Supporting Information

Selective Partial Reduction of Various Heteroaromatic Compounds with Bridgehead Nitrogen via Birch Reduction Protocol

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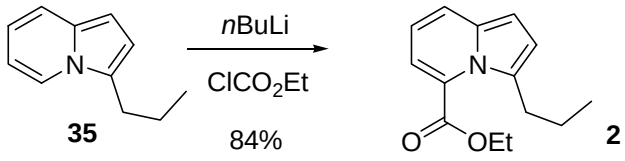
1. Preparation of Starting Materials (Experimental Details)

3-Propyl-indolizine-5-carboxylic acid ethyl ester (2)

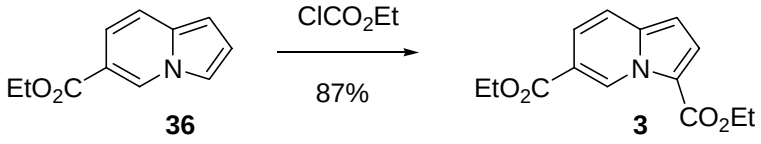


*n*BuLi (1.5 mL, 3.75 mmol; 2.5 M in hexanes) was added dropwise to a solution of 3-propyl-indolizine (490 mg, 3.08 mmol) in anhydrous THF (15 mL) at 0 ^{o}C and stirred for 30 min. After this period, ethyl chloroformate (0.45 mL, 4.72 mmol) was added to the mixture and stirred at 0 ^{o}C for 30 min. The reaction progress was monitored by TLC and GC-MS analyses. The mixture was warmed to r.t. and quenched (aqueous NH_4Cl). The phases were separated and the aqueous phase was thoroughly extracted with hexanes. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 1% EtOAc/hexanes to give 3-propyl-indolizine-5-carboxylic acid ethyl ester **2** as an oil (598 mg, 84%).

^{1}H NMR (500 MHz, C_6D_6, δ): 7.27 (1H, dd, *J* = 8.6, 1.3 Hz), 7.03 (1H, dd, *J* = 6.8, 1.3 Hz), 6.73 (1H, d, *J* = 4.0 Hz), 6.67 (1H, d, *J* = 4.0 Hz), 6.26 (1H, dd, *J* = 8.6, 6.8 Hz), 4.11 (2H, q, *J* = 7.0 Hz), 2.81 (2H, t, *J* = 7.6 Hz), 1.60-1.53 (2H, m), 1.01 (3H, t, *J* = 7.2 Hz), 0.82 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, C_6D_6, δ): 163.3, 135.1, 129.6,

127.1, 123.5, 117.6, 115.0, 113.1, 102.5, 61.3, 31.9, 20.8, 14.1 (×2). MS *m/z* (relative intensity): 231 (M^+, 33), 202 (100), 174 (54).

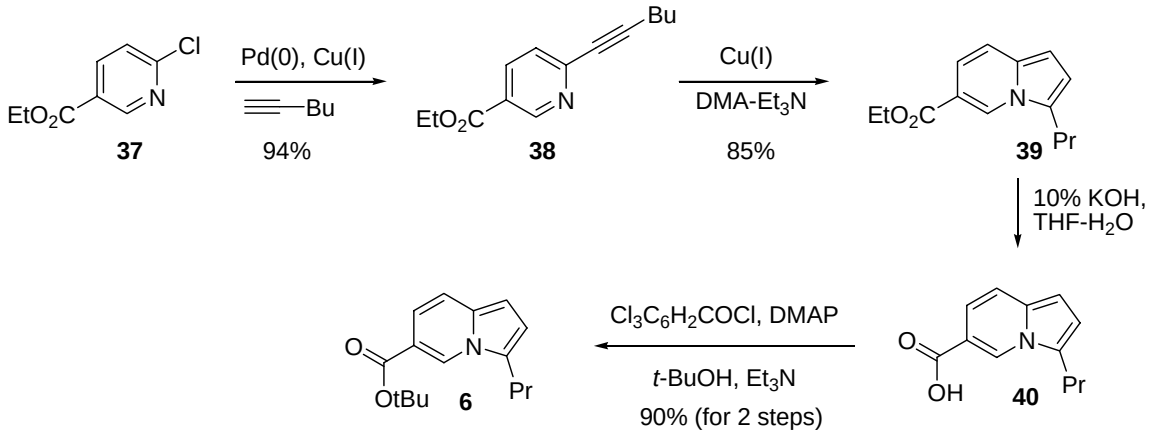
Indolizine-3,6-dicarboxylic aid diethyl ester (3)



Indolizine-6-carboxylic acid ethyl ester (513 mg, 2.7 mmol) was heated to reflux in ethyl chloroformate (8 mL) for 17 h. The mixture was cooled to r.t. and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 5% EtOAc/hexanes to give indolizine-3,6-dicarboxylic aid diethyl ester **3** (616 mg, 87%).

^{1}H NMR (500 MHz, C_6D_6, δ): 10.37 (1H, s), 7.54 (1H, d, *J* = 4.4 Hz), 7.47 (1H, dd, *J* = 9.2, 1.5 Hz), 6.91 (1H, d, *J* = 9.2 Hz), 6.17 (1H, d, *J* = 4.0 Hz), 4.18 (2H, q, *J* = 7.0 Hz), 4.10 (2H, q, *J* = 7.3 Hz), 1.10 (3H, t, *J* = 7.0 Hz), 1.02 (3H, t, *J* = 7.2). ^{13}C NMR (125 MHz, C_6D_6, δ): 165.1, 160.9, 138.2, 131.7, 123.6, 120.8, 118.1, 117.1, 115.9, 102.1, 61.0, 60.0, 14.5, 14.2. MS *m/z* (relative intensity): 261 (M^+, 95), 233 (24), 205 (100), 188 (60).

3-Propyl-indolizine-6-carboxylic acid *tert*-butyl ester (6)



The mixture of ethyl 6-chloro-nicotinate (2.13 g, 11.48 mmol), CuI (44 mg, 0.23 mmol), $Pd(PPh_3)_2Cl_2$ (161 mg, 0.23 mmol), and PPh_3 (120 mg, 0.46 mmol) in *i*-Pr_2EtN (32 mL) and Et_3N (8 mL) was stirred at r.t. *n*-Hexyne (4.0 mL, 34.57 mmol) was added to the mixture and stirred at 80 ^oC for 12 h. The reaction progress was monitored by TLC and GC-MS analyses. The mixture was cooled to r.t. and quenched (aqueous NH_4Cl). The phases were separated and the aqueous phase was thoroughly extracted with hexanes. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 5-10% EtOAc/hexanes to give 6-hex-1-ynyl-nicotinic acid ethyl ester **38** as an oil (2.5 g, 94%).

^1H NMR (400 MHz, C_6D_6, δ): 9.42 (1H, d, *J* = 2.1 Hz), 8.00 (1H, dd, *J* = 8.1, 2.2 Hz), 7.17 (1H, d, *J* = 7.3 Hz), 4.09 (2H, q, *J* = 7.0 Hz), 2.23 (1H, t, *J* = 6.9 Hz), 1.45-1.33 (4H, m), 1.03 (3H, t, *J* = 7.0 Hz), 0.83 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, C_6D_6, δ):

164.4, 151.1, 147.9, 136.6, 126.1, 124.5, 93.7, 81.4, 60.9, 30.3, 22.0, 19.0, 13.8, 13.4. MS *m/z* (relative intensity): 231 (M^+, 48), 202 (86), 189 (100), 161 (67).

The mixture of 6-hex-1-ynyl-nicotinic acid ethyl ester **38** (2.39 g, 10.33 mmol), CuCl (152 mg, 5.17 mmol), Et_3N (8 mL), and anhydrous DMA (40 mL) was stirred in a high pressure tube under argon atmosphere at 130 ^oC. The reaction was monitored by TLC and GC-MS until completion. After 12 h, the mixture was cooled to r.t. and poured into aq.NH_4Cl solution. The phases were separated and the aqueous phase was thoroughly extracted with hexanes. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes-5% EtOAc/hexanes to give 3-propyl-indolizine-6-carboxylic acid ethyl ester **39** (2.03 g, 85%).

^1H NMR (500 MHz, $CDCl_3$, δ): 8.58 (1H, s), 7.34 (1H, d, *J* = 10.0 Hz), 7.15 (1H, d, *J* = 10.7 Hz), 6.67 (1H, s), 6.42 (1H, bs), 4.39 (2H, q, *J* = 7.1 Hz), 2.85 (2H, t, *J* = 7.5 Hz), 1.82 (2H, q, J = 7.5 Hz), 1.42 (3H, t, *J* = 7.1 Hz), 1.06 (3H, t, *J* = 7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 166.7, 133.0, 127.4, 126.7, 118.8, 115.0, 114.4, 114.3, 99.8, 61.3, 28.2, 21.1, 14.8, 14.5. MS *m/z* (relative intensity): 231 (M^+, 33), 202 (100), 189 (81), 128 (24).

KOH (1.4 g, 24.95 mmol) was added to 3-propyl-indolizine-6-carboxylic acid ethyl ester **39** (1.89 g, 8.17 mmol) in a mixture of THF (20 mL) and H_2O (20 mL). After 8 h, the mixture was acidified with 2N HCl and thoroughly extracted with EtOAc. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and

concentrated under reduced pressure to give crude 3-propyl-indolizine-6-carboxylic aide **40** (1.66 g, >99%).

^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.53 (1H, s), 7.36 (1H, d, J = 9.3 Hz), 7.06 (1H, d, J = 9.3 Hz), 6.63 (1H, d, J = 3.7 Hz), 6.38 (1H, d, J = 3.7 Hz), 2.83 (2H, t, J = 7.5 Hz), 1.68 (2H, sext, J = 7.4 Hz), 0.96 (3H, t, J = 7.4 Hz). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 168.4, 132.8, 126.6, 126.2, 118.7, 117.8, 116.5, 114.2, 99.7, 27.9, 21.2 14.7. MS *m/z* (relative intensity): 203 (M^+, 24), 174 (100), 128 (19).

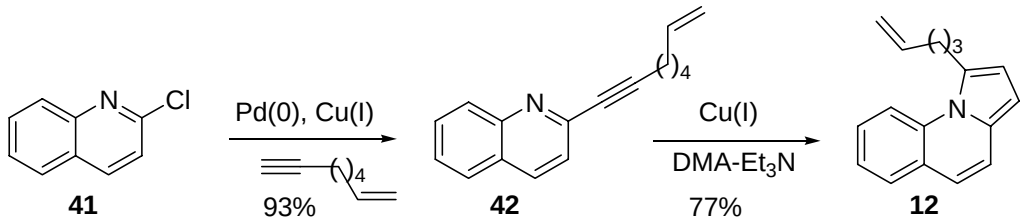
The mixture of ethyl 3-propyl-indolizine-6-carboxylic aide **40** (1.66 g, 8.17 mmol), Et_3N (12 mL, 86.09 mmol), *t*-BuOH (1.2 mL, 12.30 mmol), DMAP (5.0 g, 40.92 mmol) in toluene (100 mL) and DMF (15 mL) was stirred at r.t. 2,4,6-Trichlorobenzoyl chloride (6.4 mL, 40.93 mmol) was added to the mixture and stirred at r.t. The reaction progress was monitored by TLC and GC-MS analyses. After 12 h, the mixture was quenched (aqueous NH_4Cl). The phases were separated and the aqueous phase was thoroughly extracted with EtOAc. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 5% EtOAc/hexanes to give 3-propyl-indolizine-6-carboxylic acid *tert*-butyl ester **6** as an oil (1.9 g, 90%).

^{1}H NMR (400 MHz, C_6D_6, δ): 8.55 (1H, s), 7.13 (1H, dd, J = 9.4, 1.5 Hz), 7.15 (1H, d, J = 9.3 Hz), 6.55 (1H, d, J = 3.5 Hz), 6.43 (1H, d, J = 3.5 Hz), 2.34 (2H, t. J = 7.3 Hz), 1.51-1.46 (2H, m), 1.50 (9H, S), 0.76 (3H, t, J = 7.3 Hz). ^{13}C NMR (100 MHz, C_6D_6, δ): 165.3, 132.9, 127.0, 126.1, 118.6, 115.9, 115.1, 114.0, 99.9, 80.5, 28.2 (×3),

27.6, 120.7, 14.0. MS *m/z* (relative intensity): 259 (M^+, 13), 203 (13), 174 (100), 129 (17).

1-Propyl-pyrrolo[1,2-*a*]quinoline (10) was synthesized in 71% yield from 2-chloro-quinoline via the method described for synthesis of **12**, see below.

1-Pent-4-enyl-pyrrolo [1,2-*a*]quinoline (12)



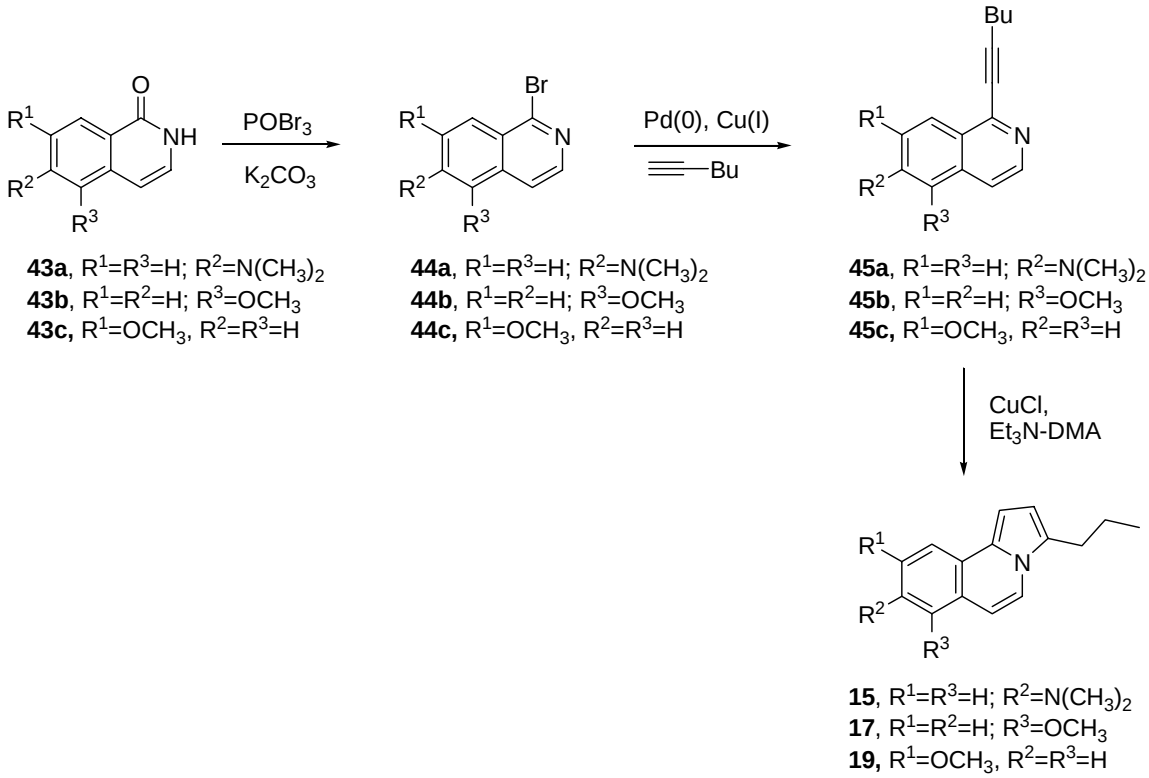
The mixture of ethyl 2-chloro-quinoline (645 mg, 3.94 mmol), CuI (15 mg, 0.08 mmol), $Pd(PPh_3)_2Cl_2$ (55 mg, 0.08 mmol), and PPh_3 (41 mg, 0.16 mmol) in *i*-Pr_2EtN (20 mL) and Et_3N (4 mL) was stirred at r.t. Oct-1-en-7-yne (1.3 g, 12.0 mmol) was added to the mixture and stirred at 80 ^oC. The reaction progress was monitored by TLC and GC-MS analyses. After 12 h The mixture was cooled to r.t. and quenched (aqueous NH_4Cl). The phases were separated and the aqueous phase was thoroughly extracted with hexanes. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 10 % EtOAc/hexanes to give 2-oct-7-en-1-ynyl-quinoline **42** as an oil (862 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.06 (1H, d, *J* = 9.2 Hz), 8.03 (1H, d, *J* = 8.6 Hz), 7.72 (1H, dd, *J* = 8.1, 0.8 Hz), 7.67 (1H, dt, *J* = 6.9, 1.4 Hz), 7.47 (1H, dt, *J* = 8.1, 1.0 Hz), 7.42 (1H, d, *J* = 8.3 Hz), 5.85-5.77 (1H, m), 5.01 (1H, dd, *J* = 17.3, 1.9 Hz), 4.95 (1H, dd, *J* = 9.9, 1.4 Hz), 2.49 (2H, t, *J* = 7.1 Hz), 2.10 (2H, q, *J* = 7.0 Hz), 1.71-1.64 (2H, m), 1.60-1.54 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.0, 144.0, 138.5, 136.0, 129.9, 129.1, 127.4, 126.9, 126.8, 124.2, 114.7, 91.9, 81.1, 33.2, 28.2, 27.7, 19.4. MS *m/z* (relative intensity): 234 (M^+-1, 38), 206 (100), 167 (95), 140 (76).

The mixture of 2-oct-7-en-1-ynyl-quinoline **42** (569 mg, 2.42 mmol), CuCl (120 mg, 1.21 mmol), Et_3N (2 mL), and anhydrous DMA (14 mL) was stirred in a high pressure tube under argon atmosphere at 130 ^{o}C. The reaction was monitored by TLC and GC-MS until completion. After 17 h, the mixture was cooled to r.t. and poured into aq. NH_4Cl solution. The phases were separated and the aqueous phase was thoroughly extracted with hexanes. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with hexanes-1% EtOAc/hexanes to give 1-pent-4-enyl-pyrrolo [1,2-*a*]quinoline **12** as an oil (436 mg, 77%).

^{1}H NMR (400 MHz, C_6D_6, δ): 8.11 (1H, d, *J* = 8.8 Hz), 7.45 (1H, dd, *J* = 7.6, 1.6 Hz), 7.25-7.22 (1H, m), 7.19 (1H, d, *J* = 9.4 Hz), 7.14 (1H, t, *J* = 7.3 Hz), 6.74 (1H, d, *J* = 8.8 Hz), 6.63 (2H, s), 5.84-5.74 (1H, m), 5.11-5.05 (2H, m), 3.05 (2H, t, *J* = 7.5 Hz), 2.06 (2H, q, *J* = 7.0 Hz), 1.80 (2H, quint, *J* = 7.7). ^{13}C NMR (100 MHz, C_6D_6, δ): 138.4, 136.1, 132.7, 131.1, 128.7, 126.6, 126.2, 123.1, 120.0, 118.0, 116.7, 115.2, 113.3, 102.8, 33.7, 31.1, 28.1. MS *m/z* (relative intensity): 235 (M^+, 11), 180 (100), 128 (6).

Synthesis of pyrroloisoquinolines (15, 17 and 19)



43a, $R^1=R^3=H$; $R^2=N(CH_3)_2$
43b, $R^1=R^2=H$; $R^3=OCH_3$
43c, $R^1=OCH_3$, $R^2=R^3=H$

44a, $R^1=R^3=H$; $R^2=N(CH_3)_2$
44b, $R^1=R^2=H$; $R^3=OCH_3$
44c, $R^1=OCH_3$, $R^2=R^3=H$

45a, $R^1=R^3=H$; $R^2=N(CH_3)_2$
45b, $R^1=R^2=H$; $R^3=OCH_3$
45c, $R^1=OCH_3$, $R^2=R^3=H$

15, $R^1=R^3=H$; $R^2=N(CH_3)_2$
17, $R^1=R^2=H$; $R^3=OCH_3$
19, $R^1=OCH_3$, $R^2=R^3=H$

7-Methoxy-2H-isoquinolin-1-one **43c** (1.8 g, 10.3 mmol), potassium carbonate (1.70 g, 12.3 mmol), and phosphorus oxybromide (3.5 g,12.2 mmol) were heated to reflux in dry acetonitrile (50 mL) for 24 h. The mixture was cooled to r.t., poured into ice, and neutralized (solid potassium carbonate). The aqueous phase was thoroughly extracted with CH_2Cl_2. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 10 % EtOAc/hexanes to give 1-bromo-7-methoxy-isoquinoline **44c** (1.12 g, 46%).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.97 (1H, d, J = 5.5 Hz), 7.46 (1H, d, J = 8.9 Hz), 7.31 (1H, d, J = 5.4 Hz), 7.21 (1H, d, J = 2.4 Hz), 7.15 (1H, dd, J = 8.9, 2.5 Hz), 3.80

(3H, s). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.3, 143.4, 139.9, 132.6, 129.9, 128.5, 124.0, 120.8, 105.8, 55.5. MS *m/z* (relative intensity): 239 (M^+, 43), 158 (100), 115 (38).

The mixture of ethyl 1-bromo-7-methoxy-isoquinoline **44c** (1.12 g, 4.7 mmol), CuI (36 mg, 0.19 mmol), and $Pd(PPh_3)_2Cl_2$ (55 mg, 0.09 mmol) in Et_3N (20 mL) was stirred at r.t. *n*-Hexyne (3.0 mL, 26.11 mmol) was added to the mixture and stirred at 50 ^oC. The reaction progress was monitored by TLC and GC-MS analyses. After 12 h The mixture was cooled to r.t. and quenched (aqueous NH_4Cl). The phases were separated and the aqueous phase was thoroughly extracted with hexanes. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 10-20% EtOAc/hexanes to give 1-hex-1-ynyl-7-methoxy-isoquinoline **45c** as an oil (1.06 g, 94%).

^{1}H NMR (500 MHz, C_6D_6, δ): 8.53 (1H, d, *J* = 5.4 Hz), 7.84 (1H, d, *J* = 2.4 Hz), 7.35 (1H, d, *J* = 8.9 Hz), 7.24 (1H, dd, *J* = 8.9, 2.5 Hz), 7.18 (1H, d, *J* = 5.5 Hz), 3.58 (3H, s), 2.38 (2H, t, *J* = 6.7 Hz), 1.50-1.44 (4H, m), 0.84 (3H, t, *J* = 7.2 Hz). ^{13}C NMR (125 MHz, C_6D_6, δ): 158.9, 143.7, 141.6, 131.4, 130.9, 128.6, 123.1, 119.7, 104.5, 94.9, 80.1, 54.7, 30.6, 22.0, 19.2, 13.6. MS *m/z* (relative intensity): 239 (M^+, 86), 210 (100), 196 (67), 126 (38).

The mixture of 1-hex-1-ynyl-7-methoxy-isoquinoline **45c** (1.0 g, 4.18 mmol), CuCl (207 mg, 2.09 mmol), Et_3N (4 mL), and anhydrous DMA (35 mL) was stirred in a high pressure tube under argon atmosphere at 130 ^oC. The reaction was monitored by TLC and GC-MS until completion. After 12 h, the mixture was cooled to r.t. and poured

into aq. NH_4Cl solution. The phases were separated and the aqueous phase was thoroughly extracted with hexanes. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 5% EtOAc/hexanes to give 9-methoxy-3-propyl-pyrrolo[2,1-*a*]isoquinoline **19** (816 mg, 82%).

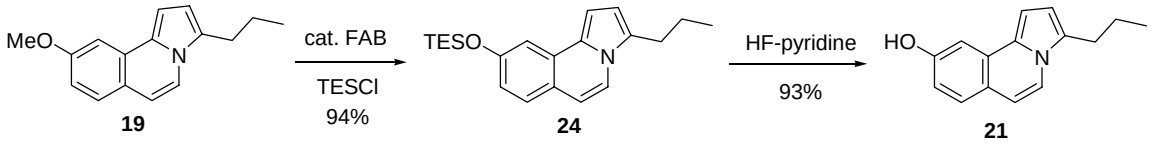
^{1}H NMR (500 MHz, C_6D_6, δ): 7.48 (1H, d, *J* = 2.6 Hz), 7.28 (1H, d, *J* = 7.3 Hz), 7.07 (1H, d, *J* = 7.3 Hz), 6.99 (1H, d, *J* = 4.0 Hz), 6.93 (1H, dd, *J* = 8.4, 2.6 Hz), 6.51 (1H, d, *J* = 4.0 Hz), 6.39 (1H, d, *J* = 7.3 Hz), 3.41 (3H, s), 2.40 (2H, t, *J* = 7.6 Hz), 1.56 (2H, sext, *J* = 7.5 Hz), 0.86 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, C_6D_6, δ): 159.6, 129.5, 128.6, 128.3, 127.1, 120.6, 119.5, 114.6, 110.2, 110.1, 103.9, 99.5, 54.8, 28.1, 21.3, 14.1. MS *m/z* (relative intensity): 239 (M^+, 22), 210 (100), 167 (52).

15: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.91 (1H, d, *J* = 8.8 Hz), 7.60 (1H, d, *J* = 7.3 Hz), 7.00 (1H, dd, *J* = 8.8, 2.6 Hz), 6.81 (1H, d, *J* = 2.6 Hz), 6.73 (1H, d, *J* = 3.4 Hz), 6.66 (1H, d, *J* = 7.7 Hz), 6.46 (1H, d, *J* = 3.7 Hz), 3.03 (6H, s), 2.81 (2H, t, *J* = 7.5 Hz), 1.81 (2H, sext, *J* = 7.5 Hz), 1.08 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 148.4, 129.9, 127.5, 125.7, 122.8, 121.7, 117.8, 114.5, 110.3, 109.2, 108.2, 95.9, 40.8 (×2), 28.0, 21.3, 14.1. MS *m/z* (relative intensity): 252 (M^+, 29), 223 (100), 207 (31), 111 (26). HRMS (EI) calcd for $C_{17}H_{20}N_2$ (M^+): 252.1627, found 252.1632.

17: Mp 93 ^{o}C. ^{1}H NMR (500 MHz, C_6D_6, δ): 7.67 (1H, d, *J* = 7.7 Hz), 7.33 (1H, d, *J* = 7.7 Hz), 7.22 (1H, d, *J* = 7.4 Hz), 7.21 (1H, t, *J* = 7.9 Hz), 7.04 (1H, d, *J* = 3.7 Hz), 6.52 (1H, d, *J* = 3.7 Hz), 6.43 (1H, d, *J* = 8.0 Hz), 3.43 (3H, s), 2.37 (2H, t, *J* = 7.5 Hz),

1.52 (2H, sext, J = 7.3 Hz), 0.82 (3H, t, J = 7.3 Hz). ^{13}C NMR (125 MHz, C_6D_6, δ): 155.6, 129.4, 128.4, 128.2, 127.0, 120.9, 117.0, 114.7, 110.3, 105.2, 104.5, 99.8, 55.0, 23.0, 21.3, 14.1. MS *m/z* (relative intensity): 239 (M^+, 27), 210 (100), 195 (24), 167 (31).

Synthesis of pyrroloisoquinolines (21 and 24)



9-Methoxy-3-propyl-pyrrolo[2,1-*a*]isoquinoline **19** (240 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) was added to the mixture of $B(C_6F_5)_3$ (50 mg, 0.1 mmol) and Et_3SiH (0.3 mL, 1.9 mmol) in anhydrous hexanes (10 mL). The reaction was monitored by TLC and GC-MS until completion. After 20 min, the reaction mixture was quenched with Et_3N (2 mL) and concentrated under reduced pressure. The residue was purified by silica gel chromatography with 5% EtOAc/hexanes to give 3-propyl-9-triethylsilanyloxy-pyrrolo[2,1-*a*]isoquinoline **24** (304 mg, 90%).

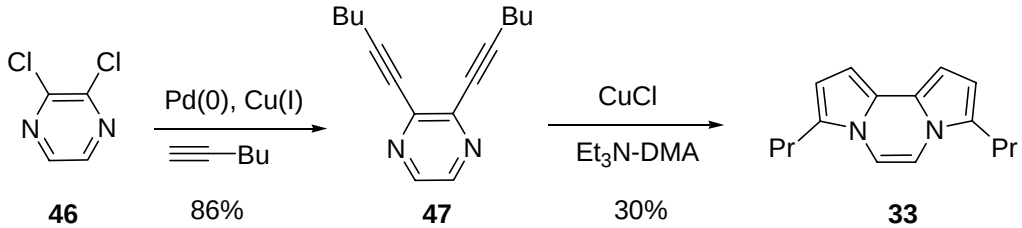
^{1}H NMR (500 MHz, C_6D_6, δ): 7.75 (1H, d, J = 2.6 Hz), 7.30 (1H, d, J = 8.4 Hz), 7.09 (1H, d, J = 7.3 Hz), 6.98 (1H, d, J = 4.0 Hz), 6.95 (1H, dd, J = 8.4, 2.6 Hz), 6.48 (1H, d, J = 3.7 Hz), 6.40 (1H, d, J = 7.3 Hz), 2.41 (2H, t, J = 7.5 Hz), 1.54 (2H, sext, J = 7.5 Hz), 1.02 (9H, t, J = 8.1 Hz), 0.85 (3H, t, J = 7.3 Hz), 0.74 (6H, q, J = 8.0 Hz). ^{13}C NMR (125 MHz, C_6D_6, δ): 155.6, 129.4, 128.9, 128.6, 127.1, 121.2, 119.8, 118.8, 111.6,

110.2, 110.1, 99.7, 28.1, 21.4, 14.0, 6.9 (×3), 5.5 (×3). MS *m/z* (relative intensity): 339 (M^+, 22), 310 (100), 224 (5), 112 (22).

HF-pyridine (0.3 mL) was added to 3-propyl-9-triethylsilanyloxy-pyrrolo[2,1-*a*]isoquinoline **5** (170 mg, 0.5 mmol) in THF (5 mL) at 0 ^{o}C. The reaction was monitored by TLC and GC-MS until completion. After 10 min, the reaction mixture was quenched with aq. NH_4Cl solution. The phases were separated and the aqueous phase was thoroughly extracted with EtOAc. The combined organic extracts were washed (brine), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure to give crude 3-propyl-pyrrolo[2,1-*a*]isoquinoline-9-ol **21** (126 mg, 93%).

Mp 140 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, δ): 7.22 (1H, d, *J* = 8.8 Hz), 7.14 (1H, d, *J* = 2.9 Hz), 7.07 (1H, d, *J* = 7.0 Hz), 6.95 (1H, d, *J* = 3.5 Hz), 6.71 (1H, dd, *J* = 8.8, 2.3 Hz), 6.54 (1H, d, *J* = 4.1 Hz), 6.38 (1H, d, *J* = 7.6 Hz), 4.59 (1H, bs), 2.42 (2H, t, *J* = 7.6 Hz), 1.55 (2H, sext, *J* = 7.3 Hz), 0.86 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, C_6D_6, δ): 155.6, 129.3, 128.7, 127.8, 127.2, 120.5, 119.4, 114.5, 110.3, 110.1, 106.7, 99.8, 28.1, 21.4, 14.0.

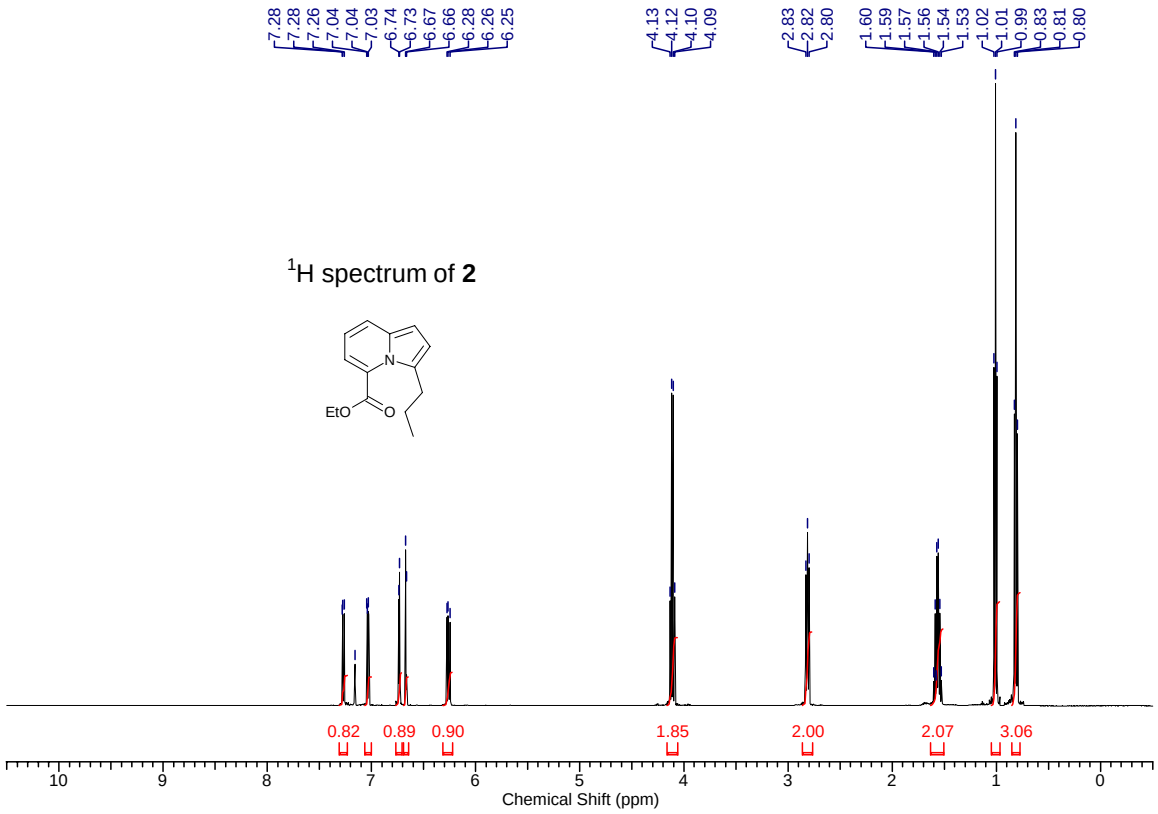
3,6-Dipropyl-3a,5a-diaza-*as*-indacene (33) was synthesized, employing our Cu-assisted double cycloisomerization technique.[3]

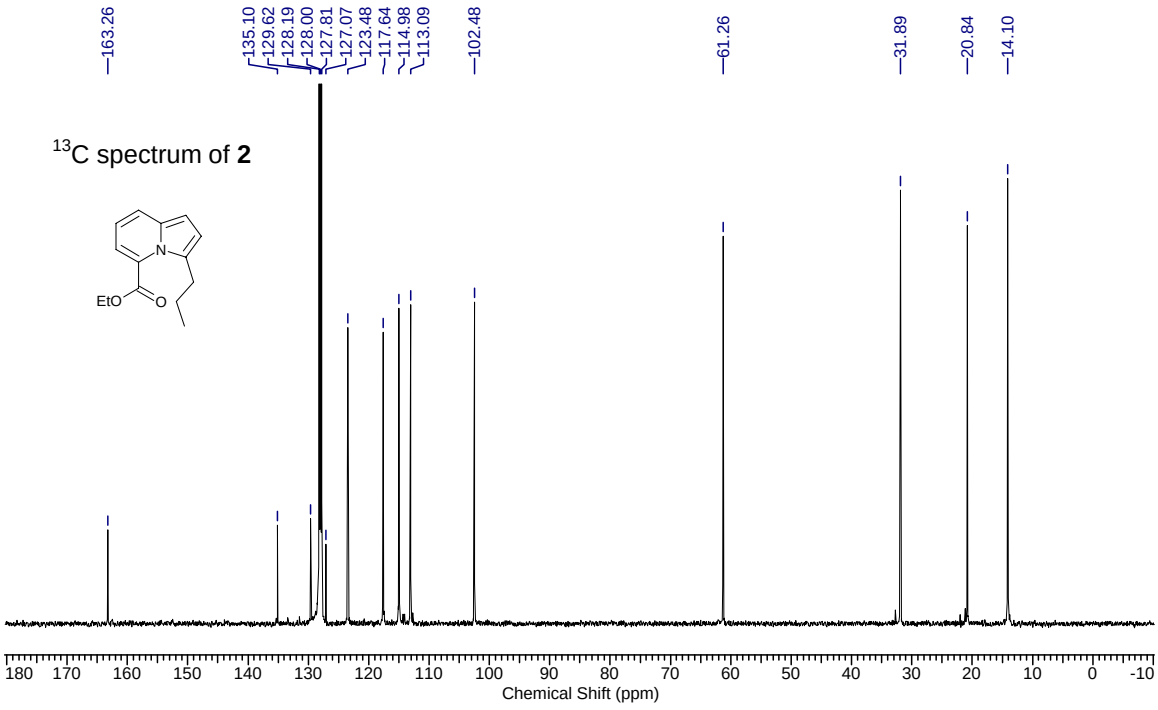


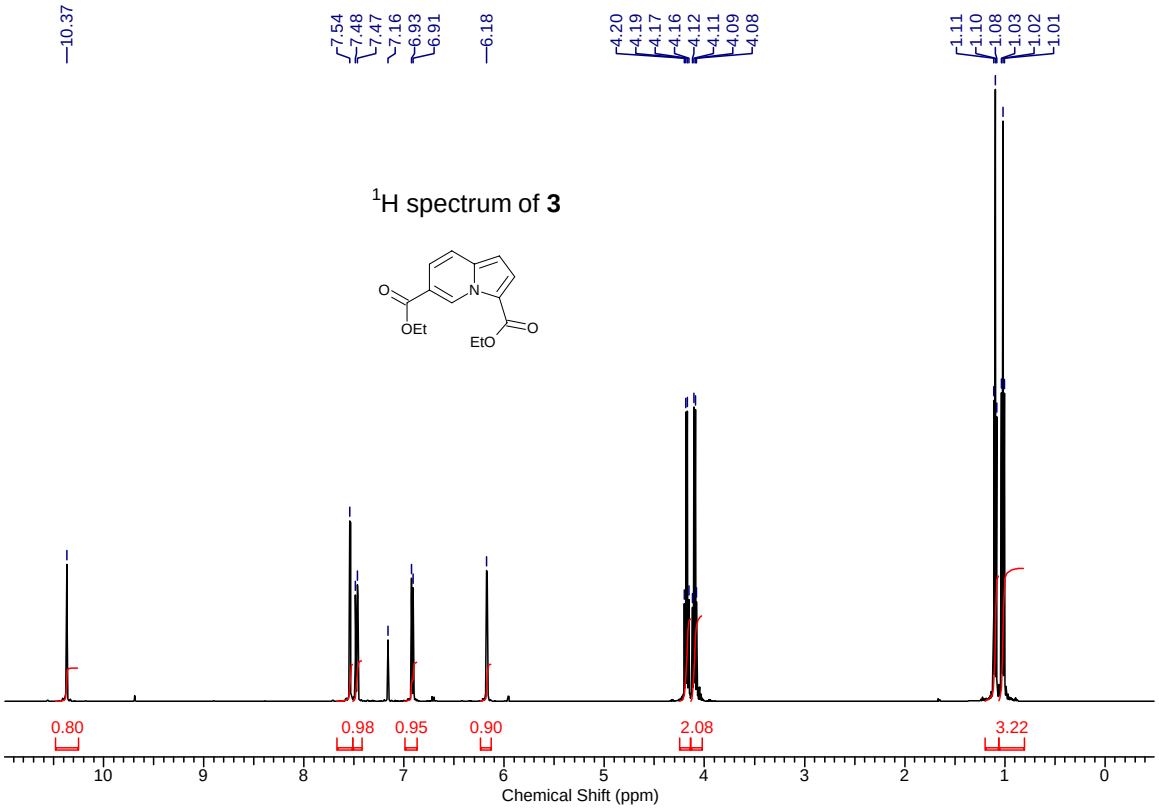
46 86% **47** 30% **33**

Mp 98 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6, δ): 6.62 (2H, d, *J* = 3.5 Hz), 6.38 (2H, s), 6.31 (2H, d, *J* = 3.5 Hz), 2.40 (4H, t, *J* = 7.6 Hz), 1.55 (4H, sext, *J* = 7.5 Hz), 0.89 (6H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, C_6D_6, δ): 126.0 (×2), 124.6 (×2), 109.4 (×2), 108.0 (×2), 98.3 (×2), 28.0 (×2), 21.9 (×2), 14.0 (×2). MS *m/z* (relative intensity): 240 (M^+, 31), 211 (100), 182 (52), 127 (5).

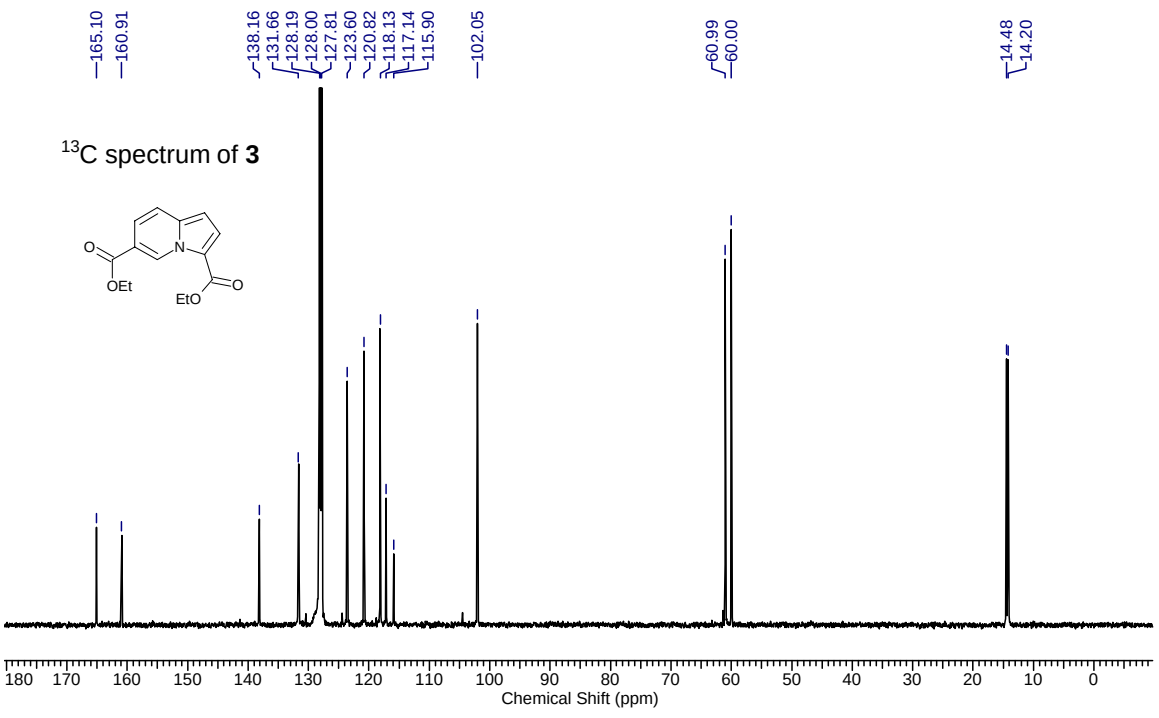
2. ^{1}H and ^{13}C NMR Spectra Data



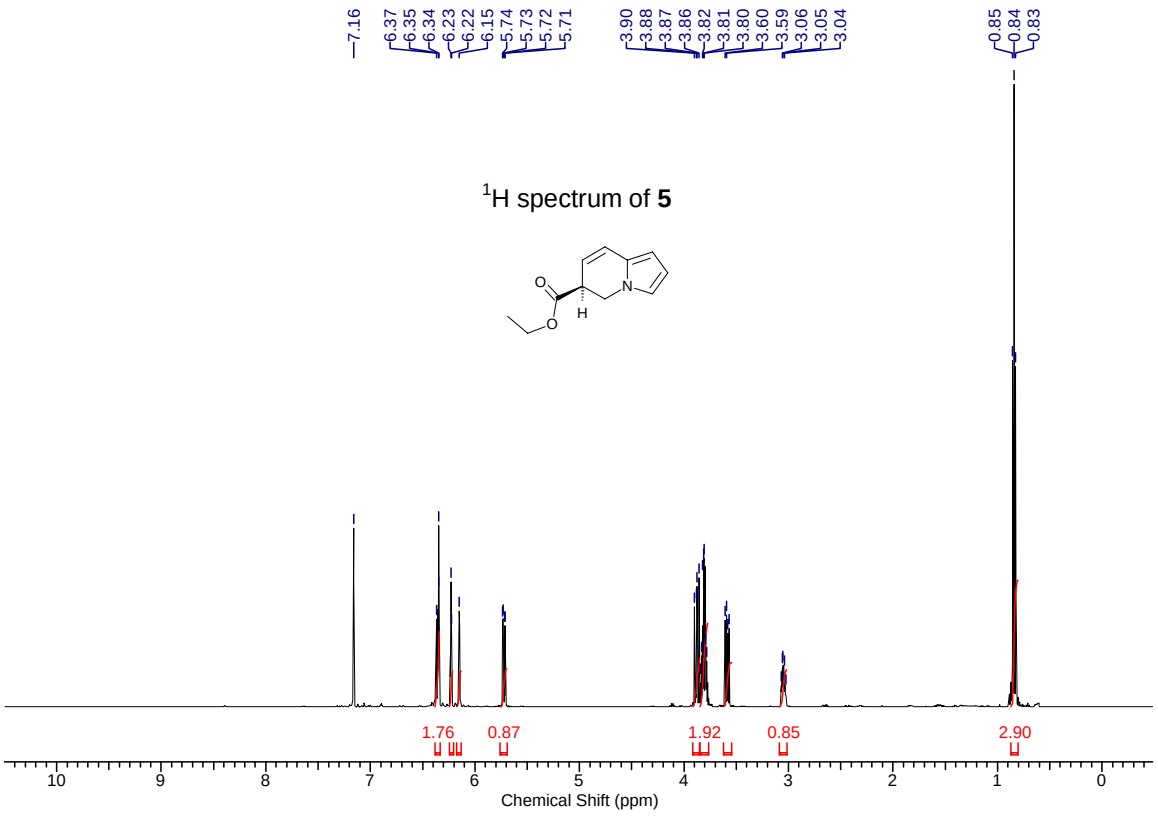


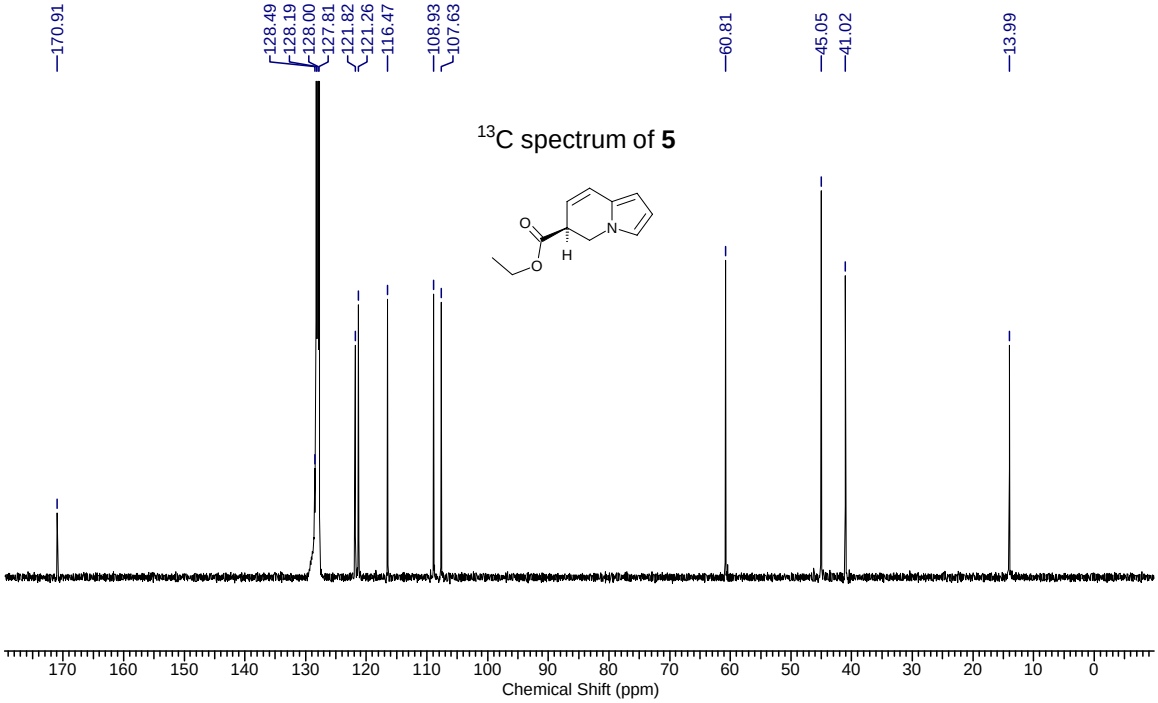


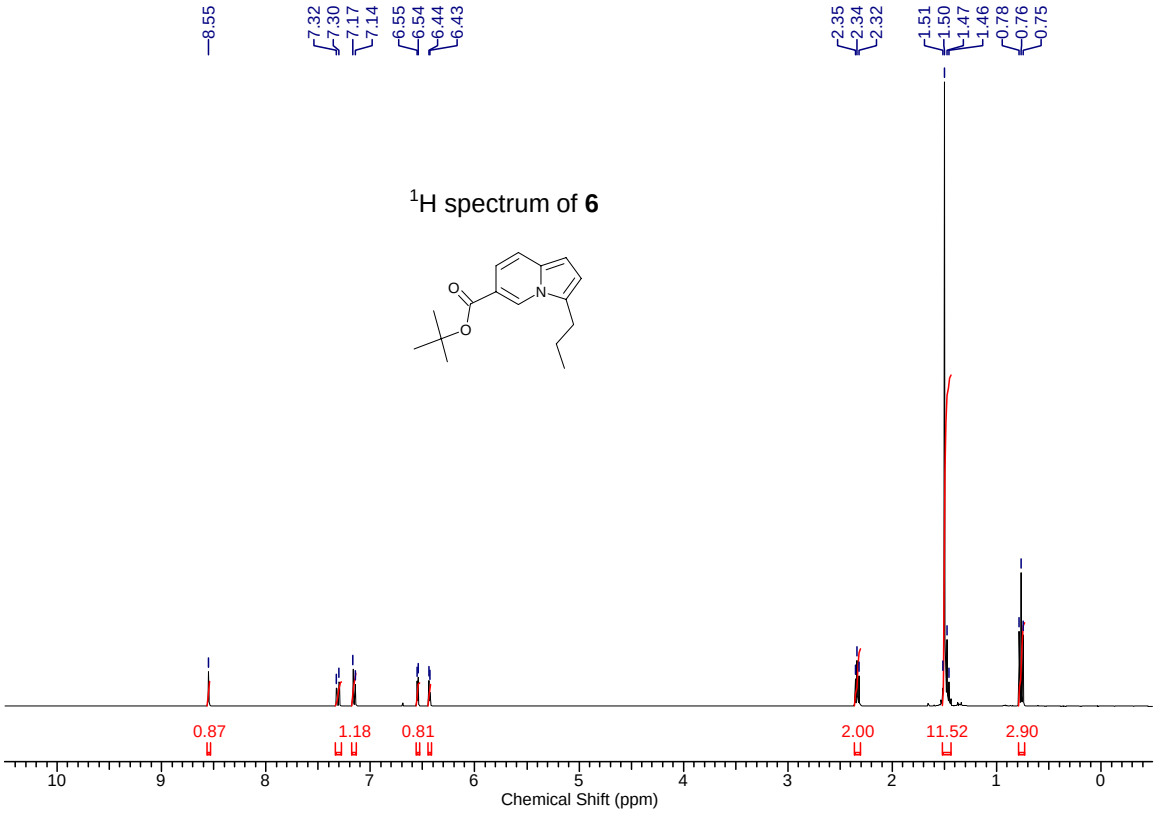
^{1}H spectrum of **3**



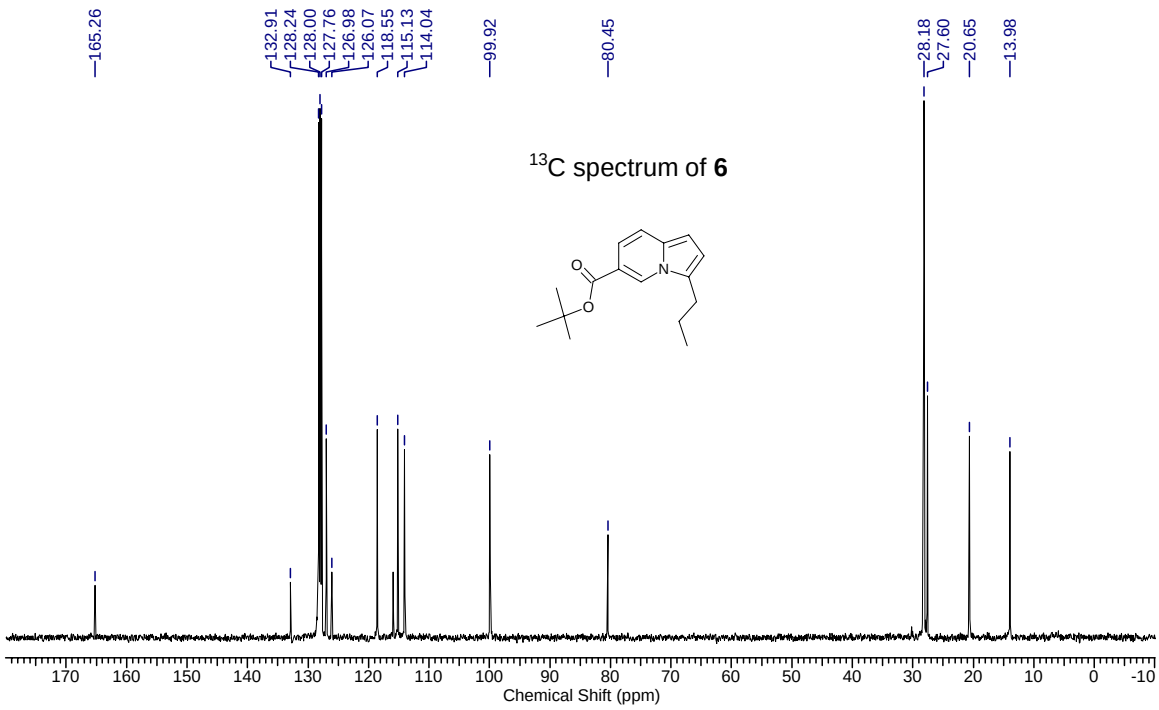
^{13}C spectrum of **3**


7.16
6.37
6.35
6.34
6.23
6.22
6.15
5.74
5.73
5.72
5.71
3.90
3.88
3.87
3.86
3.82
3.81
3.80
3.60
3.59
3.06
3.05
3.04
0.85
0.84
0.83
1H spectrum of 5
1.76
0.87
1.92
0.85
2.90
Chemical Shift (ppm)

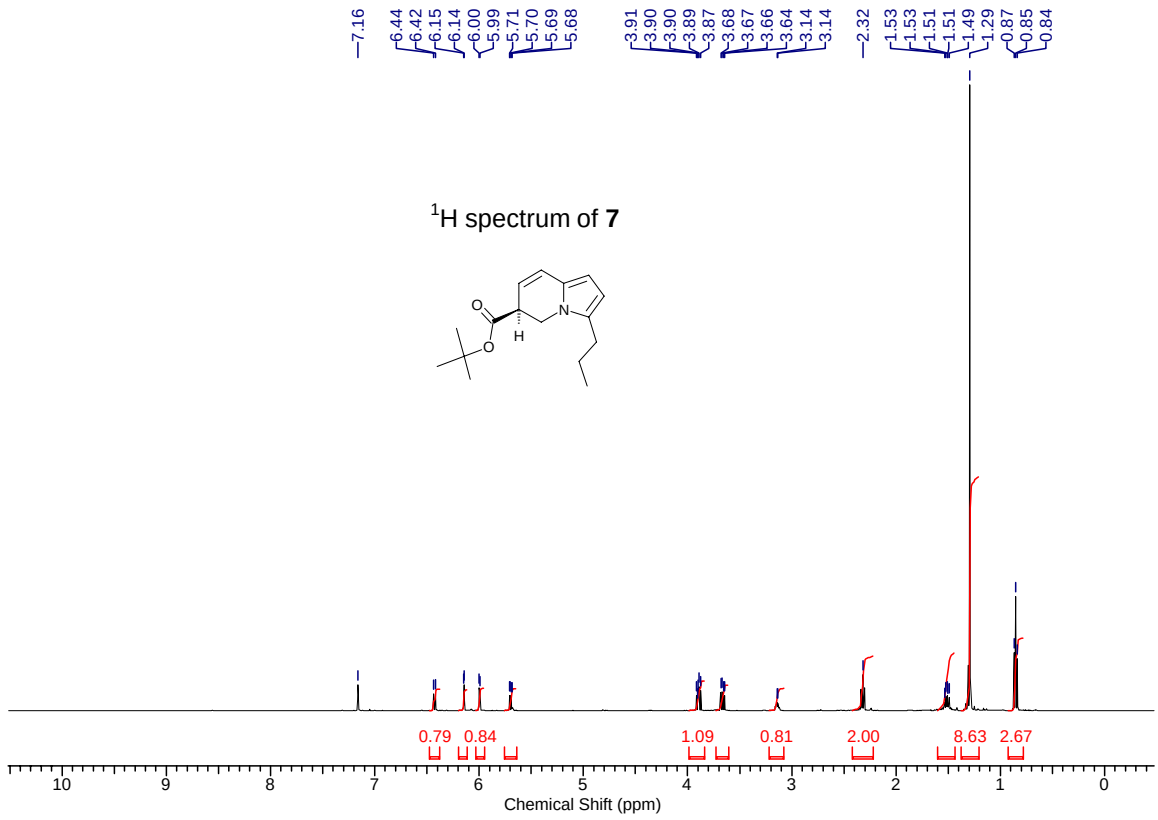

170.91
128.49
128.19
128.00
127.81
121.82
121.26
116.47
108.93
107.63
60.81
45.05
41.02
13.99
13C spectrum of 5
Chemical Shift (ppm)



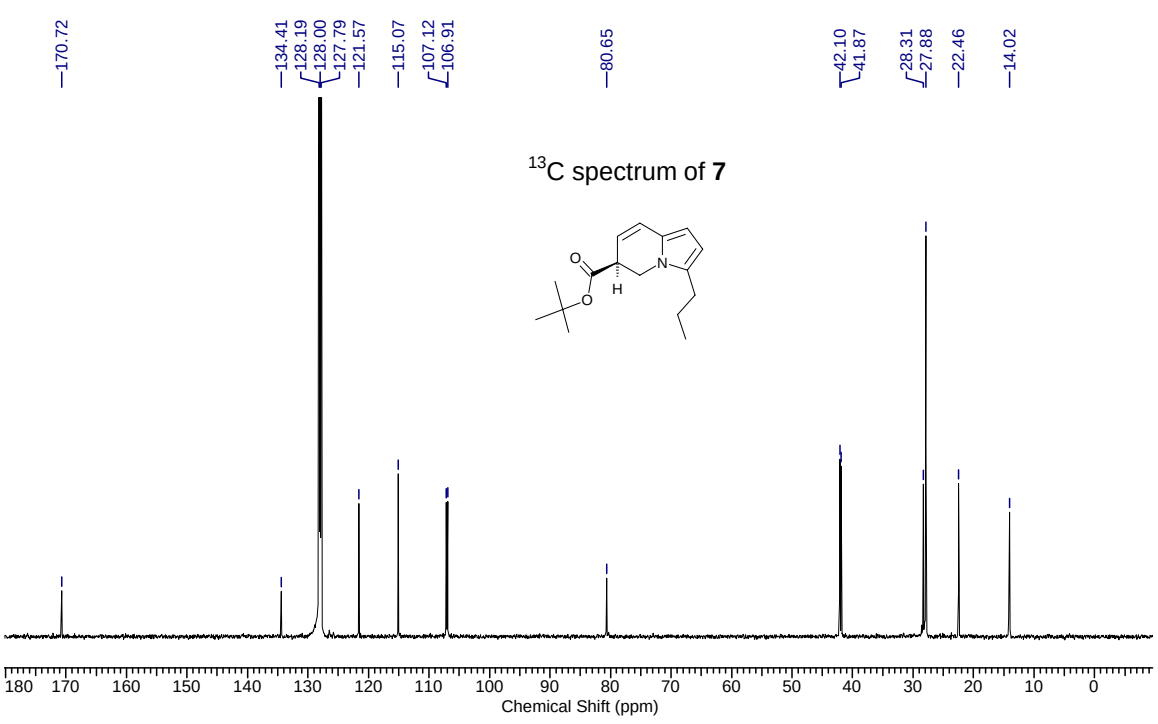
^{1}H spectrum of **6**



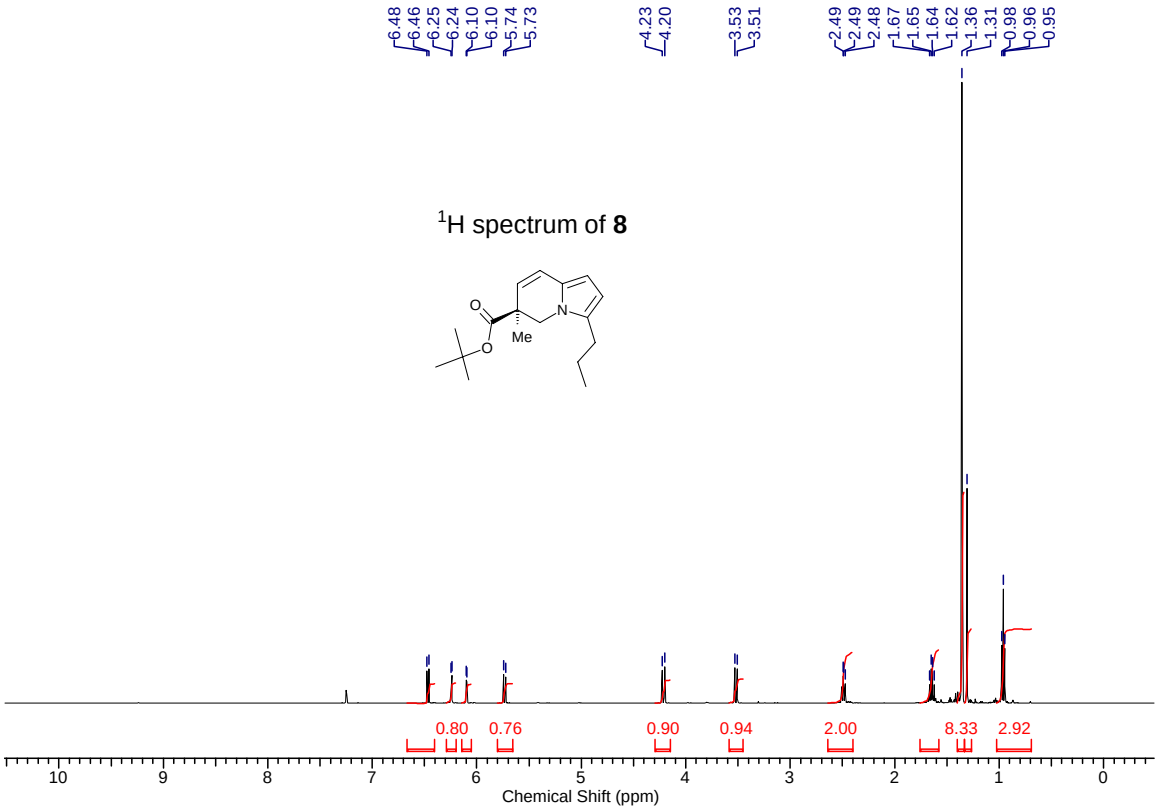
^{13}C spectrum of **6**



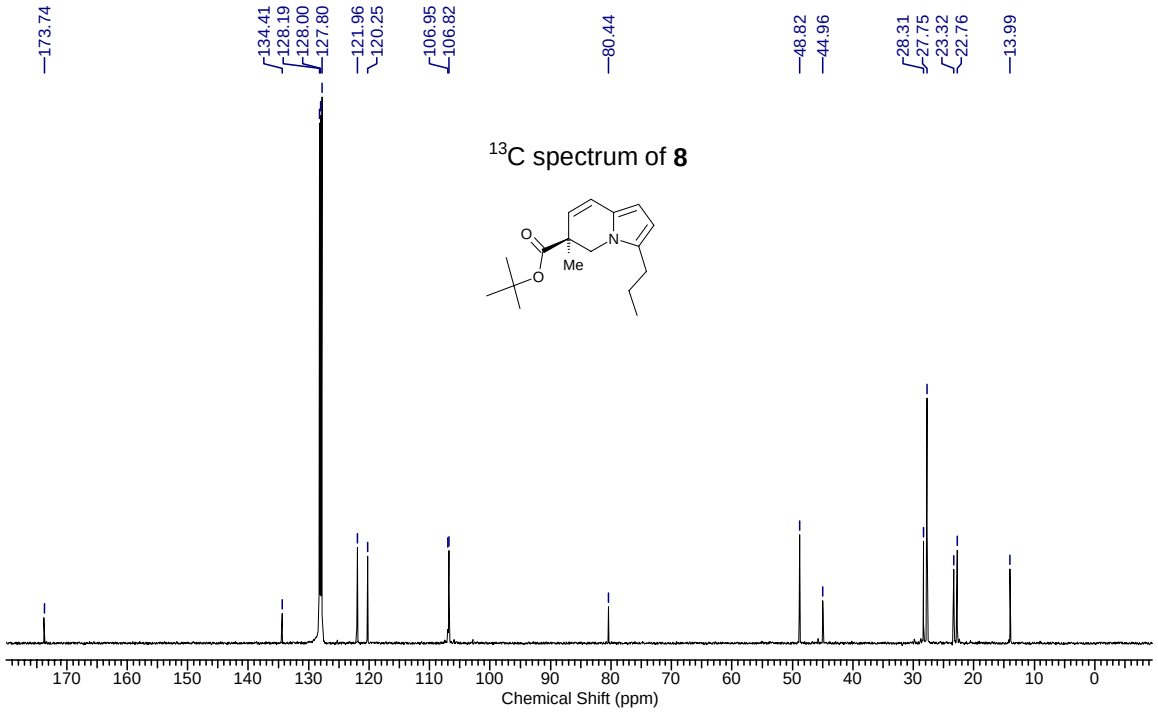
^{1}H spectrum of **7**



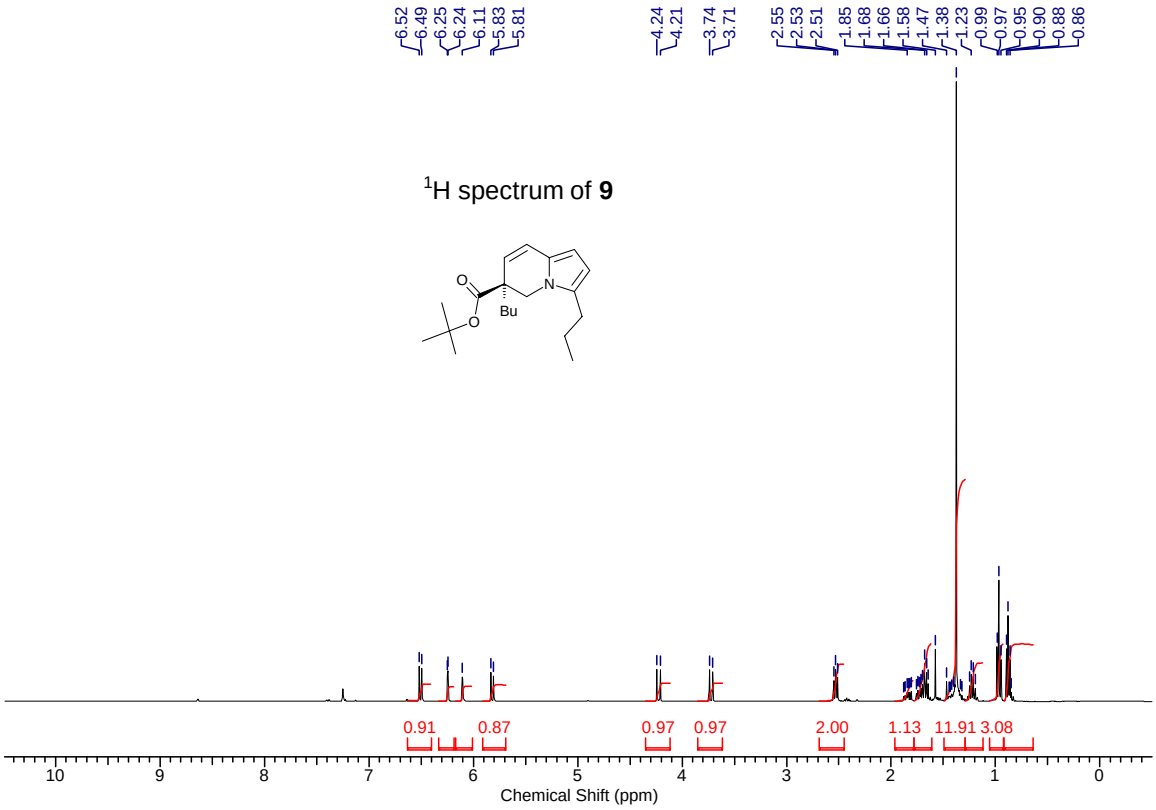
^{13}C spectrum of **7**



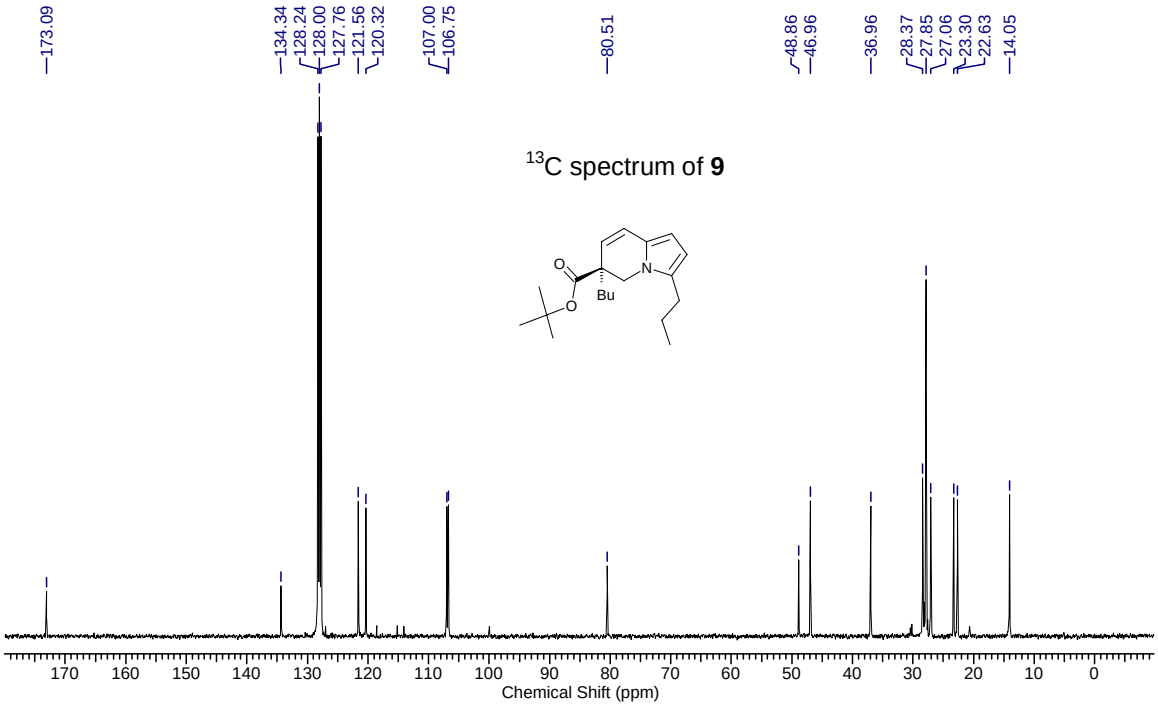
^{1}H spectrum of **8**



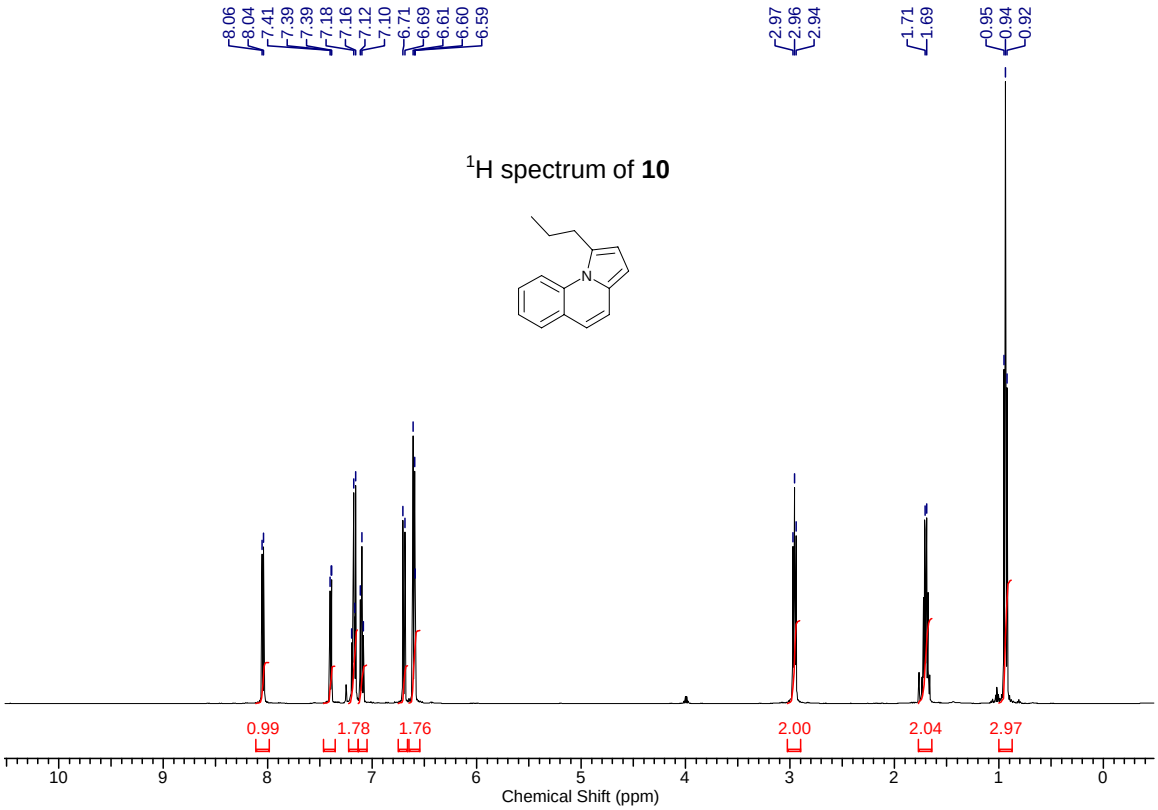
^{13}C spectrum of **8**



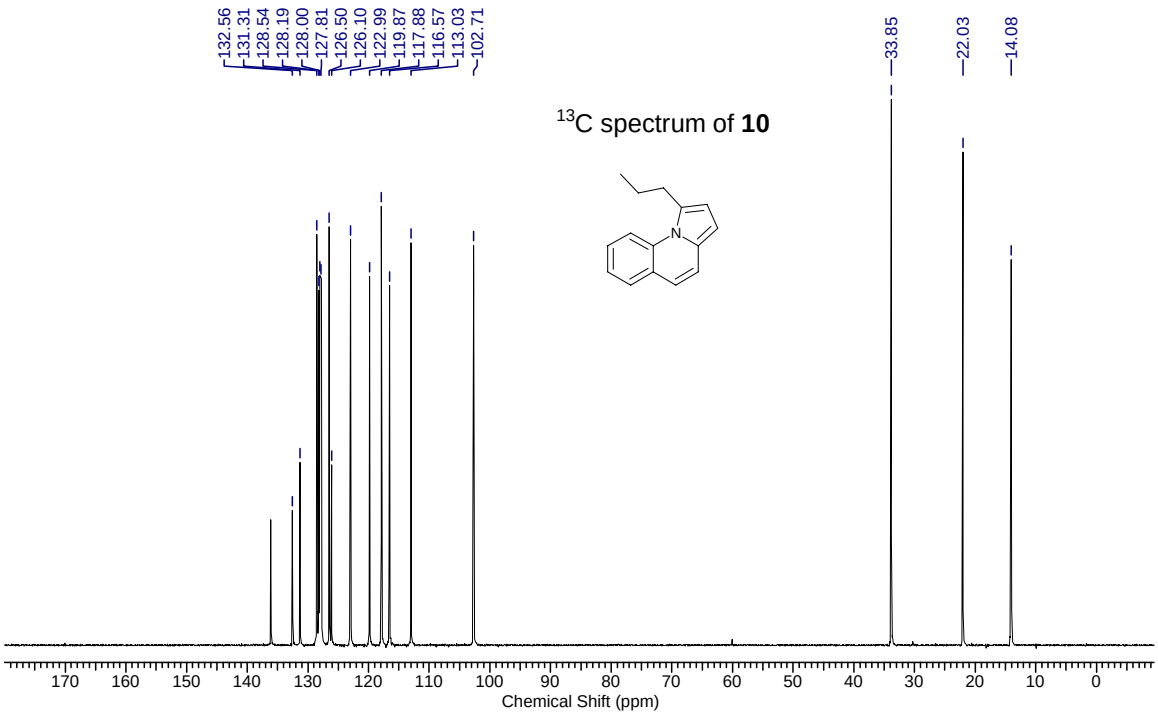
^{1}H spectrum of **9**



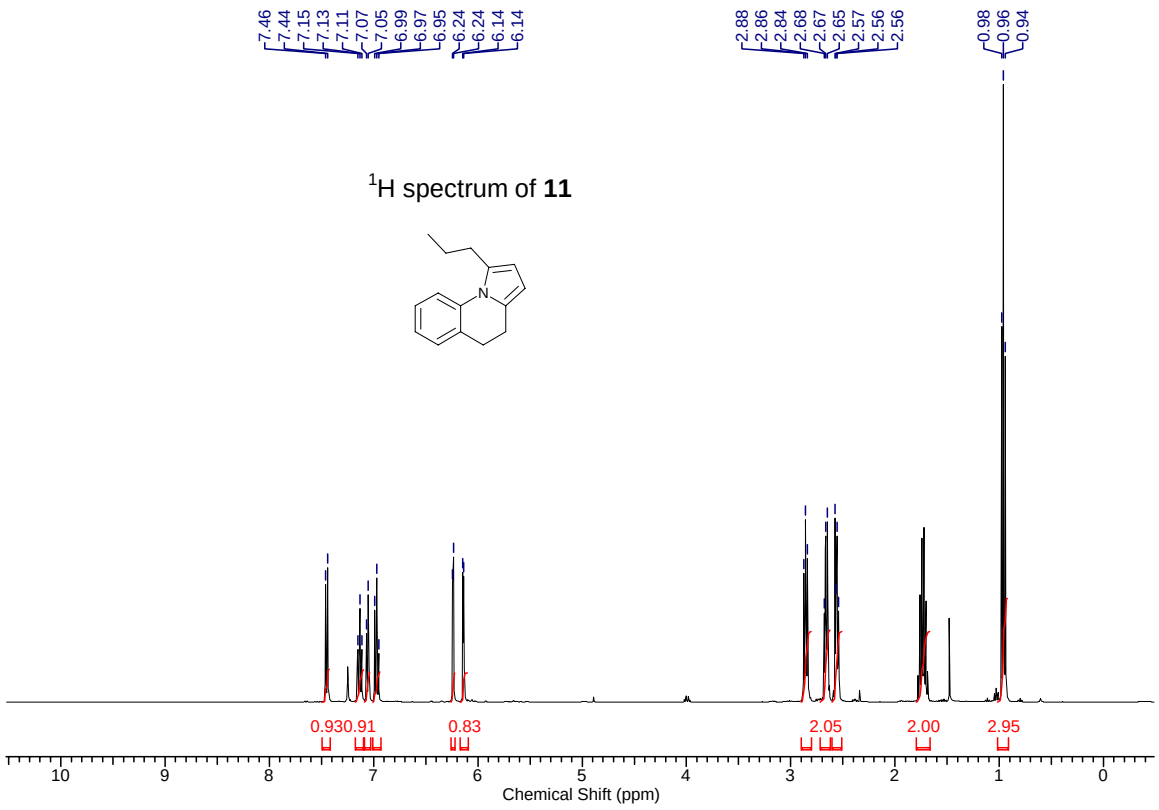
^{13}C spectrum of **9**



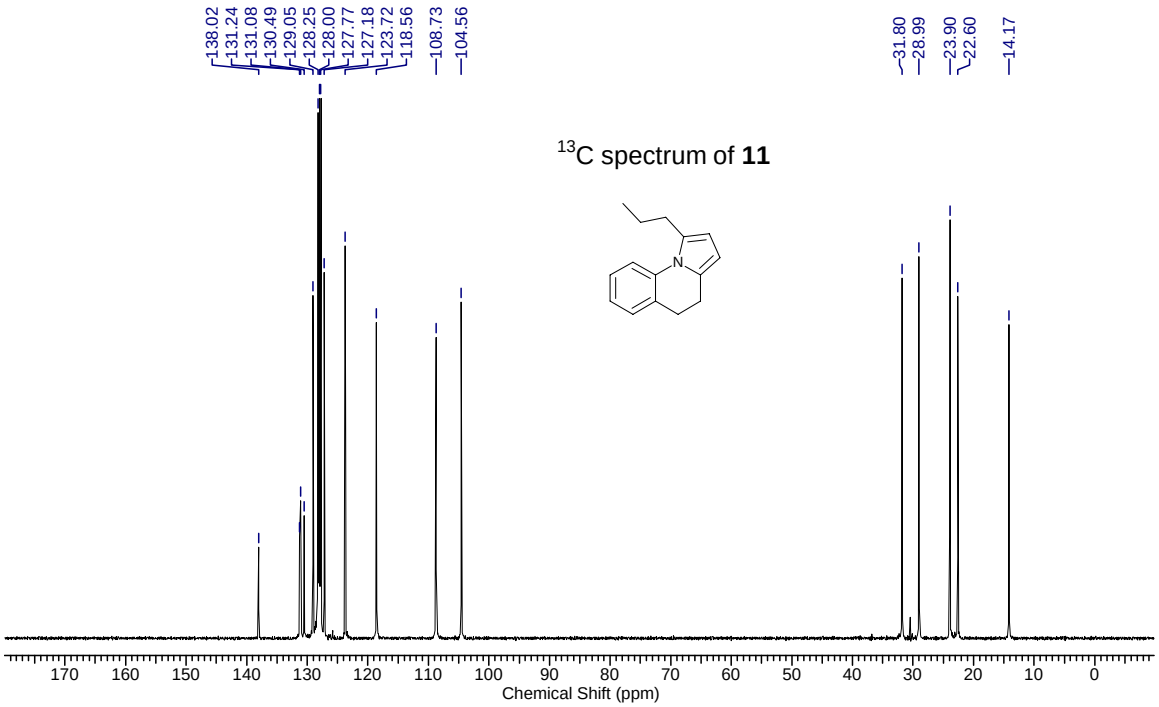
^{1}H spectrum of **10**



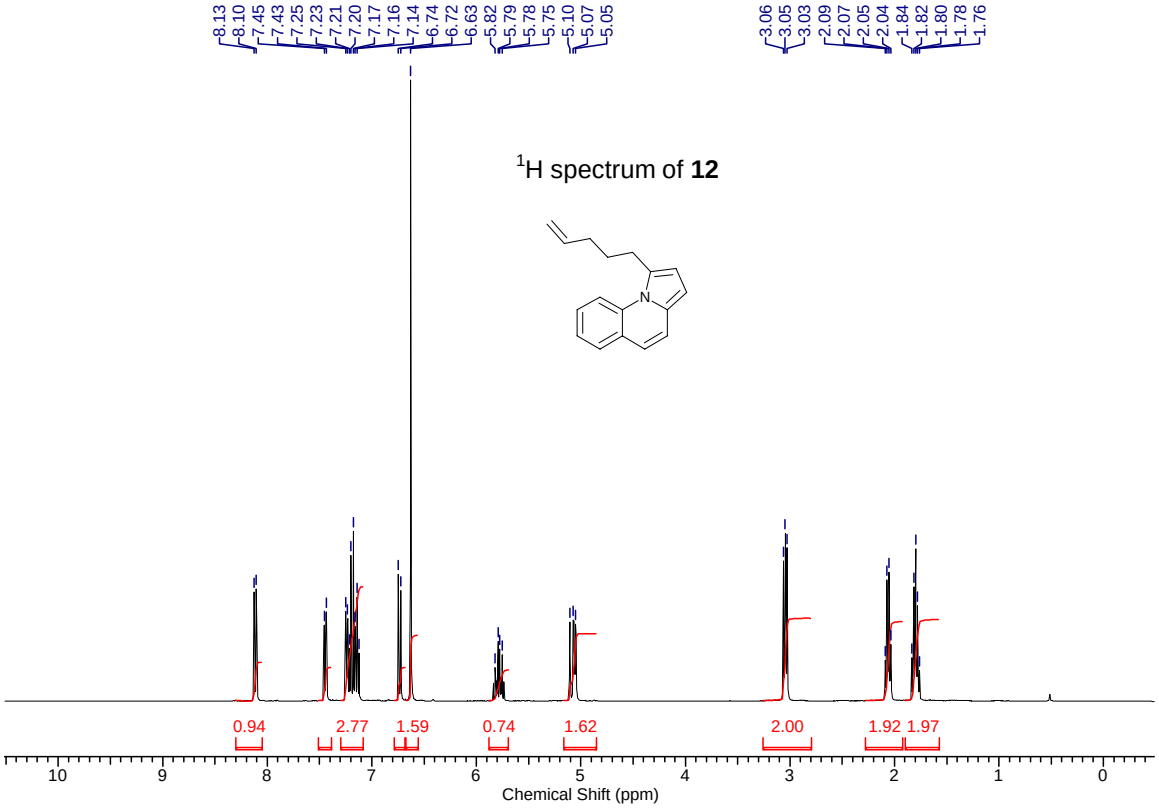
^{13}C spectrum of **10**



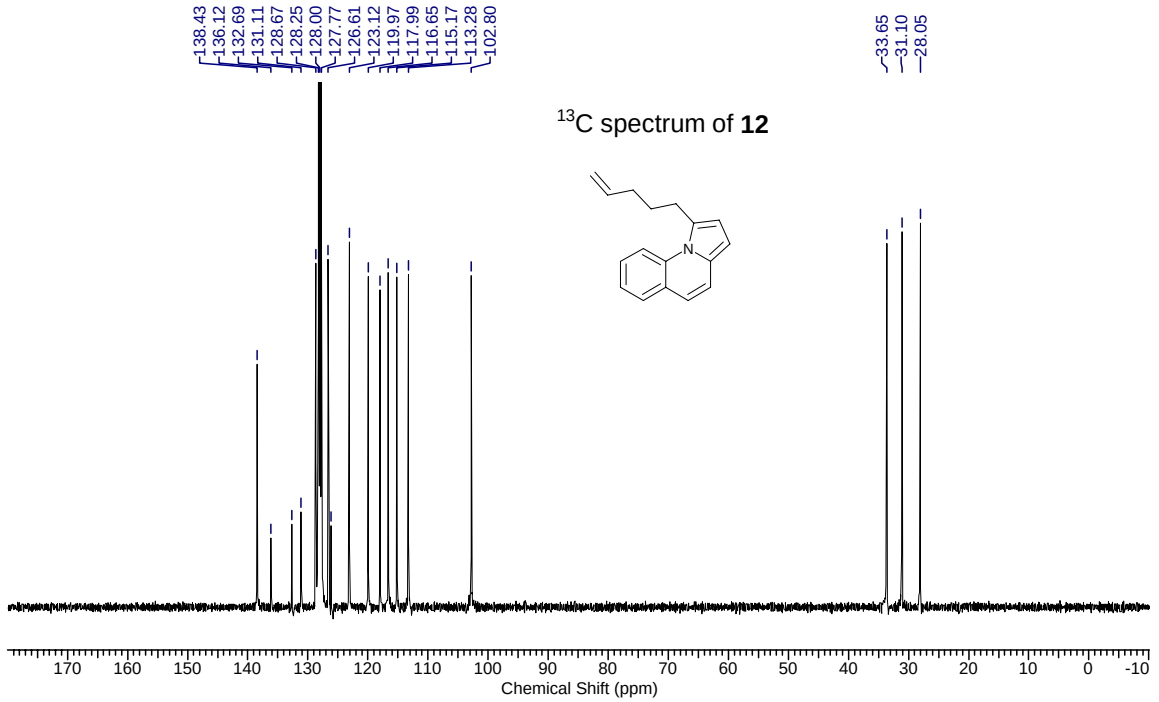
^{1}H spectrum of **11**



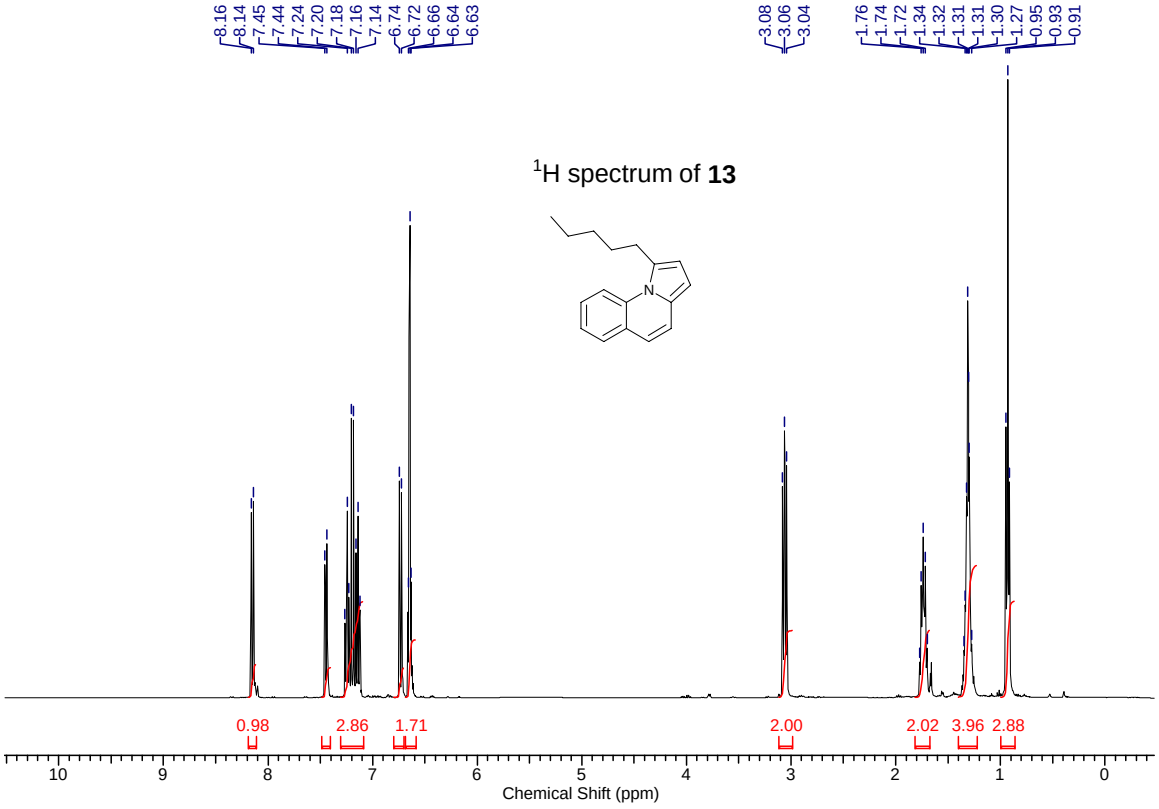
^{13}C spectrum of **11**



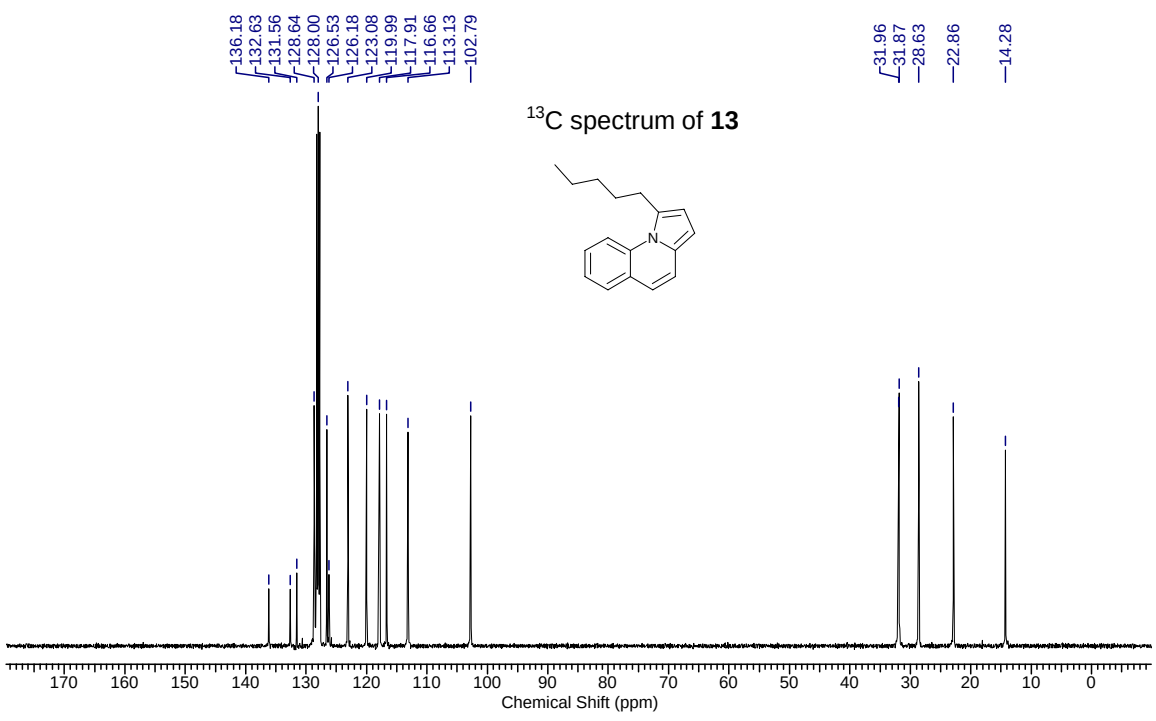
^{1}H spectrum of **12**



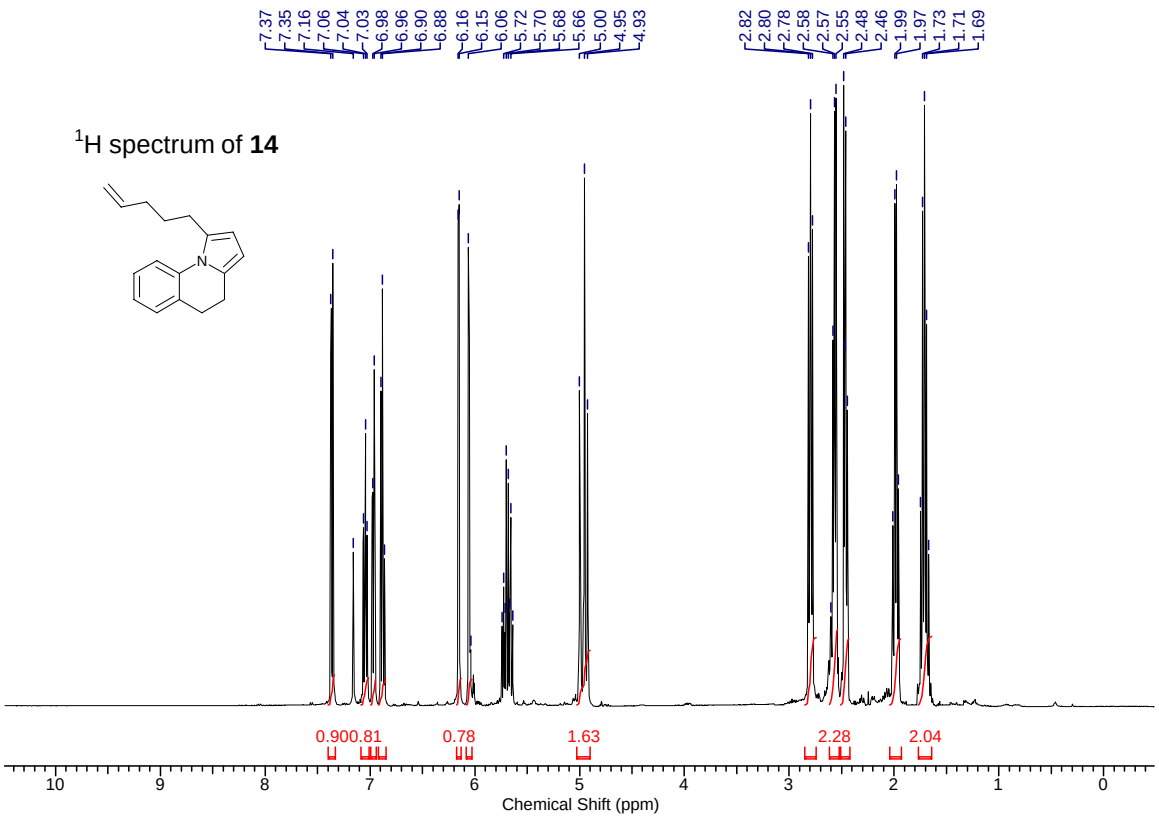
^{13}C spectrum of **12**



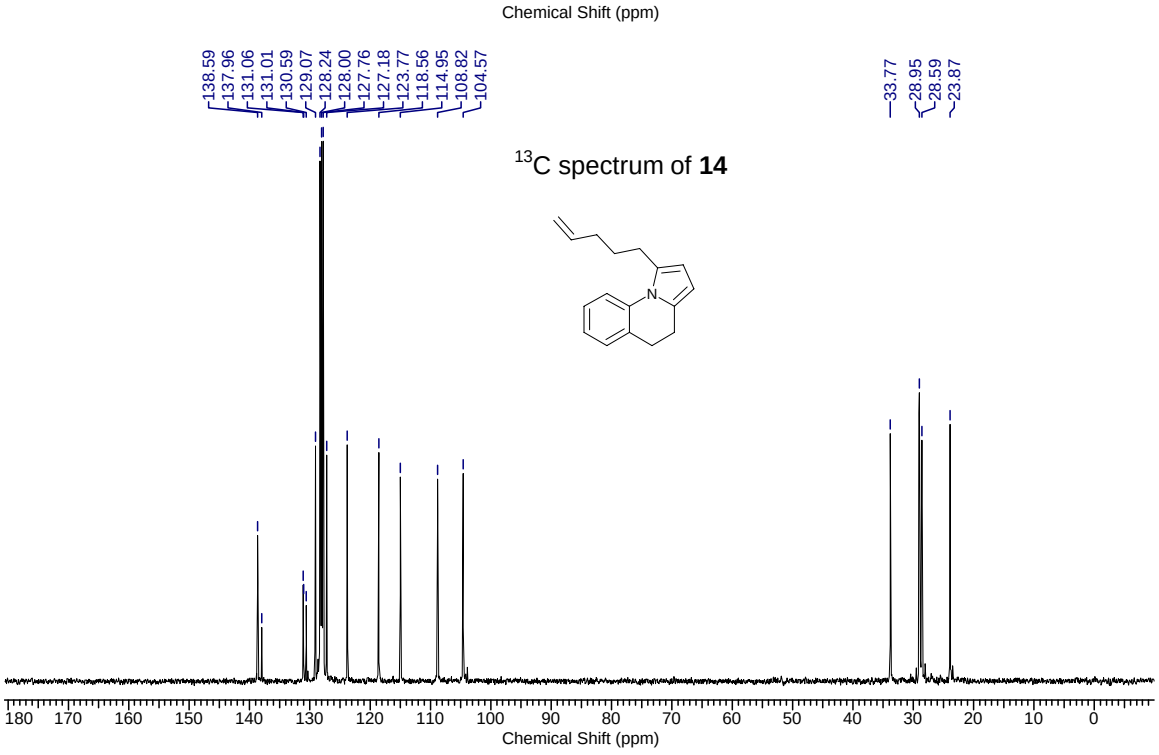
^{1}H spectrum of **13**



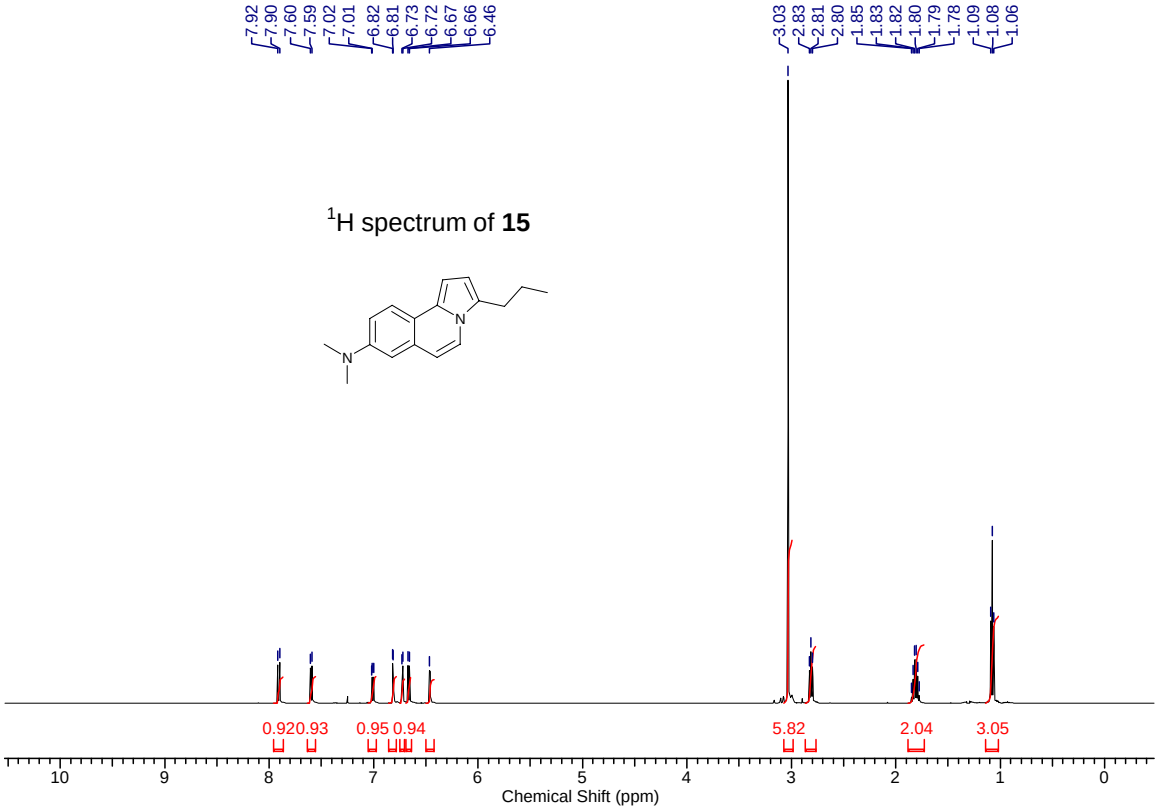
^{13}C spectrum of **13**



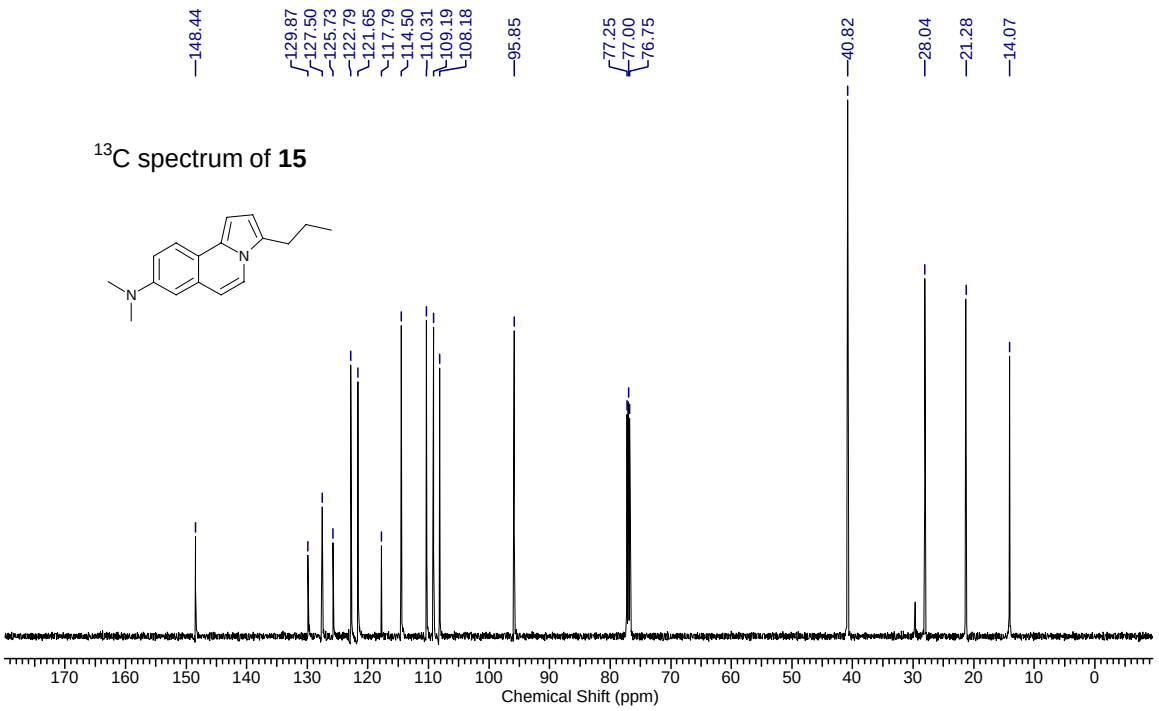
^{1}H spectrum of **14**



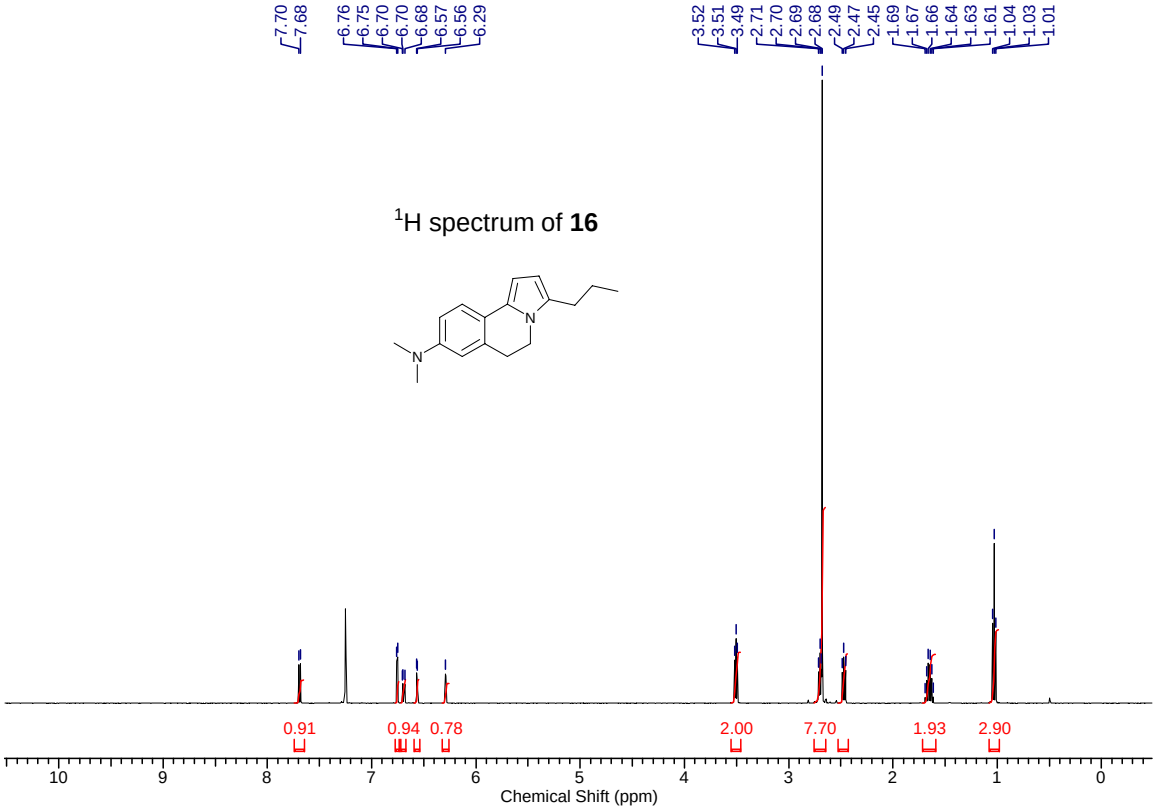
^{13}C spectrum of **14**

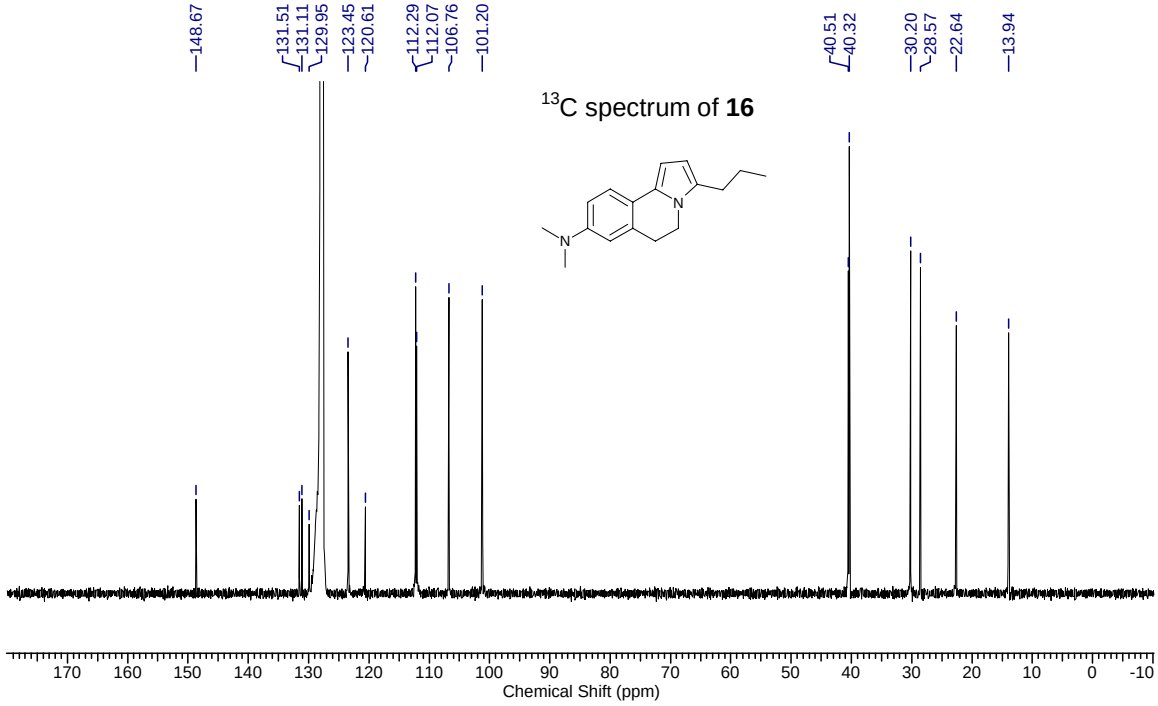


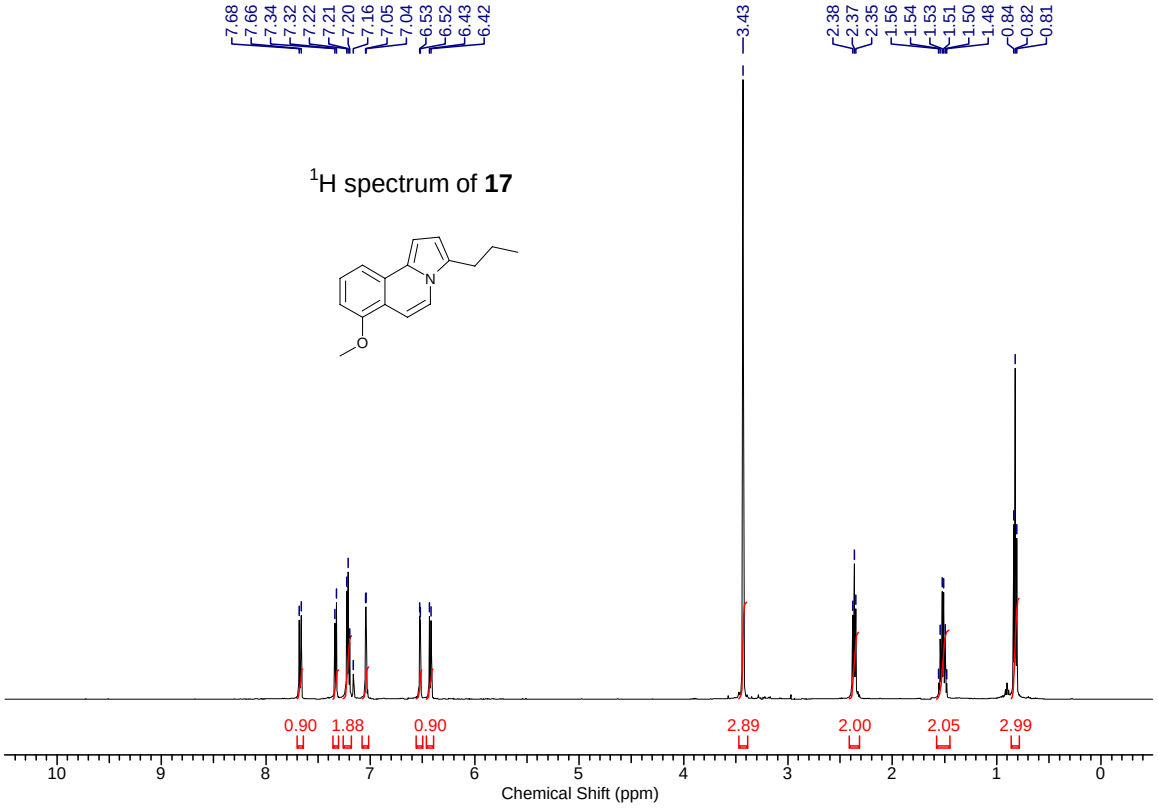
^{1}H spectrum of **15**



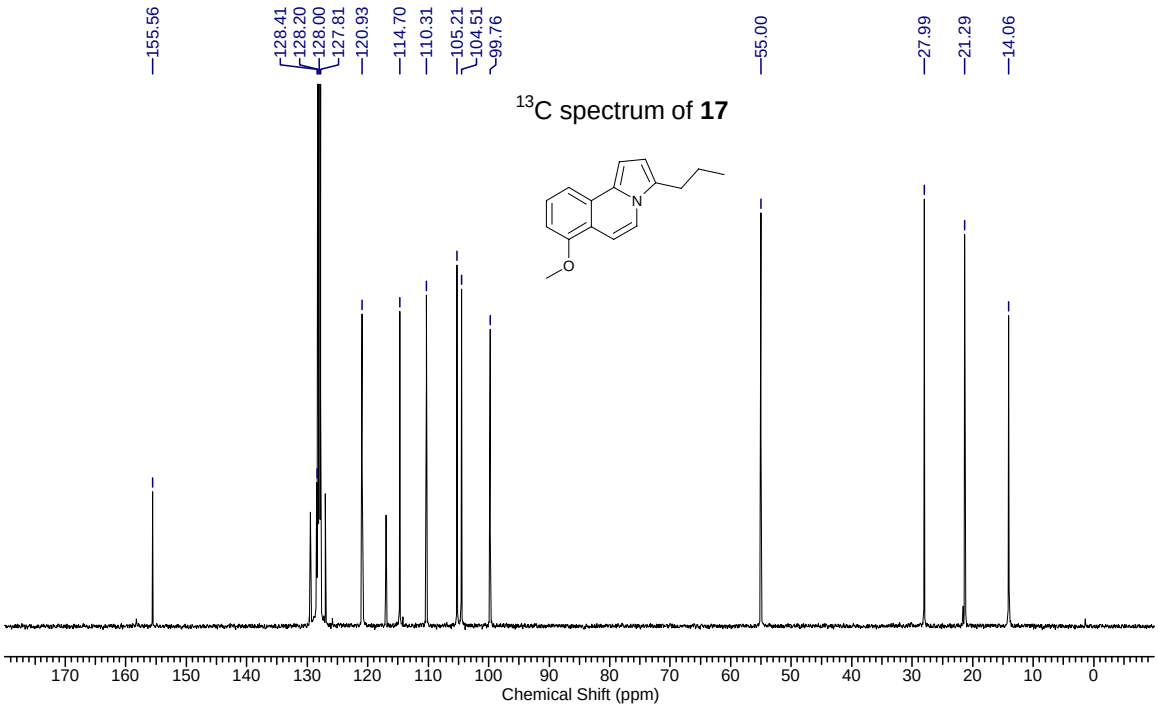
^{13}C spectrum of **15**


7.70
7.68
6.76
6.75
6.70
6.70
6.68
6.57
6.56
6.29
3.52
3.51
3.49
2.71
2.70
2.69
2.68
2.49
2.47
2.45
1.69
1.67
1.66
1.64
1.63
1.61
1.04
1.03
1.01
^{1}H spectrum of **16**
0.91
0.94
0.78
2.00
7.70
1.93
2.90
Chemical Shift (ppm)

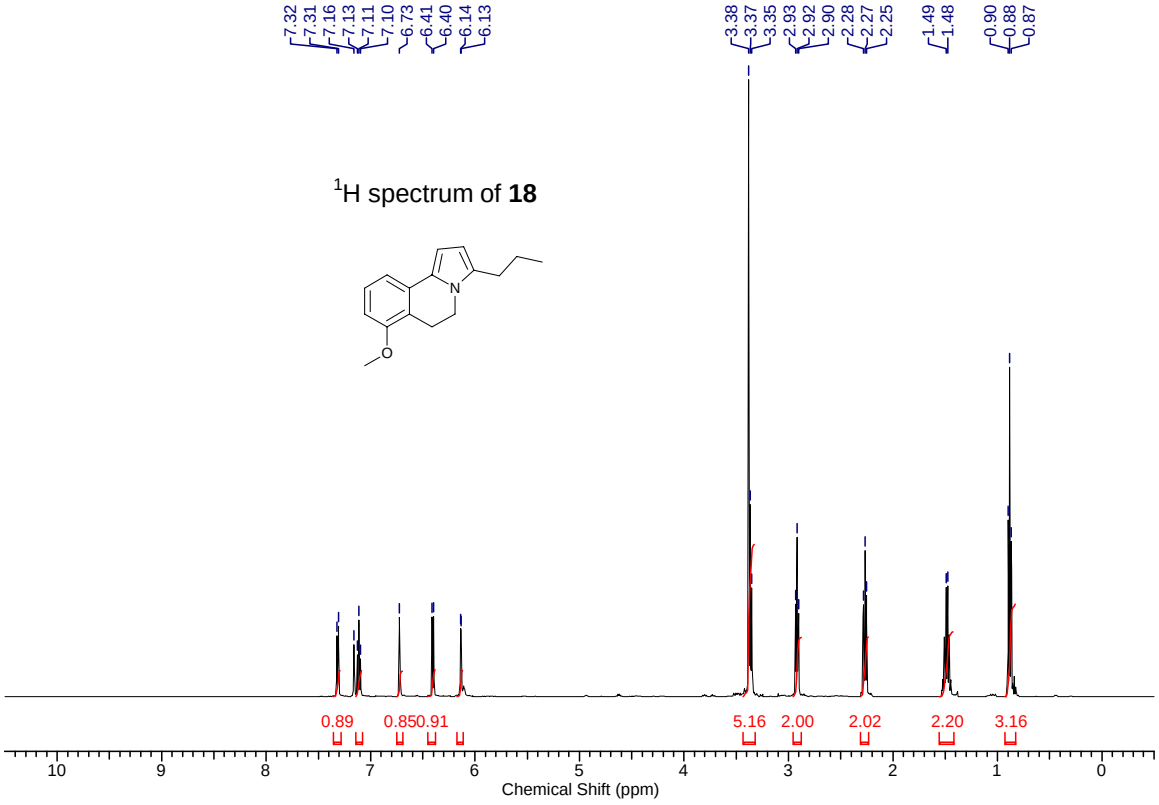

148.67
131.51
131.11
129.95
123.45
120.61
112.29
112.07
106.76
101.20
40.51
40.32
30.20
28.57
22.64
13.94
^{13}C spectrum of **16**
Chemical Shift (ppm)



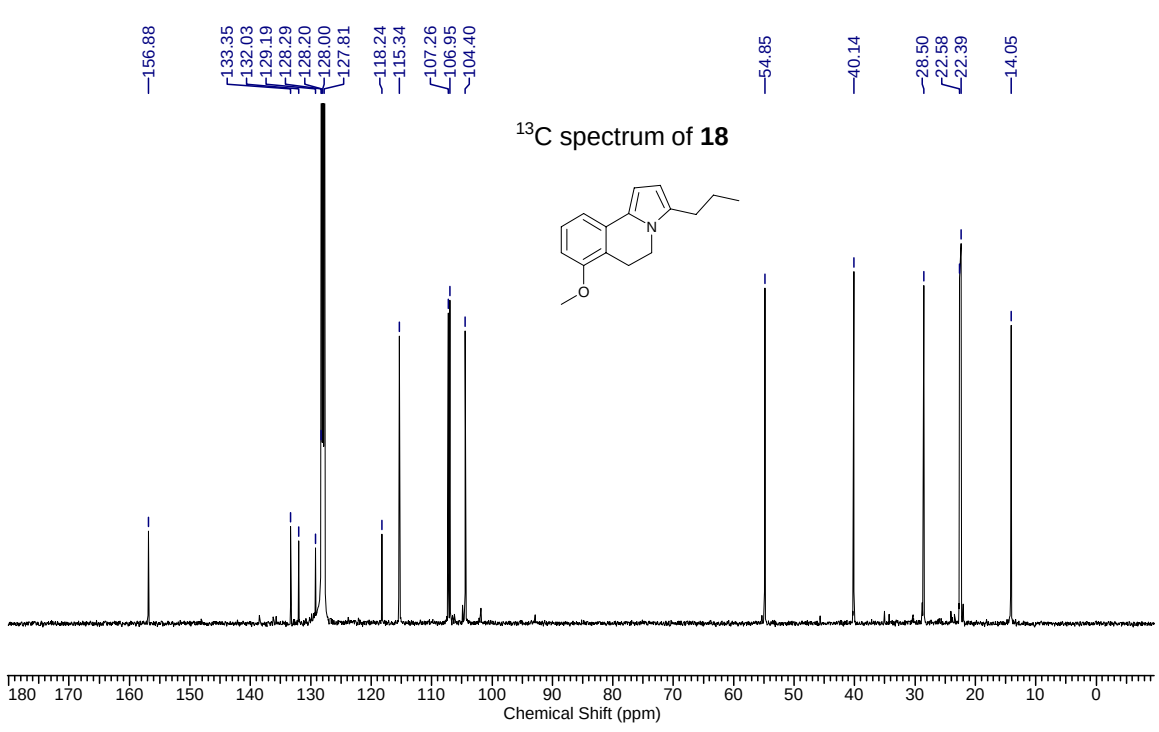
^{1}H spectrum of **17**



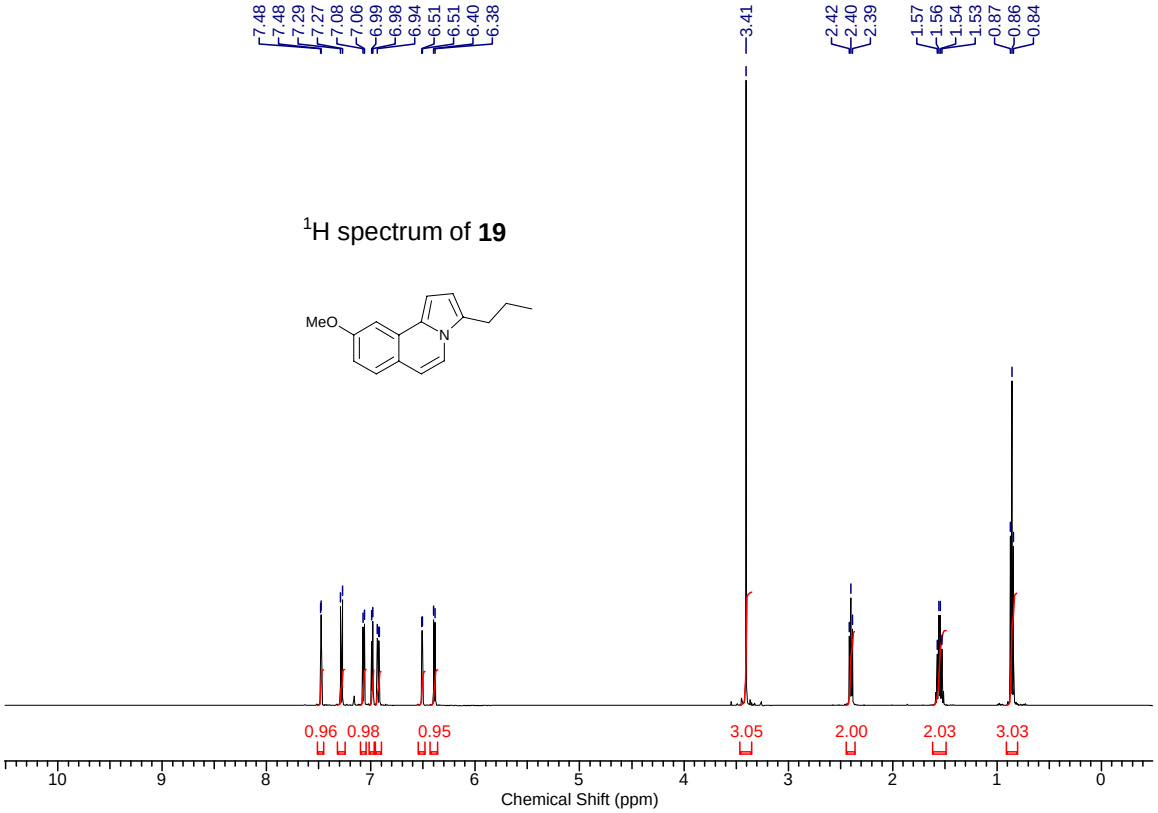
^{13}C spectrum of **17**



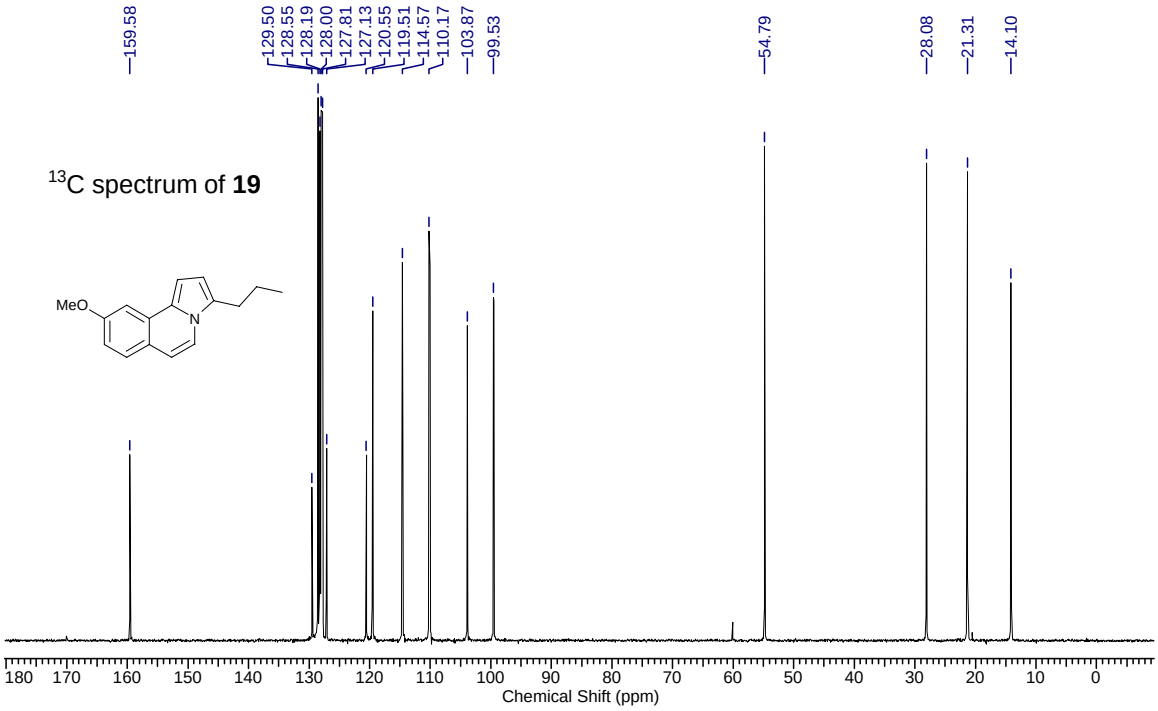
^{1}H spectrum of **18**



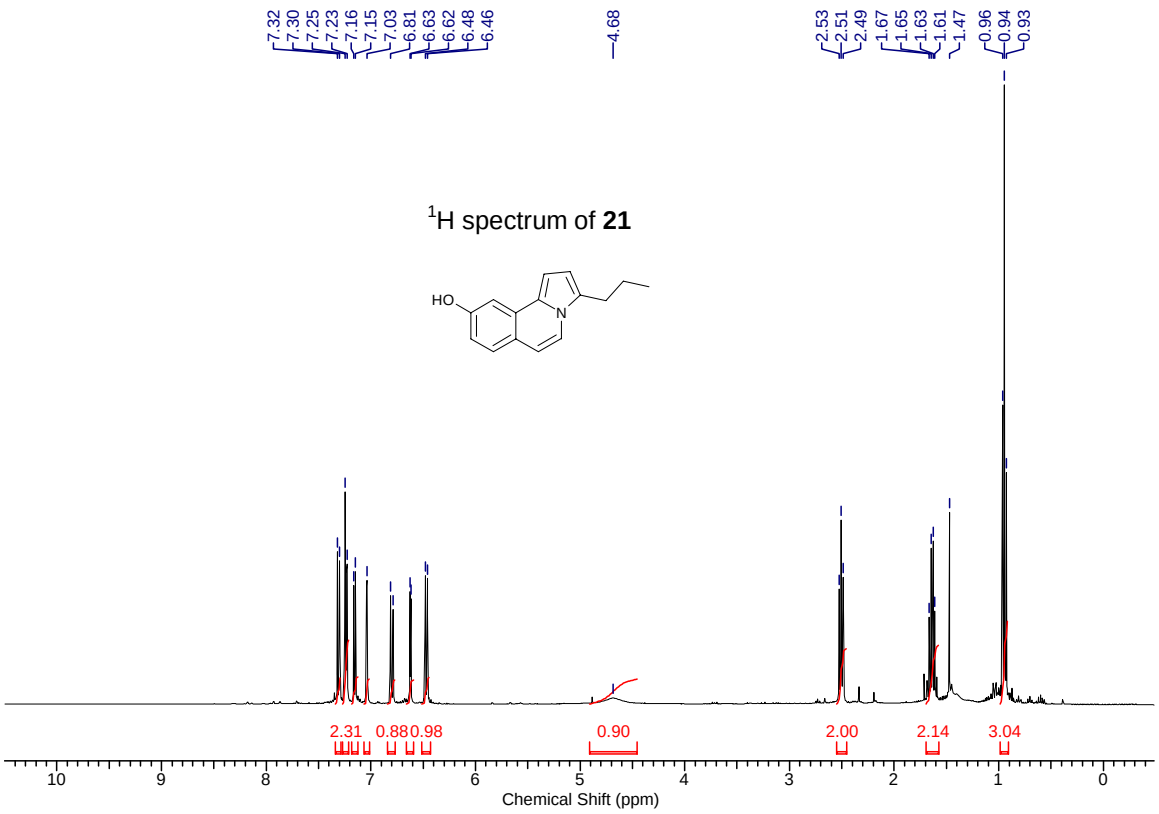
^{13}C spectrum of **18**



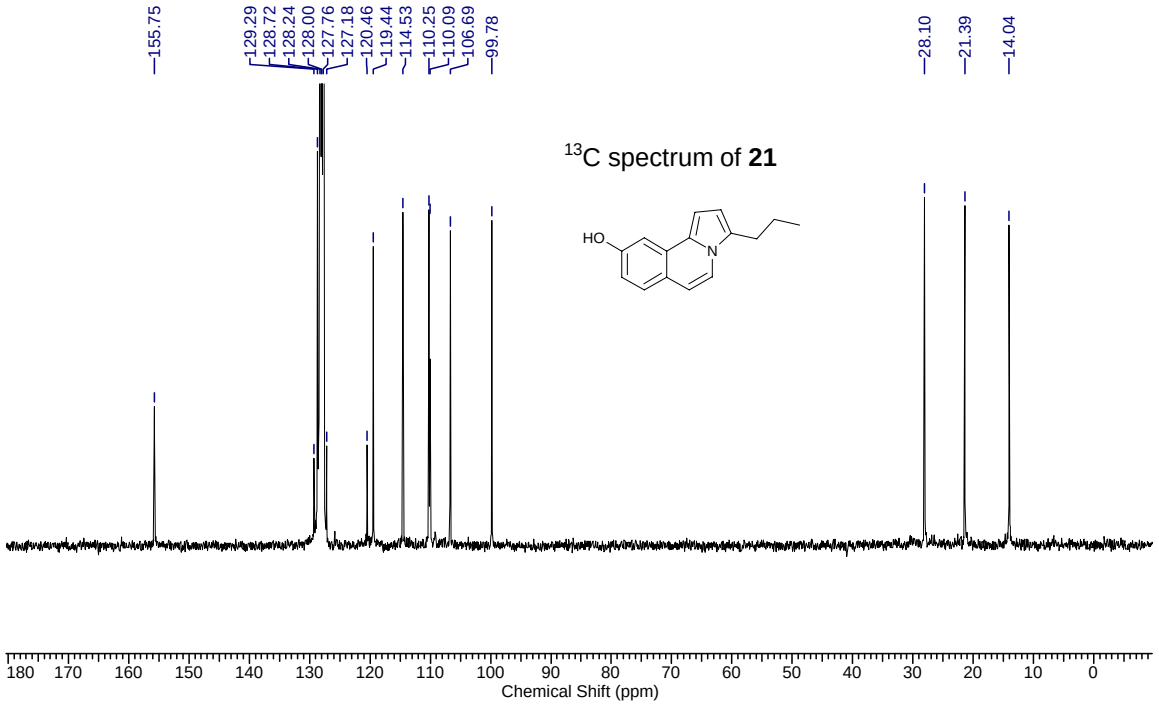
^{1}H spectrum of **19**



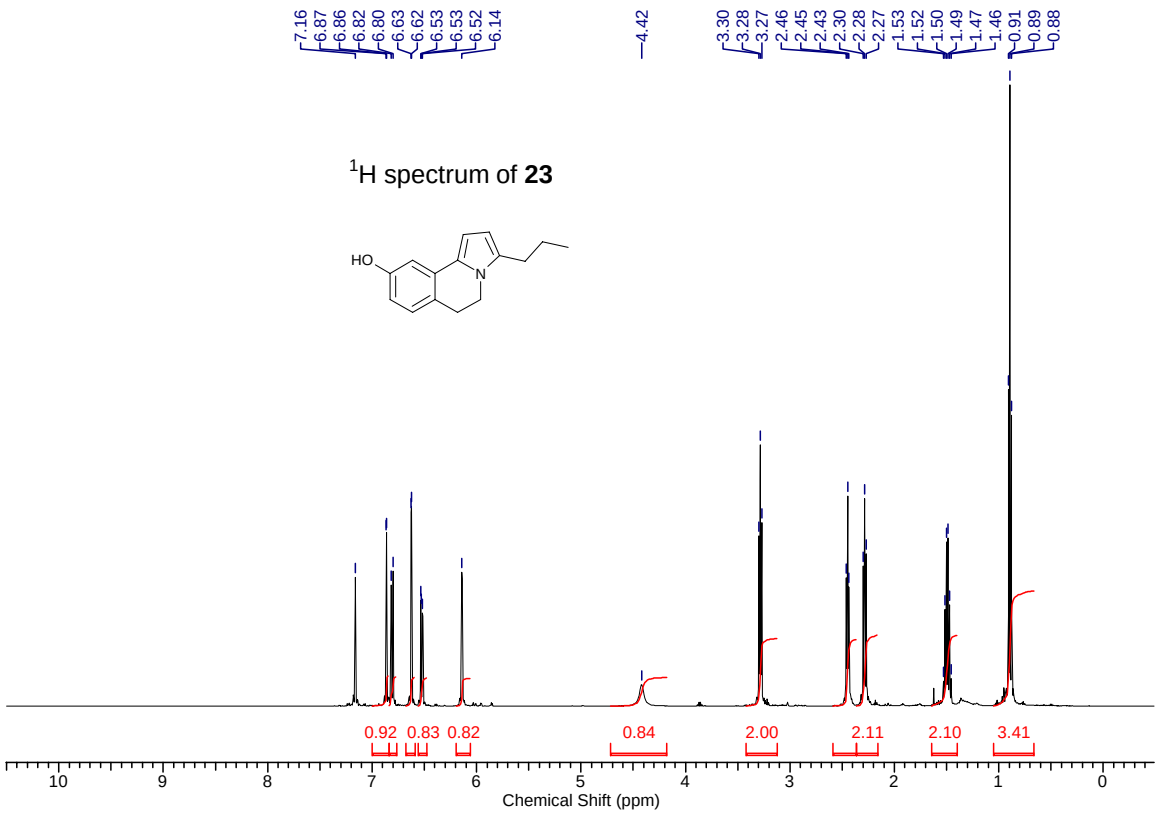
^{13}C spectrum of **19**



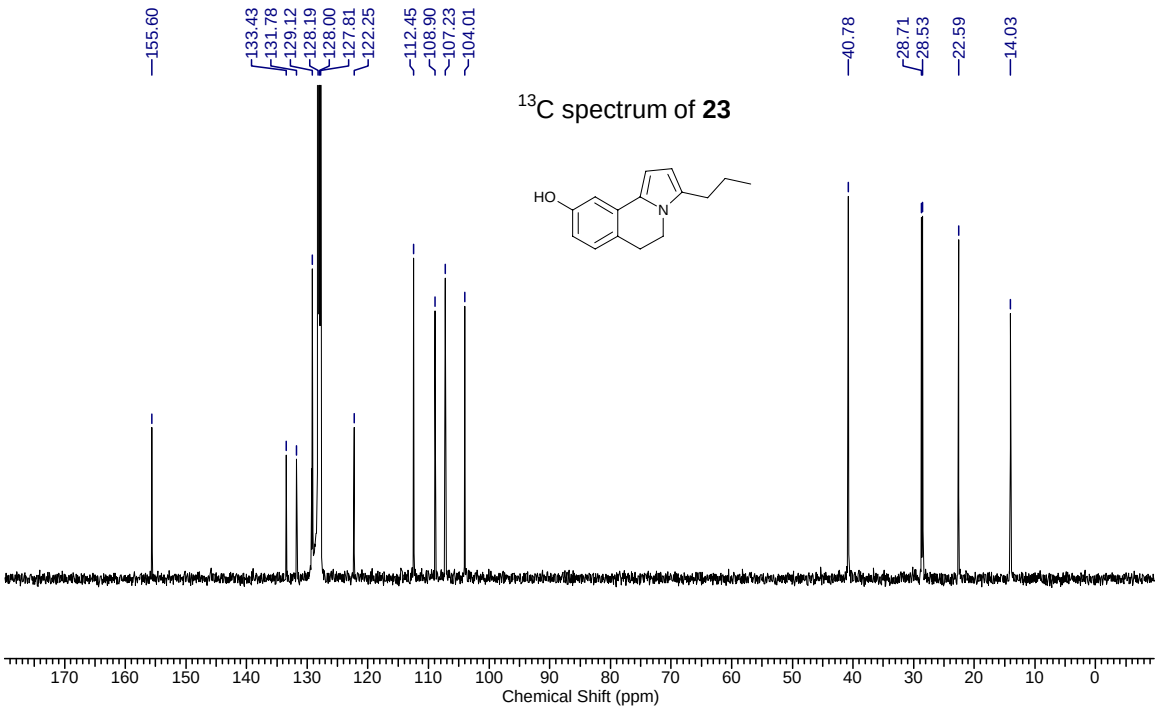
^{1}H spectrum of **21**



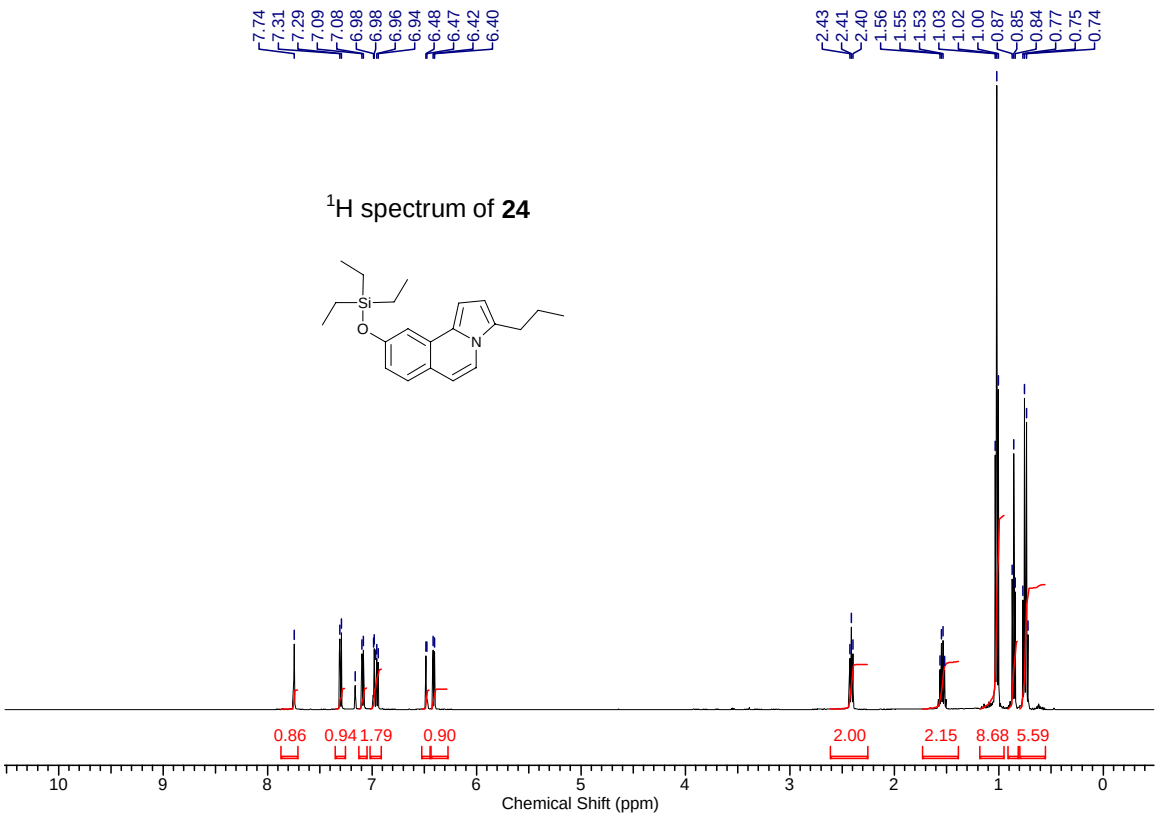
^{13}C spectrum of **21**

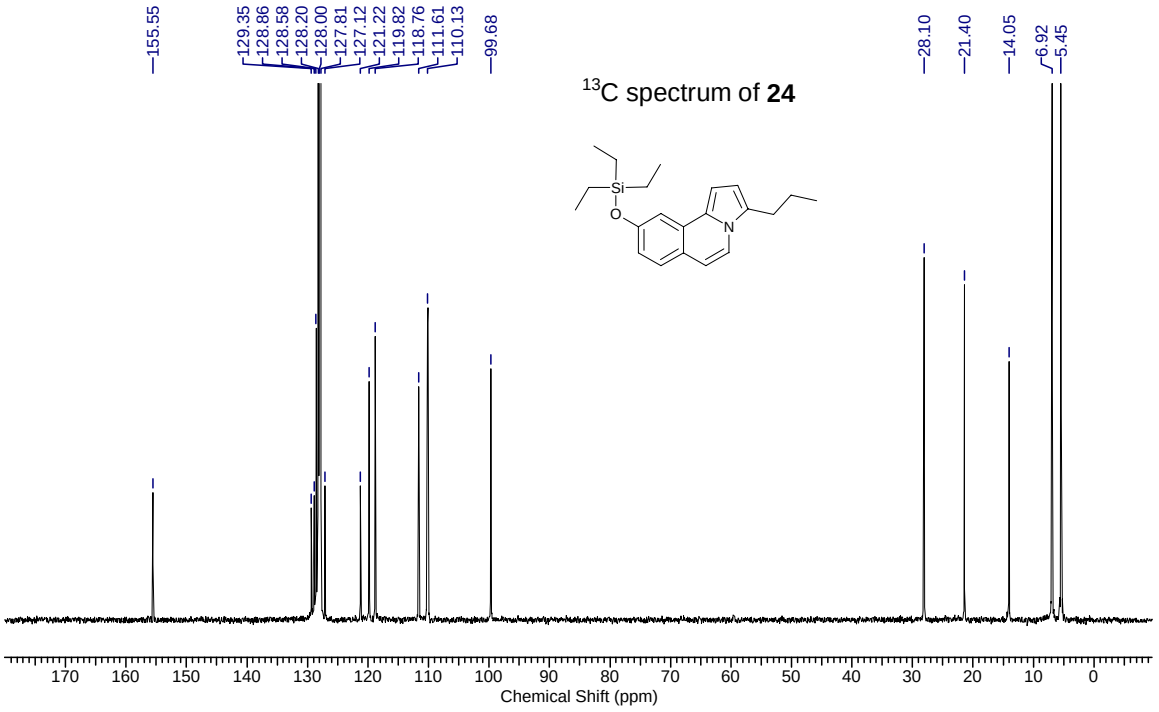


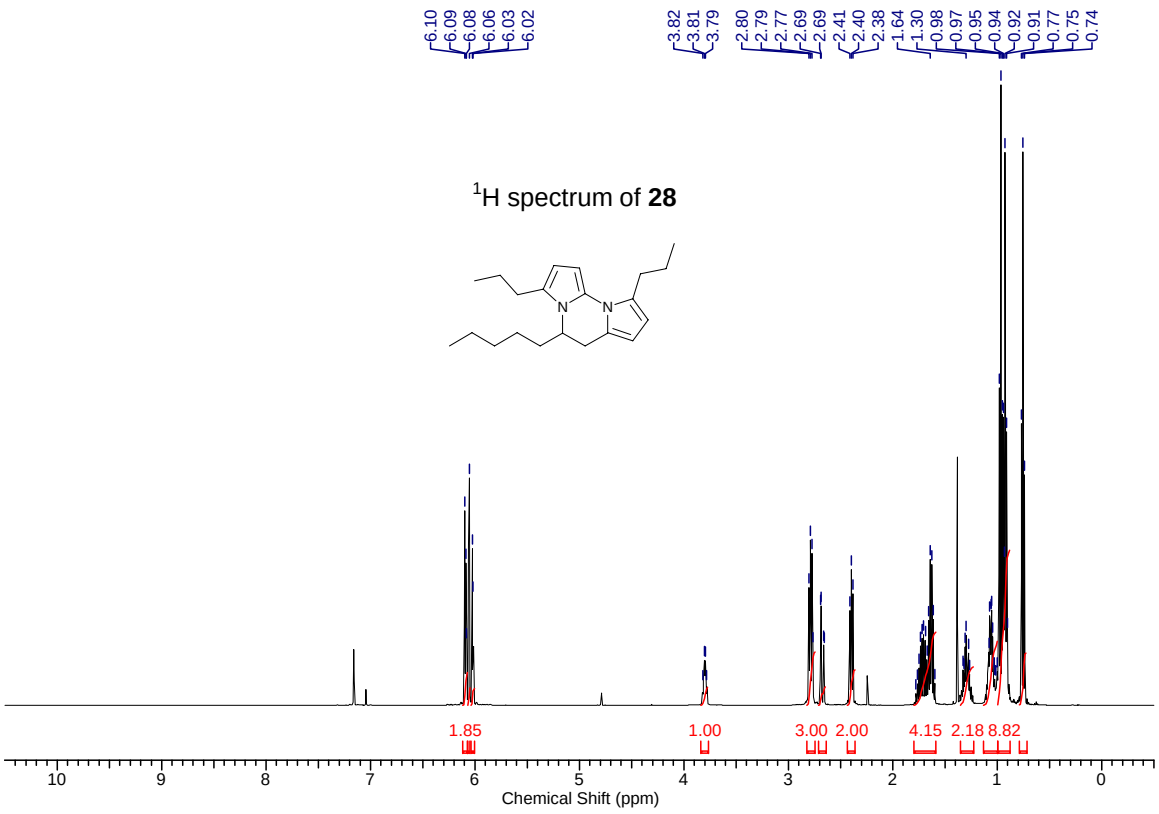
^{1}H spectrum of **23**

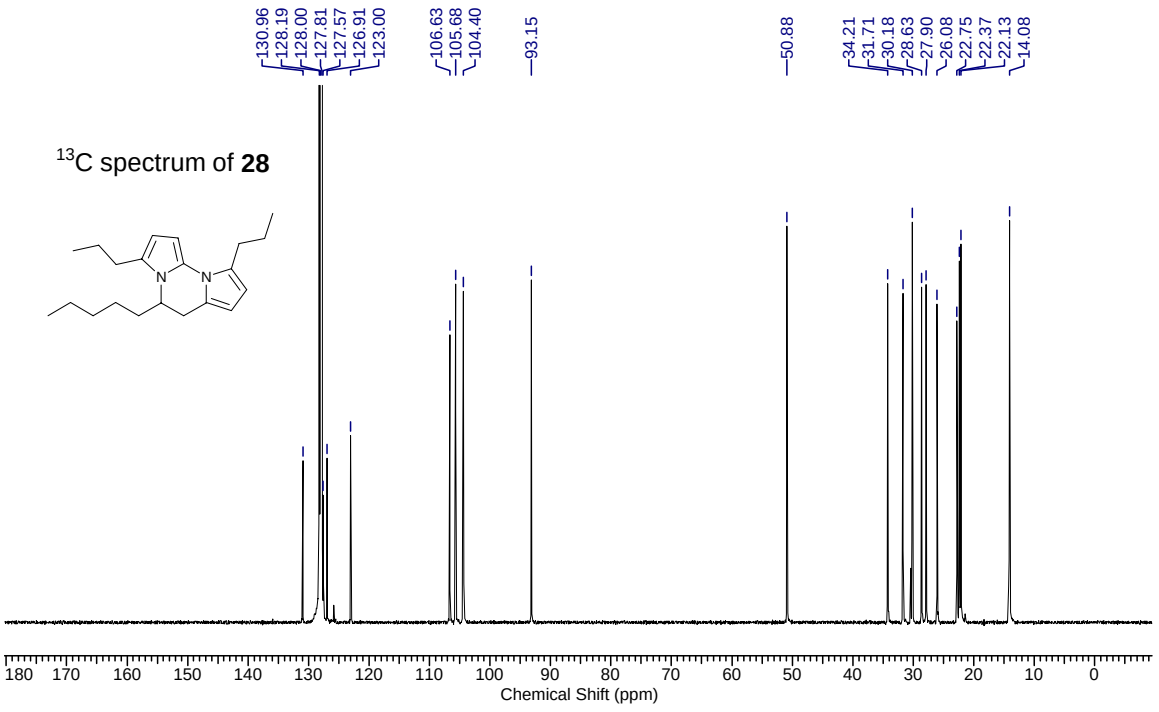


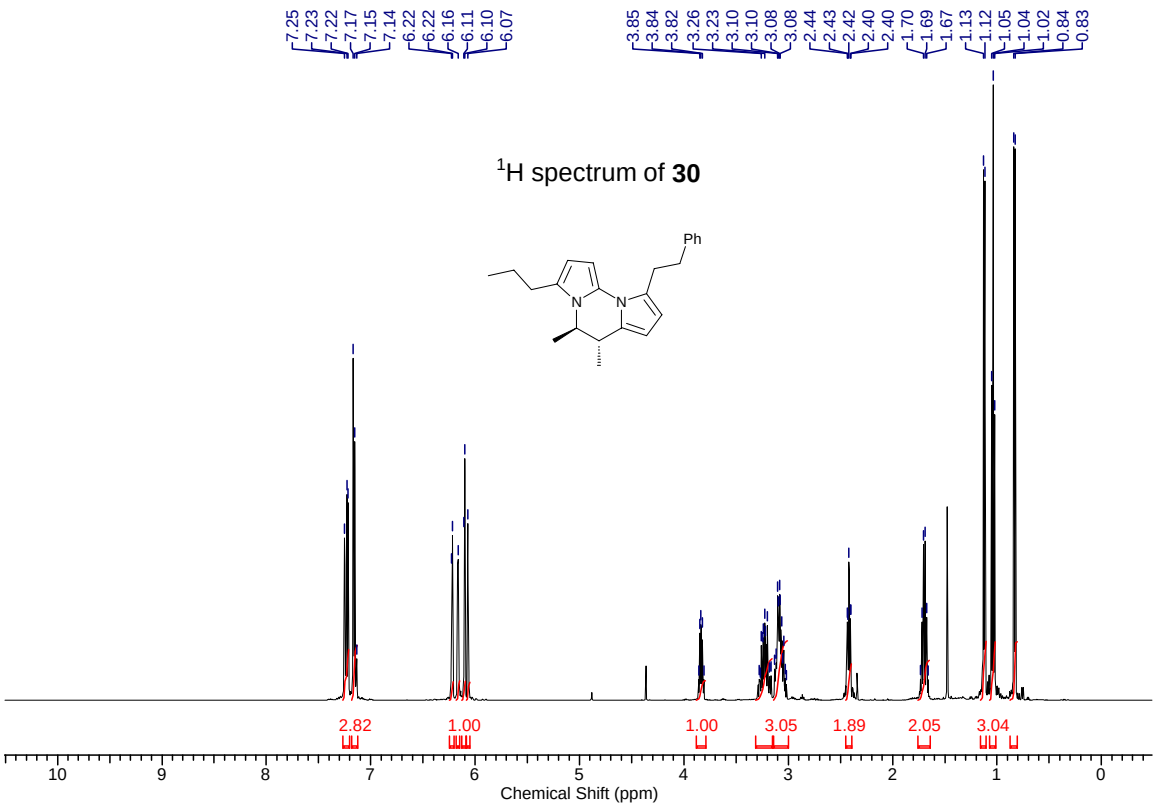
^{13}C spectrum of **23**


7.74
7.31
7.29
7.09
7.08
6.98
6.98
6.96
6.94
6.48
6.47
6.42
6.40
2.43
2.41
2.40
1.56
1.55
1.53
1.03
1.02
1.00
0.87
0.85
0.84
0.77
0.75
0.74
1H spectrum of 24
Si
O
N
0.86
0.94
1.79
0.90
2.00
2.15
8.68
5.59
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

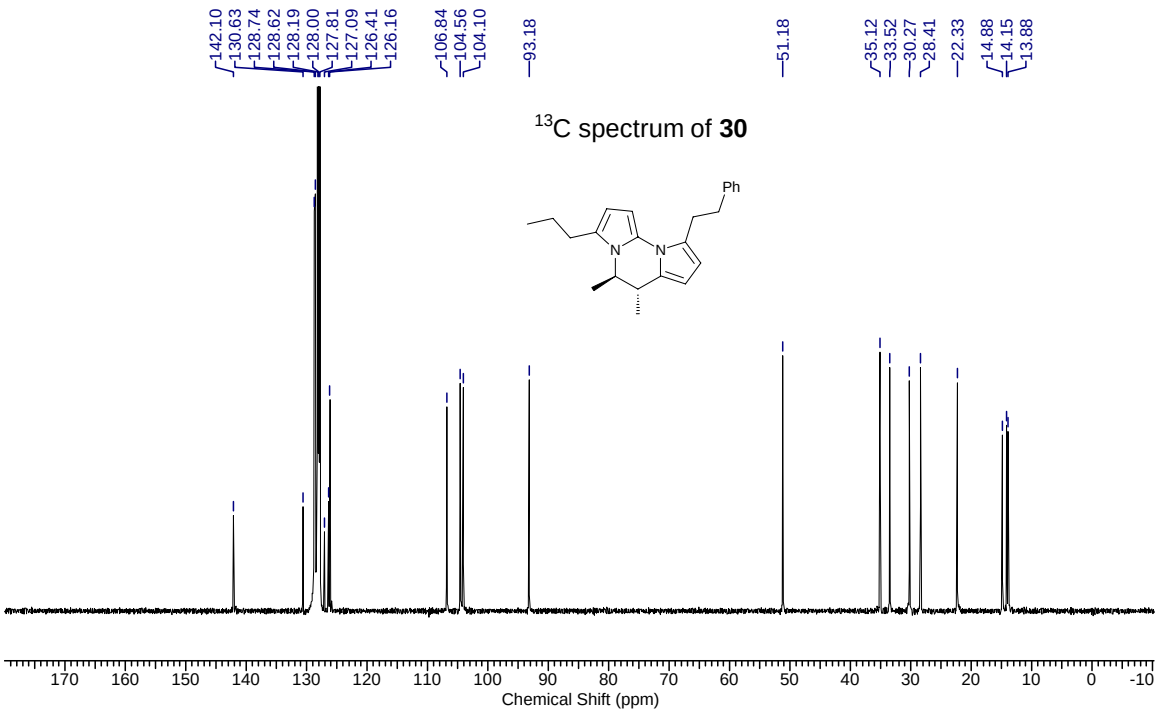

155.55
129.35
128.86
128.58
128.20
128.00
127.81
127.12
121.22
119.82
118.76
111.61
110.13
99.68
28.10
21.40
14.05
6.92
5.45
13C spectrum of 24
Si
O
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


6.10
6.09
6.08
6.06
6.03
6.02
3.82
3.81
3.79
2.80
2.79
2.77
2.69
2.69
2.41
2.40
2.38
1.64
1.30
0.98
0.97
0.95
0.94
0.92
0.91
0.77
0.75
0.74
1H spectrum of 28
N
N
1.85
1.00
3.00
2.00
4.15
2.18
8.82
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


130.96
128.19
128.00
127.81
127.57
126.91
123.00
106.63
105.68
104.40
93.15
50.88
34.21
31.71
30.18
28.63
27.90
26.08
22.75
22.37
22.13
14.08
13C spectrum of 28
N
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

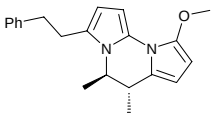


^{1}H spectrum of **30**

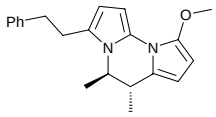


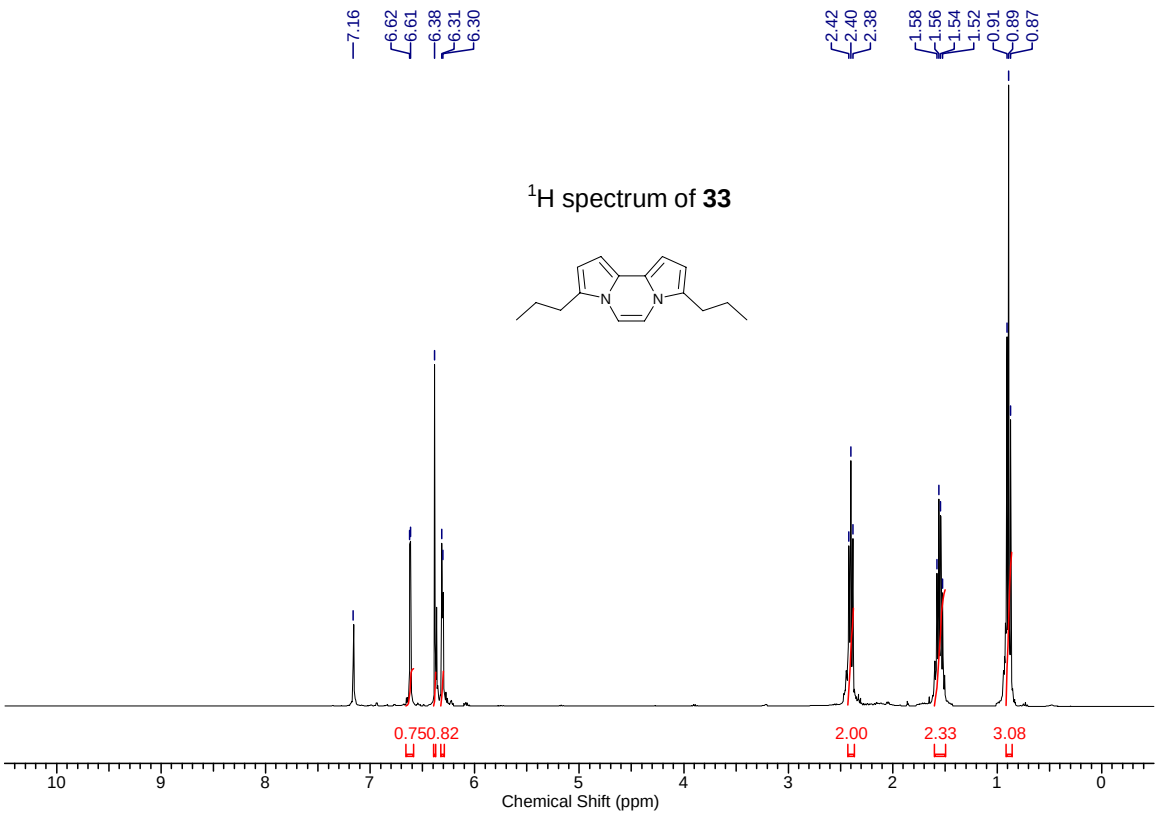
^{13}C spectrum of **30**

^{1}H spectrum of **32**

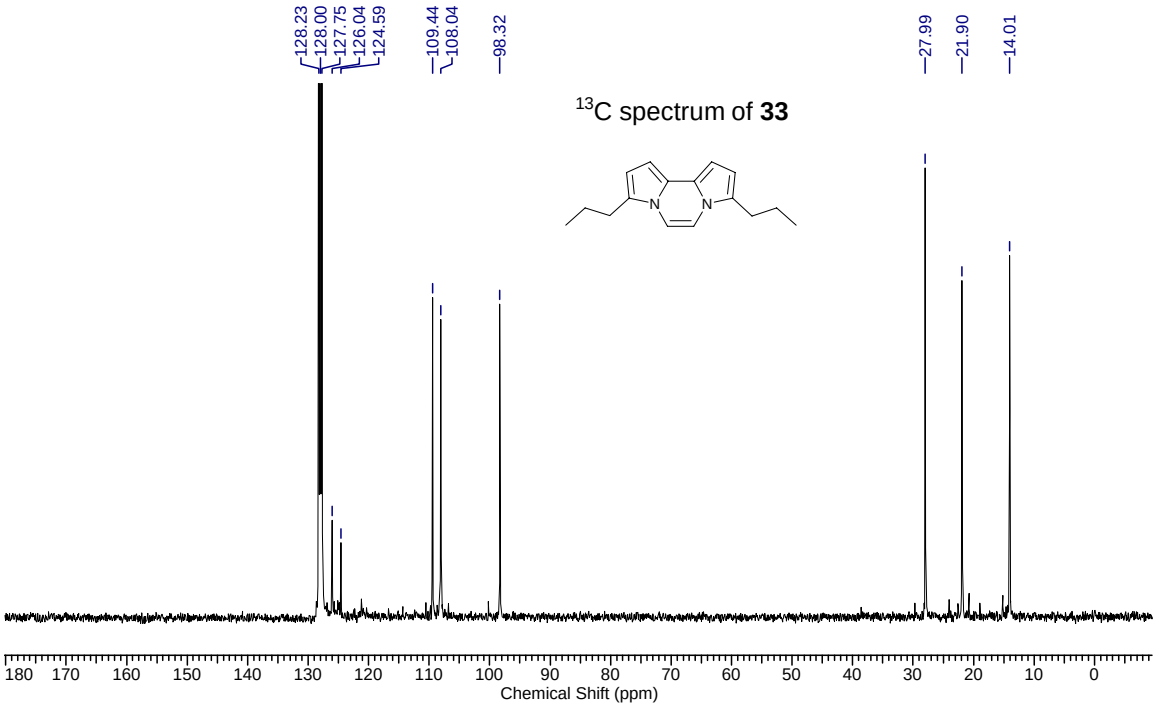


^{13}C spectrum of **32**

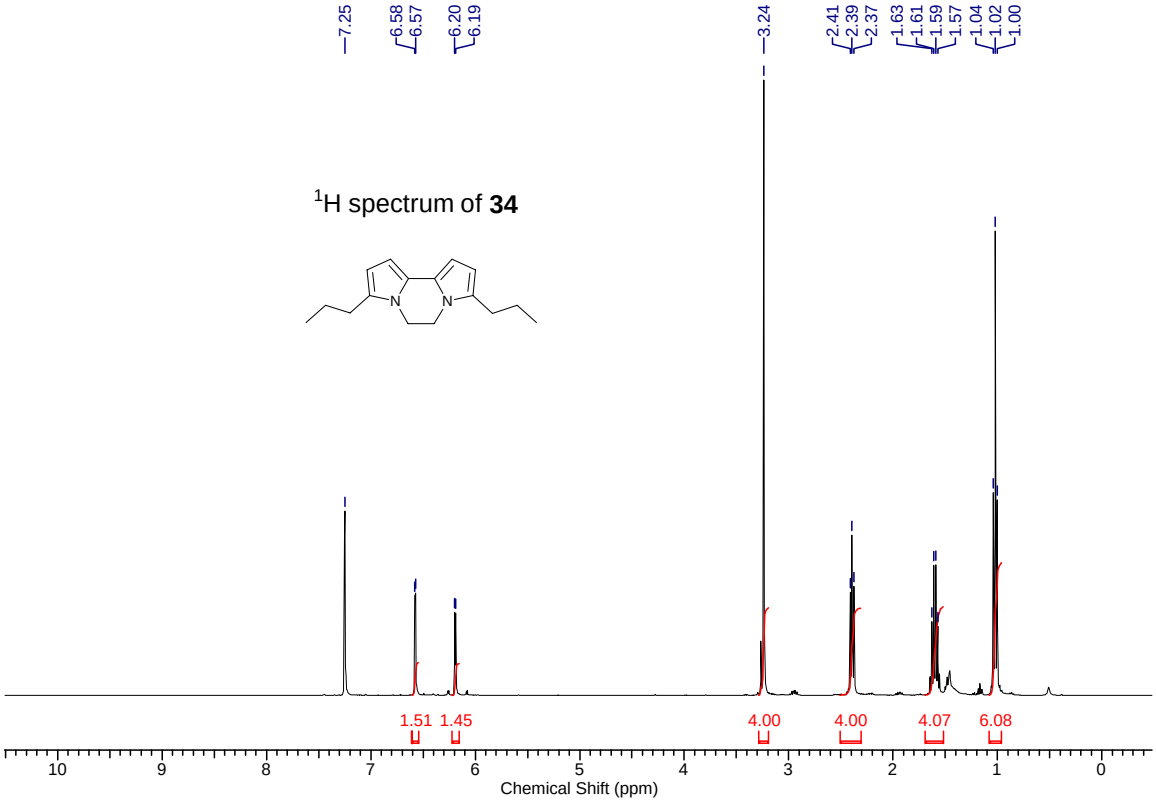




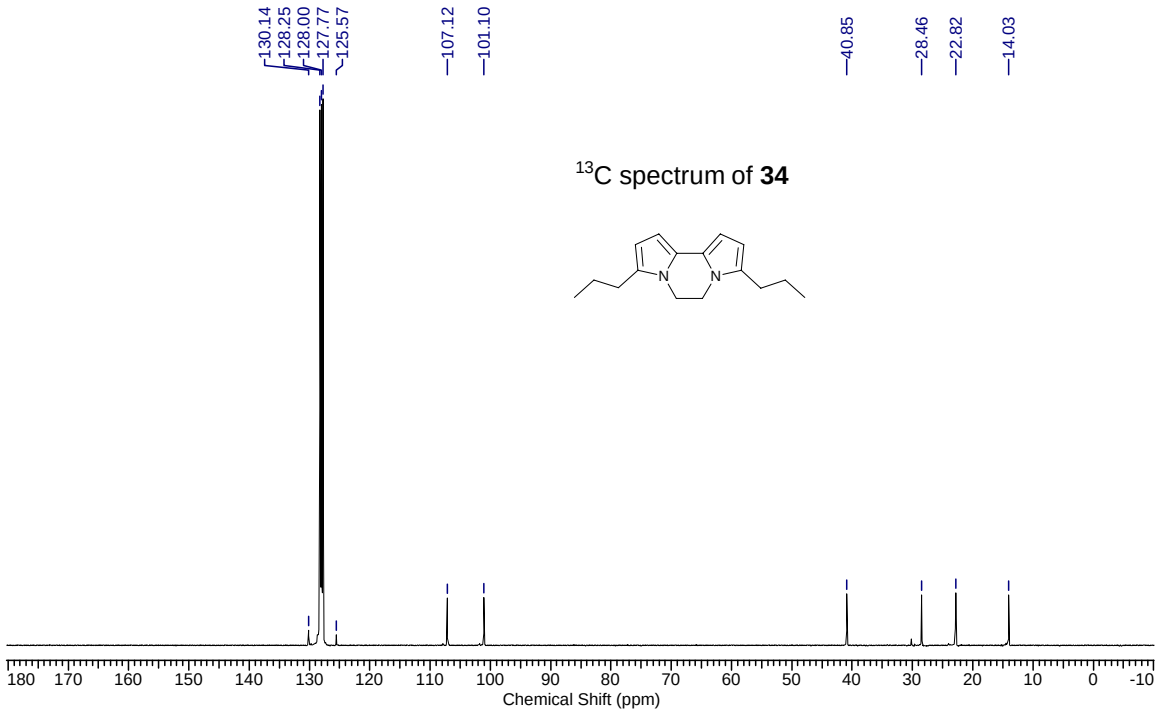
^{1}H spectrum of **33**



^{13}C spectrum of **33**



^{1}H spectrum of **34**



^{13}C spectrum of **34**