Pd Catalyzed Regioselective Intramolecular Dehydrogenative C-5 Cross Coupling in N-substituted Pyrroles-Azole System

Krishna N. Tripathi, Devalina Ray and Ravi P. Singh*

Department of Chemistry, Indian Institute of Technology Delhi, HauzKhas, New Delhi-110016, India

ravips@chemistry.iitd.ac.in

Supporting Information

Contents

Experimental Procedure:

General method

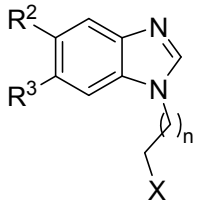
Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents with residual protonated solvent signal as internal reference on a BrückerAva-300 or BrückerAva-400. Chemical shifts are reported in parts per million using the solvent resonance internal standard (chloroform, 7.26 and 77.0 ppm or DMSO, 2.50 and 40.0 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet), coupling constant, and integration. FT-IR, infrared spectra were recorded on a Nicolet protégé 460 FTIR spectrometer and are reported in frequency of absorption. Electrospray and electron impact high resolution mass spectrometry was performed by Brücker mass spectrometer. The data is

recorded as the ionization method followed by the calculated and measured masses. Solvents for starting material preparation and coupling reactions were dried before use.

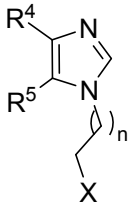
Preparation of starting materials:

Materials:

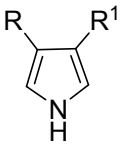
The following starting materials were either purchased or used as it is or they were synthesized using known literature procedure. Compounds (**Va**), (**Vb**) were purchased from Sigma- Aldrich and Alfa aesar, used without further purification. Compounds **I** (**a-e, g**), **II** (**a-c, f** and **g**) and **IV** (**a-e**) were prepared from Benzimidazole, imidazole and pyrrole derivatives by following literature procedure.[1] Compound **IIIa** was prepared in three steps from pyrrole following literature procedure.[2] Compounds **III** (**b-d**) were prepared by reacting TOSMIC with corresponding *α,β*-unsaturated methyl ketones or ethyl and *tert*-butyl esters *via* van-Leusen pyrrole synthesis following literature procedure.[3] Compounds **IIIe** were prepared by reacting TOSMIC with styrene following literature procedure.[4] Compound **III (f, g)** were prepared in four steps from pyrrole following literature procedure.[5] Compound **VI (a, b)** were prepared in two steps from **III (f, g)** following literature procedure.[6]



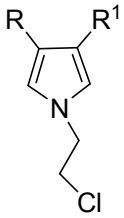
$R^2 = R^3$= H, n=1, X= Cl **(Ia)**, n=2, X= Br **(IIa)**
$R^2 = R^3$=CH_3, n=1, X=Cl **(Ib)**, n=2, X= Br **(IIb)**
$R^2 = R^3$= Cl, n=1, X=Cl **(Ic)**, n=2, X=Br **(IIc)**
$R^2 = R^3$= Br, n=1, X=Cl **(Id)**
$R^2 = R^3$= Ph, n=1, X=Cl **(Ie)**



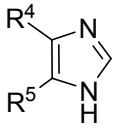
$R^4 = R^5$= Cl, n=2, X=Br **(IIf)**
$R^4 = R^5$= Ph, n=1, X=Cl **(Ig)**, n=2, X=Br **(IIg)**



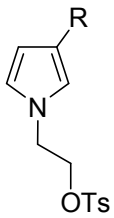
R^1 = CHO, R= H **(IIIa)**
R^1 = $COCH_3$, R= Ph **(IIIb)**
R^1 = CO_2Et, R= Ph **(IIIc)**
R^1 = $CO_2{}^tBu$, R= H **(IIId)**
R^1 = Ph, R = H **(IIIe)**
R^1 = Et, R = H **(IIIf)**
R^1 = Bu, R = H **(IIIg)**



R^1 = CHO, R= H **(IVa)**
R^1 = $COCH_3$, R= Ph **(IVb)**
R^1 = CO_2Et, R= Ph **(IVc)**
R^1 = $CO_2{}^tBu$, R= Ph **(IVd)**
R^1 = Ph, R = H **(IVe)**



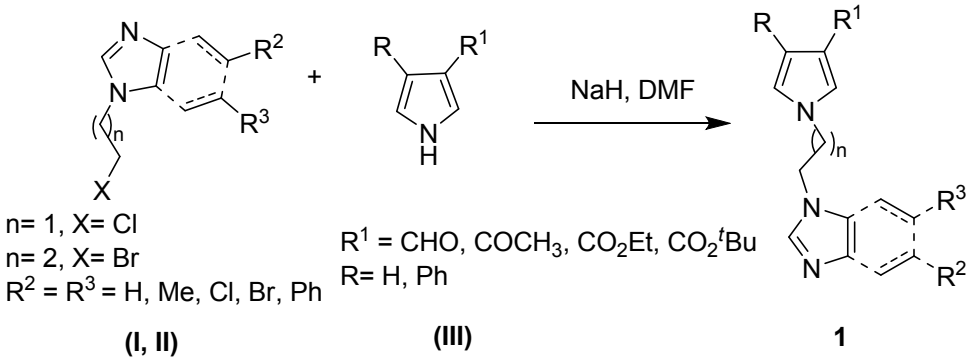
$R^4 = R^5$= Cl **(Va)**
$R^4 = R^5$= Ph **(Vb)**



R = Et **(VIa)**
R = Bu **(VIb)**

General procedure A for N-alkylation of 3-substituted and3, 4-disubstituted pyrrols:

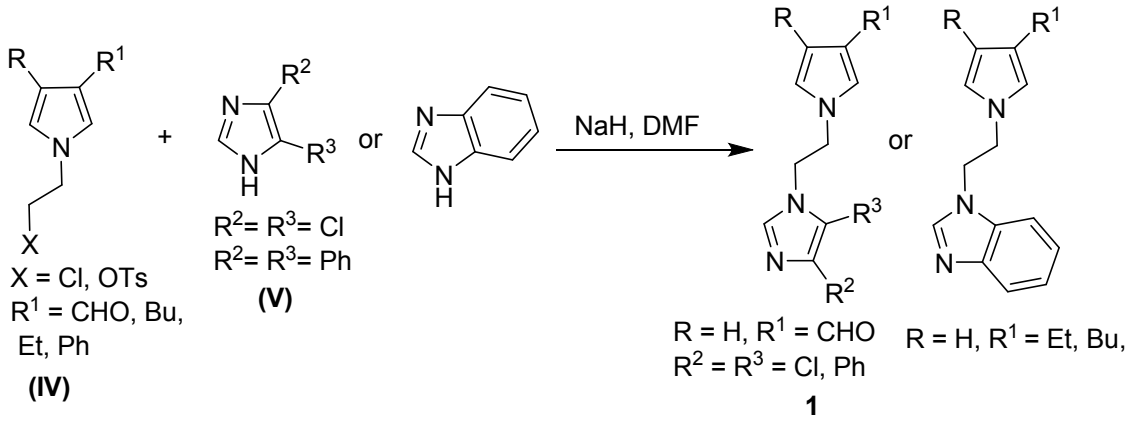
To a suspension of NaH (1.0 equivalent) in dry DMF at 0 ºC, was dropwise added a solution of 3-substituted or 3,4-disubstituted pyrrole derivatives (**IIIa-d**) (1.0 equivalent) in dry DMF and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-haloethyl)-1*H*-azole or 1-(3-halopropyl)-1*H*-azole derivatives (**Ia-e**, **Ig**, **IIa-c**, **IIf**, **IIg**) (1.2 equivalent) in DMF was added to it and the resulting solution was heated at 80 ˚C for 16 h. The completion of reaction was monitored by TLC. Once the reaction completed, saturated brine solution was added to the reaction mixture and it was extracted with EtOAc (three times).The combined organic layers were washed with brine and dried over Na_2SO_4. Further, it was filtered and concentrated under reduced pressure to provide an organic residue. The residue was purified by silica gel column chromatography to provide the desired product.



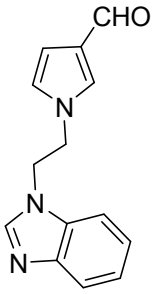
Scheme S1: Coupling of 1-(2-haloalkyl)-1*H*-azole derivatives with 3-substituted and 3,4-disubstituted pyrroles

General procedure B for N-alkylation of substituted imidazoles:

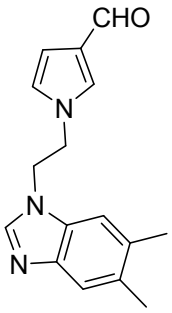
To a suspension of NaH (1.0 equivalent) in dry DMF at 0 ºC was dropwise added a solution of) or 4,5 disubstituted imidazole derivatives (**Va** and **Vb**) (1.0 equivalent) in dry DMF and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-haloethyl)-1*H*-pyrrole derivatives (**IVa-d**) (1.2 equivalent) in DMF was added to it and the resulting solution was heated at 80 °C for 16 h. The completion of reaction was monitored by TLC. Once the reaction completed, saturated brine solution was added to the reaction mixture and it was extracted with EtOAc (three times). The combined organic layers were washed with brine and dried over Na_2SO_4. The resulting solution was filtered and concentrated under reduced pressure to provide an organic residue. The residue was purified by silica gel column chromatography to provide the desired product.



Scheme S2: Coupling of 1-(2-chloroethyl)-*1H*-pyrrole derivatives with substituted azoles

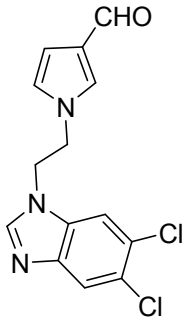


Compound 1a: Following the general procedure A, to the NaH (72 mg, 60 wt% in mineral oil, 1.80 mmol) suspension in dry DMF (4 mL) at 0 ºC was dropwise added a pyrrole-3-carboxyaldehyde (**IIIa**) (171 mg, 1.80mmol) in dry DMF (2 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloroethyl)-1*H*-benzimidazole (**Ia**) (390 mg, 2.16 mmol) in DMF (3 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 86:14) to give the product **1a** as brown solid (154 mg, yield = 36%); mp 90-94 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$): 9.44 (1H, s), 7.68 (1H, bs), 7.33 (1H, s), 7.17 (3H, bs), 6.79 (1H, s), 6.42 (1H, s), 6.31 (1H, s), 4.38 (2H, bs), 4.19 (2H, bs) ;**^{13}C NMR** (75 MHz, $CDCl_3$): 185.15, 143.60, 142.92, 133.08, 129.15, 127.09, 123.36, 123.18, 122.52, 120.36, 109.13, 103.85, 49.32, 45.86; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{14}H_{14}N_3O$: 240.1131; found 240.1135; **IR** (thin film): ν_{max} 1655, 1365, 1150, 748 cm^{-1}.

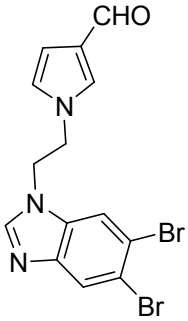


Compound1b: Following the general procedure A, to the NaH (48 mg, 60 wt% in mineral oil, 1.2mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a pyrrole-3-carboxyaldehyde (**IIIa**) (114 mg, 1.2 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloro-ethyl)-5,6-dimethyl-1*H*-benzimidazole (**Ib**) (300 g, 1.44 mmol) in DMF (4mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 84: 16) to give the product **1b** as brown solid (128 mg, yield = 40%) ^{o}C. **^{1}H NMR** (300 MHz,

$CDCl_3$): 9.63 (1H, s), 7.58 (1H, s), 7.36 (1H,s), 6.99 (1H, s), 6.94 (1H, s), 6.61 (1H, s), 6.42 (1H, d, *J* = 2.1 Hz), 4.47 (2H, t, *J* = 5.7 Hz), 4.32 (2H, t, *J* = 5.7 Hz), 2.39 (6H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.01, 142.02, 132.73, 131.57, 128.69, 127.36, 123.05, 120.67, 109.25, 109.06, 49.51, 46.08, 20.49, 20.19; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{16}H_{18}N_3O$: 268.1444; found 268.1445; **IR** (thin film): ν_{max} 2923, 1655, 1363, 1143, 748 cm^{-1}.

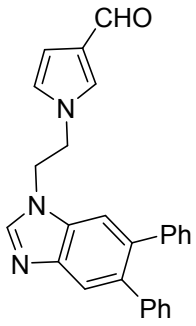


Compound1c: Following the general procedure A, to the NaH (58 mg, 60 wt% in mineral oil, 1.45mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a pyrrole-3-carboxyaldehyde (**IIIa**) (138 mg, 1.45mmol) in dry DMF (3 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 5,6-Dichloro-1-(2-chloro-ethyl)-1*H*-benzoimidazole (**Ic**) (431mg, 1.75 mmol) in DMF (3mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 90:10) to give the product **1c** as brown solid (169 mg, yield = 38%); mp 90-94 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$): 9.60 (1H, s), 7.83 (1H, s), 7.73 (1H, s), 7.30 (1H, s), 7.23 (1H, s), 6.62(1H, s), 6.55 (1H, s), 4.08 (2H, t, *J* = 4.8, 5.4 Hz), 3.93 (2H, t, *J* = 4.8, 5.9 Hz) ; **^{13}C NMR** (75 MHz, $CDCl_3$): 185.16, 144.53, 142.91, 132.30, 128.02, 127.88, 127.65, 127.15, 122.83, 121.96, 110.35, 109.99, 44.51, 46.45, 29.67; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{14}H_{11}Cl_2N_3NaO$: 330.0167; found 330.0171: **IR** (thin film): ν_{max} 2955, 1655,1373, 1148, 748 cm^{-1}.

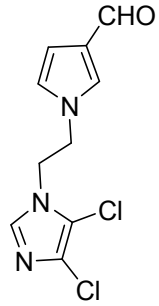


Compound1d: Following the general procedure A, to the NaH (46 mg, 60 wt% in mineral oil,1.15 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a pyrrole-3-carboxyaldehyde (**IIIa**) (109 mg, 1.15mmol) in dry DMF (3 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 5,6-Dibromo-1-(2-chloro-ethyl)-1*H*-benzoimidazole (**Id**) (463 mg, 1.36 mmol) in DMF (3 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 88:12) to give the product **1d** as brown solid (145 mg, yield = 32%). **^{1}H NMR** (300 MHz, DMSO): 9.35 (1H, s), 8.03 (1H, s), 7.96 (2H, s), 7.45 (1H, s), 6.76 (1H, s), 6.39-6.38 (1H, d, *J*= 6.0 Hz), 4.68-40.65 (2H, t, *J* = 3.0 Hz), 4.42-4.38 (2H, t, *J* = 6.0 Hz); **^{13}C NMR** (75 MHz, DMSO): 185.25, 146.63, 144.07, 134.50, 131.08, 126.70, 124.49, 124.10, 117.29, 116.48, 115.72,

107.77, 49.30, 45.74; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{14}H_{12}Br_2N_3O$: 395.9347; found 395.9155. ; **IR** (thin film): ν_{max} 2923, 1655, 1365, 1143, 755 cm^{-1}.

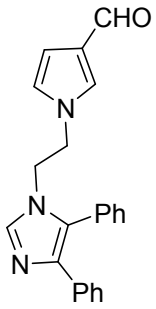


Compound1e: Following the general procedure A, to the NaH (40 mg, 60 wt% in mineral oil,0.99 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a pyrrole-3-carboxyaldehyde (**IIIa**) (94 mg, 0.99 mmol) in dry DMF (3 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 5,6-Diphenyl-1-(2-chloro-ethyl)-1*H*-benzoimidazole (**Ie**) (394 mg, 1.19 mmol) in DMF (3 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 92:8) to give the product **1e** as brown solid (124 mg, yield = 32%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.58 (1H, s), 7.91 (1H, bs), 7.83 (1H, s), 7.26-7.04 (12H, m), 6.56 (1H, s), 6.48 (1H, s), 4.60 (2H, bs), 4.38 (2H, bs); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.21, 143.59, 141.56, 141.41, 137.63, 136.91, 132.46, 130.21, 130.10, 128.79, 127.92, 127.87, 127.46, 126.62, 126.43, 123.27, 121.38, 110.81, 109.45, 49.74, 46.49; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{26}H_{22}N_3O$: 392.1757; found 392.1756. ; **IR** (thin film): ν_{max} 2930, 1658,1363, 1143, 748 cm^{-1}.

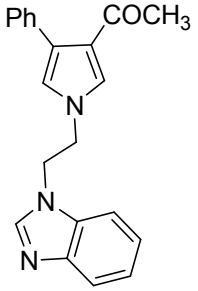


Compound1f: Following the general procedure B, to the NaH (43.6 mg, 60 wt% in mineral oil, 1.09 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a 4,5-Dichloroimidazole (**Va**) (149 mg, 1.09 mmol) in dry DMF (3 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloro-ethyl)-1*H*-pyrrole-3-carbaldehyde (**IVa**) (205 mg, 1.31 mmol) in DMF (3mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (EtOAc: MeOH 96:4) to give the product **1f** as brown solid (128 mg, yield = 46%). **^{1}H NMR** (400 MHz, $CDCl_3$): 9.68 (1H, s), 7.07 (1H, s), 6.92 (1H, s), 6.62 (1H, s), 6.48 (1H, s), 4.26-424 (4H, m); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.31, 134.87, 128.91, 127.31, 126.37, 123.18, 112.87, 109.27, 49.43, 46.97; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{10}H_9Cl_2N_3NaO$: 280.0015; found 280.0017; **IR** (thin film): ν_{max} 2945, 1655, 1483, 1251, 1164, 758 cm^{-1}.

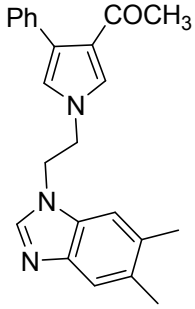
Compound1g: Following the general procedure B, to the NaH (36 mg, 60 wt% in mineral oil, 0.90 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise



added a 4,5-diphenyl-*1H*-imidazole (**Vb**) (198 mg, 0.90 mmol) in dry DMF (2mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloro-ethyl)-1*H*-pyrrole-3-carbaldehyde (**IVa**) (170 mg, 1.08 mmol) in DMF (3mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography ((EtOAc: MeOH 95:5) to give the product **1g** as brown solid (131 mg, yield = 43%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.64 (1H, s), 7.47-7.44 (5H, m), 7.31 (1H, s), 7.22-7.14 (5H, m), 6.92 (1H, s), 6.56 (1H, s), 6.33 (1H, s), 4.11 (2H, t, *J* = 5.4 Hz), 3.93 (2H, t, *J* = 5.4 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.17, 138.63, 136.79, 134.01, 130.69, 129.99, 129.46, 129.19, 128.59, 128.22, 128.07, 127.32, 126.67, 126.67, 126.59, 123.07, 109.16, 50.19, 45.85; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{22}H_{20}N_3O$: 342.1601; found 342.1584; **IR** (thin film): ν_{max} 2944, 1656, 1248, 1158, 755 cm^{-1}.

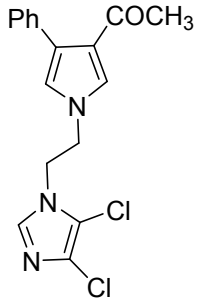


Compound1h: Following the general procedure A, to the NaH (56 mg, 60 wt% in mineral oil, 1.39mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added a 1-(4- phenyl-1*H*-pyrrole-3-yl) ethanone (**IIIb**) (257 mg, 1.39mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloroethyl)-1*H*-benzimidazole (**Ia**) (300 mg, 1.67 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1h** as brown solid (137 mg, yield = 30%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.83 (1H, s), 7.58 (1H, s), 7.29-7.19 (8H, m), 6.85 (1H, s), 6.30 (1H, s), 4.42 (2H, bs), 4.19 (2H, bs), 2.12 (3H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 193.62, 143.31, 142.91, 134.60, 133.17, 129.26, 127.88, 127.68, 127.34, 126.82, 123.91, 123.47, 122.74, 121.49, 120.48, 109.01, 49.51, 45.98, 28.52; **HRMS** (ES+) cald. for $(M+H)^+$:$C_{21}H_{20}N_3O$: 330.1601; found 330.1609. IR (thin film): ν_{max} 2923, 1709, 1450, 1367, 758 cm^{-1}.

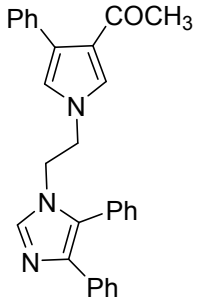


Compound1i: Following the general procedure A to the NaH (32 mg, 60 wt% in mineral oil, 0.80 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added 1-(4- phenyl-1*H*-pyrrole-3-yl) ethanone (**IIIb**) (148 mg, 0.80 mmol) in dry DMF (6 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloroethyl)-5,6-dimethyl-1*H*-benzimidazole (**Ib**) (200 mg, 0.96mmol) in DMF (6 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column

chromatography (Ethyl acetate: MeOH 98:2) to give the product **1i** as white solid (70 mg, yield = 20%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.73 (1H, s), 7.48 (2H, s), 7.19-7.16 (5H, m), 6.86 (2H, d, *J* = 2.1 Hz), 6.23 (2H, d, *J* = 2.1 Hz), 4.37 (2H, bs), 4.16 (2H, s), 2.26 (3H, s), 2.23 (3H, s), 2.04 (3H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 199.67, 134.60, 133.27, 133.32, 129.23, 127.93, 127.84, 127.23, 126.77, 123.85, 121.64, 119.68, 109.48, 49.61, 46.30, 28.54, 20.59, 20.24; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{23}H_{24}N_3O$: 358.1914; found 358.1913. IR (thin film): ν_{max} 2928, 1709, 1410, 1365, 758 cm^{-1}.

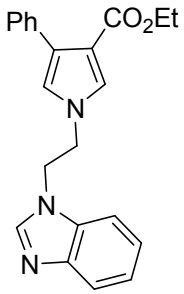


Compound1j: Following the general procedure B, to the NaH (44 mg, 60 wt% in mineral oil, 1.09mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added 4,5-dichloro-1*H*-imidazole (**Va**) (150mg, 1.09 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(1(2-chloroethyl)-4-phenyl-1*H*-pyrrole-3-yl) ethanone (**IVb**) (324 mg, 1.31 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (EtOAc) to give the product **1j** as brown solid (215 mg, yield = 60%).**^{1}H NMR** (300 MHz, $CDCl_3$): 7.24-7.14 (5H, m), 6.91 (2H, s), 6.26 (1H, s), 3.95-3.89 (4H, m), 2.19 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): 193.42, 135.04, 134.25, 129.22, 128.21, 127.82, 126.96, 126.69, 126.14, 123.51, 121.79, 112.95, 53.66, 49.24, 28.49; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{17}H_{15}Cl_2N_3NaO$: 370.0484, found 370.0496; IR (thin film): ν_{max} 2923, 1709, 1404, 1360, 758 cm^{-1}.

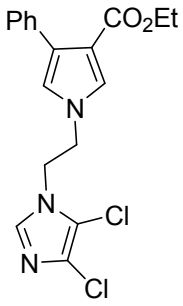


Compound1k: Following the general procedure A, to the NaH (26 mg, 60 wt% in mineral oil, 0.64mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added 1-(4-phenyl-1*H*-pyrrole-3-yl) ethanone (**IVb**) (118 mg, 0.64mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chlorooethyl)-4,5-diphenyl-1*H*-imidazole (**Vb**) (217 mg, 0.76mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (EtOAc) to give the product **1k** as brown solid (55 mg, yield = 20%).**^{1}H NMR** (300 MHz, $CDCl_3$): 7.63 (1H, bs), 7.47-7.41 (5H, m), 7.39-7.28, (5H, m), 7.26-7.17(6H, m), 6.94 (1H, d, *J* = 2.1 Hz), 6.27 (1H, d, *J* = 2.1 Hz), 4.18 (2H, bs), 3.92 (2H, bs), 2.23 (3H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 192.41, 137.03, 135.88, 133.56, 132.45, 129.62, 128.54,128.39, 128.22, 127.25, 126.83, 126.55, 126.08, 125.86, 125.69, 122.92, 120.55, 49.02, 44.91, 27.57; **HRMS**

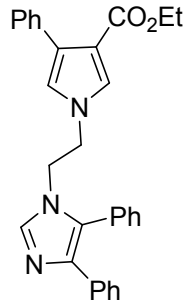
(ES+) cald. for $(M+H)^+$: $C_{29}H_{26}N_3O$: 432.2070; found 432.2063. IR (thin film): ν_{max} 2925, 1712, 1414, 1362, 758 cm^{-1}.



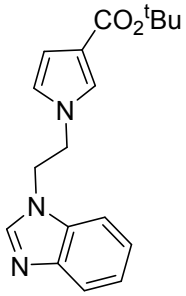
Compound1l: Following the general procedure A, to the NaH (66 mg, 60 wt% in mineral oil, 1.64 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added Ethyl 4-phenyl-1*H*-pyrrole-3-carboxylate (**IIIc**) (353 mg, 1.64 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloroethyl)-1*H*-benzimidazole (**Ia**) (354 mg, 1.96 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 99:1) to give the product **1l** as yellow solid (159 mg, yield = 27%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.86-7.83 (1H, m), 7.56 (1H, s), 7.37-7.24 (8H, m), 7.14 (1H, d, *J* = 2.4 Hz), 6.27 (1H, d, *J* = 2.4 Hz), 4.46 (2H, t, *J* = 5.4), 4.25-4.14 (4H, m), 1.22 (3H, t, *J* = 7.2 Hz), **^{13}C NMR** (75 MHz, $CDCl_3$): 164.19, 143.78, 142.83, 134.24, 129.31, 127.63, 127.31, 126.64, 123.41, 122.61, 120.83, 120.73, 114.56, 108.89, 59.61, 49.45, 46.03, 14.22; **HRMS** (ES+) cald. For $(M+Na)^+$: $C_{22}H_{21}N_3NaO_2$: 382.1531; found 382.1483; **IR** (thin film): ν_{max} 2973, 1699, 1277, 1183, 1105, 757 cm^{-1}.



Compound1m: Following the general procedure B, to the NaH (44 mg, 60 wt% in mineral oil, 1.09 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added 4,5-dichloro-1*H*-imidazole (**Va**) (150 mg, 1.09 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of Ethyl 1-(2-chloroethyl)-4-phenyl-1*H*-pyrrole-3-carboxylate (**IVc**) (362 mg, 1.3mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate) to give the product **1m** as yellow solid (192, yield = 50%).**^{1}H NMR** (300 MHz, $CDCl_3$): 7.38-7.36 (2H, m), 7.21-7.18 (3H, m), 7.10 (1H, s), 6.34 (1H, s), 4.10 (2H, q, *J* = 7.2 Hz), 4.05- 3.99 (4H, m), 1.19 (3H, t, *J* = 7.2 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 164.38, 134.99, 134.35, 132.84, 129.22, 127.70, 126.60, 126.08, 120.97, 117.99, 113.97, 112.97, 59.68, 49.17, 46.72, 14.25; **HRMS** (ES+) cald. For $(M+Na)^+$: $C_{18}H_{17}Cl_2N_3NaO_2$: 400.0590; found 400.0592; **IR** (thin film): ν_{max} 2973, 1699, 1278, 1185, 1105, 757 cm^{-1}.

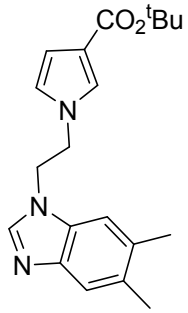


Compound1n: Following the general procedure A, to the NaH (37 mg, 60 wt% in mineral oil, 0.93mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added Ethyl 4-phenyl-1*H*-pyrrole-3-carboxylate (**IIIc**) (250 mg, 0.93mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chlorooethyl)-4,5-diphenyl-1*H*-imidazole (**Ig**) (314 mg, 1.16mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1n** as brown solid (166 mg, yield = 31%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.47 (1H, bs), 7.34-7.29 (7H, m), 7.20-7.12 (3H, m), 7.09-7.04 (5H, m), 6.89(1H, d, *J* = 2.7 Hz), 6.11 (1H, d, *J* = 2.7 Hz), 4.07-3.98 (4H, m), 3.77 (2H, t, *J* = 5.7 Hz), 1.08 (2H, t, *J* = 6.9); **^{13}C NMR** (75 MHz, $CDCl_3$): 164.27, 138.04, 136.89, 134.31, 133.57, 130.70, 129.65, 129.42, 129.31, 129.19, 128.35, 128.27, 127.76, 127.69, 127.43, 126.84, 126.76, 126.61, 120.87, 114.24, 59.61, 50.61, 50.77, 45.98; **HRMS** (ES+) cald. For $(M+H)^+$: $C_{30}H_{28}N_3O_2$: 462.2176; found 462.2179; **IR** (thin film): ν_{max} 2973, 1699, 1288, 1185, 1115, 757 cm^{-1}.

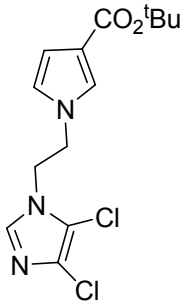


Compound1o: Following the general procedure A, to the NaH (36 mg, 60 wt% in mineral oil, 0.89 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added *tert*-butyl 1*H*-pyrrole-3-carboxyaldehyde (**IIId**) (149 mg, 0.89 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloroethyl)-1*H*-benzimidazole (**Ia**) (192 mg, 1.06 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1o** as brown solid (39 mg, yield = 14%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.82-7.67 (2H, m), 7.32-7.29 (3H, m), 7.01 (1H, bs), 6.45 (1H, bs), 6.21 (1H, bs), 4.49 (2H, d, *J* = 6.0 Hz), 4.27 (2H, d, *J* = 6.0 Hz), 1.50 (9H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 163.92, 142.80, 132.95, 125.13, 123.61, 122.88, 121.34, 120.26, 119.28, 111.12, 109.12, 79.66, 49.24, 46.35, 28.33; **HRMS** (ES+) cald. For $(M+H)^+$: $C_{18}H_{22}N_3O_2$: 312.1706; found 312.1717; **IR** (thin film): ν_{max} 2924, 2853, 1696, 1250, 1168, 763 cm^{-1}.

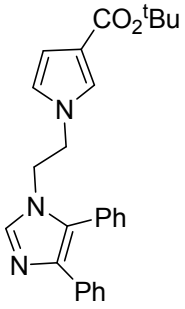
Compound1p: Following the general procedure A, to the NaH (72 mg, 60 wt% in mineral oil, 1.79mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added *tert*-butyl1*H*-pyrrole-3-carboxyalate (**IIId**) (300 mg, 1.79 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A



solution of 1-(2-chloroethyl)-5,6-dimethyl-1*H*-benzimidazole (**Ib**) (446 mg, 2.15 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1p** as white solid (103 mg, yield = 17%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.57 (1H, s), 7.38 (1H, s), 7.04 (1H, s), 6.98 (1H, s), 6.47 (1H, s), 6.20 (1H, d, *J* = 2.1 Hz), 4.45 (2H, t, *J* = 5.7 Hz), 4.24 (2H, d, *J* = 5.7 Hz), 2.38 (6H, s), 1.53 (9H, s);**^{13}C NMR** (75 MHz, $CDCl_3$): 166.94, 142.37, 142.10, 132.56, 131.68, 131.43, 125.12, 121.38, 120.63, 119.29, 111.01, 109.01, 79.61, 49.37, 46.25, 28.33, 20.47, 20.17; **HRMS** (ES+) cald. For $(M+H)^+$: $C_{20}H_{26}N_3O_2$: 340.2019; found 340.2020; **IR** (thin film): ν_{max} 2924, 2853, 1696, 1243, 1166, 763 cm-^{1}.

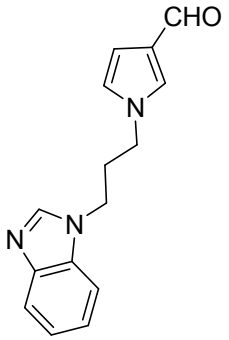


Compound1q: Following the general procedure B, to the NaH (36 mg, 60 wt% in mineral oil, 0.89 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added 4,5-dichloro-1*H*-imidazole (**Va**) (150 mg, 0.89 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of*tert*-butyl 1-(2-chloroethyl)-*1H*-pyrrole-3-carboxylate (**IVd**) (224mg, 1.07mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 96:4) to give the product **1q** as white solid (54 mg, yield = 17%). **^{1}H NMR** (300 MHz, $CDCl_3$): 6.96 (1H, s), 6.86 (1H, s), 6.39 (1H, s), 6.26 (1H, s), 4.16-4.098 (4H, m), 1.44 (9H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 164.41, 134.84, 132.77, 126.35, 125.17, 121.31, 119.18, 112.75, 111.07, 79.77, 49.13, 47.11, 28.21; **HRMS** (ES+) cald. For $(M+Na)^+$: $C_{14}H_{17}Cl_2N_3NaO_2$: 352.0600; found 352.0626; **IR** (thin film): ν_{max} 2926, 2856, 1696, 1243, 1172, 763 cm-^{1}.

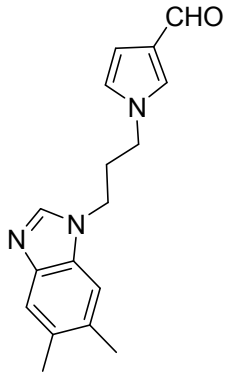


Compound1r: Following the general procedure A, to the NaH (42mg, 60 wt% in mineral oil, 1.04mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added *tert*-butyl 1*H*-pyrrole-3-carboxylate (**IIId**) (228 mg, 1.04mmol) in dry DMF (2 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chlorooethyl)-4,5-diphenyl-1*H*-imidazole (**Ig**) (285mg, 1.04mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1r** as white solid (77mg, yield = 18%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.49-7.44 (6H, m), 7.30 (1H,

s), 7.28-7.24 (2H, m), 7.21-7.15 (2H, m), 6.93 (1H, s), 6.48 (1H, s), 6.22 (1H, d, J = 2.1 Hz), 4.11(2H, t, J = 5.7 Hz), 3.89 (2H, t, J = 5.7 Hz), 1.55 (9H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 163.96, 138.66, 136.82, 134.17, 130.74, 130.18, 129.39, 129.10, 128.49, 128.17, 128.03, 126.61, 125.08, 121.28, 119.15, 110.93, 79.63, 50.01, 46.039, 28.37; **HRMS** (ES+) cald. For $(M+H)^+$: $C_{26}H_{28}N_3O_2$: 414.2176; found 414.2179; **IR** (thin film): ν_{max} 2926, 2856, 1696, 1252, 1155, 763 cm^{-1}.

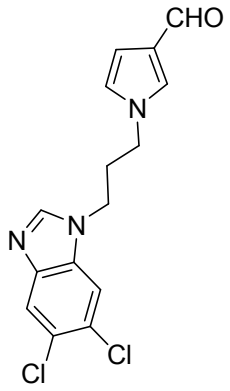


Compound1s: Following the general procedure A, to the NaH (46mg, 60 wt% in mineral oil,1.15 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added pyrrole-3-carboxyaldehyde (**IIIa**) (109 mg, 1.15mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(3-bromopropyl)-1*H*-benzo[*d*]imidazole (**IIa**)(328 mg, 1.38mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80°C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 88:12) to give the product **1s**as white solid (217mg, yield = 75%).**^{1}H NMR** (300 MHz, DMSO): 9.66(1H, s), 8.23 (1H, d, J = 1.5 Hz), 7.67 (2H, d, J = 1.5Hz), 7.55 (1H, m), 7.27- 7.22 (2H, m), 6.98 (1H, s), 6.49 (1H, d, J = 1.5Hz), 4.25 (2H, t, J = 6.9Hz), 4.04 (2H, t, J = 6.7 Hz), 2.33 (2H, t, J = 6.9 Hz);**^{13}C NMR** (75 MHz, DMSO): 185.30, 144.35, 143.97, 134.16, 131.01, 126.53, 124.42, 122.80, 122.01, 119.98, 110.70, 107.58, 47.20, 41.99, 31.13;**HRMS** (ES+) cald. For $(M+H)^+$: $C_{15}H_{16}N_3O_2$: 254.1288; found 254.1301; IR (thin film): ν_{max} 2944, 1665, 1248, 1158, 755 cm^{-1}.

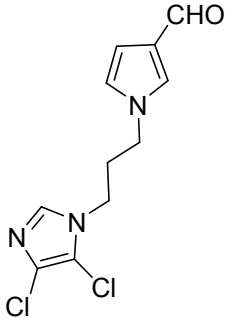


Compound1t: Following the general procedure A, to the NaH (47 mg, 60 wt% in mineral oil,1.18 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added pyrrole-3-carboxyaldehyde (**IIIa**) (112 mg, 1.18mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(3-bromopropyl)-5,6-dimethyl-*1H*-benzo[*d*]imidazole (**IIb**) (376mg, 1.42 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 90:10) to give the product **1t** as white solid (235 mg, yield = 71%). **^{1}H NMR** (300 MHz, DMSO): 9.65 (1H, s), 8.06 (1H, s), 7.68 (1H, s), 7.42 (1H, s), 7.27 (1H, s), 6.98 (1H, d, J = 2.1 Hz), 6.49 (1H, t, J = 2.1 Hz), 4.17 (2H, t, J = 7.2 Hz), 4.01 (2H, t, J = 7.2 Hz), 2.33-2.28 (8H, m); **^{13}C NMR** (75 MHz, DMSO): 185.25, 143.41, 142.45, 132.68, 131.40, 131.01, 130.29, 126.52,

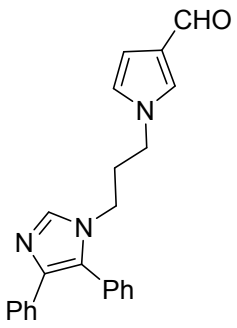
124.45, 119.98, 110.67, 107.55, 47.18, 41.86, 31.13, 20.54, 20.29; IR (thin film): ν_{max} 2944, 1666, 1244, 1144, 754 cm^{-1}.



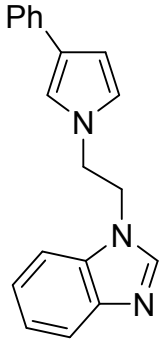
Compound1u: Following the general procedure A, to the NaH (51 mg, 60 wt% in mineral oil,1.26 mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwiseadded pyrrole-3-carboxyaldehyde (**IIIa**) (120 mg, 1.26mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(3-bromopropyl)-5,6-dichloro-1*H*-benzo[*d*]imidazole (**IIc**) (463 mg, 1.51 mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 91:9) to give the product **1u** as brown solid (316 mg, yield = 78%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.60 (1H, s), 7.83 (1H, s), 7.73 (1H, s), 7.31 (1H, s), 7.23 (1H, s), 6.62 (1H, s), 6.55 (1H, s), 4.08 (2H, t, *J*= 6.6 Hz), 3.93 (2H, t, *J*= 6.6 Hz), 2.35 (2H, t, *J*= 6.6 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.44, 144.62, 142.74, 132.63, 128.87, 127.24, 126.78, 126.53, 123.16, 121.30, 111.03, 108.88, 46.83, 42.03, 30.52; **HRMS** (ES+) cald. For $(M+H)^+$: $C_{15}H_{14}Cl_2N_3O$: 322.0508; found 322.0509. **IR** (thin film): ν_{max} 2948, 1666, 1254, 1160, 756 cm^{-1}.



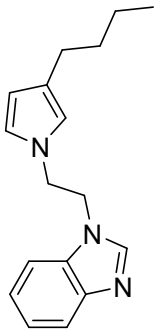
Compound1v: Following the general procedure A, to the NaH (51 mg, 60 wt% in mineral oil, 1.26mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added pyrrole-3-carboxyaldehyde (**IIIa**) (100 mg, 1.05 mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(3-bromopropyl)-4,5-dichloro-1*H*-imidazole (**IIf**) (390mg, 1.51mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 99:1) to give the product **1j** as brown solid (180 mg, yield = 52%).**^{1}H NMR** (300 MHz, $CDCl_3$): 9.64 (1H, s), 7.42 (1H, s), 7.33 (1H, s), 6.63 (1H, s), 6.56 (1H, s), 3.96-3.85 (1H, m), 2.27 (2H, q, *J* = 6.7 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.30, 134.44, 128.66, 126.89, 126.28, 123.10, 108.87, 46.72, 43.22, 30.91; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{11}H_{11}Cl_2N_3NaO$: 294.0171; found 294.0171; IR (thin film): ν_{max} 2945, 1666, 1254, 1162, 758 cm^{-1}.



Compound 1w: Following the general procedure A, to the NaH (42 mg, 60 wt% in mineral oil, 1.05mmol) suspension in dry DMF (2 mL) at 0 ºC was dropwise added pyrrole-3-carboxyaldehyde (**IIIa**) (100 mg, 1.05mmol) in dry DMF (4 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(3-bromopropyl)-4,5-diphenyl-1*H*-imidazole (**IIg**) (430 mg, 1.26mmol) in DMF (4 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: MeOH 98:2) to give the product **1j** as brown solid (250 mg, yield = 68%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.53 (1H, s), 7.67(1H, s), 7.35-7.34 (6H, m), 7.17-7.07 (4H, m), 6.91 (1H, s), 6.43 (1H, s), 6.35 (1H, s), 3.74-3.63 (4H, m), 1.91-1.84 (2H, m); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.22, 137.92, 136.80, 133.77, 130.53, 129.99, 129.42, 129.13, 128.75, 128.25, 126.70, 126.62, 123.01, 108.45, 46.76, 42.25, 31.55; **HRMS** (ES+) cald. For $(M+Na)^+$: $C_{23}H_{22}N_3O$: 356.1757; found 356.1757; IR (thin film): ν_{max} 2945, 1665, 1252, 1168, 758 cm^{-1}.

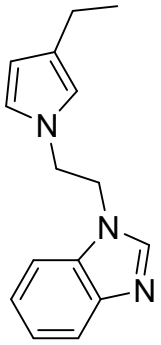


Compound 1x: Following the general procedure B, to the NaH (43 mg, 60 wt% in mineral oil, 1.09 mmol) suspension in dry DMF (4 mL) at 0 ºC was dropwise added a Benzimidazole (**IIIa**) (129 mg, 1.09 mmol) in dry DMF (2 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 1-(2-chloroethyl)-3-phenyl-1H-pyrrole (**IVe**) (270 mg, 21.31mmol) in DMF (3 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate) to give the product **1x** as brown solid (125 mg, yield = 47%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.86-7.83 (1H, m), 7.49 (1H, s), 7.43-7.41 (2H, m), 7.34-7.32 (5H, m), 7.31-7.30 (1H, m), 6.69 (1H, s), 6.41 (1H, s), 6.32 (1H, s), 4.44 (2H, t, J_1 = 5.25 Hz, J_2 = 5.25 Hz), 4.22 (2H, t, J_1= 5.25 Hz, J_2 = 5.25 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 143.10, 142.84, 135.34, 133.06, 128.56, 125.93, 125.56, 124.98, 123.36, 122.64, 121.63, 120.06, 116.94, 109.24, 107.38, 48.94, 46.36; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{19}H_{18}N_3$: 288.1501; found 288.1495;



Compound 1y: Following the general procedure B, to the NaH (32 mg, 60 wt% in mineral oil, 0.80 mmol) suspension in dry DMF (4 mL) at 0 ºC was dropwise added a Benzimidazole (**IIIa**) (95 mg, 0.80 mmol) in dry DMF (2 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 2-(3-butyl-1H-pyrrol-1-yl) ethyl 4-methylbenzenesulfonate (**VIb**) (298 mg, 0.97 mmol) in DMF (3 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate) to give the product **1z** as brown sticky solid (150 mg, yield =

54%). **^{1}H NMR** (400 MHz, $CDCl_3$): 7.82-7.80 (1H, m), 7.36 (1H, s), 7.30-7.25 (3H, m), 6.19 (1H, s), 6.25 (1H, t, J_1= 2.35 Hz, J_2 = 2.35 Hz), 6.18 (1H, s), 5.95 (1H, s) 4.41 (2H, t, J_1= 6.00 Hz, J_2 = 6.00 Hz), 4.16 (2H, t, J_1 = 6.00, J_2 = 6.00 Hz), 2.38 (2H, t, J_1= 6.00 Hz, J_2 = 6.00 Hz), 1.50-1.44 (2H, m), 1.35-1.30 (2H, m), 0.91 (3H, t, J_1= 6.00 Hz, J_2 = 6.00 Hz) ; **^{13}C NMR** (75 MHz, $CDCl_3$): 143.72, 143.23, 133.39, 126.29, 123.21, 122.42, 120.59, 120.34, 117.57, 109.70, 109.12, 49.00, 46.68, 33.42, 26.61, 22.52, 14.06;

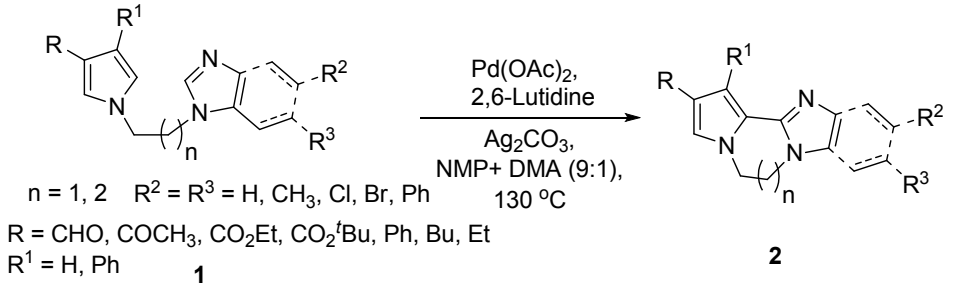


Compound 1z: Following the general procedure B, to the NaH (33.60 mg, 60 wt% in mineral oil, 0.84 mmol) suspension in dry DMF (4 mL) at 0 ºC was dropwise added a Benzimidazole (**IIIa**) (100 mg, 0.84 mmol) in dry DMF (2 mL) and the reaction mixture was allowed to stir at rt for 30 min. A solution of 2-(3-ethyl-1H-pyrrol-1-yl) ethyl 4-methylbenzenesulfonate (**VIa**) (298 mg, 1.01) in DMF (3 mL) was added to it and the resulting solution was heated at 80 °C for 16 h. The reaction mixture was quenched according to general procedure and the resulting organic residue was purified by silica gel column chromatography (Ethyl acetate: hexane 8:2) to give the product **1y** as brown sticky solid (160 mg, yield = 65%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.82 (1H, d, J = 3.80 Hz), 7.36 -7.26 (4H, m), 6.26 (1H, t, J_1= 5.2.41 Hz, J_2 = 2.41 Hz), 6.19 (1H, s), 5.97 (1H, t, J_1= 3.00 Hz, J_2 = 3.00 Hz), 4.42 (2H, t, J_1= 6.00 Hz, J_2 = 6.00 Hz), 4.17 (2H, t, J_1 = 6.00, J_2 = 6.00 Hz), 2.42 (2H, q, J_1= 7.52 Hz, J_2 = 7.52 Hz, J_3 = 7.52 Hz), 1.12 (3H, t, J_1= 7.52 Hz, J_2 = 7.52 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 143.43, 143.07, 133.16, 127.58, 123.02, 122.24, 120.25, 120.21, 116.96, 109.04, 48.72, 46.40, 19.96, 15.32;

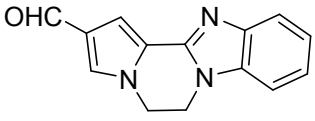
General procedure C for dehydrogenative cross coupling of N-alkylated pyrrole-3-indolecarboxaldehydes:

To a sealed tube with screw cap was loaded *N*-alkylated pyrrole-3-carbaldehyde (1 equiv), Palladium acetate (0.1 equiv), silver carbonate (2equiv), 2, 6-Lutidine (0.2 equiv) in a mixture of NMP:DMA (9:1). The reaction mixture was stirred in a preheated silicon oil bath at 130 ^{o}C for 36h.Once the reaction is completed, mixture was allowed to cool. A saturated brine solution was added to the reaction mixture and it was extracted with EtOAc (three times). The combined organic layers were washed with brine and dried over Na_2SO_4. The resulting solution was filtered and concentrated under

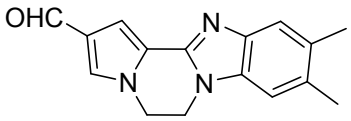
reduced pressure to provide an organic residue. The residue was purified by silica gel column chromatography to provide the desired product.



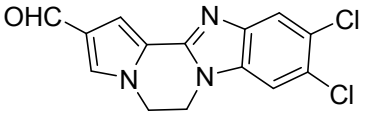
Scheme S3: Dehydrogenativecross coupling of heteroaromatics



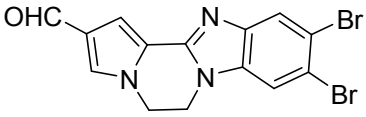
Compound 2a: Following the general procedure C, substrate **1a** (48 mg, 0.2mmol), Palladium acetate (4.5 mg, 0.02mmol), silver carbonate (111 mg, 0.4mmol) in NMP: DMA (9:1) (1mL) was heated at 130 °C for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH 96:4) to afford product **2a** as yellow solid (31 mg, yield:65%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.73 (1H, s), 7.74 (1H, bs), 7.38 (1H, s), 7.31-7.27 (3H,m) 4.44 (4H, bs); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.03, 143.57, 143.20, 133.55, 128.69, 127.24, 124.03, 123.09, 122.10, 119.59, 108.80, 108.27, 44.28, 40.45; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{18}H_{14}N_3O$: 288.1131; found 288.1118; **IR** (thin film): ν_{max} 2343, 1658, 1393, 1140, 739 cm^{-1}.



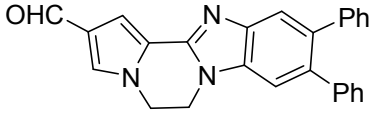
Compound 2b: Following the general procedure C, substrate **1b** (53 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 °C for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH 98:2) to afford product **2b** as yellow solid (33 mg, yield: 64%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.68 (1H, s), 7.39 (1H, s), 7.29 (1H, s), 7.19 (1H, s), 6.95 (1H, s), 4.34-4.29 (4H, m), 2.28-2.23 (6H, m); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.00, 142.43, 142.19, 132.36, 132.10, 131.85, 128.33, 127.23, 124.44, 119.70, 109.03, 107.69, 44.34, 40.398, 20.51, 20.29; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{16}H_{16}N_3O$: 266.1286; found 266.1287; **IR** (thin film): ν_{max} 2355, 1657,1388, 1235, 748 cm^{-1}



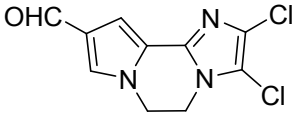
Compound 2c: Following the general procedure C, substrate **1c** (61 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH 97:3) to afford product **2c** as yellow solid (32 mg, yield: 54%). **^{1}H NMR** (300 MHz, DMSO): 9.79 (1H, s), 8.00(1H, s), 7.99 (1H, d, *J* = 1.5 Hz), 7.15 (1H, d, *J* = 1.5 Hz), 4.59 (4H, s); **^{13}C NMR** (75 MHz, DMSO): 185.79, 146.00, 143.46, 134.10, 132.33, 126.88, 125.02, 123.77, 120.17, 112.36, 107.45, 44.16, 41.21; **HRMS** (ES+) cald. for $(M+H)^{+}$: $C_{14}H_{10}Cl_2N_3O$: 306.0195; found 306.0188; **IR** (thin film): ν_{max} 2355, 1659,1388, 1242, 748 cm^{-1}.



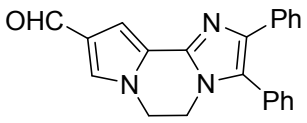
Compound 2d: Following the general procedure C, substrate **1d** (79 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH 98:2) to afford product **2d** as yellow solid (39 mg, yield: 50%). **^{1}H NMR** (300 MHz, DMSO): 9.80 (1H, s), 8.15 (1H, s), 8.04 (1H, s), 8.00 (1H, s), 7.18 (1H, s) 4.59 (4H, s); **^{13}C NMR** (75 MHz, DMSO): 185.81, 145.72, 134.86, 132.40, 126.93, 123.54, 123.17, 116.83, 115.53, 107.78, 44.16, 41.23; **HRMS** (ES+) cald. for $(M+H)^{+}$: $C_{14}H_{10}Br_2N_3O$: 395.9170; found 395.9155. **IR** (thin film): ν_{max} 2352, 1659, 1398, 1245, 748 cm^{-1}.



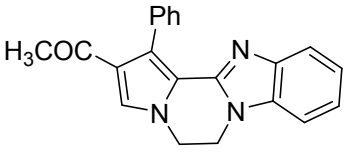
Compound 2e: Following the general procedure C, substrate **1e** (78 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate) to afford product **2e** as brown solid (38 mg, yield: 50%). **^{1}H NMR** (300 MHz, DMSO): 9.85 (1H, s), 8.14 (1H, s), 7.88 (1H, s), 7.33 (1H, s), 7.46 (1H, s), 7.45 (6H, m) 7.25-7.15 (4H, m), 4.76-4.70 (4H, m); **^{13}C NMR** (75 MHz, DMSO): 185.93, 143.13, 141.48, 137.38, 133.37, 132.54, 130.31, 128.44, 127.27, 127.1, 117.88, 113.42, 44.11, 41.57; **HRMS** (ES+) cald. for $(M+H)^{+}$: $C_{26}H_{20}N_3O$: 390.1601; found 390.1607; **IR** (thin film): ν_{max} 2355, 1658,1386, 1231, 748 cm^{-1}



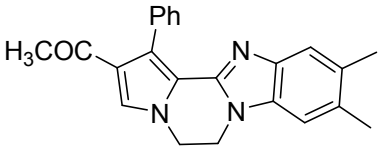
Compound 2f: Following the general procedure C, substrate **1f** (51 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH = 99:1) to afford product **2e** as brown solid (31 mg, yield: 50%). **^{1}H NMR** (400 MHz, $CDCl_3$): 9.68 (1H, s), 7.15 (1H, s), 6.99 (1H, s), 4.29 (2H, t, J_1 = 8.0 Hz, J_2 = 8.0 Hz), 4.14 (2H, t, J_1 = 8.0 Hz, J_2 = 8.0 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.06, 136.47, 128.07, 127.20, 126.84, 123.31, 112.06, 105.87, 43.97, 41.57; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{10}H_8Cl_2N_3O$: 256.0040; found 256.0039; **IR** (thin film): ν_{max} 2345, 1657,1396, 1246, 748 cm^{-1}



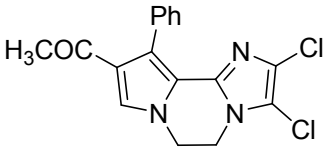
Compound 2g: : Following the general procedure C, substrate **1g**(62 mg, 0.2mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH = 98:2) to afford product **2g** as brown solid (32 mg, yield: 52%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.70 (1H, s), 7.60-7.52 (5H, m), 7.29-7.19 (4H, m), 4.29 (2H, d, J = 5.7 Hz), 4.13 (2H, d, J = 5.7 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.21, 138.88, 138.22, 133.99, 130.46, 129.64, 129.18, 128.85, 128.49, 128.22, 127.85, 127.85, 127.79, 127.50, 127.21, 127.14, 126.82, 124.95, 105.34, 44.44, 41.55, 29.67;**HRMS** (ES+) cald. for $(M+H)^+$: $C_{22}H_{18}N_3O$: 340.1444; found 340.1433; **IR** (thin film): ν_{max} 2348, 1658, 1395, 1148, 770 cm^{-1}.



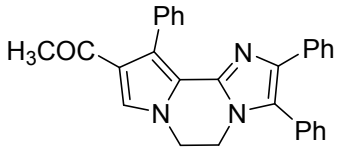
Compound 2h: Following the general procedure C, substrate **1h** (65 mg, 0.2mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane = 4:1) to afford product **2h** as brown solid (25 mg, yield: 40%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.75-7.72 (2H, m), 7.59 (1H, m), 7.40 (1H, s), 7.31 (5H, bs), 7.19-7.14 (1H, m), 4.77 (2H, bs), 4.54 (2H, bs), 2.08 (3H, s); **^{13}C NMR** (75 MHz, $CDCl_3$):193.37, 139.93, 130.58, 129.92, 128.97, 128.80, 126.41, 125.02, 124.84, 117.23, 115.29, 113.73 110.70, 44.49, 41.54, 29.21; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{21}H_{18}N_3O$: 328.1433; found 328.1444; **IR** (thin film): ν_{max} 2349, 1710, 1398, 1126 cm^{-1}.



Compound 2i: Following the general procedure C, substrate **1i** (71 mg, 0.20mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 5:1) to afford product **2i** as brown solid (24 mg, yield: 35%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.48-7.35 (6H, m), 7.26 (1H, bs), 7.03 (1H, bs), 4.40 (4H, bs), 2.35 (3H, s), 2.28 (3H, s), 2.07 (3H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 194.47, 142.54, 142.19, 133.59, 131.94, 131.26, 130.79, 127.91, 127.61, 127.10, 125.98, 120.31, 108.54, 44.59, 40.41, 29.69, 20.51, 20.16; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{23}H_{22}N_3O$: 356.1765; found 356.1757; **IR** (thin film): ν_{max} 2322, 1710, 1386, 1144 cm^{-1}.

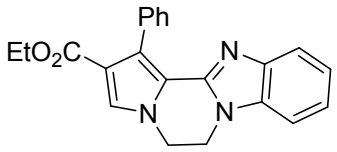


Compound 2j: Following the general procedure C, substrate **1j** (69 mg, 0.20 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 6:1) to afford product **2j** as brown solid (27 mg, yield: 40%). **^{1}H NMR** (300 MHz, DMSO): 7.84 (1H, s),7.26-7.21 (5H, m), 4.35 (2H, d, J = 5.7 Hz), 4.21 (2H, d, J = 5.7Hz), 2.12 (3H, s); **^{13}C NMR** (75 MHz, DMSO): 192.49, 136.93, 133.75, 131.75, 131.22, 129.93, 127.46, 127.21, 124.62, 123.81, 122.91, 119.75, 111.84, 43.92, 41.98, 28.98; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{17}H_{13}Cl_2N_3NaO$: 368.0238; found 368.0318; **IR** (thin film): ν_{max} 2355, 1712, 1394, 1116 cm^{-1}.

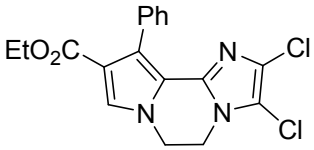


Compound 2k: Following the general procedure C, substrate **1k** (51 mg, 0.12 mmol), Palladium acetate (2.7 mg, 0.01 mmol), silver carbonate (66 mg, 0.24 mmol) in NMP: DMA (9:1) (0.5 mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 7:3) to afford product **2k** as brown solid (16 mg, yield: 32%).**^{1}H NMR** (300 MHz, $CDCl_3$): 7.64-7.62 (2H, m), 7.51-7.36 (11H, m), 715-7.13 (3H, m),4.35 (2H, bs), 4.09 (2H, bs), 2.16 (3H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 194.14, 140.82, 137.48, 133.03, 130.91, 130.76, 130.66, 129.38, 128.24, 127.88, 127.54, 127.41, 126.87, 126.66, 125.63, 44.52, 41.98, 29.18; **HRMS** (ES+)

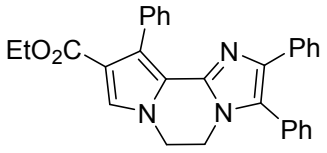
cald. for $(M+H)^+$: $C_{29}H_{24}N_3O$: 430.1914; found 430.1934; **IR** (thin film): ν_{max} 2356, 1715, 1384, 1170 cm^{-1}.



Compound 2l: Following the general procedure C, substrate **1l** (86 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^oC for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 5:1) to afford product **2j** as brown solid (27 mg, yield: 40%). **^{1}H NMR** (300 MHz, $CDCl_3$: 7.59 (1H, s), 7.51 (1H, d, J = 9.0 Hz), 7.40 (3H, bs), 7.26-7.12 (5H, m), 4.52 (4H, bs), 4.13 (2H, q, J = 6.0Hz), 1.15 (3H, t,J = 6.0 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 163.54, 142.35, 140.84, 132.59, 130.56, 129.06, 128.73, 127.41, 127.236, 127.24, 123.42, 123.26, 119.02, 116.45, 109.15, 59.91, 44.63, 40.88, 14.09; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{22}H_{20}N_3O_2$: 358.1550; found 358.1558; **IR** (thin film): ν_{max}2349, 1702, 1393, 1170 cm^{-1}.

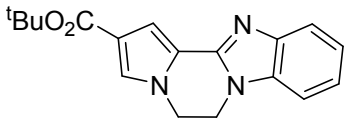


Compound 2m: Following the general procedure C, substrate **1m** (75 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^oC for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 5:1) to afford product **2m** as brown solid (33 mg, yield: 45%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.47-7.44 (2H, m), 7.39- 7.27 (4H, m), 4.24-4.11 (6H, m), 1.16 (3H, t, J = 6.9Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 163.92, 136.65, 132.35, 130.80, 127.44, 127.28, 127.19, 126.30, 125.02, 119.28, 115.71, 111.50, 59.81, 43.99, 41.42, 14.10; **HRMS** (ES+) cald. for $(M+Na)^+$: $C_{18}H_{15}Cl_2N_3NaO_2$: 398.0433; found 398.0420; **IR** (thin film): ν_{max} 2349, 1700, 1383, 1175 cm^{-1}.

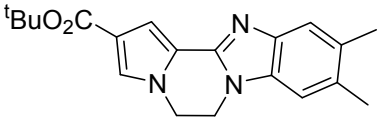


Compound 2n: Following the general procedure C, substrate **1n** (55 mg, 0.12mmol), Palladium acetate (2.7 mg, 0.01 mmol), silver carbonate (66 mg, 0.24 mmol) in NMP: DMA (9:1) (0.5 mL) was heated at 130 ^oC for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 7:3) to afford product **2n** as yellow solid (26 mg, yield: 48%). **^{1}H NMR** (300 MHz,

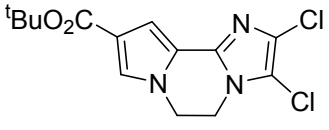
$CDCl_3$): 7.65-7.21 (14H, m), 7.14 (2H, s), 4.37 (2H, bs), 4.17-4.12 (4H, m), 1.18 (3H, t, J = 6 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): **^{13}C NMR** (75 MHz, $CDCl_3$): 163.84, 132.39, 131.05, 130.73, 129.44, 129.38, 128.59, 128.28, 128.09, 127.66, 127.42, 127.18, 127.14, 126.96, 126.73, 115.89, 59.87, 44.61, 42.05, 14.14; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{30}H_{26}N_3O_2$: 460.2019; found 460.2017; **IR** (thin film): ν_{max} 2341, 1704, 1392, 1156 cm^{-1}.



Compound 2o: Following the general procedure C, substrate **1o** (62 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 9:1) to afford product **2o** as brown solid (27 mg, yield: 45%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.59-7.57 (2H, m), 7.49-7.46 (1H, m), 7.41 (1H, s), 7.34-7.32 (1H, m), 7.29- 7.19 (1H, m), 4.65 (1H, bs),1.54 (9H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 162.44, 131.73, 129.18, 124.79, 124.51, 120.94, 116.61, 110.24, 80.72, 43.86, 41.27, 28.32; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{18}H_{20}N_3O_2$: 310.1550; found 310.1538; **IR** (thin film): ν_{max} 2349, 1702, 1391, 1170, 740 cm^{-1}.

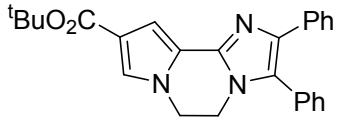


Compound 2p: Following the general procedure C, substrate **1p** (67 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 8:1) to afford product **2p** as yellow solid (33 mg, yield: 50%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.38-7.35 (3H, m), 7.12 (1H, s), 4.48 (4H, bs), 2.35 (3H, s), 2.27 (3H, s), 1.54 (9H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 162.95,141.50, 133.17, 131.01, 127.79, 120.27, 117.78, 111.93, 109.71, 80.43, 43.93, 40.88, 28.33, 20.51, 20.25; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{20}H_{24}N_3O_2$: 338.1863; found 338.1865; **IR** (thin film): ν_{max} 2333, 1700, 1311, 1179, 735 cm^{-1}.

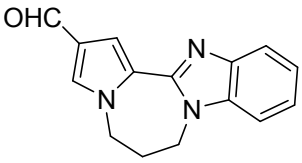


Compound 2q: Following the general procedure C, substrate **1q** (66 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane = 8:1) to afford product **2q** as yellow

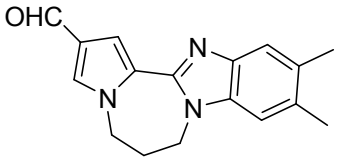
solid (26 mg, yield: 40%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.20 (1H, s), 6.98 (1H, s), 4.26 (2H, t, *J* = 5.1 Hz), 4.13 (2H, t, *J* = 5.1 Hz), 1.48 (9H, s); **^{13}C NMR** (75 MHz, $CDCl_3$): 163.31, 137.09, 126.65, 125.96, 121.85, 119.71, 111.43, 107.78, 80.22, 43.65, 41.64, 28.30; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{14}H_{16}Cl_2N_3O_2$: 328.0614; found 328.0608; **IR** (thin film): v_{max} 2345, 1701, 1314, 1184, 735 cm^{-1}.



Compound 2r: Following the general procedure C, substrate **1r** (82 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^oC for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: Hexane= 8:1) to afford product **2r** as yellow solid (20 mg, yield: 25%). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.58-7.51 (2H, m), 7.46-7.44 (3H, m), 7.35-7.33 (2H, m), 7.29, (1H, bs), 7.26 (1H, bs), 7.22-7.17 (3H, m), 4.23 (2H, d, *J* = 5.7Hz), 4.11 (2H, d, *J* = 5.7 Hz), 1.57 (9H, s), **^{13}C NMR** (100 MHz, $CDCl_3$): 162.75, 137.85, 129.45, 128.88, 128.10, 127.66, 127.15, 126.33, 126.04, 125.66, 124.49, 118.42, 106.40, 78.94, 43.16, 40.70, 27.36; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{26}H_{26}N_3O_2$: 412.2019; found 420.2020; **IR** (thin film): v_{max} 2352, 1693, 1384, 1162 cm^{-1}.

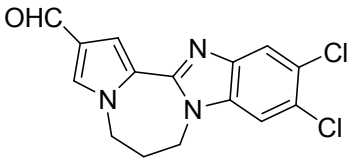


Compound 2s: Following the general procedure C, substrate **1s** (50 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^oC for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH= 95:5) to afford product **2s** as brown solid (22 mg, yield: 45%). **^{1}H NMR** (300 Hz, $CDCl_3$): 9.80 (1H, s), 7.81-7.79 (1H, m), 7.56 (1H, s), 7.43 (1H, s), 7.32-7.29 (3H, m), 4.38-4.34 (4H, m), 2.62-2.54 (2H, m); **^{13}C NMR** (75 MHz, DMSO): 185.72, 145.78, 143.12, 136.30,133.29, 127.27, 125.76, 122.74,122.55, 118.93, 112.06, 110.75, 49.73, 45.25, 26.87; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{15}H_{14}N_3O$: 252.1137; found 252.1106; **IR** (thin film): v_{max} 2374, 1666, 1353, 1145, 779 cm^{-1}.

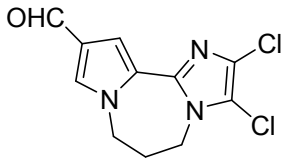


Compound 2t: Following the general procedure C, substrate **1t** (56 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^oC for 36h.

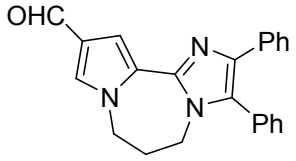
The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH= 98:2) to afford product **2t** as brown solid (22 mg, yield: 40%). **^{1}H NMR** (300 MHz, DMSO): 9.78 (1H, s), 8.00 (1H, s), 7.53 (2H, bs), 7.48 (1H, s), 4.51 (4H, bs), 2.39-2.37 (8H, m); **^{13}C NMR** (75 MHz, DMSO): 185.65, 145.05, 141.63, 134.71, 133.05, 131.34, 131.12, 127.15, 125.76, 118.98, 111.58, 110.80, 49.70, 45.16, 26.97, 20.59, 20.36; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{17}H_{18}N_3O$: 280.1450; found 280.1429; **IR** (thin film): ν_{max} 2382, 1666, 1356, 1151, 776 cm^{-1}.



Compound 2u: Following the general procedure C, substrate **1u** (64 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH= 96:4) to afford product **2u** as brown solid (31 mg, yield: 50%). **^{1}H NMR** (300 MHz, DMSO): 9.73 (1H, s), 7.93-7.87 (3H, m), 7.34 (1H, d, J = 1.2 Hz), 4.48 (2H, t, J = 5.7 Hz), 4.41 (2H, t, J = 5.7 Hz) 2.44 (2H, bs); **^{13}C NMR** (75 MHz, DMSO): 185.73, 148.15, 142.67, 135.95, 133.71, 126.37, 125.80, 125.24, 124.73, 119.77, 113.15, 112.62, 49.93, 45.92, 26.46; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{15}H_{12}Cl_2N_3O$: 320.0352; found 320.0341; **IR** (thin film): ν_{max}2339, 1667, 1393, 1144, 783 cm^{-1}.

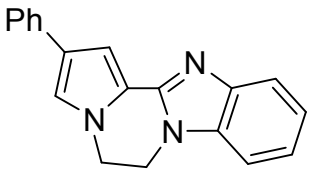


Compound 2v: Following the general procedure C, substrate **1v** (54 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 ^{o}C for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate) to afford product **2v** as brown solid (16 mg, yield: 30%). **^{1}H NMR** (300 MHz, $CDCl_3$): 9.75 (1H, s), 7.33 (1H, s), 7.26 (1H, d, J = 1.5 Hz), 4.29 (2H, t, J = 5.7 Hz), 4.15 (2H, t, J = 5.7Hz), 2.48(2H, bs); **^{13}C NMR** (75 MHz, $CDCl_3$): 185.15, 138.09, 129.32, 126.57, 126.15, 125.84, 113.18, 11.64, 48.43, 45.33, 27.42; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{11}H_{10}Cl_2N_3O$: 270.0195; found 270.0193; **IR** (thin film): ν_{max} 2348, 1665, 1395, 1139, 783 cm^{-1}.

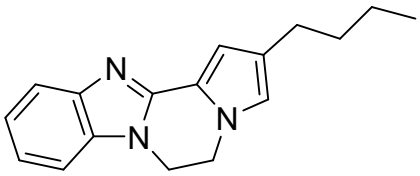


Compound 2w: Following the general procedure C, substrate **1w** (71 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111

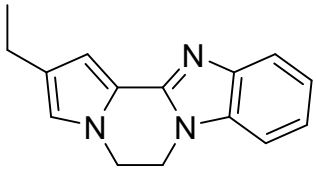
mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 °C for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: MeOH (99:1) to afford product **2w** as brown solid (28 mg, yield: 40%). **^{1}H NMR** (300 MHz, DMSO): 9.77 (1H, s), 7.96 (1H, s), 7.56 (4H, s), 7.49-4.43 (5H, m), 7.34-7.30 (2H, m), 4.46-4.44 (2H, m), 3.96 (2H, t, J = 5.4 Hz), 2.37 (2H, bs); **^{13}C NMR** (75 MHz, DMSO):185.67, 138.86, 134.00, 131.39, 130.86, 130.37, 130.16, 129.78, 128.89, 128.33, 127.66, 127.40, 125.97, 123.37, 114.85, 112.08, 48.81, 46.84, 27.03; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{23}H_{20}N_3O$: 354.1601; found 354.1600; **IR** (thin film): ν_{max} 2355, 1665, 1382, 1169, 779 cm^{-1}.



Compound 2x: Following the general procedure C, substrate **1x** (48 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 °C for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: hexane 6:4) to afford product **2y** as brown sticky solid (18 mg, yield: 38%).**^{1}H NMR** (300 MHz, DMSO): 7.64-7.54 (5H, m), 7.39-7.34 (2H, m), 7.22-7.19 (4H, m), 4.51 (4H, bs); **^{13}C NMR** (100 MHz, DMSO): 153.79, 144.63, 143.94, 134.41, 129.25, 126.26, 125.44, 125.13, 123.03, 122.41, 122.32, 121.43, 118.82, 116.06, 110.14, 106.98, 43.81, 40.97; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{19}H_{16}N_3$: 286.1341; found 286.1339;

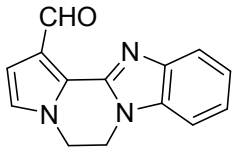


Compound 2y: Following the general procedure C, substrate **1x** (53 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 °C for 36 h. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: DCM (15:85) to afford product **2z** as brown sticky solid (26 mg, yield: 50 %). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.77-7.73 (1H, m), 7.28-7.24 (3H, m), 6.90 (1H, s), 6.63 (1H, s), 4.39-4.33 (4H, m), 2.52 (2H, t, J_1= 7.51 Hz, J_2 = 7.51 Hz), 1.63-1.58 (2H, m), 1.45-1.37 (2H, m), 0.96 (3H, t, J_1= 7.28 Hz, J_2 = 7.28 Hz) ; **^{13}C NMR** (75 MHz, $CDCl_3$): 145.11, 144.16, 133.92, 127.08, 122.51, 122.20, 121.92, 120.91, 119.35, 109.80, 108.40, 43.60, 40.95, 33.19, 26.53, 22.44, 14.04; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{17}H_{20}N_3$: 266.1653; found 266.1652;



Compound 2z: Following the general procedure C, substrate **1x** (52 mg, 0.2 mmol), Palladium acetate (4.5 mg, 0.02 mmol), silver carbonate (111 mg, 0.4 mmol) in NMP: DMA (9:1) (1mL) was heated at 130 °C for 36h.

The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate: DCM (15:85) to afford product **2y** as brown sticky solid (26 mg, yield: 55%). **^{1}H NMR** (400 MHz, $CDCl_3$): 7.79-7.77 (1H, m), 7.30 -7.27 (3H, m), 6.94 (1H, d, J = 1.47 Hz), 6.66 (1H, d, J = 0.60 Hz), 4.42-4.33 (4H, m), 2.59 (2H, q, J_1= 7.56 Hz, J_2 = 7.56 Hz, J_3 = 7.56 Hz), 1.27 (3H, t, J_1= 7.56 Hz, J_2 = 7.56 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$): 144.99, 144.07, 133.82, 128.57, 122.40, 122.10, 121.90, 120.29, 119.28, 109.23, 108.29, 43.51, 40.86, 19.97, 15.17; **HRMS** (ES+) cald. for $(M+H)^+$: $C_{15}H_{16}N_3$: 238.1339 found 238.1339;

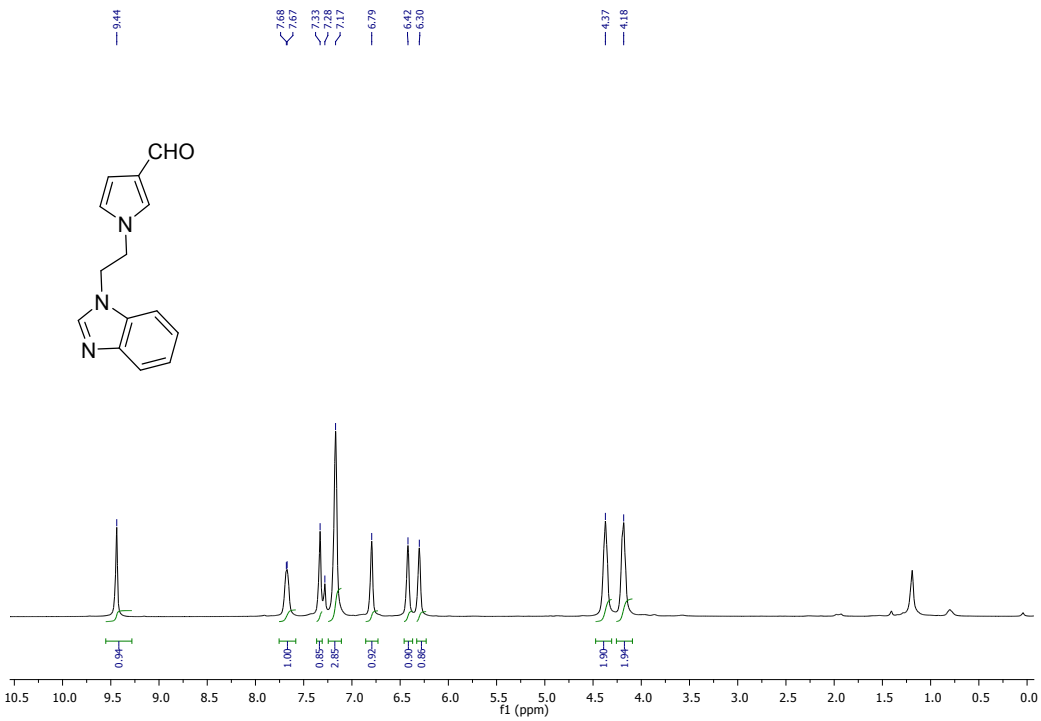


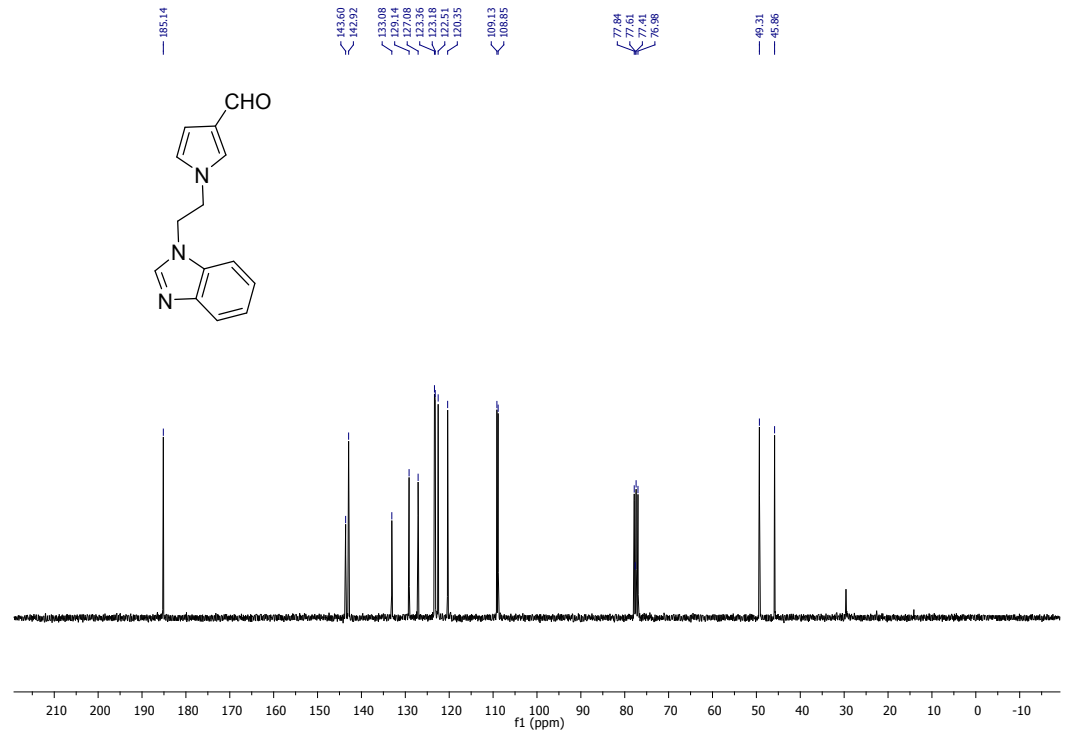
5,6-dihydrobenzo[4,5]imidazo[1,2-a]pyrrolo[2,1-c]pyrazine-1-carbaldehyde (3): The reaction was performed following the general procedure C. The reaction mixture was purified according to general procedure with silica gel column chromatography (Ethyl acetate) to afford product **2a** as brown solid mp 123-131 ^{o}C. **^{1}H NMR** (300 MHz, $CDCl_3$): 10.75 (1H, s), 7.76 (1H, dd, J_1 = 5.28 Hz, J_2 = 5.28 Hz), 7.31-7.26 (3H, m), 6.79 (1H,d, J = 2.81 Hz), 6.76 (1H, d, J = 2.81 Hz) 4.44 (4H, bs); **^{13}C NMR** (75 MHz, $CDCl_3$): 186.99, 144.08, 142.61, 135.51, 122.57, 125.66, 123.88, 123.73, 123.31, 120.32, 108.98, 44.15, 40.62**; FTIR**(thin film): ν_{max} 2924, 2853, 1658, 1462, 1259, 1090, 803 cm^{-1}; **HRMS** (ES+) calcd. for $(M+H)^+$: $C_{18}H_{14}N_3O$: 288.1131; found 288.1118

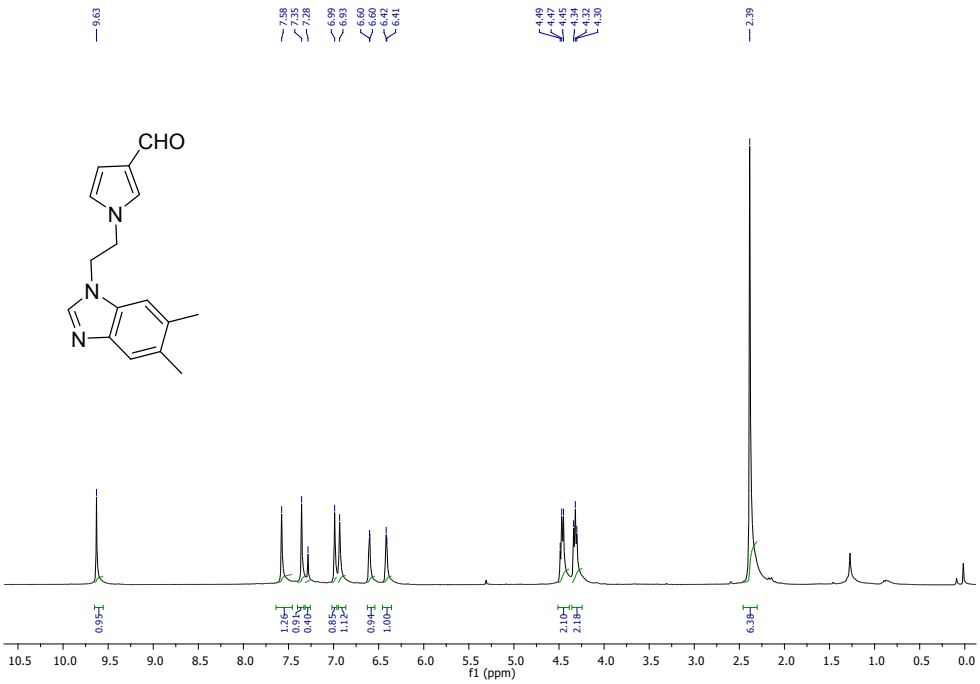
References:

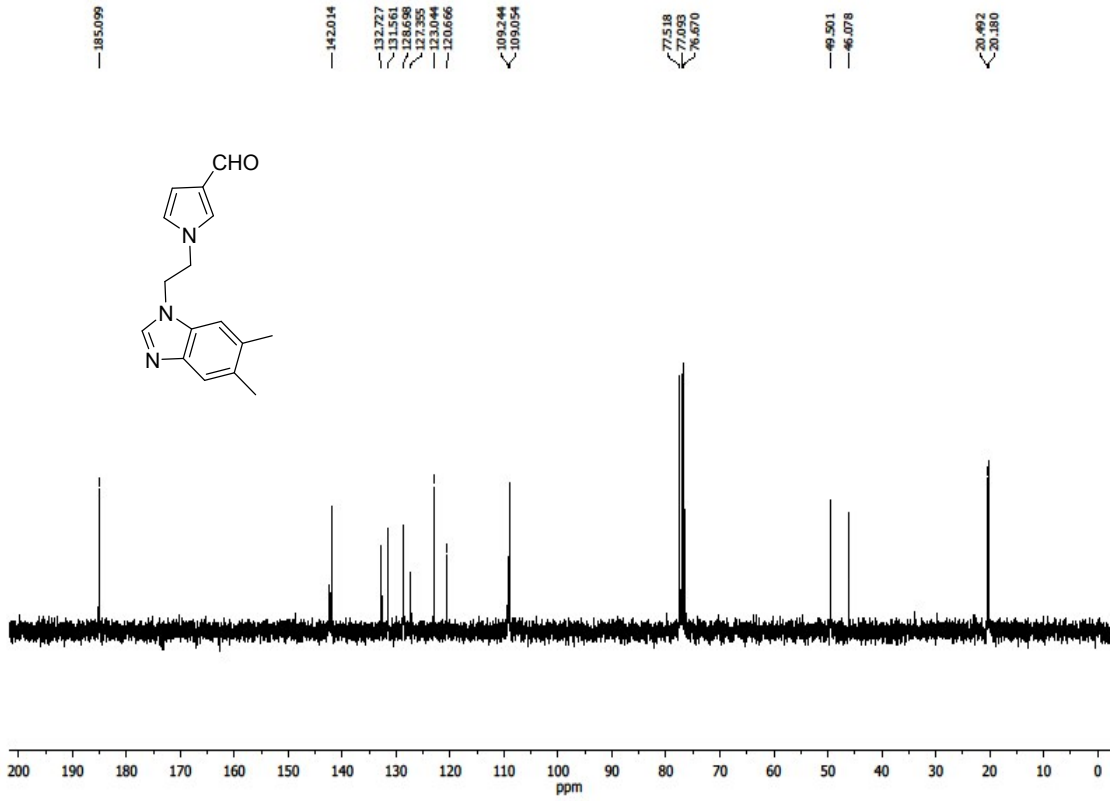
1. (a) Ray, D.; Manikandan, T.; Roy, A.; Tripathi, K. N.; Singh, R. P. *Chem. Commun.* **2015**, *51*, 7065-7068. (b) Jones, R. C. F.; Crumpling, L. J.; Iley, J. N. *ARKIVOC* **2011**, 82.
2. Arikawa, Y.; Nishida, H.; Kurasawa, O.; Hasuoka, A.; Hirase, K.; Inatomi, N.; Hori, Y.; Matsukawa, J.; Imanishi, A.; Kondo, M.; Tarui, N.; Hamada, T.; Takagi, T.; Takeuchi, T.; Kajino, M. *J. Med. Chem.* **2012**, *55*, 4446-4456.
3. Ni, L.; Li, Z.; Wu, F,; Xu, J.; Wu, X.; Kong, L.; Yao, H. *Tetrahedron Lett.* **2012**, *53*, 1271-1274.

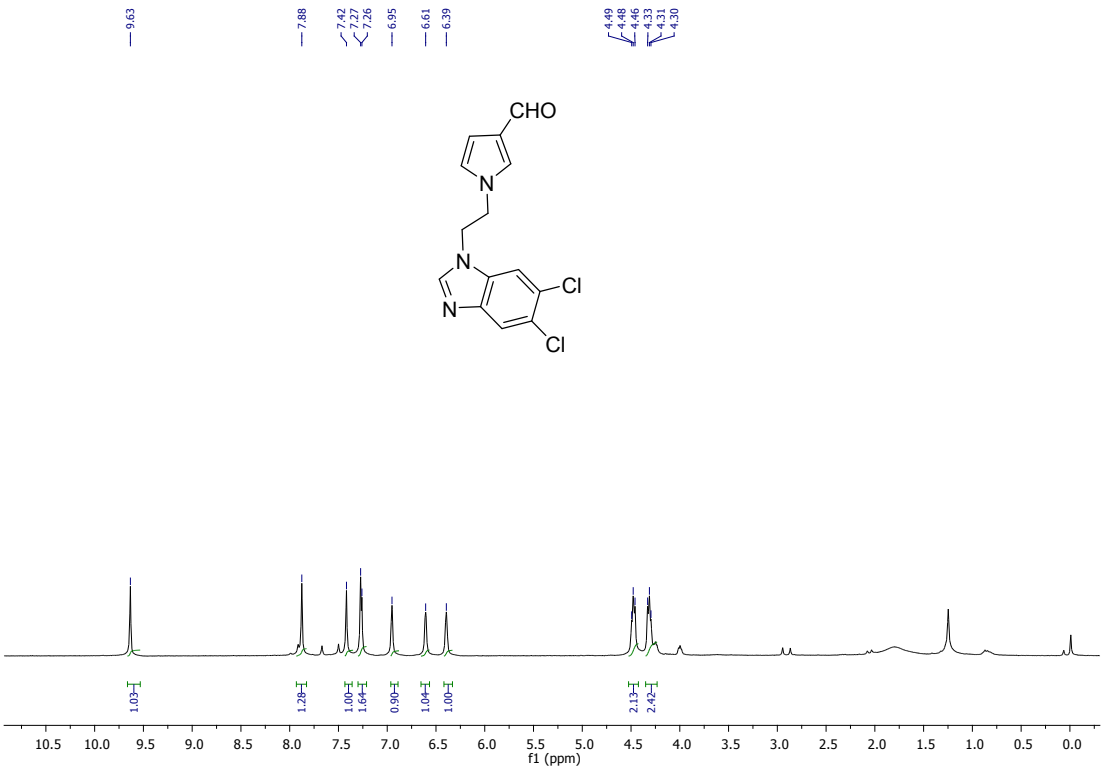
4. Smith, N. D.; Huang, D.; Cosford, N. D. P. Org. Lett. 2002, 4, 3537– 3539
5. He, Y.; Lin, M.; Li, Z.; Liang, X.; Li, G.; Antilla, J. C. Org. Lett. 2011, 13, 4490−4493
6. Schiffner, J. A.; Woeste, T. H.; Oestreich, M. Eur. J. Org. Chem. 2010, 174 – 182

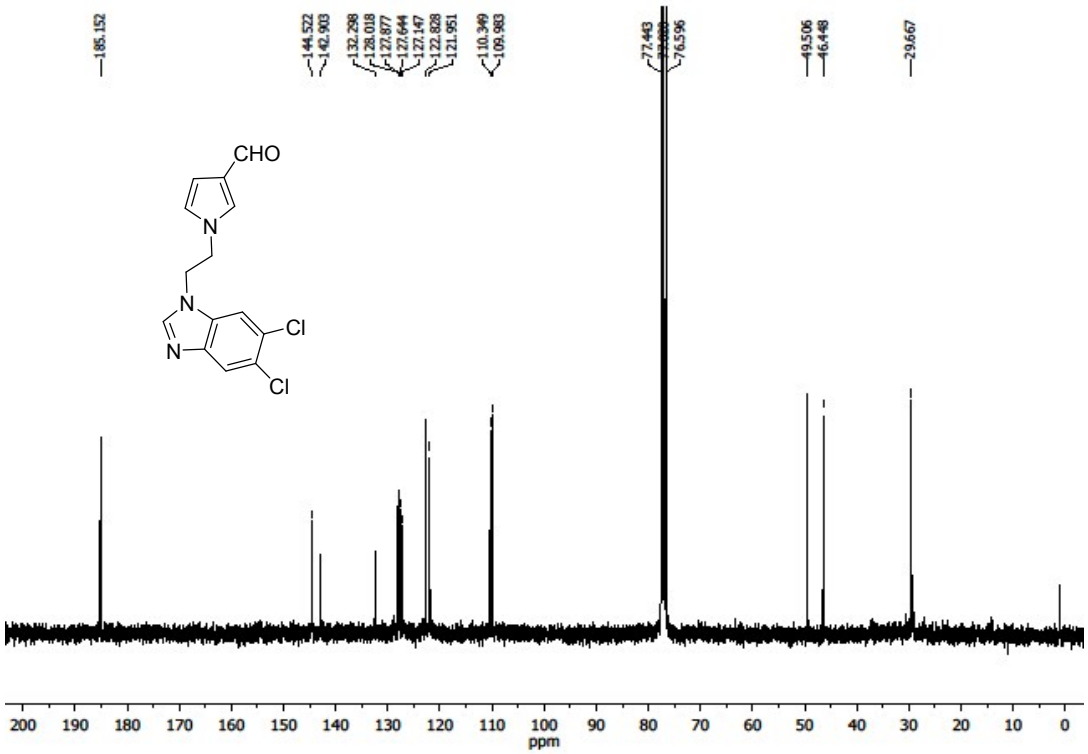


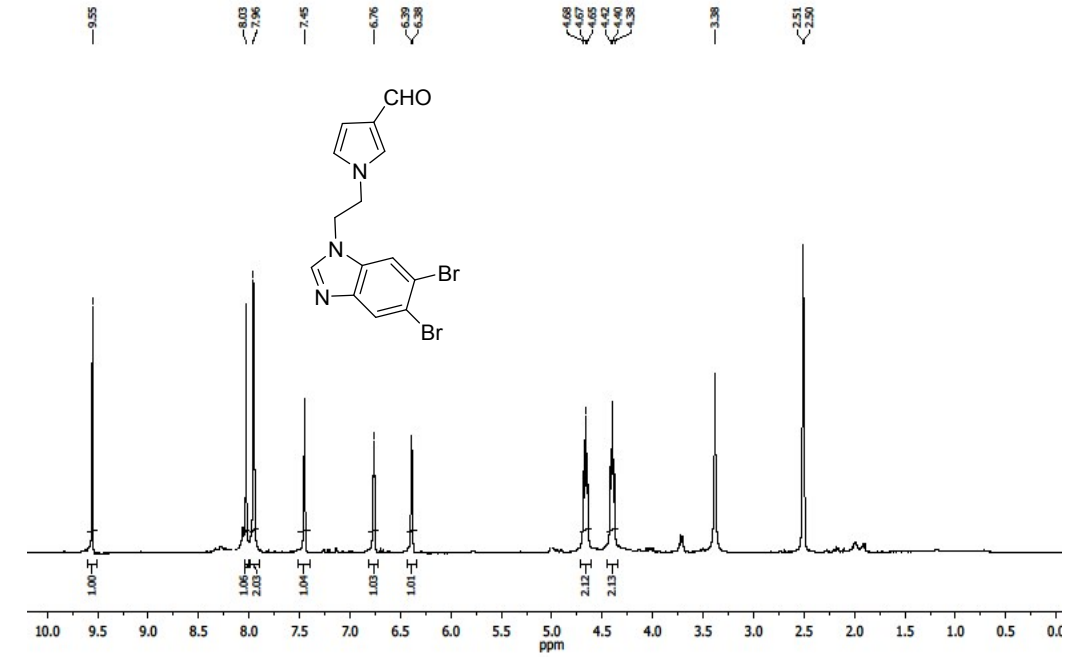

185.14
143.60
142.92
133.08
129.14
127.08
123.36
123.18
121.51
120.35
109.13
108.85
77.84
77.61
77.41
76.98
49.31
45.86
CHO
N
N
N
f1 (ppm)

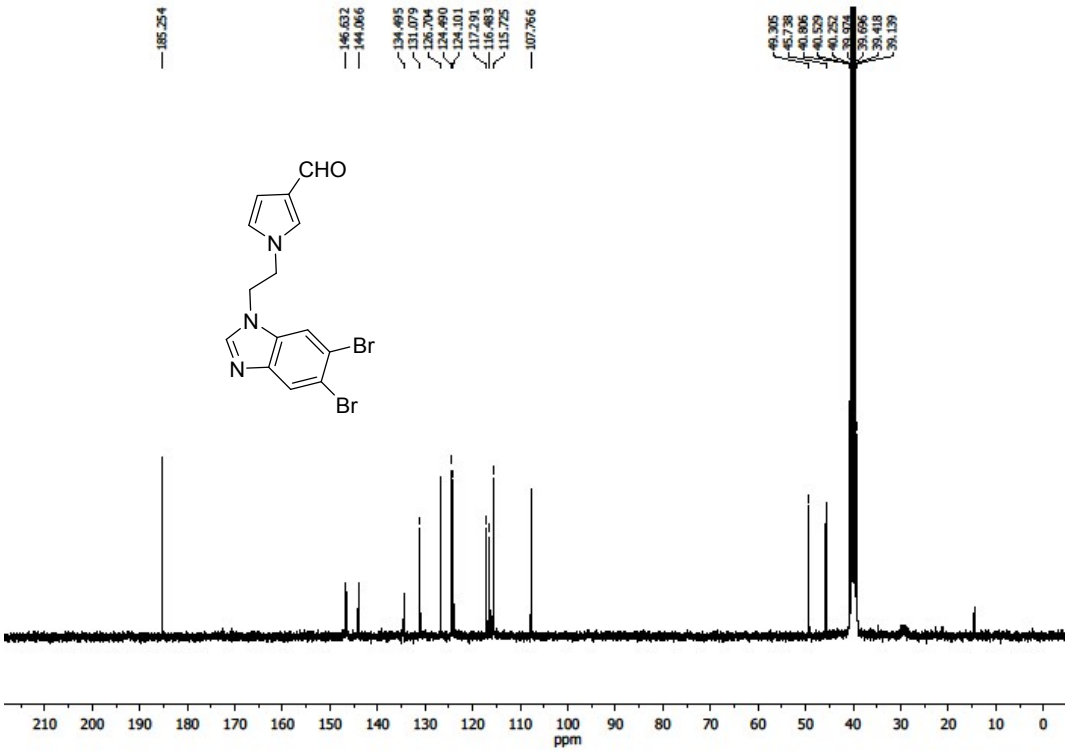

9.63
7.58
7.35
7.28
6.99
6.93
6.60
6.60
6.42
6.41
4.49
4.47
4.45
4.34
4.32
4.30
2.39
CHO
N
N
N
0.95
1.26
0.91
0.40
0.85
1.12
0.94
1.00
2.10
2.18
6.38
f1 (ppm)

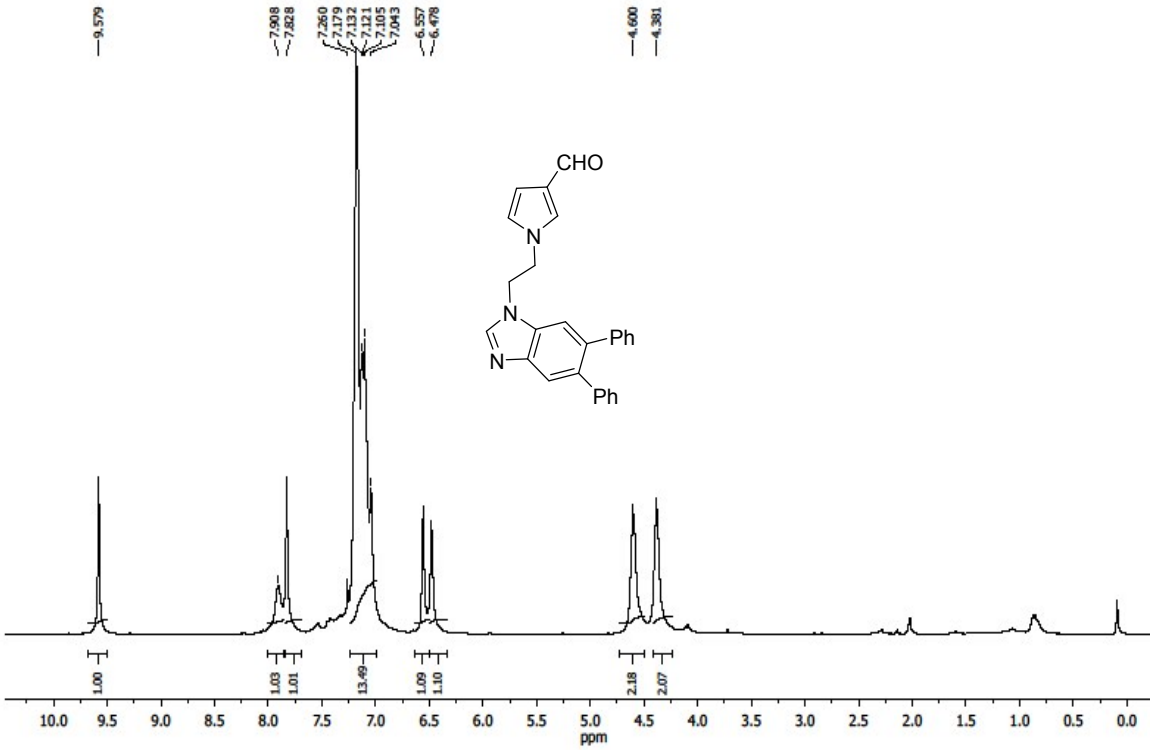

185.099
142.014
132.727
131.561
128.698
127.355
123.044
120.666
109.244
109.054
77.518
77.093
76.670
49.501
46.078
20.492
20.180
CHO
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

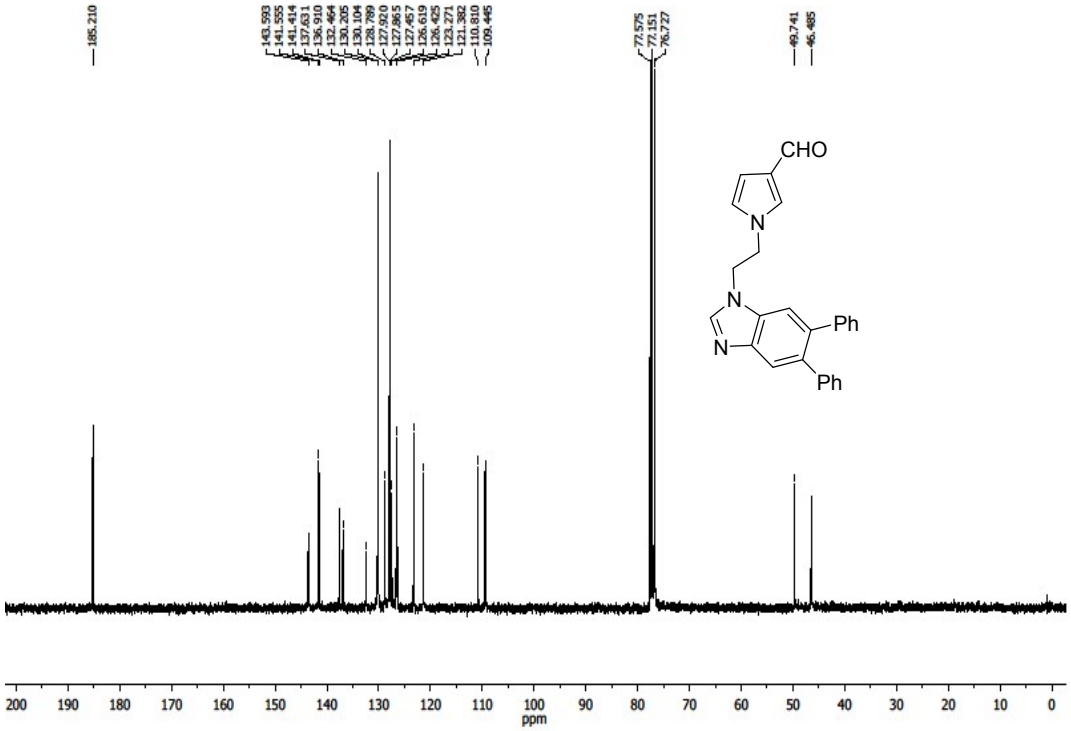

9.63
7.88
7.42
7.27
7.26
6.95
6.61
6.39
4.49
4.48
4.46
4.33
4.31
4.30
CHO
N
N
N
Cl
Cl
1.03
1.28
1.00
1.64
0.90
1.04
1.00
2.13
2.42
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

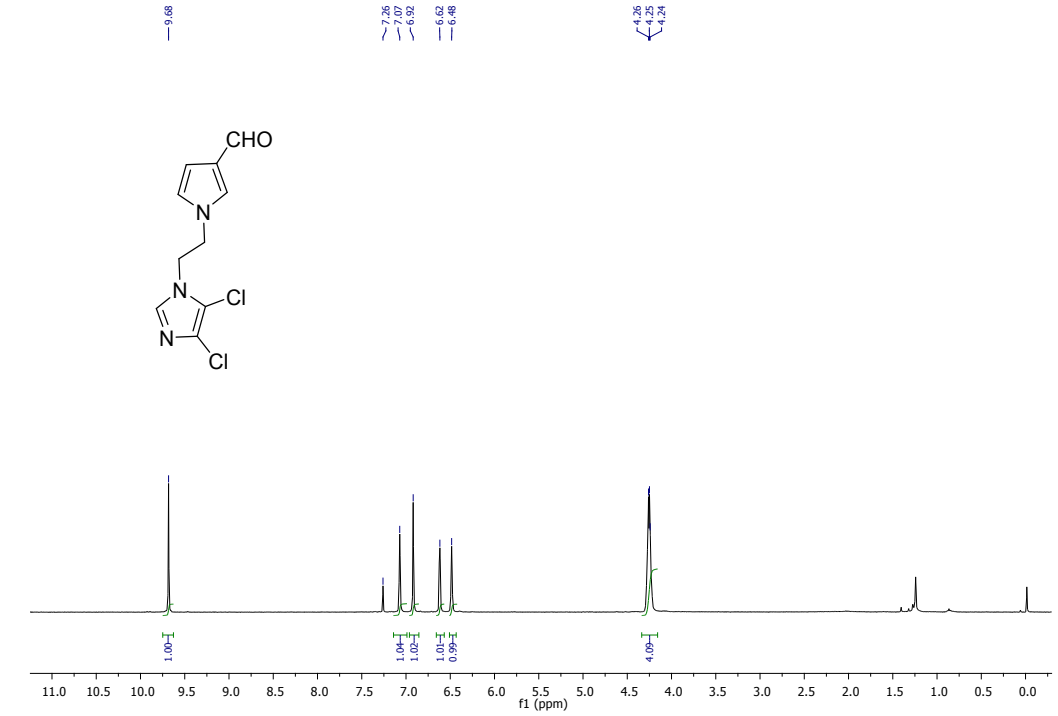

185.152
144.522
142.903
132.298
128.018
127.877
127.644
127.147
122.828
121.951
110.349
109.983
77.443
76.596
49.506
46.448
29.667
CHO
N
N
N
Cl
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

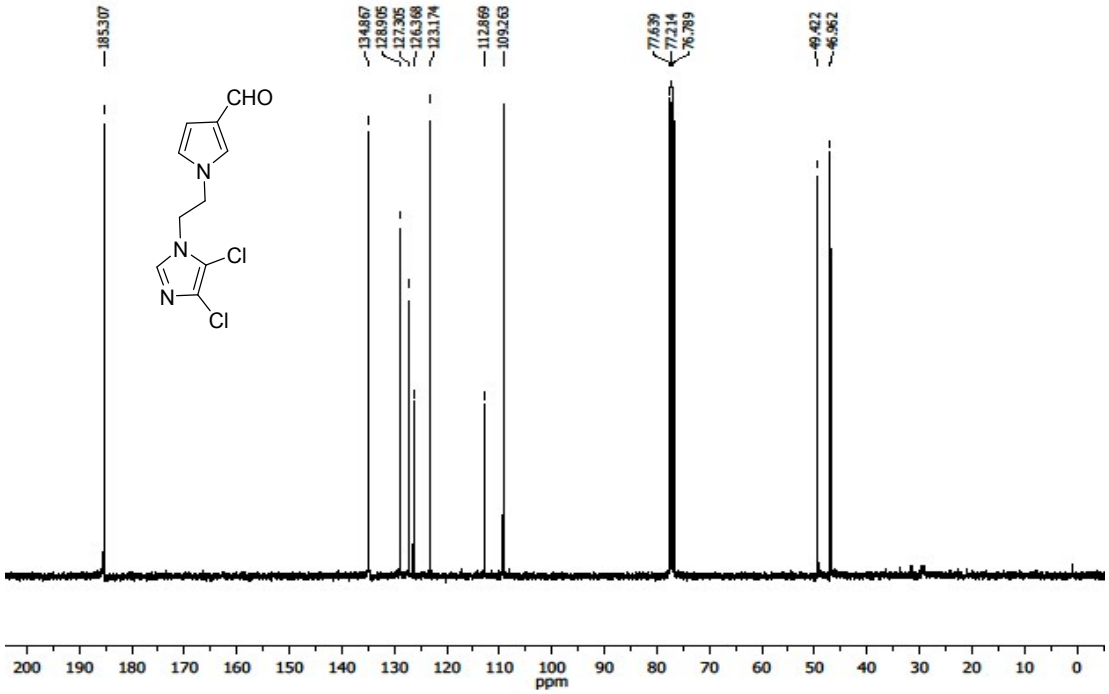

9.55
8.03
7.96
7.45
6.76
6.39
6.38
4.68
4.67
4.65
4.42
4.40
4.38
3.38
2.51
2.50
CHO
N
N
N
Br
Br
1.00
1.06
2.03
1.04
1.03
1.01
2.12
2.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

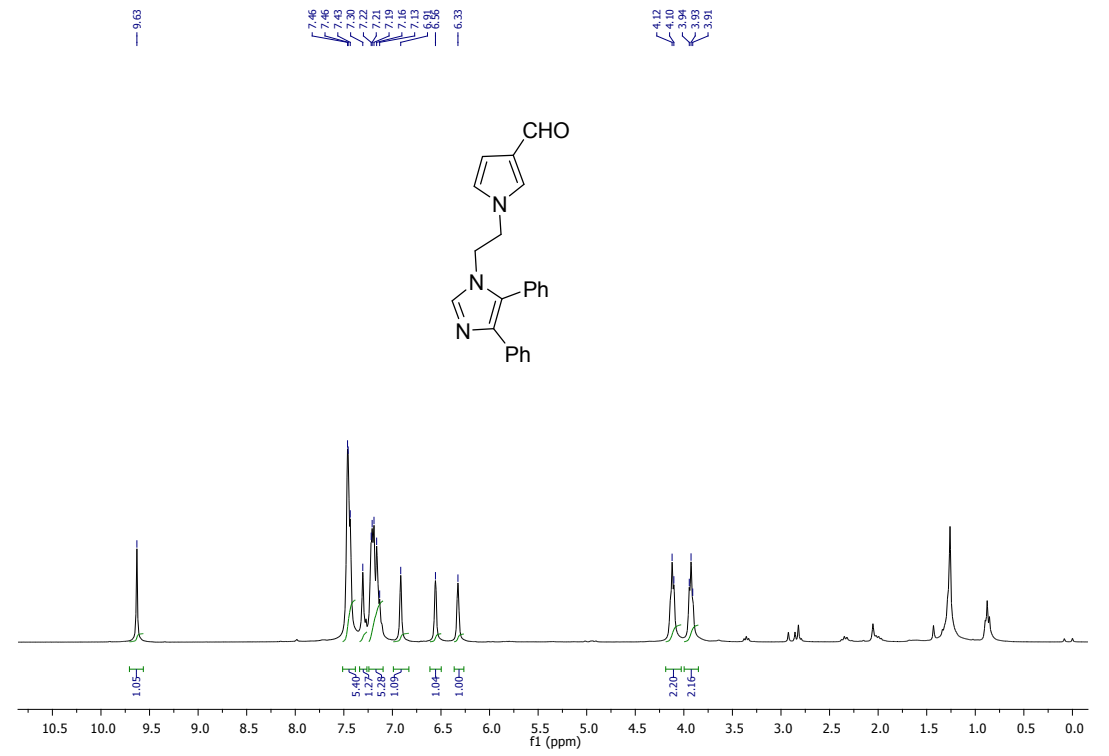

185.254
146.632
144.066
134.495
131.079
126.704
124.490
124.101
117.291
116.483
115.725
107.766
69.305
65.738
40.806
40.529
40.252
39.974
39.696
39.418
39.139
CHO
N
N
N
Br
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

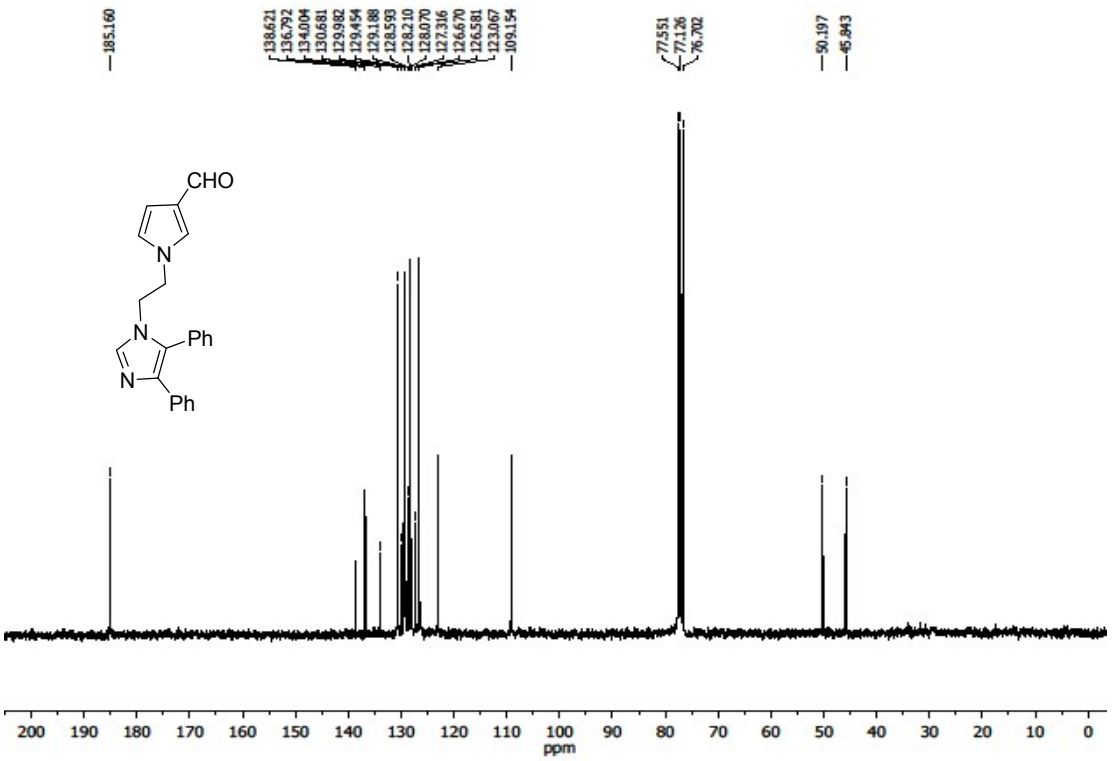

9.579
7.908
7.828
7.260
7.179
7.132
7.121
7.105
7.043
6.557
6.478
4.600
4.381
CHO
N
N
N
Ph
Ph
1.00
1.03
1.01
13.49
1.09
1.10
2.18
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

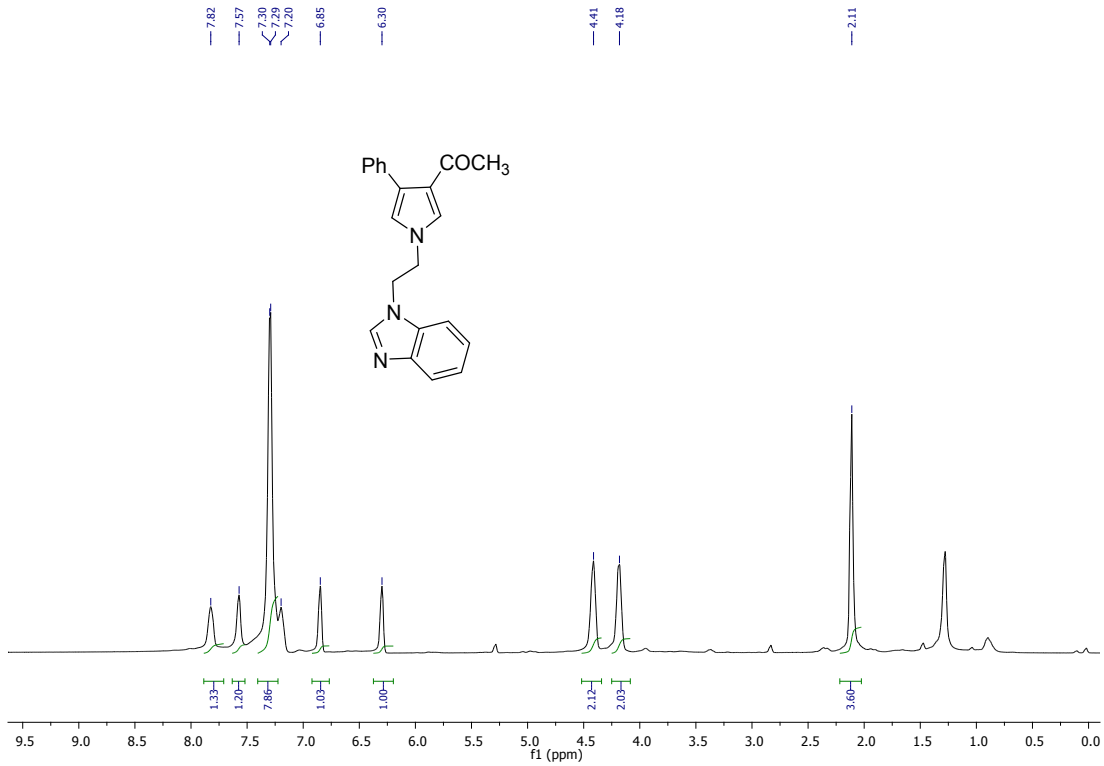

185.210
143.593
141.555
141.414
137.631
136.910
132.464
130.205
130.104
128.709
127.920
127.865
127.457
126.619
126.425
123.271
121.382
110.810
109.445
77.575
77.151
76.727
49.741
45.485
CHO
N
N
N
Ph
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

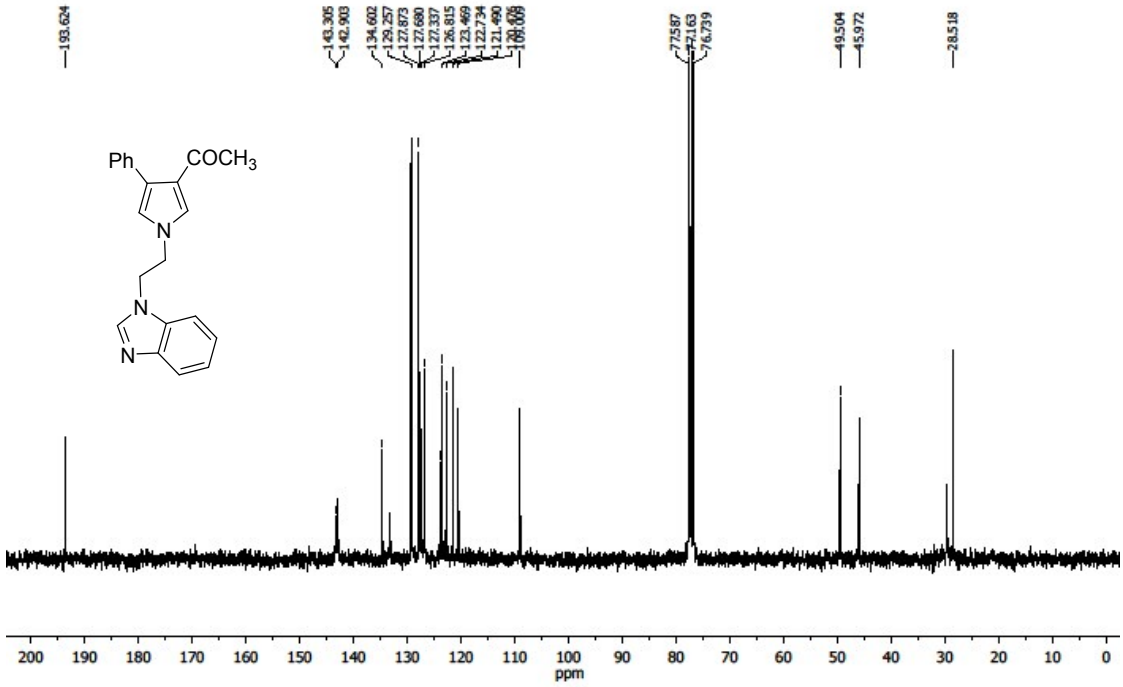

9.68
7.26
7.07
6.92
6.62
6.48
4.26
4.25
4.24
CHO
N
N
N
Cl
Cl
1.00
1.04
1.02
1.01
0.99
4.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


185.307
134.867
128.905
127.305
126.368
123.174
112.869
109.263
77.639
77.214
76.789
49.422
46.962
CHO
N
N
Cl
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

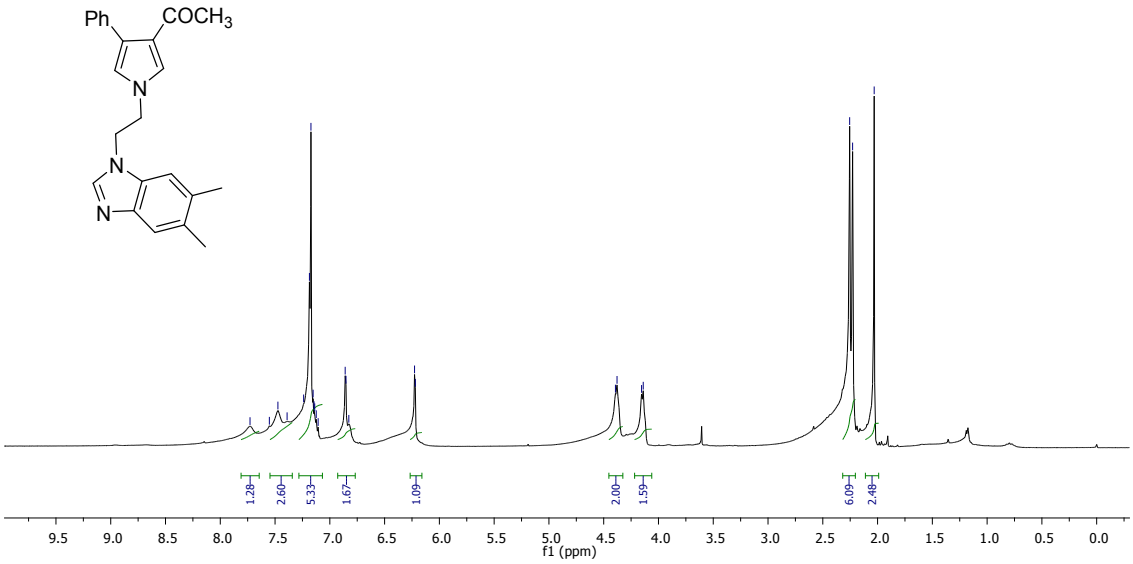

9.63
7.46
7.46
7.43
7.30
7.22
7.21
7.19
7.16
7.13
6.64
6.58
6.33
4.12
4.10
3.94
3.93
3.91
CHO
N
N
Ph
N
Ph
1.05
5.40
2.22
5.29
1.09
1.04
1.00
2.20
2.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

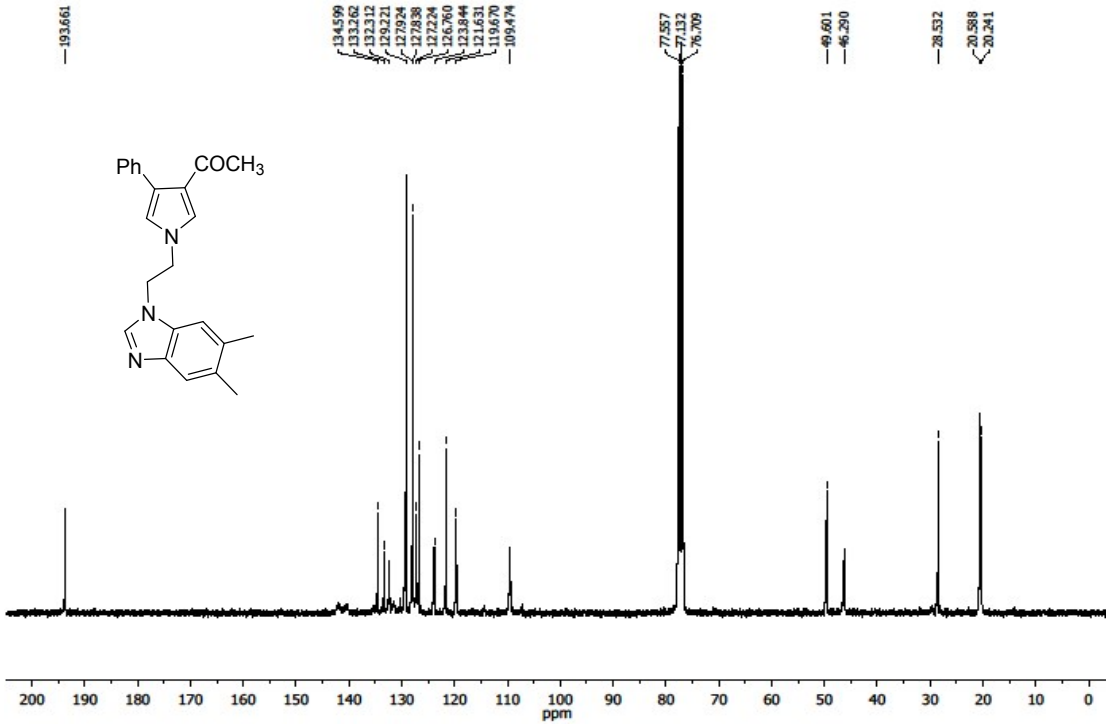

185.160
138.621
136.792
134.004
130.681
129.982
129.454
129.188
128.593
128.210
128.070
127.316
126.670
126.581
123.067
109.154
77.551
77.126
76.702
50.197
45.843
CHO
N
N
Ph
N
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

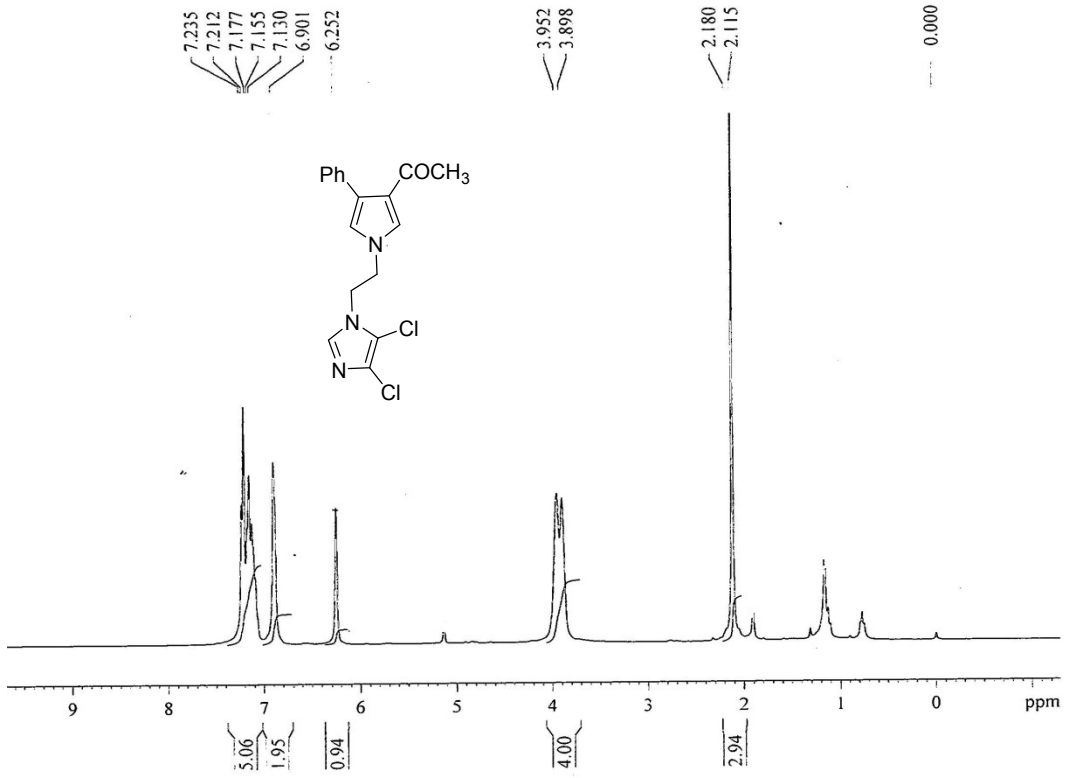

7.82
7.57
7.30
7.29
7.20
6.85
6.30
4.41
4.18
2.11
Ph
COCH3
N
N
N
1.33
1.20
7.86
1.03
1.00
2.12
2.03
3.60
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

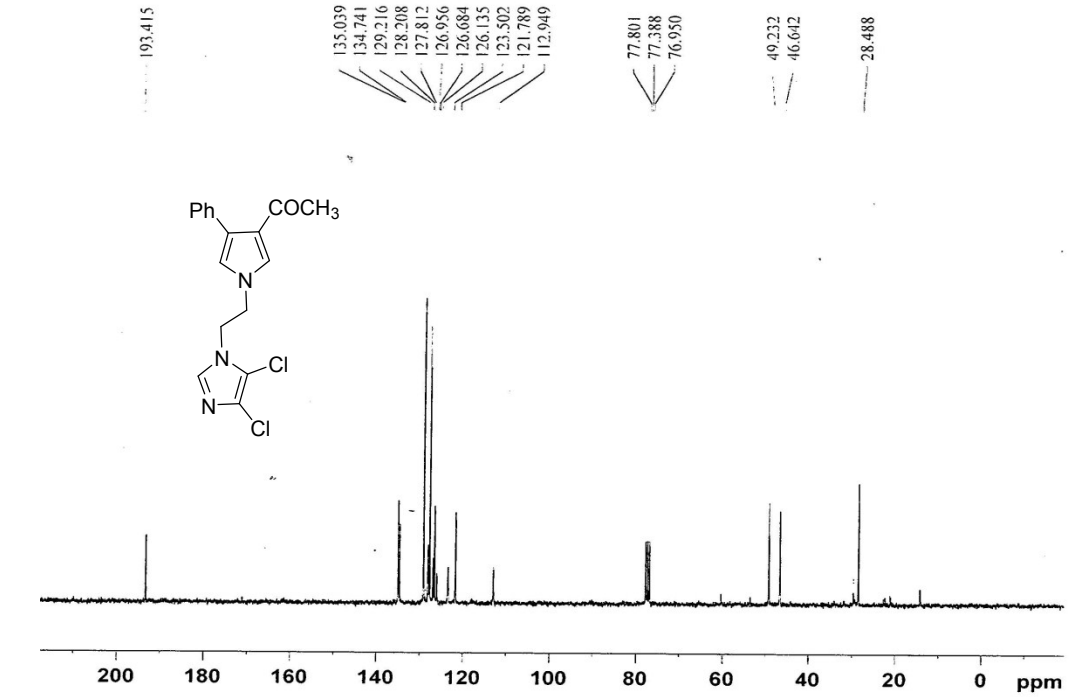

193.624
143.305
142.903
134.602
129.257
127.873
127.680
127.337
126.815
123.469
122.734
121.490
77.587
77.163
76.739
49.504
45.972
28.518
Ph
COCH3
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

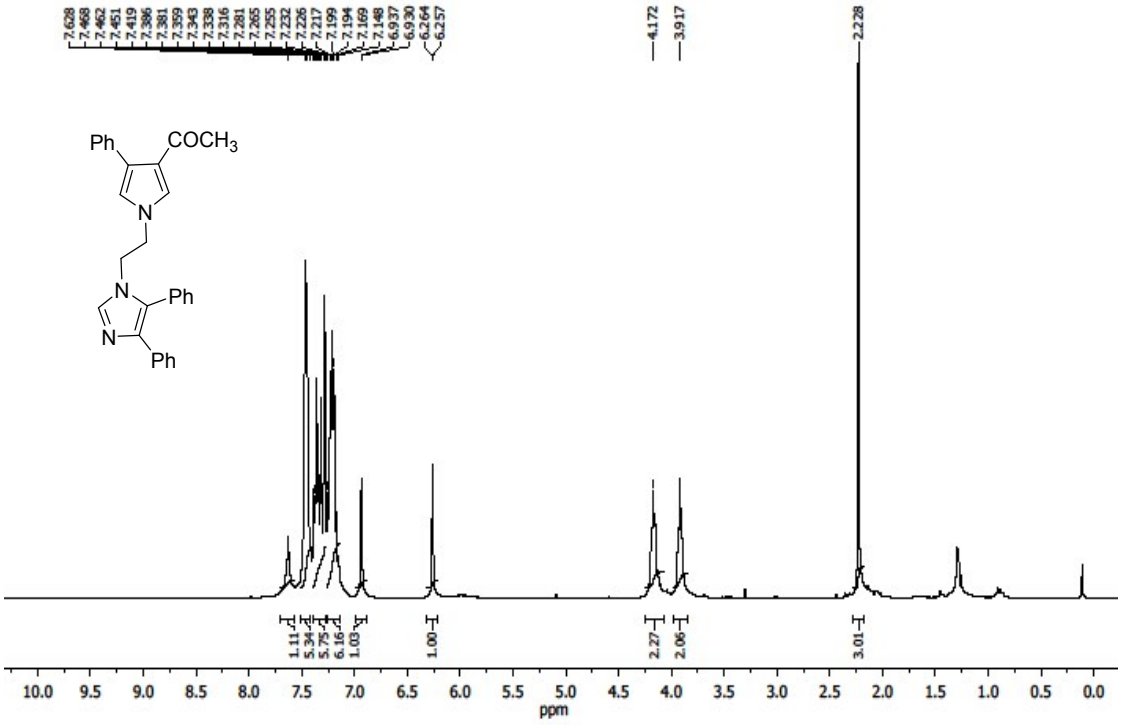

7.73
7.55
7.47
7.39
7.24
7.19
7.17
7.15
7.14
7.14
7.12
7.11
6.86
6.85
6.83
6.23
6.22
4.39
4.38
4.15
4.14
2.25
2.23
2.03

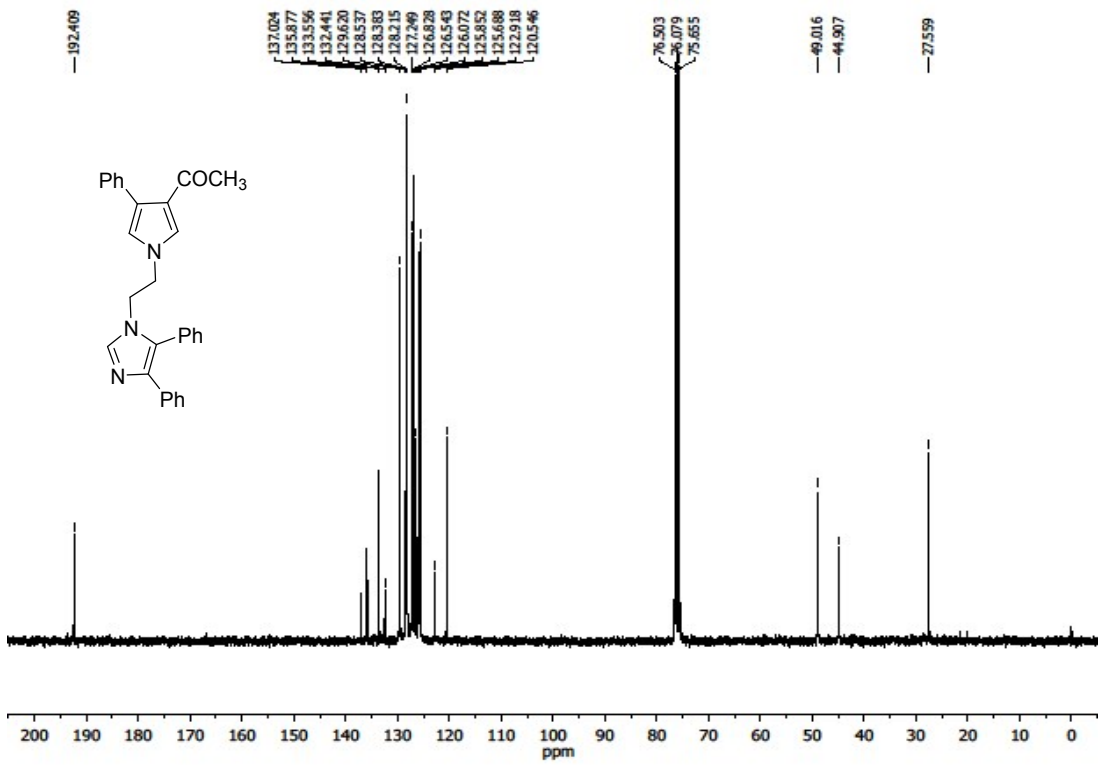

Ph
COCH3
N
N
N
1.28
2.60
5.33
1.67
1.09
2.00
1.59
6.09
2.48
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

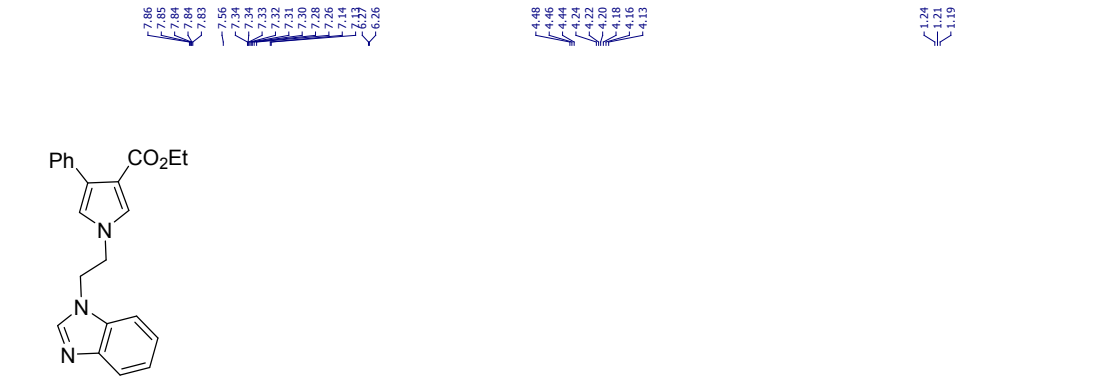

193.661
134.599
133.262
132.312
129.221
127.924
127.838
127.224
126.760
123.844
121.631
119.670
109.474
77.557
77.132
76.709
49.601
46.290
28.532
20.588
20.241
Ph
COCH3
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.235
7.212
7.177
7.155
7.130
6.901
6.252
3.952
3.898
2.180
2.115
0.000
Ph
COCH3
N
N
N
Cl
Cl
9 8 7 6 5 4 3 2 1 0 ppm
5.06
1.95
0.94
4.00
2.94

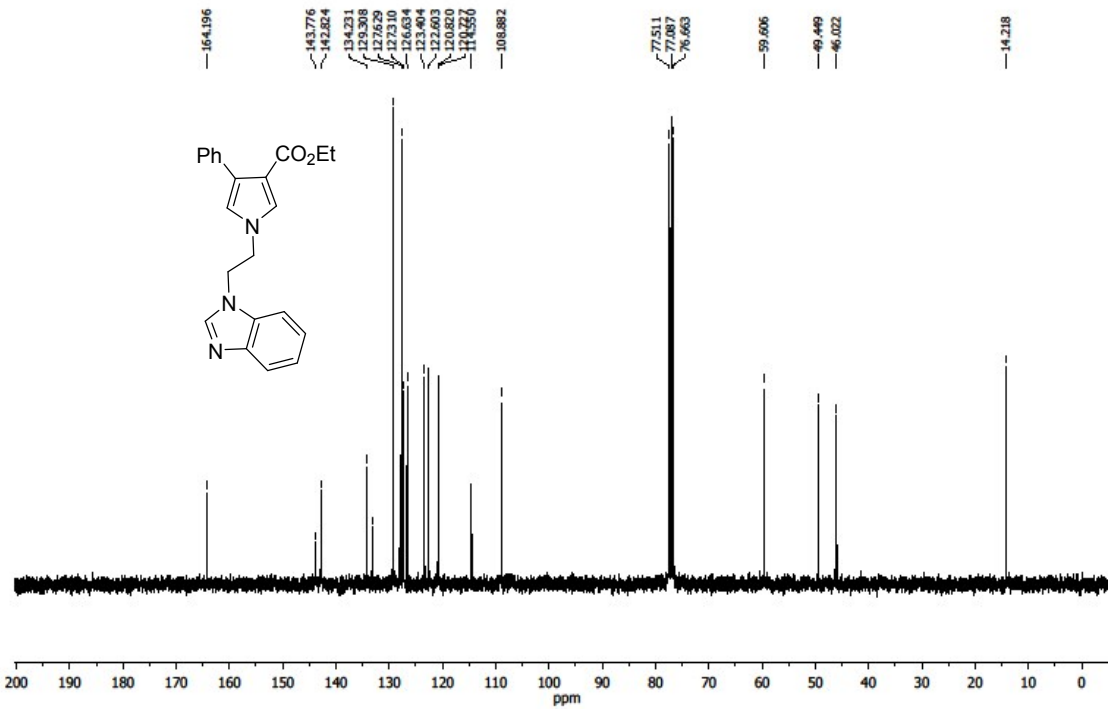

193.415
135.039
134.741
129.216
128.208
127.812
126.956
126.684
126.135
123.502
121.789
112.949
77.801
77.388
76.950
49.232
46.642
28.488
Ph
COCH3
N
N
Cl
N
Cl
200
180
160
140
120
100
80
60
40
20
0
ppm

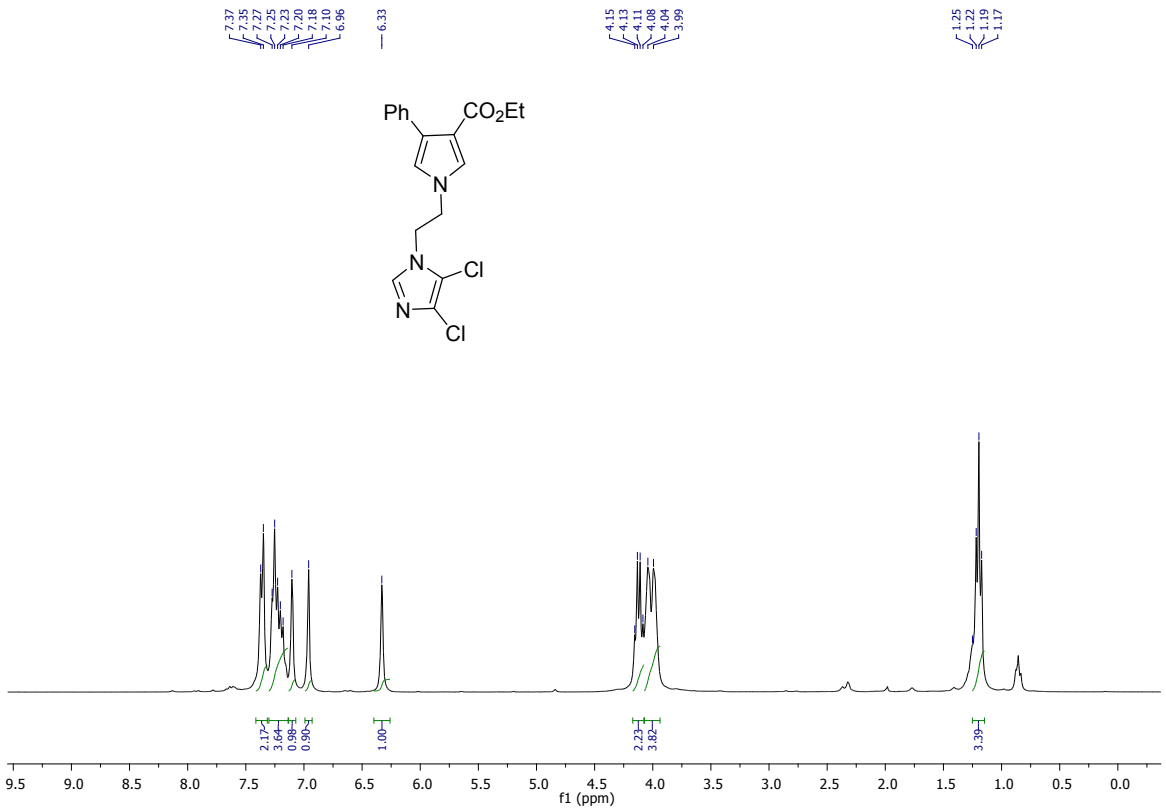

7.628
7.468
7.462
7.451
7.419
7.386
7.381
7.359
7.343
7.338
7.316
7.281
7.265
7.255
7.232
7.226
7.217
7.199
7.194
7.169
7.148
6.937
6.930
6.264
6.257
4.172
3.917
2.228
Ph
COCH3
N
N
Ph
N
Ph
1.11
5.34
5.75
6.16
1.03
1.00
2.27
2.06
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

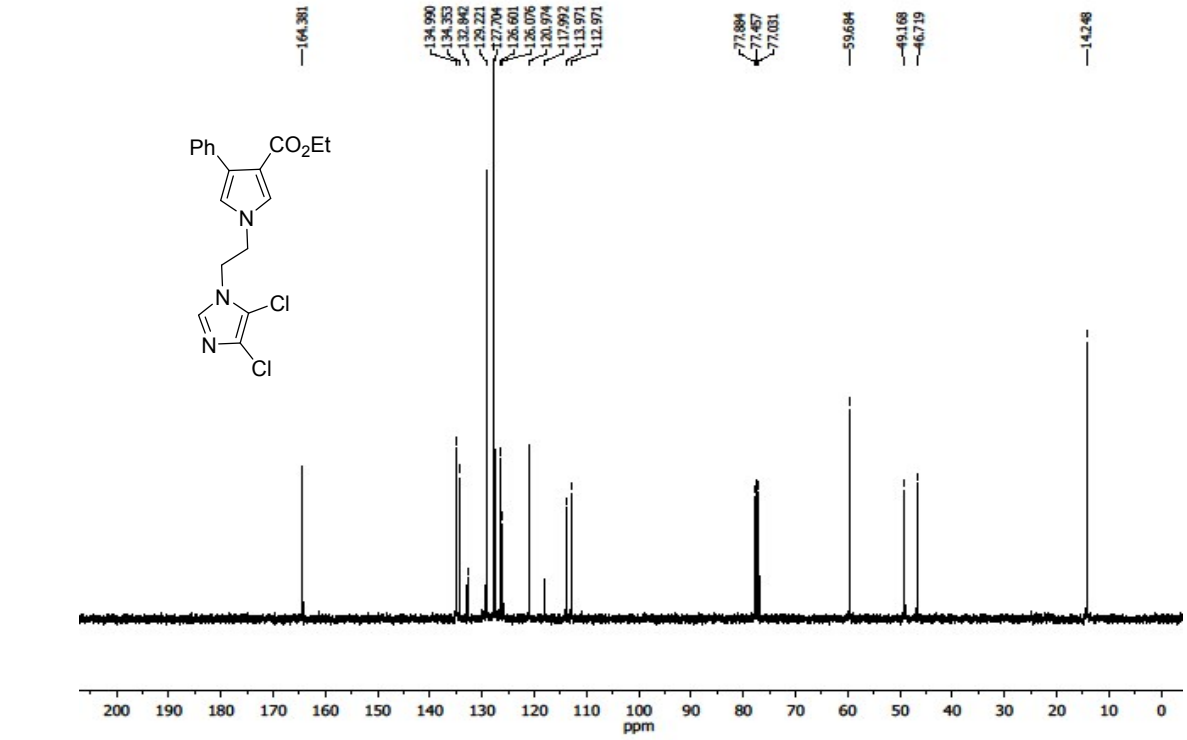

192.409
137.024
135.877
133.556
132.441
129.620
128.537
128.383
128.215
127.249
126.828
126.543
126.072
125.852
125.688
122.918
120.546
76.503
76.079
75.655
49.016
44.907
27.559
Ph
COCH3
N
N
Ph
N
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

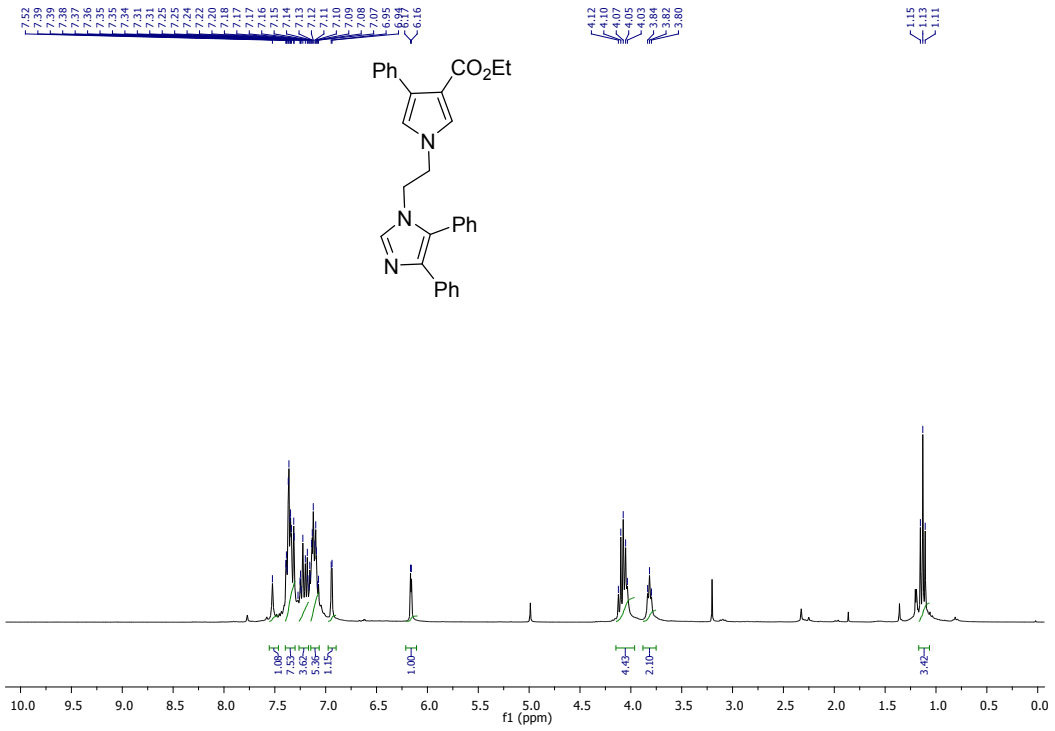

7.86
7.85
7.84
7.84
7.83
7.56
7.34
7.34
7.33
7.32
7.31
7.30
7.28
7.26
7.14
6.26
4.48
4.46
4.44
4.24
4.22
4.20
4.18
4.16
4.13
1.24
1.21
1.19

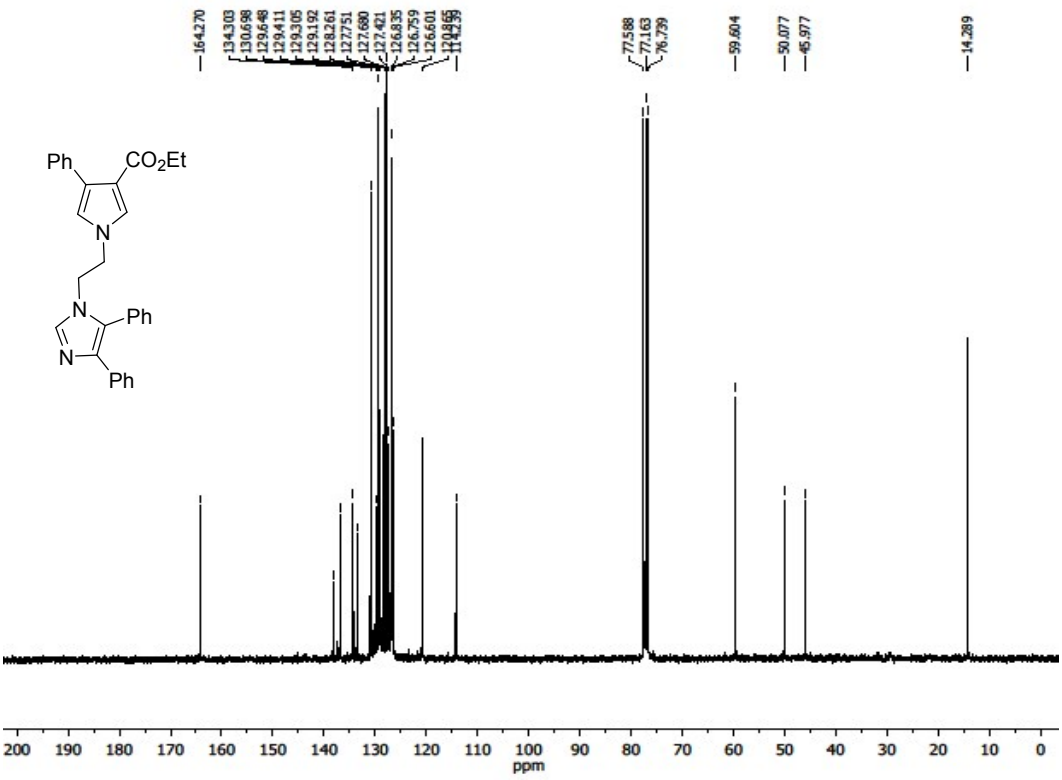
Ph
CO2Et
N
N
N
1.29
1.10
8.49
1.05
1.00
2.14
4.39
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

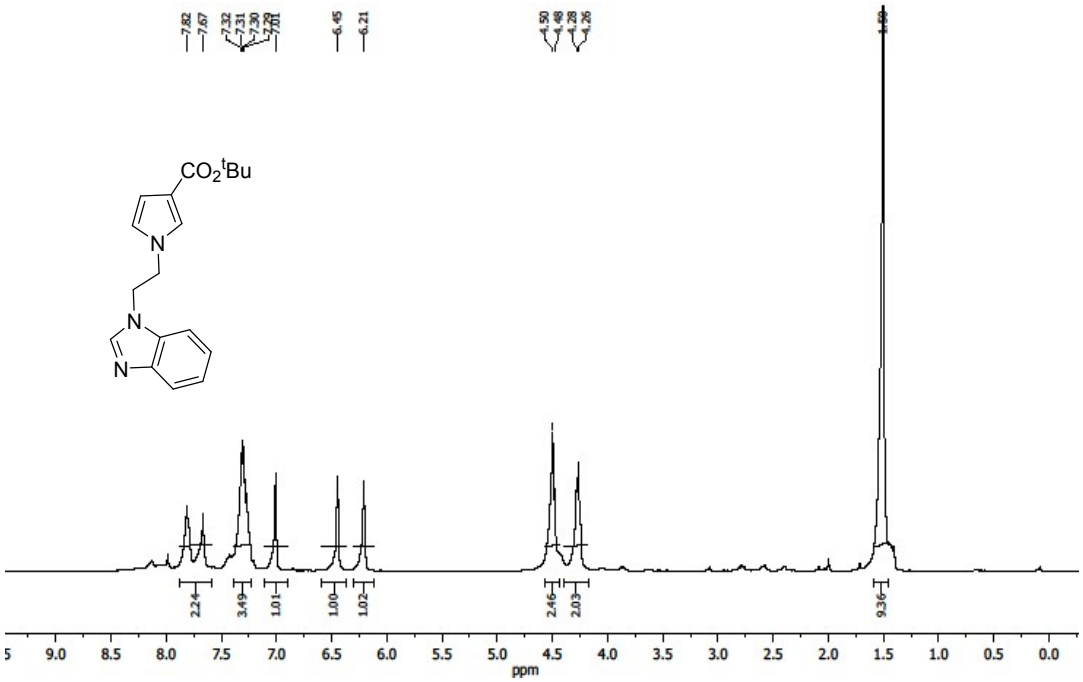

164.196
143.776
142.824
134.231
129.308
127.629
127.310
126.634
123.404
122.603
120.820
120.727
114.550
108.882
77.511
77.087
76.663
59.606
49.449
46.022
14.218
Ph
CO2Et
N
N
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

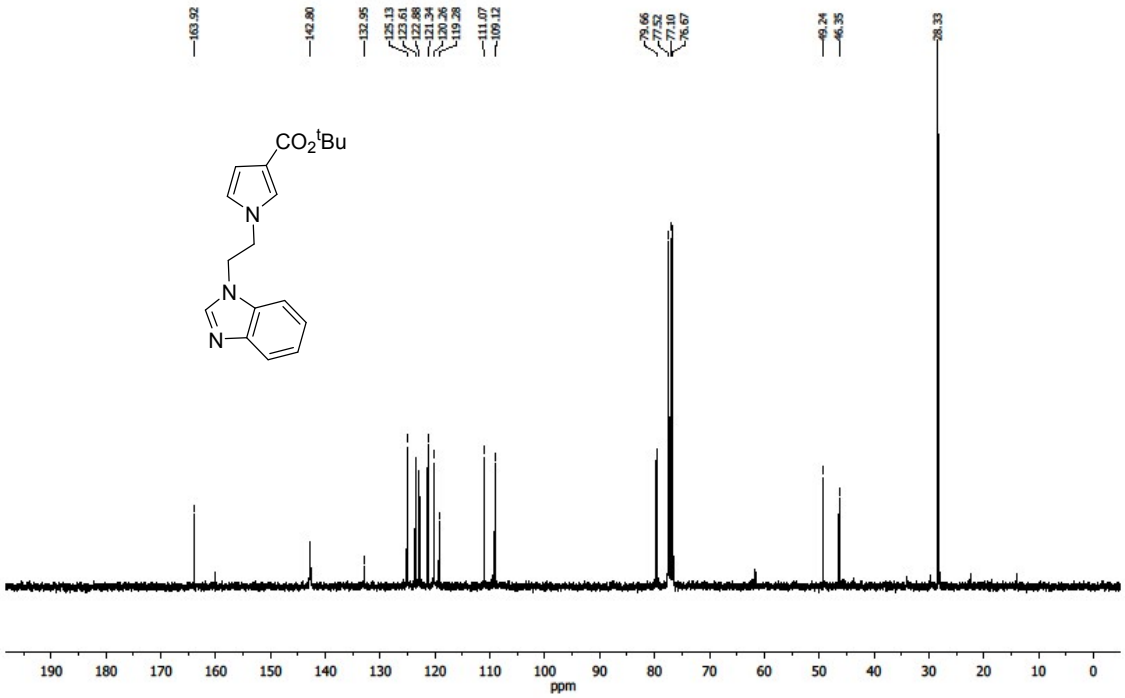

7.37
7.35
7.27
7.25
7.23
7.20
7.18
7.10
6.96
6.33
4.15
4.13
4.11
4.08
4.04
3.99
1.25
1.22
1.19
1.17
Ph
CO2Et
N
N
Cl
N
Cl
2.17
3.64
0.98
0.90
1.00
2.23
3.82
3.39
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

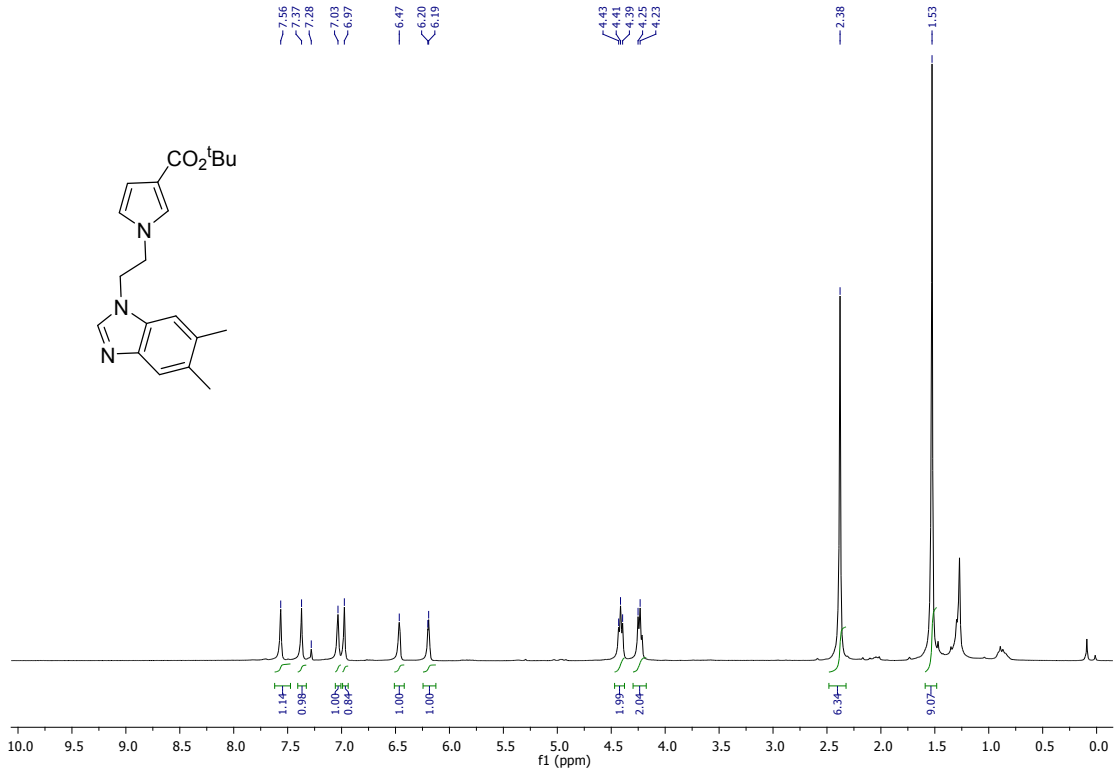

164.381
134.990
134.353
132.842
129.221
127.704
126.601
126.076
120.974
117.992
113.971
112.971
77.884
77.457
77.031
59.684
49.168
46.719
14.248
Ph
CO2Et
N
N
Cl
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

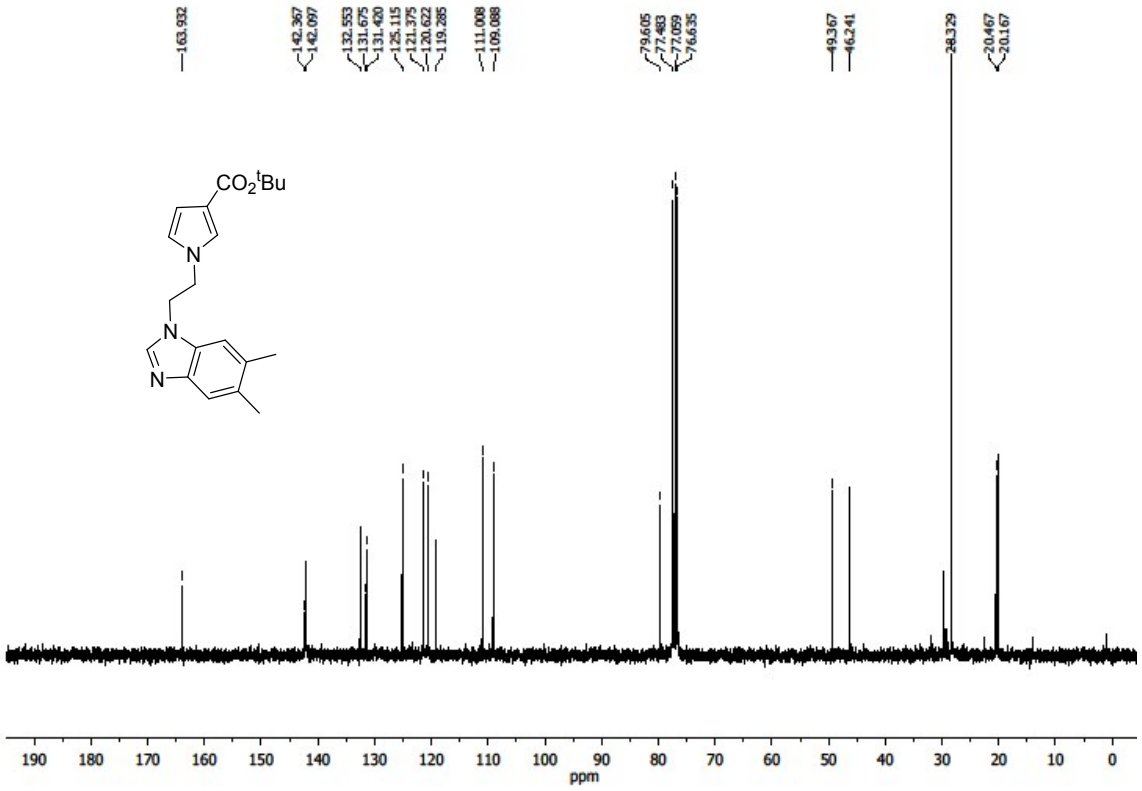

Ph
CO2Et
N
N
Ph
N
Ph
f1 (ppm)

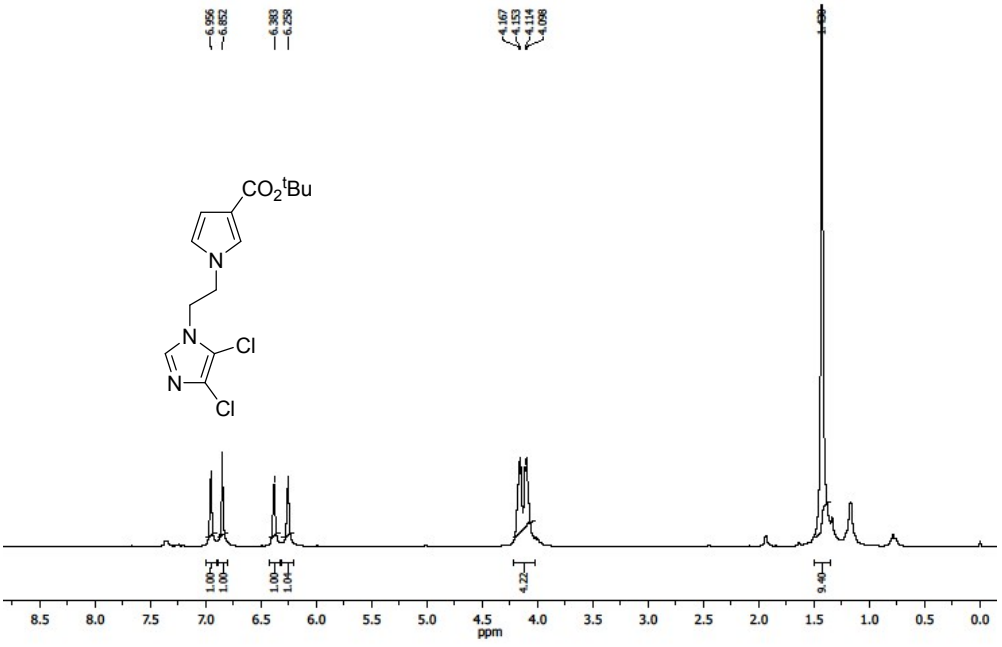

Ph
CO2Et
N
N
Ph
N
Ph
ppm

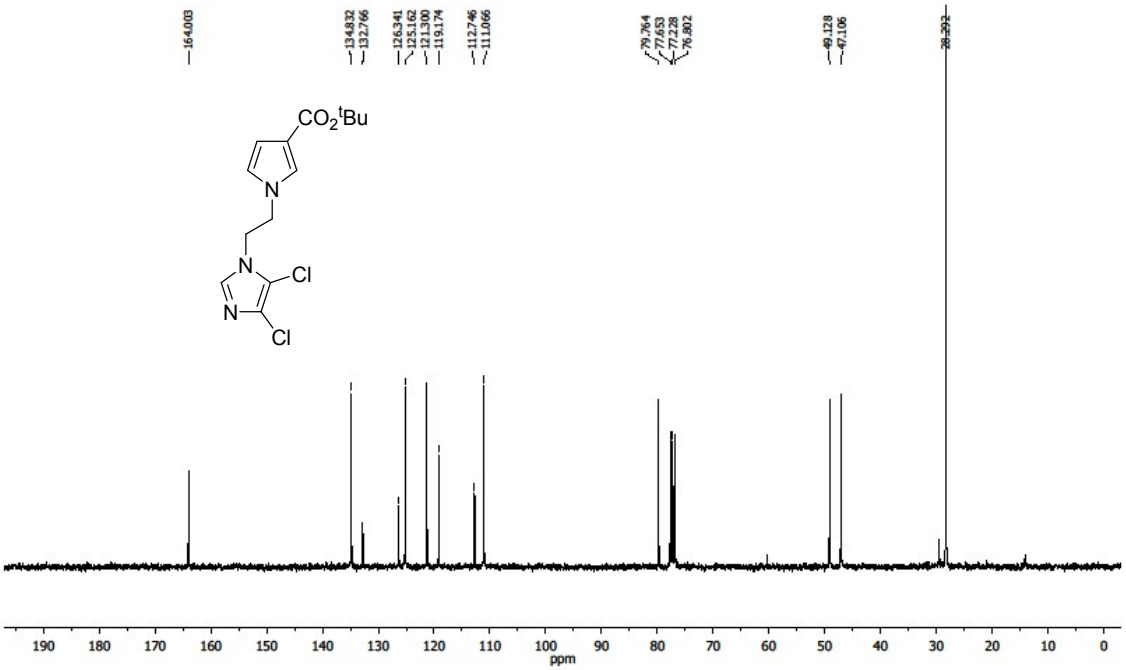

7.82
7.67
7.32
7.31
7.30
7.29
7.01
6.45
6.21
4.50
4.48
4.28
4.26
1.60
CO2tBu
N
N
N
2.24
3.49
1.01
1.00
1.02
2.46
2.03
9.36
ppm

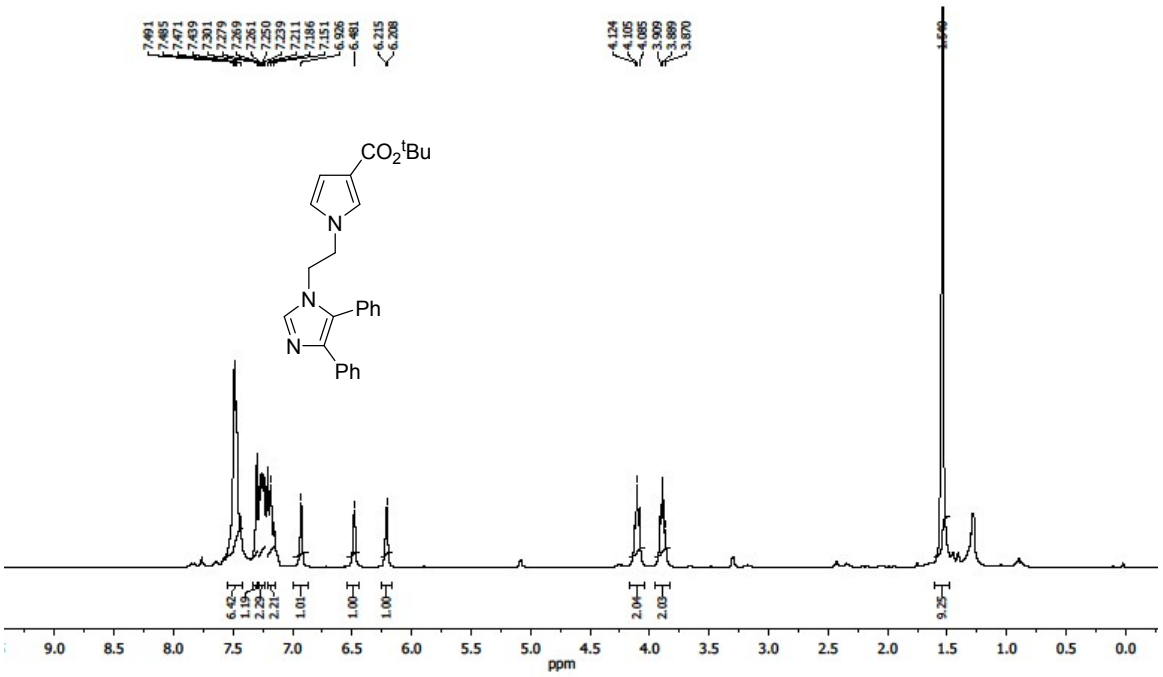

163.92
142.80
132.95
125.13
123.61
122.88
121.34
120.26
119.28
111.07
109.12
79.66
77.52
77.10
76.67
49.24
46.35
28.33
CO2tBu
N
N
N
ppm

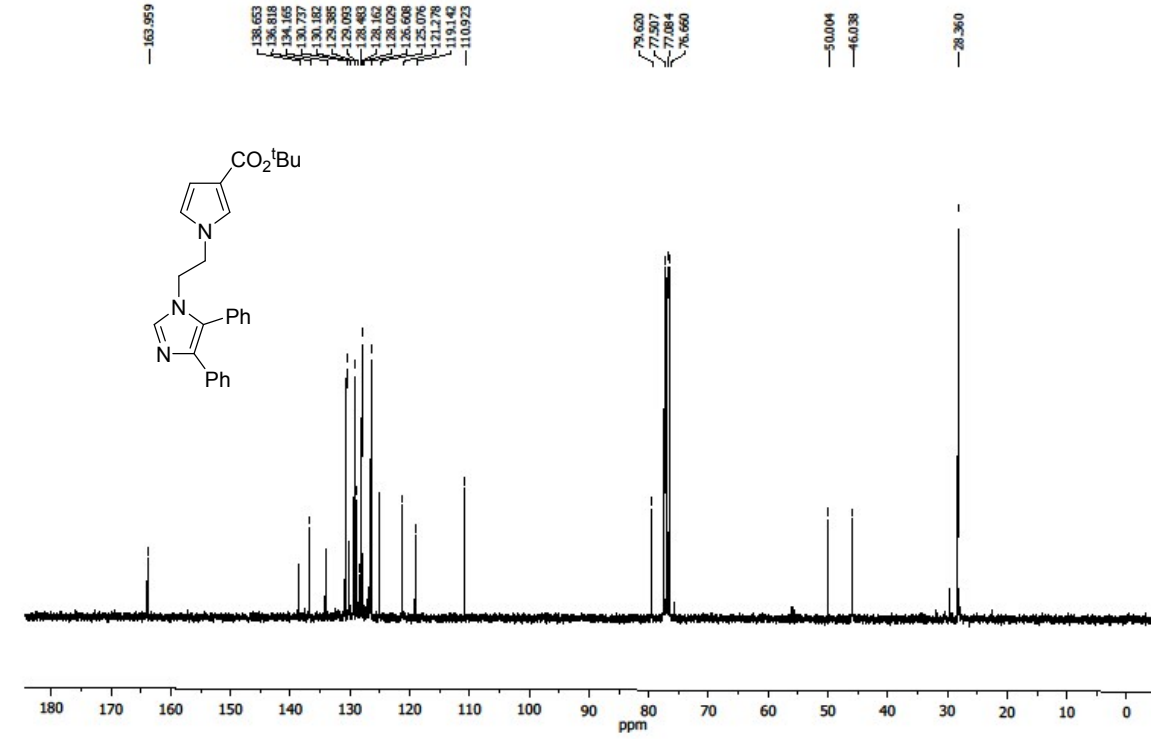

7.56
7.37
7.28
7.03
6.97
6.47
6.20
6.19
4.43
4.41
4.39
4.25
4.23
2.38
1.53
CO2tBu
N
N
N
1.14
0.98
1.00
0.84
1.00
1.00
1.99
2.04
6.34
9.07
f1 (ppm)

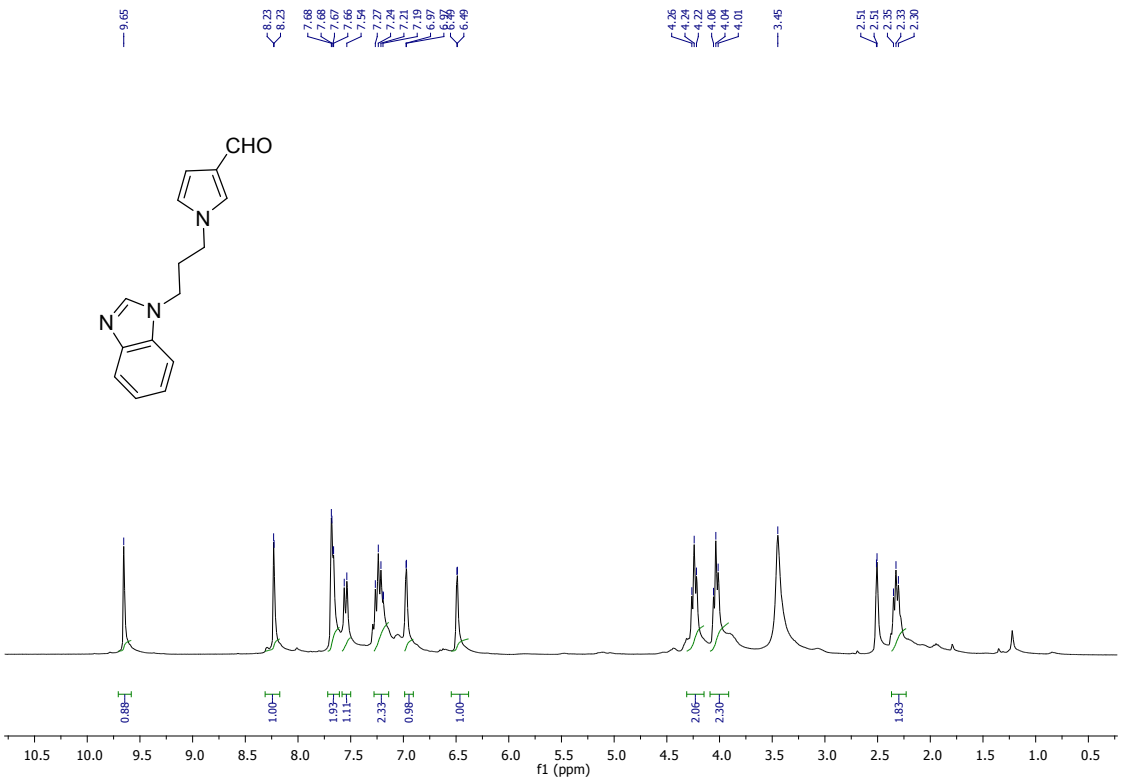

163.932
142.367
142.097
132.553
131.675
131.420
125.115
121.375
120.622
119.285
111.008
109.088
79.605
77.483
77.069
76.635
49.367
46.241
28.329
20.467
20.167
CO2tBu
N
N
N
ppm

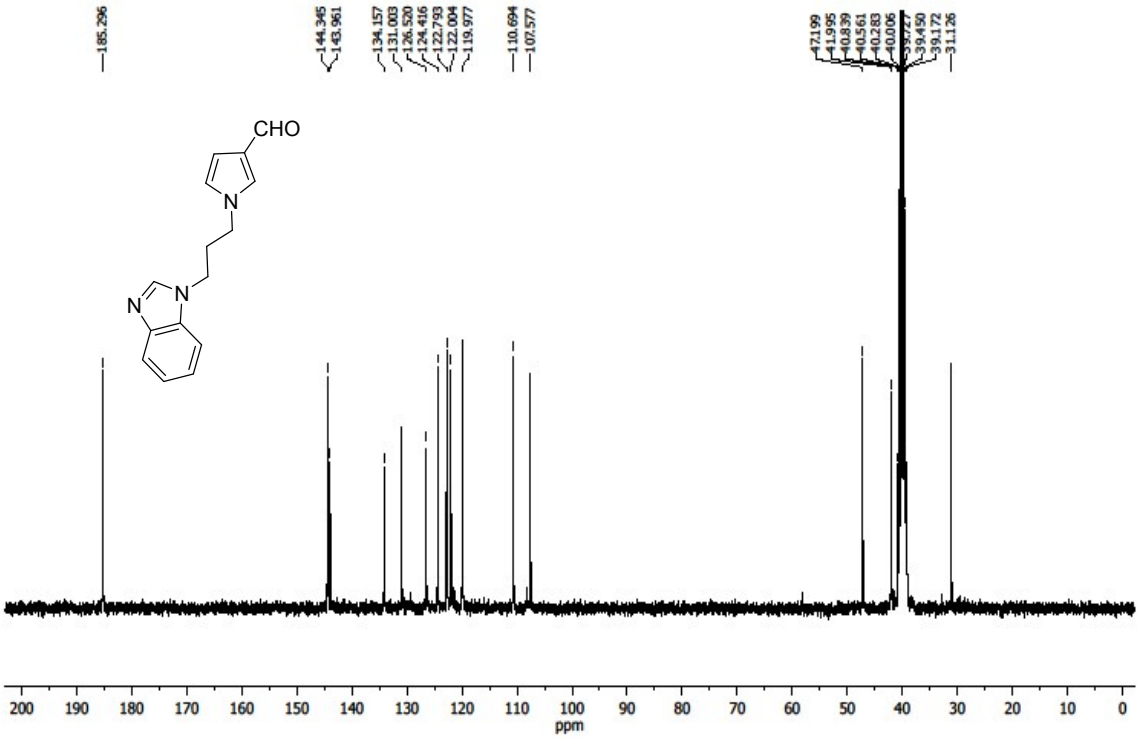

6.956
6.852
6.388
6.238
4.167
4.153
4.114
4.098
1.438
CO2tBu
N
N
Cl
N
Cl
1.00
1.00
1.00
1.04
4.22
9.40
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

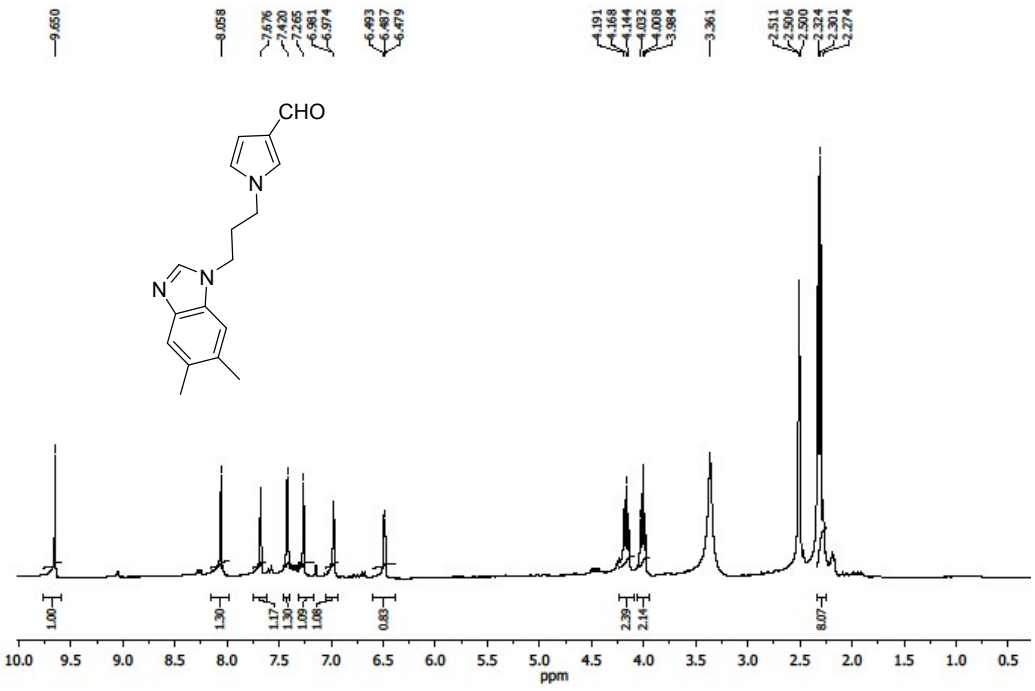

164.003
134.832
132.766
126.341
125.162
121.300
119.174
112.746
111.066
79.764
77.653
77.228
76.802
49.128
47.106
28.292
CO2tBu
N
N
Cl
N
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

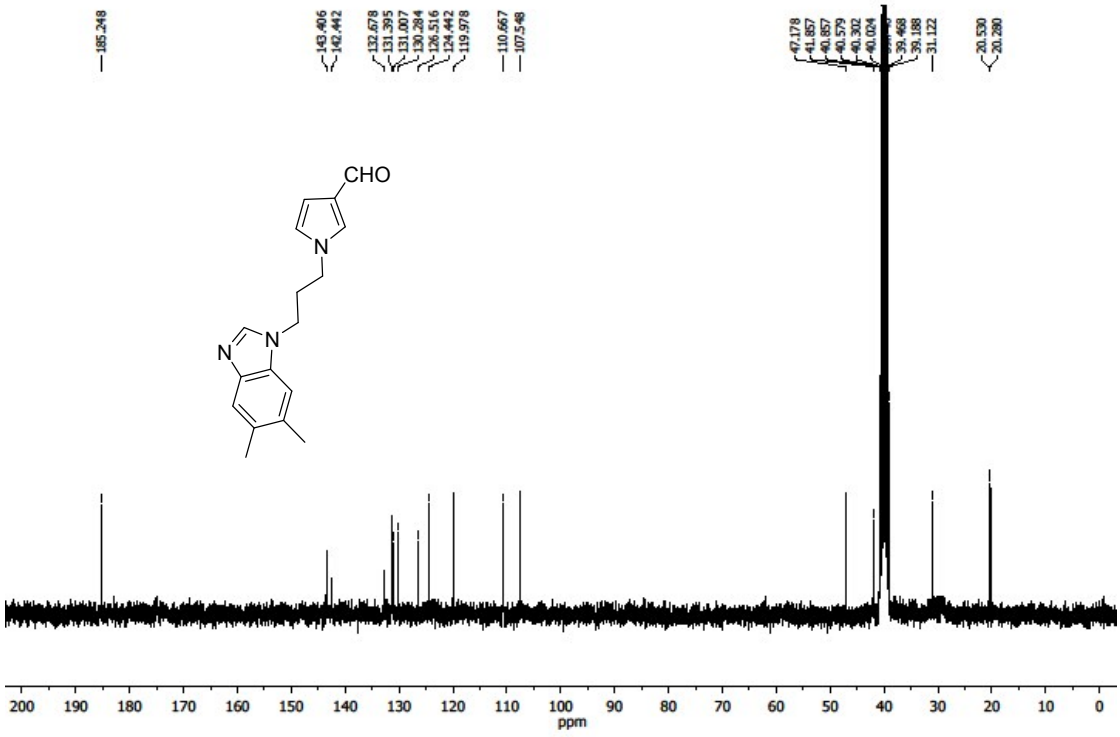

7.491
7.485
7.471
7.439
7.301
7.279
7.269
7.261
7.250
7.239
7.211
7.186
7.151
6.926
6.491
6.215
6.208
4.124
4.105
4.085
3.909
3.889
3.870
1.540
CO2tBu
N
N
N
Ph
Ph
6.42
1.19
2.29
2.21
1.01
1.00
1.00
2.04
2.03
9.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

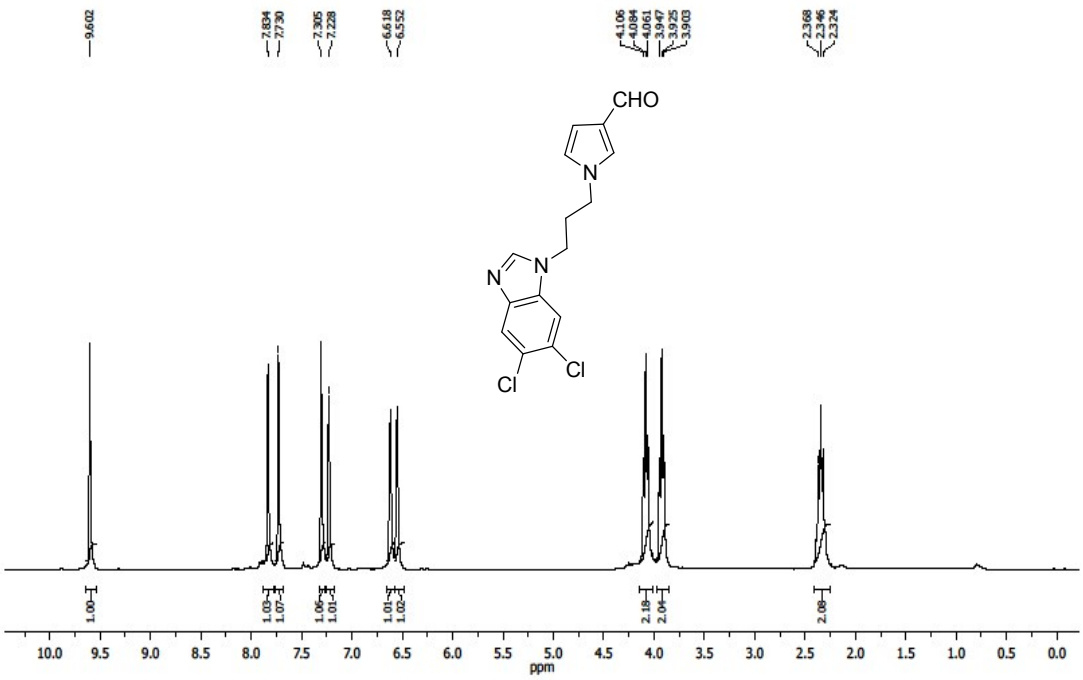

163.959
138.653
136.818
134.165
130.737
130.182
129.385
129.093
128.483
128.162
128.029
126.606
125.076
121.278
119.142
110.923
79.620
77.507
77.084
76.660
50.004
46.038
28.360
CO2tBu
N
N
N
Ph
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

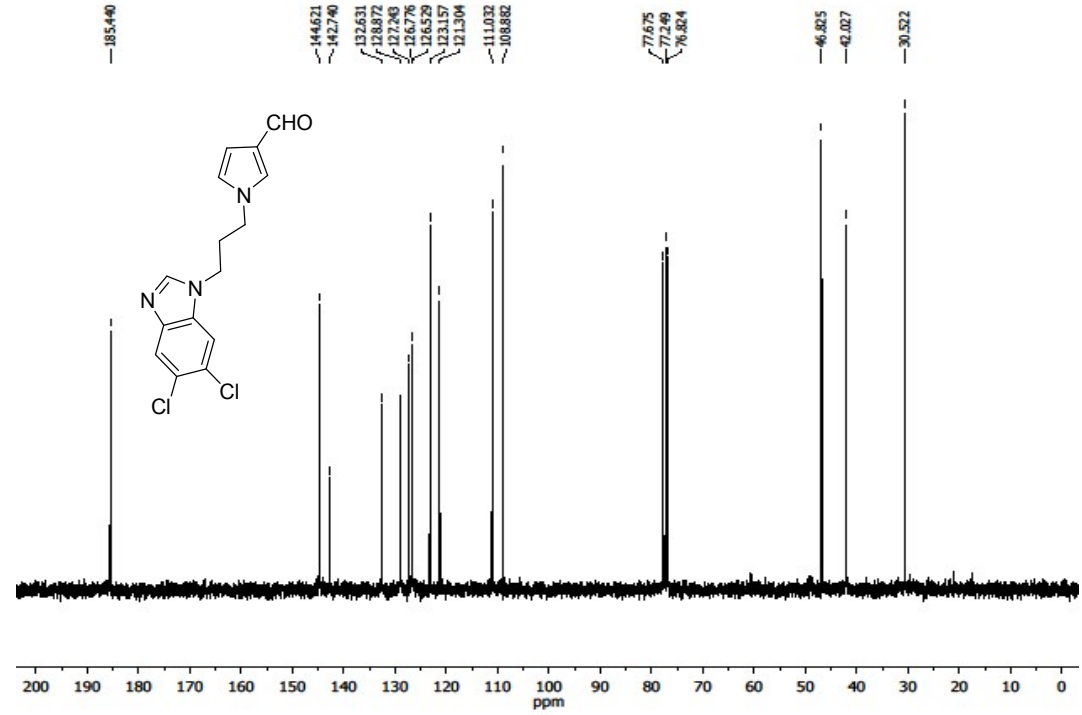

9.65
8.23
8.23
7.68
7.68
7.67
7.67
7.66
7.54
7.27
7.24
7.21
7.19
6.97
6.97
6.49
6.49
4.26
4.24
4.22
4.06
4.04
4.01
3.45
2.51
2.51
2.35
2.33
2.30
CHO
N
N
N
0.88
1.00
1.93
1.11
2.33
0.98
1.00
2.06
2.30
1.83
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

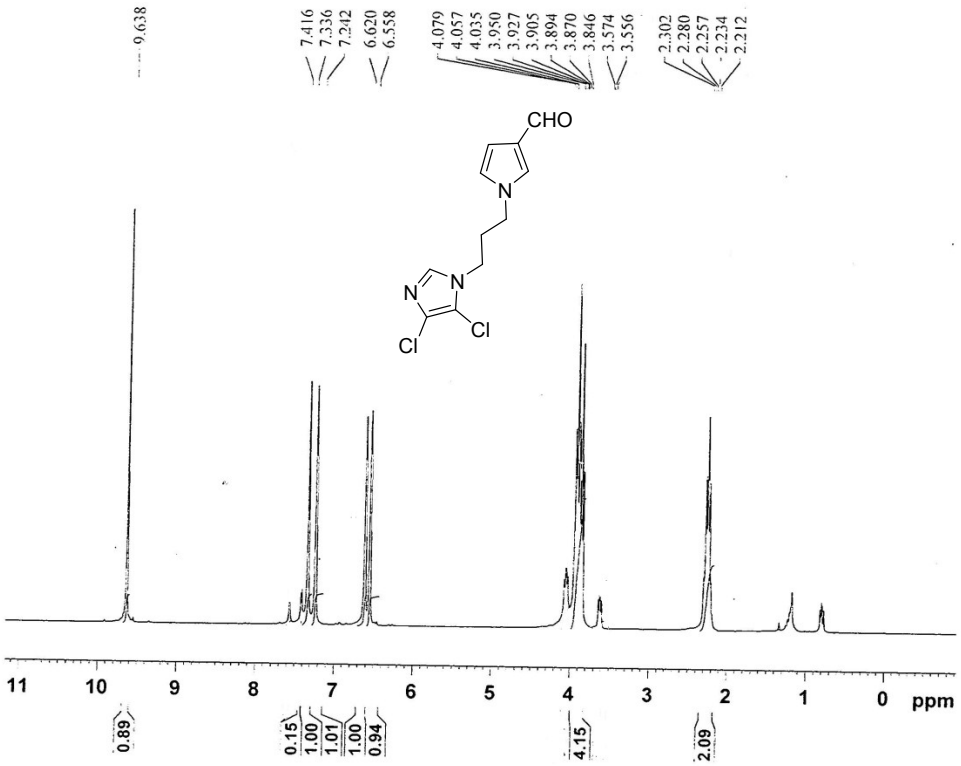

185.296
144.345
143.961
134.157
131.003
126.520
124.416
122.793
122.004
119.977
110.694
107.577
47.199
41.995
40.839
40.561
40.283
40.006
39.727
39.450
39.172
31.126
CHO
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

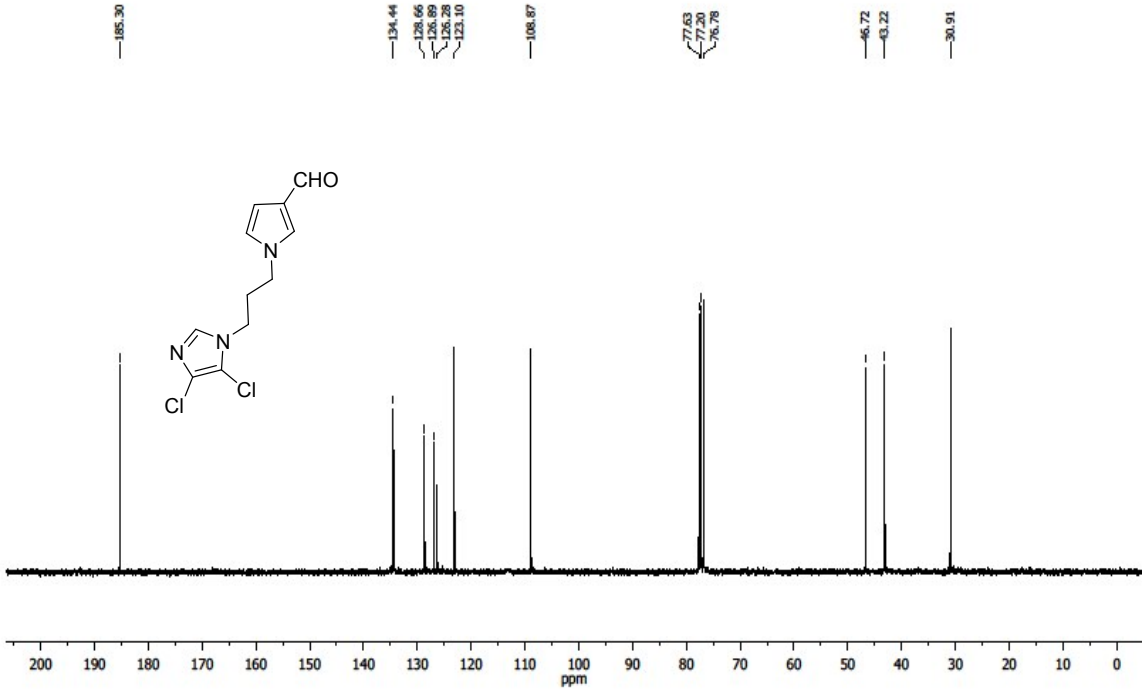

9.650
8.058
7.676
7.420
7.265
6.981
6.974
6.493
6.487
6.479
4.191
4.168
4.144
4.032
4.008
3.984
3.361
2.511
2.506
2.500
2.324
2.301
2.274
CHO
N
N
N
1.00
1.30
1.17
1.30
1.09
1.08
0.83
2.39
2.14
8.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

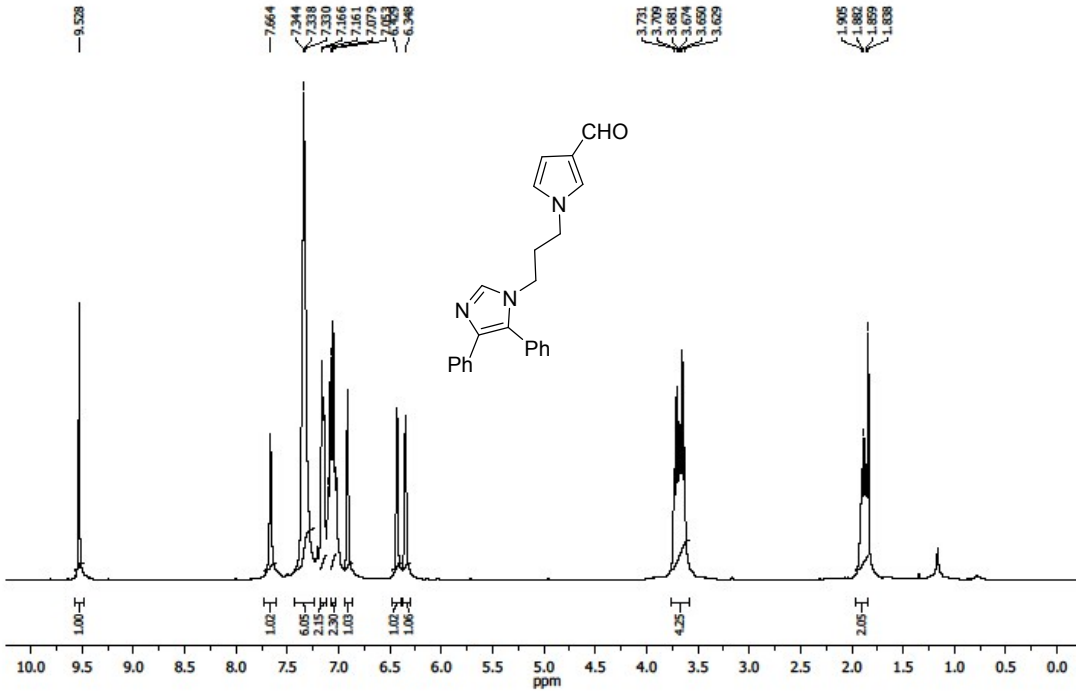

185.248
143.406
142.442
132.678
131.395
131.007
130.284
126.516
124.442
119.978
110.667
107.548
47.178
41.857
40.857
40.579
40.302
40.024
39.468
39.188
31.122
20.530
20.280
CHO
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

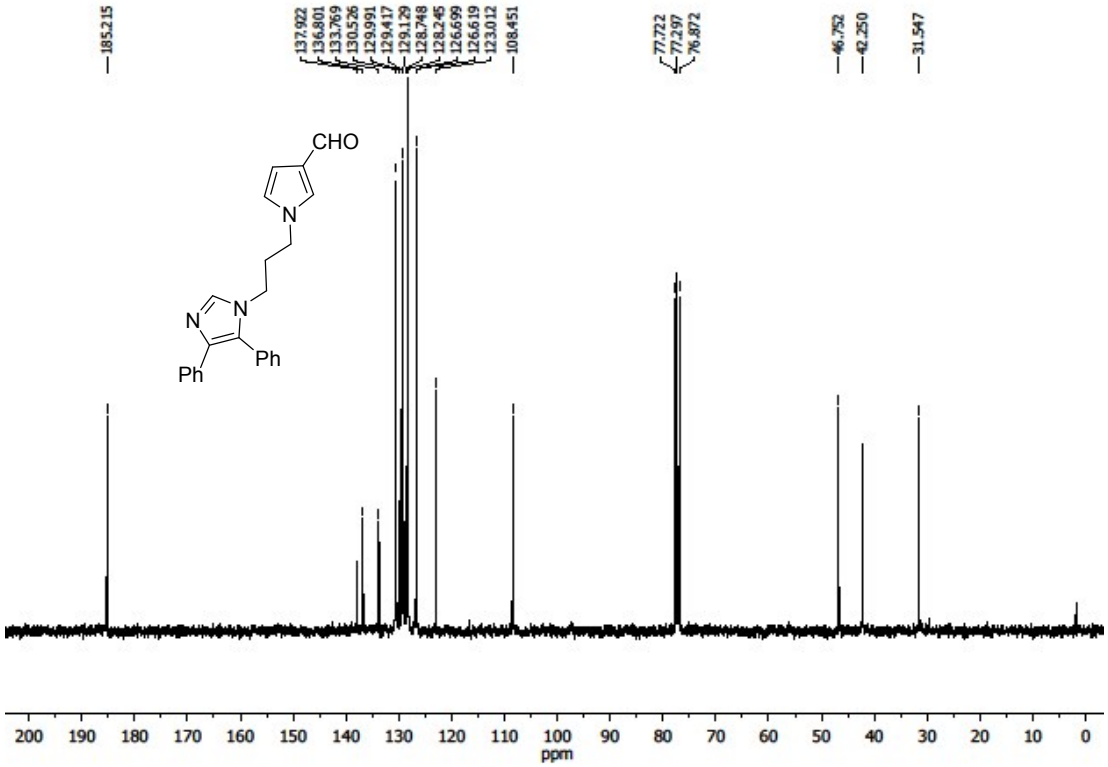

9.602
7.834
7.730
7.305
7.228
6.618
6.552
4.106
4.084
4.061
3.947
3.925
3.903
2.368
2.346
2.324
CHO
N
N
N
Cl
Cl
1.00
1.03
1.07
1.06
1.01
1.01
1.02
2.18
2.04
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

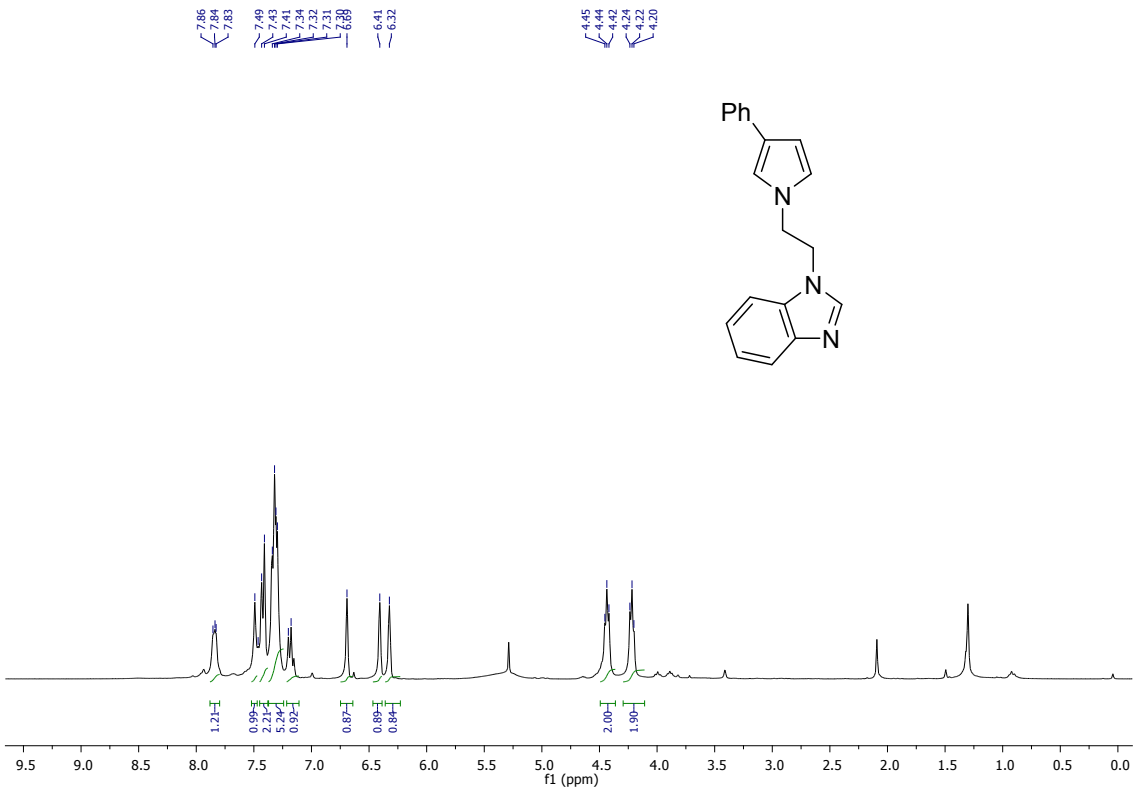

185.440
144.621
142.740
132.631
128.872
127.243
126.776
126.529
123.157
121.304
111.032
108.882
77.675
77.249
76.824
46.825
42.027
30.522
CHO
N
N
N
Cl
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

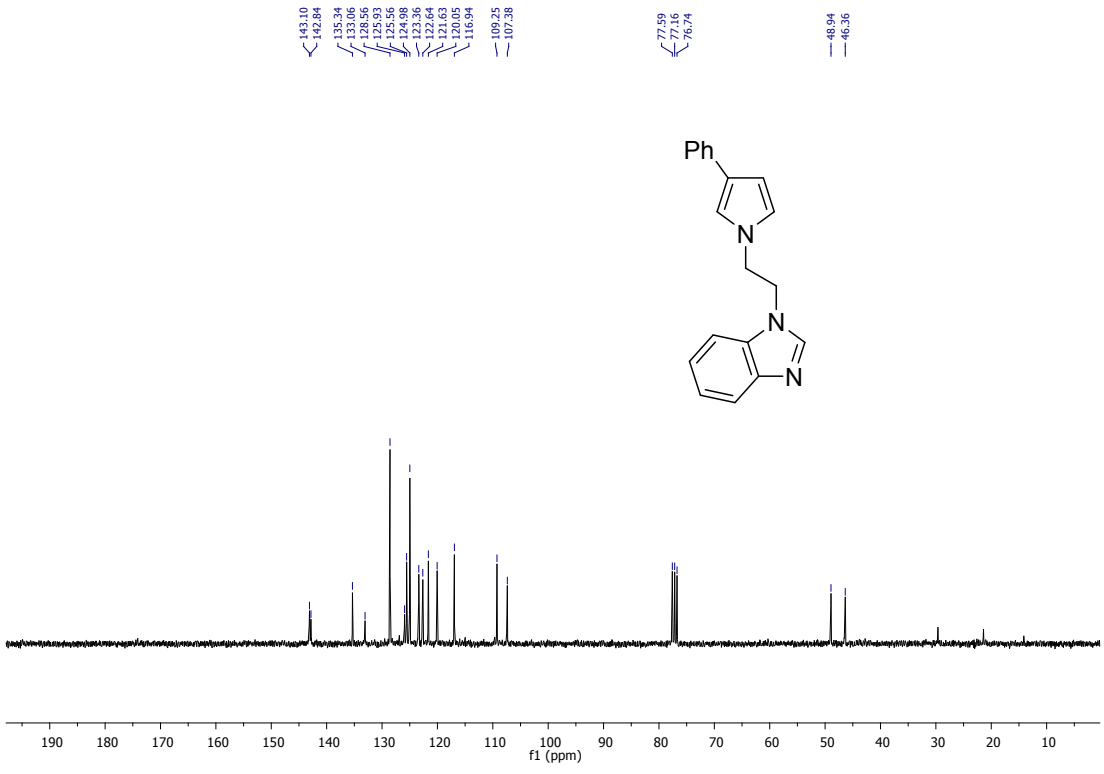

9.638
7.416
7.336
7.242
6.620
6.558
4.079
4.057
4.035
3.950
3.927
3.905
3.894
3.870
3.846
3.574
3.556
2.302
2.280
2.257
2.234
2.212
CHO
N
N
N
Cl
Cl
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.89
0.15
1.00
1.01
1.00
0.94
4.15
2.09

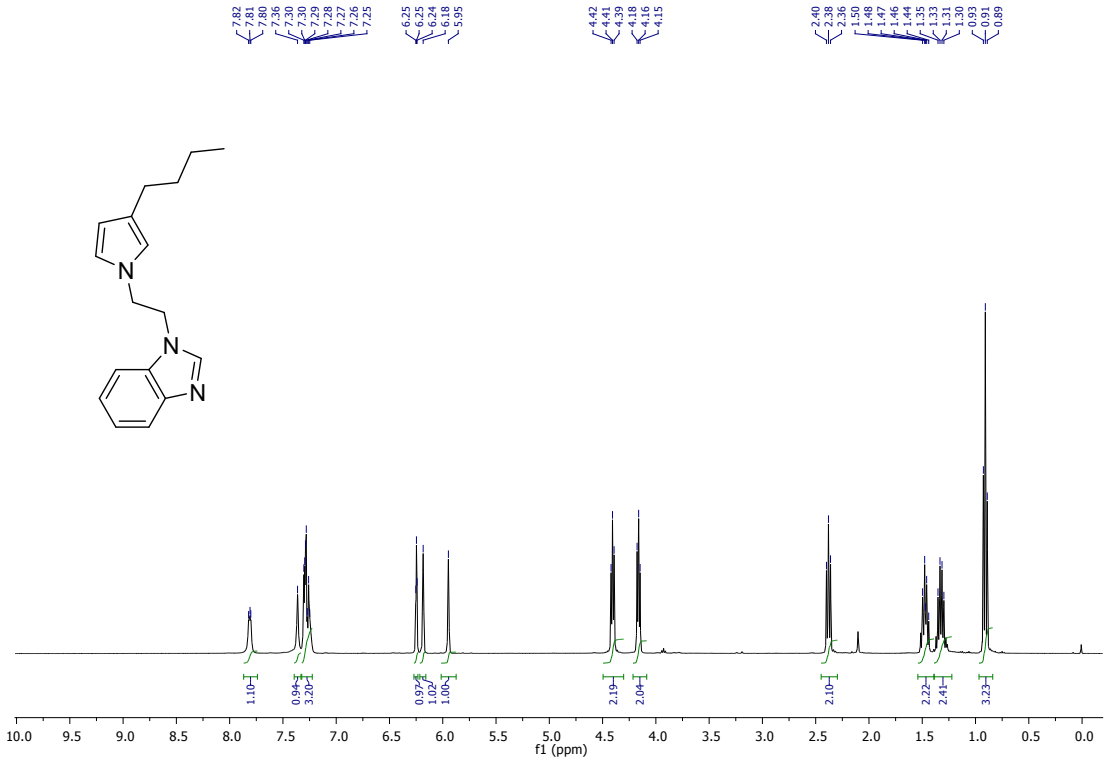

185.30
134.44
128.66
126.89
126.28
123.10
108.87
77.63
77.20
76.78
46.72
43.22
30.91
CHO
N
N
N
Cl
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

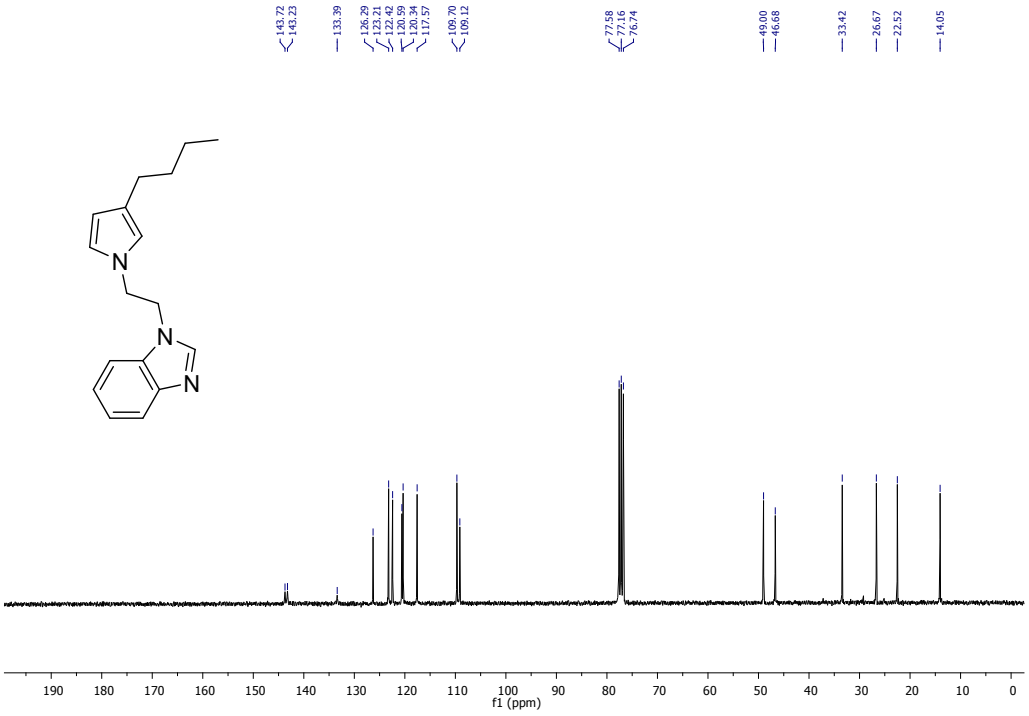

9.528
7.664
7.344
7.338
7.330
7.166
7.161
7.079
6.348
3.731
3.709
3.681
3.674
3.650
3.629
1.905
1.882
1.859
1.838
CHO
N
N
Ph
Ph
1.00
1.02
6.05
2.15
2.30
1.03
1.02
1.06
4.25
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

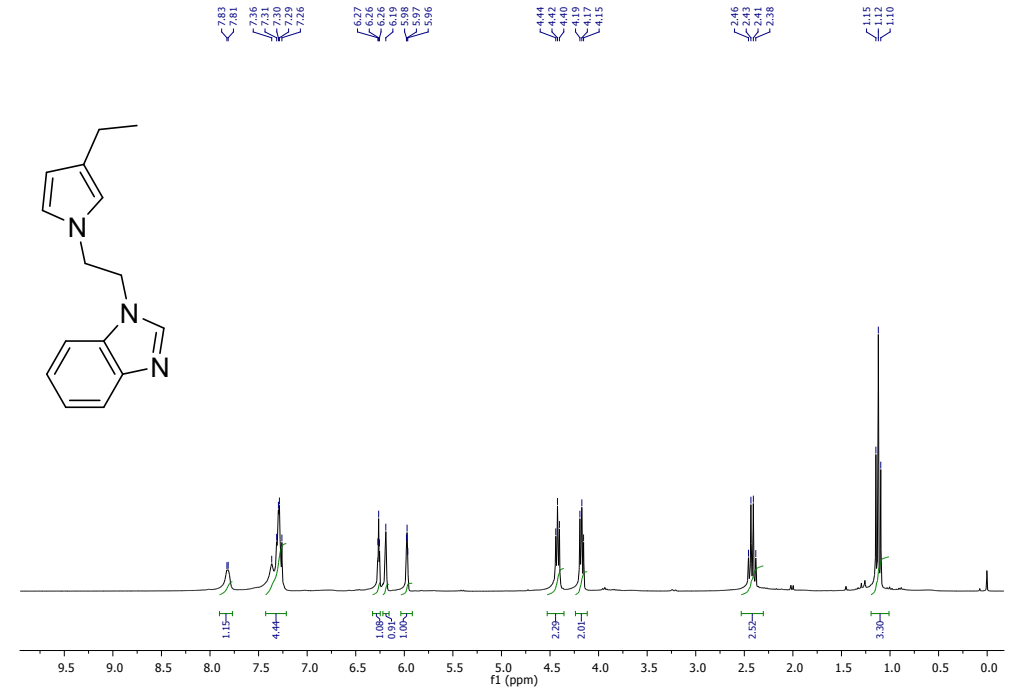

185.215
137.922
136.801
131.769
130.526
129.991
129.417
129.129
128.748
128.245
126.699
126.619
123.012
108.451
77.722
77.297
76.872
46.752
42.250
31.547
CHO
N
N
Ph
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

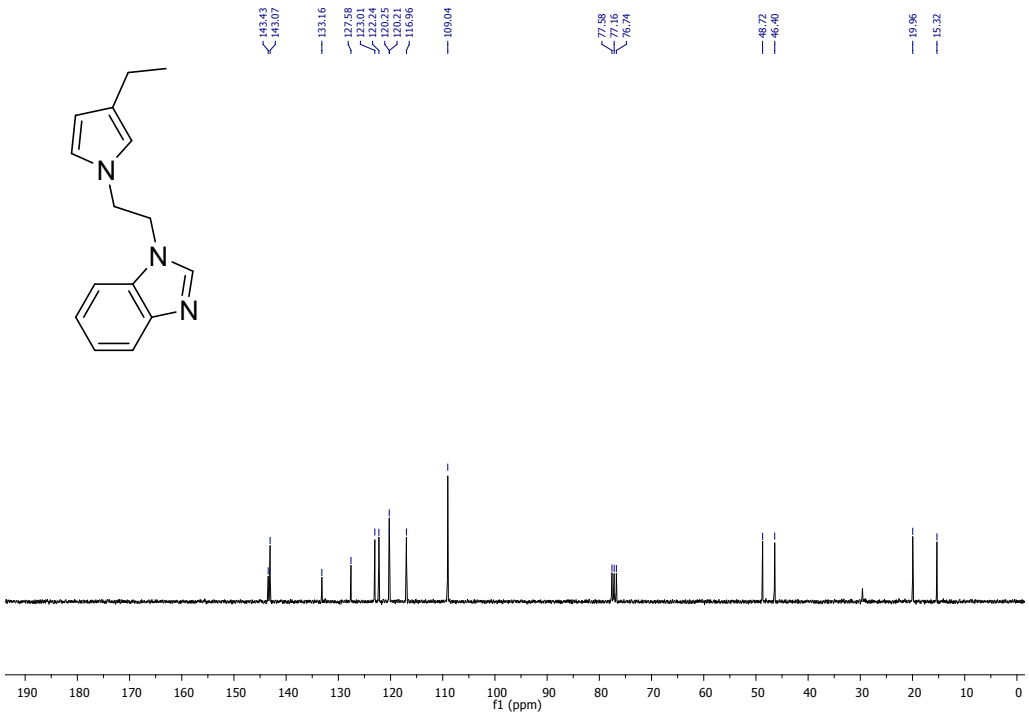

7.86
7.84
7.83
7.49
7.43
7.41
7.34
7.32
7.31
7.30
6.89
6.41
6.32
4.45
4.44
4.42
4.24
4.22
4.20
Ph
N
N
N
1.21
0.99
2.21
5.24
0.92
0.87
0.89
0.84
2.00
1.90
f1 (ppm)


143.10
142.84
135.34
133.06
128.56
125.93
125.56
124.98
123.36
122.64
121.63
120.05
116.94
109.25
107.38
77.59
77.16
76.74
48.94
46.36
Ph
N
N
N
f1 (ppm)

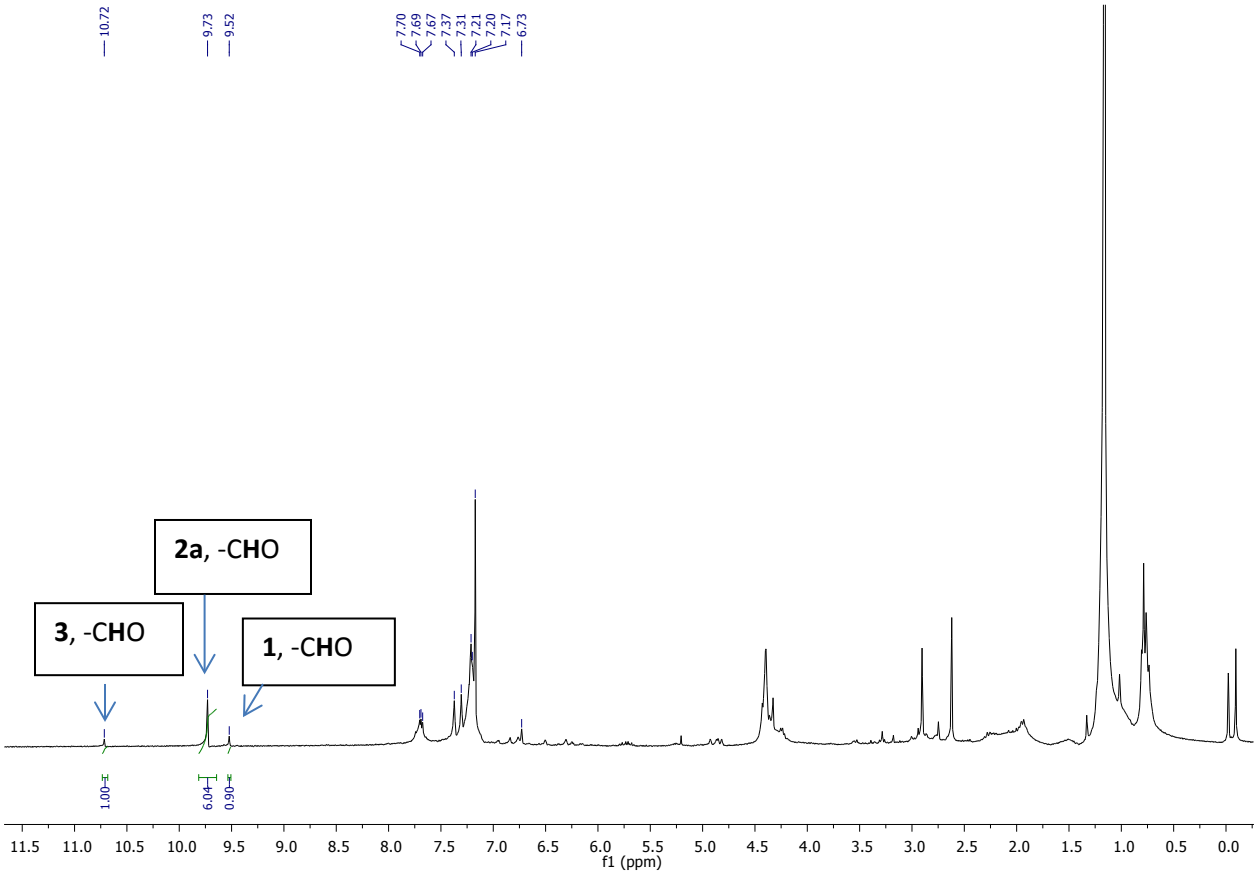

7.82
7.81
7.80
7.36
7.30
7.29
7.28
7.27
7.26
7.25
6.25
6.25
6.24
6.18
5.95
4.42
4.41
4.39
4.18
4.16
4.15
2.40
2.38
2.36
1.50
1.48
1.47
1.46
1.44
1.35
1.33
1.31
1.30
0.93
0.91
0.89
1.10
0.94
3.20
0.97
1.02
1.00
2.19
2.04
2.10
2.22
2.41
3.23
f1 (ppm)

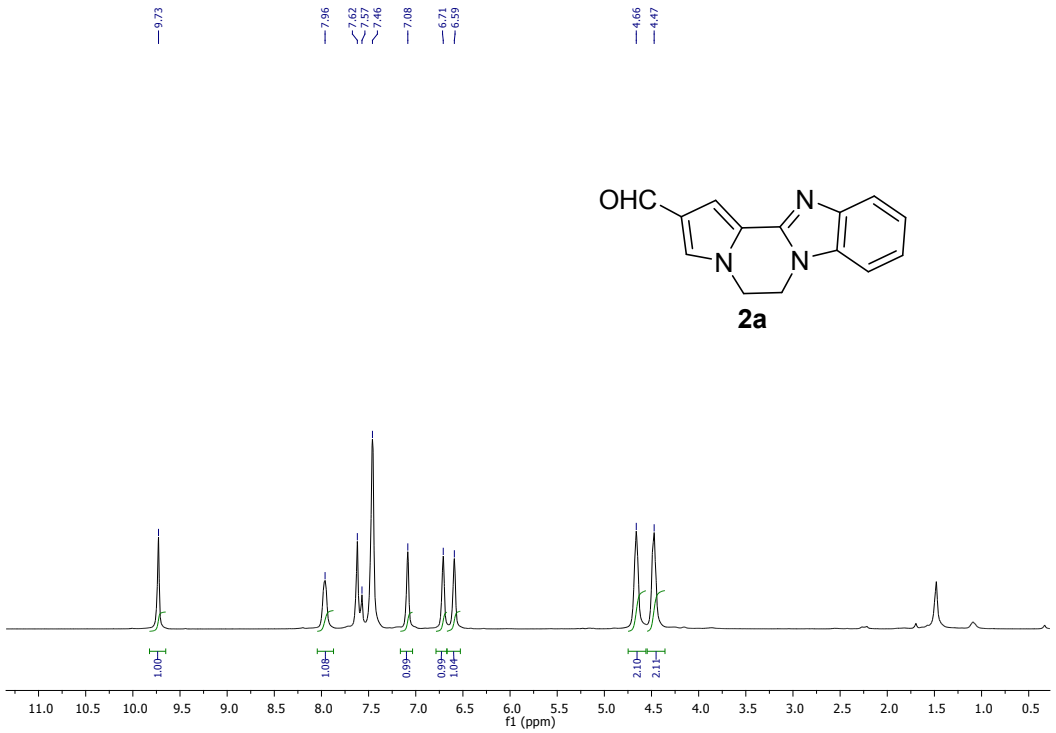

143.72
143.23
133.39
126.29
123.21
122.42
120.99
120.34
117.57
109.70
109.12
77.58
77.16
76.74
49.00
46.68
33.42
26.67
22.52
14.05
f1 (ppm)

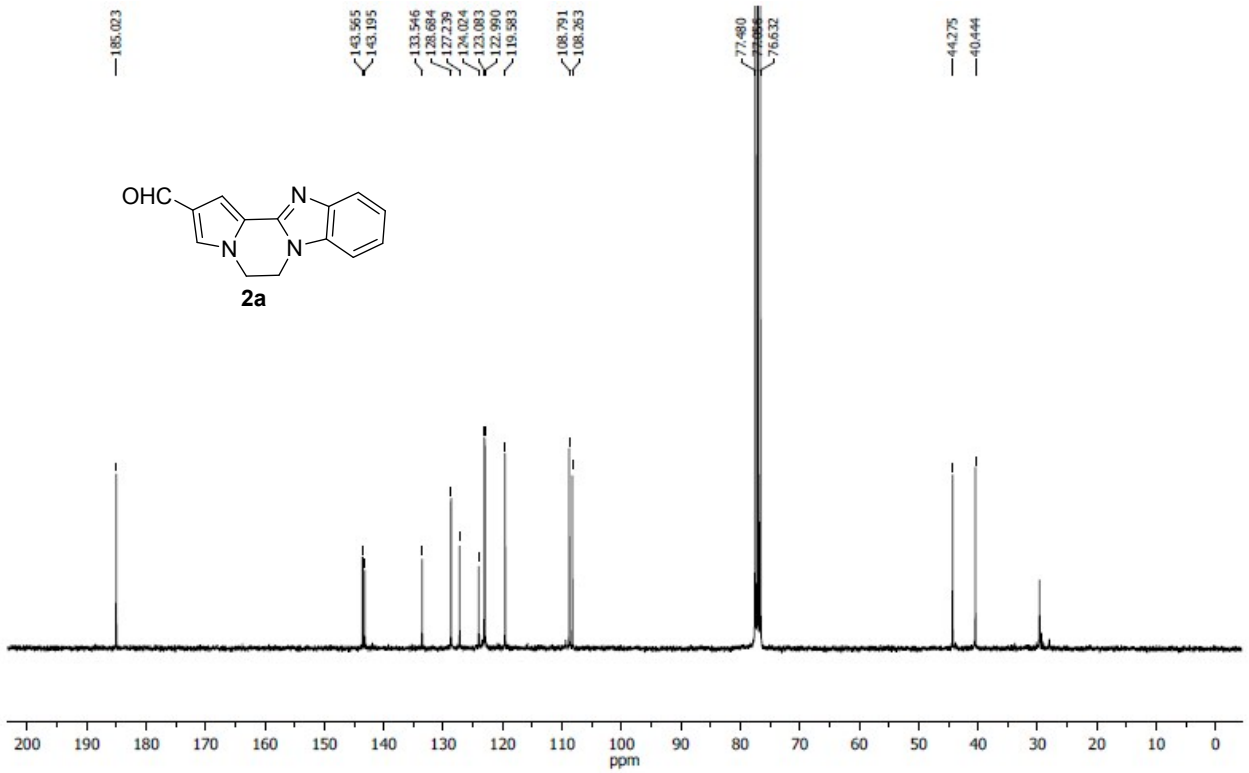

7.83
7.81
7.36
7.31
7.30
7.29
7.26
6.27
6.26
6.26
6.19
5.98
5.97
5.96
4.44
4.42
4.40
4.19
4.17
4.15
2.46
2.43
2.41
2.38
1.15
1.12
1.10
1.15
4.44
1.08
0.91
1.00
2.29
2.01
2.52
3.30
f1 (ppm)

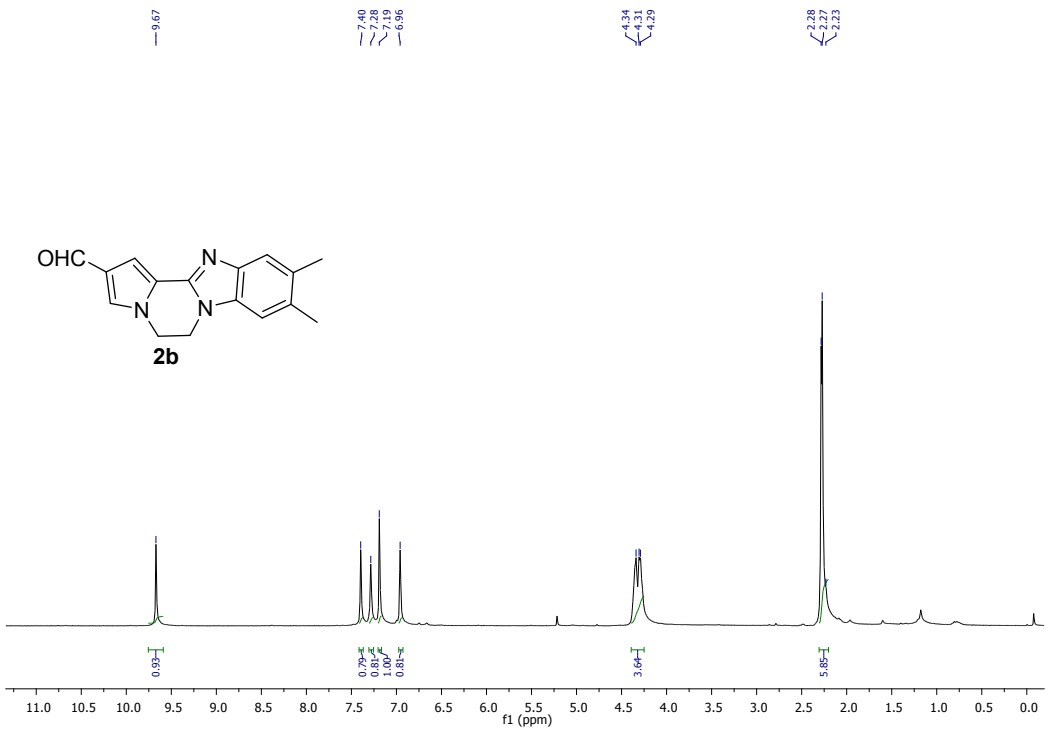

143.43
143.07
133.16
127.58
123.01
122.34
120.25
120.21
116.96
109.04
77.58
77.16
76.74
48.72
46.40
19.96
15.32
f1 (ppm)

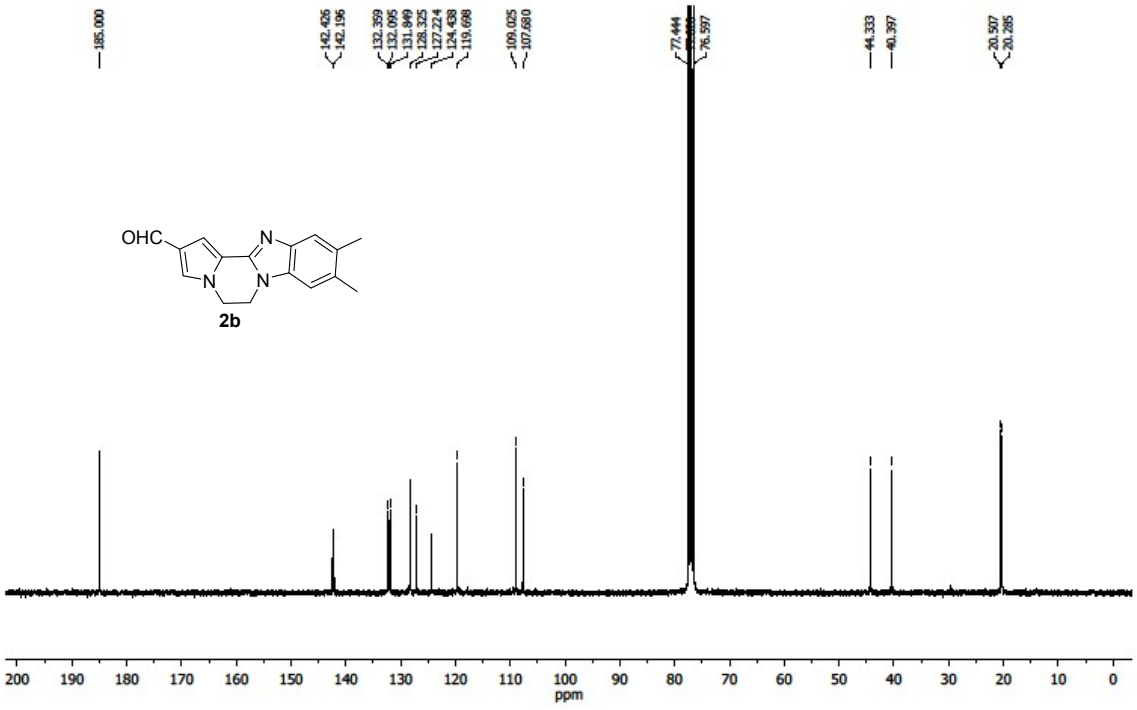
Crude ^{1}H NMR for entry 14, table 1:

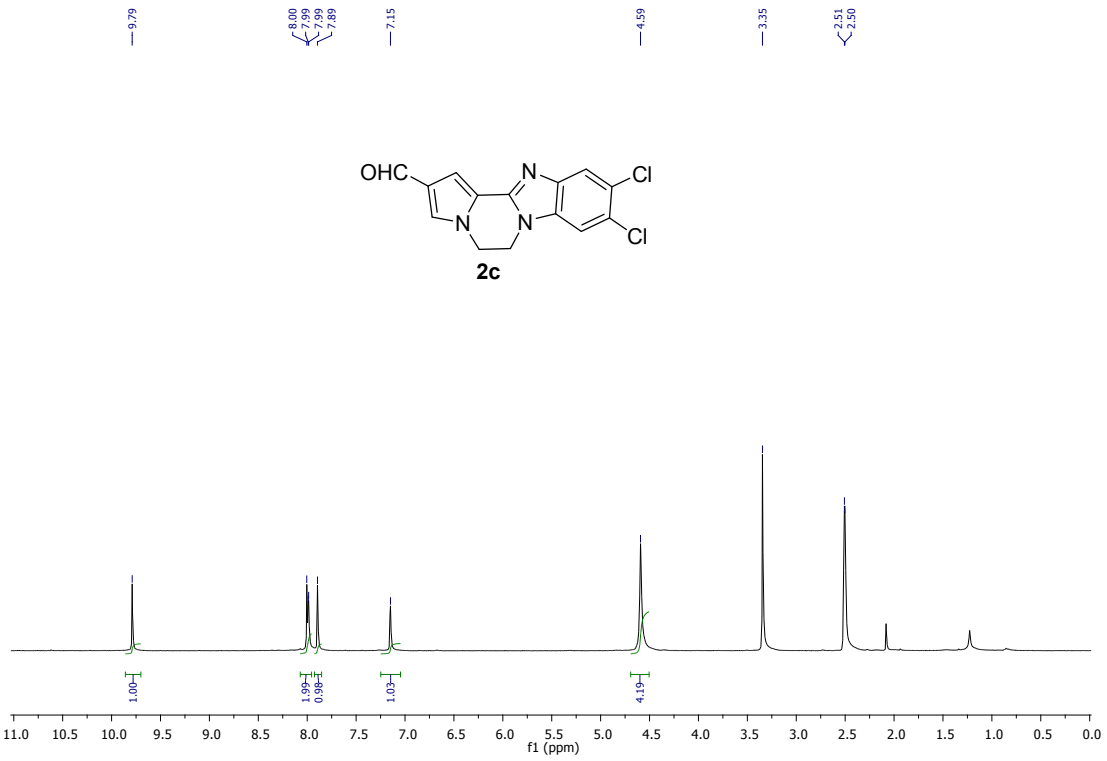


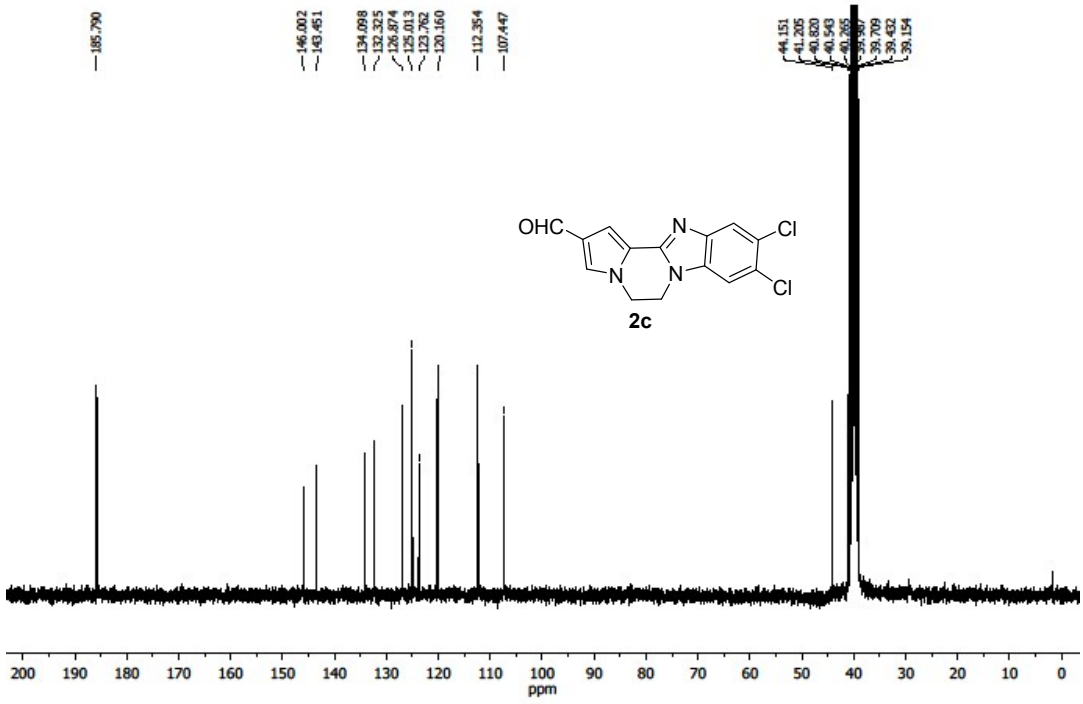

9.73
7.96
7.62
7.57
7.46
7.08
6.71
6.59
4.66
4.47
OHC
N
N
N
2a
1.00
1.08
0.99
0.99
1.04
2.10
2.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

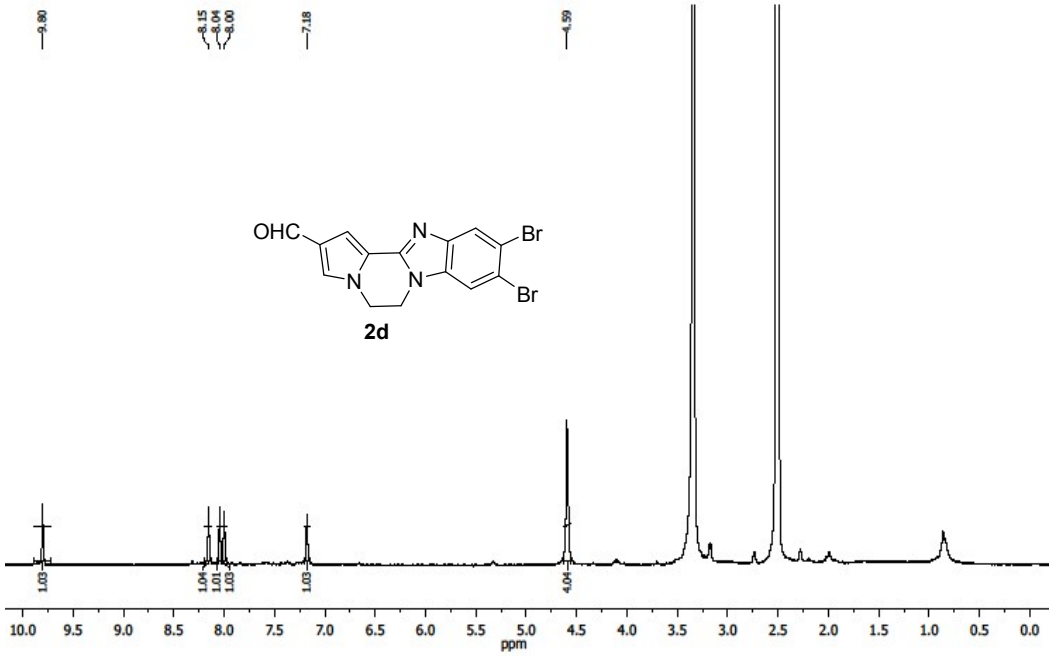

185.023
143.565
143.195
133.546
128.684
127.239
124.024
123.083
122.990
119.583
108.791
108.263
77.480
77.164
76.632
44.275
40.444
OHC
N
N
N
2a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

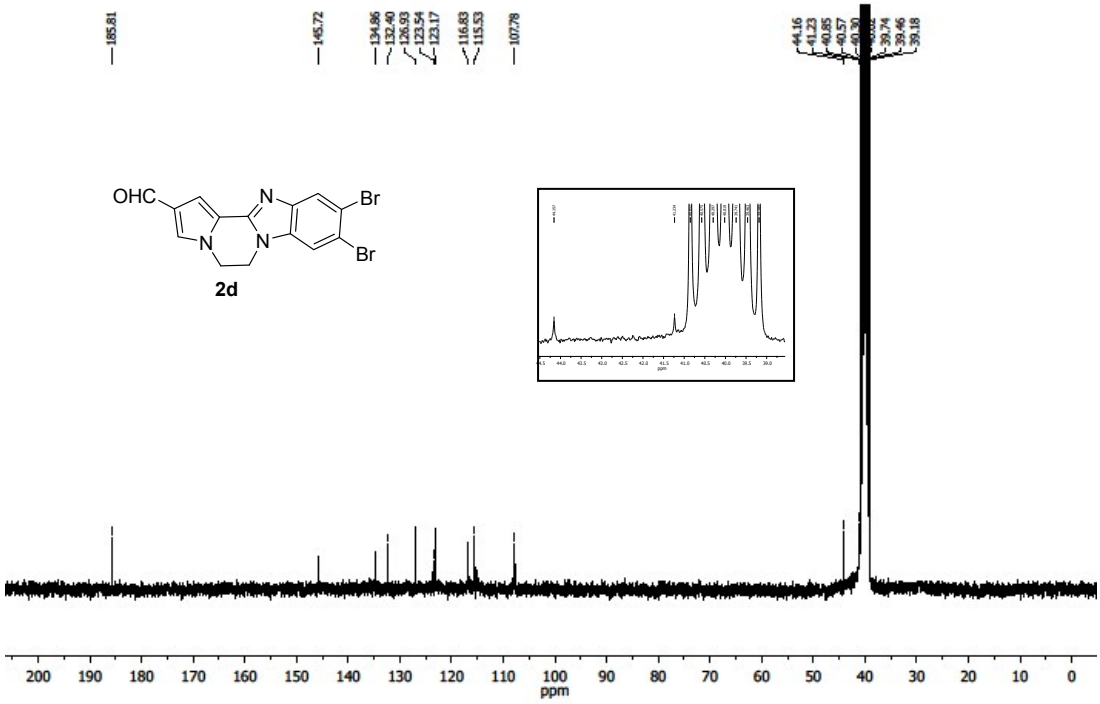

9.67
7.40
7.28
7.19
6.96
4.34
4.31
4.29
2.28
2.27
2.23
OHC
N
N
N
2b
0.93
0.79
0.81
1.00
0.81
3.64
5.85
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

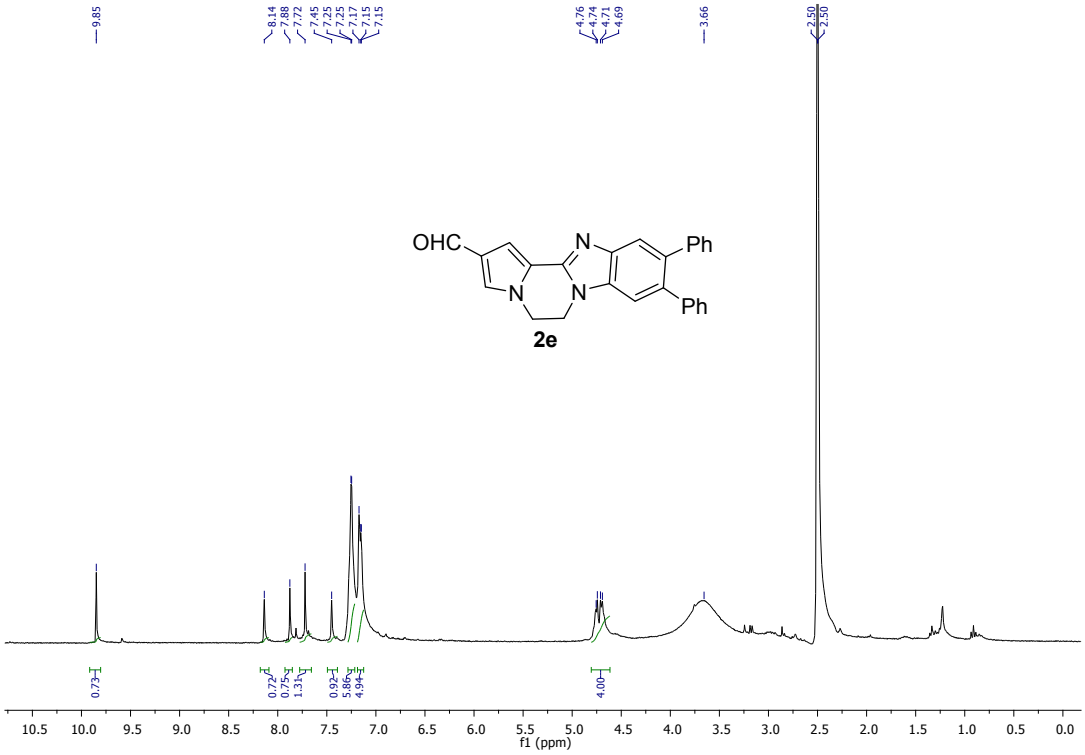

185.000
142.426
142.196
132.359
132.095
131.849
128.325
127.224
124.438
119.698
109.025
107.680
77.444
76.597
44.333
40.397
20.507
20.285
OHC
N
N
N
2b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

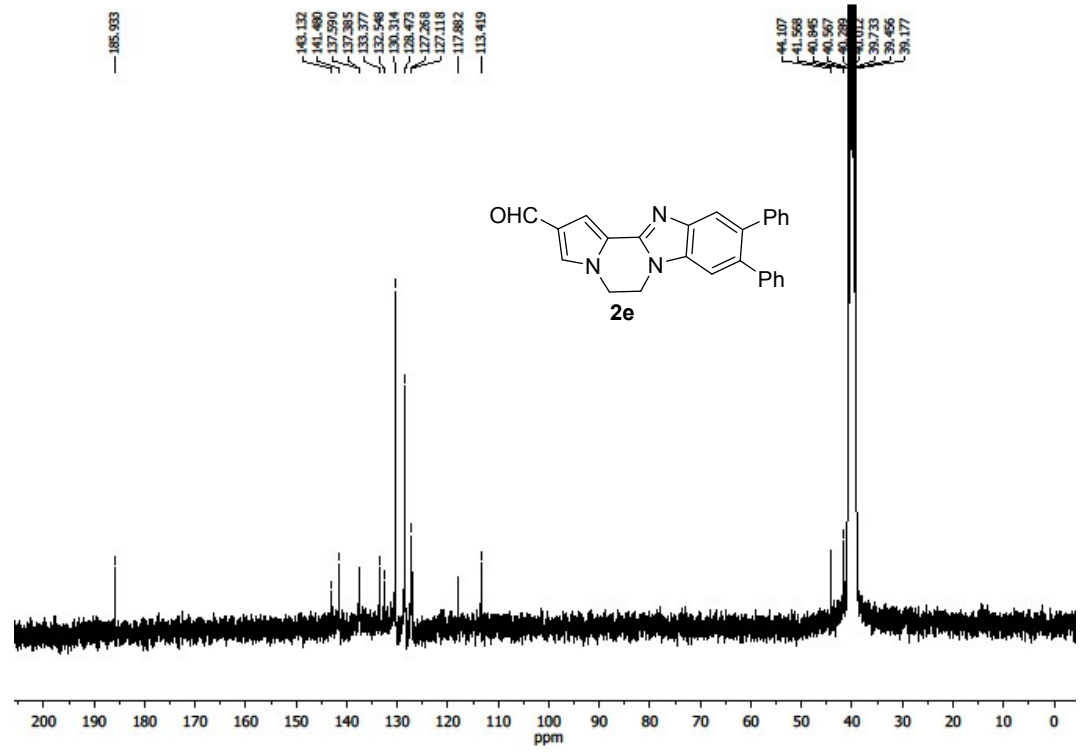

9.79
8.00
7.99
7.99
7.89
7.15
4.59
3.35
2.51
2.50
OHC
N
Cl
N
N
Cl
2c
1.00
1.99
0.98
1.03
4.19
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

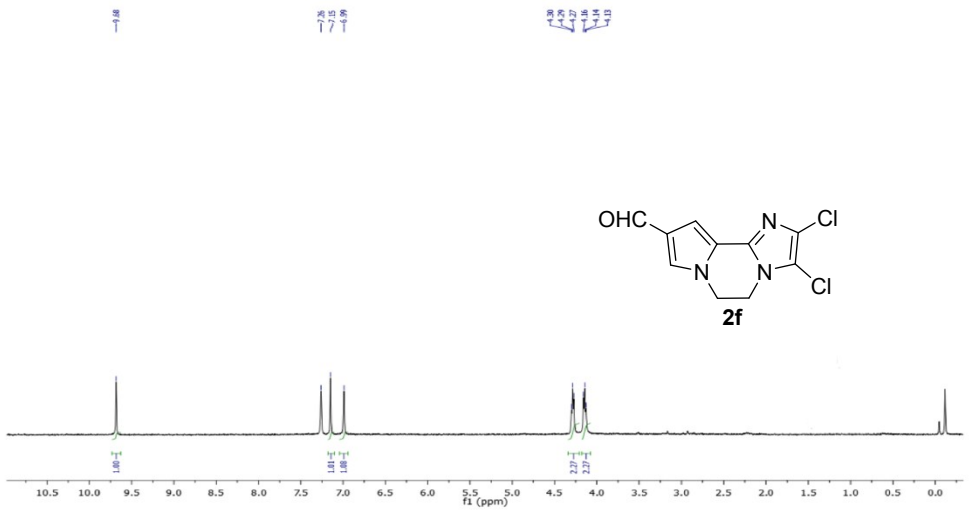

185.790
146.002
143.461
134.098
132.325
126.874
125.013
123.762
120.160
112.354
107.447
44.151
41.205
40.820
40.543
40.265
39.709
39.432
39.154
OHC
N
Cl
N
N
Cl
2c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

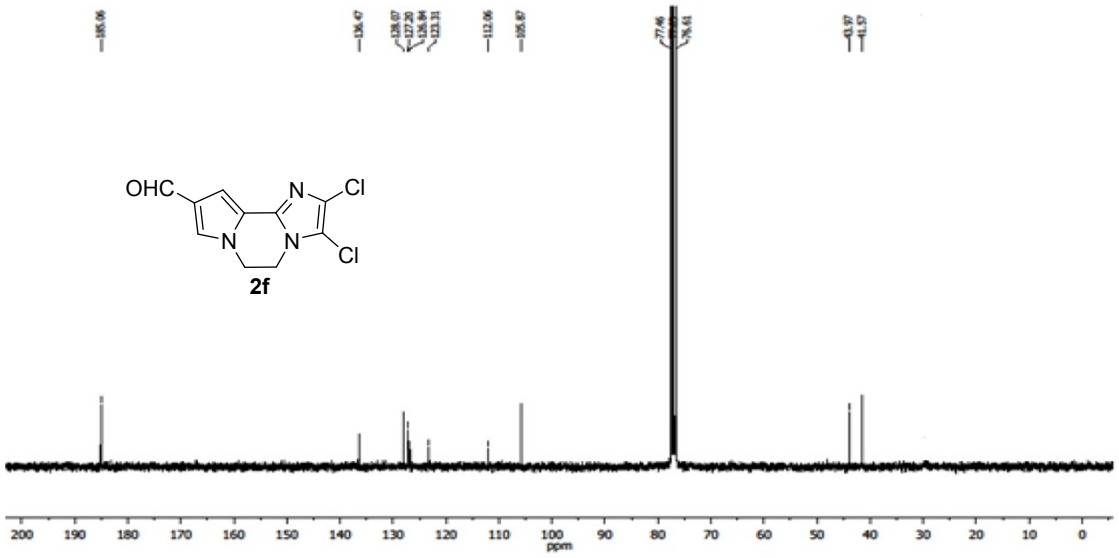

9.80
8.15
8.04
8.00
7.18
4.59
OHC
N
Br
N
N
Br
2d
1.03
1.04
1.01
1.03
1.03
4.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

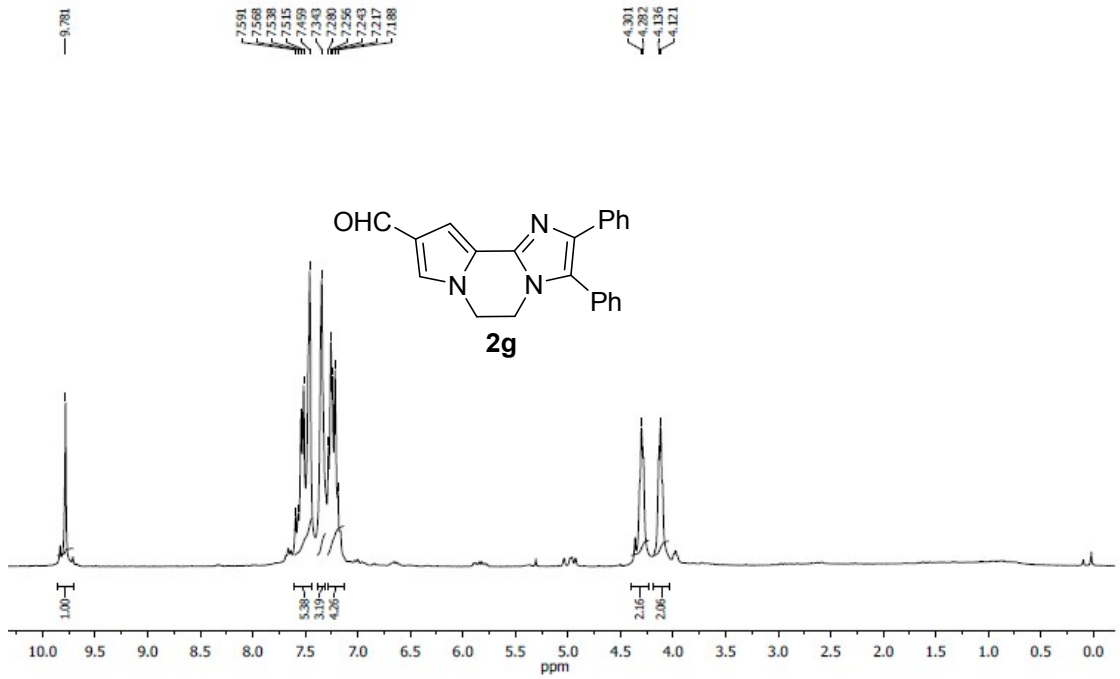

185.81
145.72
134.86
132.40
126.93
123.54
123.17
116.83
115.53
107.78
44.16
41.23
40.85
40.57
40.30
39.74
39.46
39.18
OHC
N
Br
N
N
Br
2d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

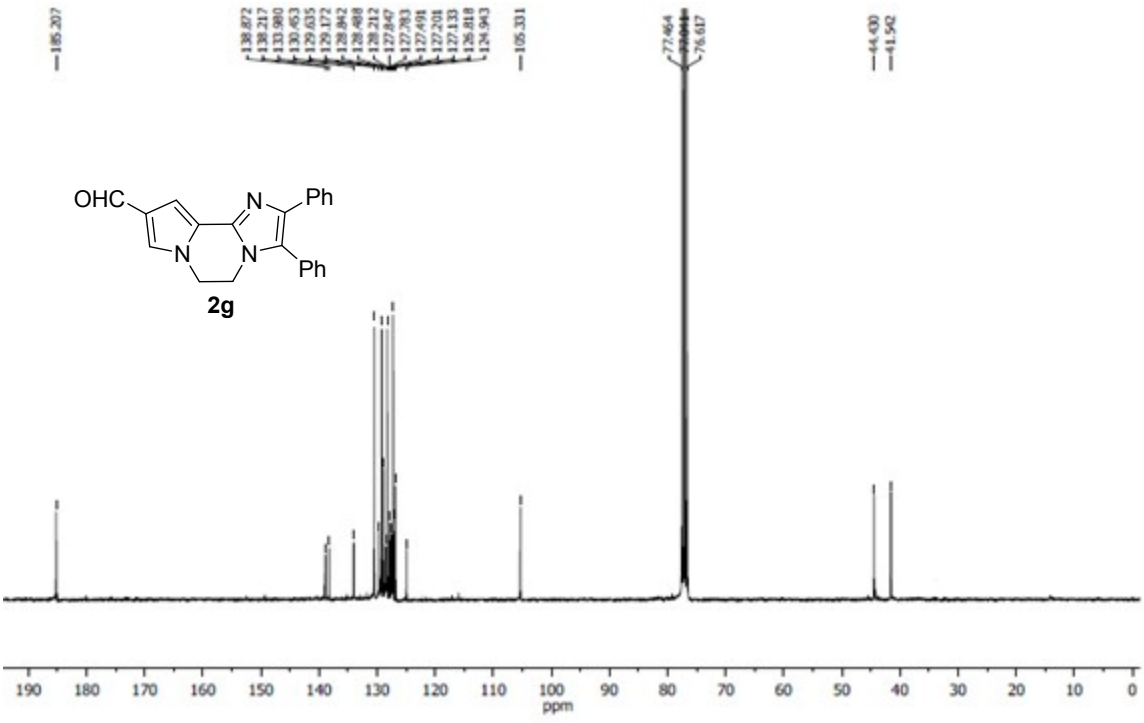

9.85
8.14
7.88
7.72
7.45
7.25
7.25
7.17
7.15
7.15
4.76
4.74
4.71
4.69
3.66
2.50
2.50
OHC
N
Ph
N
N
Ph
2e
0.73
0.72
0.75
1.31
0.92
5.86
4.94
4.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

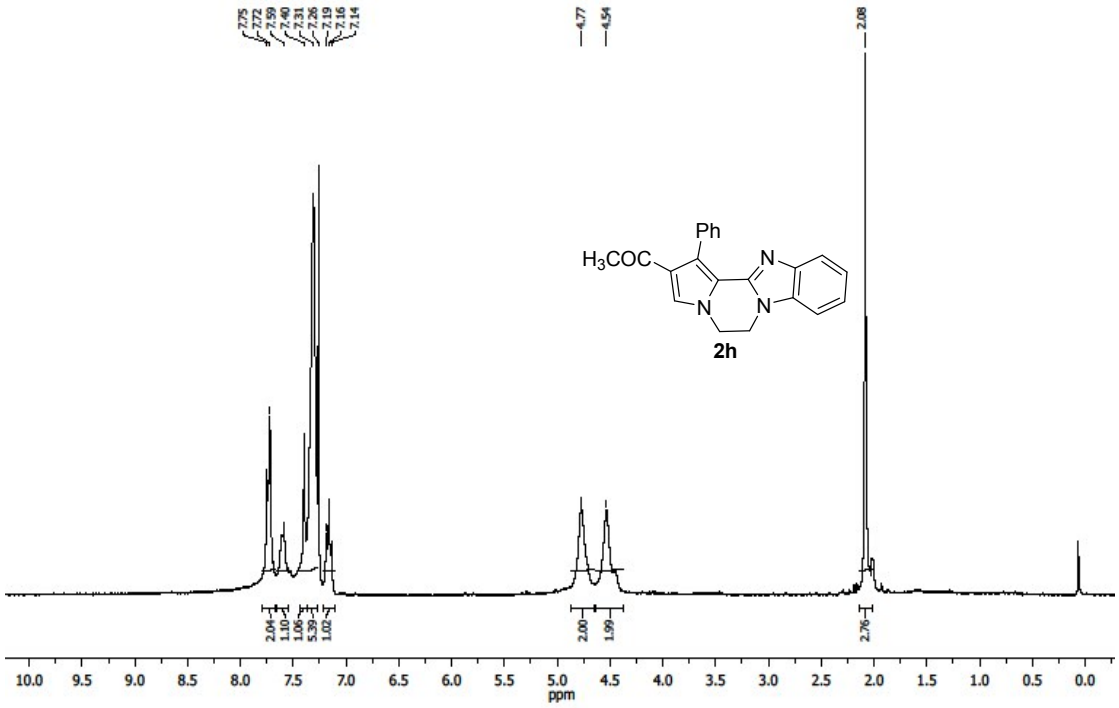

185.933
143.132
141.490
137.590
137.385
133.377
132.548
130.314
128.473
127.268
127.118
117.882
113.419
44.107
41.568
40.845
40.567
40.289
39.733
39.455
39.177
OHC
N
Ph
N
N
Ph
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

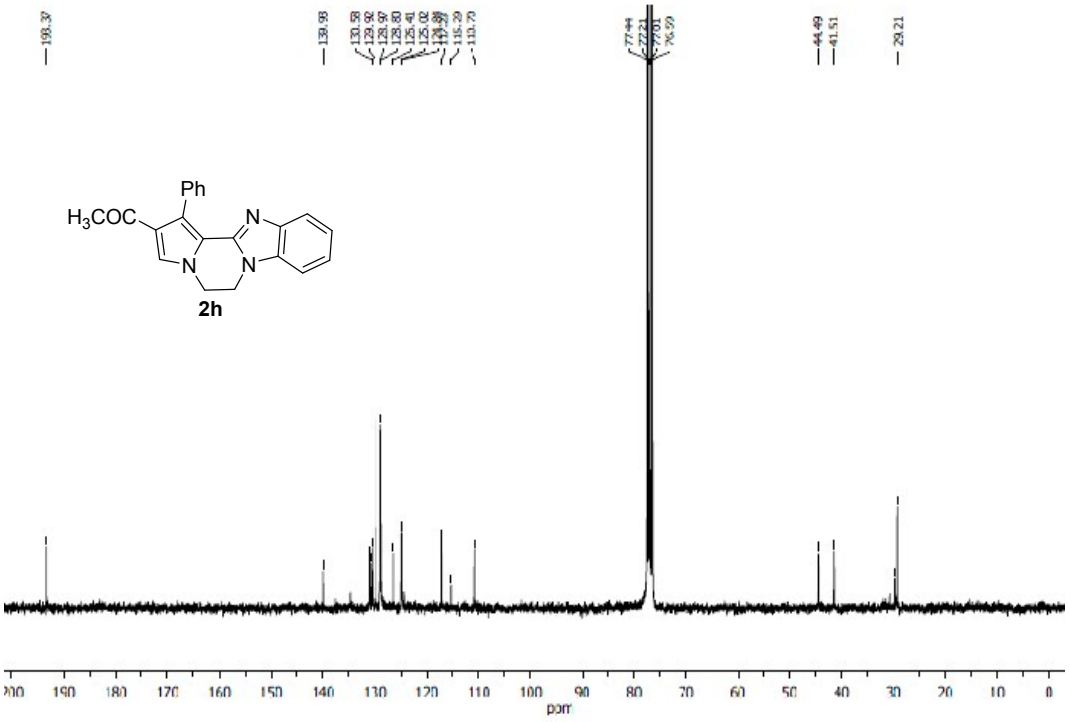

OHC
N
Cl
N
N
Cl
2f
f1 (ppm)

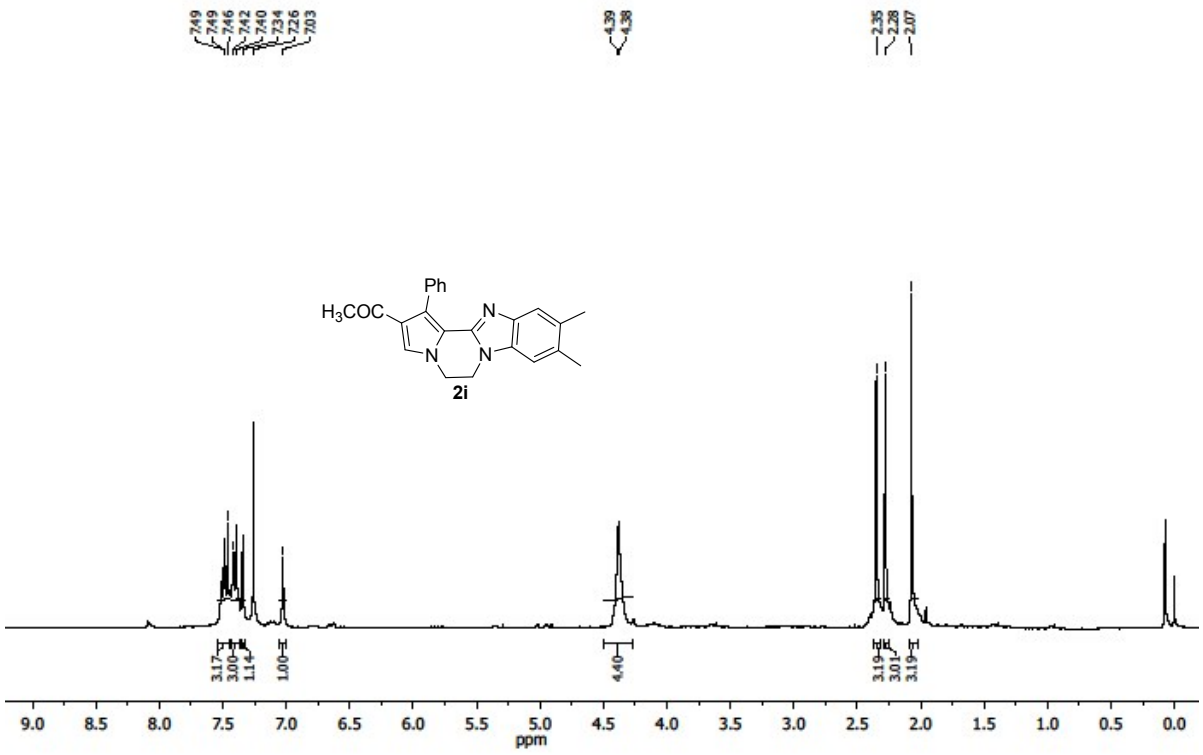

OHC
N
Cl
N
N
Cl
2f
ppm

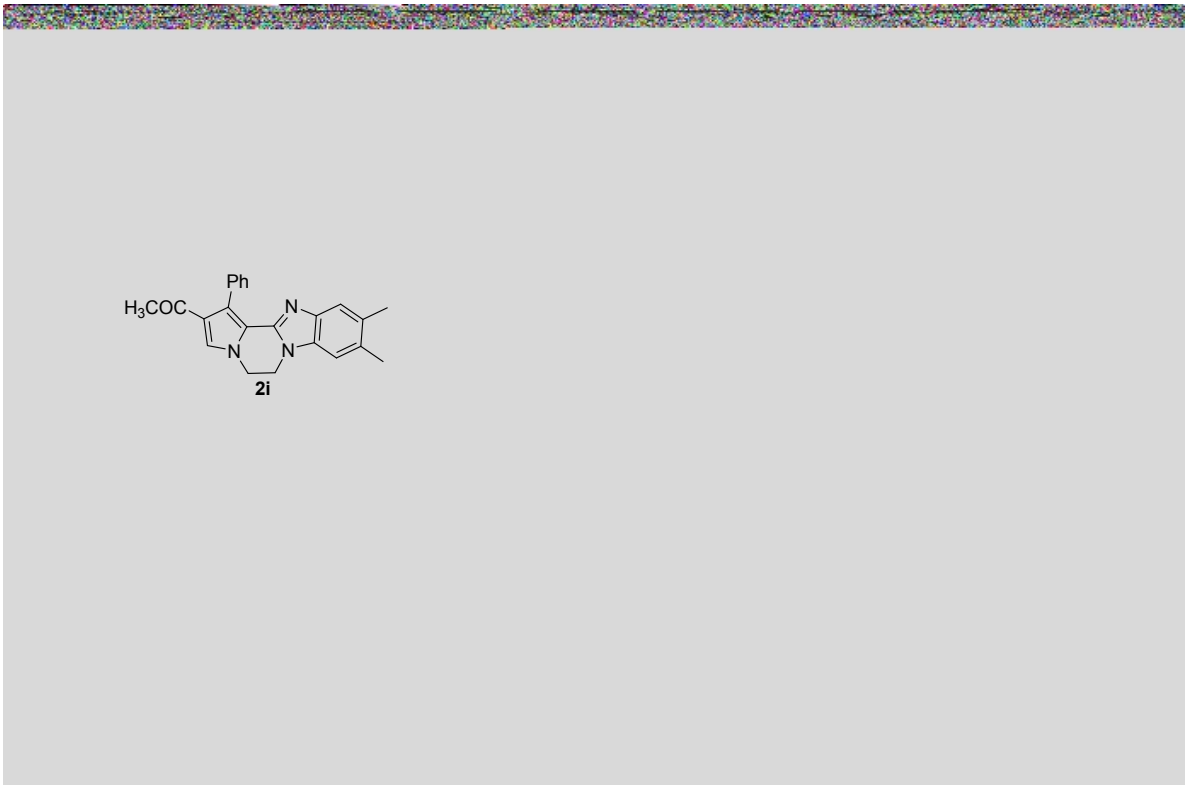

9.781
7.591
7.568
7.538
7.515
7.459
7.343
7.280
7.256
7.243
7.217
7.188
4.301
4.282
4.136
4.121
OHC
N
Ph
N
N
Ph
2g
1.00
5.38
3.19
4.26
2.16
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

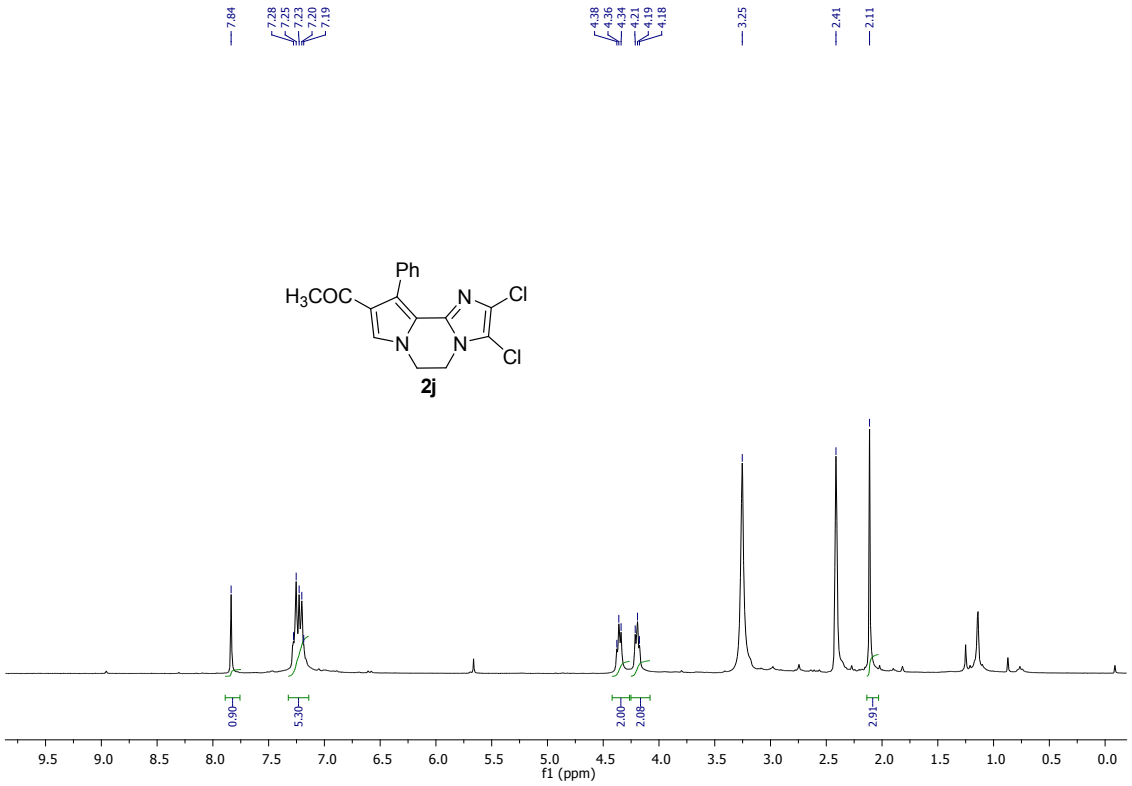

185.207
138.872
138.217
133.980
130.453
129.635
129.172
128.842
128.488
128.212
127.847
127.783
127.491
127.201
127.133
126.818
124.943
105.331
77.464
76.617
44.430
41.542
OHC
N
Ph
N
N
Ph
2g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

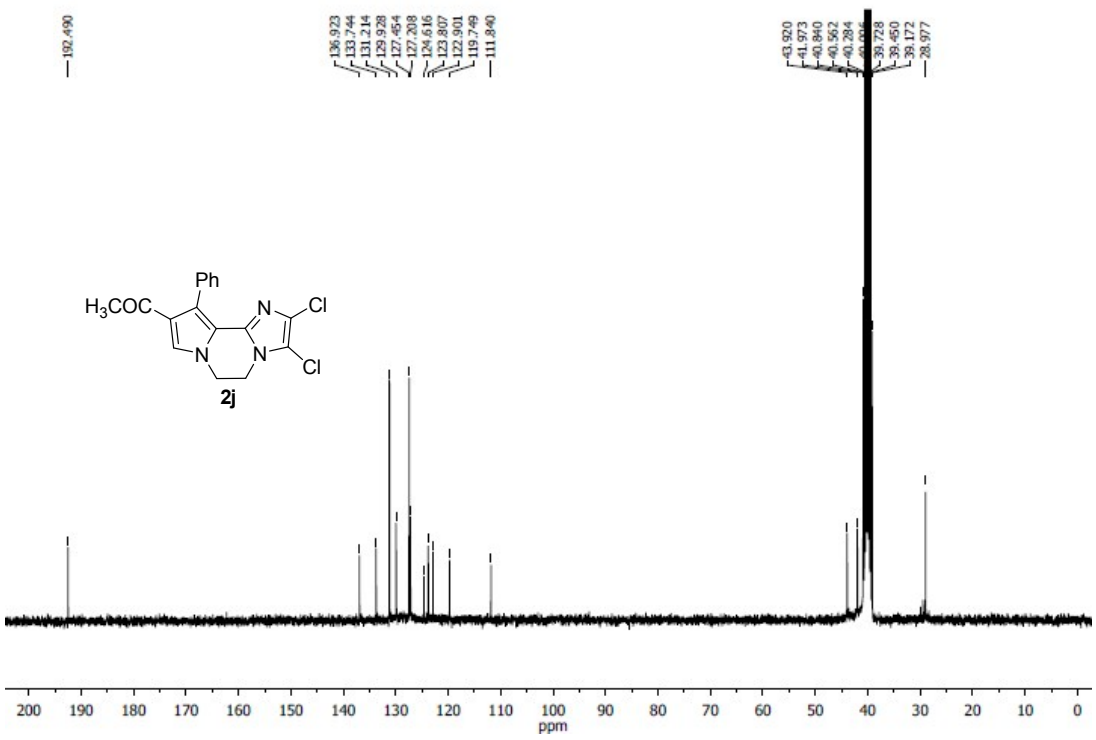

7.75
7.72
7.59
7.40
7.31
7.26
7.19
7.16
7.14
4.77
4.54
2.08
Ph
H3COC
N
N
N
2h
2.04
1.10
1.06
5.39
1.02
2.00
1.99
2.76
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

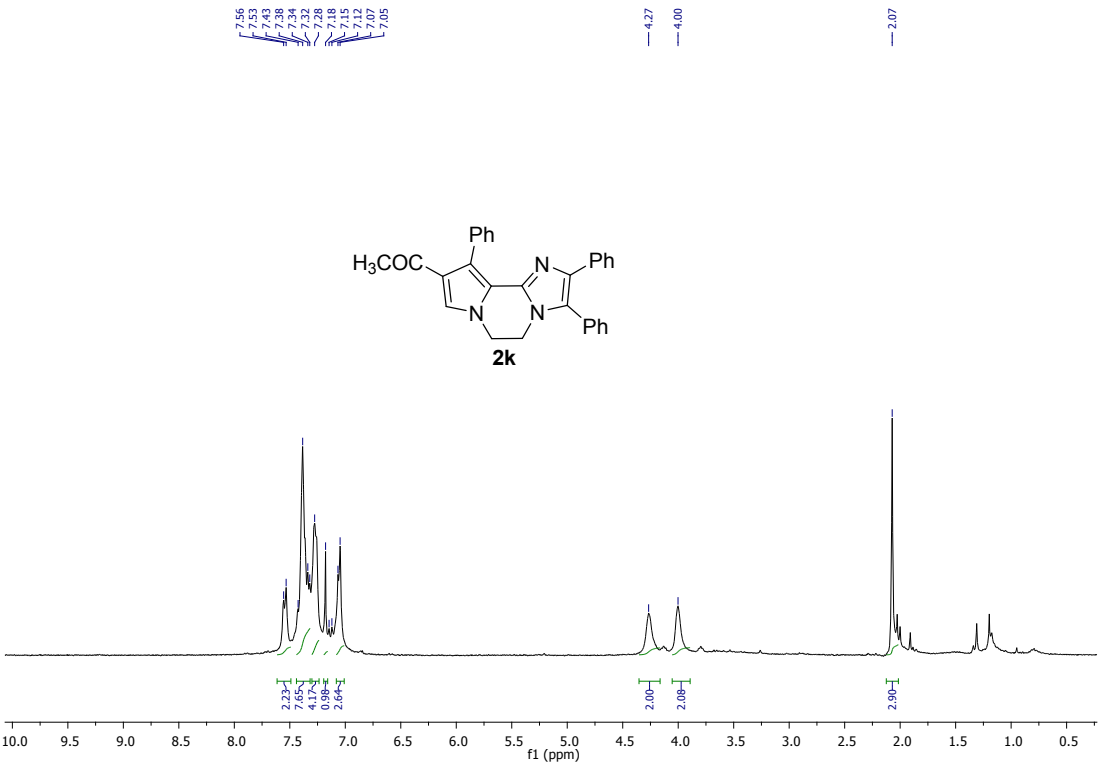

193.37
139.99
130.58
129.98
128.97
128.80
125.41
125.02
115.29
110.70
77.44
77.21
77.01
76.99
44.49
41.51
29.21
Ph
H3COC
N
N
N
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

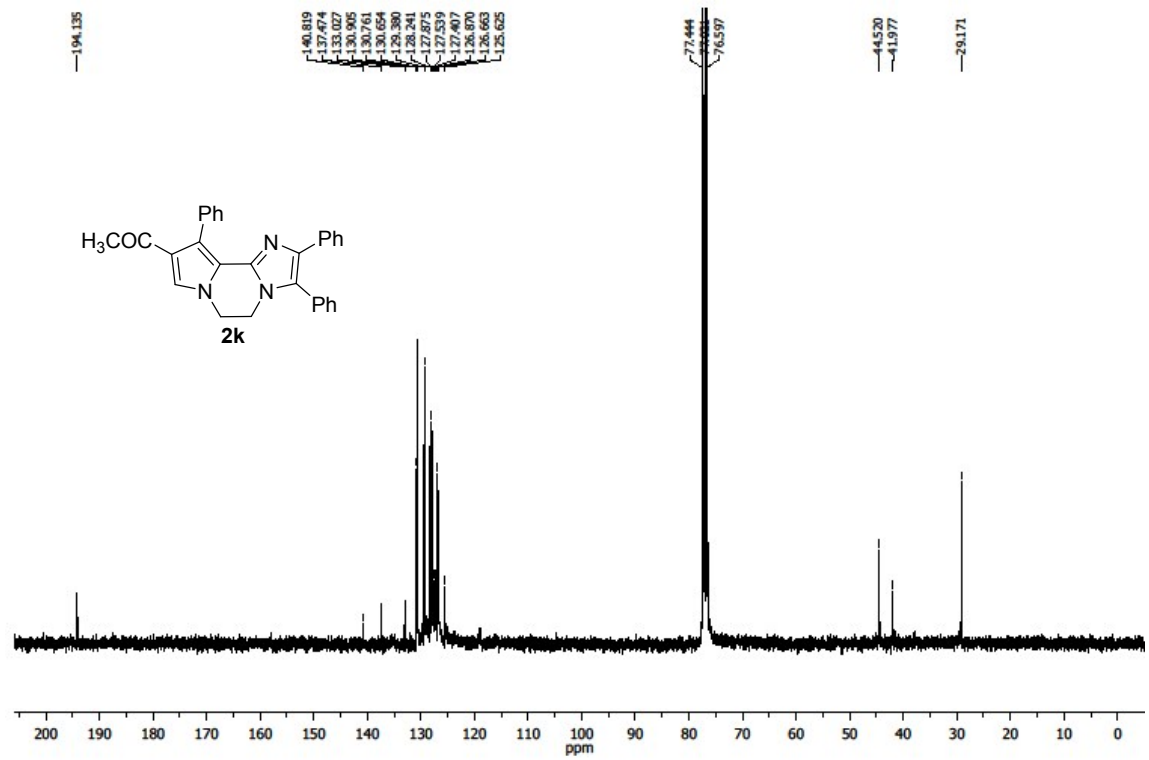

7.49
7.49
7.46
7.42
7.40
7.34
7.26
7.03
4.39
4.38
2.35
2.28
2.07
Ph
H3COC
N
N
2i
3.17
3.00
1.14
1.00
4.40
3.19
3.01
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

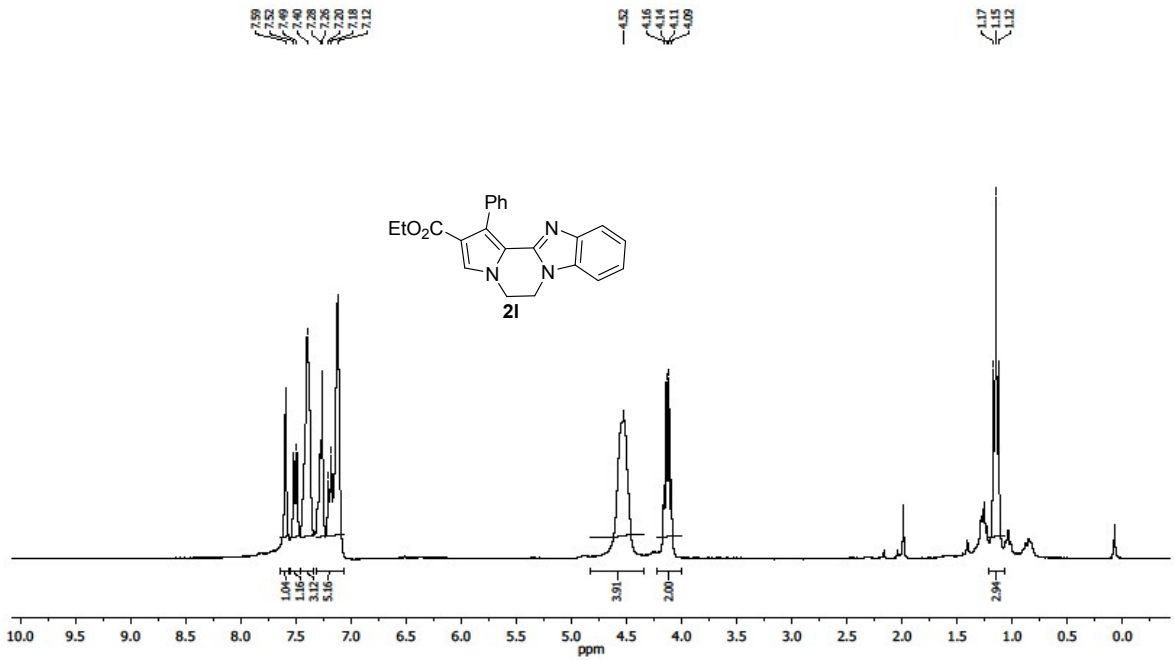

Ph
H3COC
N
N
2i

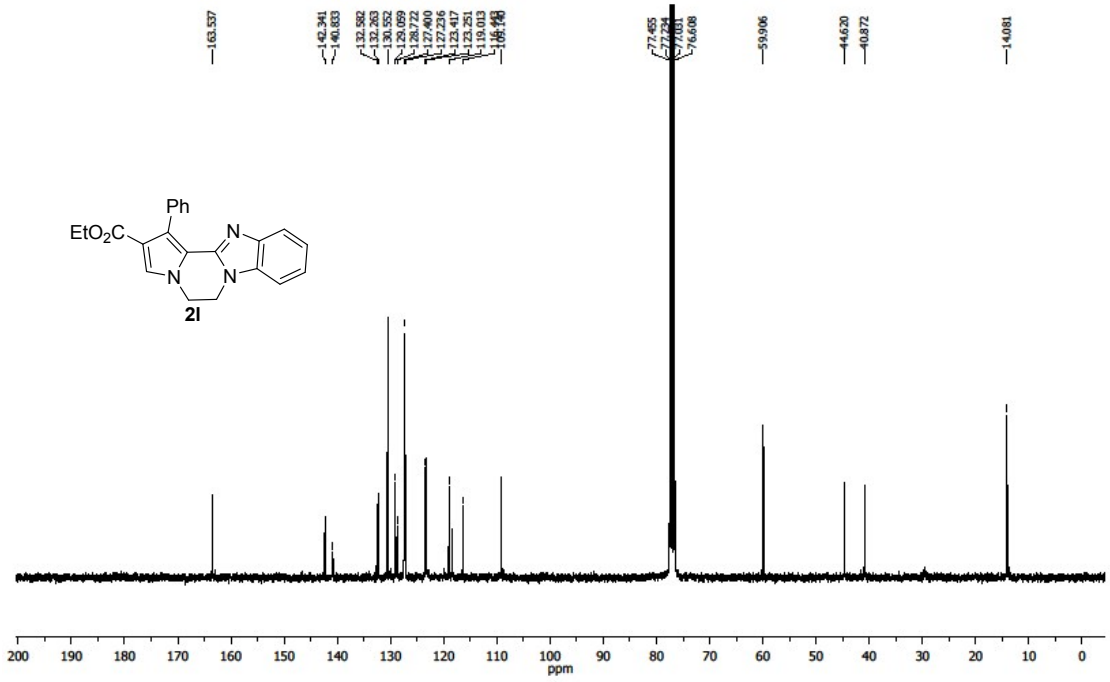

7.84
7.28
7.25
7.23
7.20
7.19
4.38
4.36
4.34
4.21
4.19
4.18
3.25
2.41
2.11
Ph
H3COC
N
Cl
N
N
Cl
2j
0.90
5.30
2.00
2.08
2.91
f1 (ppm)

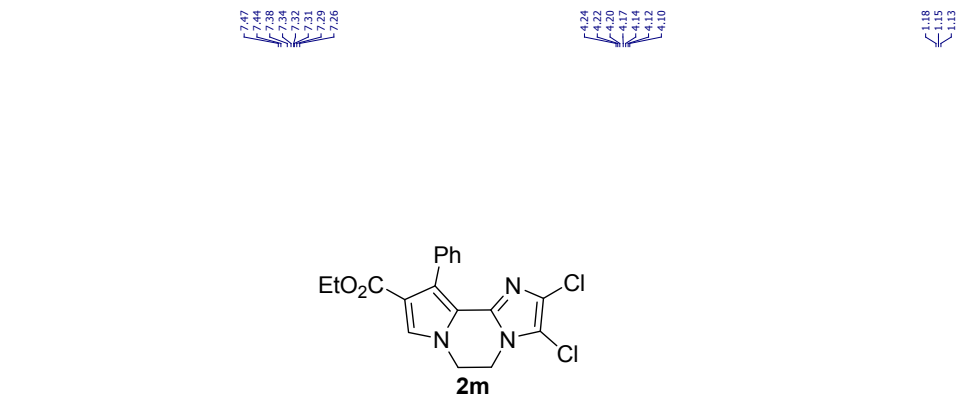

192.490
136.923
133.744
131.214
129.928
127.454
127.208
124.616
123.807
122.901
119.749
111.840
43.920
41.973
40.840
40.562
40.284
39.728
39.450
39.172
28.977
Ph
H3COC
N
Cl
N
N
Cl
2j
ppm

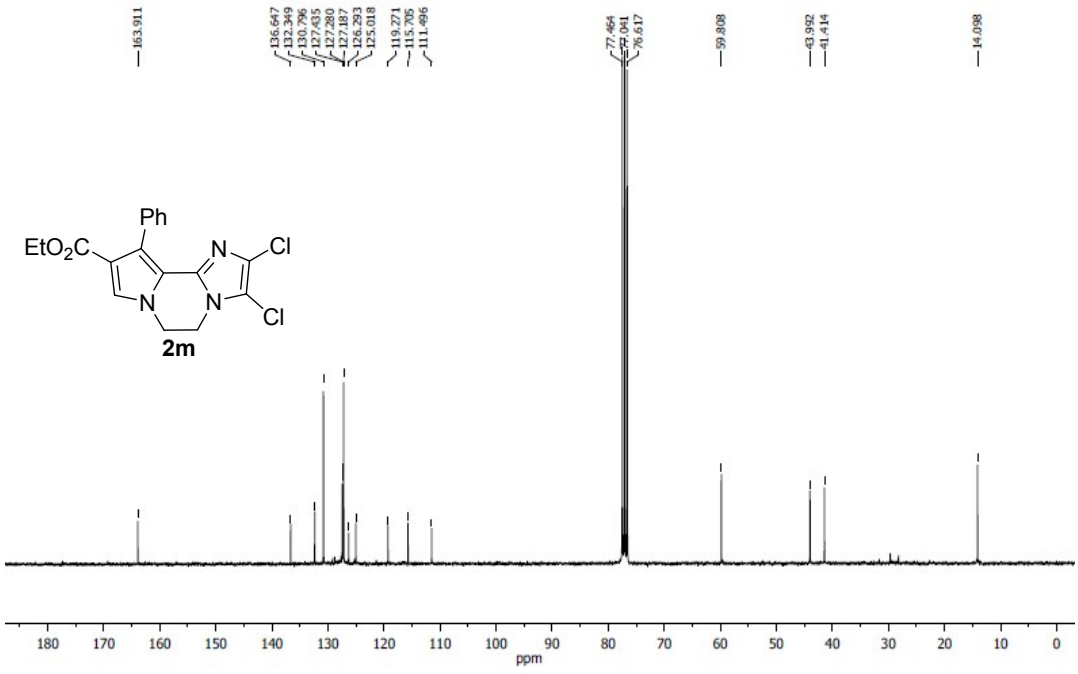

7.56
7.53
7.43
7.38
7.34
7.32
7.28
7.18
7.15
7.12
7.07
7.05
4.27
4.00
2.07
Ph
H3COC
N
Ph
N
N
Ph
2k
2.23
7.65
4.17
0.98
2.64
2.00
2.08
2.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


194.135
140.819
137.474
133.027
130.905
130.761
130.654
129.380
128.241
127.875
127.539
127.407
126.870
126.663
125.625
77.444
77.232
76.597
44.520
41.977
29.171
Ph
H3COC
N
Ph
N
N
Ph
2k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

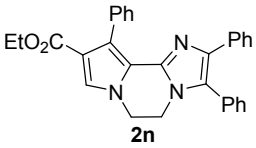

7.59
7.52
7.49
7.40
7.28
7.26
7.20
7.18
7.12
4.52
4.16
4.14
4.11
4.09
1.17
1.15
1.12
Ph
EtO2C
N
N
N
2l
1.04
1.16
3.12
5.16
3.91
2.00
2.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


163.537
142.341
140.833
132.582
132.263
130.552
129.059
128.722
127.400
127.236
123.457
123.251
119.013
116.448
108.148
77.455
77.034
76.608
59.906
44.620
40.872
14.081
Ph
EtO2C
N
N
N
2l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

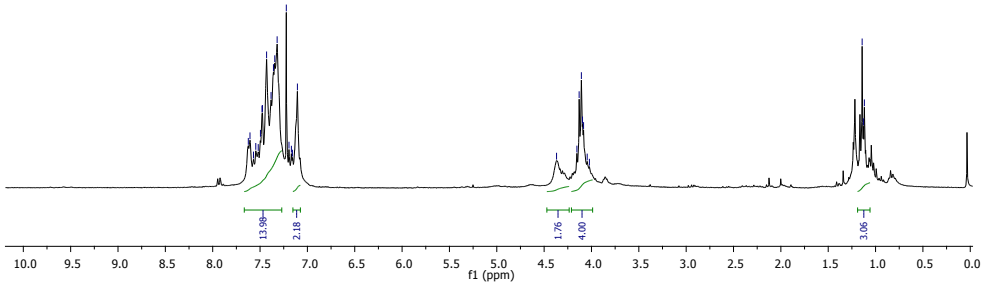

7.47
7.44
7.38
7.34
7.32
7.31
7.29
7.26
4.24
4.22
4.20
4.17
4.14
4.12
4.10
1.18
1.15
1.13
Ph
EtO2C
N
Cl
N
N
Cl
2m
2.00
4.13
5.78
3.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

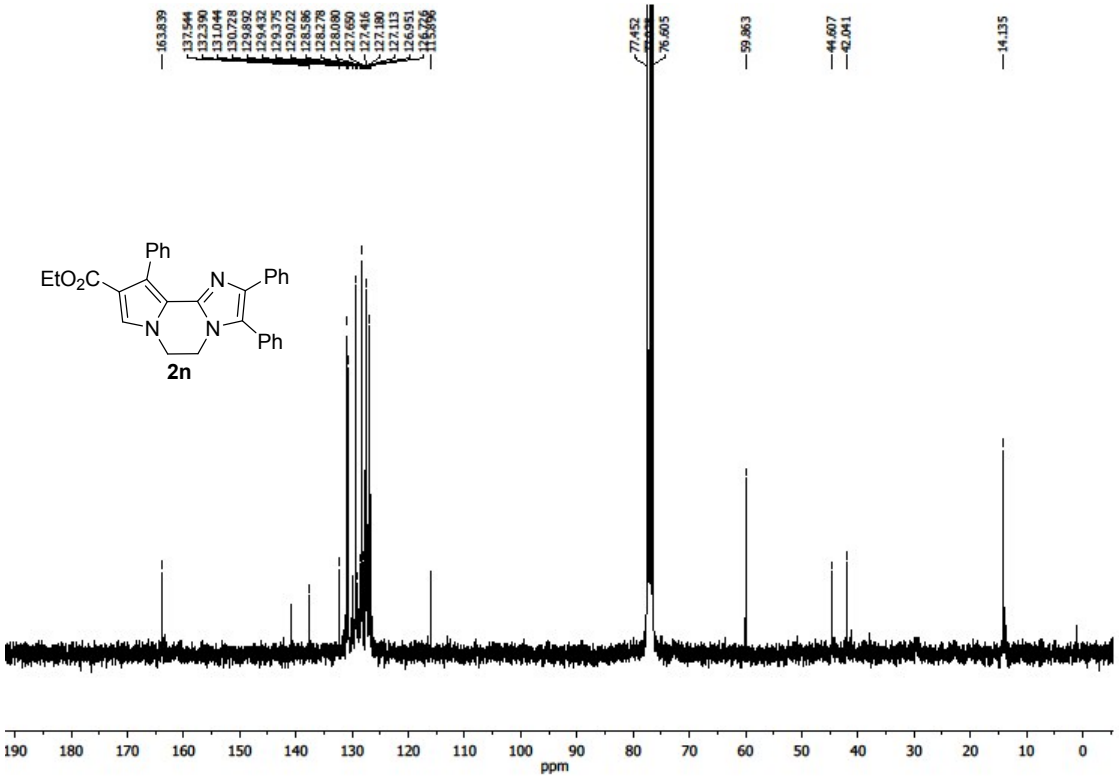

163.911
136.647
132.349
130.796
127.435
127.280
127.187
126.293
125.018
119.271
115.705
111.496
77.464
77.041
76.617
59.808
43.992
41.414
14.098
Ph
EtO2C
N
Cl
N
N
Cl
2m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.62
7.61
7.57
7.55
7.53
7.50
7.48
7.47
7.43
7.38
7.36
7.34
7.32
7.22
7.19
7.17
7.16
7.11
4.37
4.15
4.13
4.11
4.09
4.08
4.05
4.02
1.14
1.13
1.12

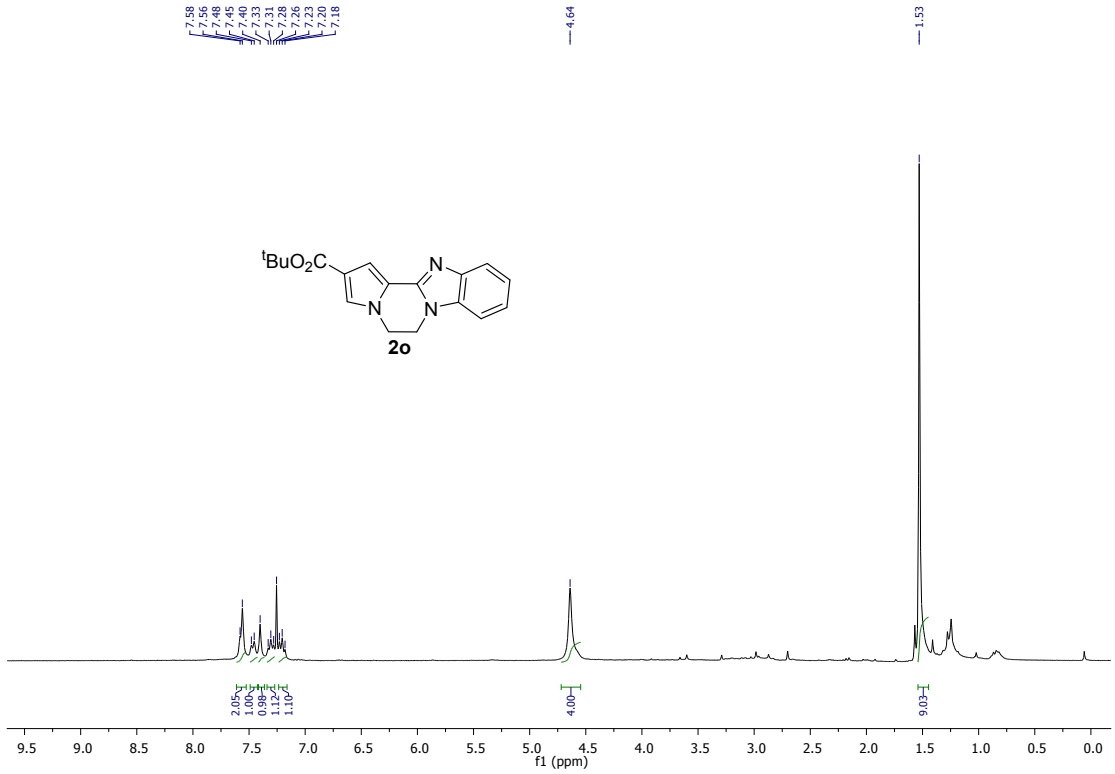

Ph
EtO2C
N
Ph
N
N
Ph

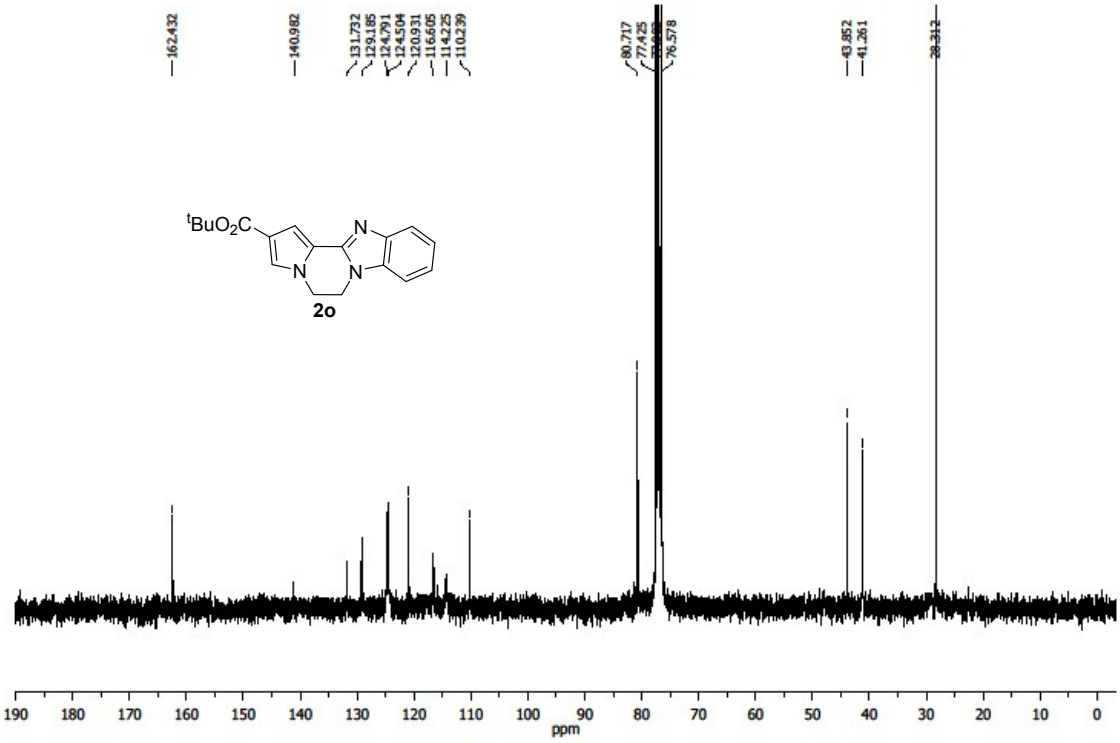
2n

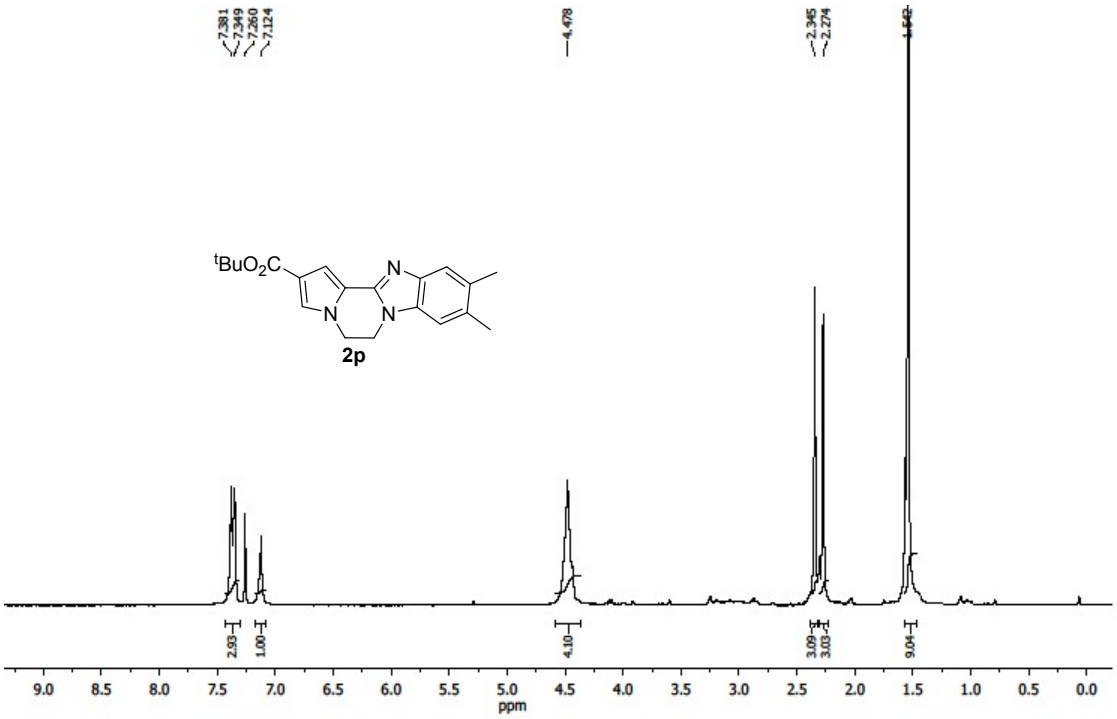

13.98
2.18
1.76
4.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

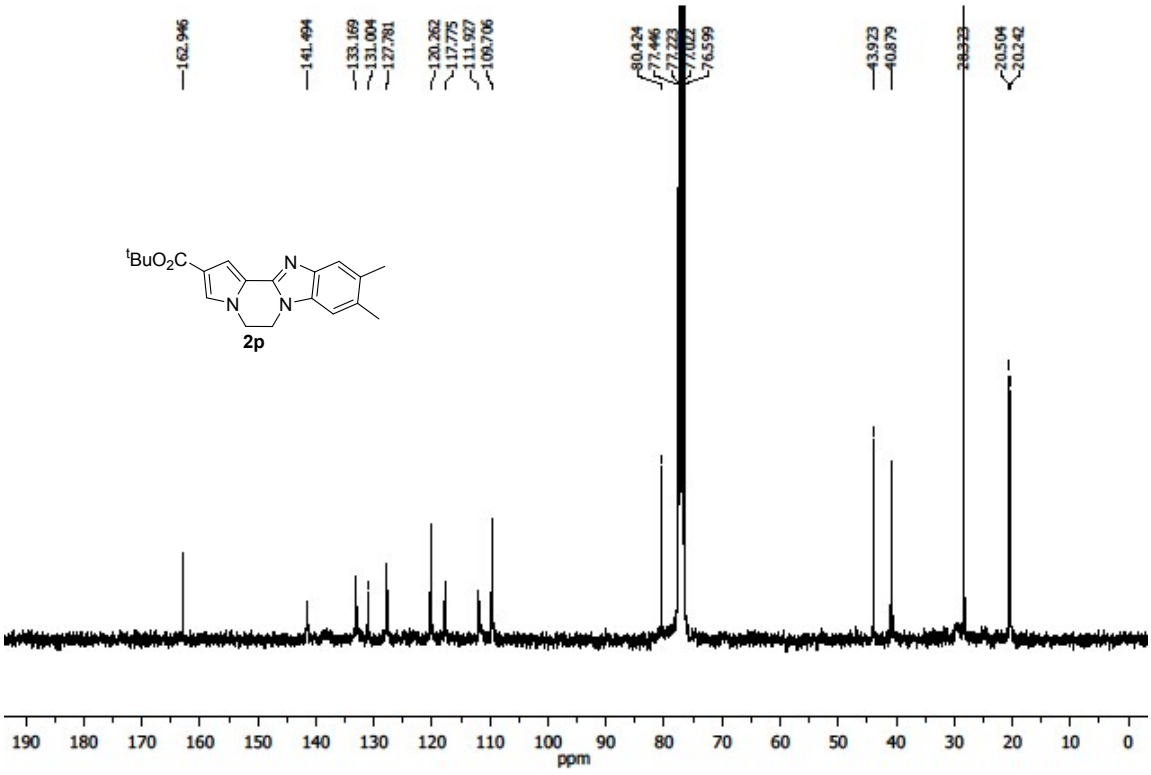

163.839
137.544
132.390
131.044
130.728
129.892
129.432
129.375
129.022
128.586
128.278
128.080
127.650
127.416
127.180
127.113
126.951
77.452
76.605
59.863
44.607
42.041
14.135
Ph
EtO2C
N
Ph
N
N
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

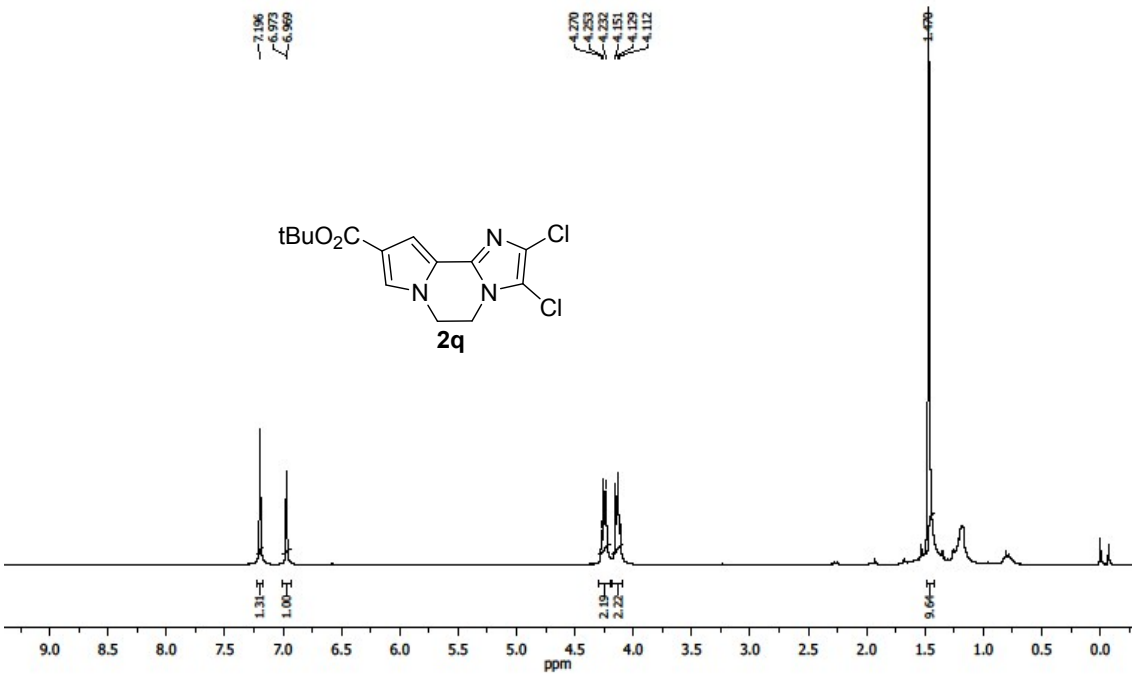
2n

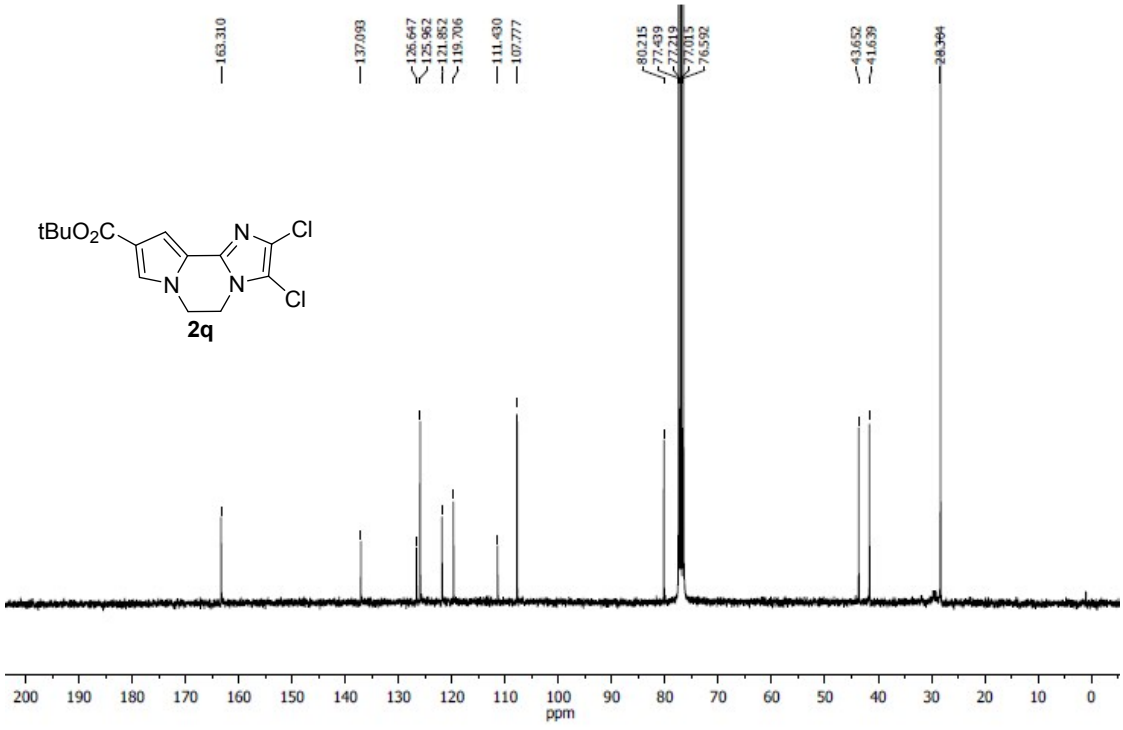

7.58
7.56
7.48
7.45
7.40
7.33
7.31
7.28
7.26
7.23
7.20
7.18
4.64
1.53
tBuO2C
N
N
N
2o
2.05
1.05
0.98
1.12
1.10
4.00
9.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

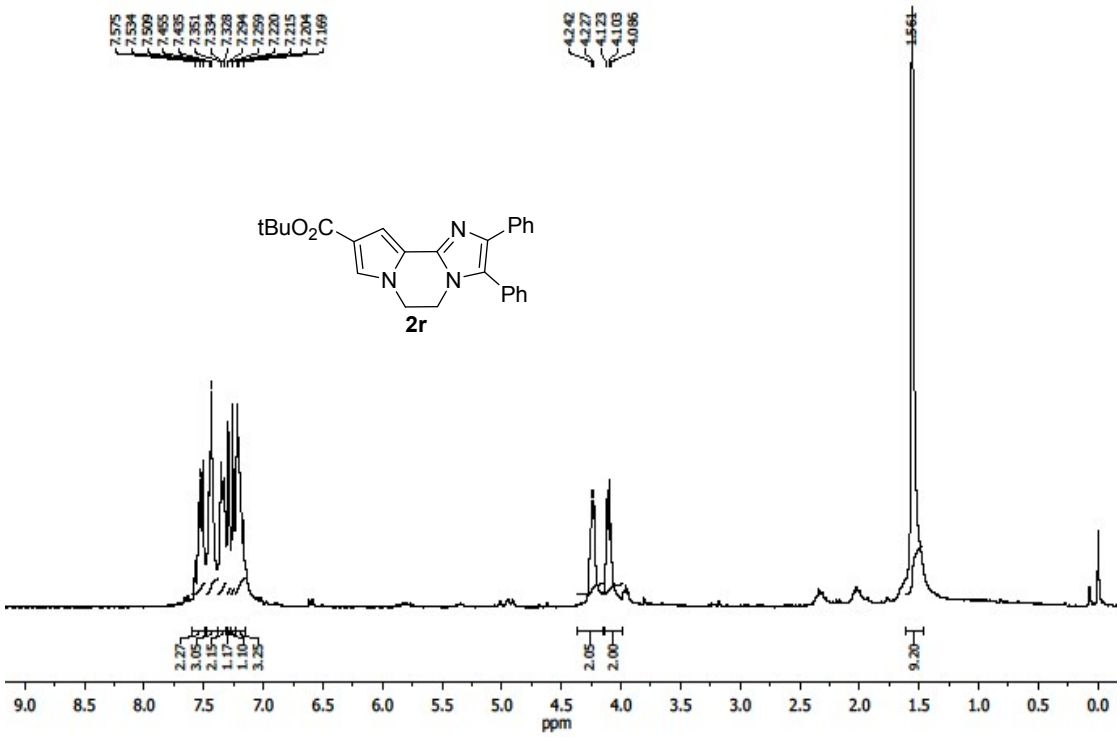

162.432
140.982
131.732
129.185
124.791
124.504
120.931
116.605
114.225
110.239
80.717
77.425
76.578
43.852
41.261
28.312
tBuO2C
N
N
N
2o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

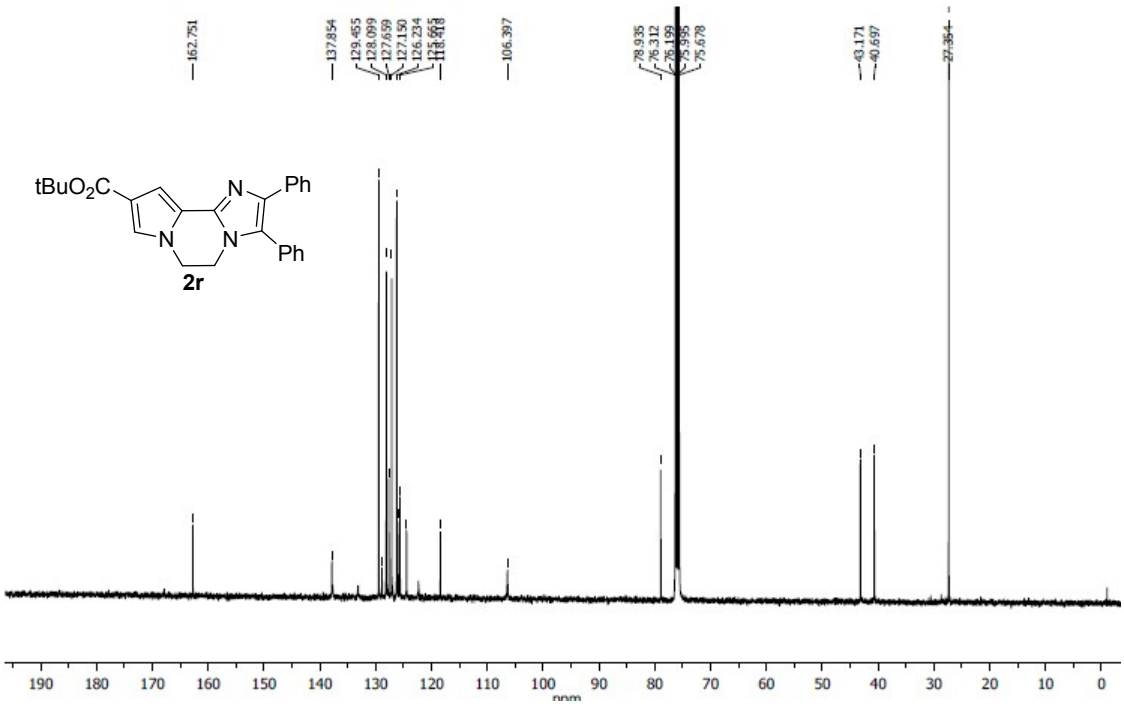

7.381
7.349
7.260
7.124
4.478
2.345
2.274
1.542
$^{t}BuO_2C$
N
N
N
2p
2.93
1.00
4.10
3.09
3.03
9.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

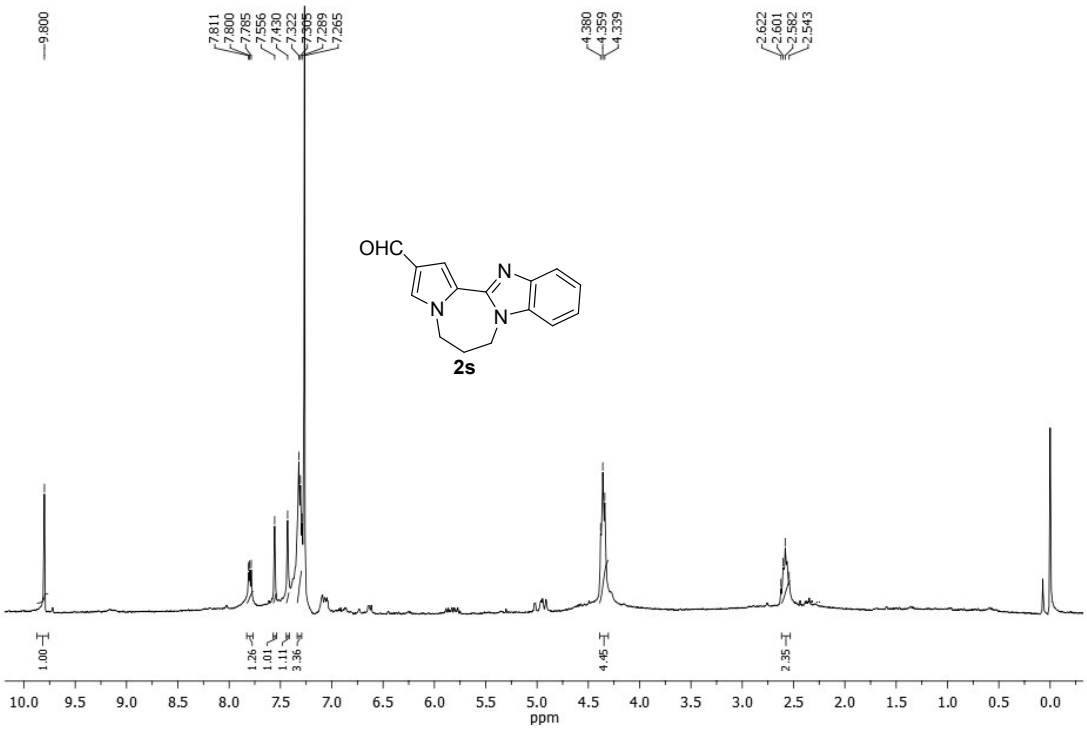

162.946
141.494
133.169
131.004
127.781
120.262
117.775
111.927
109.706
80.424
77.446
77.223
77.022
76.599
43.923
40.879
28.323
20.504
20.242
$^{t}BuO_2C$
N
N
N
2p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

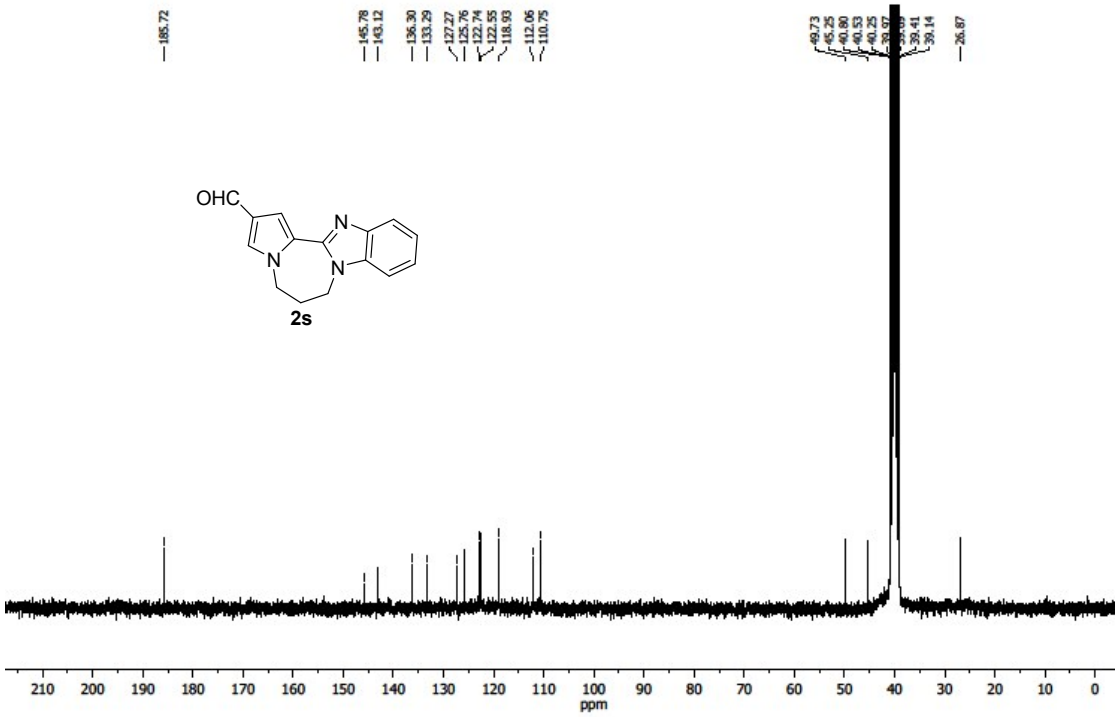

7.196
6.973
6.969
4.270
4.253
4.232
4.151
4.129
4.112
1.470
tBuO2C
N
Cl
N
N
Cl
2q
1.31
1.00
2.19
2.22
9.64
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

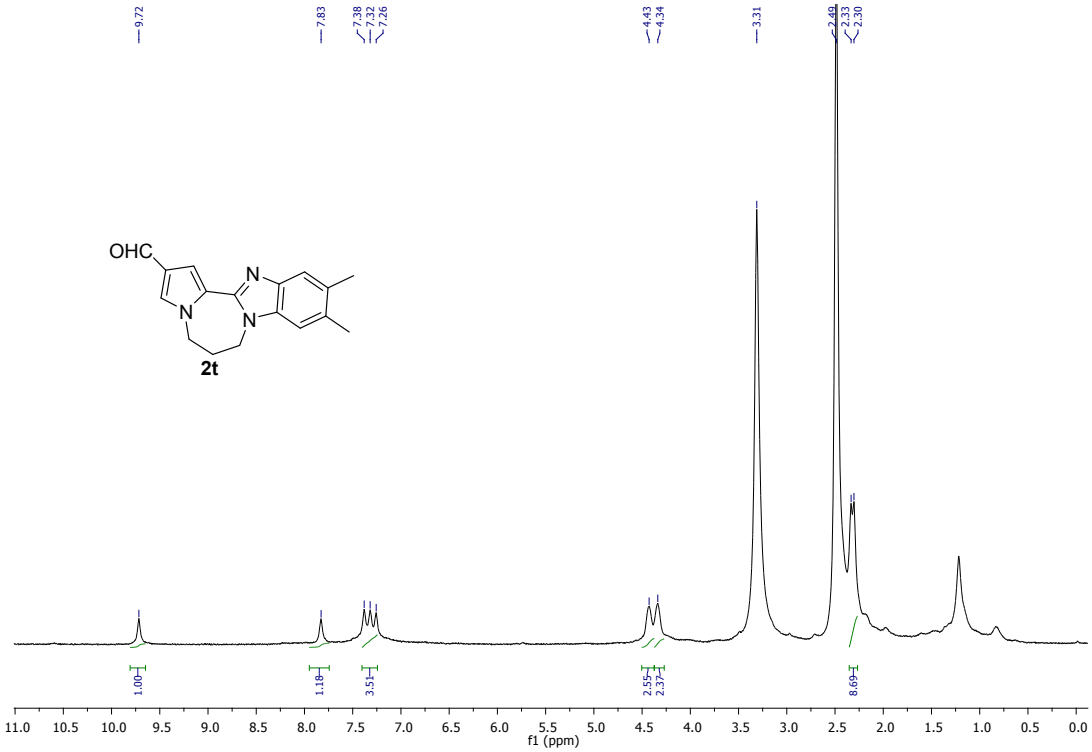

163.310
137.093
126.647
125.962
121.852
119.706
111.430
107.777
80.215
77.439
77.219
77.015
76.592
43.652
41.639
28.394
tBuO2C
N
Cl
N
N
Cl
2q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

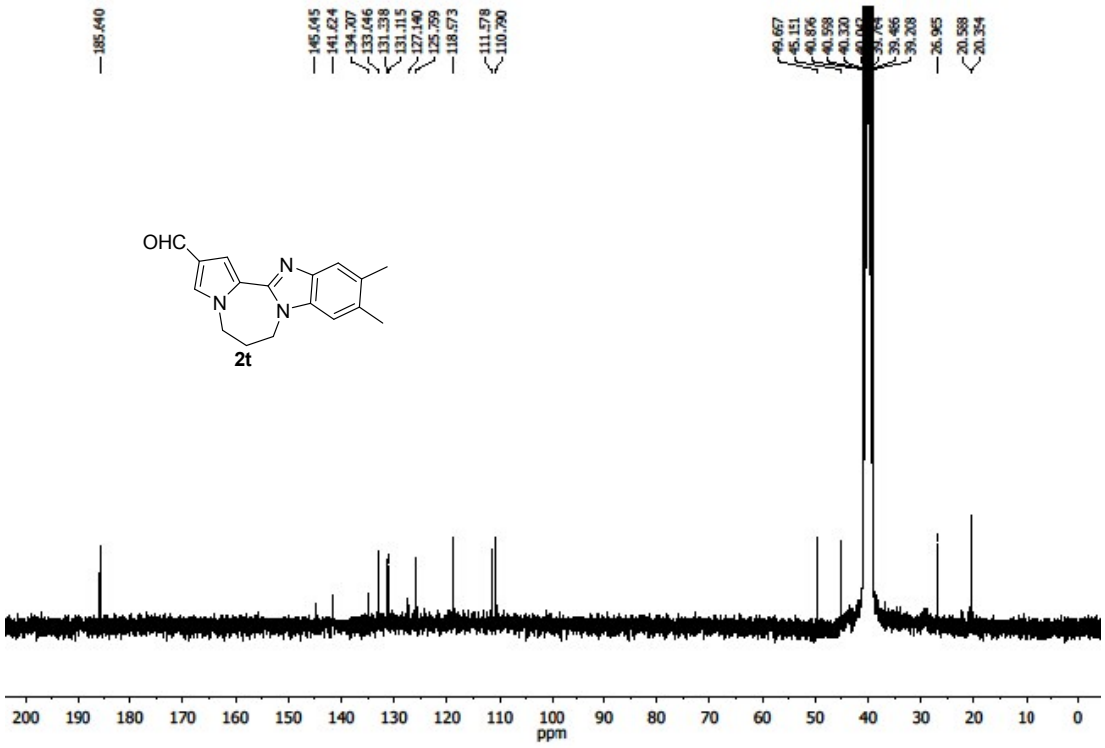

tBuO2C
N
Ph
N
N
Ph
2r
ppm

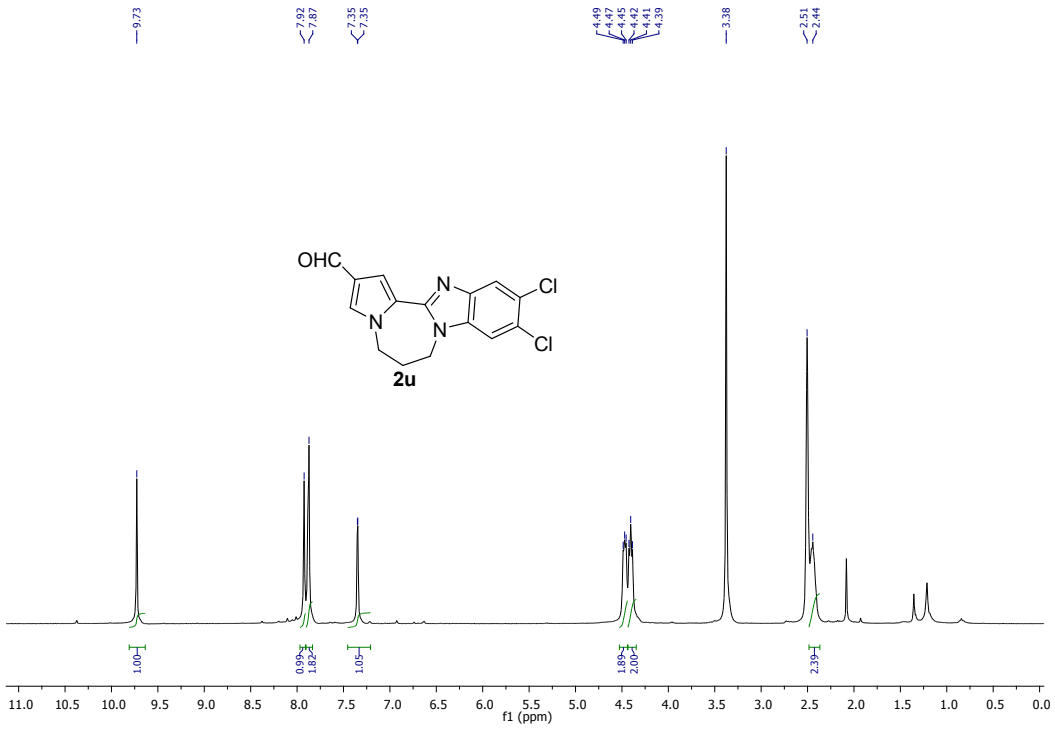

tBuO2C
N
Ph
N
N
Ph
2r
ppm

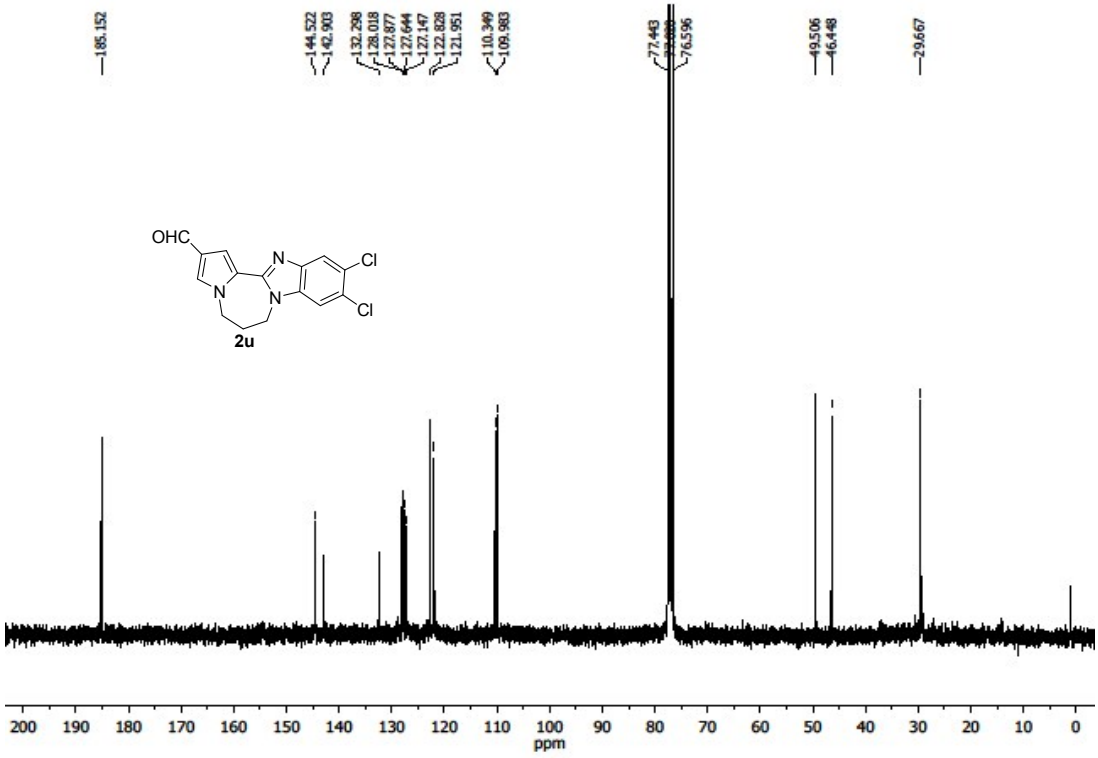

9.800
7.811
7.800
7.785
7.556
7.430
7.322
7.305
7.289
7.265
4.380
4.359
4.339
2.622
2.601
2.582
2.543
OHC
N
N
N
2s
1.00
1.26
1.01
1.11
3.36
4.45
2.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

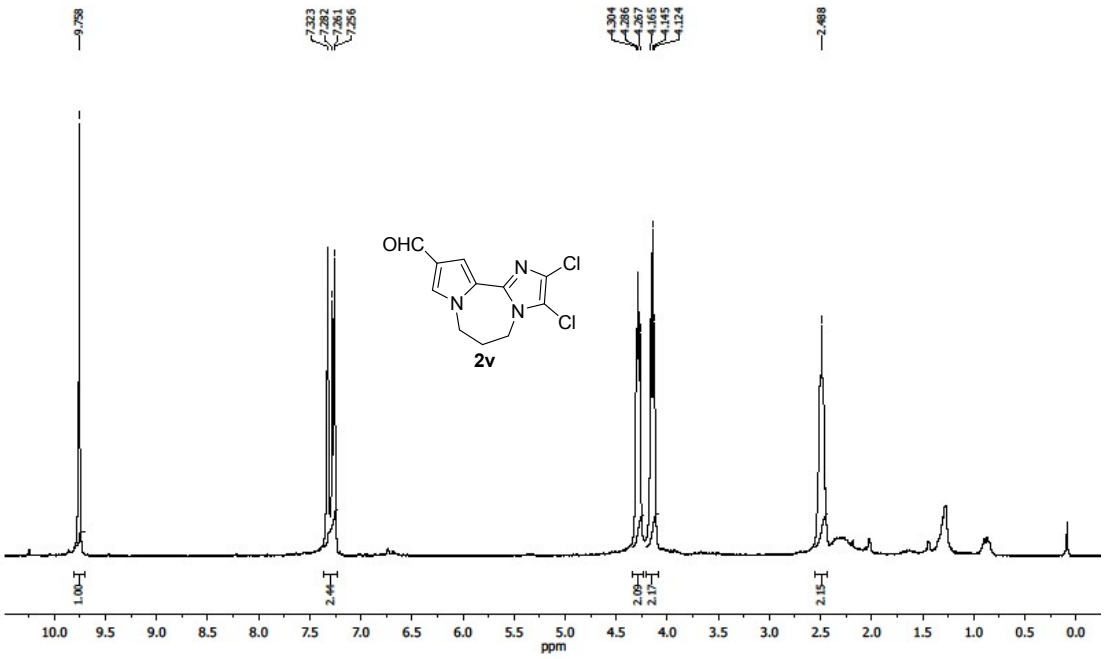

185.72
145.78
143.12
136.30
133.29
127.27
125.76
122.74
122.55
118.93
112.06
110.75
69.73
65.25
60.80
60.53
60.25
39.97
39.41
39.14
26.87
OHC
N
N
N
2s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

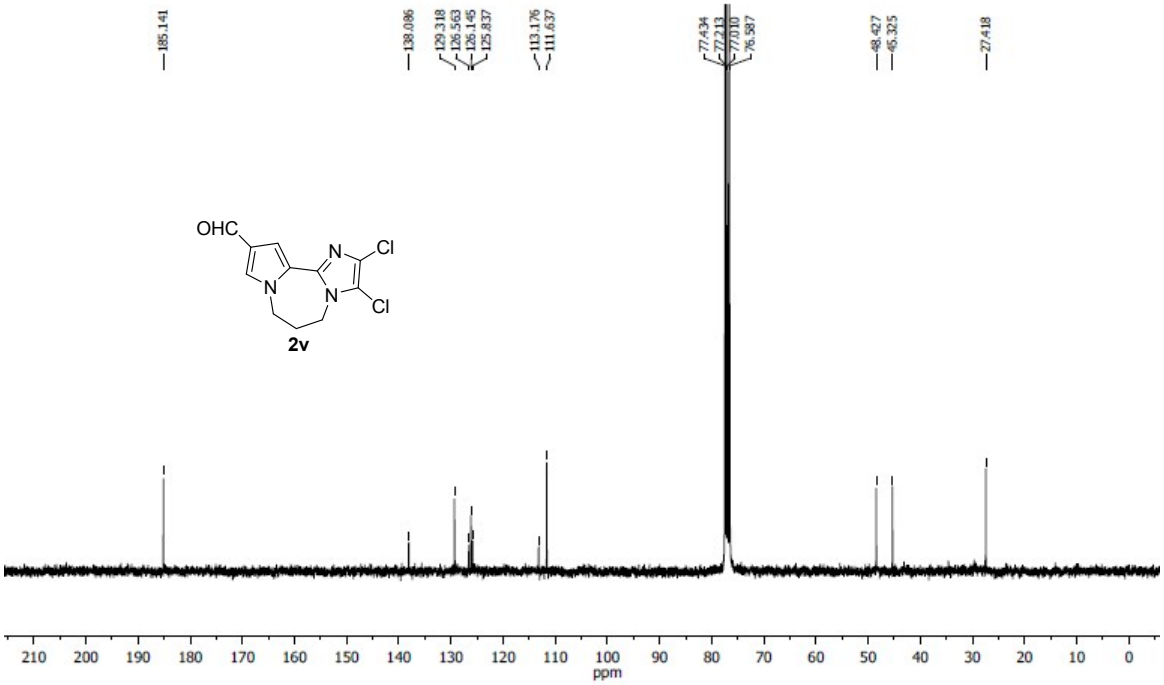

9.72
7.83
7.38
7.32
7.26
4.43
4.34
3.31
2.49
2.33
2.30
OHC
N
N
N
2t
1.00
1.18
3.51
2.55
2.37
8.69
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

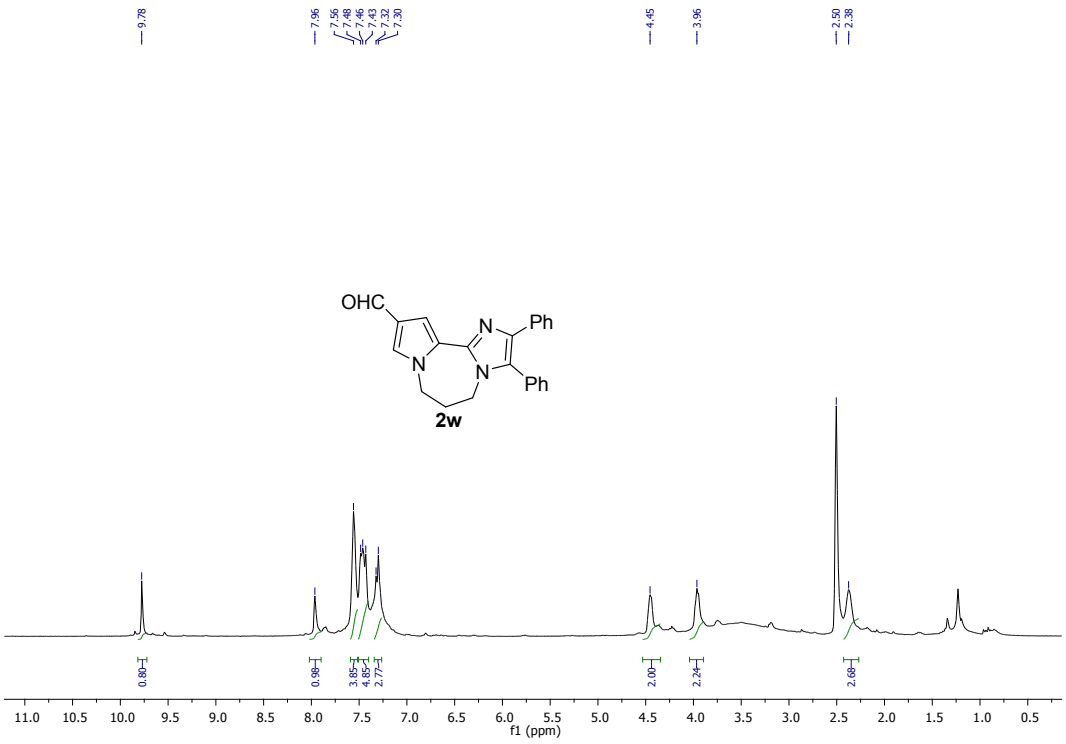

185.640
145.645
141.624
134.207
133.646
131.338
131.115
127.140
125.789
118.573
111.578
110.790
49.667
45.151
40.876
40.558
40.320
39.764
39.466
39.208
26.945
20.588
20.354
OHC
N
N
N
2t
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

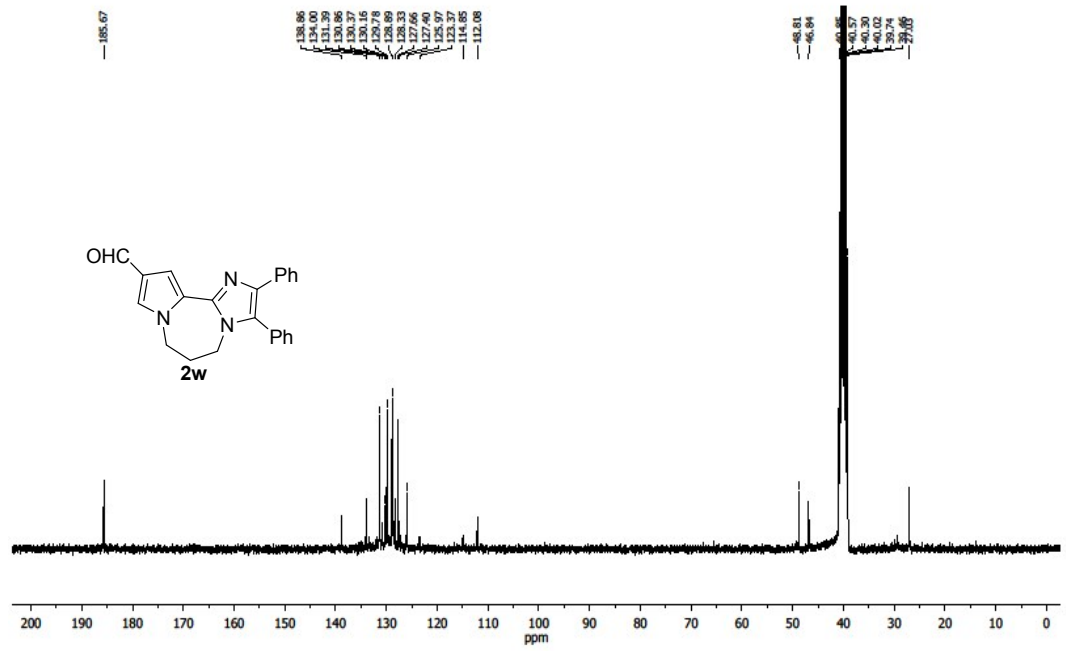

9.73
7.92
7.87
7.35
7.35
4.49
4.47
4.45
4.42
4.41
4.39
3.38
2.51
2.44
OHC
N
N
N
Cl
Cl
2u
1.00
0.99
1.82
1.05
1.89
2.00
2.39
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

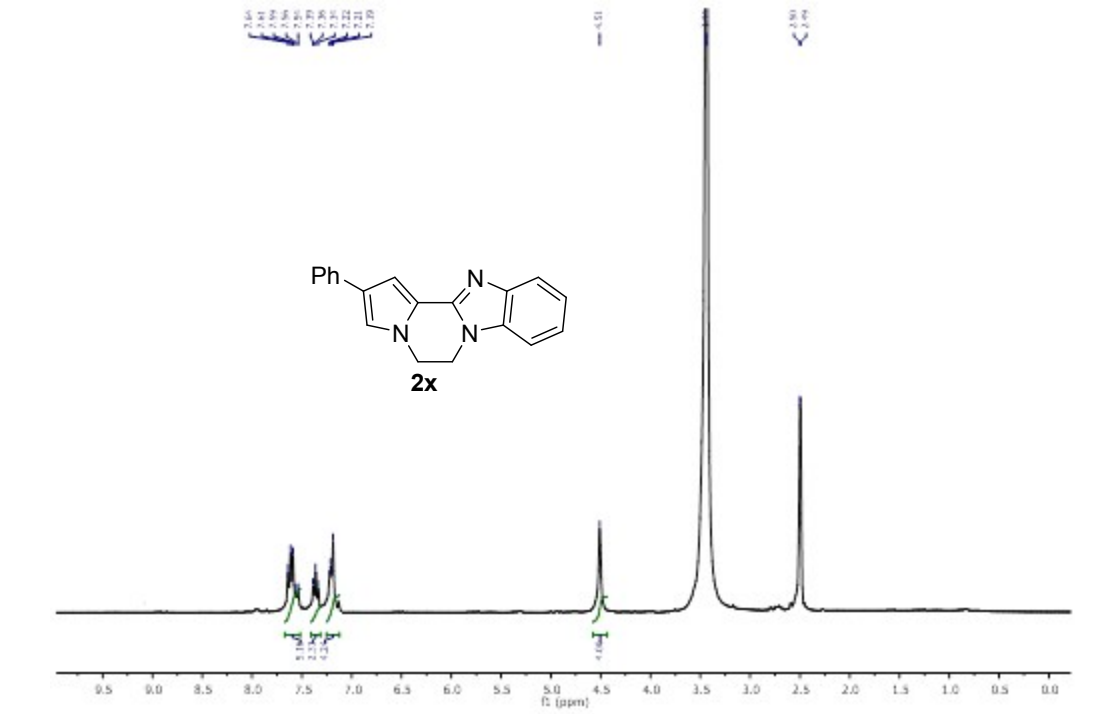

185.152
144.522
142.903
132.298
128.018
127.877
127.644
127.147
122.828
121.951
110.349
109.983
77.443
76.596
49.506
46.448
29.667
OHC
N
N
N
Cl
Cl
2u
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

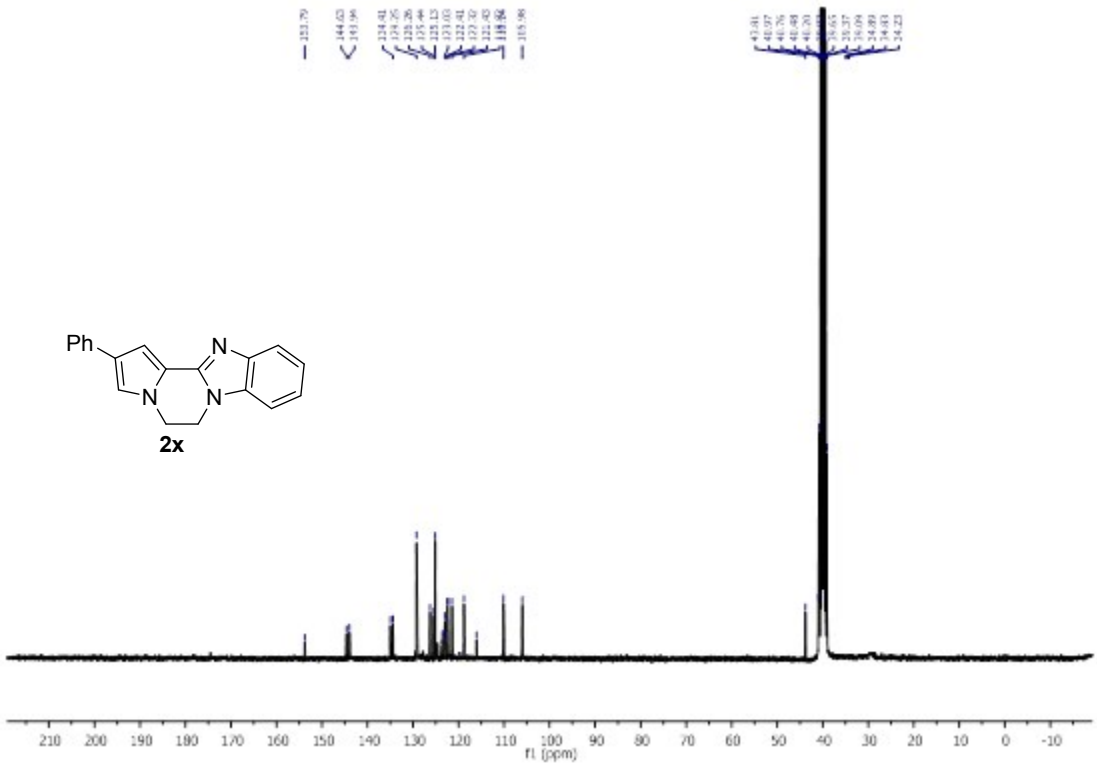

9.759
7.323
7.282
7.261
7.256
4.304
4.286
4.267
4.165
4.145
4.124
2.488
OHC
N
Cl
N
N
Cl
2v
1.00
2.44
2.09
2.17
2.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

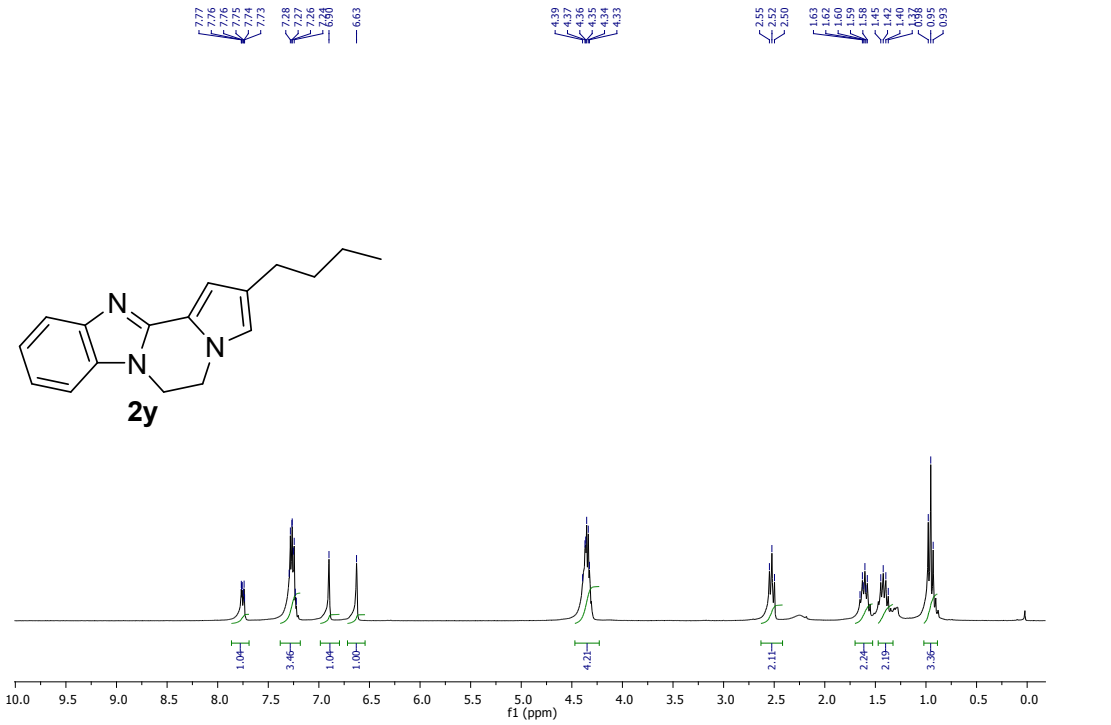

185.141
138.086
129.318
126.563
126.145
125.837
113.176
111.637
77.434
77.213
77.010
76.587
48.427
45.325
27.418
OHC
N
Cl
N
N
Cl
2v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

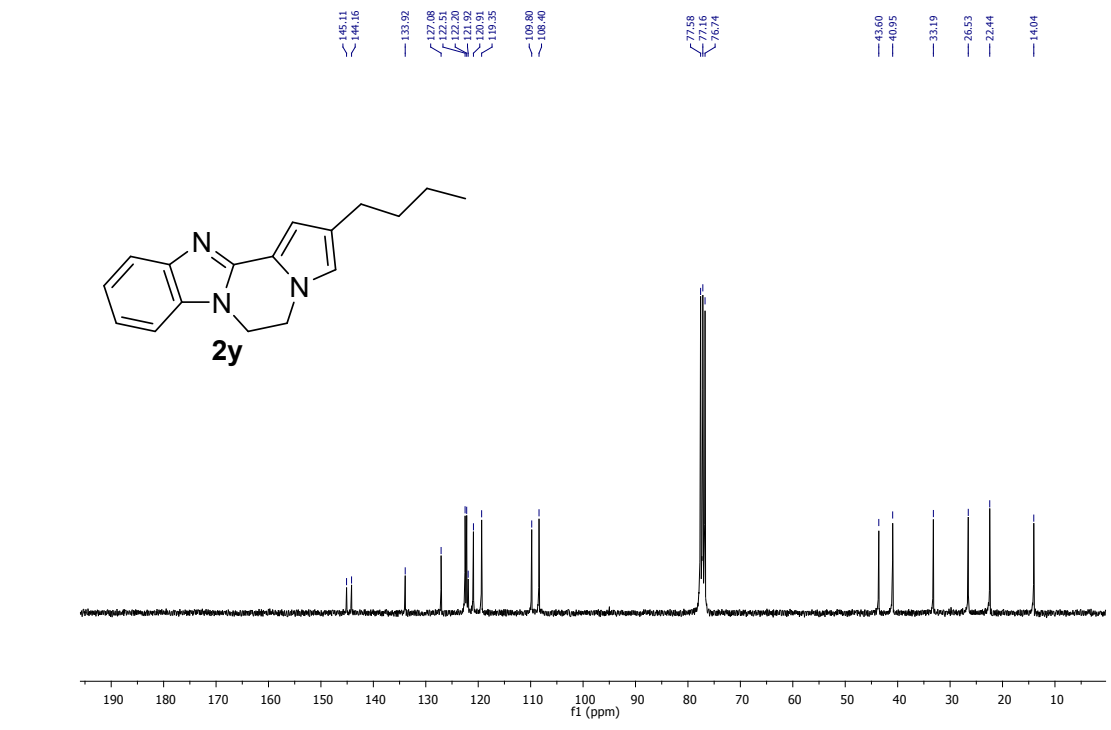

9.78
7.96
7.56
7.48
7.46
7.43
7.32
7.30
4.45
3.96
2.50
2.38
OHC
N
Ph
N
N
Ph
2w
0.80
0.98
3.85
4.85
2.77
2.00
2.24
2.68
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

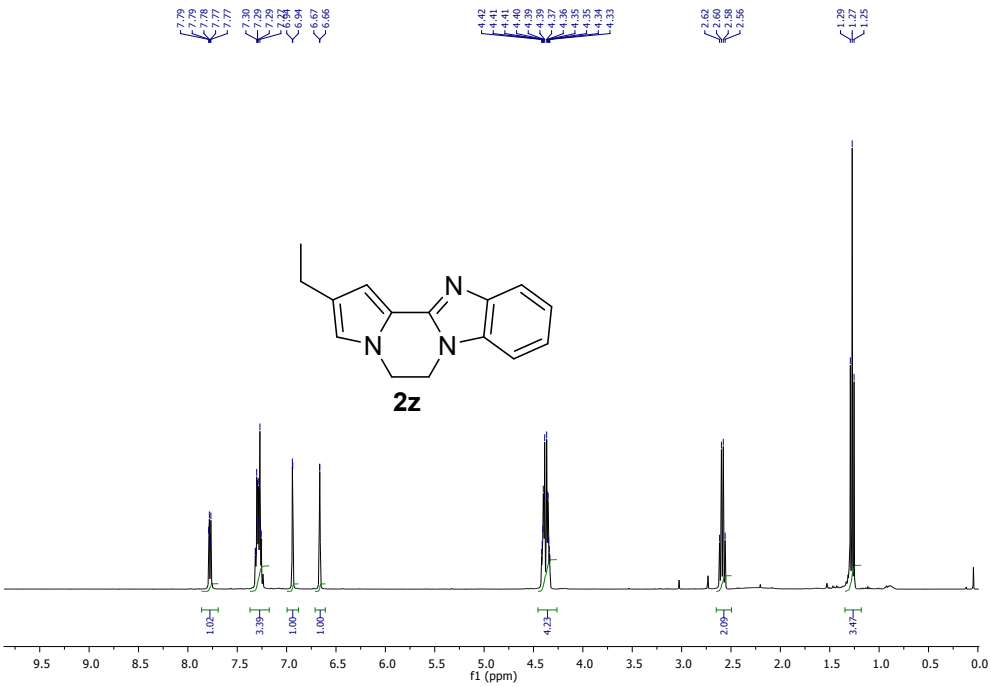

185.67
138.86
134.00
131.39
130.86
130.37
130.16
129.78
128.89
128.33
127.66
127.40
125.97
123.37
114.85
112.08
68.81
66.84
60.57
40.30
40.02
39.74
27.03
OHC
N
Ph
N
N
Ph
2w
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

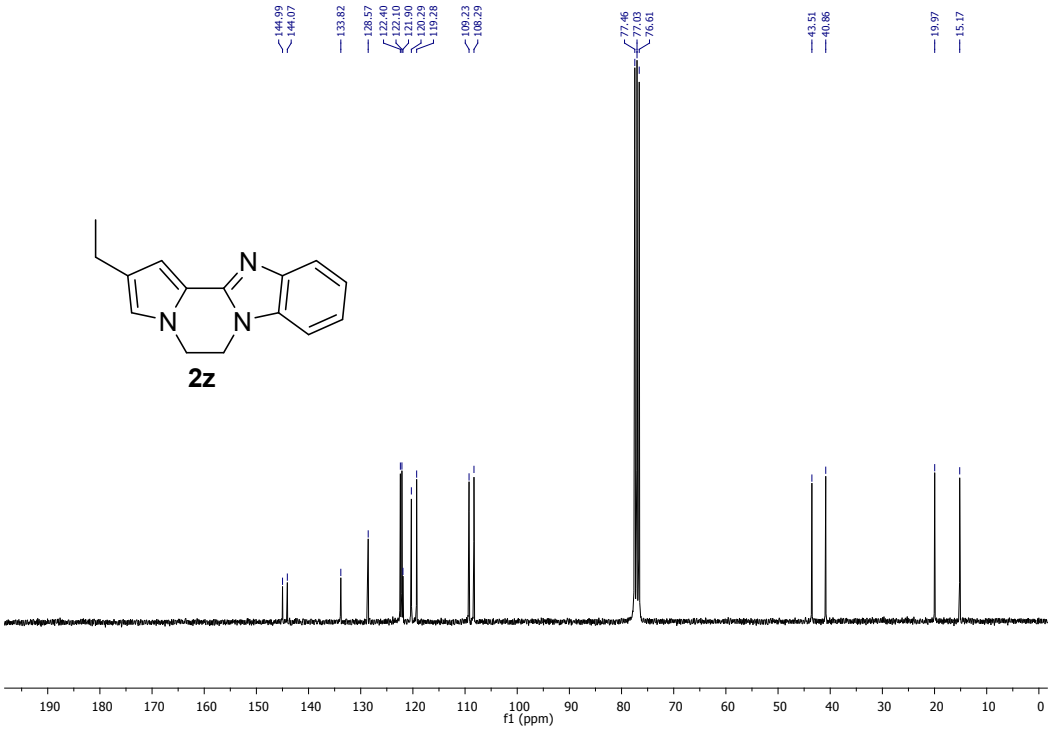

Ph
N
N
N
2x
f2 (ppm)


Ph
N
N
N
2x
f1 (ppm)

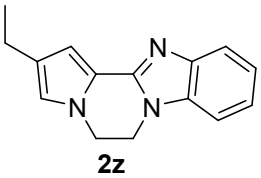

7.77
7.76
7.76
7.75
7.74
7.73
7.28
7.27
7.26
6.64
6.63
4.39
4.37
4.36
4.35
4.34
4.33
2.55
2.52
2.50
1.63
1.62
1.60
1.59
1.58
1.45
1.42
1.40
1.38
0.95
0.93
N
N
N
2y
1.04
3.46
1.04
1.00
4.21
2.11
2.24
2.19
3.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


145.11
144.16
133.92
127.08
122.51
122.20
121.92
120.91
119.35
109.80
108.40
77.58
77.16
76.74
43.60
40.95
33.19
26.53
22.44
14.04
N
N
N
2y
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

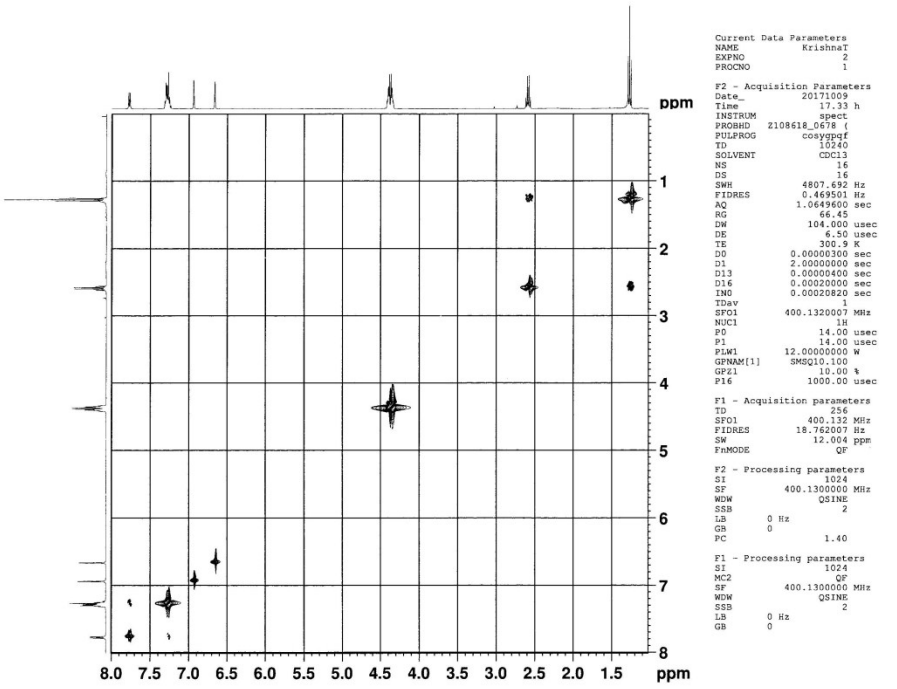

7.79
7.78
7.77
7.30
7.29
7.27
6.94
6.67
6.66
4.42
4.41
4.40
4.39
4.37
4.36
4.35
4.34
4.33
2.62
2.60
2.58
2.56
1.29
1.27
1.25
N
N
N
2z
1.02
3.39
1.00
1.00
4.23
2.09
3.47
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.99
144.07
133.82
128.57
122.40
122.10
121.90
120.29
119.28
109.23
108.29
77.46
77.03
76.61
43.51
40.86
19.97
15.17
N
N
N
2z
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

COSY spectra of compound **2z**

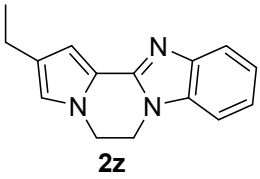


2z

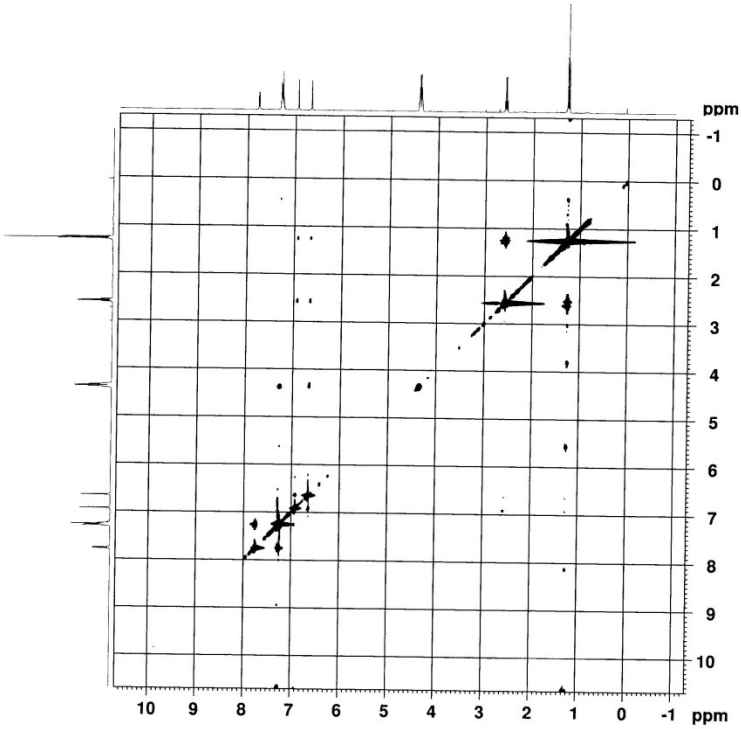



```
Current Data Parameters
NAME                 KrishnaT
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171009
Time                   17.33 h
INSTRUM                 spect
PROBHD    Z108618_0678 (
PULPROG             cosygpqf
TD                     10240
SOLVENT                CDCl3
NS                        16
DS                        16
SWH                4807.692 Hz
FIDRES            0.469501 Hz
AQ                1.0649600 sec
RG                     66.45
DW                   104.000 usec
DE                     6.50 usec
TE                    300.9 K
D0                0.00000300 sec
D1                2.00000000 sec
D13               0.00000400 sec
D16               0.00020000 sec
IN0               0.00020820 sec
TDav                        1
SFO1             400.1320007 MHz
NUC1                       1H
P0                    14.00 usec
P1                    14.00 usec
PLW1             12.00000000 W
GPNAM[1]          SMSQ10.100
GPZ1                  10.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                        256
SFO1              400.132 MHz
FIDRES           18.762007 Hz
SW                    12.004 ppm
FnMODE                    QF

F2 - Processing parameters
SI                       1024
SF               400.1300000 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
PC                      1.40

F1 - Processing parameters
SI                       1024
MC2                        QF
SF               400.1300000 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
```

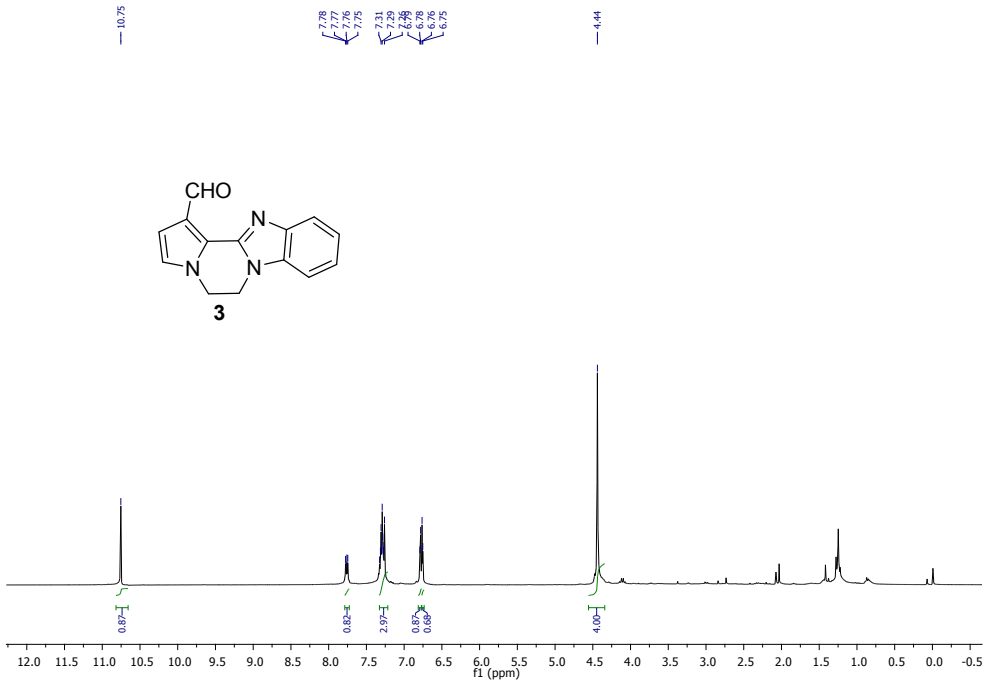
NOESY spectra of compound **2z**

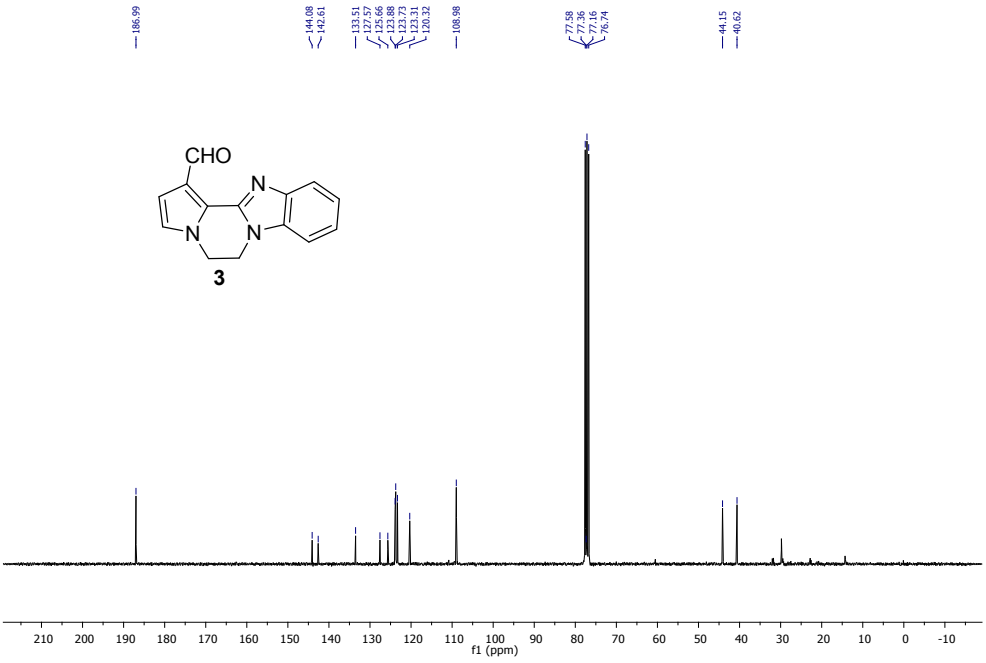


2z




```
Current Data Parameters
NAME                 KrishnaT
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_               20171009
Time                   21.05 h
INSTRUM                 spect
PROBHD    Z108618_0678 (
PULPROG          noesyesgpph
TD                     10240
SOLVENT                CDCl3
NS                          8
DS                         16
SWH                4795.396 Hz
FIDRES            0.468300 Hz
AQ                1.0676906 sec
RG                     66.45
DW                   104.267 usec
DE                     6.50 usec
TE                    299.5 K
D0                0.00008627 sec
D1                1.50000000 sec
D8                0.40000001 sec
D12               0.00002000 sec
D16               0.00020000 sec
IN0               0.00020820 sec
TDav                        1
SFO1             400.1318806 MHz
NUC1                       1H
P1                    14.00 usec
P2                    28.00 usec
P12                 2000.00 usec
PLW0       0 W
PLW1             12.00000000 W
SPNAM[1]          Sinc1.1000
SPOAL1                 0.500
SPOFFS1    0 Hz
SPW1             0.00678190 W
GPNAM[1]          SMSQ10.100
GPZ1                  31.00 %
GPNAM[2]          SMSQ10.100
GPZ2                  11.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                        512
SFO1              400.1319 MHz
FIDRES           9.381003 Hz
SW                    12.004 ppm
FnMODE          States-TPPI

F2 - Processing parameters
SI                       1024
SF               400.1300000 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
PC                      1.40

F1 - Processing parameters
SI                       1024
MC2             States-TPPI
SF               400.1300000 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
```


10.75
7.78
7.77
7.76
7.75
7.31
7.29
6.78
6.76
6.75
4.44
CHO
N
N
N
3
0.87
0.82
2.97
0.87
0.69
4.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


186.99
144.08
142.61
133.51
127.57
125.66
123.88
123.73
123.31
120.32
108.98
77.58
77.36
77.16
76.74
44.15
40.62
CHO
N
N
N
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Crystal structure for compound 2q:

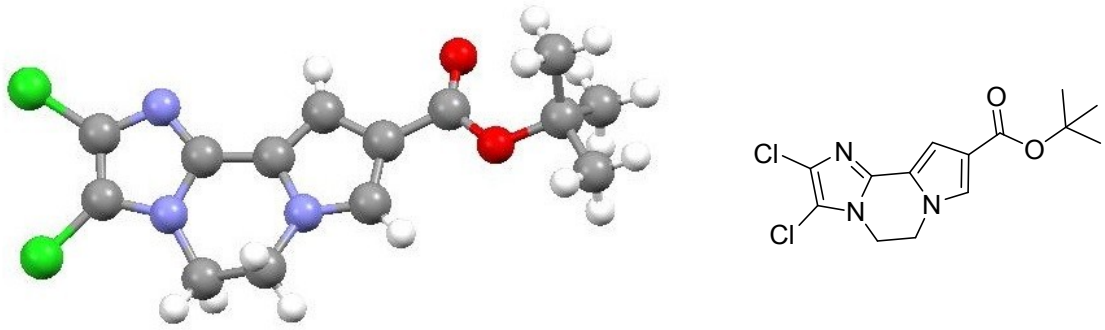


Fig S1. Molecular structure of compound **2q.** Thermal ellipsoids are drawn at the 30% probability level.