Supporting Information for

1,5-Electrocyclization of conjugated azomethine ylides derived from 3-formyl chromene and *N*-alkyl amino acids/esters

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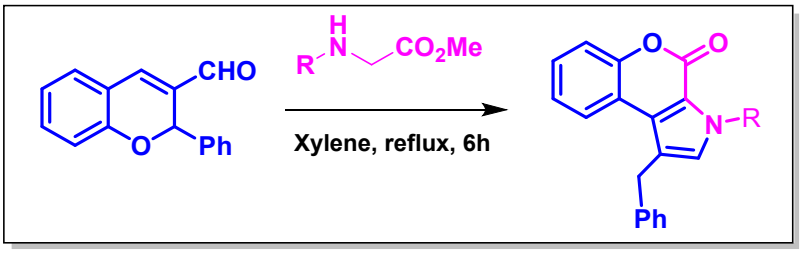

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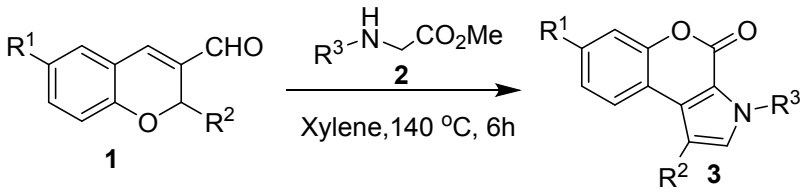
1. General Methods

All solvents were dried according to standard literature procedures. Unless otherwise noted, reactions were performed in flame-dried glassware under an atmosphere of dry argon. Dichloromethane was dried over Calcium hydride prior to use. ^{1}H NMR spectra were recorded at 500 MHz, 300 MHz and 400 MHz and ^{13}C NMR at 125 MHz, 100 MHz and 75MHz. For ^{1}H NMR, tetramethylsilane (TMS) was used as internal standard ($\delta = 0$) and the values are reported as follows: chemical shift, multiplicity, integration (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet, dd = doublet of doublet), and the coupling constants in Hz. For ^{13}C NMR, CDCl3 ($\delta = 77.00$) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS and HRMS data were obtained using ESI ionization. IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimeters (cm^{-1}). Melting points were measured on micro melting point apparatus. Crude products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to iodine vapours and/or by exposure to methanolic acidic solution of 2-napthol followed by heating (<1 min) on a hot plate (~250°C).

Experimental procedure

Preparation of 1-Benzyl-7-chloro-3-phenethylchromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3)



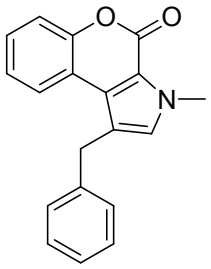
R^1 = -H, Cl, Br, OMe
R^2 = -H, Ph, O-methoxy phenyl
R^3 = -Me, Bn, CH_2-CH_2-Ph

A mixture of 2*H*-chromene-3-carbaldehyde **1** (1.1 equiv) and *N*-alkylated amino ester **2** (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the pure product.

2. Characterization data of products

1-Benzyl-3-methylchromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3a):

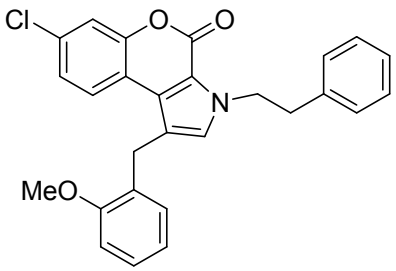
A mixture of 2-phenyl-2*H*-chromene-3-carbaldehyde **1** (1.1 equiv) and ethyl *N*-methylglycinate **2** (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (1:9 of EtOAc/hexane) to give the pure product 3a.



White solid, m.p.152-153°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.39 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.26 – 7.23 (m, 3H), 7.20 – 7.15 (m, 1H), 6.73 (s, 1H), 4.24 (s, 2H), 4.06 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 155.4, 151.3, 139.3, 132.8, 128.7, 128.5, 127.1, 126.9, 126.5, 124.0, 123.5, 118.9, 117.7, 117.3, 117.2, 36.0, 32.7; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 290; HRMS (EI): m/z calcd for $C_{19}H_{15}NO_2$: 290.11028; found: 290.11035.

7-Chloro-1-(2-methoxybenzyl)-3-phenethylchromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3b):-

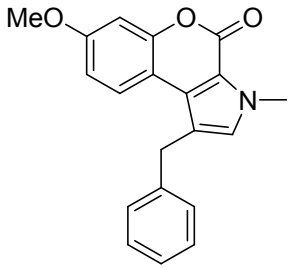
A mixture of 6-chloro-2-(2-methoxyphenyl)-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and methyl phenethylglycinate **2** (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (3:7 of EtOAc/hexane) to give the pure product 3b.



White solid, m.p.145-146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.3 Hz, 1H), 7.32 – 7.20 (m, 6H), 7.08 (d, *J* = 6.4 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 4.4 Hz, 2H), 6.54 (s, 1H), 4.62 (t, *J* = 7.0 Hz, 2H), 4.08 (s, 2H), 3.90 (s, 3H), 3.13 (t, *J* = 7.0 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 154.6, 149.6, 137.8, 132.6, 129.7, 129.2, 128.9, 128.5, 127.7, 127.2, 126.9, 126.7, 126.2, 123.4, 120.6, 120.2, 118.2, 117.5, 116.2, 110.2, 55.4, 50.7, 38.1, 25.6 ppm; IR (KBr): ν_{max} 3456, 2987, 1655, 1484, 1209 cm^{-1}; MS (EI): m/z ([M+1]): 444; HRMS (EI): m/z calcd for $C_{27}H_{22}ClNO_3$: 444.12882; found: 444.12890.

1-Benzyl-7-methoxy-3-methylchromeno [3,4-*b*]pyrrol-4(3*H*)-one(3c):-

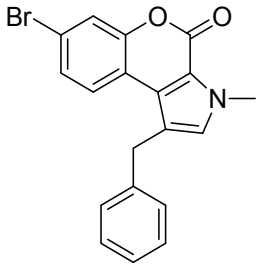
A mixture of 6-methoxy-2-phenyl-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and ethyl methylglycinate **2** (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (2:8 of EtOAc/hexane) to give the pure product 3c.



White solid, m.p.129-130 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.10 (d, *J* = 2.9 Hz, 1H), 6.86 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.81 (s, 1H), 4.24 (s, 2H), 4.08 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 145.6, 139.3, 132.8, 128.7, 128.3, 126.9, 126.5, 117.9, 117.6, 117.1, 114.3, 106.9, 55.6, 36.0, 32.6.; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 320; HRMS (EI): m/z calcd for $C_{20}H_{17}NO_3$: 320.12084; found: 320.12096.

1-Benzyl-7-bromo-3-methylchromeno [3, 4-*b*] pyrrol-4(3H)-one (3d):-

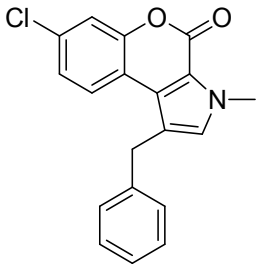
A mixture of 6-bromo-2-phenyl-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and ethyl methylglycinate **2** (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (1:9 of EtOAc/hexane) to give the pure product 3d.



White solid, m.p.167-168 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.3 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.34 (dd, *J* = 10.1, 4.8 Hz, 2H), 7.26–7.23 (m, 4H), 6.74 (s, 1H), 4.20 (s, 2H), 4.05 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 141.5, 133.5, 131.1, 128.6, 128.3, 125.8, 124.1, 123.1, 122.0, 120.8, 116.3, 116.1, 111.8, 36.3, 31.7; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 368; HRMS (EI): m/z calcd for $C_{19}H_{14}BrNO_2$: 368.02079; found: 368.102085.

1-Benzyl-7-chloro-3-methylchromeno [3,4-*b*]pyrrol-4(3*H*)-one (3e):-

A mixture of 6-chloro-2-phenyl-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and ethyl methylglycinate **2** (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (1:9 of EtOAc/hexane) to give the pure product 3e.

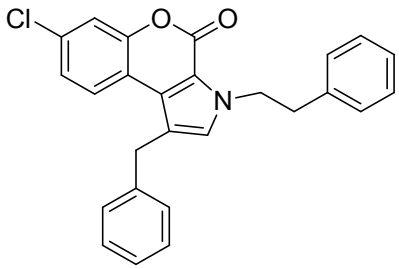


White solid, m.p.145-146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.34 (dd, *J* = 13.8, 6.6 Hz, 2H), 7.27 (dd, *J* = 13.3, 5.0 Hz, 5H), 6.73 (s, 1H), 4.20 (s, 2H), 4.05 (s, 3H).; ^{13}C NMR (125

MHz, $CDCl_3$) δ 154.9, 149.6, 138.9, 132.9, 129.3, 128.8, 128.6, 127.0, 126.6, 125.7, 123.2, 120.1, 118.4, 118.3, 117.4, 36.1, 32.7.; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 324; HRMS (EI): m/z calcd for $C_{19}H_{14}ClNO_2$: 324.07131; found: 324.07145.

1-Benzyl-7-chloro-3-phenethylchromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3f):-

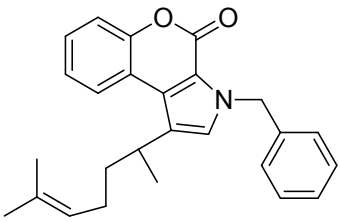
A mixture of 6-chloro-2-phenyl-2H-chromene-3-carbaldehyde 1 (1.1 equiv) and methyl phenethylglycinate 2 (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (2:8 of EtOAc/hexane) to give the pure product 3f.



White solid, m.p.125-126 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (t, J = 10.6 Hz, 1H), 7.34 – 7.22 (m, 8H), 7.15 – 7.03 (m, 4H), 6.44 (s, 1H), 4.61 (t, J = 7.0 Hz, 2H), 4.11 (s, 2H), 3.12 (t, J = 7.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 151.3, 139.2, 137.9, 132.6, 128.9, 128.6, 128.5, 128.5, 127.4, 127.2, 126.6, 126.4, 124.0, 123.6, 118.9, 117.2, 117.1, 116.2, 50.7, 38.1, 32.6; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 414; HRMS (EI): m/z calcd for $C_{26}H_{20}ClNO_2$: 414.10921; found: 414.11166.

3-Benzyl-1-(6-methylhept-5-en-2-yl) chromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3g):-

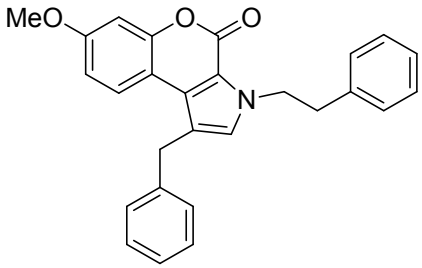
A mixture of 2-methyl-2-(4-methylpent-3-en-1-yl)-2H-chromene-3-carbaldehyde 1 (1.1 equiv) and ethyl benzylglycinate 2 (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (3:7 of EtOAc/hexane) to give the pure product 3g.



White solid, m.p.132-133 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 1H), 7.41 – 7.22 (m, 8H), 7.05 – 7.01 (m, 1H), 5.70 (q, *J* = 15.1 Hz, 2H), 5.22 – 5.09 (m, 1H), 3.35 – 3.20 (m, 1H), 2.13 – 2.02 (m, 2H), 1.86 – 1.73 (m, 1H), 1.69 (s, 3H), 1.60 (dd, *J* = 14.8, 7.0 Hz, 1H), 1.53 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3, 151.2, 137.6, 132.1, 129.0, 128.8, 128.4, 127.8, 127.4, 127.1, 126.6, 126.4, 124.0, 123.7, 119.1, 117.3, 116.4, 51.8, 37.4, 30.4, 25.8, 20.9, 17.6 ; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 386; HRMS (EI): m/z calcd for $C_{26}H_{27}NO_2$: 386.20418; found: 386.20424.

1-Benzyl-7-methoxy-3-phenethylchromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3h):-

A mixture of 6-methoxy-2-phenyl-2H-chromene-3-carbaldehyde 1 (1.1 equiv) and methyl phenethylglycinate 2 (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (3:7 of EtOAc/hexane) to give the pure product 3h.

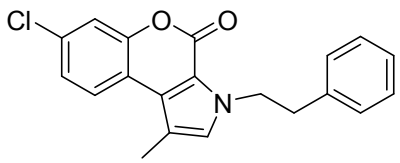


White solid, m.p.162-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 7H), 7.10 (dd, *J* = 11.6, 7.0 Hz, 5H), 6.87 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.51 (s, 1H), 4.63 (t, *J* = 7.0 Hz, 2H), 4.14 (s, 2H), 3.62 (s, 3H), 3.14 (t, *J* = 7.0 Hz, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 155.2, 145.6,

139.3, 138.0, 132.6, 129.0, 128.6, 128.5, 128.3, 127.4, 126.6, 126.4, 119.1, 117.9, 116.5, 114.5, 106.8, 55.6, 50.7, 38.1, 32.5.; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 410; HRMS (EI): m/z calcd for $C_{27}H_{23}NO_3$: 410.16779; found: 410.16786.

7-Chloro-1-methyl-3-phenethylchromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3i):-

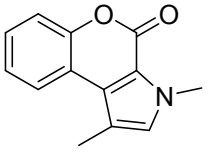
A mixture of 6-chloro-2H-chromene-3-carbaldehyde 1 (1.1 equiv) and methyl phenethylglycinate 2 (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (3:7 of EtOAc/hexane) to give the pure product 3i.



White solid, m.p.150-151 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.3 Hz, 1H), 7.46 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.33 – 7.24 (m, 5H), 7.17 – 7.13 (m, 2H), 6.73 (s, 1H), 4.67 – 4.60 (m, 2H), 3.14 (t, *J* = 7.3 Hz, 2H), 2.41 (d, *J* = 0.5 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 150.1, 137.8, 131.9, 129.8, 128.9, 128.5, 126.7, 126.3, 125.8, 121.2, 118.8, 116.8, 116.0, 114.0, 50.5, 38.3, 12.1.; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 338; HRMS (EI): m/z calcd for $C_{20}H_{16}ClNO_2$: 338.79954; found: 338.79967.

1,3-Dimethylchromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3j):-

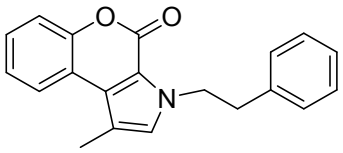
A mixture of 2H-chromene-3-carbaldehyde 1 (1.1 equiv) and ethyl methylglycinate 2 (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (1:9 of EtOAc/hexane) to give the pure product 3j.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.36 (dd, *J* = 9.8, 8.3 Hz, 2H), 7.30 – 7.27 (m, 1H), 6.91 (s, 1H), 4.07 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 141.7, 131.3, 125.7, 123.0, 121.9, 120.7, 120.0, 117.1, 114.6, 36.3, 32.1 ppm; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 214; HRMS (EI): m/z calcd for $C_{13}H_{11}NO_2$: 214.07898; found: 338.07910.

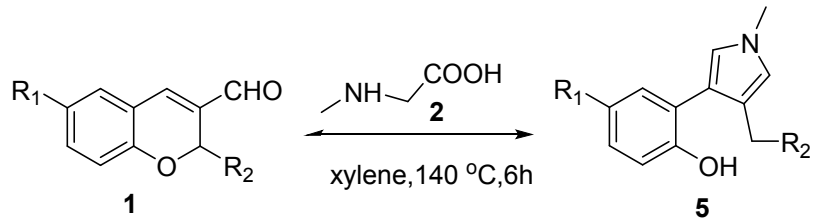
1-Methyl-3-phenethylchromeno [3, 4-*b*] pyrrol-4(3*H*)-one (3k):-

A mixture of 2H-chromene-3-carbaldehyde 1 (1.1 equiv) and methyl phenethylglycinate 2 (3.0 equiv) in xylene (5 mL) was stirred at 140 ºC for 6 h. The progress of the reaction was monitored by TLC. Up on completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (3:7 of EtOAc/hexane) to give the pure product 3k.



White solid, m.p.155-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.42 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.31 – 7.26 (m, 2H), 7.26 – 7.19 (m, 2H), 7.16 – 7.11 (m, 2H), 6.70 (s, 1H), 4.64 – 4.58 (m, 2H), 3.12 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 151.2, 147.5, 138.0, 131.7, 128.9, 128.5, 127.6, 127.0, 126.6, 123.9, 123.2, 119.4, 117.1, 50.5, 38.3, 12.2; IR (KBr): ν_{max} 3449, 2925, 1652, 1489, 1208, 766 cm^{-1}; MS (EI): m/z ([M+1]): 304; HRMS (EI): m/z calcd for $C_{20}H_{17}NO_2$: 304.35448; found: 304.35456.

Preparation of 2-(4-benzyl-1-methyl-1H-pyrrol-3-yl)phenol (5)



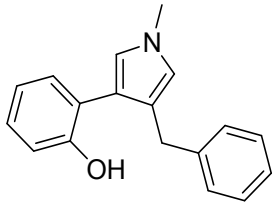
R_1 = -H, Cl, Br, OMe
R_2 = -H, Ph

Typical experimental procedure:

A mixture of 2*H*-chromene-3-carbaldehyde **1** (1.1 equiv) and sarcocine (**4)** (3.0 equiv) in xylene (5 mL) at 140 ºC for 6 h and then the mixture was cooled and filtered. The progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/hexane) to give the pure product.

2-(4-Benzyl-1-methyl-1*H*-pyrrol-3-yl) phenol (5a):-

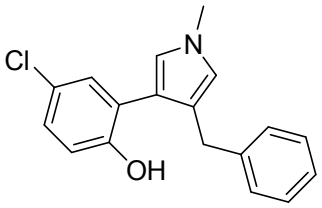
A mixture of 2-phenyl-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and sarcocine (**4)** (3.0 equiv) in xylene (5 mL) at 140 ºC for 6 h and then the mixture was cooled and filtered. The progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (2:8 of EtOAc/hexane) to give the pure product.



Colorless liquid ;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.08 (m, 7H), 6.95 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.87 (tdd, *J* = 7.4, 2.4, 1.1 Hz, 1H), 6.59 (d, *J* = 2.1 Hz, 1H), 6.36 (s, 1H), 5.54 – 5.51 (m, 1H), 3.68 (s, 2H), 3.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 141.9, 131.1, 128.6, 128.4, 128.3, 125.7, 123.2, 121.9, 120.7, 120.0, 117.3, 114.6, 36.3, 31.7; IR (KBr): ν_{max} 3487, 3059, 2930, 1490, 1206, 1036, 761 cm^{-1}; MS (EI): m/z ([M+1]): 264; HRMS (EI): m/z calcd for $C_{18}H_{17}NO$: 264.13101; found: 264.13116.

2-(4-Benzyl-1-methyl-1*H*-pyrrol-3-yl)-4-chlorophenol (5b):-

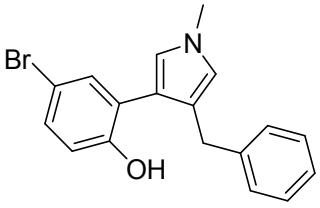
A mixture of 6-chloro-2-phenyl-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and sarcocine (**4)** (3.0 equiv) in xylene (5 mL) at 140 ºC for 6 h and then the mixture was cooled and filtered. The progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (3:7 of EtOAc/hexane) to give the pure product.



Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H), 7.16 – 7.12 (m, 2H), 7.07 (dd, *J* = 11.9, 4.9 Hz, 3H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.59 (d, *J* = 2.2 Hz, 1H), 6.38 (d, *J* = 1.7 Hz, 1H), 5.45 (s, 1H), 3.66 (s, 2H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 141.5, 133.5, 131.1, 128.6, 128.3, 125.8, 124.1, 123.1, 122.0, 120.8, 116.3, 116.1, 111.8, 36.3, 31.7; IR (KBr): ν_{max} 3487, 3059, 2930, 1490, 1206, 1036, 761 cm^{1}; MS (EI): m/z ([M+1]): 298; HRMS (EI): m/z calcd for $C_{18}H_{16}ClNO$: 298.09241; found: 298.09249.

2-(4-Benzyl-1-methyl-1*H*-pyrrol-3-yl)-4-bromophenol (5c):-

A mixture of 6-bromo-2-phenyl-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and sarcocine (**4)** (3.0 equiv) in xylene (5 mL) at 140 ºC for 6 h and then the mixture was cooled and filtered. The progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (3:7 of EtOAc/hexane) to give the pure product.

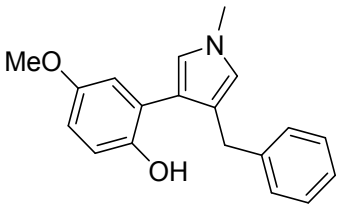


Colorless liquid ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.25 – 7.22 (m, 2H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.11 – 7.07 (m, 2H), 6.82 (d, *J* = 8.6 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 6.39 (d, *J* = 2.3 Hz, 1H), 5.48 (s, 1H), 3.66 (s, 2H), 3.62 (s, 3H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$) δ 152.8, 141.5, 133.5, 131.1, 128.6, 128.3, 125.8, 124.1, 123.1, 122.0, 120.8, 116.3, 116.1, 111.8, 36.3, 31.7 ppm. IR (KBr): ν_{max} 3487, 3059, 2930, 1490, 1206, 1036, 761 cm^{-1}; MS (EI): m/z ([M+1]): 342; HRMS (EI): m/z calcd for $C_{18}H_{16}BrNO$: 342.22974; found: 342.22976.

2-(4-Benzyl-1-methyl-1*H*-pyrrol-3-yl)-4-methoxyphenol (5d):-

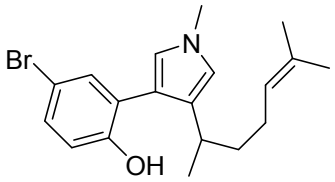
A mixture of 6-methoxy-2-phenyl-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and sarcocine (**4)** (3.0 equiv) in xylene (5 mL) at 140 ºC for 6 h and then the mixture was cooled and filtered. The progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (3:7 of EtOAc/hexane) to give the pure product.



Colorless liquid ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 7.9, 7.1 Hz, 2H), 7.16 – 7.10 (m, 3H), 6.87 (dd, *J* = 8.8, 1.1 Hz, 1H), 6.75 (ddd, *J* = 8.8, 3.0, 1.1 Hz, 1H), 6.66 – 6.61 (m, 2H), 6.40 – 6.38 (m, 1H), 5.18 (d, *J* = 2.0 Hz, 1H), 3.71 (s, 2H), 3.66 (s, 3H), 3.61 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 147.6, 141.9, 128.6, 128.2, 127.4, 125.7, 122.9, 122.3, 122.0, 120.7, 117.6, 115.9, 115.1, 114.1, 55.7, 36.3, 31.7; IR (KBr): ν_{max} 3487, 3059, 2930, 1490, 1206, 1036, 761 cm^{-1}; MS (EI): m/z ([M+1]): 294; HRMS (EI): m/z calcd for $C_{19}H_{20}NO_2$: 294.14158; found: 294.14167.

4-Bromo-2-(1-methyl-4-(6-methylhept-5-en-2-yl)-1*H*-pyrrol-3-yl) phenol (5e):-

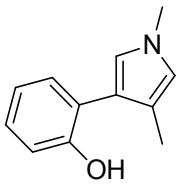
A mixture of 6-bromo-2-methyl-2-(4-methylpent-3-en-1-yl)-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and sarcocine (**4)** (3.0 equiv) in xylene (5 mL) at 140 ºC for 6 h and then the mixture was cooled and filtered. The progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (1:9 of EtOAc/hexane) to give the pure product.



Colorless liquid ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.52 (dd, *J* = 12.2, 2.3 Hz, 2H), 5.48 (s, 1H), 4.95 (dd, *J* = 7.7, 6.5 Hz, 1H), 3.66 (d, *J* = 2.3 Hz, 3H), 2.57 – 2.47 (m, 1H), 1.85 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.63 (s, 3H), 1.46 – 1.33 (m, 3H), 1.26 (s, 3H), 1.08 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 133.4, 131.4, 131.0, 130.0, 124.6, 124.4, 120.5, 119.5, 116.1, 115.4, 111.7, 38.8, 36.3, 29.7, 26.0, 25.6, 22.2, 17.6 ppm; IR (KBr): ν_{max} 3487, 3059, 2930, 1490, 1206, 1036, 761 cm^{-1}; MS (EI): m/z ([M+1]): 362; HRMS (EI): m/z calcd for $C_{19}H_{24}BrNO$: 362.10413; found: 362.10418.

2-(1, 4-Dimethyl-1*H*-pyrrol-3-yl) phenol (5f):-

A mixture of 2H-chromene-3-carbaldehyde **1** (1.1 equiv) and sarcocine (**4)** (3.0 equiv) in xylene (5 mL) at 140 ºC for 6 h and then the mixture was cooled and filtered. The progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (1:9 of EtOAc/hexane) to give the pure product.

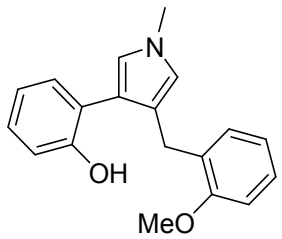


Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 2H), 7.01 – 6.86 (m, 2H), 6.63 – 6.50 (m, 2H), 5.55 (s, 1H), 3.65 (s, 3H), 1.99 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 141.7, 131.3, 125.7, 123.0, 121.9, 120.7, 120.0, 117.1, 114.6, 36.3, 32.1 ppm; IR (KBr): ν_{max} 3487, 3059, 2930, 1490, 1206, 1036, 761 cm^{-1}; MS (EI): m/z ([M+1]): 188; HRMS (EI): m/z calcd for $C_{12}H_{13}NO$: 188.18734; found: 188.18739.

2-(4-(2-methoxybenzyl)-1-methyl-1*H*-pyrrol-3-yl)phenol (5g):-

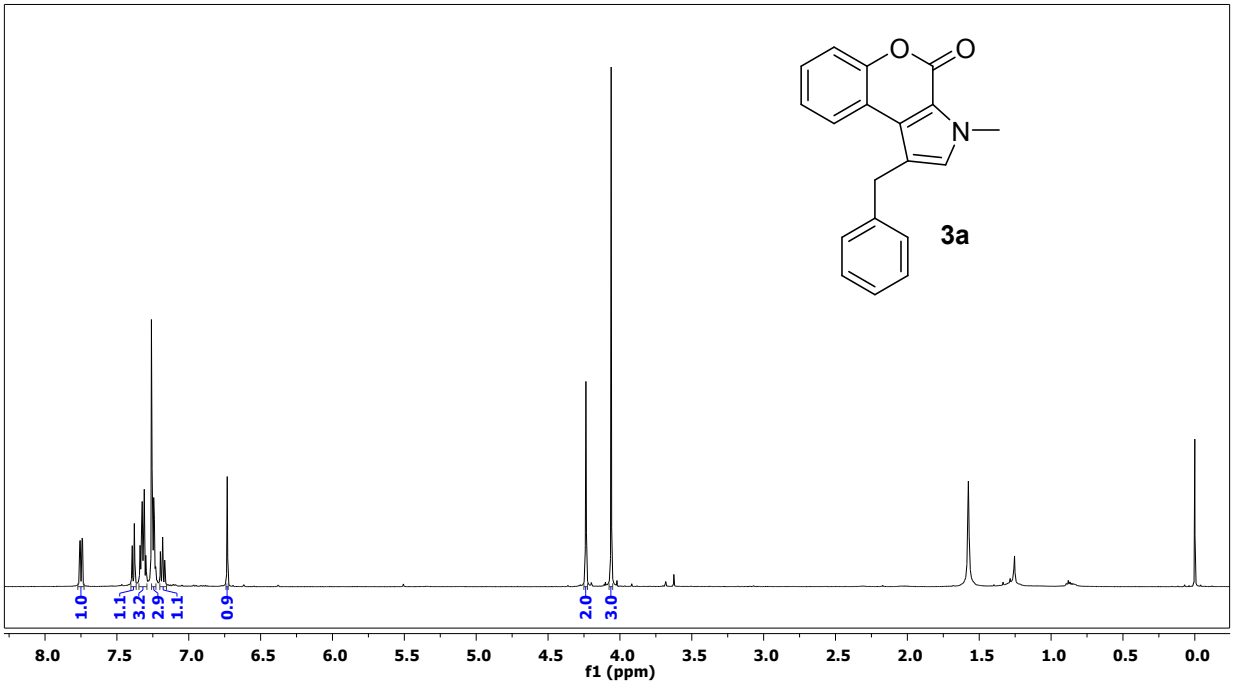
A mixture of 2-(2-methoxyphenyl)-2H-chromene-3-carbaldehyde **1** (1.1 equiv) and sarcocine (**4)** (3.0 equiv) in xylene (5 mL) at 140 ºC for 6 h and then the mixture was cooled and filtered. The

progress of the reaction was monitored by TLC; upon completion, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (1:9 of EtOAc/hexane) to give the pure product.

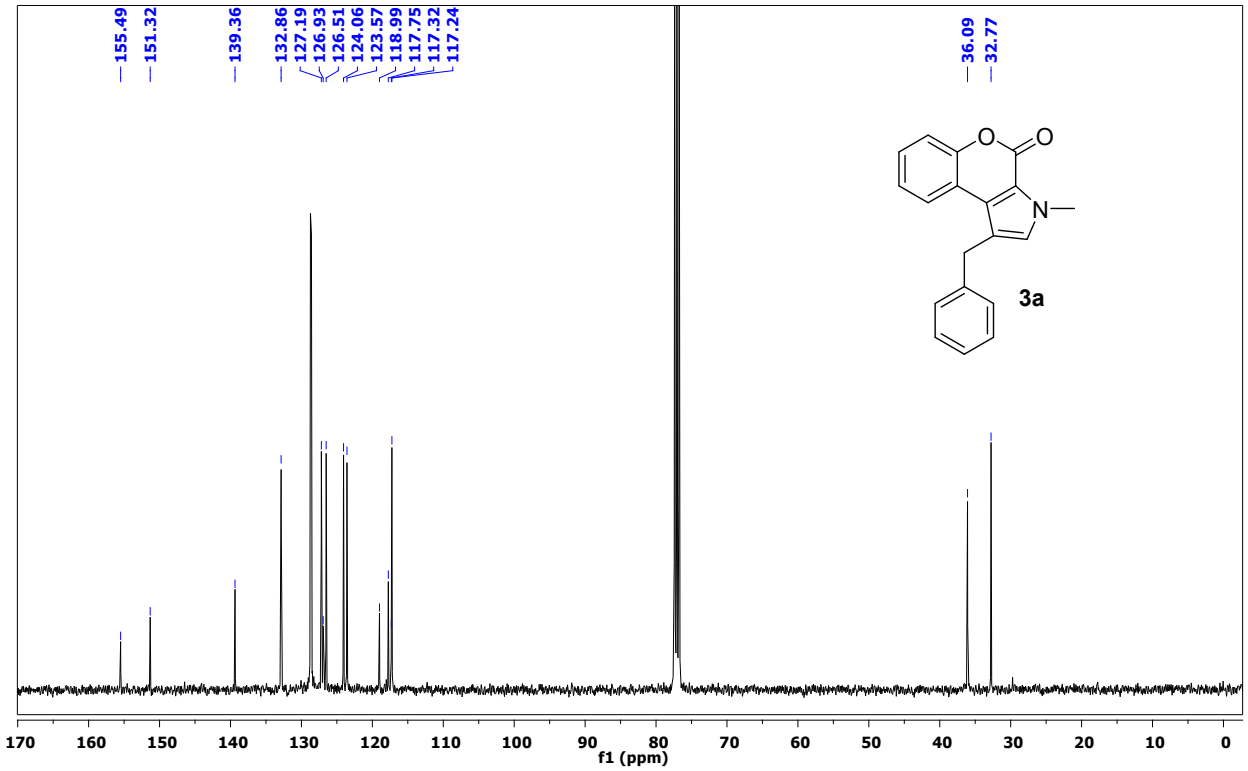


Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 3H), 7.04 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.97 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.91 – 6.81 (m, 3H), 6.57 (d, *J* = 2.4 Hz, 1H), 6.29 (d, *J* = 2.3 Hz, 1H), 5.80 (s, 1H), 3.76 (s, 3H), 3.66 (s, 2H), 3.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 153.7, 131.2, 130.3, 130.1, 128.3, 127.1, 122.5, 122.1, 121.7, 120.5, 120.4, 119.9, 117.55, 114.6, 110.3, 55.3, 36.3, 26.0; IR (KBr): ν_{max} 3489, 3058, 2931, 1493, 1209, 1038, 767 cm^{-1}; MS (EI): m/z ([M+1]): 294; HRMS (EI): m/z calcd for $C_{19}H_{20}NO_2$: 294.14155; found: 294.14162.

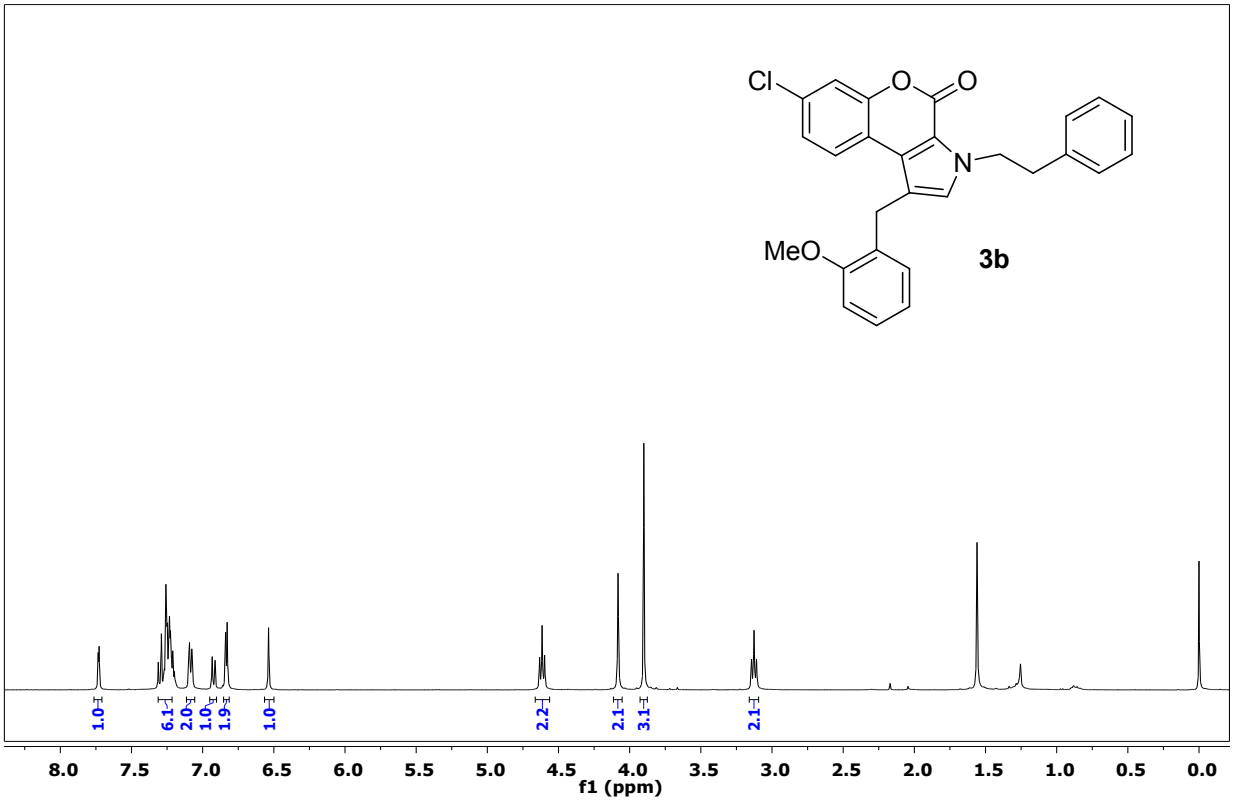
3. NMR spectra of products



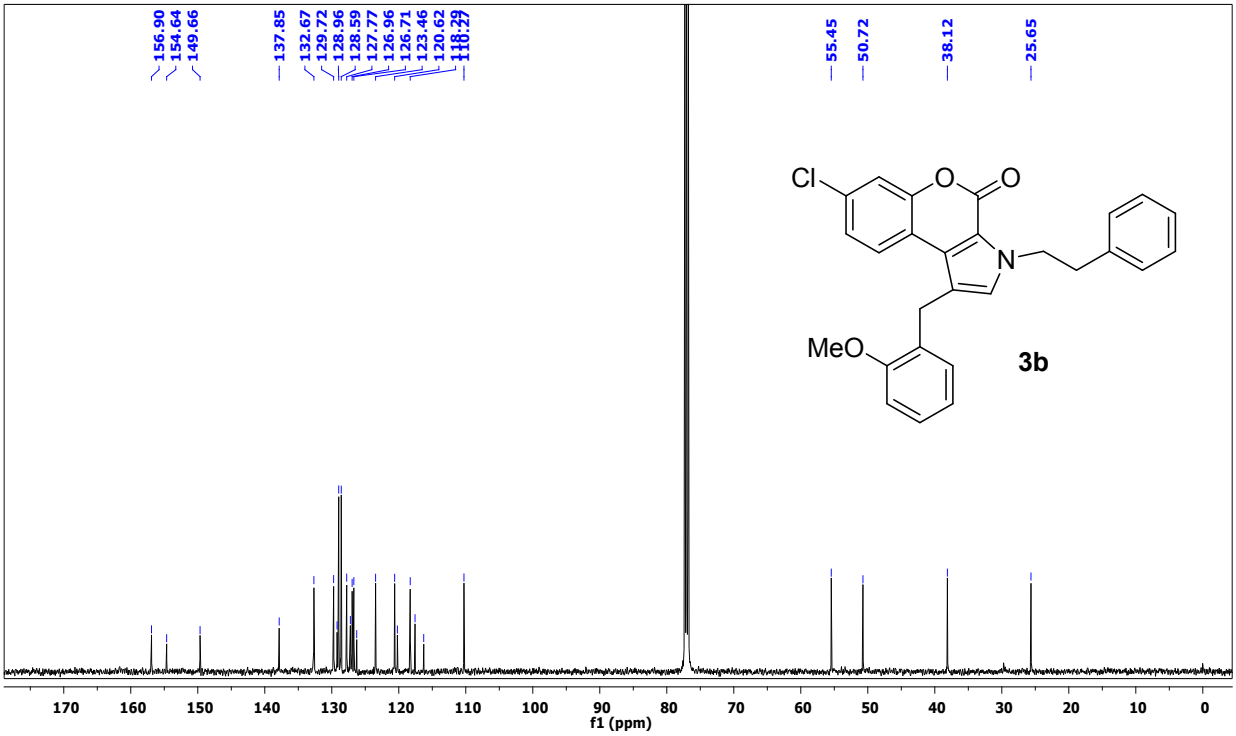
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3a



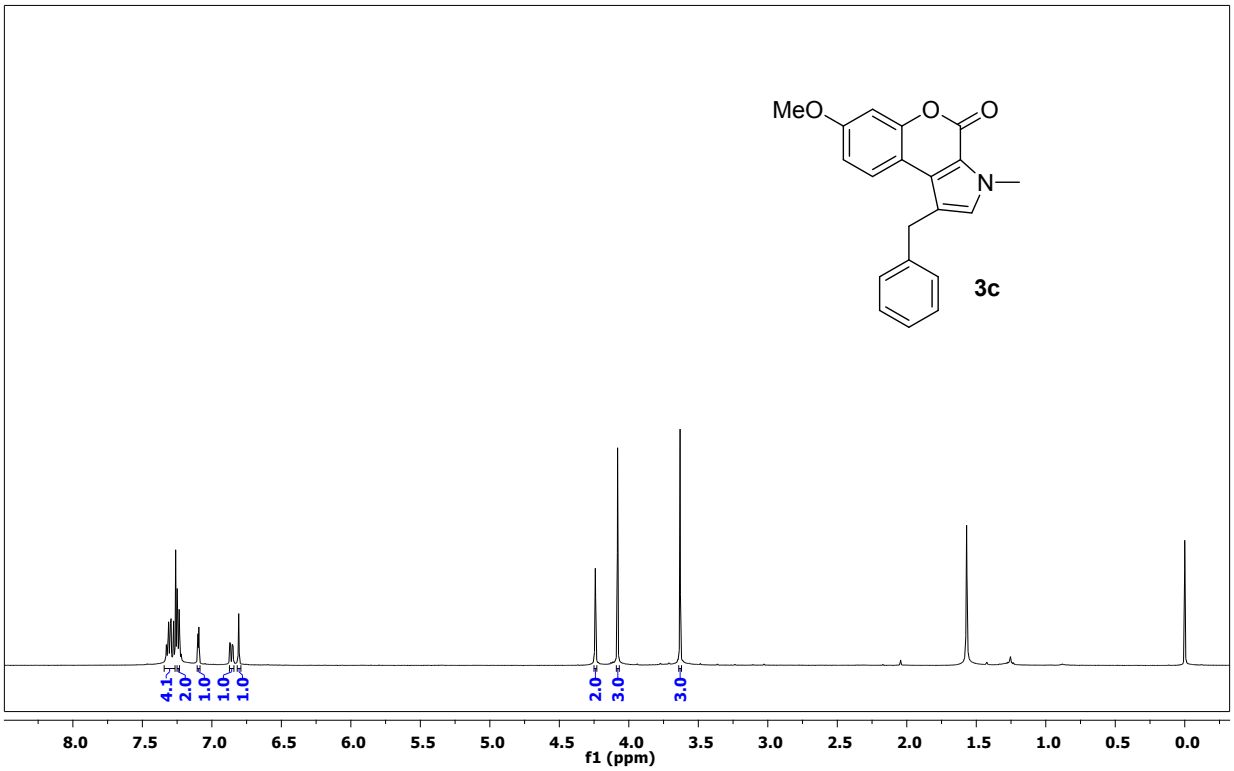
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3a



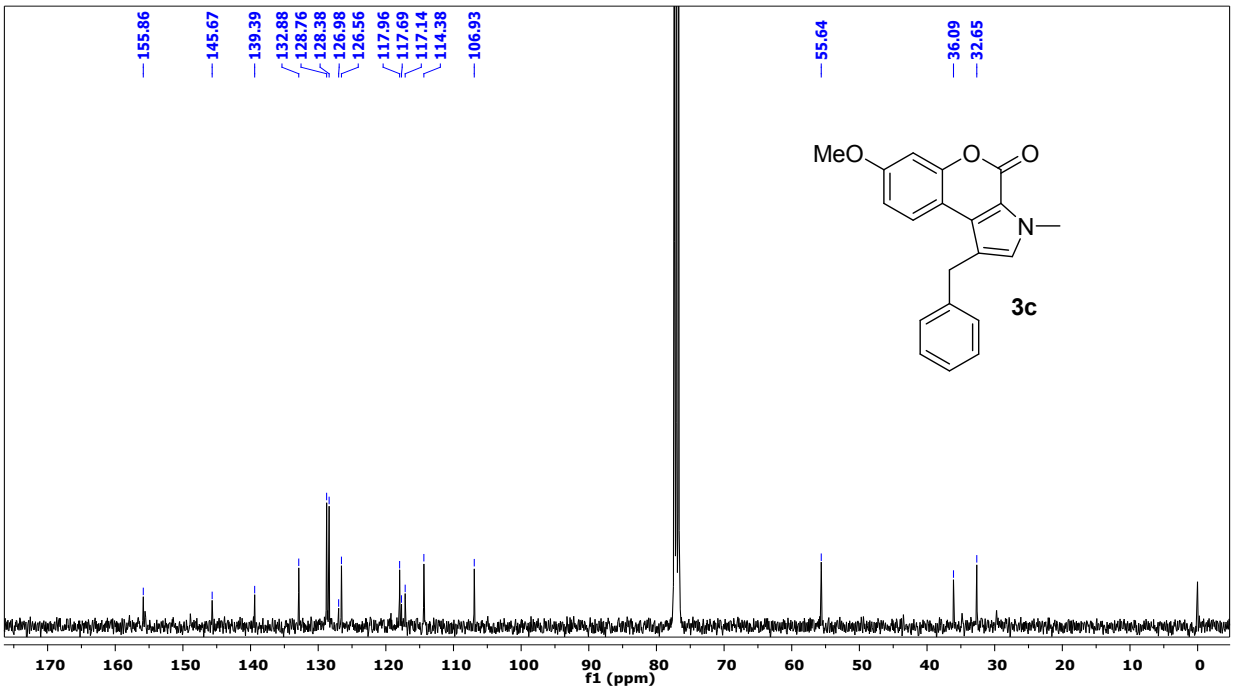
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3b



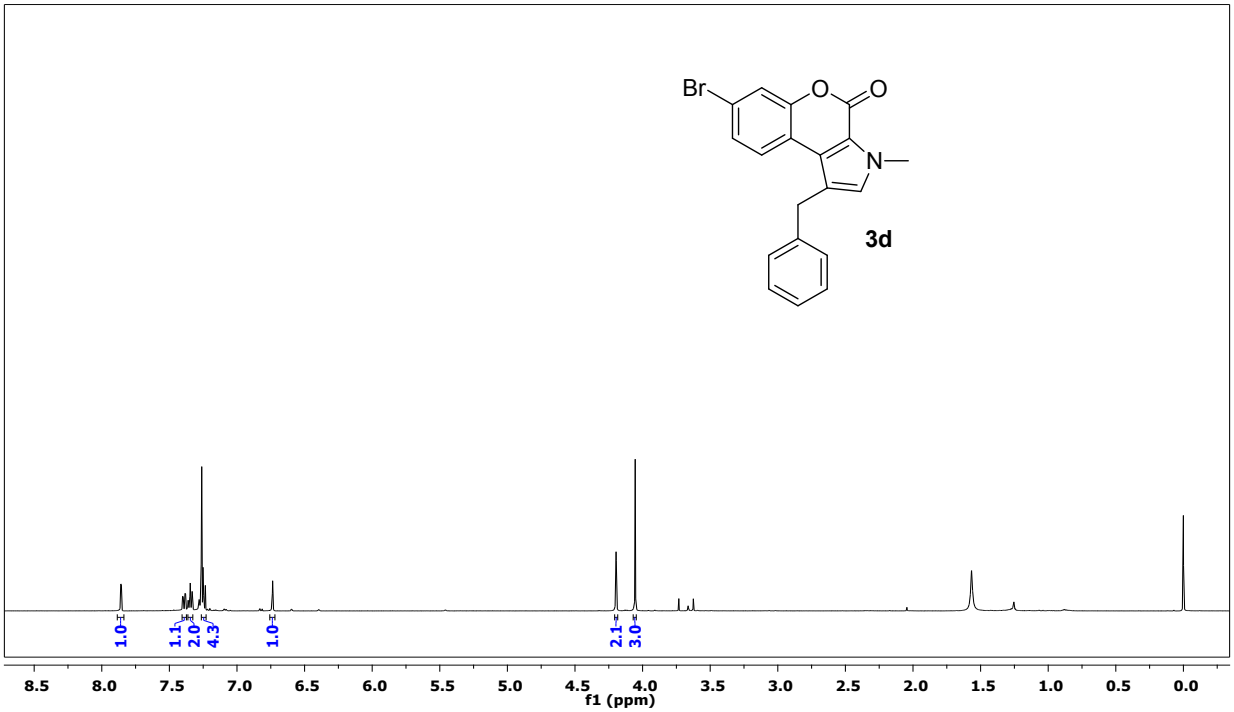
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3b



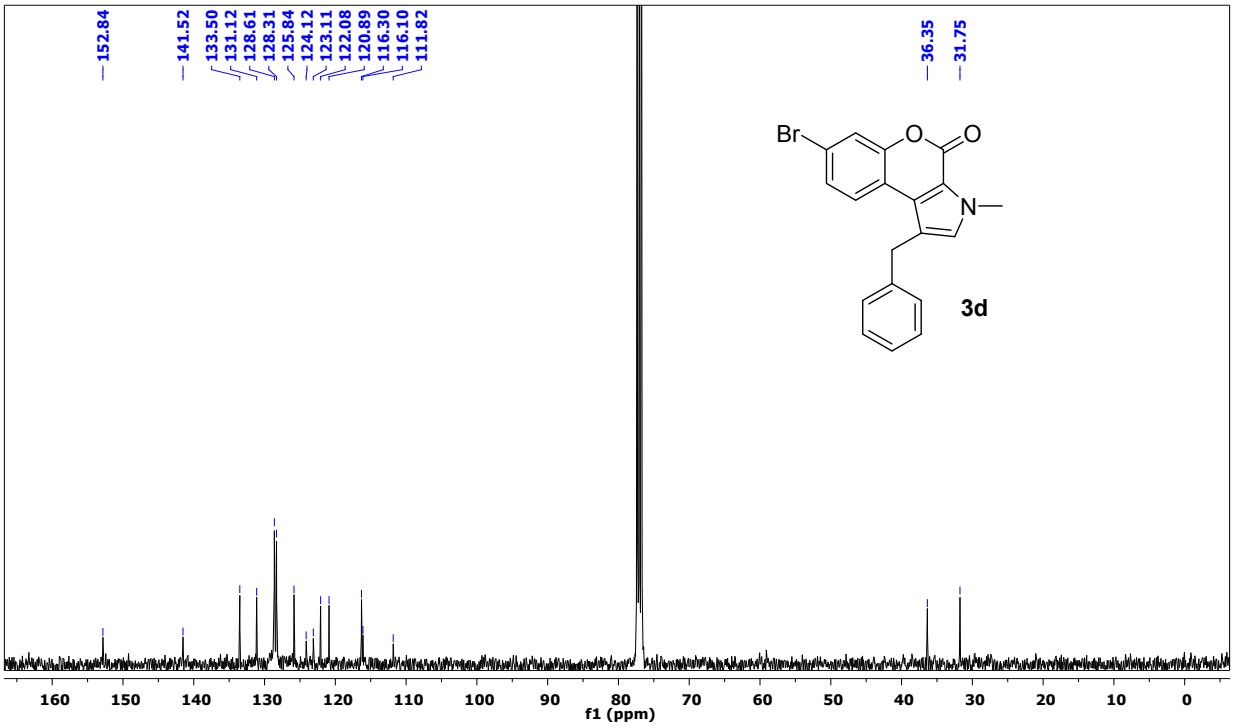
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3c



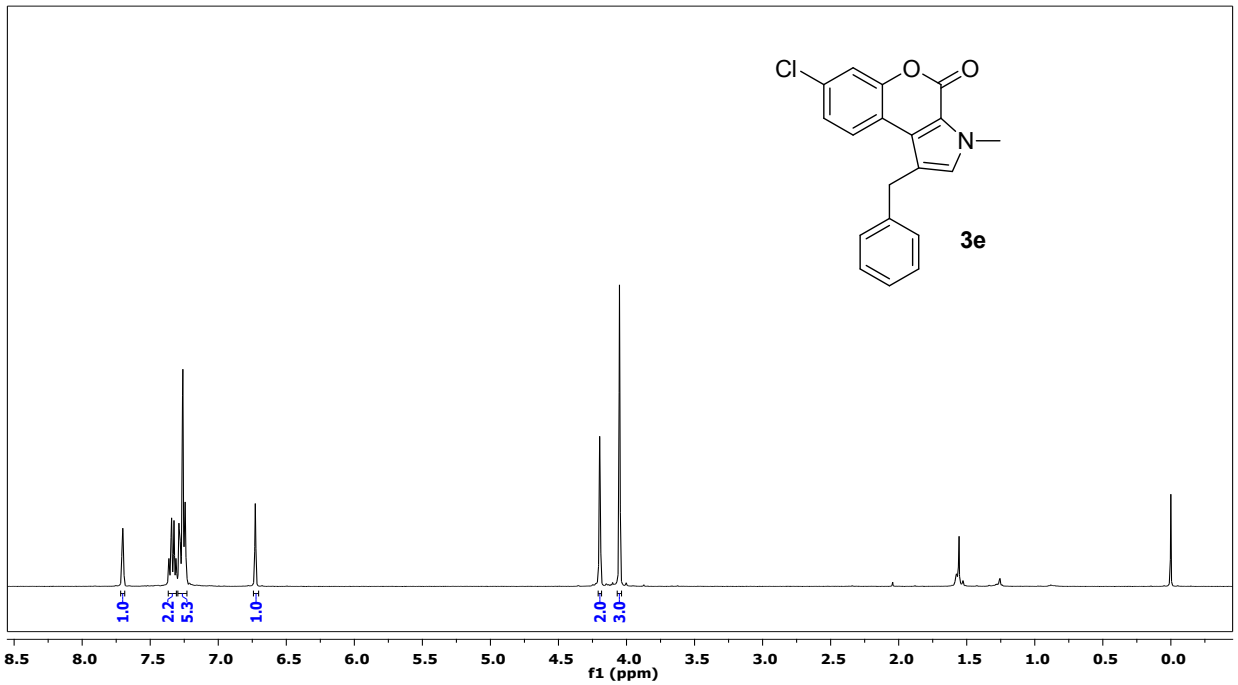
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3c



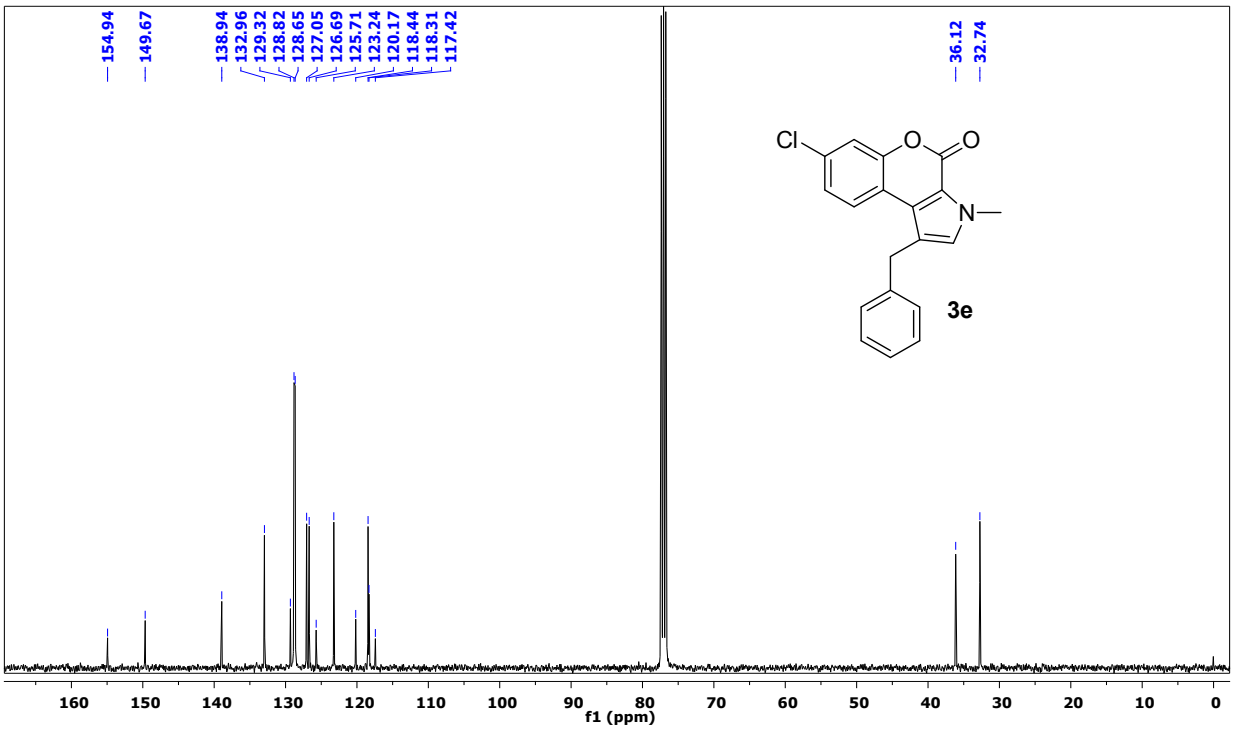
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3d



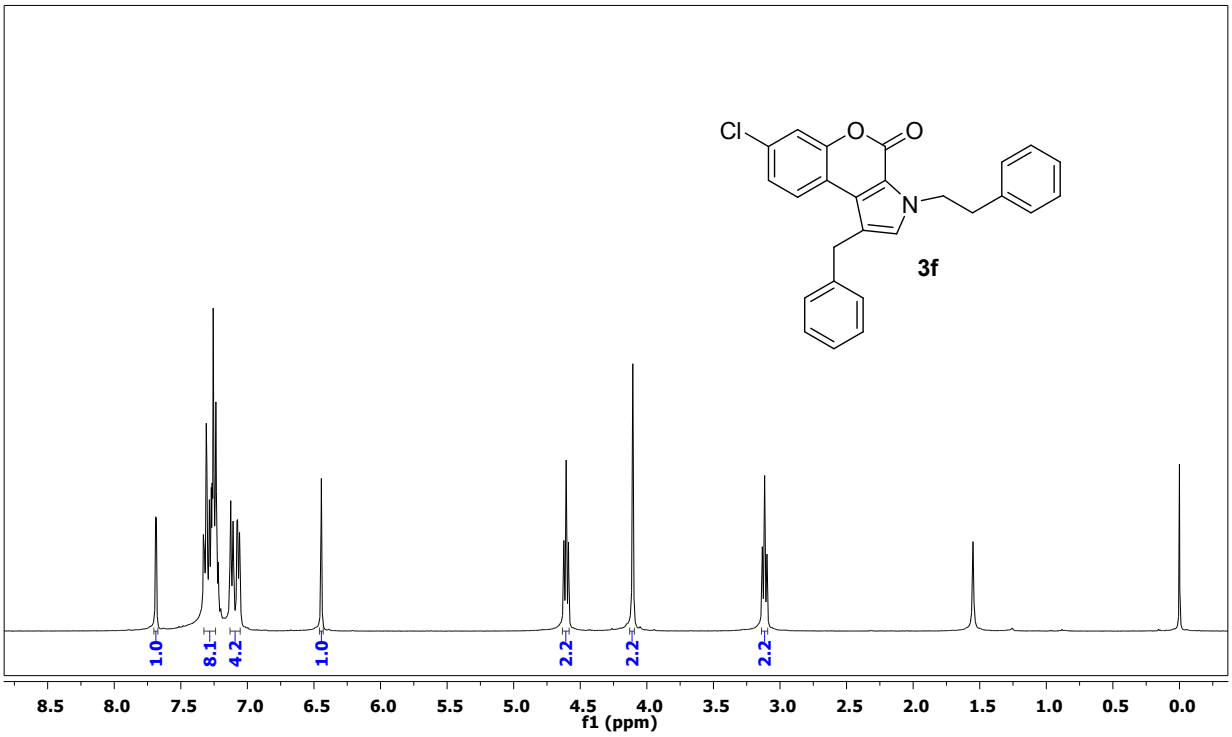
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3d



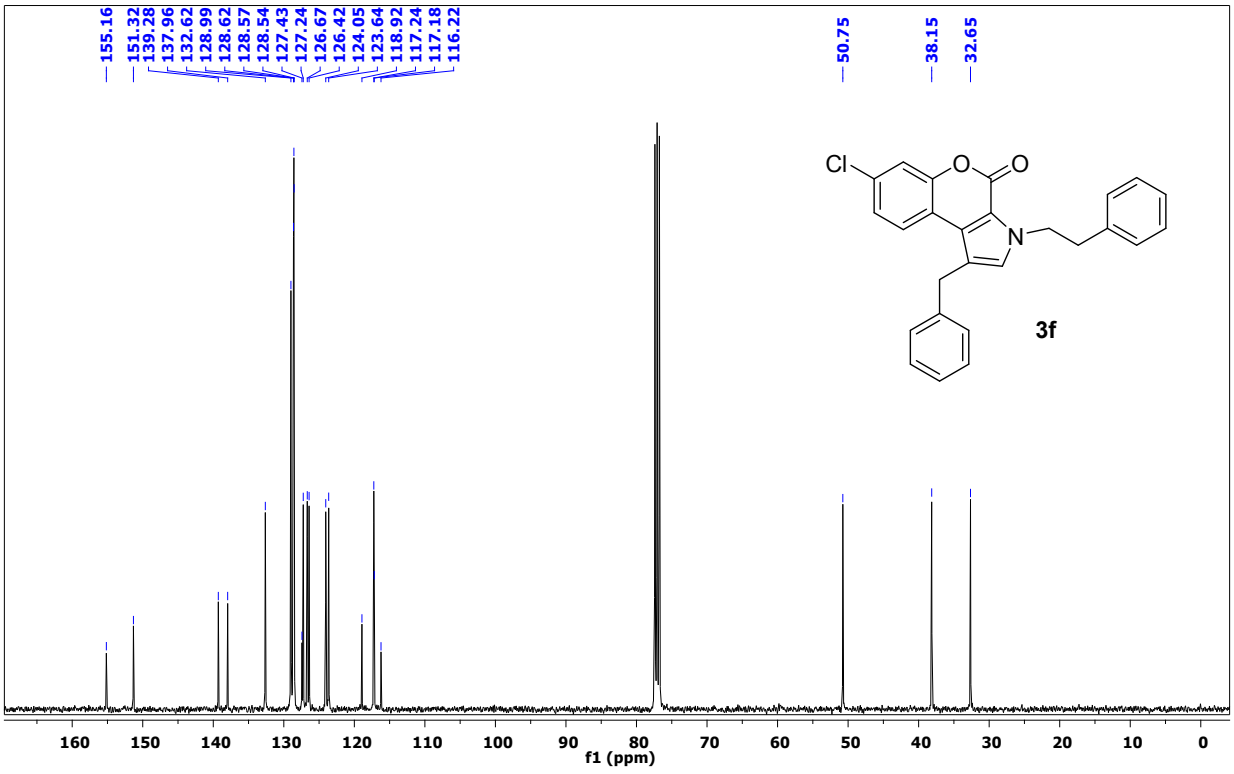
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3e



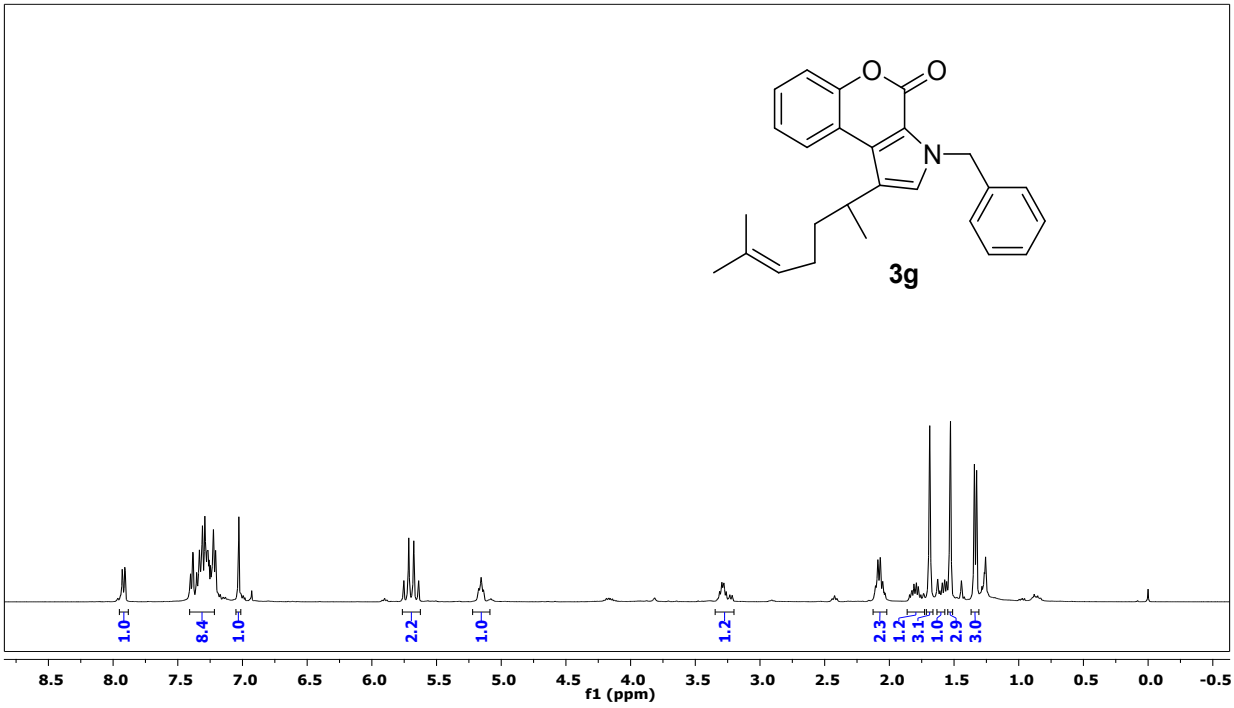
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3e



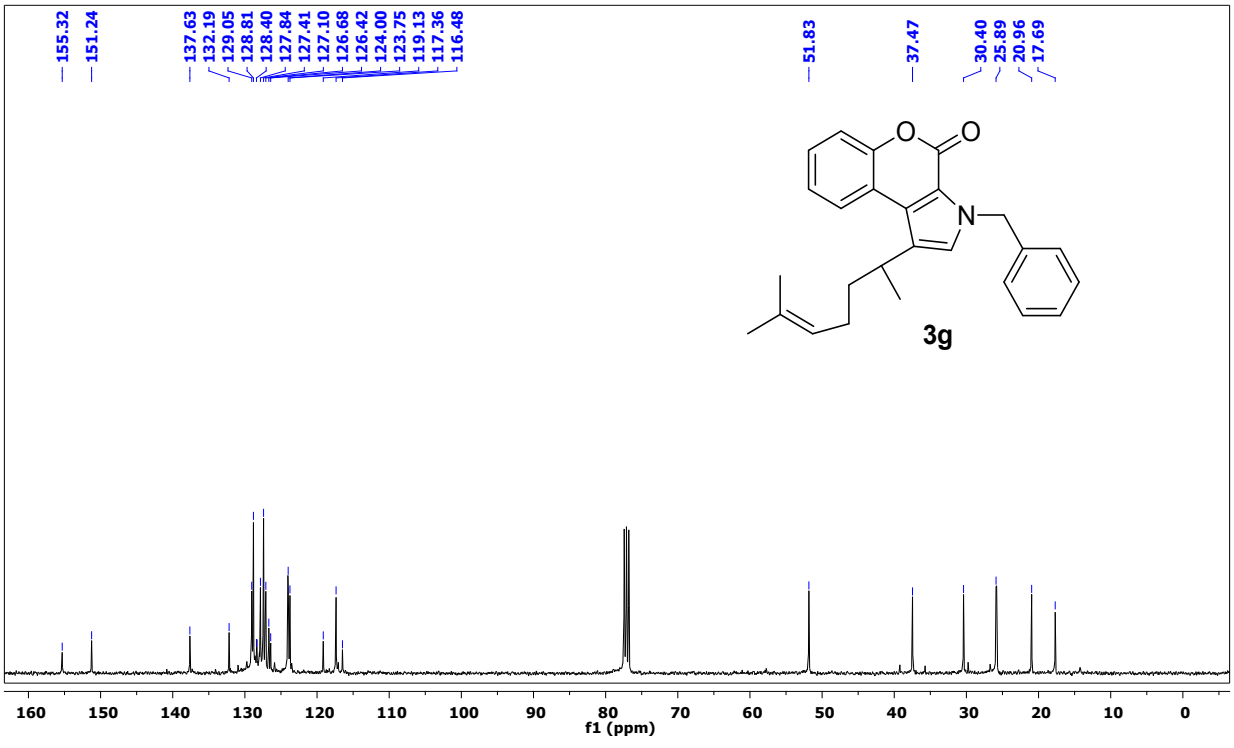
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3f



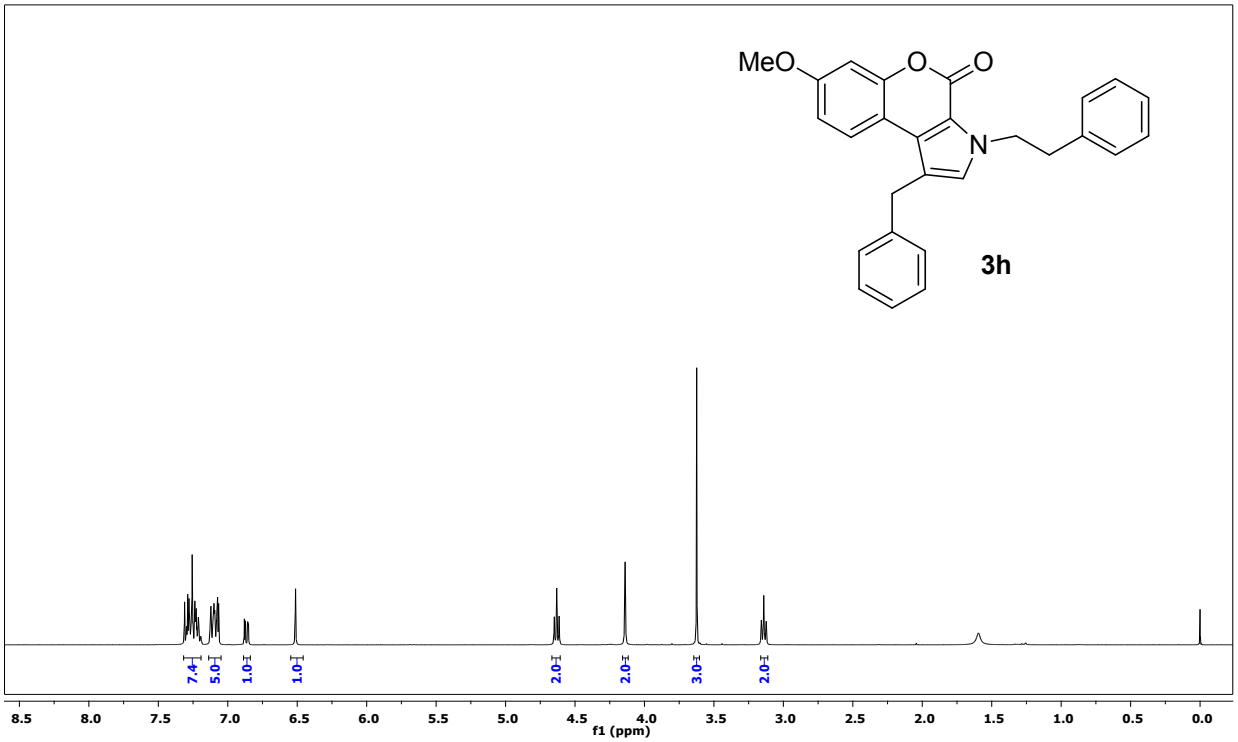
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3f



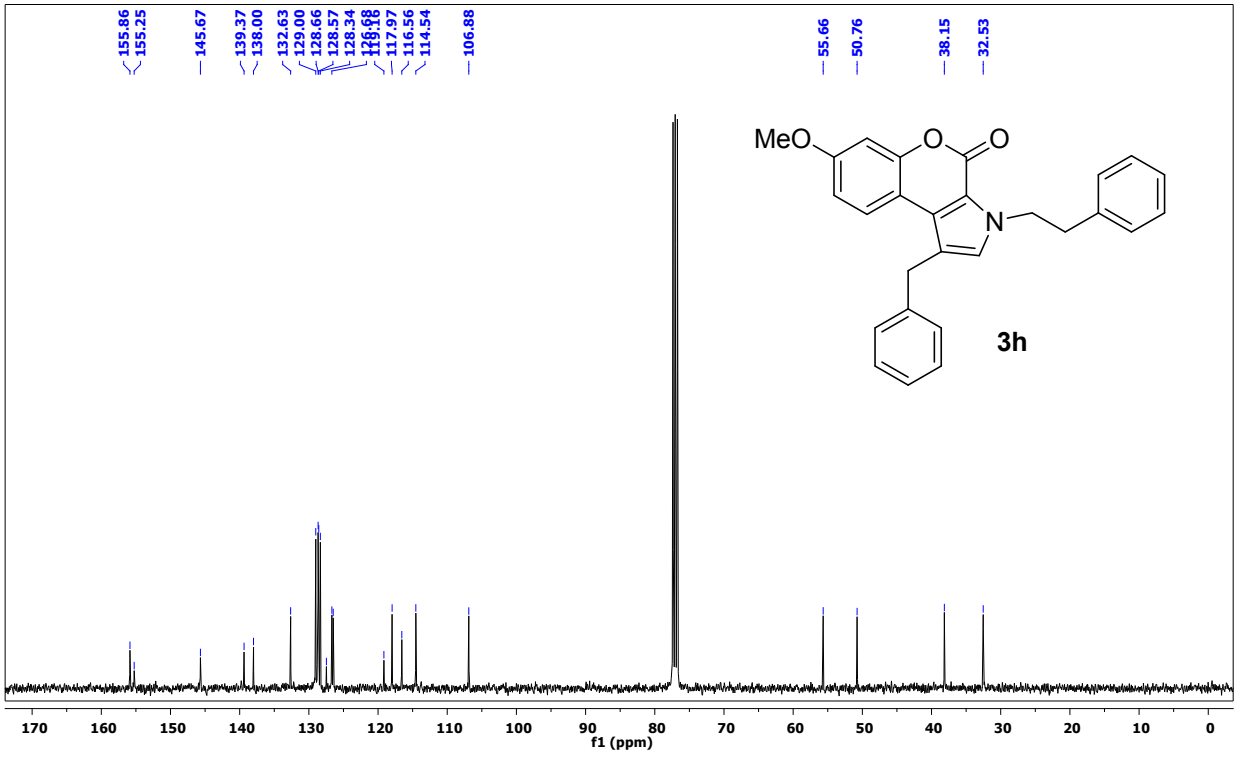
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3g



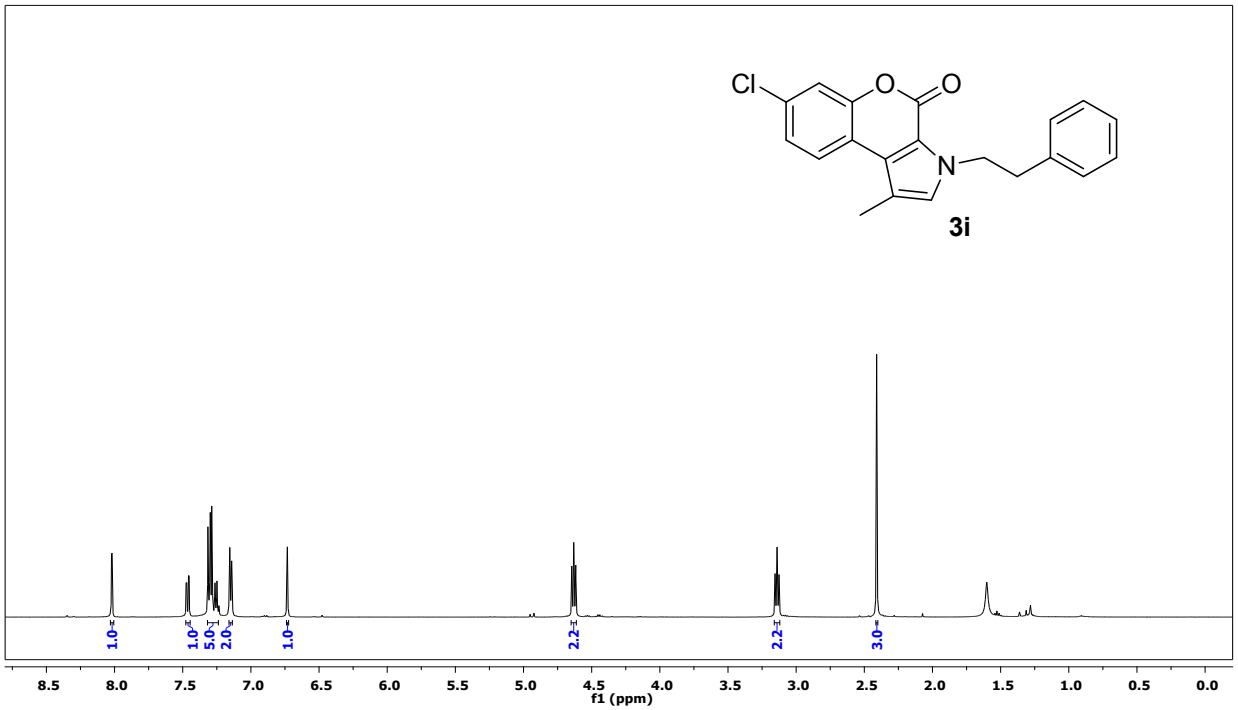
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3g



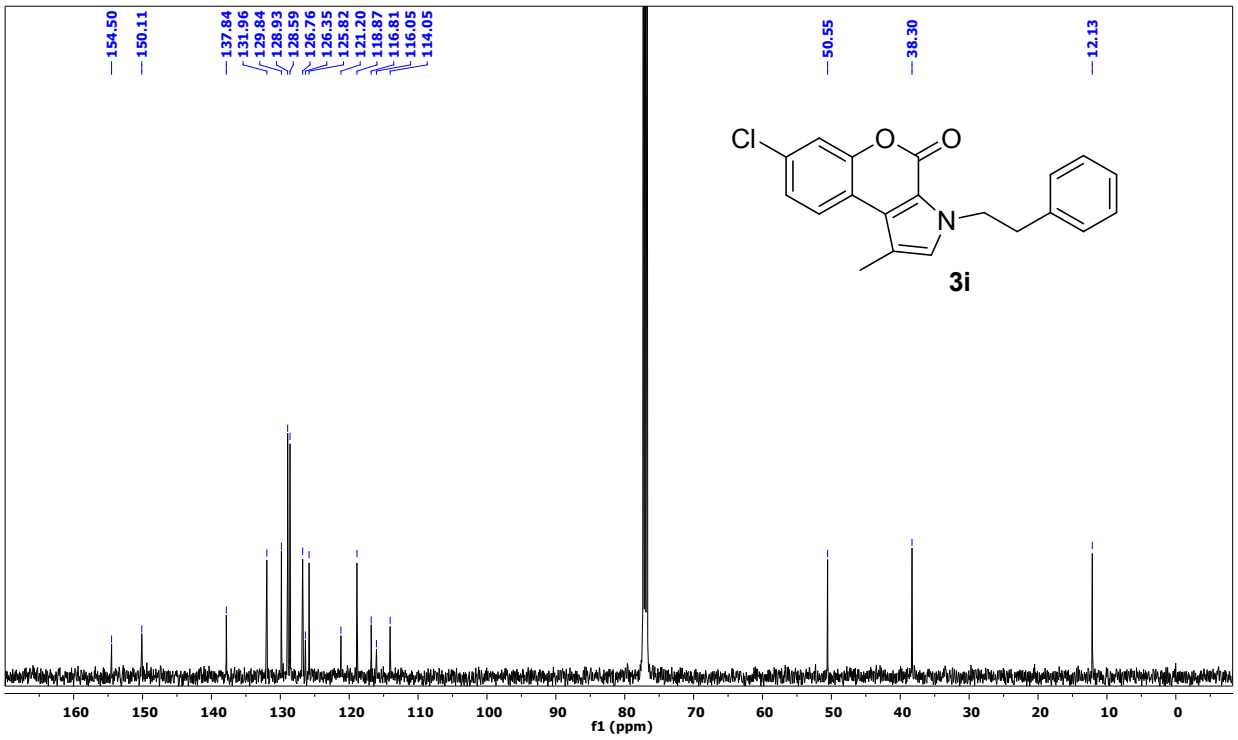
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3h



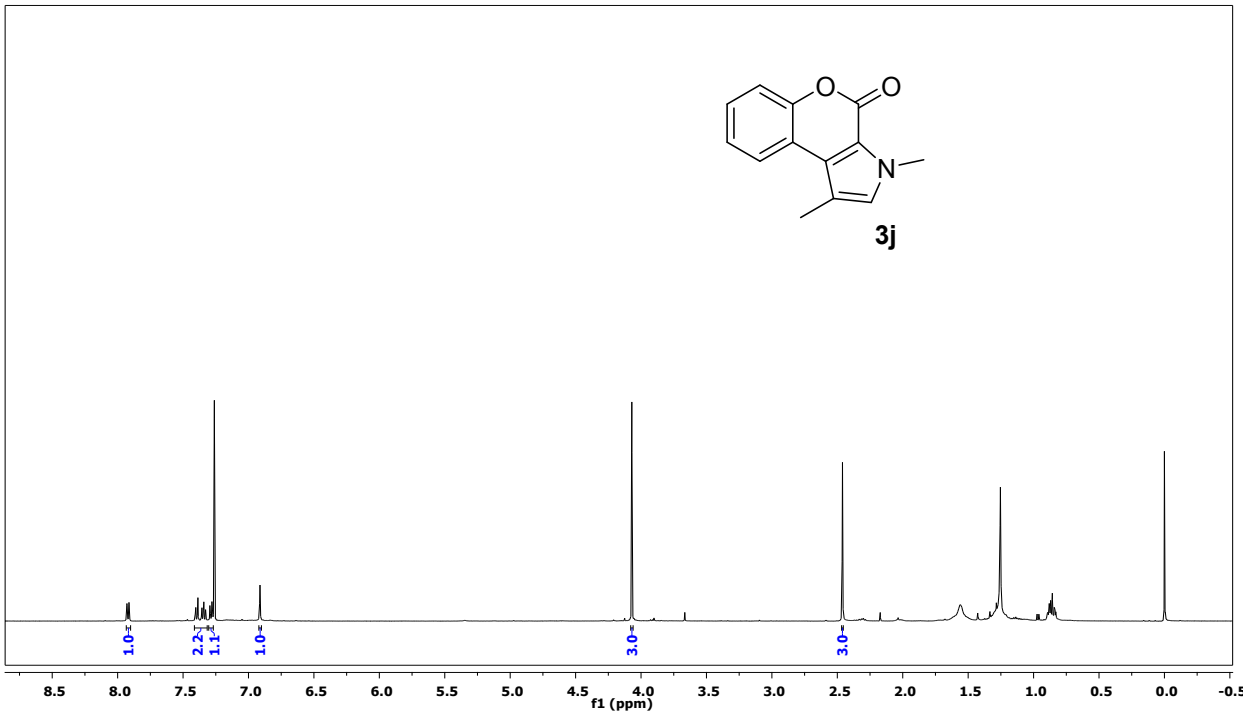
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3h



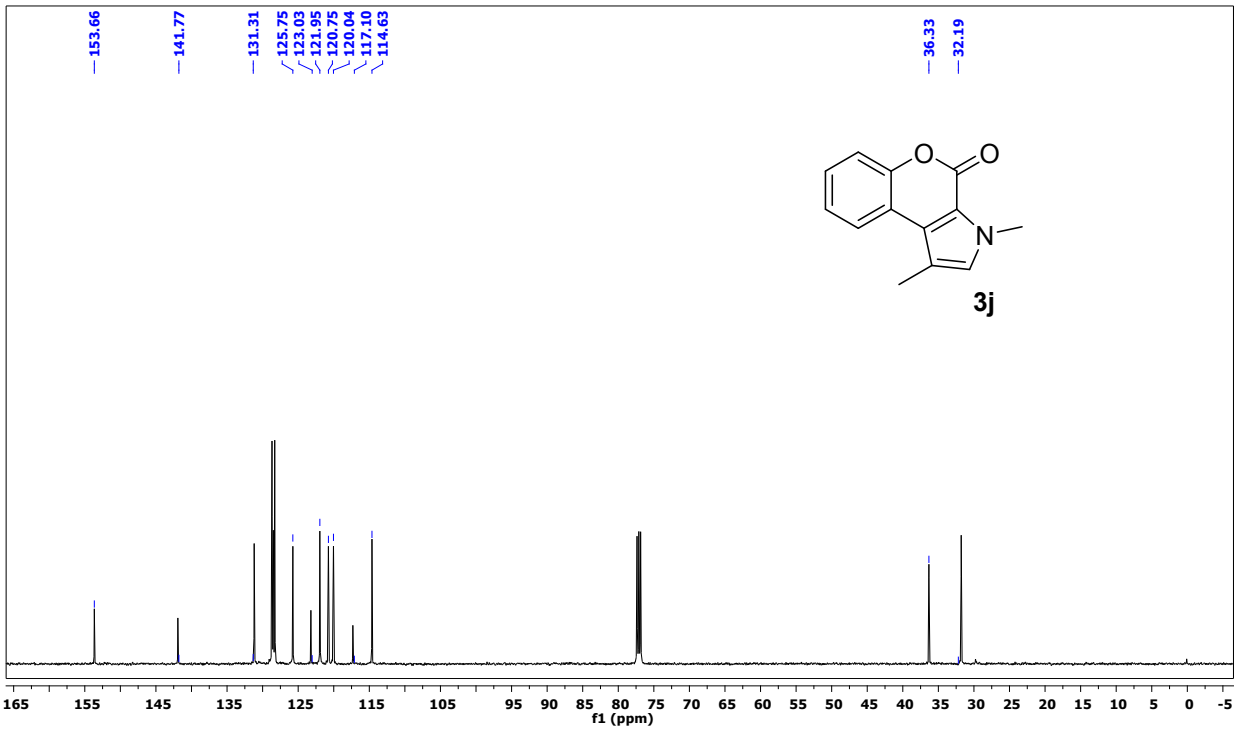
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3i



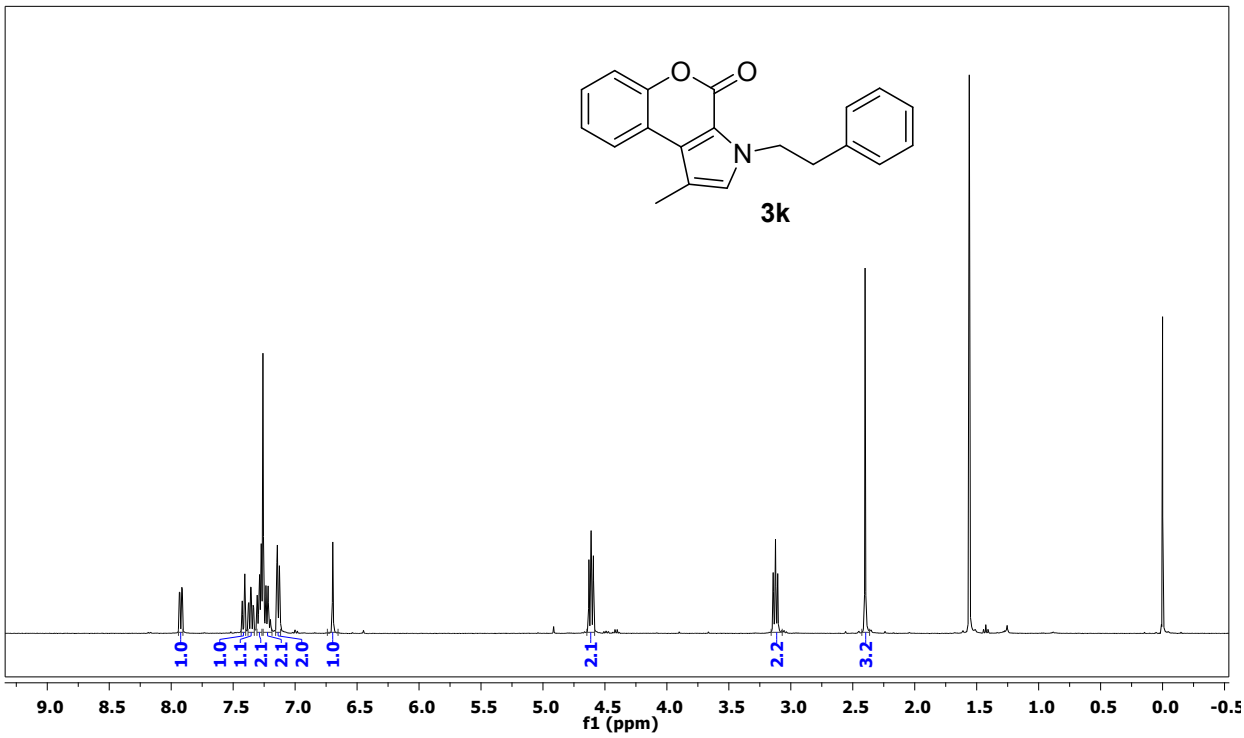
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3i



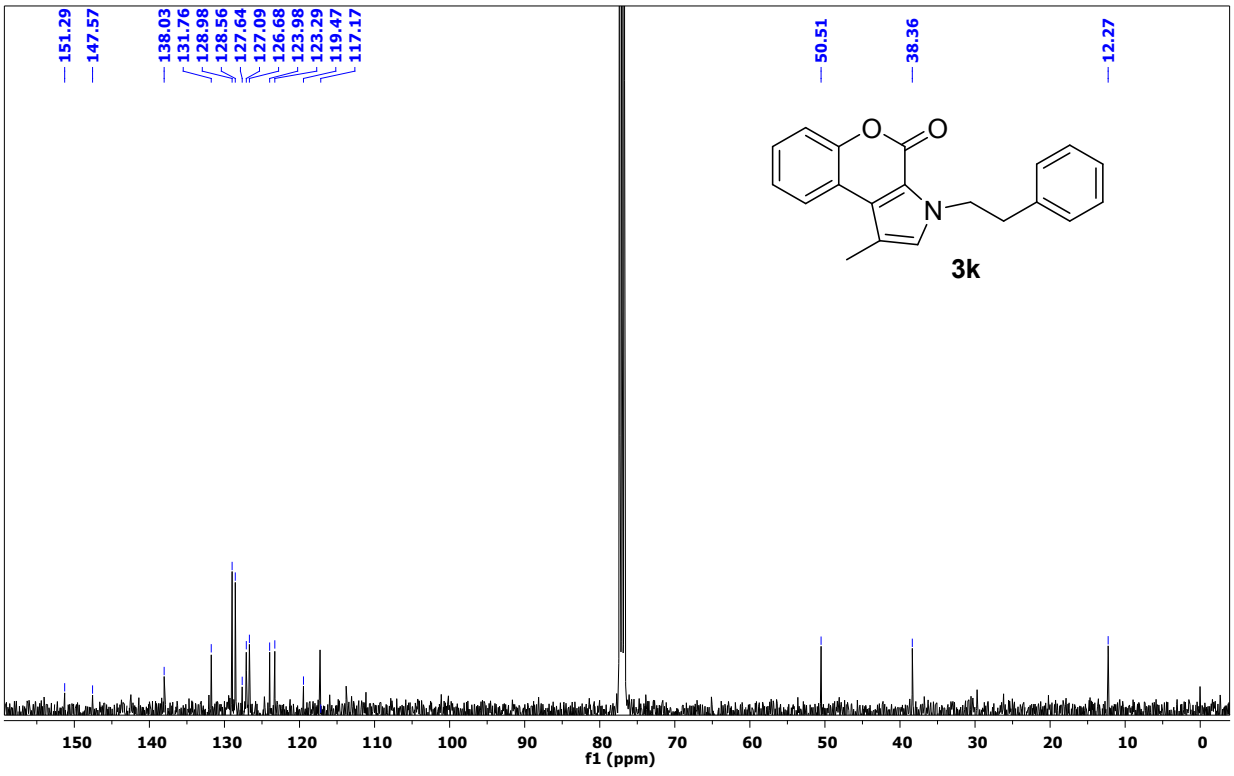
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3j



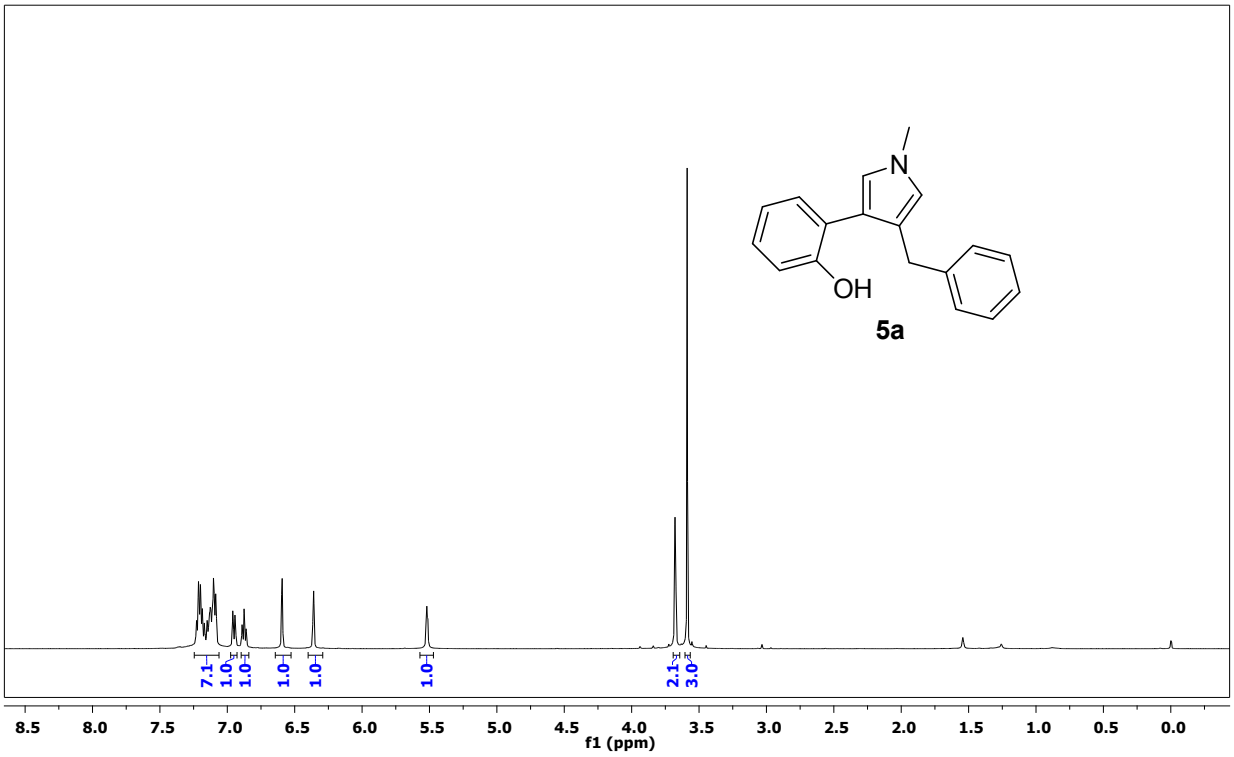
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 3j



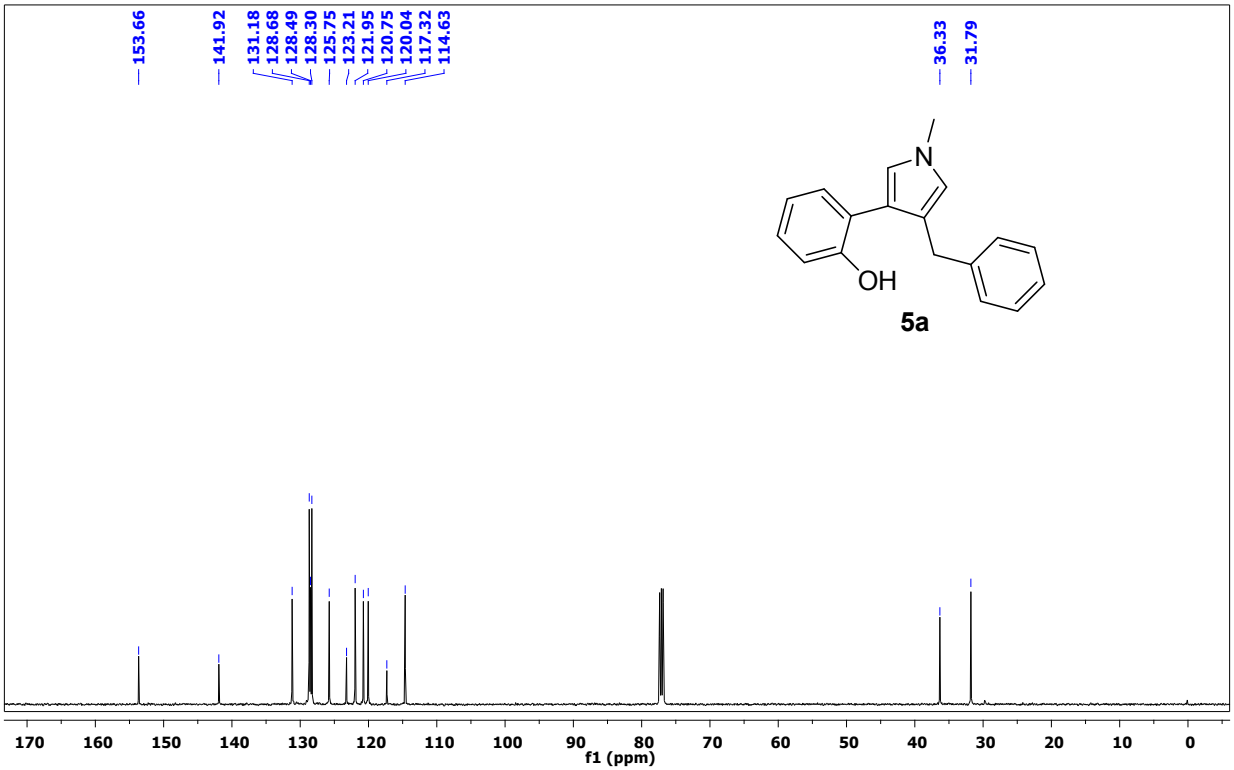
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3k



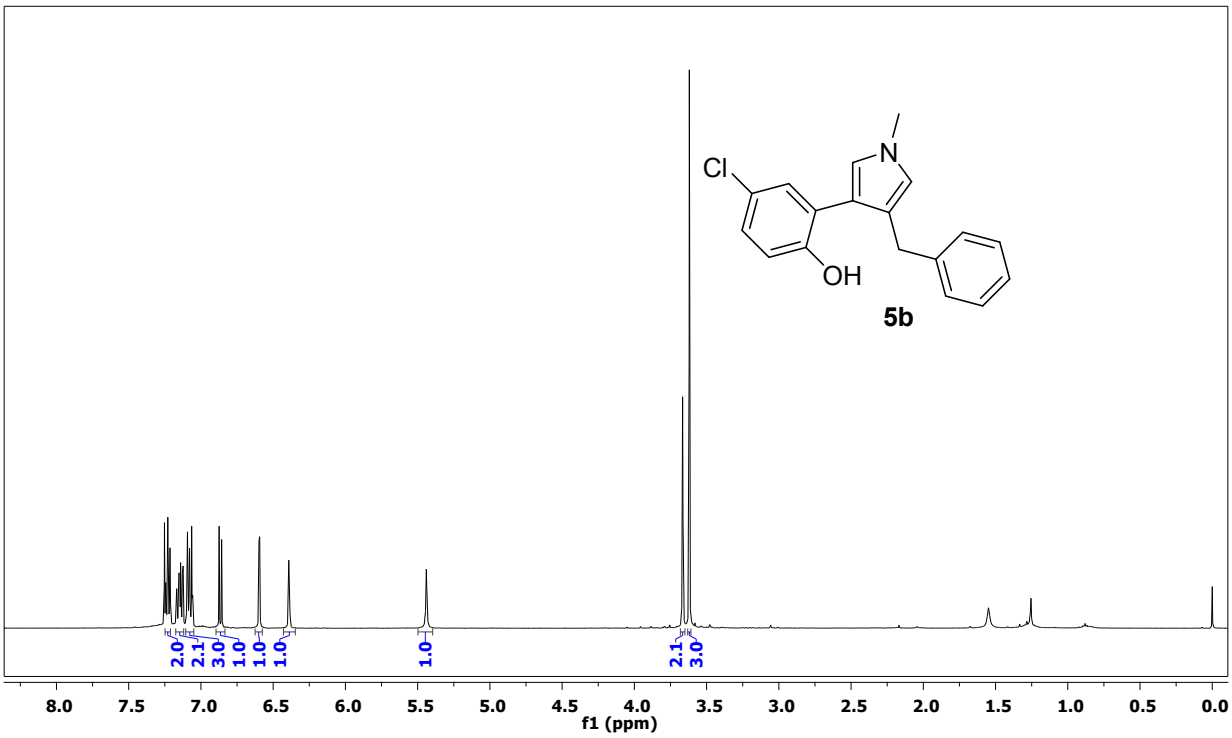
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 3k



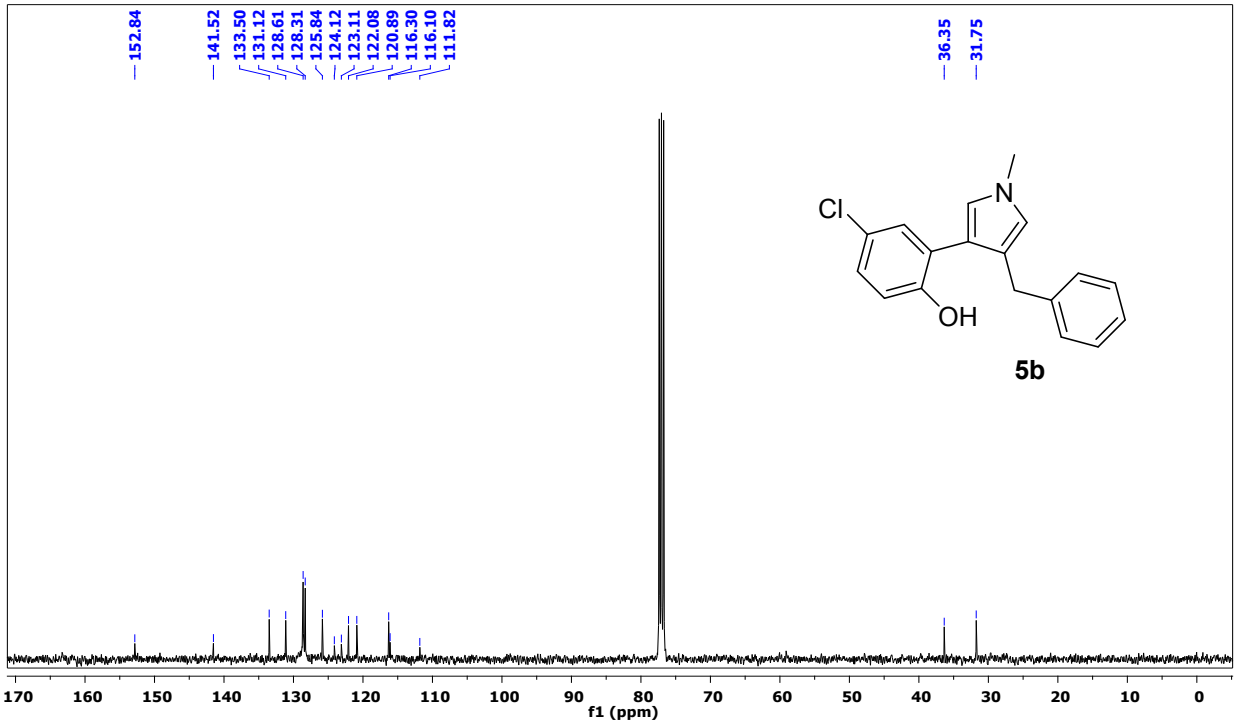
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5a



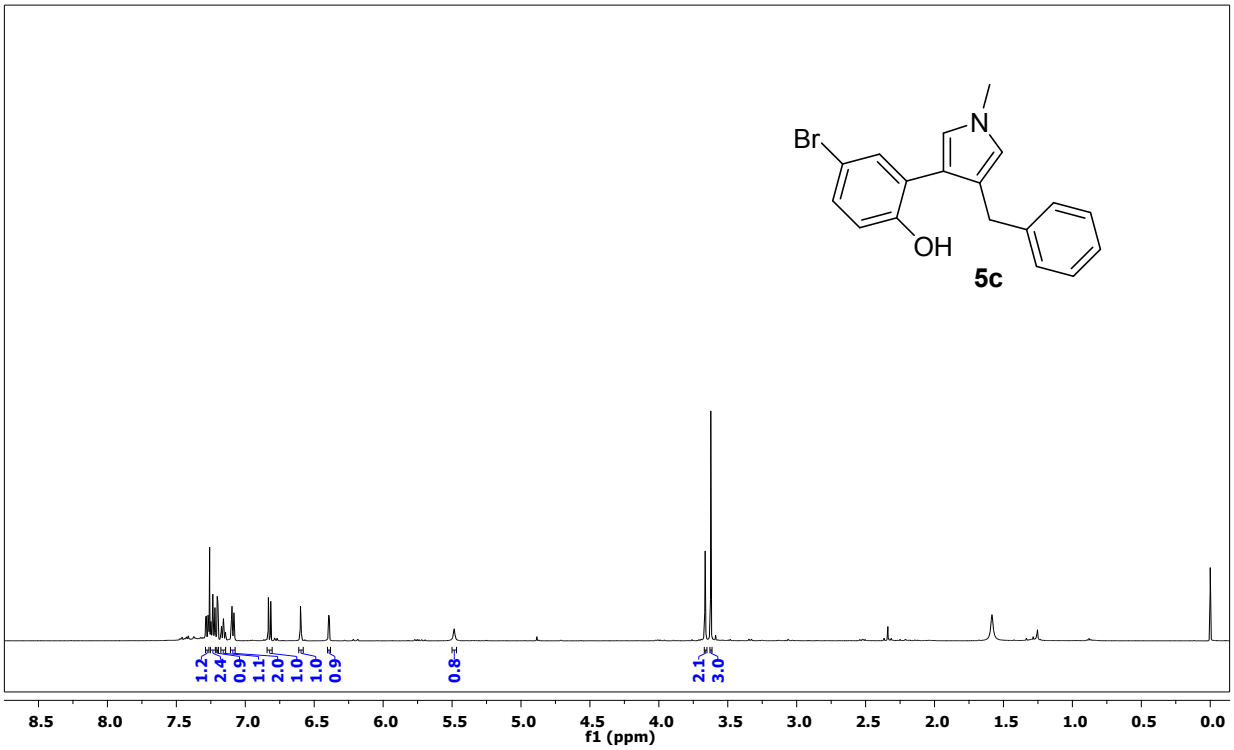
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5a



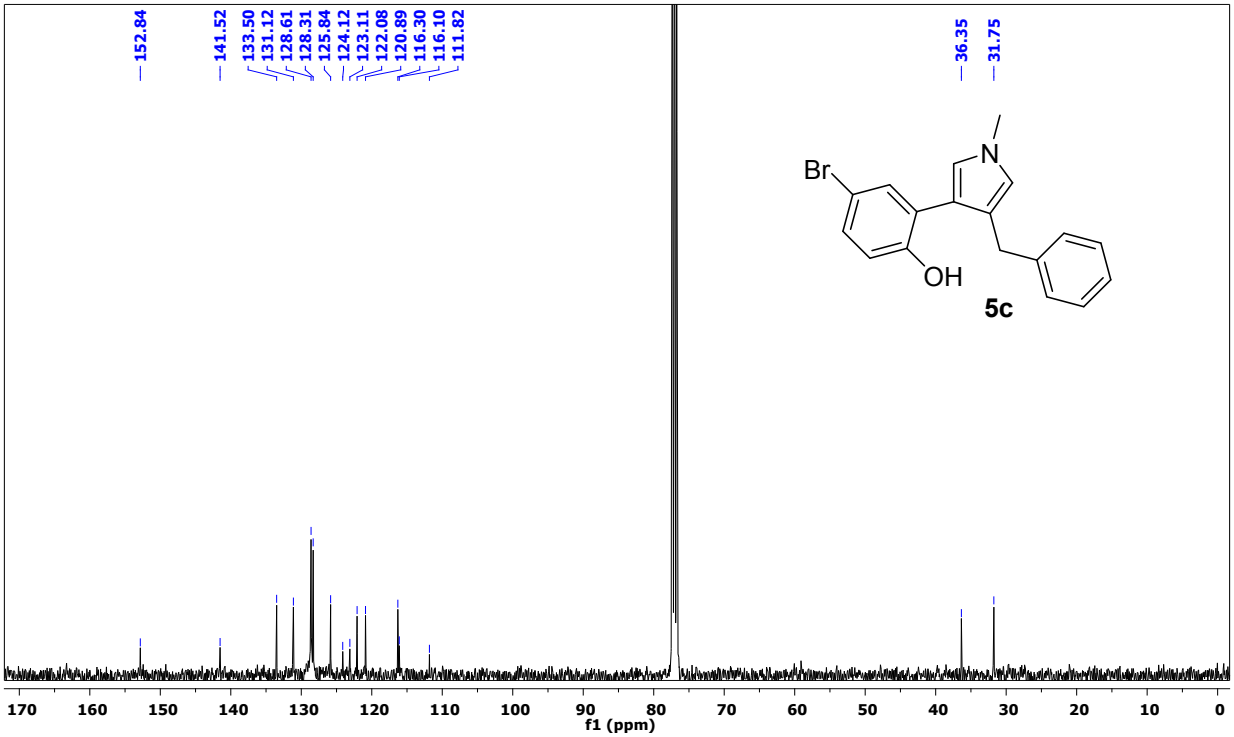
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5b



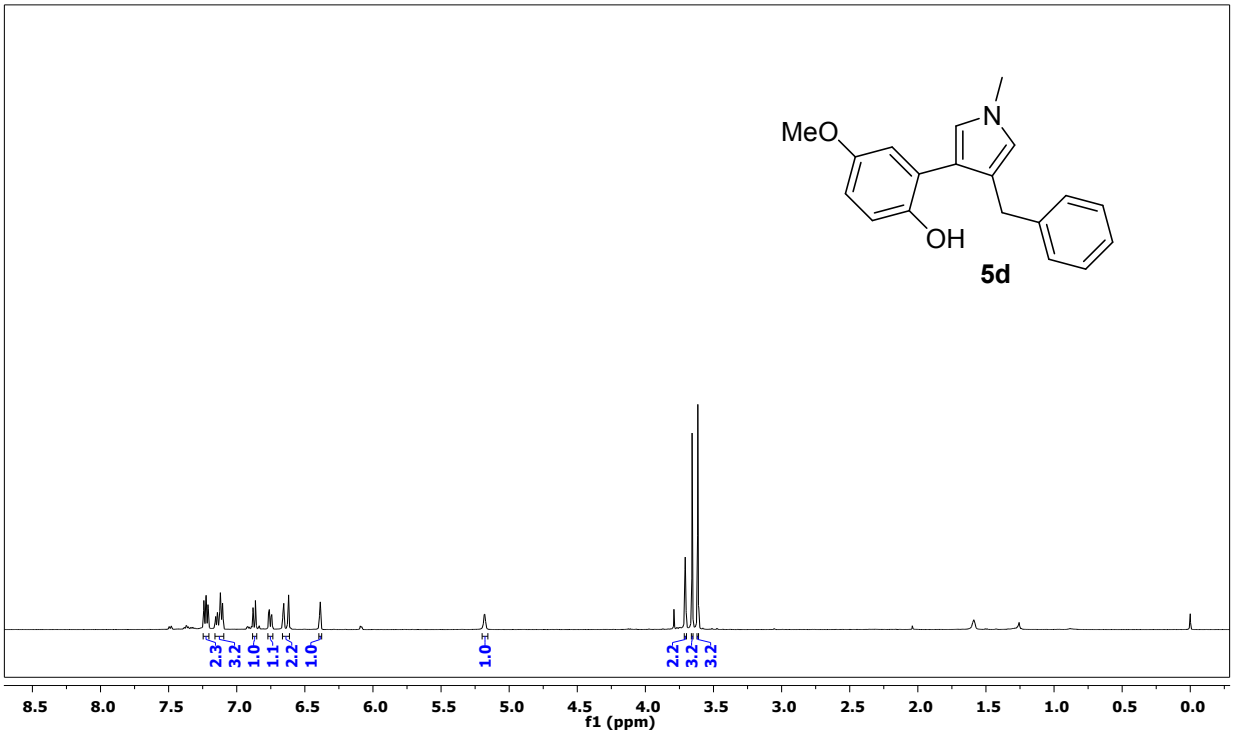
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 5b



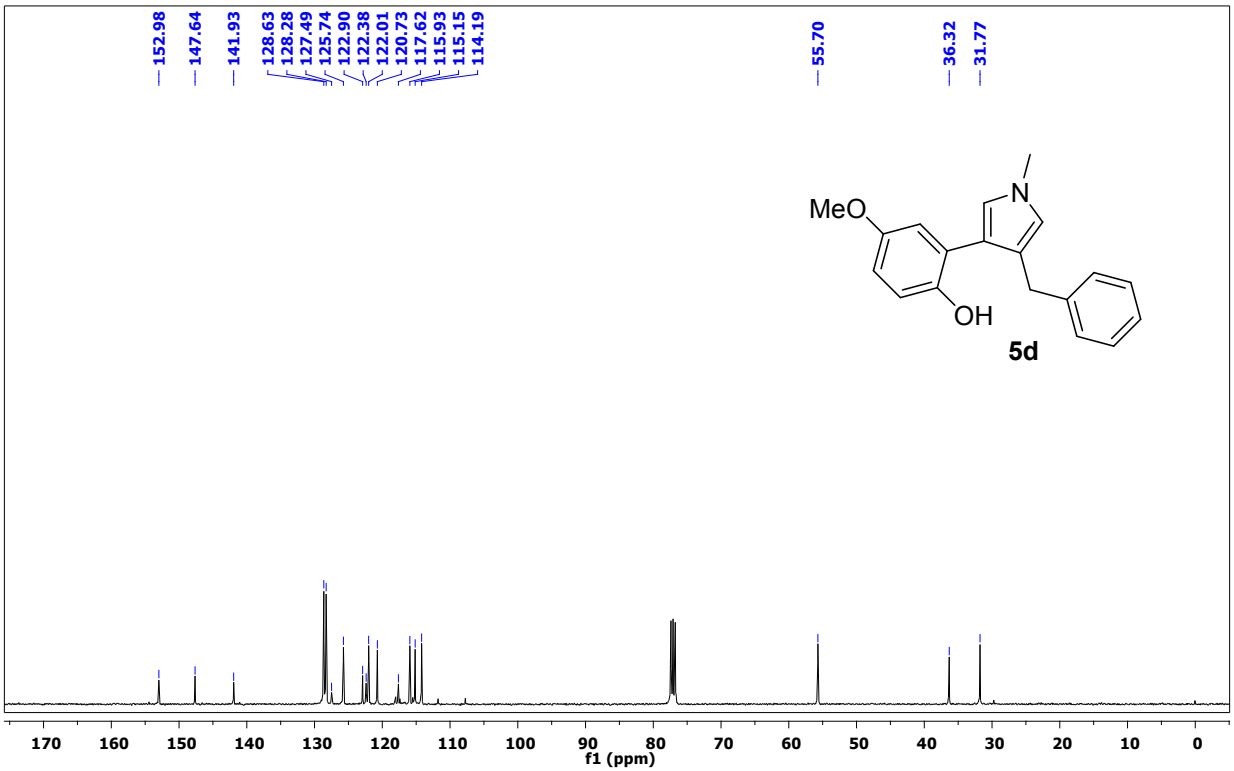
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5c



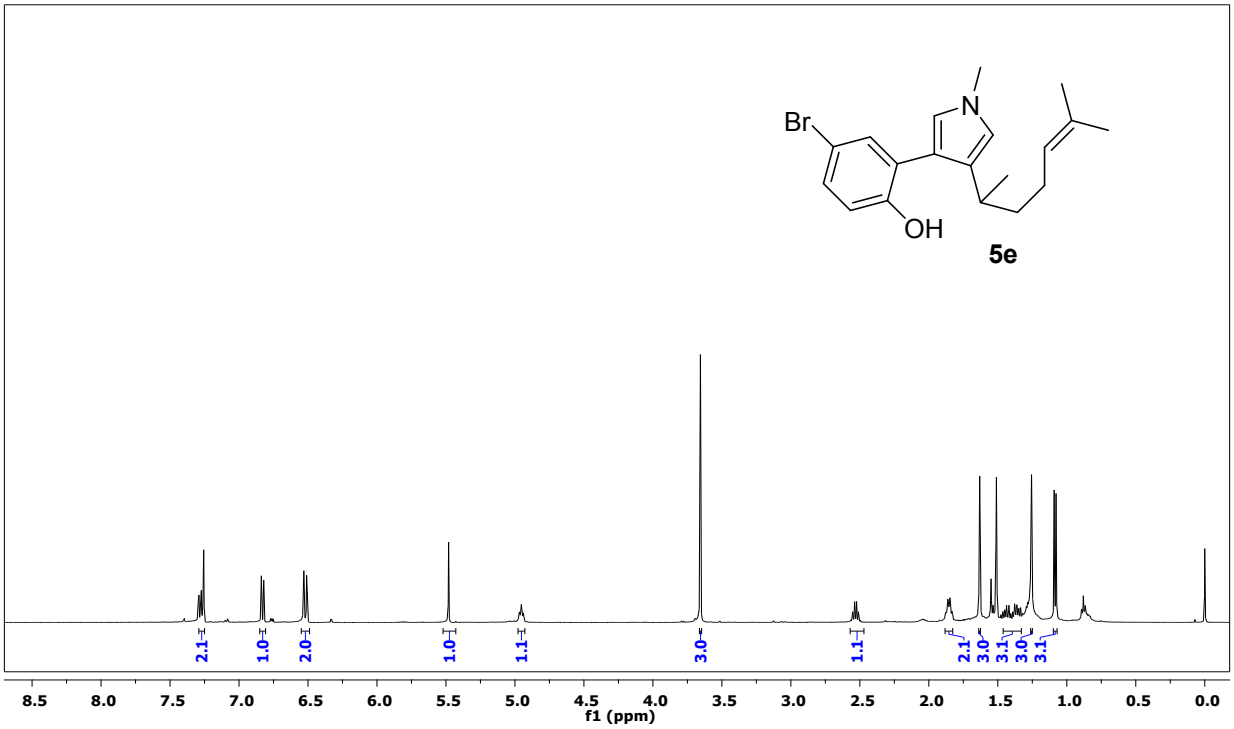
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 5c



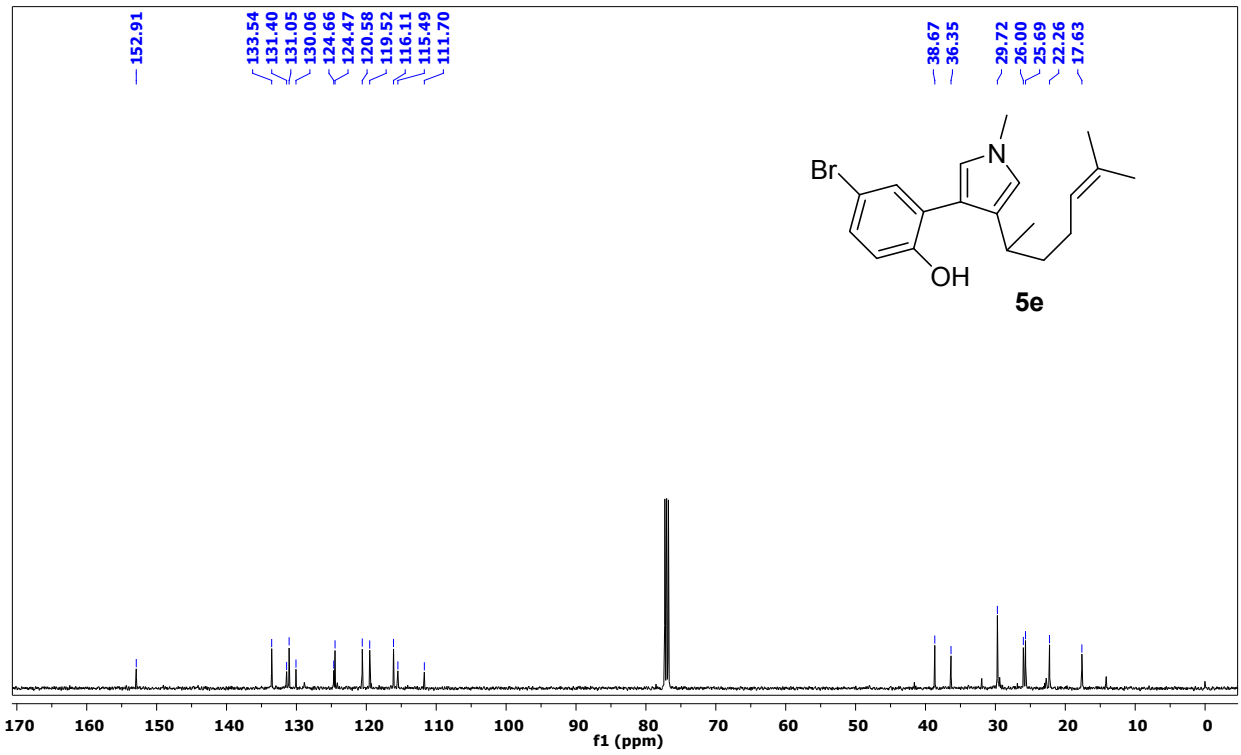
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5d



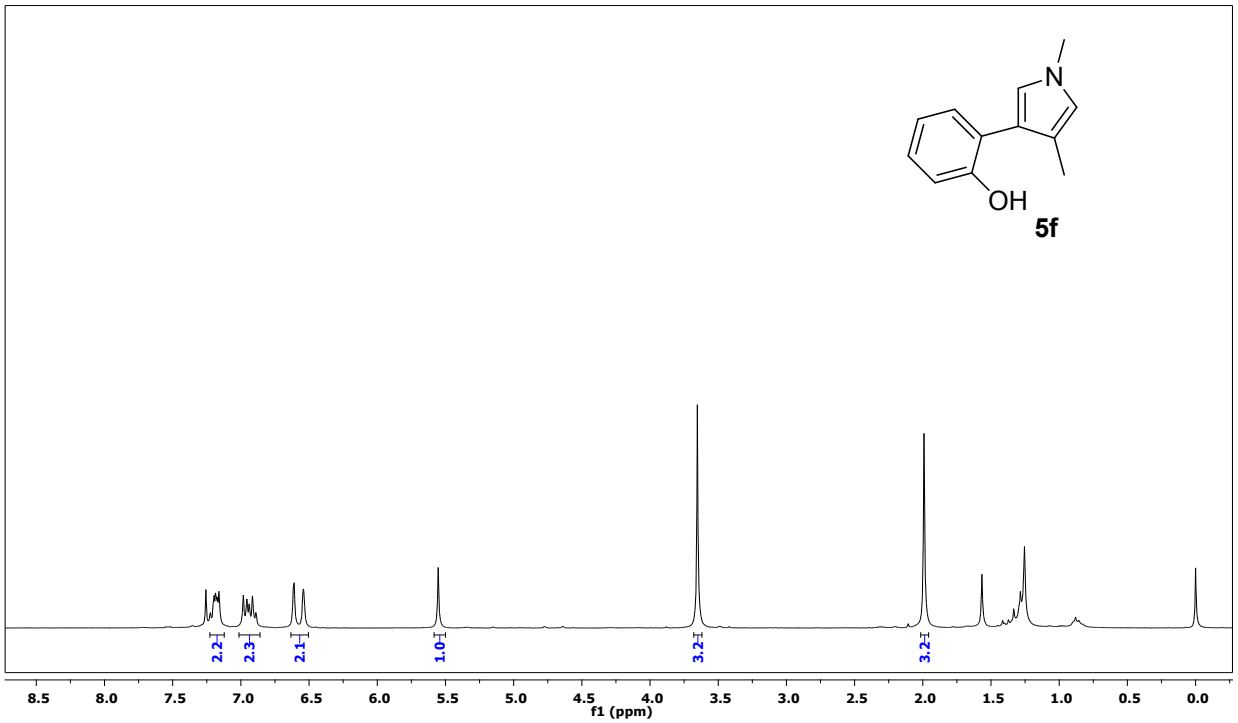
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 5d



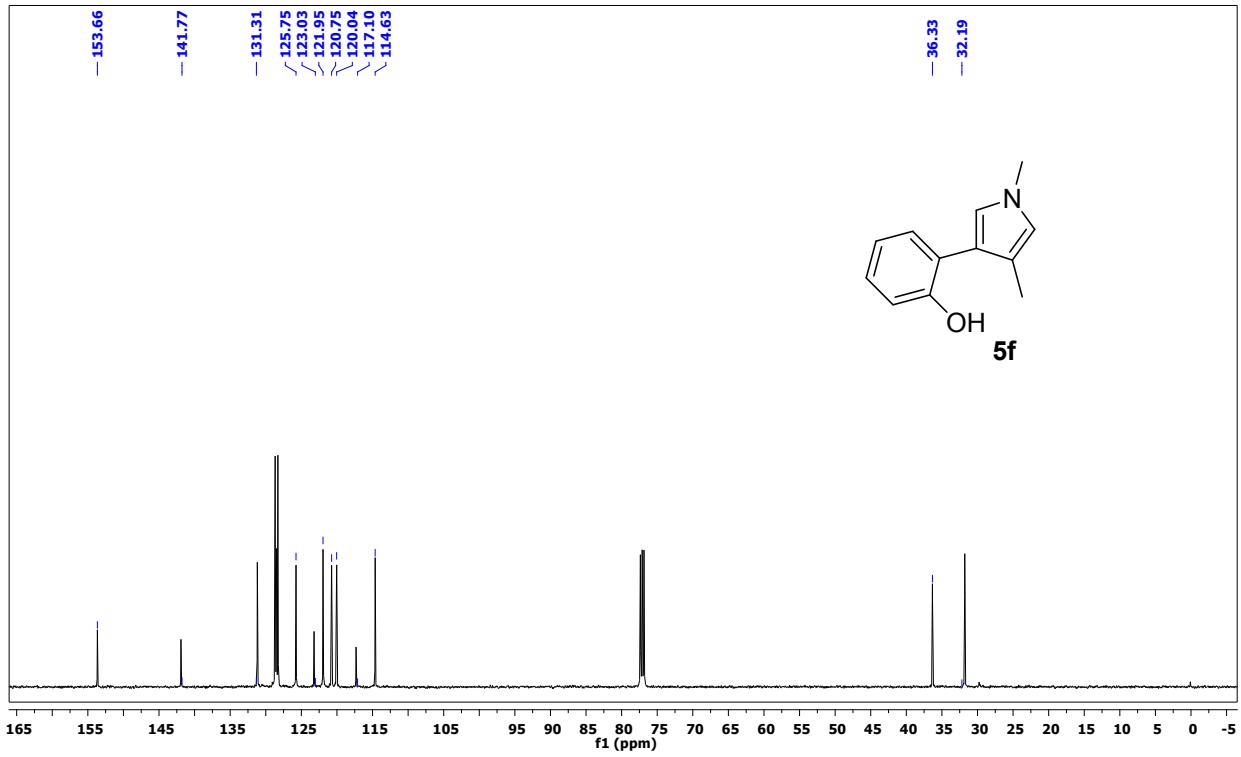
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5e



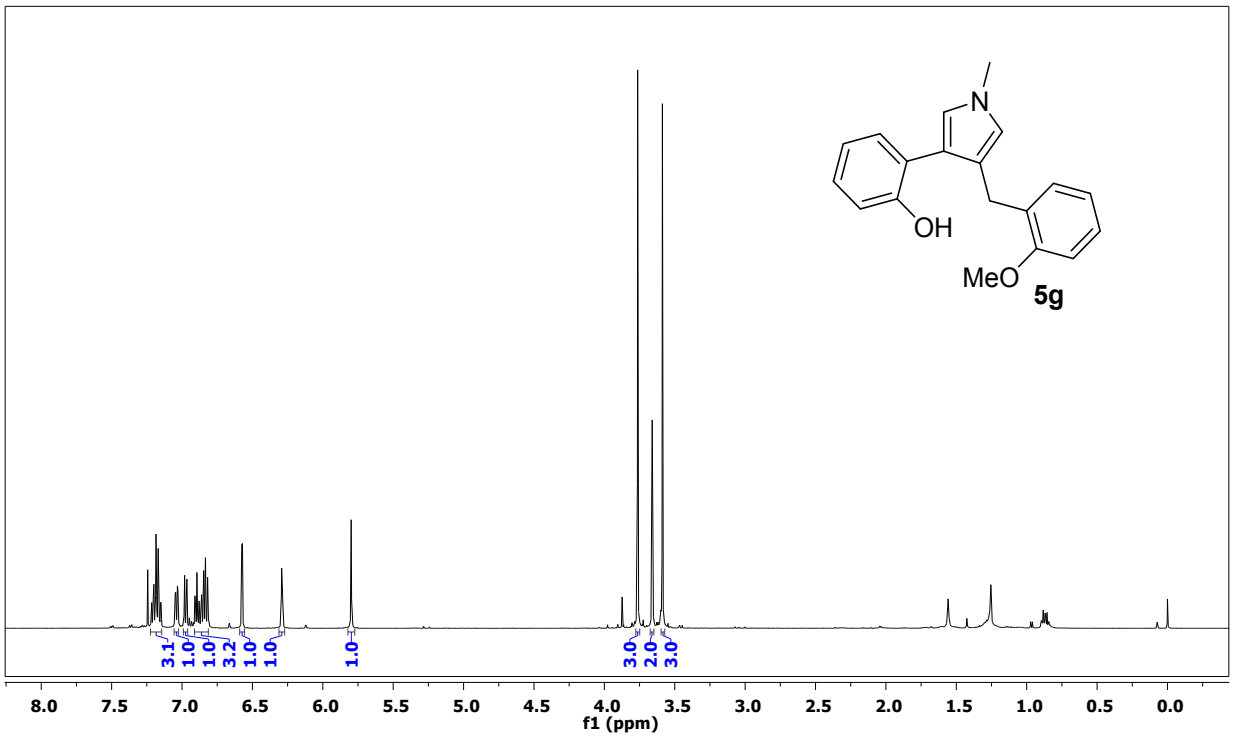
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound 5e



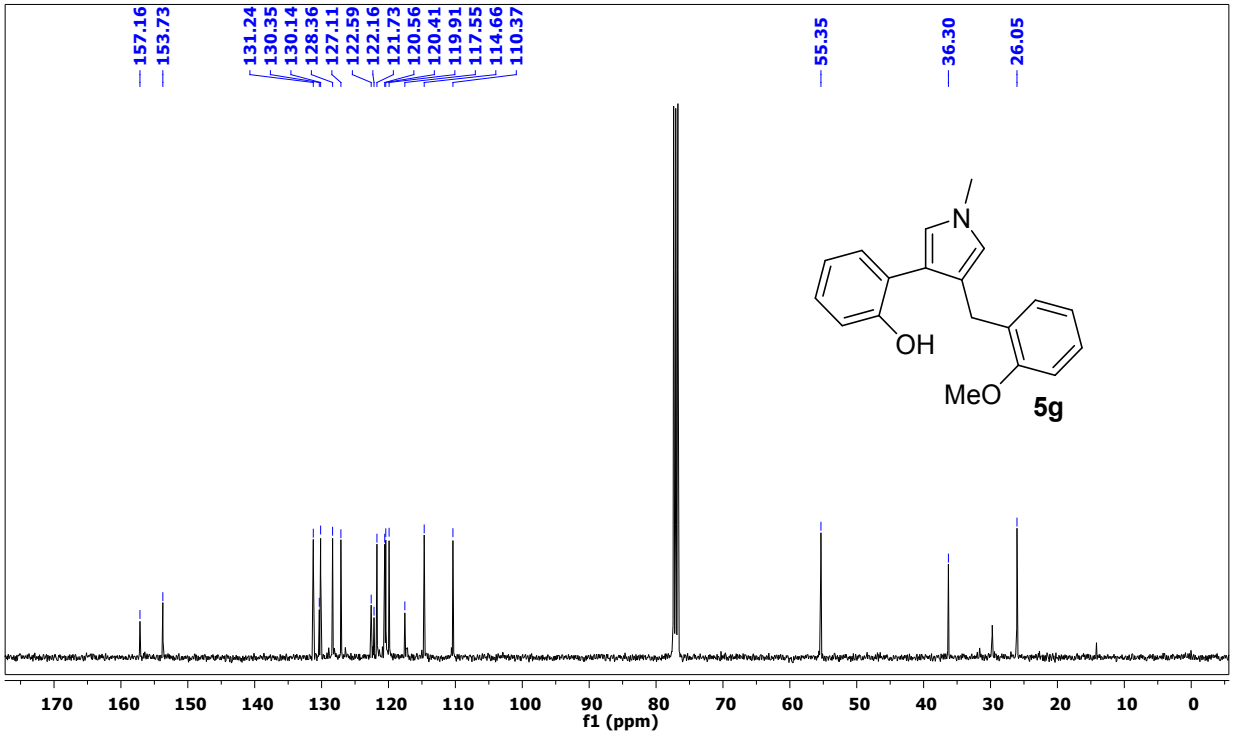
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of compound 5f



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 5f



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 5g



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 5g

4. X-ray Crystallography.

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data was accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS [2] and refinement was carried out by full-matrix least-squares technique using SHELXL [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms with U_{iso}(H) 1.2U_{eq}(C).

Crystal Data for 3b: $C_{27}H_{22}NO_3Cl$ (M =443.93 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 12.0549(11) Å, b = 8.6910(8) Å, c = 21.1744(19) Å, β = 103.921(1)°, V = 2153.3(3) Å^3, Z = 4, T = 294.15 K, μ(Mo Kα) = 0.208 mm^{-1}, *Dcalc* = 1.3693 g/cm^3, 24460 reflections measured (3.96° ≤ 2Θ ≤ 56.74°), 5229 unique (R_{int} = 0.0219, R_{sigma} = 0.0167) which were used in all calculations. The final R_1 was 0.0449 (I>2σ(I)) and wR_2 was 0.1430 (all data). CCDC 1532822 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015**)** Acta Crystallogr C71: 3-8.

Figure Caption

Fig.1. A view of **3b**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.