Table of Content:

Full lists of authors for references 5 and 7:

[5] M. Gallant, C. Beaulieu, C. Berthelette, J. Colucci, M. A. Crackower, C. Dalton, D. Denis, Y. Ducharme, R. W. Friesen, D. Guay, F. G. Gervais, M. Hamel, R. Houle C. M. Krawczyk, B. Kosjek, S. Lau, Y. Leblanc, E. E. Lee, J.-F. Levesque, C. Mellon, C. Molinaro, W. Mullet, G. P. O'Neill, P. O'Shea, N. Sawyer, S. Sillaots, D. Simard, D. Slipetz, R. Stocco, D. Sørensen, V. L. Truong, E. Wong, J. Wu, H. Zaghdane, Z. Wang, *Bioorg. Med. Chem. Lett.*, **2011**, *21*, 288–293.

[7] R. Snoeck, G. Andrei, B. Bodaghi, L. Lagneaux, D. Daelemans, E. de Clercq, J. Neyts, D. Schols, L. Naesens, S. Michelson, D. Bron, M. J. Otto, A. Bousseau, C. Nemecek, C. Roy, *Antiviral Res.* **2002**, *55*, 413−424.

General Methods

Experimental Procedures, Reagents and Glassware

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. Toluene, THF and Et_2O were purified by an Innovative Technology Solvent Delivery System. Chemicals were used as obtained from the suppliers unless otherwise stated. Solvent compositions are given in (v/v).

Chromatography

Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were visualised under UV-light at 254 nm.

NMR Spectroscopy

Proton nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker AVANCEIII-400 spectrometer, 500 MHz on a AVANCENEO-500, 600 MHz on a Bruker DRX-600 or at 800 MHz on a AVANCEII-800 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm). Proton decoupled Carbon-13 nuclear magnetic resonance (^{13}C{^{1}H}NMR) data were acquired at 101 MHz on a Bruker AVANCEIII-400 spectrometer, 126 MHz on a AVANCENEO-500, 151 MHz on a Bruker DRX-600 or at 201 MHz on a AVANCEII-800 spectrometer. Chemical shifts are reported in ppm relative to residual chloroform (77.16 ppm). The assignment of proton and carbon signals was assisted by COSY, HSQC, HMBC and DEPT-135 experiments where necessary. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; hept, heptet; dd, doublet of doublets; dt, doublet of triplets; ddd, doublet of doublets of doublets; tt, triplet of triplets; tq, triplet of quartets; qt, quartet of triplets; m, multiplet. All NMR data were recorded at 298 K.

Infrared Spectroscopy

Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}).

Mass Spectrometry

HRMS measurements were performed on an Agilent LC-MS TOF (Multimode: ESI + APCI) or Waters Xevo G2-S QTOF (APPI or APCI). High resolution mass are given in *m/z*.

Melting Points

Melting points were measured on a Büchi B-540 and are uncorrected.

Enantiomeric excesses

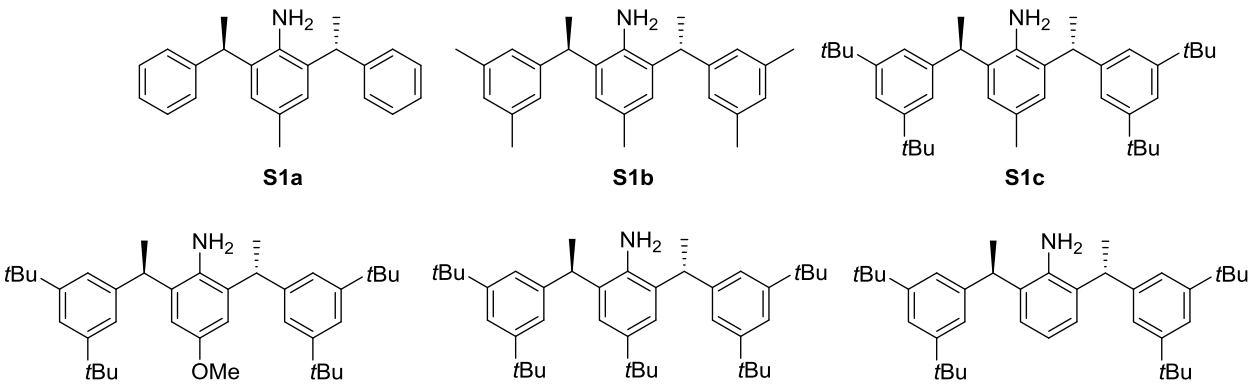
Enantiomeric excesses were measured on an Agilent or Waters HPLC, or on a Thar SFC Investigator system using chiral stationary phase columns. Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter.

X-Ray analyses

X-ray analysis of compounds **2a** and **L8**•HCl was performed by Dr. R. Scopelliti and Dr. F. Fadaei Tirani at the EPF Lausanne.

General Procedure for the Synthesis of Ligands L5 and L7 - L11 (GP1)

Chiral Anilines S1a – S1f

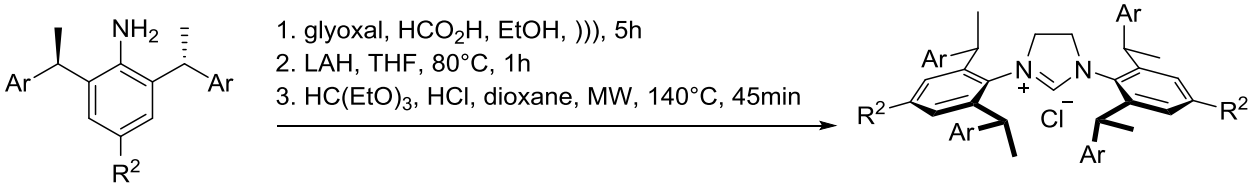


S1a **S1b** **S1c**

S1d **S1e** **S1f**

Ligands **L1- L4, L6** and chiral anilines **S1** were obtained as described previously:
J. Diesel, A. Finogenova, N. Cramer, *J. Am. Chem. Soc.* **2018**, *140*, 4489–4493.

General Procedure for the Preparation of the Imidazolium Salts (GP1)



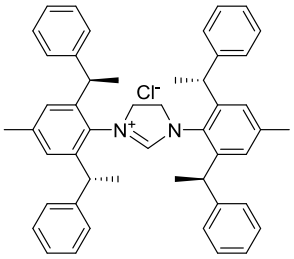
S1 **L5•HCl , L7-L11•HCl**

Aniline **S1** (1.0 eq) was suspended in EtOH (1 M) and a 40% solution of glyoxal (0.5 eq) in water, and catalytic amounts of formic acid (0.1 eq) were added. The mixture was sonicated for 5h and subsequently the crude solid was coevaporated with THF. The crude product was dissolved in THF (0.15 M), cooled to 0 °C and $LiAlH_4$ (2 eq) was added. The mixture was allowed to warm to ambient temperature and stirred for 1 h at 80°C. Subsequently the reaction mixture was quenched at 0°C with 10% aq NaOH and extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was dissolved in dioxane (0.5 M) inside a microwave vial and triethyl orthoformate (1.15 eq) was added. To this mixture a 4 M solution of HCl (1.15 eq) in dioxane was added. The vial was sealed and heated for 45 min at 140 °C inside the microwave reactor. The reaction mixture was

filtered to yield the crude imidazolium salt as off white powder. The crude solid was recrystallized two times from dioxane to yield the ligands **L** as white powder.

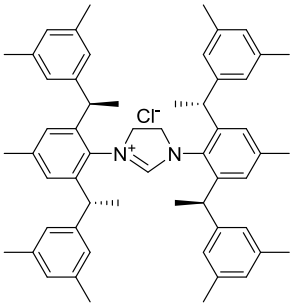
Characterization Data for Imidazolium Salts of Ligands L5 and L7 - L11

1,3-bis(4-methyl-2,6-bis((*R*)-1-phenylethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**L5**•HCl):



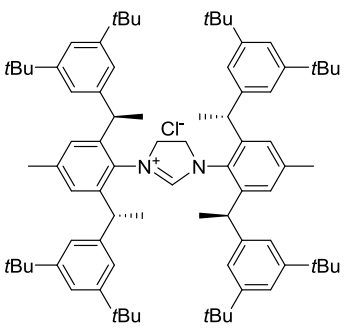
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.31 (s, 1H), 7.37 (d, *J* = 6.8 Hz, 8 H), 7.22 – 7.09 (m, 10 H), 6.94 – 6.90 (m, 6 H), 4.36 (q, *J* = 7.1 Hz, 2 H), 4.25 (q, *J* = 6.9 Hz, 2 H), 3.70 – 3.60 (m, 2 H), 3.08 – 2.97 (m, 2 H), 2.34 (s, 6 H), 1.73 (d, *J* = 7.5 Hz, 6 H), 1.44 (d, *J* = 6.9 Hz, 1 H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 161.9, 146.1, 143.9, 143.8, 142.1, 141.0, 129.4, 129.1, 128.8, 128.4, 128.1, 127.6, 127.4, 126.7, 126.7, 52.9, 40.1, 38.4, 23.3, 21.7 ppm; **IR (ATR):** $\tilde{\nu}$ 3333, 3058, 3026, 2969, 2932, 2874, 2790, 2626, 2189, 2175, 2158, 1617, 1493, 1446, 1378, 1265, 1211, 1187, 1061, 1029, 1014, 985, 928,911, 864, 756, 729, 701, 638, 582, 560. cm^{-1}; **HRMS (ESI)** calculated for $[C_{49}H_{51}N_2]^+$: 667.4047, found: 667.4055; **$[\alpha]_D^{20}$:** 132.1° (c = 0.1, CH_2Cl_2). **m.p.:** 258-260 °C.

1,3-bis(2,6-bis((*R*)-1-(3,5-dimethylphenyl)ethyl)-4-methylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**L7**•HCl):



^{1}H NMR (600 MHz, $CDCl_3$) δ = 10.83 (s, 1 H), 7.14 (s, 2 H), 7.02 (s, 4 H), 6.93 (s, 2 H), 6.86 (s, 2 H), 6.78 (s, 2 H), 6.48 (s, 4 H), 4.26 (s, 2 H), 4.07 (s, 2 H), 3.72 (d, *J* = 15.0 Hz, 2 H), 3.25 (s, 2 H), 2.34 (d, *J* = 7.5 Hz, 12 H), 2.20 (s, 12 H), 1.73 (s, 6 H), 1.41 (s, 6 H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 162.7, 146.2, 144.4, 143.4, 142.2, 141.0, 138.6, 138.3, 129.0, 128.6, 128.5, 128.4, 128.0, 125.4, 125.0, 53.5, 40.2, 38.3, 23.2, 22.2, 21.9, 21.6, 21.5 ppm; **IR (ATR):** $\tilde{\nu}$ 2968, 2917, 2873, 2733, 1617, 1462, 1377, 1263, 1038, 924, 863, 848, 726, 708 cm^{-1}; **HRMS (ESI)** calculated for $[C_{57}H_{67}N_2]^+$: 779.5299, found: 779.5202; **$[\alpha]_D^{20}$:** 145.1° (c = 0.1, CH_2Cl_2). **m.p.:** 254-256 °C.

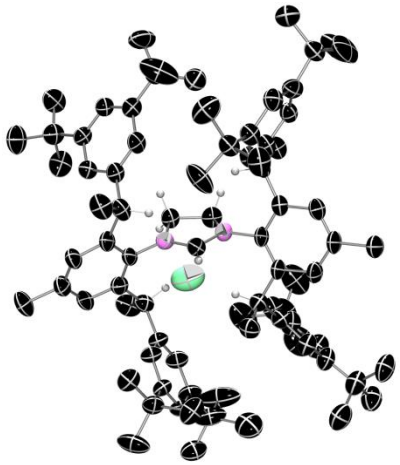
1,3-bis(2,6-bis((*R*)-1-(3,5-di-*tert*-butylphenyl)ethyl)-4-methylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**L8**•HCl):



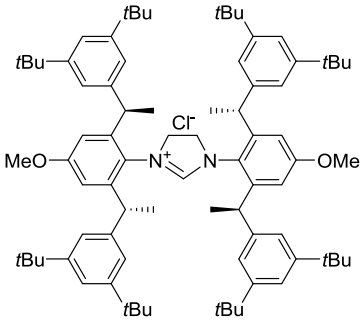
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.24 (s, 1 H), 7.26 (s, 4 H), 7.01 (s, 4 H), 6.90 (s, 8 H), 4.42 (d, *J* = 13.8 Hz, 2 H), 4.40 – 4.30 (m, 2 H),

4.18 (s, 2 H), 3.85 (q, J = 6.9 Hz, 2 H), 2.29 (s, 6 H), 1.81 (d, *J* = 6.9 Hz, 6 H), 1.28 (s, 36 H), 1.17 (s, 36 H), 1.03 (d, *J* = 7.0 Hz, 6 H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 158.5, 151.2, 151.0, 144.0, 143.7, 143.3, 143.2, 141.4, 128.6, 128.3, 128.0, 121.7, 121.1, 120.8, 120.8, 54.3, 40.4, 38.6, 34.9, 34.9, 31.5, 31.5, 23.2, 22.9, 21.7 ppm; **IR (ATR):** $\tilde{\nu}$ 2961, 2904, 2867, 2176, 1635, 1617, 1595, 1460, 1393, 1362, 1248, 1202, 989, 923, 908, 873, 727, 637, 541 cm^{-1}; **HRMS (ESI)** calculated for $[C_{49}H_{51}N_2]^+$: 1115.9055, found: 1115.9085; **$[\alpha]_D^{20}$:** 115.5° (c = 0.1, CH_2Cl_2). **m.p.:** 274-276 °C.

L8•HCl was crystallised by slow evaporation from dioxane and its absolute configuration assigned by X-ray crystallography as *(R;R;R;R).*

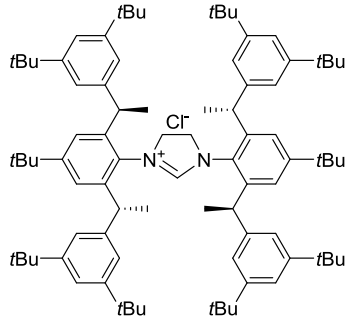


1,3-bis(2,6-bis((*R*)-1-(3,5-di-*tert*-butylphenyl)ethyl)-4-methoxyphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**L9**•HCl):



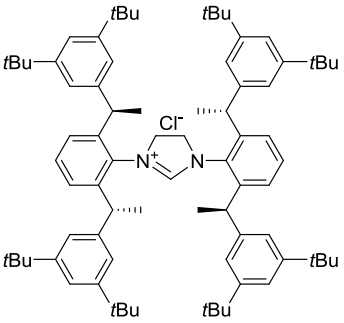
^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.32 (s, 1H), 7.26 (dq, *J* = 3.4, 1.7 Hz, 4 H), 6.96 – 6.91 (m, 8 H), 6.73 (d, *J* = 2.8 Hz, 2 H), 6.67 (d, *J* = 2.8 Hz, 2 H), 4.43 (d, *J* = 8.9 Hz, 2 H), 4.40 (t, *J* = 7.1 Hz, 2 H), 4.19 (s, 2 H), 3.88 (q, *J* = 7.0 Hz, 2 H), 3.69 (s, 6 H), 1.81 (d, *J* = 7.0 Hz, 6 H), 1.28 (s, 36 H), 1.17 (s, 36 H), 1.04 (d, *J* = 7.0 Hz, 6 H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 160.9, 159.2, 151.3, 151.0, 146.0, 145.8, 143.0, 142.9, 129.0, 128.2, 125.3, 123.7, 121.7, 121.2, 120.9, 120.8, 113.4, 112.4, 55.4, 54.3, 40.6, 39.0, 34.9, 34.9, 31.5, 31.5, 23.2, 23.1 ppm; **IR (ATR):** $\tilde{\nu}$ 2960, 2904, 2868, 2178, 1632, 1612, 1596, 1464, 1438, 1393, 1362, 1325,1248, 1205, 1149, 1042, 997, 925, 910, 874, 855, 804, 729, 637, 597 cm^{-1}; **HRMS (ESI)** calculated for $[C_{49}H_{51}N_2]^+$: 1147.8953, found: 1147.8959; **$[\alpha]_D^{20}$:** 171.3° (c = 0.1, CH_2Cl_2). **m.p.:** 247-248 °C.

1,3-bis(4-(*tert*-butyl)-2,6-bis((*R*)-1-(3,5-di-*tert*-butylphenyl)ethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**L10**•HCl):



^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.30 – 7.27 (m, 4 H), 7.21 (d, *J* = 1.7 Hz, 2 H), 6.96 (d, *J* = 1.8 Hz, 4 H), 6.86 (d, *J* = 1.7 Hz, 4 H), 4.50 (d, *J* = 11.9 Hz, 2 H), 4.44 (q, *J* = 7.1 Hz, 2 H), 4.31 – 4.22 (m, 2 H), 3.95 (q, *J* = 7.0 Hz, 2 H), 1.83 (d, *J* = 7.1 Hz, 6 H), 1.28 (s, 36 H), 1.21 (s, 18 H), 1.12 (s, 36 H), 1.08 (d, *J* = 7.1 Hz, 6 H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 158.2, 154.1, 151.2, 150.9, 143.5, 143.3, 143.2, 143.0, 128.3, 124.9, 124.5, 121.6, 121.2, 120.8, 120.7, 54.4, 40.7, 39.2, 35.1, 34.9, 34.8, 31.5, 31.4, 31.1, 23.5, 23.3 ppm; **IR (ATR):** $\tilde{\nu}$ 3068, 2961, 2904, 2868, 2161, 1634, 1616, 1596, 1477, 1460, 1393, 1362, 1248, 1200, 923, 898, 874, 728 cm^{-1}; **HRMS (ESI)** calculated for $[C_{49}H_{51}N_2]^+$: 1199.9994, found: 1199.9999; **$[\alpha]_D^{20}$:** 131.1° (c = 0.1, CH_2Cl_2). **m.p.:** 240-242 °C.

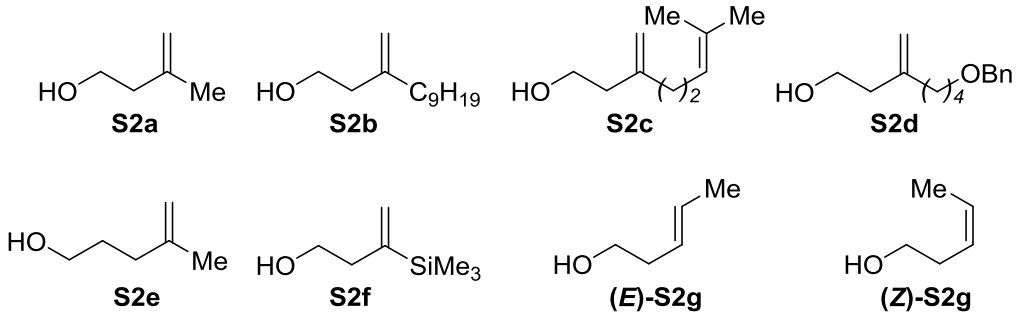
1,3-bis(2,6-bis((*R*)-1-(3,5-di-*tert*-butylphenyl)ethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**L11**•HCl):



^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.51 (s, 1H), 7.44 (t, J = 7.8 Hz, 3H), 7.21 (dt, J = 12.3, 5.9 Hz, 6H), 6.93 – 6.89 (m, 11H), 4.50 (d, J = 11.3 Hz, 2H), 4.45 (q, J = 7.0 Hz, 2H), 4.30 (d, J = 11.8 Hz, 2H), 3.97 (q, J = 7.0 Hz, 2H), 1.83 (d, J = 6.9 Hz, 6H), 1.27 (s, 36H), 1.23 (d, J = 4.7 Hz, 6H), 1.17 (s, 36H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 158.5, 151.3, 151.0, 144.5, 144.2, 143.3, 143.1, 131.3, 130.8, 128.1, 127.4, 121.7, 121.3, 120.9, 120.8, 54.4, 40.4, 38.8, 34.9, 34.9, 31.5, 31.5, 23.2, 23.0 ppm; **IR (ATR):** $\tilde{\nu}$ 2961, 2904, 2867, 2176, 1614, 1595, 1475, 1459, 1393, 1362, 1298, 1248, 1200, 1064, 988, 908, 873, 812, 758, 727, 637 cm^{-1}; **HRMS (ESI)** calculated for $[C_{49}H_{51}N_2]^+$: 1087.8742, found: 1087.8748; **$[\alpha]_D^{20}$:** 222.3° (c = 0.1, CH_2Cl_2). **m.p.:** 222-224 °C.

General Procedures for the Synthesis of Indoles 1a-1s and Pyrolles 3a-3f

Unsaturated Alcohols S2a-S2h



S2a is commercially available (CAS#: 763-32-6); other alcohols were synthesized following literature procedures:

S2b-S2d: K. H. Yong, J. A. Lotoski, J. M. Chong, *J. Org. Chem.* **2001**, *66*, 8248-8251.

S2e: P. A. Clarke, M. Grist, M. Ebden, C. Wilson, A. J. Blake, *Tetrahedron* **2005**, *61*, 353-363.

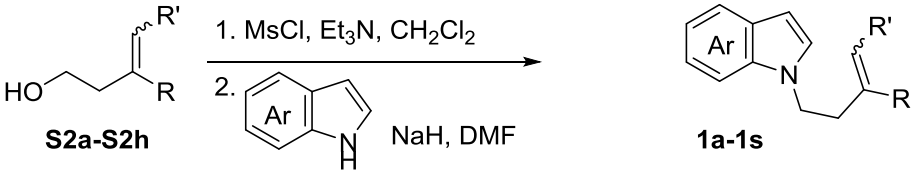
S2f: I. M. Dawson, J. A. Gregory, R. B. Herbert, P. G. Sammes, *J. Chem. Soc., Chem. Commun.* **1986**, 620-621.

(*E*)-S2g: W.-Y. Kim, B. G. Kim, T. Kang, H.-Y. Lee, *Chem. Asian J.* **2011**, *6*, 1931-1935.

(*Z*)-S2g: L. C. Morrill, S. M. Smith, A. M. Z. Slawin, A. D. Smith, *J. Org. Chem.* **2014**, *79*, 1640-1655.

S2h: H. M. C. Ferraz, L. S. Longo, *J. Org. Chem.* **2002**, *67*, 3518-3521.

General Procedure for the Alkylation of Indoles (GP2)

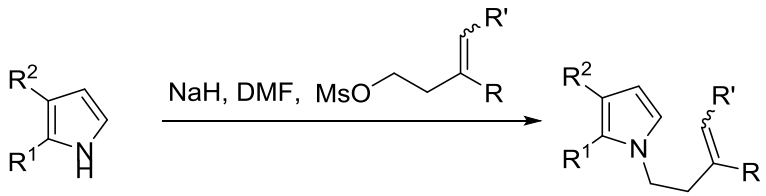


To a solution of the corresponding alcohol (5.00 mmol, 1.0 eq) and Et_3N (658 mg, 6.50 mmol, 1.3 eq) in CH_2Cl_2 (10 mL) was added MsCl (0.41 mL, 5.25 mmol, 1.05 eq) at 0 °C. The reaction mixture was allowed to warm to ambient temperature overnight and then was diluted with CH_2Cl_2, washed with 1M HCl, saturated aqueous $NaHCO_3$, brine and dried over Na_2SO_4. The resulting solution was concentrated under reduced pressure to afford the crude mesylate that was used in the next step without further purification.

To a suspension of NaH (60% in mineral oil; 112 mg, 2.8 mmol, 1.4 eq) in DMF (4.0 mL) was added the corresponding indole (2 mmol, 1.0 eq) in one portion at 0 °C. The resulting mixture

was heated to 50 °C, kept at this temperature for 30 min and then cooled to 0 °C. A solution of the mesylate (2.2 mmol, 1.1 eq) in DMF (0.5 mL) was added, and the resulting mixture was allowed to warm to ambient temperature overnight. Then, the reaction was quenched by addition of water, and the aqueous phase was extracted with EtOAc (*3). The combined organic extracts were washed with water (*5), brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluting with mixtures of pentane:EtOAc or pentane:Et_2O).

General Procedure for the Alkylation of Pyrroles (GP3)



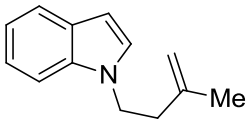
S3a ($R^1 = CO_2Me$, $R^2 = H$)
S3b ($R^1 = H$, $R^2 = CO_2Me$)

3a-3f

To a suspension of NaH (60% in oil; 48.0 mg, 1.2 mmol, 1.2 eq) in DMF (0.8 mL) was added a solution of the corresponding pyrrole (1 mmol, 1.0 eq) in DMF (0.8 mL) at 0 °C. The resulting mixture was warmed to room temperature, kept stirring for 30 min and then cooled to 0 °C. A solution of the corresponding mesylate (1.2 mmol, 1.2 eq) in DMF (0.4 mL) was added, and the resulting mixture was allowed to warm to ambient temperature overnight. Then, the reaction was quenched by addition of water, and the aqueous phase was extracted with EtOAc (*3). The combined organic extracts were washed with water (*5), brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluting with mixtures of pentane:EtOAc or pentane:Et_2O).

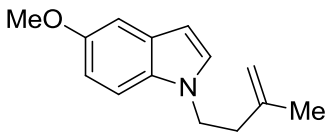
Characterization Data for Indoles 1a-1s and Pyrroles 3a-3f

1-(3-Methylbut-3-en-1-yl)-1*H*-indole (**1a**):



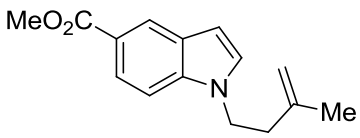
Yield: 48%; **appearance**: yellow oil; R_f: 0.2 (pentane:EtOAc, 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 (dt, *J* = 7.9, 1.0 Hz, 1 H), 7.36 (d, *J* = 8.2 Hz, 1 H), 7.21 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1 H), 7.14–7.05 (m, 2 H), 6.48 (dd, *J* = 3.2, 0.8 Hz, 1 H), 4.83–4.81 (m, 1 H), 4.73–4.71 (m, 1 H), 4.30–4.19 (m, 2 H), 2.54 (td, *J* = 7.4, 1.1 Hz, 2 H), 1.78 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 142.5, 135.9, 128.7, 127.8, 121.5, 121.1, 119.4, 112.6, 109.4, 101.2, 45.2, 38.3, 22.7 ppm; **IR (ATR):** $\tilde{\nu}$ = 3073, 3054, 2967, 2935, 1650, 1612, 1512, 1463, 1315, 1176, 891, 738, 715, 425 cm^{-1}; **HRMS (APPI)** calculated for $[C_{13}H_{15}N+H]^+$ 186.1277, found 186.1273.

5-Methoxy-1-(3-methylbut-3-en-1-yl)-1*H*-indole (**1b**):



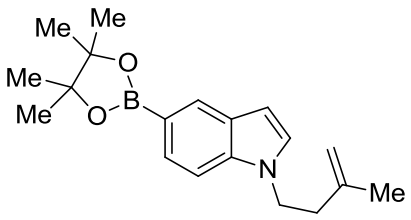
Yield: 35%; **appearance**: yellow oil; R_f: 0.25 (pentane:EtOAc, 40:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.9 Hz, 1 H), 7.08 (dd, *J* = 10.0, 2.8 Hz, 2 H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.40 (d, *J* = 3.1 Hz, 1 H), 4.86–4.79 (m, 1 H), 4.76–4.66 (m, 1 H), 4.29–4.15 (m, 2 H), 3.85 (s, 3 H), 2.59–2.43 (m, 2 H), 1.77 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 154.1, 142.5, 131.3, 129.0, 128.3, 112.6, 111.9, 110.1, 102.7, 100.7, 56.0, 45.4, 38.4, 22.7 ppm; **IR (ATR):** $\tilde{\nu}$ = 3075, 2936, 2831, 1649, 1621, 1576, 1488, 1450, 1362, 1238, 1150, 1033, 892, 797, 716, 433 cm^{-1}; **HRMS (APPI)** calculated for $[C_{14}H_{17}NO+H]^+$ 216.1383, found 216.1389.

Methyl 1-(3-methylbut-3-en-1-yl)-1*H*-indole-5-carboxylate (**1c**):



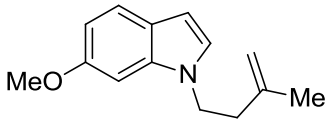
Yield: 28%; **appearance**: colorless oil; R_f: 0.35 (pentane:Et_2O, 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 1.1 Hz, 1 H), 7.92 (dd, *J* = 8.7, 1.6 Hz, 1 H), 7.35 (d, *J* = 8.7 Hz, 1 H), 7.15 (d, *J* = 3.2 Hz, 1 H), 6.62–6.55 (m, 1 H), 4.81 (s, 1 H), 4.69 (s, 1 H), 4.29–4.22 (m, 2 H), 3.93 (s, 3 H), 2.53 (t, *J* = 7.4 Hz, 2 H), 1.77 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 168.4, 142.0, 138.4, 129.2, 128.2, 124.2, 123.0, 121.5, 112.9, 109.0, 102.9, 52.0, 45.4, 38.2, 22.6 ppm; **IR (ATR):** $\tilde{\nu}$ = 3077, 2948, 1709, 1612, 1450, 1434, 1347, 1309, 1258, 1193, 1098, 1085, 897, 753, 411 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{15}H_{17}NO_2 + H]^+$ 244.1332, found 244.1340.

1-(3-Methylbut-3-en-1-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**1d**):



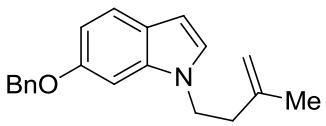
Yield: 9%; **appearance**: colorless oil; R_f: 0.3 (pentane:Et_2O, 99:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 1.0 Hz, 1 H), 7.65 (dd, *J* = 8.3, 1.1 Hz, 1 H), 7.34 (d, *J* = 8.3 Hz, 1 H), 7.10–7.05 (m, 1 H), 6.49 (dd, *J* = 3.2, 0.8 Hz, 1 H), 4.80 (p, *J* = 1.6 Hz, 1 H), 4.69 (dt, *J* = 2.0, 1.0 Hz, 1 H), 4.29–4.20 (m, 2 H), 2.52 (t, *J* = 7.5 Hz, 2 H), 1.76 (s, 3 H), 1.36 (s, 12 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 142.4, 137.9, 129.1, 128.5, 127.9, 127.6, 112.6, 108.8, 102.0, 83.5 (2 C), 45.2, 38.3, 25.1 (4 C), 22.7 ppm; **IR (ATR):** $\tilde{\nu}$ = 2977, 2934, 1609, 1515, 1439, 1369, 1350, 1303, 1269, 1192, 1139, 1070, 964, 858, 722, 683 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{19}H_{26}BNO_2 + H]^+$ 312.2129, found 312.2137.

6-Methoxy-1-(3-methylbut-3-en-1-yl)-1*H*-indole (**1e**):



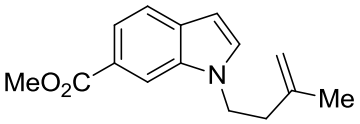
Yield: 45%; **appearance**: colorless oil; R_f: 0.35 (pentane:Et_2O, 40:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.5 Hz, 1 H), 6.99 (d, *J* = 3.2 Hz, 1 H), 6.84–6.75 (m, 2 H), 6.43–6.38 (m, 1 H), 4.82 (s, 1 H), 4.73 (s, 1 H), 4.18 (dd, *J* = 8.3, 6.9 Hz, 2 H), 3.88 (s, 3 H), 2.57–2.48 (m, 2 H), 1.78 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 156.3, 142.5, 136.7, 126.8, 123.1, 121.7, 112.5, 109.1, 101.1, 93.3, 55.9, 45.2, 38.1, 22.8 ppm; **IR (ATR):** $\tilde{\nu}$ = 3100, 3074, 2937, 2832, 1622, 1513, 1491, 1456, 1362, 1327, 1246, 1212, 1162, 1034, 809, 709, 615, 432 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{14}H_{17}NO + H]^+$ 216.1383, found 216.1395.

6-(Benzyloxy)-1-(3-methylbut-3-en-1-yl)-1*H*-indole (**1f**):



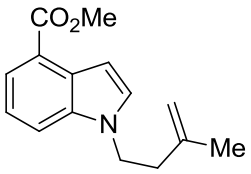
Yield: 32%; **appearance**: colorless oil; R_f: 0.2 (pentane:Et_2O, 40:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.54–7.45 (m, 3 H), 7.40 (ddt, *J* = 8.9, 6.1, 1.9 Hz, 2 H), 7.33 (tt, *J* = 7.5, 1.6 Hz, 1 H), 6.99 (t, *J* = 2.6 Hz, 1 H), 6.91–6.83 (m, 2 H), 6.42 (d, *J* = 3.2 Hz, 1 H), 5.15 (s, 2 H), 4.81 (p, *J* = 1.6 Hz, 1 H), 4.71 (s, 1 H), 4.21–4.09 (m, 2 H), 2.49 (t, *J* = 7.4 Hz, 2 H), 1.76 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 155.4, 142.5, 137.7, 136.6, 128.7 (2 C), 128.0, 127.7 (2 C), 127.0, 123.3, 121.6, 112.5, 109.8, 101.1, 94.9, 71.0, 45.2, 38.1, 22.7 ppm; **IR (ATR):** $\tilde{\nu}$ = 3066, 3031, 2966, 2934, 1622, 1573, 1513, 1488, 1454, 1325, 1219, 1025, 807, 697, 433 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{20}H_{21}NO + H]^+$ 292.1696, found 292.1703.

Methyl 1-(3-methylbut-3-en-1-yl)-1*H*-indole-6-carboxylate (**1g**):



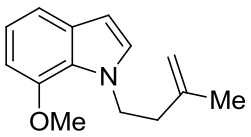
Yield: 42%; **appearance**: yellow oil; R_f: 0.25 (pentane:Et_2O, 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 7.79 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.31–7.23 (m, 2 H), 6.56–6.48 (m, 1 H), 4.85–4.78 (m, 1 H), 4.69 (s, 1 H), 4.35–4.25 (m, 2 H), 3.95 (s, 3 H), 2.55 (t, *J* = 7.5 Hz, 2 H), 1.78 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 168.4, 142.1, 135.3, 132.4, 131.1, 123.2, 120.7, 120.5, 112.9, 111.9, 101.6, 52.1, 45.3, 38.3, 22.7 ppm; **IR (ATR):** $\tilde{\nu}$ = 3076, 2968, 2948, 1615, 1504, 1434, 1353, 1323, 1271, 1231, 1108, 987, 890, 773, 726, 427 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{15}H_{17}NO_2 + H]^+$ 244.1332, found 244.1330.

Methyl 1-(3-methylbut-3-en-1-yl)-1*H*-indole-4-carboxylate (**1h**):



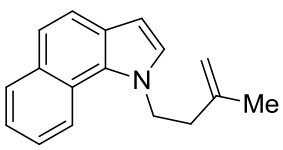
Yield: 43%; **appearance**: colorless oil; R_f: 0.25 (pentane:Et_2O, 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$): 7.90 (dd, *J* = 7.5, 0.9 Hz, 1 H), 7.56 (d, *J* = 8.2 Hz, 1 H), 7.29–7.22 (m, 2 H), 7.11 (dd, *J* = 3.2, 0.9 Hz, 1 H), 4.81 (p, *J* = 1.5 Hz, 1 H), 4.69 (dt, *J* = 1.9, 1.0 Hz, 1 H), 4.33–4.23 (m, 2 H), 3.98 (s, 3 H), 2.60–2.45 (m, 2 H), 1.77 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 168.2, 142.1, 136.8, 130.0, 128.2, 123.2, 121.8, 120.7, 114.2, 112.9, 102.5, 51.9, 45.4, 38.3, 22.7 ppm; **IR (ATR):** $\tilde{\nu}$ = 3065, 2952, 1713, 1619, 1444, 1421, 1359, 1312, 1263, 1184, 1101, 1076, 902, 745, 511 cm^{-1}; **HRMS (APPI)** calculated for $[C_{15}H_{17}NO_2 + H]^+$ 244.1332, found 244.1336.

7-Methoxy-1-(3-methylbut-3-en-1-yl)-1*H*-indole (**1i**):



Yield: 50%; **appearance**: colorless oil; R_f: 0.35 (pentane:Et_2O, 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 7.8 Hz, 1 H), 7.06–6.91 (m, 2 H), 6.63 (d, *J* = 7.7 Hz, 1 H), 6.42 (s, 1 H), 4.80 (s, 1 H), 4.72 (s, 1 H), 4.55–4.40 (m, 2 H), 3.95 (s, 3 H), 2.59–2.45 (m, 2 H), 1.79 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 147.6, 143.0, 131.1, 129.0, 125.6, 119.8, 113.9, 112.1, 102.3, 101.2, 55.4, 48.5, 40.7, 22.7 ppm; **IR (ATR):** $\tilde{\nu}$ = 3072, 2936, 2835, 1649, 1575, 1492, 1455, 1430, 1365, 1314, 1255, 1167, 1092, 1062, 971, 889, 780, 717, 685, 504 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{14}H_{17}NO + H]^+$ 216.1383, found 216.1389.

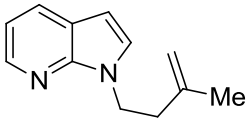
1-(3-Methylbut-3-en-1-yl)-1*H*-benzo[*g*]indole (**1j**):



Yield: 38%; **appearance**: white solid; **m.p.**: 82-83 °C; R_f: 0.4 (pentane:Et_2O, 80:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.30 (dd, *J* = 8.6,

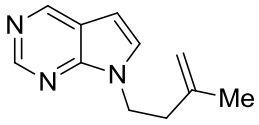
1.1 Hz, 1 H), 7.97 (dd, *J* = 8.1, 1.4 Hz, 1 H), 7.72 (d, *J* = 8.6 Hz, 1 H), 7.60–7.50 (m, 2 H), 7.45 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1 H), 7.12 (d, *J* = 3.0 Hz, 1 H), 6.62 (d, *J* = 3.0 Hz, 1 H), 4.91 (q, *J* = 1.6 Hz, 1 H), 4.81 (dd, *J* = 2.0, 1.1 Hz, 1 H), 4.74–4.64 (m, 2 H), 2.73–2.62 (m, 2 H), 1.84 (s, 3 H) ppm; **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$): δ = 142.3, 131.5, 129.6, 129.0, 128.5, 126.4, 125.5, 123.3, 123.0, 121.4, 121.2, 120.7, 112.6, 102.5, 49.3, 38.7, 23.0 ppm; **IR (ATR):** $\tilde{\nu}$ = 3071, 2965, 2930, 2853, 1649, 1505, 1438, 1367, 1312, 1144, 892, 804, 723, 687, 563, 422 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{17}H_{17}N + H]^+$ 236.1434, found 236.1434.

1-(3-Methylbut-3-en-1-yl)-1*H*-pyrrolo[2,3-*b*]pyridine (**1k**):



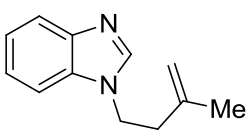
Yield: 55%; **appearance**: colorless oil; R_f: 0.25 (pentane:Et_2O, 10:1); **^1H NMR** (400 MHz, $CDCl_3$): δ = 8.25 (dd, *J* = 4.7, 1.4 Hz, 1 H), 7.82 (dd, *J* = 7.8, 1.4 Hz, 1 H), 7.14 (d, *J* = 3.5 Hz, 1 H), 6.97 (dd, *J* = 7.8, 4.7 Hz, 1 H), 6.36 (d, *J* = 3.5 Hz, 1 H), 4.69 (s, 1 H), 4.61 (s, 1 H), 4.42–4.27 (m, 2 H), 2.51 (t, *J* = 7.3 Hz, 2 H) ppm; **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$): δ = 147.4, 142.6, 142.5, 128.9, 128.1, 120.8, 115.7, 112.5, 99.5, 43.1, 38.4, 22.6 ppm; **IR (ATR):** $\tilde{\nu}$ = 3075, 3051, 2967, 2934, 1650, 1593, 1509, 1425, 1346, 1306, 1204, 892, 796, 772, 716, 483 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{12}H_{14}N_2 + H]^+$ 187.1230, found 187.1229.

7-(3-methylbut-3-en-1-yl)-7H-pyrrolo[2,3-*d*]pyrimidine (**1l**):



Yield: 40%; **appearance**: colorless oil; R_f: 0.25 (pentane:EtOAc, 1:1); **^1H NMR** (400 MHz, $CDCl_3$): δ = 8.94 (s, 1 H), 8.88 (s, 1 H), 7.22 (d, *J* = 3.5 Hz, 1 H), 6.54 (d, *J* = 3.6 Hz, 1 H), 4.75 (t, *J* = 1.6 Hz, 1 H), 4.64 (s, 1 H), 4.41 (t, *J* = 7.3 Hz, 2 H), 2.57 (t, *J* = 7.2 Hz, 2 H), 1.79 (s, 3 H) ppm; **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$): δ = 151.2, 150.5, 149.2, 141.8, 129.1, 119.0, 113.0, 99.6, 42.9, 38.3, 22.4. ppm; **IR (ATR):** $\tilde{\nu}$ = 3077, 3048, 2971, 2937, 1650, 1587, 1561, 1514, 1474, 1417, 1375, 1354, 1322, 1250, 1168, 1102, 899, 781, 727, 598 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{11}H_{13}N_3 + H]^+$ 188.1182, found: 188.1185.

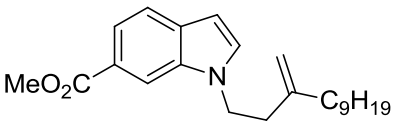
1-(3-Methylbut-3-en-1-yl)-1*H*-benzo[*d*]imidazole (**1m**):



Yield: 69%; **appearance**: yellow oil; R_f: 0.35 (EtOAc); **^1H NMR** (400 MHz, $CDCl_3$): δ = 7.90 (s, 1 H), 7.85–7.75 (m, 1 H), 7.46–7.38 (m, 1 H), 7.35–7.23 (m, 2 H), 4.83 (p, *J* = 1.6 Hz, 1 H), 4.65 (t, *J* = 1.3 Hz, 1 H), 4.28 (t, *J* =

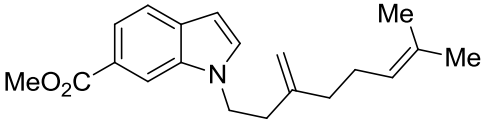
7.3 Hz, 2 H), 2.64–2.50 (m, 2 H), 1.83–1.72 (m, 3 H) ppm; **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ = 143.8, 143.0, 141.2, 133.7, 123.0, 122.3, 120.5, 113.5, 109.7, 43.7, 37.9, 22.5 ppm; **IR (ATR):** $\tilde{\nu}$ = 3410, 3075, 2970, 2935, 1650, 1615, 1495, 1458, 1366, 1330, 1286, 1260, 1201, 1170, 891, 742, 427 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{12}H_{14}N_2 + H]^+$ 187.1230, found 187.1236.

Methyl 1-(3-methylenedodecyl)-1*H*-indole-6-carboxylate (**1n**):



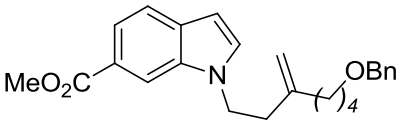
Yield: 23%; **appearance**: colorless oil; R_f: 0.35 (pentane:Et_2O, 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 7.79 (dd, *J* = 8.3, 1.3 Hz, 1 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.31–7.20 (m, 2 H), 6.51 (d, *J* = 3.3 Hz, 1 H), 4.87–4.78 (m, 1 H), 4.72 (s, 1 H), 4.30 (t, *J* = 7.5 Hz, 2 H), 3.95 (s, 3 H), 2.54 (t, *J* = 7.5 Hz, 2 H), 2.03 (t, *J* = 7.7 Hz, 2 H), 1.46–1.36 (m, 2 H), 1.34–1.20 (m, 12 H), 0.88 (t, *J* = 6.8 Hz, 3 H) ppm; **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ = 168.4, 146.4, 135.4, 132.4, 131.2, 123.2, 120.6, 120.5, 111.9, 111.5, 101.6, 52.1, 45.6, 36.6, 36.4, 32.1, 29.7, 29.7, 29.5, 27.9, 22.8, 14.3 ppm; **IR (ATR):** $\tilde{\nu}$ = 2925, 2854, 1714, 1615, 1505, 1466, 1434, 1353, 1323, 1272, 1230, 1108, 893, 773, 723, 427 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{23}H_{33}NO_2 + H]^+$ 356.2584, found 356.2581.

Methyl 1-(7-methyl-3-methyleneoct-6-en-1-yl)-1*H*-indole-6-carboxylate (**1o**):



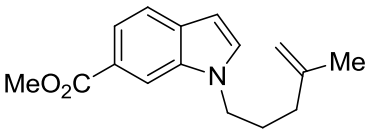
Yield: 49%; **appearance**: colorless oil; R_f: 0.3 (pentane:Et_2O, 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.16–8.08 (m, 1 H), 7.79 (dd, *J* = 8.3, 1.4 Hz, 1 H), 7.63 (dd, *J* = 8.3, 0.7 Hz, 1 H), 7.31–7.21 (m, 2 H), 5.16–5.04 (m, 1 H), 4.89–4.81 (m, 1 H), 4.75 (d, *J* = 1.3 Hz, 1 H), 4.35–4.24 (m, 2 H), 3.95 (s, 3 H), 2.61–2.49 (m, 2 H), 2.19–2.00 (m, 4 H), 1.69 (d, *J* = 1.3 Hz, 3 H), 1.60 (d, *J* = 1.1 Hz, 3 H) ppm; **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ = 168.4, 146.0, 135.3, 132.4, 132.2, 131.2, 123.8, 123.2, 120.6, 120.5, 111.9, 111.7, 101.6, 52.1, 45.5, 36.8, 36.3, 26.4, 25.8, 17.9 ppm; **IR (ATR):** $\tilde{\nu}$ = 3096, 2947, 2926, 2855, 1711, 1615, 1486, 1434, 1376, 1323, 1272, 1230, 1108, 774, 725 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{20}H_{25}NO_2 + H]^+$ 312.1958, found 312.1964.

Methyl 1-(7-(benzyloxy)-3-methyleneheptyl)-1*H*-indole-6-carboxylate (**1p**):



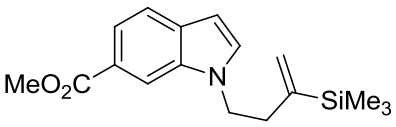
Yield: 43%; **appearance**: colorless oil; R_f: 0.3 (pentane:Et_2O, 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (s, 1 H), 7.79 (dd, *J* = 8.3, 1.4 Hz, 1 H), 7.63 (d, *J* = 8.3 Hz, 1 H), 7.33 (d, *J* = 4.3 Hz, 4 H), 7.28 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.23 (d, *J* = 3.0 Hz, 1 H), 6.54–6.47 (m, 1 H), 4.83 (d, *J* = 1.6 Hz, 1 H), 4.78–4.69 (m, 1 H), 4.50 (s, 2 H), 4.36–4.24 (m, 2 H), 3.94 (s, 3 H), 3.46 (t, *J* = 6.3 Hz, 2 H), 2.54 (t, *J* = 7.5 Hz, 2 H), 2.05 (t, *J* = 7.5 Hz, 2 H), 1.68–1.57 (m, 2H), 1.56–1.45 (m, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 168.4, 145.9, 138.7, 135.3, 132.4, 131.2, 128.5 (2 C), 127.8 (2 C), 127.7, 123.2, 120.6, 120.5, 111.9, 111.8, 101.6, 73.1, 70.2, 52.1, 45.5, 36.6, 36.1, 29.5, 24.4 ppm; **IR (ATR):** $\tilde{\nu}$ = 2942, 2859, 1711, 1615, 1504, 1454, 1434, 1354, 1323, 1272, 1231, 1109, 894, 774, 732, 698, 426 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{25}H_{29}NO_3 + H]^+$ 392.2220, found 392.2230.

Methyl 1-(4-methylpent-4-en-1-yl)-1*H*-indole-6-carboxylate (**1q**):



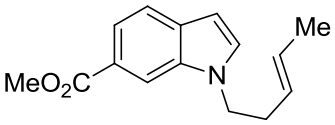
Yield: 60%; **appearance**: colorless oil; R_f: 0.4 (pentane:Et_2O, 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.16–8.08 (m, 1 H), 7.79 (dd, *J* = 8.3, 1.5 Hz, 1 H), 7.63 (d, *J* = 8.3 Hz, 1 H), 7.26 (d, *J* = 2.0 Hz, 2 H), 6.53 (dd, *J* = 3.0, 0.9 Hz, 1 H), 4.84–4.76 (m, 1 H), 4.75–4.66 (m, 1 H), 4.19 (td, *J* = 5.7, 4.6, 2.1 Hz, 2 H), 3.95 (s, 3 H), 2.08–1.94 (m, 4 H), 1.72 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 168.4, 144.3, 135.5, 132.4, 131.2, 123.2, 120.6, 120.4, 112.0, 111.1, 101.6, 52.1, 46.1, 34.9, 28.1, 22.5 ppm; **IR (ATR):** $\tilde{\nu}$ = 3078, 2947, 1711, 1615, 1504, 1435, 1354, 1321, 1274, 1258, 1229, 1109, 888, 774, 726, 426 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{16}H_{19}NO_2 + H]^+$ 258.1489, found 258.1490.

Methyl 1-(3-(trimethylsilyl)but-3-en-1-yl)-1*H*-indole-6-carboxylate (**1r**):



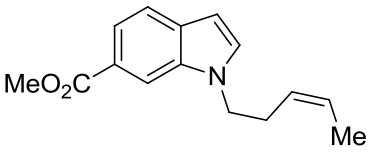
Yield: 42%; **appearance**: colorless oil; R_f: 0.35 (pentane:Et_2O, 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.13 (s, 1 H), 7.79 (dd, *J* = 8.3, 1.4 Hz, 1 H), 7.63 (d, *J* = 8.4 Hz, 1 H), 7.24 (d, *J* = 3.1 Hz, 1 H), 6.56–6.46 (m, 1 H), 5.56 (dt, *J* = 2.6, 1.5 Hz, 1 H), 5.45 (d, *J* = 2.5 Hz, 1 H), 4.34–4.17 (m, 2 H), 3.95 (s, 3 H), 2.65 (t, *J* = 7.7 Hz, 2 H), 0.13 (s, 9 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 168.4, 148.5, 135.3, 132.4, 131.2, 126.9, 123.2, 120.6, 120.5, 112.0, 101.5, 52.1, 46.5, 36.0, -1.4 (3 C) ppm; **IR (ATR):** $\tilde{\nu}$ = 3050, 2951, 1713, 1615, 1504, 1435, 1354, 1322, 1273, 1229, 1108, 989, 931, 837, 774, 758, 724, 427 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{17}H_{23}NO_2Si + H]^+$ 302.1571, found 302.1580.

Methyl (*E*)-1-(pent-3-en-1-yl)-1*H*-indole-6-carboxylate ((*E*)-**1s**):



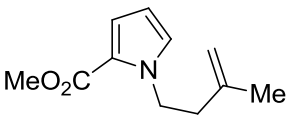
Yield: 378 mg, 50%; **appearance**: colorless oil; R_f: 0.35 (pentane:Et_2O, 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.14 – 8.08 (m, 1 H), 7.79 (dq, *J* = 8.3, 1.5 Hz, 1 H), 7.65 – 7.59 (m, 1 H), 7.24 (d, *J* = 3.1 Hz, 1 H), 6.53 – 6.49 (m, 1 H), 5.54 – 5.33 (m, 2 H), 4.24 – 4.16 (m, 2 H), 3.95 (d, *J* = 1.3 Hz, 3 H), 2.52 (qd, *J* = 7.5, 7.0, 3.2 Hz, 2 H), 1.62 (dq, *J* = 6.0, 1.2 Hz, 3 H); **^{13}C{^{1}H} NMR** δ = 168.3, 135.3, 132.2, 131.1, 128.5, 126.7, 123.0, 120.4, 120.3, 111.9, 101.3, 51.9, 46.7, 33.6, 18.0; **IR (ATR):** $\tilde{\nu}$ = 3099, 2948, 2918, 1710, 1615, 1504, 1434, 1270, 1231, 1106, 969, 774, 749, 726, 426 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{15}H_{17}NO_2 + H]^+$ 244.1332, found 244.1337.

Methyl (*Z*)-1-(pent-3-en-1-yl)-1*H*-indole-6-carboxylate ((*Z*)-**1s**):



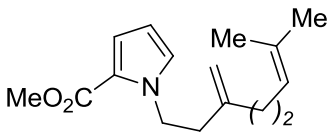
Yield: 378 mg, 50%; **appearance**: colorless oil; R_f: 0.35 (pentane:Et_2O, 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.19 – 8.10 (m, 1 H), 7.79 (dd, *J* = 8.4, 1.4 Hz, 1 H), 7.63 (d, *J* = 8.2 Hz, 1 H), 7.28 – 7.21 (m, 1 H), 6.52 (dd, *J* = 3.1, 0.9 Hz, 1 H), 5.62 – 5.50 (m, 1 H), 5.39 (dtq, *J* = 10.9, 7.3, 1.8 Hz, 1 H), 4.21 (t, *J* = 7.0 Hz, 2 H), 3.95 (s, 3 H), 2.59 (q, *J* = 7.1 Hz, 2 H), 1.44 (ddd, *J* = 6.8, 1.8, 0.8 Hz, 1 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 168.3, 135.3, 132.3, 131.2, 127.4, 125.7, 123.0, 120.5, 120.3, 111.8, 101.4, 52.0, 46.2, 27.9, 12.7 ppm; **IR (ATR):** $\tilde{\nu}$ = 3097, 3016, 2948, 1706, 1614, 1503, 1487, 1466, 1433, 1403, 1352, 1322, 1307, 1271, 1228, 1205, 1189, 1109, 1076, 987, 909, 829, 773, 747, 720 cm^{-1}; **HRMS (APPI)** calculated for $[C_{15}H_{17}NO_2+H]^+$ 244.1332, found 244.1335.

Methyl 1-(3-methylbut-3-en-1-yl)-1*H*-pyrrole-2-carboxylate (**3a**):



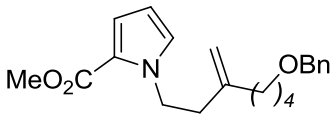
Yield: 71%; **appearance**: colorless oil; R_f: 0.6 (pentane:Et_2O, 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.94 (dd, *J* = 4.0, 1.8 Hz, 1 H), 6.83 (t, *J* = 2.2 Hz, 1 H), 6.10 (dd, *J* = 4.0, 2.6 Hz, 1 H), 4.78 (p, *J* = 1.6 Hz, 1 H), 4.68 (dq, *J* = 2.0, 1.0 Hz, 1 H), 4.47–4.35 (m, 2 H), 3.81 (s, 3 H), 2.46 (td, *J* = 7.5, 1.3 Hz, 2 H), 1.76 (s, 3 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 161.6, 142.5, 128.8, 121.5, 118.3, 112.4, 108.0, 51.2, 48.1, 39.9, 22.6 ppm; **IR (ATR):** $\tilde{\nu}$ = 3077, 2949, 1703, 1650, 1531, 1473, 1437, 1409, 1330, 1242, 1106, 891, 736, 612 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{11}H_{15}NO_2 + H]^+$ 194.1176, found 194.1166.

Methyl 1-(7-methyl-3-methyleneoct-6-en-1-yl)-1*H*-pyrrole-2-carboxylate (**3b**):



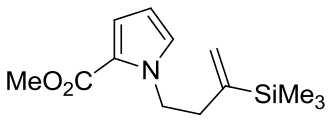
Yield: 62%; **appearance**: colorless oil; R_f: 0.4 (pentane:Et_2O, 60:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.94 (dd, *J* = 4.0, 1.8 Hz, 1 H), 6.82 (dd, *J* = 2.5, 1.8 Hz, 1 H), 6.10 (dd, *J* = 4.0, 2.5 Hz, 1 H), 5.11 (ddp, *J* = 6.9, 5.7, 1.4 Hz, 1 H), 4.81 (q, *J* = 1.5 Hz, 1 H), 4.78–4.68 (m, 1 H), 4.48–4.34 (m, 2 H), 3.81 (s, 3 H), 2.46 (td, *J* = 7.4, 1.1 Hz, 2 H), 2.12 (q, *J* = 7.4 Hz, 2 H), 2.04 (dd, *J* = 9.0, 6.1 Hz, 2 H), 1.69 (s, 3 H), 1.61 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 161.6, 146.3, 131.9, 128.8, 124.1, 121.5, 118.3, 111.4, 108.0, 51.2, 48.4, 38.3, 36.3, 26.5, 25.8, 17.9 ppm; **IR (ATR):** $\tilde{\nu}$ = 2924, 2856, 1705, 1645, 1531, 1473, 1437, 1409, 1329, 1241, 1189, 1105, 1079, 892, 735, 612 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{16}H_{23}NO_2 + H]^+$ 262.1802, found 262.1799.

Methyl 1-(7-(benzyloxy)-3-methyleneheptyl)-1*H*-pyrrole-2-carboxylate (**3c**):



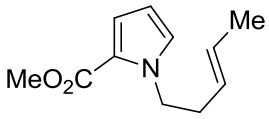
Yield: 50%; **appearance**: colorless oil; R_f: 0.45 (pentane:Et_2O, 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 4.4 Hz, 4 H), 7.28 (dd, *J* = 5.1, 3.7 Hz, 1 H), 6.94 (dd, *J* = 4.0, 1.8 Hz, 1 H), 6.81 (t, *J* = 2.3 Hz, 1 H), 6.09 (dd, *J* = 4.0, 2.5 Hz, 1 H), 4.79 (d, J = 1.5 Hz, 1 H), 4.72 (s, 1 H), 4.50 (s, 2 H), 4.47–4.32 (m, 2H), 3.80 (s, 3 H), 3.48 (t, *J* = 6.4 Hz, 2 H), 2.44 (t, *J* = 7.5 Hz, 2 H), 2.03 (t, *J* = 7.6 Hz, 2 H), 1.70–1.58 (m, 2 H), 1.53 (qd, J = 7.5, 2.8 Hz, 2 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 161.6, 146.2, 138.8, 128.8, 128.5 (2 C), 127.8 (2 C), 127.6, 121.5, 118.3, 111.4, 108.0, 73.0, 70.4, 51.2, 48.4, 38.1, 36.0, 29.5, 24.4 ppm; **IR (ATR):** $\tilde{\nu}$ = 2940, 2858, 1704, 1531, 1473, 1437, 1410, 1330, 1242, 1106, 736, 698, 612 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{21}H_{27}NO_3 + H]^+$ 342.2064, found 342.2072.

Methyl 1-(3-(trimethylsilyl)but-3-en-1-yl)-1*H*-pyrrole-2-carboxylate (**3d**):



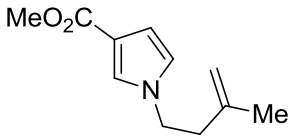
Yield: 26%; **appearance**: colorless oil; R_f: 0.5 (pentane:Et_2O, 20:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.95 (dd, *J* = 4.0, 1.8 Hz, 1 H), 6.81 (t, *J* = 2.2 Hz, 1 H), 6.10 (dd, *J* = 4.0, 2.6 Hz, 1 H), 5.57 (dt, *J* = 2.8, 1.5 Hz, 1 H), 5.43 (d, *J* = 2.6 Hz, 1 H), 4.42–4.28 (m, 2 H), 3.81 (s, 3 H), 2.65–2.47 (m, 2 H), 0.11 (s, 9 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 161.5, 148.7, 128.8, 126.6, 121.6, 118.3, 108.0, 51.2, 49.2, 37.6, -1.5 (3 C) ppm; **IR (ATR):** $\tilde{\nu}$ = 3049, 2952, 2856, 1708, 1531, 1473, 1438, 1410, 1330, 1245, 1148, 1106, 1078, 932, 838, 760, 735 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{13}H_{21}NO_2Si + H]^+$ 252.1414, found 252.1391.

Methyl (*E*)-1-(pent-3-en-1-yl)-1*H*-pyrrole-2-carboxylate (**3e**):



Yield: 55%; **appearance**: colorless oil; R_f: 0.3 (pentane:Et_2O, 50:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.94 (dd, *J* = 3.9, 1.8 Hz, 1 H), 6.81 (t, *J* = 2.2 Hz, 1 H), 6.10 (dd, *J* = 3.9, 2.5 Hz, 1 H), 5.51 – 5.30 (m, 2 H), 4.30 (t, *J* = 7.2 Hz, 2 H), 3.81 (s, 3 H), 2.42 (q, *J* = 6.9 Hz, 2 H), 1.62 (dd, *J* = 6.0, 1.4 Hz, 3 H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 161.5, 128.8, 127.8, 126.9, 121.4, 118.1, 107.7, 51.0, 49.3, 34.8, 18.0 ppm; **IR (ATR):** $\tilde{\nu}$ = 3111, 3022, 2989, 2948, 2918, 2855, 1703, 1530, 1473, 1436, 1409, 1364, 1328, 1240, 1190, 1103, 1077, 1025, 998, 967, 933, 889, 799, 760, 736 cm^{-1}; **HRMS (APPI)** calculated for $[C_{11}H_{15}NO_2 + H]^+$ 194.1176, found 194.1172.

Methyl 1-(3-methylbut-3-en-1-yl)-1*H*-pyrrole-3-carboxylate (**3f**):



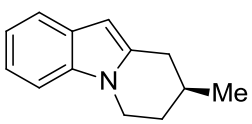
Yield: 378 mg, 71%; **appearance**: colorless oil; R_f: 0.6 (pentane:Et_2O, 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28 (t, *J* = 1.9 Hz, 1 H), 6.62 – 6.50 (m, 2 H), 4.83 – 4.74 (m, 1 H), 4.71 – 4.63 (m, 1 H), 3.98 (t, *J* = 7.3 Hz, 2 H), 3.78 (s, 3 H), 2.46 (t, *J* = 7.4 Hz, 2 H), 1.73 (t, *J* = 1.1 Hz, 1 H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 165.3, 141.4, 125.9, 121.5, 115.6, 112.9, 110.0, 51.0, 48.6, 39.3, 22.3. ppm; **IR (ATR):** $\tilde{\nu}$ = 3130, 3076, 2971, 2946, 2912, 2852, 1792, 1702, 1650, 1540, 1509, 1438, 1400, 1365, 1196, 1115, 1075, 1002, 924, 894, 820, 791, 762, 715 cm^{-1}; **HRMS (APPI)** calculated for $[C_{11}H_{15}NO_2+H]^+$ 194.1176, found 194.1173.

Nickel-Catalyzed Enantioselective Indole and Pyrrole C-H Functionalization

General procedure 4 (GP4)

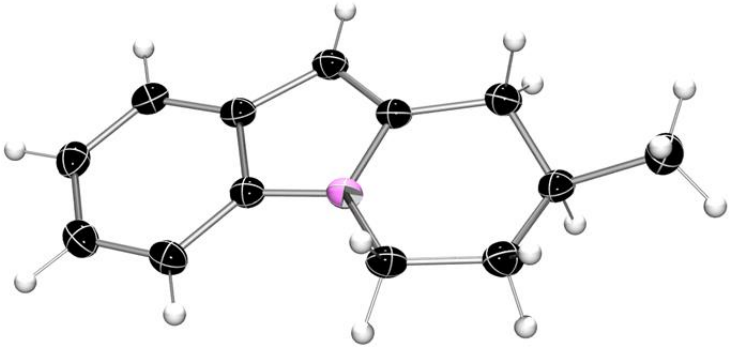
Inside a glove box a tube containing a magnetic stirring bar was charged with $Ni(cod)_2$ (1.4 mg, 5 mol%), **L8**•HCl (6.3 mg, 5.5 mol%), NaO*t*Bu (2.4 mg, 25 mol%) and the substrate (0.1 mmol). The mixture was dissolved in $PhCF_3$ (0.2 mL) and was stirred for 24 h at 60 °C. Subsequently the reaction mixture was cooled to ambient temperature, was filtered over a short plug of silica gel (EtOAc), and was concentrated under reduced pressure to afford the crude product, which was purified by silica gel column (Pentane/EtOAc).

(*S*)-8-Methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**2a**):

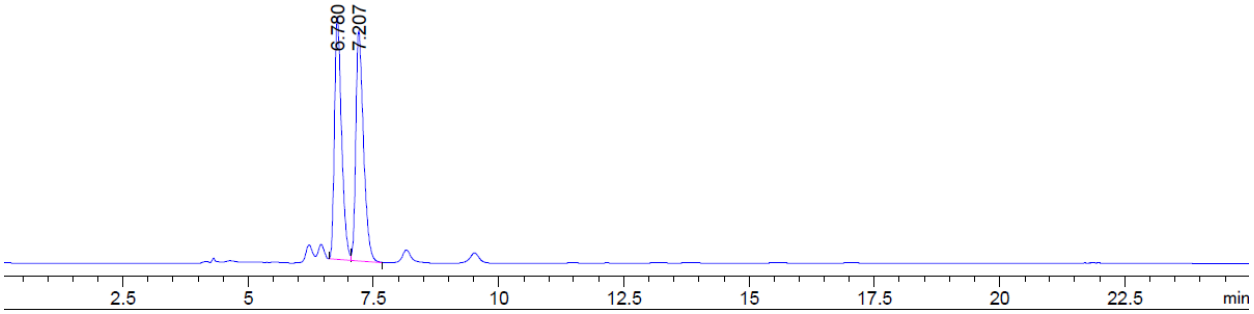


Obtained as white solid in 92% (17 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.81 – 7.66 (m, 1H), 7.37 – 7.24 (m, 2 H), 7.17 – 7.13 (m, 1 H), 6.27 (d, *J* = 1.3 Hz, 1 H), 3.60 (ddd, *J* = 11.6, 5.7, 2.9 Hz, 1 H), 3.21 (td, *J* = 11.4, 4.9 Hz, 1 H), 2.70 (ddd, *J* = 15.8, 4.6, 1.8 Hz, 1 H), 2.17 (ddd, *J* = 15.9, 10.8, 1.5 Hz, 1 H), 1.47 – 1.27 (m, 2 H), 1.07 (dd, *J* = 13.1, 5.7 Hz, 1 H), 0.74 (d, *J* = 6.5 Hz, 3 H) ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 136.5, 136.4, 129.1, 120.2, 119.9, 119.8, 108.7, 97.8, 41.1, 32.3, 30.9 27.5, 20.9 ppm; **IR (ATR):** $\tilde{\nu}$ 3050, 2952, 2927, 2869, 2830, 1543, 1475, 1459, 1413, 1358, 1324, 1313, 1167, 1011, 769, 741, 622, 545, 473 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{15}N+H]^+$: 186.1277, found: 186.283; **R_f:** 0.3 (pentane/EtOAc 99:1); **$[\alpha]_D^{20}$:** 46.8 (*c* = 0.1, CH_2Cl_2); **m.p.:** 77-78 °C.

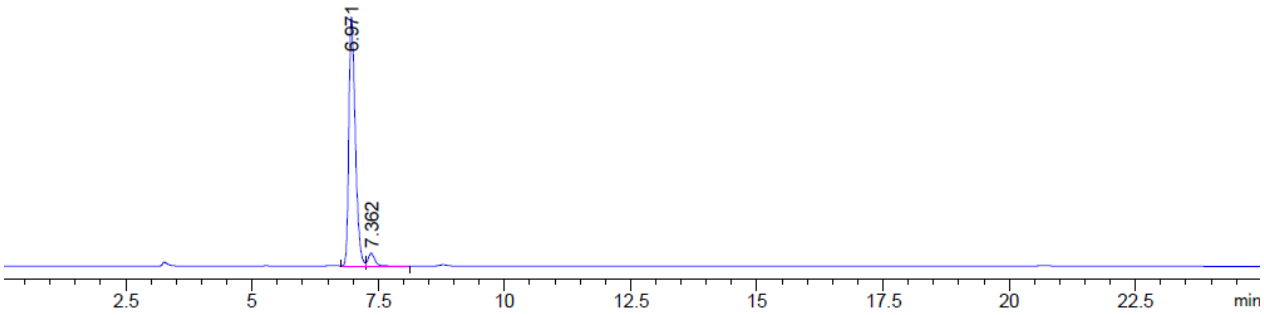
This compound was crystallised by slow evaporation from toluene and its absolute configuration assigned by X-ray crystallography as *R*:



Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 99:1, 1.0 mL/min, 282 nm; t_R (major) = 7.0 min, t_R (minor) = 7.4 min), 94.8:5.2 er.

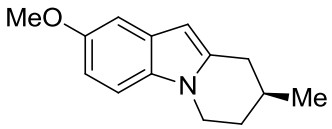


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.780	BV	0.1505	7690.22900	783.68555	49.2208
2	7.207	VB	0.1625	7933.72412	743.26611	50.7792



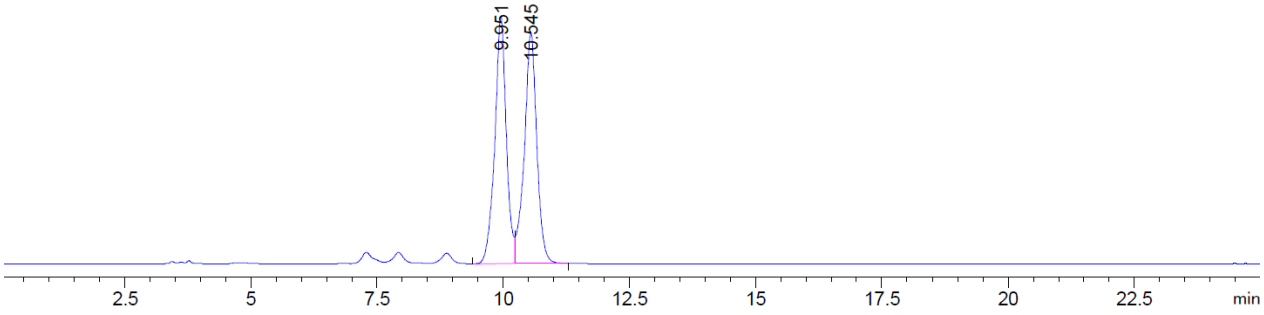
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.971	VV	0.1346	7333.37305	833.59821	94.7596
2	7.362	VB	0.1390	405.55322	43.40305	5.2404

(*S*)-2-Methoxy-8-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**2b**):

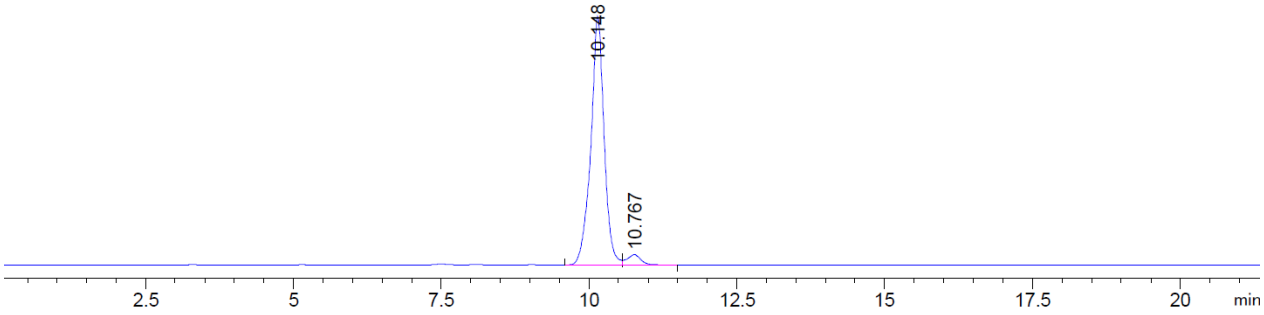


Obtained as white solid in 88% (19 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.20 (d, *J* = 2.4 Hz, 1 H), 7.13 (dd, *J* = 8.7, 2.4 Hz, 1 H), 7.03 (d, *J* = 8.7 Hz, 1 H), 6.26 (d, *J* = 1.3 Hz, 1 H), 3.59 (s, 3 H), 3.56 (dq, *J* = 8.6, 2.8 Hz, 1 H), 3.20 (td, *J* = 11.4, 4.9 Hz, 1 H), 2.73 (ddd, *J* = 15.9, 4.6, 1.8 Hz, 1 H), 2.20 (ddd, *J* = 15.8, 10.8, 1.4 Hz, 1 H), 1.41 (s, 1 H), 1.37 (dd, *J* = 13.1, 2.6 Hz, 1 H), 1.08 (dtd, *J* = 13.1, 11.2, 5.7 Hz, 1 H), 0.75 (d, *J* = 6.6 Hz, 3 H) ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 154.6, 137.0, 131.9, 129.4, 110.3, 109.3, 101.9, 97.6, 55.0, 41.2, 32.3, 30.9, 27.4, 20.9; **IR (ATR):** $\tilde{\nu}$ = 3008, 2949, 2927, 2867, 2827, 1617, 1579, 1486, 1471, 1450, 1420, 1355, 1338, 1271, 1233, 1202, 1168, 1157, 1131, 1111, 1037, 826, 801, 778, 769 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{14}H_{17}NO+H]^+$ 216.1383, found 216.1378; **R_f:** 0.2 (pentane:EtOAc 80:1); **$[\alpha]_D^{20}$:** 36.3 (*c* = 0.1, CH_2Cl_2); **m.p.:** 78-80 °C.

Chiral HPLC: (Chiralpak IA, 4.6 x 250 mm; hexane:*i*-PrOH 99:1, 1.0 mL/min, 280 nm; t_R (major) = 10.1 min, t_R (minor) = 10.8 min), 95.9:4.1 er.

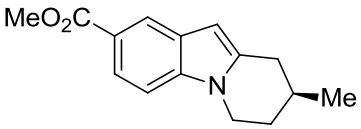


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.951	BV	0.2329	3114.81763	196.49290	49.7600
2	10.545	VB	0.2501	3144.86499	183.38817	50.2400



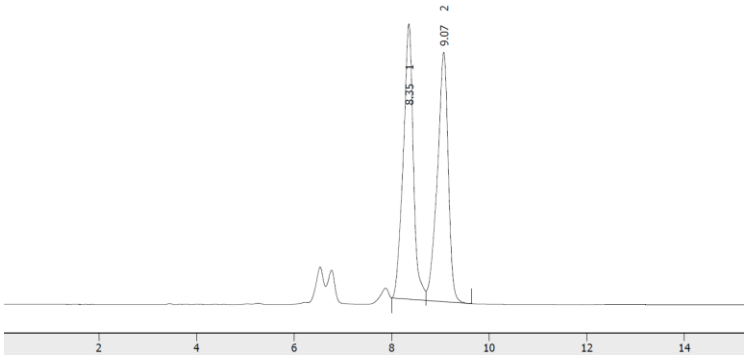
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.148	BV	0.2289	1.01650e4	648.35162	95.8719
2	10.767	VB	0.2406	437.68863	26.79069	4.1281

Methyl (*S*)-8-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-2-carboxylate (**2c**):

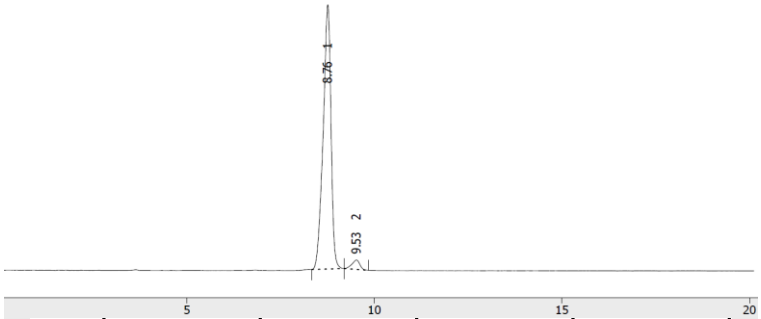


Obtained as white solid in 82% (20 mg). **^{1}H NMR (800 MHz, C_6D_6)** δ = 8.76 (d, *J* = 1.5 Hz, 1 H), 8.33 (dd, *J* = 8.5, 1.6 Hz, 1 H), 6.99 (d, *J* = 8.6 Hz, 1 H), 6.19 (d, *J* = 1.4 Hz, 1 H), 3.67 (s, 3 H), 3.45 (ddd, *J* = 11.7, 5.8, 2.9 Hz, 1 H), 3.06 (td, *J* = 11.6, 5.0 Hz, 1 H), 2.67–2.53 (m, 1 H), 2.05 (ddd, *J* = 16.1, 11.0, 1.5 Hz, 1 H), 1.34 (tddd, *J* = 11.2, 7.0, 4.5, 2.8 Hz, 1 H), 1.30 (ddt, *J* = 13.3, 5.0, 2.5 Hz, 1 H), 0.98 (dtd, *J* = 13.2, 11.4, 5.8 Hz, 1 H), 0.70 (d, *J* = 6.7 Hz, 3 H) ppm; **^{13}C NMR (201 MHz, C_6D_6)** δ = 168.2, 139.1, 138.3, 128.8, 123.2, 122.6, 122.4, 108.7, 99.5, 51.4, 41.6, 32.4, 30.9, 27.5, 21.1 ppm; **IR (ATR):** $\tilde{\nu}$ = 3054, 2947, 2872, 1711, 1609, 1448, 1435, 1412, 1358, 1330, 1304, 1292, 1278, 1264, 1240, 1212, 1169, 1123, 1087, 764, 735, 704 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{15}H_{17}NO_2+H]^+$ 244.1332, found 244.1331; **R_f:** 0.45 (pentane:EtOAc 20:1); **$[\alpha]_D^{20}$:** 12.8 (*c* = 0.1, CH_2Cl_2); **m.p.:** 136-137 °C.

Chiral HPLC: (Chiralpak IA, 4.6 x 250 mm; hexane:*i*-PrOH 90:10, 1.0 mL/min, 294 nm; t_R (major) = 8.8 min, t_R (minor) = 9.5 min), 96.6:3.4 er.

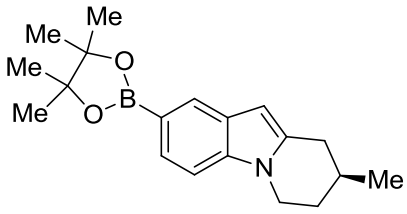


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]
1	8.353	4239.971	294.223	50.5
2	9.067	4160.180	266.448	49.5



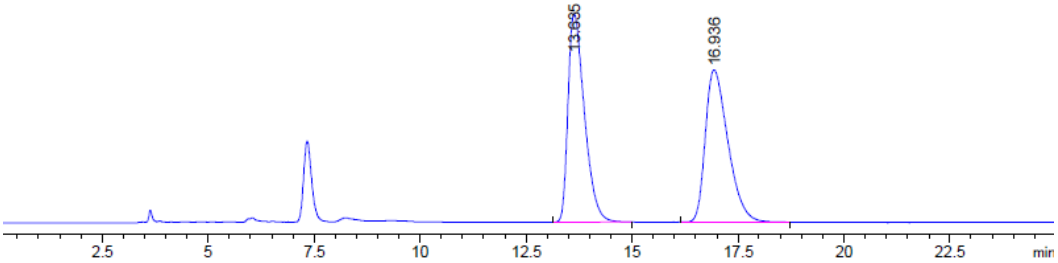
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]
1	8.757	1141.339	78.283	96.6
2	9.525	40.455	2.774	3.4

(*S*)-8-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**2d**):

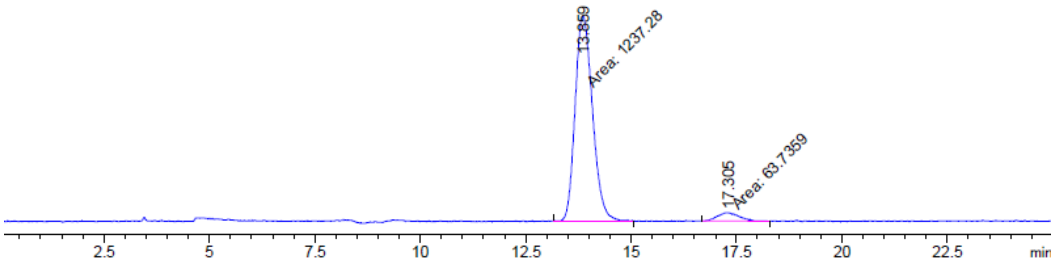


Obtained as white solid in 63% (19.5 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 8.75 (s, 1 H), 8.26 (dd, *J* = 8.2, 1.1 Hz, 1 H), 7.19 (d, *J* = 8.1 Hz, 1 H), 6.26 (d, *J* = 1.3 Hz, 1 H), 3.54 (ddd, *J* = 11.7, 5.7, 2.9 Hz, 1 H), 3.14 (td, *J* = 11.6, 5.0 Hz, 1 H), 2.69–2.60 (m, 1 H), 2.10 (ddd, *J* = 16.0, 10.9, 1.5 Hz, 1 H), 1.36 (dttd, *J* = 13.7, 7.0, 4.2, 2.4 Hz, 1 H), 1.30 (ddq, *J* = 12.8, 5.0, 2.7 Hz, 1 H), 1.22 (s, 12 H), 0.99 (dtd, *J* = 13.2, 11.3, 5.7 Hz, 1 H), 0.70 (d, *J* = 6.6 Hz, 3 H) ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 138.9, 136.9, 129.1, 128.6, 128.4, 127.4, 108.6, 98.8, 83.3 (2 C), 41.5, 32.6, 31.2, 27.7, 25.2 (4 C), 21.3 ppm; **IR (ATR):** $\tilde{\nu}$ = 2977, 2946, 2865, 1604, 1556, 1445, 1387, 1372, 1352, 1323, 1294, 1275, 1265, 1213, 1151, 1123, 1069, 966, 859, 815, 774, 751, 685 cm^{-1}; **HRMS (Multimode)** calculated for $[C_{19}H_{26}BNO_2+H]^+$ 312.2129, found 312.2132; **R_f:** 0.2 (pentane:EtOAc 99:1); **$[\alpha]_D^{20}$:** 11.9 (*c* = 0.1, CH_2Cl_2); **m.p.:** 165-166 °C.

Chiral HPLC: (Chiralpak IG, 4.6 x 250 mm; hexane:*i*-PrOH 99:1, 1.0 mL/min, 280 nm; t_R (major) = 13.9 min, t_R (minor) = 17.3 min), 95.1:4.9 er.

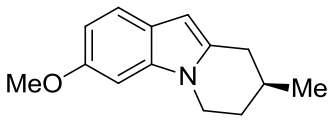


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.635	BB	0.4124	8863.31250	328.92957	49.7851
2	16.936	BB	0.5620	8939.82910	240.31593	50.2149



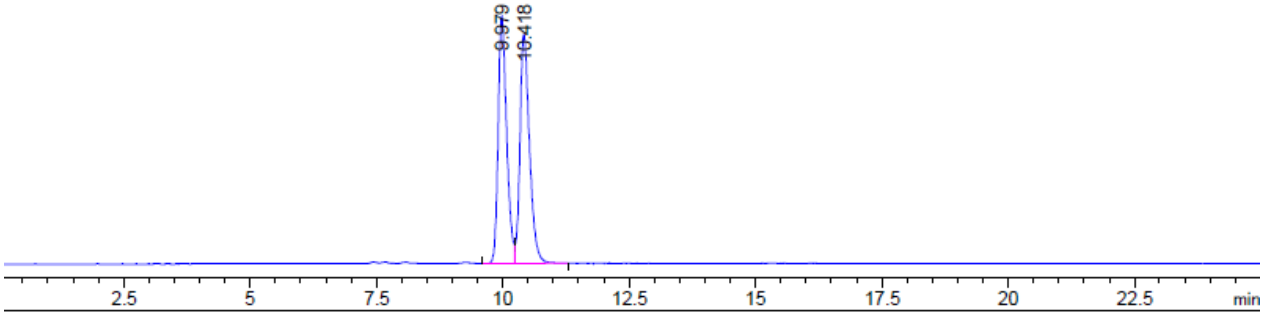
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.859	MM	0.4743	1237.27600	43.47823	95.1010
2	17.305	MM	0.5929	63.73594	1.79173	4.8990

(*S*)-3-Methoxy-8-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**2e**):

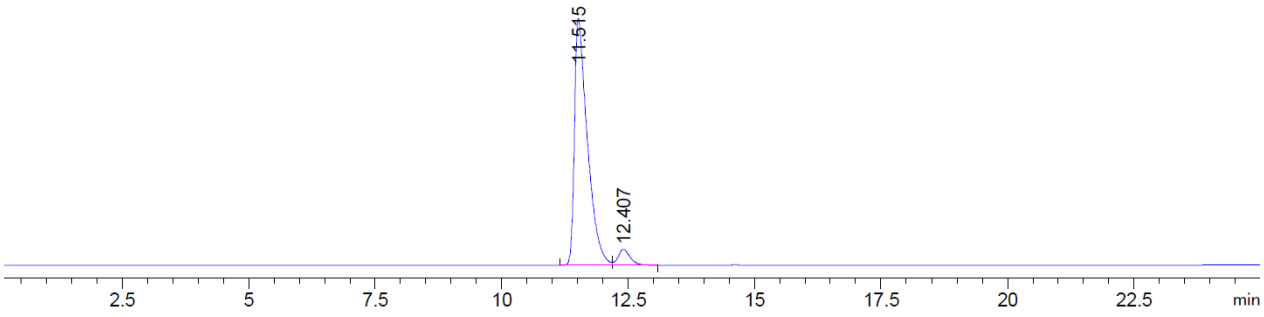


Obtained as white solid in 88% (19 mg). **^{1}H NMR (500 MHz, C_6D_6)** δ = 7.56 (d, *J* = 8.5 Hz, 1 H), 7.01 (dd, *J* = 8.5, 2.3 Hz, 1 H), 6.76 (d, *J* = 2.3 Hz, 1 H), 6.22 (d, *J* = 1.3 Hz, 1 H), 3.60 (s, 3 H), 3.54 (ddd, *J* = 11.5, 5.7, 3.0 Hz, 1 H), 3.18 (td, *J* = 11.4, 5.0 Hz, 1 H), 2.71 (dddd, *J* = 15.8, 4.5, 2.1, 0.8 Hz, 1 H), 2.19 (ddd, *J* = 15.8, 10.8, 1.6 Hz, 1 H), 1.50 – 1.32 (m, 2 H), 1.17 – 1.04 (m, 1 H), 0.75 (d, *J* = 6.6 Hz, 3 H) ppm; **^{13}C NMR (126 MHz, C_6D_6)** δ = 155.8, 137.3, 135.3, 123.4, 120.3, 108.9, 97.6, 93.3, 55.1, 41.2, 32.4, 31.0, 27.6, 20.9 ppm; **IR (ATR):** $\tilde{\nu}$ 2950, 2926, 2868, 2829, 2279, 1620, 1548, 1489, 1454, 1412, 1360, 1347, 1329, 1246, 1227, 1212, 1159, 1033, 811, 516, 490 cm^{-1}; **HRMS (ESI)** calculated for $[C_{14}H_{17}NO+H]^+$: 216.1383, found: 216.1382; **R_f:** 0.2 (pentane:EtOAc 50:1); **$[\alpha]_D^{20}$:** 18.8 (*c* = 0.1, CH_2Cl_2); **m.p.:** 74-75 °C.

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 99:1, 1.0 mL/min, 298 nm; t_R (major) = 11.5 min, t_R (minor) = 12.4 min), 94.4:5.6 er.

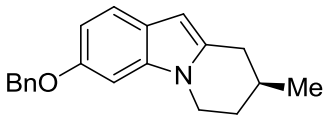


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.979	BV	0.1786	1803.40808	154.04082	49.1600
2	10.418	VB	0.1962	1865.03638	142.99574	50.8400



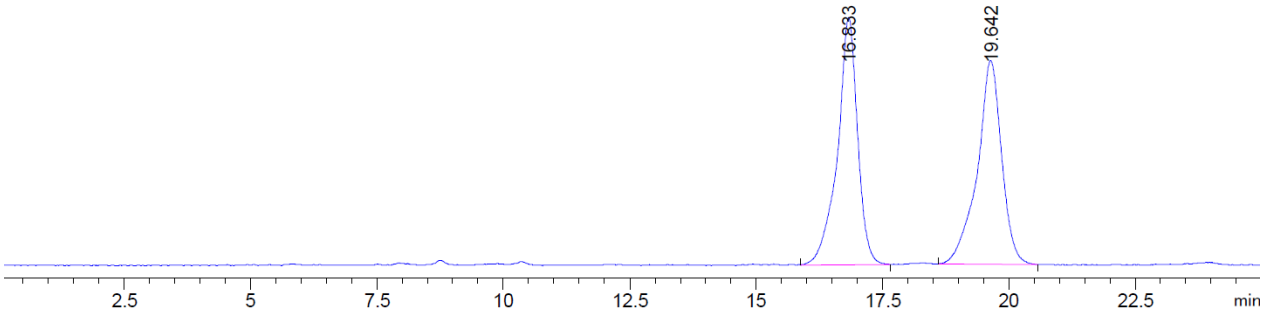
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.515	BV	0.2588	9891.62598	557.96674	94.4041
2	12.407	VB	0.2439	586.33624	35.64983	5.5959

(*S*)-3-(Benzyloxy)-8-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**2f**):

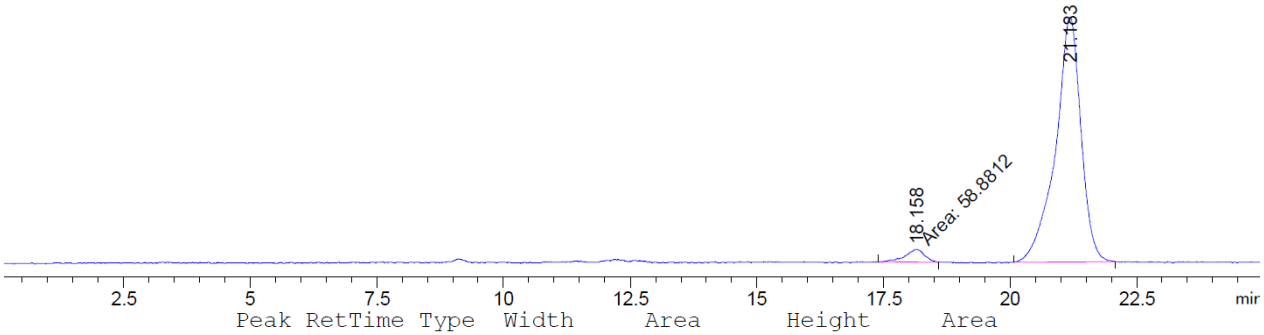


Obtained as white solid in 84% (24.5 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.56 (d, *J* = 8.4 Hz, 1 H), 7.41 (d, *J* = 7.5 Hz, 2 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.12 – 7.02 (m, 2 H), 6.85 (d, *J* = 2.2 Hz, 1 H), 6.21 (s, 1 H), 4.99 (s, 2 H), 3.53 (ddd, *J* = 11.5, 5.7, 2.9 Hz, 1 H), 3.16 (td, *J* = 11.4, 5.0 Hz, 1 H), 2.69 (ddd, *J* = 15.8, 4.6, 1.8 Hz, 1 H), 2.16 (ddd, *J* = 15.8, 10.9, 1.5 Hz, 1 H), 1.49 – 1.38 (m, 1 H), 1.34 (ddt, *J* = 13.8, 6.0, 3.0 Hz, 1 H), 1.06 (dd, *J* = 13.1, 5.7 Hz, 1 H), 0.73 (d, J = 6.6 Hz, 3 H); **^{13}C NMR (151 MHz, C_6D_6)** δ = 154.9, 138.2, 137.293, 135.6, 128.3, 128.0, 127.4, 123.7, 120.4, 109.7, 97.6, 94.7, 70.5, 41.2, 32.4, 30.9, 27.5, 20.9 ppm; **IR (ATR):** $\tilde{\nu}$ 3063, 3031, 2950, 2950, 2925, 2867, 2831, 1620, 1548, 1487, 1475, 1454, 1412, 1379, 1359, 1346, 1336, 1292, 1259, 1245, 1218, 1200, 1161, 1110, 1103, 1024, 808, 734, 696 cm^{-1}; **HRMS (ESI)** calculated for $[C_{20}H_{21}NO]^+$: 292.1696, found: 292.1697; **R_f:** 0.25 (pentane:EtOAc 60:1); **$[\alpha]_D^{20}$:** 8.3 (*c* = 0.1, CH_2Cl_2); **m.p.:** 86-87 °C.

Chiral HPLC: (Chiralpak IA, 4.6 x 250 mm; hexane:*i*-PrOH 99:1, 1.0 mL/min, 296 nm; t_R (minor) = 18.2 min, t_R (major) = 21.2 min), 96.0:4.0 er.

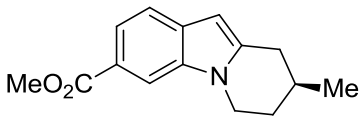


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.833	BB	0.3986	2533.89331	91.62320	50.0209
2	19.642	BB	0.4813	2531.77466	75.48514	49.9791



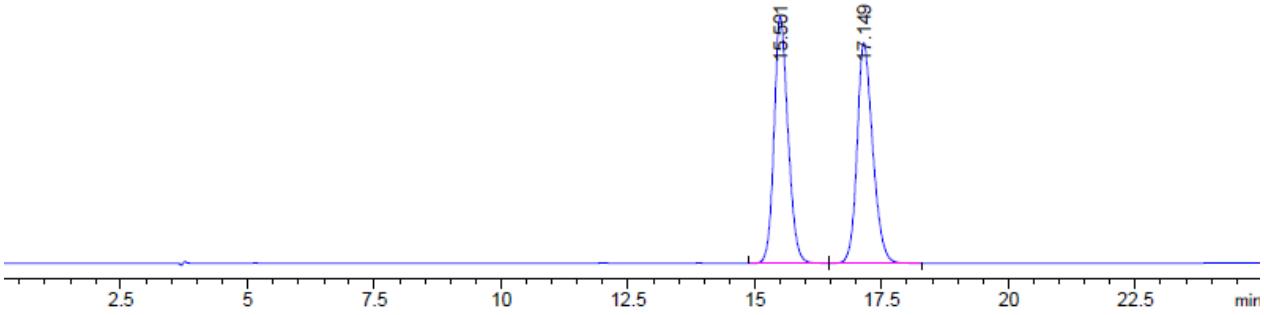
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.144	BB	0.3450	69.05689	2.51023	3.9589
2	21.187	BB	0.4961	1675.30591	48.12834	96.0411

Methyl (*S*)-8-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-3-carboxylate (**2g**):

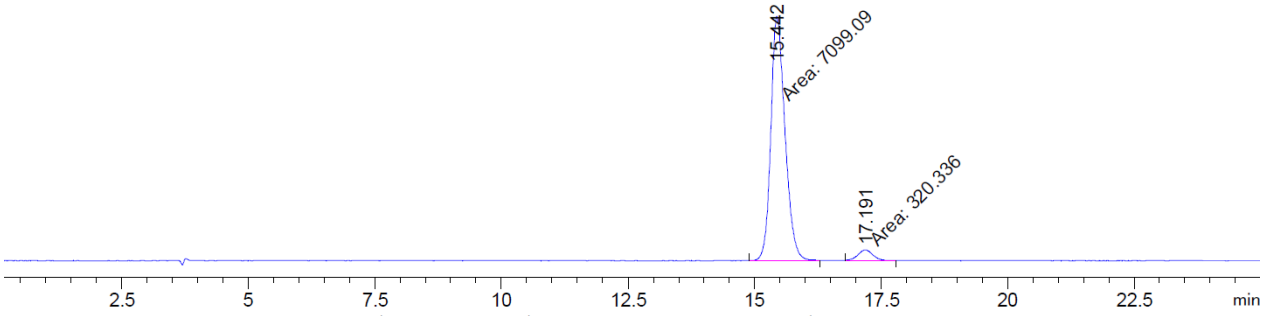


Obtained as white solid in 80% (19.5 mg). **^{1}H NMR (500 MHz, C_6D_6)** δ = 8.26 (s, 1 H), 8.23 (dd, *J* = 8.3, 1.5 Hz, 1 H), 7.58 (d, *J* = 8.2 Hz, 1 H), 6.13 (d, *J* = 1.2 Hz, 1 H), 3.69 (s, 3 H), 3.45 (ddd, *J* = 11.8, 5.7, 2.8 Hz, 1 H), 3.07 (td, *J* = 11.6, 4.9 Hz, 1 H), 2.67 – 2.50 (m, 1 H), 2.03 (ddd, *J* = 16.3, 10.7, 1.4 Hz, 1 H), 1.38 – 1.19 (m, 2 H), 1.01 – 0.86 (m, 1 H), 0.67 (d, *J* = 6.5 Hz, 3 H) ppm; **^{13}C NMR (126 MHz, C_6D_6)** δ = 167.9, 140.3, 135.8, 132.5, 122.2, 121.2, 119.1, 111.4, 98.2, 51.1, 41.0, 32.1, 30.5, 27.0, 20.7. ppm; **IR (ATR):** $\tilde{\nu}$ 3052, 2948, 2868, 2839, 1699, 1609, 1529, 1456, 1432, 1347, 1330, 1263, 1251, 1234, 1164, 1164, 1123, 1093, 1093, 997, 776, 737cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{17}NO_2+H]^+$: 244.1332, found: 244.1322; **R_f:** 0.32 (pentane:EtOAc 20:1); **$[\alpha]_D^{20}$:** 41.6 (*c* = 0.1, CH_2Cl_2); **m.p.:** 148-149 °C.

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 294 nm; t_R (major) = 15.4 min, t_R (minor) = 17.2 min), 95.7:4.3 er.

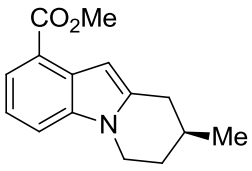


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.501	BB	0.2937	5144.43604	268.31009	49.9694
2	17.149	BB	0.3229	5150.72998	239.51312	50.0306



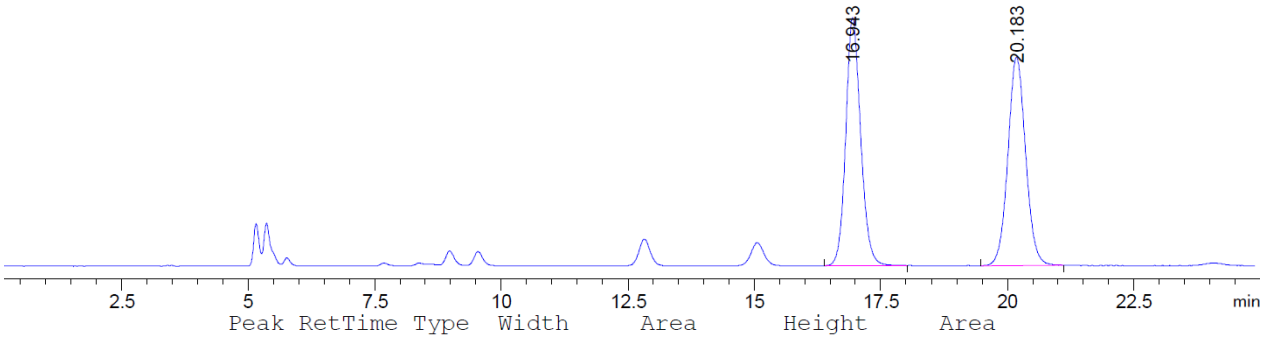
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.442	MF	0.3246	7099.09229	364.46478	95.6825
2	17.191	FM	0.3420	320.33636	15.61202	4.3175

Methyl (*S*)-8-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-1-carboxylate (**2h**):

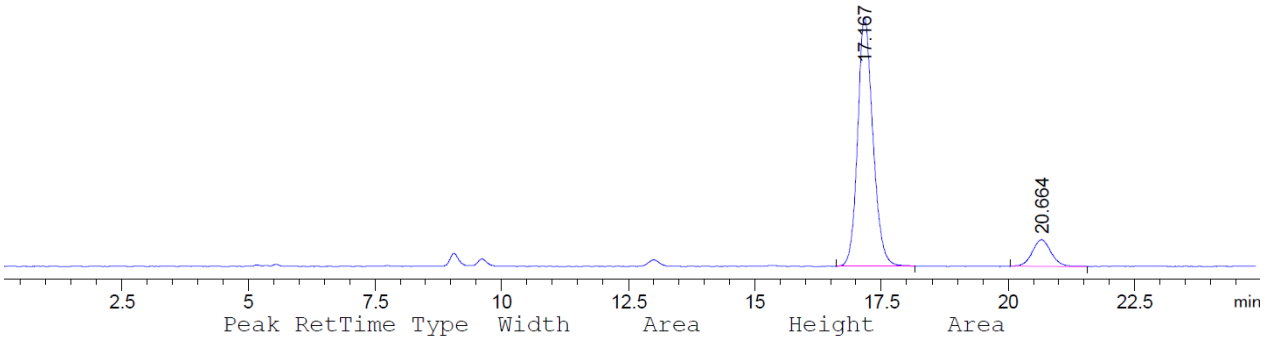


Obtained as white solid in 78% (19 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 8.32 (dd, *J* = 6.9, 1.6 Hz, 1 H), 7.36 (d, *J* = 1.2 Hz, 1 H), 7.15 – 7.10 (m, 2 H), 3.67 (s, 3 H), 3.49 (dq, *J* = 8.6, 2.8 Hz, 1 H), 3.12 (td, *J* = 11.4, 5.0 Hz, 1 H), 2.74 – 2.66 (m, 1 H), 2.14 (ddd, *J* = 16.3, 10.7, 1.4 Hz, 1 H), 1.37 (dddd, *J* = 15.3, 8.6, 4.5, 1.2 Hz, 1 H), 1.33 – 1.29 (m, 1 H), 1.03 – 0.96 (m, 1H), 0.69 (s, 3H) ppm; **^{13}C NMR (201 MHz, C_6D_6)** δ = 167.7, 139.2, 137.3, 129.0, 123.2, 120.9, 119.1, 113.0, 100.0, 50.9, 41.1, 32.1, 30.6, 27.2, 20.8 ppm; **IR (ATR):** $\tilde{\nu}$ 3067, 2950, 2928, 2871, 1709, 1537, 1438, 1417, 1363, 1330, 1281, 1268, 1252, 1193, 1164, 1137, 779, 751 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{17}NO_2+H]^+$: 244.1332, found: 244.1328; **R_f:** 0.2 (pentane:EtOAc 20:1); **$[\alpha]_D^{20}$:** 11.8 (*c* = 0.1, CH_2Cl_2); **m.p.:** 87-88 °C.

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 90:10, 1.0 mL/min, 326 nm; t_R (major) = 17.2 min, t_R (minor) = 20.6 min), 88.3:11.7 er.

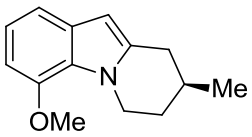


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.943	BB	0.3117	3552.65625	172.94423	50.0760
2	20.183	BB	0.3742	3541.87769	145.39845	49.9240



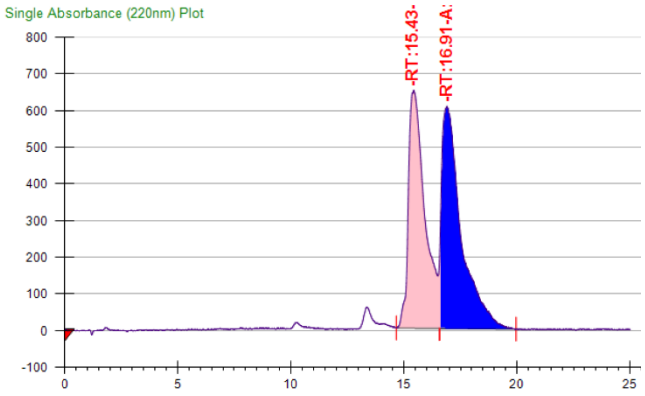
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.167	BB	0.3188	5531.99902	263.65854	88.2902
2	20.664	BB	0.3833	733.69873	28.21832	11.7098

(*S*)-4-Methoxy-8-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (**2i**):

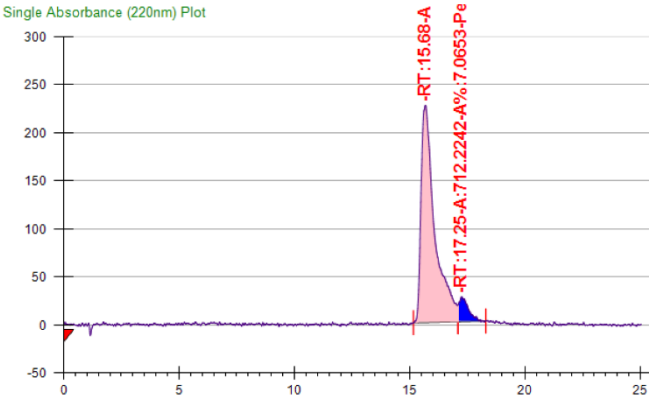


Obtained as white solid in 86% (18.5 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = δ 7.42 (dd, *J* = 7.9, 0.8 Hz, 1 H), 7.14 (t, *J* = 7.8 Hz, 1 H), 6.49 (d, *J* = 7.7 Hz, 1 H), 6.27 (t, *J* = 1.0 Hz, 1 H), 3.94 – 3.85 (m, 1 H), 3.47 (s, 3 H), 2.72 (ddd, *J* = 15.8, 4.5, 2.1 Hz, 1 H), 2.20 (ddd, *J* = 15.8, 10.8, 1.5 Hz, 1 H), 1.47 (dddd, *J* = 14.9, 6.6, 4.3, 2.3 Hz, 2 H), 1.39 – 1.29 (m, 1 H), 1.28 – 1.17 (m, 1 H), 0.74 (d, *J* = 6.4 Hz, 3 H).ppm; **^{13}C NMR (201 MHz, C_6D_6)** δ = 147.8, 136.7, 131.2, 126.5, 112.0, 113.2, 101.7, 98.8, 54.6, 45.2, 32.6, 31.8, 27.2, 20.9 ppm; **IR (ATR):** $\tilde{\nu}$ 2951, 2928, 2869, 2833, 1577, 1552, 1493, 1441, 1413, 1365, 1342, 1325, 1306, 1296, 1253, 1167, 1131, 1096, 976, 782, 725 cm^{-1}; **HRMS (ESI)** calculated for $[C_{14}H_{17}NO+H]^+$: 216.1383, found: 216.1385; **R_f:** 0.22 (pentane:EtOAc 50:1); **$[\alpha]_D^{20}$:** 44.2 (*c* = 0.1, CH_2Cl_2); **m.p.:** 58 °C.

SFC: (OD-H column, 1.0 ppm MeOH in supercritical CO_2 as eluent, 4 mL/min., 220 nm; t_R (major) = 15.7 min, t_R (minor) = 17.3 min, 92.9:7.1 er.

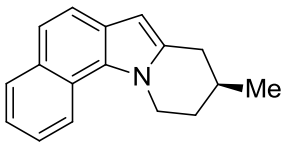


Peak No	% Area	Area	Ret. Time
1	47.6201	32897.7135	15.43 min
2	52.3799	36185.9081	16.91 min



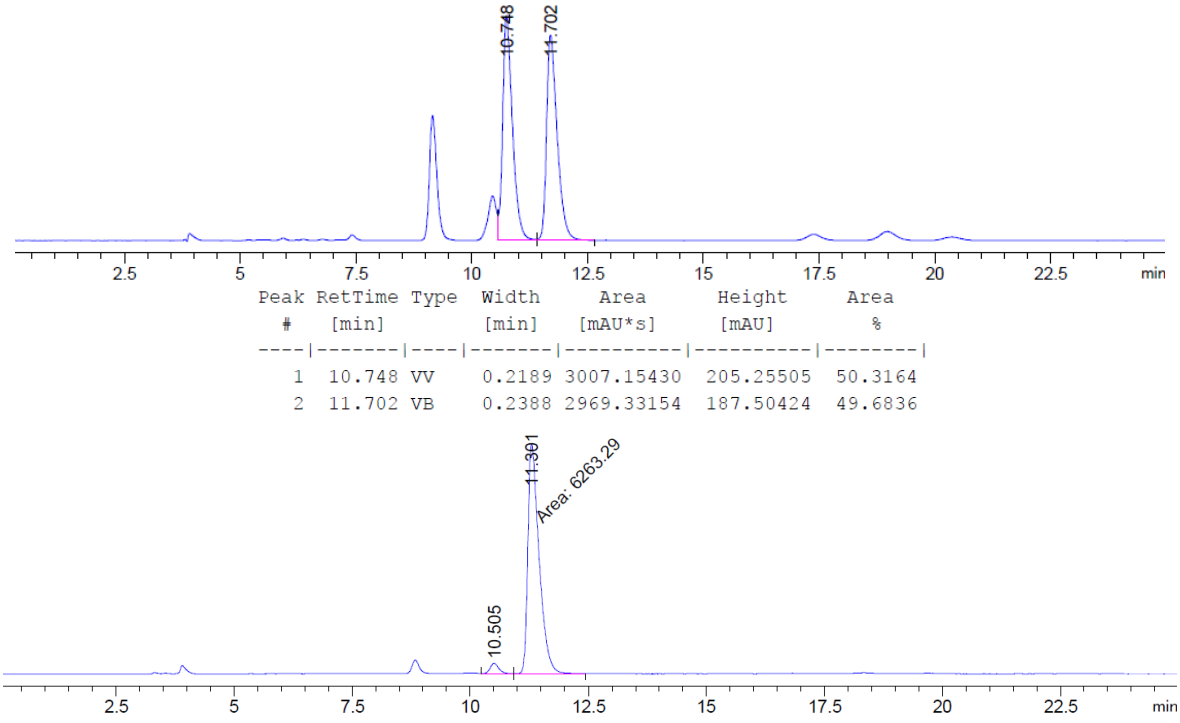
Peak No	% Area	Area	Ret. Time
1	92.9347	9368.3411	15.68 min
2	7.0653	712.2242	17.25 min

(*S*)-9-Methyl-8,9,10,11-tetrahydrobenzo[*g*]pyrido[1,2-*a*]indole (**2j**):



Obtained as white solid in 85% (20 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 8.25 (d, *J* = 8.7 Hz, 1 H), 7.97 (dd, *J* = 8.1, 1.3 Hz, 1 H), 7.79 (d, *J* = 8.3 Hz, 1 H), 7.58 (d, *J* = 8.3 Hz, 1 H), 7.47 – 7.43 (m, 1 H), 7.37 (ddd, *J* = 7.9, 6.8, 1.0 Hz, 1 H), 6.40 (t, *J* = 1.1 Hz, 1 H), 4.21 (ddd, *J* = 11.3, 6.1, 2.7 Hz, 1 H), 3.78 (td, *J* = 11.2, 5.4 Hz, 1 H), 2.79 (ddd, *J* = 15.7, 4.4, 2.1 Hz, 1 H), 2.25 (ddd, *J* = 15.6, 10.9, 1.4 Hz, 1 H), 1.49 – 1.37 (m, 2 H), 1.07 (dtd, *J* = 13.2, 11.5, 6.1 Hz, 1 H), 0.76 (d, *J* = 6.6 Hz, 3 H) ppm; **^{13}C NMR (201 MHz, C_6D_6)** δ = 135.0, 131.3, 129.5, 129.4, 125.7, 124.7, 123.8, 122.3, 121.1, 122.0, 120.7, 99.9, 46.0, 33.9, 31.5, 26.1, 20.7 ppm; **IR (ATR):** $\tilde{\nu}$ 2957, 2920, 2867, 2183, 2169, 2157, 1521, 1450, 1414, 1375, 1352, 1343, 1318, 1383, 1262, 1205, 1132, 1004, 975, 953, 939, 920, 892, 854, 820, 808, 782, 762, 741, 688, 665, 632,623, 594, 584 cm^{-1}; **HRMS (ESI)** calculated for $[C_{17}H_{17}N+H]^+$: 236.1434, found: 236.1434; **R_f:** 0.3 (pentane:EtOAc 80:1); **$[\alpha]_D^{20}$:** 69.5 (*c* = 0.1, CH_2Cl_2); **m.p.:** 114-118 °C.

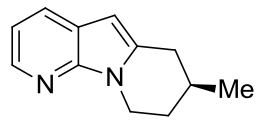
Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 99:1, 1.0 mL/min, 282 nm; t_R (minor) = 10.5 min, t_R (major) = 11.3 min), 96.6:3.4 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.748	VV	0.2189	3007.15430	205.25505	50.3164
2	11.702	VB	0.2388	2969.33154	187.50424	49.6836

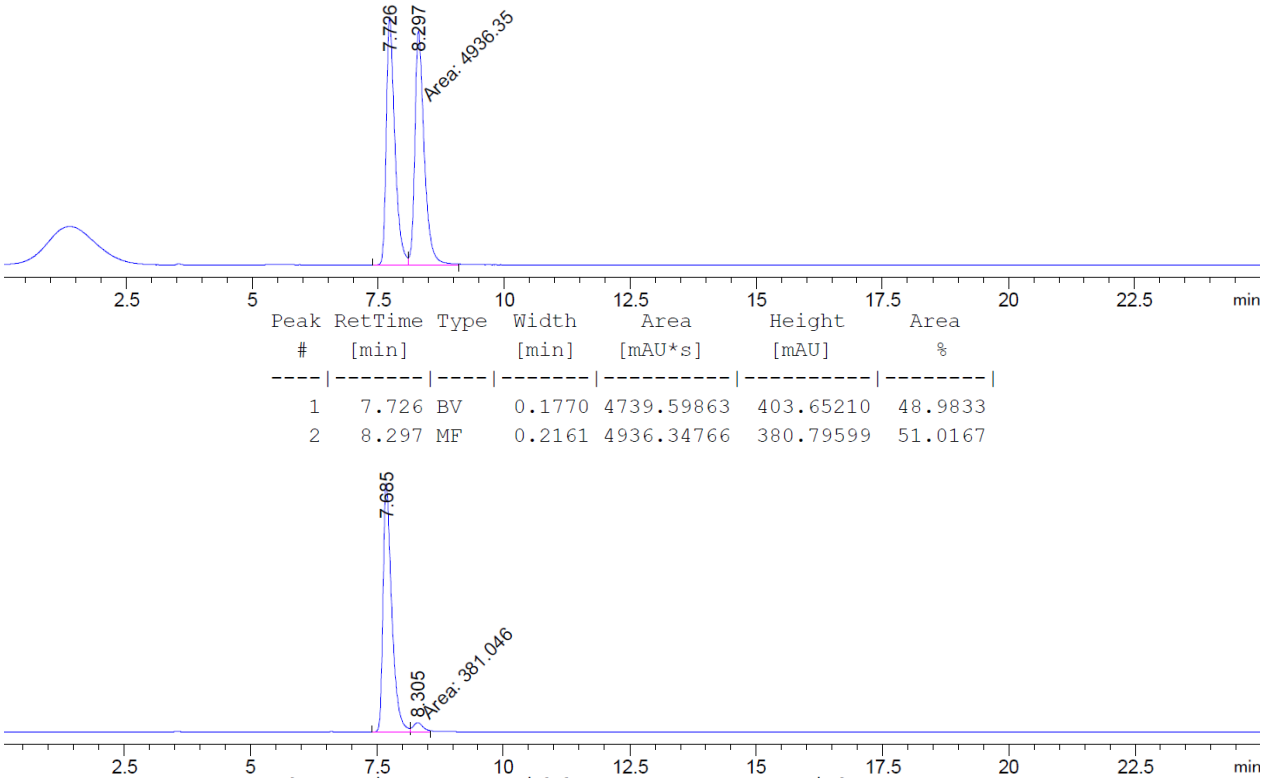
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.505	VB	0.1969	221.86896	17.15424	3.4212
2	11.301	MF	0.2747	6263.28662	379.96674	96.5788

(*S*)-7-methyl-6,7,8,9-tetrahydropyrido[3,2-*b*]indolizine (**2k**):



Obtained as white solid in 91% (17 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 8.46 (dd, *J* = 4.7, 1.6 Hz, 1 H), 7.67 (dd, *J* = 7.7, 1.6 Hz, 1 H), 6.90 (dd, *J* = 7.7, 4.7 Hz, 1 H), 6.08 (t, *J* = 1.2 Hz, 1 H), 4.43 (ddd, *J* = 12.7, 5.7, 2.9 Hz, 1 H), 3.64 (ddd, *J* = 12.7, 11.4, 4.8 Hz, 1 H), 2.73 – 2.55 (m, 1 H), 2.12 (ddd, *J* = 16.3, 10.7, 1.5 Hz, 1 H), 1.45 – 1.28 (m, 2 H), 1.13 – 0.95 (m, 1 H), 0.68 (d, *J* = 6.5 Hz, 3 H) ppm; **^{13}C NMR (201 MHz, C_6D_6)** δ = 148.3, 141.5, 137.5, 126.4, 121.0, 115.8, 95.5, 40.5, 32.3, 30.5, 27.3, 20.8 ppm; **IR (ATR):** $\tilde{\nu}$ 3068, 3046, 2951, 2927, 2870, 1594, 1573, 1540, 1481, 1438, 1428, 1402, 1371, 1352, 1308, 1290, 1167, 795, 770, 746 cm^{-1}; **HRMS (ESI)** calculated for $[C_{12}H_{14}N_2+H]^+$: 187.1230, found: 187.1234; **R_f:** 0.25 (pentane:EtOAc 20:1); **$[\alpha]_D^{20}$:** 26.4 (*c* = 0.1, CH_2Cl_2); **m.p.:** 90-91 °C.

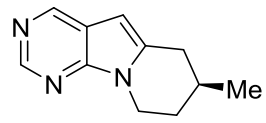
Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 95:5, 1.0 mL/min, 292 nm; t_R (major) = 7.7 min, t_R (minor) = 8.3 min), 95.8:4.2 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.726	BV	0.1770	4739.59863	403.65210	48.9833
2	8.297	MF	0.2161	4936.34766	380.79599	51.0167

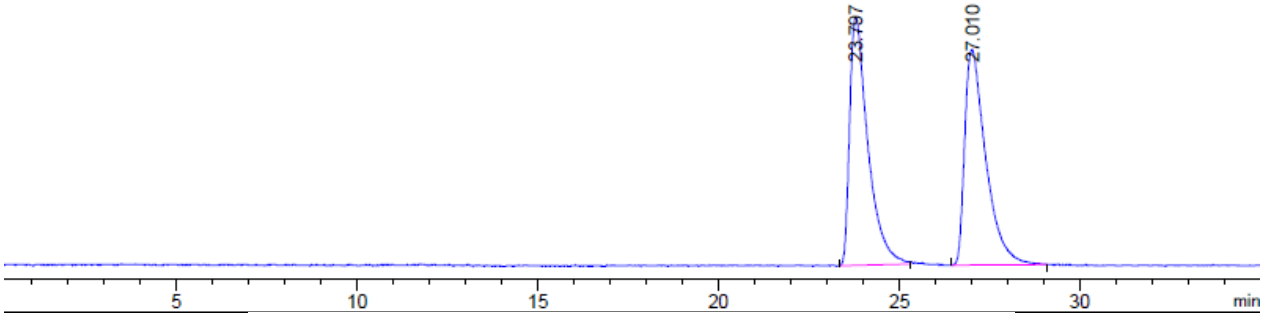
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.685	BV	0.1797	8790.48633	734.06293	95.8453
2	8.305	MF	0.2305	381.04559	27.55416	4.1547

(*S*)-7-methyl-6,7,8,9-tetrahydropyrimido[5,4-b]indolizine (**2l**):

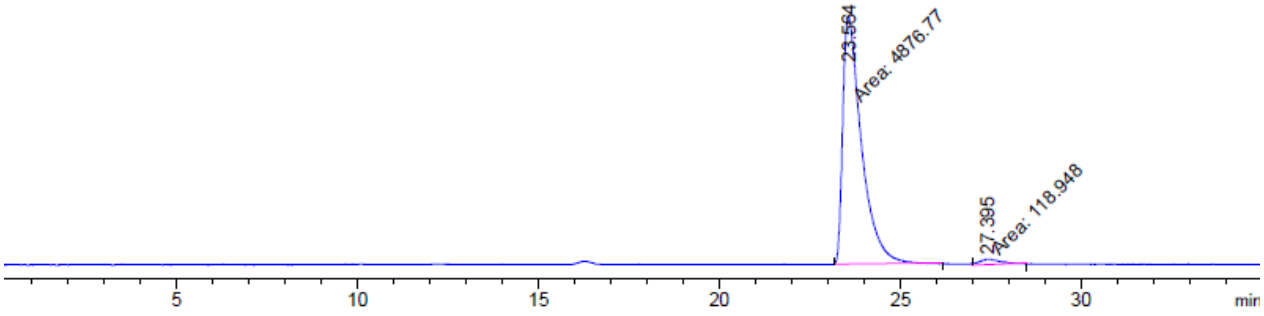


Obtained as white solid in 85% (16 mg). **^{1}H NMR (500 MHz, C_6D_6)** δ = 9.25 (s, 1 H), 8.90 (s, 1 H), 5.84 (t, *J* = 1.2 Hz, 1 H), 4.17 (ddd, *J* = 12.8, 5.7, 2.8 Hz, 1 H), 3.39 (ddd, *J* = 12.8, 11.6, 4.9 Hz, 1 H), 2.47 (ddd, J = 16.5, 4.6, 1.8 Hz, 1 H), 1.93 (ddd, *J* = 16.5, 10.8, 1.6 Hz, 1 H), 1.33 – 1.17 (m, 2 H), 0.94 – 0.81 (m, 1 H), 0.63 (d, *J* = 6.4 Hz, 3 H).ppm; **^{13}C NMR (126 MHz, C_6D_6)** δ = 150.9, 150.9, 147.6, 138.1, 119.3, 94.6, 40.3, 31.9, 30.0, 27.0, 20.7 ppm; **IR (ATR):** $\tilde{\nu}$ 3092, 2955, 2926, 2896, 2870, 1581, 1562, 1542, 1464, 1447, 1432, 1394, 1384, 1355, 1321, 1240, 1173, 1101, 930, 914, 774, 708, 531 cm^{-1}; **HRMS (ESI)** calculated for $[C_{11}H_{13}N_3+H]^+$: 188.1182, found: 188.1183; **R_f:** 0.15 (EtOAc); **$[\alpha]_D^{20}$:** 17.3 (*c* = 0.1, CH_2Cl_2); **m.p.:** 135 °C.

Chiral HPLC: (Chiralpak IC, 4.6 x 250 mm; hexane:*i*-PrOH 70:30, 1.0 mL/min, 274 nm; t_R (major) = 18.6 min, t_R (minor) = 19.8 min), 97.6:2.4 er.

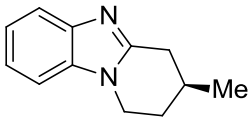


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.794	BB	0.4962	1187.48828	34.27606	49.5317
2	27.009	BB	0.5867	1209.94238	29.86349	50.4683



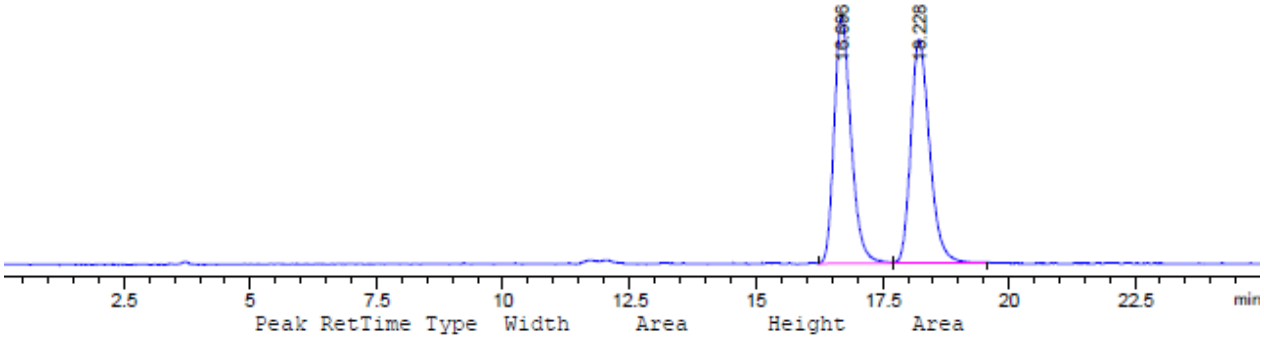
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.564	MM	0.5998	4876.76563	135.51544	97.6190
2	27.395	MM	0.6643	118.94834	2.98425	2.3810

(*S*)-3-Methyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (**2m**):

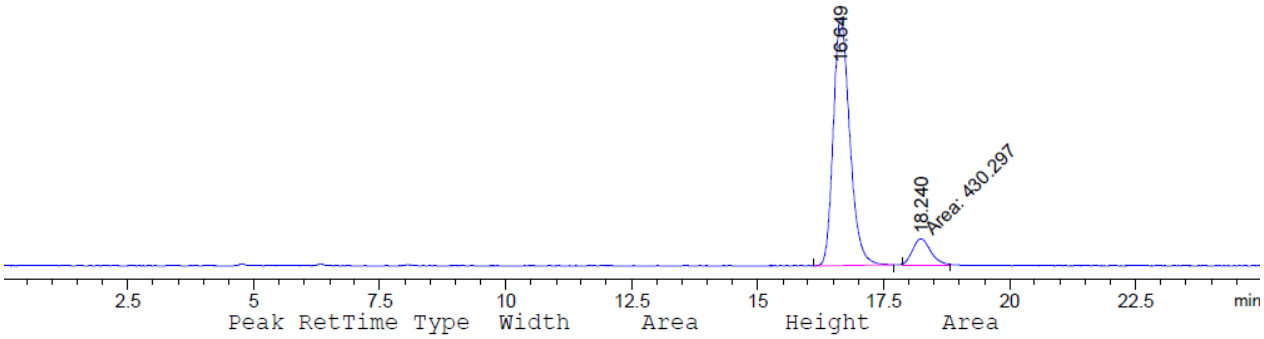


Obtained as white solid in 86% (16 mg). **^{1}H NMR (600 MHz, $CDCl_3$)** δ = 7.71 (d, *J* = 7.4 Hz, 1 H), 7.36 – 7.28 (m, 1 H), 7.29 – 7.22 (m, 2 H), 4.24 (s, 1 H), 3.99 (td, *J* = 11.4, 4.9 Hz, 1H), 3.27 (d, J = 17.1 Hz, 1 H), 2.67 (dd, *J* = 17.1, 10.5 Hz, 1 H), 2.25 – 2.13 (m, 2 H), 1.87 – 1.74 (m, 1 H), 1.20 (d, J = 6.5 Hz, 3 H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 151.7, 141.7, 134.1, 122.6, 122.1, 118.6, 109.0, 41.7, 33.1, 30.4, 27.5, 21.1 ppm; **IR (ATR):** $\tilde{\nu}$ 3074, 3051, 2954, 2922, 2865, 1650, 1614, 1514, 1486, 1458, 1417, 1373, 1321, 1285, 1266, 1231, 1165, 1004, 890, 765, 739 cm^{-1}; **HRMS (ESI)** calculated for $[C_{12}H_{14}N_2+H]^+$: 187.1230, found: 187.1225; **R_f:** 0.2 (EtOAc); **$[\alpha]_D^{20}$:** 22.8 (*c* = 0.1, CH_2Cl_2); **m.p.:** 128-129 °C.

Chiral HPLC: (Chiralpak IC, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 274 nm; t_R (major) = 16.6 min, t_R (minor) = 18.2 min), 89.6:10.4 er.

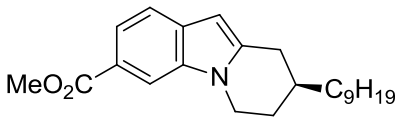


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.696	BV	0.3543	1615.14087	69.70731	49.8488
2	18.228	VB	0.3948	1624.94043	63.02063	50.1512



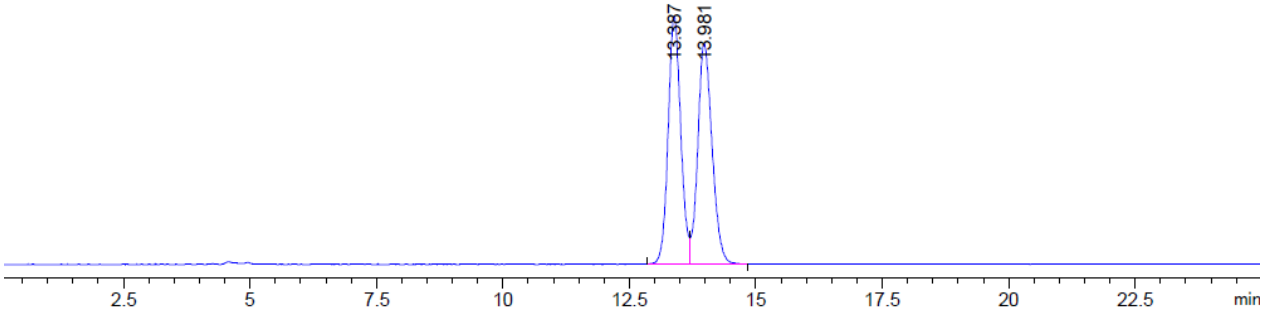
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.649	BB	0.3535	3722.43091	163.54837	89.6382
2	18.240	MM	0.4148	430.29715	17.29127	10.3618

Methyl (*S*)-8-nonyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-3-carboxylate (**2n**):

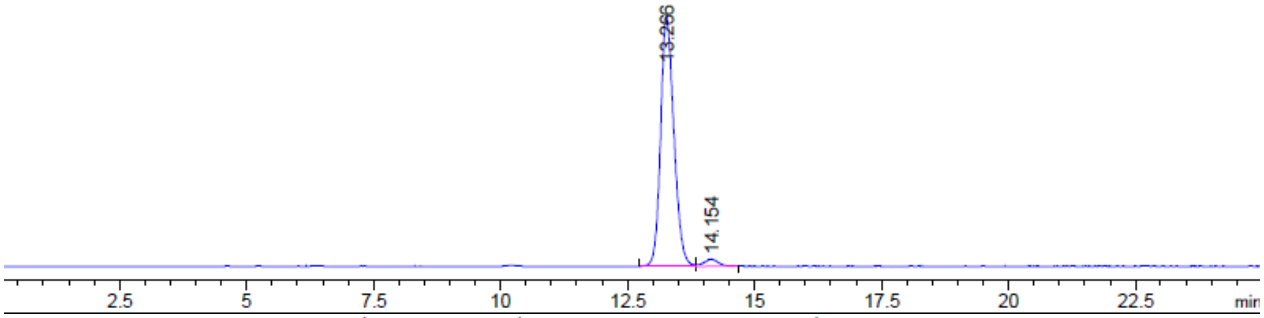


Obtained as white solid in 80% (28.5 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 8.31 (s, 1 H), 8.26 (dd, *J* = 8.3, 1.5 Hz, 1 H), 7.61 (d, *J* = 8.2 Hz, 1 H), 6.19 (d, *J* = 1.2 Hz, 1 H), 3.69 (s, 3 H), 3.51 (ddd, *J* = 11.8, 5.7, 2.9 Hz, 1 H), 3.11 (td, *J* = 11.5, 4.9 Hz, 1 H), 2.73 (ddd, J = 16.4, 4.6, 1.8 Hz, 1 H), 2.11 (ddd, *J* = 16.2, 10.8, 1.4 Hz, 1 H), 1.39 (ddq, *J* = 12.8, 4.9, 2.5 Hz, 1 H), 1.36 – 1.24 (m, 11 H), 1.21 (p, *J* = 6.8 Hz, 2 H), 1.17 – 1.09 (m, 2 H), 1.07 – 0.95 (m, 3 H), 0.93 (t, *J* = 6.8 Hz, 3 H).ppm; **^{13}C NMR (201 MHz, C_6D_6)** δ = 167.9, 140.4, 135.8, 132.6, 122.2, 121.2, 119.2, 111.4, 98.4, 51.1, 41.1, 35.6, 32.1, 32.0, 30.2, 29.8, 29.8 (2C), 29.5, 28.8, 26.7, 22.8, 14.0 ppm; **IR (ATR):** $\tilde{\nu}$ 2923, 2852, 1711, 1612, 1534, 1455, 1433, 1335, 1302, 1233, 1189, 1125, 1090, 998, 882, 828, 776, 738 cm^{-1}; **HRMS (ESI)** calculated for $[C_{23}H_{33}NO_2+H]^+$: 356.2584, found: 356.2589; **R_f:** 0.2 (pentane:EtOAc 20:1); **$[\alpha]_D^{20}$:** 24.3 (*c* = 0.1, CH_2Cl_2); **m.p.:** 64 °C.

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 324 nm; t_R (major) = 13.3 min, t_R (minor) = 14.2 min), 97.1:2.9 er.

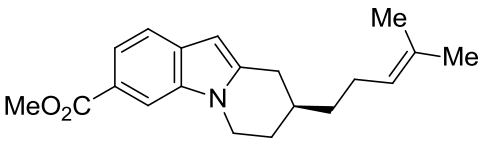


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.387	BV	0.2681	2627.68945	151.68370	49.8450
2	13.981	VB	0.2987	2644.03101	134.87874	50.1550



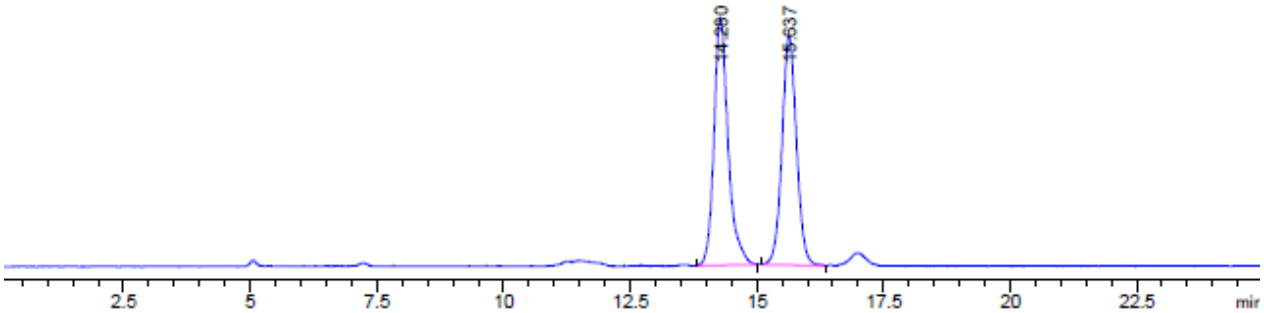
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.266	BV	0.2785	5658.69238	310.68732	97.0673
2	14.154	VB	0.2938	170.96814	8.75621	2.9327

Methyl (*S*)-8-(4-methylpent-3-en-1-yl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-3-carboxylate (**2o**):

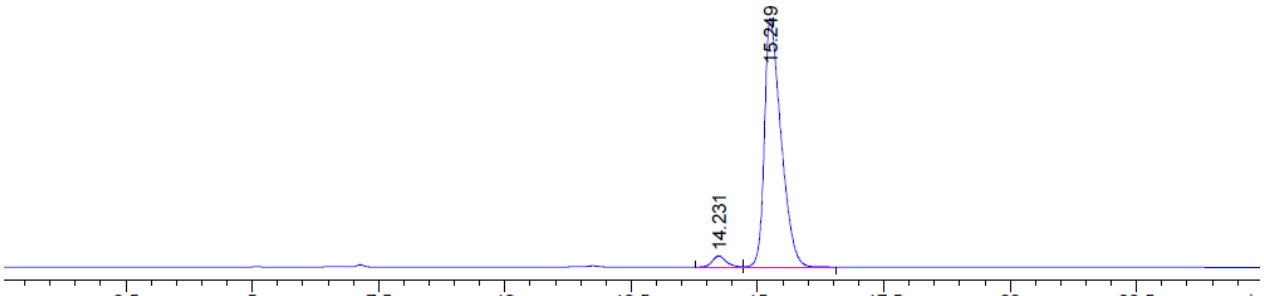


Obtained as white solid in 80% (28.5 mg). **^{1}H NMR (800 MHz, C_6D_6)** δ = 8.29 (s, 1 H), 8.25 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1 H), 6.17 (s, 1 H), 5.16 – 5.06 (m, 1 H), 3.70 (s, 3 H), 3.50 (ddd, *J* = 11.6, 5.7, 3.0 Hz, 1 H), 3.10 (td, *J* = 11.4, 4.9 Hz, 1 H), 2.72 (ddd, *J* = 16.1, 4.7, 1.7 Hz, 1 H), 2.12 (ddd, *J* = 16.1, 10.8, 1.4 Hz, 1 H), 1.96 – 1.83 (m, *J* = 7.3 Hz, 2 H), 1.69 (d, *J* = 1.9 Hz, 3 H), 1.56 (s, 3 H), 1.39 (ddt, *J* = 13.1, 5.0, 2.5 Hz, 1 H), 1.31 (dh, *J* = 13.6, 3.7 Hz, 1 H), 1.11 (qd, *J* = 7.2, 3.5 Hz, 2 H), 1.01 – 0.96 (m, 1 H) ppm; **^{13}C NMR (201 MHz, C_6D_6)** δ = 167.9, 140.4, 135.8, 132.6, 131.2, 124.3, 122.2, 121.2, 119.2, 111.4, 98.4, 51.1, 41.1, 35.6, 31.5, 30.3, 28.7, 25.5, 25.1, 17.4 ppm; **IR (ATR):** $\tilde{\nu}$ 2913, 2853, 1707, 1612, 1533, 1454, 1433, 1418, 1368, 1334, 1302, 1232, 1189, 1170, 1126, 1115, 1086, 996, 828, 776, 738 cm^{-1}; **HRMS (ESI)** calculated for $[C_{20}H_{25}NO_2+H]^+$: 312.1958, found: 312.1958; **R_f:** 0.18 (pentane:EtOAc 20:1); **$[\alpha]_D^{20}$:** -4 (*c* = 0.1, CH_2Cl_2); **m.p.:** 66 °C.

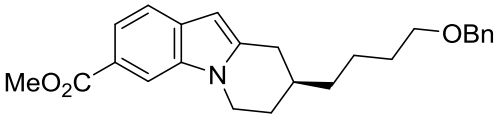
Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 324 nm; t_R (minor) = 14.2 min, t_R (major) = 15.2 min), 96.4:3.6 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.280	BB	0.2930	1392.39880	71.54711	51.4492
2	15.637	BB	0.3076	1313.95984	66.19458	48.5508



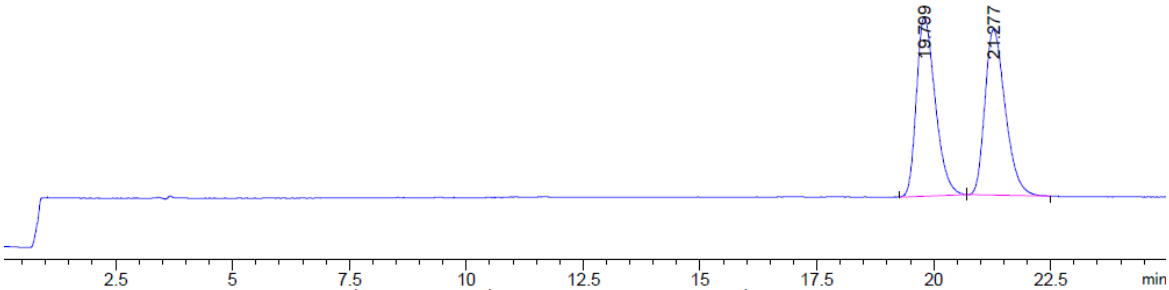
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.231	BV	0.2839	535.08496	27.87713	3.6317
2	15.249	VB	0.3418	1.41985e4	623.22760	96.3683



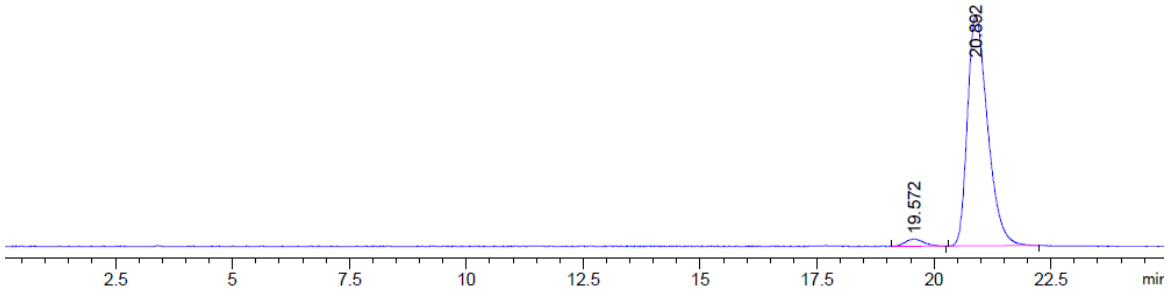
Methyl (*S*)-8-(4-(benzyloxy)butyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-3-carboxylate (**2p**):

Obtained as white solid in 84% (33 mg). **^{1}H NMR (800 MHz, C_6D_6)** δ = 8.30 (d, *J* = 11.3 Hz, 1 H), 8.26 (tt, *J* = 8.0, 1.5 Hz, 1 H), 7.61 (dd, *J* = 8.2, 4.8 Hz, 1 H), 7.34 (d, J = 7.5 Hz, 1 H), 7.21 (t, J = 7.5 Hz, 2 H), 7.16 (s, 1 H), 7.12 (t, *J* = 7.4 Hz, 1 H), 6.17 (d, *J* = 3.9 Hz, 1 H), 4.38 (s, 2 H), 3.70 (d, *J* = 1.3 Hz, 3 H), 3.49 (ddt, *J* = 10.5, 5.0, 2.2 Hz, 1 H), 3.31 (t, *J* = 6.3 Hz, 2 H), 3.09 (td, *J* = 11.5, 4.9 Hz, 1 H), 2.69 (dd, *J* = 16.4, 4.5 Hz, 1 H), 2.12 – 2.01 (m, 1 H), 1.49 (p, *J* = 6.8 Hz, 2 H), 1.38 – 1.33 (m, 1 H), 1.22 (dp, *J* = 14.2, 7.8, 6.7 Hz, 3 H), 1.05 – 0.91 (m, 3 H) ppm; **^{13}C NMR (201 MHz, C_6D_6)** δ = 167.9, 140.5, 139.1, 135.8, 132.6, 128.3, 128.0, 127.4, 122.2, 121.2, 119.6, 111.4, 98.4, 72.8, 69.9, 51.1, 41.1, 35.3, 32.0, 30.3, 30.0, 28.7, 23.4. ppm; **IR (ATR):** $\tilde{\nu}$ 3029, 2932, 2855, 1705, 1612, 1532, 1454, 1432, 1418, 1334, 1302, 1231, 1188, 1113, 1090, 1027, 997, 881, 828, 776, 735, 697 cm^{-1}; **HRMS (ESI)** calculated for $[C_{25}H_{29}NO_3+H]^+$: 392.2220, found: 392.2222; **R_f:** 0.2 (pentane:EtOAc 12:1); **$[\alpha]_D^{20}$:** 33.5 (*c* = 0.1, CH_2Cl_2); **m.p.:** 85-86 °C.

Chiral HPLC: (Chiralpak ID, 4.6 x 250 mm; hexane:*i*-PrOH 90:10, 1.0 mL/min, 294 nm; t_R (minor) = 19.6 min, t_R (major) = 20.9 min), 2.8:97.2 er.

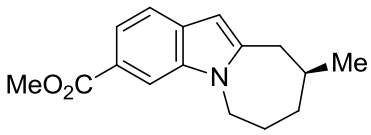


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.799	BB	0.4260	4370.49365	156.43188	49.8496
2	21.277	BB	0.4622	4396.87012	144.83839	50.1504



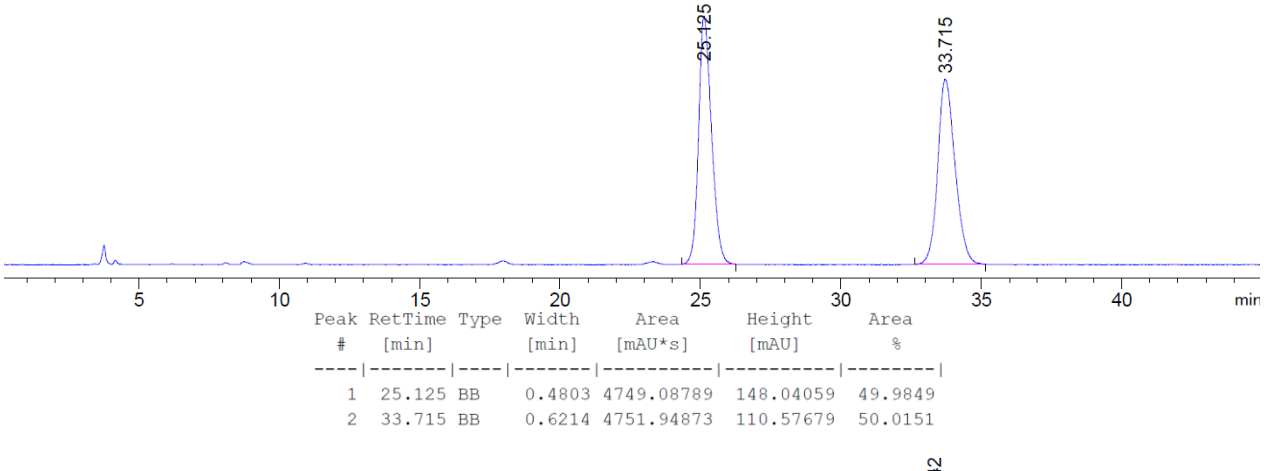
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.572	BB	0.3409	190.22879	6.87277	2.7569
2	20.892	BV	0.4556	6709.76855	223.92914	97.2431

Methyl (*S*)-9-methyl-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]indole-3-carboxylate (**2q**):

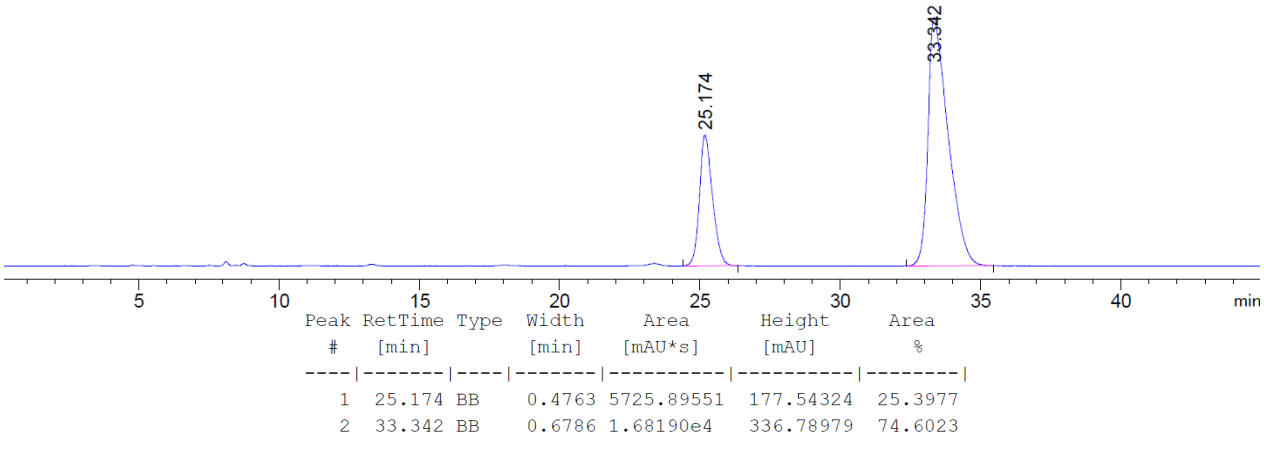


Obtained as white solid in 82% (21 mg). **^{1}H NMR (500 MHz, C_6D_6)** δ = 8.43 (d, *J* = 1.3 Hz, 1 H), 8.30 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.68 (d, *J* = 8.3 Hz, 1 H), 6.31 (s, 1 H), 3.81 (d, *J* = 6.3 Hz, 1 H), 3.78 (s, 3 H), 3.33 (dd, *J* = 14.5, 10.0 Hz, 1 H), 2.67 (dt, *J* = 14.8, 1.6 Hz, 1 H), 2.31 (dd, *J* = 14.7, 9.8 Hz, 1 H), 1.58 – 1.48 (m, 2 H), 1.40 (dtd, *J* = 14.9, 6.8, 2.3 Hz, 1 H), 1.16 – 1.07 (m, 1 H), 1.04 (s, 1 H), 0.81 (d, *J* = 6.7 Hz, 3 H) ppm; **^{13}C NMR (126 MHz, C_6D_6)** δ = 167.8, 144.4, 136.6, 131.9, 122.6, 120.6, 119.5, 111.2, 100.7, 51.1, 43.9, 38.5, 35.8, 32.8, 27.4, 21.9.; **IR (ATR):** $\tilde{\nu}$ 2949, 2925, 2869, 2843, 1707, 1611, 1537, 1460, 1433, 1415, 1353, 1341, 1307, 1275, 1259, 1235, 1207, 1184, 1126, 1115, 1084, 989, 828, 779, 742 cm^{-1}; **HRMS (ESI)** calculated for $[C_{16}H_{19}NO_2+H]^+$: 258.1489, found: 258.1491; **R_f:** 0.2 (pentane:EtOAc 20:1); **$[\alpha]_D^{20}$:** -67.9 (*c* = 0.1, CH_2Cl_2); **m.p.:** 97-98 °C.

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 294 nm; t_R (minor) = 25.17 min, t_R (major) = 33.3 min), 25.4:74.6 er.

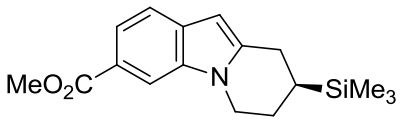


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.125	BB	0.4803	4749.08789	148.04059	49.9849
2	33.715	BB	0.6214	4751.94873	110.57679	50.0151



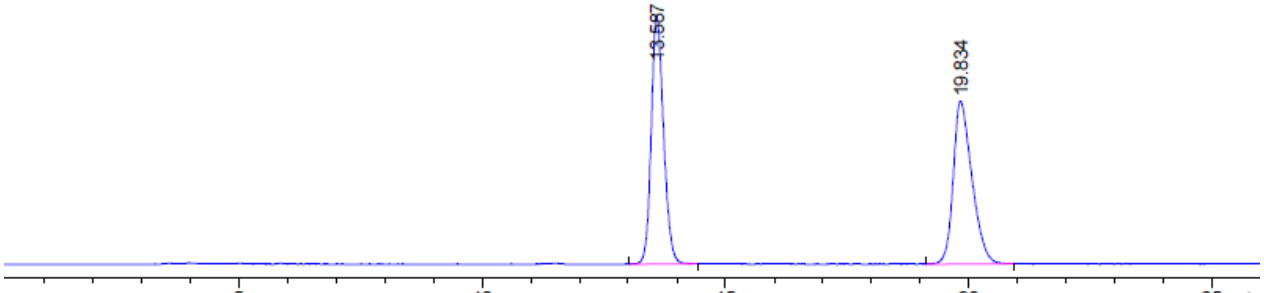
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.174	BB	0.4763	5725.89551	177.54324	25.3977
2	33.342	BB	0.6786	1.68190e4	336.78979	74.6023

Methyl (*S*)-8-(trimethylsilyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-3-carboxylate (**2r**):

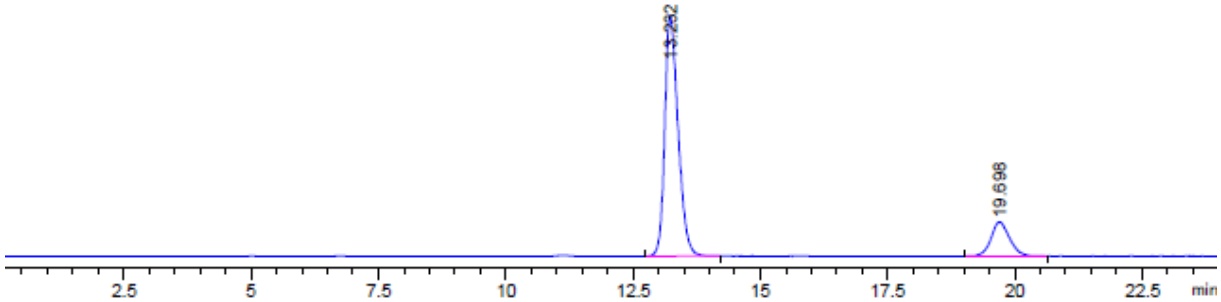


Obtained as white solid in 86% (26 mg). **^{1}H NMR (500 MHz, C_6D_6)** δ = 8.36 (dd, *J* = 1.5, 0.8 Hz, 1 H), 8.27 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.64 (d, J = 8.3 Hz, 1H), 6.20 (d, J = 1.3 Hz, 1H), 3.71 (s, 3 H), 3.59 (ddd, *J* = 11.6, 5.6, 2.1 Hz, 1 H), 3.10 (td, *J* = 11.7, 4.9 Hz, 1 H), 2.72 – 2.61 (m, 1 H), 2.32 (ddd, *J* = 16.6, 12.8, 1.5 Hz, 1 H), 1.46 – 1.34 (m, 1 H), 1.12 – 1.01 (m, 1 H), 0.41 (dd, J = 4.3, 2.3 Hz, 1 H), -0.16 (s, 9 H). ppm; **^{13}C NMR (126 MHz, C_6D_6)** δ = 167.9, 140.7, 135.9, 132.3, 122.2, 121.3, 119.1, 111.1, 98.0, 51.1, 42.4, 24.9, 23.6, 19.3, -4.1. ppm; **IR (ATR):** $\tilde{\nu}$ 2949, 2898, 2874, 283, 1709, 1612, 1529, 1455, 1433, 1417, 1348, 1335, 1300, 1276, 1247, 1231, 1184, 1126, 1117, 1090, 999, 880, 854, 833, 776, 738 cm^{-1}; **HRMS (ESI)** calculated for $[C_{17}H_{23}NO_2Si+H]^+$: 302.1571, found: 302.1570; **R_f:** 0.25 (pentane:EtOAc 50:1); **$[\alpha]_D^{20}$:** 41.3 (*c* = 0.1, CH_2Cl_2); **m.p.:** 114-115 °C.

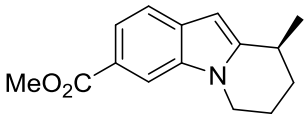
Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 294 nm; t_R (major) = 13.2 min, t_R (minor) = 19.7 min), 83.5:16.5 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.587	BB	0.2671	6274.56299	356.86661	50.1194
2	19.834	BB	0.4000	6244.67822	233.50555	49.8806



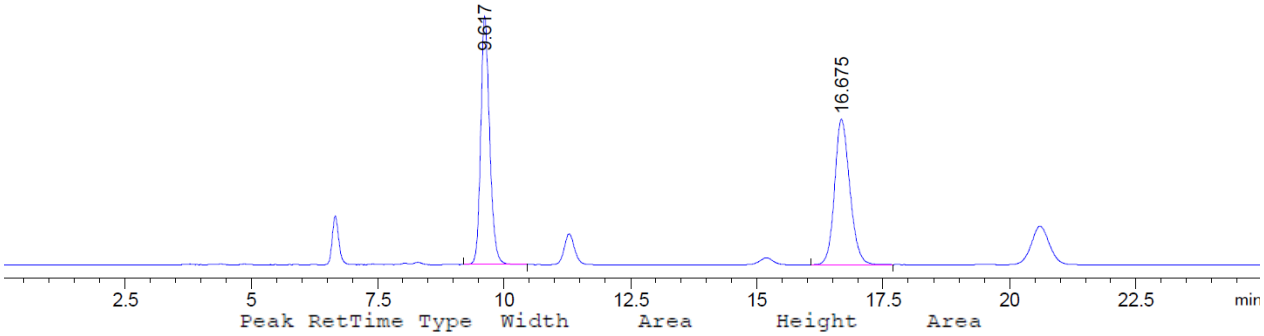
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.232	BB	0.2751	1.02288e4	565.17267	83.5006
2	19.698	BB	0.3710	2021.17419	79.93562	16.4994



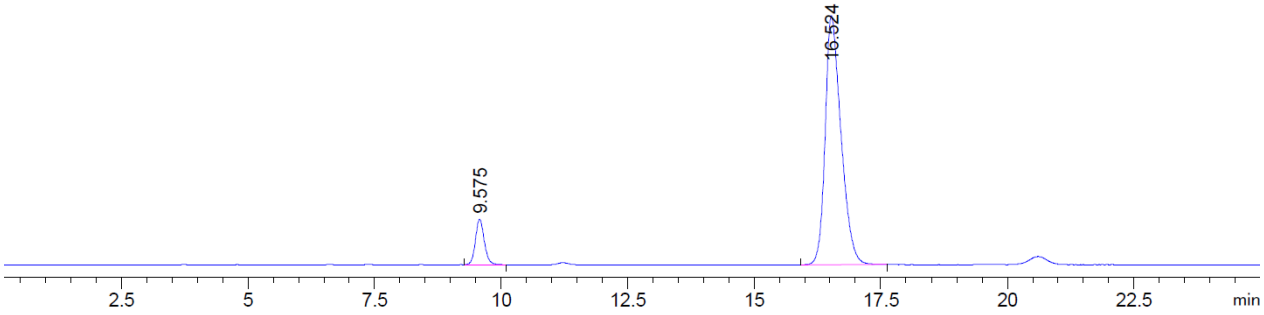
Methyl (*S*)-9-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-3-carboxylate ((+)-**2s**):

Obtained as white solid in 84% (20.5 mg). **^{1}H NMR (400 MHz, C_6D_6)** δ = 8.30 – 8.21 (m, 2 H), 7.60 (d, *J* = 8.7 Hz, 1 H), 6.20 (s, 1 H), 3.69 (s, 3 H), 3.44 – 3.32 (m, 1 H), 3.04 (td, *J* = 11.4, 4.8 Hz, 1 H), 2.61 – 2.45 (m, 1 H), 1.35 (dddd, *J* = 12.9, 10.6, 5.4, 2.5 Hz, 2 H), 1.28 – 1.14 (m, 1 H), 1.11 (d, *J* = 6.9 Hz, 3 H), 0.90 – 0.79 (m, 1 H) ppm; **^{13}C NMR (101 MHz, C_6D_6)** δ = 167.9, 145.8, 135.9, 132.3, 122.4, 121.1, 119.3, 111.5, 97.5, 51.1, 41.5, 29.9, 29.2, 21.9, 20.0 ppm; **IR (ATR):** $\tilde{\nu}$ 2947, 2868, 1707, 1611, 1527, 1456, 1433, 1417, 1358, 1342, 1325, 1299, 1264, 1243, 1206, 1189, 1173, 1118, 1095, 993, 829, 779, 742 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{17}NO_2+H]^+$: 244.1332, found: 244.1335; **R_f:** 0.35 (pentane:EtOAc 50:1); **$[\alpha]_D^{20}$:** 6.2 (*c* = 0.1, CH_2Cl_2); **m.p.:** 102-103 °C.

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 294 nm; t_R (minor) = 9.6 min, t_R (major) = 16.5 min), 90.7:9.3 er.

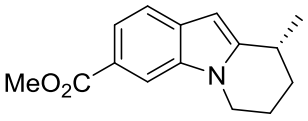


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.587	BB	0.2671	6274.56299	356.86661	50.1194
2	19.834	BB	0.4000	6244.67822	233.50555	49.8806



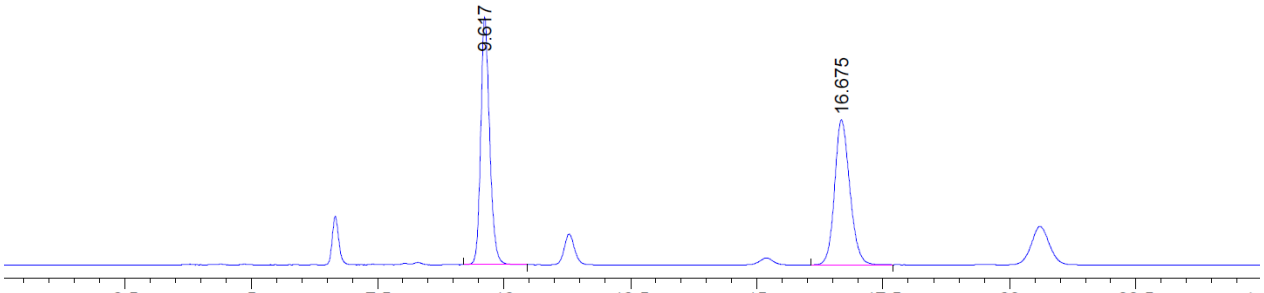
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.575	BB	0.1859	1273.46509	104.71303	9.3010
2	16.524	BB	0.3239	1.24182e4	570.53564	90.6990

Methyl (*R*)-9-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-3-carboxylate ((-)-**2s**):

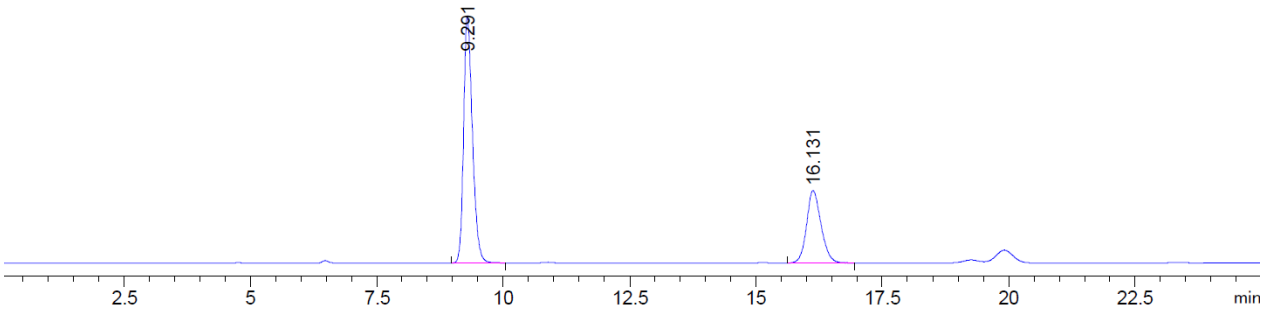


Obtained as white solid in 78% (19 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 8.27 (d, *J* = 8.2 Hz, 2 H), 7.61 (d, *J* = 8.2 Hz, 1 H), 6.21 (s, 1 H), 3.69 (s, 3 H), 3.42 – 3.31 (m, 1 H), 3.02 (td, *J* = 11.3, 4.8 Hz, 1 H), 2.58 – 2.47 (m, 1 H), 1.34 (dddt, *J* = 18.5, 10.5, 5.3, 2.7 Hz, 2 H), 1.19 (ddtt, *J* = 19.3, 8.2, 5.6, 3.3 Hz, 1 H), 1.11 (d, *J* = 6.9 Hz, 3 H), 0.89 – 0.80 (m, 1 H) ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 167.9, 145.8, 135.9, 132.3, 122.4, 121.1, 119.3, 111.5, 97.5, 51.1, 41.5, 29.9, 29.2, 21.9, 20.0 ppm; **IR (ATR):** $\tilde{\nu}$ 2946, 2868, 1708, 1611, 1527, 1457, 1433, 1358, 1342, 1325, 1299, 1264, 1243, 1206, 1118, 1095, 993, 830, 779, 740 cm^{-1}; **HRMS (ESI)** calculated for $[C_{15}H_{17}NO_2+H]^+$: 244.1332, found: 244.1336; **R_f:** 0.35 (pentane:EtOAc 50:1); **$[\alpha]_D^{20}$:** -9.2 (*c* = 0.1, CH_2Cl_2); **m.p.:** 102-103 °C.

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 294 nm; t_R (major) = 9.3 min, t_R (minor) = 16.1 min), 67.4:32.6 er.

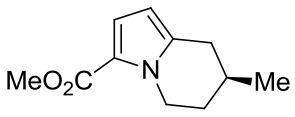


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.587	BB	0.2671	6274.56299	356.86661	50.1194
2	19.834	BB	0.4000	6244.67822	233.50555	49.8806



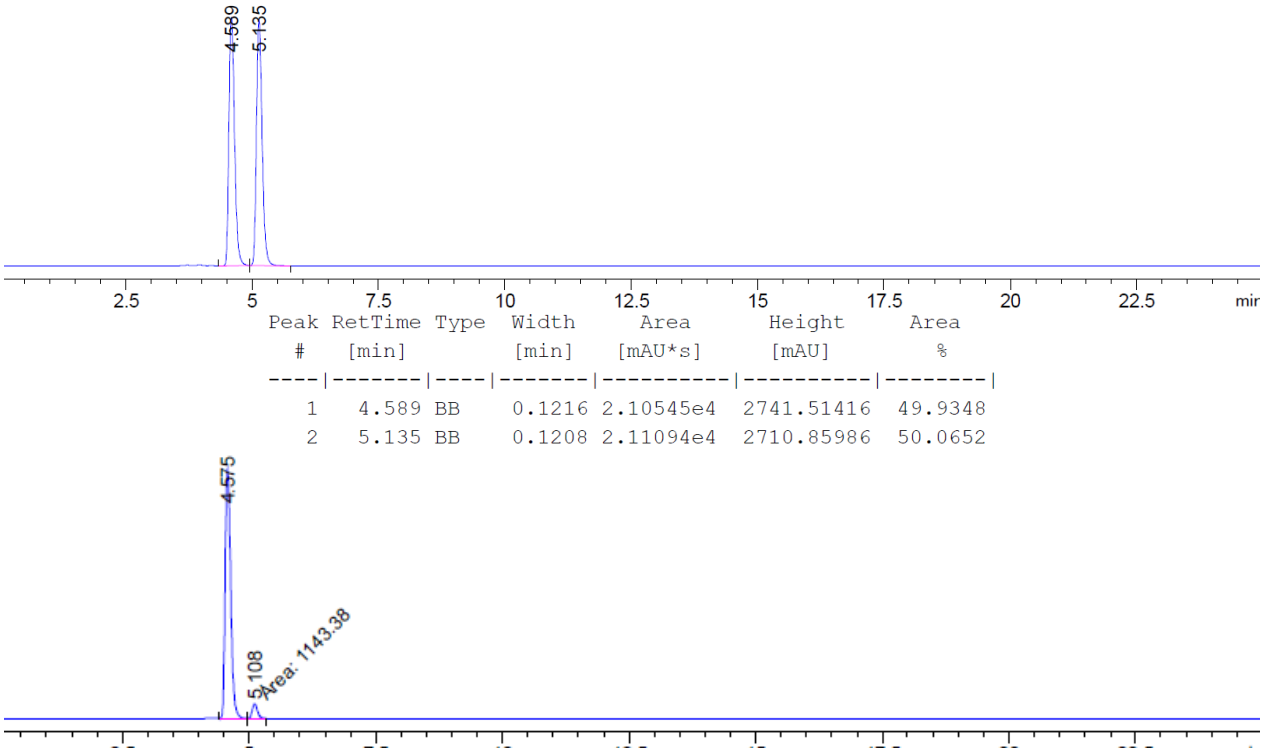
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.291	BB	0.1833	6875.17480	567.54163	67.3952
2	16.131	BB	0.3021	3326.10913	167.15417	32.6048

(*S*)-Methyl 7-methyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (**4a**):



Obtained as colourless oil 78% (15 mg). **^{1}H NMR (400 MHz, C_6D_6)** δ = 7.28 (d, *J* = 3.9 Hz, 1 H), 5.86 (d, *J* = 3.9 Hz, 1 H), 4.67 (ddd, *J* = 14.0, 5.7, 2.8 Hz, 1 H), 3.82 (ddd, *J* = 13.9, 11.5, 4.8 Hz, 1 H), 3.57 (s, 3H), 2.46 (ddd, *J* = 16.3, 4.7, 2.1 Hz, 1 H), 1.92 (dd, *J* = 16.3, 10.5 Hz, 1H), 1.29 (tdd, *J* = 12.4, 6.5, 2.2 Hz, 2 H), 0.95 (dtd, *J* = 13.7, 11.4, 5.5 Hz, 1 H), 0.62 (d, *J* = 6.4 Hz, 3 H). ppm; **^{13}C NMR (101 MHz, C_6D_6)** δ = 161.4, 136.5, 120.8, 117.8, 105.9, 50.1, 44.9, 32.0, 30.9, 26.2, 20.7.ppm; **IR (ATR):** $\tilde{\nu}$ 2951, 2926, 2886, 2871, 1698, 1490, 1470, 1435, 1397, 1337, 1274, 1249, 1223, 1182, 1146, 1075, 1025, 937, 753 cm^{-1}; **HRMS (ESI)** calculated for $[C_{11}H_{15}NO_2+H]^+$: 194.1176, found: 194.1171; **R_f:** 0.3 (pentane:EtOAc 40:1); **$[\alpha]_D^{20}$:** 28.8 (*c* = 0.1, CH_2Cl_2).

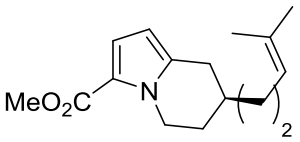
Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 312 nm; t_R (major) = 4.6 min, t_R (minor) = 5.1 min), 94.5:5.5 er.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.589	BB	0.1216	2.10545e4	2741.51416	49.9348
2	5.135	BB	0.1208	2.11094e4	2710.85986	50.0652

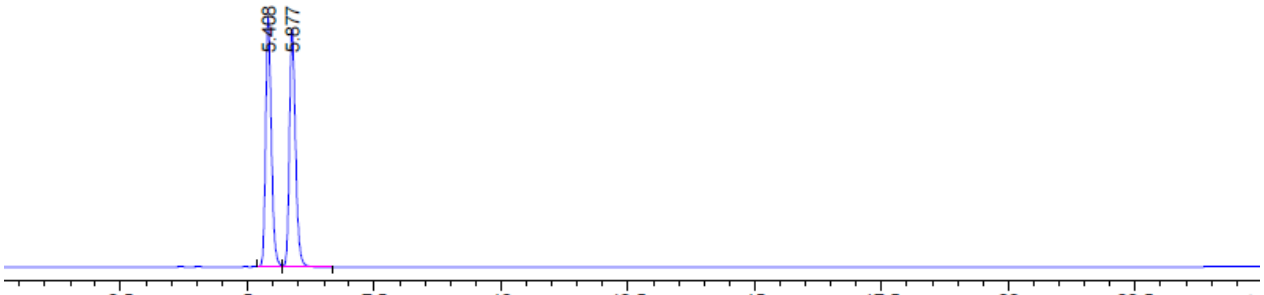
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.575	VV	0.1206	1.97803e4	2604.87524	94.5355
2	5.108	MF	0.1218	1143.37976	156.42924	5.4645

Methyl (*S*)-7-(3-methylbut-2-en-1-yl)-5,6,7,8-tetrahydroindolizine-3-carboxylate (**4b**):

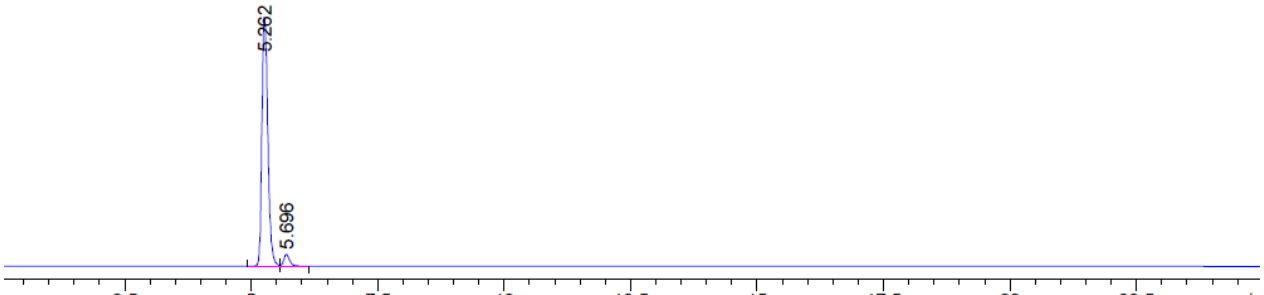


Obtained as colourless oil 73% (19 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.29 (d, *J* = 3.9 Hz, 1 H), 5.88 (d, *J* = 3.8 Hz, 1 H), 5.09 – 5.03 (m, 1 H), 3.81 (ddd, *J* = 13.8, 11.4, 4.9 Hz, 1 H), 3.57 (s, 3 H), 2.59 (ddd, *J* = 16.2, 4.9, 1.8 Hz, 1 H), 1.98 (dd, *J* = 16.2, 10.6 Hz, 1 H), 1.83 (hept, *J* = 7.3 Hz, 2 H), 1.66 (d, *J* = 1.5 Hz, 3 H), 1.51 (s, 3 H), 1.40 (ddq, *J* = 13.0, 5.0, 2.5 Hz, 1 H), 1.24 (dddd, *J* = 13.1, 9.1, 6.6, 3.0 Hz, 1 H), 1.10 – 0.93 (m, 3 H) ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 161.4, 136.5, 131.0, 124.4, 120.7, 117.8, 106.0, 50.1, 45.0, 35.6, 30.7, 30.2, 29.1, 25.5, 25.1, 17.3 ppm; **IR (ATR):** $\tilde{\nu}$ 2913, 2852, 1697, 1490, 1469, 1443, 1435, 1398, 1355, 1324, 1277, 1239, 1220, 1182, 1142, 1075, 1031, 937, 752 cm^{-1}; **HRMS (ESI)** calculated for $[C_{16}H_{23}NO_2+H]^+$: 262.1802, found: 262.1803; **R_f:** 0.35 (pentane:EtOAc 60:1); **$[\alpha]_D^{20}$:** 16.3 (*c* = 0.1, CH_2Cl_2).

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 90:10, 1.0 mL/min, 274 nm; t_R (major) = 5.3 min, t_R (minor) = 5.7 min), 95.5:4.5 er.

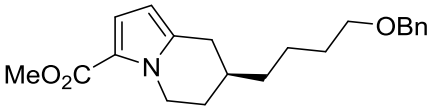


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.408	VV	0.1218	1.60775e4	2043.69385	49.6912
2	5.877	VB	0.1271	1.62773e4	1954.94775	50.3088



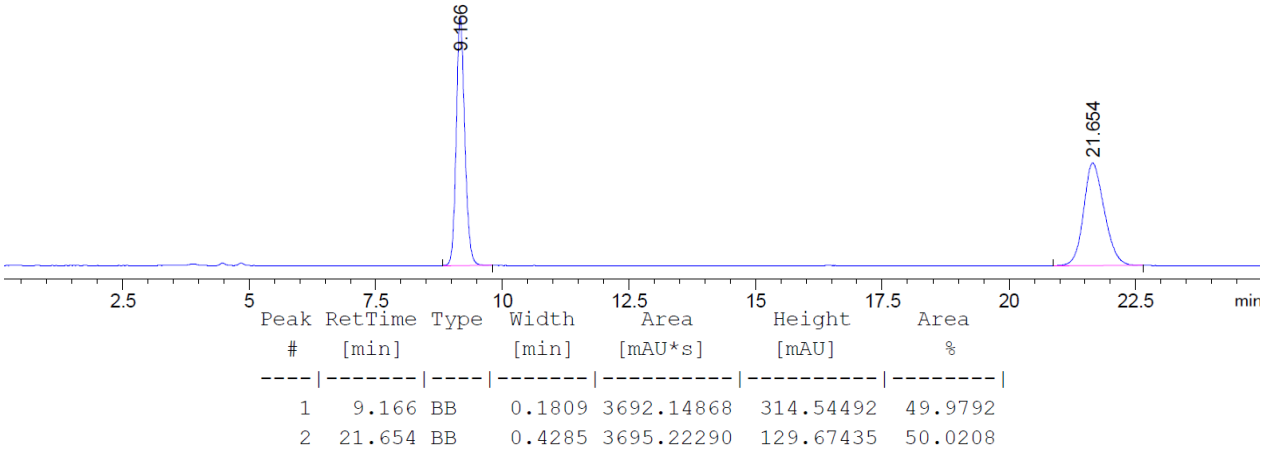
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.262	VV	0.1272	2.14709e4	2630.11621	95.4735
2	5.696	VB	0.1229	1017.96552	125.19469	4.5265

Methyl (*S*)-7-(4-(benzyloxy)butyl)-5,6,7,8-tetrahydroindolizine-3-carboxylate (**4c**):

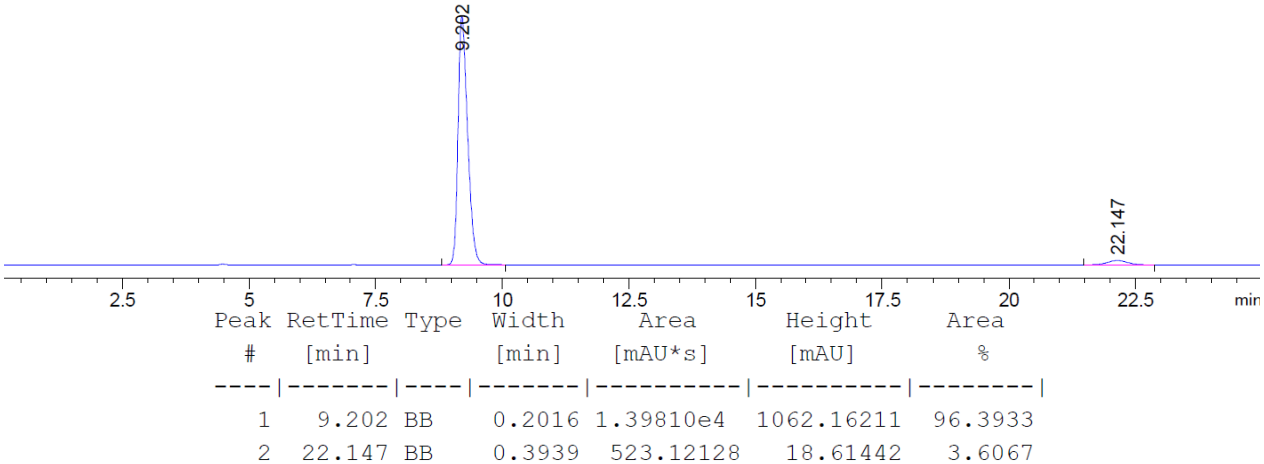


Obtained as colourless oil in 81% (27.5 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.35 – 7.32 (m, 2 H), 7.30 (d, *J* = 3.9 Hz, 1 H), 7.20 (t, *J* = 7.6 Hz, 2 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 5.89 (d, *J* = 3.9 Hz, 1 H), 4.36 (s, 2 H), 3.82 (ddd, *J* = 13.8, 11.4, 4.9 Hz, 1 H), 3.58 (s, 3 H), 3.28 (t, *J* = 6.4 Hz, 2 H), 2.57 (ddd, *J* = 16.3, 4.9, 1.8 Hz, 1 H), 1.95 (dd, *J* = 16.2, 10.6 Hz, 1 H), 1.45 (p, *J* = 7.0 Hz, 2 H), 1.38 (ddq, *J* = 13.0, 5.0, 2.5 Hz, 1 H), 1.17 (tdd, *J* = 13.2, 8.5, 6.1 Hz, 3 H), 1.02 – 0.85 (m, 3 H) ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 161.4, 139.1, 136.6, 128.3, 127.4, 127.4, 120.7, 117.8, 106.0, 72.7, 69.9, 50.1, 45.0, 35.3, 31.1, 30.2, 29.9, 29.2, 23.3; **IR (ATR):** $\tilde{\nu}$ 3029, 2933, 2855, 1696, 1490, 1468, 1443, 1434, 1357, 1320, 1273, 1247, 1225, 1182, 1145, 1101, 1027, 936, 751, 697 cm^{-1}; **HRMS (ESI)** calculated for $[C_{21}H_{27}NO_3+H]^+$: 342.2064, found: 342.2056; **R_f:** 0.2 (pentane:EtOAc 60:1); **$[\alpha]_D^{20}$:** 55.2 (*c* = 0.1, CH_2Cl_2).

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 80:20, 1.0 mL/min, 274 nm; t_R (major) = 9.2 min, t_R (minor) = 22.1 min), 96.4:3.6 er.

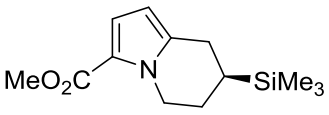


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.166	BB	0.1809	3692.14868	314.54492	49.9792
2	21.654	BB	0.4285	3695.22290	129.67435	50.0208



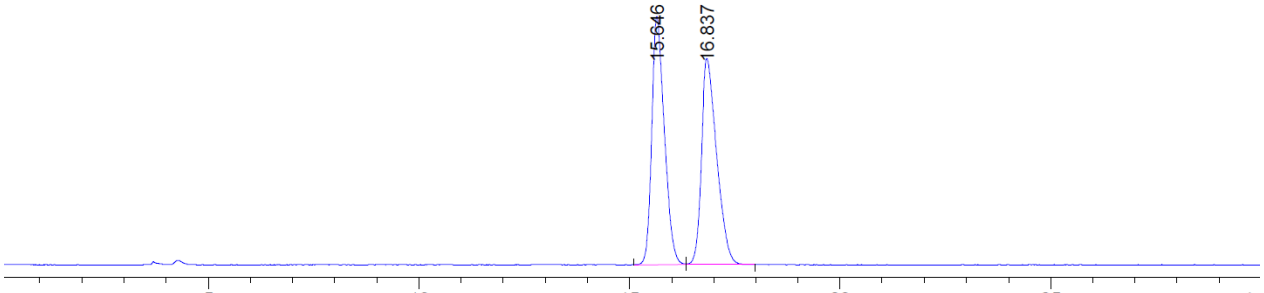
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.202	BB	0.2016	1.39810e4	1062.16211	96.3933
2	22.147	BB	0.3939	523.12128	18.61442	3.6067

Methyl (*S*)-7-(trimethylsilyl)-5,6,7,8-tetrahydroindolizine-3-carboxylate (**4d**):

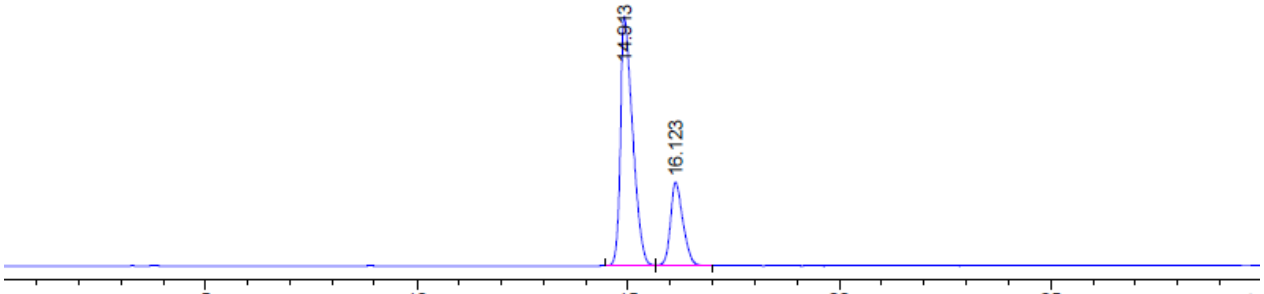


Obtained as colourless oil in 76% (19 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.33 (d, *J* = 3.9 Hz, 1 H), 5.91 (d, *J* = 3.9 Hz, 1 H), 3.74 (td, *J* = 12.8, 4.8 Hz, 1 H), 3.61 (s, 3 H), 2.52 (ddd, *J* = 16.5, 4.7, 1.8 Hz, 1 H), 2.20 (dd, *J* = 16.4, 12.7 Hz, 1 H), 1.46 – 1.32 (m, H), 1.10 – 0.98 (m, 1 H), 0.35 (tdd, *J* = 12.8, 4.7, 2.3 Hz, 1 H), -0.20 (s, 9 H). ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 161.4, 136.9, 120.7, 117.6, 105.9, 50.1, 46.1, 24.7, 23.9, 18.2, -4.2. ppm; **IR (ATR):** $\tilde{\nu}$ 2950, 2847, 1699, 1490, 1467, 1441, 1396, 1346, 1324, 1311, 1244,1216, 1182, 1165, 1138, 1059, 1023, 925, 881, 835, 750, 690 cm^{-1}; **HRMS (ESI)** calculated for $[C_{13}H_{21}NO_2Si+H]^+$: 252.1414, found: 252.1413; **R_f:** 0.3 (pentane:EtOAc 60:1); **$[\alpha]_D^{20}$:** 15.4 (*c* = 0.1, CH_2Cl_2).

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 98:2, 1.0 mL/min, 276 nm; t_R (major) = 14.9 min, t_R (minor) = 16.1 min), 74.4:25.6 er.

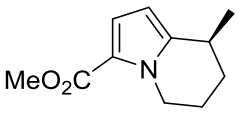


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.646	BV	0.3150	1.02937e4	494.23776	50.0262
2	16.837	VB	0.3740	1.02829e4	410.79575	49.9738



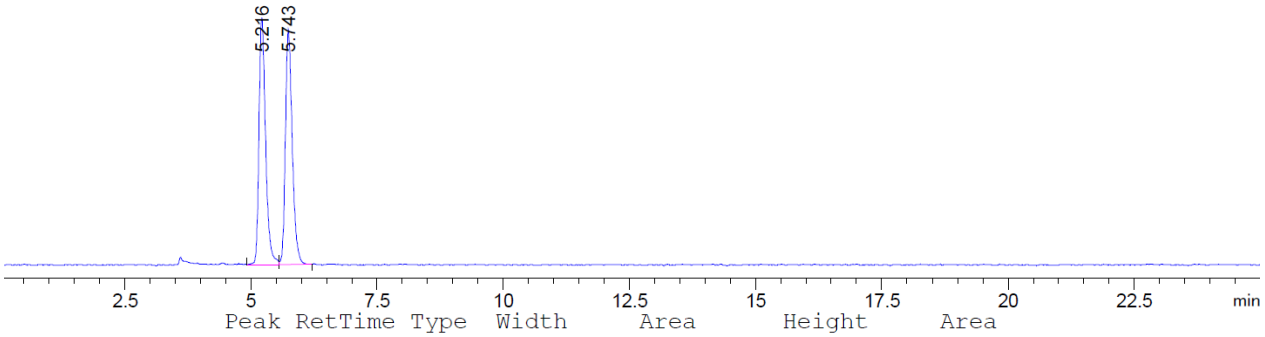
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.913	BV	0.2999	1.84862e4	922.20782	74.4386
2	16.123	VB	0.3078	6347.95557	308.88663	25.5614

Methyl (*S*)-8-methyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (**4e**):

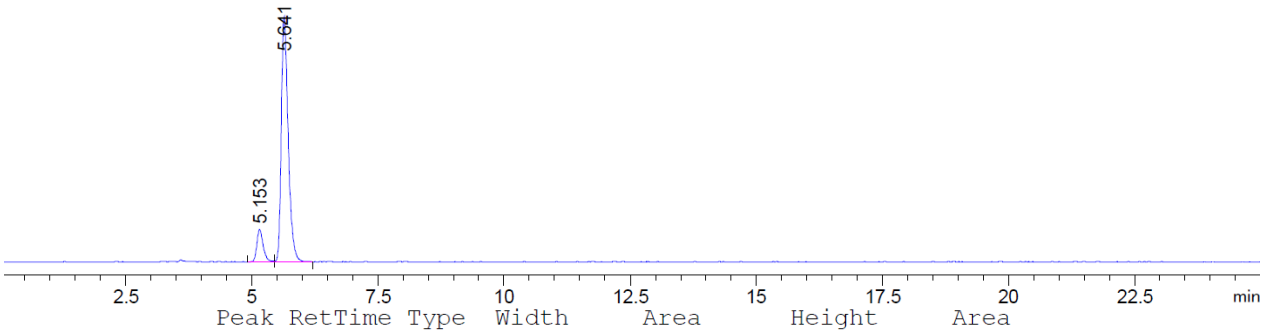


Obtained as colourless oil in 72% (14 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.28 (d, *J* = 4.0 Hz, 1 H), 5.96 (dd, *J* = 4.0, 1.0 Hz, 1 H), 4.55 – 4.47 (m, 1 H), 3.85 (dddd, *J* = 19.0, 14.0, 10.1, 5.0 Hz, 1 H), 3.57 (s, 3 H), 2.48 – 2.39 (m, 1 H), 1.43 – 1.34 (m, 1 H), 1.33 – 1.28 (m, 1 H), 1.26 – 1.18 (m, 1 H), 1.02 (d, *J* = 6.9 Hz, 3 H), 0.88 – 0.78 (m, 1 H) ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 161.5, 142.0, 120.7, 117.7, 105.1, 50.1, 45.3, 29.6, 28.5, 22.2, 20.4 ppm; **IR (ATR):** $\tilde{\nu}$ 2948, 2861, 1697, 1536, 1486, 1473, 1433, 1355, 1323, 1305, 1233, 1215, 1149, 1076, 948, 919, 752 cm^{-1}; **HRMS (ESI)** calculated for $[C_{11}H_{15}NO_2+H]^+$: 194.1176, found: 194.1170; **R_f:** 0.2 (pentane:EtOAc 40:1); **$[\alpha]_D^{20}$:** -17.6 (*c* = 0.1, CH_2Cl_2).

Chiral HPLC: (Chiralpak IB, 4.6 x 250 mm; hexane:*i*-PrOH 98:2, 1.0 mL/min, 292 nm; t_R (minor) = 5.2 min, t_R (major) = 5.6 min), 89.1:10.9 er.

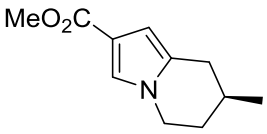


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.216	BV	0.1382	646.19110	70.95435	50.4789
2	5.743	VB	0.1438	633.93127	67.34781	49.5211



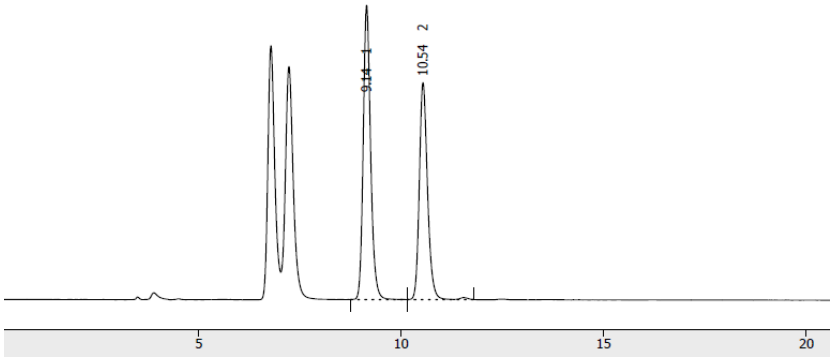
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.153	BV	0.1321	269.03897	30.75523	10.9366
2	5.641	VB	0.1450	2190.94849	230.19301	89.0634

Methyl (*S*)-7-methyl-5,6,7,8-tetrahydroindolizine-2-carboxylate (**4f**):

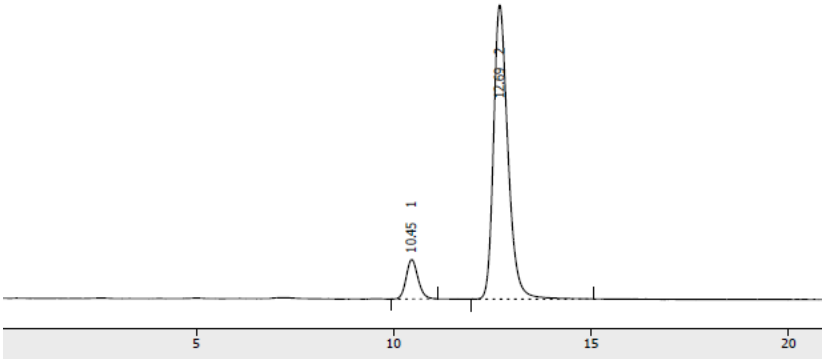


Obtained as colourless oil in 57% (11 mg). **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.11 (d, *J* = 1.7 Hz, 1 H), 6.60 (q, *J* = 1.3 Hz, 1 H), 3.13 (ddd, *J* = 12.4, 5.5, 2.9 Hz, 1 H), 3.00 (td, *J* = 12.0, 4.7 Hz, 1 H), 2.46 – 2.33 (m, 1 H), 1.89 – 1.81 (m, 1 H), 1.26 – 1.17 (m, 1 H), 1.08 (ddq, *J* = 13.0, 4.7, 2.6 Hz, 1 H), 0.83 (dtd, *J* = 13.2, 11.4, 5.5 Hz, 1 H), 0.62 (d, *J* = 6.6 Hz, 3 H) ppm; **^{13}C NMR (151 MHz, C_6D_6)** δ = 165.0, 129.6, 123.9, 116.0, 106.0, 50.2, 44.4, 31.1, 30.9, 27.3, 20.8 ppm; **IR (ATR):** $\tilde{\nu}$ 2951, 2928, 2895, 2872, 2841, 1712, 1522, 1451, 1443, 1389, 1276, 1245, 1205, 1139, 1091, 1000, 928, 820, 773, 751 cm^{-1}; **HRMS (ESI)** calculated for $[C_{11}H_{15}NO_2+H]^+$: 194.1176, found: 194.1181; **R_f:** 0.2 (pentane:EtOAc 40:1); **$[\alpha]_D^{20}$:** 26.6 (*c* = 0.1, CH_2Cl_2).

Chiral HPLC: (Chiralpak OJH, 4.6 x 250 mm; hexane:*i*-PrOH 90:10, 1.0 mL/min, 254 nm; t_R (minor = 10.5 min, t_R (major) = 12.7 min), 90.1:9.9 er.



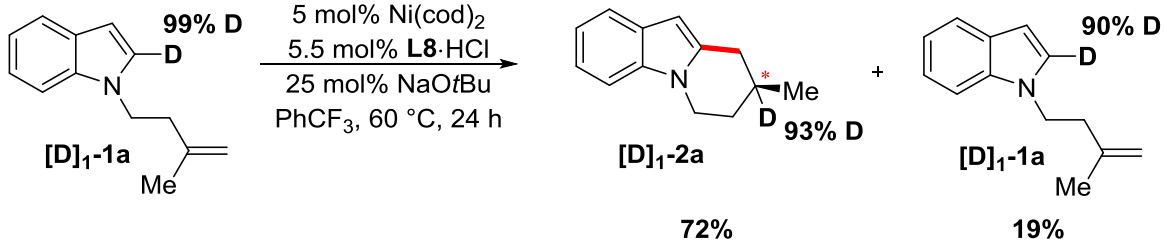
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]
1	9.144	1408.225	111.022	54.9	57.6
2	10.537	1156.908	81.855	45.1	42.4



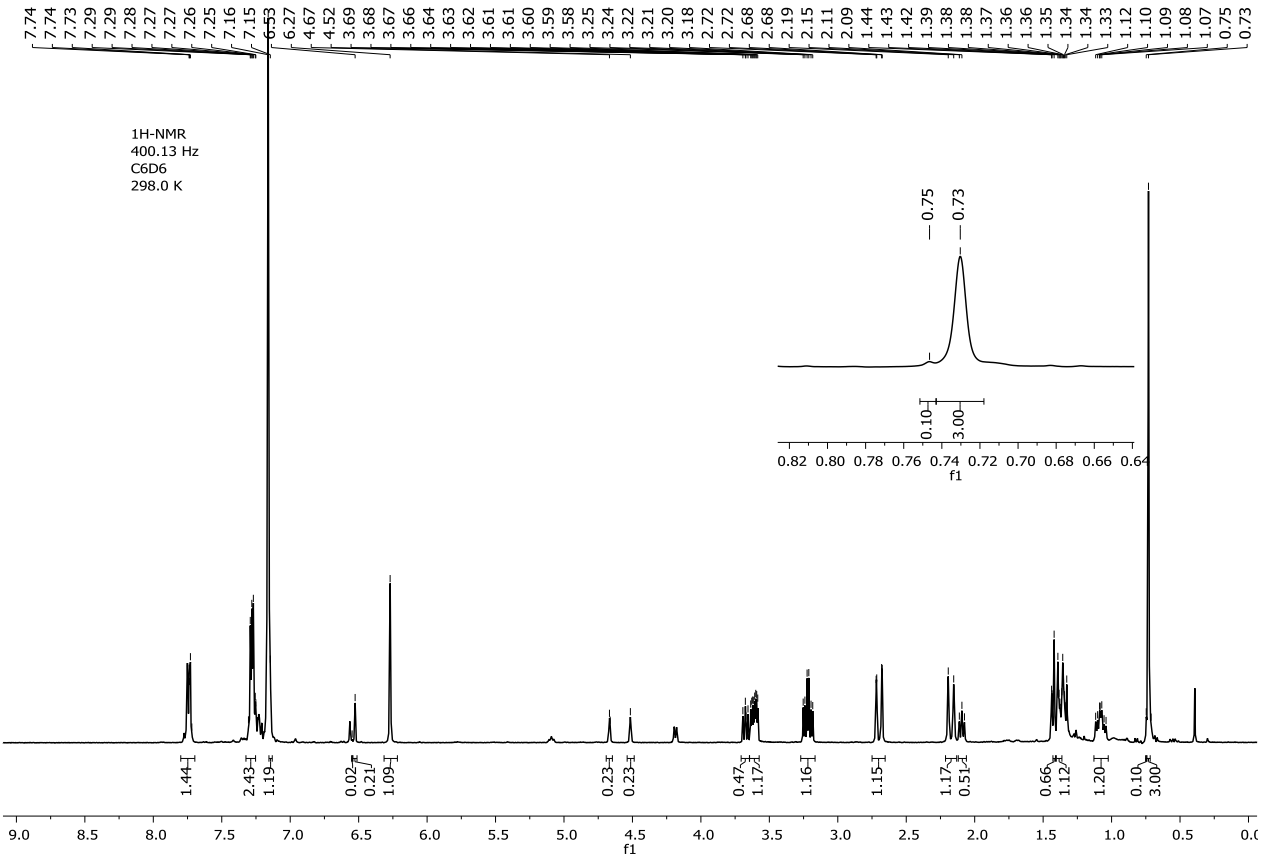
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]
1	10.455	202.063	9.715	9.9
2	12.685	1839.260	72.432	90.1

Mechanistic Studies

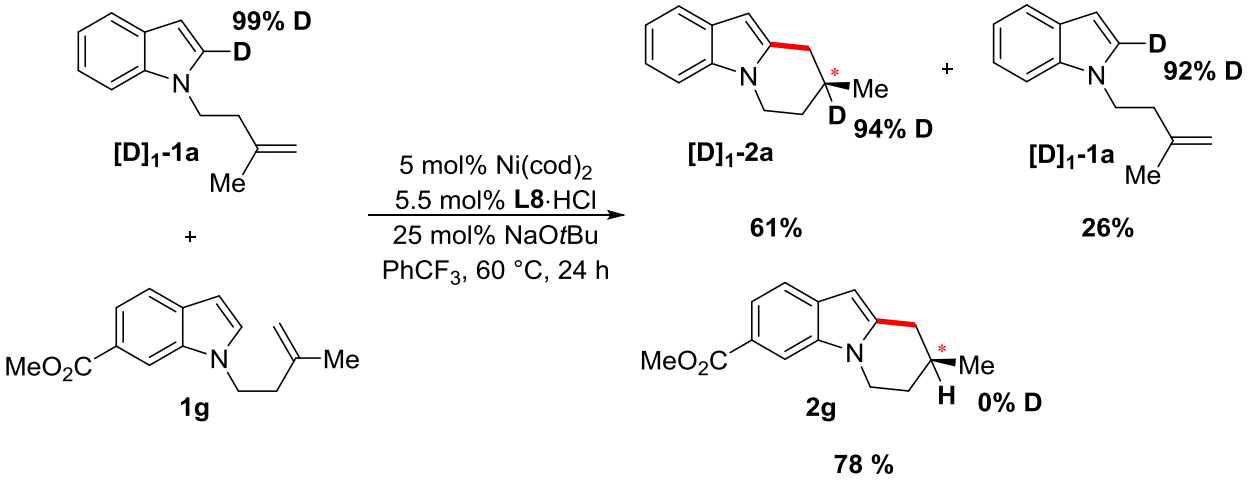
Deuterium labeling experiment



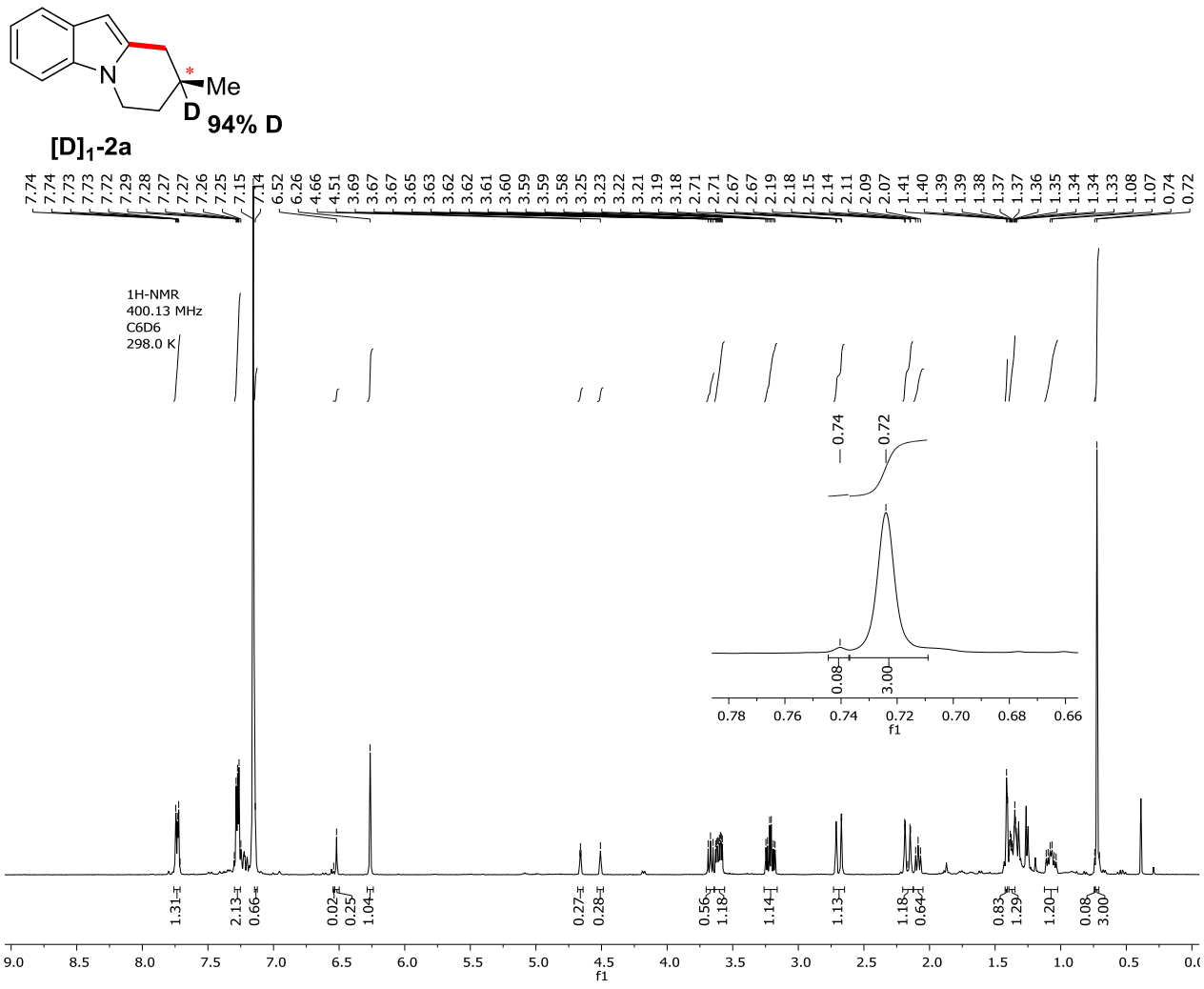
Inside a glove box a tube containing a magnetic stirring bar was charged with $Ni(cod)_2$ (1.4 mg, 5 mol%), **L8**•HCl (6.3 mg, 5.5 mol%), NaO*t*Bu (2.4 mg, 25 mol%) and **$[D]_1$-1a** (0.1 mmol). The mixture was dissolved in $PhCF_3$ (0.2 mL) and was stirred for 24 h at 60 °C. Subsequently the reaction mixture was cooled to ambient temperature, was filtered over a short plug of silica gel (EtOAc), and was concentrated under reduced pressure to afford the crude product, which was purified by silica gel column (Pentane/EtOAc) to afford the mixture of product and reisolated starting material as a white solid in 91 % (17 mg) yield.

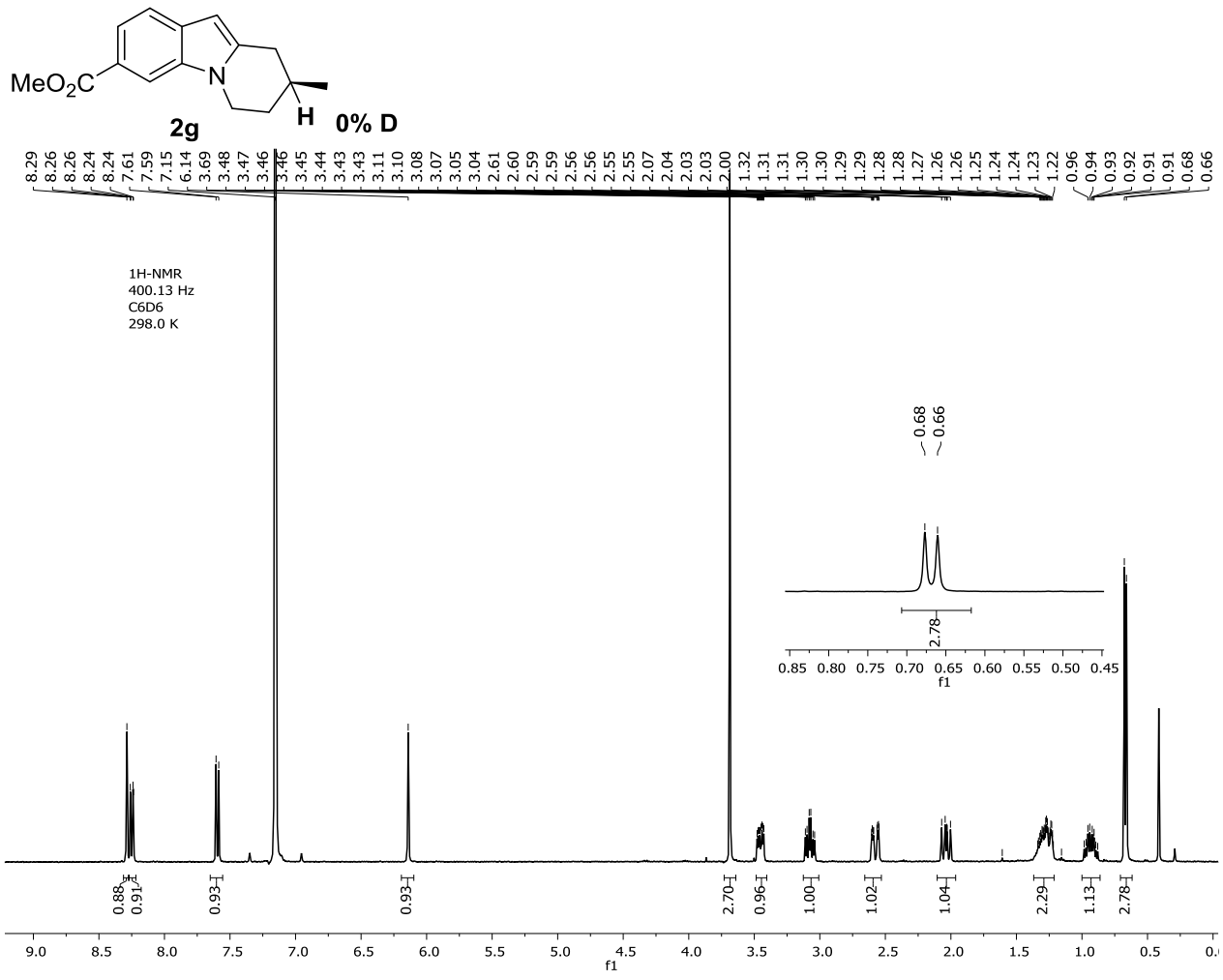


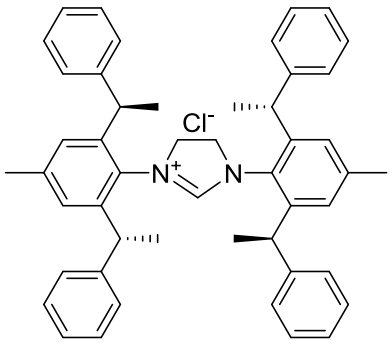
Deuterium scrambling experiment



Inside a glove box a tube containing a magnetic stirring bar was charged with $Ni(cod)_2$ (1.4 mg, 5 mol%), **L8**•HCl (6.3 mg, 5.5 mol%), NaO*t*Bu (2.4 mg, 25 mol%), **[D]$_1$-1a** (0.05 mmol) and **1g** (0.05 mmol). The mixture was dissolved in $PhCF_3$ (0.2 mL) and was stirred for 24 h at 60 °C. Subsequently the reaction mixture was cooled to ambient temperature, was filtered over a short plug of silica gel (EtOAc), and was concentrated under reduced pressure to afford the crude product, which was purified by silica gel column (Pentane/EtOAc) to afford **[D]$_1$-2a** as a white solid in 61 % (6 mg) yield and **2g** as a white solid in 78 % (9.5 mg).

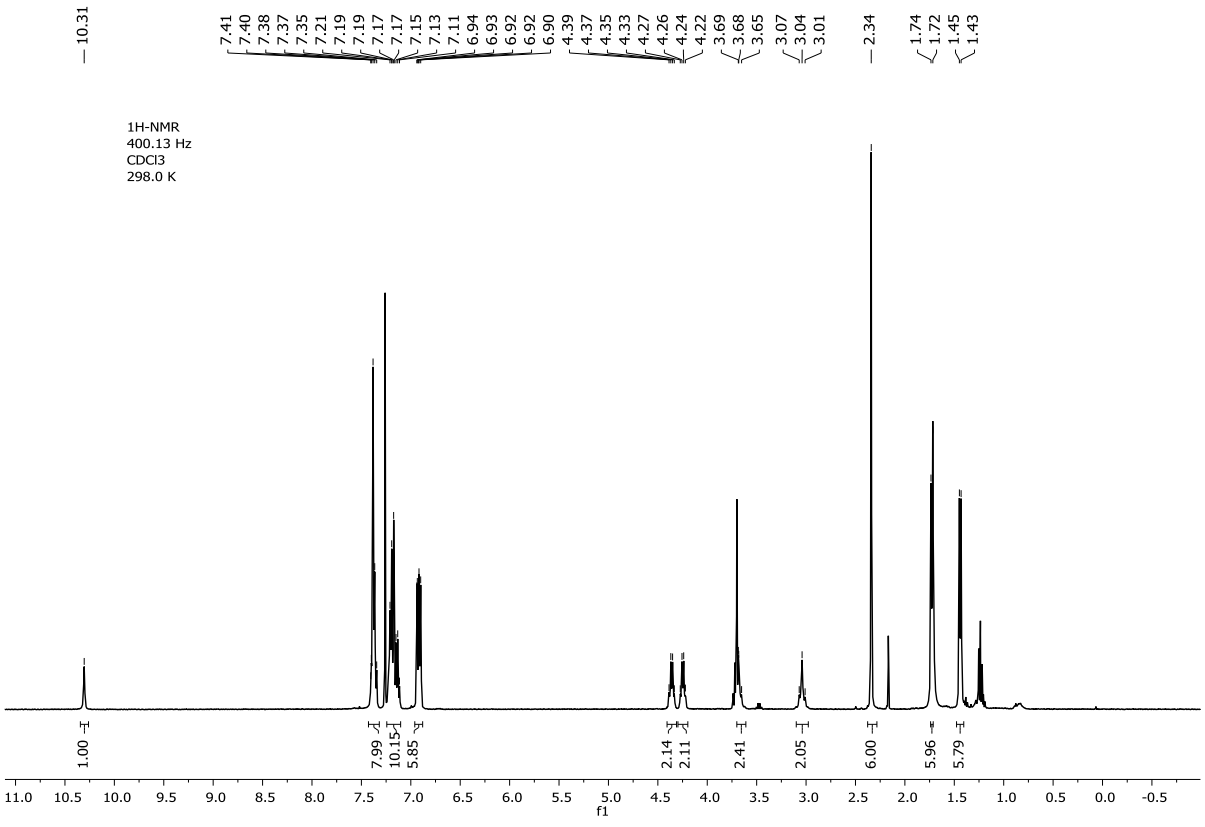

N
*
Me
D
94% D
[D]1-2a
1H-NMR
400.13 MHz
C6D6
298.0 K
f1

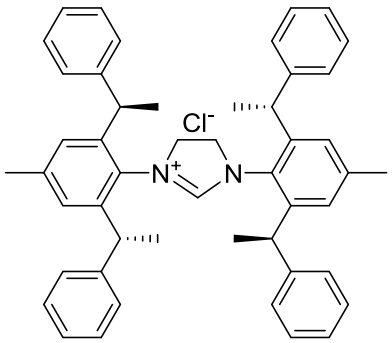

MeO2C
N
H
2g
0% D
1H-NMR
400.13 Hz
C6D6
298.0 K
f1



L5·HCl

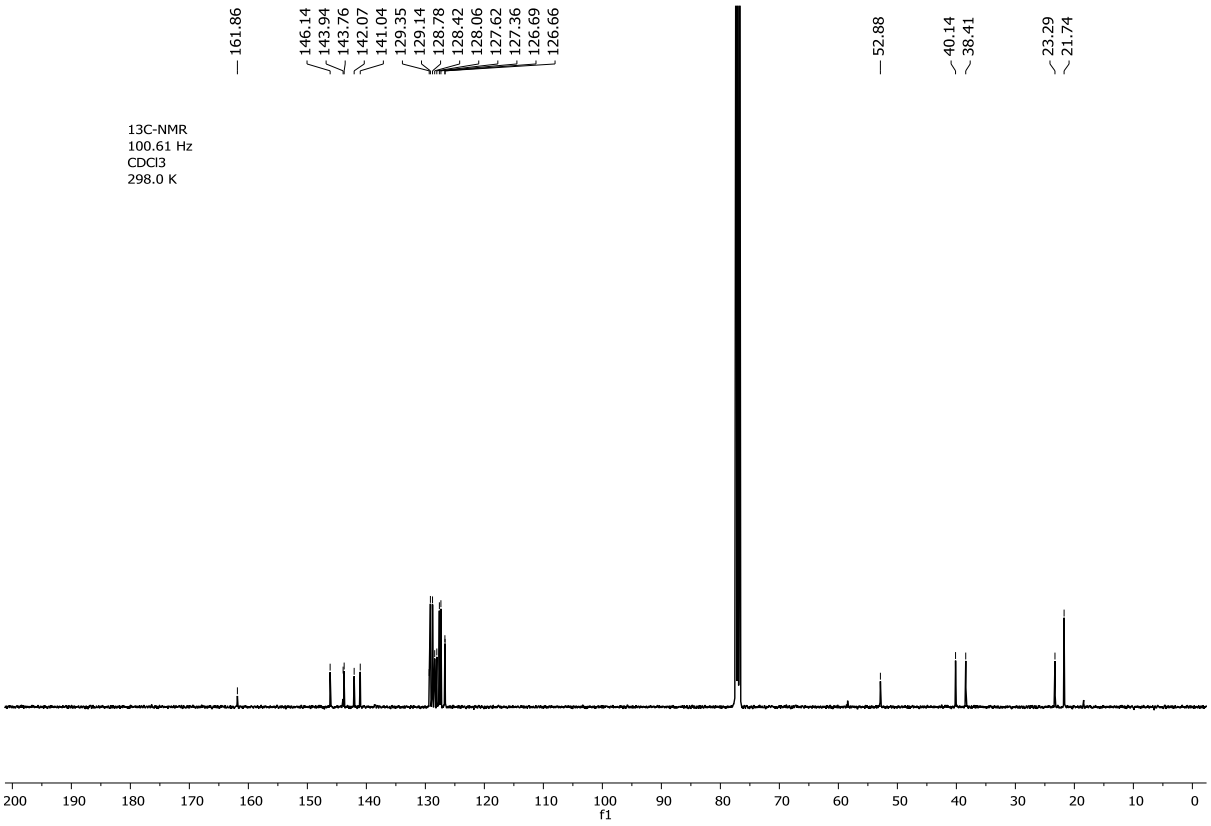
^{1}H NMR, 400 MHz, $CDCl_3$

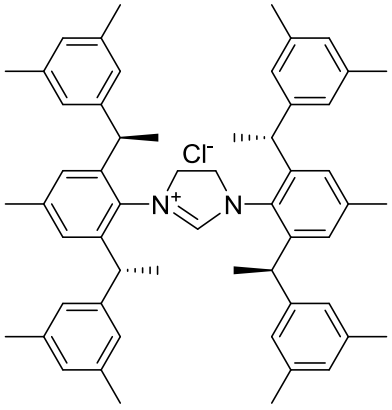




L5·HCl

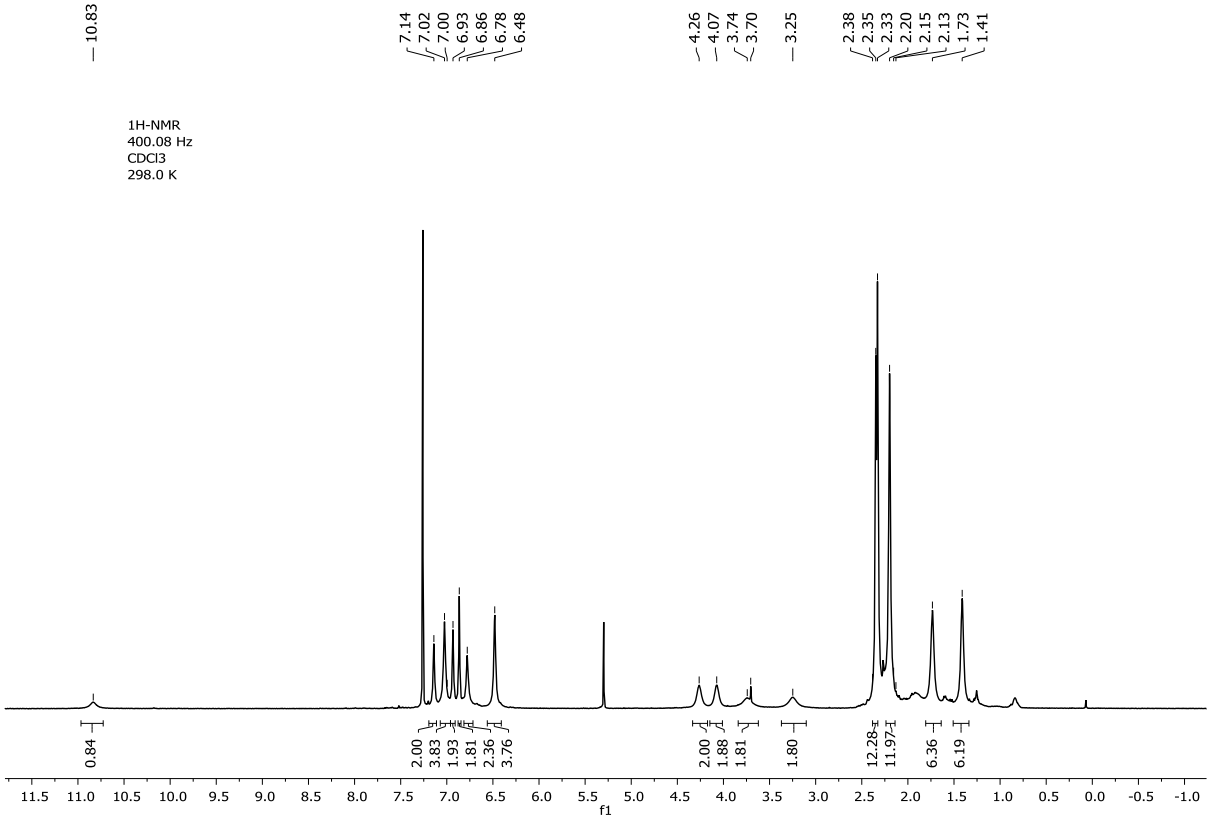
^{13}C NMR, 101 MHz, $CDCl_3$

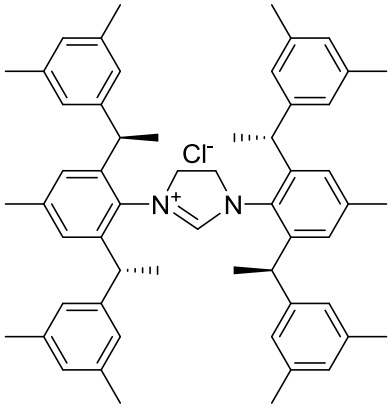




L7·HCl

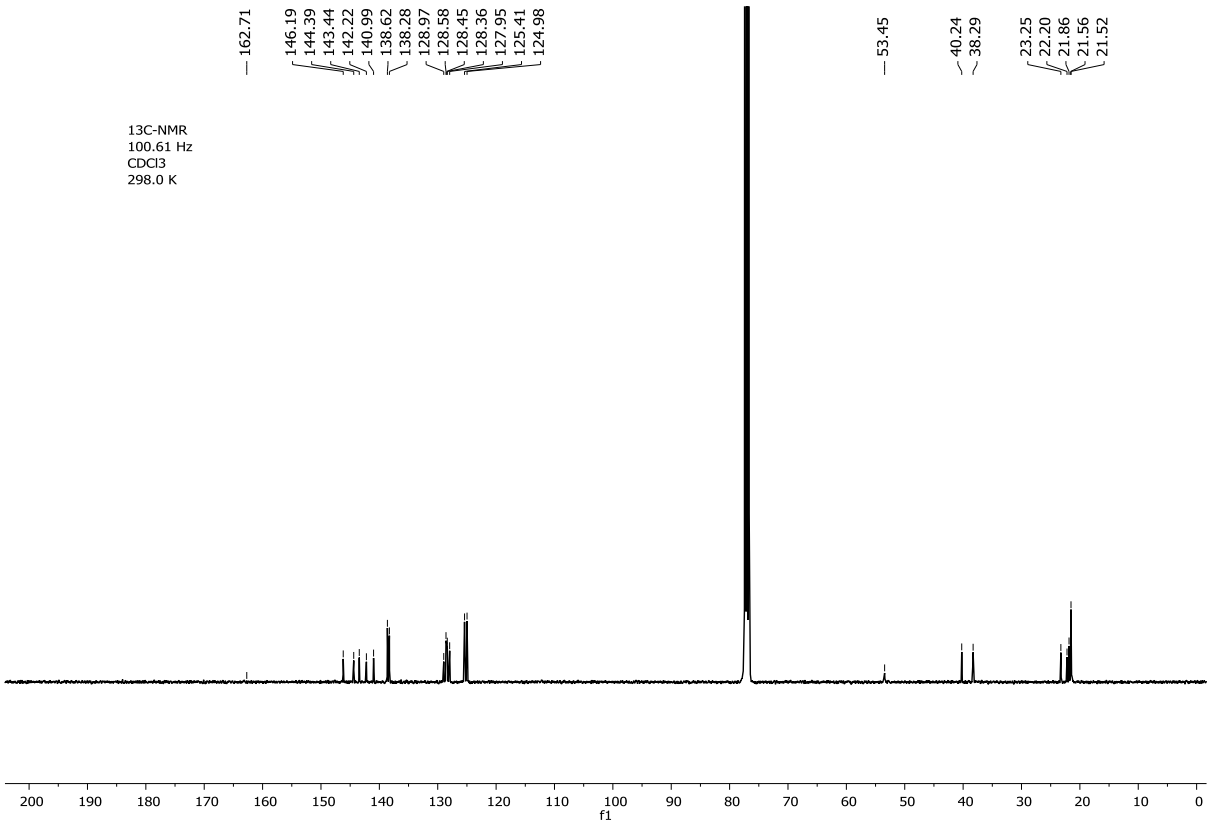
^{1}H NMR, 400 MHz, $CDCl_3$

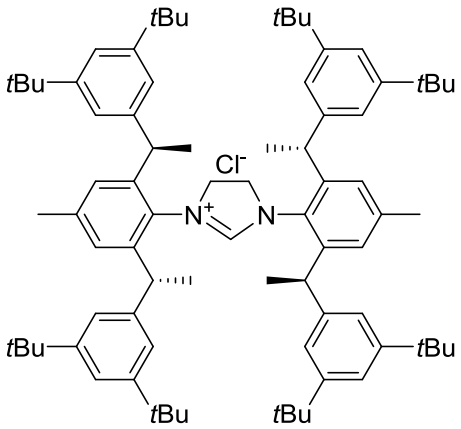




L7·HCl

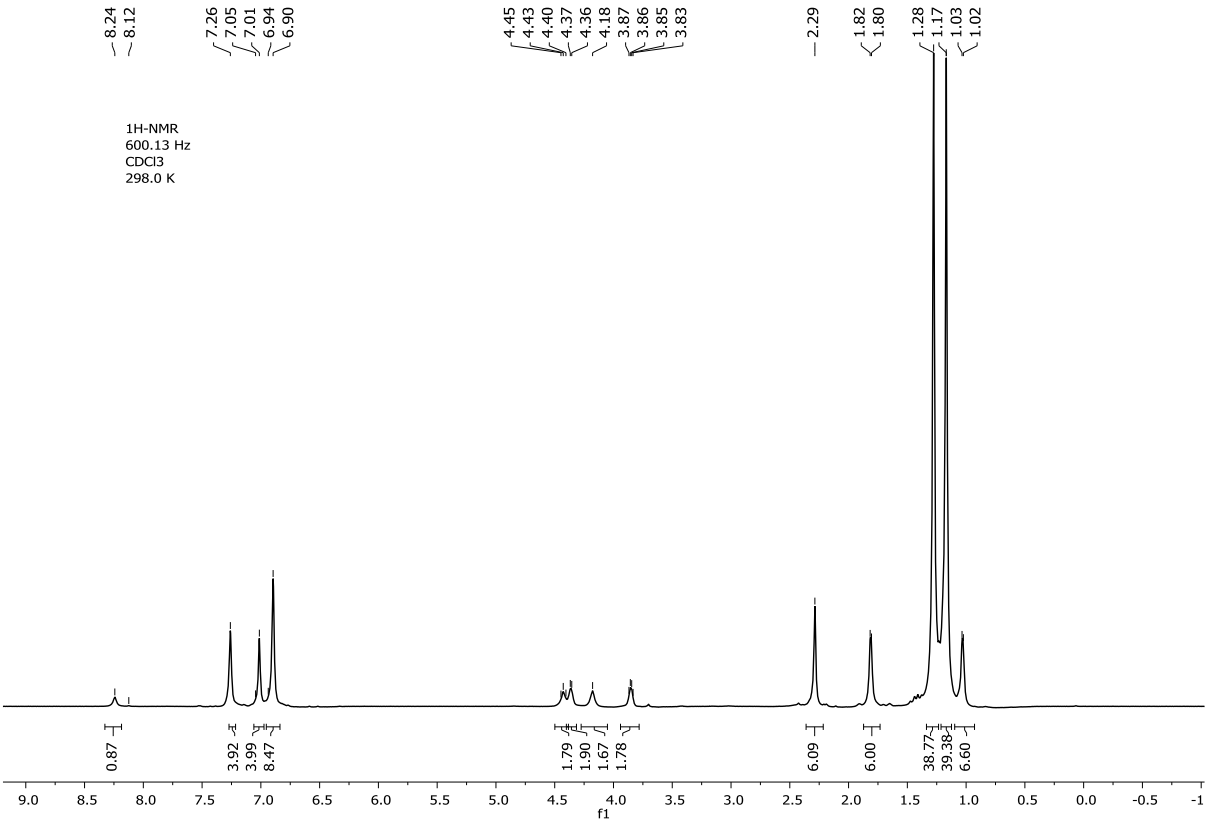
^{13}C NMR, 101 MHz, $CDCl_3$

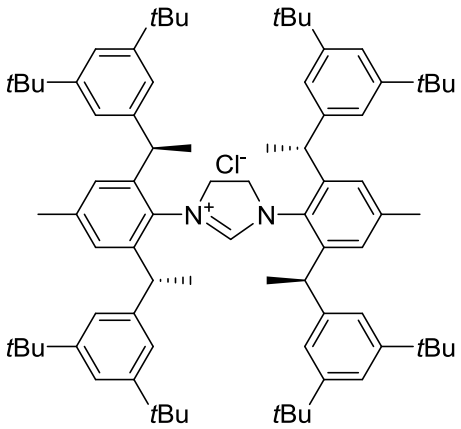




L8·HCl

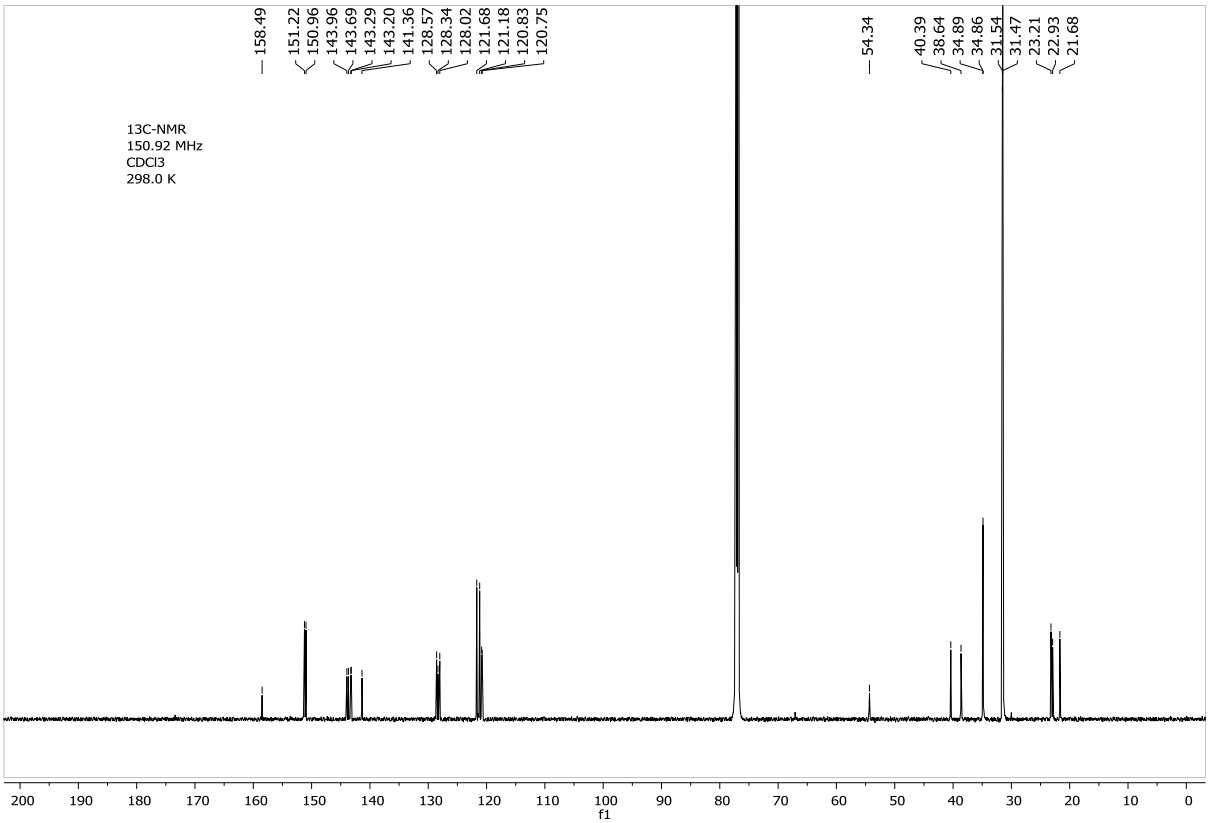
^{1}H NMR, 600 MHz, $CDCl_3$

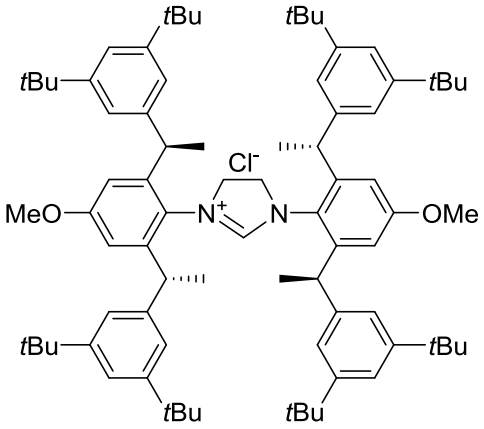




L8·HCl

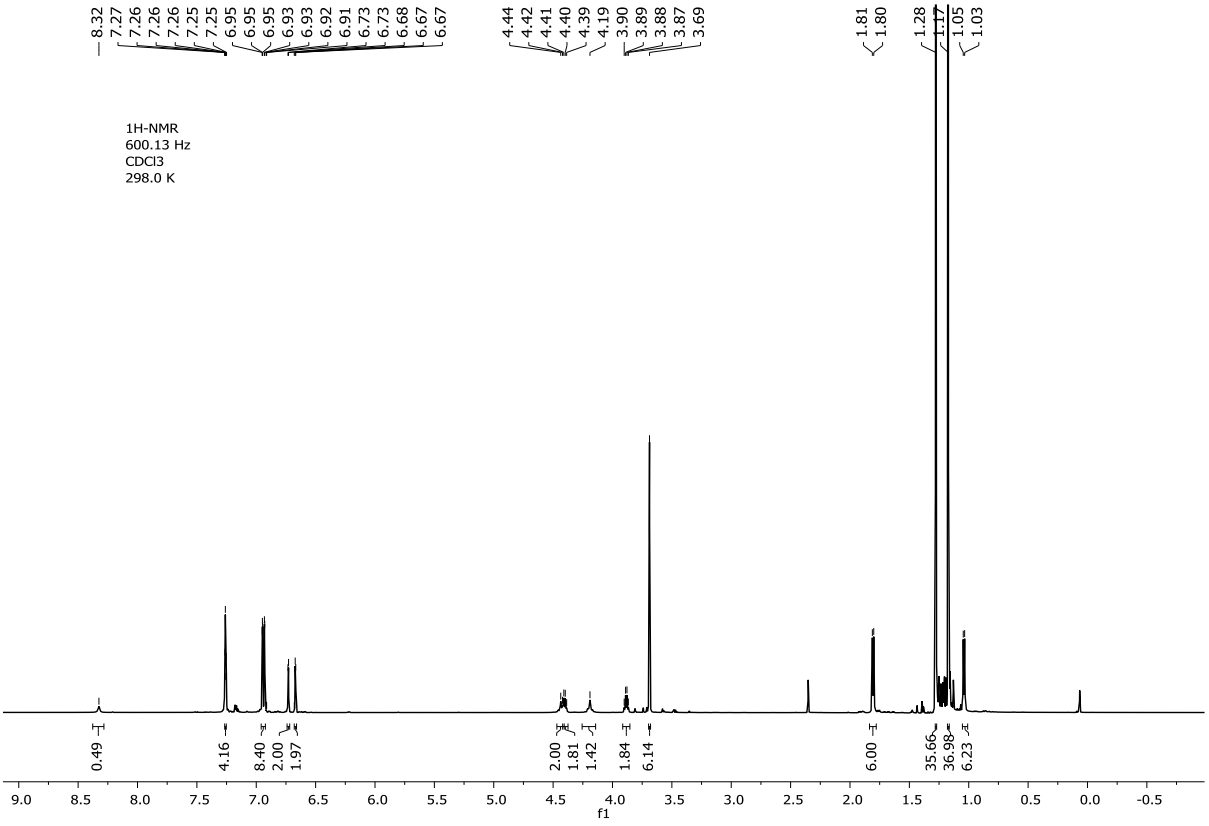
^{13}C NMR, 151 MHz, $CDCl_3$

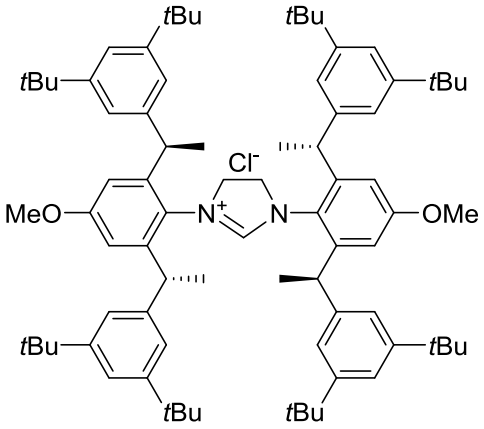




L9·HCl

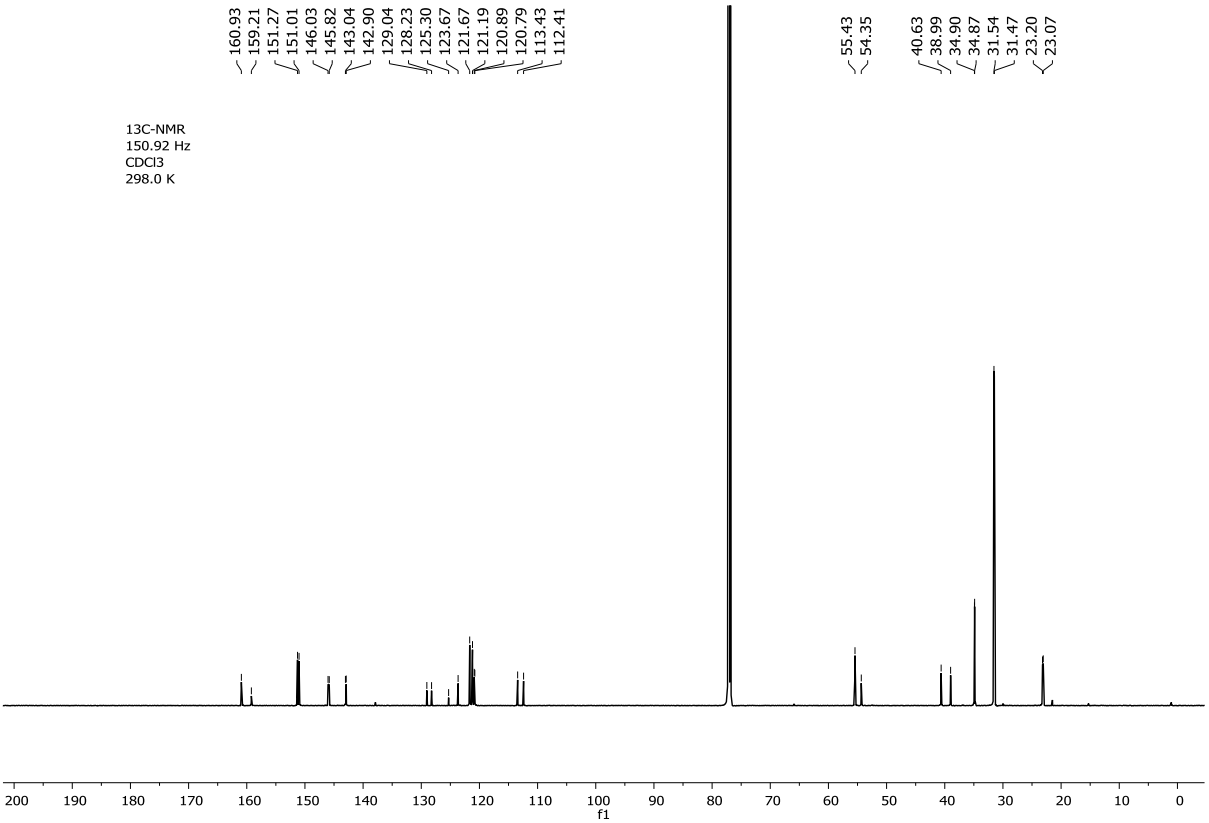
^{1}H NMR, 600 MHz, $CDCl_3$

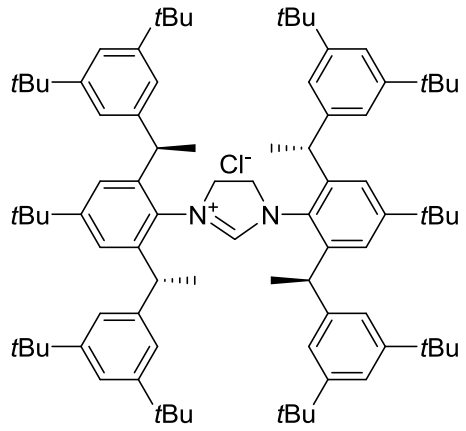




L9·HCl

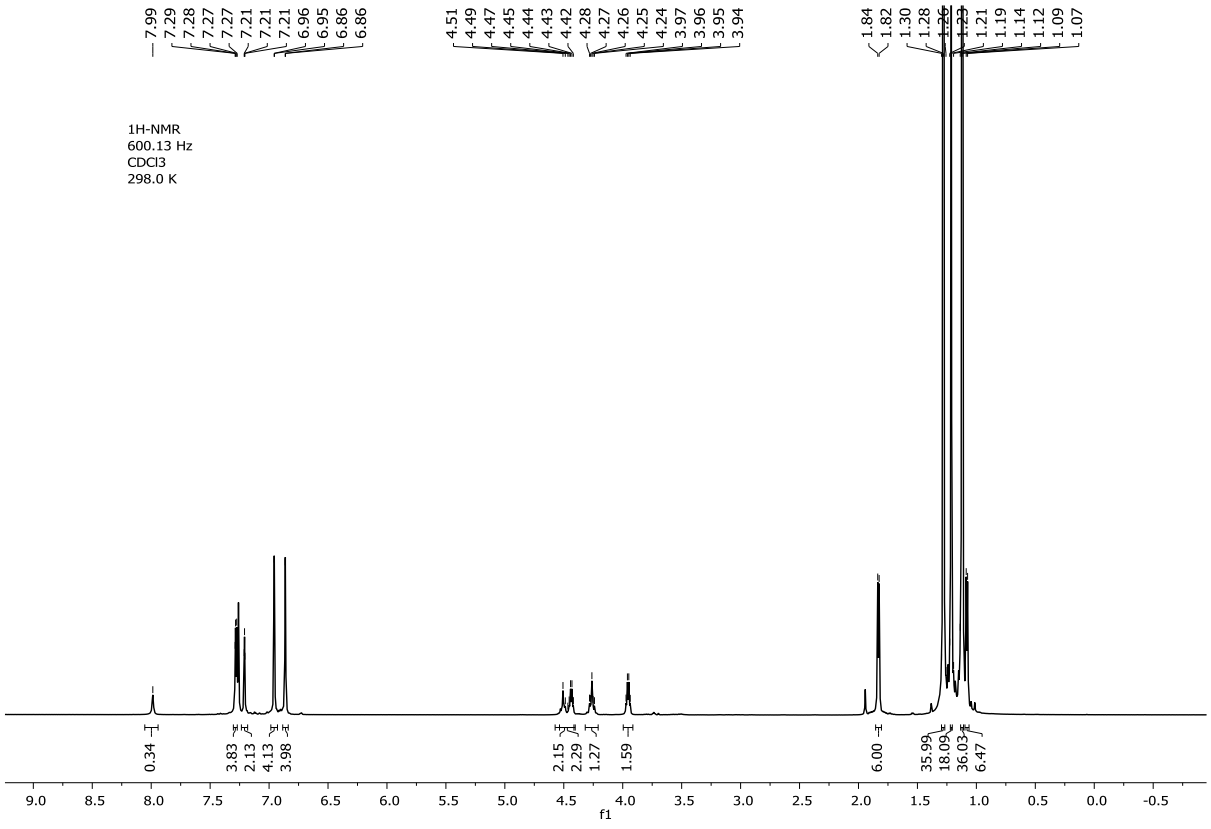
^{13}C NMR, 151 MHz, $CDCl_3$

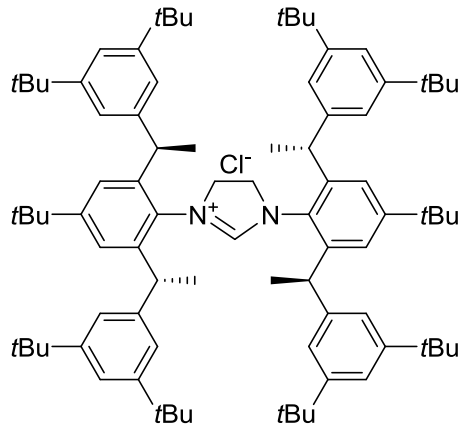




L10·HCl

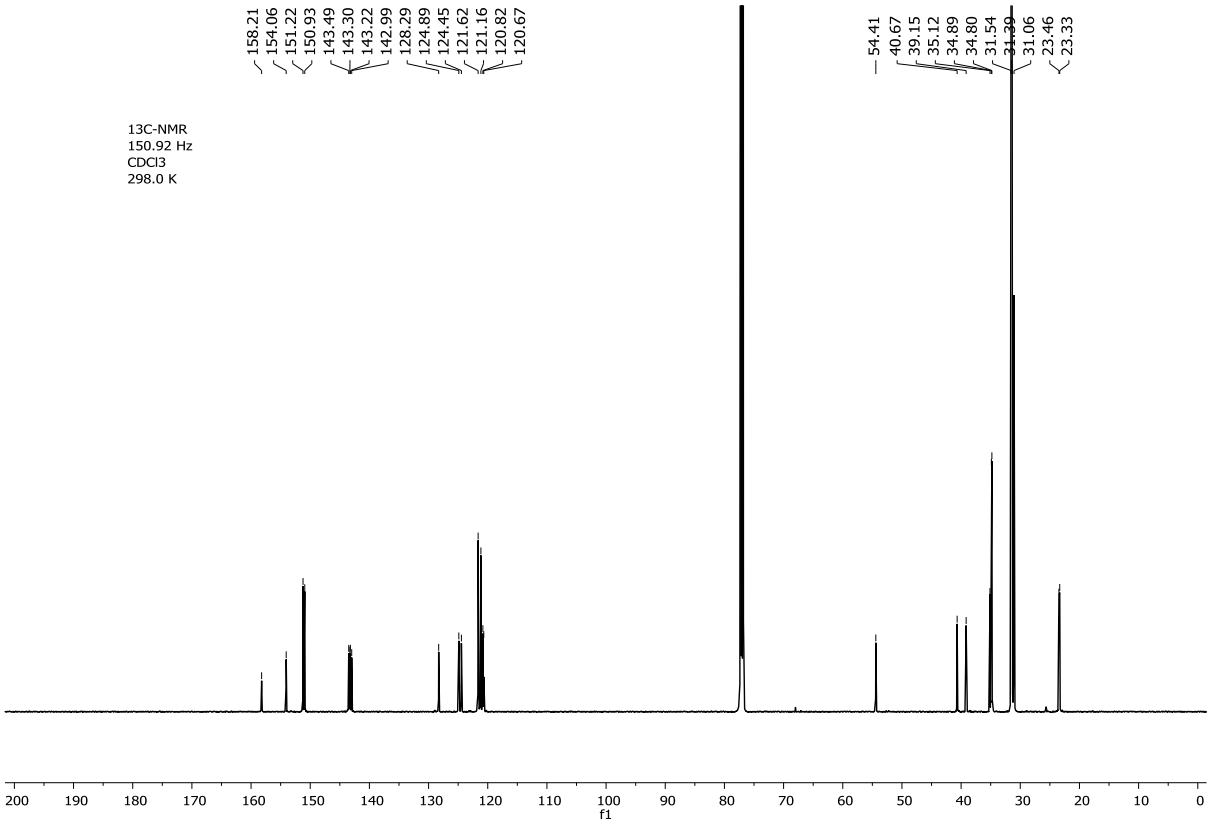
^{1}H NMR, 600 MHz, $CDCl_3$

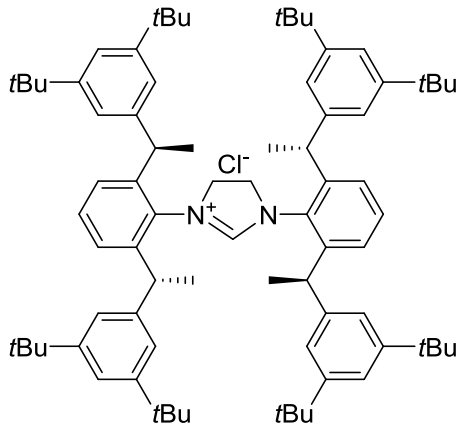




L10·HCl

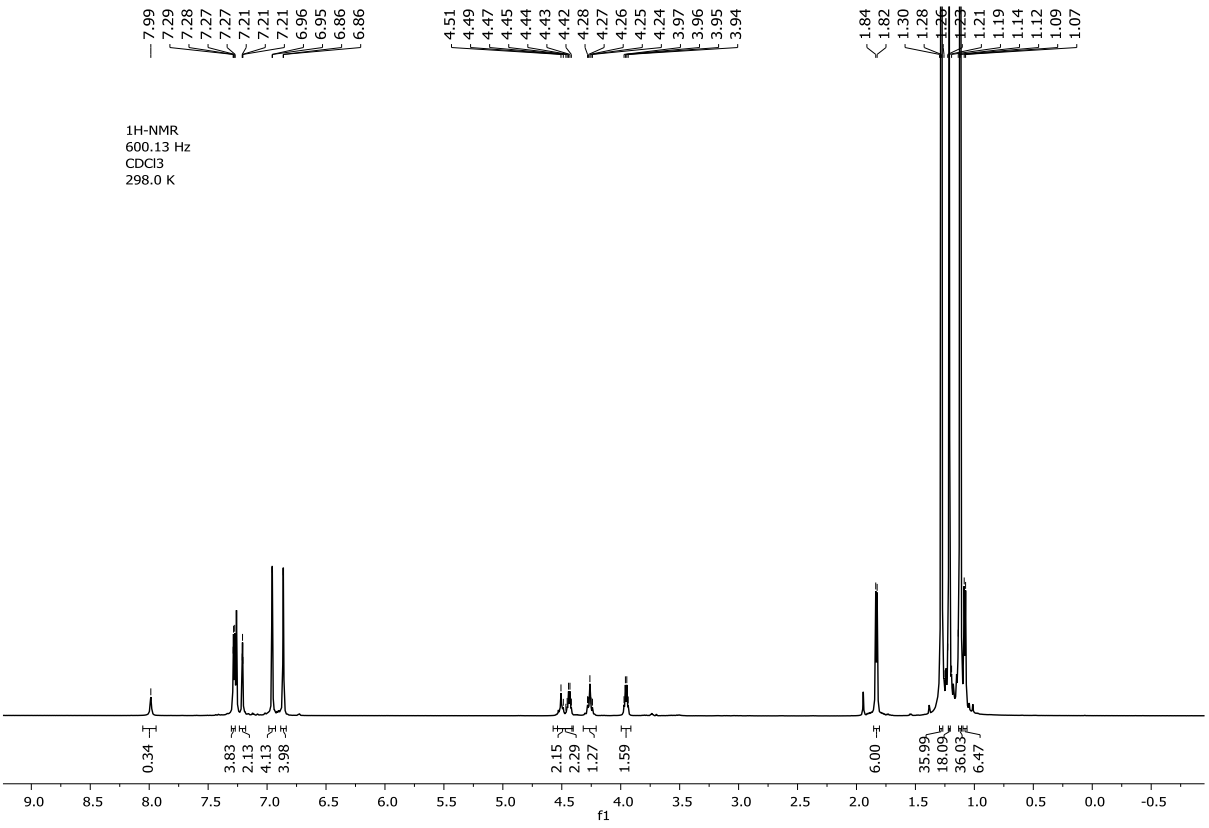
^{13}C NMR, 151 MHz, $CDCl_3$

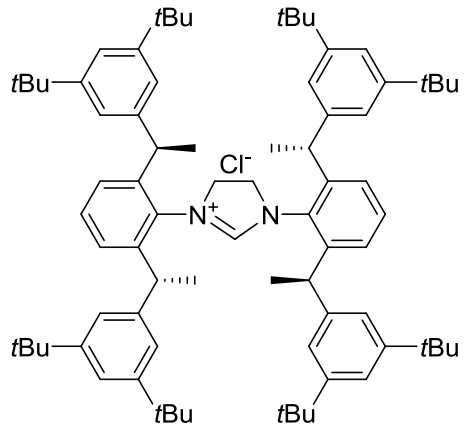




L11·HCl

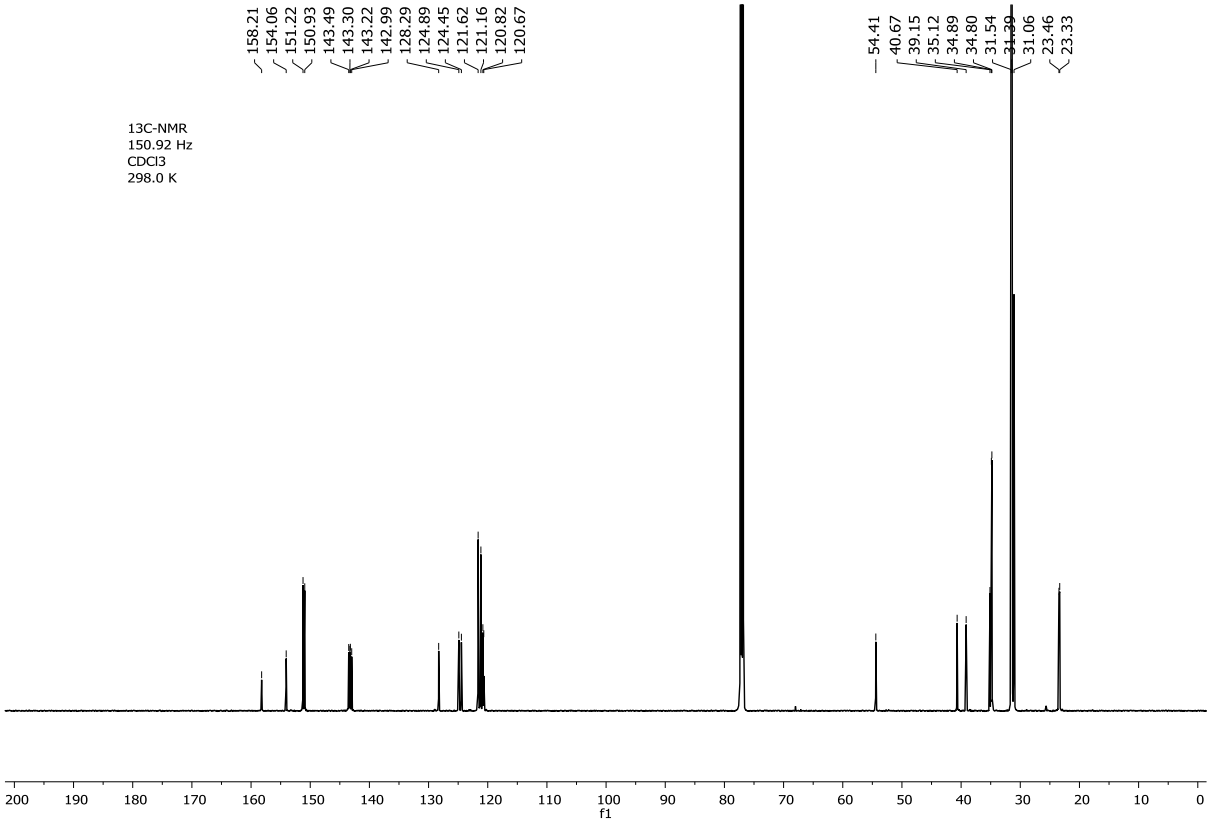
^{1}H NMR, 600 MHz, $CDCl_3$

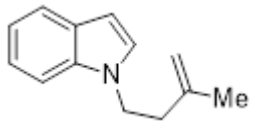




L11·HCl

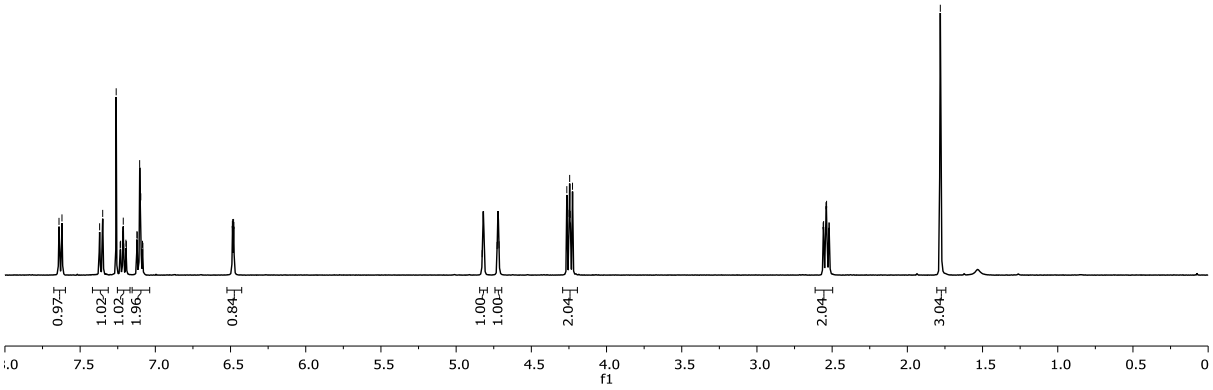
^{13}C NMR, 151 MHz, $CDCl_3$

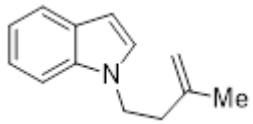




1a

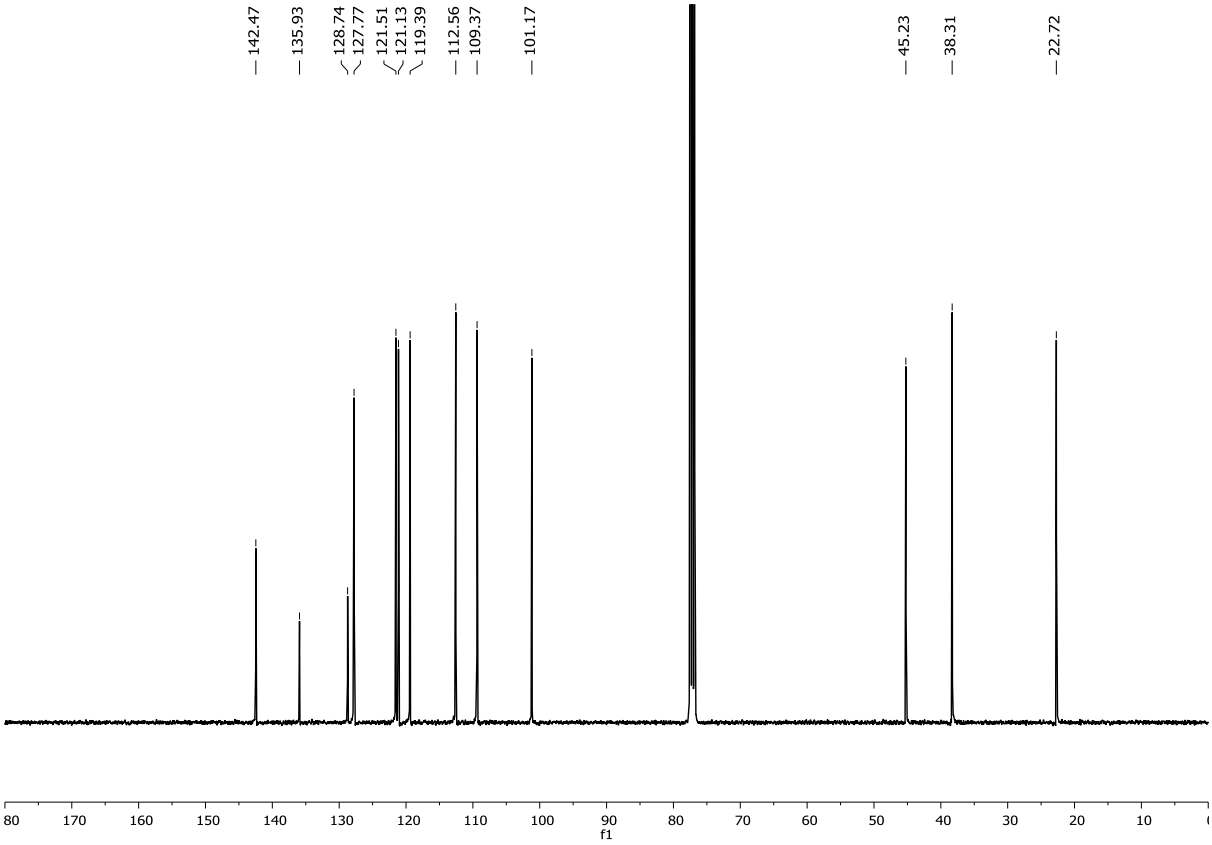
^{1}H NMR, 400 MHz, $CDCl_3$

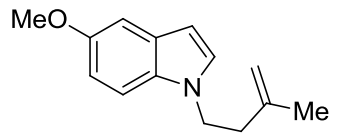




1a

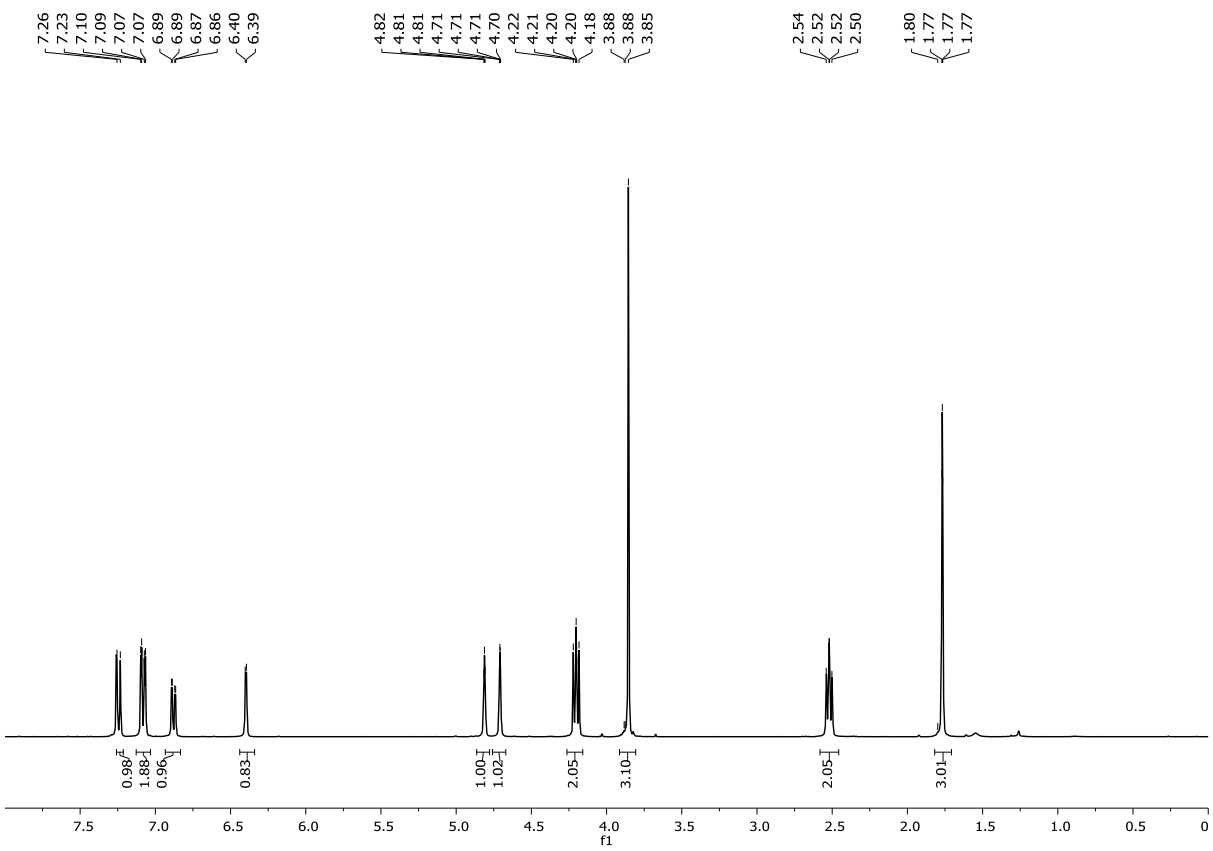
^{13}C NMR, 101 MHz, $CDCl_3$

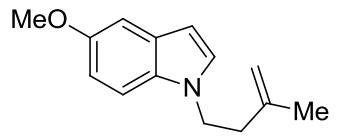




1b

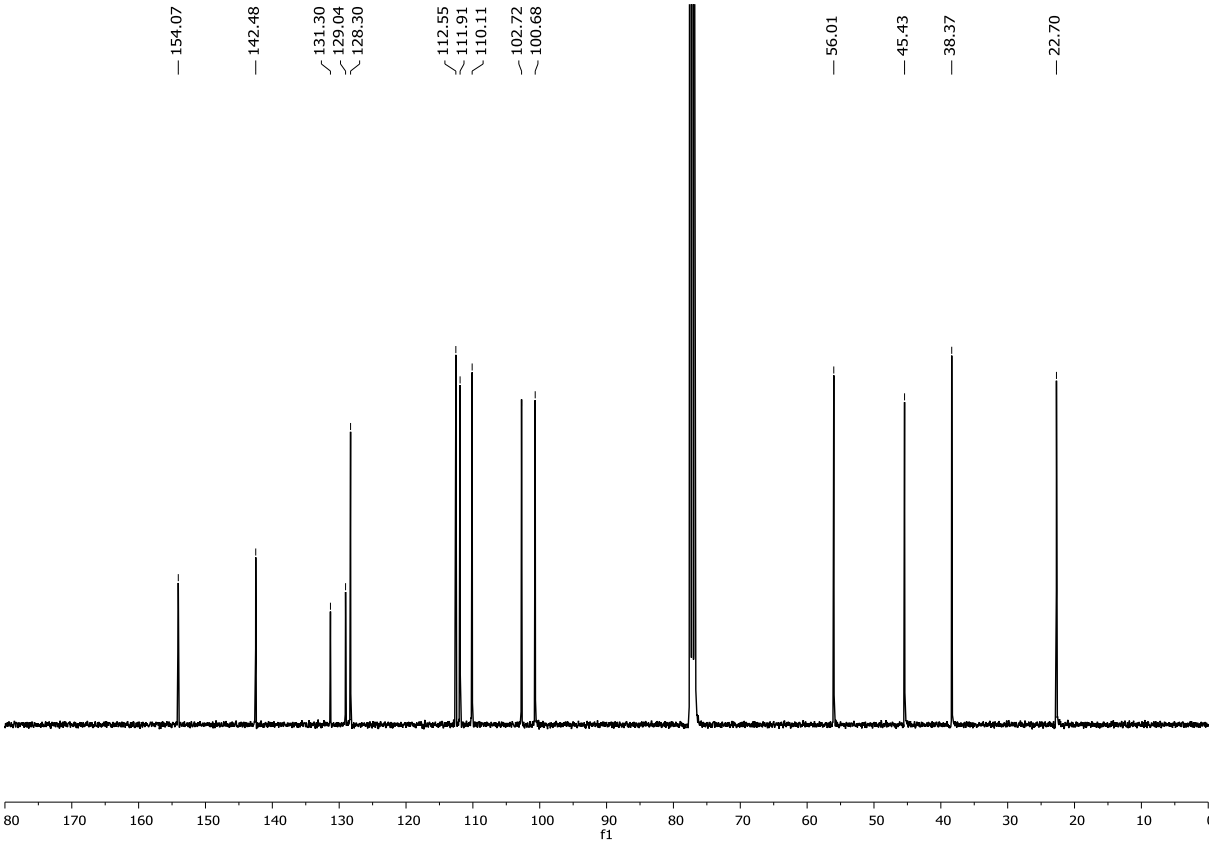
^{1}H NMR, 400 MHz, $CDCl_3$

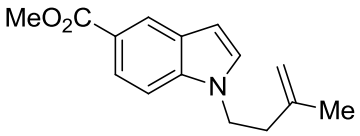




1b

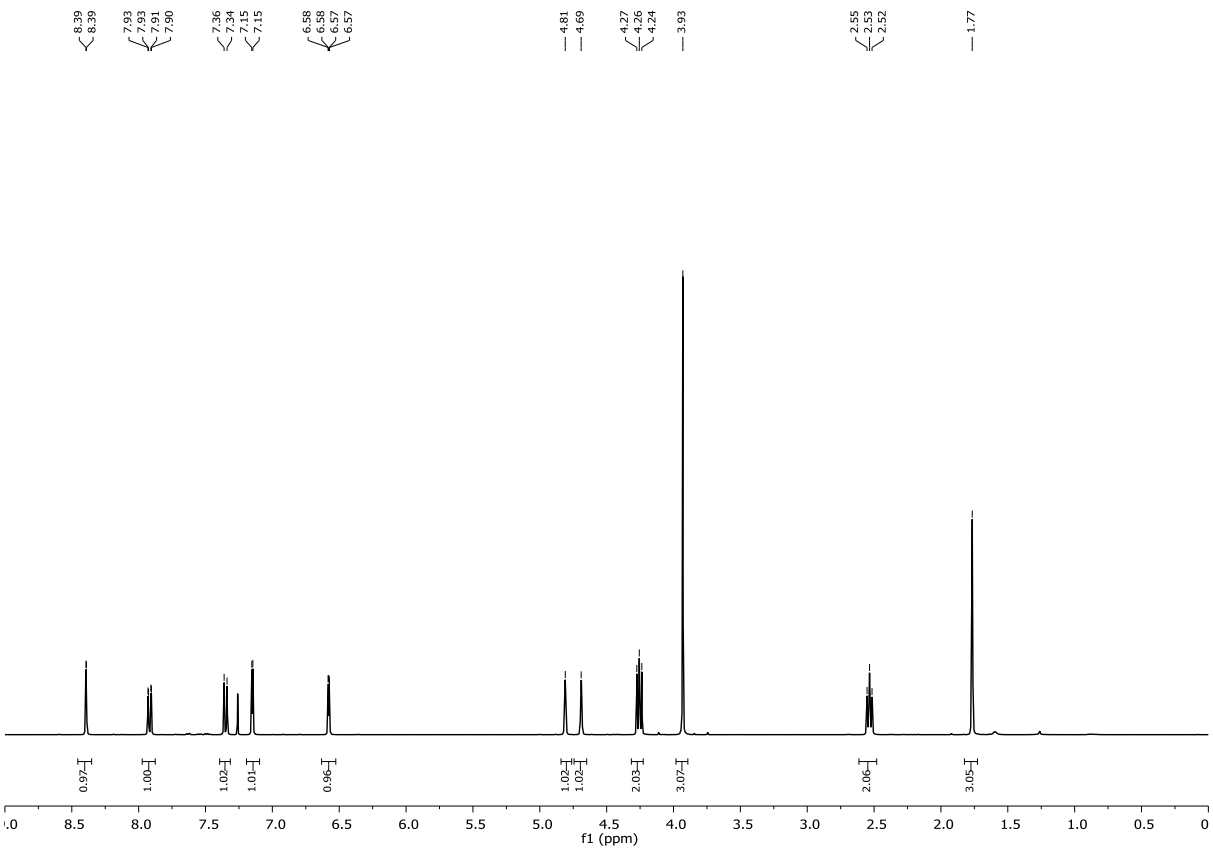
^{13}C NMR, 101 MHz, $CDCl_3$

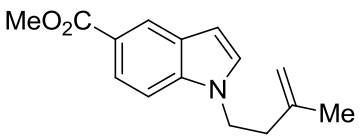




1c

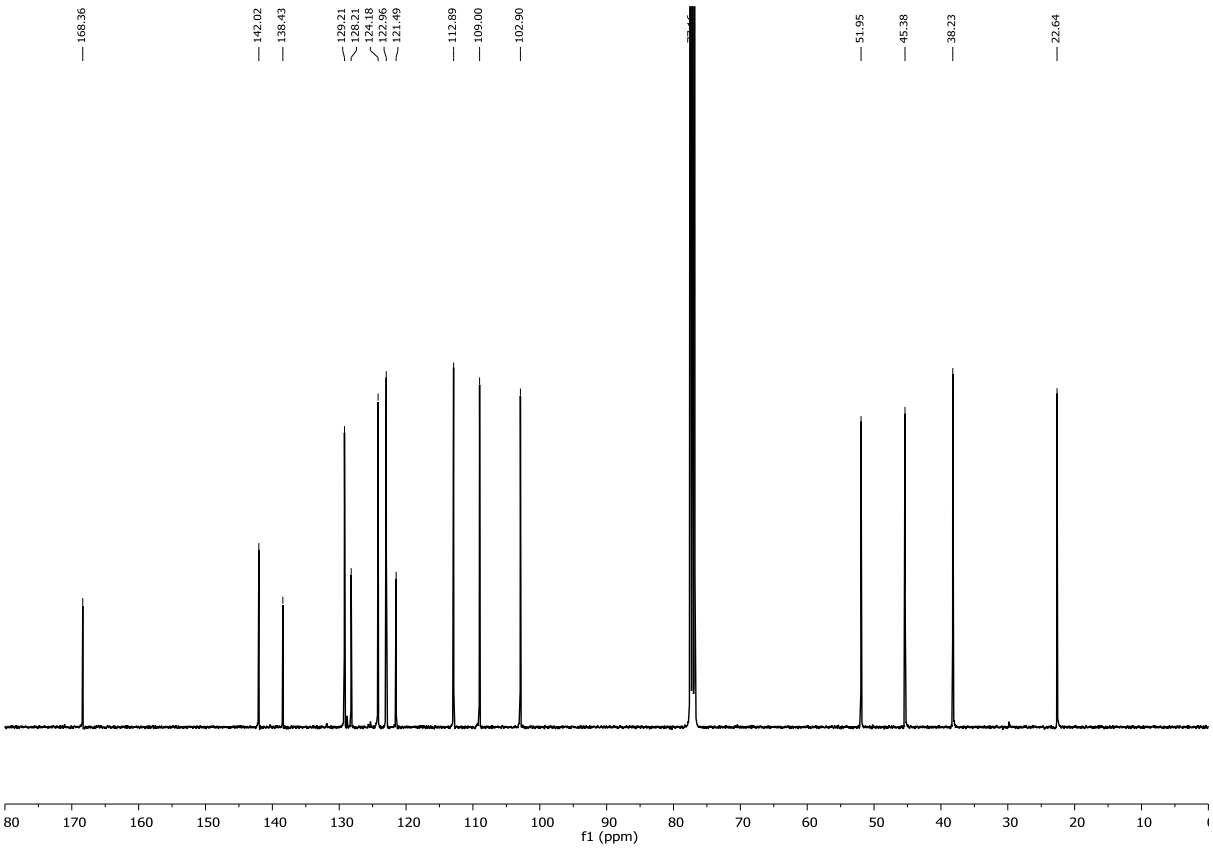
^{1}H NMR, 400 MHz, $CDCl_3$

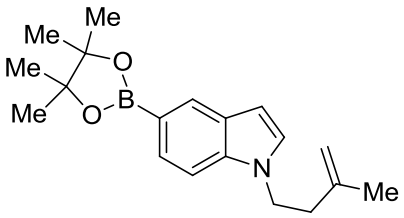




1c

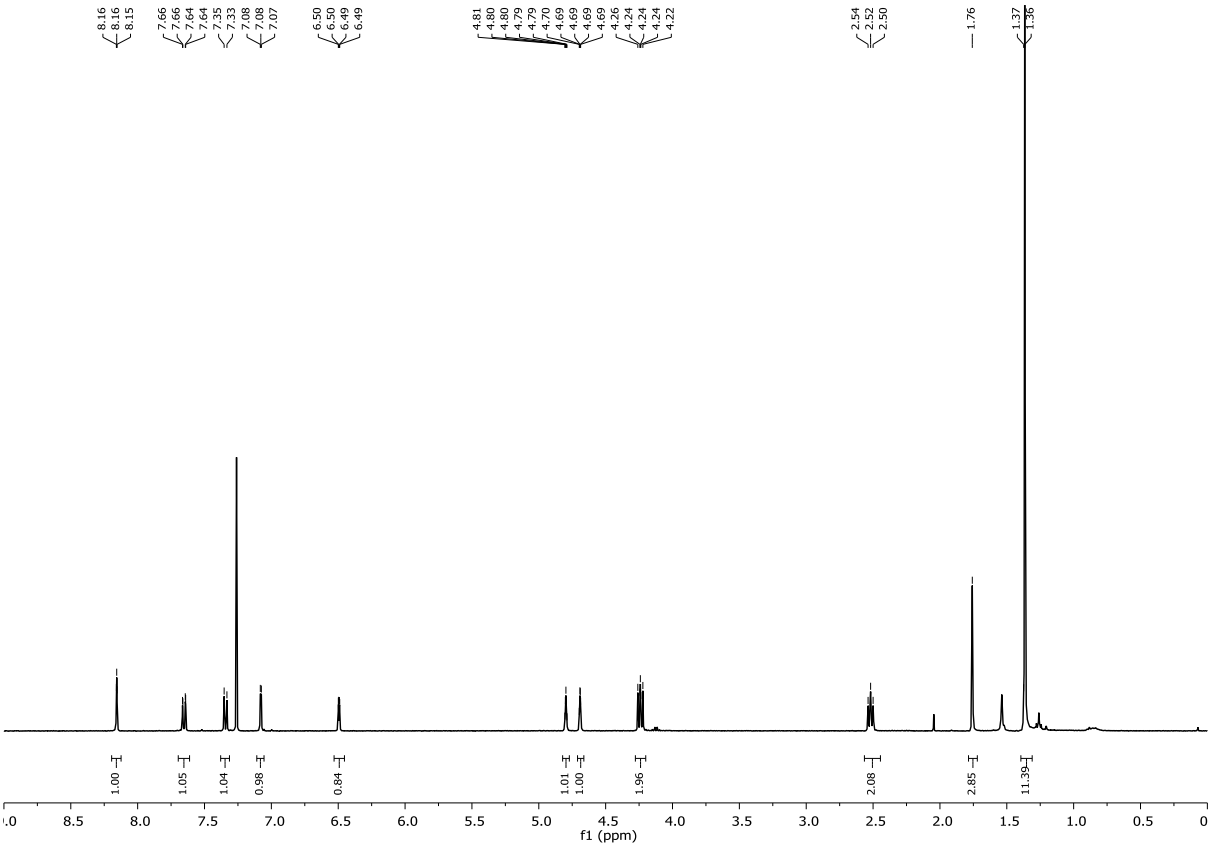
^{13}C NMR, 100 MHz, $CDCl_3$

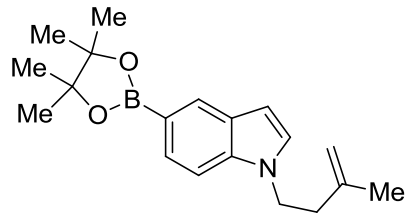




1d

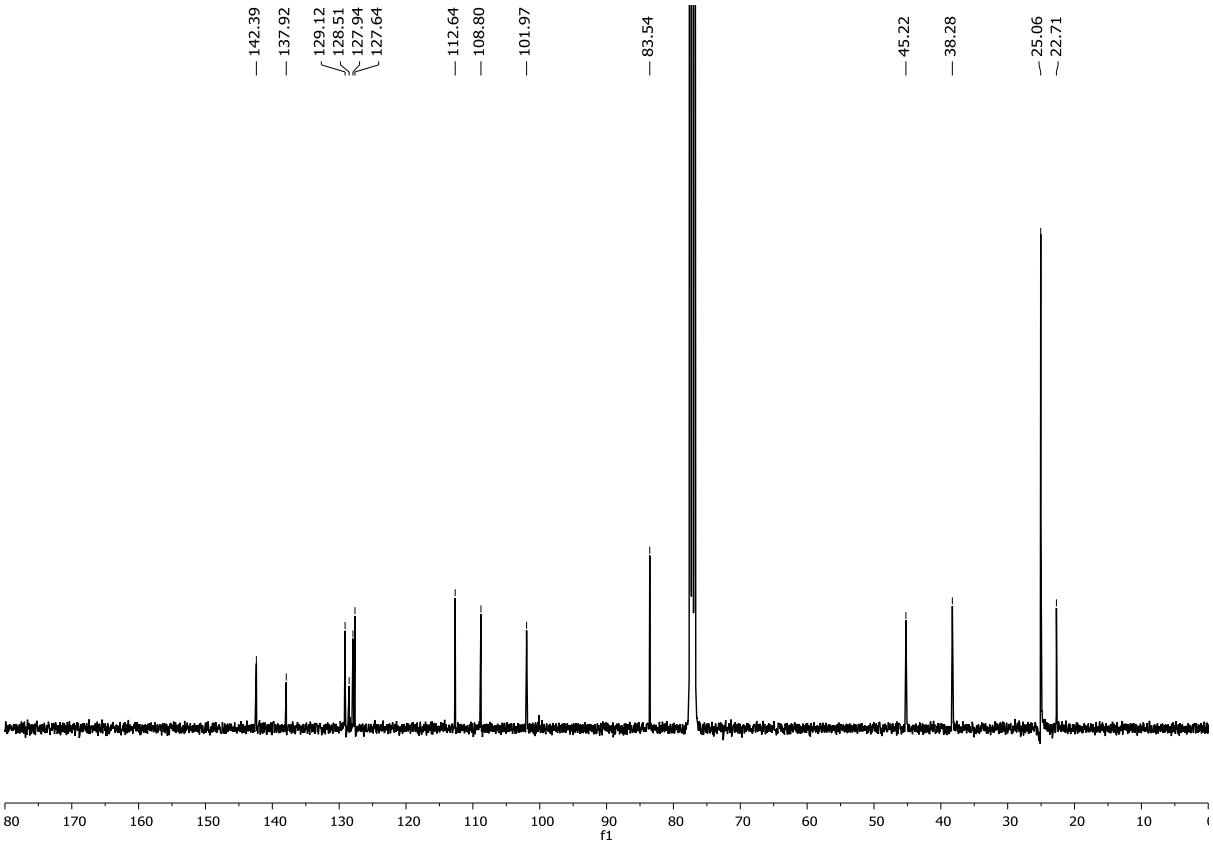
^{1}H NMR, 400 MHz, $CDCl_3$

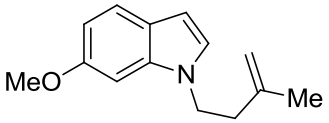




1d

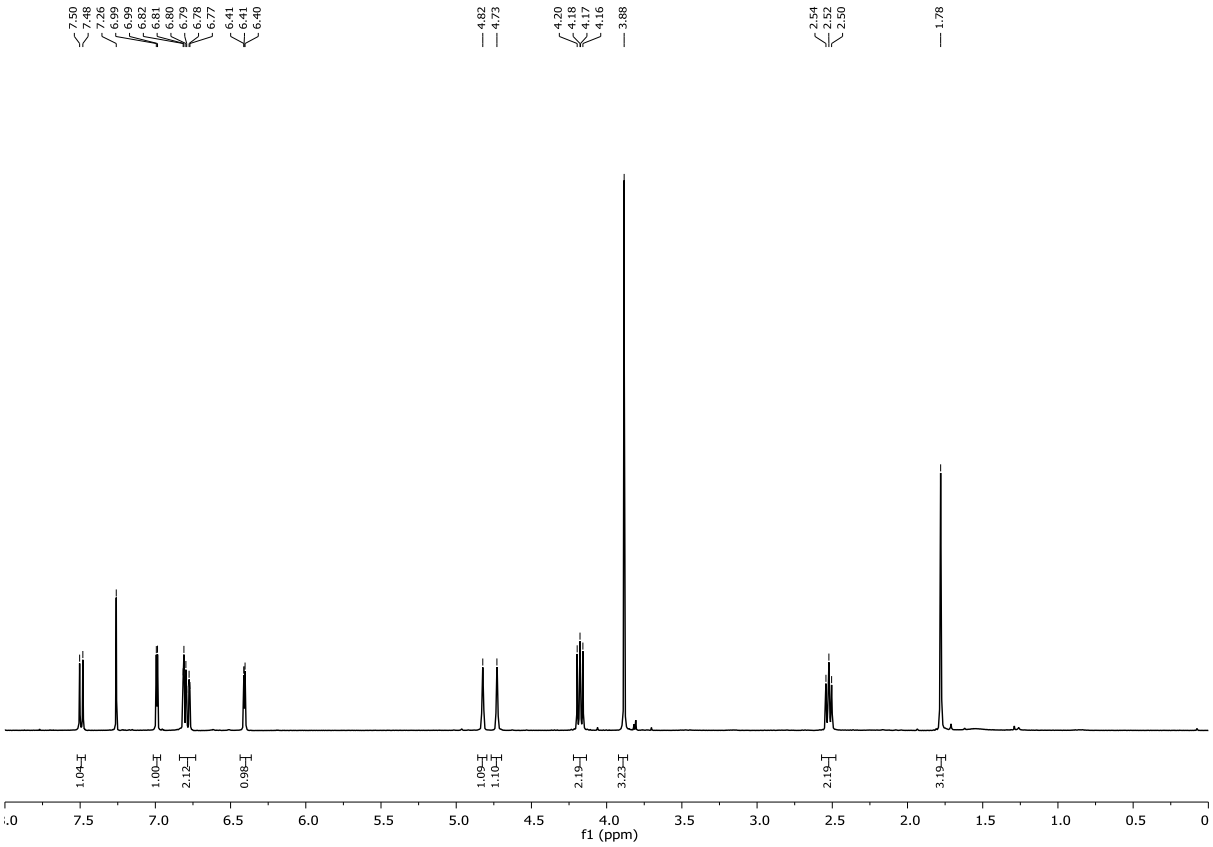
^{13}C NMR, 100 MHz, $CDCl_3$

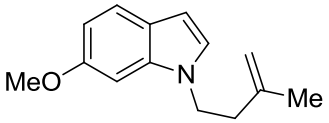




1e

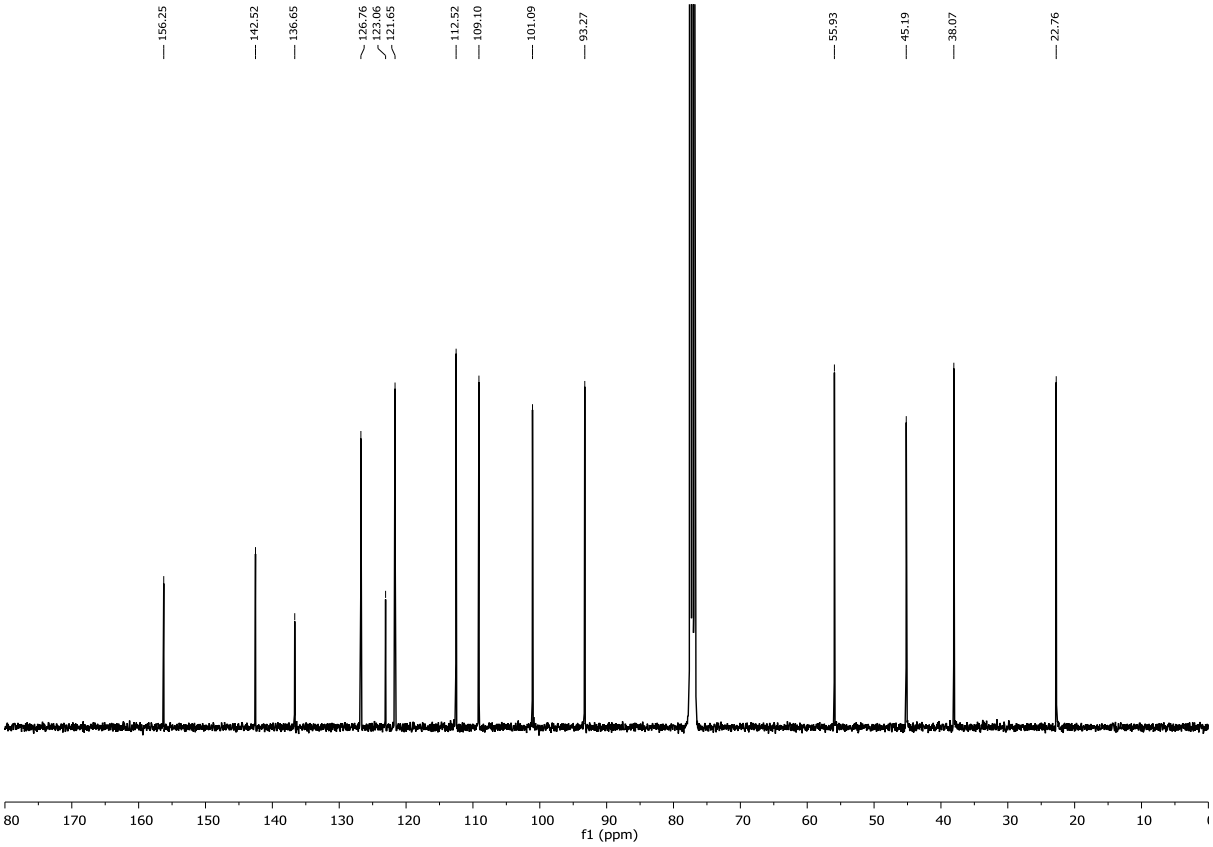
^{1}H NMR, 400 MHz, $CDCl_3$

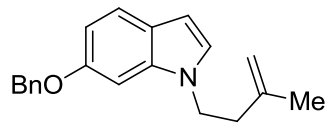




1e

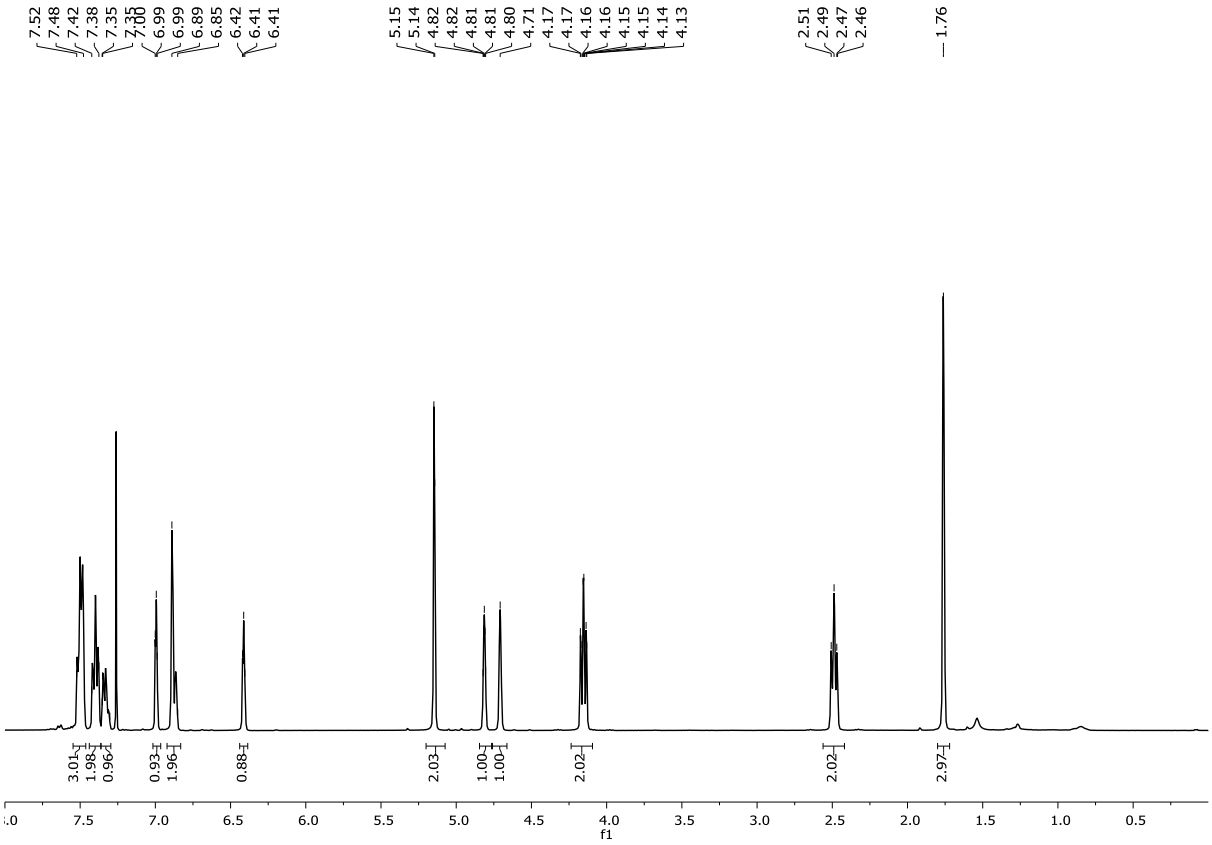
^{13}C NMR, 100 MHz, $CDCl_3$

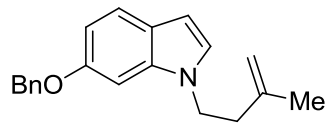




1f

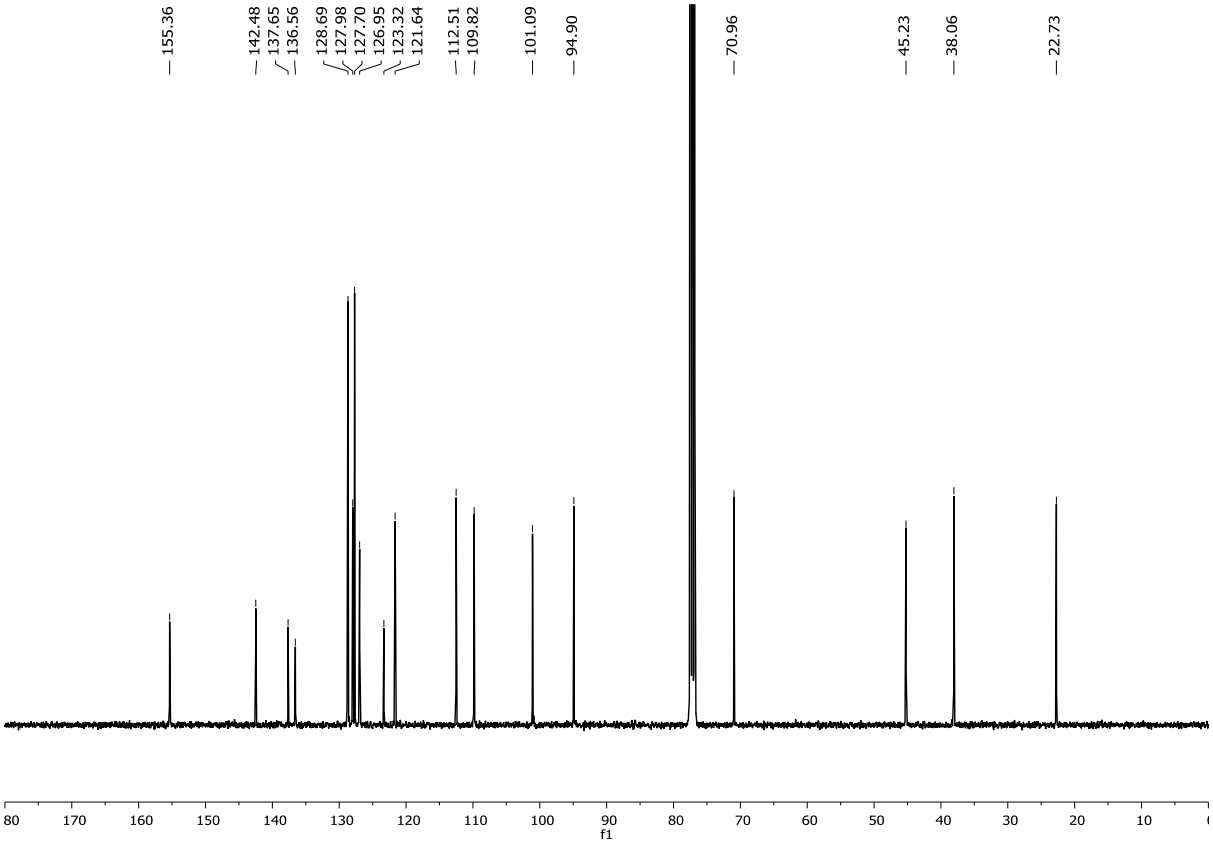
^{1}H NMR, 400 MHz, $CDCl_3$

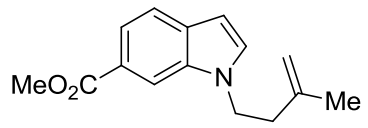




1f

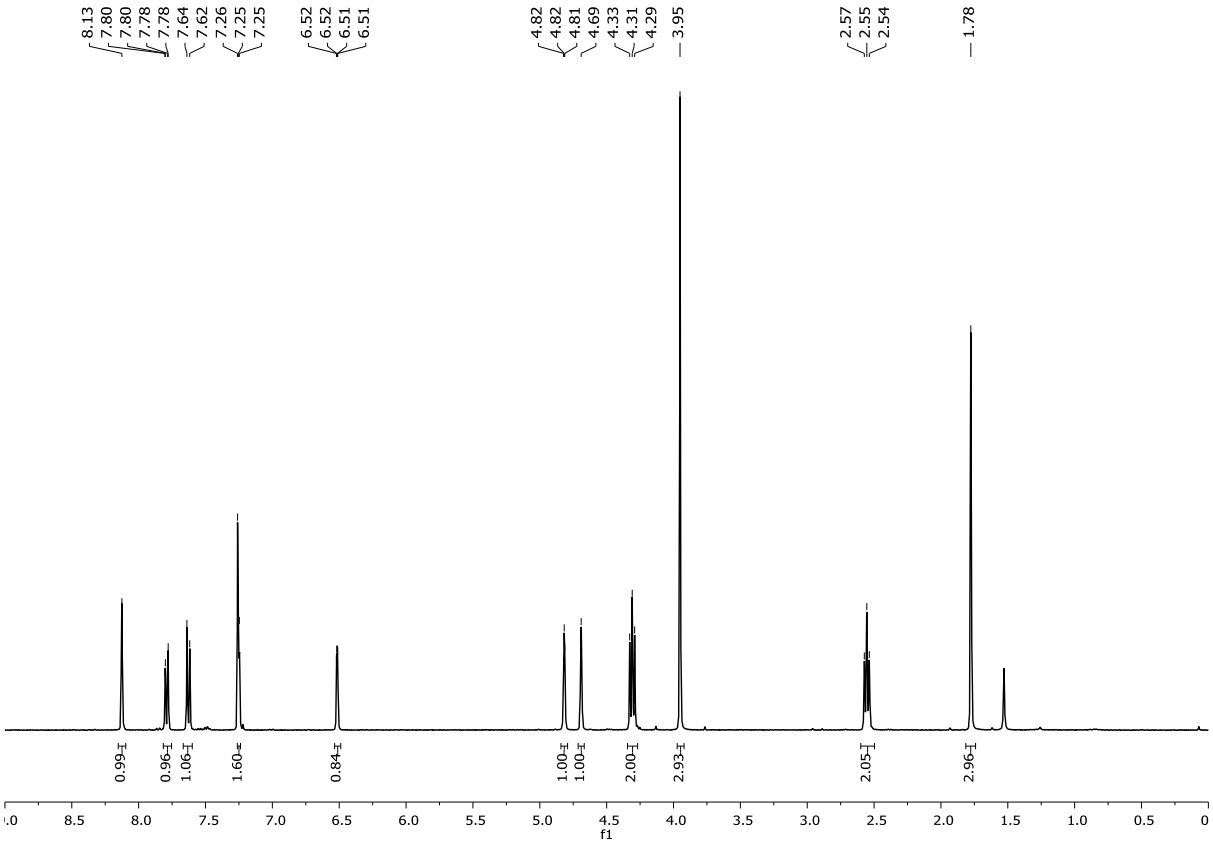
^{13}C NMR, 100 MHz, $CDCl_3$

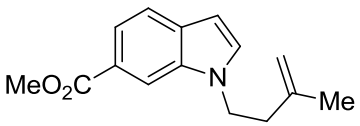




1g

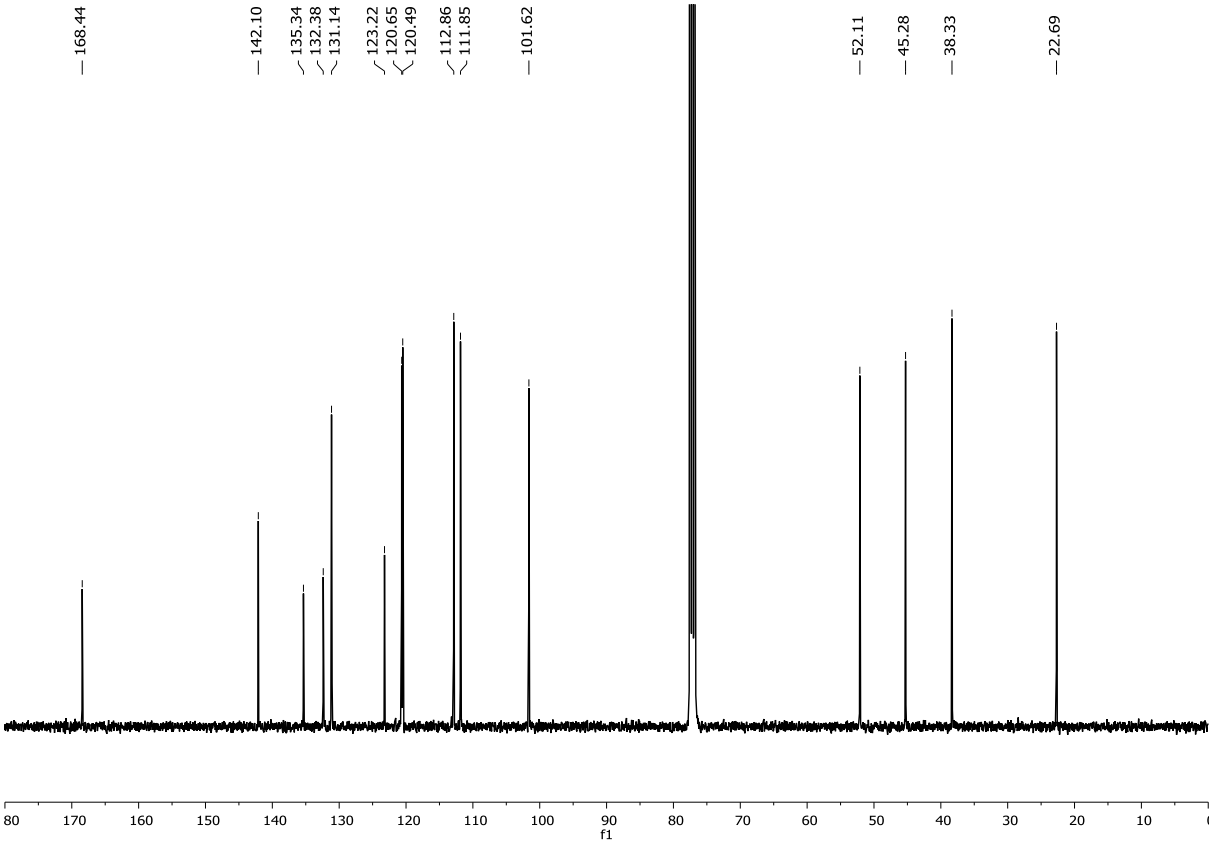
^{1}H NMR, 400 MHz, $CDCl_3$

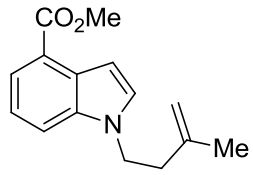




1g

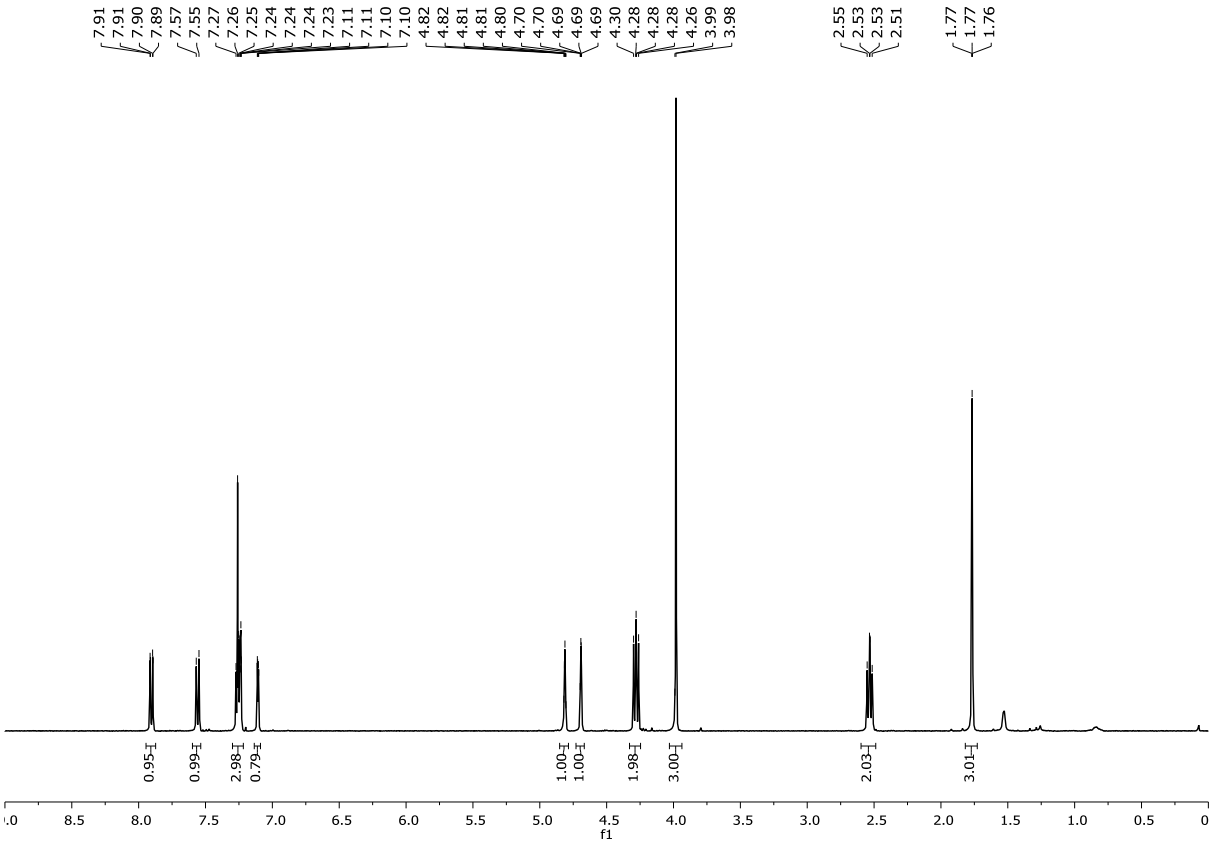
^{13}C NMR, 101 MHz, $CDCl_3$

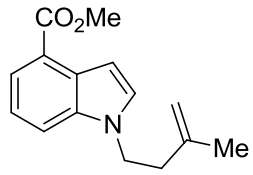




1h

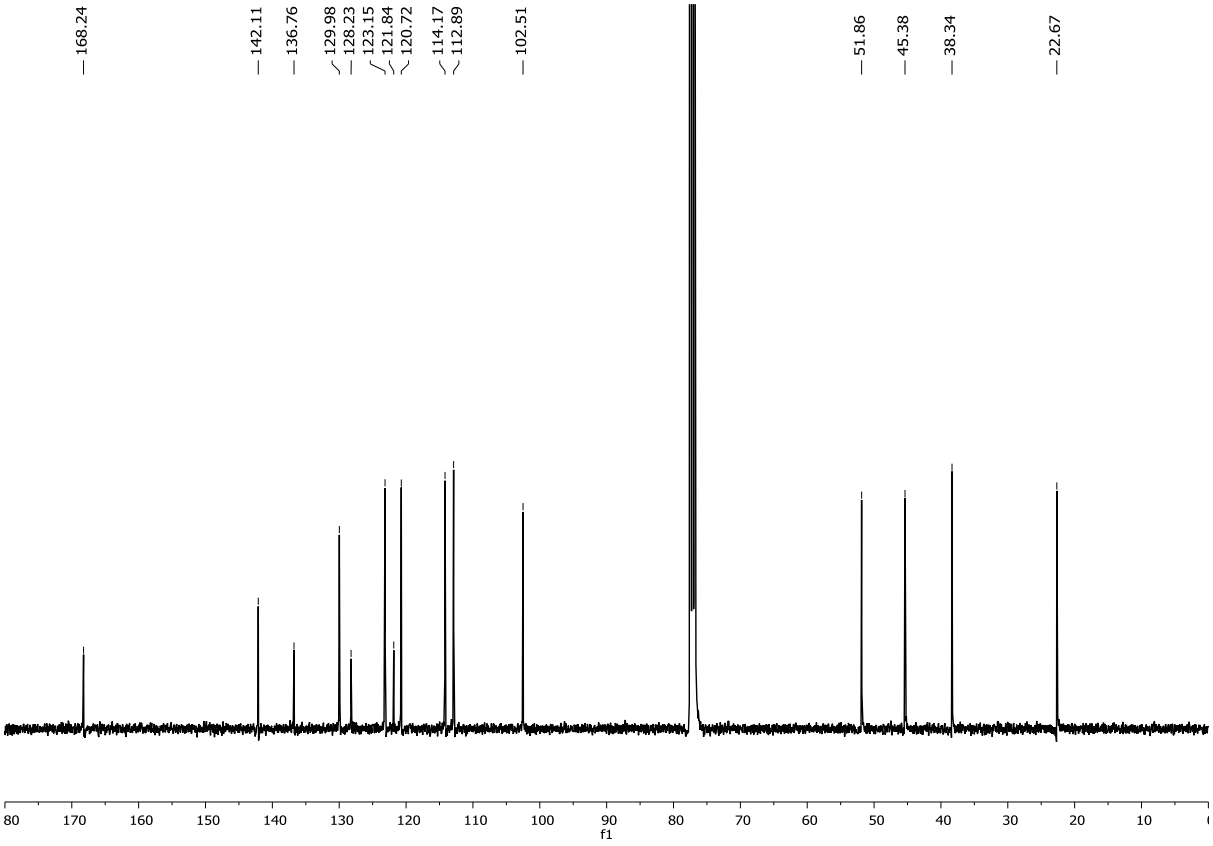
^{1}H NMR, 400 MHz, $CDCl_3$

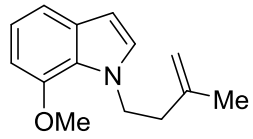




1h

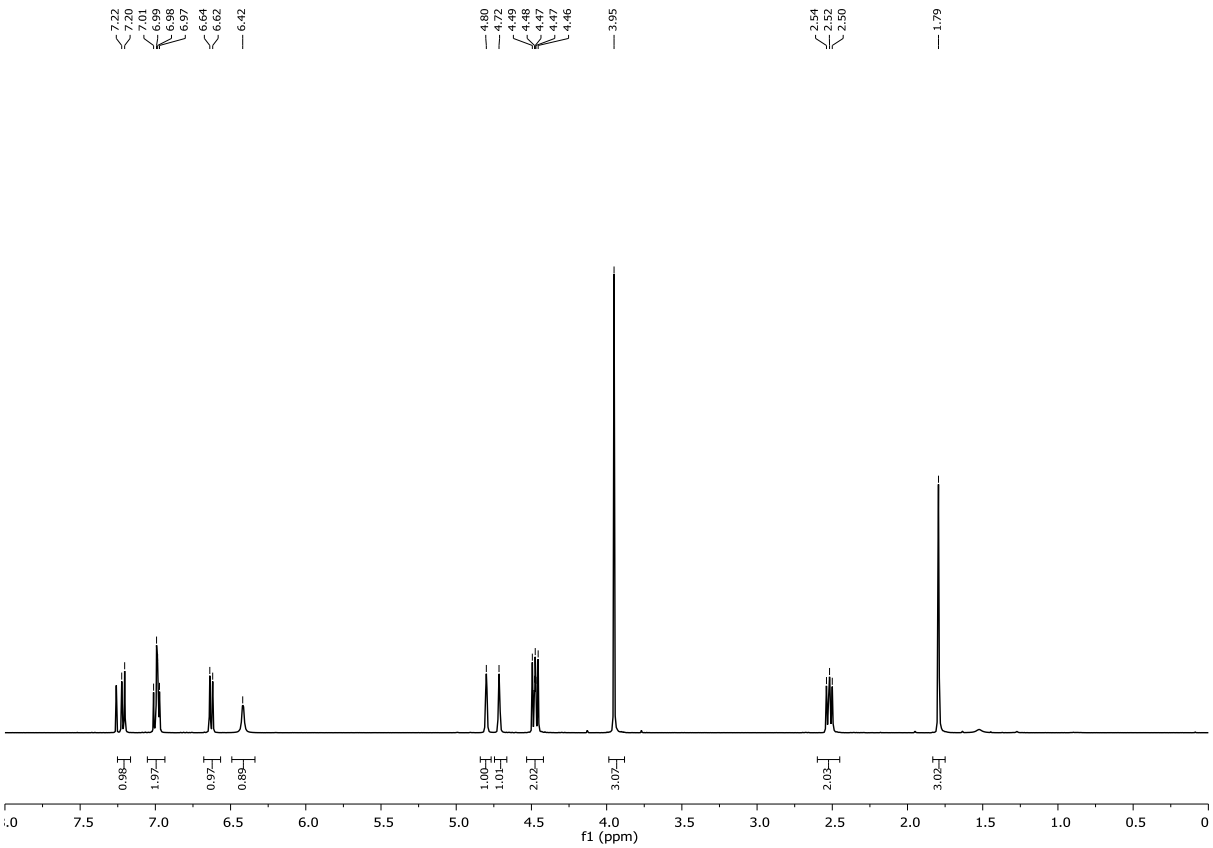
^{13}C NMR, 100 MHz, $CDCl_3$

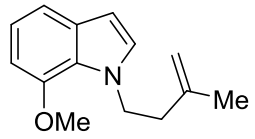




1i

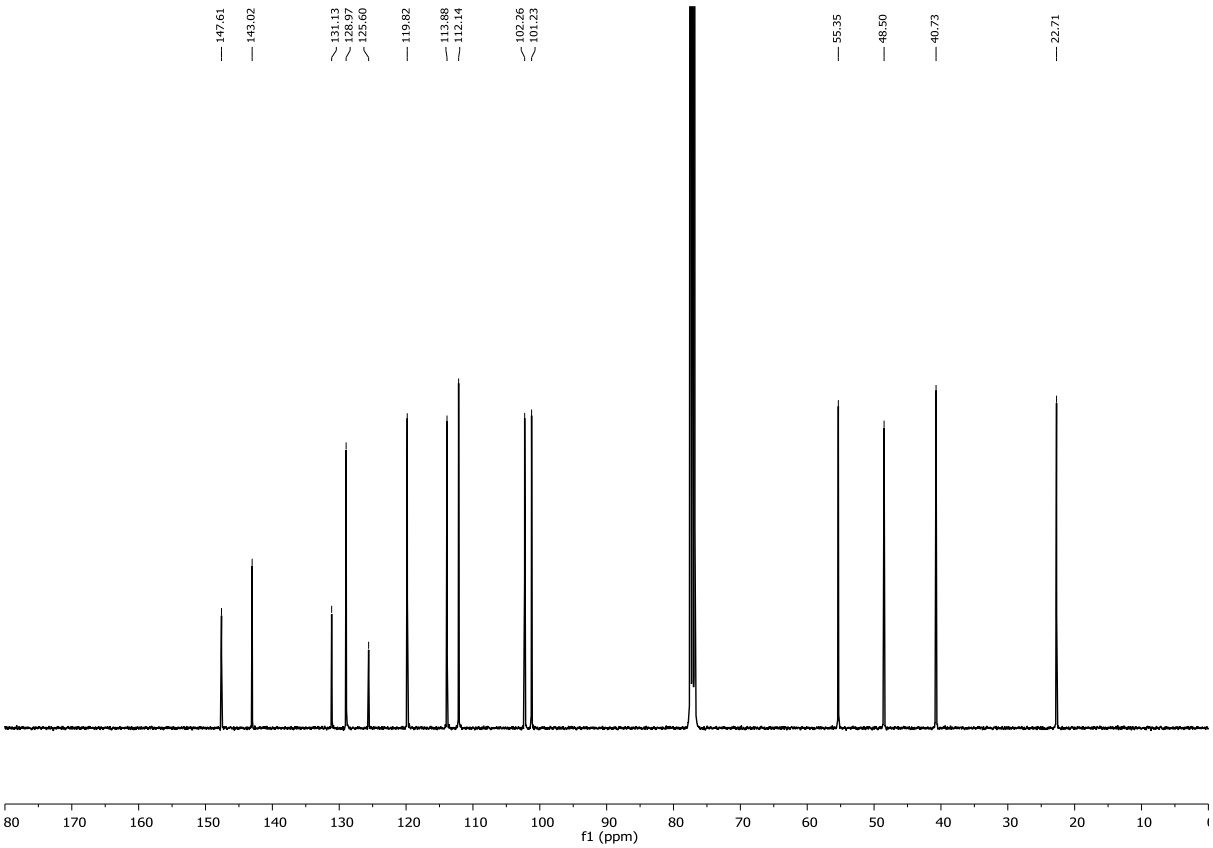
^{1}H NMR, 400 MHz, $CDCl_3$

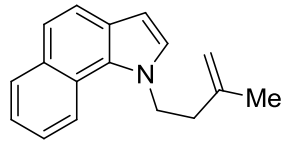




1i

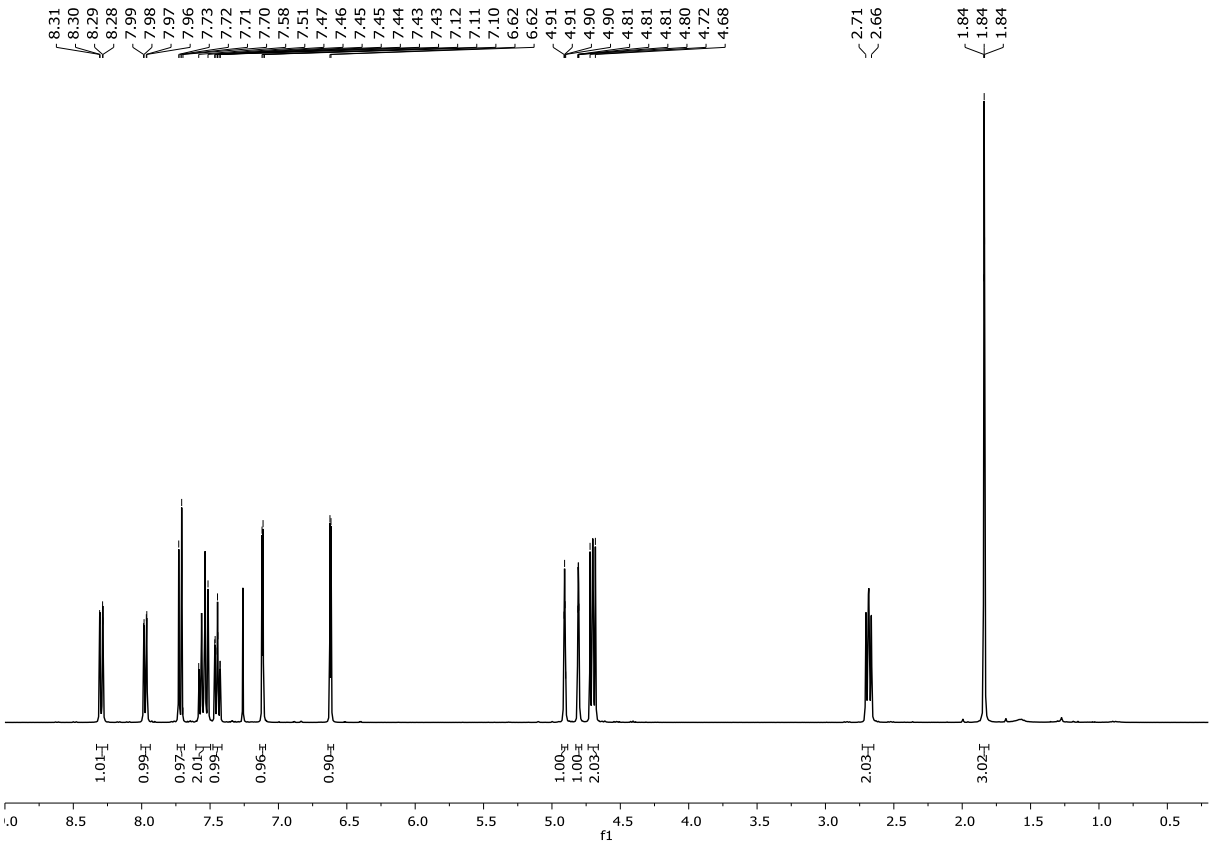
^{13}C NMR, 100 MHz, $CDCl_3$

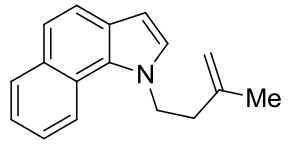




1j

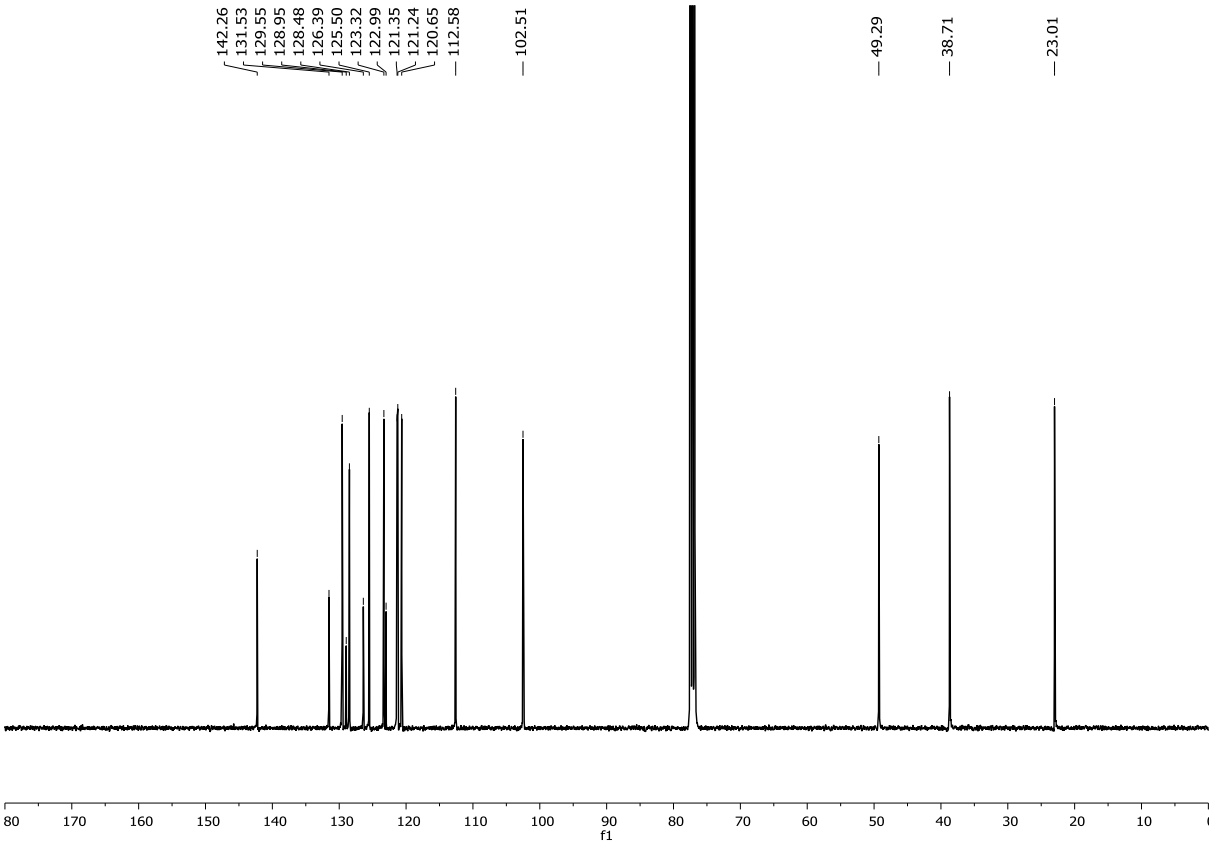
^{1}H NMR, 400 MHz, $CDCl_3$

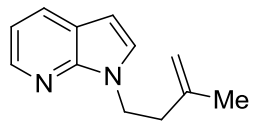




1j

^{13}C NMR, 100 MHz, $CDCl_3$





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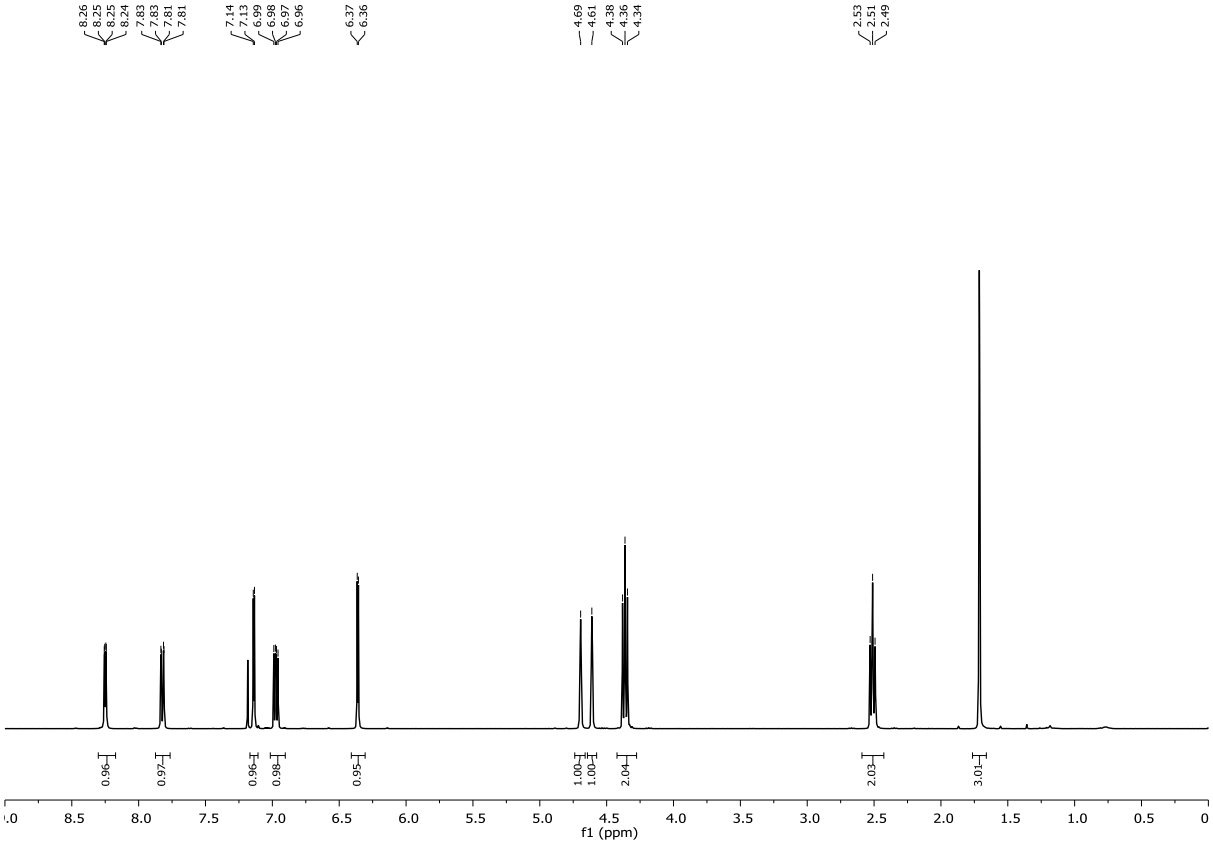
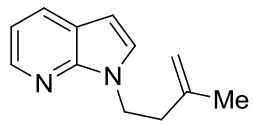
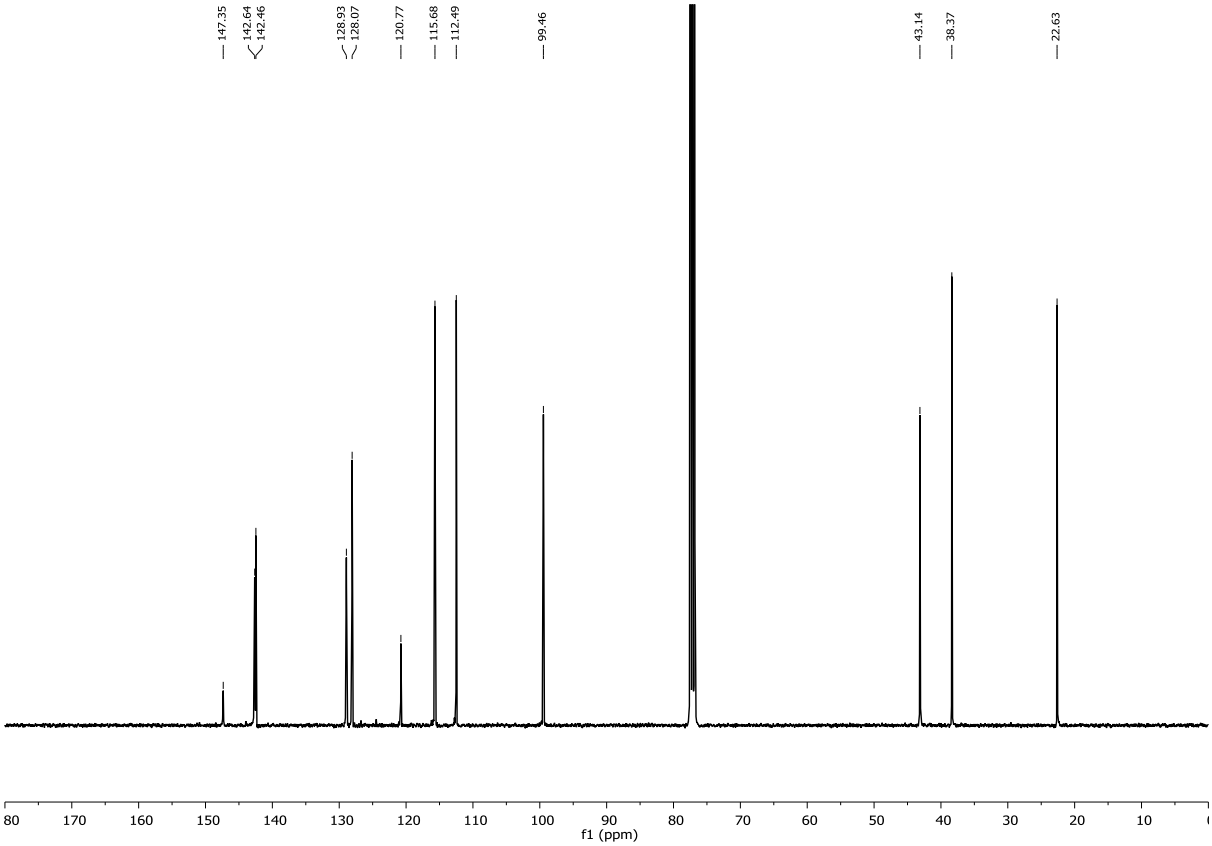
^{1}H NMR, 400 MHz, $CDCl_3$

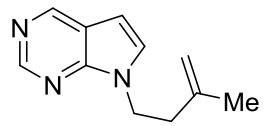




1k

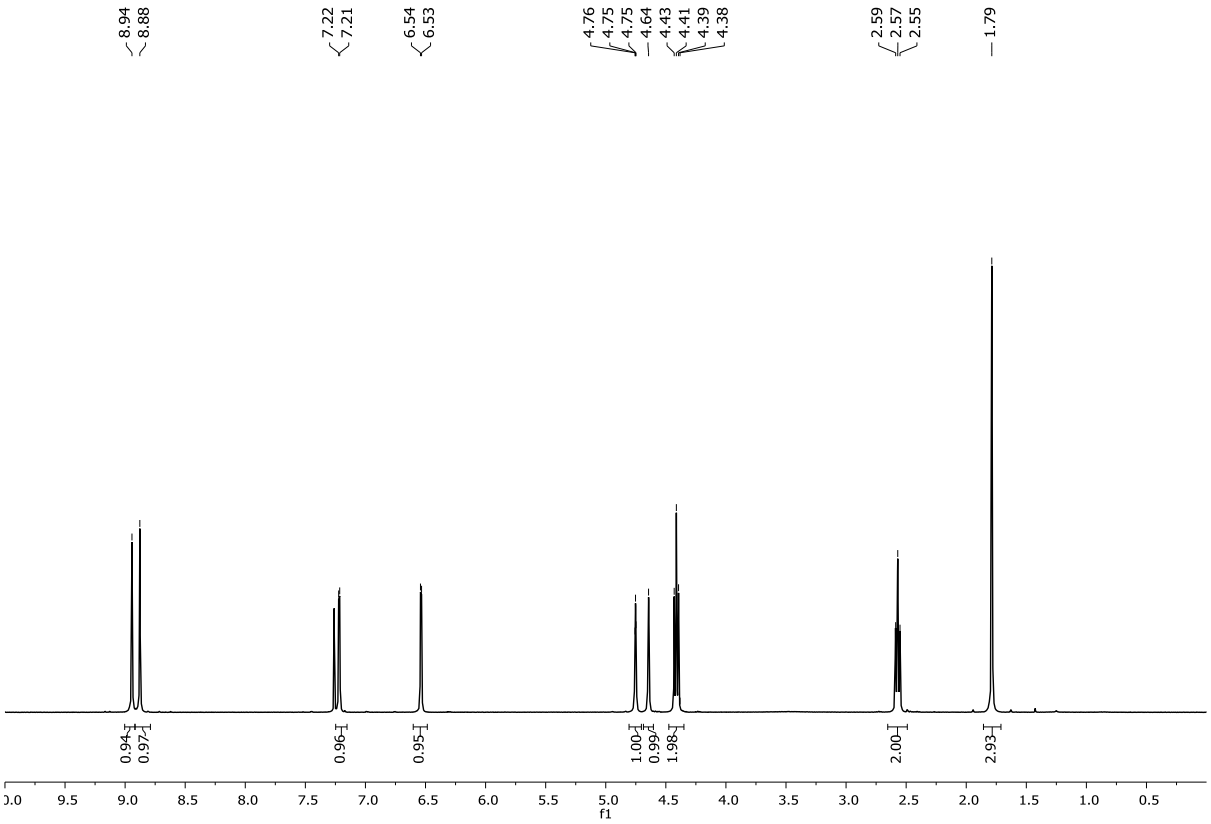
^{13}C NMR, 100 MHz, $CDCl_3$

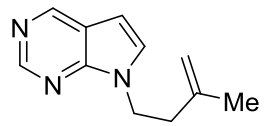




1l

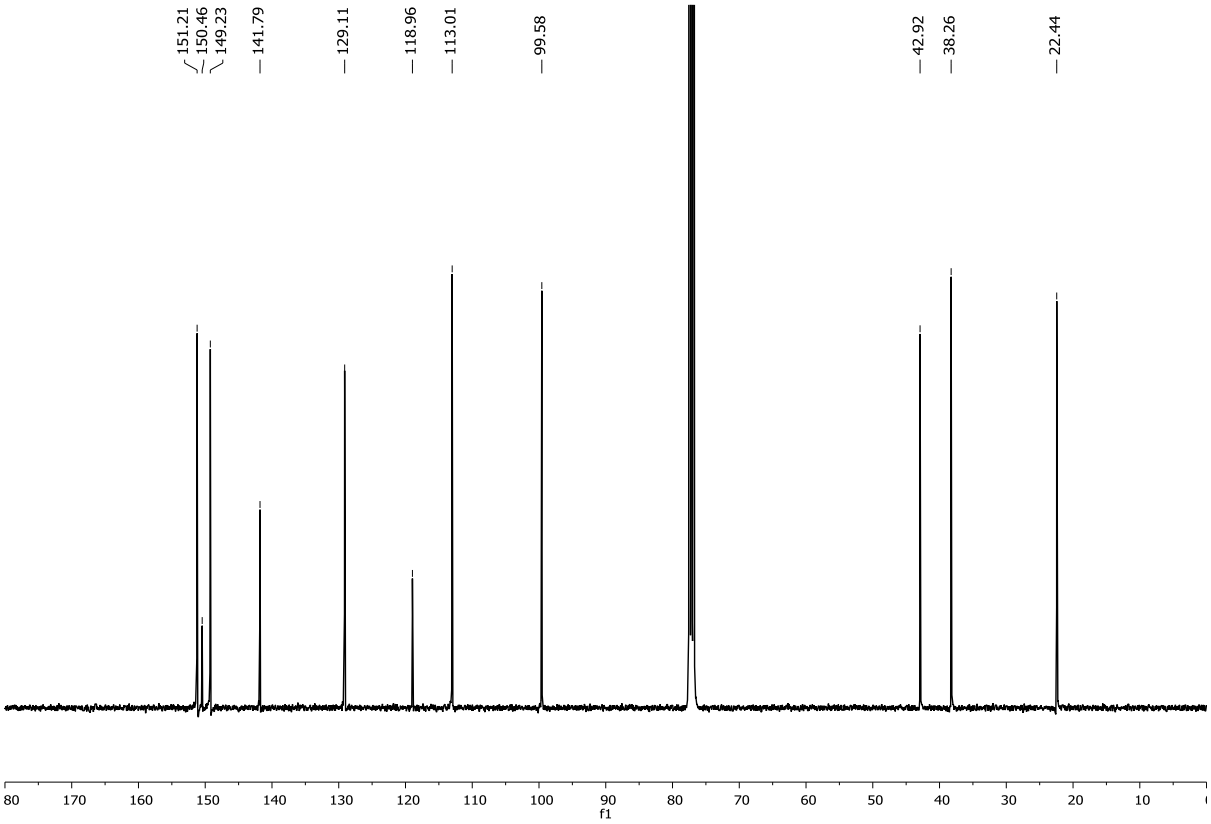
^{1}H NMR, 400 MHz, $CDCl_3$

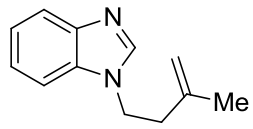




1l

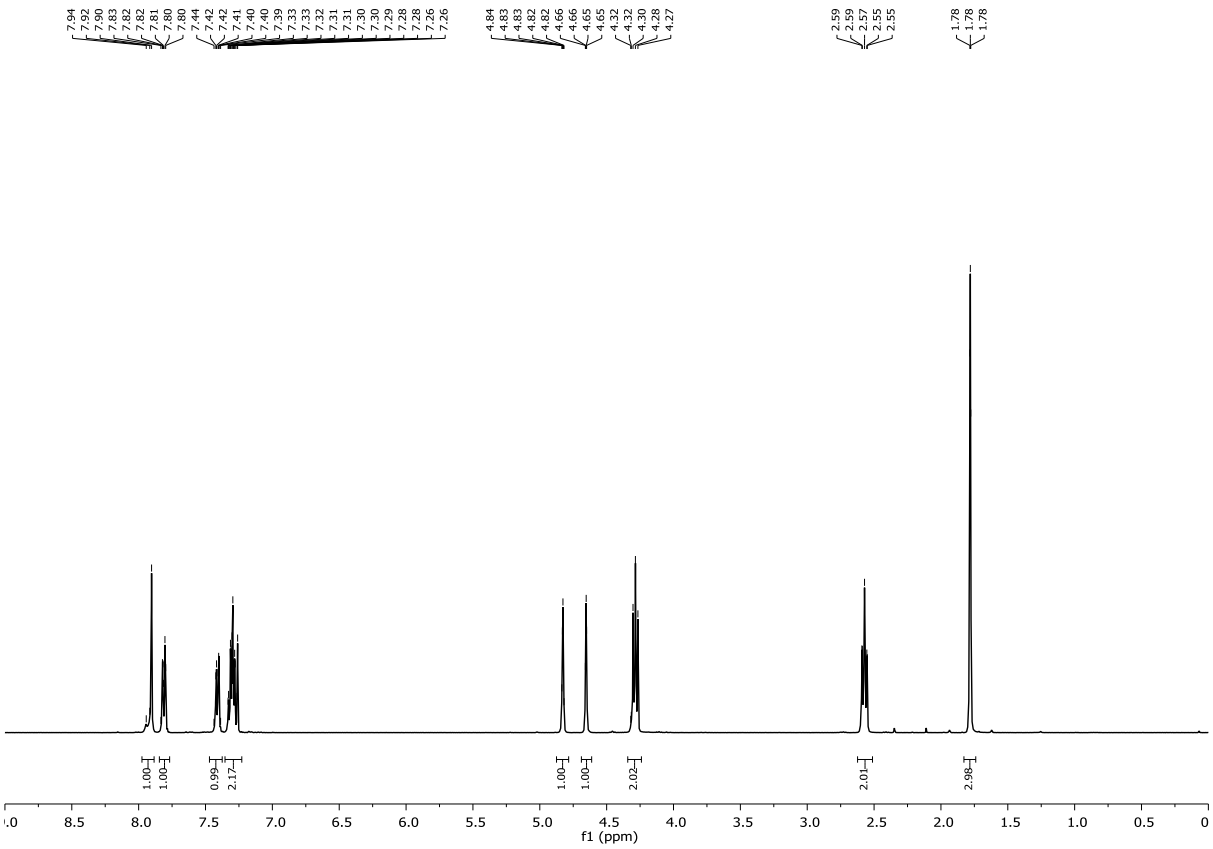
^{13}C NMR, 100 MHz, $CDCl_3$

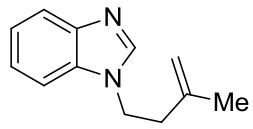




1m

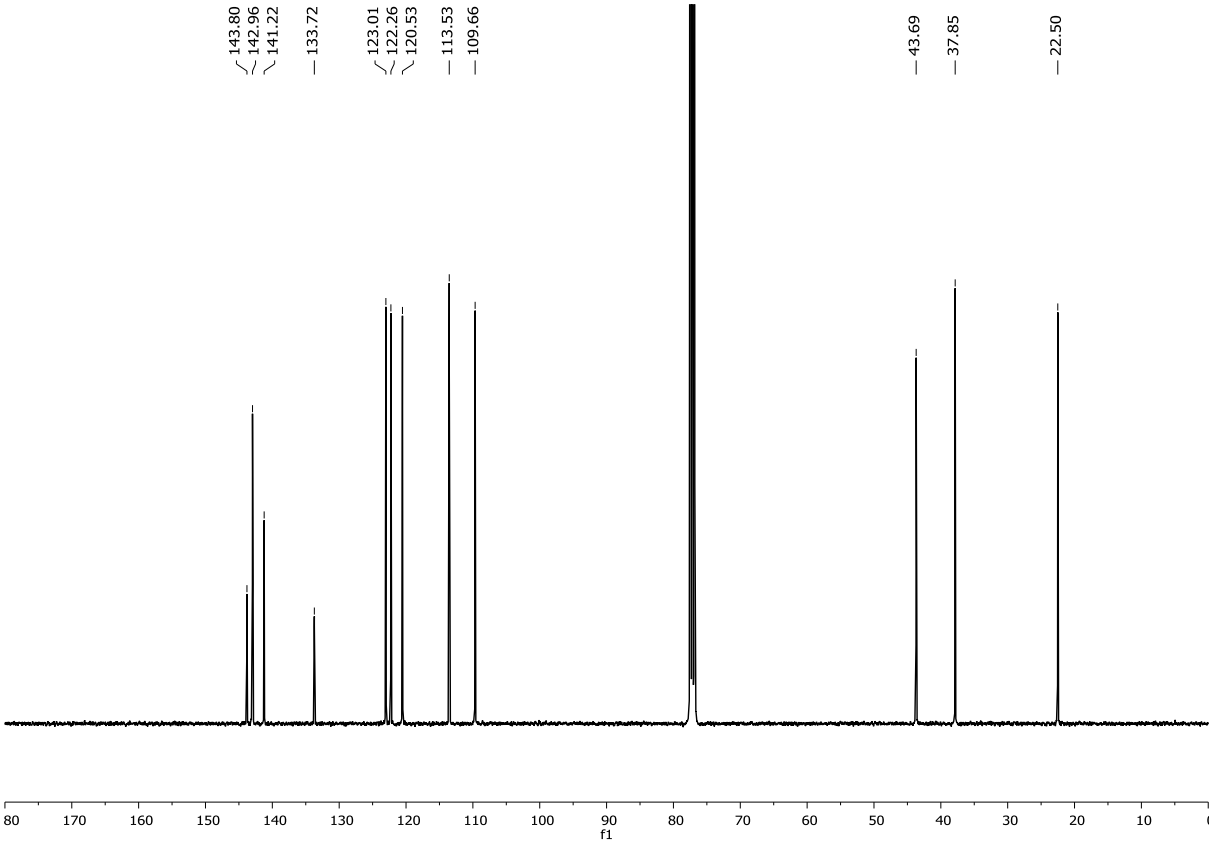
^{1}H NMR, 400 MHz, $CDCl_3$

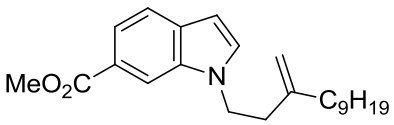




1m

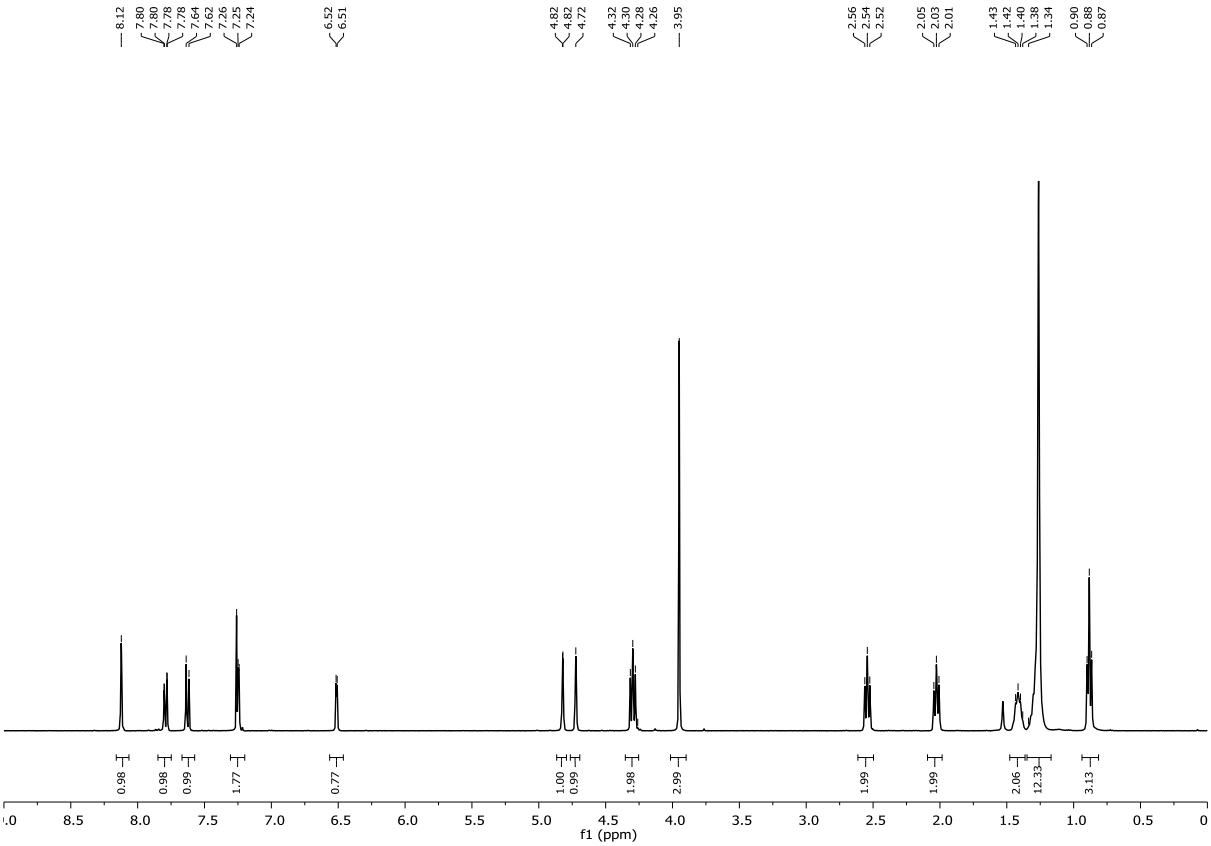
^{13}C NMR, 100 MHz, $CDCl_3$

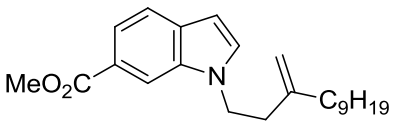




1n

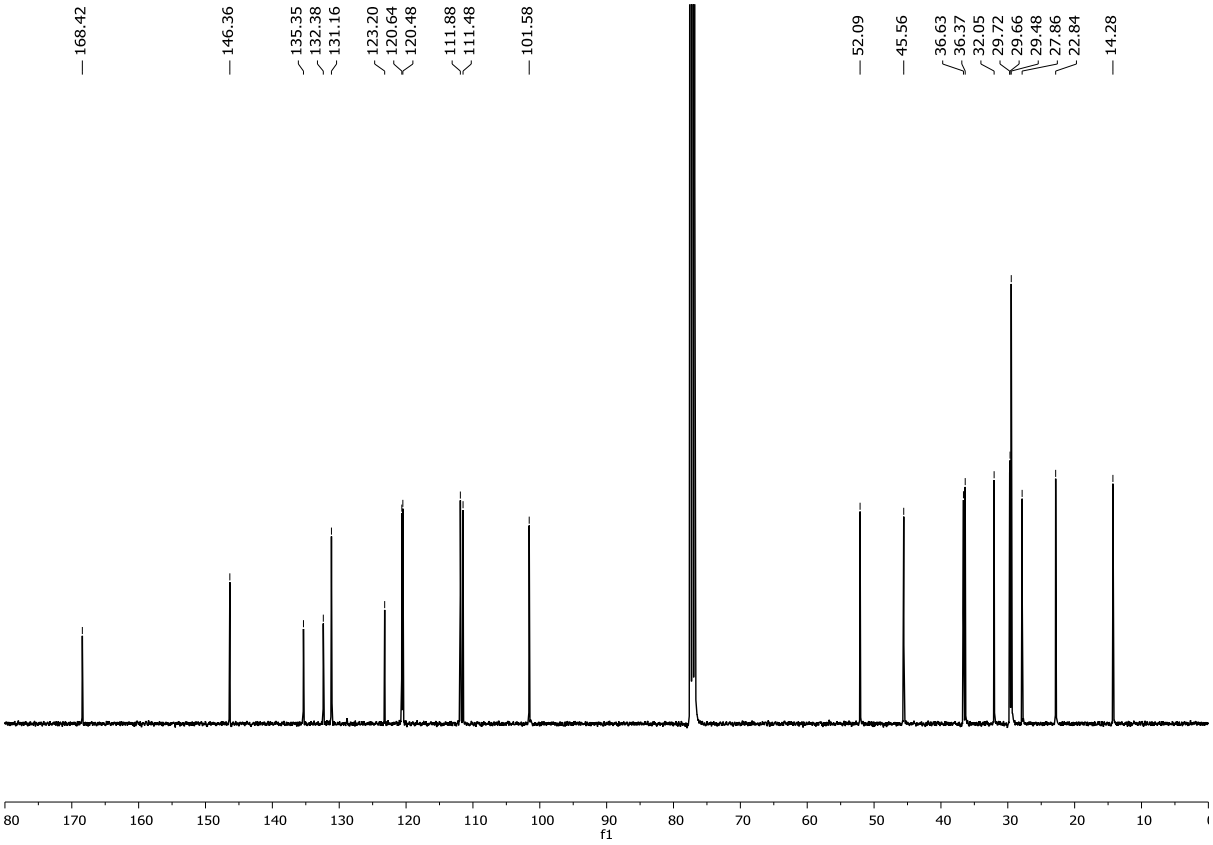
^{1}H NMR, 400 MHz, $CDCl_3$

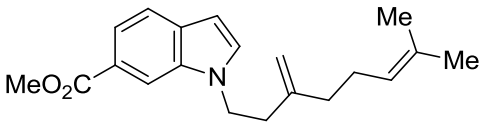




1n

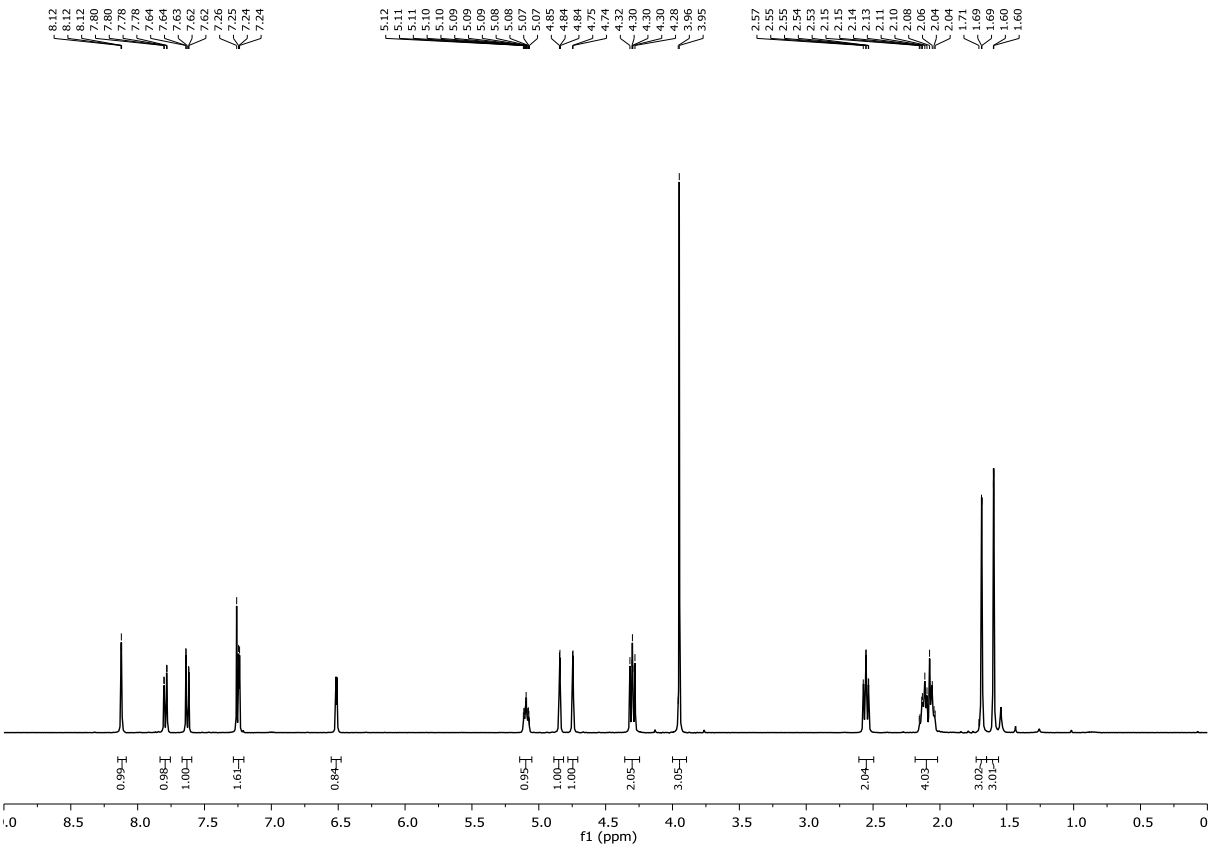
^{13}C NMR, 100 MHz, $CDCl_3$

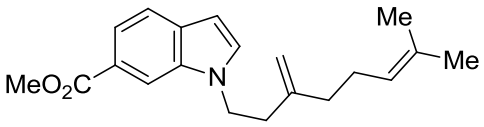




1o

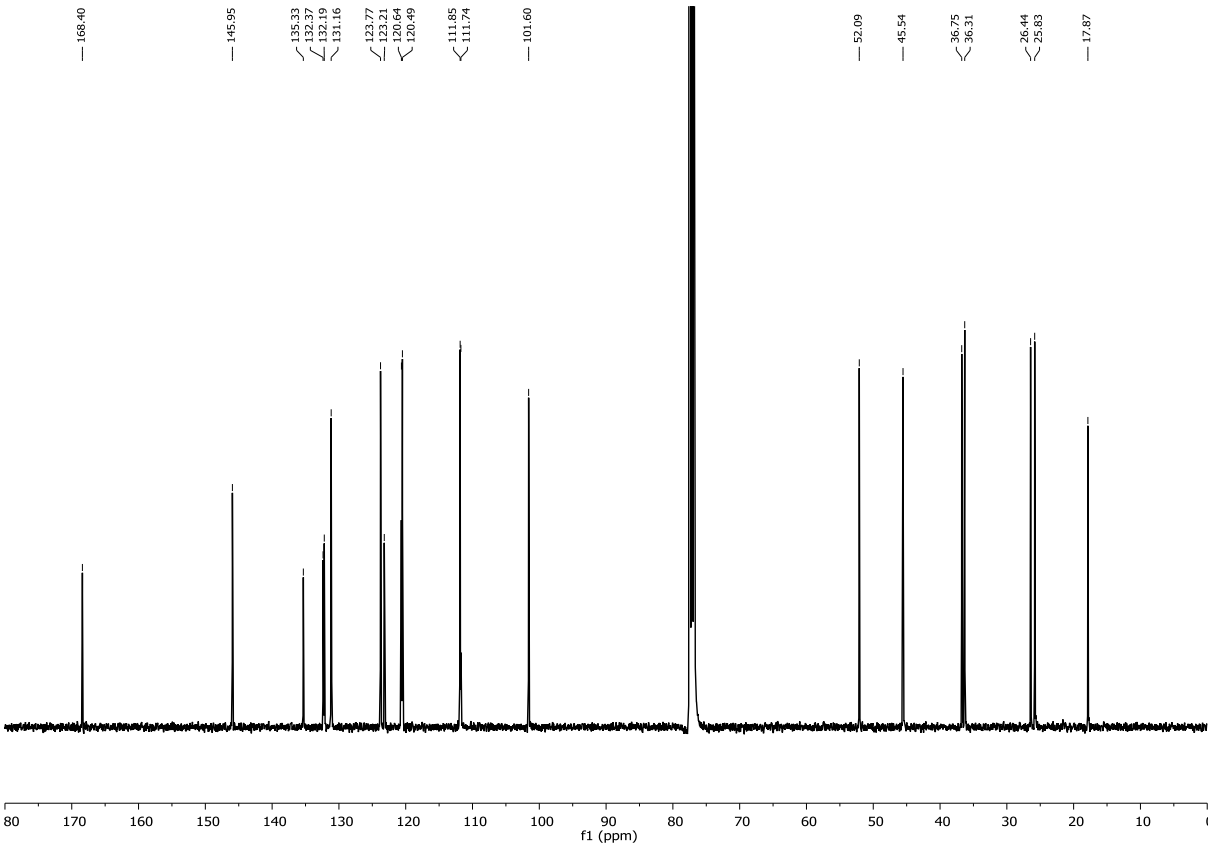
^{1}H NMR, 400 MHz, $CDCl_3$

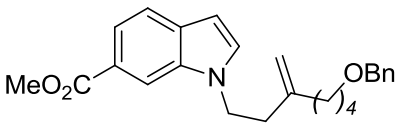




1o

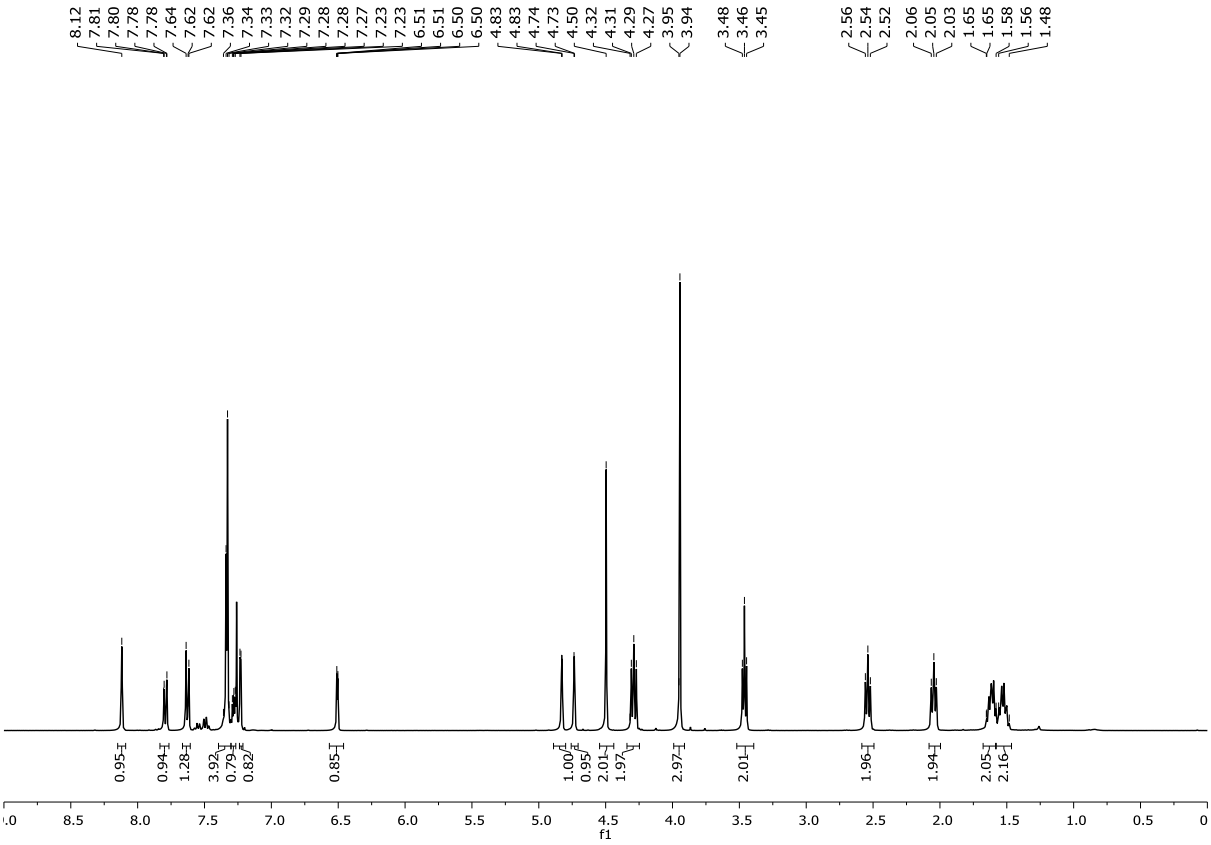
^{13}C NMR, 100 MHz, $CDCl_3$

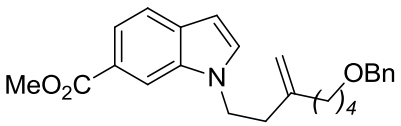




1p

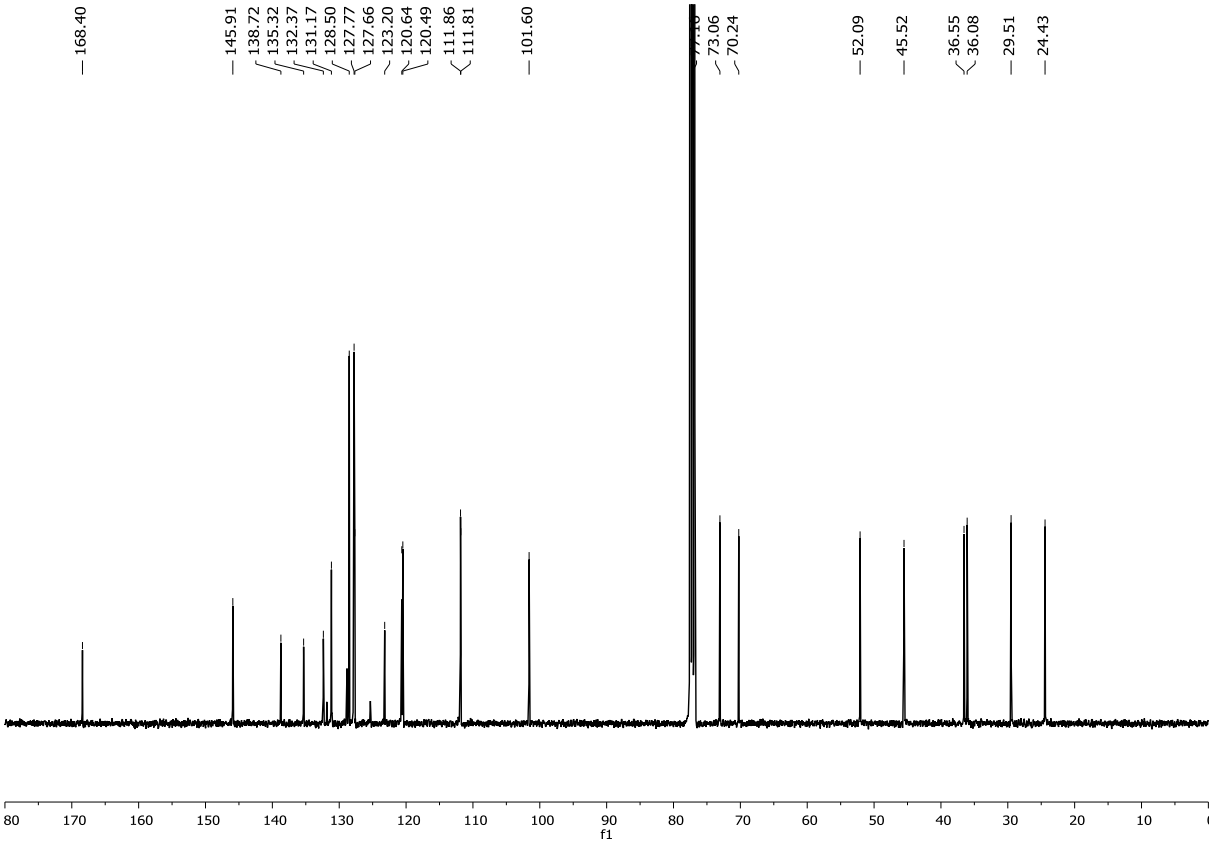
^{1}H NMR, 400 MHz, $CDCl_3$

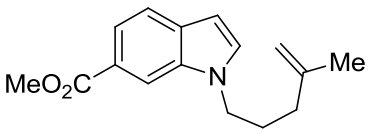




1p

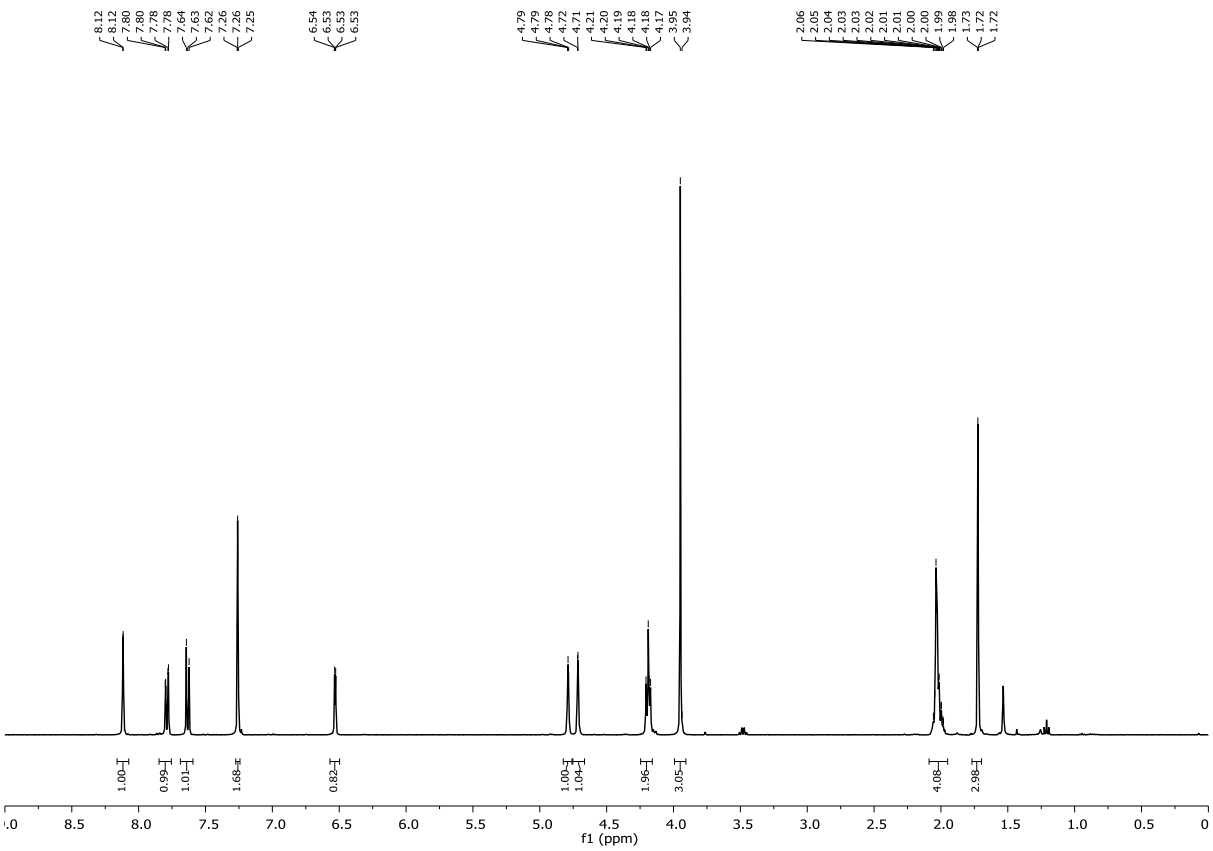
^{13}C NMR, 101 MHz, $CDCl_3$

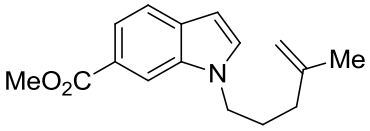




1q

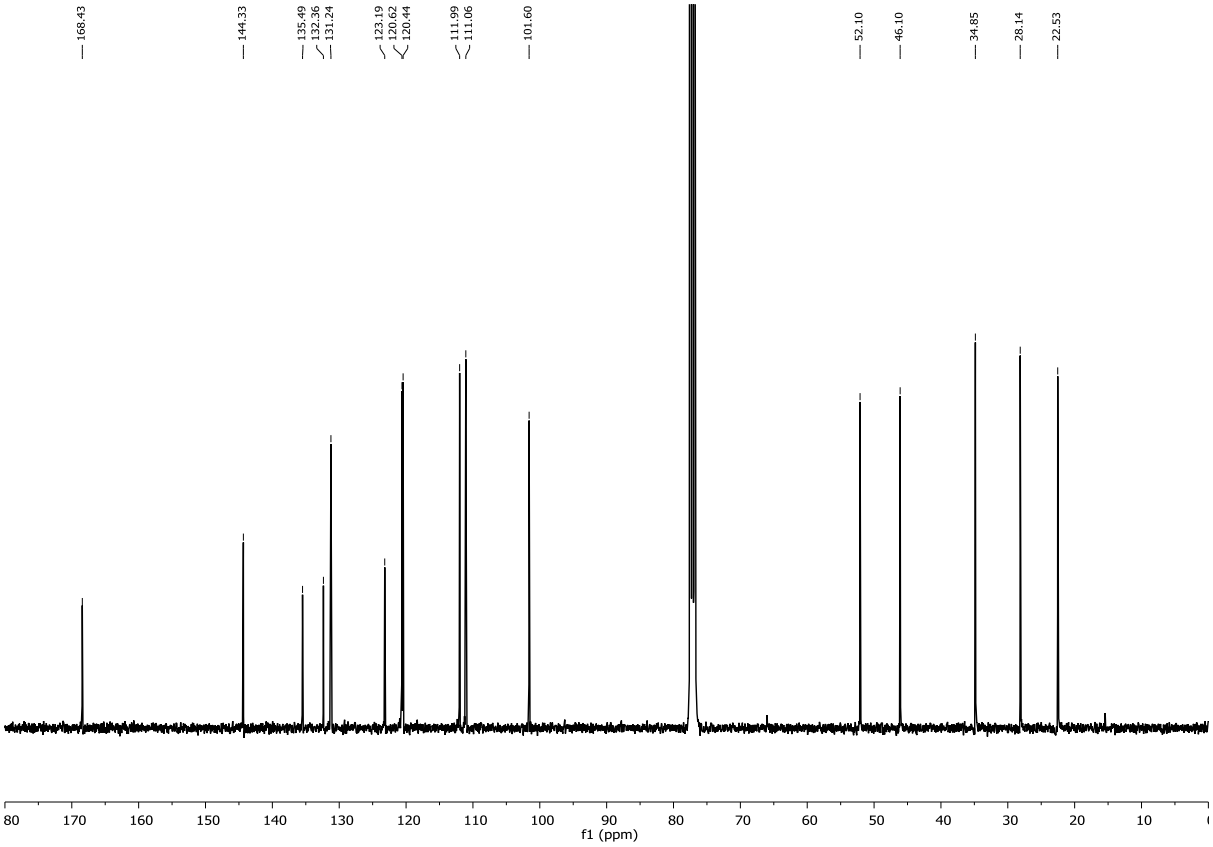
^{1}H NMR, 400 MHz, $CDCl_3$

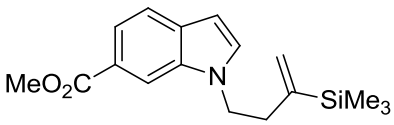




1q

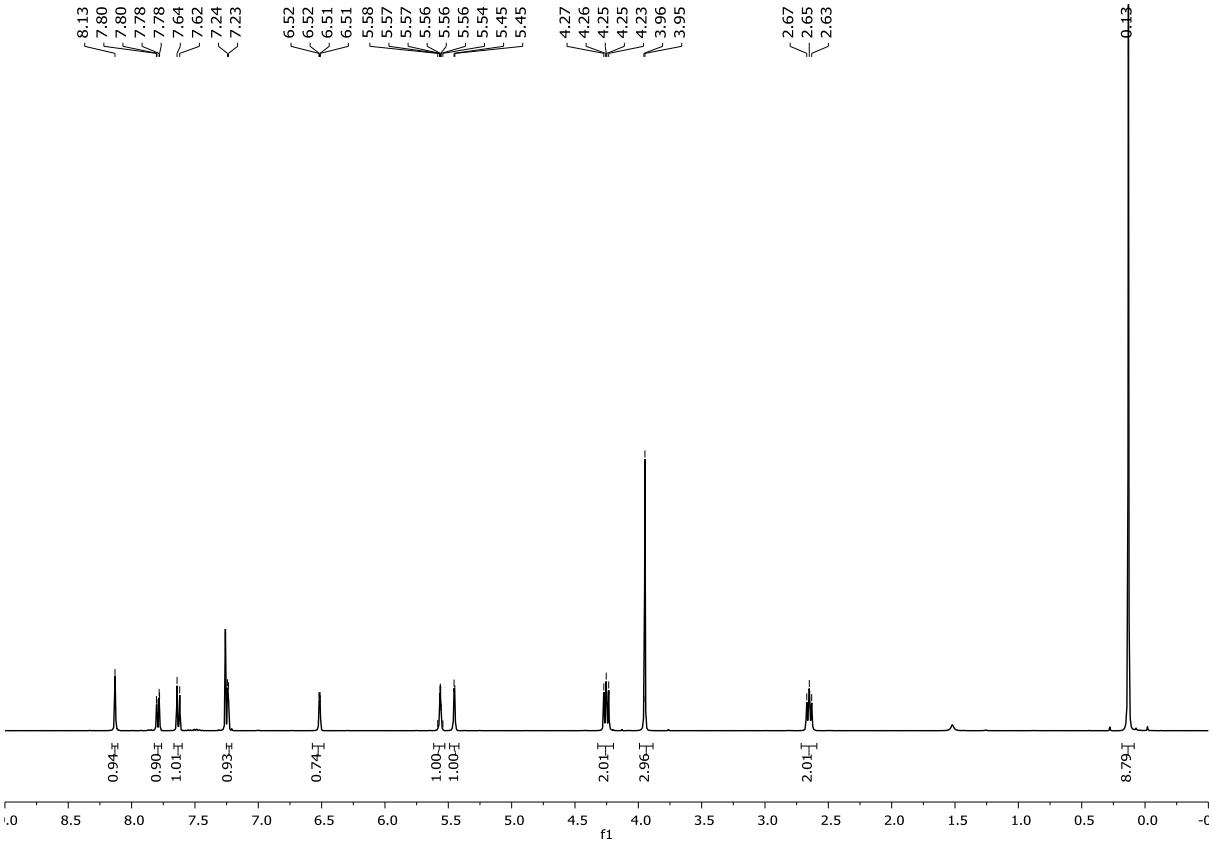
^{13}C NMR, 100 MHz, $CDCl_3$

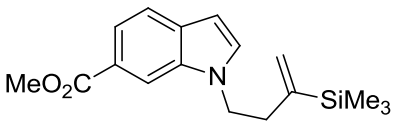




1r

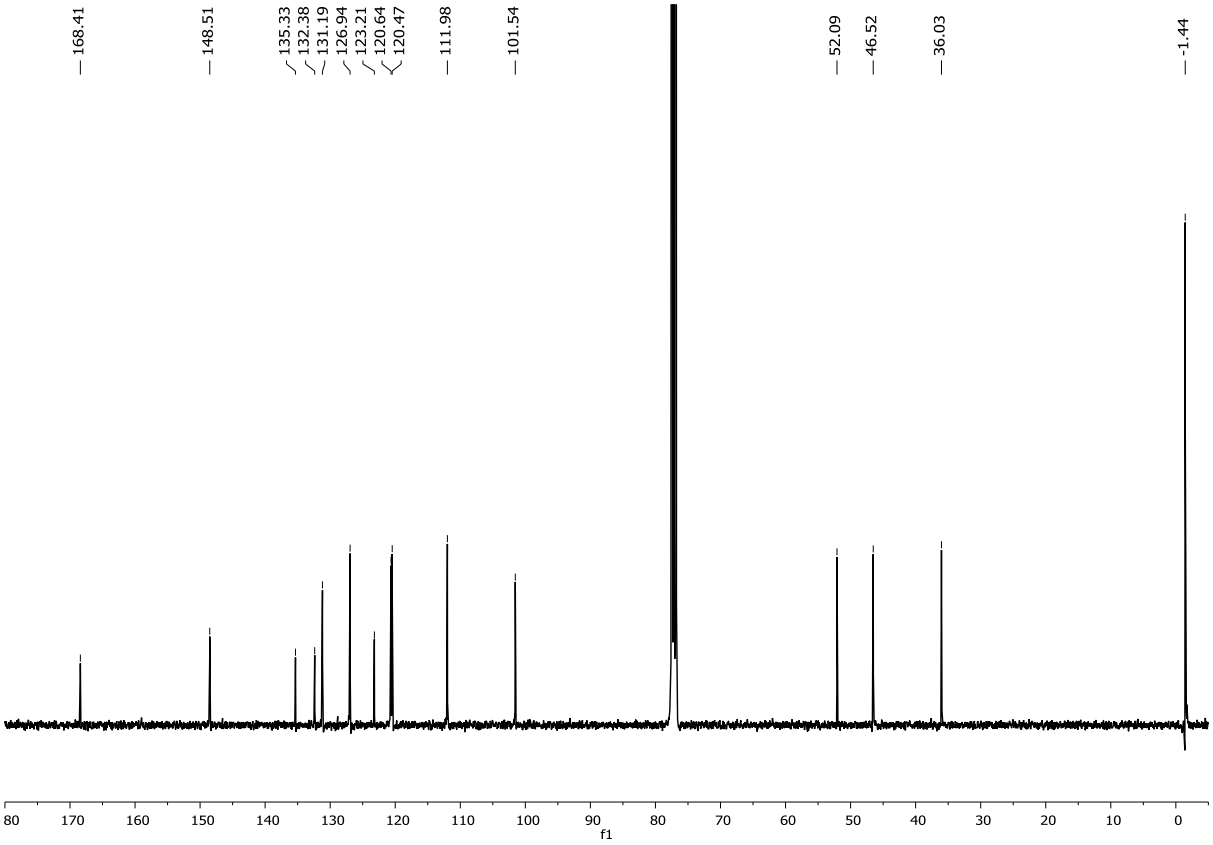
^{1}H NMR, 400 MHz, $CDCl_3$

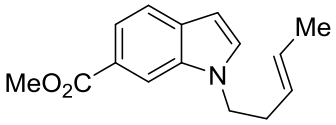




1r

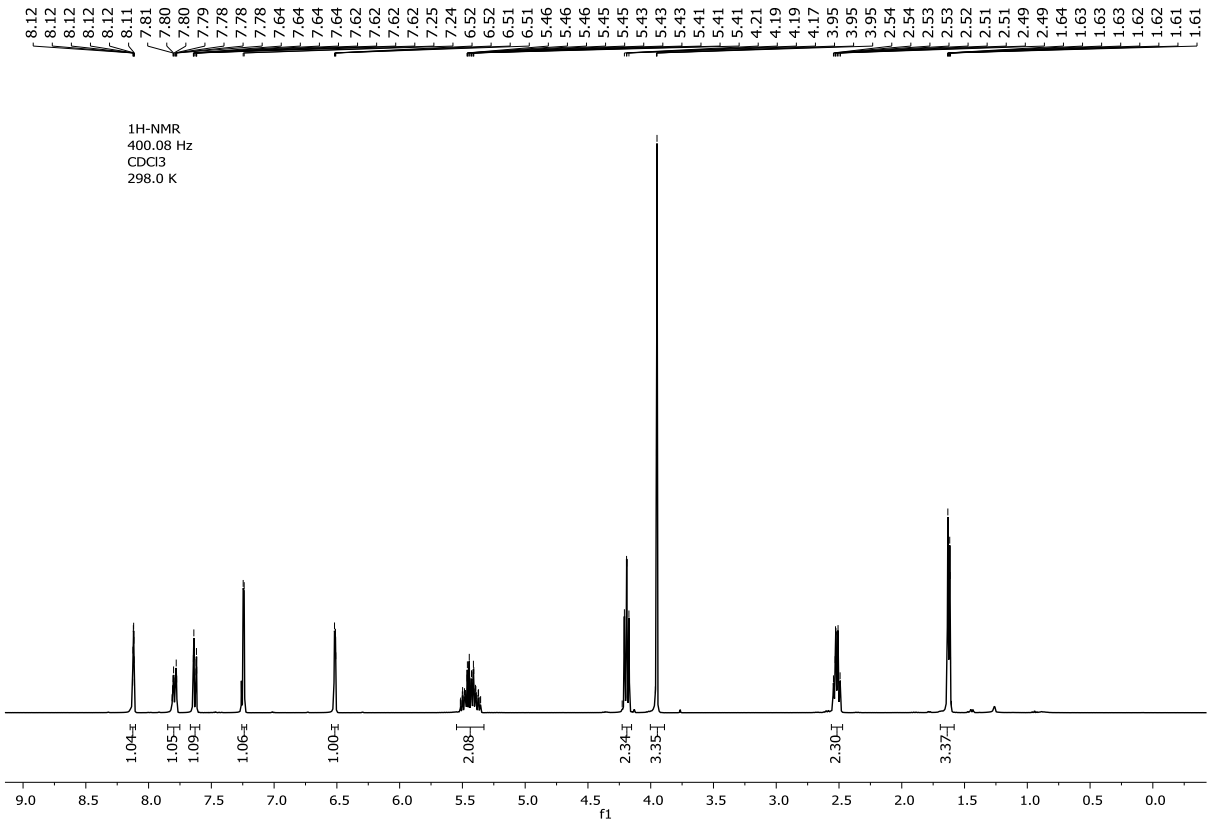
^{13}C NMR, 100 MHz, $CDCl_3$

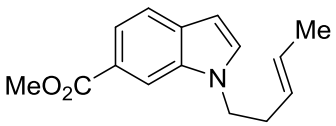




***E*-1s**

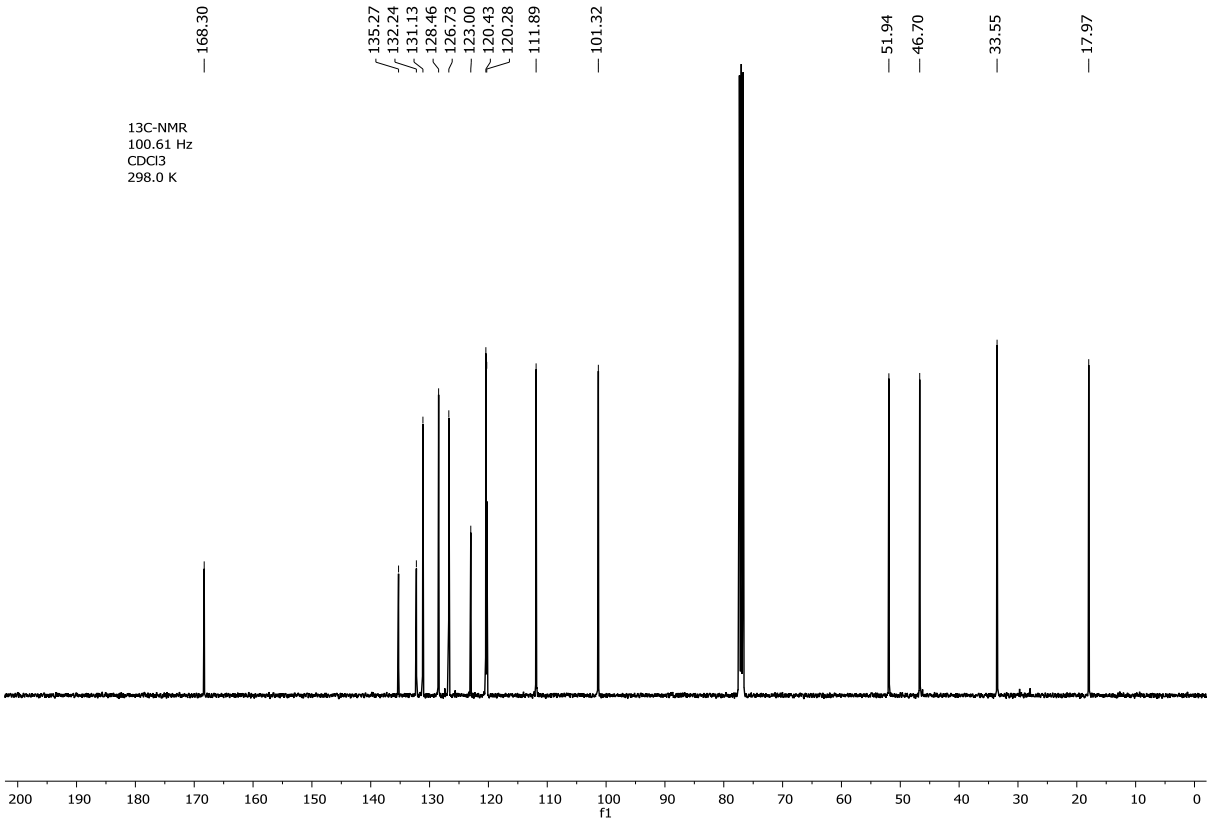
^{1}H NMR, 400 MHz, $CDCl_3$

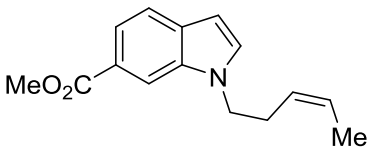




***E*-1s**

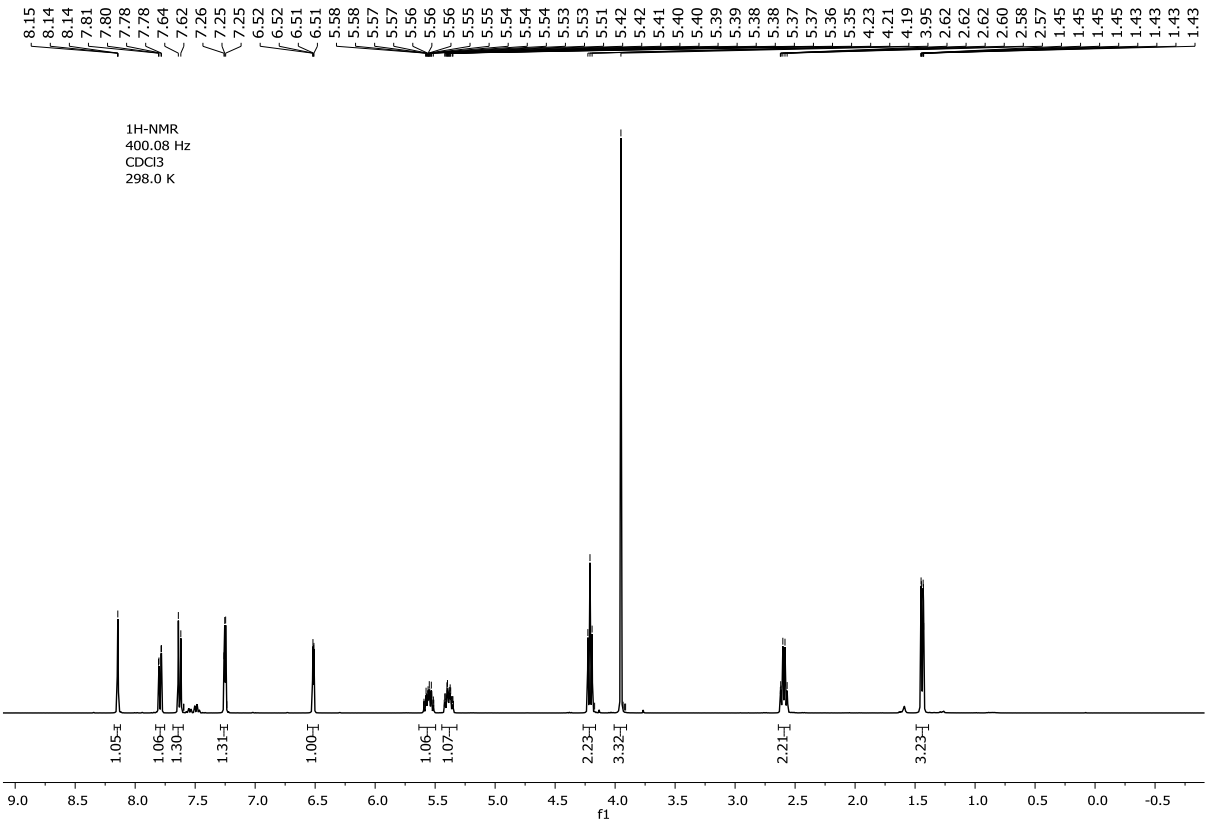
^{13}C NMR, 100 MHz, $CDCl_3$

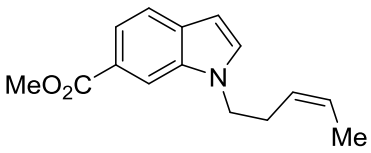




***Z*-1s**

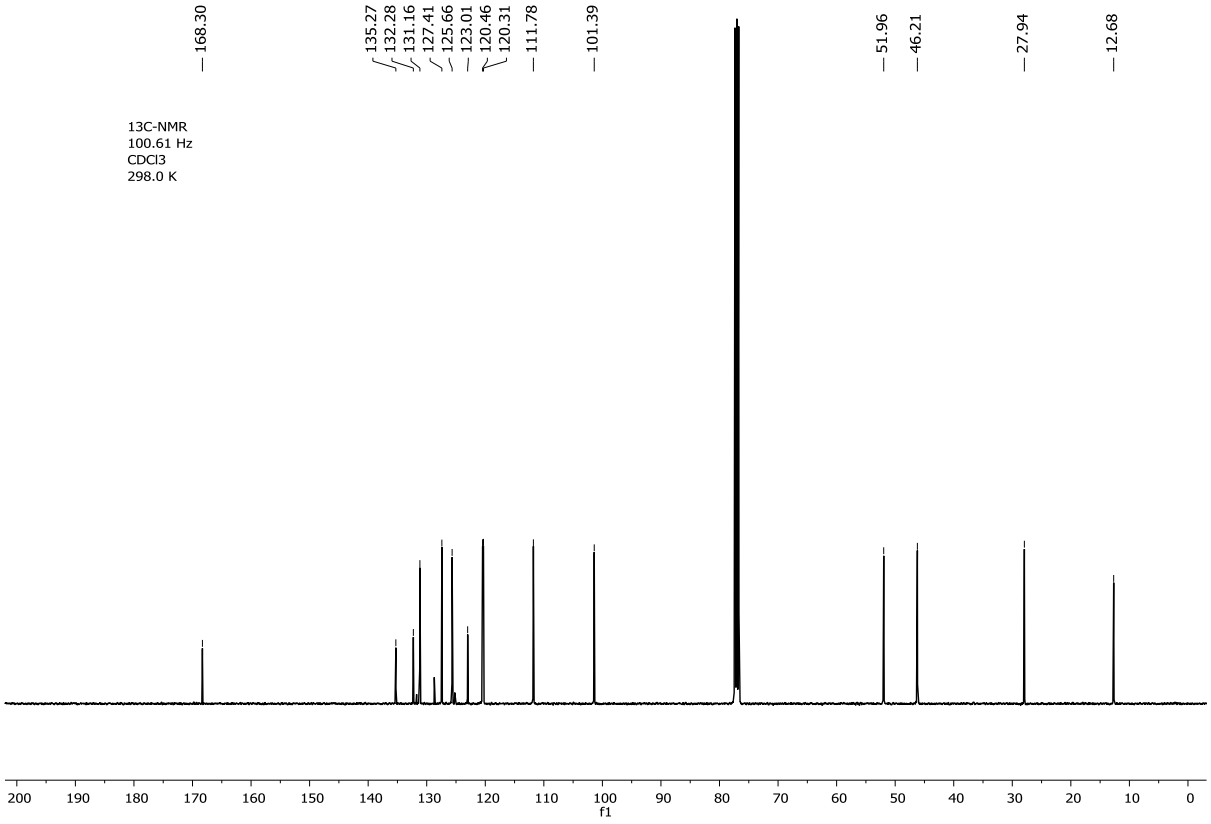
^{1}H NMR, 400 MHz, $CDCl_3$

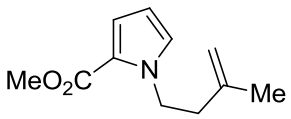




***Z*-1s**

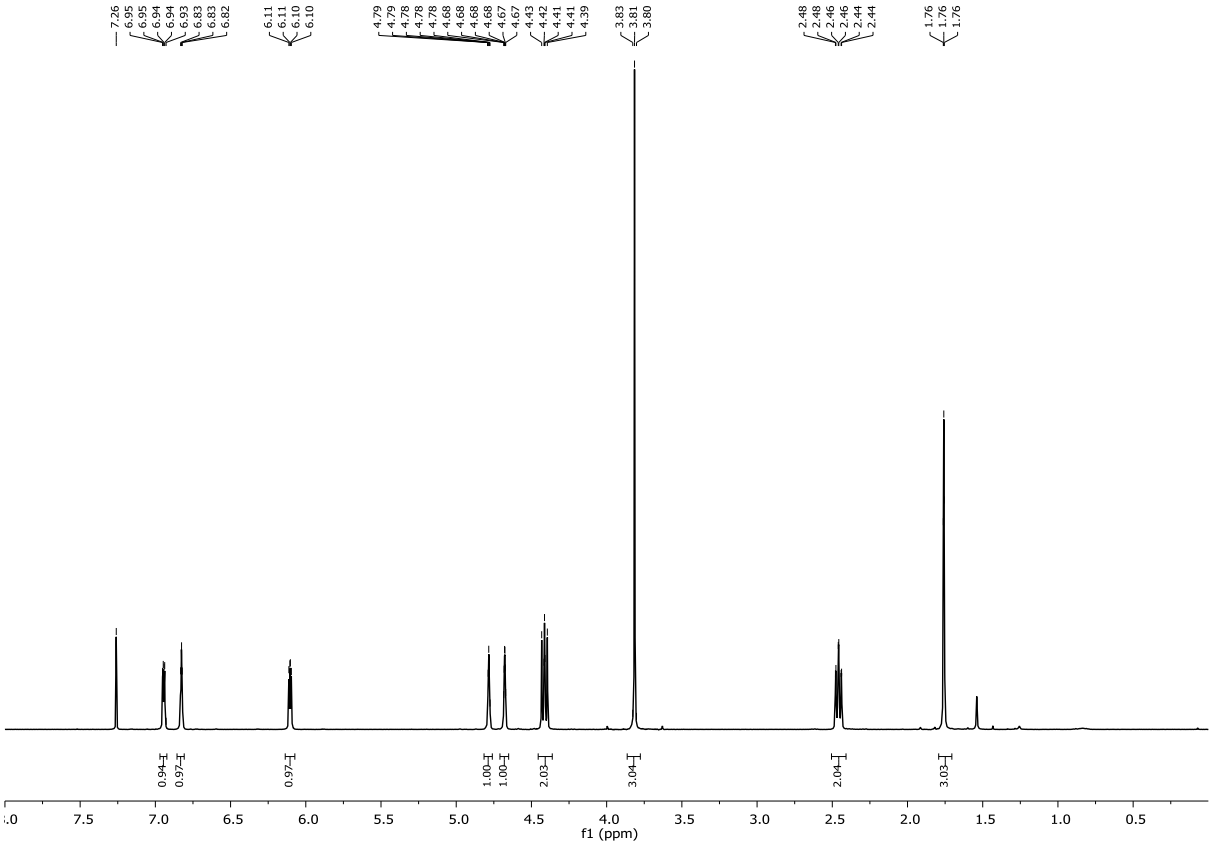
^{13}C NMR, 100 MHz, $CDCl_3$

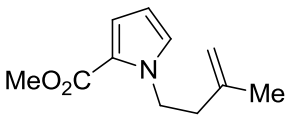




3a

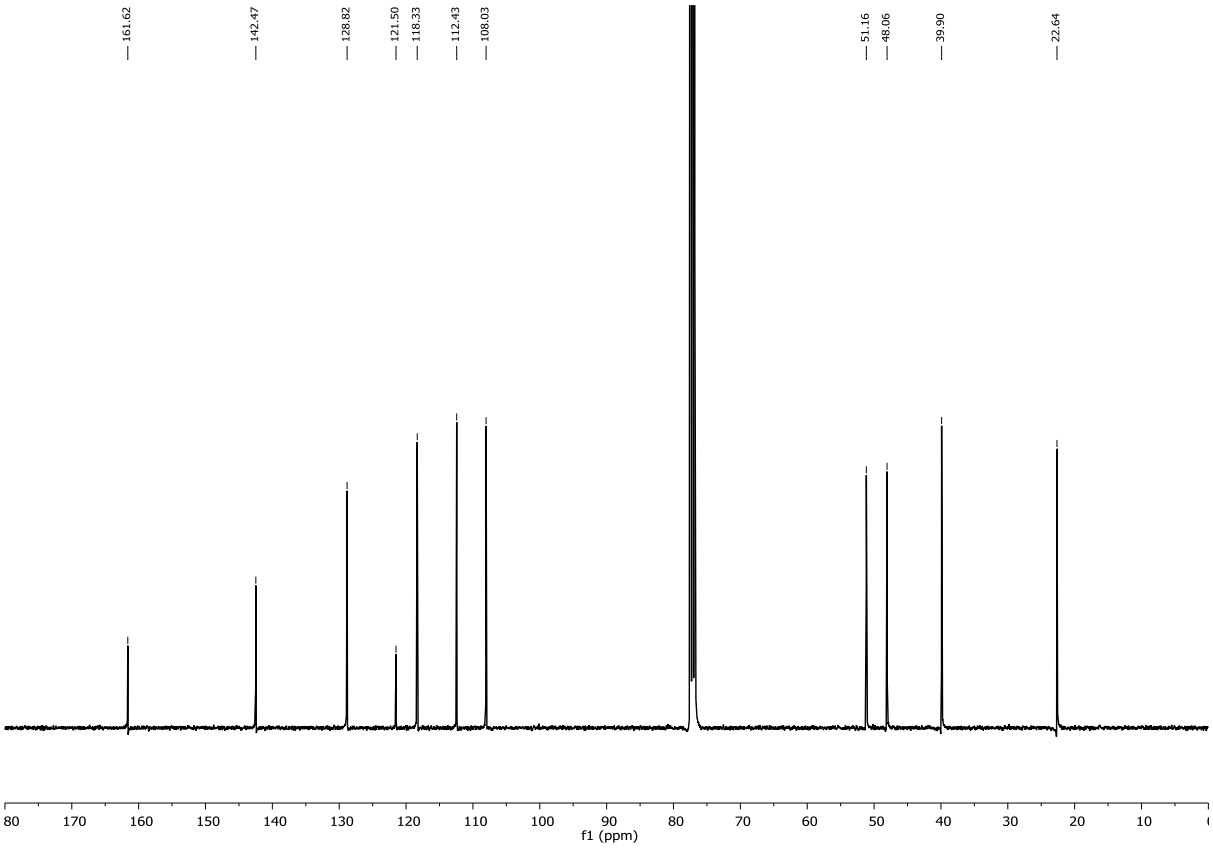
^{1}H NMR, 400 MHz, $CDCl_3$

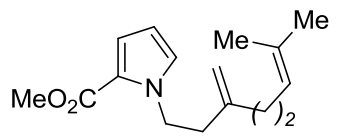




3a

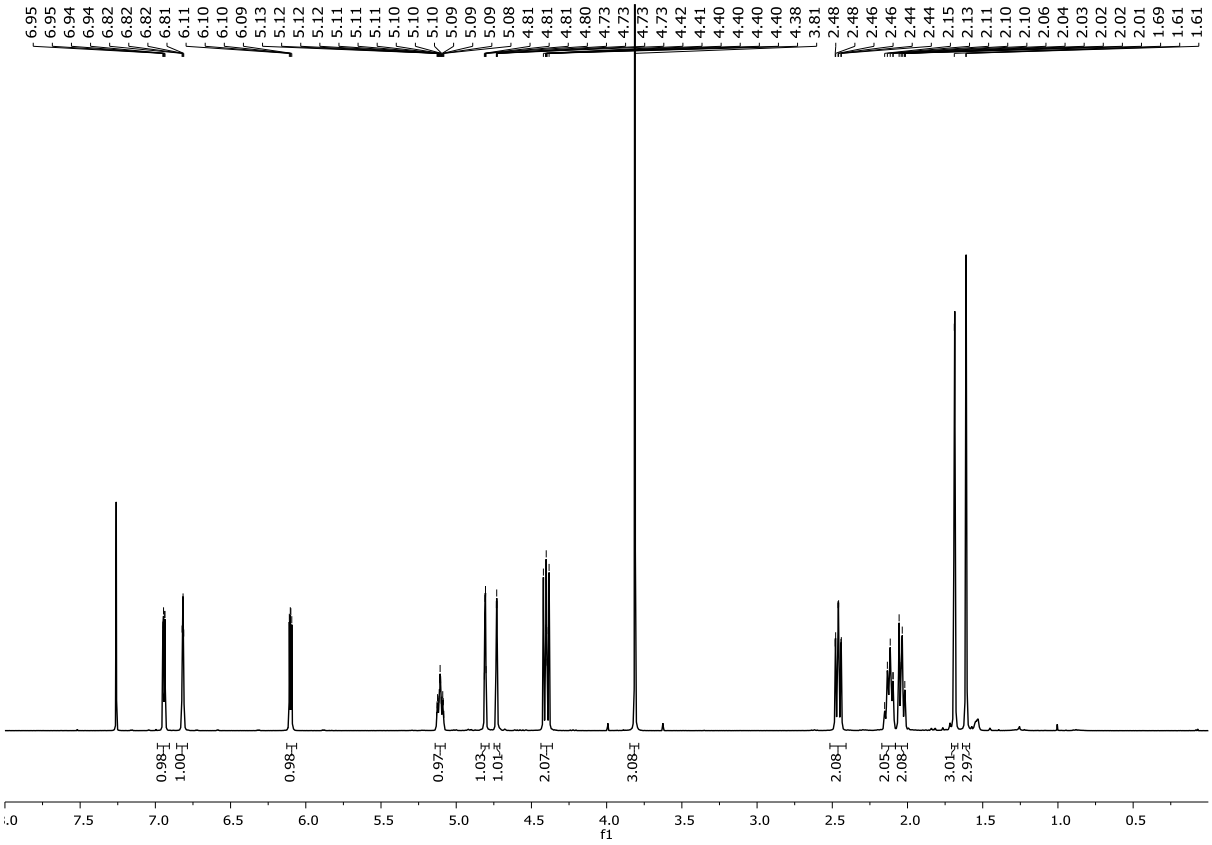
^{13}C NMR, 100 MHz, $CDCl_3$

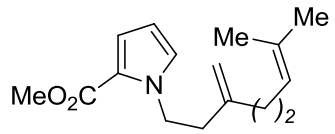




3b

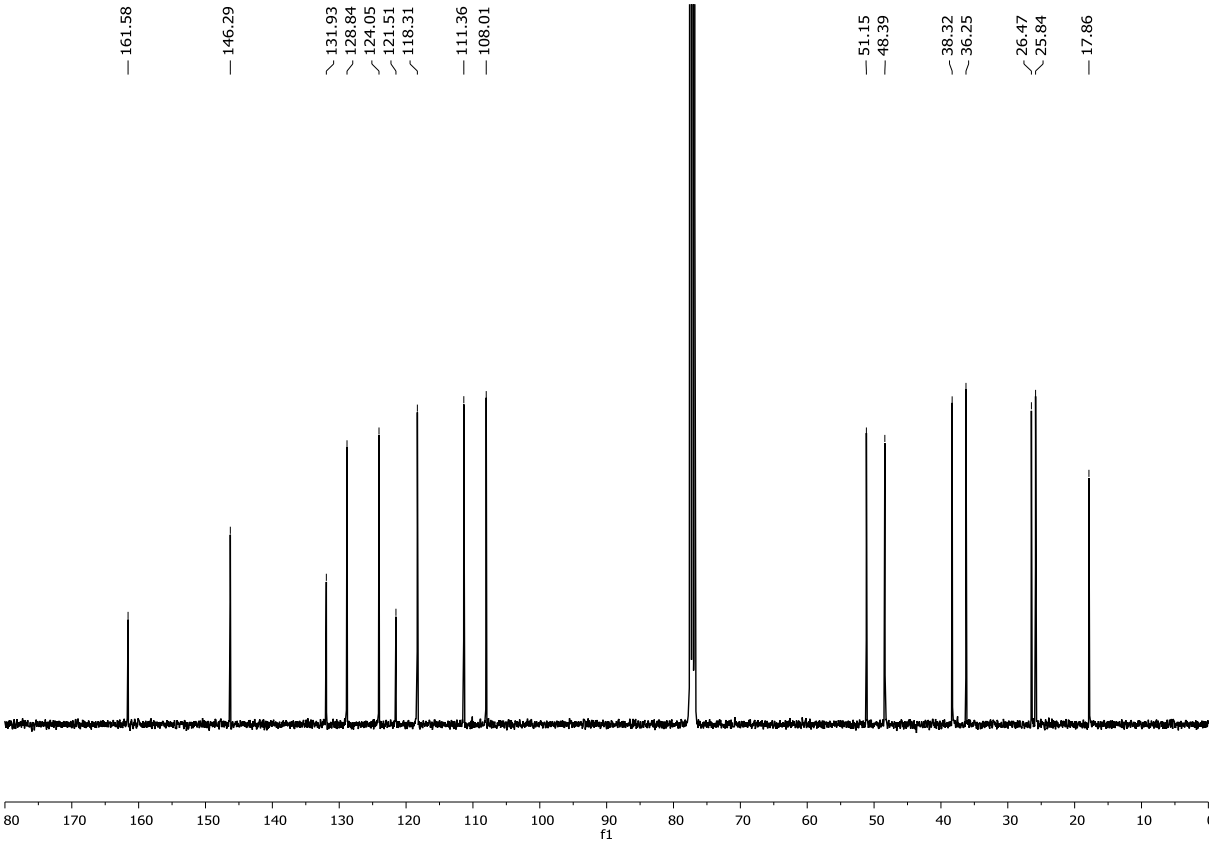
^{1}H NMR, 400 MHz, $CDCl_3$

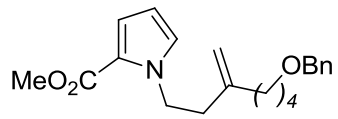




3b

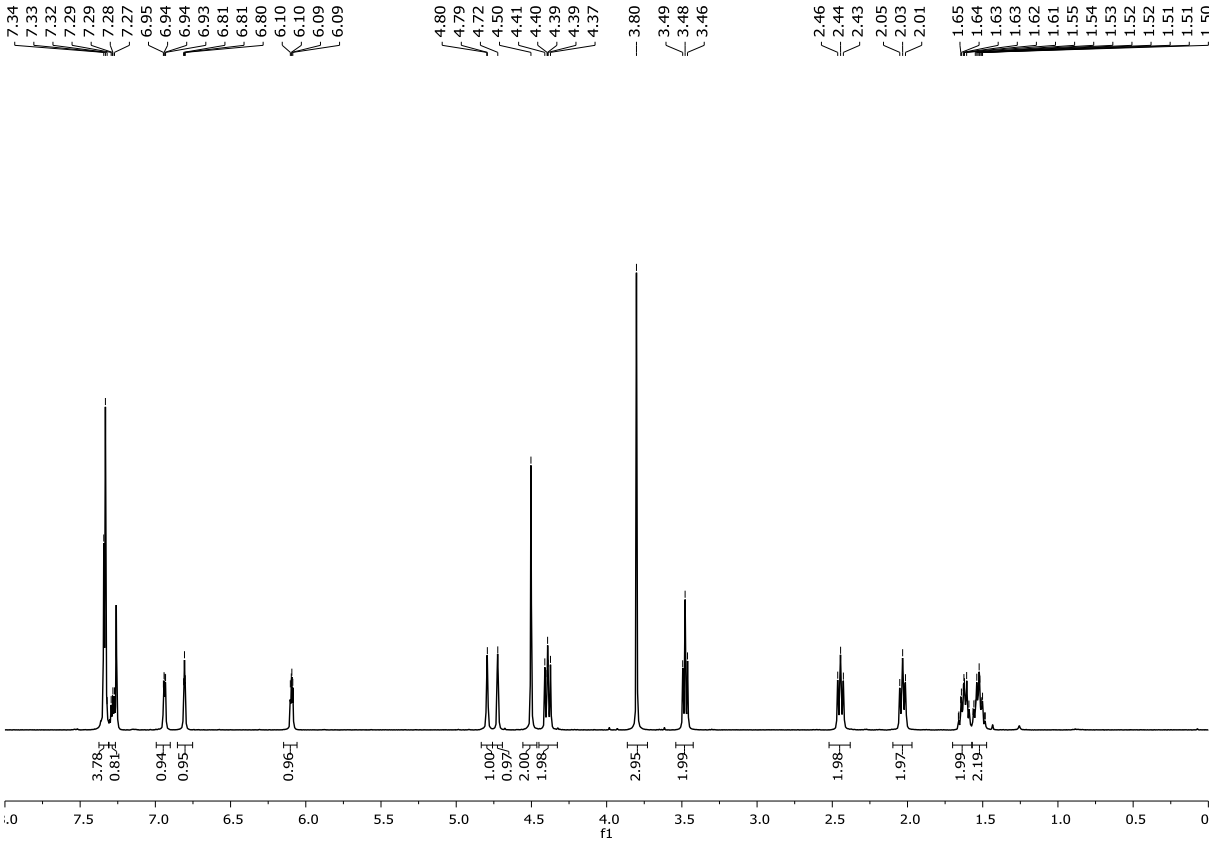
^{13}C NMR, 101 MHz, $CDCl_3$

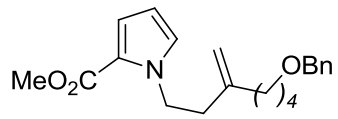




3c

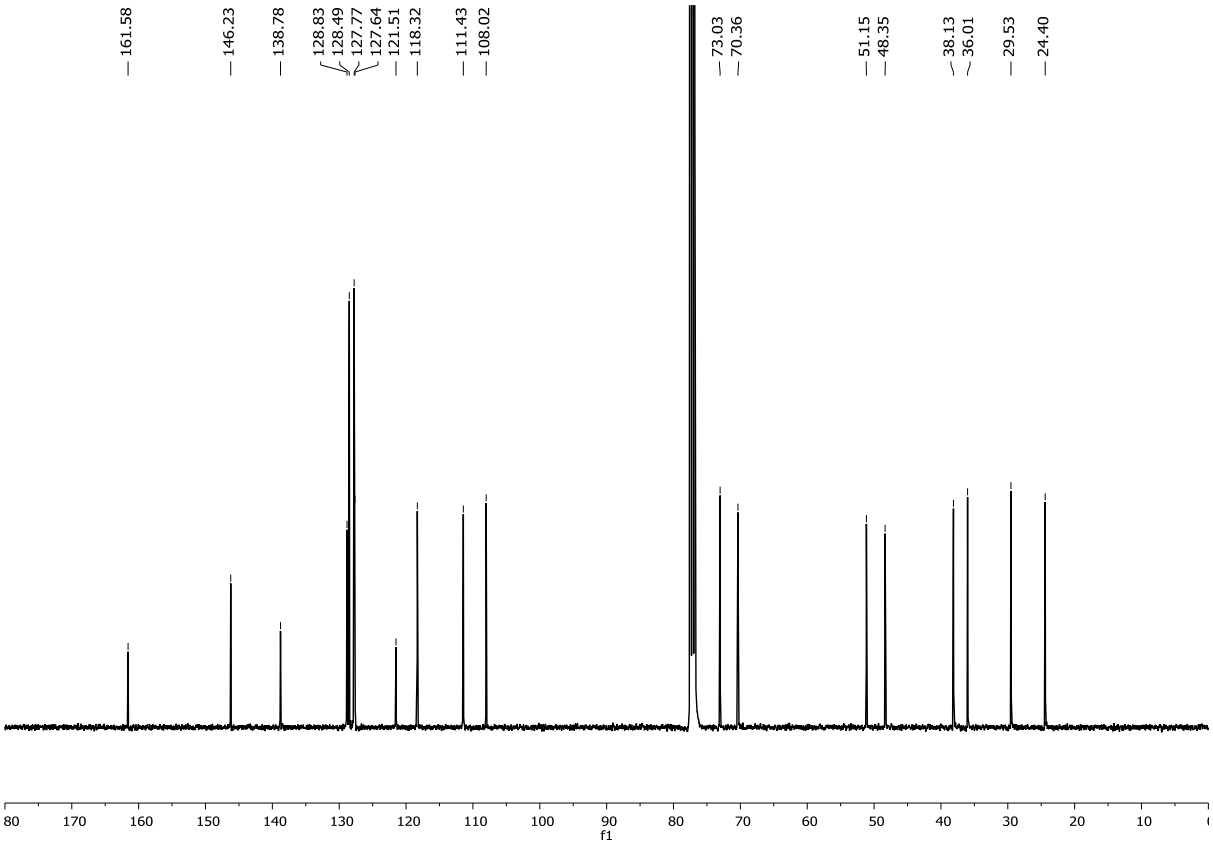
^{1}H NMR, 400 MHz, $CDCl_3$

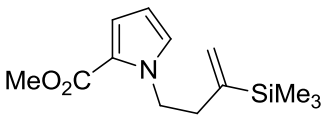




3c

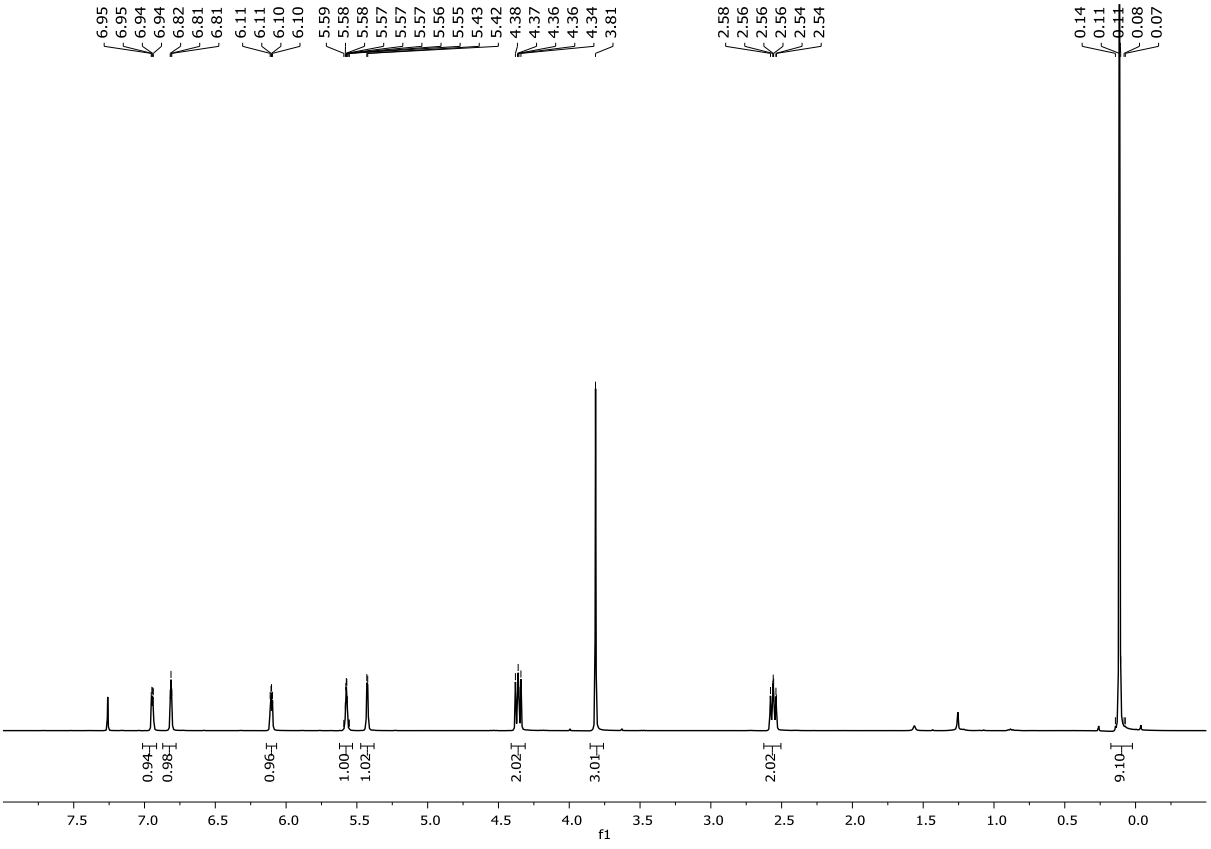
^{13}C NMR, 101 MHz, $CDCl_3$

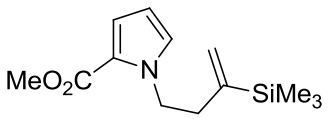




3d

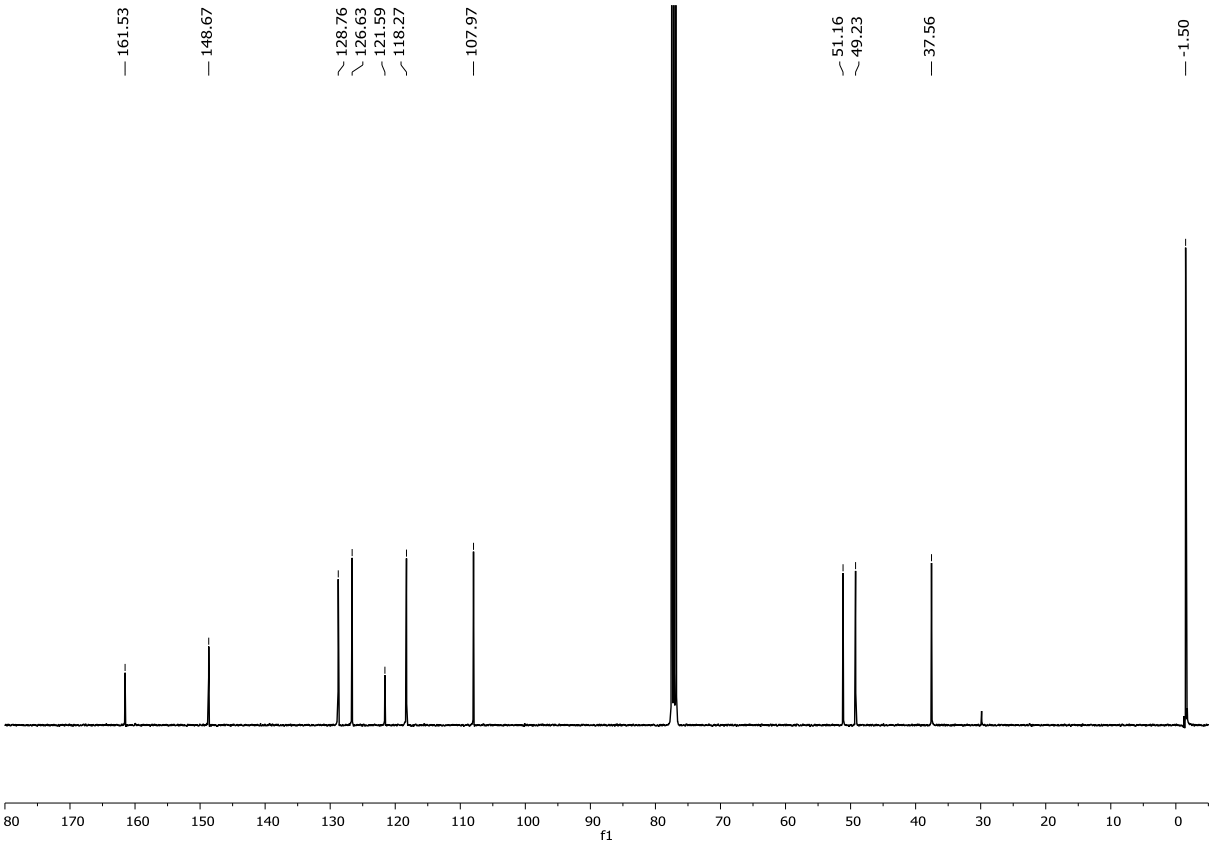
^{1}H NMR, 400 MHz, $CDCl_3$

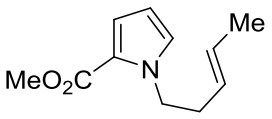




3d

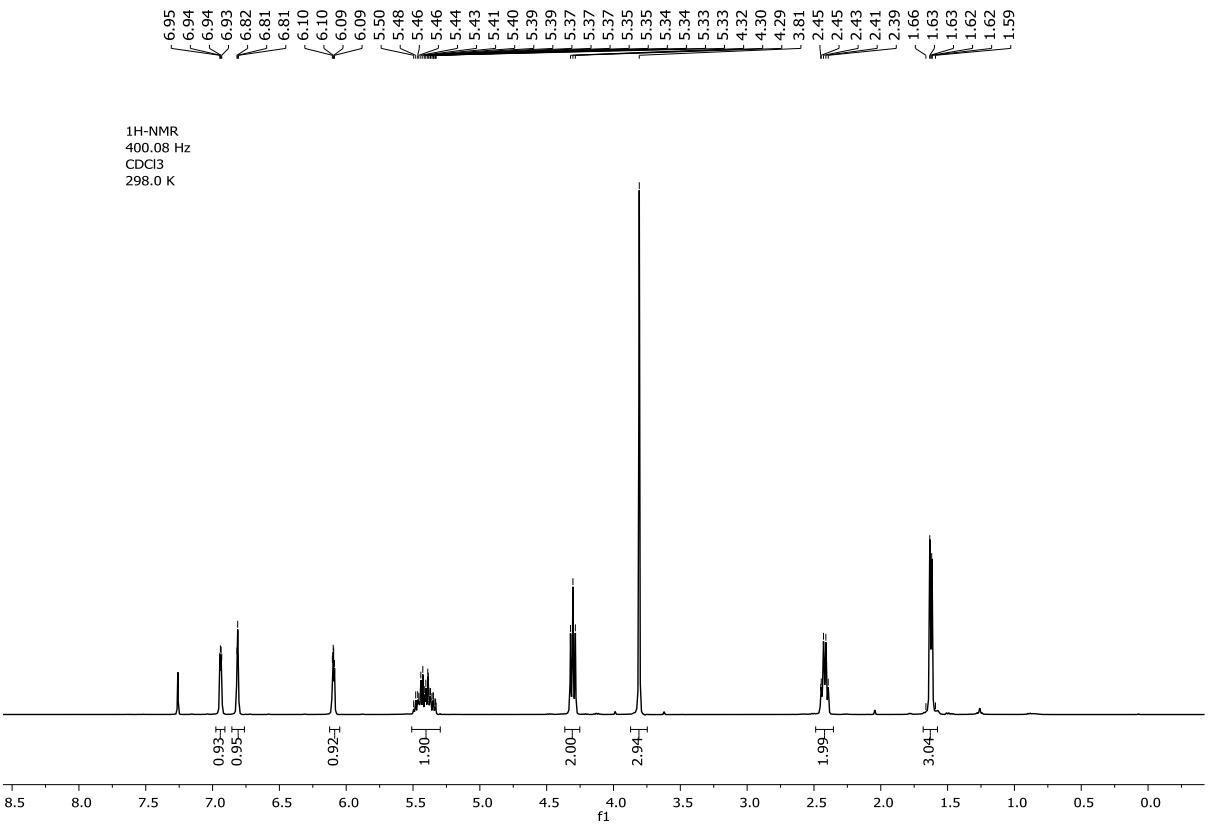
^{13}C NMR, 101 MHz, $CDCl_3$

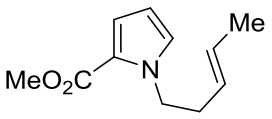




3e

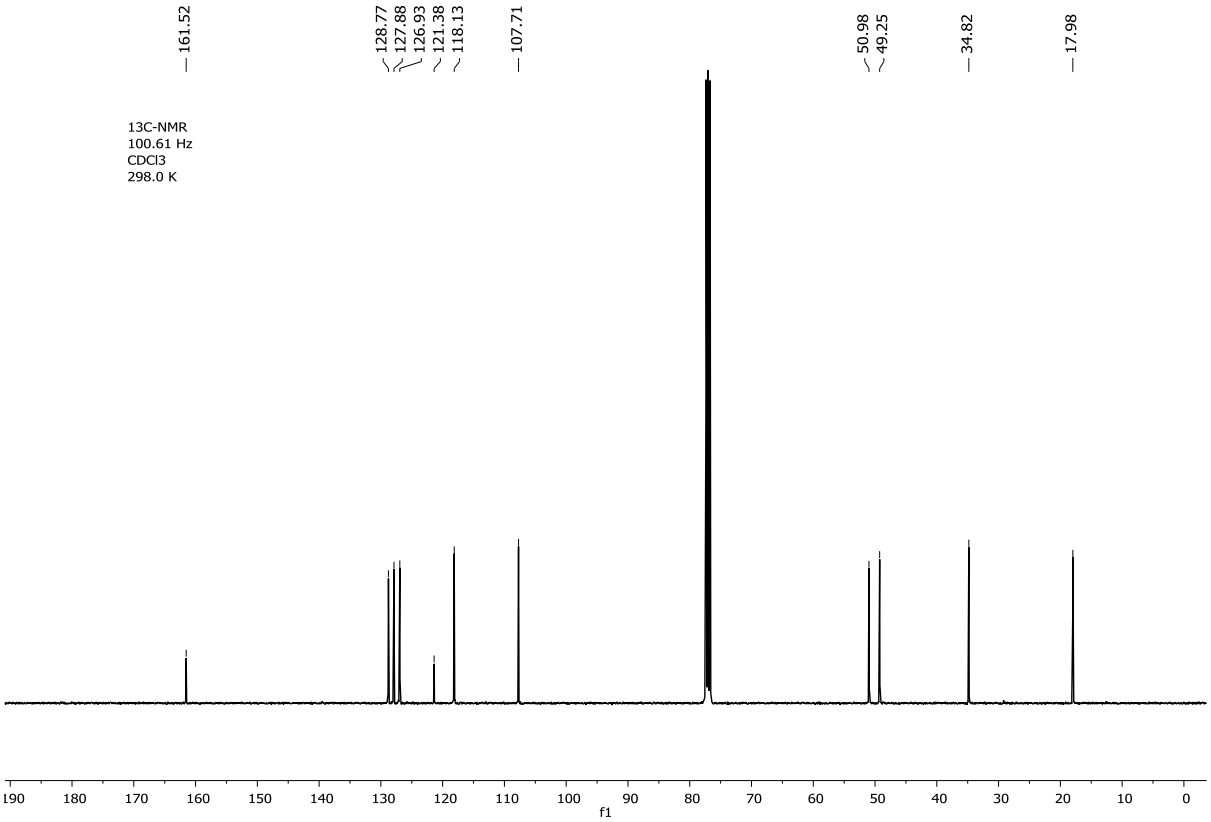
^{1}H NMR, 400 MHz, $CDCl_3$

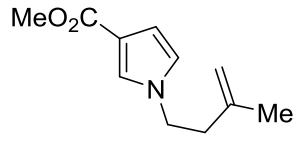




3e

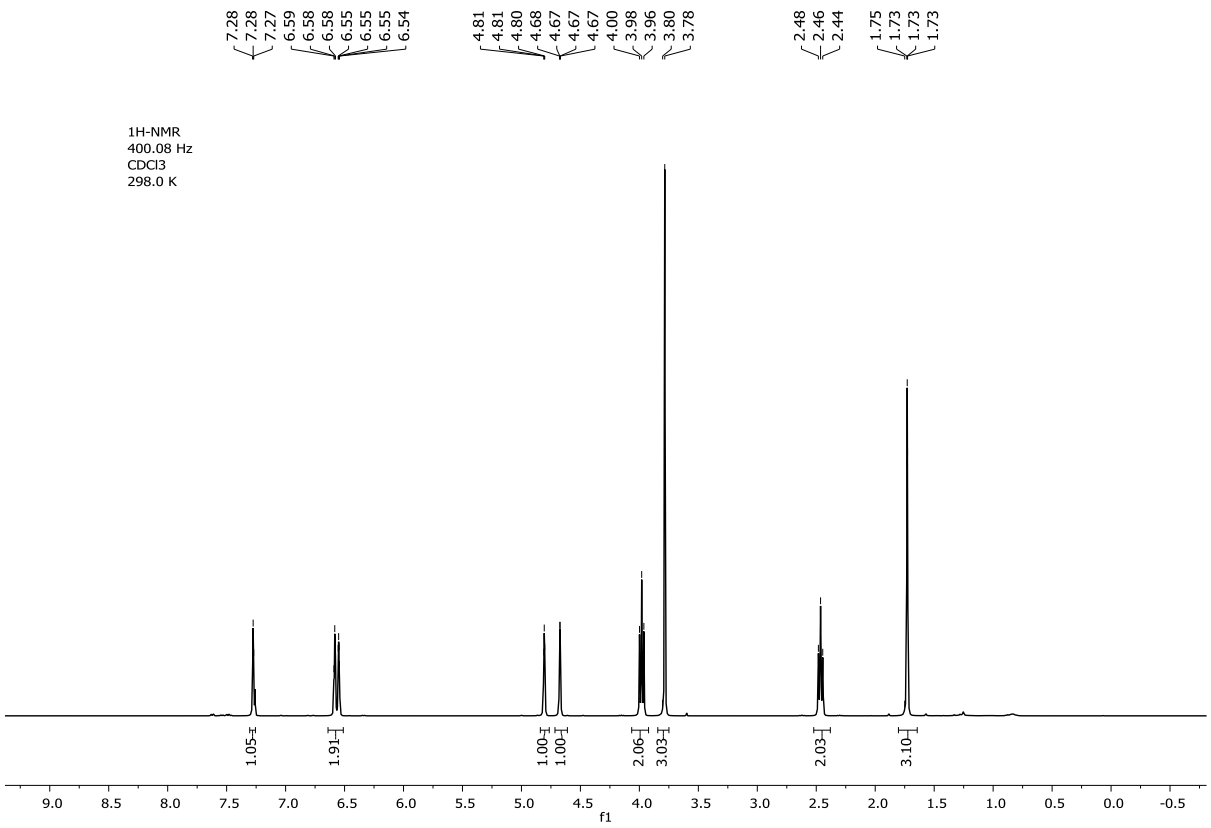
^{13}C NMR, 101 MHz, $CDCl_3$

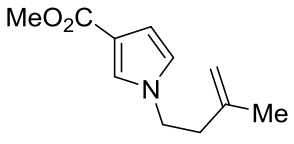




3f

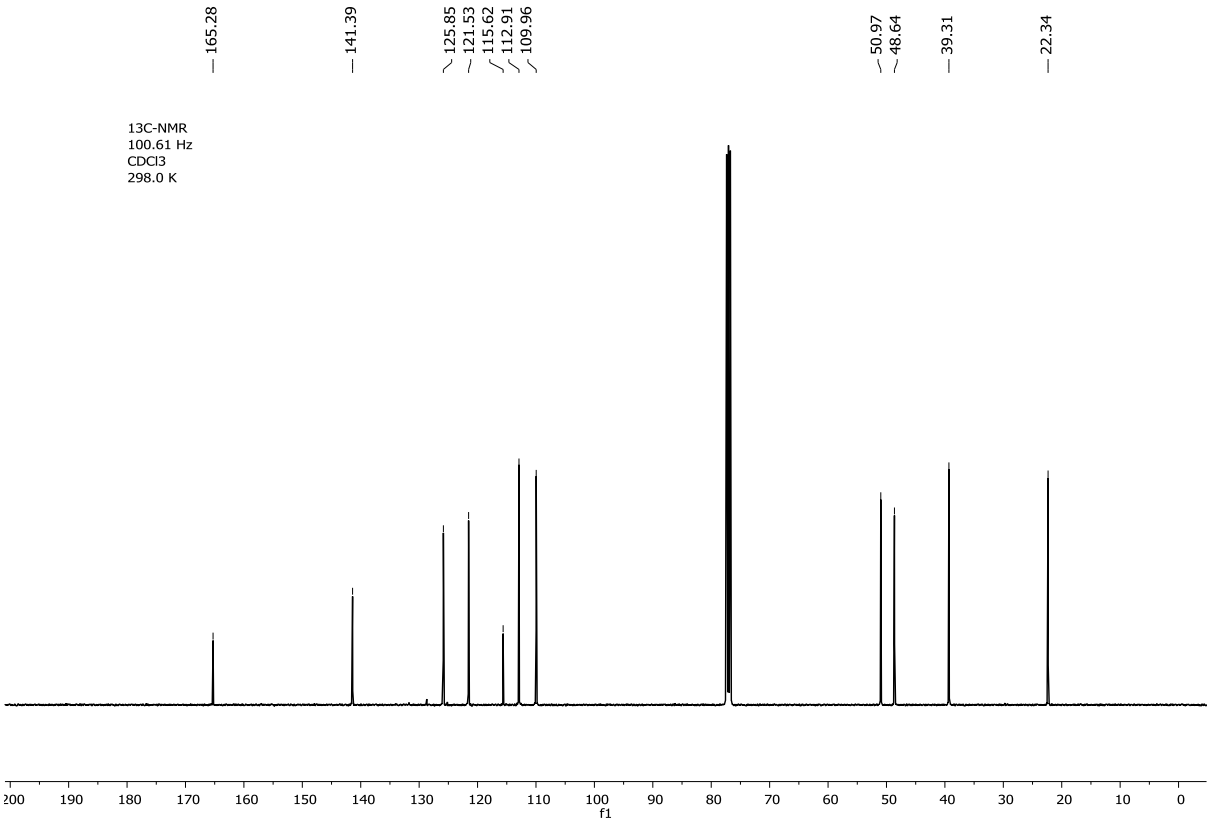
^{1}H NMR, 400 MHz, $CDCl_3$

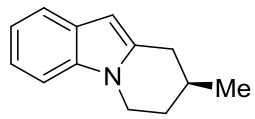




3f

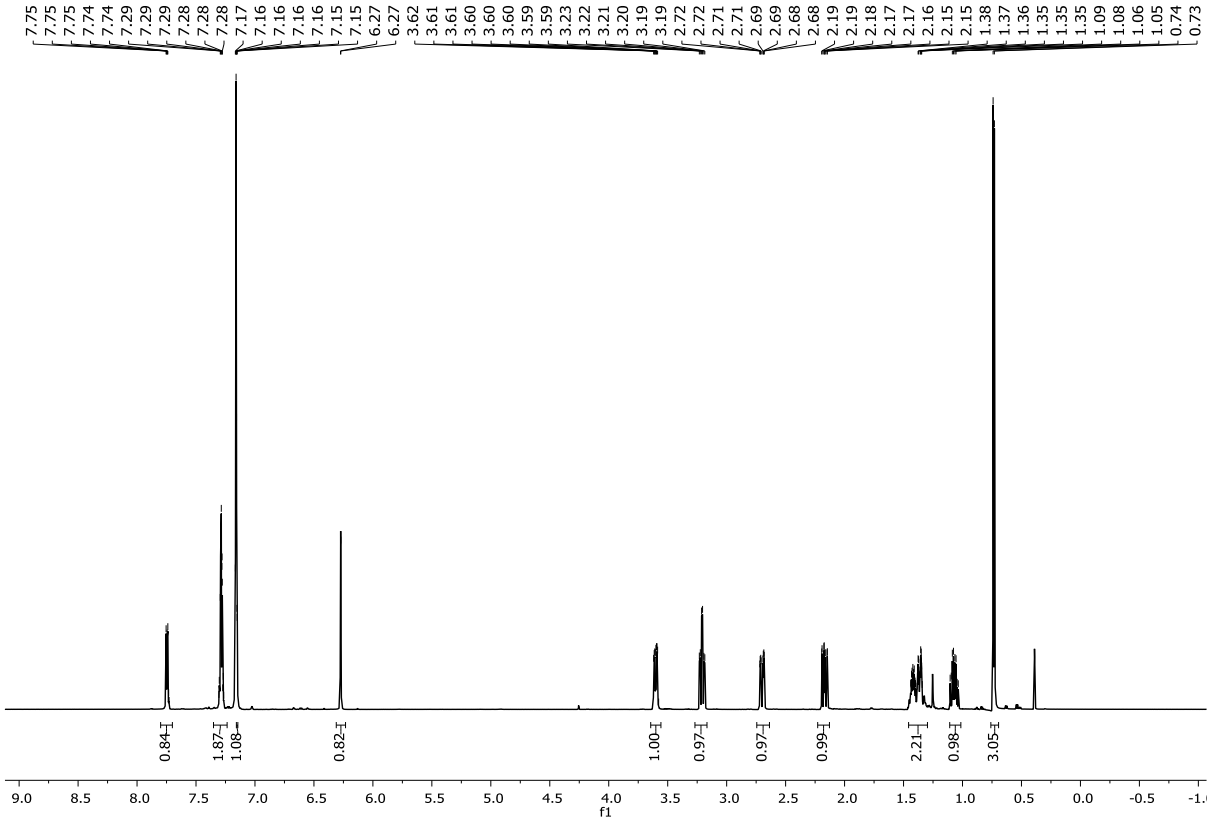
^{13}C NMR, 101 MHz, $CDCl_3$

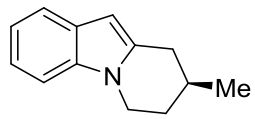




2a

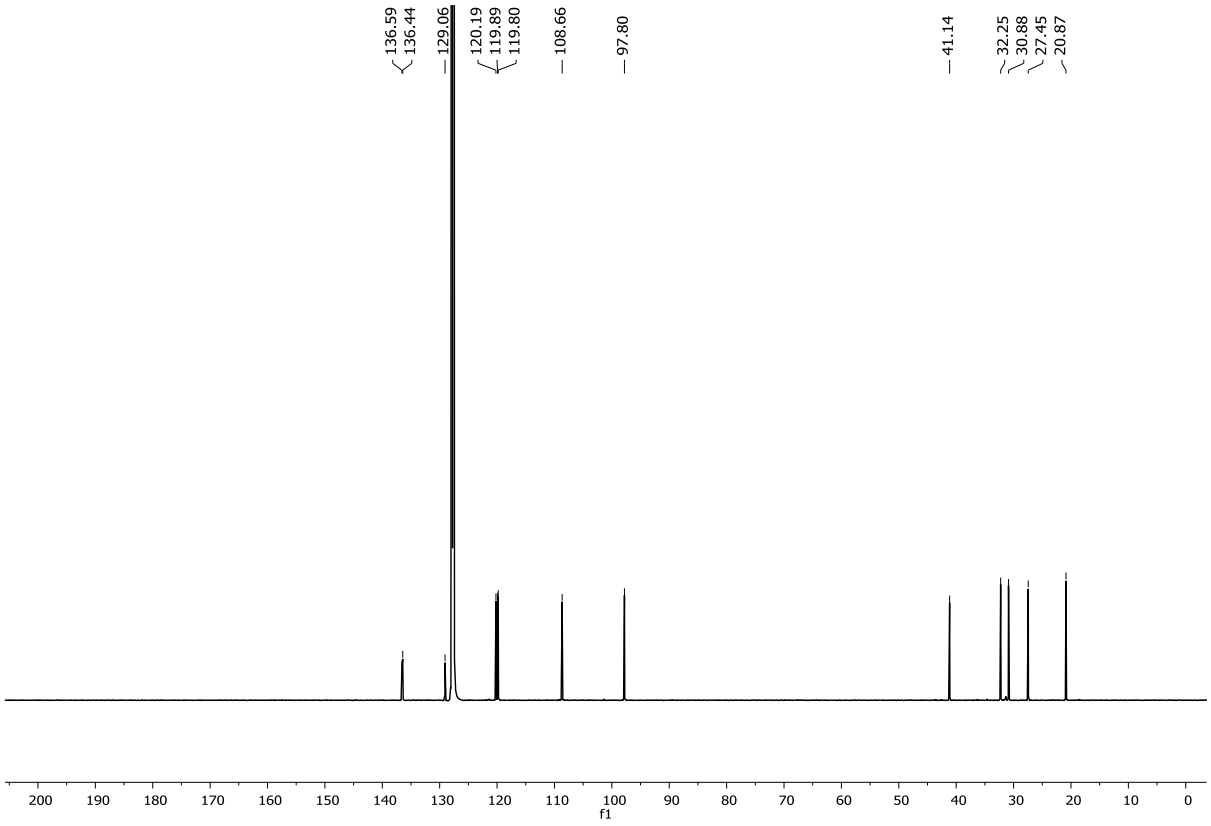
^{1}H NMR, 600 MHz, C_6D_6

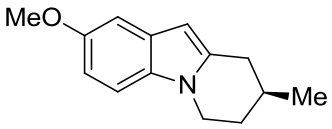




2b

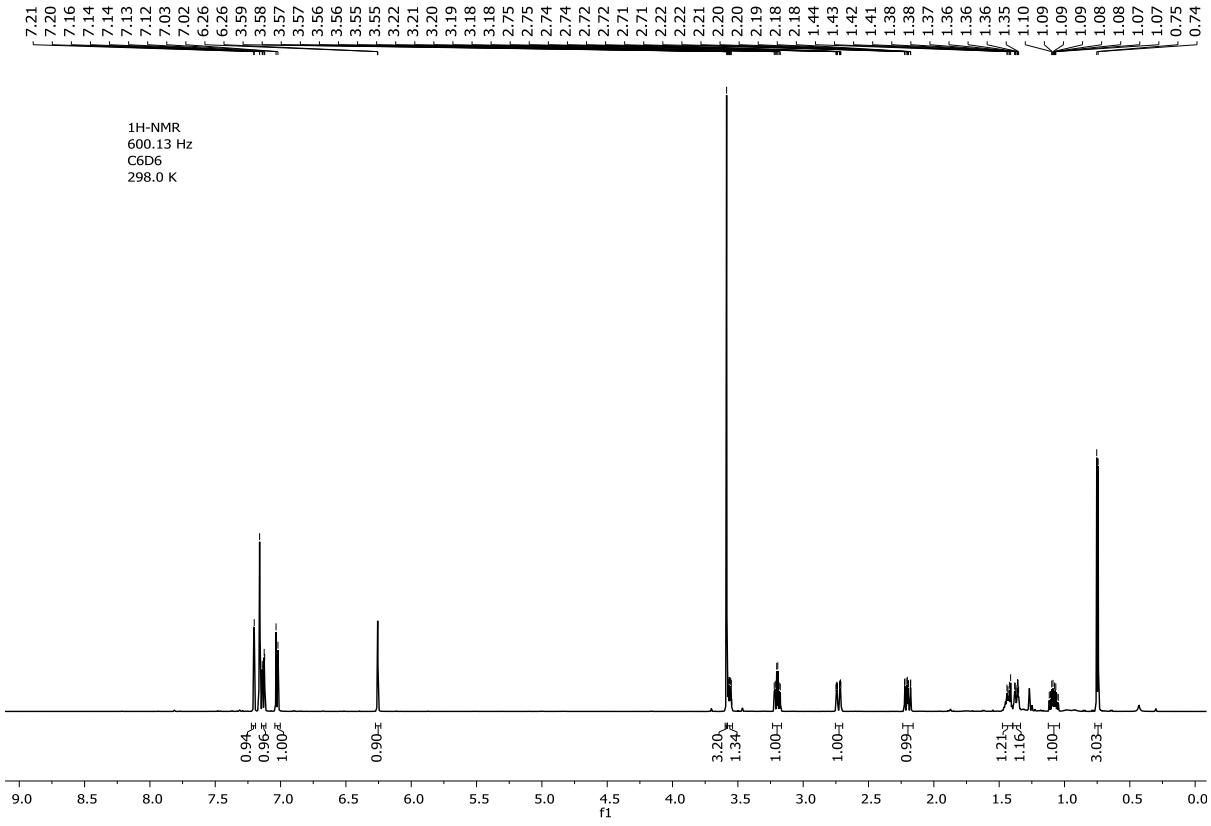
^{13}C NMR, 151 MHz, C_6D_6

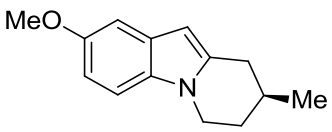




2b

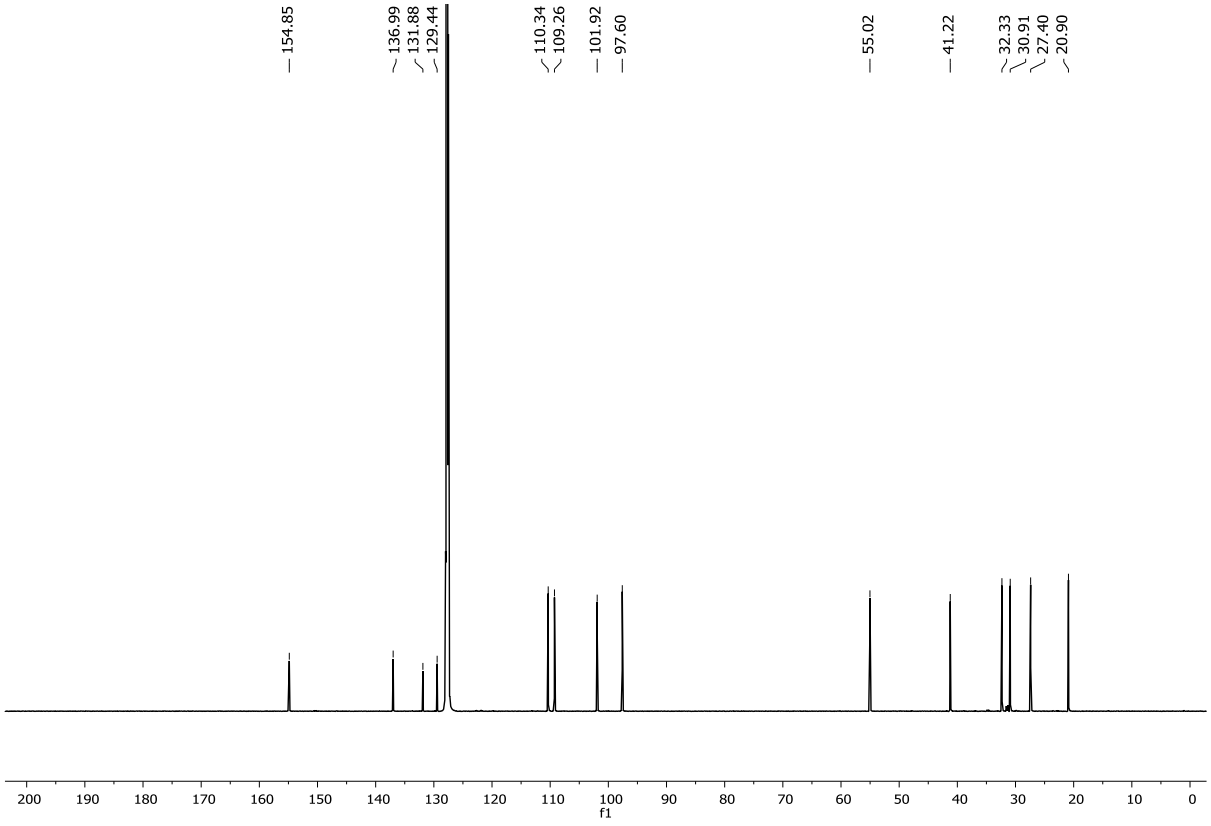
^{1}H NMR, 600 MHz, C_6D_6

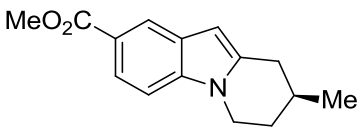




2b

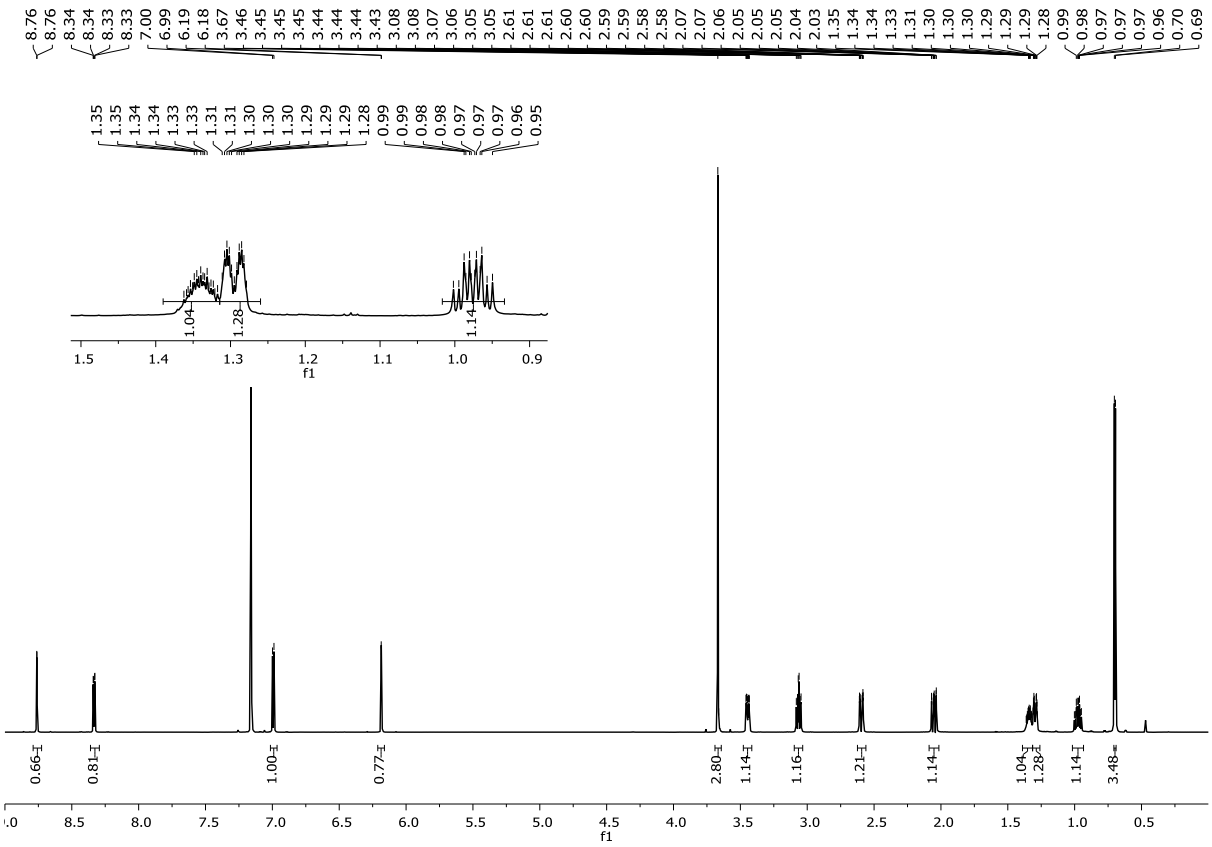
^{13}C NMR, 151 MHz, C_6D_6

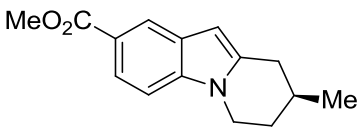




2c

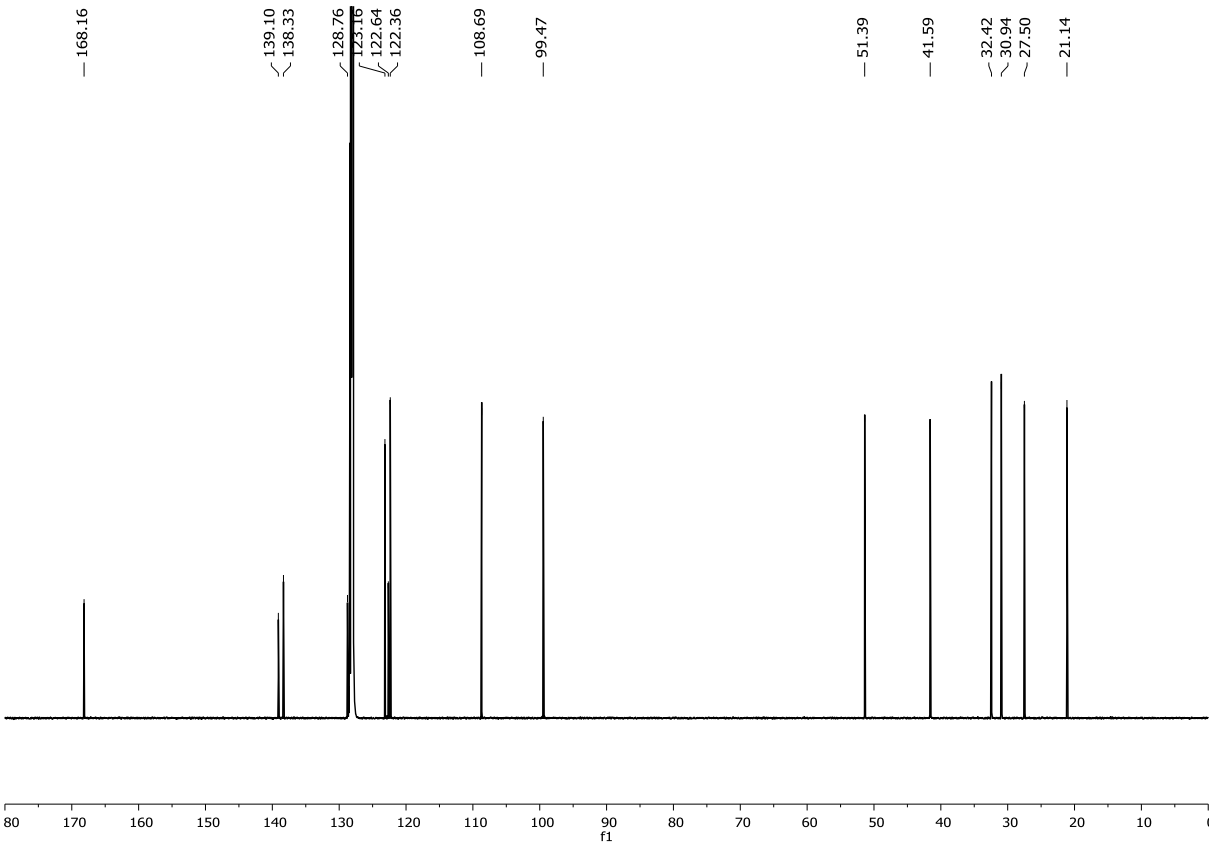
^{1}H NMR, 800 MHz, C_6D_6

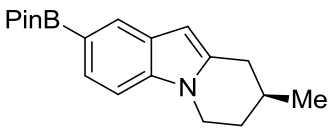




2c

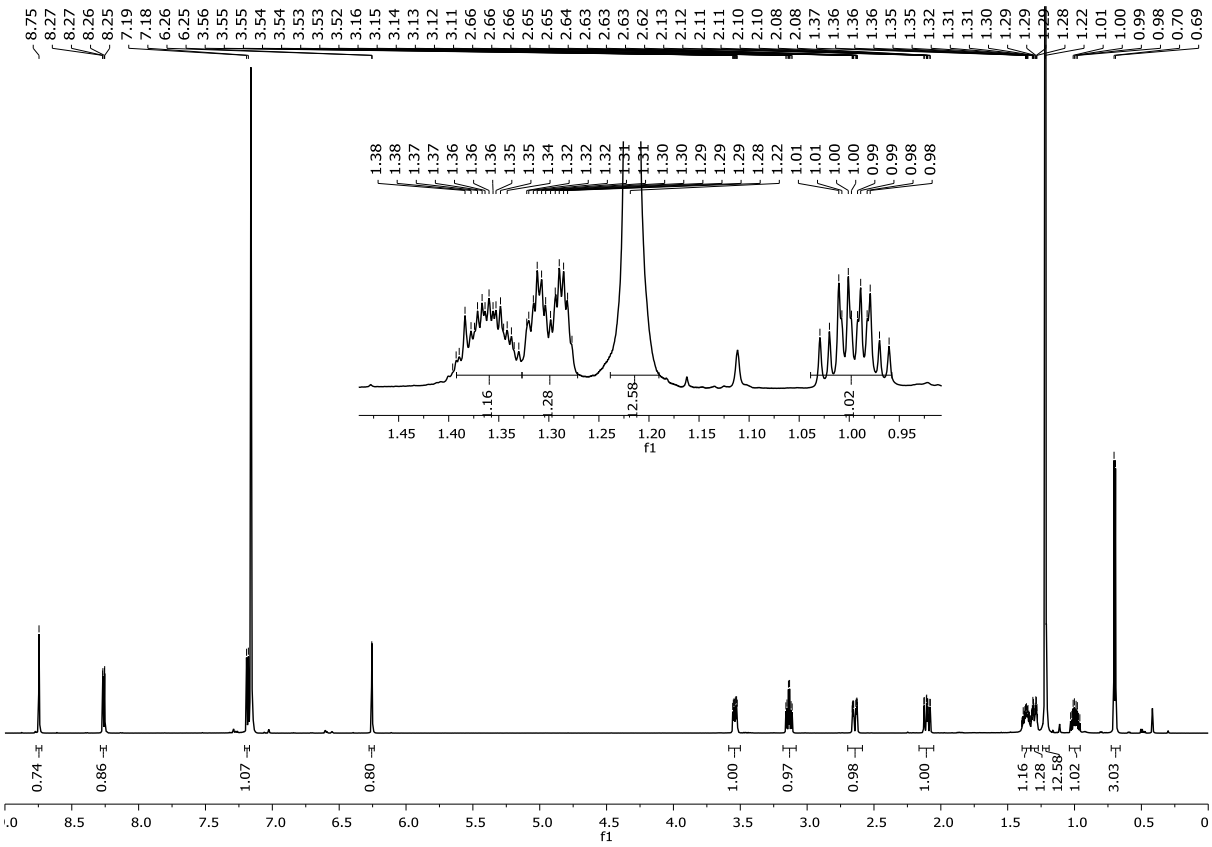
^{13}C NMR, 201 MHz, C_6D_6

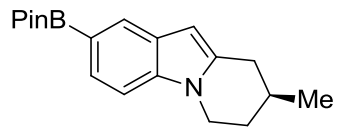




2d

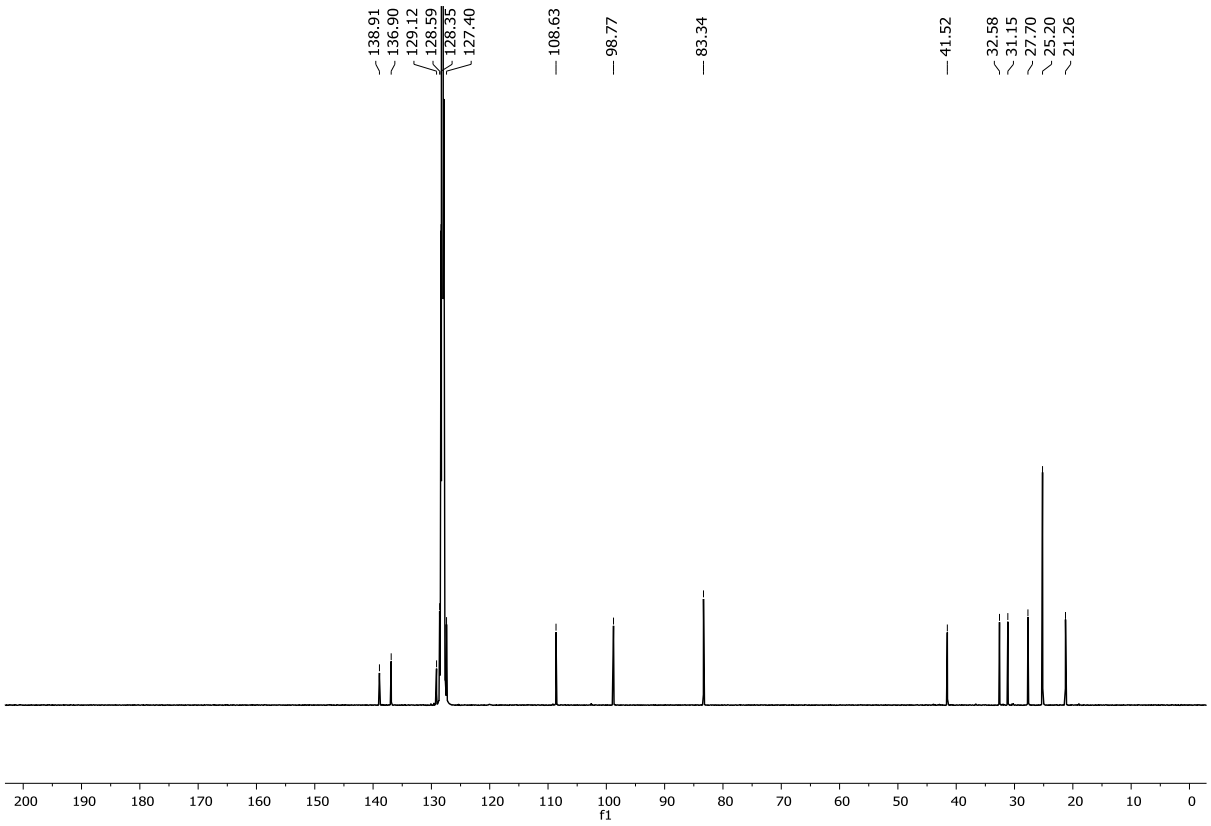
^{1}H NMR, 600 MHz, C_6D_6

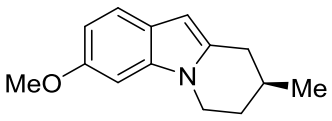




2d

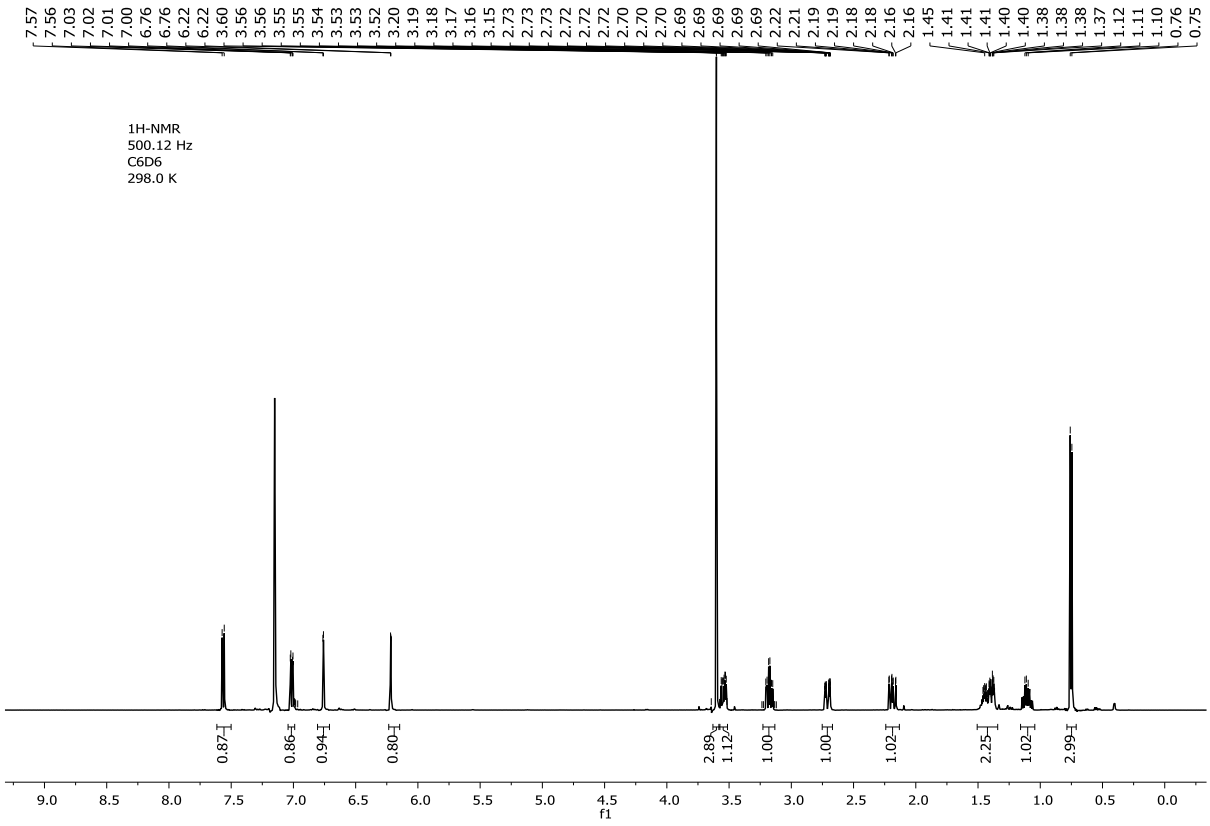
^{13}C NMR, 201 MHz, C_6D_6

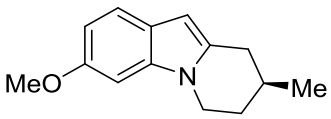




2e

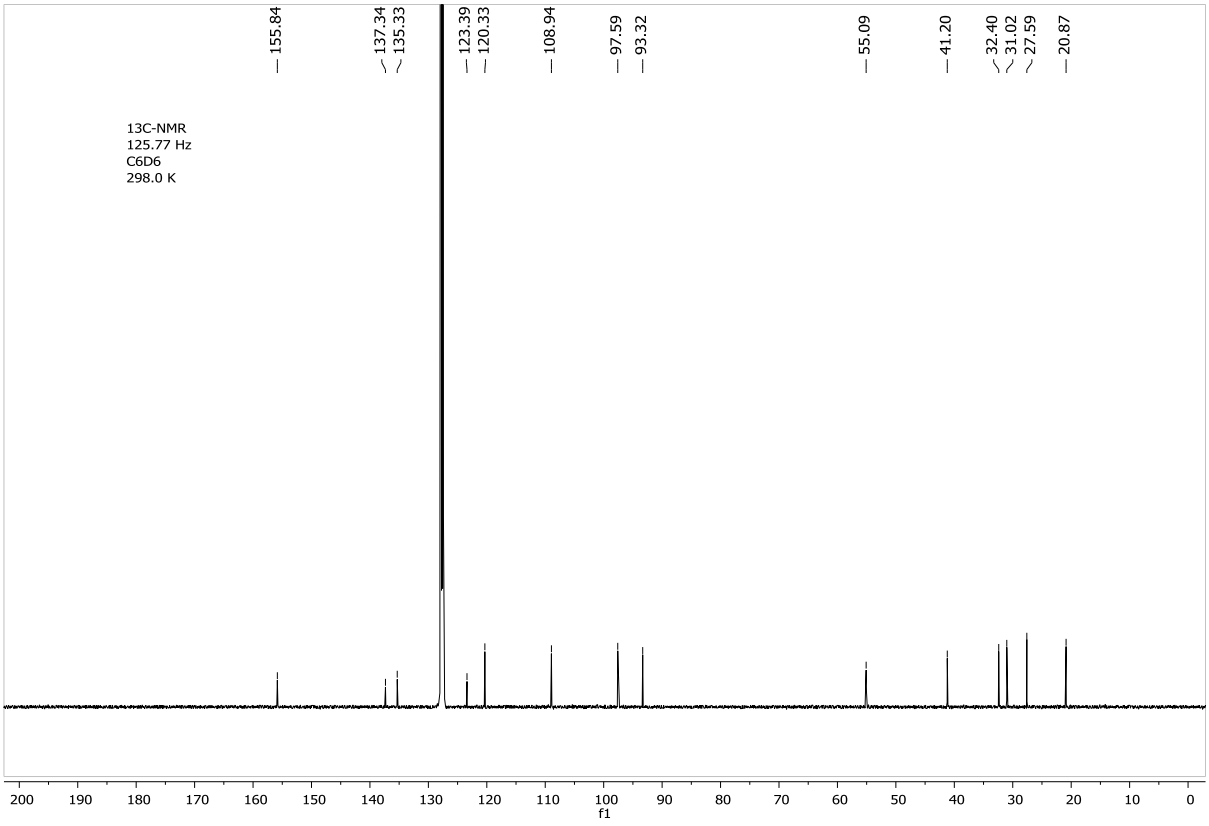
^{1}H NMR, 500 MHz, C_6D_6

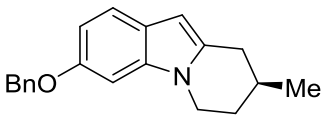




2e

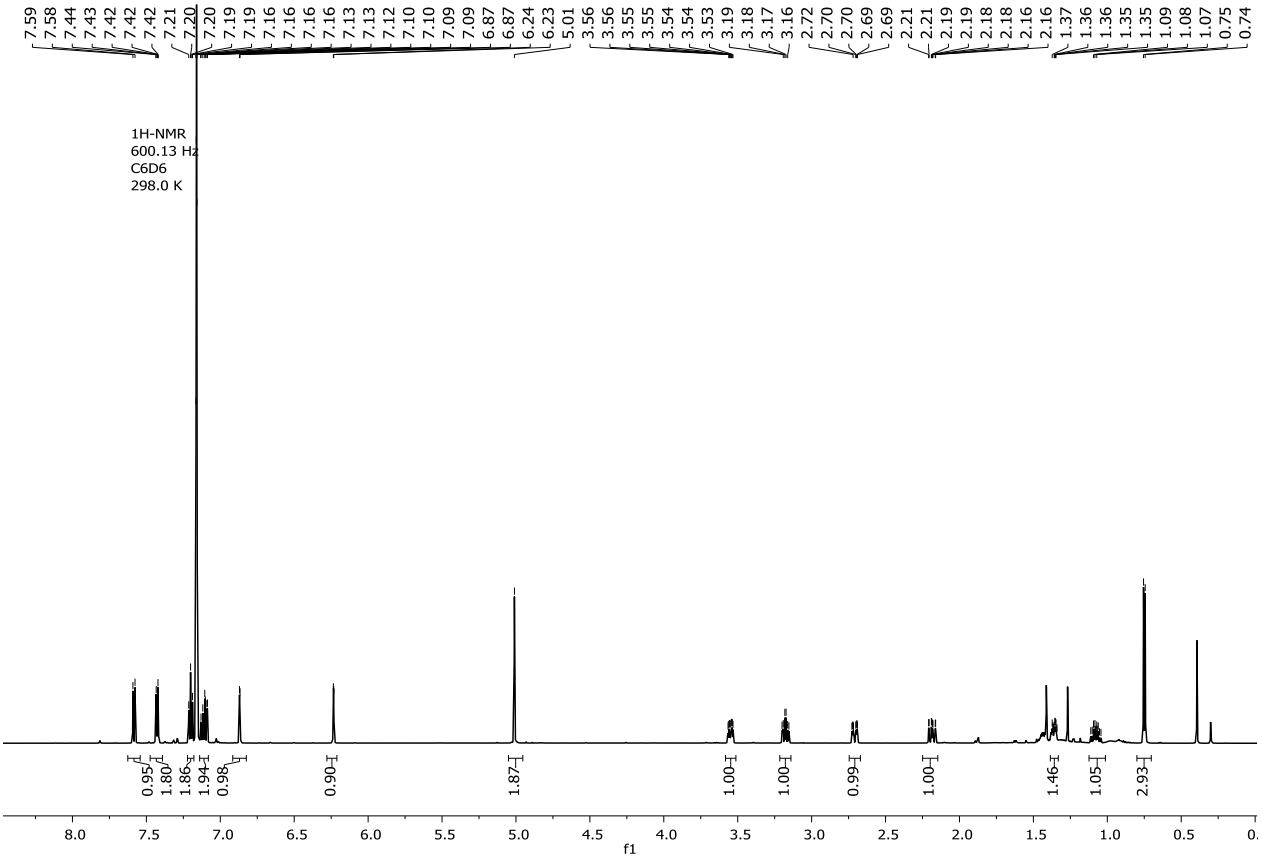
^{13}C NMR, 126 MHz, C_6D_6

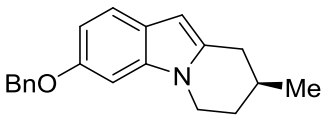




2f

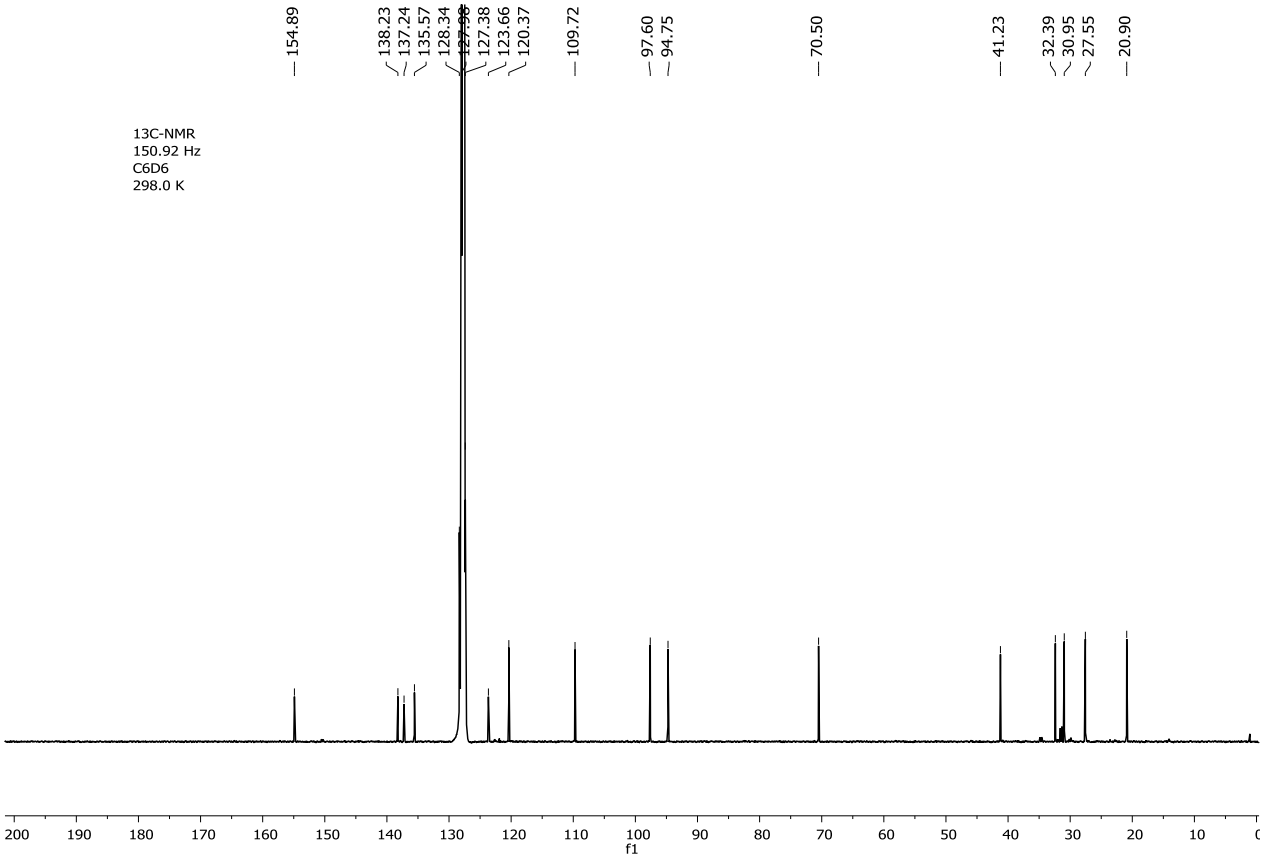
^{1}H NMR, 600 MHz, C_6D_6

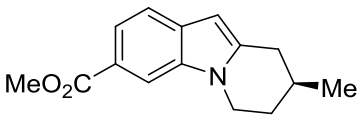




2f

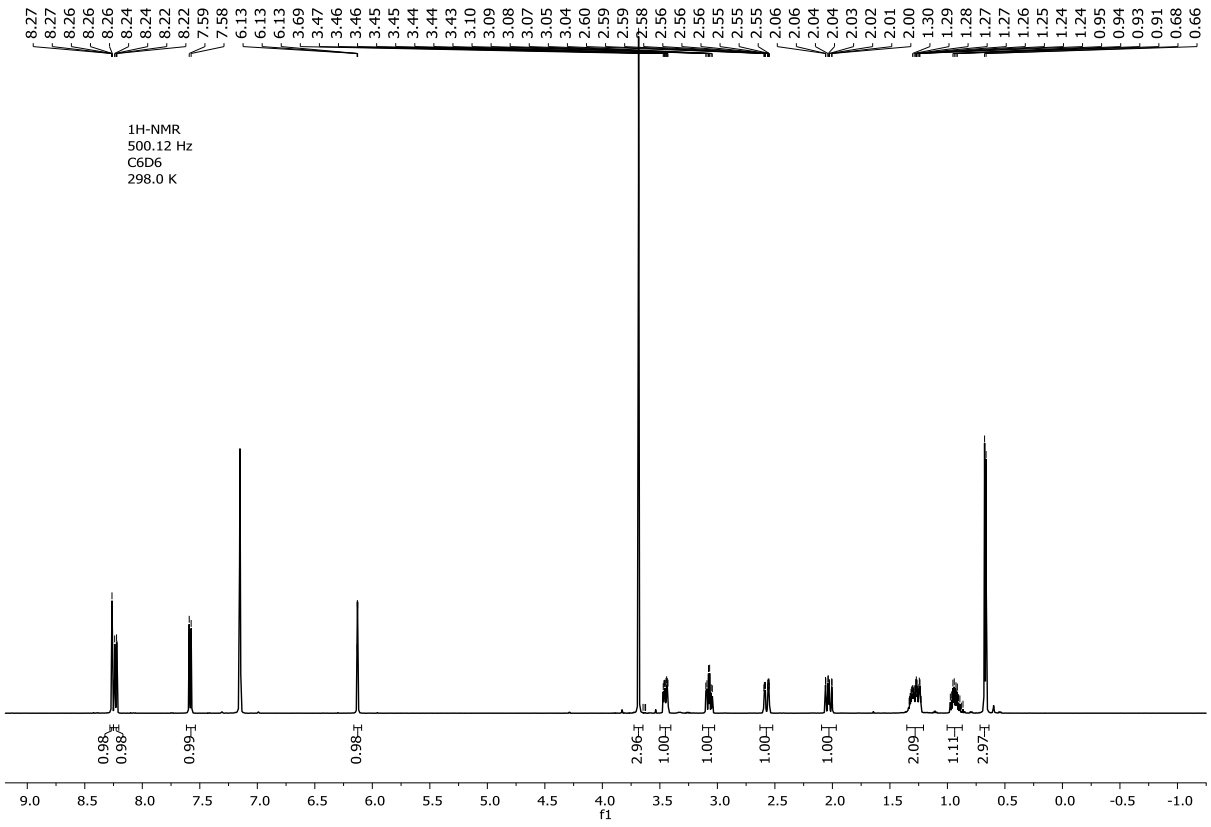
^{13}C NMR, 151 MHz, C_6D_6

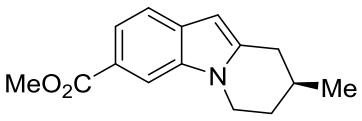




2g

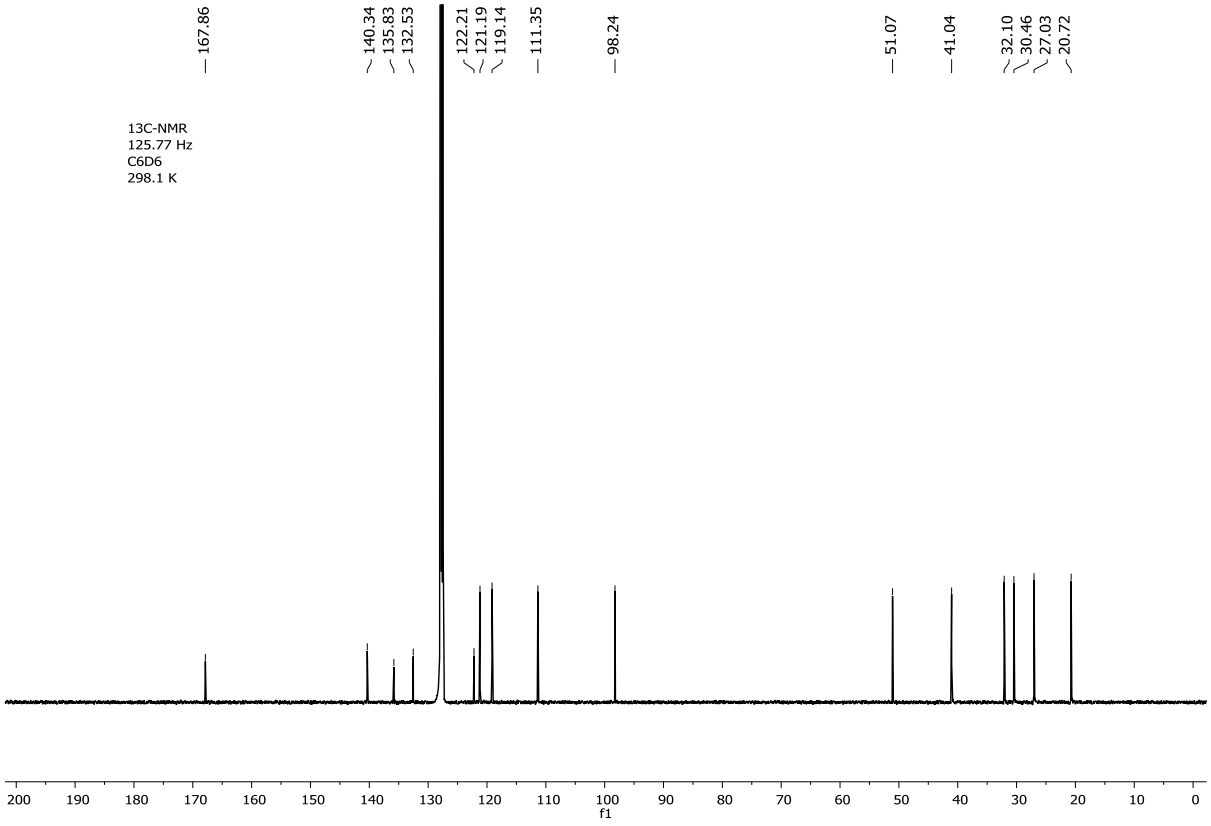
^{1}H NMR, 500 MHz, C_6D_6

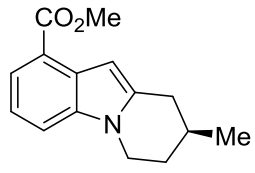




2g

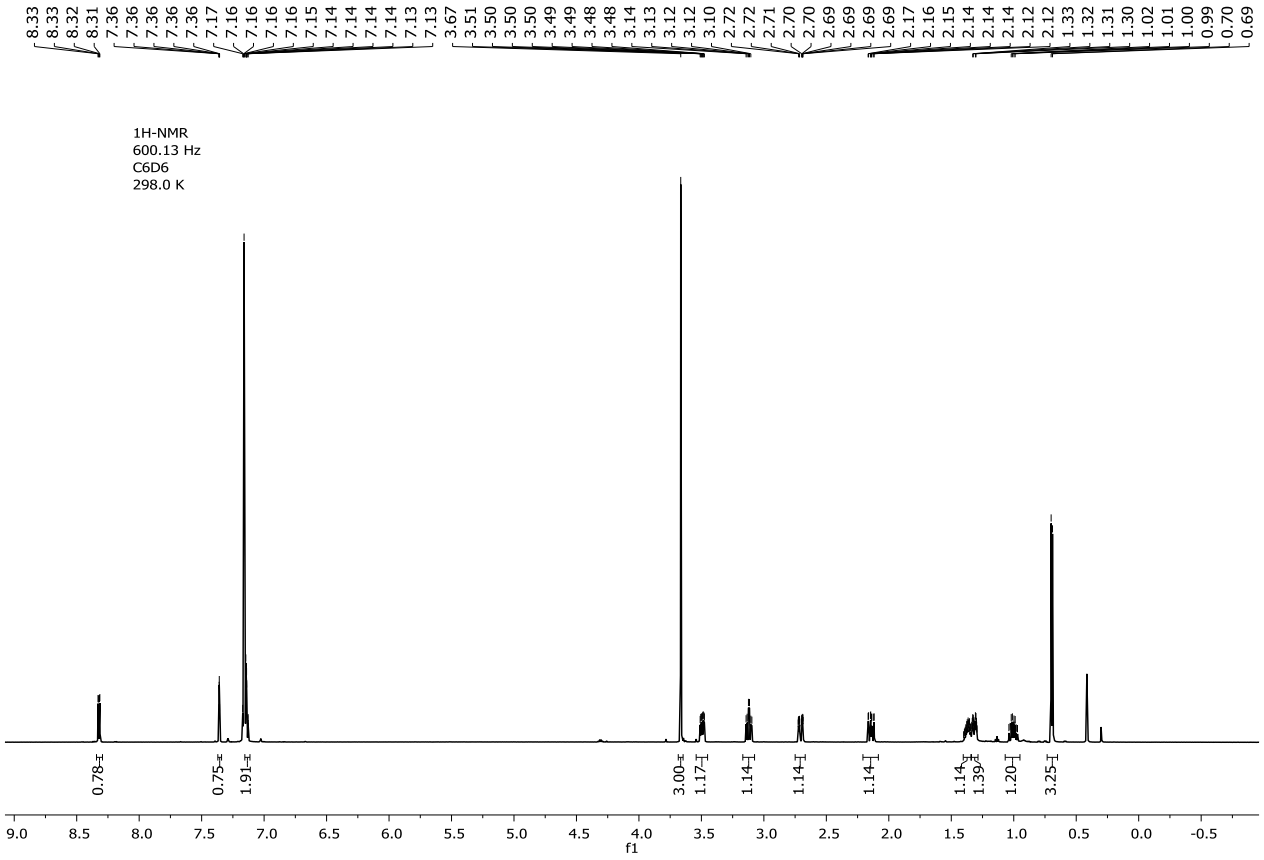
^{13}C NMR, 126 MHz, C_6D_6

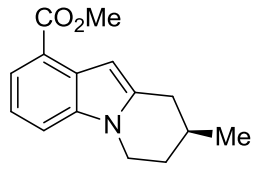




2h

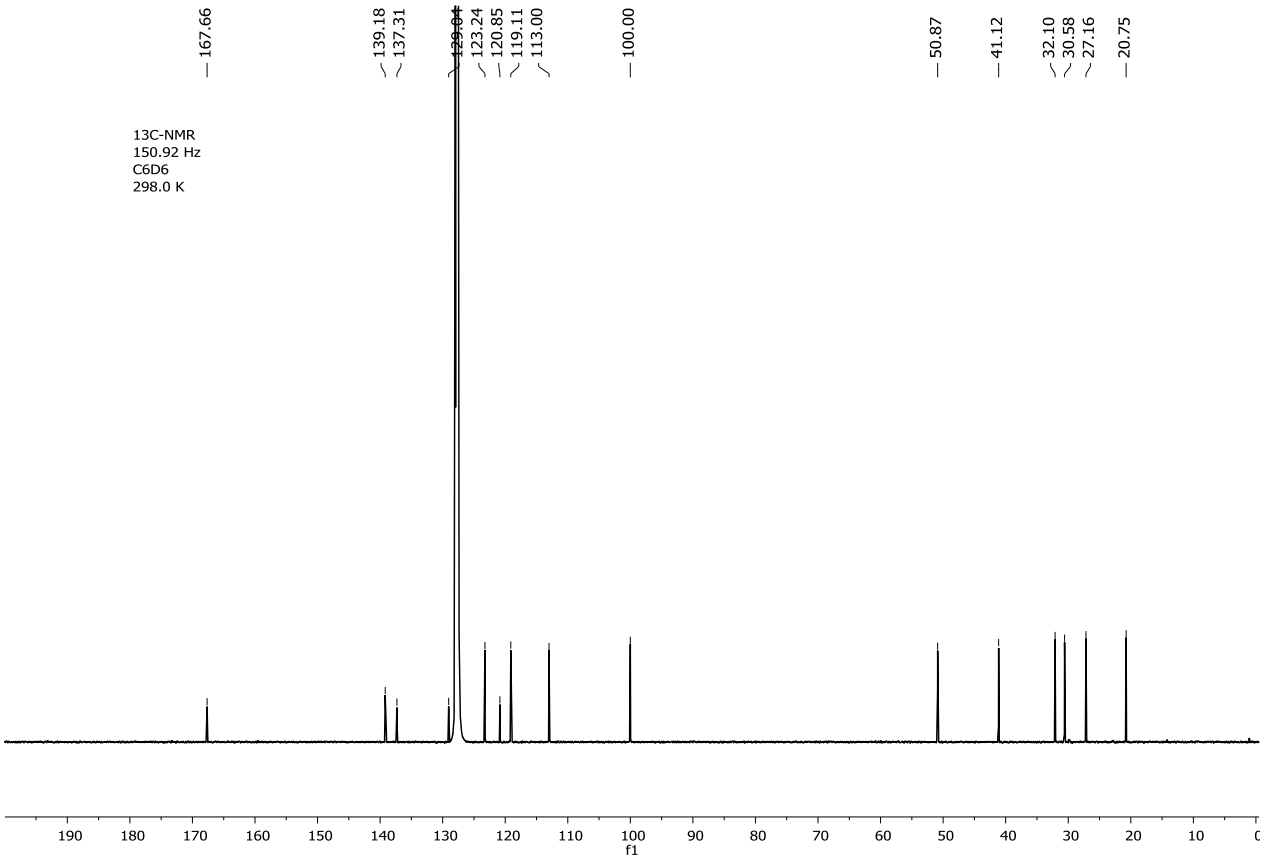
^{1}H NMR, 600 MHz, C_6D_6

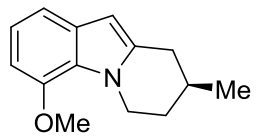




2h

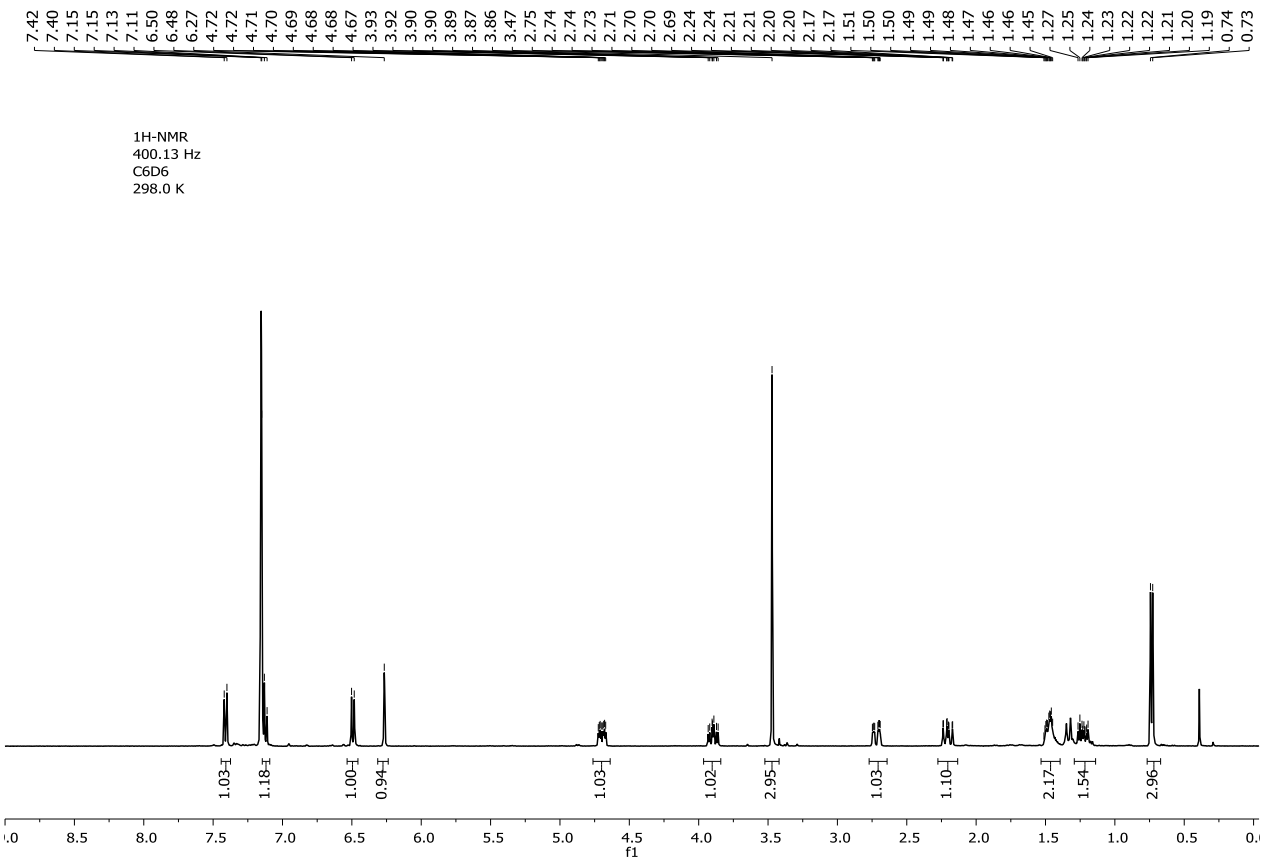
^{13}C NMR, 151 MHz, C_6D_6

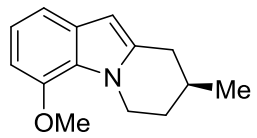




2i

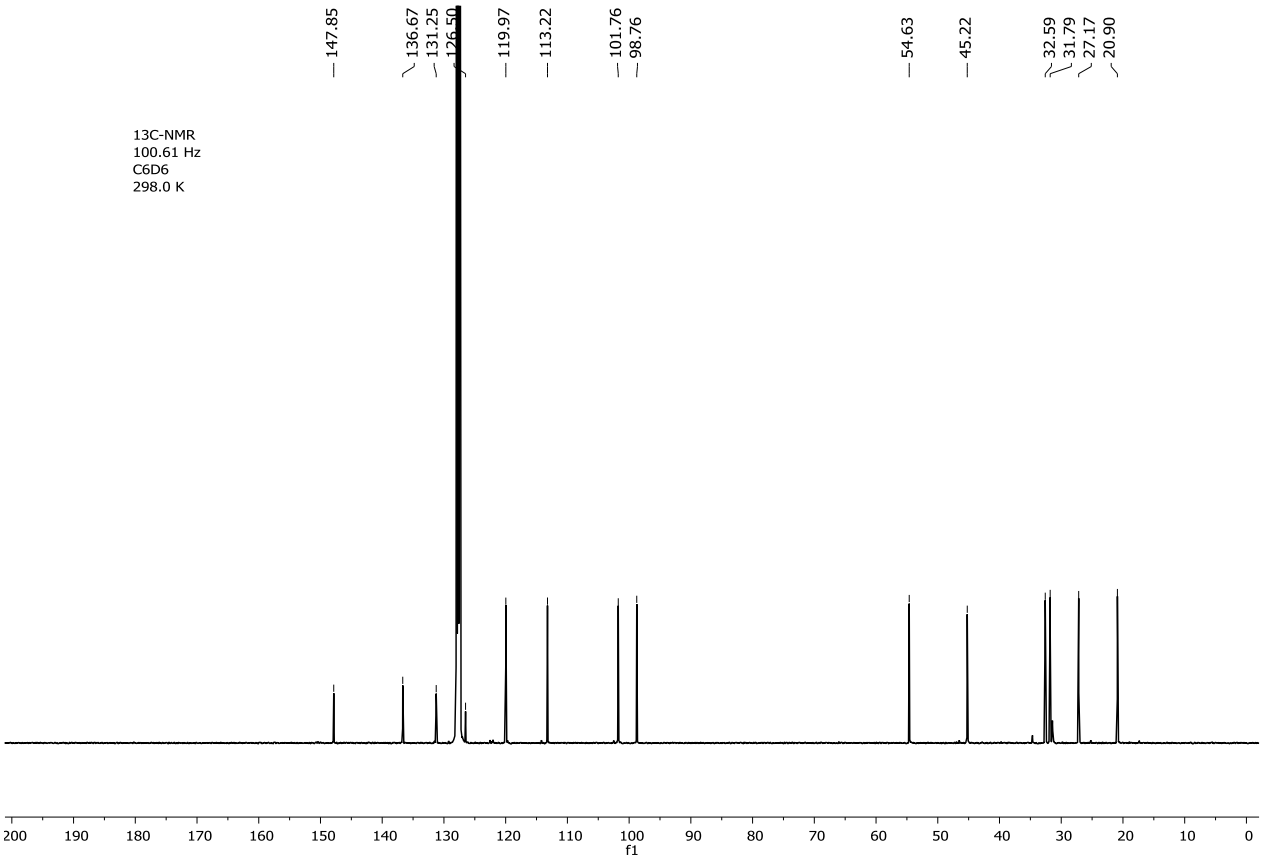
^{1}H NMR, 600 MHz, C_6D_6

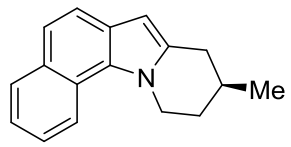




2i

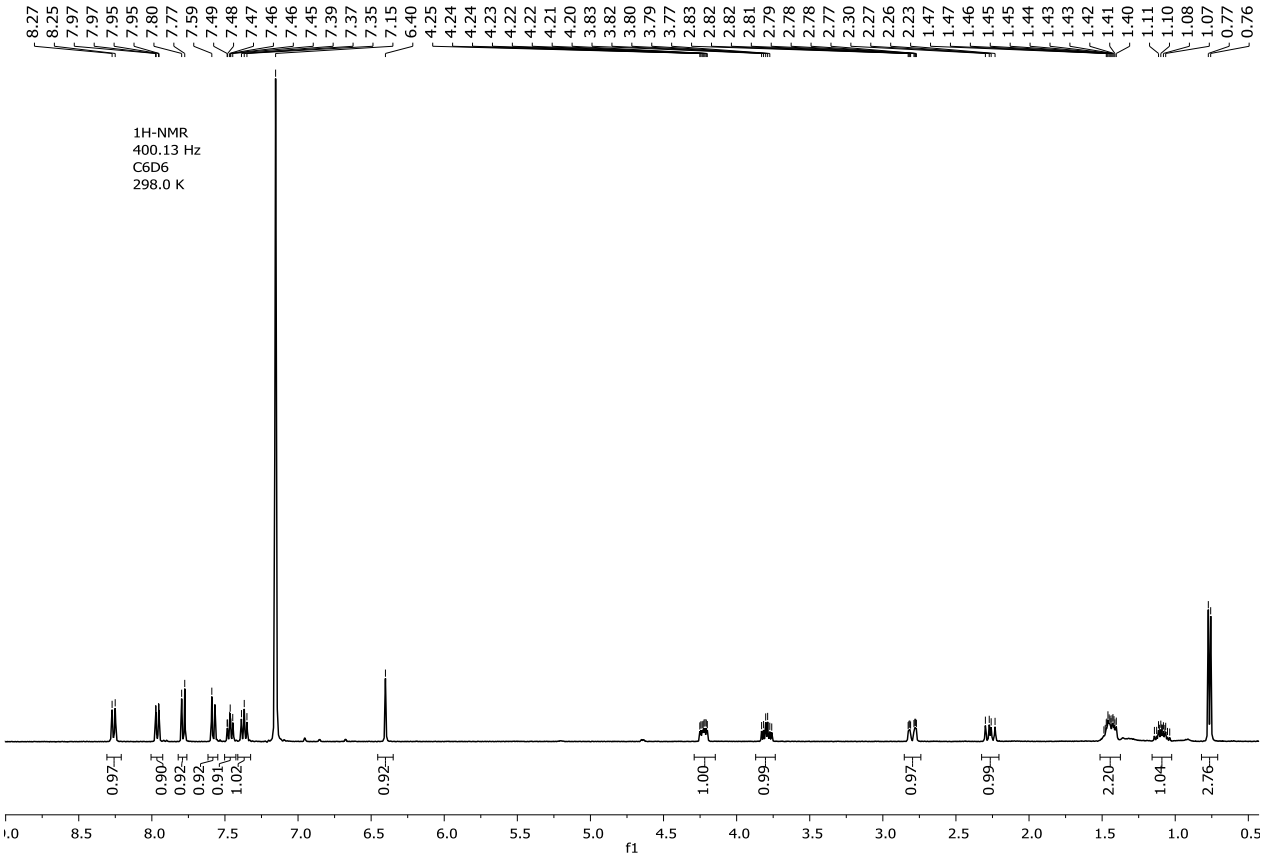
^{13}C NMR, 151 MHz, C_6D_6

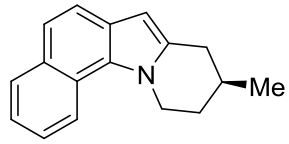




2j

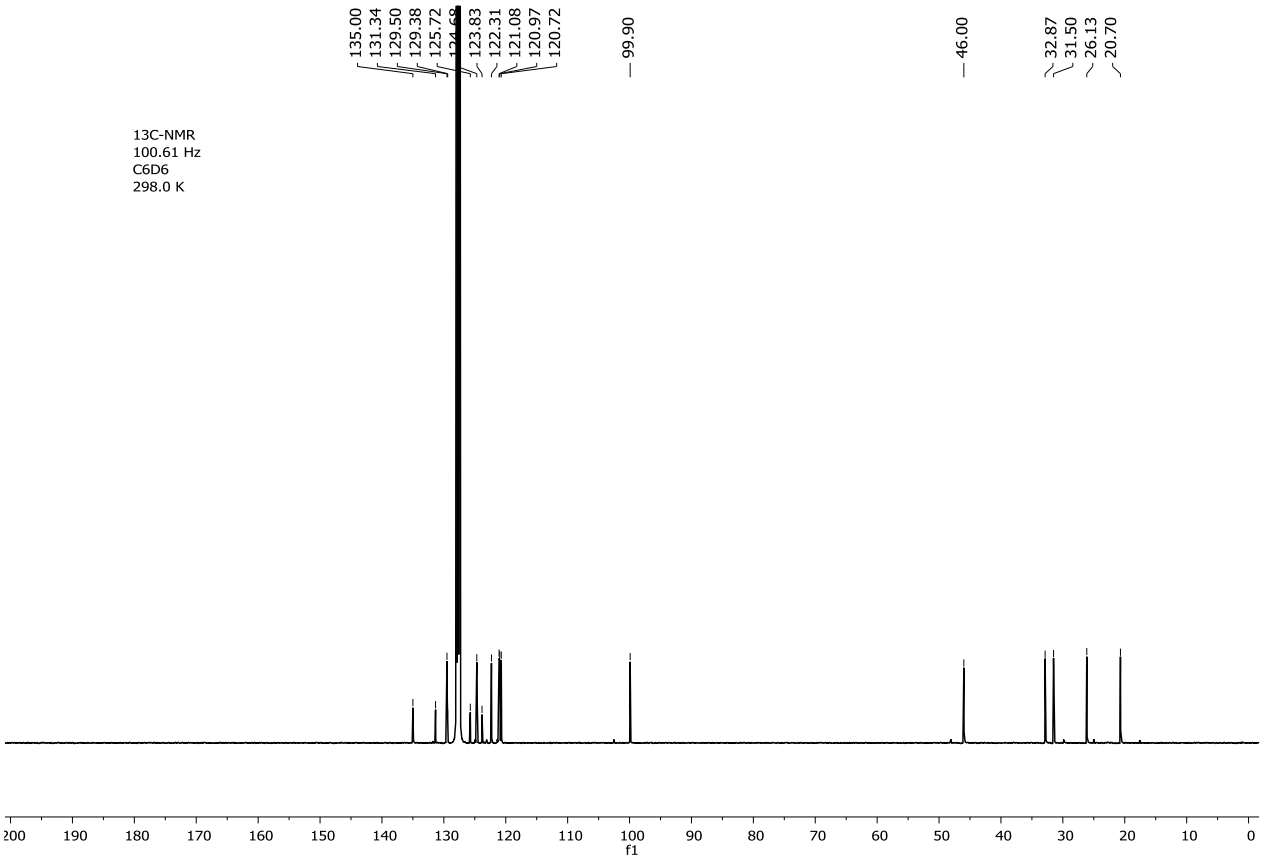
^{1}H NMR, 800 MHz, C_6D_6

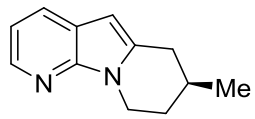




2j

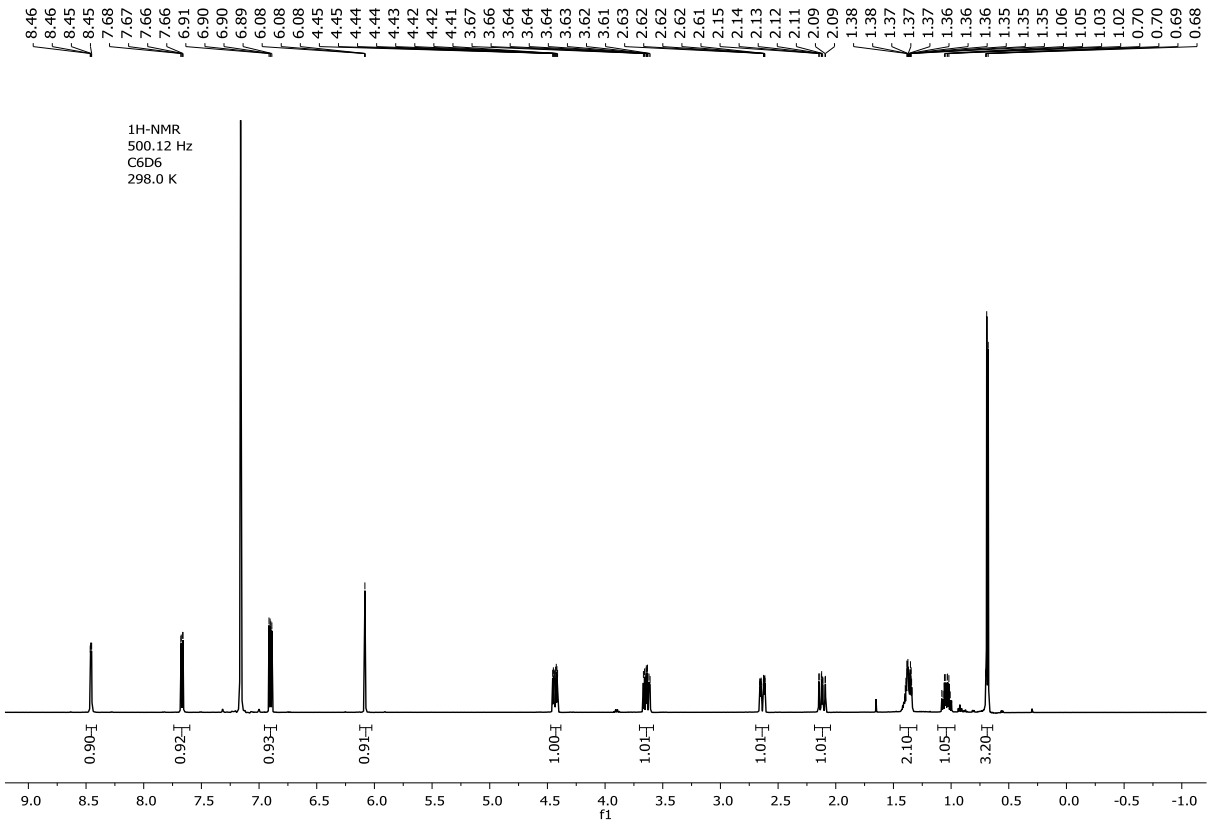
^{13}C NMR, 201 MHz, C_6D_6

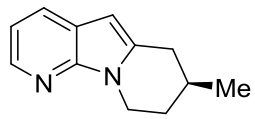




2k

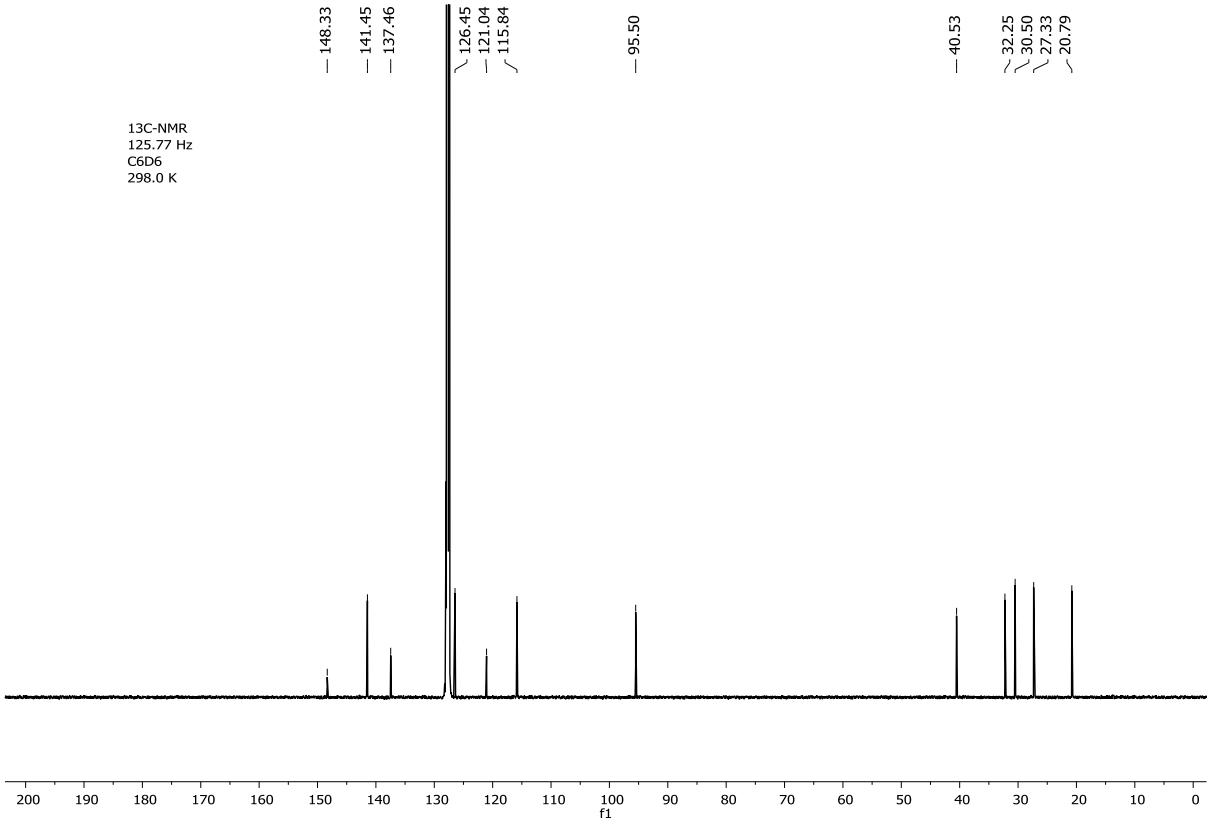
^{1}H NMR, 500 MHz, C_6D_6

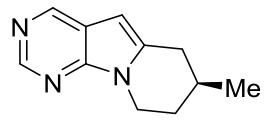




2k

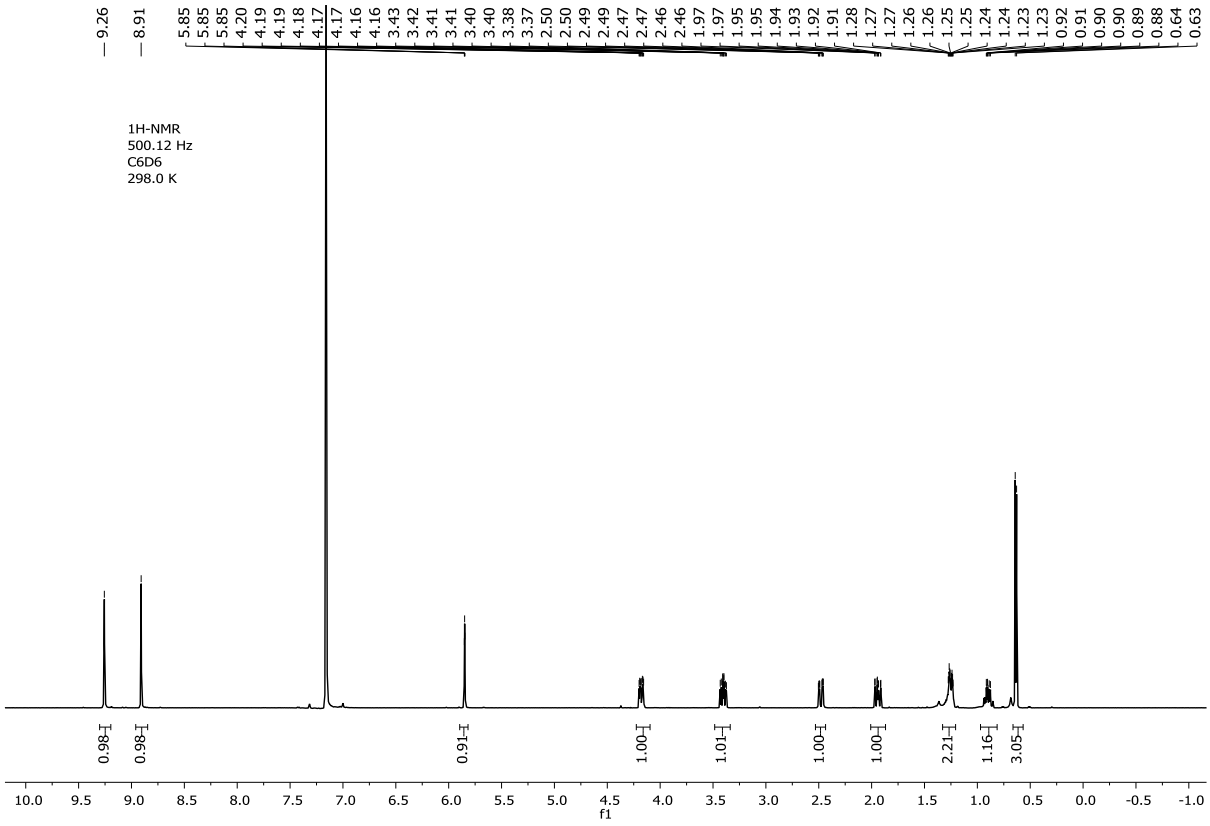
^{13}C NMR, 126 MHz, C_6D_6

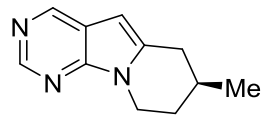




2l

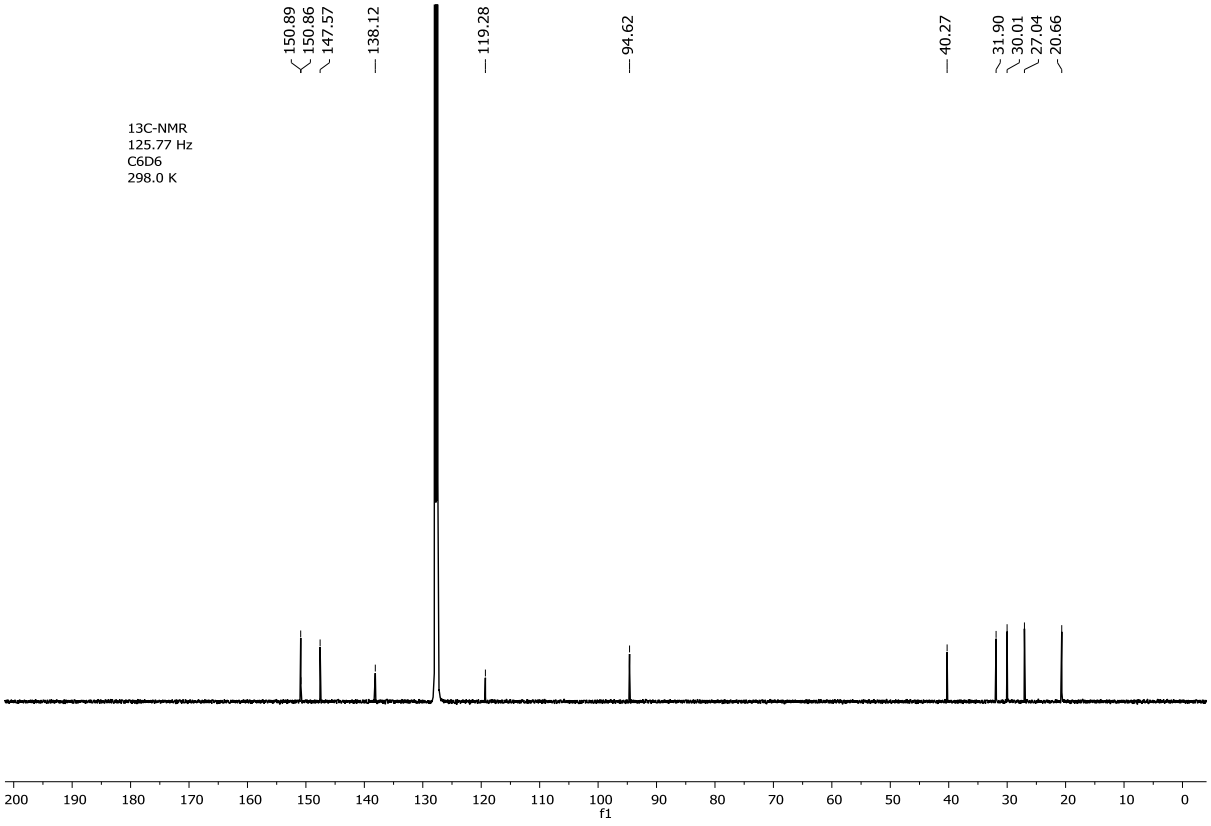
^{1}H NMR, 500 MHz, C_6D_6

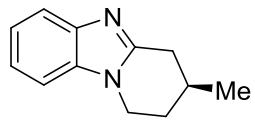




2l

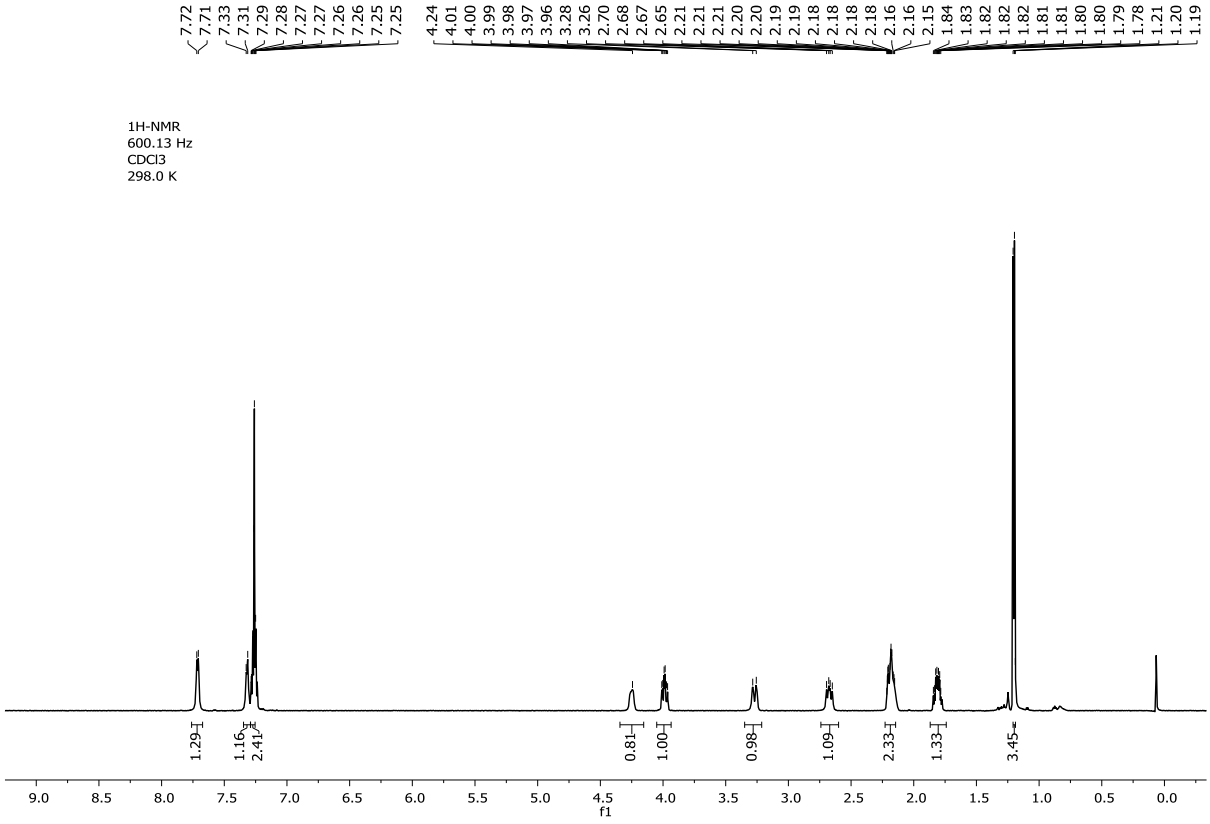
^{13}C NMR, 126 MHz, C_6D_6

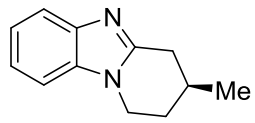




2m

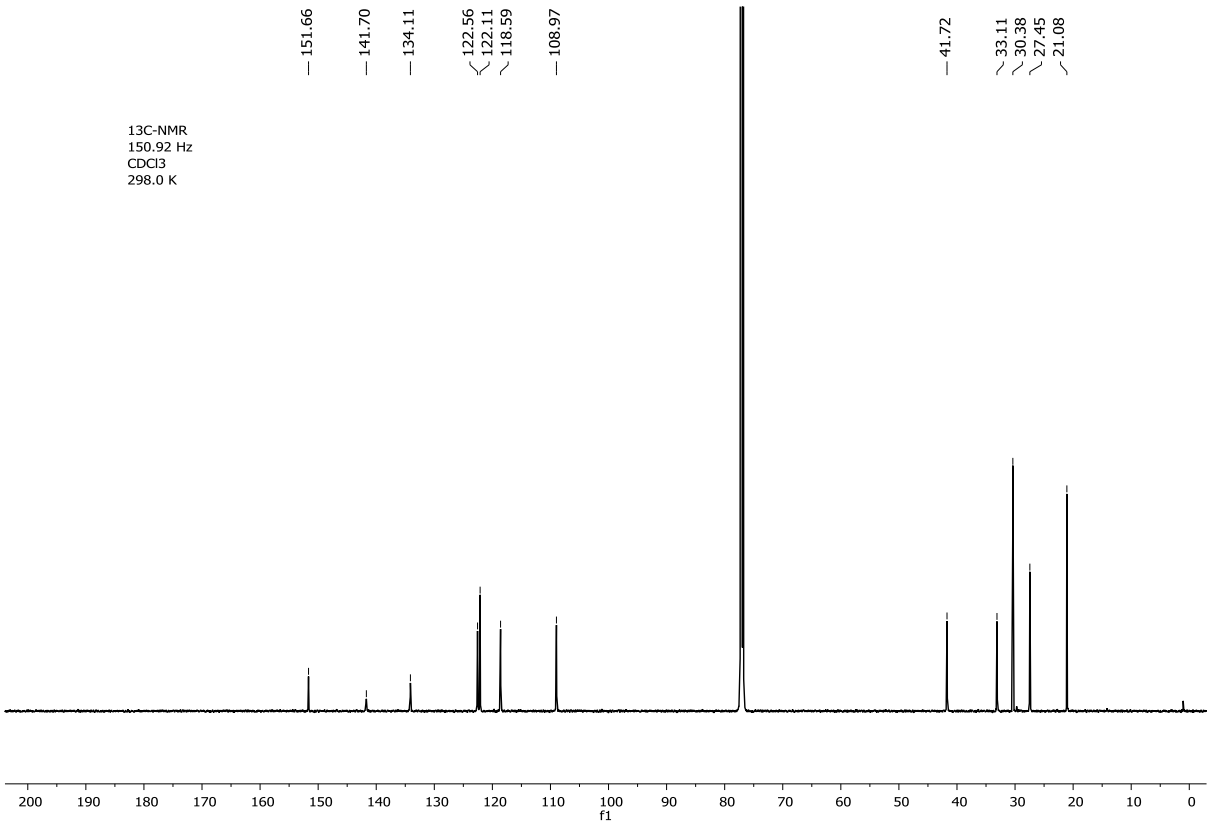
^{1}H NMR, 600 MHz, $CDCl_3$

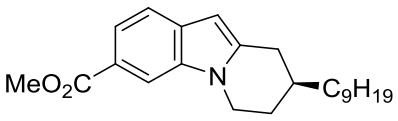




2m

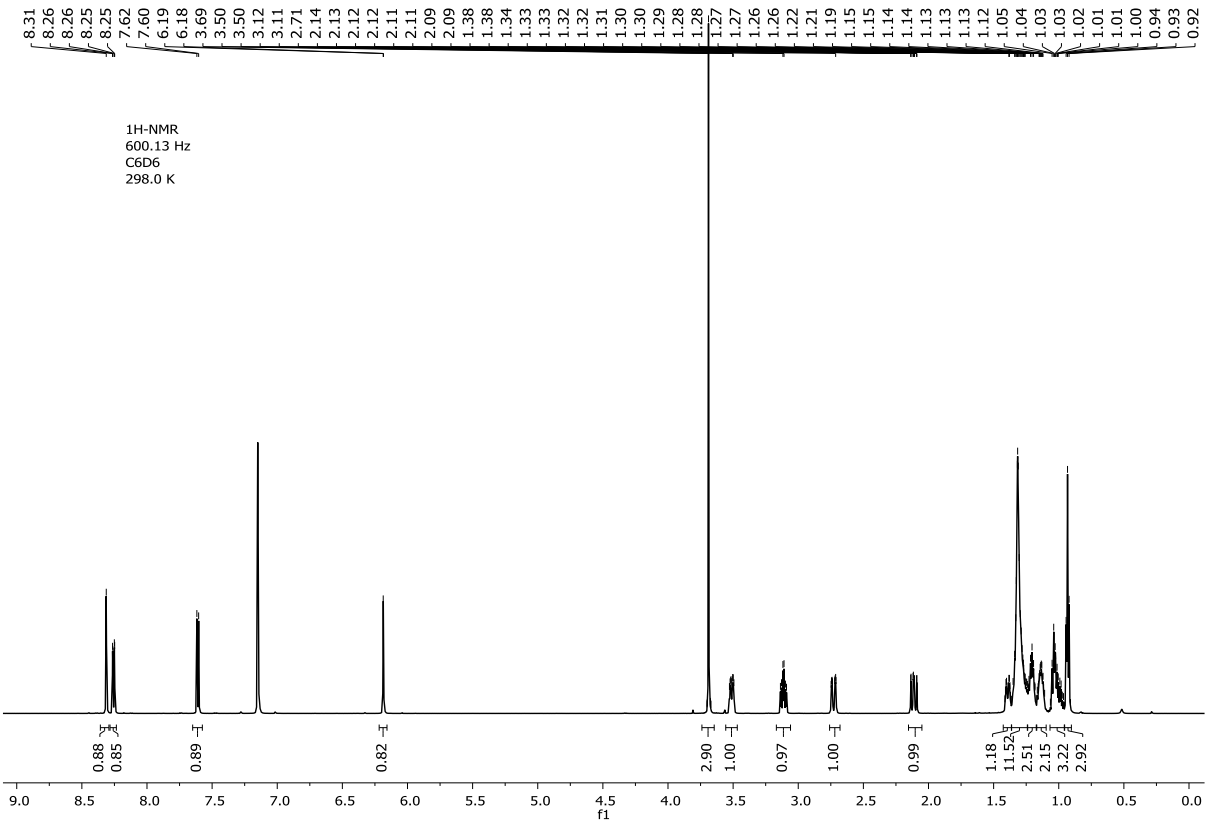
^{13}C NMR, 151 MHz, $CDCl_3$

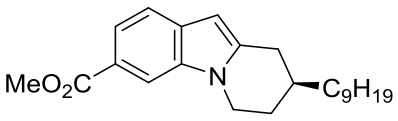




2n

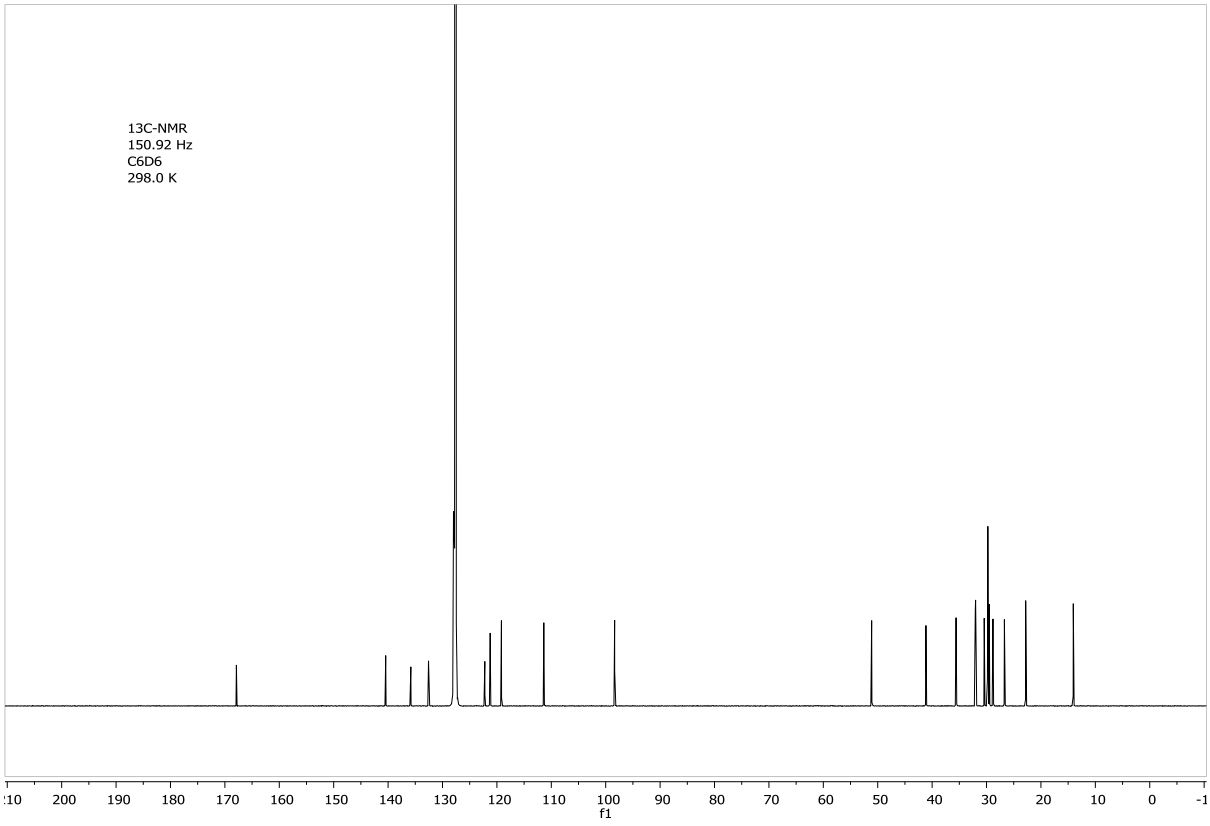
^{1}H NMR, 600 MHz, C_6D_6

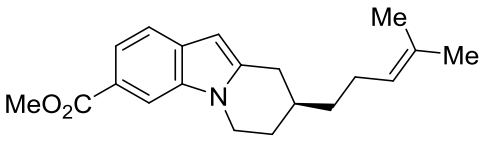




2n

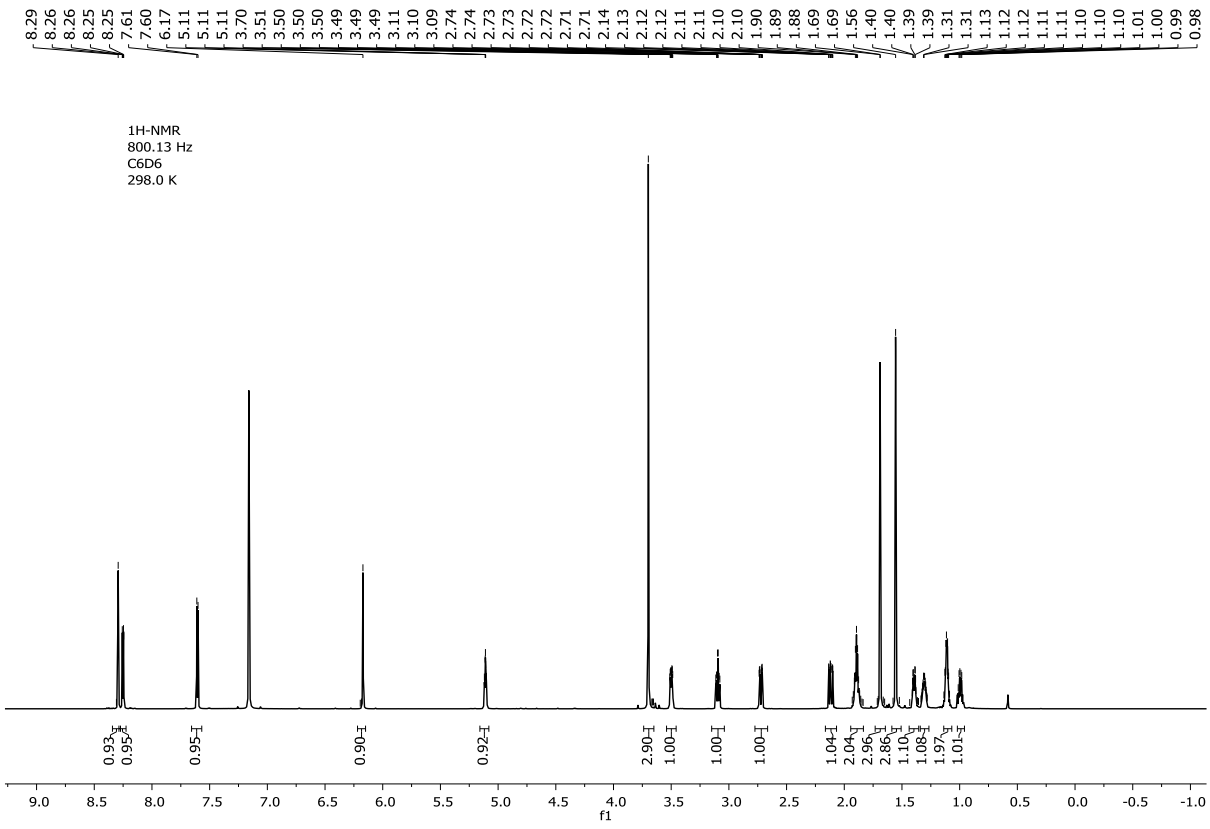
^{13}C NMR, 151 MHz, C_6D_6

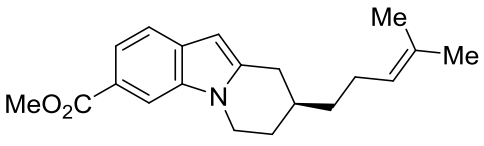




2o

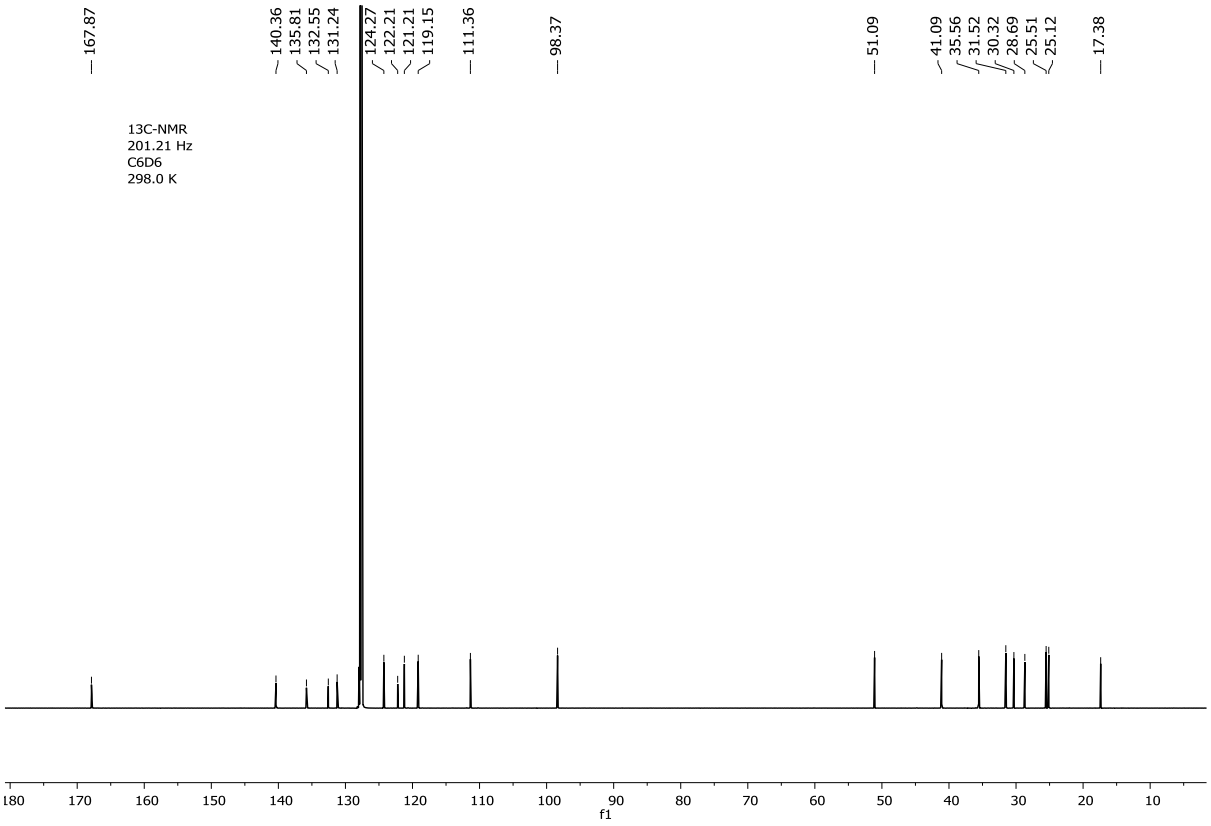
^{1}H NMR, 800 MHz, C_6D_6

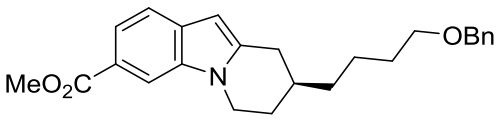




2o

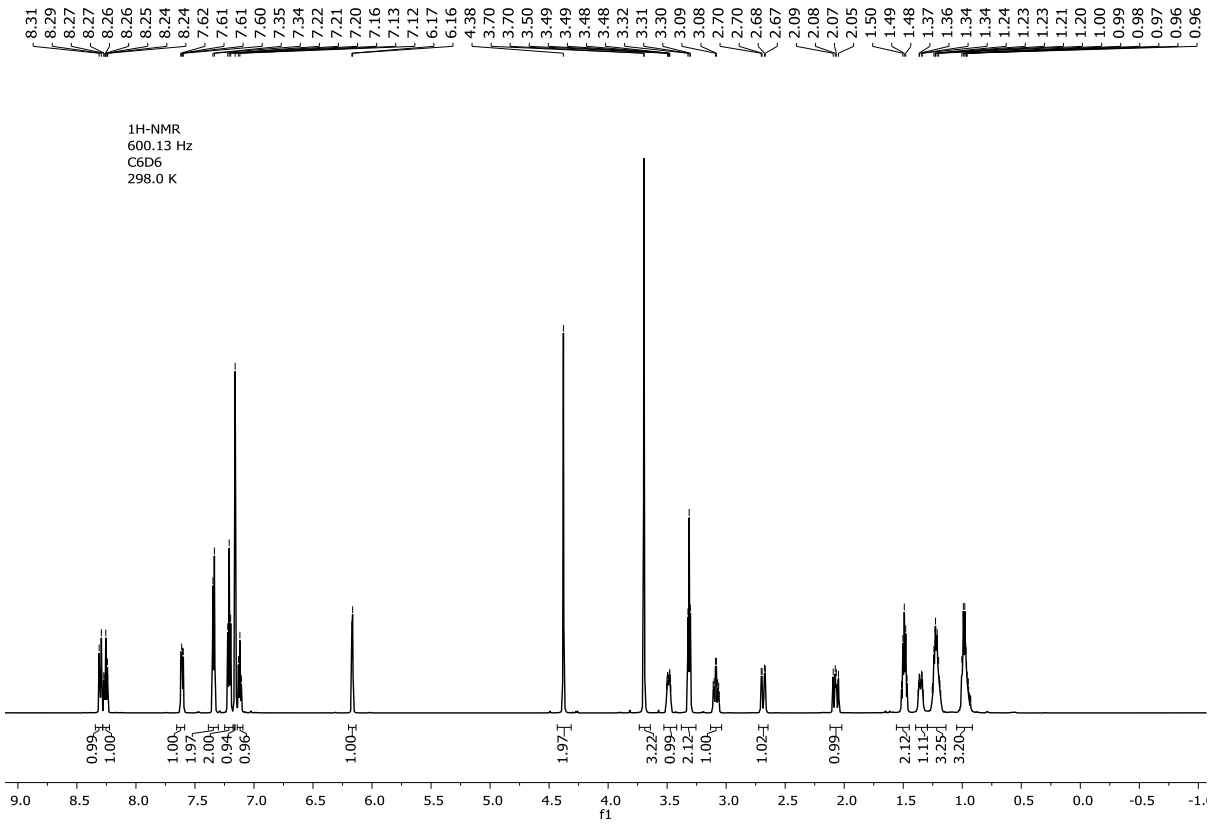
^{13}C NMR, 201 MHz, C_6D_6

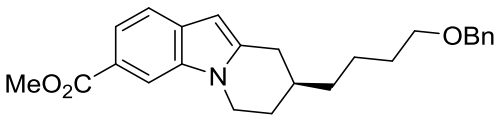




2p

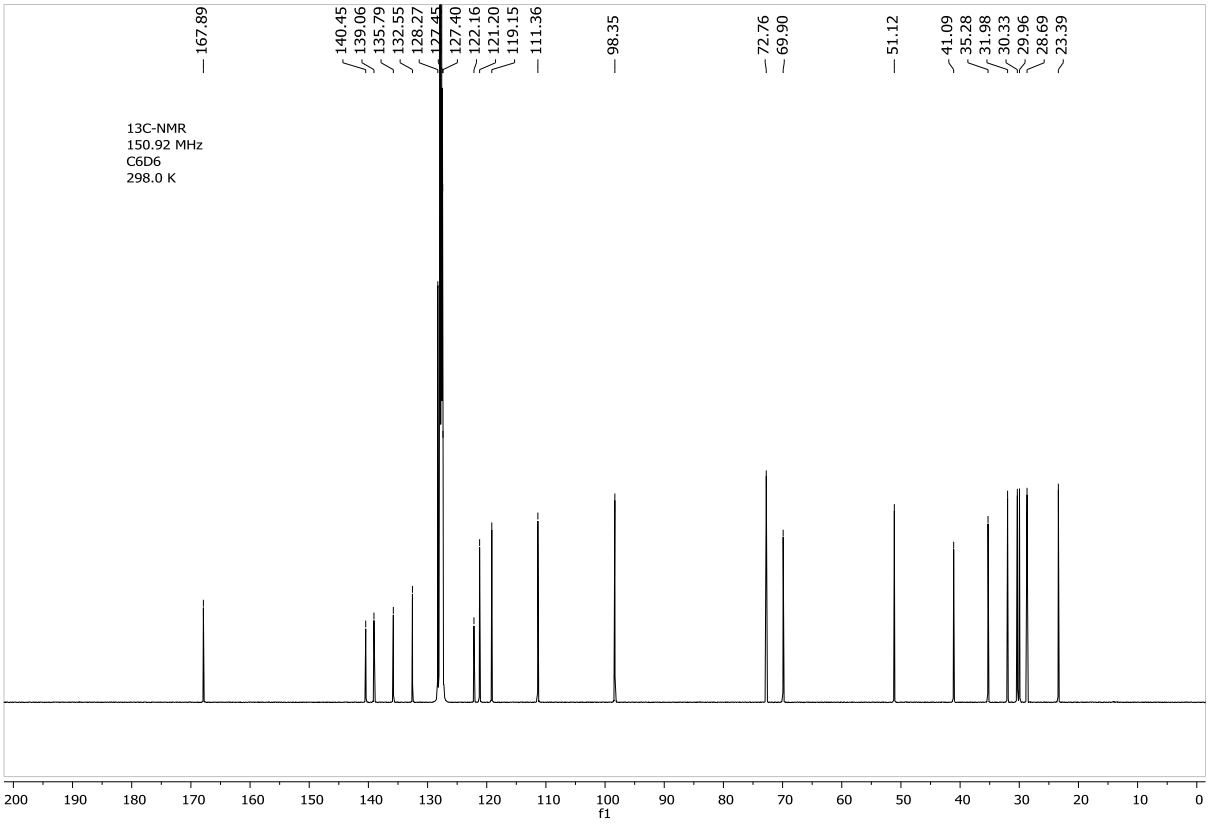
^{1}H NMR, 600 MHz, C_6D_6

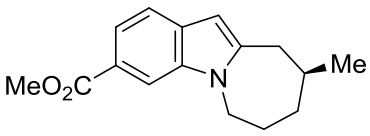




2p

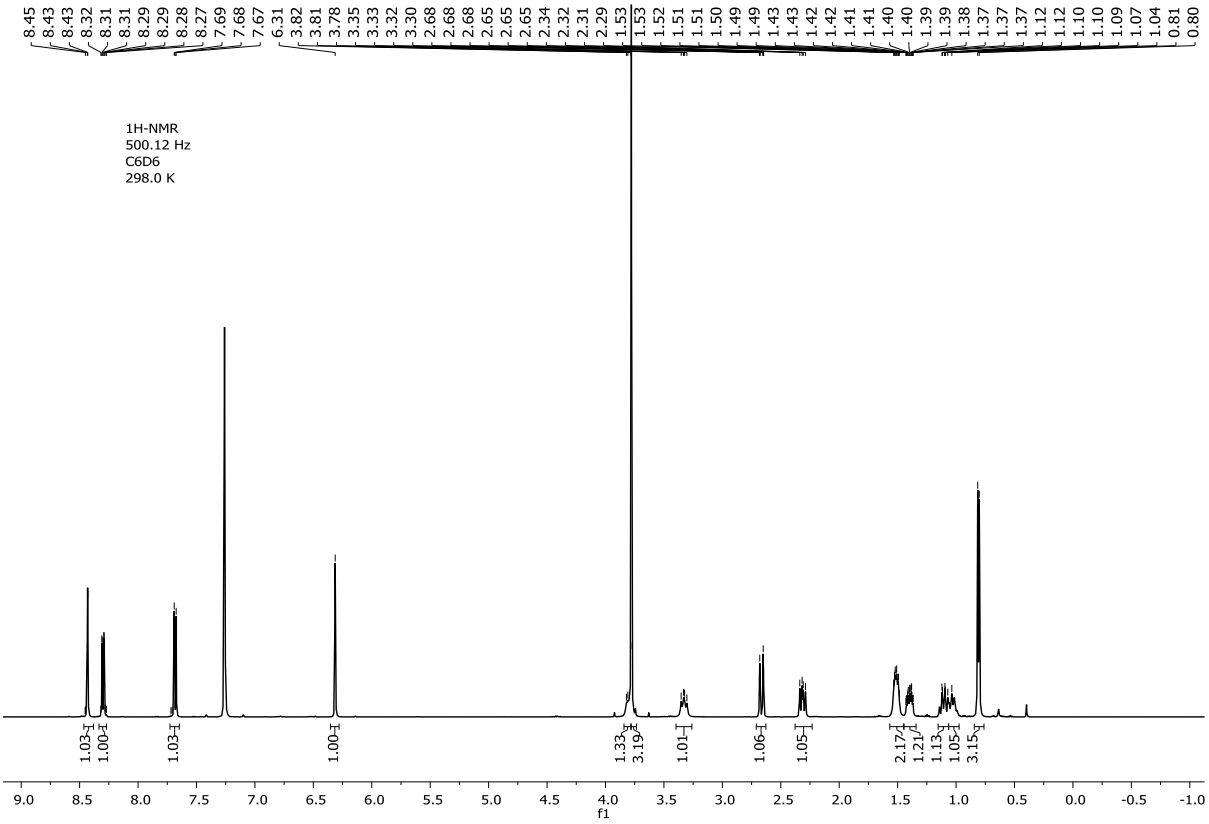
^{13}C NMR, 151 MHz, C_6D_6

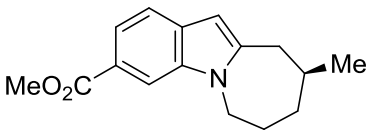




2q

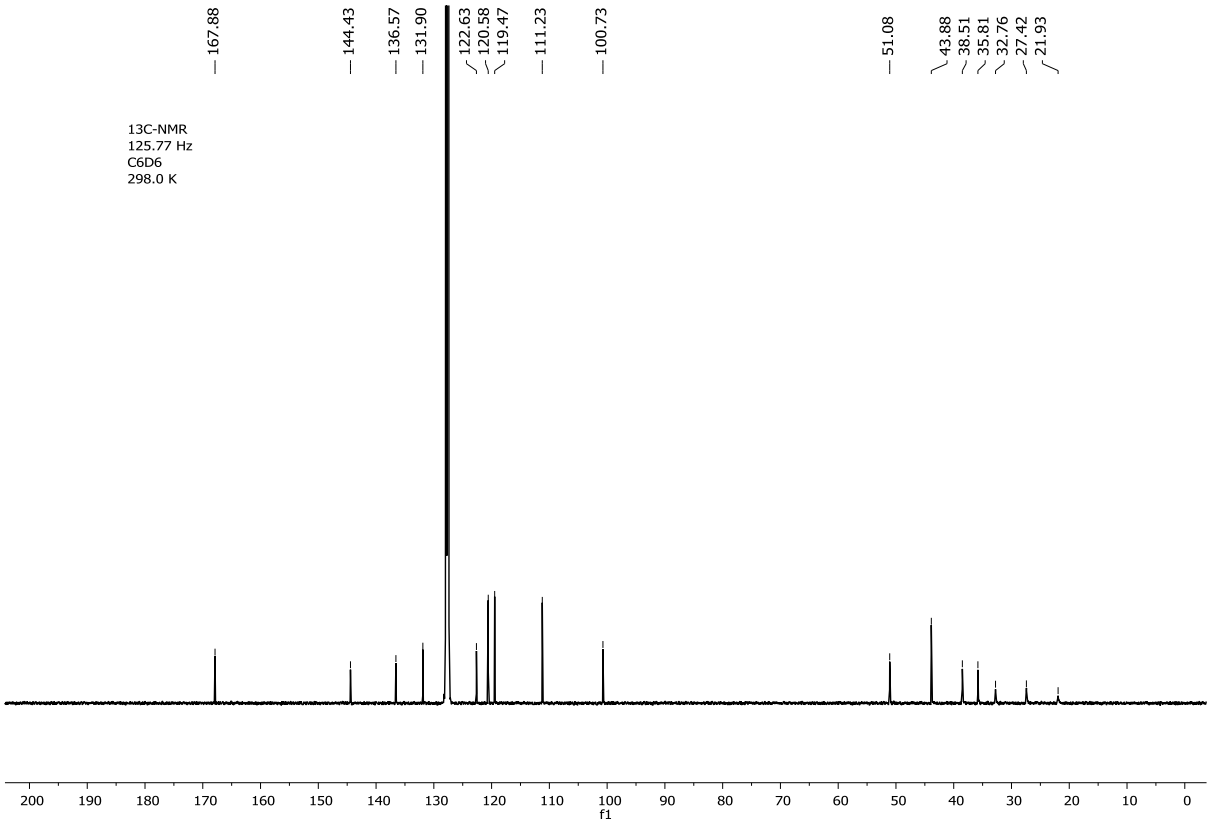
^{1}H NMR, 500 MHz, C_6D_6

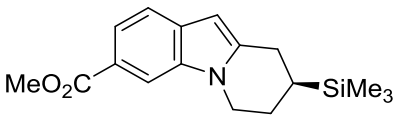




2q

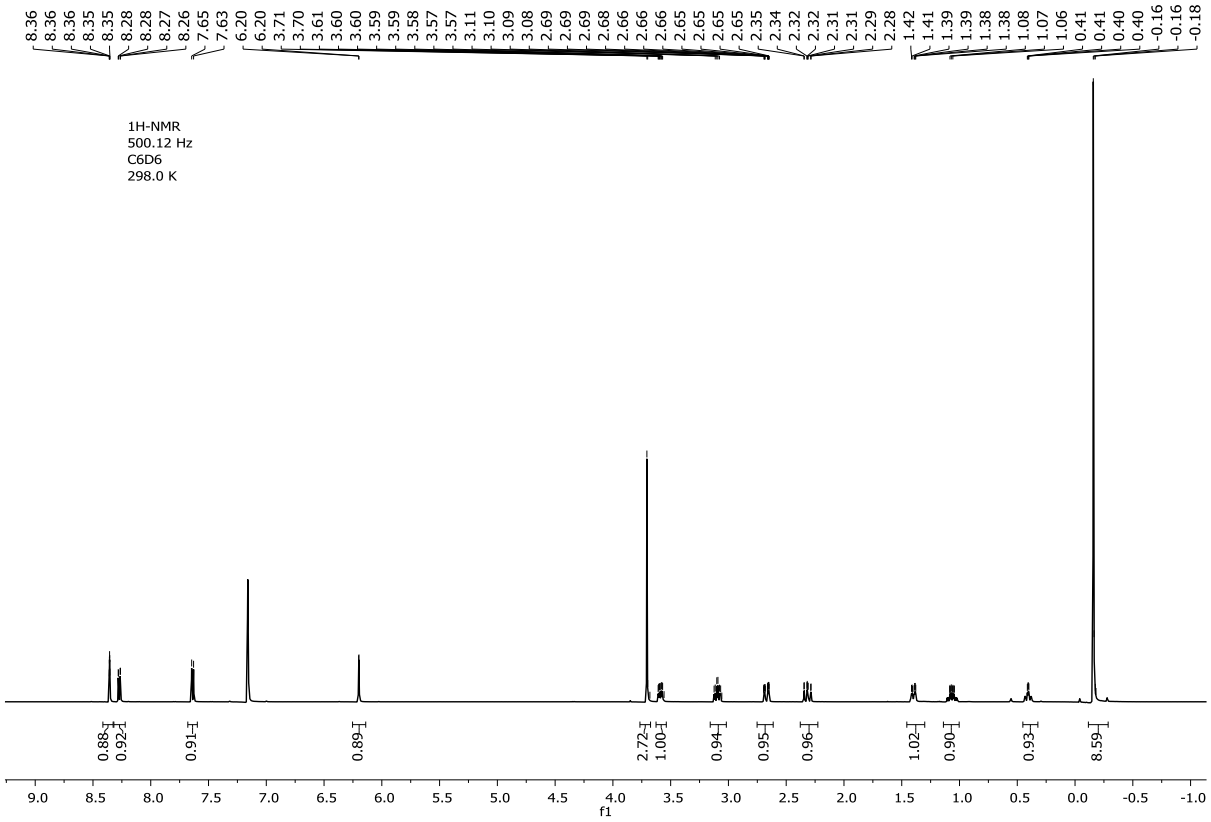
^{13}C NMR, 126 MHz, C_6D_6

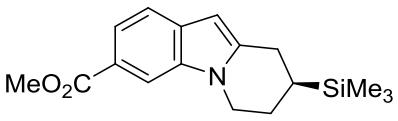




2r

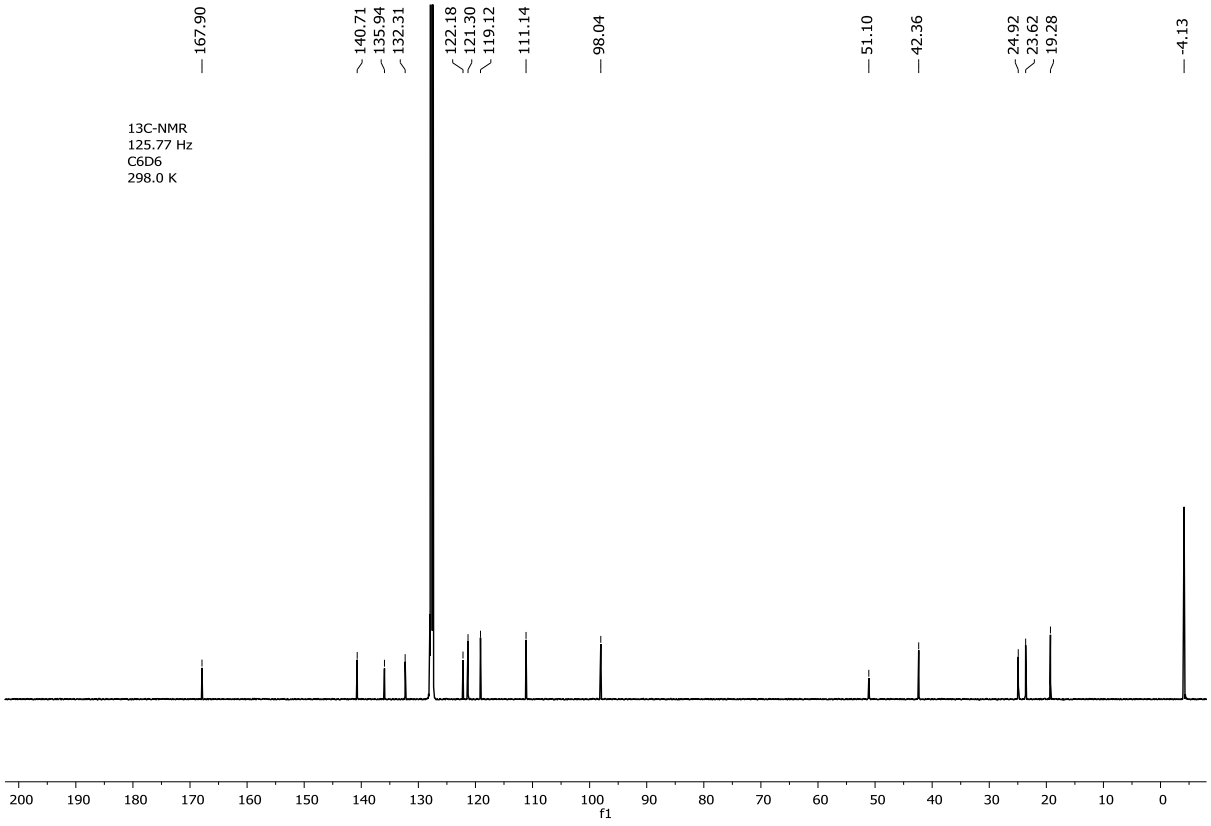
^{1}H NMR, 500 MHz, C_6D_6

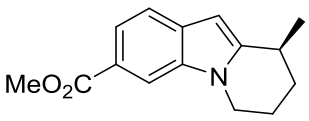




2r

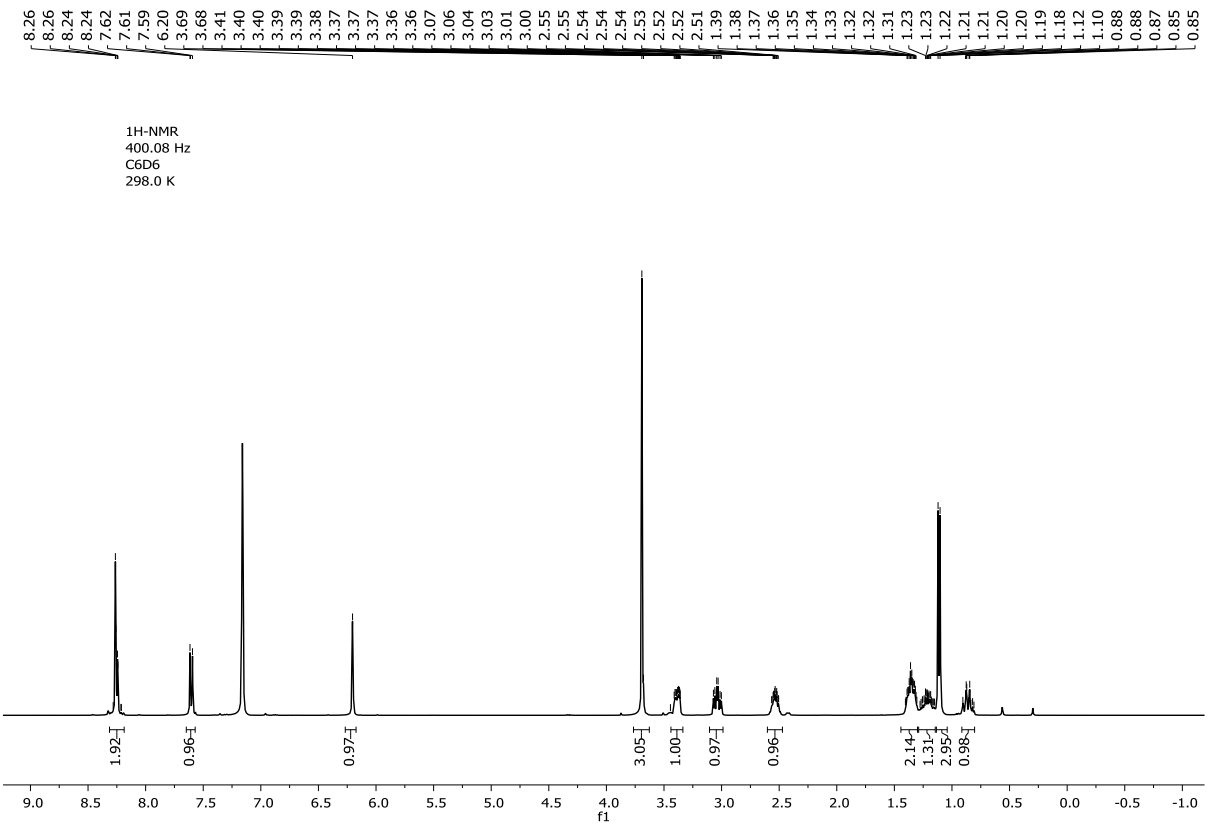
^{13}C NMR, 126 MHz, C_6D_6

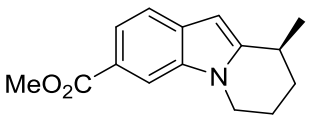




(+)-2s

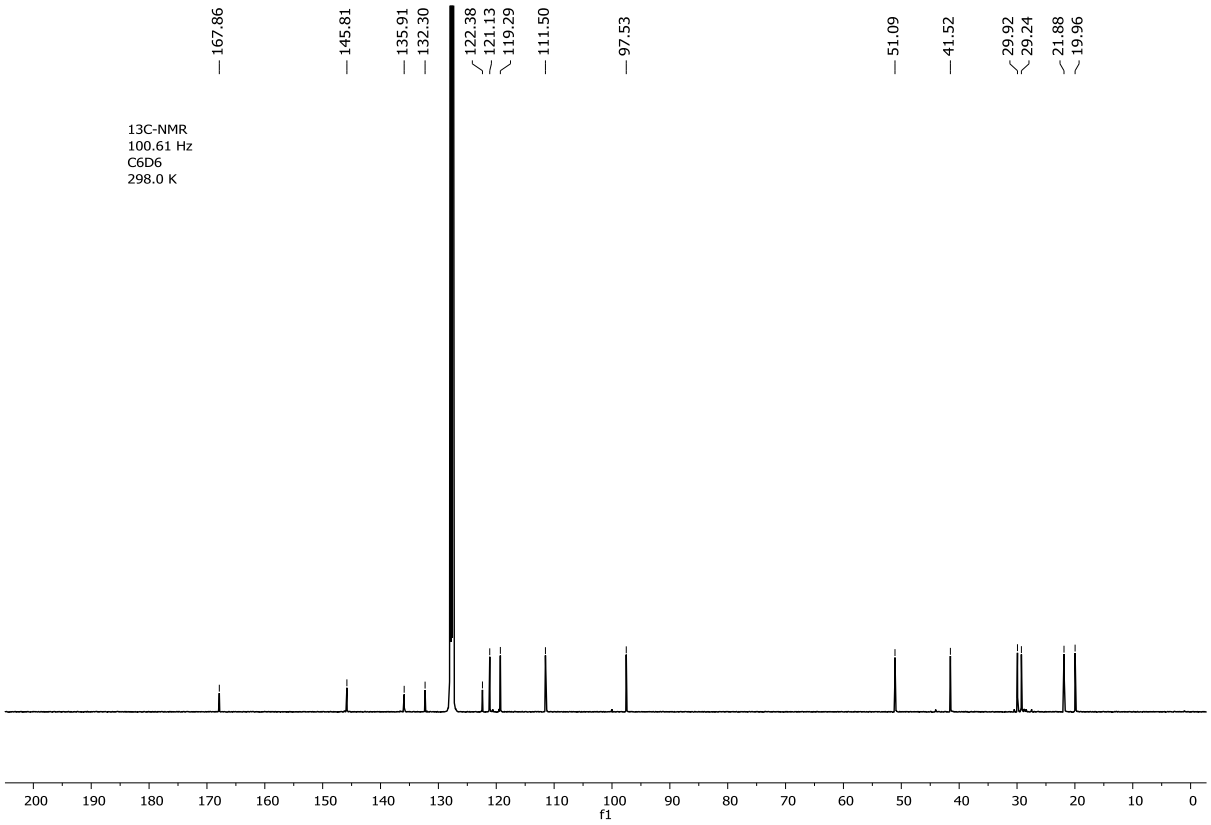
^{1}H NMR, 400 MHz, C_6D_6

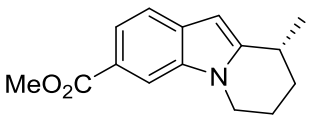




(+)-2s

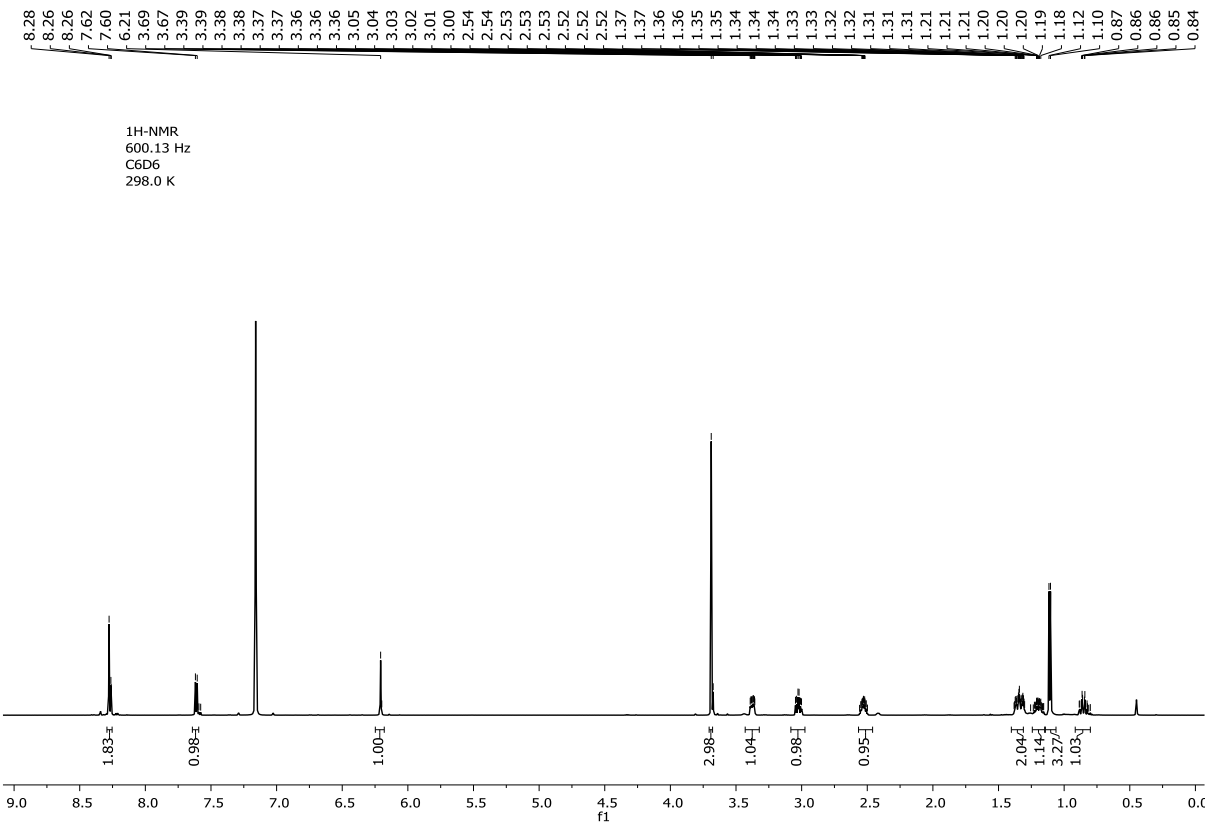
^{13}C NMR, 101 MHz, C_6D_6

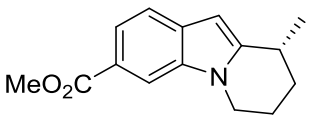




(-)-2s

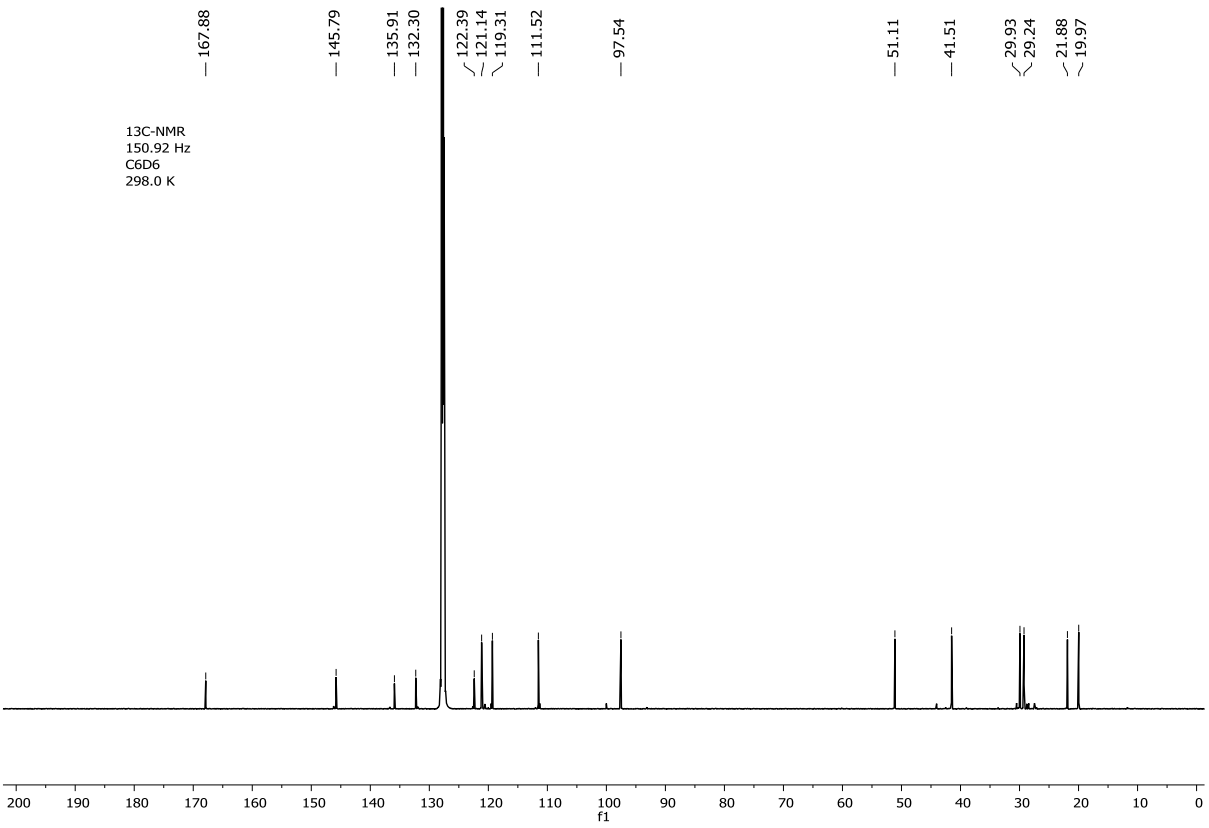
^{1}H NMR, 600 MHz, C_6D_6

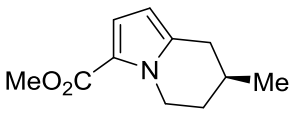




(-)-2s

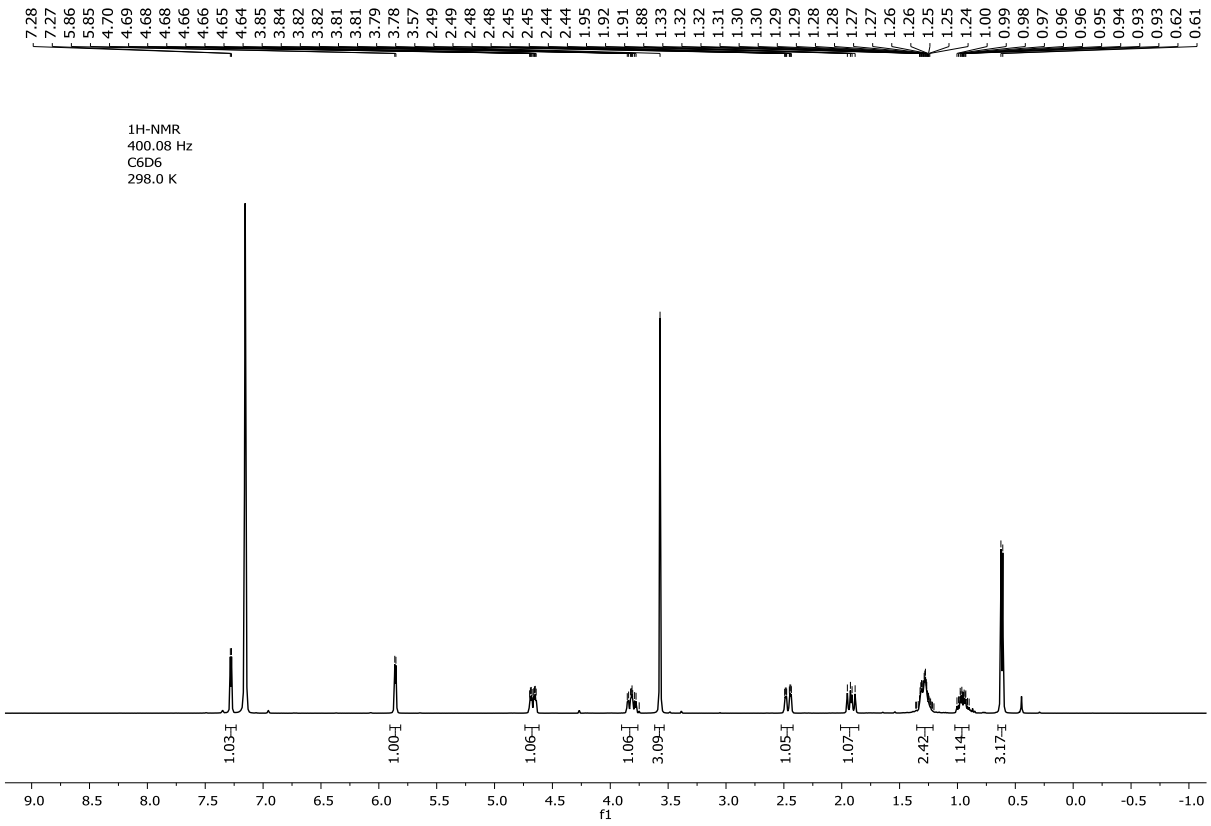
^{13}C NMR, 151 MHz, C_6D_6

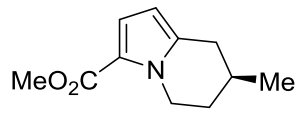




4a

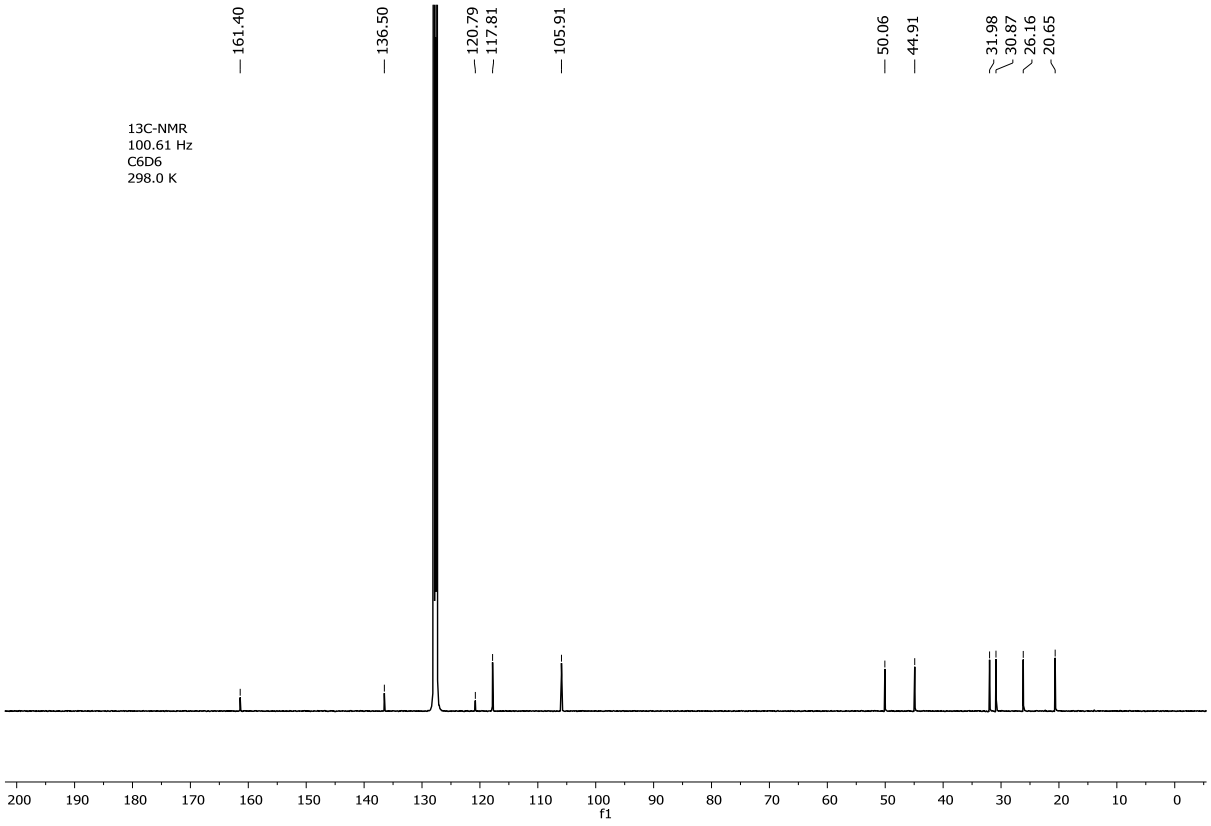
^{1}H NMR, 400 MHz, C_6D_6

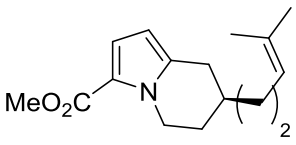




4a

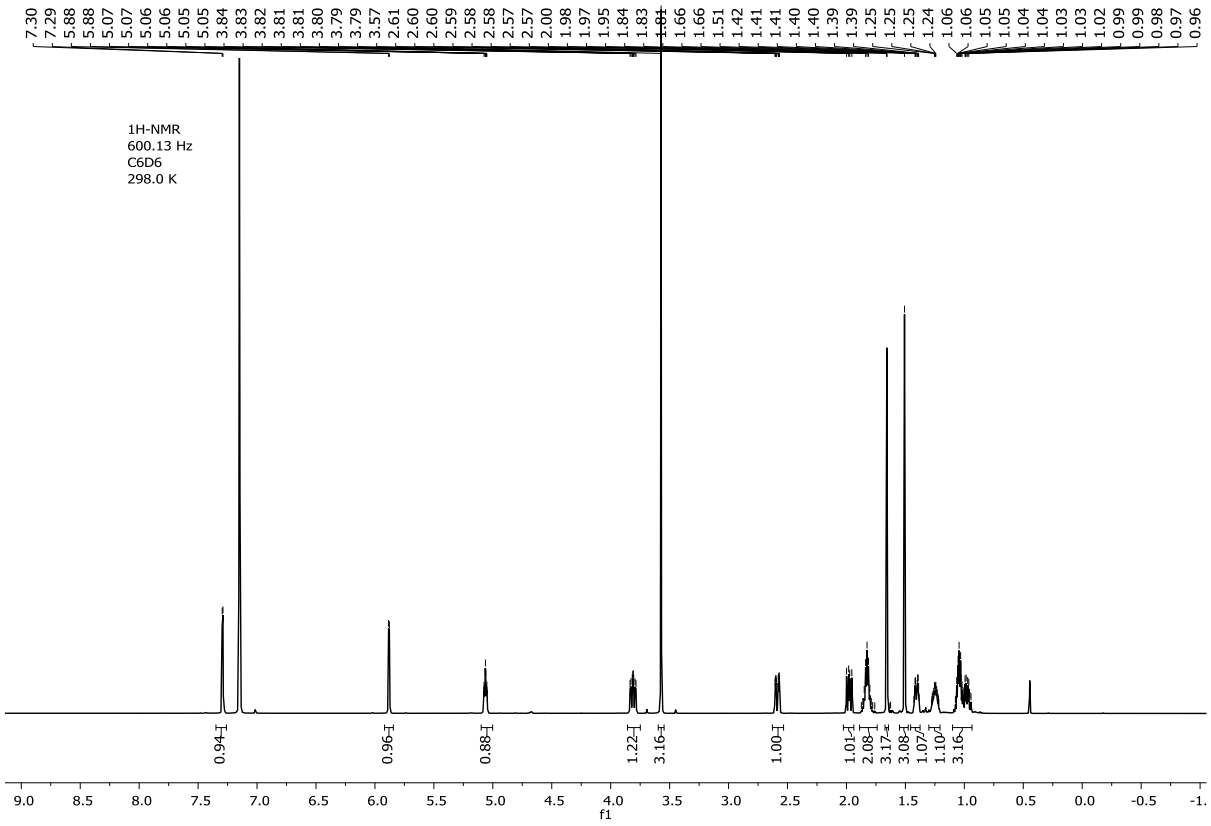
^{13}C NMR, 101 MHz, C_6D_6

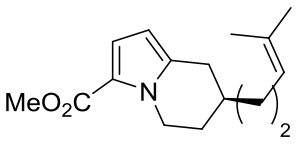




4b

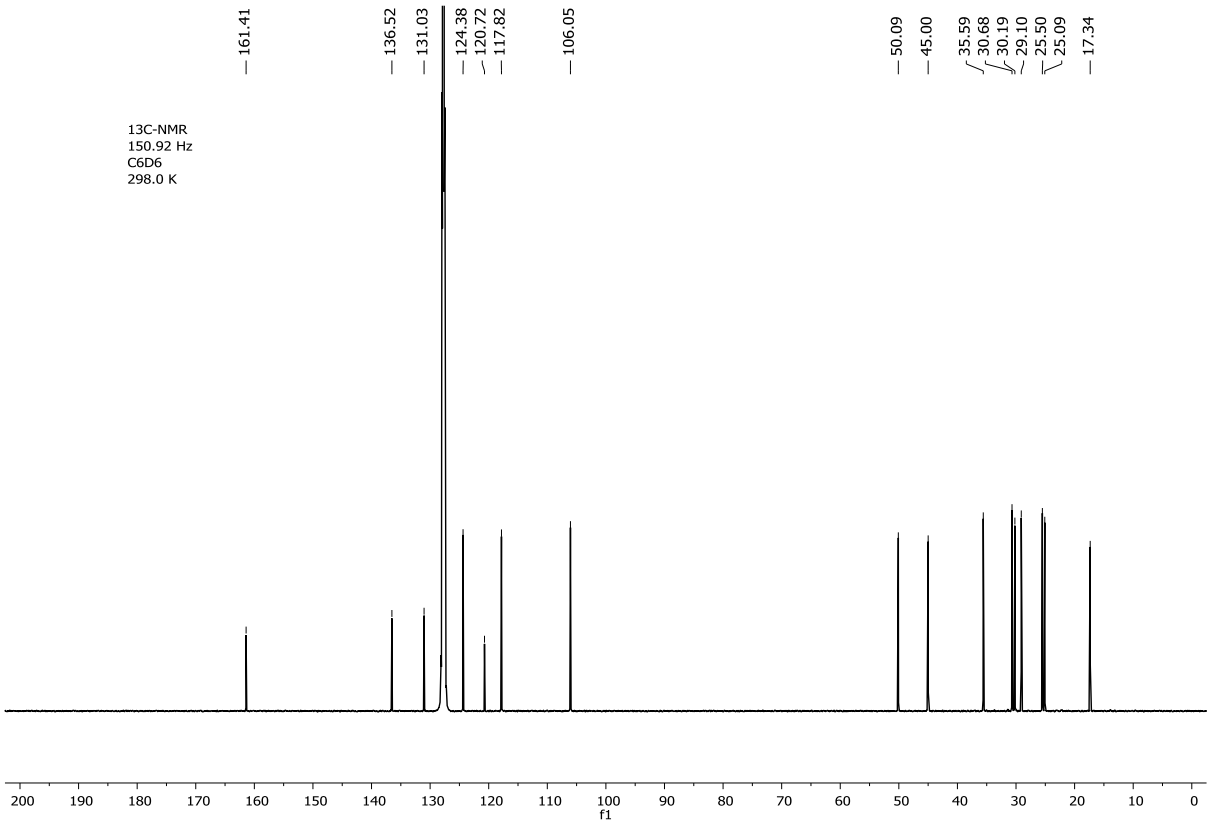
^{1}H NMR, 600 MHz, C_6D_6

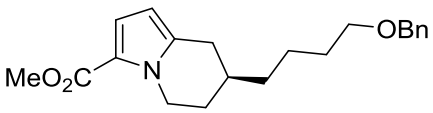




4b

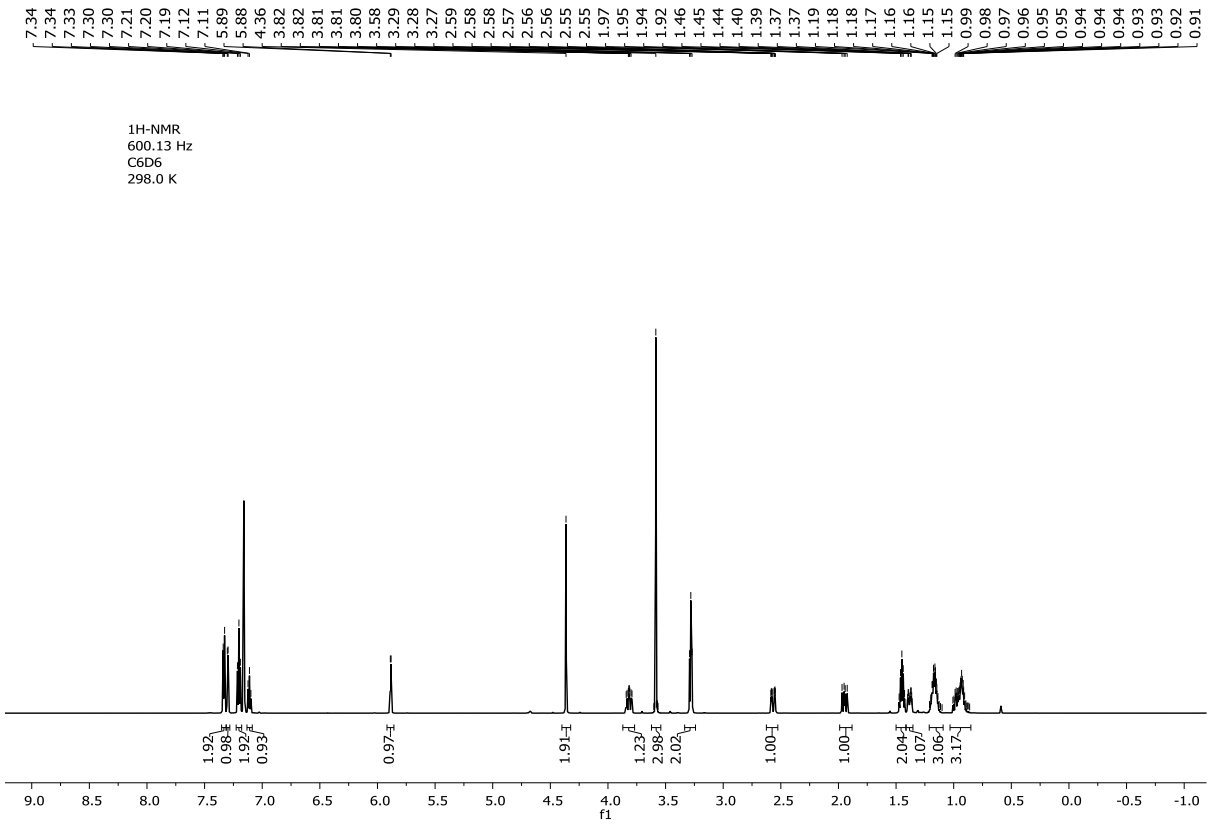
^{13}C NMR, 151 MHz, C_6D_6

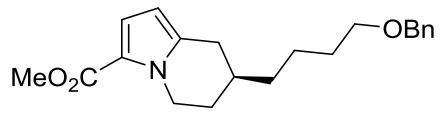




4c

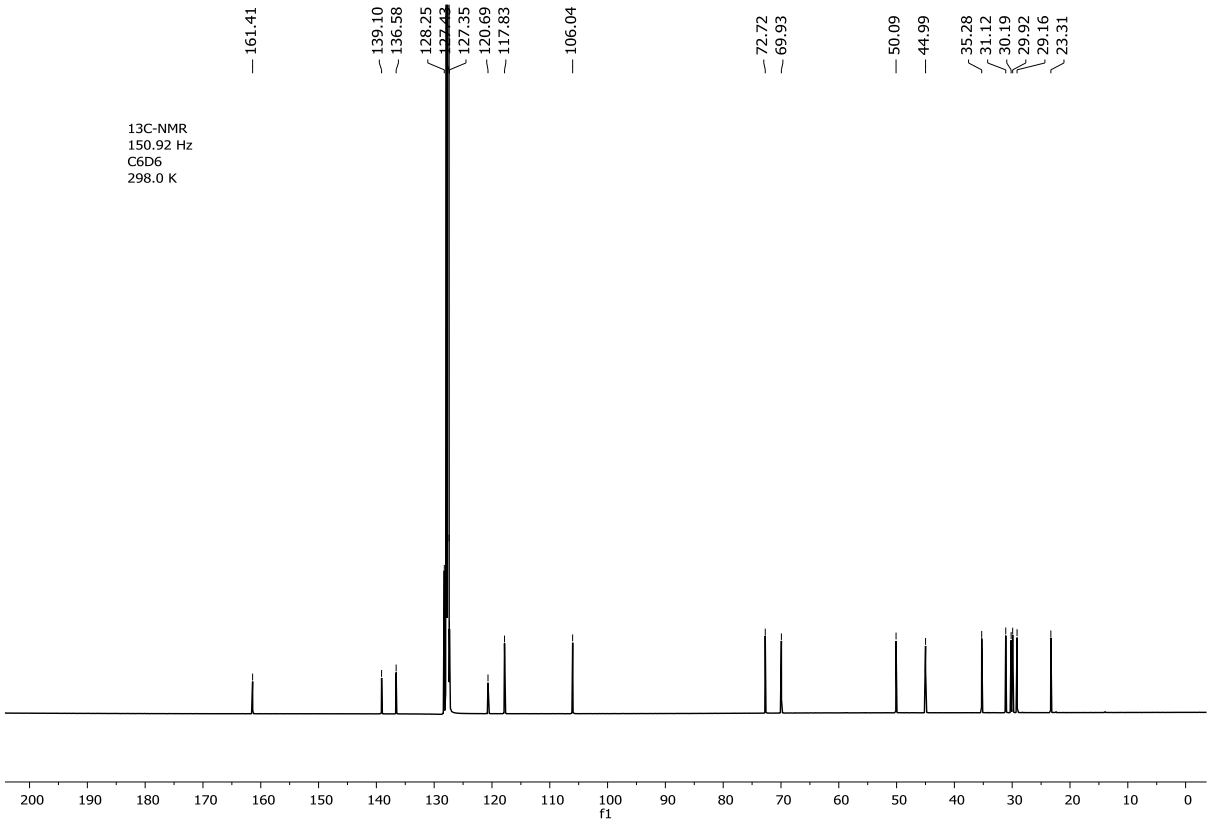
^{1}H NMR, 600 MHz, C_6D_6

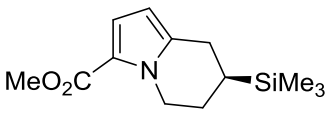




4c

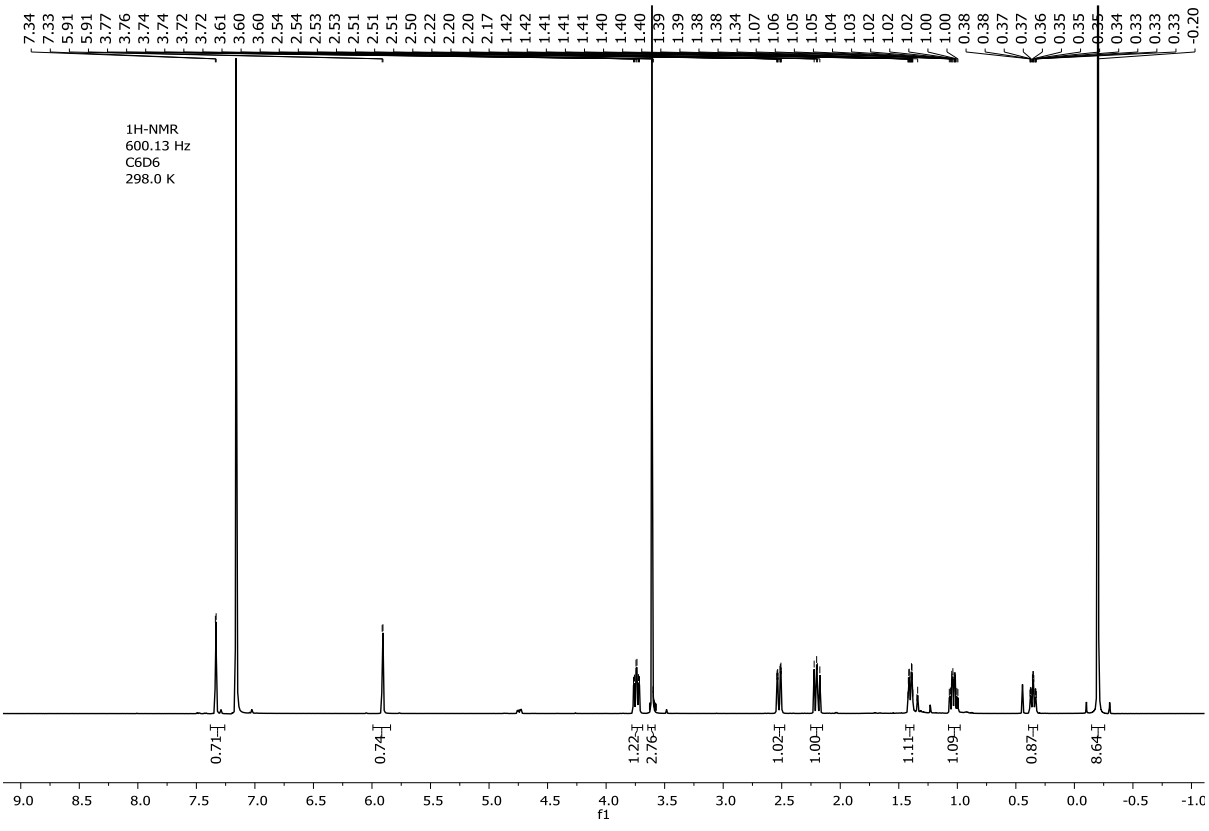
^{13}C NMR, 151 MHz, C_6D_6

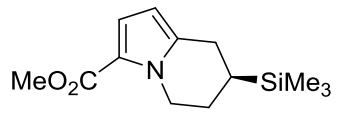




4d

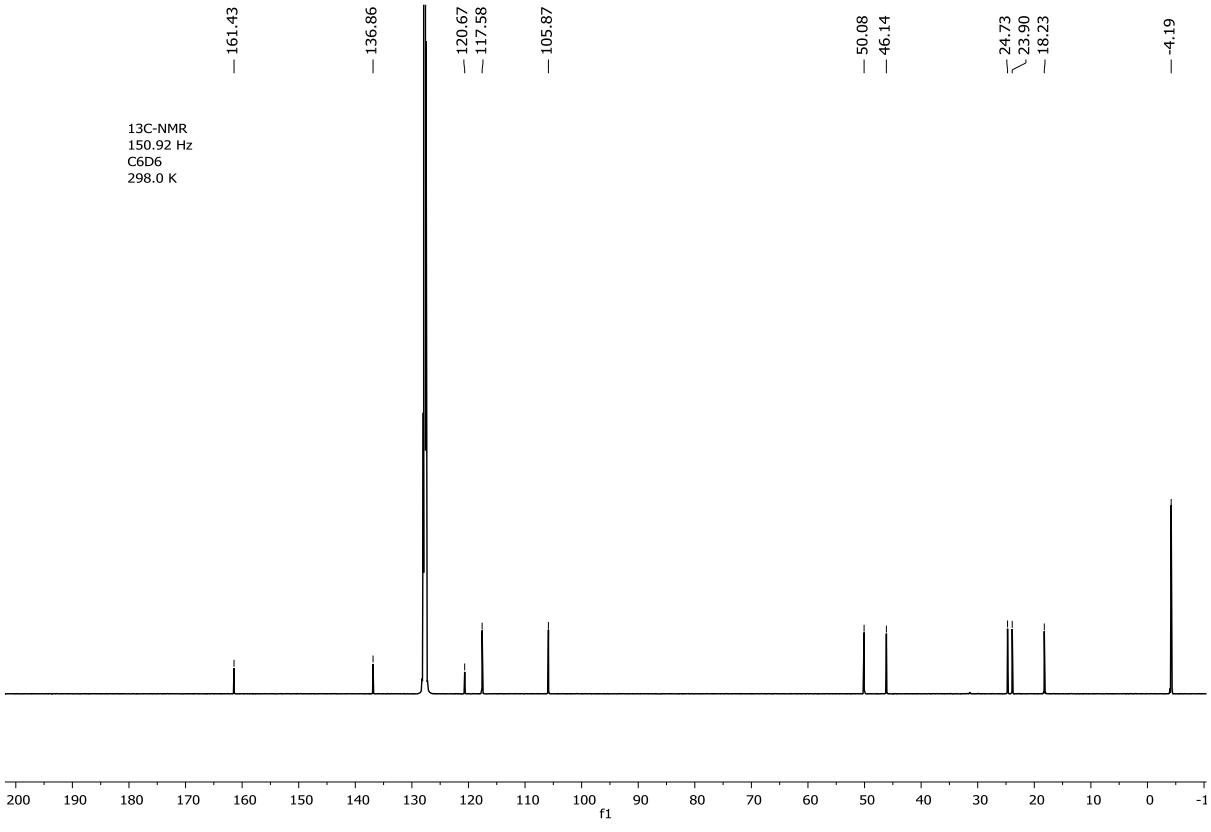
^{1}H NMR, 600 MHz, C_6D_6

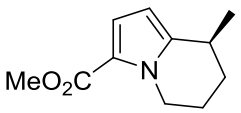




4d

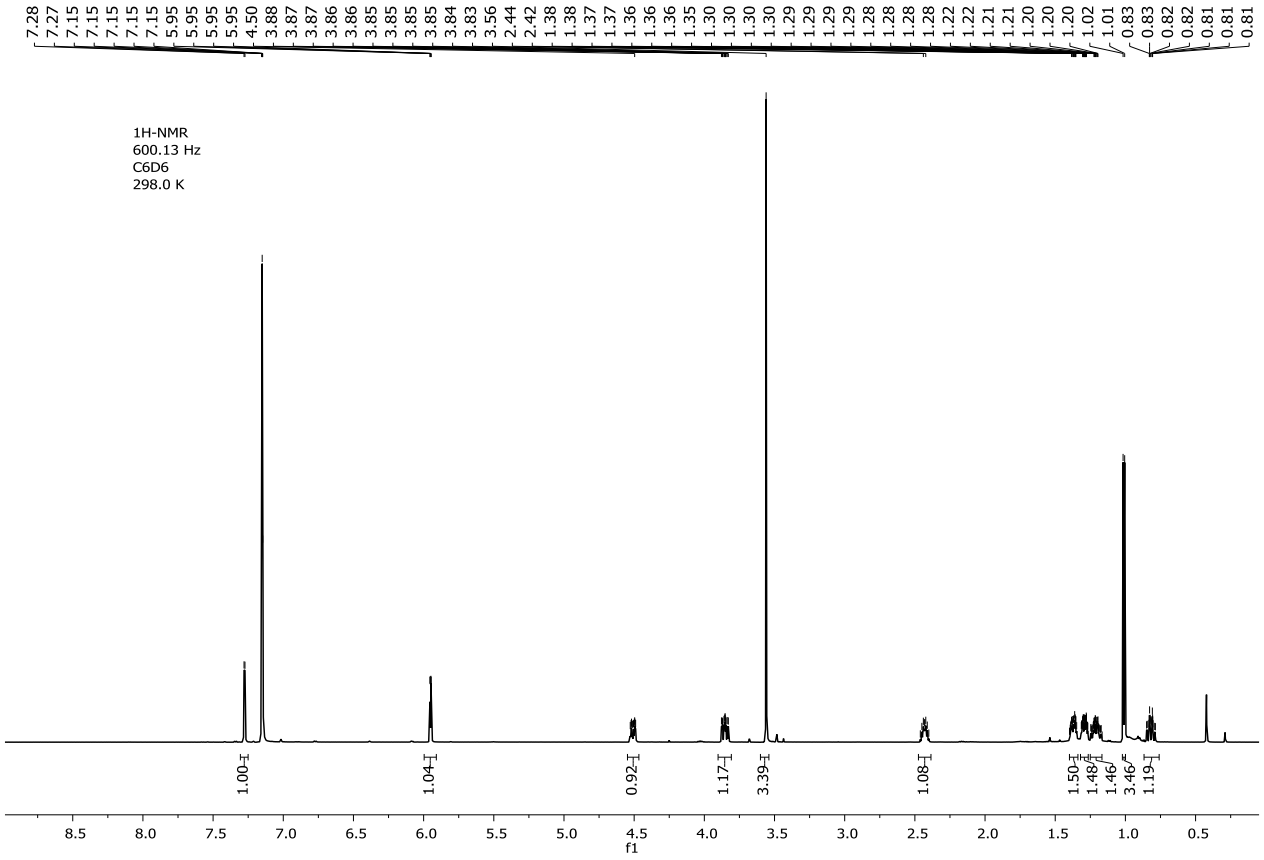
^{13}C NMR, 151 MHz, C_6D_6

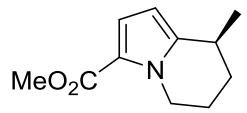




4e

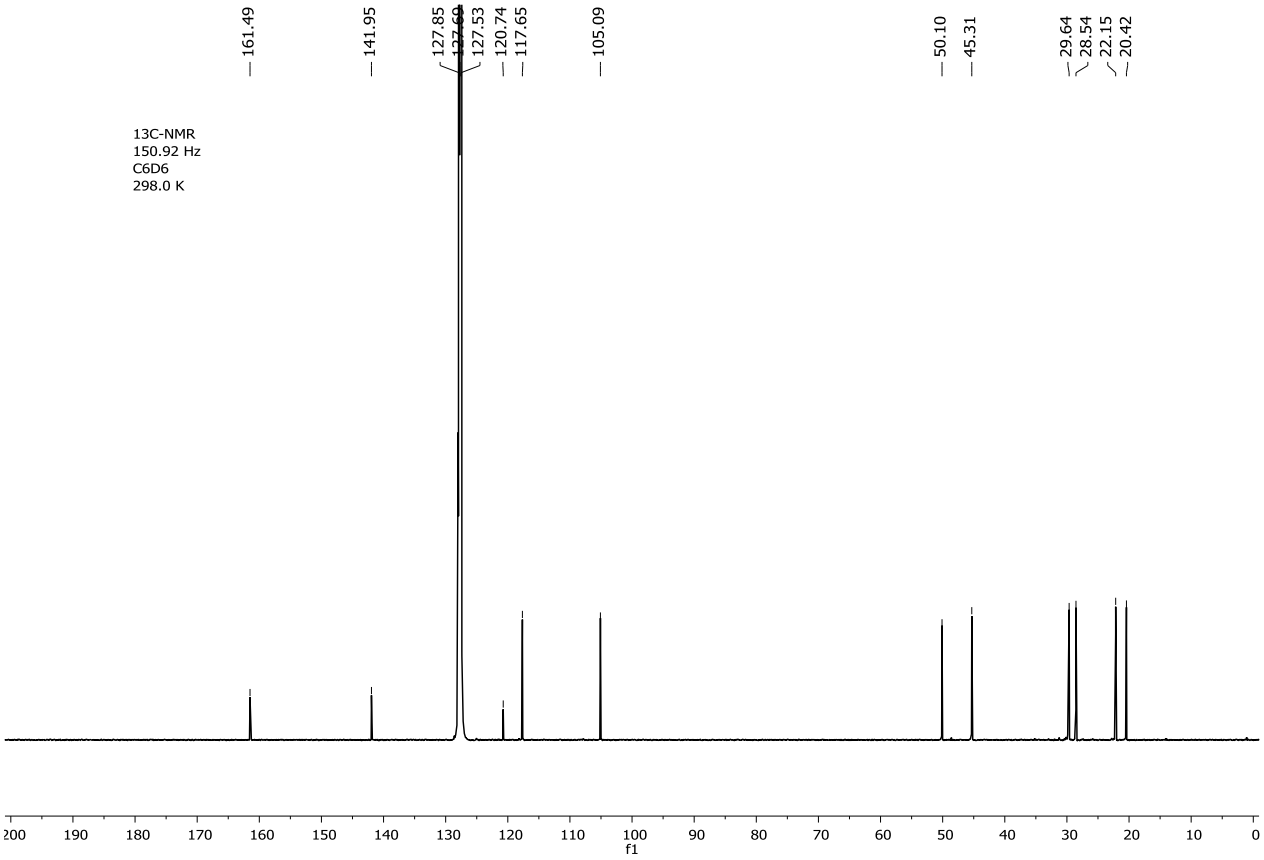
^{1}H NMR, 600 MHz, C_6D_6

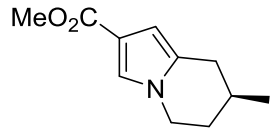




4e

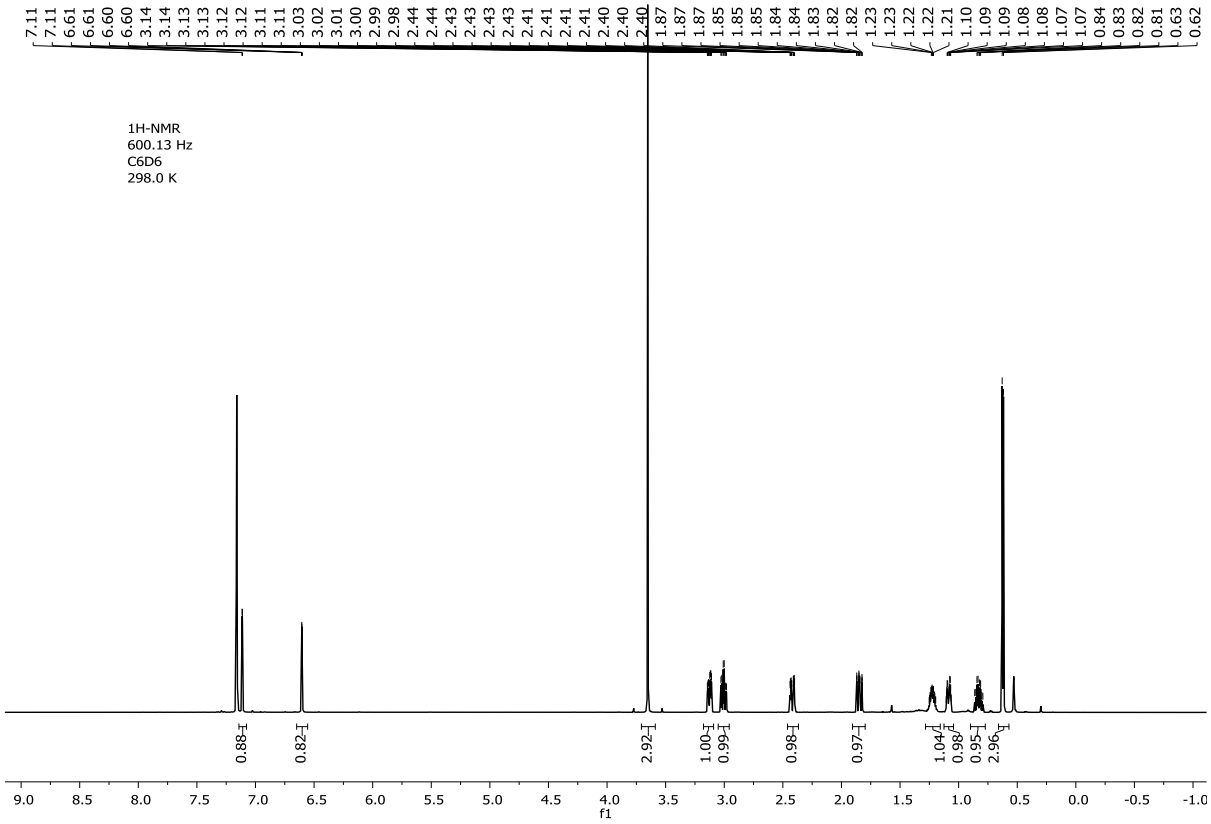
^{13}C NMR, 151 MHz, C_6D_6

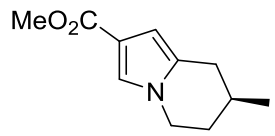




4f

^{1}H NMR, 600 MHz, C_6D_6





4f

^{13}C NMR, 151 MHz, C_6D_6