Imidazo[1,5-a]pyridine: A versatile architecture for stable N-heterocyclic carbenes

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SUPPORTING INFORMATION

General Experimental Procedures: Melting points were determined using a metal block and are uncorrected. Optical rotations were measured at room temperature. ^{1}H and ^{13}C-NMR spectra were obtained in $CDCl_3$, C_6D_6, or acetone-d_6 as the solvent. EI-mass spectra were recorded at 70 eV, using an ionizing current of 100 mA, an accelerating voltage of 4kV, and a resolution of 1000 or 10000 (10% valley definition). The reactions were monitored by TLC. Solvents were dried using standard techniques.

2,5-Dimethylimidazo[1,5-a]pyridinium iodide (2a): To a solution of **1** (600 mg, 4.6 mmol) in dry THF (2 mL) was added MeI (3.2 g, 23 mmol) and the mixture was stirred at 40 ºC for 24 h. The yellow precipitate formed was filtered, washed with dry Et_2O and dried *in vacuo* to afford **1** in 97% yield as a hygroscopic powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 8.13 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 9.3 Hz, 1H), 7.17 (dd, *J* = 6.9, 9.3 Hz, 1H), 6.88 (d, *J* = 6.9 Hz ,1H), 4.46 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.6, 130.7, 126.1, 126.0, 117.1, 116.2, 115.2, 38.7, 19.7. Anal. Calcd for $C_9H_{11}N_2I$ (%): C 39.44; H 4.04; N 10.22, found: C 39.49; H 4.12; N 10.19.

2-Benzyl-5-methylimidazo[1,5-a]pyridinium bromide (2b): To a solution of **1** (1g, 7.6 mmol) in dry THF (5 mL) was added BnBr (5.2 g, 30.3 mmol) and the mixture was heated at 60 ºC overnight. The hygroscopic off-white precipitate formed was washed and dried *in vacuo* to give **2b** in 94% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ 11.24 (s, 1H), 8.07 (d, *J* = 1.4 Hz,1H), 7.69 (m, 2H), 7.50 (d, *J* = 9.3 Hz, 1H), 7.32 (m, 3H), 7.09 (dd, *J*

= 6.8, 9.3 Hz, 1H), 6.80 (d, *J* = 6.8 Hz, 1H), 6.01 (s, 2H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 130.4, 129.5, 129.4, 129.0, 128.4, 125.7, 125.4, 116.4, 115.8, 113.0, 54.1, 18.9. Anal. Calcd for $C_{15}H_{15}N_2Br$ (%): C 59.42; H 4.99; N 9.24, found: C 59.19; H 4.68; N 8.98.

2-Isopropyl-3-phenylimidazo[1,5-a]pyridinium iodide (10a): To a solution of 3-phenylimidazo[1,5-a]pyridine (980 mg, 5 mmol) in toluene (5 mL) was added isopropyl iodide (5.1 g. 30.0 mmol) and the mixture was heated at 60 ºC for 3 days. The hygroscopic off-white precipitate formed was filtered, washed with pentane, and dried *in vacuo* to afford **10a** in 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.95 (d, *J* = 9.6 Hz, 1H), 7.60-7.80 (m, 6H), 7.20 (dd, *J* = 9.2, 6.8 Hz, 1H), 7.05 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.70 (m, *J* = 6.8 Hz, 1H), 1.66 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2, 132.5, 131.0, 130.7, 130.3, 124.7, 121.5, 120.4, 119.7, 118.9, 111.9, 53.0, 23.8. Anal. Calcd for $C_{16}H_{17}N_2I$ (%): C 52.76; H 4.70; N 7.69, found: C 52.84; H 4.62; N 7.75.

General procedure for the direct synthesis of imidazo[1,5-a]pyridinium salts: To a solution of amide **5c-f** or *N*-mesityl, *N*-(pyridin-2-yl)methy benzamide (4 mmol) in toluene (10 mL) was added $POCl_3$ (410 µl, 4.4 mmol) and the mixture was stirred at 80º C overnight. Solvents were then removed *in vacuo* and residue was purified by column chromatography (95:5→90:10 DCM:MeOH) to afford salts **2** or **10b** as chlorides. Hexafluorophosphates were obtained by addition of a saturated solution of KPF_6 (1.1 eq.) in water to solutions of the chlorides in the minimum amount of water. The white precipitates formed were filtered, washed with Et_2O and crystallised from acetone- Et_2O.

2-Benzylimidazo[1,5-a]pyridinium chloride (2c): 50% yield. ^{1}H NMR (300 MHz, CD_3OD) δ 9.52 (s, 1H), 8.45 (d, *J* = 6.6 Hz, 1H), 8.10 (s, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.45-7.55 (m, 5H), 7.22-7.28 (m, 1H), 7.15 (t, *J* = 6.6 Hz, 1H), 5.72 (s, 2H); ^{13}C NMR (75 MHz, CD_3OD) δ 129.5, 129.4, 128.9, 125.1, 125.0, 124.0, 118.2, 118.0, 113.3, 54.1. Anal. Calcd for $C_{14}H_{13}ClN_2$: C 68.71; H 5.35; N11.45. Found C 68.45; H 5.67; N 11.67.

2-Benzylimidazo[1,5-a]quinolinium chloride [2d(Cl)]: 59% yield. ^{1}H NMR (300 MHz, CD_3OD) δ 10.45 (s, 1H), 8.26-8.42 (m, 1H), 8.02-8.15 (m, 1H), 7.35-7.95 (m, 10H), 5.75 (br s, 2H); ^{13}C NMR (75 MHz, CD_3OD) δ 134.0, 130.5, 129.8, 129.4, 129.3, 128.8, 127.1, 124.8, 116.4, 115.3, 114.7, 54.3. Anal. Calcd for $C_{18}H_{15}N_2Cl$ (%): C 73.34; H 5.13; N 9.50; found: C 72.94; H 4.86; N 9.23.

2-Benzylimidazo[1,5-a]quinolinium hexafluorophosphate [2d(PF_6)]: 58% yield; m.p. 144-146 ºC. ^{1}H NMR (300 MHz, acetone-d_6) δ 10.45 (s, 1H), 8.46 (d, *J* = 8.2 Hz, 1H), 8.25 (s, 1H), 8.05 (d, *J* = 7.1 Hz,1H), 7.95-7.56 (m, 6H), 7.43 (br s, 3H), 5.89 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 131.3, 130.7, 130.4, 130.3, 130.2, 130.1, 129.7, 128.4, 127.8, 125.5, 117.3, 116.3, 115.9, 55.0. Anal. Calcd for $C_{18}H_{15}N_2F_6P$ (%): C 53.47; H 3.74; N 6.93, found: C 59.19; H 4.68; N 8.98.

2-Mesityl-5-methylimidazo[1,5-a]pyridinium hexafluorophosphate (2e): 52 % yield; m.p. 218-219 ºC. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.80 (s, 1H), 8.34 (d, *J* = 1.5 Hz, 1H), 7.94 (s, 1H), 7.45 (dd, *J* = 9.3, 6.9Hz, 1H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.19 (s, 2H), 2.86 (s, 3H), 2.39 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6) δ 142.1, 135.5, 134.8, 132.6, 132.3, 130.3, 126.9, 126.0, 117.9, 117.1, 116.1, 21.0, 17.9, 17.2. Anal. Calcd for $C_{17}H_{19}N_2F_6P$ (%): C 51.52; H 4.83; N 7.07 found: C 51.43; H 4.38; N 7.01.

2-*t*-Butylimidazo[1,5-a]pyridinium hexafluorophosphate (2f): 48% yield. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.69 (s, 1H), 8.52 (d, *J* = 7.2 Hz, 1H), 8.39 (s, 1H), 7.84 (d, *J* = 9.3 Hz, 1H), 7.33 (t, *J* = 6.6 Hz, 1H), 7.25 (t, *J* = 6.9 Hz, 1H), 1.87 (s, 9H). ^{13}C NMR (75 MHz, acetone-d_6) δ 131.1, 125.7, 125.5, 124.9, 119.1, 118.6, 112.1, 62.3, 29.9. Anal. Calcd for $C_{11}H_{15}N_2F_6P$ (%): C 41.26; H 4.72; N 8.75, found: C 41.31; H 4.28; N 8.50

2-Mesityl-3-phenylimidazo[1,5-a]pyridinium chloride (10b): This product was prepared following the general procedure but heating was prolonged for 7 days. Very hygroscopic yellow foam. 58% yield. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.51 (s, 1H), 8.47 (d, *J* = 6.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.61 (m, 3H), 7.47 (t, *J* = 6.8 Hz, 1H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.06 (s, 2H), 2.29 (s, 3H), 2.06 (s, 6H); ^{13}C

NMR (100 MHz, acetone-d_6) δ 142.0, 135.7, 135.3, 133.4, 131.9, 1301.6, 131.0, 130.6, 130.5, 126.6, 124.2, 122.1, 120.0, 119.7, 116.4, 21.0, 17.8. Anal. Calcd for $C_{22}H_{21}N_2Cl$ (%): C 75.74; H 6.07; N 8.03, found: C 76.01; H 6.31; N 7.87.

General procedure for the synthesis of carbenes 4: Inside a dry box, a schlenk flask equipped with a magnetic stir bar was charged with **2** (1 mmol), NaH (29 mg, 1.1 mmol) and a catalytic amount of KO^{t}Bu. Dry THF (5 mL) was added and the resulting pink-orange mixture was stirred for 2 hours at r.t. Then the solvent was evaporated *in vacuo* and dry toluene (10 mL) was added *via* syringe. The mixture was then filtered through a celite plug and washed again with toluene (10 mL). Combined filtrates were evaporated *in vacuo* to afford crude free carbenes **4** as syrups. These compounds were used without further purification.

2,5-Dimethylimidazo[1,5-a]pyridine-3-ylidene (4a): ^{1}H NMR (500 MHz, C_6D_6) δ 6.87 (d, *J* = 9.5 Hz, 1H), 6.59 (s, 1H), 6.34 (dd, *J* = 6.5, 9.5 Hz, 1H), 5.86 (d, *J* = 6.5 Hz, 1H), 3.60 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (125MHz, C_6D_6) δ 206.9, 139.6, 131.5, 121.1, 114.5, 110.1, 108.9, 38.4, 19.8.

2-Benzyl-5-methylimidazo[1,5-a]pyridine-3-ylidene (4b): ^{1}H NMR (300 MHz, C_6D_6) δ 7.16-6.98 (m, 5H), 6.80 (d, *J* = 9.9 Hz, 1H), 6.64 (s, 1H), 6.31 (dd, *J* = 6.6, 9.0 Hz, 1H), 5.85 (d, *J* = 6.3 Hz, 1H), 5.28 (s, 2H), 2.77 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ 206.2, 139.7, 138.4, 131.8, 128.4, 127.8, 127.4, 121.2, 114.8, 109.3, 109.1, 55.9, 19.8.

2-Mesyl-5-methyl imidazo[1,5-a]pyridine-3-ylidene (4e): ^{1}H NMR (300 MHz, C_6D_6) δ 6.90 (d, *J* = 9.0 Hz, 1H), 6.76 (s, 2H) 6.68 (s, 1H), 6.35 (dd, *J* = 6.6, 9.3 Hz, 1H), 5.89 (d, *J* = 6.2 Hz, 1H), 2.71 (s, 3H), 2.12 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 206.9, 140.0, 139.0, 137.2, 134.7 131.2, 128.7, 121.4, 115.0, 111.1, 109.5, 20.6, 19,7, 17.4.

2-Benzylimidazo[1,5-a]quinoline-3-ylidene (4d): ^{1}H NMR (500 MHz, C_6 D_6) δ 9.44 (d, *J* = 8.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* =6.5 Hz, 2H), 7.09 (d, *J* = 7.0 Hz, 2H),

7.05-6.98 (m, 4H), 6.61 (d, *J* = 9.5 Hz, 1H), 5.56 (d, *J* = 9.5 Hz, 1H), 6.48 (s, 1H), 5.25 (s, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ 208.7, 138.3, 137.3, 136.5, 129.7, 128.8, 128.5, 127.5, 124.7, 123.8, 122.9, 117.6, 115.7, 111.7, 55.8.

General procedure for the synthesis of complexes 5 and 11: To a solution of **2a-c**, **2d(Cl)**, or **10a** (3 mmol) in CH_2Cl_2 (50 mL) was added solid Ag_2O (370.7 mg, 1.6 mmol) and the mixture was stirred in darkness at r.t. during two hours. The solution was then filtered through a celite plug and the filtrate was evaporated *in vacuo***.**

Iodo(2,5-dimethylimidazo[1,5-a]pyridine-3-ylidene)silver (I) (5a): Folowing the general procedure but using 300 ml of DCM. White solid, 63% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.31 (d, *J* = 9.2 Hz,1H), 6.83 (dd, *J* = 5.8, 9.3 Hz, 1H), 6.47 (d, *J* = 5.8 Hz, 1H), 4.30 (s, 3H), 3.01 (s, 3H). Anal. Calcd for $C_9H_{10}N_2AgI$ (%): C 28.30; H 2.90; N 7.33, found: C 27.94; H 2.65; N 6.98. No further characterization was done due to the poor solubility of **5a** in all common organic solvents.

Bromo(2-benzyl-5-methylimidazo[1,5-a]pyridine-3-ylidene)silver (I) (5b): Off white solid, 92% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45-7.25 (m, 7H), 6.78 (dd, *J* = 6.7, 9.3 Hz, 1H), 6.53 (dt, *J* = 1.1, 6.7 Hz, 1H), 5.64 (s, 2H), 3.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 135.2, 132.9, 129.2, 128.9, 128.1, 123.1, 115.9, 114.3, 111.7, 58.0, 21.7, Carbene carbon signal not found. Anal. Calcd for $C_{15}H_{14}N_2AgBr$ (%): C 43.83; H 3.68; N 6.81, found: C 44.09; H 3.84; N 6.97.

Chloro(2-benzylimidazo[1,5-a]quinoline-3-ylidene)silver (I) (5d): White foam, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.48 (dt, *J* =7.6, 1.6 Hz, 1H), 7.41 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.32-7.28 (m, 6H), 7.10 (s, 2H), 5.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 135.1, 133.2, 131.0, 129.6, 129.3, 129.0, 128.1, 127.1, 125.3, 124.6, 116.1, 115.1, 113.7, 58.2. Anal. Calcd for $C_{18}H_{14}N_2AgCl$ (%): C 53.83; H 3.51; N 6.97, found: C 54.15; H 3.76; N 7.12.

(2-Benzylimidazo[1,5-a]pyridine-3-ylidene) chloro silver (I) (5c): White foam, 98% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.2, 0.9 Hz, 1H,.), 7.40-7.20 (m, 6H), 6.86 (dd, *J* =8.7, 2.4 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 5.50 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 135.4, 131.9, 129.5, 129.2, 128.7, 128.3, 123.7, 117.7, 114.5, 111.2, 57.3. Anal. Calcd for $C_{14}H_{12}N_2AgCl$ (%): C 47.83; H 3.44; N 7.97, found: C 47.98; H 3.77; N 7.66.

Iodo(2-Isopropyl-3-phenylimidazo[1,5-a]pyridine-1-ylidene)silver (I) (11): White foam, 89% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.79 (d, *J* = 9.5 Hz, 1H), 7.73 (m, 3H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.50 (m, 2H), 6.88 (dd, *J* = 9.0, 6.5 Hz, 1H), 6.80 (t, *J* = 6.0 Hz, 1H), 4.76 (sep, *J* = 6.5 Hz, 1H), 1.76 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 150.8, 137.5, 133.5, 132.1, 130.7, 130.5, 125.5, 123.9, 121.1, 119.9, 117.9, 52.0, 24.7. Anal. Calcd for $C_{16}H_{16}N_2AgI$ (%): C 40.79; H 3.42; N 5.95, found: C 41.04; H 3.34; N 5.69.

General procedure for the synthesis of complexes 6 and 12 by transmetallation from silver carbenes: To a solution of **5** or **11** (1 mmol) in CH_2Cl_2 (20 mL) was added $[RhCl(COD)]_2$ (246 mg, 0.5 mmol) and the mixture was stirred during three hours. The reaction mixture was then filtered through a celite plug and concentrated to afford **6**. as a yellow solid that was purified by crystallization from CH_2Cl_2-Et_2O (**6a**, **6b**, and **6e)** or by column chromatography (1:2 AcOEt-Hexane) (**6f** and **12**).

Chloro(1,5-cyclooctadiene)(2,5-dimethylimidazo[1,5-a]pyridine-3-ylidene)rhodium (I) (6a) 91% yield. m.p. 156-157 ºC (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.04 (d, *J* = 9.2 Hz, 1H), 6.63 (dd, *J* = 6.5, 9.2 Hz, 1H), 6.30 (dt, *J* = 1.0, 6.5 Hz, 1H), 5.07 (m, 2H), 4.58 (s, 3H), 3.78 (s, 3H), 3.18 (m, 2H), 2.60-2.30 (m, 4H), 2.07-1.73 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.3 (d, $J_{C\text{-}Rh}$ = 51 Hz), 137.8, 133.9, 122.2, 115.7, 113.0, 112.9, 97.6 (d, $J_{C\text{-}Rh}$ = 7.5 Hz), 95.9 (d, $J_{C\text{-}Rh}$ = 7.5 Hz), 69.9 (d, $J_{C\text{-}Rh}$ = 15 Hz), 68.0 (d, $J_{C\text{-}Rh}$ = 15 Hz), 40.8, 33.7, 32,7, 29.7, 29.1, 24.0. Anal. Calcd for $C_{17}H_{22}N_2RhCl$ (%): C 51.99; H 5.65; N 7.13, found: C 51.87; H 5.83; N 7.21.

(2-Benzyl-5-methylimidazo[1,5-a]pyridine-3-ylidene)chloro(1,5-cyclooctadiene)rhodium (I) (6b) 96% yield. m.p. 177-178 ºC (dec). This procedure invariably affords complex **6b** contaminated with a 15% of the bromide analogue **(6bBr):** The mixture was transformed in **6bBr** by addition of NaBr to a solution of **6b** in $CHCl_3$. **6b** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.38 (m, 3H), 7.00 (s, 1H), 6.98 (d, *J* = 9.2 Hz, 1H), 6.75 (d, *J* =14.6 Hz, 1H), 6.61 (dd, *J* = 6.5, 9.2 Hz, 1H), 6.31 (d, *J* = 6.5 Hz, 1H), 6.11 (d, *J* = 14.6 Hz,1H). 5.11 (br s, 2H), 3.84 (s, 3H), 3.28 (br s, 2H), 2.50-2.25 (m, 4H), 2.07-1.70 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.7 (d, $J_{C\text{-}Rh}$ = 50.2 Hz), 138.0, 136.6, 134.2, 129.4, 129.1, 128.8, 122.4, 116.0, 113.1, 111.4, 97.9 (d, $J_{C\text{-}Rh}$ = 7.5 Hz), 96.0 (d, $J_{C\text{-}Rh}$ = 7.5 Hz), 70.2 (d, $J_{C\text{-}Rh}$ = 15 Hz), 68.3 (d, $J_{C\text{-}Rh}$ = 15 Hz), 57.8, 33.5, 32,8, 29.7, 29.2, 23.9; **6bBr** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.36 (m, 3H), 6.98 (s, 1H), 6.95 (d, *J* = 9.2 Hz, 1H), 6.66 (d, *J* =14.6 Hz, 1H), 6.61 (dd, *J* = 6.5, 9.2 Hz, 1H), 6.30 (d, *J* = 6.5 Hz, 1H), 6.07 (d, *J* = 14.6 Hz, 1H), 5.19 (br s, 2H), 3.81 (s, 3H), 3.37 (m, 2H), 2.60-2.28 (m, 4H), 2.09-1.94 (m, 1H), 1.90-1.73 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.4 (d, $J_{C\text{-}Rh}$ = 50.0 Hz), 137.9, 136.5, 134.3, 129.4, 129.2, 128.8, 122.3, 116.0, 113.1, 111.6, 97.2 (d, $J_{C\text{-}Rh}$ = 7.0 Hz), 95.6 (d, $J_{C\text{-}Rh}$ = 7.0 Hz), 70.2 (d, $J_{C\text{-}Rh}$ = 15 Hz), 69.2 (d, $J_{C\text{-}Rh}$ = 15 Hz), 57.7, 33.6, 32,4, 30.1, 29.2, 23.8. Anal. Calcd for $C_{23}H_{22}N_2RhBr$ (%): C 53.82; H 5.11; N 5.46, found: C 53.80; H 5.42; N 5.32.

(2-Benzylimidazo[1,5-a]quinoline-3-ylidene)chloro(1,5-cyclooctadiene)rhodium (I) (6d): 92% yield. m.p. 243-245 ºC (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.56 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 8.4 Hz,1H), 7.62-7.30 (m, 5H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.92 (s, 1H), 6.56 (d, *J* = 14.7 Hz, 1H), 6.17 (d, *J* = 14.7 Hz, 1H), 5.30 (m, 1H). 5.18 (m, 1H), 3.29 (m, 1H), 3.18 (m, 1H), 2.55 (m, 1H), 2.50-2.20 (m, 3H), 2.10-1.75 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4 (d, $J_{C\text{-}Rh}$ = 63.7 Hz), 136.3, 134.6, 131.8, 129.3, 129.0, 128.8, 128.7, 128.4, 126.4, 125.1, 124.5, 121.1, 115.6, 113.3, 98.8 (d, $J_{C\text{-}Rh}$ = 7.3 Hz), 97.2 (d, $J_{C\text{-}Rh}$ = 7.2 Hz), 70.7 (d, $J_{C\text{-}Rh}$ = 14.5 Hz), 69.4 (d, $J_{C\text{-}Rh}$ = 14.7 Hz), 57.9, 33.0, 32,9, 29.5, 29.3. Anal. Calcd for $C_{26}H_{26}N_2RhCl$ (%): C 61.85; H 5.19; N 5.55, found: C 61.76; H 5.23; N 5.43.

(2-Benzylimidazo[1,5-a]pyridine-3-ylidene)chloro(1,5-cyclooctadiene)rhodium (I) (6c): 96% yield. m.p. 178-179 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.40-7.26 (m, 5H), 7.04 (d, *J* = 9.6 Hz, 1H), 6.95 (s, 1H), 6.70 (dd, *J* = 6.4, 0.8 Hz, 1H), 6.52 (dt, *J* = 6.4, 0.8 Hz, 1H), 6.02 (d, *J* = 14.8 Hz, 1H), 5.94 (d, *J* = 14.8 Hz, 1H), 5.13 (m, 1H) 3.35 (m, 1H), 3.25 (m, 1H), 2.60-2.33 (m, 3H), 2.25 (m. 1H), 1.97 (m, 3H), 1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7 (d, $J_{C\text{-}Rh}$ = 52.7 Hz), 136.2, 131.7, 129.0, 128.6, 128.5, 128.4, 122.3, 117.4, 112.4, 110.7, 99.94 (d, $J_{C\text{-}Rh}$ = 4.8 Hz), 68.8 (d, $J_{C\text{-}Rh}$ = 14.2 Hz), 68.6 (d, $J_{C\text{-}Rh}$ = 14.4 Hz), 55.9, 33.2, 32,9, 29.0, 28.9. Anal. Calcd for $C_{22}H_{24}N_2RhCl$ (%): C 58.10; H 5.32; N 6.16, found: C 57.98; H 5.45; N 6.40.

Chloro(1,5-cyclooctadiene)(2-Isopropyl-3-phenylimidazo[1,5-a]pyridine-1-ylidene)iridium (I) (12): 38% yield, yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 1H), 7.70-7.55 (m, 3H), 7.42 (d, *J* = 6.0 Hz, 1H), 7.38 (d, *J* = 6.4 Hz, 1H), 7.20 (d, *J* = 5.2 Hz, 1H), 6.63-6.54 (m, 2H), 5.90 (sep, *J* = 6.8 Hz, 1H), 4.56 (m, 1H), 4.42 (m, 1H), 3.12 (m, 1H), 3.04 (m, 1H), 2.33 (m, 2H), 2.18 (m, 2H), 1.77 (m, 1H), 1.61 (m, 3H), 1.53 (d, *J* = 6.8 Hz, 3H), 1.49 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 131.8, 131.6, 131.5, 130.6, 129.9, 129.7, 125.9, 125.8, 119.7, 117.6, 116.3, 81.4, 81.0, 57.9, 53.3, 50,7, 34.5, 33.3, 30.3, 29.6, 23.9, 23.2. Anal. Calcd for $C_{24}H_{28}N_2RhCl$ (%): C 50.38; H 4.93; N 4.90, found: C 50.29; H 4.86; N 4.78.

General procedure for the direct synthesis of complexes (6): To a solution of carbene **4** (0.4 mL) in toluene (5 mL) was added $[Rh(cod)Cl]_2$ (93 mg, 0.19 mmol) and the mixture was stirred at room temperature for 2 h. Products **6** were isolated and purified as described above to afford **6a** (93%), **6b** (94%), or **6d** (91%).

General procedure for the synthesis of complexes 7: To a slurry of $[Rh(COD)Cl]_2$ (74 mg, 0.15 mmol) in THF (4 mL) was added solid KO^{t}Bu (68 mg, 0.6 mmol). The mixture was stirred for 5 min, and salt **2d(PF_6)**, **2e**, or **2f** was then added in one portion (0.6 mmol). The reaction mixture was stirred under argon overnight and the yellow-orange solid formed was filtered and washed with Et_2O (2 × 2 mL). Crystallization was performed by slow diffusion of Et_2O in a DCM solution of the complex.

Bis(2-benzylimidazo[1,5-a]quinoline-3-ylidene)(1,5-cyclooctadiene)rhodium (I) hexafluorophosphate (7d): 71% yield. m.p. 220-221 ºC (dec). ^{1}H NMR (400 MHz, acetone-d_6) δ 12.00 (d, *J* = 8.4 Hz, 2H), 7.92 (t, *J* = 6.8 Hz, 2H), 7.71 (d, *J* = 6.4 Hz, 2H), 7.64 (t, *J* = 6.8 Hz, 2H), 7.51 (s, 2H), 7.17 (d, *J* = 9.6 Hz, 2H), 7.11 (d, *J* = 9.6 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 4H), 6.25 (d, *J* = 7.2 Hz, 4H), 6.12 (d, *J* = 16 Hz, 2H), 5.68 (d, *J* = 16 Hz, 2H), 5.33 (t, *J* = 7.2 Hz, 2H), 3.88 (dd, *J* =14.8, 6.8 Hz, 2H), 3.22 (m, 2H), 2.55 (dd, *J* = 15.6, 6.4 Hz, 2H), 2.20 (m, 2H), 1.85 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6) δ 173.5 (d, *J* =54.4 Hz), 136.4, 134.6, 133.7, 130.0, 128.8, 128.1, 128.0, 127.6, 126.7, 125.9, 124.9, 121.8, 117.1, 116.8, 94.3 (d, *J* = 8.7 Hz), 87.1 (d, *J* = 7.6 Hz), 56.8, 35.6, 27.7. Anal. Calcd for $C_{44}H_{40}N_4RhF_6P$ (%): C 60.56; H 4.62; N 6.42, found C 60.41; H 4.48; N 6.26.

Bis(2-mesityl-5-methylimidazo[1,5-a]pyridine-3-ylidene)(1,5-cyclooctadiene)rhodium (I) hexafluorophosphate (7e): 72% yield. m.p. 152-153 ºC (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.8 Hz, 2H), 7.10 (s, 2H), 7.07 (s, 2H), 6.87 (dd, *J* = 8.8, 6.4 Hz, 2H), 6.38 (d, *J* = 6.4 Hz, 2H), 5.10 (t, *J* = 7.2 Hz, 2H), 3.60 (q, *J* = 7.9 Hz, 2H), 3.25 (s, 6H), 2.26 (s, 6H), 2.30 (m, 2H), 1.97 (m, 4H), 1.73 (s, 6H), 1.45 (m, 2H), 0.76 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7 (d, *J* = 53.9 Hz), 140.2, 138.6, 136.8, 135.2, 134.9, 134.8, 131.3, 129.7, 122.9, 116.6, 116.2, 115.2, 90.1 (d, *J* = 9.8 Hz), 82.9 (d, *J* = 7.8 Hz), 34.8, 27.0, 22.1, 21.4, 18.2, 17.2. Anal. Calcd for $C_{42}H_{48}N_4RhF_6P$(%): C 58.88; H 5.65; N 6.54, found: C 58.96; H 5.72; N 6.35.

Bis(2-*t*-butylimidazo[1,5-a]pyridine-3-ylidene)(1,5-cyclooctadiene)rhodium (I) hexafluorophosphate (7f): 84 % yield**.** m.p. 201-202 ºC. ^{1}H NMR (400 MHz, acetone-d_6) δ 9.62 (dd, *J* = 7.2, 0.8 Hz, 2H), 7.88 (s, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.03-6.96 (m, 6H), 4.82 (t, *J* = 7.2 Hz, 2H), 3.80 (q, J = 7.2 Hz, 2H), 2.98 (m, 2H), 2.48 (m, 2H), 2.28 (m, 2H), 1.87 (m, 2H), 1.57 (s, 18H). ^{13}C NMR (100 MHz, acetone-d_6) δ 167.2 (d, *J* =54.9 Hz), 132.3, 131.4, 122.7, 119.3 114.3, 93.6 (d, *J* = 8.8 Hz), 87.6 (d, *J* = 8.1 Hz), 60.2, 35.5, 31.2, 26.8. Anal. Calcd for $C_{30}H_{40}N_4RhF_6P$ (%): C 51.14; H 5.72; N 7.95, found: C 50.96; H 5.72; N 7.55.

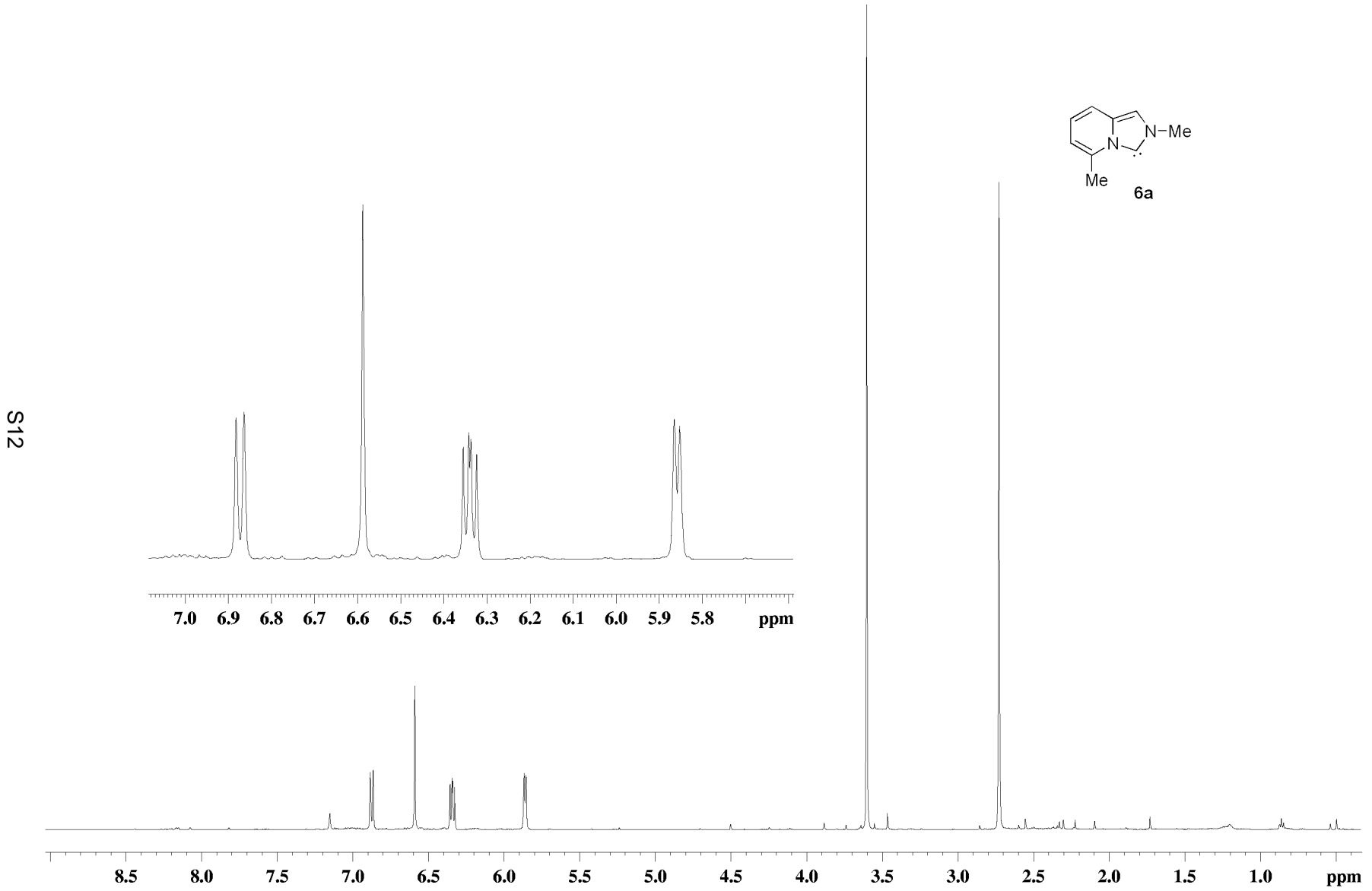
Chloro(1,5-cyclooctadiene)(2-mesityl-3-phenylimidazo[1,5-a]pyridine-1-ylidene)rhodium (I) (13): To a slurry of $[Rh(COD)Cl]_2$ (74 mg, 0.15 mmol) in dry THF (4 mL) was added solid $KN(SiMe_3)_2$ (60 mg, 0.3 mmol). The resulting solution was stirred for for 5 min, and salt **10b** (0.3 mmol) was then added in one portion. The reaction mixture was stirred under argon overnight, concentrated, and the yellow residue was purified by column chromatography(1:2 AcOEt-hexane) to afford **13** in 39% yield. Crystals suitable for X-ray diffraction may be grown by slow diffusion of pentane in a CH_2Cl_2 solution of the complex. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (m, 1H), 7.89 (m, 1H), 7.34 (m, 3H), 7.16 (m, 2H), 7.11 (br s, 1H), 6.76 (m, 2H), 6.67 (br s, 1H), 4.18 (br s, 2H), 3.58 (br s, 1H), 2.80 (br s, 1H), 2.60 (br s, 3H), 2.46 (br s, 1H), 2.31 (s, 3H), 2.18 (br s, 1H), 2.02 (br s, 1H), 1.87 (br s, 1H), 1.76 (br s, 1H), 1.67 (br s, 1H), 1.42 (br s, 3H) ^{13}C NMR (125MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}Rh}$ = 47.5 Hz), 138.8, 135.8, 134.1, 132.8, 130.1, 129.3, 128.7, 128.6, 128.1, 124.1, 119.7, 118.8, 117.2, 95.2 (br s), 69.4 (br s), 65.9 (br s), 34.5 (br s), 31.5 (br s), 29.7 (br s), 28.0, 21.1, 20.9 (br s), 17.8 (br s). Anal. Calcd for $C_{30}H_{32}N_2RhCl$ (%): C 64.46; H 5.77; N 5.01, found C 64.32; H 5.89; N 4.93.

Seleno lactame (15): KHMDS (100 mg, 0.5 mmol) and Se powder (80 mg, 1mmol) were added in one portion to a suspension of **10b** (174 mg, 0.5 mmol) in THF (4 mL). After stirring for two days, the mixture was concentrated and the residue was purified by column chromatography (3:1 AcOEt/hexane) to afford **15** in 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz,1H), 7.98 (d, *J* = 5.7 Hz, 1H), 7.52 (m, 3H), 7.39 (m, 2H), 6.93 (s, 2H), 6.70 (m, 2H), 2.30 (s, 3H), 1.99 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 139.8, 135.7, 132.1, 131.8, 131.1, 130.9, 129.6, 129.0, 128.8, 124.3, 123.3, 119.9, 119.8, 118.1, 21.3, 18.6. HRMS: *m/z* calculated for $C_{22}H_{20}N_2Se$ 392.0792, found 392.0781.

Chlorodicarbonyl(2,5-dimethylimidazo[1,5-a]pyridine-3-ylidene)rhodium (I) (16): A schlenk flask was charged with **6a** (197 mg, 0.5 mmol) and dry THF (6 mL). CO was bubled for 10 min and the solvent was evaporated *in vacuo*. The remaining oil was washed with hexane and dried to afford **16** in quantitative yield. ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.37 (s, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.77 (dd, *J* = 6.6, 9.0 Hz, 1H), 6.41 (dt, *J* = 0.9, 6.2 Hz, 1H), 4.30 (d, J = 0.6 Hz, 3H), 3.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.6 (d, J_{CO-Rh} = 33.0 Hz) , 182.4 (d, J_{CO-Rh} = 44.7 Hz), 136.7, 133.6, 128.7, 122.8, 115.5, 113.9, 113.6, 41.1, 24.5; FTIR (CH_2Cl_2), ν_{CO} = 2079, 2000 cm^{-1}. HRMS: *m/z* calculated for $C_{11}H_{10}N_2O_2Rh$ 339.9486, found 339.9483.

Chlorodicarbonyl(2-mesityl-3-phenylimidazo[1,5-a]pyridine-1-ylidene)rhodium (I) (17): Starting from **13**, reaction with CO as above yielded **17** in quantitative yield as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (m, 1H), 7.94 (m, 1H), 7.42 (m, 3H), 7.24 (m, 3H), 6.88 (s, 2H), 6.84 (d, *J* = 1.2 Hz, 1H), 2.28 (s, 3H), 1.98 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.2 (d, J_{CO-Rh} = 52.6 Hz), 184.1 (br. s), 154.9 (d, J_{C-Rh} = 40.05), 139.8, 135.8, 134.9, 133.3, 131.2, 129.8, 129.6, 127.0, 123.8, 120.5, 119.3, 119.1, 21.4, 19.1 FTIR (CH_2Cl_2), ν_{CO} = 2072, 1992 cm^{-1}. Anal. Calcd for $C_{24}H_{20}N_2O_2RhCl$ (%): C 56.88; H 3.98; N 5.53, found C: 56.70; H: 4.08; N: 5.76 .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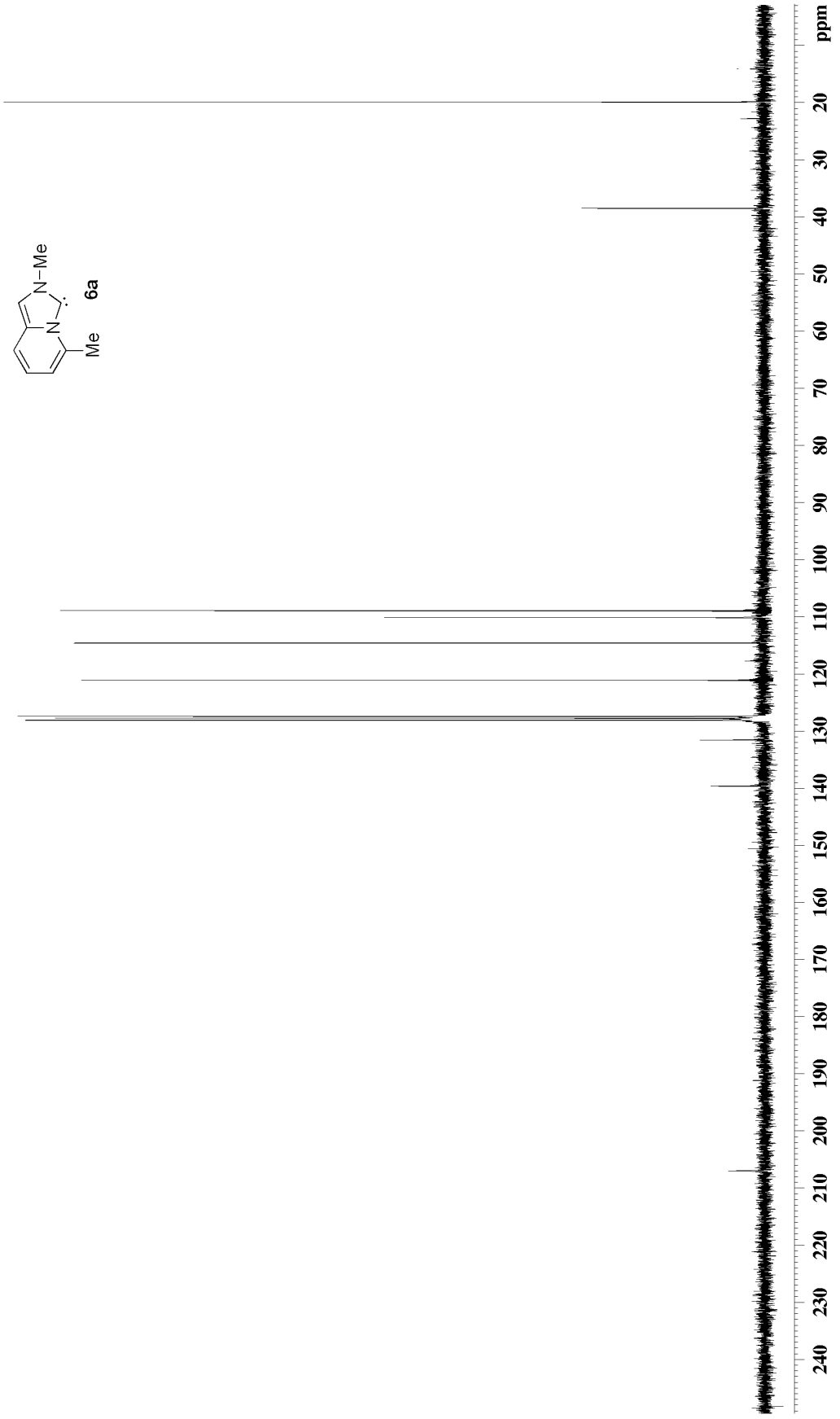
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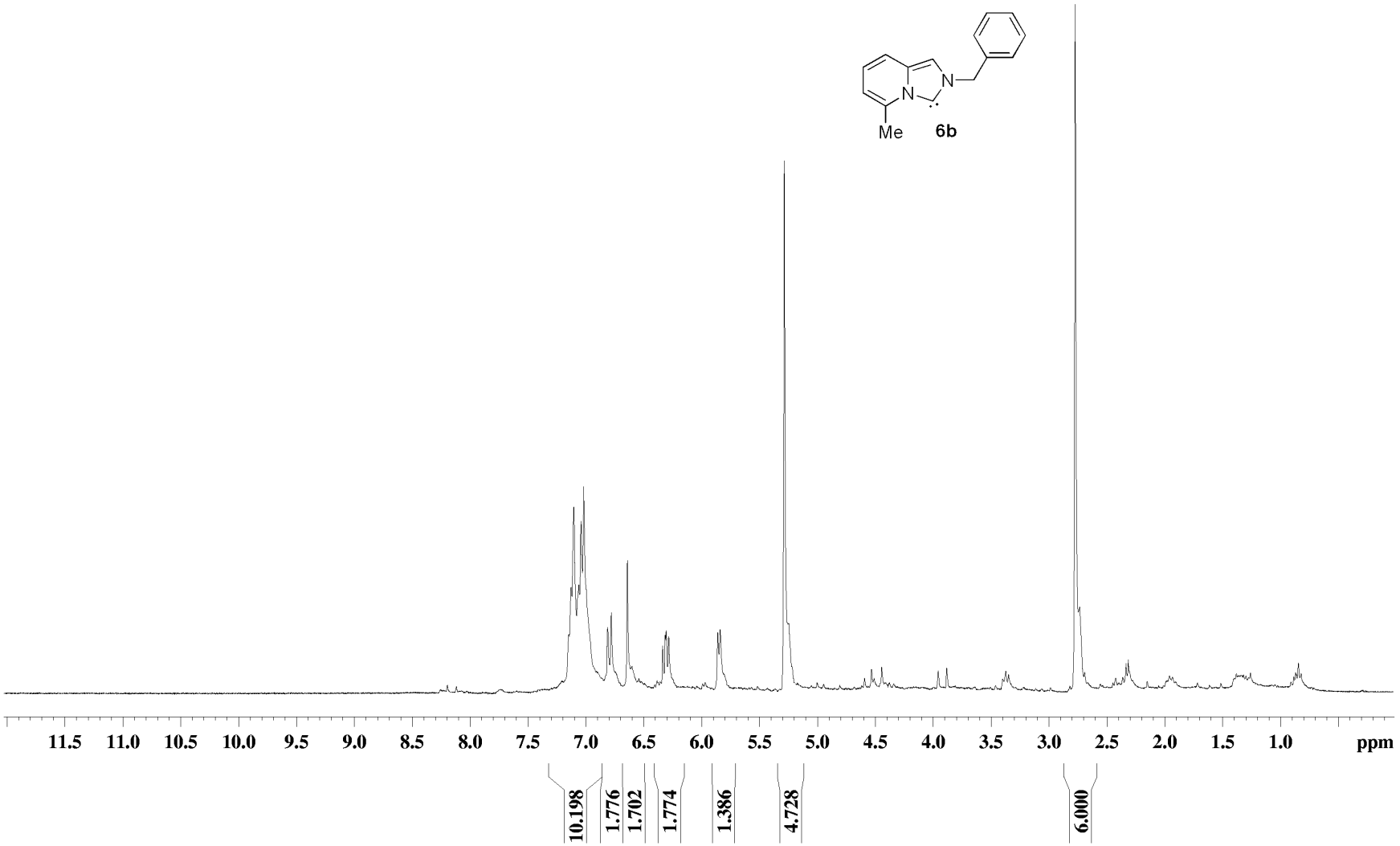
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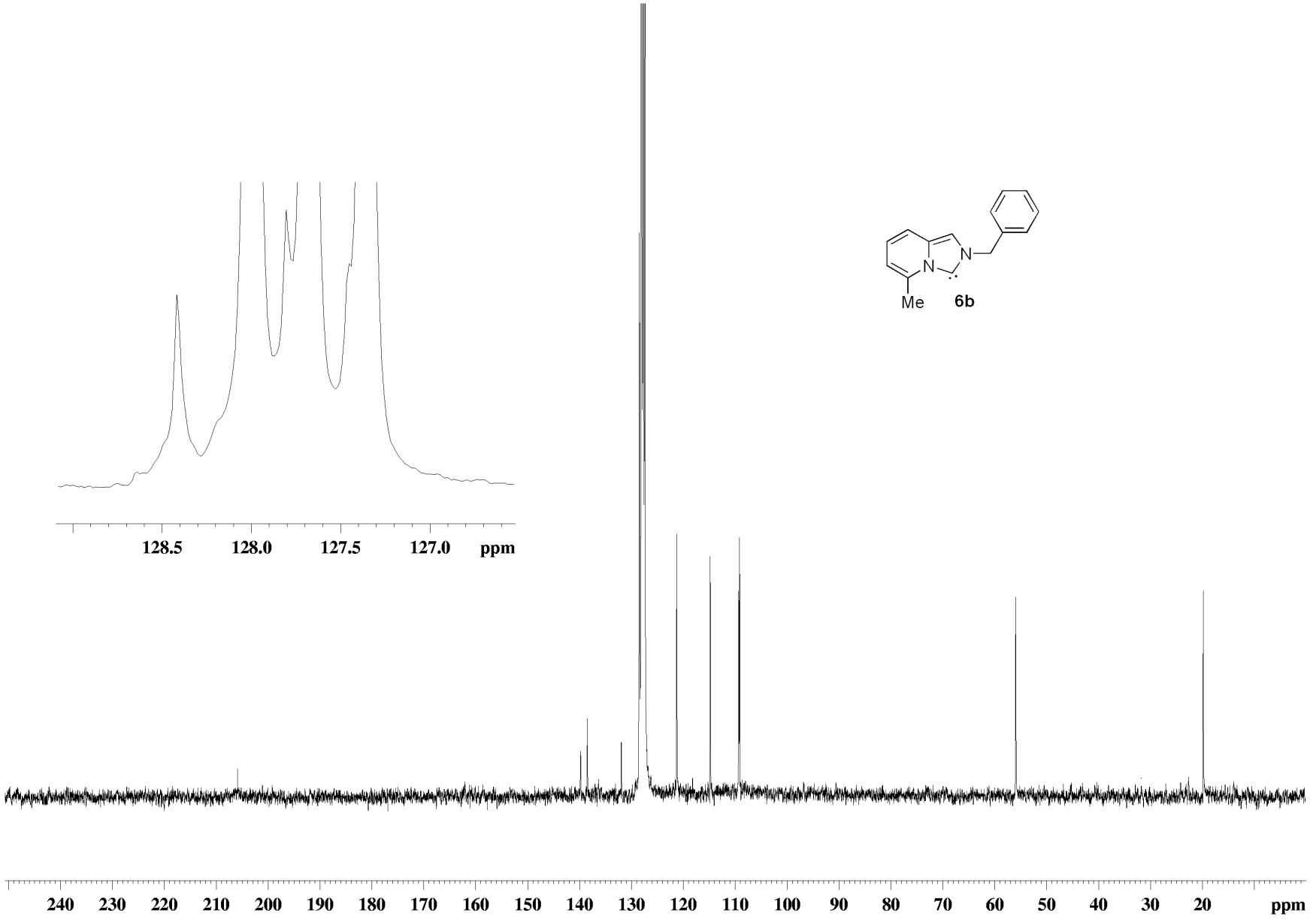
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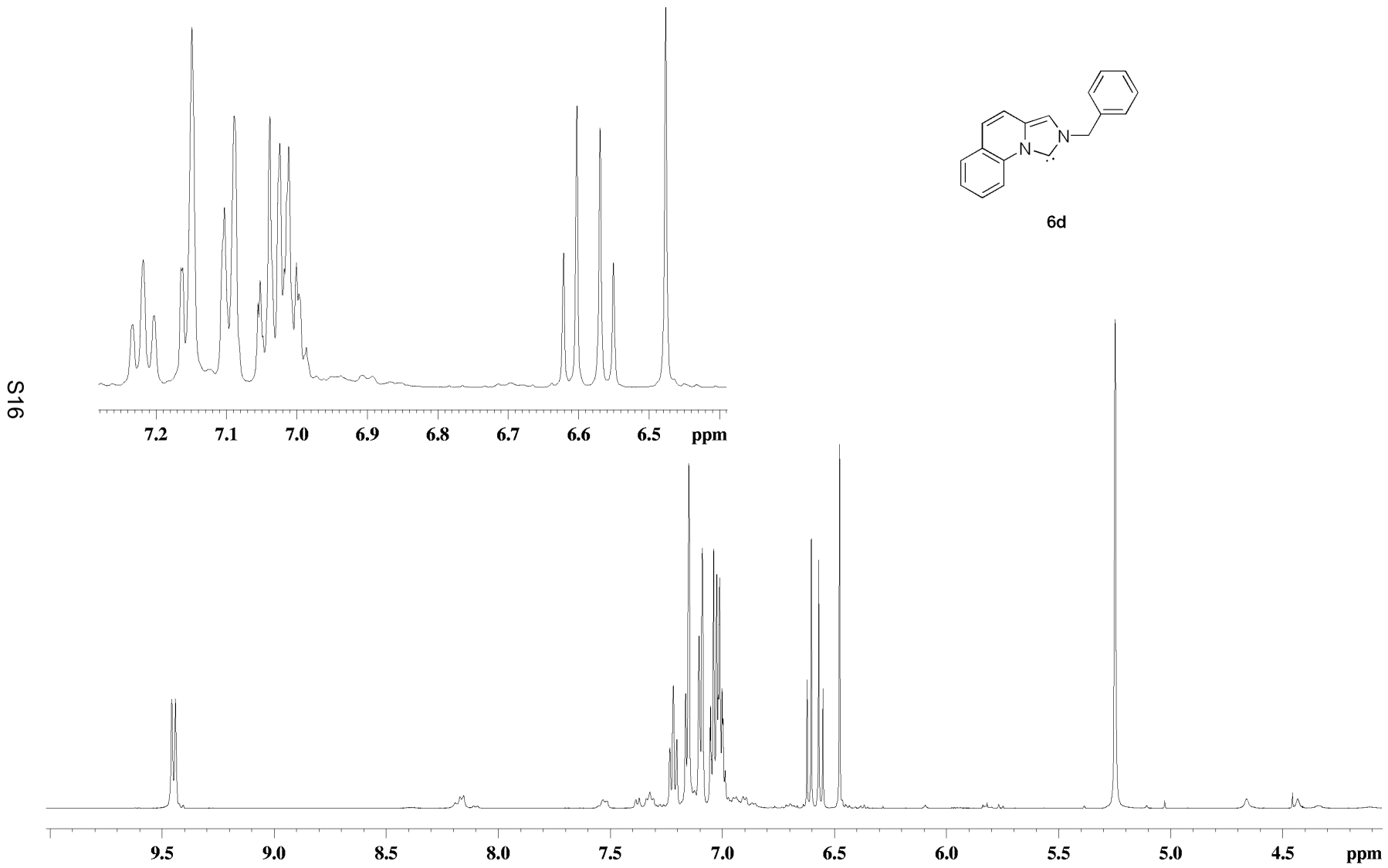
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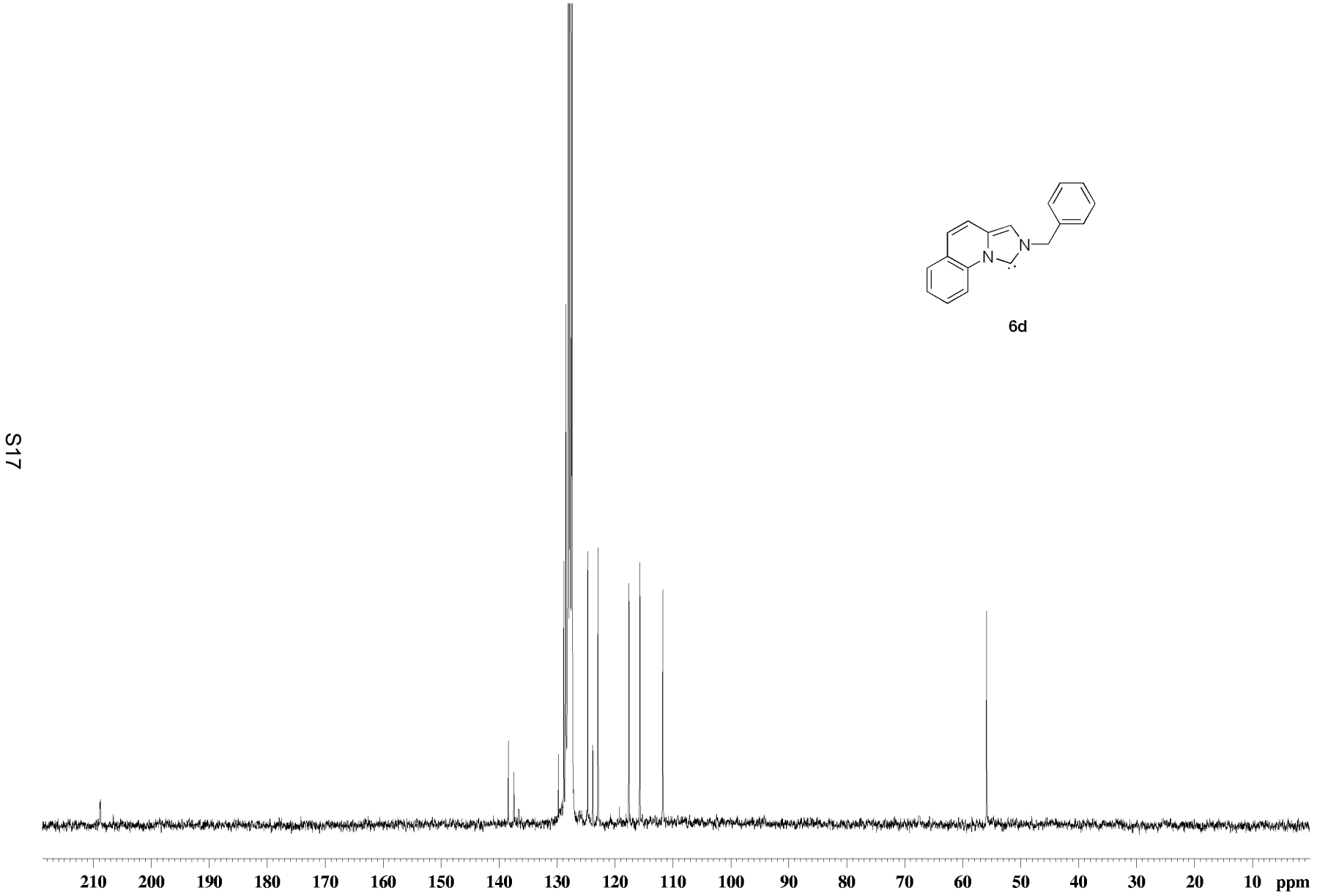
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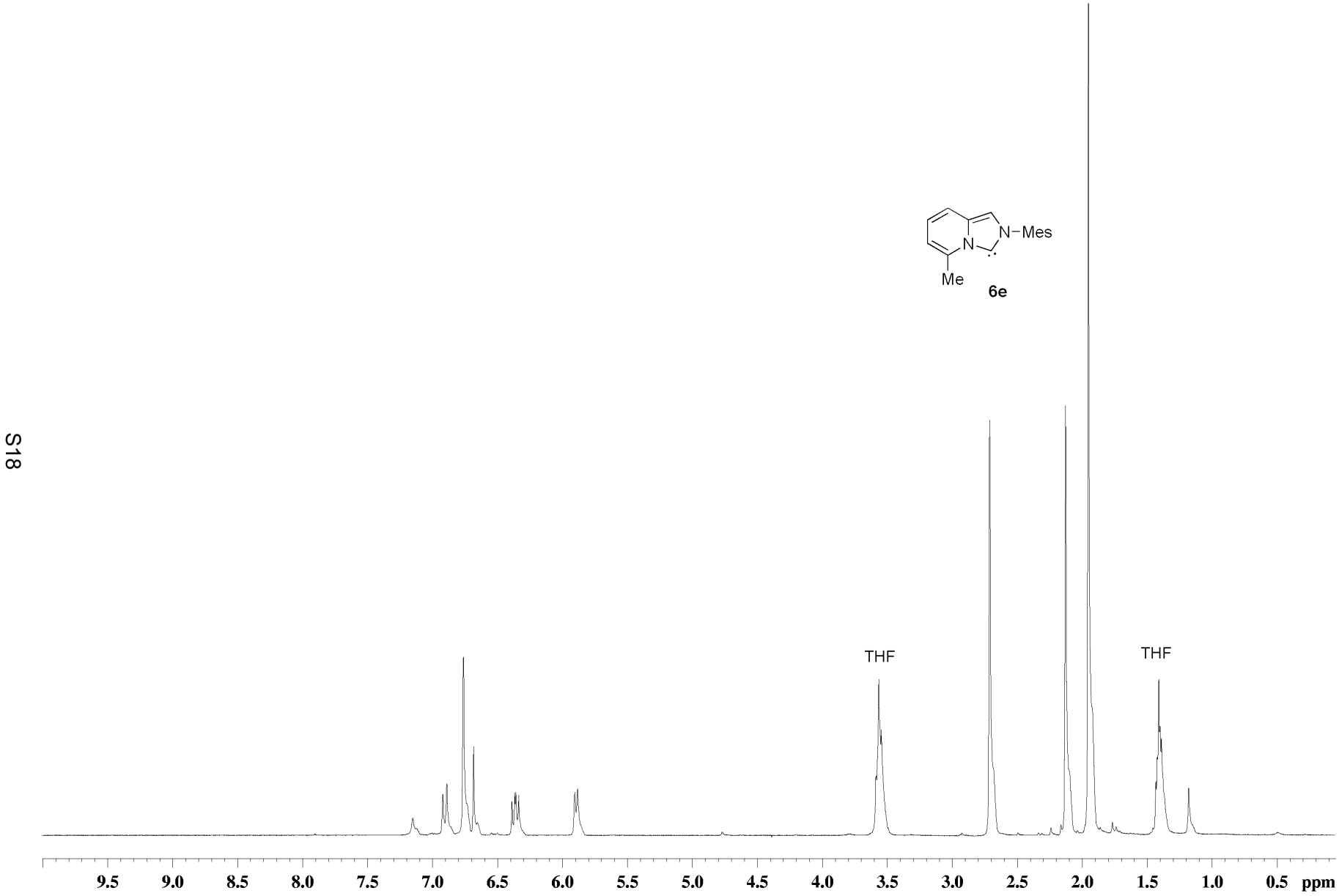
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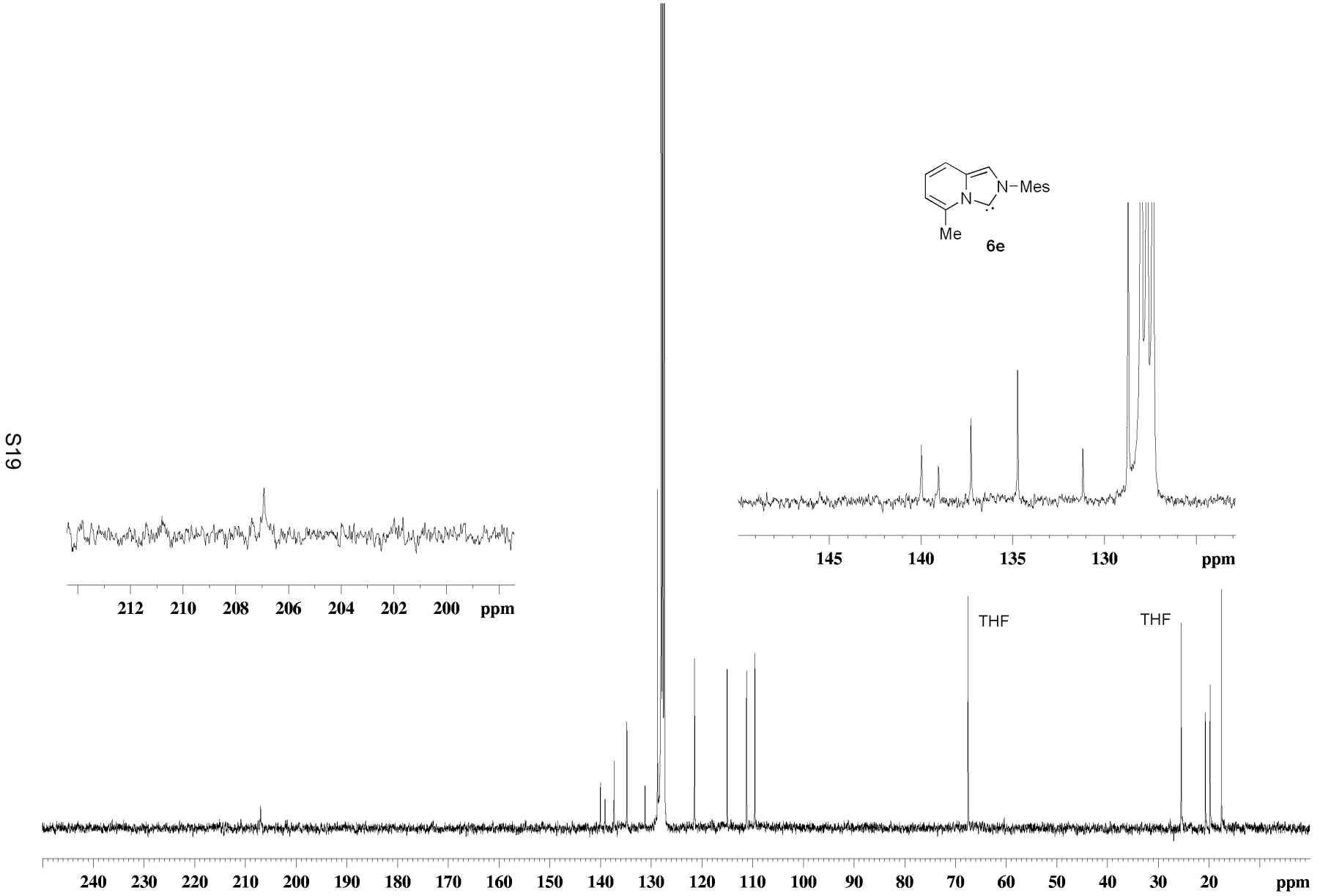
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