Electronic Supplementary Information for

Sterically Enriched Bulky 1,3-Bis(*N,N'*-Aralkyl)Benzimidazolium based Pd-PEPPSI Complexes for Buchwald-Hartwig Amination Reactions

Motakatla Venkata Krishna Reddy, Gokanapalli Anusha and Peddiahgari Vasu Govardhana Reddy*

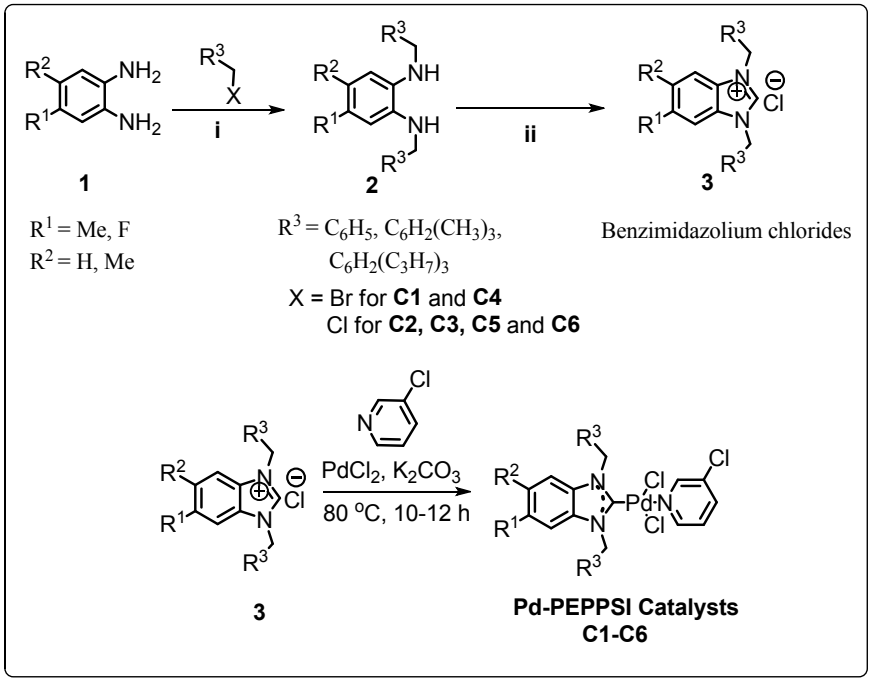
Department of Chemistry, Yogi Vemana University, Kadapa – 516005, Andhra Pradesh, India

*Corresponding Author Phone: +91-856225410; fax: +91-8562225419

E-mail: pvgr@yogivemanauniversity.ac.in

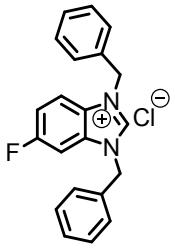
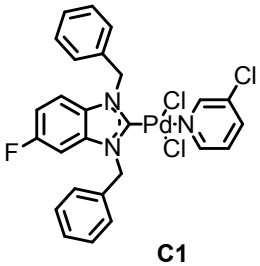
Table of Contents

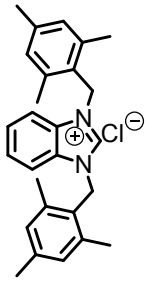
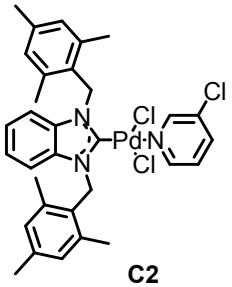
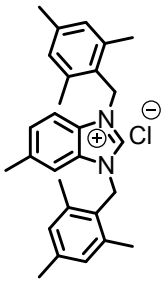
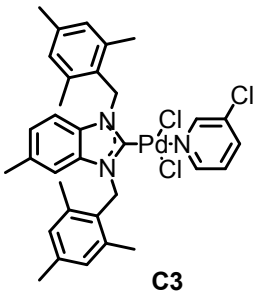
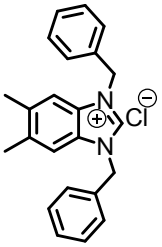
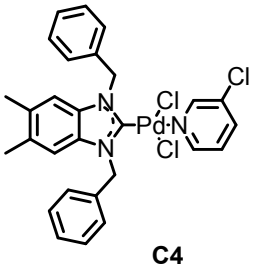
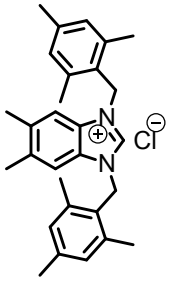
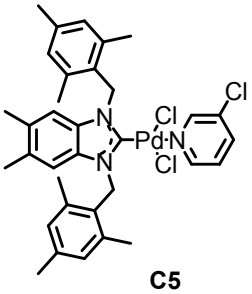
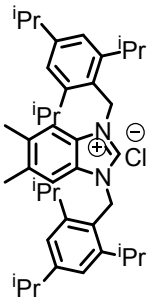
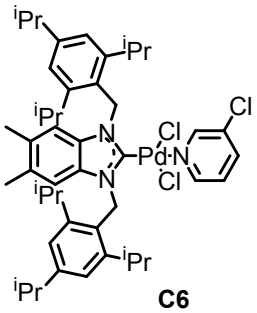
I. General Scheme for the preparation of benzimidazolium Pd-PEPPSI complexes **C1-C6**



Reagents and conditions for benzimidazolium chlorides: (i) *o*-phenylenediamine (1.0 mmol), aralkyl halide (2.0 mmol), NEt_3 (2.0 mmol), acetonitrile (10 mL), reflux, 3h; (ii) $HC(OEt)_3$ (1.0 mmol), conc. HCl (1.0 mmol), 120 °C, 3h.

II. Table 1. Preparation of Pd-PEPPSI complexes **C1-C6**

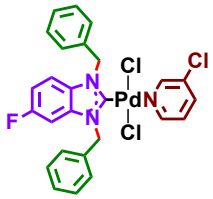
Entry	Benzimidazolium chloride	Pd-PEPPSI Complex	Time (h)	Yield[a] (%)
1		 **C1**	12	63

2		 **C2**	10	71
3		 **C3**	11	85
4		 **C4**	10	69
5		 **C5**	10	82
6		 **C6**	10	79

Reaction conditions: benzimidazolium chloride (1.0 mmol), $PdCl_2$ (1.0 mmol), K_2CO_3 (3.0 mmol), 3-chloro pyridine (4 mL), 80 ^oC. Non-inert atmosphere. [a]Isolated yield.

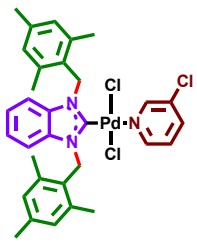
III. Characteristic data of Pd-PEPPSI complexes **C1-C6**

C1: [1,3-Dibenzyl)-5-fluorobenzimidazol-2-ylidene]-*N*-(3-chloropyridine)dichloropalladium(II)



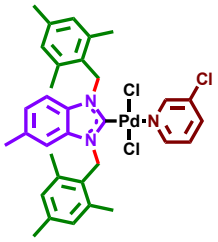
Yellow solid (381 mg, 63%); m.p. 146-148 ^{o}C; *v*max (KBr)/cm^{-1}: 3095 (Ar-C-H), 2911 (Ali-C-H), 1714 (-C=N), 1552 (Ar-C=C), 1410 (Pd-Ccarbene); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.05 (d, *J* = 2.8 Hz, 1H, Ar-H), 8.95 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.61 (t, *J* = 6.8 Hz, 6H, Ar-H), 7.41 (d, *J* = 4.8 Hz, 4H, Ar-H), 7.40 (s, 1H, Ar-H), 7.38-7.30 (m, 2H, Ar-H), 6.81 (d, *J* = 9.2 Hz, 2H, Ar-H), 6.22 (d, *J* = 9.6 Hz, 4H, Ar-C$\underline{H}_2$-); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.08 (d, *J* = 1.4 Hz, Ar-C), 156.36 (Ar-C), 150.40 (Ar-C), 149.31 (Ar-C), 138.34 (Ar-C), 134.69 (Ar-C), 134.45 (Ar-C), 132.80 (Ar-C), 131.10 (Ar-C), 129.17 (Ar-C), 129.11 (Ar-C), 128.60 (Ar-C), 128.53 (Ar-C), 128.07 (Ar-C), 128.03 (Ar-C), 124.99 (Ar-C), 112.45 (d, *J* = 10.1 Hz, Ar-C), 111.75 (d, *J* = 25.4 Hz, Ar-C), 99.13 (Ar-C), 98.85 (Ar-C), 53.57 (Ar-$\underline{C}H_2$); HRMS (ESI-TOF) calcd for $C_{26}H_{22}Cl_3FN_3Pd$ $[M+H]^+$ m/z = 605.9898, found 605.9905.

C2: [Bis-1,3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]-*N*-(3-chloropyridine)dichloropalladium(II)



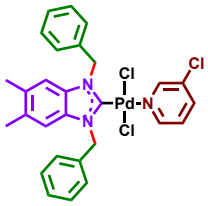
Yellow solid (477 mg, 71%); m.p. 140-142 ^{o}C; vmax (KBr)/cm^{-1}: 3020 (Ar-C-H), 2950 (Ali-C-H), 1699 (-C=N), 1533 (Ar-C=C), 1406 (Pd-Ccarbene); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.93 (s, 1H, Ar-H), 8.88 (d, J = 5.6 Hz, 1H, Ar-H), 7.77 (d, J = 8.4 Hz, 1H, Ar-H), 7.32 (t, J = 6.0 Hz, 1H, Ar-H), 6.91 (s, 4H, Ar-H), 6.87-6.84 (m, 2H, Ar-H), 6.50 (d, J = 3.2 Hz, 2H, Ar-H), 6.20 (s, 4H, Ar-C$\underline{H}_2$), 2.32 (s, 18H, Ar-C$\underline{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.96 (Ar-C), 150.37 (Ar-C), 149.28 (Ar-C), 138.83 (Ar-C), 138.60 (Ar-C), 138.14 (Ar-C), 134.83 (Ar-C), 132.63 (Ar-C), 129.74 (Ar-C), 127.69 (Ar-C), 124.87 (Ar-C), 122.94 (Ar-C), 111.26 (Ar-C), 50.24 (Ar-$\underline{C}H_2$), 21.17 (Ar-$\underline{C}H_3$), 20.94 (Ar-$\underline{C}H_3$); HRMS (ESI-TOF) calcd for $C_{32}H_{35}Cl_3N_3Pd$ $[M+H]^+$ m/z = 672.0931, found 672.0937.

C3: [Bis-1,3-(2,4,6-trimethylbenzyl)-5-methylbenzimidazol-2-ylidene]-*N*-(3-chloropyridine)dichloropalladium(II)



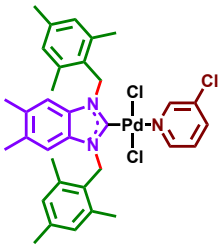
Yellow solid (583 mg, 85%); m.p. 150-152 ^{o}C; vmax (KBr)/cm^{-1} : 3065 (Ar-C-H), 2918 (Ali-C-H), 1700 (-C=N), 1561 (Ar-C=C), 1407 (Pd-Ccarbene); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.89 (s, 1H, Ar-H), 8.85 (d, J = 5.6 Hz, 1H, Ar-H), 7.76 (d, J = 8.4 Hz, 1H, Ar-H), 7.31 (t, J = 8.0 Hz, 1H, Ar-H), 6.92 (d, J = 4.4 Hz, 4H, Ar-H), 6.68 (d, J = 8.4 Hz, 1H, Ar-H), 6.34 (t, J = 8.0 Hz, 2H, Ar-H), 6.17 (s, 2H, Ar-C$\underline{H}_2$), 6.11 (s, 2H, Ar-C$\underline{H}_2$), 2.32 (s, 18H, Ar-C$\underline{H}_3$), 2.14 (s, 3H, Ar-C$\underline{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.87 (Ar-C), 150.36 (Ar-C), 149.26 (Ar-C), 138.86 (Ar-C), 138.54 (Ar-C), 138.47 (Ar-C), 138.08 (Ar-C), 135.20 (Ar-C), 132.83 (Ar-C), 132.57 (Ar-C), 129.66 (Ar-C), 127.96 (Ar-C), 124.83 (Ar-C), 124.26 (Ar-C), 111.19 (Ar-C), 110.80 (Ar-C), 50.23 (Ar-$\underline{C}H_2$), 49.72 (Ar-$\underline{C}H_2$), 21.54 (Ar-$\underline{C}H_3$), 21.18 (Ar-$\underline{C}H_3$), 21.15 (Ar-$\underline{C}H_3$), 20.99 (Ar-$\underline{C}H_3$), 20.91 (Ar-$\underline{C}H_3$); HRMS (ESI-TOF) calcd for $C_{33}H_{37}Cl_3N_3Pd$ $[M+H]^+$ m/z = 686.1088, found 686.1095.

C4: [1,3-Dibenzyl)-5,6-dimethylbenzimidazol-2-ylidene]-*N*-(3-chloropyridine)dichloropalladium(II)



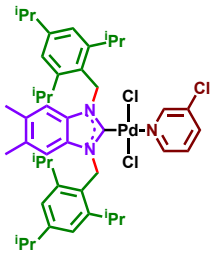
Yellow solid (425 mg, 69%); m.p. 164-166 ^{o}C; *v*max (KBr)/cm^{-1} : 3076 (Ar-C-H), 2921 (Ali-C-H), 1691 (-C=N), 1558 (Ar-C=C), 1414 (Pd-Ccarbene); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.02 (d, *J* = 2.8 Hz, 1H, Ar-H), 8.92 (d, *J* = 5.6 Hz, 1H, Ar-H), 7.58 (d, *J* = 8.0 Hz, 4H, Ar-H), 7.38 (t, *J* = 7.6 Hz, 5H, Ar-H), 7.32-7.24 (m, 2H, Ar-H), 6.85 (s, 3H, Ar-H), 6.16 (s, 4H, Ar-C$\underline{H}_2$), 2.16 (s, 6H, Ar-C$\underline{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.21 (Ar-C), 151.77 (Ar-C), 150.39 (Ar-C), 149.32 (Ar-C), 138.19 (Ar-C), 135.34 (Ar-C), 133.22 (Ar-C), 132.70 (Ar-C), 128.95 (Ar-C), 128.20 (Ar-C), 127.95 (Ar-C), 124.92 (Ar-C), 111.72 (Ar-C), 52.99 (Ar-$\underline{C}H_2$), 20.32 (Ar-$\underline{C}H_3$); HRMS (ESI-TOF) calcd for $C_{28}H_{27}Cl_3N_3Pd$ $[M+H]^+$ m/z = 616.0305, found 616.0309.

C5: [Bis-1,3-(2,4,6-trimethylbenzyl)-5,6-dimethylbenzimidazol-2-ylidene]-*N*-(3-chloropyridine) dichloropalladium(II)



Yellow solid (574 mg, 82%); m.p. 163-164 ^{o}C; vmax (KBr)/cm^{-1} : 3076 (Ar-C-H), 2926 (Ali-C-H), 1693 (-C=N), 1569 (Ar-C=C), 1409 (Pd-Ccarbene); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.86 (d, J = 2.4 Hz, 1H, Ar-H), 8.82 (dd, J = 1.2 Hz and 1.6 Hz, 1H, Ar-H), 7.76 (qd, J = 1.2 Hz and 1.2 Hz, 1H, Ar-H), 7.30 (q, J = 5.6 Hz and 5.6 Hz, 1H, Ar-H), 6.90 (s, 4H, Ar-H), 6.23 (s, 2H, Ar-H), 6.09 (s, 4H, Ar-C$\underline{H}_2$), 2.31 (S, 18H, Ar-C$\underline{H}_3$), 2.01 (s, 6H, Ar-C$\underline{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.51 (Ar-C), 150.36 (Ar-C), 149.26 (Ar-C), 138.91 (Ar-C), 138.43 (Ar-C), 138.00 (Ar-C), 133.47 (Ar-C), 132.53 (Ar-C), 131.82 (Ar-C), 129.57 (Ar-C), 128.04 (Ar-C), 124.77 (Ar-C), 111.46 (Ar-C), 49.78 (Ar-$\underline{C}H_2$), 21.13 (Ar-$\underline{C}H_3$), 20.93 (Ar-$\underline{C}H_3$), 20.38 (Ar-$\underline{C}H_3$); HRMS (ESI-TOF) calcd for $C_{34}H_{39}Cl_3N_3Pd$ $[M+H]^+$ m/z = 700.1244, found 700.1251.

C6: [Bis-1,3-(2,4,6-triisopropylbenzyl)-5,6-dimethylbenzimidazol-2-ylidene]-*N*-(3-Chloropyridine)dichloropalladium(II)

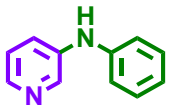


Yellow solid (686 mg, 79%); m.p. 172-174 ^{o}C; vmax (KBr)/cm^{-1}: 3080 (Ar-C-H), 2957 (Ali-C-H), 1695 (-C=N), 1550 (Ar-C=C), 1409 (Pd-Ccarbene); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.18 (s, 1H, Ar-H), 9.10 (d, J = 3.6 Hz, 1H, Ar-H), 7.82 (d, J = 6.4 Hz, 1H, Ar-H), 7.40 (t, J = 4.4 Hz, 1H, Ar-H), 7.11 (s, 4H, Ar-H), 6.35 (s, 4H, Ar-H), 5.75 (s, 2H, Ar-H), 3.50-3.44 (m, 4H, Ar-$\underline{C}H(CH_3)_2$), 3.01-2.93 (m, 2H, Ar-$\underline{C}H(CH_3)_2$), 1.85 (s, 6H, Ar-C$\underline{H}_3$), 1.32 (d, J = 5.6 Hz, 12H, Ar-CH(C$\underline{H}_3$)$_2$), 1.12 (s, 24H, Ar-CH(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.50 (Ar-C), 150.49 (Ar-C), 150.30 (Ar-C), 149.58 (Ar-C), 149.46 (Ar-C), 138.12 (Ar-C), 133.76 (Ar-C), 132.77 (Ar-C), 130.79 (Ar-C), 125.47 (Ar-C), 124.98 (Ar-C), 121.56 (Ar-C), 112.31 (Ar-C), 48.73 (Ar-$\underline{C}H_2$), 34.52 (Ar-$\underline{C}H(CH_3)_2$),

29.70 (Ar-<u>C</u>H(CH_3)$_2$), 24.24 (Ar-CH(<u>C</u>H_3)$_2$), 24.22 (Ar-CH(<u>C</u>H_3)$_2$), 19.88 (Ar-<u>C</u>H_3); HRMS (ESI-TOF) calcd for $C_{46}H_{63}Cl_3N_3Pd$ $[M+H]^+$ m/z = 868.3122, found 868.3127.

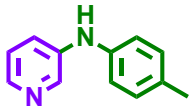
IV. Characteristic data of compounds 6a - 6cb

N-Phenyl pyridin-3-amine (**6a**)[1]



Pale brown solid (156 mg, 91%); m.p. 90-92 ˚C; *v*max (KBr)/cm^{-1}: 3321 (Ar-NH-Ar), 3062 (Ar-C-H), 1634 (Ar-C=N), 1437 (Ar-C=C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.37 (s, 1H, Ar-H), 8.16 (s, 1H, Ar-H), 7.41 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.31 (t, *J* = 8.4 Hz, 2H, Ar-H), 7.18 (q, *J* = 4.8 Hz and 4.8 Hz, 1H, Ar-H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 5.814 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 147.23 (Ar-C), 141.95 (Ar-C), 140.11 (Ar-C), 139.84 (Ar-C), 129.56 (Ar-C), 123.70 (Ar-C), 123.45 (Ar-C), 122.07 (Ar-C), 118.35 (Ar-C); HRMS (ESI-TOF) calcd for $C_{11}H_{11}N_2$ $[M+H]^+$ m/z = 171.0922, found 171.0920.

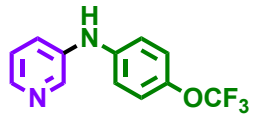
N-p-Tolyl pyridin-3-amine (**6b**)[1]



Pale brown solid (181 mg, 98%); m.p. 85-88 ˚C; *v*max (KBr)/cm^{-1}: 3325 (Ar-NH-Ar), 3051 (Ar-C-H), 2972 (Ali-C-H), 1627 (Ar-C=N), 1425 (Ar-C=C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.32 (s, 1H, Ar-H), 8.11 (s, 1H, Ar-H), 7.33 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.14 - 7.10 (m, 3H, Ar-H), 7.01 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.73 (s, 1H, Ar-NH), 2.31 (s, 3H, Ar-C<u>H</u>$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 141.18 (Ar-C), 140.64 (Ar-C), 139.33 (Ar-C), 139.09 (Ar-C), 132.05 (Ar-C), 130.07 (Ar-C), 123.70 (Ar-C), 122.41 (Ar-C), 119.39 (Ar-C), 20.74 (Ar-<u>C</u>H_3); HRMS (ESI-TOF) calcd for $C_{12}H_{13}N_2$ $[M+H]^+$ m/z = 185.1079, found 185.1081.

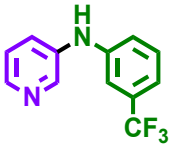
N-(4-(Trifluoromethoxy)phenyl)pyridin-3-amine (**6c**)[1]

Colourless crystalline solid (235 mg, 92%); m. p. 93-95 ˚C; *v*max



(KBr)/cm^{-1}: 3313 (Ar-NH-Ar), 3057 (Ar-C-H), 1614 (Ar-C=N), 1431 (Ar-C=C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.38 (d, *J* = 2.8 Hz, 1H, Ar-H), 8.21 (dd, *J* = 0.8 Hz and 1.2 Hz, 1H, Ar-H), 7.42 (qd, *J* = 1.6 Hz and 1.2 Hz, 1H, Ar-H), 7.21 (q, *J* = 4.8 Hz and 4.8 Hz, 1H, Ar- H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.07 - 7.04 (m, 2H, Ar-H), 5.94 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.57 (Ar-C), 142.55 (Ar-C), 141.00 (Ar-C), 140.20 (Ar-C), 139.39 (Ar-C), 123.98 (d, *J* = 16.6 Hz, Ar-O$\underline{C}F_3$), 122.53 (Ar-C), 121.84 (Ar-C), 119.29 (Ar-C), 118.86 (Ar-C); HRMS (ESI-TOF) calcd for $C_{12}H_{10}F_3N_2O$ $[M+H]^+$ m/z = 255.0745, found 255.0737.

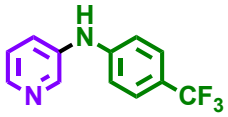
N-(3-(Trifluoromethyl)phenyl)pyridin-3-amine (**6d**)



Colourless solid (198 mg, 83%); m. p. 85-87 ˚C; *v*max (KBr)/cm^{-1}: 3317 (Ar-NH-Ar), 3042 (Ar-C-H), 1618 (Ar-C=N), 1429 (Ar-C=C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.35 (s, 1H, Ar-H), 8.18 (s, 1H, Ar-H), 7.39 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.32 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.15 (t, *J* = 8.4 Hz, 4H, Ar-H), 6.16 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.04 (Ar-C), 141.04 (Ar-C), 132.49 (q, *J* = 35.4 Hz and 32.0 Hz, Ar-C), 130.08 (Ar-C), 128.00 (Ar-C), 125.29 (Ar-C), 124.79 (Ar-C), 122.58 (Ar-C), 120.27 (Ar-C), 119.87 (Ar-C), 118.05 (q, *J* = 3.7 Hz and 3.9 Hz, Ar-C), 113.91 (d, *J* = 3.9 Hz, Ar-C); HRMS (ESI-TOF) calcd for $C_{12}H_{10}F_3N_2$ $(M+H)^+$ m/z = 239.0796, found 239.0793.

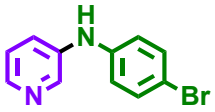
N-(4-(Trifluoromethyl)phenyl)pyridin-3-amine (**6e**)

Colorless solid (213 mg, 89%); m. p. 113-115 ˚C; *v*max (KBr)/cm^{-1}: 3328 (Ar-NH-Ar), 3057 (Ar-C-H), 1622 (Ar-C=N), 1431 (Ar-C=C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.46 (s, 1H, Ar-H), 8.29 (d, *J* = 4.0 Hz, 1H, Ar-H), 7.52 (d, *J* = 8.4 Hz, 3H, Ar-H), 7.27 (t, *J* = 4 Hz, 1H, Ar-



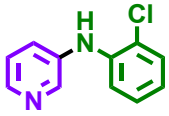
H), 7.080 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.11 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 145.76 (Ar-C), 143.77 (Ar-C), 142.01 (Ar-C), 138.02 (Ar-C), 126.96 (q, *J* = 3.7 Hz and 3.7 Hz, Ar-C), 126.05 (Ar-C), 123.89 (Ar-C), 123.05 (d, *J* = 5.6 Hz, Ar-C), 115.89 (Ar-C); HRMS (ESI-TOF) calcd for $C_{12}H_{10}F_3N_2$ $(M+H)^+$ m/z = 239.0796, found 239.0793.

N-(4-Bromophenyl)pyridin-3-amine (**6f**)[2]



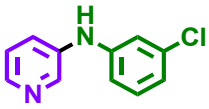
Pale black solid (219 mg, 88%); m. p. 108-110 ˚C; *v*max (KBr)/cm^{-1}: 3331 (Ar-NH-Ar), 3049 (Ar-C-H), 1613 (Ar-C=N), 1426 (Ar-C=C), 653 (C-Br); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.37 (s, 1H, Ar-H), 8.20 (d, *J* = 4.0 Hz, 1H, Ar-H), 7.39 (d, *J* = 8.8 Hz, 3H, Ar-H), 7.20 (q, *J* = 4.8 Hz and 4.4 Hz, 1H, Ar-H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.86 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 142.27 (Ar-C), 140.75 (Ar-C), 140.27 (Ar-C), 139.53 (Ar-C), 129.52 (Ar-C), 126.68 (Ar-C), 123.81 (Ar-C), 123.75 (Ar-C), 119.40 (Ar-C). HRMS (ESI-TOF) calcd for $C_{11}H_{10}BrN_2$ $(M+H)^+$ m/z = 249.0027, found 249.0037.

N-(2-Chlorophenyl)pyridin-3-amine (**6g**)



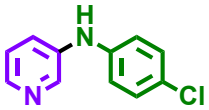
Colourless solid (162 mg, 79%); m. p. 80-81 ˚C; *v*max (KBr)/cm^{-1}: 3332 (Ar-NH-Ar), 3051 (Ar-C-H), 1621 (Ar-C=N), 1421 (Ar-C=C), 694 (Ar-Cl); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.47 (s, 1H, Ar-H), 8.27 (d, *J* = 4.4 Hz, 1H, Ar-H), 7.49 (qd, *J* = 1.2 Hz and 1.2 Hz, 1H, Ar-H), 7.40 (dd, *J* = 1.2 Hz and 1.2 Hz, 1H, Ar-H), 7.25 (q, *J* = 4.8 Hz and 4.8 Hz, 1H, Ar-H), 7.17 (t, *J* = 7.2 Hz, 1H, Ar-H), 6.90 (t, *J* = 8.0 Hz, 1H, Ar-H), 6.09 (s, 1H, Ar-N<u>H</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.48 (Ar-C), 142.06 (Ar-C), 139.26 (Ar-C), 138.36 (Ar-C), 130.02 (Ar-C), 127.60 (Ar-C), 126.08 (Ar-C), 123.79 (Ar-C), 122.47 (Ar-C), 121.62 (Ar-C), 116.08 (Ar-C); HRMS (ESI-TOF) calcd for $C_{11}H_{10}ClN_2$ $(M+H)^+$ m/z = 205.0533, found 205.0537.

N-(3-Chlorophenyl)pyridin-3-amine (**6h**)



Colourless solid (170 mg, 83%); m. p. 88-90 ˚C; *v*max (KBr)/cm^{-1}: 3332 (Ar-NH-Ar), 3051 (Ar-C-H), 1620 (Ar-C=N), 1469 (Ar-C=C), 693 (Ar-Cl); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.39 (d, *J* = 2.8 Hz, 1H, Ar-H), 8.22 (dd, *J* = 1.2 Hz and 1.2 Hz, 1H, Ar-H), 7.46 (qd, *J* = 1.2 Hz and 1.6 Hz, 1H, Ar-H), 7.22 - 7.16 (m, 2H, Ar-H), 7.05 (t, *J* = 2.0 Hz, 1H, Ar-H), 6.935 (qd, *J* = 2.0 Hz and 1.6 Hz, 2H, Ar-H), 6.14 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.74 (Ar-C), 142.80 (Ar-C), 140.98 (Ar-C), 138.93 (Ar-C), 135.21 (Ar-C), 130.55 (Ar-C), 124.71 (Ar-C), 123.86 (Ar-C), 121.54 (Ar-C), 117.32 (Ar-C), 115.63 (Ar-C); HRMS (ESI-TOF) calcd for $C_{11}H_{10}ClN_2$ $(M+H)^+$ m/z = 205.0533, found 205.0537.

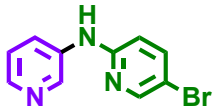
N-(4-Chlorophenyl)pyridin-3-amine (**6i**)[3]



Off white solid (178 mg, 87%); m. p. 90-92 ˚C; *v*max (KBr)/cm^{-1}: 3330 (Ar-NH-Ar), 3053 (Ar-C-H), 1618 (Ar-C=N), 1449 (Ar-C=C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.36 (d, *J* = 2.4 Hz, 1H, Ar-H), 8.18 (dd, *J* = 1.2 Hz and 1.2 Hz, 1H, Ar-H), 7.39 (qd, *J* = 1.2 Hz and 1.2 Hz, 1H, Ar-H), 7.26-7.22 (m, 2H, Ar-H), 7.19 (q, *J* = 4.8 Hz and 4.4 Hz, 1H, Ar-H), 7.02-6.98 (m, 2H, Ar-H), 6.00 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 168.37 (Ar-C), 157.97 (Ar-C), 156.29 (Ar-C), 152.73 (Ar-C), 139.76 (Ar-C), 135.52 (Ar-C), 129.62(Ar-C), 125.62 (Ar-C), 124.96 (Ar-C); HRMS (ESI-TOF) calcd for $C_{11}H_{10}ClN_2$ $(M+H)^+$ m/z = 205.0533, found 205.0537.

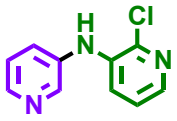
5-Bromo-*N*-(pyridin-3-yl)pyridin-2-amine (**6j**)

Pale yellow crystalline solid (212 mg, 85%); m. p. 85-88 ˚C; *v*max (KBr)/cm^{-1}: 3445 (Ar-NH-Ar), 3051 (Ar-C-H), 1611 (Ar-C=N), 1467



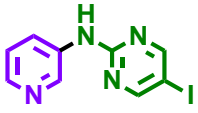
(Ar-C=C), 684 (C-Br); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08 (s, 2H, Ar-H), 7.49 (dd, *J* = 2.4 Hz and 2.8 Hz, 2H, Ar-H), 6.42 (d, *J* = 8.8 Hz, 3H, Ar-H), 4.685 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 157.17 (Ar-C), 148.55 (Ar-C), 140.12 (Ar-C), 110.14 (Ar-C), 108.09 (Ar-C); HRMS (ESI-TOF) calcd for $C_{10}H_9BrN_3$ $(M+H)^+$ m/z = 249.9980, found 249.9982.

2-Chloro-*N*-pyridin-3-yl)pyridin-3-amine (**6k**)[4]



Pale black solid (167 mg, 81%); m. p. 81-83 ˚C; *v*max (KBr)/cm^{-1}: 3331 (Ar-NH-Ar), 3150 (Ar-C-H), 1609 (Ar-C=N), 1512 (Ar-C=C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (t, *J* = 2.8 Hz, 2H, Ar-H), 7.04 (d, *J* = 3.2 Hz, 5H, Ar-H), 4.167 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 139.75 (Ar-C), 138.51 (Ar-C), 136.90 (Ar-C), 123.38 (Ar-C), 122.44 (Ar-C); HRMS (ESI-TOF) calcd for $C_{10}H_9ClN_3$ $(M+H)^+$ = 206.0485, found 206.0486.

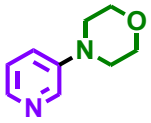
5-Iodo-*N*-(pyrid-3-yl)pyrimidin-2-amine (**6l**)



Colourless solid (245 mg, 82%); m. p. 90-93 ˚C; *v*max (KBr)/cm^{-1}: 3323 (Ar-NH-Ar), 3175 (Ar-C-H), 1636 (Ar-C=N), 1474 (Ar-C=C), 527 (C-I); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.40 (s, 4H, Ar-H), 7.26 (s, 2H, Ar-H), 5.06 (s, 1H, Ar-NH); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 142.52 (Ar-C), 141.28 (Ar-C), 140.51 (Ar-C), 139.25 (Ar-C), 132.45 (Ar-C), 124.01 (Ar-C), 123.80 (Ar-C), 119.59 (Ar-C), 113.89 (Ar-C); HRMS (ESI-TOF) calcd for $C_9H_8IN_4$ $(M+H)^+$ m/z = 298.9794, found 298.9794.

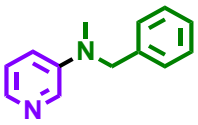
4-(Pyridin-3-yl)morpholine (**6aa**)[5]

Pale yellow liquid (153 mg, 93%); νmax (KBr)/cm^{-1}: 3019 (Ar-C-H),



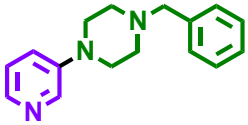
2962 (Ali-C-H), 1621 (Ar-C=N), 1483 (Ar-C=C), 1242 (C-N), 1121 (C-O); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.31 (s, 1H, Ar-H), 8.13 (s, 1H, Ar-H), 7.18 (s, 2H, Ar-H), 3.88 (t, J = 4.8 Hz, 4H, -C$\underline{H}_2$-O-C$\underline{H}_2$-), 3.20 (t, J = 4.8 Hz, 4H, Ar-N-C$\underline{H}_2$-); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 146.75 (Ar-C), 141.02 (Ar-C), 138.23 (Ar-C), 123.57 (Ar-C), 122.13 (Ar-C), 66.66 (-$\underline{C}H_2$-O-$\underline{C}H_2$-), 48.58 (Ar-N-$\underline{C}H_2$-); HRMS (ESI-TOF) calcd for $C_9H_{13}N_2O$ $(M+H)^+$ m/z = 165.1028, found 165.1022.

N-Benzyl-*N*-methyl pyridin-3-amine (**6ab**)[6]



Pale yellow liquid (179 mg, 90%); dried to solid slowly upon washing with ether; m. p. 89-91 ˚C; *v*max (KBr)/cm^{-1}: 3021 (Ar-C-H), 2985 (Ali-C-H), 1617 (Ar-C=N), 1483 (Ar-C=C); 1367 (C-N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16 (d, *J* = 2.8 Hz, 1H, Ar-H), 7.95 (d, *J* = 3.6 Hz, 1H, Ar-H), 7.32 (t, *J* = 6.8 Hz, 2H, Ar-H), 7.25 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.19 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.08 (q, *J* = 4.8 Hz and 4.8 Hz, 1H, Ar-H), 6.97 (dd, *J* = 2.0 Hz and 1.6 Hz, 1H, Ar-H), 4.51 (s, 2H, Ar-C$\underline{H}_2$-), 3.03 (s, 3H, Ar-N-C$\underline{H}_3$-); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 145.36 (Ar-C), 137.91 (Ar-C), 134.97 (Ar-C), 128.74 (Ar-C), 127.19 (Ar-C), 126.66 (Ar-C), 123.49 (Ar-C), 118.61 (Ar-C), 56.18 (Ar-$\underline{C}H_2$-), 38.38 (Ar-N-$\underline{C}H_3$-); HRMS (ESI-TOF) calcd for $C_{13}H_{15}N_2$ $(M+H)^+$ m/z = 199.1235, found 199.1236.

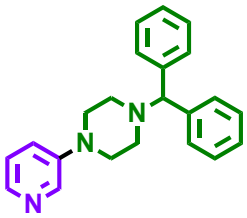
1-Benzyl-4-(pyridin-3-yl)piperazine (**6ac**)[7]



*P*ale brown solid (221 mg, 87%); m. p. 63-65 ˚C; *v*max (KBr)/cm^{-1} : 3032 (Ar-C-H), 2957 (Ali-C-H), 1611 (Ar-C=N), 1477 (Ar-C=C); 1243 (C-N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.29 (s, 1H, Ar-H), 8.08 (dd, *J* = 2.0 Hz and 2.0 Hz, 1H, Ar-H), 7.36-7.27 (m, 5H, Ar-H), 7.16 (t, *J* = 2.4 Hz, 2H, Ar-H), 3.57 (s, 2H, Ar-C$\underline{H}_2$-), 3.23 (t, *J* = 4.8 Hz, 4H, Ar-N-C$\underline{H}_2$-), 2.62 (t, *J* = 5.2 Hz, 4H, Ar-CH_2-N-C$\underline{H}_2$-);

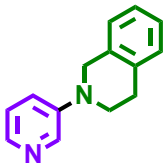
^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 147.02 (Ar-C), 140.51 (Ar-C), 138.45 (Ar-C), 137.80 (Ar-C), 129.20 (Ar-C), 128.33 (Ar-C), 127.24 (Ar-C), 123.47 (Ar-C), 122.28 (Ar-C), 63.01 (Ar-$\underline{C}H_2$-), 52.78 (Ar-N-$\underline{C}H_2$-), 48.41 (Ar-CH_2-N-$\underline{C}H_2$-); HRMS (ESI-TOF) calcd for $C_{16}H_{20}N_3$ $(M+H)^+$ m/z = 254.1657, found 254.1649.

1-Benzhydryl-4-(pyridin-3-yl)piperazine (**6ad**)



Brown liquid (277 mg, 84%); *v*max (KBr)/cm^{-1}: 3039 (Ar-C-H), 1624 (Ar-C=N), 1475 (Ar-C=C); 1325 (C-N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.27 (s, 1H, Ar-H), 8.08 (t, *J* = 2.8 Hz, 1H, Ar-H), 7.45 (d, *J* = 7.2 Hz, 4H, Ar-H), 7.30 (t, *J* = 7.2 Hz, 4H, Ar-H), 7.21 (t, *J* = 7.2 Hz, 2H, Ar-H), 7.14 (q, *J* = 1.6 Hz and 1.2 Hz, 2H, Ar-H), 4.27 (s, 1H, $(Ar)_2$-C$\underline{H}$-), 3.23 (t, *J* = 4.8 Hz, 4H, Ar-N-$C\underline{H}_2$-), 2.57 (t, *J* = 5.2 Hz, 4H, $(Ar)_2$-CH-N-$C\underline{H}_2$-); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 146.97 (Ar-C), 142.46 (Ar-C), 140.42 (Ar-C), 138.21 (Ar-C), 128.61 (Ar-C), 127.90 (Ar-C), 127.12 (Ar-C), 123.46 (Ar-C), 122.10 (Ar-C), 76.15 $(Ar)_2$-$\underline{C}$H-), 51.65 (Ar-N-$\underline{C}H_2$), 48.52 ($(Ar)_2$-CH-N-$\underline{C}H_2$-); HRMS (ESI-TOF) calcd for $C_{22}H_{24}N_3$ $(M+H)^+$ m/z = 330.1970, found 330.1972.

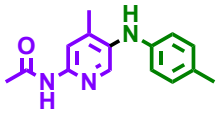
2-(Pyridin-3-yl)-1,2,3,4-tetrahydroisoquinoline (**6ae**)[8]



Brown liquid (192 mg, 91%); *v*max (KBr)/cm^{-1}: 3036 (Ar-C-H), 2921 (Ali-C-H), 1608 (Ar-C=N), 1429 (Ar-C=C); 1322 (C-N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.57 (d, *J* = 2.4 Hz, 1H, Ar-H), 8.37 (dd, *J* = 1.6 Hz and 1.6 Hz, 1H, Ar-H), 8.24 (d, *J* = 2.0 Hz, 1H, Ar-H), 8.05 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.95 (d, *J* = 3.2 Hz, 1H, Ar-H), 7.69 (qd, *J* = 1.6 Hz and 1.2 Hz, 1H, Ar-H), 7.39 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.35-7.21 (m, 1H, Ar-H), 4.30 (s, 2H, Ali-H), 3.91 (t, *J* = 6.4 Hz, 1H, Ali-H), 3.45 (d, *J* = 6.0 Hz, 1H, Ali-H), 3.05 (t, *J*

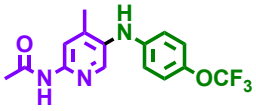
= 6.4 Hz, 1H, Ali-H); 2.88 (t, *J* = 6.0 Hz, 1H, Ali-H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.34 (Ar-C), 146.91 (Ar-C), 139.34 (Ar-C), 137.13 (Ar-C), 134.56 (Ar-C), 128.51 (Ar-C), 126.26 (Ar-C), 123.59 (Ar-C), 121.04 (Ar-C), 49.75 (Ali-CH), 45.64 (Ali-CH), 28.78 (Ali-CH); HRMS (ESI-TOF) calcd for $C_{14}H_{15}N_2$ $(M+H)^+$ *m/z* = 211.1235, found 211.1237.

N-(4-Methyl-5-(p-tolylamino)pyridin-2-yl)acetamide (**6ba**)



Colourless solid (213 mg, 83%); m. p. 120-122 ˚C; νmax (KBr)/cm^{-1}: 3026 (Ar-C-H), 2897 (Ali-C-H), 1611 (Ar-C=N), 1438 (Ar-C=C); 1322 (C-N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.70 (s, 1H, Ar-H), 8.07 (s, 2H, Ar-H), 7.05 (d, J = 6.0 Hz, 2H, Ar-H), 6.75 (d, J = 6.4 Hz, 2H, Ar-H), 5.19 (s, 1H, Ar-H), 2.28 (s, 3H, Ar-NHCOCH_3), 2.25 (s, 3H, Ar-CH_3), 2.16 (s, 3H, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 168.48 (Ar-NHCO-), 146.73 (Ar-C), 141.95 (Ar-C), 141.64 (Ar-C), 139.78 (Ar-C), 135.07 (Ar-C), 130.19 (Ar-C), 129.99 (Ar-C), 116.89 (Ar-C), 115.90 (Ar-C), 24.59 (Ar-NHCO$\underline{C}H_3$), 20.58 (Ar-CH_3), 17.97 (Ar-CH_3); HRMS (ESI-TOF) calcd for $C_{15}H_{18}N_3O$ $(M+H)^+$ m/z = 256.1450, found 256.1451.

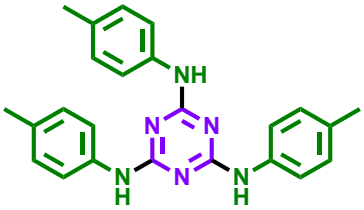
N-(4-Methyl-5-(4-(trifluoromethoxy)phenyl)amino)pyridin-2-yl)acetamide (**6bb**)



Colourless solid (258 mg, 79%); m. p. 125-127 ˚C; *ν*max (KBr)/cm^{-1}: 3039 (Ar-C-H), 2921 (Ali-C-H), 1623 (Ar-C=N), 1429 (Ar-C=C); 1322 (C-N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (s, 1H, Ar-N$\underline{H}$-CO-), 8.04 (d, *J* = 16.8 Hz, 2H, Ar-H), 6.98 (d, *J* = 5.6 Hz, 2H, Ar-H), 6.64 (d, *J* = 6.4 Hz, 2H, Ar-H), 5.30 (s, 1H, Ar-NH-), 2.17 (s, 3H, Ar-NHCOC$\underline{H}_3$), 2.10 (s, 3H, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 168.63 (Ar-

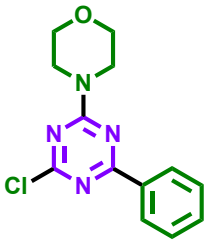
NHCO-), 147.93 (Ar-C), 144.28 (Ar-C), 143.71 (Ar-C), 142.24 (Ar-C), 133.65 (Ar-O$\underline{C}F_3$), 122.53 (Ar-C), 121.60 (Ar-C), 119.59 (Ar-C), 116.00 (Ar-C), 24.60 (Ar-NHCO$\underline{C}H_3$), 17.98 (Ar-CH_3); HRMS (ESI-TOF) calcd for $C_{15}H_{15}F_3N_3O_2$ $(M+H)^+$ m/z = 326.1116, found 326.1120.

N^2,*N*^{4},*N*^{6}-Tri-p-tolyl-1,3,5-triazine-2,4,6-triamine (**6ca**)



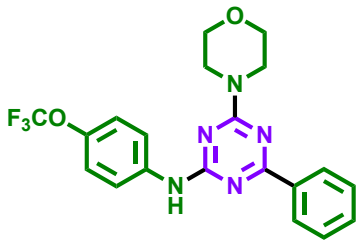
Colourless solid (365 mg, 92%); m. p. 137-139 ˚C; *v*max (KBr)/cm^{-1}: 3043 (Ar-C-H), 2947 (Ali-C-H), 1611 (Ar-C=N), 1429 (Ar-C=C); 1322 (C-N); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, *J* = 8.0 Hz, 6H, Ar-H), 7.11 (d, *J* = 8.0 Hz, 6H, Ar-H), 7.05 (s, 3H, Ar-NH-), 2.32 (s, 9H, Ar-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.30 (Ar-C), 135.94 (Ar-C), 133.10 (Ar-C), 129.38 (Ar-C), 121.06 (Ar-C), 20.93 (Ar-CH_3); HRMS (ESI-TOF) calcd for $C_{24}H_{25}N_6$ $(M+H)^+$ m/z = 397.2141, found 397.2137.

4-(4-chloro-6-phenyl-1,3,5-triazin-2-yl)morpholine (Step ii, int **2** in **6cb** synthesis)



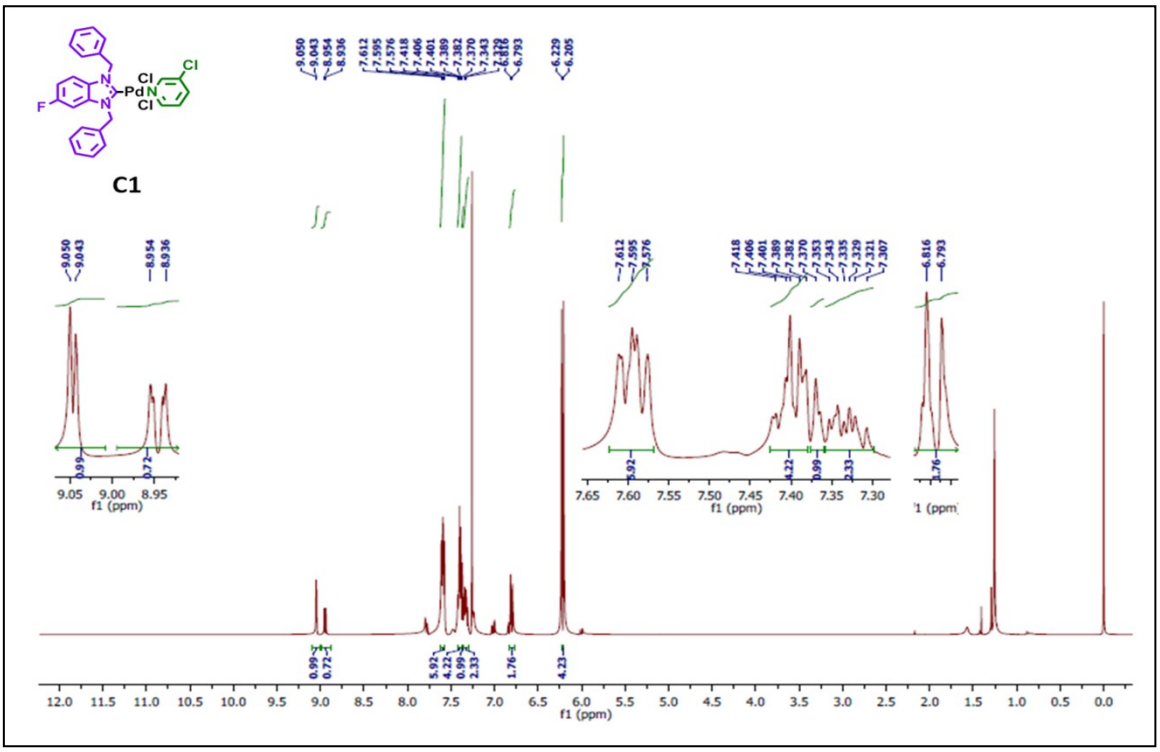
Colorless solid (94%); m. p. 87-89 ˚C; vmax (KBr)/cm^{-1}: 3016 (Ar-C-H), 2958 (Ali-C-H), 1617 (Ar-C=N), 1421 (Ar-C=C); 1328 (C-N), 1161 (C-O); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.41-8.39 (m, 2H, Ar-H), 7.57-7.54 (m, 1H, Ar-H), 7.48-7.45 (m, 2H, Ar-H), 4.06 (t, J = 3.6 Hz, 2H, -$\underline{C}H_2$-N-$\underline{C}H_2$-), 3.93 (t, J = 3.6 Hz, 2H, -$\underline{C}H_2$-N-$\underline{C}H_2$-), 3.81-3.77 (m, 4H, -$\underline{C}H_2$-O-$\underline{C}H_2$-); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 172.33 (Ar-C), 170.99 (Ar-C), 164.75 (Ar-C), 134.92 (Ar-C), 132.73 (Ar-C), 128.90 (Ar-C), 128.47 (Ar-C), 66.58 (-$\underline{C}H_2$-O-$\underline{C}H_2$-), 44.12 (-$\underline{C}H_2$-N-$\underline{C}H_2$-), 43.58 (-$\underline{C}H_2$-N-$\underline{C}H_2$-).

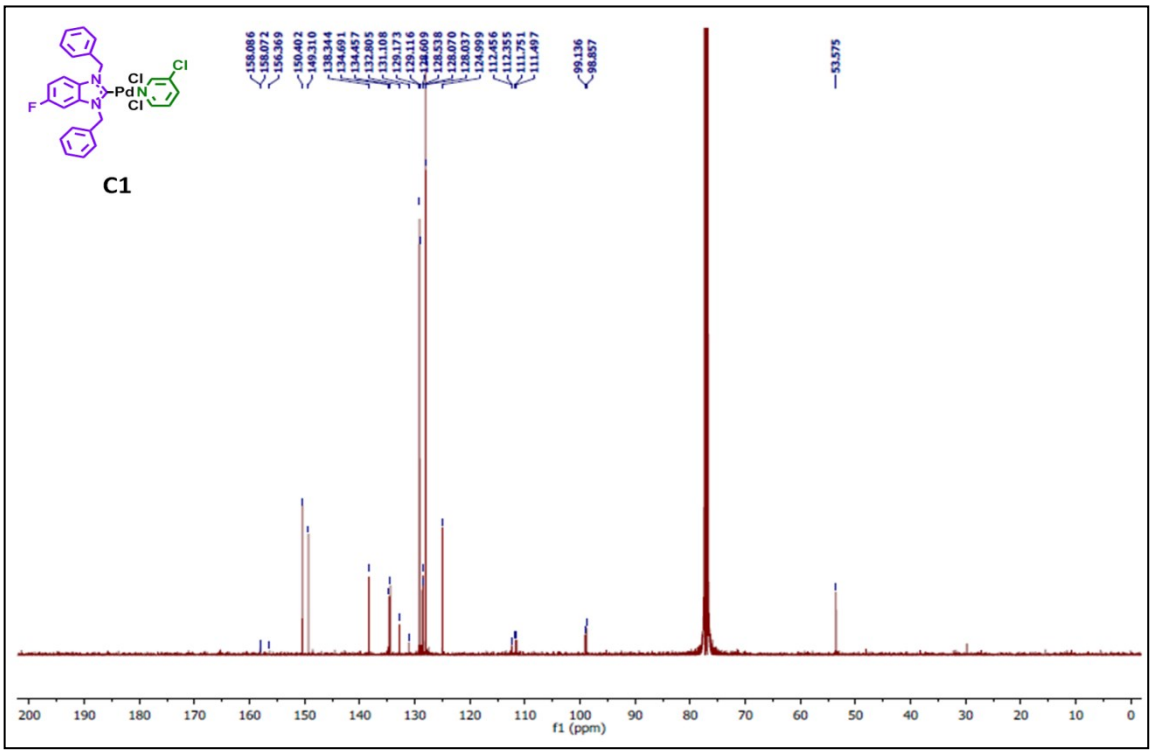
4-Morpholino-6-phenyl-*N*-(4-(trifluoromethoxy)phenyl)-1,3,5-triazin-2-amine (**6cb**)

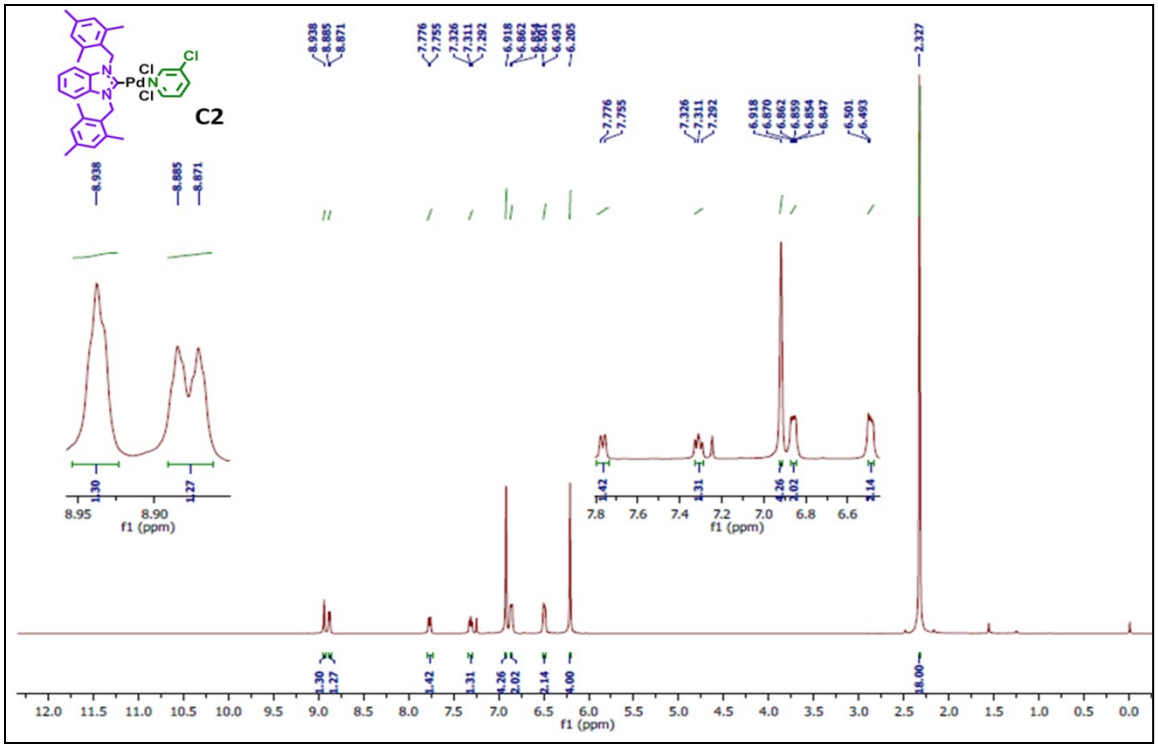


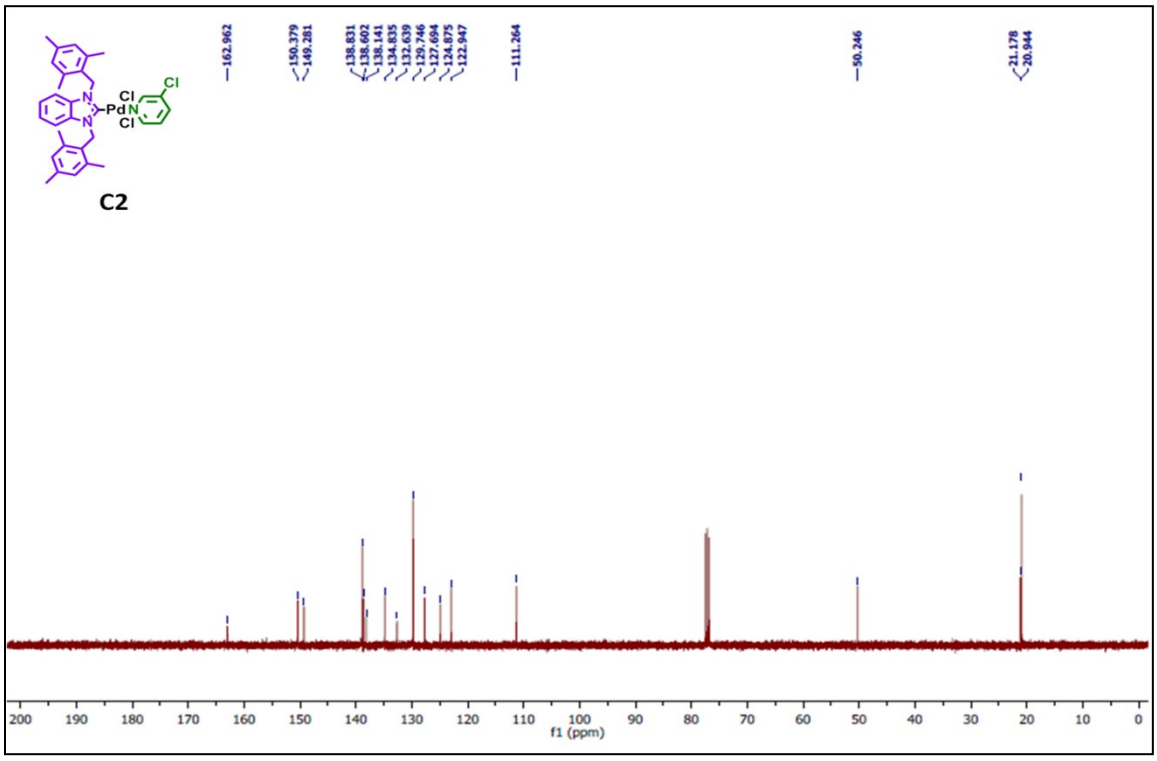
Colourless solid (347 mg, 83%); m. p. 141-143 ˚C; *ν*max (KBr)/cm^{-1}: 3029 (Ar-C-H), 2953 (Ali-C-H), 1601 (Ar-C=N), 1421 (Ar-C=C); 1318 (C-N), 1167 (C-O); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.38 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.64 (d, *J* = 9.2 Hz, 2H, Ar-H), 7.52-7.43 (m, 3H, Ar-H), 7.20 (d, *J* = 8.8 Hz, 3H, Ar-H & Ar-NH), 4.01-3.88 (m, 4H, -C$\underline{H_2}$-O-C$\underline{H_2}$-), 3.80 (t, *J* = 5.2 Hz, 4H, Ar-N-C$\underline{H_2}$); ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 171.26 (Ar-C), 165.22 (Ar-C), 164.57 (Ar-C), 144.41 (d, *J* = 2.0 Hz, Ar-C), 137.71 (Ar-C), 136.75 (Ar-C), 131.82 (Ar-C), 128.43 (d, *J* = 2.3 Hz, Ar-O$\underline{C}F_3$), 121.91 (Ar-C), 121.70 (Ar-C), 120.92 (Ar-C), 66.86 (-$\underline{C}H_2$-*O*-$\underline{C}H_2$-), 43.87 (Ar-*N*-$\underline{C}H_2$); HRMS (ESI-TOF) calcd for $C_{20}H_{19}F_3N_5O_2$ $(M+H)^+$ m/z = 418.1491, found 418.1496.

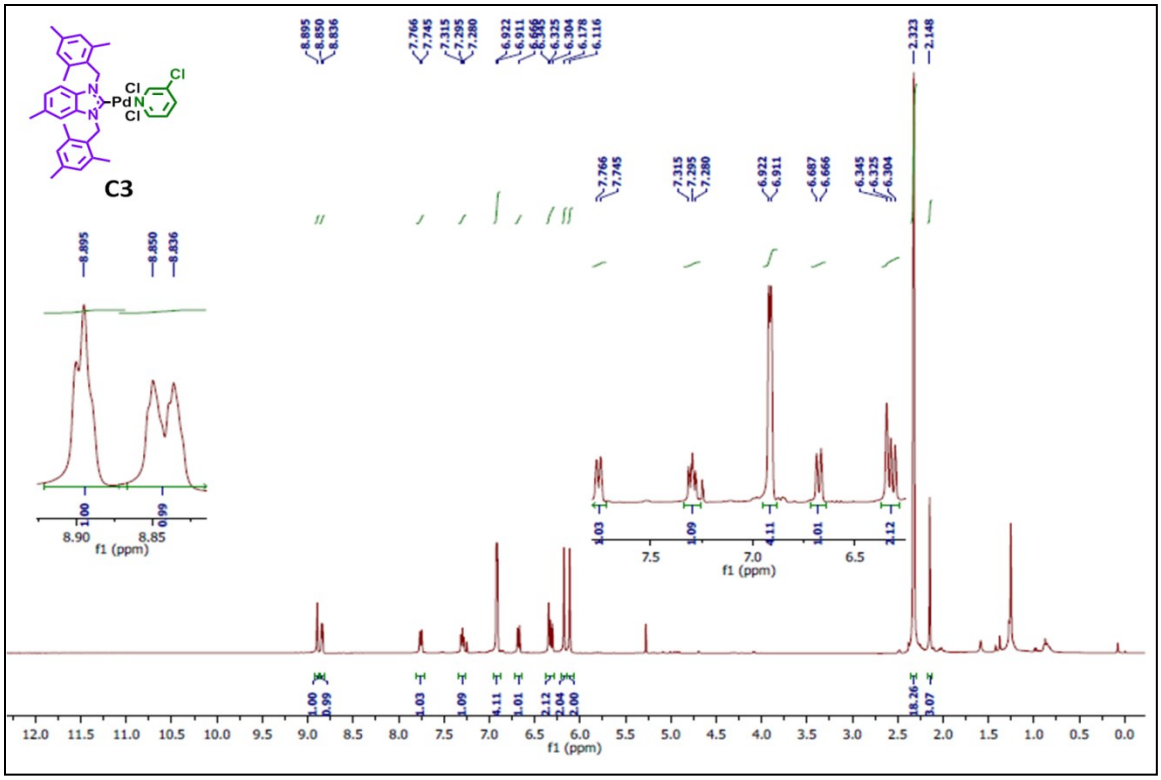
V. ^{1}H and ^{13}C NMR Spectra

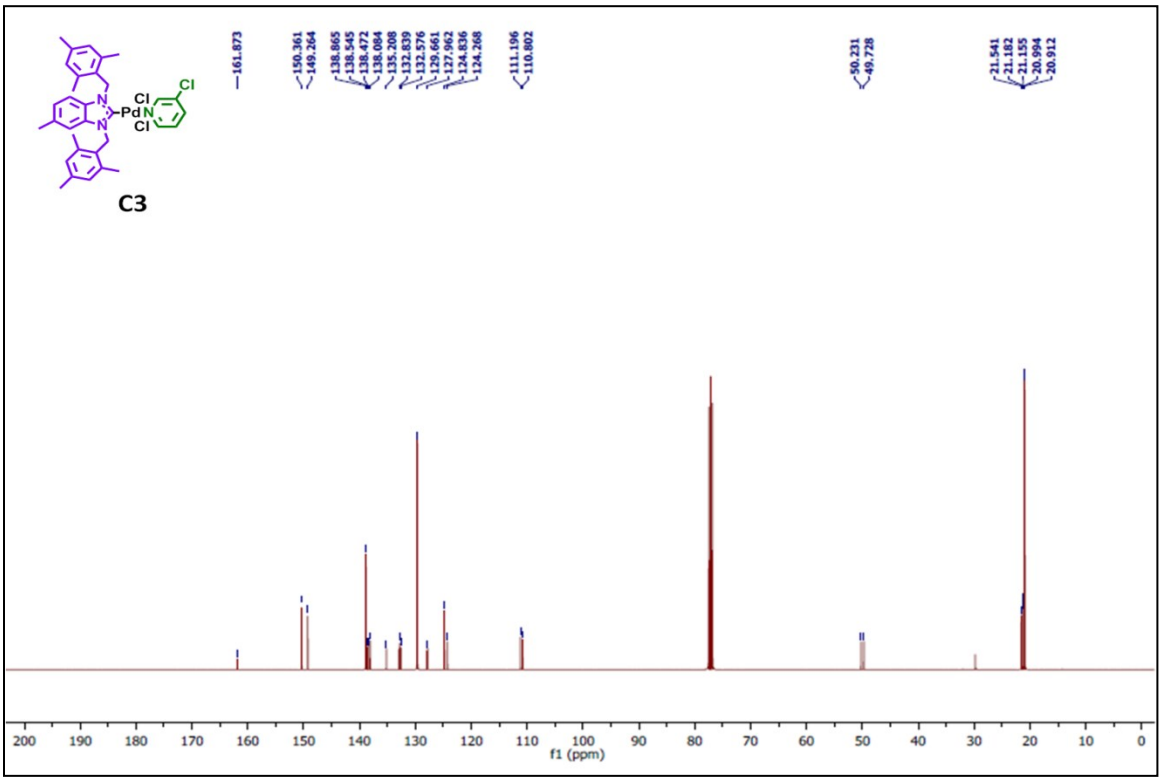


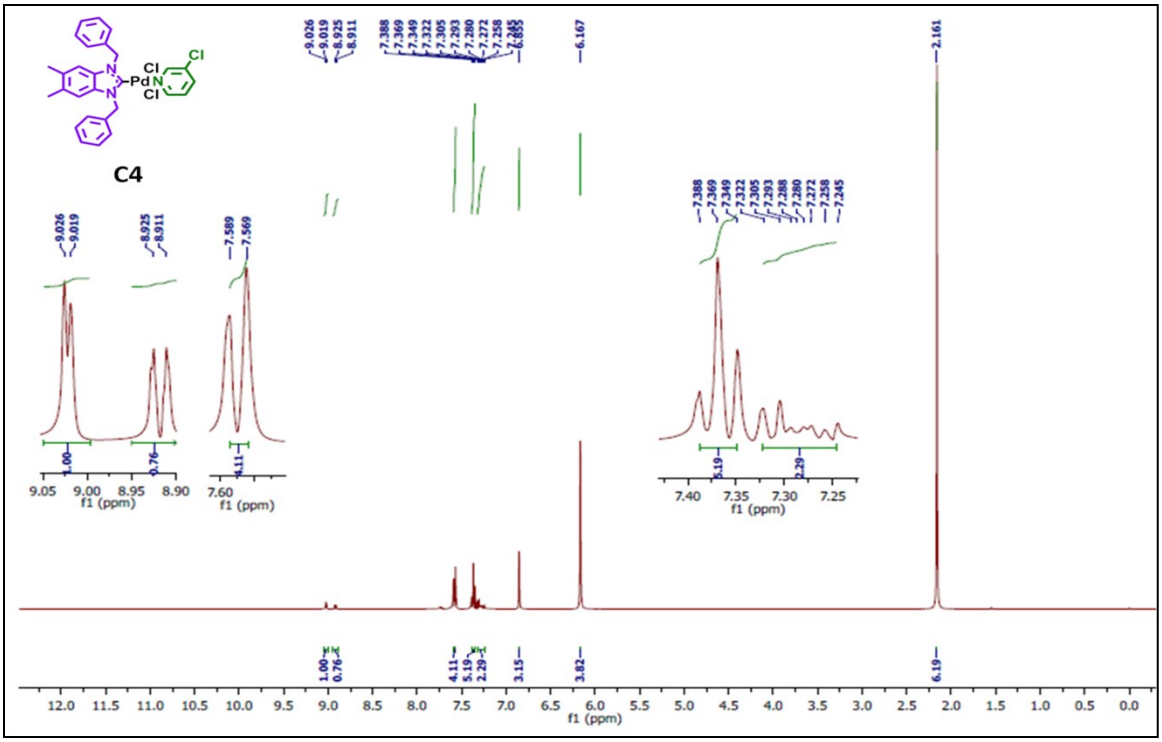


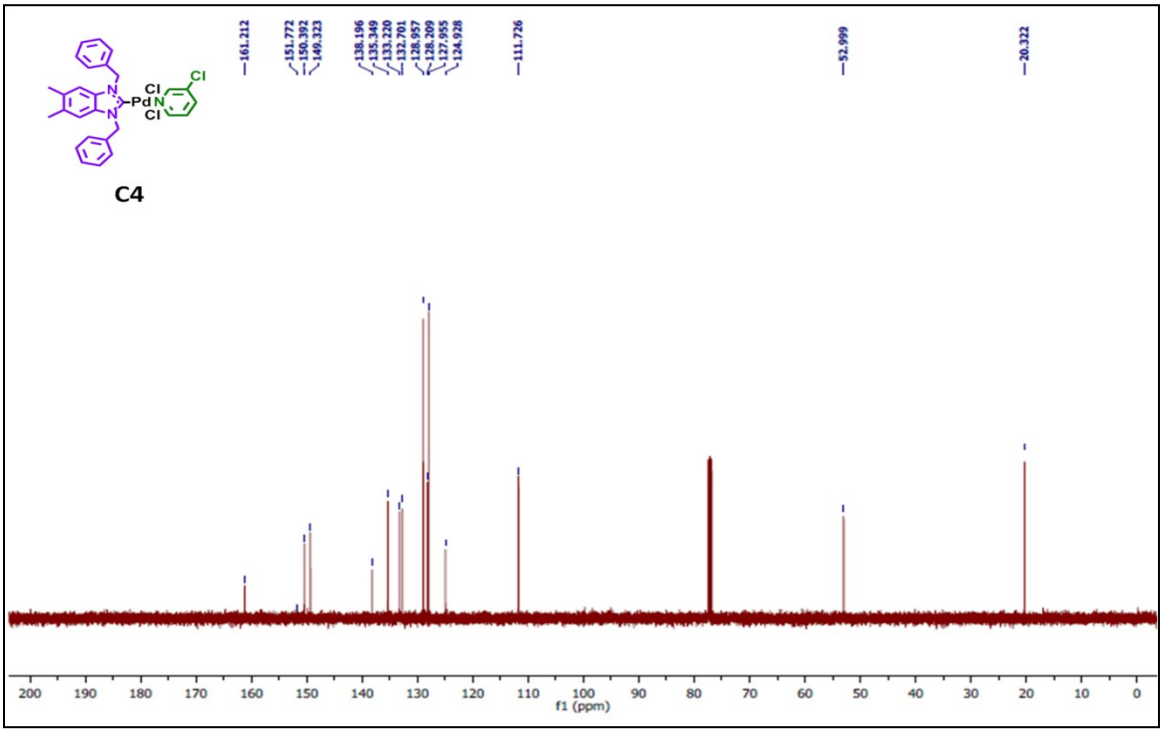

C2
8.938
8.885
8.871
7.776
7.755
7.326
7.311
7.292
6.918
6.862
6.493
6.205
2.327
f1 (ppm)

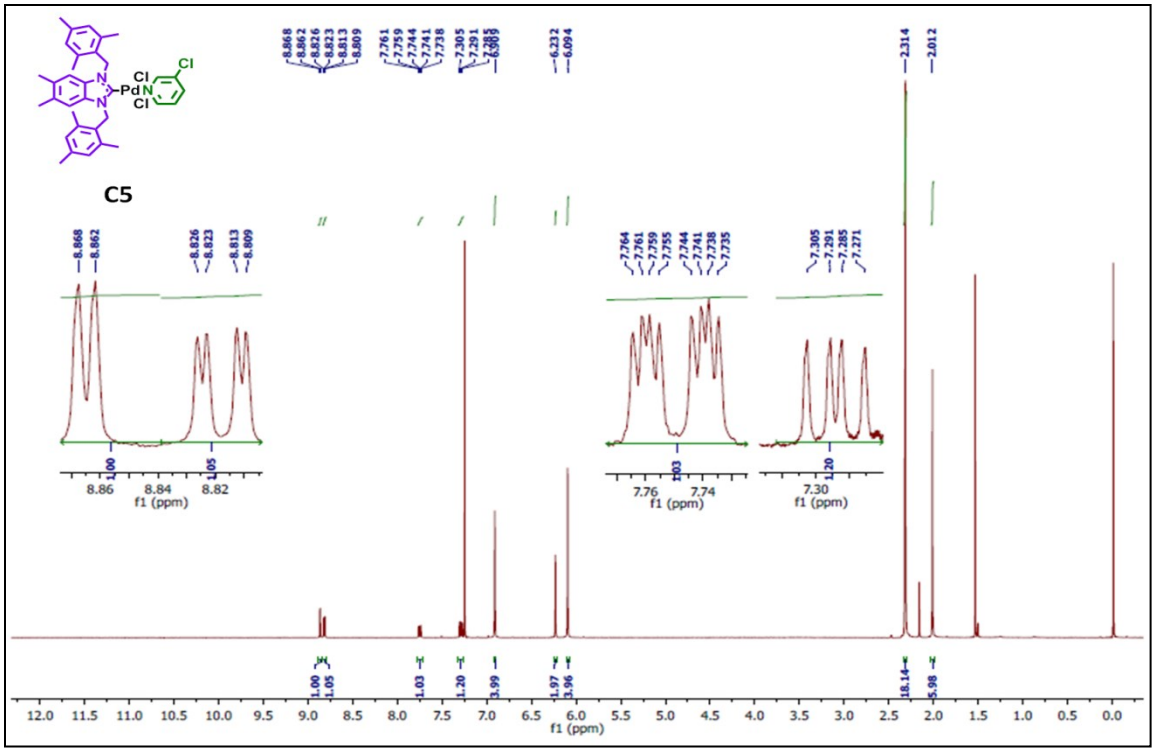

C2
162.962
150.379
149.281
138.831
138.602
138.141
134.835
132.639
129.746
127.694
124.875
122.947
111.264
50.246
21.178
20.944
f1 (ppm)

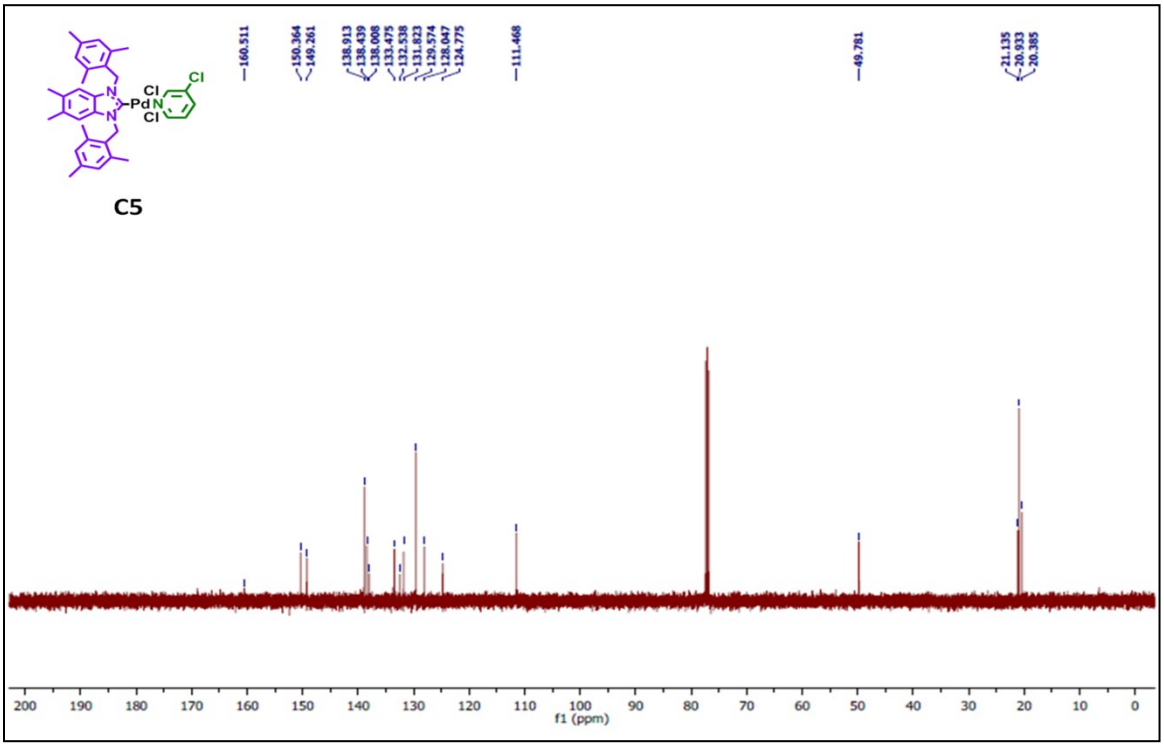

C3
f1 (ppm)

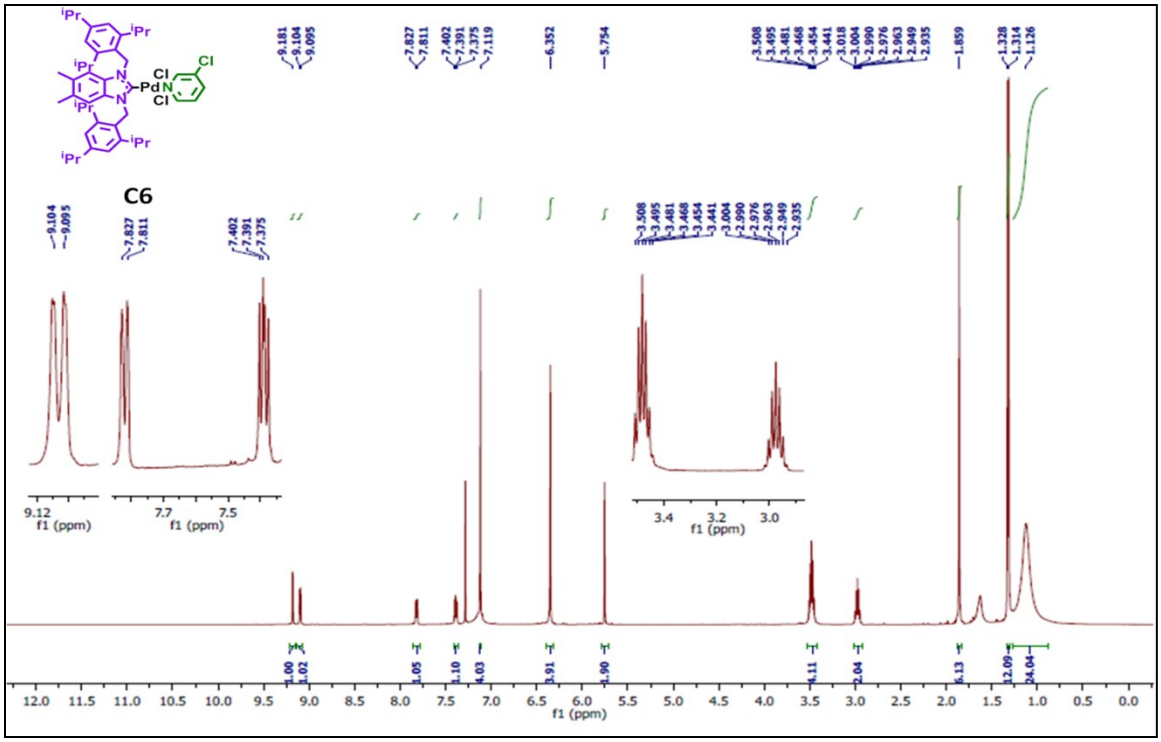

C3
f1 (ppm)

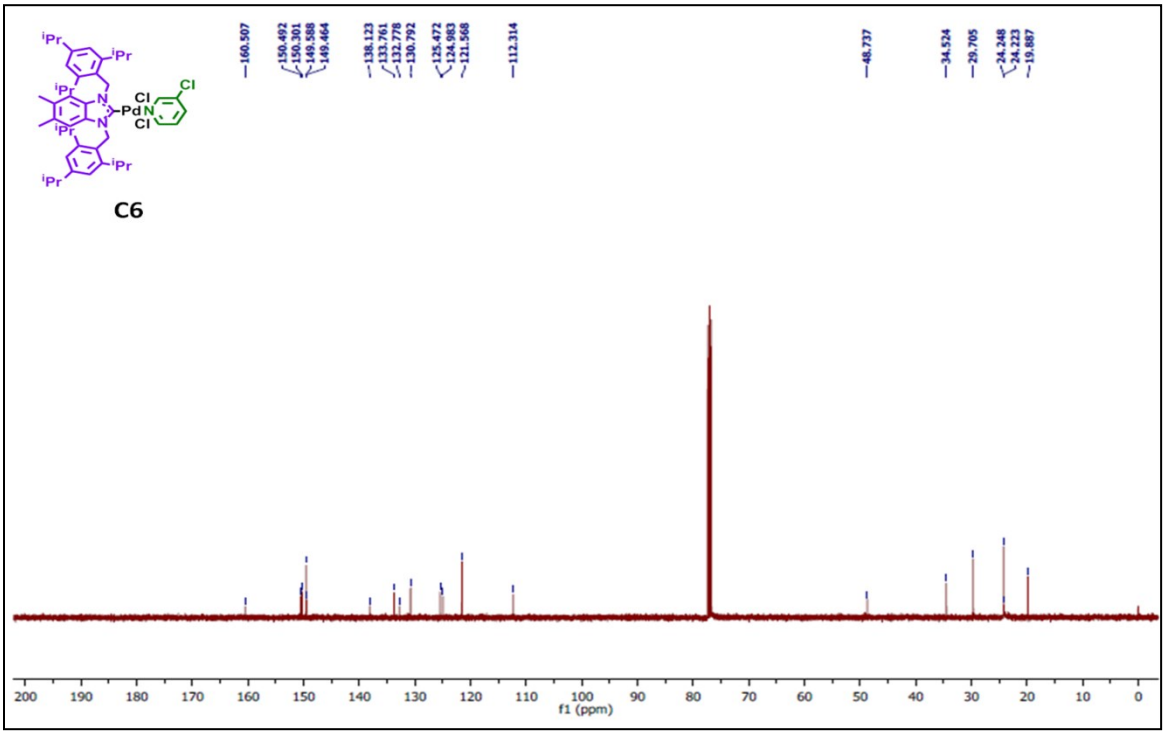

C4
f1 (ppm)

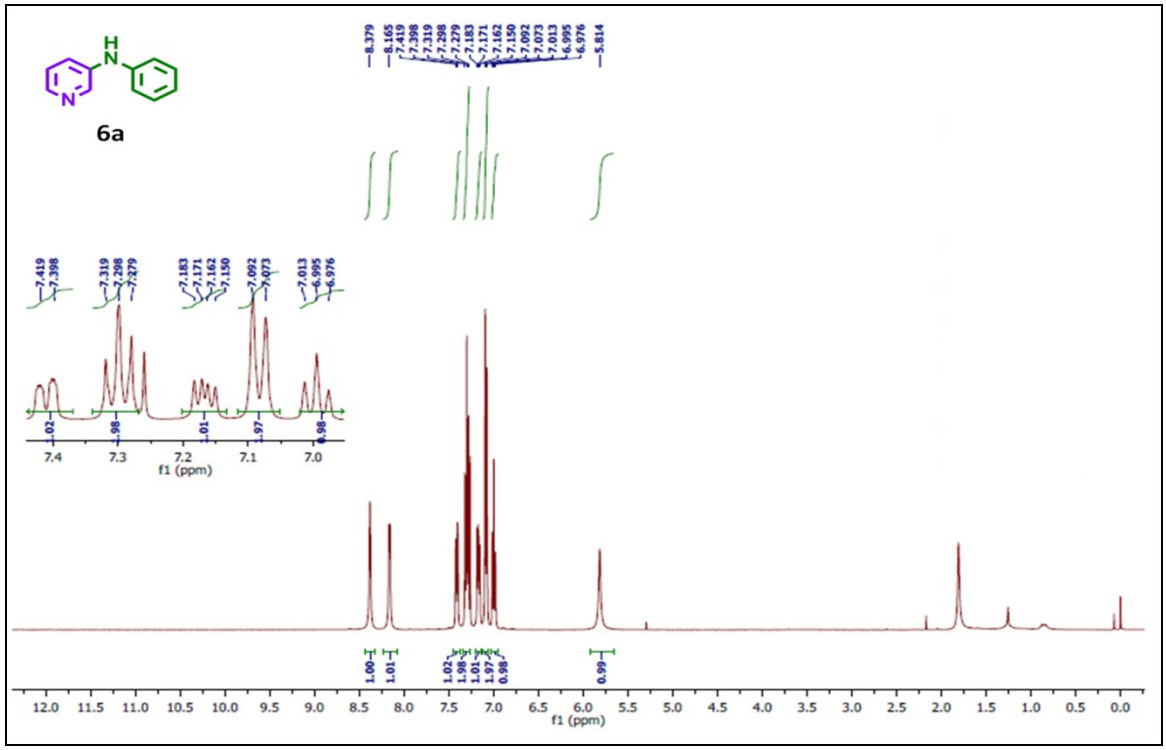

C4
f1 (ppm)

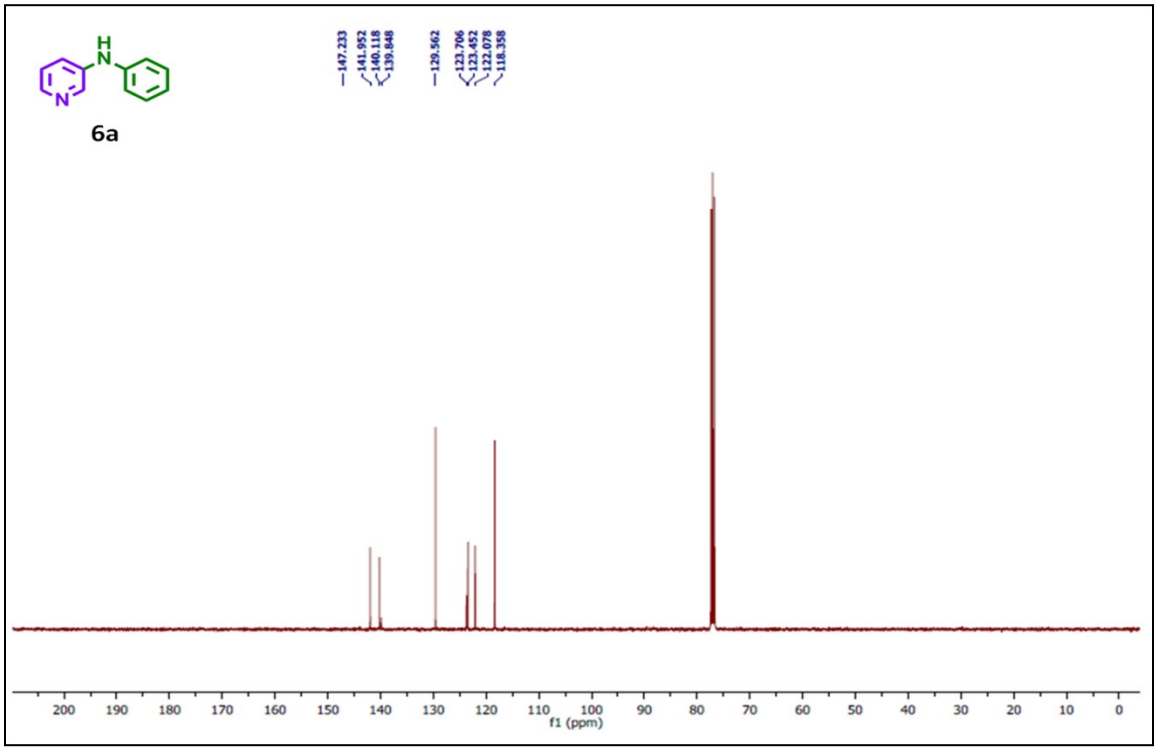

C5
f1 (ppm)

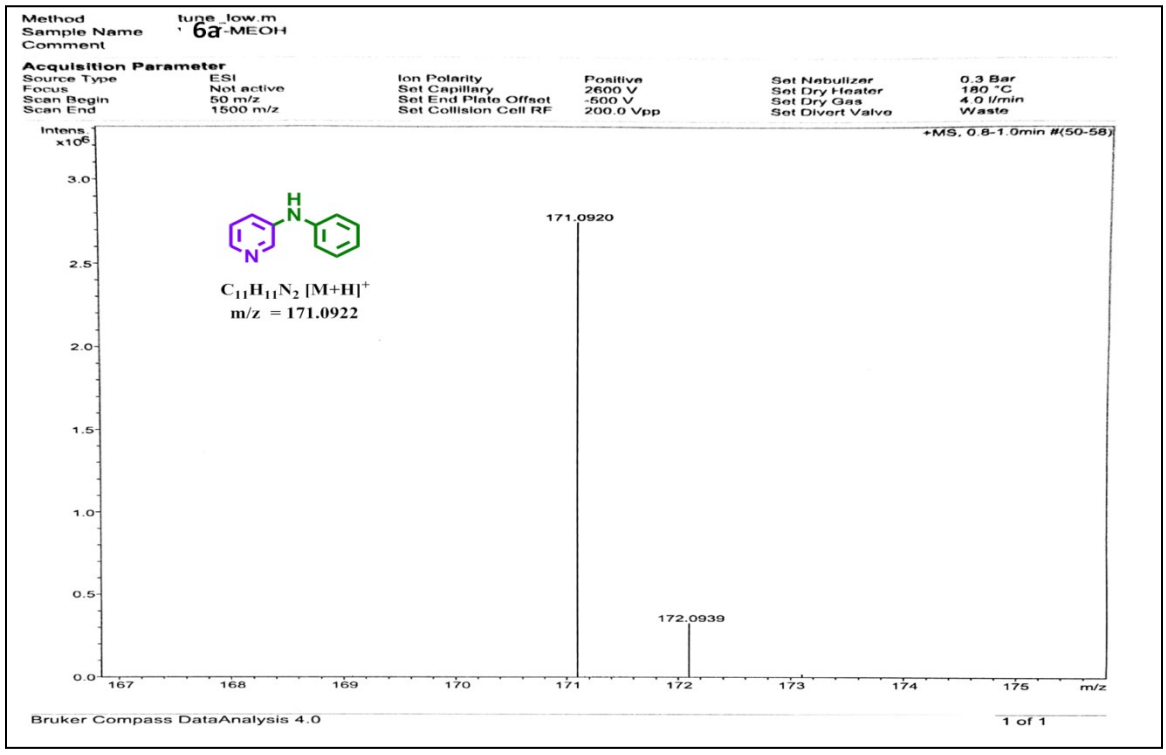

C5
f1 (ppm)

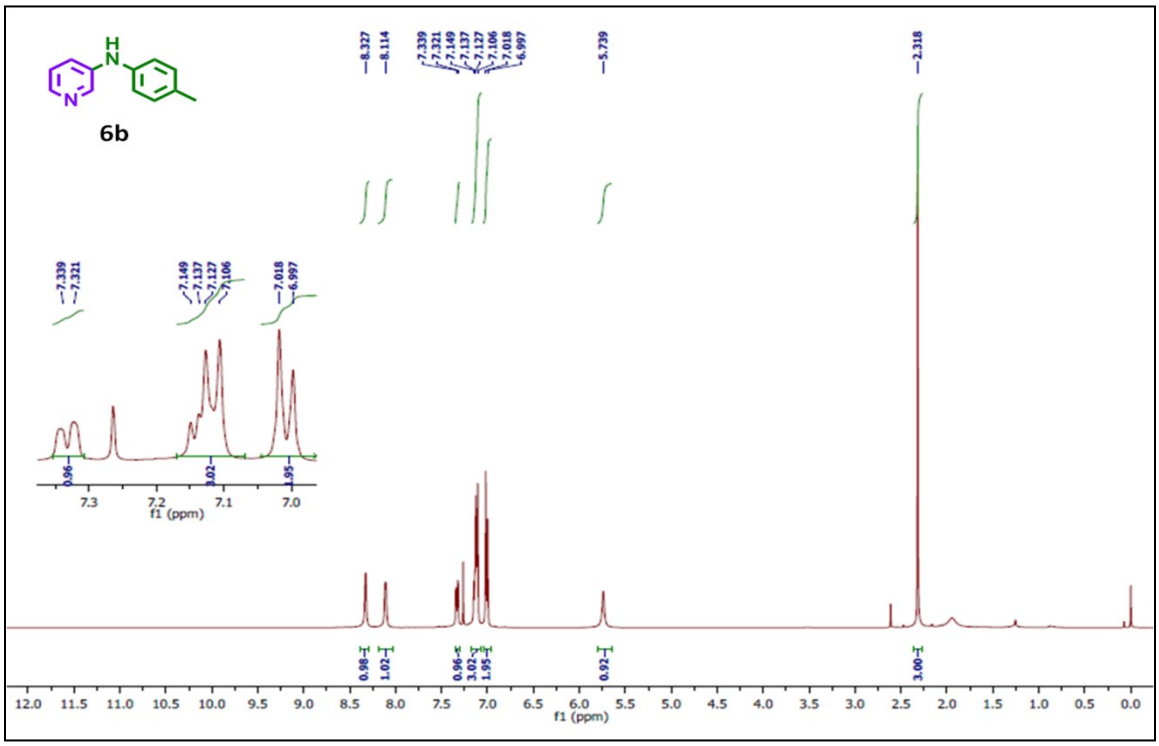

C6
f1 (ppm)

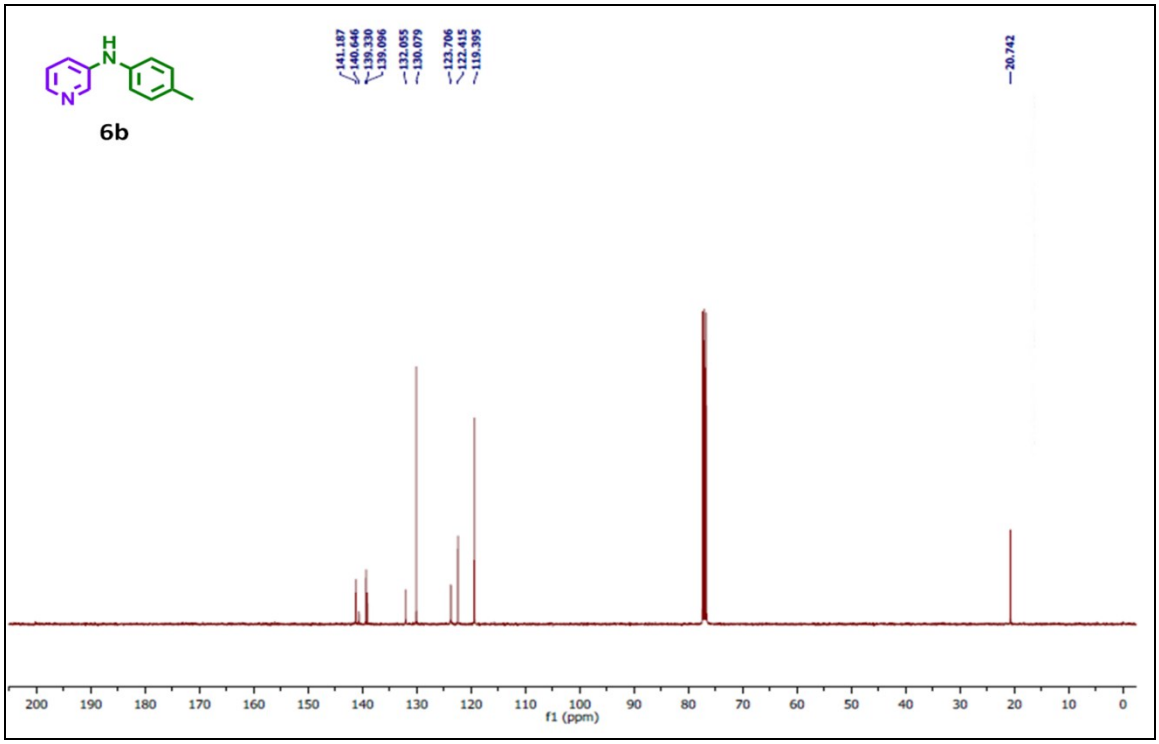

C6
f1 (ppm)

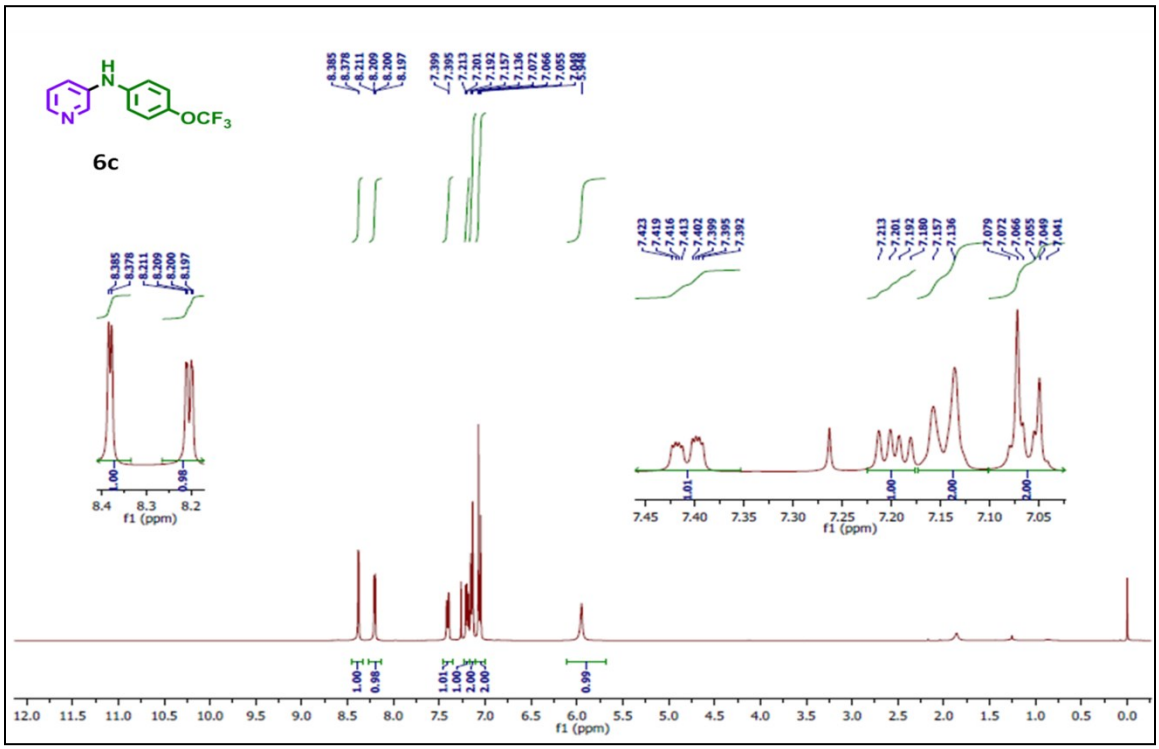

6a
8.379
8.165
7.419
7.398
7.319
7.288
7.279
7.183
7.171
7.162
7.150
7.092
7.073
7.013
6.995
6.976
5.814
1.00
1.01
1.02
1.98
1.01
1.97
0.98
0.99
f1 (ppm)

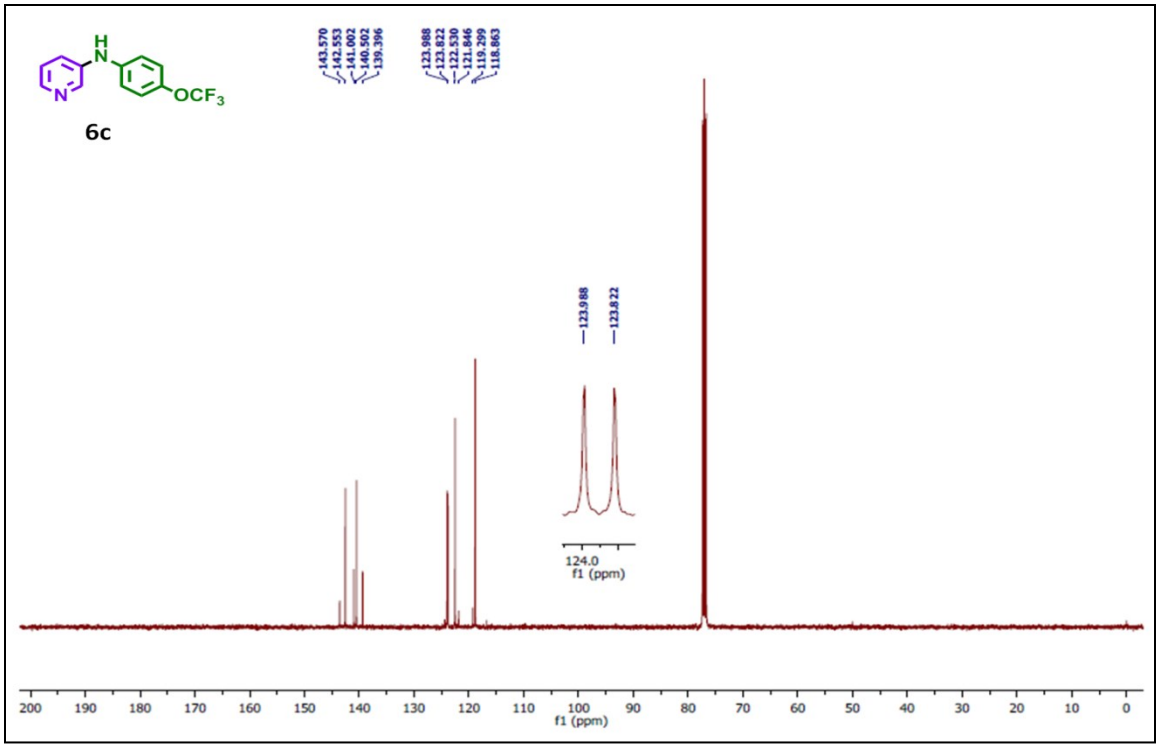

6a
147.233
141.952
140.118
139.848
129.562
123.706
123.452
122.078
118.358
f1 (ppm)

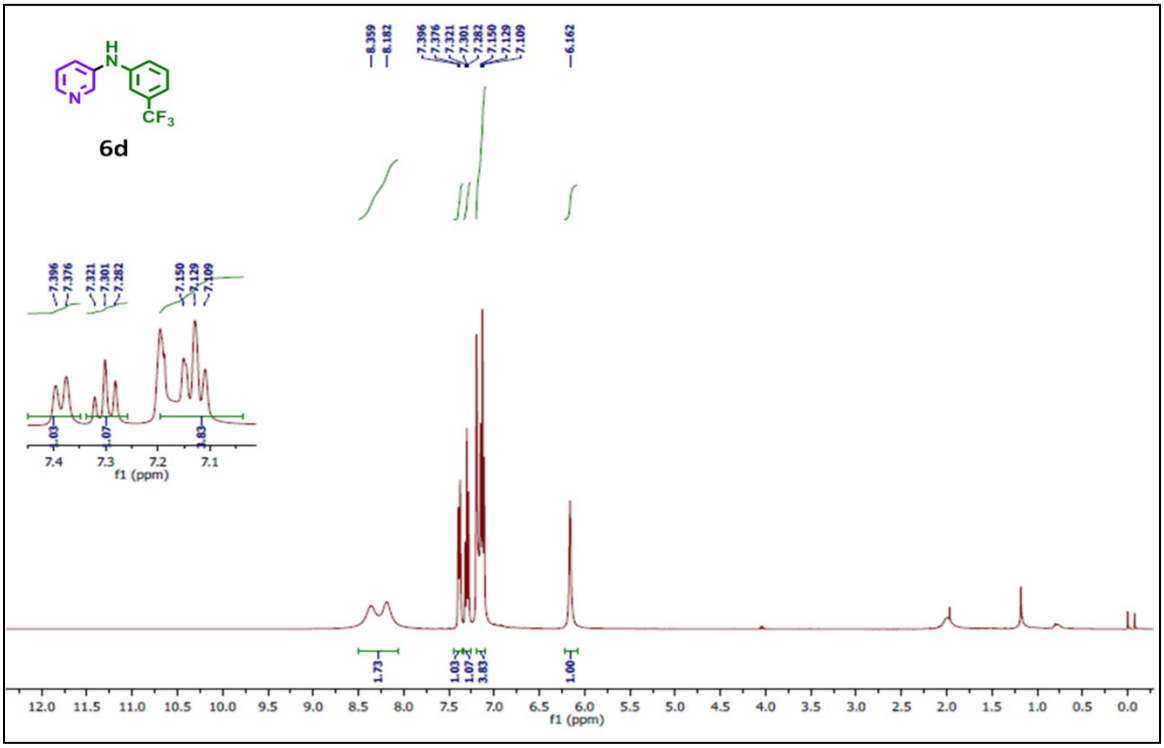

Method tune_low.m
Sample Name 6a-MEOH
Comment
Acquisition Parameter
Source Type ESI
Focus Not active
Scan Begin 50 m/z
Scan End 1500 m/z
Ion Polarity Positive
Set Capillary 2600 V
Set End Plate Offset -500 V
Set Collision Cell RF 200.0 Vpp
Set Nebulizer 0.3 Bar
Set Dry Heater 180 °C
Set Dry Gas 4.0 l/min
Set Divert Valve Waste
+MS, 0.8-1.0min #(50-58)
Intens. x10^6
171.0920
172.0939
C11H11N2 [M+H]+
m/z = 171.0922
m/z
Bruker Compass DataAnalysis 4.0
1 of 1

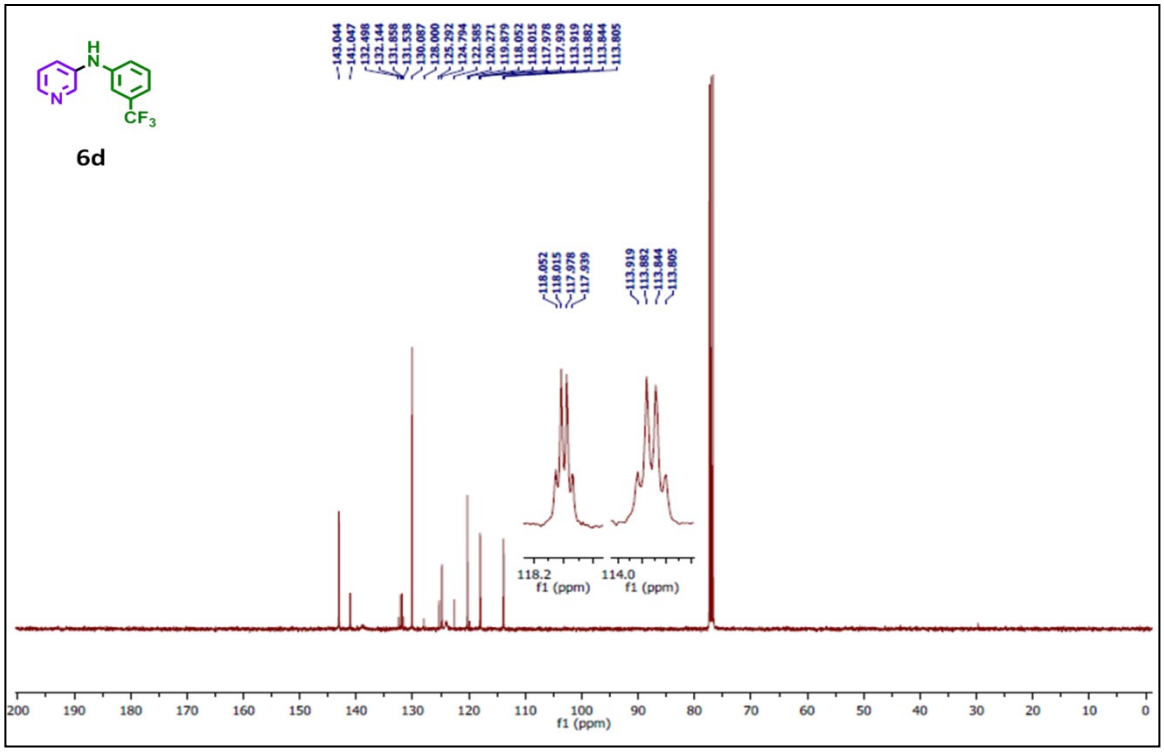

6b
8.327
8.114
7.339
7.321
7.149
7.137
7.127
7.106
7.018
6.997
5.739
2.318
f1 (ppm)

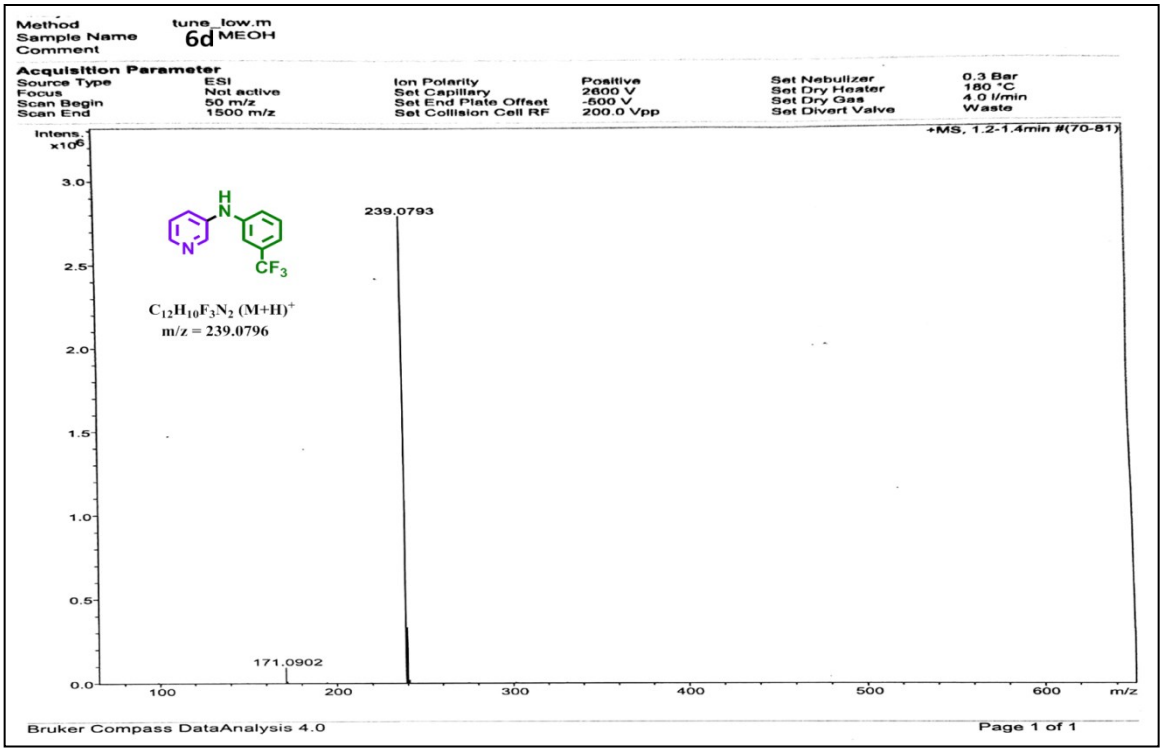

6b
141.187
140.646
139.330
139.096
132.055
130.079
123.706
122.415
119.395
20.742
f1 (ppm)

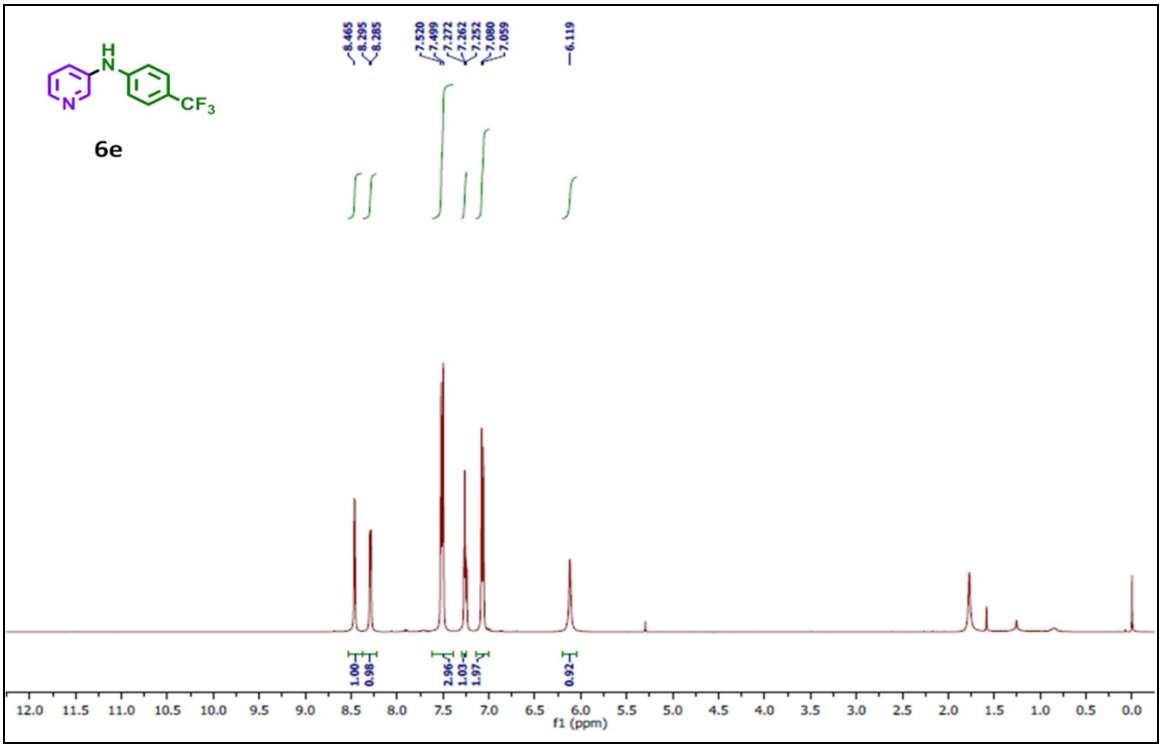

6c
OCF3
8.385
8.378
8.211
8.209
8.200
8.197
7.399
7.395
7.213
7.201
7.192
7.180
7.157
7.136
7.072
7.066
7.055
7.049
7.041
7.423
7.419
7.416
7.413
7.402
7.399
7.395
7.392
f1 (ppm)

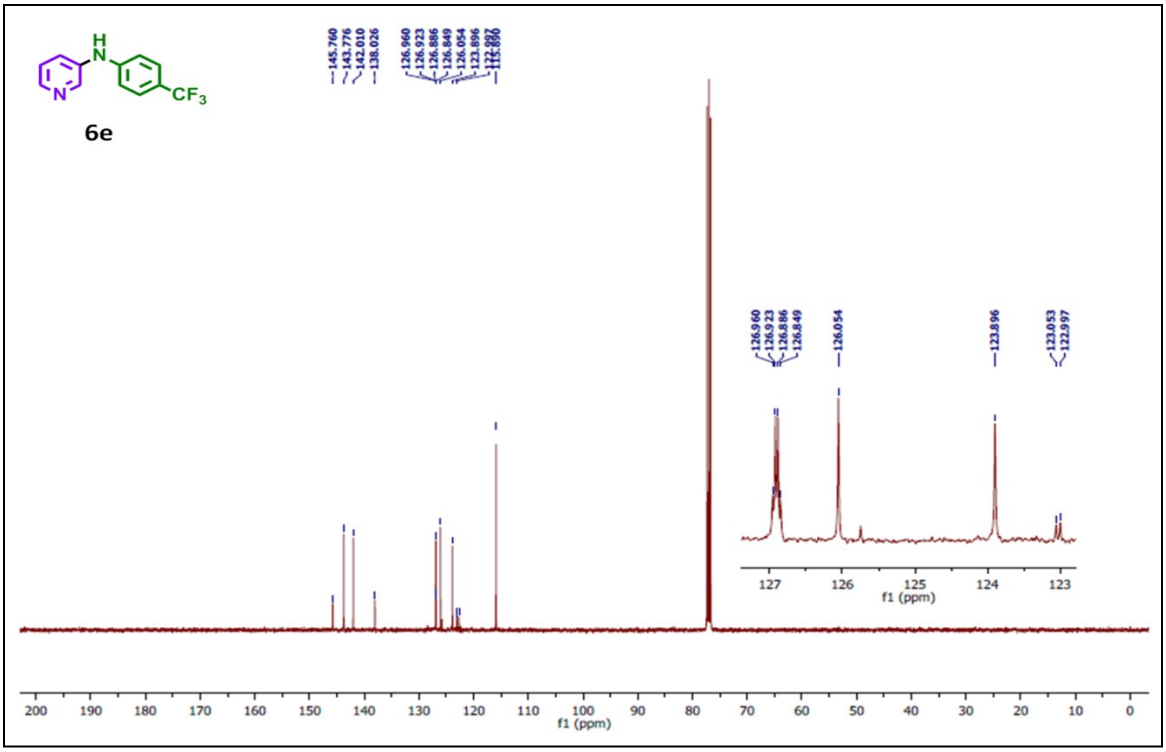

6c
143.570
142.553
141.002
140.502
139.396
123.988
123.822
122.530
121.846
119.299
118.863
124.0
f1 (ppm)
f1 (ppm)

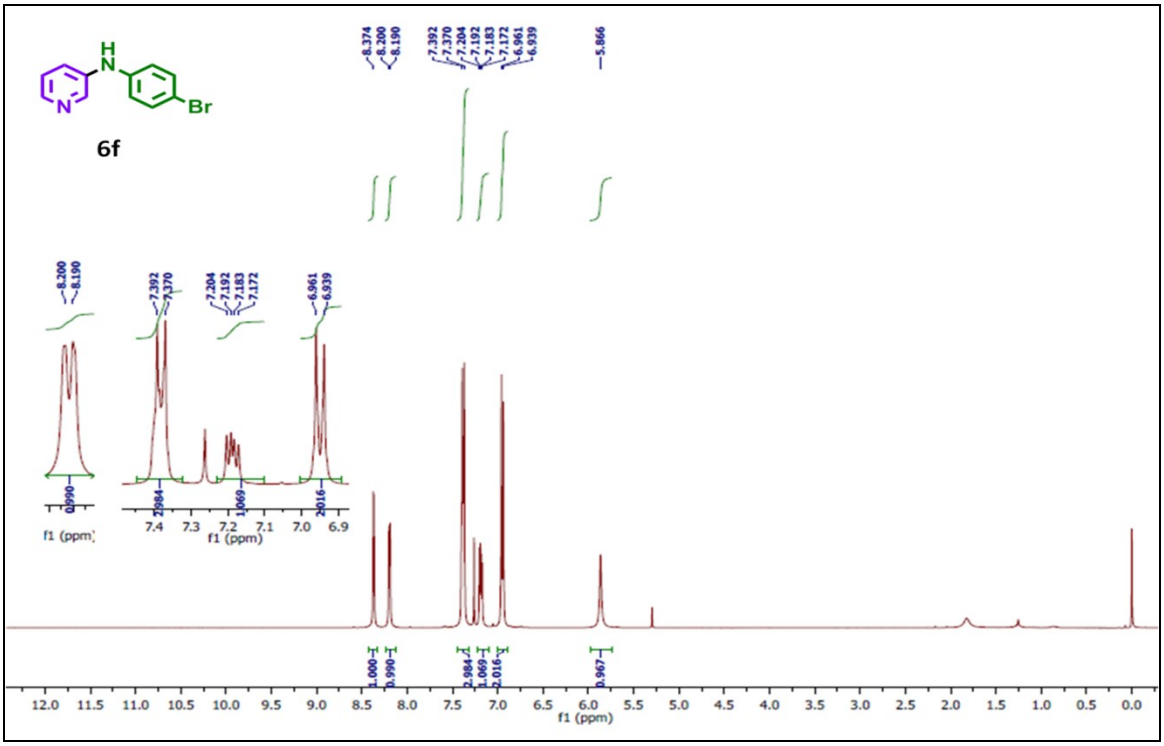

6d
8.359
8.182
7.396
7.376
7.321
7.301
7.282
7.150
7.129
7.109
6.162
1.73
1.03
1.07
3.83
1.00
f1 (ppm)
f1 (ppm)

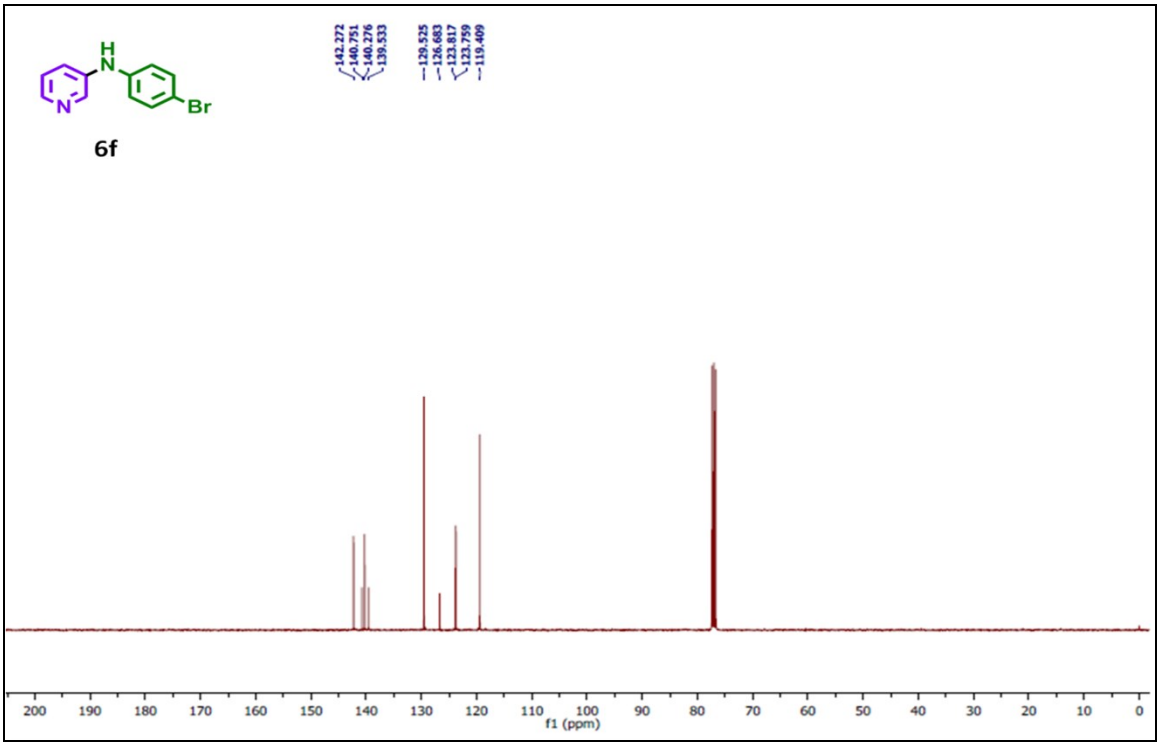

6d
143.044
141.047
132.498
132.144
131.858
131.538
130.087
128.000
125.292
124.794
122.585
120.271
119.879
118.052
118.015
117.978
117.939
113.919
113.882
113.844
113.805
118.2
f1 (ppm)
114.0
f1 (ppm)
f1 (ppm)

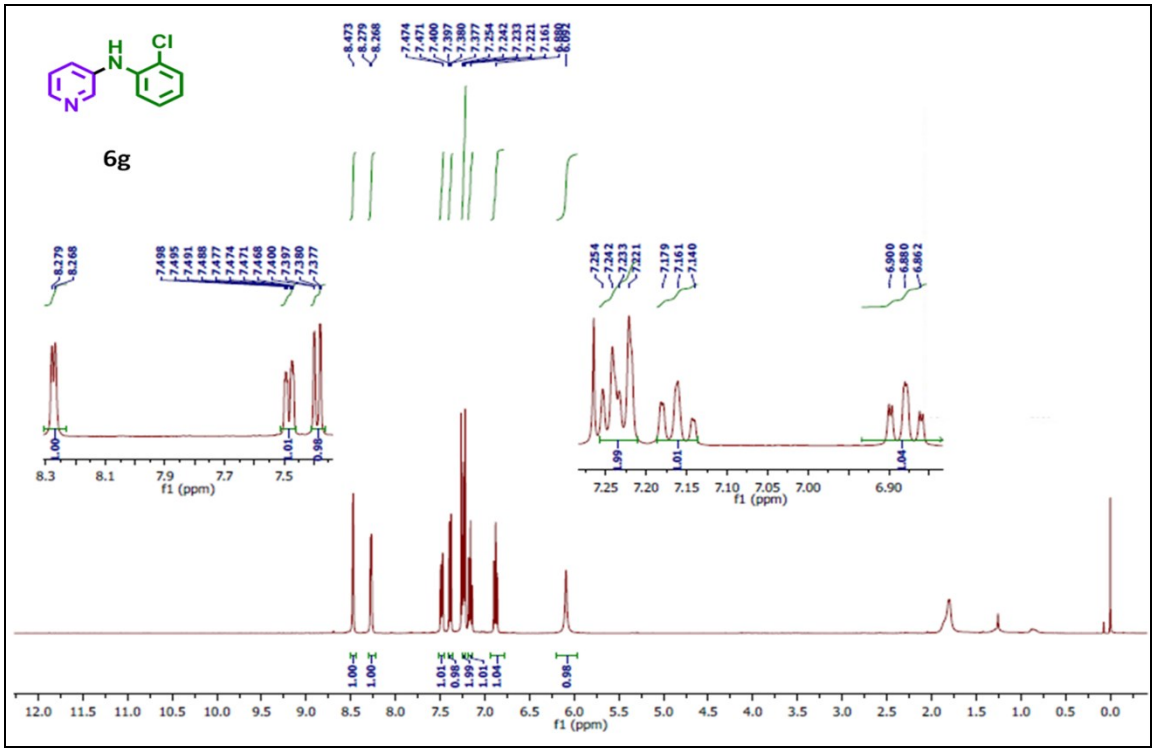

Method tune_low.m
Sample Name 6d MEOH
Comment
Acquisition Parameter
Source Type ESI
Focus Not active
Scan Begin 50 m/z
Scan End 1500 m/z
Ion Polarity Positive
Set Capillary 2600 V
Set End Plate Offset -500 V
Set Collision Cell RF 200.0 Vpp
Set Nebulizer 0.3 Bar
Set Dry Heater 180 °C
Set Dry Gas 4.0 l/min
Set Divert Valve Waste
+MS, 1.2-1.4min #(70-81)
Intens. x10^6
239.0793
171.0902
C12H10F3N2 (M+H)+
m/z = 239.0796
m/z
Bruker Compass DataAnalysis 4.0
Page 1 of 1

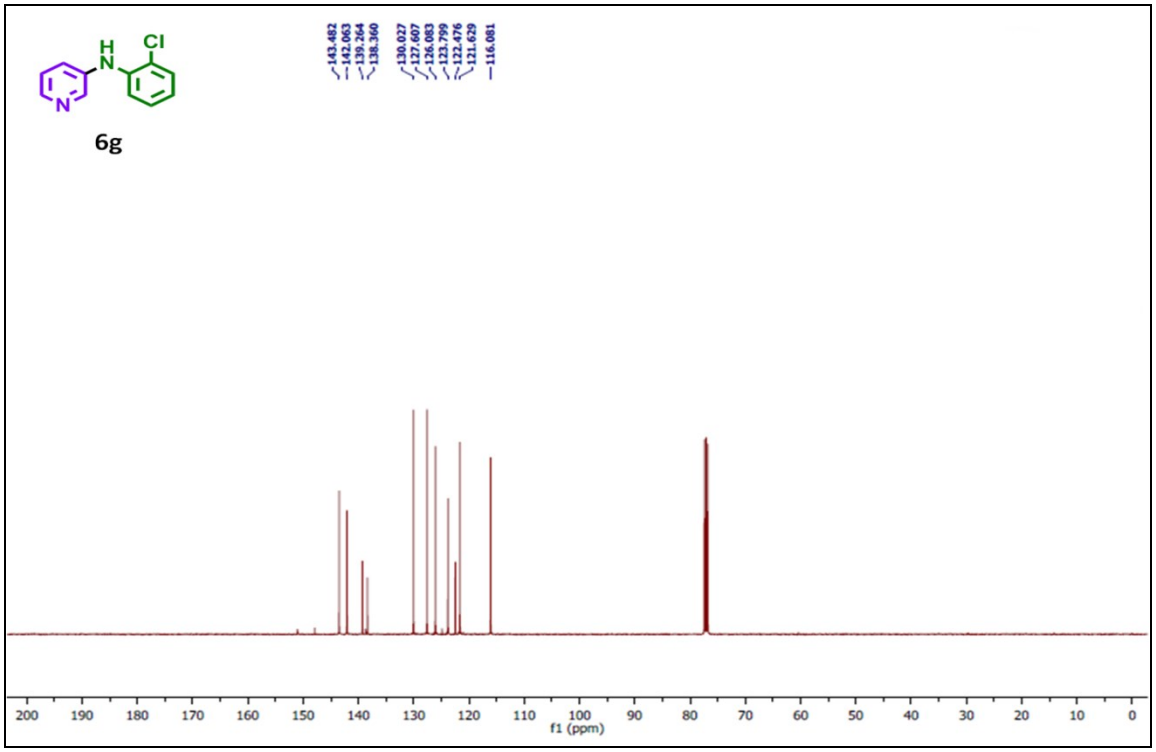

6e
8.465
8.295
8.285
7.520
7.499
7.272
7.262
7.252
7.080
7.059
6.119
1.00
0.98
2.96
1.03
1.97
0.92
f1 (ppm)

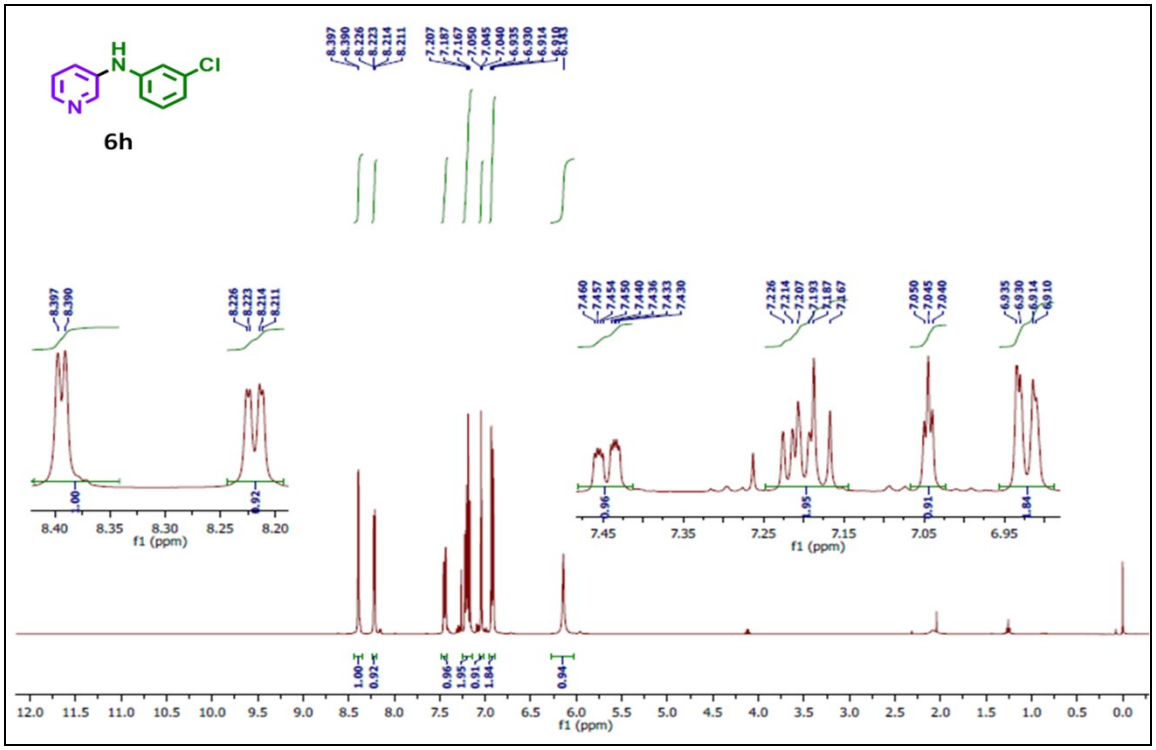

6e
145.760
143.776
142.010
138.026
126.960
126.923
126.886
126.849
126.054
123.896
f1 (ppm)

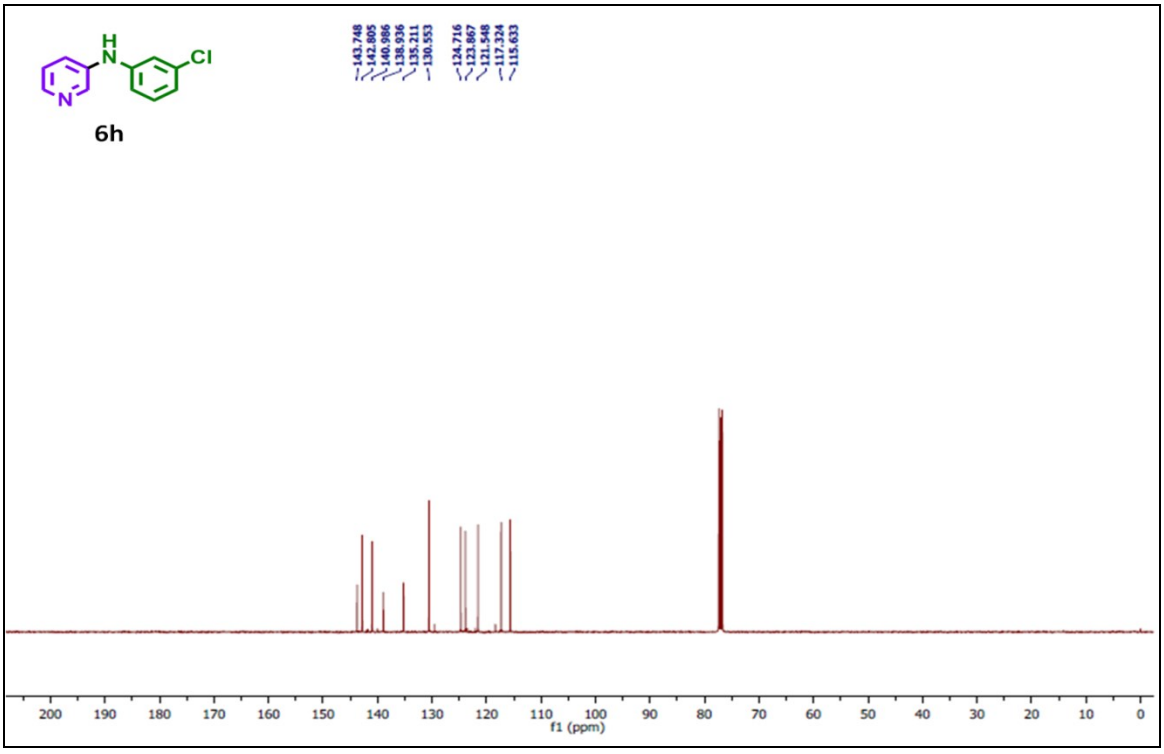

6f
8.374
8.200
8.190
7.392
7.370
7.204
7.192
7.183
7.172
6.961
6.939
5.866
f1 (ppm)

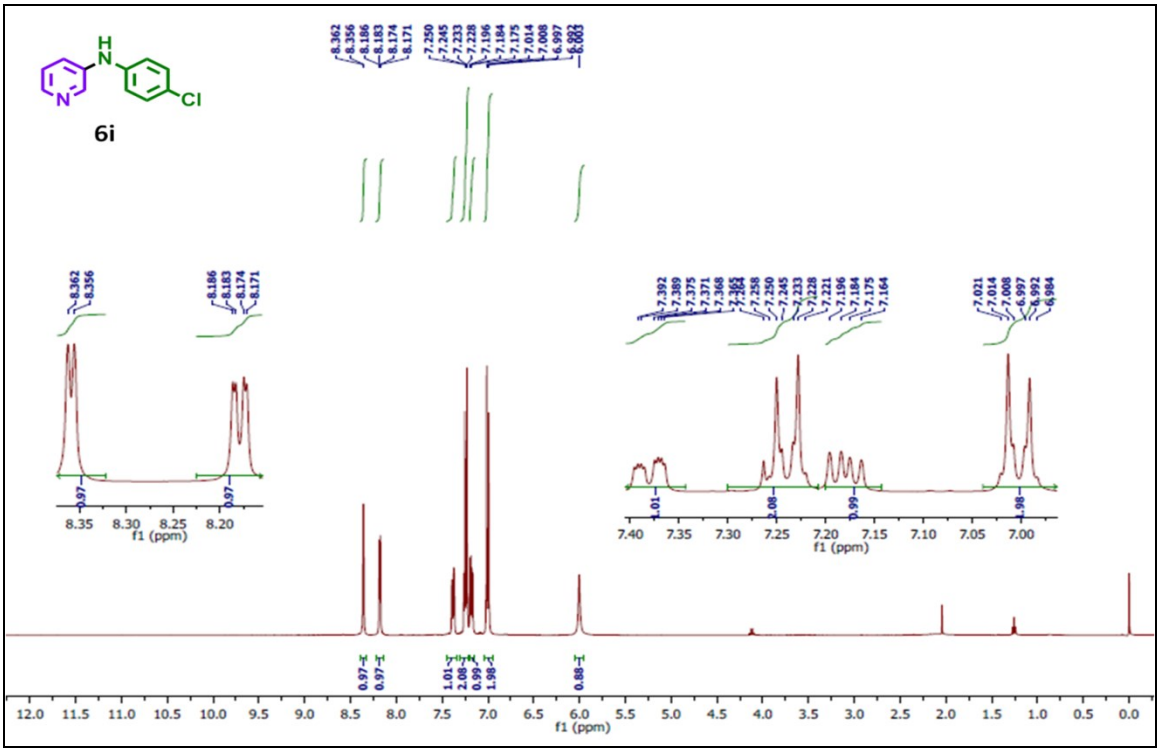

6f
142.272
140.751
140.276
139.533
129.525
126.683
123.817
123.759
119.469
f1 (ppm)

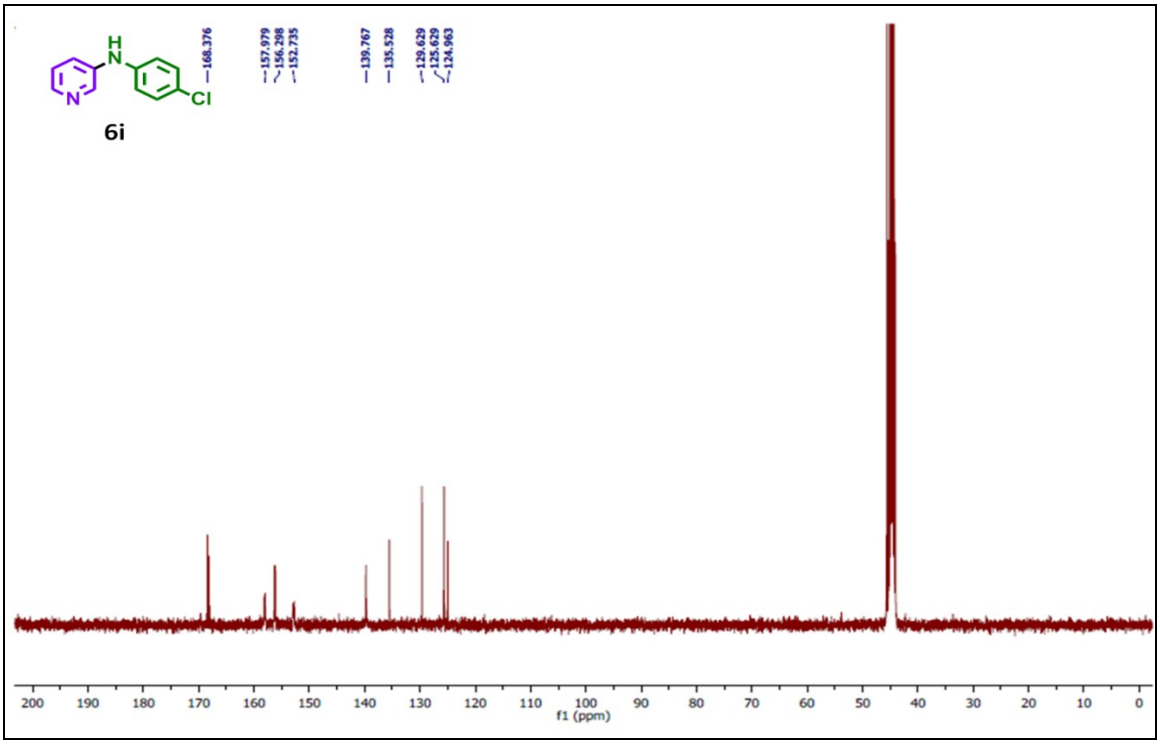

6g
8.473
8.279
8.268
7.474
7.471
7.400
7.397
7.389
7.377
7.254
7.242
7.233
7.221
7.161
6.880
6.862
f1 (ppm)

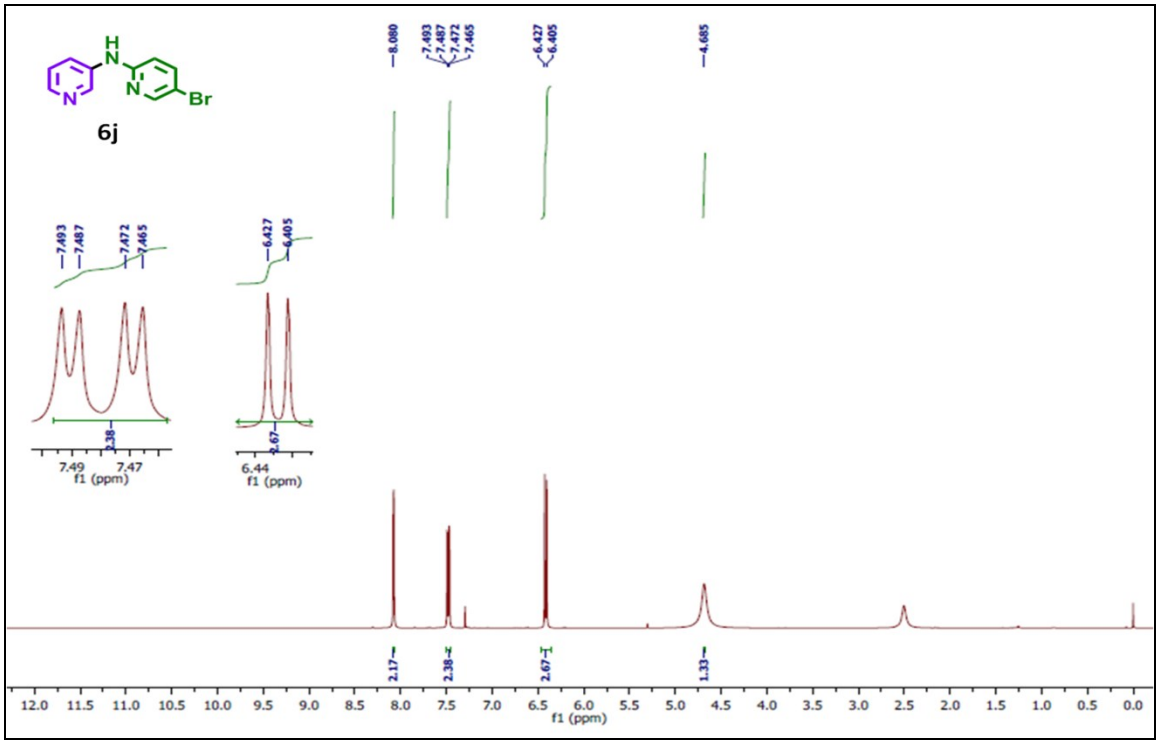

6g
143.482
142.063
139.264
138.360
130.027
127.607
126.083
123.799
122.476
121.629
116.081
f1 (ppm)

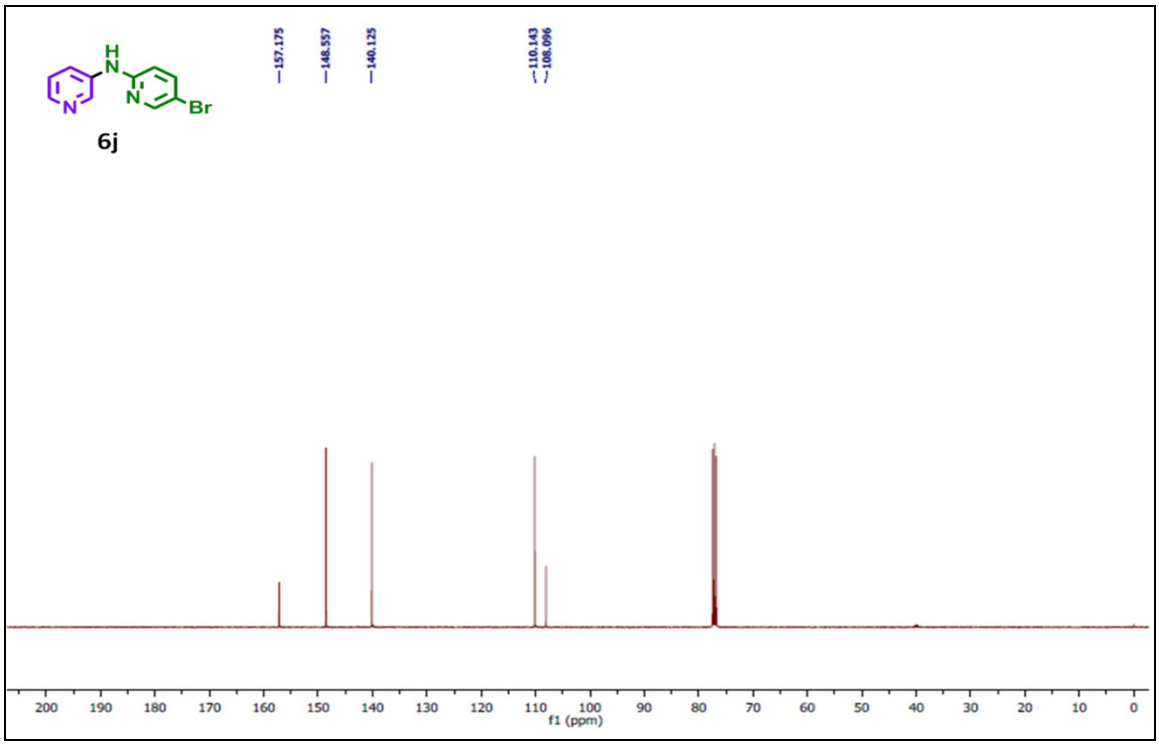

6h
8.397
8.390
8.226
8.223
8.214
8.211
7.207
7.187
7.167
7.050
7.045
7.040
6.935
6.930
6.914
6.910
6.143
7.460
7.457
7.454
7.450
7.440
7.436
7.433
7.430
7.226
7.214
7.207
7.193
7.187
7.167
7.050
7.045
7.040
6.935
6.930
6.914
6.910
1.00
0.92
0.96
1.95
0.91
1.84
0.94
f1 (ppm)

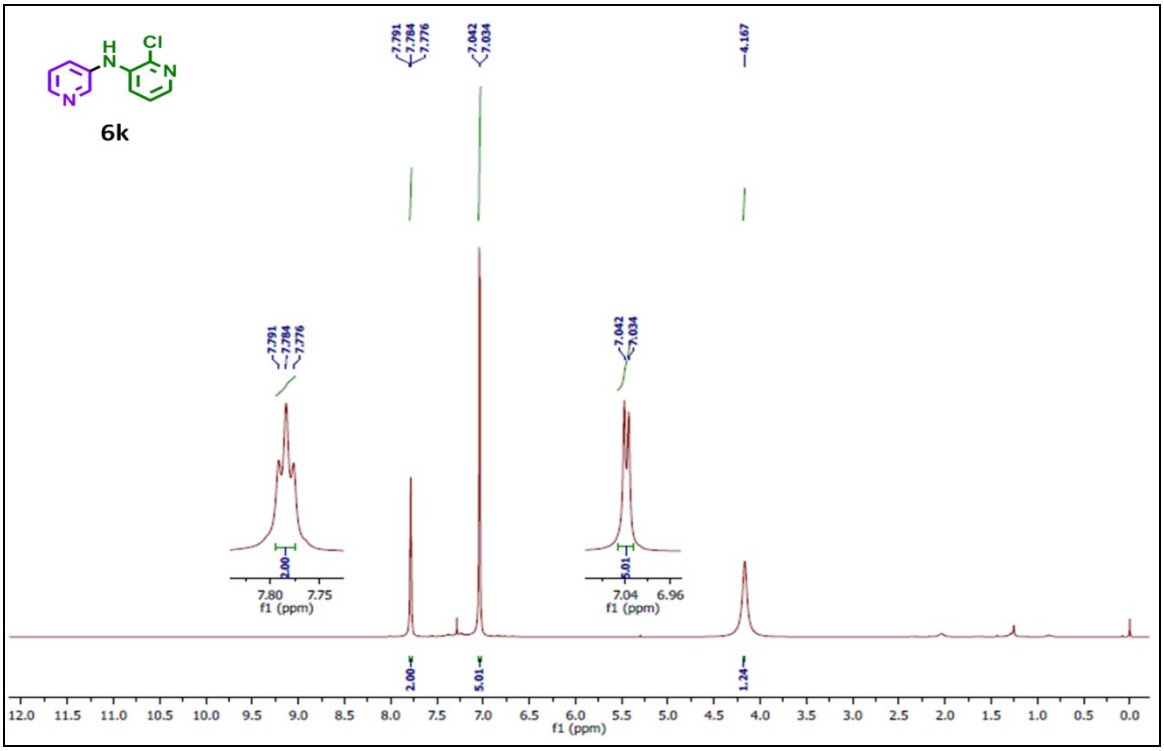

6h
143.748
142.805
140.986
138.936
135.211
130.553
124.716
123.867
121.548
117.324
115.633
f1 (ppm)

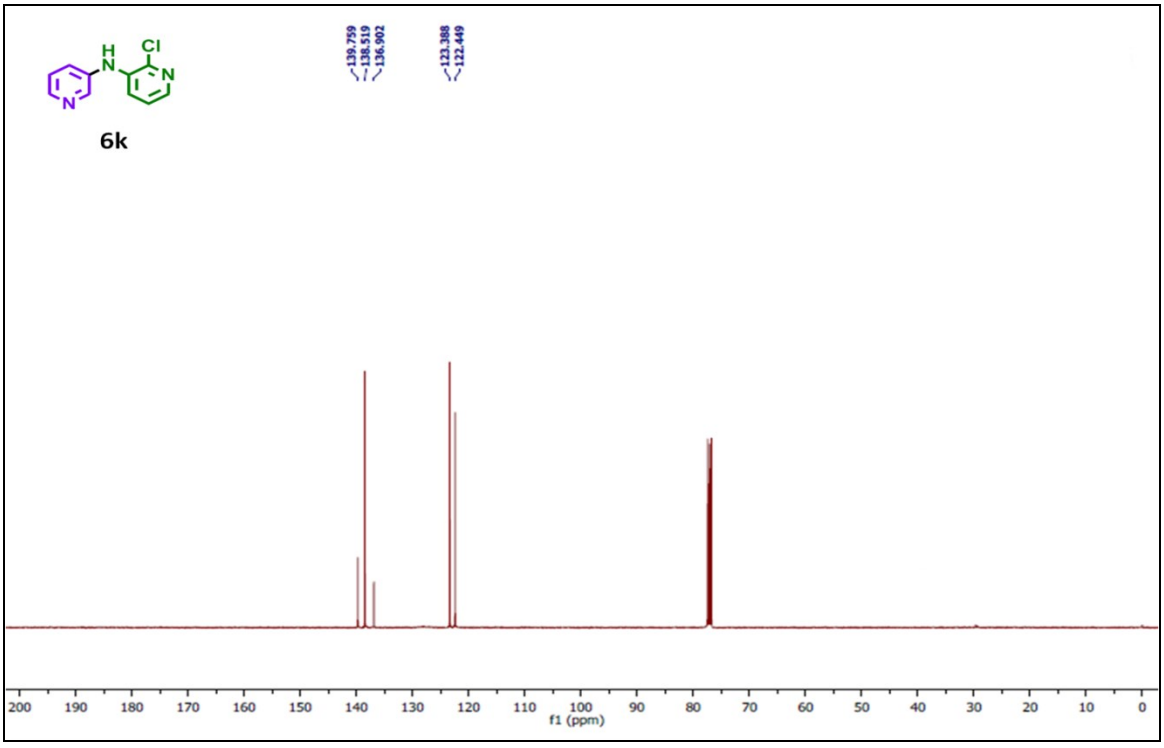

6i
f1 (ppm)

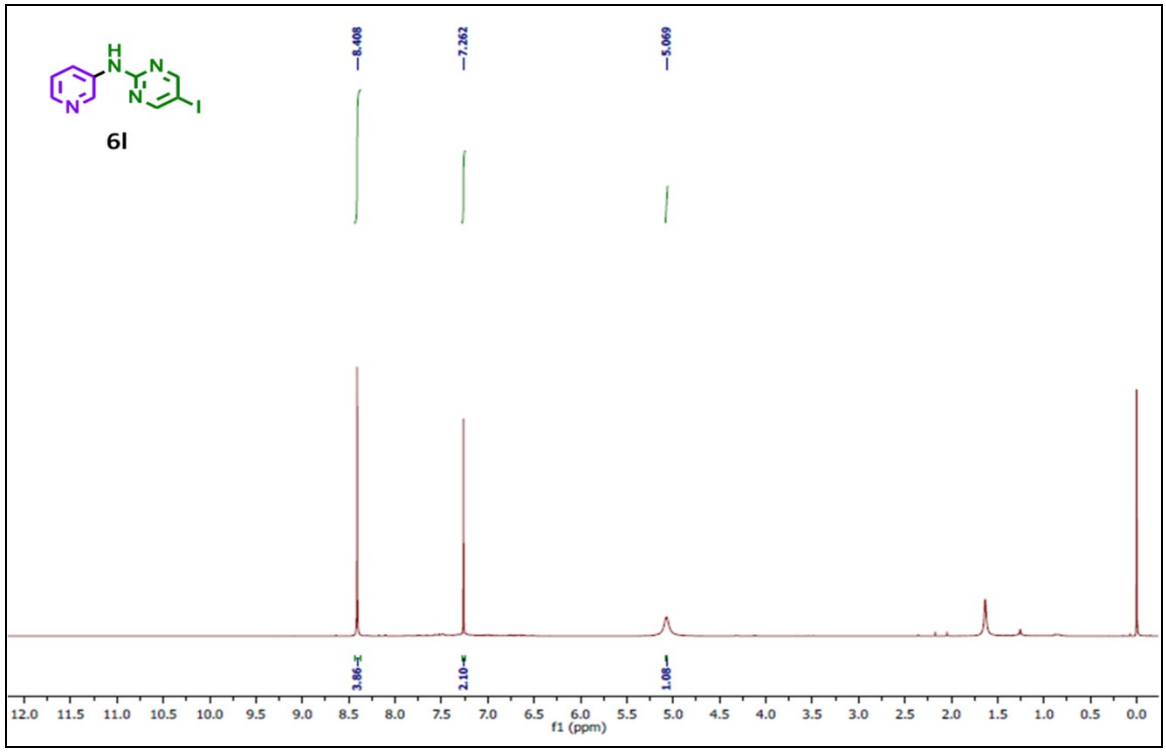

6i
f1 (ppm)

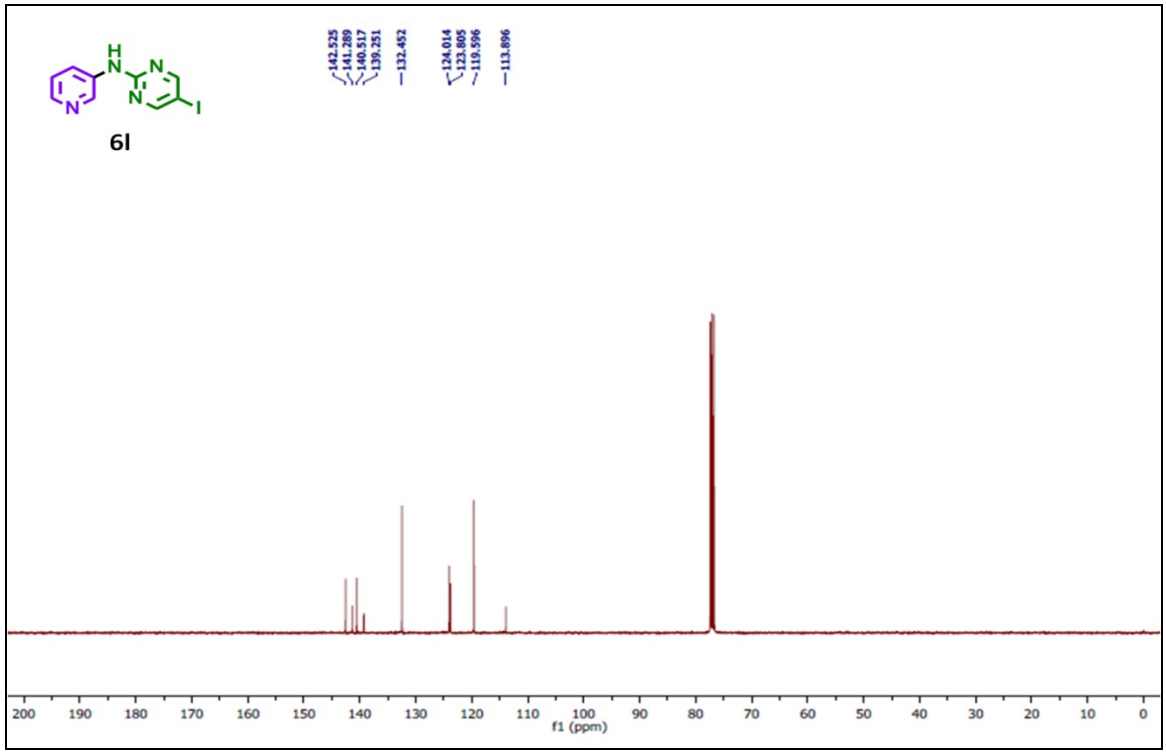

6j
8.000
7.493
7.487
7.472
7.465
6.427
6.405
4.685
2.17
2.38
2.67
1.33
f1 (ppm)

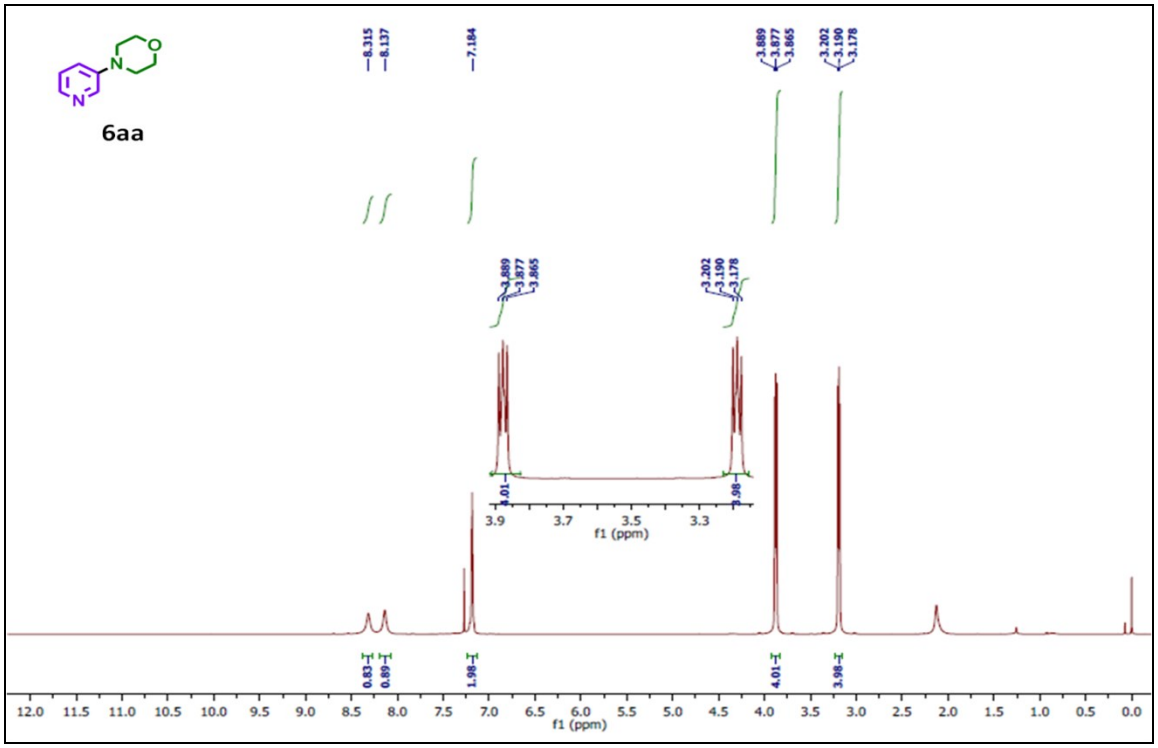

6j
157.175
148.557
140.125
110.143
108.096
f1 (ppm)

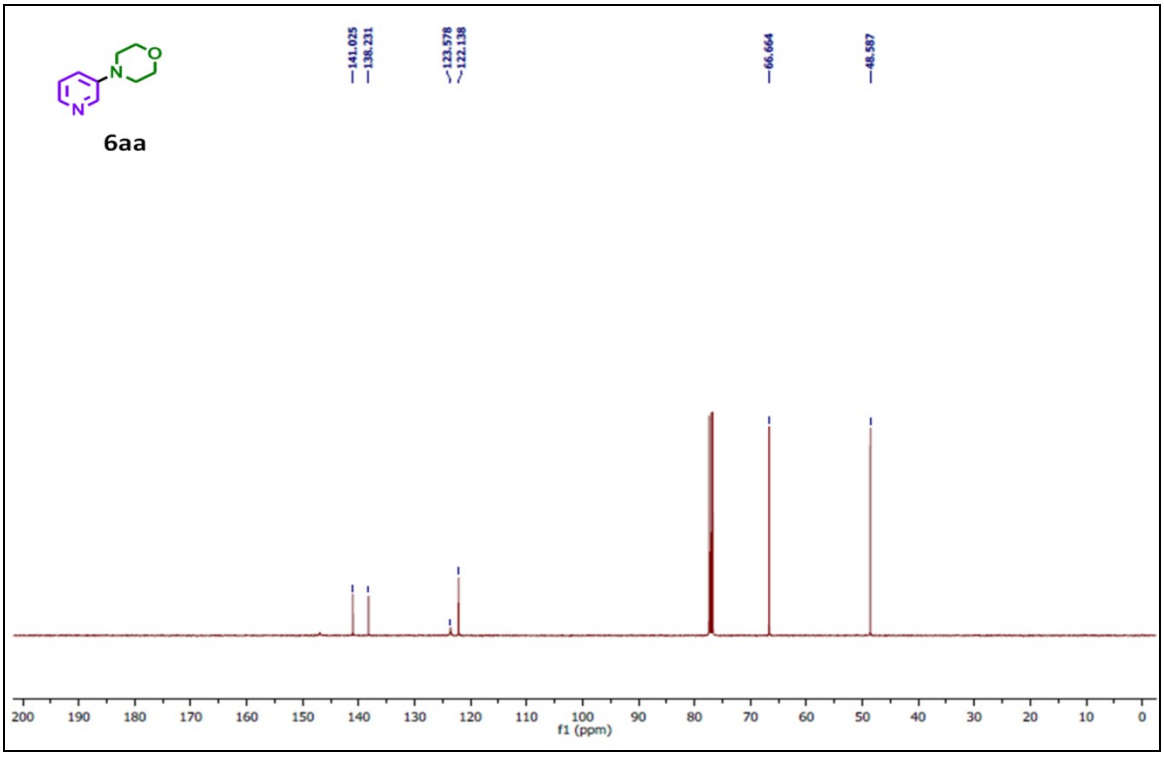

6k
7.791
7.784
7.776
7.042
7.034
4.167
2.00
5.01
1.24
f1 (ppm)

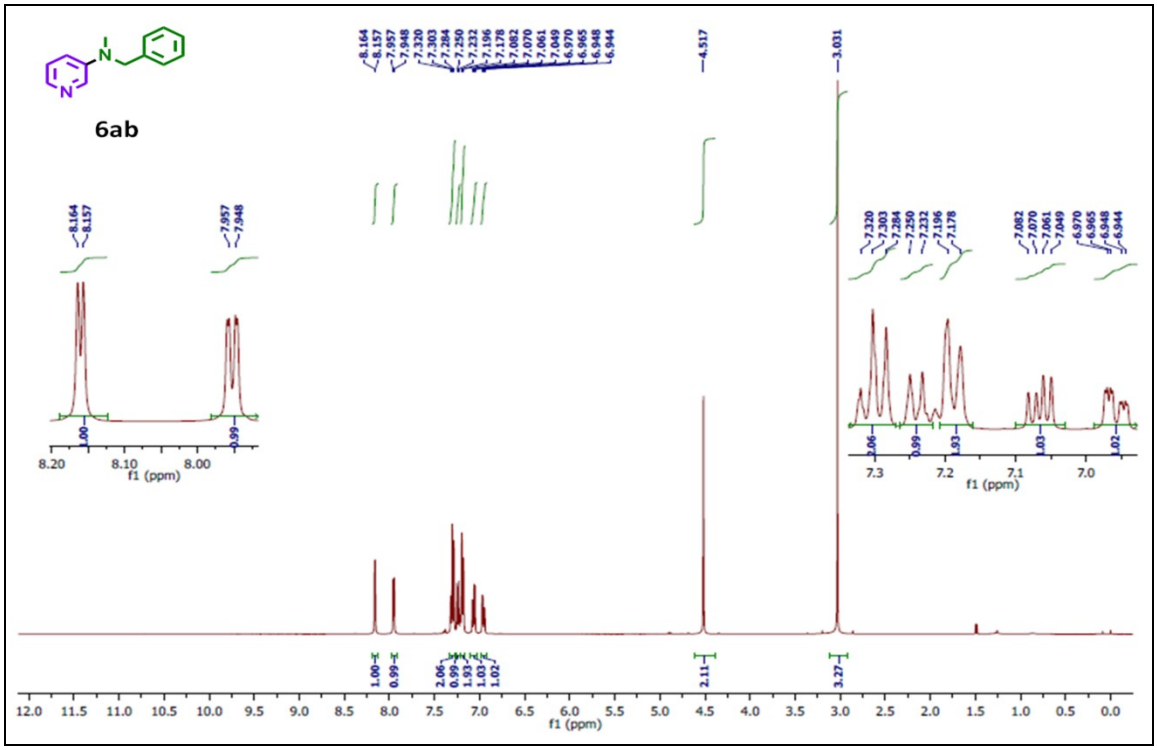

6k
139.759
138.519
136.902
123.388
122.449
f1 (ppm)

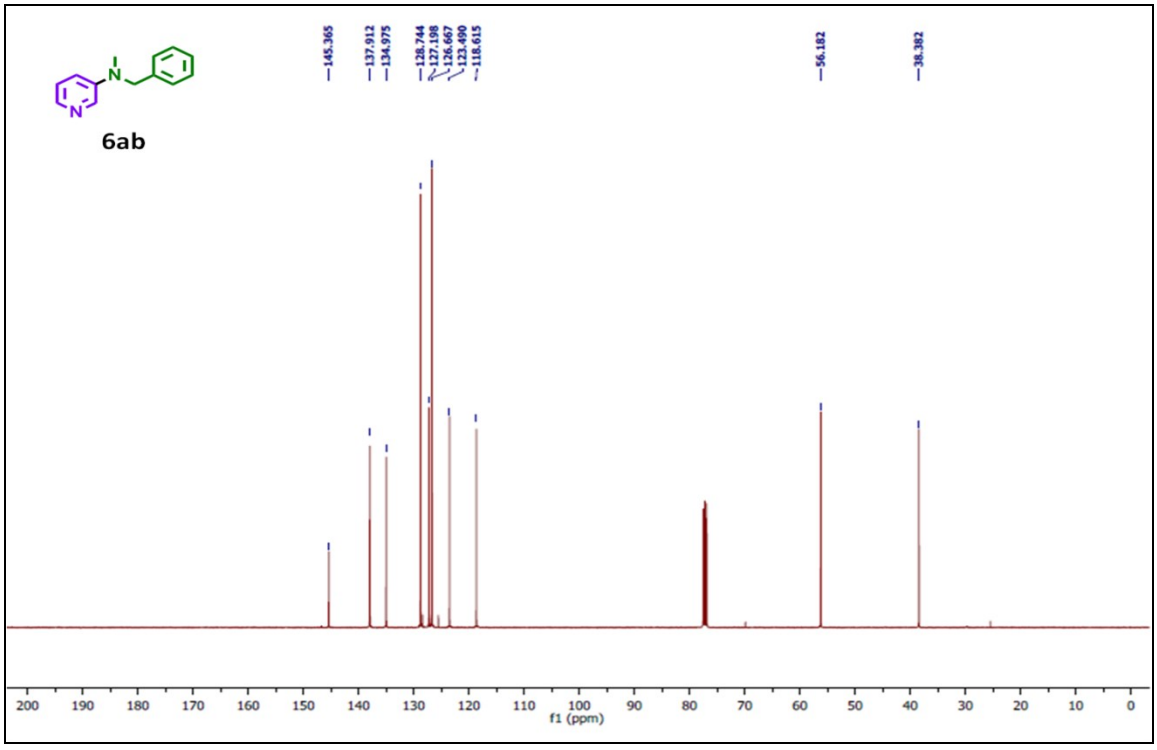

6l
8.408
7.262
5.069
3.86
2.10
1.08
f1 (ppm)

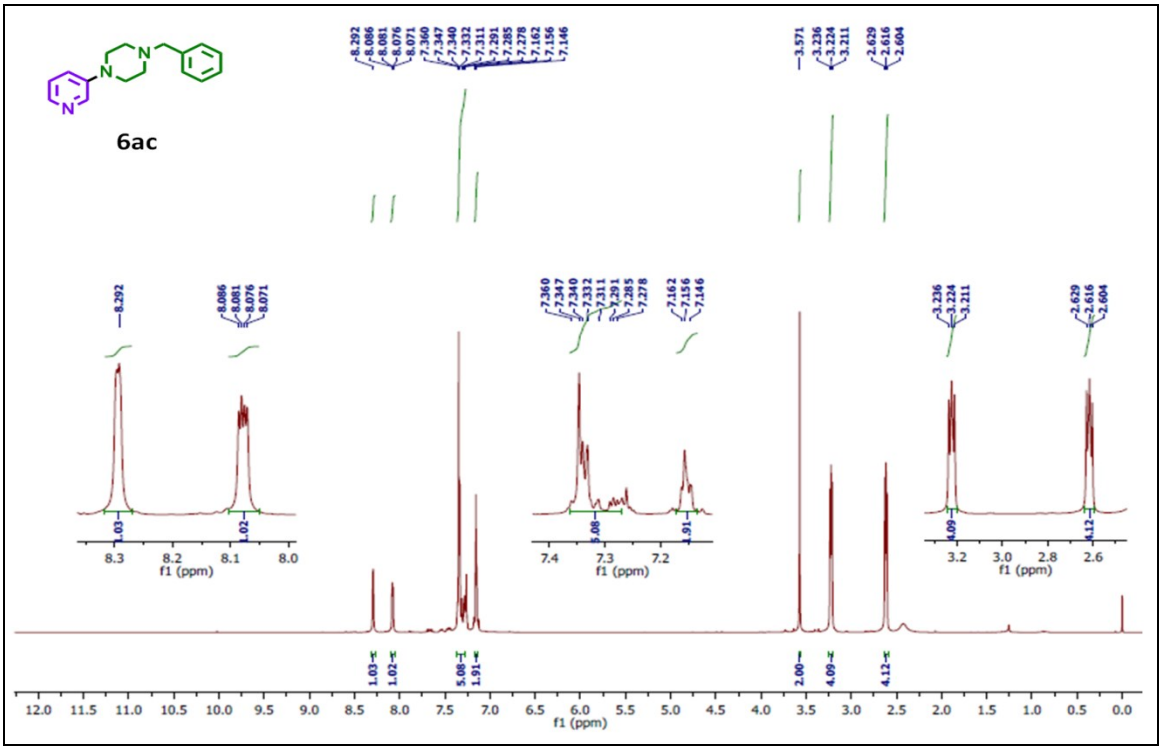

6l
142.525
141.289
140.517
139.251
132.452
124.014
123.805
119.596
113.896
f1 (ppm)

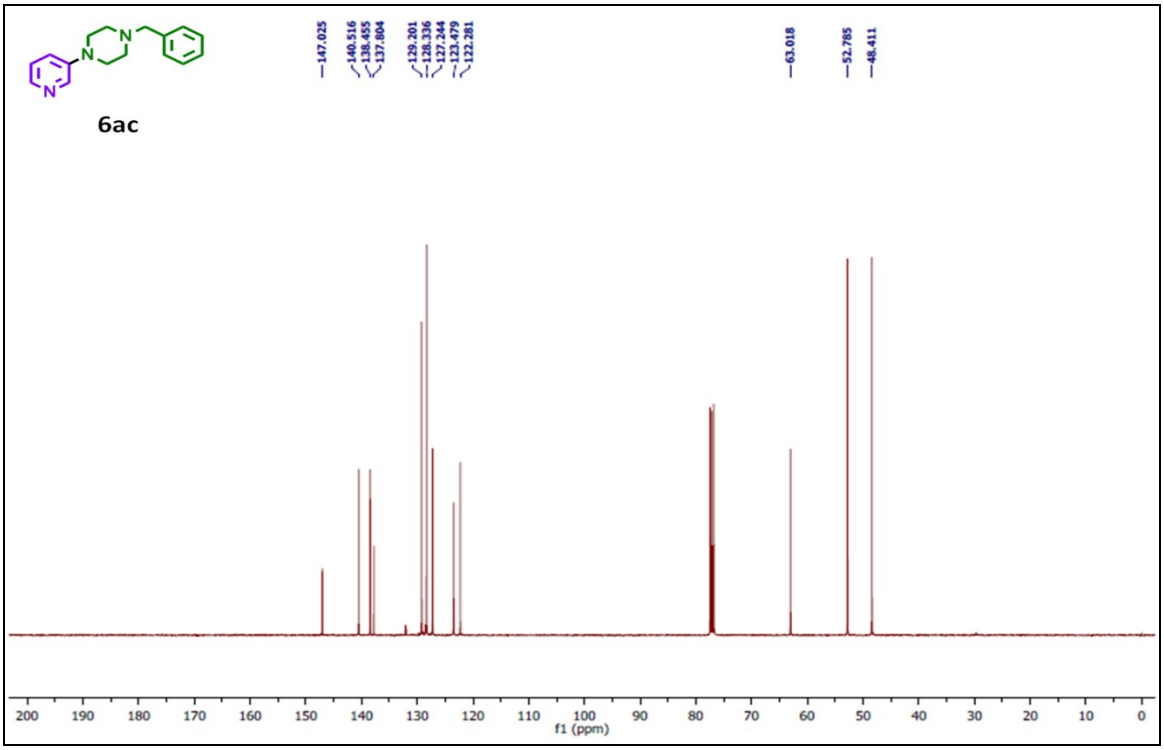

6aa
8.315
8.137
7.184
3.889
3.877
3.865
3.202
3.190
3.178
0.83
0.89
1.98
4.01
3.98
f1 (ppm)

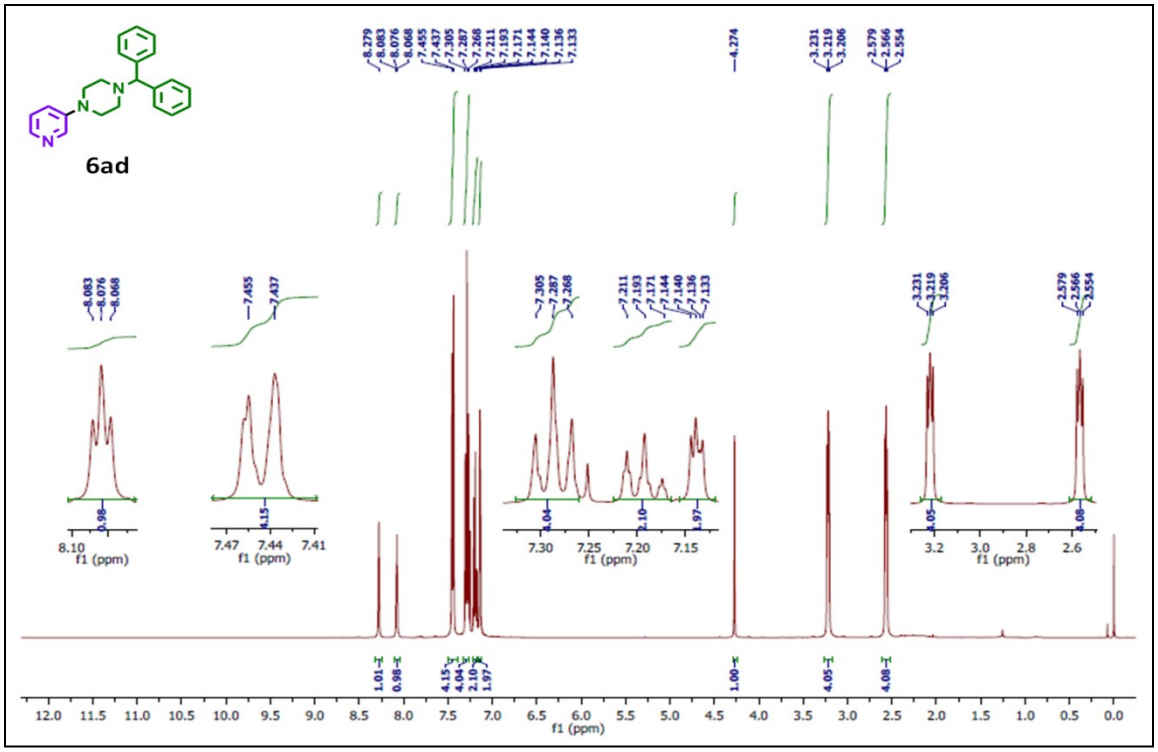

6aa
141.025
138.231
123.578
122.138
66.664
48.587
f1 (ppm)

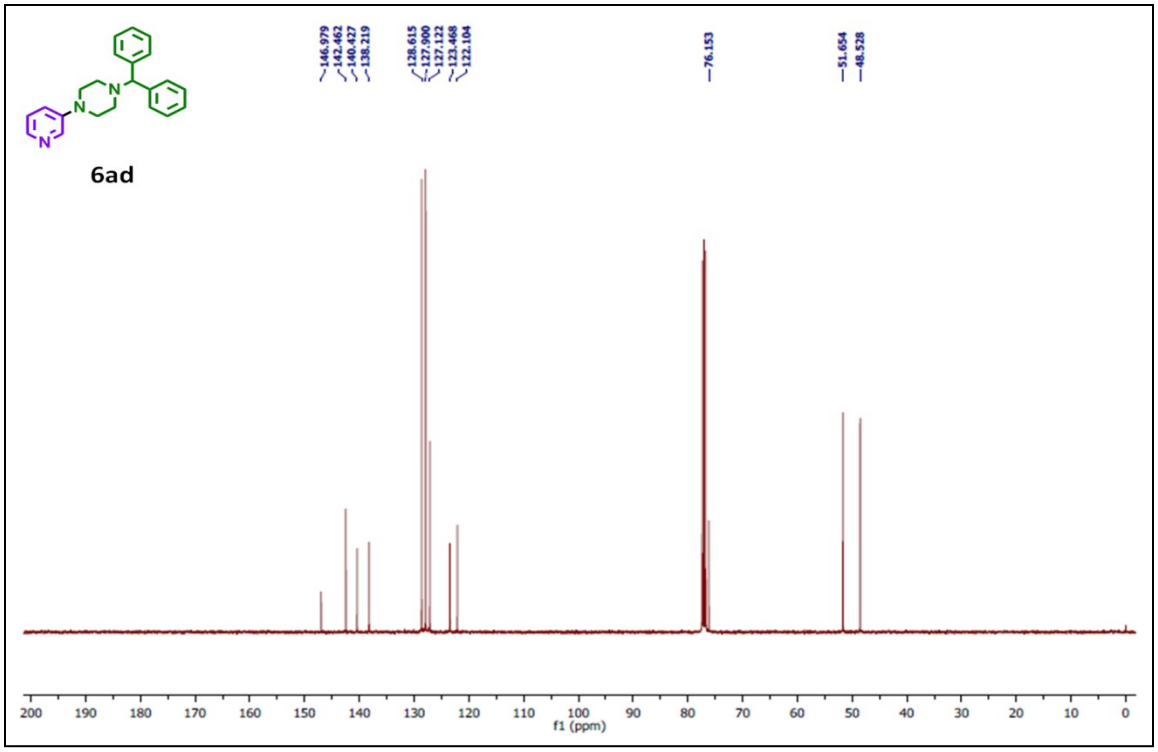

6ab
8.164
8.157
7.957
7.948
7.320
7.303
7.284
7.250
7.232
7.196
7.178
7.082
7.070
7.061
7.049
6.970
6.965
6.948
6.944
4.517
3.031
f1 (ppm)

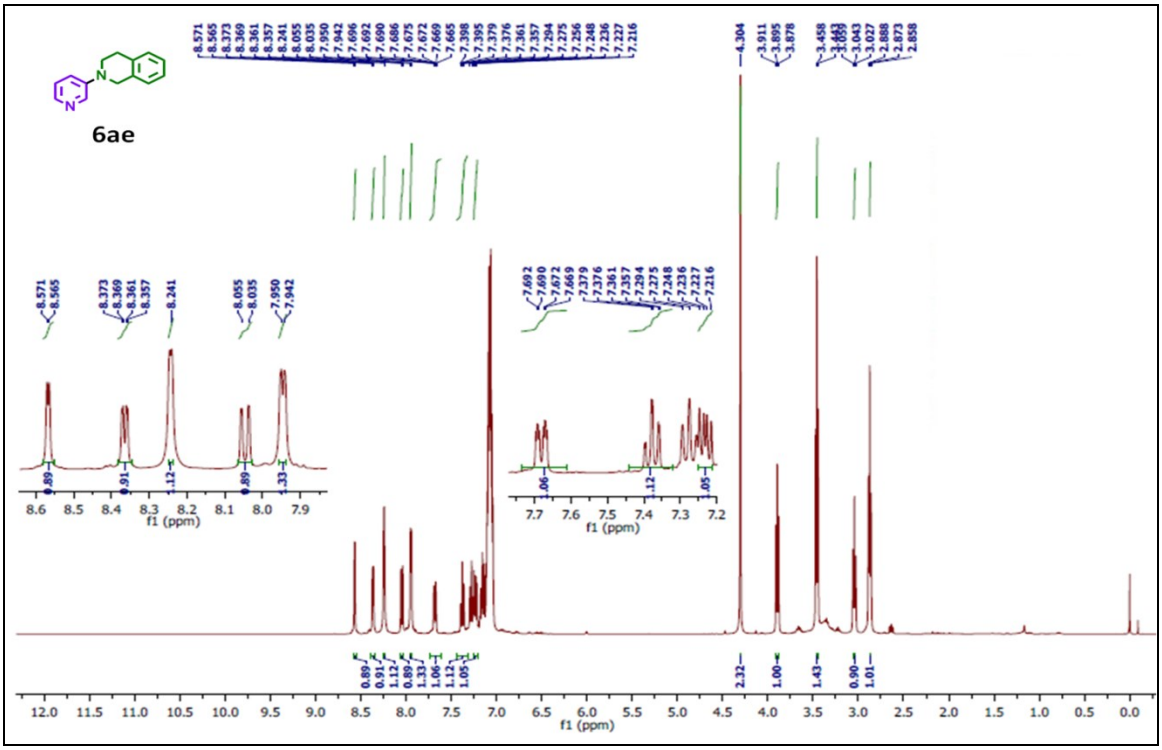

6ab
145.365
137.912
134.975
128.744
127.198
126.667
123.490
118.615
56.182
38.382
f1 (ppm)

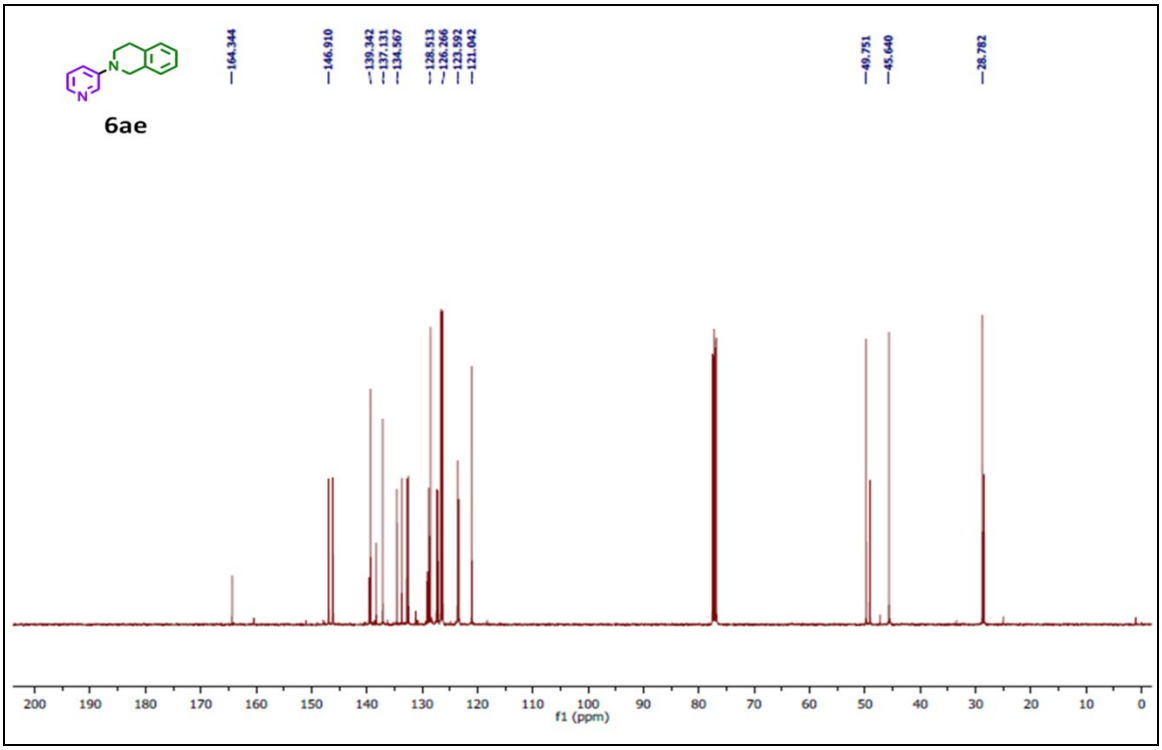

6ac
8.292
8.086
8.081
8.076
8.071
7.360
7.347
7.340
7.332
7.311
7.291
7.285
7.278
7.162
7.156
7.146
3.571
3.236
3.224
3.211
2.629
2.616
2.604
1.03
1.02
5.08
1.91
2.00
4.09
4.12
f1 (ppm)

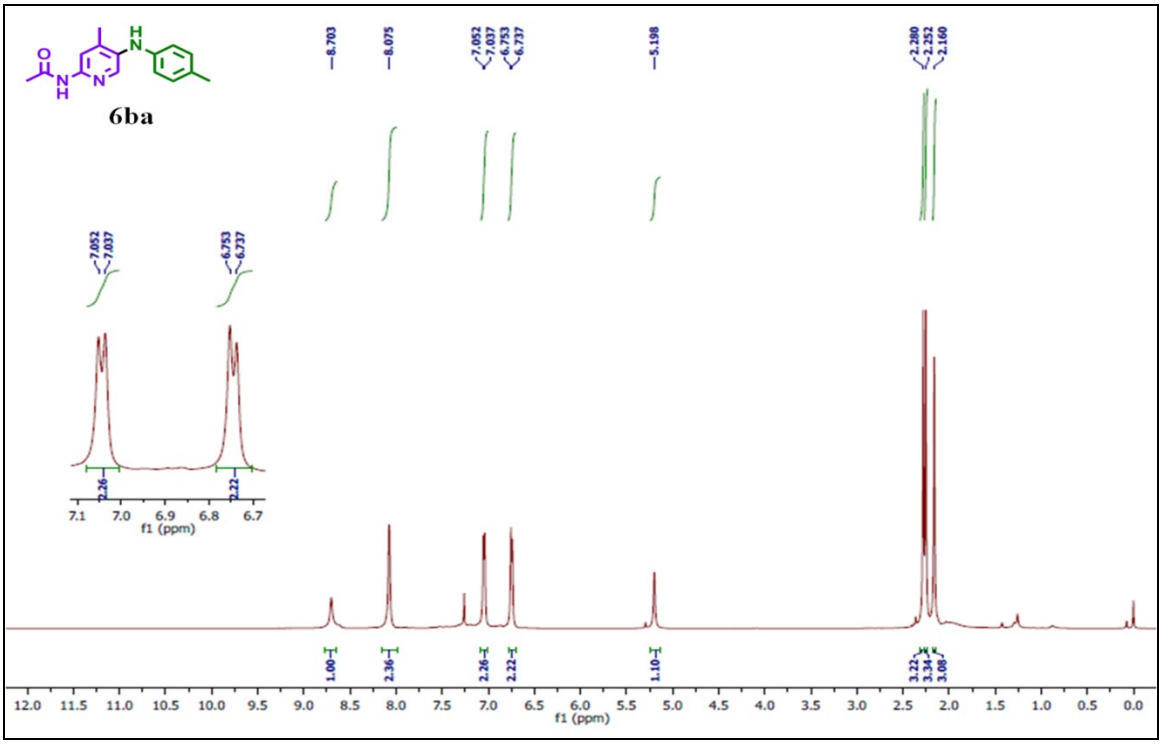

6ac
147.025
140.516
138.455
137.804
129.201
128.336
127.244
123.479
122.281
63.018
52.785
48.411
f1 (ppm)

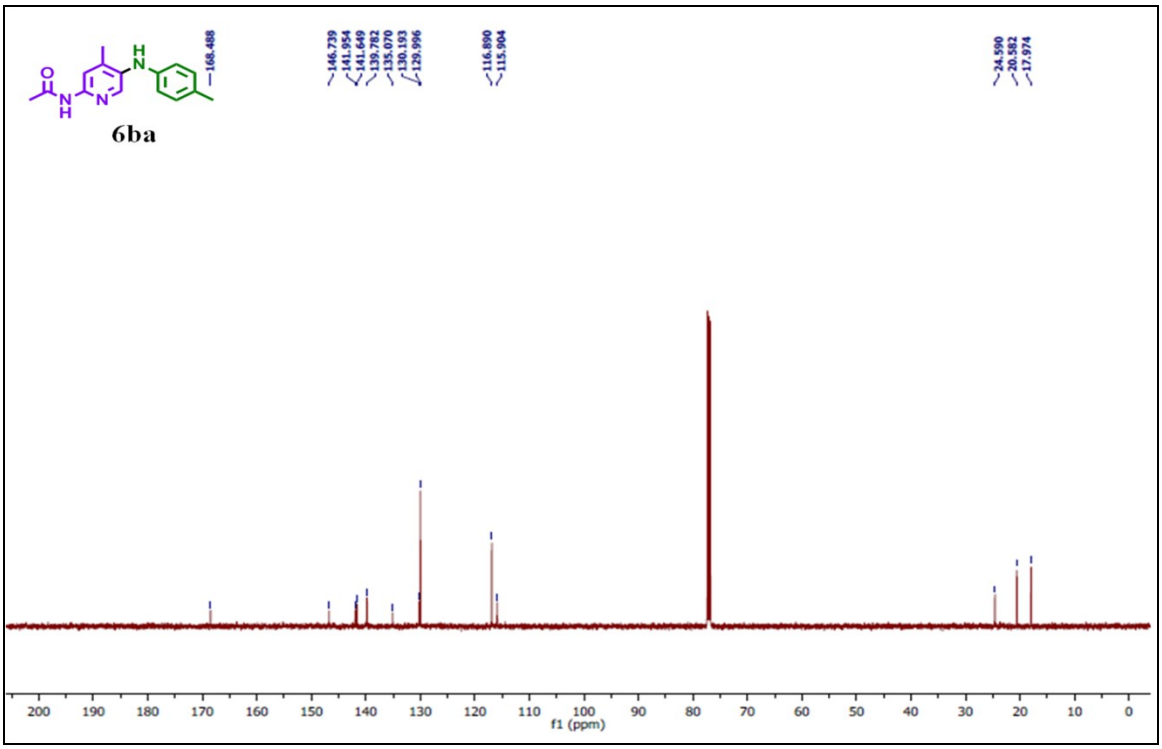

6ad
8.279
8.083
8.076
8.068
7.455
7.437
7.305
7.287
7.268
7.211
7.193
7.171
7.144
7.140
7.136
7.133
4.274
3.231
3.219
3.206
2.579
2.566
2.554
f1 (ppm)

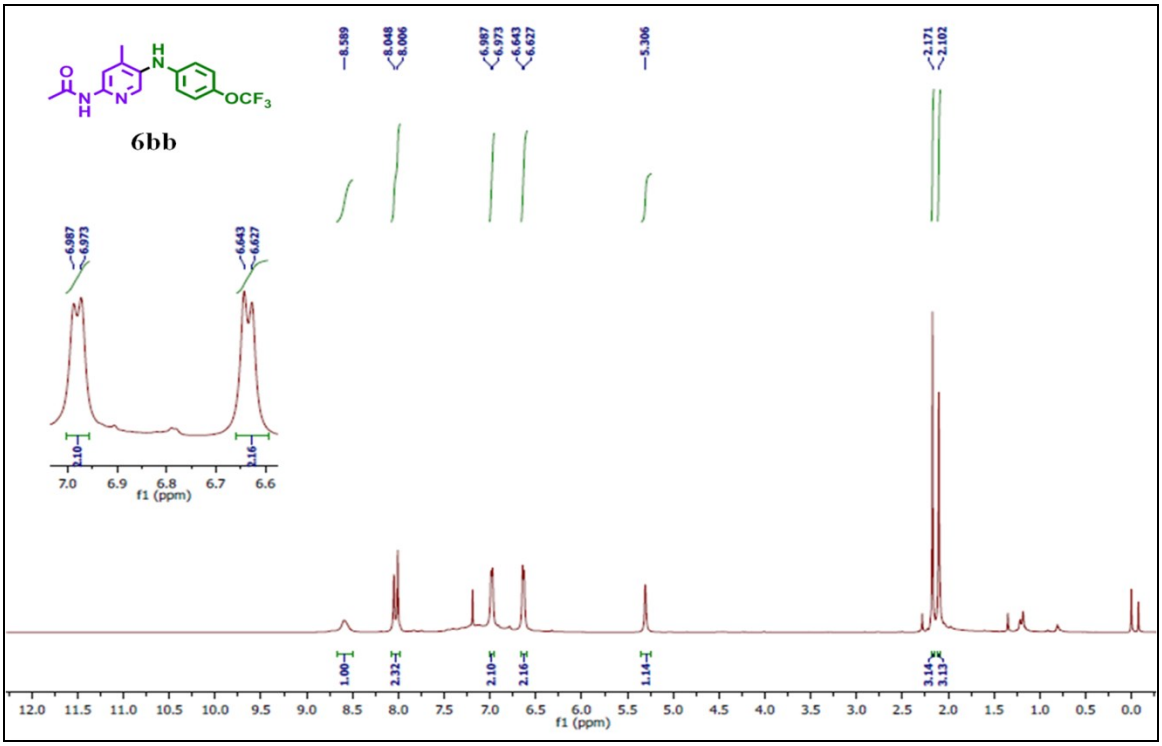

6ad
146.979
142.462
140.427
138.219
128.615
127.900
127.122
123.468
122.104
76.153
51.654
48.528
f1 (ppm)

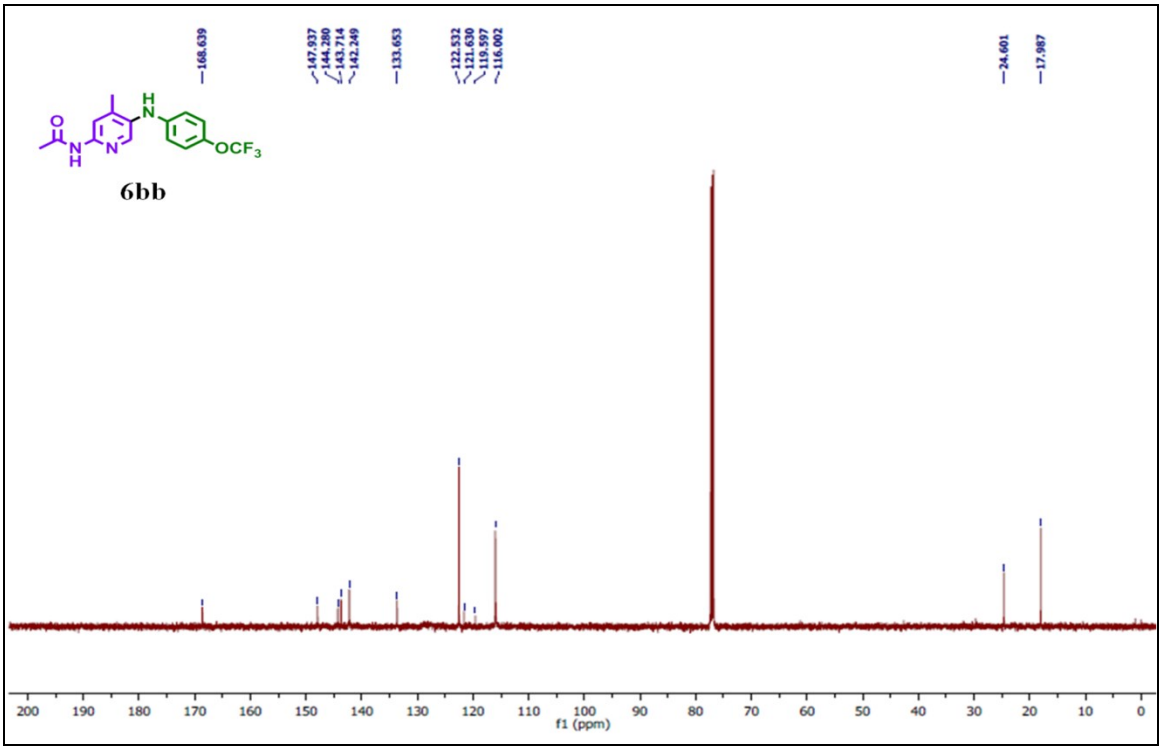

6ae
f1 (ppm)

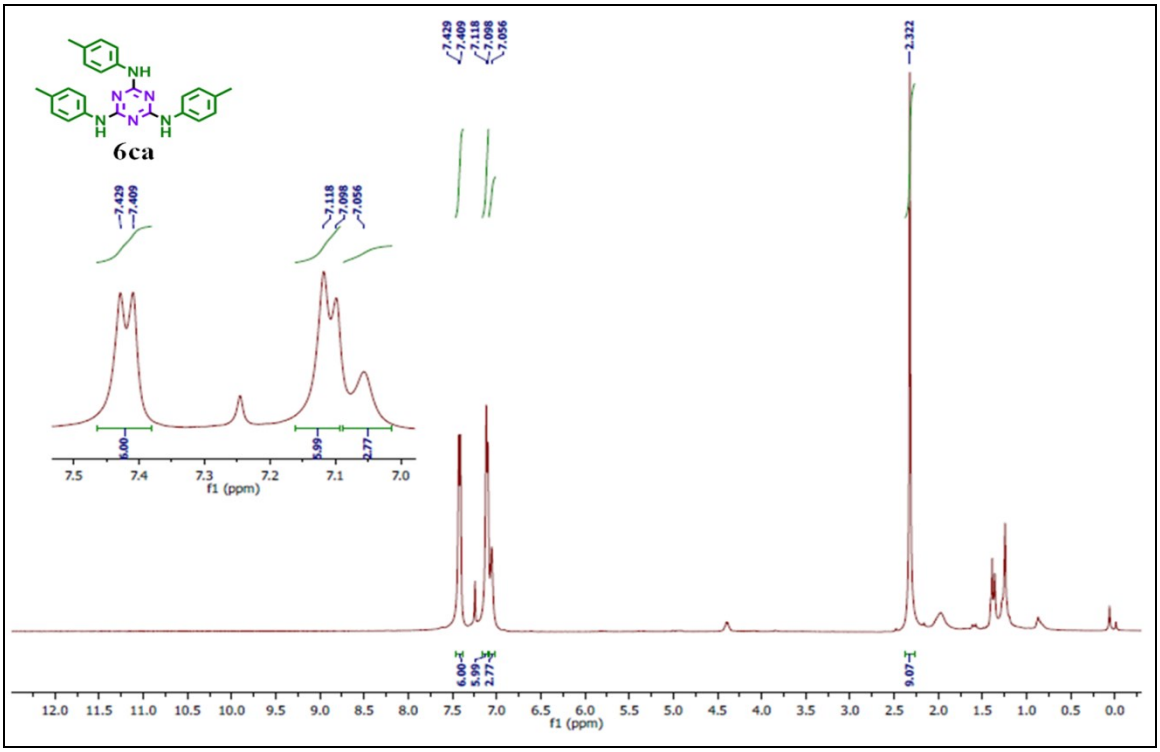

6ae
f1 (ppm)

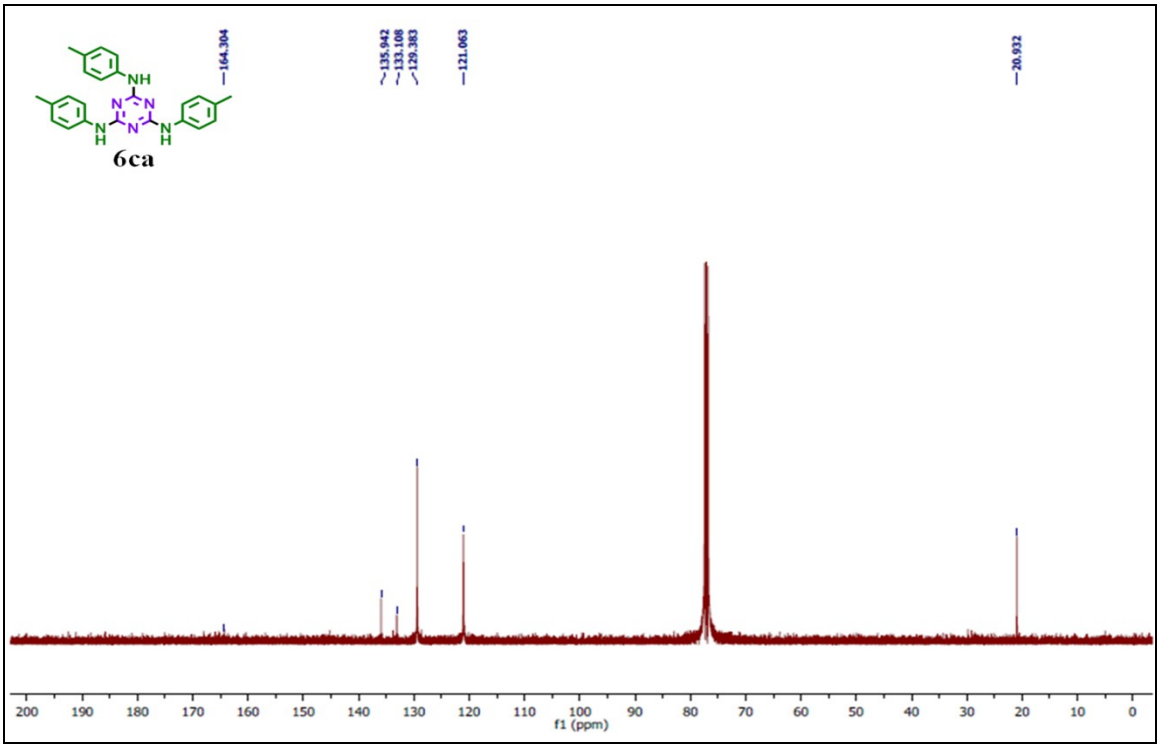

6ba
8.703
8.075
7.052
7.037
6.753
6.737
5.198
2.280
2.252
2.160
1.00
2.36
2.26
2.22
1.10
3.22
3.34
3.08
f1 (ppm)

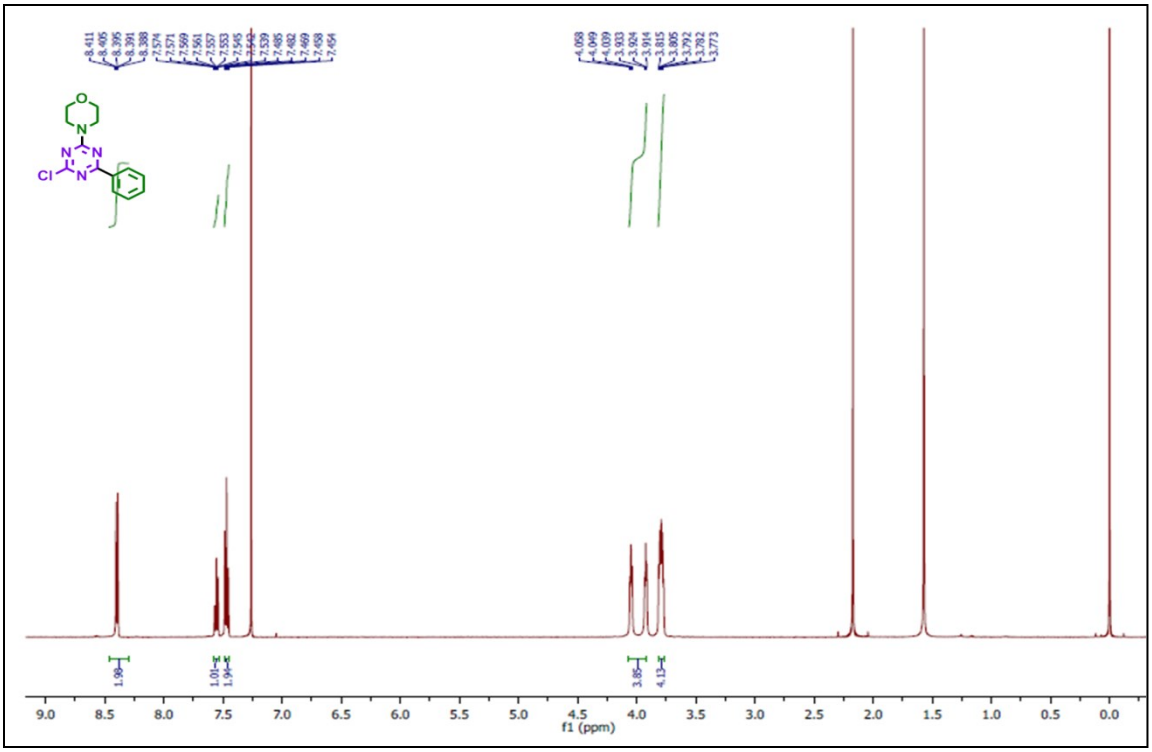

6ba
168.488
146.739
141.954
141.649
139.782
135.070
130.193
129.996
116.890
115.904
24.590
20.582
17.974
f1 (ppm)

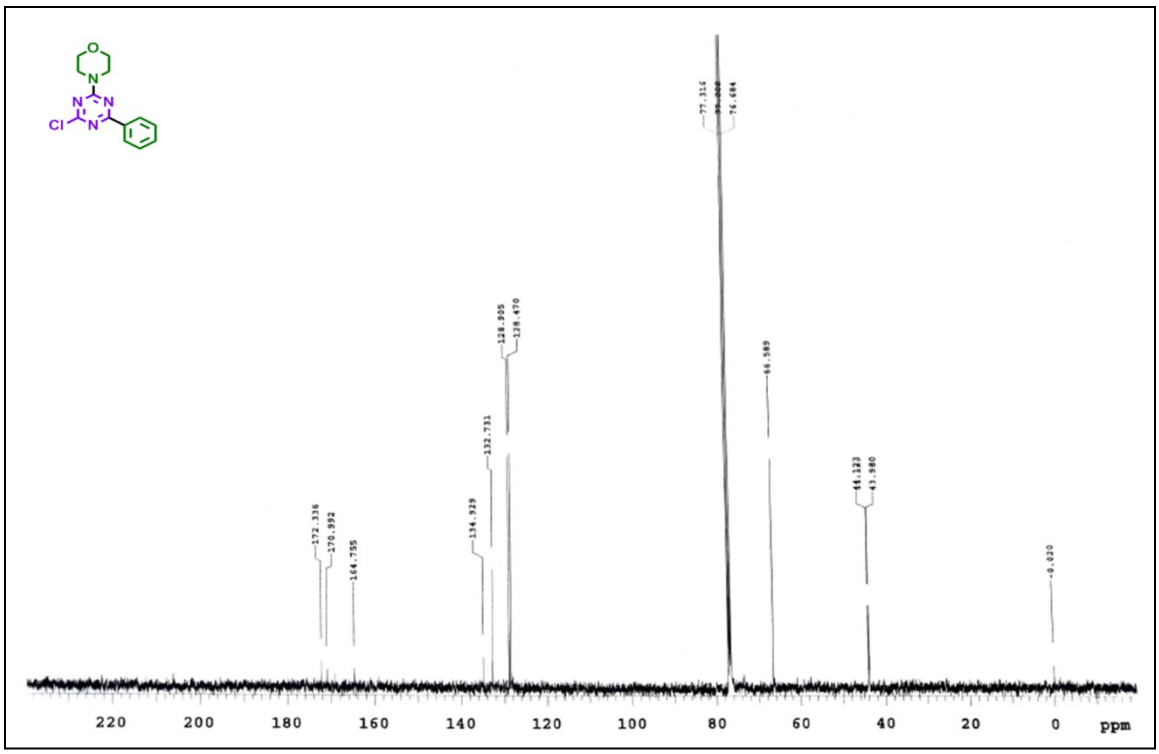

6bb
8.589
8.048
8.006
6.987
6.973
6.643
6.627
5.306
2.171
2.102
1.00
2.32
2.10
2.16
1.14
3.14
3.13
f1 (ppm)

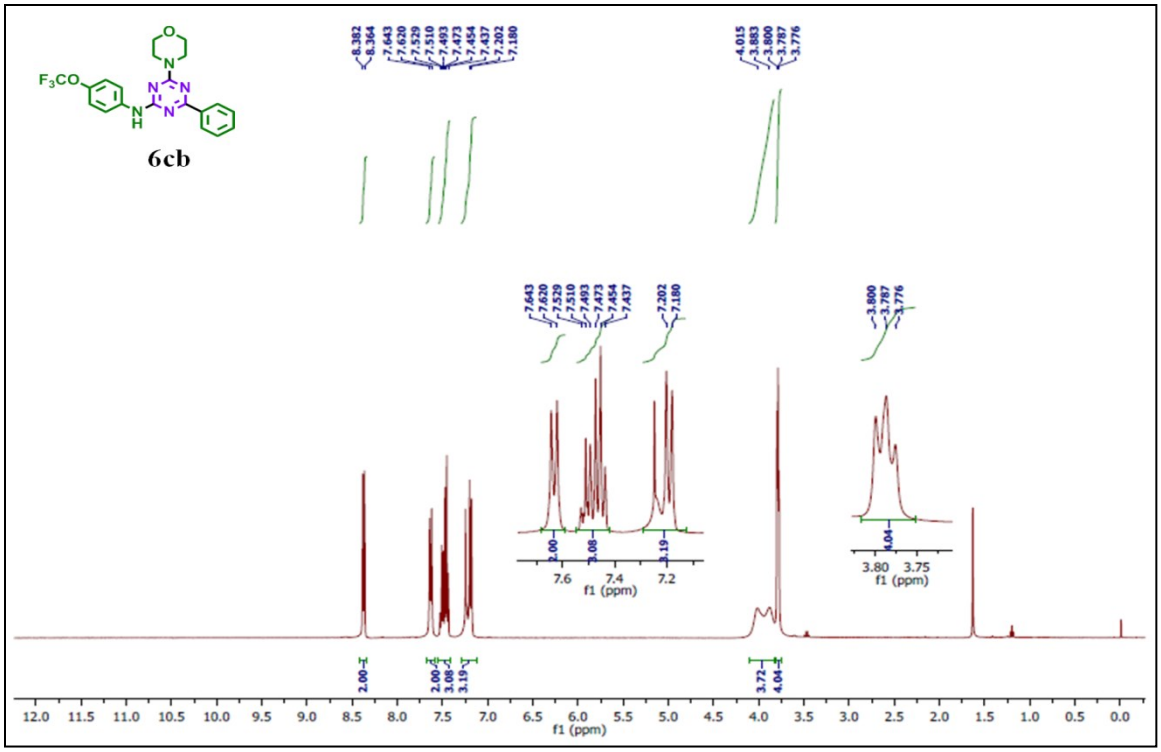

6bb
168.639
147.937
144.280
143.714
142.249
133.653
122.532
121.630
119.597
116.002
24.601
17.987
f1 (ppm)

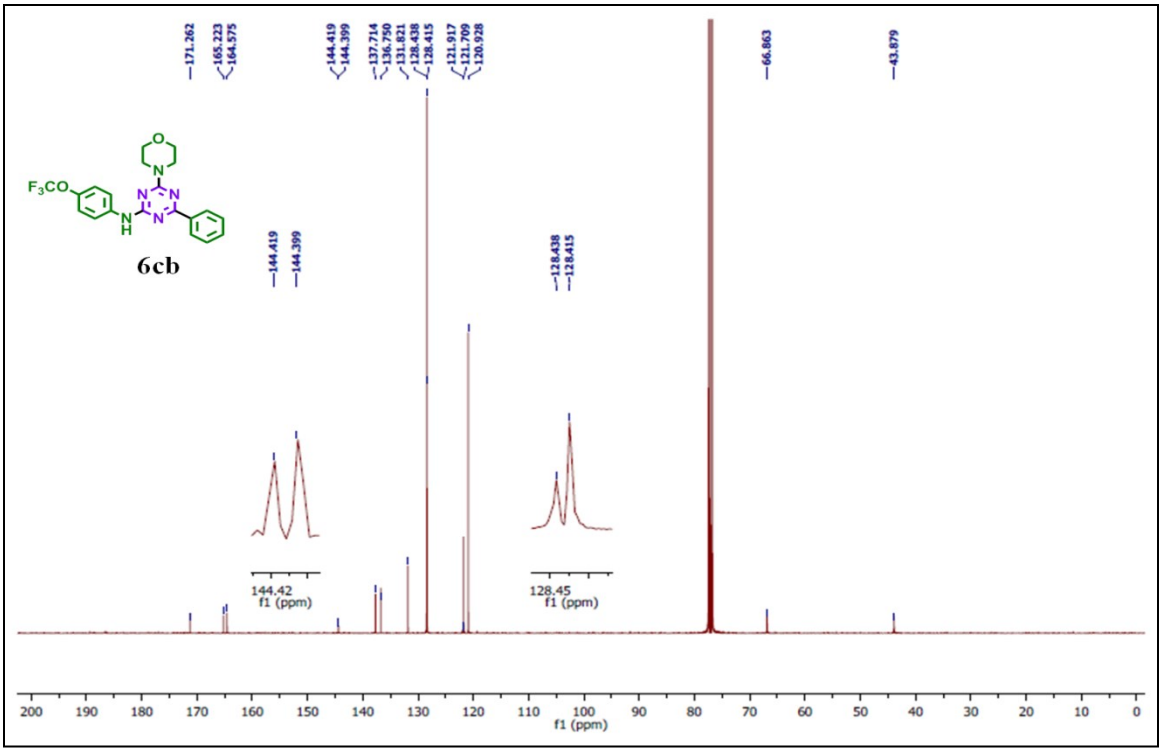

6ca
7.429
7.409
7.118
7.098
7.056
2.322
6.00
5.99
2.77
9.07
f1 (ppm)


6ca
164.304
135.942
133.108
129.383
121.063
20.932
f1 (ppm)


8.411
8.405
8.395
8.391
8.388
7.574
7.571
7.569
7.561
7.557
7.553
7.545
7.542
7.539
7.485
7.482
7.469
7.466
7.454
4.058
4.049
4.039
3.933
3.924
3.914
3.815
3.805
3.792
3.782
3.773
Cl
1.98
1.01
1.94
3.85
4.13
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)


Cl
172.336
170.992
164.755
134.929
132.731
128.905
128.470
77.316
76.684
66.589
44.123
43.980
0.020
220
200
180
160
140
120
100
80
60
40
20
0
ppm


6cb
8.382
8.364
7.643
7.620
7.529
7.510
7.493
7.473
7.454
7.437
7.202
7.180
4.015
3.883
3.800
3.787
3.776
2.00
2.00
3.08
3.19
3.72
4.04
f1 (ppm)


6cb
171.262
165.223
164.575
144.419
144.399
137.714
136.750
131.821
128.438
128.415
121.917
121.709
120.928
66.863
43.879
144.42
128.45
f1 (ppm)

VI. X-ray cystallography data for Pd-PEPPSI complex, C6

Table 2. Crystal data and structure refinement.

Identification code	1982273
Empirical formula	$C_{46}H_{62}Cl_3N_3Pd$
Formula weight	869.73
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 18.9613(9) Å a= 90°.
b = 9.3523(4) Å	b= 91.116(2)°.
c = 26.6508(12) Å	g = 90°.
Volume	4725.1(4) Å3
Z	4
Density (calculated)	1.223 Mg/m3
Absorption coefficient	0.594 mm-1
F(000)	1824
Crystal size	0.200 x 0.150 x 0.150 mm3
Theta range for data collection	2.149 to 25.000°.
Index ranges	-22<=h<=22, -11<=k<=11, -31<=l<=31
Reflections collected	60323
Independent reflections	8307 [R(int) = 0.0764]
Completeness to theta = 25.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7453 and 0.6238
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	8307 / 294 / 601

Goodness-of-fit on F2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1151
R indices (all data)	R1 = 0.0966, wR2 = 0.1440
Extinction coefficient	0.00137(17)
Largest diff. peak and hole	0.594 and -1.046 e.Å-3

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **C6**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	X	**y**	**z**	**U(eq)**
Pd(1)	6672(1)	7884(1)	5265(1)	53(1)
Cl(1)	7724(1)	9024(2)	5137(1)	90(1)
Cl(2)	5698(1)	6465(1)	5410(1)	75(1)
Cl(3)	4406(1)	11187(2)	6007(1)	132(1)
C(1)	5185(3)	11218(6)	5681(2)	75(2)
C(2)	5456(4)	12465(6)	5508(3)	80(2)
C(3)	6062(4)	12404(6)	5254(3)	84(2)
C(4)	6390(3)	11102(6)	5181(2)	80(2)
C(5)	5526(3)	9941(6)	5597(2)	69(2)
C(6)	7903(3)	4246(5)	5357(2)	57(1)
C(7)	7833(3)	4352(5)	4843(2)	57(1)
C(8)	8179(3)	3391(6)	4536(2)	72(2)
C(9)	8600(3)	2349(6)	4748(3)	75(2)
C(10)	8685(3)	2268(6)	5270(3)	71(2)
C(11)	8334(3)	3209(6)	5577(2)	72(2)
C(12)	9172(3)	1160(6)	5510(3)	102(2)
C(13)	8956(4)	1278(7)	4413(3)	113(3)
C(14)	7195(3)	6264(6)	4272(2)	73(2)
C(15)	7441(3)	5515(6)	3810(2)	70(2)
C(16)	8087(4)	5869(7)	3597(2)	82(2)

C(17)	8301(4)	5113(8)	3176(3)	102(2)
C(18)	7900(5)	4027(8)	2967(3)	103(2)
C(19)	7269(4)	3725(7)	3178(2)	97(2)
C(20)	7028(4)	4418(6)	3597(2)	77(2)
C(21)	6327(4)	3984(8)	3818(3)	96(2)
C(22)	5712(4)	4723(9)	3549(3)	126(3)
C(23)	6225(6)	2390(9)	3833(4)	169(4)
C(24)	8583(12)	6920(20)	3864(11)	124(6)
C(25)	8589(16)	8230(30)	3539(12)	151(9)
C(26)	9306(12)	6210(20)	3922(14)	153(8)
C(24')	8554(13)	7130(20)	3781(9)	122(6)
C(25')	8935(17)	8040(30)	3395(10)	155(8)
C(26')	9078(15)	6690(30)	4205(10)	151(8)
C(27)	8155(14)	3120(20)	2528(6)	156(5)
C(28)	8633(17)	1940(30)	2712(8)	181(9)
C(29)	8380(20)	4010(30)	2107(11)	187(9)
C(27')	8200(20)	3210(50)	2522(11)	161(8)
C(28')	8940(20)	2700(70)	2584(17)	177(11)
C(29')	7990(30)	3880(60)	2033(15)	173(11)
C(30)	7317(4)	5676(7)	6085(2)	91(2)
C(31)	7809(4)	5023(7)	6477(2)	81(2)
C(32)	8435(5)	5698(7)	6596(3)	98(2)
C(33)	8863(5)	5101(9)	6977(3)	118(3)
C(34)	8677(5)	3868(9)	7219(3)	111(3)
C(35)	8061(4)	3238(8)	7087(3)	102(2)
C(36)	7608(4)	3771(8)	6713(2)	90(2)
C(37)	6957(5)	2916(12)	6560(3)	126(3)
C(38)	6333(6)	3270(15)	6874(4)	203(6)
C(39)	7077(6)	1323(12)	6531(4)	188(5)

C(40)	9296(12)	3200(20)	7544(8)	167(7)
C(41)	9024(12)	3130(30)	8056(9)	186(9)
C(42)	9529(8)	1768(18)	7369(5)	170(7)
C(40')	9092(15)	3070(40)	7647(10)	144(8)
C(41')	8686(17)	2610(40)	8092(13)	142(9)
C(42')	9693(15)	4010(30)	7831(12)	184(11)
C(43)	8770(20)	6970(30)	6337(12)	133(7)
C(44)	9220(20)	6630(40)	5876(12)	136(9)
C(45)	9190(30)	8080(30)	6636(11)	162(9)
C(43')	8594(12)	7077(16)	6330(8)	122(5)
C(44')	9322(13)	6910(30)	6119(11)	171(8)
C(45')	8572(16)	8337(16)	6671(6)	141(7)
C(46)	7212(2)	6141(5)	5185(2)	49(1)
N(1)	6118(2)	9864(4)	5354(2)	61(1)
N(2)	7500(2)	5356(4)	5559(2)	58(1)
N(3)	7406(2)	5553(4)	4749(2)	53(1)

Table 4. Bond lengths [Å] and angles [°]

Pd(1)-C(46)	1.939(5)
Pd(1)-N(1)	2.144(4)
Pd(1)-Cl(1)	2.2939(15)
Pd(1)-Cl(2)	2.3139(14)
Cl(3)-C(1)	1.729(6)
C(1)-C(2)	1.358(8)
C(1)-C(5)	1.378(7)
C(2)-C(3)	1.347(8)
C(3)-C(4)	1.383(8)
C(4)-N(1)	1.351(7)
C(5)-N(1)	1.309(7)

C(6)-C(7)	1.377(7)
C(6)-C(11)	1.390(7)
C(6)-N(2)	1.401(6)
C(7)-C(8)	1.389(7)
C(7)-N(3)	1.405(6)
C(8)-C(9)	1.375(8)
C(9)-C(10)	1.398(8)
C(9)-C(13)	1.512(8)
C(10)-C(11)	1.382(8)
C(10)-C(12)	1.521(8)
C(14)-N(3)	1.484(6)
C(14)-C(15)	1.499(7)
C(15)-C(16)	1.400(8)
C(15)-C(20)	1.403(8)
C(16)-C(17)	1.394(8)
C(16)-C(24)	1.528(15)
C(16)-C(24')	1.546(14)
C(17)-C(18)	1.381(9)
C(18)-C(19)	1.362(9)
C(18)-C(27')	1.528(17)
C(18)-C(27)	1.530(12)
C(19)-C(20)	1.377(8)
C(20)-C(21)	1.519(9)
C(21)-C(23)	1.504(10)
C(21)-C(22)	1.524(10)
C(24)-C(25)	1.493(17)
C(24)-C(26)	1.532(19)
C(24')-C(25')	1.531(18)
C(24')-C(26')	1.546(17)

C(27)-C(29)	1.466(17)
C(27)-C(28)	1.505(16)
C(27')-C(29')	1.495(19)
C(27')-C(28')	1.50(2)
C(30)-N(2)	1.481(6)
C(30)-C(31)	1.516(8)
C(31)-C(32)	1.377(9)
C(31)-C(36)	1.387(9)
C(32)-C(33)	1.402(9)
C(32)-C(43')	1.505(13)
C(32)-C(43)	1.519(16)
C(33)-C(34)	1.371(10)
C(34)-C(35)	1.350(10)
C(34)-C(40')	1.564(17)
C(34)-C(40)	1.575(14)
C(35)-C(36)	1.394(9)
C(36)-C(37)	1.521(11)
C(37)-C(38)	1.498(12)
C(37)-C(39)	1.509(13)
C(40)-C(41)	1.470(16)
C(40)-C(42)	1.486(16)
C(40')-C(41')	1.488(19)
C(40')-C(42')	1.511(19)
C(43)-C(45)	1.523(19)
C(43)-C(44)	1.545(19)
C(43')-C(45')	1.490(16)
C(43')-C(44')	1.509(17)
C(46)-N(3)	1.342(6)
C(46)-N(2)	1.346(6)

C(46)-Pd(1)-N(1)	177.45(19)
C(46)-Pd(1)-Cl(1)	84.93(14)
N(1)-Pd(1)-Cl(1)	92.54(13)
C(46)-Pd(1)-Cl(2)	87.77(14)
N(1)-Pd(1)-Cl(2)	94.74(13)
Cl(1)-Pd(1)-Cl(2)	172.47(6)
C(2)-C(1)-C(5)	120.5(6)
C(2)-C(1)-Cl(3)	121.2(5)
C(5)-C(1)-Cl(3)	118.4(5)
C(3)-C(2)-C(1)	117.8(6)
C(2)-C(3)-C(4)	119.8(6)
N(1)-C(4)-C(3)	122.1(6)
N(1)-C(5)-C(1)	122.5(5)
C(7)-C(6)-C(11)	120.9(5)
C(7)-C(6)-N(2)	106.5(4)
C(11)-C(6)-N(2)	132.5(5)
C(6)-C(7)-C(8)	120.2(5)
C(6)-C(7)-N(3)	106.2(4)
C(8)-C(7)-N(3)	133.5(5)
C(9)-C(8)-C(7)	119.4(6)
C(8)-C(9)-C(10)	120.2(5)
C(8)-C(9)-C(13)	119.2(7)
C(10)-C(9)-C(13)	120.5(6)
C(11)-C(10)-C(9)	120.4(5)
C(11)-C(10)-C(12)	118.7(6)
C(9)-C(10)-C(12)	120.8(6)
C(10)-C(11)-C(6)	118.7(6)
N(3)-C(14)-C(15)	114.3(4)
C(16)-C(15)-C(20)	119.7(5)

C(16)-C(15)-C(14)	120.7(5)
C(20)-C(15)-C(14)	119.6(6)
C(17)-C(16)-C(15)	118.5(6)
C(17)-C(16)-C(24)	121.0(13)
C(15)-C(16)-C(24)	120.0(13)
C(17)-C(16)-C(24')	117.9(12)
C(15)-C(16)-C(24')	123.5(12)
C(18)-C(17)-C(16)	122.1(7)
C(19)-C(18)-C(17)	117.9(6)
C(19)-C(18)-C(27')	124(2)
C(17)-C(18)-C(27')	118(2)
C(19)-C(18)-C(27)	119.7(12)
C(17)-C(18)-C(27)	122.4(13)
C(18)-C(19)-C(20)	123.1(7)
C(19)-C(20)-C(15)	118.8(6)
C(19)-C(20)-C(21)	119.6(6)
C(15)-C(20)-C(21)	121.6(6)
C(23)-C(21)-C(20)	113.0(7)
C(23)-C(21)-C(22)	111.4(8)
C(20)-C(21)-C(22)	111.3(6)
C(25)-C(24)-C(16)	106(2)
C(25)-C(24)-C(26)	113.6(17)
C(16)-C(24)-C(26)	107.7(17)
C(25')-C(24')-C(26')	109.5(15)
C(25')-C(24')-C(16)	119(2)
C(26')-C(24')-C(16)	112.8(16)
C(29)-C(27)-C(28)	118.9(15)
C(29)-C(27)-C(18)	112(2)
C(28)-C(27)-C(18)	110.8(14)

C(29')-C(27')-C(28')	118(2)
C(29')-C(27')-C(18)	112(3)
C(28')-C(27')-C(18)	116(3)
N(2)-C(30)-C(31)	114.8(5)
C(32)-C(31)-C(36)	121.8(6)
C(32)-C(31)-C(30)	119.4(7)
C(36)-C(31)-C(30)	118.9(7)
C(31)-C(32)-C(33)	117.9(7)
C(31)-C(32)-C(43')	117.6(10)
C(33)-C(32)-C(43')	124.3(11)
C(31)-C(32)-C(43)	128.1(17)
C(33)-C(32)-C(43)	113.7(18)
C(34)-C(33)-C(32)	121.7(8)
C(35)-C(34)-C(33)	118.3(7)
C(35)-C(34)-C(40')	113.7(13)
C(33)-C(34)-C(40')	128.0(14)
C(35)-C(34)-C(40)	127.0(11)
C(33)-C(34)-C(40)	113.5(12)
C(34)-C(35)-C(36)	123.2(7)
C(31)-C(36)-C(35)	117.1(7)
C(31)-C(36)-C(37)	123.4(7)
C(35)-C(36)-C(37)	119.3(7)
C(38)-C(37)-C(39)	111.6(10)
C(38)-C(37)-C(36)	112.3(9)
C(39)-C(37)-C(36)	114.2(8)
C(41)-C(40)-C(42)	111.2(17)
C(41)-C(40)-C(34)	104.9(18)
C(42)-C(40)-C(34)	114.1(13)
C(41')-C(40')-C(42')	108(2)

C(41')-C(40')-C(34)	117(2)
C(42')-C(40')-C(34)	108.9(19)
C(32)-C(43)-C(45)	121(2)
C(32)-C(43)-C(44)	116(3)
C(45)-C(43)-C(44)	105.0(18)
C(45')-C(43')-C(32)	112.5(14)
C(45')-C(43')-C(44')	110.2(15)
C(32)-C(43')-C(44')	106.3(17)
N(3)-C(46)-N(2)	107.6(4)
N(3)-C(46)-Pd(1)	126.5(4)
N(2)-C(46)-Pd(1)	125.8(4)
C(5)-N(1)-C(4)	117.2(5)
C(5)-N(1)-Pd(1)	121.9(4)
C(4)-N(1)-Pd(1)	120.8(4)
C(46)-N(2)-C(6)	109.7(4)
C(46)-N(2)-C(30)	119.4(4)
C(6)-N(2)-C(30)	130.6(4)
C(46)-N(3)-C(7)	109.9(4)
C(46)-N(3)-C(14)	118.9(4)
C(7)-N(3)-C(14)	131.1(4)

Symmetry transformations are used to generate equivalent atoms

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	60(1)	42(1)	56(1)	-1(1)	0(1)	2(1)
Cl(1)	68(1)	61(1)	142(2)	-9(1)	14(1)	-17(1)
Cl(2)	62(1)	47(1)	118(1)	8(1)	7(1)	-3(1)

Cl(3)	120(2)	81(1)	198(2)	3(1)	73(2)	21(1)
C(1)	77(4)	57(4)	92(5)	-3(3)	9(3)	10(3)
C(2)	97(5)	47(3)	97(5)	1(3)	-5(4)	14(3)
C(3)	101(5)	50(4)	103(5)	15(3)	6(4)	4(3)
C(4)	91(4)	59(4)	90(5)	16(3)	16(4)	3(3)
C(5)	81(4)	52(3)	75(4)	-1(3)	11(3)	2(3)
C(6)	59(3)	47(3)	65(4)	-5(3)	0(3)	6(2)
C(7)	62(3)	44(3)	65(4)	-4(3)	4(3)	4(2)
C(8)	97(4)	48(3)	72(4)	-2(3)	12(3)	10(3)
C(9)	79(4)	44(3)	102(5)	-4(3)	28(4)	4(3)
C(10)	58(3)	43(3)	111(5)	-2(3)	-1(3)	3(3)
C(11)	78(4)	60(4)	76(4)	-1(3)	-10(3)	17(3)
C(12)	75(4)	57(4)	172(7)	-5(4)	-30(4)	17(3)
C(13)	142(7)	61(4)	137(7)	3(4)	58(5)	33(4)
C(14)	106(5)	59(3)	53(3)	2(3)	1(3)	13(3)
C(15)	99(5)	57(3)	53(3)	-4(3)	8(3)	1(3)
C(16)	95(5)	76(4)	76(4)	-15(3)	10(4)	-13(4)
C(17)	119(6)	101(5)	87(5)	-13(4)	44(4)	-15(5)
C(18)	152(7)	85(5)	74(5)	-23(4)	36(5)	-19(5)
C(19)	135(6)	84(5)	74(5)	-14(4)	19(4)	-26(5)
C(20)	108(5)	65(4)	58(4)	3(3)	13(3)	-11(4)
C(21)	106(5)	89(5)	94(5)	12(4)	14(4)	-21(4)
C(22)	113(6)	140(7)	125(7)	15(6)	5(5)	-32(6)
C(23)	197(11)	107(7)	205(11)	33(7)	60(9)	-45(7)
C(24)	128(11)	118(11)	128(12)	-27(10)	27(10)	-40(10)
C(25)	178(19)	106(13)	170(18)	-26(13)	31(16)	-75(15)
C(26)	136(15)	154(16)	169(18)	-49(14)	-18(14)	-56(13)
C(24')	130(11)	120(12)	117(11)	-26(11)	14(10)	-40(10)
C(25')	170(18)	109(13)	186(17)	-3(13)	54(14)	-62(14)

C(26')	149(16)	154(16)	151(17)	-28(14)	-9(14)	-57(14)
C(27)	227(13)	147(11)	97(9)	-34(8)	77(9)	-17(10)
C(28)	234(19)	147(16)	164(14)	-59(12)	71(13)	31(14)
C(29)	240(20)	201(15)	122(14)	-25(12)	103(15)	-43(17)
C(27')	229(16)	154(14)	103(13)	-35(13)	77(13)	-9(14)
C(28')	220(20)	170(20)	144(19)	-32(19)	68(19)	20(20)
C(29')	230(20)	210(20)	85(15)	-53(16)	80(20)	-30(20)
C(30)	119(5)	106(5)	47(3)	2(3)	-3(3)	48(4)
C(31)	115(5)	76(4)	53(4)	-2(3)	-15(4)	24(4)
C(32)	152(7)	69(4)	73(5)	10(4)	-25(5)	0(5)
C(33)	149(7)	108(6)	97(6)	17(5)	-45(5)	-28(6)
C(34)	144(7)	99(6)	89(5)	20(5)	-51(5)	-1(5)
C(35)	135(7)	86(5)	84(5)	22(4)	-20(5)	-3(5)
C(36)	115(6)	90(5)	65(4)	-1(4)	-16(4)	11(4)
C(37)	117(7)	160(9)	100(6)	9(6)	-13(5)	-19(7)
C(38)	145(10)	306(17)	159(10)	-11(11)	31(8)	-44(11)
C(39)	223(13)	150(10)	190(12)	-19(9)	-24(9)	-63(10)
C(40)	220(15)	158(11)	119(11)	75(9)	-77(11)	-36(12)
C(41)	200(20)	199(19)	159(14)	39(15)	-39(16)	45(15)
C(42)	190(14)	181(15)	136(12)	26(11)	-28(10)	104(12)
C(40')	171(16)	178(14)	81(12)	77(12)	-64(13)	-16(13)
C(41')	150(20)	158(19)	119(15)	90(14)	-39(16)	-28(16)
C(42')	190(20)	200(20)	154(19)	76(17)	-104(17)	-29(18)
C(43)	178(16)	106(12)	115(12)	16(11)	-17(13)	-24(13)
C(44)	165(18)	122(16)	121(19)	-7(15)	-20(16)	-39(14)
C(45)	230(20)	110(15)	145(16)	9(13)	-6(19)	-47(17)
C(43')	164(12)	93(8)	109(9)	15(8)	-20(9)	-19(9)
C(44')	201(16)	147(15)	166(18)	29(15)	3(16)	-56(14)
C(45')	228(19)	78(9)	117(10)	10(8)	-19(13)	-42(12)

C(46)	55(3)	42(3)	51(3)	-4(2)	1(2)	-3(2)
N(1)	75(3)	46(3)	62(3)	1(2)	-1(2)	5(2)
N(2)	69(3)	56(3)	50(3)	-3(2)	-4(2)	13(2)
N(3)	63(3)	47(2)	50(2)	-3(2)	2(2)	4(2)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **C6**.

	x	y	z	U(eq)
H(2)	5231	13332	5564	97
H(3)	6260	13237	5127	101
H(4)	6811	11077	5009	96
H(5)	5329	9103	5719	83
H(8)	8126	3452	4189	87
H(11)	8385	3150	5924	86
H(12A)	9650	1359	5420	153
H(12B)	9042	224	5392	153
H(12C)	9132	1198	5868	153
H(13A)	8831	1473	4069	169
H(13B)	8807	330	4498	169
H(13C)	9459	1351	4458	169
H(14A)	7381	7230	4274	87
H(14B)	6684	6332	4256	87
H(17)	8729	5346	3032	122
H(19)	6987	3017	3033	117
H(21)	6331	4321	4166	115
H(22A)	5706	4461	3200	189
H(22B)	5764	5740	3579	189
H(22C)	5277	4433	3697	189
H(23A)	6087	2053	3506	253

H(23B)	5864	2160	4068	253
H(23C)	6659	1938	3936	253
H(24)	8400	7165	4195	149
H(25A)	8894	8934	3689	227
H(25B)	8757	7978	3213	227
H(25C)	8119	8604	3508	227
H(26A)	9266	5380	4133	230
H(26B)	9468	5919	3598	230
H(26C)	9635	6867	4070	230
H(24')	8225	7788	3941	146
H(25D)	8609	8313	3131	232
H(25E)	9120	8887	3555	232
H(25F)	9315	7504	3256	232
H(26D)	8839	6120	4448	227
H(26E)	9458	6154	4066	227
H(26F)	9263	7537	4365	227
H(27)	7731	2630	2402	187
H(28A)	8418	1455	2986	271
H(28B)	8711	1276	2444	271
H(28C)	9077	2340	2822	271
H(29A)	8023	4714	2033	280
H(29B)	8814	4484	2196	280
H(29C)	8448	3421	1818	280
H(27')	7927	2318	2522	193
H(28D)	9010	2298	2913	266
H(28E)	9038	1988	2336	266
H(28F)	9260	3493	2544	266
H(29D)	7498	4155	2042	259
H(29E)	8271	4707	1975	259

H(29F)	8050	3202	1766	259
H(30A)	6843	5335	6142	109
H(30B)	7316	6705	6129	109
H(33)	9284	5552	7067	142
H(35)	7932	2406	7253	122
H(37)	6832	3223	6218	151
H(38A)	5932	2730	6757	305
H(38B)	6232	4273	6847	305
H(38C)	6437	3032	7218	305
H(39A)	7238	977	6852	282
H(39B)	7427	1124	6284	282
H(39C)	6644	855	6438	282
H(40)	9700	3851	7542	200
H(41A)	8588	2605	8053	280
H(41B)	8946	4077	8179	280
H(41C)	9362	2649	8271	280
H(42A)	9923	1452	7571	254
H(42B)	9666	1830	7024	254
H(42C)	9148	1098	7397	254
H(40')	9299	2209	7500	173
H(41D)	9002	2500	8375	212
H(41E)	8458	1714	8021	212
H(41F)	8337	3319	8166	212
H(42D)	9525	4963	7878	276
H(42E)	10060	4005	7588	276
H(42F)	9875	3642	8144	276
H(43)	8364	7509	6199	160
H(44A)	9404	7509	5742	204
H(44B)	9605	6022	5976	204

H(44C)	8935	6164	5625	204
H(45A)	9358	8801	6413	243
H(45B)	8893	8508	6882	243
H(45C)	9583	7619	6801	243
H(43')	8252	7213	6054	147
H(44D)	9330	6098	5900	256
H(44E)	9441	7756	5934	256
H(44F)	9658	6778	6389	256
H(45D)	8676	9189	6486	212
H(45E)	8110	8416	6810	212
H(45F)	8915	8219	6938	212

Table 7. Torsion angles [°]

C(5)-C(1)-C(2)-C(3)	0.3(10)
Cl(3)-C(1)-C(2)-C(3)	-179.5(5)
C(1)-C(2)-C(3)-C(4)	-0.7(10)
C(2)-C(3)-C(4)-N(1)	0.8(10)
C(2)-C(1)-C(5)-N(1)	0.1(10)
Cl(3)-C(1)-C(5)-N(1)	179.9(5)
C(11)-C(6)-C(7)-C(8)	1.9(8)
N(2)-C(6)-C(7)-C(8)	179.7(5)
C(11)-C(6)-C(7)-N(3)	-176.1(5)
N(2)-C(6)-C(7)-N(3)	1.7(5)
C(6)-C(7)-C(8)-C(9)	-1.1(8)
N(3)-C(7)-C(8)-C(9)	176.2(5)
C(7)-C(8)-C(9)-C(10)	-0.6(9)
C(7)-C(8)-C(9)-C(13)	178.1(5)
C(8)-C(9)-C(10)-C(11)	1.6(9)
C(13)-C(9)-C(10)-C(11)	-177.2(6)

C(8)-C(9)-C(10)-C(12)	-177.5(5)
C(13)-C(9)-C(10)-C(12)	3.8(9)
C(9)-C(10)-C(11)-C(6)	-0.8(9)
C(12)-C(10)-C(11)-C(6)	178.3(5)
C(7)-C(6)-C(11)-C(10)	-0.9(8)
N(2)-C(6)-C(11)-C(10)	-178.1(5)
N(3)-C(14)-C(15)-C(16)	-91.4(7)
N(3)-C(14)-C(15)-C(20)	86.7(7)
C(20)-C(15)-C(16)-C(17)	0.1(10)
C(14)-C(15)-C(16)-C(17)	178.2(6)
C(20)-C(15)-C(16)-C(24)	-172.2(13)
C(14)-C(15)-C(16)-C(24)	5.9(15)
C(20)-C(15)-C(16)-C(24')	175.5(12)
C(14)-C(15)-C(16)-C(24')	-6.4(14)
C(15)-C(16)-C(17)-C(18)	-0.4(11)
C(24)-C(16)-C(17)-C(18)	171.8(14)
C(24')-C(16)-C(17)-C(18)	-176.1(13)
C(16)-C(17)-C(18)-C(19)	1.4(12)
C(16)-C(17)-C(18)-C(27')	-176.8(19)
C(16)-C(17)-C(18)-C(27)	-175.5(12)
C(17)-C(18)-C(19)-C(20)	-2.1(12)
C(27')-C(18)-C(19)-C(20)	176(2)
C(27)-C(18)-C(19)-C(20)	174.9(12)
C(18)-C(19)-C(20)-C(15)	1.8(11)
C(18)-C(19)-C(20)-C(21)	-178.2(7)
C(16)-C(15)-C(20)-C(19)	-0.7(9)
C(14)-C(15)-C(20)-C(19)	-178.9(6)
C(16)-C(15)-C(20)-C(21)	179.3(6)
C(14)-C(15)-C(20)-C(21)	1.1(9)

C(19)-C(20)-C(21)-C(23)	42.2(10)
C(15)-C(20)-C(21)-C(23)	-137.8(8)
C(19)-C(20)-C(21)-C(22)	-83.9(8)
C(15)-C(20)-C(21)-C(22)	96.1(8)
C(17)-C(16)-C(24)-C(25)	76(2)
C(15)-C(16)-C(24)-C(25)	-111.7(19)
C(17)-C(16)-C(24)-C(26)	-45(3)
C(15)-C(16)-C(24)-C(26)	127(2)
C(17)-C(16)-C(24')-C(25')	35(3)
C(15)-C(16)-C(24')-C(25')	-141(2)
C(17)-C(16)-C(24')-C(26')	-96(2)
C(15)-C(16)-C(24')-C(26')	89(2)
C(19)-C(18)-C(27)-C(29)	130(2)
C(17)-C(18)-C(27)-C(29)	-53(3)
C(19)-C(18)-C(27)-C(28)	-95(2)
C(17)-C(18)-C(27)-C(28)	82(2)
C(19)-C(18)-C(27')-C(29')	91(4)
C(17)-C(18)-C(27')-C(29')	-91(4)
C(19)-C(18)-C(27')-C(28')	-130(4)
C(17)-C(18)-C(27')-C(28')	48(5)
N(2)-C(30)-C(31)-C(32)	81.9(8)
N(2)-C(30)-C(31)-C(36)	-99.3(7)
C(36)-C(31)-C(32)-C(33)	-1.5(11)
C(30)-C(31)-C(32)-C(33)	177.1(7)
C(36)-C(31)-C(32)-C(43')	-178.0(11)
C(30)-C(31)-C(32)-C(43')	0.7(13)
C(36)-C(31)-C(32)-C(43)	172.9(19)
C(30)-C(31)-C(32)-C(43)	-8(2)
C(31)-C(32)-C(33)-C(34)	1.2(13)

C(43')-C(32)-C(33)-C(34)	177.4(12)
C(43)-C(32)-C(33)-C(34)	-174.0(16)
C(32)-C(33)-C(34)-C(35)	-0.7(14)
C(32)-C(33)-C(34)-C(40')	179.9(19)
C(32)-C(33)-C(34)-C(40)	167.2(12)
C(33)-C(34)-C(35)-C(36)	0.6(14)
C(40')-C(34)-C(35)-C(36)	-180.0(16)
C(40)-C(34)-C(35)-C(36)	-165.6(13)
C(32)-C(31)-C(36)-C(35)	1.4(10)
C(30)-C(31)-C(36)-C(35)	-177.3(6)
C(32)-C(31)-C(36)-C(37)	-174.0(7)
C(30)-C(31)-C(36)-C(37)	7.3(10)
C(34)-C(35)-C(36)-C(31)	-0.9(12)
C(34)-C(35)-C(36)-C(37)	174.7(8)
C(31)-C(36)-C(37)-C(38)	-96.4(10)
C(35)-C(36)-C(37)-C(38)	88.3(11)
C(31)-C(36)-C(37)-C(39)	135.3(9)
C(35)-C(36)-C(37)-C(39)	-40.0(11)
C(35)-C(34)-C(40)-C(41)	-71(2)
C(33)-C(34)-C(40)-C(41)	122.2(17)
C(35)-C(34)-C(40)-C(42)	51(3)
C(33)-C(34)-C(40)-C(42)	-115.8(17)
C(35)-C(34)-C(40')-C(41')	-46(3)
C(33)-C(34)-C(40')-C(41')	133(3)
C(35)-C(34)-C(40')-C(42')	-169(2)
C(33)-C(34)-C(40')-C(42')	10(3)
C(31)-C(32)-C(43)-C(45)	146(3)
C(33)-C(32)-C(43)-C(45)	-40(4)
C(31)-C(32)-C(43)-C(44)	-85(4)

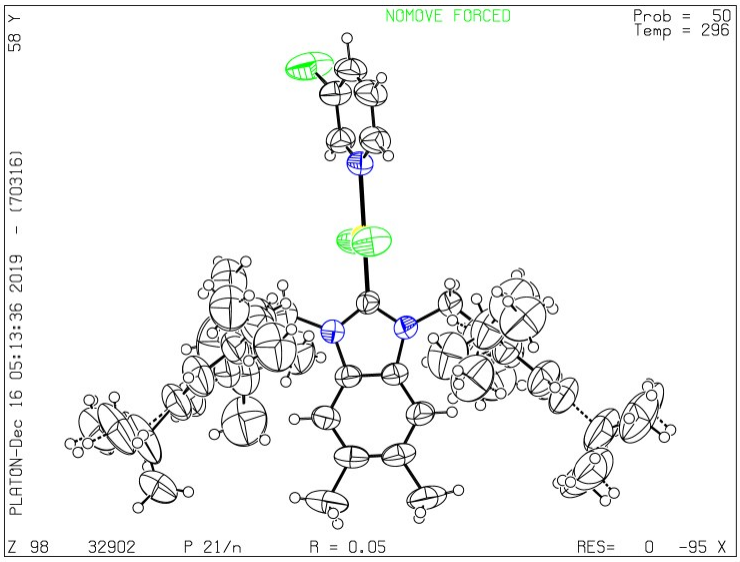
C(33)-C(32)-C(43)-C(44)	89(3)
C(31)-C(32)-C(43')-C(45')	110.9(18)
C(33)-C(32)-C(43')-C(45')	-65(2)
C(31)-C(32)-C(43')-C(44')	-128.4(17)
C(33)-C(32)-C(43')-C(44')	55(2)
C(1)-C(5)-N(1)-C(4)	-0.1(9)
C(1)-C(5)-N(1)-Pd(1)	176.4(4)
C(3)-C(4)-N(1)-C(5)	-0.3(9)
C(3)-C(4)-N(1)-Pd(1)	-176.9(5)
N(3)-C(46)-N(2)-C(6)	1.2(5)
Pd(1)-C(46)-N(2)-C(6)	-174.7(3)
N(3)-C(46)-N(2)-C(30)	-174.1(5)
Pd(1)-C(46)-N(2)-C(30)	10.0(7)
C(7)-C(6)-N(2)-C(46)	-1.9(6)
C(11)-C(6)-N(2)-C(46)	175.6(6)
C(7)-C(6)-N(2)-C(30)	172.7(6)
C(11)-C(6)-N(2)-C(30)	-9.8(10)
C(31)-C(30)-N(2)-C(46)	-164.1(5)
C(31)-C(30)-N(2)-C(6)	21.7(10)
N(2)-C(46)-N(3)-C(7)	-0.1(5)
Pd(1)-C(46)-N(3)-C(7)	175.8(3)
N(2)-C(46)-N(3)-C(14)	-176.3(4)
Pd(1)-C(46)-N(3)-C(14)	-0.4(7)
C(6)-C(7)-N(3)-C(46)	-1.1(6)
C(8)-C(7)-N(3)-C(46)	-178.7(6)
C(6)-C(7)-N(3)-C(14)	174.6(5)
C(8)-C(7)-N(3)-C(14)	-3.0(10)
C(15)-C(14)-N(3)-C(46)	179.9(5)
C(15)-C(14)-N(3)-C(7)	4.6(8)

Table 8. Hydrogen Symmetry transformations used to generate equivalent atoms bonds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4)...Cl(1)	0.93	2.60	3.194(6)	121.9
C(5)-H(5)...Cl(2)	0.93	2.70	3.306(6)	123.8
C(14)-H(14A)...Cl(1)	0.97	2.91	3.591(6)	128.1

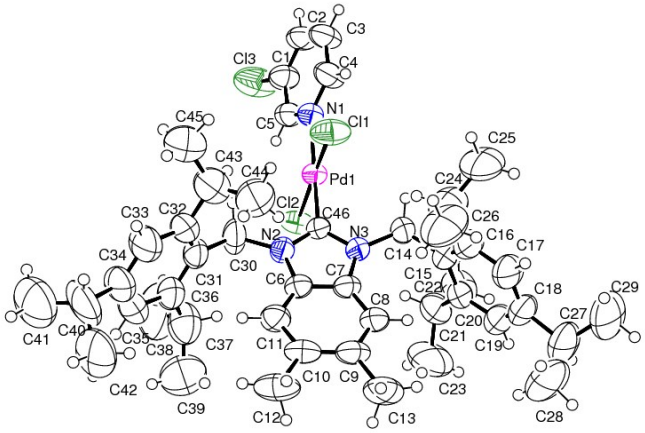
Symmetry transformations used to generate equivalent atoms

VII. X-ray Crystallography Structure of Pd-PEPPSI complex C6



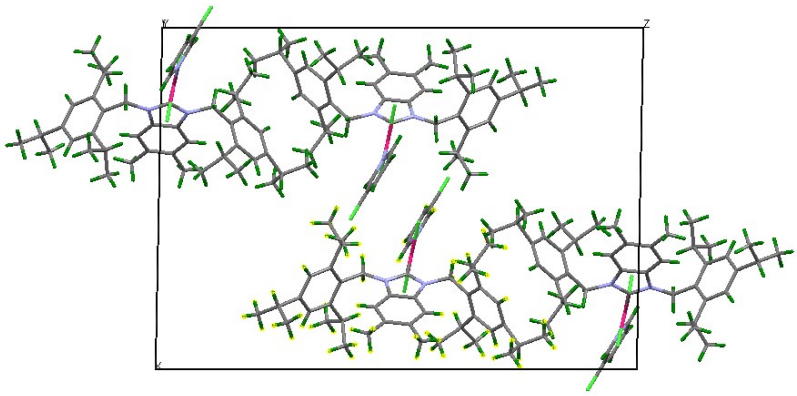
Single crystal XRD Structure for **C6**

Packed structures

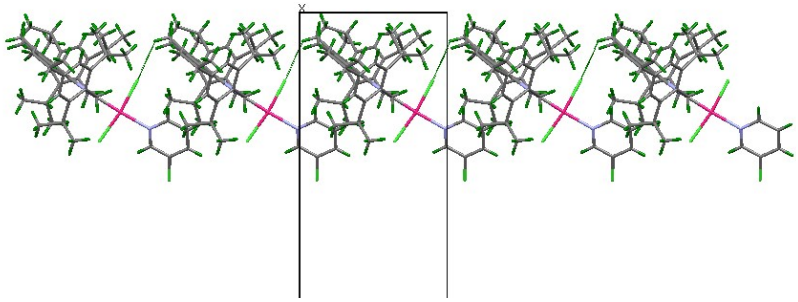


(1)

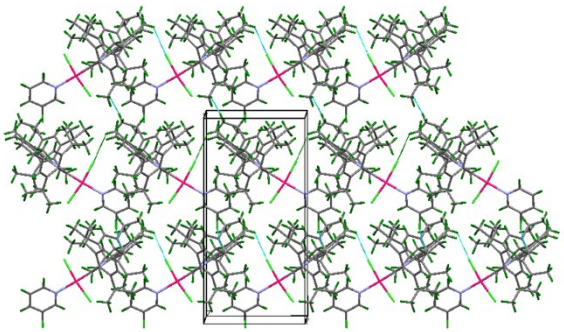
ORTEP diagrams drawn with 50% ellipsoid probability for non-H atoms of the crystal structure of Pd-PEPPSI complex **C6** determined at 296 K (CCDC Deposit No. 1982273).



(2)



(3)



(4) Crystal packing of **C6** displaying non-linear interactions

VIII. References

[1] Q. Deng, Y. Zhang, H. Zhu, T. Tu, *Asian J. Org. Chem.,* 2017, **12**, 2364-2368.

[2] S. Xia, L. -Y. Wang, H. -Z. Sun, H. Yue, X. -H. wang, J. -L. Tan, Y. Wang, D. Hou, X. -Y. He, K. -C. Mun, B. P. Kumar, H. Zuo, D. -S. Shin, *Bull. Korean Chem. Soc.,* 2013, **34**, 394-398.

[3] C. Salome, P. Wagner, M. Bollenbach, F. Bihel, J. J. Bourguignon, M. Schmitt, *Tetrahedron,* 2014, **70**, 3413-3421.

[4] S. Blanchard, I. Grig-Alexa, O. -I. Patriciu, A. Fînaru, G. Guillaumet, *St. Cerc. St. CICBIA.,* 2010, **11**, 45-65.

[5] T. Wang, K. Xu, L. Liu, H. Xie, Y. Li, W. -X. Zhao, *Transition Met. Chem.,* 2016, **41**, 525-529.

[6] S. Roy, M. J. Sarma, B. Kashyap, P. Prodeep, *Chem. Commun.,* 2016, **52**, 1170-1173.

[7] T. B. Bach, A. A. Jensen, J. G. Peterson, T. E. Sorensen, S. D. Volpe, J. Liu, A. R. Blaazer, J. E. van Muilwijk-Koezen, T. Balle, B. Frolund, *Eur. J. Med. Chem.,* 2015, **102**, 425-444

[8] J. A. Forni, M. Brzozowski, J. Tsanaktsidis, G. P. Savage, A. Polyzos, *Aus. J. Chem.,* 2015, **68**, 1890-1893.