

## Supplemental Data

### Synthesis of 3-aryl-2-phosphinoimidazo[1,2-*a*]pyridine ligands for use in palladium-catalyzed cross-coupling reactions

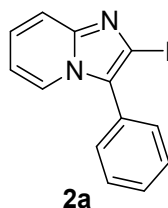
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#### General Considerations

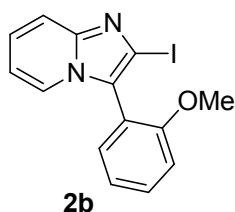
<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were obtained on a JEOL 500 MHz NMR at 500 MHz, 125 MHz, and 201 MHz, respectively, as solutions in CDCl<sub>3</sub> or in DMSO-*d*<sub>6</sub>. Chemical shifts were reported in parts per million (ppm, δ). TLC analyses were performed on Whatman flexible aluminum backed TLC plates with a fluorescent indicator. Detection was conducted by UV absorption (254 nm). High-purity grade silica gel (Merck Grade 7734), pore size 60 Å, 70-230 mesh was used for all chromatographic separations. All chemicals used for synthetic procedures were reagent grade or better. Solutions were concentrated *in vacuo* with a rotary evaporator and the residue was purified by column chromatography using silica gel.

#### Preparation of 2-iodo-3-arylimidazo[1,2-*a*]pyridines 2a–d:

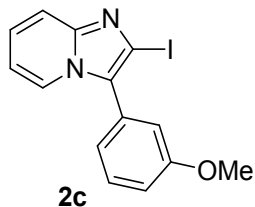


**2-Iodo-3-phenylimidazo[1,2-*a*]pyridine (2a):** A mixture of 2-aminopyridine (**1**, 200 mg, 2.13 mmol), phenylacetylene (217 mg, 2.13 mmol), iodine (540 mg, 2.13 mmol), and copper acetate monohydrate (43 mg, 0.213 mmol) in 1,2-dichlorobenzene (25 mL) was stirred overnight at 120

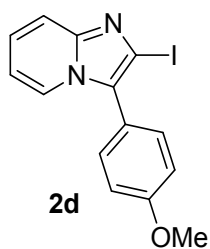
°C under a balloon of oxygen. The reaction was quenched with water and was extracted with dichloromethane (3 x 25 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and condensed *in vacuo*. Column chromatography was performed using acetone:dichloromethane (3:97) eluent system to yield a yellow solid (209 mg, 30%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.84 (dd, *J* = 27.3, 21.3 Hz, 1H), 7.38 (dd, *J* = 10.0, 5.1 Hz, 1H), 7.35 – 7.28 (m, 5H), 7.27 – 7.20 (m, 1H), 6.98 – 6.90 (m, 1H), 6.50 (td, *J* = 6.9, 1.1 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 147.0, 130.2, 129.3, 128.3, 127.2, 125.2, 123.3, 117.3, 113.1, 93.8.



**2-Iodo-3-(2-methoxyphenyl)imidazo[1,2-a]pyridine (2b):** 2-Aminopyridine (**1**, 1.00 g, 10.6 mmol), 2-ethynylanisole (1.40 g, 10.6 mmol), iodine (2.70 g, 10.6 mmol) and copper acetate monohydrate (212 mg, 1.06 mmol) were dissolved in 1,2-dichlorobenzene (100 mL). Septa was added and O<sub>2</sub> was bubbled into flask through two needles and was stirred at 120 °C overnight. The reaction was quenched with water (25 mL) and was extracted with dichloromethane (5 x 200 mL). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and condensed *in vacuo*. Column chromatography was performed using ethyl acetate:hexanes (2:1) to give a yellow solid (1.47 g, 39%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 6.9 Hz, 1H), 7.53 (dd, *J* = 5.5, 4.5 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.39 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.66 (td, *J* = 6.8, 1.1 Hz, 1H), 3.69 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.6, 147.0, 133.4, 131.3, 125.0, 124.8, 124.7, 121.1, 116.9, 116.8, 112.1, 111.5, 94.7, 55.6.

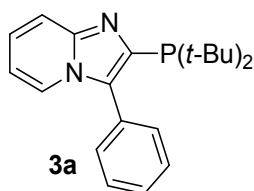


**2-Iodo-3(3-methoxyphenyl)imidazo[1,2-a]pyridine (2c):** A mixture of 2-aminopyridine (**1**, 1.00 g, 10.6 mmol), 3-methoxyphenylacetylene (1.41 g, 10.6 mmol), iodine (2.70 g, 10.6 mmol), and copper acetate monohydrate (213 mg, 1.06 mmol) in 1,2-dichlorobenzene (100 mL) was stirred overnight at 120 °C under a balloon of oxygen. The reaction was quenched with water and was extracted with dichloromethane (3 x 25 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and condensed *in vacuo*. Column chromatography was performed using hexanes:ethyl acetate (2:1) eluent system to yield a yellow solid (1.12 g, 30%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.90 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.98 – 6.92 (m, 1H), 6.91 – 6.86 (m, 2H), 6.83 – 6.78 (m, 1H), 6.53 (td, *J* = 6.9, 1.0 Hz, 1H), 3.66 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 160.1, 146.8, 132.4, 130.5, 129.4, 127.8, 125.0, 123.3, 117.0, 115.6, 114.6, 112.9, 93.9, 55.5.

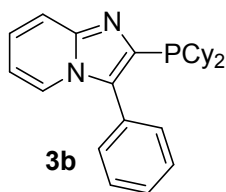


**2-Iodo-3(4-methoxyphenyl)imidazo[1,2-a]pyridine (2d):** A mixture of 2-aminopyridine (**1**, 400 mg, 4.25 mmol), 4-methoxyphenylacetylene (562 mg, 4.25 mmol), iodine (1.08 g, 4.25 mmol), and copper acetate monohydrate (86 mg, 0.425 mmol) in 1,2-dichlorobenzene (40 mL) was stirred overnight at 120 °C under a balloon of oxygen. The reaction was quenched with water and was extracted with dichloromethane (3 x 25 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and condensed *in vacuo*. Column chromatography was performed using

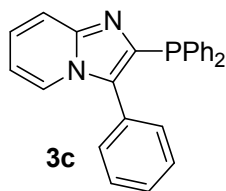
hexanes:ethyl acetate (2:1) eluent system to yield a yellow solid (634 mg, 43%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 6.9$  Hz, 1H), 7.50 (d,  $J = 9.1$  Hz, 1H), 7.38 – 7.34 (m, 2H), 7.07 (td,  $J = 8.8, 6.8, 0.9$  Hz, 1H), 6.99 (d,  $J = 8.7$  Hz, 2H), 6.65 (t,  $J = 6.9$  Hz, 1H), 3.84 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  160.2, 146.8, 131.6, 129.2, 127.0, 124.8, 123.2, 120.5, 114.8, 112.7, 93.9, 55.5.



**2-(Di-tert-butylphosphino)-3-phenylimidazo[1,2-a]pyridine (3a):** To a vial was added 2-iodo-3-phenylimidazo[1,2-a]pyridine (**2a**, 200 mg, 0.630 mmol),  $\text{Cs}_2\text{CO}_3$  (244 mg, 0.760 mmol), DIPPf (7 mg, 0.016 mmol), and  $\text{Pd}(\text{OAc})_2$  (3 mg, 0.0126 mmol) in 1,4-dioxane (4.0 mL) was purged with nitrogen. The reaction was capped and was stirred at room temperature for 1 h. The reaction was purged with nitrogen for 5 minutes and di-*tert*-butylphosphine (92 mg, 0.63 mmol) was added and was capped in a vial. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using hexanes:ethyl acetate (3:2) eluent was performed to give a reddish solid (89 mg, 41%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 6.9$  Hz, 1H), 7.52 – 7.41 (m, 5H), 7.16 – 7.11 (m, 1H), 6.73 – 6.64 (m, 1H), 1.24 (d,  $J = 11.9$  Hz, 18H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  145.4, 131.3, 129.0, 125.1, 124.3, 123.6, 118.1, 112.4, 111.7, 33.1, 30.7, 26.9.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.2.

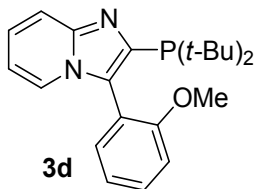


**2-(Dicyclohexylphosphino)-3-phenylimidazo[1,2-a]pyridine (3b):** To a vial was added 2-iodo-3-phenylimidazo[1,2-a]pyridine (**2a**, 114 mg, 0.356 mmol), Cs<sub>2</sub>CO<sub>3</sub> (139 mg, 0.427 mmol), DIPPF (4 mg, 0.0089 mmol), and Pd(OAc)<sub>2</sub> (2 mg, 0.00712 mmol) in 1,4-dioxane (2.0 mL) and was purged with nitrogen for five minutes. The reaction was capped and was stirred at room temperature for 1 h. The reaction was purged with nitrogen for 5 minutes and dicyclohexylphosphine (71 mg, 0.356 mmol) was added. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using ethyl acetate:dichloromethane (3:7) eluent was performed to give a white solid (70 mg, 50%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.99 (d, *J* = 7.0 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.40 (m, 5H), 7.19 – 7.13 (m, 1H), 6.69 (t, *J* = 6.6 Hz, 1H), 2.25 – 2.18 (m, 2H), 1.84 – 1.61 (m, 9H), 1.42 – 1.09 (m, 11H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.0, 147.0, 141.4, 140.4, 134.1, 133.6, 131.1, 128.9, 128.6, 124.5, 123.4, 118.0, 112.0, 33.9, 31.1, 29.6, 27.5, 26.3. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -22.8.

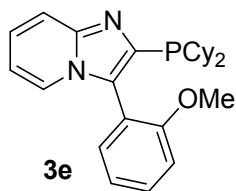


**2-(Diphenylphosphino)-3-phenylimidazo[1,2-a]pyridine (3c):** 2-Iodo-3-phenylimidazo[1,2-a]pyridine (**2a**, 132 mg, 0.410 mmol), Cs<sub>2</sub>CO<sub>3</sub> (159 mg, 0.492 mmol), DIPPF (4 mg, 0.0103 mmol), and Pd(OAc)<sub>2</sub> (2 mg, 0.0082 mmol) were dissolved in 1,4-dioxane (4.0 mL) in a vial while purging with nitrogen. The reaction was capped and was stirred at room temperature for 1 h. The reaction was purged with nitrogen for 5 minutes and diphenylphosphine (74 mg, 0.410 mmol) was added and was capped. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and washed with dichloromethane. The filtrate was condensed

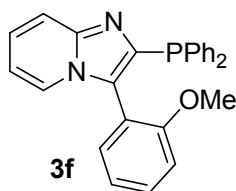
*in vacuo*. Column chromatography using acetone:dichloromethane (5:95) eluent was performed to give a white solid (95 mg, 61%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.07 (d, *J* = 6.9 Hz, 1H), 7.66 (d, *J* = 9.2 Hz, 1H), 7.55 – 7.45 (m, 10H), 7.32 – 7.25 (m, 5H), 7.17 (ddd, *J* = 9.2, 6.4, 1.2 Hz, 1H), 6.72 (td, *J* = 6.9, 1.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 146.7, 140.0, 137.8, 137.7, 133.9, 133.7, 130.7, 129.0, 128.9, 128.8, 128.4, 124.9, 123.7, 118.6, 112.4. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -28.8.



**2-(Di-tert-butylphosphino)-3-(2-methoxyphenyl)imidazo[1,2-a]pyridine (3d):** 2-Iodo-3-(2-methoxyphenyl)imidazo[1,2-*a*]pyridine (**2b**, 200 mg, 0.571 mmol), Cs<sub>2</sub>CO<sub>3</sub> (222 mg, 0.686 mmol), DIPPF (24 mg, 0.057 mmol), and Pd(OAc)<sub>2</sub> (6.5 mg, 0.029 mmol) were dissolved in 1,4-dioxane (3.0 mL) in a vial while purging with nitrogen. The reaction was capped and was stirred at room temperature for 2 h. The reaction was purged with nitrogen for 5 minutes and di-*tert*-butylphosphine (83 mg, 0.572 mmol) was added and was capped. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using ethyl acetate:hexanes (1:2) eluent was performed to give a white solid (111 mg, 53%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.72 (d, *J* = 6.9 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.14 – 7.06 (m, 2H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.61 (dd, *J* = 9.9, 3.7 Hz, 1H), 3.67 (s, 3H), 1.35 (d, *J* = 11.9 Hz, 9H), 1.12 (d, *J* = 11.9 Hz, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.0, 145.6, 141.5, 131.6, 134.4, 130.7, 124.7, 124.0, 120.9, 118.6, 117.8, 110.0, 55.3, 32.7, 31.0, 30.2. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 8.7.

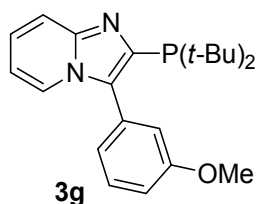


**2-(Dicyclohexylphosphino)-3-(2-methoxyphenyl)imidazo[1,2-a]pyridine (3e):** 2-Iodo-3-(2-methoxyphenyl)imidazo[1,2-a]pyridine (**2b**, 300 mg, 0.857 mmol), Cs<sub>2</sub>CO<sub>3</sub> (333 mg, 1.03 mmol), DIPPF (9 mg, 0.0214 mmol), and Pd(OAc)<sub>2</sub> (4.0 mg, 0.0171 mmol) were dissolved in 1,4-dioxane (3.0 mL) in a vial while purging with nitrogen. The reaction was capped and was stirred at room temperature for 2 h. The reaction was purged with nitrogen for 5 minutes and dicyclohexylphosphine (170 mg, 0.8568 mmol) was added and was capped. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using ethyl acetate:hexanes (1:2) eluent was performed to give a white solid (300 mg, 83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.72 (d, *J* = 9.1 Hz, 1H), 7.60 (d, *J* = 6.9 Hz, 1H), 7.48 – 7.38 (m, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.07 – 6.98 (m, 2H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.56 (t, *J* = 6.7 Hz, 1H), 3.62 (s, 3H), 2.42 – 2.25 (m, 2H), 1.97 -1.83 (m, 2H), 1.71 – 1.45 (m, 9H), 1.29 – 0.90 (m, 9H) <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.0, 146.0, 140.3, 134.2, 130.7, 124.8, 124.3, 120.9, 118.1, 117.5, 111.1, 55.5, 34.2, 32.9, 30.3, 29.1, 27.1, 26.6. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -22.2.



**2-(Diphenylphosphino)-3-(2-methoxyphenyl)imidazo[1,2-a]pyridine (3f):** 2-Iodo-3-(2-methoxyphenyl)imidazo[1,2-a]pyridine (**2b**, 300 mg, 0.857 mmol) was dissolved in 1,4-dioxane

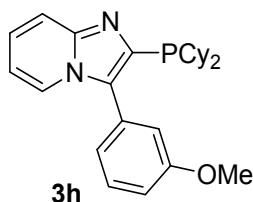
(3 mL) and purged under nitrogen in a brown vial. Cs<sub>2</sub>CO<sub>3</sub> (333 mg, 1.02 mmol), DIPPF (9 mg, 0.0214 mmol), and Pd(OAc)<sub>2</sub> (4 mg, 0.0171 mmol) were added and stirred at room temperature for 2 h. The reaction was purged with nitrogen for 5 minutes and diphenylphosphine (160 mg, 0.857 mmol) was added and was stirred overnight at 80 °C. The solids were removed by filtration over Celite and washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using acetone:dichloromethane (4:96) eluent gave a white solid (240 mg, 69%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.71 – 7.60 (m, 4H), 7.47 – 7.42 (m, 3H), 7.34 – 7.21 (m, 7H), 7.17 – 7.13 (m, 1H), 7.06 – 6.98 (m, 2H), 6.69 (t, *J* = 6.9 Hz, 1H), 3.64 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 157.8, 146.8, 140.3, 138.1, 134.2, 133.6, 133.4, 131.0, 130.1, 128.5, 128.1, 124.9, 124.7, 120.8, 118.2, 117.5, 111.7, 55.3. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -27.8 .



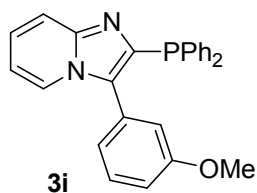
**2-(Di-tert-butylphosphino)-3-(3-methoxyphenyl)imidazo[1,2-a]pyridine (3g):** 2-Iodo-3(3-methoxyphenyl)imidazo[1,2-a]pyridine (**2c**, 300 mg, 0.857 mmol), Cs<sub>2</sub>CO<sub>3</sub> (333 mg, 1.03 mmol), DIPPF (9.0 mg, 0.0214 mmol), and Pd(OAc)<sub>2</sub> (4.0 mg, 0.0171 mmol) were dissolved in 1,4- dioxane (3.0 mL) in a vial while purging with nitrogen. The reaction was capped and was stirred at room temperature for 2 h. The reaction was purged with nitrogen for 5 minutes and di-*tert*-butylphosphine (125 mg, 0.857 mmol) was added and was capped. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and were washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using ethyl acetate:hexanes (3:7) eluent was performed to give a white solid (197 mg, 62%). <sup>1</sup>H NMR



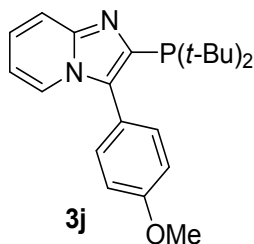
(CDCl<sub>3</sub>) δ 7.88 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.65 (dt, *J* = 9.2, 1.2 Hz, 1H), 7.41 (td, *J* = 7.8, 0.8 Hz, 1H), 7.14 (ddd, *J* = 9.1, 6.6, 1.3 Hz, 1H), 7.05 – 6.92 (m, 3H), 6.65 (td, *J* = 6.8, 1.2 Hz, 1H), 3.83 (s, 3H), 1.24 (d, *J* = 11.9 Hz, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 159.8, 145.4, 141.2, 131.3, 130.0, 129.9, 124.3, 123.7, 123.5, 118.0, 117.0, 114.1, 111.7, 55.3, 33.0, 30.7. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 8.2.



**2-(Dicyclohexylphosphino)-3-(3-methoxyphenyl)imidazo[1,2-a]pyridine (3h):** 2-Iodo-3(3-methoxyphenyl)imidazo[1,2-a]pyridine (**2c**, 300 mg, 0.857 mmol), Cs<sub>2</sub>CO<sub>3</sub> (333 mg, 1.03 mmol), DIPPF (9.0 mg, 0.0214 mmol), and Pd(OAc)<sub>2</sub> (4.0 mg, 0.0171 mmol) were dissolved in 1,4-dioxane (3.0 mL) in a vial while purging with nitrogen. The reaction was capped and was stirred at room temperature for 2 h. The reaction was purged with nitrogen for 5 minutes and dicyclohexylphosphine (170 mg, 0.857 mmol) was added and was capped. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and were washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using ethyl acetate:hexanes (3:7) eluent was performed to give a white solid (257 mg, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.04 (d, *J* = 6.9 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.68 (t, *J* = 6.8 Hz, 1H), 3.83 (s, 3H), 2.21 (tq, *J* = 11.9, 3.5 Hz, 2H), 1.89 – 1.81 (m, 2H), 1.75 – 1.53 (m, 10H), 1.37 – 1.05 (m, 11H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 159.8, 145.8, 140.2, 133.8, 130.6, 129.9, 124.6, 123.7, 117.8, 116.7, 114.1, 111.9, 55.3, 33.9, 30.8, 29.8, 27.1, 26.6. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -22.6.

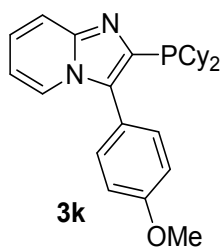


**2-(Diphenylphosphino)-3-(3-methoxyphenyl)imidazo[1,2-a]pyridine (3i):** 2-Iodo-3-(3-methoxyphenyl)imidazo[1,2-*a*]pyridine (**2c**, 160 mg, 0.457 mmol), Pd(OAc)<sub>2</sub> (2.0 mg, 0.009 mmol), Cs<sub>2</sub>CO<sub>3</sub> (177 mg, 0.548 mmol) and DIPPF (4.4 mg, 0.0105 mmol) were dissolved in dioxane (3 mL) while purging with nitrogen. After stirring for 2 h at room temperature capped in a brown vial, diphenylphosphine (85 mg, 0.457 mmol) was added while purging. Vial purged an additional five minutes, capped, and was heated overnight at 80 °C. The mixture was filtered over Celite washing with ethyl acetate and was purified by silica gel column chromatography with a dichloromethane:acetone system (98:2) to give a white solid (148 mg, 79%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.11 (d, *J* = 6.9 Hz, 1H), 7.67 (d, *J* = 9.2 Hz, 1H), 7.51-7.48 (m, 4H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.27-7.24 (m, 6H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 5.7 Hz, 1H), 6.89 (s, 1H), 6.67 (t, *J* = 6.9 Hz, 1H), 3.71 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 159.9, 146.6, 140.1, 137.8, 133.9, 132.9, 130.0, 128.5, 128.4, 125.0, 123.8, 122.8, 118.5, 116.2, 116.1, 114.8, 112.5, 55.4. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -28.3.



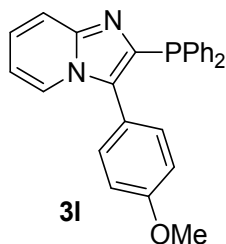
**2-(Di-tert-butylphosphino)-3-(4-methoxyphenyl)imidazo[1,2-a]pyridine (3j):** 2-Iodo-3-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (**2d**, 155 mg, 0.443 mmol), Cs<sub>2</sub>CO<sub>3</sub> (172 mg, 0.531

mmol), DIPPF (5.0 mg, 0.0111 mmol), and Pd(OAc)<sub>2</sub> (2.0 mg, 0.0089 mmol) were dissolved in 1,4-dioxane (3.0 mL) in a vial while purging with nitrogen. The reaction was capped and was stirred at room temperature for 2 h. The reaction was purged with nitrogen for 5 minutes and di-*tert*-butylphosphine (65 mg, 0.443 mmol) was added and was capped. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and were washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using ethyl acetate:hexanes (3:7) eluent was performed to give a white solid (119 mg, 73%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.83 (d, *J* = 6.9 Hz, 1H), 7.63 (d, *J* = 9.1 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.13 – 7.07 (m, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.62 (t, *J* = 6.7 Hz, 1H), 3.85 (s, 3H), 1.30 (d, *J* = 13.8 Hz, 9H), 1.23 (d, *J* = 11.9 Hz, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 159.8, 145.2, 132.5, 124.1, 123.7, 122.1, 118.1, 114.5, 111.6, 55.3, 32.9, 30.7, 30.6, 26.9. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 8.3.

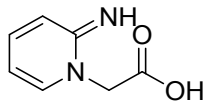


**2-(Dicyclohexylphosphino)-3-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (3k):** 2-Iodo-3-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (**2d**, 160 mg, 0.457 mmol), Cs<sub>2</sub>CO<sub>3</sub> (177 mg, 0.549 mmol), DIPPF (5.0 mg, 0.011 mmol), and Pd(OAc)<sub>2</sub> (2.0 mg, 0.00914 mmol) were dissolved in 1,4-dioxane (2.0 mL) in a vial while purging with nitrogen. The reaction was capped and was stirred at room temperature for 2 h. The reaction was purged with nitrogen for 5 minutes and dicyclohexylphosphine (91 mg, 0.457 mmol) was added and was capped. The reaction was stirred overnight at 80 °C. The solids were removed by filtration over Celite and were washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using ethyl

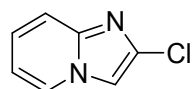
acetate:hexane (3:7) eluent was performed to give a white solid (106 mg, 55%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 7.0$  Hz, 1H), 7.64 (d,  $J = 9.1$  Hz, 1H), 7.34 (d,  $J = 8.6$  Hz, 2H), 7.16 – 7.00 (m, 1H), 7.01 (d,  $J = 8.7$  Hz, 2H), 6.65 (td,  $J = 6.9, 0.8$  Hz, 1H), 3.83 (s, 3H), 2.22 – 2.15 (m, 2H), 1.80 - 1.59 (m, 8H), 1.33 – 1.04 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  159.8, 145.7, 140.0, 132.3, 124.5, 123.6, 121.5, 117.8, 114.5, 111.8, 55.4, 33.8, 30.8, 29.8, 27.1, 26.6.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -22.6.



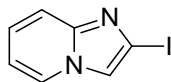
**2-Diphenylphosphino-3-(4-methoxyphenyl)imidazo[1,2-a]pyridine (3l):** To a vial was added 2-iodo-3-(4-methoxyphenyl)imidazo[1,2-a]pyridine (**2d**, 155 mg, 0.443 mmol),  $\text{Cs}_2\text{CO}_3$  (172 mg, 0.532 mmol), DIPPF (5.0 mg, 0.0111 mmol), and  $\text{Pd}(\text{OAc})_2$  (2.0 mg, 0.0089 mmol) in 1,4-dioxane (2.0 mL) under nitrogen. The reaction was capped and was stirred at room temperature for 1 h. The reaction was purged with nitrogen for 5 minutes and diphenylphosphine (233 mg, 0.714 mmol) was added and was stirred overnight at 80 °C. The solids were removed by filtration over Celite and washed with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using acetone:dichloromethane (3:97) eluent gave a white solid (108 mg, 59%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 6.9$  Hz, 1H), 7.75–7.80 (m, 1H), 7.61 (d,  $J = 9.2$  Hz, 1H), 7.48-7.51 (m, 3H), 7.25-7.31 (m, 8H), 7.17 (t,  $J = 9.2$  Hz, 1H), 7.00 (d,  $J = 8.6$  Hz, 2H), 6.72 (t,  $J = 6.3$  Hz, 1H), 3.87 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  160.1, 146.4, 139.3, 137.6, 133.9, 132.7, 132.0, 130.9, 128.4, 125.1, 123.7, 120.7, 118.4, 114.5, 112.5, 55.4.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  22.2.



**(2-Iminopyridin-1(2H)-yl)acetic acid<sup>1</sup>:** To a 50 mL round bottom flask was added 2-aminopyridine (15.0 g, 160 mmol), chloroacetic acid (12.7 g, 133 mmol) in water (20 mL). Triethylamine (23 mL, 153 mmol) was dropwise added to the solution. The reaction was stirred at 90 °C for 5 h. The reaction mixture was allowed to cool to room temperature then added 15 mL ice-cold ethanol and stirred on an ice-bath for another 2 h. The white solid was collected using vacuum filtration and washed with ice-cold ethanol (3 x 50 mL) yielding 15.7 g (65%). <sup>1</sup>H NMR (D<sub>2</sub>O) δ 7.75 (td, *J* = 6.9 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 6.81 (td, *J* = 6.9 Hz, 1H), 4.65 (s, 2H).

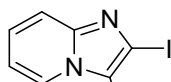


**2-Chloroimidazo[1,2-a]pyridine<sup>1</sup>:** To a 500 mL round bottom flask was added (2-iminopyridin-1(2H)-yl)acetic acid (15.7 g, 104 mmol) in toluene (100 mL). Phosphorus oxychloride (30 mL, 310 mmol) was dropwise added to the mixture. The reaction was heated under reflux for 16 h. The reaction mixture was allowed to cool to room temperature then 200 mL ice-cold water was added and was stirred for 15 minutes. The reaction was quenched with 50% NaOH (75 mL) and the organic layers were extracted. The aqueous layer was further extracted with dichloromethane (5 x 30 mL). The combined organic layers were dried over sodium sulfate and condensed *in vacuo* yielding a brown solid (13.6 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.96 (d, *J* = 6.9 Hz, 1H), 7.39 (t, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 6.9 Hz, 1H).



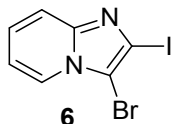
4

**2-Iodoimidazo[1,2-*a*]pyridine (4)<sup>2</sup>:** To a 500 mL round bottom flask was added 2-chloroimidazo[1,2-*a*]pyridine (6.0 g, 39.2 mmol), NaI (17.7 g, 118 mmol) in acetonitrile (173 mL). The first portion of 57% w/w HI (17.3 mL) was added to the reaction mixture and was stirred under reflux for 6 h. The second portion of HI (11.1 mL) was added. Mixture was stirred under reflux for another 6 h. The reaction mixture was allowed to cool to room temperature, neutralized with 50% w/w NaOH (60 mL), saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (30 mL) and extracted with dichloromethane (5 x 40 mL). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and condensed *in vacuo*. The crude product was collected and was crystallized from hexanes/ethyl acetate (1:1) yielding a brown solid (5.70 g, 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.82 (d, *J* = 6.9 Hz, 1H), 7.40 (s, 1H), 7.22 (d, *J* = 9.2 Hz, 1H), 6.86 (td, *J* = 8.3 Hz, 1H), 6.45 (td, *J* = 7.7 Hz, 1H).

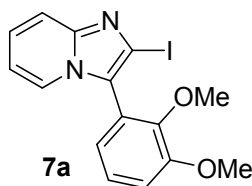


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**2,3-Diiodoimidazo[1,2-*a*]pyridine (5):** To a 100 mL round bottom flask was added 2-iodoimidazo[1,2-*a*]pyridine (4, 2.0 g, 8.2 mmol), NIS (2.0 g, 9.0 mmol) in acetonitrile (35 mL) was stirred at room temperature for 3 h under nitrogen. The reaction mixture was quenched with water (20 mL), 10% KOH (20 mL), saturated sodium thiosulfate (15 mL) and extracted with dichloromethane (4 x 25 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo* yielding a brown solid (2.90 g, 97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.05 (dt, *J* = 9.2 Hz, 1H), 7.51 (dt, *J* = 10.3 Hz, 1H), 7.18 (td, *J* = 8.0 Hz, 1H), 6.89 (td, *J* = 6.9 Hz, 1H).

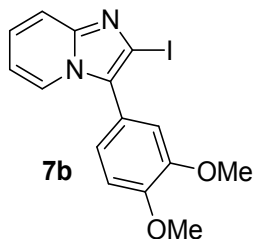


**3-Bromo-2-iodoimidazo[1,2-a]pyridine (6):** To a 100 mL round bottom flask was added 2-iodoimidazo[1,2-a]pyridine (**4**, 2.0 g, 8.2 mmol), NBS (1.6 g, 9.0 mmol) in acetonitrile (35 mL) was stirred at room temperature for 3 h under nitrogen. The reaction mixture was quenched with water (20 mL), 10% KOH (20 mL), saturated sodium thiosulfate (15 mL) and extracted with dichloromethane (4 x 25 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo* yielding a green solid (2.60 g, 98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.77 (d, *J* = 6.9 Hz, 1H), 7.29 (d, *J* = 9.7 Hz, 1H), 6.97 (td, *J* = 8.0 Hz, 1H), 6.67 (td, *J* = 6.9 Hz, 1H).

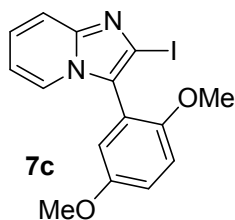


**3-(2,3-Dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (7a):** To a 25 mL reaction vial was added 2,3-diiodoimidazo[1,2-a]pyridine (**5**, 1.3 g, 4.0 mmol), 2,3-dimethoxyphenylboronic acid (650 mg, 4.40 mmol), Na<sub>2</sub>CO<sub>3</sub> (848 mg, 8.00 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (232 mg, 0.20 mmol) in 1,4-dioxane/H<sub>2</sub>O (12 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 35 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using dichloromethane:acetone (95:5) eluent to give a colorless oil (790 mg, 59%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.01 (d, *J* = 6.9 Hz, 1H), 7.53 (d, *J* = 9.2 Hz, 1H), 7.11 (td, *J* = 8.0 Hz, 1H), 6.97-7.03 (m, 3H), 6.69 (td, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H). <sup>13</sup>C

NMR (CDCl<sub>3</sub>)  $\delta$  149.7, 149.4, 146.8, 127.0, 124.8, 123.3, 122.9, 120.6, 117.2, 113.2, 112.8, 111.7, 93.9, 56.2, 56.1.



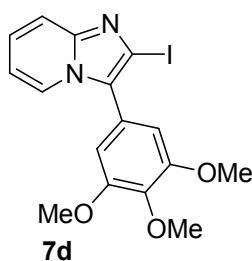
**3-(3,4-Dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (7b):** To a 25 mL reaction vial was added 2,3-diiodoimidazo[1,2-a]pyridine (**5**, 650 mg, 2.0 mmol), 3,4-dimethoxyphenylboronic acid (325 mg, 2.20 mmol), Na<sub>2</sub>CO<sub>3</sub> (424 mg, 4.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.10 mmol) in 1,4-dioxane/H<sub>2</sub>O (15 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 25 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using dichloromethane:acetone (95:5) eluent to give a yellow oil (360 mg, 54%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.90 (d, *J* = 6.9 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.86-6.90 (m, 3H), 6.58 (t, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 3.80 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  149.6, 146.6, 126.9, 124.8, 123.2, 122.7, 120.5, 116.9, 113.2, 112.8, 111.6, 93.9, 56.2, 56.0.



**3-(2,5-Dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (7c):** To a 25 mL reaction vial was added 2,3-diiodoimidazo[1,2-a]pyridine (**5**, 650 mg, 2.0 mmol), 2,5-dimethoxyphenylboronic

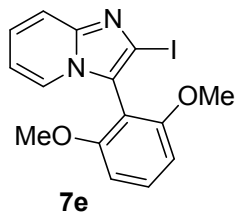


acid (325 mg, 2.2 mmol), Na<sub>2</sub>CO<sub>3</sub> (424 mg, 4.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.10 mmol) in 1,4-dioxane/H<sub>2</sub>O (15 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 25 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using dichloromethane:acetone (95:5) eluent to give a yellow oil (390 mg, 58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.59 (d, *J* = 6.9 Hz, 1H), 7.49 (d, *J* = 9.2 Hz, 1H), 7.06 (td, *J* = 8.0 Hz, 1H), 6.86-6.93 (m, 3H), 6.63 (td, *J* = 6.9 Hz, 1H), 3.71 (s, 3H), 3.58 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.6, 151.7, 146.9, 124.9, 118.6, 117.5, 116.7, 116.2, 112.6, 112.1, 94.6, 56.1, 55.9.

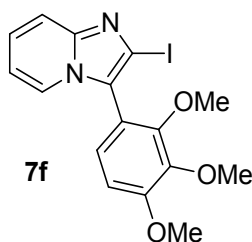


**2-Iodo-3-(3,4,5-trimethoxyphenyl)imidazo[1,2-a]pyridine (7d);** To a 25 mL reaction vial was added 2,3-diiodoimidazo[1,2-a]pyridine (**5**, 1.0 g 2.7 mmol), 3,4,5-trimethoxyphenylboronic acid (630 mg, 3.0 mmol), Na<sub>2</sub>CO<sub>3</sub> (573 mg, 5.4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (156 mg, 0.14 mmol) in 1,4-dioxane/H<sub>2</sub>O (12 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 35 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using dichloromethane:acetone (95:5) eluent to give a yellow solid (564 mg, 50%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (dd, *J* = 4.4, 3.5 Hz, 1H), 7.48 (dt, *J* = 9.1, 1.0 Hz, 1H), 7.09 (ddd, *J* = 9.0, 6.8, 1.2 Hz, 1H), 6.71 – 6.64 (m, 3H), 3.85 (s, 3H), 3.81 (s,

6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 146.8, 138.6, 127.0, 125.0, 123.5, 123.3, 117.1, 113.0, 107.3, 93.7, 61.0, 56.4.

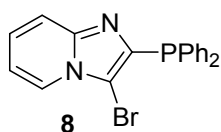


**3-(2,6-Dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (7e):** To a 25 mL reaction vial was added 2,3-diiodoimidazo[1,2-a]pyridine (**5**, 1.30 g, 3.50 mmol), 2,6-dimethoxyphenylboronic acid (700 mg, 3.85 mmol),  $\text{Na}_2\text{CO}_3$  (742 mg, 7.00 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (202 mg, 0.180 mmol) in 1,4-dioxane/ $\text{H}_2\text{O}$  (12 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 25 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using dichloromethane:acetone (95:5) eluent to give a colorless oil (534 mg, 40%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.53 (t,  $J = 9.2$  Hz, 2H), 7.41 (t,  $J = 8.6$  Hz, 1H), 7.09 (td,  $J = 6.9$  Hz, 1H), 6.62-6.65 (m, 3H), 3.69 (s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  159.3, 146.9, 131.9, 124.5, 124.3, 121.6, 116.7, 111.9, 104.2, 96.6, 55.9.

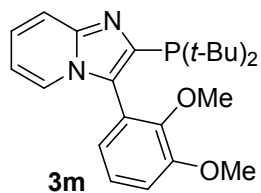


**2-Iodo-3-(2,3,4-trimethoxyphenyl)imidazo[1,2-a]pyridine (7f):** To a 25 mL reaction vial was added 2,3-diiodoimidazo[1,2-a]pyridine (**5**, 1.30 g, 3.50 mmol), 2,3,4-trimethoxyphenylboronic

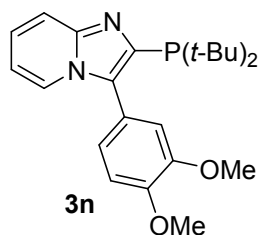
acid (819 mg, 3.86 mmol), Na<sub>2</sub>CO<sub>3</sub> (742 mg, 7.00 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (203 mg, 0.175 mmol) in 1,4-dioxane/H<sub>2</sub>O (12 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 25 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using dichloromethane:acetone (95:5) eluent to give a yellow oil (848 mg, 58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.58 (d, *J* = 6.9 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.62 (t, *J* = 6.3 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.43 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.1, 152.6, 146.9, 142.4, 127.8, 124.8, 116.7, 114.7, 112.3, 107.8, 94.8, 61.3, 61.2, 56.2.



**3-Bromo-2-(diphenylphosphino)imidazo[1,2-a]pyridine (8):** To a 25 mL reaction vial was added 3-bromo-2-iodoimidazo[1,2-a]pyridine (**6**, 1.0 g, 3.09 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.20 g, 3.71 mmol), DIPPF (33 mg, 0.0773 mmol), and Pd(OAc)<sub>2</sub> (14 mg, 0.0620 mmol) in 1,4-dioxane (6 mL) was purged with argon. The reaction vial was capped and stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes then added diphenylphosphine (576 mg, 3.09 mmol) was added and capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over Celite washing with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography was performed using hexanes:ethyl acetate (3:1) eluent to give a white solid (815 mg, 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.01 (d, *J* = 6.9 Hz, 1H), 7.59-7.67 (m, 5H), 7.33-7.38 (m, 6H), 7.11 (td, *J* = 9.2 Hz, 1H), 6.76 (td, *J* = 8.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 147.3, 141.4, 136.5, 134.1, 133.9, 128.9, 125.3, 124.0, 118.3, 113.3, 104.1, 103.8.

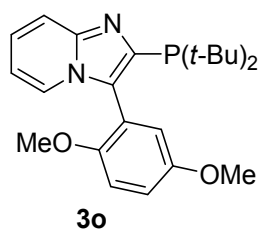


**2-(Di-tert-butylphosphino)-3-(3,4-dimethoxyphenyl)imidazo[1,2-a]pyridine (3m):** To a 25 mL reaction vial was added 3-(3,4-dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (**7b**, 385 mg, 1.0 mmol), Cs<sub>2</sub>CO<sub>3</sub> (393 mg, 1.2 mmol), DIPPF (43 mg, 0.10 mmol), and Pd(OAc)<sub>2</sub> (12 mg, 0.050 mmol) in 1,4-dioxane (3 mL) was purged with argon. The reaction vial was capped and was stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes then added di-tert-butylphosphine (189 μL, 1.0 mmol) and capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over Celite washing with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography was performed using hexanes: ethyl acetate (3:2) eluent to give a yellow solid (290 mg, 64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.62 (d, *J* = 9.2 Hz, 2H), 7.08-7.12 (m, 2H), 6.98-7.03 (m, 2H), 6.59 (td, *J* = 8.0 Hz, 1H), 3.91 (d, *J* = 7.9 Hz, 3H), 3.53 (s, 3H), 1.38 (d, *J* = 12.0 Hz, 9H), 1.19 (d, *J* = 12.0 Hz, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 152.8, 147.8, 145.6, 141.3, 131.5, 131.1, 126.1, 125.3, 124.2, 122.5, 117.6, 113.2, 111.1, 60.8, 55.9, 33.3, 33.1, 31.1, 31.0. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 8.2.



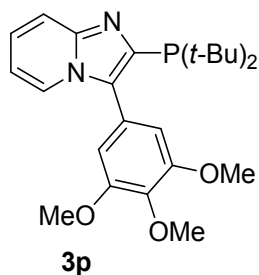
**2-(Di-tert-butylphosphino)-3-(2,3-dimethoxyphenyl)imidazo[1,2-a]pyridine (3n):** To a 25 mL reaction vial was added 3-(2,3-dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (**7a**, 280 mg,

0.74 mmol), Cs<sub>2</sub>CO<sub>3</sub> (287 mg, 0.89 mmol), DIPPF (31 mg, 0.070 mmol), and Pd(OAc)<sub>2</sub> (10 mg, 0.040 mmol) in 1,4-dioxane (3 mL) was purged with argon. The reaction vial was capped and was stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes then added di-*tert*-butylphosphine (140 μL, 0.74 mmol) was added and capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over Celite washing with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography was performed using hexanes:ethyl acetate (1:1) eluent to give an orange oil (91 mg, 31%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.83 (d, *J* = 6.9 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.10 (td, *J* = 9.2 Hz, 1H), 6.94-6.98 (m, 2H), 6.88 (s, 1H), 6.63 (td, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 3.83 (s, 3H), 1.23 (d, *J* = 11.5 Hz, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 149.3, 149.1, 145.3, 141.1, 140.9, 134.3, 133.9, 124.2, 123.9, 123.7, 122.3, 118.0, 114.3, 111.7, 111.5, 56.0, 55.9, 33.0, 32.8, 30.7, 30.6. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 8.4.

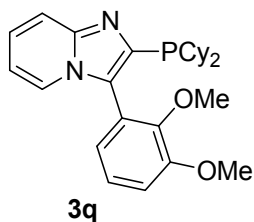


**2-(Di-*tert*-butylphosphino)-3-(2,5-dimethoxyphenyl)imidazo[1,2-*a*]pyridine (3o):** To a 25 mL reaction vial was added 3-(2,5-dimethoxyphenyl)-2-iodoimidazo[1,2-*a*]pyridine (**7c**, 350 mg, 0.92 mmol), Cs<sub>2</sub>CO<sub>3</sub> (360 mg, 1.1 mmol), DIPPF (48 mg, 0.12 mmol), and Pd(OAc)<sub>2</sub> (21 mg, 0.09 mmol) in 1,4-dioxane (5 mL) was purged with argon. The reaction vial was capped and was stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes then added di-*tert*-butylphosphine (200 μL, 0.92 mmol) and capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over Celite washing with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography was performed using hexanes:ethyl acetate (3:1)

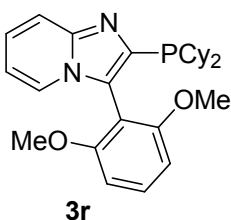
eluent to give a yellow solid (224 mg, 61%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 9.2$  Hz, 1H), 7.53 (d,  $J = 7.5$  Hz, 1H), 7.11 (t,  $J = 8.0$  Hz, 1H), 6.89-6.97 (m, 3H), 6.61 (t,  $J = 6.3$  Hz, 1H), 3.76 (s, 3H), 3.61 (s, 3H), 1.35 (d,  $J = 11.5$  Hz, 9H), 1.12 (d,  $J = 12.0$  Hz, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  153.3, 152.3, 145.6, 141.3, 131.6, 124.7, 124.1, 119.7, 119.3, 117.8, 115.6, 111.9, 111.1, 55.8, 55.7, 31.0, 30.1, 30.4, 30.3.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.5.



**2-(Di-tert-butylphosphino)-3-(3,4,5-dimethoxyphenyl)imidazo[1,2-a]pyridine (3p):** To a vial was added 2-iodo-3-(3',4',5'-dimethoxyphenyl)imidazo[1,2-a]pyridine (**7d**, 200 mg, 0.490 mmol),  $\text{Cs}_2\text{CO}_3$  (190 mg, 0.590 mmol), DIPPF (5.0 mg, 0.0120 mmol), and  $\text{Pd}(\text{OAc})_2$  (2.5 mg, 0.0090 mmol) in 1,4-dioxane (4.0 mL) under nitrogen. The reaction was capped and was stirred at room temperature for 1 hour. The reaction was purged with nitrogen for 5 minutes and di-tert-butylphosphine (1.0 mL, 0.500 mmol, 0.5 M in hexanes) was added and was stirred overnight at 80 °C. The solids were removed by filtration over Celite washing with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography using hexanes:ethyl acetate (2:1) eluent gave a brownish white solid (130 mg, 62%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 6.9$  Hz, 1H), 7.63 (d,  $J = 9.1$  Hz, 1H), 7.12 (t,  $J = 9.0$  Hz, 1H), 6.66 (t,  $J = 9.8, 3.8$  Hz, 1H), 6.58 (s, 2H), 3.92 (s, 3H), 3.82 (s, 5H), 1.24 (d,  $J = 12.0$  Hz, 18H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 145.2, 140.8, 138.3, 134.0, 124.2, 118.1, 111.7, 108.5, 76.8, 60.9, 56.2, 32.8, 30.7, 26.9.  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  8.3.

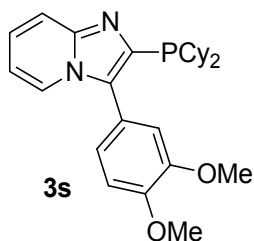


**2-(Dicyclohexylphosphino)-3-(2,3-dimethoxyphenyl)imidazo[1,2-a]pyridine (3q):** To a 25 mL reaction vial was added 3-(2,3-dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (**7a**, 280 mg, 0.74 mmol), Cs<sub>2</sub>CO<sub>3</sub> (287 mg, 0.89 mmol), DIPPF (31 mg, 0.07 mmol), and Pd(OAc)<sub>2</sub> (10 mg, 0.04 mmol) in 1,4-dioxane (3 mL) was purged with argon. The reaction vial was capped and was stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes then added dicyclohexylphosphine (163 μL, 0.74 mmol) and capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over Celite washing with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography was performed using hexanes:ethyl acetate (1:1) eluent to give an orange oil (153 mg, 46%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.10 (td, *J* = 8.6 Hz, 1H), 6.88-6.97 (m, 3H), 6.63 (t, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 2.14-2.19 (m, 2H), 1.54-1.63 (m, 9H), 1.07-1.17 (m, 11H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 149.3, 149.1, 140.1, 133.8, 133.5, 124.4, 123.7, 121.7, 117.8, 114.07, 111.8, 56.0, 55.9, 33.8, 30.8, 29.8, 27.2, 27.0, 26.6. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -22.6.



**2-(Dicyclohexylphosphino)-3-(2,6-dimethoxyphenyl)imidazo[1,2-a]pyridine (3r):** To a 30 mL reaction vial was added 3-(2,6-dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (**7e**, 520 mg, 1.4

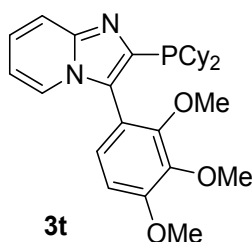
mmol), Cs<sub>2</sub>CO<sub>3</sub> (542 mg, 1.7 mmol), DIPPF (15 mg, 0.035 mmol), and Pd(OAc)<sub>2</sub> (6.2 mg, 0.028 mmol) in 1,4-dioxane (6 mL) was purged with argon. The reaction vial was capped and was stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes; dicyclohexylphosphine (1.4 mmol, 2.8 mL, 0.5 M in hexanes) was added and the vial capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over Celite washing with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography was performed using hexanes: ethyl acetate (3:2) eluent to give a yellow solid (328 mg, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 9.1 Hz, 1H), 7.45 (d, *J* = 6.9 Hz, 1H), 7.34 (t, *J* = 8.5 Hz, 1H), 7.03 (t, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 2H), 6.53 (t, *J* = 6.8, 1H), 3.60 (s, 6H), 2.05–2.22 (m, 2H), 1.51–1.72 (m, 8H), 1.30 – 1.01 (m, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.4, 146.4, 141.1, 131.4, 124.3, 117.5, 110.9, 106.4, 103.9, 77.3, 55.4, 33.3, 30.4, 26.6. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ -20.8.



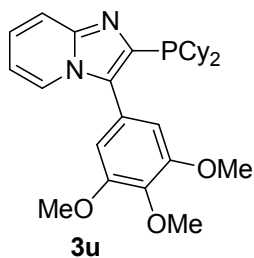
**2-(Dicyclohexylphosphino)-3-(3,4-dimethoxyphenyl)imidazo[1,2-a]pyridine (3s):** To a 25 mL reaction vial was added 3-(3,4-dimethoxyphenyl)-2-iodoimidazo[1,2-a]pyridine (**7b**, 385 mg, 1.0 mmol), Cs<sub>2</sub>CO<sub>3</sub> (393 mg, 1.2 mmol), DIPPF (43 mg, 0.10 mmol), and Pd(OAc)<sub>2</sub> (11 mg, 0.050 mmol) in 1,4-dioxane (3 mL) was purged with argon. The reaction vial was capped and stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes then added dicyclohexylphosphine (223 μL, 1.0 mmol) and capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over Celite washing with ethyl acetate. The filtrate was



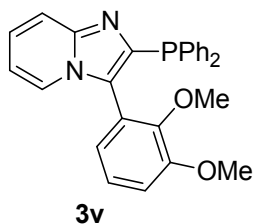
condensed *in vacuo*. Column chromatography was performed using hexanes: ethyl acetate (3:2) eluent to give a yellow solid (238 mg, 52%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.64 (t, *J* = 6.9 Hz, 2H), 7.09-7.14 (m, 2H), 6.94-7.00 (m, 2H), 6.60 (td, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.43 (s, 3H), 2.19-2.23 (m, 2H), 1.03-1.71 (m, 20H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 152.9, 147.6, 145.8, 131.3, 131.0, 125.9, 125.6, 124.3, 123.1, 117.0, 113.3, 111.6, 60.8, 55.9, 34.2, 31.3, 30.7, 30.1, 29.8, 27.2, 26.4. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -23.1.



**2-(Dicyclohexylphosphino)-3-(2,3,4-trimethoxyphenyl)imidazo[1,2-a]pyridine (3t):** To a 25 mL reaction vial was added 2-iodo-3-(2,3,4-trimethoxyphenyl)imidazo[1,2-a]pyridine (**7f**, 350 mg, 0.85 mmol), Cs<sub>2</sub>CO<sub>3</sub> (331 mg, 1.02 mmol), DIPPF (36 mg, 0.09 mmol), and Pd(OAc)<sub>2</sub> (10 mg, 0.04 mmol) in 1,4-dioxane (3 mL) was purged with argon. The reaction vial was capped and stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes then added dicyclohexylphosphine (190 μL, 0.85 mmol) and capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over Celite washing with ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography was performed using hexanes:ethyl acetate (3:1) eluent to give a brown solid (85 mg, 21%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.12 (t, *J* = 6.9 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.63 (t, *J* = 6.9 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.50 (s, 3H), 2.25-2.27 (m, 2H), 1.09-1.79 (m, 20H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 154.7, 152.5, 146.1, 142.2, 140.3, 131.5, 128.7, 125.2, 124.5, 117.4, 115.6, 107.5, 61.1, 61.0, 56.0, 34.2, 33.9, 31.3, 29.5, 27.2, 26.6. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -23.0.

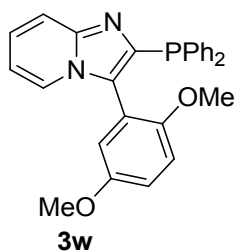


**2-(Dicyclohexylphosphino)-3-(3,4,5-trimethoxyphenyl)imidazo[1,2-a]pyridine (3u):** To a 25 mL reaction vial was added 2-iodo-3-(3,4,5-trimethoxyphenyl)imidazo[1,2-a]pyridine (**7d**, 290 mg, 0.71 mmol), Cs<sub>2</sub>CO<sub>3</sub> (275 mg, 0.85 mmol), DIPPF (30 mg, 0.07 mmol), and Pd(OAc)<sub>2</sub> (9 mg, 0.04 mmol) in 1,4-dioxane (3 mL) was purged with argon. The reaction vial was capped and stirred at room temperature for 2 h. The reaction was purged with argon for 5 minutes then added dicyclohexylphosphine (190 μL, 0.85 mmol) and capped. The reaction was stirred overnight at 80 °C. The reaction mixture was filtered over celite and transferred using ethyl acetate. The filtrate was condensed in vacuo. Column chromatography was performed using hexanes: ethyl acetate (1:1) eluent to give an orange oil (183 mg, 55%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.91 (d, *J* = 6.9 Hz, 1H), 7.58 (d, *J* = 9.2 Hz, 1H), 7.06 (td, *J* = 7.5 Hz, 1H), 6.56-6.62 (m, 3H), 3.82 (s, 3H), 3.77 (s, 6H), 2.12-2.16 (m, 2H), 1.04-1.53 (m, 20H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.5, 145.7, 140.0, 139.8, 138.2, 133.9, 124.7, 124.5, 123.7, 117.8, 111.9, 108.1, 60.9, 56.2, 33.8, 30.8, 29.8, 27.1, 26.9, 26.5. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -22.5.



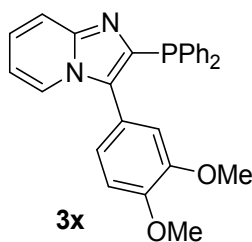
**2-(Diphenylphosphino)-3-(2,3-dimethoxyphenyl)imidazo[1,2-a]pyridine (3v):** To a 25 mL reaction vial was added 3-bromo-2-(diphenylphosphino)imidazo[1,2-a]pyridine (**8**, 233 mg,

0.610 mmol), 2,3-dimethoxyphenylboronic acid (122 mg, 0.670 mmol), Na<sub>2</sub>CO<sub>3</sub> (129 mg, 1.20 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.0305 mmol) in 1,4-dioxane/H<sub>2</sub>O (6 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 15 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using chloroform:acetone (96:4) eluent to give a colorless oil (135 mg, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (dd, *J* = 9.3 Hz, 1H), 7.71 – 7.60 (m, 3H), 7.50 – 7.43 (m, 2H), 7.37 – 7.29 (m, 3H), 7.28 – 7.20 (m, 3H), 7.19 – 7.13 (m, 2H), 7.06 (dd, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 6.0 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H), 3.92 (s, 3H), 3.41 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 153.0, 147.7, 146.9, 140.0, 137.8, 133.9, 133.6, 133.5, 130.6, 130.2, 128.6, 128.5, 128.4, 128.3, 128.2, 125.5, 125.2, 124.5, 123.2, 118.0, 113.6, 111.9, 60.9, 56.0. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ -29.2.

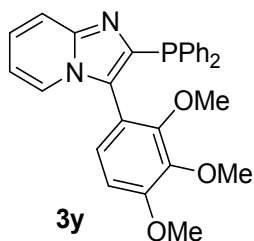


**2-(Diphenylphosphino)-3-(2,5-dimethoxyphenyl)imidazo[1,2-a]pyridine (3w):** To a 25 mL reaction vial was added 3-bromo-2-(diphenylphosphino)imidazo[1,2-a]pyridine (**8**, 190 mg, 0.52 mmol), 2,5-dimethoxyphenylboronic acid (106 mg, 0.58 mmol), Na<sub>2</sub>CO<sub>3</sub> (110 mg, 1.04 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg, 0.026 mmol) in 1,4-dioxane/H<sub>2</sub>O (6 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 hours. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 15 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using chloroform:acetone (96:4) eluent to give a colorless oil (149 mg, 68%). <sup>1</sup>H NMR (500

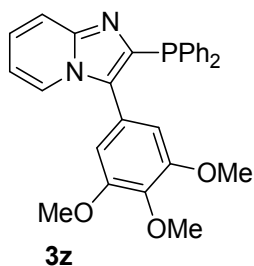
MHz, CDCl<sub>3</sub>)  $\delta$  7.73 – 7.61 (m, 4H), 7.44 (td,  $J$  = 7.5 Hz, 2H), 7.34 – 7.20 (m, 6H), 7.19 – 7.13 (m, 1H), 6.95 (dt,  $J$  = 6.0 Hz, 2H), 6.80 (d,  $J$  = 2.1 Hz, 1H), 6.70 (t,  $J$  = 6.9 Hz, 1H), 3.66 (s, 3H), 3.59 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  153.4, 152.0, 146.7, 140.3, 137.8, 134.3, 134.1, 133.5, 133.3, 130.1, 129.8, 128.6, 128.2, 125.0, 118.6, 118.1, 116.3, 112.5, 111.9, 55.9, 55.7. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>)  $\delta$  -27.3.



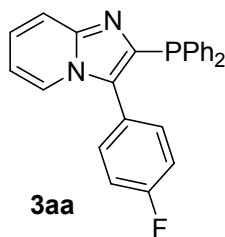
**2-(Diphenylphosphino)-3-(3,4-dimethoxyphenyl)imidazo[1,2-a]pyridine (3x):** To a 25 mL reaction vial was added 3-bromo-2-(diphenylphosphino)imidazo[1,2-a]pyridine (**8**, 190 mg, 0.52 mmol), 3,4-dimethoxyphenylboronic acid (106 mg, 0.58 mmol), Na<sub>2</sub>CO<sub>3</sub> (110 mg, 1.04 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg, 0.026 mmol) in 1,4-dioxane/H<sub>2</sub>O (6 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 15 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using chloroform:acetone (96:4) eluent to give a colorless oil (146 mg, 67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.05 (d,  $J$  = 7.5 Hz, 1H), 7.63 (d,  $J$  = 9.2 Hz, 1H), 7.51-7.55 (m, 4H), 7.27-7.33 (m, 6H), 7.12-7.14 (m, 1H), 6.96-7.02 (m, 2H), 6.85 (s, 1H), 6.71 (td,  $J$  = 8.0 Hz, 1H), 3.92 (s, 3H), 3.73 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  149.6, 149.2, 146.4, 139.8, 137.7, 133.9, 128.5, 124.8, 123.7, 123.1, 121.0, 118.4, 113.9, 112.4, 111.5, 56.1, 55.9. <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  -27.9.



**2-(Diphenylphosphino)-3-(2,3,4-trimethoxyphenyl)imidazo[1,2-a]pyridine (3y):** To a 25 mL reaction vial was added 3-bromo-2-(diphenylphosphino)imidazo[1,2-a]pyridine (**8**, 190 mg, 0.52 mmol), 2,3,4-trimethoxyphenylboronic acid (123 mg, 0.58 mmol), Na<sub>2</sub>CO<sub>3</sub> (110 mg, 1.04 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg, 0.026 mmol) in 1,4-dioxane/H<sub>2</sub>O (6 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 hours. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 25 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using hexanes:acetone (3:1) eluent to give a colorless oil (126 mg, 52%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.73 (d, *J* = 6.9 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.62 (td, *J* = 8.0 Hz, 2H), 7.45 (td, *J* = 9.2 Hz, 2H), 7.30-7.35 (m, 3H), 7.23-7.27 (m, 3H), 7.17 (td, *J* = 8.0 Hz, 1H), 6.97 (dd, *J* = 9.7 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 1H), 6.71 (td, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.46 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.0, 152.5, 146.8, 142.4, 137.9, 134.0, 133.8, 133.5, 128.5, 128.3, 125.2, 124.9, 118.1, 115.2, 111.9, 107.6, 61.3, 61.1, 56.1. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -28.9.

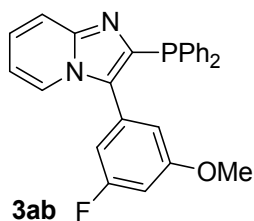


**2-(Diphenylphosphino)-3-(3,4,5-trimethoxyphenyl)imidazo[1,2-*a*]pyridine (3z):** To a 25 mL reaction vial was added 3-bromo-2-(diphenylphosphino)imidazo[1,2-*a*]pyridine (**8**, 190 mg, 0.52 mmol), 3,4,5-trimethoxyphenylboronic acid (123 mg, 0.58 mmol), Na<sub>2</sub>CO<sub>3</sub> (110 mg, 1.04 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg, 0.026 mmol) in 1,4-dioxane/H<sub>2</sub>O (6 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 15 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using chloroform:acetone (96:4) eluent to give a colorless foam (149 mg, 64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.09 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.49-7.52 (m, 4H), 7.27-7.32 (m, 6H), 7.13-7.15 (m, 1H), 6.73 (t, *J* = 8.0 Hz, 1H), 6.55 (s, 2H), 3.91 (s, 3H), 3.71 (s, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 153.5, 146.4, 140.0, 138.4, 137.5, 133.9, 133.8, 128.6, 128.3, 124.8, 124.1, 123.7, 118.5, 112.6, 107.7, 61.0, 56.1. <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ -26.8.

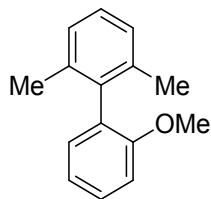


**2-(Diphenylphosphino)-3-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (3aa):** To a 25 mL reaction vial was added 3-bromo-2-(diphenylphosphino)imidazo[1,2-*a*]pyridine (**8**, 200 mg, 0.52 mmol), 4-fluorophenylboronic acid (81 mg, 0.600 mmol), Na<sub>2</sub>CO<sub>3</sub> (106 mg, 1.02 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (29 mg, 0.025 mmol) in 1,4-dioxane/H<sub>2</sub>O (6 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 15 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using methylene chloride:ethyl

acetate (96:4) eluent to give a colorless oil (80 mg, 40%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 6.9$  Hz, 1H), 7.66 (d,  $J = 9.2$  Hz, 1H), 7.50-7.54 (m, 4H), 7.39-7.42 (m, 2H), 7.29-7.31 (m, 6H), 7.16-7.20 (m, 3H), 6.74 (td,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  164.0, 162.0, 146.6, 140.3, 137.5, 133.9, 128.4, 125.1, 123.5, 118.6, 116.3, 116.1, 112.6.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -28.7.

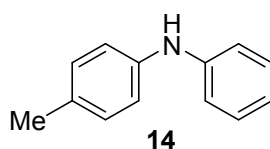


**2-(Diphenylphosphino)-3-(3-fluoro-5-methoxyphenyl)imidazo[1,2-a]pyridine (3ab):** To a 25 mL reaction vial was added 3-bromo-2-(diphenylphosphino)imidazo[1,2-a]pyridine (**8**, 300 mg, 0.790 mmol), 3-fluoro-5-methoxyphenylboronic acid (148 mg, 0.870 mmol),  $\text{Na}_2\text{CO}_3$  (168 mg, 1.58 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (46 mg, 0.0395 mmol) in 1,4-dioxane/ $\text{H}_2\text{O}$  (10 mL, 2:1) was purged with argon. Reaction vial was capped and stirred at 100 °C for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane (3 x 15 mL). The organic layers were dried over sodium sulfate and condensed *in vacuo*. Column chromatography was performed using hexanes:ethyl acetate (1:1) eluent to give a colorless oil (133 mg, 39%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.10 (d,  $J = 6.9$  Hz, 1H), 7.66 (d,  $J = 9.2$  Hz, 1H), 7.51-7.55 (m, 4H), 7.29-7.32 (m, 6H), 7.18 (td,  $J = 8.0$  Hz, 1H), 6.68-6.77 (m, 4H), 3.73 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  164.7, 162.7, 161.3, 146.7, 137.4, 133.9, 128.6, 128.4, 125.2, 123.7, 118.6, 112.8, 109.6, 109.4, 102.5, 55.7.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -27.9.



**11**

**2,6-Dimethyl-(2'-methoxy)biphenyl (11)<sup>3</sup>:** In a 25 mL brown vial, 2-bromo-*m*-xylene (**9**, 200 mg, 1.10 mmol) was dissolved in 1,4-dioxane (5 mL). To the vial was added 2-methoxyphenyl boronic acid (**10**, 243 mg, 1.60 mmol), Cs<sub>2</sub>CO<sub>3</sub> (888 mg, 2.75 mmol), Pd(OAc)<sub>2</sub> (6.2 mg, 0.0275 mmol), and ligand **3r** (25 mg, 0.055 mmol). The vial was purged with nitrogen for 10 min. The reaction was stirred overnight at 80° C and the crude mixture was filtered over Celite washing with ethyl acetate. The mixture was purified utilizing column chromatography using 9:1 hexanes:ethyl acetate (9:1) eluent to give a yellow oil (225 mg, 96%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.51 (t, 1H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 3H), 2.20 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 156.8, 138.5, 136.82, 130.9, 129.8, 128.7, 127.3, 121.0, 111.1, 55.6, 20.7.



**14**

**4-Methyl-N-phenylaniline (14)<sup>4</sup>:** To a 25 mL reaction vial, aniline (100 mg, 1.07 mmol), 4-chlorotoluene (204 mg, 1.61 mmol), Cs<sub>2</sub>CO<sub>3</sub> (876 mg, 2.69 mmol), ligand **3e** (23 mg, 0.0537 mmol), and Pd(OAc)<sub>2</sub> (12 mg, 0.0537 mmol) were dissolved in 1,4 dioxane (4 mL) while purging with argon. The reaction vial was capped and stirred overnight at 100 °C. The reaction mixture was filtered over Celite and transferred using ethyl acetate. The filtrate was condensed *in vacuo*. Column chromatography was performed using gradient of 10–20% ethyl



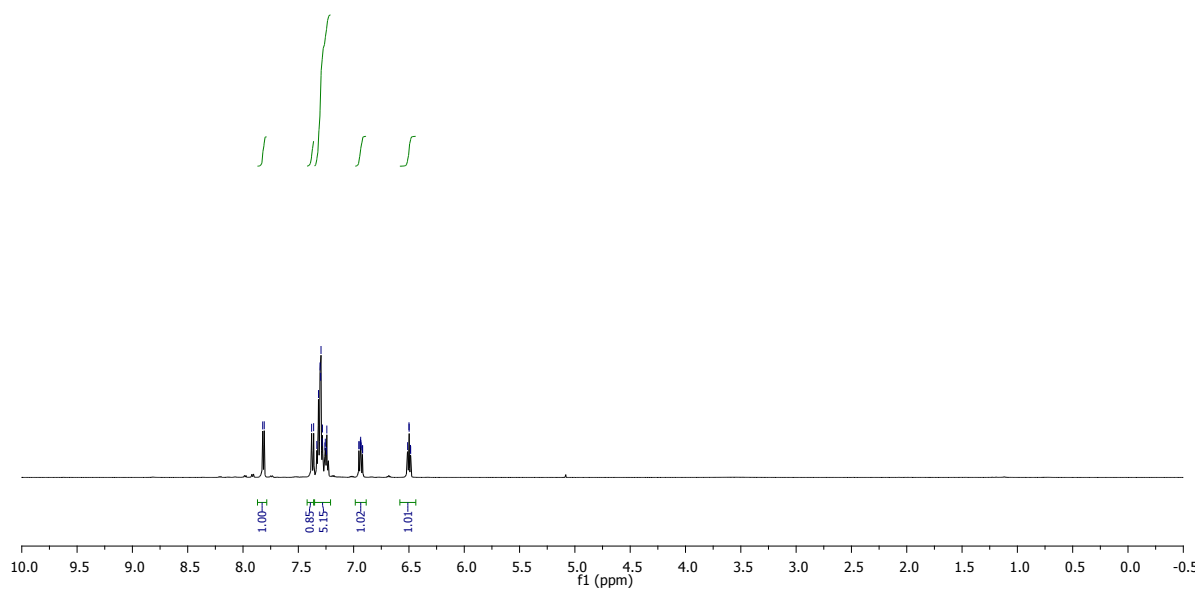
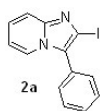
acetate/petroleum ether eluent to give a light yellow solid (156 mg, 79%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.19 (m, 2H), 7.09 (dd,  $J = 7.2, 1.4$  Hz, 2H), 7.04 – 7.00 (m, 4H), 6.88 (tq,  $J = 7.4, 1.0$  Hz, 1H), 5.60 (bs, 1H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 140.4, 131.0, 130.0, 129.4, 120.4, 119.0, 117.0, 20.8.

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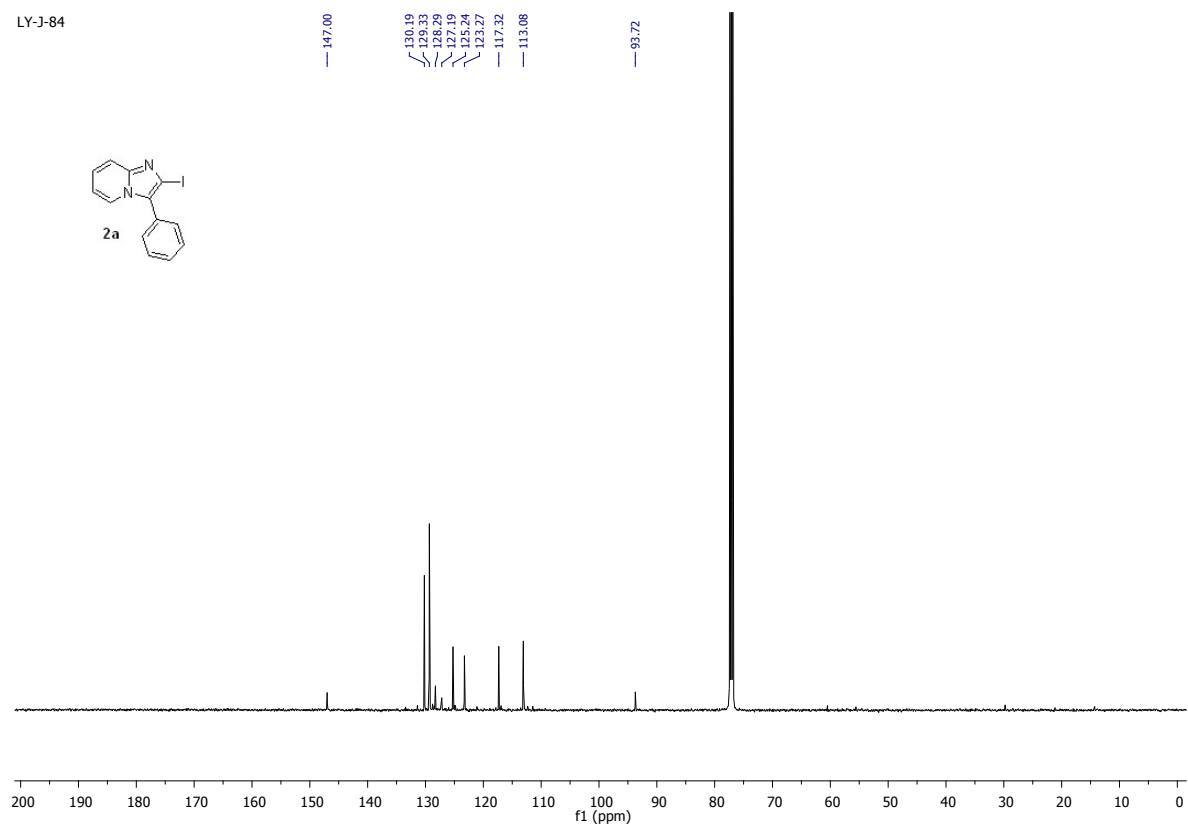
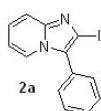
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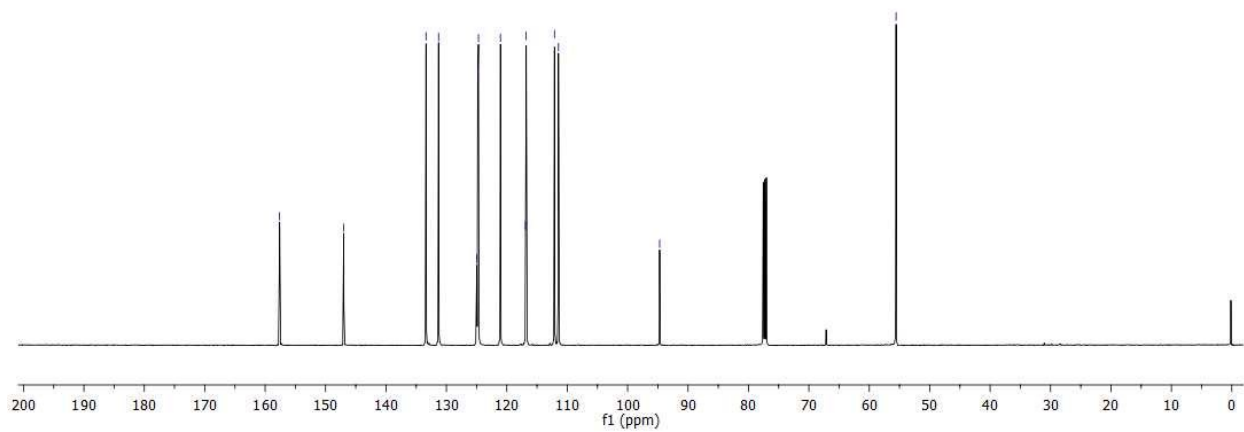
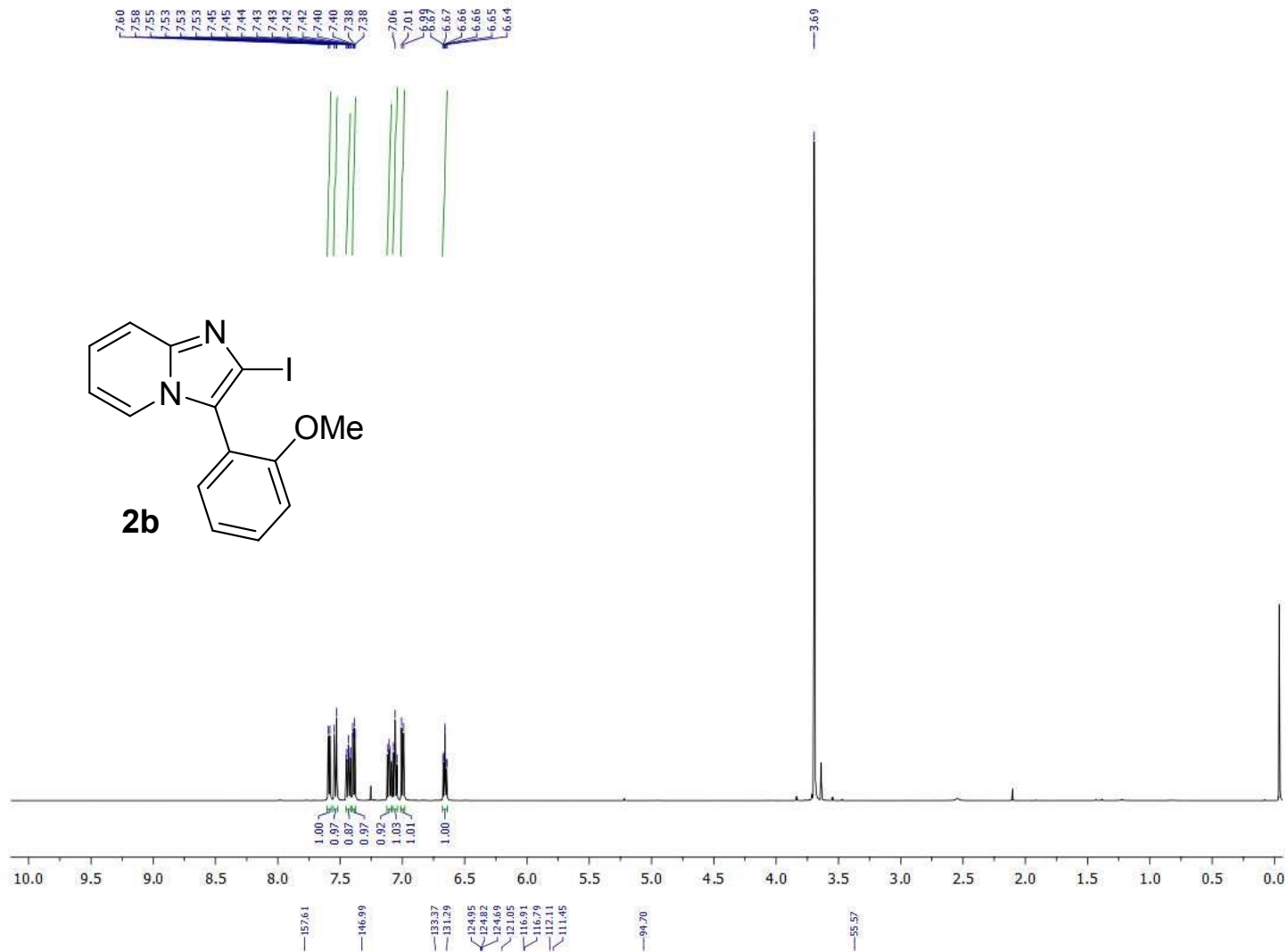
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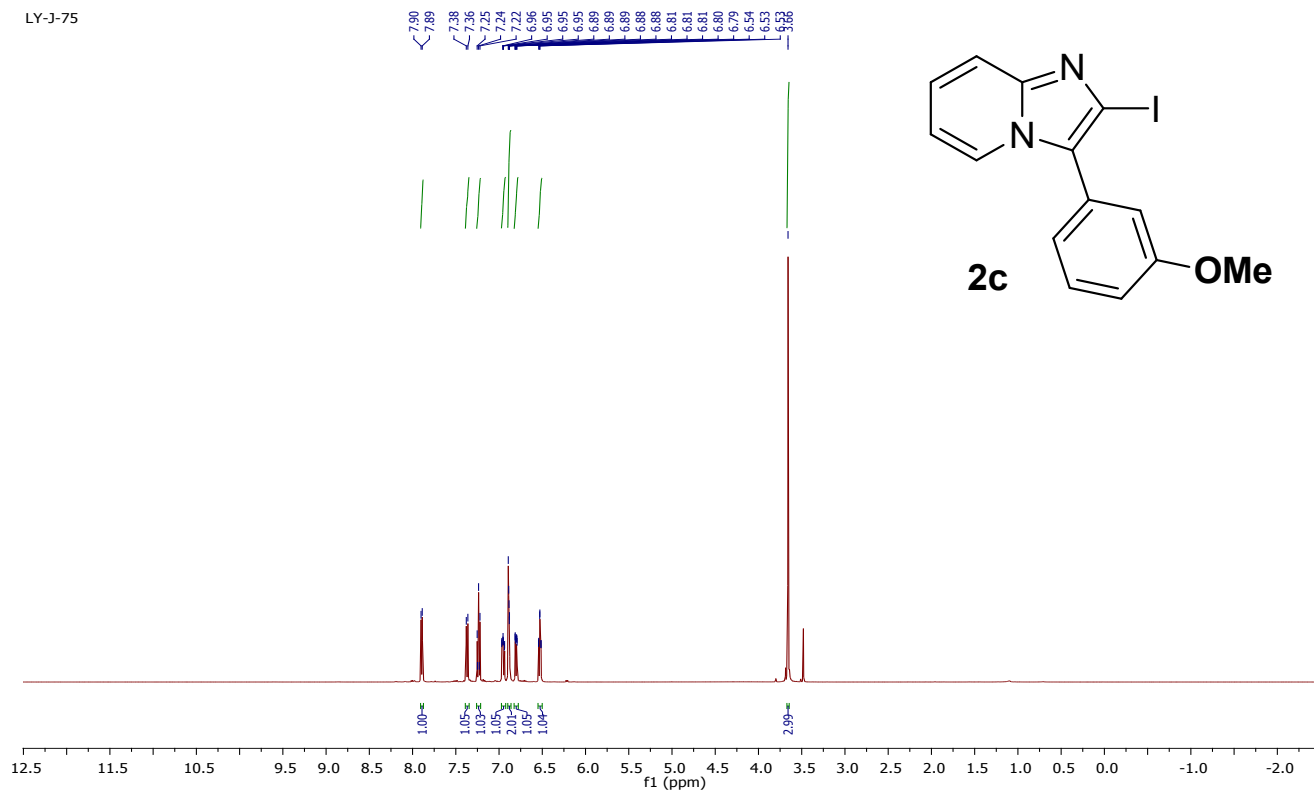
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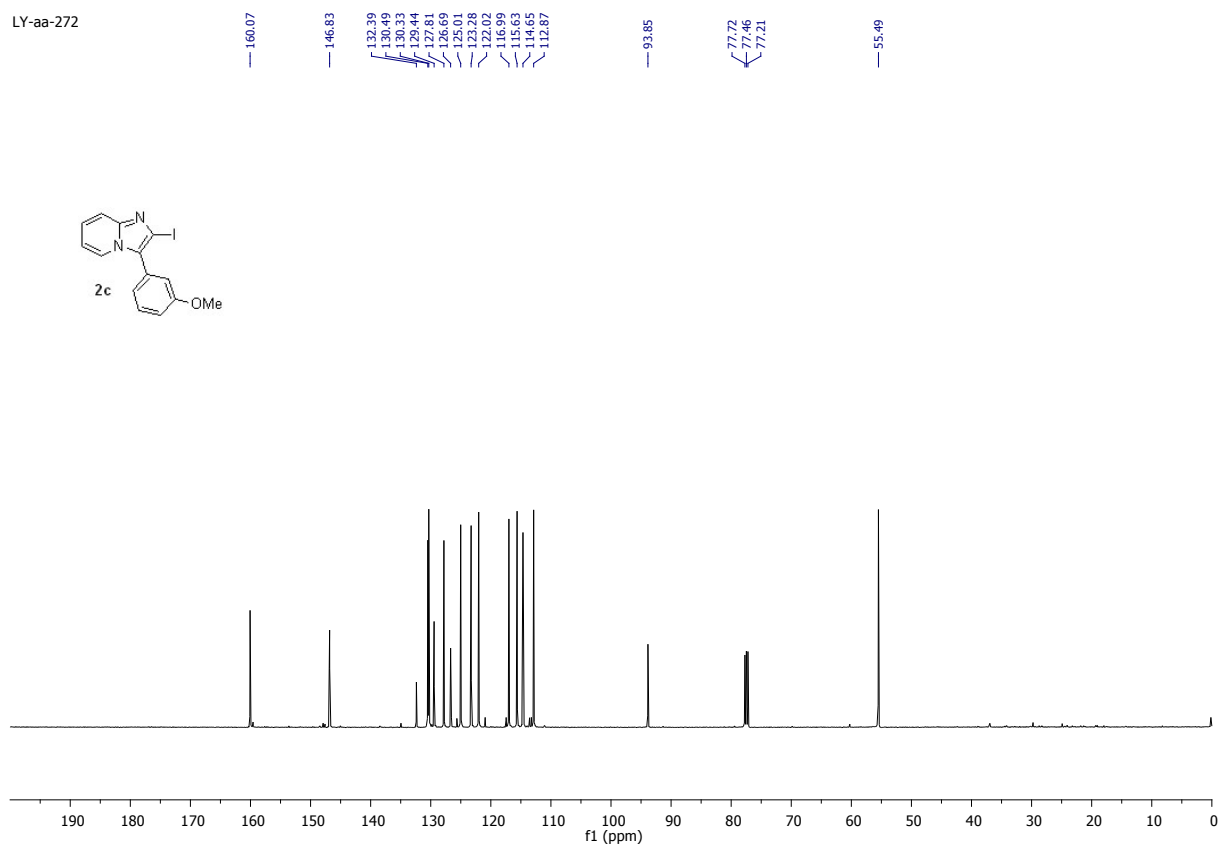




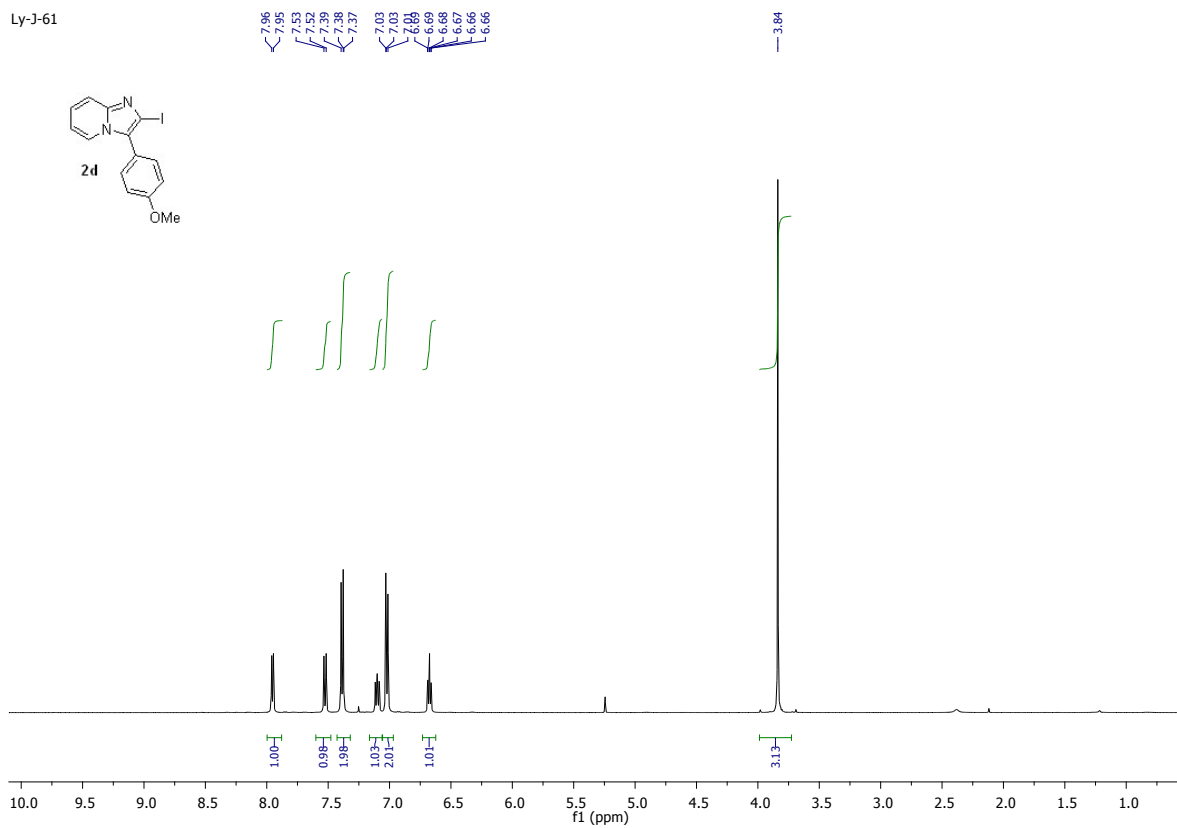
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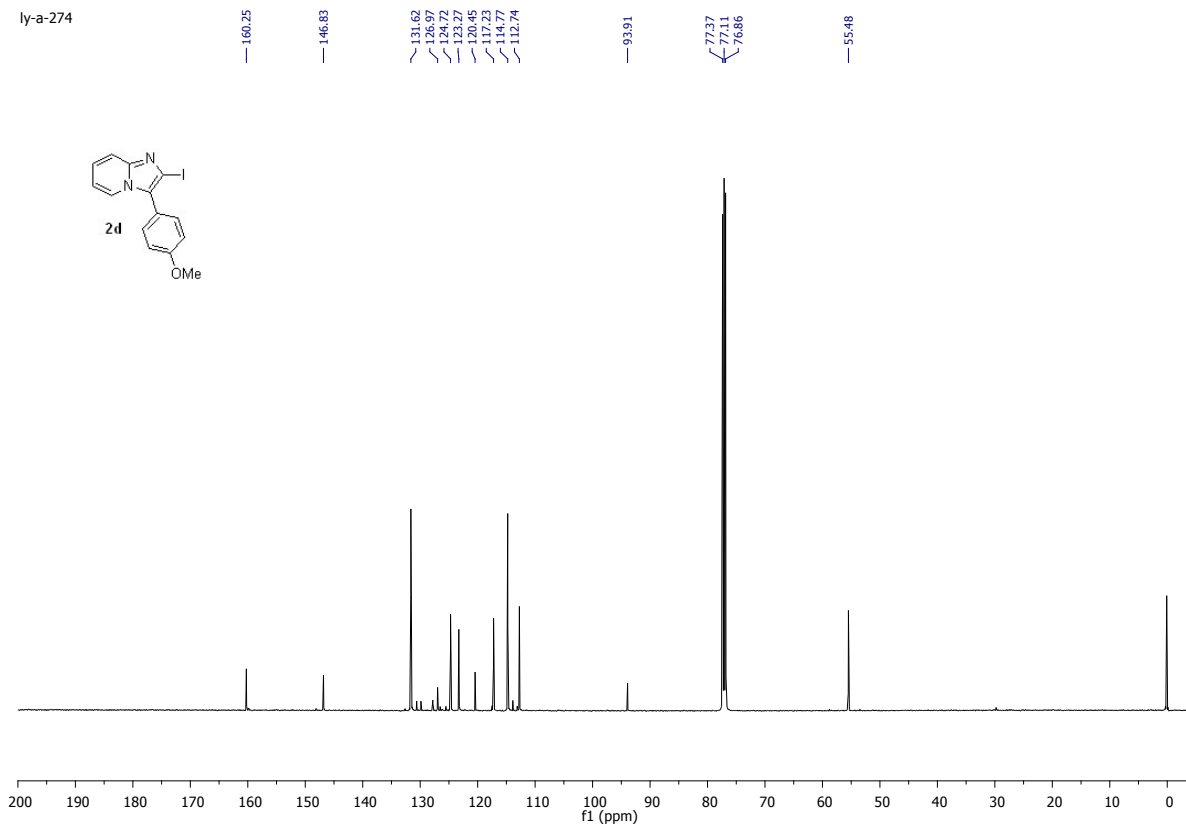
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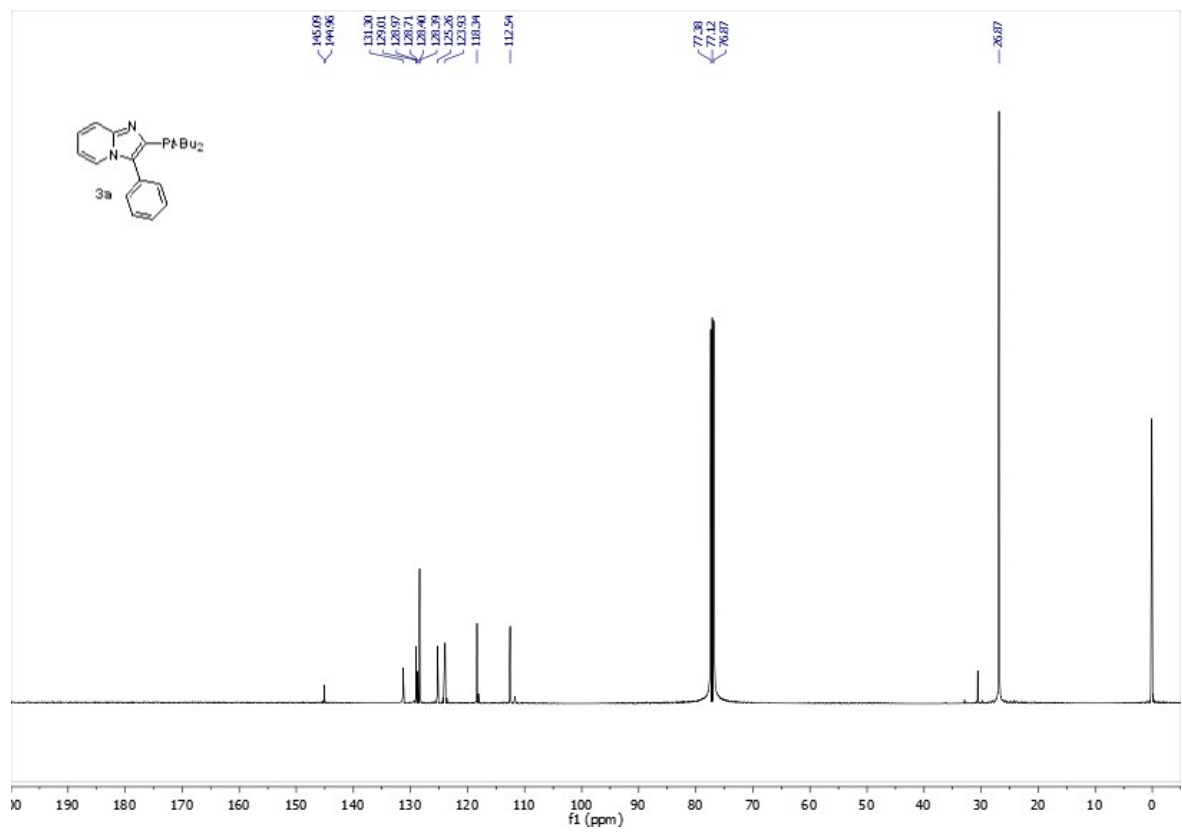
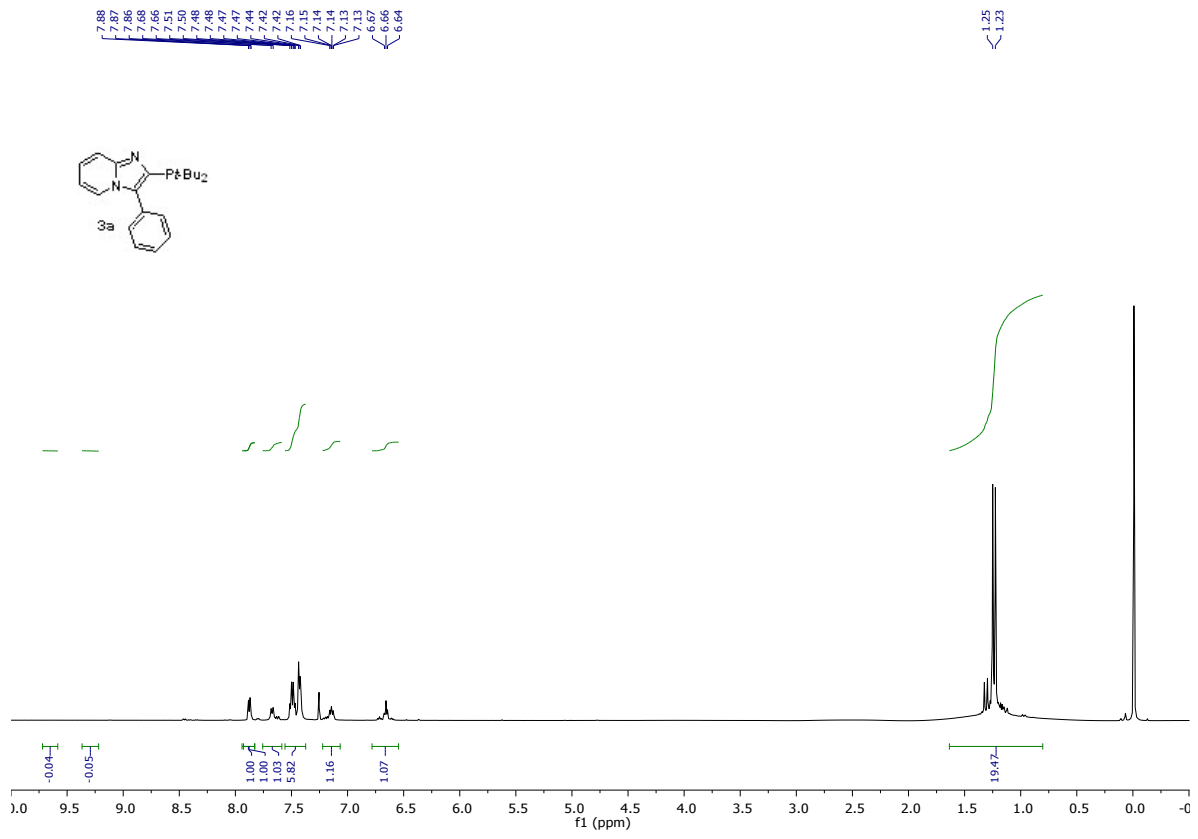


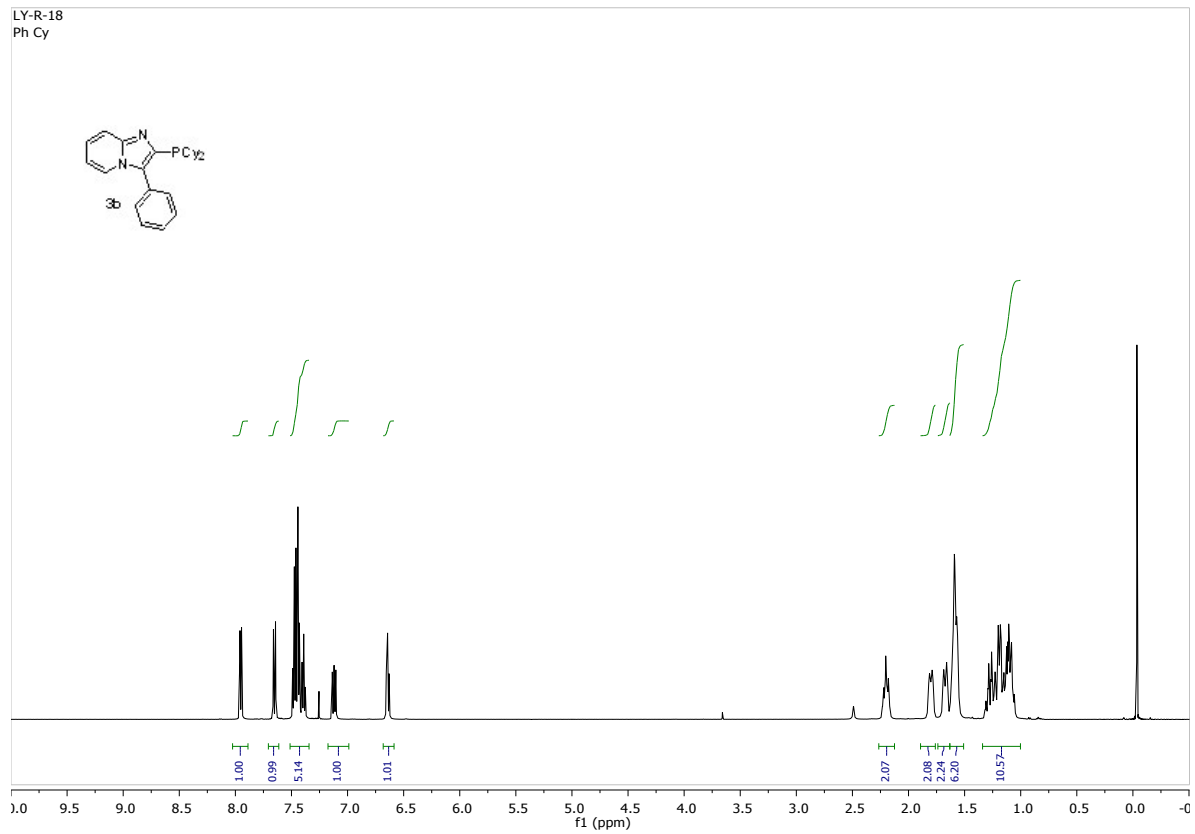
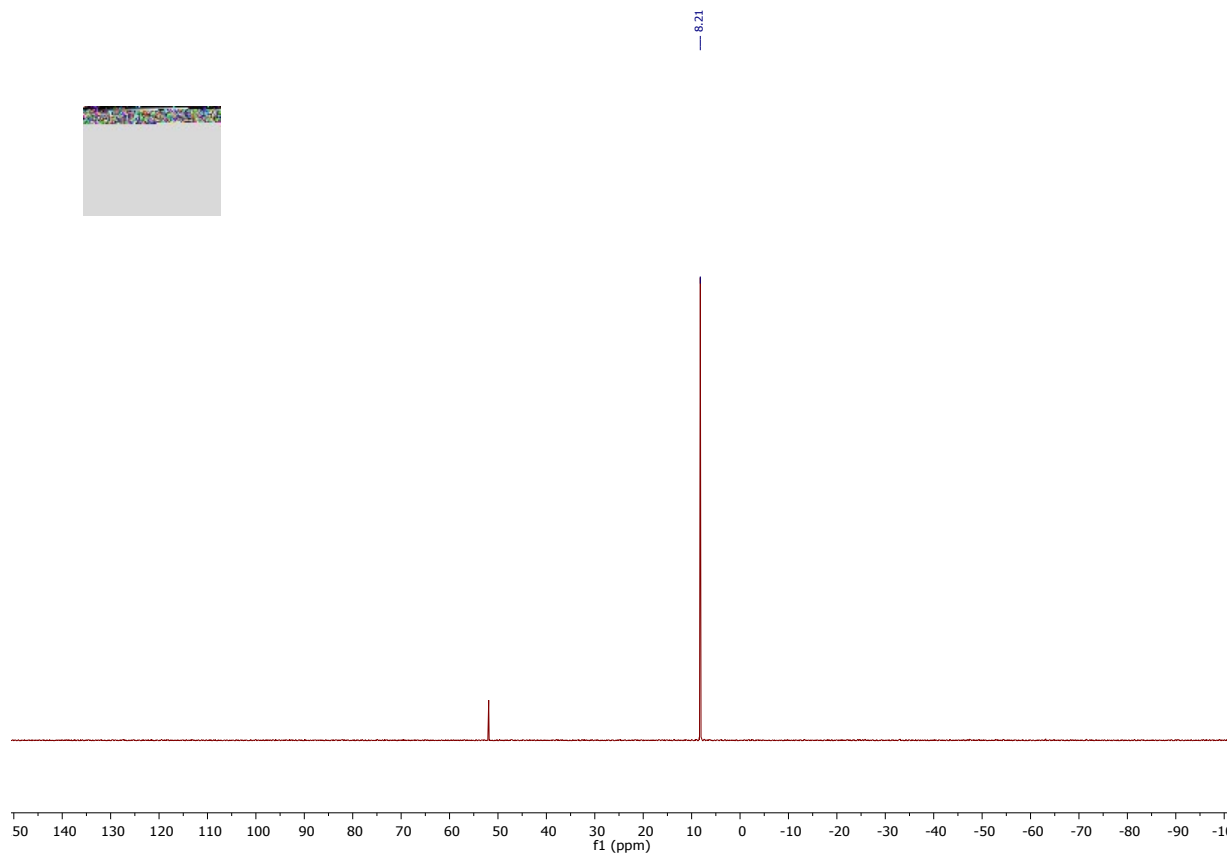
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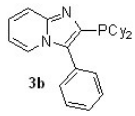
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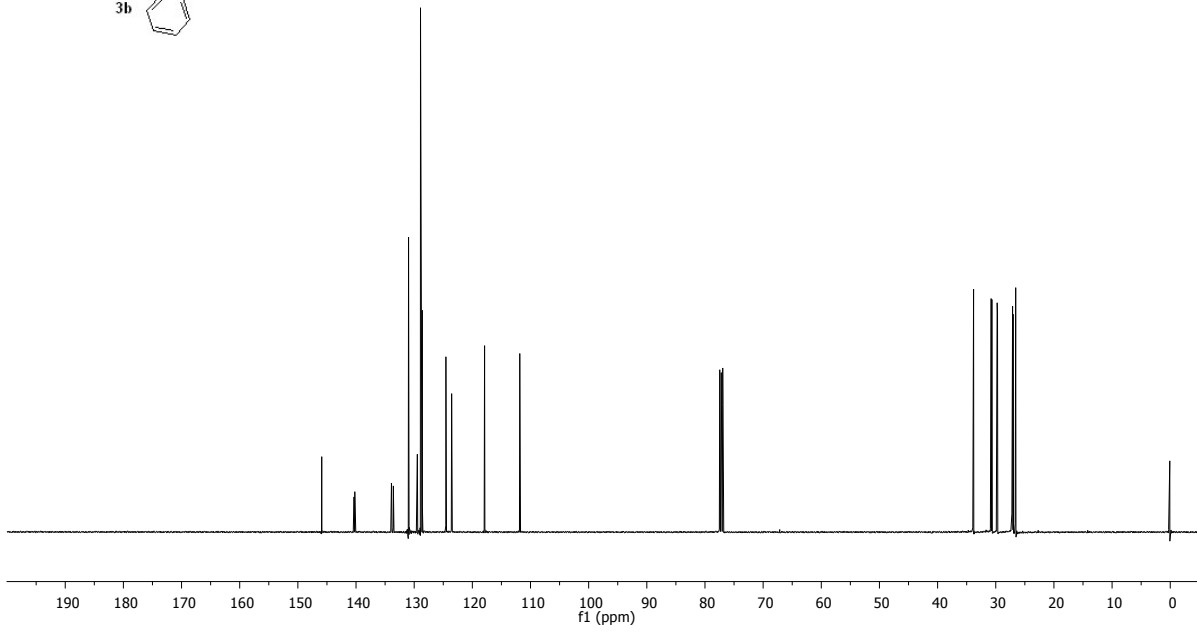
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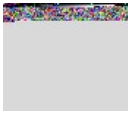
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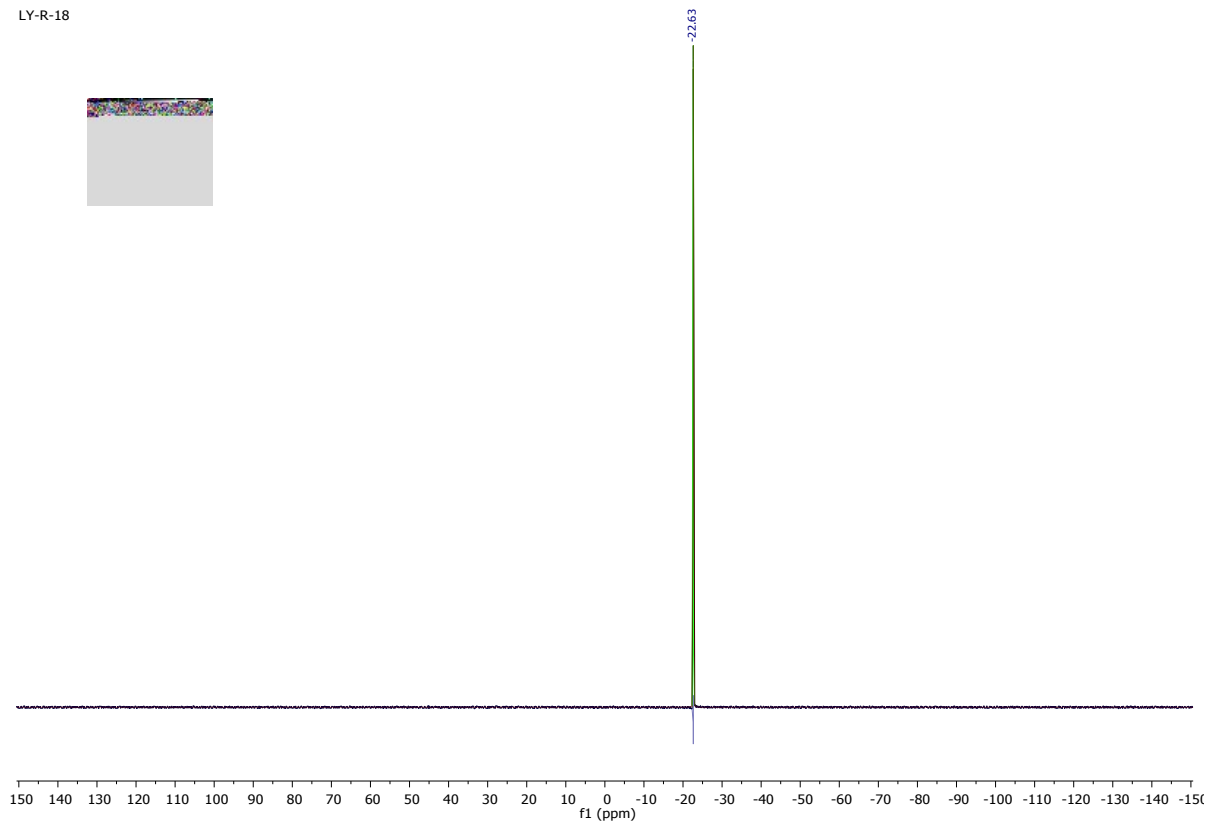
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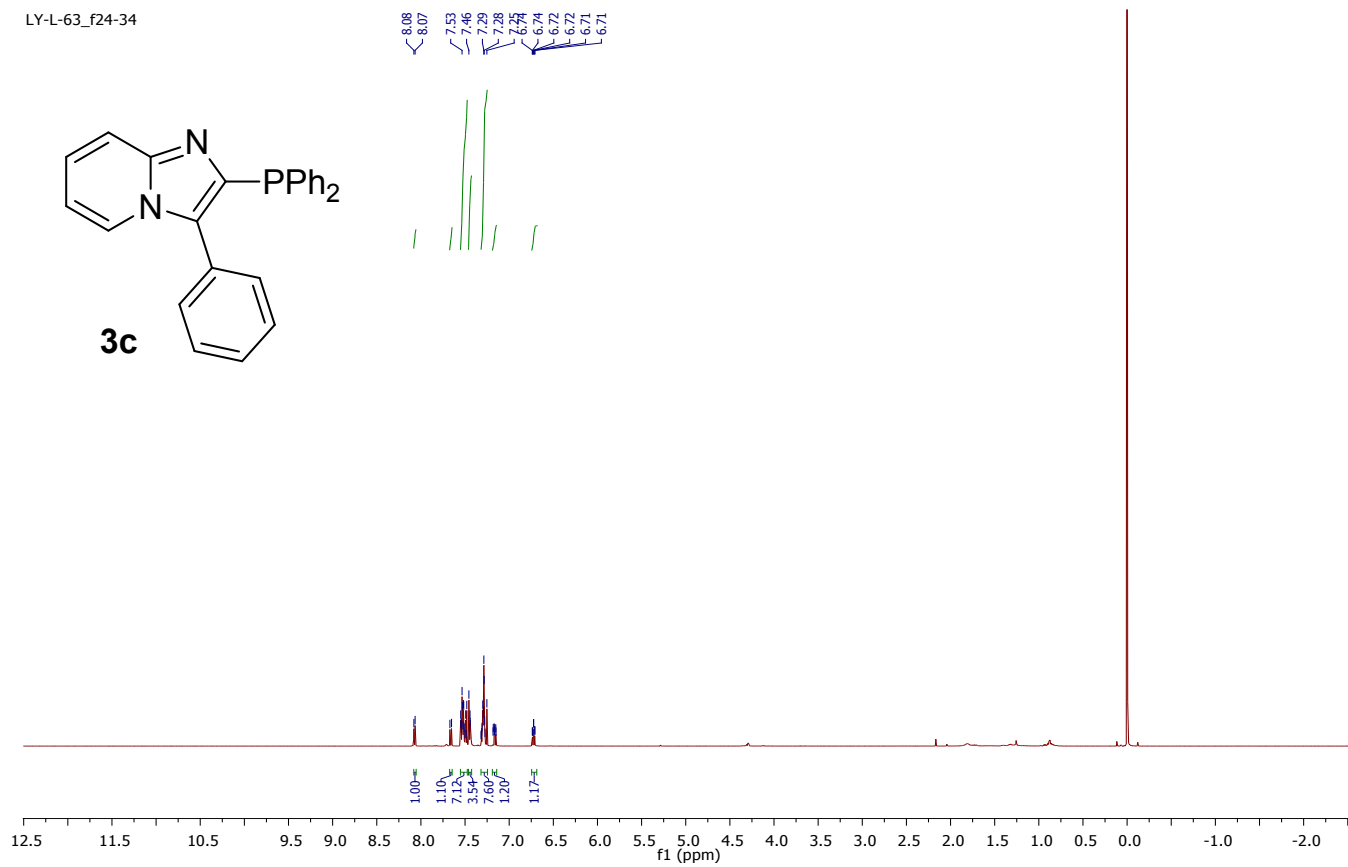
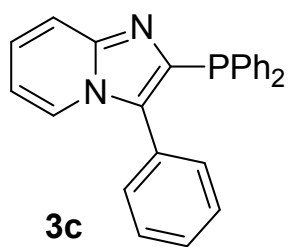


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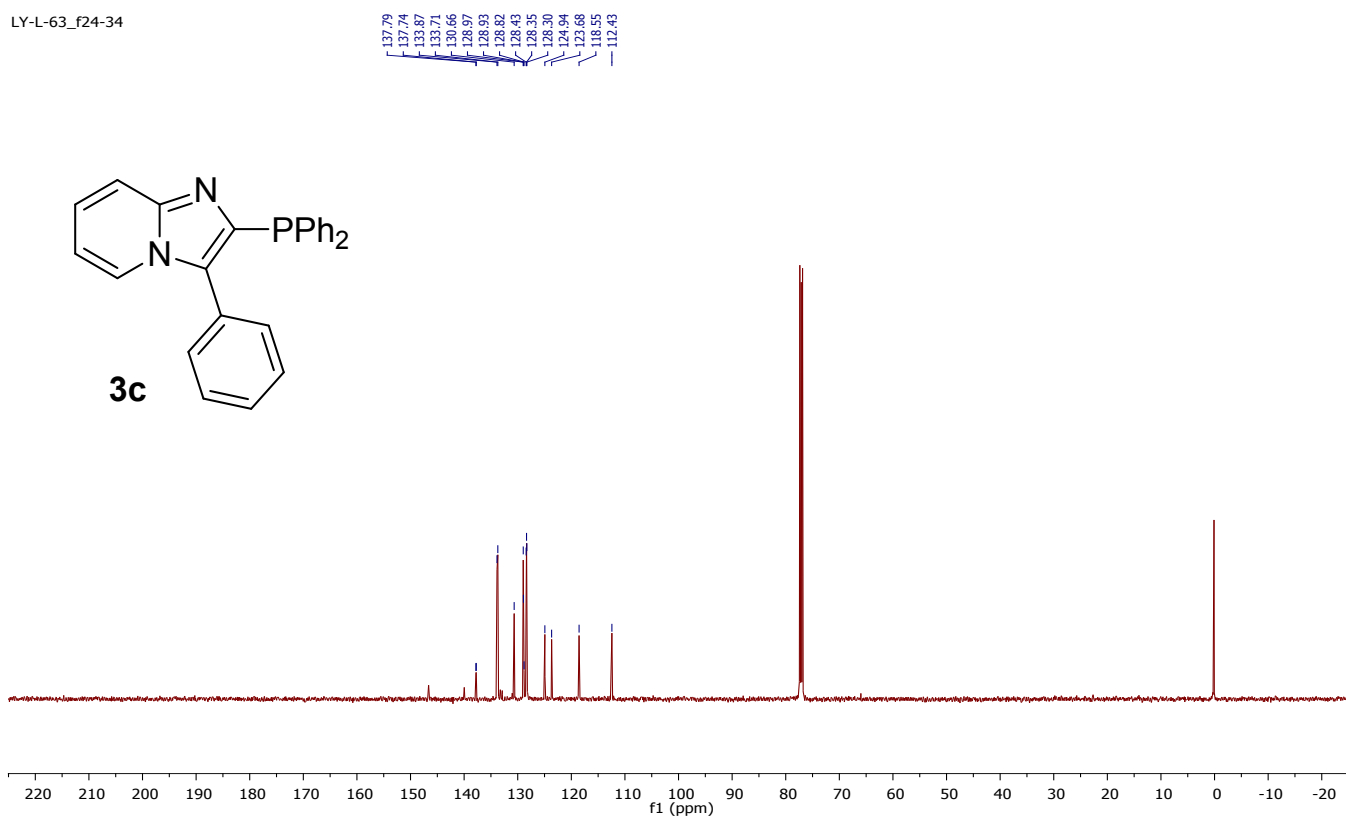
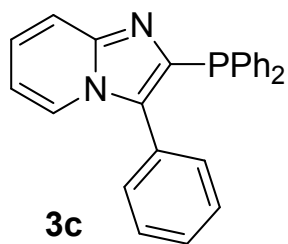




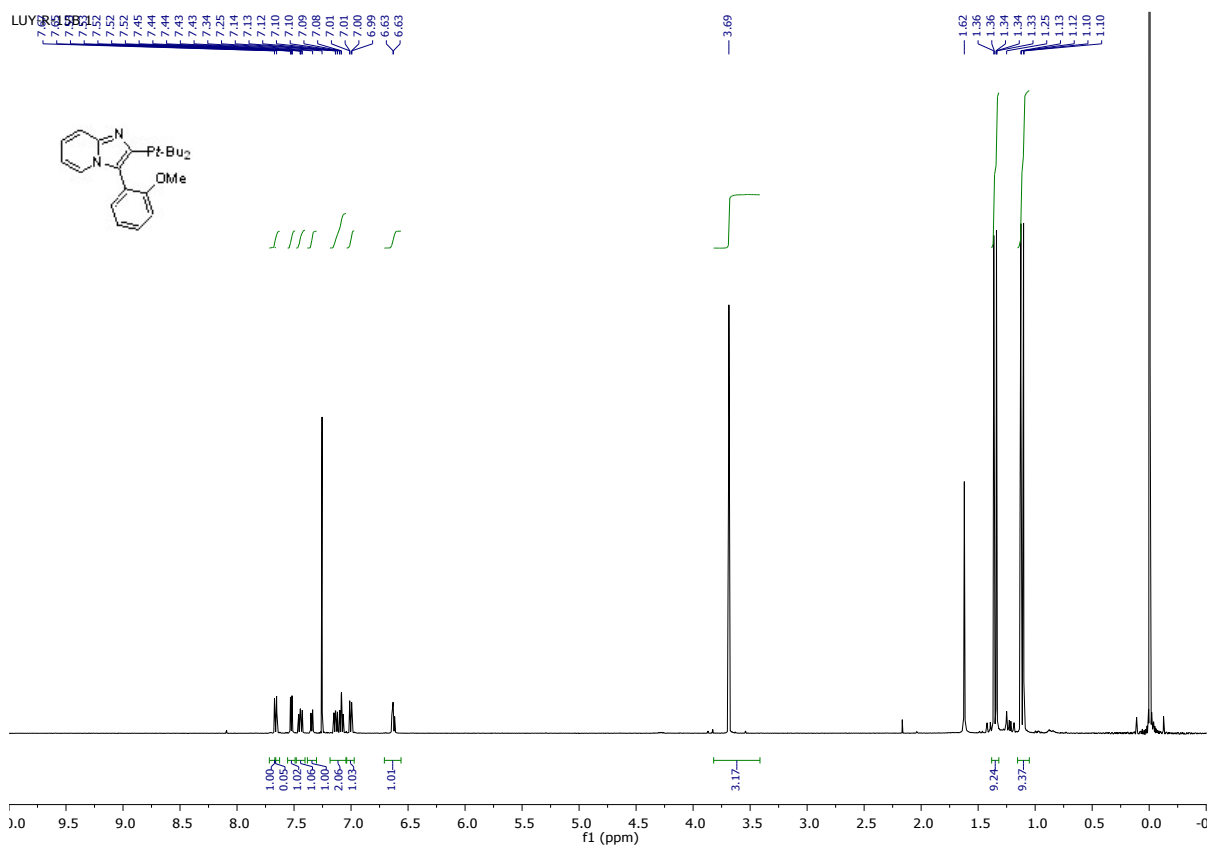
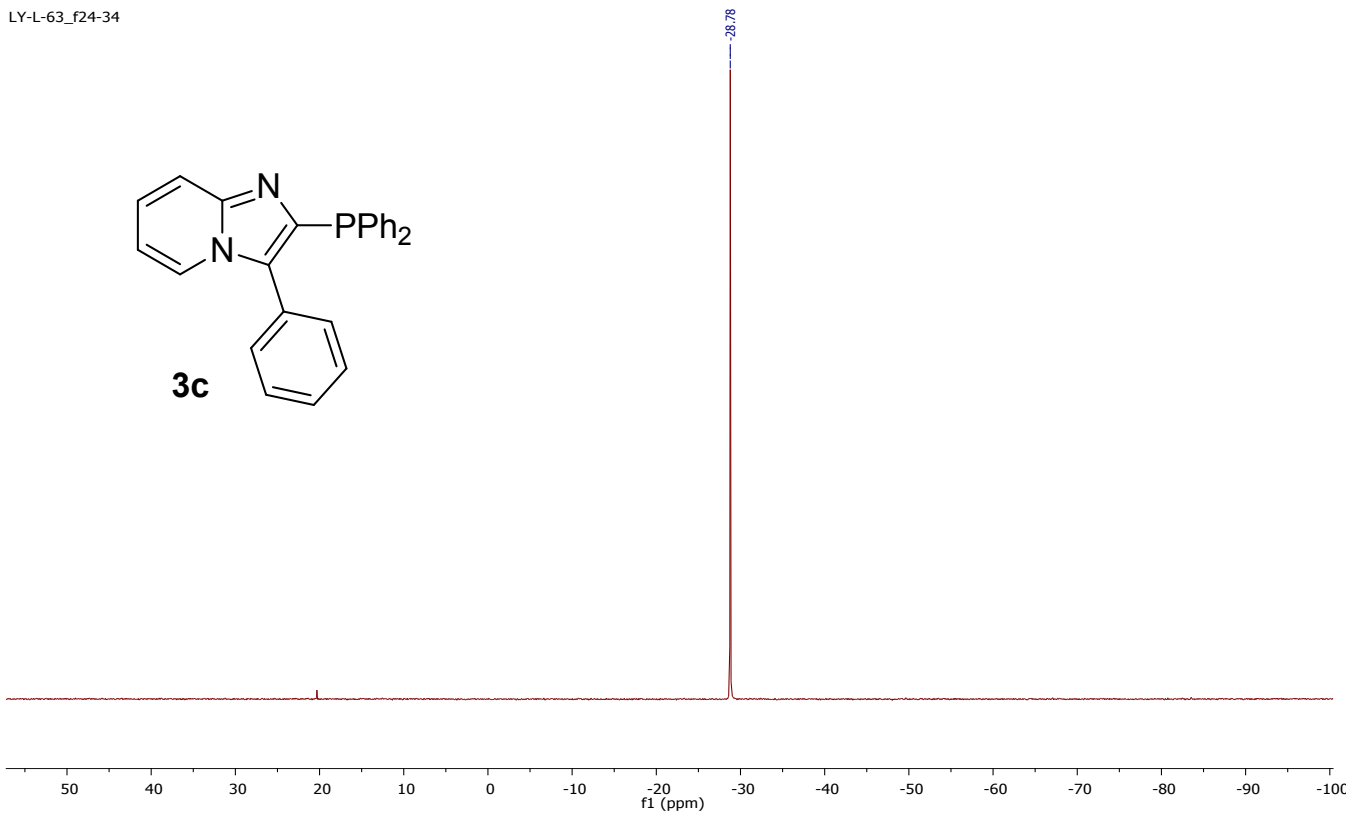
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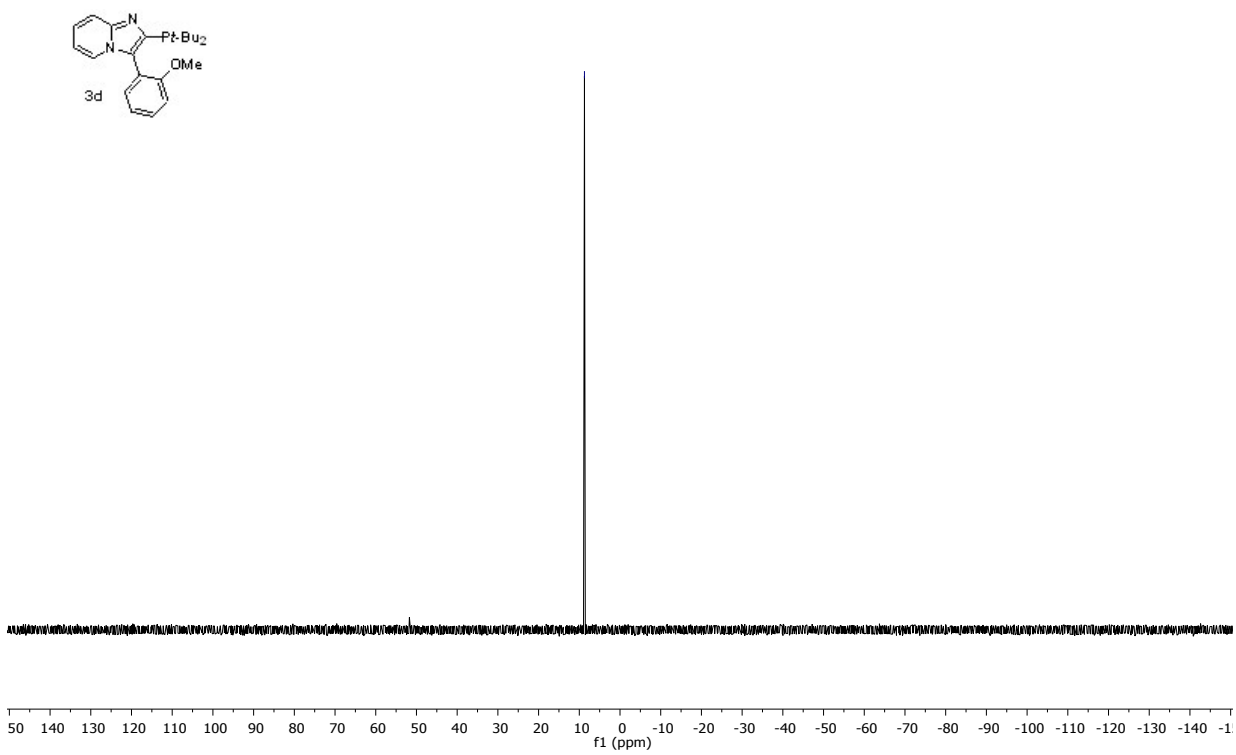
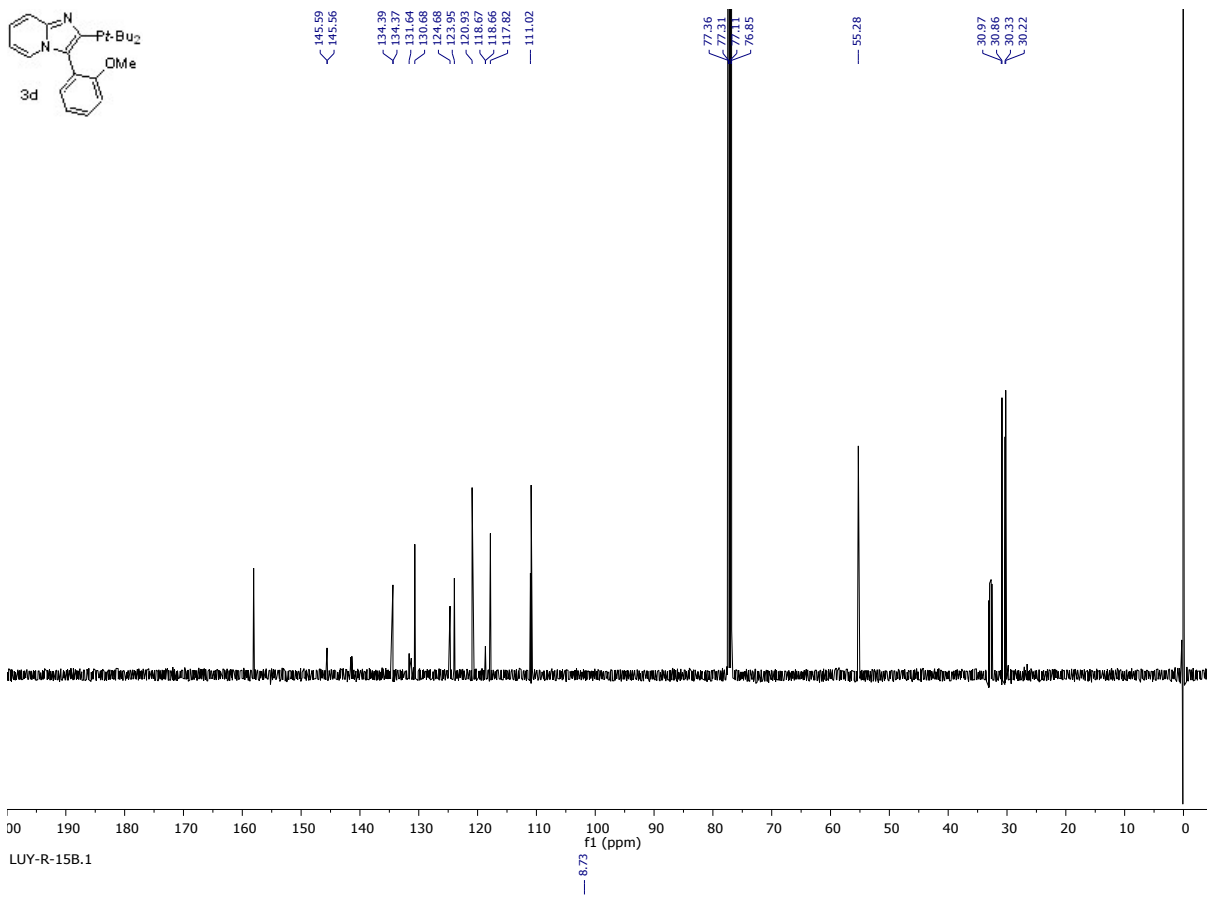


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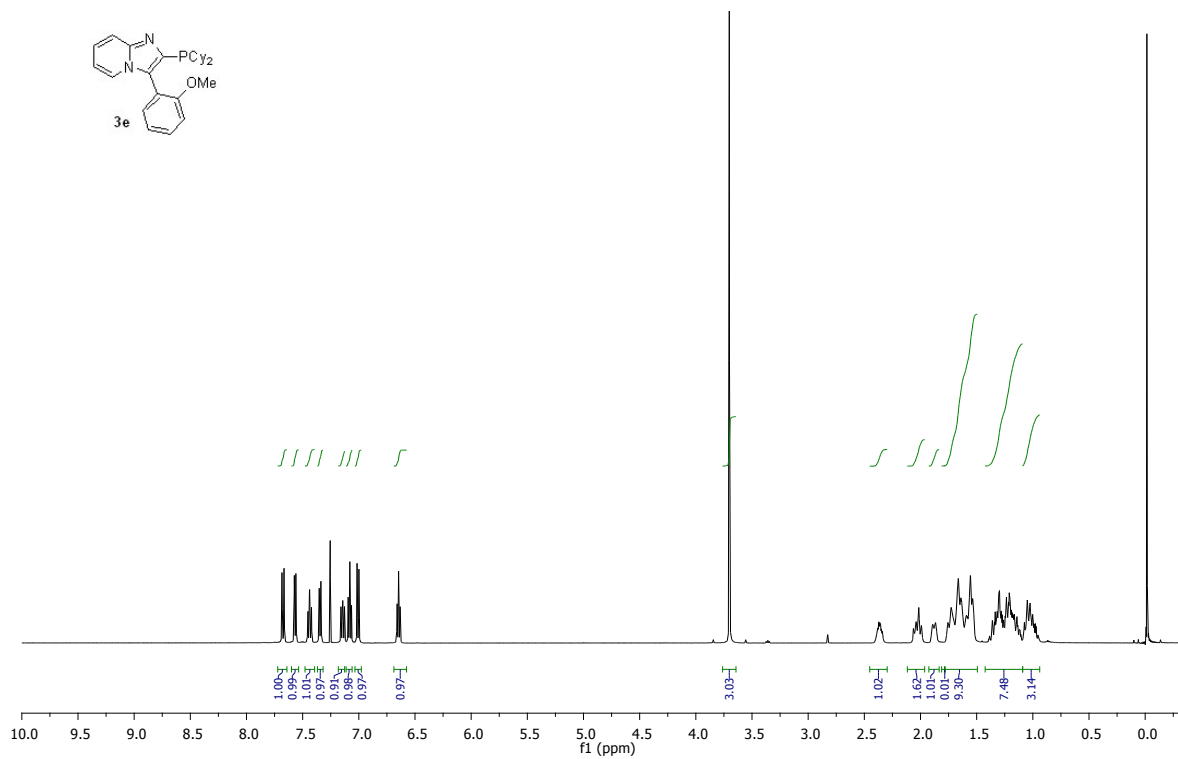
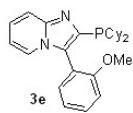


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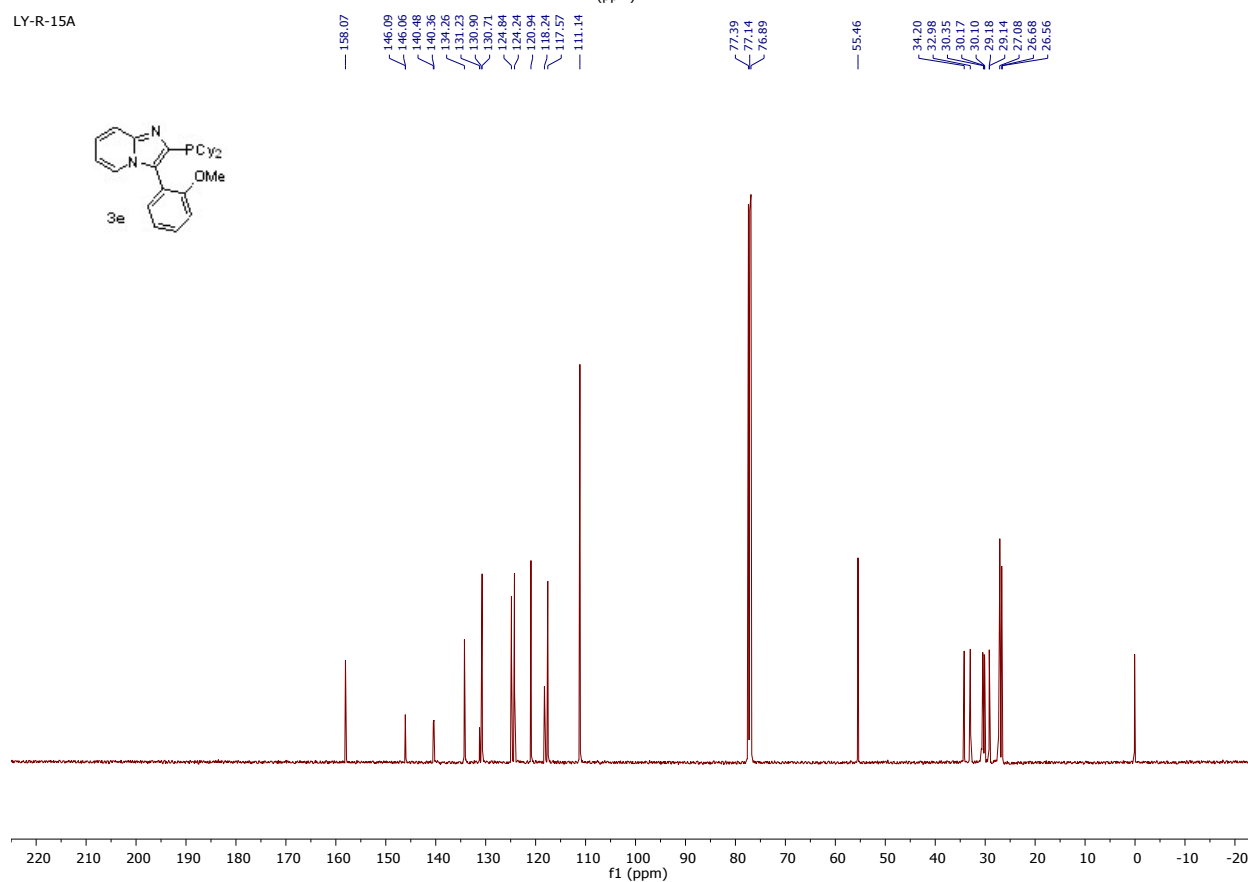
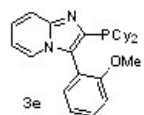




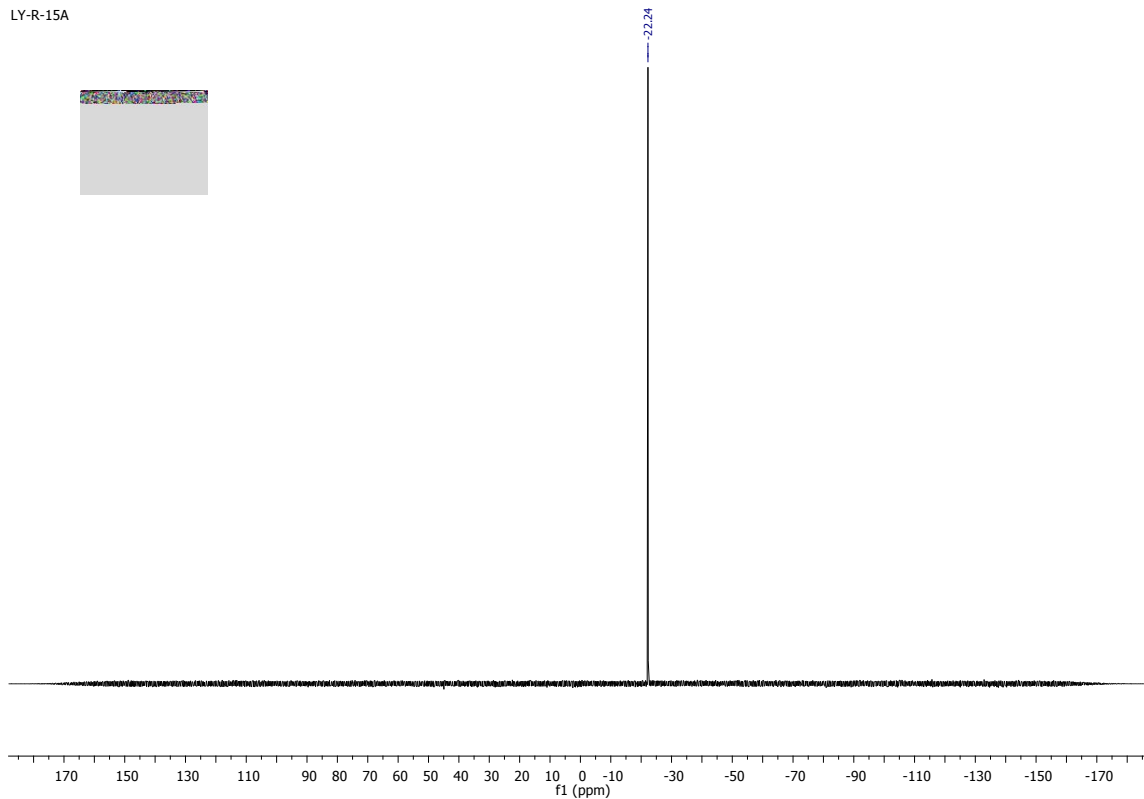
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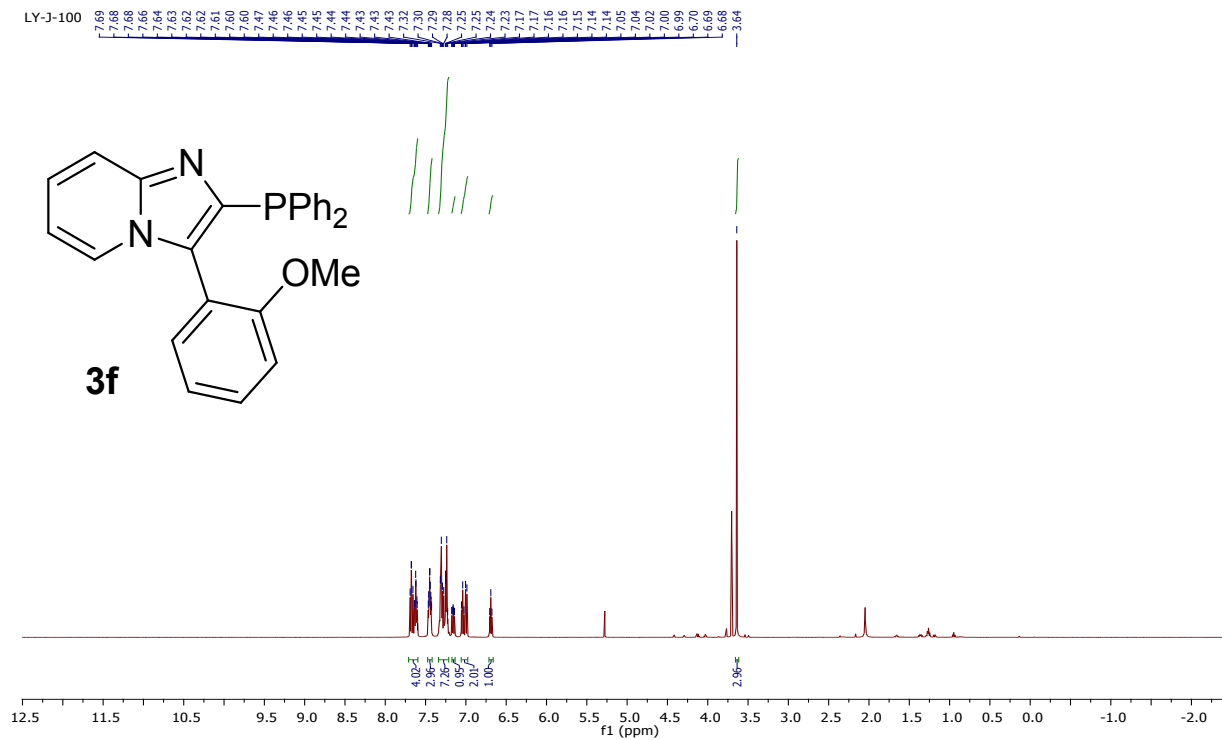
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LY-R-15A



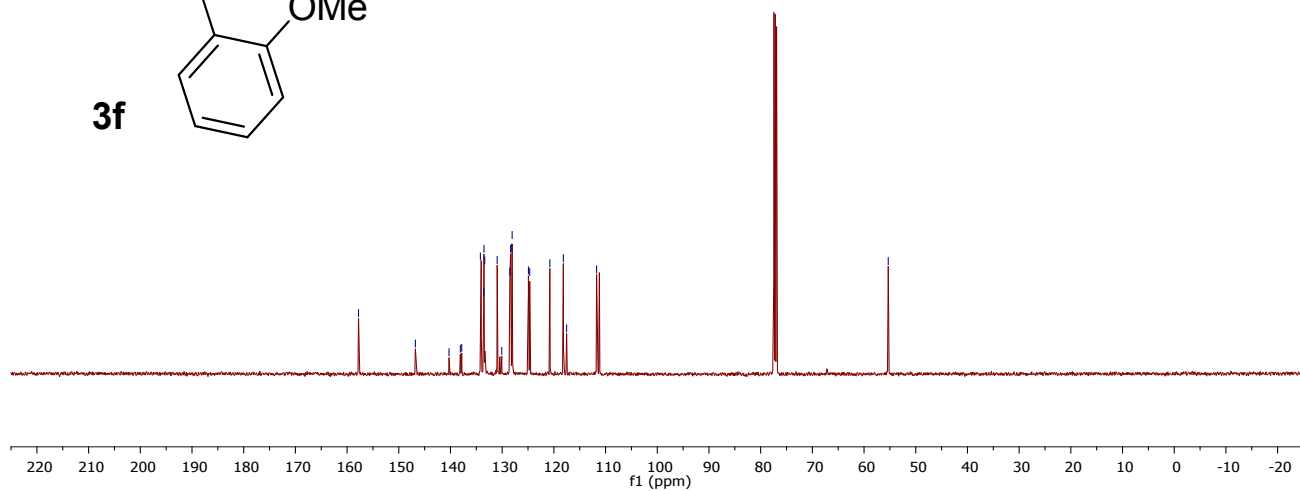
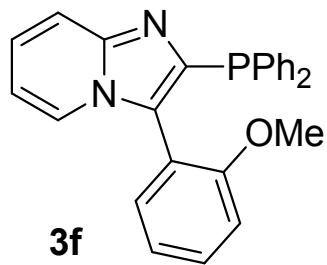
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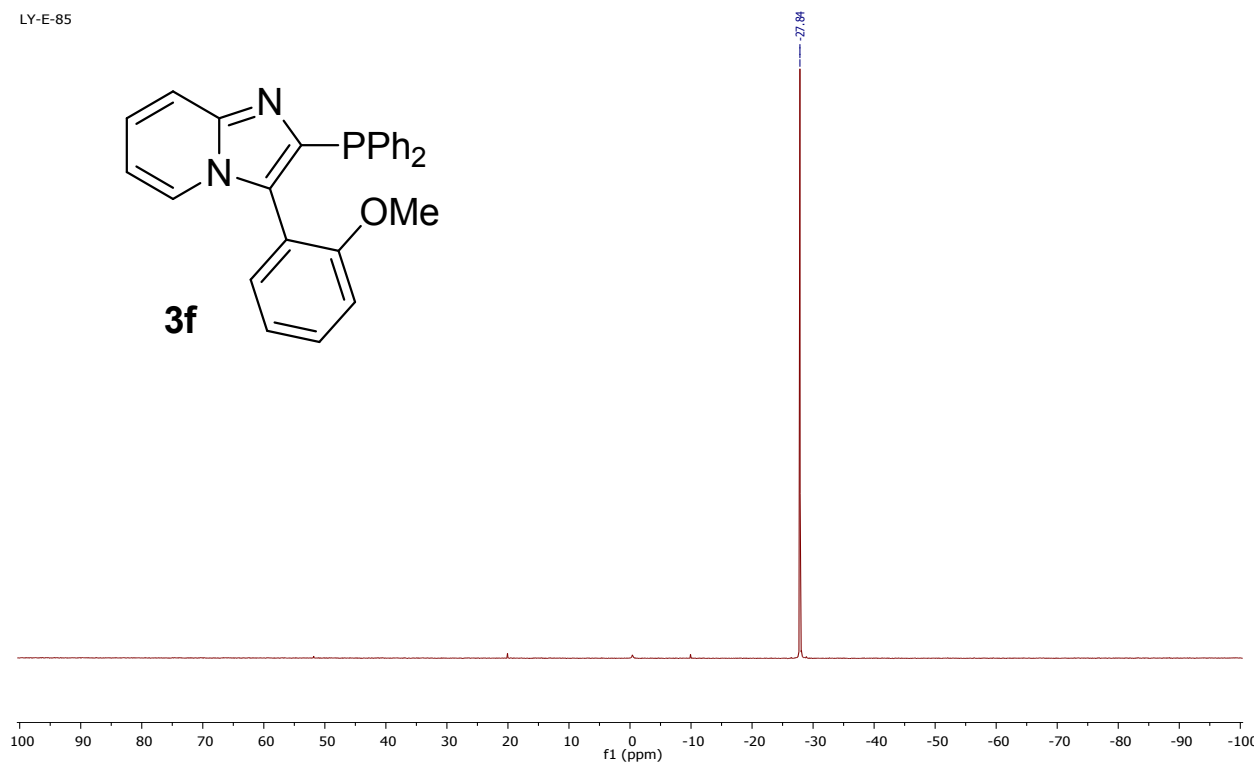
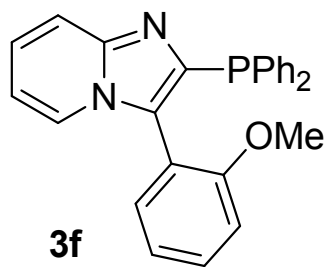
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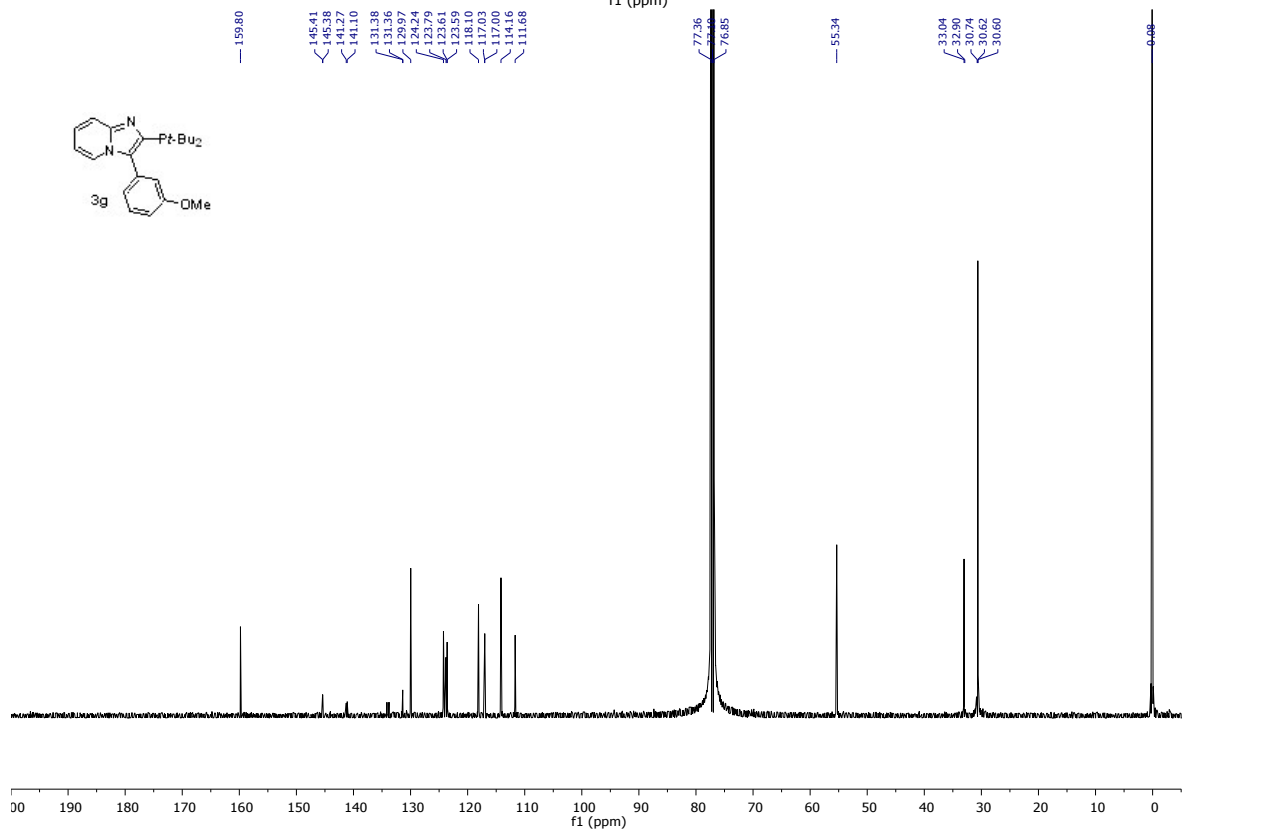
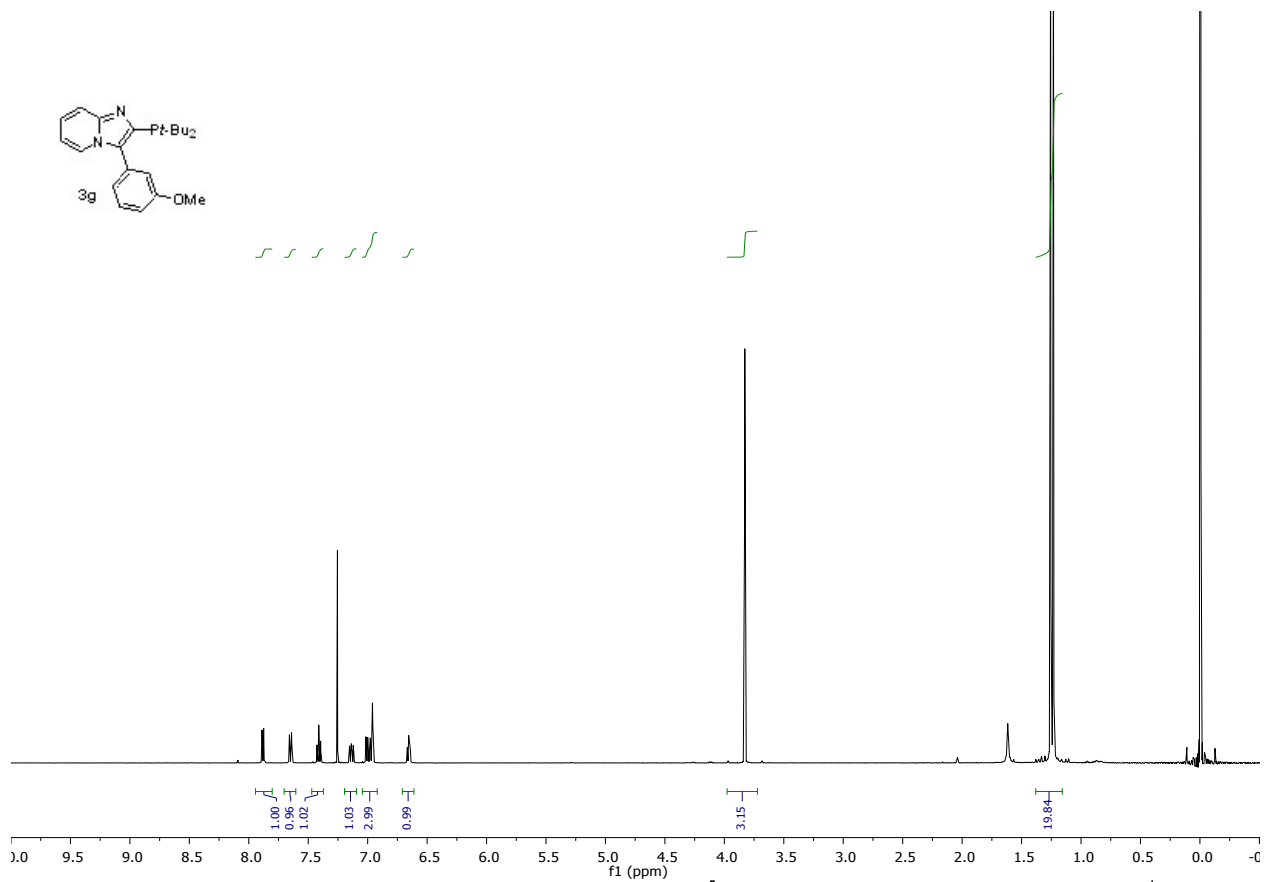
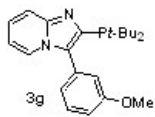
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111.74

55.32

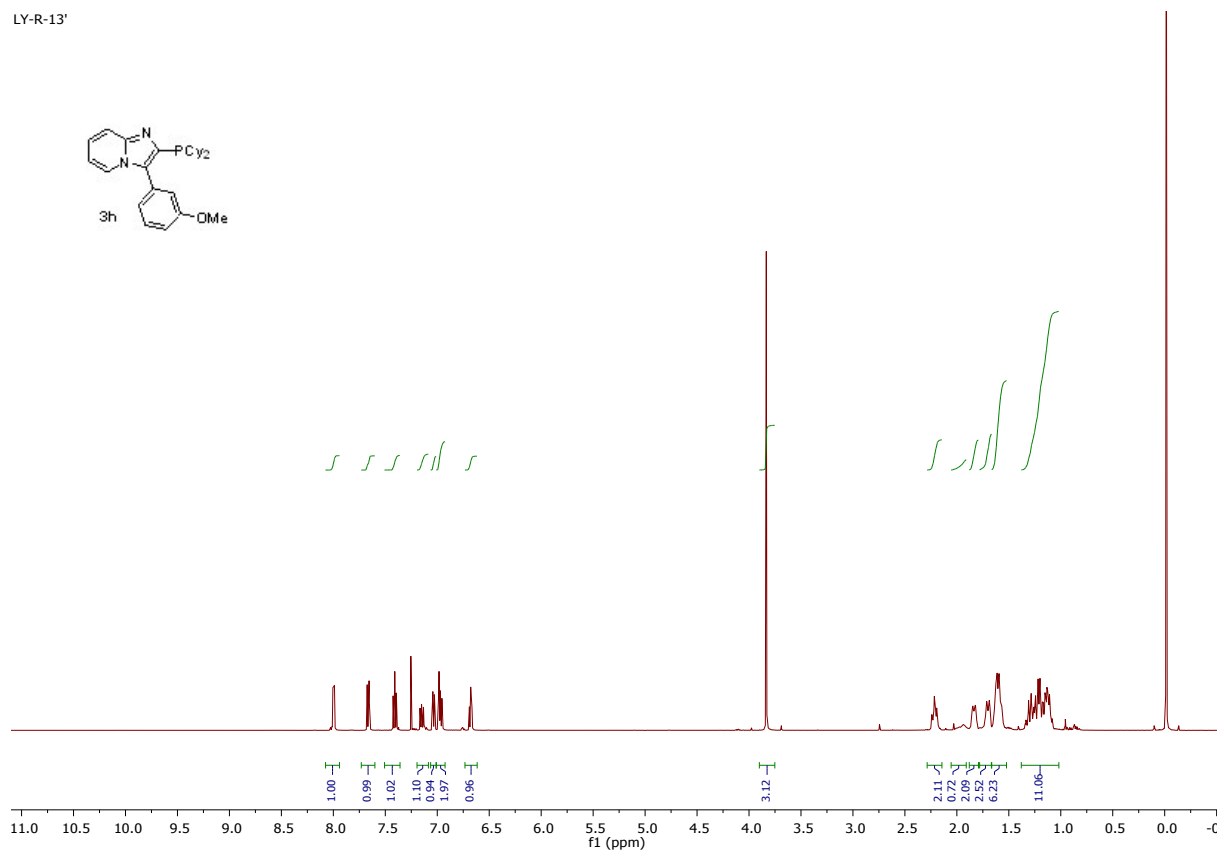


LY-E-85

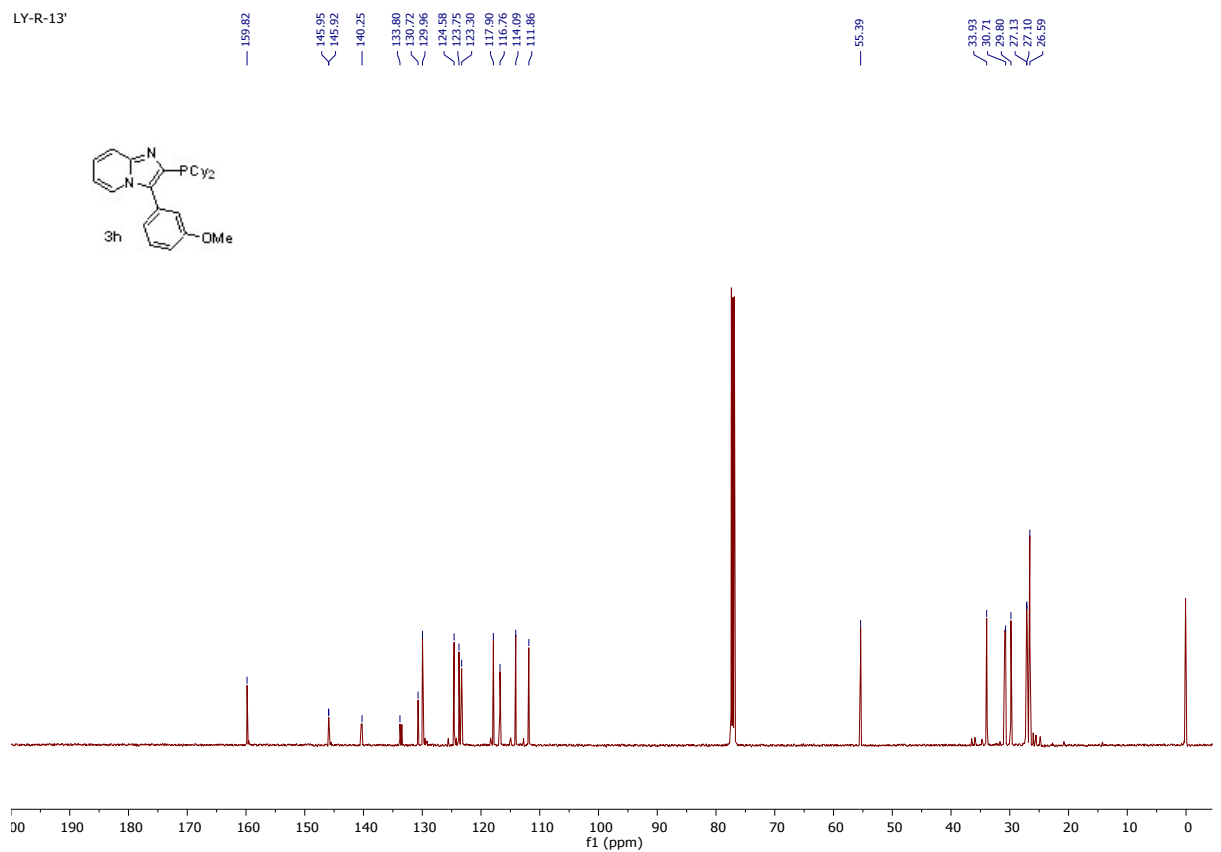




LY-R-13'

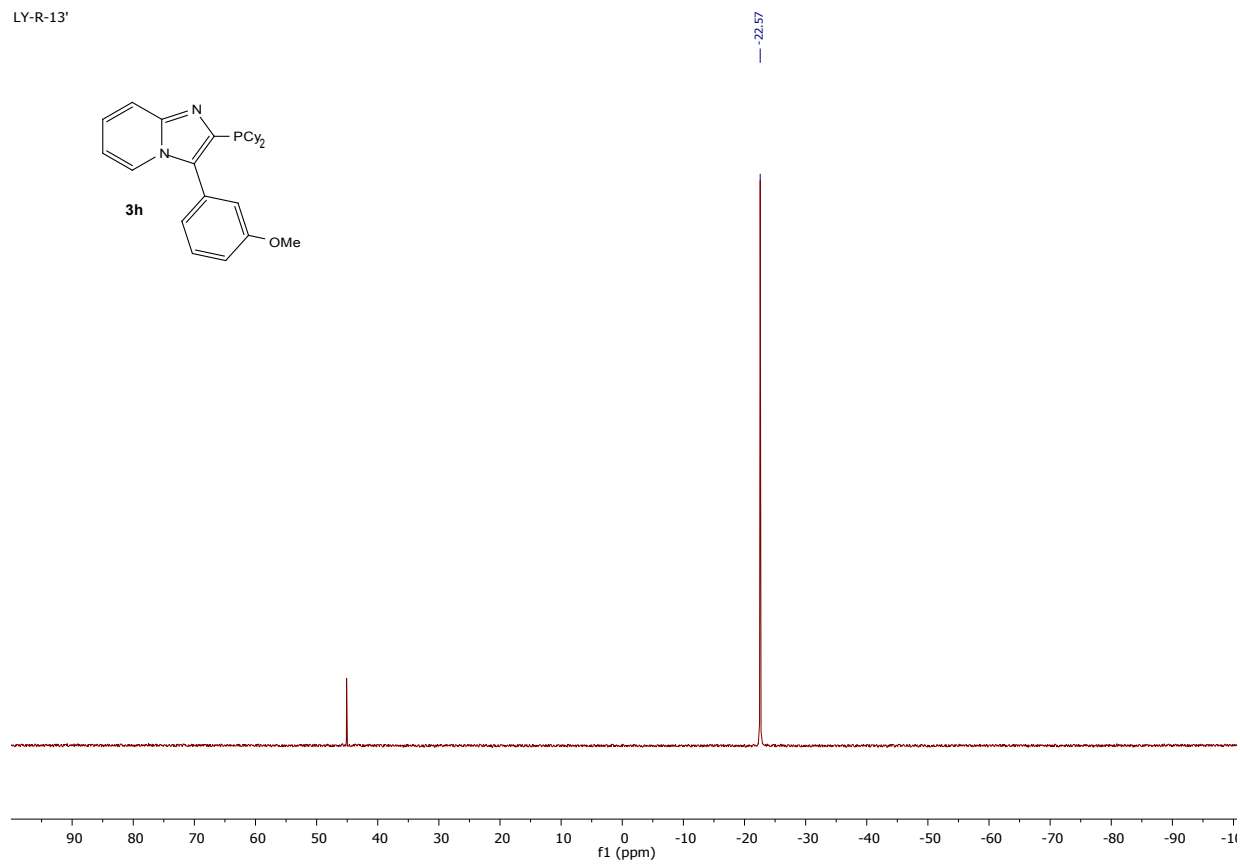
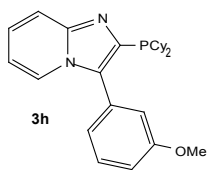


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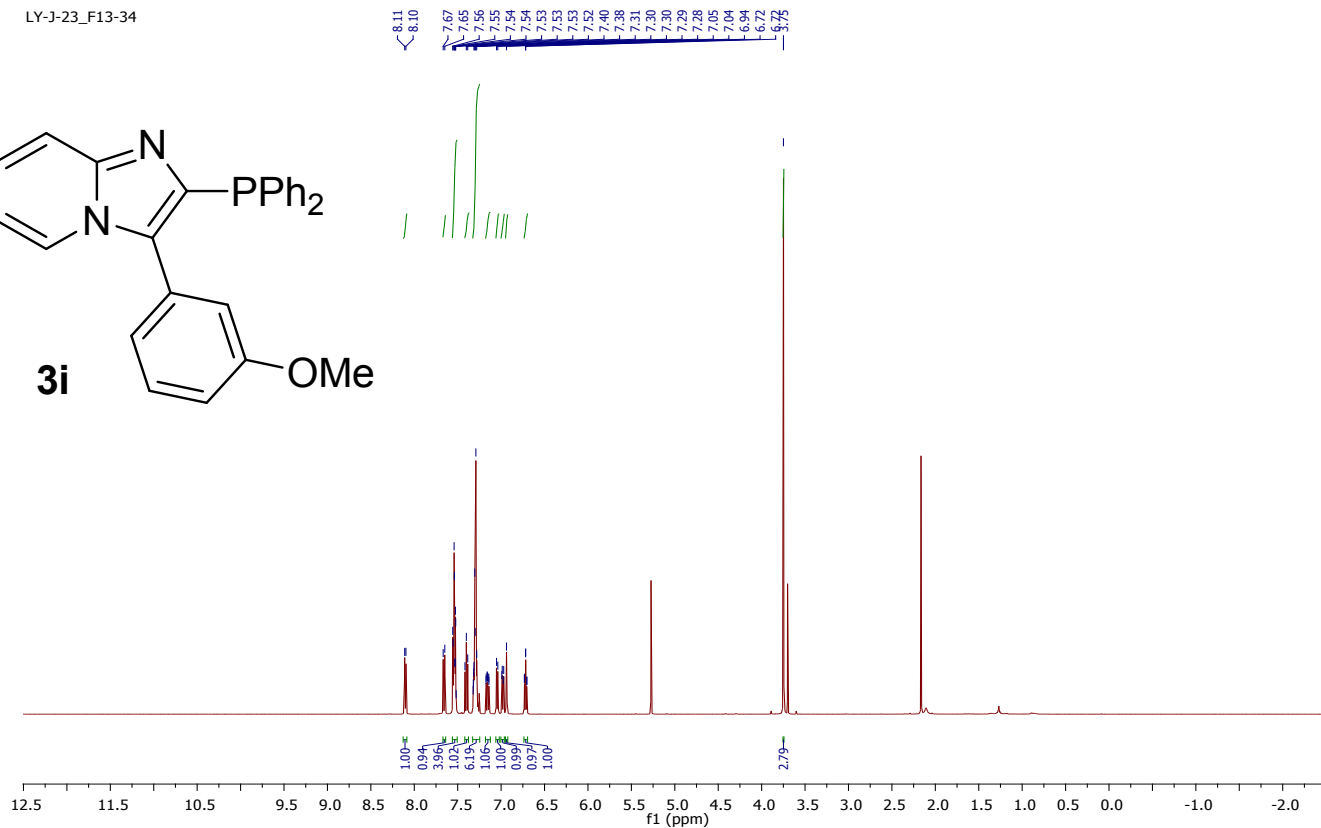
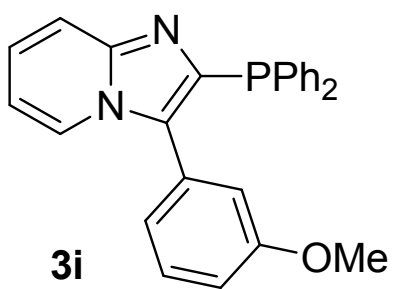




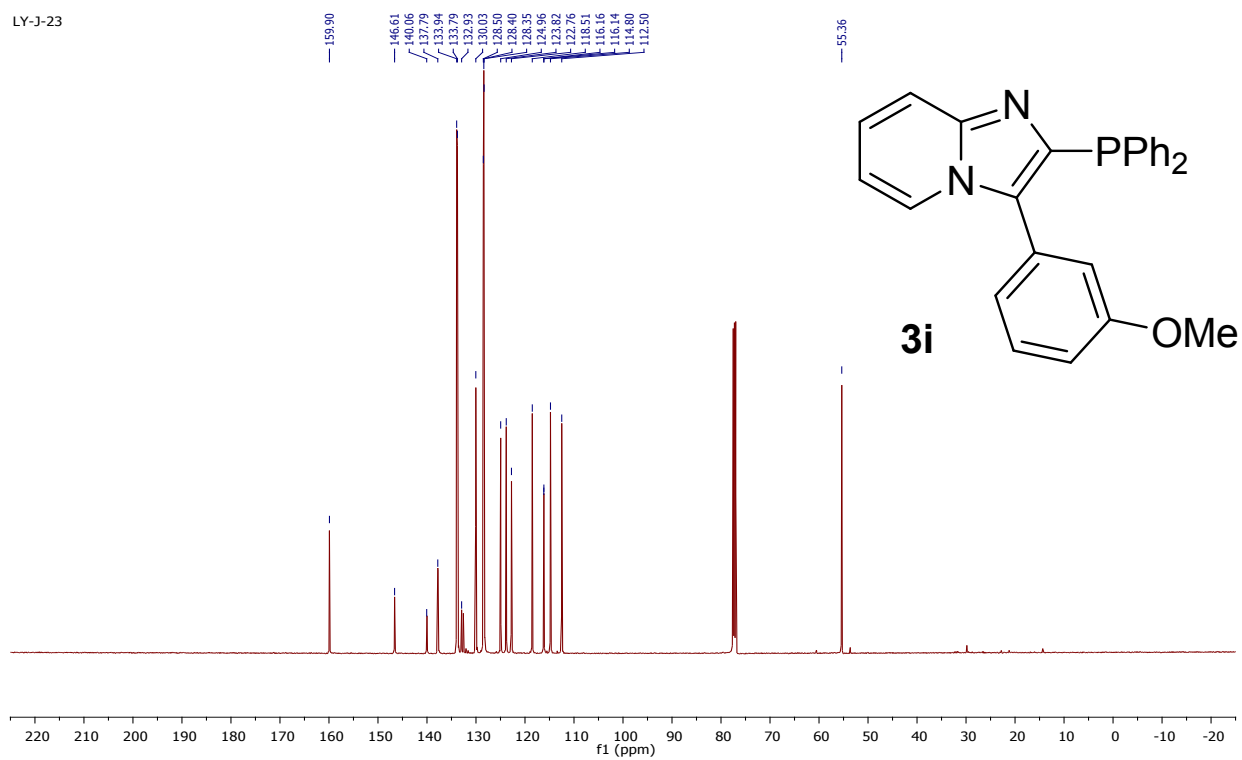
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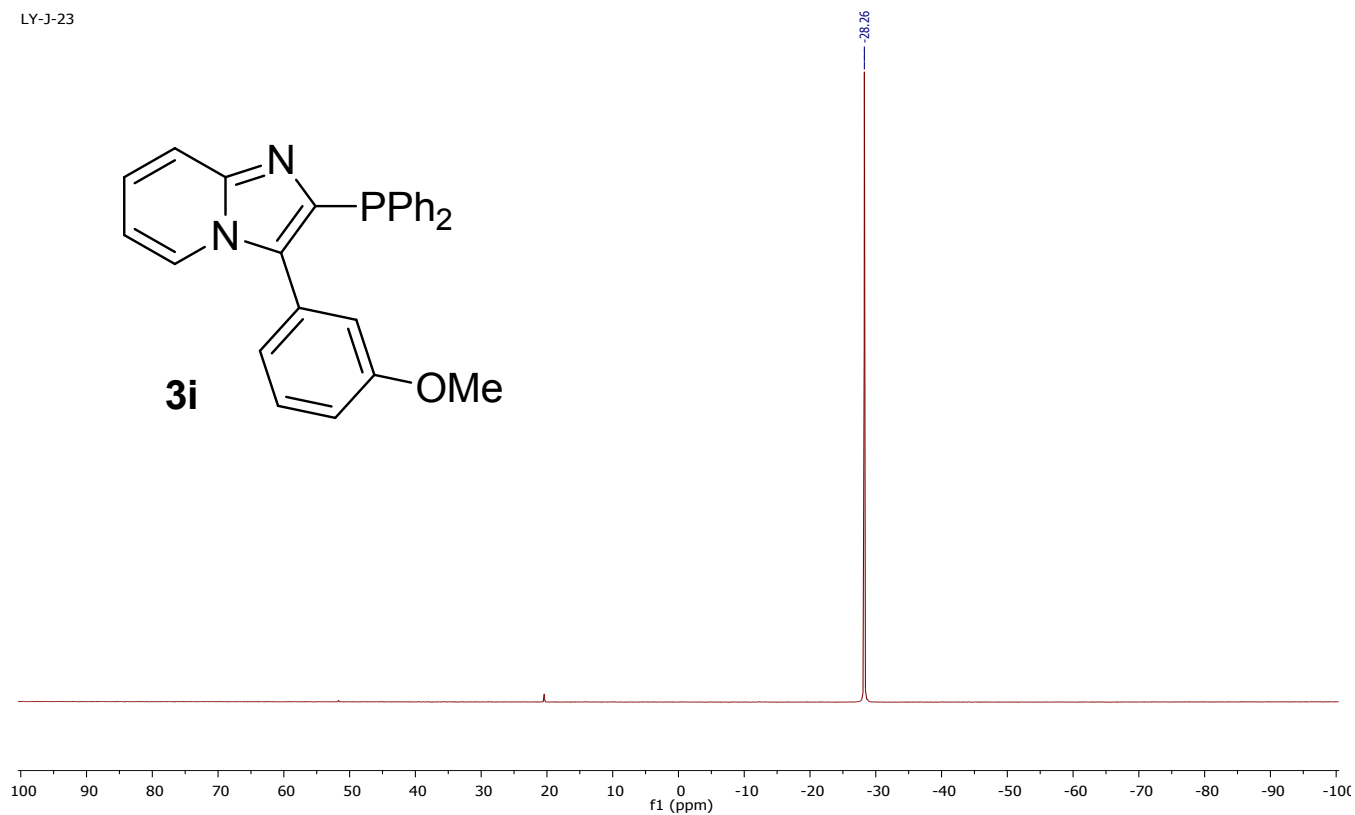
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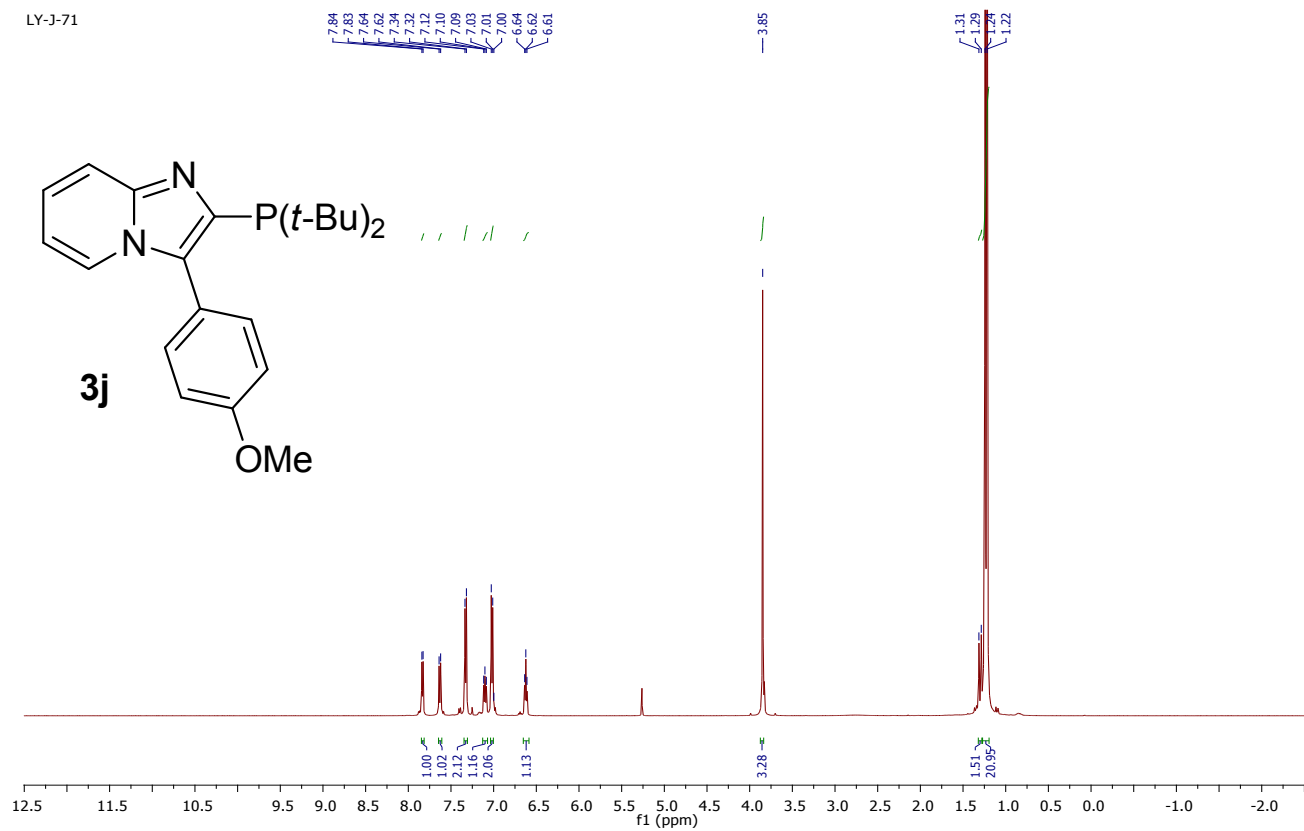
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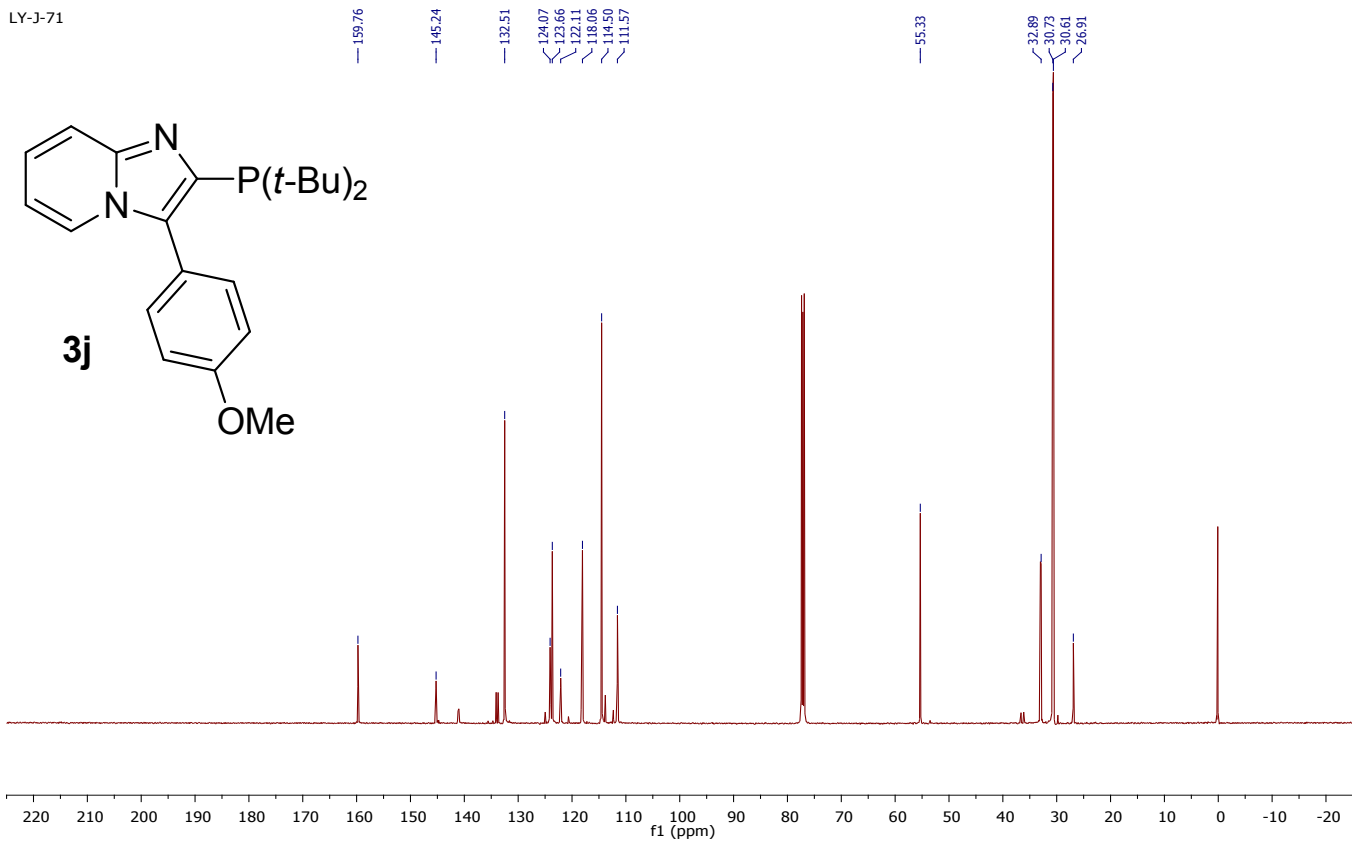
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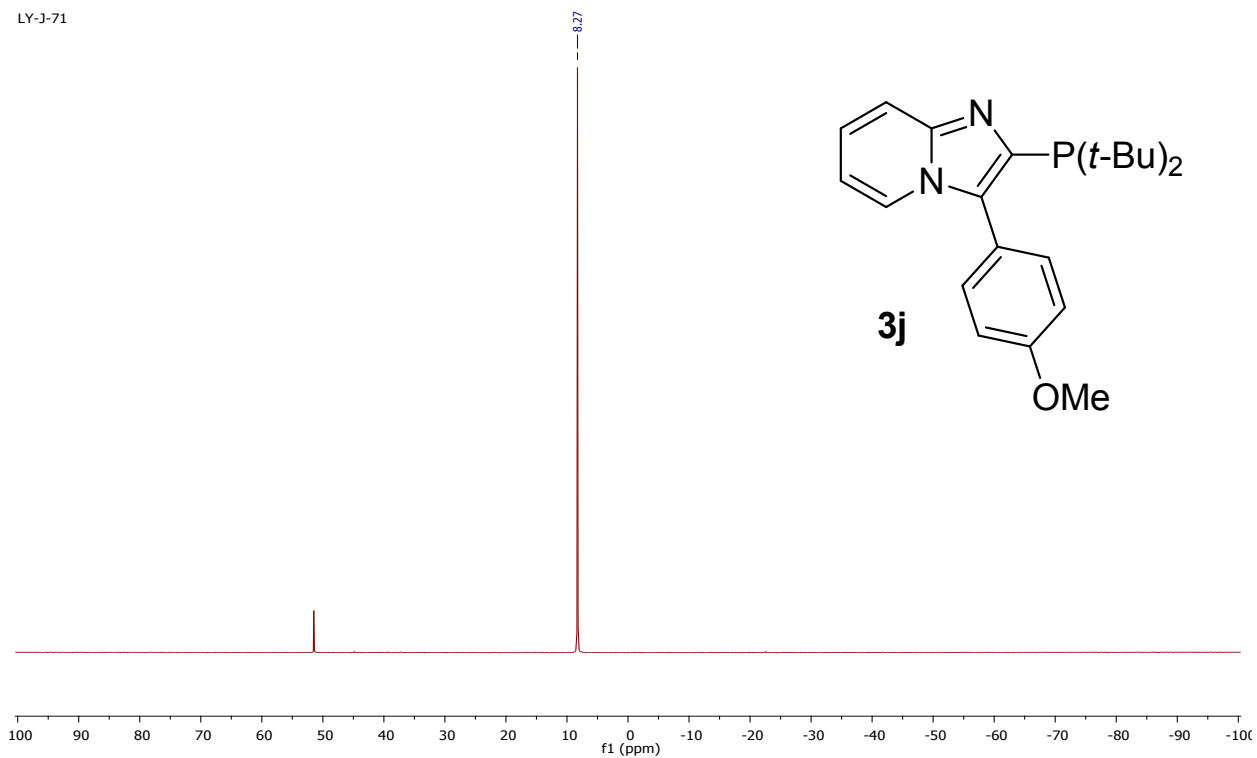
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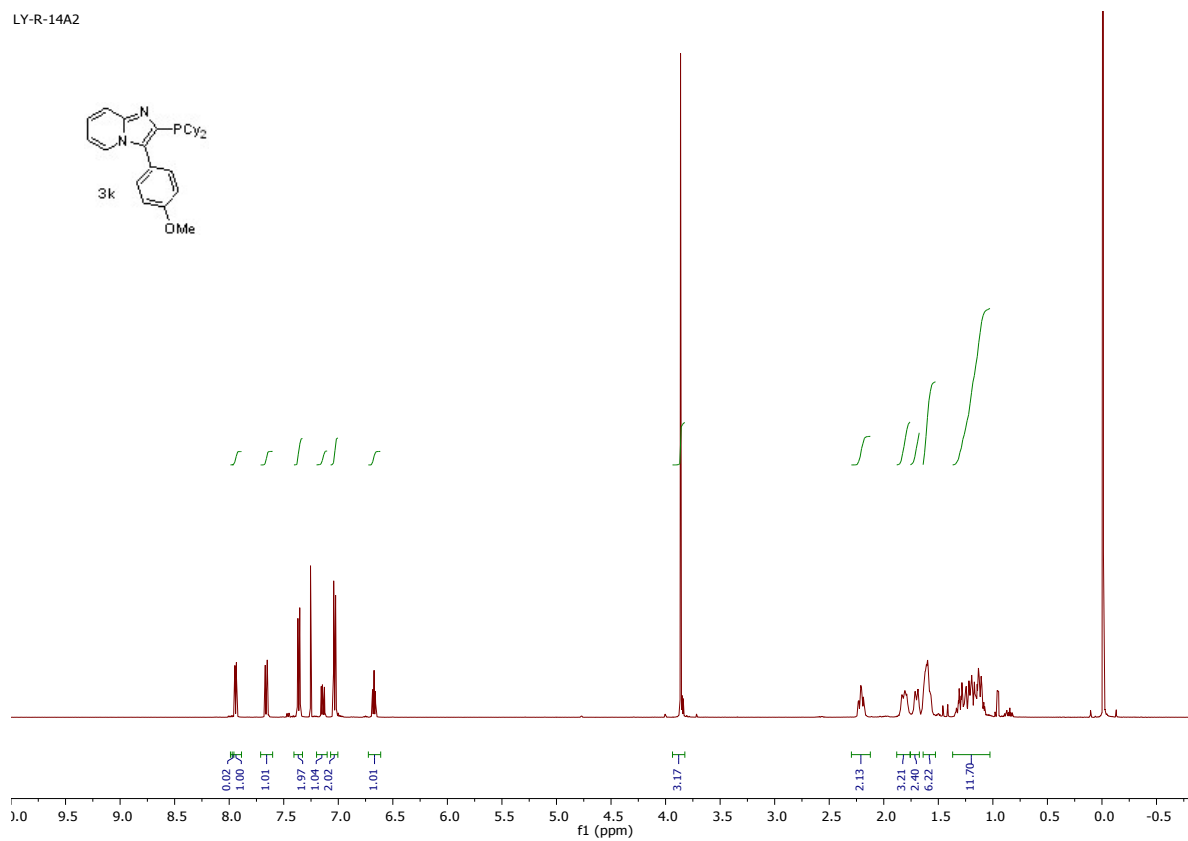
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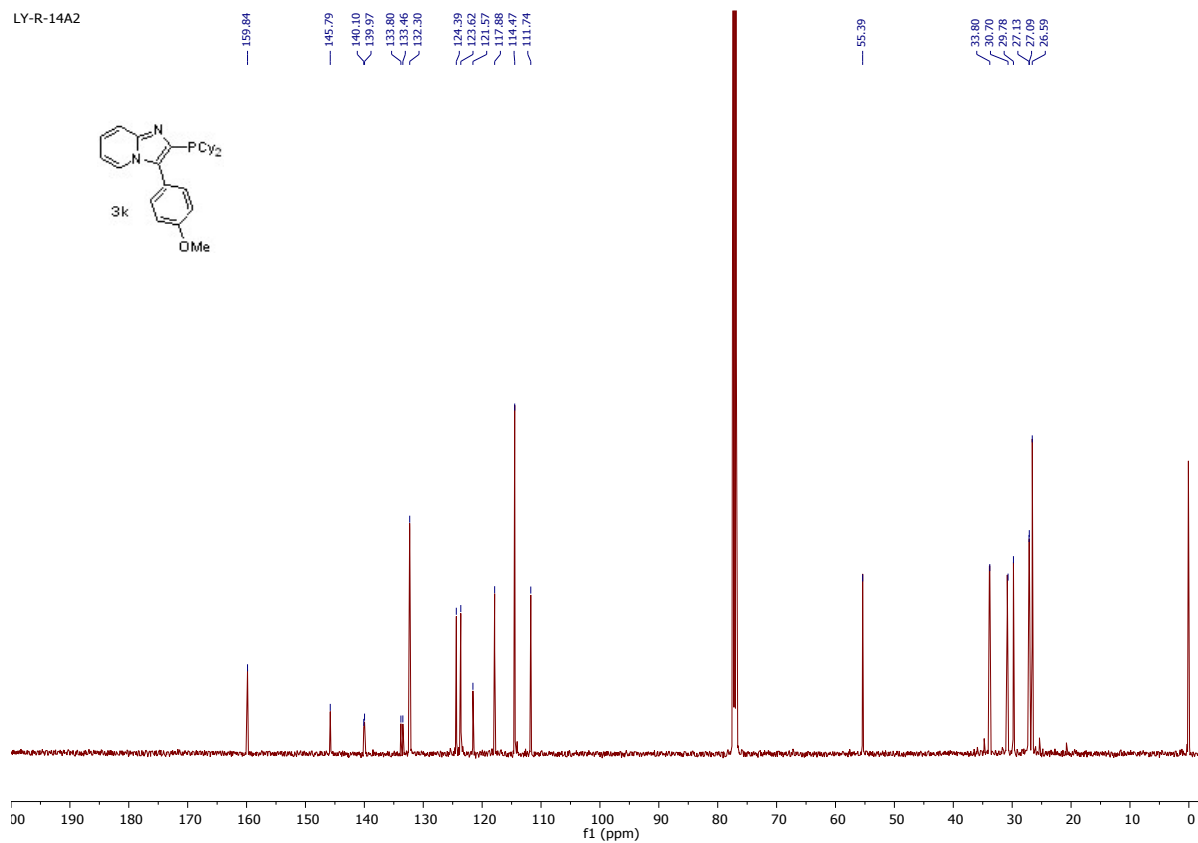
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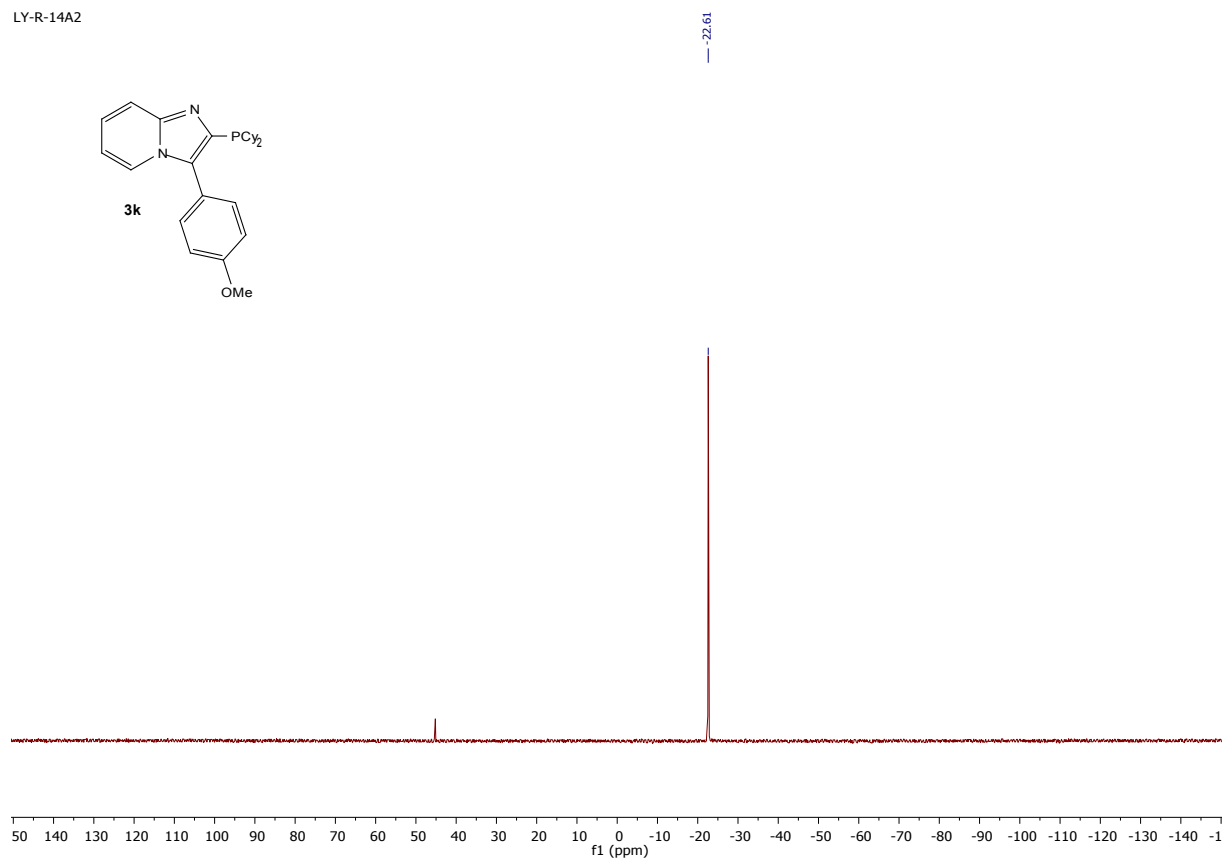
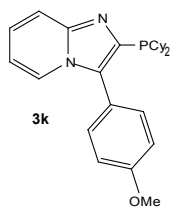
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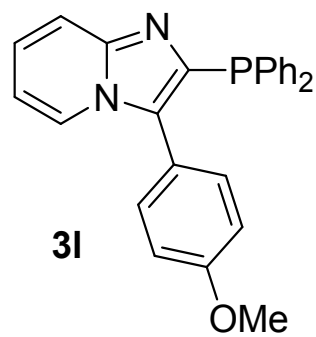
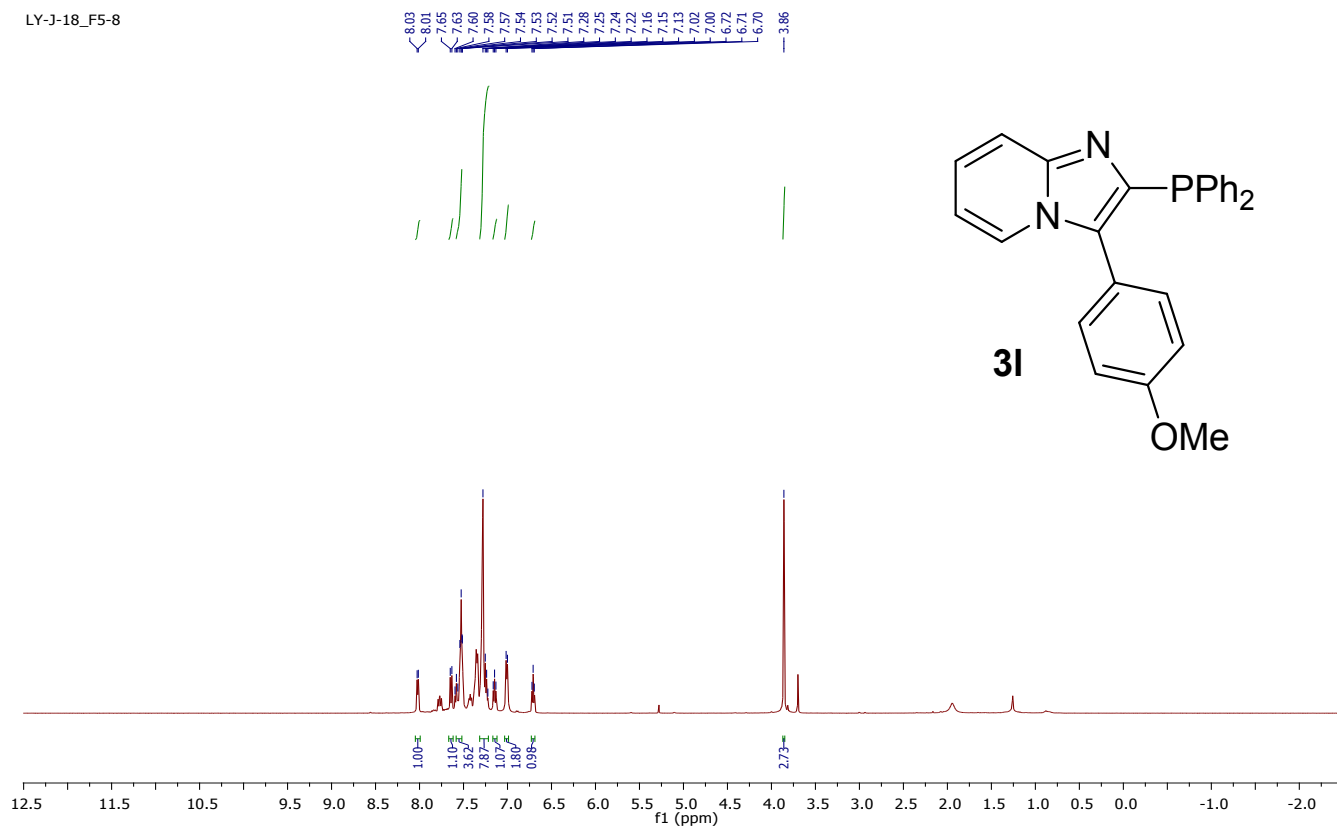
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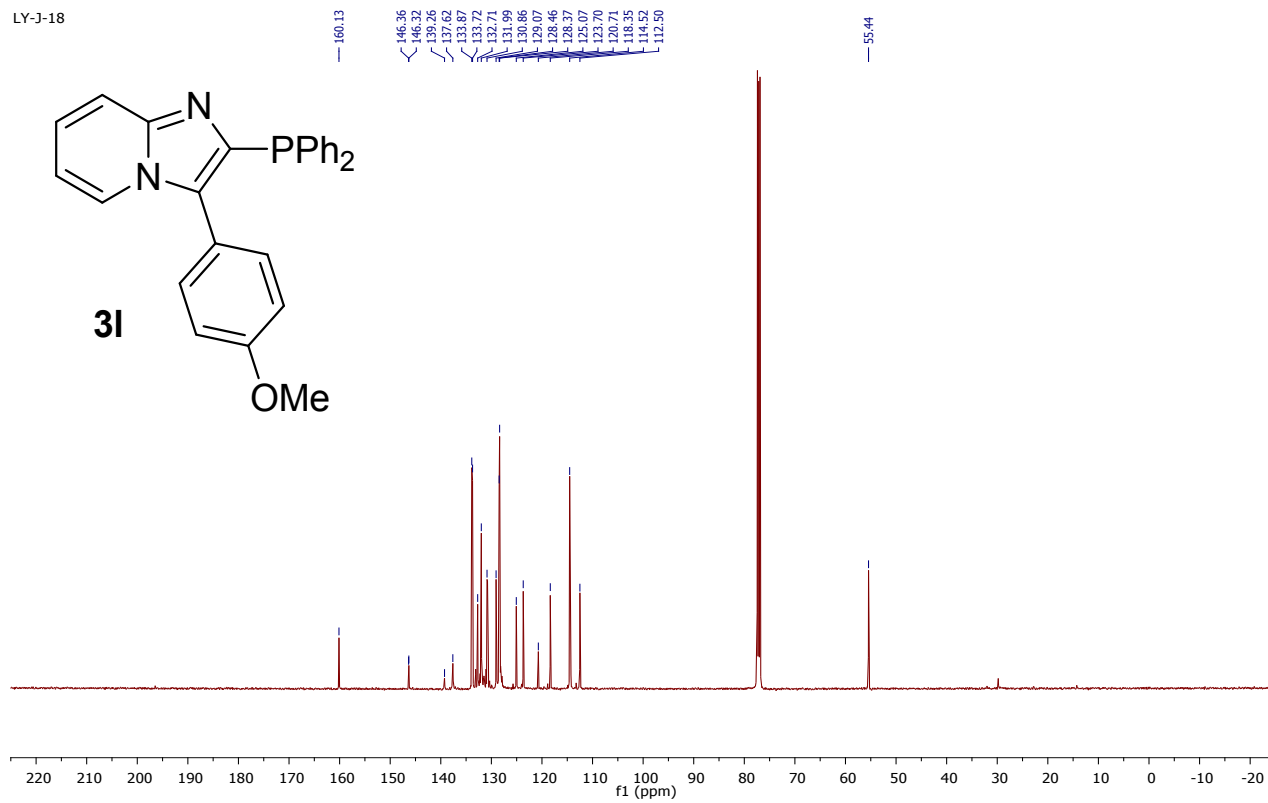
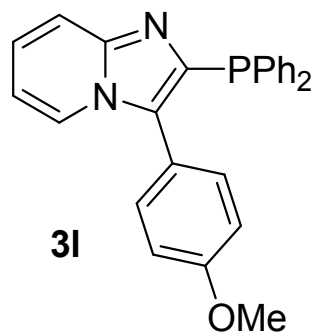
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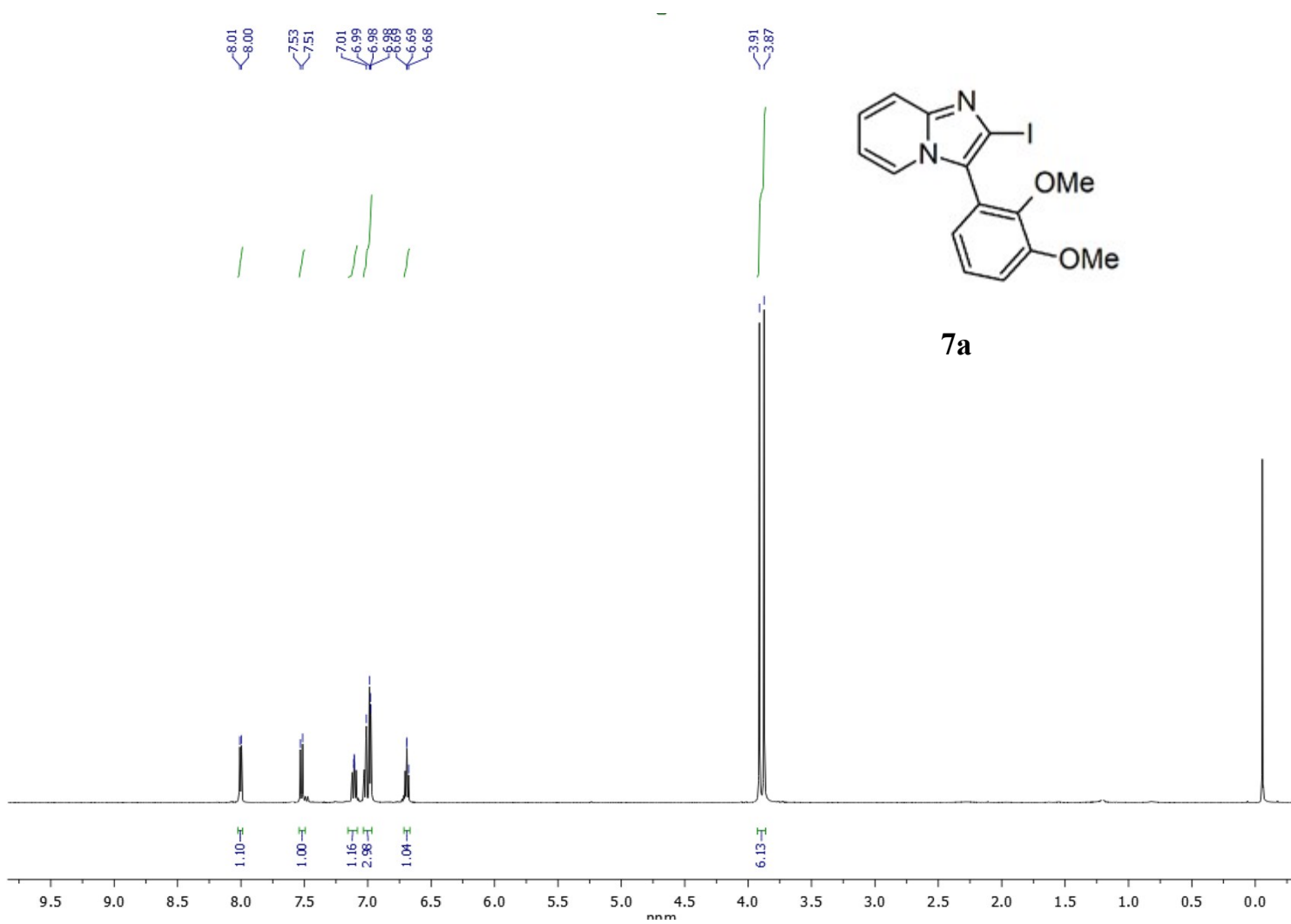


LY-J-18\_F5-8

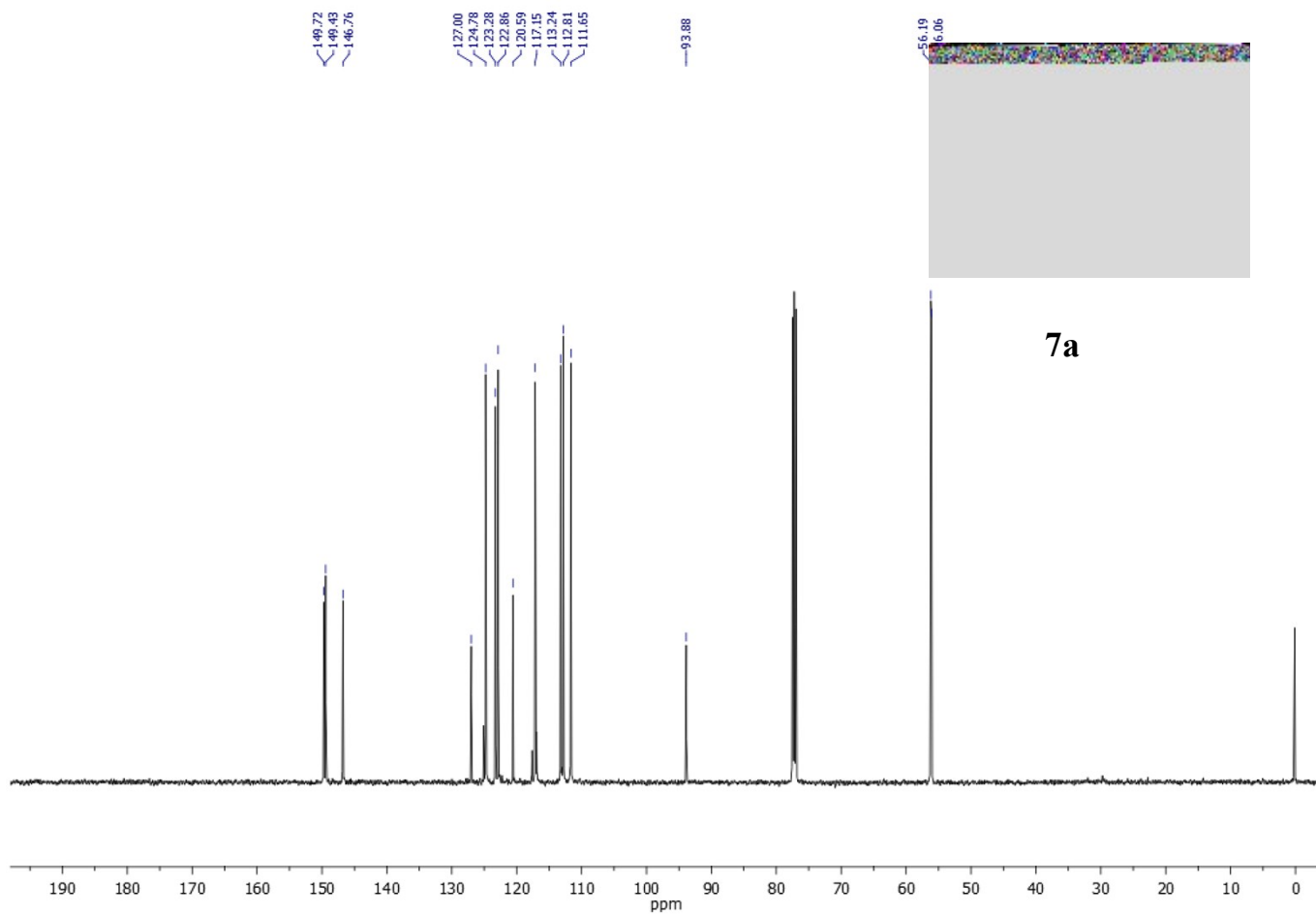


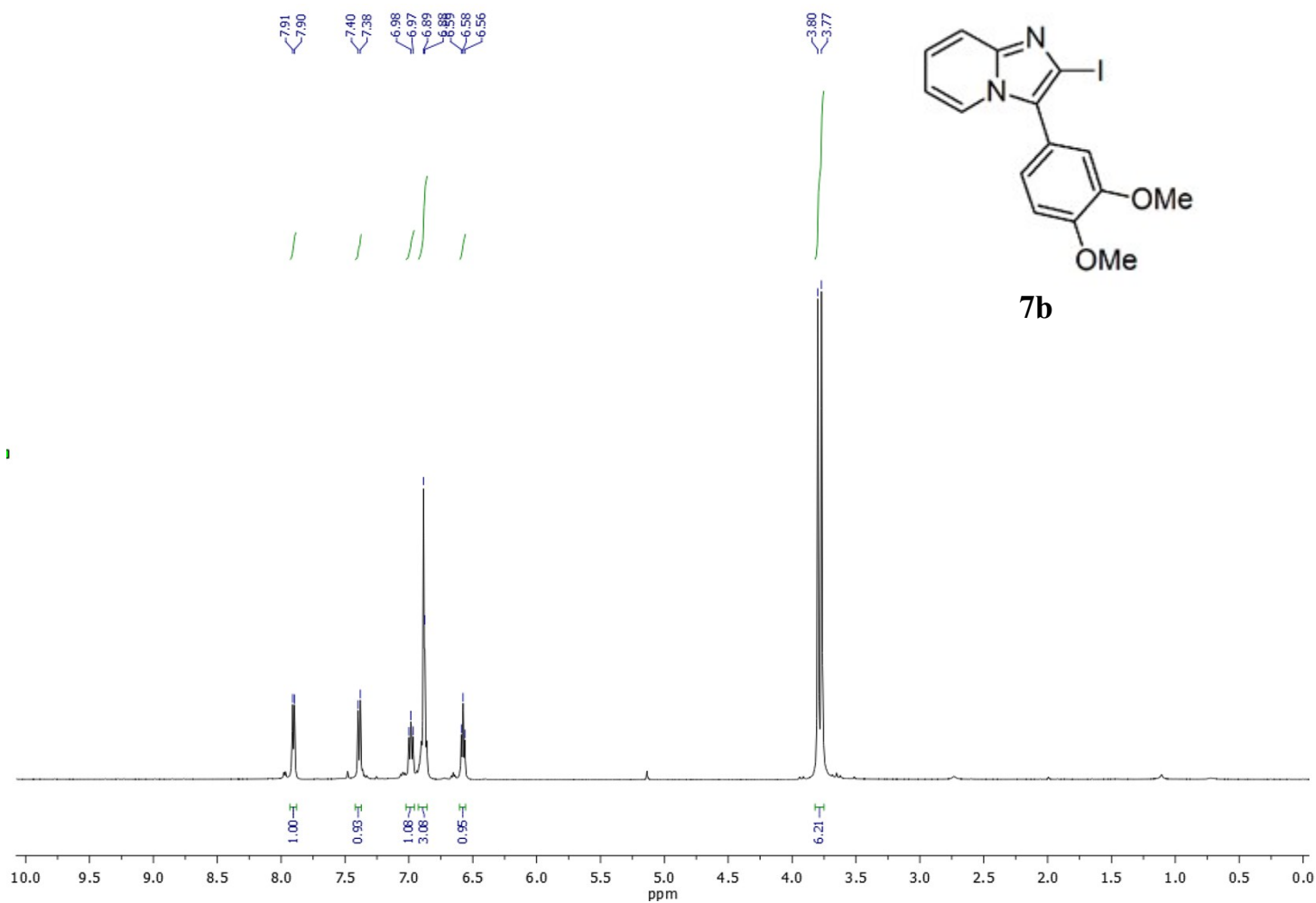
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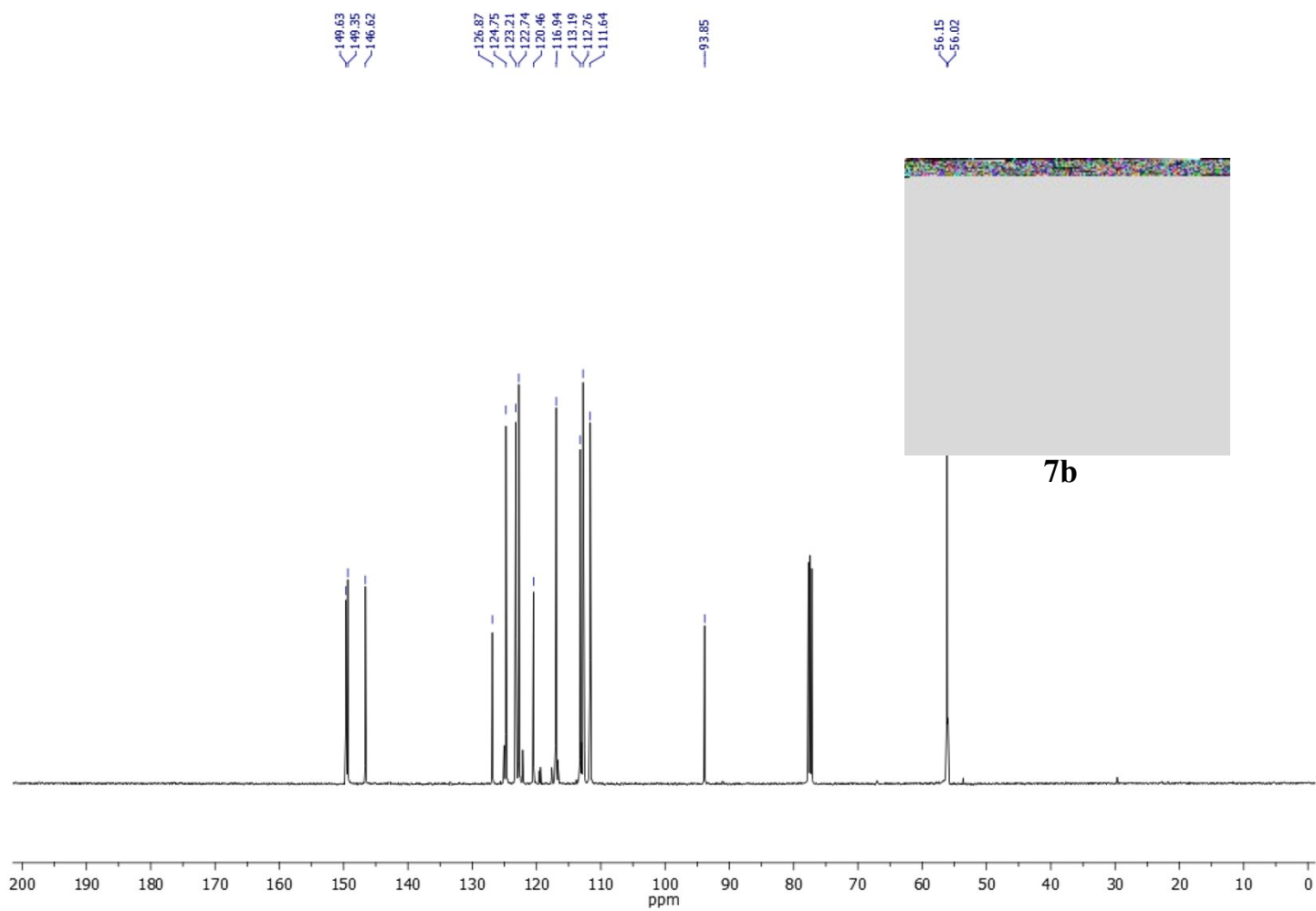


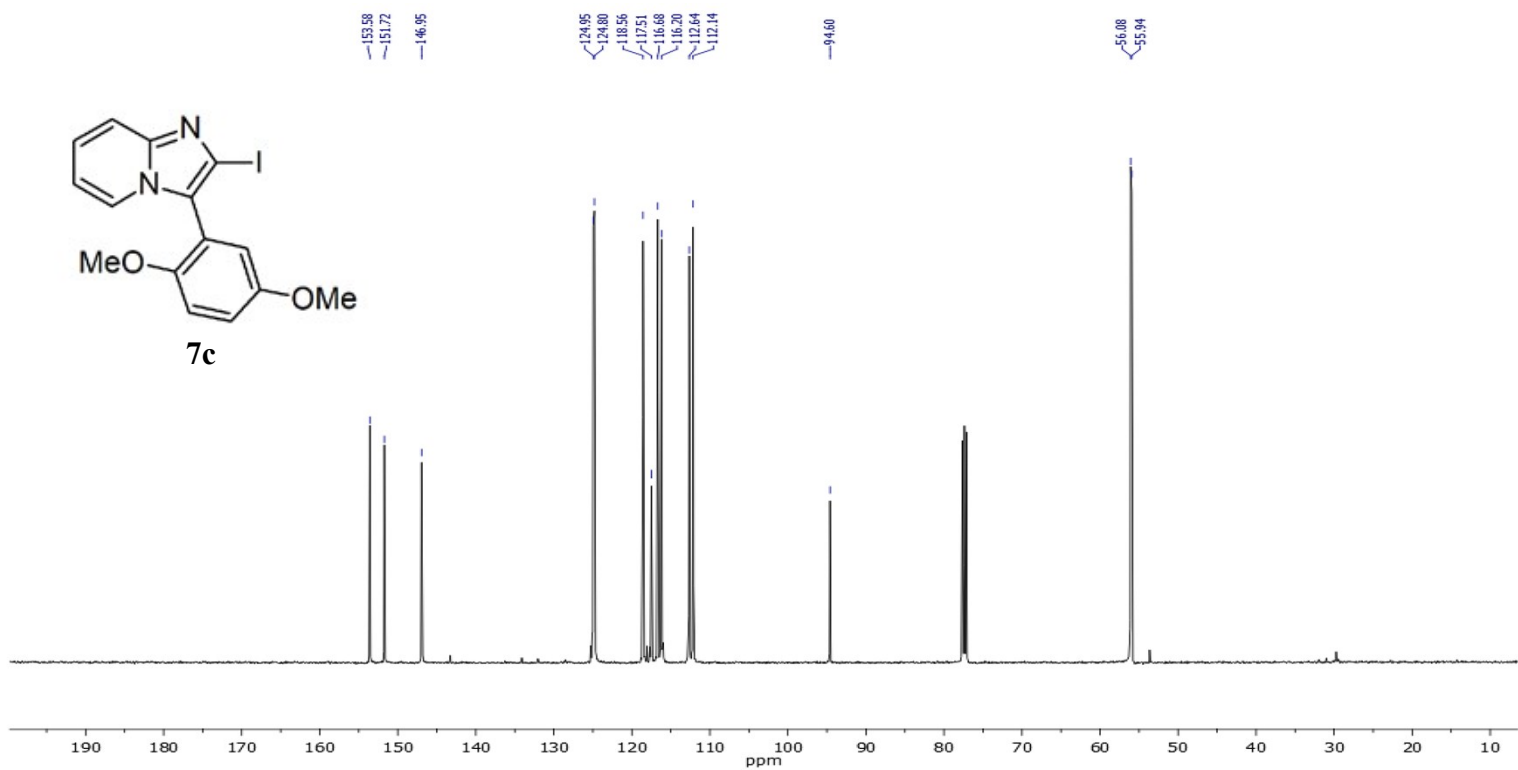
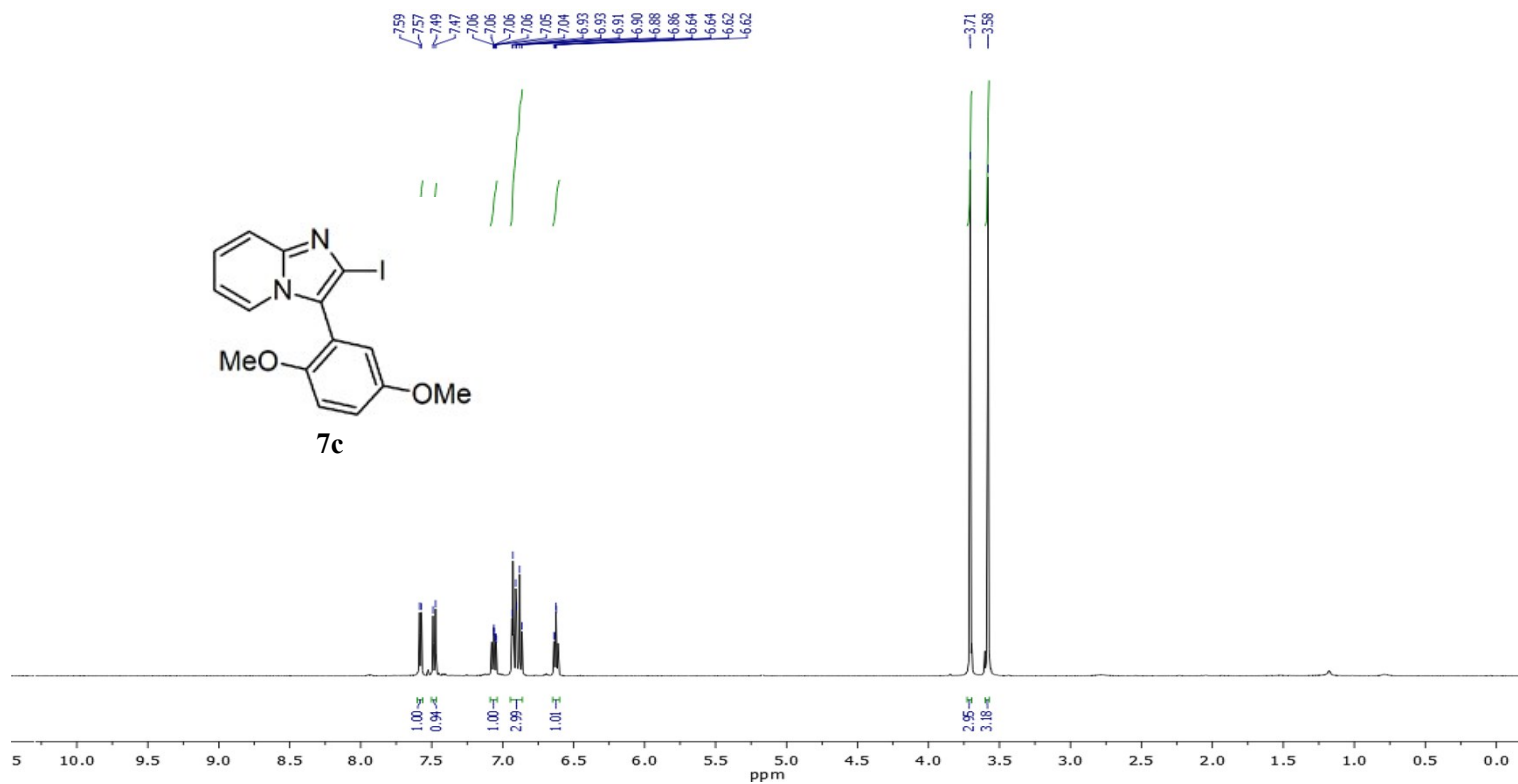


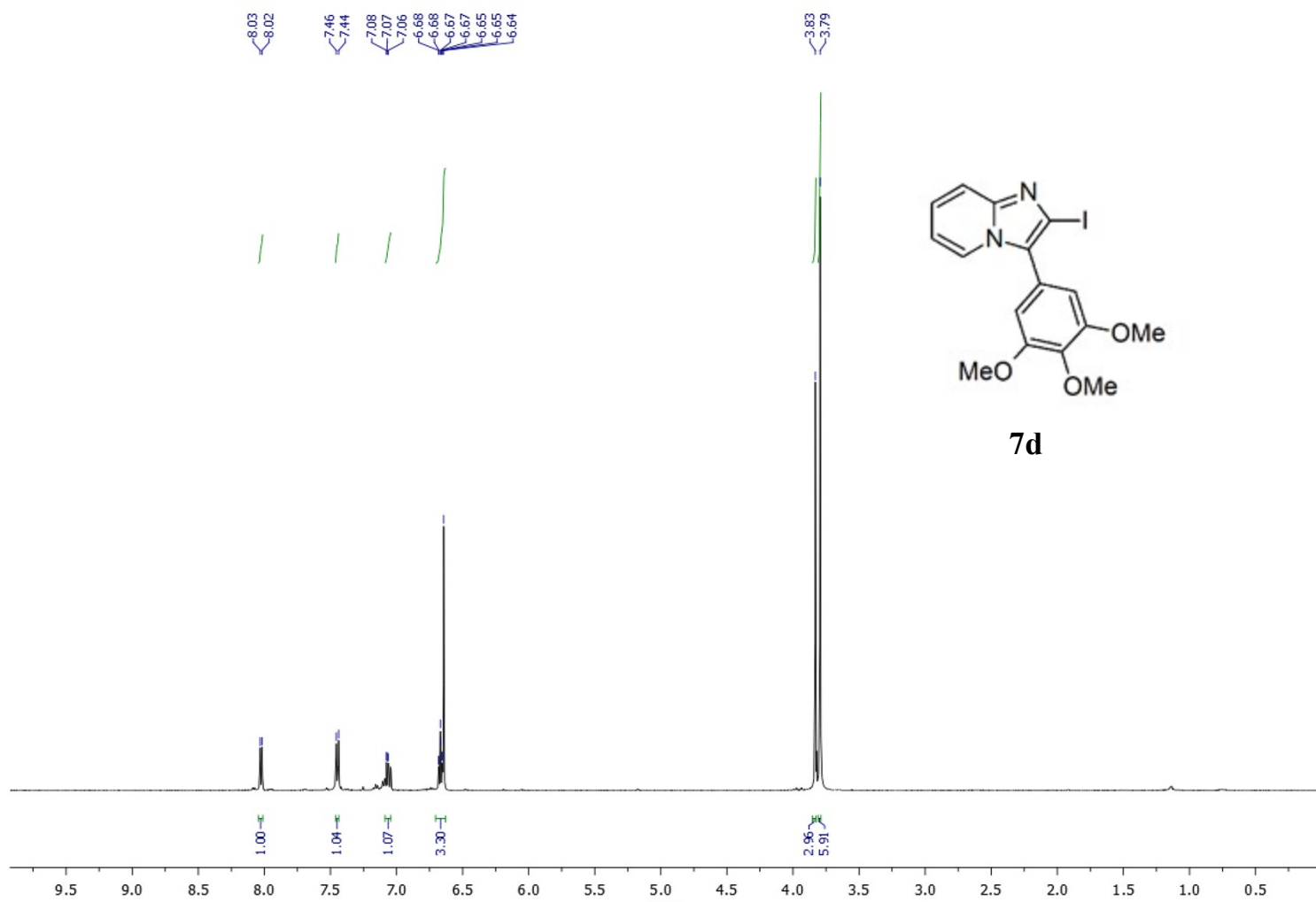


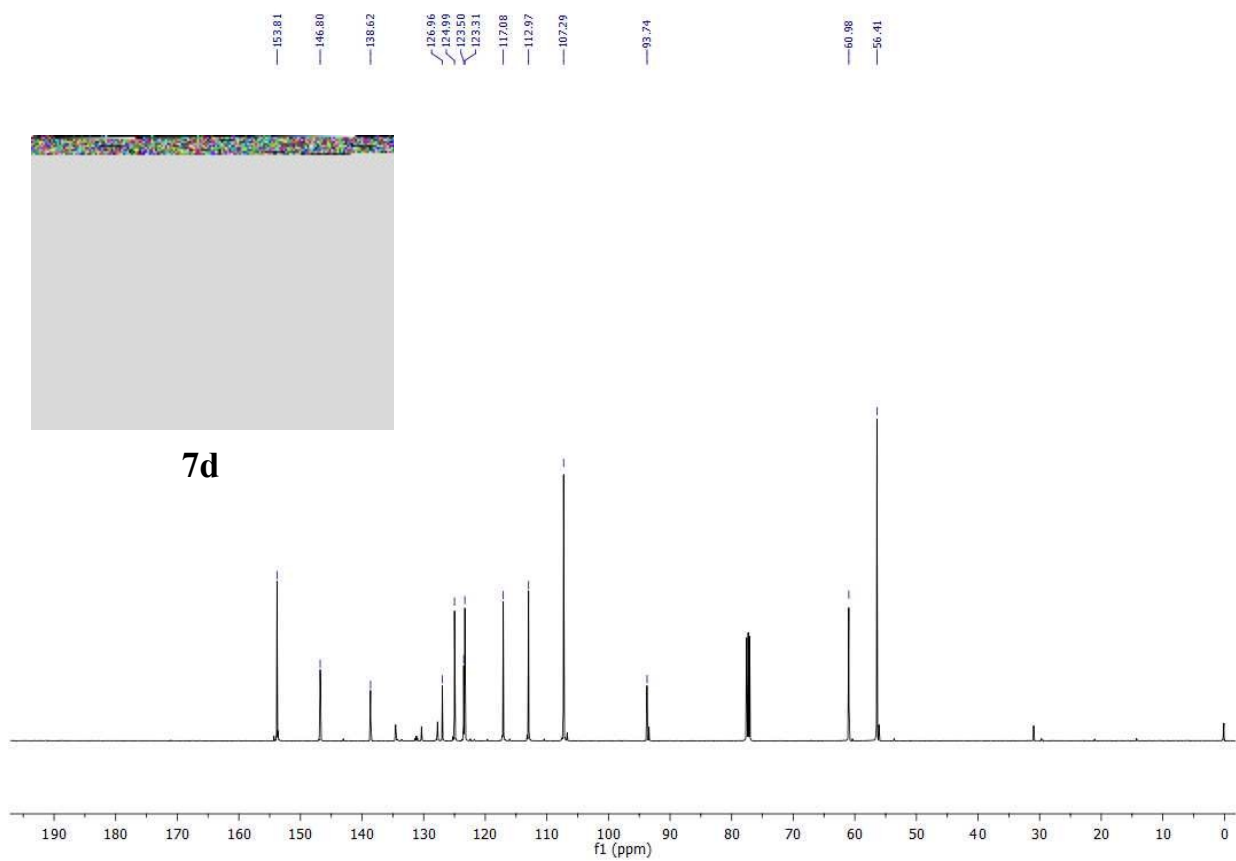


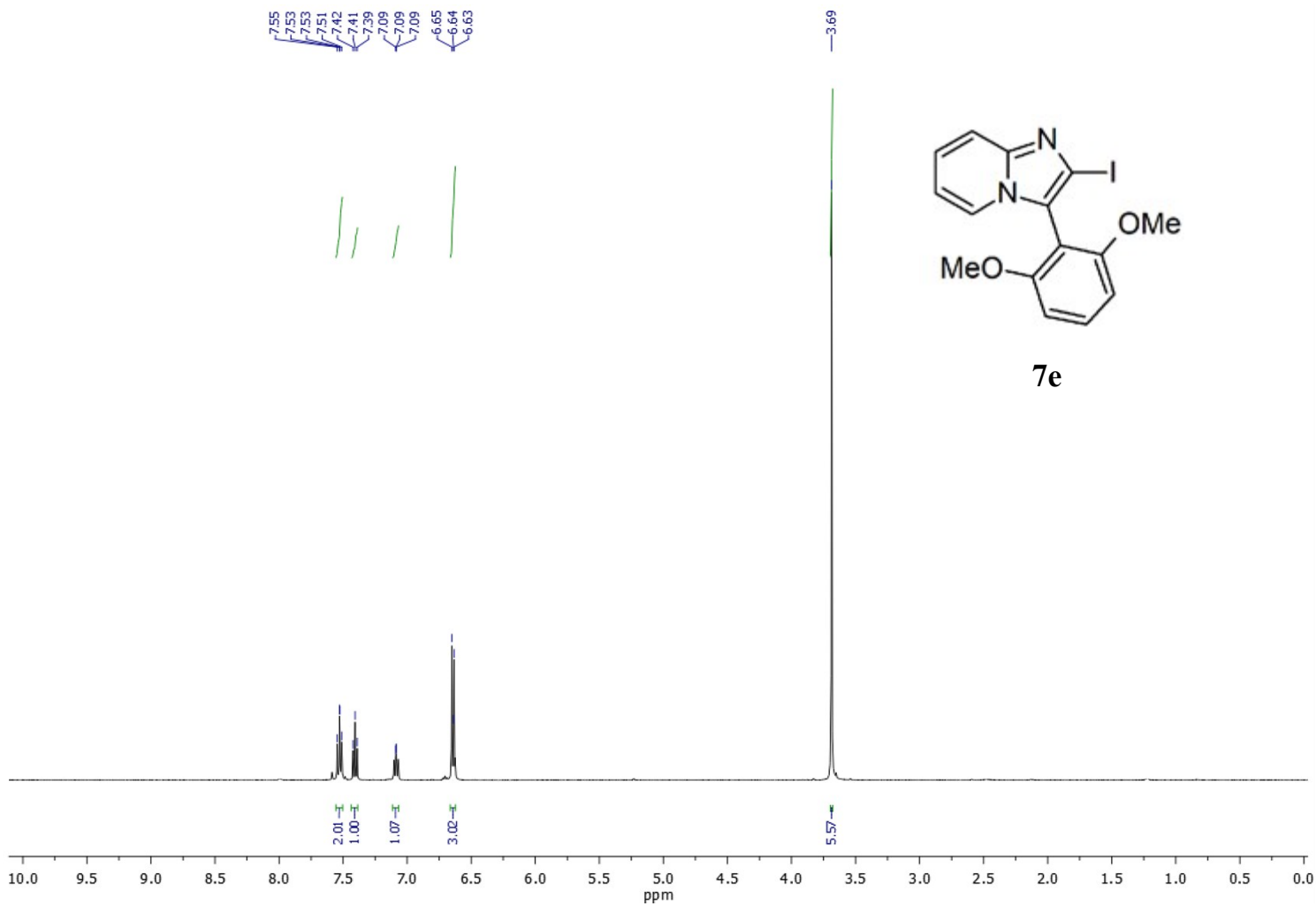


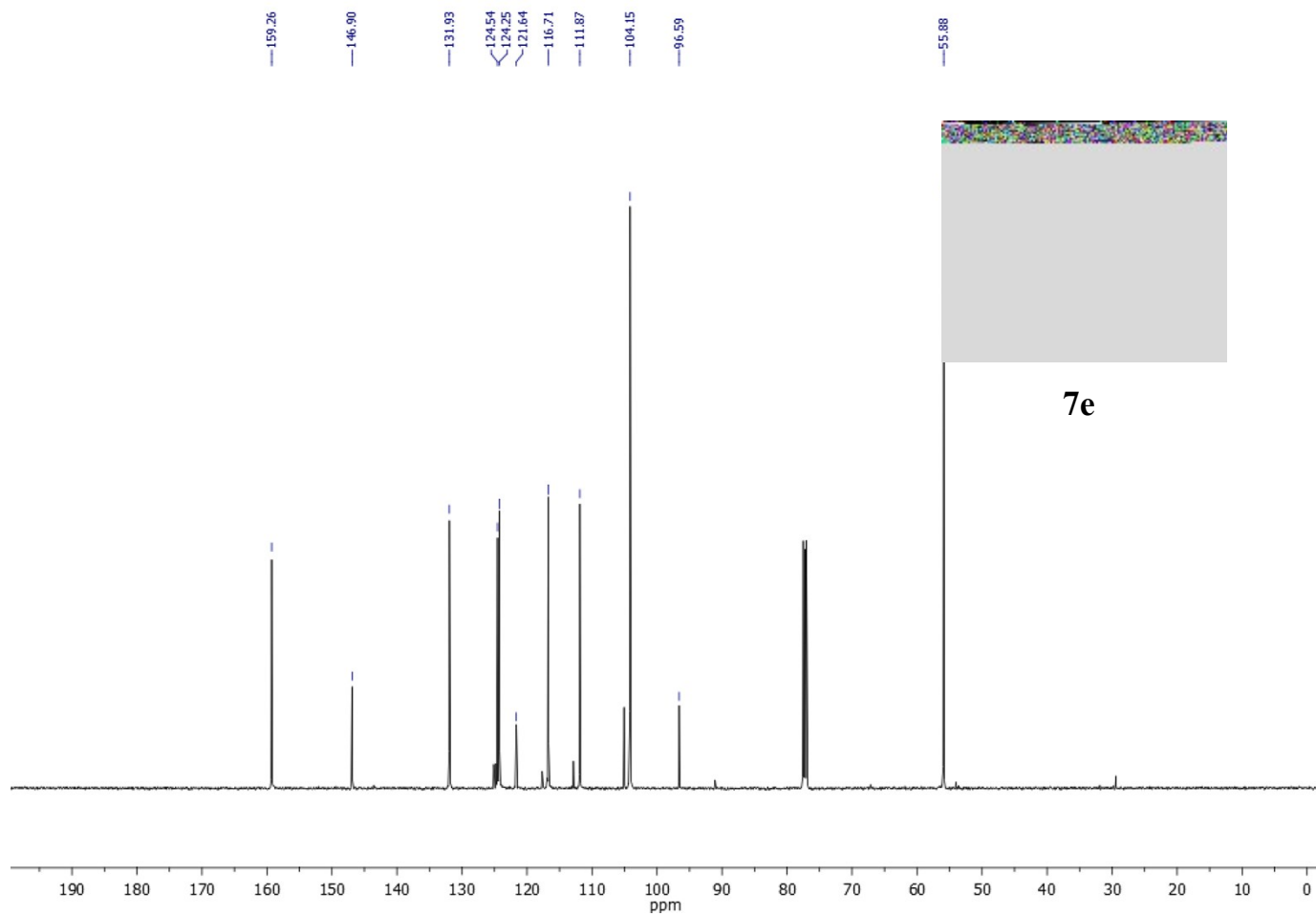




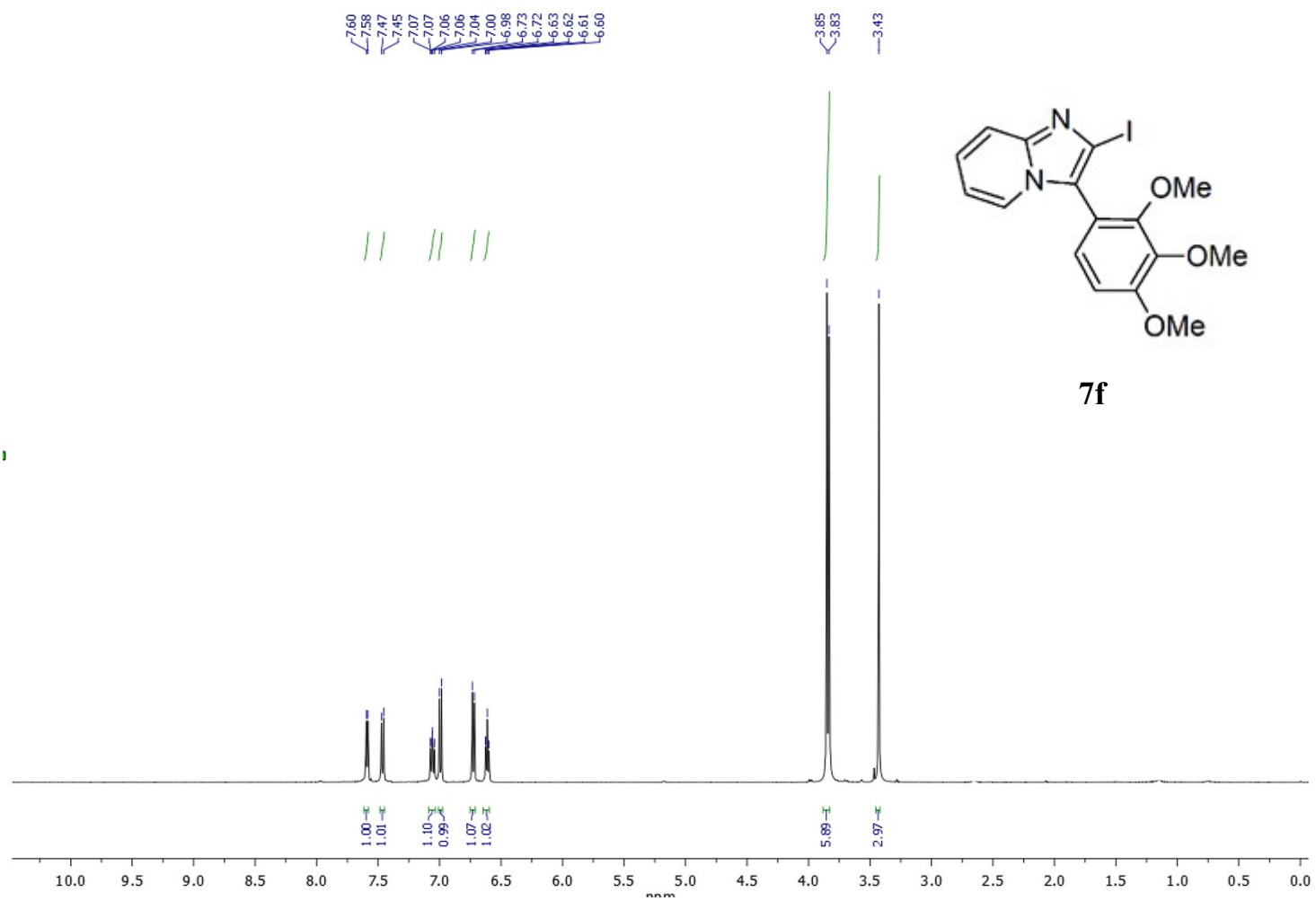


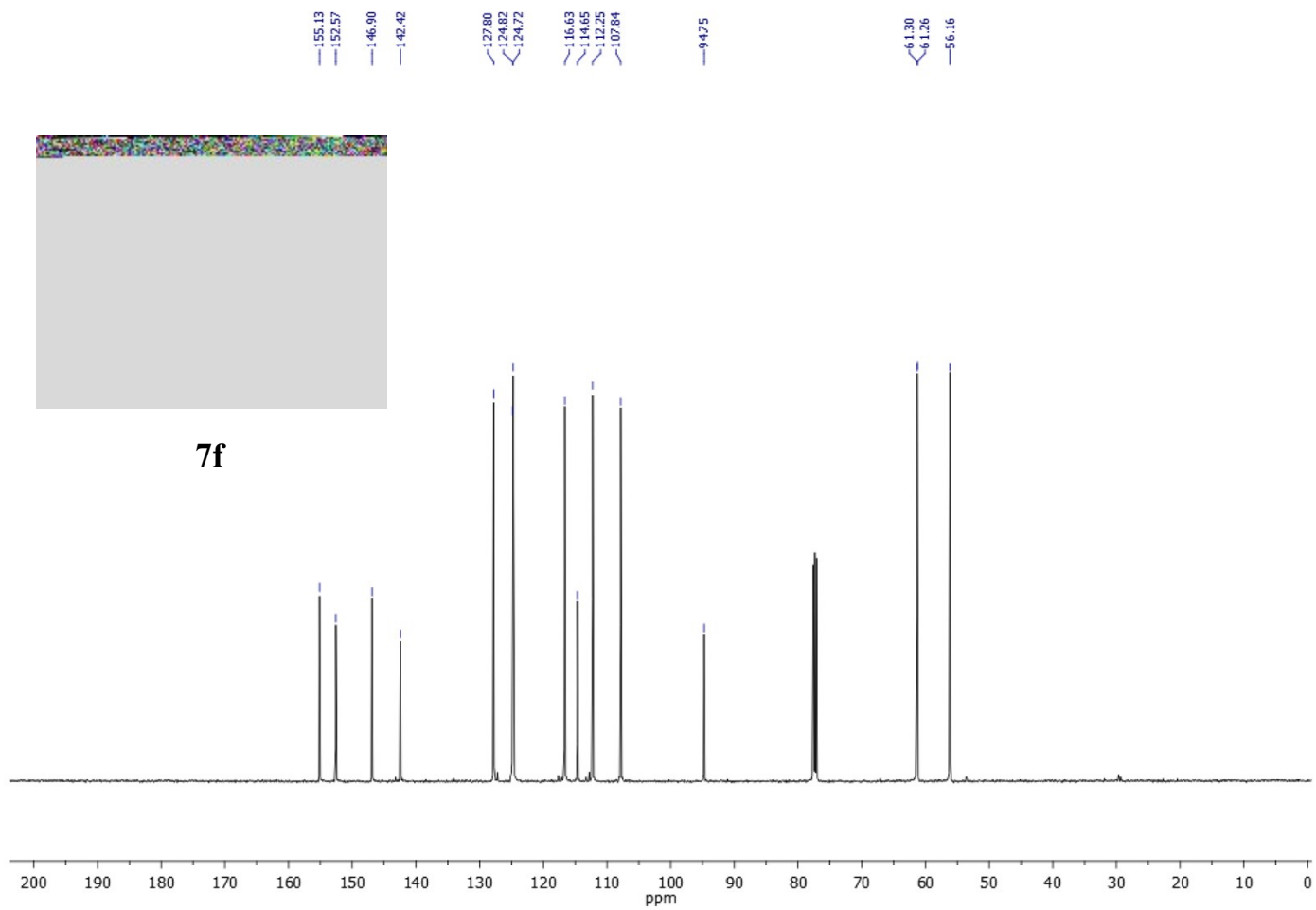




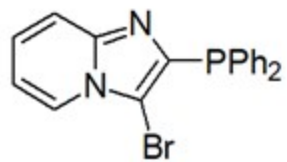
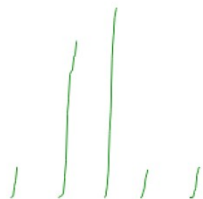




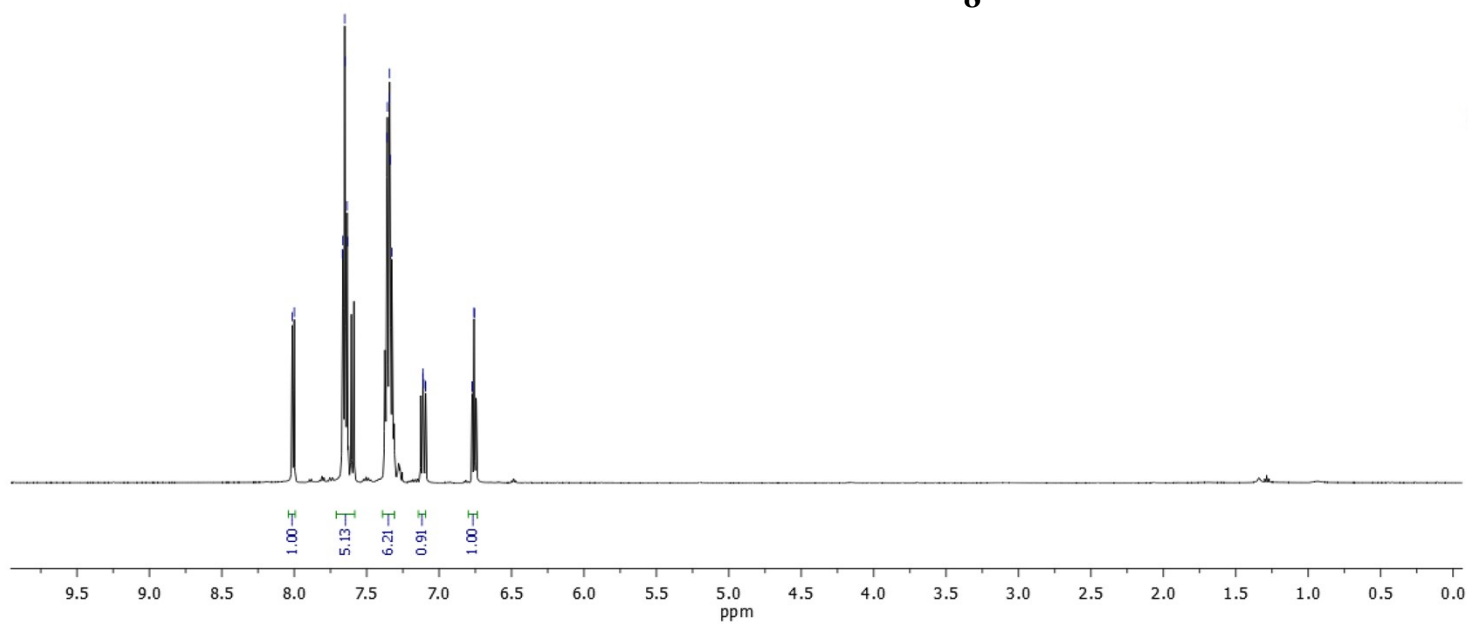


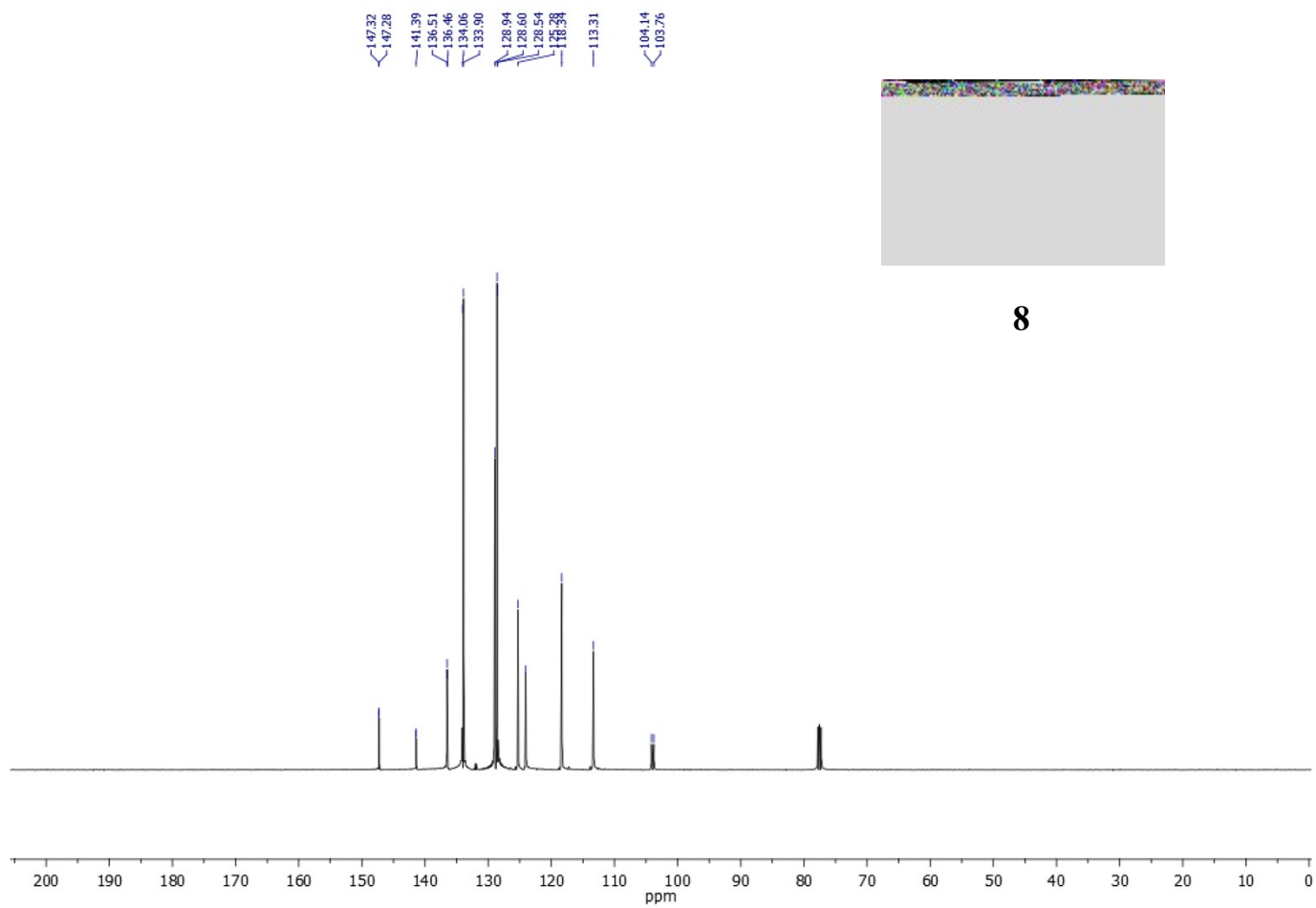


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8.00  
7.65  
7.64  
7.36  
7.35  
7.34  
6.77  
6.76

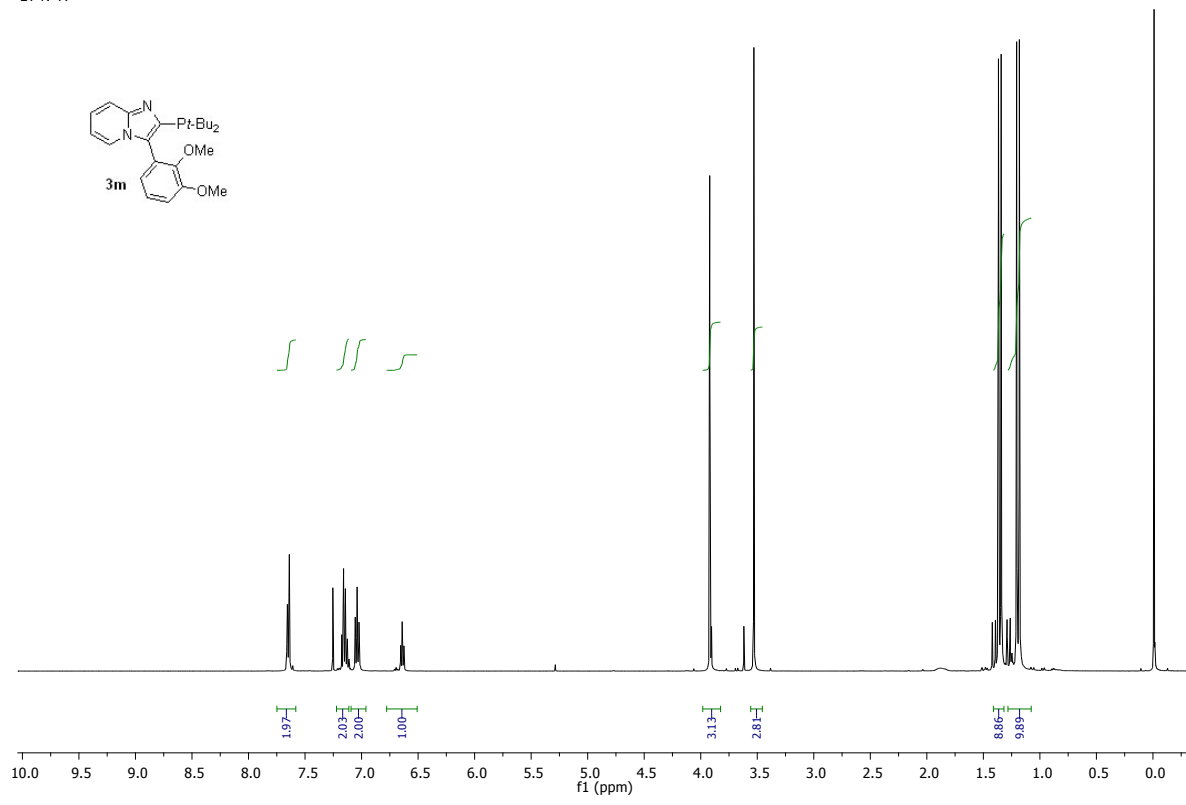


8

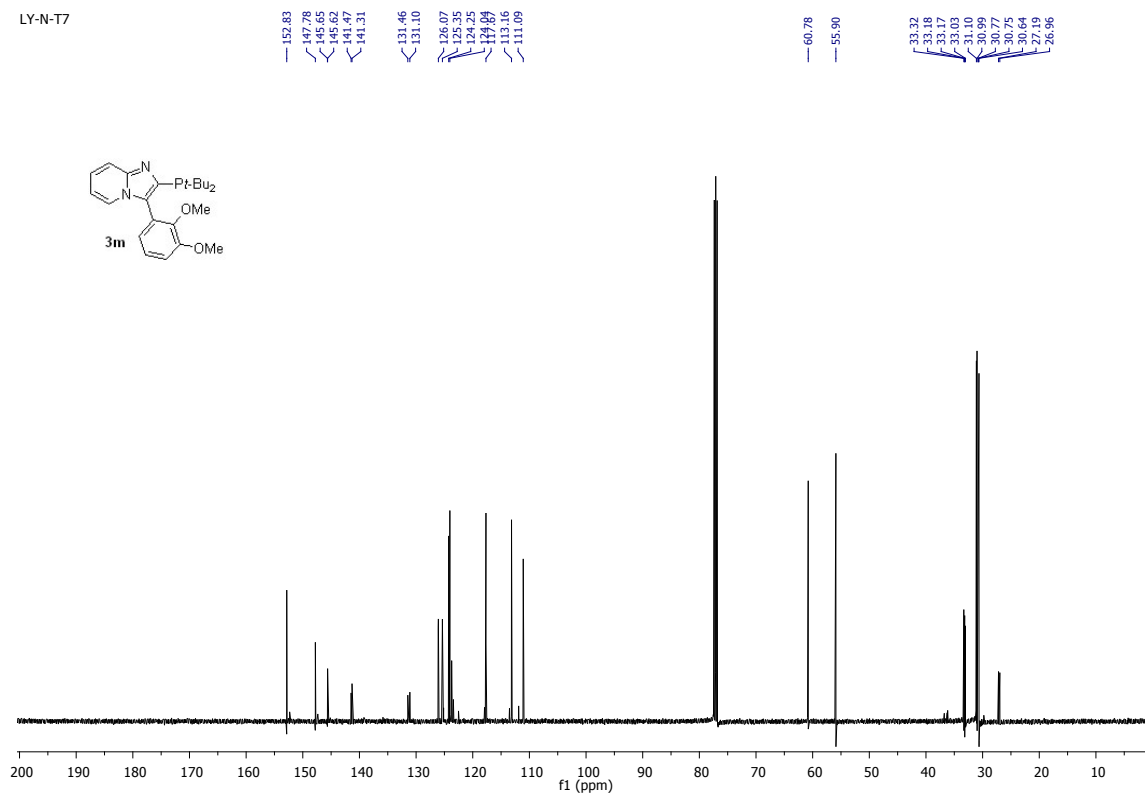




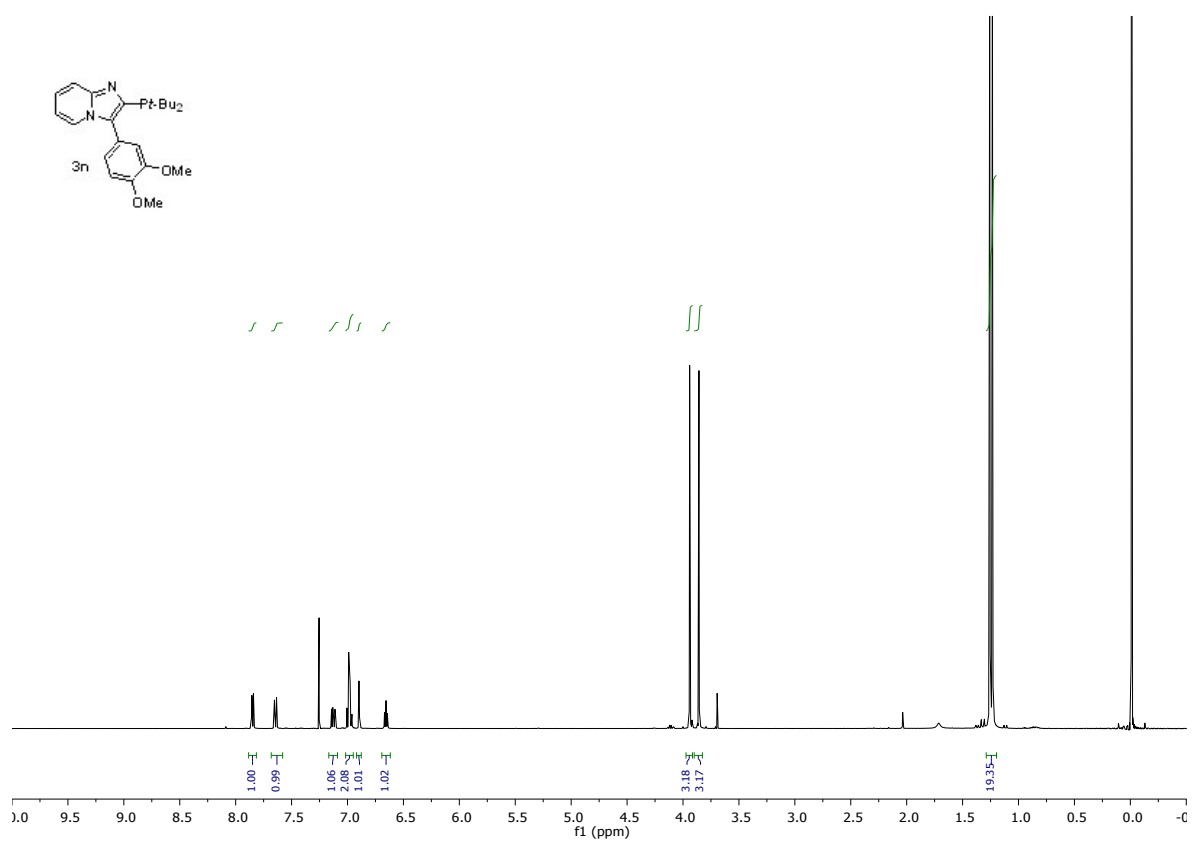
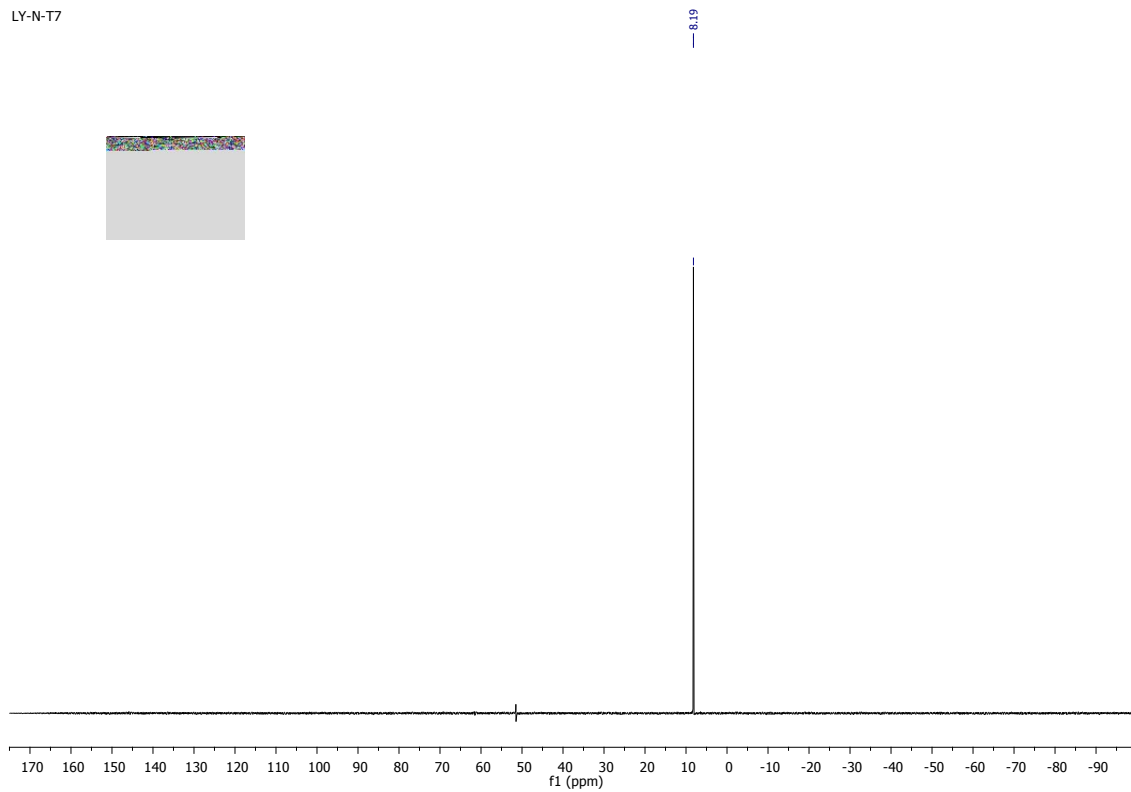
LY-N-T7

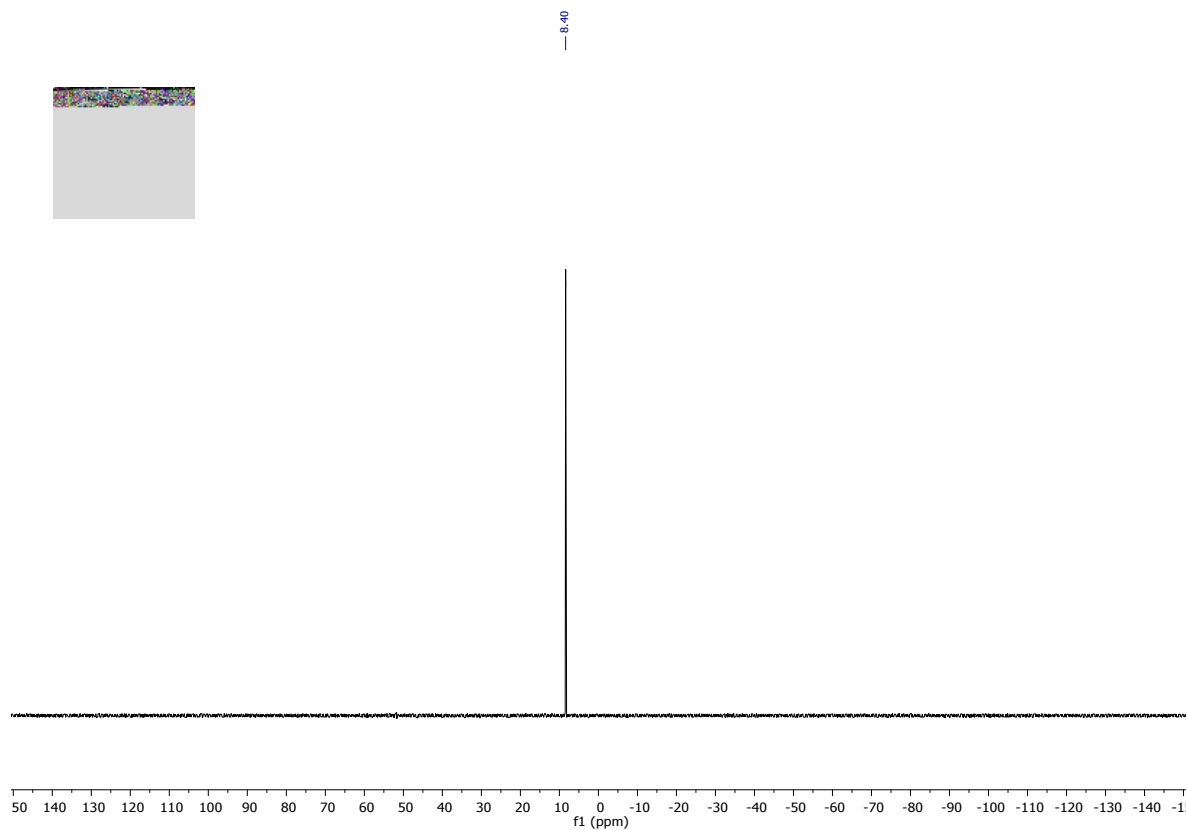
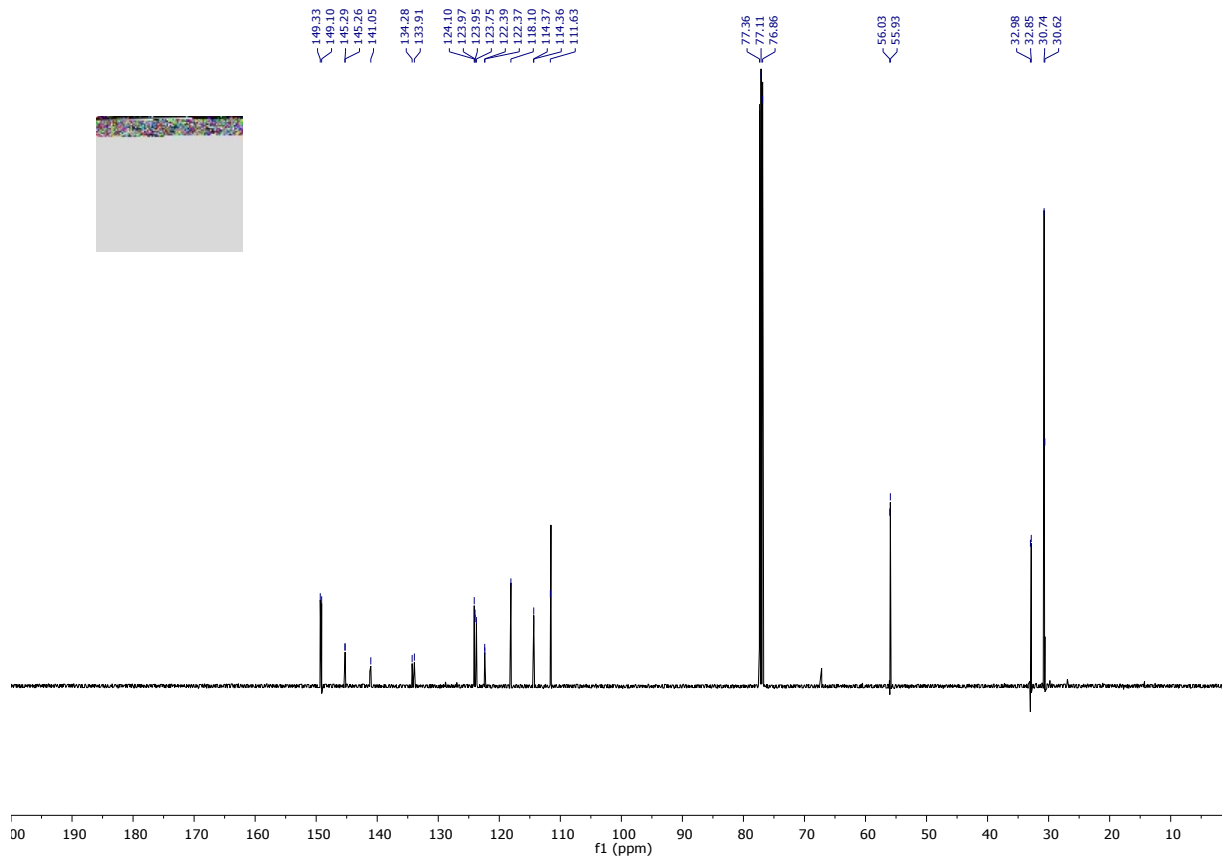


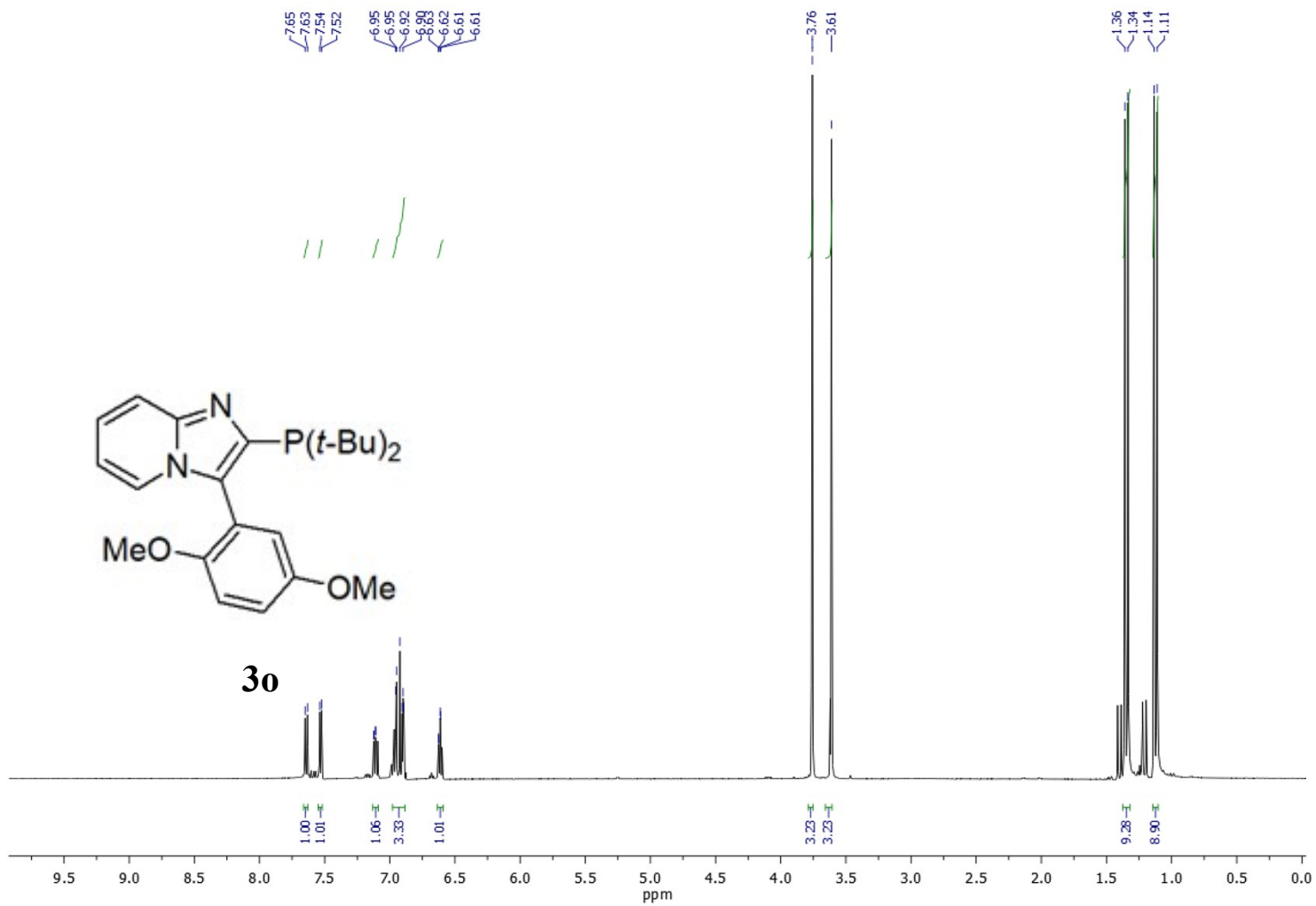
LY-N-T7



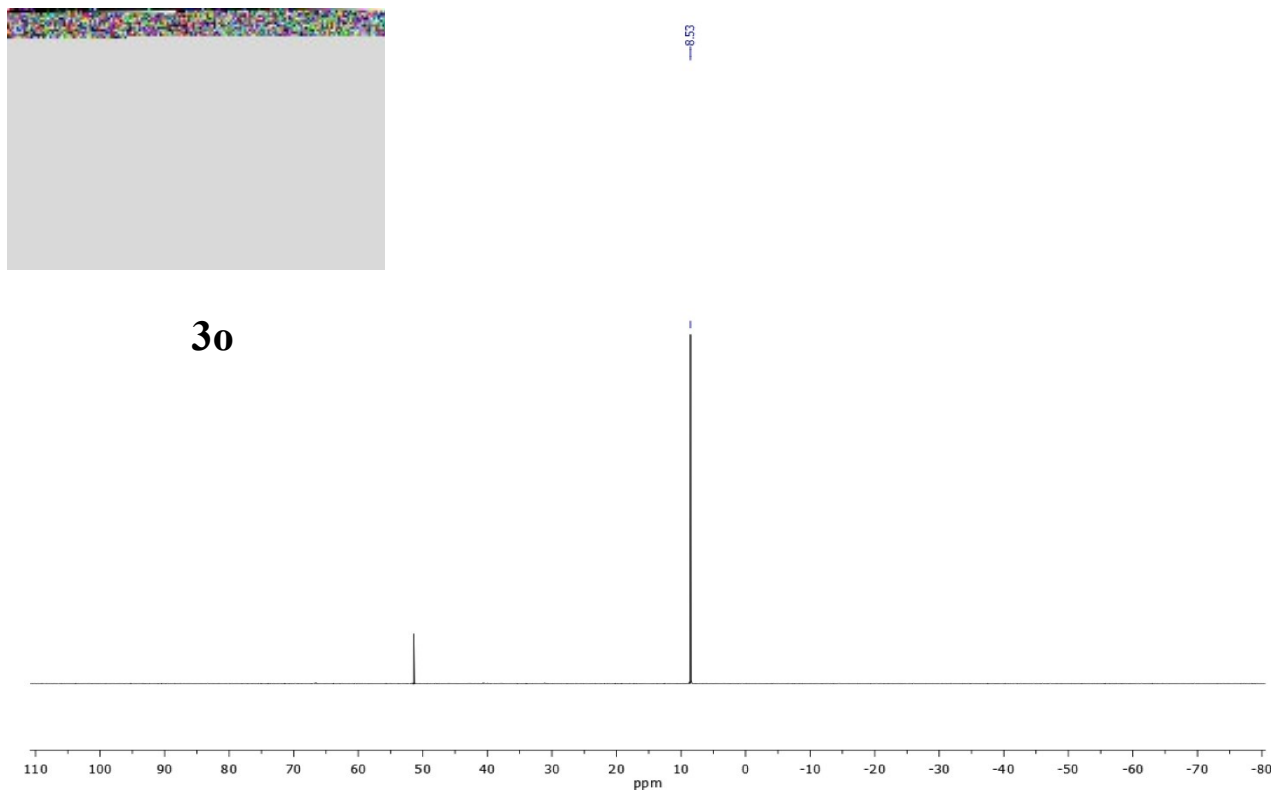
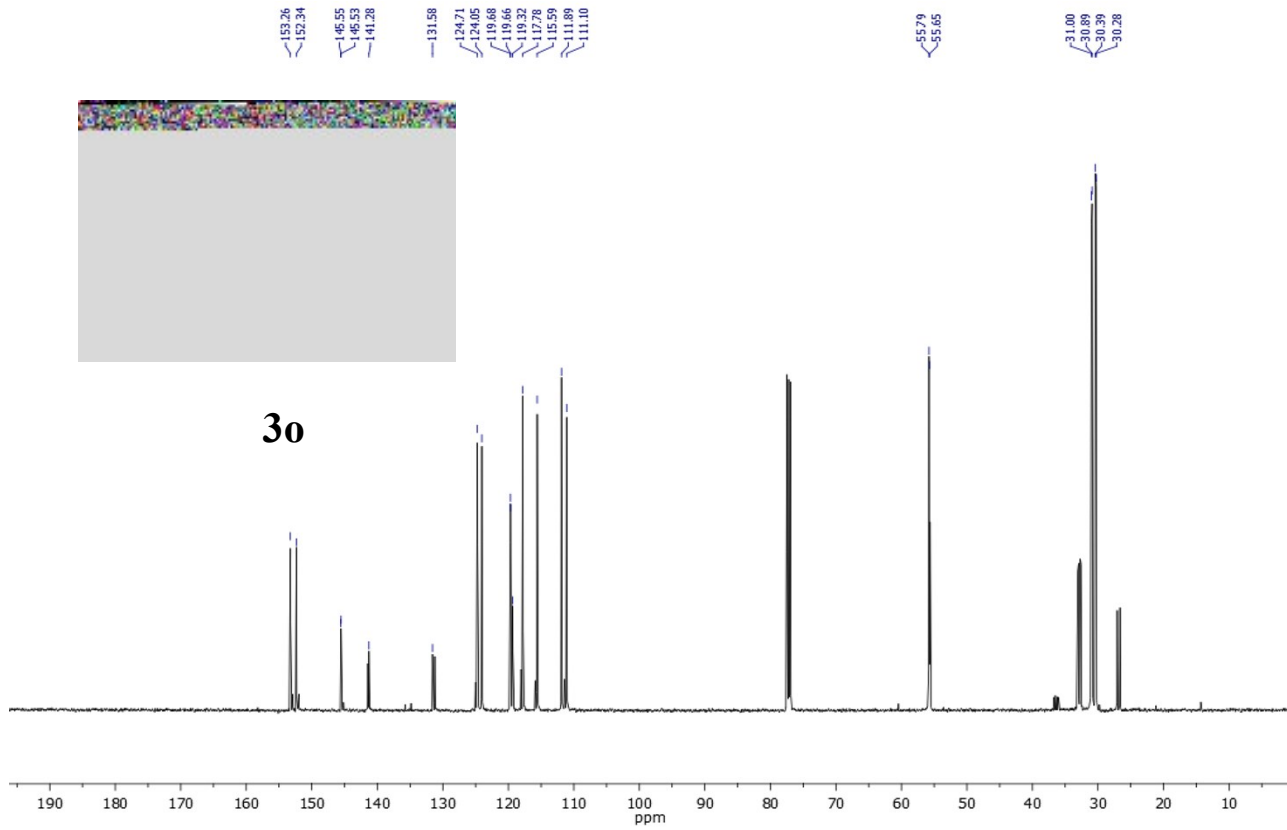
LY-N-T7



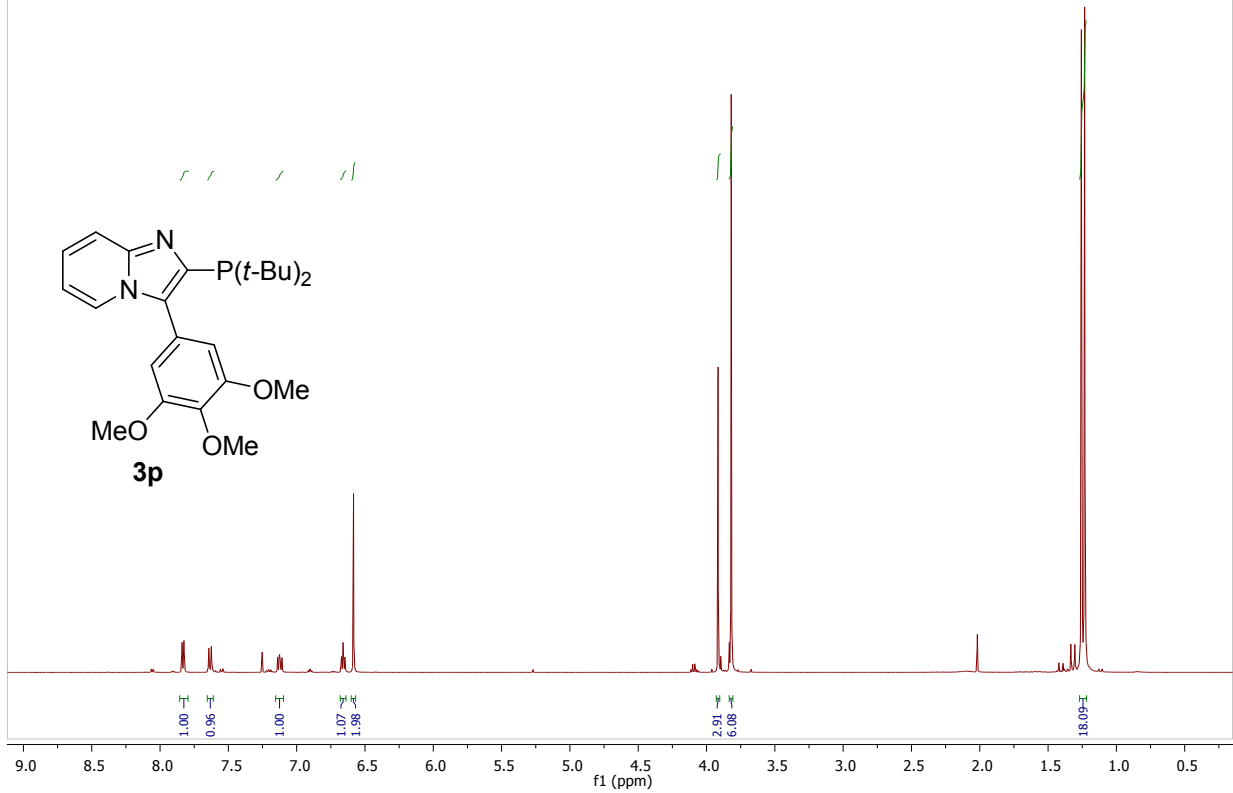


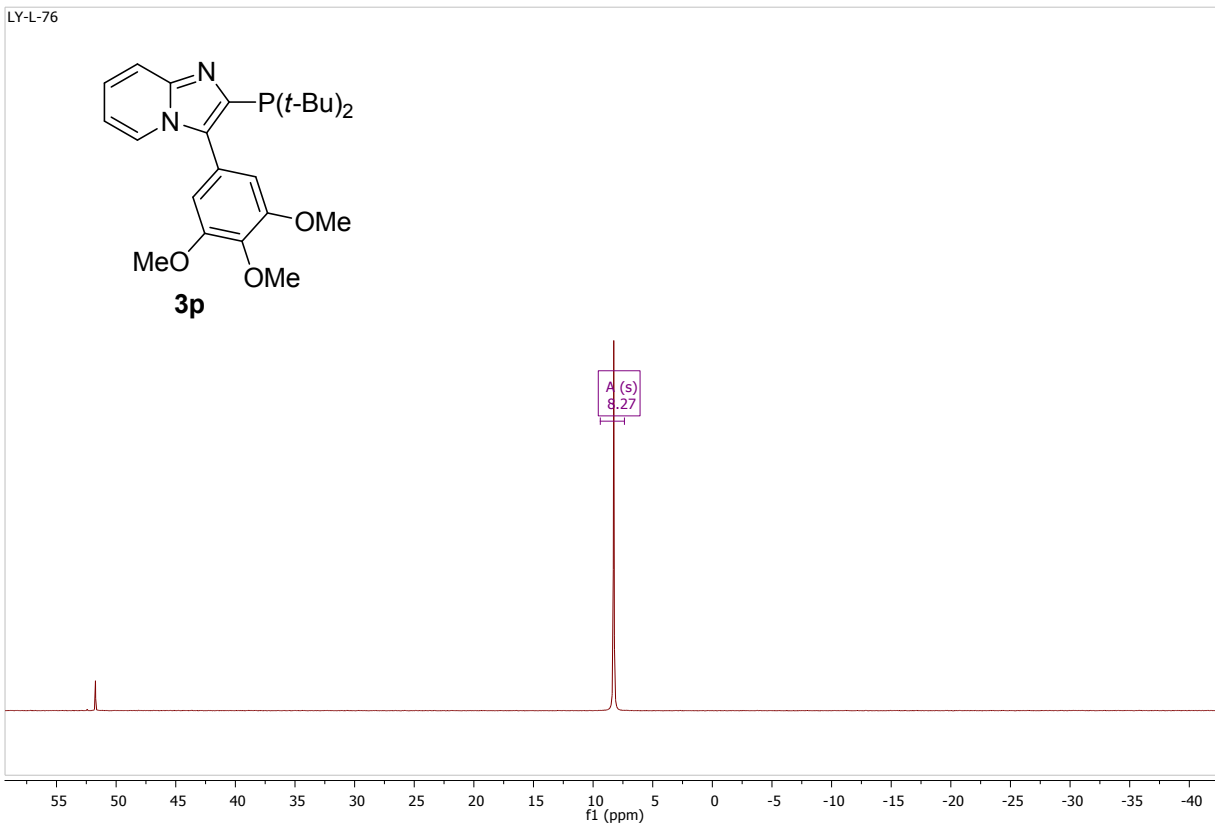
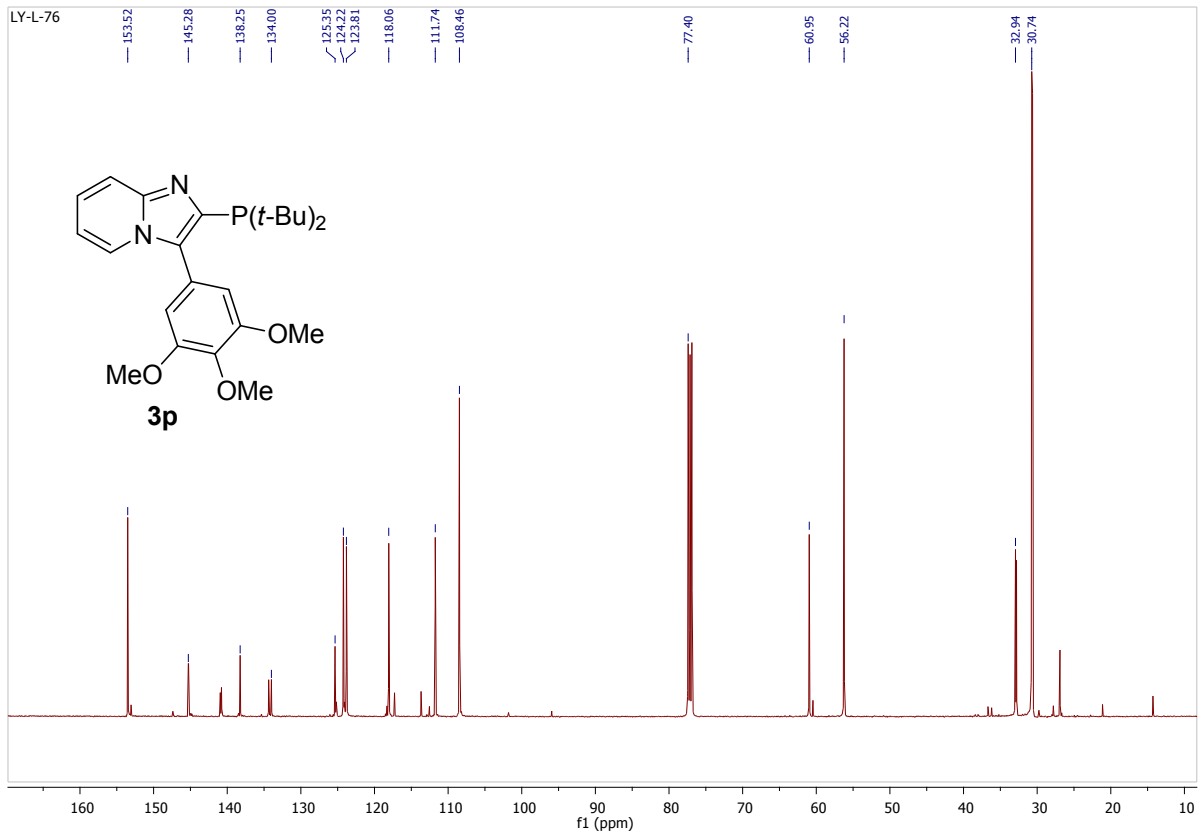


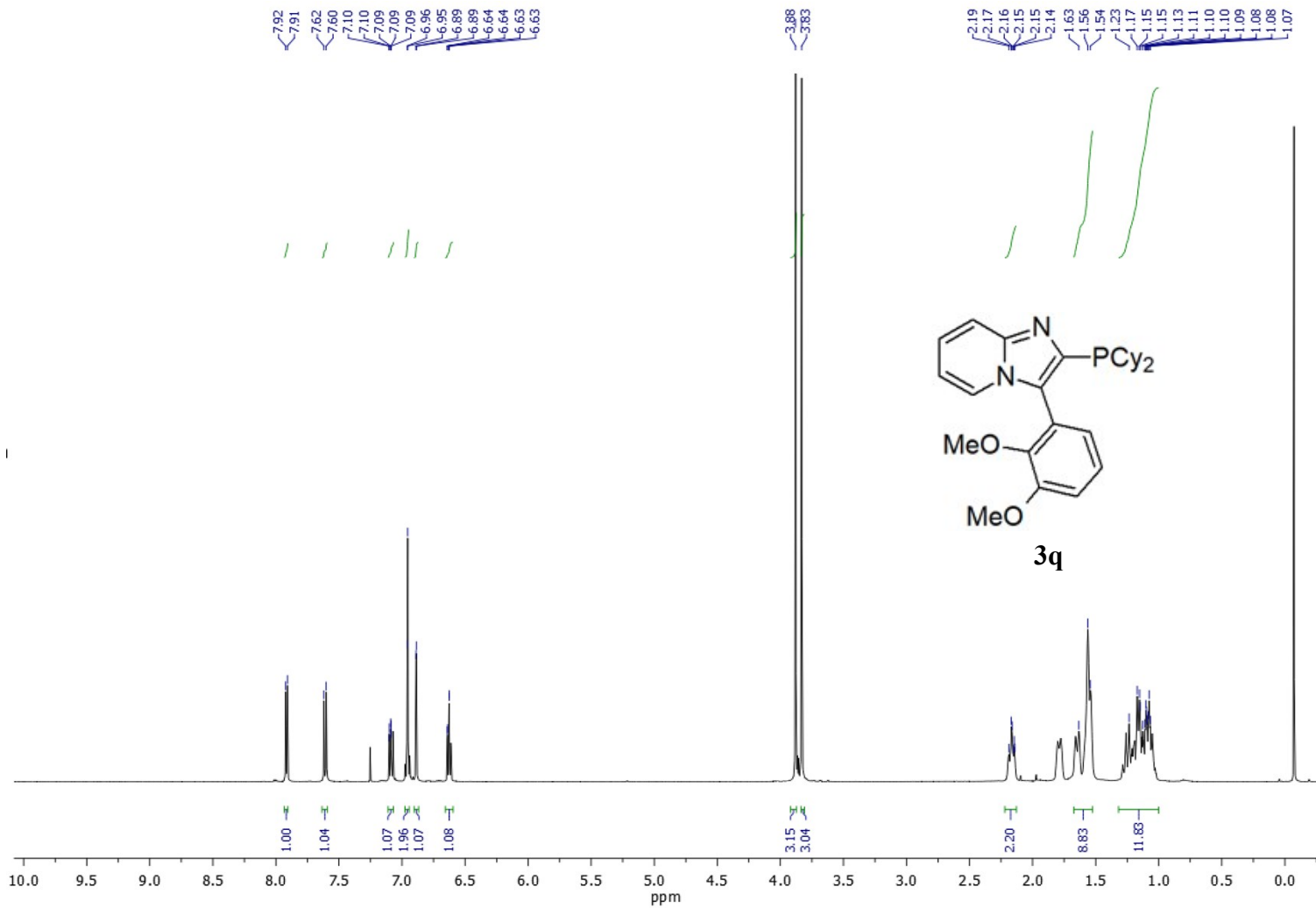


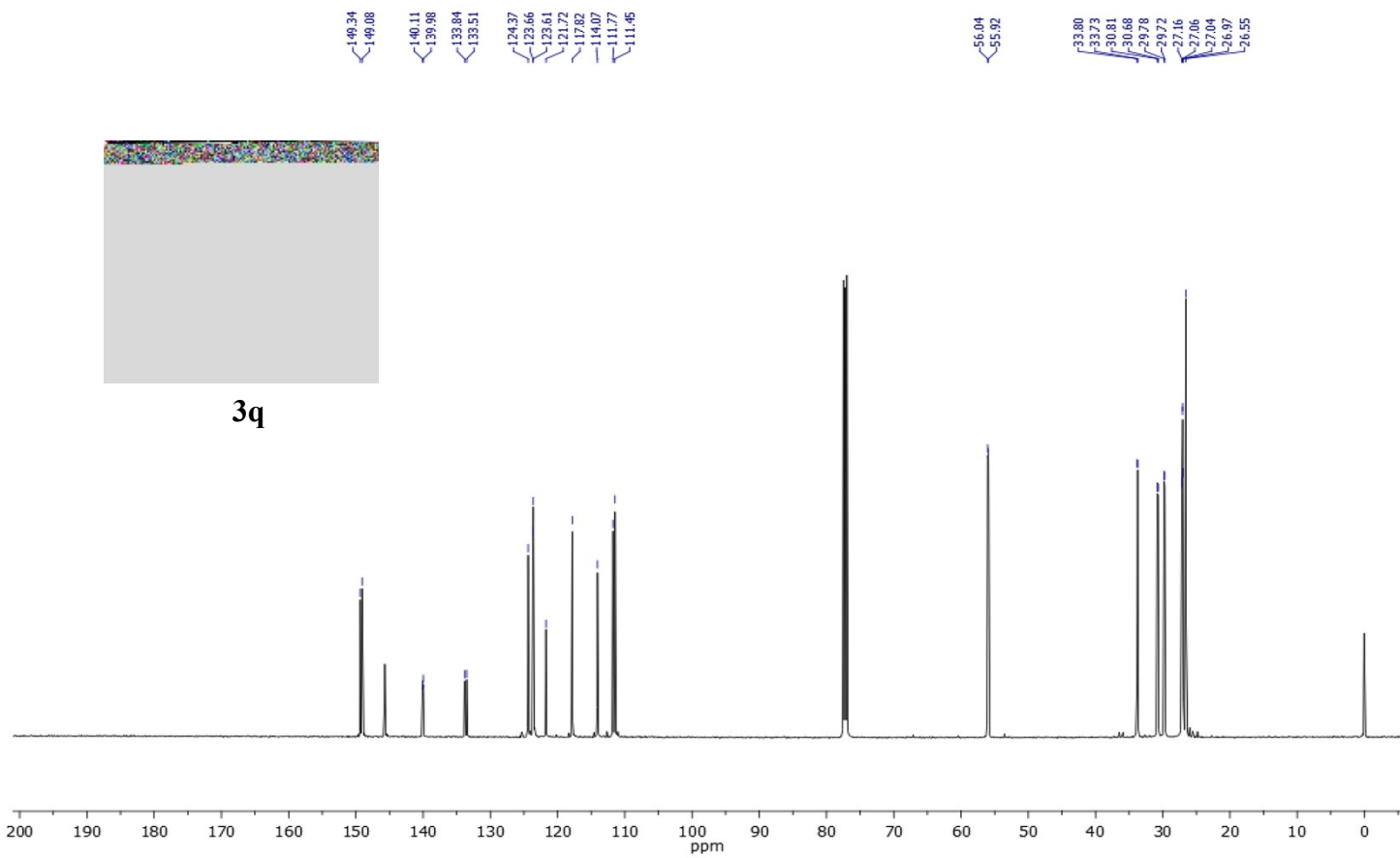


LY-L-75  
3

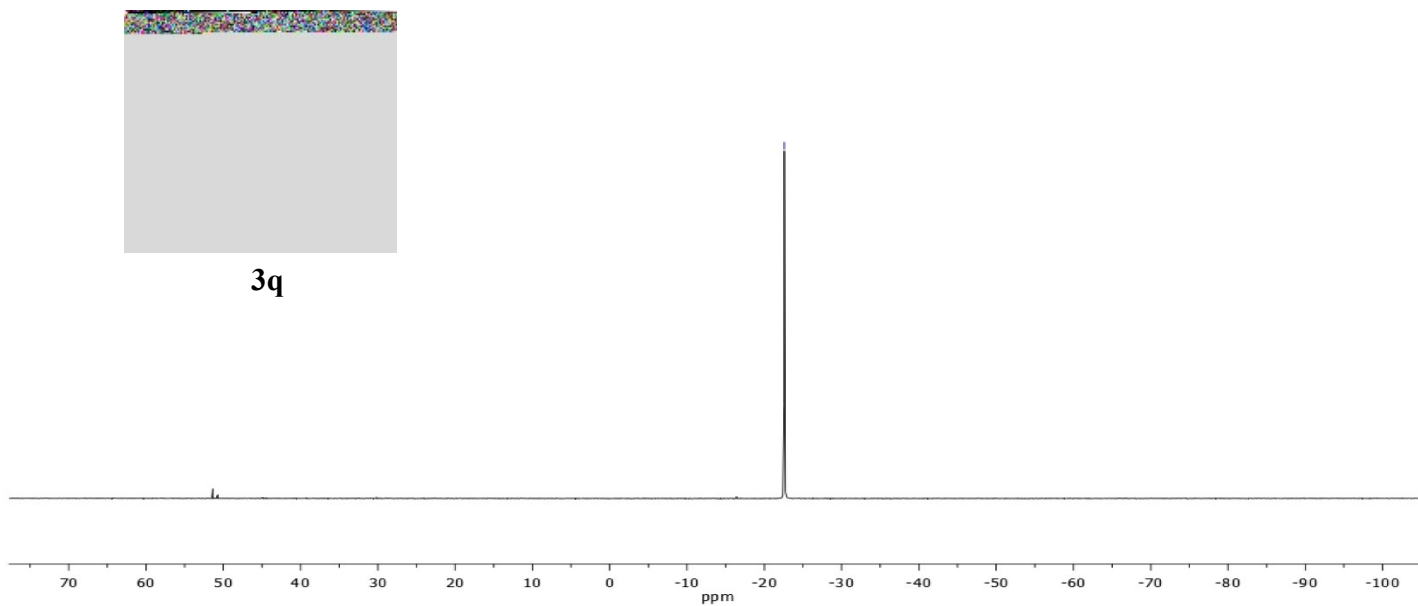




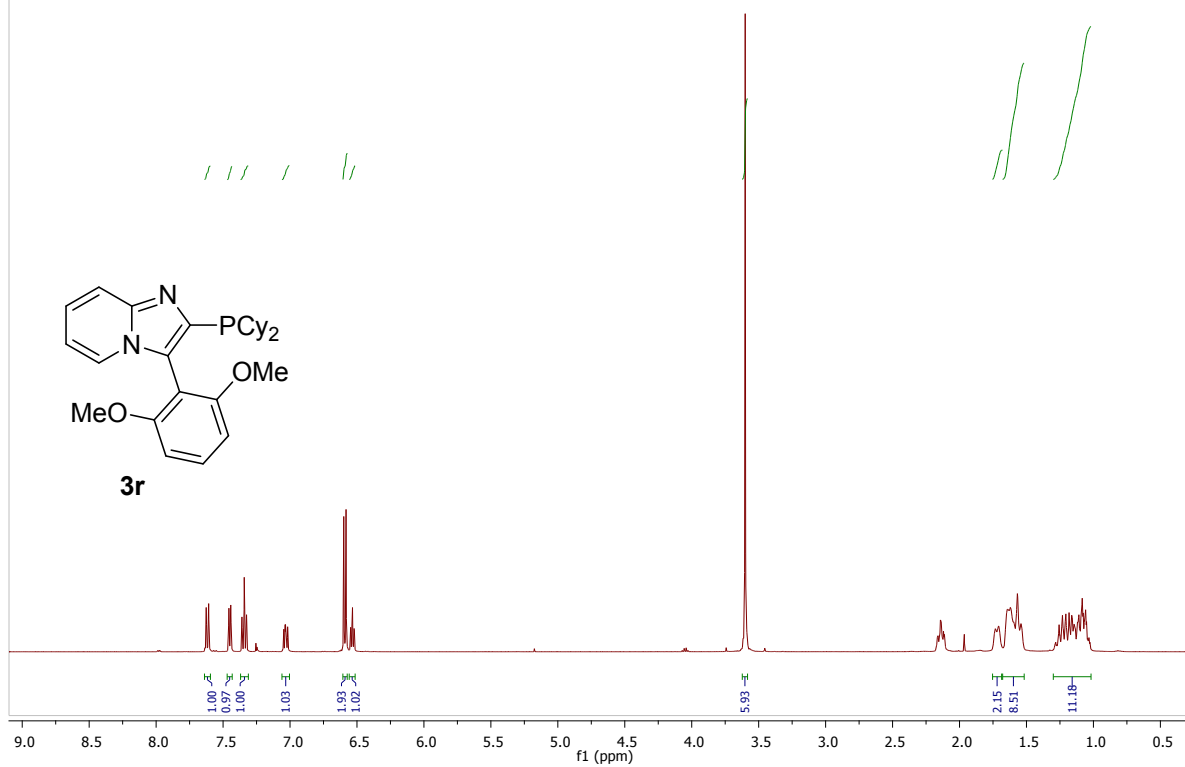




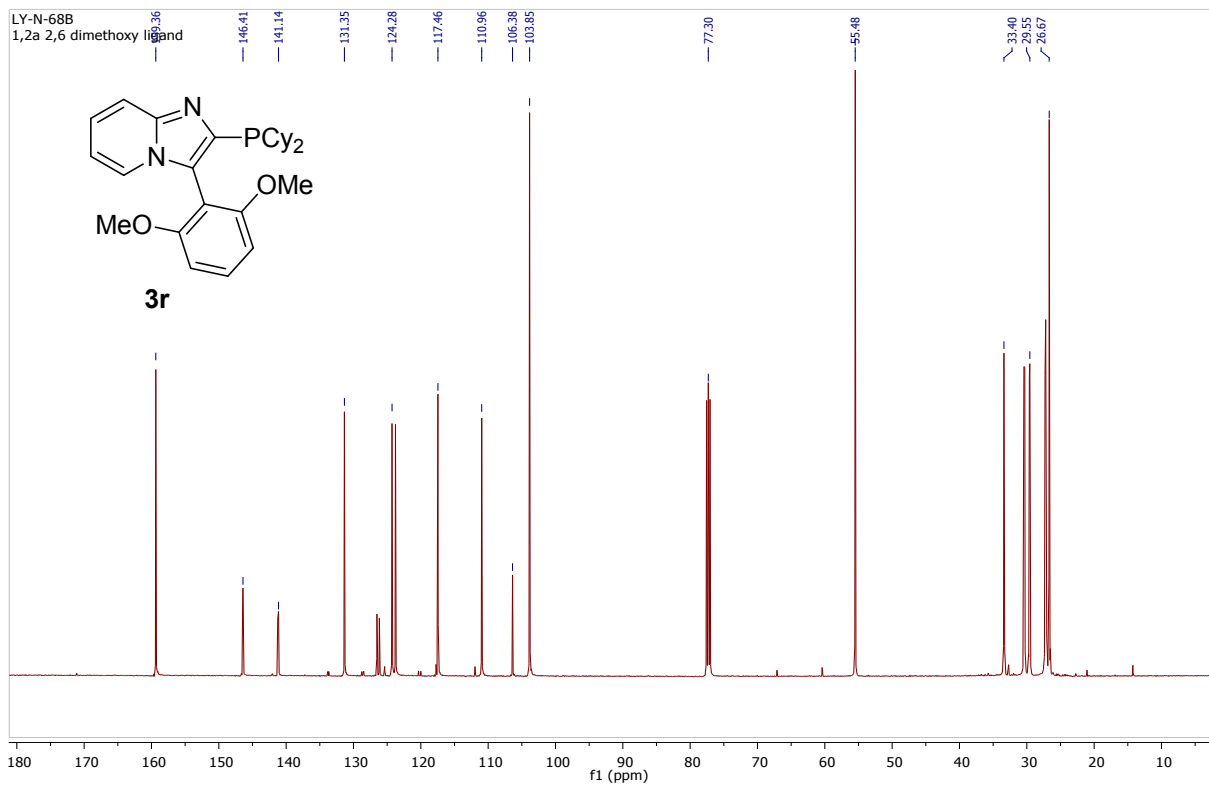
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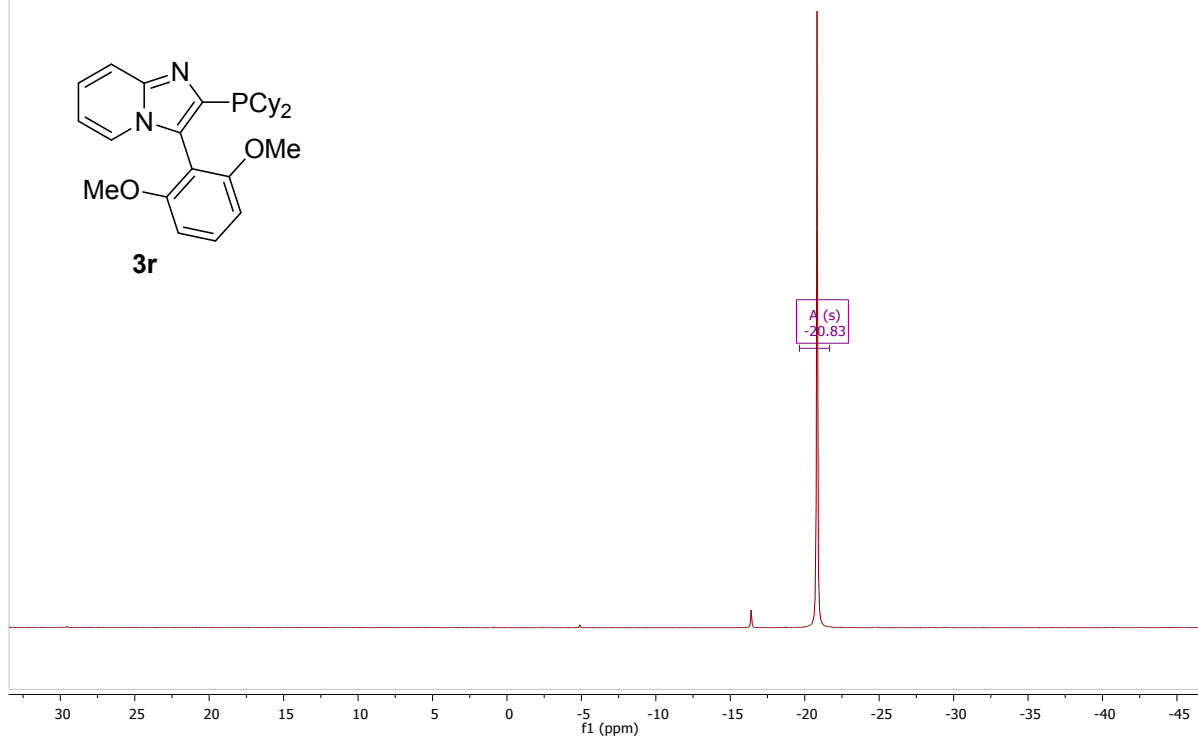
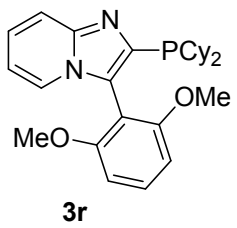
LY-N-68B  
1,2a,2,6 dimethoxy ligand

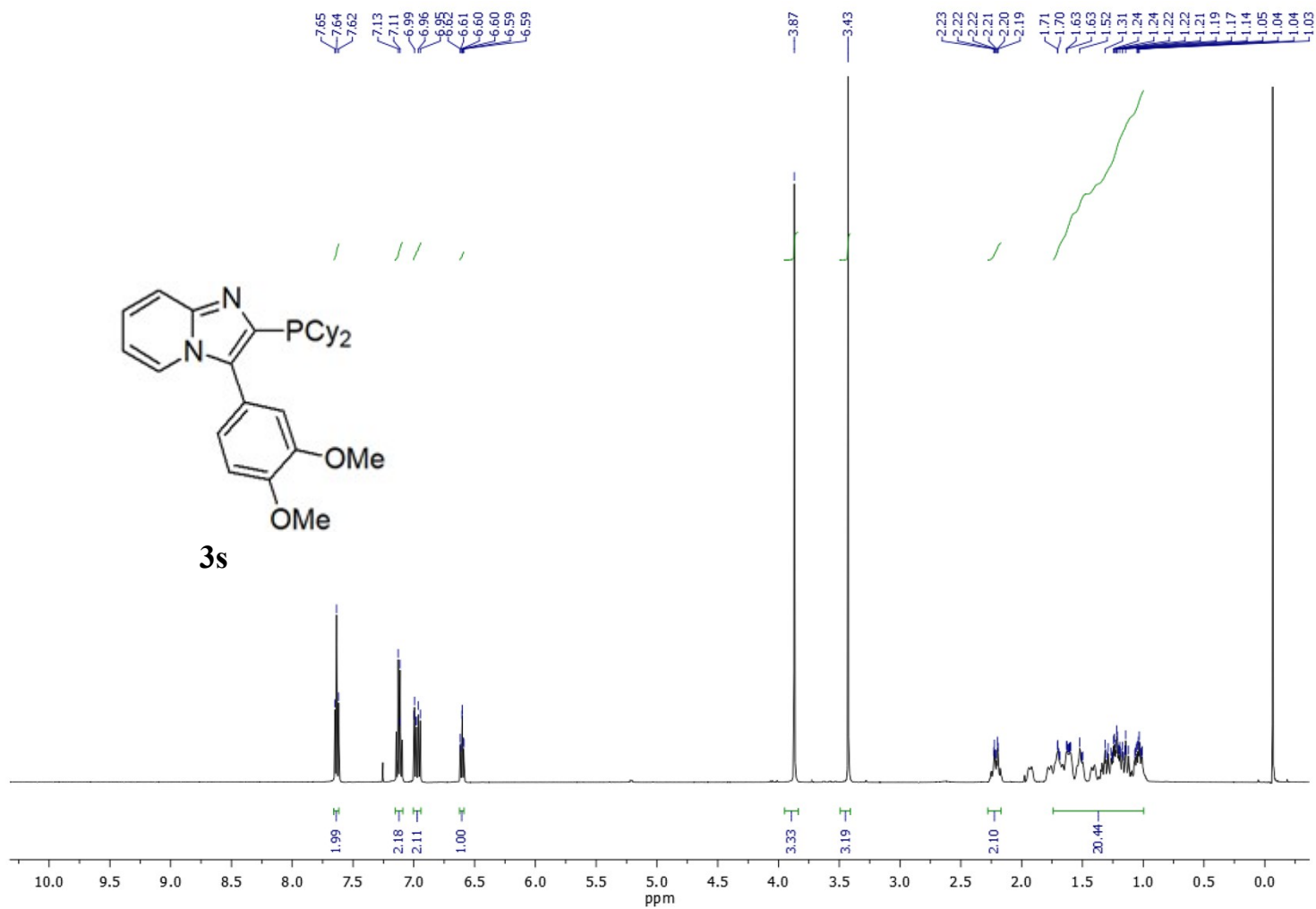


LY-N-68B  
1,2a,2,6 dimethoxy ligand

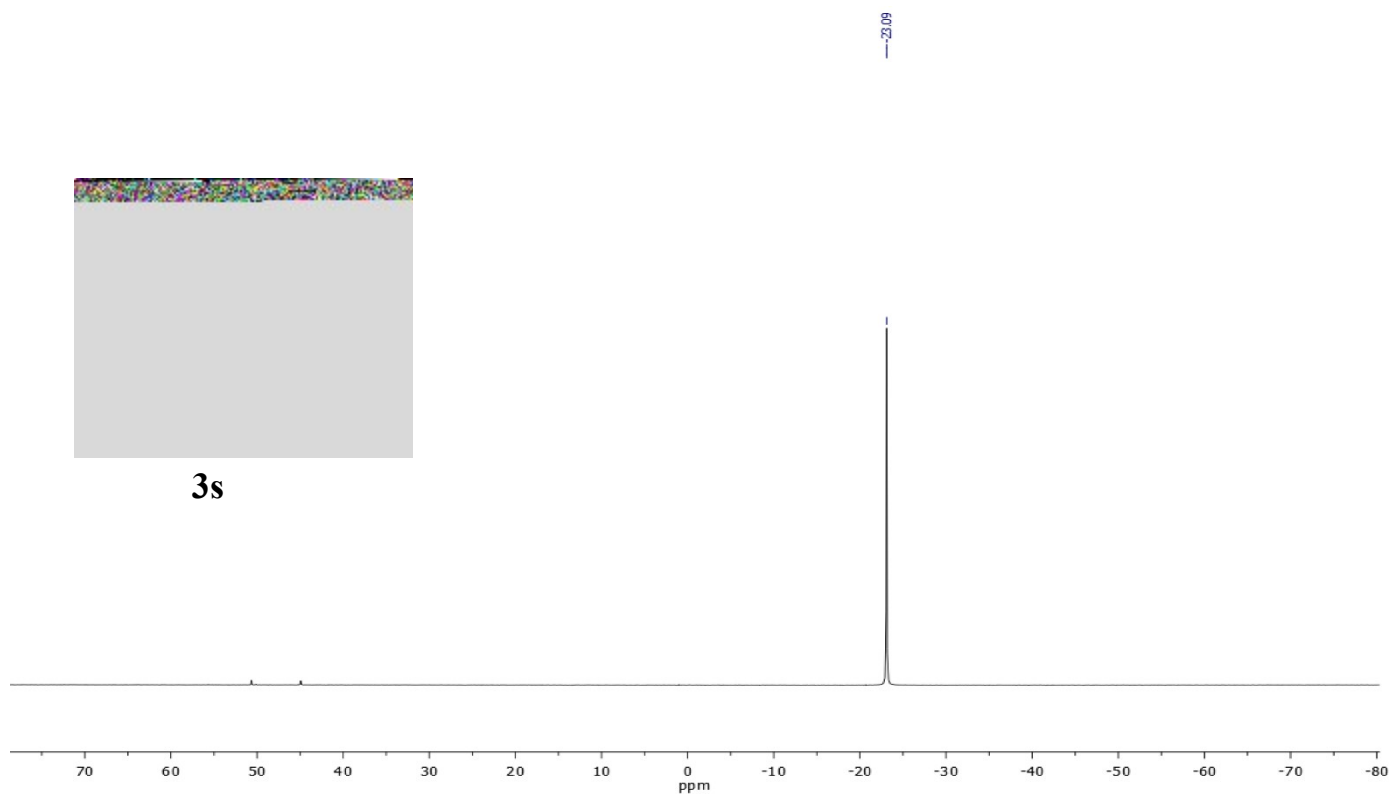
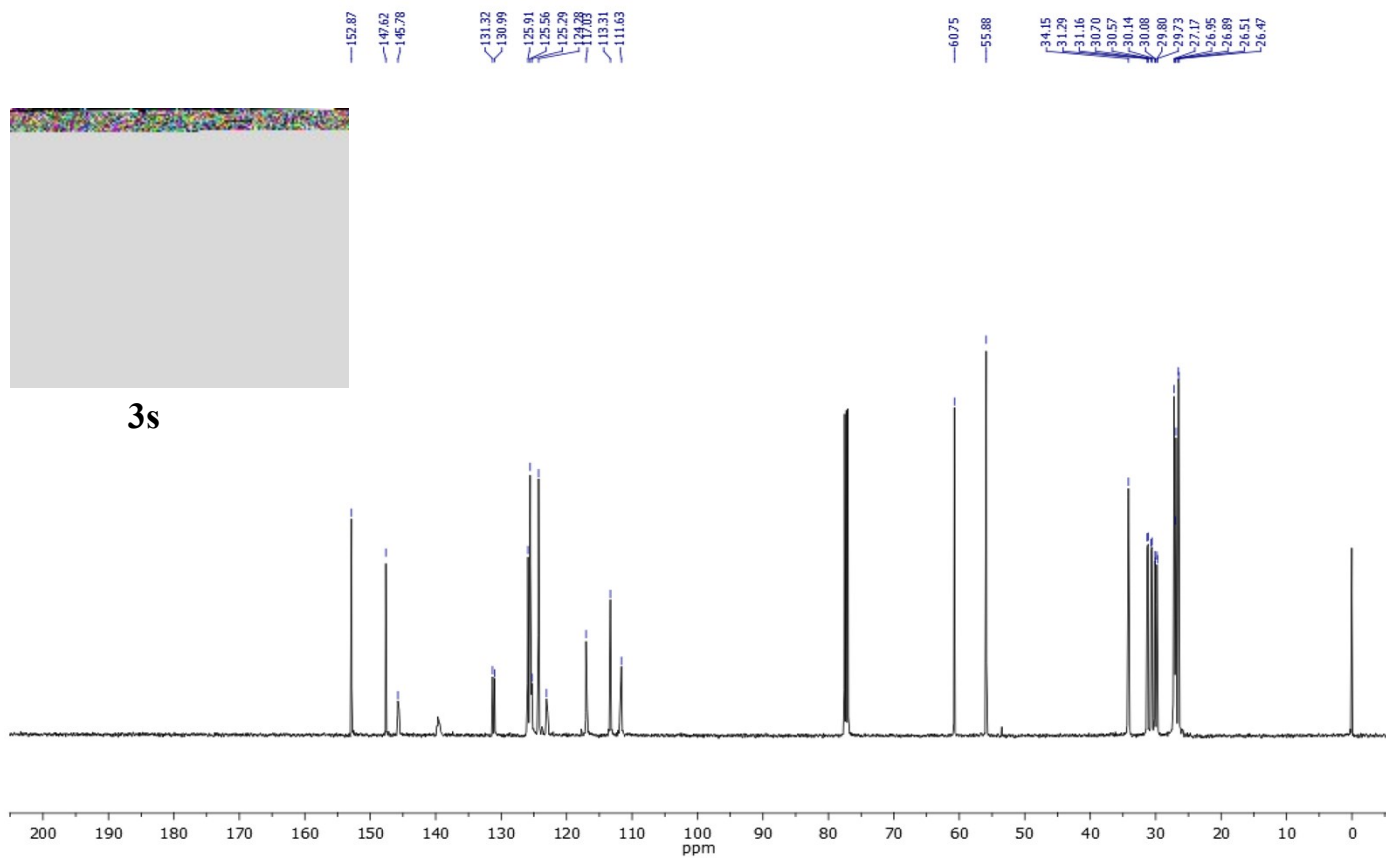


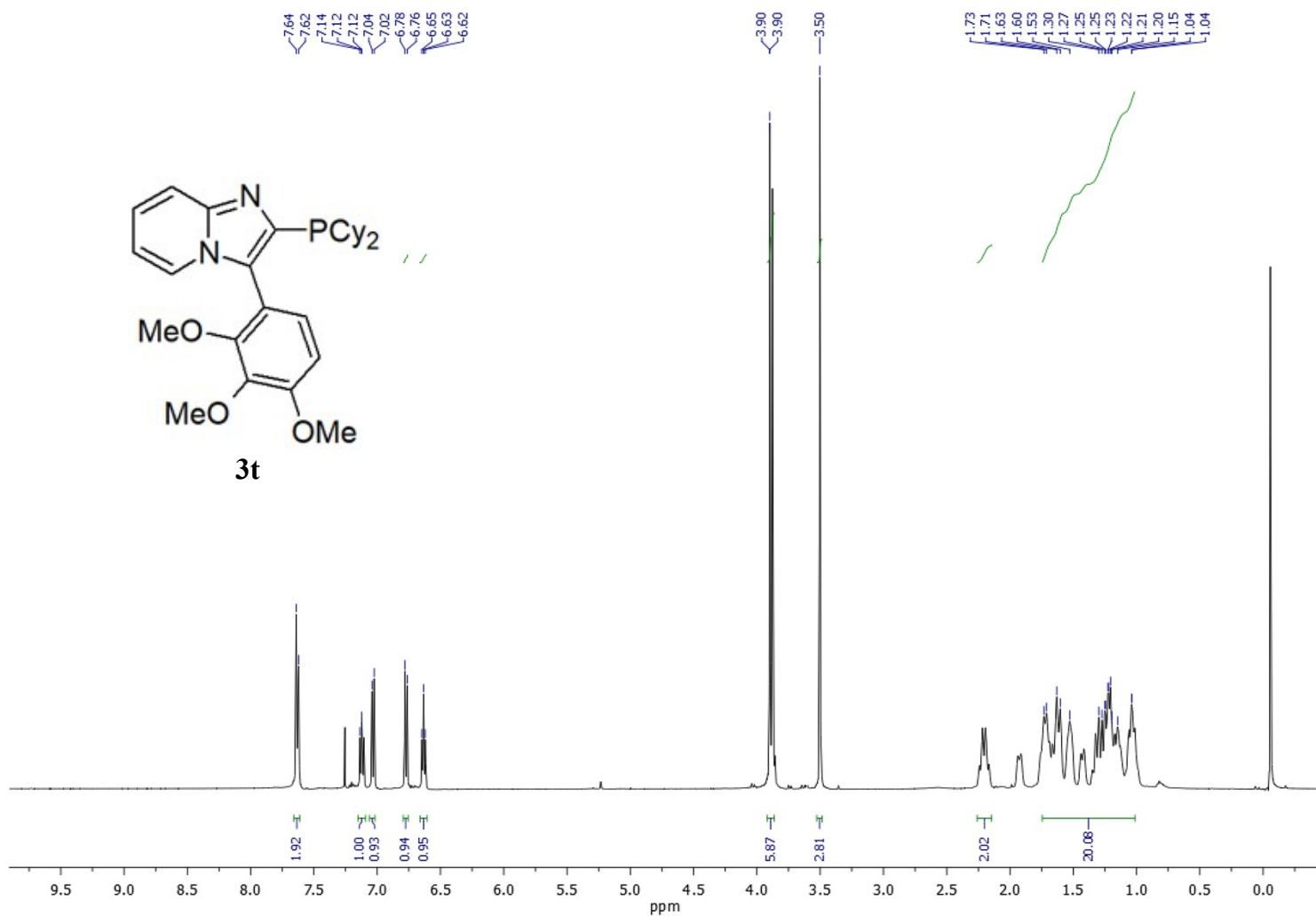
LY-N-68B  
1,2a,2,6 dimethoxy ligand

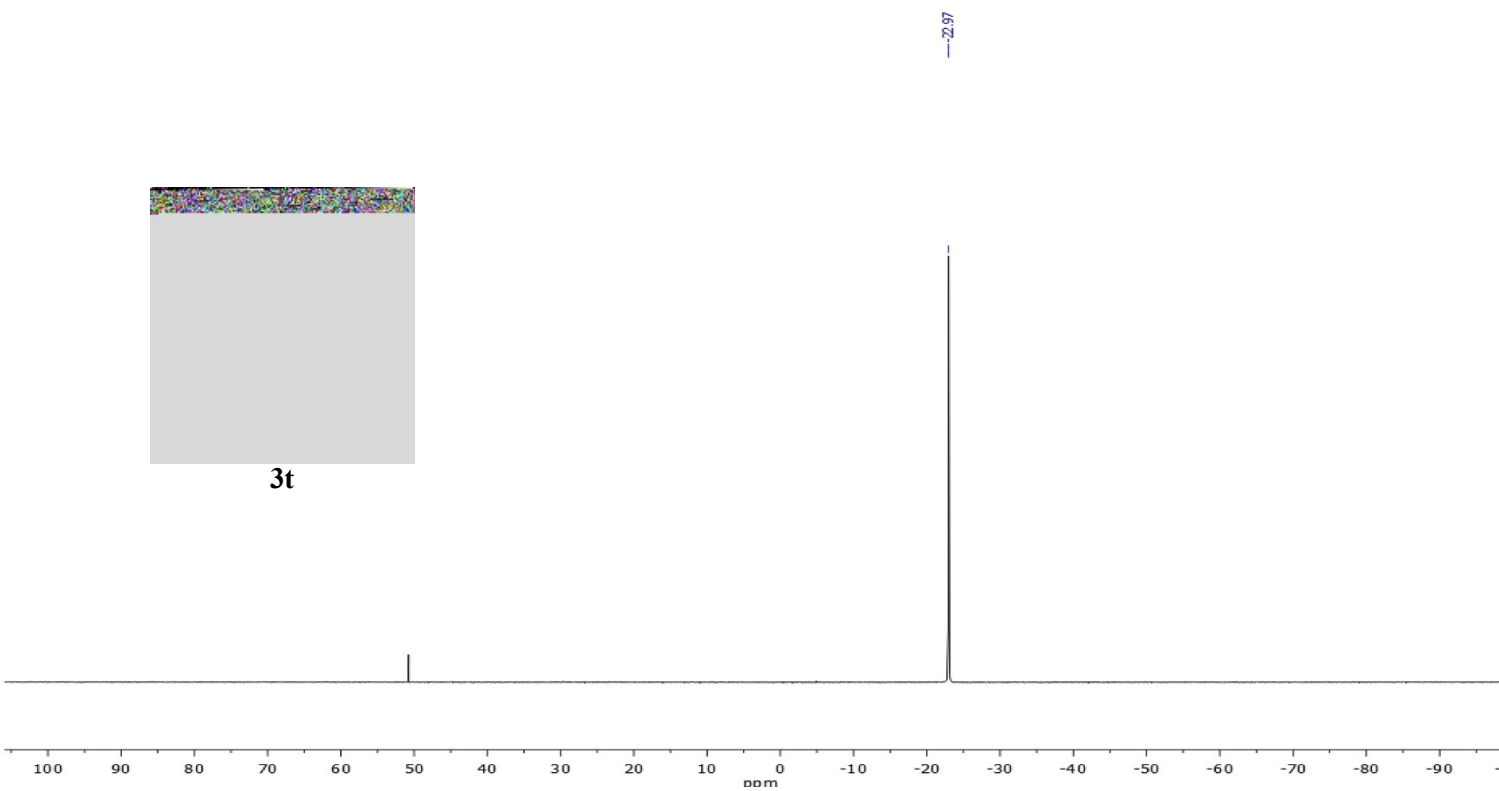
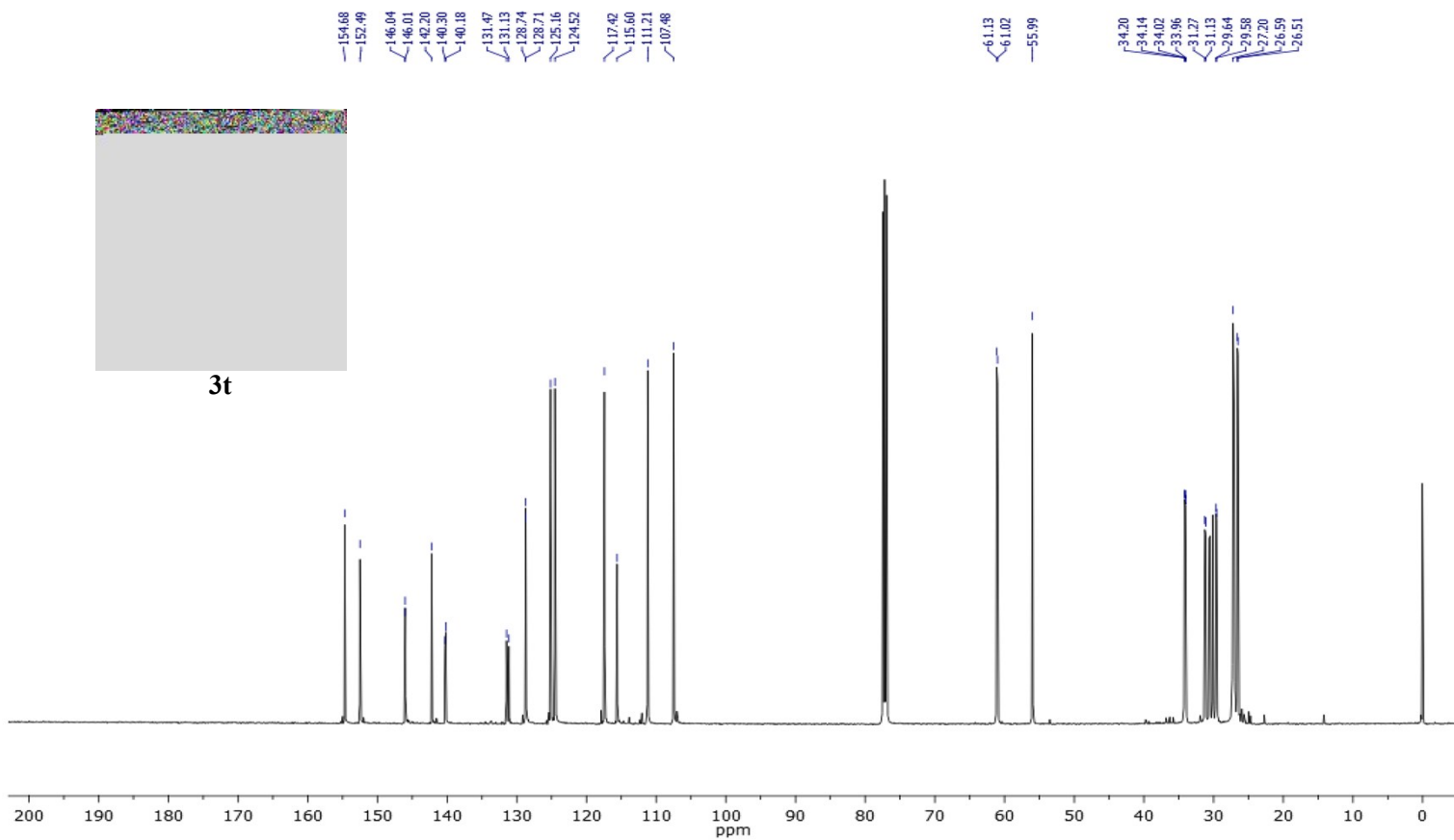


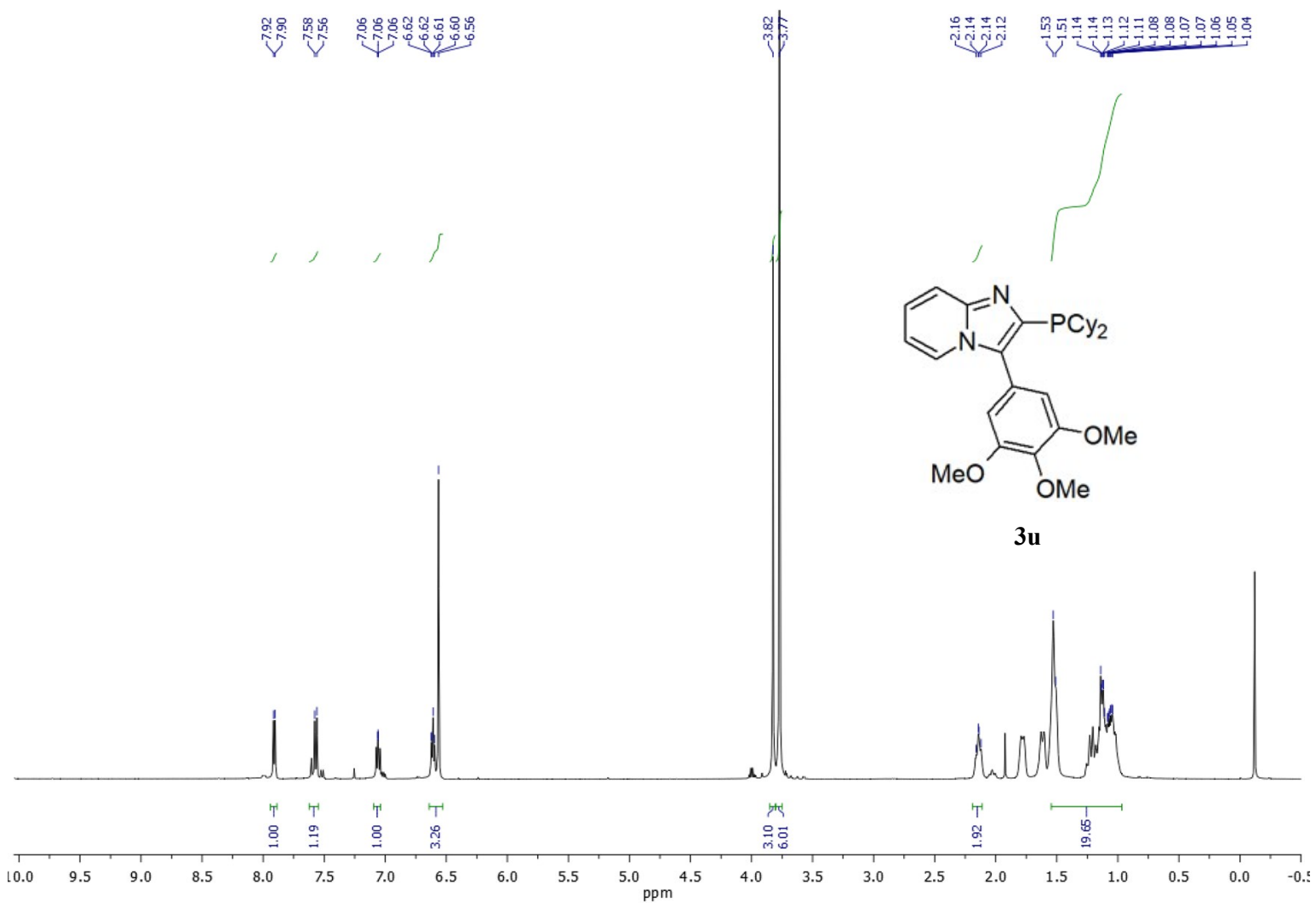


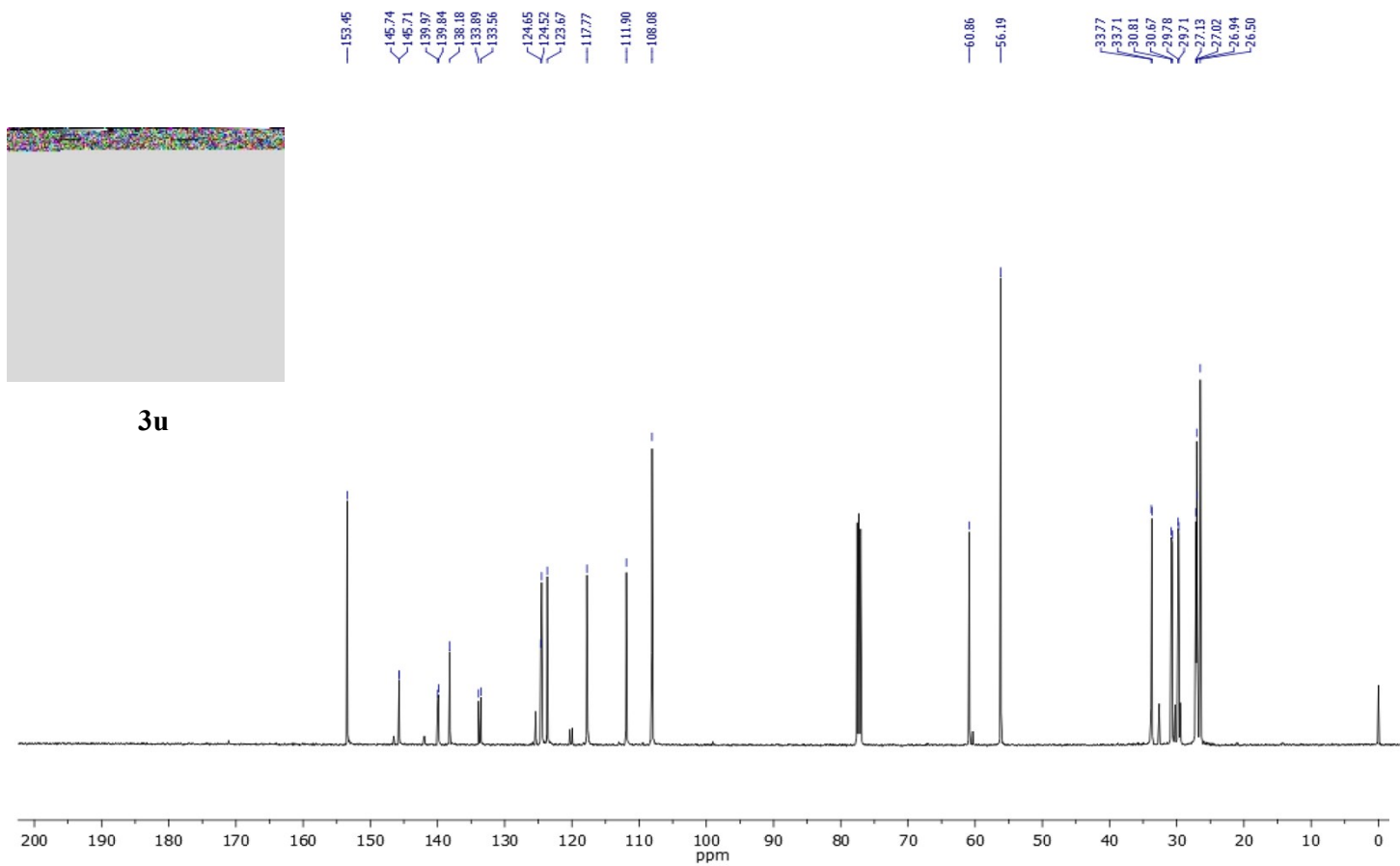




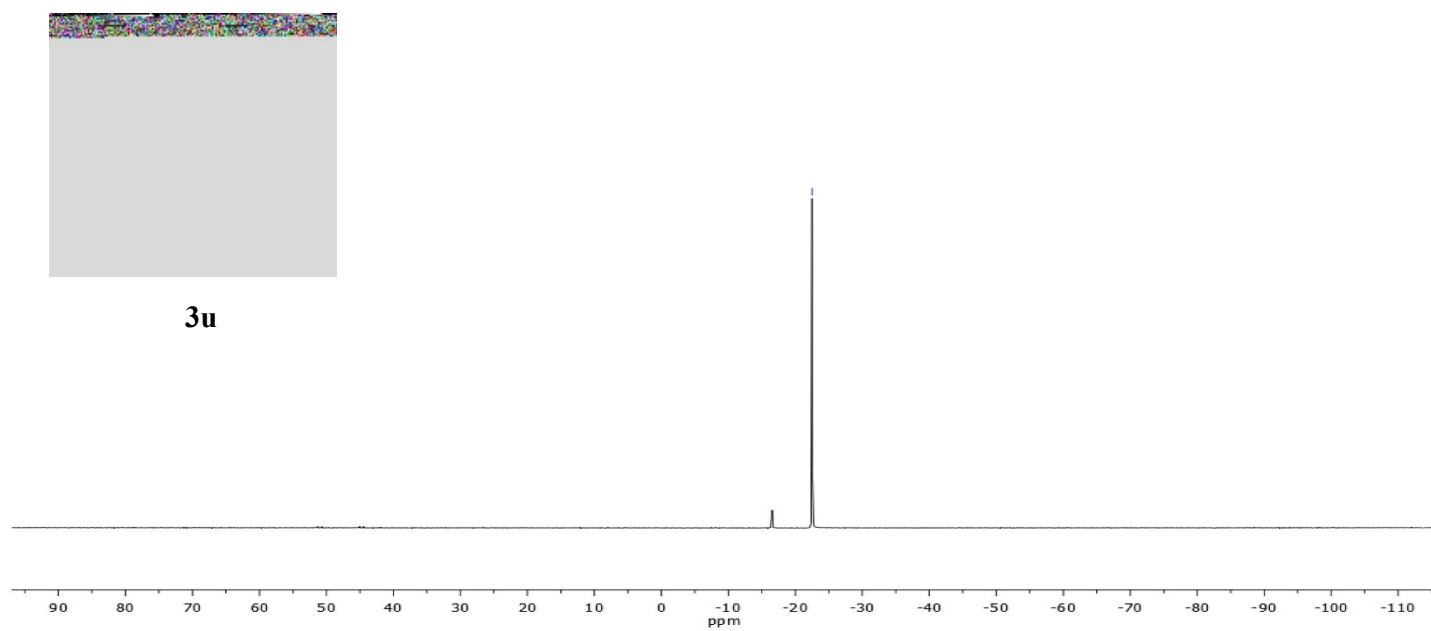


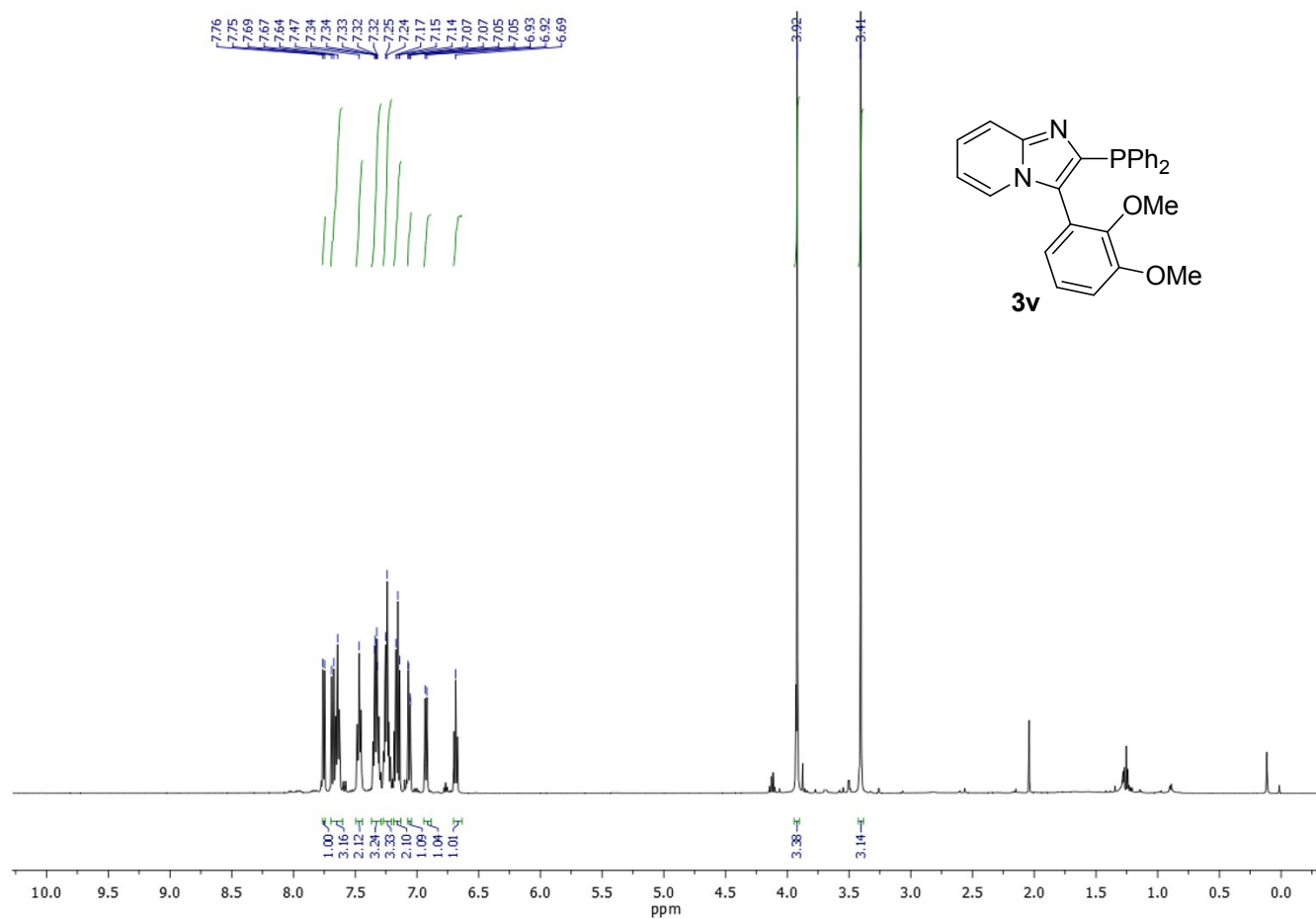


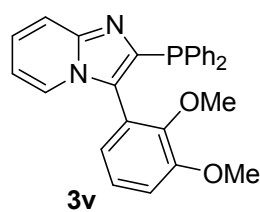
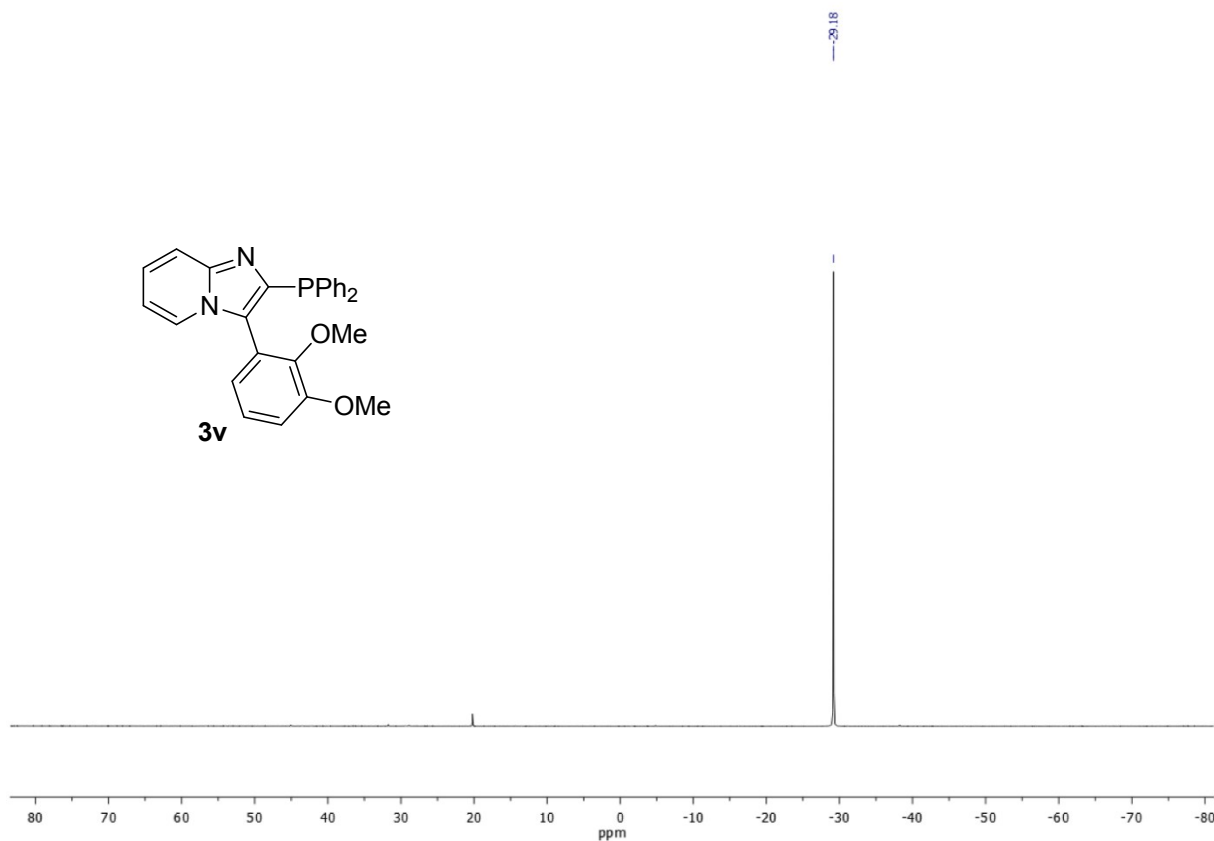
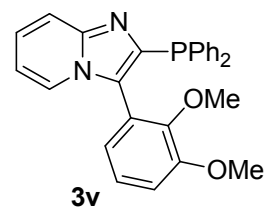
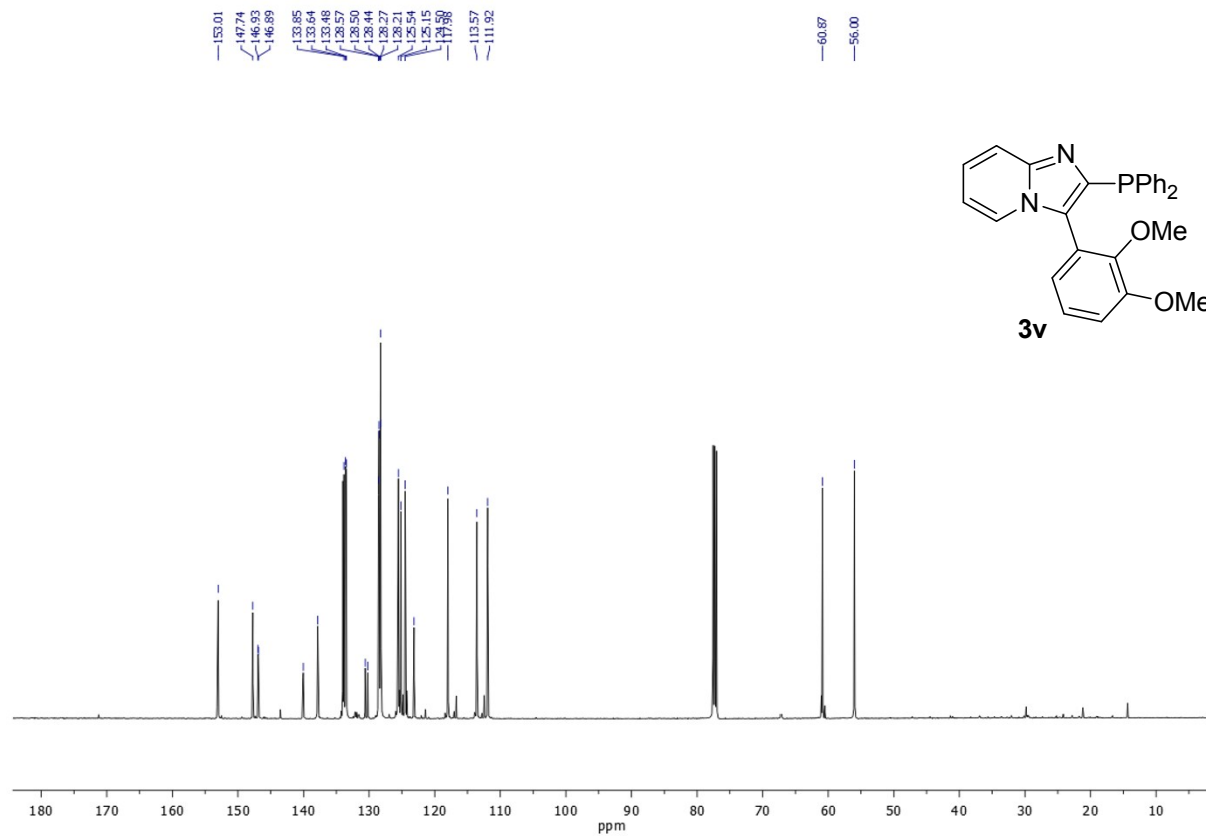


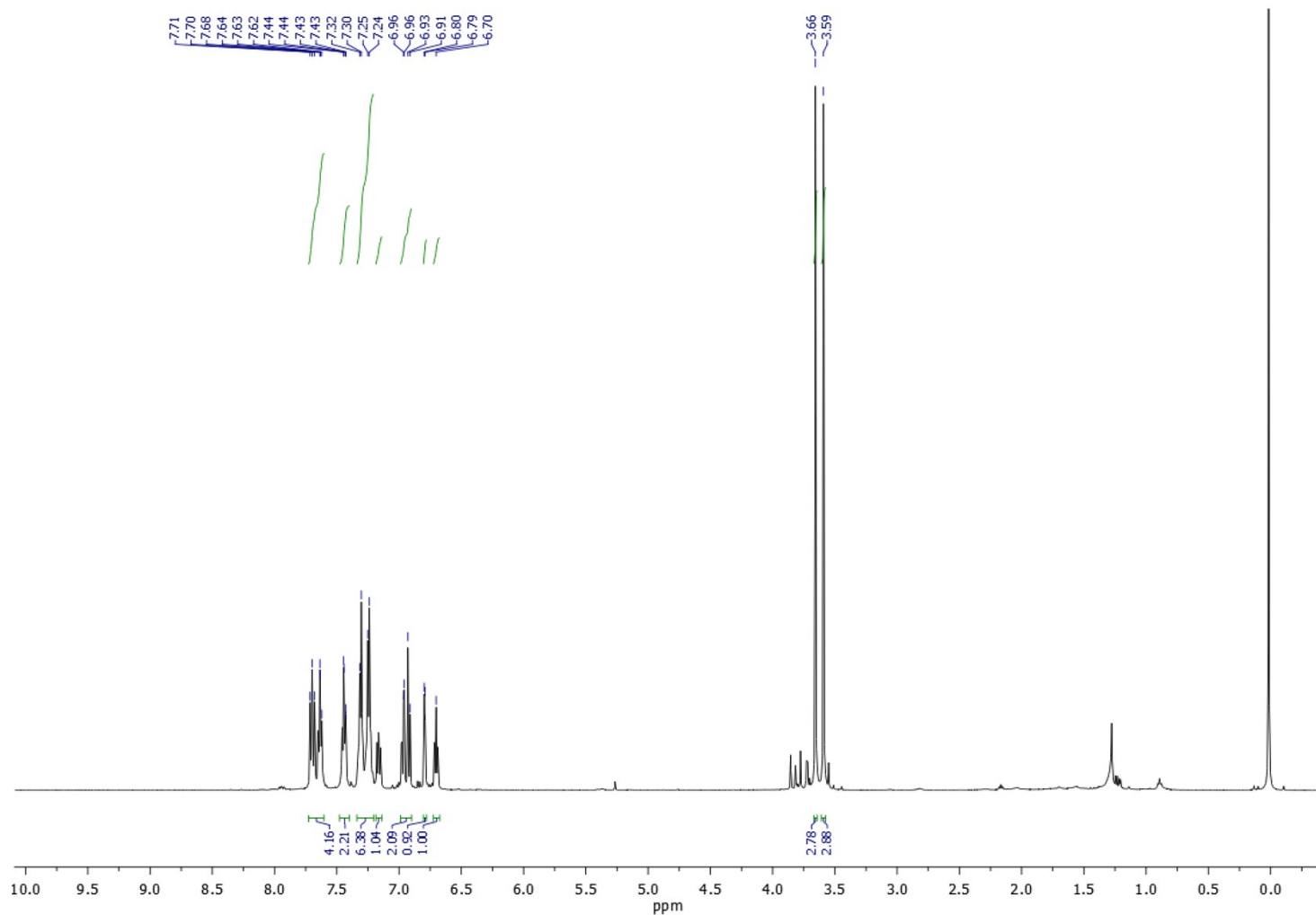


77.09

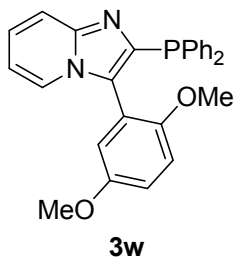
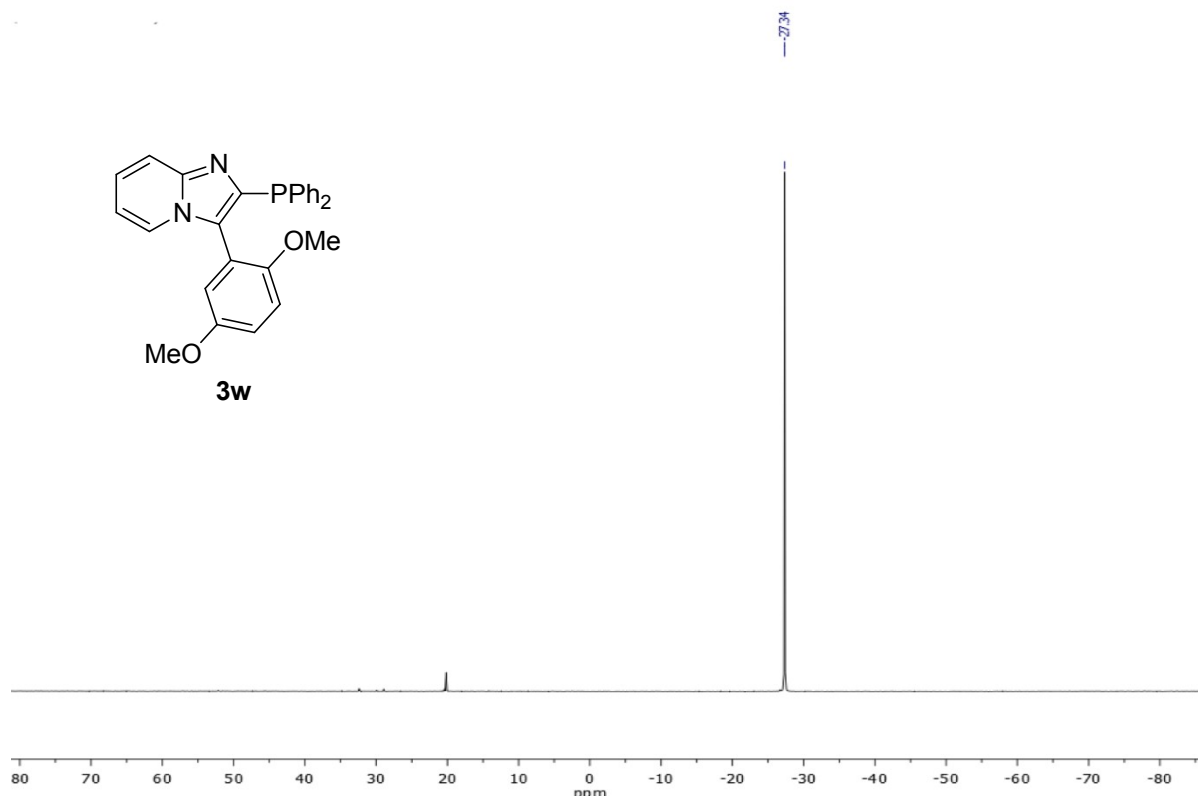
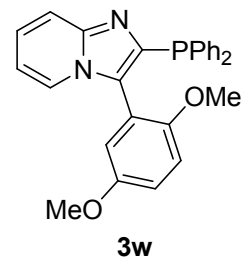
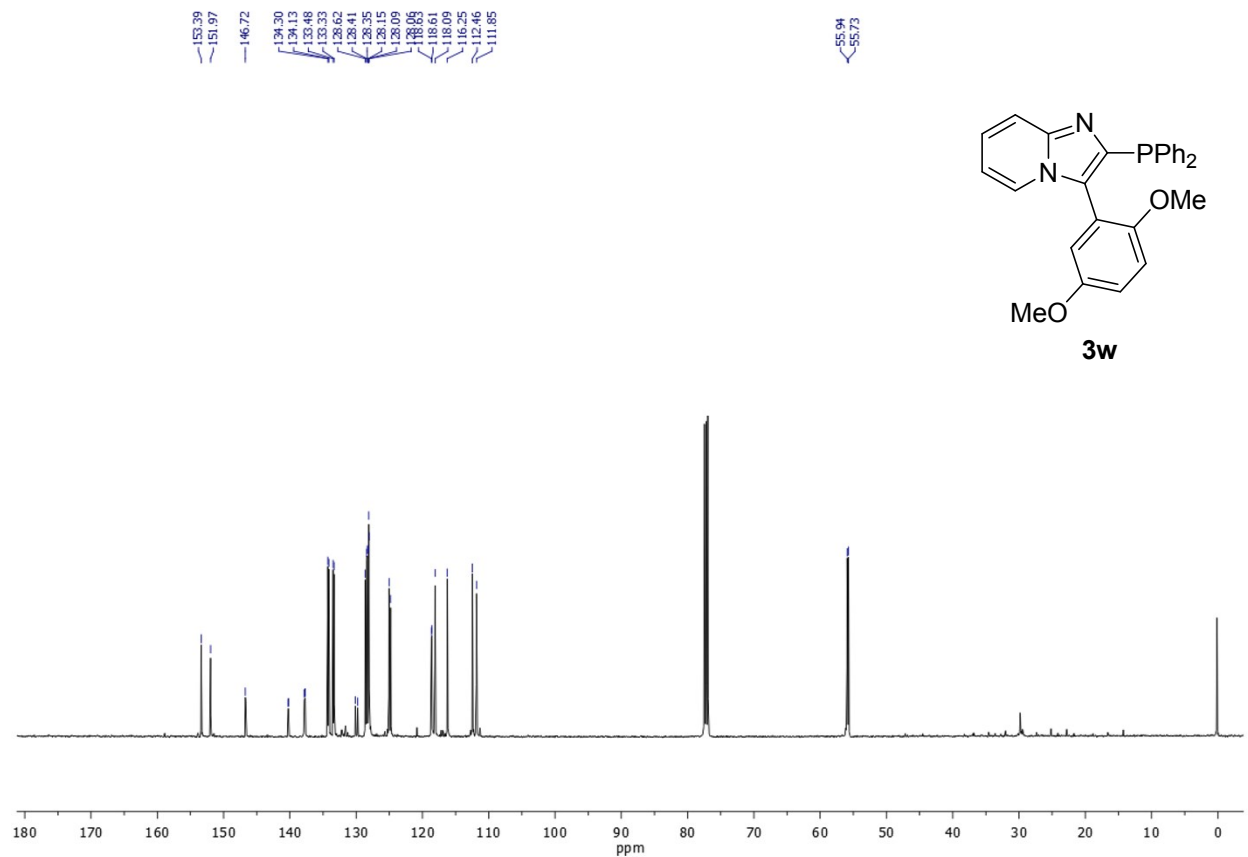


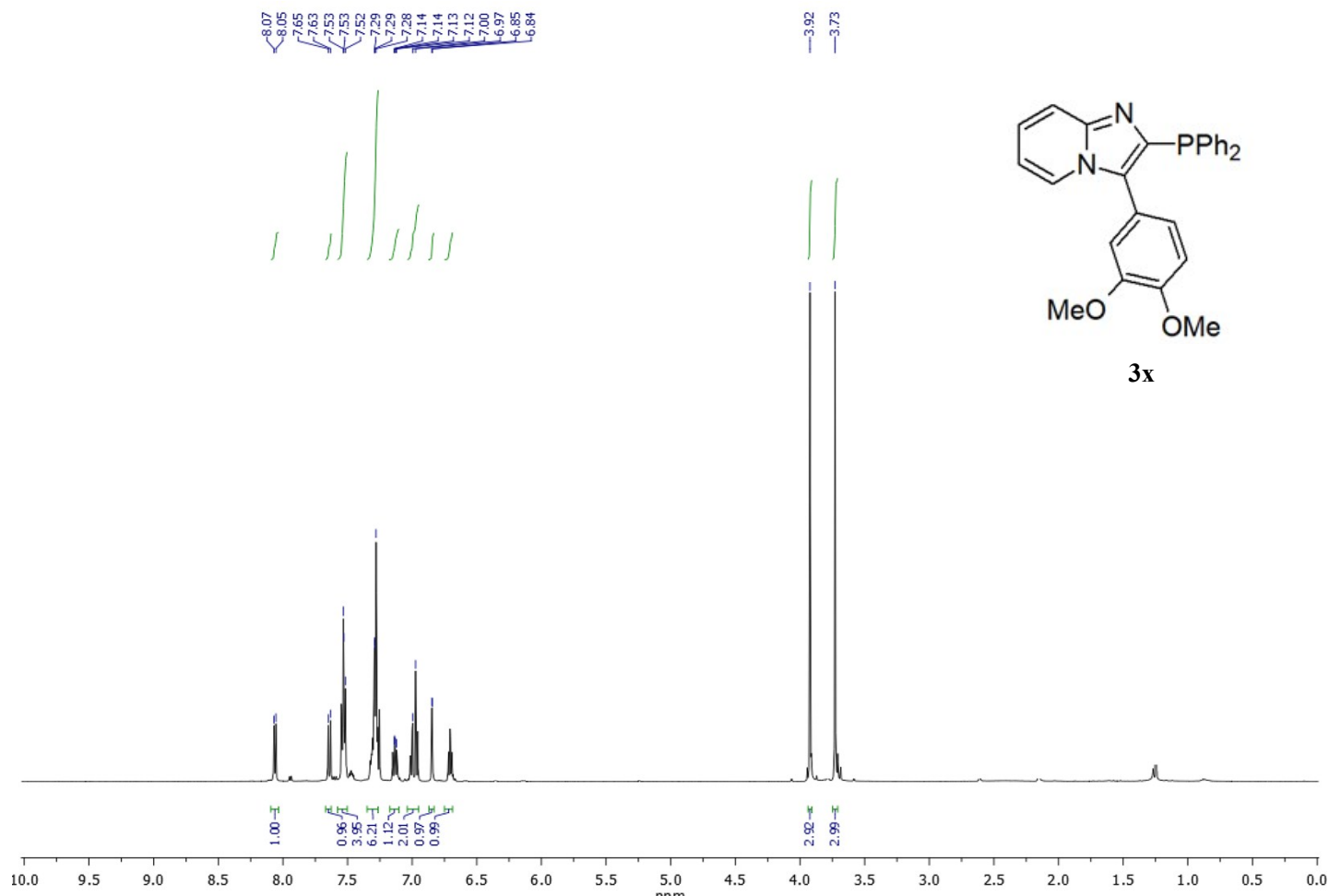


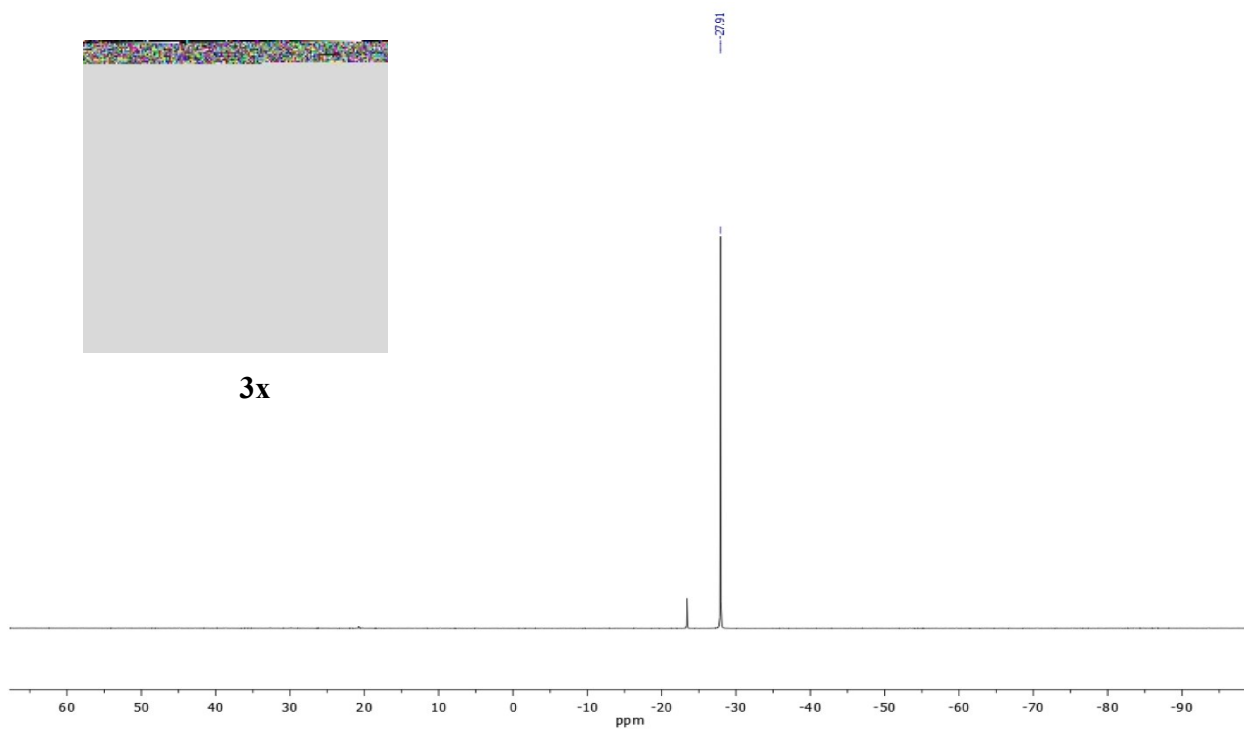
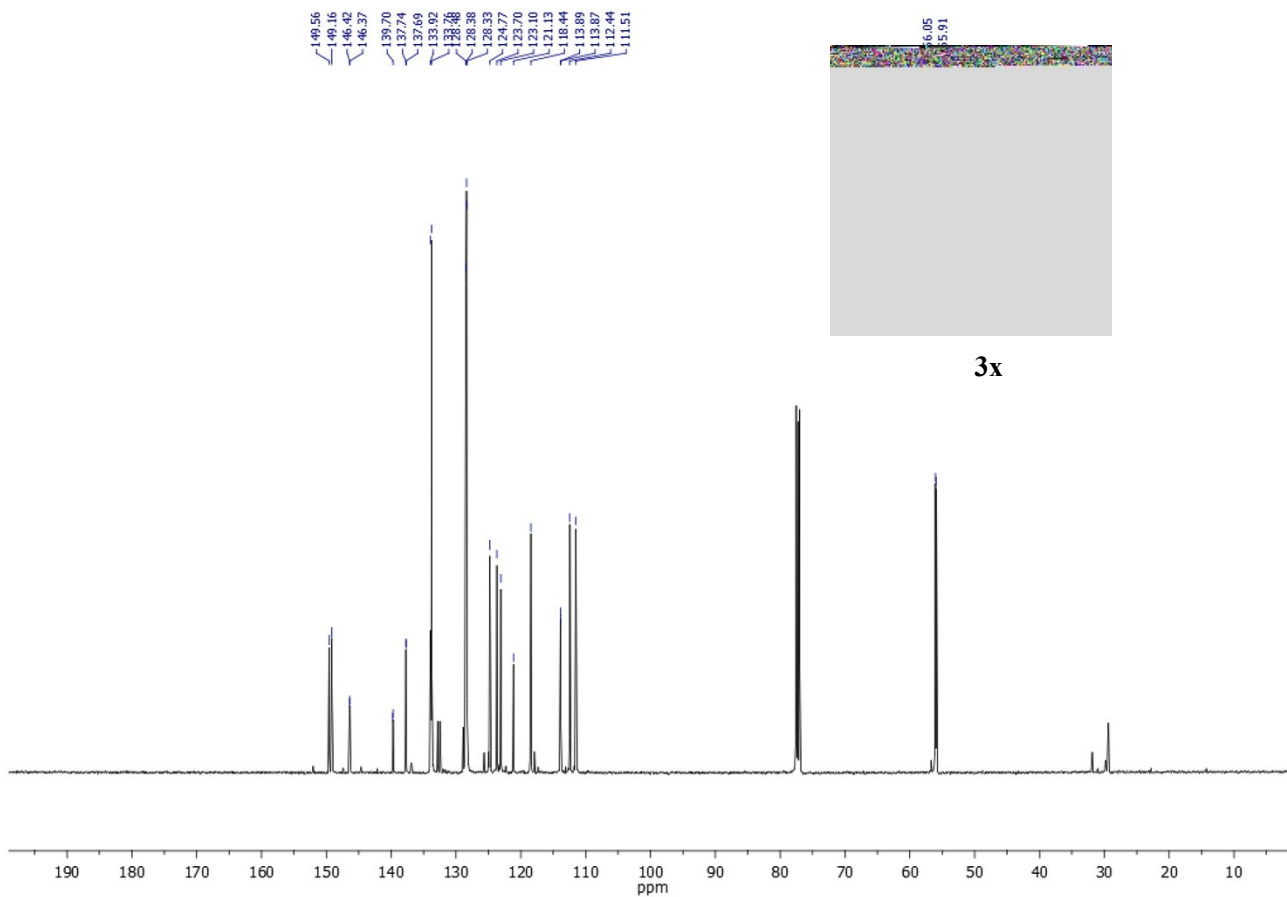


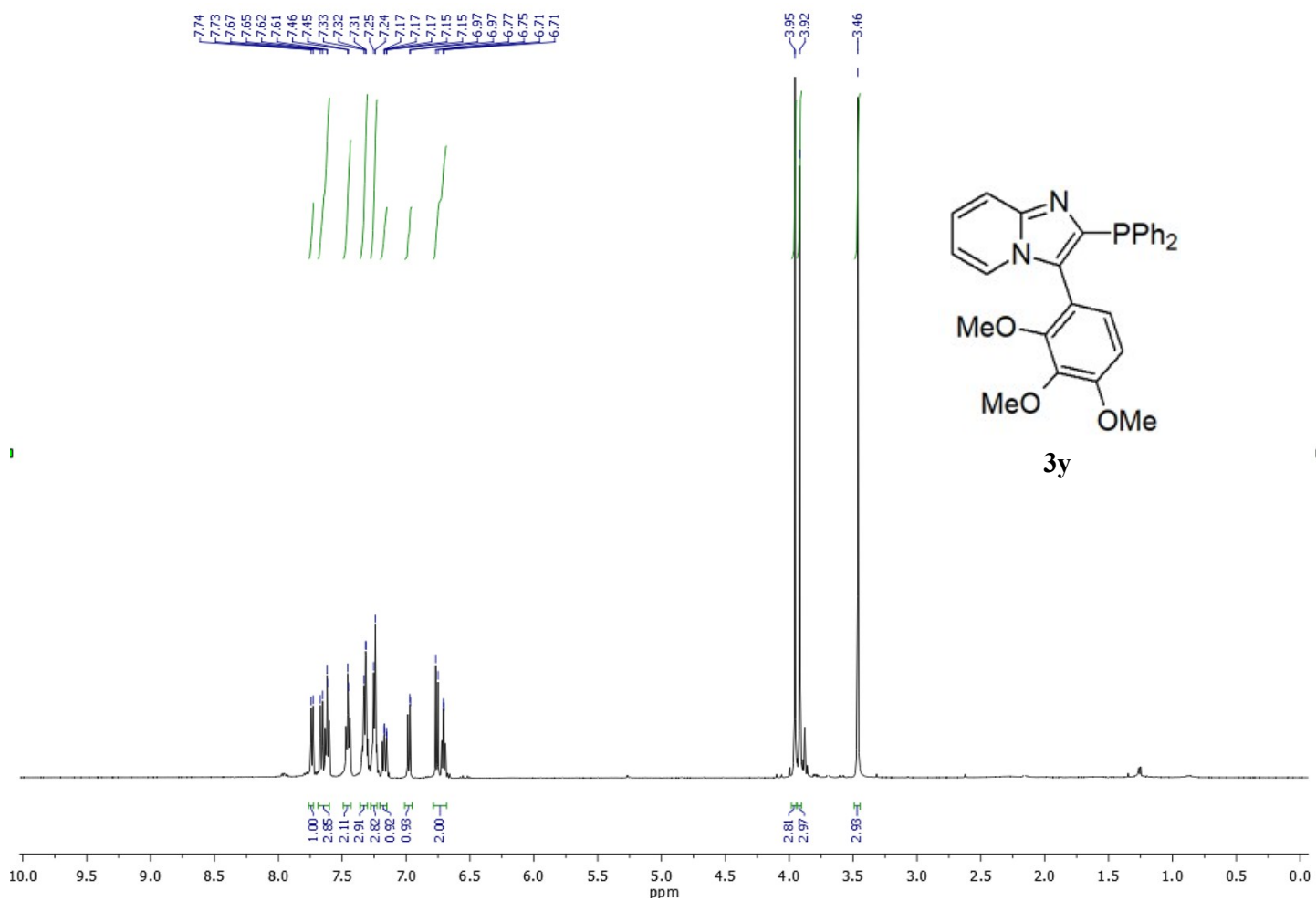


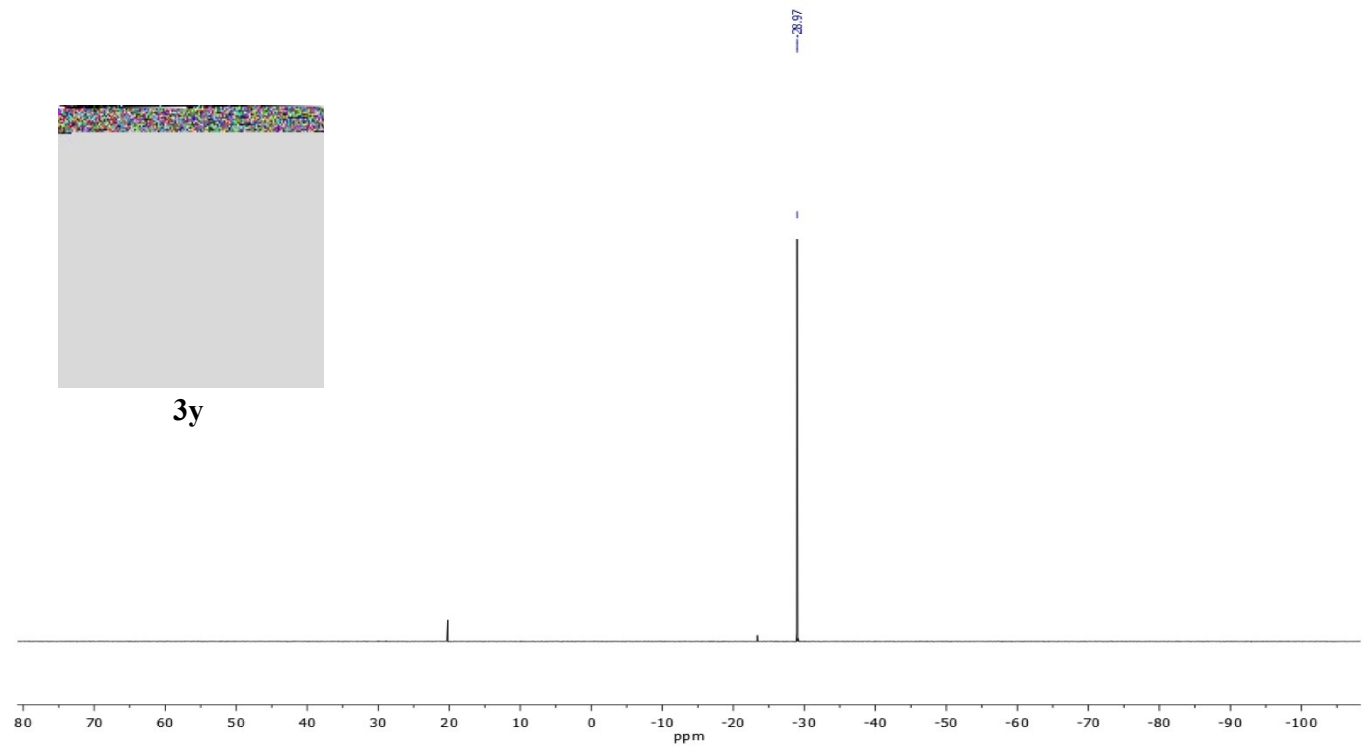
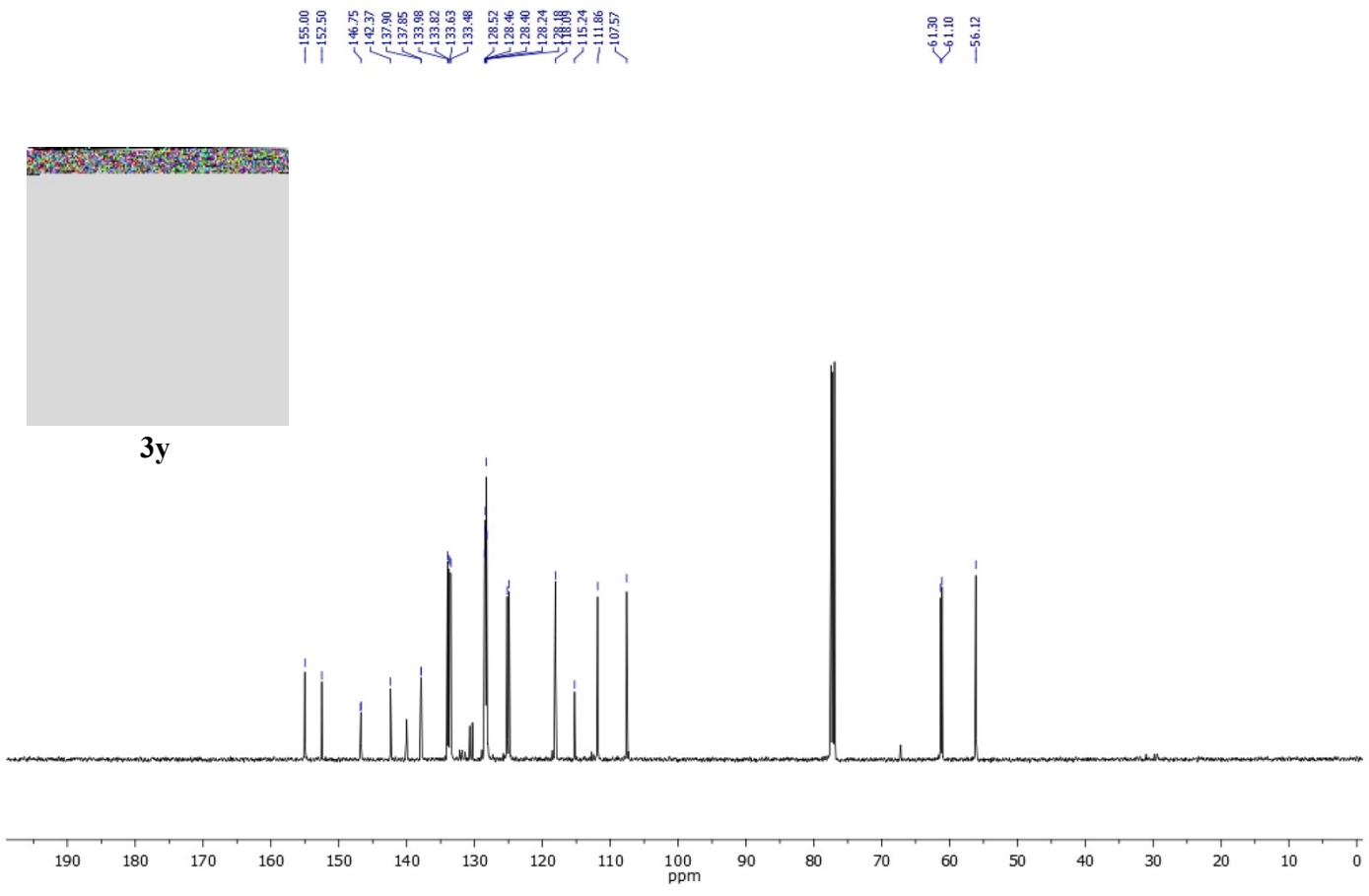


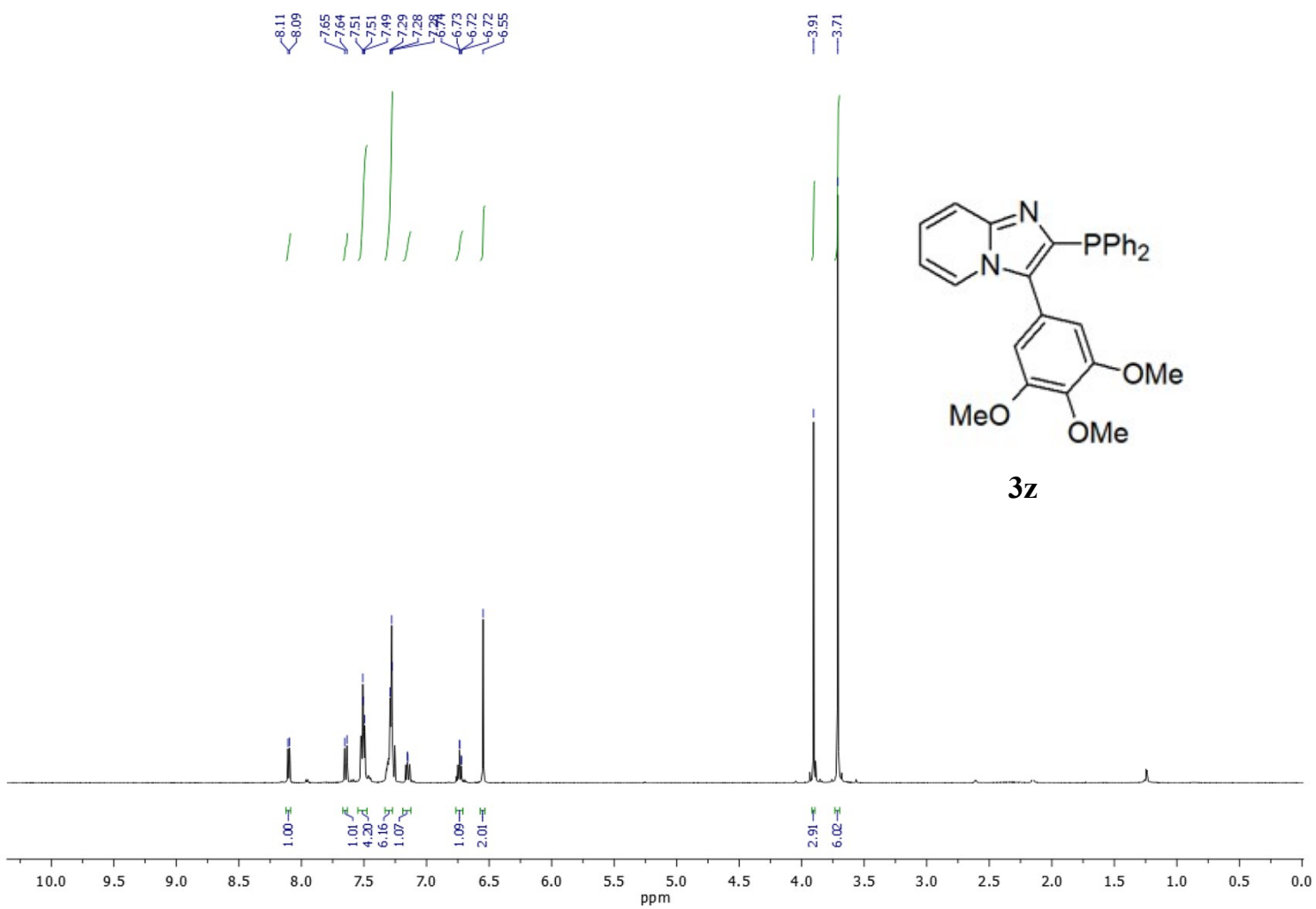


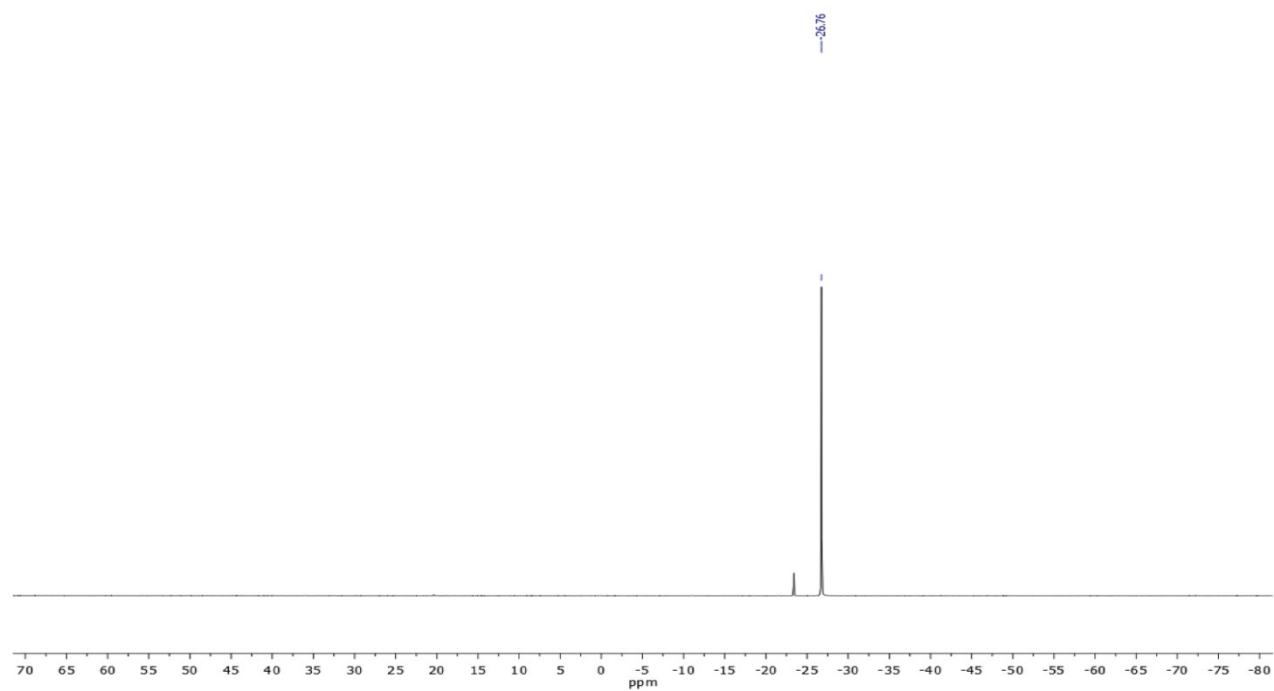
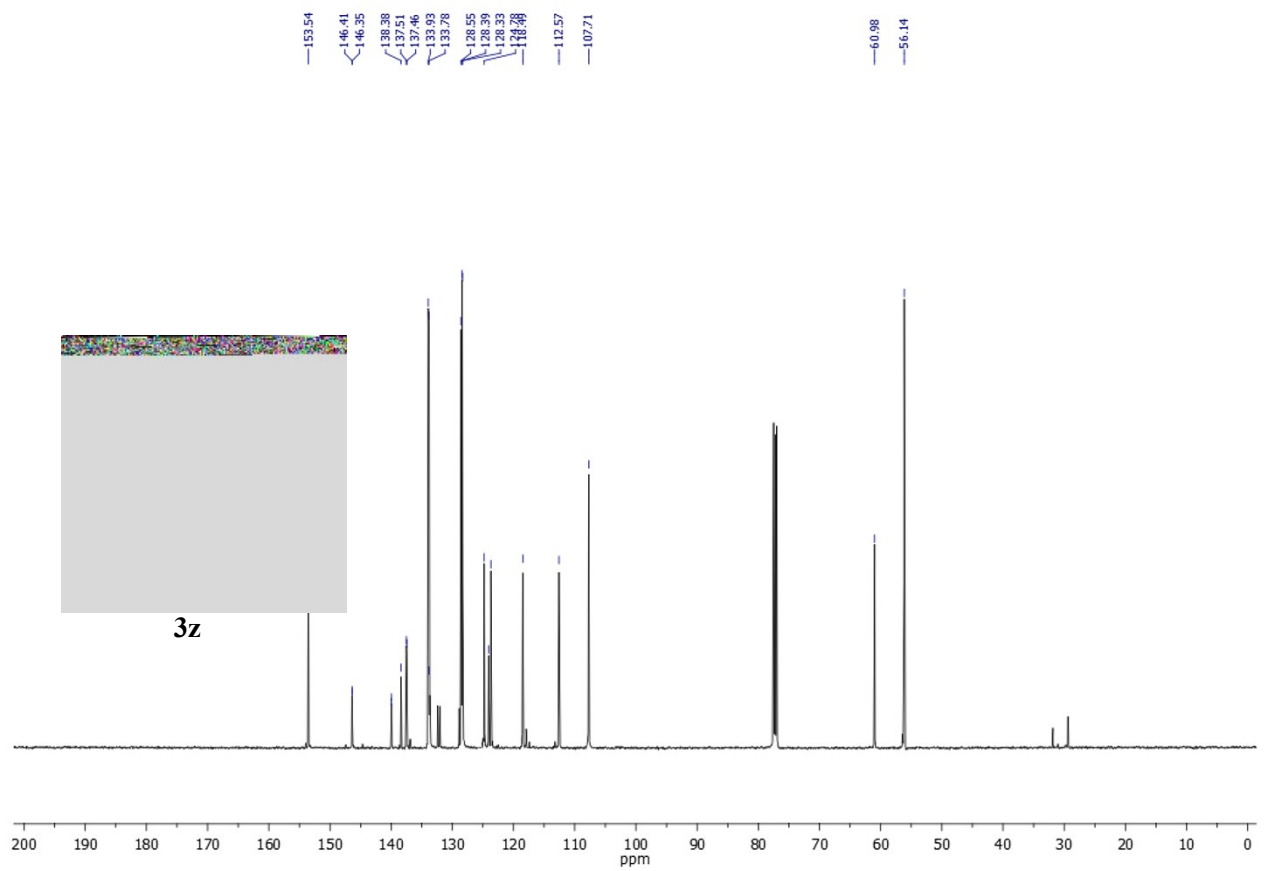












8.00  
7.98  
7.52  
7.30  
7.29  
7.29  
6.75  
6.74  
6.73  
6.72

