

Supporting Information

Electrochemical oxidation of 3-substituted indoles

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General experimental information

Unless otherwise noted, all reactions were performed under an atmosphere of dry nitrogen in oven-dried (100 °C) glassware. Commercially available starting materials and reagents were used as received unless otherwise noted. All the solvents used were dried by passage through a column of activated alumina under nitrogen using an LC Technology solvent purification system. Thin-layer chromatography (TLC) was performed using F254 0.2 mm silica plates, followed by visualisation with UV irradiation at 254 nm, and staining with ethanolic vanillin or potassium permanganate solution. Flash column chromatography was performed using 63–100 μm silica gel. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded with an FT-IR spectrometer using a diamond ATR sampling accessory. NMR spectra were recorded at ambient temperature in CDCl_3/TMS , $(\text{CD}_3)_2\text{CO}$ or $(\text{CD}_3)_2\text{SO}$ solutions using a spectrometer operating at 400 MHz for ^1H nuclei, 100 MHz for ^{13}C nuclei and 376 MHz for ^{19}F nuclei. All chemical shifts are reported in ppm on the δ scale and were measured relative to the tetramethylsilane peak recorded as δ 0.00 in CDCl_3/TMS , the residual $(\text{CD}_3)_2\text{CO}$ (δ 2.05) peak, or the residual $(\text{CD}_3)_2\text{SO}$ (δ 2.50) peak. Coupling constants, J , are reported in Hertz [Hz] where applicable. Multiplicities are reported as "s" (singlet), "d" (doublet), "t" (triplet), "q" (quartet), "p" (pentet), "m" (multiplet), "br" (broad or combination thereof). Where distinguishable from those due to a major isomer/diastereomer or rotamer, resonances due to the minor isomer, diastereomer and rotamer are denoted by an asterisk (*). High-resolution mass spectra were recorded on a microTOF QII (electrospray ionisation, ESI) mass spectrometer.

General electrochemical experimental information

With no precautions to exclude air or moisture, the ElectraSyn vial (5 mL) with a stirrer bar was charged with KBr (1-2 eq.) and a mixture of MeCN-water (5:1, 3 mL). The ElectraSyn vial cap equipped with an anode (glassy carbon) and cathode (glassy carbon) were inserted into the mixture (**Figure S1**). The reaction mixture was electrolysed with stirring at a constant current of 2.5 mA for 2 min, after this, the reaction was stopped and the indole (0.23 mmol) was added. The vial cap was replaced, and the mixture electrolysed at 2.5 mA until 2 F/mol had been consumed. Upon completion, the ElectraSyn vial cap was removed, and the electrodes rinsed with EtOAc and water. The resulting mixture was diluted with EtOAc (10 mL) and sodium thiosulfate (sat. sol. 10 mL) was added. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic extracts were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude oxindole was purified by flash chromatography on silica gel eluting with EtOAc-light petroleum to give the desired oxindole.

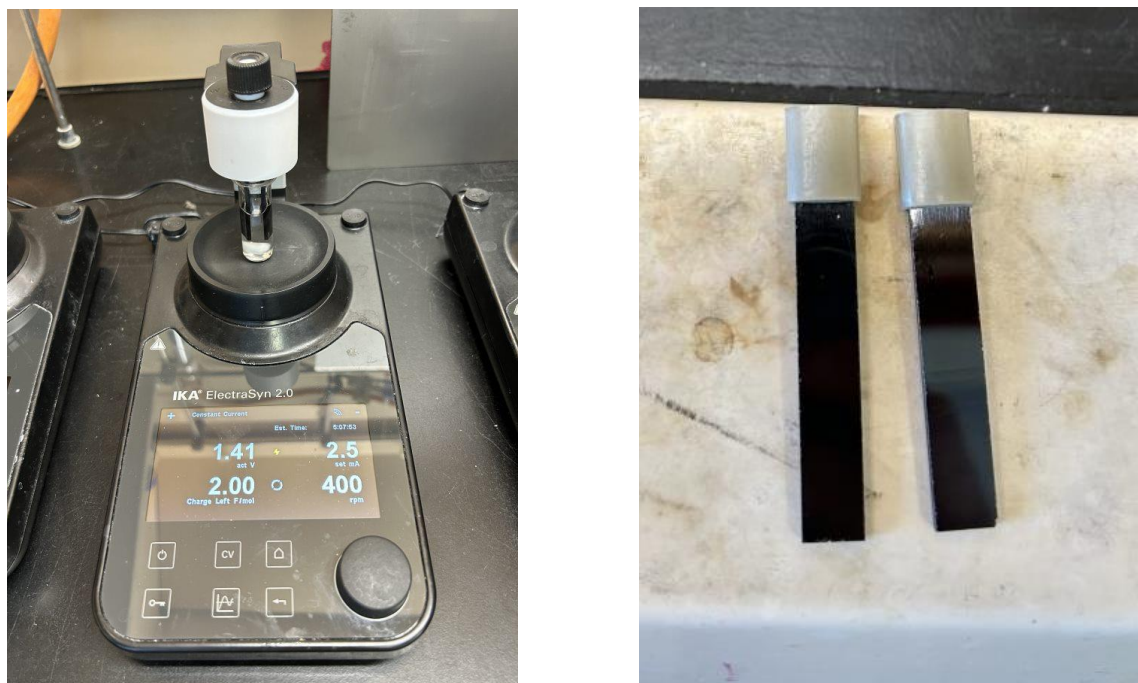
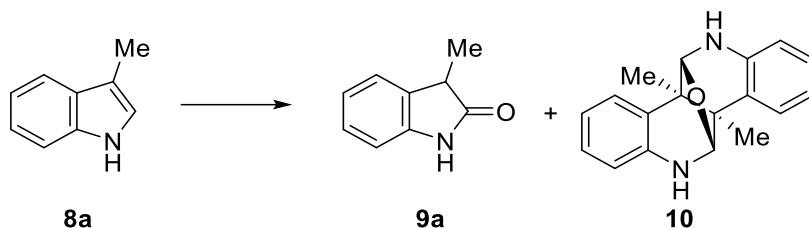


Figure S1, IKA ElectraSyn 2.0 and a 5 mL ElectraSyn undivided vial (left) fitted with ElectraSyn glassy carbon electrodes (4 x 0.8 x 0.2 cm; 4.0 cm² area exposed to the electrolyte; right) were used unless otherwise stated.

Experimental procedures and characterisation data

3-Methylindolin-2-one (**9a**) and (4bR,5R,10bR,11R)-4b,10b-dimethyl-4b,5,6,10b,11,12-hexahydro-5,11-epoxydibenzo[*c,h*][2,6]naphthyridine (**10**)

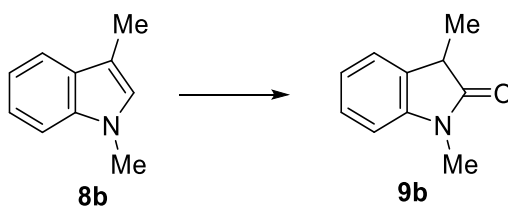


Prepared according to the general electrochemical procedure from 3-methylindole (**8a**, 30 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the compounds **9a** and **10**.

9a; pale-yellow solid (25 mg, 0.17 mmol, 74%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.12 (br s, 1 H, NH), 7.21 (t, J 7.4, 2 H, ArH), 7.03 (td, J 7.4, 1.0, 1 H, ArH), 6.92 (d, J 7.5, 1 H, ArH), 3.47 (q, J 7.7, 1 H, CH), 1.51 (d, J 7.6, 3 H, Me). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 181.7, 141.3, 131.3, 127.9, 123.8, 122.4, 109.8, 41.1, 15.3. NMR Spectroscopic data in accordance with previous reports.¹

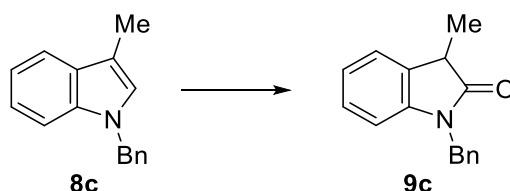
10; yellow solid, could be obtained in trace amounts (≤ 1 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 (dd, J 7.7, 1.3, 2 H, ArH), 7.11 (td, J 7.5, 1.5, 2 H, ArH), 6.83 (td, J 7.5, 1.5, 2 H, ArH), 6.57 (dd, J 7.9, 1.2, 2 H, ArH), 4.99 (d, J 2.7 Hz, 2 H), 4.90 (br s, 2H, 2 x NH), 1.34 (s, 6H, 2 x Me). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 141.8, 128.9, 128.1, 126.6, 119.7, 115.2, 95.8, 43.7, 13.3. NMR Spectroscopic data in accordance with previous reports.²

1,3-Dimethylindolin-2-one (**9b**)



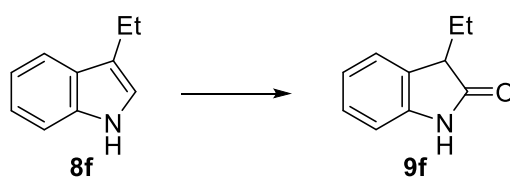
Prepared according to the general electrochemical procedure from 1,3-dimethylindole³ (**8b**, 33 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a yellow oil (15 mg, 0.09, mmol, 40%). ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.22 (m, 2 H, ArH), 7.06 (td, *J* 7.5, 1.0, 1 H, ArH), 6.83 (d, *J* 7.8, 1 H, ArH), 3.43 (q, *J* 7.6, 1 H, CH), 3.21 (s, 3 H, Me), 1.48 (d, *J* 7.5, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ 178.8, 144.1, 130.8, 128.0, 123.6, 122.5, 108.1, 40.7, 26.3, 15.5. NMR Spectroscopic data in accordance with previous reports.⁴

1-Benzyl-3-methylindolin-2-one (**9c**)



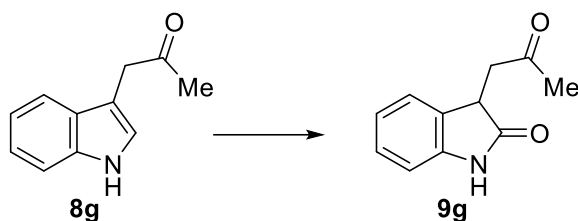
Prepared according to the general electrochemical procedure from 1-benzyl-3-methylindole³ (**8c**, 51 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (5% EtOAc in light petroleum) gave the *title compound* (19 mg, 0.08 mmol, 35%). ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.23 (m, 6 H, ArH), 7.18-7.12 (m, 1 H, ArH), 7.04-6.99 (m, 1 H, ArH), 6.71 (d, *J* 8.0, 1 H, ArH), 4.91 (s, 2 H, CH₂), 3.53 (q, *J* 7.6, 1 H, CH), 1.54 (d, *J* 7.7, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ 178.9, 143.2, 136.1, 130.8, 128.9, 127.9, 127.7, 127.4, 123.4, 122.5, 109.1, 43.8, 40.7, 15.7. NMR Spectroscopic data in accordance with previous reports.⁵

3-Ethylindolin-2-one (**9f**)



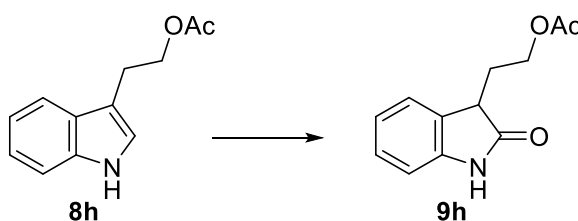
Prepared according to the general electrochemical procedure from 3-ethylindole⁶ (**8f**, 31 mg, 0.21 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a pale-yellow solid (20 mg, 0.12 mmol, 54%). ¹H NMR (400 MHz, CDCl₃) δ 8.95 (br s, 1 H, NH), 7.24-7.18 (m, 2 H, ArH), 7.03 (td, *J* 7.5, 1.1, 1 H, ArH), 6.91 (d, *J* 7.7, 1 H, ArH), 3.46 (t, *J* 5.8, 1 H, CH), 2.07-2.00 (m, 2 H, CH₂), 0.92 (t, *J* 7.4, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ 180.8, 142.0, 129.7, 127.9, 124.2, 122.4, 109.8, 47.3, 23.7, 10.1. NMR Spectroscopic data in accordance with previous reports.⁷

3-(2-Oxopropyl)indolin-2-one (**9g**)



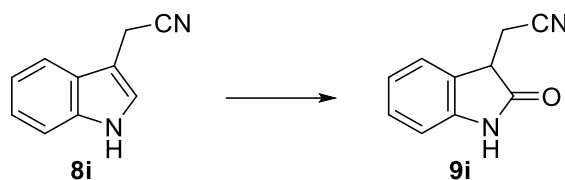
Prepared according to the general electrochemical procedure from 1-(indol-3-yl)propan-2-one⁸ (**8g**, 40 mg, 0.23 mmol) and KBr (1 eq.). Purification by flash chromatography on silica gel (50% EtOAc in light petroleum) gave the *title compound* as a pale-yellow oil (21 mg, 0.11 mmol, 49%). ¹H NMR (400 MHz, CDCl₃) δ 8.92 (br s, 1 H, NH), 7.22-7.15 (m, 2 H, ArH), 6.98 (t, *J* 7.5, 1 H, ArH), 6.89 (d, *J* 7.8, 1 H, ArH), 3.88 (dd, *J* 8.6, 3.5, 1 H, CH), 3.25 (dd, *J* 18.4, 3.6, 1 H, CH₂), 2.89 (dd, *J* 18.4, 8.6, 1 H, CH₂), 2.22 (s, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ 205.5, 179.7, 141.4, 129.6, 128.3, 124.6, 122.7, 109.8, 44.4, 41.5, 30.1. NMR Spectroscopic data in accordance with previous reports.⁹

2-(2-Oxoindolin-3-yl)ethyl acetate (**9h**)



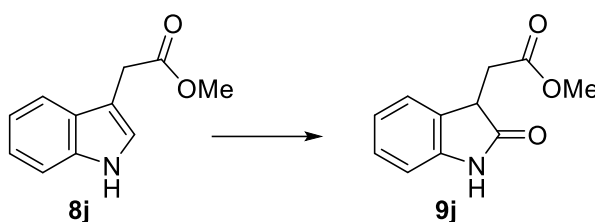
Prepared according to the general electrochemical procedure from 2-(indol-3-yl)ethyl acetate¹⁰ (**8h**, 47 mg, 0.23 mmol) and KBr (1 eq.). Purification by flash chromatography on silica gel (50% EtOAc in light petroleum) gave the *title compound* as a yellow oil (19 mg, 0.09 mmol, 38%). ¹H NMR (400 MHz, CDCl₃) δ 8.87 (br s, 1 H, NH), 7.25-7.19 (m, 2 H, ArH), 7.05-7.00 (m, 1 H, ArH), 6.92 (d, *J* 7.7, 1 H, ArH), 4.32-4.25 (m, 1 H, CH₂), 4.22-4.15 (m, 1 H, CH₂), 3.57 (t, *J* 6.2, 1 H, CH), 3.39-3.23 (m, 2 H, CH₂), 1.96 (s, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ 180.2, 171.0, 141.7, 128.8, 128.3, 124.3, 122.5, 110.1, 61.3, 43.2, 29.2, 20.9. NMR Spectroscopic data in accordance with previous reports.¹¹

2-(2-Oxoindolin-3-yl)acetonitrile (**9i**)



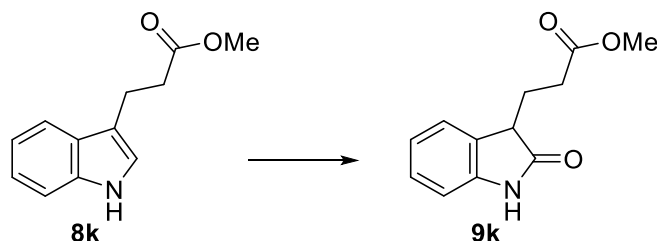
Prepared according to the general electrochemical procedure from 2-(indol-3-yl)acetonitrile (**8i**, 36 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) to afford the *title compound* as a yellow oil (18 mg, 0.10 mmol, 45%). ¹H NMR (400 MHz, CDCl₃) δ 8.55 (br s, 1 H, NH), 7.49 (d, *J* 7.5, 1 H, ArH), 7.33-7.28 (m, 1 H, ArH), 7.14-7.09 (m, 1 H, ArH), 6.95 (d, *J* 7.8, 1 H, ArH), 3.71 (dd, *J* 8.8, 4.8, 1 H, CH), 3.09 (dd, *J* 16.9, 8.9, 1 H, CH₂), 2.75 (dd, *J* 16.9, 8.9, 1 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 176.6, 141.3, 129.6, 126.3, 124.7, 123.4, 117.2, 110.5, 42.0, 19.0. NMR Spectroscopic data in accordance with previous reports.¹²

Methyl 2-(2-oxoindolin-3-yl)acetate (**9j**)



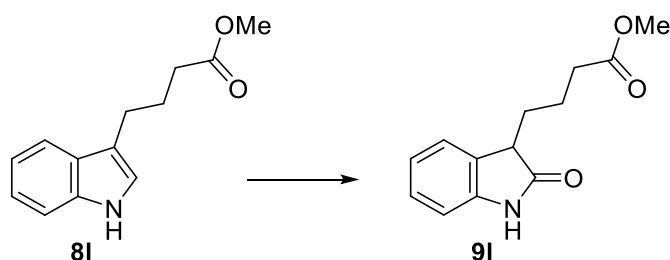
Prepared according to the general electrochemical procedure from methyl 2-(indol-3-yl)acetate¹³ (**8j**, 43 mg, 0.23 mmol) and KBr (1 eq.). Purification by flash chromatography on silica gel (50% EtOAc in light petroleum) gave the *title compound* as a pale-yellow oil (23 mg, 0.11 mmol, 49%). ¹H NMR (400 MHz, CDCl₃) δ 8.75 (br s, 1 H, NH), 7.24-7.20 (m, 2 H, ArH), 7.01 (t, *J* 7.6, 1 H, ArH), 6.90 (d, *J* 8.1, 1 H, ArH), 3.83 (dd, *J* 8.1, 4.5, 1 H, CH), 3.70 (s, 3 H, Me), 3.09 (dd, *J* 16.9, 4.5, 1 H, CH₂), 2.84 (dd, *J* 16.9, 8.0, 1 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 179.0, 171.7, 141.6, 128.8, 128.5, 124.3, 122.7, 110.0, 52.2, 42.4, 34.7. NMR Spectroscopic data in accordance with previous reports.⁷

Methyl 3-(2-oxoindolin-3-yl)propanoate (**9k**)



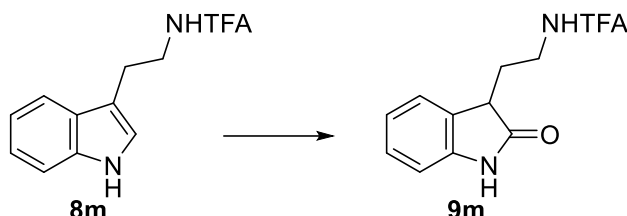
Prepared according to the general electrochemical procedure from methyl 3-(indol-3-yl)propanoate³ (**8k**, 47 mg, 0.23 mmol) and KBr (1 eq.). Purification by flash chromatography on silica gel (50% EtOAc in light petroleum) gave the *title compound* as a clear oil (44 mg, 0.20 mmol, 87%). ¹H NMR (400 MHz, CDCl₃) δ 9.18 (br s, 1 H, NH), 7.25-7.18 (m, 2 H, ArH), 7.05-7.00 (m, 1 H, ArH), 6.90 (d, *J* 7.6, 1 H, ArH), 3.63 (s, 3 H, Me), 2.55-2.45 (m, 1 H, CH₂), 2.43-2.35 (m, 1 H, CH₂), 2.34-2.22 (m, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 180.2, 173.5, 141.8, 128.8, 128.3, 124.3, 122.5, 110.1, 51.8, 45.0, 30.2, 25.6. NMR Spectroscopic data in accordance with previous reports.¹¹

Methyl 4-(2-oxoindolin-3-yl)butanoate (**9l**)



Prepared according to the general electrochemical procedure from methyl 4-(indol-3-yl)butanoate¹³ (**8l**, 50 mg, 0.23 mmol) and KBr (1 eq.). Purification by flash chromatography on silica gel (50% EtOAc in light petroleum) gave the *title compound* as a pale-yellow oil (36 mg, 0.15 mmol, 67%). **HRMS** (ESI) m/z calculated for $[\text{C}_{13}\text{H}_{15}\text{NO}_3 + \text{Na}]^+$ ($\text{M} + \text{Na}$)⁺ 256.0944, found 256.0944; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat): 3210, 2952, 1705, 1621, 1471, 1437, 1207, 753; **¹H NMR** (400 MHz, CDCl_3) δ 9.04 (br s, 1 H, NH), 7.23 (d, J 7.1, 1 H, ArH), 7.20-7.17 (m, 1 H, ArH), 7.02 (td, J 7.5, 1.1, 1 H, ArH), 6.90 (d, J 7.6, 1 H, ArH), 3.64 (s, 3 H, Me), 3.48 (t, J 6.0, 1 H, CH), 2.33 (t, J 7.5, 2 H, CH_2), 2.06-1.92 (m, 2 H, CH_2), 1.79-1.64 (m, 2 H, CH_2); **¹³C NMR** (100 MHz, CDCl_3) δ 180.5, 173.7, 141.8, 129.4, 128.1, 124.2, 122.5, 110.0, 51.7, 45.9, 34.0, 29.9, 21.3. NMR Spectroscopic data in accordance with previous reports.¹⁴

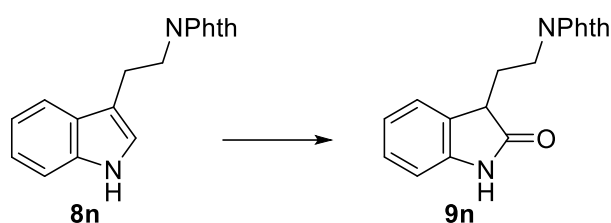
2,2,2-Trifluoro-*N*-(2-(2-oxoindolin-3-yl)ethyl)acetamide (**9m**)



Prepared according to the general electrochemical procedure from *N*-(2-(indol-3-yl)ethyl)-2,2,2-trifluoroacetamide¹⁵ (**8m**, 59 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash

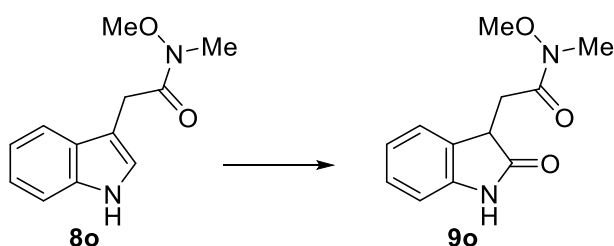
chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a colourless solid (44 mg, 0.16 mmol, 70%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.28 (br s, 1 H, NH), 8.17 (br s, 1 H, NH), 7.30-7.24 (m, 2 H, ArH), 7.10 (t, J 7.5, 1 H, ArH), 6.91 (d, J 7.7, 1 H, ArH), 3.84-3.74 (m, 1 H), 3.59-3.47 (m, 2 H), 2.43-2.34 (m, 1 H), 2.09-1.99 (m, 1 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 180.8, 157.6, 157.2, 140.8, 128.7, 128.6, 124.0, 123.2, 110.1, 45.3, 38.5, 29.0. NMR Spectroscopic data in accordance with previous reports.¹⁵

2-(2-(2-Oxoindolin-3-yl)ethyl)isoindoline-1,3-dione (9n)



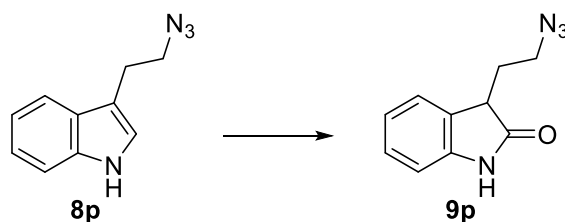
Prepared according to the general electrochemical procedure from 2-(2-(indol-3-yl)ethyl)isoindoline-1,3-dione¹⁶ (**8n**, 67 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a colourless solid (42 mg, 0.14 mmol, 60%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.69 (br s, 1 H, NH), 7.77-7.74 (m, 2 H, ArH), 7.66-7.62 (m, 2 H, ArH), 7.28 (d, J 7.4, 1 H, ArH), 7.08 (t, J 7.7, 1 H, ArH), 6.87 (t, J 7.5, 1 H, ArH), 6.82 (d, J 7.7, 1 H, ArH), 4.00-3.92 (m, 1 H, CH_2), 3.84-3.76 (m, 1 H, CH_2), 3.53 (t, J 6.0, 1 H, CH), 2.55-2.45 (m, 1 H, CH_2), 2.38-2.29 (m, 1 H, CH_2); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 179.5, 168.3, 141.7, 133.9, 132.1, 128.7, 128.1, 124.1, 123.2, 122.4, 110.1, 44.1, 35.2, 28.5. NMR Spectroscopic data in accordance with previous reports.¹⁷

N-Methoxy-*N*-methyl-2-(2-oxoindolin-3-yl)acetamide (9o)



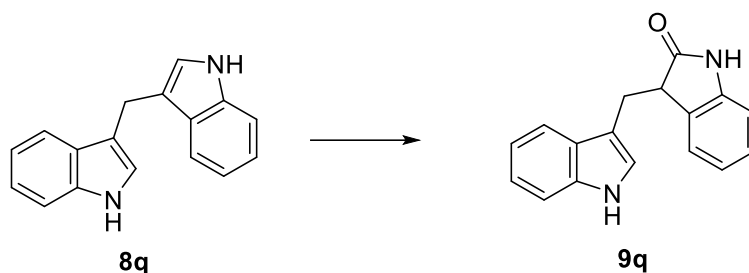
Prepared according to the general electrochemical procedure from 2-(indol-3-yl)-*N*-methoxy-*N*-methylacetamide⁸ (**8o**, 42 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a yellow solid (23 mg, 0.10 mmol, 43%). **mp** 101-103 °C; **HRMS** (ESI) *m/z* calculated for [C₁₂H₁₄N₂O₃ + Na]⁺ (*M* + Na)⁺ 257.0897, found 257.0896; **ν_{max}/cm⁻¹** (neat): 3268, 3209, 2917, 1712, 1690, 1652, 1622, 1471, 1419, 1386, 1335, 1231, 1178, 1096, 987, 925, 739, 669; **¹H NMR** (400 MHz, CDCl₃) δ 8.29 (br s, 1 H, NH), 7.29-7.26 (m, 1 H, ArH), 7.22-7.17 (m, 1 H, ArH), 6.99 (td, *J* 7.5, 0.9, 1 H, ArH), 6.87 (d, *J* 7.9, 1 H, ArH), 3.92 (dd, *J* 8.7, 3.7, 1 H, CH), 3.68 (s, 3 H, Me), 3.29-3.22 (m, 1 H, CH₂), 3.21 (s, 3 H, Me), 2.93 (dd, *J* 17.0, 8.7, 1 H, CH₂); **¹³C NMR** (100 MHz, CDCl₃) δ 179.8, 171.7, 141.6, 129.8, 128.2, 124.7, 122.5, 109.7, 61.4, 42.1, 33.3, 32.5.

3-(2-Azidoethyl)indolin-2-one (**9p**)



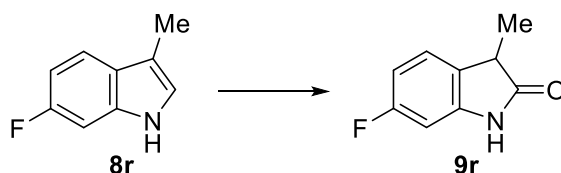
Prepared according to the general electrochemical procedure from 3-(2-azidoethyl)indole¹⁸ (**8p**, 43 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (50% EtOAc in light petroleum) gave the *title compound* as a pale-yellow oil (14 mg, 0.07 mmol, 30%). **¹H NMR** (400 MHz, CDCl₃) δ 8.56 (br s, 1 H, NH), 7.22 (d, *J* 7.5, 2 H, ArH), 7.07-7.02 (m, 1 H, ArH), 6.92 (d, *J* 7.6, 1 H, ArH), 3.58 (t, *J* 6.5, 1 H, CH), 3.55-3.43 (m, 2 H, CH₂), 2.29-2.16 (m, 2 H, CH₂); **¹³C NMR** (100 MHz, CDCl₃) δ 179.7, 141.5, 128.52, 128.46, 124.2, 122.7, 110.1, 48.3, 43.3, 29.8. NMR Spectroscopic data in accordance with previous reports.¹⁷

3-((Indol-3-yl)methyl)indolin-2-one (9q)



Prepared according to the general electrochemical procedure from di(indol-3-yl)methane (**8q**, 42 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (50% EtOAc in light petroleum) to afford the *title compound* as a yellow solid (31 mg, 0.12 mmol, 51%). $^1\text{H NMR}$ (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 10.00 (br s, 1 H, NH), 9.28 (br s, 1 H, NH), 7.63 (d, J 8.0, 1 H, ArH), 7.35 (dt, J 8.0, 1.0, 1 H, ArH), 7.11-6.93 (m, 5 H, ArH), 6.84-6.78 (m, 2 H, ArH), 3.78 (dd, J 8.2, 4.7, 1 H, CH), 3.54 (ddd, J 14.4, 5.0, 0.8, 1 H, CH_2), 3.16 (dd, J 14.5, 8.6, 1 H, CH_2); $^{13}\text{C NMR}$ (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 179.3, 143.7, 137.5, 130.9, 128.6, 128.4, 125.4, 124.3, 122.1, 121.9, 119.5, 119.4, 112.3, 112.1, 109.9, 47.1, 26.8. NMR Spectroscopic data in accordance with previous reports.¹⁹

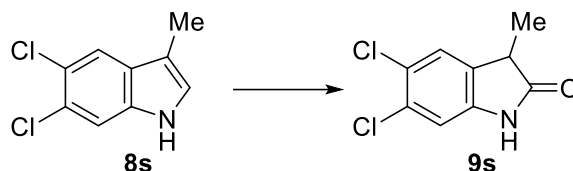
6-Fluoro-3-methylindolin-2-one (9r)



Prepared according to the general electrochemical procedure from 6-fluoro-3-methylindole⁶ (**8r**, 34 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a yellow solid (23 mg, 0.14 mmol, 61%). **mp** 120-122 °C; **HRMS** (ESI) m/z calculated for $[\text{C}_9\text{H}_8\text{FNO} - \text{H}]^-$ ($\text{M} - \text{H}$)⁻ 164.0517, found 164.0514; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat): 3204, 2971, 2937, 2880, 1723, 1671, 1615, 1499, 1456, 1378, 1337, 1238, 1212, 1131, 1098, 1003, 960, 844, 805, 787, 766, 732, 707, 667; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.38 (br s, 1 H, NH), 7.13 (dd, J 8.1, 5.3, 1 H, ArH), 6.74-6.65 (m, 2 H,

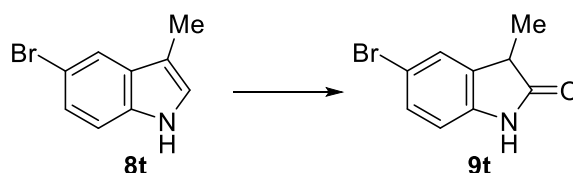
ArH), 3.43 (q, J 7.6, 1 H, CH), 1.48 (d, J 7.6, 3 H, Me); ^{13}C NMR (100 MHz, CDCl_3) δ 182.3, 162.8 (d, J : 244, 1 C), 142.6 (d, J : 12, 1 C), 126.7 (d, J : 3, 1 C), 124.7 (d, J : 10, 1 C), 108.8 (d, J : 22, 1 C), 98.6 (d, J : 27, 1 C), 40.8, 15.4; ^{19}F NMR (376 MHz, CDCl_3) δ -112.9.

5,6-Dichloro-3-methylindolin-2-one (9s)



Prepared according to the general electrochemical procedure from 5,6-dichloro-3-methylindole (8s, 46 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (8s, 40% EtOAc in light petroleum) gave the *title compound* as a colourless solid (36 mg, 0.17 mmol, 73%). **mp** 183-185 °C; **HRMS** (ESI) m/z calculated for $[\text{C}_9\text{H}_7\text{Cl}_2\text{NO} - \text{H}]^-$ ($\text{M} - \text{H}$)⁻ 213.9832, found 213.9829; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat): 3224, 2981, 1717, 1688, 1619, 1470, 1360, 1308, 1236, 1218, 1166, 1106, 1008, 945, 883, 851, 802, 723, 697, 636, 619; ^1H NMR (400 MHz, CDCl_3) δ 9.05 (br s, 1 H, NH), 7.28 (s, 1 H, ArH), 7.02 (s, 1 H, ArH), 3.49-3.42 (m, 1 H, CH), 1.49 (d, J 7.6, 3 H, Me); ^{13}C NMR (100 MHz, CDCl_3) δ 181.0, 140.8, 131.8, 131.3, 126.1, 125.9, 111.9, 41.0, 15.2. NMR Spectroscopic data in accordance with previous reports.²⁰

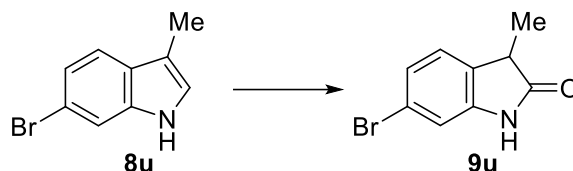
5-Bromo-3-methylindolin-2-one (9t)



Prepared according to the general electrochemical procedure from 5-bromo-3-methylindole³ (8t, 48 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a pale-yellow solid (43 mg, 0.19 mmol, 83%). ^1H NMR (400 MHz, CDCl_3) δ 8.91 (br s, 1 H, NH), 7.35-7.32 (m, 2 H, ArH),

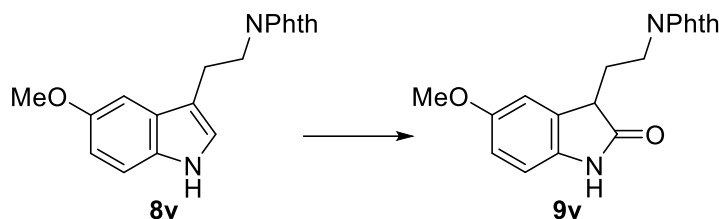
6.79 (d, J 8.5, 1 H, ArH), 3.47 (q, J 7.7, 1 H, CH), 1.49 (d, J 7.6, 3 H, Me); ^{13}C NMR (100 MHz, CDCl_3) δ 181.1, 140.4, 133.4, 130.9, 127.2, 115.2, 111.4, 41.3, 15.2. NMR Spectroscopic data in accordance with previous reports.²¹

6-Bromo-3-methylindolin-2-one (9u)



Prepared according to the general electrochemical procedure from 6-bromo-3-methylindole²² (**8u**, 48 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) to afford the *title compound* as a pale-yellow solid (40 mg, 0.18 mmol, 77%). **HRMS** (ESI) m/z calculated for $[\text{C}_9\text{H}_8\text{BrNO} + \text{Na}]^+$ ($\text{M} + \text{Na}$)⁺ 247.9681, found 247.9681; ^1H NMR (400 MHz, CDCl_3) δ 9.32 (br s, 1 H, NH), 7.17 (dd, J 7.9, 1.6, 1 H, ArH), 7.09 (d, J 1.5, 1 H, ArH), 7.07 (d, J 8.0, 1 H, ArH), 3.42 (q, J 7.6, 1 H, CH), 1.48 (d, J 7.6, 3 H, Me); ^{13}C NMR (100 MHz, CDCl_3) δ 181.4, 142.6, 130.2, 125.4, 125.2, 121.4, 113.3, 40.9, 15.2. NMR Spectroscopic data in accordance with previous reports.²¹

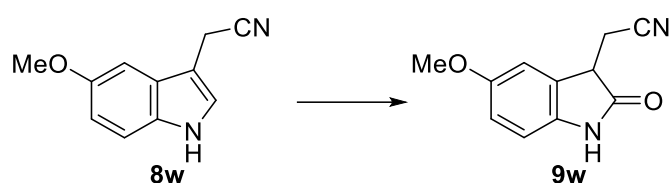
2-(2-(5-Methoxy-2-oxoindolin-3-yl)ethyl)isoindoline-1,3-dione (9v)



Prepared according to the general electrochemical procedure from 2-(2-(5-methoxy-1H-indol-3-yl)ethyl)isoindoline-1,3-dione¹⁶ (**8v**, 74 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a pale-yellow solid (18 mg, 0.05 mmol, 23%). **mp** 207-209 °C; **HRMS** (ESI) m/z calculated for $[\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_4 + \text{H}]^+$ ($\text{M} + \text{H}$)⁺ 337.1183, found 337.1183; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat): 3188, 2927, 1772,

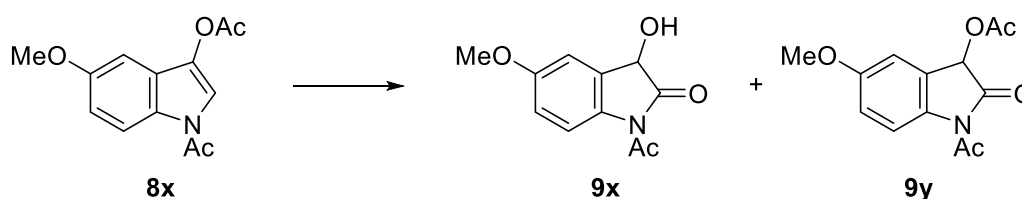
1697, 1598, 1485, 1468, 1401, 1312, 1262, 1210, 1045, 1033, 1004, 876, 803, 718, 656; ^1H NMR (400 MHz, CDCl_3); 8.17 (br s, 1 H, NH), 7.76-7.71 (m, 2 H, ArH), 7.67-7.63 (m, 2 H, ArH), 6.86 (d, J 2.0, 1 H, ArH), 6.69 (d, J 8.5, 1 H, ArH), 6.54 (dd, J 8.5, 2.5, 1 H, ArH), 4.01-3.92 (m, 1 H, CH_2), 3.80-3.73 (m, 1 H, CH_2), 3.65 (s, 3 H, Me), 3.52 (t, J 5.8, 1 H, CH), 2.59-2.49 (m, 1 H, CH_2), 2.38-2.29 (m, 1 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 179.1, 168.2, 155.8, 134.9, 133.9, 132.1, 130.0, 123.2, 112.8, 110.9, 110.4, 55.7, 44.5, 35.1, 28.2.

2-(5-Methoxy-2-oxoindolin-3-yl)acetonitrile (9w)



Prepared according to the general electrochemical procedure from 2-(5-methoxy-1H-indol-3-yl)acetonitrile (**8w**, 42 mg, 0.23 mmol) and KBr (1 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compound* as a yellow oil (14 mg, 0.07 mmol, 30%). ^1H NMR (400 MHz, CDCl_3) δ 8.35 (br s, 1 H, NH), 7.09 (br s, 1 H, ArH), 6.87-6.80 (m, 2 H, ArH), 3.80 (s, 3 H, Me), 3.71-3.66 (m, 1 H, CH), 3.09 (dd, J 16.9, 4.7, 1 H, CH_2), 2.75 (dd, J 16.9, 8.9, 1 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 176.4, 156.4, 134.6, 127.6, 117.2, 114.3, 111.6, 110.9, 56.0, 42.4, 19.1. NMR Spectroscopic data in accordance with previous reports.²³

1-Acetyl-3-hydroxy-5-methoxyindolin-2-one (9x) and 1-acetyl-3-hydroxy-5-methoxyindolin-2-one (9y)

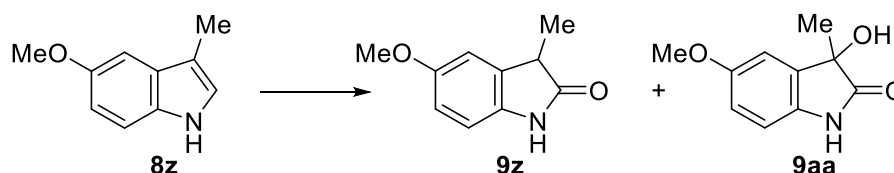


Prepared according to the general electrochemical procedure from 5-methoxy-indol-3-yl acetate²⁴ (**8x**, 42 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (50% EtOAc in light petroleum) gave the *title compounds* **9x** and **9y**

9x; yellow solid (15 mg, 0.09 mmol, 29%). **mp** 164-166 °C; **HRMS** (ESI) *m/z* calculated for [C₁₁H₁₁NO₄ – H][–] (M – H)[–] 220.0615, found 220.0608; **v**_{max}/cm^{–1} (neat): 3286, 2968, 1717, 1628, 1488, 1471, 1456, 1386, 1329, 1314, 1276, 1250, 1200, 1132, 1100, 1010, 928, 870, 837, 808, 766, 728, 656; **¹H NMR** (400 MHz, (CD₃)₂CO) δ 8.38 (d, *J* 9.0, 1 H, ArH), 7.30 (dd, *J* 9.0, 2.9, 1 H, ArH), 7.12 (d, *J* 2.8, 1 H, ArH), 6.26 (d, *J* 9.0, 1 H, OH), 5.50 (d, *J* 9.0, 1 H, CH), 3.85 (s, 3 H, Me), 2.38 (s, 3 H, Me); **¹³C NMR** (100 MHz, (CD₃)₂CO) δ 196.6, 169.7, 157.4, 148.4, 126.2, 123.9, 119.8, 106.1, 82.9, 56.2, 23.6.

9y; yellow solid (31 mg, 0.12 mmol, 51%). **mp** 107-109 °C; **HRMS** (ESI) *m/z* calculated for [C₁₃H₁₃NO₅ + Na]⁺ (M + Na)⁺ 286.0686, found 286.0684; **v**_{max}/cm^{–1} (neat): 3022, 2844, 1746, 1728, 1666, 1489, 1438, 1385, 1369, 1324, 1274, 1222, 1154, 1019, 943, 920, 883, 835, 778, 728, 655; **¹H NMR** (400 MHz, (CD₃)₂CO) δ 8.34 (d, *J* 9.0, 1 H, ArH), 7.32 (dd, *J* 9.0, 2.7, 1 H, ArH), 7.16 (d, *J* 2.8, 1 H, ArH), 6.47 (s, 1 H, CH), 3.87 (s, 3 H, Me), 2.28 (s, 3 H, Me), 2.19 (s, 3 H, Me); **¹³C NMR** (100 MHz, (CD₃)₂CO) δ 192.6, 169.7, 169.3, 157.6, 148.5, 126.0, 124.3, 119.8, 106.2, 81.4, 56.2, 23.5, 20.5.

5-Methoxy-3-methylindolin-2-one (9z) and 3-hydroxy-5-methoxy-3-methylindolin-2-one (9aa)



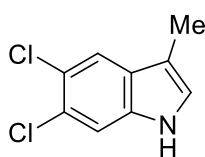
Prepared according to the general electrochemical procedure from 5-methoxy-3-methylindole³ (**8z**, 37 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave the *title compounds* **9z** and **9aa**

9z; pale-yellow solid (13 mg, 0.07 mmol, 32%). ¹H NMR (400 MHz, CDCl₃) δ 8.59 (br s, 1 H, NH), 6.84-6.79 (m, 2 H, ArH), 6.74 (dd, *J* 8.5, 2.5, 1 H, ArH), 3.79 (s, 3 H, Me), 3.45 (q, *J* 7.6, 1 H, CH), 1.49 (d, *J* 7.6, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ 181.3, 156.0, 134.7, 132.8, 112.5, 111.3, 110.1, 55.9, 41.7, 15.4. NMR Spectroscopic data in accordance with previous reports.²¹

9aa; pale-brown solid (6 mg, 0.03 mmol, 14%). HRMS (ESI) *m/z* calculated for [C₁₀H₁₁NO₃ + Na]⁺ (*M* + Na)⁺ 216.0631, found 216.0627; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (br s, 1 H, NH), 7.01-6.99 (m, 1 H, ArH), 6.79 (d, *J* 1.4, 2 H, ArH), 3.80 (s, 3 H, Me), 2.99 (br s, 1 H, OH), 1.61 (s, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ 180.5, 156.5, 133.1, 133.0, 114.7, 111.0, 110.7, 74.5, 56.0, 25.1. NMR Spectroscopic data in accordance with previous reports.²⁵

Indole derivatives

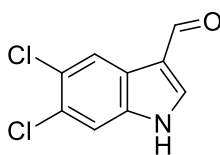
5,6-Dichloro-3-methylindole (**8s**)



To a cold stirring solution of LiAlH₄ (2 eq.) in THF (2 M, 0.51 mL) was added dropwise a solution of 5,6-dichloroindole-3-carbaldehyde (**13**, 110 mg, 0.51 mmol) in dry THF (3 mL). The reaction mixture was allowed to warm up to rt and stirred at rt for 20 h. The reaction mixture was quenched (H₂O) and stirred at rt for 30 min. The reaction mixture was extracted with EtOAc (3 x 20), dried (Na₂SO₄), filtered through celite and concentrated under reduce pressure. Purification by flash chromatography on silica gel (30% EtOAc in light petroleum)

gave the *title compound* as a colourless solid (85 mg, 0.43 mmol, 83%). **mp** 86-88 °C; **HRMS** (ESI) m/z calculated for $[C_9H_7Cl_2N - H]^- (M - H)^-$ 197.9883, found 197.9877; $\nu_{\max}/\text{cm}^{-1}$ (neat): 3431, 2920, 1740, 1616, 1570, 1449, 1399, 1381, 1323, 1280, 1230, 1112, 1095, 1069, 952, 841, 837, 803, 655; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.58 (br s, 1 H, NH), 7.61 (s, 1 H, ArH), 7.41 (s, 1 H, ArH), 6.98-6.97 (m, 1 H, ArH), 2.27 (s, 3 H, Me); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 135.1, 128.3, 125.8, 123.7, 123.4, 120.1, 112.5, 111.8, 9.6.

5,6-Dichloroindole-3-carbaldehyde (13)



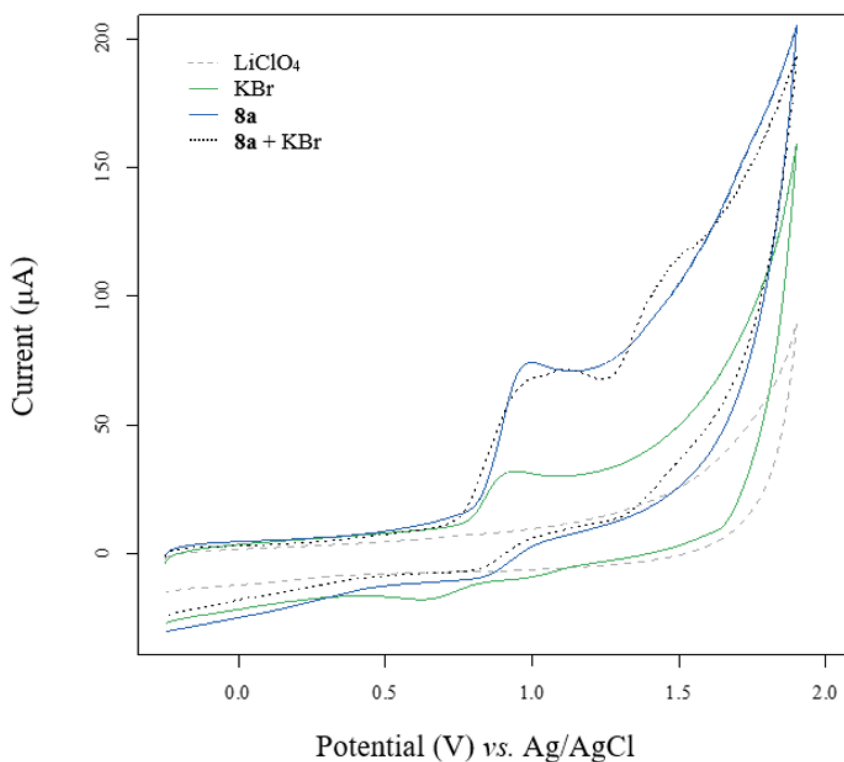
To a cold stirring solution of 5,6-dichloroindole (150 mg, 0.81 mmol) in DMF (1 mL) was added dropwise phosphorus oxychloride (1.4 eq.). The reaction mixture was allowed to warm up to rt and it was stirred at rt for 3 hours. The reaction mixture was quenched (H_2O) and the pH was adjusted (pH 7-8) with NaOH (1 M). Then, the reaction mixture was stirred at 70 °C for 30 minutes. The reaction mixture was allowed to cool down to rt and the precipitate was filtered, washed with cold water and dried (desiccator) to afford *title compound* as a pale-pink powder (150 mg, 0.70 mmol, 87%). **mp** 288-290 °C (charred); **HRMS** (ESI) m/z calculated for $[C_9H_5Cl_2NO - H]^- (M - H)^-$ 211.9675, found 211.9672; $\nu_{\max}/\text{cm}^{-1}$ (neat): 3117, 3025, 2886, 2820, 1636, 1619, 1569, 1527, 1482, 1444, 1423, 1389, 1306, 1265, 1244, 1145, 1114, 1084, 937, 883, 846, 820, 696, 657; **$^1\text{H NMR}$** (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 12.34 (s, 1 H, NH), 9.93 (s, 1 H, CH), 8.41 (s, 1 H, ArH), 8.23 (s, 1 H, ArH), 7.79 (s, 1 H, ArH); **$^{13}\text{C NMR}$** (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ 185.2, 140.2, 135.9, 125.7, 124.8, 124.0, 121.5, 117.3, 114.3.

Mechanistic studies

Procedures for cyclic voltammetry

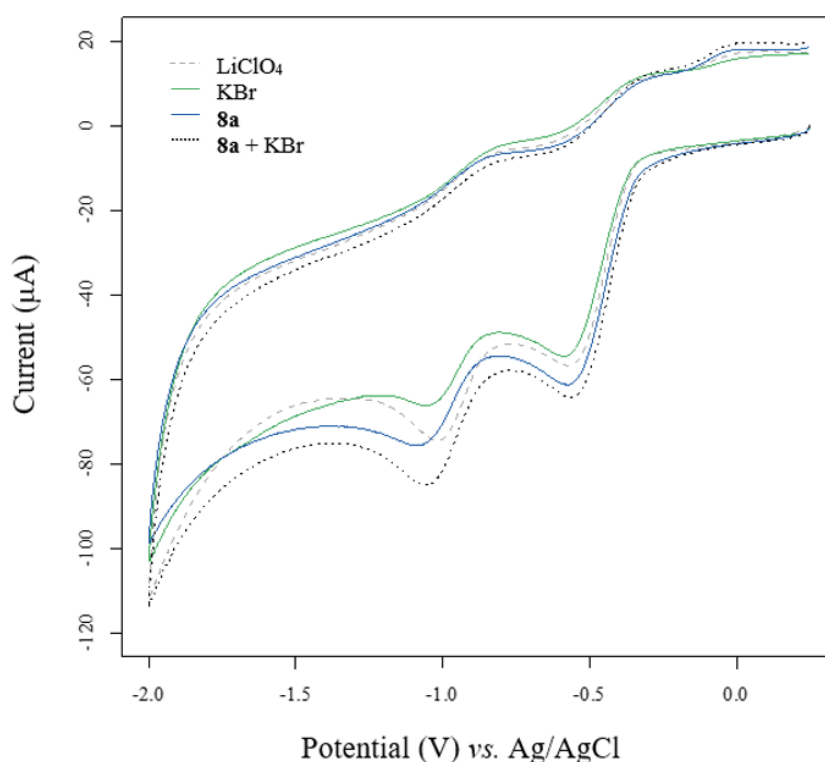
Experiment 1: Determination of oxidation potential of **8a** using a three-electrode cell

Cyclic voltammetry experiments were conducted with a CH660 potentiostat, with a three-electrode cell (**Figure S3**). The redox behaviour of the reaction mixture [3-methylindole (**8a**, blue line), KBr (green line) and a mixture of KBr and 3-methylindole (**8a**, dotted black line)] was studied in MeCN-H₂O (5:1) containing LiClO₄ (0.1 M) as the supporting electrolyte at room temperature. The electrochemical cell was made up of a BASi platinum wire auxiliary electrode (7.5 cm), a BASi glassy carbon working electrode (\varnothing 3.0 mm) and a BASi Ag/AgCl (3 M NaCl) reference electrode (**Figure S2**). The substrate concentration was 1 mM, and the potential was scanned from -0.25 V to 1.9 V with a scan rate of 0.1 Vs⁻¹. All experiments were done in triplicate.



Experiment 2: Determination of reduction potential of **8a** using a three-electrode cell

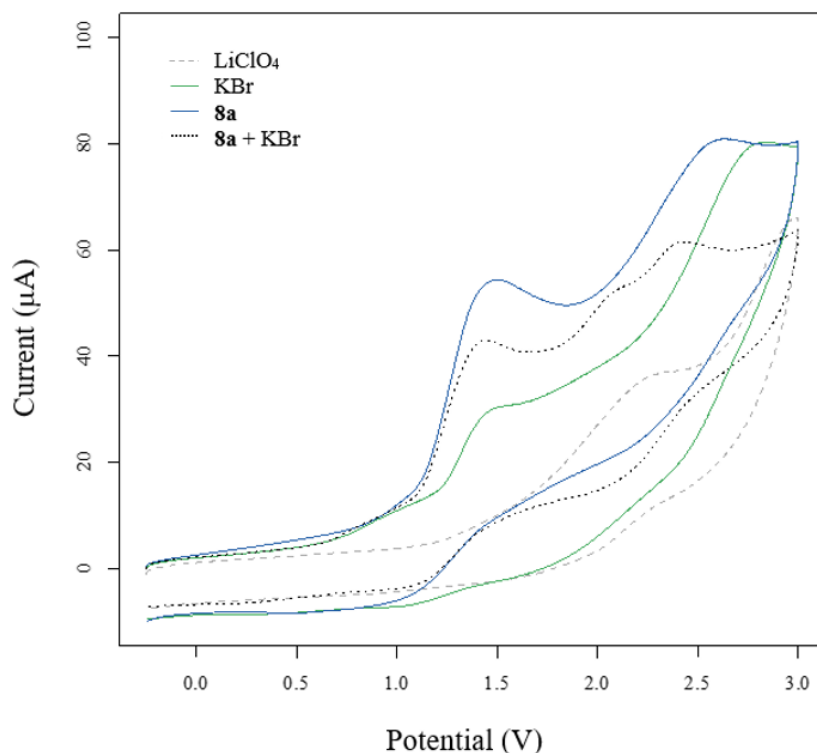
Cyclic voltammetry experiments were conducted with a CH660 potentiostat, with a three-electrode cell (**Figure S3**). The redox behaviour of the reaction mixture [3-methylindole (**8a**, blue line), KBr (green line) and a mixture of KBr and 3-methylindole (**8a**, dotted black line)] was studied in MeCN-H₂O (5:1) containing LiClO₄ (0.1 M) as the supporting electrolyte at room temperature. The electrochemical cell was made up of a BASi platinum wire auxiliary electrode (7.5 cm), a BASi glassy carbon working electrode (\varnothing 3.0 mm) and a BASi Ag/AgCl (3 M NaCl) reference electrode (**Figure S2**). The substrate concentration was 1 mM, and the potential was scanned from 0.25 V to -2.0 V with a scan rate of 0.1 Vs⁻¹. All experiments were done in triplicate.



Experiment 3: Determination of oxidation potential of **8a** using a two-electrode cell

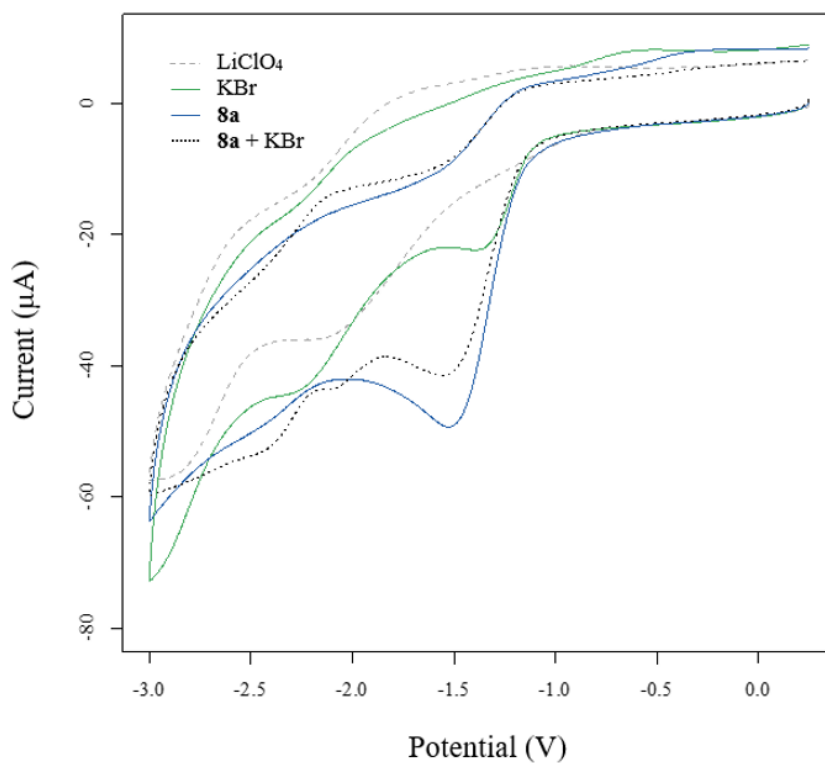
Cyclic voltammetry experiments were conducted with a CH660 potentiostat, with a two-electrode cell (**Figure S4**). The redox behaviour of the reaction mixture [3-methylindole (**8a**, blue line), KBr (green line) and a mixture of KBr and 3-methylindole (**8a**, dotted black line)]

was studied in MeCN-H₂O (5:1) containing LiClO₄ (0.1 M) as the supporting electrolyte at room temperature. The electrochemical cell was made up of BASi glassy carbon electrodes (\varnothing 3.0 mm) used as working and counter/reference electrodes (**Figure S2**). The substrate concentration was 1 mM, and the potential was scanned from -0.25 V to 3.0 V with a scan rate of 0.1 Vs⁻¹. All experiments were done in triplicate.



Experiment 4: Determination of reduction potential of **8a** using a two-electrode cell

Cyclic voltammetry experiments were conducted with a CH660 potentiostat, with a two-electrode cell (**Figure S4**). The redox behaviour of the reaction mixture [3-methylindole (**8a**, blue line), KBr (green line) and a mixture of KBr and 3-methylindole (**8a**, dotted black line)] was studied in MeCN-H₂O (5:1) containing LiClO₄ (0.1 M) as the supporting electrolyte at room temperature. The electrochemical cell was made up of BASi glassy carbon electrodes (\varnothing 3.0 mm) used as working and counter/reference electrodes (**Figure S2**). The substrate concentration was 1 mM, and the potential was scanned from 0.25 V to -3.0 V with a scan rate of 0.1 Vs⁻¹. All experiments were done in triplicate.



Set-up for cyclic voltammetry



Figure S2, Electrodes used for cyclic voltammetry; from left to right, BASi Ag/AgCl (3 M NaCl) reference electrode, 2 x BASi glassy carbon electrodes (\varnothing 3.0 mm) and a BASi platinum wire auxiliary electrode (7.5 cm).



Figure S3, Three-electrode cell made up of a BASi Ag/AgCl (3 M NaCl) reference electrode, a BASi glassy carbon working electrode (\varnothing 3.0 mm) and a BASi platinum wire auxiliary electrode (7.5 cm).

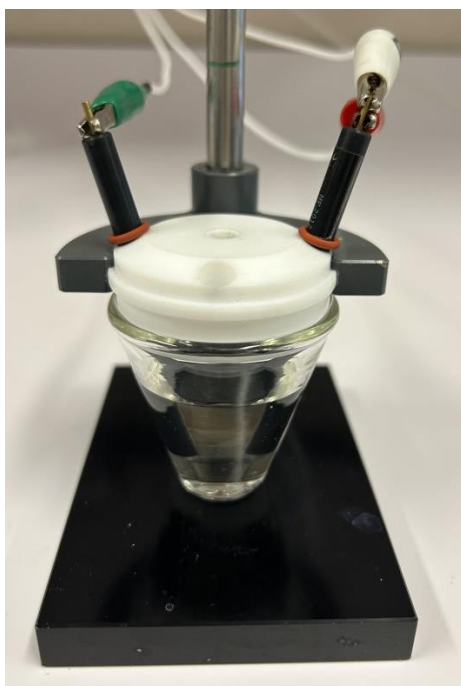
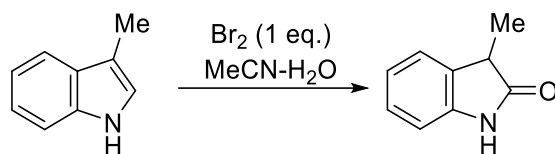
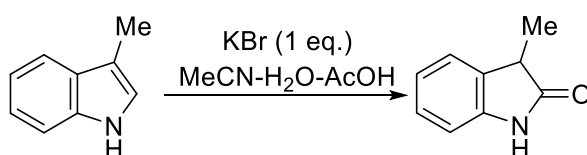


Figure S4, Two-electrode cell made up of BASi glassy carbon electrodes (\varnothing 3.0 mm) used as working and counter/reference electrodes.

Active brominating species investigation

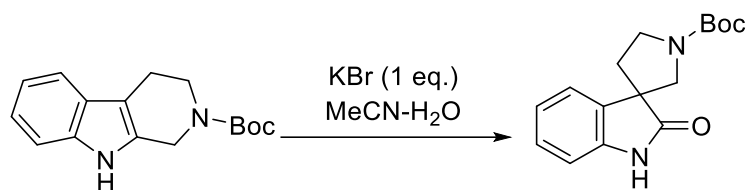


To a stirring solution of 3-methylindole (**8a**, 30 mg, 0.23 mmol) in MeCN-H₂O (5:1, 3 mL) was added dropwise elemental bromine (1 eq.). The reaction mixture was stirred at rt for 5 minutes. Then, sodium thiosulfate (sat. sol., 10 mL) was added and the mixture was extracted with EtOAc (3 x 20 mL). The organic extracts were combined, dried (Na₂SO₄) and concentrated under reduced pressure. Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave 3-methylindolin-2-one as a pale-yellow powder (**9a**, 22 mg, 0.15 mmol, 65%). NMR Spectroscopic data as previously reported.

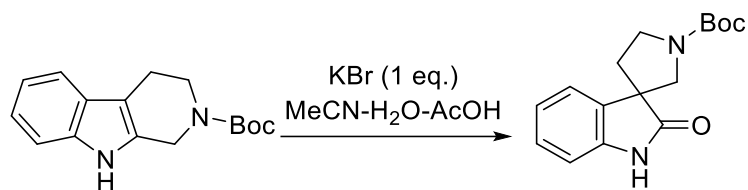


With no precautions to exclude air or moisture, the ElectraSyn vial (5 mL) with a stirrer bar was charged KBr (1 eq., 27 mg), 3-methylindole (**8a**, 30 mg, 0.23 mmol) and a mixture of MeCN-H₂O-AcOH (15:2.4:2, 3 mL). The ElectraSyn vial cap equipped with an anode (glassy carbon) and cathode (glassy carbon) were inserted into the mixture. The reaction mixture was electrolysed with stirring at a constant current of 2.5 mA until 2 F/mol had been consumed. Upon completion, the ElectraSyn vial cap was removed, and the electrodes rinsed with EtOAc and water. The resulting mixture was diluted with EtOAc (10 mL) and sodium thiosulfate (sat. sol. 10 mL) was added. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic extracts were combined, dried (Na₂SO₄), filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave 3-

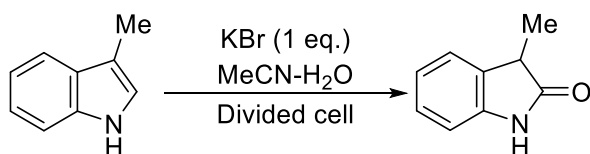
methylindolin-2-one as a pale-yellow solid (19 mg, 0.14 mmol, 56%). NMR Spectroscopic data as previously reported.



With no precautions to exclude air or moisture, the ElectraSyn vial (5 mL) with a stirrer bar was charged KBr (1 eq., 27 mg), *tert*-butyl 1,3,4,9-tetrahydro-pyrido[3,4-*b*]indole-2-carboxylate²⁶ (**11**, 63 mg, 0.23 mmol) and a mixture of MeCN-H₂O (5:1, 3 mL). The ElectraSyn vial cap equipped with an anode (glassy carbon) and cathode (glassy carbon) were inserted into the mixture. The reaction mixture was electrolysed with stirring at a constant current of 2.5 mA until 2 F/mol had been consumed. Upon completion, the ElectraSyn vial cap was removed, and the electrodes rinsed with EtOAc and water. The resulting mixture was diluted with EtOAc (10 mL) and sodium thiosulfate (sat. sol. 10 mL) was added. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic extracts were combined, dried (Na₂SO₄), filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (30% EtOAc in light petroleum) gave the *tert*-Butyl 2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate as a pale-yellow oil (**12**, 12 mg, 0.04 mmol, 18%); mixture of two rotational isomers (~1:0.7). **HRMS** (ESI) *m/z* calculated for [C₁₆H₂₀N₂O₃ + Na]⁺ (M + Na)⁺ 311.1366 found 311.1365; **¹H NMR** (400 MHz, CDCl₃) δ 9.55 (br s, 0.58 H, NH), 9.47 (br s, 0.40 H, NH), 7.25-7.15 (m, 2 H, ArH), 7.08-7.01 (m, 1 H, ArH), 7.00-6.95 (m, 1 H, ArH), 3.92-3.69 (m, 3 H), 3.67-3.55 (m, 1 H), 2.47-2.38 (m, 1 H), 2.15-2.02 (m, 1 H), 1.49 (d, *J* 24.2, 9 H, 3 x Me); **¹³C NMR** (100 MHz, CDCl₃) δ 180.8, 180.4, 154.6, 140.5, 140.4, 133.2, 132.7, 128.5, 123.0, 122.8, 110.3, 80.0, 79.9, 54.4, 53.9, 53.5, 52.6, 45.6, 45.3, 36.4, 35.6, 28.6, 28.5. NMR Spectroscopic data in accordance with previous reports.²⁷



With no precautions to exclude air or moisture, the ElectraSyn vial (5 mL) with a stirrer bar was charged KBr (1 eq., 27 mg), *tert*-butyl 1,3,4,9-tetrahydro-pyrido[3,4-*b*]indole-2-carboxylate²⁶ (**11**, 63 mg, 0.23 mmol) and a mixture of MeCN-H₂O-AcOH (15:2.4:2, 3 mL). The ElectraSyn vial cap equipped with an anode (glassy carbon) and cathode (glassy carbon) were inserted into the mixture. The reaction mixture was electrolysed with stirring at a constant current of 2.5 mA until 2 F/mol had been consumed. Upon completion, the ElectraSyn vial cap was removed, and the electrodes rinsed with EtOAc and water. The resulting mixture was diluted with EtOAc (10 mL) and sodium thiosulfate (sat. sol. 10 mL) was added. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic extracts were combined, dried (Na₂SO₄), filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave *tert*-butyl 2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate as a pale-yellow oil (**12**, 53 mg, 0.18 mmol, 80%). NMR Spectroscopic data as previously reported.



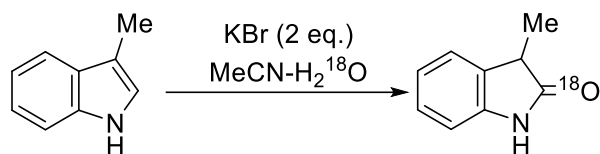
With no precautions to exclude air or moisture, each of the compartments of the IKA Pro-Divide with a stirrer bar were charged with KBr (1 eq., 27 mg) and a mixture of MeCN-H₂O (5:1, 3 mL). The cell was equipped with an anode (glassy carbon) and cathode (glassy carbon). The reaction mixture was electrolysed with stirring at a constant current of 2.5 mA for 2 min, after this, the reaction was stopped and 3-methylindole (**8a**, 30 mg, 0.23 mmol) was added. The vial cap was replaced, and the mixture electrolysed at 2.5 mA until 2 F/mol had been consumed.

Upon completion, the ElectraSyn vial cap was removed, and the electrodes rinsed with EtOAc and water. The resulting mixture was diluted with EtOAc (10 mL) and sodium thiosulfate (sat. sol. 10 mL) was added. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic extracts were combined, dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave 3-methylindolin-2-one as a pale-yellow solid (21 mg, 0.14 mmol, 62%). NMR Spectroscopic data as previously reported.



Figure S5, IKA ElectraSyn 2.0 and an ElectraSyn Pro-divide fitted with a glass frit (pore size 10-16 μm) and ElectraSyn glassy carbon electrodes (4 x 0.8 x 0.2 cm).

Labelling experiments



With no precautions to exclude air or moisture, the ElectraSyn vial (5 mL) with a stirrer bar was charged with KBr (2 eq., 55 mg, 0.46 mmol) and a mixture of MeCN-H₂¹⁸O (5:1, 3 mL, 10% ¹⁸O-water). The ElectraSyn vial cap equipped with an anode (glassy carbon) and cathode (glassy carbon) were inserted into the mixture. The reaction mixture was electrolysed with stirring at a constant current of 2.5 mA for 2 min, after this, the reaction was stopped and the 3-methylindole (**8a**, 30 mg, 0.23 mmol) was added. The vial cap was replaced, and the mixture electrolysed at 2.5 mA until 2 F/mol had been consumed. Upon completion, the ElectraSyn vial cap was removed, and the electrodes rinsed with EtOAc and water. The resulting mixture was diluted with EtOAc (10 mL) and sodium thiosulfate (sat. sol. 10 mL) was added. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic extracts were combined, dried (Na₂SO₄), filtered and concentrated under reduced pressure. purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave 3-methylindolin-2-one-¹⁸O as a pale-yellow solid (**9a-¹⁸O**, 20 mg, 0.14 mmol, 59%); Mixture of ¹⁶O : ¹⁸O (~9:1). **HRMS** (ESI) *m/z* calculated for [C₉H₉NO + Na]⁺ (M + Na)⁺ 170.0576 found 170.0576 (ESI) *m/z* calculated for [C₉H₉N¹⁸O + Na]⁺ (M + Na)⁺ 172.0619 found 172.0659; **¹H NMR** (400 MHz, CDCl₃) δ 9.13 (br s, 1 H, NH), 7.21 (t, *J* 7.5, 2 H, ArH), 7.03 (t, *J* 7.5, 1 H, ArH), 6.92 (d, *J* 7.6, 1 H, ArH), 3.47 (q, *J* 7.6, 1 H, CH), 1.50 (s, 3 H, Me). **¹³C NMR** (100 MHz, CDCl₃) δ 181.8, 141.4, 131.4, 128.0, 123.9, 122.5, 109.9, 41.2, 15.3.

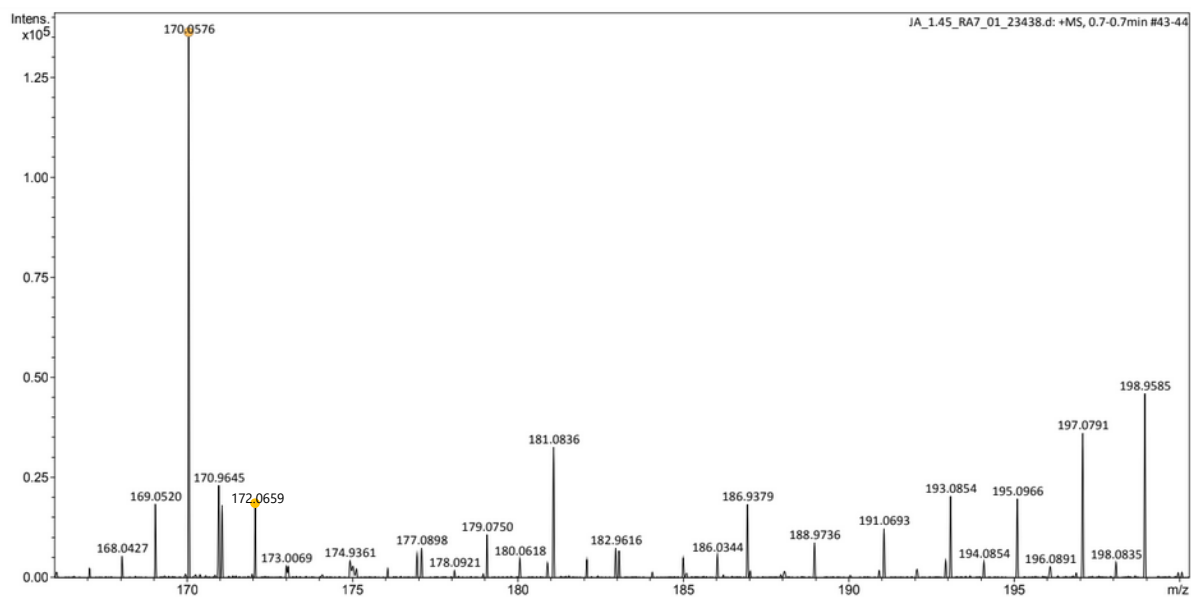
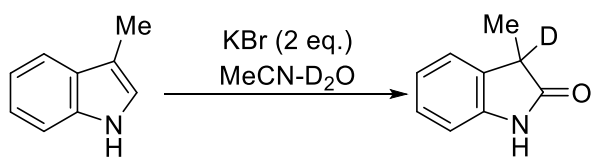


Figure S6, HRMS spectrum of 9a-18O; showing 9a $[M + Na]^+$ $m/z = 170.0576$ (calc. 170.0576) and 9a-18O $[M + Na]^+$ $m/z = 172.0659$ (calc. 172.0619) in a ~9:1 ratio.



With no precautions to exclude air or moisture, the ElectraSyn vial (5 mL) with a stirrer bar was charged with KBr (2 eq., 55 mg, 0.46 mmol) and a mixture of MeCN-D₂O (5:1, 3 mL). The ElectraSyn vial cap equipped with an anode (glassy carbon) and cathode (glassy carbon) were inserted into the mixture. The reaction mixture was electrolysed with stirring at a constant current of 2.5 mA for 2 min, after this, the reaction was stopped and the 3-methylindole (**8a**, 30 mg, 0.23 mmol) was added. The vial cap was replaced, and the mixture electrolysed at 2.5 mA until 2 F/mol had been consumed. Upon completion, the ElectraSyn vial cap was removed, and the electrodes rinsed with EtOAc and water. The resulting mixture was diluted with EtOAc (10 mL) and sodium thiosulfate (sat. sol. 10 mL) was added. The aqueous layer was extracted with EtOAc (3 x 10 mL). The organic extracts were combined, dried (Na₂SO₄), filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave 3-methylindolin-2-one-3-D as a pale-yellow solid (**9a-²H**, 26 mg, 0.17 mmol, 76%); Mixture of the 3-methylindolin-2-one-3-D and non-deuterated 3-methylindolin-2-one (D:H, ~8:2, by ¹H NMR integration). ¹H NMR (400 MHz, CDCl₃) δ 9.08 (br s, 1 H, NH), 7.21 (t, *J* 7.4, 2 H, ArH), 7.03 (t, *J* 7.5, 1 H, ArH), 6.92 (d, *J* 7.9, 1 H, ArH), 3.46 (q, *J* 7.6, 0.2 H, CH), 1.50 (s, 3 H, Me); ¹³C NMR (100 MHz, CDCl₃) δ 181.8, 141.5, 131.4, 128.0, 123.9, 122.5, 109.9, 41.2, 41.1, 40.9, 40.7, 15.3. NMR Spectroscopic data in accordance with previous reports.²⁸

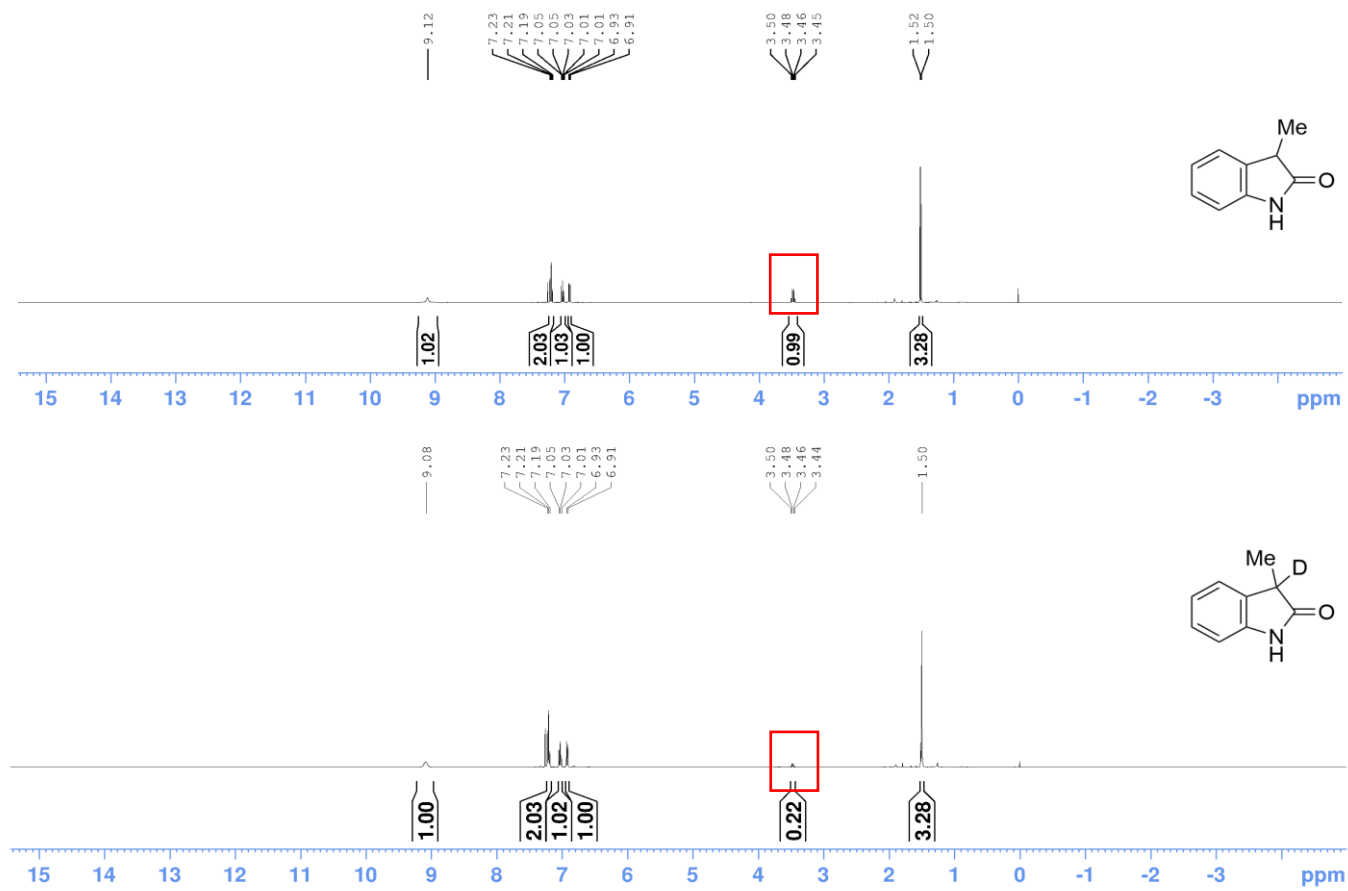
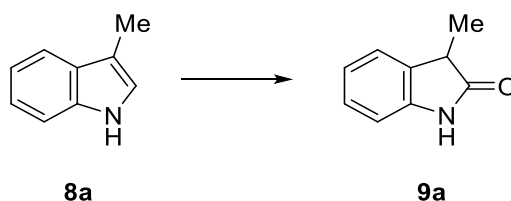


Figure S7, ^1H NMR of 3-methylindolin-2-one (top) and ^1H NMR spectra of 3-methylindolin-2-one-3-D (bottom)

Larger scale reaction



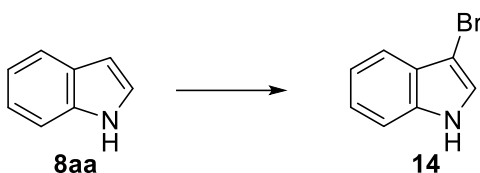
A current of 3.8 mA was used to maintain the reaction conditions identical to that of the smaller scale reaction (4 x 0.8 x 0.2 cm; 6.1 cm² area exposed to the electrolyte; 0.625 mAcm⁻²).

With no precautions to exclude air or moisture, the ElectraSyn vial (20 mL) with a stirrer bar was charged with KBr (2 eq., 357 mg, 3.0 mmol) and a mixture of MeCN-H₂O (5:1, 20 mL). The ElectraSyn vial cap equipped with an anode (glassy carbon) and cathode (glassy carbon) were inserted into the mixture (**Figure S8**). The reaction mixture was electrolysed with stirring at a constant current of 3.8 mA for 2 min, after this, the reaction was stopped and the 3-methylindole (**8a**, 198 mg, 1.5 mmol) was added. The vial cap was replaced, and the mixture electrolysed at 3.8 mA until 2 F/mol had been consumed. Upon completion, the ElectraSyn vial cap was removed, and the electrodes rinsed with EtOAc and water. The resulting mixture was diluted with EtOAc (25 mL) and sodium thiosulfate (sat. sol. 25 mL) was added. The aqueous layer was extracted with EtOAc (3 x 20 mL). The organic extracts were combined, dried (Na₂SO₄), filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (40% EtOAc in light petroleum) gave 3-methylindolin-2-one as a pale-yellow solid (**9a**, 145 mg, 0.99 mmol, 66%). NMR Spectroscopic data as previously reported.



Figure S8, IKA ElectraSyn 2.0 and a 20 mL ElectraSyn undivided vial fitted with ElectraSyn glassy carbon electrodes (4 x 0.8 x 0.2 cm; 6.1 cm² area exposed to the electrolyte).

3-Bromoindole (**14**)



Prepared according to the general electrochemical procedure from indole (**8aa**, 27 mg, 0.23 mmol) and KBr (2 eq.). Purification by flash chromatography on silica gel (10% EtOAc in light petroleum) gave the *title compound* as a colourless solid (18 mg, 0.09 mmol, 40%). ¹H NMR (400 MHz, CDCl₃) δ 8.12 (br s, 1 H, NH), 7.58 (d, *J* 7.7, 1 H, ArH), 7.34 (d, *J* 7.5, 1 H, ArH), 7.27-7.17 (m, 3 H, ArH). NMR Spectroscopic data in accordance with previous reports.²⁹

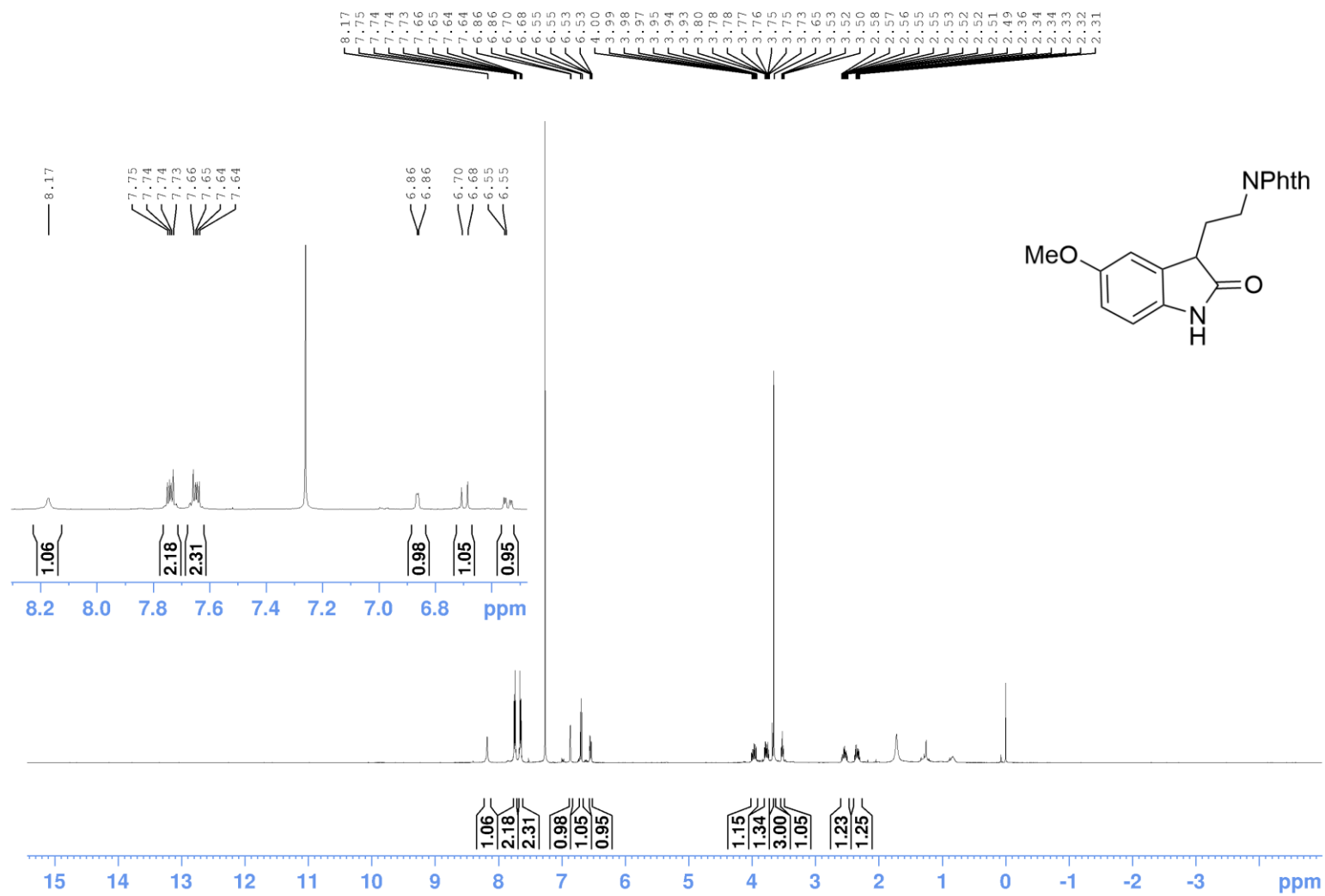
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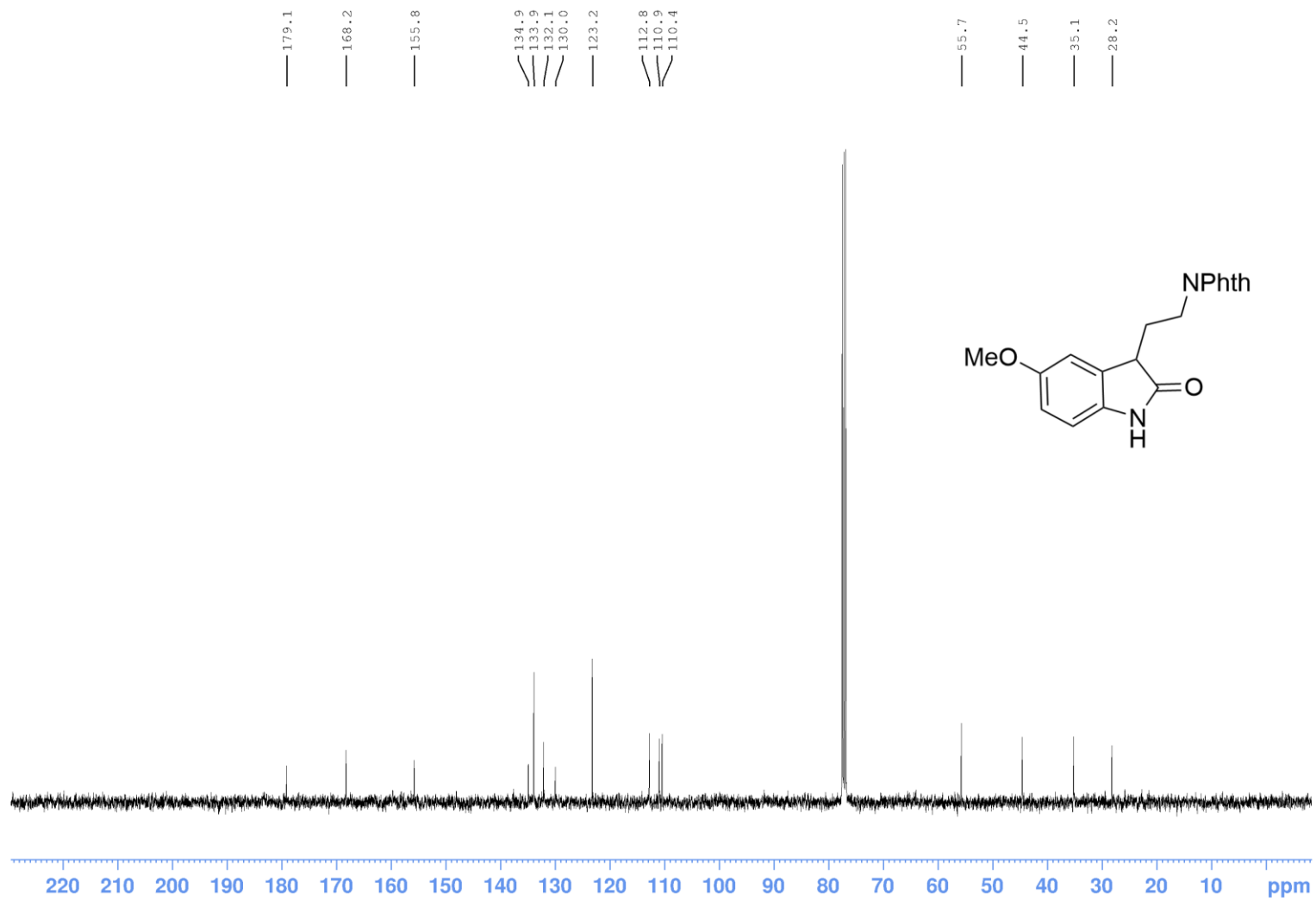
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NMR Spectra of novel compounds

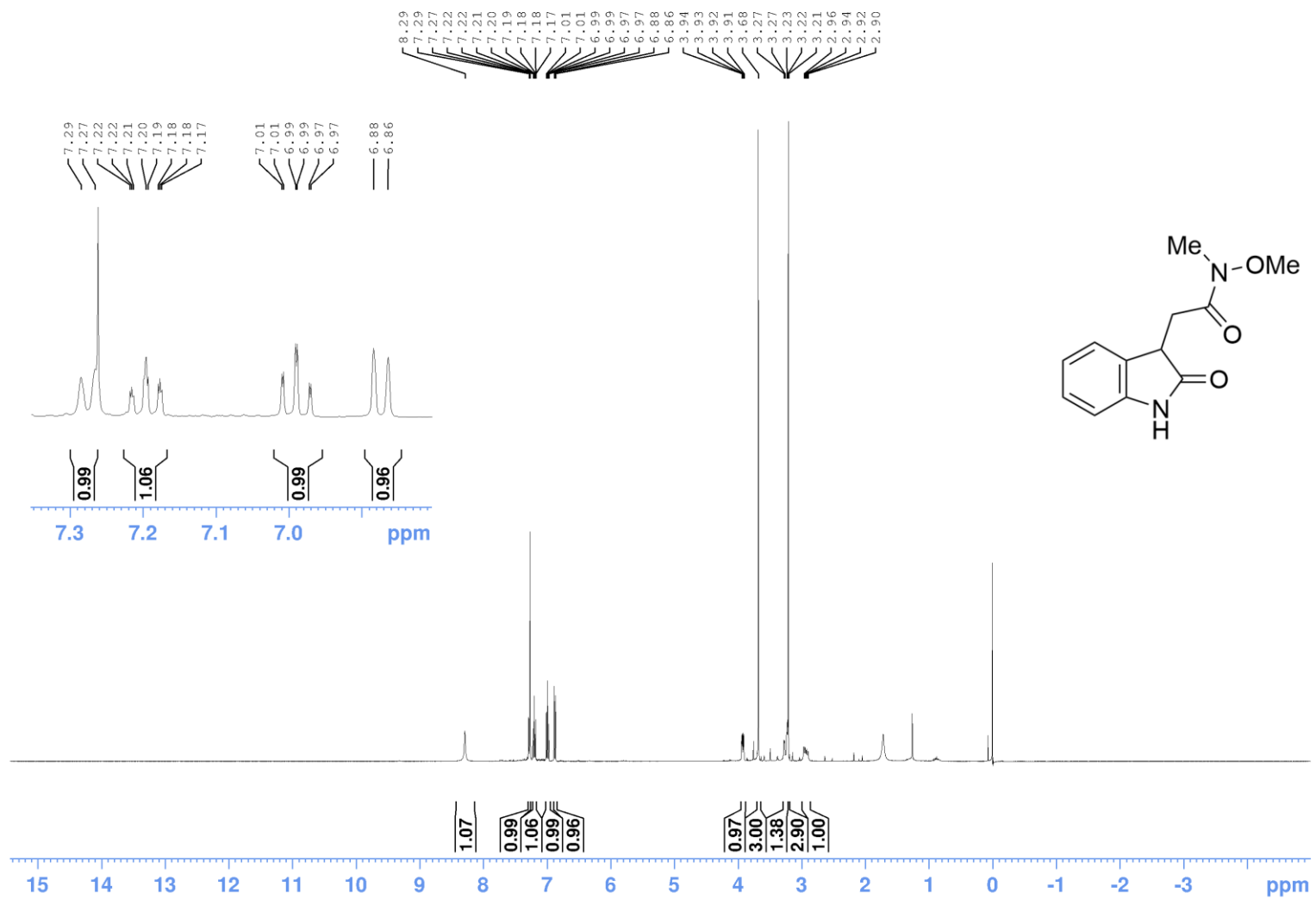
¹H NMR spectrum of **9v** (400 MHz, CDCl₃)



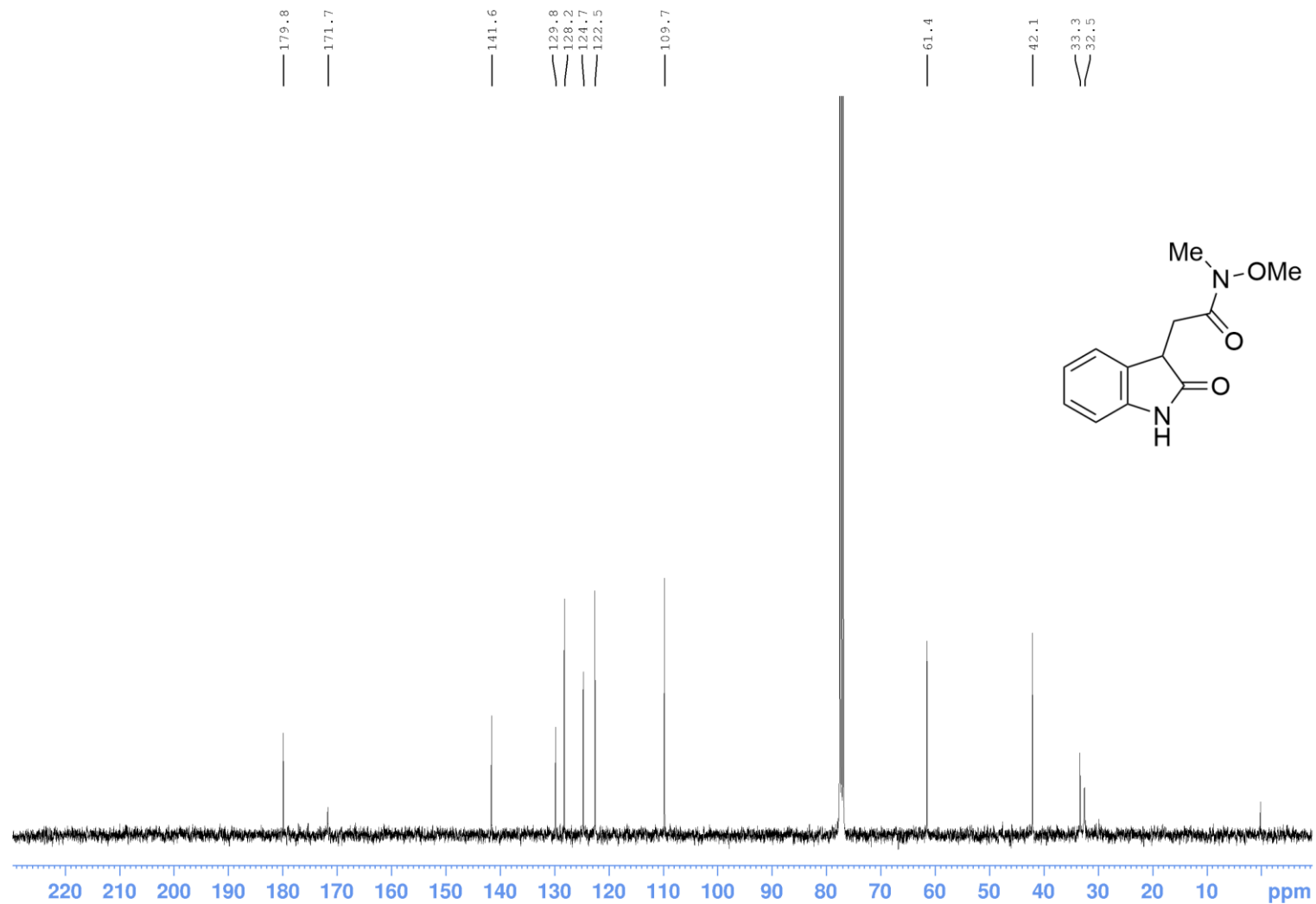
^{13}C NMR spectrum of **9v** (100 MHz, CDCl_3)



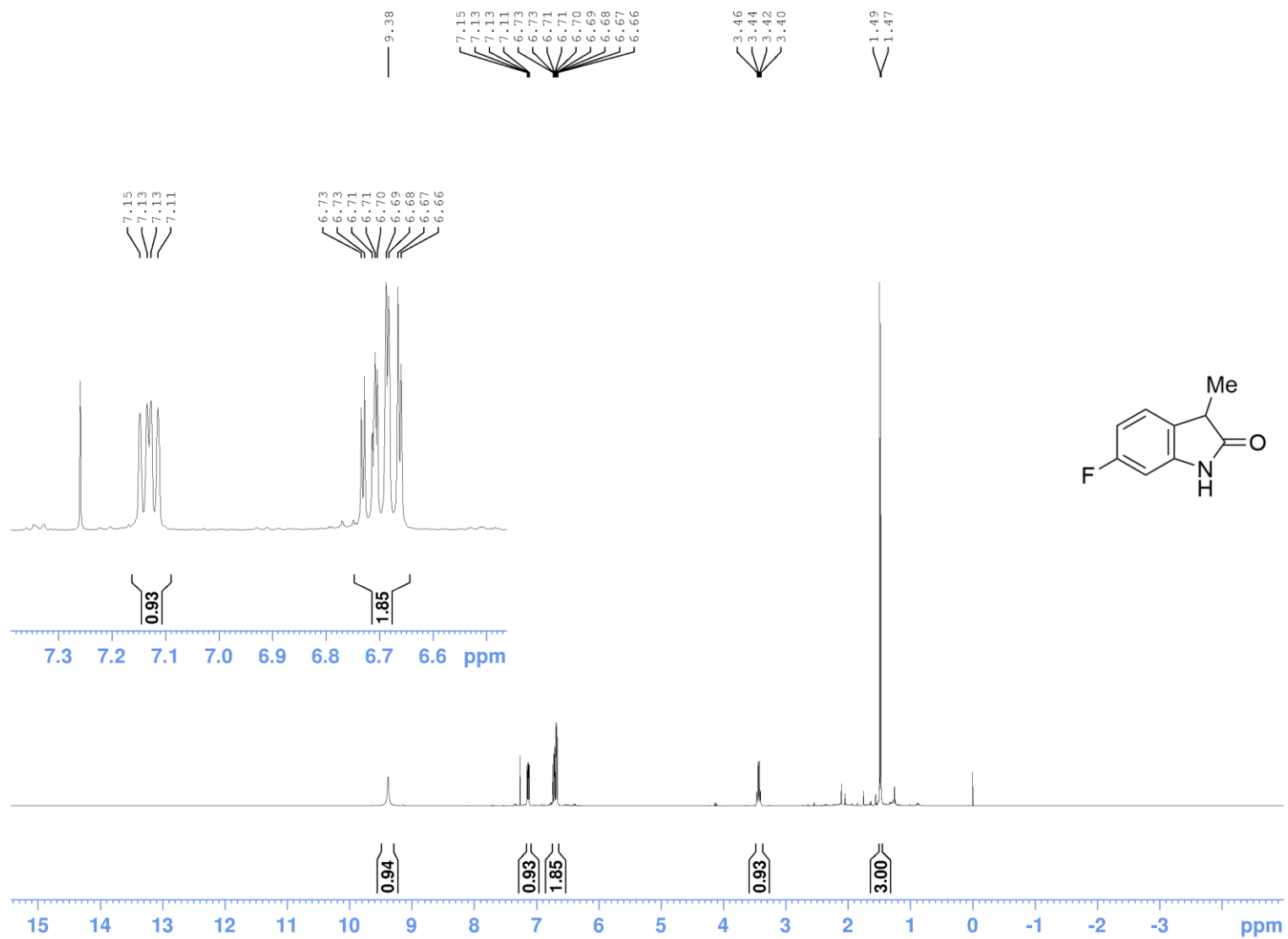
^1H NMR spectrum of **9o** (400 MHz, CDCl_3)



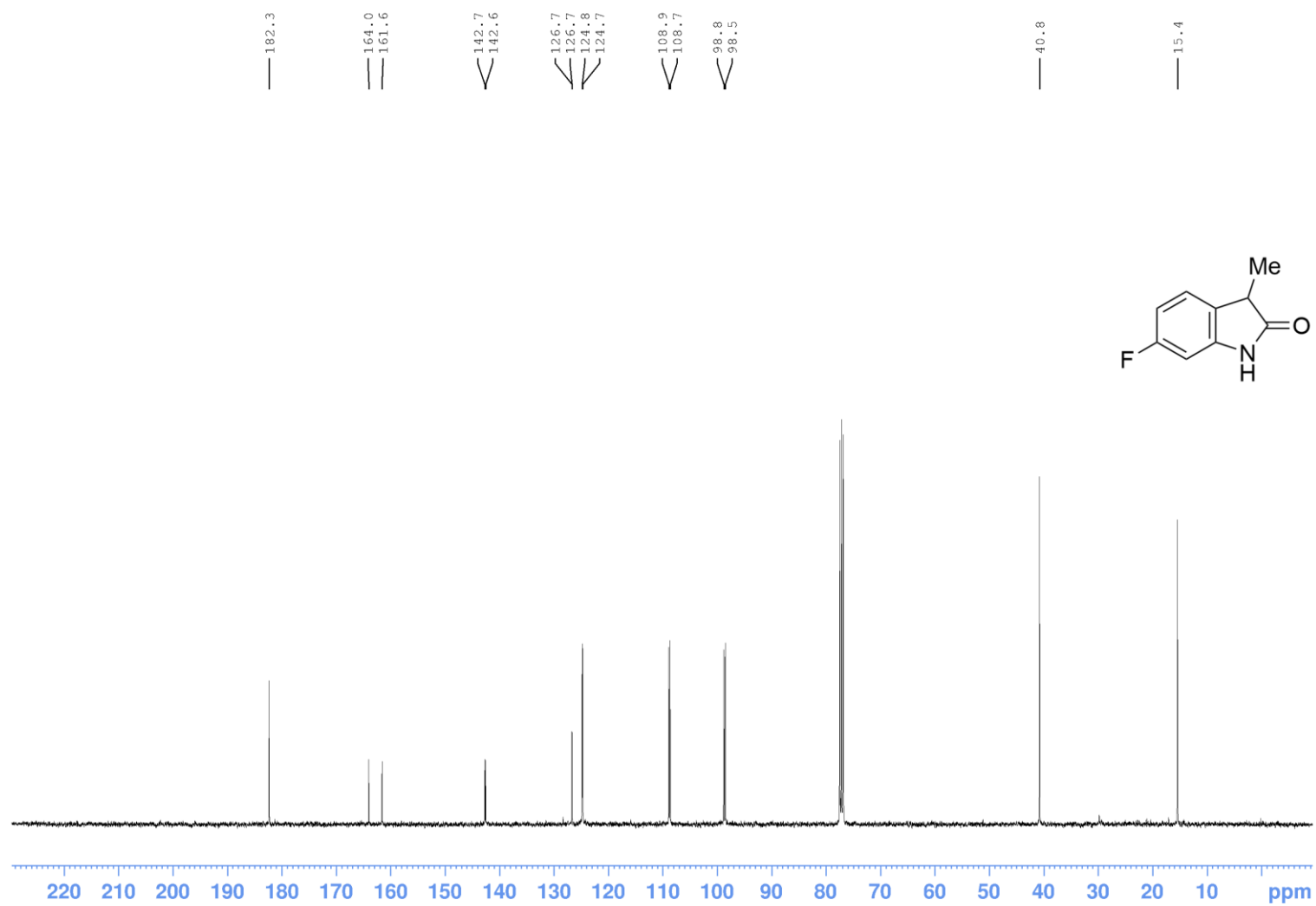
^{13}C NMR spectrum of **9o** (100 MHz, CDCl_3)



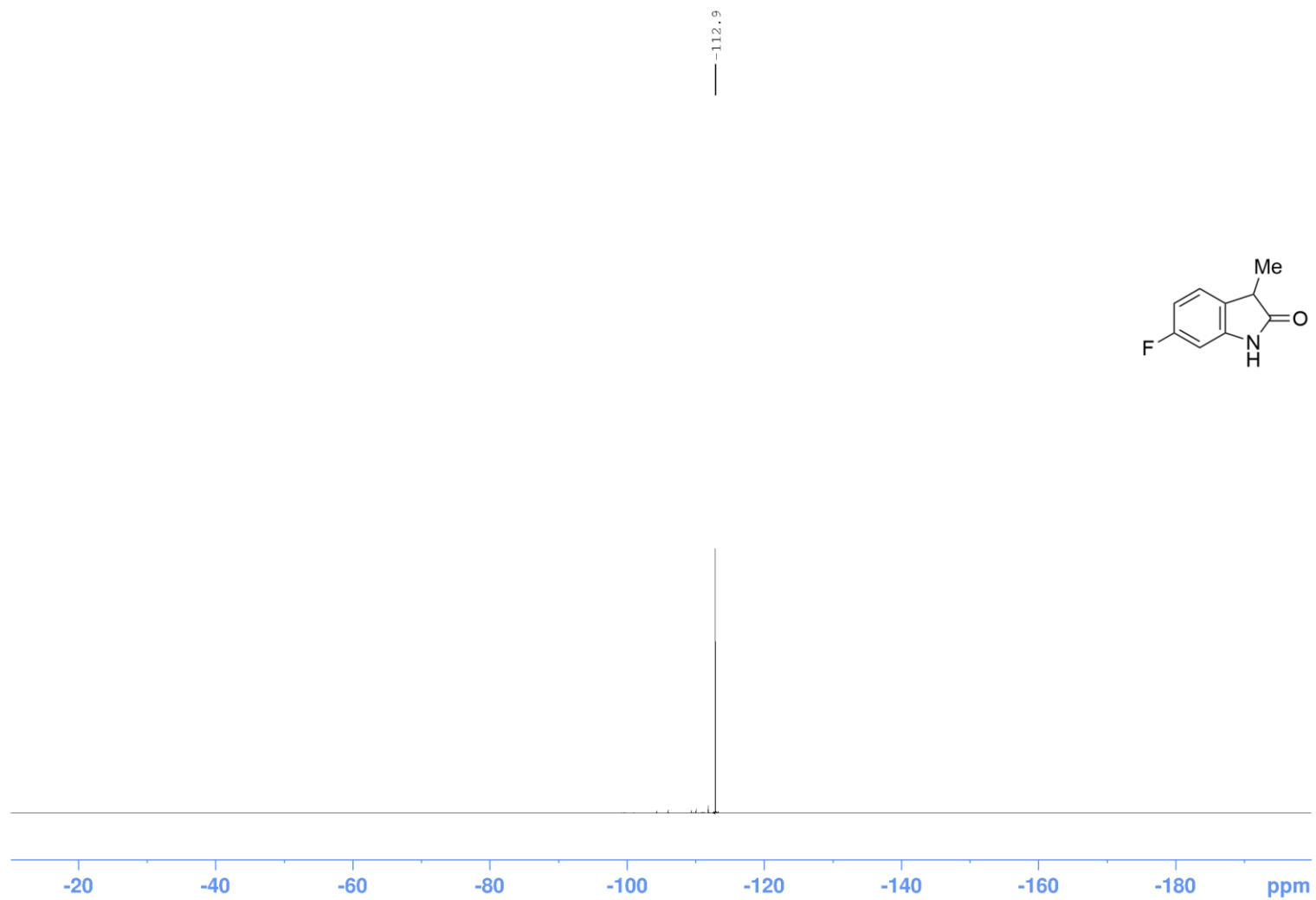
^1H NMR spectrum of **9r** (400 MHz, CDCl_3)



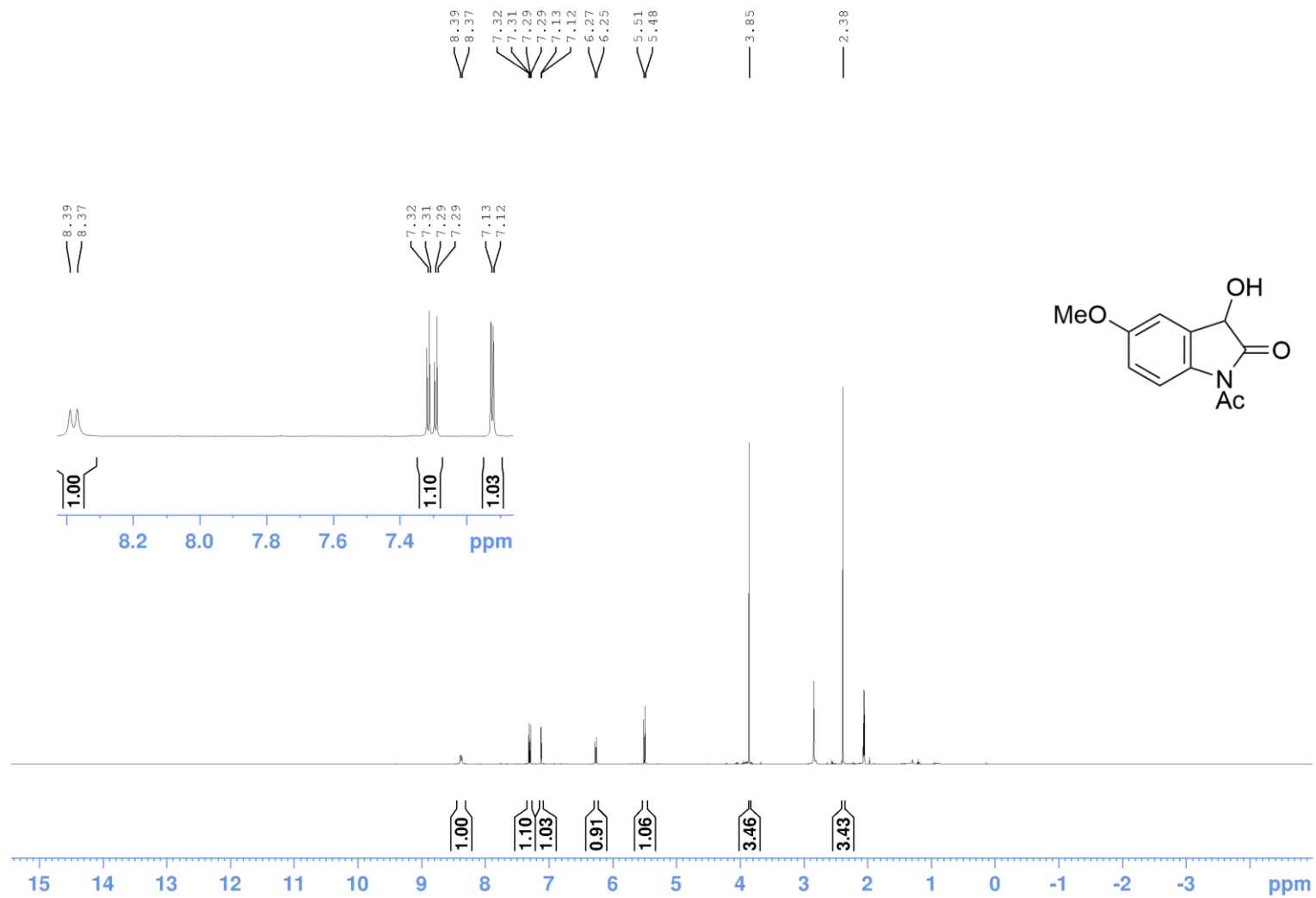
^{13}C NMR spectrum of **9r** (100 MHz, CDCl_3)



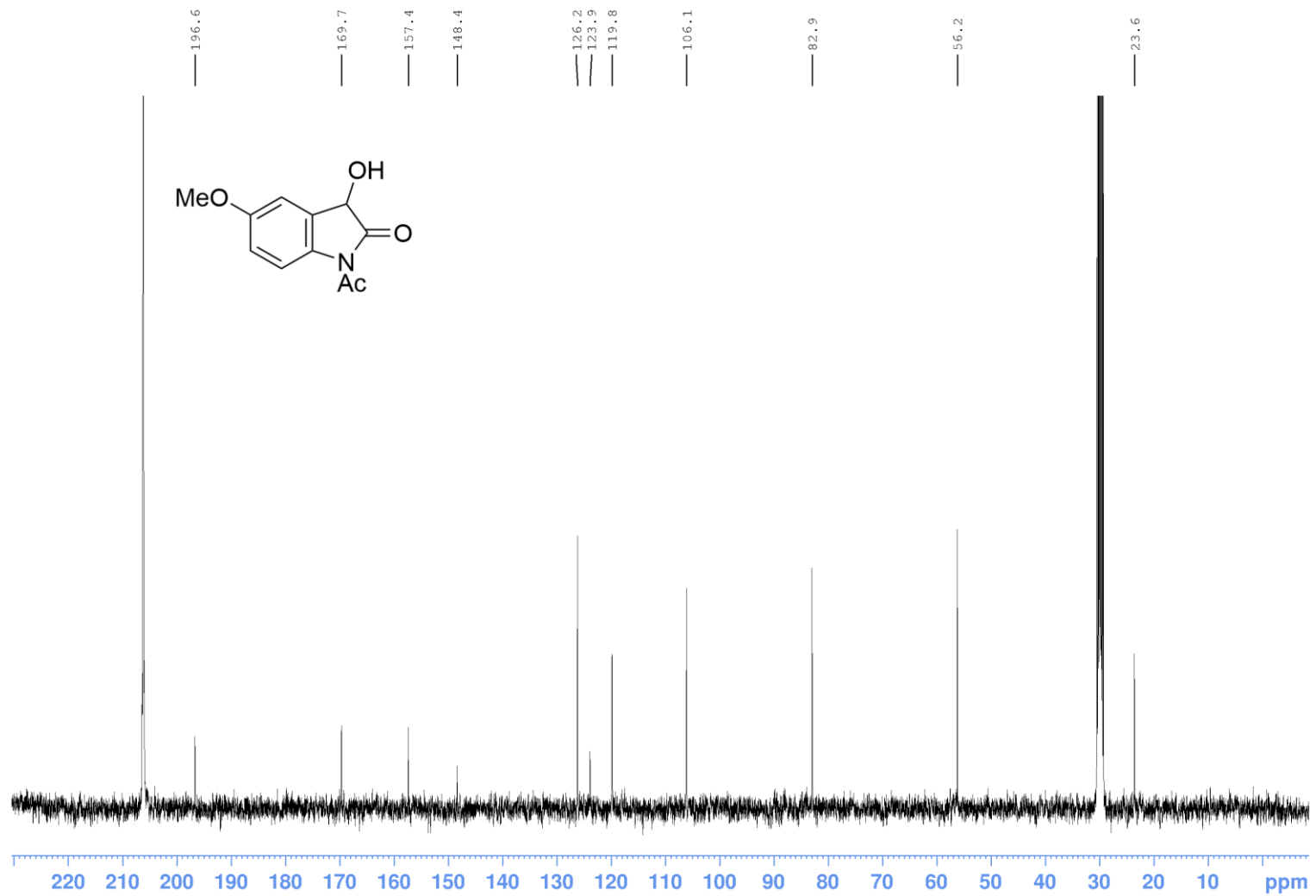
^{19}F NMR spectrum of **9r** (376 MHz, CDCl_3)



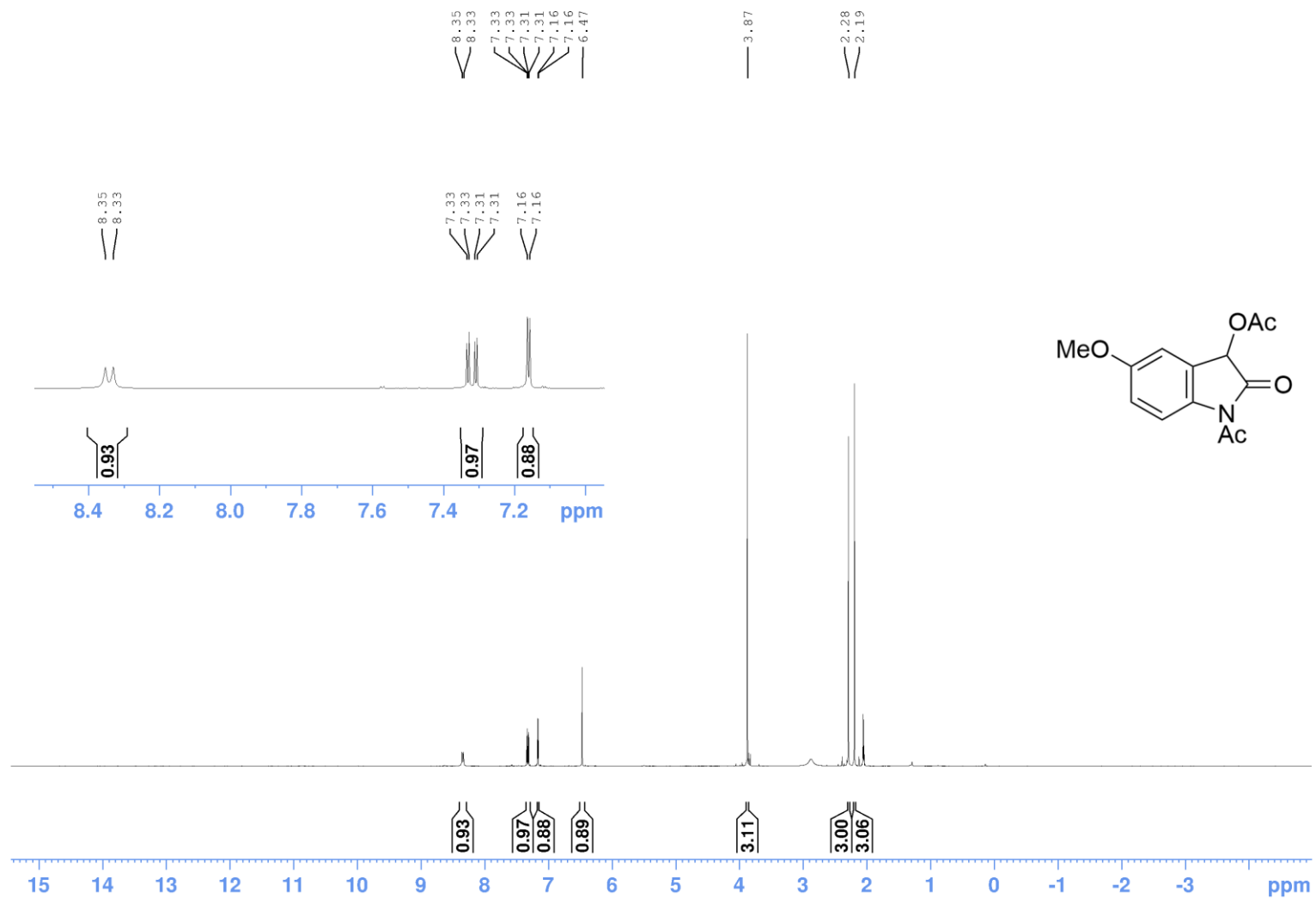
^1H NMR spectrum of **9x** (400 MHz, $(\text{CD}_3)_2\text{CO}$)



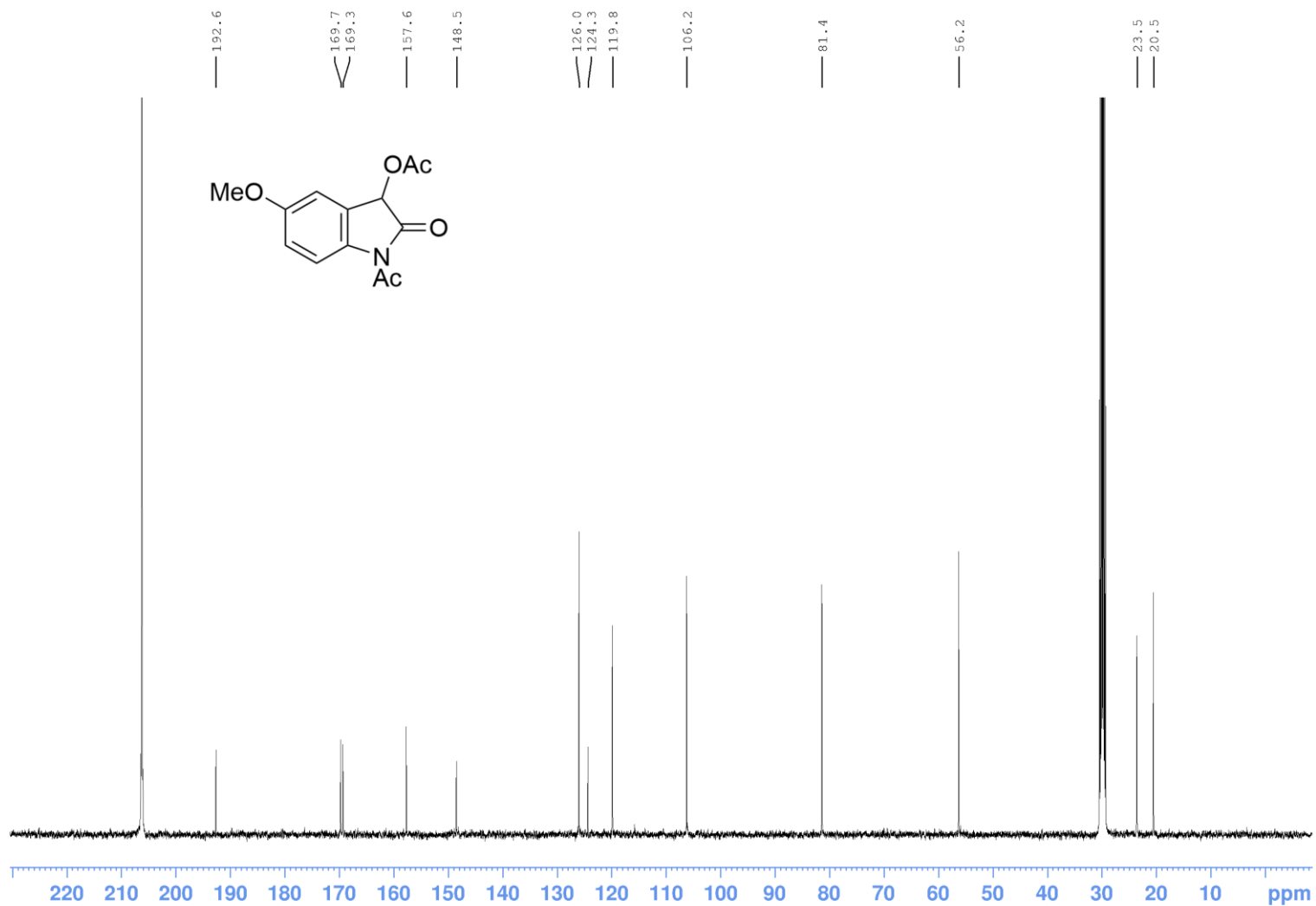
^{13}C NMR spectrum of **9x** (100 MHz, $(\text{CD}_3)_2\text{CO}$)



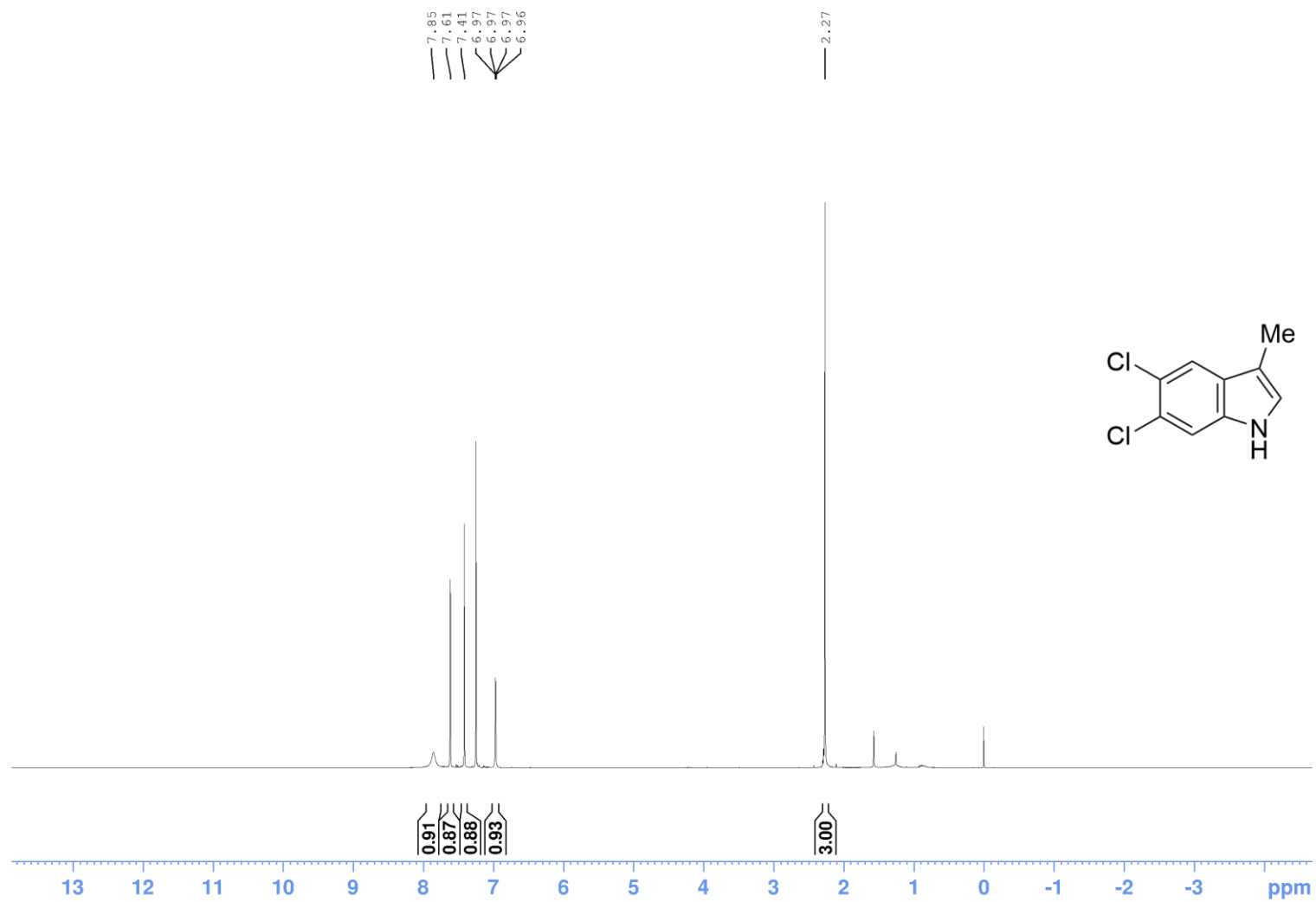
^1H NMR spectrum of **9y** (400 MHz, $(\text{CD}_3)_2\text{CO}$)



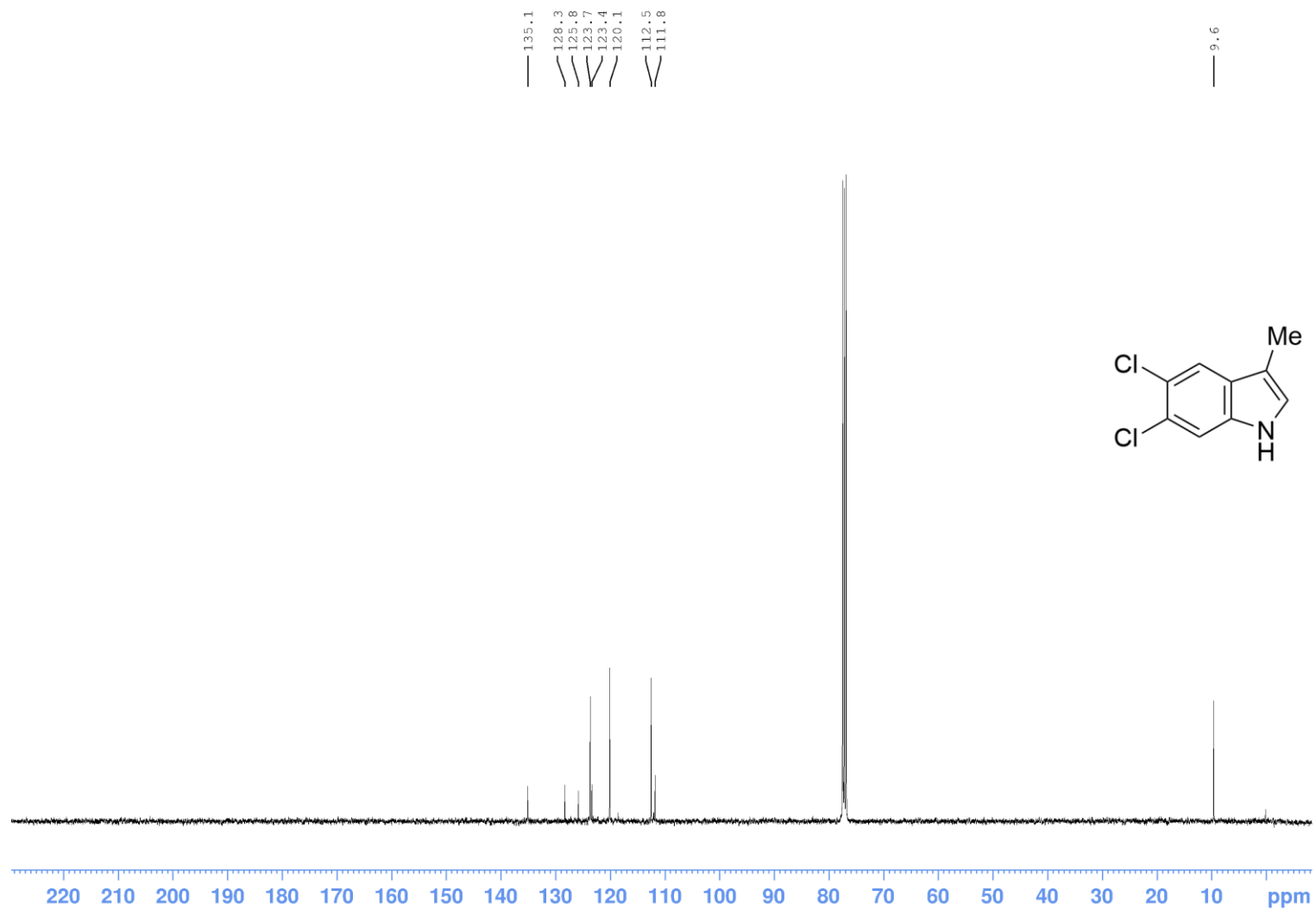
^{13}C NMR spectrum of **9y** (100 MHz, $(\text{CD}_3)_2\text{CO}$)



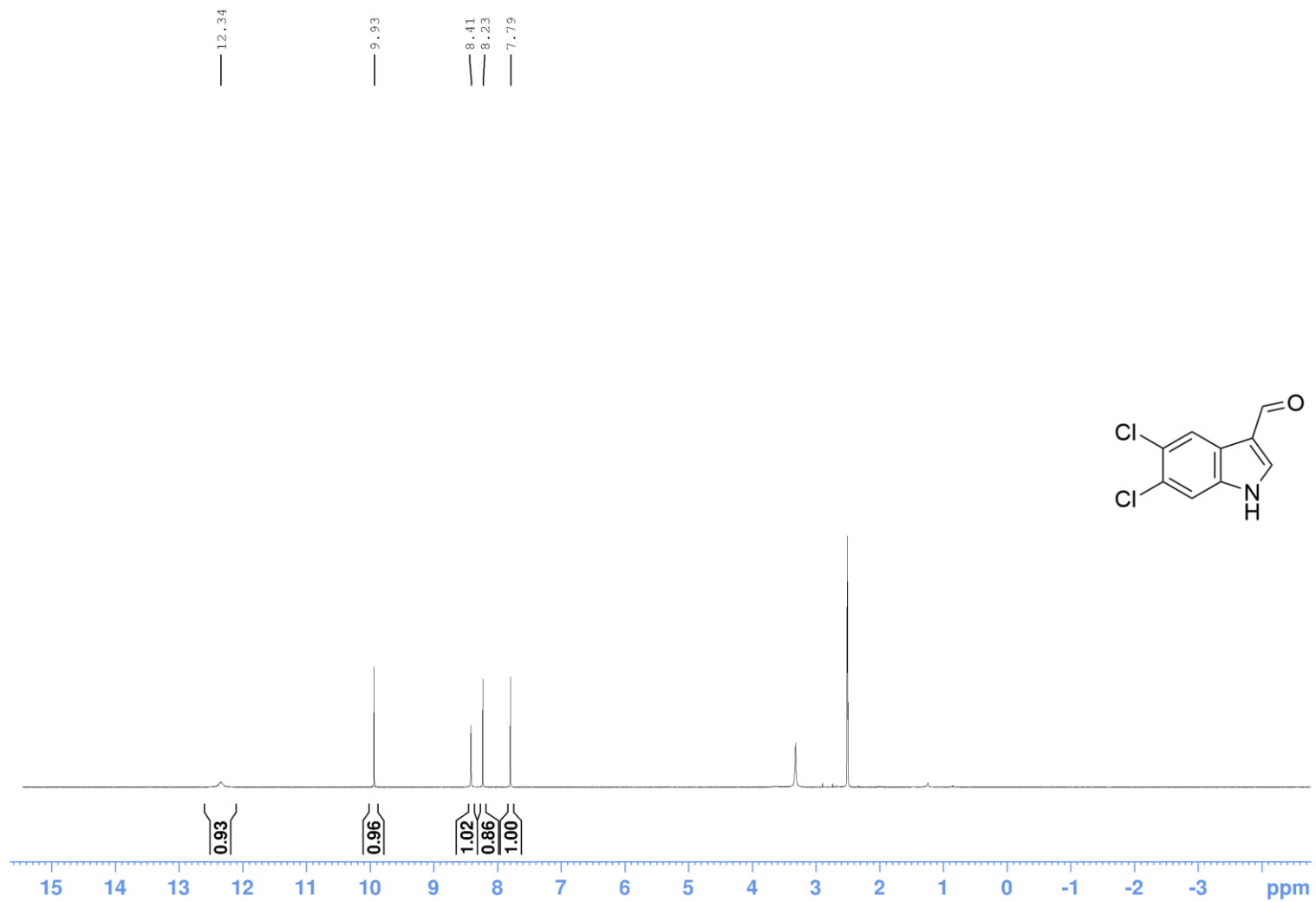
^1H NMR spectrum of **8s** (400 MHz, CDCl_3)



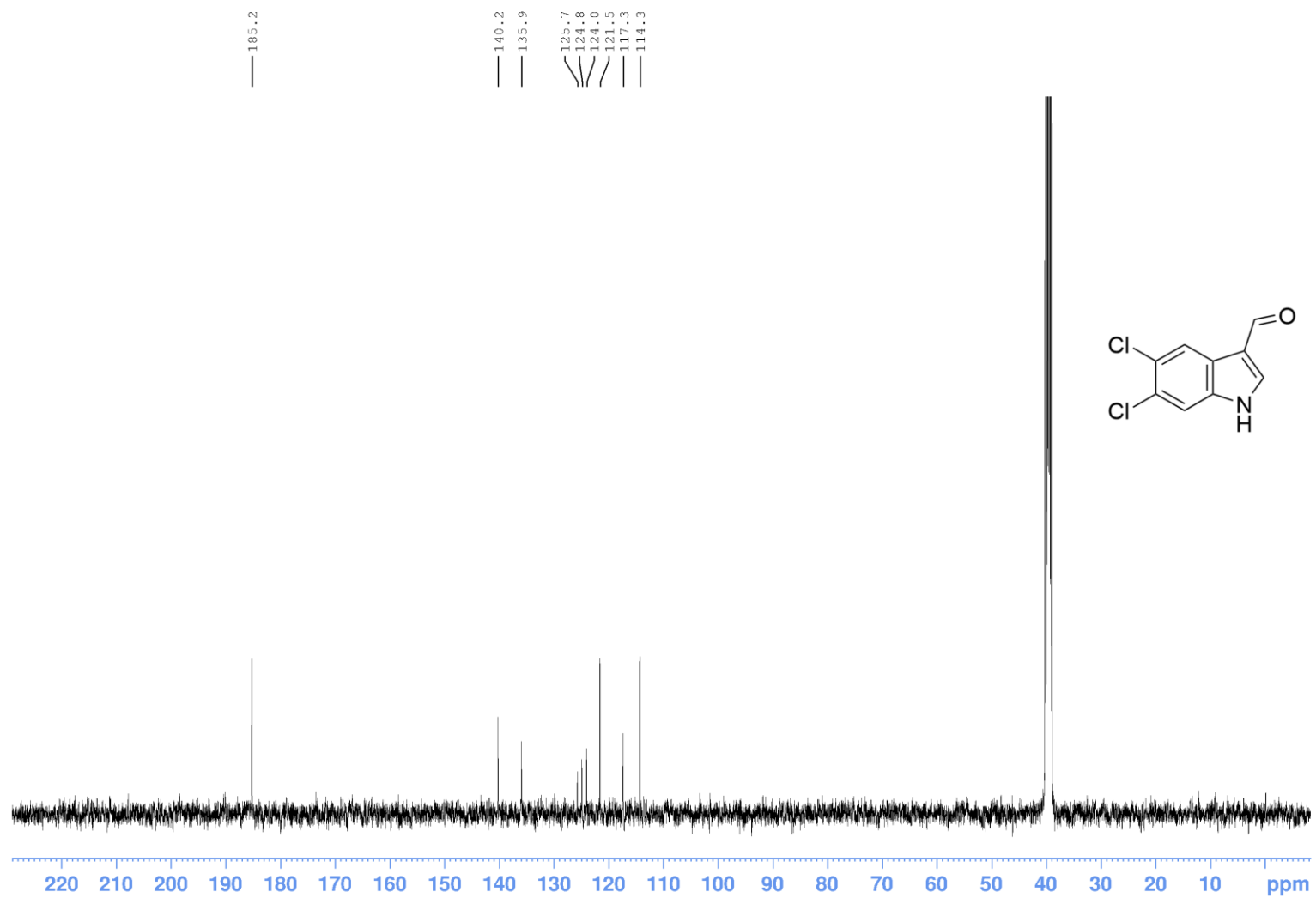
^{13}C NMR spectrum of **8s** (100 MHz, CDCl_3)



^1H NMR spectrum of **13** (400 MHz, $(\text{CD}_3)_2\text{SO}$)

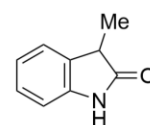
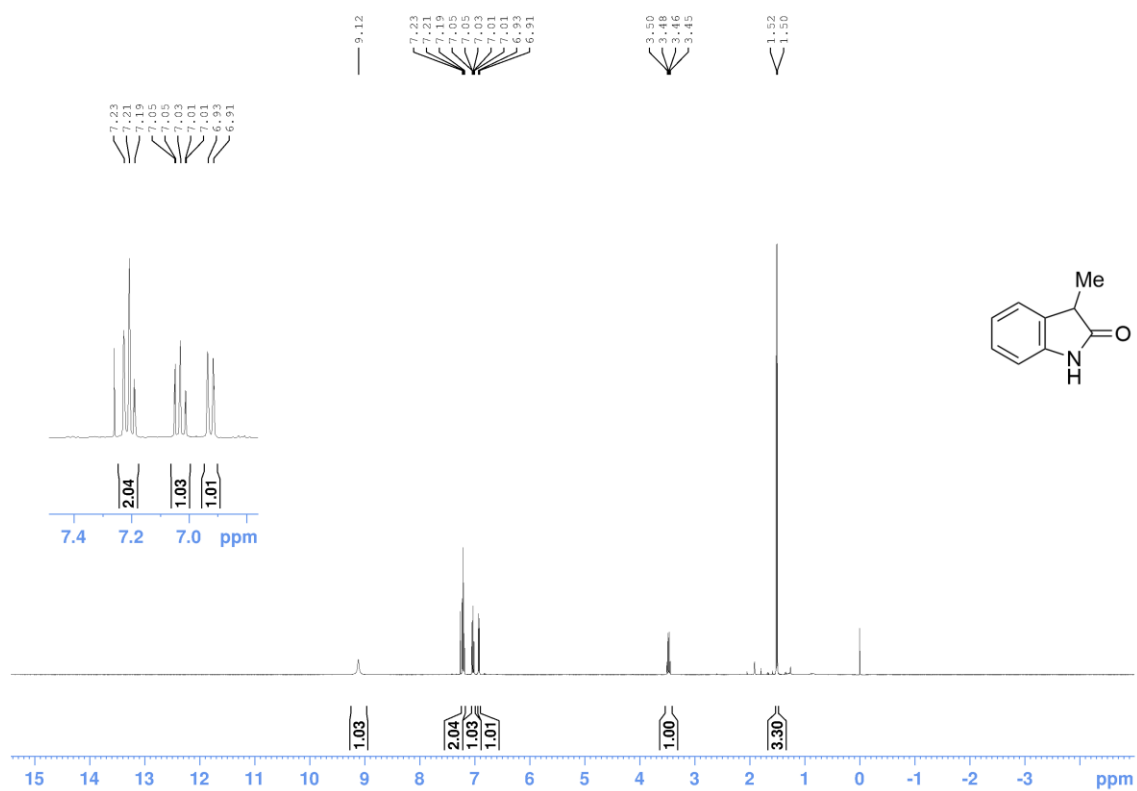


^{13}C NMR spectrum of **13** (100 MHz, $(\text{CD}_3)_2\text{SO}$)

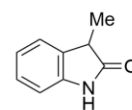
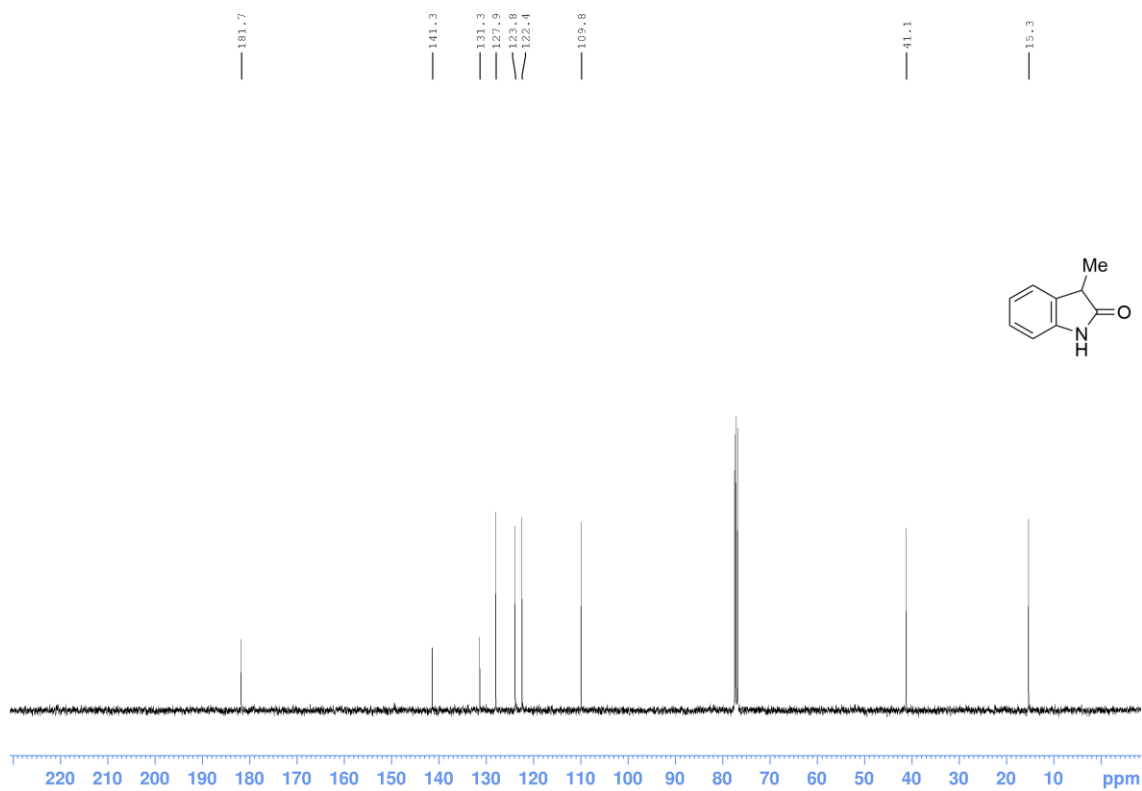


NMR Spectra of known compounds

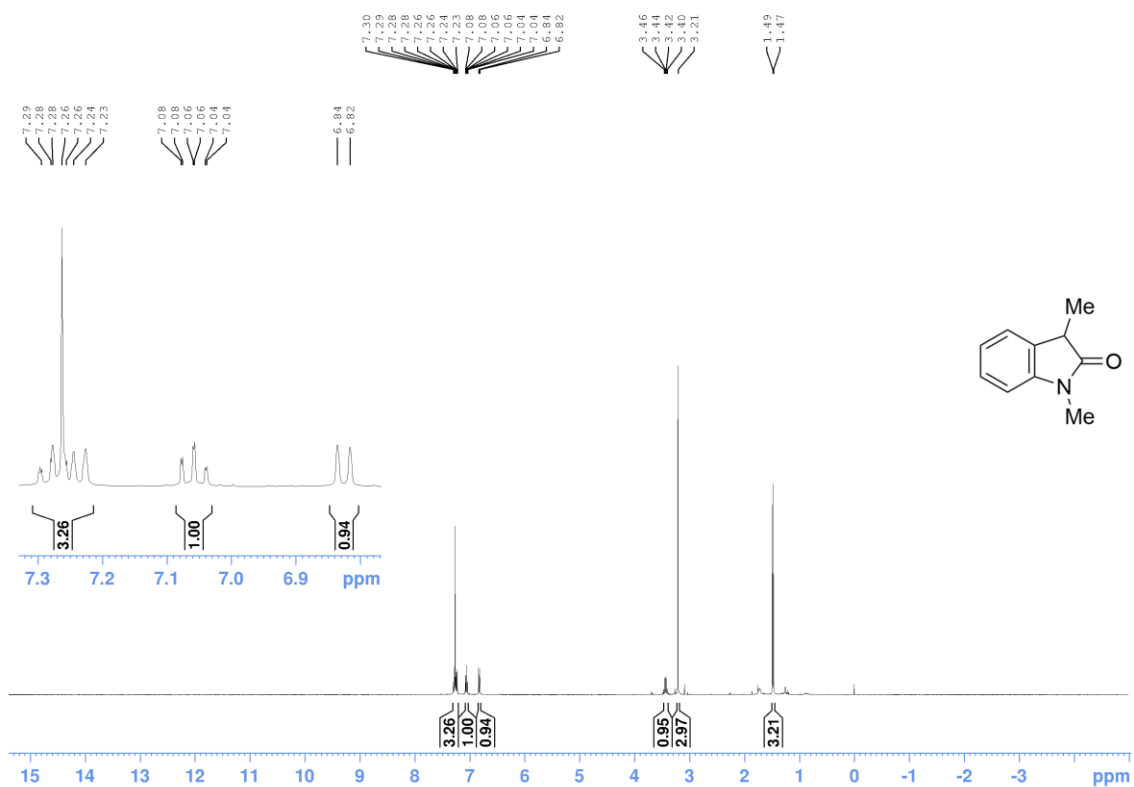
^1H NMR spectrum of **9a** (400 MHz, CDCl_3)



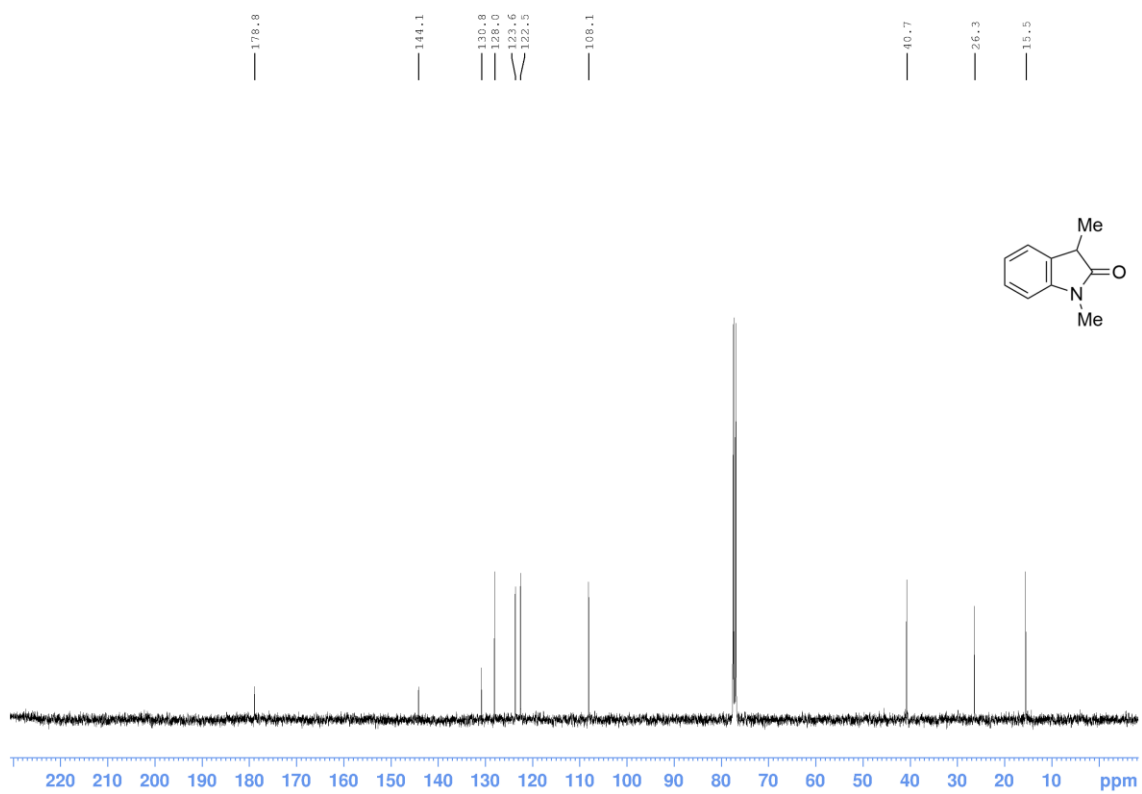
^{13}C NMR spectrum of **9a** (400 MHz, CDCl_3)



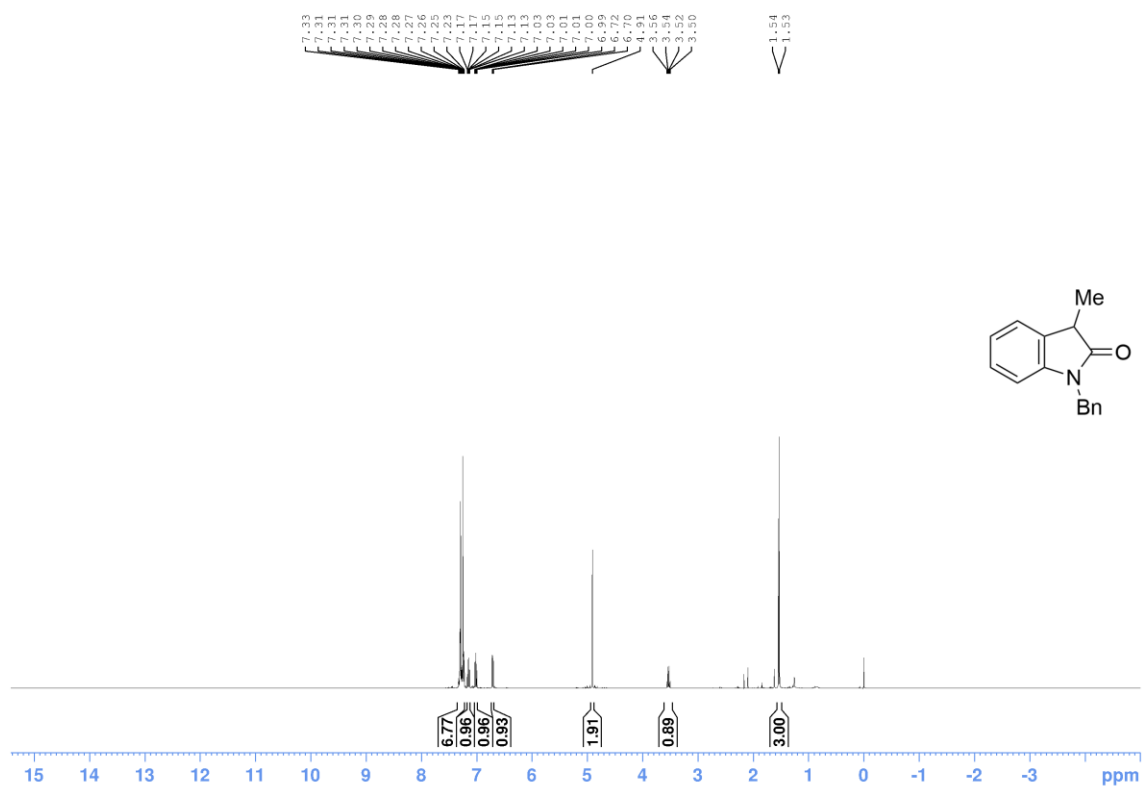
^1H NMR spectrum of **9b** (400 MHz, CDCl_3)



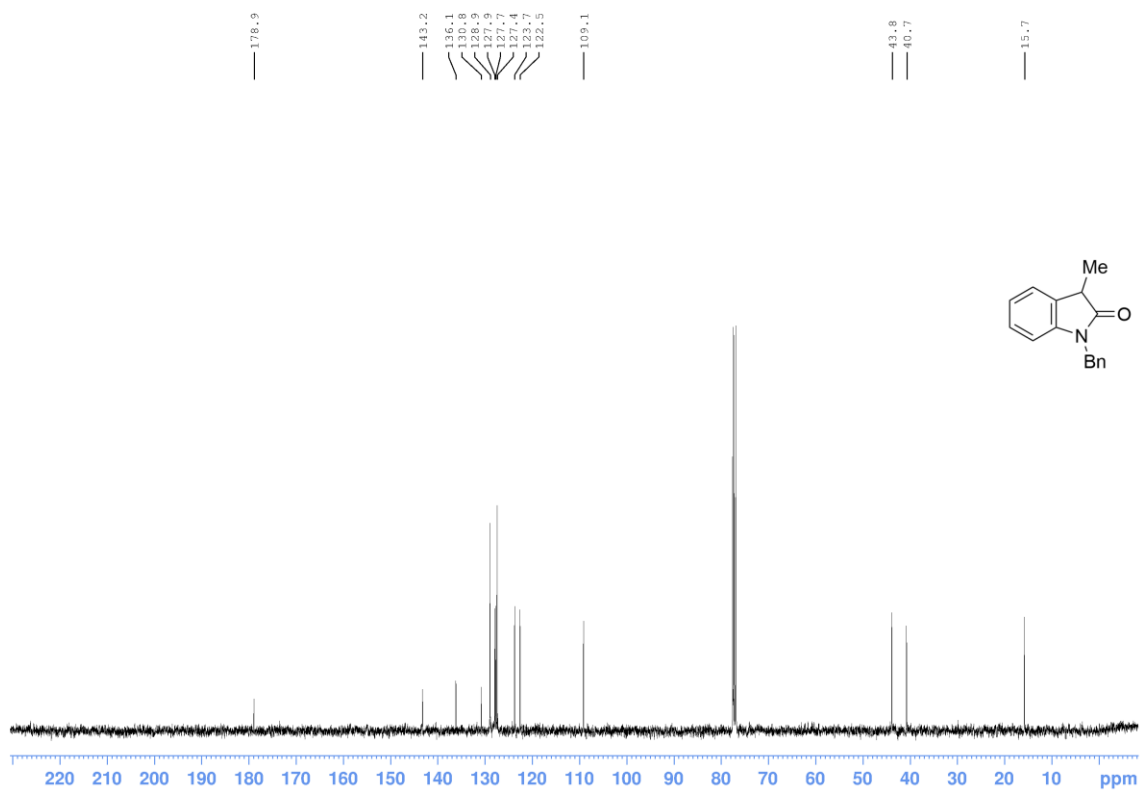
^{13}C NMR spectrum of **9b** (400 MHz, CDCl_3)



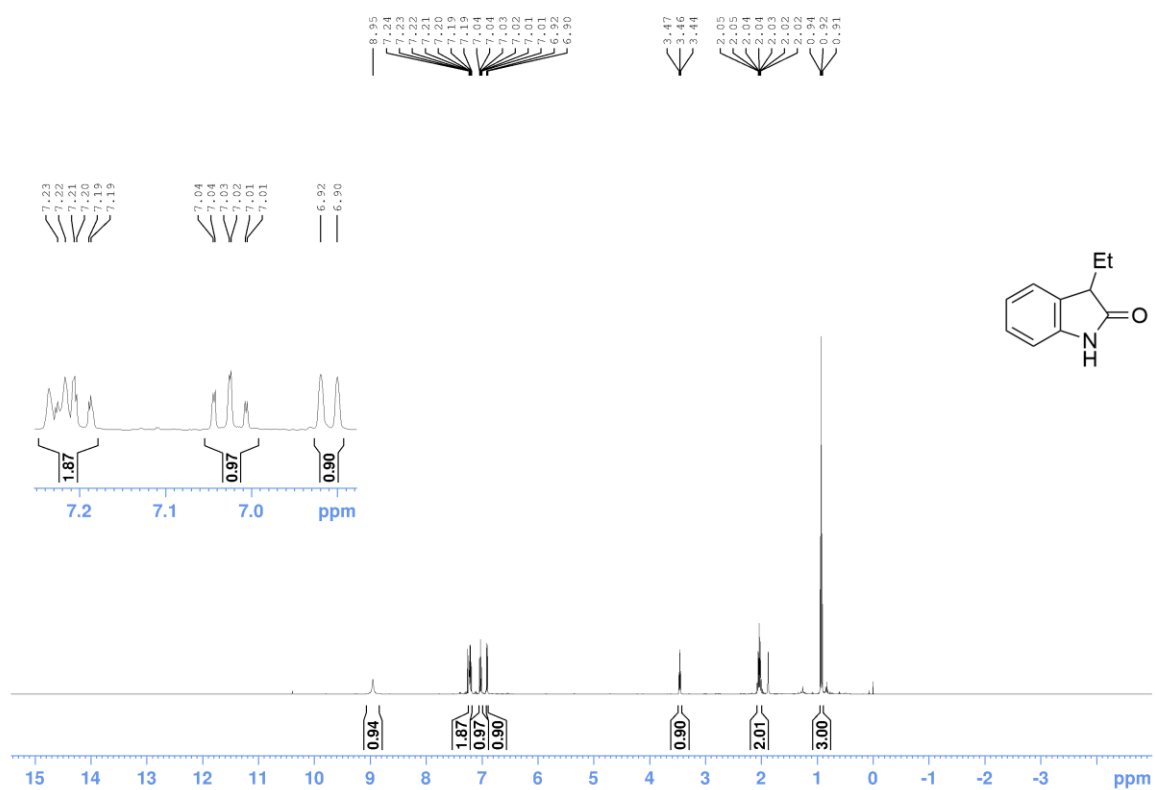
^1H NMR spectrum of **9c** (400 MHz, CDCl_3)



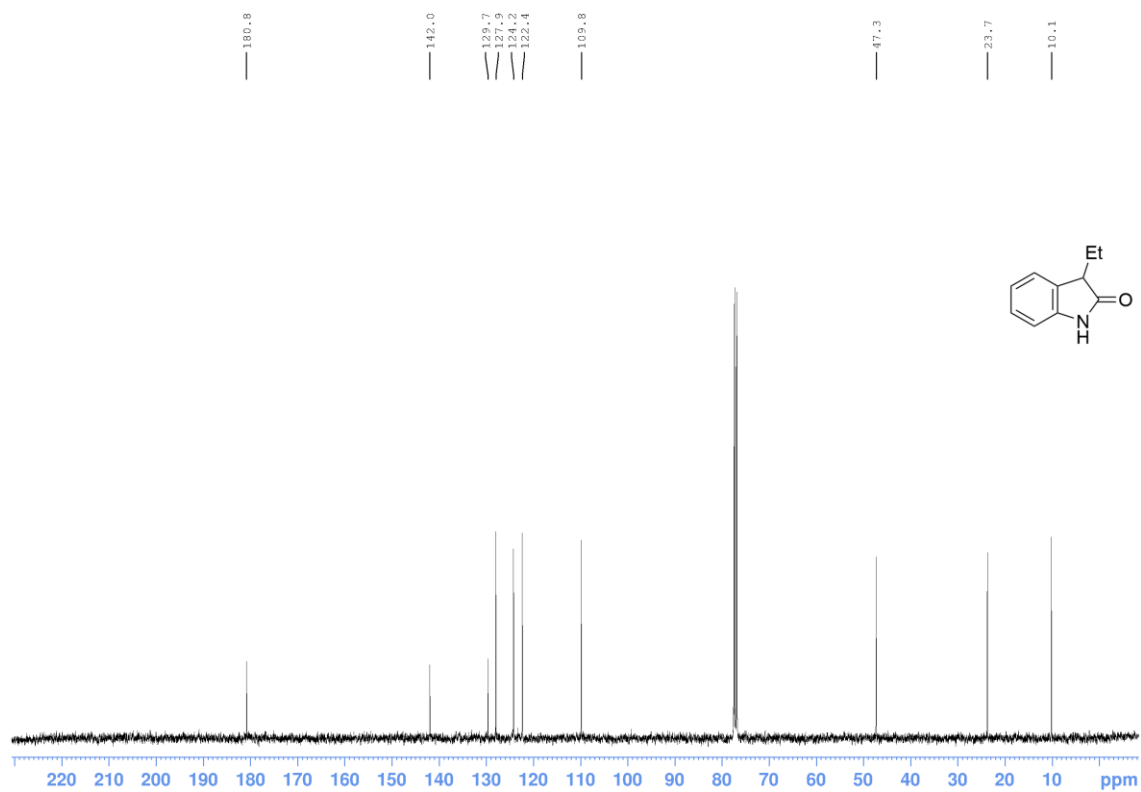
^{13}C NMR spectrum of **9c** (400 MHz, CDCl_3)



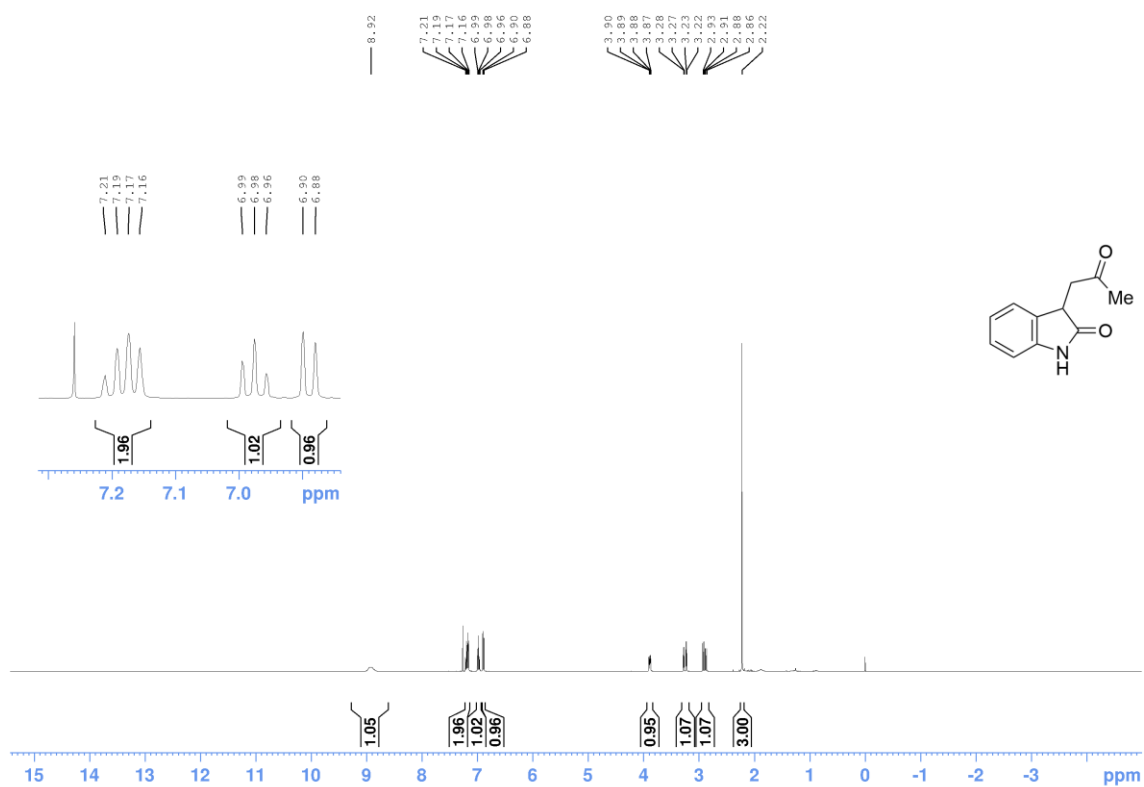
^1H NMR spectrum of **9f** (400 MHz, CDCl_3)



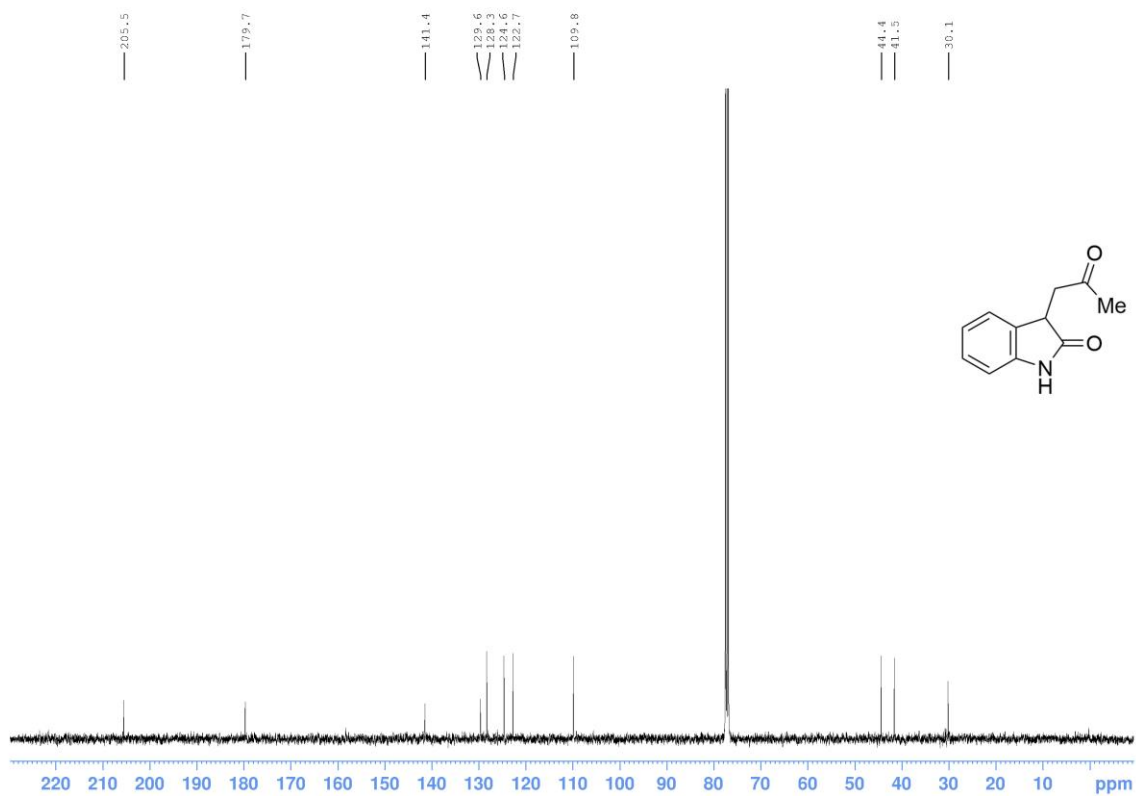
^{13}C NMR spectrum of **9f** (400 MHz, CDCl_3)



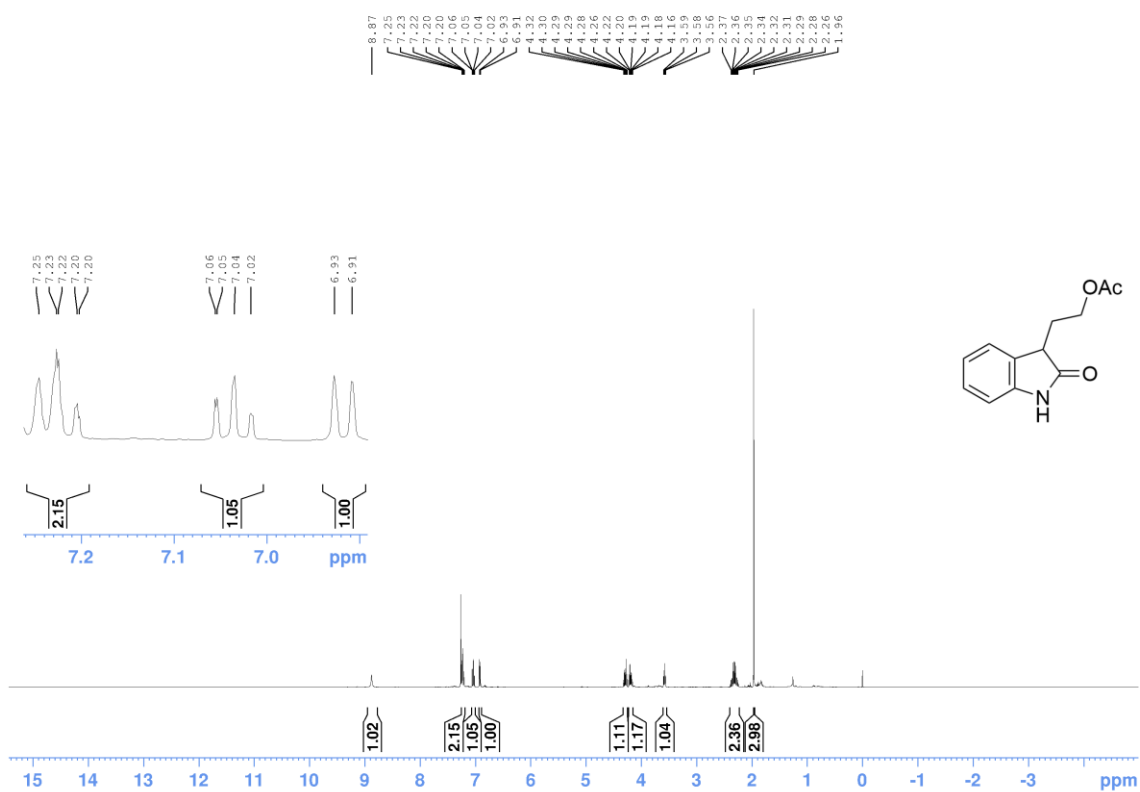
^1H NMR spectrum of **9g** (400 MHz, CDCl_3)



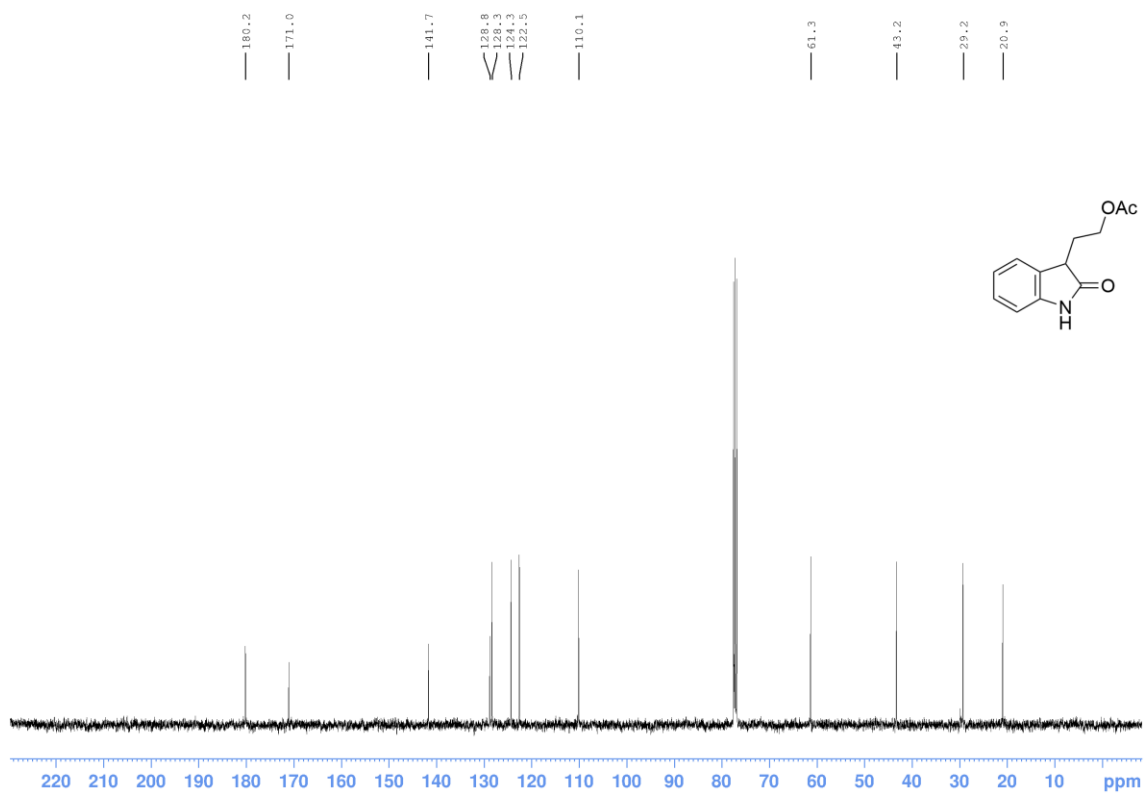
^{13}C NMR spectrum of **9g** (400 MHz, CDCl_3)



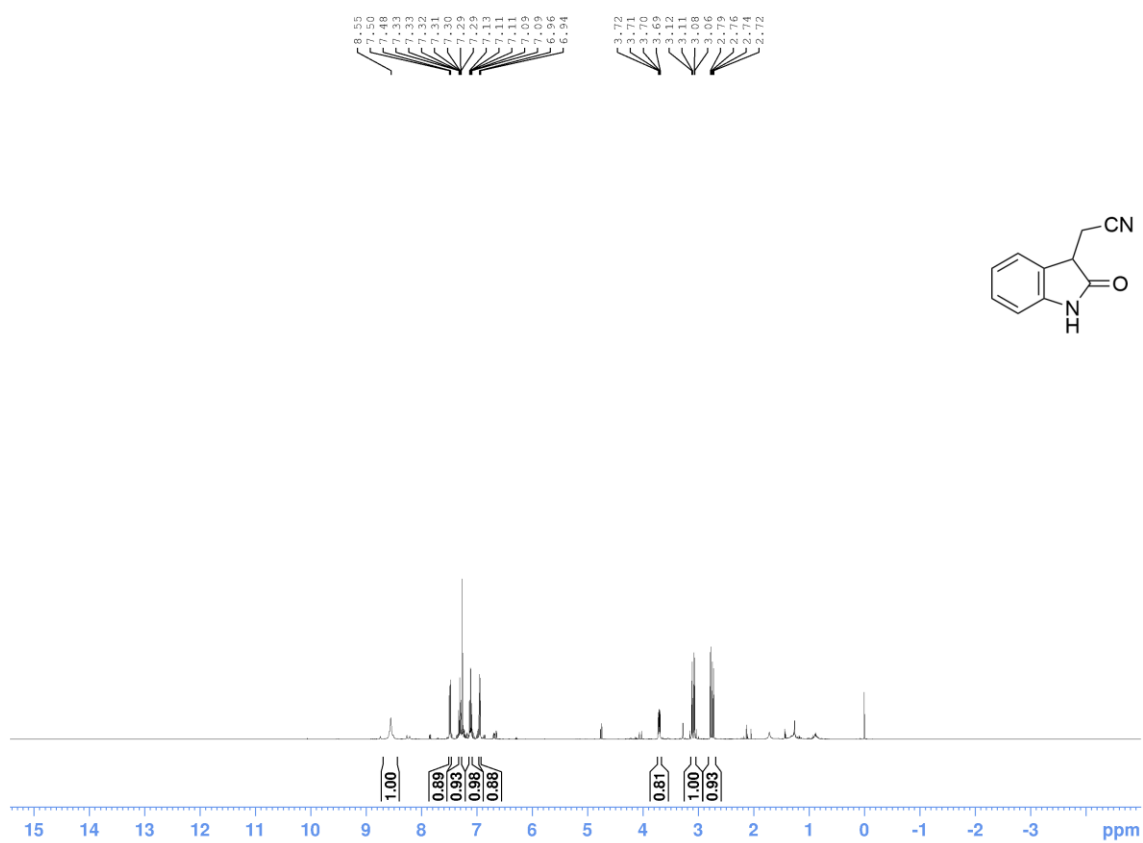
^1H NMR spectrum of **9h** (400 MHz, CDCl_3)



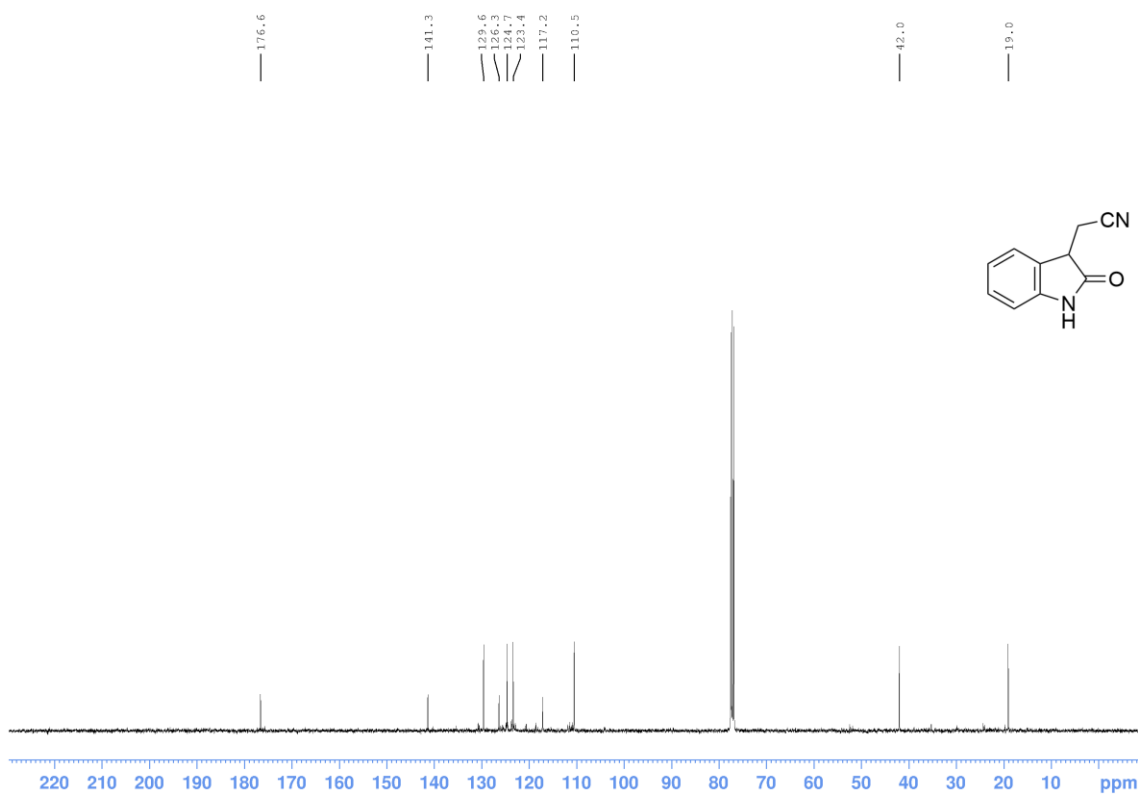
^{13}C NMR spectrum of **9h** (400 MHz, CDCl_3)



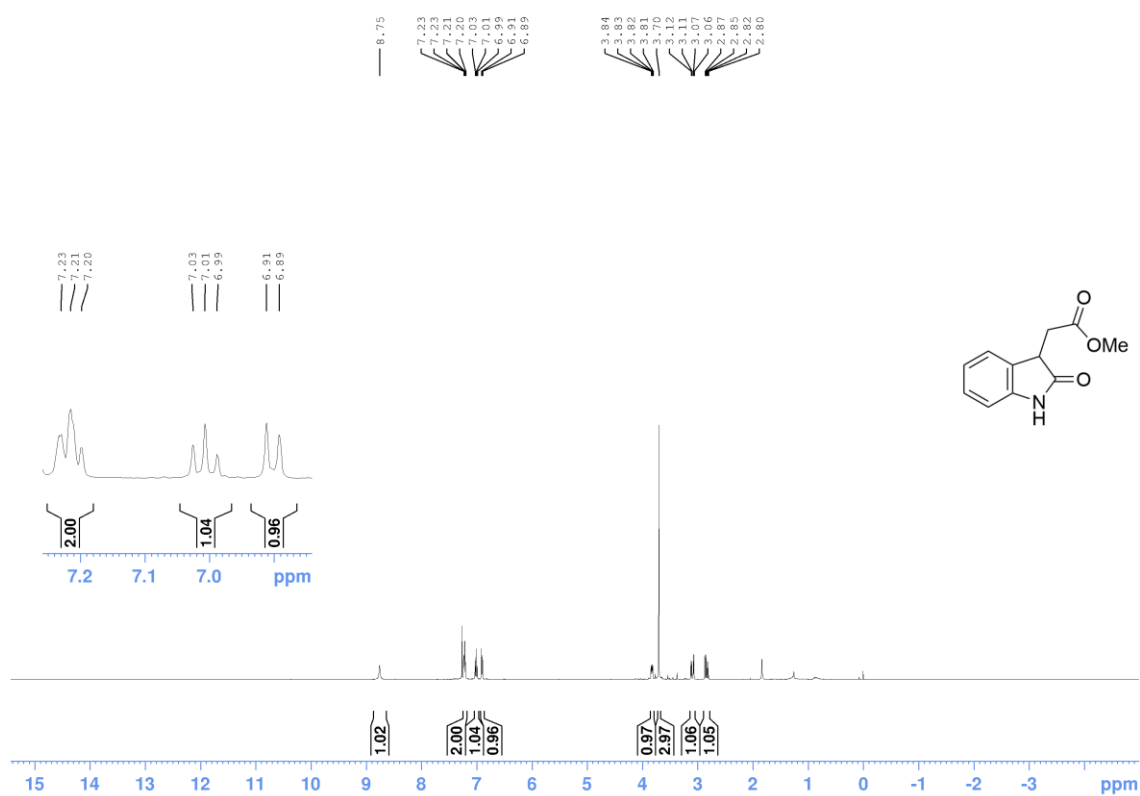
^1H NMR spectrum of **9i** (400 MHz, CDCl_3)



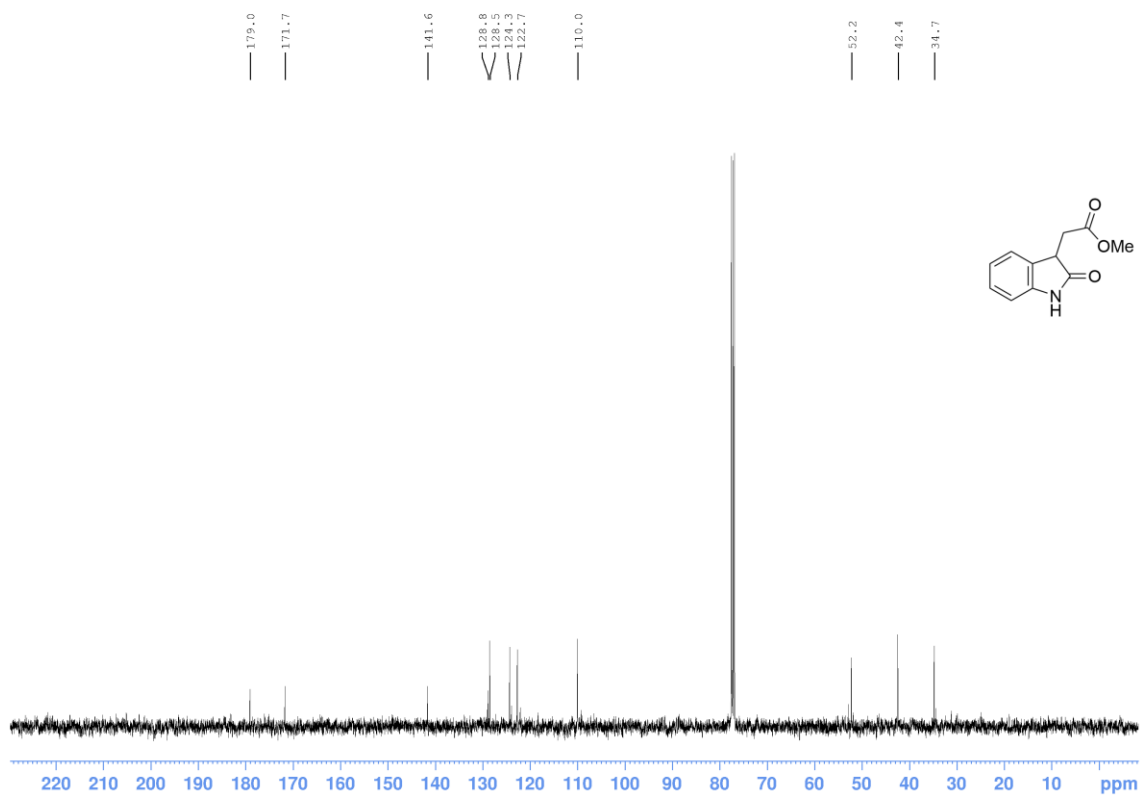
^{13}C NMR spectrum of **9i** (400 MHz, CDCl_3)



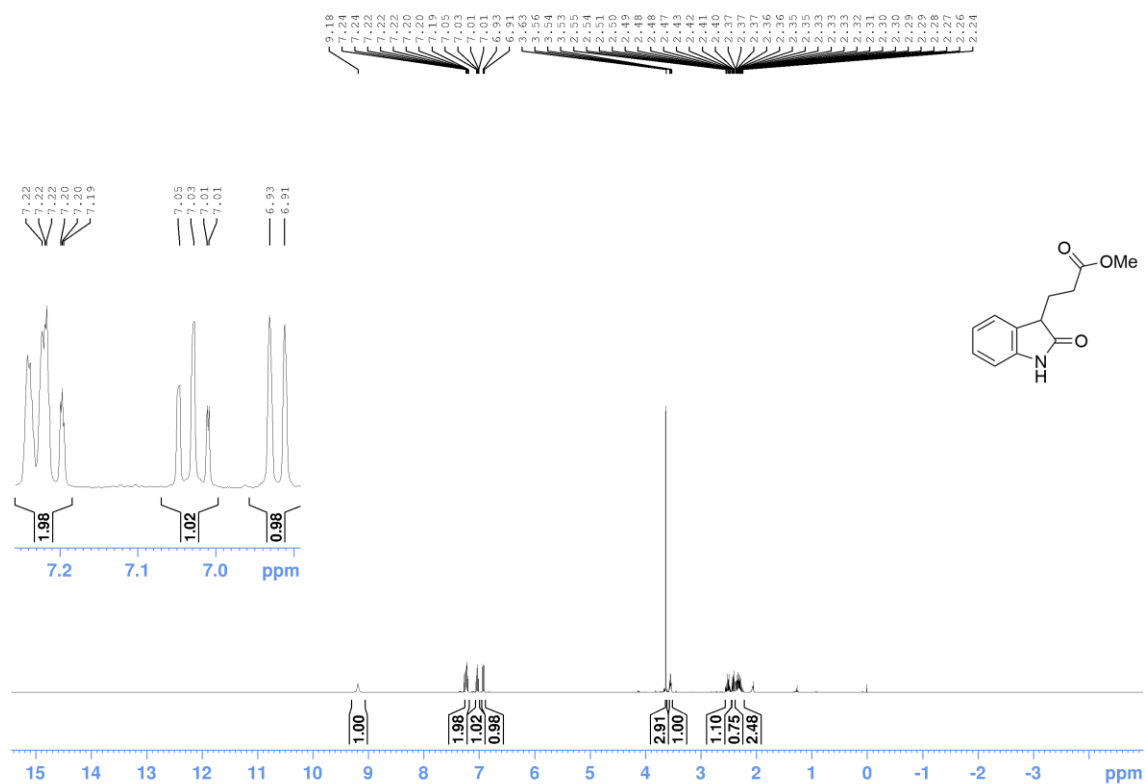
^1H NMR spectrum of **9j** (400 MHz, CDCl_3)



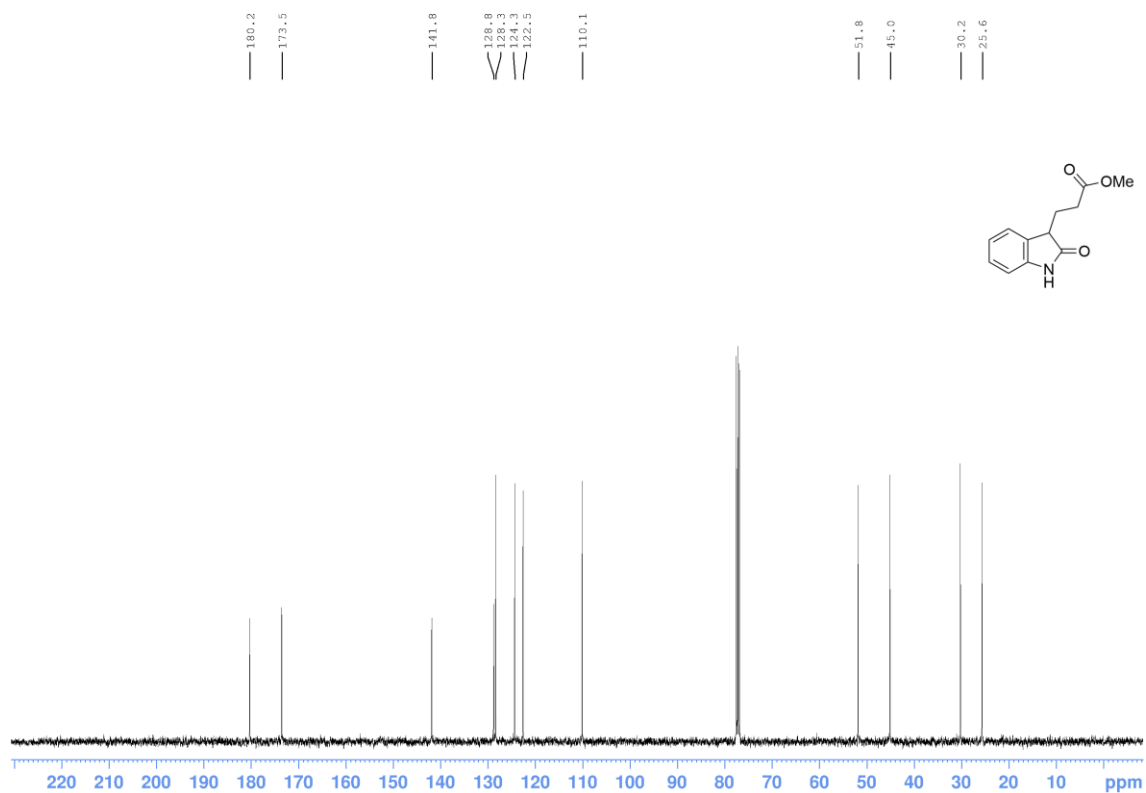
^{13}C NMR spectrum of **9j** (400 MHz, CDCl_3)



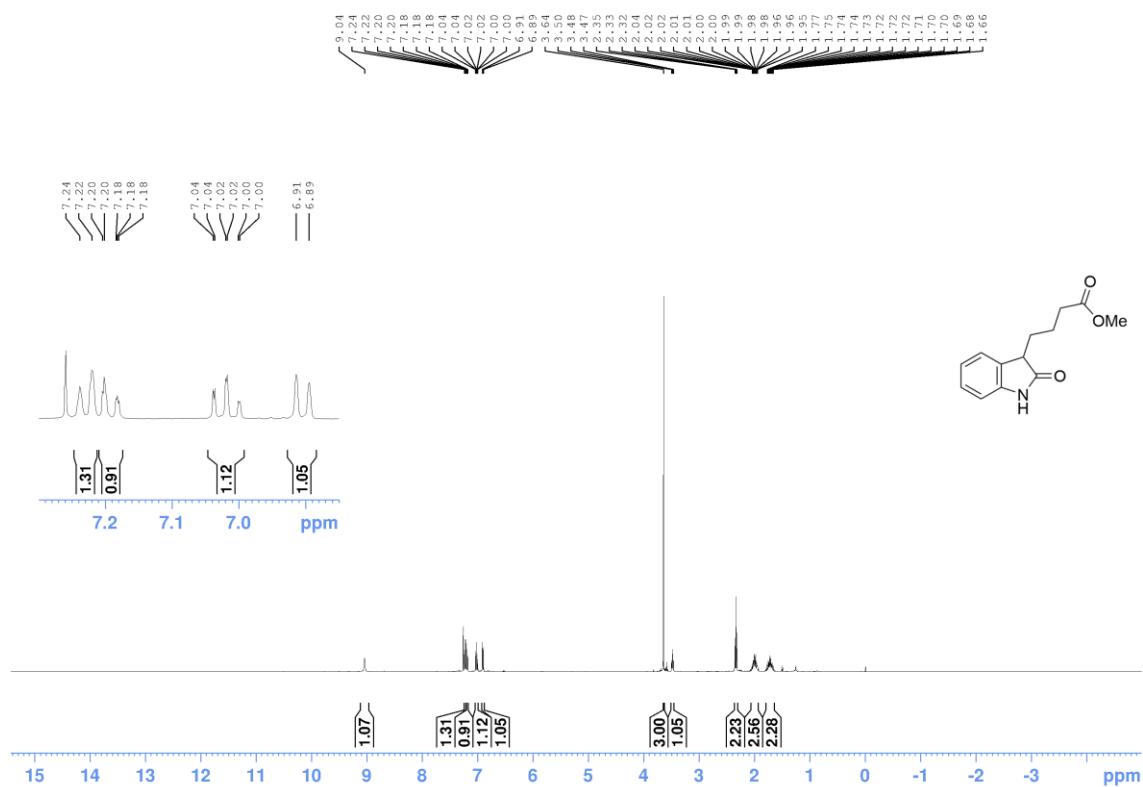
^1H NMR spectrum of **9k** (400 MHz, CDCl_3)



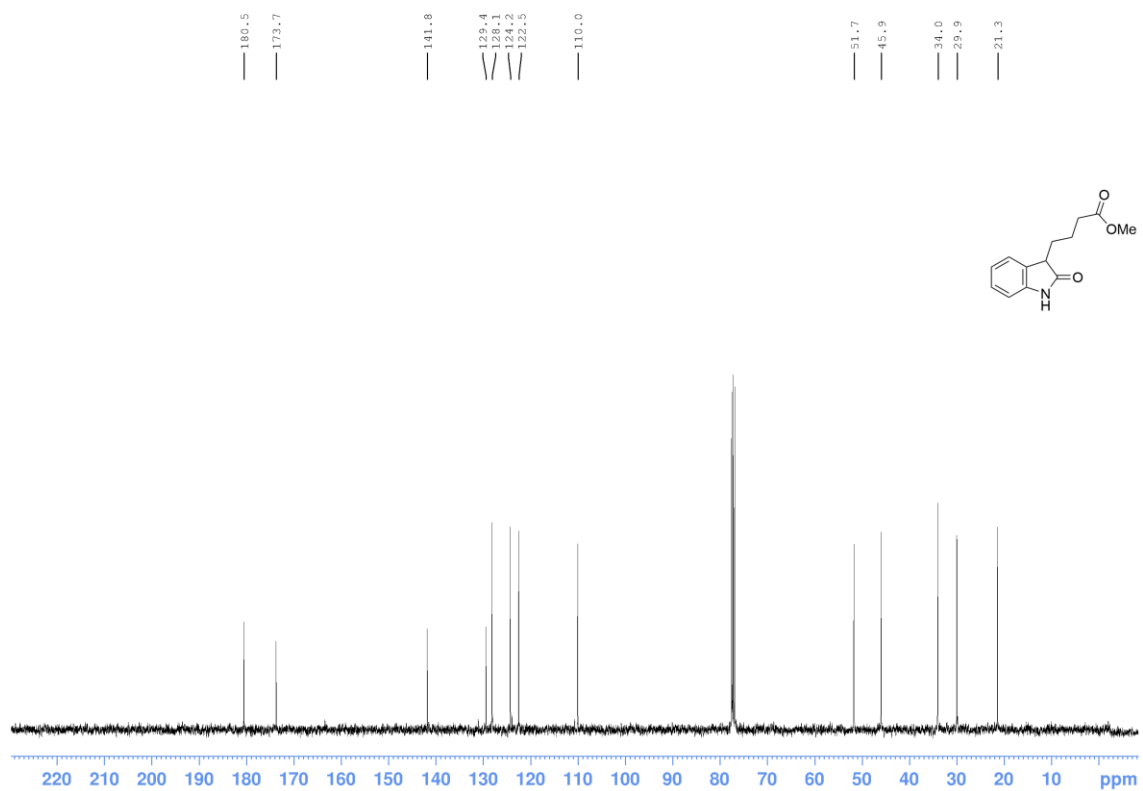
^{13}C NMR spectrum of **9k** (400 MHz, CDCl_3)



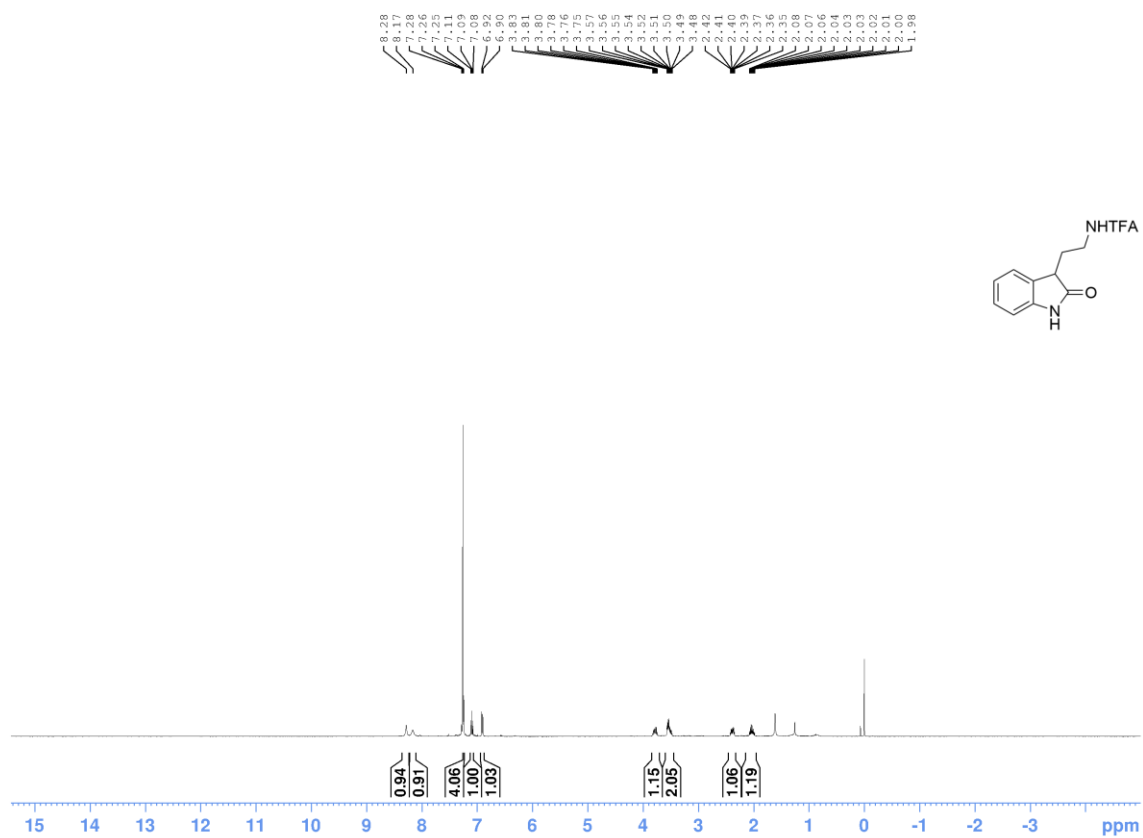
^1H NMR spectrum of **91** (400 MHz, CDCl_3)



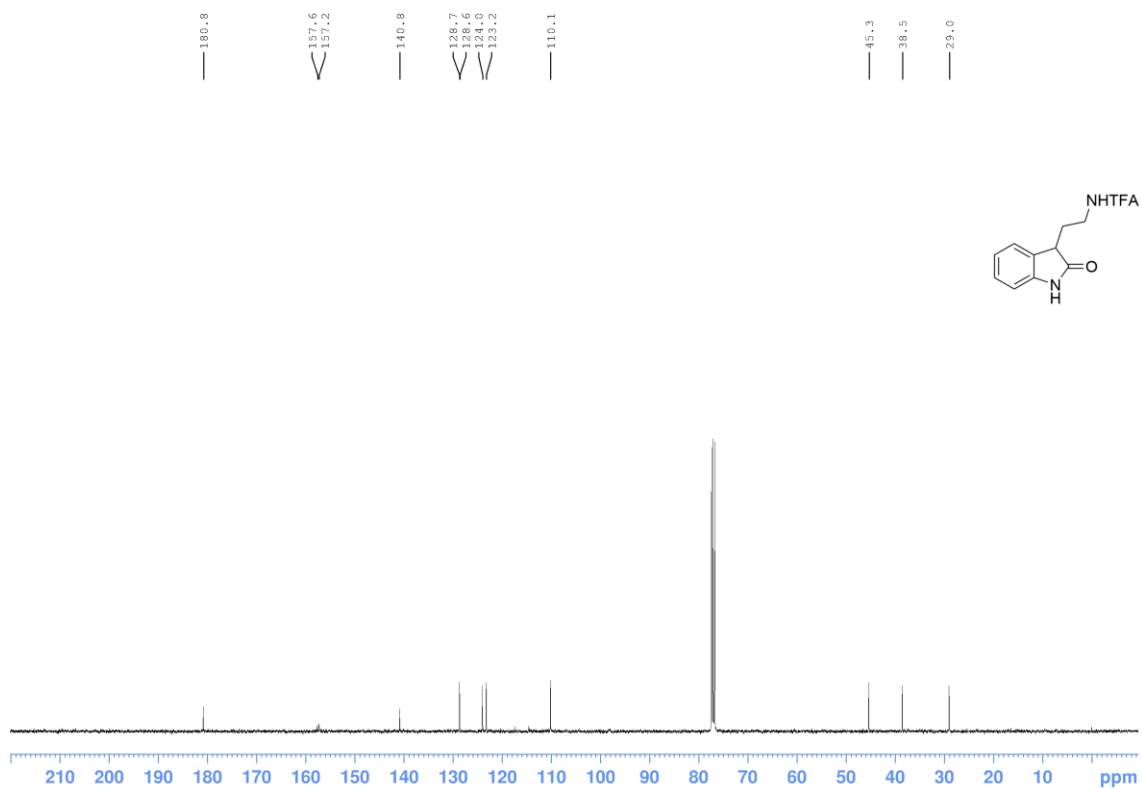
^{13}C NMR spectrum of **91** (400 MHz, CDCl_3)



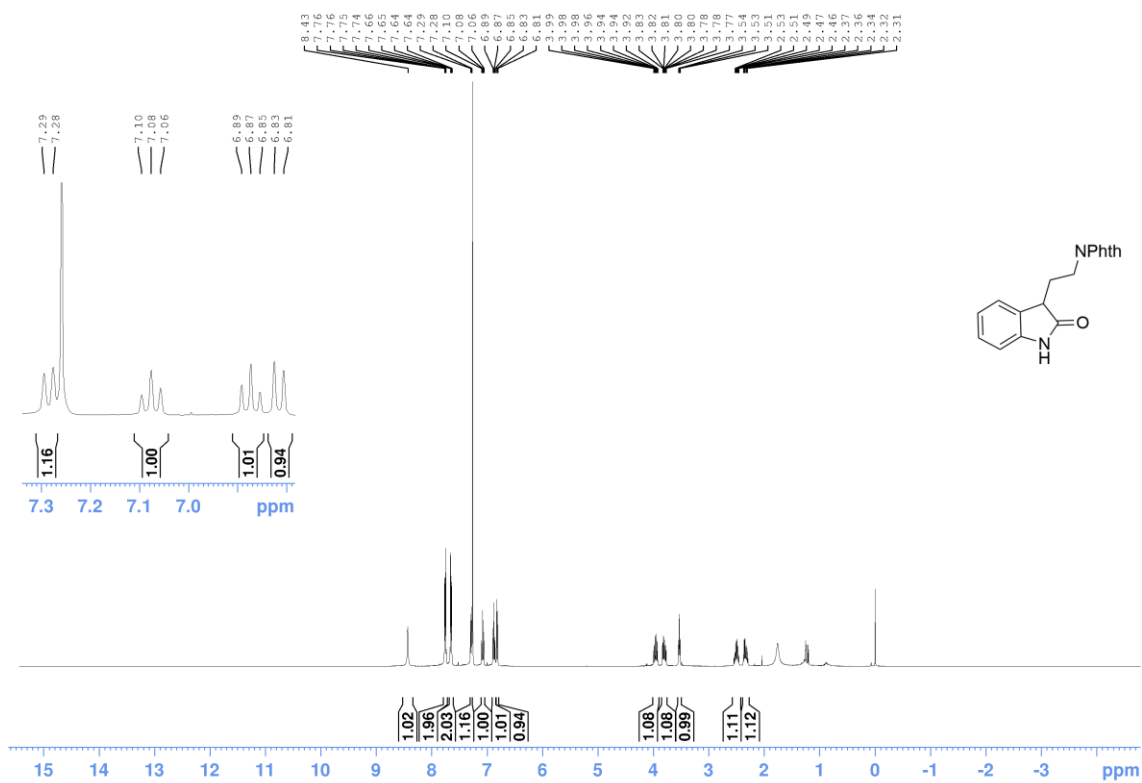
^1H NMR spectrum of **9m** (400 MHz, CDCl_3)



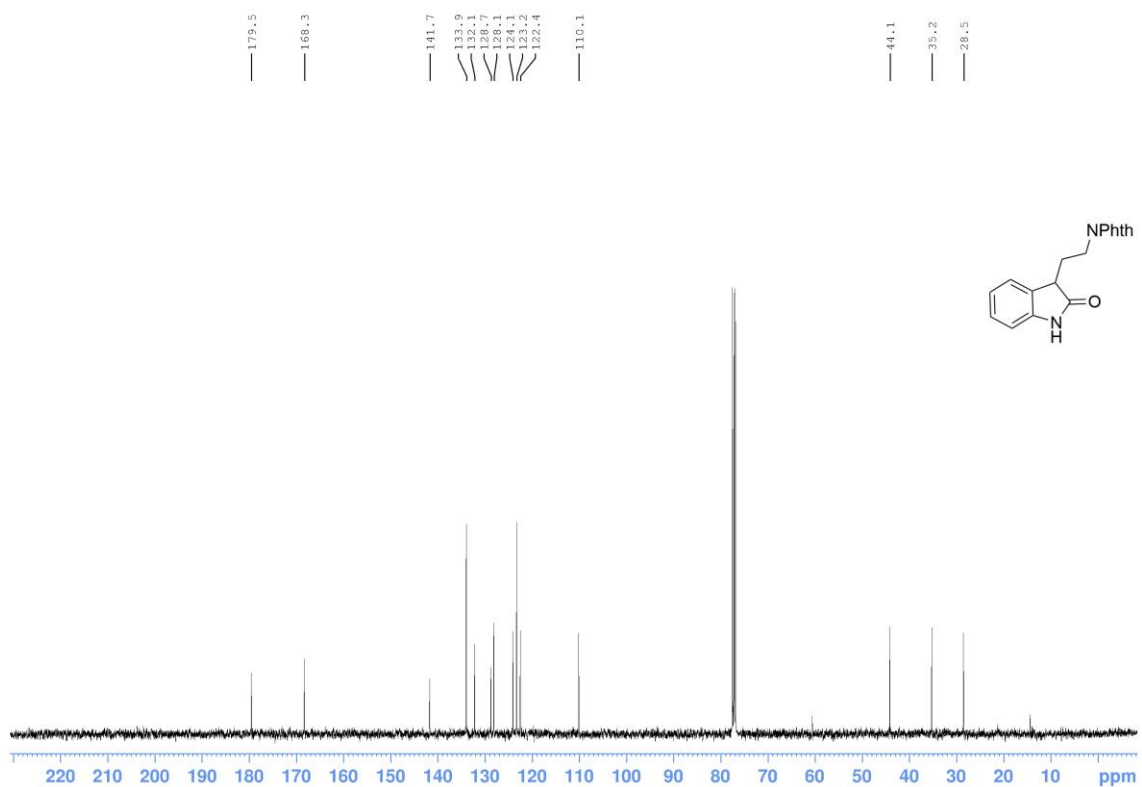
^{13}C NMR spectrum of **9m** (400 MHz, CDCl_3)



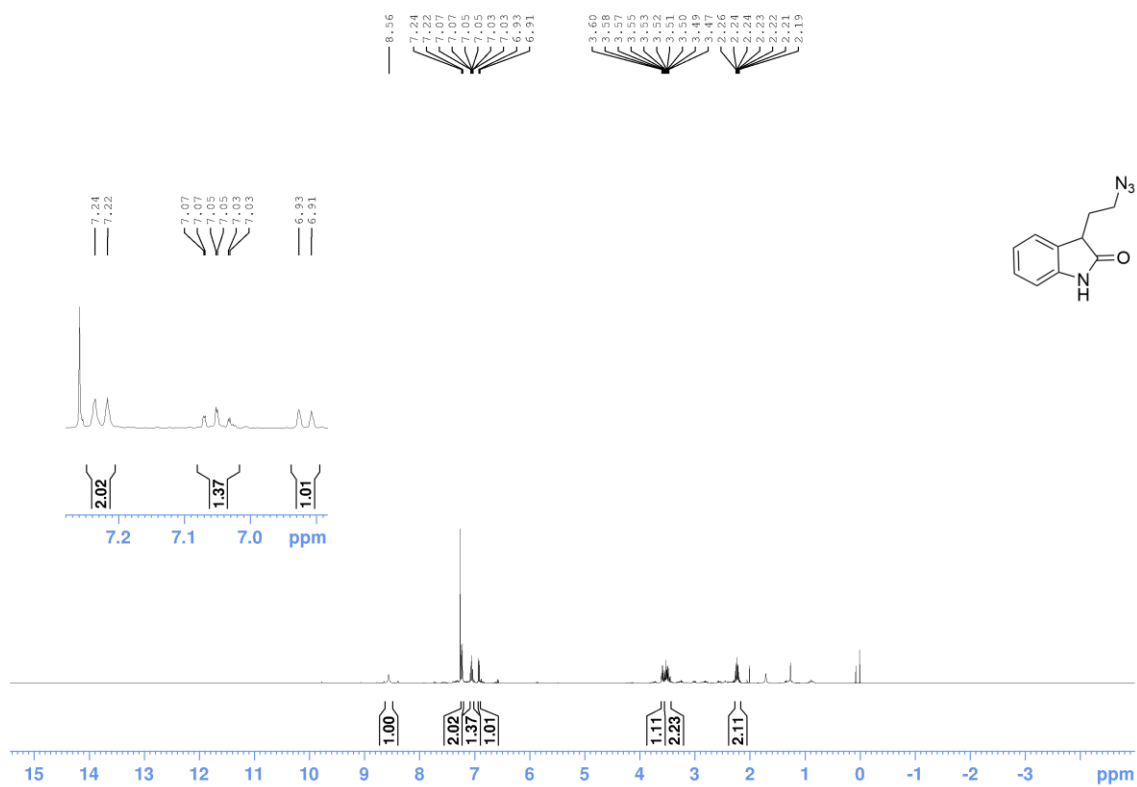
^1H NMR spectrum of **9n** (400 MHz, CDCl_3)



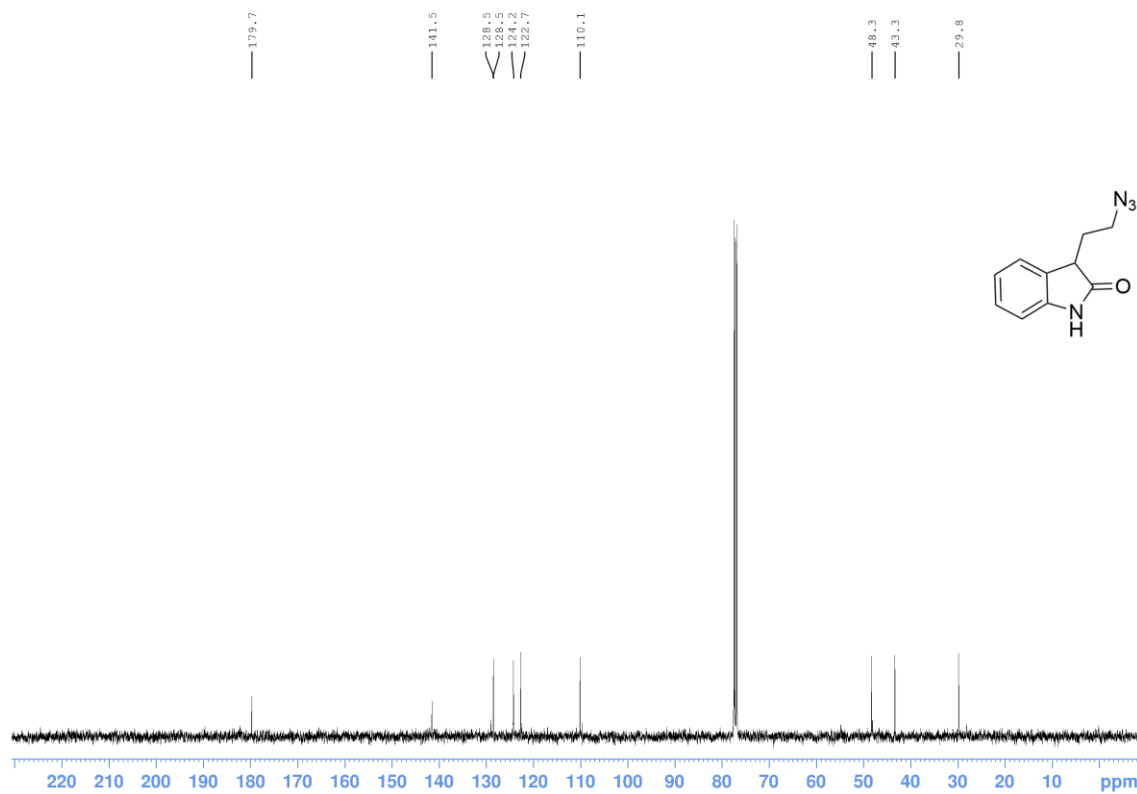
^{13}C NMR spectrum of **9n** (400 MHz, CDCl_3)



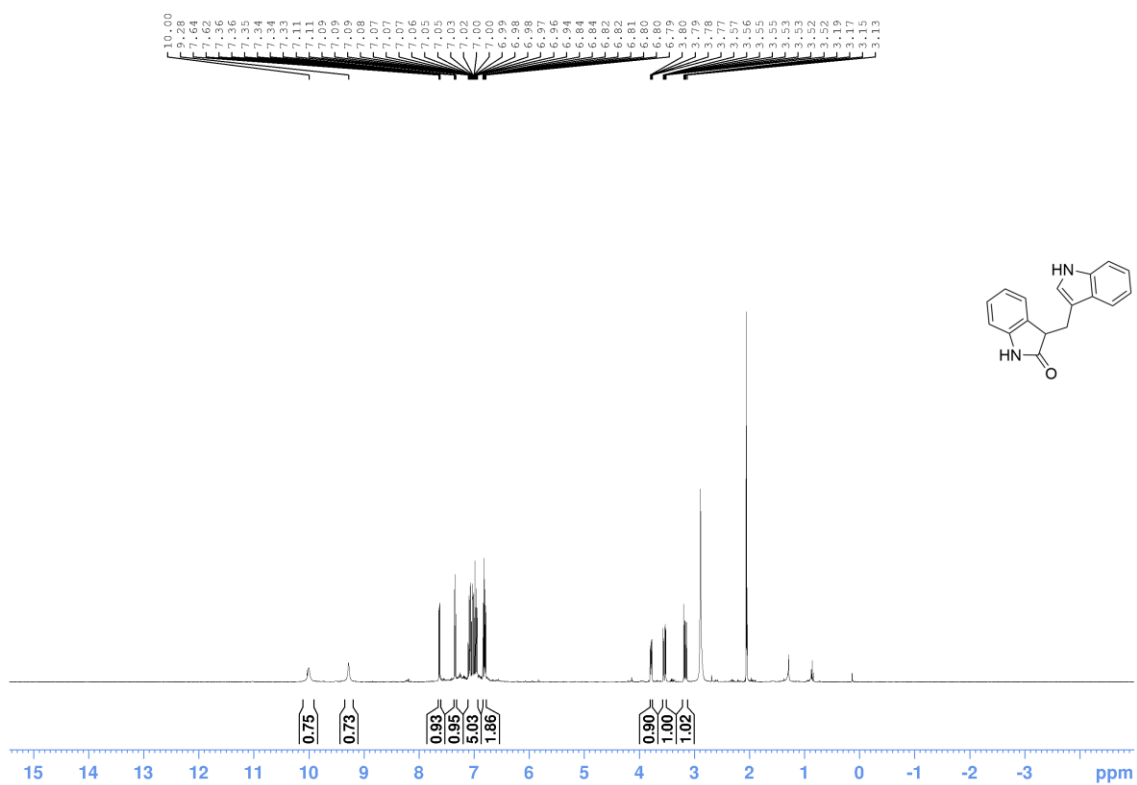
^1H NMR spectrum of **9p** (400 MHz, CDCl_3)



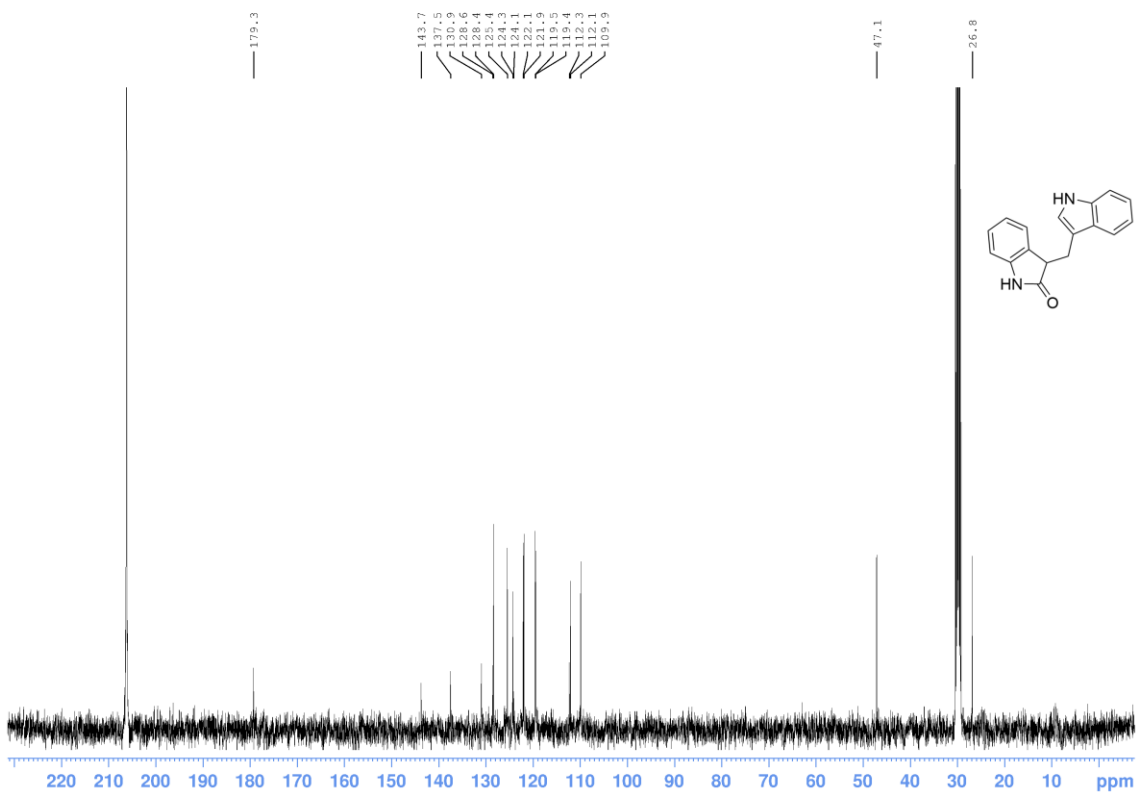
^{13}C NMR spectrum of **9p** (400 MHz, CDCl_3)



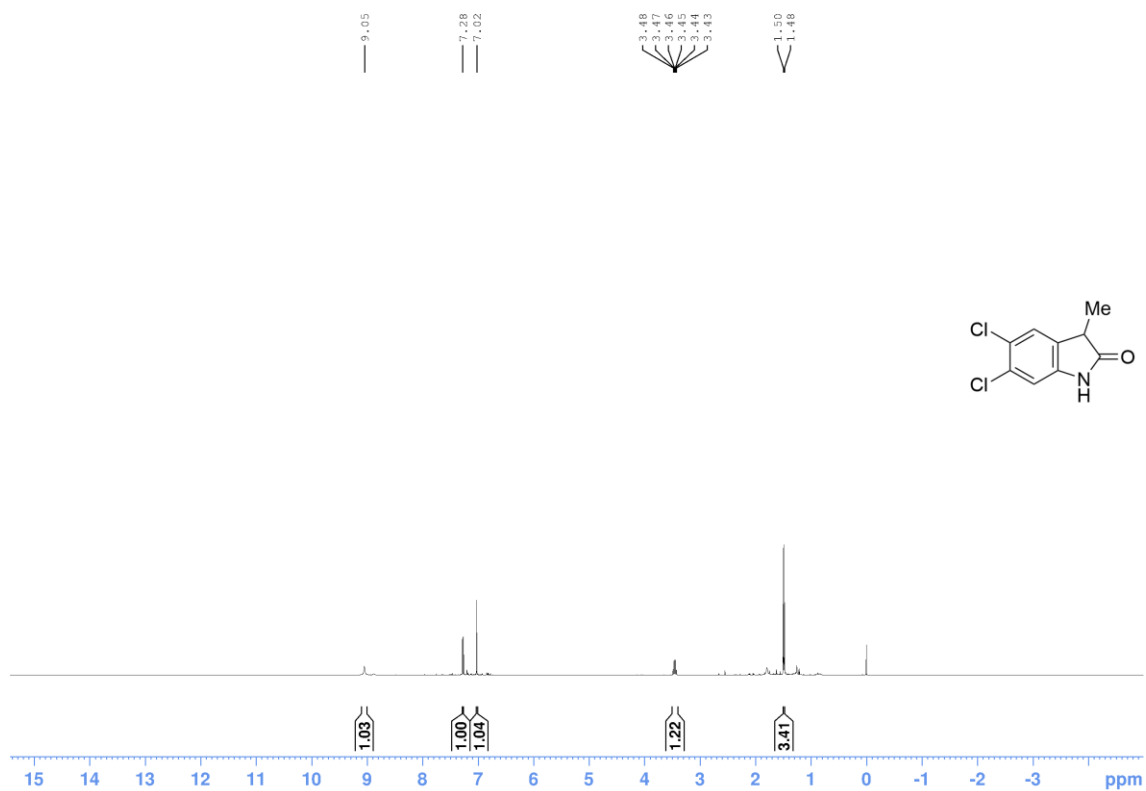
^1H NMR spectrum of **9q** (400 MHz, $(\text{CD}_3)_2\text{CO}$)



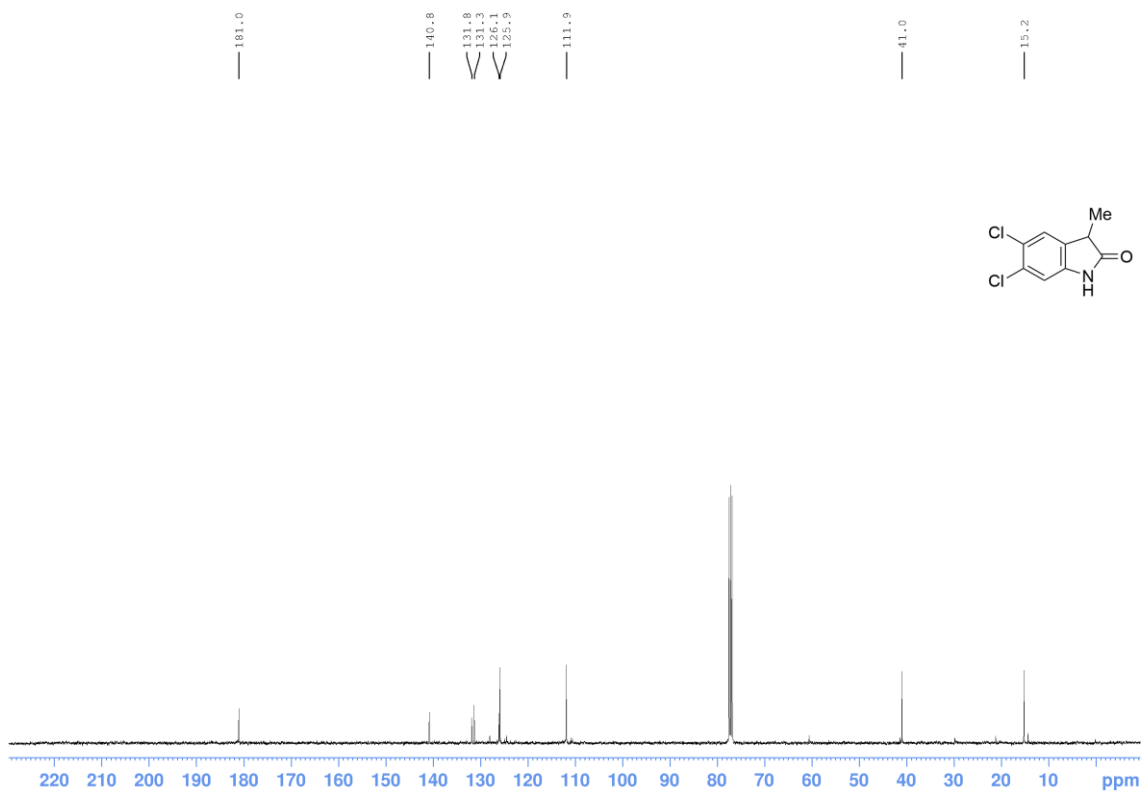
^{13}C NMR spectrum of **9q** (400 MHz, $(\text{CD}_3)_2\text{CO}$)



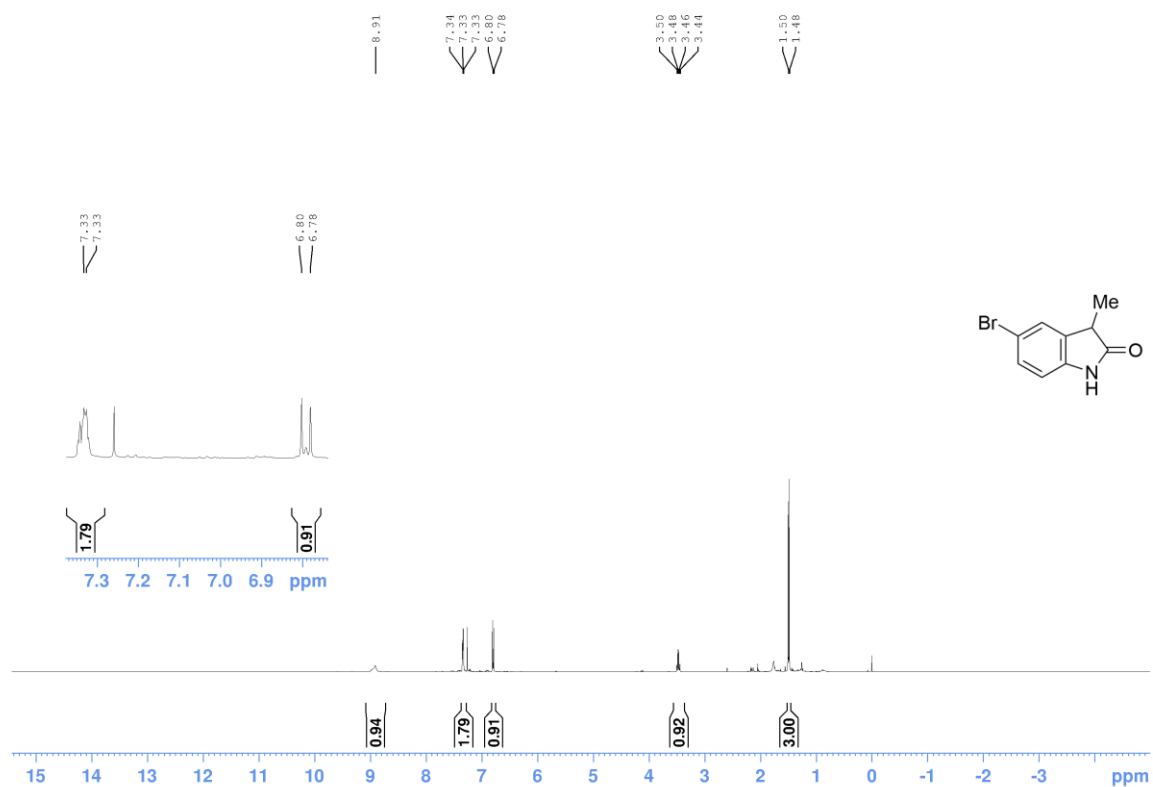
^1H NMR spectrum of **9s** (400 MHz, CDCl_3)



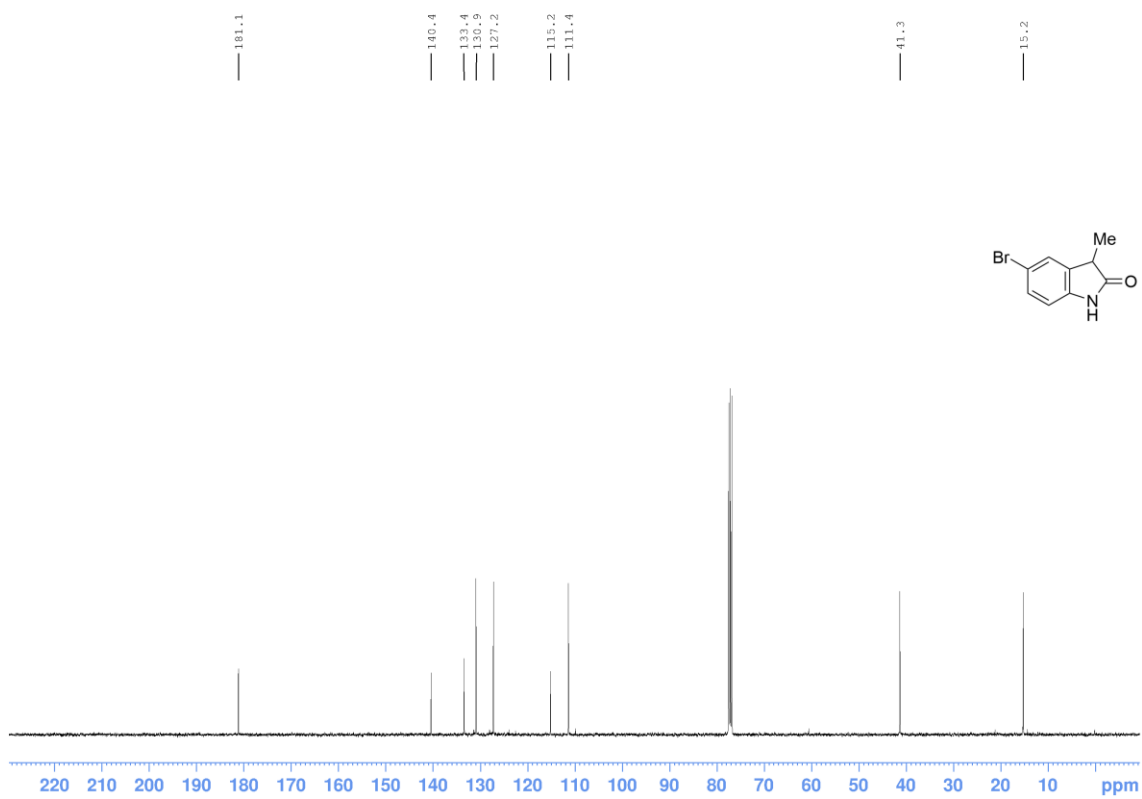
^{13}C NMR spectrum of **9s** (400 MHz, CDCl_3)



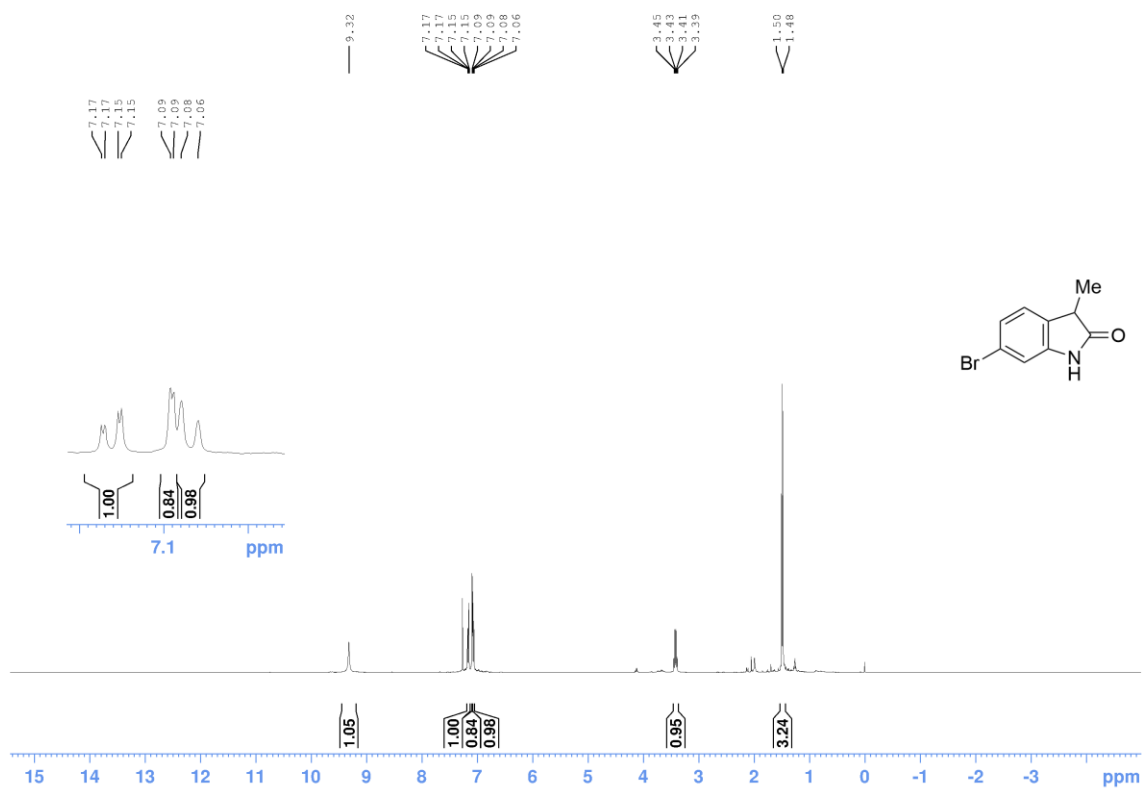
^1H NMR spectrum of **9t** (400 MHz, CDCl_3)



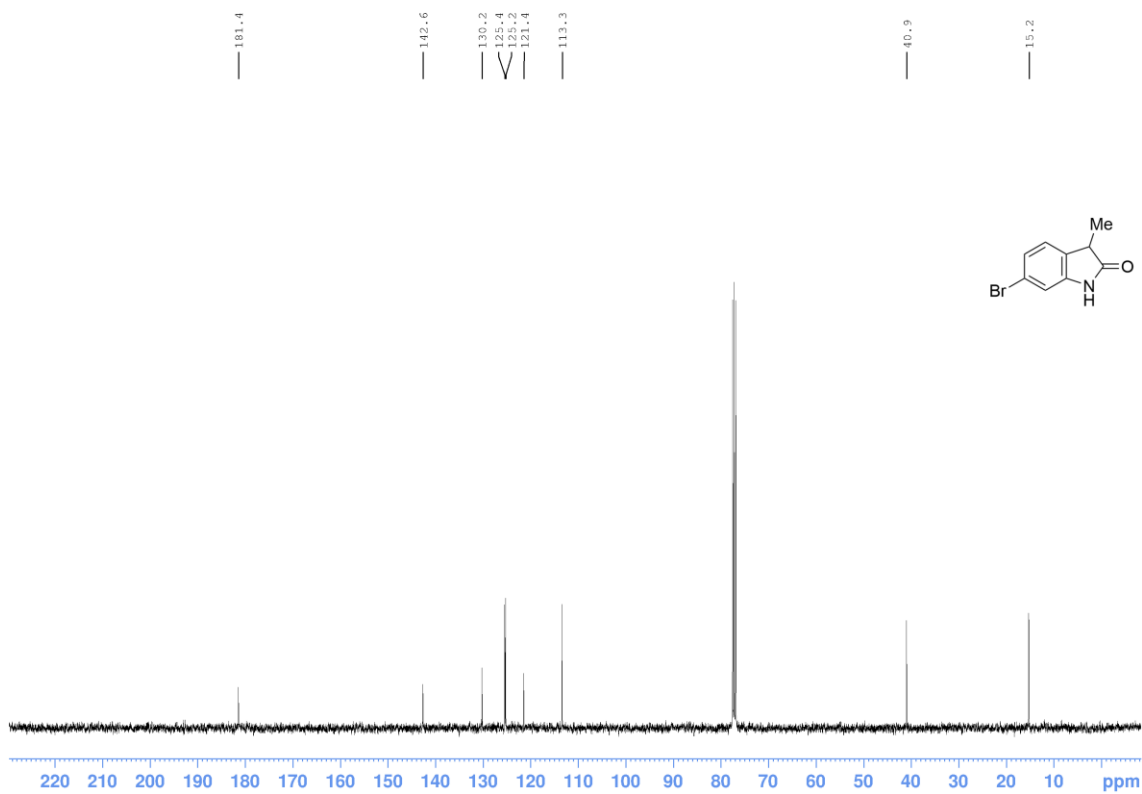
^{13}C NMR spectrum of **9t** (400 MHz, CDCl_3)



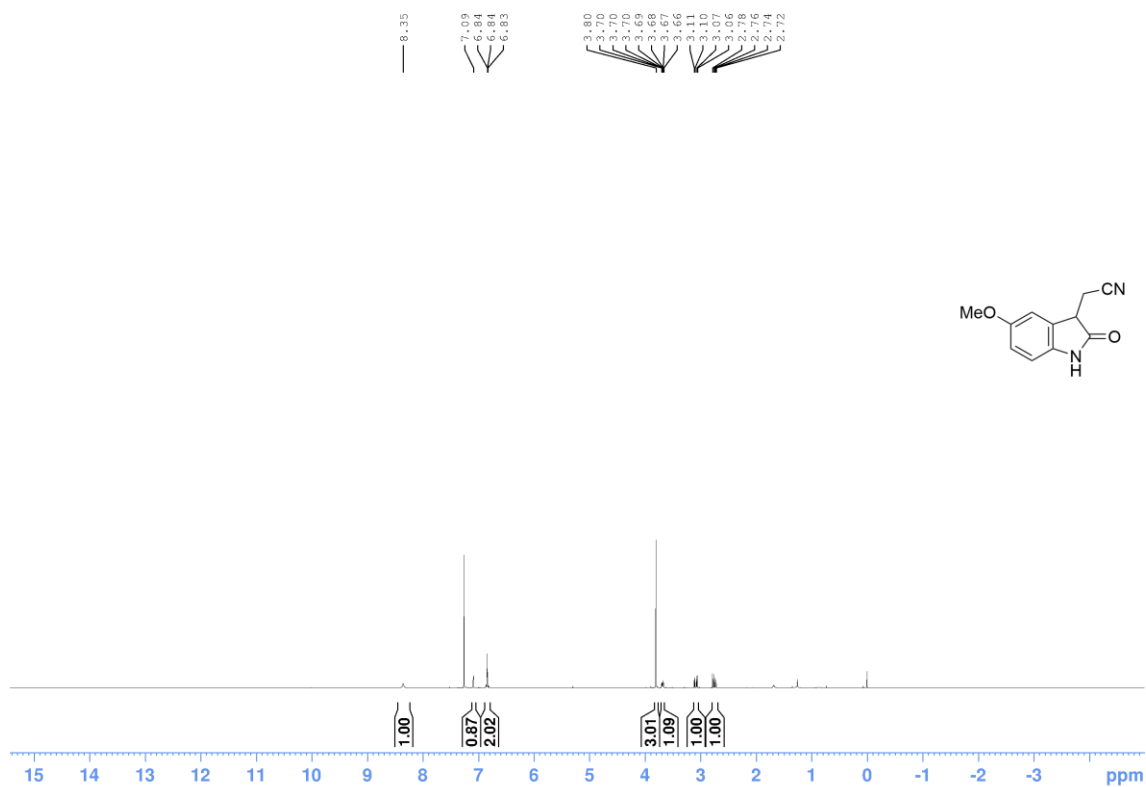
^1H NMR spectrum of **9u** (400 MHz, CDCl_3)



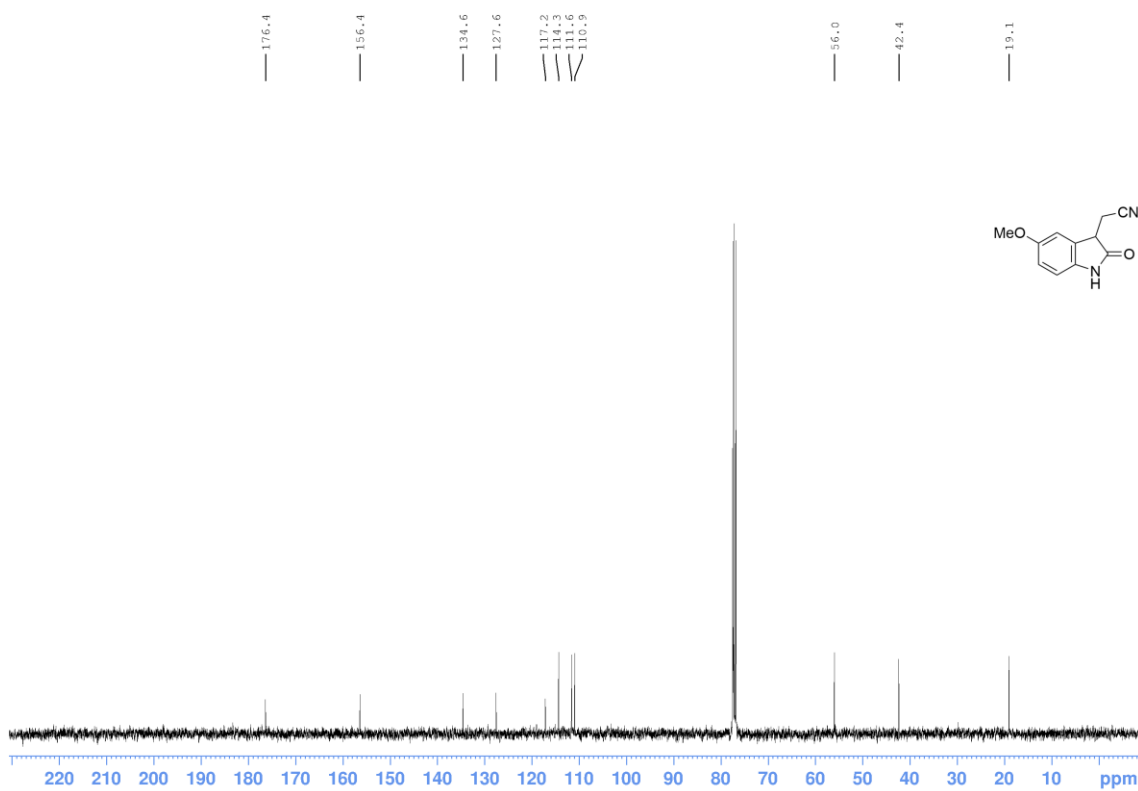
^{13}C NMR spectrum of **9u** (400 MHz, CDCl_3)



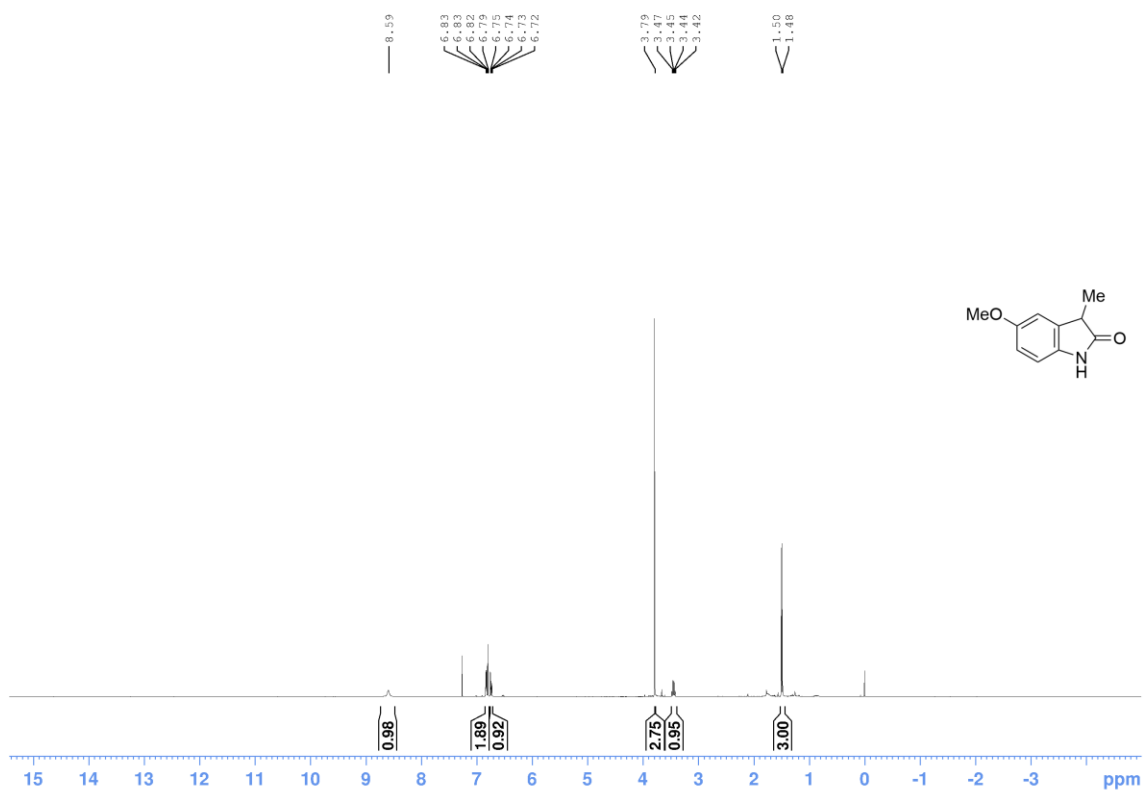
^1H NMR spectrum of **9w** (400 MHz, CDCl_3)



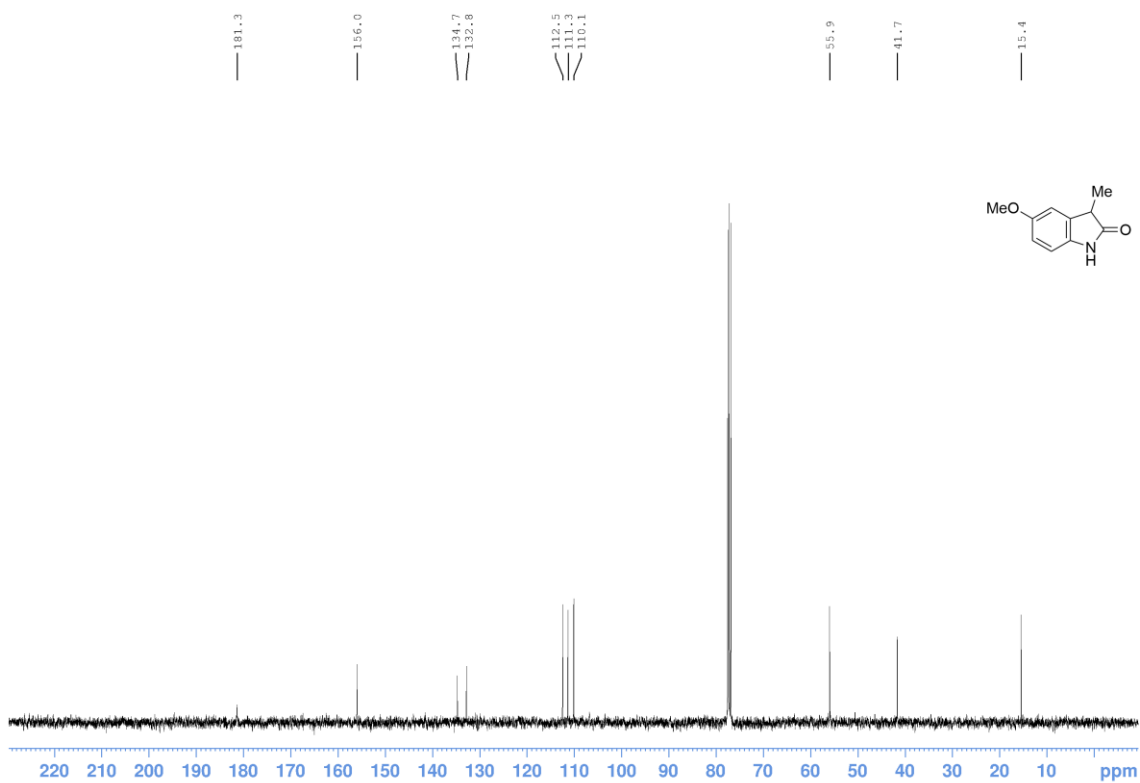
^{13}C NMR spectrum of **9w** (400 MHz, CDCl_3)



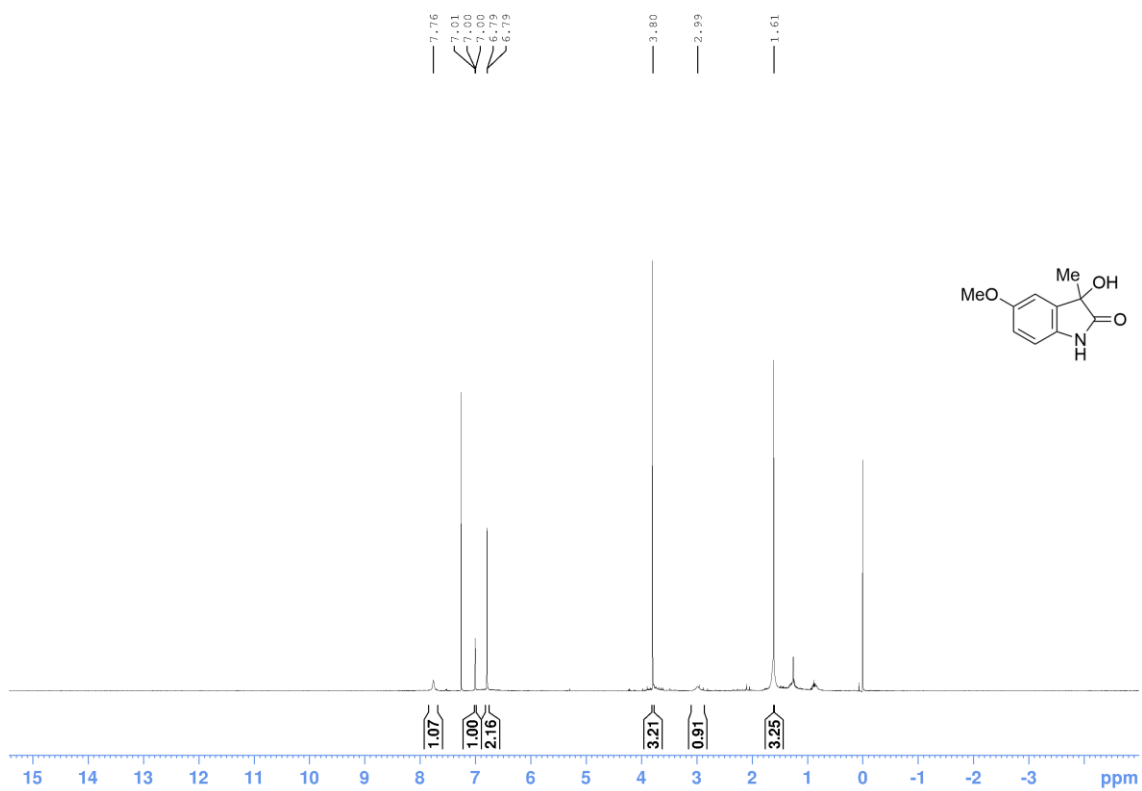
^1H NMR spectrum of **9z** (400 MHz, CDCl_3)



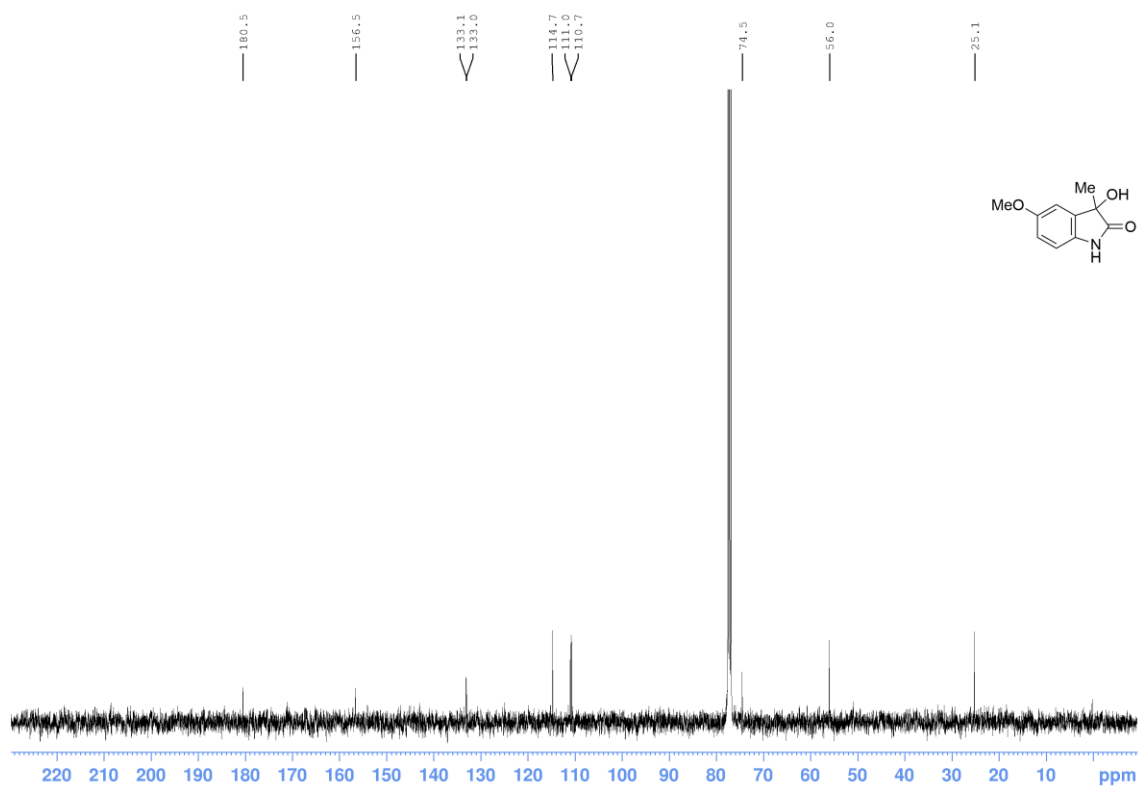
^{13}C NMR spectrum of **9z** (400 MHz, CDCl_3)



^1H NMR spectrum of **9aa** (400 MHz, CDCl_3)



^{13}C NMR spectrum of **9aa** (400 MHz, CDCl_3)



^1H NMR spectrum of **14** (400 MHz, CDCl_3)

