Cascade synthesis of indolizines and pyrrolo[1,2-*a*]pyrazines from 2-formyl-1-propargylpyrroles

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SUPPLEMENTARY INFORMATION

1. Experimental Section

General

Melting points were determined on a Krüss KSP 1N capillary melting point apparatus. IR spectra were recorded on a Perkin-Elmer 2000 spectrophotometer. ^{1}H and ^{13}C NMR spectra were captured on Varian Mercury (300 MHz), Varian VNMR (500 MHz), Bruker 600AVANCE III (600 MHz) and Bruker Ascend (750 MHz) instruments, with $CDCl_3$ as the solvent and TMS as internal standard. Signal assignments were based on 2D NMR spectra (HMQC, HMBC and ROESY). Mass spectra (MS) were recorded on Thermo Polaris Q-Trace GC Ultra and Hewlett-Packard 5971A spectrometers. High-resolution mass spectra (HRMS) were obtained (in electron impact mode) on a Jeol JSM-GCMateII spectrometer. Analytical thin-layer chromatography was carried out with E. Merck silica gel 60 F254 coated 0.25 plates, visualized by using a long- and short-wavelength UV lamp. Flash column chromatography was performed over Natland International Co. silica gel (230-400 mesh). All air moisture sensitive reactions were conducted under N_2 with oven-dried glassware. Triethylamine (TEA) was distilled on NaOH. Before their application, THF and toluene were freshly distilled over sodium, as were DMF, DMAc, and CH_2Cl_2 over CaH_2. MeOH and EtOH were distilled over sodium. K_2CO_3 was dried overnight at 200 °C prior to use. All other reagents were employed without further purification.

1-(Propa-1,2-dien-1-yl)-1*H*-pirrole-2-carbaldehyde (5).[1] Method A: In a threaded ACE glass pressure tube equipped with a sealed Teflon screw cap and a magnetic stirring bar, a mixture of **2a** (0.100 g, 0.75 mmol) and sodium hydride (0.057 g, 2.37 mmol) in dry DMF (2.0 mL) and under N_2 atmosphere was heated at 0 °C for 1 h. The mixture was extracted with hexane/EtOAc (1:1, 40 mL) and washed with water (2 x 20 mL). The organic layer was dried (Na_2SO_4), the solvent removed under vacuum, and the residue purified by column chromatography over silica gel (30 g/g crude, hexane/EtOAc, 99:1) to provide **5** (0.09 g, 90%) as a yellow oil.

Method B: To a solution of **1** (0.300 g, 3.15 mmol) in dry DMF (6.0 mL) at 0 °C and under N_2, NaH (60%, 0.189 g, 4.73 mmol) was added. The mixture was stirred at 0 °C for 15 min, then propargyl bromide (0.450 g, 3.78 mmol) was added dropwise, and stirring continued at 0 °C for 4 h. Hexane/EtOAc (1:1, 60 mL) was added, the mixture washed with water (2 x 30 mL), the organic layer dried (Na_2SO_4) and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane) to give **5** (0.197 g, 47%) as a yellow oil. *Rf* 0.66 (hexane/EtOAc, 7:3). IR (film): ῡ 2923, 2853, 1666,1470, 1417, 1371, 1305, 738 cm^{-1}. ^{1}H NMR (300

MHz, $CDCl_3$): δ 5.52 (d, *J* = 6.6 Hz, 2H, H-3'), 6.31 (dd, *J* = 3.9, 2.6 Hz, 1H, H-4), 6.98 (dd, *J* = 3.9, 1.8 Hz, 1H, H-3), 7.20-7.24 (m, 1H, H-5), 8.14 (t, *J* = 6.6 Hz, 1H, H-1'), 9.66 (d, *J* = 1.2 Hz, 1H, C*H*O). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 87.4 (C-3'), 98.5 (C-1'), 111.3 (C-4), 125.4 (C-3), 127.9 (C-5), 130.64 (C-2), 179.7 (*C*HO), 202.7 (C-2'). MS (70 eV): *m/z* 133 (M^+, 100), 104 (84), 78 (19), 65 (3), 51 (8).

1-(Prop-2-ynyl)-1*H*-pyrrole-2-carbaldehyde (2a).[1-3] To a solution of **1** (0.300 g, 3.15 mmol) in dry DMF (6.0 mL) at 0 °C and under N_2, NaH (60%, 0.138 g, 3.30 mmol) was added. The mixture was stirred at 0 °C for 15 min, then propargyl bromide (0.450 g, 3.78 mmol) was added dropwise, and stirring continued at 0 °C for 4 h. Subsequently, hexane/EtOAc (1:1, 60 mL) was added, the mixture washed with water (2 x 30 mL), the organic layer dried (Na_2SO_4), and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane) to obtain **2a** (0.399 g, 95%) as a yellow oil. *Rf* 0.65 (hexane/EtOAc, 7:3). IR (film): ῡ 3289, 1660, 1529, 1477, 1405, 1370, 1338, 1315, 1219, 1076, 1031, 747 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.49 (t, *J* = 2.6 Hz, 1H, H-3'), 5.19 (d, *J* = 2.6 Hz, 2H, H-1'), 6.27 (dd, *J* = 4.2, 2.7 Hz, 1H, H-4), 6.96 (dd, *J* = 4.2, 1.8 Hz, 1H, H-3), 7.24-7.27 (m, 1H, H-5), 9.54 (d, *J* = 1.2 Hz, 1H, C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.0 (C-1'), 74.3 (C-3'), 77.4 (C-2'), 110.0 (C-4), 124.9 (C-3), 130.3 (C-5), 130.9 (C-2), 179.4 (*C*HO). MS (70 eV): *m/z* 133 (M^+, 47), 104 (100), 78 (40), 65 (12), 51 (34).

1-(3-Phenylprop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2b).[2,3] In a threaded ACE glass pressure tube equipped with a sealed Teflon screw cap and a magnetic stirring bar, a mixture of **2a** (0.200 g, 1.50 mmol), iodobenzene (0.386 g, 1.65 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol), CuI (0.011 g, 0.06 mmol), and K_2CO_3 (1.035 mmol, 7.50 mmol) in dry DMF (2.0 mL) was heated at 60 °C for 4 h. The mixture was diluted with aqueous HCl (5%, 10 mL) and extracted twice with hexane/EtOAc (1:1, 2 x 40 mL). The organic layer was dried (Na_2SO_4) and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane/EtOAc, 98:2) to afford **2b** (0.226 g, 72%) as a pale yellow solid. *Rf* 0.67 (hexane/EtOAc, 7:3); mp 55–56 °C [Lit.[2] 58-60 ºC]. IR (film): ῡ 2810, 1662, 1529, 1478, 1406, 1370, 1337, 1314, 1217, 1074, 1030, 789, 756, 691 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.43 (s, 2H, H-1'), 6.30 (dd, *J* = 4.0, 2.5 Hz, 1H, H-4), 6.98 (dd, *J* = 4.0, 1.5 Hz, 1H, H-3), 7.30-7.35 (m, 3H, H-3'', H-4''), 7.37 (br s, 1H, H-5), 7.43-7.47 (m, 2H, H-2''), 9.58 (d, *J* = 1.0 Hz, 1H, C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.0 (C-1'), 82.7 (C-2'), 86.1 (C-3'), 110.0 (C-4), 122.1 (C-1''), 125.0 (C-3), 128.3 (C-3''), 128.7 (C-4''), 130.4 (C-5), 131.0 (C-2), 131.8 (C-2''), 179.5 (*C*HO). HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{11}NO$: 209.0841; found: 209.0841.

1-(3-(*p*-Tolyl)prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2c). Following the method of preparation for **2b**, a mixture of **2a** (0.200 g, 1.50 mmol), 4-iodotoluene (0.360 g, 1.65 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol), CuI (0.011 g, 0.06 mmol), and K_2CO_3 (1.035 mmol, 7.50 mmol) in dry DMF was heated at 60 °C for 4 h to produce **2c** (0.235 g, 70%) as a brown solid. *Rf* 0.70 (hexane/EtOAc, 7:3); mp 45–46 °C. IR (film): ῡ 2922, 2808, 1661, 1509, 1479, 1406, 1369, 1337, 1314, 1289, 1216, 1074, 1031, 817, 746 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.34 (s, 3H, C*H*$_3$), 5.41 (s, 2H, H-1'), 6.29 (ddd, *J* = 4.0, 3.0, 1.5 Hz, 1H, H-4), 6.97 (dt, *J* = 4.0, 1.0 Hz,1H, H-3), 7.12 (br d, *J* = 7.7 Hz, 2H, H-3''), 7.34 (br d, *J* = 7.7 Hz, 2H, H-2''), 7.37 (br s, 1H, H-5), 9.58 (d, *J* = 1.0 Hz, 1H, C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3 (*C*H_3), 39.0 (C-1'), 81.9 (C-2'), 86.1 (C-3'), 109.8 (C-4), 119.0 (C-1''), 124.7 (C-3), 129.0 (C-3''), 130.4 (C-5), 131.1 (C-2), 131.6 (C-2''), 138.7 (C-4''), 179.3 (*C*HO). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{13}NO$: 223.0997; found: 223.0993.

1-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2d).[2] Following the method of preparation for **2b**, a mixture of **2a** (0.200 g, 1.50 mmol), 4-iodoanisole (0.386 g, 1.65 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol), CuI (0.011 g, 0.06 mmol), and K_2CO_3 (1.035 g, 7.50 mmol) in dry DMF (2 mL) was heated at 60 °C for 4 h, resulting in **2d** (0.216 g, 60%) as a brown solid. *Rf* 0.62 (hexane/EtOAc, 7:3); mp 71–72 °C [Lit.[2] 69-71 ºC]. IR (film): ῡ 2927, 2837, 1662, 1606, 1509, 1405, 1338, 1290, 1250, 1216, 1174, 1074, 1032, 833, 747 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.81 (s, 3H, OC*H*$_3$), 5.40 (s, 2H, H-1'), 6.29 (dd, *J* = 4.0, 2.5 Hz, 1H, H-4), 6.82-6.86 (m, 2H, H-3''), 6.98 (dd, *J* = 4.0, 2.0 Hz, 1H, H-3), 7.36-7.40 (m, 3H, H-2'', H-5), 9.57 (d, *J* = 1.0 Hz, 1H, *C*HO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.1 (C-1'), 55.3 (O*C*H_3), 81.2 (C-2'), 86.1 (C-3'), 109.9 (C-4), 113.9 (C-3''), 114.1 (C-1''), 124.9 (C-3), 130.4 (C-5), 131.0 (C-2), 133.3 (C-2''), 159.8 (C-4''), 179.5 (*C*HO). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{13}NO_2$: 239.0946; found: 239.0948.

1-(3-(4-Formylphenyl)prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2e). In a threaded ACE glass pressure tube equipped with a sealed Teflon screw cap and a magnetic stirring bar, a mixture of **2a** (0.200 g, 1.50 mmol), 4-bromobenzaldehyde (0.278 g, 1.50 mmol) and $PdCl_2(PPh_3)_2$ (0.042 g, 0.06 mmol) in dry TEA (1.0 mL) was stirred at 80 °C for 1 h. The mixture was diluted with aqueous HCl (5%, 10 mL) and extracted with hexane/EtOAc (1:1, 2 x 40 mL). The organic layer was dried (Na_2SO_4) and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane/EtOAc, 98:2) to furnish **2e** (0.197 g, 55%) as a pale yellow solid. *Rf* 0.50 (hexane/EtOAc, 7:3); mp 90–92 °C. IR (film): ῡ 3108, 2811, 1701, 1658, 1603, 1405, 1335, 1311, 1288, 1207, 1167, 1076, 831, 788, 744 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.46 (s, 2H, H-1'), 6.31 (dd, *J* = 4.0, 3.0 Hz, H-4), 6.99 (dd, *J* = 4.0, 1.5 Hz, 1H, H-3), 7.30 (br s, 1H, H-5), 7.58 (br d, *J* = 8.3

Hz, 2H, H-2''), 7.83 (br d, *J* = 8.3 Hz, 2H, H-3''), 9.59 (s, 1H, C*H*O), 10.00 (s, 1H, ArC*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.8 (C-1'), 84.8 (C-3'), 86.9 (C-2'), 110.3 (C-4), 125.0 (C-3), 128.4 (C-1''), 129.5 (C-3''), 130.4 (C-5), 131.1 (C-2), 132.3 (C-2''), 135.8 (C-4''), 179.6 (*C*HO), 191.3 (ArC*H*O). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{11}NO_2$: 237.0790; found: 237.0791.

1-(3-(4-Acetylphenyl)prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2f). Following the method of preparation for **2e**, a mixture of **2a** (0.200 g, 1.50 mmol), 1-(4-bromophenyl)ethan-1-one (0.299 g, 1.50 mmol) and $PdCl_2(PPh_3)_2$ (0.042 g, 0.06 mmol) in dry TEA (1.0 mL) was heated at 60 °C for 2 h to obtain **2f** (0.204 g, 54%) as a pale yellow solid. *Rf* 0.38 (hexane/EtOAc, 8:2); mp 63–65 °C. IR (film): ῡ 3112, 2808, 1683, 1661, 1602, 1404, 1264, 1075, 838, 764, 749 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.59 (s, 3H, COC*H*$_3$), 5.46 (s, 2H, H-1'), 6.31 (dd, *J* = 4.0, 2.5 Hz, 1H, H-4), 6.99 (dd, *J* = 4.0, 1.5 Hz, 1H, H-3), 7.30-7.32 (m, 1H, H-5), 7.55-7.49 (m, 2H, H-2''), 7.92-7.88 (m, 2H, H-3''), 9.59 (d, *J* = 1.0 Hz, 1H, C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.6 (CO*C*H$_3$), 38.8 (C-1'), 85.0 (C-3'), 86.1 (C-2'), 110.2 (C-4), 124.9 (C-3), 127.0 (C-1''), 128.2 (C-3''), 130.4 (C-5), 131.1 (C-2), 131.9 (C-2''), 136.6 (C-4''), 179.6 (*C*HO), 197.2 (*C*OCH$_3$). HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{13}NO_2$: 251.0946; found: 251.0946.

1-(3-(3-Methoxyphenyl)prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2g). Following the method of preparation for **2b**, a mixture of **2a** (0.200 g, 1.50 mmol), 3-iodoanisole (0.386 g, 1.65 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol), CuI (0.011 g, 0.06 mmol), and K_2CO_3 (1.035 mmol, 7.50 mmol) in dry DMF was heated at 60 °C for 4 h to yield **2g** (0.230 g, 64%) as a yellow oil. *Rf* 0.62 (hexane/EtOAc, 7:3). IR (film): ῡ 2937, 2834, 1661, 1597, 1575, 1479, 1404, 1337, 1316, 1289, 1204, 1164, 1074, 1042, 784, 745, 686 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, 3H, OC*H*$_3$), 5.42 (s, 2H, H-1'), 6.30 (dd, *J* = 4.0, 2.5 Hz, 1H, H-4), 6.89 (ddd, *J* = 8.5, 3.0, 1.0 Hz, 1H, H-4''), 6.96-6.98 (m, 1H, H-2''), 6.98 (dd, *J* = 4.0, 1.5 Hz, 1H, H-3), 7.04 (dt, *J* = 7.5, 1.5 Hz, 1H, H-6''), 7.22 (dd, *J* = 8.5, 7.5 Hz, 1H, H-5''), 7.36 (br s, 1H, H-5), 9.57 (d, *J* = 1.0 Hz, 1H, C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.9 (C-1'), 55.2 (O*C*H$_3$), 82.5 (C-2'), 85.9 (C-3'), 110.0 (C-4), 115.3 (C-4''), 116.6 (C-2''), 123.1 (C-1''), 124.3 (C-6''), 125.0 (C-3), 129.4 (C-5''), 130.4 (C-5), 131.1 (C-2), 159.2 (C-3''), 179.5 (*C*HO). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{13}NO_2$: 239.0946; found: 239.0943.

1-(3-(3-Nitrophenyl)prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2h).[2] Following the method of preparation for **2b**, a mixture of **2a** (0.200 g, 1.50 mmol), 1-iodo-3-nitrobenzene (0.411 g, 1.65 mmol), $PdCl_2(PPh_3)_2$ (0.021 g, 0.03 mmol), and CuI (0.011 g. 0.06 mmol) in dry TEA (1.515 g, 15.00 mmol) was stirred at 80 °C for 1 h to provide **2h** (0.328 g, 86%) as a pale yellow solid. *Rf* 0.62

(hexane/EtOAc, 7:3); mp 84-86 °C [Lit.[2] 107-108 °C]. IR (film): ῡ 3084, 2813, 1662, 1529, 1478, 1405, 1351, 1315, 1218, 1076, 1031, 874, 808, 753, 736, 674 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.46 (s, 2H, H-1'), 6.31-6.34 (m, 1H, H-4), 7.00 (dt, *J* = 4.0, 1.5 Hz, 1H, H-3), 7.27-7.30 (m, 1H, H-5), 7.50 (t, *J* = 8.3 Hz, 1H, H-5''), 7.74 (dt, *J* = 8.3, 1.5 Hz, 1H, H-6''), 8.18 (dm, *J* = 8.3 Hz 1H, H-4''), 8.28 (br s, 1H, H-2''), 9.59 (d, *J* = 1.0 Hz, 1H, C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.7 (C-1'), 83.2 (C-3'), 85.7 (C-2'), 110.4 (C-4), 123.4 (C-4''), 123.9 (C-1''), 125.1 (C-3), 126.6 (C-2''), 129.4 (C-5''), 130.5 (C-5), 131.1 (C-2), 137.5 (C-6''), 148.0 (C-3''), 179.7 (*C*HO). HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{10}N_2O_3$: 254.0692; found: 254.0701.

1-(3-(3-Formylphenyl)prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2i). Following the method of preparation for **2e**, a mixture of **2a** (0.200 g, 1.50 mmol), 3-bromobenzaldehyde (0.278 g, 1.50 mmol), and $PdCl_2(PPh_3)_2$ (0.42 g, 0.06 mmol) in dry TEA (1.0 mL) was stirred at 80 °C for 1 h to give **2i** (0.147 g, 41%) as a yellow oil. *Rf* 0.48 (hexane/EtOAc, 7:3). IR (film): ῡ 2932, 1713, 1506, 1383, 1261, 1209, 1160, 1029, 804, 734, 701 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 5.45 (s, 2H, H-1'), 6.31 (dd, *J* = 3.9, 2.4 Hz, 1H, H-4), 6.99 (dd, *J* = 3.9, 1.2 Hz, 1H, H-3), 7.32 (br s, 1H, H-5), 7.50 (t, *J* = 7.8 Hz, 1H, H-5''), 7.68 (d, *J* = 7.8 Hz, 1H, H-6''), 7.84 (d, *J* = 7.8 Hz, 1H, H-4''), 7.94 (s, 1H, H-2''), 9.59 (s, 1H, C*H*O), 9.98 (s, 1H, PhC*H*O). ^{13}C NMR (150 MHz, $CDCl_3$): δ 38.8 (C-1'), 84.3 (C-3'), 84.5 (C-2'), 110.2 (C-4), 123.3 (C-1''), 125.0 (C-3), 129.1 (C-5''), 129.4 (C-4''), 130.4 (C-5), 131.0 (C-2), 133.0 (C-2''), 136.3 (C-3''), 137.3 (C-6''), 179.6 (*C*HO), 191.3 (Ph*C*HO). HRMS (EI): m/z [M^+] calcd for $C_{15}H_{11}NO_2$: 237.0790; found: 237.0786.

1-(3-(3-Fluorophenyl)prop-2-yn-1-yl)-1*H*-pyrrole-2-carbaldehyde (2j). Following the method of preparation for **2b**, a mixture of **2a** (0.200 g, 1.50 mmol), 3-fluoro-1-iodobenzene(0.366 g, 1.65 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol), CuI (0.011 g, 0.06 mmol), and K_2CO_3 (1.035 mmol, 7.50 mmol) in dry DMF was heated at 60 °C for 2 h to produce **2j** (0.250 g, 73%) as a reddish oil. *Rf* 0.69 (hexane/EtOAc, 8:2). IR (film): ῡ 3112, 3072, 2812, 1661, 1609, 1582, 1486, 1406, 1338, 1218, 1173, 1152, 874, 786, 747, 682 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.42 (s, 2H, H-1'), 6.30 (dd, *J* = 4.0, 2.5 Hz, 1H, H-4), 6.97 (dd, *J* = 4.0, 1.7 Hz, 1H, H-3), 7.03 (tdd, *J* = 8.5, 2.5, 1.0 Hz, 1H, H-4''), 7.13 (ddd, *J* = 9.3, 2.5, 1.5 Hz, 1H, H-2''), 7.21 (dt, *J* = 7.8, 1.2 Hz, 1H, H-6''), 7.27 (td, *J* = 7.8, 5.8 Hz, 1H, H-5''), 7.31 (br s, 1H, H-5), 9.58 (d, *J* = 1.0 Hz, 1H, C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.8 (C-1'), 83.8 (C-2'), 84.6 (d, $J_{C,F}$ = 3.3 Hz, C-3'), 110.1 (C-4), 116.0 (d, $J_{C,F}$ = 21.0 Hz, C-4''), 118.6 (d, $J_{C,F}$ = 22.8 Hz, C-2''), 123.9 (d, $J_{C,F}$ = 9.3 Hz, C-1''), 124.9 (C-3), 127.6 (d, $J_{C,F}$ = 3.1 Hz, C-6''), 129.8 (d, $J_{C,F}$ = 8.5 Hz, C-5''), 130.3 (C-5), 131.1 (C-2), 162.2 (d, $J_{C,F}$ = 246.9 Hz, C-3''), 179.5 (C*H*O). HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{10}NOF$: 227.0746; found: 227.0747.

(*E*)-2-(2-Nitrovinyl)-1-(prop-2-yn-1-yl)-1*H*-pyrrole (2k). In a threaded ACE glass pressure tube equipped with a sealed Teflon screw cap and a magnetic stirring bar, a mixture of **2a** (0.100 g, 0.75 mmol), **3a** (0.229 g, 3.76 mmol), and NH_4OAc (0.058 g, 0.75 mmol) in dry toluene (0.5 mL) was heated at 100 °C for 20 h. The mixture was diluted with an aqueous saturated solution of $NaHCO_3$ (10 mL) and extracted twice with CH_2Cl_2 (2 x 40 mL). The organic layer was dried (Na_2SO_4) and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane/EtOAc, 9:1) to afford **2k** (0.115 g, 87%) as a reddish solid. *Rf* 0.40 (hexane/EtOAc, 8:2); mp 107–109 °C. IR (film): ῡ 3294, 3120, 2970, 1661, 1615, 1471, 1307, 1268, 1245, 1202, 1126, 1079,947, 816, 745, 733, 673 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 2.54 (t, *J* = 2.6 Hz, 1H, H-3'), 4.81 (d, *J* = 2.6 Hz, 2H, H-1'), 6.31 (ddd, *J* = 4.0, 2.7, 0.6 Hz, 1H, H-4), 6.83 (dd, *J* = 4.0, 1.3 Hz, 1H, H-3), 7.11 (dd, *J* = 2.7, 1.3 Hz, 1H, H-5), 7.49 (d, *J* = 13.2 Hz, 1H, H-2''), 8.05 (d, *J* = 13.2 Hz, 1H, H-1''). ^{13}C NMR (150 MHz, $CDCl_3$): δ 37.2 (C-1'), 75.3 (C-3'), 76.5 (C-2'), 111.4 (C-4), 116.6 (C-3), 124.2 (C-2), 126.8 (C-1''), 129.2 (C-5), 132.4 (C-2''). HRMS (EI): *m/z* [M^+] calcd for $C_9H_8N_2O_2$: 176.0586; found: 176.0589.

6-(4-Methoxybenzyl)-7-nitroindolizine (4d). Following the method of preparation for **4b**, a mixture of **2d** (0.060 g, 0.25 mmol), DBU (0.088 g, 0.58 mmol), and **3a** (0.017 g, 0.28 mmol) in dry DMF (1.5 mL) gave **4d** (0.021 g, 30%) as a reddish oil. *Rf* 0.72 (hexane/EtOAc, 7:3). IR (film): ῡ 2929, 1611, 1542, 1517, 1429, 1402, 1316, 1247, 1177, 1037, 828, 722 cm^{-1}. ^1H NMR (750 MHz, $CDCl_3$): δ 3.79 (s, 3H, OC*H*$_3$), 4.23 (s, 2H, C*H*$_2$), 6.83-6.88 (m, 3H, H-1, H-3'), 6.92 (br s, 1H, H-2), 7.12 (d, *J* = 7.5 Hz, 2H, H-2'), 7.41 (br s, 1H, H-3), 7.54 (s, 1H, H-5), 8.38 (s, 1H, H-8). ^{13}C NMR (187.5 MHz, $CDCl_3$): δ 35.9 (*C*H_2), 55.2 (*C*H_3O), 107.7 (C-1), 114.1 (C-3'), 116.5 (C-3), 117.1 (C-2), 118.2 (C-6), 119.3 (C-8), 125.0 (C-5), 129.2 (C-8a), 130.0 (C-2'), 130.4 (C-1'), 139.4 (C-7), 158.3 (C-4'). HRMS (EI): m/z [M^+] calcd for $C_{16}H_{14}N_2O_3$: 282.1005; found: 282.0998.

1-(4-((7-Nitroindolizin-6-yl)methyl)phenyl)ethanone (4f). Following the method of preparation for **4b**, a mixture of **2f** (0.050 g, 0.20 mmol), DBU (0.046 g, 0.30 mmol), and **3a** (0.018 g, 0.30 mmol) in dry DMF (1.0 mL) was stirred at rt for 1 h to produce **4f** (0.019 g, 33%) as a reddish solid. *Rf* 0.21 (hexane/EtOAc, 7:3); mp 134–136 °C. IR (film): ῡ 2926, 1678, 1606, 1544, 1495, 1438, 1355, 1313, 1268, 1038, 723 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 2.58 (s, 3H, COC*H*$_3$), 4.35 (s, 2H, C*H*$_2$), 6.91 (d, *J* = 4.0 Hz, 1H, H-1), 6.97 (dd, *J* = 4.0, 2.4 Hz, 1H, H-2), 7.29 (d, *J* = 8.1 Hz, 2H, H-2'), 7.47 (br s, 1H, H-3), 7.66 (s, 1H, H-5), 7.89 (d, *J* = 8.1 Hz, 2H, H-3'), 8.44 (s, 1H, H-8). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.6 (CO*C*H_3), 37.1 (*C*H_2Ar), 108.3 (C-1), 116.4 (C-6), 116.8 (C-3), 117.5 (C-2), 119.7 (C-8), 125.3

(C-5), 128.7 (C-3'), 128.9 (C-2'), 129.3 (C-8a), 135.6 (C-4'), 138.8 (C-7), 144.4 (C-1'), 197.7 (*C*OCH$_3$). HRMS (EI): m/z [M$^+$] calcd for $C_{17}H_{14}N_2O_3$: 294.1005; found: 294.1002.

6-(3-Methoxybenzyl)-7-nitroindolizine (4g). Following the method of preparation for **4b**, a mixture of **2g** (0.050 g, 0.21 mmol), DBU (0.073 g, 0.48 mmol), and **3a** (0.014 g, 0.23 mmol) in dry DMF (1.0 mL) furnished **4g** (0.028 g, 41%) as a reddish oil. *Rf* 0.62 (hexane/EtOAc, 7:3). IR (film): ῡ 2919, 1719, 1600, 1548, 1543, 1490, 1437, 1313, 1267, 1039, 846, 782, 736 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.78 (s, 3H, C*H*$_3$O), 4.27 (s, 2H, C*H*$_2$), 6.74 (br s, 1H, H-2'), 6.77-6.83 (m, 2H, H-4', H-6'), 6.87 (d, *J* = 3.5 Hz, 1H, H-1), 6.93 (dd, *J* = 3.5, 2.0 Hz, 1H, H-2), 7.32 (t, *J* = 6.5 Hz, 1H, H-5'), 7.42 (br s, 1H, H-3), 7.57 (s, 1H, H-5), 8.41 (s, 1H, H-8). ^{13}C NMR (150 MHz, $CDCl_3$): δ 36.8 (*C*H$_2$), 55.2 (*C*H$_3$O), 107.8 (C-1), 111.7 (C-4'), 114.9 (C-2'), 116.6 (C-3), 117.2 (C-2), 117.4 (C-6), 119.4 (C-8), 121.3 (C-6'), 125.2 (C-5), 129.2 (C-8a), 129.6 (C-5'), 139.2 (C-7), 140.2 (C-1'), 159.8 (C-3'). HRMS (EI): m/z [M$^+$] calcd for $C_{16}H_{14}N_2O_3$: 282.1005; found: 282.1006.

6-(3-Fluorobenzyl)-7-nitroindolizine (4j). Following the method of preparation for **4b**, a mixture of **2j** (0.050 g, 0.22 mmol), DBU (0.050 g, 0.33 mmol), and **3a** (0.017 g, 0.29 mmol) in dry DMF (1.0 mL) was heated at 80 °C for 2 h to obtain **4j** (0.032 g, 54%) as a reddish solid. *Rf* 0.50 (hexane/EtOAc, 8:2); mp 103–105 °C. IR (film): ῡ 1612, 1588, 1544, 1483, 1448, 1438, 1311, 1269, 1219, 1130, 1039, 790, 736, 725 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.28 (s, 2H, C*H*$_2$), 6.85-6.93 (m, 3H, H-1, H-2', H-4'), 6.95 (dd, *J* = 4.0, 2.5 Hz, 1H, H-2), 6.98 (dm, *J* = 8.0 Hz, 1H, H-6'), 7.22-7.27 (m, 1H, H-5'), 7.45 (ddd, *J* = 2.5, 1.2, 0.7 Hz, 1H, H-3), 7.63-7.62 (m, 1H, H-5), 8.42 (s, 1H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.7 (d, $J_{C,F}$ = 1.7 Hz, *C*H$_2$), 108.1 (C-1), 113.5 (d, $J_{C,F}$ = 21.0 Hz, C-2'), 115.6 (d, $J_{C,F}$ = 21.5 Hz, C-4'), 116.6 (C-6), 116.7 (C-3), 117.4 (C-2), 119.6 (C-8), 124.4 (d, $J_{C,F}$ = 2.9 Hz, C-6'), 125.2 (C-5), 129.2 (C-8a), 130.0 (d, $J_{C,F}$ = 8.3 Hz, C-5'), 138.9 (C-7), 141.3 (d, $J_{C,F}$ = 7.1 Hz, C-1'), 162.9 (d, $J_{C,F}$ = 245.0 Hz, C-3'). HRMS (EI): *m/z* [M$^+$] calcd for $C_{15}H_{11}FN_2O_2$: 270.0805; found: 270.0805.

Methyl 6-benzylindolizine-7-carboxylate (8b). Following the method of preparation for **8a**, a mixture of **2b** (0.050 g, 0.24 mmol), DBU (0.055 g, 0.36 mmol), and **3b** (0.038 g, 0.29 mmol) in dry DMF (1.5 mL) was heated at 80 ºC for 2 h to provide **8b** (0.011 g, 17%) as a brown solid. *Rf* 0.48 (hexane/EtOAc, 9:1); mp 63–65 °C. IR (film): ῡ 1712, 1453, 1352, 1263, 1252, 1191, 1184, 1153, 1078, 780, 716, 697 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.77 (s, 3H, CO_2CH_3), 4.28 (s, 2H, C*H*$_2$Ar), 6.66 (d, *J* = 4.0 Hz, 1H, H-1), 6.82 (dd, *J* = 4.0, 2.4 Hz, 1H, H-2), 7.17–7.22 (m, 3H, H-2', H-4'), 7.27–7.31 (m, 3H, H-3, H-3'), 7.56 (s, 1H, H-5), 8.18 (s, 1H, H-8). ^{13}C NMR (150 MHz, $CDCl_3$): δ 37.3 (*C*H$_2$Ar), 51.7 (CO_2CH_3), 103.9 (C-1), 114.7 (C-3), 115.2 (C-2), 118.9 (C-7), 122.2 (C-6), 124.5 (C-8),

124.8 (C-5), 126.1 (C-4'), 128.4 (C-3'), 128.9 (C-2'), 130.5 (C-8a), 140.4 (C-1'), 166.9 (*C*O_2CH_3). HRMS (EI): m/z [M^+] calcd for $C_{17}H_{15}NO_2$: 265.1103; found: 265.1107.

Methyl 6-(4-methylbenzyl)indolizine-7-carboxylate (8c). Following the method of preparation for **8a**, a mixture of **2c** (0.050 g, 0.22 mmol), DBU (0.052 g, 0.34 mmol), and **3b** (0.034 g, 0.26 mmol) in dry DMF (1.5 mL) was heated at 140 °C for 12 h to give **8c** (0.005 g, 15%) as a brown oil. *Rf* 0.48 (hexane/EtOAc, 9:1). IR (film): ῡ 2925, 1713, 1460, 1441, 1350, 1251, 1262, 1189, 1080, 781, 714 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 2.32 (s, 3H, C*H*$_3$), 3.78 (s, 3H, CO_2CH_3), 4.23 (s, 2H, C*H*$_2$Ar), 6.65 (d, *J* = 3.6 Hz, 1H, H-1), 6.81 (dd, *J* = 3.6, 2.7 Hz, 1H, H-2), 7.06–7.11 (m, 4H, H-2', H-3'), 7.30 (br s, 1H, H-3), 7.54 (s, 1H, H-5), 8.17 (s, 1H, H-8). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.0 (*C*H_3), 36.8 (*C*H_2Ar), 51.7 (CO_2CH_3), 103.8 (C-1), 114.6 (C-3), 115.1 (C-2), 119.0 (C-7), 122.5 (C-6), 124.5 (C-8), 124.7 (C-5), 128.8 (C-2'), 129.1 (C-3'), 130.5 (C-8a), 135.5 (C-4'), 137.2 (C-1'), 166.9 (*C*O_2CH_3). HRMS (EI): m/z [M^+] calcd for $C_{18}H_{17}NO_2$: 279.1259; found: 279.1260.

Methyl 6-(4-methoxybenzyl)indolizine-7-carboxylate (8d). Following the method of preparation for **8a**, a mixture of **2d** (0.060 g, 0.25 mmol), DBU (0.057 g, 0.38 mmol), and **3b** (0.043 g, 0.33 mmol) in dry DMF (1.5 mL) was heated at 140 °C for 12 h to produce **8d** (0.009 g, 12%) as a brown oil. *Rf* 0.33 (hexane/EtOAc, 7:3). IR (film): ῡ 1713, 1511, 1461, 1441, 1262, 1249, 1178, 1080, 1035 cm^{-1}. ^1H NMR (750 MHz, $CDCl_3$): δ 3.79 (s, 6H, OC*H*$_3$, CO_2CH_3), 4.21 (s, 2H, C*H*$_2$Ar), 6.65 (d, *J* = 3.8 Hz, 1H, H-1), 6.81 (dd, *J* = 3.8, 2.4 Hz, 1H, H-2), 6.82–6.86 (m, 2H, H-3'), 7.11 (d, *J* = 8.4 Hz, 2H, H-2'), 7.30 (br s, 1H, H-3), 7.53 (s, 1H, H-5), 8.17 (s, 1H, H-8). ^{13}C NMR (187.5 MHz, $CDCl_3$): δ 36.4 (*C*H_2Ar), 51.7 (CO_2CH_3), 55.2 (*C*H_3O), 103.8 (C-1), 113.8 (C-3'), 114.7 (C-3), 115.1 (C-2), 119.0 (C-7), 122.8 (C-6), 124.5 (C-8), 124.6 (C-5), 130.0 (C-2'), 130.5 (C-8a), 132.3 (C-1'), 157.9 (C-4'), 166.9 (*C*O_2CH_3). HRMS (EI): m/z [M^+] calcd for $C_{18}H_{17}NO_3$: 295.1208; found: 295.1208.

Methyl 6-(3-fluorobenzyl)indolizine-7-carboxylate (8g). Following the method of preparation for **8a**, a mixture of **2f** (0.050 g, 0.22 mmol), DBU (0.034 g, 0.22 mmol), and **3b** (0.036 g, 0.27 mmol) in dry DMF (1.0 mL) was stirred at rt for 7 h to obtain **8g** (0.028 g, 45%) as a yellow solid. *Rf* 0.60 (hexane/EtOAc, 8:2); mp 75–77 °C. IR (film): ῡ 1714, 1614, 1584, 1485, 1446, 1352, 1258, 1244, 1188, 1158, 1062, 776, 714, 685 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.77 (s, 3H, CO_2CH_3), 4.27 (s, 2H, C*H*$_2$Ar), 6.68 (d, *J* = 4.0 Hz, 1H, H-1), 6.83–6.86 (m, 1H, H-2), 6.86–6.91 (m, 2H, H-2', H-4'), 6.97 (d, *J* = 8.0 Hz, 1H, H-6'), 7.21–7.26 (m, 1H, H-5'), 7.32–7.35 (m, 1H, H-3), 7.61 (s, 1H, H-5), 8.21 (s, 1H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 37.1 (d, *J* = 1.8 Hz, *C*H_2Ar), 51.7 (CO_2CH_3), 104.2 (C-1), 112.9 (d, $J_{C,F}$ = 21.1 Hz, C-4'), 114.8 (C-3), 115.3 (C-2), 115.6 (d, $J_{C,F}$ = 21.3 Hz, C-2'), 118.5 (C-7),

121.4 (C-6), 124.4 (d, $J_{C,F}$ = 2.8 Hz, C-6'), 124.7 (C-8), 124.8 (C-5), 129.7 (d, $J_{C,F}$ = 8.3 Hz, C-5'), 130.6 (C-8a), 143.3 (d, $J_{C,F}$ = 7.1 Hz, C-1'), 162.9 (d, $J_{C,F}$ = 243.9 Hz, C-3'), 166.6 (CO_2CH_3). HRMS (EI): m/z [M^+] calcd for $C_{17}H_{14}FNO_4$: 283.1009; found: 283.1007.

6-Benzylindolizine-7-carbonitrile (8i). Following the method of preparation for **8a**, a mixture of **2b** (0.050 g, 0.24 mmol), **3d** (0.029 g, 0.29 mmol), and DBU (0.055 g, 0.36 mmol) in dry DMF (1.5 mL) was heated at 80 °C for 12 h to provide **8i** (0.022 g, 40%) as a yellow solid. *Rf* 0.64 (hexane/EtOAc, 8:2); mp 123–125 °C. IR (film): ῡ 2217, 1493, 1454, 1350, 1275, 1267, 1255, 1069, 916, 772, 741, 721, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 4.03 (s, 2H, CH_2Ph), 6.67 (d, *J* = 3.5 Hz, 1H, H-1), 6.86 (dd, *J* = 3.5, 2.5 Hz, 1H, H-2), 7.24–7.31 (m, 3H, H-2', H-4'), 7.32–7.37 (m, 3H, H-3, H-3'), 7.58 (s, 1H, H-5), 7.80 (s, 1H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 37.1 (CH_2Ph), 101.5 (C-7), 104.4 (C-1), 115.8 (C-2), 116.1 (C-3), 118.3 (CN), 122.0 (C-6), 124.0 (C-5), 126.9 (C-4'), 127.0 (C-8), 128.7 (C-3'), 129.1 (C-2'), 129.9 (C-8a), 138.0 (C-1'). HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{12}N_2$: 232.1000; found: 232.1001.

6-(4-Methoxybenzyl)indolizine-7-carbonitrile (8j). Following the method of preparation for **8a**, a mixture of **2d** (0.050 g, 0.21 mmol), **3d** (0.025 g, 0.25 mmol), and DBU (0.047 g, 0.31 mmol) in dry DMF (1.5 mL) was heated at 140 °C for 24 h to give **8j** (0.013 g, 24%) as a brown solid. *Rf* 0.35 (hexane/EtOAc, 9:1); mp 72–74 °C. IR (film): ῡ 2218, 1717, 1609, 1509, 1346, 1243, 1178, 1028, 835, 724, 718 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.81 (s, 3H, CH_3O), 3.97 (s, 2H, CH_2Ar), 6.67 (br d, *J* = 4.5 Hz, 1H, H-1), 6.86 (dd, *J* = 4.5, 3.0 Hz, 1H, H-2), 6.87–6.91 (m, 2H, H-3'), 7.18–7.22 (m, 2H, H-2'), 7.33–7.35 (m, 1H, H-3), 7.56 (br s, 1H, H-5), 7.80 (s, 1H, H-8). ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.3 (CH_2Ar), 55.3 (CH_3O), 101.4 (C-7), 104.4 (C-1), 114.1 (C-3'), 115.8 (C-2), 116.1 (C-3), 118.3 (CN), 122.5 (C-6), 123.8 (C-5), 127.0 (C-8), 129.9 (C-8a, C-1'), 130.2 (C-2'), 158.5 (C-4'). HRMS (EI): *m/z* [M^+] calcd for $C_{17}H_{14}N_2O$: 262.1106; found: 262.1108.

6-(4-Acetylbenzyl)indolizine-7-carbonitrile (8k). Following the method of preparation for **8a**, a mixture of **2f** (0.050 g, 0.20 mmol), **3d** (0.024 g, 0.24 mmol), and DBU (0.046 g, 0.30 mmol) in dry DMF (1.5 mL) was heated at 80 °C for 2 h to produce **8k** (0.025 g, 46%) as a brown solid. *Rf* 0.43 (hexane/EtOAc, 8:2); mp 142–144 °C. IR (film): ῡ 2218, 1675, 1605, 1346, 1266, 1184, 885, 728 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.59 (s, 3H, $COCH_3$), 4.08 (s, 2H, CH_2), 6.70 (d, *J* = 4.0 Hz, 1H, H-1), 6.89 (dd, *J* = 4.0, 2.7 Hz, 1H, H-2), 7.36–7.39 (m, 3H, H-2', H-3), 7.66–7.67 (m, 1H, H-5), 7.81 (s, 1H, H-8), 7.92–7.95 (m, 2H, H-3'). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.6 ($COCH_3$), 37.0 (CH_2Ar), 101.0 (C-7), 104.7 (C-1), 116.0 (C-2), 116.3 (C-3), 118.1 (CN), 120.8 (C-6), 124.1 (C-5), 127.2 (C-8), 128.8

(C-3'), 129.2 (C-2'), 129.8 (C-8a), 135.8 (C-4'), 143.6 (C-1'), 197.7 (*C*OCH$_3$). HRMS (EI): *m/z* [M$^+$] calcd for $C_{18}H_{14}N_2O$: 274.1106; found: 274.1103.

6-(3-Nitrobenzyl)indolizine-7-carbonitrile (8l). Method A: Following the method of preparation for **8a**, a mixture of **2h** (0.050 g, 0.20 mmol), **3d** (0.024 g, 0.24 mmol), and DBU (0.046 g, 0.30 mmol) in dry DMF (1.5 mL) was heated at 80 °C for 2 h to furnish **8l** (0.031 g, 57%) as a yellow solid.

Method B: Following the method of preparation for **8a**, a mixture of **2h** (0.100 g, 0.394 mmol), **3e** (0.037 g, 0.56 mmol), and DBU (0.137 g, 0.90 mmol) in dry DMF (1.5 mL) was stirred at rt for 8 h to afford **8l** (0.055 g, 50%) as a yellow solid. *Rf* 0.45 (hexane/EtOAc, 7:3); mp 172–174 °C. IR (film): ῡ 2212, 1633, 1525, 1456, 1349, 1270, 1097, 1068, 1034, 800, 723 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.13 (s, 2H, C*H*$_2$), 6.73 (br d, *J* = 4.0 Hz, 1H, H-1), 6.92 (dd, *J* = 4.0, 2.5 Hz, 1H, H-2), 7.43 (br s, 1H, H-3), 7.52 (t, *J* = 7.5 Hz, 1H, H-5'), 7.66 (br d, *J* = 7.5 Hz, 1H, H-6'), 7.75 (s, 1H, H-5), 7.83 (s, 1H, H-8), 8.10 (br s, 1H, H-2'), 8.12 (d, *J* = 7.5 Hz, 1H, H-4'). ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.8 (*C*H$_2$), 100.8 (C-7), 105.1 (C-1), 116.3 (C-2), 116.5 (C-3), 118.0 (CN), 120.2 (C-6), 122.1 (C-4'), 123.6 (C-2'), 124.2 (C-5), 127.5 (C-8), 129.7 (C-5'), 129.9 (C-8a), 135.3 (C-6'), 140.3 (C-1'), 148.5 (C-3'). HRMS (EI): *m/z* [M$^+$] calcd for $C_{16}H_{11}N_3O_2$: 277.0851; found: 277.0850.

(*E*)-Methyl 3-(1-(3-(3-nitrophenyl)prop-2-yn-1-yl)-1*H*-pyrrol-2-yl)acrylate (10). In a round-bottomed flask (100 mL) equipped with a magnetic stirring bar, trimethyl phosphonoacetate (0.086 g, 0.471 mmol) in anhydrous THF (10 mL) was added to a suspension of NaH (60%, 0.024 g, 0.600 mmol) in anhydrous THF (20 mL) under N_2 atmosphere at 0 ºC. After stirring at 0 ºC for 30 min, **2h** (0.100 g, 0.39 mmol) was added and stirring continued at rt for 4 h. The solvent was removed under vacuum, and the residue purified by column chromatography over silica gel (30 g/g crude, hexane/EtOAc, 9:1) led to **10** (0.12 g, 98%) as a yellow solid. *Rf* 0.50 (hexane/EtOAc, 7:3); mp 74–75 ºC. IR (film): ῡ 3085, 2950, 1699, 1622, 1531, 1468, 1435, 1350, 1327, 1279, 1170, 1131, 1080, 1030, 968, 874, 852, 807, 735, 674 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79 (s, 3H, CO_2C*H*$_3$), 5.01 (s, 2H, H-1''), 6.22 (d, *J* = 15.5 Hz, 1H, H-2), 6.24-6.26 (m, 1H, H-4'), 6.72 (dd, *J* = 4.0, 1.5 Hz, 1H, H-3'), 6.97 (dd, *J* = 2.5, 1.5 Hz, 1H, H-5'), 7.50 (dd, *J* = 8.5, 7.5 Hz, 1H, H-5'''), 7.70-7.73 (m, 1H, H-6'''), 7.73 (d, *J* = 15.5 Hz, 1H, H-3), 8.17 (ddd, *J* = 8.5, 2.5, 1.0 Hz, 1H, H-4'''), 8.26 (dd, *J* = 2.0, 1.5 Hz, 1H, H-2'''). ^{13}C NMR (125 MHz, $CDCl_3$): δ 37.4 (C-1''), 51.6 (CO_2C*H*$_3$), 83.5 (C-3''), 85.4 (C-2''), 110.1 (C-4'), 112.7 (C-3'), 113.3 (C-2), 123.5 (C-4'''), 123.7 (C-1'''), 125.7 (C-5'), 126.6 (C-2'''), 128.8 (C-2'), 129.4 (C-5'''), 131.9 (C-3), 137.5 (C-6'''), 148.0 (C-3'''), 168.0 (CO_2Me). HRMS (EI): *m/z* [M$^+$] calcd for $C_{17}H_{14}N_2O_4$: 310.0954; found: 310.0955.

(*E*)-Methyl 3-(5-formyl-1-(3-(3-nitrophenyl)prop-2-yn-1-yl)-1*H*-pyrrol-2-yl)acrylate (11). In a round-bottomed flask (100 mL) equipped with a magnetic stirring bar, a mixture of **10** (0.363 g, 1.17 mmol) and anhydrous DMF (0.128 g, 1.75 mmol) was stirred at rt for 15 min under N_2 atmosphere. Subsequently, $POCl_3$ (0.268 g, 1.75 mmol) was added followed by stirring for 24 h, and then a cold 10% aqueous solution of KOH (10 mL) was added followed by stirring for 20 min. The mixture was extracted with CH_2Cl_2 (2 x 10 mL), and the organic layer was dried (Na_2SO_4) and removed under vacuum. The residue was purified by column chromatography over silica gel (30 g/g crude, hexane/EtOAc, 96:4) to deliver **11** (0.303 g, 76%) as a white solid. *Rf* 0.42 (hexane/EtOAc, 7:3); mp 136 °C-decomp. IR (film): ῡ 3083, 2951, 2850, 1710, 1659, 1631, 1529, 1474, 1448, 1409, 1351, 1313, 1279, 1233, 1196, 1167, 1049, 968, 782, 736, 674 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H, CO_2CH_3), 5.64 (s, 2H, H-1''), 6.49 (d, *J* = 15.7 Hz, 1H, H-2), 6.73 (d, *J* = 4.5 Hz, 1H, H-3'), 6.98 (d, *J* = 4.5 Hz, 1H, H-4'), 7.47 (t, *J* = 8.0 Hz, 1H, H-5'''), 7.69 (dt, *J* = 8.0, 1.5 Hz, 1H, H-6'''), 7.82 (d, *J* = 15.7 Hz, 1H, H-3), 8.14 (ddd, *J* = 8.0, 2.3, 1.0 Hz, 1H, H-4'''), 8.22 (t, *J* = 2.0 Hz, 1H, H-2'''), 9.63 (s, 1H, C*H*O). ^{13}C NMR (125 MHz, $CDCl_3$): δ 35.1 (C-1''), 52.0 (CO_2CH_3), 82.8 (C-3''), 85.9 (C-2''), 111.8 (C-3'), 121.0 (C-2), 123.4 (C-4'''), 123.8 (C-1'''), 124.8 (C-4'), 126.7 (C-2'''), 129.3 (C-5'''), 130.3 (C-3), 132.9 (C-5'), 137.4 (C-2'), 137.5 (C-6'''), 148.0 (C-3'''), 166.7 (CO_2Me), 180.0 (CHO). HRMS (EI): *m/z* [M^+] calcd for $C_{18}H_{14}N_2O_5$: 338.0903; found: 338.0896.

(*E*)-Dimethyl 2-((5-(3-methoxy-3-oxoprop-1-en-1-yl)-1-(propa-1,2-dien-1-yl)-1*H*-pyrrol-2-yl)methylene)malonate (6b). In a round-bottomed flask (50 mL) equipped with a magnetic stirring bar, a mixture of **6a** (0.300 g, 1.38 mmol), **3b** (0.219 g, 1.66 mmol), piperidine (0.047 g, 0.55 mmol), and glacial acetic acid (0.050 g, 0.83 mmol) in CH_2Cl_2 (20 mL) was heated at 150 ºC for 8 h under N_2 atmosphere. The mixture was diluted with CH_2Cl_2 (50 mL) and washed with an aqueous saturated solution of $NaHCO_3$ (100 mL). The aqueous layer was washed with CH_2Cl_2 (3 x 50 mL), the organic extracts were dried (Na_2SO_4), and the solvent was removed under vacuum. The residue was purified by column chromatography over silica gel (30 g/g crude, hexane/EtOAc, 9:1) to provide **6b** (0.389 g, 85%) as a yellow oily solid. *Rf* 0.40 (hexano/AcOEt, 7:3). IR (film): ῡ 2953, 1716, 1606, 1527, 1435, 1388, 1364, 1309, 1228, 1071, 971, 924, 896, 851, 770, 743 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, 3H, $CHCO_2CH_3$), 3.82 (s, 3H, CO_2CH_3), 3.88 (s, 3H, CO_2CH_3), 5.49 (d, *J* = 6.5 Hz, 2H, H-3'''), 6.30 (d, *J* = 15.5 Hz, 1H, H-2^{IV}), 6.66 (br d, *J* = 4.3 Hz, 1H, H-3''), 6.73 (br d, *J* = 4.3 Hz, 1H, H-4''), 6.79 (t, *J* = 6.5 Hz, 1H, H-1'''), 7.65 (d, *J* = 15.5 Hz, 1H, H-1^{IV}), 7.76 (s, 1H, H-1'). ^{13}C NMR (125 MHz, $CDCl_3$): δ 51.5 ($CHCO_2CH_3$), 52.3 (CO_2CH_3), 52.5 (CO_2CH_3), 84.6 (C-3'''), 93.1 (C-1'''), 113.1 (C-4''), 115.5 (C-3''), 116.7 (C-2^{IV}), 120.6 (C-2), 129.3 (C-1'), 129.9 (C-2''), 131.4 (C-1^{IV}), 133.6 (C-5''), 164.5

(CO_2CH_3), 166.9 (CO_2CH_3), 167.1 ($CHCO_2CH_3$), 208.0 (C-2'''). HRMS (EI): *m/z* [M^+] calcd for $C_{17}H_{17}NO_6$: 331.1056; found: 331.1040.

Methyl 6-(4-acetylbenzyl)-3-formylindolizine-7-carboxylate (12a). $POCl_3$ (0.017 g, 1.10 mmol) was added to anhydrous DMF (0.008 g, 1.10 mmol) at 0 ºC, and the mixture was stirred for 10 min. Subsequently, a solution of **8e** (0.030 g, 0.10 mmol) in anhydrous CH_2Cl_2 (3.0 mL) was added dropwise and stirred at 0 °C for 2 h. The reaction mixture was quenched with a 1 M aqueous solution of KOH until neutral, CH_2Cl_2 (30 mL) was added, the organic layer dried (Na_2SO_4) and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane/EtOAc, 98:2) to furnish **12a** (0.021 g, 64%) as a pale yellow solid. *Rf* 0.29 (hexane/EtOAc, 8:2); mp 187–189 °C. IR (film): ῡ 1717, 1678, 1639, 1604, 1454, 1392, 1373, 1334, 1261, 1206, 1026, 783 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 2.56 (s, 3H, $COCH_3$), 3.78 (s, 3H, CO_2CH_3), 4.43 (s, 2H, CH_2Ar), 6.76 (d, *J* = 4.5 Hz, 1H, H-1), 7.25 (d, *J* = 8.0 Hz, 2H, H-2'), 7.48 (d, *J* = 4.5 Hz, 1H, H-2), 7.86 (d, *J* = 8.0 Hz, 2H, H-3'), 8.26 (s, 1H, H-8), 9.58 (s, 1H, H-5), 9.79 (s, 1H, CHO). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.5 ($COCH_3$), 37.4 (CH_2Ar), 52.3 (CO_2CH_3), 106.3 (C-1), 122.9 (C-8), 124.9 (C-6), 125.0 (C-3), 126.2 (C-7), 126.8 (C-2), 128.4 (C-5), 128.5 (C-3'), 128.7 (C-2'), 135.3 (C-4'), 137.2 (C-8a), 145.8 (C-1'), 165.7 (CO_2CH_3), 178.4 (CHO), 197.7 ($COCH_3$). HRMS (EI): *m/z* [M^+] calcd for $C_{20}H_{17}NO_4$: 335.1158; found: 335.1152.

Methyl 3-(4-acetylphenyl)-2-bromo-6-(3-nitrobenzyl)indolizine-7-carboxylate (13b). Methyl 3-(4-acetylphenyl)-6-(3-nitrobenzyl)indolizine-7-carboxylate (13c). In a threaded ACE glass pressure tube equipped with a sealed Teflon screw cap and a magnetic stirring bar, a mixture of **13a** (0.050 g, 0.11 mmol), (4-acetylphenyl)boronic acid (0.026 g, 0.16 mmol), $Pd(PPh_3)_4$ (0.006 g, 0.005 mmol), and K_2CO_3 (0.022 g, 0.16 mmol) in dry DMF/EtOH (1:1, 2 mL) was heated at 70 ºC for 8 h. A solution of brine was added (20 mL), the mixture extracted with EtOAc (40 mL), the organic layer dried (Na_2SO_4), and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane/EtOAc, 1:1) to generate a mixture of **13b**/**13c** (6:1, 0.022 g, 66%) as a yellow solid. *Rf* 0.69 (hexane/EtOAc, 8:2); mp 140–143 ºC. IR (film): ῡ 1715, 1676, 1600, 1526, 1440, 1350, 1254, 1196, 1187, 958, 820, 736 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ 2.64 (s, 3H, $COCH_3$), 3.80 (s, 3H, CO_2CH_3), 4.38 (s, 2H, CH_2Ar), 7.07 (s, 1H, H-1), 7.43 (t, *J* = 7.9 Hz, 1H, H-5''), 7.49–7.52 (m, 1H, H-6''), 7.62 (d, *J* = 8.4 Hz, 2H, H-2'), 7.99 (s, 1H, H-2''), 8.02–8.09 (m, 4H, H-4'', H-3', H-5), 8.26 (s, 1H, H-8). Signals attributed to minor isomer **13c**: 2.65 (s, $COCH_3$), 3.77 (s, CO_2CH_3), 6.85 (d, *J* = 4.2 Hz, H-1), 7.05 (d, *J* = 4.2 Hz, H-2), 7.42 (t, *J* = 7.9 Hz, H-5''), 7.53 (m, H-6''), 7.67 (d, *J* = 8.4 Hz, H-2'), 7.72 (d, *J* = 8.3 Hz, H-3'), 8.12 (s, 1H, H-5), 8.30 (s, 1H, H-8). ^{13}C NMR (150 MHz, $CDCl_3$): δ

26.6 (CO*C*H_3), 37.2 (ArC*H*$_2$), 52.0 (CO_2*C*H_3), 93.3 (C-2), 118.4 (C-1), 119.7 (C-6), 121.4 (C-4'), 122.5 (C-5), 123.2 (C-2'), 123.9 (C-8), 126.8 (C-3), 127.4 (C-1''), 127.6 (C-2'), 129.2 (C-5'), 129.3 (C-3'), 130.1 (C-8a), 134.8 (C-6'), 142.4 (C-1'), 148.3 (C-3'), 165.7 (*C*$O_2$$CH_3$), 197.1 (*C*O$CH_3$). Signals attributed to minor isomer **13c**: 26.8 (CO*C*H_3), 37.4 (Ar*C*H_2), 51.9 (CO_2C*H*$_3$), 106.1 (C-1), 117.2 (C-2), 122.3 (C-5), 125.6 (C-8), 127.4 (C-3'), 127.5 (C-2'), 129.0 (C-5'), 166.1 (*C*$O_2$$CH_3$), 197.6 (*C*O$CH_3$). HRMS (EI): *m/z* [$M^+$] calcd for $C_{25}H_{19}N_2O_5Br$: 506.0477; found: 506.0489.

3-(4-Methylbenzyl)pyrrolo[1,2-*a*]pyrazine (14c). Following the method of preparation for **14a**, a mixture of **2c** (0.050 g, 0.22 mmol), DBU (0.038 g, 0.25 mmol), and NH_4OAc (0.022 g, 0.29 mmol) in dry DMF (1.0 mL) was heated at 140 °C for 12 h to give **14c** (0.023 g, 46%) as a brown solid. *Rf* 0.29 (hexane/EtOAc, 7:3); mp 42–44 °C. IR (film): ῡ 1616, 1513, 1442, 1425, 1345, 1302, 1245, 1030, 937, 797, 760, 731, 721 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.33 (s, 3H, C*H*$_3$Ar), 3.98 (s, 2H, C*H*$_2$Ar), 6.72 (dm, *J* = 4.0 Hz, 1H, H-8), 6.80 (dd, *J* = 4.0, 2.5 Hz, 1H, H-7), 7.13 (d, *J* = 8.0 Hz, 2H, H-3'), 7.19 (d, *J* = 8.0 Hz, 2H, H-2'), 7.27–7.29 (m, 1H, H-6), 7.49 (br s, 1H, H-4), 8.75 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.0 (*C*H_3Ar), 40.5 (*C*H_2Ar), 103.2 (C-8), 114.6 (C-6), 114.7 (C-7), 115.6 (C-4), 127.3 (C-8a), 129.0 (C-2'), 129.3 (C-3'), 135.8 (C-1'), 136.0 (C-4'), 138.9 (C-3), 144.6 (C-1). HRMS (EI): m/z [M^+] calcd for $C_{15}H_{14}N_2$: 222.1157; found: 222.1158.

3-(4-Methoxybenzyl)pyrrolo[1,2-*a*]pyrazine (14d). Following the method of preparation for **14a**, a mixture of **2d** (0.050 g, 0.21 mmol), DBU (0.038 g, 0.25 mmol), and NH_4OAc (0.032 g, 0.42 mmol) in dry DMF (1.0 mL) was heated at 140 °C for 24 h to furnish **14d** (0.021 g, 43%) as a brown solid. *Rf* 0.31 (hexane/EtOAc, 7:3); mp 127–129 °C. IR (film): ῡ 2921, 1601, 1583, 1486, 1439, 1344, 1305, 1260, 1151, 1038, 942, 771, 721, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79 (s, 3H, OC*H*$_3$), 3.97 (s, 2H, C*H*$_2$Ar), 6.72 (d, *J* = 3.7 Hz, 1H, H-8), 6.78–6.81 (m, 1H, H-7), 6.87 (d, *J* = 8.5 Hz, 2H, H-3'), 7.22 (d, *J* = 8.5 Hz, 2H, H-2'), 7.29 (br s, 1H, H-6), 7.49 (s, 1H, H-4), 8.75 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.2 (*C*H_2Ar), 55.2 (C*H*$_3$O), 103.0 (C-8), 114.0 (C-3'), 114.6 (C-6), 114.7 (C-7), 115.6 (C-4), 127.4 (C-8a), 130.1 (C-2'), 131.1 (C-1'), 139.2 (C-3), 144.7 (C-1), 158.3 (C-4'). HRMS (EI): m/z [M^+] calcd for $C_{15}H_{14}N_2O$: 238.1106; found: 238.1105.

4-(Pyrrolo[1,2-*a*]pyrazin-3-ylmethyl)benzaldehyde (14e). Following the method of preparation for **14a**, a mixture of **2e** (0.060 g, 0.25 mmol), DBU (0.046 g, 0.30 mmol), and NH_4OAc (0.023 g, 0.30 mmol) in dry DMF (1.5 mL) was heated at 60 ºC for 1 h to produce **14e** (0.010 g, 17%) as a brown oil. *Rf* 0.21 (hexane/EtOAc, 7:3). IR (film): ῡ 2922, 2835, 1599, 1584, 1489, 1445, 1303, 1258, 1153, 1073, 1048, 889, 770, 721, 696 cm^{-1}. ^{1}H NMR (750 MHz, $CDCl_3$): δ 4.09 (s, 2H, C*H*$_2$Ar), 6.77 (br d, *J*

= 3.5 Hz, 1H, H-8), 6.83–6.86 (m, 1H, H-7), 7.36 (br s, 1H, H-6), 7.48 (d, *J* = 8.0 Hz, 2H, H-2'), 7.63 (s, 1H, H-4), 7.84 (d, *J* = 8.0 Hz, 2H, H-3'), 8.76 (s, 1H, H-1), 9.99 (s, 1H, C*H*O). ^{13}C NMR (187.5 MHz, $CDCl_3$): δ 41.1 (*C*H_2Ar), 103.5 (C-8), 114.8 (C-6), 115.0 (C-7), 115.9 (C-4), 127.4 (C-8a), 129.7 (C-2'), 130.1 (C-3'), 134.9 (C-4'), 137.4 (C-3), 145.0 (C-1), 146.5 (C-1'), 192.0 (*C*HO). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{12}N_2O$: 236.0950; found: 236.0953.

1-(4-(Pyrrolo[1,2-*a*]pyrazin-3-ylmethyl)phenyl)ethanone (14f). Following the method of preparation for **14a**, a mixture of **2f** (0.050 g, 0.20 mmol), DBU (0.036 g, 0.24 mmol), and NH_4OAc (0.031 g, 0.40 mmol) in dry DMF (1.0 mL) was heated at 60 °C for 1 h to afford **14f** (0.035 g, 70%) as a brown solid. *Rf* 0.19 (hexane/EtOAc, 7:3); mp 95–97 °C. IR (film): ῡ 2920, 1681, 1606, 1427, 1356, 1303, 1270, 1073, 960, 797, 721 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59 (s, 3H, COC*H*$_3$), 4.07 (s, 2H, C*H*$_2$Ar), 6.75 (dm, *J* = 4.1 Hz, 1H, H-8), 6.84 (dd, *J* = 4.1, 2.4 Hz, 1H, H-7), 7.32–7.36 (m, 1H, H-6), 7.37–7.43 (m, 2H, H-2'), 7.60 (s, 1H, H-4), 7.88–7.95 (m, 2H, H-3'), 8.76 (s, 1H, H-1). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 26.6 (COC*H*$_3$), 40.9 (*C*H_2Ar), 103.4 (C-8), 114.8 (C-6), 114.9 (C-7), 115.9 (C-4), 127.3 (C-8a), 128.7 (C-3'), 129.3 (C-2'), 135.5 (C-4'), 137.6 (C-3), 144.8 (C-1'), 144.9 (C-1), 197.8 (*C*OCH_3). HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{14}N_2O$: 250.1106; found: 250.1107.

3-(3-Methoxybenzyl)pyrrolo[1,2-*a*]pyrazine (14g). Following the method of preparation for **14a**, a mixture of **2g** (0.050 g, 0.21 mmol), DBU (0.038 g, 0.25 mmol), and NH_4OAc (0.032 g, 0.42 mmol) in dry DMF (1.0 mL) was heated at 120 °C for 12 h to yield **14g** (0.016 g, 33%) as a brown solid. *Rf* 0.29 (hexane/EtOAc, 7:3); mp 43–45 °C. IR (film): ῡ 2922, 1599, 1584, 1489, 1445, 1348, 1303, 1258, 1153, 1048, 770, 721, 696 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79 (s, 3H, C*H*$_3$O), 4.00 (s, 2H, C*H*$_2$Ar), 6.73 (dm, *J* = 4.0 Hz, 1H, H-8), 6.79 (dd, *J* = 8.0, 2.5 Hz, 1H, H-4'), 6.81 (dd, *J* = 4.0, 2.5 Hz, 1H, H-7), 6.85 (br s, 1H, H-2'), 6.89 (d, *J* = 8.0 Hz, 1H, H-6'), 7.24 (t, *J* = 8.0 Hz, 1H, H-5'), 7.30 (br s, 1H, H-6), 7.53 (s, 1H, H-4), 8.76 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 41.1 (*C*H_2Ar), 55.2 (*C*H_3O), 103.2 (C-8), 111.9 (C-4'), 114.6 (C-6), 114.7 (C-7), 114.9 (C-2'), 115.8 (C-4), 121.5 (C-6'), 127.4 (C-8a), 129.6 (C-5'), 138.6 (C-3), 140.6 (C-1'), 144.7 (C-1), 159.8 (C-3'). HRMS (EI): m/z [M^+] calcd for $C_{15}H_{14}N_2O$: 238.1106; found: 238.1109.

3-(3-Fluorobenzyl)pyrrolo[1,2-*a*]pyrazine (14i). Following the method of preparation for **14a**, a mixture of **2j** (0.050 g, 0.22 mmol), DBU (0.040 g, 0.26 mmol), and NH_4OAc (0.034 g, 0.44 mmol) in dry DMF (1.0 mL) was heated at 80 °C for 2 h to provide **14i** (0.025 g, 51%) as a brown oil. *Rf* 0.21 (hexane/EtOAc, 7:3). IR (film): ῡ 3079, 2924, 1715, 1615, 1589, 1488, 1447, 1349, 1304, 1246, 1134, 1074, 963, 787, 754, 722, 693 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.01 (s, 2H, C*H*$_2$Ar), 6.75 (d, *J* =

4.0 Hz, 1H, H-8), 6.83 (dd, *J* = 4.0, 2.5 Hz, 1H, H-7), 6.92 (td, *J* = 8.5, 2.5 Hz, 1H, H-4'), 7.00 (br d, *J* = 9.5 Hz, 1H, H-2'), 7.08 (d, *J* = 7.5 Hz, 1H, H-6'), 7.24–7.30 (m, 1H, H-5'), 7.32–7.34 (m, 1H, H-6), 7.57 (s, 1H, H-4), 8.77 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.7 (d, $J_{C,F}$ = 1.75 Hz, CH_2Ar), 103.5 (C-8), 113.4 (d, J_{CF} = 21.0 Hz, C-4'), 114.8 (C-6), 115.0 (C-7), 115.9 (C-4), 116.0 (d, J_{CF} = 21.1 Hz, C-2'), 124.7 (d, J_{CF} = 2.8 Hz, C-6'), 127.4 (C-8a), 130.0 (d, J_{CF} = 8.4 Hz, C-5'), 137.9 (C-3), 141.7 (d, J_{CF} = 7.3 Hz, C-1'), 144.8 (C-1), 162.9 (d, J_{CF} = 244.5 Hz, C-3'). HRMS (EI): m/z [M^+] calcd for $C_{15}H_{11}N_2F$: 226.0906; found: 226.0907.

6-Bromo-3-(4-methoxybenzyl)pyrrolo[1,2-*a*]pyrazine (15c). Following the method of preparation for **15a**, a mixture of **14d** (0.030 g, 0.13 mmol) and NBS (0.023 g, 0.13 mmol) in dry CH_2Cl_2 (15 mL) furnished **15c** (0.03 g, 76%) as a dark brown oil. *Rf* 0.31 (hexane/EtOAc, 7:3). IR (film): ῡ 1616, 1508, 1439, 1296, 1248, 1239, 1178, 1032, 927, 820, 778, 745, 709 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79 (s, 3H, CH_3O), 4.02 (s, 2H, CH_2Ar), 6.79 (dd, *J* = 4.3, 0.5 Hz, 1H, H-8), 6.84 (d, *J* = 4.3 Hz, 1H, H-7), 6.85–6.89 (m, 2H, H-3'), 7.22–7.25 (m, 2H, H-2'), 7.62 (s, 1H, H-4), 8.69 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.4 (*C*H_2Ar), 55.3 (*C*H_3O), 96.5 (C-6), 104.3 (C-8), 113.0 (C-4), 114.0 (C-3'), 116.9 (C-7), 128.4 (C-8a), 130.0 (C-2'), 131.0 (C-1'), 140.4 (C-3), 144.2 (C-1), 158.3 (C-4'). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{13}BrN_2O$: 316.0211; found: 316.0206.

6-Bromo-3-(3-nitrobenzyl)pyrrolo[1,2-*a*]pyrazine (15d). Following the method of preparation for **15a**, a mixture of **14h** (0.050 g, 0.20 mmol) and NBS (0.037 mg, 0.20 mmol) in dry CH_2Cl_2 (15 mL) produced **15d** (0.048 g, 73%) as a pale yellow solid. *Rf* 0.32 (hexane/EtOAc, 7:3); mp 153–155 ºC. IR (film): ῡ 1617, 1515, 1420, 1342, 1304, 1299, 1242, 1195, 1042, 912, 798, 737, 719, 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.16 (s, 2H, CH_2Ar), 6.85 (d, *J* = 4.3 Hz, 1H, H-8), 6.90 (d, *J* = 4.3 Hz, 1H, H-7), 7.50 (t, *J* = 7.8 Hz, 1H, H-5'), 7.69 (br d, *J* = 7.8 Hz, 1H, H-6'), 7.78 (s, 1H, H-4), 8.02–8.14 (br d, *J* = 7.8 Hz, 1H, H-4'), 8.17 (br s, 1H, H-2'), 8.70 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.7 (*C*H_2Ar), 97.0 (C-6), 104.9 (C-8), 113.5 (C-4), 117.3 (C-7), 121.7 (C-4'), 123.9 (C-2'), 128.4 (C-8a), 129.4 (C-5'), 135.3 (C-6'), 138.2 (C-3), 141.3 (C-1'), 144.6 (C-1), 148.4 (C-3'). HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{10}BrN_3O_2$: 330.9956; found: 330.9920.

6,7-Dibromo-3-(4-methoxybenzyl)pyrrolo[1,2-*a*]pyrazine (16b). Following the method of preparation for **16a**, a mixture of **14d** (0.040 g, 0.17 mmol) and NBS (0.060 mg, 0.34 mmol) in dry CH_2Cl_2 (15 mL) yielded **16b** (0.04 g, 61%) as a dark brown solid. *Rf* 0.61 (hexane/EtOAc, 7:3); mp 115–117 ºC. IR (film): ῡ 1608, 1508, 1430, 1316, 1293, 1240, 1177, 1033, 819, 810, 760 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.79 (s, 3H, OCH_3), 4.02 (s, 2H, CH_2Ar), 6.85 (s, 1H, H-8), 6.87 (br d, *J* =

8.7 Hz, 2H, H-3'), 7.22 (d, *J* = 8.7 Hz, 2H, H-2'), 7.55 (s, 1H, H-4), 8.67 (s, 1H, H-1). ^{13}C NMR (150 MHz, $CDCl_3$): δ 40.4 (*C*H_2Ar), 55.3 (O*C*H_3), 90.7 (C-7), 96.4 (C-6), 112.9 (C-4), 114.1 (C-3'), 118.3 (C-8), 126.2 (C-8a), 130.0 (C-2'), 130.6 (C-1'), 141.1 (C-3), 143.1 (C-1), 158.4 (C-4'). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{12}Br_2N_2O$: 393.9316; found: 393.9313.

3-Methyl-6-(*p*-tolyl)pyrrolo[1,2-*a*]pyrazine (17a). In a threaded ACE glass pressure tube equipped with a sealed Teflon screw cap and a magnetic stirring bar, a mixture of **14a** (0.040 g, 0.30 mmol), 4-iodotoluene (0.098 g, 0.45 mmol), $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol), and KOAc (0.060 g, 0.61 mmol) in dry DMAc (2 mL) was heated at 150 ºC for 24 h. A 5% aqueous solution of HCl (2 mL) was then added and stirred for 5 min. The mixture was extracted with EtOAc (30 mL) and washed with water (20 mL). The organic layer was dried (Na_2SO_4) and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane/EtOAc, 1:1) to obtain **17a** (0.02 g, 30%) as a dark brown solid. *Rf* 0.17 (hexane/EtOAc, 7:3); mp 103–105 ºC. IR (film): ῡ 1621, 1473, 1448, 1385, 1323, 1241, 1194, 1038, 915, 801, 780, 767, 715 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.38 (d, *J* = 1.0 Hz, 3H, C*H*$_3$-3), 2.43 (s, 3H, C*H*$_3$Ar), 6.82 (d, *J* = 4.2 Hz, 1H, H-8), 6.86 (d, *J* = 4.2 Hz, 1H, H-7), 7.31 (d, *J* = 8.0 Hz, 2H, H-3'), 7.45 (d, *J* = 8.0 Hz, 2H, H-2'), 7.90 (s, 1H, H-4), 8.76 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1 (*C*H_3-3), 21.3 (*C*H_3Ar), 104.1 (C-8), 111.7 (C-4), 114.8 (C-7), 127.9 (C-6), 128.0 (C-2'), 128.3 (C-8a), 129.1 (C-1'), 129.8 (C-3'), 135.7 (C-3), 137.9 (C-4'), 144.7 (C-1). HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{14}N_2$: 222.1157; found: 222.1157.

3-Methyl-6-(3-nitrophenyl)pyrrolo[1,2-*a*]pyrazine (17b). Following the method of preparation for **17a**, a mixture of **14a** (0.040 g, 0.30 mmol), 1-iodo-3-nitrobenzene (0.112 g, 0.45 mmol), $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol), and KOAc (0.060 g, 0.61 mmol) in dry DMAc (2 mL) provided **17b** (0.05 g, 65%) as a pale yellow solid. *Rf* 0.16 (hexane/EtOAc, 7:3); mp 169–171 ºC. IR (film): ῡ 1621, 1542, 1526, 1506, 1343, 1325, 1241, 1197, 919, 797, 736, 728, 685 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.44 (s, 3H, C*H*$_3$), 6.88 (dd, *J* = 4.3, 0.7 Hz, 1H, H-8), 6.99 (d, *J* = 4.3 Hz, 1H, H-7), 7.70 (t, *J* = 8.0 Hz, 1H, H-5'), 7.89–7.92 (m, 2H, H-4, H-6'), 8.22 (br d, *J* = 8.0 Hz, 1H, H-4'), 8.43 (t, *J* = 2.0 Hz, 1H, H-2'), 8.83 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.2 (*C*H_3), 104.7 (C-8), 111.2 (C-4), 115.9 (C-7), 122.4 (C-4'), 122.5 (C-2'), 124.4 (C-6), 128.7 (C-8a), 130.2 (C-5'), 133.0 (C-1'), 133.5 (C-6'), 137.0 (C-3), 145.1 (C-1), 148.9 (C-3'). HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{11}N_3O_2$: 253.0851; found: 253.0849.

3-Methyl-6-phenylpyrrolo[1,2-*a*]pyrazine (17d). In a threaded ACE glass pressure tube equipped with a sealed Teflon screw cap and a magnetic stirring bar, a mixture of **15a** (0.051 g, 0.24 mmol), phenylboronic acid (0.044 g, 0.36 mmol), $Pd(OAc)_2$ (0.002 g, 0.01 mmol), and K_2CO_3 (0.050 g, 0.36

mmol) in a solution of DMF/EtOH (1:1, 1.0 mL) was heated at 70 ºC for 8 h. A solution of brine (20 mL) was added and the mixture extracted with EtOAc (40 mL), the organic layer dried (Na_2SO_4), and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel (20 g/g crude, hexane/EtOAc, 1:1) to furnish **17d** (0.021 g, 41%) as a yellow solid. *Rf* 0.17 (hexane/EtOAc, 7:3); mp 97–99 ºC. IR (film): ῡ 1620, 1601, 1441, 1407, 1385, 1323, 1275, 1195, 915, 751, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.42 (s, 3H, C*H*$_3$), 6.92–6.96 (m, 2H, H-7, H-8), 7.38–7.45 (m, 2H, H-2'), 7.50–7.60 (m, 3H, H-3', H-4'), 7.92 (s, 1H, H-4), 8.93 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.7 (*C*H$_3$), 105.5 (C-8), 112.2 (C-4), 115.7 (C-7), 127.5 (C-6), 127.9 (C-8a), 128.1 (C-2'), 128.2 (C-4'), 129.2 (C-3'), 131.0 (C-1'), 135.3 (C-3), 144.0 (C-1). HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{12}N_2$: 208.1001; found: 208.1001.

6-(4-Methoxyphenyl)-3-(3-nitrobenzyl)pyrrolo[1,2-*a*]pyrazine (17f). Following the method of preparation for **17d**, a mixture of **15d** (0.050 g, 0.15 mmol), (4-methoxyphenyl)boronic acid (0.035 g, 0.23 mmol), $Pd(OAc)_2$ (0.0016 g, 0.007 mmol), and K_2CO_3 (0.043 g, 0.31 mmol) produced **17f** (0.04 g, 74%) as a dark yellow solid. *Rf* 0.21 (hexane/EtOAc, 7:3); mp 185–187 ºC. IR (film): ῡ 1611, 1520, 1475, 1348, 1242, 1180, 1035, 922, 837, 804, 768, 699 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 3.89 (s, 3H, C*H*$_3$O), 4.06 (s, 2H, C*H*$_2$Ar), 6.85–6.89 (m, 2H, H-7, H-8), 7.03–7.07 (m, 2H, H-3''), 7.43–7.49 (m, 3H, H-5', H-2''), 7.65 (br d, *J* = 7.5 Hz, 1H, H-6'), 7.96 (s, 1H, H-4), 8.07 (br d, *J* = 7.5 Hz, 1H, H-4'), 8.13 (br s, 1H, H-2'), 8.77 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.7 (*C*H$_2$Ar), 55.4 (*C*H$_3$O), 104.7 (C-8), 112.8 (C-4), 114.7 (C-3''), 115.3 (C-7), 121.6 (C-4'), 123.2 (C-1''), 123.7 (C-2'), 127.8 (C-8a), 128.0 (C-6), 129.3 (C-5'), 129.5 (C-2''), 135.2 (C-6'), 137.2 (C-3), 141.7 (C-1'), 145.5 (C-1), 148.4 (C-3'), 159.6 (C-4''). HRMS (EI): *m/z* [M^+] calcd for $C_{21}H_{17}N_3O_3$: 359.1270; found: 359.1270.

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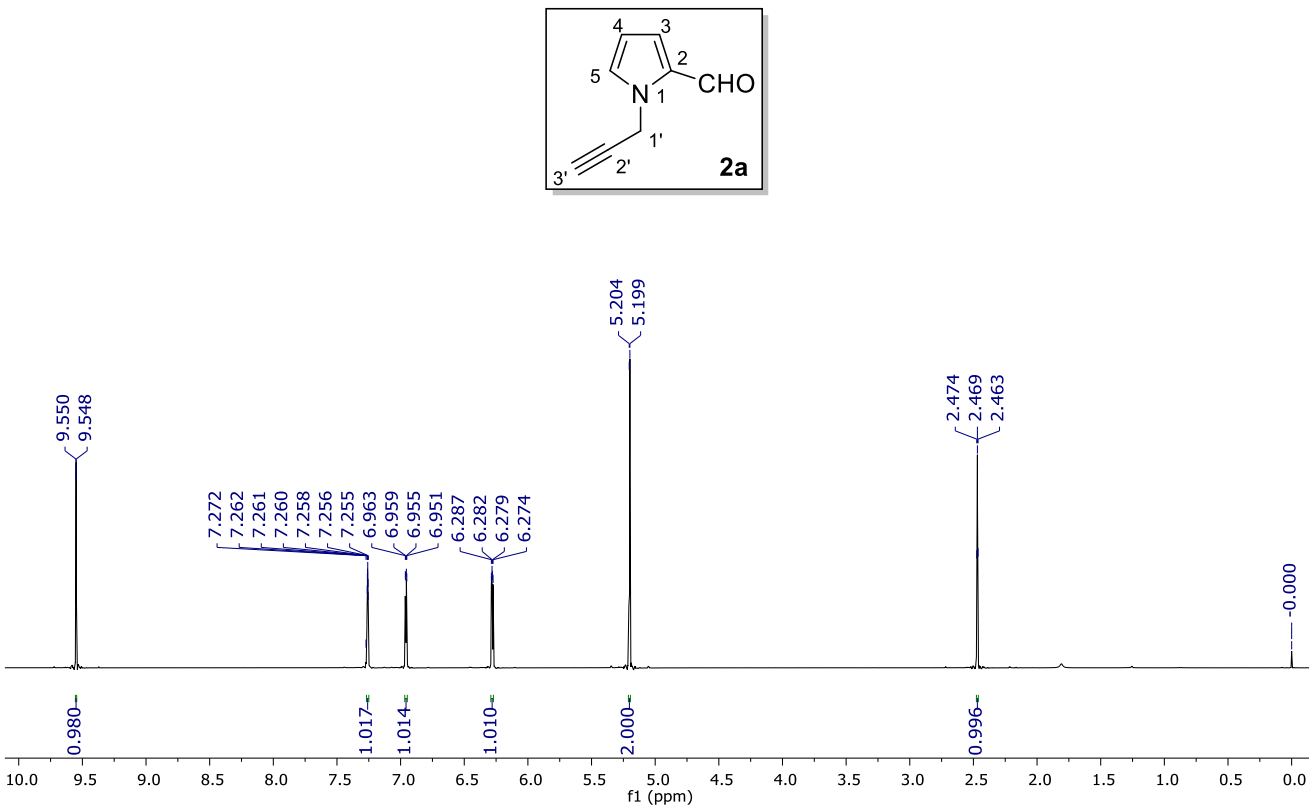
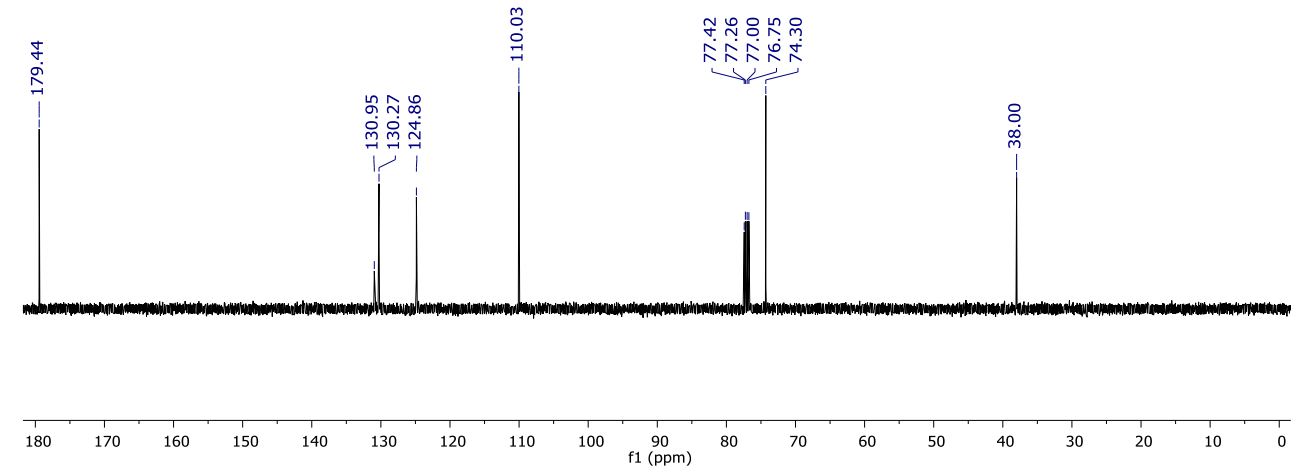
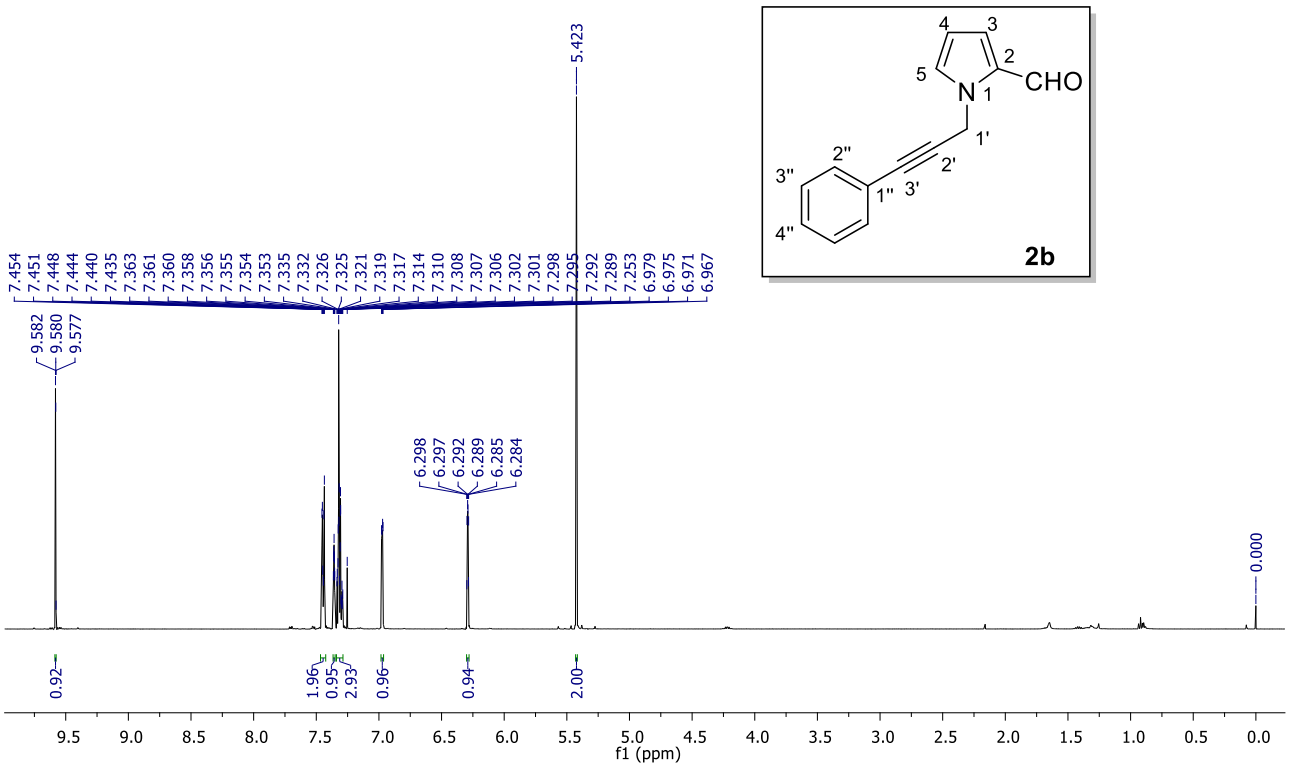
3 O. Sari, A. F. Seybek, S. Kaya, N. Menges, S. S. Erdem and M. Balci, *Eur. J. Org. Chem.*, 2019, 5261–5274.



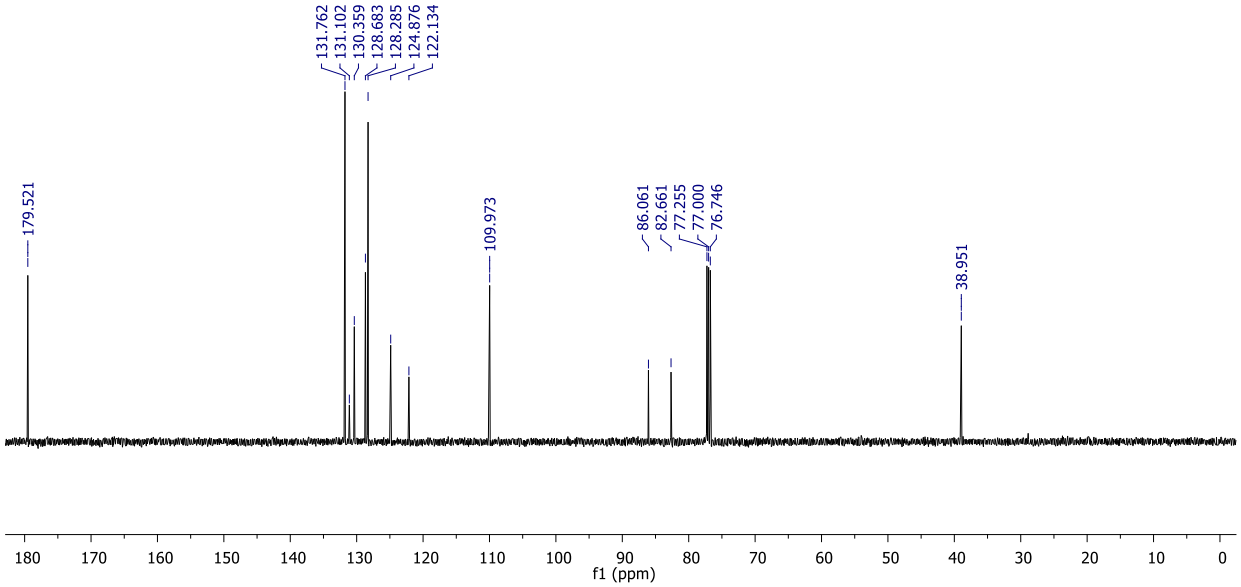
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2a**.



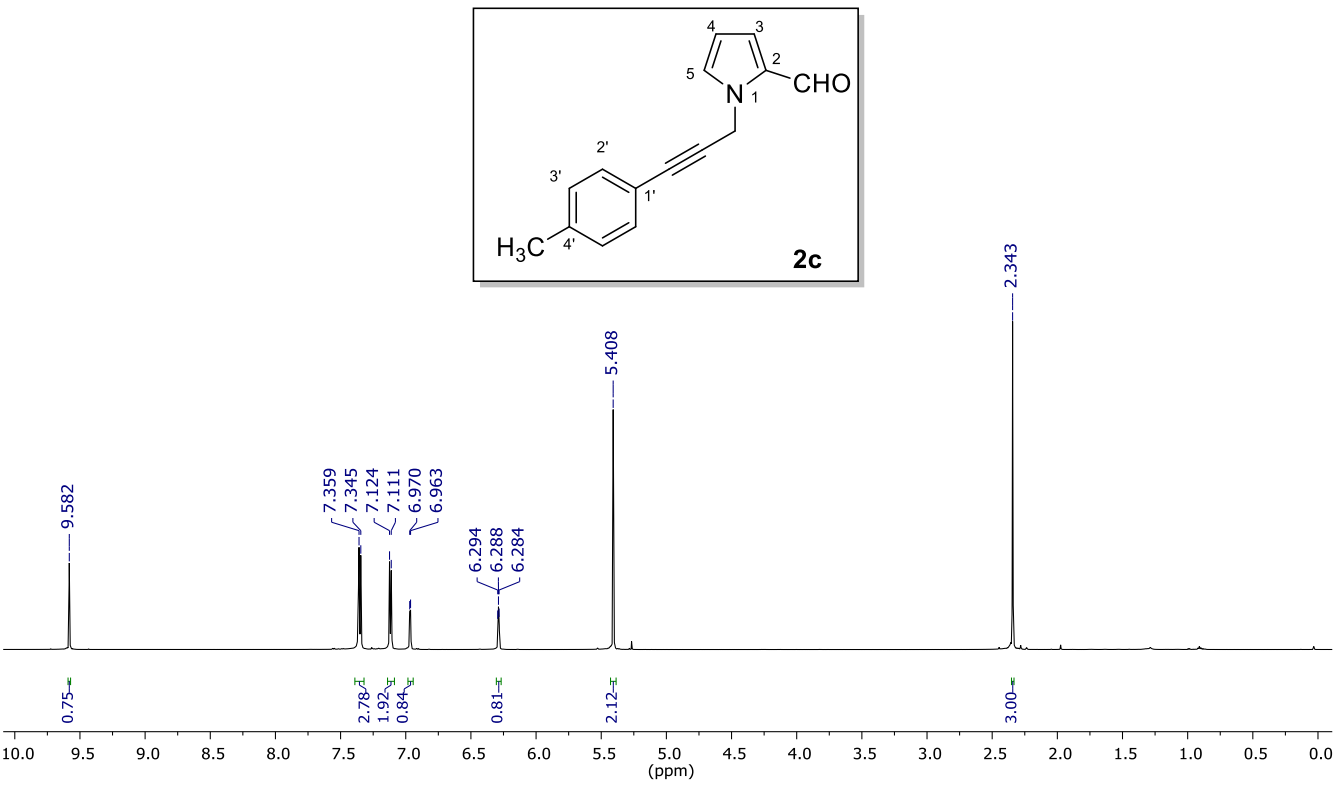
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2a**.



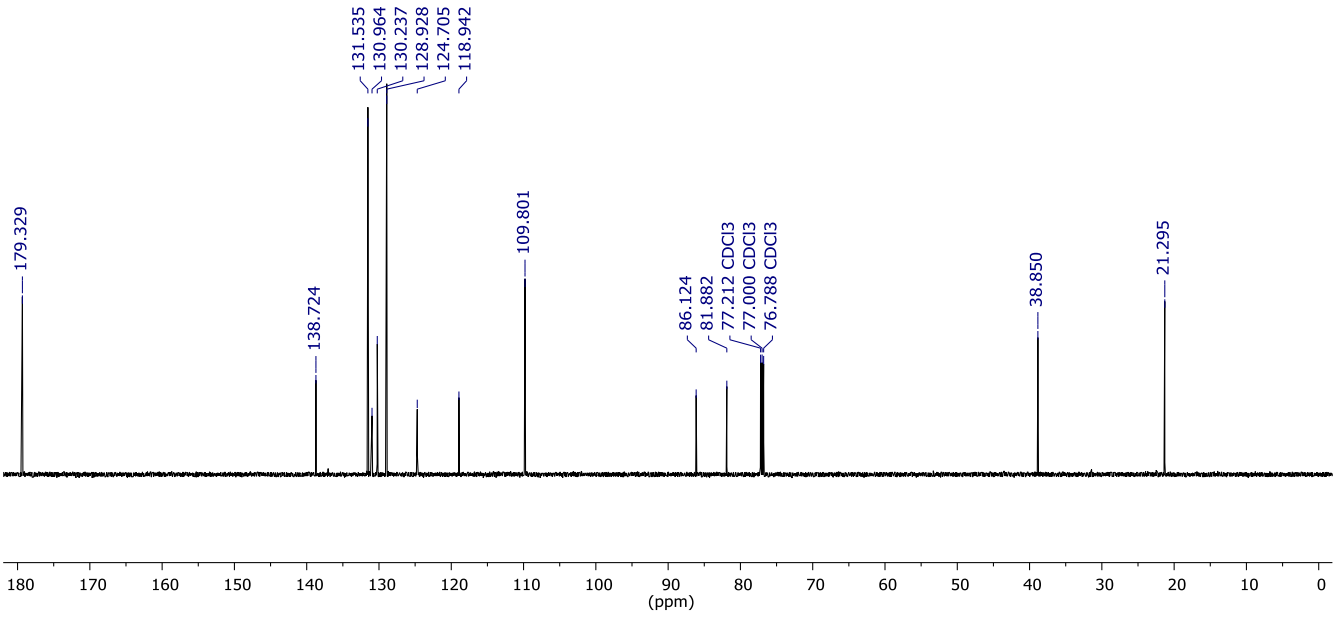
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2b**.



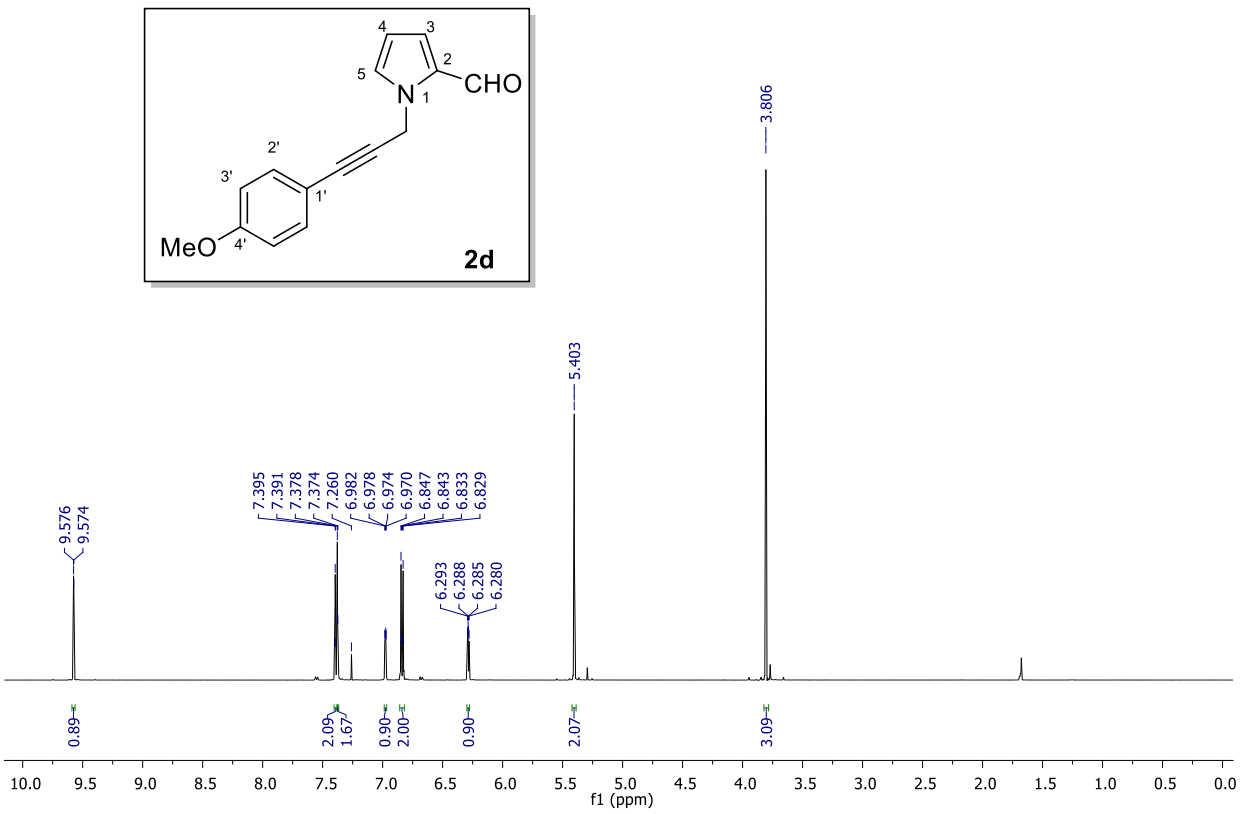
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2b**.



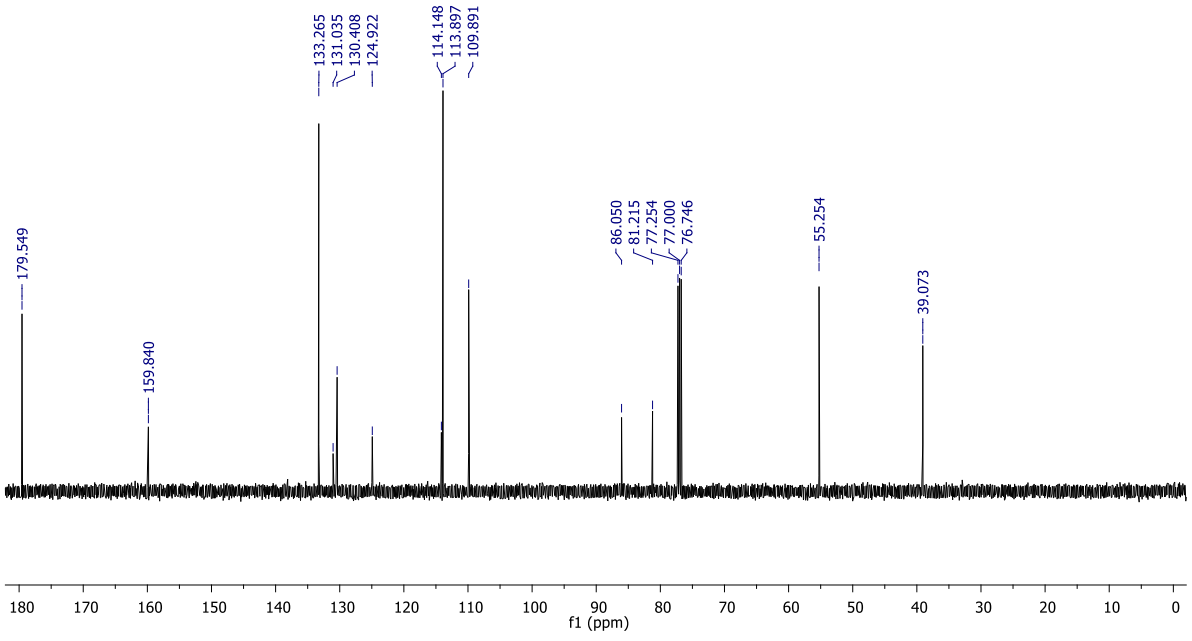
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2c**.



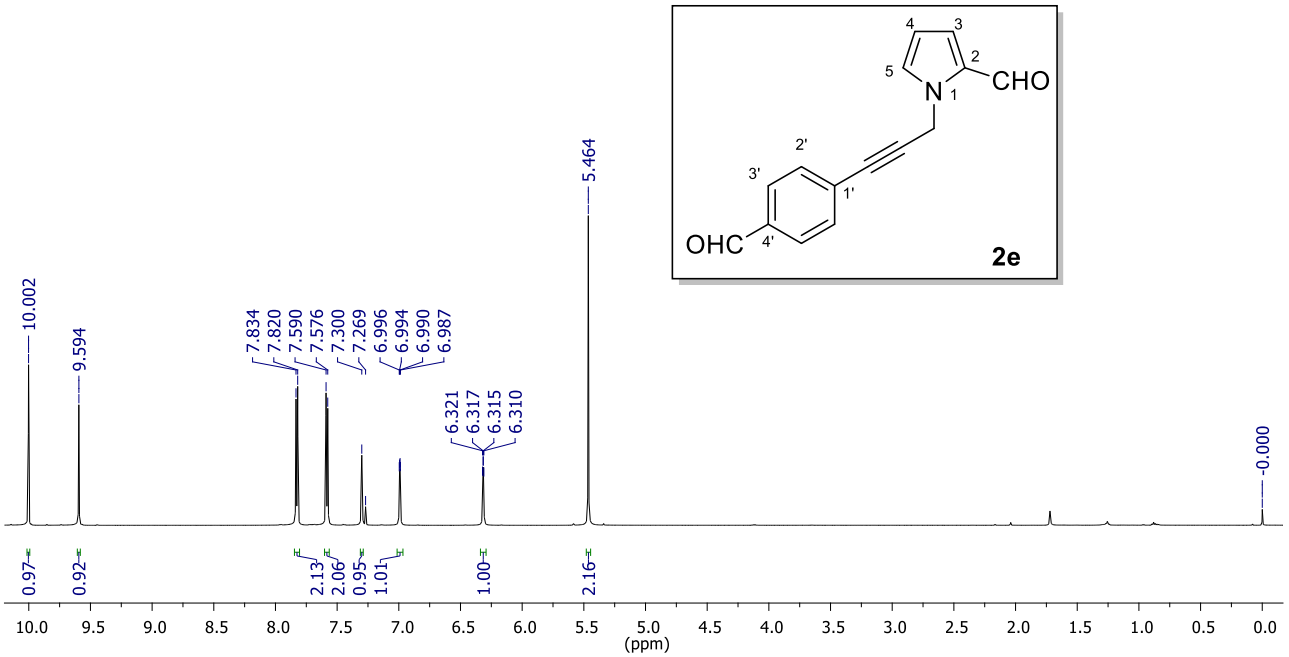
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2c**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **2d**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **2d**.



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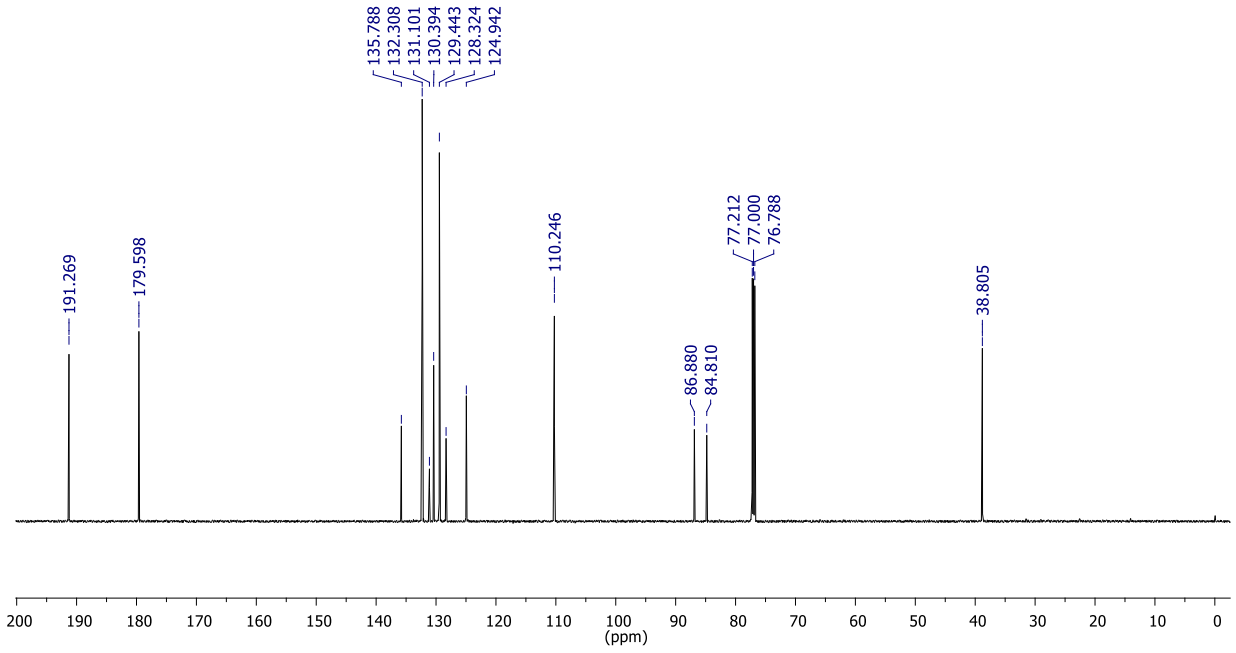
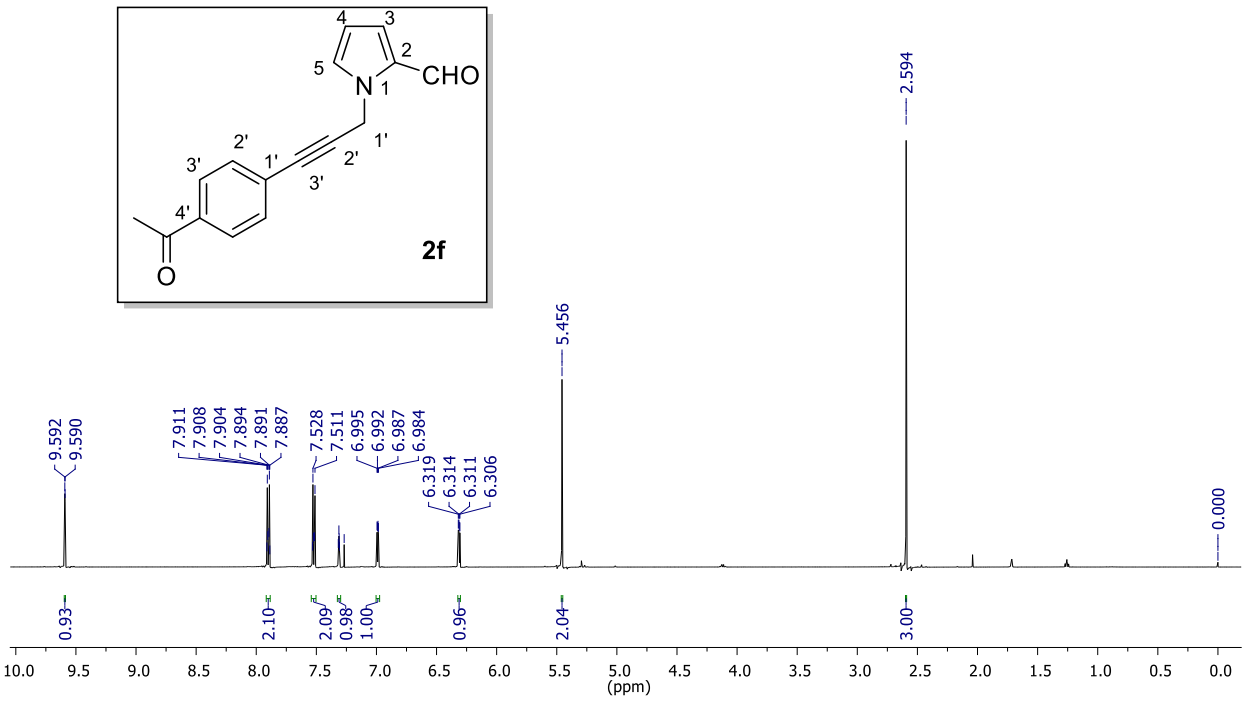
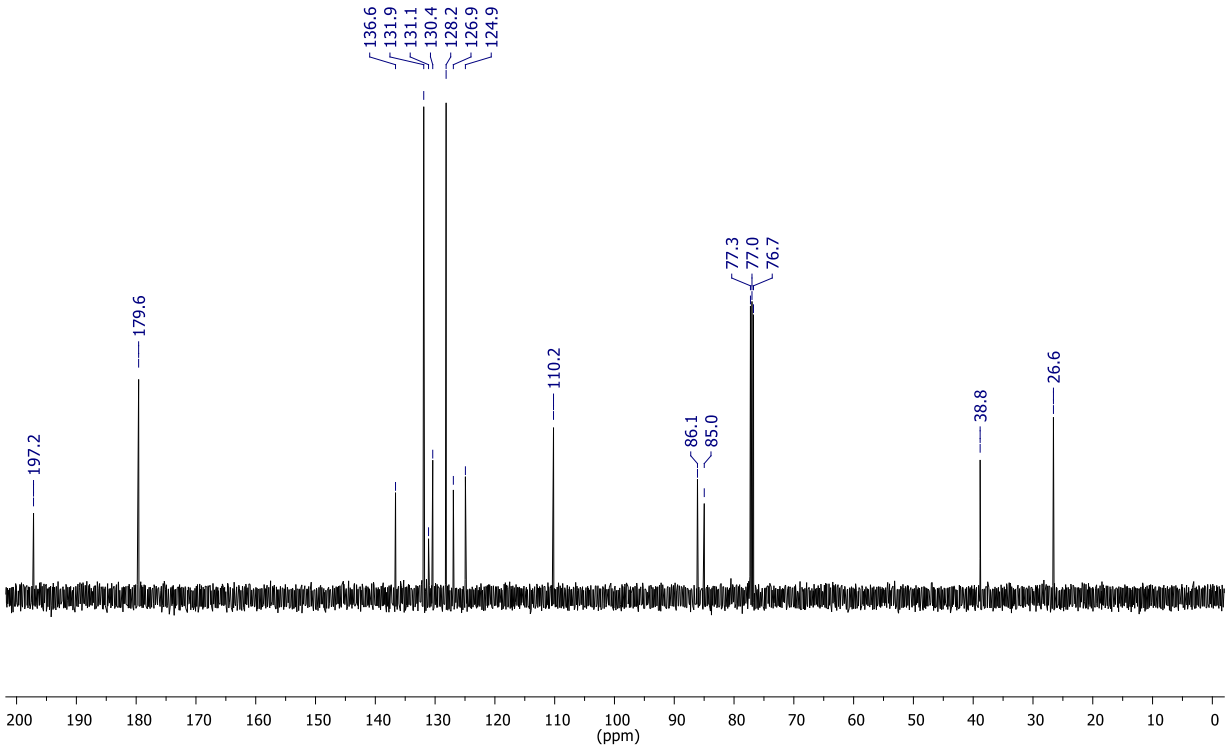


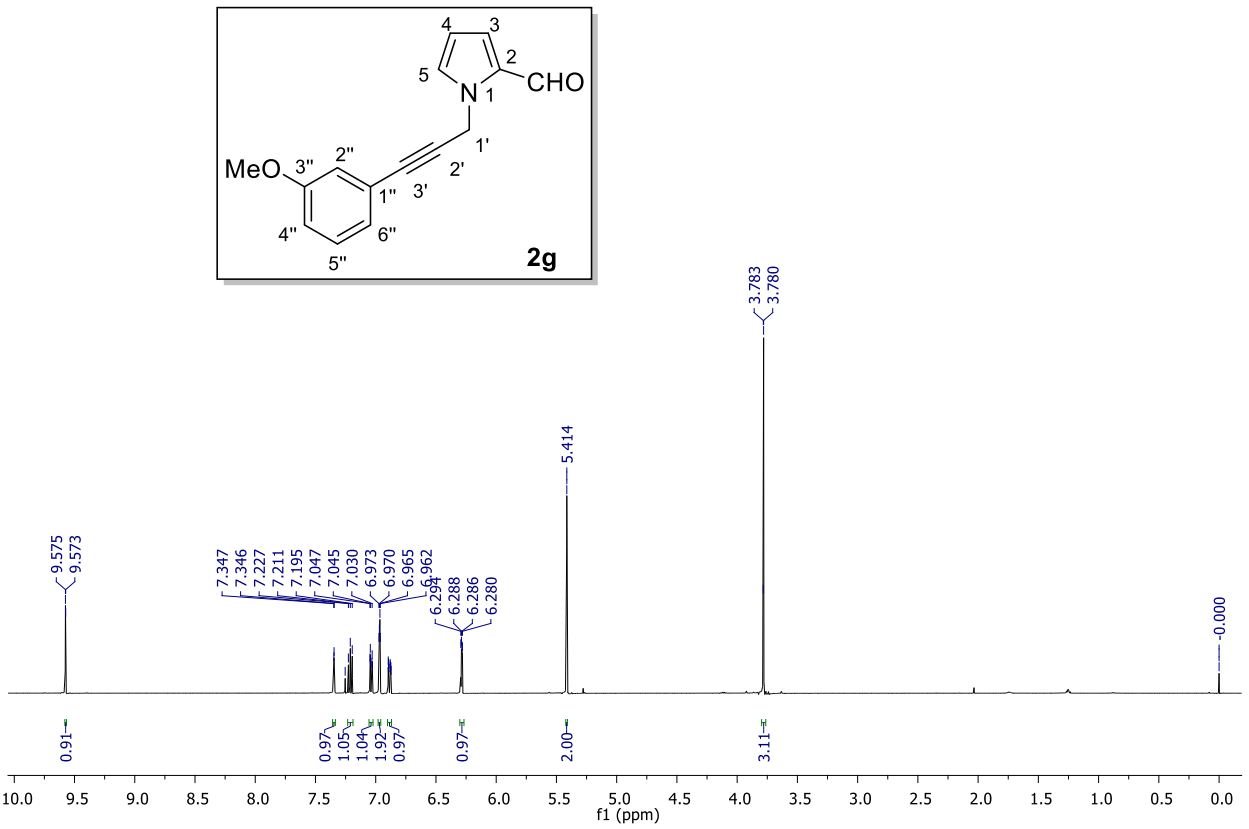
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2e**.



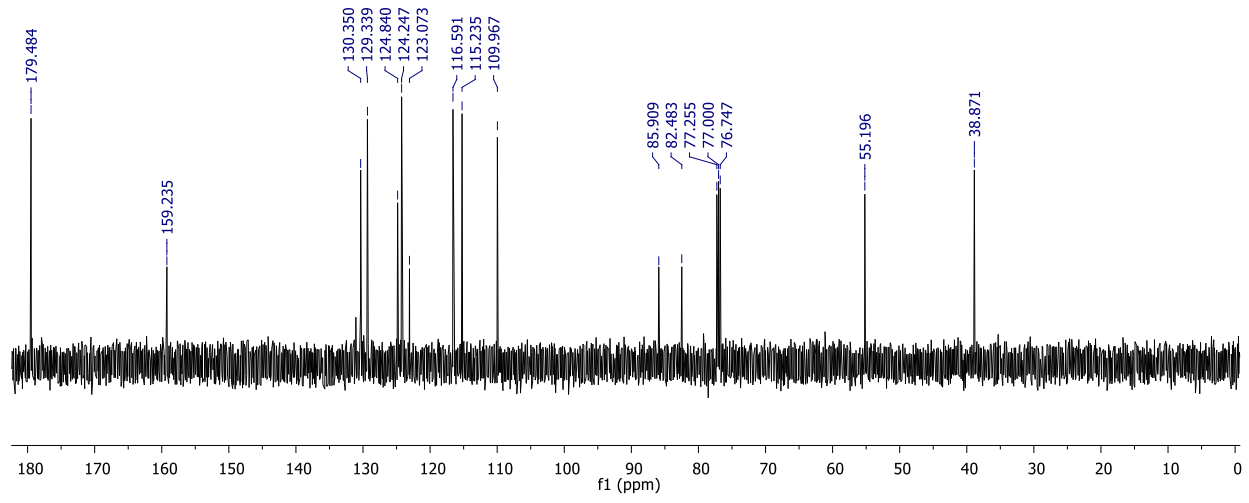
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2f**.



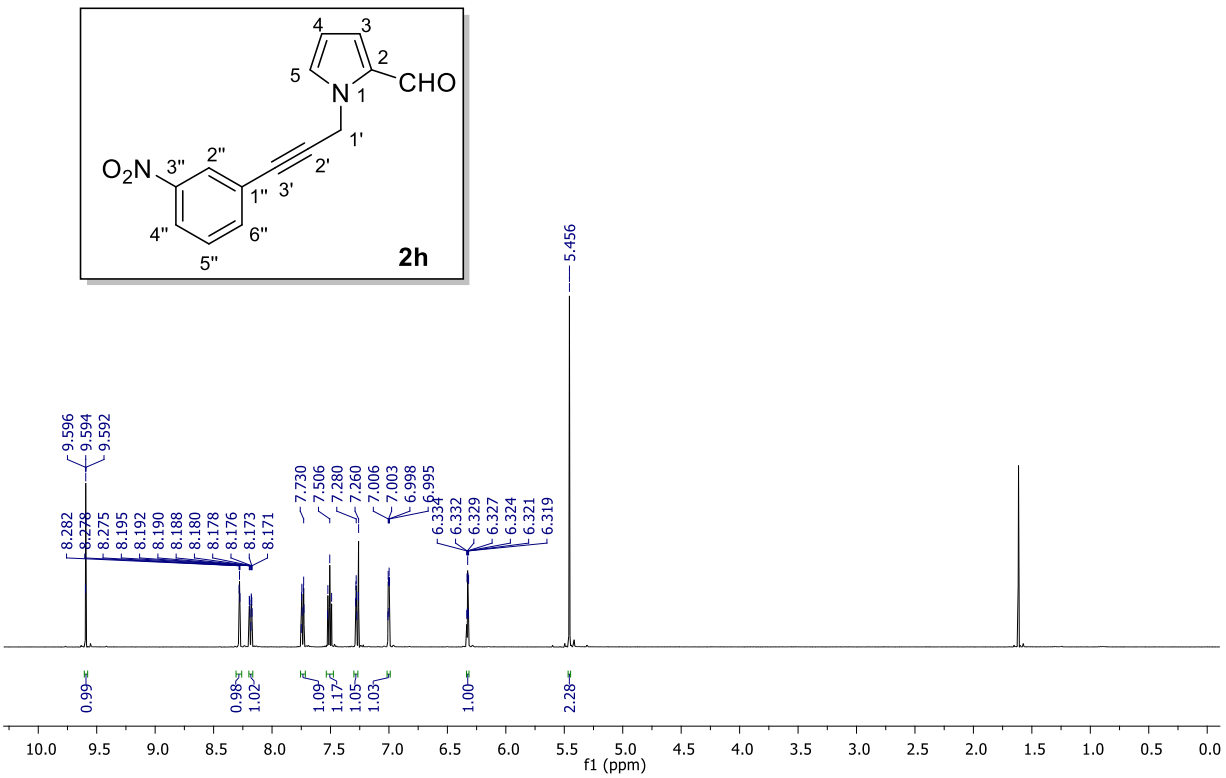
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2f**.



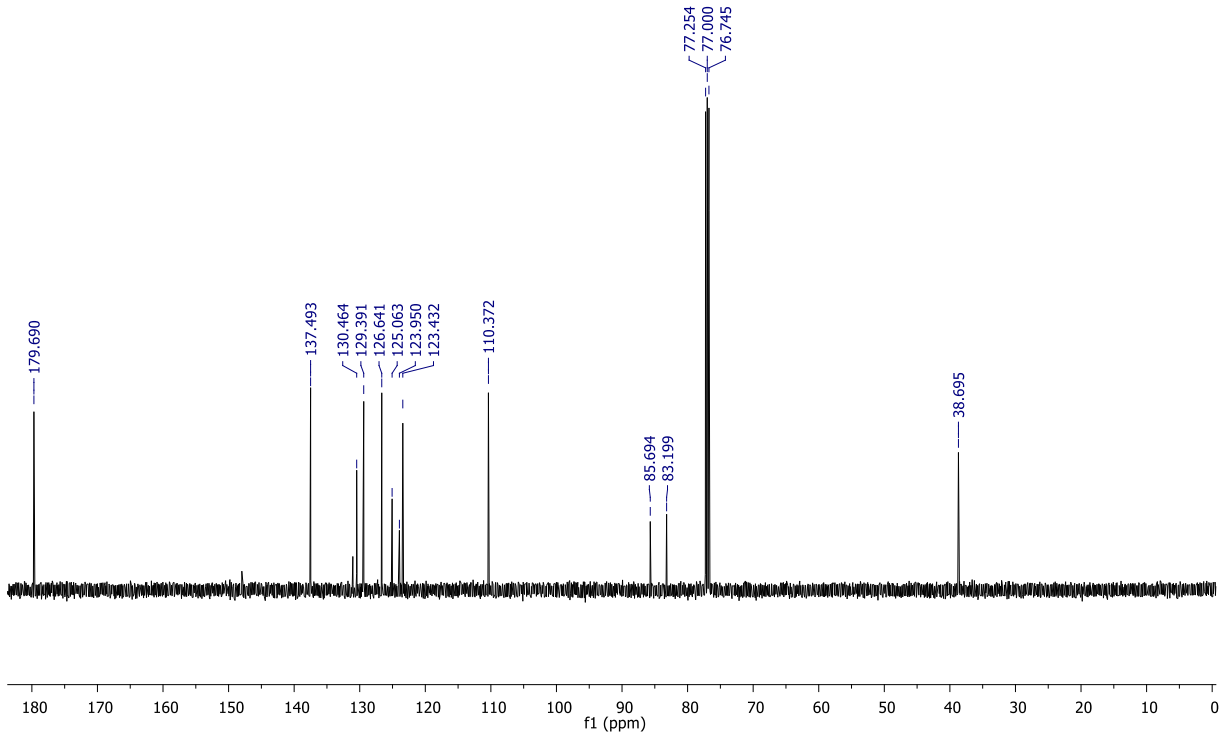
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2g**.



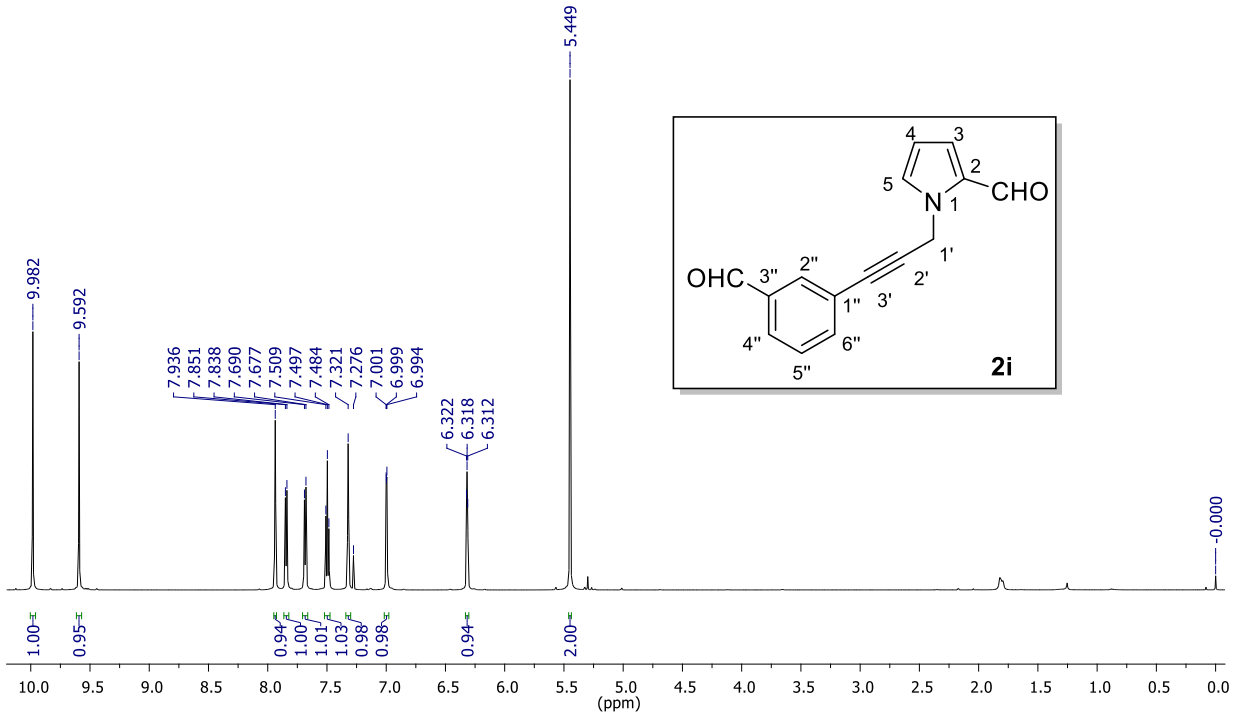
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2g**.



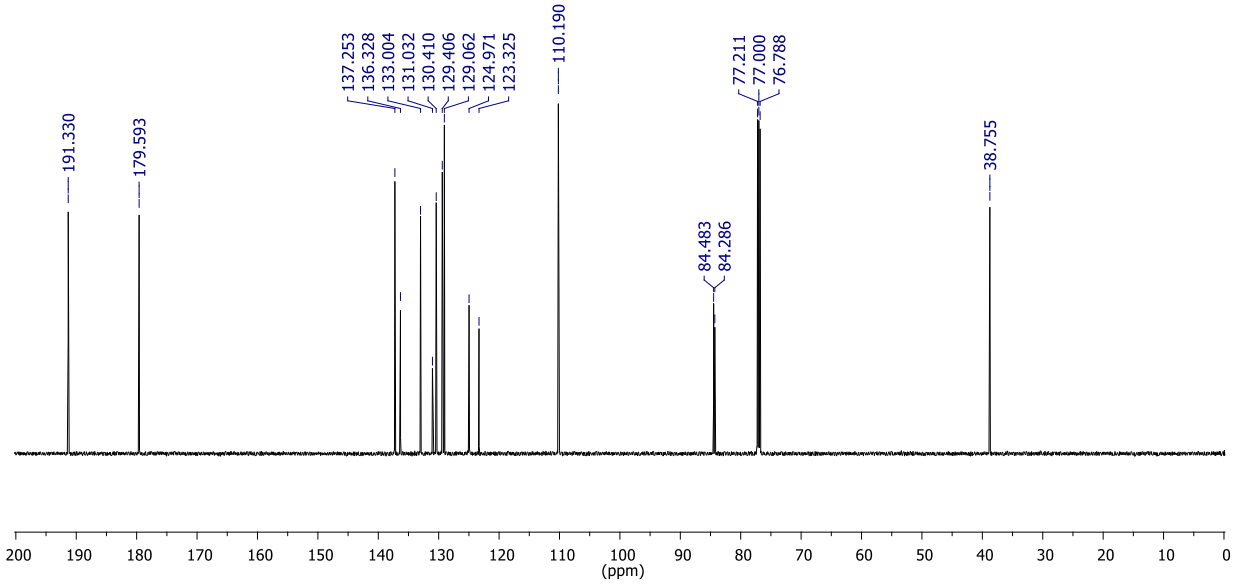
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2h**.



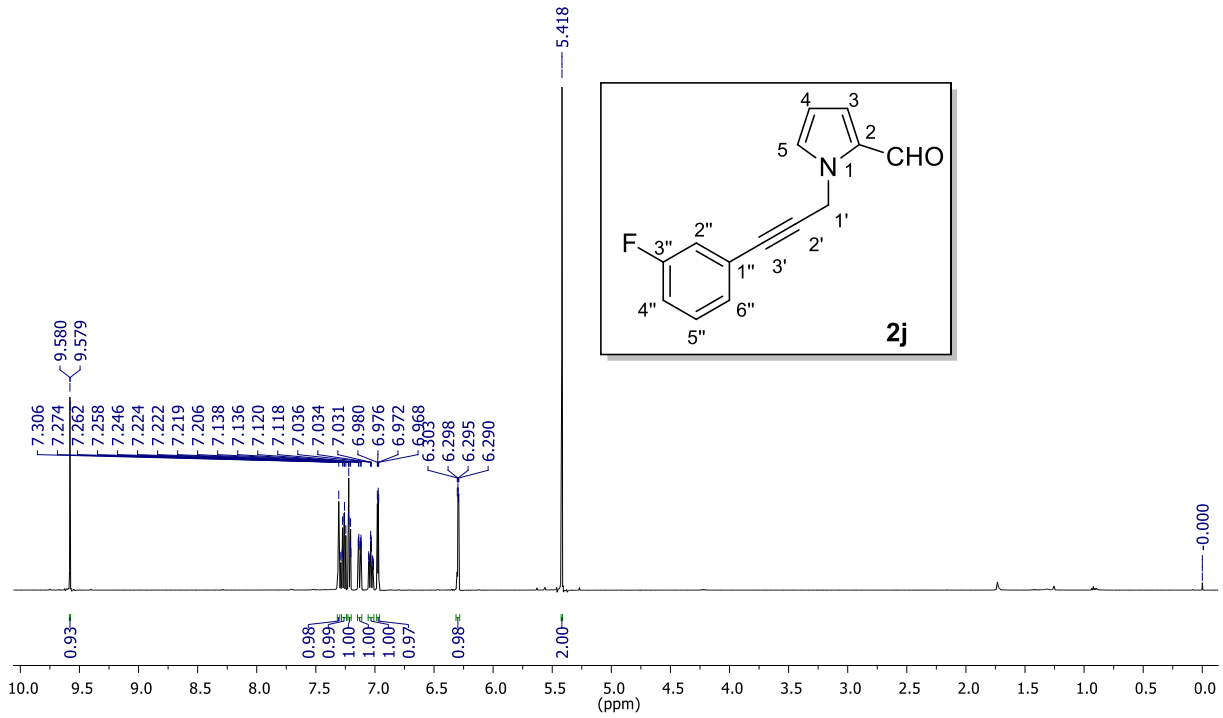
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2h**.



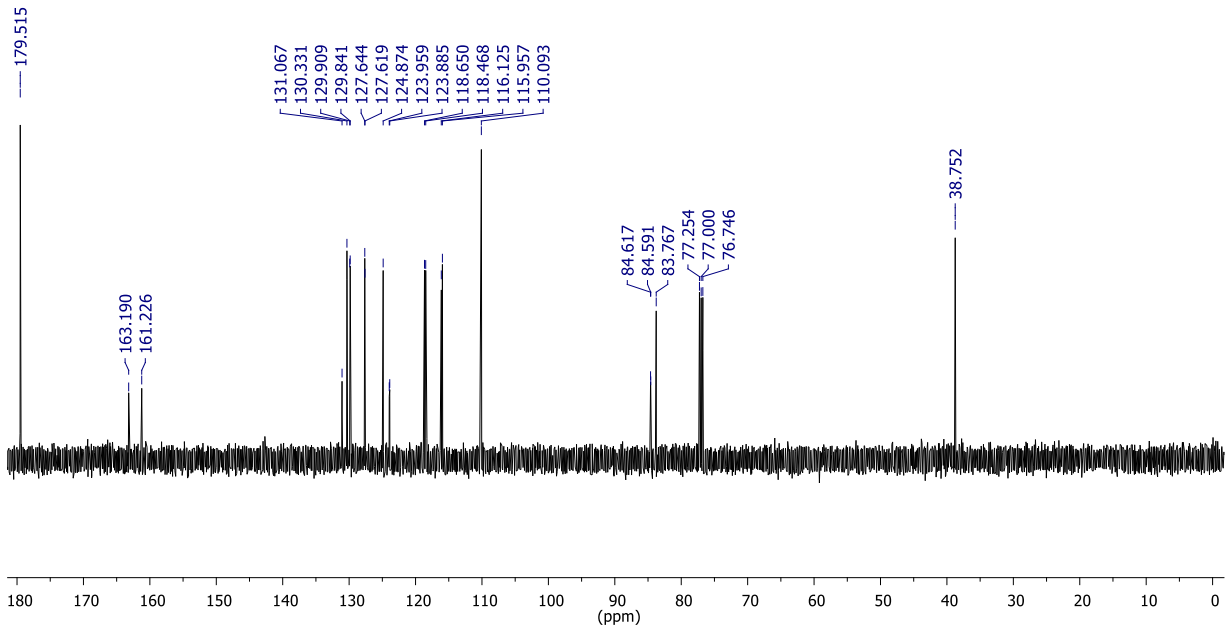
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2i**.



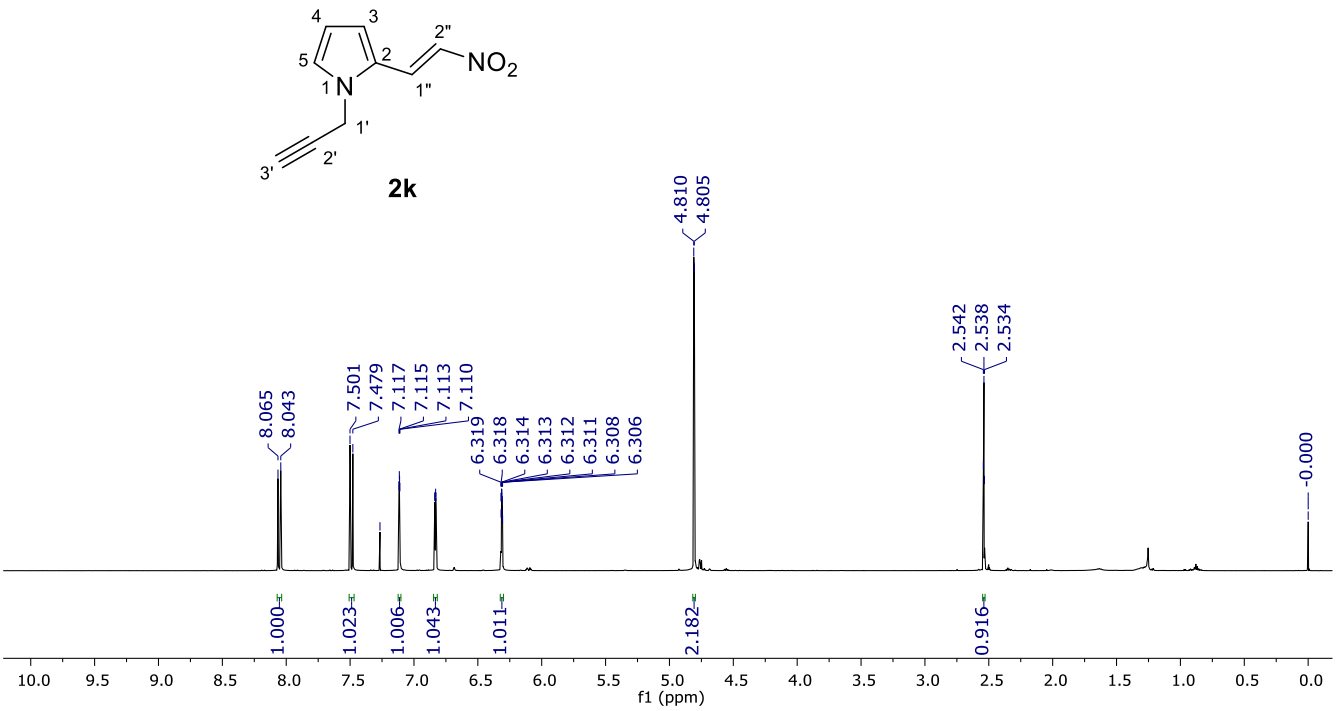
^{13}C NMR (150 MHz, $CDCl_3$) of compound **2i**.



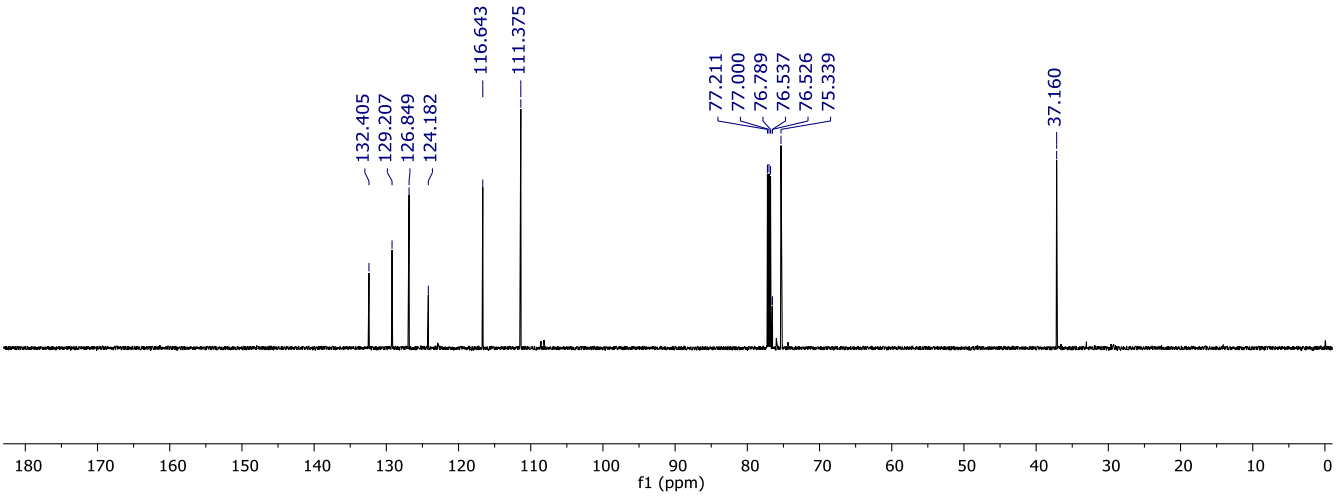
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2j**.



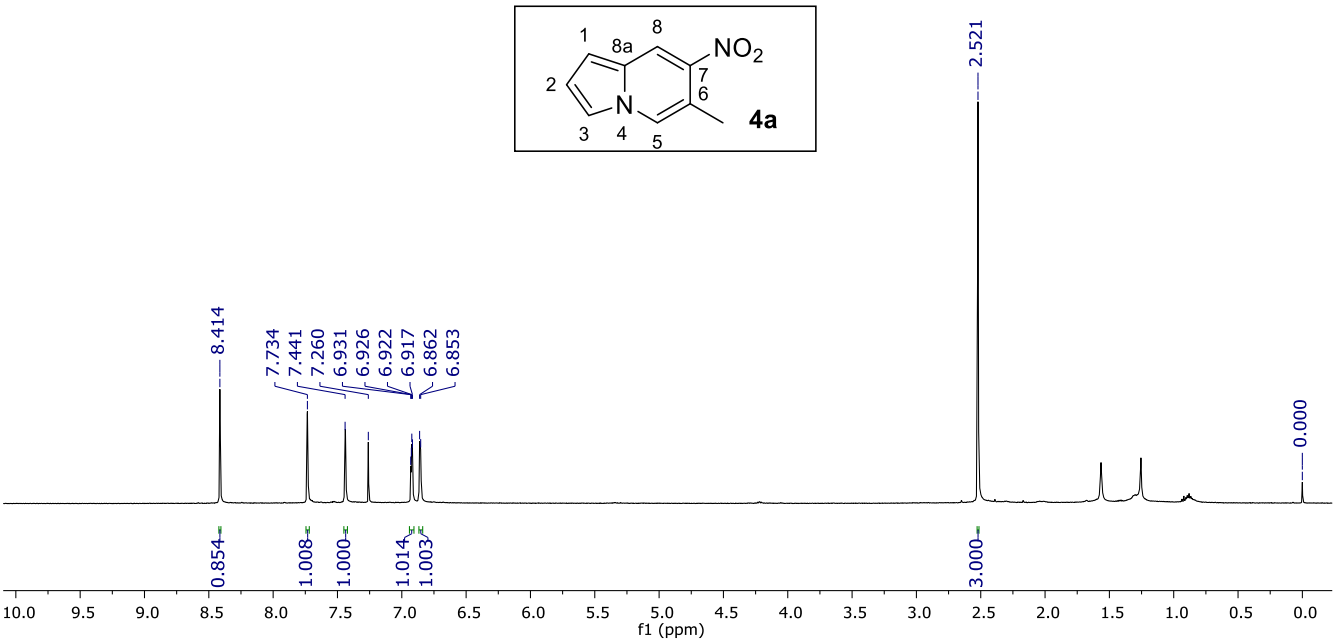
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2j**.



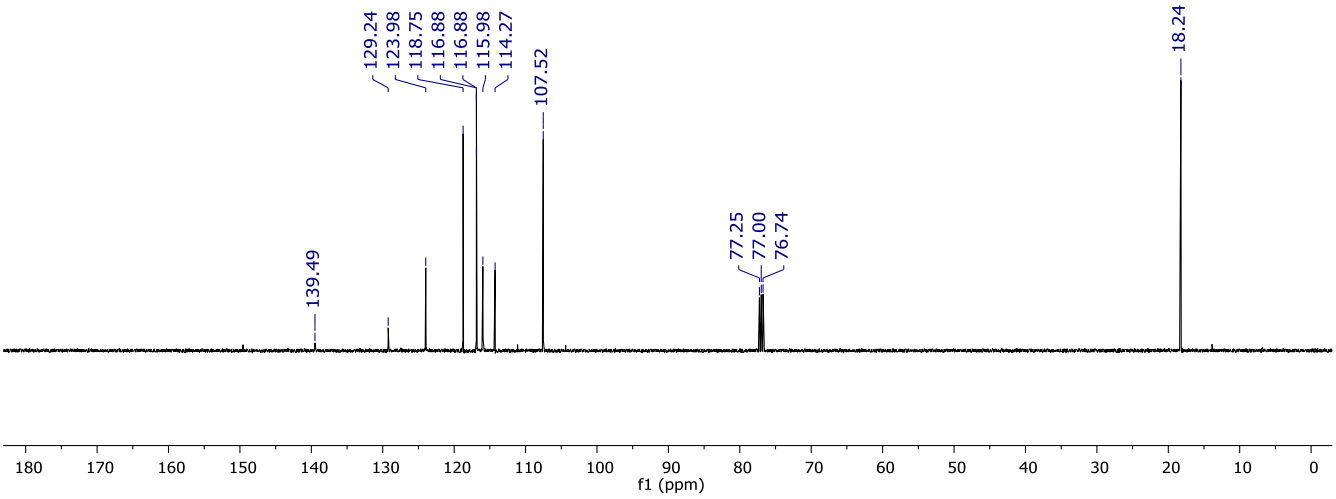
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2k**.



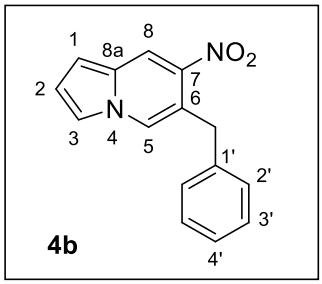
^{13}C NMR (150 MHz, $CDCl_3$) of compound **2k**.

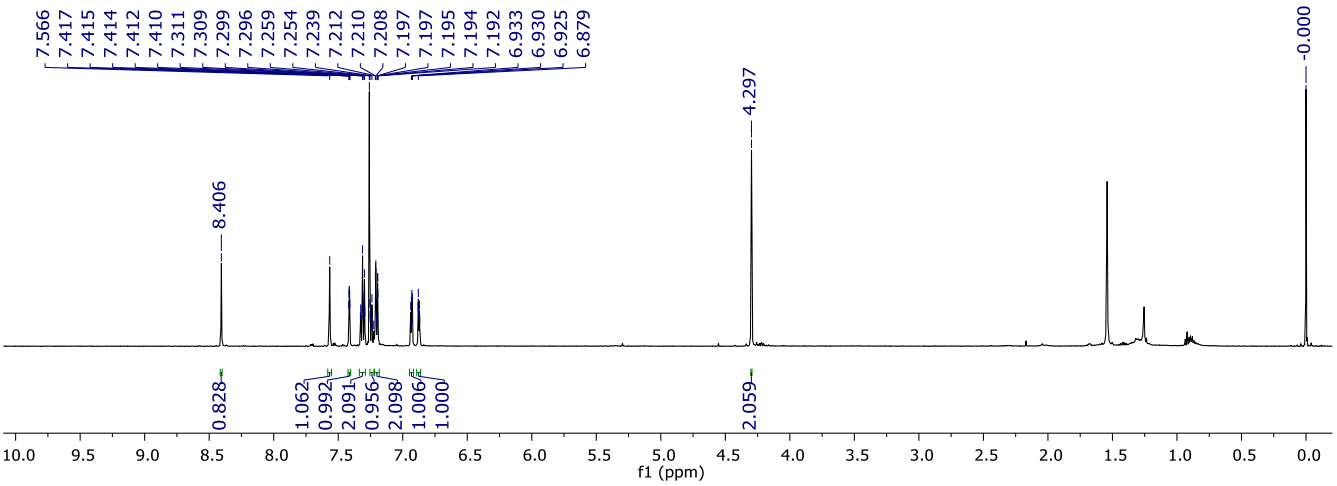


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4a**.

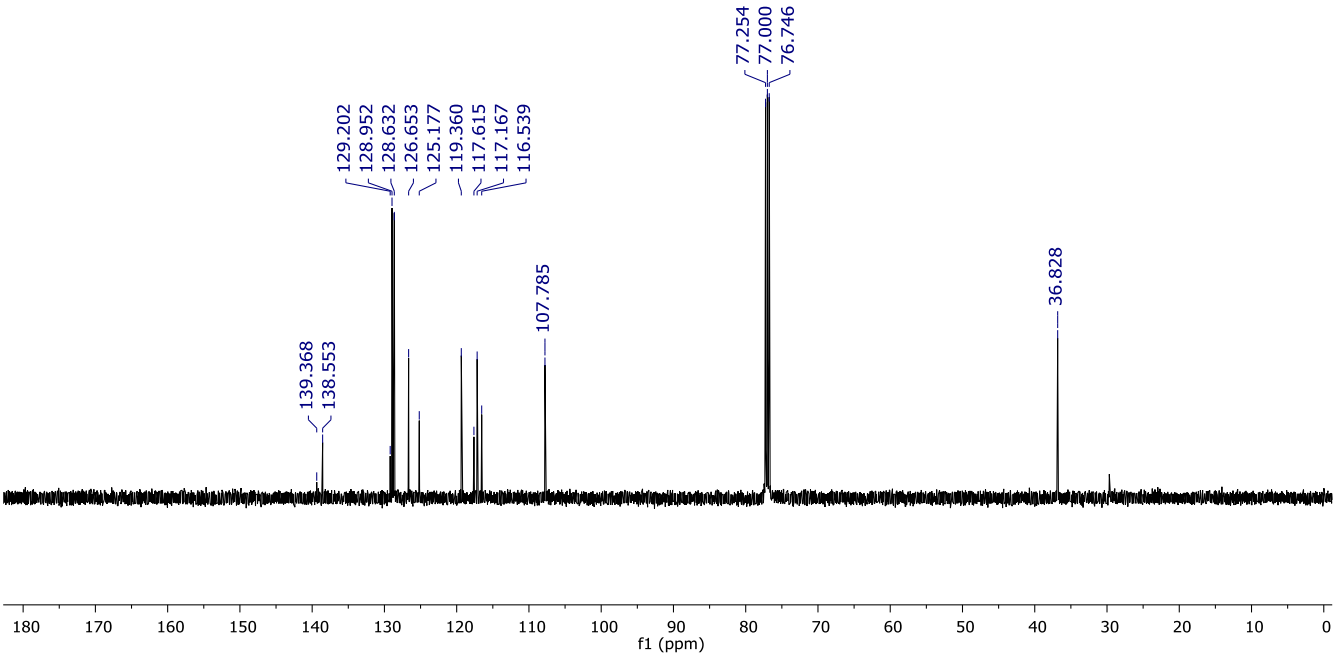


^{13}C NMR (125 MHz, $CDCl_3$) of compound **4a**.

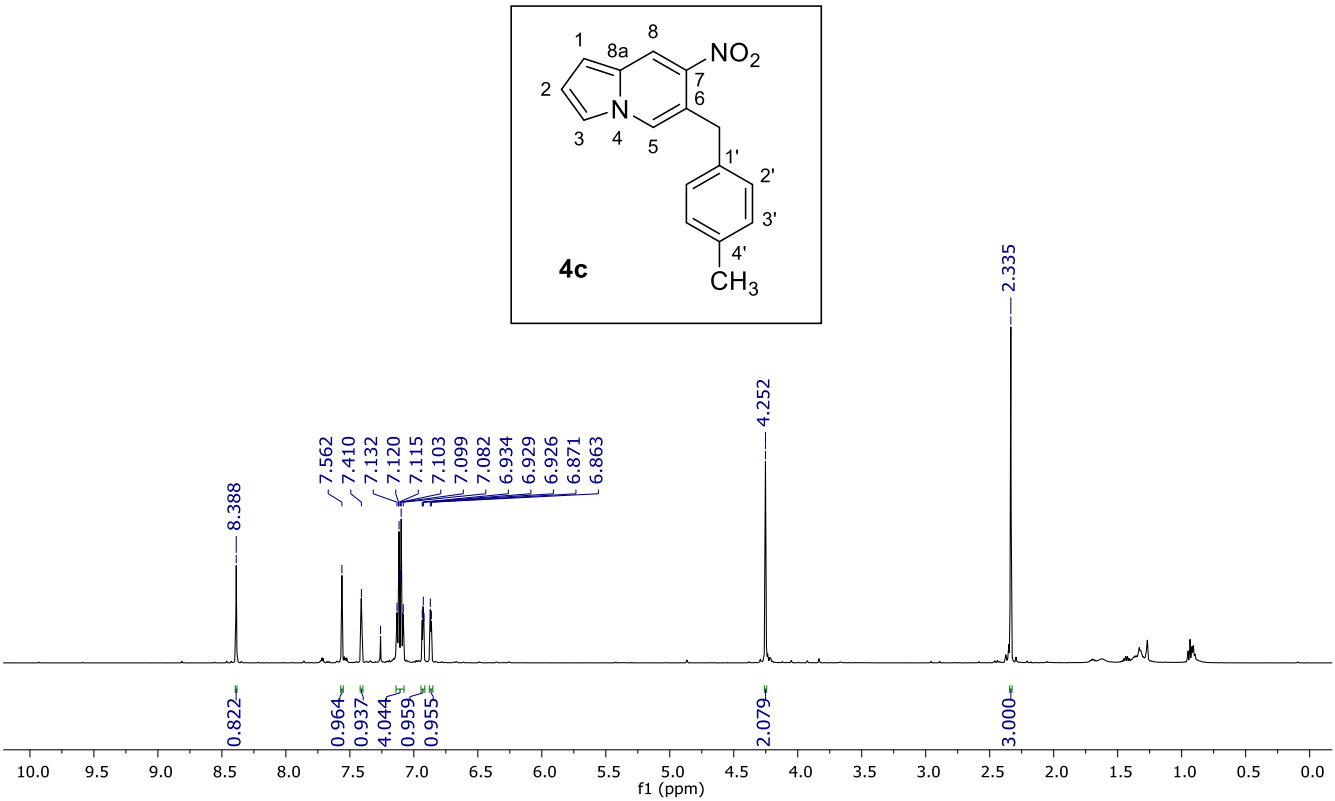




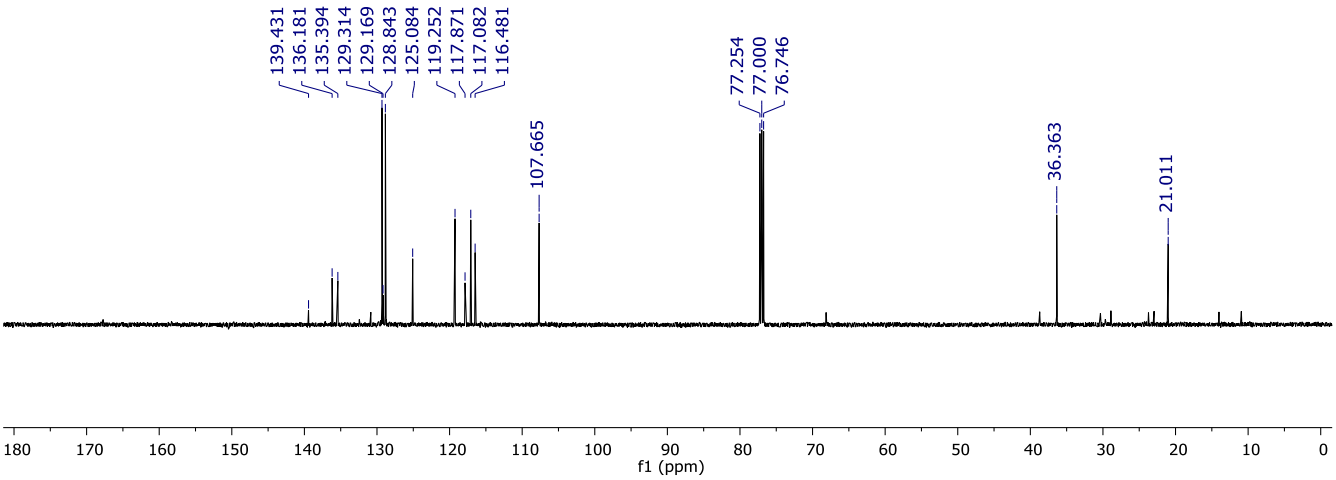
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b**.



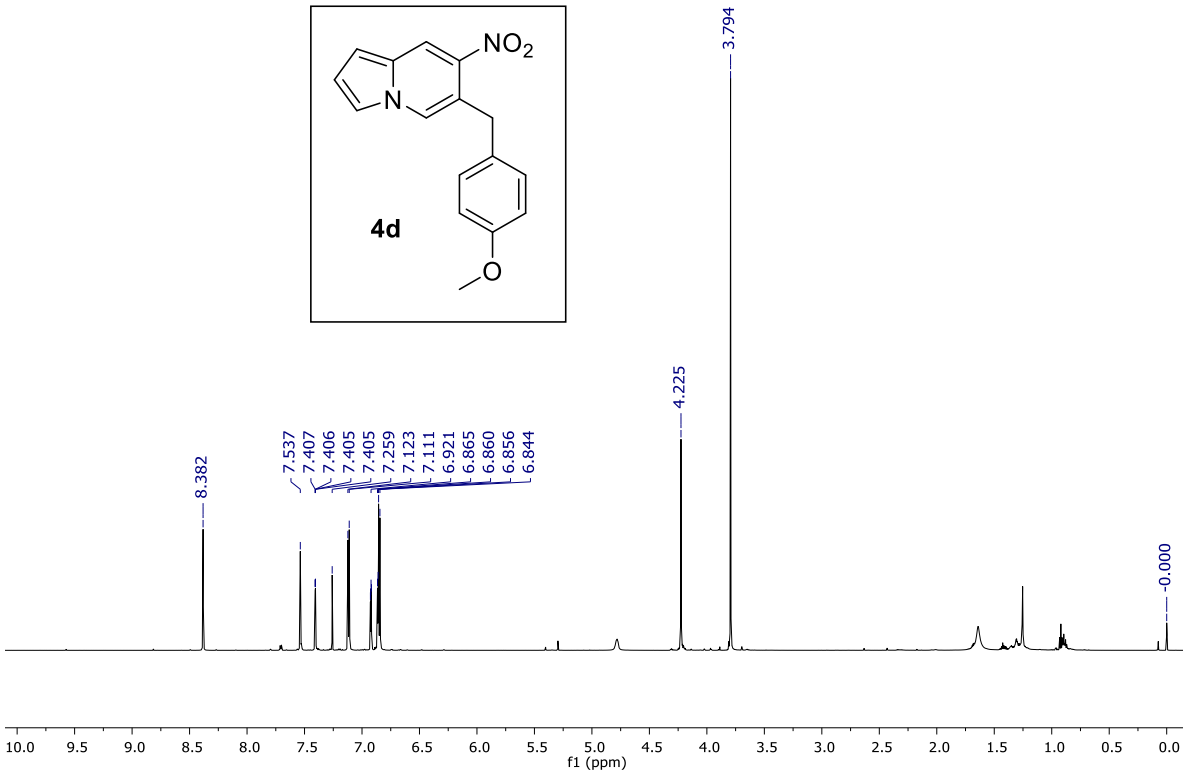
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4b**.



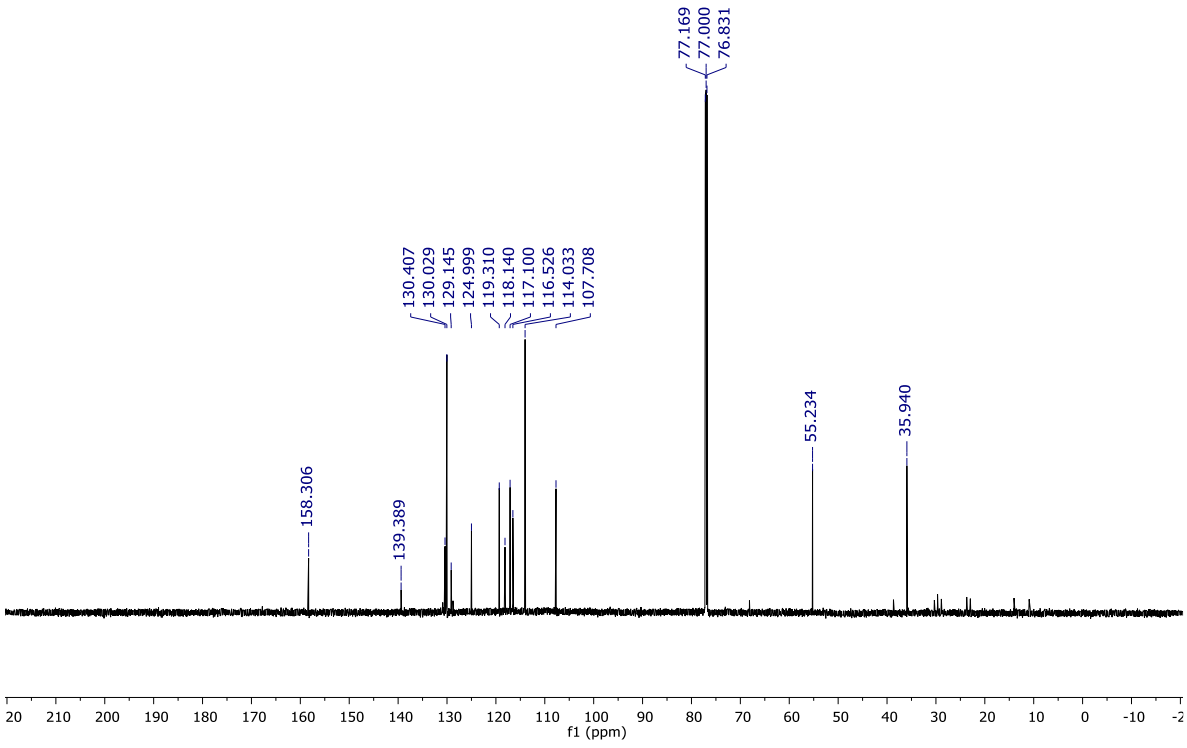
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4c**.



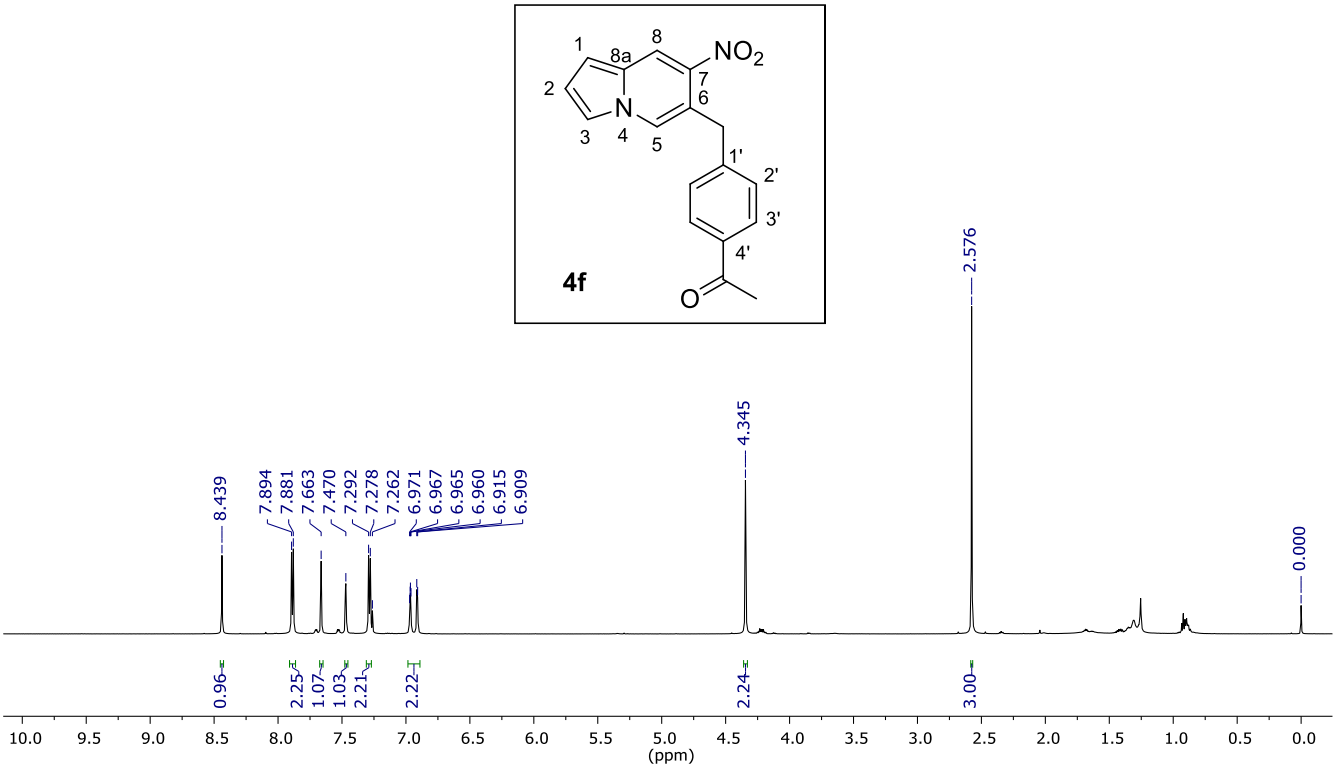
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4c**.



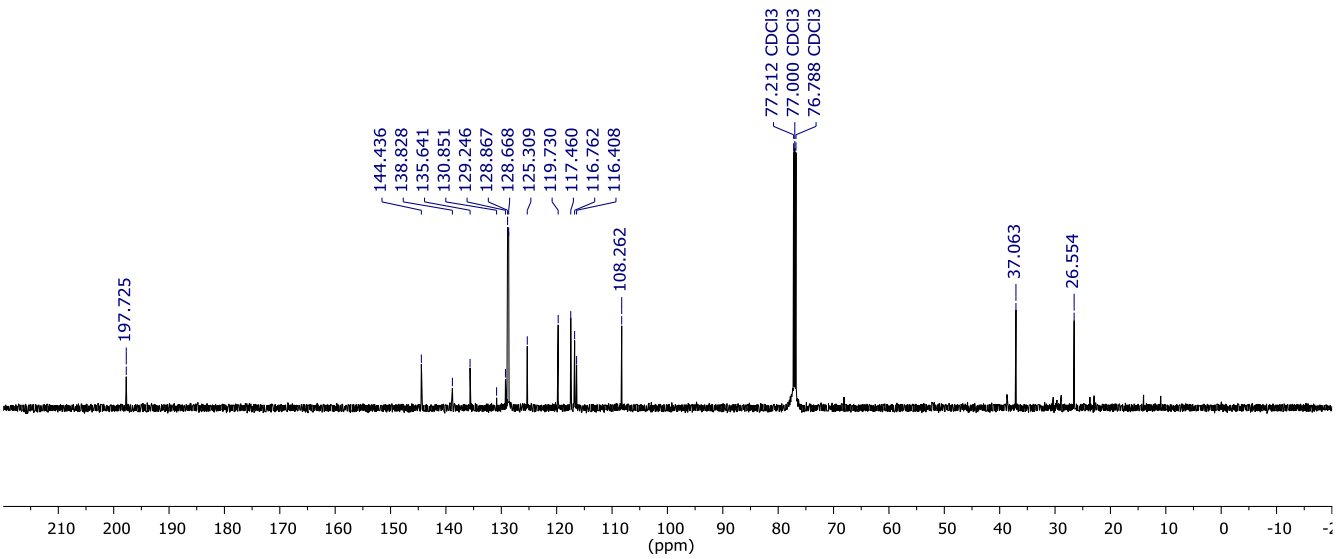
^{1}H NMR (750 MHz, $CDCl_3$) of compound **4d**.



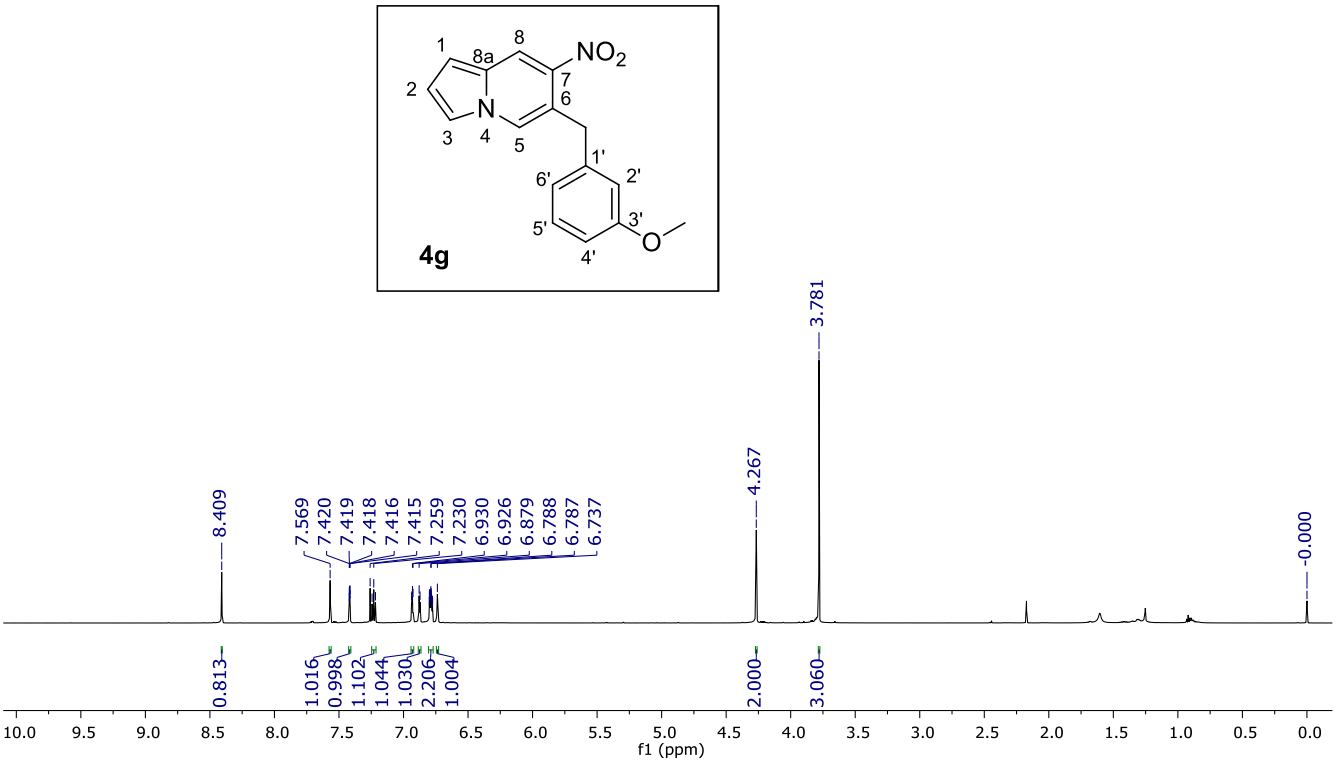
^{13}C NMR (187.5 MHz, $CDCl_3$) of compound **4d**.



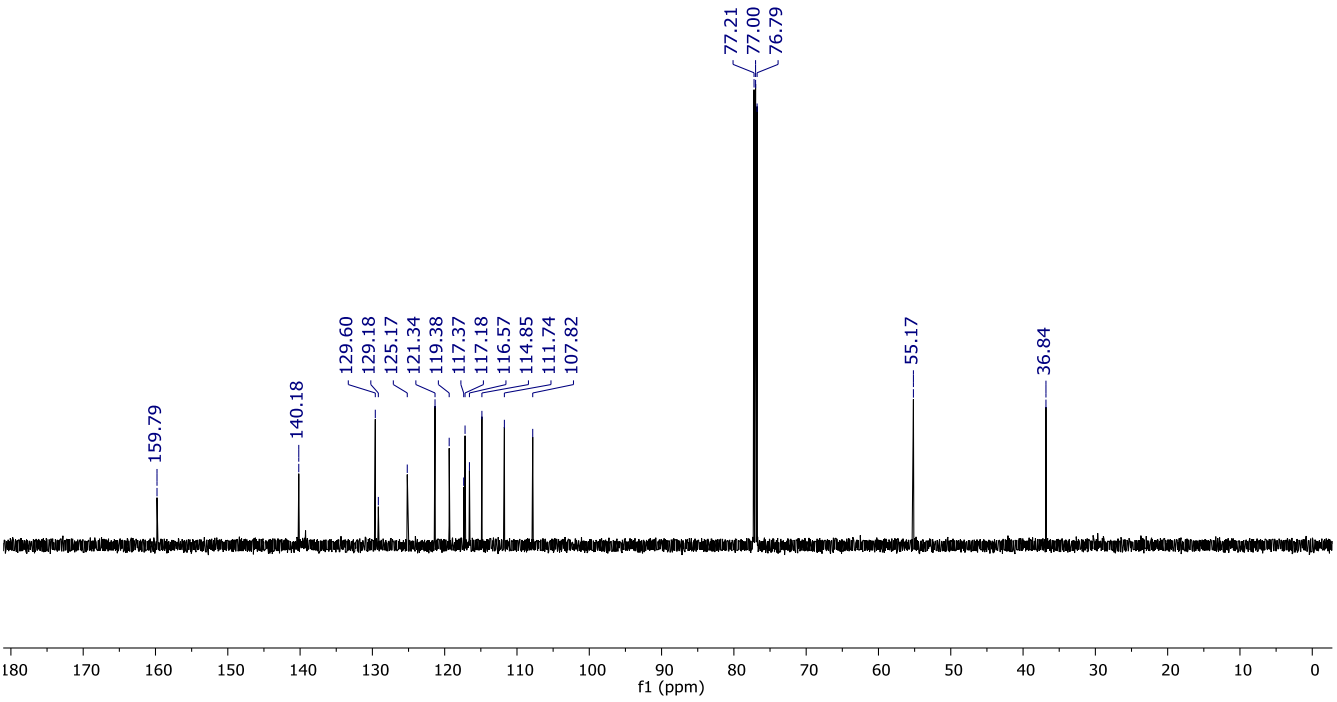
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4f**.



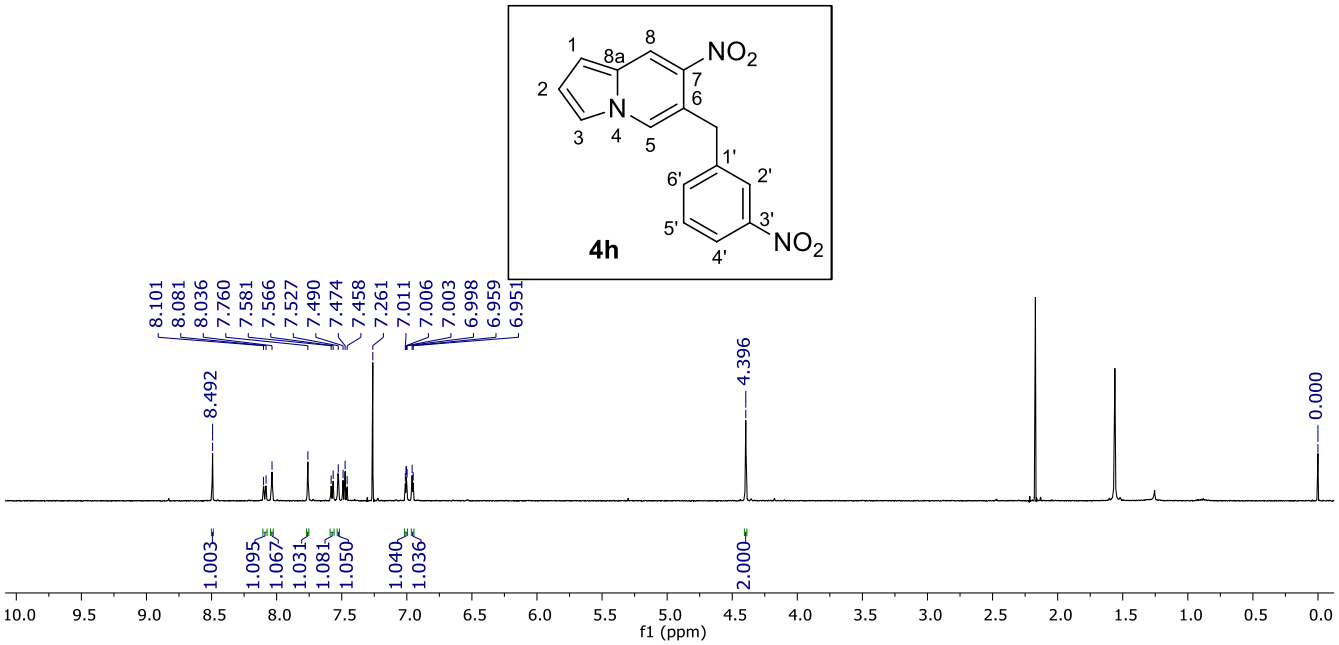
^{13}C NMR (150 MHz, $CDCl_3$) of compound **4f**.



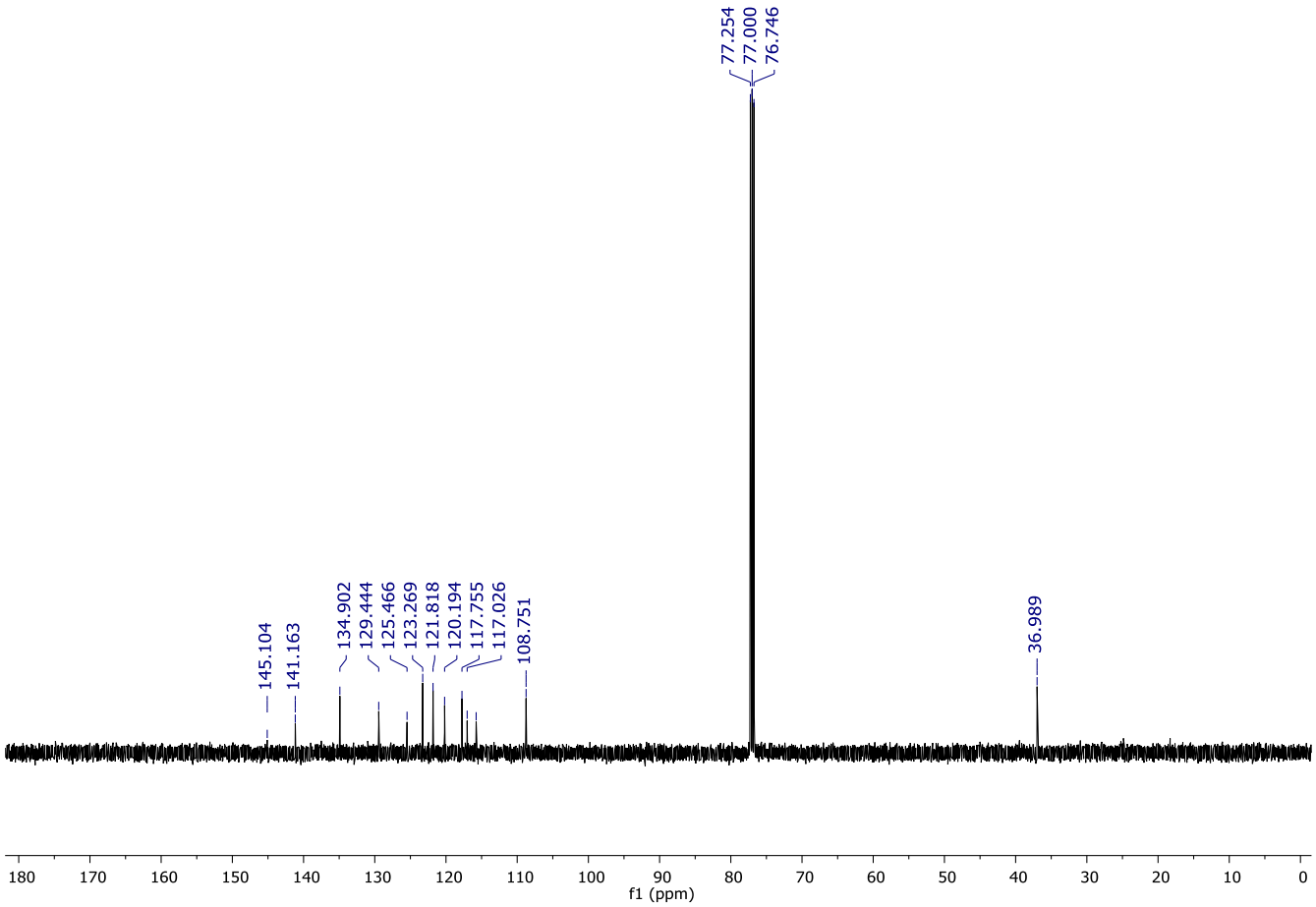
^{1}H NMR (600 MHz, $CDCl_3$) of compound **4g**.



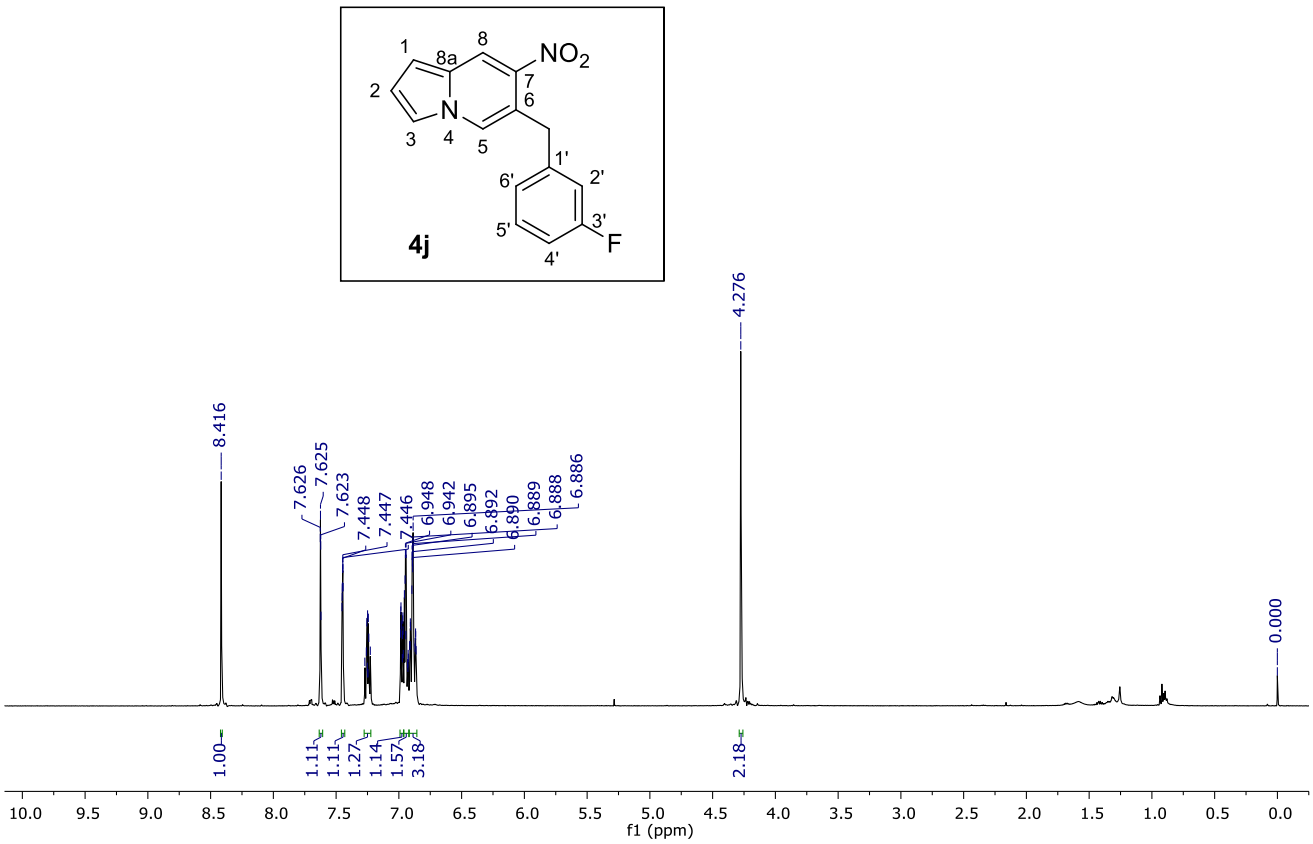
^{13}C NMR (150 MHz, $CDCl_3$) of compound **4g**.



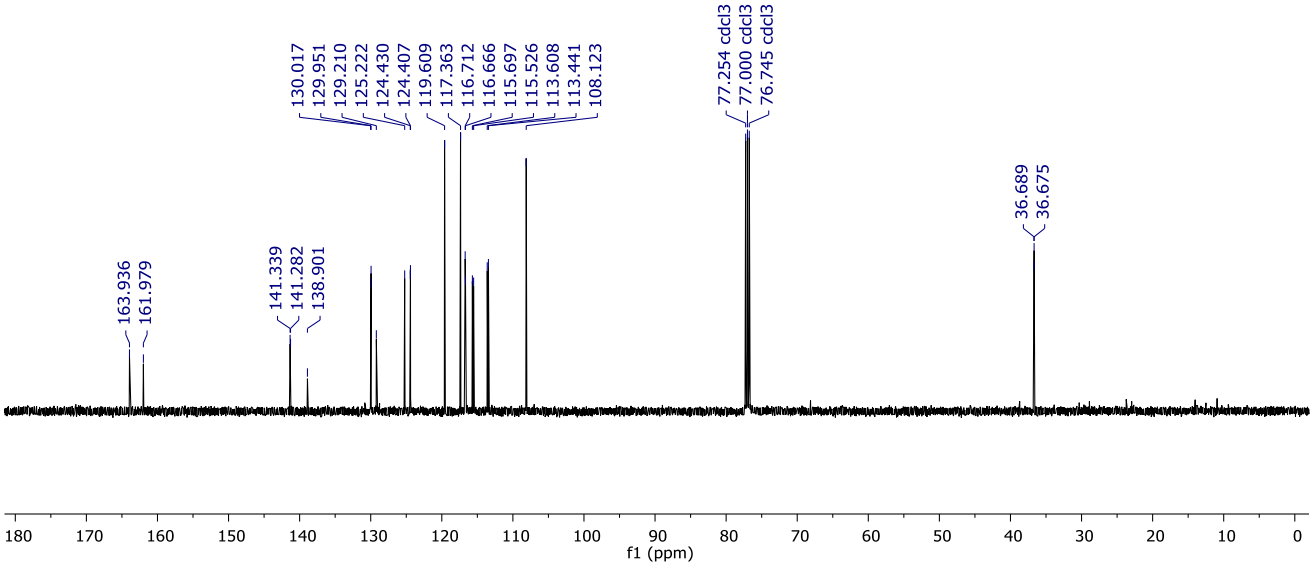
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4h**.



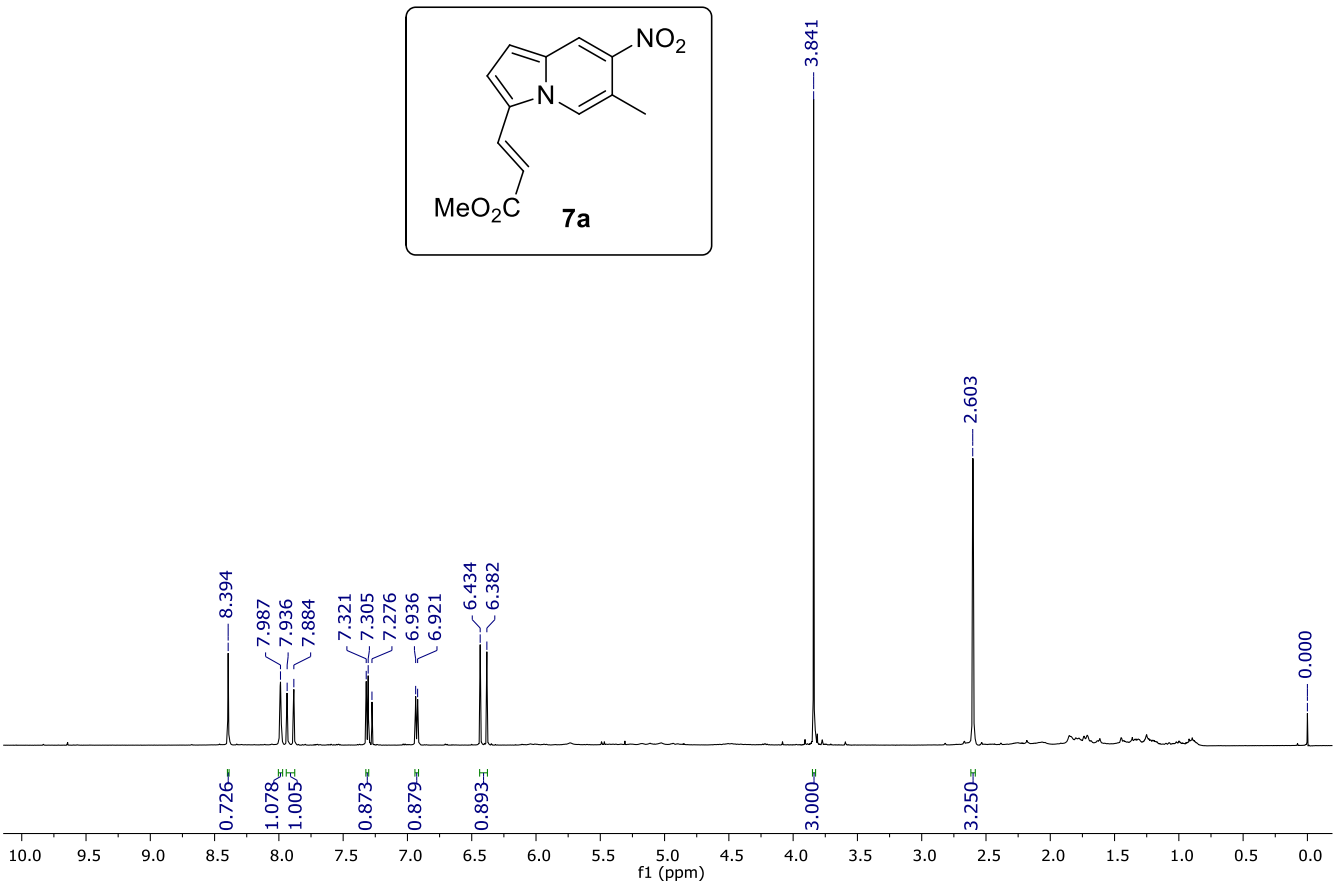
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4h**.



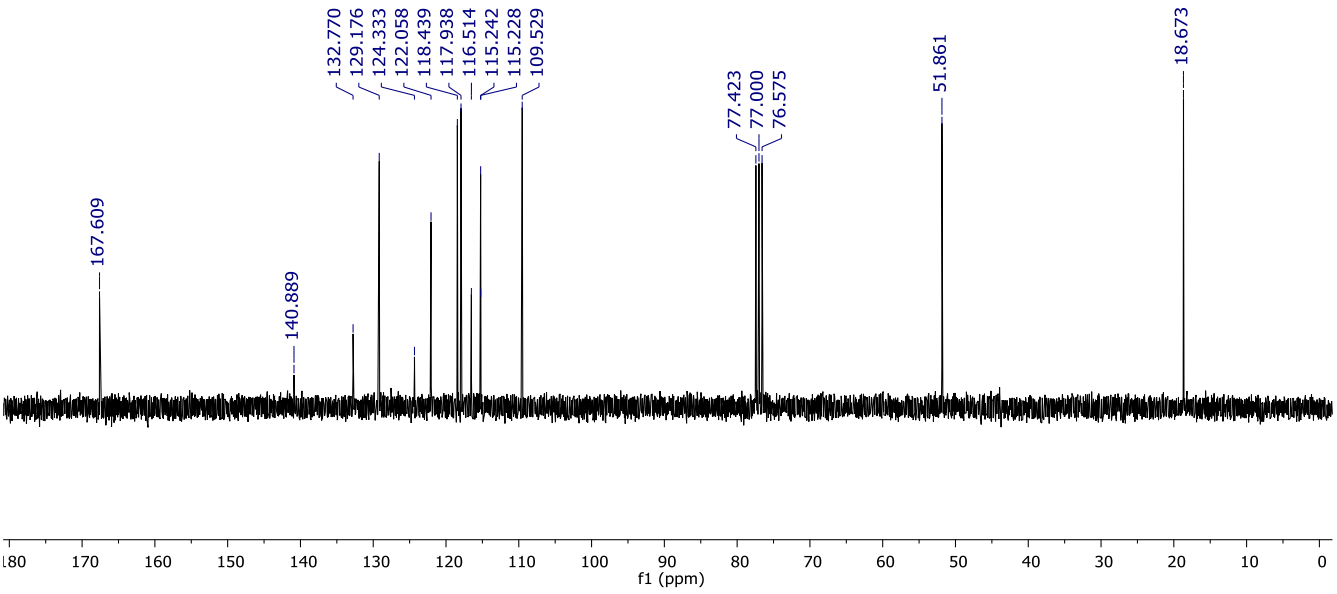
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4j**.



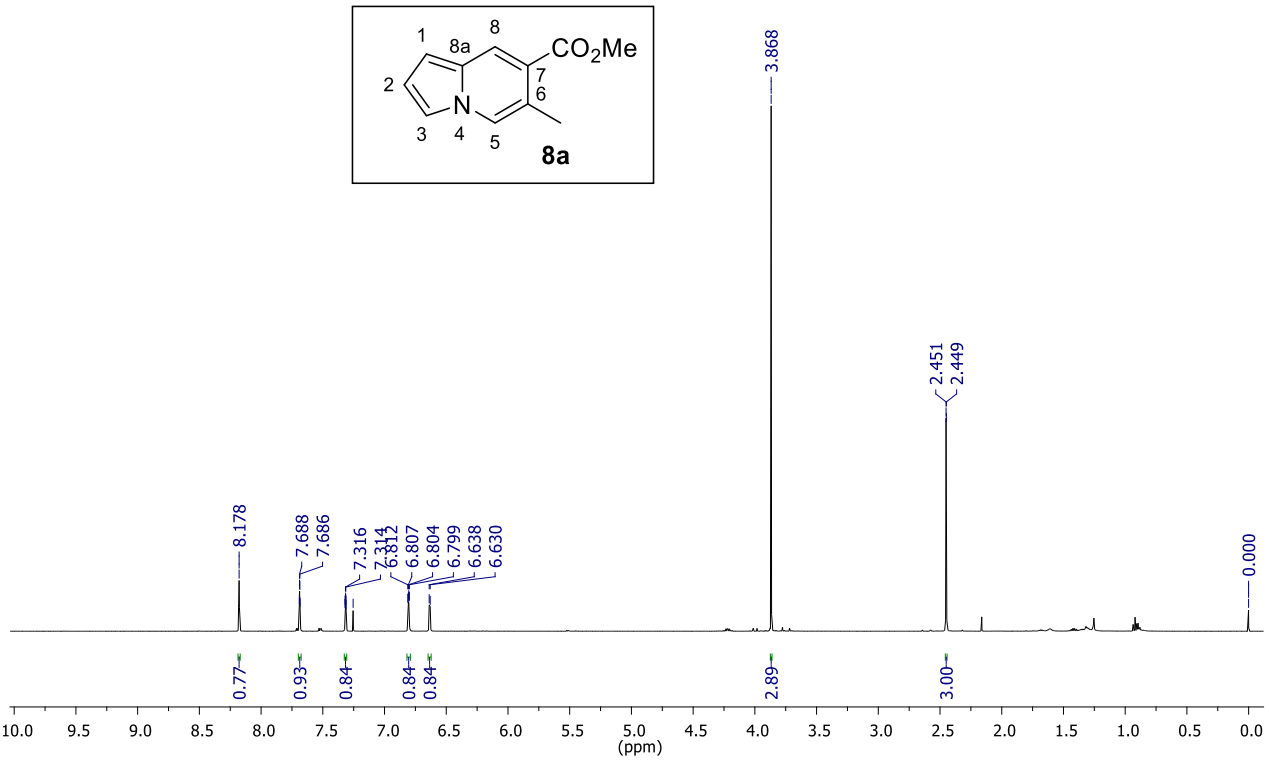
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4j**.



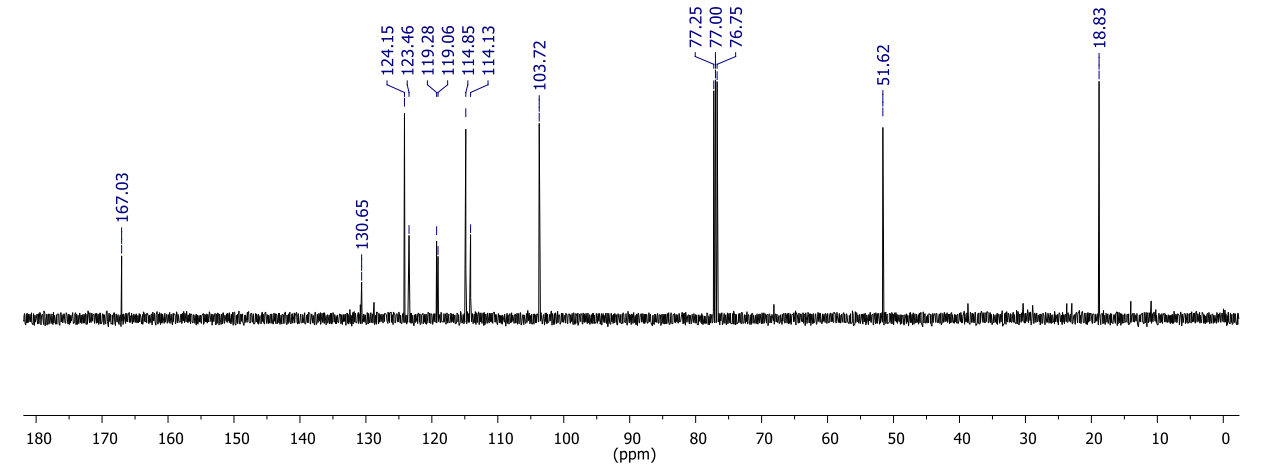
^{1}H NMR (300 MHz, $CDCl_3$) of compound **7a**.



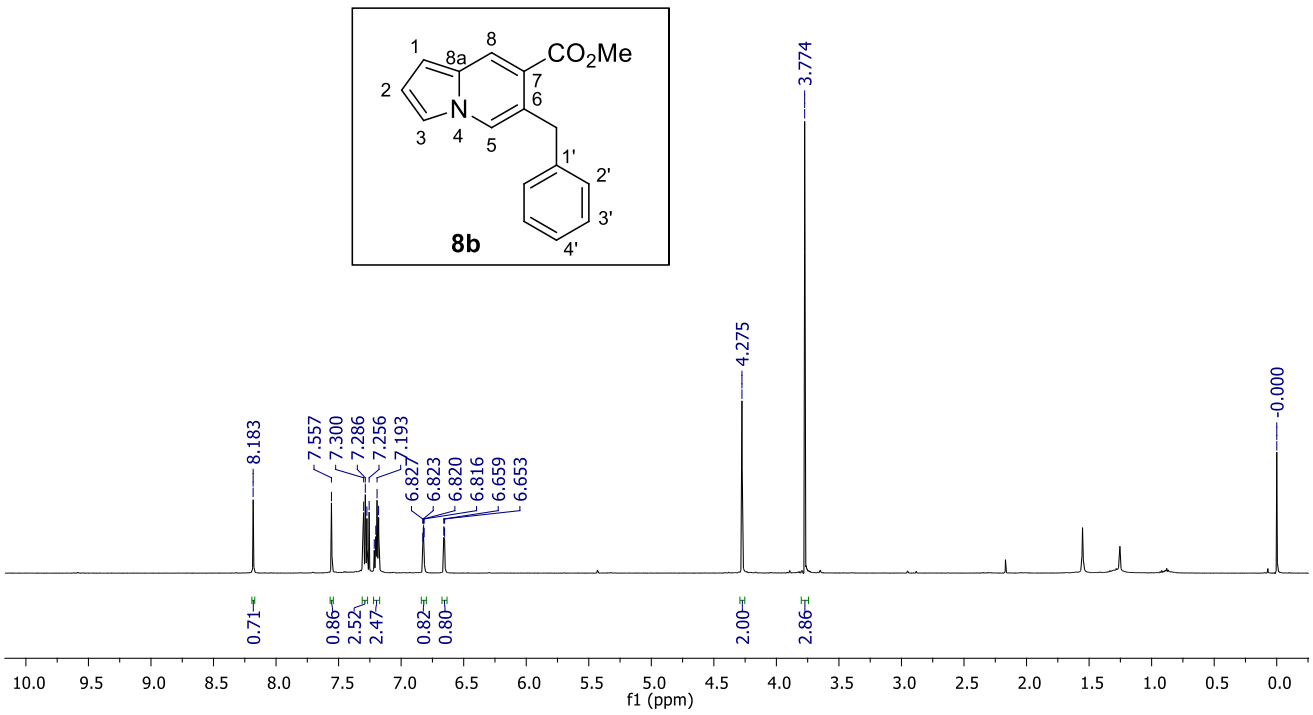
^{13}C NMR (75.4 MHz, $CDCl_3$) of compound **7a**.



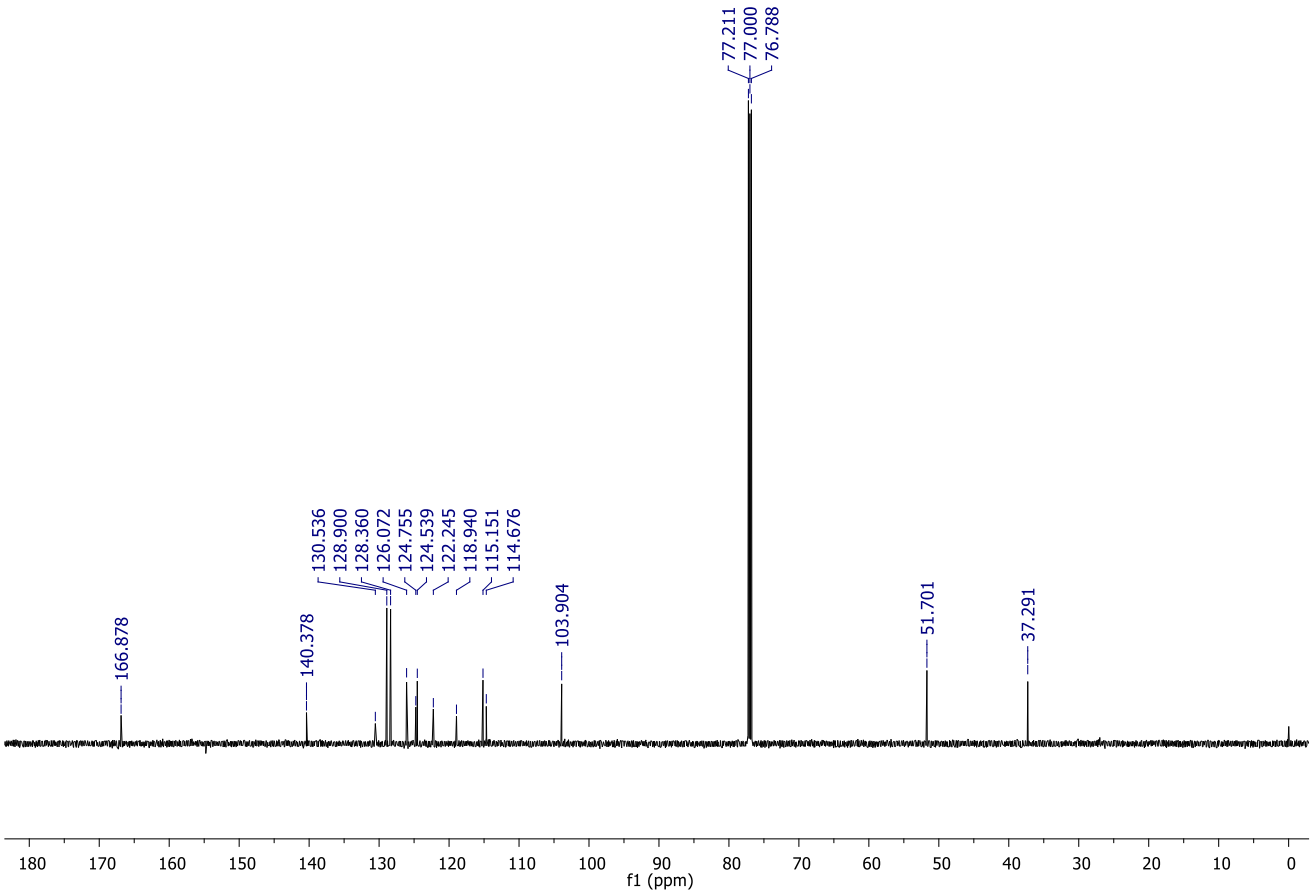
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8a**.



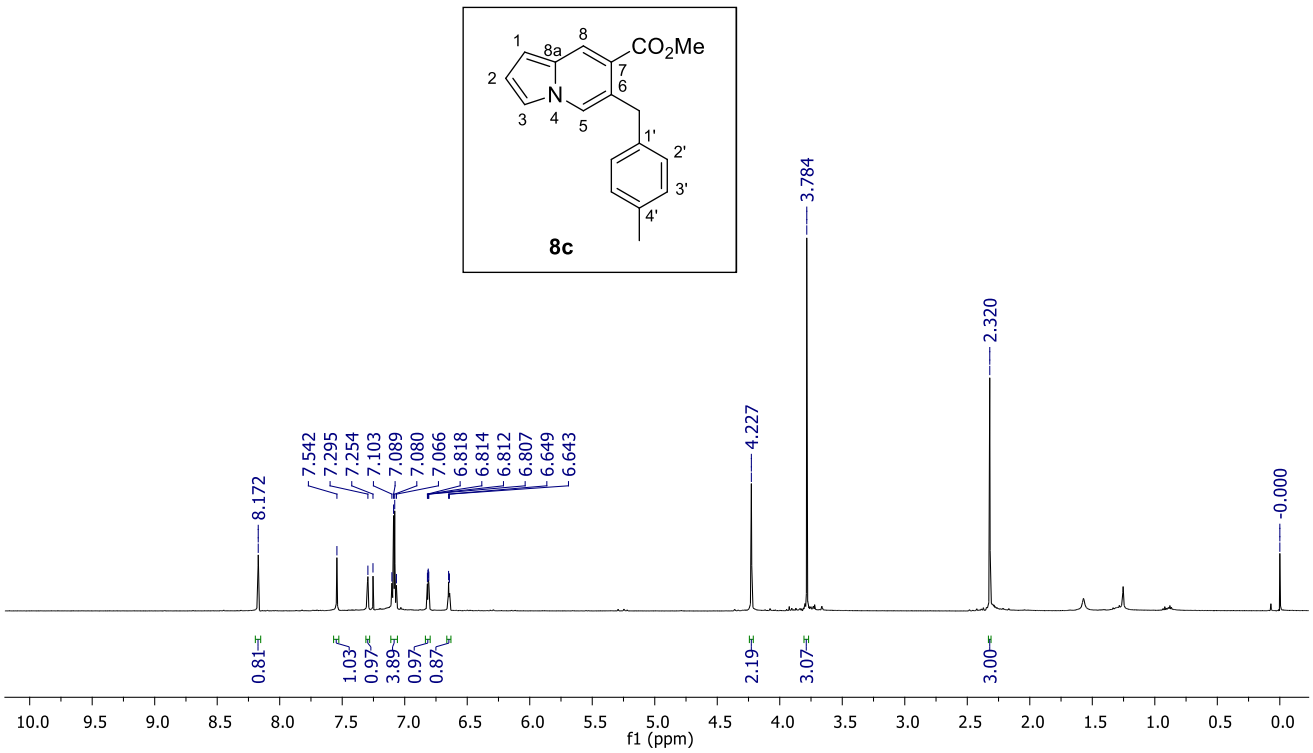
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8a**.



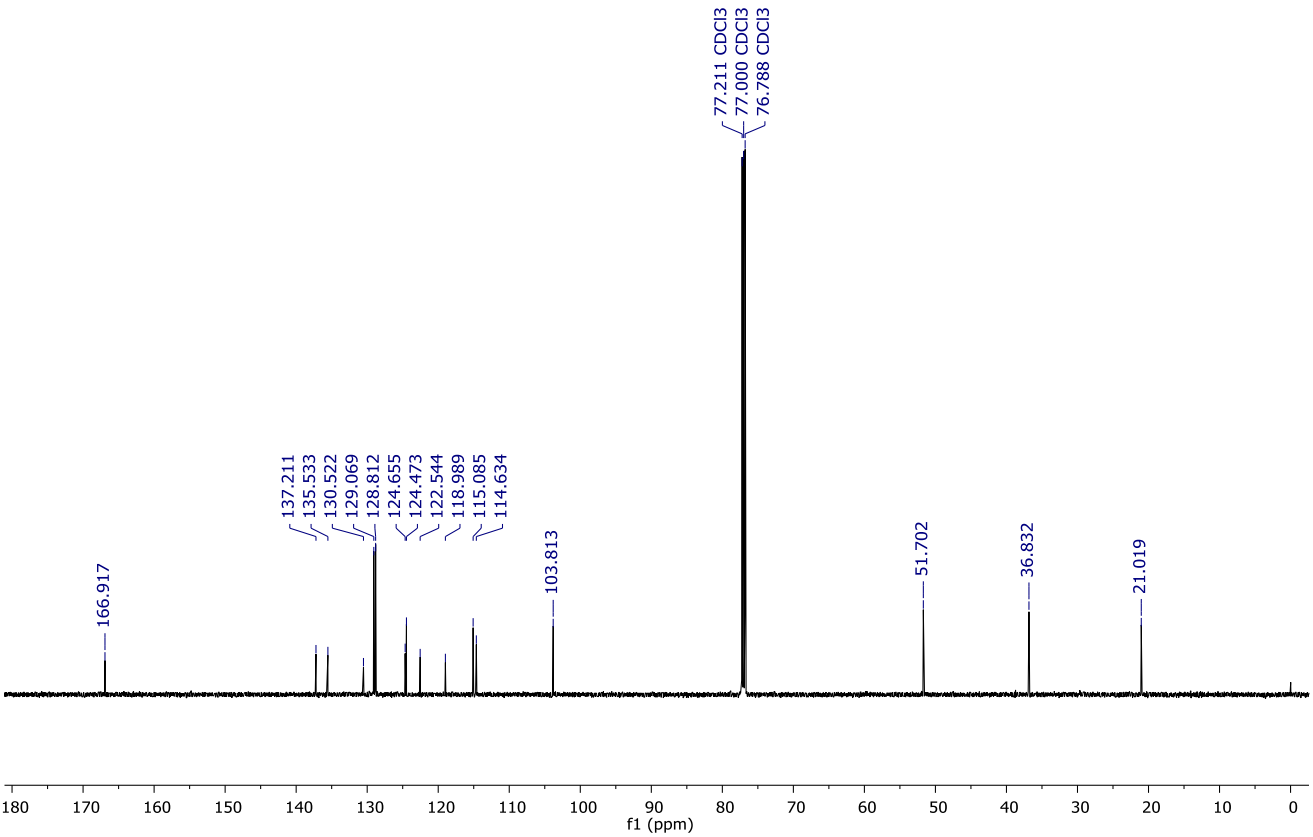
^{1}H NMR (600 MHz, $CDCl_3$) of compound **8b**.



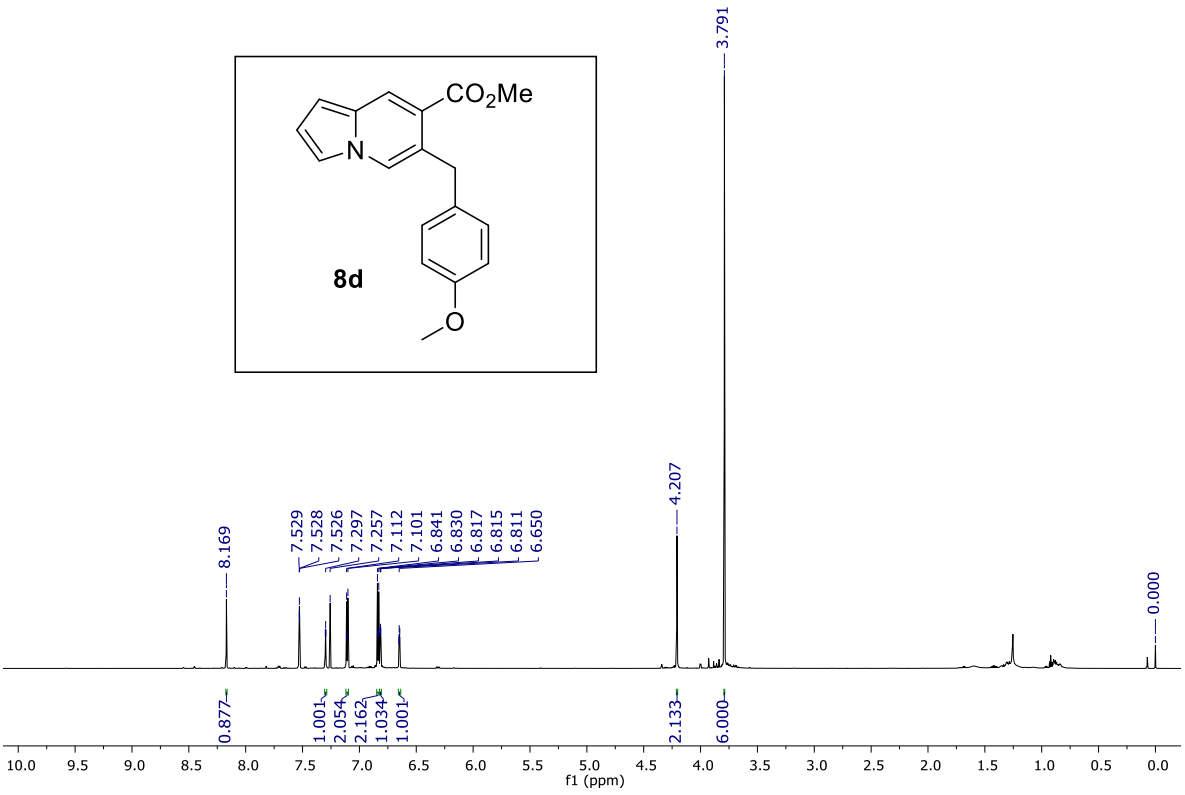
^{13}C NMR (150 MHz, $CDCl_3$) of compound **8b**.



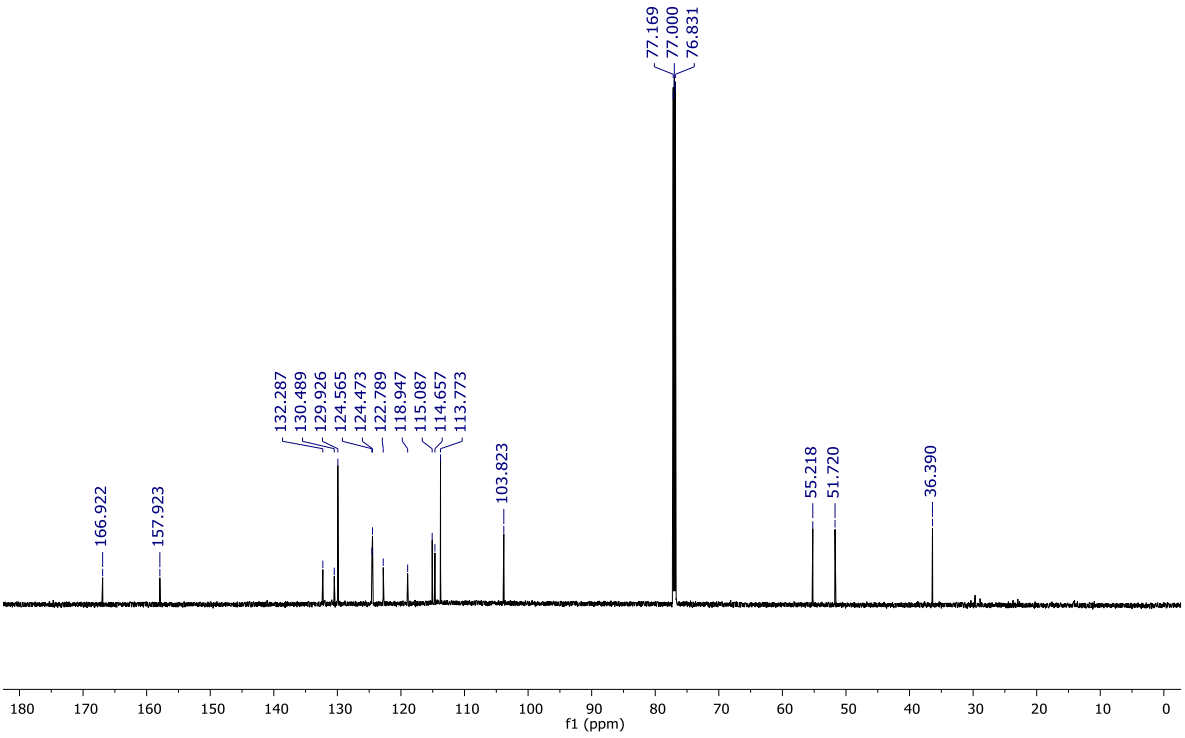
^{1}H NMR (600 MHz, $CDCl_3$) of compound **8c**.



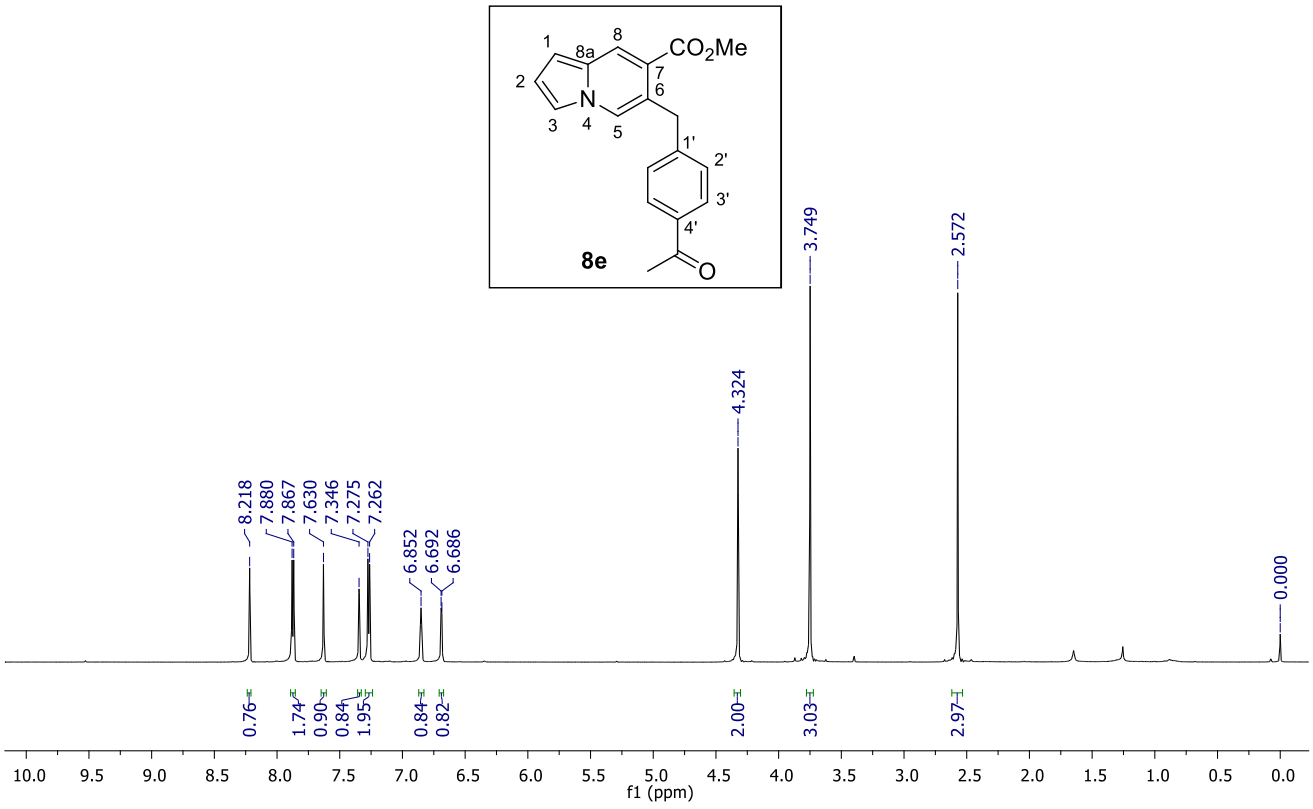
^{13}C NMR (150 MHz, $CDCl_3$) of compound **8c**.



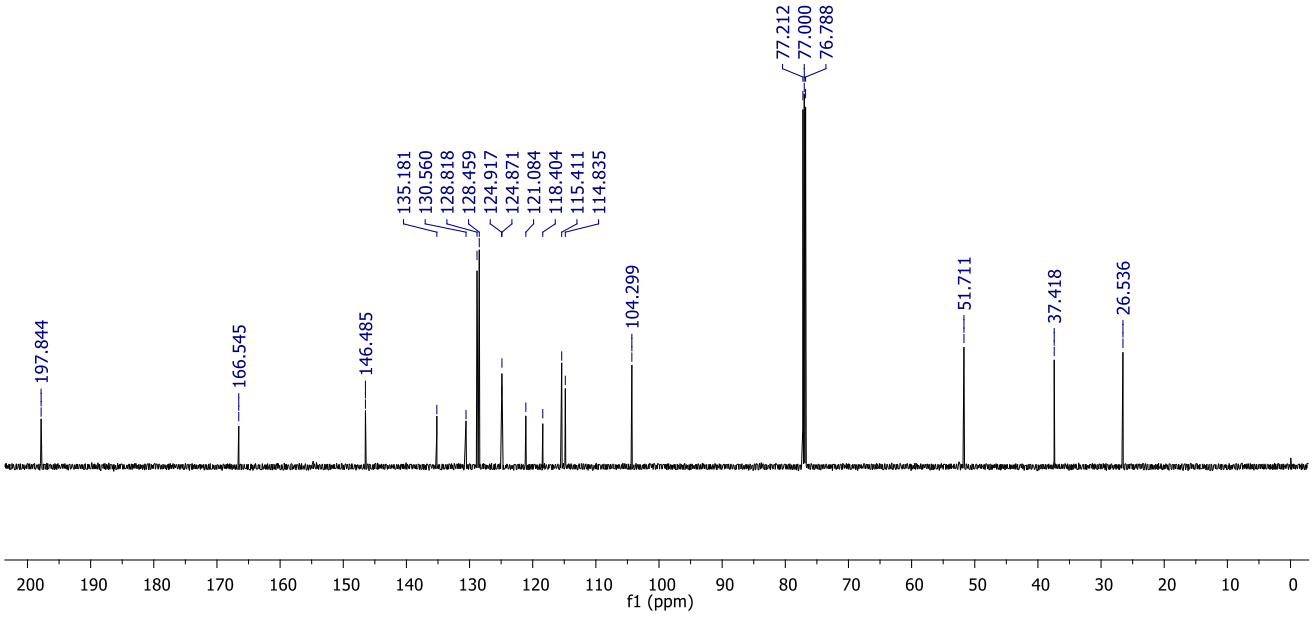
^{1}H NMR (750 MHz, $CDCl_3$) of compound **8d**.



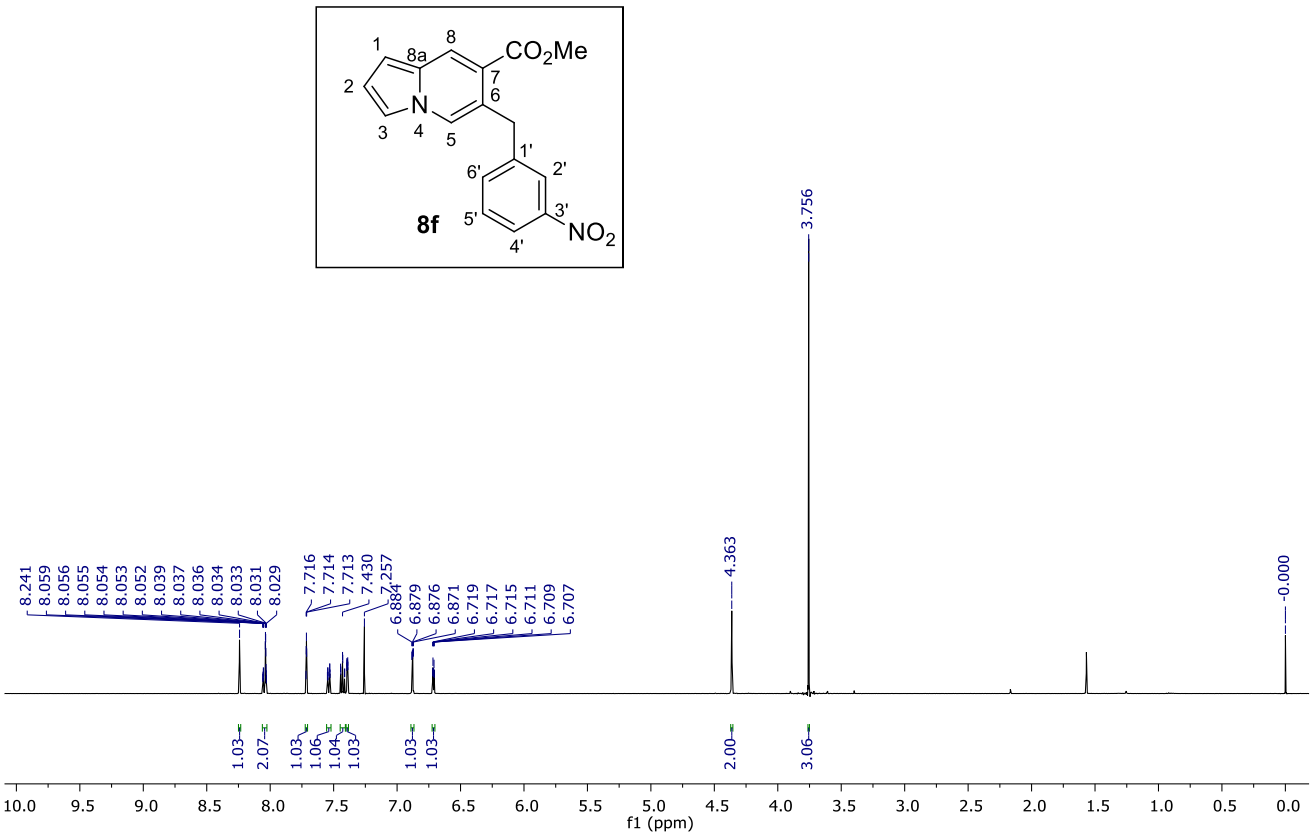
^{13}C NMR (187.5 MHz, $CDCl_3$) of compound **8d**.



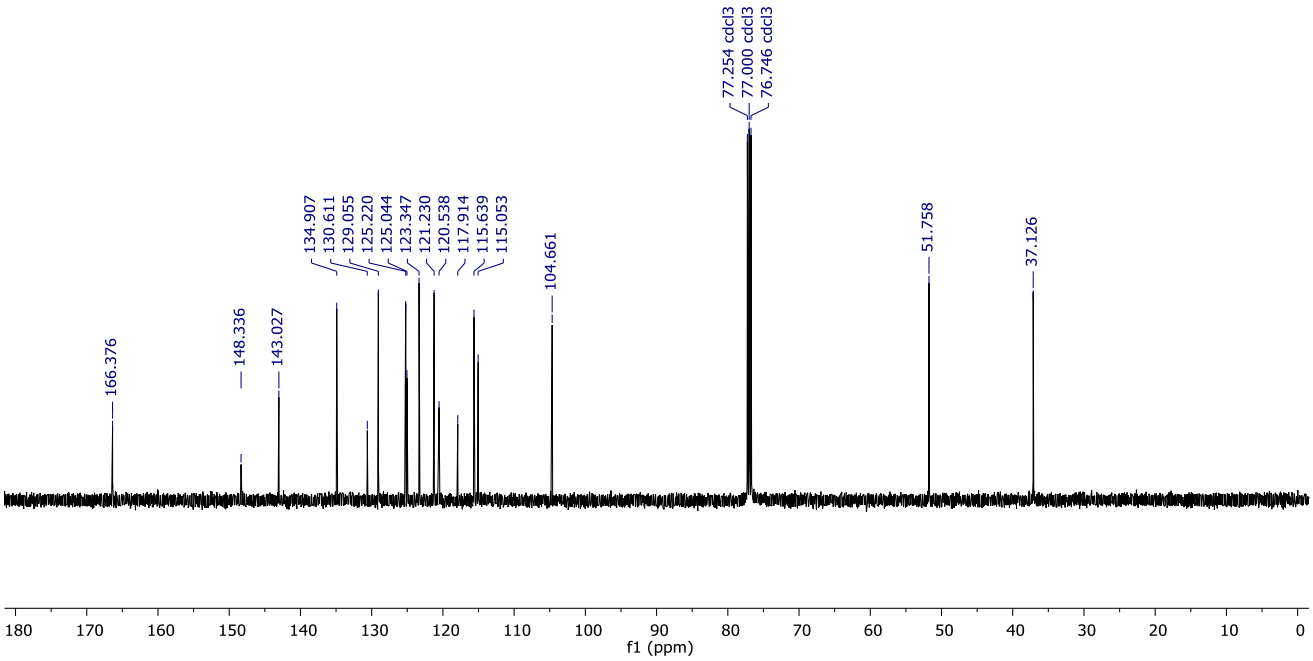
^{1}H NMR (600 MHz, $CDCl_3$) of compound **8e**.



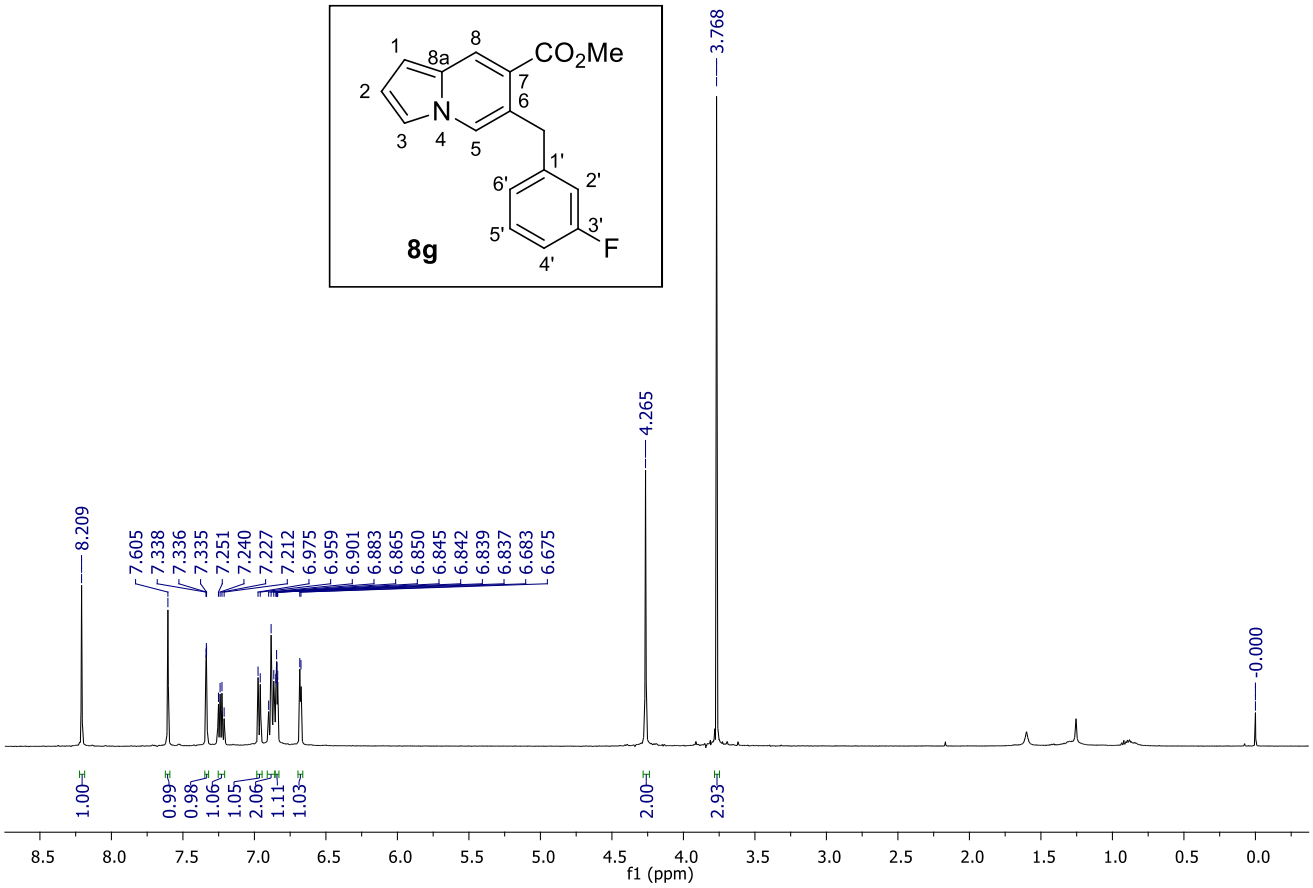
^{13}C NMR (150 MHz, $CDCl_3$) of compound **8e**.



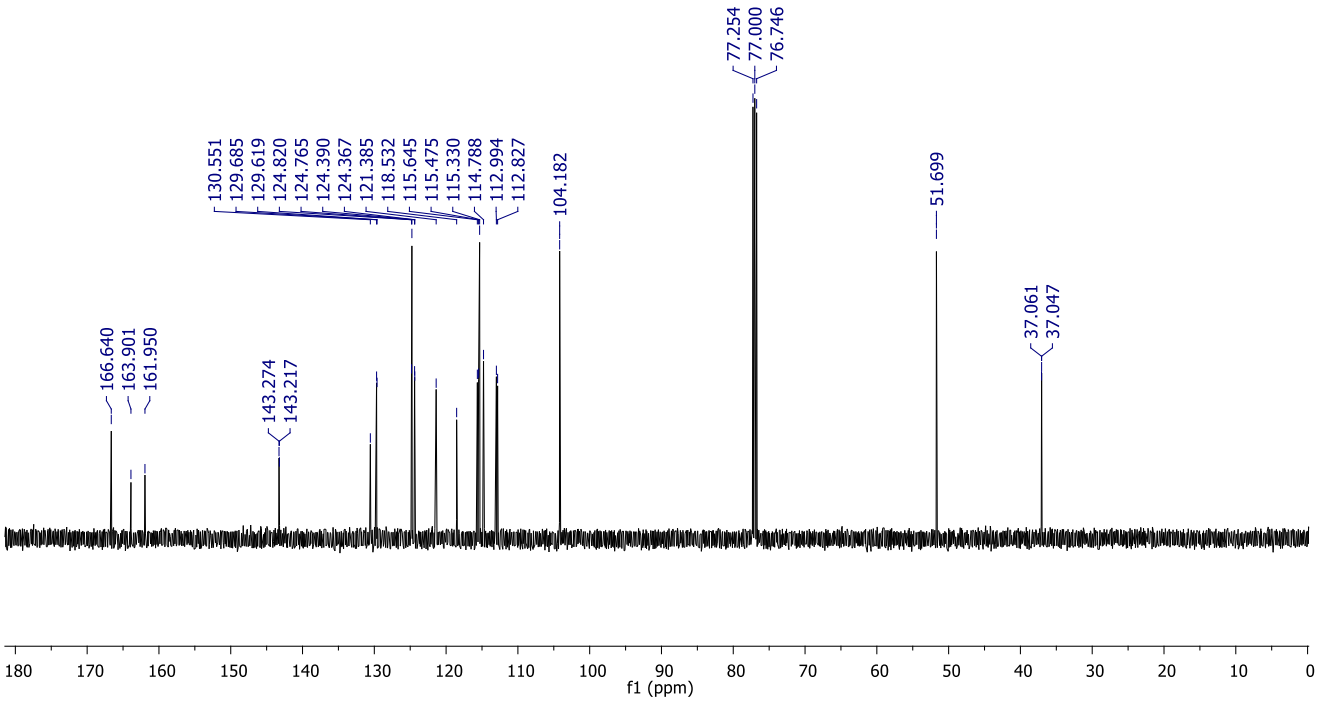
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8f**.



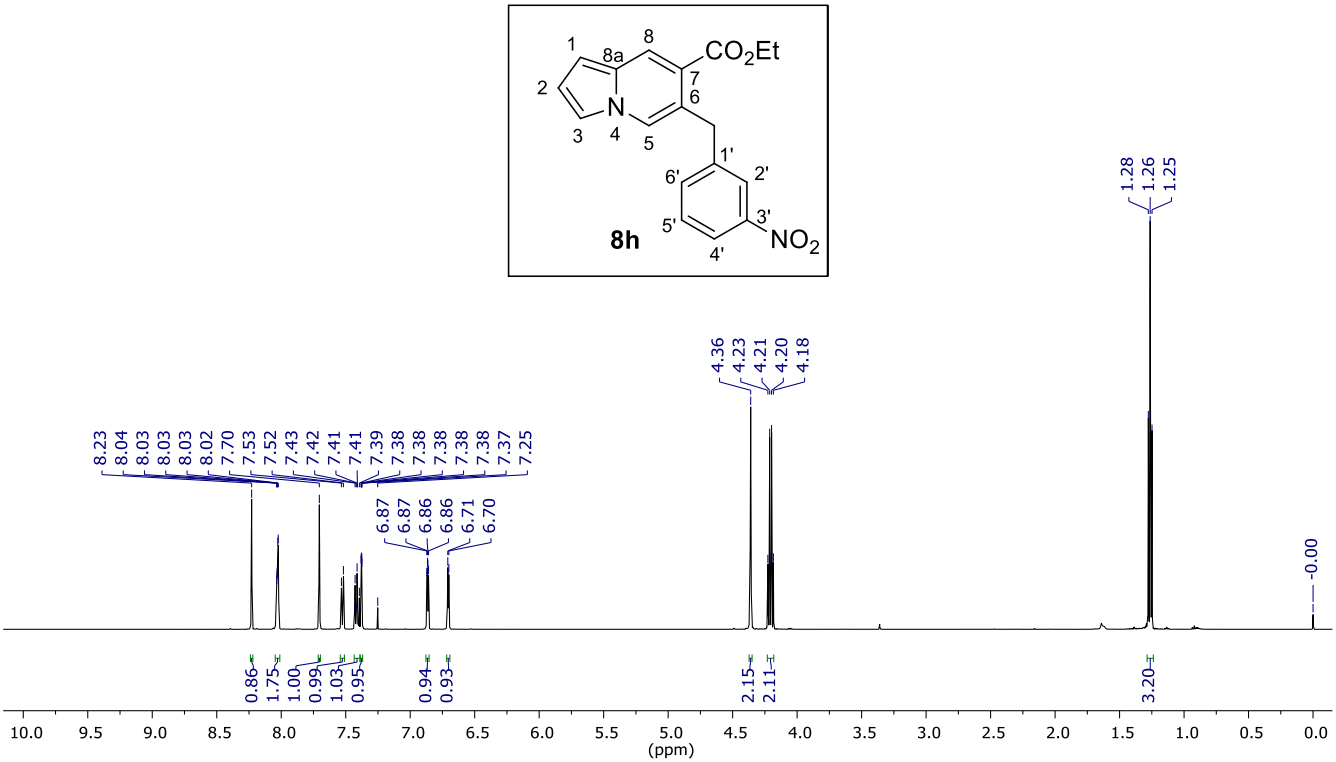
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8f**.



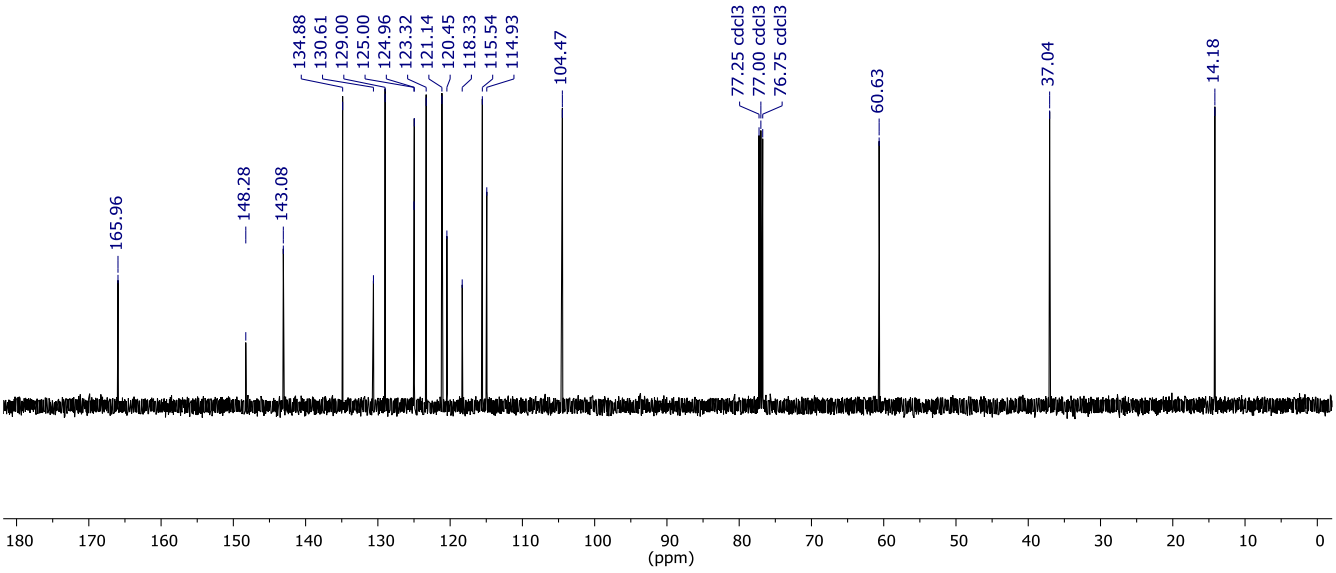
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8g**.



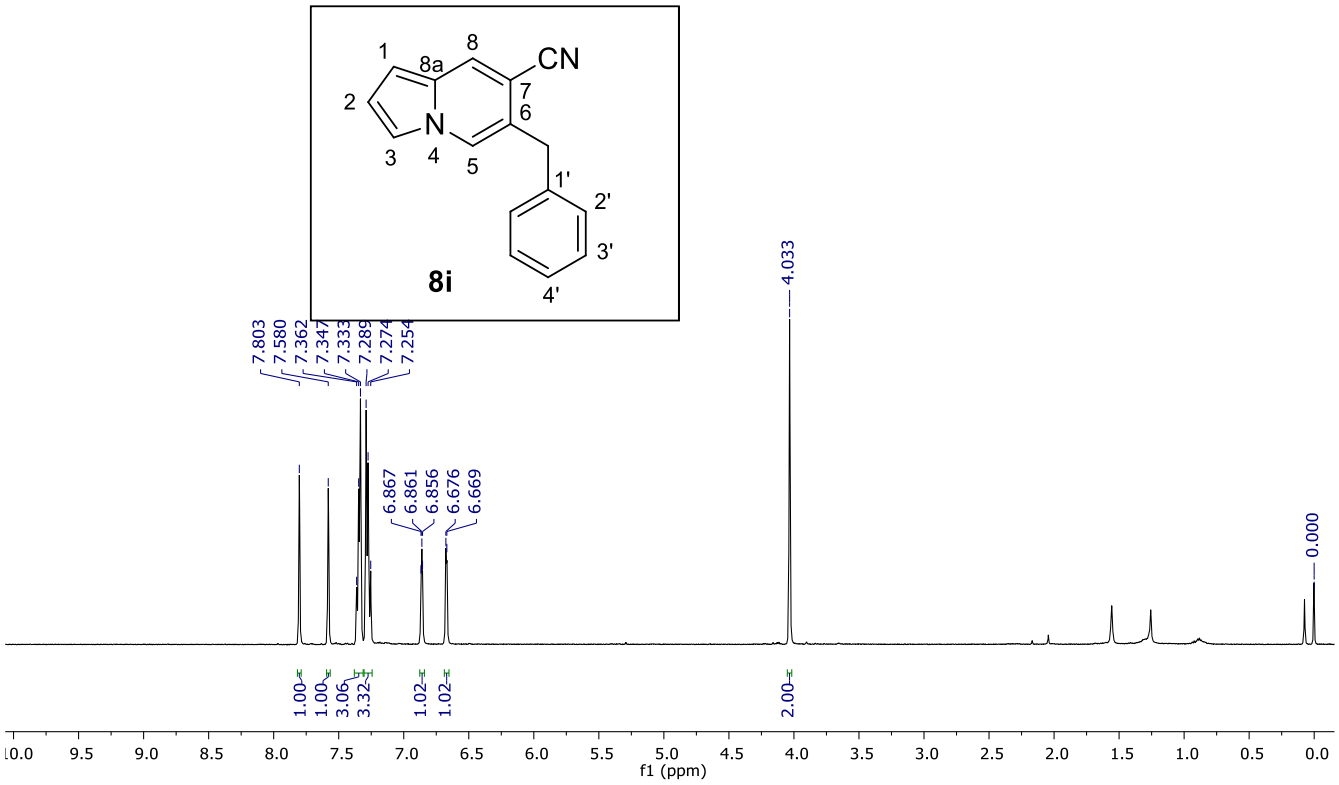
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8g**.



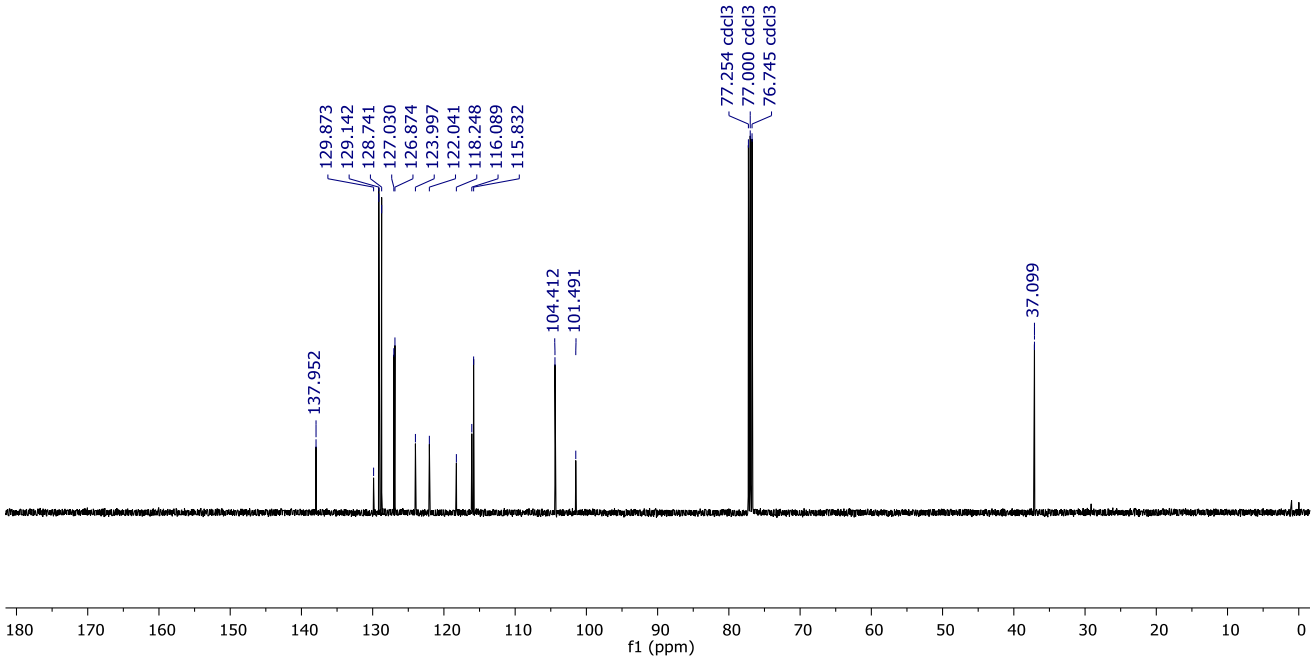
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8h**.



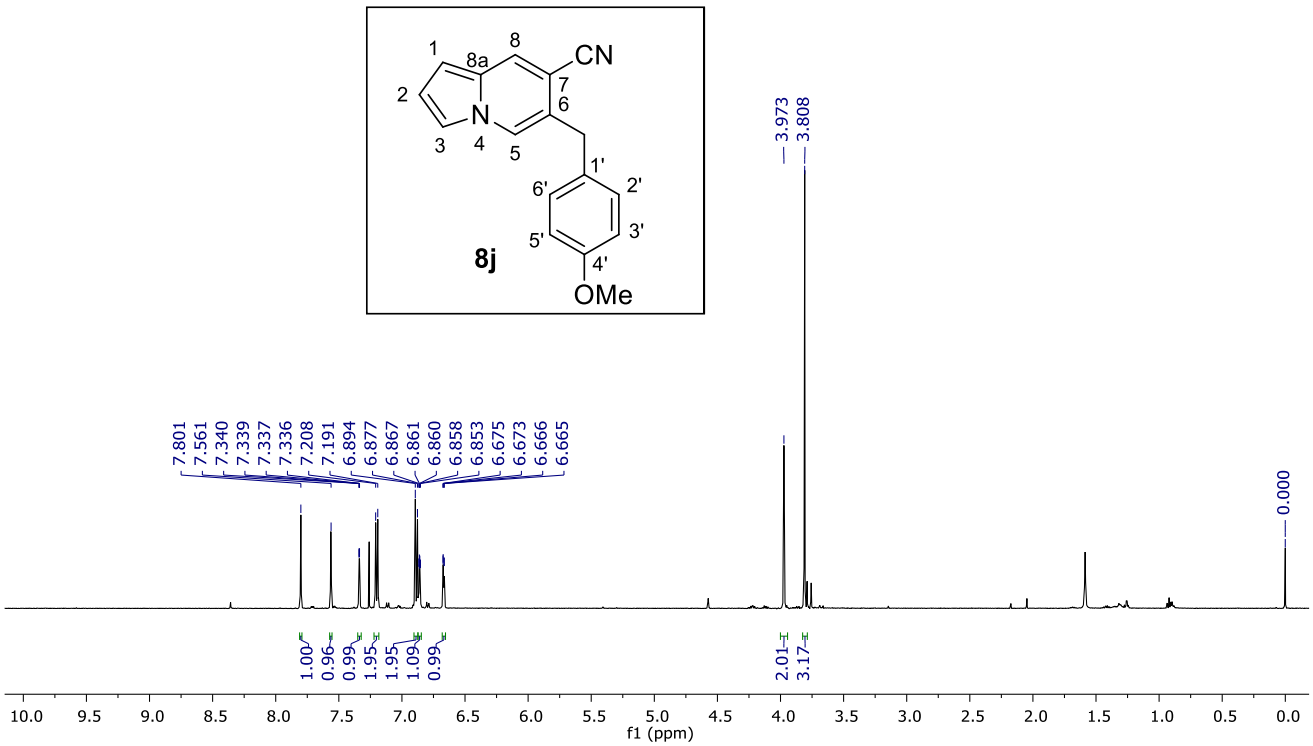
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8h**.



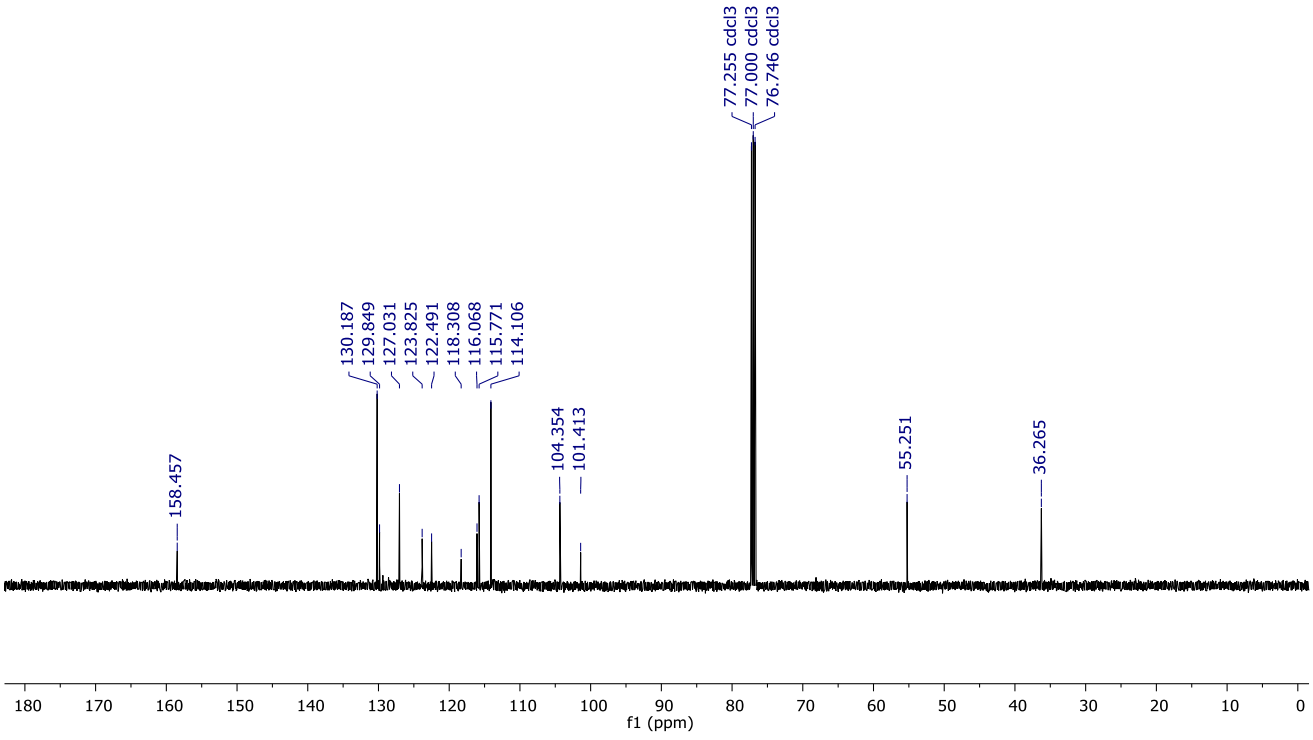
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8i**.



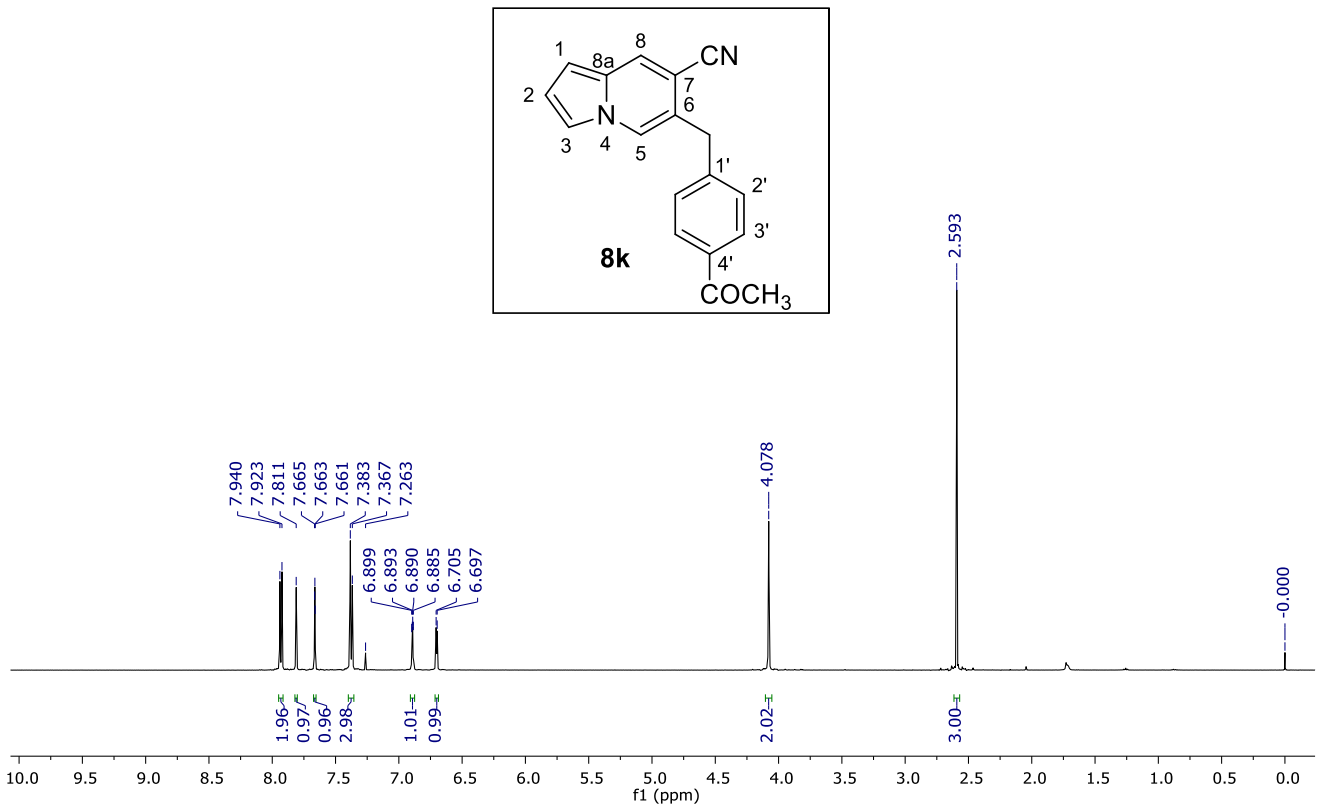
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8i**.



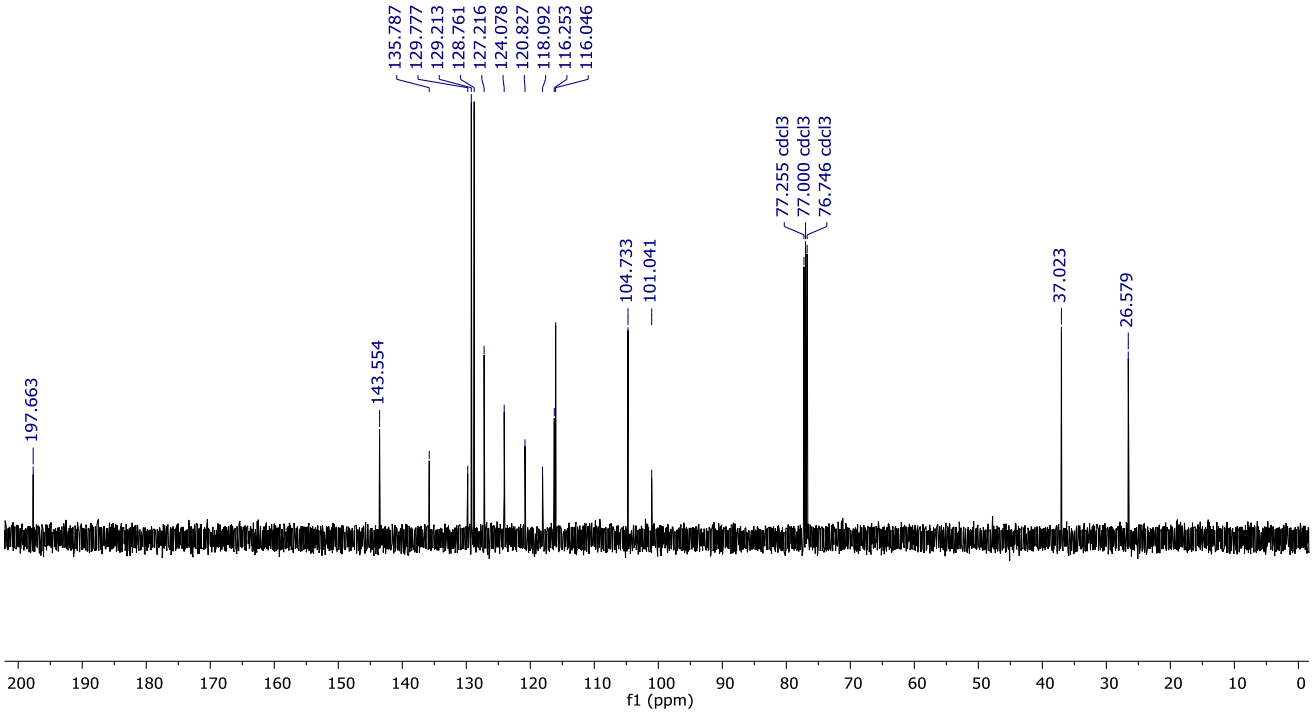
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8j**.



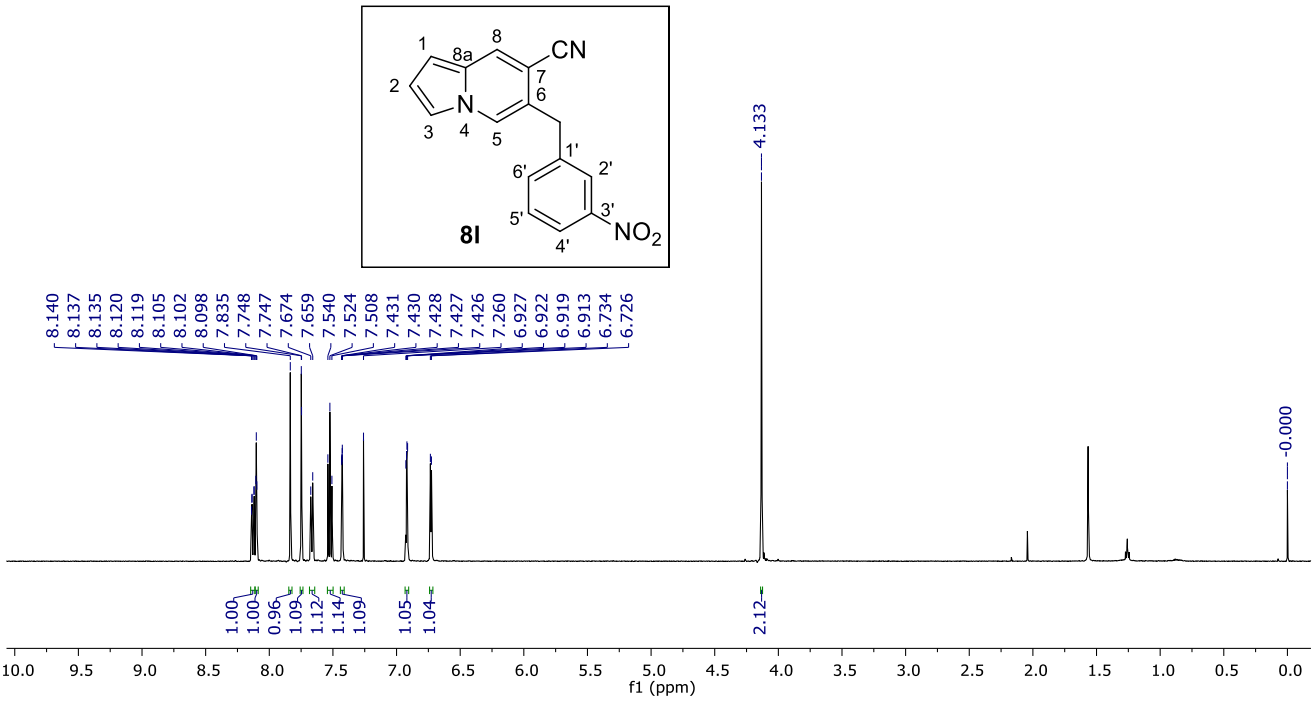
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8j**.



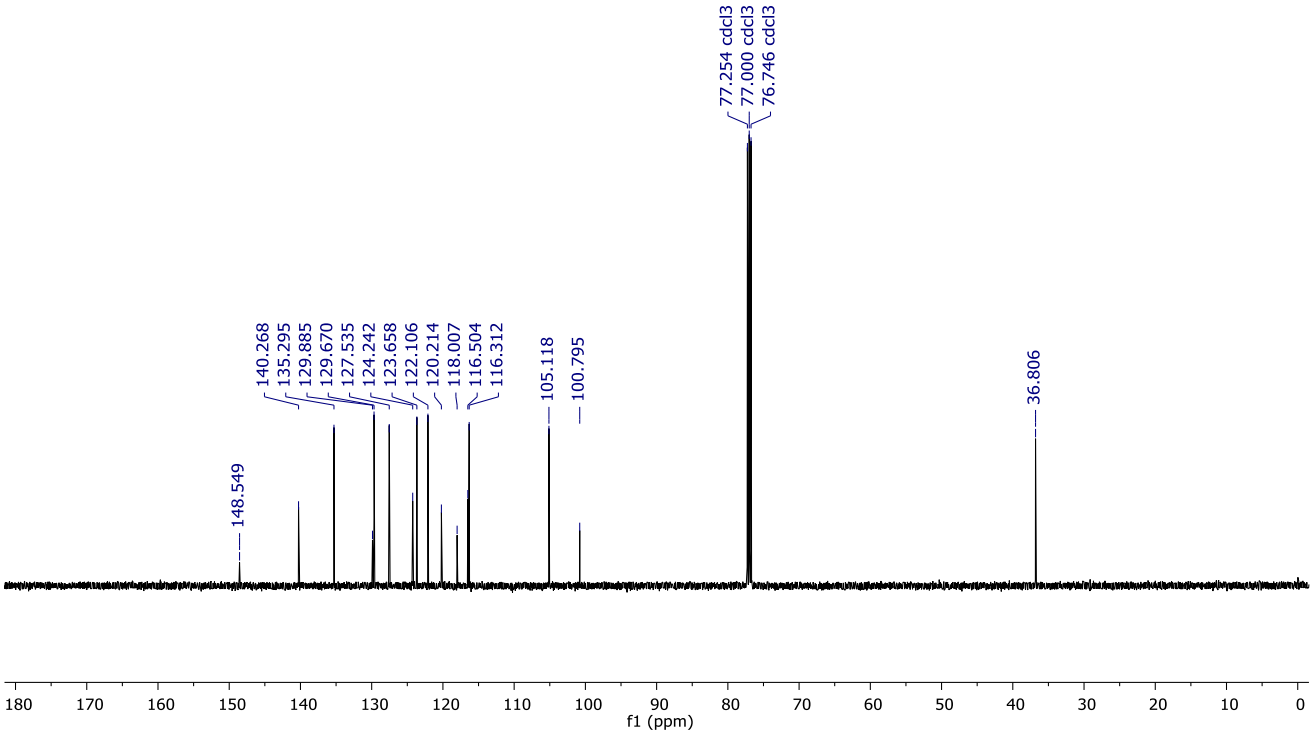
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8k**.



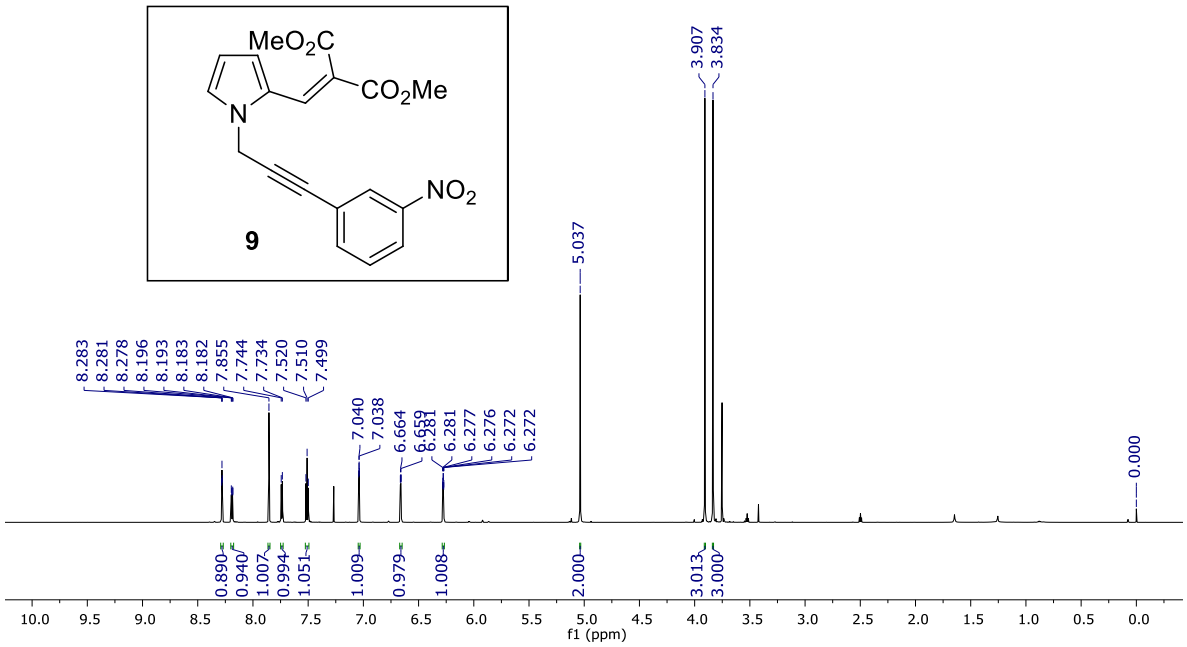
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8k**.



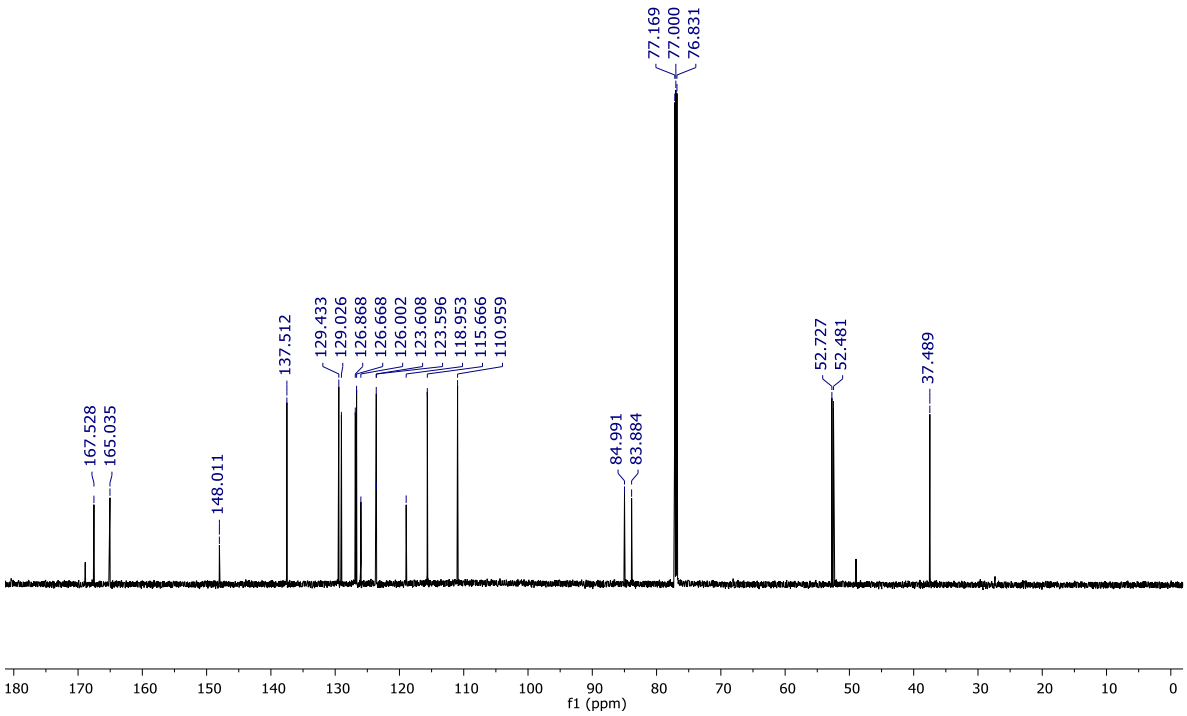
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8l**.



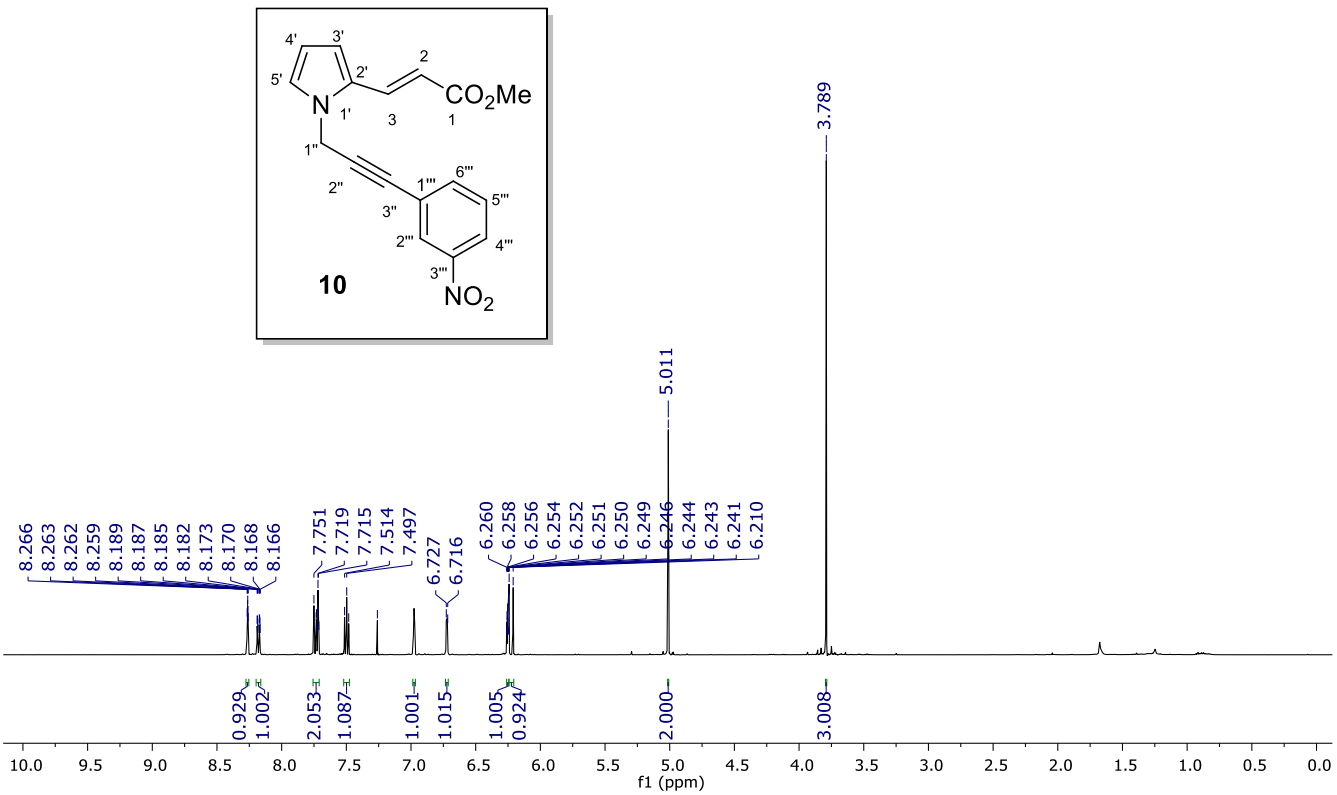
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8l**.



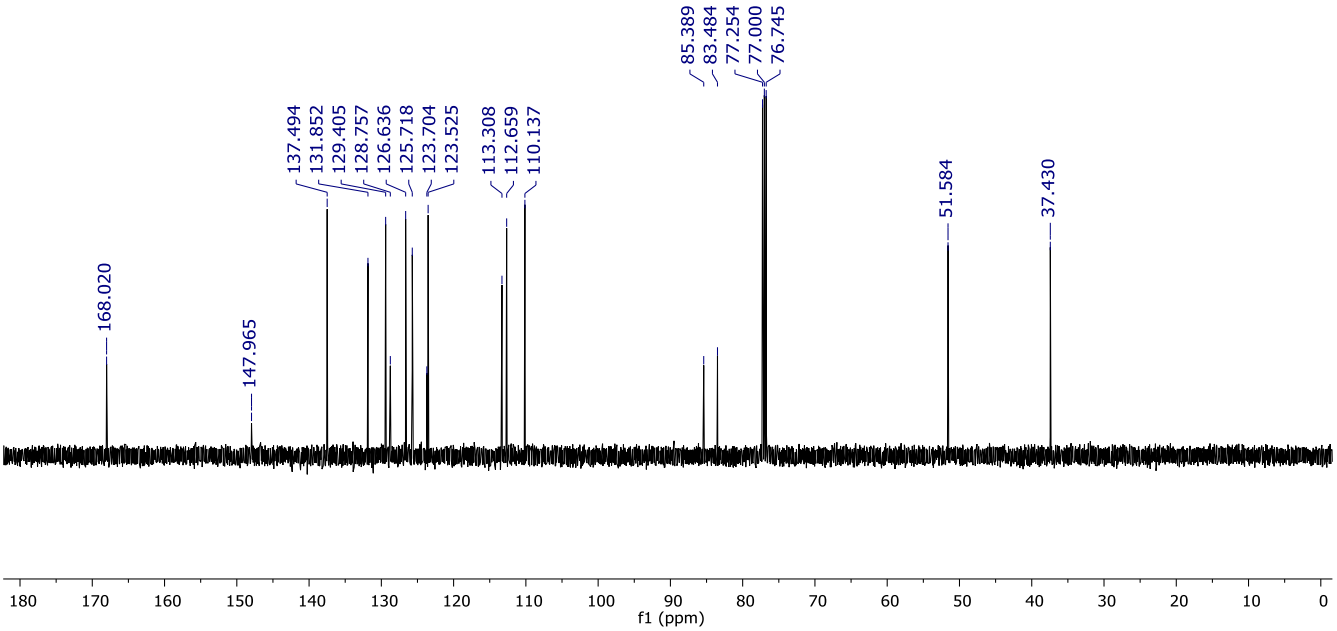
^{1}H NMR (750 MHz, $CDCl_3$) of compound **9**.



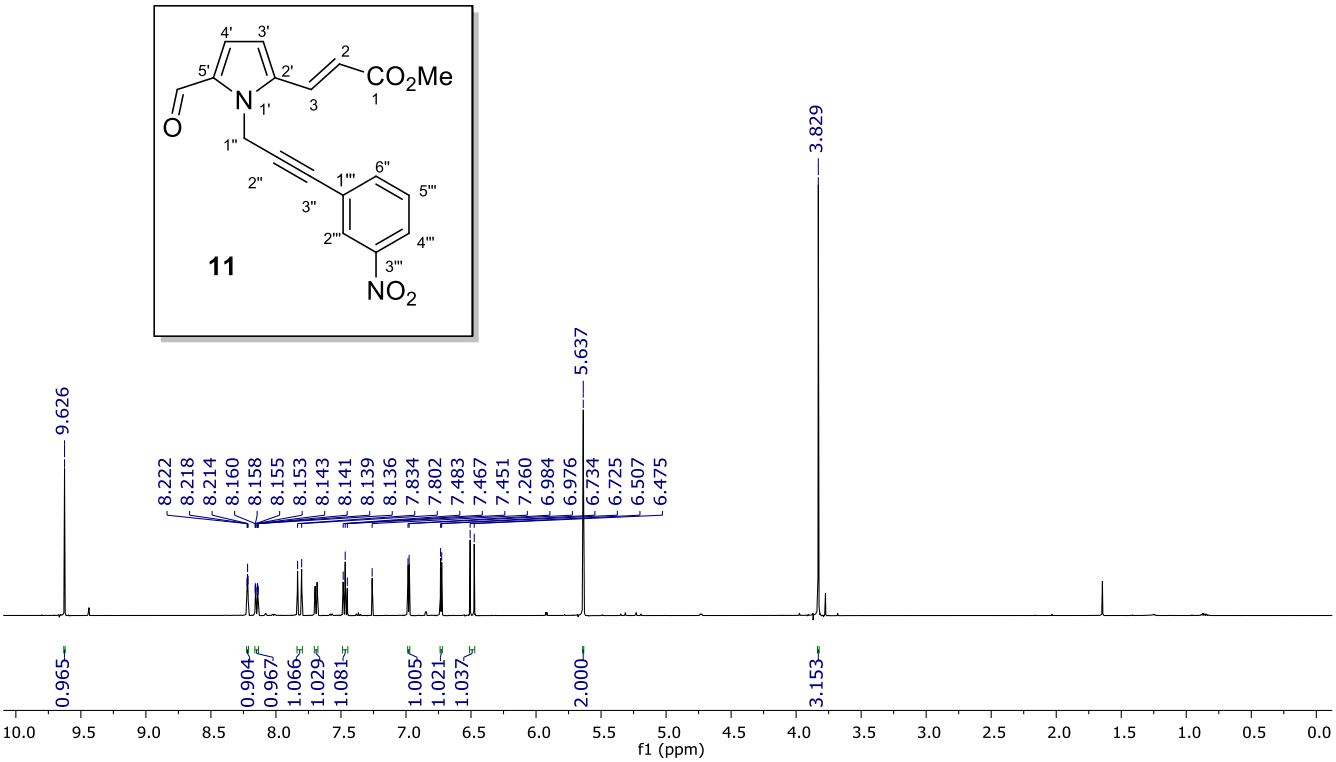
^{13}C NMR (187.5 MHz, $CDCl_3$) of compound **9**.



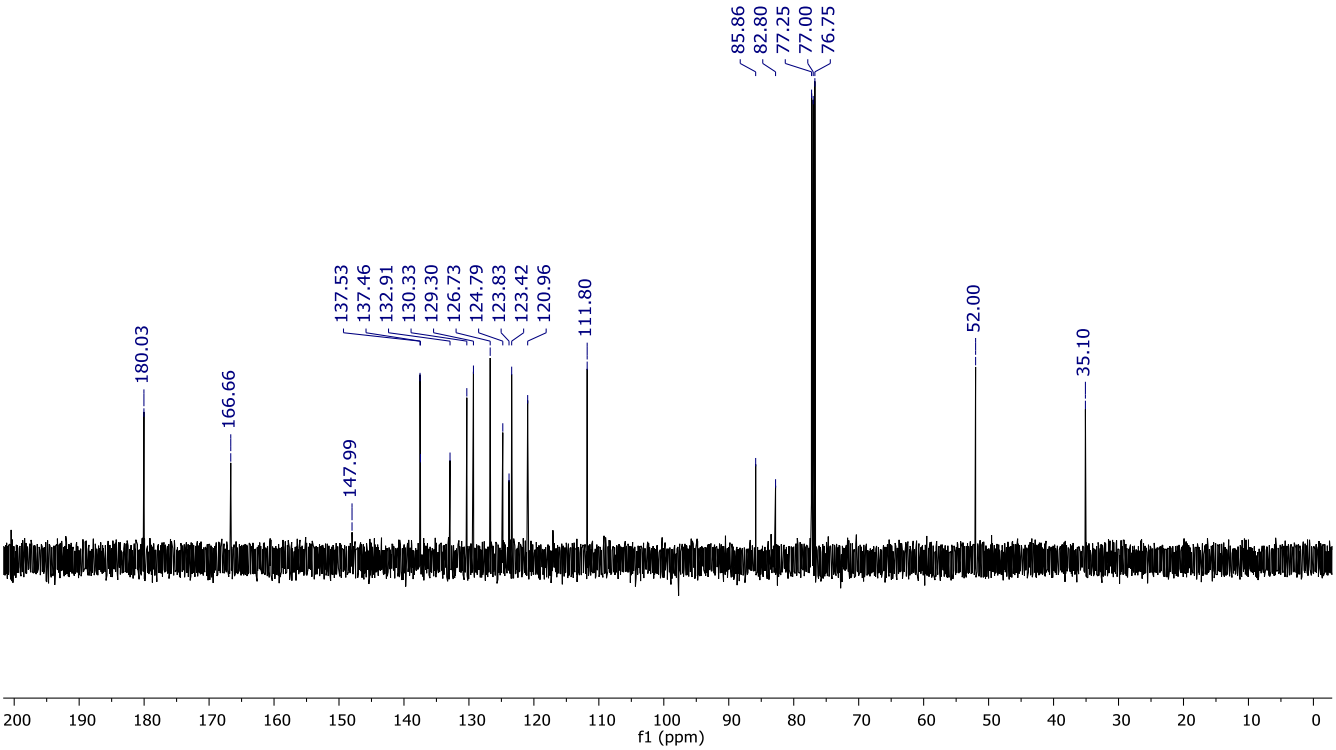
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10**.



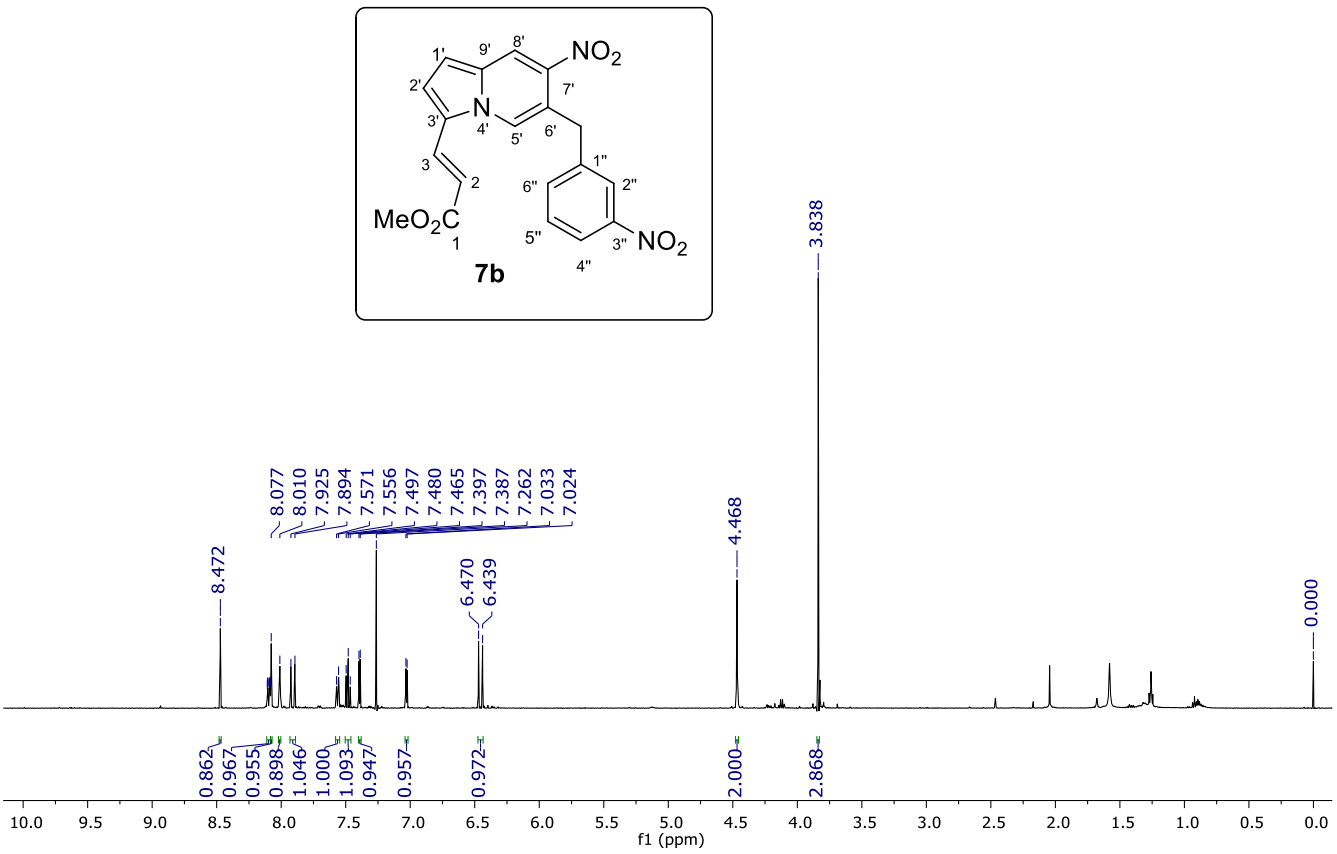
^{13}C NMR (125 MHz, $CDCl_3$) of compound **10**.



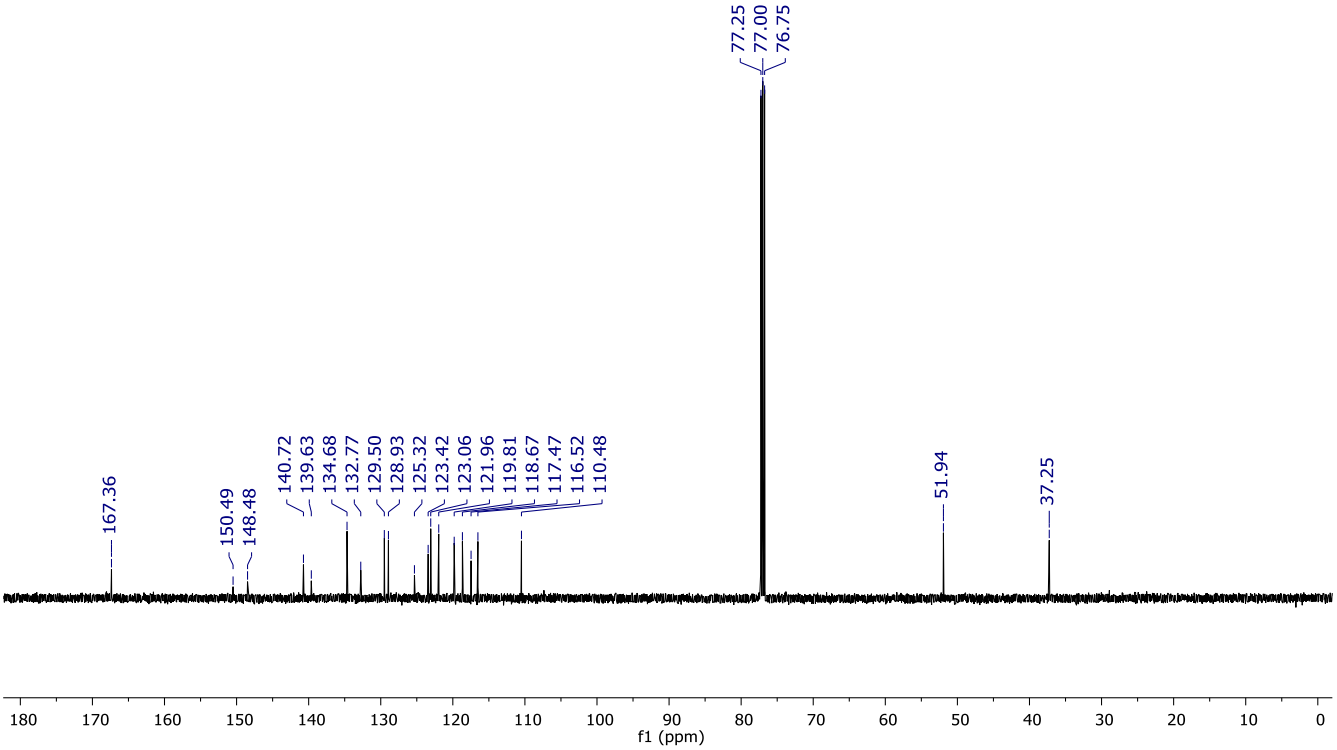
^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.



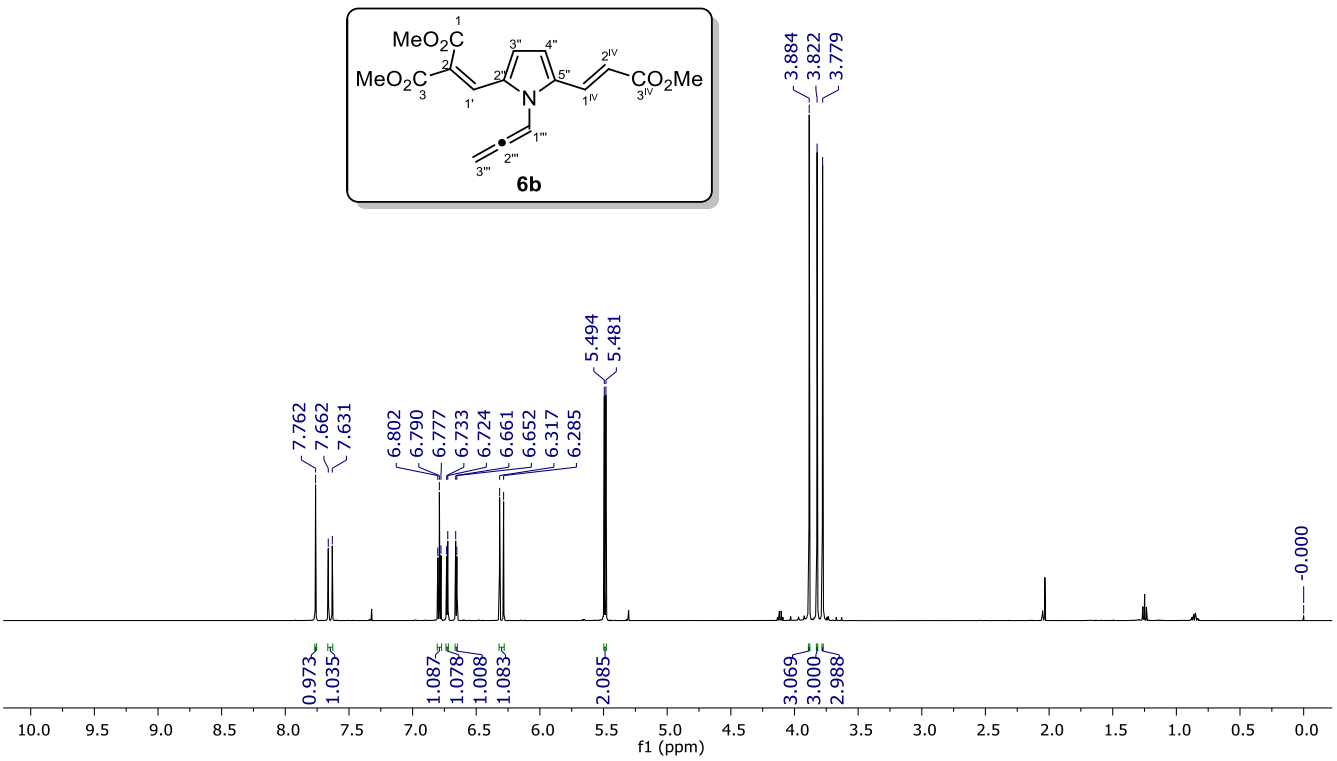
^{13}C NMR (125 MHz, $CDCl_3$) of compound **11**.



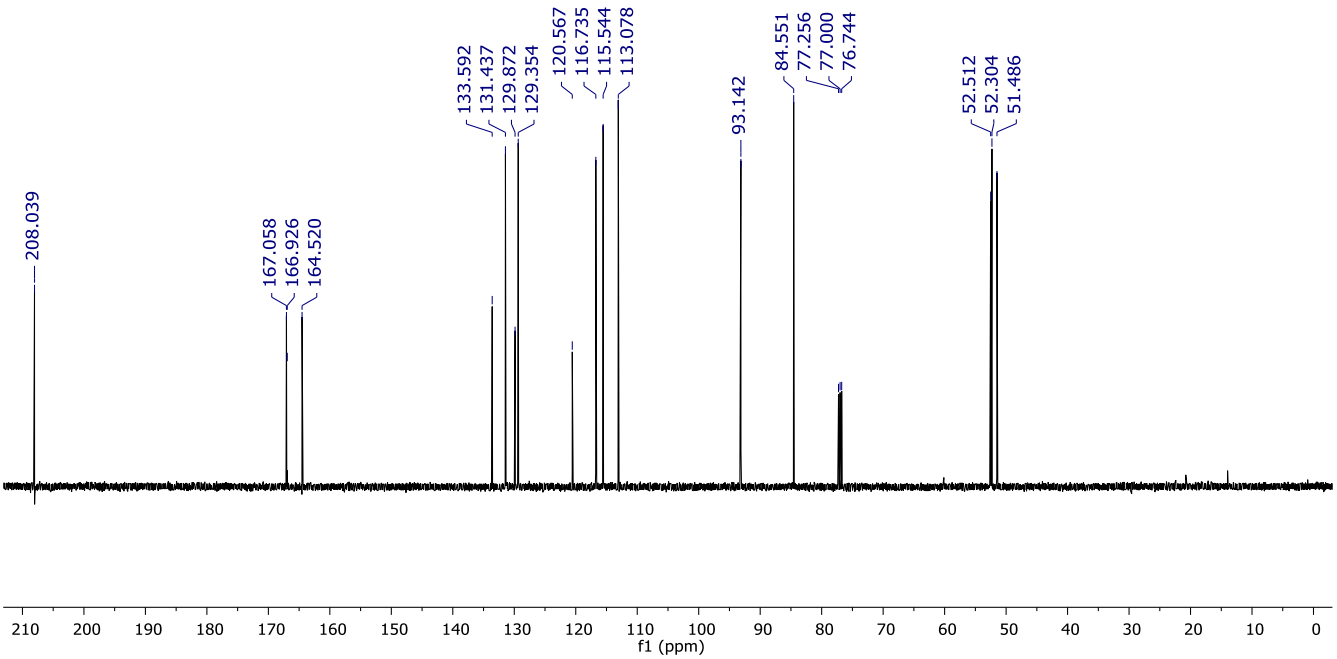
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7b**.



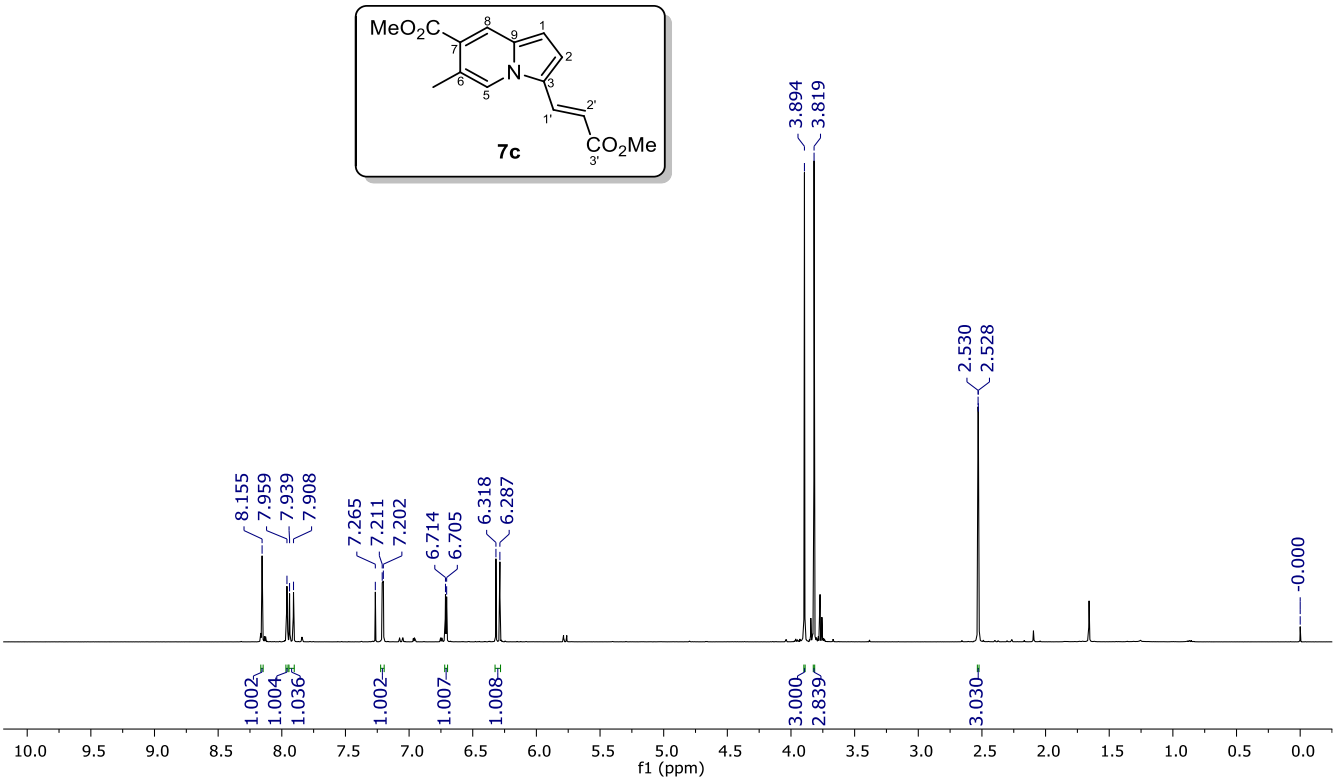
^{13}C NMR (125 MHz, $CDCl_3$) of compound **7b**.



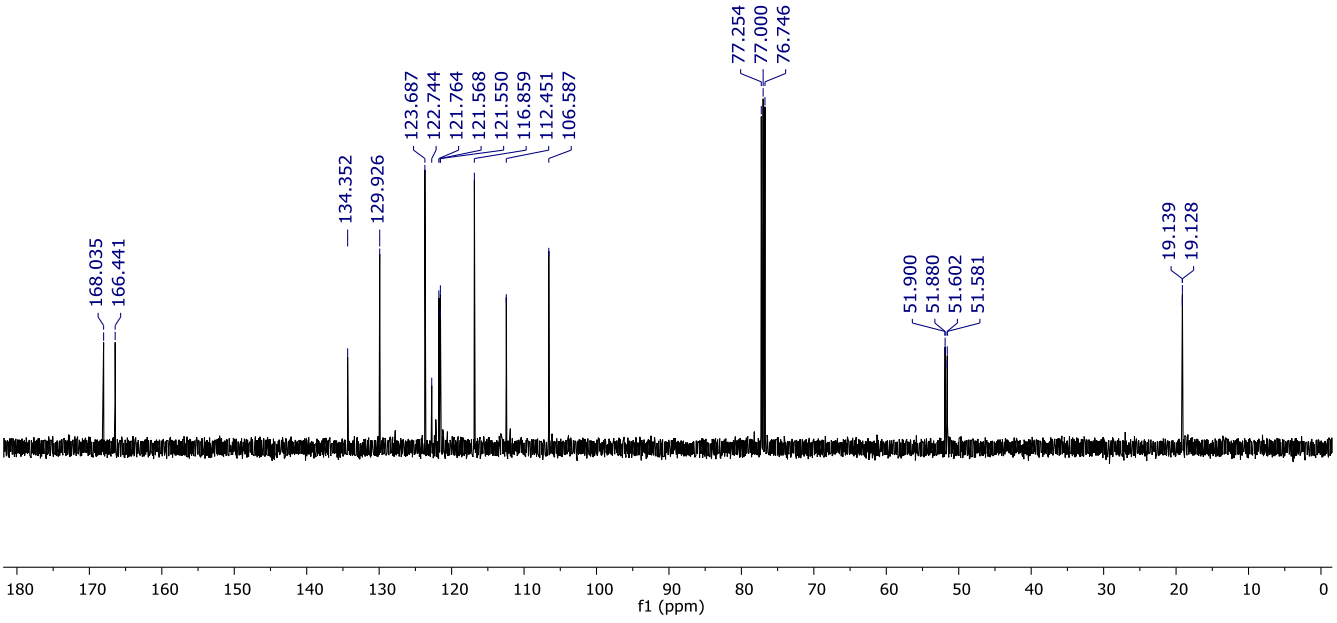
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6b**.



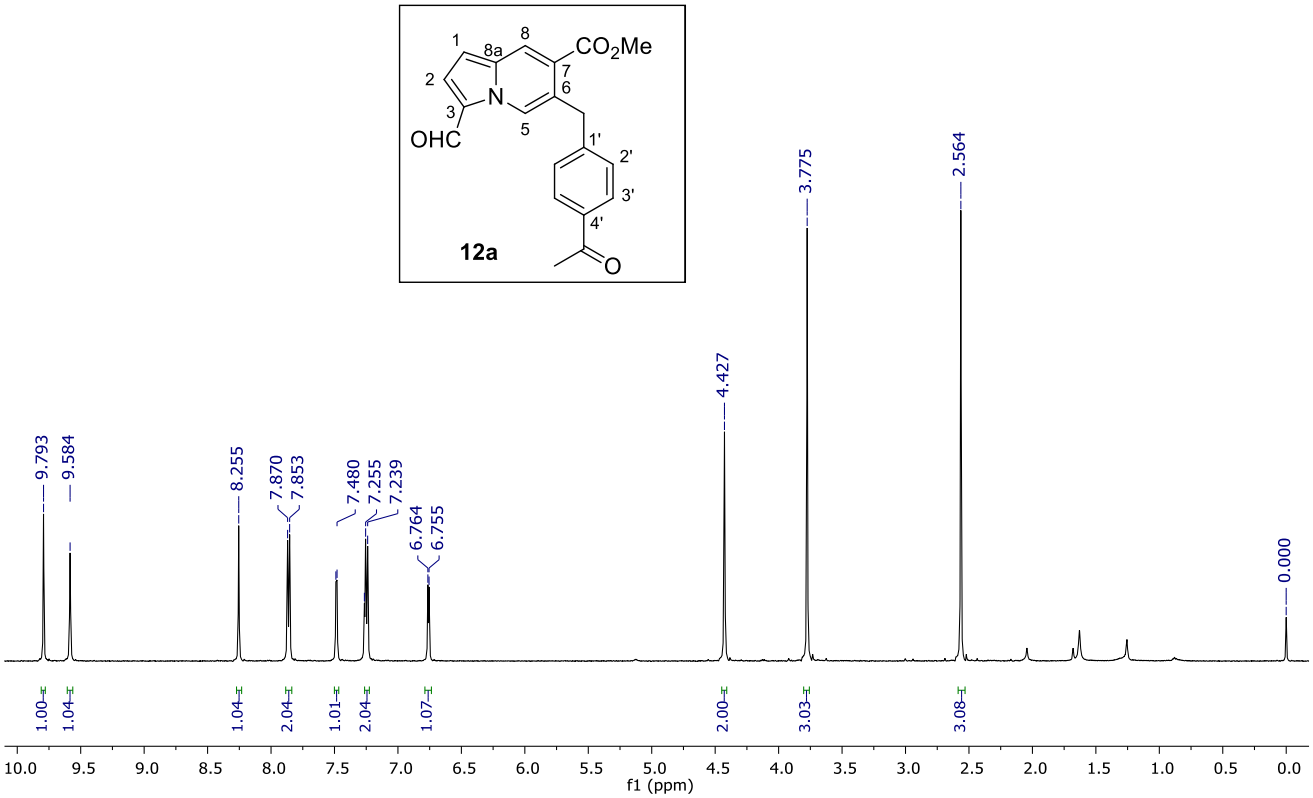
^{13}C NMR (125 MHz, $CDCl_3$) of compound **6b**.



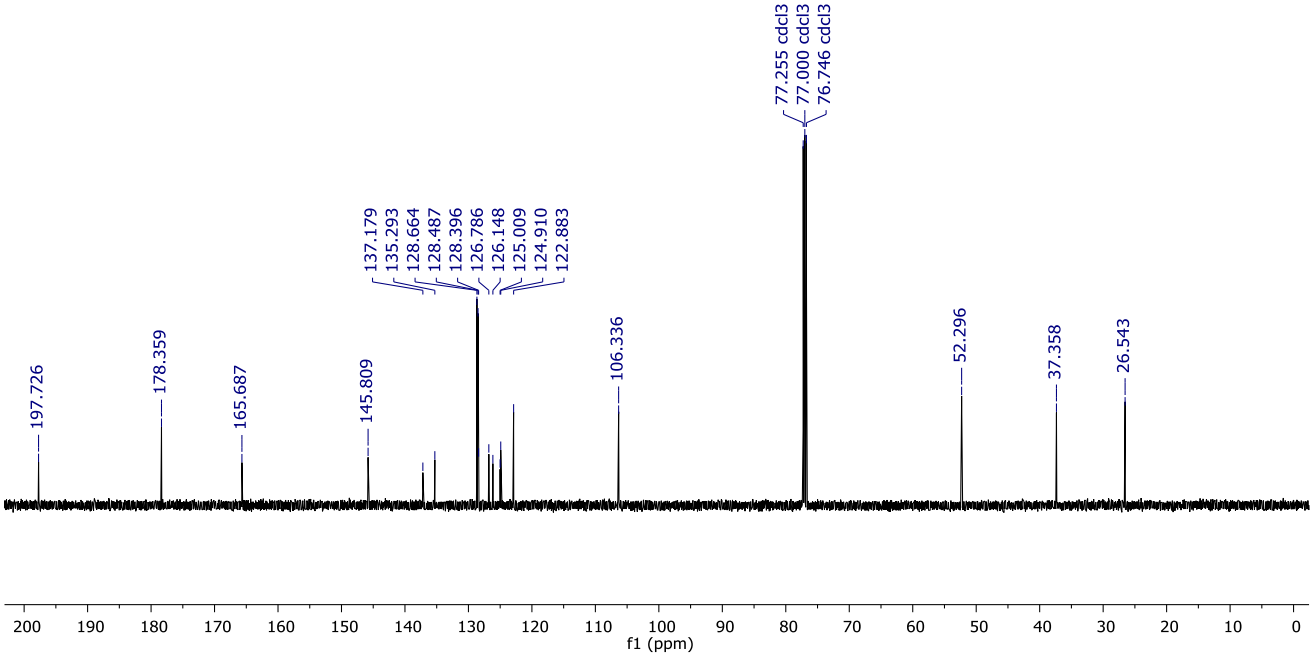
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7c**.



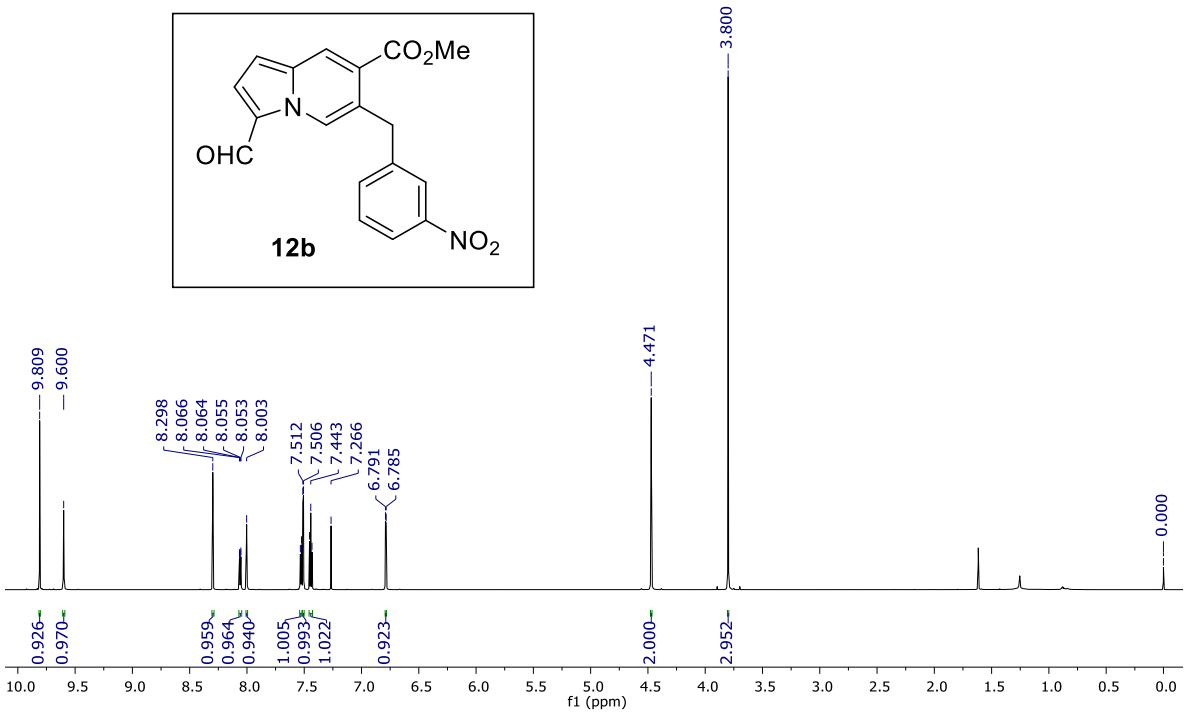
^{13}C NMR (125 MHz, $CDCl_3$) of compound **7c**.



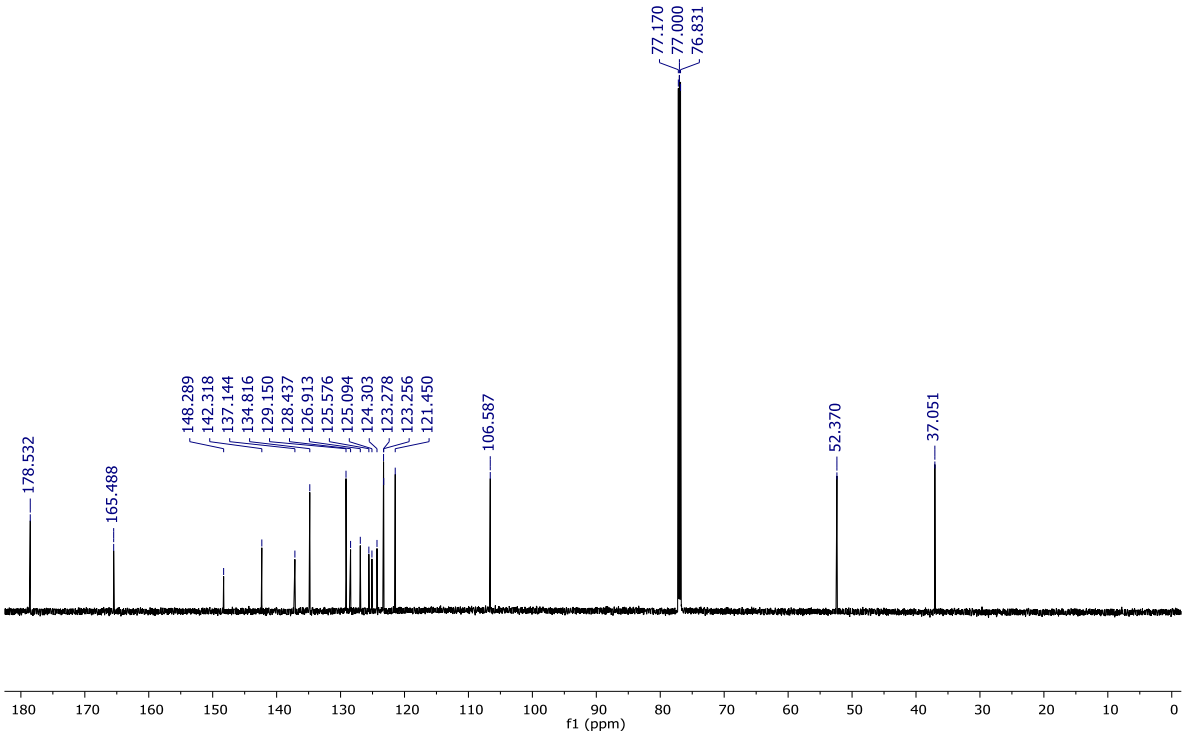
^{1}H NMR (600 MHz, $CDCl_3$) of compound **12a**.



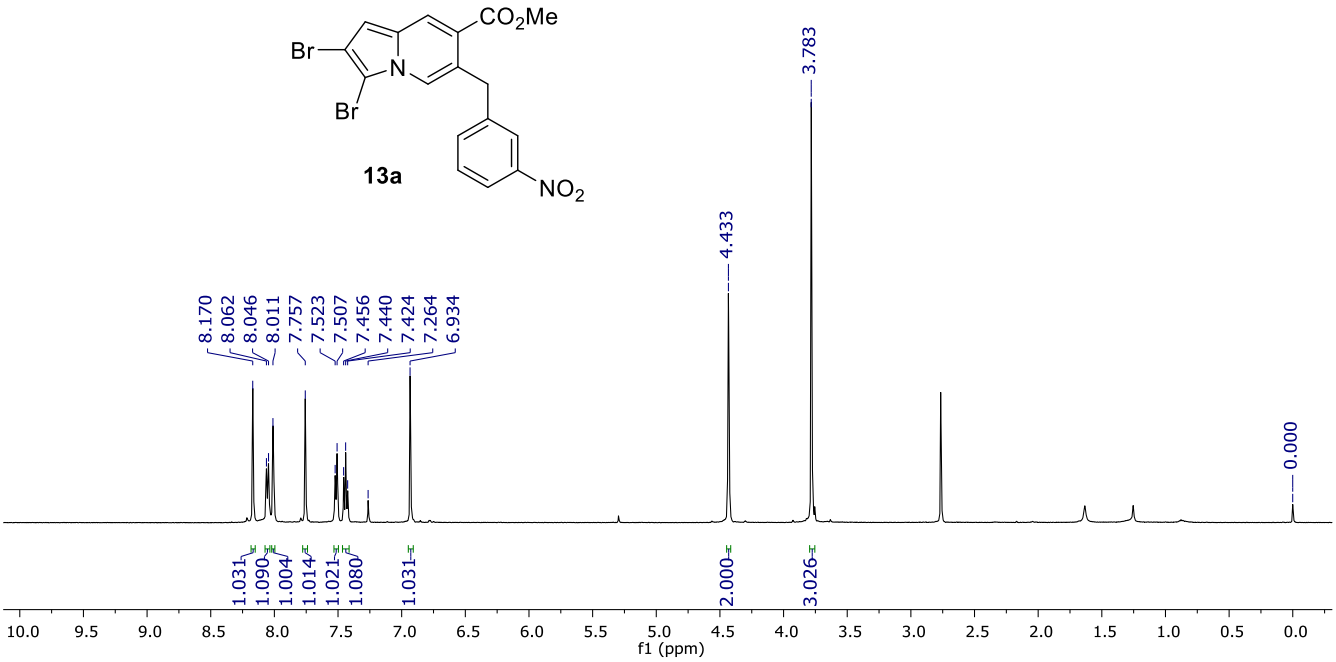
^{13}C NMR (150 MHz,$CDCl_3$) of compound **12a**.



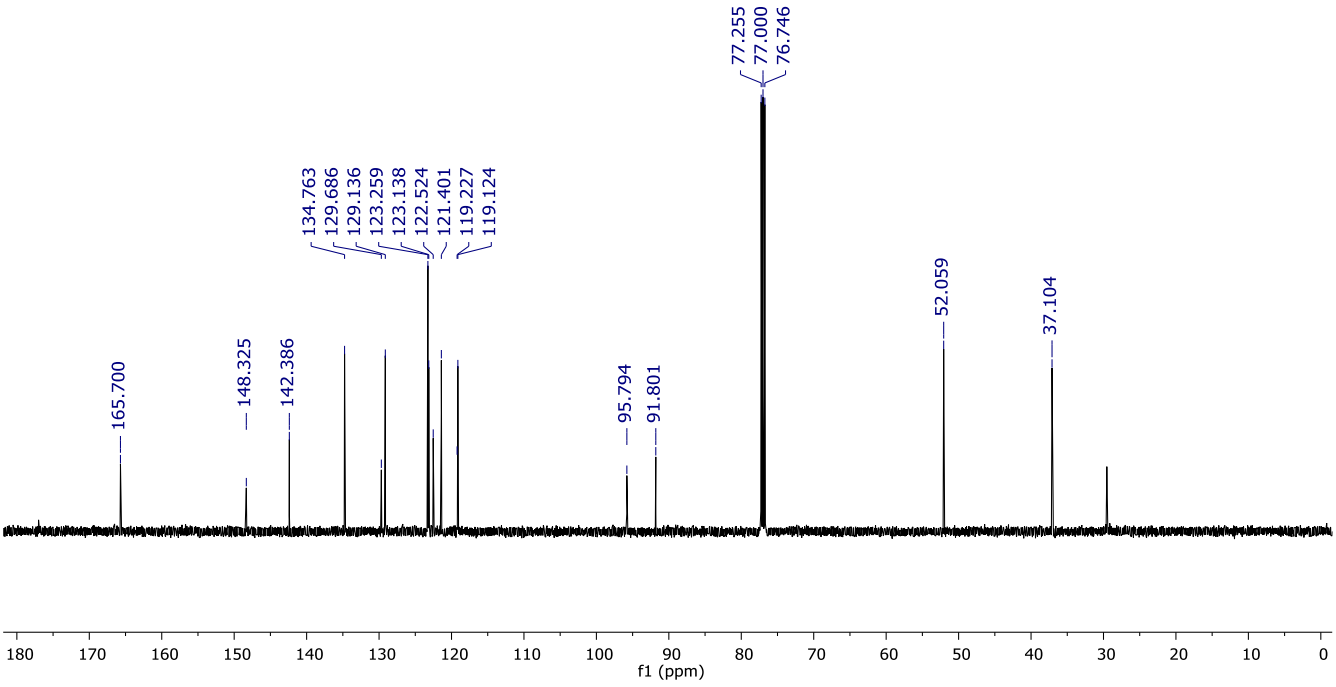
^{1}H NMR (750 MHz, $CDCl_3$) of compound **12b**.



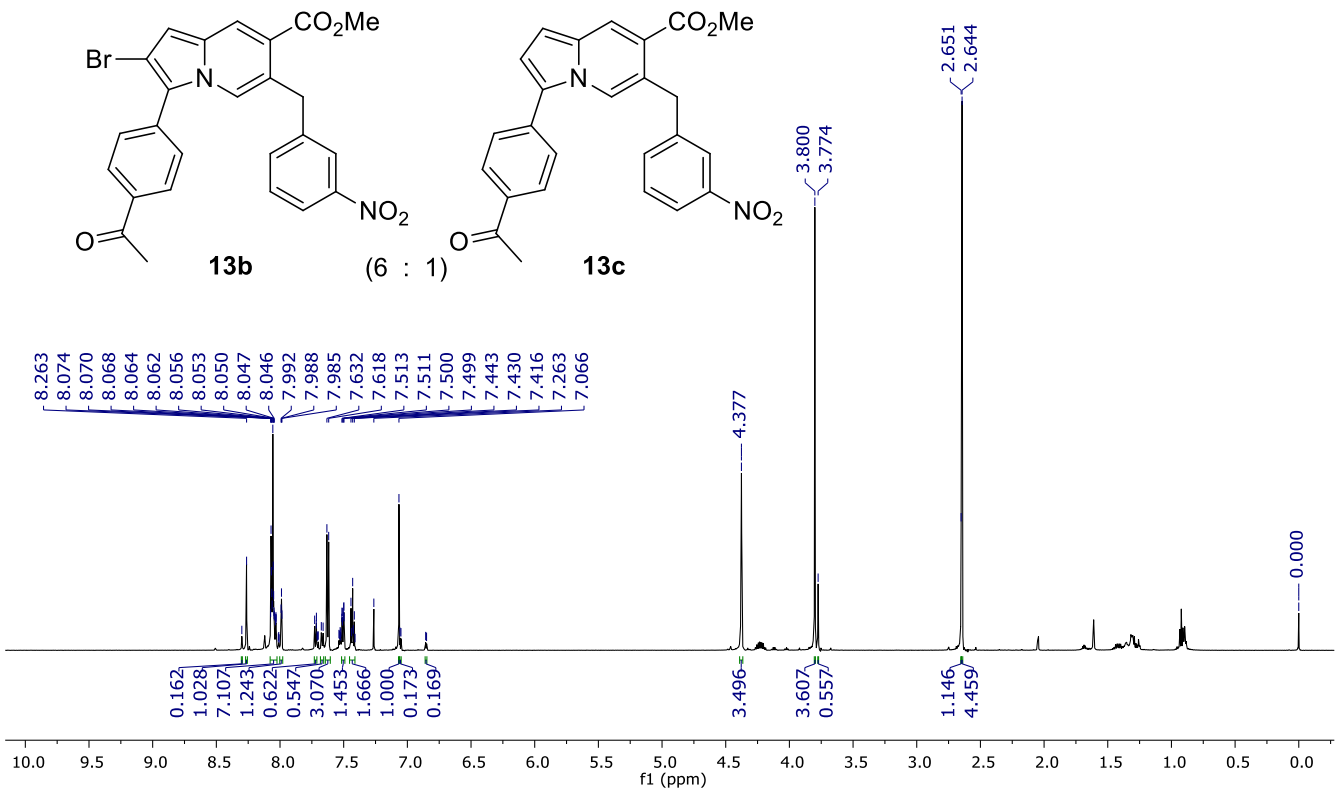
^{13}C NMR (187.5 MHz, $CDCl_3$) of compound **12b**.



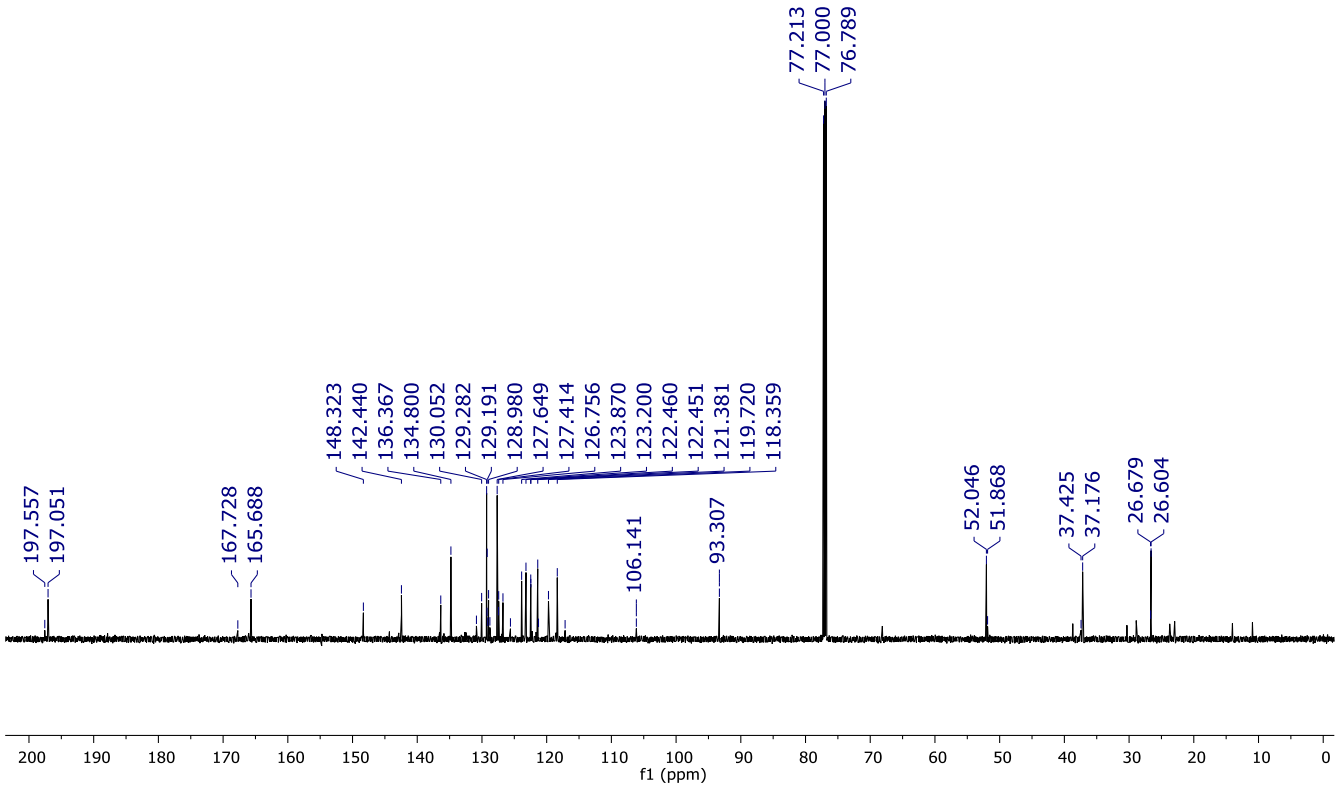
^{1}H NMR (500 MHz, $CDCl_3$) of compound **13a**.



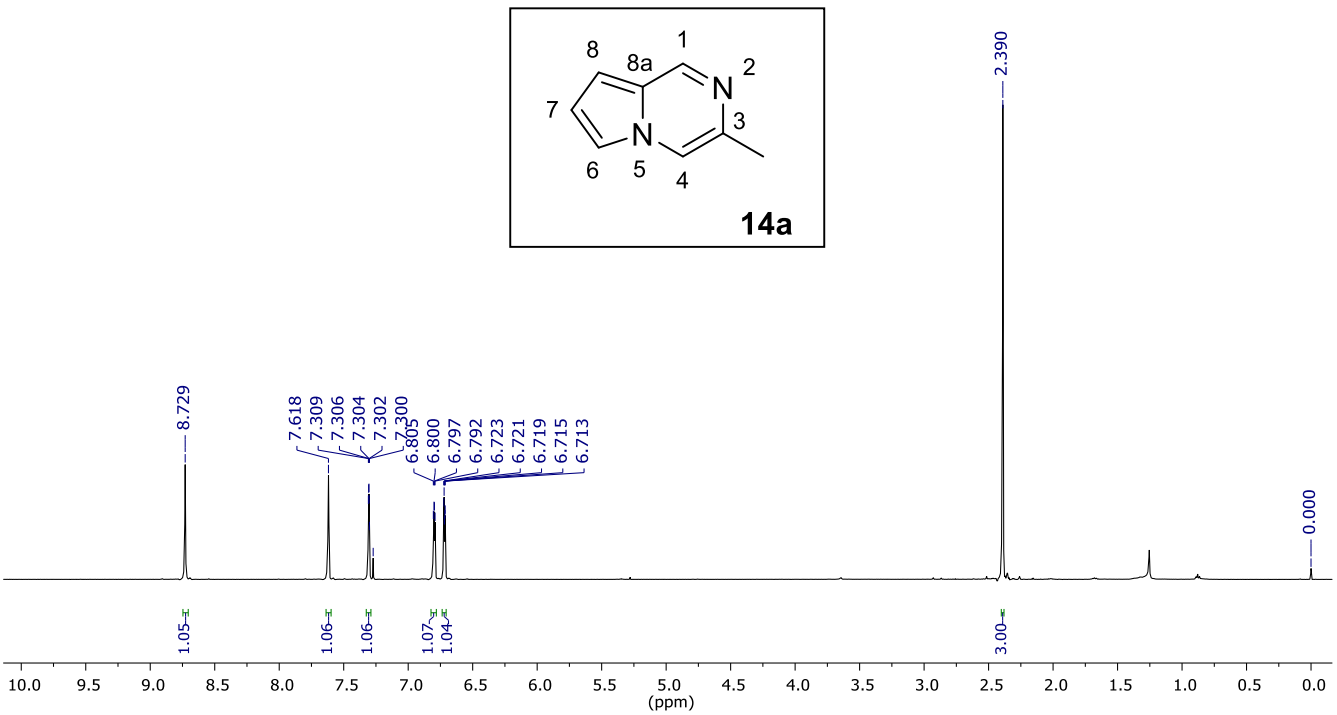
^{13}C NMR (125 MHz, $CDCl_3$) of compound **13a**.



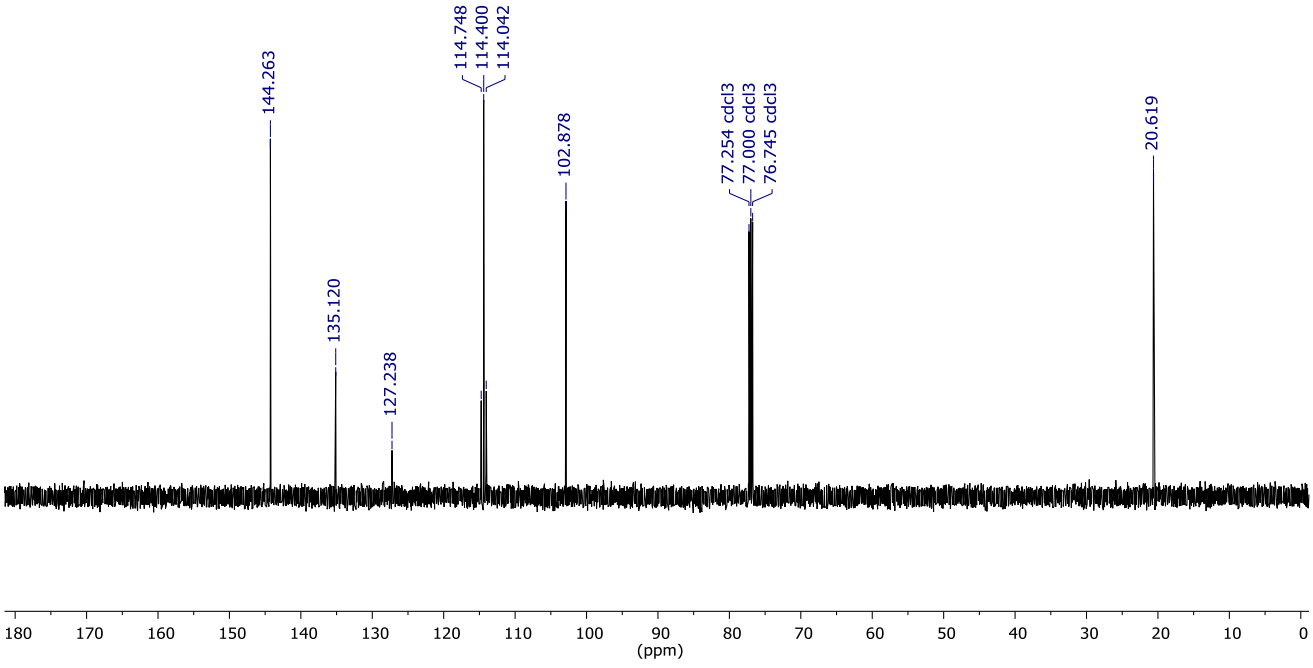
^{1}H NMR (600 MHz, $CDCl_3$) of compounds **13b**/**13c**.



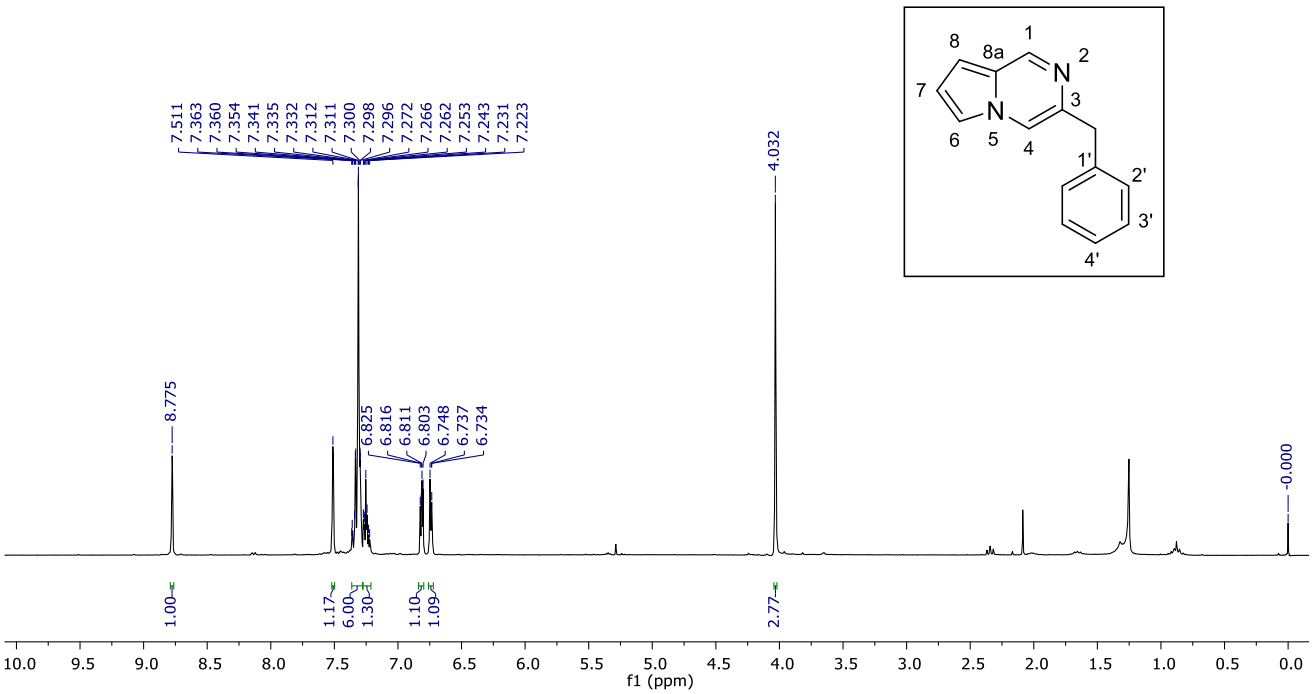
^{13}C NMR (150 MHz, $CDCl_3$) of compounds **13b**/**13c**.



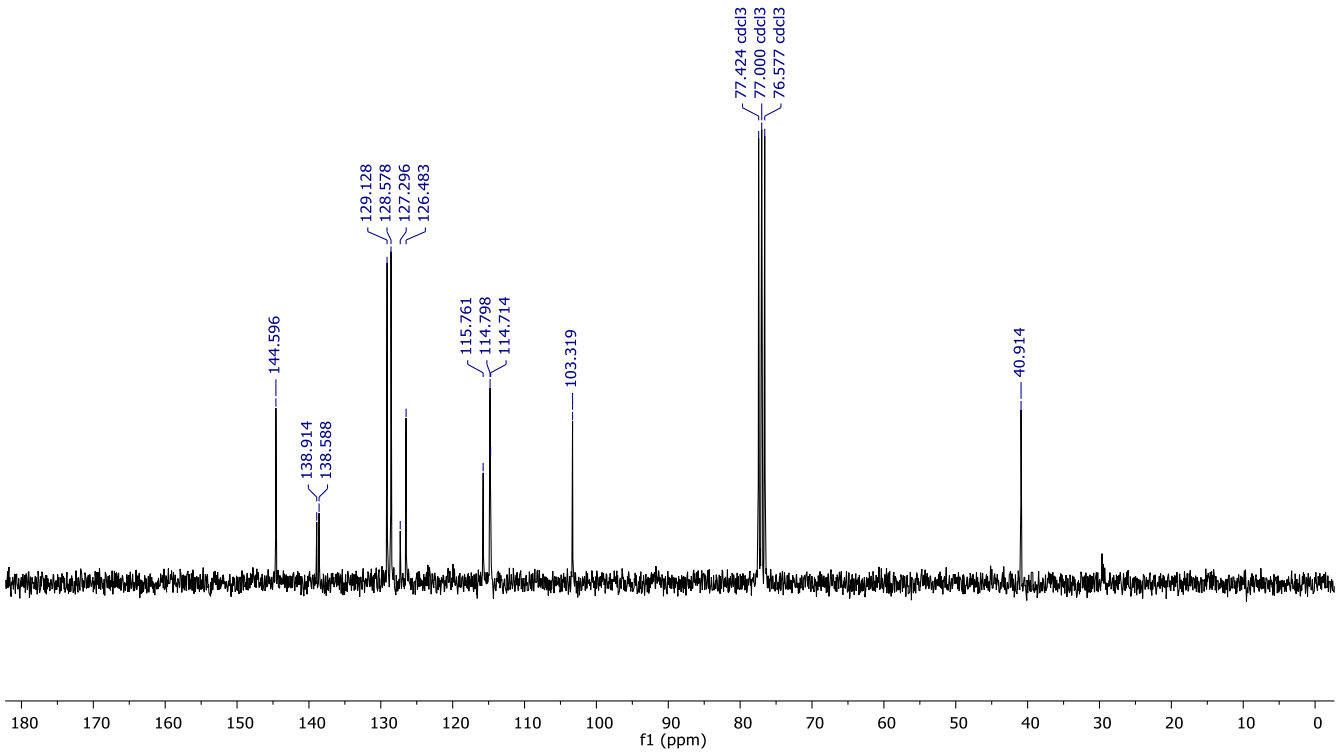
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14a**.



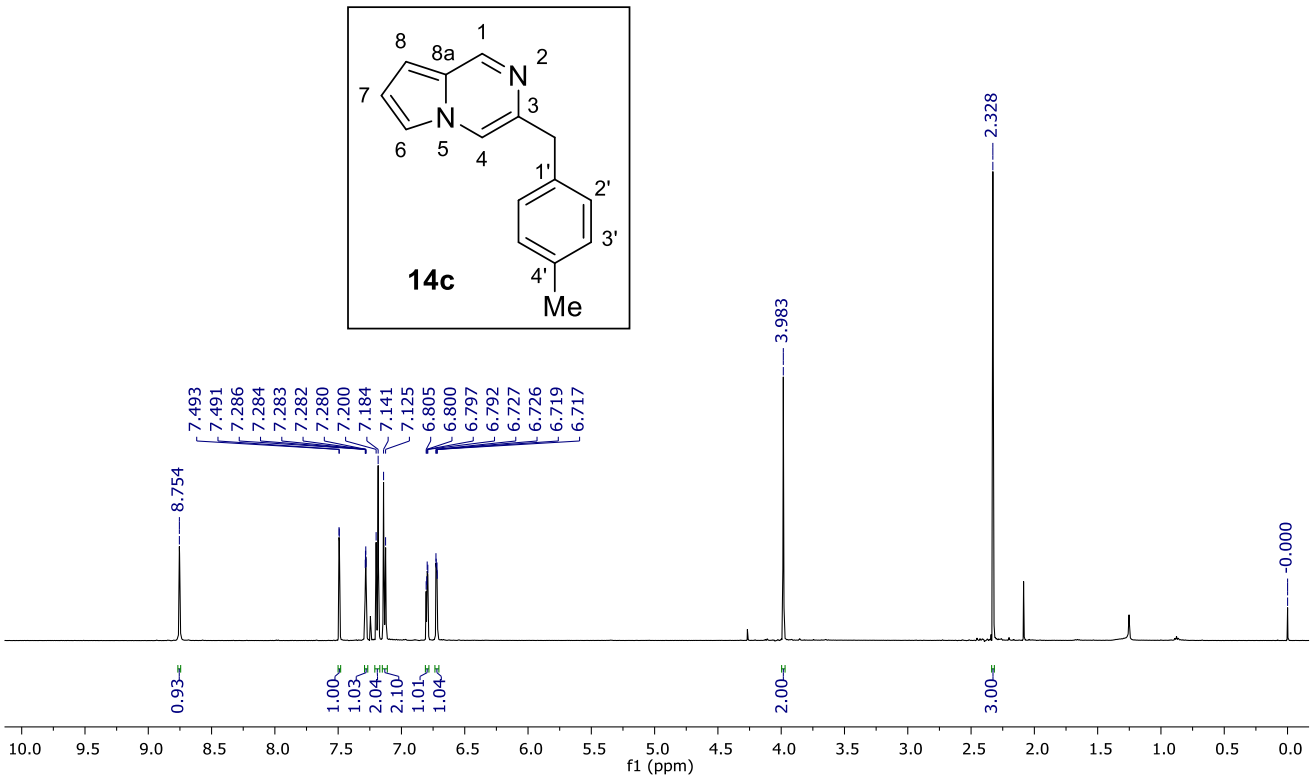
^{13}C NMR (125 MHz, $CDCl_3$) of compound **14a**.



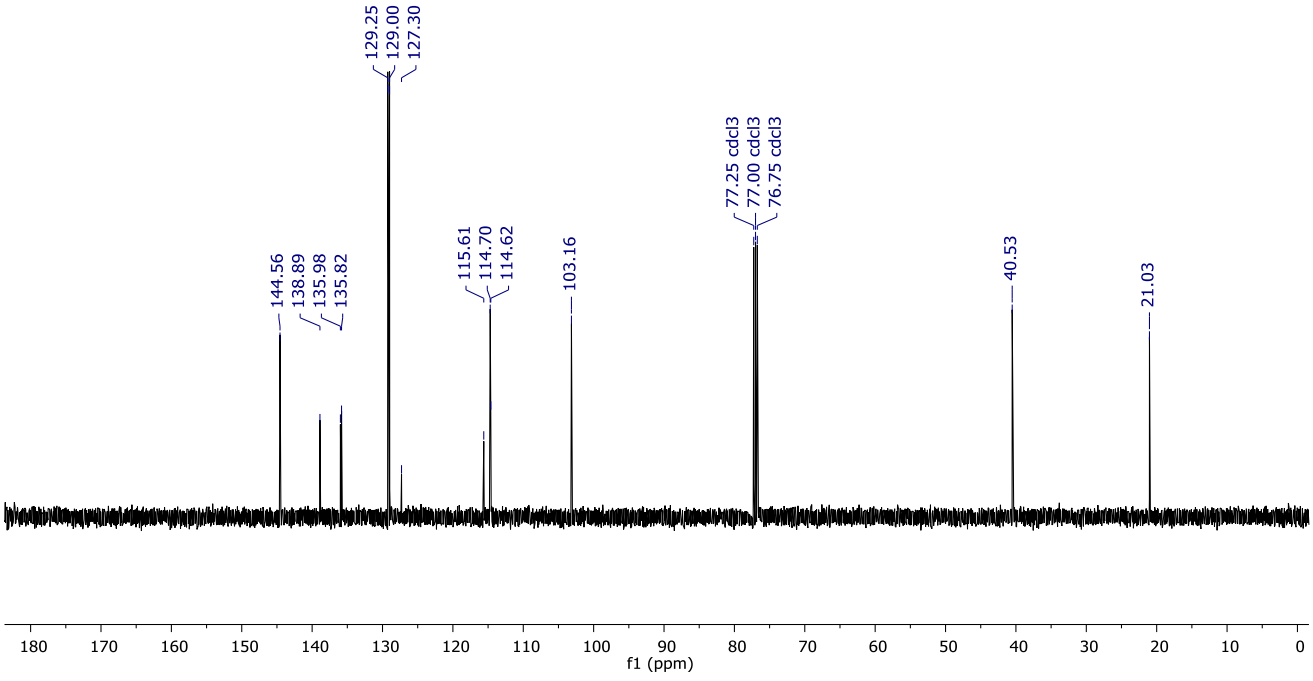
^{1}H NMR (300 MHz, $CDCl_3$) of compound **14b**.



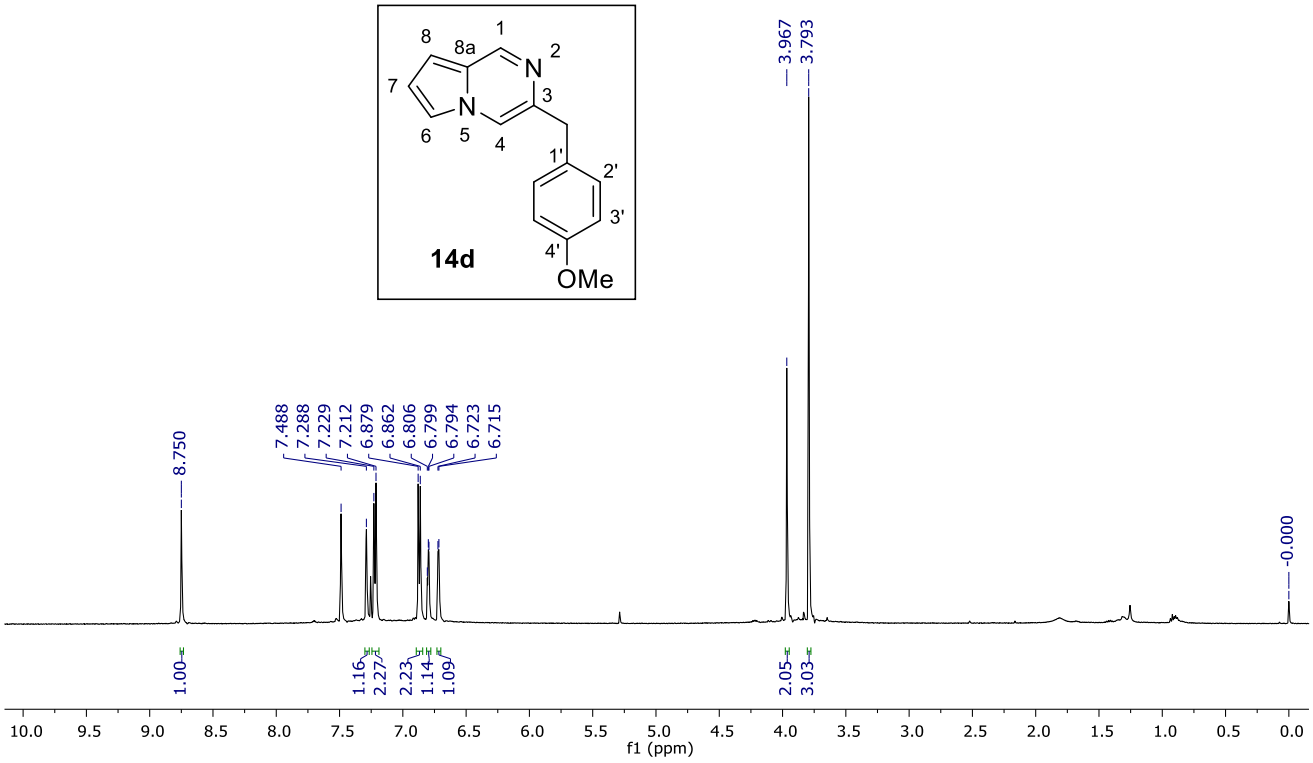
^{13}C NMR (75.4 MHz, $CDCl_3$) of compound **14b**.



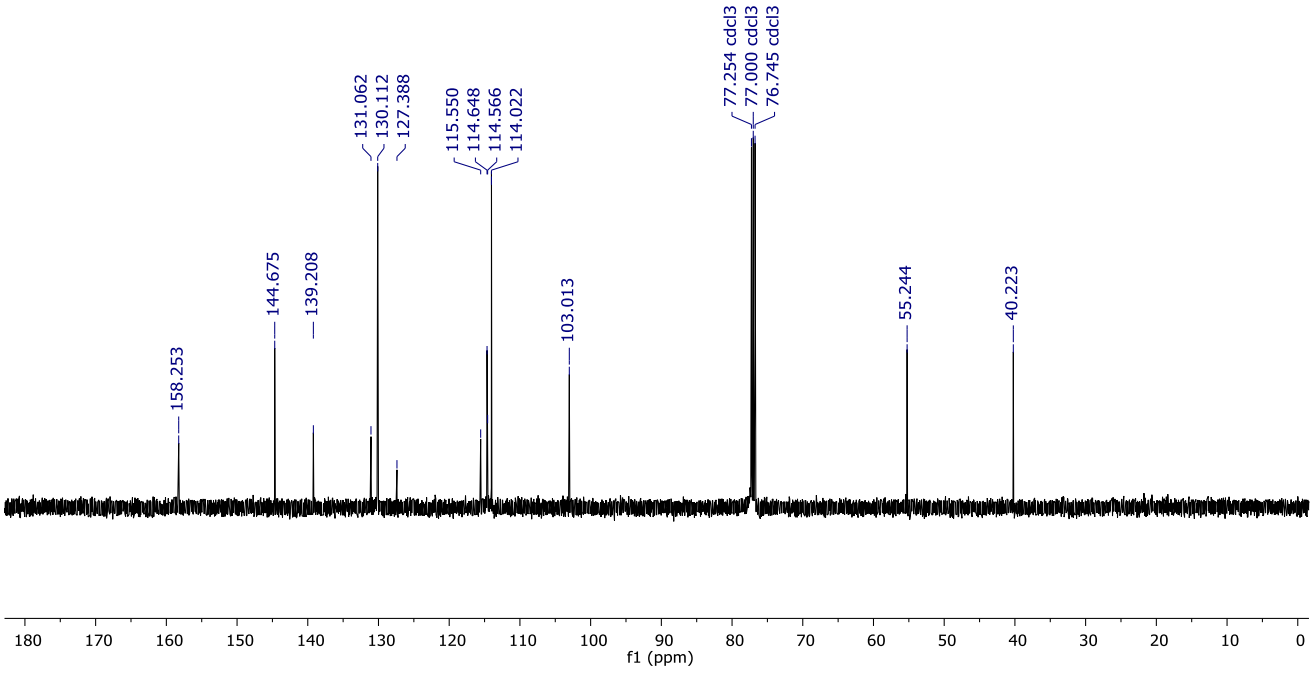
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14c**.



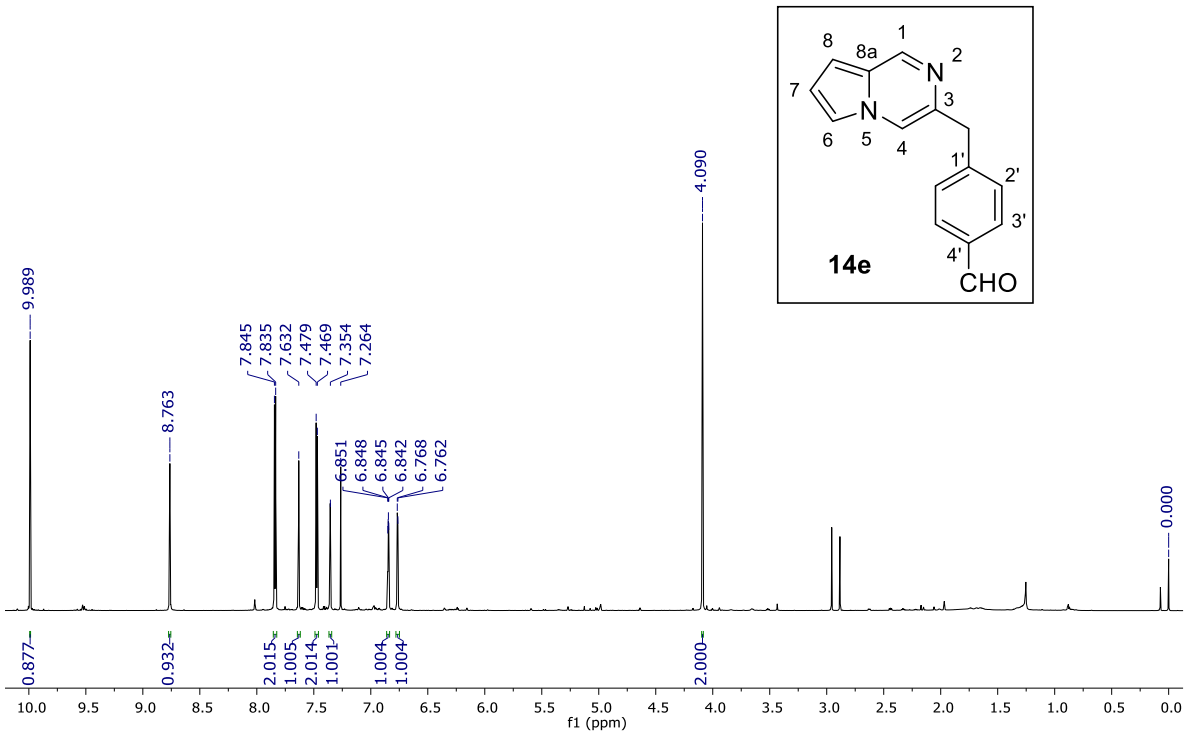
^{13}C NMR (125 MHz, $CDCl_3$) of compound **14c**.



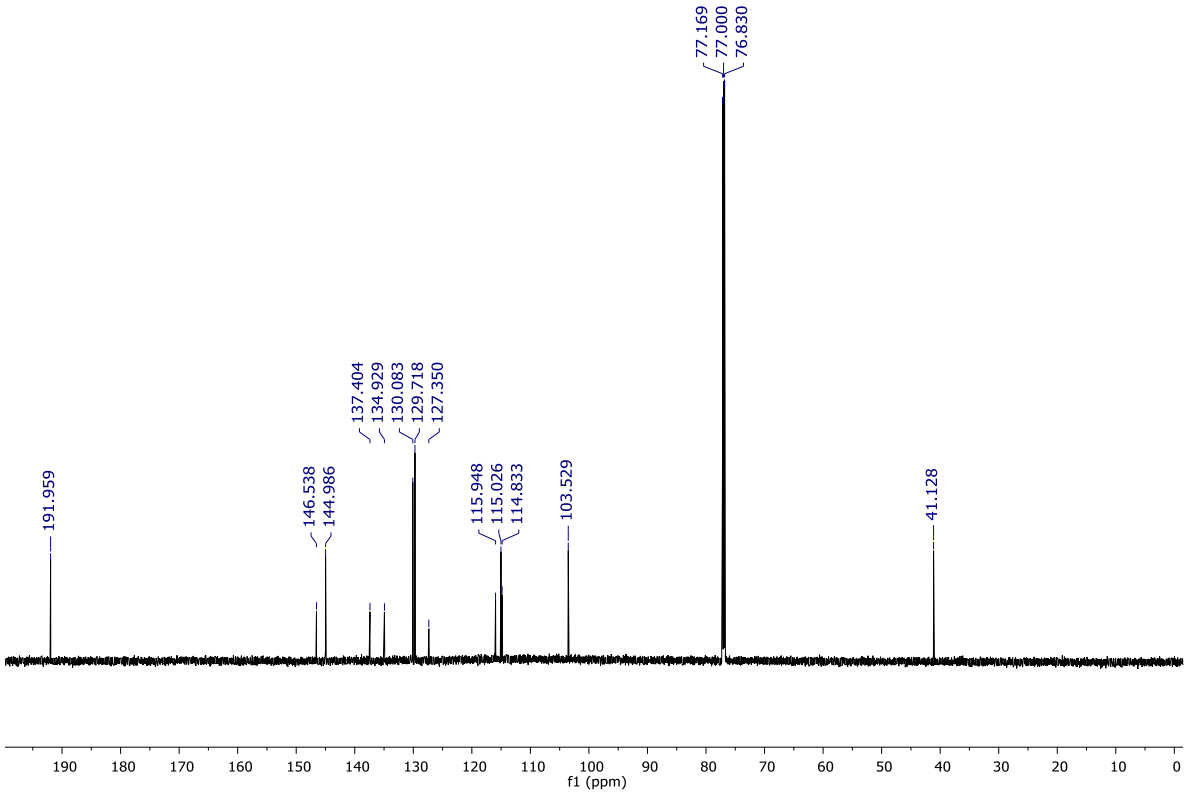
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14d**.



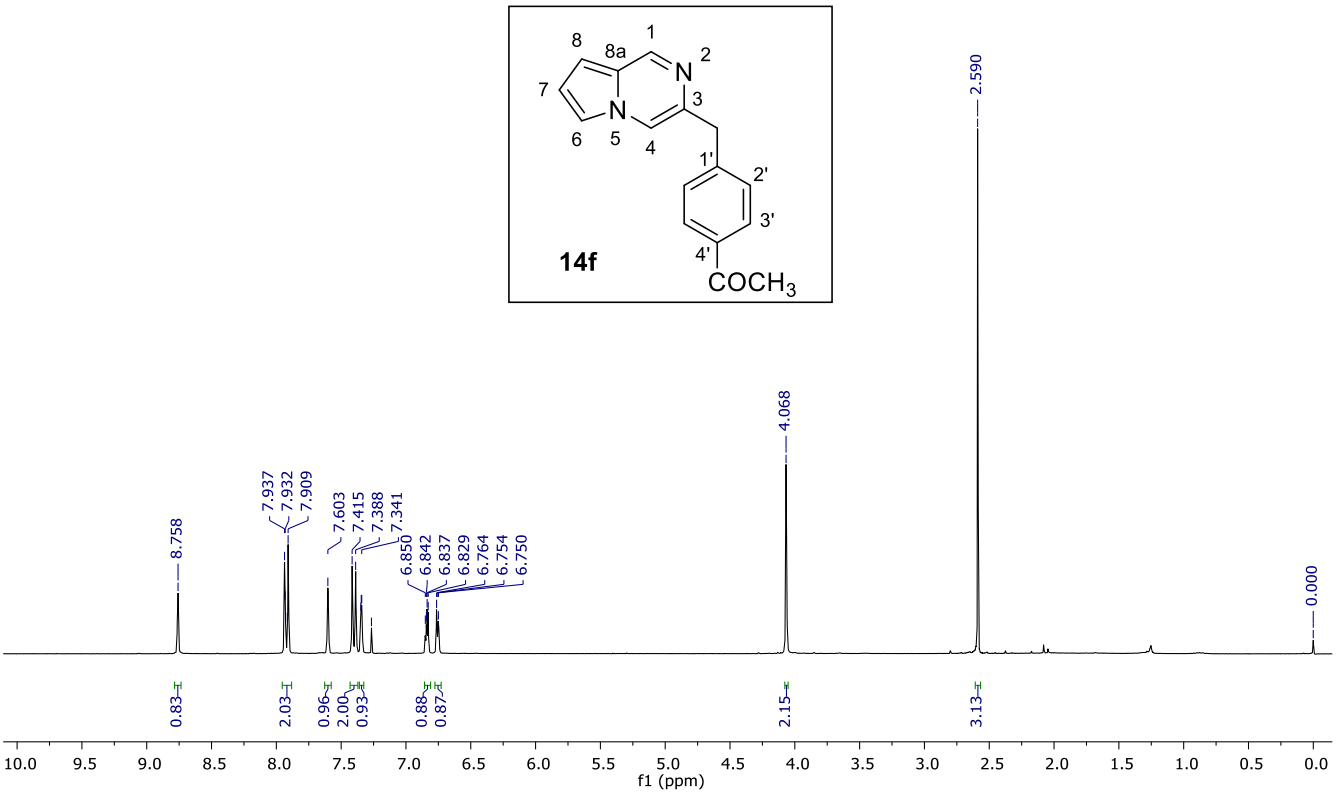
^{13}C NMR (125 MHz, $CDCl_3$) of compound **14d**.



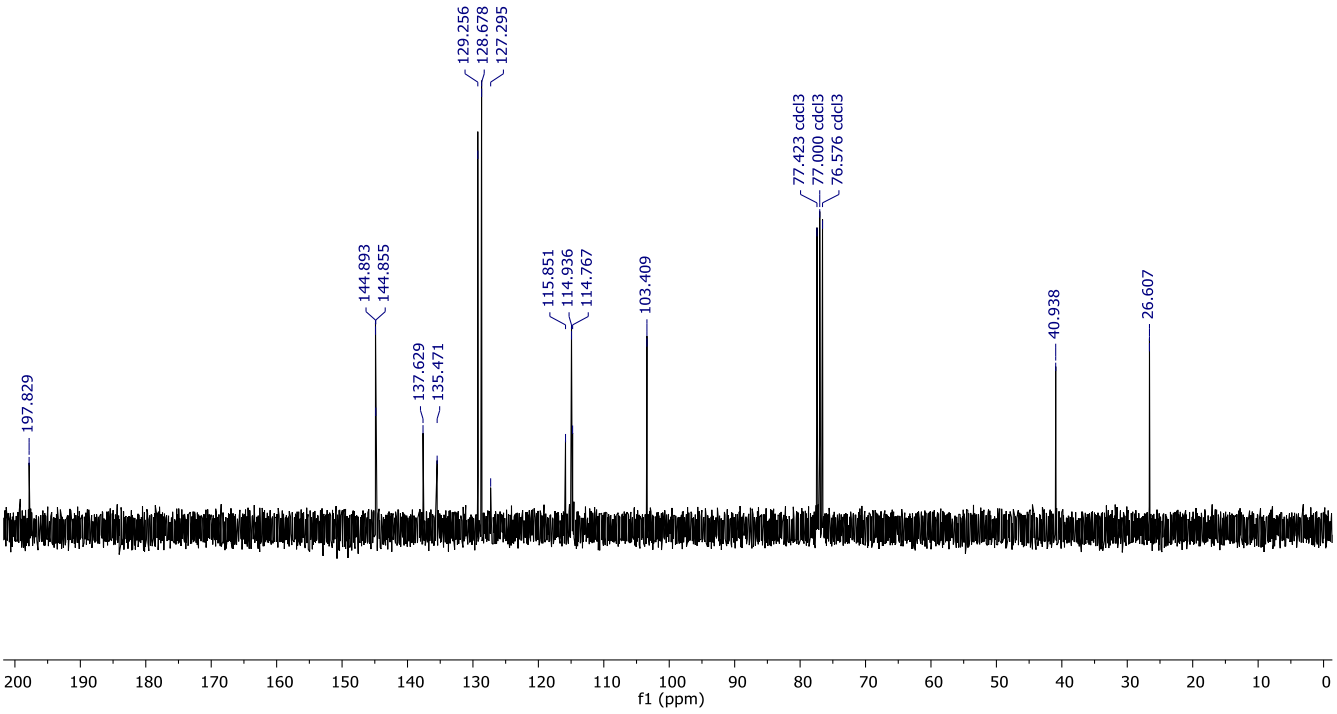
^{1}H NMR (750 MHz, $CDCl_3$) of compound **14e**.



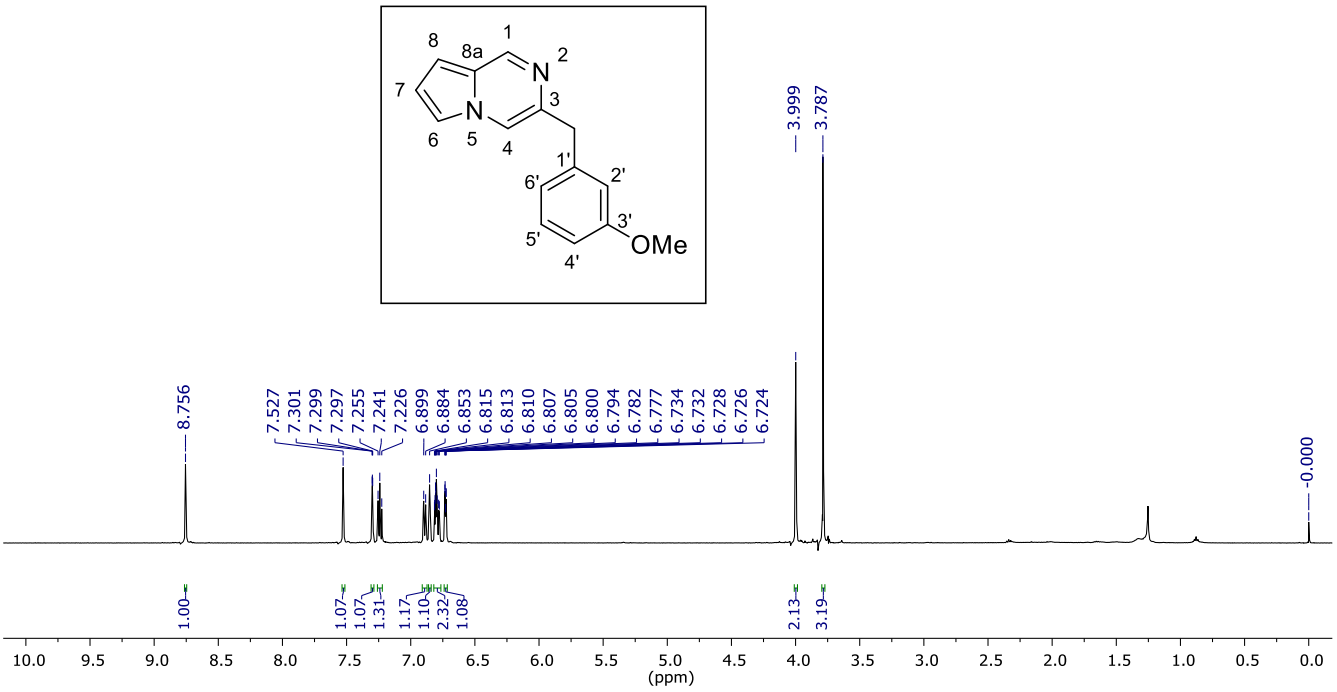
^{13}C NMR (187.5 MHz, $CDCl_3$) of compound **14e**.



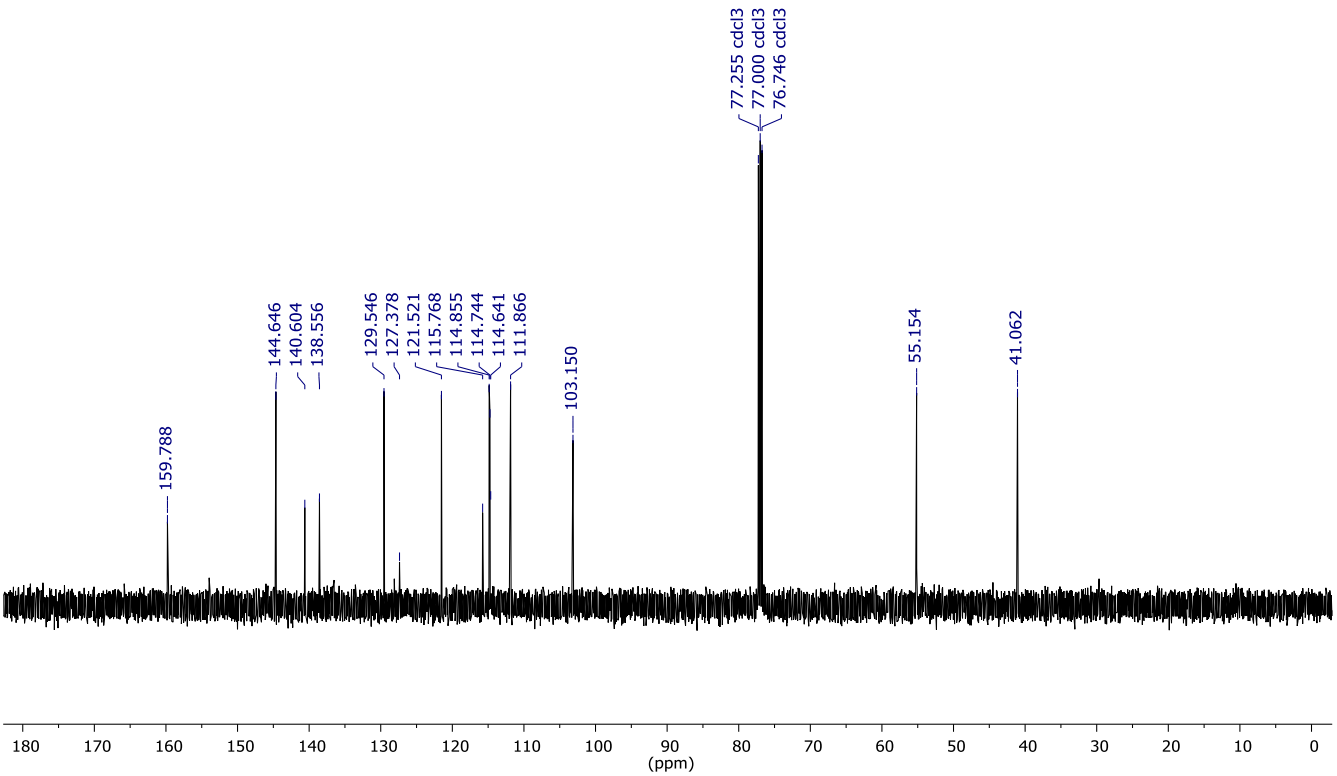
^{1}H NMR (300 MHz, $CDCl_3$) of compound **14f**.



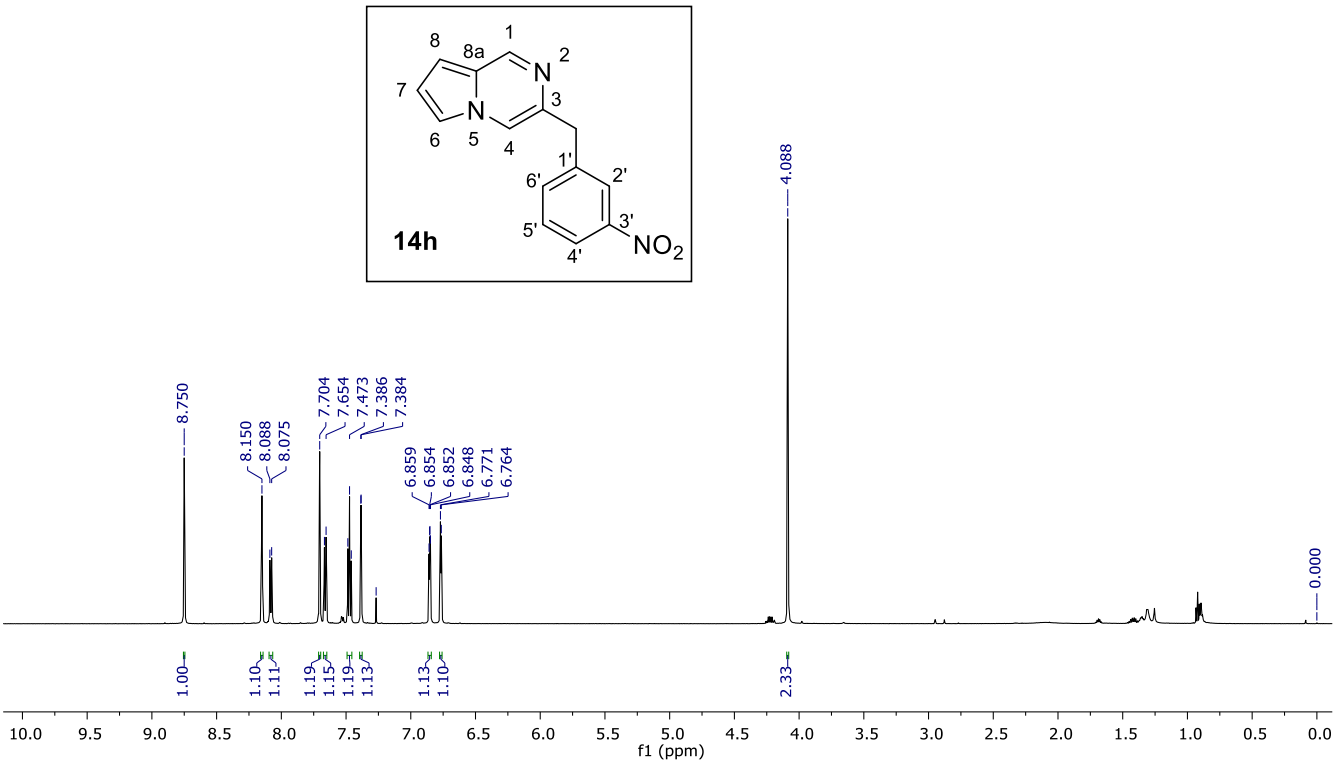
^{13}C NMR (75.4 MHz, $CDCl_3$) of compound **14f**.



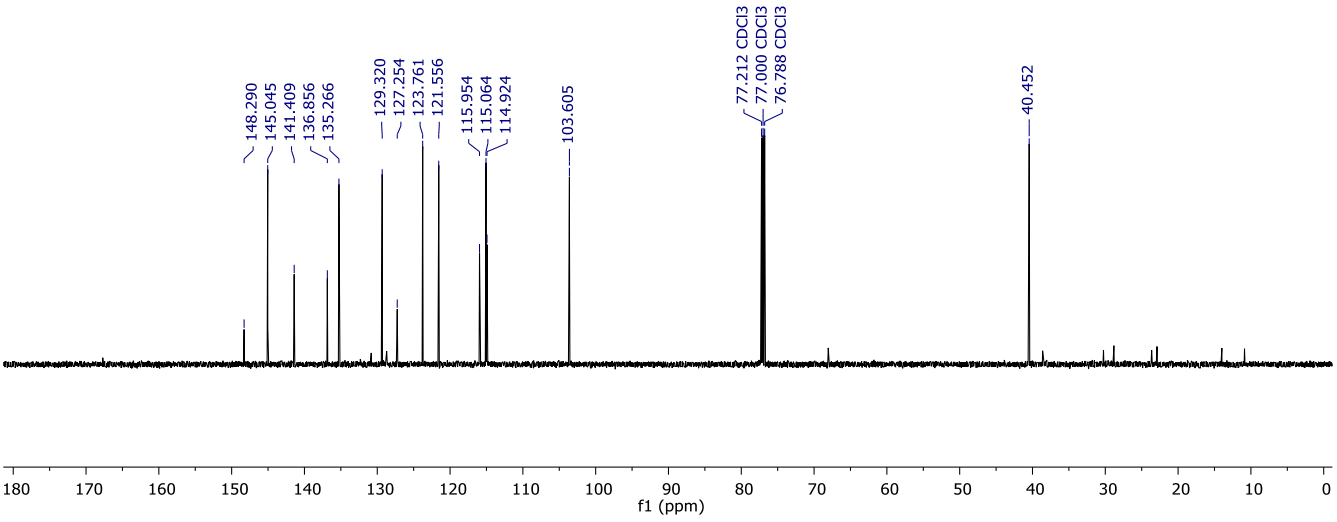
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14g**.



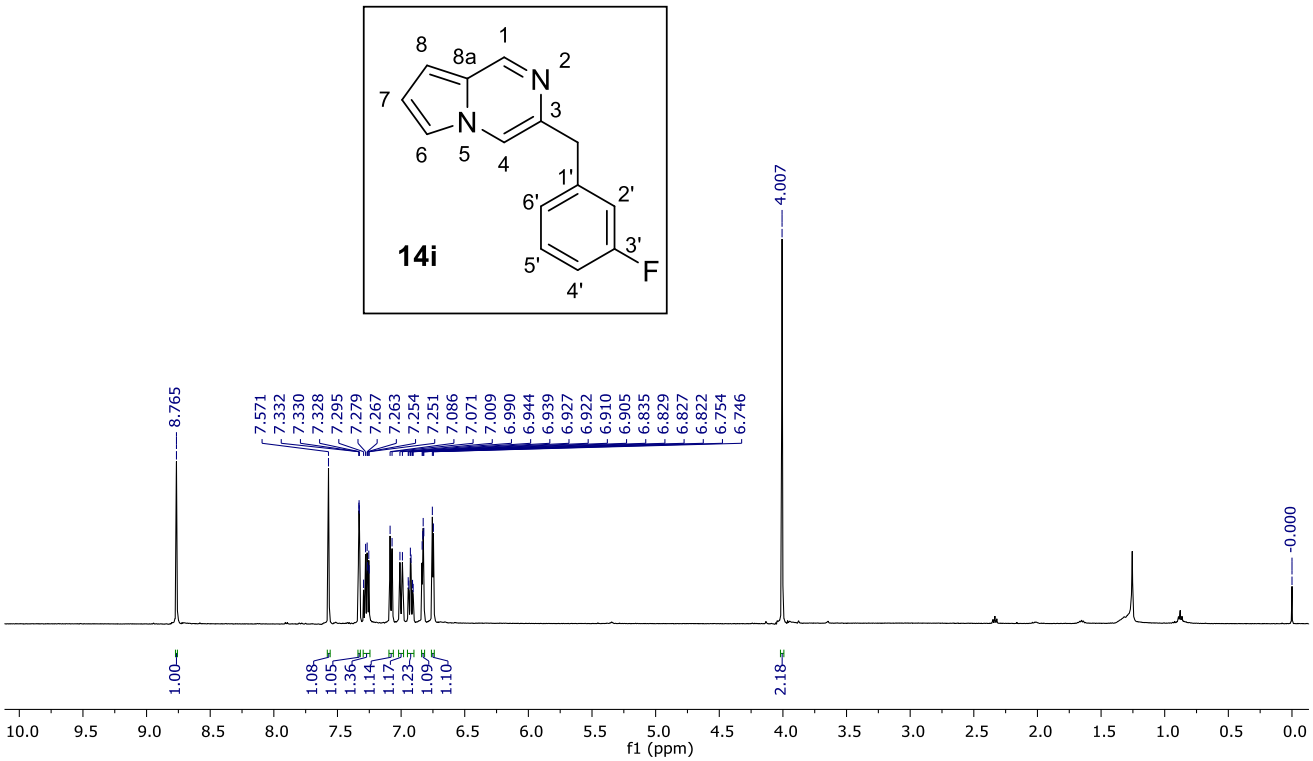
^{13}C NMR (125 MHz, $CDCl_3$) of compound **14g**.



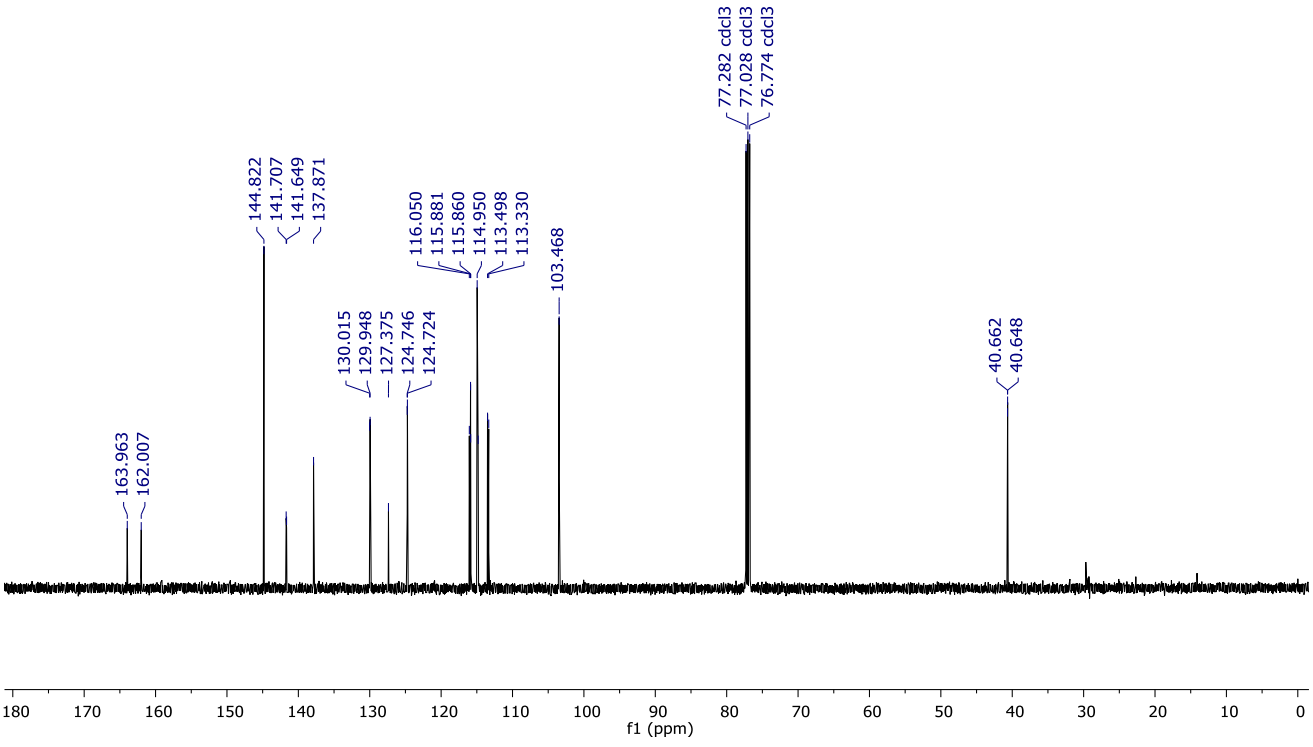
^{1}H NMR (600 MHz, $CDCl_3$) of compound **14h**.



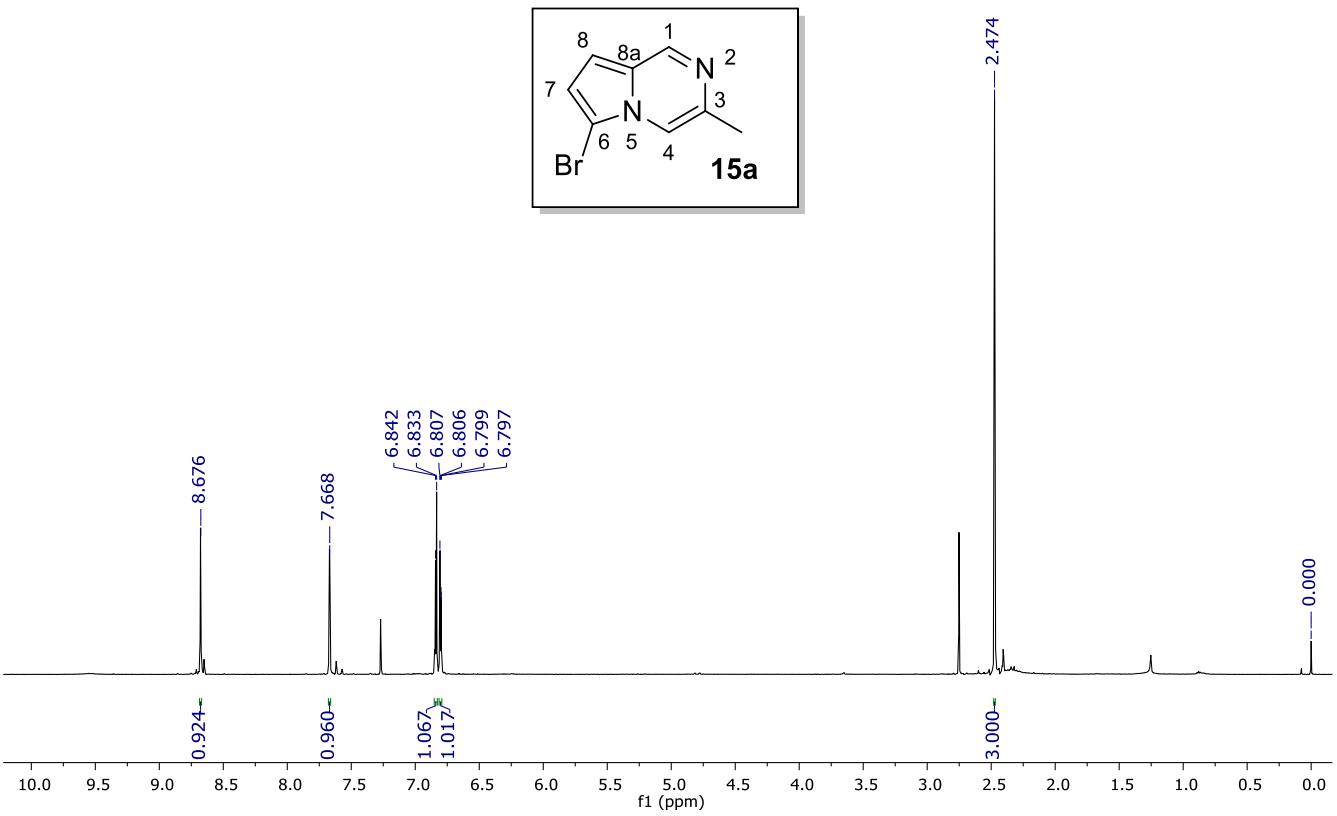
^{13}C NMR (150 MHz, $CDCl_3$) of compound **14h**.



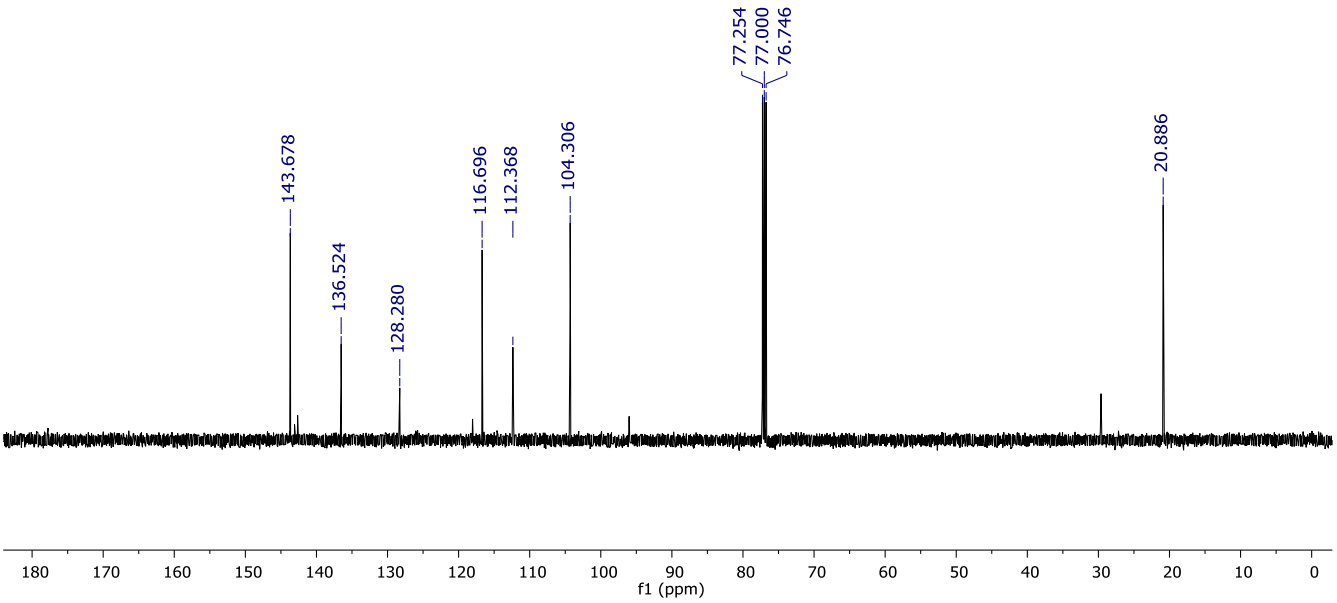
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14i**.



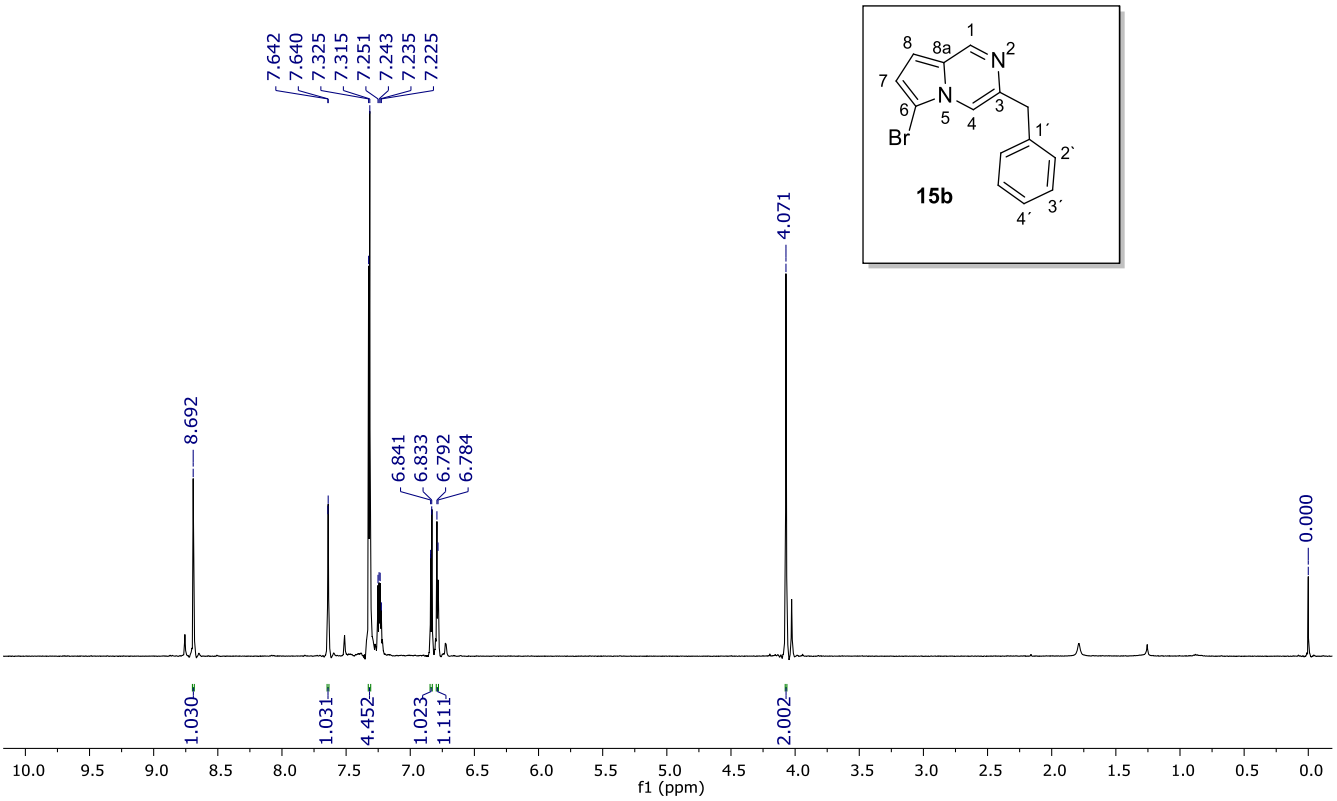
^{13}C NMR (125 MHz, $CDCl_3$) of compound **14i**.



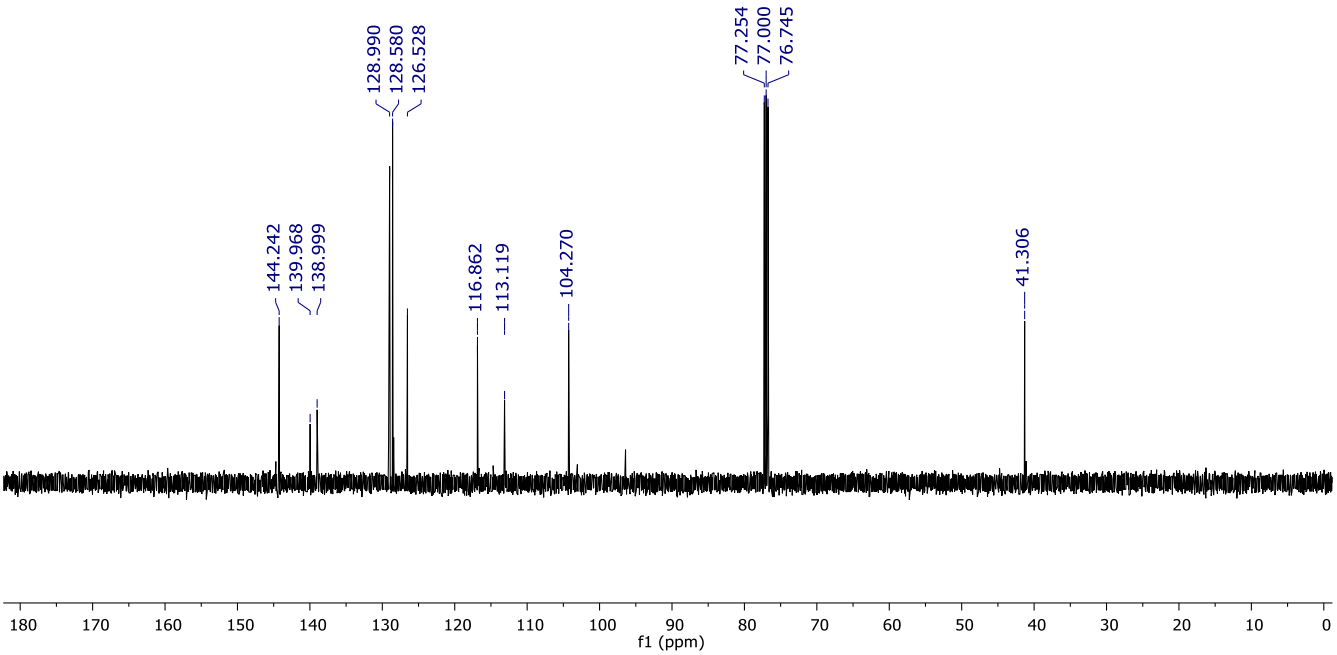
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15a**.



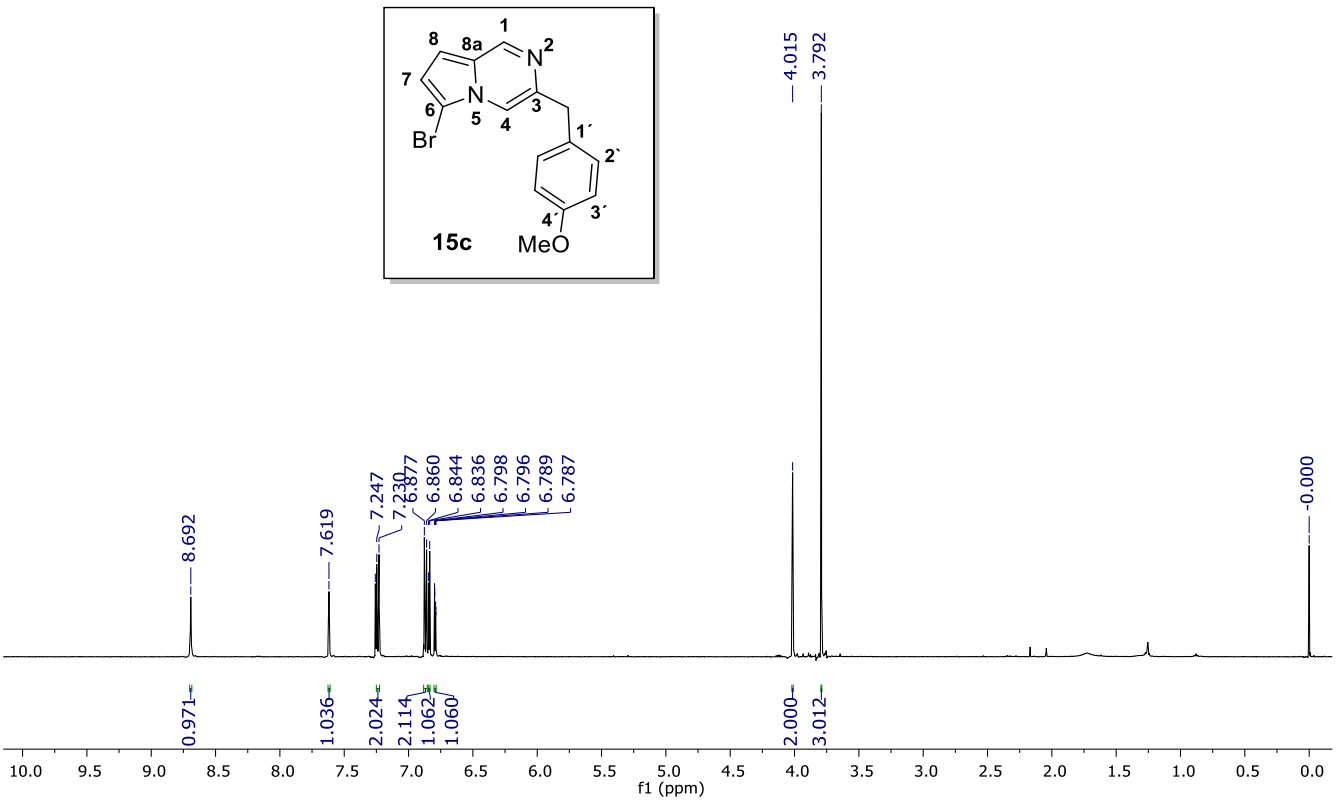
^{13}C NMR (125 MHz, $CDCl_3$) of compound **15a**.



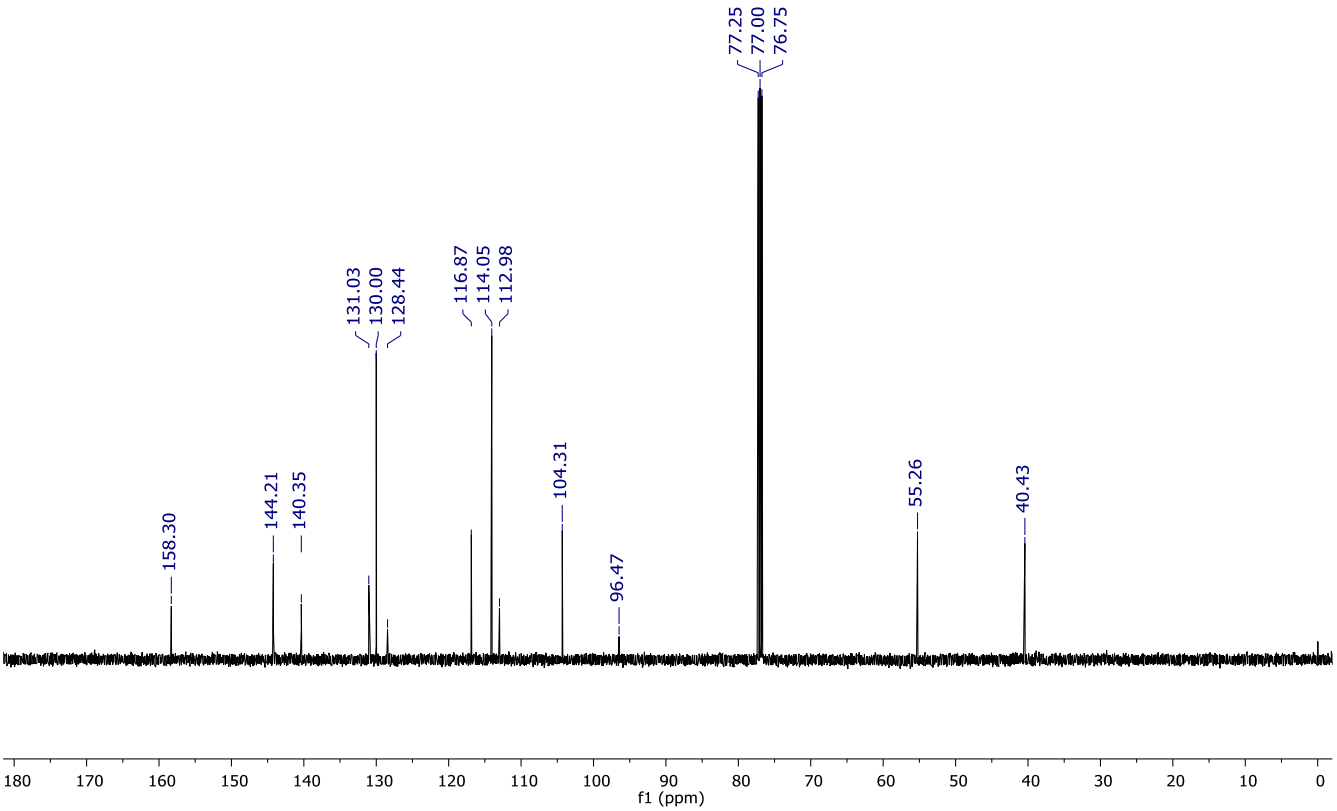
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15b**.



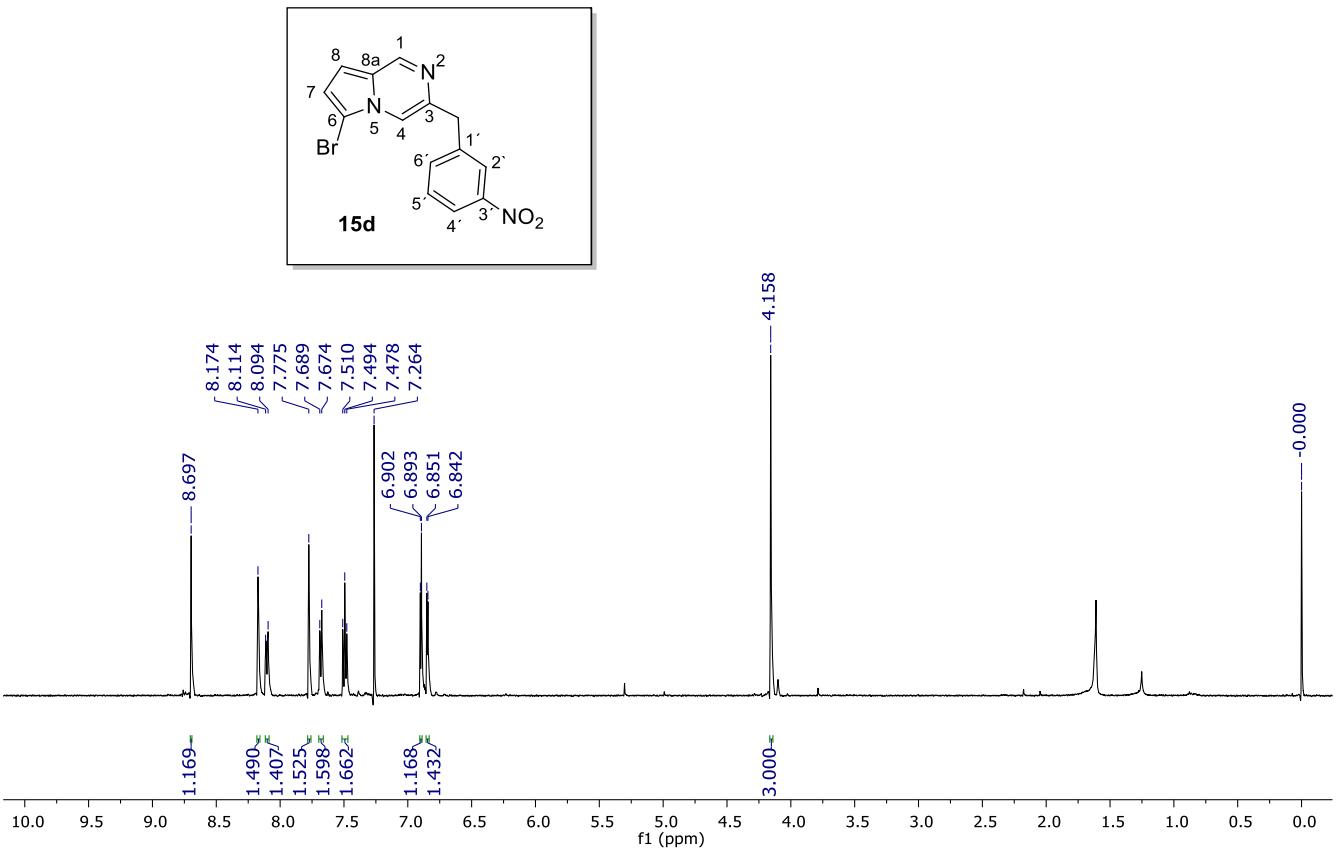
^{13}C NMR (125 MHz, $CDCl_3$) of compound **15b**.



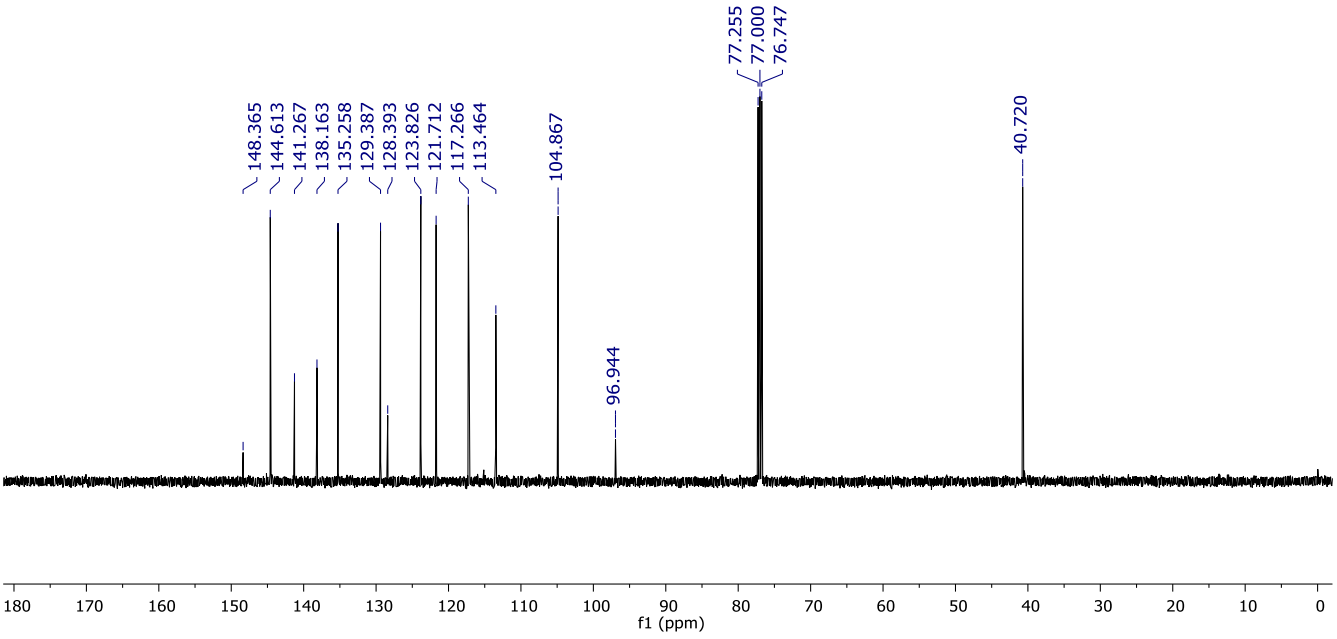
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15c**.



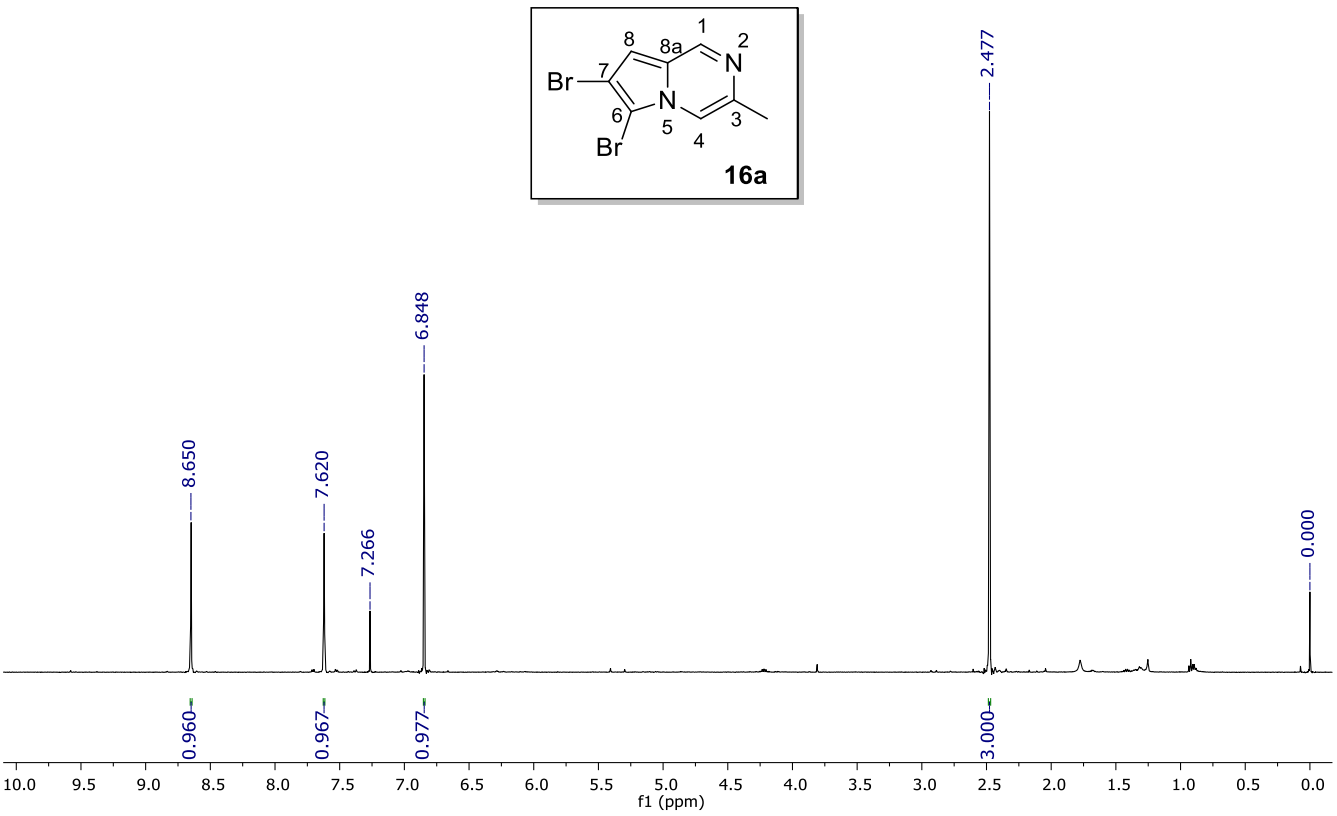
^{13}C NMR (125 MHz, $CDCl_3$) of compound **15c**.



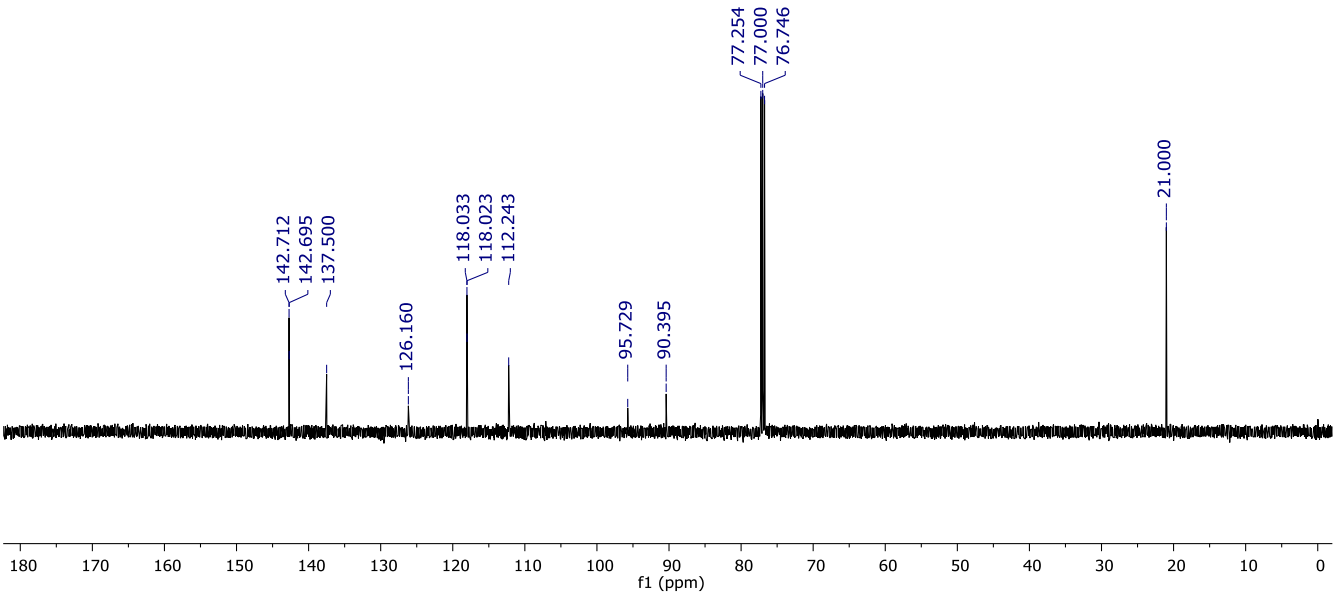
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15d**.



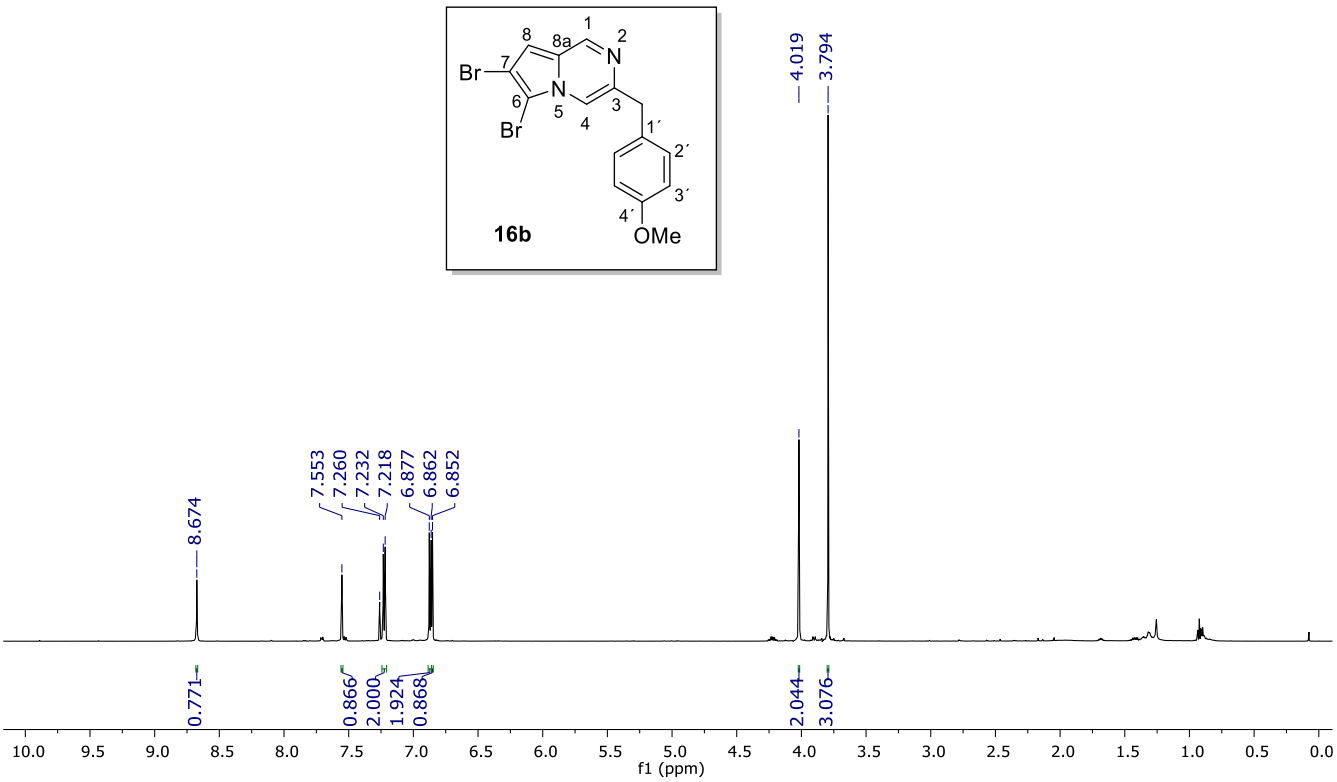
^{13}C NMR (125 MHz, $CDCl_3$) of compound **15d**.



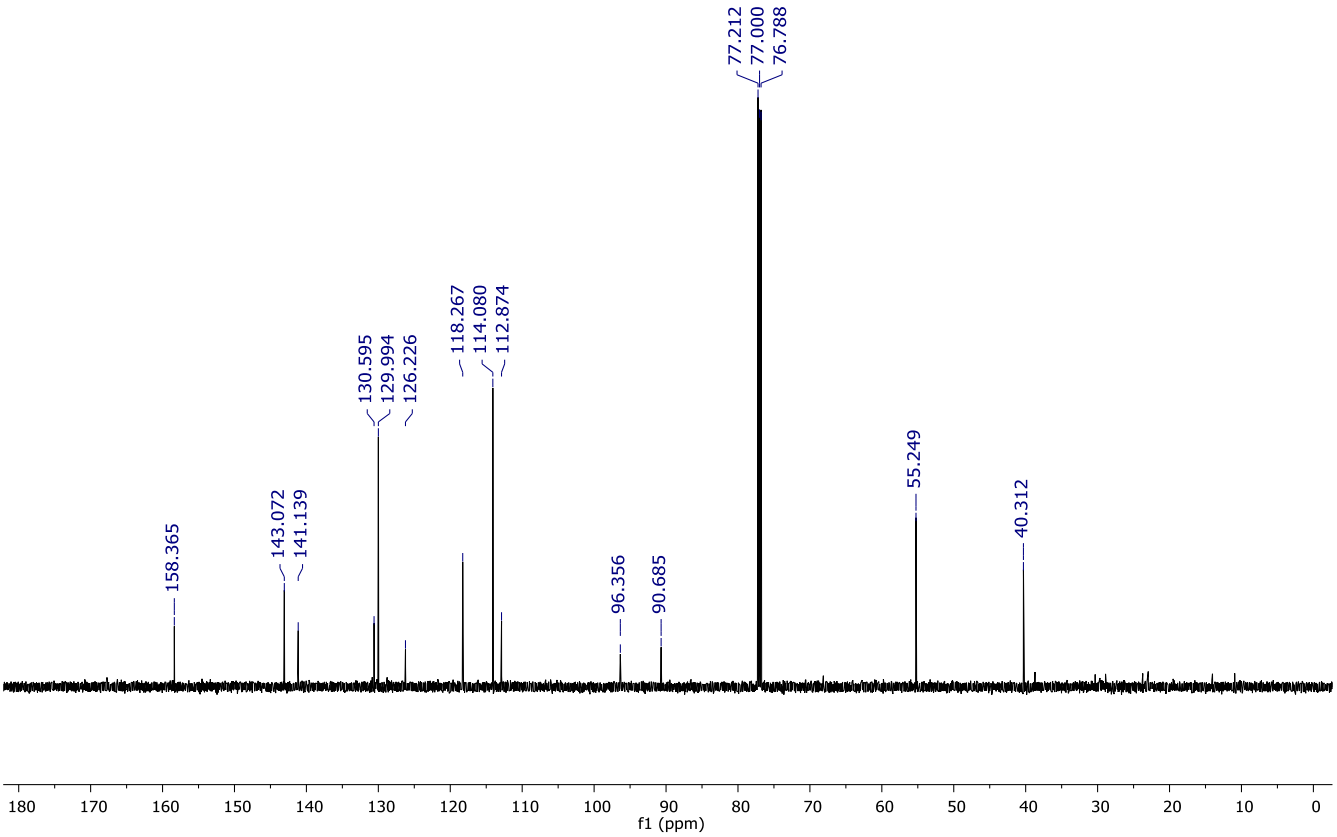
^{1}H NMR (500 MHz, $CDCl_3$) of compound **16a**.



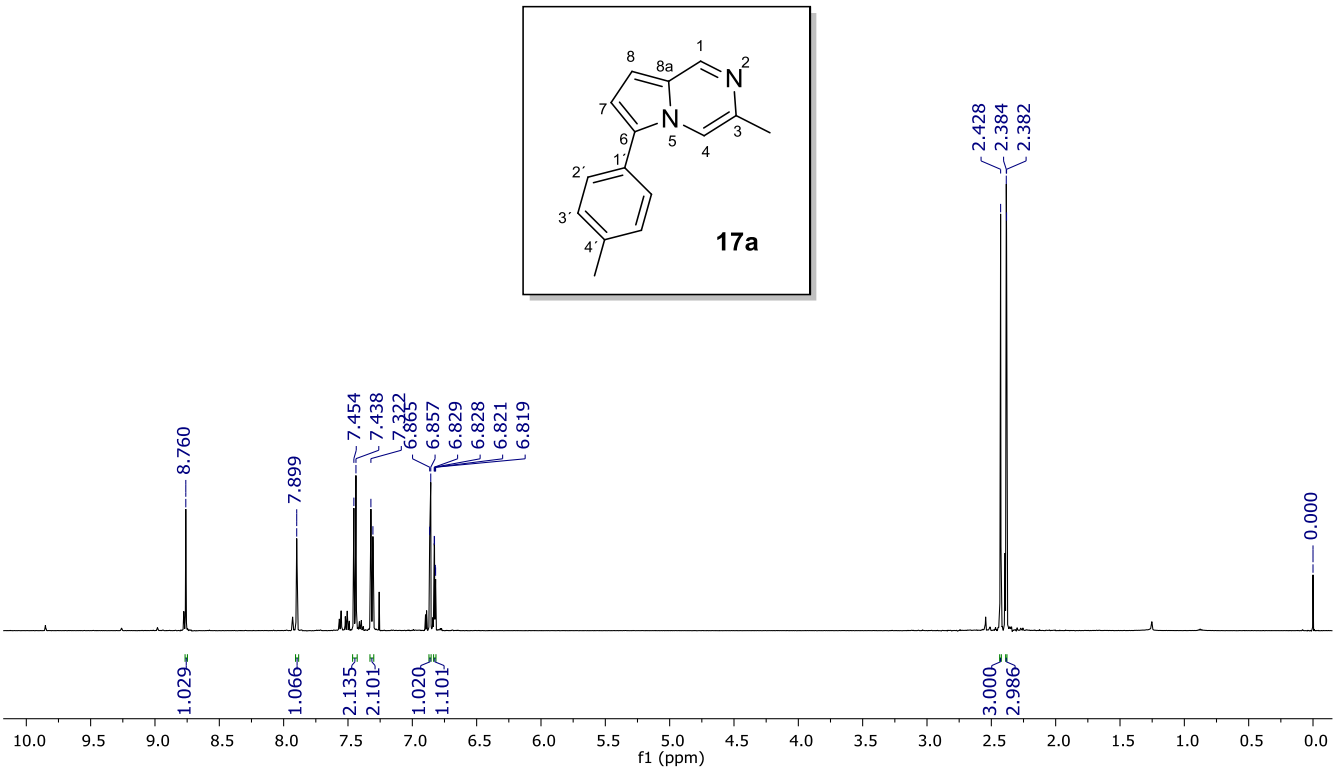
^{13}C NMR (125 MHz, $CDCl_3$) of compound **16a**.



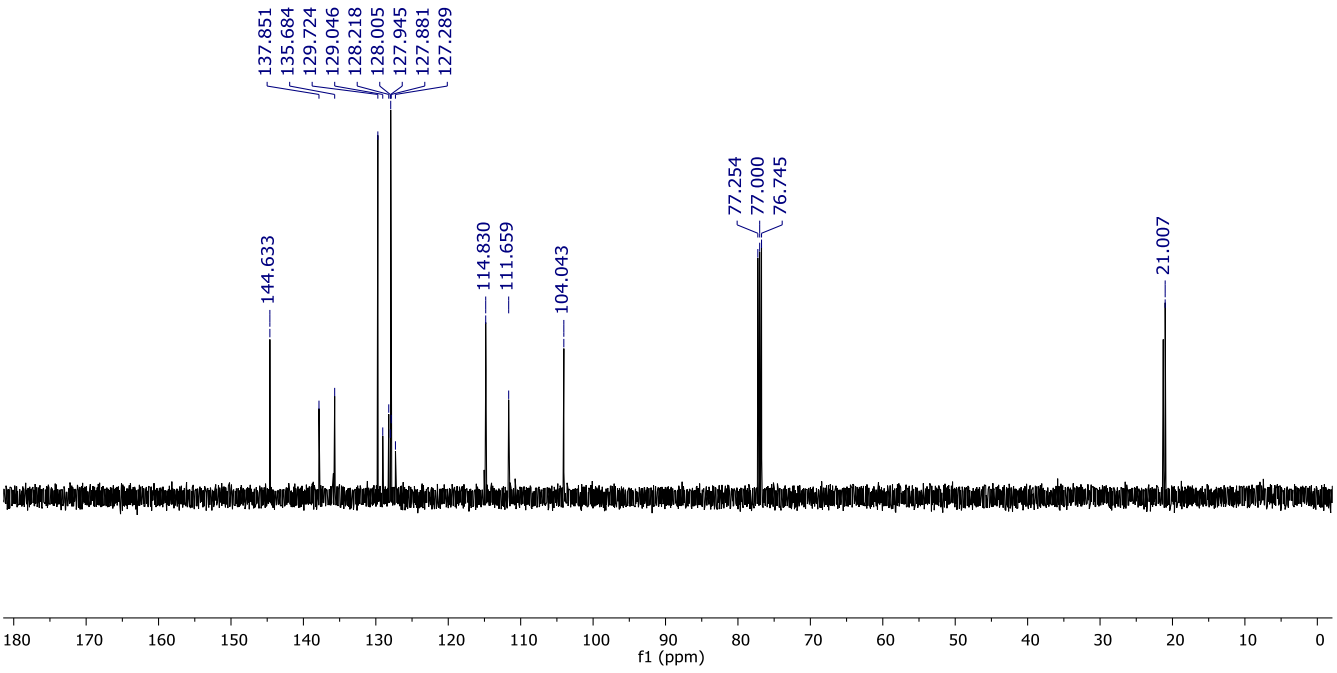
^{1}H NMR (600 MHz, $CDCl_3$) of compound **16b**.



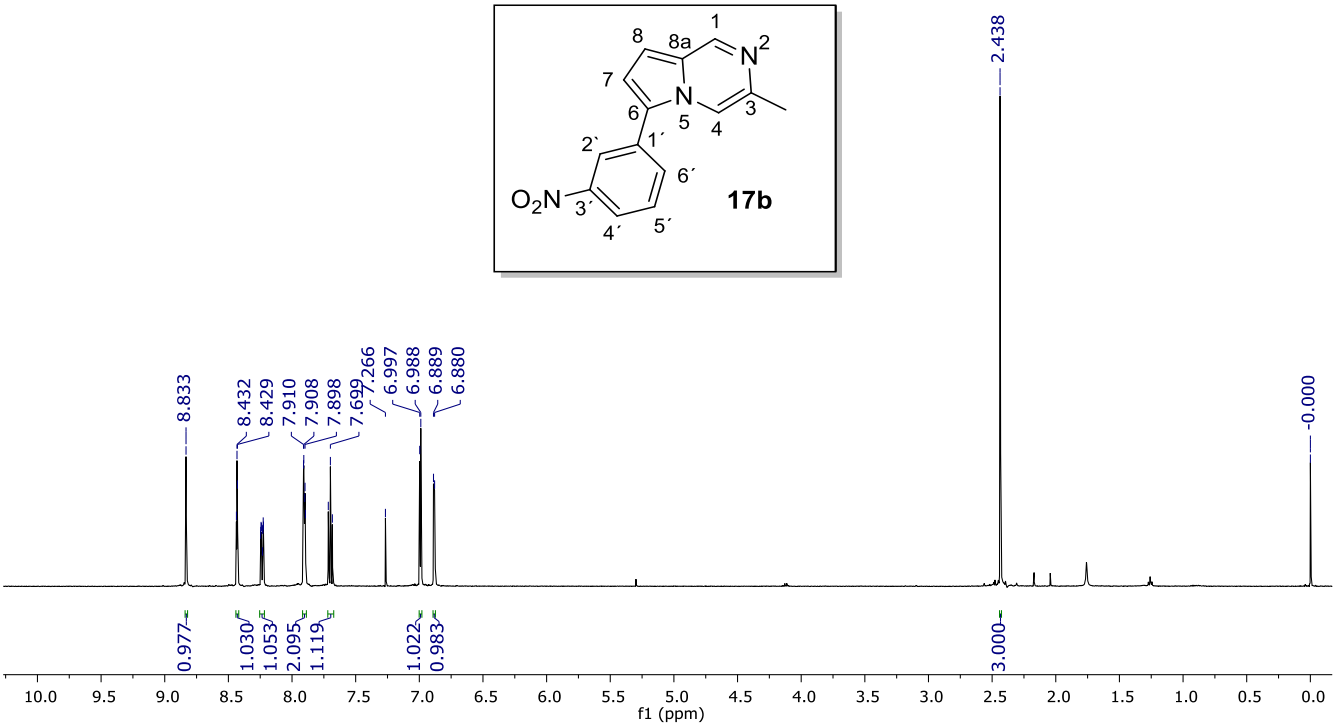
^{13}C NMR (150 MHz, $CDCl_3$) of compound **16b**.



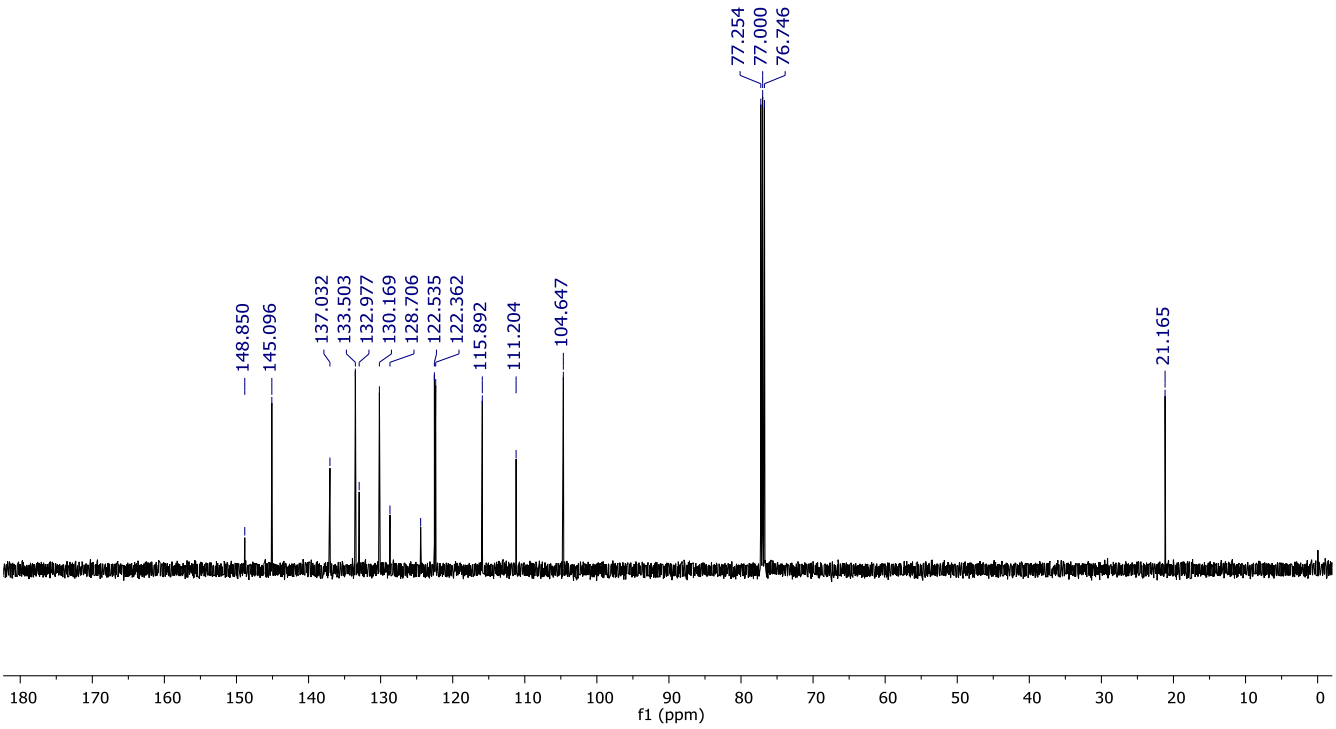
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17a**.



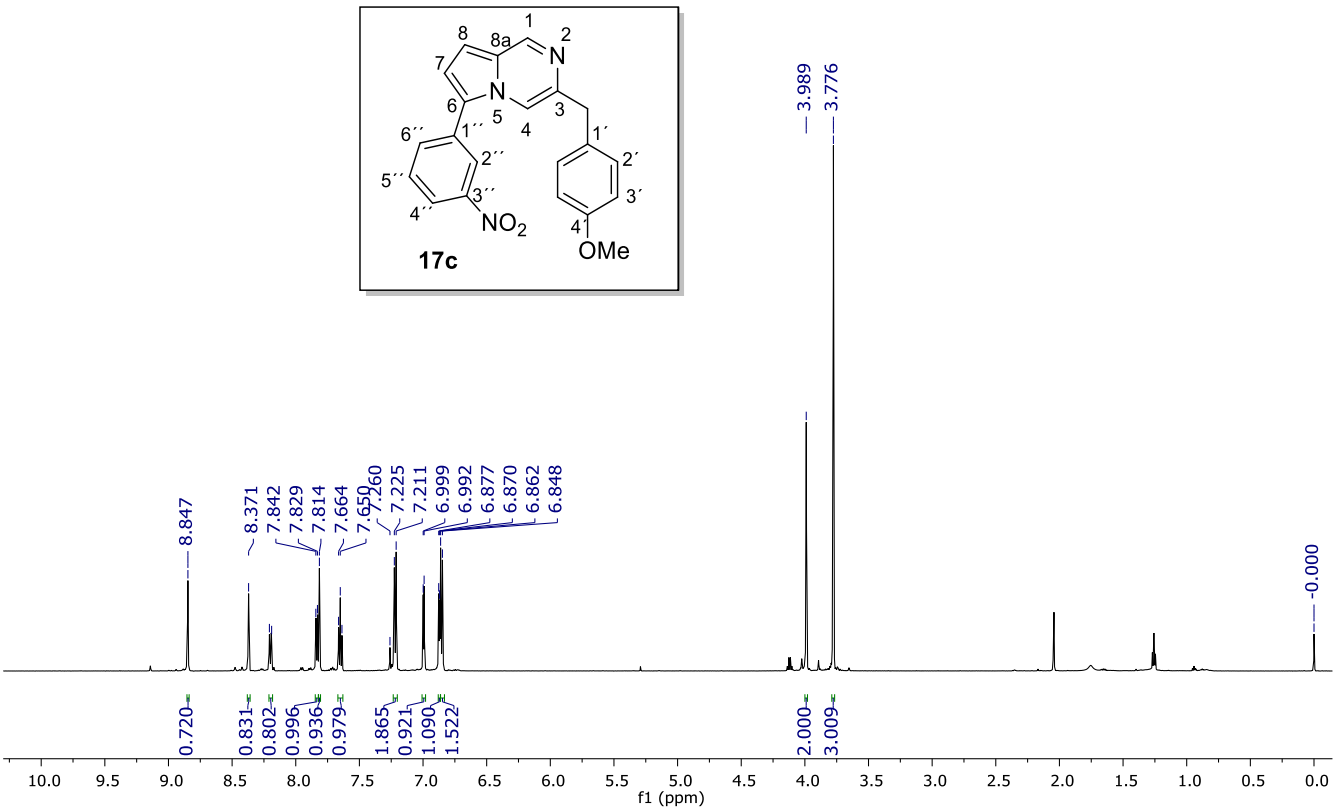
^{13}C NMR (125 MHz, $CDCl_3$) of compound **17a**.



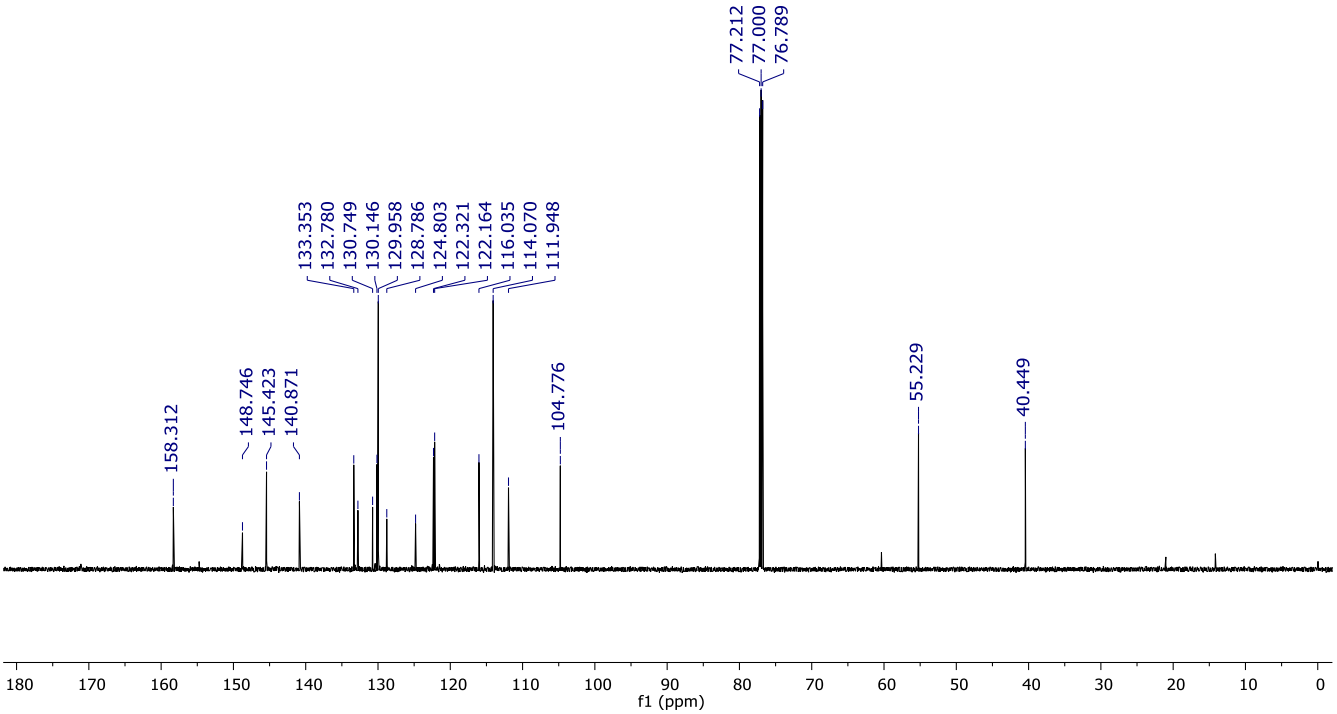
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17b**.



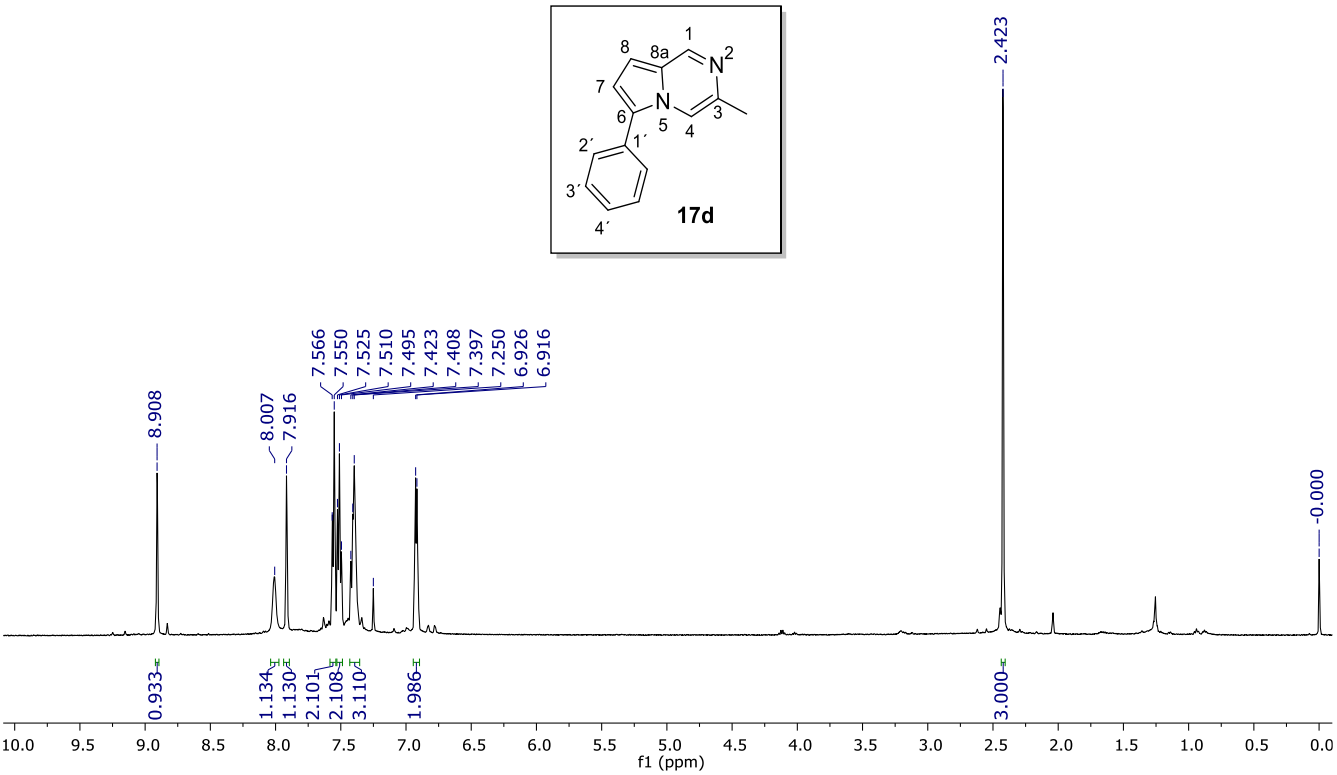
^{13}C NMR (125 MHz, $CDCl_3$) of compound **17b**.



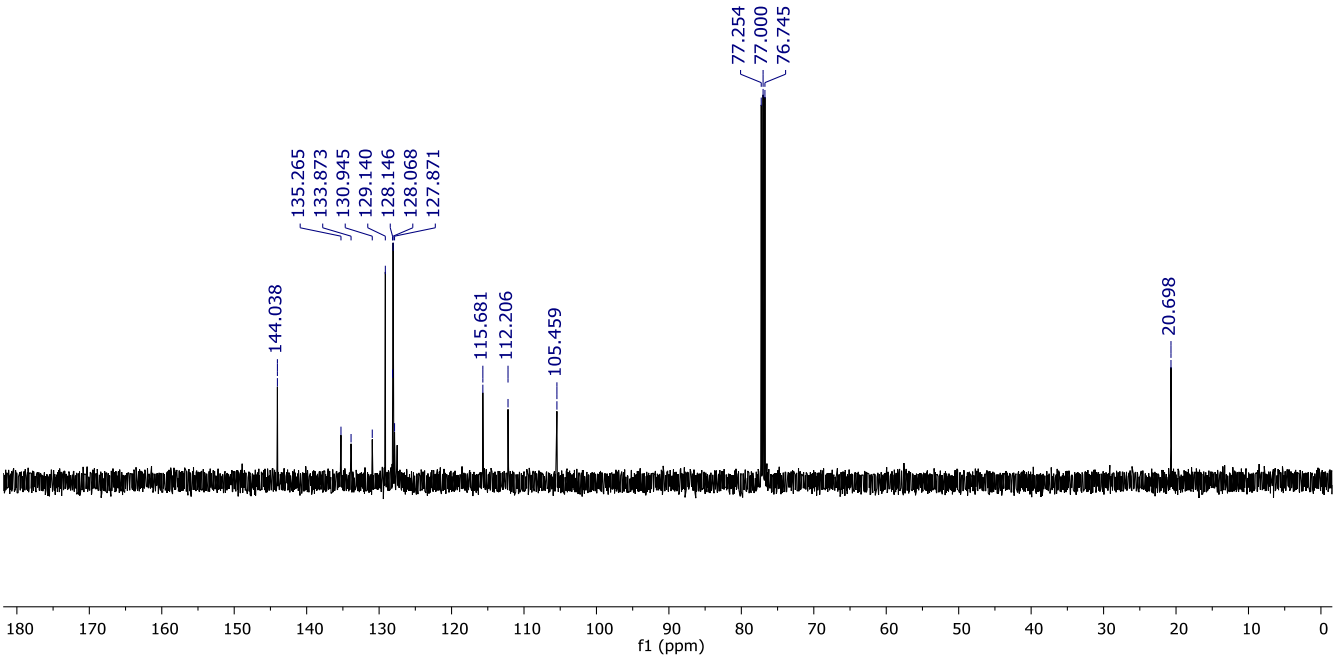
^{1}H NMR (600 MHz, $CDCl_3$) of compound **17c**.



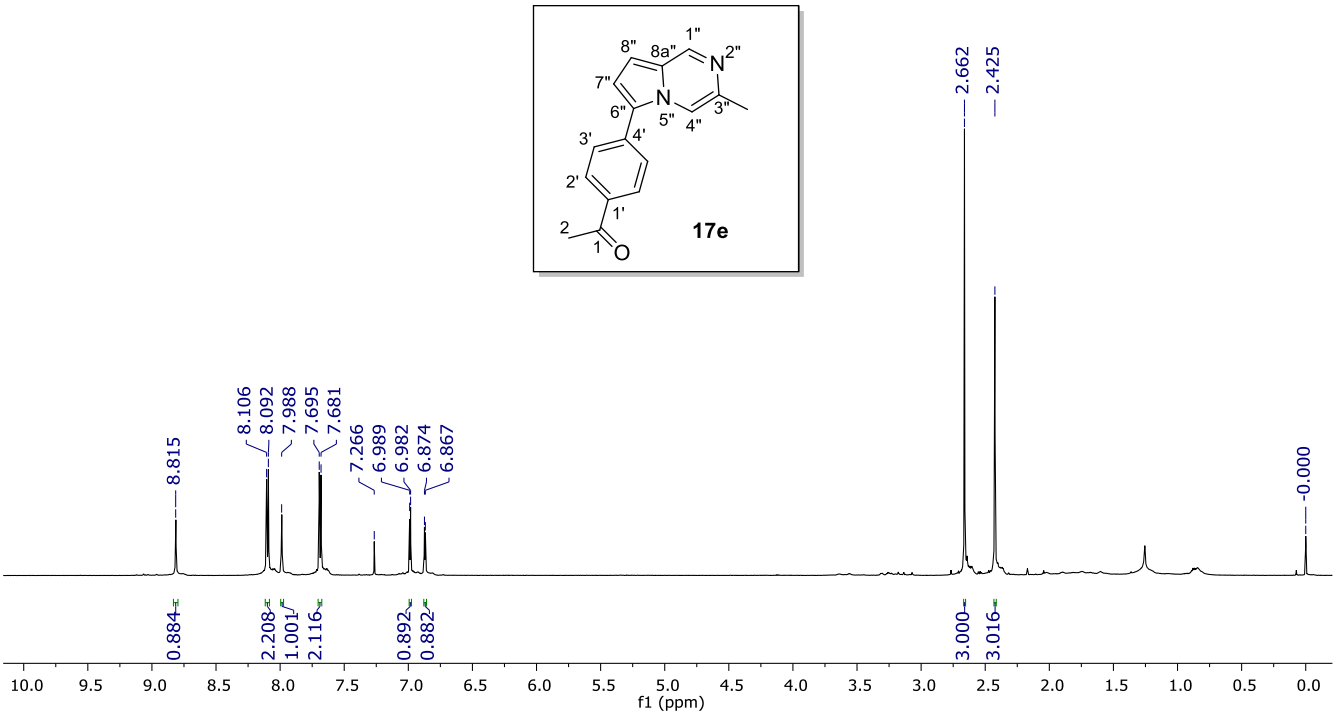
^{13}C NMR (150 MHz, $CDCl_3$) of compound **17c**.



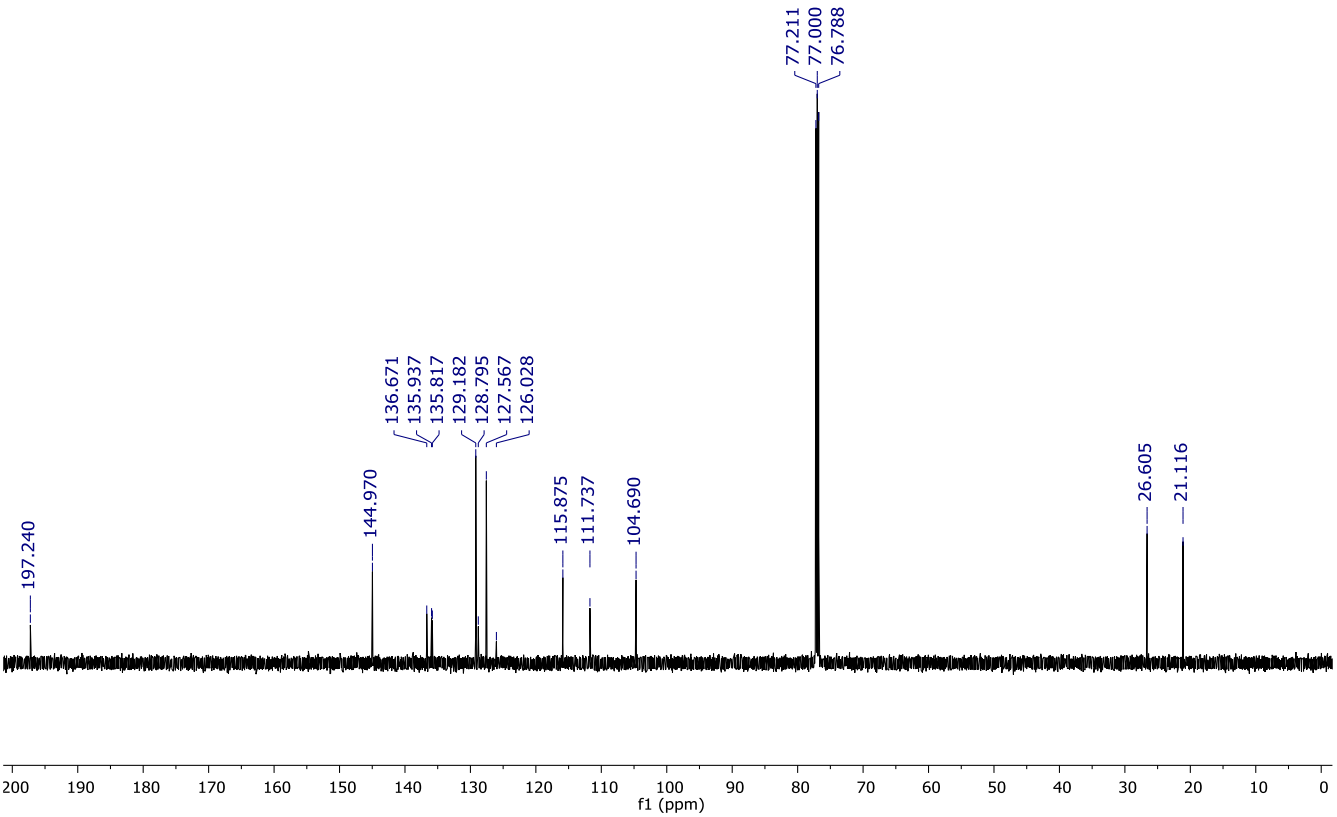
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17d**.



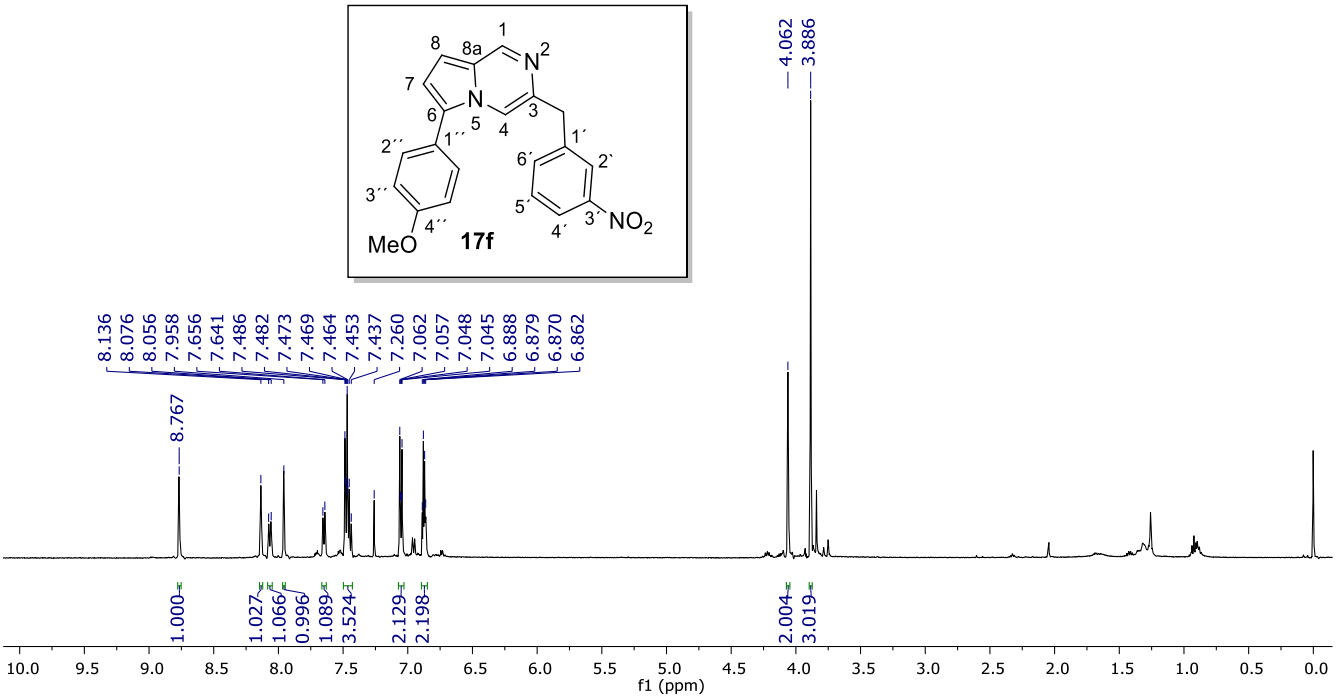
^{13}C NMR (125 MHz, $CDCl_3$) of compound **17d**.



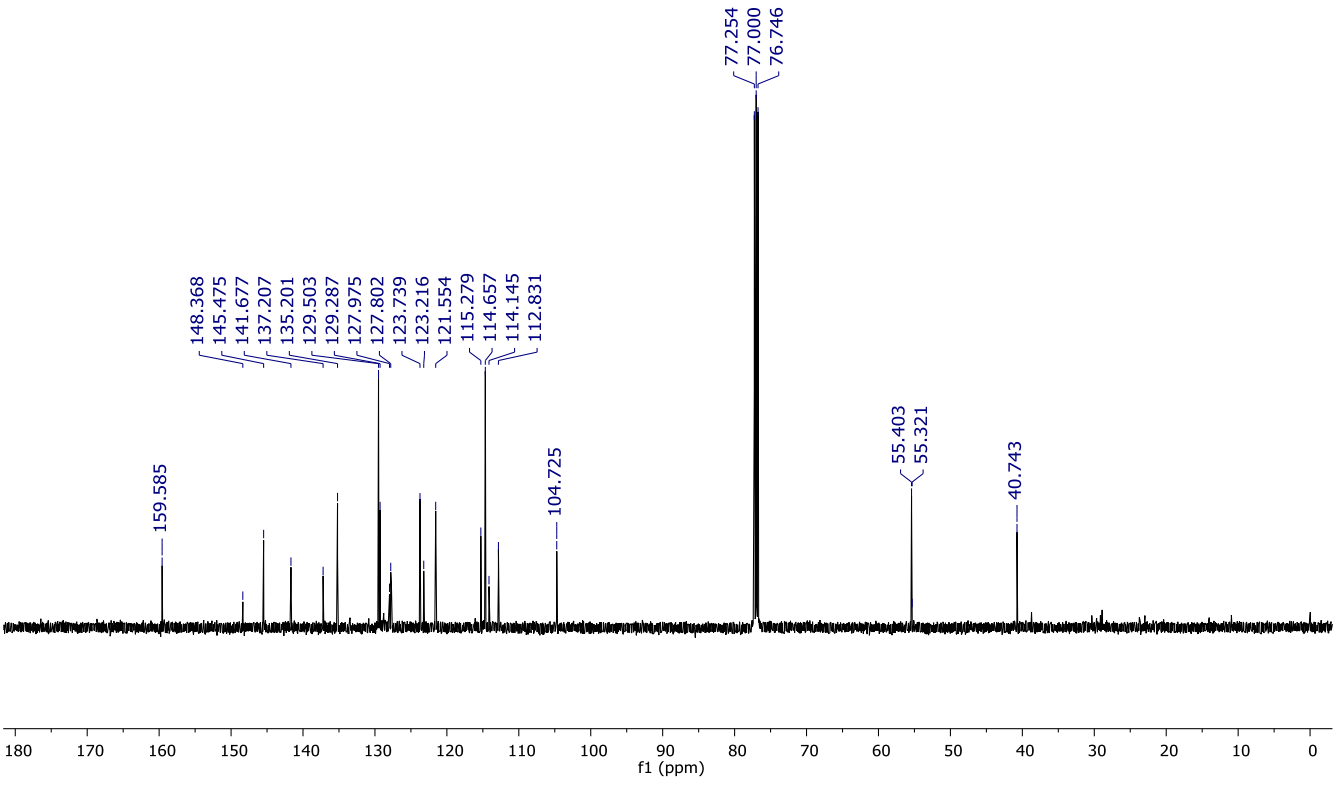
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17e**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **17e**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **17f**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **17f**.