Supporting Information

Microwave assisted aminocatalyzed [3+2] annulation between α-iminonitrile and succinaldehyde: Synthesis of pyrrole-3-methanols and related polycyclic ring systems

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Table of Contents:

General Experimental Methods…….S2

Typical experimental procedure and characterization data for all compounds .....….....S3-S14

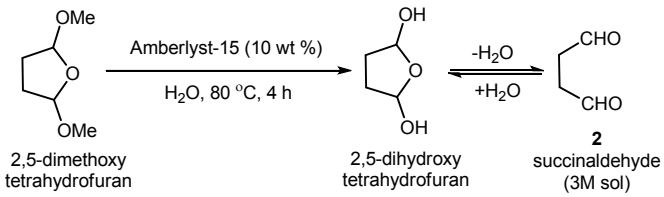
Copies of ^{1}H and ^{13}C-NMR Spectra for all compounds.....S15-S40

General Experimental Methods:

General Remarks: Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents employed in the reactions were distilled from appropriate drying agents prior to use. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F254 pre-coated plates (0.25 mm). The column chromatography was performed on silica gel (100-200) using mixture of hexane/EtOAc. Chemical yields refer to pure isolated substances. ^{1}H-NMR spectra were recorded on a BRUKER-AV400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$ = δ 7.26 for ^{1}H, and 77.00 for ^{13}C NMR). Data are reported as follows: chemical shift, multiciplity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C-NMR spectra were recorded on a BRUKER-AV400 (75 MHz) spectrometer with complete proton decoupling. High resolution mass spectra were recorded using quadrupole electrospray ionization (ESI) technique.

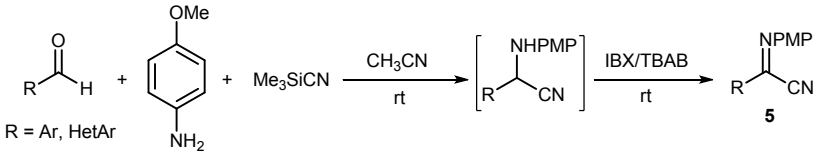
Preparation of succinaldehyde 2 (3M sol):

To a stirred solution of 2,5-dimethoxytetrahydrofuran (2.0 g, 15.15 mmol) in H_2O (5.0 mL) was added Amberlyst-15 (10 wt %) and further heated at 80 ^{o}C for 4 h in an open flask. The resulting solution was cooled to rt and used directly for the said reaction.



General experimental procedure for the synthesis of imino-nitriles 5:[1]

To a stirred solution of aldehyde (0.3 mmol) and *p*-anisidine (0.3 mmol, 1.0 equiv) in acetonitrile (0.3 mL, 1.0 M sol) was added TMSCN (0.33 mmol, 1.1 equiv) at room temperature, and the mixture was stirred for one hour. IBX (0.33 mmol, 1.1 equiv) and *n*-$Bu_4N^+Br^-$ (TBAB, 0.33 mmol, 1.1 equiv) were then added at the same temperature until starting materials consumed completely by TLC. The reaction mixture was then filtered over celite and concentrated under vacuo. The crude product was purified by silica-gel column chromatograph using hexane:AcOEt (99.5:0.5) to afford pure α-imino-nitrile.

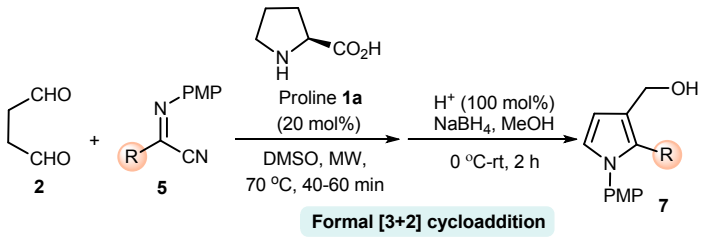


Scheme 1: Preperation of imino-nitriles **5** from Ar/HetAr aldehydes

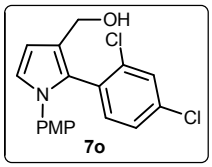
[1] P, Fontaine, A. Chiaroni, G. Masson and J. Zhu; *Org. Lett*., 2008, **10**, 1509.

Typical procedure for the synthesis of pyrrole-3-methylenealcohols (7)

Succinaldehyde **2** (0.3 mL, 0.9 mmol, 3M solution) was added to a mixture of preformed N-PMP-iminonitrile **5** (0.3 mmol), $PhCO_2H$ (7.3 mg, 0.06 mmol), and proline **1a** (7.0 mg, 0.06 mmol) in DMSO (3.0 mL) and irradiated under microwave condition at 70 °C until the α-iminonitrile 5 was consumed as monitored by TLC. Once the imine consumed, reaction was taken to 0 °C and cold MeOH (2.0 mL), CH_3CO_2H (100 mol%, 18 μL) was added. To this solution NaBH4 was added cautiously, and stirred for additional 2 h. The reaction was subsequently quenched with aqueous $NaHCO_3$ (20 % sol, 5.0 mL). The aqueous solution was extracted with EtOAc (2 × 8.0 mL) and combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuo after filtration. The residue was purified by silica gel column chromatography eluting with hexane:EtOAc to afford pyrrole-3-methylenealcohols **7** with 50-75% yields.



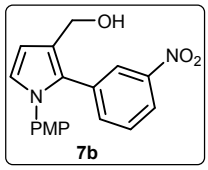
^{1}H and ^{13}C NMR data for prepared compounds:



(1-(4-methoxyphenyl)-2-(2-nitrophenyl)-1*H*-pyrrol-3-yl) methanol (7a):

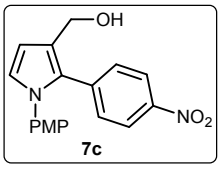
(66 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.47 ((d, *J* = 12.0 Hz, 1H), 6.45 (d, *J* = 2.6 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.37, 57.77, 109.50, 114.16 (2C), 123.42, 123.60, 124.34, 126.60, 126.68 (2C), 126.86, 128.82, 132.32, 132.48, 134.08, 149.66, 158.33; HRMS (ESI): Calcd for $C_{18}H_{16}N_2O_4$ (MH^+) 325.1178; Found 325.1176.

(1-(4-methoxyphenyl)-2-(3-nitrophenyl)-1*H*-pyrrol-3-yl) methanol (7b):



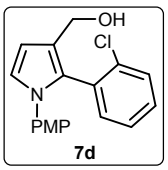
(69 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.56 (s, 2H), 6.45 (d, *J* = 2.3 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 2.2 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.41, 57.82, 109.94, 114.38 (2C), 121.44, 123.81, 124.26, 124.59, 126.99 (2C), 128.87, 129.35, 132.63, 133.32, 135.79, 147.96, 158.52; HRMS (ESI): Calcd for $C_{18}H_{16}N_2O_4$ (MH^+) 325.1178; Found 325.1181.

(1-(4-methoxyphenyl)-2-(4-nitrophenyl)-1*H*-pyrrol-3-yl) methanol (7c):



(72 mg, 75% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.55 (s, 2H), 6.45 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 2.1 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.36, 57.69, 110.40, 114.36 (2C), 123.21(2C), 124.60, 124.99, 126.78 (2C), 129.46, 130.12 (2C), 132.67, 138.18, 145.89, 158.47; IR (KBr)/cm^{-1}; HRMS (ESI): Calcd for $C_{18}H_{16}N_2O_4$ (MH^+) 325.1178; Found 325.1182.

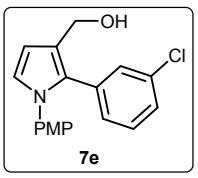
(2-(2-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7d):



7d

(60 mg, 65% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 6.47 (s, 1H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.92 (s, 1H), 7.00 (d, *J* = 8.3 Hz, 2H), 7.21 (dd, *J* = 13.0, 6.8 Hz, 3H), 7.35 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.33, 58.15, 108.76, 113.90 (2C), 122.74, 123.67, 126.24 (2C), 126.42, 128.62, 129.48, 129.49, 131.20, 133.20, 133.59, 135.49, 158.04; HRMS (ESI): Calcd for $C_{18}H_{16}ClNO_2$ (MH^+) 314.0948; Found 314.0947.

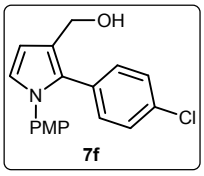
(2-(3-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7e):



7e

(65 mg, 70% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.55 (s, 2H), 6.44 (d, *J* = 1.3 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 1.5 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 3H), 7.15 (d, *J* = 7. 8 Hz, 1H), 7.20 (d, *J* = 14.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.37, 57.88, 109.57, 114.14 (2C), 123.20, 123.53, 126.77 (2C), 126.88, 128.31, 129.14, 129.95, 130.26, 133.03, 133.38, 133.78, 158.21; HRMS (ESI): Calcd for $C_{18}H_{16}ClNO_2$ (MH^+) 314.0948; Found 314.0946.

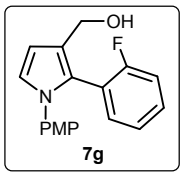
(2-(4-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7f):



7f

(67 mg, 72% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.54 (s, 2H), 6.43 (d, *J* = 2.8 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 2.8 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.40, 58.01, 109.56, 114.13 (2C), 122.79, 123.38, 126.82 (2C), 128.27 (2C), 129.94, 130.65, 131.33 (2C), 132.80, 133.06, 158.15 HRMS (ESI): Calcd for $C_{18}H_{16}ClNO_2$ (MH^+) 314.0948; Found 314.0950.

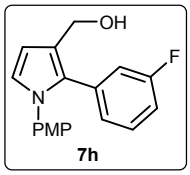
(2-(2-fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7g):



7g

(55 mg, 63% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.52 (s, 2H), 6.51 (d, *J* = 2.5 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 2.4 Hz, 1H), 7.00-7.06 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.32, 58.04, 109.20, 113.94 (2C), 115.49, 115.72, 123.44, 123.84, 124.13, 125.16, 126.23 (2C), 129.58, 129.98, 133.31, 158.11, 161.42; HRMS (ESI): Calcd for $C_{18}H_{16}FNO_2$ (MH^+) 298.1243; Found 298.1240.

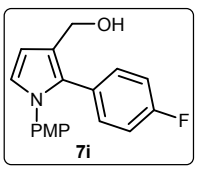
(2-(3-fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7h):



7h

(57 mg, 65% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.56 (s, 2H), 6.44 (d, *J* = 2.6 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.86-6.97 (m, 4H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.36, 57.90, 109.55, 113.81, 114.10 (2C), 116.94, 123.02, 123.50, 125.85, 126.73 (2C), 129.37, 130.45, 133.03, 133.63, 158.15, 161.30; HRMS (ESI): Calcd for $C_{18}H_{16}FNO_2$ (MH^+) 298.1243; Found 298.1241.

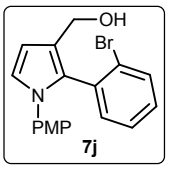
(2-(4-fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7i):



7i

(64 mg, 73% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.53 (s, 2H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 2.5 Hz, 1H), 6.91-6.99 (m, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3 6, 58.01, 109.35, 114.07 (2C), 114.92, 115.14, 122.53, 122.98, 126.83 (2C), 127.57, 130.90, 131.81, 131.89, 133.18, 158.13, 163.02; HRMS (ESI): Calcd for $C_{18}H_{16}FNO_2$ (MH^+) 298.1243; Found 298.1245.

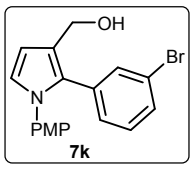
(2-(2-bromophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7j):



7j

(63 mg, 60% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 6.46 (d, *J* = 2.9 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 2.9 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 7.15 (ddd, *J* = 8.1, 5.6, 3.6 Hz, 1H), 7.21–7.25 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.32, 58.19, 108.63, 113.87 (2C), 122.51, 123.38, 126.34 (2C), 126.98, 129.70 130.43, 132.57, 133.13, 133.35, 133.70, 158.04; HRMS (ESI): Calcd for $C_{18}H_{16}BrNO_2$ (MH^+) 358.0442; Found 358.0446.

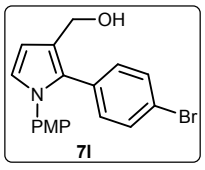
(2-(3-bromophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7k):



7k

(69 mg, 65% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.55 (s, 2H), 6.43 (d, *J* = 2.8 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 2.8 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 7.03 (s, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.37 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.43, 57.93, 109.57, 114.14 (2C), 121.98, 123.10, 123.59, 126.80 (2C), 128.76, 129.45 129.82, 130.19, 132.81, 132.96, 133.58, 158.20; HRMS (ESI): Calcd for $C_{18}H_{16}BrNO_2$ (MH^+) 358.0442; Found 358.0445.

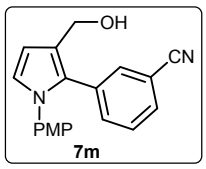
(2-(4-bromophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7l):



7l

(77 mg, 73% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 4.53 (s, 2H), 6.41 (d, *J* = 1.9 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 2.1 Hz, 1H), 6.98 (dd, *J* = 11.9, 8.5 Hz, 5H), 7.43 (d, *J* = 6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.46, 57.92, 109.56, 114.26 (2C), 115,89, 116.11, 123.09, 123.51, 126.91 (2C), 129.20, 129.51, 130.72, 130.79, 132.87, 134.91, 158.37; HRMS (ESI): Calcd for $C_{18}H_{16}BrNO_2$ (MH^+) 358.0442; Found 358.0444.

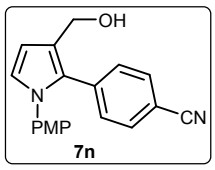
3-(3-(hydroxymethyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-2-yl) benzonitrile (7m):



7m

(56 mg, 62% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 4.96 (s, 2H), 6.46 (d, *J* = 2.8 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.34-7.38 (m, 2H), 7.43 (s, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.43, 59.72, 109.69, 112.33, 114.34 (2C), 118.53, 118.55, 124.17, 126.88 (2C), 128.99, 130.55, 130.59, 132.40, 132.67, 133.39, 134.36, 158.50; HRMS (ESI): Calcd for $C_{19}H_{16}N_2O_2$ (MH^+) 305.1290; Found 305.1294.

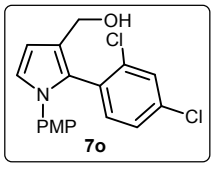
4-(3-(hydroxymethyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-2-yl) benzonitrile (7n):



7n

(63 mg, 70% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 4.58 (s, 2H), 6.48 (d, *J* = 2.4 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 2.5 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.44, 57.88, 110.23, 114.37 (2C), 118.89, 124.21, 124.66, 126.84 (2C), 129.91, 130.25 (2C), 131.75 (2C), 132.09, 132.81, 136.23, 158.51; HRMS (ESI): Calcd for $C_{19}H_{16}N_2O_2$ (MH^+) 305.1290; Found 305.1293.

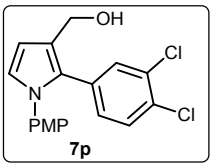
(2-(2,4-dichlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl)methanol (7o):



7o

(62 mg, 60% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 4.26 (d, *J* = 11.4 Hz, 1H), 4.36 (d, *J* = 11.4 Hz, 1H), 6.42 (d, *J* = 2.8 Hz, 1H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 2.8 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 7.19 (s, 2H), 7.35 (d, *J* = 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.32, 58.19, 108.63, 113.87 (2C), 122.51, 123.38, 126.34, 126.38 (2C), 126.98, 129.70, 130.43, 132.57, 133.13, 133.35, 133.70, 158.04; HRMS (ESI): Calcd for $C_{18}H_{15}Cl_2NO_2$ (MH^+) 348.0558; Found 348. 0552.

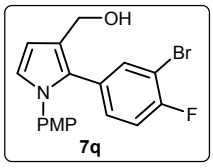
(2-(3, 4-dichlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7p):



7p

(65 mg, 63% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 4.54 (s, 2H), 6.42 (d, *J* = 2.7 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 2.7 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 1.7 Hz, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 55.43, 57.93, 109.57, 114.14 (2C), 121.98, 123.10, 123.59, 126.80 (2C), 128.76, 129.45, 129.82, 130.19, 132.88, 132.96, 133.58, 158.20; HRMS (ESI): Calcd for $C_{18}H_{15}Cl_2NO_2$ (MH^+) 348.0558; Found 348.0556.

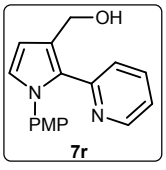
(2-(3-bromo-4-fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrrol-3-yl) methanol (7q):



7q

(77 mg, 69% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.41 (s, 1H), 4.56 (s, 1H), 6.47 (m, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.87 (t, *J* = 2.8 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 7.07 (dd, *J* = 14.7, 7.7 Hz, 1H), 7.30-7.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.44, 57.98, 109.58, 110.90, 114.20 (2C), 120.84, 121.94, 123.60, 126.84 (2C), 128.79, 129.27, 129.35, 129.84, 132.88, 133.30, 158.18; HRMS (ESI): Calcd for $C_{18}H_{15}BrFNO_2$ (MH^+) 376.0348; Found 376.0344.

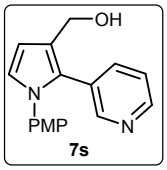
(1-(4-methoxyphenyl)-2-(pyridin-2-yl)-1*H*-pyrrol-3-yl) methanol (7r):



7r

(54 mg, 65% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 4H), 4.50 (s, 2H), 6.35 (d, *J* = 2.6 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 7.05 (dd, *J* = 7.3, 5.0 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.39 (td, *J* = 8.3, 1.6 Hz, 1H), 8.56 (d, *J* = 4.9 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.48, 58.05, 110.54, 114.42 (2C), 120.44, 123.20, 124.96, 126.94 (2C), 128.66, 130.35, 133.50, 135.94, 148.41, 150.70, 158.62; HRMS (ESI): Calcd for $C_{17}H_{16}N_2O_2$ (MH^+) 281.1290; Found 281.1293.

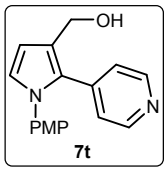
(1-(4-methoxyphenyl)-2-(pyridin-3-yl)-1*H*-pyrrol-3-yl) methanol (7s):



7s

(55 mg, 67% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.55 (s, 2H), 6.46 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 2.5 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.18 (dd, *J* = 7.5, 5.1 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 8.41 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.41, 57.78, 109.87, 114.33 (2C), 122.97, 123.84, 124.10, 127.02 (2C), 127.89, 128.20, 132.78, 137.35, 147.53, 150.41, 158.44; HRMS (ESI): Calcd for $C_{17}H_{16}N_2O_2$ (MH^+) 281.1290; Found 281.1292.

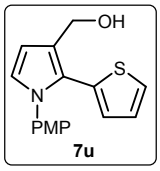
(1-(4-methoxyphenyl)-2-(pyridin-4-yl)-1*H*-pyrrol-4-yl) methanol (7t):



7t

(56 mg, 68% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 1H), 3.80 (s, 3H), 4.57 (s, 2H), 6.45 (d, *J* = 2.5 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 2.6 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 4.5 Hz, 2H), 8.44 (bs, 2H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.44, 57.67, 109.54, 114.41 (2C), 124.25, 125.06, 125.30, 126.06, 126.83 (2C), 128.53, 132.67, 138.48, 140.11, 148.29, 158.58; HRMS (ESI): Calcd for $C_{17}H_{16}N_2O_2$ (MH^+) 281.1290; Found 281.1294.

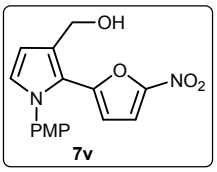
(1-(4-methoxyphenyl)-2-(thiophen-2-yl)-1*H*-pyrrol-3-yl) methanol (7u):



7u

(50 mg, 60% yield); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 4.61 (s, 2H), 6.41 (d, *J* = 2.5 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 4H), 6.4 (t, 3.8 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 5.1 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.40, 58.11, 109.38, 113.97 (2C), 123.63, 123.98,125.17, 126.22, 126.76, 127.40 (2C) , 128.05 , 132.45 , 132.96 , 158.62 ; HRMS (ESI): Calcd for $C_{16}H_{15}SNO_2$ (MH^+) 286.0901; Found 281.0905.

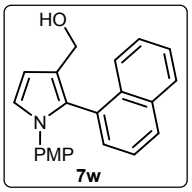
(1-(4-methoxyphenyl)-2-(5-nitrofuran-2-yl)-1*H*-pyrrol-3-yl) methanol (7v):



7v

(63 mg, 67% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 4.84 (s, 2H), 5.63 (d, *J* = 3.9 Hz, 1H), 6.44 (d, *J* = 2.7 Hz, 1H), 6.87 (d, *J* = 2.7 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 3.9 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 2H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.59, 58.32, 108.43, 111.17, 113.85, 114.52 (2C), 120.14, 127.26, 127.93 (2C), 128.59, 132.12, 139.28, 150.23, 159.74; HRMS (ESI): Calcd for $C_{16}H_{14}N_2O_5$(MH^+) 315.0981; Found 315.0985.

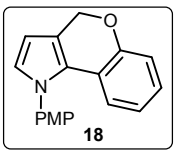
(1-(4-methoxyphenyl)-2-(naphthalen-1-yl)-1*H*-pyrrol-3-yl) methanol (7w):



7w

(54 mg, 55% yield); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.65 (s, 3H), 4.31 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 6.55 (d, *J* = 2.9 Hz, 1H), 6.59 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 2.9 Hz, 1H), 7.33 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.36–7.40 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 3H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.22, 58.22, 108.80, 113.75 (2C), 114.07, 122.65, 124.05, 125.07, 125.80, 125.85, 125.90 (2C), 126.29, 128.13, 128.44, 129.52, 129.99, 133.36, 133.41, 133.44, 157.71; HRMS (ESI): Calcd for $C_{22}H_{19}NO_2$ (MH^+) 330.1494; Found 330.1498.

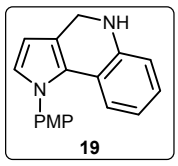
1-(4-methoxyphenyl)-1,4-dihydrochromeno [4, 3-*b*] pyrrole (18): In a two-necked round bottom flask fitted with condenser, substrate **7j** (0.05 g, 0.14 mmol), KO^{t}Bu (31



18

mg, 0.28 mmol), and $Pd(OAc)_2$ (1.0 mg, 2 mol %), PPh_3 (7.3 mg, 20 mol %), added in dry DMF (3 mL) was taken and degassed for 10 minutes with N_2 and reaction mixture was heated at 110 ^oC for 3 h. The reaction mixture was allowed to cool to rt and quenched with saturated $NaHCO_3$ solution (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The organic solvent was evaporated under vacuo and purified through silica gel column chromatography by eluting with hexane/EtOAc (90:10). The product **18** was obtained as colorless oil (24 mg, 63% isolated yield). ^1H NMR (400 MHz, $CDCl_3$) δ ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.53 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.37 (td, *J* = 7.4, 0.9 Hz, 1H), 7.23–7.26 (m, 2H), 7.12 – 7.17 (m, 1H), 6.89 – 6.94 (m, 3H), 6.84–6.86 (m, 1H), 6.18 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.41, 57.82, 109.94, 114.38 (2C), 121.44, 123.81, 124.26, 124.59, 126.99 (2C), 128.87, 129.35, 132.63, 133.32, 135.79, 147.96, 158.52; HRMS (ESI): Calcd for $C_{18}H_{15}NO_2$ (MH^+) 278.1181; Found 278.1184.

1-(4-methoxyphenyl)-4, 5-dihydro-1H-pyrrolo [3, 2-*c*] quinoline (19):



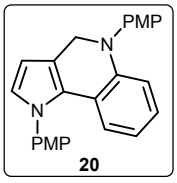
19

To a stirred solution of compound **7a** (97 mg, 0.3 mmol) in CH_2Cl_2 (3 mL) was added Et_3N (3.0 equiv, 0.9 mmol) at rt. Reaction was taken to 0 ^oC and TsCl (68 mg, 0.36 mmol) in CH_2Cl_2 (2.0 mL) was added drop wise and then stirred at rt for additional 4 hr. Progress of the reaction was monitored by TLC. Reaction was stirred with NH_4Cl (20% sol. 5.0 mL) and extracted with additional CH_2Cl_2 (5.0 mL). The combined organic layer was washed with brine solution and concentrated under vacuo to give crude solid mass. This was used further without purification at this stage. To this crude mass was added ethanol and acetic acid (3mL, 2:1 ratio respectively) and Fe powder (125 mg, 7.5 equiv, 2.2 mmol) and $FeCl_3$ (9.5 mg, 0.2 equiv, 0.06 mmol) were added while stirring. The reaction mixture was

refluxed for 6 hours and monitored by TLC. After completion of the reaction, ethanol was evaporated under reduced pressure. The reaction mixture was filtered through celite and washed with the CH_2Cl_2 (10 mL). The organic layer was stirred with $NaHCO_3$ solution (5 mL) and extracted with CH_2Cl_2 (10 mL). The combined organic layer was washed with brine solution, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica-gel column chromatography (EtOAc/hexanes) to afford **19** as brownish pasty liquid (48 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.14 (m, 1H), 7.05 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 3.1 Hz, 1H), 6.87 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.76 (d, *J* = 9.0 Hz, 2H), 6.67 (s, 1H), 6.62 – 6.66 (m, 2H), 6.62 (d, *J* = 3.1 Hz, 1H), 3.82 (d, *J* = 19.7 Hz, 1H), 3.75 (s, 3H), 3.69 (d, *J* = 12.6 Hz, 1H); ^{13}C ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.34, 59.93, 109.37, 113.76, 114.03 (2C), 115.35, 118.14, 120.42, 124.43, 125.40, 125.80 (2C), 129.92, 132.45, 138.30, 145.84, 158.28; HRMS (ESI): Calcd for $C_{18}H_{16}N_2O$ (MH^+); 277.1341 Found 277.1345.

1, 5-bis(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrrolo[3,2-*c*] quinoline (20):

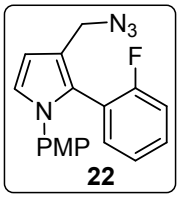


20

To a stirred solution of compound **7a** (90 mg, 0.28 mmol) in CH_2Cl_2 (3 mL) was added Et_3N (3.0 equiv, 0.83 mmol) at rt. Reaction was taken to 0 ^{o}C and TsCl (63 mg, 0.33 mmol) in CH_2Cl_2 (2.0 mL) was added drop wise and then stirred at rt for additional 4 hr. Progress of the reaction was monitored by TLC. Reaction was stirred with NH_4Cl (20% sol. 5 mL) and extracted with additional CH_2Cl_2 (5.0 mL). The combined organic layer was washed with brine solution and concentrated under vacuo to give crude solid mass. This was used further without purification at this stage. To this crude mass in DMF (3 mL) was added *p*-anisidine (34 mg, 0.27 mmol, 1.0 equiv) and heated at 80 ^{o}C for 2 hr. Next, to this reaction mixture, K_2CO_3 (76 mg, 0.55 mmol, 2.0 equiv.), CuI (10 mg, 20 mol %), L-proline as

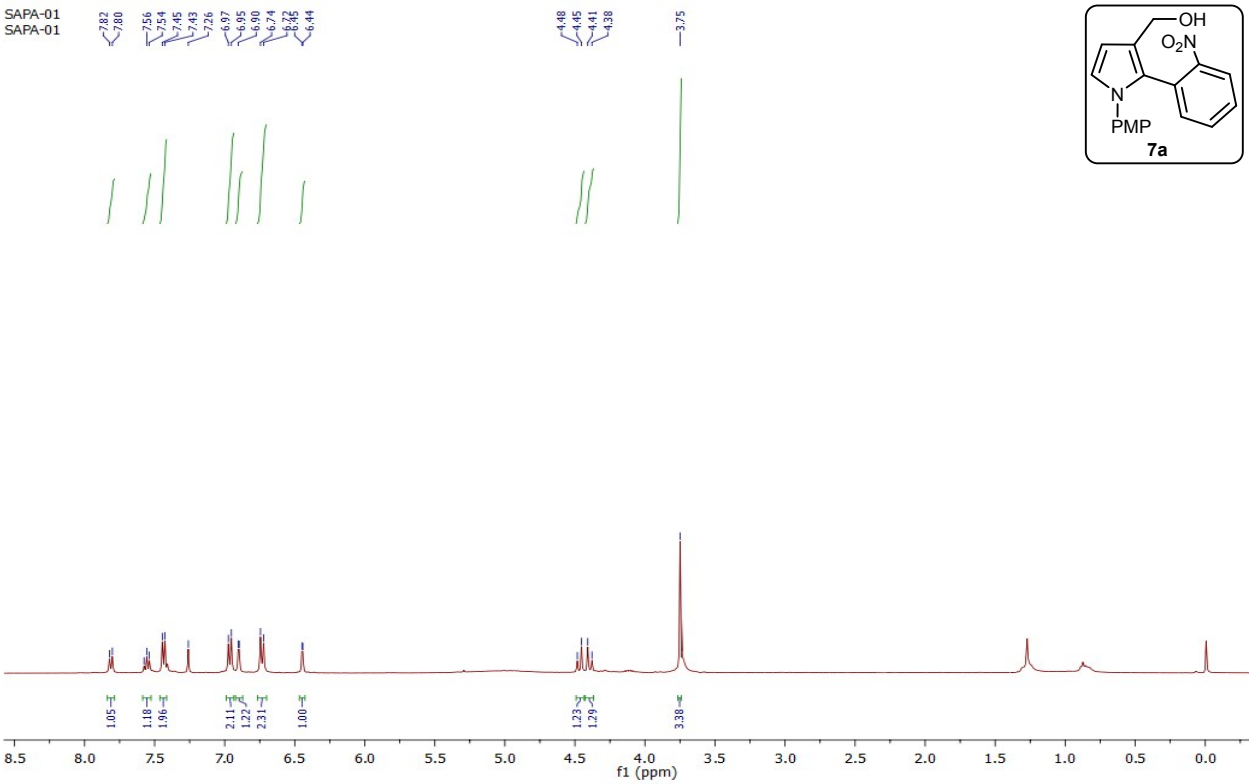
ligand (13 mg, 40 mol %) were added and further heated at 110 °C for additional 3 h under an N_2 atmosphere. Progress of this reaction was monitored by TLC. The reaction was cooled to rt and quenched with water (8.0 mL) and extracted with EtOAc (3 × 8.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuo. The crude mass was purified using silica-gel column chromatography by eluting with hexane/EtOAc to afford **20** as yellow pasty liquid (93 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.56 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.28 – 7.33 (m, 1H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.08 – 7.14 (m, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.74 (d, *J* = 1.8 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.47 (d, *J* = 8.9 Hz, 2H), 6.25 (dd, *J* = 2.8, 1.8 Hz, 1H), 5.80 (s, 1H), 3.81 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.62, 151.97, 142.23, 141.30, 134.14, 132.93, 128.44, 128.15, 127.80, 126.79, 123.57, 121.93 (2C), 119.96, 118.18, 114.77 (2C), 114.55 (2C), 114.25 (2C), 109.20, 56.26, 55.70, 55.52; HRMS (ESI): Calcd for $C_{25}H_{22}N_2O_2$ (MH^+) 383.1759; Found 383.1762.

3-(azidomethyl)-2-(2-fluorophenyl)-1-(4-methoxyphenyl)-1H-pyrrole (22):



22

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 4.63 (s, 2H), 6.46 (d, *J* = 2.5 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.96 (d, *J* = 9.3 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.20 – 7.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.32, 56.04, 109.20, 113.94 (2C), 115.49, 115.72, 123.44, 123.84, 124.13, 125.16, 126.23 (2C), 129.58, 132.98, 133.31, 158.11, 161.42; IR (KBr)/cm^{-1} 2965, 2052, 1612, 1512, 1466, 1319, 1134, 1034, 964; HRMS (ESI): Calcd for $C_{18}H_{15}FN_4O$ ($M\text{-}H^+$) 322.1308; Found 322.1312.


SAPA-01
SAPA-01
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7.56
7.54
7.45
7.43
7.26
6.97
6.95
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6.74
6.72
6.45
6.44
4.48
4.45
4.41
4.38
3.75
1.05
1.18
1.96
2.11
1.22
2.31
1.00
1.23
1.29
3.38
8.5
8.0
7.5
7.0
6.5
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4.5
4.0
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3.0
2.5
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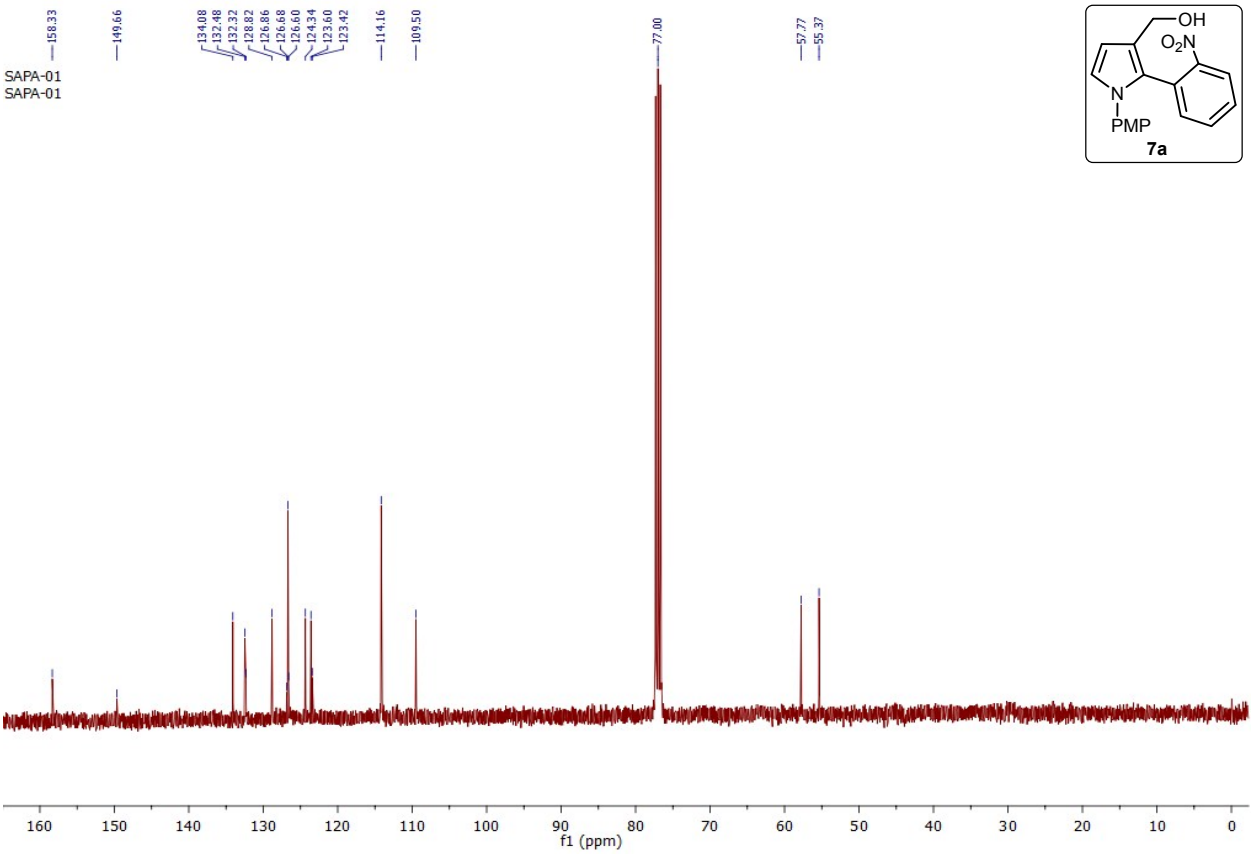
0.0
f1 (ppm)
OH
O2N
N
PMP
7a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20
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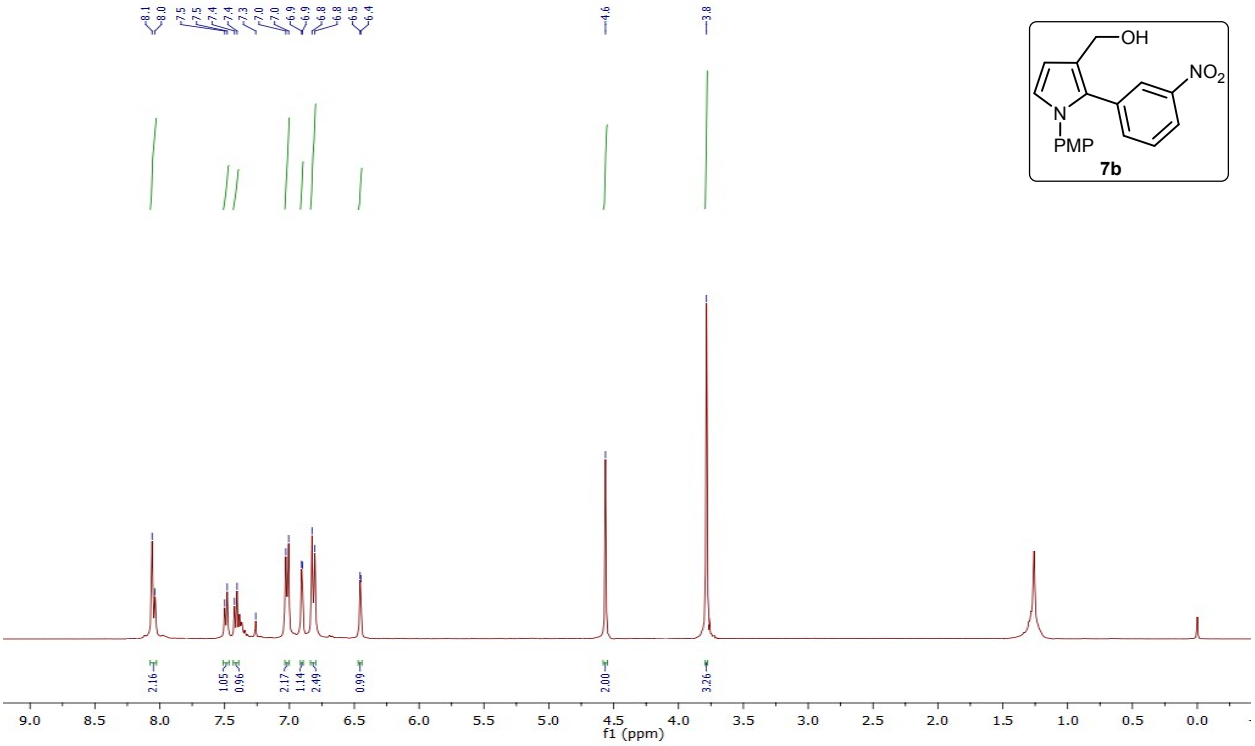
N
PMP
7a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3.8
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0.99
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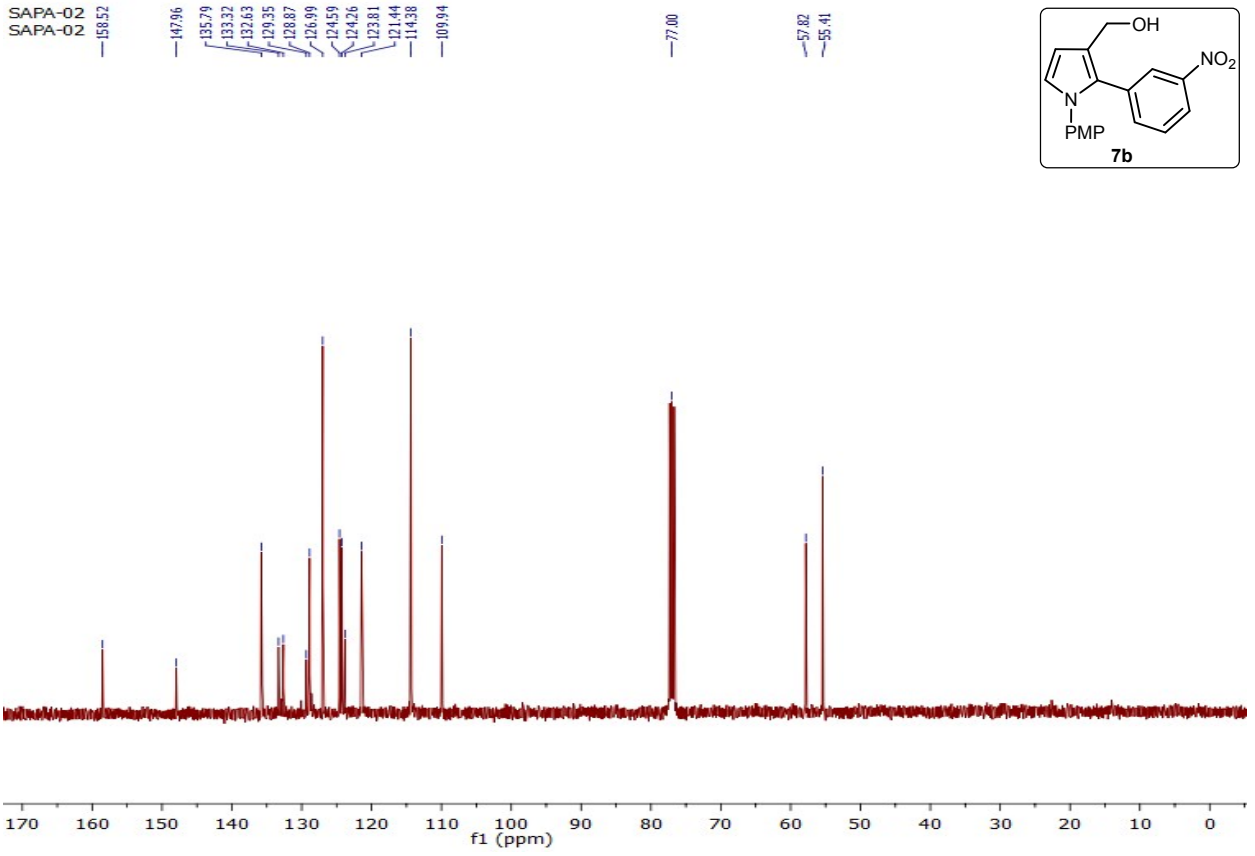
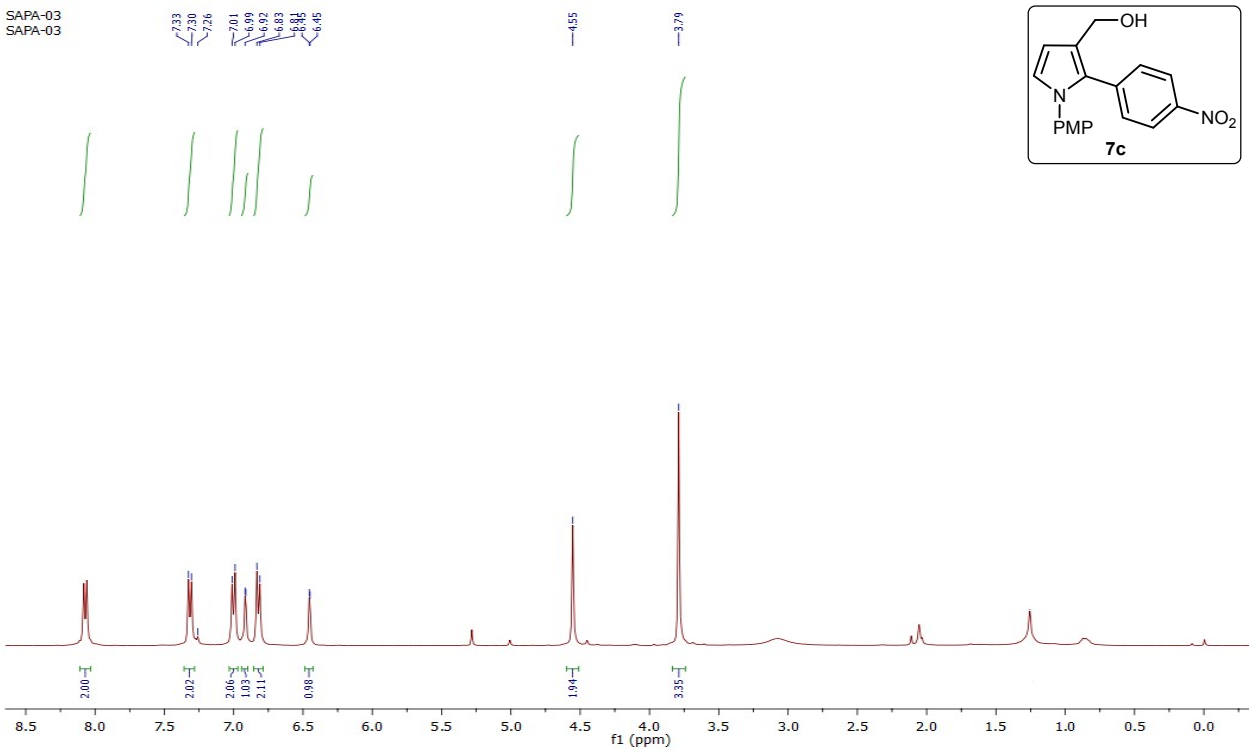
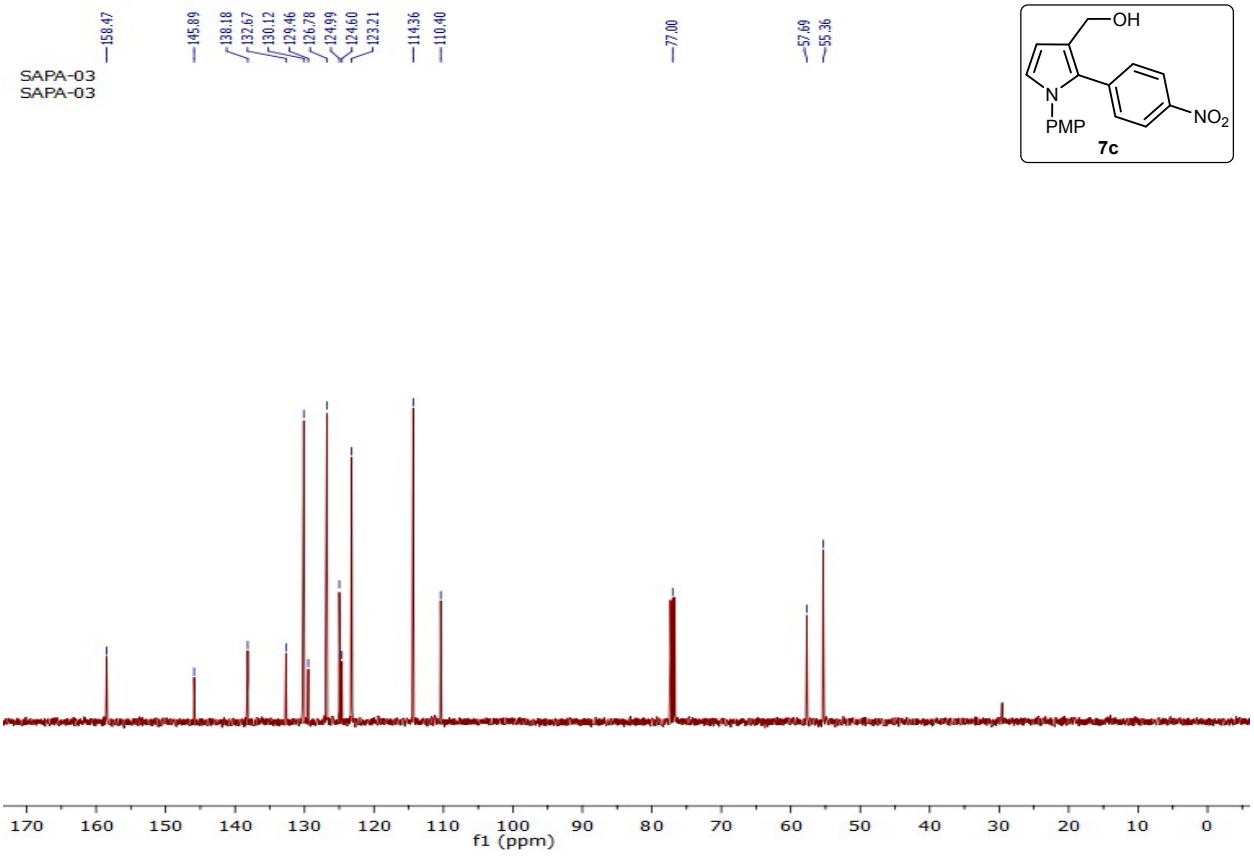
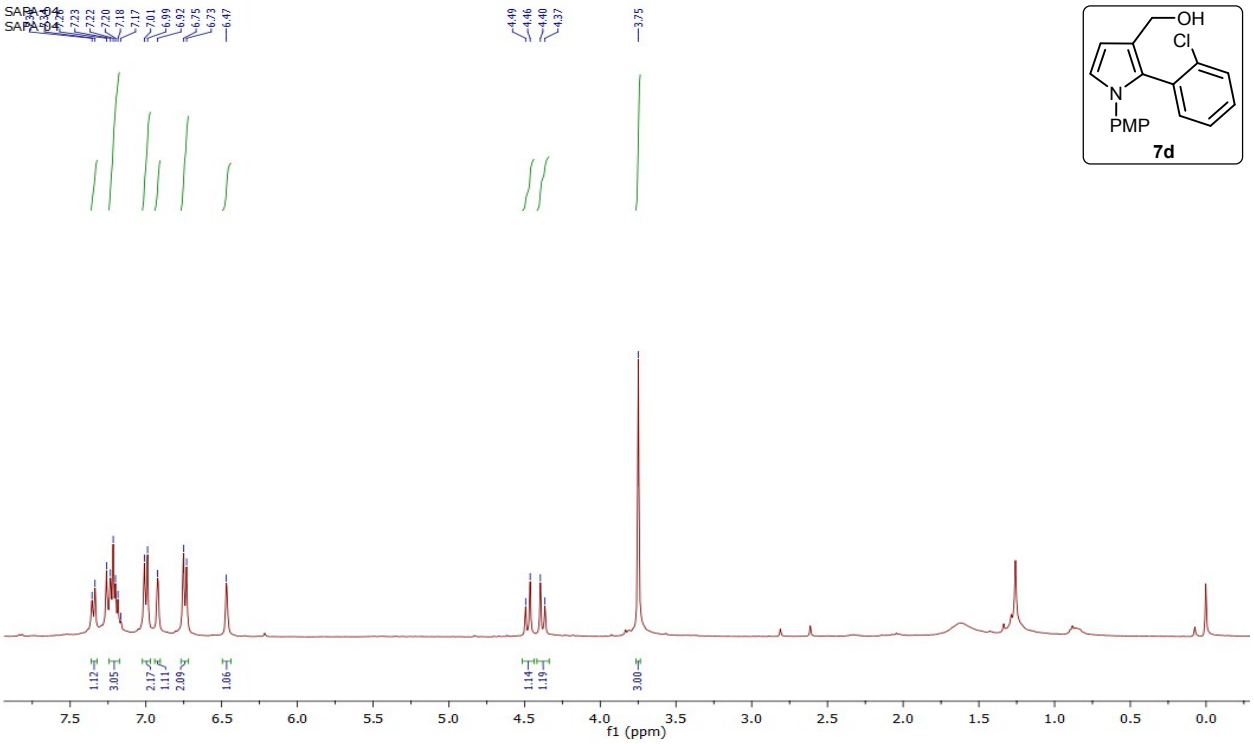
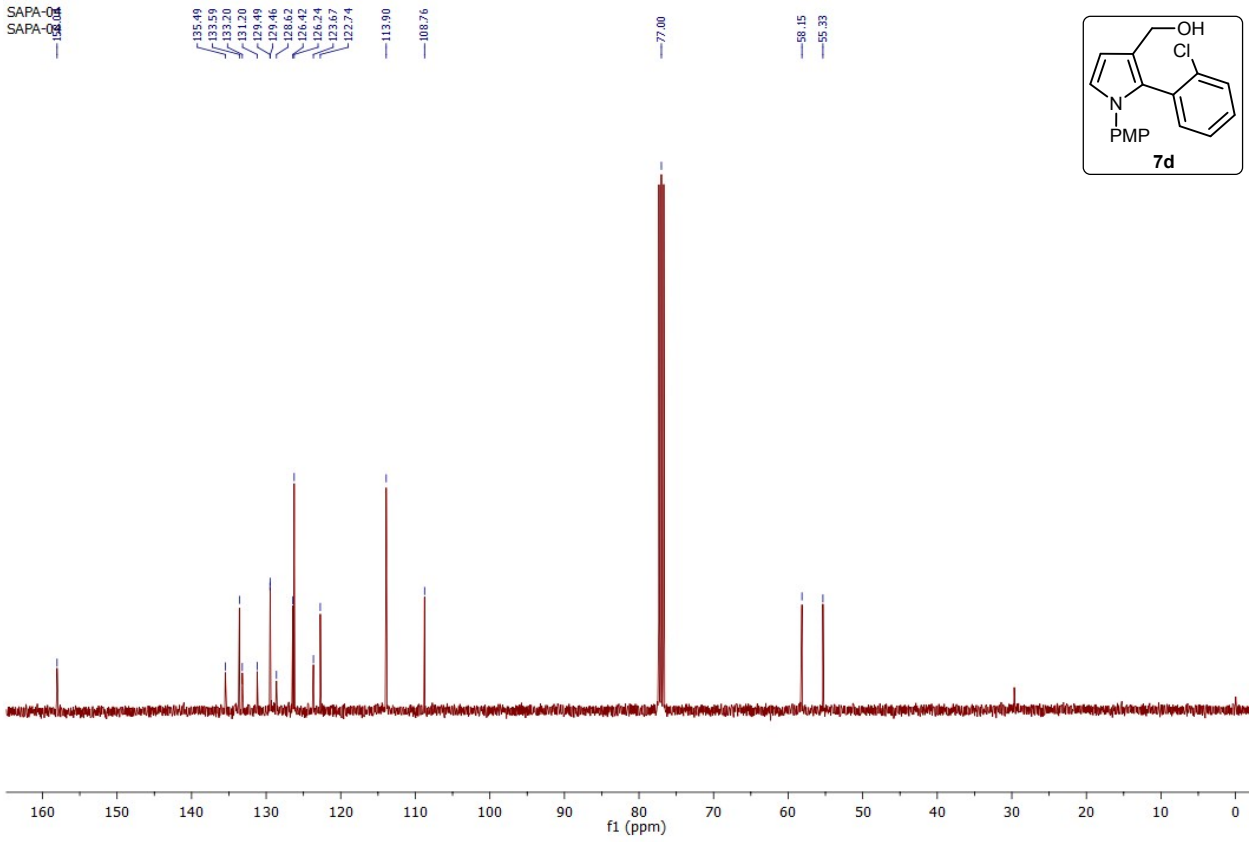
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

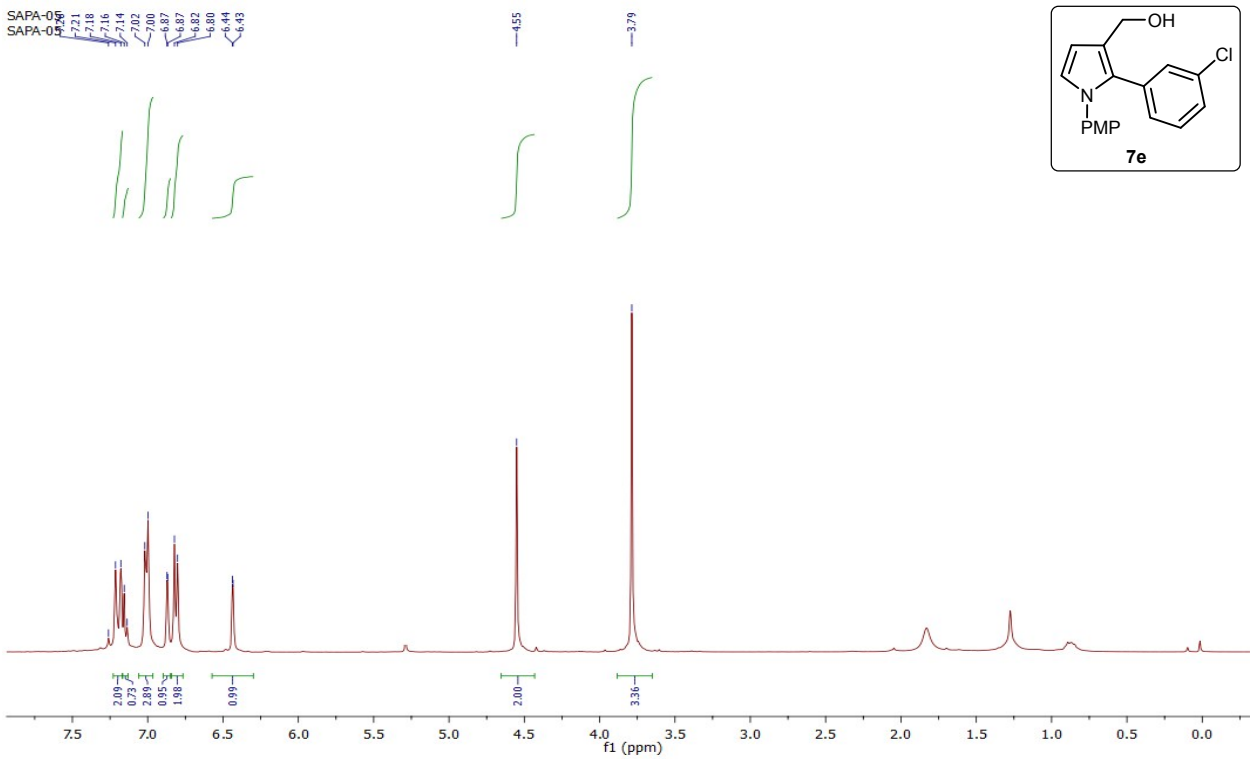

SAPA-02
SAPA-02
158.52
147.96
135.79
133.32
132.63
129.35
128.87
126.99
124.59
124.26
123.81
121.44
114.38
109.94
77.00
57.82
55.41
OH
NO2
N
PMP
7b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

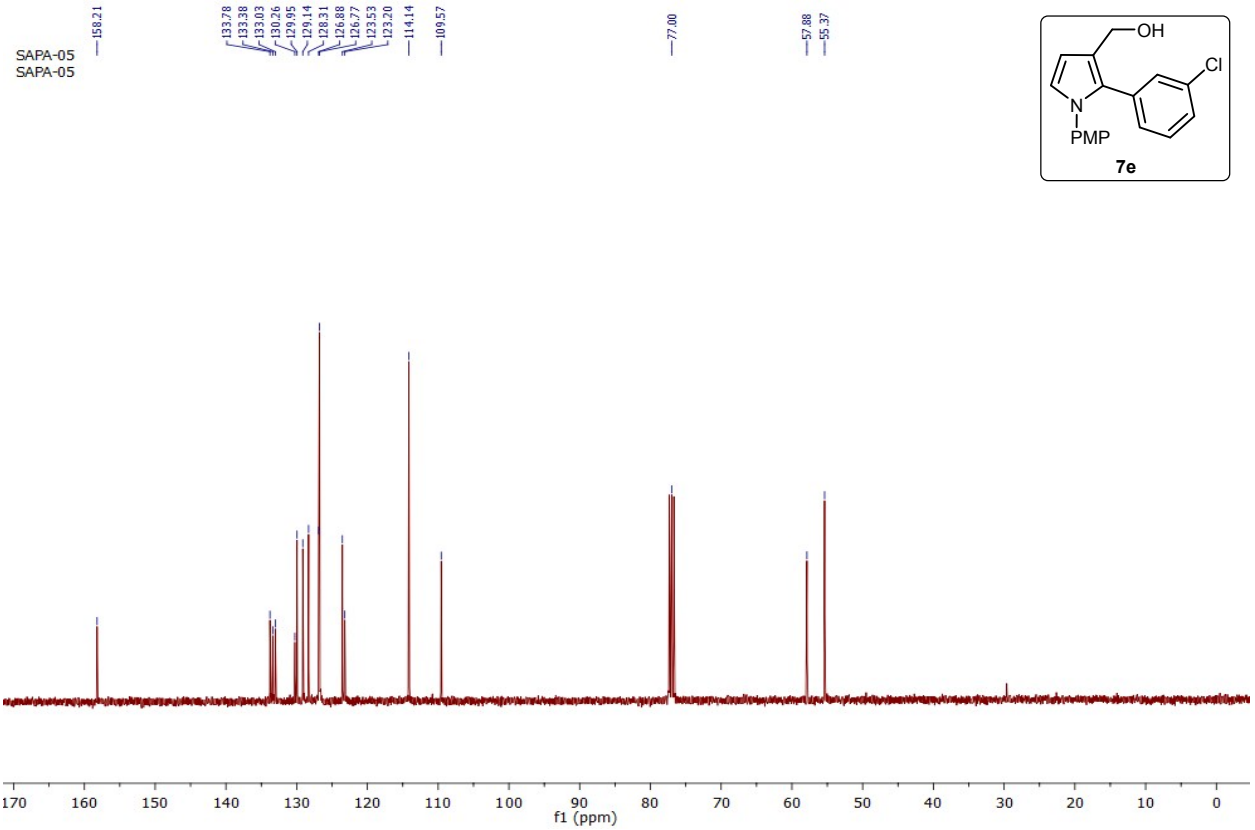

SAPA-03
SAPA-03
7.33
7.30
7.26
7.01
6.99
6.92
6.83
6.81
6.45
4.55
3.79
OH
N
PMP
NO2
7c
2.00
2.02
2.06
1.03
2.11
0.98
1.94
3.35
f1 (ppm)

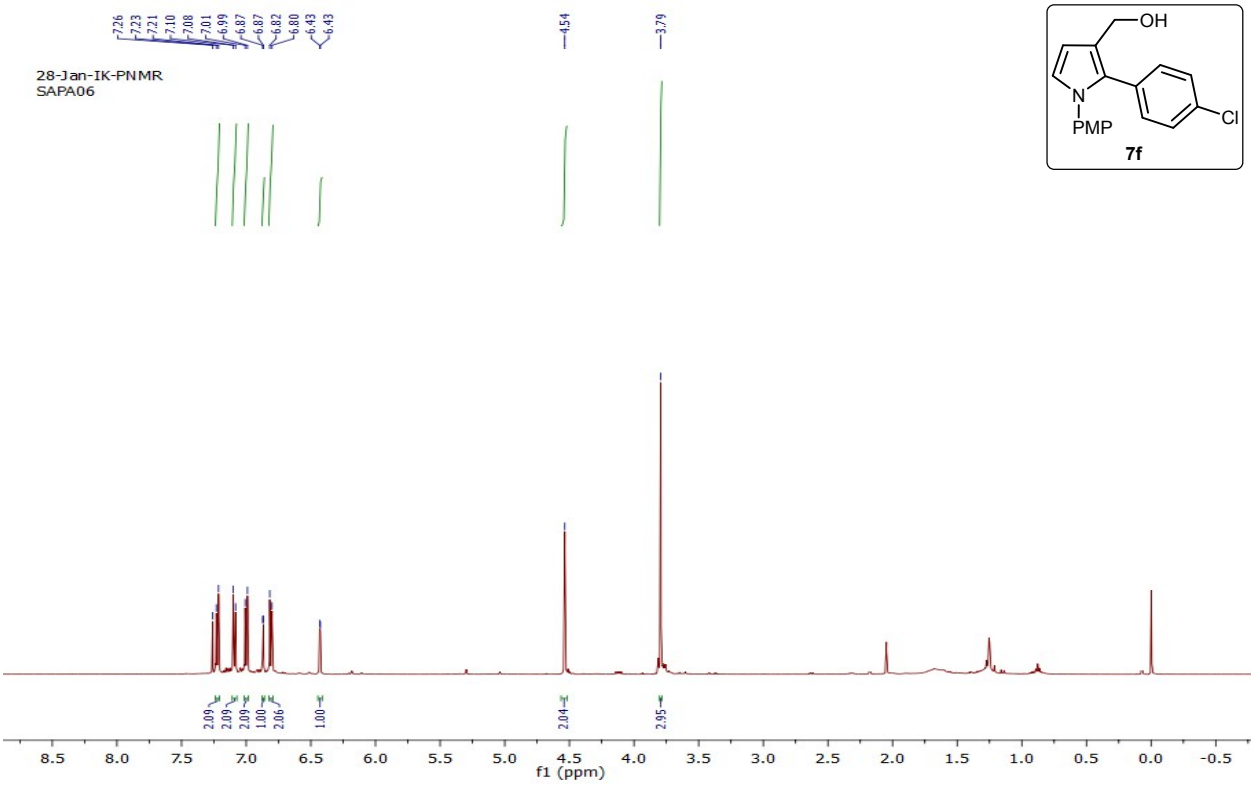

158.47
145.89
138.18
132.67
130.12
129.46
126.78
124.99
124.60
123.21
114.36
110.40
77.00
57.69
55.36
SAPA-03
SAPA-03
OH
N
PMP
NO2
7c
f1 (ppm)

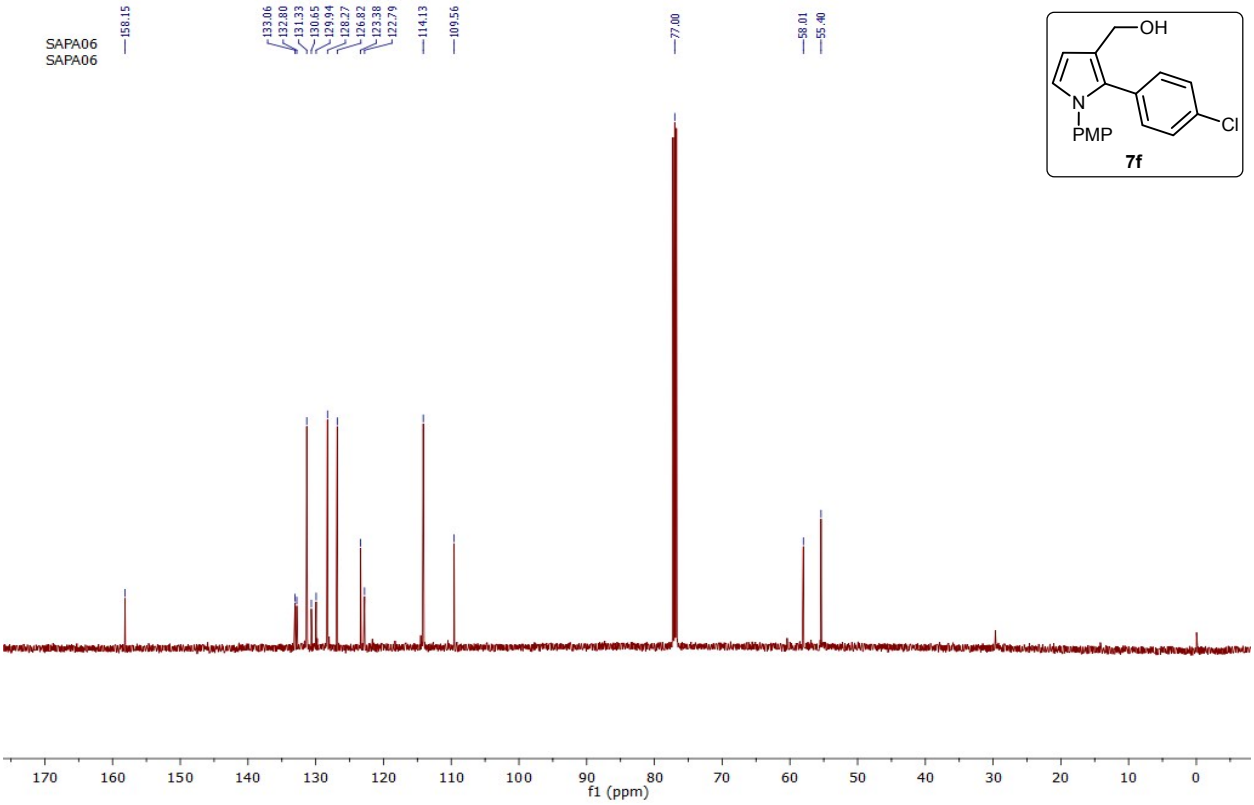

SAPA-04
SAPA-04
7.23
7.22
7.20
7.18
7.17
7.01
6.99
6.92
6.75
6.73
6.47
4.49
4.46
4.40
4.37
3.75
OH
Cl
N
PMP
7d
1.12
3.05
2.17
1.11
2.09
1.06
1.14
1.19
3.00
f1 (ppm)

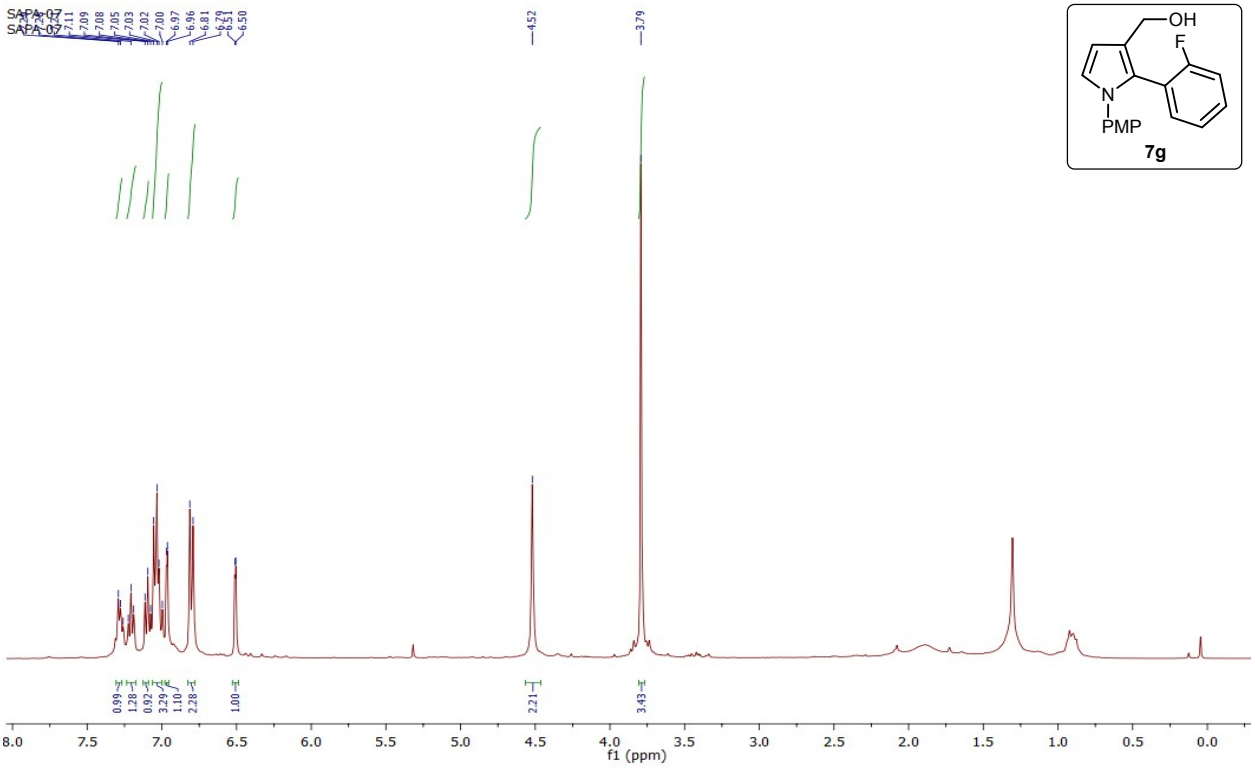

SAPA-04
SAPA-04
135.49
133.59
133.20
131.20
129.49
129.46
128.62
126.42
126.24
123.67
122.74
113.90
108.76
77.00
58.15
55.33
OH
Cl
N
PMP
7d
f1 (ppm)

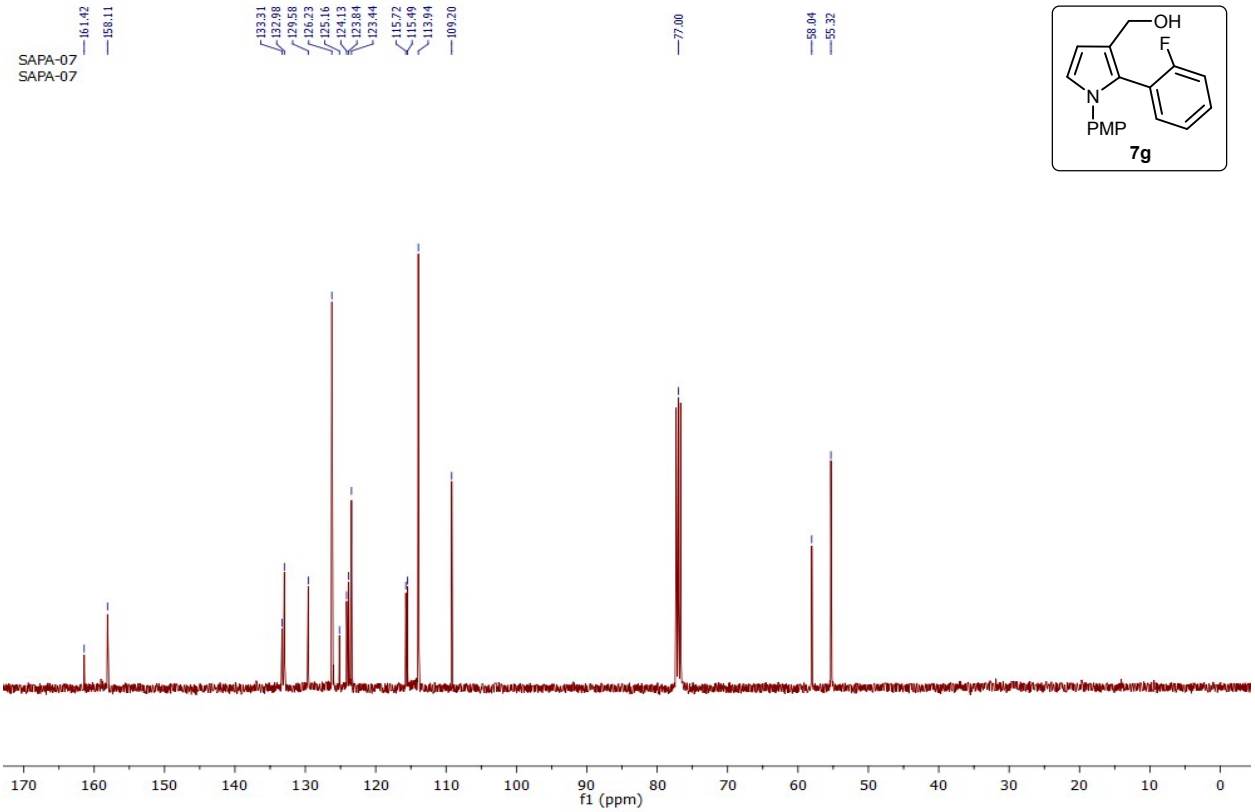

SAPA-05
SAPA-05
7.24
7.21
7.18
7.16
7.14
7.02
7.00
6.87
6.87
6.82
6.80
6.44
6.43
4.55
3.79
OH
Cl
N
PMP
7e
2.09
0.73
2.89
0.95
1.98
0.99
2.00
3.36
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

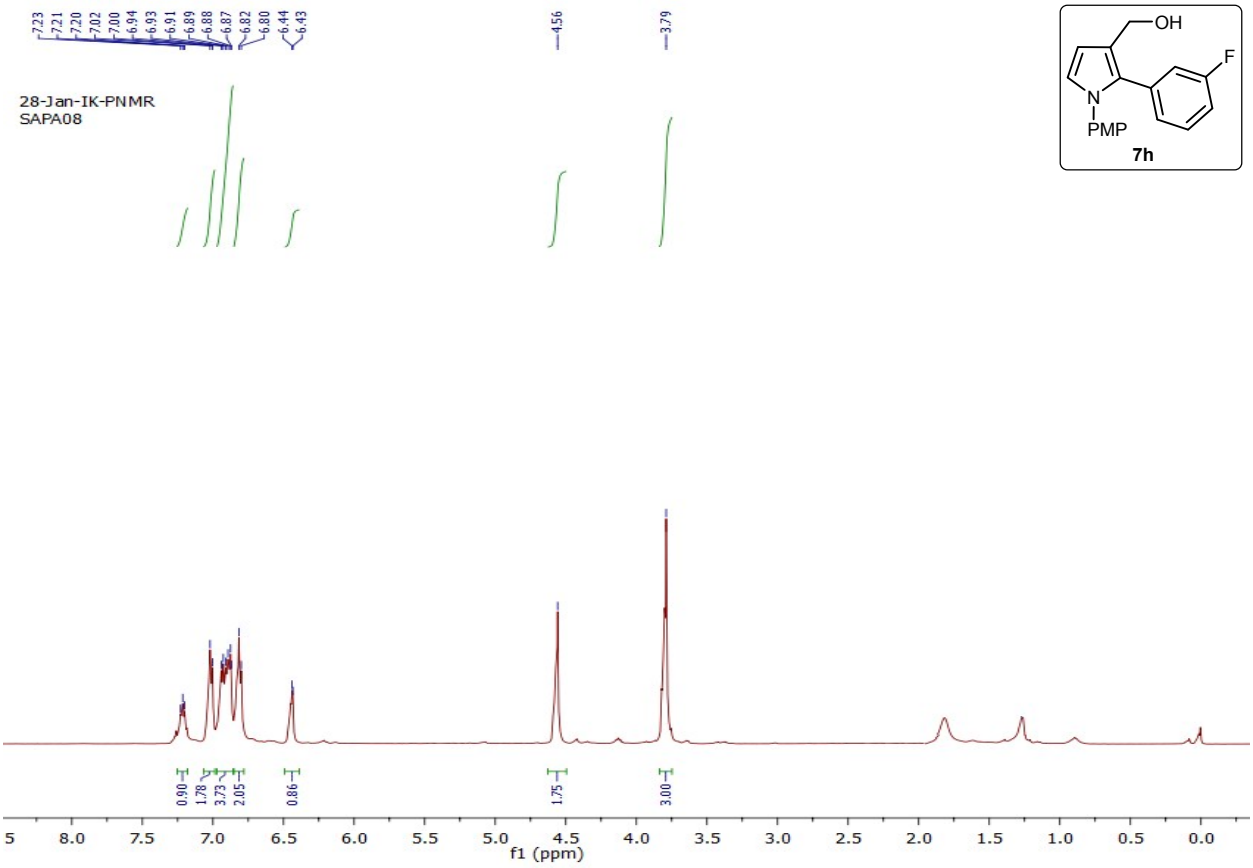

SAPA-05
SAPA-05
158.21
133.78
133.38
133.03
130.26
129.95
129.14
128.31
126.88
126.77
123.53
123.20
114.14
109.57
77.00
57.88
55.37
OH
Cl
N
PMP
7e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

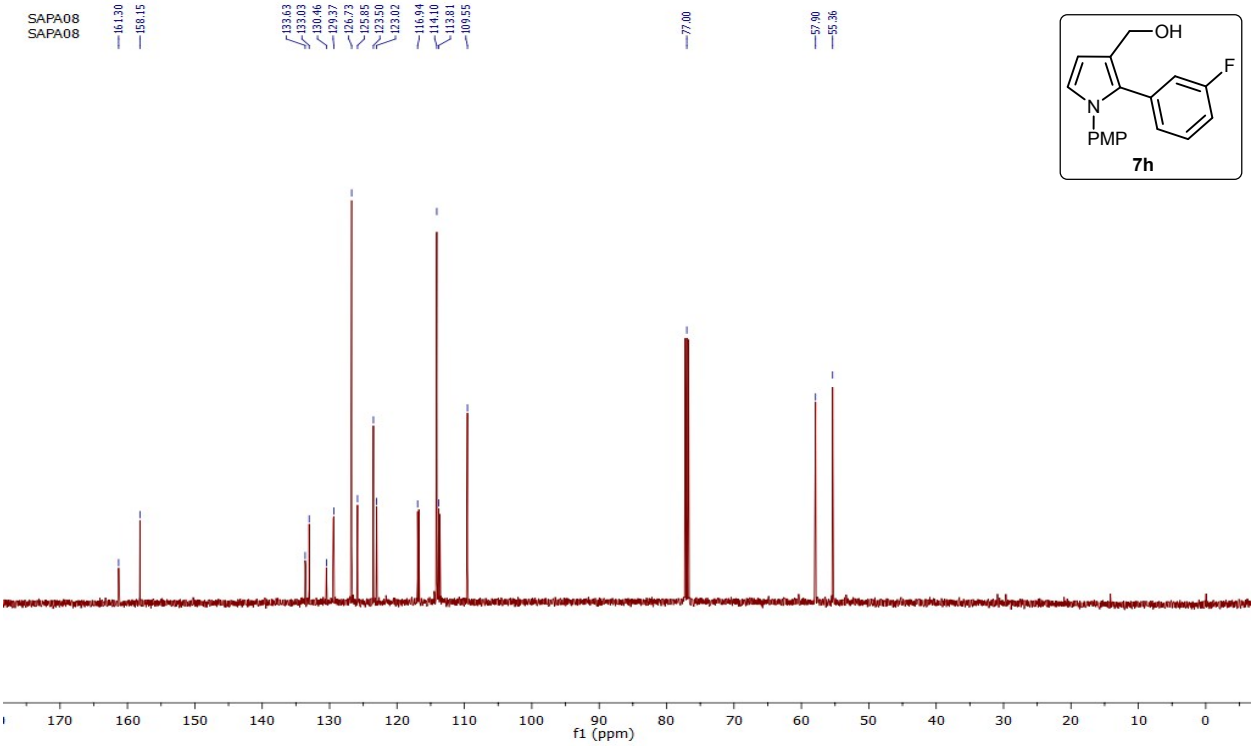

7.26
7.23
7.21
7.10
7.08
7.01
6.99
6.87
6.87
6.82
6.80
6.43
6.43
4.54
3.79
28-Jan-IK-PNMR
SAPA06
OH
N
PMP
Cl
7f
2.09
2.09
2.09
1.00
2.06
1.00
2.04
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

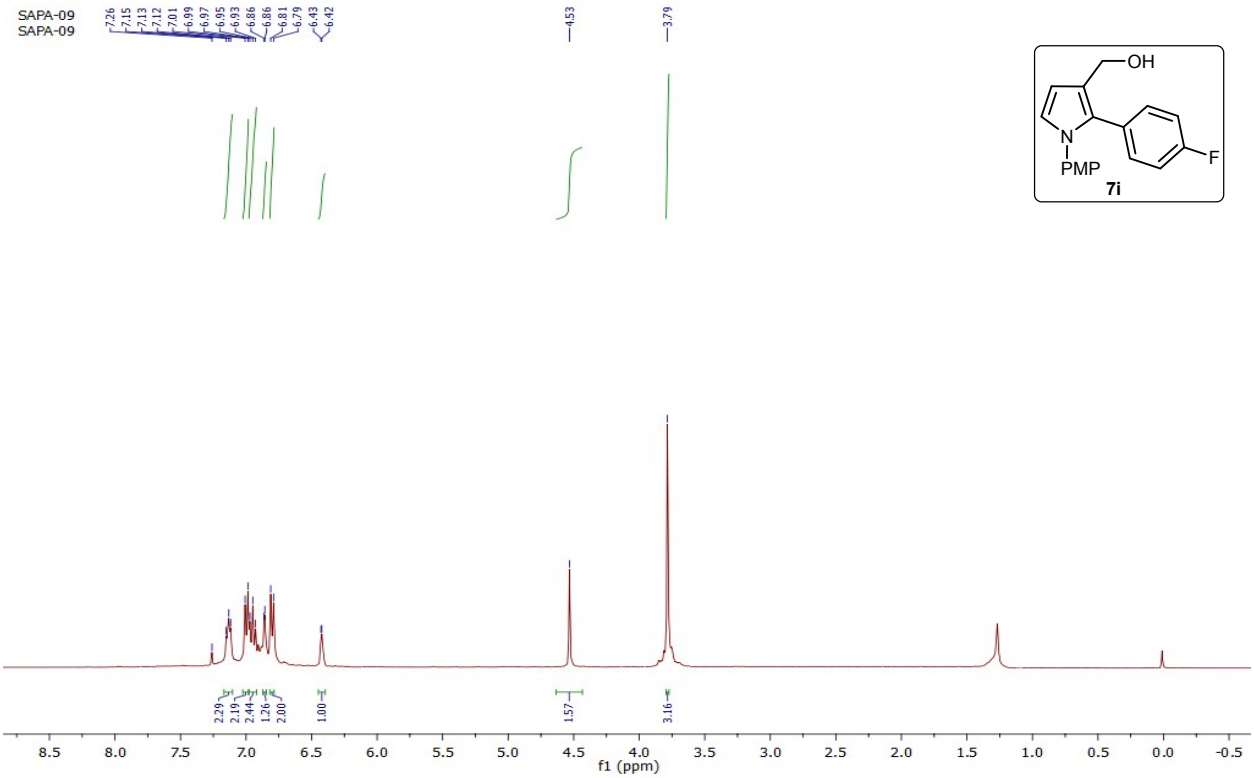

158.15
133.06
132.80
131.33
130.65
129.94
128.27
126.82
123.38
122.79
114.13
109.56
77.00
58.01
55.40
SAPA06
SAPA06
OH
N
PMP
Cl
7f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

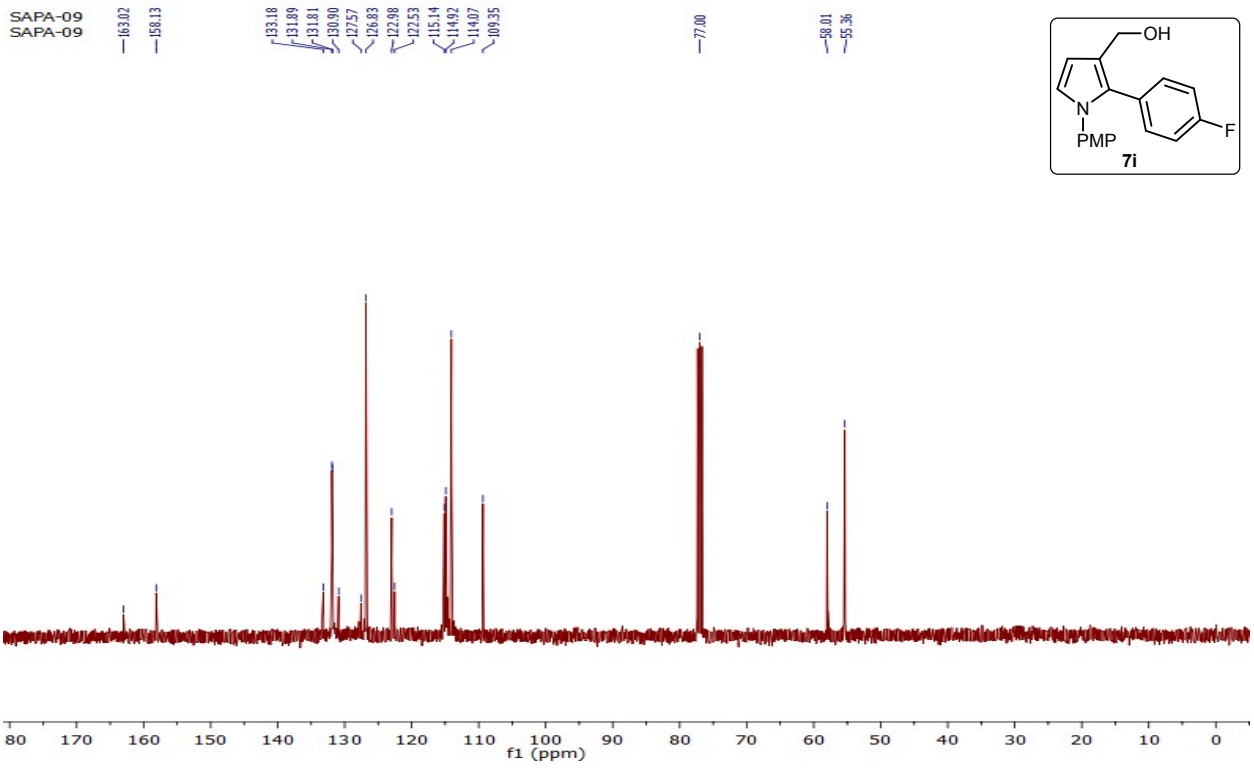

SAPA-07
SAPA-07
7.11
7.09
7.08
7.05
7.03
7.02
7.00
6.97
6.96
6.81
6.51
6.50
4.52
3.79
0.99
1.28
0.92
3.29
1.10
2.28
1.00
2.21
3.43
f1 (ppm)
OH
F
N
PMP
7g

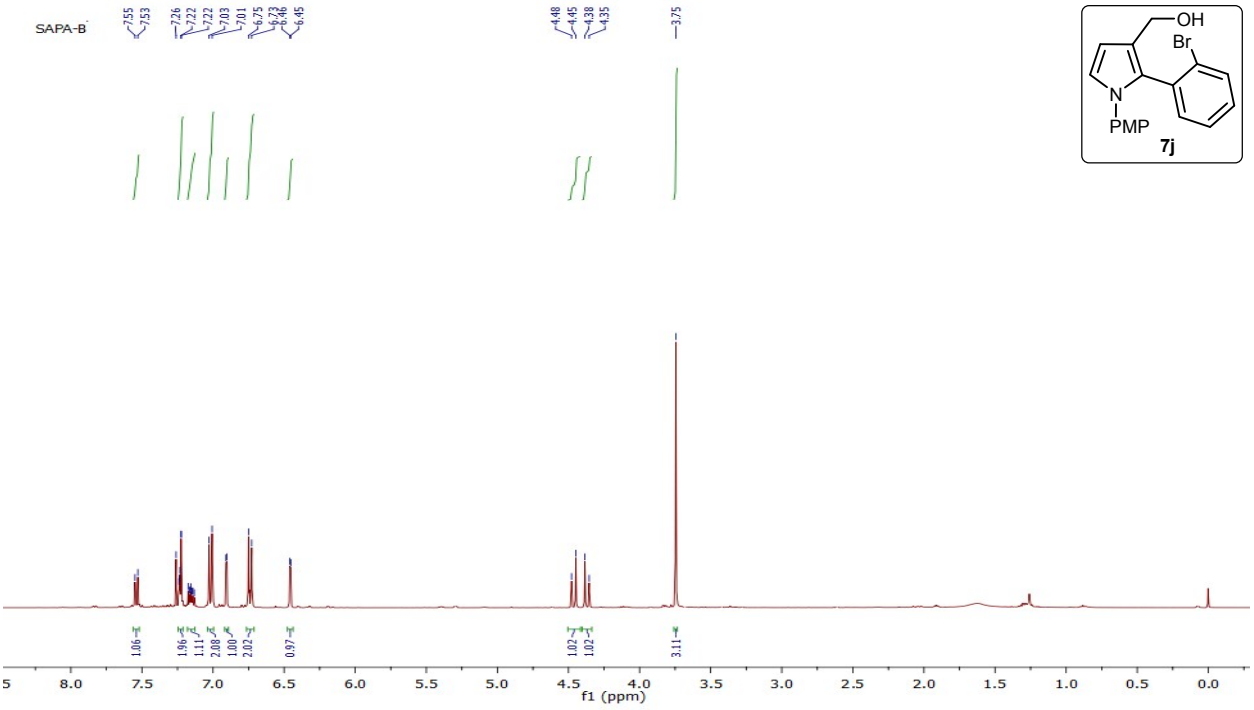

SAPA-07
SAPA-07
161.42
158.11
133.31
132.98
129.58
126.23
125.16
124.13
123.84
123.44
115.72
115.49
113.94
109.20
77.00
58.04
55.32
f1 (ppm)
OH
F
N
PMP
7g

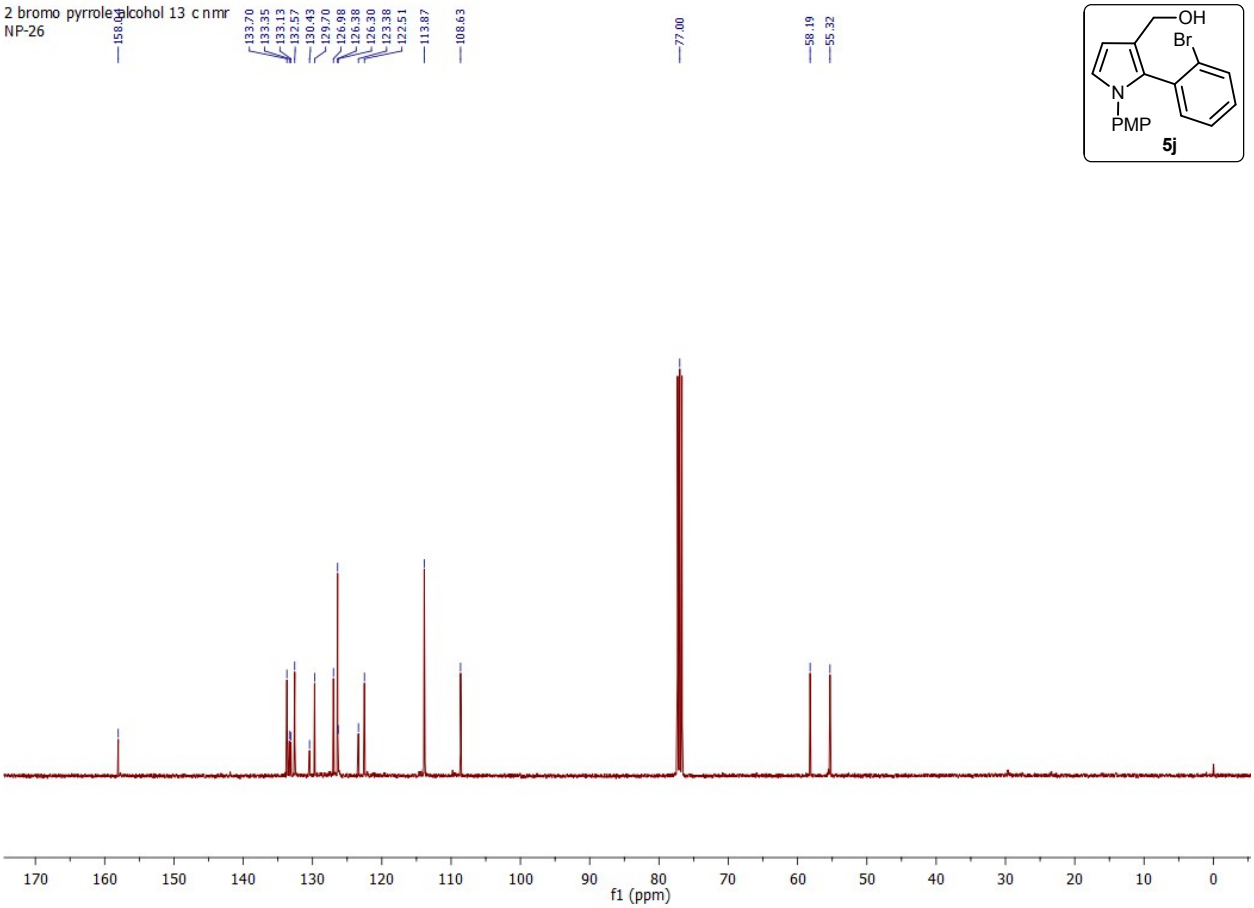

7.23
7.21
7.20
7.02
7.00
6.94
6.93
6.91
6.89
6.88
6.87
6.82
6.80
6.44
6.43
4.56
3.79
28-Jan-IK-PNMR
SAPA08
OH
F
N
PMP
7h
0.90
1.78
3.73
2.05
0.86
1.75
3.00
f1 (ppm)

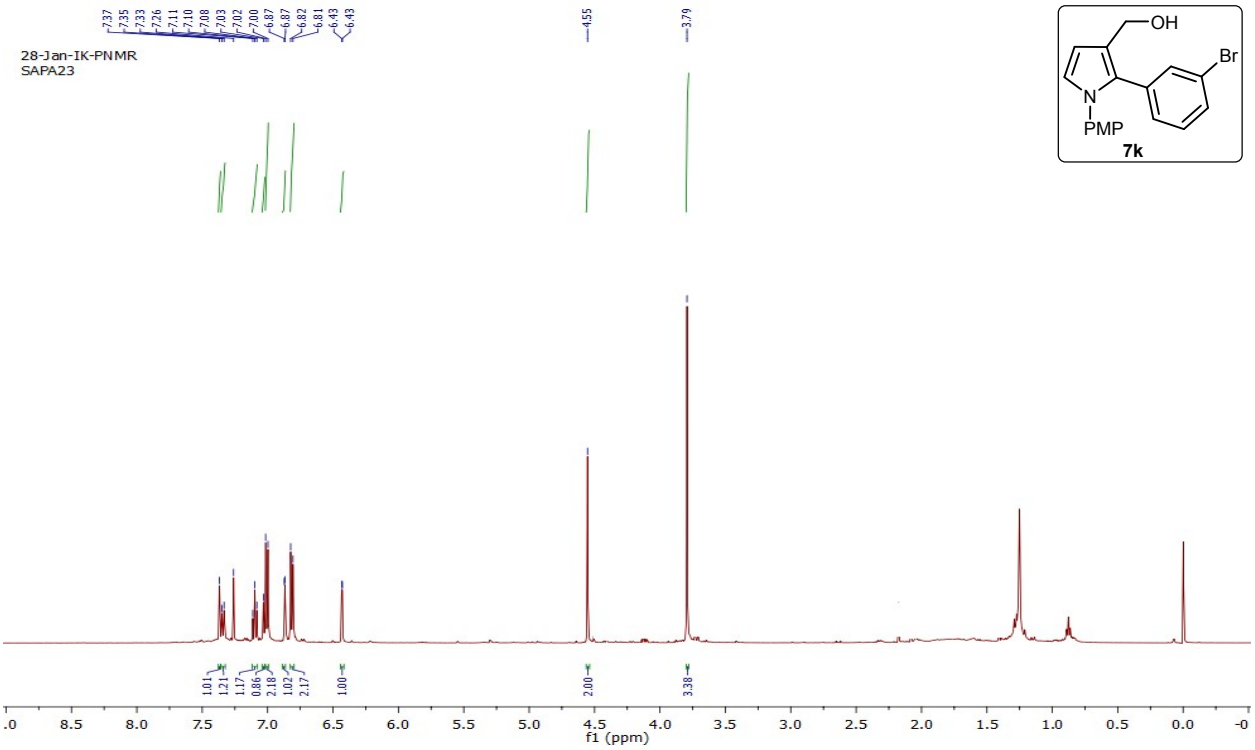

SAPA08
SAPA08
161.30
158.15
133.63
133.03
130.46
129.37
126.73
125.85
123.50
123.02
116.94
114.10
113.81
109.55
77.00
57.90
55.36
OH
F
N
PMP
7h
f1 (ppm)

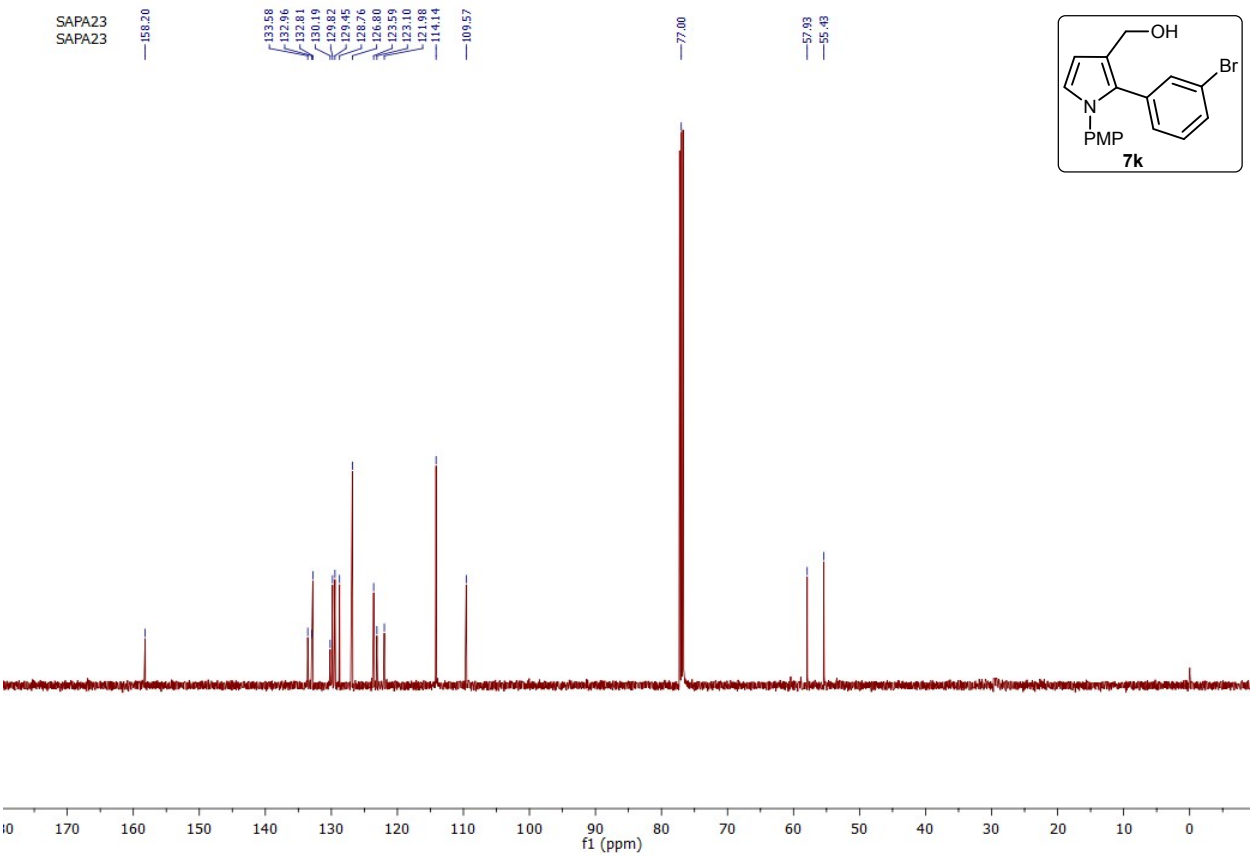

SAPA-09
SAPA-09
7.26
7.15
7.13
7.12
7.01
6.99
6.97
6.95
6.93
6.86
6.86
6.81
6.79
6.43
6.42
4.53
3.79
OH
N
PMP
F
7i
2.29
2.19
2.44
1.26
2.00
1.00
1.57
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

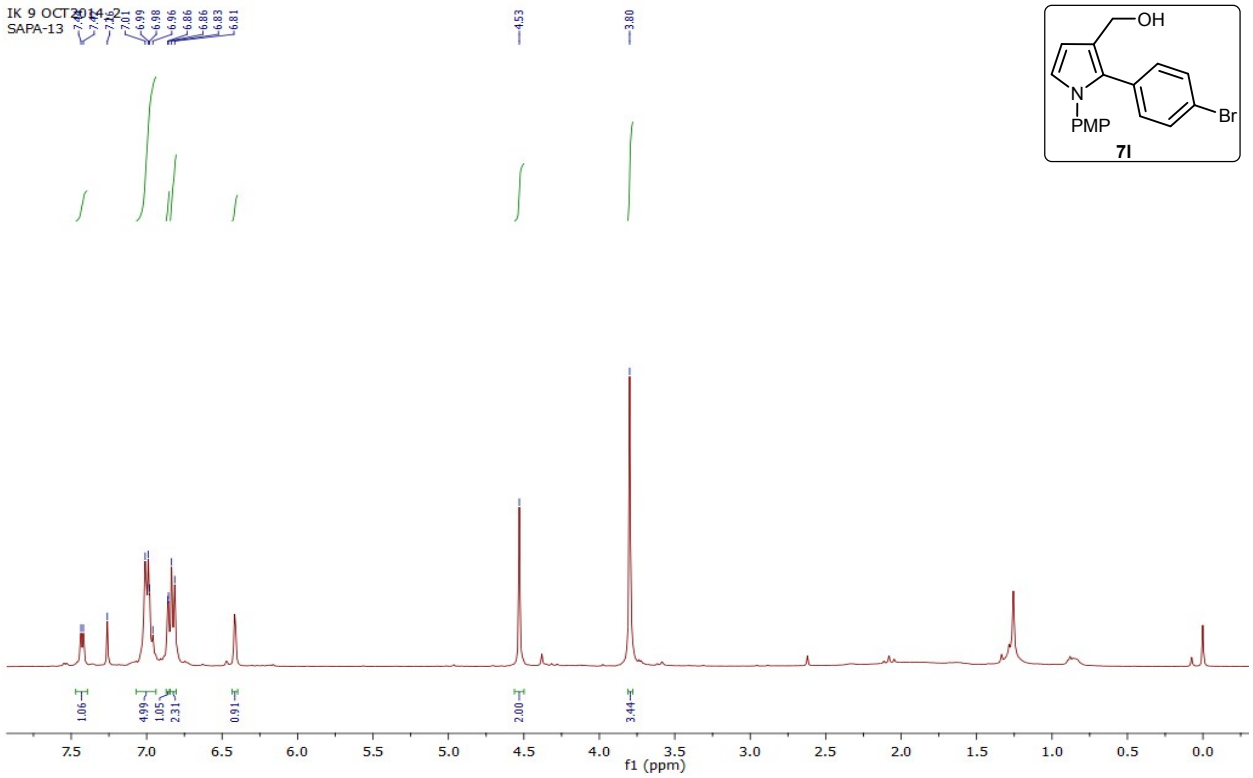

SAPA-09
SAPA-09
163.02
158.13
133.18
131.89
131.81
130.90
127.57
126.83
122.98
122.53
115.14
114.92
114.07
109.35
77.00
58.01
55.36
OH
N
PMP
F
7i
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

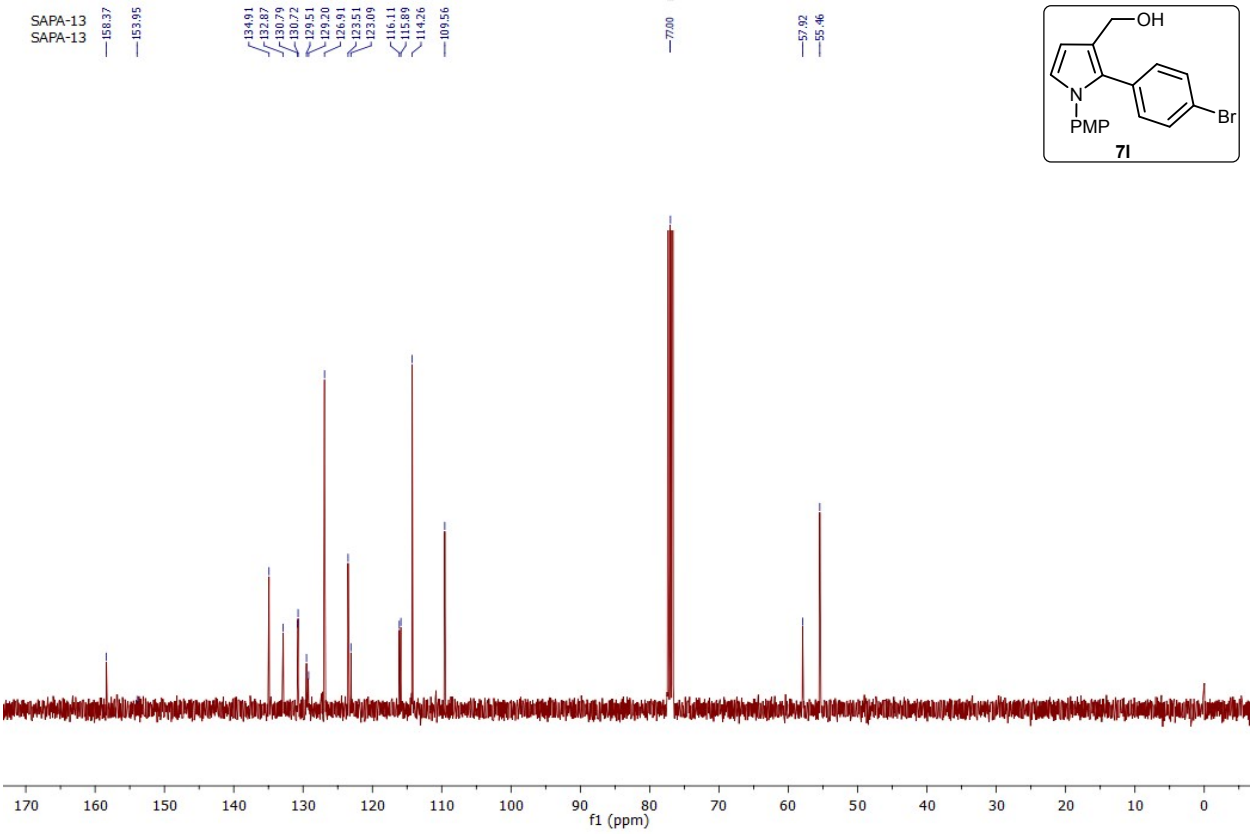

SAPA-B
7.55
7.53
7.26
7.22
7.22
7.03
7.01
6.75
6.73
6.48
6.45
4.48
4.45
4.38
4.35
3.75
OH
Br
N
PMP
7j
1.06
1.96
1.11
2.08
1.00
2.02
0.97
1.02
1.02
3.11
f1 (ppm)

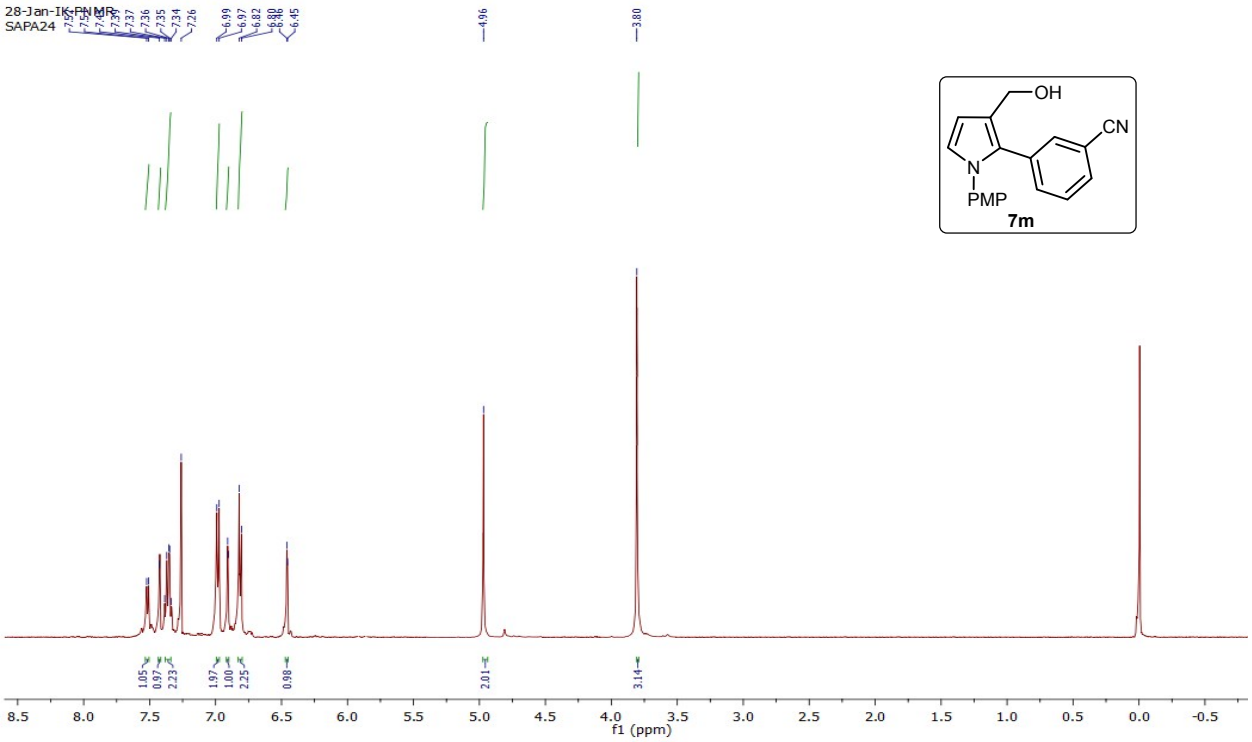

2 bromo pyrrole alcohol 13 c nmr
NP-26
158.94
133.70
133.35
133.13
132.57
130.43
129.70
126.98
126.38
126.30
123.38
122.51
113.87
108.63
77.00
58.19
55.32
OH
Br
N
PMP
5j
f1 (ppm)

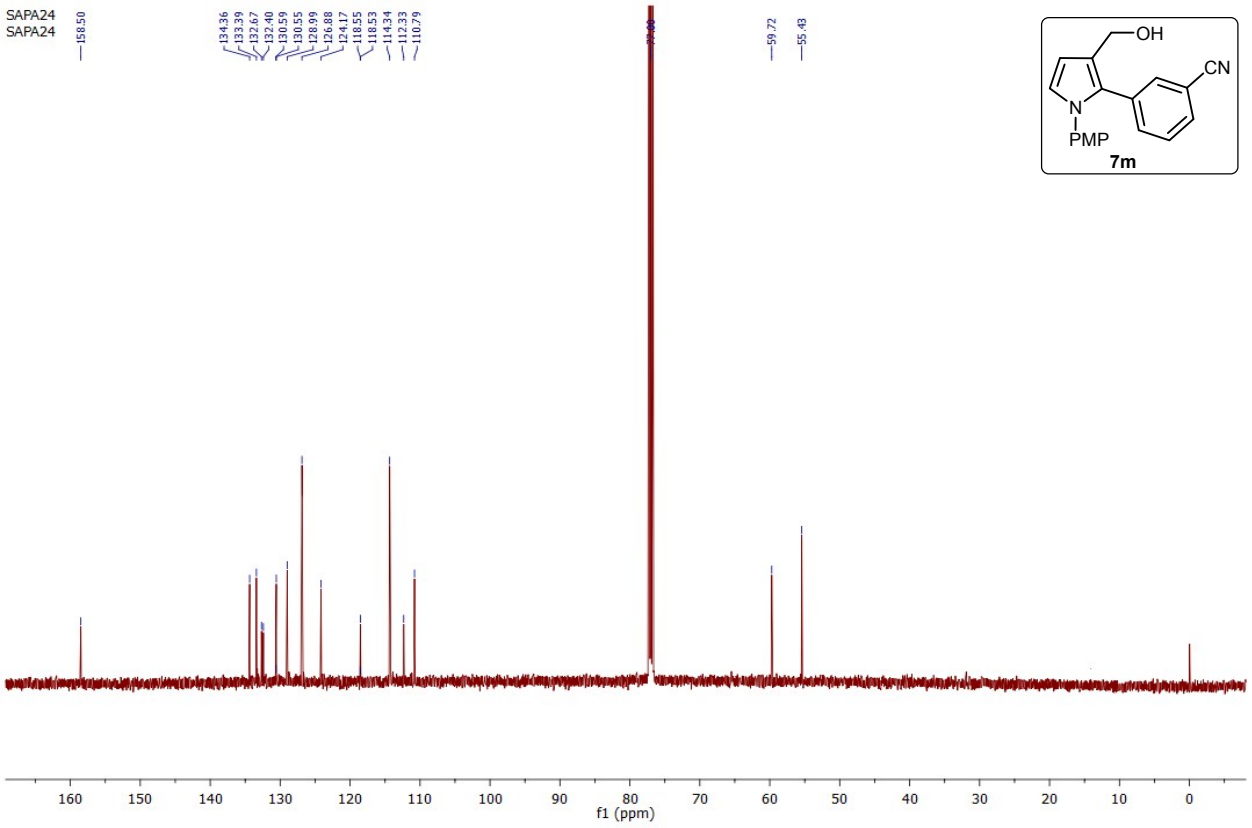

28-Jan-IK-PNMR
SAPA23
7.37
7.35
7.33
7.26
7.11
7.10
7.08
7.03
7.02
7.00
6.87
6.82
6.81
6.43
6.43
4.55
3.79
1.01
1.21
1.17
0.86
2.18
1.02
2.17
1.00
2.00
3.38
f1 (ppm)
OH
Br
N
PMP
7k

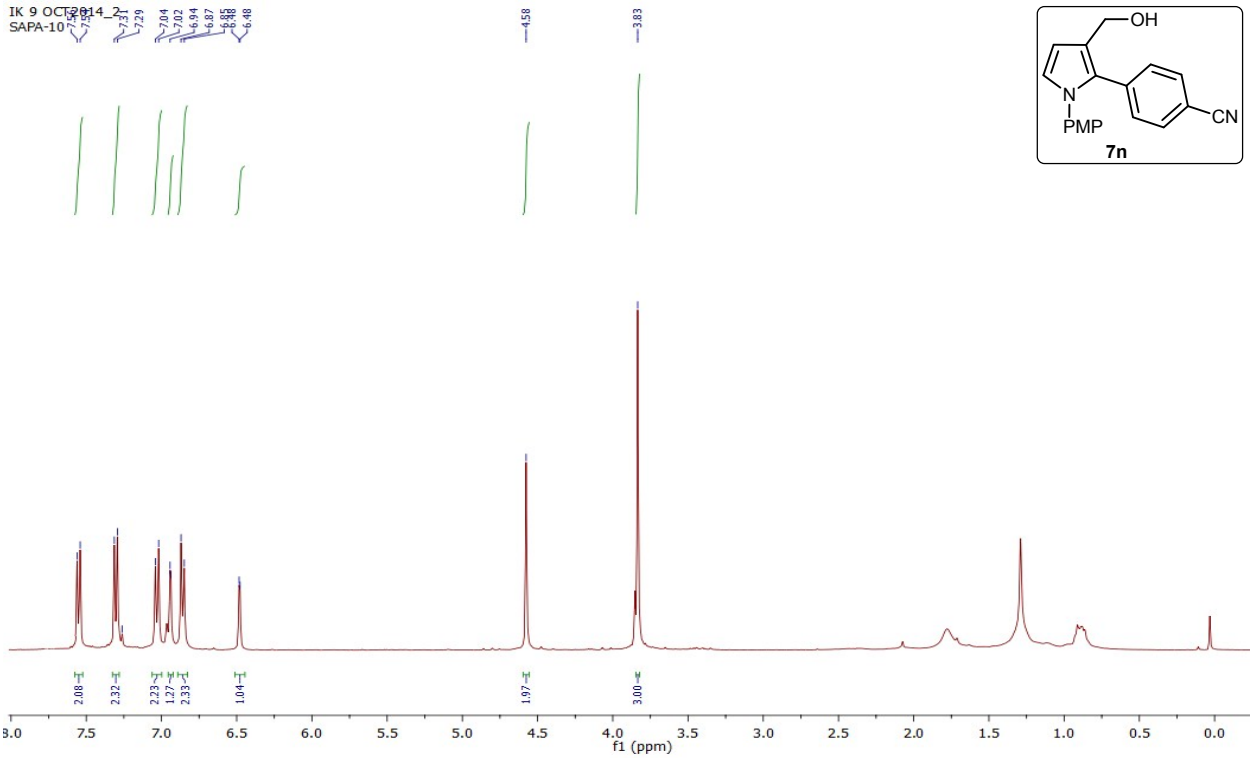

SAPA23
SAPA23
158.20
133.58
132.96
132.81
130.19
129.82
129.45
128.76
126.80
123.59
123.10
121.98
114.14
109.57
77.00
57.93
55.43
f1 (ppm)
OH
Br
N
PMP
7k

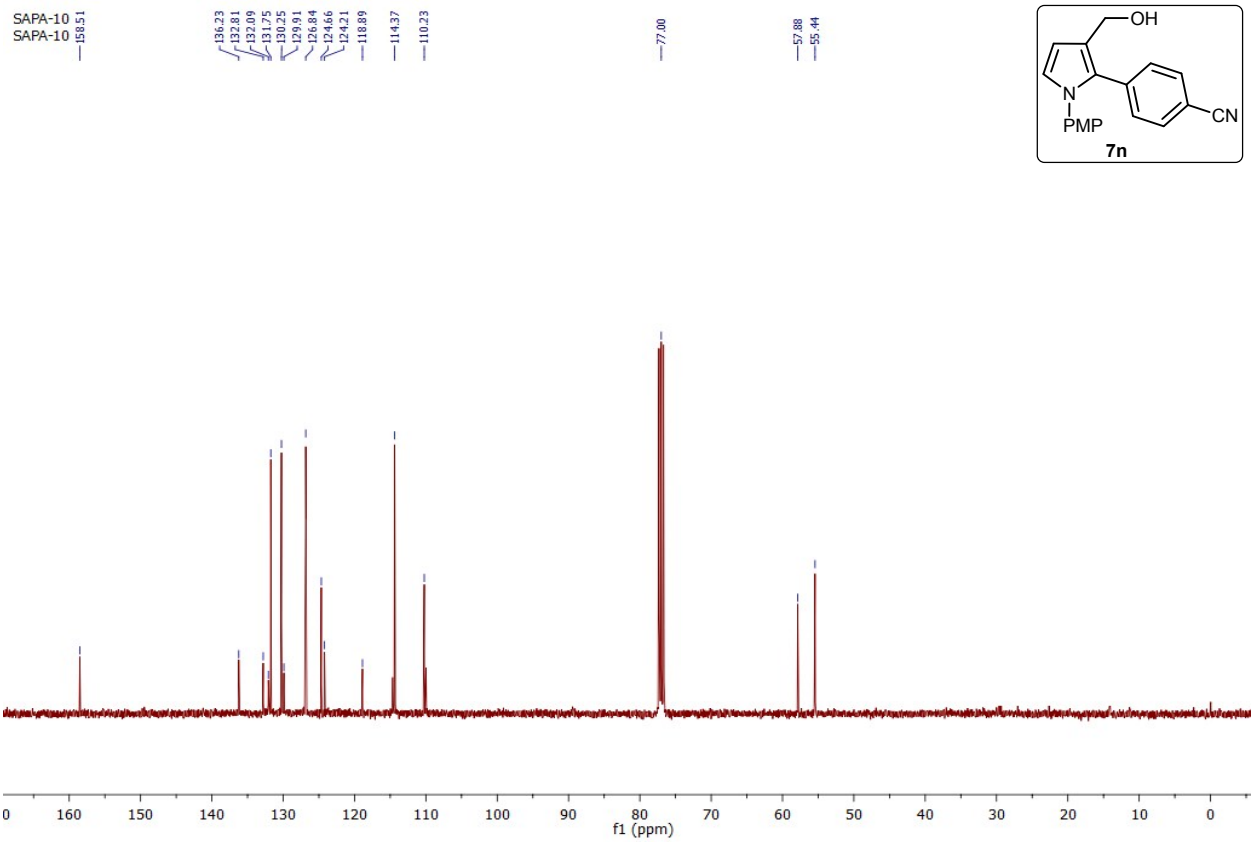

IK 9 OCT2014
SAPA-13
4.53
3.80
OH
N
PMP
Br
7l
1.06
4.99
1.05
2.31
0.91
2.00
3.44
f1 (ppm)

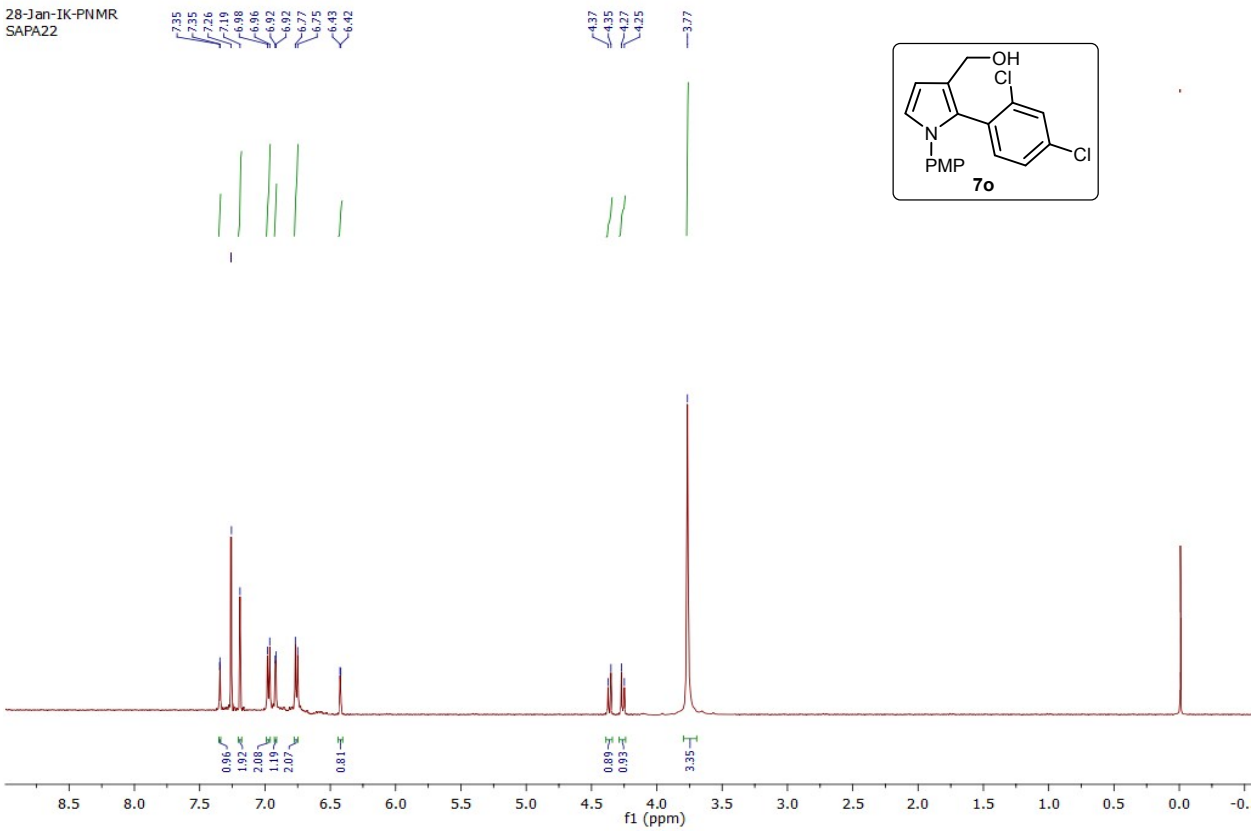

SAPA-13
SAPA-13
158.37
153.95
134.91
132.87
130.79
130.72
129.51
129.20
126.91
123.51
123.09
116.11
115.89
114.26
109.56
77.00
57.92
55.46
OH
N
PMP
Br
7l
f1 (ppm)

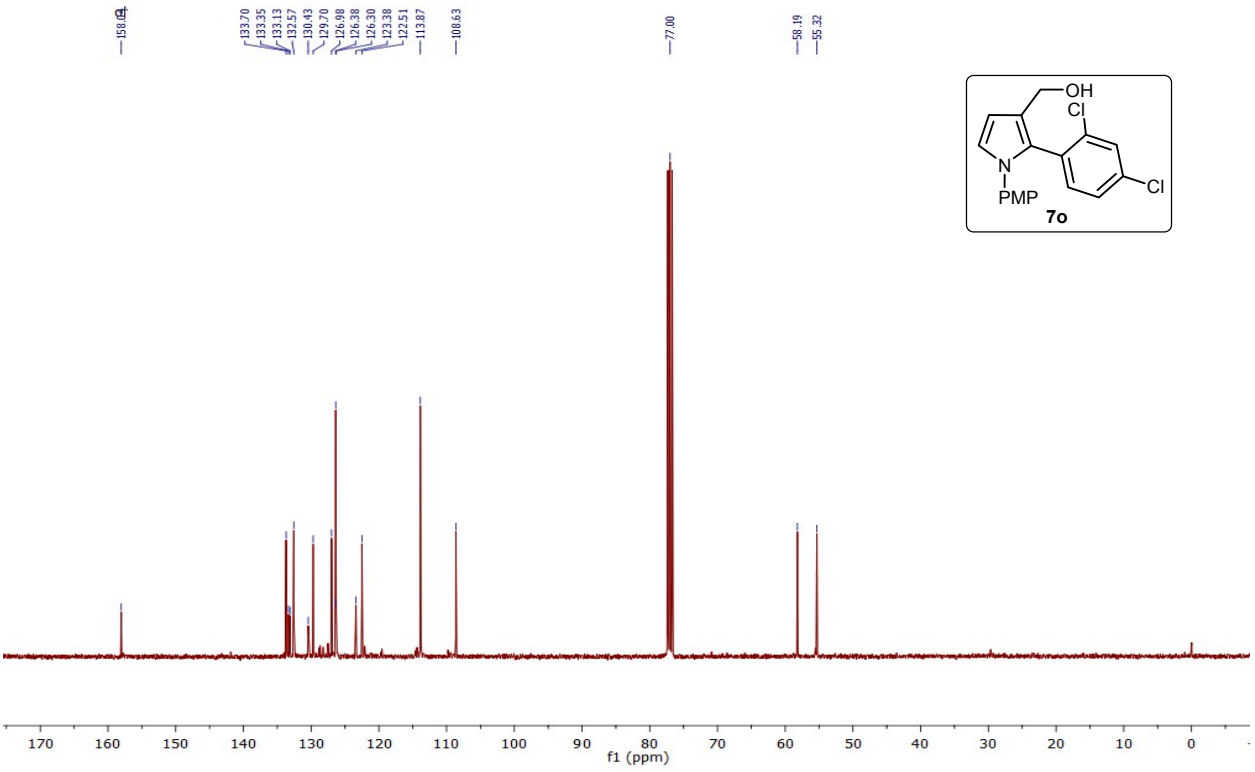

28-Jan-IK-PNMR
SAPA24
7.52
7.51
7.48
7.39
7.37
7.36
7.35
7.34
7.26
6.99
6.97
6.82
6.80
6.80
6.45
4.96
3.80
OH
CN
N
PMP
7m
1.05
0.97
2.23
1.97
1.00
2.25
0.98
2.01
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

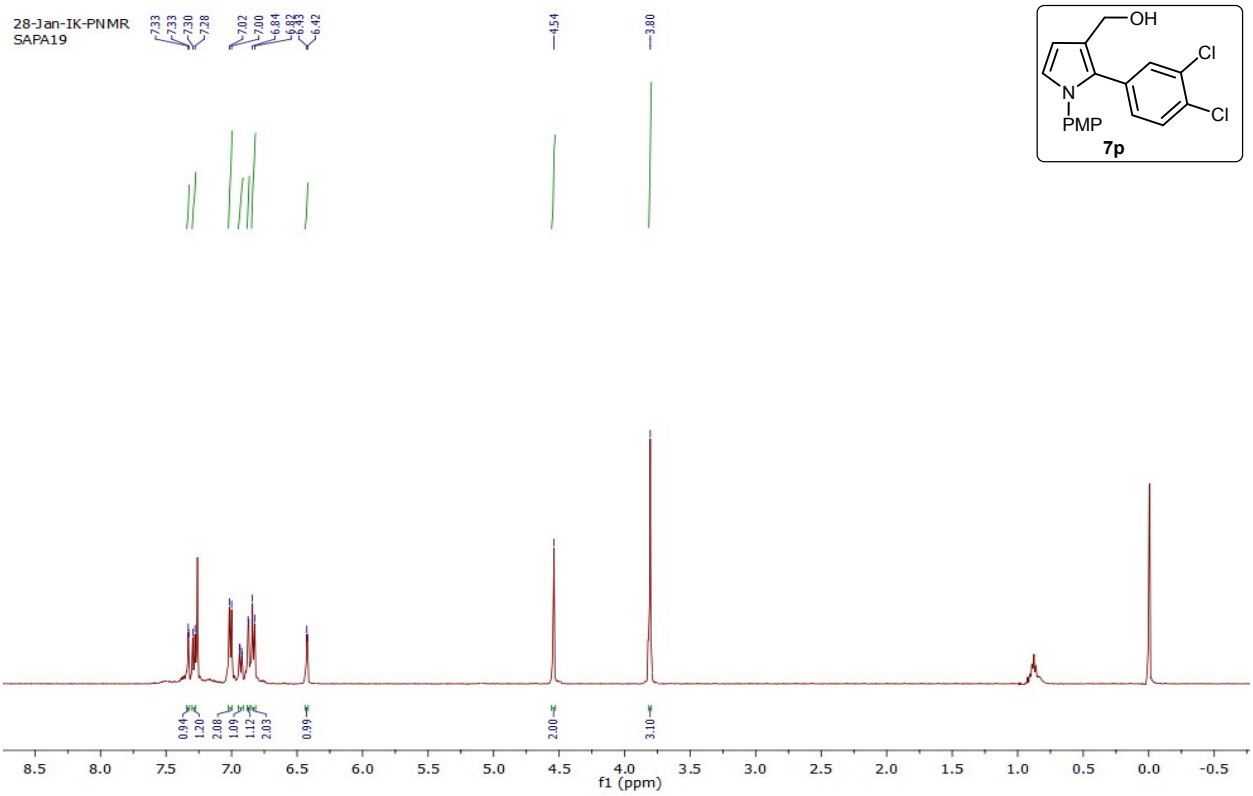

SAPA24
SAPA24
158.50
134.36
133.39
132.67
132.40
130.59
130.55
128.99
126.88
124.17
118.55
118.53
114.34
112.33
110.79
77.00
59.72
55.43
OH
CN
N
PMP
7m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

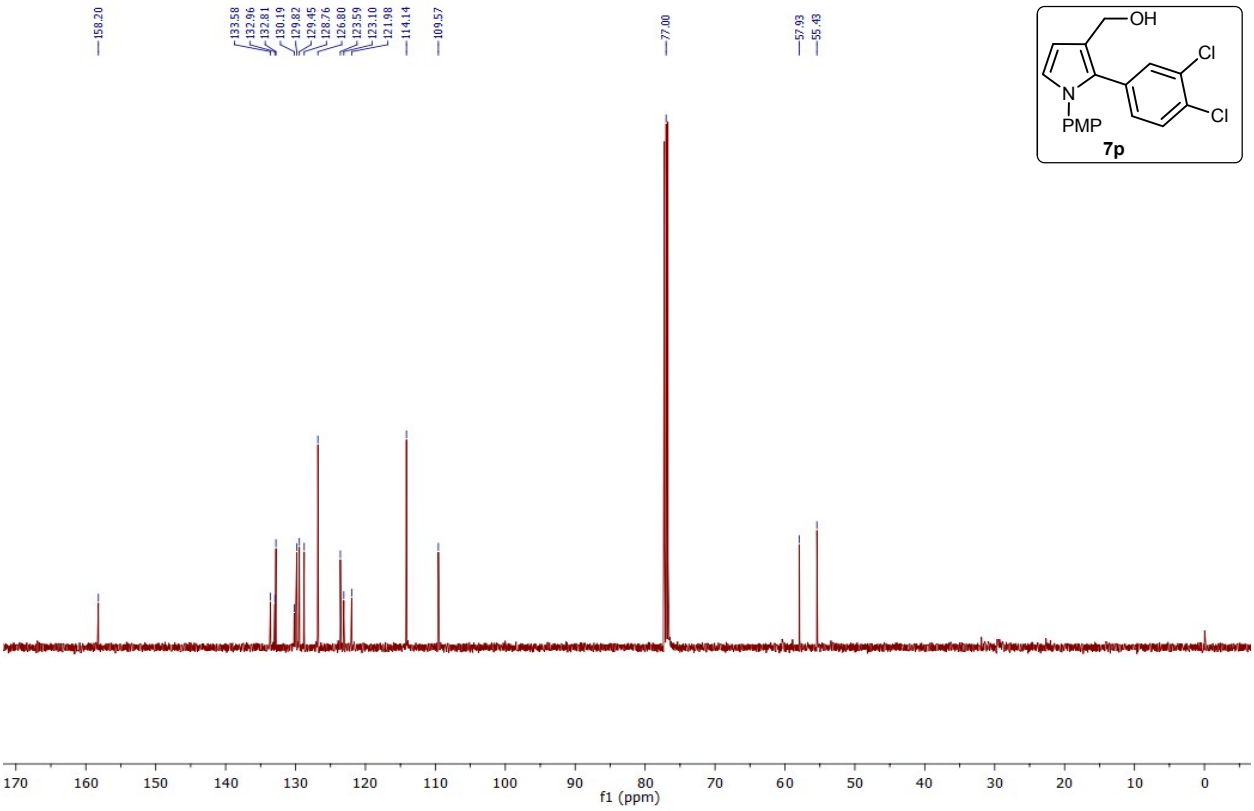

IK 9 OCT2014_2
SAPA-10
7.58
7.56
7.31
7.29
7.04
7.02
6.94
6.87
6.85
6.48
4.58
3.83
OH
N
PMP
CN
7n
2.08
2.32
2.23
1.27
2.33
1.04
1.97
3.00
f1 (ppm)

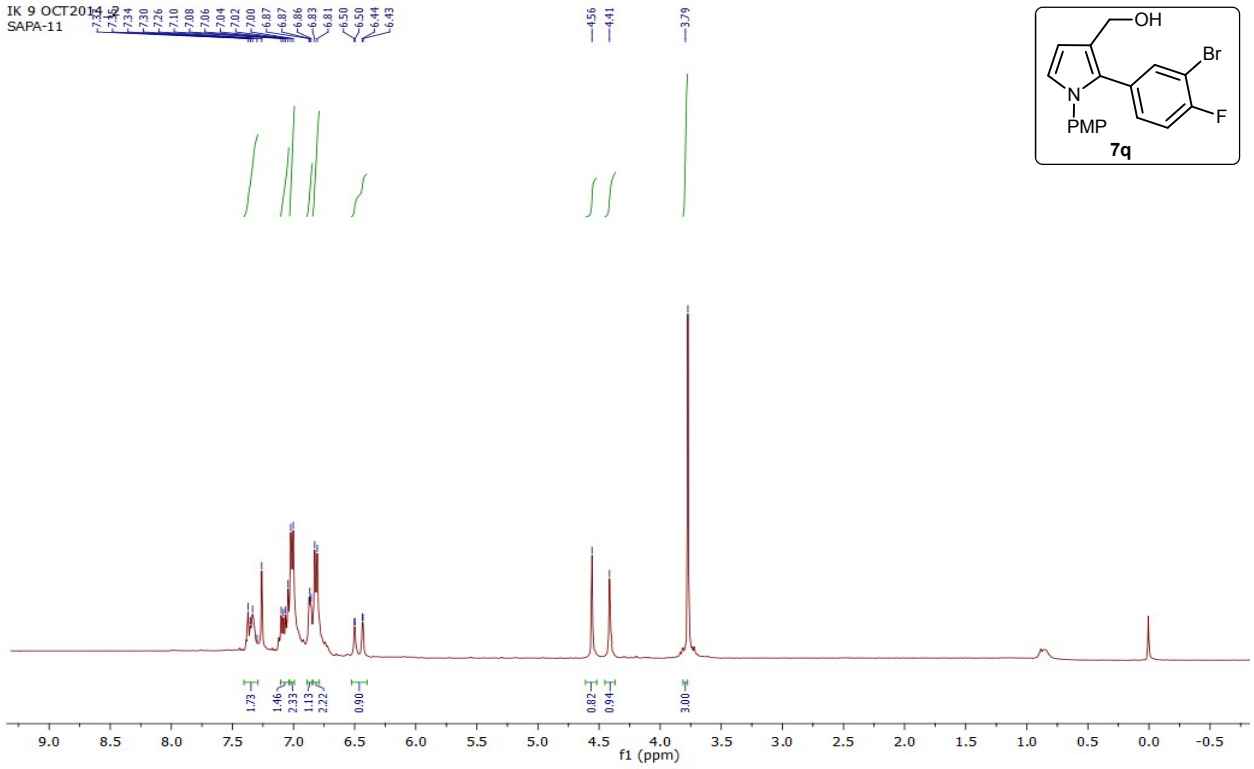

SAPA-10
SAPA-10
158.51
136.23
132.81
132.09
131.75
130.25
129.91
126.84
124.66
124.21
118.89
114.37
110.23
77.00
57.88
55.44
OH
N
PMP
CN
7n
f1 (ppm)

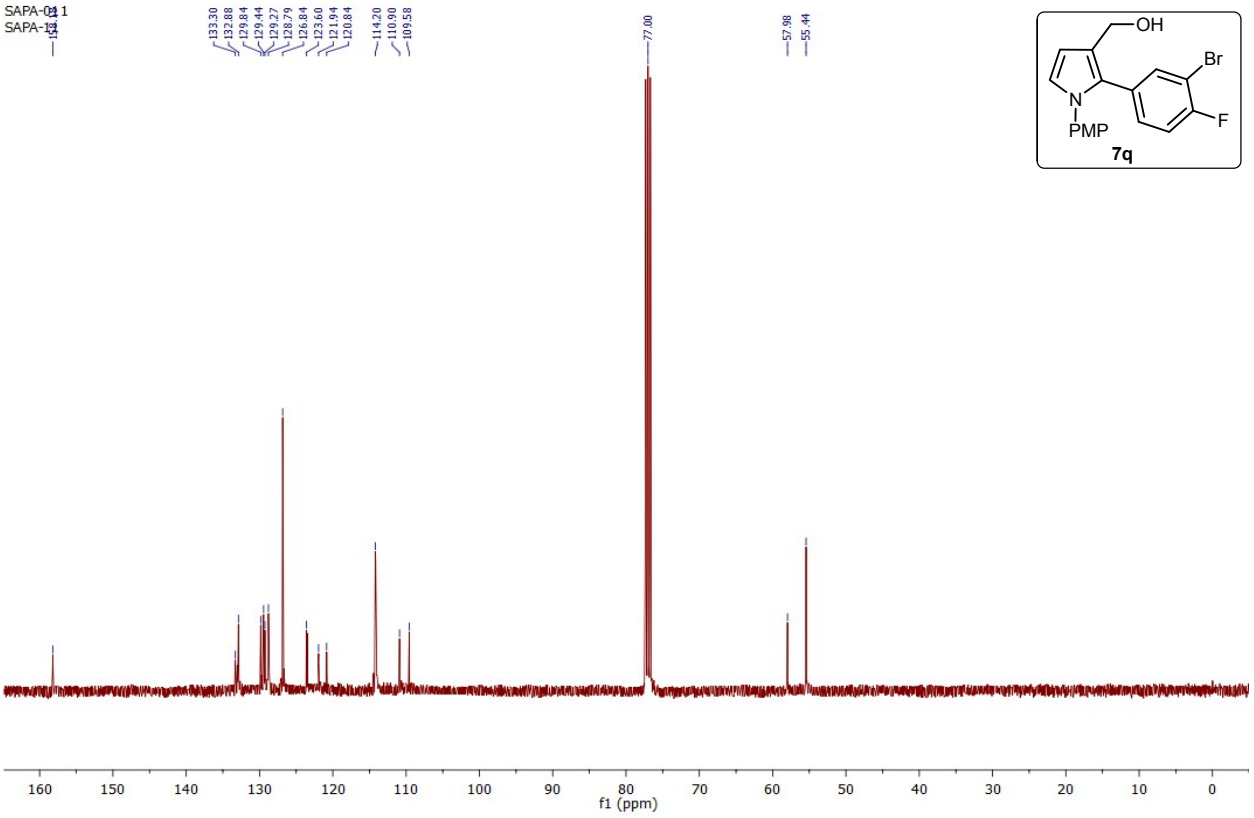

28-Jan-IK-PNMR
SAPA22
7.35
7.35
7.26
7.19
6.98
6.96
6.92
6.92
6.77
6.75
6.43
6.42
4.37
4.35
4.27
4.25
3.77
OH
Cl
N
PMP
Cl
7o
0.96
1.92
2.08
1.19
2.07
0.81
0.89
0.93
3.35
f1 (ppm)

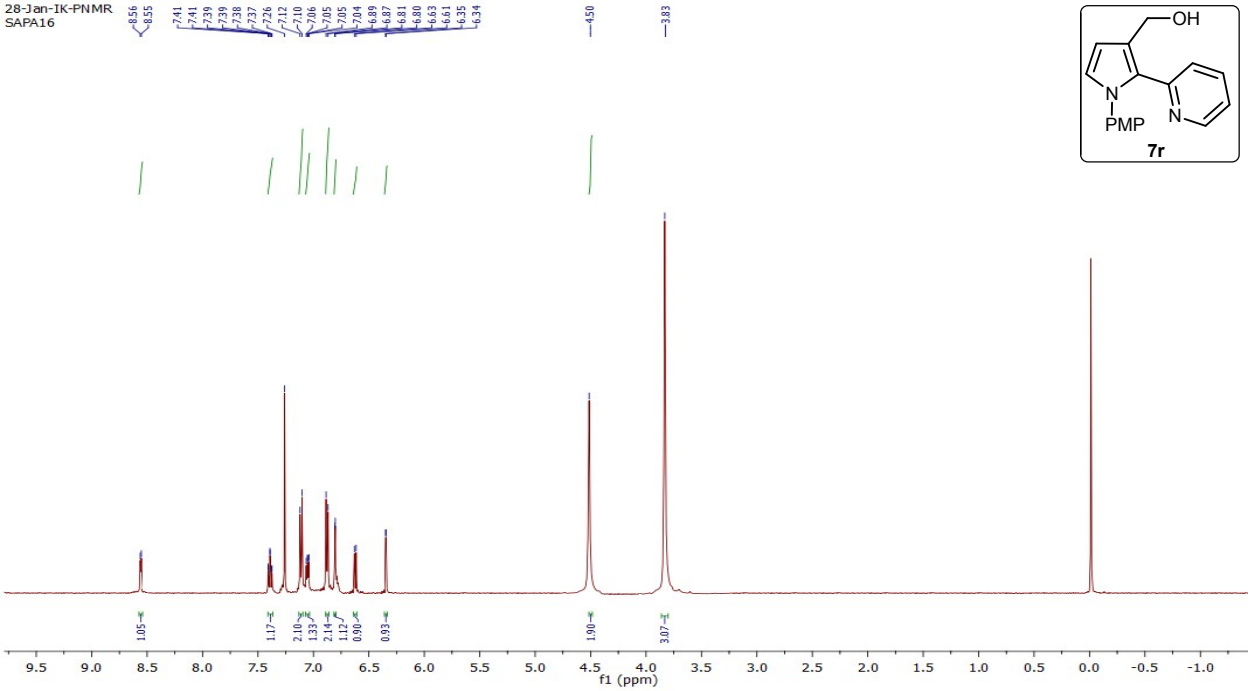

158.04
133.70
133.35
133.13
132.57
130.43
129.70
126.98
126.38
126.30
123.38
122.51
113.87
108.63
77.00
58.19
55.32
OH
Cl
N
PMP
Cl
7o
f1 (ppm)

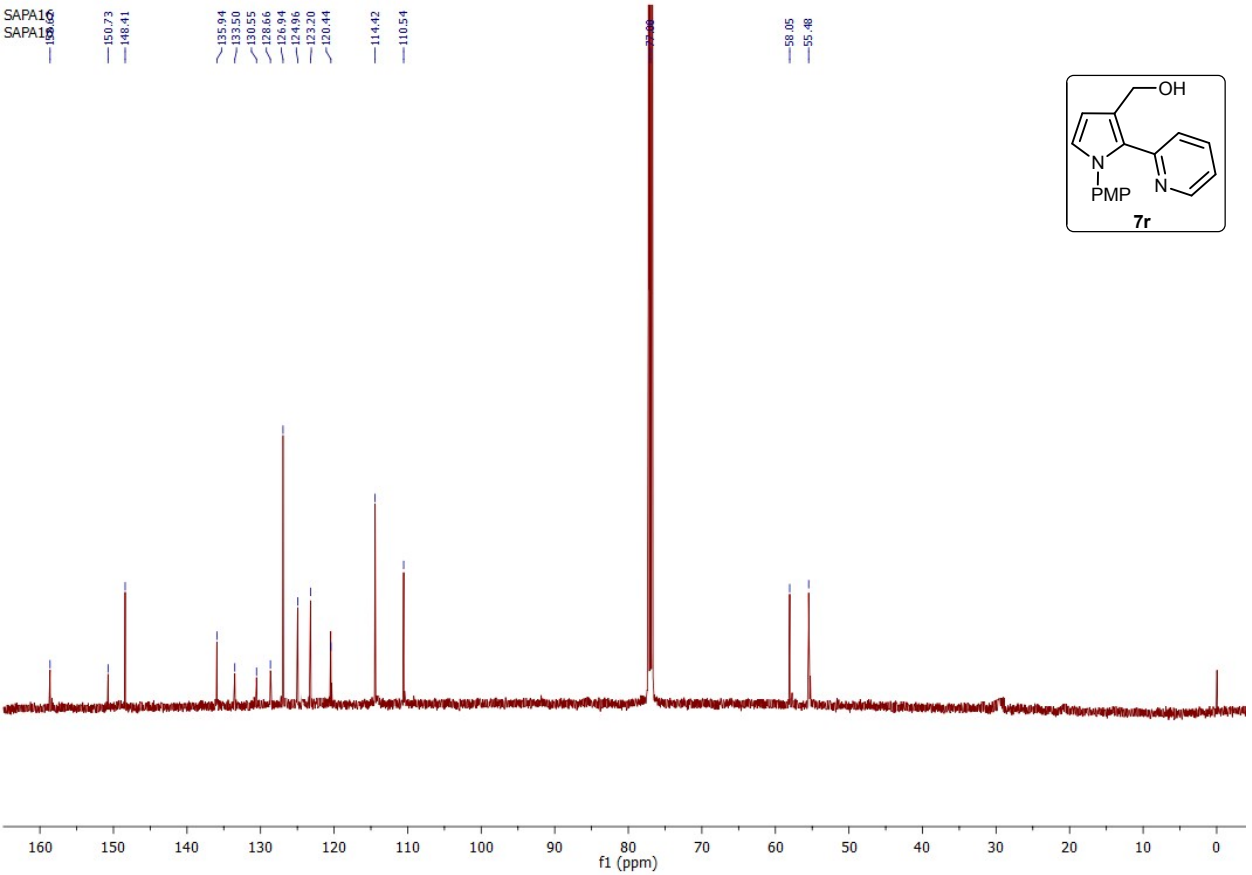

28-Jan-IK-PNMR
SAPA19
7.33
7.33
7.30
7.28
7.02
7.00
6.84
6.83
6.83
6.42
4.54
3.80
OH
Cl
N
PMP
Cl
7p
0.94
1.20
2.08
1.09
1.12
2.03
0.99
2.00
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

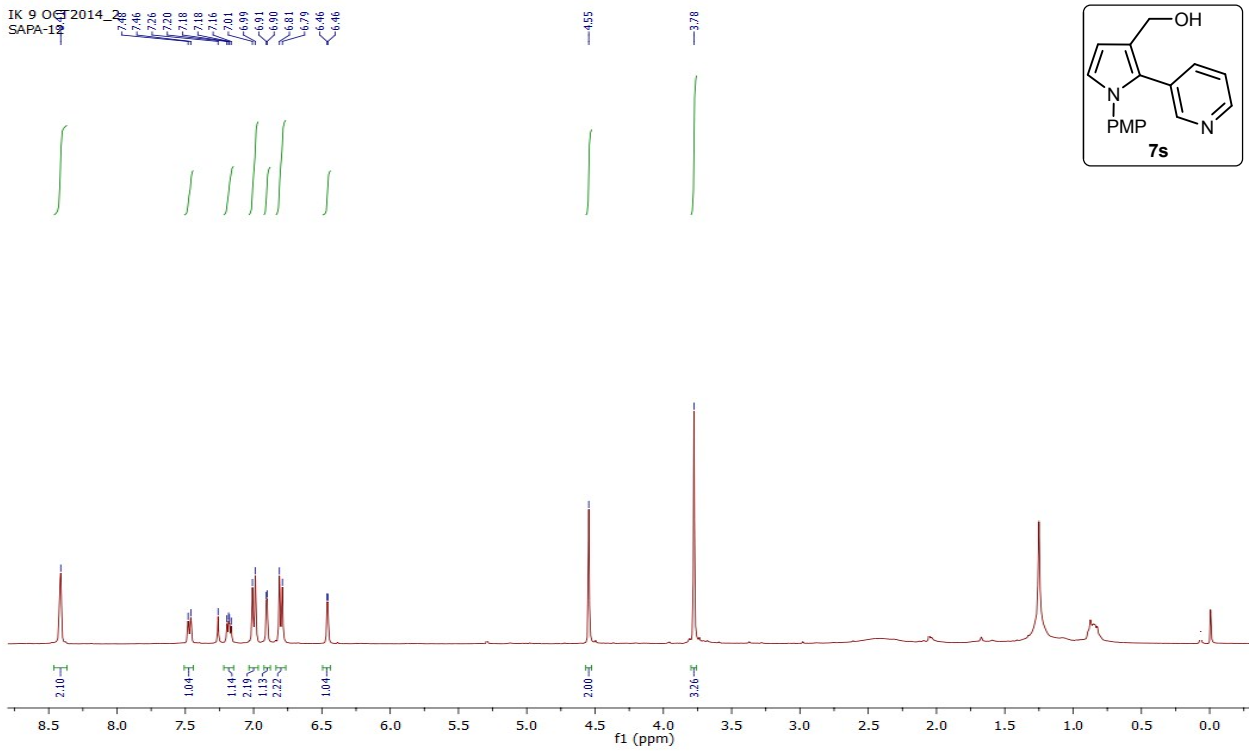

158.20
133.58
132.96
132.81
130.19
129.82
129.45
128.76
126.80
123.59
123.10
121.98
114.14
109.57
77.00
57.93
55.43
OH
Cl
N
PMP
Cl
7p
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

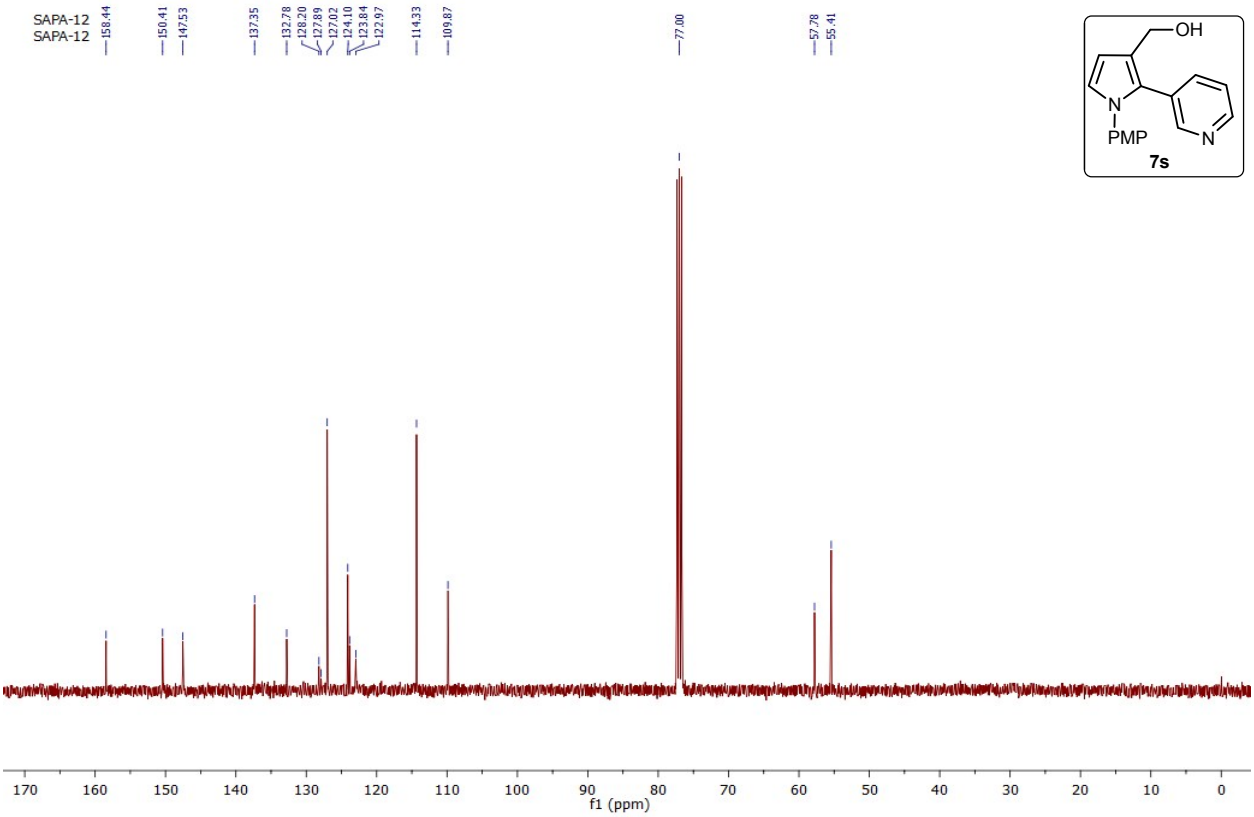

IK 9 OCT2014
SAPA-11
OH
Br
N
PMP
F
7q
f1 (ppm)

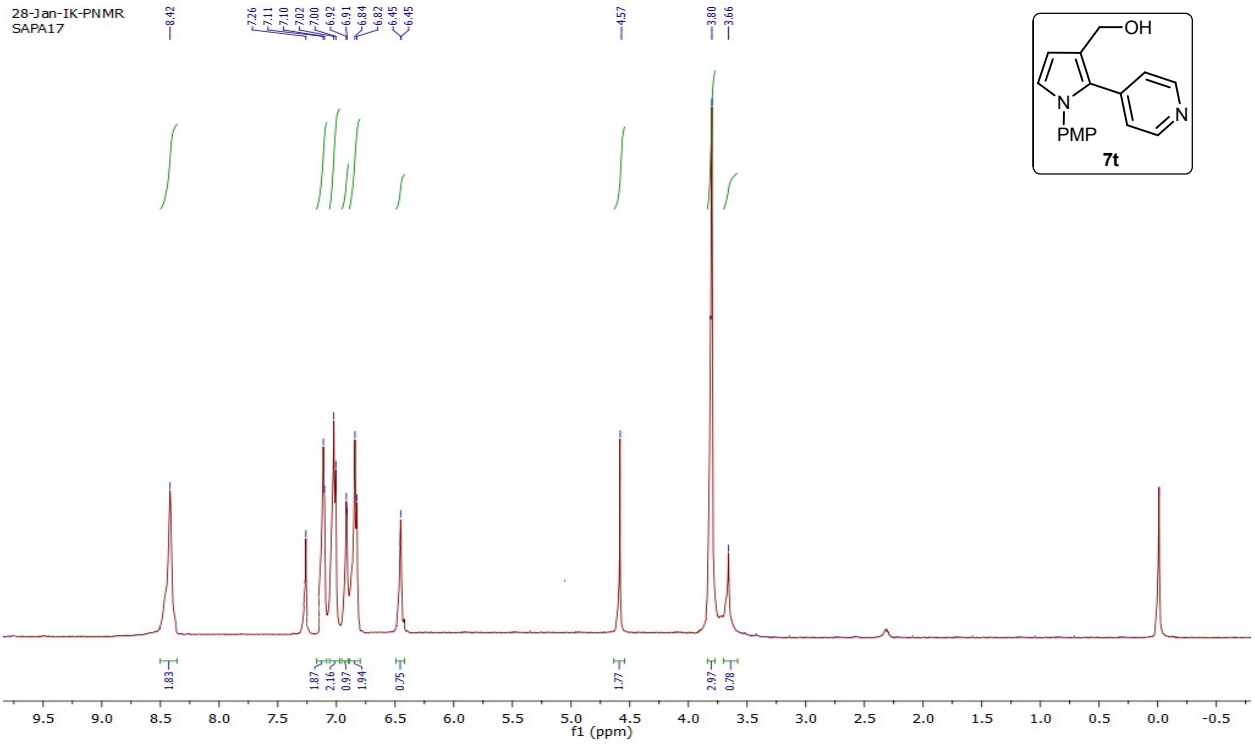

SAPA-11
SAPA-11
OH
Br
N
PMP
F
7q
f1 (ppm)

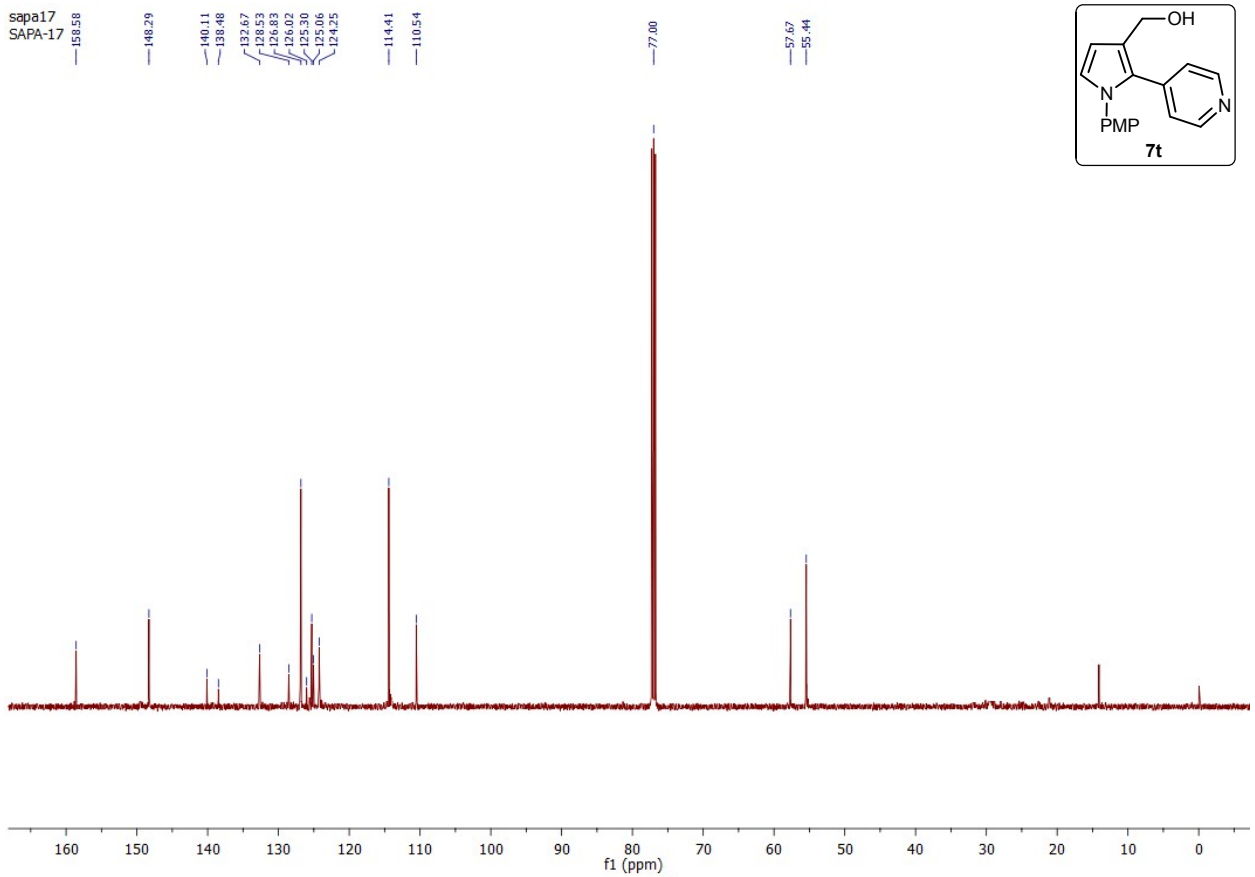

28-Jan-IK-PNMR
SAPA16
OH
N
PMP
N
7r
f1 (ppm)

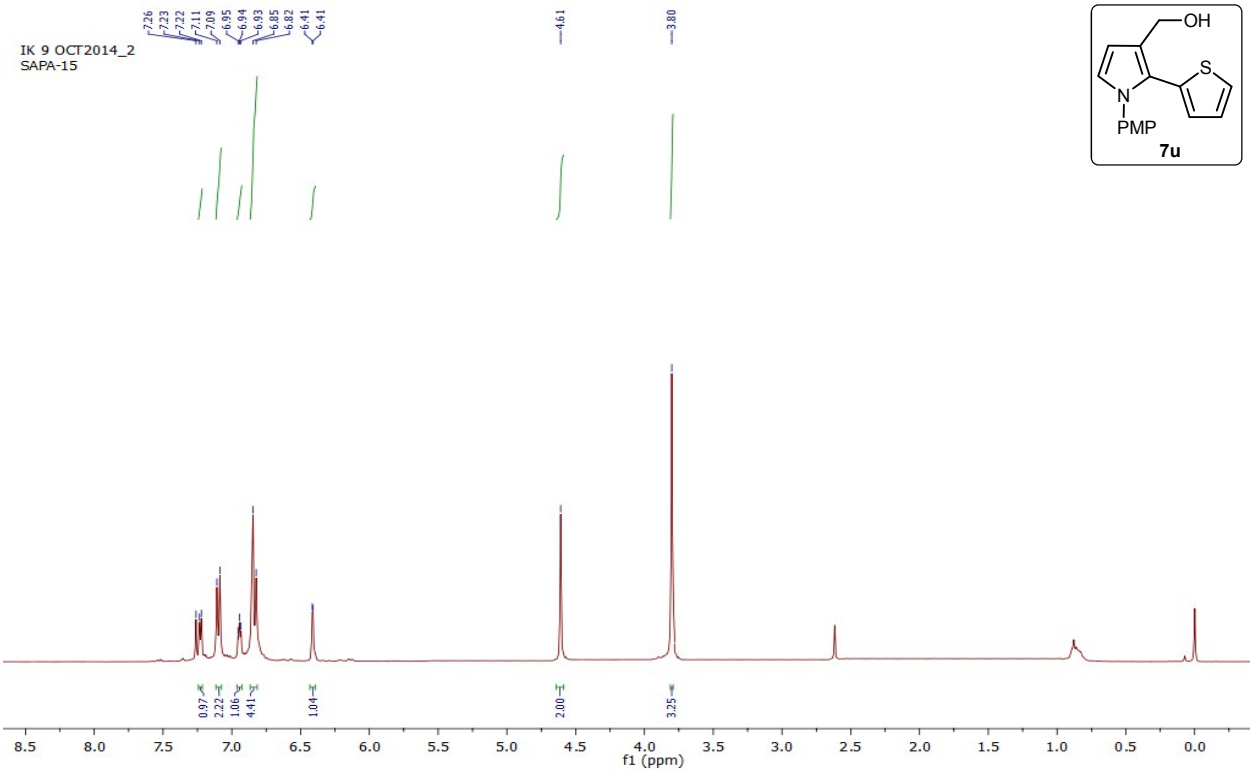

SAPA16
OH
N
PMP
N
7r
f1 (ppm)

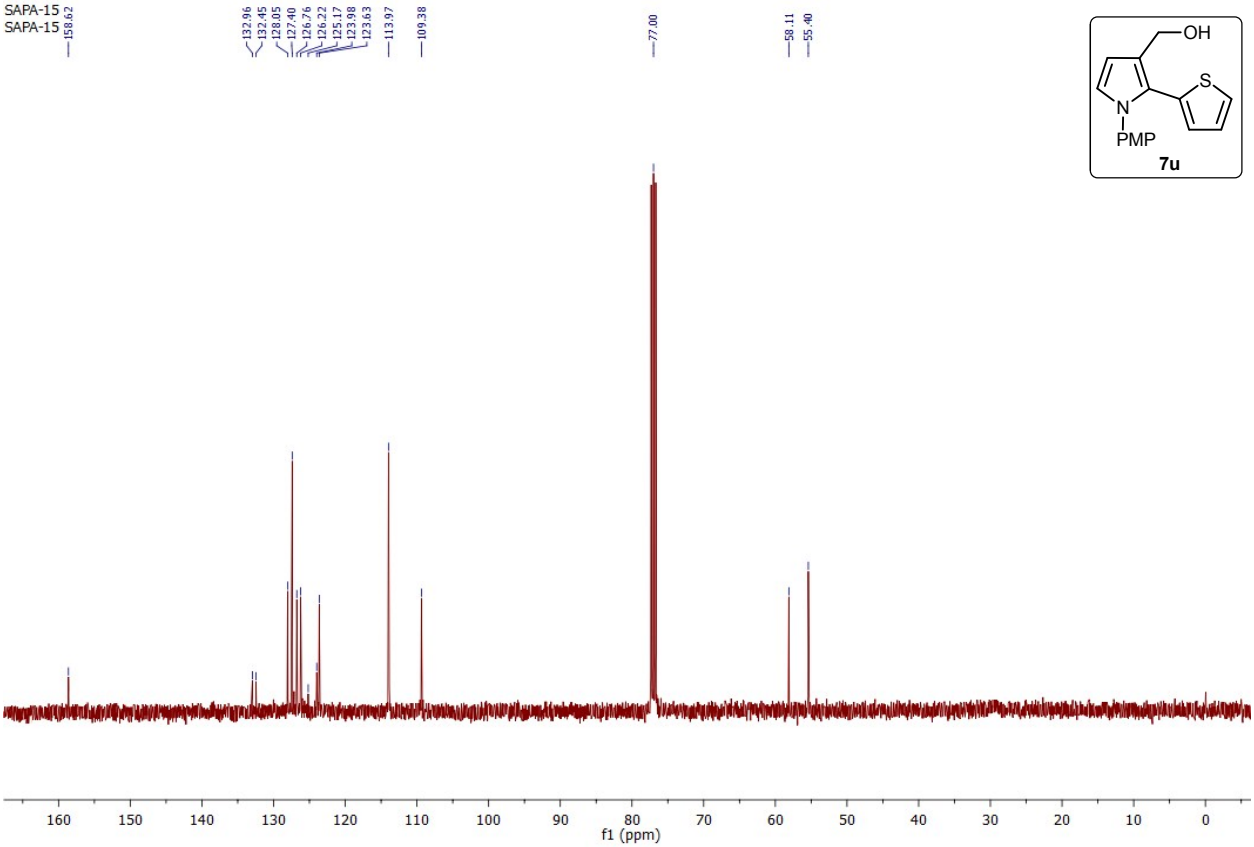

IK 9 OCT2014_2
SAPA-12
7.48
7.46
7.26
7.20
7.18
7.18
7.16
7.01
6.99
6.91
6.90
6.81
6.79
6.46
6.46
4.55
3.78
OH
N
PMP
N
7s
2.10
1.04
1.14
2.19
1.13
2.22
1.04
2.00
3.26
f1 (ppm)

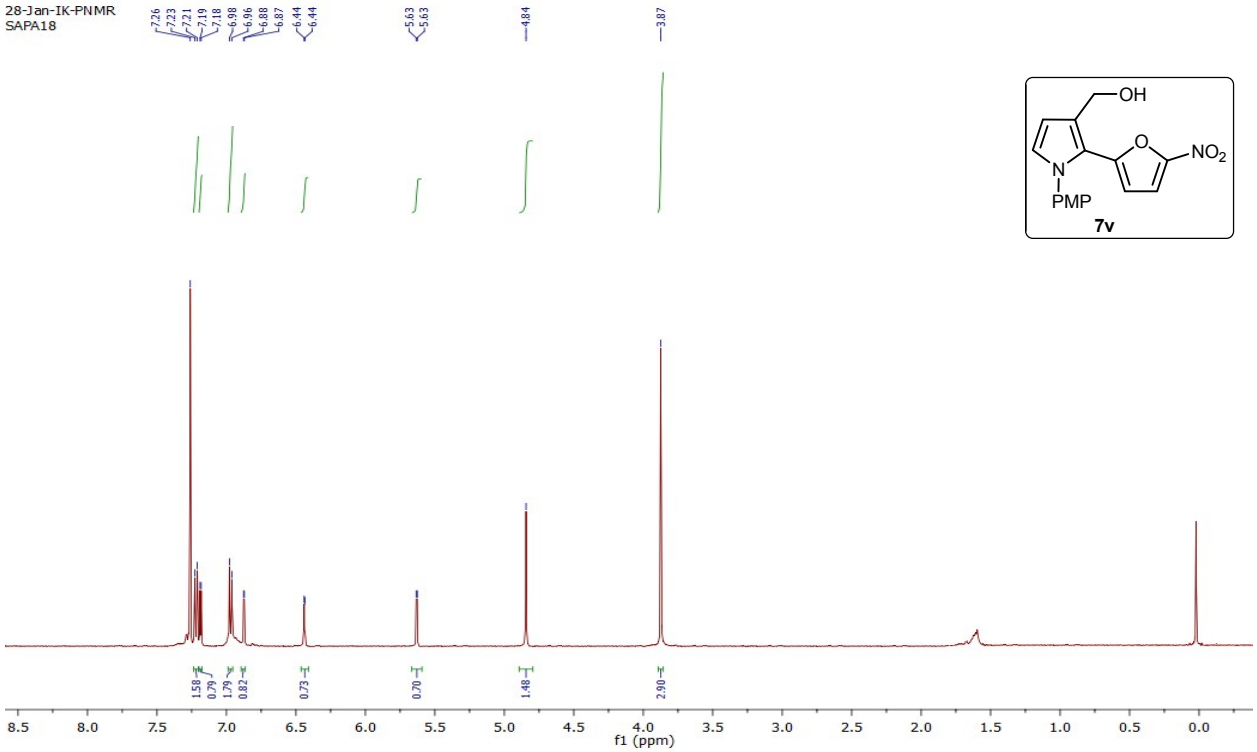

SAPA-12
SAPA-12
158.44
150.41
147.53
137.35
132.78
128.20
127.89
127.02
124.10
123.84
122.97
114.33
109.87
77.00
57.78
55.41
OH
N
PMP
N
7s
f1 (ppm)

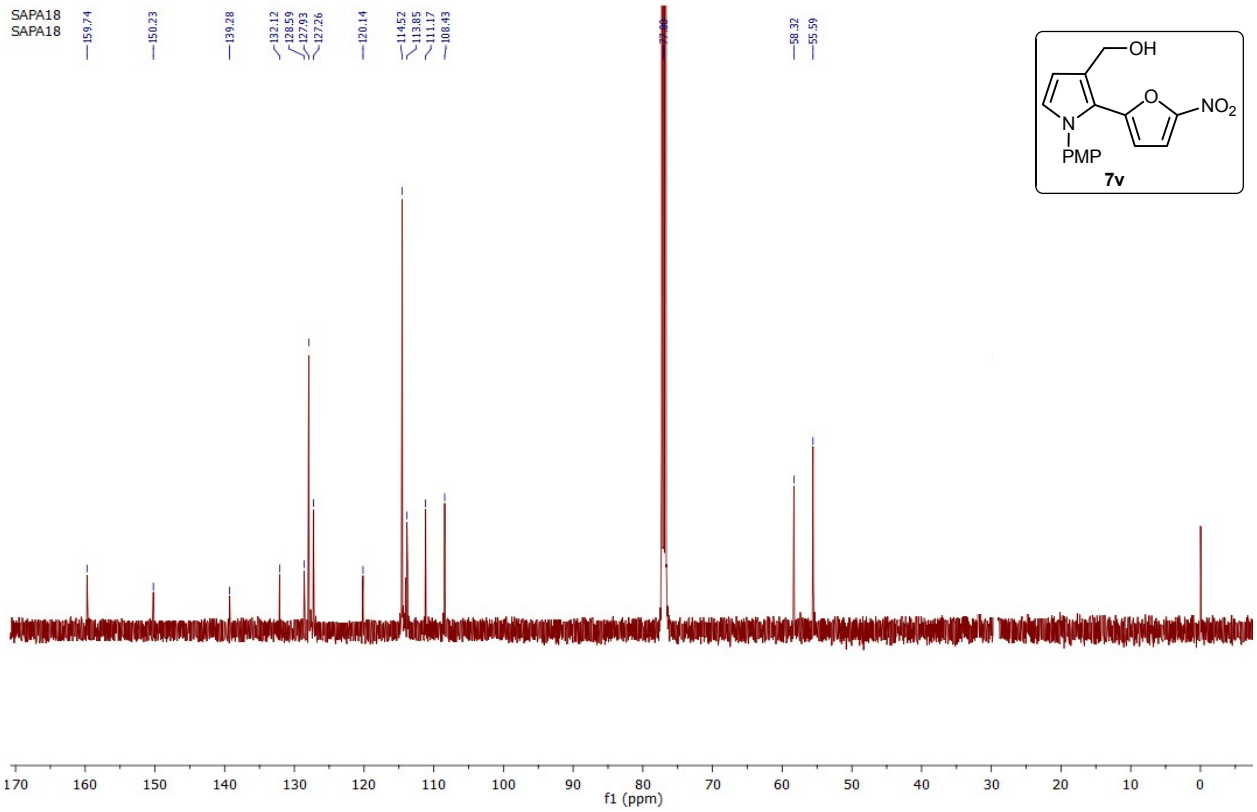

28-Jan-IK-PNMR
SAPA17
8.42
7.26
7.11
7.10
7.02
7.00
6.92
6.91
6.84
6.82
6.45
6.45
4.57
3.80
3.66
OH
N
PMP
N
7t
1.83
1.87
2.16
0.97
1.94
0.75
1.77
2.97
0.78
f1 (ppm)

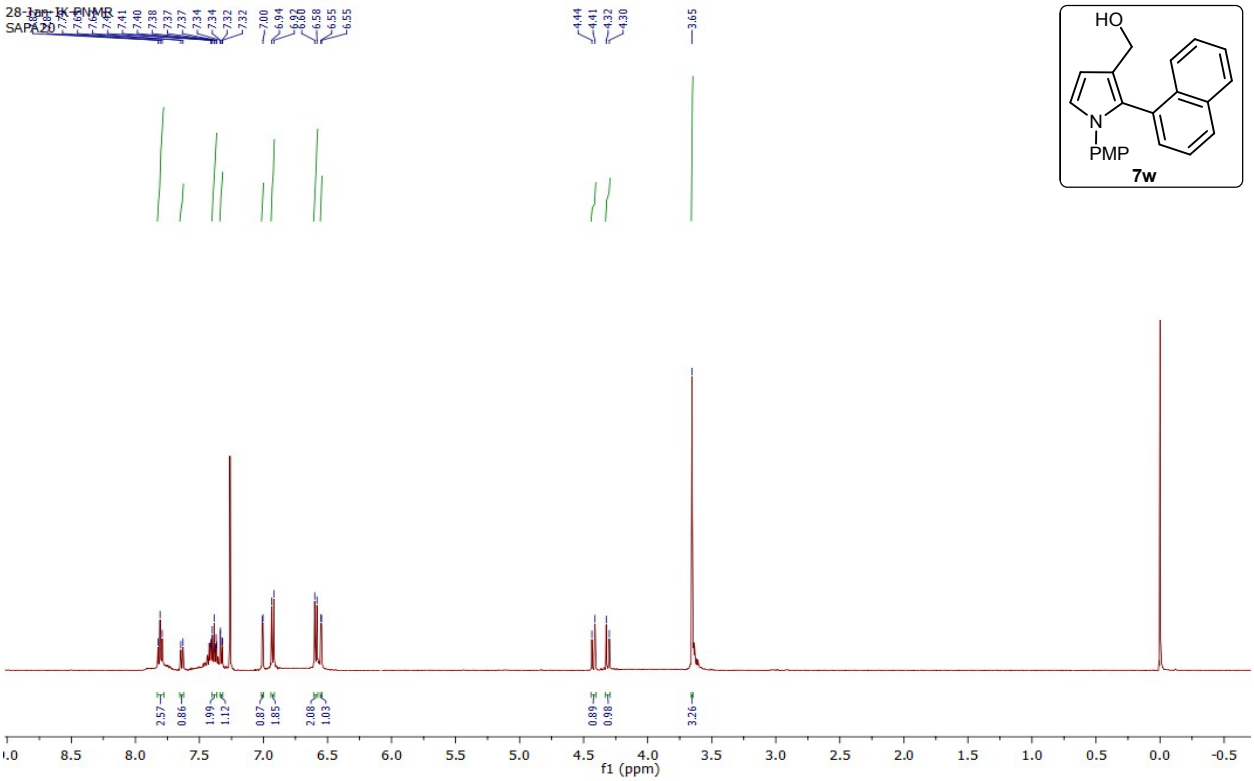

sapa17
SAPA-17
158.58
148.29
140.11
138.48
132.67
128.53
126.83
126.02
125.30
125.06
124.25
114.41
110.54
77.00
57.67
55.44
OH
N
PMP
N
7t
f1 (ppm)

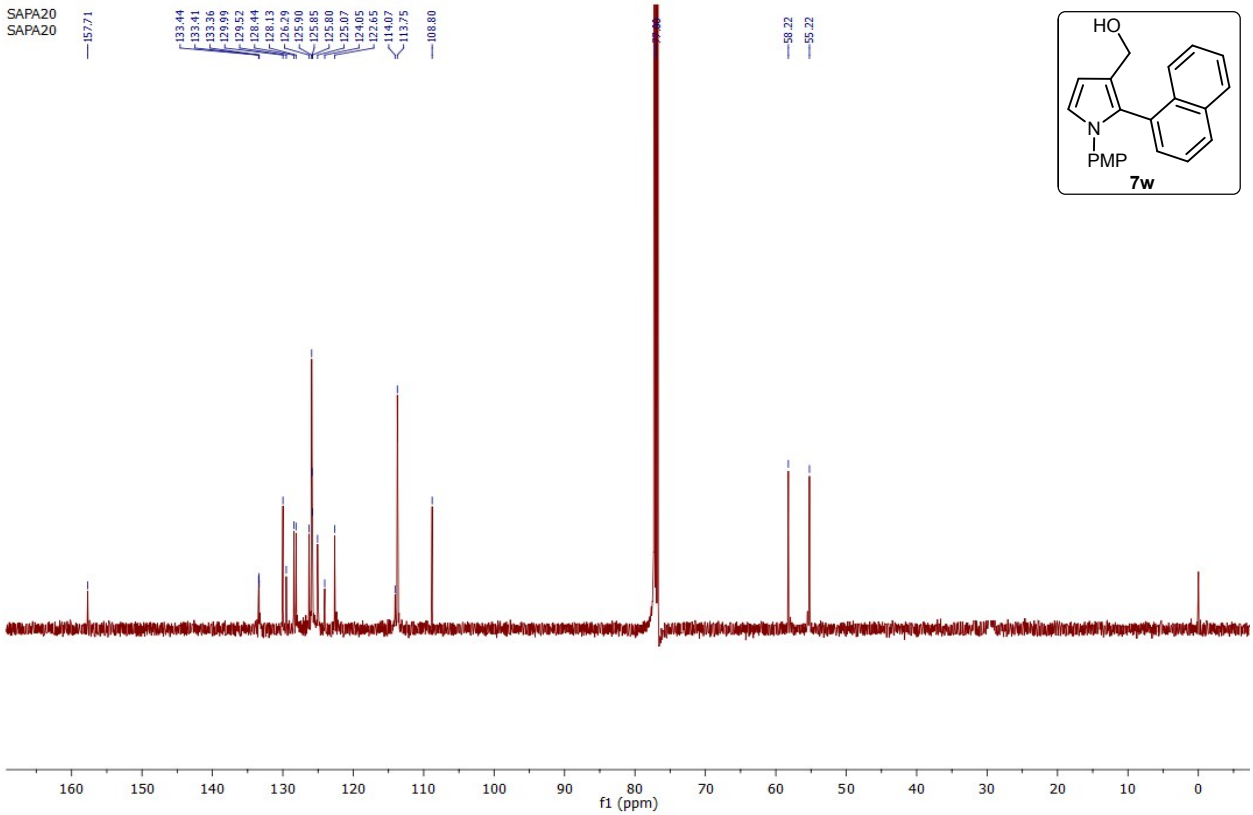

IK 9 OCT2014_2
SAPA-15
7.26
7.23
7.22
7.11
7.09
6.95
6.94
6.93
6.85
6.82
6.41
6.41
4.61
3.80
OH
S
N
PMP
7u
0.97
2.22
1.06
4.41
1.04
2.00
3.25
f1 (ppm)

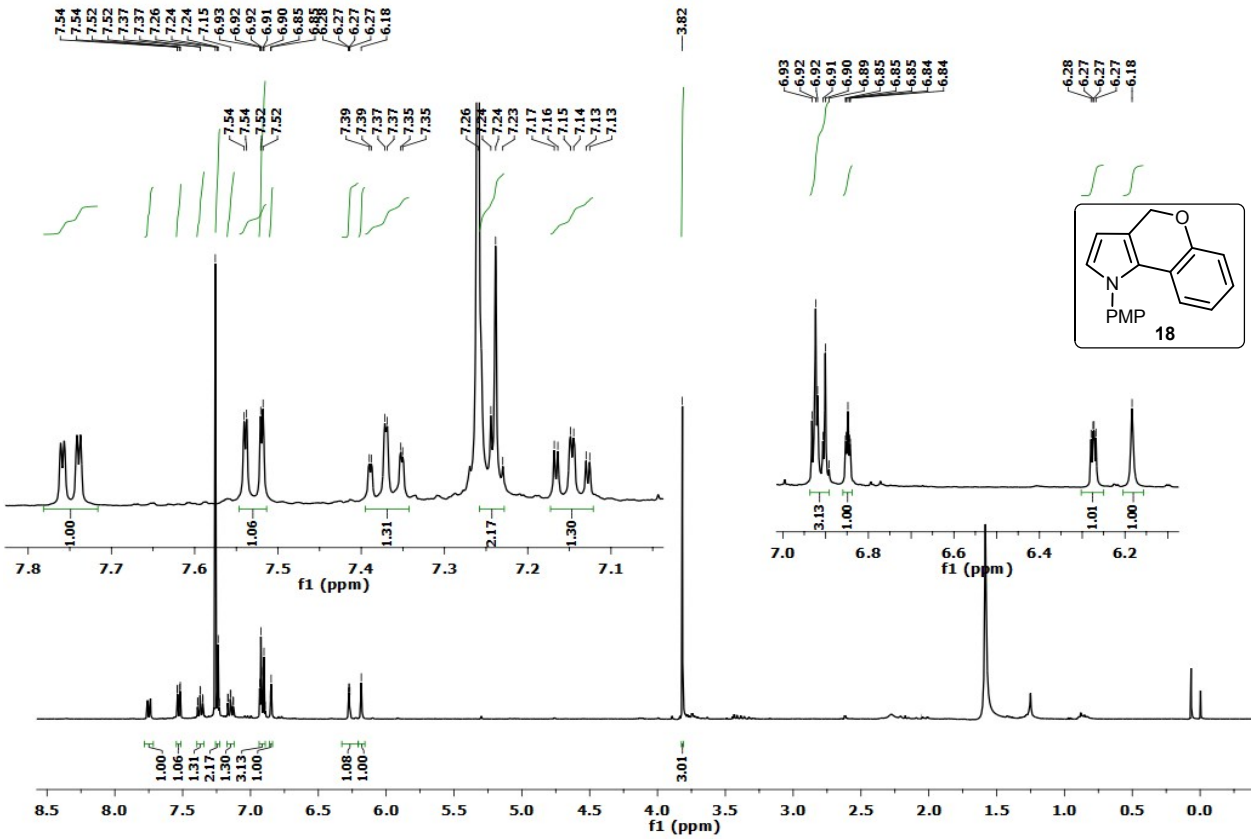

SAPA-15
SAPA-15
158.62
132.96
132.45
128.05
127.40
126.76
126.22
125.17
123.98
123.63
113.97
109.38
77.00
58.11
55.40
OH
S
N
PMP
7u
f1 (ppm)

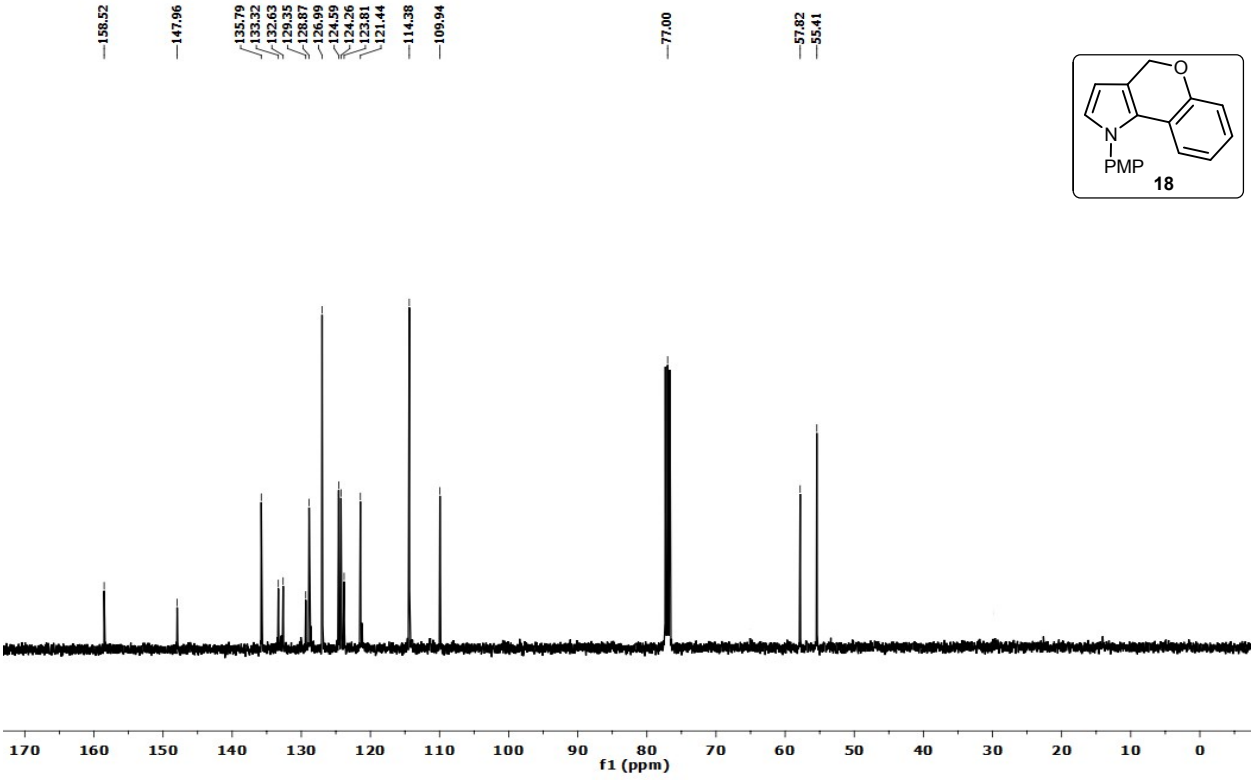

28-Jan-IK-PNMR
SAPA18
7.26
7.23
7.21
7.19
7.18
6.98
6.96
6.88
6.87
6.44
6.44
5.63
5.63
4.84
3.87
OH
O
NO2
N
PMP
7v
1.58
0.79
1.79
0.82
0.73
0.70
1.48
2.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

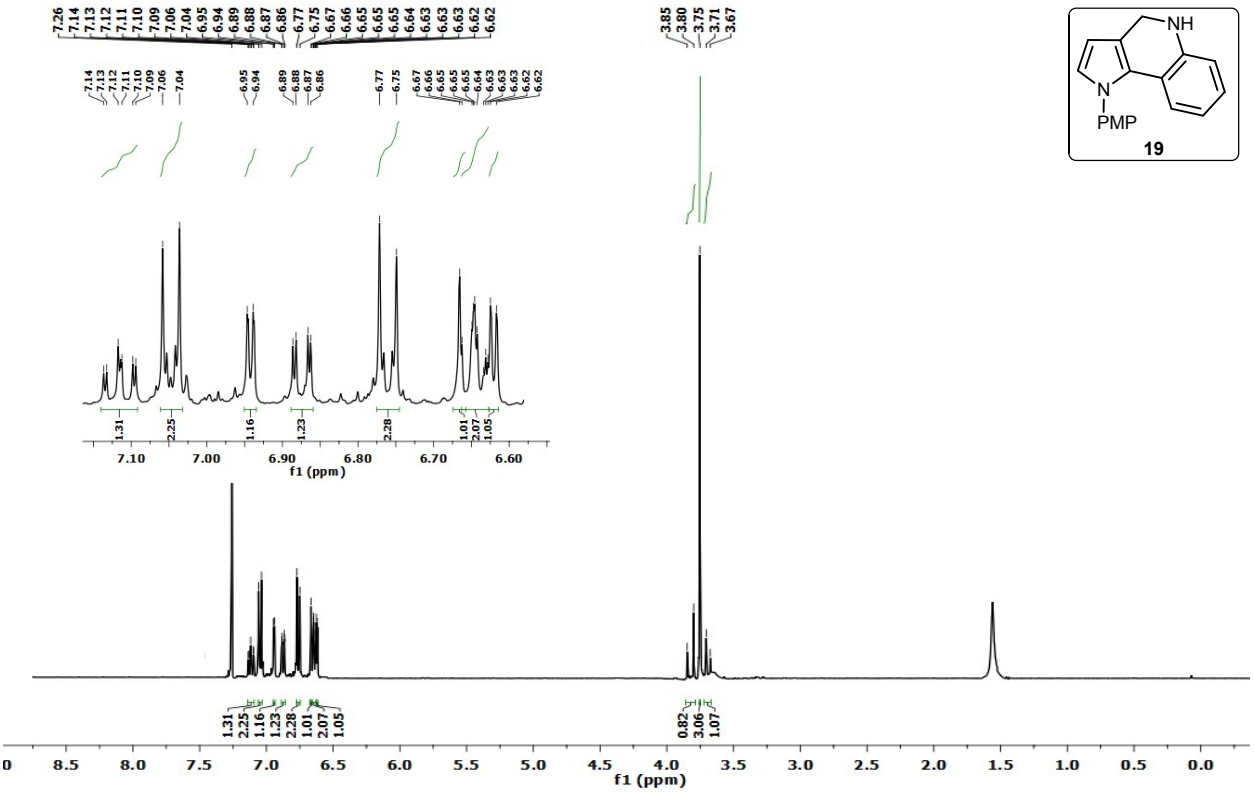

SAPA18
SAPA18
159.74
150.23
139.28
132.12
128.59
127.93
127.26
120.14
114.52
113.85
111.17
108.43
58.32
55.59
OH
O
NO2
N
PMP
7v
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

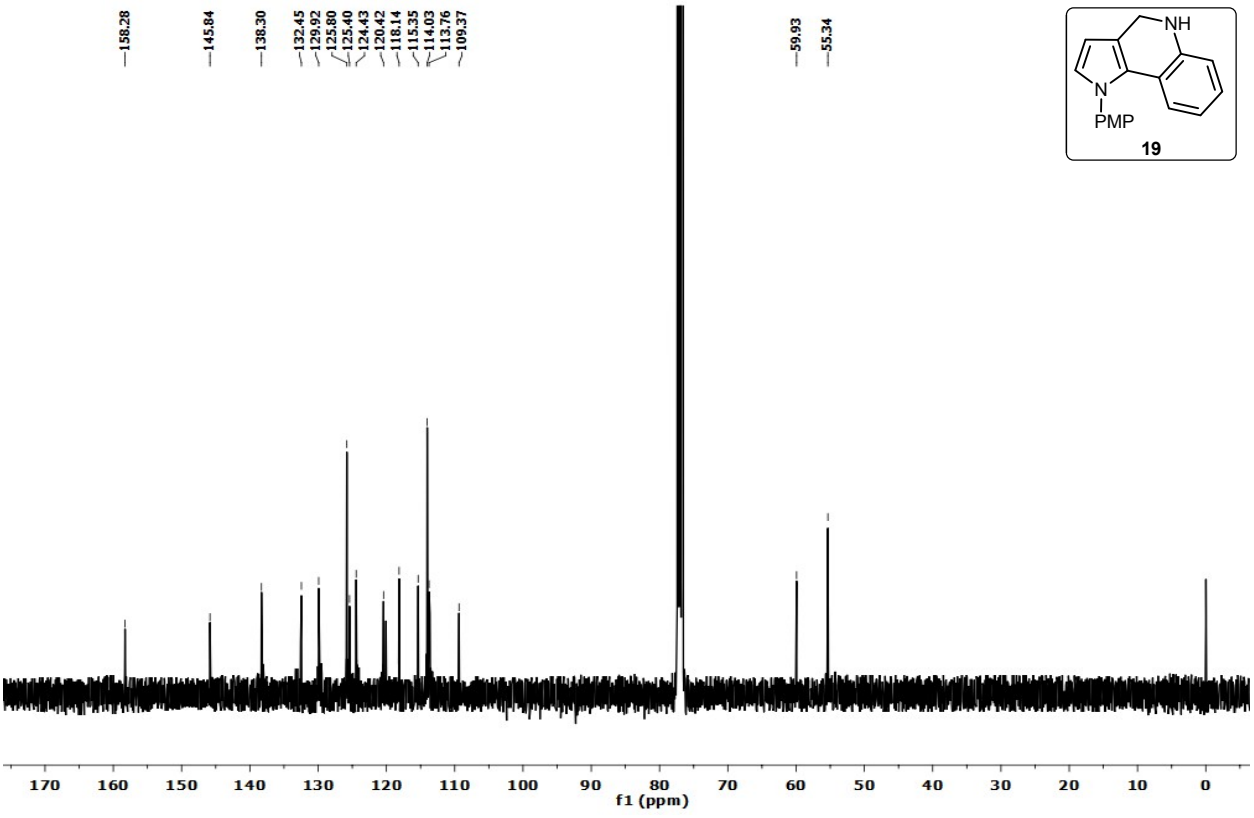

28-1pr-1K-PNMR
SAPA20
HO
N
PMP
7w
f1 (ppm)

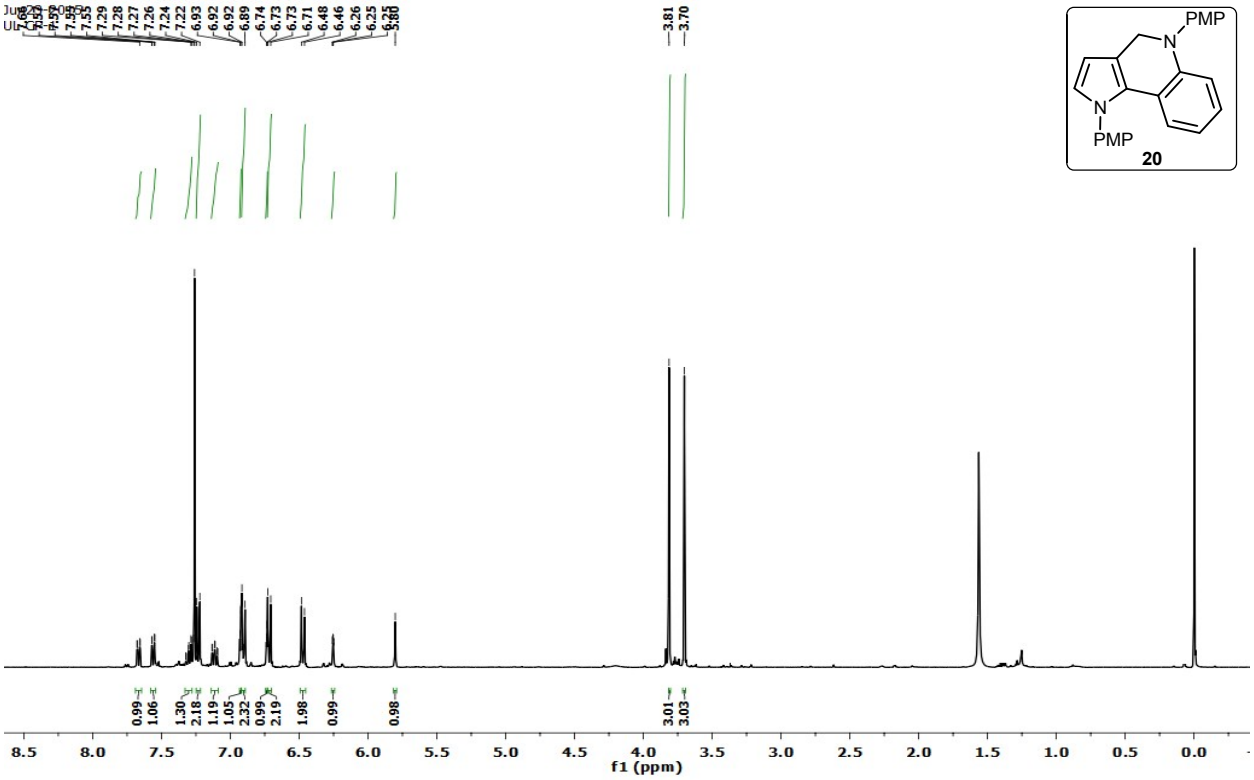

SAPA20
SAPA20
HO
N
PMP
7w
f1 (ppm)

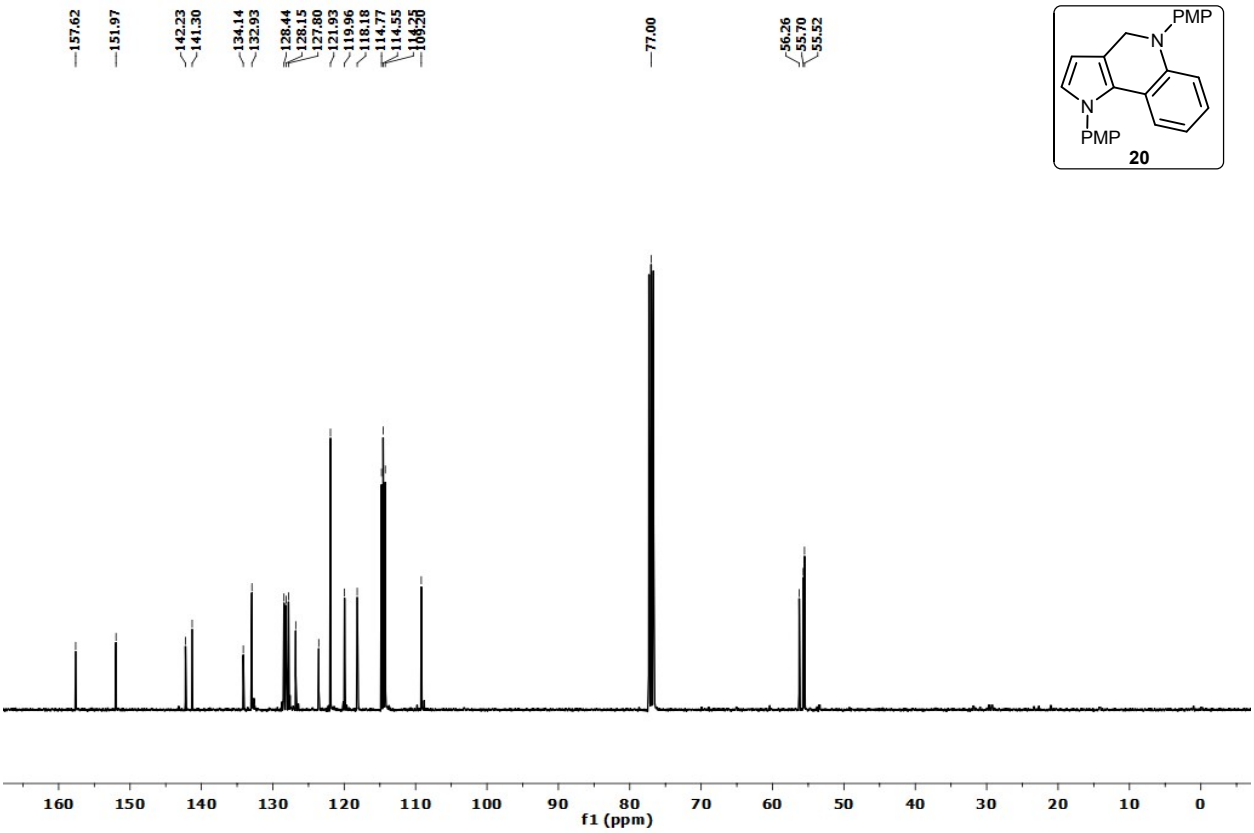

PMP
18
f1 (ppm)

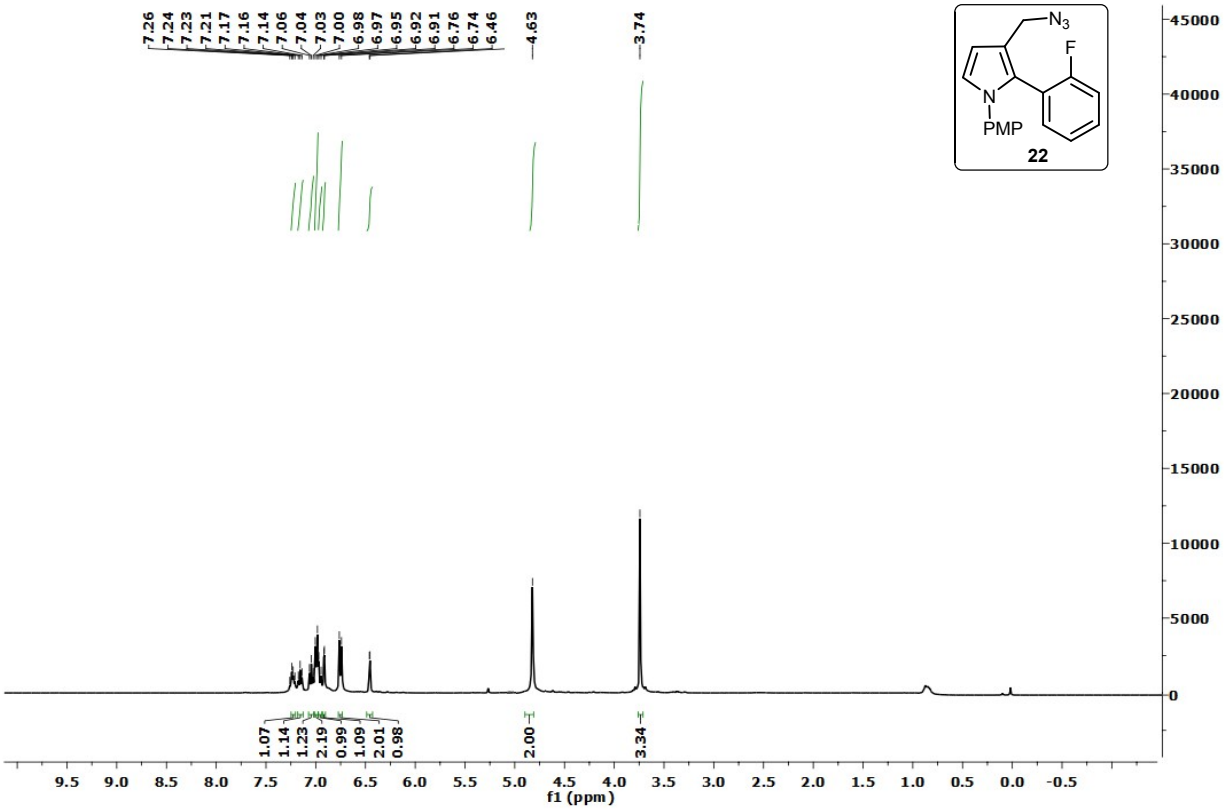

PMP
18
f1 (ppm)

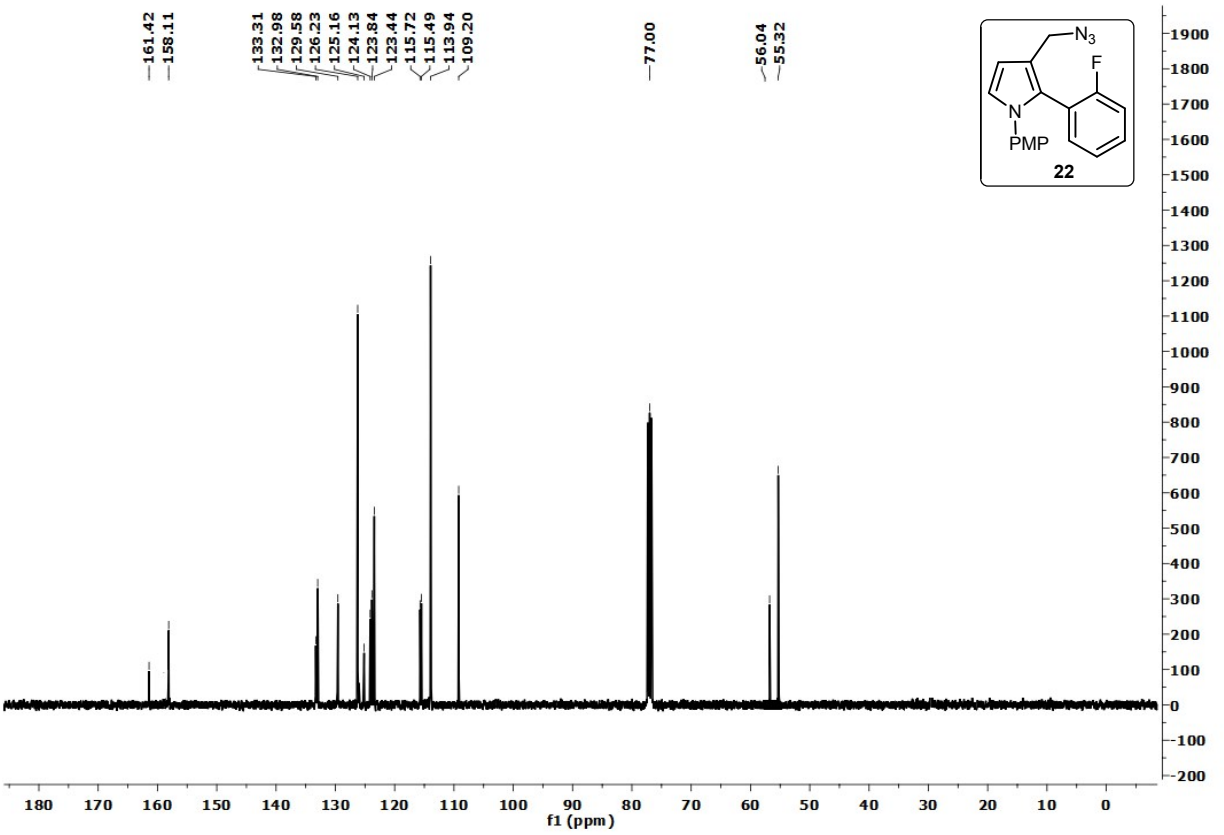

NH
N
PMP
19
f1 (ppm)


NH
N
PMP
19
f1 (ppm)


PMP
N
N
PMP
20
f1 (ppm)


PMP
N
N
PMP
20
f1 (ppm)


7.26
7.24
7.23
7.21
7.17
7.16
7.14
7.06
7.04
7.03
7.00
6.98
6.97
6.95
6.92
6.91
6.76
6.74
6.46
4.63
3.74
N3
F
N
PMP
22
1.07
1.14
1.23
2.19
0.99
1.09
2.01
0.98
2.00
3.34
f1 (ppm)


161.42
158.11
133.31
132.98
129.58
126.23
125.16
124.13
123.84
123.44
115.72
115.49
113.94
109.20
77.00
56.04
55.32
N3
F
N
PMP
22
f1 (ppm)