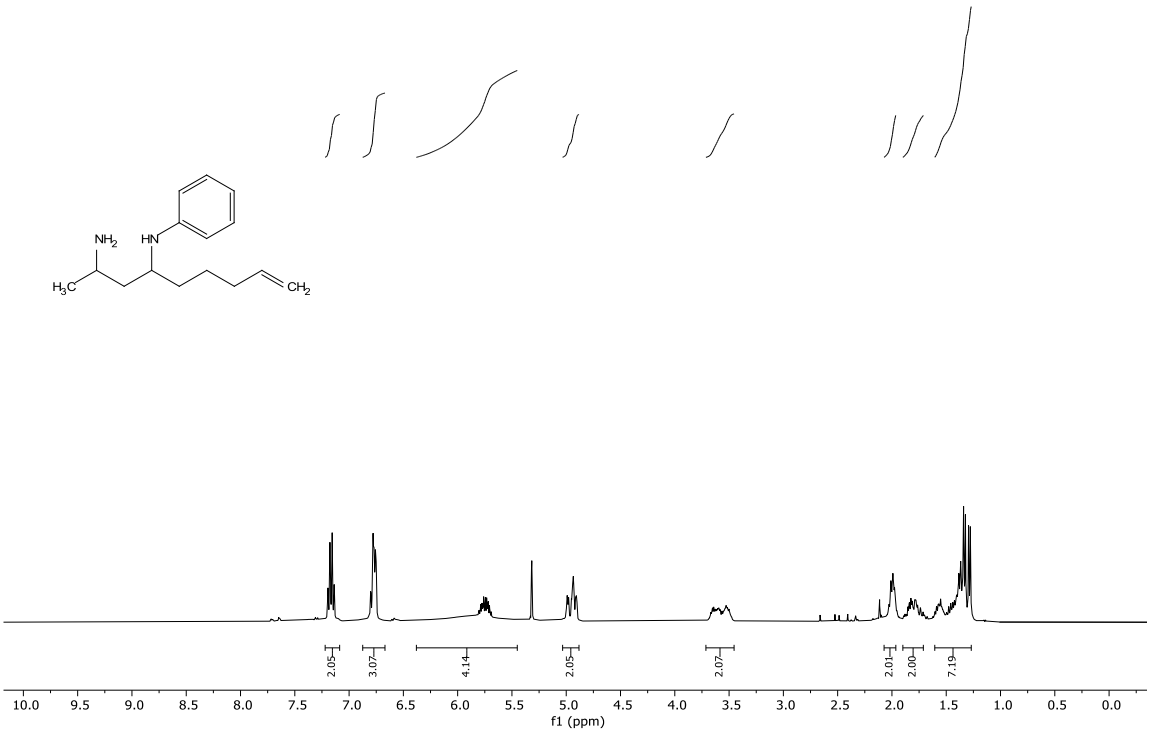
^{1}H NMR spectrum for **6m**



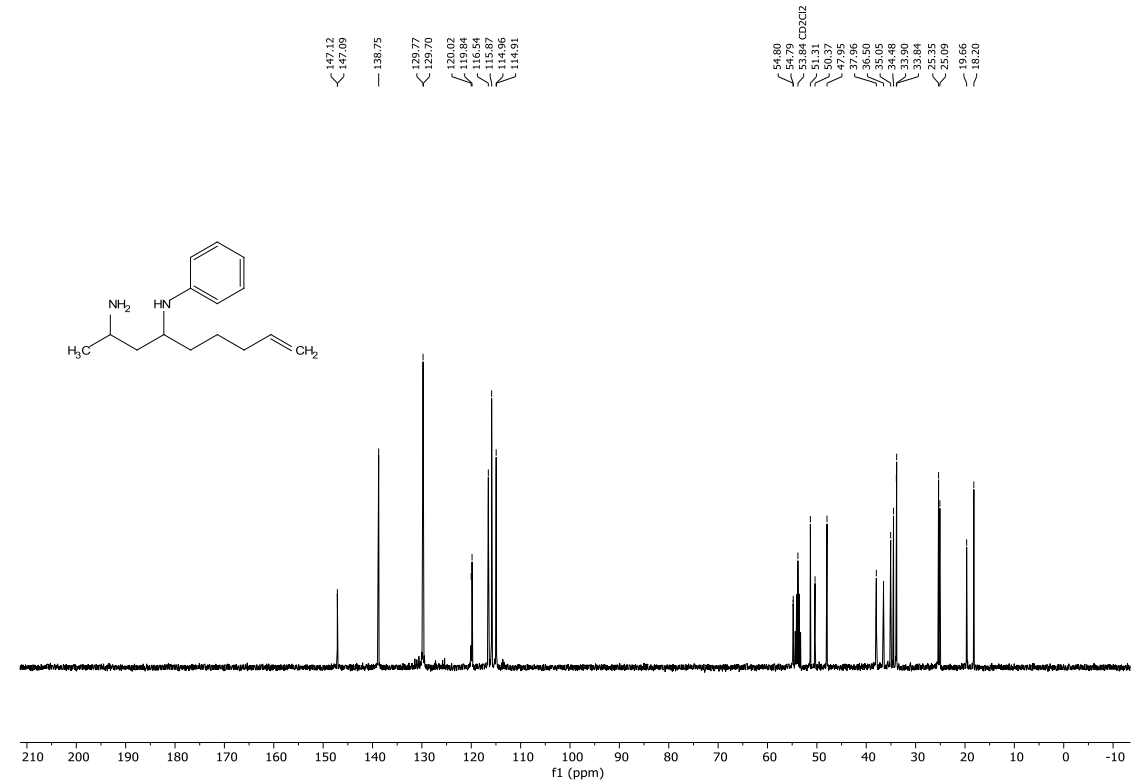
^{13}C NMR spectrum for **6m**



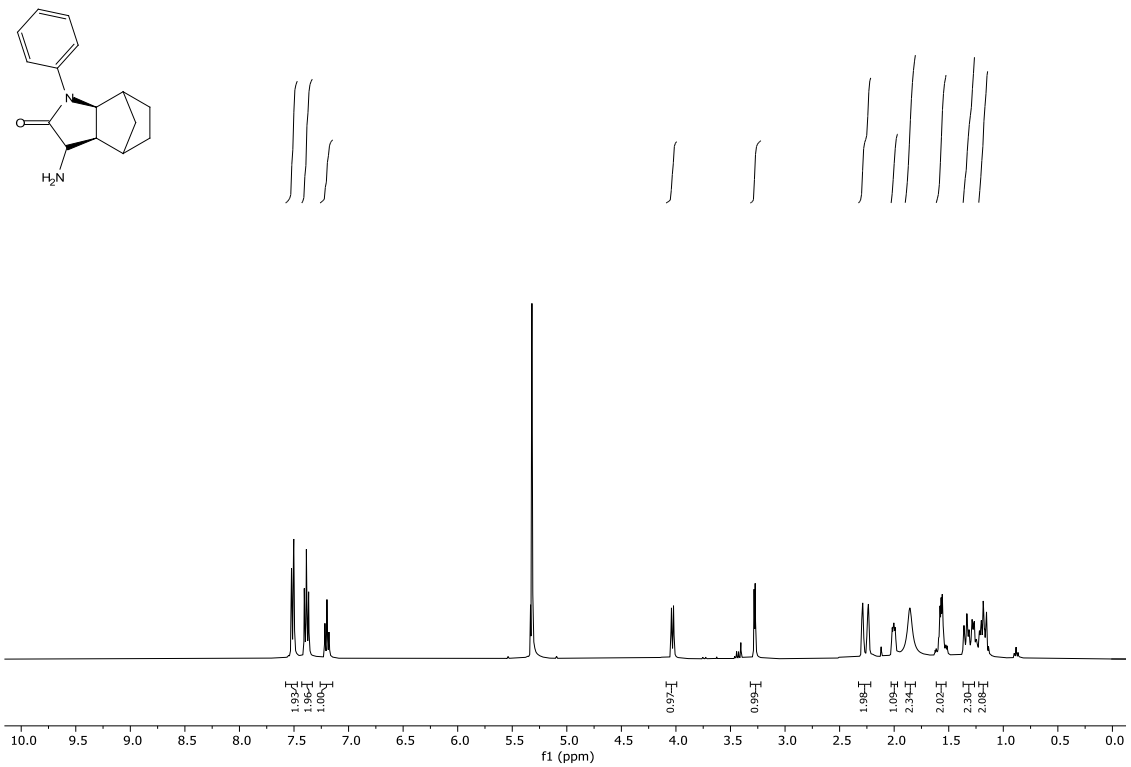
^{1}H NMR spectrum for **6n**



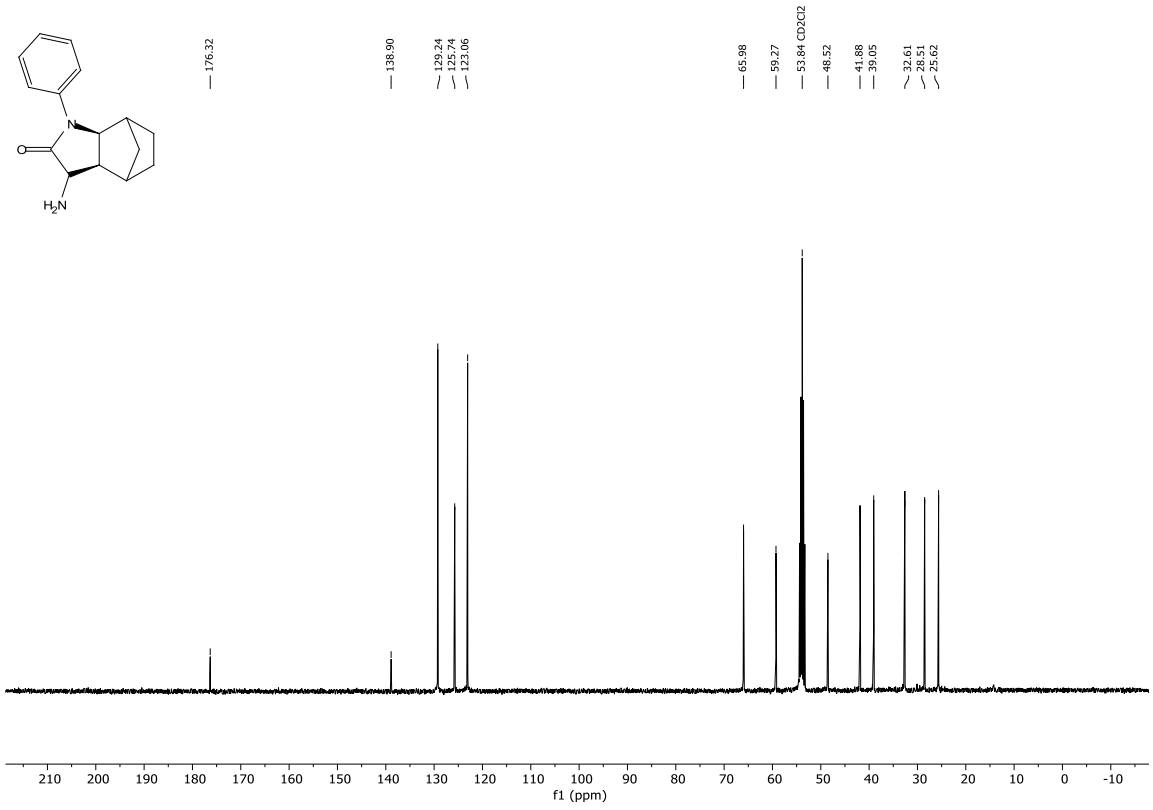
^{13}C NMR spectrum for **6n**



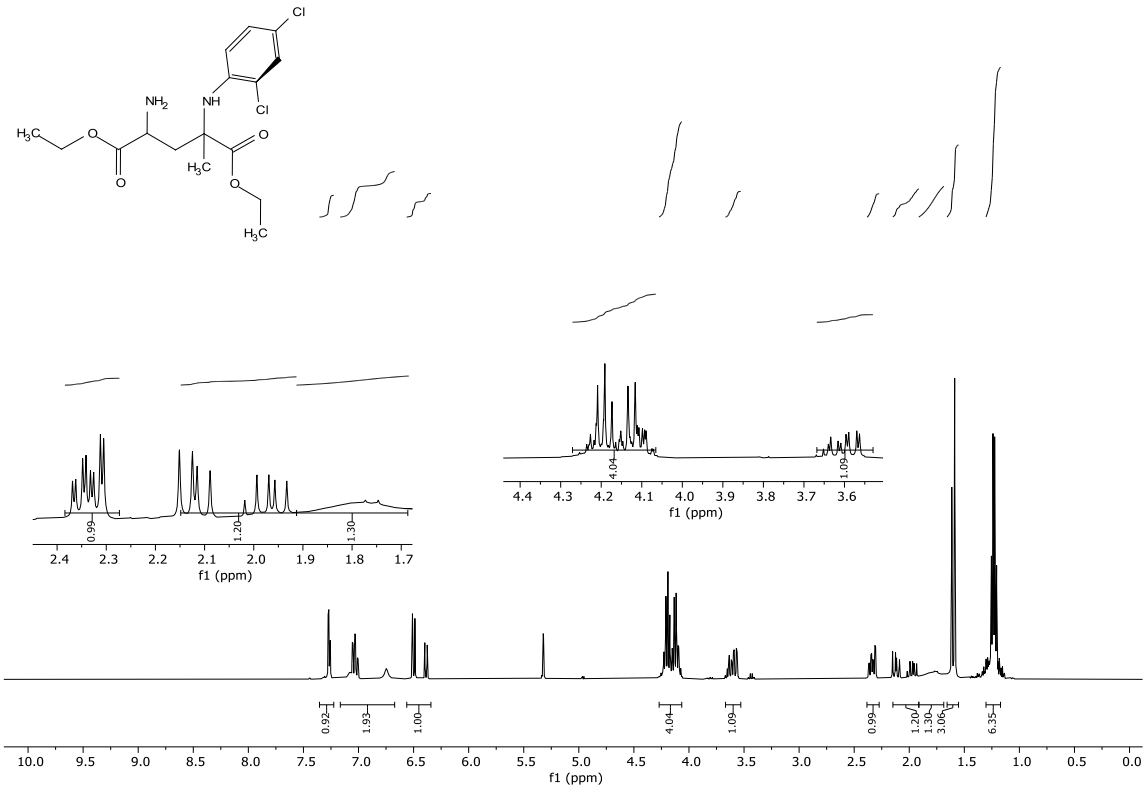
^{1}H NMR spectrum for **6o**



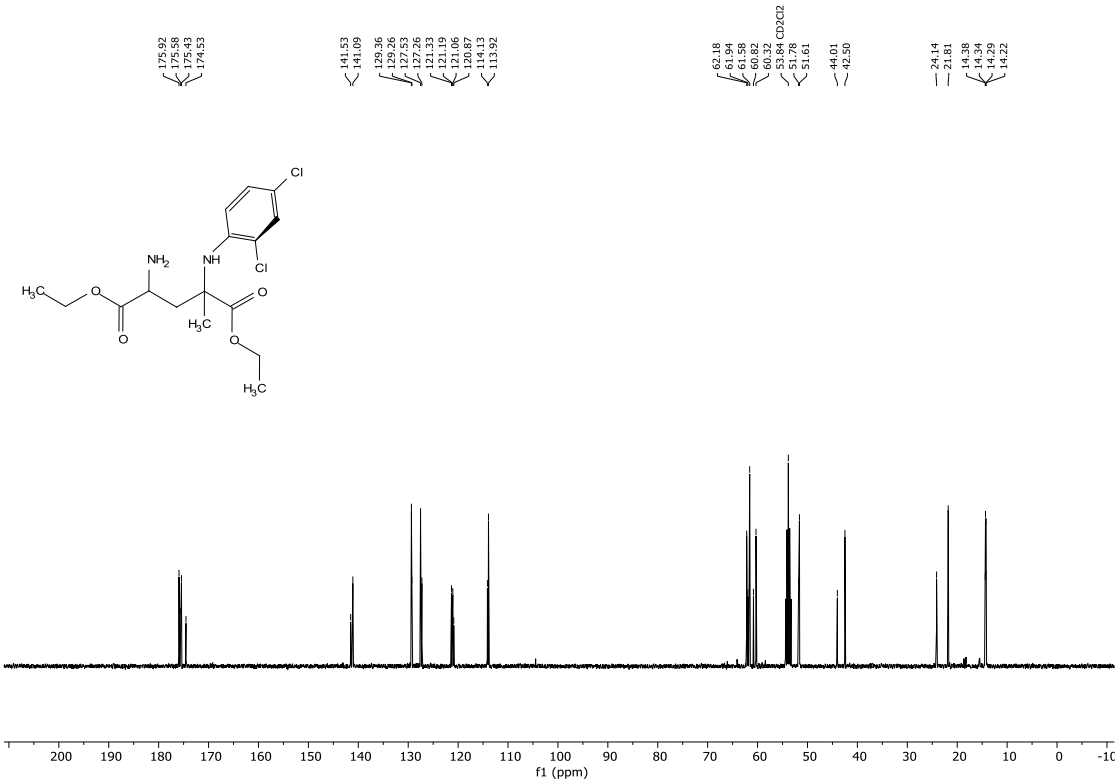
^{13}C NMR spectrum for **6o**



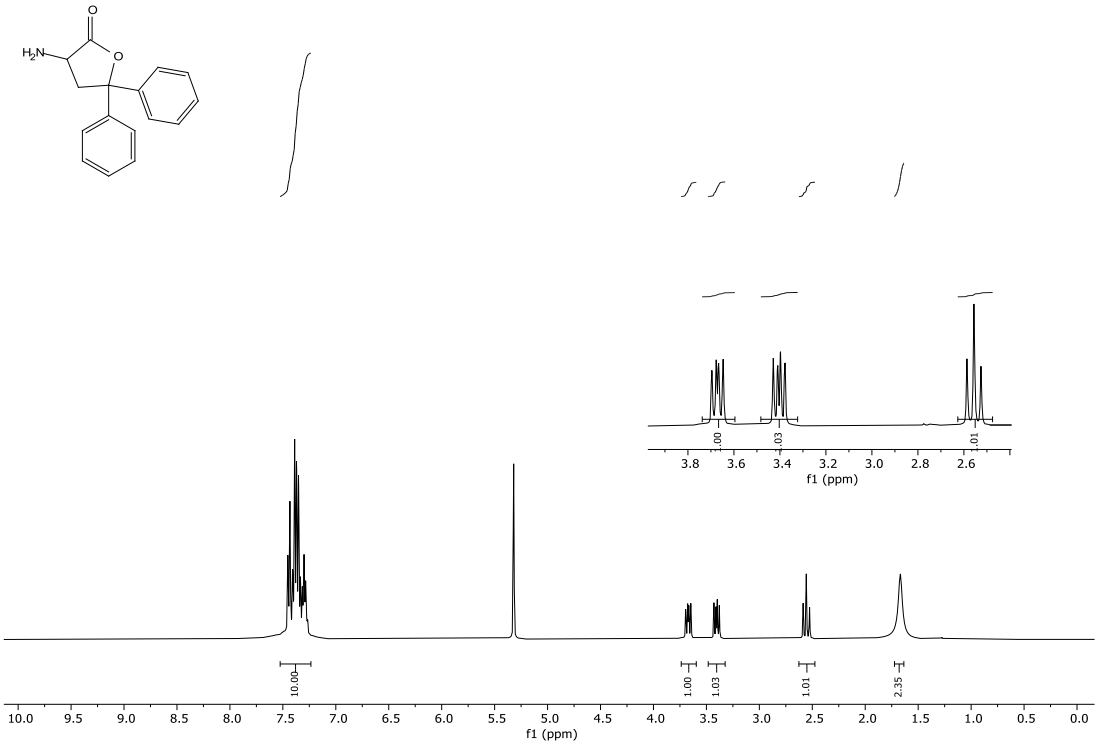
^{1}H NMR spectrum for **6p**



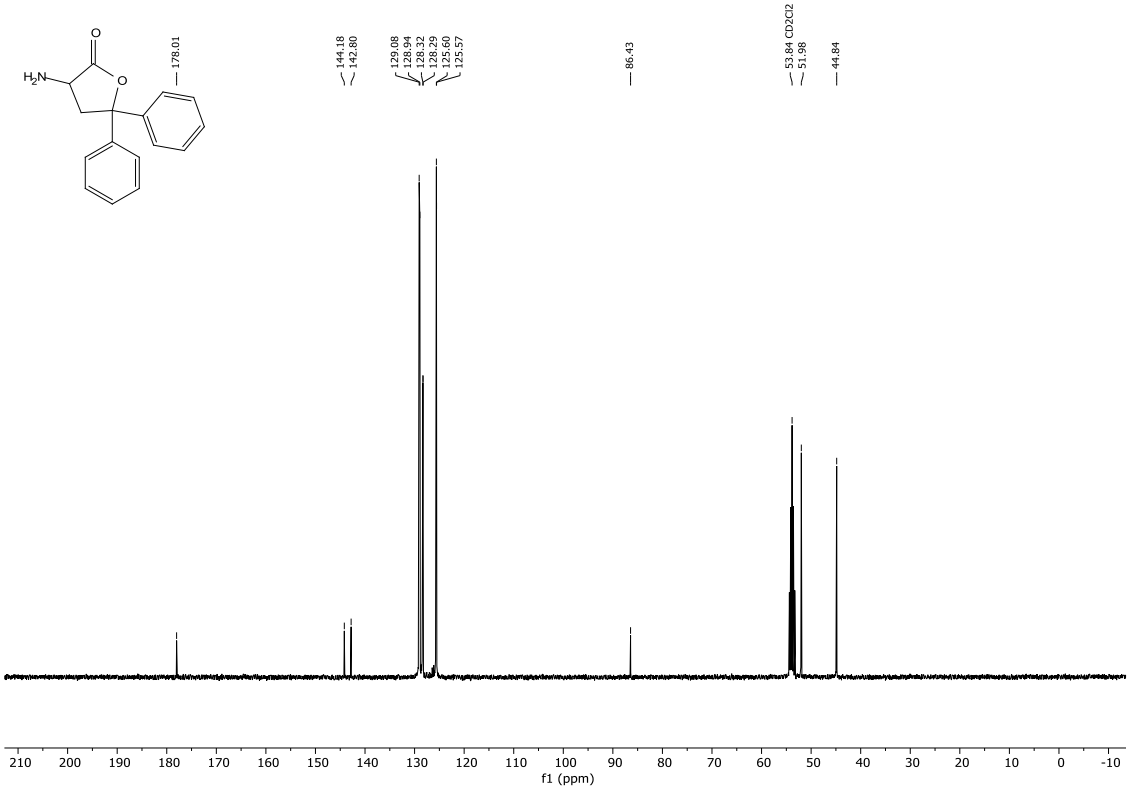
^{13}C NMR spectrum for **6p**



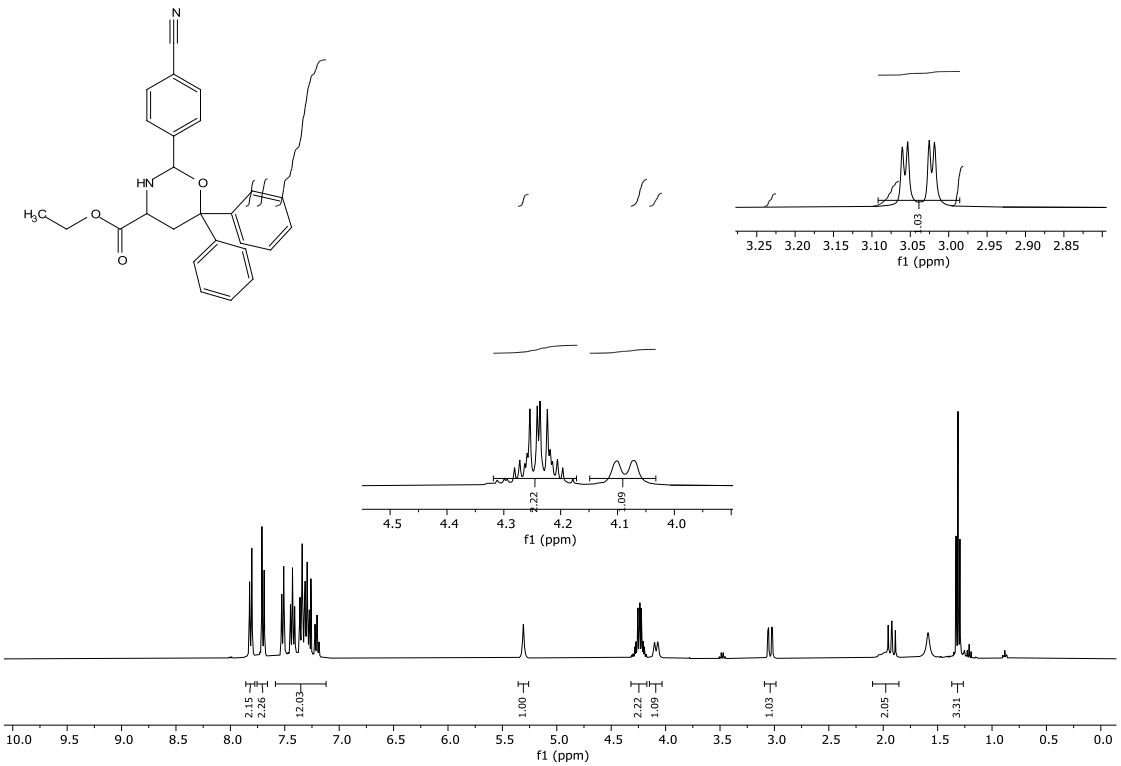
^{1}H NMR spectrum for **7a**



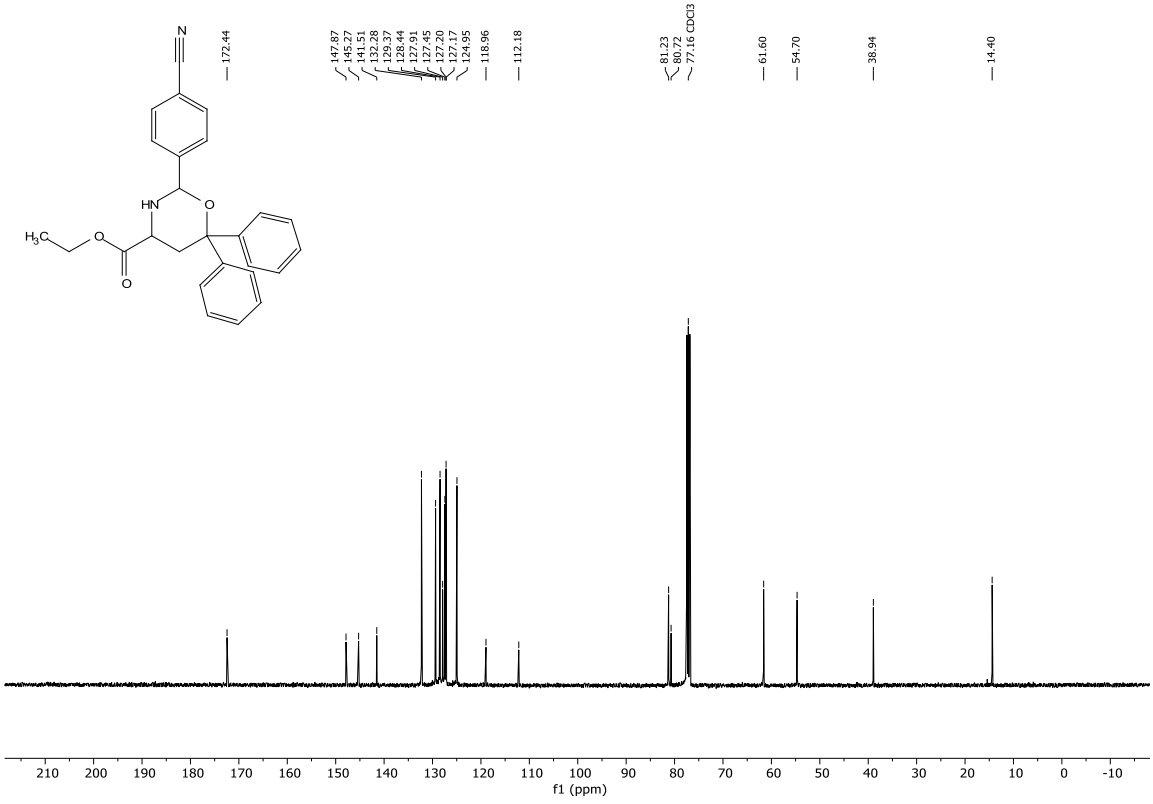
^{13}C NMR spectrum for **7a**



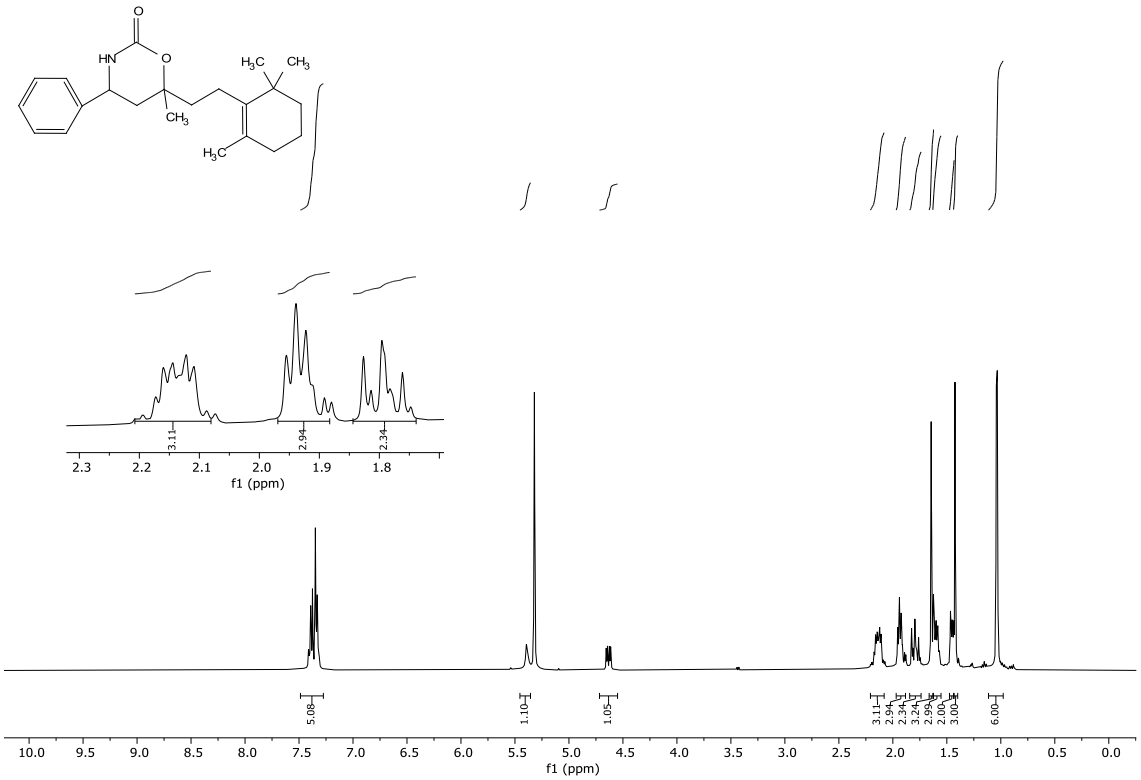
^{1}H NMR spectrum for **7b**



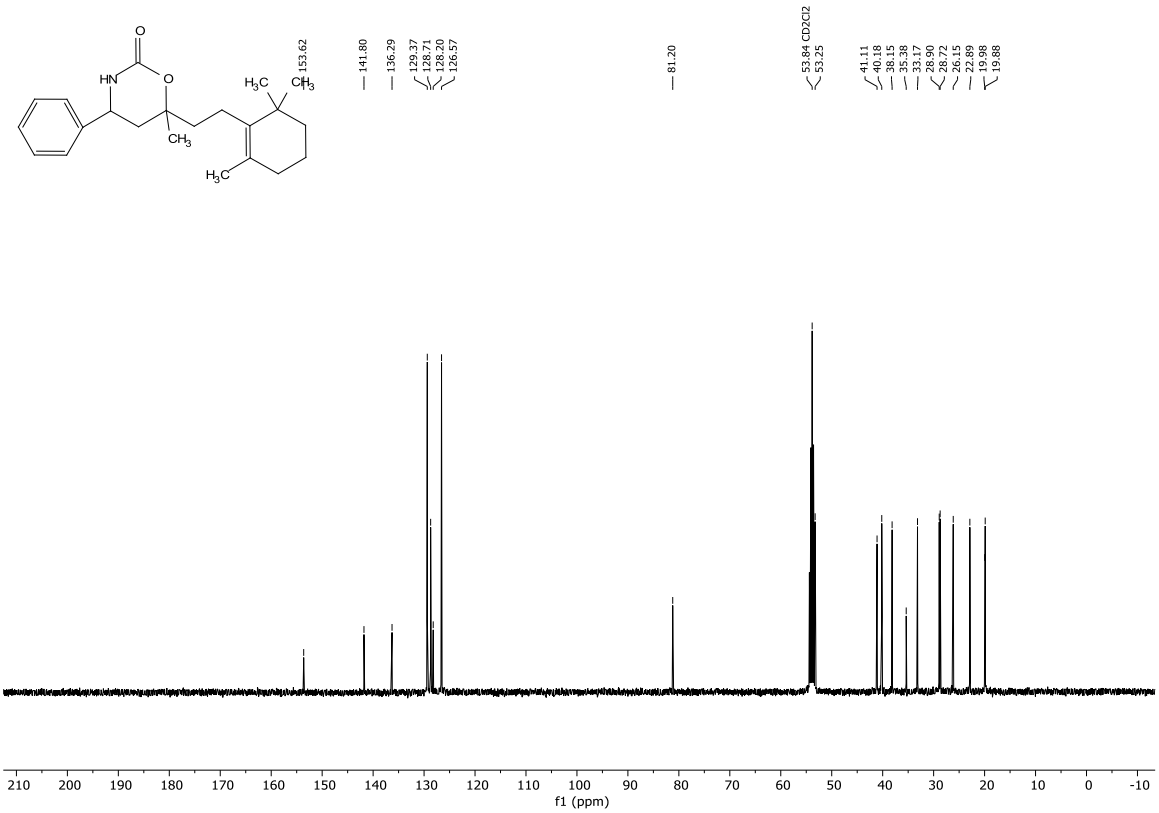
^{13}C NMR spectrum for **7b**



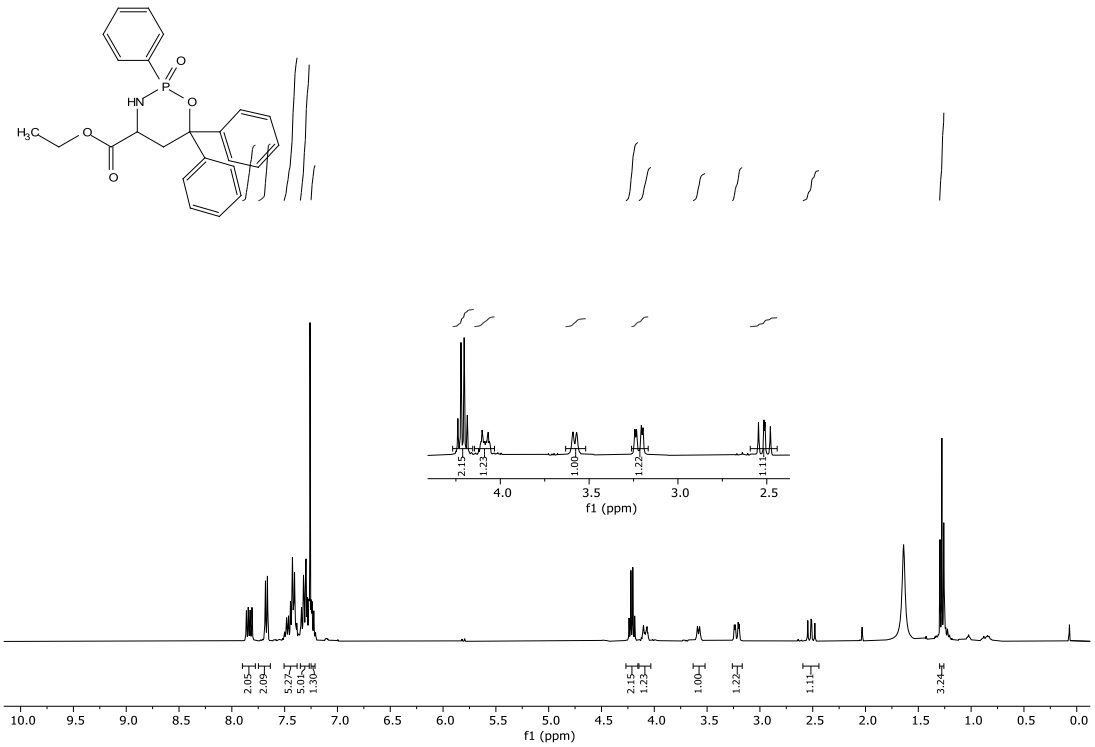
^{1}H NMR spectrum for **7c**



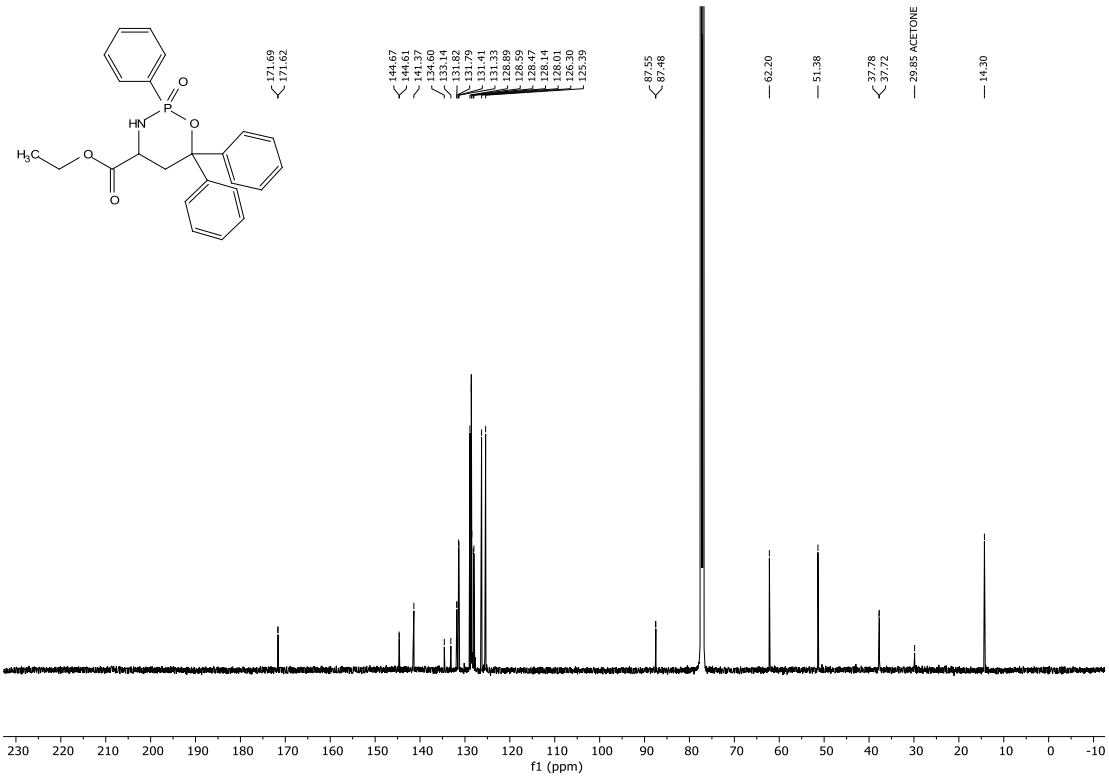
^{13}C NMR spectrum for **7c**



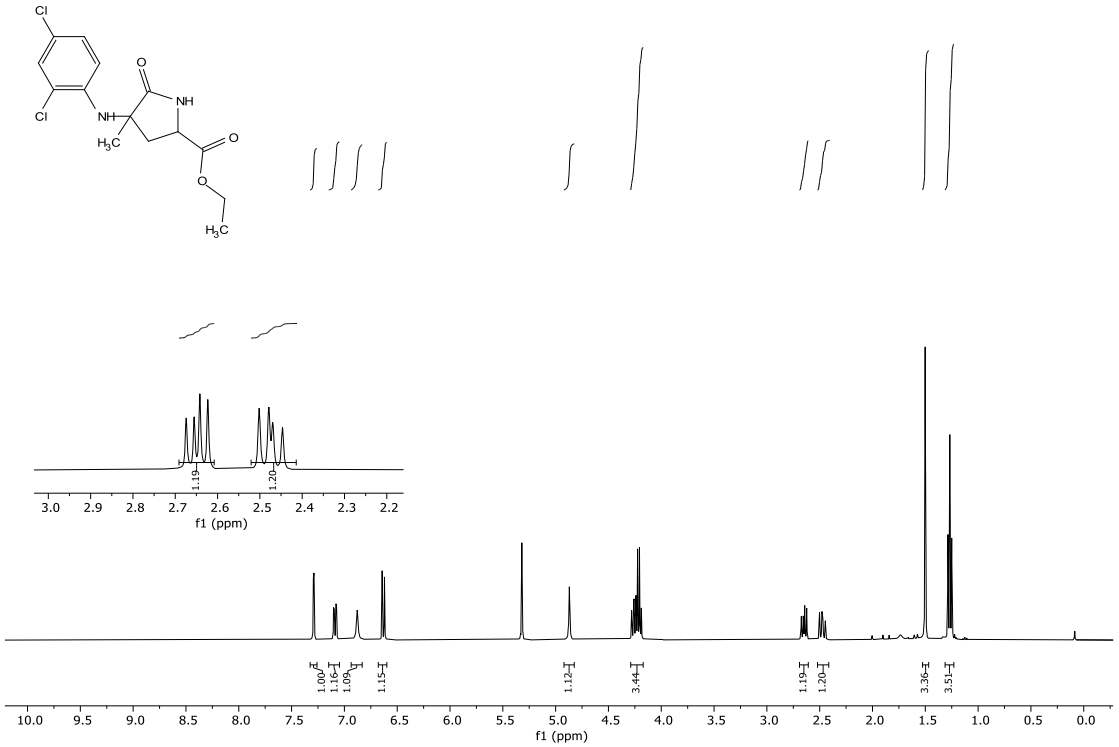
^{1}H NMR spectrum for **7d**



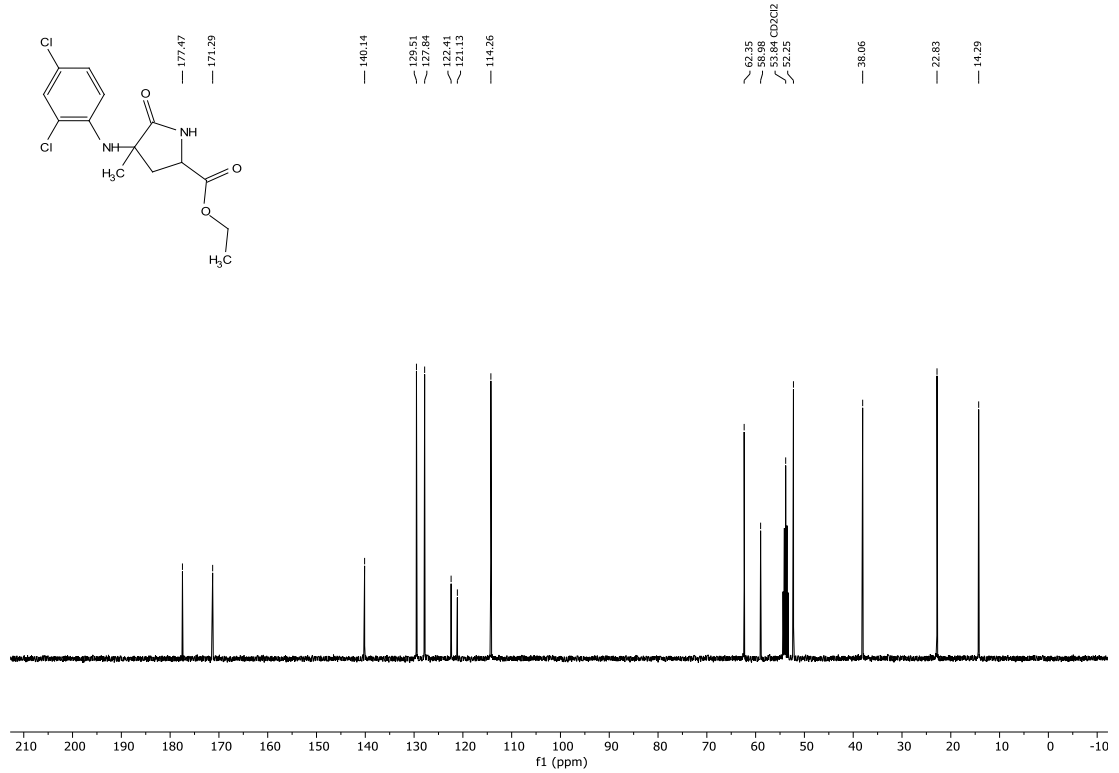
^{13}C NMR spectrum for **7d**



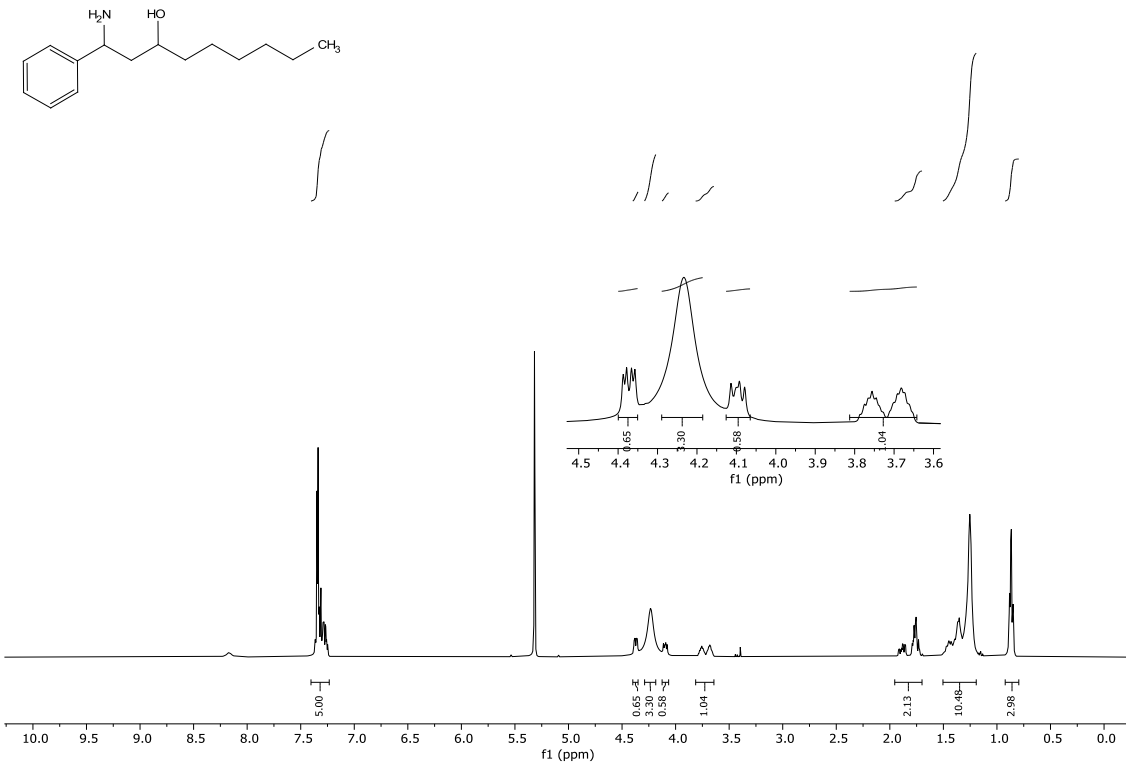
^{1}H NMR spectrum for **7e**



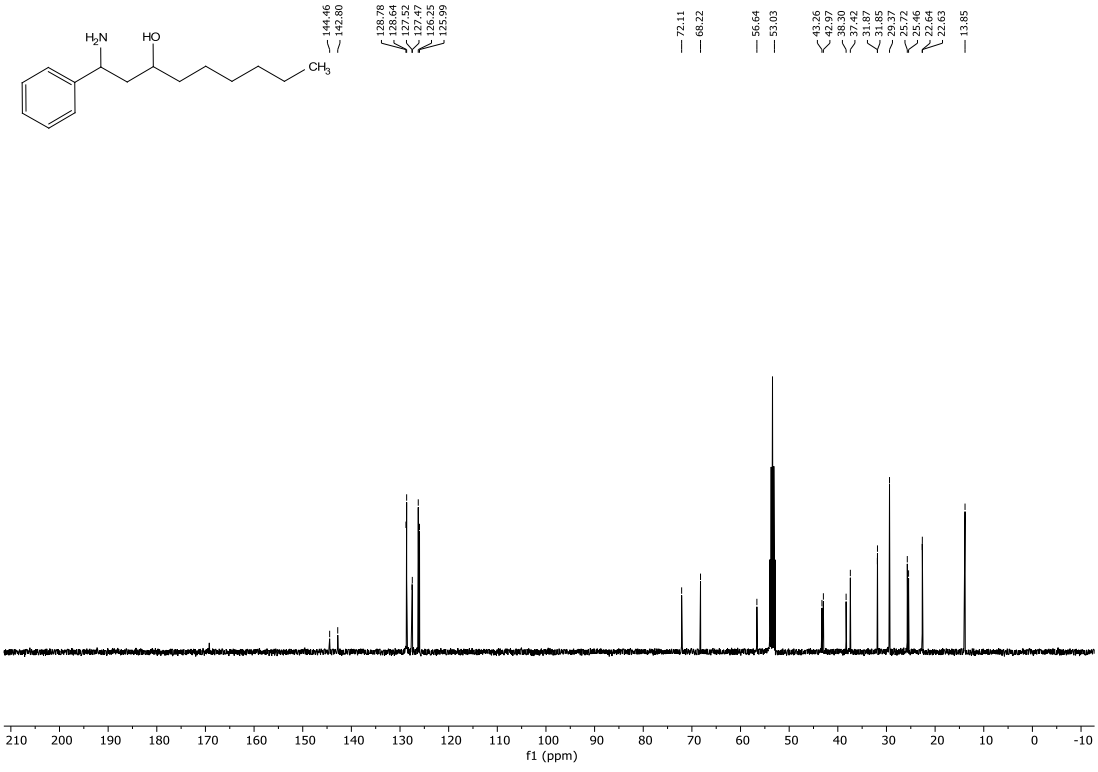
^{13}C NMR spectrum for **7e**



^{1}H NMR spectrum for **4q**



^{13}C NMR spectrum for **4q**



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