Supporting Information

A novel approach on rhodium(III)-catalyzed C−H functionalization of 2,2'-bipyridine derivatives with alkynes: significant substituent effect

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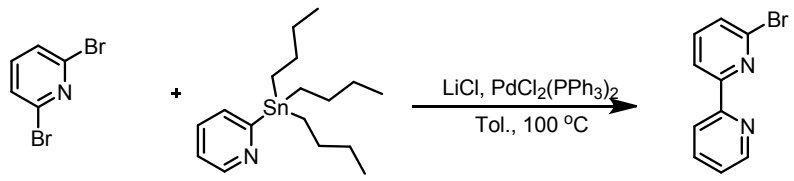
General Information

The ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded with Bruker 400 MHz nuclear spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource.

Preparation of Starting Materials

Synthesis of 1a

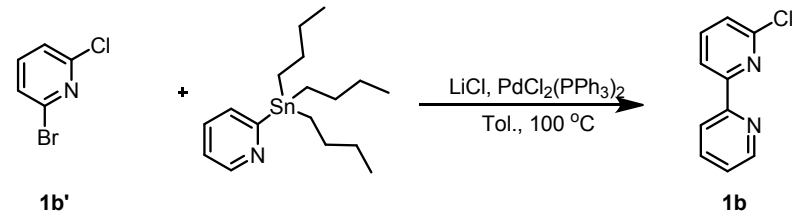


1a' **1a**

A toluene solution (35.0 mL) containing **1a'** (1.26 g, 5.3 mmol), 2-(tri-n-butylstannyl)pyridine (1.95 g, 5.3 mmol), LiCl (2.5 g, 53.0 mmol) and $[PdCl_2(PPh_3)_2]$ (294.8 mg, 0.42 mmol) was deaerated by bubbling N_2 through it. The mixture was then refluxed under N_2 for 18 h, and an aqueous solution (10.0 mL) of NaF (2.2 g, 53.0 mmol) was added to the solution at room temperature. The resultant solution was further stirred at ambient temperature for 30 min. An insoluble solid was filtered off, and the filtrate was treated with a 5% Na_2CO_3 aqueous solution in a separating funnel. The organic layer was dried with anhydrous sodium sulfate, and the solvents were

evaporated to dryness under reduced pressure. The obtained yellow solid was dissolved in PE/EA (95:5, v/v), and purified on a silica gel column.

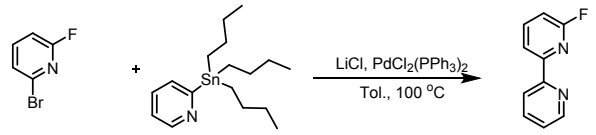
Synthesis of 1b



1b' **1b**

A toluene solution (35.0 mL) containing **1b'** (1.02 g, 5.3 mmol), 2-(tri-n-butylstannyl)pyridine (2.95 g, 8.0 mmol), LiCl (2.5 g, 53.0 mmol) and $[PdCl_2(PPh_3)_2]$ (294.8 mg, 0.42 mmol) was deaerated by bubbling N_2 through it. The mixture was then refluxed under N_2 for 18 h, and an aqueous solution (10.0 mL) of NaF (2.2 g, 53.0 mmol) was added to the solution at room temperature. The resultant solution was further stirred at ambient temperature for 30 min. An insoluble solid was filtered off, and the filtrate was treated with a 5% Na_2CO_3 aqueous solution in a separating funnel. The organic layer was dried with anhydrous sodium sulfate, and the solvents were evaporated to dryness under reduced pressure. The obtained yellow solid was dissolved in PE/EA (95:5, v/v), and purified on a silica gel column.

Synthesis of 1c

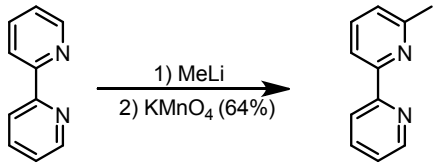


1c' **1c**

A toluene solution (35.0 mL) containing **1c'** (932.7 mg, 5.3 mmol), 2-(tri-n-butylstannyl)pyridine (2.95 g, 8.0 mmol), LiCl (2.5 g, 53.0 mmol) and $[PdCl_2(PPh_3)_2]$ (294.8 mg, 0.42 mmol) was deaerated by bubbling N_2 through it. The mixture was then refluxed under N_2 for 18 h, and an aqueous solution (10.0 mL) of NaF (2.2 g, 53.0 mmol) was added to the solution at room temperature. The resultant solution was further stirred at ambient temperature for 30 min. An insoluble solid was filtered off,

and the filtrate was treated with a 5% Na_2CO_3 aqueous solution in a separating funnel. The organic layer was dried with anhydrous sodium sulfate and the solvents were evaporated to dryness under reduced pressure. The obtained white solid was dissolved in PE/EA (95:5, v/v) and purified on a silica gel column.

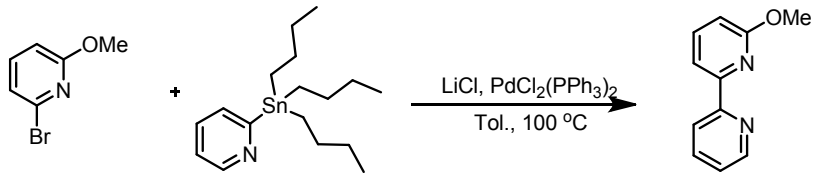
Synthesis of 1d



1d

4.0 mL of 1.6 M methyllithium in diethyl ether (67.5 mmol) was added dropwise to 40.0 mL of a diethyl ether solution containing 2,2'-bi-pyridine (1.0 g, 6.4 mmol) at 0 °C. After complete addition (approximately 1 h), the resulting brown solution was gently refluxed for 3 h under N_2. It was then allowed to cool to room temperature and water was added with stirring, resulting in a biphasic yellow solution. The aqueous layer was separated from the organic layer and extracted three times with diethyl ether. The combined organic layers were washed twice with brine followed by addition of anhydrous Na_2SO_4 to remove residual water. The solution was then decanted into a round-bottom flask and the ether was removed by rotary evaporation. The resulting orange oil was oxidized with approximately 100.0 mL of a saturated $KMnO_4$/acetone solution until formation of MnO_2 ceased. The MnO_2 was removed by vacuum filtration through celite. The filtrate was placed in a round-bottom flask and acetone was removed by rotary evaporation. The purification of the crude product by columnchromatography (heptane/EtOAc: 1/1) give the desired product **1d**.

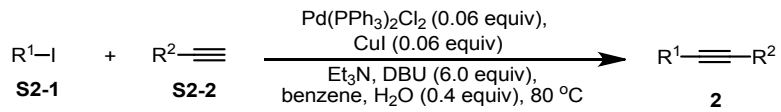
Synthesis of 1e



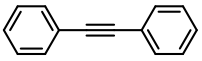
1e' **1e**

A toluene solution (35.0 mL) containing **1e'** (996.5 mg, 5.3 mmol), 2-(tri-n-butylstannyl)pyridine (2.95 g, 8.0 mmol), LiCl (2.5 g, 53.0 mmol) and $[PdCl_2(PPh_3)_2]$ (294.8 mg, 0.42 mmol) was deaerated by bubbling N_2 through it. The mixture was then refluxed under N_2 for 18 h, and an aqueous solution (10.0 mL) of NaF (2.2 g, 53.0 mmol) was added to the solution at room temperature. The resultant solution was further stirred at ambient temperature for 30 min. An insoluble solid was filtered off, and the filtrate was treated with a 5% Na_2CO_3 aqueous solution in a separating funnel. The organic layer was dried with anhydrous sodium sulfate and the solvents were evaporated to dryness under reduced pressure. The obtained oil was dissolved in PE/EA (95:5, v/v), and purified on a silica gel column.

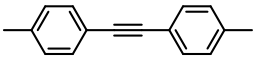
Synthesis of 2



The preparation of the symmetrical and unsymmetrical alkyne by the coupling of iodide derivatives with alkyne derivatives. In a 50 mL vessel with $Pd(PPh_3)_2Cl_2$ (421.1 mg, 0.6 mmol), DBU (9.13 g, 60.0 mmol), CuI (114.3 mg, 0.6 mmol) and H_2O (72.0 mg, 4.0 mmol) in benzene (25.0 mL), **S2-1** (10.0 mmol), **S2-2** (10.0 mmol) were added, respectively. The resulting product was extracted with diethyl ether (2 × 30 mL). The solution was concentrated in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether) to afford the desired pure products **2**.



2a



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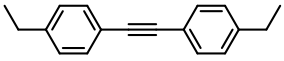
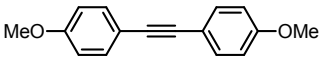


2c



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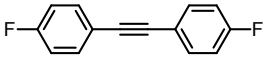

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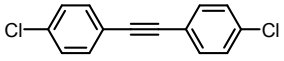

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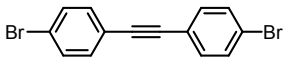

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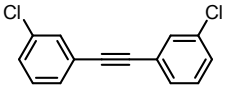
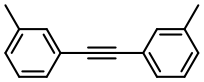
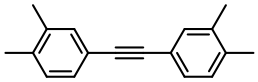


2h



2i



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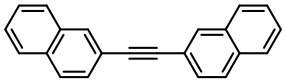

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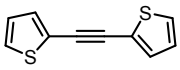

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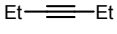
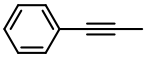
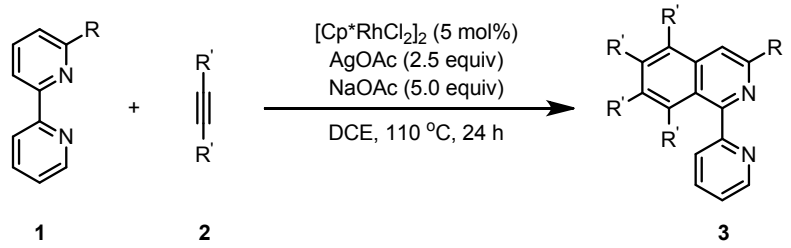


2n



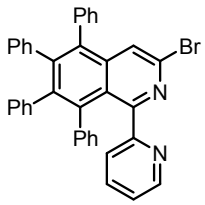
2o

Synthesis of 3



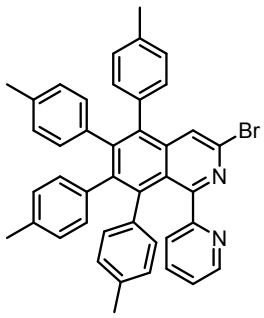
1 **2** **3**

A sealed tube contained **1** (0.2 mmol), **2** (0.5 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 5 mol%, 0.01 mmol), AgOAc (83.5 mg, 0.5 mmol) and NaOAc (82.0 mg, 1.0 mmol) was filled and purged with nitrogen gas three times. Then DCE (2.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 110 °C for 24 h. The reaction solution was concentrated in vacuum and the residue was purified by column chromatography on silica gel to afford the desired pure product **3**.



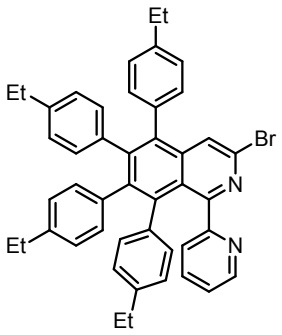
3-bromo-5,6,7,8-tetraphenyl-1-(pyridin-2-yl)isoquinoline

3aa: yield: 92%, 109.2 mg; appearance: yellow solid (M.p.: 273-275 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.16 (m, 1H), 7.65 (s, 1H), 7.38 – 7.36 (m, 2H), 7.28 – 7.26 (m, 1H), 7.25 – 7.19 (m, 3H), 6.86 – 6.71 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.5, 148.1, 143.9, 142.3, 139.8, 139.4, 139.3, 139.2, 138.8, 137.7, 136.8, 135.8, 133.9, 132.0, 131.1, 131.0, 130.5, 127.9, 127.1, 126.7, 126.5, 126.4, 125.8, 125.8, 125.4, 124.9, 124.7, 122.4, 121.7. ESI-MS: Calcd for: $C_{38}H_{25}BrN_2$ [M+H$^+$] 589.1279, found 589.1289.



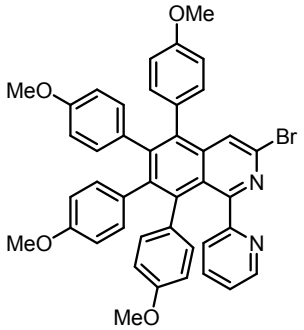
3-bromo-1-(pyridin-2-yl)-5,6,7,8-tetra-p-tolylisoquinoline

3ab: yield: 85%, 109.5 mg; appearance: yellow solid (M.p.: 168-170 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.15 (m, 1H), 7.63 (s, 1H), 7.37 – 7.33 (m, 1H), 7.30 – 7.27 (m, 1H), 7.10 – 7.05 (m, 4H), 6.87 – 6.84 (m, 1H), 6.67 – 6.45 (m, 12H), 2.31 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.5, 147.8, 144.3, 142.5, 139.5, 138.7, 137.0, 136.7, 136.7, 136.4, 136.4, 135.7, 135.1, 134.9, 134.6, 133.5, 131.9, 131.0, 130.8, 130.4, 128.6, 127.4, 127.3, 127.2, 125.4, 124.9, 122.6, 121.2, 21.2, 21.2, 21.0, 20.8. ESI-MS: Calcd for: $C_{42}H_{33}BrN_2$ [M+H$^+$] 645.1905, found 645.1907.



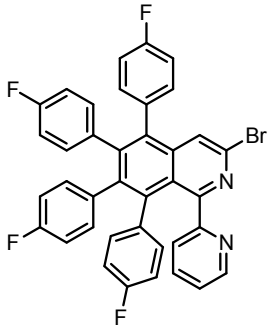
3-bromo-5,6,7,8-tetrakis(4-ethylphenyl)-1-(pyridin-2-yl)isoquinoline

3ac: yield: 89%, 124.6 mg; appearance: yellow solid (M.p.: 148-150 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 4.8 Hz, 1H), 7.70 (s, 1H), 7.33 (d, J = 4.0 Hz, 2H), 7.07 (s, 4H), 6.82 – 6.78 (m, 1H), 6.66 – 6.51 (m, 12H), 2.61 (q, J = 7.6 Hz, 2H), 2.40 – 2.29 (m, 6H), 1.21 (t, J = 7.6 Hz, 3H), 1.04 – 0.95 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 159.6, 148.0, 144.3, 142.6, 142.6, 141.3, 141.3, 141.0, 139.4, 138.6, 137.2, 136.9, 136.6, 135.5, 135.1, 133.5, 131.0, 130.4, 127.2, 126.0, 125.8, 125.1, 124.7, 122.5, 121.5, 28.4, 28.4, 28.3, 15.6, 15.5, 15.4, 15.3. ESI-MS: Calcd for $C_{46}H_{41}BrN_2$: [M+H$^+$] 701.2531, found 701.2552.



3-bromo-5,6,7,8-tetrakis(4-methoxyphenyl)-1-(pyridin-2-yl)isoquinoline

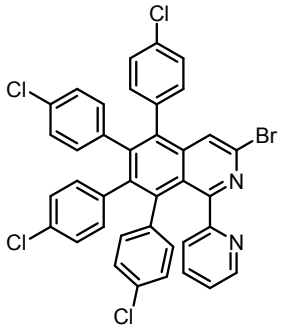
3ad: yield: 90%, 127.4 mg; appearance: yellow solid (M.p.: 183-185 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.8 Hz, 1H), 7.64 (s, 1H), 7.41 – 7.33 (m, 2H), 7.05 (s, 2H), 6.88 – 6.80 (m, 3H), 6.64 – 6.62 (m, 5H), 6.44 – 6.36 (m, 5H), 6.25 – 6.24 (m, 2H), 3.81 (s, 3H), 3.63 (s, 3H), 3.61 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 159.3, 158.4, 157.4, 157.2, 157.1, 147.7, 144.3, 142.5, 139.7, 138.4, 136.6, 136.1, 133.5, 133.1, 132.6, 132.2, 132.0, 131.8, 131.6, 130.2, 125.5, 124.9, 122.6, 121.6, 113.4, 112.3, 112.1, 55.1, 55.1, 55.0, 55.0. ESI-MS: Calcd for $C_{42}H_{33}BrN_2O_4$: [M+H$^+$] 709.1702, found 709.1702.



3-bromo-5,6,7,8-tetrakis(4-fluorophenyl)-1-(pyridin-2-yl)isoquinoline

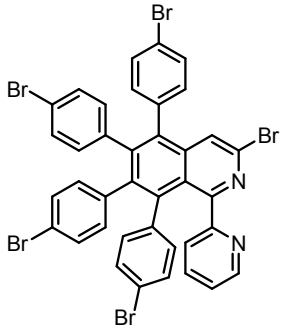
3ae: yield: 52%, 68.4 mg; appearance: yellow solid (M.p.: 265-267 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19– 8.17 (m, 1H), 7.60 (s, 1H), 7.49 – 7.40 (m, 2H), 7.11 (m, 2H), 7.02 – 6.91 (m, 3H), 6.71 – 6.55 (m, 10H), 6.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.2, 162.1 (d, *J* = 3.0 Hz), 160.7, 160.5, 159.8, 159.7 (d, *J* = 3.0 Hz), 159.3, 148.3, 143.3, 141.4, 139.5, 138.5, 136.4, 136.1, 135.6 (d, *J* = 3.0 Hz), 135.1 (d, *J* = 4.0 Hz), 134.8 (d, *J* = 3.0 Hz), 134.4, 133.5, 133.3 (d, *J* = 4.0 Hz), 132.6 (d, *J* = 8.0 Hz), 132.3 (d, *J* = 8.0 Hz), 131.9 (d, *J* = 8.0 Hz), 125.1, 124.7, 122.3, 122.1, 115.5, 115.3, 114.4, 114.2 (d, *J* = 4.0 Hz), 113.9 (d, *J* = 4.0 Hz), 113.7. ^{19}F NMR (376

MHz, $CDCl_3$) δ -113.8, -115.2, -115.5, -115.7. ESI-MS: Calcd for $C_{38}H_{21}BrF_4N_2$: [M+H$^+$] 661.0902, found 661.0910.



3-bromo-5,6,7,8-tetrakis(4-chlorophenyl)-1-(pyridin-2-yl)isoquinoline

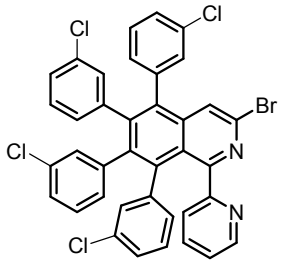
3af: yield: 63%, 91.4 mg; appearance: yellow solid (M.p.: 192-194 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.16 (m, 1H), 7.57 (s, 1H), 7.50 – 7.47 (m, 1H), 7.42 – 7.40 (m, 1H), 7.30 – 7.28 (m, 2H), 7.08 – 7.06 (m, 2H), 7.00 – 6.96 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.70 – 6.55 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.0, 148.2, 142.7, 140.8, 139.3, 138.3, 137.8, 137.2, 137.0, 136.3, 136.2, 135.6, 134.7, 133.8, 133.1, 132.6, 132.5, 132.3, 132.2, 132.0, 131.5, 128.6, 127.6, 127.4, 127.1, 125.0, 124.8, 122.3, 122.1. ESI-MS: Calcd for $C_{38}H_{21}BrCl_4N_2$: [M+H$^+$] 726.9691, found 726.9695.



3-bromo-5,6,7,8-tetrakis(4-bromophenyl)-1-(pyridin-2-yl)isoquinoline

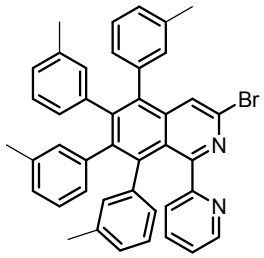
3ag: yield: 55%, 99.4 mg; appearance: yellow solid (M.p.: 210-212 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 4.4 Hz, 1H), 7.56 (s, 1H), 7.52 – 7.39 (m, 4H), 7.09 – 6.97 (m, 7H), 6.87 – 6.85 (m, 2H), 6.59 – 6.49 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 158.9, 148.2, 142.4, 140.5, 139.2, 138.2, 137.6, 137.4, 136.2, 136.1, 136.0, 134.7, 133.3, 132.4, 132.3, 131.8, 131.5, 130.5, 130.3, 130.0, 124.8, 124.8,

122.2, 122.0, 120.9, 120.8, 120.5. ESI-MS: Calcd for $C_{38}H_{21}Br_5N_2$: [M+H$^+$] 904.7659, found 904.7661.



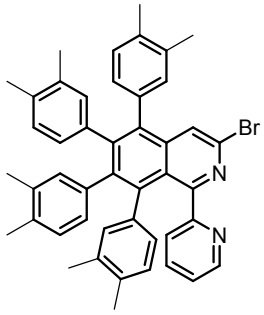
3-bromo-5,6,7,8-tetrakis(3-chlorophenyl)-1-(pyridin-2-yl)isoquinoline

3ah: yield: 75%, 108.8 mg; appearance: yellow solid (M.p.: 135-137 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.60 (s, 1H), 7.47 (s, 2H), 7.29 – 7.26 (m, 1H), 7.23 – 6.59 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 158.8, 148.2, 142.2, 140.7, 140.5, 140.1, 140.0, 139.0, 138.6, 138.1, 136.0, 136.0, 134.9, 134.3, 134.1, 133.0, 132.8, 132.7, 132.6, 131.8, 130.7, 130.6, 130.2, 129.6, 129.0, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 126.8, 126.5, 124.5, 122.3, 122.2. ESI-MS: Calcd for $C_{38}H_{21}BrCl_4N_2$: [M+H$^+$] 726.9691, found 726.971.



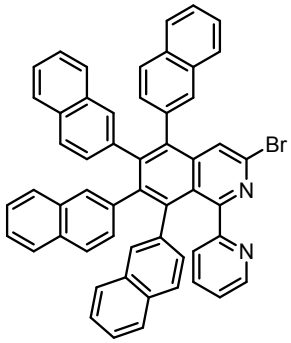
3-bromo-1-(pyridin-2-yl)-5,6,7,8-tetra-m-tolylisoquinoline

3ai: yield: 43%, 55.4 mg; appearance: yellow solid (M.p.: 76-78 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.66 (s, 1H), 7.34 (s, 2H), 7.17 – 7.13 (m, 1H), 7.03 – 6.44 (m, 16H), 2.27 (d, *J* = 13.2 Hz, 3H), 2.01 – 1.93 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.6, 147.9, 144.1, 142.4, 139.7, 139.4, 139.4, 139.3, 139.3, 139.2, 138.7, 138.6, 137.7, 137.3, 137.2, 137.2, 136.7, 135.9, 135.8, 135.6, 135.5, 135.4, 133.7, 133.0, 131.8, 131.4, 128.1, 127.8, 127.6, 126.4, 126.3, 126.1, 126.0, 124.9, 124.5, 122.6, 121.6, 21.3, 21.0, 20.9, 20.8. ESI-MS: Calcd for $C_{42}H_{33}BrN_2$: [M+H$^+$] 645.1905, found 645.1922.



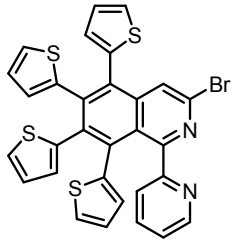
3-bromo-5,6,7,8-tetrakis(3,4-dimethylphenyl)-1-(pyridin-2-yl)isoquinoline

3ak: yield: 88%, 123.2 mg; appearance: yellow solid (M.p.: 135-137 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.64 (s, 1H), 7.28 – 7.27 (m, 1H), 7.23 (m, 1H), 6.99 – 6.80 (m, 4H), 6.58 – 6.40 (m, 9H), 2.20 – 2.14 (m, 6H), 1.96 – 1.84 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 159.7, 147.7, 144.3, 144.3, 142.5, 139.5, 139.4, 138.4, 138.3, 137.4, 137.1, 136.8, 136.5, 135.6, 135.5, 135.4, 134.8, 134.0, 133.8, 133.7, 133.6, 133.4, 133.3, 133.2, 132.8, 132.3, 131.9, 129.0, 128.9, 128.5, 128.4, 127.8, 127.7, 127.5, 125.2, 124.5, 122.6, 120.8, 19.6, 19.4, 19.4, 19.1, 19.1, 19.1, 19.0. ESI-MS: Calcd for $C_{46}H_{41}BrN_2$: [M+H$^+$] 701.2531, found 701.2548.



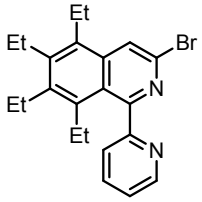
3-bromo-5,6,7,8-tetra(naphthalen-2-yl)-1-(pyridin-2-yl)isoquinoline

3al: yield: 66%, 104.1 mg; appearance: yellow solid (M.p.: 194-196 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (m, 1H), 7.93 – 7.30 (m, 19H), 7.20 – 6.85 (m, 12H), 6.43 – 6.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 159.5, 148.2, 144.4, 144.2, 142.3, 140.0, 139.3, 137.5, 137.3, 137.1, 136.9, 136.8, 136.6, 135.3, 134.4, 133.0, 132.9, 132.3, 132.2, 132.1, 131.7, 131.5, 131.4, 131.3, 131.0, 130.9, 130.7, 130.6, 130.4, 130.3, 130.1, 129.9, 129.7, 129.5, 129.2, 128.9, 128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 127.3, 127.1, 126.5, 126.2, 125.7, 125.6, 125.5, 125.5, 124.3, 122.7, 121.1. ESI-MS: Calcd for $C_{54}H_{33}BrN_2$: [M+H$^+$] 789.1905, found 789.1916.



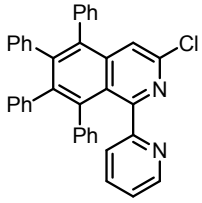
3-bromo-1-(pyridin-2-yl)-5,6,7,8-tetra(thiophen-2-yl)isoquinoline

3am: yield: 79%, 96.6 mg; appearance: brown solid (M.p.: 92-94 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.8 Hz, 1H), 7.85 (s, 1H), 7.54 – 7.51 (m, 2H), 7.38 (d, *J* = 4.8 Hz, 1H), 7.10 (d, *J* = 4.8 Hz, 1H), 7.07 – 7.01(m, 3H), 6.99 – 6.95 (m, 1H), 6.93 – 6.92 (m, 1H), 6.70 – 6.65 (m, 2H), 6.59 – 6.55 (m, 2H), 6.38 – 6.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.1, 148.3, 140.3, 139.6, 139.4, 139.3, 137.5, 137.0, 136.0, 134.9, 134.6, 132.0, 131.4, 130.2, 129.6, 129.3, 127.4, 126.7, 126.6, 126.4, 126.3, 126.0, 125.8, 125.7, 124.3, 122.0, 121.9. ESI-MS: Calcd for $C_{30}H_{17}BrN_2S_4$: [M+H$^+$] 612.9536, found 612.9549.



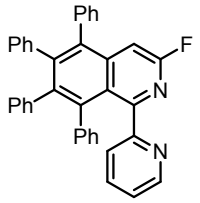
3-bromo-5,6,7,8-tetraethyl-1-(pyridin-2-yl)isoquinoline

3an: yield: 45%, 35.7 mg; appearance: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.8 Hz, 1H), 8.01 (s, 1H), 7.88 – 7.79 (m, 2H), 7.36 – 7.32 (m, 1H), 3.05 (q, *J* = 7.6 Hz, 2H), 2.88 – 2.77 (m, 4H), 2.37 (m, 2H), 1.32 – 1.17 (m, 9H), 0.72 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 159.1, 148.6, 143.8, 141.4, 138.6, 137.8, 136.8, 133.9, 132.5, 124.2, 123.8, 122.8, 120.4, 23.2, 22.9, 22.8, 21.7, 16.7, 15.6, 15.4. ESI-MS: Calcd for $C_{22}H_{25}BrN_2$: [M+H$^+$] 397.1279, found 397.1295.



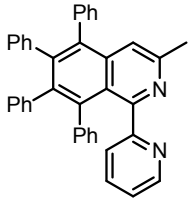
3-chloro-5,6,7,8-tetraphenyl-1-(pyridin-2-yl)isoquinoline

3ba: yield: 80%, 87.1 mg; appearance: yellow solid (M.p.: 255-257 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.4 Hz, 1H), 7.40 (s, 1H), 7.25 (s, 1H), 7.16 – 7.09 (m, 5H), 6.73 – 6.60 (m, 17H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 159.5, 148.1, 143.9, 143.7, 142.1, 139.8, 139.4, 139.2, 138.8, 137.7, 136.9, 135.7, 132.0, 131.0, 131.0, 130.4, 127.9, 127.1, 126.7, 126.5, 126.4, 125.8, 125.8, 125.4, 124.7, 124.6, 121.7, 118.5. ESI-MS: Calcd for $C_{38}H_{25}ClN_2$: [M+H$^+$] 545.1785, found 545,1790.



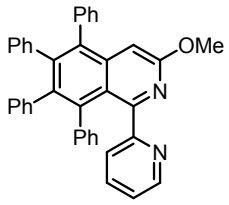
3-fluoro-5,6,7,8-tetraphenyl-1-(pyridin-2-yl)isoquinoline

3ca: yield: 20%, 21.2 mg; appearance: white solid (M.p.: 290-292 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.18 (m, 1H), 7.38 – 7.26 (m, 4H), 7.25 – 7.19 (m, 3H), 7.07 (d, *J* = 1.6 Hz, 1H), 7.86 – 6.70 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 159.4, 159.3, 159.2, 158.1, 148.3, 143.8, 141.7, 141.7, 141.2 (d, *J* = 2.0 Hz), 140.0, 139.6, 139.4, 138.9, 138.1, 137.4, 137.3, 135.7, 132.1, 131.1, 130.5, 127.9, 127.1, 126.7, 126.5 (d, *J* = 8.0 Hz), 125.8 (d, *J* = 4.0 Hz), 125.4, 124.6, 121.8, 102.0, 101.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.6. ESI-MS: Calcd for $C_{38}H_{25}FN_2$: [M+H$^+$] 529.2080, found 529.2088.



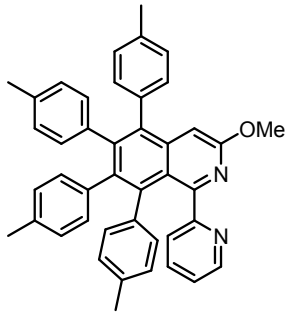
3-methyl-5,6,7,8-tetraphenyl-1-(pyridin-2-yl)isoquinoline

3da: yield: 24%, 25.2 mg; appearance: white solid (M.p.: 120-122 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.20 (m, 1H), 7.35 – 7.26 (m, 4H), 7.26 – 7.20 (m, 4H), 6.85 – 6.70 (m, 16H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 159.3, 149.8, 148.2, 142.8, 140.8, 140.4, 140.0, 139.8, 138.7, 138.4, 137.8, 136.9, 135.6, 131.2, 130.7, 127.7, 126.7, 126.6, 126.4, 126.4, 125.6, 125.2, 124.7, 124.0, 121.3, 117.3, 24.2. ESI-MS: Calcd for $C_{39}H_{28}N_2$: [M+H$^+$] 525.2331, found 525.2327.



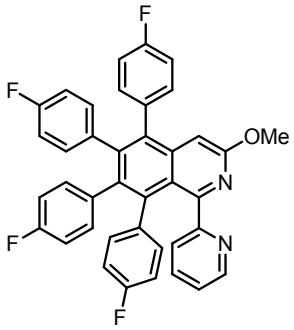
3-methoxy-5,6,7,8-tetraphenyl-1-(pyridin-2-yl)isoquinoline

3ea: yield: 88%, 95.1 mg; appearance: yellow solid (M.p.: 146-148 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.15 (m, 1H), 7.38 – 7.36 (m, 2H), 7.24 – 7.28 (m, 5H), 6.85 – 6.77 (m, 13H), 6.69 – 6.68 (m, 4H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 159.2, 158.3, 148.1, 142.8, 141.2, 140.6, 140.1, 139.9, 139.2, 138.8, 138.4, 136.5, 135.4, 132.1, 131.3, 131.1, 130.6, 127.7, 126.7, 126.6, 126.4, 126.3, 125.5, 125.1, 124.6, 122.4, 121.3, 100.6, 54.1. ESI-MS: Calcd for $C_{39}H_{28}N_2O$: [M+H$^+$] 541.2208, found 541.2283.



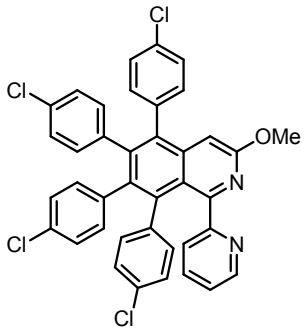
3-methoxy-1-(pyridin-2-yl)-5,6,7,8-tetra-p-tolylisoquinoline

3eb: yield: 45%, 53.7 mg; appearance: yellow solid (M.p.: 94-96 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 4.8 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.13 – 7.04 (m, 5H), 6.83 – 6.81 (m, 1H), 6.79 (s, 1H), 6.65 – 6.46 (m, 11H), 3.90 (s, 3H), 2.30 (s, 3H), 2.09 (s, 3H), 2.06 (s, 1H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 159.0, 158.3, 148.0, 143.0, 141.3, 139.3, 138.2, 137.7, 137.3, 137.0, 136.3, 136.0, 135.9, 135.1, 134.6, 134.5, 134.2, 131.1, 131.0, 130.5, 128.4, 127.2, 127.1, 127.0, 124.7, 122.8, 120.7, 100.3, 54.1, 21.2, 21.1, 21.0, 20.9. ESI-MS: Calcd for $C_{43}H_{36}N_2O$: [M+H$^+$] 597.2906, found 597.2922.



5,6,7,8-tetrakis(4-fluorophenyl)-3-methoxy-1-(pyridin-2-yl)isoquinoline

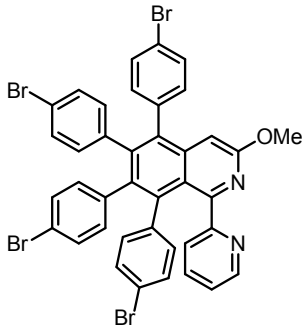
3ee: yield: 77%, 94.3 mg; appearance: yellow solid (M.p.: 193-195 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 4.4 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.13 – 7.10 (m, 2H), 6.98 – 6.89 (m, 3H), 6.76 (s, 1H), 6.74 – 6.67 (m, 4H), 6.62 – 6.51 (m, 6H), 6.43 – 6.39 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.0, 161.8 (d, *J* = 2.0 Hz), 160.4, 160.2, 159.5, 159.4, 158.3, 148.2, 142.0, 141.2, 138.2, 137.9, 136.3 (d, *J* = 3.0 Hz), 136.0, 135.7, 135.6, 135.4 (d, *J* = 4.0 Hz), 134.3 (d, *J* = 3.0 Hz), 133.5, 132.5 (d, *J* = 8.0 Hz), 131.9 (d, *J* = 8.0 Hz), 124.6, 122.4, 121.6, 115.1, 114.9, 114.1, 113.9 (d, *J* = 3.0 Hz), 113.7, 113.6, 113.4, 100.5, 54.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.8, -115.9, -116.4, -116.4. ESI-MS: Calcd for $C_{39}H_{24}F_4N_2O$: [M+H$^+$] 613.1903, found 613.1933.



5,6,7,8-tetrakis(4-chlorophenyl)-3-methoxy-1-(pyridin-2-yl)isoquinoline

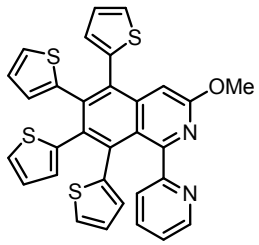
3ef: yield: 66%, 89.3 mg; appearance: yellow solid (M.p.: 155-157 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 4.4 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.40 – 7.38 (m, 1H), 7.26 – 7.24 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.96 – 6.89 (m, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.72 (s, 1H), 6.68 – 6.65 (m, 6H), 6.57 (m, 2H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.5, 158.3, 148.2, 141.4, 141.1, 138.6, 137.9, 137.8, 137.6, 137.5 136.6, 135.9, 135.8, 133.2, 132.4, 132.2, 132.2, 131.9, 131.8, 131.6, 128.4,

127.4, 127.2, 126.9, 124.7, 122.2, 121.6, 100.6, 54.2. ESI-MS: Calcd for $C_{39}H_{24}Cl_4N_2O$: [M+H$^+$] 677.0721, found 677.0747.



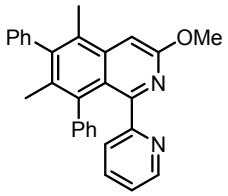
5,6,7,8-tetrakis(4-bromophenyl)-3-methoxy-1-(pyridin-2-yl)isoquinoline

3eg: yield: 78%, 133.4 mg; appearance: yellow solid (M.p.: 210-212 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 3.2 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.07 – 6.98 (m, 7H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.71 (s, 1H), 6.62 – 6.51 (m, 6H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.6, 158.3, 148.3, 141.2, 141.1, 139.0, 138.3, 138.1, 137.8, 137.3, 137.1, 135.8, 135.7, 133.5, 132.7, 132.5, 132.0, 131.4, 130.4, 130.1, 129.8, 124.7, 122.2, 121.5, 121.5, 120.5, 120.4, 120.2, 100.7, 100.7, 54.2. ESI-MS: Calcd for $C_{39}H_{24}Br_4N_2O$: [M+H$^+$] 856.8659, found 856.8658.



3-methoxy-1-(pyridin-2-yl)-5,6,7,8-tetra(thiophen-2-yl)isoquinoline

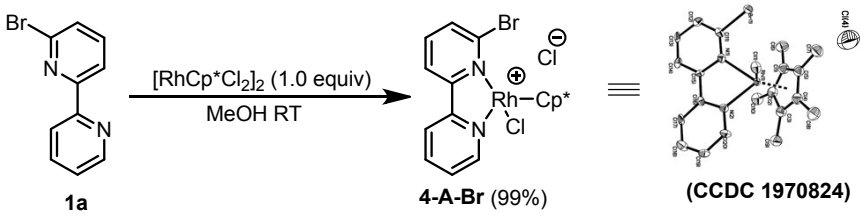
3em: yield: 50%, 56.4 mg; appearance: brown solid (M.p.: 176-178 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 4.8 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.34 (d, *J* = 4.8 Hz, 1H), 7.08 – 6.94 (m, 6H), 6.89 (d, *J* = 5.2 Hz, 1H), 6.69 – 6.64 (m, 2H), 6.58 (d, *J* = 3.2 Hz, 1H), 6.55 (d, *J* = 3.2 Hz, 1H), 6.39 – 6.35 (m, 2H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 148.0, 142.4, 140.2, 138.6, 138.5, 135.7, 134.2, 133.6, 131.8, 131.2, 129.7, 129.6, 129.1, 126.8, 126.5, 126.2, 126.1, 125.8, 125.6, 125.6, 124.3, 123.7, 121.5, 100.5, 54.3. ESI-MS: Calcd for $C_{21}H_{20}N_2OS_4$: [M+H$^+$] 565.0537, found 565.0542.



3-methoxy-5,7-dimethyl-6,8-diphenyl-1-(pyridin-2-yl)isoquinoline

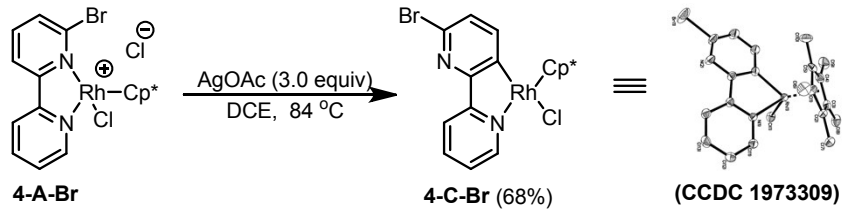
3eo: yield: 52%, 43.3 mg; appearance: yellow solid (M.p.: 183-185 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.65 (m, 1H), 7.84 (d, *J* = 3.6 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.28 (s, 1H), 7.15 – 6.95 (m, 10H), 4.09 (s, 3H), 2.38 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 159.2, 157.7, 148.5, 143.1, 141.4, 141.2, 141.1, 140.1, 136.5, 130.8, 130.5, 123.0, 127.7, 127.3, 127.3, 126.1, 125.9, 124.1, 123.1, 122.5, 98.9, 54.3, 22.2, 17.0. ESI-MS: Calcd for $C_{29}H_{24}N_2O$: [M+H$^+$] 417.1967, found 417.1984.

Mechanistic studies



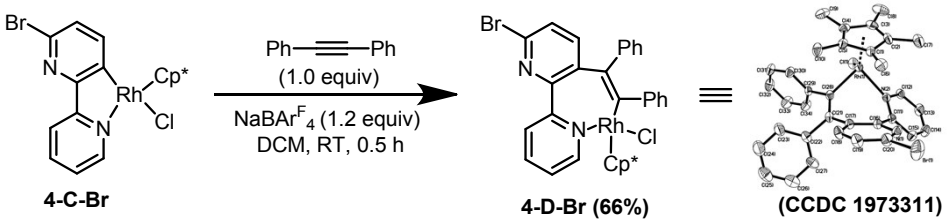
A sealed tube contained $[Cp^*RhCl_2]_2$ (61.8 mg, 0.1 mmol) and **1a** (47.0 mg, 0.2 mmol) was filled and purged with nitrogen gas three times. Then MeOH (10.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at room temperature for 1 h. The reaction solution was concentrated in vacuum. Cyclometalated compound **4-A-Br** was isolated as an orange solid (90.4 mg, 99%). **4-A-Br** was recrystallized from MeOH at −10 °C.

4-A-Br: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 4.0 Hz, 1H), 8.42 – 8.37 (m, 2H), 7.84 – 7.80 (m, 1H), 7.69 – 7.65 (m, 1H), 7.50 – 7.48 (m, 1H), 7.35 – 7.31 (m, 1H), 1.62 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 141.6, 139.2, 137.0, 128.0, 124.3, 121.5, 119.7, 94.1, 9.4.



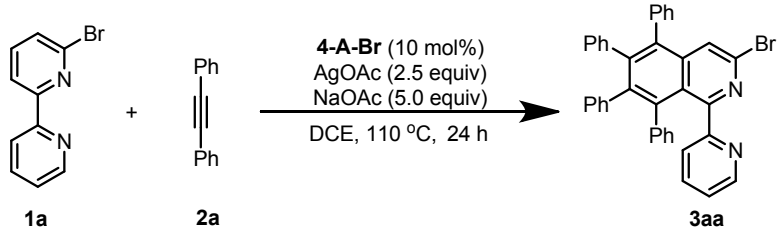
A sealed tube contained **4-A-Br** (90.4 mg, 0.2 mmol) and AgOAc (100.1 mg, 0.6 mmol) was filled and purged with nitrogen gas three times. Then DCE (10.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 84 °C for 3 h. The reaction solution was concentrated in vacuum and the residue was purified by column chromatography on aluminium oxide gel (ethyl acetate) to afford the desired pure product **4-C-Br**. Cyclometalated compound **4-C-Br** was isolated as an orange solid (69.0 mg, 68%). **4-C-Br** were recrystallized from n-hexane/CH_2Cl_2 (2:1) at −10 °C.

4-C-Br: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.6 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.78(m, 1H), 7.30 – 7.26 (m, 2H), 1.61 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 162.4, 161.1, 150.8, 146.9, 137.7, 137.3, 129.0, 124.3, 122.0, 96.2, 96.2, 9.2.



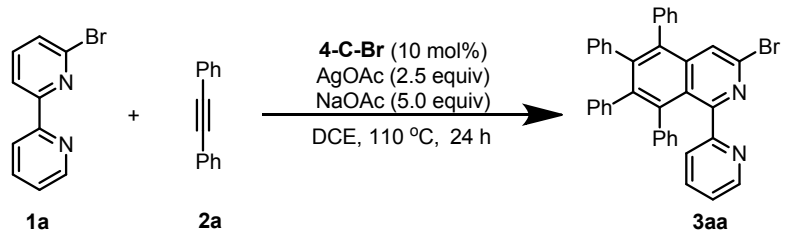
A sealed tube contained **4-C-Br** (101.0 mg, 0.2 mmol), diphenylacetylene (36.0 mg, 0.2 mmol) and $NaBAr^F_4$ (213.0 mg, 0.24 mmol) was filled and purged with nitrogen gas three times. Then DCE (10.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at room temperature for 0.5 h. The reaction solution was concentrated in vacuum and the residue was purified by column chromatography on aluminium oxide gel (petroleum ether/ethyl acetate, 1:1) to afford the desired pure product **4-D-Br**. Cyclometalated compound **4-D-Br** was isolated as an orange solid (91.0 mg, 66%). **4-D-Br** were recrystallized from n-hexane/CH_2Cl_2 (2:1) at −10 °C.

4-D-Br: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (d, *J* = 5.2 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.39 – 7.33 (m, 3H), 7.11 – 7.08 (m, 2H), 6.95 – 6.85 (m, 3H), 6.77 – 6.69 (m, 4H), 5.97 (s, 1H), 1.33 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 176.6, 161.4, 154.5, 154.3, 152.7, 145.6, 143.3, 141.4, 137.7, 136.9, 135.6, 131.1, 128.0, 127.6, 127.2, 124.9, 124.3, 123.2, 96.2, 96.1, 9.1.

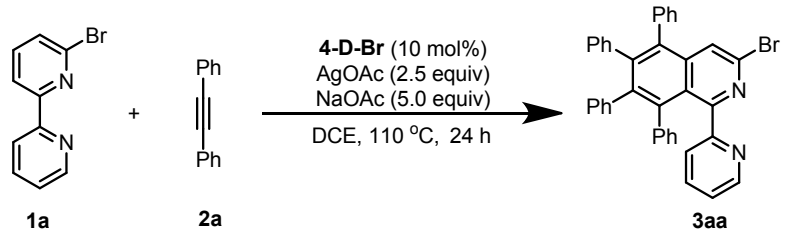


A sealed tube contained **1a** (47.0 mg, 0.2 mmol), diphenylacetylene (89.0 mg, 0.5 mmol), **4-A-Br** (11.0 mg, 0.02 mmol), AgOAc (84.0 mg, 0.5 mmol) and NaOAc

(82.0 mg, 1.0 mmol) was filled and purged with nitrogen gas three times. Then DCE (2.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 110 °C for 24 h. The product **3aa** was obtained in 61% isolated yield.



A sealed tube contained **1a** (47.0 mg, 0.2 mmol), diphenylacetylene (89.0 mg, 0.5 mmol), **4-C-Br** (10.0 mg, 0.02 mmol), AgOAc (84.0 mg, 0.5 mmol) and NaOAc (82.0 mg, 1.0 mmol) was filled and purged with nitrogen gas three times. Then DCE (2.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 110 °C for 24 h. The product **3aa** was obtained in 64% isolated yield.



A sealed tube contained **1a** (47 mg, 0.2 mmol), diphenylacetylene (89.0 mg, 0.5 mmol), **4-D-Br** (14.0 mg, 0.02 mmol), AgOAc (84.0 mg, 0.5 mmol) and NaOAc (8.02 mg, 1.0 mmol) was filled and purged with nitrogen gas three times. Then DCE (2.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 110 °C for 24 h. The product **3aa** was obtained in 87% isolated yield.

DFT analysis

1. Computational methods
2. Bond dissociation energy (BDE) calculation
3. Calculated total energies, Gibb free energies and geometrical coordinates for structures in the main text

1. Computational methods

All the calculations were performed at the B3LYP-D3(BJ) method [1] using the Gaussian09 suite of programs.[2] For Rh, the SDD basis set with Effective Core Potential (ECP) was used; and for other atoms, 6-31g* basis set was used. Structures were optimized with the SMD method and the dichloroethane solvent in the experiments was used for solvent effects. Harmonic vibration frequency calculations are used to confirm the stationary points and to obtain thermodynamic data. The 3D figures of molecular structure were prepared by CYLView.[3]

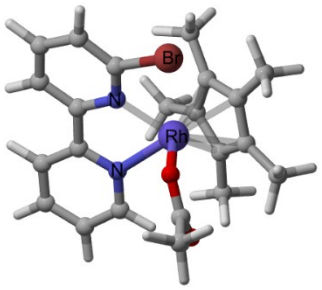
1 a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104. b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* 2011, **32**, 1456.

2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G.

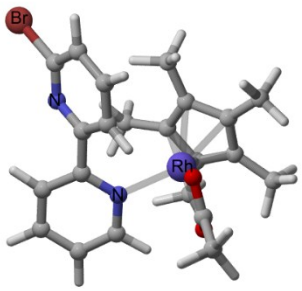
Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision E.01; Gaussian, Inc.: Wallingford, CT, 2009.

3 Legault, C. *CYLview, 1.0b*; Université de Sherbrooke: Quebec, Canada, 2009.

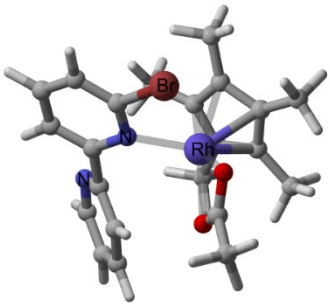
2. Bond dissociation energy (BDE) calculation



4-A-Br



4-B-Br



4-B'-Br

E(4-B-Br) – E(4-A-Br) = 6.7 kcal/mol

E(4-B'-Br) – E(4-A-Br) = 15.0 kcal/mol

The values of BDE in Scheme 4b were estimated by the above formula.

3. Calculated total energies, Gibb free energy and geometrical coordinates for structures in the main text

4-A-H

E = -1224.6586094 hartree; G = -1224.275139 hartree

Rh	0.47384900	0.15386100	-0.01721600
C	-2.35161800	-0.65107700	-0.46180600
C	-3.46236400	-1.43376400	-0.78324100
C	-3.27289700	-2.75390100	-1.18228400
C	-1.97866100	-3.26652500	-1.24265700
C	-0.91456200	-2.43798600	-0.90253200
C	-2.43512000	0.74875600	-0.00853400
C	-3.63446200	1.44153900	0.17093600
C	-3.60203200	2.75205800	0.63901000
C	-2.37265300	3.34159200	0.92748100
C	-1.21410900	2.59912600	0.72578400
H	-4.46125300	-1.02092900	-0.71986000
H	-4.12714100	-3.37237200	-1.43746300
H	-1.78618200	-4.29104300	-1.54054100
H	0.10599500	-2.78985500	-0.90671900
H	-4.58166800	0.96330500	-0.04553600
H	-4.52702100	3.30066500	0.78268800
H	-2.30207800	4.35582400	1.30383200

H	-0.23490600	3.00491300	0.94120300
N	-1.24650000	1.34368100	0.25801200
N	-1.09830300	-1.16281000	-0.53344700
O	0.08488800	-0.35834600	1.97941300
C	0.34074600	-1.57502100	2.37030200
O	0.79469200	-2.47900000	1.65995700
C	0.02846400	-1.80386800	3.84250900
H	0.66074000	-1.15588200	4.46054600
H	-1.01389100	-1.54144100	4.05390400
H	0.20618100	-2.84679200	4.11429900
C	2.29228600	-0.70017100	-0.93078300
C	1.61761100	0.15719100	-1.89328400
C	2.23101400	1.45925200	-0.05779100
C	1.59808900	1.48443000	-1.36376300
C	2.67787700	0.11264800	0.18030900
C	3.41849100	-0.35745000	1.38718400
H	4.49841500	-0.28447800	1.20108000
H	3.18745100	0.25750500	2.26048700
H	3.17757600	-1.39690800	1.61572100
C	2.52152500	2.63694500	0.81732400
H	2.35612000	2.40079200	1.87272000
H	3.57071500	2.93981800	0.70477500
H	1.90250600	3.49791400	0.55433500
C	1.04396300	2.69779600	-2.03499000
H	0.64786500	3.41325600	-1.31011200

H	1.84078200	3.20263300	-2.59652400
H	0.24806600	2.44044300	-2.73805500
C	1.09309200	-0.28178900	-3.22200100
H	0.32585200	0.40103900	-3.59567900
H	1.90844000	-0.30908600	-3.95645100
H	0.66262300	-1.28555500	-3.16705100
C	2.63792500	-2.14269300	-1.10952400
H	3.71090200	-2.24650400	-1.31673100
H	2.40645300	-2.70754600	-0.20318000
H	2.09558900	-2.58331000	-1.94980100

4-A-Br

E = -3795.456209 hartree; G = -3795.087808 hartree

Rh	-0.31148800	-0.43065100	-0.12621800
C	-1.09397100	2.42153600	0.04623200
C	-1.91089300	3.55318200	0.01184100
C	-3.28224000	3.40878500	0.20866300
C	-3.80188900	2.14249500	0.46433900
C	-2.93554900	1.05332000	0.47879900
C	0.37809000	2.47180000	-0.03790000
C	1.09154500	3.66076600	-0.17845300
C	2.48225700	3.63202000	-0.12305000

C	3.12804500	2.42573400	0.11692800
C	2.34362100	1.28012700	0.24148100
H	-1.48768800	4.53621600	-0.15109900
H	-3.92894000	4.27961900	0.18123600
H	-4.85821500	1.98845800	0.65418000
H	-3.26796700	0.05011100	0.70246800
H	0.57327800	4.60034300	-0.31737800
H	3.05587100	4.54560800	-0.23691800
H	4.20448300	2.36575000	0.21550900
N	1.01601500	1.27644900	0.11555600
N	-1.62292200	1.19055000	0.24526600
O	-0.08523000	-0.69464200	1.93399000
C	-1.10438100	-1.14172800	2.60835800
O	-2.22365400	-1.39179000	2.14207600
C	-0.79522600	-1.36596200	4.08133200
H	-0.08464600	-2.19511100	4.18234700
H	-0.32451400	-0.47750600	4.51491600
H	-1.70696600	-1.60779000	4.63225200
C	-1.66695300	-1.69974600	-1.29821500
C	-0.95899600	-0.78688100	-2.18414200
C	0.60577000	-2.18065700	-1.15779200
C	0.43418800	-1.09561400	-2.09848600
C	-0.69865600	-2.54768900	-0.67741300
C	-0.97133800	-3.67035300	0.26546200
H	-1.01058900	-4.61152800	-0.29961000

H	-0.17342600	-3.76155400	1.00750700
H	-1.91787500	-3.53327900	0.78741500
C	1.84181000	-2.98642400	-0.91807800
H	1.97703500	-3.21502500	0.14253200
H	1.74967200	-3.94228000	-1.45109900
H	2.73732600	-2.48557800	-1.28672400
C	1.52872300	-0.42177100	-2.85854600
H	2.48587700	-0.49936300	-2.33824500
H	1.64281600	-0.90100100	-3.83943800
H	1.30921400	0.63569300	-3.02705100
C	-1.59507400	0.23810900	-3.06712900
H	-0.88837200	1.02903700	-3.33204500
H	-1.94294900	-0.22836000	-3.99772900
H	-2.46028900	0.69795000	-2.58133800
C	-3.14733200	-1.83295700	-1.16891700
H	-3.49287200	-2.63871900	-1.83028300
H	-3.43112300	-2.09033700	-0.14611300
H	-3.66714200	-0.91861100	-1.46326500
Br	3.21185900	-0.34770100	0.66547400

4-A-Cl

E = -1684.2443325 hartree; G = -1683.875034 hartree

Rh	-0.46346000	-0.10519900	-0.07588300
C	1.92247600	1.65599300	-0.08354800
C	2.68473800	2.80949500	-0.27928100
C	2.05574700	4.05203500	-0.25809600
C	0.68588400	4.11622700	-0.01479100
C	-0.01963400	2.92914100	0.15822000
C	2.49803000	0.30158000	0.02477900
C	3.86802000	0.05271100	-0.02194900
C	4.33501700	-1.23996200	0.20170500
C	3.42900100	-2.24722800	0.50727600
C	2.07466800	-1.91703900	0.53377400
H	3.75390500	2.74471100	-0.43780300
H	2.63499400	4.95621900	-0.41351100
H	0.16162900	5.06356900	0.04039300
H	-1.07818000	2.90915400	0.37278800
H	4.56607800	0.85609900	-0.21550900
H	5.39764800	-1.45429500	0.16297300
H	3.74662200	-3.25866300	0.72781900
N	1.60384600	-0.70006000	0.25848000
N	0.58217900	1.73318800	0.09427100
O	-0.61995100	-0.17831500	2.00710200
C	-1.38860200	0.68499700	2.60465300
O	-2.04374100	1.57462200	2.04635500
C	-1.44110100	0.49475500	4.11358000
H	-1.98670000	-0.42807600	4.34510800

H	-0.43165100	0.39017700	4.52422700
H	-1.94936700	1.33672800	4.58893100
C	-2.19211100	0.53274400	-1.25781400
C	-1.08561700	0.20811200	-2.14881700
C	-1.68964600	-1.72324200	-0.98366000
C	-0.78377300	-1.17703000	-1.97650600
C	-2.55502500	-0.66099000	-0.55704400
C	-3.66683300	-0.79582400	0.42851600
H	-4.59092000	-1.06081900	-0.10277500
H	-3.45871600	-1.58766400	1.15282400
H	-3.83144100	0.13776600	0.96829800
C	-1.89315900	-3.16643800	-0.65003700
H	-2.04201700	-3.31920100	0.42221400
H	-2.79603200	-3.52417100	-1.16293800
H	-1.05692900	-3.78459400	-0.97837600
C	0.27787500	-1.94467700	-2.69407200
H	0.68555700	-2.74292600	-2.06892500
H	-0.14660600	-2.40924200	-3.59346000
H	1.09964500	-1.29598900	-3.00671400
C	-0.43595600	1.15558100	-3.10444400
H	0.58462300	0.84691000	-3.34381200
H	-1.00612300	1.19029900	-4.04163300
H	-0.40168200	2.17020800	-2.69904500
C	-2.92821700	1.82886600	-1.18062800
H	-3.86659200	1.74742200	-1.74493100

H	-3.17301500	2.07039400	-0.14372500
H	-2.35340300	2.65136000	-1.61066200
Cl	0.93476800	-3.15133100	0.97677200

4-A-F

E = -1323.893255 hartree; G = -1323.520837 hartree

Rh	-0.47881100	-0.11201200	-0.03158700
C	2.26714900	1.02860800	-0.35596100
C	3.27997200	1.93986900	-0.66155800
C	2.94883300	3.27172300	-0.89610800
C	1.61620200	3.66547700	-0.80143200
C	0.65407400	2.70763000	-0.49633700
C	2.51430800	-0.38566200	-0.02745900
C	3.78126400	-0.95729800	0.05950800
C	3.90363700	-2.29148900	0.45051700
C	2.76485000	-3.02376700	0.76320900
C	1.54676800	-2.36811400	0.64428800
H	4.31286500	1.61827000	-0.71132200
H	3.72482900	3.99019900	-1.13823800
H	1.31489100	4.69536800	-0.95657400
H	-0.38832200	2.96324900	-0.38292200
H	4.66452400	-0.37273800	-0.16174200

H	4.88367200	-2.75050300	0.52222000
H	2.79560300	-4.05558700	1.09105800
N	1.39882300	-1.11547900	0.24576400
N	0.97066200	1.41990300	-0.29975300
O	-0.32593600	0.21730400	2.03242600
C	-0.76783400	1.34863400	2.50365000
O	-1.29515000	2.24743300	1.83730500
C	-0.55362900	1.49779100	4.00287400
H	-0.87349600	0.59458200	4.53237800
H	0.51566500	1.63560000	4.20454300
H	-1.10068200	2.36362100	4.38279300
C	-2.23475300	0.68162100	-1.07477200
C	-1.38137400	-0.02277100	-2.02126000
C	-2.11249800	-1.54652900	-0.41080700
C	-1.31613600	-1.39024000	-1.61491000
C	-2.68627800	-0.26711400	-0.10316500
C	-3.60522400	0.01621700	1.03705200
H	-4.64255100	-0.14974300	0.71675100
H	-3.40484400	-0.64975800	1.88021600
H	-3.50598200	1.04836300	1.37550900
C	-2.45465200	-2.82843100	0.27912300
H	-2.42743300	-2.71786100	1.36675600
H	-3.47326500	-3.13051300	0.00195400
H	-1.77597000	-3.63396600	-0.00310600
C	-0.57831700	-2.48463300	-2.31407200

H	-0.25133200	-3.25632700	-1.61392500
H	-1.23966300	-2.95957700	-3.05031800
H	0.29671100	-2.10279400	-2.84614600
C	-0.74123600	0.58436900	-3.22722600
H	0.11347400	-0.00733100	-3.56477700
H	-1.46515100	0.63331700	-4.05084100
H	-0.39740000	1.60316200	-3.02603700
C	-2.69255200	2.09865300	-1.17558800
H	-3.71574000	2.12377800	-1.57287200
H	-2.69518500	2.57394900	-0.19228700
H	-2.06172000	2.68139700	-1.85012500
F	0.42331700	-3.02153100	0.94790400

4-B-H

E = -1224.6355851 hartree; G = -1224.256381 hartree

Rh	-0.87178600	-0.00136800	0.09601000
C	2.01157800	1.25437400	0.00638100
C	2.88874100	2.27220300	-0.38348300
C	2.40589900	3.55527800	-0.61224700
C	1.04465100	3.80103000	-0.43554300
C	0.22140600	2.74669600	-0.06572600
C	2.56310900	-0.09558400	0.29797200

C	2.17323600	-0.81885900	1.42965600
C	2.79540300	-2.03995200	1.68606900
C	3.77653600	-2.49723000	0.80897100
C	4.09839600	-1.70383600	-0.29416200
H	3.94064400	2.03670500	-0.48961100
H	3.08035400	4.35093900	-0.91220900
H	0.61775100	4.78616200	-0.58731600
H	-0.84428600	2.88390200	0.06522600
H	1.41277400	-0.43024800	2.09429000
H	2.51977300	-2.61837400	2.56295100
H	4.28693300	-3.44077800	0.97180700
H	4.85832700	-2.02548700	-1.00262900
N	3.51577300	-0.52667400	-0.55037400
N	0.68484600	1.49424000	0.13663400
O	-0.73933900	-0.32856800	2.31025700
C	-1.47832300	0.68816700	2.50580900
O	-1.93814800	1.29980800	1.48209200
C	-1.76812000	1.19010300	3.88836500
H	-1.68621900	0.38114700	4.61795700
H	-1.03160100	1.96293400	4.14181500
H	-2.76289900	1.64088300	3.93197100
C	-1.71610400	0.07412900	-1.87546600
C	-0.45322500	-0.61330000	-1.97170200
C	-1.84877800	-1.84246100	-0.55600100
C	-0.51551900	-1.77713500	-1.14000400

C	-2.59140600	-0.72003500	-1.02557800
C	-4.00549800	-0.38124600	-0.69735700
H	-4.65564900	-0.69378700	-1.52492500
H	-4.33888700	-0.89153000	0.20874100
H	-4.13293000	0.69609400	-0.56082800
C	-2.33404800	-2.92157300	0.35292300
H	-3.14456600	-2.57004100	0.99599300
H	-2.71168100	-3.76378700	-0.24158400
H	-1.52465900	-3.29565000	0.98551900
C	0.54539300	-2.81082500	-0.97578100
H	0.55583500	-3.21304700	0.03959800
H	0.34743200	-3.64437000	-1.66331300
H	1.53444600	-2.41221300	-1.20329500
C	0.70809000	-0.17370800	-2.79868700
H	1.65611200	-0.53753900	-2.39902700
H	0.59169800	-0.57137200	-3.81545000
H	0.75490100	0.91562500	-2.87210100
C	-2.09927000	1.32212500	-2.59818900
H	-2.53049200	1.06991200	-3.57605200
H	-2.84885200	1.88884700	-2.03931300
H	-1.23120600	1.96356200	-2.76856400

4-B'-H

E = -1224.6355875 hartree; G = -1224.255096 hartree

Rh	-0.87160500	0.00148700	0.09610600
C	2.56287700	0.09600900	0.29807000
C	2.17208800	0.82042000	1.42867200
C	2.79417600	2.04173000	1.68444800
C	3.77610900	2.49807700	0.80779300
C	4.09876100	1.70361500	-0.29436600
C	2.01161800	-1.25417900	0.00719600
C	2.88894200	-2.27207400	-0.38216800
C	2.40616800	-3.55524800	-0.61050600
C	1.04490600	-3.80104000	-0.43392800
C	0.22153400	-2.74666700	-0.06448400
H	1.41067800	0.43303500	2.09294500
H	2.51776200	2.62101900	2.56051000
H	4.28650500	3.44170500	0.97016900
H	4.85928000	2.02456200	-1.00252300
H	3.94084200	-2.03658500	-0.48829900
H	3.08070200	-4.35100000	-0.91005100
H	0.61814700	-4.78626600	-0.58548900
H	-0.84410600	-2.88386100	0.06665400
N	0.68498700	-1.49415700	0.13758800
N	3.51629000	0.52626200	-0.54991600
O	-1.93727800	-1.29963900	1.48269900
C	-1.47864900	-0.68693500	2.50612000

O	-0.74081200	0.33071200	2.31030100
C	-1.76704500	-1.18728300	3.88951100
H	-2.73877600	-1.68599300	3.92396700
H	-0.99590500	-1.91764300	4.16511300
H	-1.73610600	-0.36630800	4.60985800
C	-0.51587500	1.77631800	-1.14149300
C	-0.45334900	0.61170600	-1.97210600
C	-2.59146000	0.71878200	-1.02591100
C	-1.71604900	-0.07584600	-1.87529500
C	-1.84904600	1.84183700	-0.55739700
C	-2.33471300	2.92185300	0.35020600
H	-2.71207900	3.76339500	-0.24543100
H	-3.14549200	2.57104000	0.99333200
H	-1.52566700	3.29676000	0.98276600
C	-4.00533000	0.37960600	-0.69706600
H	-4.33890000	0.89092100	0.20837200
H	-4.65582400	0.69050400	-1.52497100
H	-4.13201500	-0.69761200	-0.55892400
C	-2.09882100	-1.32457100	-2.59697800
H	-2.84902800	-1.89020600	-2.03790300
H	-2.52917600	-1.07339000	-3.57549200
H	-1.23076100	-1.96639100	-2.76589800
C	0.70801200	0.17160600	-2.79875200
H	0.75555500	-0.91782100	-2.87045400
H	0.59106700	0.56759700	-3.81609500

H	1.65592100	0.53664800	-2.39989900
C	0.54496200	2.81022800	-0.97818200
H	0.34806600	3.64233800	-1.66776800
H	0.55417300	3.21465000	0.03633300
H	1.53425600	2.41101700	-1.20361300

4-B-Br

E = -3795.4455149 hartree; G = -3795.079802 hartree

Rh	-1.58671100	-0.20529300	0.03928800
C	0.72842600	1.92054700	0.09827800
C	1.31319200	3.10466400	-0.35971200
C	0.51135200	4.11306400	-0.88316200
C	-0.86824100	3.91779700	-0.92879000
C	-1.38591700	2.71079400	-0.47755300
C	1.59048400	0.87554400	0.70654600
C	1.24027300	0.21815700	1.88764200
C	2.14457500	-0.69493700	2.43206900
C	3.35681700	-0.93131000	1.78953600
C	3.59320800	-0.21663300	0.61373400
H	2.38801300	3.21816100	-0.28634000
H	0.95476200	5.03745200	-1.23901900
H	-1.53929400	4.67683900	-1.31504600

H	-2.44757500	2.50391800	-0.51086400
H	0.29283900	0.41943000	2.36992600
H	1.90803700	-1.21660000	3.35436300
H	4.08370700	-1.63294600	2.17984000
N	2.76587500	0.65968900	0.08097000
N	-0.60782800	1.72240000	0.01167700
O	-1.80553700	-0.17711800	2.26824000
C	-2.83617900	0.56100700	2.15971300
O	-3.24388000	0.84874600	0.98315300
C	-3.52432400	1.11813900	3.36923100
H	-3.43961100	0.42569300	4.21048700
H	-3.03229800	2.05841400	3.64851700
H	-4.57478700	1.32842800	3.15512000
C	-2.06614300	-0.65126500	-1.99955800
C	-0.65310600	-0.87787000	-1.83269800
C	-1.79766500	-2.33379500	-0.40814100
C	-0.47743000	-1.88833200	-0.83246800
C	-2.77178100	-1.59219500	-1.13956500
C	-4.25410900	-1.72071200	-1.04363500
H	-4.61114200	-2.40091200	-1.82803600
H	-4.56047200	-2.12693800	-0.07717800
H	-4.74582400	-0.75543600	-1.18881300
C	-2.05199500	-3.40937100	0.59414400
H	-3.04209500	-3.31509800	1.04629800
H	-1.99474800	-4.38909300	0.10178200

H	-1.30130000	-3.39268200	1.38900600
C	0.81168400	-2.48684600	-0.38365800
H	0.79800400	-2.71274100	0.68475300
H	0.97907200	-3.42979600	-0.92157700
H	1.65531300	-1.82790500	-0.59029200
C	0.42850400	-0.16983500	-2.57732500
H	1.36723000	-0.15899400	-2.02101800
H	0.60354300	-0.68905800	-3.52876700
H	0.14623700	0.85993500	-2.80896100
C	-2.70135200	0.30752900	-2.95046400
H	-2.90244600	-0.19248000	-3.90707600
H	-3.65332300	0.67774000	-2.56054300
H	-2.04986400	1.16225900	-3.14711900
Br	5.24078300	-0.51948300	-0.33263000

4-B'-Br

E = -3795.4323204 hartree; G = -3795.065909 hartree

Rh	0.27354800	-0.73985800	-0.00607100
C	-2.40425400	1.27340800	0.35923200
C	-2.60171000	0.52456500	1.52140000
C	-3.83259400	-0.10327800	1.70883700
C	-4.82276400	0.05035700	0.74126600

C	-4.53936500	0.83784100	-0.37699800
C	-1.15347400	2.04896200	0.14282400
C	-1.27732200	3.38742900	-0.23244900
C	-0.14046300	4.17339500	-0.37257100
C	1.10111100	3.60427800	-0.11299600
C	1.14560800	2.25638600	0.23113300
H	-1.81573300	0.44083600	2.25781700
H	-4.01446100	-0.69097400	2.60352800
H	-5.79652100	-0.41596900	0.84896500
H	-5.28888500	0.98949800	-1.15030700
H	-2.26867000	3.79150500	-0.39407800
H	-0.21550400	5.21725600	-0.65916600
H	2.01569500	4.17941500	-0.17977800
N	0.06438900	1.46507700	0.33588000
N	-3.36258100	1.44278500	-0.57175700
O	1.59491500	-1.05476300	1.71449400
C	0.62389200	-1.40183200	2.46238100
O	-0.54120500	-1.42469000	1.94917300
C	0.84132600	-1.72345000	3.91076400
H	1.85535400	-2.09581400	4.07508100
H	0.71147000	-0.80518400	4.49726800
H	0.10771200	-2.45640400	4.25592000
C	-0.96265500	-1.69975100	-1.52433600
C	-0.29150300	-0.59466200	-2.13400100
C	1.33478300	-2.07424300	-1.34603500

C	1.13282700	-0.80224300	-2.00264500
C	0.04832900	-2.61985500	-1.02130600
C	-0.22765700	-3.92514500	-0.35382900
H	-0.32219000	-4.71457500	-1.11095600
H	0.58089100	-4.20454700	0.32620000
H	-1.16111800	-3.88683000	0.21278100
C	2.65680000	-2.68427200	-1.03226400
H	2.57987000	-3.41415900	-0.22397800
H	3.03508200	-3.19976700	-1.92491100
H	3.38912200	-1.92408900	-0.74909300
C	2.18870500	0.05520600	-2.61636600
H	3.16326700	-0.10708100	-2.15398800
H	2.27487000	-0.19241600	-3.68294900
H	1.93796400	1.11640700	-2.54413300
C	-0.91649900	0.56484100	-2.83301300
H	-0.31500300	1.46960800	-2.71526700
H	-0.97162100	0.34129600	-3.90685000
H	-1.92604300	0.76916000	-2.47303400
C	-2.43237000	-1.92645300	-1.43886100
H	-2.72214800	-2.69671300	-2.16588100
H	-2.71969500	-2.28472200	-0.44658700
H	-2.99137300	-1.01815500	-1.66043500
Br	2.86860400	1.52107800	0.55993800

4-B-Cl

E = -1684.234249 hartree; G = -1683.865231 hartree

Rh	-1.22622000	-0.14605800	0.05096100
C	1.25196300	1.77779500	0.03844100
C	1.90970900	2.92787700	-0.40839000
C	1.17194700	4.00694200	-0.88264900
C	-0.21898400	3.91541300	-0.89343400
C	-0.81236500	2.73985500	-0.45364100
C	2.05878200	0.65756300	0.58843200
C	1.72186300	0.00079000	1.77352100
C	2.59215300	-0.97307300	2.26555000
C	3.75915300	-1.27099100	1.56872000
C	3.98598400	-0.55197900	0.39398900
H	2.99163600	2.95945800	-0.36546900
H	1.67355800	4.90505400	-1.22844300
H	-0.84191900	4.73103900	-1.24326200
H	-1.88690800	2.61267400	-0.46078000
H	0.81179700	0.25181600	2.30189000
H	2.36329700	-1.49312300	3.19059300
H	4.46232600	-2.01831000	1.91529700
N	3.19122200	0.38108000	-0.09064700
N	-0.09764900	1.68463400	-0.00858100
O	-1.31867200	-0.07596200	2.29797100

C	-2.30233700	0.72760000	2.22854400
O	-2.74929200	1.02909100	1.06955000
C	-2.89667700	1.34254800	3.45961500
H	-2.78729300	0.67154600	4.31504700
H	-2.35965400	2.27345200	3.68121400
H	-3.95029800	1.58368300	3.29912600
C	-1.78715000	-0.57621600	-1.97227700
C	-0.39581100	-0.92482600	-1.82904000
C	-1.63896200	-2.25298200	-0.36137500
C	-0.29251100	-1.93233400	-0.81761200
C	-2.55651900	-1.44027600	-1.08823500
C	-4.04273800	-1.44072200	-0.97239900
H	-4.46496200	-2.08444300	-1.75538700
H	-4.37215800	-1.82430400	-0.00433700
H	-4.45233200	-0.43701200	-1.11044600
C	-1.96452600	-3.28898300	0.66180900
H	-2.95268400	-3.12923700	1.09910200
H	-1.95536600	-4.28210400	0.19362700
H	-1.22365500	-3.29496900	1.46612500
C	0.94448200	-2.64023800	-0.38169400
H	0.93378500	-2.83912000	0.69234600
H	1.00546100	-3.60729700	-0.89895300
H	1.84338500	-2.07180000	-0.62232200
C	0.72806200	-0.32927200	-2.60889700
H	1.67939900	-0.40840700	-2.08076200

H	0.82215100	-0.86502000	-3.56248800
H	0.54274500	0.72344500	-2.83671300
C	-2.35585200	0.41654500	-2.93030900
H	-2.61702900	-0.08173900	-3.87327900
H	-3.26512600	0.87381500	-2.53057000
H	-1.63691400	1.20791500	-3.15517000
Cl	5.44396200	-0.89503900	-0.54334300

4-B-F

E = -1323.8743358 hartree; G = -1323.504784 hartree

Rh	-1.04182500	-0.09160200	0.07225800
C	1.60509900	1.60223600	0.02257700
C	2.33746300	2.71129800	-0.41223700
C	1.67616700	3.87744800	-0.78039100
C	0.28517600	3.91429900	-0.69616000
C	-0.38692300	2.77384300	-0.27762500
C	2.33918400	0.38825100	0.46543200
C	2.00423700	-0.30321400	1.62985200
C	2.80121600	-1.38664300	2.01281700
C	3.89566800	-1.74607200	1.23479300
C	4.12725600	-0.97102900	0.09980000
H	3.41794400	2.64082600	-0.44371300

H	2.23670000	4.74399700	-1.11621900
H	-0.27908200	4.80237600	-0.95816100
H	-1.46691500	2.74617000	-0.21567900
H	1.15352700	-0.00088400	2.22571400
H	2.56964100	-1.94050300	2.91723100
H	4.54814100	-2.57493300	1.48241600
N	3.40732600	0.05519400	-0.29119900
N	0.25133500	1.63291000	0.06036500
O	-1.00242600	-0.18293200	2.31135100
C	-1.89747200	0.71922500	2.36410400
O	-2.38430900	1.14186500	1.26050400
C	-2.33356700	1.30983700	3.67081600
H	-2.23151000	0.57866900	4.47640100
H	-1.68678400	2.16636100	3.89962000
H	-3.36481800	1.66566700	3.60942100
C	-1.75854900	-0.32578200	-1.93448700
C	-0.40417700	-0.81885900	-1.90160700
C	-1.68913900	-2.11214300	-0.43875000
C	-0.34507900	-1.89506500	-0.95908600
C	-2.55868000	-1.16535100	-1.05450400
C	-4.02437700	-1.01654900	-0.82764600
H	-4.57082100	-1.54900000	-1.61703800
H	-4.32403400	-1.43475900	0.13569900
H	-4.32567400	0.03349100	-0.86206400
C	-2.06363100	-3.16739200	0.54725400

H	-2.99151100	-2.91921600	1.06823400
H	-2.21060100	-4.12285500	0.02684300
H	-1.27450300	-3.31042100	1.29042600
C	0.84025200	-2.74050300	-0.64155600
H	0.86649800	-3.01297800	0.41570300
H	0.78611500	-3.67024800	-1.22398200
H	1.77314800	-2.23709400	-0.89601600
C	0.72786500	-0.27882600	-2.70997500
H	1.69586700	-0.51570500	-2.26586700
H	0.69362200	-0.72302900	-3.71324100
H	0.65460400	0.80579400	-2.82477800
C	-2.28156500	0.76920600	-2.80283700
H	-2.65607600	0.34847100	-3.74536700
H	-3.11037000	1.29548500	-2.32120200
H	-1.50075700	1.49390500	-3.04580600
F	5.17605200	-1.27833300	-0.68585700

TS-Decomplexation-H

E = -1224.6196938 hartree; G = -1224.240585 hartree

Rh	-0.54069600	-0.17410400	0.06219700
C	2.19632000	1.01043100	-0.48630500

C	3.15521900	1.93795100	-0.88609600
C	2.74346800	3.12590300	-1.48764300
C	1.38002700	3.35499900	-1.66354200
C	0.47487100	2.39425800	-1.22877500
C	2.57392300	-0.28537600	0.15146100
C	2.89489500	-0.33602200	1.51162400
C	3.22977500	-1.56946800	2.07100900
C	3.24230000	-2.69593900	1.25031700
C	2.91017500	-2.54364900	-0.09727900
H	4.20518000	1.71702300	-0.72920300
H	3.47522200	3.85915800	-1.81122000
H	1.01247400	4.26635900	-2.12167600
H	-0.59254400	2.53821500	-1.30898100
H	2.87219600	0.56839100	2.10968800
H	3.47977200	-1.64515600	3.12487600
H	3.50577000	-3.67393000	1.63950700
H	2.91174200	-3.40079200	-0.76543500
N	2.57160700	-1.36916900	-0.64647100
N	0.87776100	1.24500200	-0.65592500
O	-0.46153600	0.79192000	1.89339700
C	-0.98352700	1.98207000	2.01832000
O	-1.57629500	2.59239800	1.12235500
C	-0.79274600	2.58008800	3.40195000
H	-1.16283800	1.89031200	4.16807300
H	0.27529500	2.73838900	3.59173900

H	-1.31855800	3.53392700	3.48124700
C	-2.29367700	-0.04062700	-1.12642200
C	-1.35146400	-0.87849600	-1.85024000
C	-1.87279500	-1.91044000	0.18733200
C	-1.08942800	-2.01769400	-1.04532100
C	-2.64407800	-0.72021100	0.11495600
C	-3.62591600	-0.20622600	1.11187900
H	-4.64187600	-0.45345400	0.77674700
H	-3.47294200	-0.65466600	2.09586100
H	-3.55370800	0.87965100	1.20377000
C	-1.87278200	-2.92342500	1.28328900
H	-2.27982200	-2.51004800	2.20861200
H	-2.48692200	-3.78607000	0.99371500
H	-0.86105200	-3.29045700	1.48170300
C	-0.20633900	-3.16744500	-1.37977100
H	0.30625400	-3.54702700	-0.49283100
H	-0.82706200	-3.98323900	-1.77570600
H	0.53573900	-2.90411600	-2.13455500
C	-0.76719800	-0.57728000	-3.19124600
H	0.20790800	-1.05512800	-3.31241000
H	-1.43195100	-0.94782100	-3.98175200
H	-0.64158200	0.49905500	-3.33582000
C	-2.92319100	1.21823900	-1.61119500
H	-3.95549900	1.00698900	-1.92159400
H	-2.94985400	1.96342800	-0.81205800

H	-2.38993300	1.63047900	-2.47021000

TS-Decomplexation-Br

E = -3795.4295077 hartree; G = -3795.063381 hartree

Rh	-0.95985600	-0.46357700	0.06540500
C	0.22261400	2.26959000	-0.53722200
C	0.28227800	3.57051900	-1.02920900
C	-0.72137100	4.02074500	-1.88601000
C	-1.75867100	3.15460100	-2.22537800
C	-1.76337800	1.87145100	-1.69178600
C	1.28175200	1.72742000	0.36858800
C	1.25401400	1.96476000	1.74247800
C	2.26477700	1.41077900	2.53142200
C	3.26909300	0.65931000	1.92778800
C	3.19733000	0.50141600	0.54211000
H	1.11065300	4.20928800	-0.74400900
H	-0.69197000	5.03145400	-2.28004600
H	-2.56276300	3.46270900	-2.88413200
H	-2.56032900	1.17079500	-1.89847200
H	0.45479900	2.55121400	2.17856800
H	2.27442400	1.56815900	3.60527900

H	4.07656300	0.22130800	2.50157400
N	2.24498000	0.99344300	-0.22738200
N	-0.79104800	1.43969600	-0.86797500
O	-1.67010100	0.56267100	1.70597500
C	-2.84783700	1.12503100	1.65941500
O	-3.63619800	1.03524500	0.71312000
C	-3.16933100	1.94973600	2.89439100
H	-2.88457600	1.41434400	3.80544600
H	-2.59202300	2.88219100	2.86506100
H	-4.23309900	2.19576300	2.92356200
C	-2.23516700	-1.80743800	-0.96586900
C	-0.96592600	-1.77986100	-1.67789800
C	-0.60199300	-2.57326700	0.49678700
C	0.03667700	-2.22272700	-0.77705200
C	-1.99773600	-2.34828700	0.36749900
C	-3.06094200	-2.57010400	1.39017600
H	-3.57701800	-3.51563400	1.17870900
H	-2.64558400	-2.62686200	2.39840000
H	-3.80343400	-1.76853400	1.36208100
C	0.12949000	-3.07545700	1.69536200
H	-0.49023900	-3.02957800	2.59318800
H	0.42943800	-4.11927400	1.53588900
H	1.04114800	-2.49532900	1.87162800
C	1.49366300	-2.34677600	-1.05721800
H	2.08601900	-2.23224700	-0.14786300

H	1.70105200	-3.34619200	-1.46369700
H	1.82817000	-1.60751000	-1.78711600
C	-0.76963200	-1.34609000	-3.09236700
H	0.25388100	-1.00472100	-3.26437000
H	-0.96741200	-2.18851400	-3.76726800
H	-1.45302000	-0.53719400	-3.36178300
C	-3.57530800	-1.46804200	-1.51683500
H	-4.14310900	-2.39422800	-1.67891600
H	-4.12819700	-0.84215000	-0.81156000
H	-3.49890700	-0.94527600	-2.47236200
Br	4.59015800	-0.48949100	-0.33832300

TS-Decomplexation-Cl

E = -1684.217984 hartree; G = -1683.853224 hartree

Rh	-0.66930500	-0.38160700	0.06262700
C	0.90934900	2.13012200	-0.57918800
C	1.14237500	3.42492900	-1.03732400
C	0.17516600	4.05451500	-1.81949300
C	-1.00033800	3.36962900	-2.12014500
C	-1.17544700	2.08551300	-1.61895600
C	1.92073000	1.41196900	0.25250600

C	2.11631300	1.76235800	1.58881400
C	3.09109500	1.07994100	2.31871900
C	3.85107400	0.09843200	1.68916100
C	3.57219200	-0.15484100	0.34474700
H	2.07392400	3.91887300	-0.78479100
H	0.33820200	5.06269400	-2.18651000
H	-1.78182600	3.81939700	-2.72223400
H	-2.08400400	1.52768200	-1.79655500
H	1.51231300	2.54010600	2.04102800
H	3.26601900	1.31844800	3.36299400
H	4.63413200	-0.44018700	2.20882600
N	2.63345900	0.44846100	-0.36304100
N	-0.23926900	1.48123800	-0.86439400
O	-1.11707500	0.70111400	1.76928800
C	-2.25715500	1.33519100	1.83113600
O	-3.10802600	1.34800000	0.93510100
C	-2.46398800	2.07522900	3.14151700
H	-2.44498700	1.36529700	3.97624300
H	-1.65044100	2.79123200	3.30229900
H	-3.41979600	2.60329300	3.13579100
C	-2.18895500	-1.42720400	-0.98953500
C	-0.94268800	-1.63393700	-1.70967400
C	-0.73454900	-2.53614400	0.44315000
C	-0.04866000	-2.29721000	-0.82927100
C	-2.05746400	-2.03585200	0.33018100

C	-3.14041000	-2.08349500	1.35355700
H	-3.81861000	-2.91538400	1.12254200
H	-2.73775200	-2.24157500	2.35648000
H	-3.72102500	-1.15851500	1.34857400
C	-0.11882600	-3.21127000	1.62250400
H	-0.68190400	-3.01103200	2.53664500
H	-0.09848400	-4.29691200	1.46125400
H	0.91412100	-2.88121500	1.77019500
C	1.34619200	-2.72202400	-1.12563600
H	1.97229400	-2.68584800	-0.23214100
H	1.33489100	-3.76277800	-1.47794400
H	1.80278300	-2.10574300	-1.90144100
C	-0.65902800	-1.20981500	-3.11306200
H	0.40327700	-0.99420900	-3.25261900
H	-0.93932000	-2.01132900	-3.80803700
H	-1.23048600	-0.31800400	-3.38180800
C	-3.44518400	-0.83584900	-1.52465000
H	-4.17811800	-1.63800400	-1.68523400
H	-3.86319800	-0.12435800	-0.80809300
H	-3.28043500	-0.33321900	-2.48002700
Cl	4.55811000	-1.34342900	-0.50947500

TS-Decomplexation-F

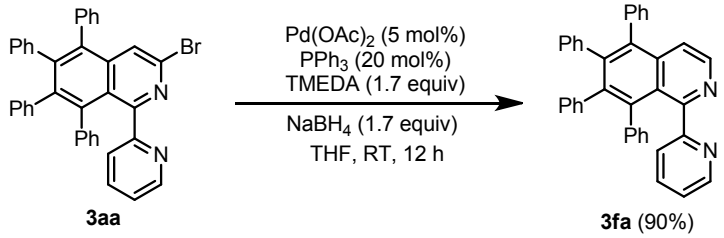
E = -1323.8590403 hartree; G = -1323.489969 hartree

Rh	-0.57371000	-0.35811500	0.09810700
C	1.35961400	1.99592900	-0.36344600
C	1.77285000	3.27374900	-0.73140500
C	0.88811400	4.10627200	-1.41520600
C	-0.38985000	3.63534100	-1.70613800
C	-0.74398300	2.35446800	-1.29706600
C	2.28648400	1.06029100	0.34309300
C	2.48867700	1.13882000	1.71976200
C	3.35720700	0.21744300	2.31767100
C	3.99235700	-0.73431600	1.52801900
C	3.70909600	-0.70030500	0.16396400
H	2.77872000	3.59718600	-0.48770300
H	1.19363500	5.10421600	-1.71294800
H	-1.11467600	4.24725000	-2.23135000
H	-1.73578200	1.95867100	-1.45877600
H	1.97883400	1.89521800	2.30522500
H	3.53700500	0.24667100	3.38754900
H	4.67967700	-1.46853700	1.93149600
N	2.89222200	0.13801700	-0.43345000
N	0.11417200	1.55072500	-0.64225700

O	-1.26665200	0.68097100	1.74657000
C	-2.32635700	1.44051400	1.67181800
O	-3.03320000	1.57588800	0.66728400
C	-2.62412100	2.18030500	2.96503600
H	-2.64715900	1.48213700	3.80842100
H	-1.82715500	2.90696300	3.16281100
H	-3.57894000	2.70545500	2.89389800
C	-1.93239400	-1.18123100	-1.30836200
C	-0.59320400	-1.52247000	-1.76027800
C	-0.95783000	-2.49559200	0.34089800
C	0.00503500	-2.31665400	-0.74711000
C	-2.16170900	-1.83634800	-0.02739600
C	-3.43951400	-1.77827500	0.73749500
H	-4.15213100	-2.48947800	0.29940700
H	-3.29325100	-2.04554200	1.78604100
H	-3.87678300	-0.77908500	0.68452800
C	-0.70528300	-3.28194400	1.58381100
H	-1.37807400	-2.97992400	2.38994100
H	-0.86452200	-4.35036200	1.38752800
H	0.32584100	-3.15886800	1.92751000
C	1.36882300	-2.91199200	-0.76367200
H	1.83555300	-2.87242600	0.22421300
H	1.28742500	-3.97187100	-1.04198500
H	2.02129400	-2.41840600	-1.48310300
C	0.01664600	-1.10050300	-3.05613100

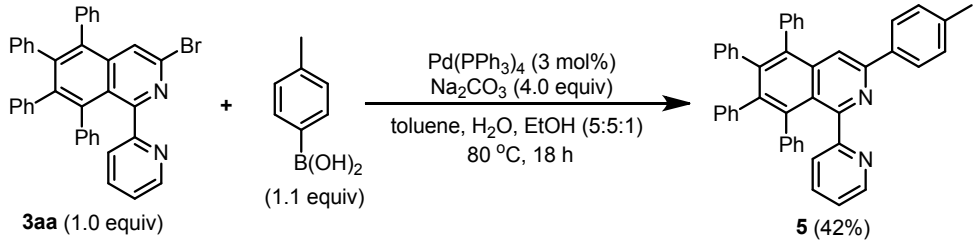
H	1.10713600	-1.14663300	-3.01620900
H	-0.32608200	-1.76275100	-3.86124900
H	-0.27577200	-0.07965700	-3.31686000
C	-2.95712300	-0.41556200	-2.06841900
H	-3.66775100	-1.11910400	-2.52323300
H	-3.51065100	0.24790000	-1.39943500
H	-2.50544900	0.17413300	-2.86906900
F	4.29987600	-1.60574300	-0.63822000

Derivatization



To a 100 mL round-bottom flask equipped with a magnetic stirring bar were added **3aa** (118.0 mg, 0.2 mmol), $Pd(OAc)_2$ (3.0 mg, 0.01 mmol), PPh_3 (11.0 mg, 0.04 mmol), TMEDA (40.0 mg, 0.34 mmol), $NaBH_4$ (13.0 mg, 0.34 mmol) and THF (20.0 ml). The mixture was stirred at RT for 12 h. The solvent was removed in vacuum, and the crude product was purified by column chromatography using PE/EA (2:1) to give the product **3fa** (92.0 mg, 90%) as a white (M.p.: 230-232 ºC).

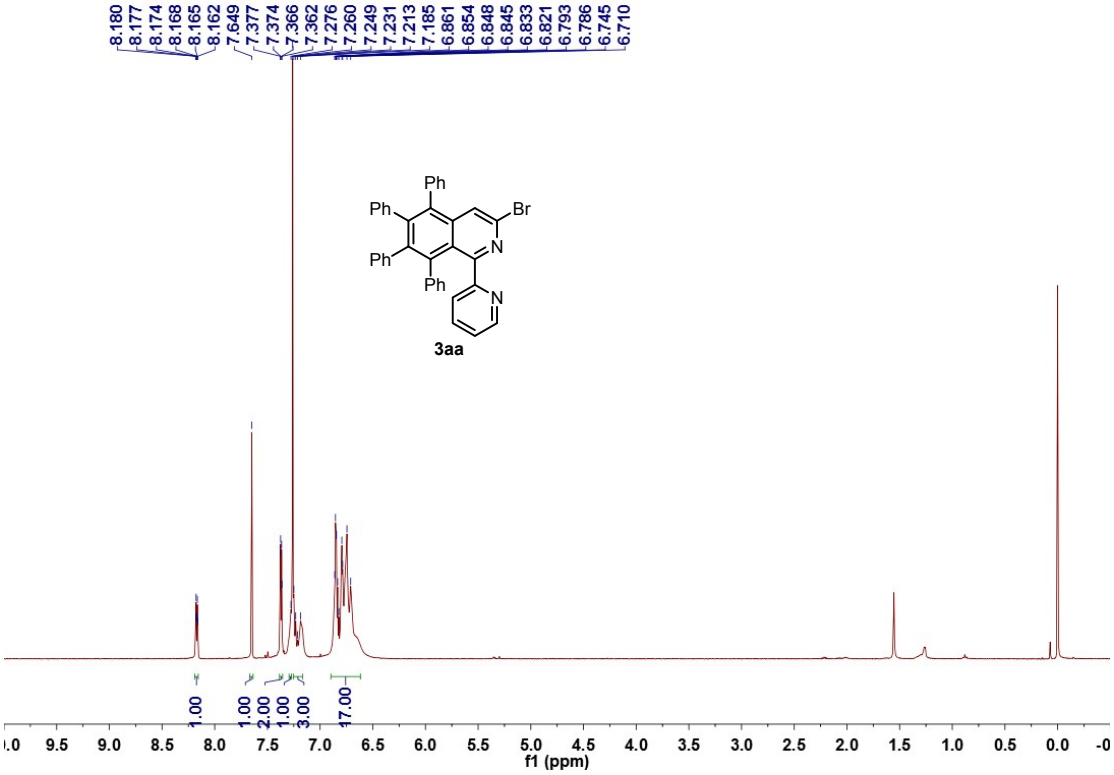
3fa: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 5.6 Hz, 1H), 8.20 (d, J = 4.8 Hz, 1H), 7.47 (d, J = 5.6 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.24 – 7.19 (m, 4H), 6.85 – 6.71 (m, 17H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 159.7, 148.1, 142.9, 141.8, 141.0, 140.2, 139.8, 139.6, 138.5, 138.4, 137.5, 137.1, 135.5, 132.1, 131.1, 130.6, 127.7, 126.8, 126.6, 126.4, 126.4, 125.7, 125.6, 125.6, 125.3, 124.4, 121.3, 119.2. ESI-MS: Calcd for $C_{38}H_{26}N_2$: [M+H$^+$] 511.2174, found 511.2173.



To a 100 mL round-bottom flask equipped with a magnetic stirring bar were added **3aa** (118.0 mg, 0.2 mmol), p-tolylboronic acid (30.0 mg, 0.22 mmol), $Pd(PPh_3)_4$ (7.0 mg, 0.006 mmol), Na_2CO_3 (85.0 mg, 0.8 mmol), toluene (10.0 ml), ethanol (2.0 ml), water (10.0 ml). The mixture was stirred at 80 ºC for 18 h. The solvent was removed in vacuum, and the crude product was purified by column chromatography using PE/EA (5:1) to give the product **5** (51.0 mg, 42%) as a white solid (M.p.: 177-179 ºC).

5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.4 Hz, 1H), 7.90 – 7.89 (m, 2H), 7.84 (m, 1H), 7.56 – 7.54 (m, 1H), 7.44 – 7.40 (m, 1H), 7.29 – 7.27 (m, 3H), 7.25 – 7.20 (m, 4H), 6.88 – 6.72 (m, 17H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 159.3, 148.8, 148.0, 142.8, 141.2, 140.5, 140.0, 139.8, 138.6, 138.5, 138.3, 138.3, 137.7, 136.3, 135.6, 131.3, 131.2, 130.7, 129.3, 127.7, 126.8, 126.6, 126.4, 126.4, 125.6, 125.6, 125.3, 124.8, 124.8, 121.4, 114.4, 21.2. ESI-MS: Calcd for $C_{45}H_{32}N_2$: [M+H$^+$] 601.2644, found 601.2675.

NMR Spectra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Ph
Ph
Br
N
Ph
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N
3aa
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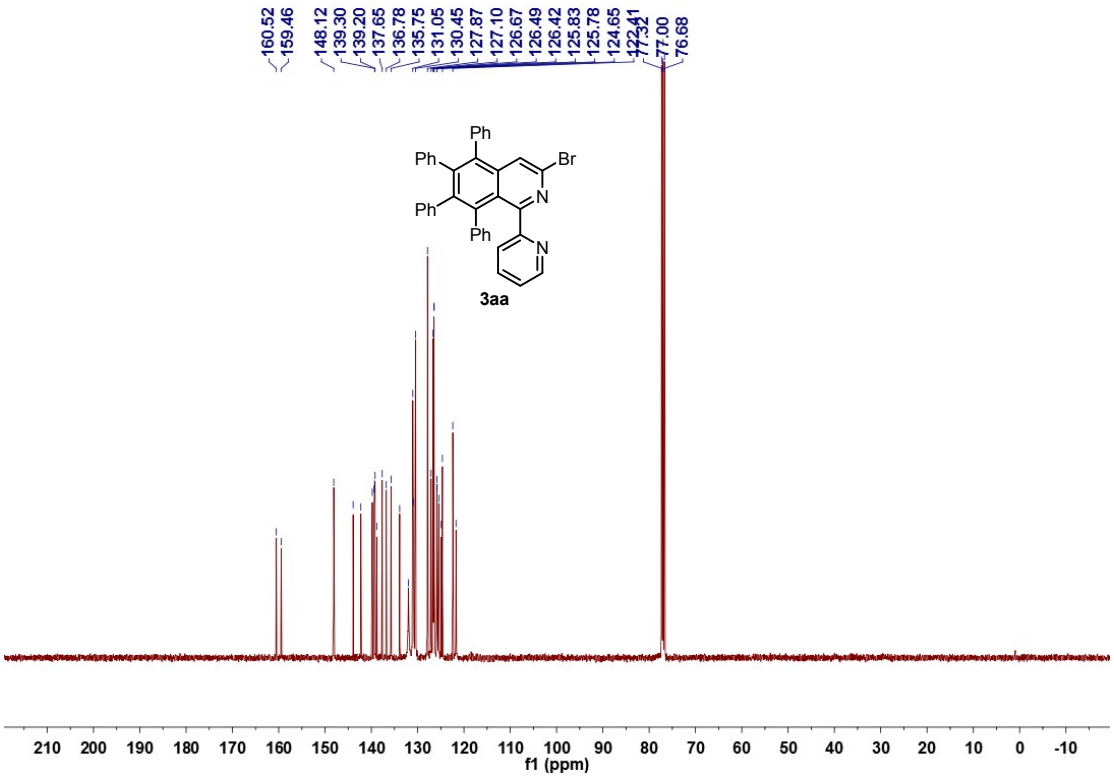
1.00
2.00
1.00
3.00
17.00
f1 (ppm)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135.75
131.05
130.45
127.87
127.10
126.67
126.49
126.42
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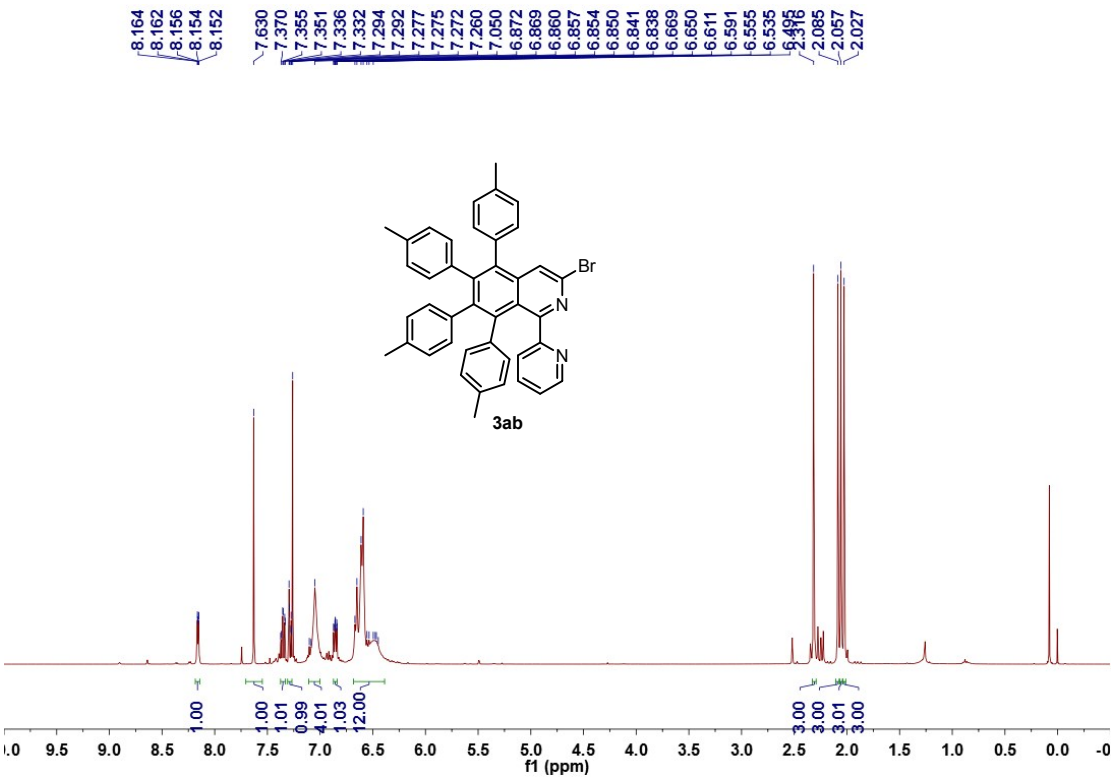
125.78
124.65
77.00
76.68
Ph
Ph
Br
N
Ph
Ph
N
3aa
f1 (ppm)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7.355
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7.336
7.332
7.294
7.292
7.277
7.275
7.272
7.260
7.050
6.872
6.869
6.860
6.857
6.854
6.850
6.841
6.838
6.669
6.650
6.611
6.591
6.555
6.535
2.085
2.057
2.027
Br
N
N
3ab
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1.00
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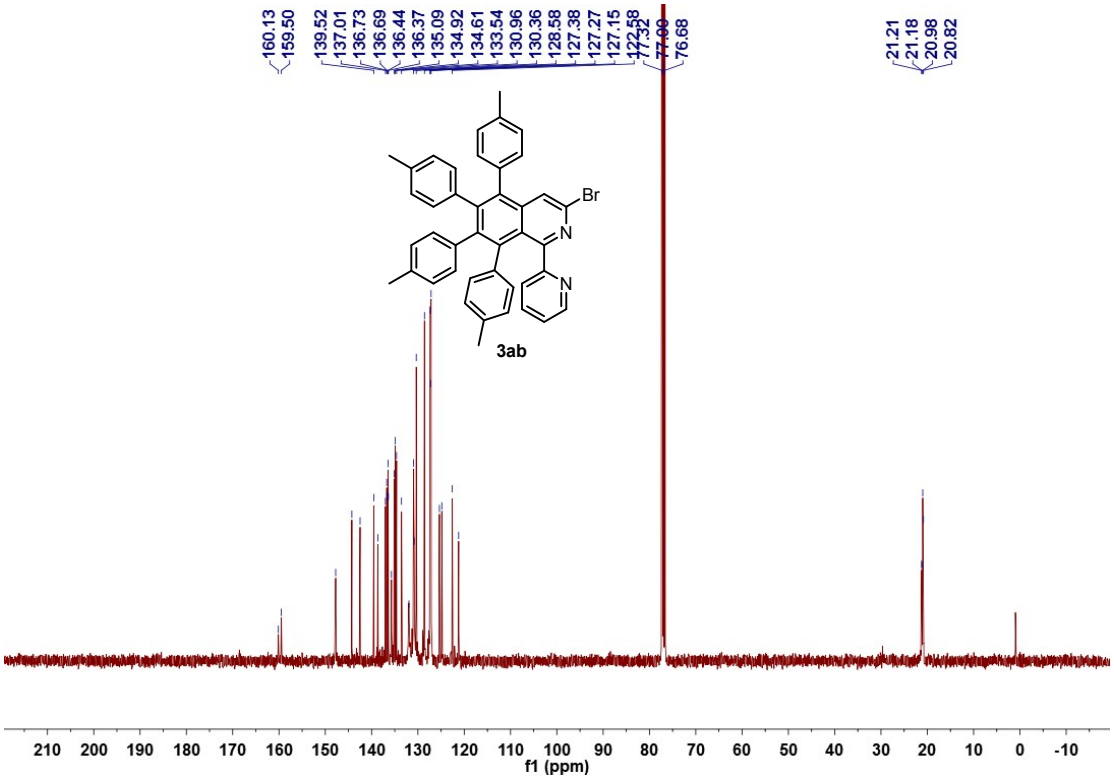
0.99
4.01
1.03
12.00
3.00
3.00
3.01
3.00
f1 (ppm)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134.92
134.61
133.54
130.96
130.36
128.58
127.38
127.27
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76.68
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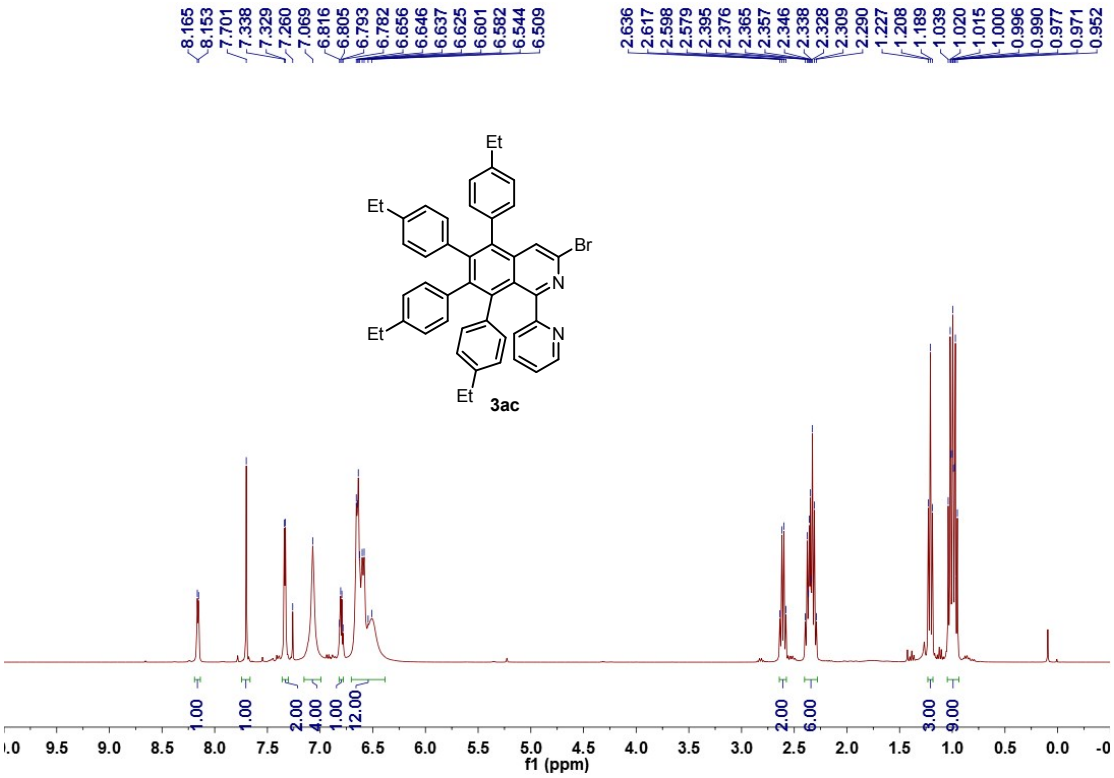
20.82
Br
N
N
3ab
f1 (ppm)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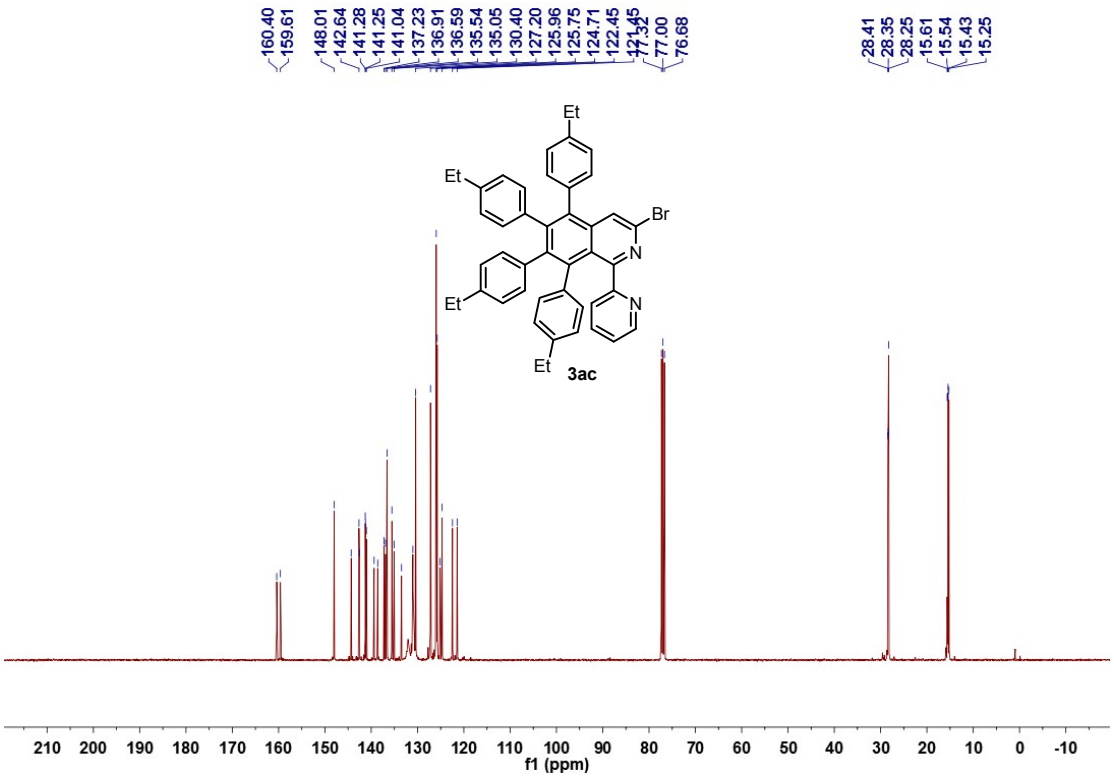
7.338
7.329
7.260
7.069
6.816
6.805
6.793
6.782
6.656
6.646
6.637
6.625
6.601
6.582
6.544
6.509
2.636
2.617
2.598
2.579
2.395
2.376
2.365
2.357
2.346
2.338
2.328
2.309
2.290
1.227
1.208
1.189
1.039
1.020
1.015
1.000
0.996
0.990
0.977
0.971
0.952
Et
Et
Br
N
Et
N
Et
3ac
1.00
1.00
2.00
4.00
1.00
12.00
2.00
6.00
3.00
9.00
f1 (ppm)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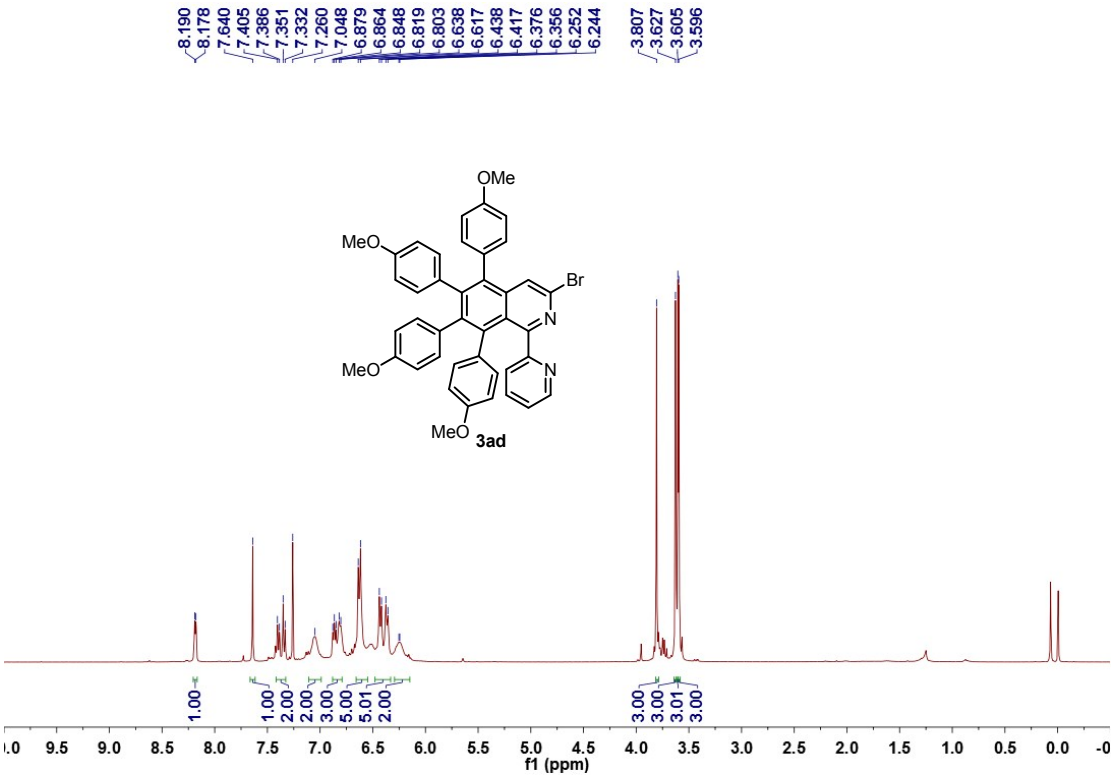
135.54
135.05
130.40
127.20
125.96
125.75
124.71
122.45
121.45
77.32
77.00
76.68
28.41
28.35
28.25
15.61
15.54
15.43
15.25
Et
Et
Br
N
Et
N
Et
3ac
f1 (ppm)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7.386
7.351
7.332
7.260
7.048
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6.864
6.848
6.819
6.803
6.638
6.617
6.438
6.417
6.376
6.356
6.252
6.244
3.807
3.627
3.605
3.596
OMe
MeO
Br
N
MeO
N
MeO
3ad
1.00
1.00
2.00
2.00
3.00
5.00
5.01
2.00
3.00
3.00
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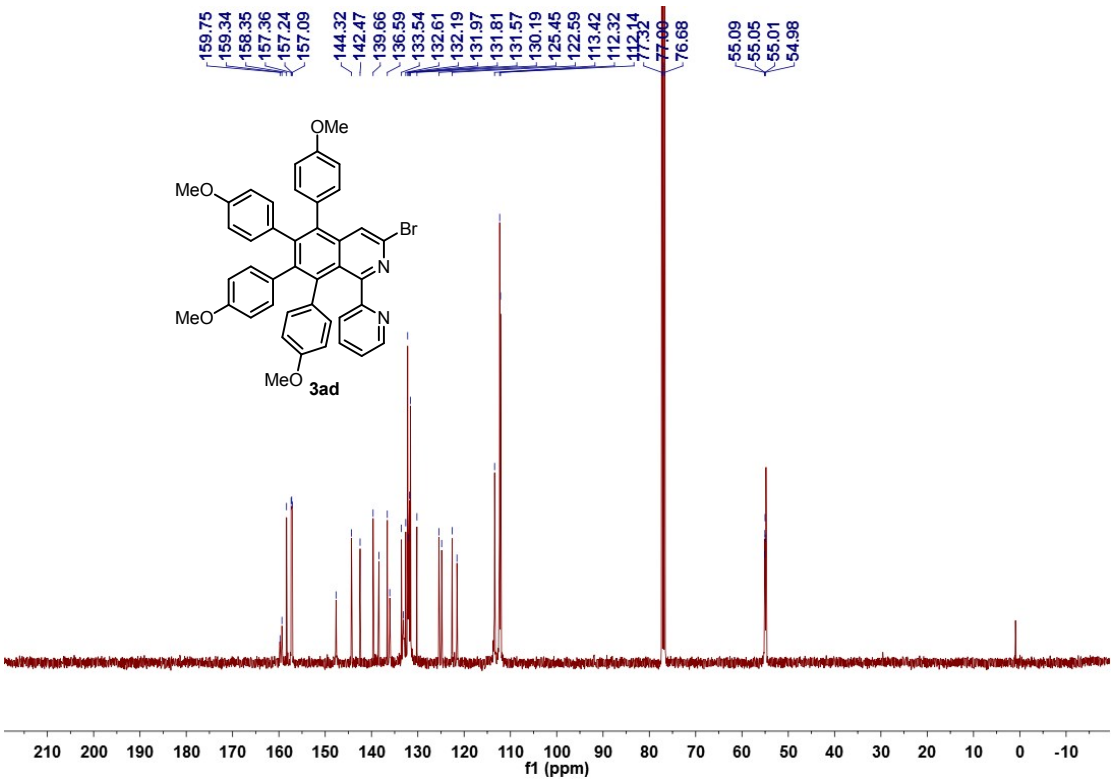
3.00
f1 (ppm)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157.09
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142.47
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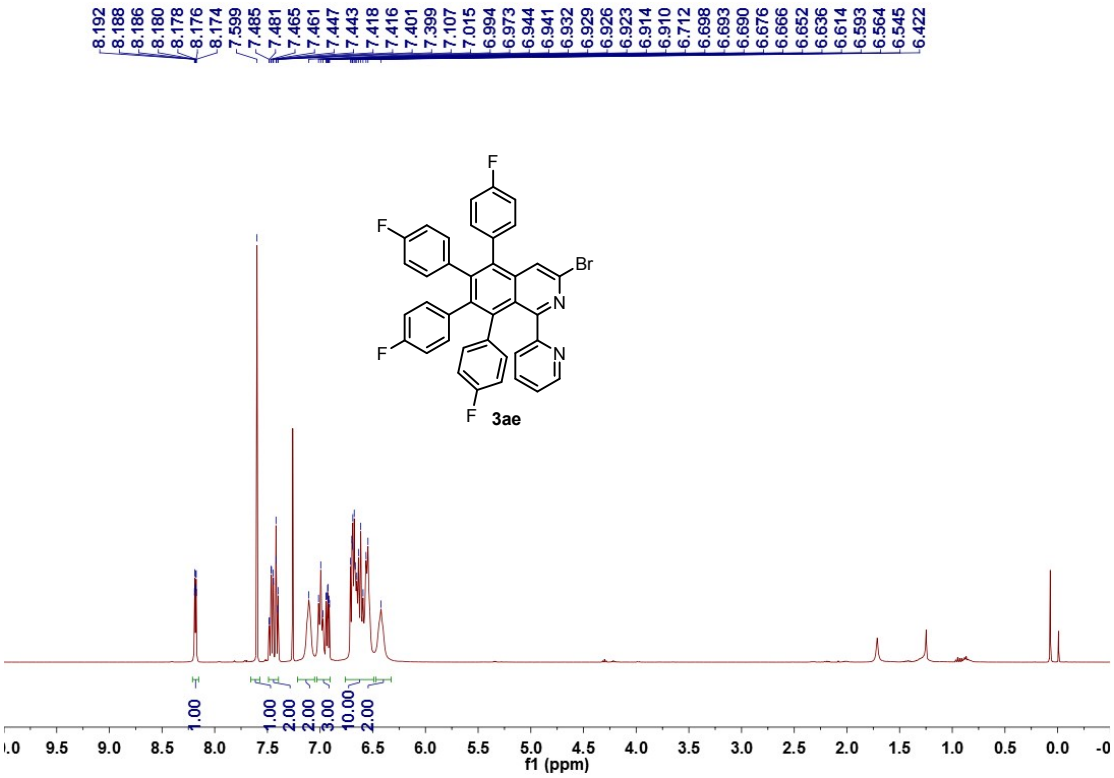
136.59
133.54
132.61
132.19
131.97
131.81
131.57
130.19
125.45
122.59
113.42
112.32
112.14
77.32
77.00
76.68
55.09
55.05
55.01
54.98
OMe
MeO
Br
N
MeO
N
MeO
3ad
f1 (ppm)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8.176
8.174
7.599
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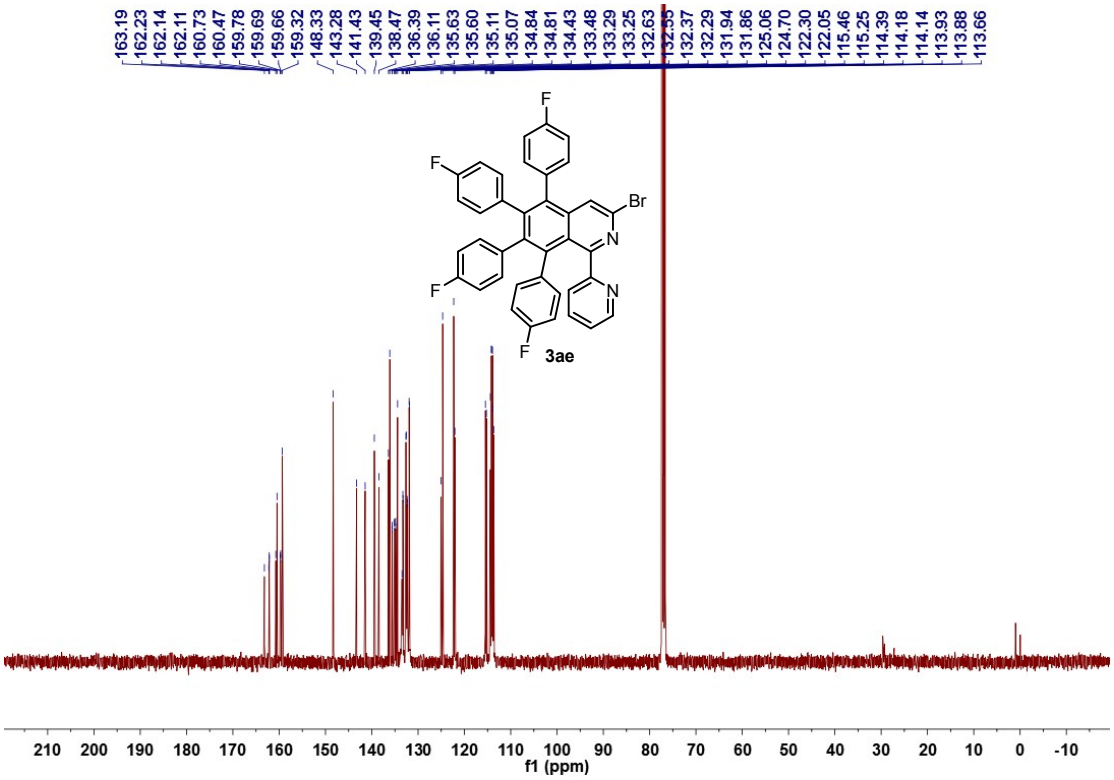
7.481
7.465
7.461
7.447
7.443
7.418
7.416
7.401
7.399
7.107
7.015
6.994
6.973
6.944
6.941
6.932
6.929
6.926
6.923
6.914
6.910
6.712
6.698
6.693
6.690
6.676
6.666
6.652
6.636
6.614
6.593
6.564
6.545
6.422
F
F
Br
N
F
N
F
3ae
1.00
1.00
2.00
2.00
3.00
10.00
2.00
f1 (ppm)


163.19
162.23
162.14
162.11
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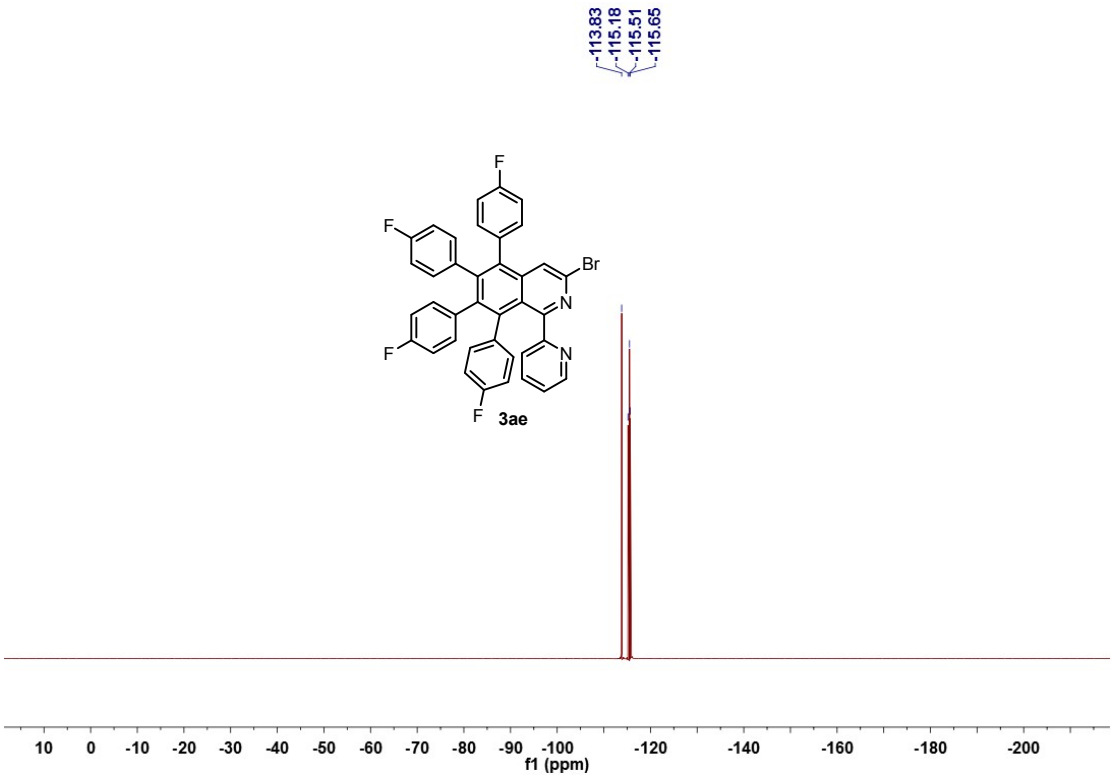
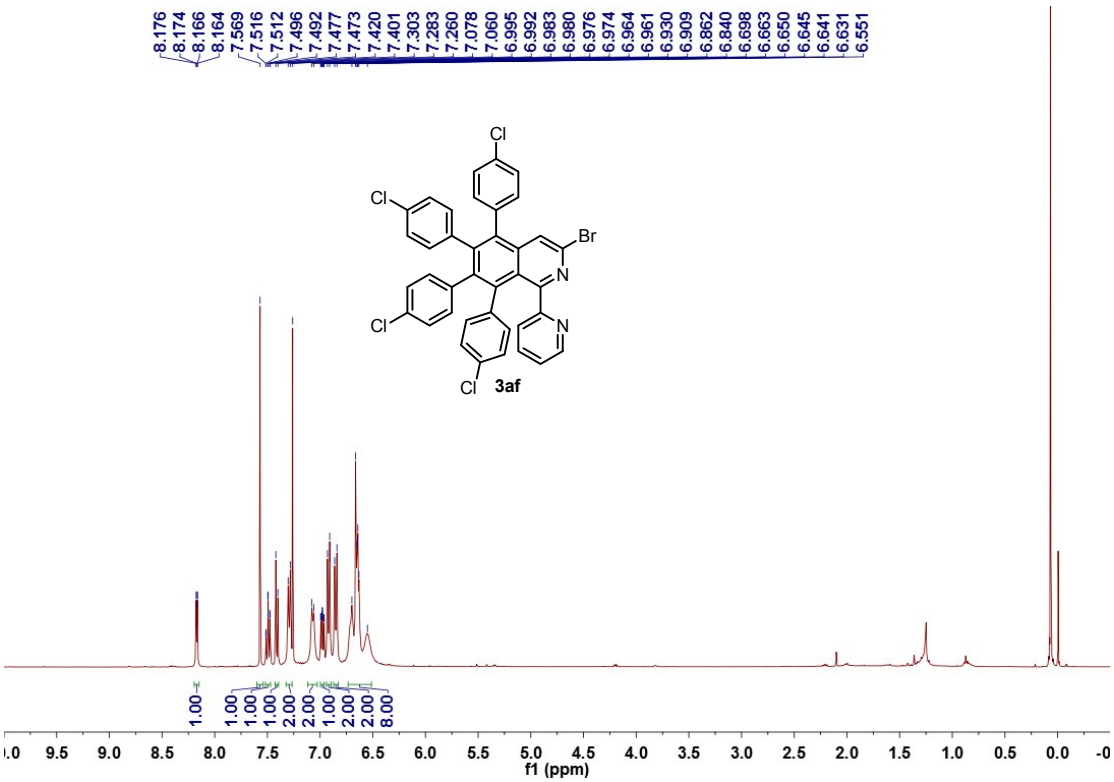
160.47
159.78
159.69
159.66
159.32
148.33
143.28
141.43
139.45
138.47
136.39
136.11
135.63
135.60
135.11
135.07
134.84
134.81
134.43
133.48
133.29
133.25
132.63
132.37
132.29
131.94
131.86
125.06
124.70
122.30
122.05
115.46
115.25
114.39
114.18
114.14
113.93
113.88
113.66
F
F
Br
N
F
N
F
3ae
f1 (ppm)


-113.83
-115.18
-115.51
-115.65
F
F
Br
N
F
N
F
3ae
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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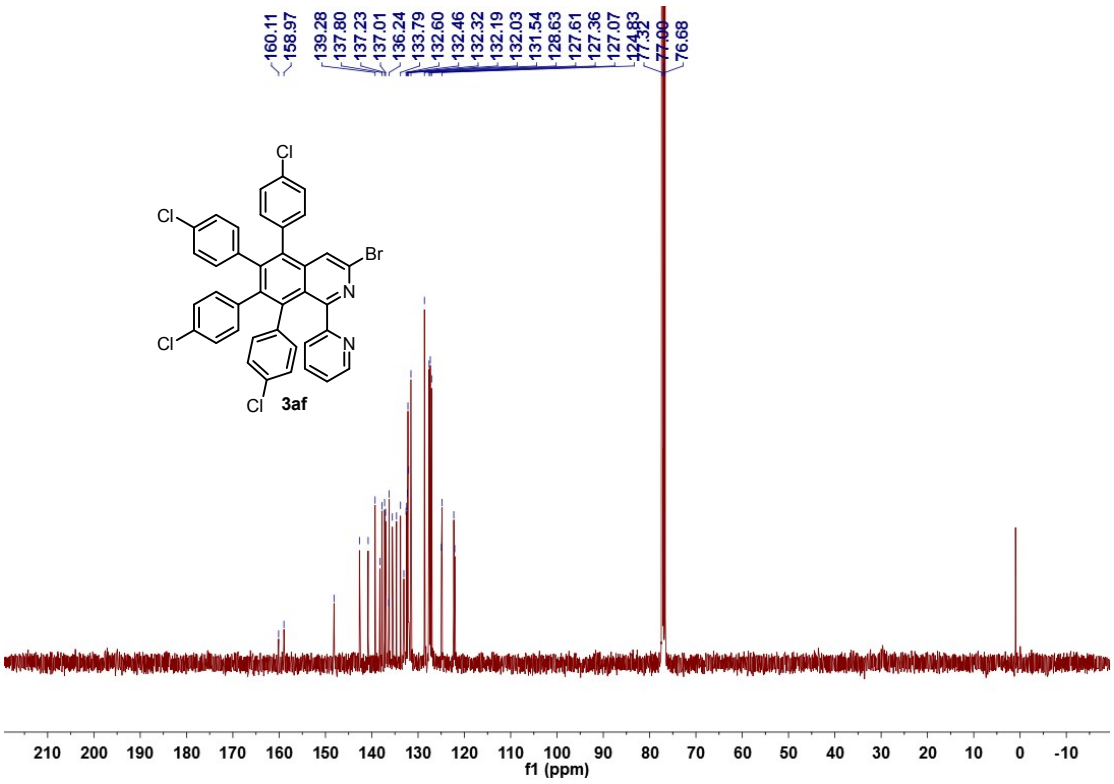
7.512
7.496
7.492
7.477
7.473
7.420
7.401
7.303
7.283
7.260
7.078
7.060
6.995
6.992
6.983
6.980
6.976
6.974
6.964
6.961
6.930
6.909
6.862
6.840
6.698
6.663
6.650
6.645
6.641
6.631
6.551
Cl
Cl
Br
N
Cl
N
Cl
3af
1.00
1.00
1.00
1.00
2.00
2.00
1.00
2.00
2.00
8.00
f1 (ppm)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137.01
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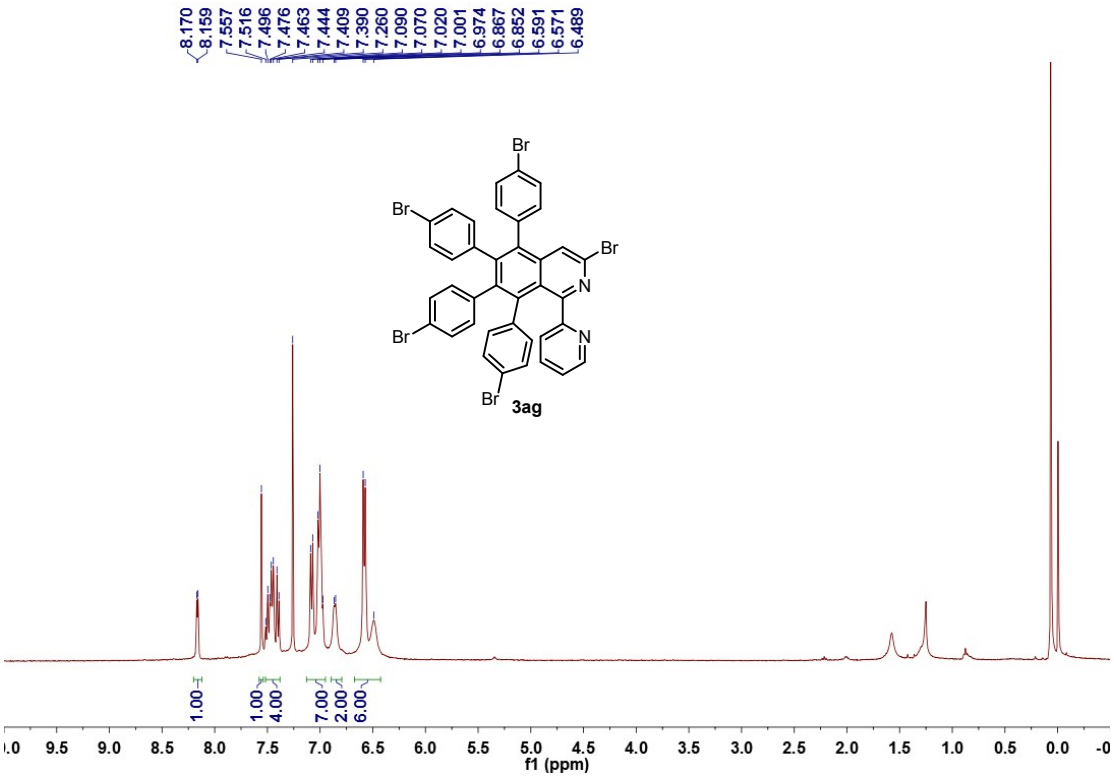
132.46
132.32
132.19
132.03
131.54
128.63
127.61
127.36
127.07
124.83
77.32
77.00
76.68
Cl
Cl
Br
N
Cl
N
Cl
3af
f1 (ppm)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7.476
7.463
7.444
7.409
7.390
7.260
7.090
7.070
7.020
7.001
6.974
6.867
6.852
6.591
6.571
6.489
Br
Br
Br
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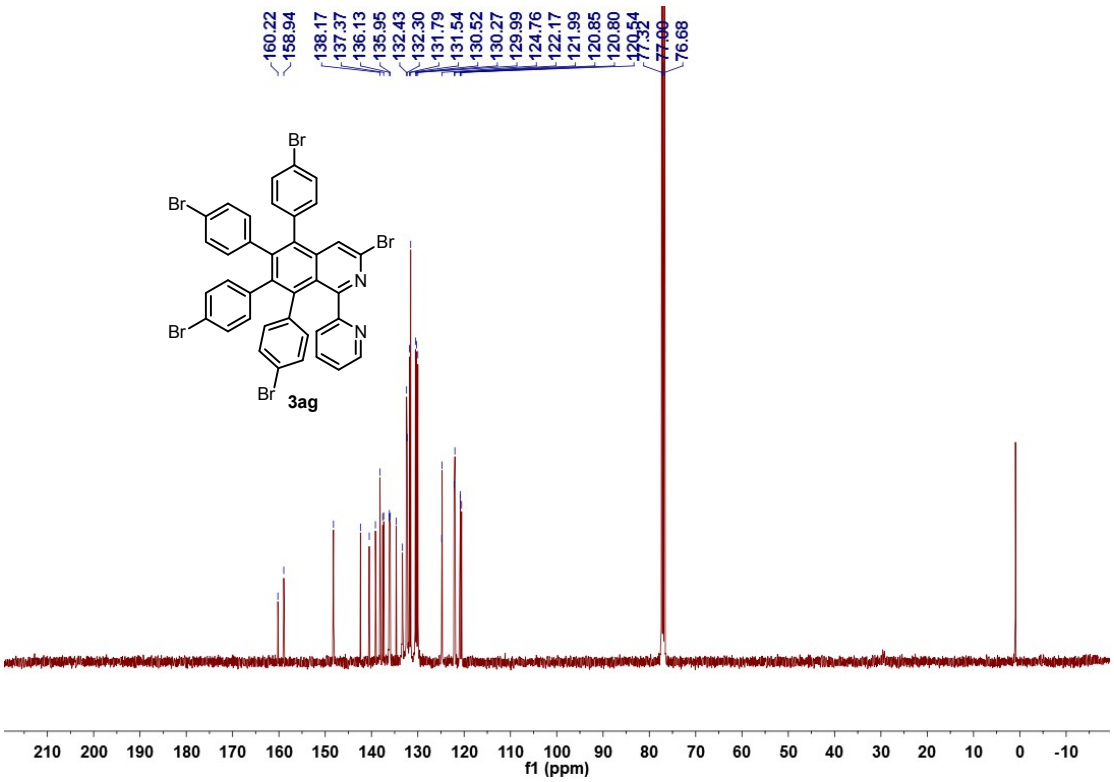
Br
N
Br
3ag
1.00
1.00
4.00
7.00
2.00
6.00
f1 (ppm)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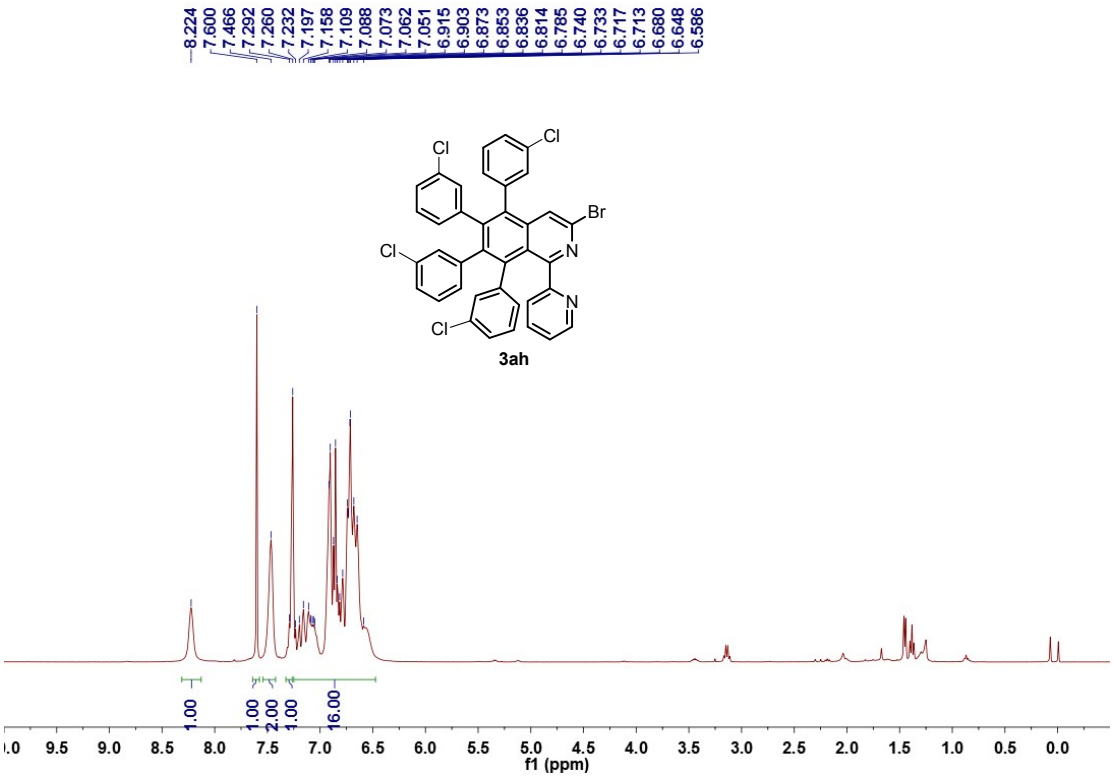
136.13
135.95
132.43
132.30
131.79
131.54
130.52
130.27
129.99
124.76
122.17
121.99
120.85
120.80
77.00
76.68
Br
Br
Br
N
Br
N
Br
3ag
f1 (ppm)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7.051
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6.903
6.873
6.853
6.836
6.814
6.785
6.740
6.733
6.717
6.713
6.680
6.648
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Cl
Cl
Br
Cl
N
N
Cl
3ah
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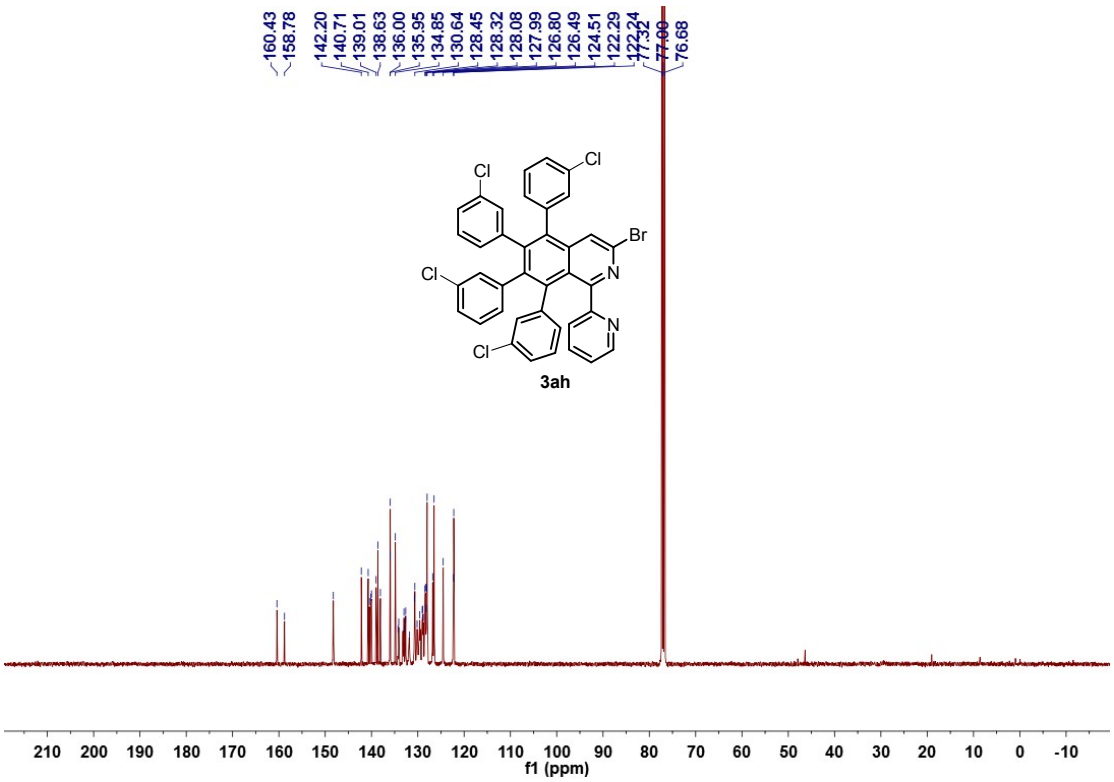
1.00
2.00
1.00
16.00
f1 (ppm)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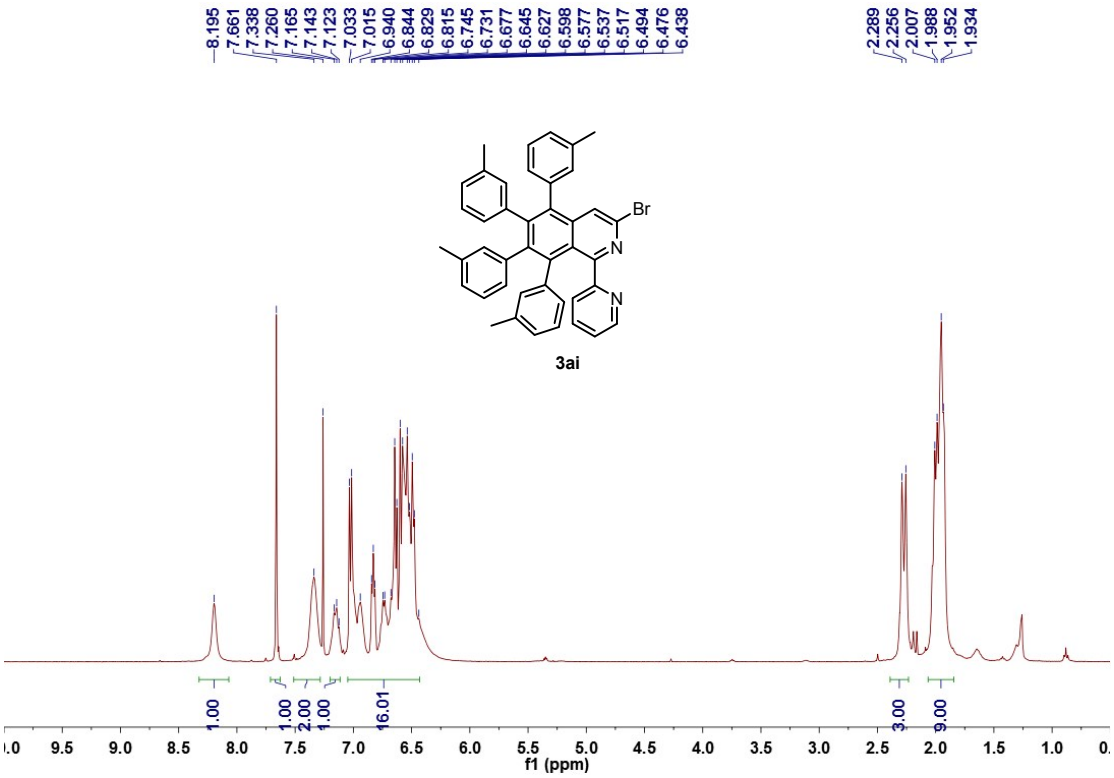
135.95
134.85
130.64
128.45
128.32
128.08
127.99
126.80
126.49
124.51
122.29
122.24
77.00
76.68
Cl
Cl
Br
Cl
N
N
Cl
3ah
f1 (ppm)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6.829
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6.745
6.731
6.677
6.645
6.627
6.598
6.577
6.537
6.517
6.494
6.476
6.438
2.289
2.256
2.007
1.988
1.952
1.934
Br
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N
3ai
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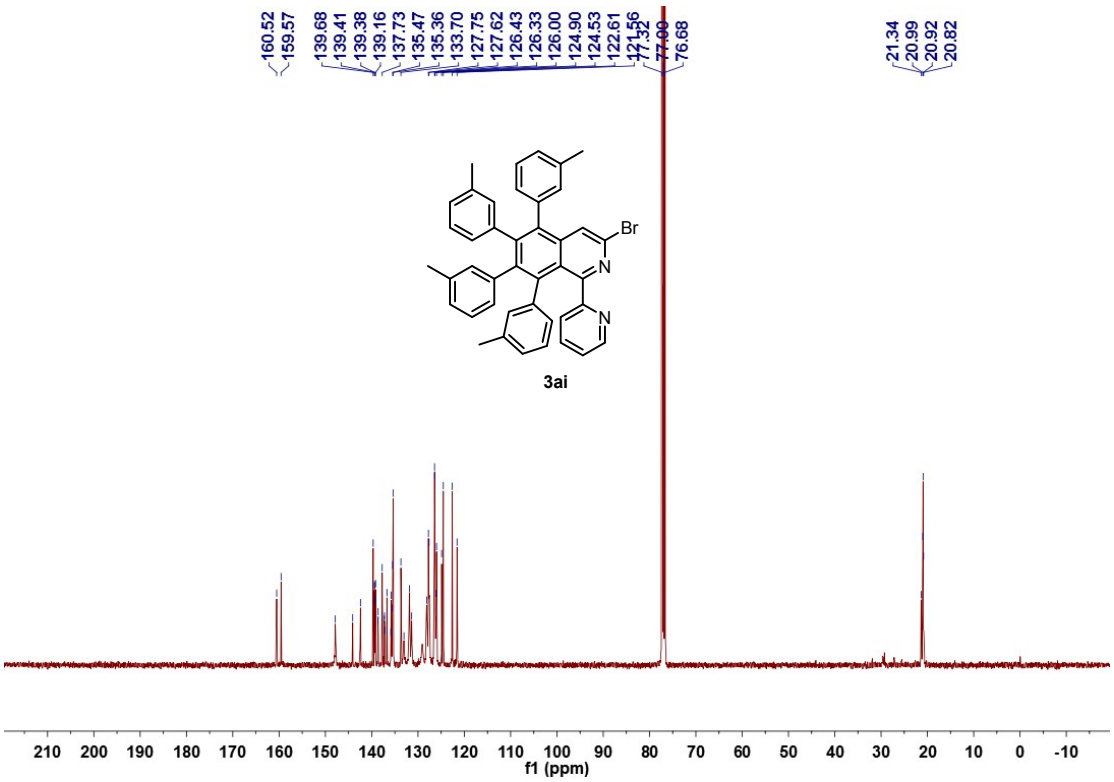
1.00
2.00
1.00
16.01
3.00
9.00
f1 (ppm)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133.70
127.75
127.62
126.43
126.33
126.00
124.90
124.53
122.61
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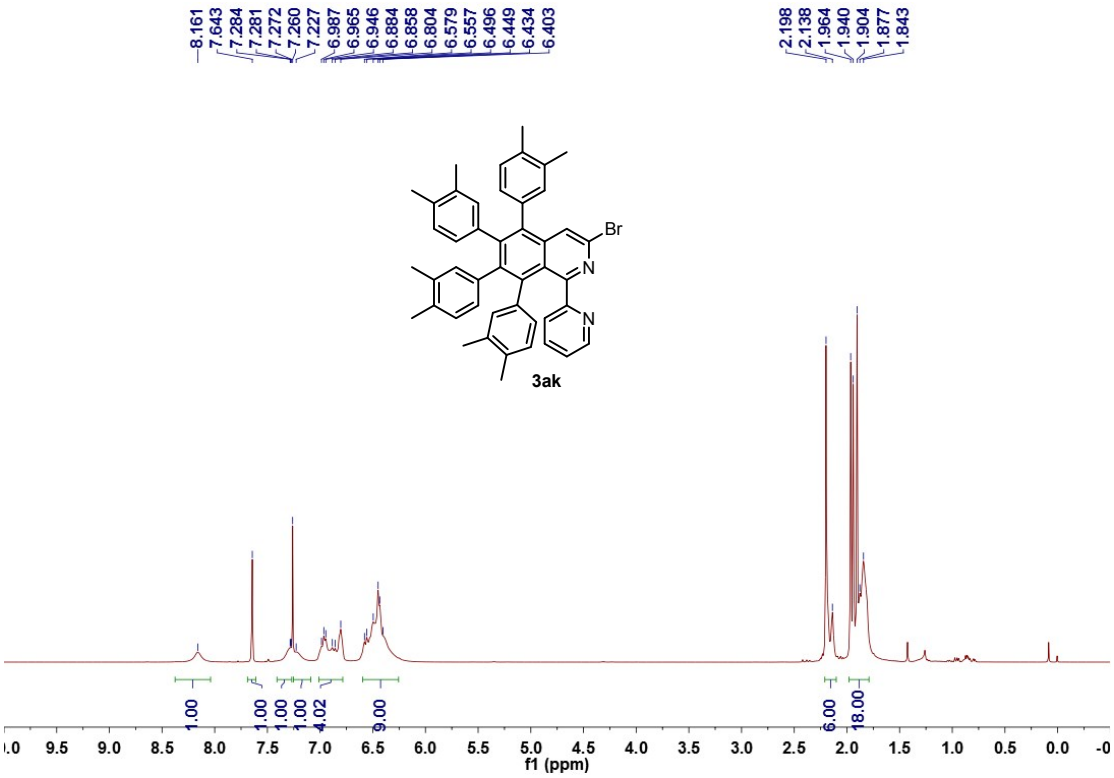
77.00
76.68
21.34
20.99
20.92
20.82
Br
N
N
3ai
f1 (ppm)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6.557
6.496
6.449
6.434
6.403
2.198
2.138
1.964
1.940
1.904
1.877
1.843
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1.00
1.00
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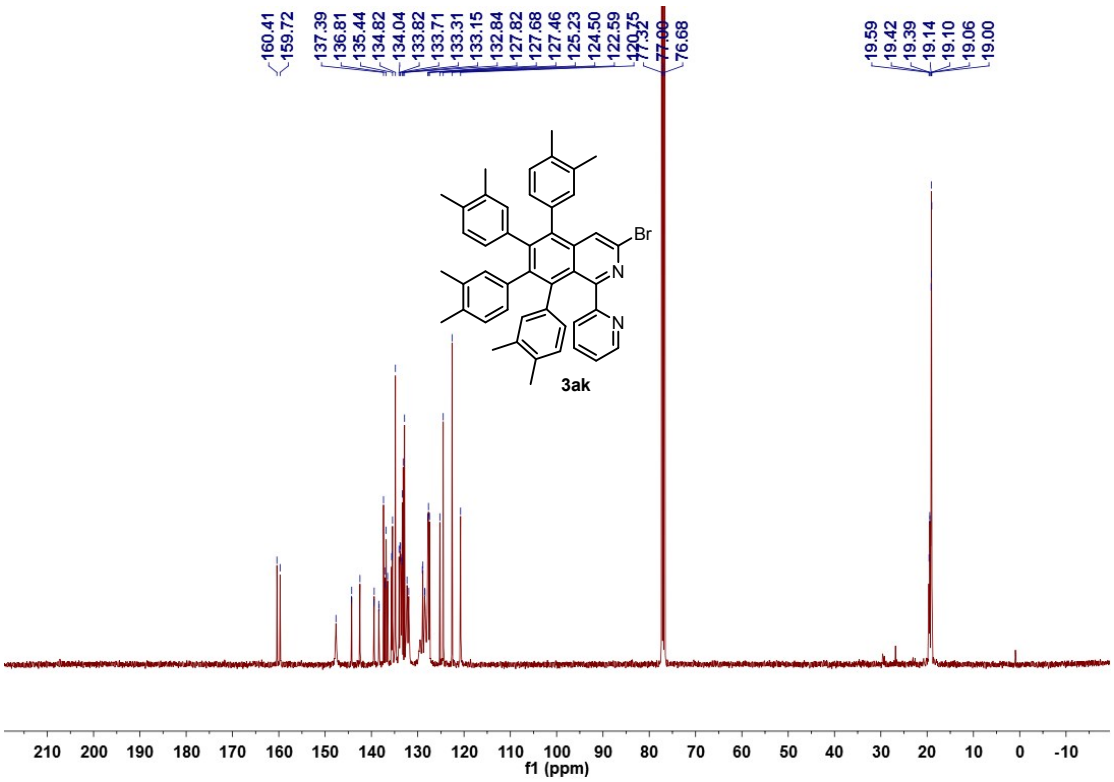
9.00
6.00
18.00
f1 (ppm)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132.84
127.82
127.68
127.46
125.23
124.50
122.59
120.75
77.32
77.00
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19.39
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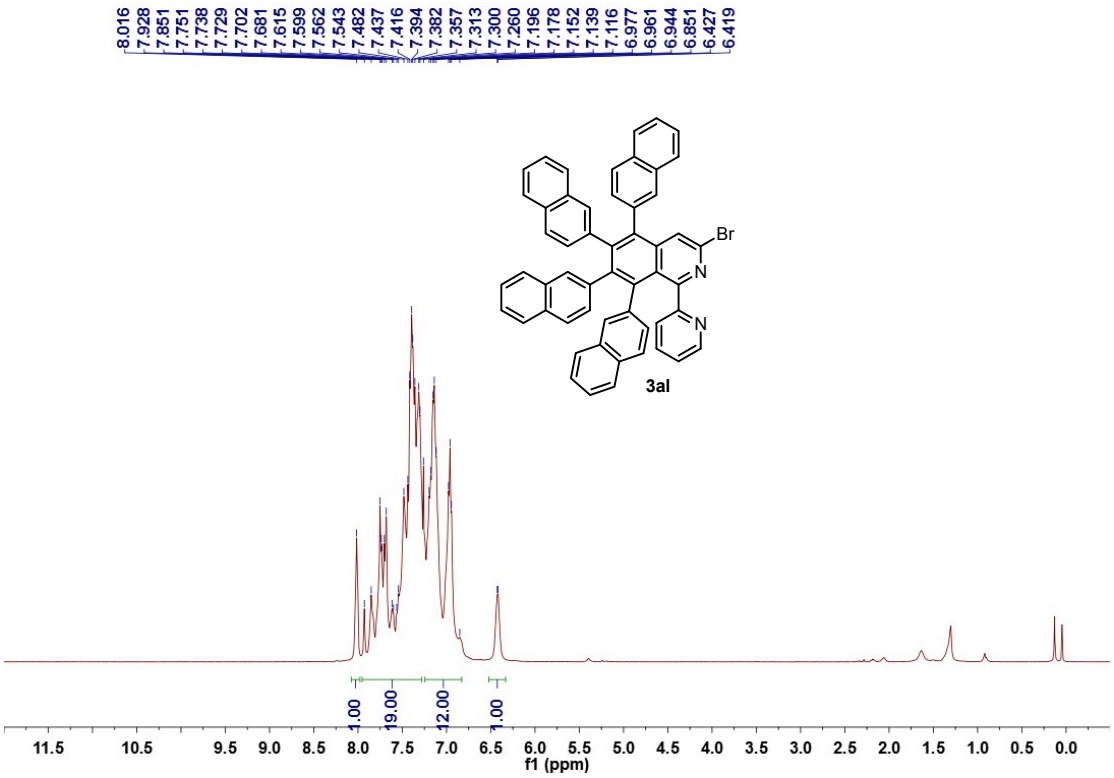
19.10
19.06
19.00
Br
N
N
3ak
f1 (ppm)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7.599
7.562
7.543
7.482
7.437
7.416
7.394
7.382
7.357
7.313
7.300
7.260
7.196
7.178
7.152
7.139
7.116
6.977
6.961
6.944
6.851
6.427
6.419
Br
N
N
3al
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19.00
12.00
1.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
2.0
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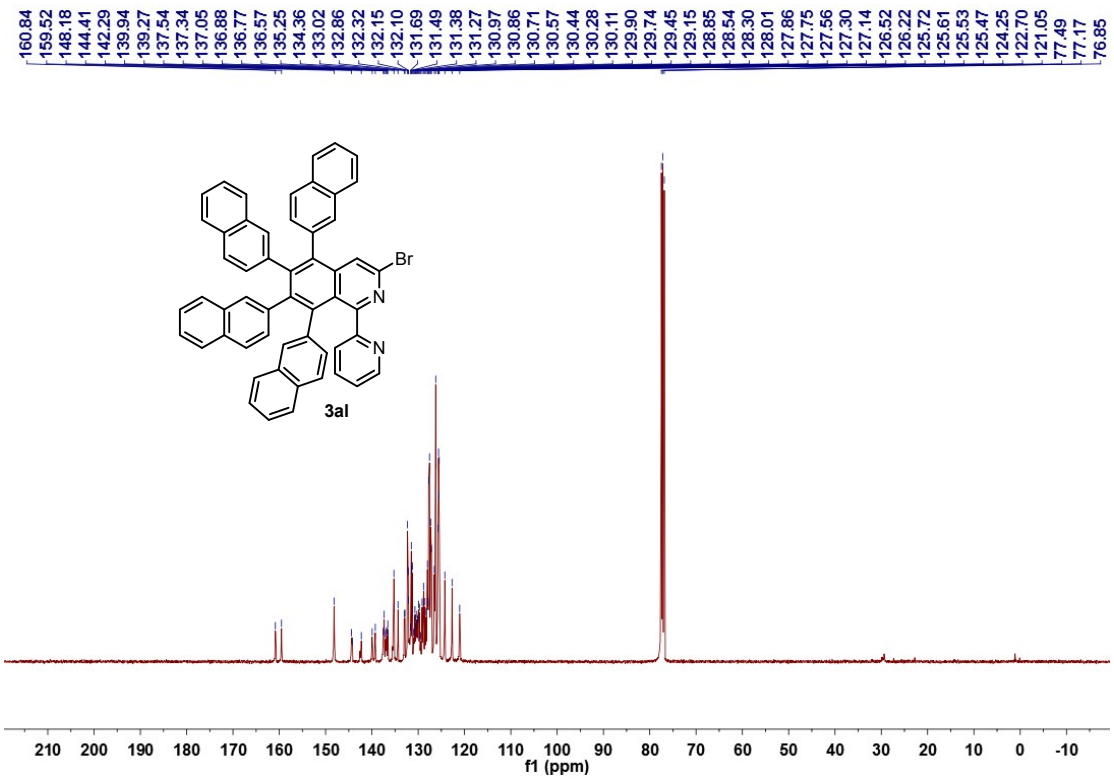
0.0
f1 (ppm)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133.02
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132.10
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130.97
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130.71
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130.11
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129.45
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128.85
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128.30
128.01
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127.75
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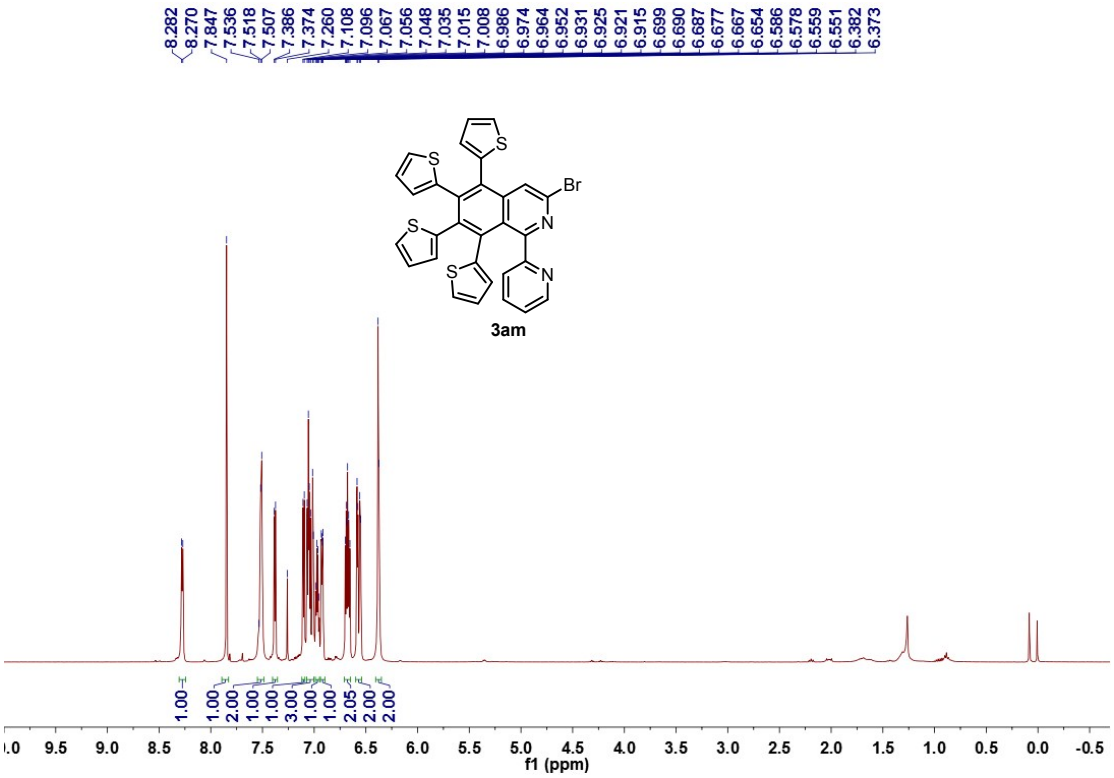
127.30
127.14
126.52
126.22
125.72
125.61
125.53
125.47
124.25
122.70
121.05
77.49
77.17
76.85
Br
N
N
3al
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.374
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7.108
7.096
7.067
7.056
7.048
7.035
7.015
7.008
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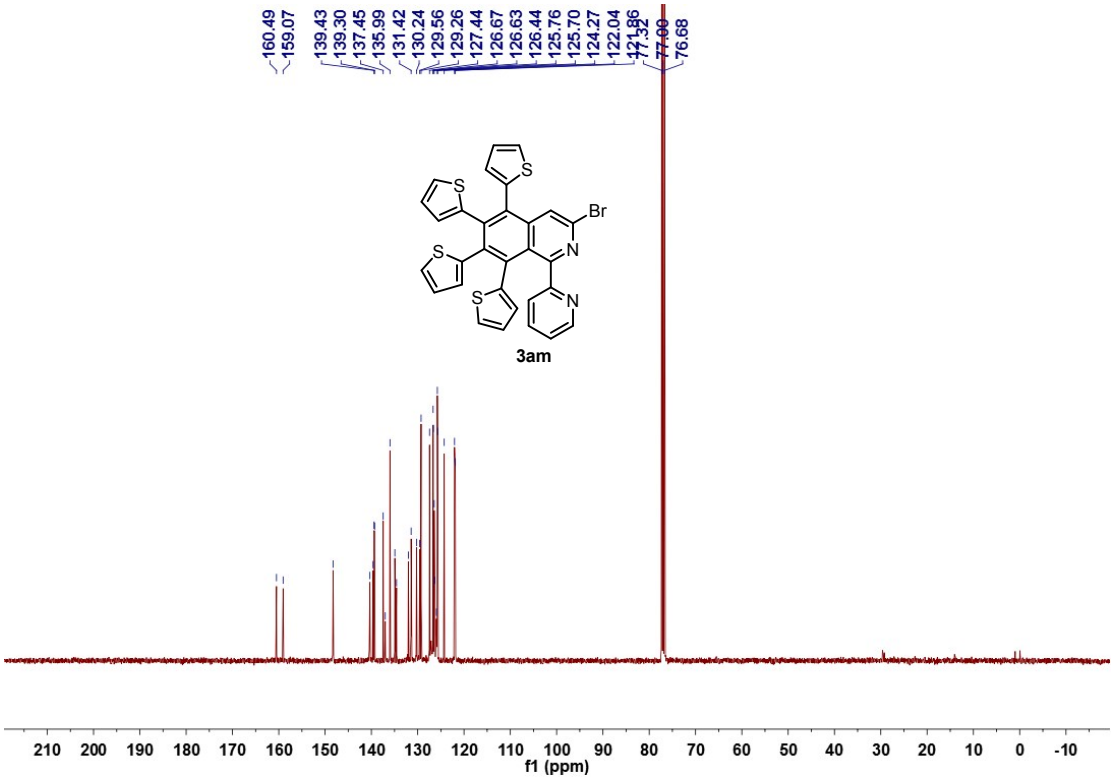
6.931
6.925
6.921
6.915
6.699
6.690
6.687
6.677
6.667
6.654
6.586
6.578
6.559
6.551
6.382
6.373
S
S
S
S
Br
N
N
3am
1.00
1.00
2.00
1.00
1.00
3.00
1.00
1.00
2.05
2.00
2.00
f1 (ppm)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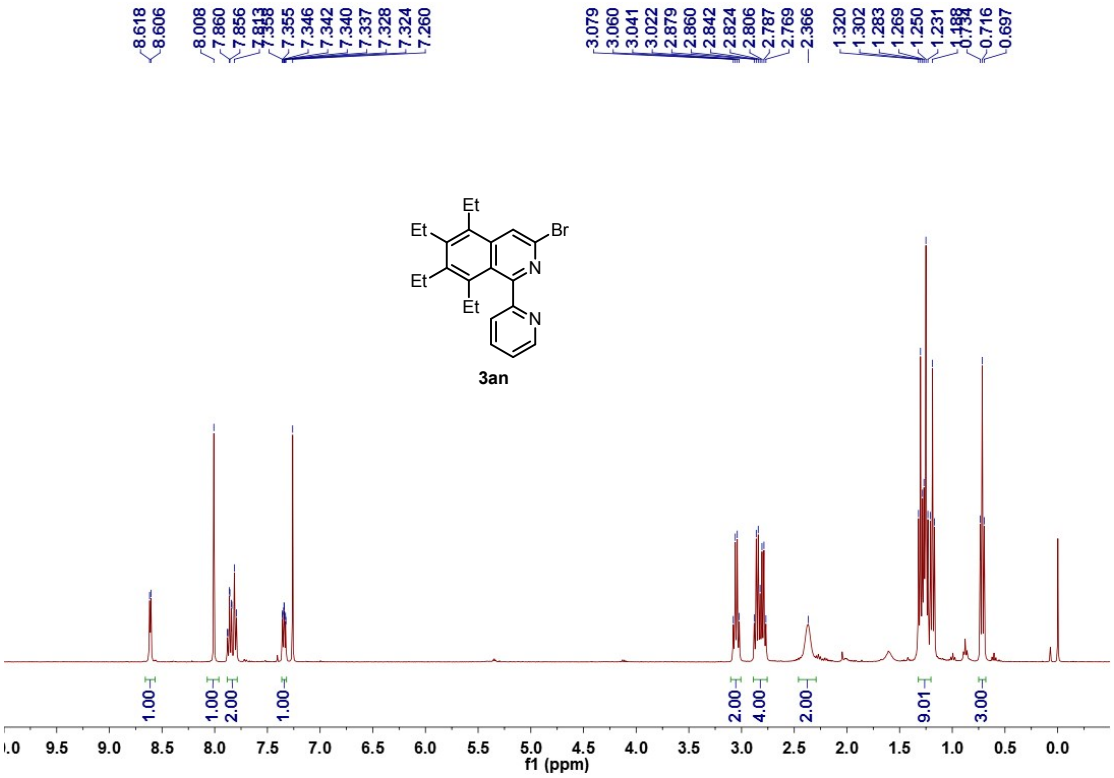
126.63
126.44
125.76
125.70
124.27
122.04
121.86
77.32
77.00
76.68
S
S
S
S
Br
N
N
3am
f1 (ppm)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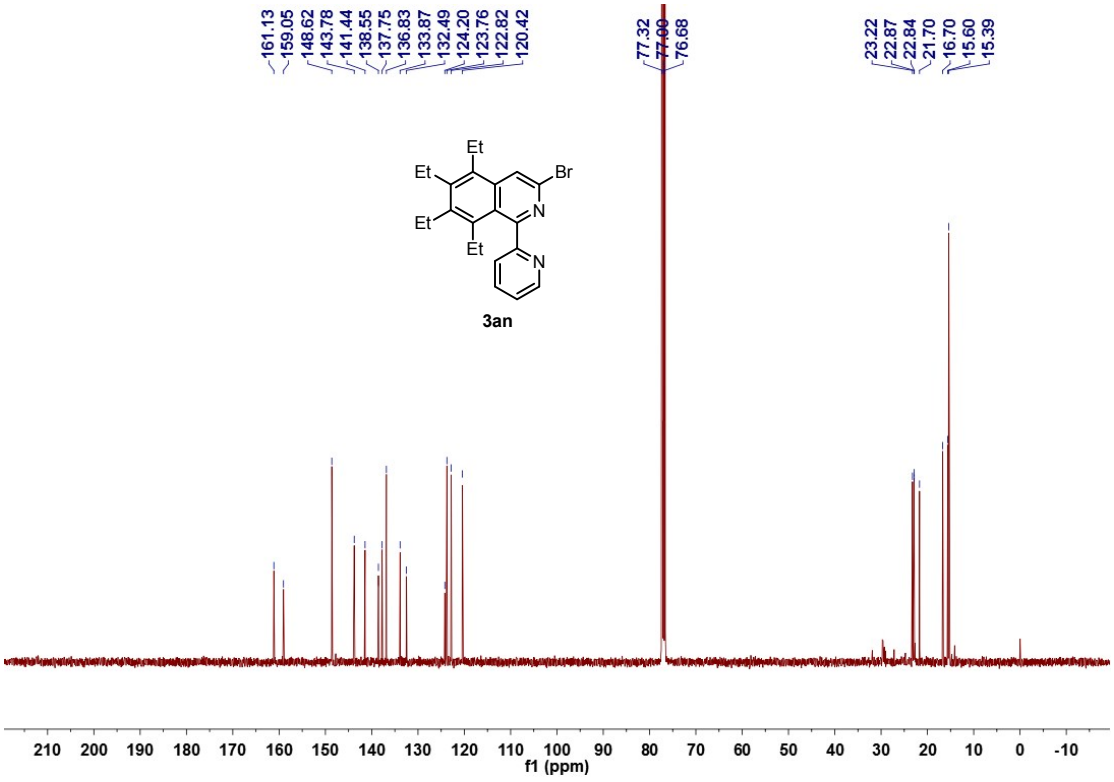
8.008
7.860
7.856
7.355
7.346
7.342
7.340
7.337
7.328
7.324
7.260
3.079
3.060
3.041
3.022
2.879
2.860
2.842
2.824
2.806
2.787
2.769
2.366
1.320
1.302
1.283
1.269
1.250
1.231
0.716
0.697
Et
Et
Et
Et
Br
N
N
3an
1.00
1.00
2.00
1.00
2.00
4.00
2.00
9.01
3.00
f1 (ppm)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148.62
143.78
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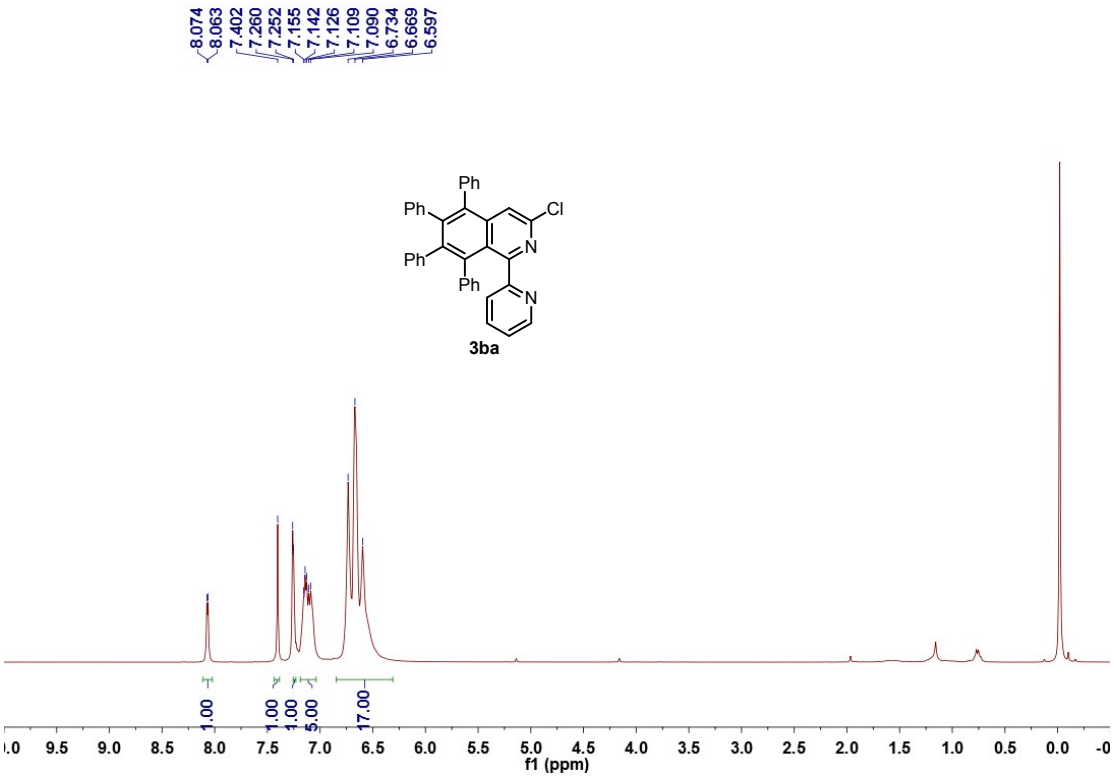
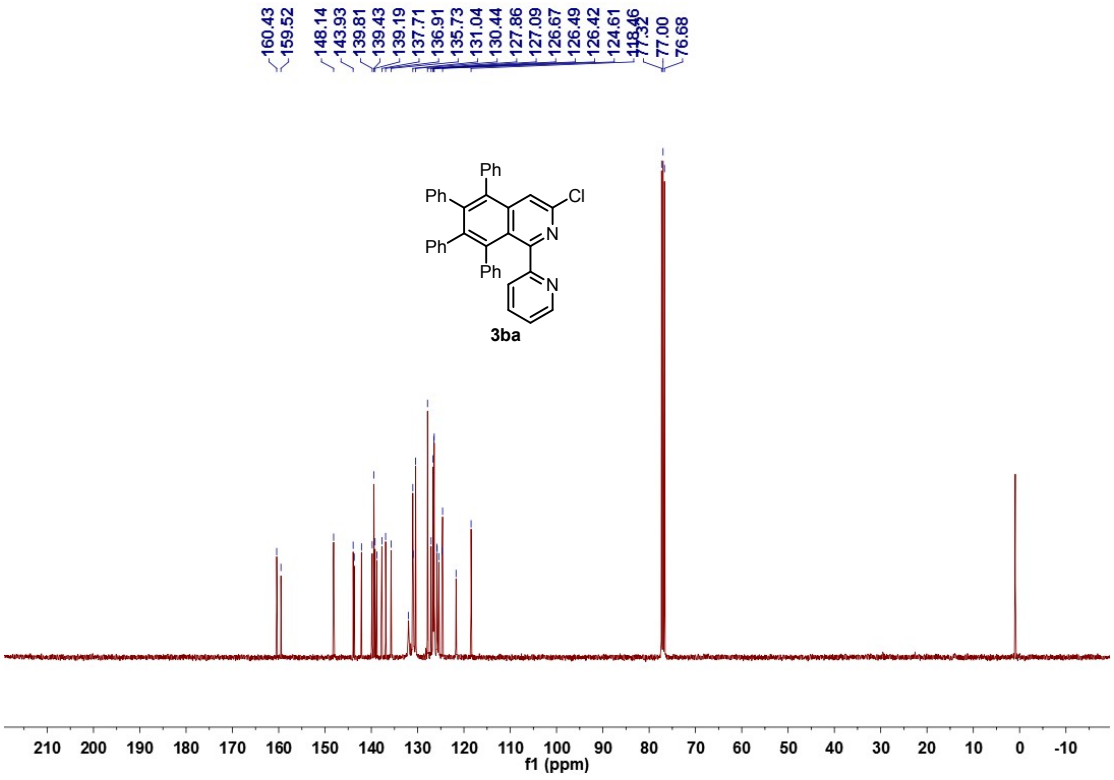
138.55
137.75
136.83
133.87
132.49
124.20
123.76
122.82
120.42
77.32
77.00
76.68
23.22
22.87
22.84
21.70
16.70
15.60
15.39
Et
Et
Et
Et
Br
N
N
3an
f1 (ppm)


8.074
8.063
7.402
7.260
7.252
7.155
7.142
7.126
7.109
7.090
6.734
6.669
6.597
Ph
Ph
Cl
Ph
N
Ph
N
3ba
1.00
1.00
1.00
5.00
17.00
f1 (ppm)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159.52
148.14
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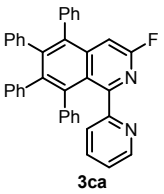
139.81
139.43
139.19
137.71
136.91
135.73
131.04
130.44
127.86
127.09
126.67
126.49
126.42
124.61
77.00
76.68
Ph
Ph
Cl
Ph
N
Ph
N
3ba
f1 (ppm)

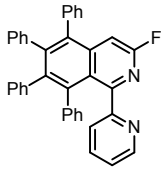

8.195
8.192
8.191
8.188
8.182
8.180
8.179
8.176
7.398
7.394
7.378
7.374
7.360
7.356
7.348
7.345
7.342
7.329
7.326
7.323
7.293
7.277
7.260
7.248
7.244
7.240
7.226
7.208
7.204
7.186
7.070
7.066
6.864
6.860
6.856
6.852
6.848
6.842
6.834
6.830
6.794
6.786
6.772
6.709
6.703


Ph
Ph
F
Ph
N
Ph
N

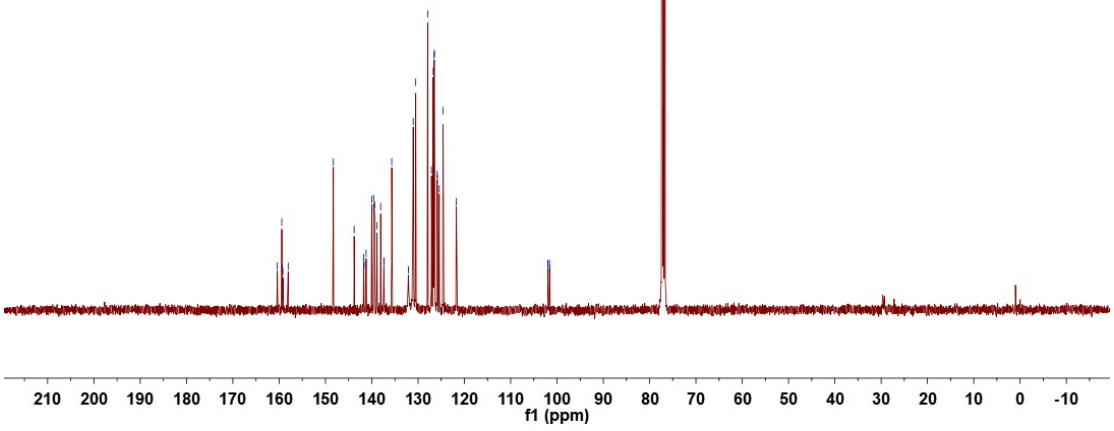
3ca

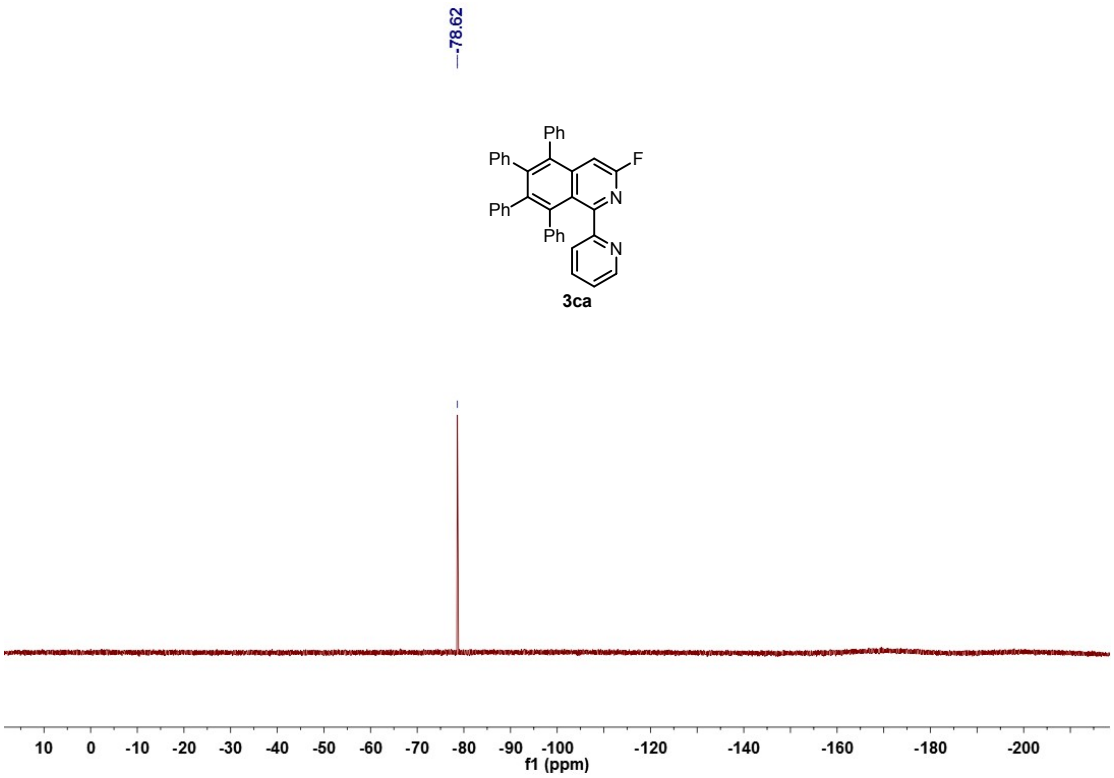
1.00
5.01
3.00
1.00
16.00
f1 (ppm)

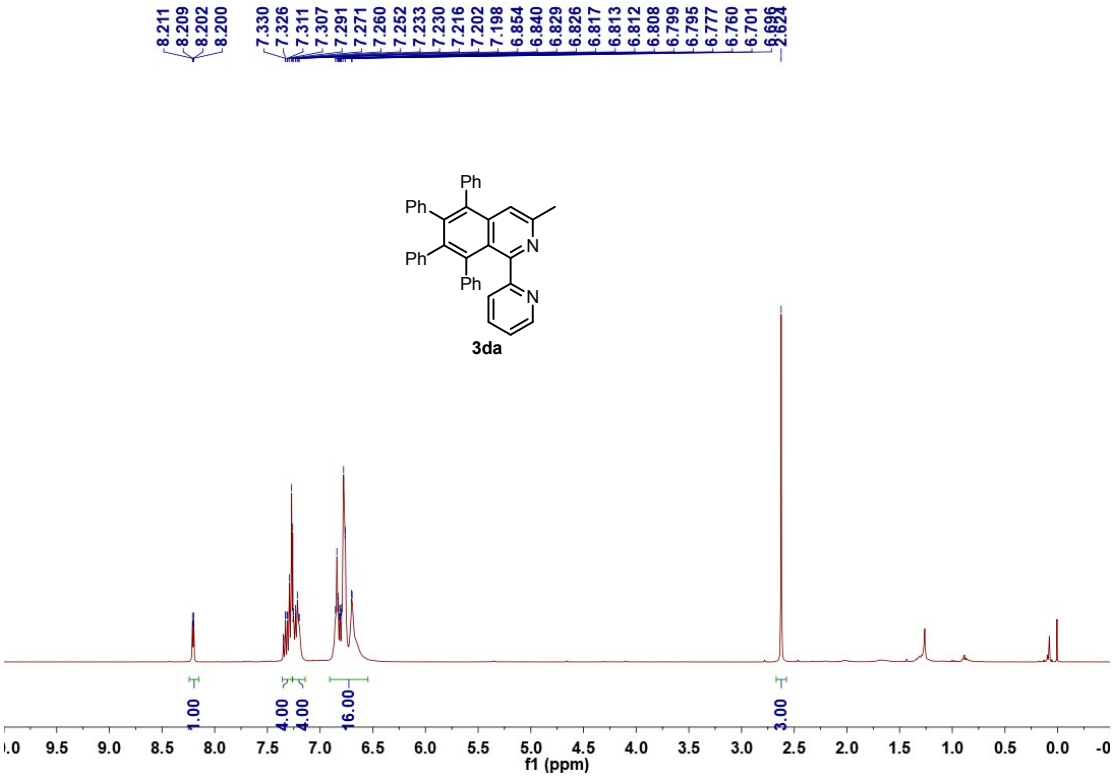

160.39
159.44
159.34
159.20
158.05
148.29
135.69
131.05
130.51
127.94
127.11
126.72
126.55
126.47
101.95
101.61
101.59
77.32
77.00
76.68


Ph
Ph
F
Ph
N
Ph
N

3ca


f1 (ppm)


-78.62
Ph
Ph
Ph
Ph
F
N
N
3ca
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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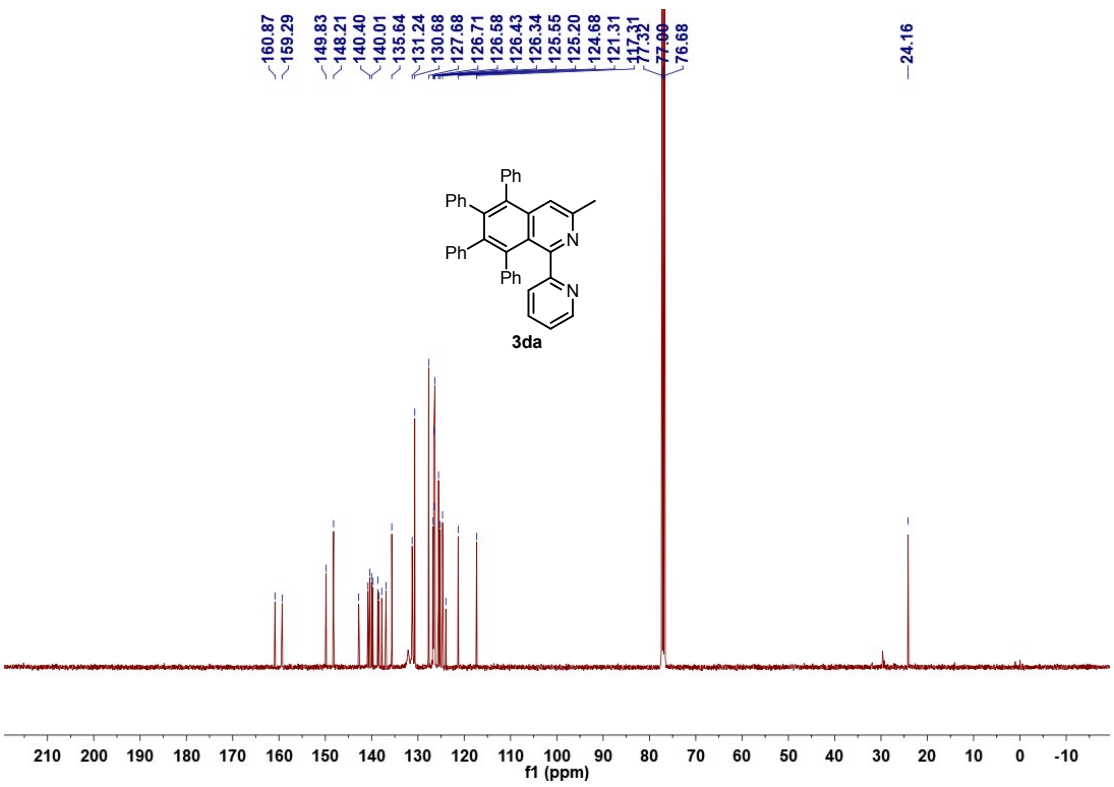
8.209
8.202
8.200
7.330
7.326
7.311
7.307
7.291
7.271
7.260
7.252
7.233
7.230
7.216
7.202
7.198
6.854
6.840
6.829
6.826
6.817
6.813
6.812
6.808
6.799
6.795
6.777
6.760
6.701
6.686
2.824
Ph
Ph
Ph
Ph
N
N
3da
1.00
4.00
4.00
16.00
3.00
f1 (ppm)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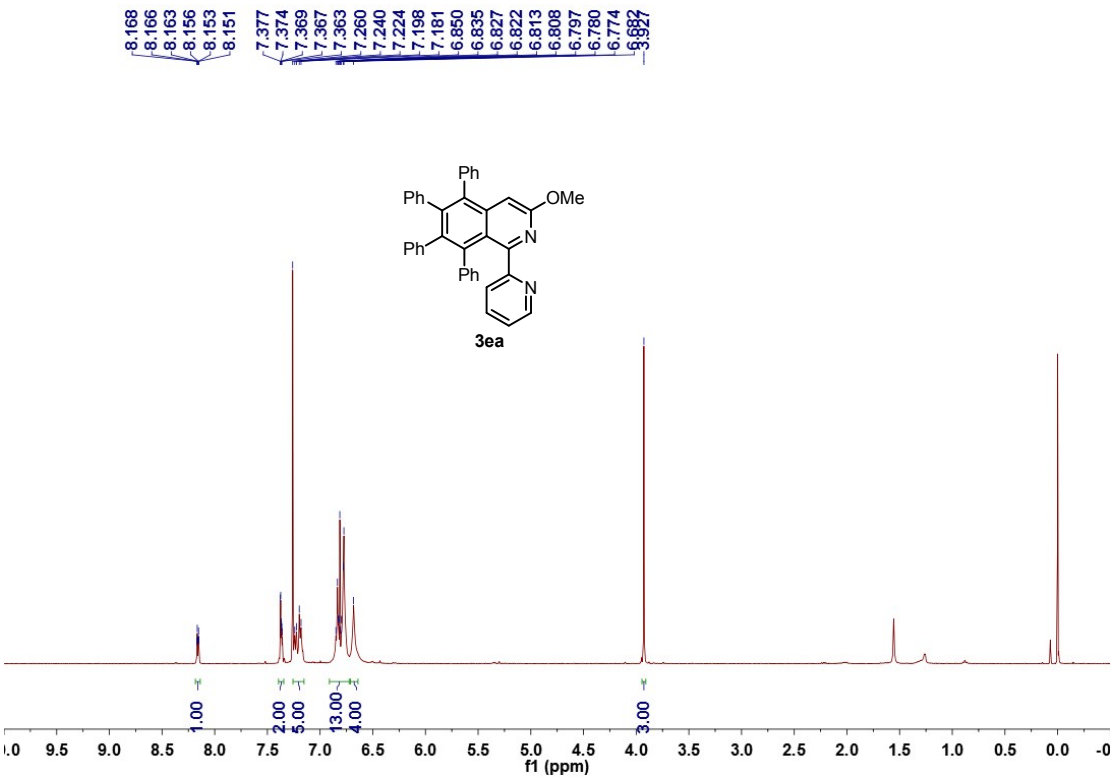
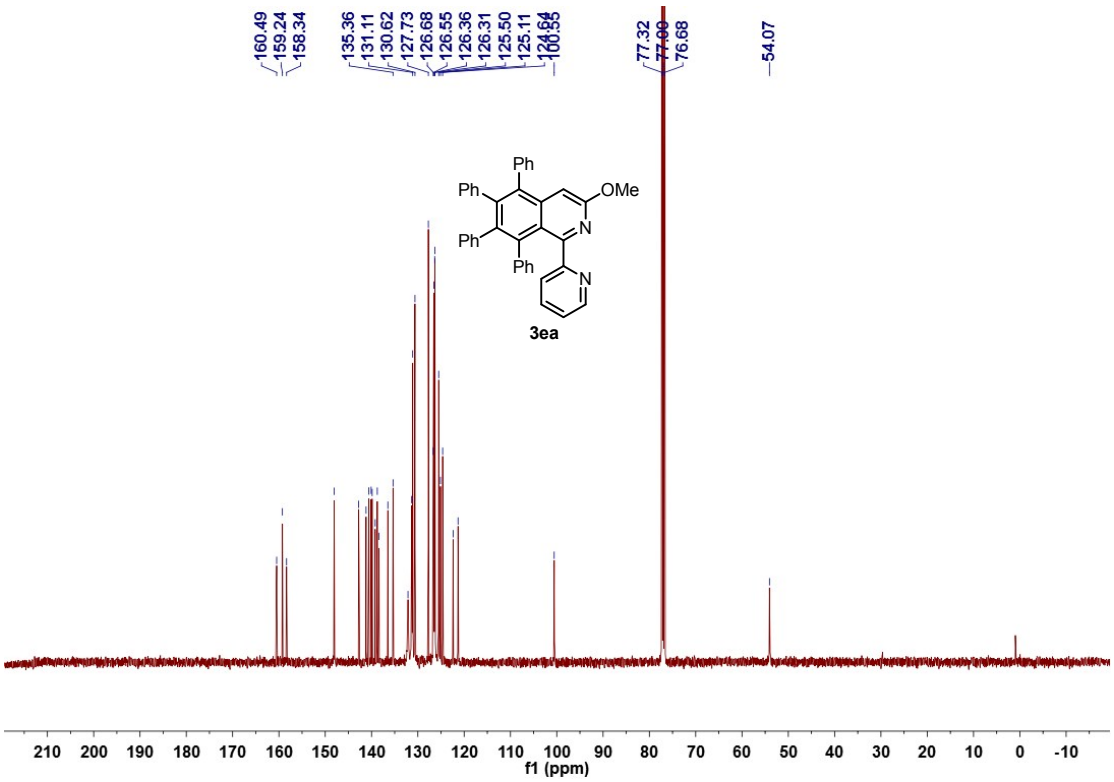
140.40
140.01
135.64
131.24
130.68
127.68
126.71
126.58
126.43
126.34
125.55
125.20
124.68
121.31
117.31
77.32
77.00
76.68
24.16
Ph
Ph
Ph
Ph
N
N
3da
f1 (ppm)


8.168
8.166
8.163
8.156
8.153
8.151
7.377
7.374
7.369
7.367
7.363
7.260
7.240
7.224
7.198
7.181
6.850
6.835
6.827
6.822
6.813
6.808
6.797
6.780
6.774
3.927
Ph
Ph
Ph
Ph
OMe
N
N
3ea
1.00
2.00
5.00
13.00
4.00
3.00
f1 (ppm)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158.34
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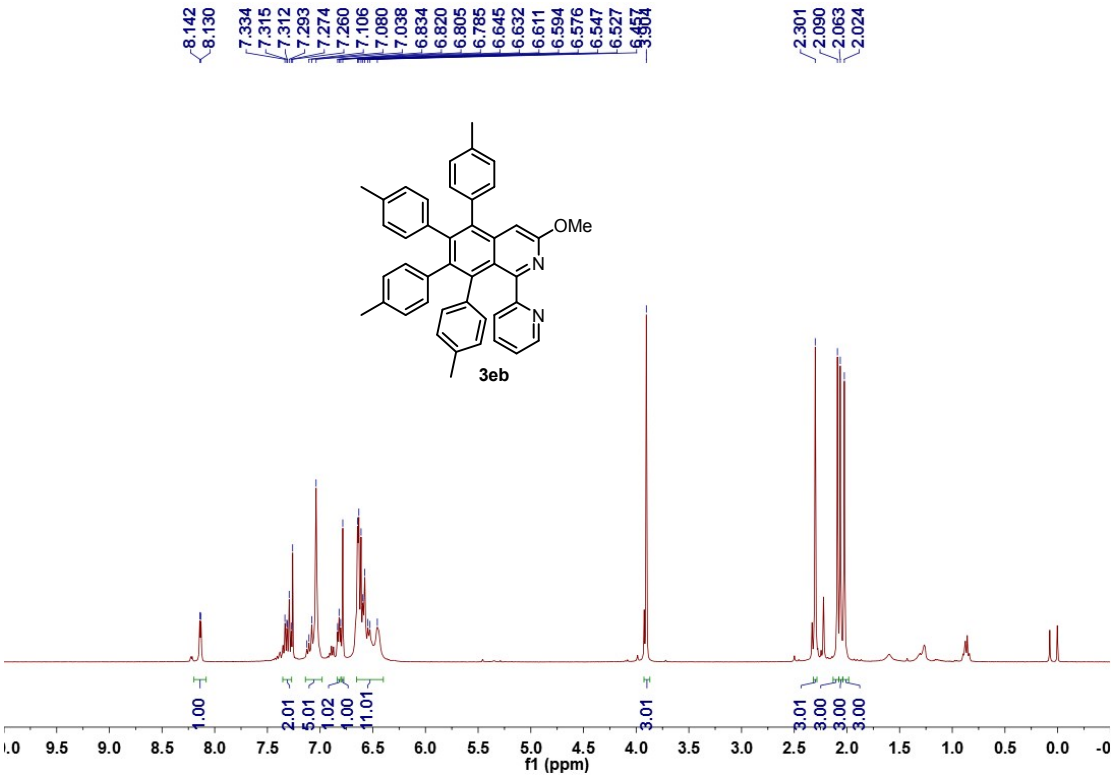
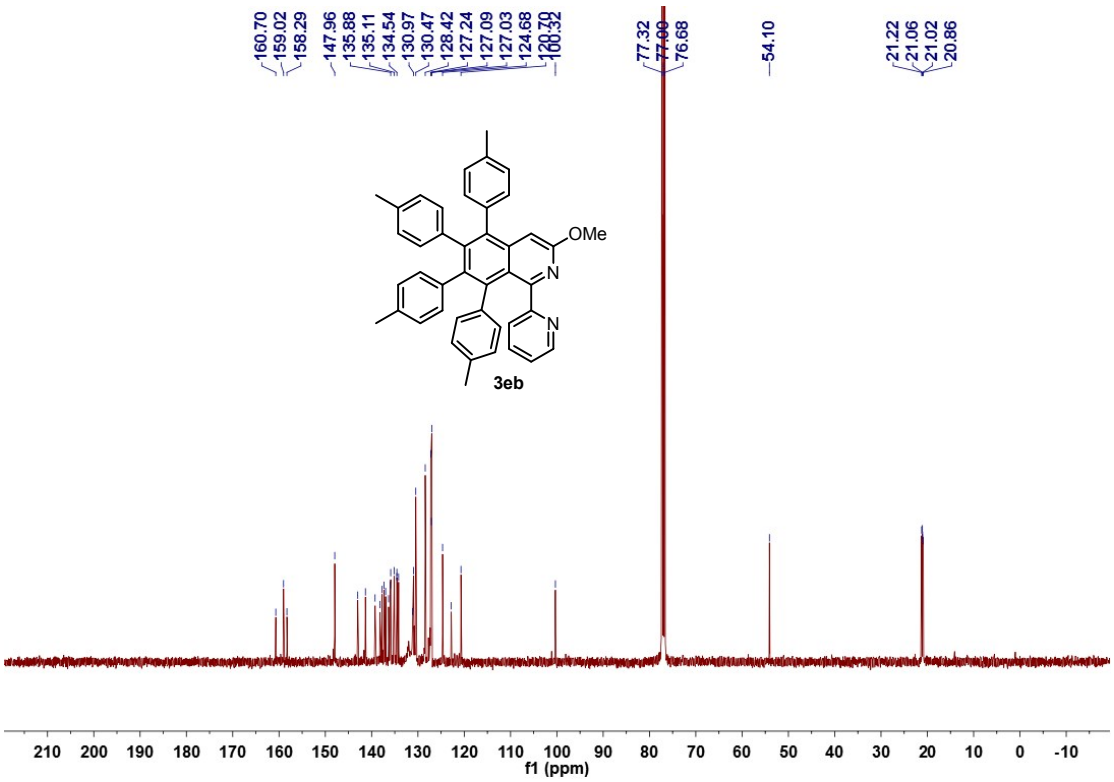
131.11
130.62
127.73
126.68
126.55
126.36
126.31
125.50
125.11
77.32
77.00
76.68
54.07
Ph
Ph
Ph
Ph
OMe
N
N
3ea
f1 (ppm)


8.142
8.130
7.334
7.315
7.312
7.293
7.274
7.260
7.106
7.080
7.038
6.834
6.820
6.805
6.785
6.645
6.632
6.611
6.594
6.576
6.547
6.527
3.904
2.301
2.090
2.063
2.024
OMe
N
N
3eb
1.00
2.01
5.01
1.02
1.00
11.01
3.01
3.01
3.00
3.00
3.00
f1 (ppm)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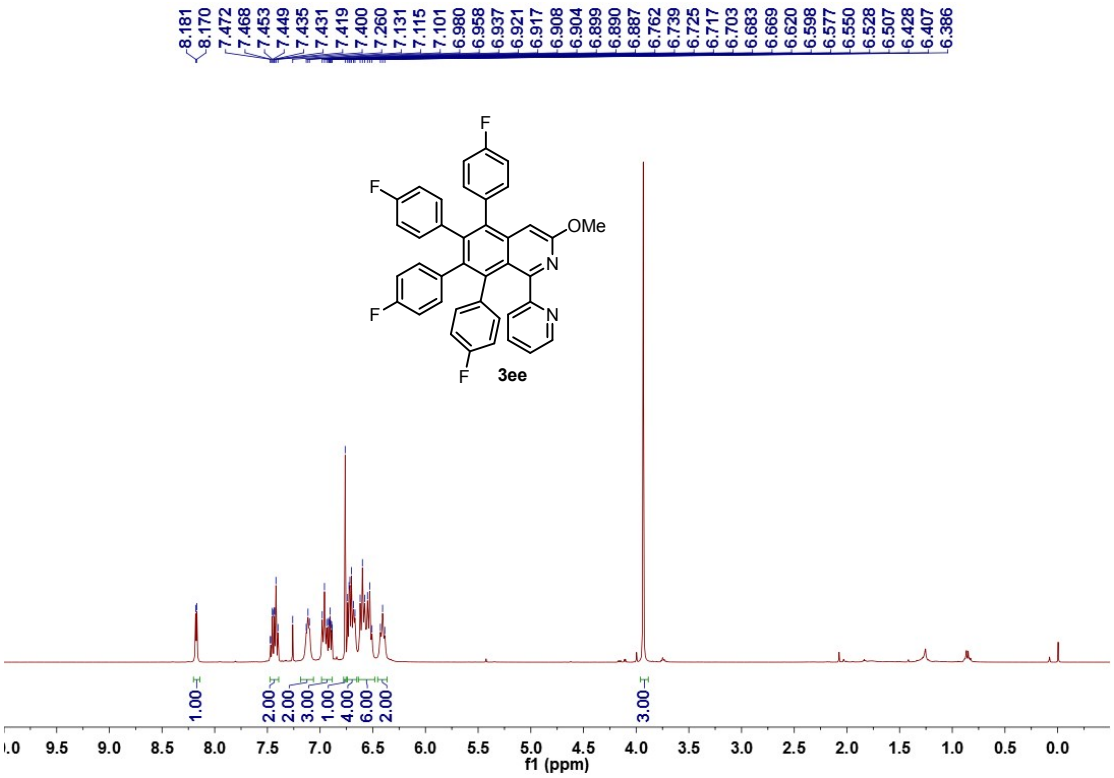
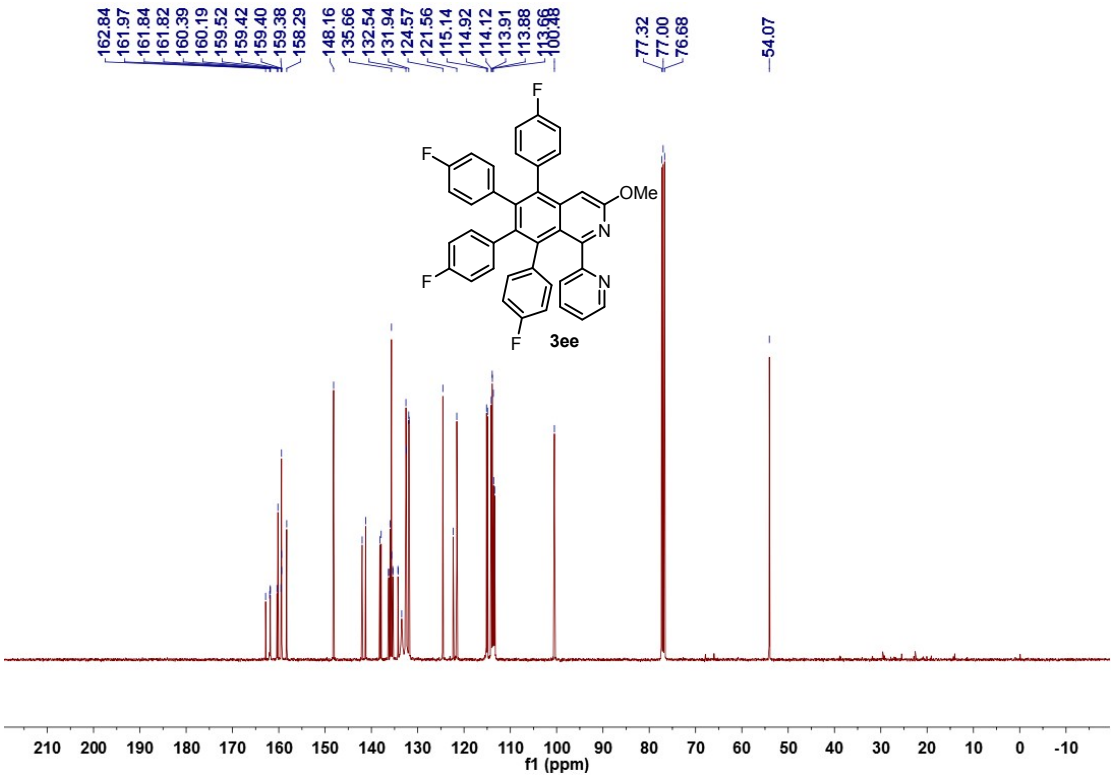
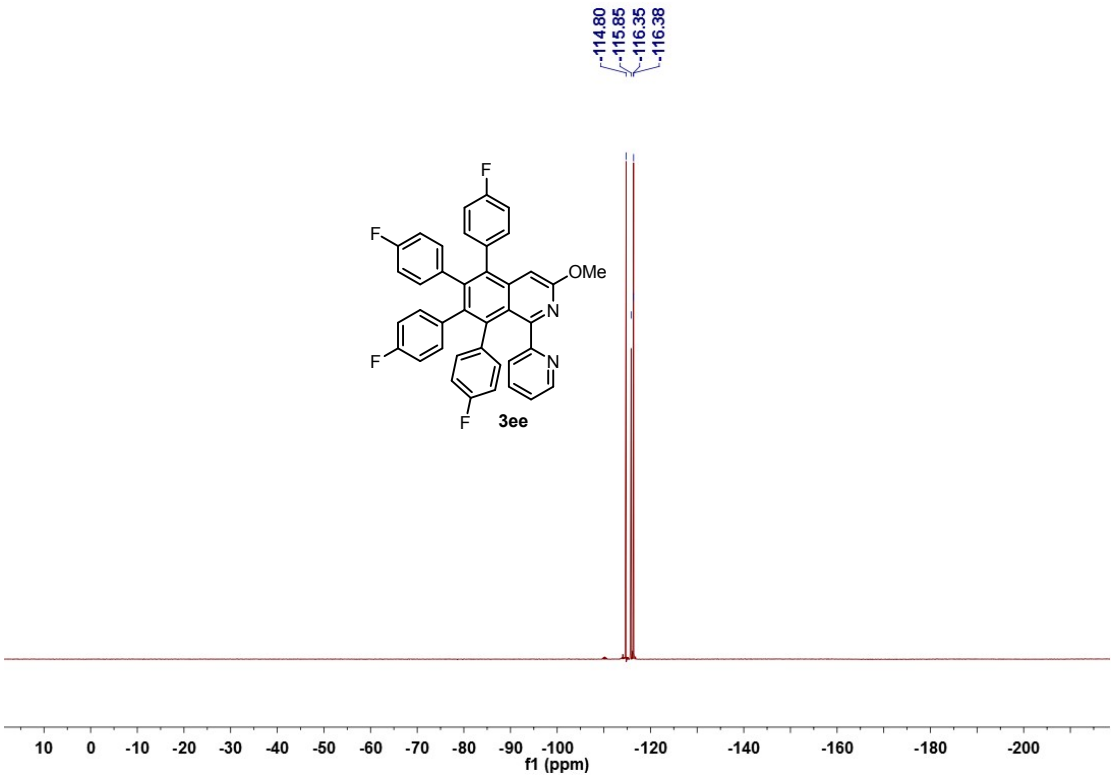
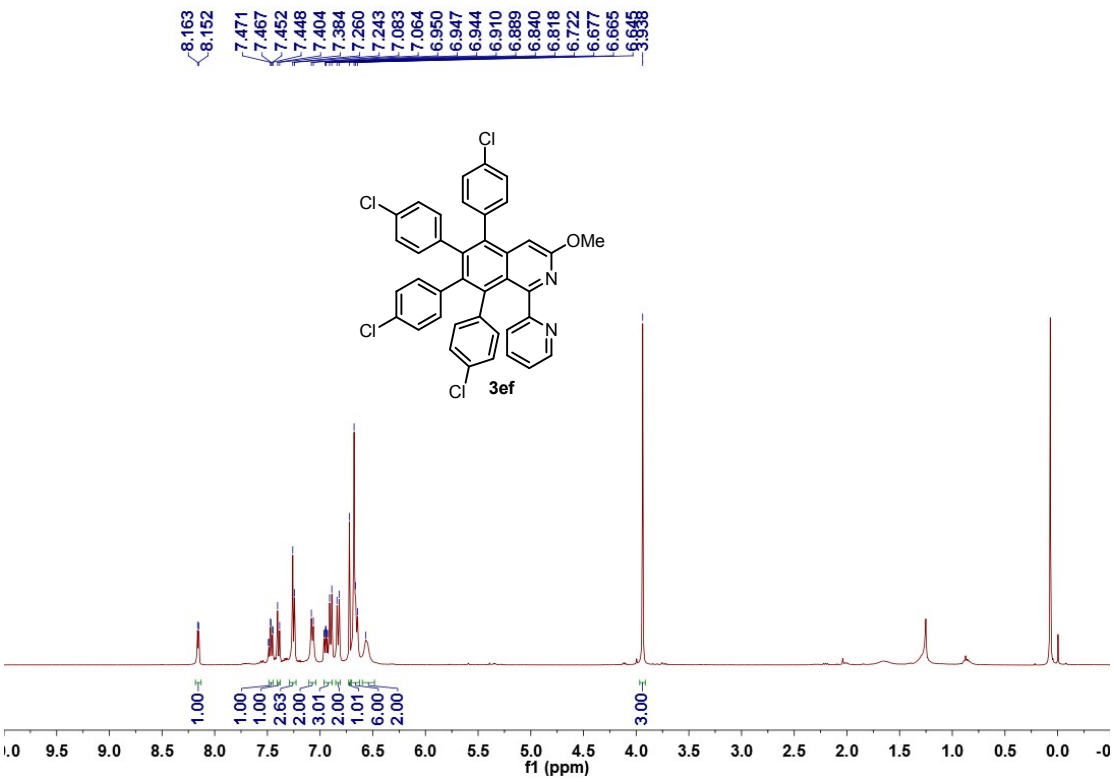
135.88
135.11
134.54
130.97
130.47
128.42
127.24
127.09
127.03
124.68
77.32
77.00
76.68
54.10
21.22
21.06
21.02
20.86
OMe
N
N
3eb
f1 (ppm)


8.181
8.170
7.472
7.468
7.453
7.449
7.435
7.431
7.419
7.400
7.260
7.131
7.115
7.101
6.980
6.958
6.937
6.921
6.917
6.908
6.904
6.899
6.890
6.887
6.762
6.739
6.725
6.717
6.703
6.683
6.669
6.620
6.598
6.577
6.550
6.528
6.507
6.428
6.407
6.386
F
F
OMe
N
F
N
F
3ee
1.00
2.00
2.00
3.00
1.00
4.00
6.00
2.00
3.00
f1 (ppm)


162.84
161.97
161.84
161.82
160.39
160.19
159.52
159.42
159.40
159.38
158.29
148.16
135.66
132.54
131.94
124.57
121.56
115.14
114.92
114.12
113.91
113.88
77.32
77.00
76.68
54.07
F
F
OMe
N
F
N
F
3ee
f1 (ppm)


-114.80
-115.85
-116.35
-116.38
F
F
OMe
N
F
N
F
3ee
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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8.152
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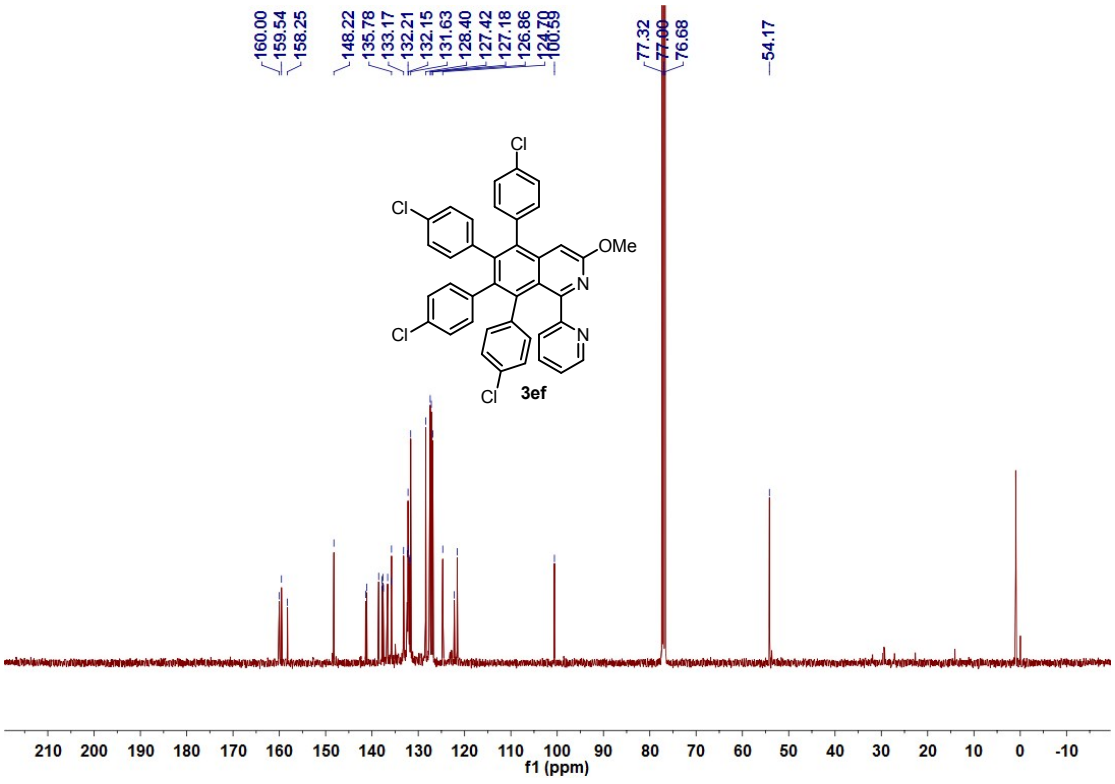
7.452
7.448
7.404
7.384
7.260
7.243
7.083
7.064
6.950
6.947
6.944
6.910
6.889
6.840
6.818
6.722
6.677
6.665
Cl
Cl
OMe
N
Cl
N
Cl
3ef
1.00
1.00
1.00
2.63
2.00
3.01
2.00
1.01
6.00
2.00
3.00
f1 (ppm)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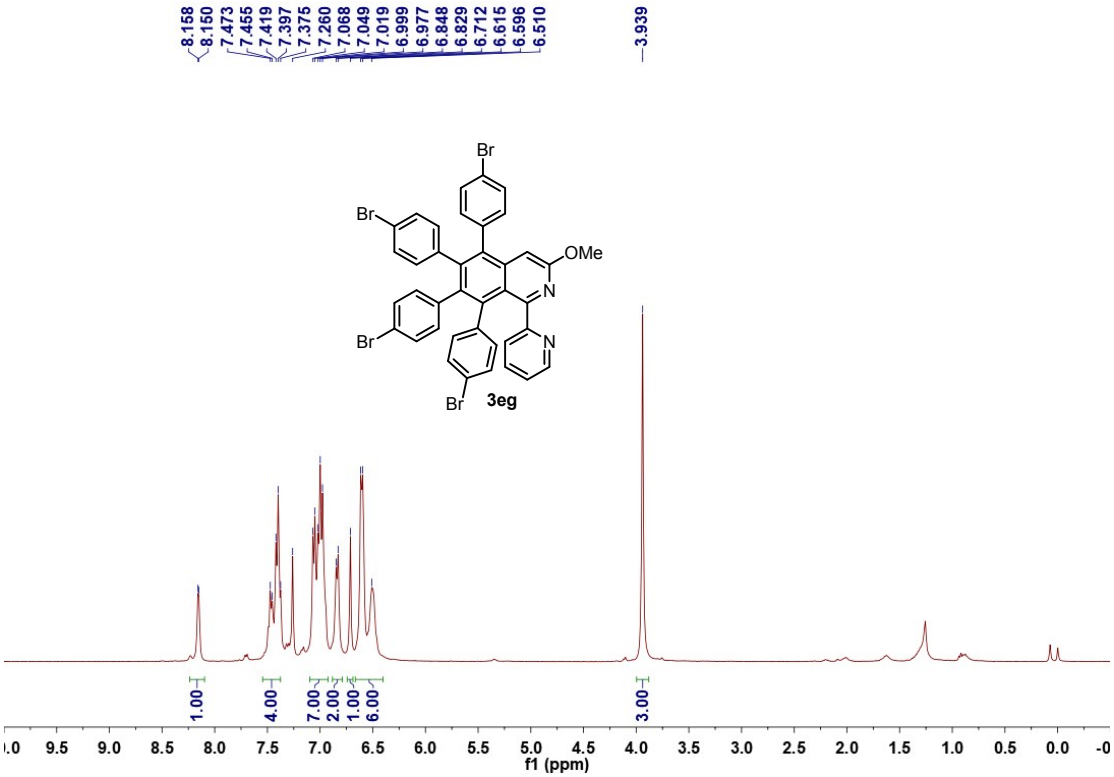
148.22
135.78
133.17
132.21
132.15
131.63
128.40
127.42
127.18
126.86
77.32
77.00
76.68
54.17
Cl
Cl
OMe
N
Cl
N
Cl
3ef
f1 (ppm)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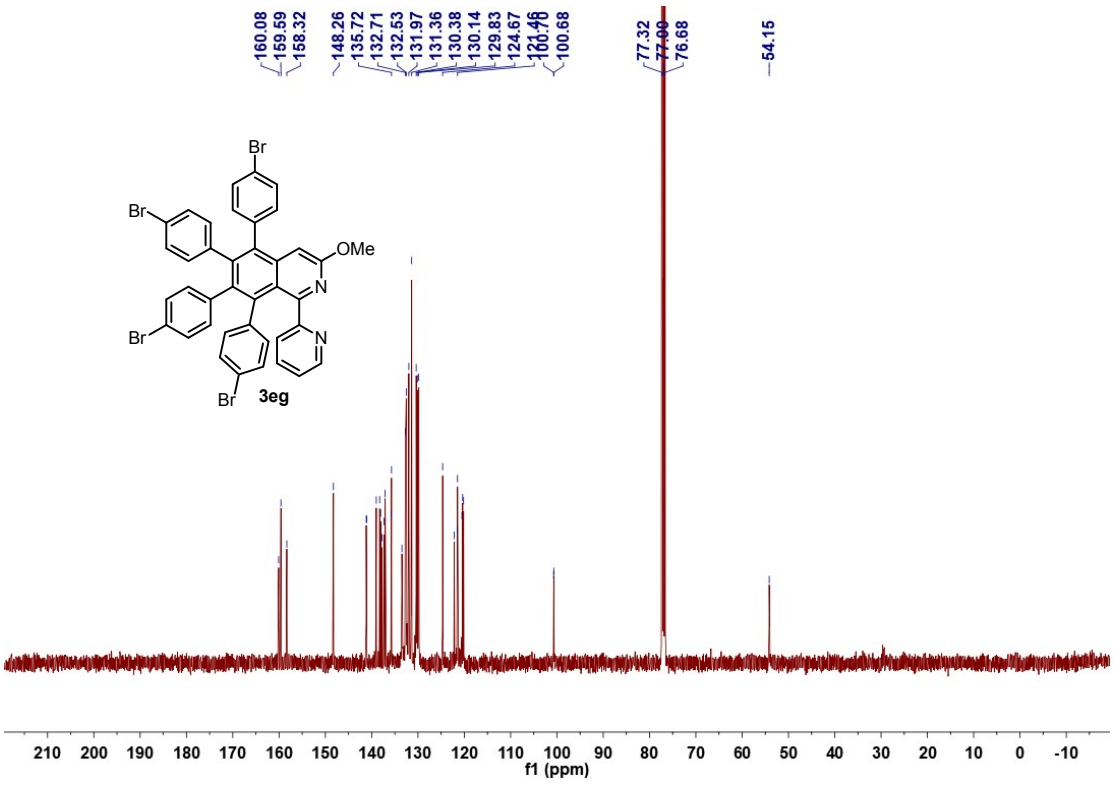
7.397
7.375
7.260
7.068
7.049
7.019
6.999
6.977
6.848
6.829
6.712
6.615
6.596
6.510
3.939
Br
Br
Br
Br
OMe
N
N
3eg
1.00
4.00
7.00
2.00
1.00
6.00
3.00
f1 (ppm)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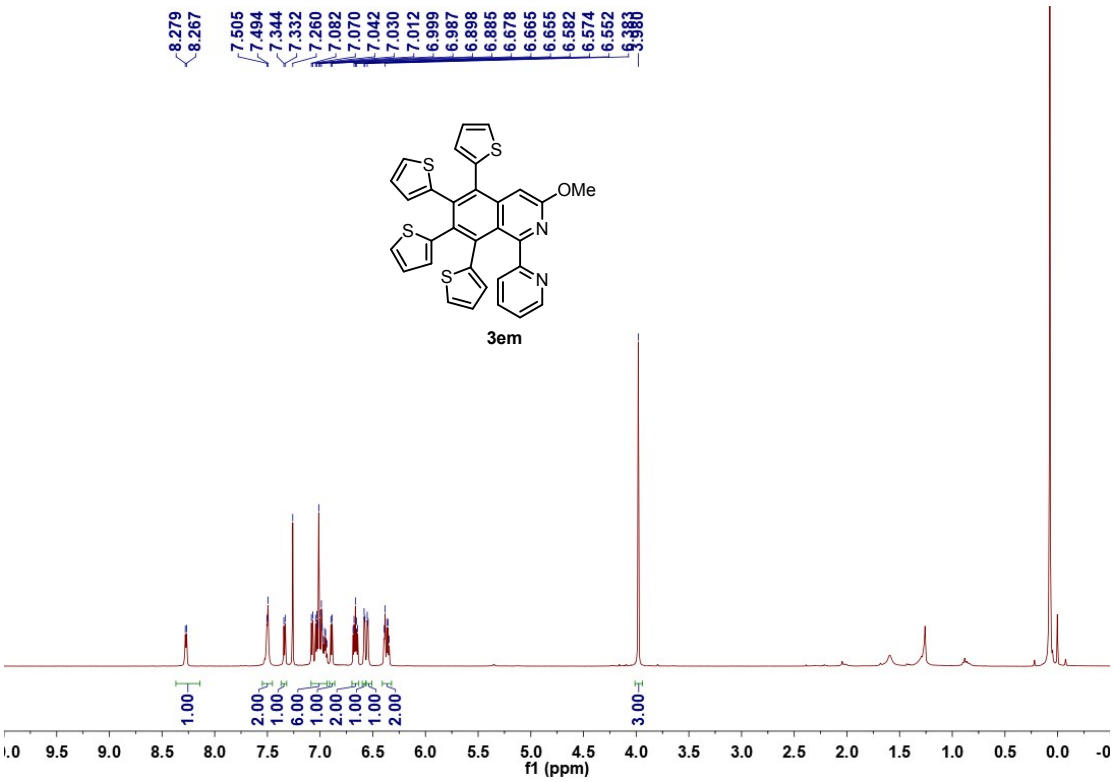
148.26
135.72
132.71
132.53
131.97
131.36
130.38
130.14
129.83
124.67
100.68
77.32
77.00
76.68
54.15
Br
Br
Br
Br
OMe
N
N
3eg
f1 (ppm)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8.267
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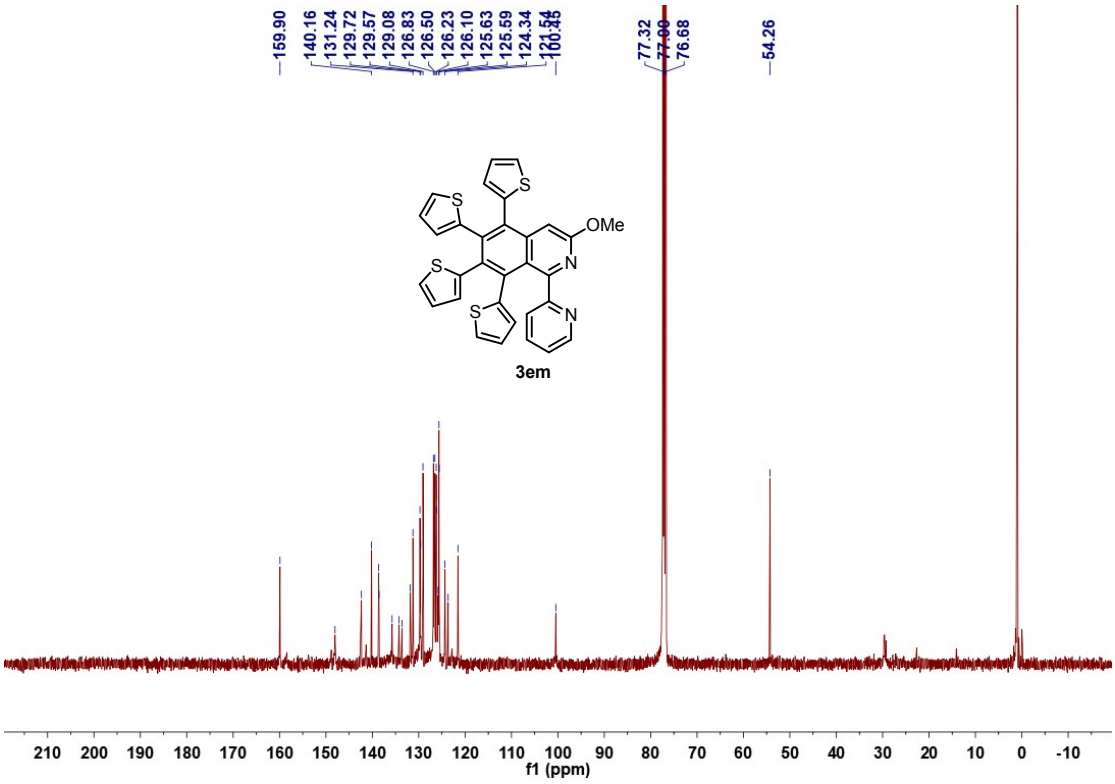
7.494
7.344
7.332
7.260
7.082
7.070
7.042
7.030
7.012
6.999
6.987
6.898
6.885
6.678
6.665
6.655
6.582
6.574
6.552
3.980
OMe
N
N
S
S
S
S
3em
1.00
2.00
1.00
6.00
1.00
2.00
1.00
1.00
2.00
3.00
f1 (ppm)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140.16
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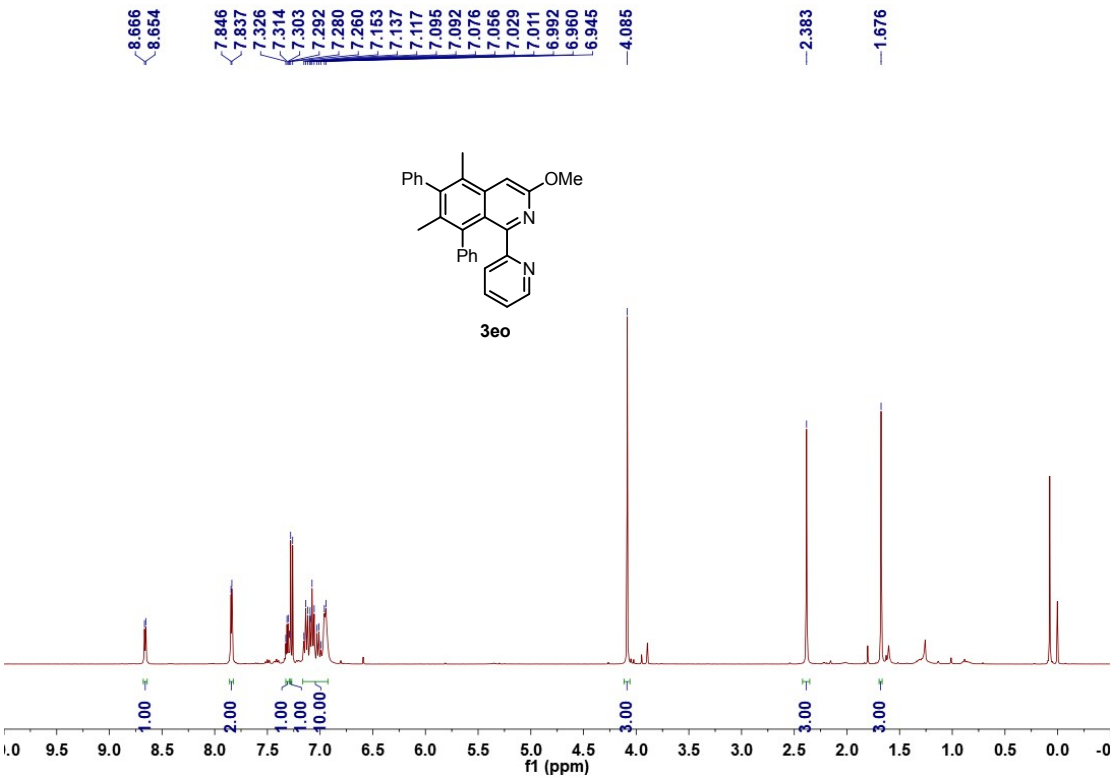
129.57
129.08
126.83
126.50
126.23
126.10
125.63
125.59
124.34
77.32
77.00
76.68
54.26
OMe
N
N
S
S
S
S
3em
f1 (ppm)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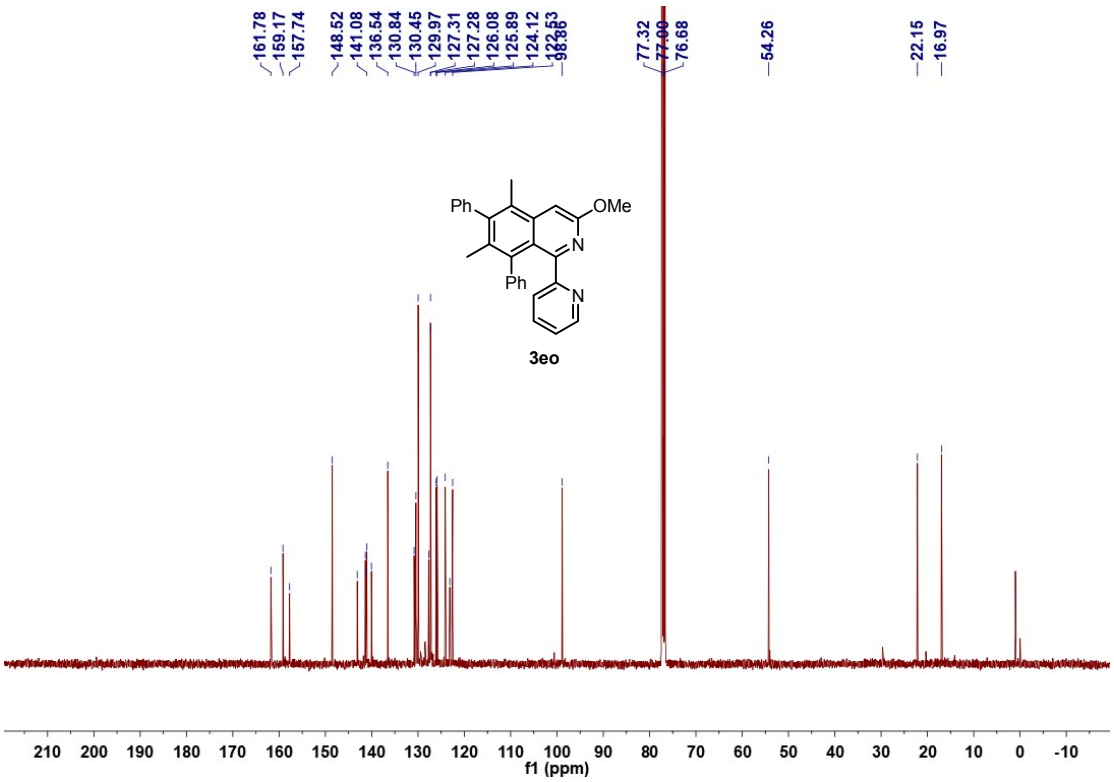
7.314
7.303
7.292
7.280
7.260
7.153
7.137
7.117
7.095
7.092
7.076
7.056
7.029
7.011
6.992
6.960
6.945
4.085
2.383
1.676
Ph
OMe
N
Ph
N
3eo
1.00
2.00
1.00
1.00
10.00
3.00
3.00
3.00
f1 (ppm)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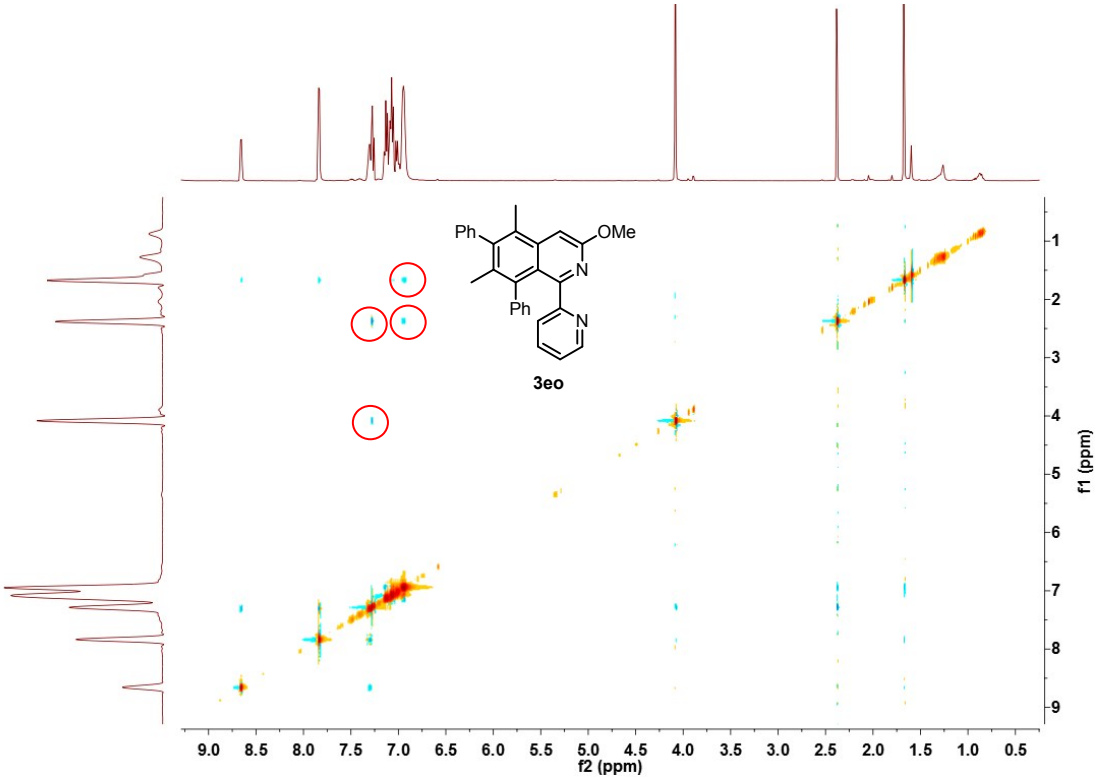
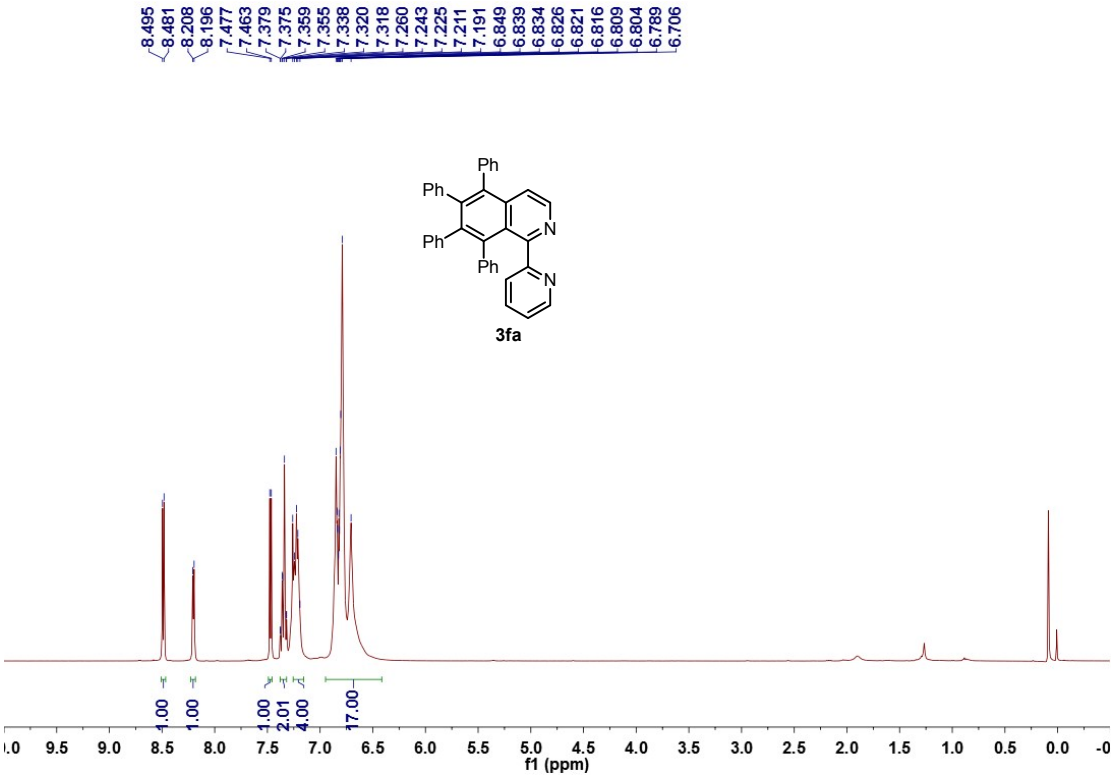
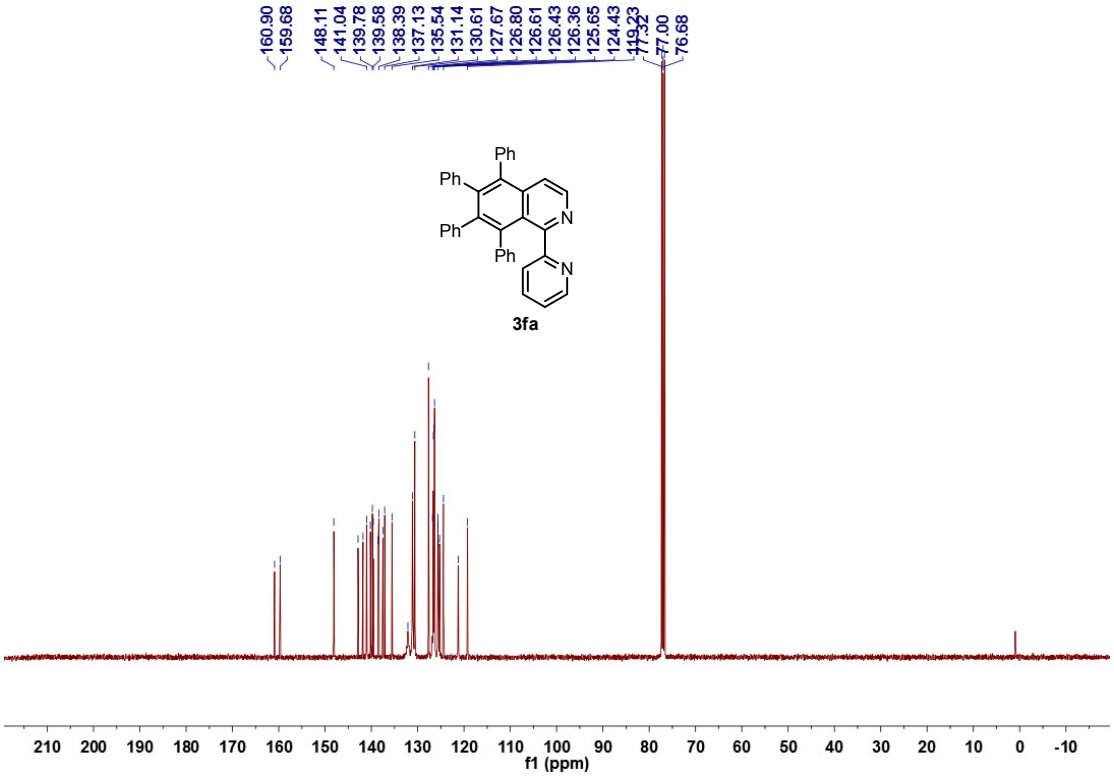
136.54
130.84
130.45
129.97
127.31
127.28
126.08
125.89
124.12
77.32
77.00
76.68
54.26
22.15
16.97
Ph
OMe
N
Ph
N
3eo
f1 (ppm)


Ph
OMe
N
Ph
N
3eo
f1 (ppm)
f2 (ppm)


8.495
8.481
8.208
8.196
7.477
7.463
7.379
7.375
7.359
7.355
7.338
7.320
7.318
7.260
7.243
7.225
7.211
7.191
6.849
6.839
6.834
6.826
6.821
6.816
6.809
6.804
6.789
6.706
Ph
Ph
Ph
Ph
N
N
3fa
1.00
1.00
1.00
2.01
4.00
17.00
f1 (ppm)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139.58
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137.13
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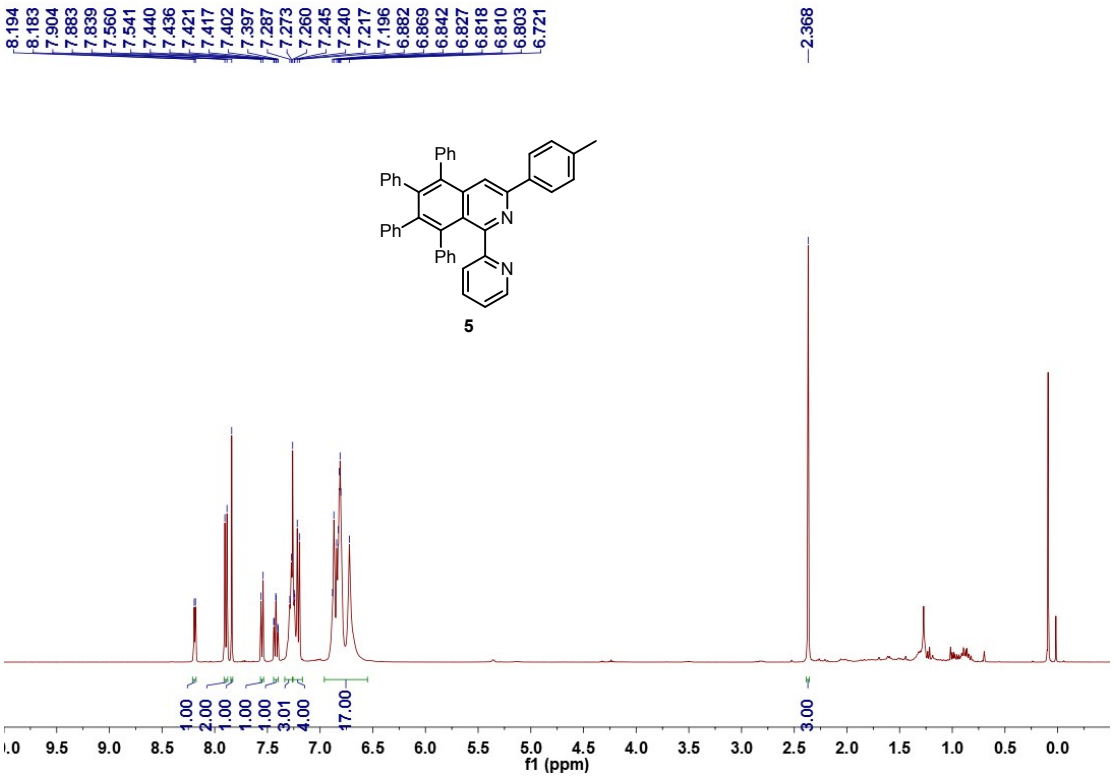
131.14
130.61
127.67
126.80
126.61
126.43
126.36
125.65
124.43
119.23
77.32
77.00
76.68
Ph
Ph
Ph
Ph
N
N
3fa
f1 (ppm)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7.240
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7.196
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6.842
6.827
6.818
6.810
6.803
6.721
2.368
Ph
Ph
Ph
Ph
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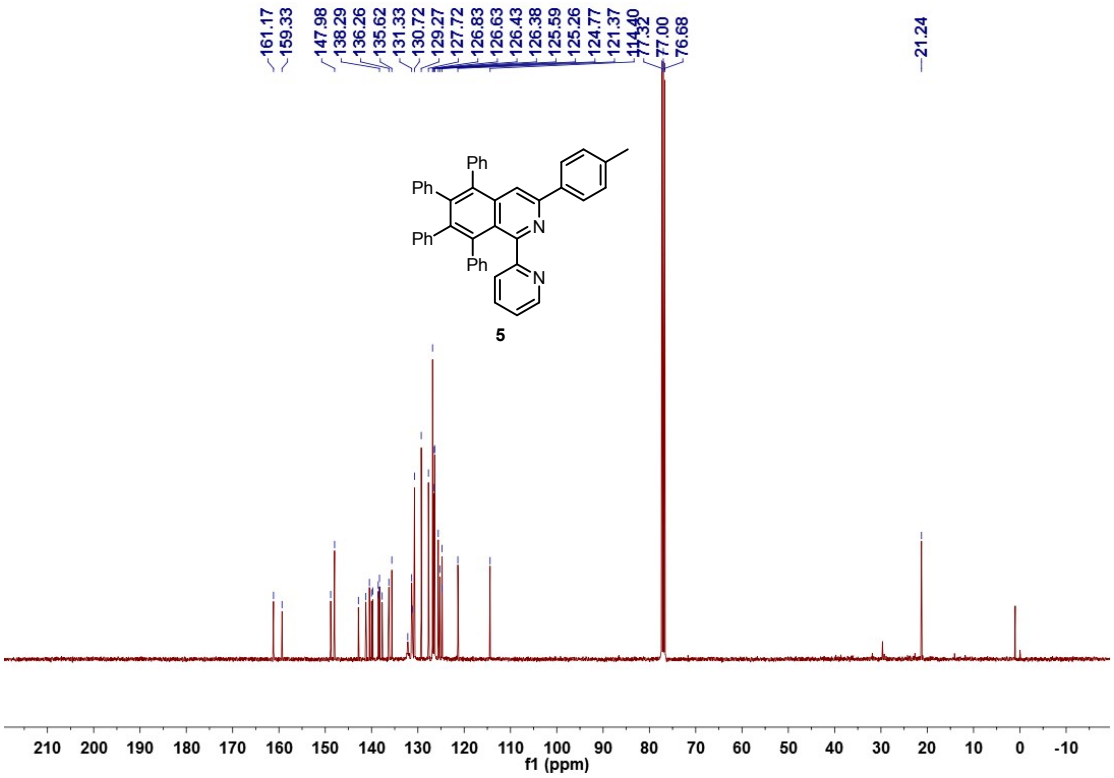
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126.38
125.59
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Ph
Ph
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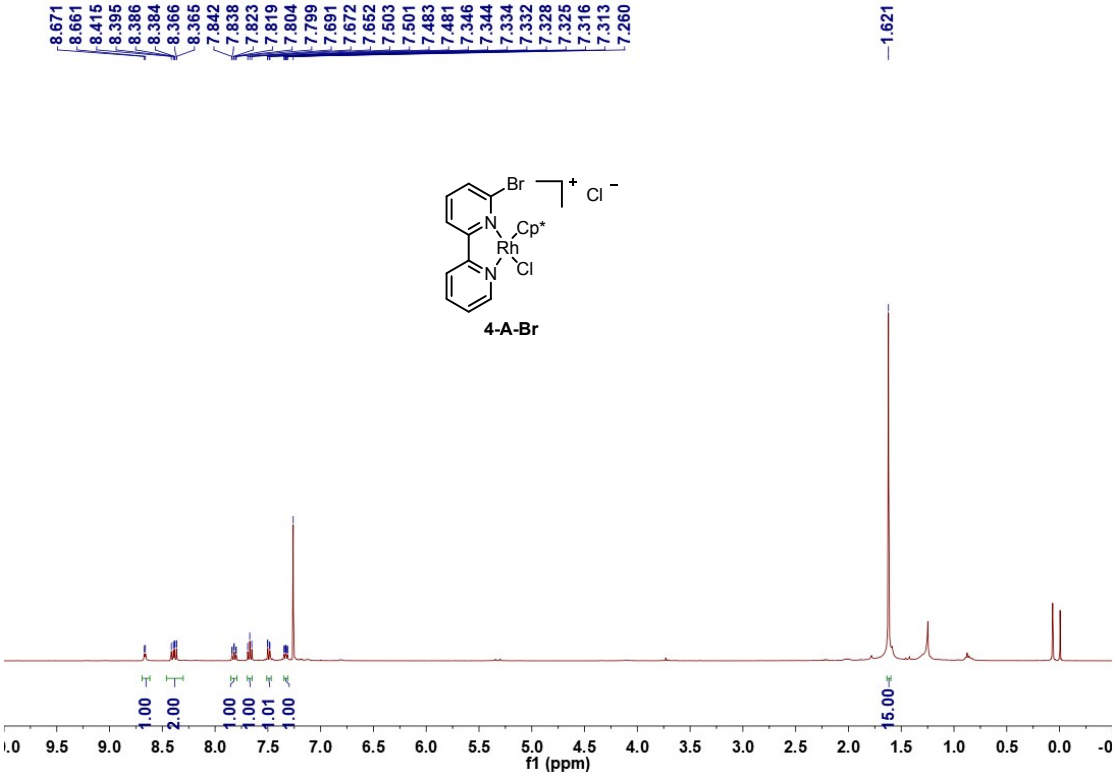
N
5
f1 (ppm)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7.652
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7.346
7.344
7.334
7.332
7.328
7.325
7.316
7.313
7.260
1.621
Br
Cl
N
Cp*
Rh
Cl
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4-A-Br
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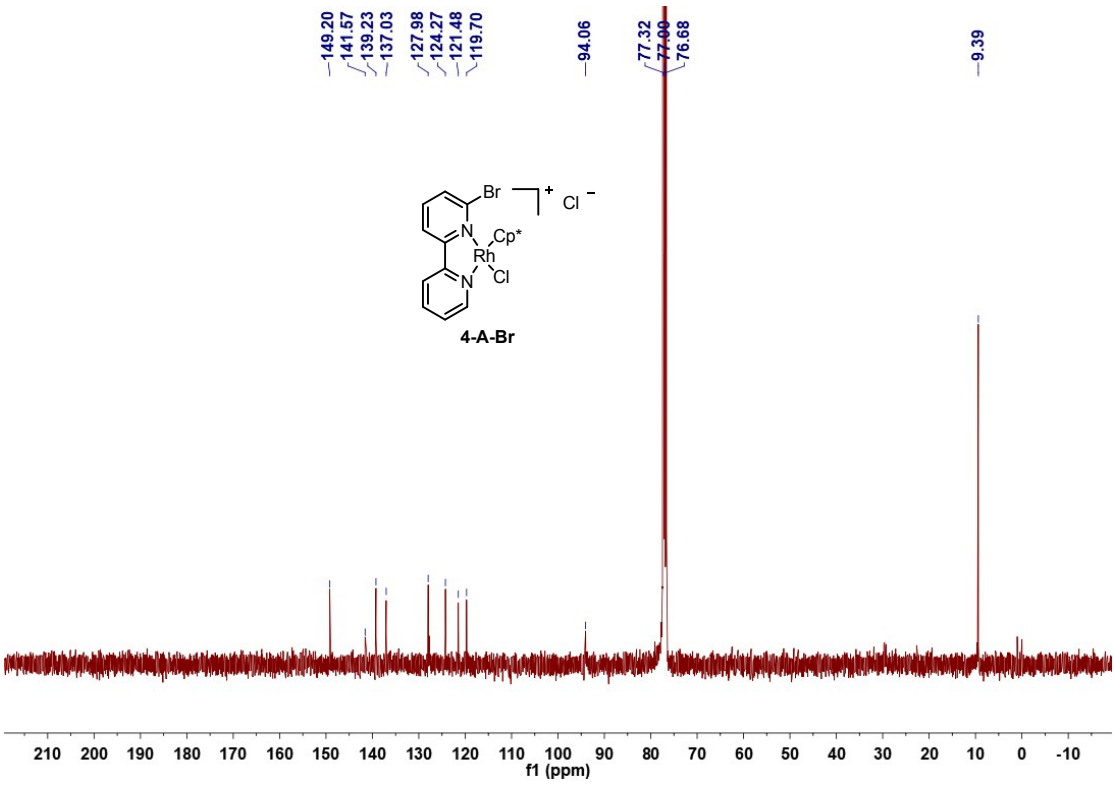
f1 (ppm)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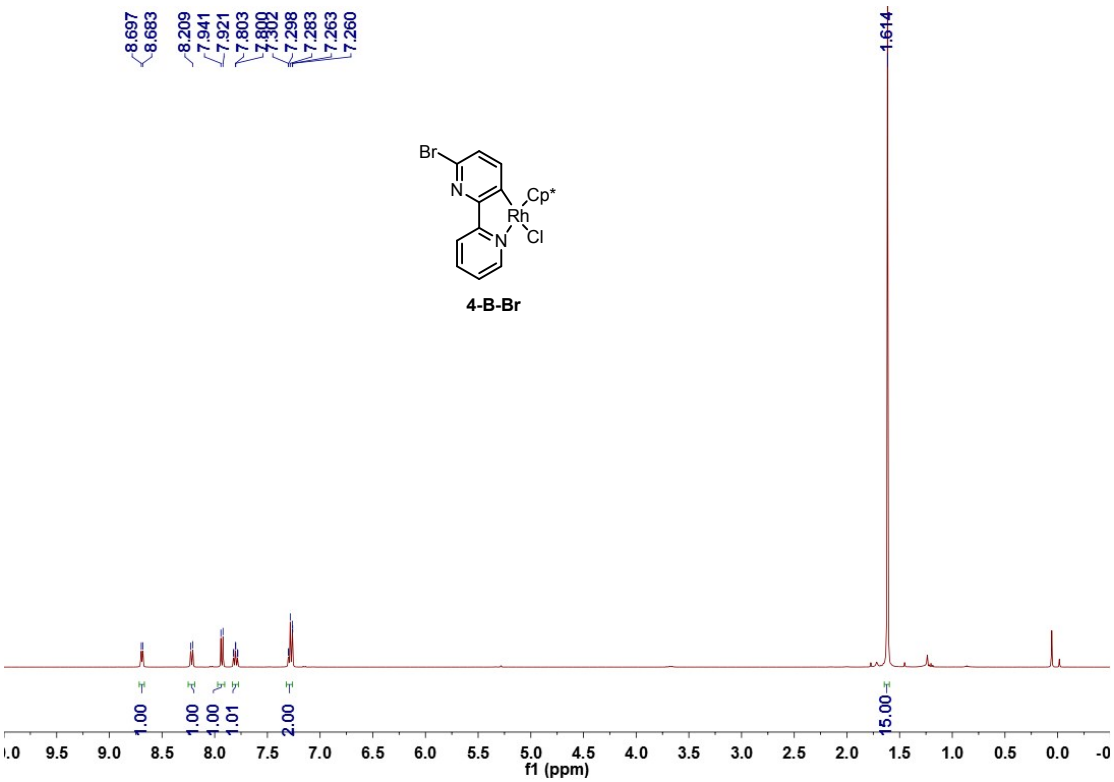
9.39
Br
Cl
N
Cp*
Rh
Cl
N
4-A-Br
f1 (ppm)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7.283
7.263
7.260
1.614
Br
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N
Cl
4-B-Br
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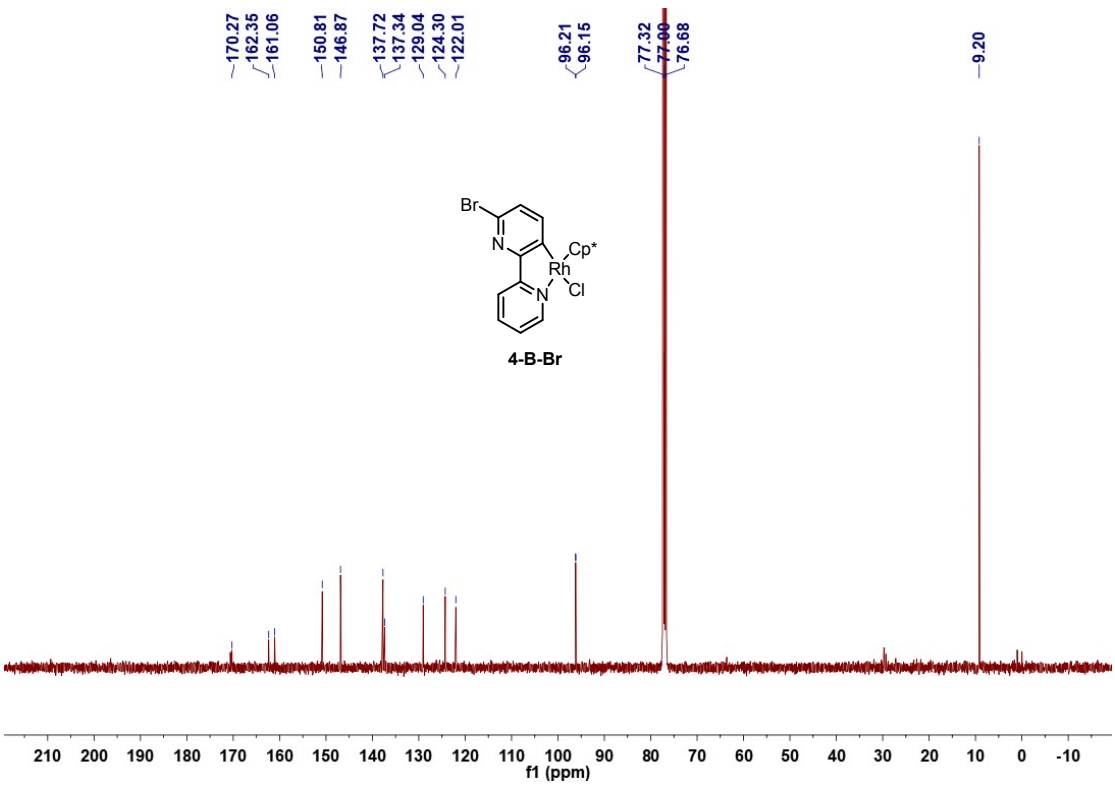
1.00
1.00
1.01
2.00
15.00
f1 (ppm)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150.81
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137.34
129.04
124.30
122.01
96.21
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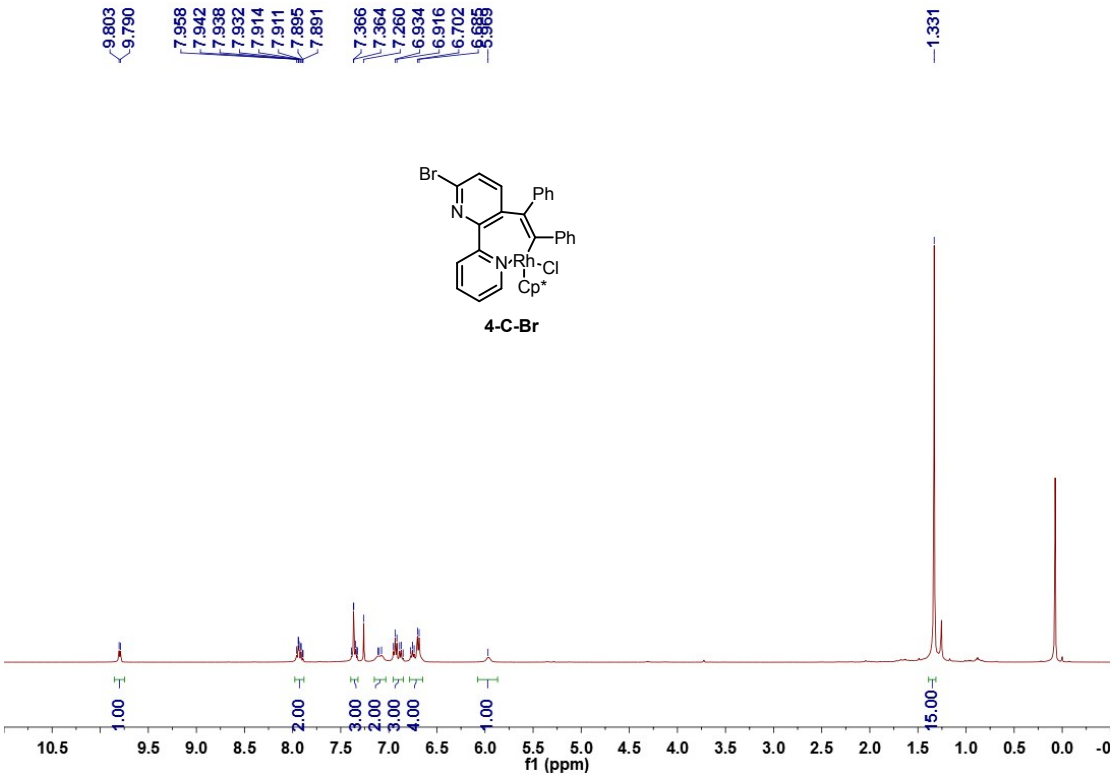
77.00
76.68
9.20
Br
N
Cp*
Rh
N
Cl
4-B-Br
f1 (ppm)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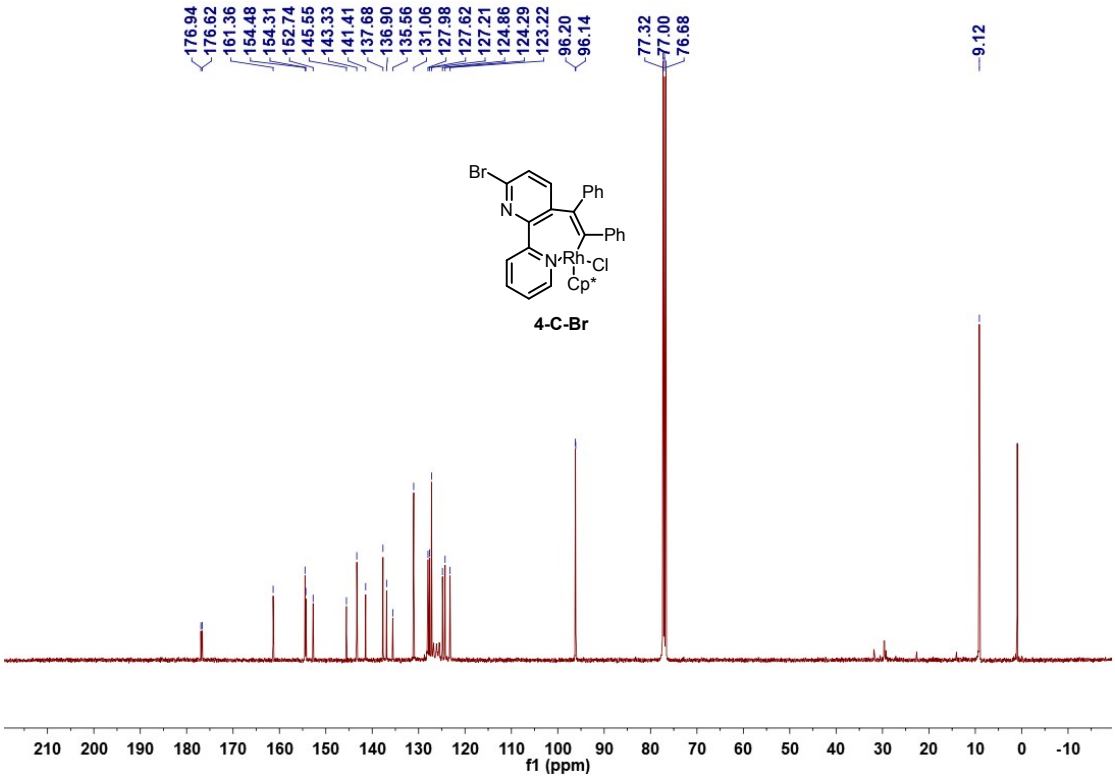
7.932
7.914
7.911
7.895
7.891
7.366
7.364
7.260
6.934
6.916
6.702
1.331
Br
N
Ph
Ph
N
Rh
Cl
Cp*
4-C-Br
1.00
2.00
3.00
2.00
3.00
4.00
1.00
15.00
f1 (ppm)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127.98
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127.21
124.86
124.29
123.22
96.20
96.14
77.32
77.00
76.68
9.12
Br
N
Ph
Ph
N
Rh
Cl
Cp*
4-C-Br
f1 (ppm)

X-Ray Crystallographic Data

X-Ray Crystallographic Data of **3aa**

Table 1. Crystal Data and Summary of X-ray Data Collection for **3aa.**

	3aa
Empirical formula	$C_{38}H_{25}BrN_2$
Formula weight	589.51
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 21.018(9) A alpha = 90 deg.
	b = 10.048(4) A beta = 90 deg.
	c = 27.166(12) A gamma = 90 deg.
Volume	5737(4) A^3
Z, Calculated density	8, 1.365 Mg/m^3
Absorption coefficient	1.463 mm^-1
F(000)	2416
Crystal size	0.220x0.210x0.180 mm
Theta range for data collection	1.499 to 26.499 deg.
Limiting indices	-26<=h<=25, -6<=k<=12, -33<=l<=34
Reflections collected/unique	33597/5953 [R(int) = 0.2061]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5953/0/370
Goodness-of-fit on F^2	0.771
Final R indices [I>2sigma(I)]	R1 = 0.0855, wR2 = 0.1898
R indices (all data)	R1 = 0.1919, wR2 = 0.2298
Extinction coefficient	n/a
Largest diff. peak and hole	1.687 and -1.087 e.A^-3

Table 2. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (A^2 x 10^3) for **3aa**. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U (eq)
Br(1)	8875(1)	7238(1)	5303(1)	67(1)
N(1)	8726(2)	5230(4)	4627(2)	50(1)
N(2)	8207(2)	3957(5)	3600(2)	59(1)
C(1)	9153(2)	6148(5)	4776(2)	49(1)
C(2)	9736(2)	6352(5)	4570(2)	48(1)
C(3)	9928(2)	5504(5)	4188(2)	45(1)
C(4)	9532(2)	4415(4)	4065(2)	44(1)
C(5)	8903(2)	4405(5)	4274(2)	46(1)
C(6)	8367(2)	3616(5)	4056(2)	51(1)
C(7)	8064(3)	2635(6)	4319(3)	69(2)
C(8)	7566(3)	1961(6)	4101(3)	78(2)
C(9)	7393(3)	2291(7)	3641(3)	78(2)
C(10)	7709(3)	3305(7)	3411(3)	70(2)
C(11)	9751(2)	3400(5)	3742(2)	45(1)
C(12)	9455(2)	2033(5)	3766(2)	49(1)
C(13)	9497(2)	1356(5)	4205(2)	59(2)
C(14)	9242(3)	82(6)	4263(3)	74(2)
C(15)	8948(3)	-498(6)	3862(3)	74(2)
C(16)	8906(2)	150(6)	3432(3)	68(2)
C(17)	9162(2)	1427(5)	3368(2)	58(2)
C(18)	10292(2)	3633(4)	3460(2)	45(1)
C(19)	10495(2)	2677(5)	3079(2)	51(2)
C(20)	10718(2)	1403(6)	3198(2)	63(2)
C(21)	10890(3)	502(6)	2832(3)	74(2)
C(22)	10838(3)	831(7)	2347(3)	82(2)
C(23)	10610(3)	2088(7)	2226(3)	74(2)
C(24)	10446(3)	2982(6)	2579(2)	59(2)
C(25)	10660(2)	4816(5)	3553(2)	47(1)
C(26)	11244(2)	5074(5)	3257(2)	51(1)
C(27)	11782(3)	4267(6)	3300(3)	73(2)

C(28)	12339(3)	4610(7)	3047(3)	88(2)
C(29)	12356(3)	5720(9)	2762(3)	92(2)
C(30)	11816(3)	6481(8)	2704(3)	82(2)
C(31)	11270(3)	6166(6)	2953(2)	62(2)
C(32)	10513(2)	5683(4)	3922(2)	45(1)
C(33)	10962(2)	6783(5)	4069(2)	48(1)
C(34)	10799(3)	8118(6)	4047(2)	71(2)
C(35)	11216(4)	9073(6)	4196(3)	88(2)
C(36)	11811(4)	8772(8)	4346(3)	91(2)
C(37)	11983(3)	7458(8)	4367(3)	81(2)
C(38)	11562(3)	6457(6)	4236(2)	60(2)

Table 3. Bond Lengths [A] and Angles [deg] for **3aa**.

Br(1)-C(1)	1.895(5)
N(1)-C(5)	1.321(6)
N(1)-C(1)	1.349(7)
N(2)-C(6)	1.328(7)
N(2)-C(10)	1.337(7)
C(1)-C(2)	1.362(7)
C(2)-C(3)	1.403(7)
C(2)-H(2)	0.9300
C(3)-C(4)	1.414(7)
C(3)-C(32)	1.438(7)
C(4)-C(11)	1.423(7)
C(4)-C(5)	1.439(7)
C(5)-C(6)	1.499(7)
C(6)-C(7)	1.375(8)
C(7)-C(8)	1.381(8)
C(7)-H(7)	0.9300
C(8)-C(9)	1.343(9)
C(8)-H(8)	0.9300
C(9)-C(10)	1.366(9)
C(9)-H(9)	0.9300

C(10)-H(10)	0.9300
C(11)-C(18)	1.389(7)
C(11)-C(12)	1.509(7)
C(12)-C(13)	1.376(8)
C(12)-C(17)	1.385(7)
C(13)-C(14)	1.397(8)
C(13)-H(13)	0.9300
C(14)-C(15)	1.383(8)
C(14)-H(14)	0.9300
C(15)-C(16)	1.341(9)
C(15)-H(15)	0.9300
C(16)-C(17)	1.401(8)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
C(18)-C(25)	1.441(7)
C(18)-C(19)	1.477(7)
C(19)-C(24)	1.396(8)
C(19)-C(20)	1.401(8)
C(20)-C(21)	1.393(8)
C(20)-H(20)	0.9300
C(21)-C(22)	1.363(9)
C(21)-H(21)	0.9300
C(22)-C(23)	1.390(9)
C(22)-H(22)	0.9300
C(23)-C(24)	1.359(8)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-C(32)	1.363(7)
C(25)-C(26)	1.489(7)
C(26)-C(31)	1.373(8)
C(26)-C(27)	1.396(7)
C(27)-C(28)	1.403(8)
C(27)-H(27)	0.9300
C(28)-C(29)	1.358(10)
C(28)-H(28)	0.9300

C(29)-C(30)	1.377(10)
C(29)-H(29)	0.9300
C(30)-C(31)	1.370(8)
C(30)-H(30)	0.9300
C(31)-H(31)	0.9300
C(32)-C(33)	1.507(7)
C(33)-C(38)	1.378(7)
C(33)-C(34)	1.386(8)
C(34)-C(35)	1.359(9)
C(34)-H(34)	0.9300
C(35)-C(36)	1.352(10)
C(35)-H(35)	0.9300
C(36)-C(37)	1.369(10)
C(36)-H(36)	0.9300
C(37)-C(38)	1.387(8)
C(37)-H(37)	0.9300
C(38)-H(38)	0.9300
C(5)-N(1)-C(1)	117.4(4)
C(6)-N(2)-C(10)	115.5(5)
N(1)-C(1)-C(2)	125.3(5)
N(1)-C(1)-Br(1)	114.6(4)
C(2)-C(1)-Br(1)	120.1(4)
C(1)-C(2)-C(3)	118.1(5)
C(1)-C(2)-H(2)	120.9
C(3)-C(2)-H(2)	120.9
C(2)-C(3)-C(4)	118.4(4)
C(2)-C(3)-C(32)	122.8(4)
C(4)-C(3)-C(32)	118.8(5)
C(3)-C(4)-C(11)	120.7(4)
C(3)-C(4)-C(5)	117.0(4)
C(11)-C(4)-C(5)	122.4(4)
N(1)-C(5)-C(4)	122.7(4)
N(1)-C(5)-C(6)	114.0(4)
C(4)-C(5)-C(6)	122.6(5)
N(2)-C(6)-C(7)	123.6(6)

N(2)-C(6)-C(5)	115.0(5)
C(7)-C(6)-C(5)	121.4(6)
C(6)-C(7)-C(8)	118.6(7)
C(6)-C(7)-H(7)	120.7
C(8)-C(7)-H(7)	120.7
C(9)-C(8)-C(7)	118.9(7)
C(9)-C(8)-H(8)	120.5
C(7)-C(8)-H(8)	120.5
C(8)-C(9)-C(10)	118.6(6)
C(8)-C(9)-H(9)	120.7
C(10)-C(9)-H(9)	120.7
N(2)-C(10)-C(9)	124.7(7)
N(2)-C(10)-H(10)	117.6
C(9)-C(10)-H(10)	117.6
C(18)-C(11)-C(4)	118.9(4)
C(18)-C(11)-C(12)	120.9(4)
C(4)-C(11)-C(12)	119.5(4)
C(13)-C(12)-C(17)	119.2(5)
C(13)-C(12)-C(11)	117.4(5)
C(17)-C(12)-C(11)	123.4(5)
C(12)-C(13)-C(14)	121.8(6)
C(12)-C(13)-H(13)	119.1
C(14)-C(13)-H(13)	119.1
C(15)-C(14)-C(13)	117.9(6)
C(15)-C(14)-H(14)	121.0
C(13)-C(14)-H(14)	121.0
C(16)-C(15)-C(14)	120.8(6)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(15)-C(16)-C(17)	121.9(6)
C(15)-C(16)-H(16)	119.1
C(17)-C(16)-H(16)	119.1
C(12)-C(17)-C(16)	118.4(6)
C(12)-C(17)-H(17)	120.8
C(16)-C(17)-H(17)	120.8

C(11)-C(18)-C(25)	118.9(5)
C(11)-C(18)-C(19)	120.9(4)
C(25)-C(18)-C(19)	120.2(5)
C(24)-C(19)-C(20)	116.8(5)
C(24)-C(19)-C(18)	121.2(5)
C(20)-C(19)-C(18)	121.9(6)
C(21)-C(20)-C(19)	121.1(6)
C(21)-C(20)-H(20)	119.5
C(19)-C(20)-H(20)	119.5
C(22)-C(21)-C(20)	120.8(6)
C(22)-C(21)-H(21)	119.6
C(20)-C(21)-H(21)	119.6
C(21)-C(22)-C(23)	118.5(6)
C(21)-C(22)-H(22)	120.7
C(23)-C(22)-H(22)	120.7
C(24)-C(23)-C(22)	121.4(7)
C(24)-C(23)-H(23)	119.3
C(22)-C(23)-H(23)	119.3
C(23)-C(24)-C(19)	121.5(6)
C(23)-C(24)-H(24)	119.2
C(19)-C(24)-H(24)	119.2
C(32)-C(25)-C(18)	122.2(5)
C(32)-C(25)-C(26)	118.2(4)
C(18)-C(25)-C(26)	119.5(5)
C(31)-C(26)-C(27)	118.9(5)
C(31)-C(26)-C(25)	119.7(5)
C(27)-C(26)-C(25)	121.3(5)
C(26)-C(27)-C(28)	119.5(6)
C(26)-C(27)-H(27)	120.3
C(28)-C(27)-H(27)	120.3
C(29)-C(28)-C(27)	120.2(6)
C(29)-C(28)-H(28)	119.9
C(27)-C(28)-H(28)	119.9
C(28)-C(29)-C(30)	120.0(6)
C(28)-C(29)-H(29)	120.0

C(30)-C(29)-H(29)	120.0
C(31)-C(30)-C(29)	120.4(7)
C(31)-C(30)-H(30)	119.8
C(29)-C(30)-H(30)	119.8
C(30)-C(31)-C(26)	120.9(6)
C(30)-C(31)-H(31)	119.5
C(26)-C(31)-H(31)	119.5
C(25)-C(32)-C(3)	118.9(4)
C(25)-C(32)-C(33)	121.4(4)
C(3)-C(32)-C(33)	119.6(5)
C(38)-C(33)-C(34)	118.0(5)
C(38)-C(33)-C(32)	119.0(5)
C(34)-C(33)-C(32)	122.9(5)
C(35)-C(34)-C(33)	120.8(6)
C(35)-C(34)-H(34)	119.6
C(33)-C(34)-H(34)	119.6
C(36)-C(35)-C(34)	121.9(7)
C(36)-C(35)-H(35)	119.1
C(34)-C(35)-H(35)	119.1
C(35)-C(36)-C(37)	118.2(6)
C(35)-C(36)-H(36)	120.9
C(37)-C(36)-H(36)	120.9
C(36)-C(37)-C(38)	121.4(7)
C(36)-C(37)-H(37)	119.3
C(38)-C(37)-H(37)	119.3
C(33)-C(38)-C(37)	119.7(6)
C(33)-C(38)-H(38)	120.1
C(37)-C(38)-H(38)	120.1

Table 4. Anisotropic Displacement Parameters (A^2 x 10^3) for **3aa**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	65(1)	55(1)	80(1)	-17(1)	11(1)	0(1)
N(1)	47(2)	39(2)	65(3)	-6(2)	2(2)	3(2)
N(2)	47(3)	58(3)	73(4)	-10(3)	-4(2)	9(2)
C(1)	49(3)	41(3)	57(4)	-8(3)	3(3)	2(3)
C(2)	49(3)	39(3)	56(4)	2(3)	4(3)	-6(2)
C(3)	44(3)	34(3)	57(4)	5(2)	-2(3)	1(2)
C(4)	41(3)	31(2)	60(4)	3(2)	3(2)	-2(2)
C(5)	38(3)	38(3)	60(4)	3(3)	4(3)	-1(2)
C(6)	40(3)	43(3)	71(4)	-11(3)	13(3)	2(2)
C(7)	54(4)	69(4)	84(5)	-2(4)	11(3)	-12(3)
C(8)	54(4)	61(4)	120(7)	-9(4)	10(4)	-22(3)
C(9)	54(4)	66(4)	114(7)	-26(5)	-10(4)	3(3)
C(10)	50(4)	72(4)	87(5)	-16(4)	-15(3)	16(3)
C(11)	44(3)	38(3)	53(4)	-1(3)	-2(2)	-1(2)
C(12)	43(3)	43(3)	61(4)	-7(3)	3(3)	1(2)
C(13)	50(3)	47(3)	79(5)	0(3)	0(3)	-5(3)
C(14)	67(4)	47(3)	108(6)	13(4)	-6(4)	-4(3)
C(15)	68(4)	41(3)	113(6)	-4(4)	0(4)	-14(3)
C(16)	56(4)	50(3)	98(5)	-18(4)	-10(4)	-9(3)
C(17)	56(3)	48(3)	68(4)	-12(3)	-2(3)	-2(3)
C(18)	46(3)	36(3)	52(4)	1(2)	-4(3)	-1(2)
C(19)	38(3)	41(3)	73(5)	-9(3)	5(3)	-6(2)
C(20)	58(4)	52(3)	78(5)	0(3)	0(3)	2(3)
C(21)	55(4)	52(3)	116(6)	-19(4)	14(4)	0(3)
C(22)	66(4)	70(5)	110(7)	-36(5)	24(4)	-21(4)
C(23)	77(4)	75(5)	71(5)	-21(4)	15(3)	-10(4)
C(24)	61(4)	54(3)	62(4)	-5(3)	2(3)	-3(3)
C(25)	37(3)	44(3)	60(4)	1(3)	1(2)	-4(2)
C(26)	43(3)	45(3)	66(4)	-7(3)	6(3)	-6(2)
C(27)	51(4)	56(3)	111(6)	-8(4)	7(3)	3(3)

C(28)	50(4)	81(5)	135(7)	-15(5)	18(4)	2(3)
C(29)	60(5)	120(6)	95(6)	-6(5)	20(4)	-26(4)
C(30)	74(5)	94(5)	79(5)	10(4)	2(4)	-28(4)
C(31)	49(3)	70(4)	68(4)	2(3)	-1(3)	-10(3)
C(32)	44(3)	31(3)	61(4)	0(3)	5(3)	-6(2)
C(33)	49(3)	43(3)	53(4)	-2(3)	6(3)	-4(2)
C(34)	77(4)	49(3)	85(5)	3(3)	-12(4)	-6(3)
C(35)	126(6)	44(3)	93(6)	3(4)	-12(5)	-21(4)
C(36)	113(6)	78(5)	82(6)	-3(4)	-6(5)	-56(5)
C(37)	59(4)	106(6)	77(5)	5(4)	-10(4)	-25(4)
C(38)	54(3)	56(3)	71(4)	-1(3)	1(3)	-14(3)

Table 5. Hydrogen Coordinates (× 10^4) and Isotropic Displacement Parameters (A^2 × 10^3) for **3aa**.

	x	y	z	U (eq)
H(2)	9999	7035	4679	58
H(7)	8191	2429	4638	83
H(8)	7353	1289	4269	94
H(9)	7066	1840	3482	94
H(10)	7568	3559	3100	84
H(13)	9701	1758	4470	71
H(14)	9270	-361	4563	88
H(15)	8777	-1348	3891	89
H(16)	8702	-258	3169	82
H(17)	9135	1856	3065	69
H(20)	10752	1155	3527	75
H(21)	11042	-335	2920	89
H(22)	10952	229	2102	98
H(23)	10569	2322	1896	89
H(24)	10297	3816	2485	71
H(27)	11770	3508	3496	87
H(28)	12699	4076	3074	106
H(29)	12731	5966	2605	110
H(30)	11822	7213	2495	99
H(31)	10911	6698	2916	75

H(34)	10400	8364	3930	85
H(35)	11087	9958	4193	105
H(36)	12097	9438	4433	109
H(37)	12390	7232	4472	97
H(38)	11683	5569	4261	72

Table 6. Torsion Angles [deg] for **3aa**

C(5)-N(1)-C(1)-C(2)	4.8(8)
C(5)-N(1)-C(1)-Br(1)	-177.3(4)
N(1)-C(1)-C(2)-C(3)	-3.6(8)
Br(1)-C(1)-C(2)-C(3)	178.7(4)
C(1)-C(2)-C(3)-C(4)	-5.3(7)
C(1)-C(2)-C(3)-C(32)	175.8(5)
C(2)-C(3)-C(4)-C(11)	-169.3(5)
C(32)-C(3)-C(4)-C(11)	9.8(7)
C(2)-C(3)-C(4)-C(5)	11.9(7)
C(32)-C(3)-C(4)-C(5)	-169.1(5)
C(1)-N(1)-C(5)-C(4)	2.8(7)
C(1)-N(1)-C(5)-C(6)	-167.8(5)
C(3)-C(4)-C(5)-N(1)	-11.1(7)
C(11)-C(4)-C(5)-N(1)	170.1(5)
C(3)-C(4)-C(5)-C(6)	158.7(5)
C(11)-C(4)-C(5)-C(6)	-20.1(8)
C(10)-N(2)-C(6)-C(7)	1.9(8)
C(10)-N(2)-C(6)-C(5)	-176.9(4)
N(1)-C(5)-C(6)-N(2)	109.1(5)
C(4)-C(5)-C(6)-N(2)	-61.5(6)
N(1)-C(5)-C(6)-C(7)	-69.7(6)
C(4)-C(5)-C(6)-C(7)	119.6(6)
N(2)-C(6)-C(7)-C(8)	0.1(9)
C(5)-C(6)-C(7)-C(8)	178.8(5)
C(6)-C(7)-C(8)-C(9)	-0.4(10)
C(7)-C(8)-C(9)-C(10)	-1.5(10)
C(6)-N(2)-C(10)-C(9)	-4.0(8)
C(8)-C(9)-C(10)-N(2)	3.9(10)

C(3)-C(4)-C(11)-C(18)	-14.7(7)
C(5)-C(4)-C(11)-C(18)	164.1(5)
C(3)-C(4)-C(11)-C(12)	156.2(5)
C(5)-C(4)-C(11)-C(12)	-25.0(7)
C(18)-C(11)-C(12)-C(13)	110.8(6)
C(4)-C(11)-C(12)-C(13)	-59.9(7)
C(18)-C(11)-C(12)-C(17)	-67.6(7)
C(4)-C(11)-C(12)-C(17)	121.7(6)
C(17)-C(12)-C(13)-C(14)	-1.2(8)
C(11)-C(12)-C(13)-C(14)	-179.6(5)
C(12)-C(13)-C(14)-C(15)	0.7(9)
C(13)-C(14)-C(15)-C(16)	-0.5(9)
C(14)-C(15)-C(16)-C(17)	0.7(10)
C(13)-C(12)-C(17)-C(16)	1.3(8)
C(11)-C(12)-C(17)-C(16)	179.7(5)
C(15)-C(16)-C(17)-C(12)	-1.1(9)
C(4)-C(11)-C(18)-C(25)	8.2(7)
C(12)-C(11)-C(18)-C(25)	-162.6(5)
C(4)-C(11)-C(18)-C(19)	-172.9(5)
C(12)-C(11)-C(18)-C(19)	16.3(8)
C(11)-C(18)-C(19)-C(24)	109.5(6)
C(25)-C(18)-C(19)-C(24)	-71.6(7)
C(11)-C(18)-C(19)-C(20)	-67.5(7)
C(25)-C(18)-C(19)-C(20)	111.4(6)
C(24)-C(19)-C(20)-C(21)	1.0(8)
C(18)-C(19)-C(20)-C(21)	178.1(5)
C(19)-C(20)-C(21)-C(22)	-0.8(9)
C(20)-C(21)-C(22)-C(23)	0.1(9)
C(21)-C(22)-C(23)-C(24)	0.5(10)
C(22)-C(23)-C(24)-C(19)	-0.4(9)
C(20)-C(19)-C(24)-C(23)	-0.4(8)
C(18)-C(19)-C(24)-C(23)	-177.5(5)
C(11)-C(18)-C(25)-C(32)	3.2(8)
C(19)-C(18)-C(25)-C(32)	-175.7(5)
C(11)-C(18)-C(25)-C(26)	179.5(5)

C(19)-C(18)-C(25)-C(26)	0.6(7)
C(32)-C(25)-C(26)-C(31)	-67.5(7)
C(18)-C(25)-C(26)-C(31)	116.0(6)
C(32)-C(25)-C(26)-C(27)	109.1(6)
C(18)-C(25)-C(26)-C(27)	-67.4(7)
C(31)-C(26)-C(27)-C(28)	2.0(9)
C(25)-C(26)-C(27)-C(28)	-174.6(6)
C(26)-C(27)-C(28)-C(29)	0.1(11)
C(27)-C(28)-C(29)-C(30)	-2.8(12)
C(28)-C(29)-C(30)-C(31)	3.4(11)
C(29)-C(30)-C(31)-C(26)	-1.2(10)
C(27)-C(26)-C(31)-C(30)	-1.5(9)
C(25)-C(26)-C(31)-C(30)	175.3(5)
C(18)-C(25)-C(32)-C(3)	-8.0(8)
C(26)-C(25)-C(32)-C(3)	175.5(5)
C(18)-C(25)-C(32)-C(33)	169.5(5)
C(26)-C(25)-C(32)-C(33)	-6.9(7)
C(2)-C(3)-C(32)-C(25)	-179.5(5)
C(4)-C(3)-C(32)-C(25)	1.6(7)
C(2)-C(3)-C(32)-C(33)	3.0(7)
C(4)-C(3)-C(32)-C(33)	-176.0(5)
C(25)-C(32)-C(33)-C(38)	-60.4(7)
C(3)-C(32)-C(33)-C(38)	117.1(6)
C(25)-C(32)-C(33)-C(34)	120.2(6)
C(3)-C(32)-C(33)-C(34)	-62.3(8)
C(38)-C(33)-C(34)-C(35)	-1.1(10)
C(32)-C(33)-C(34)-C(35)	178.4(6)
C(33)-C(34)-C(35)-C(36)	3.2(12)
C(34)-C(35)-C(36)-C(37)	-2.8(12)
C(35)-C(36)-C(37)-C(38)	0.4(12)
C(34)-C(33)-C(38)-C(37)	-1.2(9)
C(32)-C(33)-C(38)-C(37)	179.3(6)
C(36)-C(37)-C(38)-C(33)	1.6(10)

X-Ray Crystallographic Data of **3ef**

Table 1. Crystal Data and Structure Refinement for **3ef**.

Identification code	**3ef**
Empirical formula	$C_{39}H_{24}Cl_4N_2O$
Formula weight	678.40
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Iba2
a/Å	38.6912(8)
b/Å	13.8512(3)
c/Å	12.5280(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6714.0(3)
Z	8
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	3.471
F(000)	2784.0
Crystal size/mm^3	0.22×0.2×0.17
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	4.568 to 134.126
Index ranges	-41≤h≤46, -11≤k≤16, -14≤l≤12
Reflections collected	7707
Independent reflections	4117 [R_{int}]= 0.0238, R_{sigma}=
Data/restraints/parameters	4117/43/416
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1= 0.0560, wR_2= 0.1584
Final R indexes [all data]	R_1= 0.0595, wR_2= 0.1636
Largest diff. peak/hole/e Å^{-3}	0.59/-0.36
Flack parameter	0.042(15)

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3ef**. U (eq) is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U (eq)
Cl1	7479.1(6)	6999(2)	1310(2)	130.4(10)
Cl2	6815.5(6)	11315.1(14)	3955(4)	144.7(13)
Cl3	5353.1(6)	10960.8(13)	7707(2)	110.4(7)
Cl4	4531.1(3)	6411.6(15)	8725.5(13)	88.3(5)
O1	5852.2(11)	3037(3)	5892(5)	81.0(13)
N1	6257(1)	3898(3)	4954(4)	53.5(9)
N2	7020.9(10)	4769(4)	4467(6)	83.9(16)
C1	6401.2(9)	4734(3)	4684(4)	48.9(10)
C2	6271.9(9)	5647(3)	5045(4)	44.7(9)
C3	6405.1(9)	6579(3)	4724(4)	44.6(9)
C4	6272.1(10)	7402(3)	5180(4)	49.2(9)
C5	5994.2(10)	7357(3)	5932(4)	47.9(9)
C6	5852.5(9)	6488(3)	6213(4)	45.1(9)
C7	5992.9(9)	5615(3)	5785(4)	47.0(9)
C8	5853.5(10)	4717(3)	6058(4)	51.7(10)
C9	5988.8(11)	3903(4)	5615(4)	57.0(11)
C10	6014(2)	2182(5)	5523(8)	100(3)
C11	6718.6(11)	4585(3)	4016(5)	58.0(11)
C12	7305.3(16)	4594(6)	3875(10)	106(3)
C13	7292(3)	4264(7)	2887(10)	114(3)
C14	6980(4)	4039(9)	2427(10)	139(4)
C15	6679(2)	4187(7)	3016(7)	101(2)
C16	6673.3(10)	6692(3)	3865(4)	48.7(9)
C17	7004.3(11)	6985(4)	4116(5)	58.3(11)
C18	7249.7(12)	7094(4)	3334(6)	68.9(15)
C19	7162.6(15)	6919(4)	2304(6)	75.7(17)
C20	6833.1(18)	6647(6)	2024(5)	87(2)
C21	6593.4(13)	6527(5)	2813(5)	68.2(14)
C22	6410.0(11)	8376(3)	4877(5)	55.6(11)
C23	6594.9(14)	8916(4)	5586(6)	72.0(15)

C24	6727.3(16)	9831(6)	5307(9)	96(3)
C25	6661.4(15)	10163(5)	4292(9)	92(2)
C26	6479.5(16)	9656(5)	3573(8)	94(2)
C27	6354.3(14)	8759(4)	3857(6)	71.3(14)
C28	5843.4(10)	8274(3)	6365(4)	51(1)
C29	5867.9(14)	8489(4)	7426(5)	65.4(13)
C30	5717.2(15)	9304(4)	7860(6)	74.0(15)
C31	5539.8(14)	9918(4)	7187(6)	72.7(15)
C32	5508.4(13)	9726(4)	6121(6)	70.5(15)
C33	5659.0(12)	8897(4)	5718(5)	60.9(12)
C34	5531.1(11)	6453(3)	6883(4)	48.4(9)
C35	5528.6(12)	6141(4)	7923(5)	62.1(12)
C36	5224.6(14)	6127(5)	8516(5)	71.5(14)
C37	4918.6(11)	6741(4)	7002(5)	59.0(12)
C38	5223.8(10)	6749(4)	6427(4)	54.1(10)
C39	4923.1(12)	6431(4)	8027(5)	62.4(13)

Table 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3ef**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
Cl1	114.8(14)	163.3(19)	113.2(16)	-39.5(15)	71.9(13)	-61.3(13)
Cl2	111.2(14)	78.9(9)	244(4)	37.2(16)	55.2(19)	-18.9(9)
Cl3	116.4(14)	76.0(9)	138.8(19)	-33.6(11)	3.7(13)	21.0(9)
Cl4	54.8(6)	140.7(13)	69.4(9)	-24(1)	25.5(6)	-18.8(7)
O1	69(2)	57.2(19)	117(4)	-7(2)	31(2)	-14.9(16)
N1	44.9(17)	57.4(19)	58(2)	0.5(18)	3.5(16)	-2.0(15)
N2	40(2)	100(3)	112(4)	19(3)	7(2)	0(2)
C1	32.6(17)	64(2)	50(2)	2(2)	0.7(16)	-1.8(15)
C2	29.0(15)	58(2)	47(2)	2.6(18)	-2.9(15)	-0.3(15)
C3	30.6(17)	59(2)	44(2)	2.0(18)	-4.1(15)	-1.2(15)
C4	36.6(17)	57(2)	54(3)	3.8(19)	-3.8(17)	-2.5(16)
C5	36.0(17)	58(2)	50(2)	2(2)	-3.3(16)	0.6(16)
C6	32.3(16)	57(2)	46(2)	-0.2(18)	-3.6(16)	1.3(15)
C7	30.0(16)	62(2)	49(2)	0.8(18)	-4.3(16)	-1.3(15)
C8	38.2(17)	59(2)	58(3)	3(2)	8.1(17)	-6.5(16)
C9	44(2)	61(2)	66(3)	-1(2)	2(2)	-7.8(18)
C10	119(5)	61(3)	119(6)	-17(4)	48(5)	-18(3)
C11	46(2)	60(2)	68(3)	9(2)	11(2)	8.4(17)
C12	55(3)	102(4)	160(8)	27(5)	14(4)	4(3)
C13	103(5)	106(5)	134(7)	23(5)	62(5)	32(4)
C14	171(8)	143(7)	103(6)	-21(6)	51(6)	40(7)
C15	105(5)	126(6)	70(4)	-19(4)	16(4)	22(4)
C16	36.0(18)	56(2)	54(3)	-1(2)	2.9(17)	-4.2(15)
C17	41(2)	72(3)	62(3)	4(2)	-5(2)	-5.1(18)
C18	39(2)	75(3)	93(5)	0(3)	11(2)	-10(2)
C19	65(3)	79(3)	83(4)	-15(3)	34(3)	-23(3)
C20	89(4)	120(5)	51(3)	-17(3)	12(3)	-37(4)
C21	49(2)	97(4)	58(3)	-6(3)	2(2)	-22(2)
C22	42(2)	58(2)	67(3)	3(2)	13.0(19)	-1.1(17)
C23	62(3)	72(3)	82(4)	-3(3)	6(3)	-12(2)
C24	62(3)	84(4)	142(8)	-31(5)	19(4)	-16(3)

C25	58(3)	80(4)	140(7)	22(5)	26(4)	1(3)
C26	65(3)	89(4)	126(7)	43(5)	22(4)	9(3)
C27	57(2)	77(3)	80(4)	18(3)	14(3)	5(2)
C28	36.6(18)	56(2)	60(3)	-1(2)	4.6(18)	-3.7(15)
C29	59(3)	67(3)	70(4)	-4(2)	1(2)	4(2)
C30	76(3)	76(3)	70(4)	-22(3)	5(3)	0(3)
C31	65(3)	59(3)	94(5)	-11(3)	8(3)	-1(2)
C32	57(3)	64(3)	90(4)	6(3)	3(3)	5(2)
C33	53(2)	65(3)	65(3)	2(2)	4(2)	2(2)
C34	39.7(18)	58(2)	47(2)	-4.1(18)	3.9(17)	-3.1(16)
C35	45(2)	90(3)	52(3)	1(2)	0(2)	-5(2)
C36	66(3)	98(4)	51(3)	4(3)	7(2)	-16(3)
C37	37(2)	75(3)	66(3)	-12(2)	1(2)	-2.1(18)
C38	38.7(19)	75(3)	49(2)	-3(2)	0.4(18)	-2.9(18)
C39	43(2)	85(3)	59(3)	-22(3)	13(2)	-13(2)

Table 4. Bond Lengths for **3ef**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C19	1.750(6)	C13	C14	1.376(17)
Cl2	C25	1.755(7)	C14	C15	1.393(13)
Cl3	C31	1.741(6)	C16	C17	1.380(6)
Cl4	C39	1.751(5)	C16	C21	1.373(8)
O1	C9	1.356(6)	C17	C18	1.372(8)
O1	C10	1.416(8)	C18	C19	1.356(10)
N1	C1	1.329(6)	C19	C20	1.375(9)
N1	C9	1.327(7)	C20	C21	1.365(8)
N2	C11	1.323(7)	C22	C23	1.364(8)
N2	C12	1.349(10)	C22	C27	1.399(9)
C1	C2	1.433(6)	C23	C24	1.412(10)
C1	C11	1.500(6)	C24	C25	1.376(15)
C2	C3	1.447(6)	C25	C26	1.341(14)
C2	C7	1.424(6)	C26	C27	1.380(9)
C3	C4	1.374(6)	C28	C29	1.365(8)
C3	C16	1.504(6)	C28	C33	1.383(7)
C4	C5	1.431(6)	C29	C30	1.383(8)
C4	C22	1.500(6)	C30	C31	1.381(10)
C5	C6	1.369(6)	C31	C32	1.367(11)
C5	C28	1.499(6)	C32	C33	1.383(8)
C6	C7	1.429(6)	C34	C35	1.373(8)
C6	C34	1.501(6)	C34	C38	1.381(6)
C7	C8	1.399(6)	C35	C36	1.392(8)
C8	C9	1.361(7)	C36	C39	1.384(8)
C11	C15	1.378(11)	C37	C38	1.383(6)
C12	C13	1.320(17)	C37	C39	1.354(8)

Table 5. Bond Angles for **3ef.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O1	C10	119.0(5)	C18	C17	C16	120.8(5)
C9	N1	C1	118.9(4)	C19	C18	C17	119.2(5)
C11	N2	C12	116.9(7)	C18	C19	Cl1	119.5(4)
N1	C1	C2	122.8(4)	C18	C19	C20	121.5(5)
N1	C1	C11	111.5(4)	C20	C19	Cl1	119.0(6)
C2	C1	C11	125.7(4)	C21	C20	C19	118.6(6)
C1	C2	C3	125.1(4)	C20	C21	C16	121.4(5)
C7	C2	C1	116.3(4)	C23	C22	C4	121.0(5)
C7	C2	C3	118.6(4)	C23	C22	C27	117.9(5)
C2	C3	C16	122.5(4)	C27	C22	C4	121.1(5)
C4	C3	C2	119.4(4)	C22	C23	C24	121.4(7)
C4	C3	C16	118.0(4)	C25	C24	C23	117.5(8)
C3	C4	C5	121.3(4)	C24	C25	Cl2	117.6(7)
C3	C4	C22	120.5(4)	C26	C25	Cl2	119.5(8)
C5	C4	C22	118.2(4)	C26	C25	C24	122.9(6)
C4	C5	C28	119.6(4)	C25	C26	C27	118.8(8)
C6	C5	C4	120.6(4)	C26	C27	C22	121.5(7)
C6	C5	C28	119.7(4)	C29	C28	C5	120.7(5)
C5	C6	C7	119.7(4)	C29	C28	C33	118.0(5)
C5	C6	C34	120.2(4)	C33	C28	C5	121.1(5)
C7	C6	C34	119.9(4)	C28	C29	C30	122.2(6)
C2	C7	C6	120.4(4)	C31	C30	C29	118.2(6)
C8	C7	C2	118.6(4)	C30	C31	Cl3	119.2(5)
C8	C7	C6	120.9(4)	C32	C31	Cl3	119.4(5)
C9	C8	C7	119.3(4)	C32	C31	C30	121.4(6)
O1	C9	C8	118.5(4)	C31	C32	C33	118.7(6)
N1	C9	O1	117.4(4)	C28	C33	C32	121.4(6)
N1	C9	C8	124.0(4)	C35	C34	C6	123.1(4)
N2	C11	C1	117.3(5)	C35	C34	C38	118.7(4)
N2	C11	C15	124.3(6)	C38	C34	C6	118.2(4)
C15	C11	C1	118.1(5)	C34	C35	C36	121.2(5)
C13	C12	N2	123.1(8)	C39	C36	C35	118.1(5)

C12	C13	C14	120.4(8)	C39	C37	C38	119.0(5)
C13	C14	C15	118.6(10)	C34	C38	C37	121.1(5)
C11	C15	C14	116.6(9)	C36	C39	Cl4	120.3(5)
C17	C16	C3	120.5(5)	C37	C39	Cl4	117.9(4)
C21	C16	C3	121.0(4)	C37	C39	C36	121.8(5)
C21	C16	C17	118.5(5)				

Table 6. Torsion Angles for **3ef.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C19	C20	C21	175.9(6)	C7	C2	C3	C16	-173.5(4)
Cl2	C25	C26	C27	-178.7(5)	C7	C6	C34	C35	75.6(6)
Cl3	C31	C32	C33	179.8(4)	C7	C6	C34	C38	-104.2(5)
N1	C1	C2	C3	-176.0(4)	C7	C8	C9	O1	179.6(5)
N1	C1	C2	C7	4.8(6)	C7	C8	C9	N1	2.4(8)
N1	C1	C11	N2	-108.5(5)	C9	N1	C1	C2	-2.3(7)
N1	C1	C11	C15	65.8(7)	C9	N1	C1	C11	174.8(4)
N2	C11	C15	C14	-4.7(12)	C10	O1	C9	N1	3.9(9)
N2	C12	C13	C14	-3.0(14)	C10	O1	C9	C8	-173.5(7)
C1	N1	C9	O1	-178.7(5)	C11	N2	C12	C13	0.8(11)
C1	N1	C9	C8	-1.4(7)	C11	C1	C2	C3	7.2(7)
C1	C2	C3	C4	-176.0(4)	C11	C1	C2	C7	-172.0(4)
C1	C2	C3	C16	7.2(6)	C12	N2	C11	C1	177.2(5)
C1	C2	C7	C6	178.3(4)	C12	N2	C11	C15	3.3(10)
C1	C2	C7	C8	-3.6(6)	C12	C13	C14	C15	1.3(16)
C1	C11	C15	C14	-178.7(8)	C13	C14	C15	C11	2.3(15)
C2	C1	C11	N2	68.6(6)	C16	C3	C4	C5	174.3(4)
C2	C1	C11	C15	-117.1(6)	C16	C3	C4	C22	-4.2(6)
C2	C3	C4	C5	-2.7(6)	C16	C17	C18	C19	0.7(8)
C2	C3	C4	C22	178.9(4)	C17	C16	C21	C20	0.1(10)
C2	C3	C16	C17	-110.8(5)	C17	C18	C19	Cl1	-176.9(4)
C2	C3	C16	C21	70.7(6)	C17	C18	C19	C20	0.8(10)
C2	C7	C8	C9	0.3(6)	C18	C19	C20	C21	-1.8(12)
C3	C2	C7	C6	-1.0(6)	C19	C20	C21	C16	1.4(12)
C3	C2	C7	C8	177.1(4)	C21	C16	C17	C18	-1.1(8)
C3	C4	C5	C6	-0.3(6)	C22	C4	C5	C6	178.2(4)

C3	C4	C5	C28	-176.7(4)	C22	C4	C5	C28	1.8(6)
C3	C4	C22	C23	-111.2(5)	C22	C23	C24	C25	0.3(9)
C3	C4	C22	C27	68.6(6)	C23	C22	C27	C26	-0.4(8)
C3	C16	C17	C18	-179.7(5)	C23	C24	C25	Cl2	178.3(5)
C3	C16	C21	C20	178.6(6)	C23	C24	C25	C26	0.0(10)
C4	C3	C16	C17	72.4(6)	C24	C25	C26	C27	-0.5(10)
C4	C3	C16	C21	-106.1(6)	C25	C26	C27	C22	0.7(9)
C4	C5	C6	C7	2.6(6)	C27	C22	C23	C24	-0.1(8)
C4	C5	C6	C34	-171.6(4)	C28	C5	C6	C7	179.0(4)
C4	C5	C28	C29	-116.0(5)	C28	C5	C6	C34	4.7(6)
C4	C5	C28	C33	67.8(5)	C28	C29	C30	C31	-0.6(9)
C4	C22	C23	C24	179.7(5)	C29	C28	C33	C32	1.2(7)
C4	C22	C27	C26	179.8(5)	C29	C30	C31	Cl3	-179.0(5)
C5	C4	C22	C23	70.3(6)	C29	C30	C31	C32	0.9(9)
C5	C4	C22	C27	-109.9(5)	C30	C31	C32	C33	-0.1(9)
C5	C6	C7	C2	-1.9(6)	C31	C32	C33	C28	-1.0(8)
C5	C6	C7	C8	-180.0(4)	C33	C28	C29	C30	-0.4(8)
C5	C6	C34	C35	-110.1(6)	C34	C6	C7	C2	172.3(4)
C5	C6	C34	C38	70.0(6)	C34	C6	C7	C8	-5.8(6)
C5	C28	C29	C30	-176.8(5)	C34	C35	C36	C39	0.4(9)
C5	C28	C33	C32	177.6(4)	C35	C34	C38	C37	0.6(7)
C6	C5	C28	C29	67.7(6)	C35	C36	C39	Cl4	179.0(4)
C6	C5	C28	C33	-108.6(5)	C35	C36	C39	C37	-0.3(9)
C6	C7	C8	C9	178.4(4)	C38	C34	C35	C36	-0.6(8)
C6	C34	C35	C36	179.6(5)	C38	C37	C39	Cl4	-178.9(4)
C6	C34	C38	C37	-179.6(4)	C38	C37	C39	C36	0.4(8)
C7	C2	C3	C4	3.2(6)	C39	C37	C38	C34	-0.6(8)

Table 7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3ef**.

Atom	x	y	z	U(eq)
H8	5670	4675	6537	62
H10A	5934	2039	4815	150
H10B	5957	1657	5991	150
H10C	6260	2272	5513	150
H12	7521	4710	4178	127
H13	7495	4183	2501	137
H14	6969	3794	1736	167
H15	6463	4024	2748	121
H17	7062	7111	4823	70
H18	7473	7285	3509	83
H20	6775	6547	1312	104
H21	6371	6330	2633	82
H23	6635	8676	6269	86
H24	6854	10197	5791	115
H26	6438	9905	2895	112
H27	6230	8401	3360	86
H29	5990	8074	7871	78
H30	5735	9436	8586	89
H32	5388	10145	5675	85
H33	5636	8755	4996	73
H35	5734	5935	8236	74
H36	5224	5918	9222	86
H37	4713	6947	6690	71
H38	5222	6956	5720	65

X-Ray Crystallographic Data of **4-A-Br**

Table 1. Crystal Data and Structure Refinement for **4-A-Br.**

Identification code	**4-A-Br**
Empirical formula	$C_{40}H_{52}Br_2Cl_4N_4O_4Rh_2$
Formula weight	1160.29
Temperature/K	29
Crystal system	orthorhombic
Space group	Pbcn
a/Å	29.056(6)
b/Å	9.526(2)
c/Å	33.069(8)
α/°	90
β/°	90
γ/°	90
Volume/Å3	9153(3)
Z	8
ρcalcg/cm3	1.684
ɯ/mm-1	2.744
F(000)	4640.0
Crystal size/mm3	0.25×0.22×0.21
Radiation	MoKα (λ=0.71073)
2Θ range for data	2.464 to 50.018
Index ranges	-34≤h≤22, -10≤k≤11, -39≤l≤37
Reflections collected	47032
Independent reflections	8071 [Rint=0.1938, Rsigma=0.1360]
Data/restraints/parameters	8071/170/524
Goodness-of-fit on F2	1.102
Final R indexes [I>=2σ	R1=0.0935, wR2=0.1352
Final R indexes [all data]	R1=0.1615, wR2=0.1588
Largest diff. peak/hole/e	1.38/-1.12

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4-A-Br**. U (eq) is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U (eq)
Rh1	1416.0(3)	7205.7(10)	3081.7(3)	24.0(2)
Rh2	3544.5(3)	2045.3(9)	465.9(3)	22.8(2)
Br1	2578.8(5)	5822.0(15)	2948.8(4)	38.6(3)
Br2	2435.1(5)	648.5(14)	183.0(4)	37.4(3)
Cl1	1876.3(12)	8581(4)	3537.5(9)	38.4(8)
Cl2	2992.0(12)	3436(4)	827.9(10)	39.3(8)
Cl3	4223.9(15)	2623(6)	8786.3(15)	83.1(15)
Cl4	4185.5(16)	7436(7)	1268.2(16)	95.9(18)
O1	5008(5)	4975(11)	8798(5)	87(4)
O2	3188(4)	6318(13)	1347(3)	66(3)
O3	4964(5)	8467(17)	636(4)	91(4)
O4	5004(4)	8778(12)	1794(4)	94(4)
N1	1903(3)	7529(11)	2599(3)	31(3)
N2	1198(3)	9064(11)	2803(3)	31(2)
N3	3145(3)	2356(10)	-84(3)	22(2)
N4	3811(4)	3873(10)	221(3)	32(3)
C1	1334(5)	4922(15)	3069(5)	51(2)
C2	963(5)	5592(15)	2878(5)	50(2)
C3	727(5)	6406(15)	3165(5)	49(2)
C4	976(5)	6319(15)	3526(5)	49(2)
C5	1355(5)	5372(15)	3464(5)	49(2)
C6	1613(5)	3807(16)	2878(5)	68(3)
C7	1661(5)	4941(17)	3797(5)	66(3)
C8	833(5)	7016(17)	3926(5)	64(3)
C9	281(5)	7163(16)	3101(5)	57(3)
C10	780(5)	5374(17)	2450(5)	64(3)
C11	2307(4)	6915(13)	2535(4)	33(3)
C12	2547(4)	7033(13)	2175(4)	36(3)
C13	2370(5)	7859(14)	1872(4)	40(4)
C14	1969(5)	8562(14)	1940(4)	36(3)

C15	1741(4)	8388(12)	2303(3)	22(3)
C16	1338(4)	9223(12)	2413(4)	26(3)
C17	1129(5)	10215(14)	2176(4)	40(4)
C18	786(5)	11062(15)	2323(5)	53(4)
C19	670(5)	10964(14)	2720(5)	46(4)
C20	880(4)	9923(13)	2953(4)	38(3)
C21	3993(4)	311(13)	326(4)	33.5(18)
C22	4215(4)	1200(13)	606(4)	36.6(19)
C23	3946(4)	1281(13)	960(4)	35.8(18)
C24	3561(4)	345(13)	910(4)	34.2(18)
C25	3598(4)	-265(13)	530(4)	35.1(18)
C26	4162(5)	-104(15)	-76(4)	48(3)
C27	4672(4)	1885(14)	533(4)	46(3)
C28	4067(5)	2094(15)	1336(4)	49(3)
C29	3197(5)	54(15)	1223(4)	46(3)
C30	3327(4)	-1470(13)	379(4)	43(3)
C31	2741(4)	1807(11)	-189(4)	28(3)
C32	2533(4)	2069(14)	-563(4)	39(3)
C33	2755(5)	2942(14)	-827(4)	39(3)
C34	3168(4)	3559(13)	-720(4)	33(3)
C35	3350(4)	3283(11)	-348(3)	16(2)
C36	3738(4)	4056(13)	-180(4)	32(3)
C37	4016(5)	4960(16)	-403(4)	49(4)
C38	4336(6)	5773(17)	-216(5)	63(5)
C39	4381(5)	5694(15)	198(5)	53(4)
C40	4117(5)	4731(13)	408(4)	39(4)

Table 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4-A-Br**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
Rh1	28.3(6)	28.1(5)	15.6(5)	2.0(4)	-0.6(4)	0.6(4)
Rh2	24.8(5)	24.8(5)	18.9(5)	2.1(4)	-1.0(4)	-2.1(4)
Br1	36.3(8)	44.3(8)	35.2(8)	5.3(7)	-0.7(6)	8.1(6)
Br2	32.4(8)	40.0(8)	39.7(8)	3.6(7)	-1.3(6)	-7.3(6)
Cl1	50(2)	43(2)	21.7(19)	-3.6(15)	-8.8(14)	-4.4(16)
Cl2	44(2)	44(2)	30(2)	-1.3(16)	2.2(15)	12.3(16)
Cl3	57(3)	99(4)	94(4)	-14(3)	2(2)	-6(3)
Cl4	55(3)	147(5)	85(4)	37(4)	-4(2)	-3(3)
O1	109(10)	46(7)	106(11)	8(8)	-36(9)	-2(7)
O2	87(10)	64(9)	49(8)	6(6)	12(6)	-12(6)
O3	93(10)	103(10)	76(10)	40(9)	-11(7)	-18(9)
O4	90(10)	103(10)	88(10)	-43(8)	18(7)	-17(8)
N1	31(7)	38(7)	25(6)	4(5)	-7(5)	-7(5)
N2	30(7)	35(6)	27(6)	-1(5)	-5(5)	4(5)
N3	32(6)	24(6)	9(5)	2(4)	-8(4)	7(4)
N4	46(7)	34(6)	16(6)	7(5)	-7(5)	-4(5)
C1	51(3)	50(3)	53(2)	0.2(18)	1.9(17)	-0.9(18)
C2	51(3)	50(3)	50(2)	0.2(18)	0.9(17)	-2.3(18)
C3	49(3)	48(3)	50(2)	1.2(18)	0.0(17)	-0.7(18)
C4	49(3)	49(3)	49(2)	1.2(18)	0.5(17)	-2.9(18)
C5	49(3)	48(3)	51(2)	3.3(18)	-0.7(17)	-2.6(18)
C6	65(5)	63(4)	75(5)	-10(3)	5(4)	6(3)
C7	66(4)	70(5)	64(4)	11(4)	-11(3)	2(3)
C8	68(5)	68(5)	55(3)	-6(3)	6(3)	1(4)
C9	52(4)	59(5)	61(5)	1(4)	-3(3)	4(3)
C10	67(5)	68(5)	57(3)	-7(3)	-6(3)	-2(4)
C11	40(9)	39(8)	21(7)	0(6)	-16(6)	-2(6)
C12	37(8)	35(8)	37(8)	-11(7)	8(6)	1(6)
C13	60(10)	36(8)	24(8)	11(7)	17(6)	-1(7)
C14	48(9)	42(8)	20(7)	-1(6)	8(6)	-6(7)
C15	16(7)	36(7)	14(7)	-7(6)	-7(5)	-1(5)

C16	33(8)	18(6)	28(8)	1(6)	-6(5)	-6(5)
C17	64(11)	41(9)	16(8)	13(6)	8(6)	4(7)
C18	62(11)	42(9)	55(11)	3(8)	-7(8)	17(8)
C19	41(10)	41(9)	57(11)	-2(8)	13(7)	17(7)
C20	34(8)	39(8)	41(9)	-4(7)	-5(6)	16(6)
C21	34(2)	33(3)	34(2)	1.4(17)	0.3(16)	2.7(17)
C22	36(2)	36(3)	37(2)	0.7(18)	-0.4(16)	-0.1(18)
C23	36(2)	35(3)	36(2)	0.7(18)	-1.6(16)	1.4(17)
C24	35(2)	33(3)	34(2)	3.2(17)	0.0(17)	2.4(17)
C25	34(2)	36(2)	36(2)	1.2(17)	-0.7(17)	0.3(17)
C26	51(4)	51(5)	41(3)	-5(3)	7(3)	3(4)
C27	40(3)	48(4)	49(4)	-1(3)	2(3)	-6(3)
C28	52(5)	53(4)	42(3)	-8(3)	-6(3)	1(3)
C29	47(4)	48(5)	43(4)	6(3)	9(3)	0(3)
C30	42(4)	39(4)	46(4)	-2(3)	-4(3)	-2(3)
C31	27(7)	16(6)	40(8)	-8(6)	-12(6)	4(5)
C32	25(8)	48(9)	43(9)	3(7)	-11(6)	6(7)
C33	54(10)	47(9)	15(7)	1(7)	-5(6)	14(7)
C34	38(9)	37(8)	25(8)	5(6)	0(6)	3(6)
C35	20(7)	20(6)	9(6)	-6(5)	-6(4)	5(5)
C36	33(8)	26(7)	38(9)	9(6)	9(6)	7(6)
C37	55(10)	71(11)	21(9)	15(8)	7(7)	-16(8)
C38	69(12)	59(11)	61(12)	12(9)	7(9)	-31(9)
C39	36(9)	56(10)	67(12)	17(9)	-31(8)	-25(7)
C40	54(10)	34(8)	30(9)	2(7)	-5(7)	-16(7)

Table 4. Bond Lengths for **4-A-Br**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rh1	Cl1	2.404(3)	C3	C9	1.499(18)
Rh1	N1	2.156(10)	C4	C5	1.437(19)
Rh1	N2	2.093(10)	C4	C8	1.536(19)
Rh1	C1	2.189(15)	C5	C7	1.474(19)
Rh1	C2	2.132(15)	C11	C12	1.384(16)
Rh1	C3	2.159(14)	C12	C13	1.374(17)
Rh1	C4	2.123(15)	C13	C14	1.362(17)
Rh1	C5	2.163(14)	C14	C15	1.381(16)
Rh2	Cl2	2.401(3)	C15	C16	1.461(16)
Rh2	N3	2.178(8)	C16	C17	1.370(16)
Rh2	N4	2.071(10)	C17	C18	1.369(18)
Rh2	C21	2.155(12)	C18	C19	1.360(19)
Rh2	C22	2.157(13)	C19	C20	1.395(18)
Rh2	C23	2.137(13)	C21	C22	1.409(17)
Rh2	C24	2.187(12)	C21	C25	1.442(17)
Rh2	C25	2.217(12)	C21	C26	1.472(17)
Br1	C11	1.892(12)	C22	C23	1.410(17)
Br2	C31	1.877(13)	C22	C27	1.500(17)
N1	C11	1.328(15)	C23	C24	1.442(17)
N1	C15	1.361(14)	C23	C28	1.504(17)
N2	C16	1.359(14)	C24	C25	1.388(16)
N2	C20	1.331(15)	C24	C29	1.507(17)
N3	C31	1.332(14)	C25	C30	1.477(16)
N3	C35	1.375(13)	C31	C32	1.398(16)
N4	C36	1.356(15)	C32	C33	1.369(17)
N4	C40	1.356(15)	C33	C34	1.382(17)
C1	C2	1.403(19)	C34	C35	1.366(15)
C1	C5	1.376(19)	C35	C36	1.455(16)
C1	C6	1.477(19)	C36	C37	1.392(17)
C2	C3	1.405(19)	C37	C38	1.358(19)
C2	C10	1.53(2)	C38	C39	1.380(19)
C3	C4	1.400(19)	C39	C40	1.385(18)

Table 5. Bond Angles for **4-A-Br**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Rh1	Cl1	91.2(3)	C2	C3	Rh1	69.9(9)
N1	Rh1	C1	101.5(5)	C2	C3	C9	126.4(14)
N1	Rh1	C3	138.9(5)	C4	C3	Rh1	69.5(9)
N1	Rh1	C5	127.0(5)	C4	C3	C2	107.0(13)
N2	Rh1	Cl1	89.0(3)	C4	C3	C9	126.5(14)
N2	Rh1	N1	75.6(4)	C9	C3	Rh1	127.9(10)
N2	Rh1	C1	143.0(5)	C3	C4	Rh1	72.3(9)
N2	Rh1	C2	106.5(5)	C3	C4	C5	108.0(13)
N2	Rh1	C3	94.3(5)	C3	C4	C8	124.6(14)
N2	Rh1	C4	117.4(5)	C5	C4	Rh1	71.9(8)
N2	Rh1	C5	156.2(5)	C5	C4	C8	127.1(14)
C1	Rh1	Cl1	127.9(4)	C8	C4	Rh1	125.9(10)
C2	Rh1	Cl1	159.2(4)	C1	C5	Rh1	72.6(9)
C2	Rh1	N1	105.9(5)	C1	C5	C4	107.4(13)
C2	Rh1	C1	37.9(5)	C1	C5	C7	130.4(14)
C2	Rh1	C3	38.2(5)	C4	C5	Rh1	68.9(8)
C2	Rh1	C5	63.4(6)	C4	C5	C7	121.9(14)
C3	Rh1	Cl1	128.9(4)	C7	C5	Rh1	127.7(11)
C3	Rh1	C1	63.3(5)	N1	C11	Br1	119.8(9)
C3	Rh1	C5	64.2(5)	N1	C11	C12	123.1(11)
C4	Rh1	Cl1	96.8(4)	C12	C11	Br1	117.2(10)
C4	Rh1	N1	164.8(5)	C13	C12	C11	119.0(12)
C4	Rh1	C1	63.4(6)	C14	C13	C12	118.9(12)
C4	Rh1	C2	64.0(6)	C13	C14	C15	119.6(12)
C4	Rh1	C3	38.2(5)	N1	C15	C14	122.1(11)
C4	Rh1	C5	39.2(5)	N1	C15	C16	115.2(10)
C5	Rh1	Cl1	96.9(4)	C14	C15	C16	122.5(11)
C5	Rh1	C1	36.8(5)	N2	C16	C15	114.6(10)
N3	Rh2	Cl2	89.2(3)	N2	C16	C17	119.1(11)
N3	Rh2	C24	132.3(4)	C17	C16	C15	126.0(12)
N3	Rh2	C25	104.6(4)	C18	C17	C16	121.7(13)
N4	Rh2	Cl2	88.9(3)	C19	C18	C17	118.8(14)

N4	Rh2	N3	76.0(4)	C18	C19	C20	118.3(13)
N4	Rh2	C21	109.5(4)	N2	C20	C19	122.4(13)
N4	Rh2	C22	93.4(4)	C22	C21	Rh2	71.0(7)
N4	Rh2	C23	112.4(4)	C22	C21	C25	106.6(11)
N4	Rh2	C24	151.3(4)	C22	C21	C26	127.1(12)
N4	Rh2	C25	147.8(4)	C25	C21	Rh2	73.1(7)
C21	Rh2	Cl2	159.2(4)	C25	C21	C26	125.9(12)
C21	Rh2	N3	104.3(4)	C26	C21	Rh2	127.0(9)
C21	Rh2	C22	38.1(5)	C21	C22	Rh2	70.8(7)
C21	Rh2	C24	64.1(5)	C21	C22	C23	109.0(12)
C21	Rh2	C25	38.5(4)	C21	C22	C27	124.1(12)
C22	Rh2	Cl2	134.6(4)	C23	C22	Rh2	70.1(8)
C22	Rh2	N3	135.3(4)	C23	C22	C27	126.8(12)
C22	Rh2	C24	63.9(5)	C27	C22	Rh2	127.1(9)
C22	Rh2	C25	63.0(5)	C22	C23	Rh2	71.6(8)
C23	Rh2	Cl2	99.9(4)	C22	C23	C24	107.4(11)
C23	Rh2	N3	167.6(4)	C22	C23	C28	125.8(12)
C23	Rh2	C21	64.7(5)	C24	C23	Rh2	72.4(7)
C23	Rh2	C22	38.3(5)	C24	C23	C28	126.6(12)
C23	Rh2	C24	38.9(5)	C28	C23	Rh2	125.7(9)
C23	Rh2	C25	63.3(5)	C23	C24	Rh2	68.7(7)
C24	Rh2	Cl2	95.1(3)	C23	C24	C29	125.4(12)
C24	Rh2	C25	36.7(4)	C25	C24	Rh2	72.8(7)
C25	Rh2	Cl2	123.1(3)	C25	C24	C23	107.7(11)
C11	N1	Rh1	129.4(8)	C25	C24	C29	126.8(12)
C11	N1	C15	117.2(10)	C29	C24	Rh2	125.7(9)
C15	N1	Rh1	113.0(8)	C21	C25	Rh2	68.4(7)
C16	N2	Rh1	115.0(8)	C21	C25	C30	124.1(12)
C20	N2	Rh1	124.5(9)	C24	C25	Rh2	70.5(7)
C20	N2	C16	119.4(11)	C24	C25	C21	109.0(11)
C31	N3	Rh2	129.3(8)	C24	C25	C30	126.2(12)
C31	N3	C35	118.0(9)	C30	C25	Rh2	134.6(9)
C35	N3	Rh2	112.7(7)	N3	C31	Br2	118.6(9)
C36	N4	Rh2	115.6(8)	N3	C31	C32	122.8(12)
C36	N4	C40	118.2(11)	C32	C31	Br2	118.6(9)

C40	N4	Rh2	124.9(8)	C33	C32	C31	117.8(12)
C2	C1	Rh1	68.9(9)	C32	C33	C34	120.4(12)
C2	C1	C6	123.8(15)	C35	C34	C33	119.0(12)
C5	C1	Rh1	70.6(9)	N3	C35	C36	114.8(9)
C5	C1	C2	108.6(13)	C34	C35	N3	121.8(10)
C5	C1	C6	127.3(14)	C34	C35	C36	123.0(11)
C6	C1	Rh1	131.5(11)	N4	C36	C35	115.4(10)
C1	C2	Rh1	73.2(9)	N4	C36	C37	120.4(12)
C1	C2	C3	108.8(14)	C37	C36	C35	124.2(12)
C1	C2	C10	128.6(14)	C38	C37	C36	120.7(14)
C3	C2	Rh1	71.9(9)	C37	C38	C39	119.1(14)
C3	C2	C10	122.1(14)	C38	C39	C40	118.8(13)
C10	C2	Rh1	127.4(11)	N4	C40	C39	122.2(13)

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4-A-Br**.

Atom	x	y	z	U (eq)
H1A	4810	4335	8755	130
H1B	5266	4573	8762	130
H2A	3421	6806	1283	100
H2B	3110	5802	1149	100
H3A	5228	8411	746	136
H3B	4777	8480	834	136
H4A	5250	8552	1671	141
H4B	4787	8501	1641	141
H6A	1728	4135	2623	101
H6B	1425	2991	2836	101
H6C	1866	3572	3051	101
H7A	1917	4426	3689	99
H7B	1493	4356	3982	99
H7C	1771	5759	3936	99
H8A	1102	7320	4069	96
H8B	666	6354	4088	96
H8C	640	7812	3869	96
H9A	274	7993	3266	86
H9B	30	6560	3175	86
H9C	252	7422	2822	86
H10A	676	6255	2342	96
H10B	527	4724	2456	96
H10C	1020	5004	2281	96
H12	2824	6560	2139	43
H13	2521	7936	1625	48
H14	1849	9156	1743	44
H17	1222	10315	1909	49
H18	636	11692	2154	64
H19	457	11574	2834	56
H20	795	9827	3222	45
H26A	3907	-192	-258	72

H26B	4319	-988	-57	72
H26C	4370	598	-176	72
H27A	4682	2249	263	69
H27B	4913	1205	568	69
H27C	4714	2638	723	69
H28A	4305	2759	1274	74
H28B	4173	1459	1541	74
H28C	3800	2584	1431	74
H29A	3075	926	1322	69
H29B	3330	-462	1444	69
H29C	2953	-487	1104	69
H30A	3032	-1484	510	64
H30B	3488	-2326	437	64
H30C	3286	-1381	92	64
H32	2252	1663	-629	46
H33	2628	3121	-1080	46
H34	3320	4153	-899	40
H37	3983	5008	-682	59
H38	4522	6375	-366	75
H39	4586	6277	334	63
H40	4149	4670	688	47

X-Ray Crystallographic Data of **4-C-Br**

Table 1 Crystal Data and Structure Refinement for **4-C-Br**.

Identification code	**4-C-Br**
Empirical formula	$C_{20}H_{21}BrClN_2Rh$
Formula weight	507.66
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a=8.968(3) A alpha=65.119(5) deg.
	b=11.141(4) A beta=83.659(6) deg.
	c=11.249(3) A gamma=80.437(6) deg.
Volume	1004.4(5) A^3
Z, Calculated density	2, 1.679 Mg/m^3
Absorption coefficient	2.977 mm^-1
F(000)	504
Crystal size	0.220x0.210x0.180 mm
Theta range for data collection	1.998 to 26.497 deg.
Limiting indices	-9<=h<=11, -12<=k<=13, -9<=l<=14
Reflections collected/unique	6337/4117 [R(int)=0.0411]
Completeness to theta = 25.242	98.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4117/0/226
Goodness-of-fit on F^2	1.078
Final R indices [I>2sigma(I)]	R1=0.0603, wR2=0.1799
R indices (all data)	R1=0.0686, wR2=0.1917
Extinction coefficient	n/a
Largest diff. peak and hole	1.426 and -2.606 e.A^-3

Table 2. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (A^2 x 10^3) for **4-C-Br**. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U (eq)
Rh(1)	2068(1)	3538(1)	2919(1)	27(1)
Br(1)	2516(2)	234(1)	9339(1)	103(1)
Cl(1)	-625(2)	4051(2)	3029(2)	42(1)
N(1)	1836(6)	1549(5)	3380(4)	30(1)
N(2)	2268(7)	610(6)	6790(5)	43(1)
C(1)	4264(8)	3589(7)	1958(6)	39(1)
C(2)	3250(7)	4239(6)	897(5)	34(1)
C(3)	2428(7)	5341(6)	1061(6)	36(1)
C(4)	2926(8)	5419(7)	2196(6)	42(2)
C(5)	4147(7)	4368(7)	2691(6)	39(1)
C(6)	5391(9)	2380(8)	2151(8)	58(2)
C(7)	3185(9)	3826(8)	-201(6)	46(2)
C(8)	1201(9)	6312(7)	227(7)	52(2)
C(9)	2447(11)	6539(8)	2614(8)	64(2)
C(10)	5161(10)	4132(10)	3766(8)	65(2)
C(11)	1534(8)	1078(7)	2526(6)	40(1)
C(12)	1424(8)	-242(7)	2873(6)	44(2)
C(13)	1607(9)	-1131(7)	4168(7)	46(2)
C(14)	1880(8)	-655(6)	5059(6)	38(1)
C(15)	1983(7)	695(6)	4648(5)	32(1)
C(16)	2138(7)	1362(6)	5494(5)	33(1)
C(17)	2050(7)	2749(6)	4886(5)	31(1)
C(18)	1995(8)	3401(7)	5718(6)	42(2)
C(19)	2102(10)	2647(8)	7056(7)	52(2)
C(20)	2281(10)	1288(7)	7496(6)	51(2)

Table 3 Bond Lengths [A] and Angles [deg] for **4-C-Br**.

Rh(1)-C(17)	2.007(6)
Rh(1)-N(1)	2.094(5)
Rh(1)-C(1)	2.137(7)
Rh(1)-C(4)	2.146(7)
Rh(1)-C(5)	2.159(6)
Rh(1)-C(3)	2.245(6)
Rh(1)-C(2)	2.270(6)
Rh(1)-Cl(1)	2.3896(18)
Br(1)-C(20)	1.920(6)
N(1)-C(11)	1.342(7)
N(1)-C(15)	1.348(7)
N(2)-C(20)	1.309(9)
N(2)-C(16)	1.348(8)
C(1)-C(5)	1.414(9)
C(1)-C(2)	1.438(8)
C(1)-C(6)	1.494(10)
C(2)-C(3)	1.395(9)
C(2)-C(7)	1.498(8)
C(3)-C(4)	1.438(9)
C(3)-C(8)	1.497(9)
C(4)-C(5)	1.428(9)
C(4)-C(9)	1.495(9)
C(5)-C(10)	1.501(9)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600

C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(12)	1.371(9)
C(11)-H(11)	0.9300
C(12)-C(13)	1.384(9)
C(12)-H(12)	0.9300
C(13)-C(14)	1.375(9)
C(13)-H(13)	0.9300
C(14)-C(15)	1.391(9)
C(14)-H(14)	0.9300
C(15)-C(16)	1.462(8)
C(16)-C(17)	1.394(8)
C(17)-C(18)	1.398(8)
C(18)-C(19)	1.386(9)
C(18)-H(18)	0.9300
C(19)-C(20)	1.368(11)
C(19)-H(19)	0.9300
C(17)-Rh(1)-N(1)	78.6(2)
C(17)-Rh(1)-C(1)	115.2(2)
N(1)-Rh(1)-C(1)	98.5(2)
C(17)-Rh(1)-C(4)	108.0(2)
N(1)-Rh(1)-C(4)	163.2(2)
C(1)-Rh(1)-C(4)	64.7(3)
C(17)-Rh(1)-C(5)	93.6(2)
N(1)-Rh(1)-C(5)	127.2(2)
C(1)-Rh(1)-C(5)	38.4(2)
C(4)-Rh(1)-C(5)	38.8(3)
C(17)-Rh(1)-C(3)	145.7(2)
N(1)-Rh(1)-C(3)	135.2(2)
C(1)-Rh(1)-C(3)	62.6(2)
C(4)-Rh(1)-C(3)	38.1(2)
C(5)-Rh(1)-C(3)	63.1(2)

C(17)-Rh(1)-C(2)	153.1(2)
N(1)-Rh(1)-C(2)	103.9(2)
C(1)-Rh(1)-C(2)	37.9(2)
C(4)-Rh(1)-C(2)	63.0(2)
C(5)-Rh(1)-C(2)	63.1(2)
C(3)-Rh(1)-C(2)	36.0(2)
C(17)-Rh(1)-Cl(1)	89.30(18)
N(1)-Rh(1)-Cl(1)	89.55(15)
C(1)-Rh(1)-Cl(1)	155.21(17)
C(4)-Rh(1)-Cl(1)	105.7(2)
C(5)-Rh(1)-Cl(1)	142.97(19)
C(3)-Rh(1)-Cl(1)	95.36(17)
C(2)-Rh(1)-Cl(1)	117.36(16)
C(11)-N(1)-C(15)	118.4(5)
C(11)-N(1)-Rh(1)	125.4(4)
C(15)-N(1)-Rh(1)	116.1(4)
C(20)-N(2)-C(16)	114.6(6)
C(5)-C(1)-C(2)	108.9(6)
C(5)-C(1)-C(6)	125.5(6)
C(2)-C(1)-C(6)	125.3(6)
C(5)-C(1)-Rh(1)	71.6(4)
C(2)-C(1)-Rh(1)	76.1(4)
C(6)-C(1)-Rh(1)	124.2(5)
C(3)-C(2)-C(1)	106.9(5)
C(3)-C(2)-C(7)	127.8(6)
C(1)-C(2)-C(7)	125.2(6)
C(3)-C(2)-Rh(1)	71.0(3)
C(1)-C(2)-Rh(1)	66.0(3)
C(7)-C(2)-Rh(1)	130.4(5)
C(2)-C(3)-C(4)	109.3(5)
C(2)-C(3)-C(8)	127.2(6)
C(4)-C(3)-C(8)	123.5(6)
C(2)-C(3)-Rh(1)	73.0(3)
C(4)-C(3)-Rh(1)	67.2(3)
C(8)-C(3)-Rh(1)	125.4(5)

C(5)-C(4)-C(3)	107.0(5)
C(5)-C(4)-C(9)	126.4(7)
C(3)-C(4)-C(9)	125.6(7)
C(5)-C(4)-Rh(1)	71.1(4)
C(3)-C(4)-Rh(1)	74.6(4)
C(9)-C(4)-Rh(1)	128.1(5)
C(1)-C(5)-C(4)	107.4(5)
C(1)-C(5)-C(10)	125.4(7)
C(4)-C(5)-C(10)	127.2(7)
C(1)-C(5)-Rh(1)	69.9(4)
C(4)-C(5)-Rh(1)	70.1(4)
C(10)-C(5)-Rh(1)	126.4(5)
C(1)-C(6)-H(6A)	109.6
C(1)-C(6)-H(6B)	109.2
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.6
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.4
C(2)-C(7)-H(7B)	109.6
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.4
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.6
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.4
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.4
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5

H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.4
H(10A)-C(10)-	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-	109.5
H(10B)-C(10)-	109.5
N(1)-C(11)-C(12)	123.1(6)
N(1)-C(11)-H(11)	118.4
C(12)-C(11)-H(11)	118.4
C(11)-C(12)-C(13)	118.7(6)
C(11)-C(12)-H(12)	120.6
C(13)-C(12)-H(12)	120.6
C(14)-C(13)-C(12)	118.7(6)
C(14)-C(13)-H(13)	120.6
C(12)-C(13)-H(13)	120.6
C(13)-C(14)-C(15)	119.9(6)
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-H(14)	120.0
N(1)-C(15)-C(14)	121.0(5)
N(1)-C(15)-C(16)	112.8(5)
C(14)-C(15)-C(16)	126.1(5)
N(2)-C(16)-C(17)	125.6(6)
N(2)-C(16)-C(15)	118.1(6)
C(17)-C(16)-C(15)	116.2(5)
C(16)-C(17)-C(18)	116.1(5)
C(16)-C(17)-Rh(1)	115.2(4)
C(18)-C(17)-Rh(1)	128.7(5)
C(19)-C(18)-C(17)	119.2(6)
C(19)-C(18)-H(18)	120.4
C(17)-C(18)-H(18)	120.4
C(20)-C(19)-C(18)	117.8(6)
C(20)-C(19)-H(19)	121.1
C(18)-C(19)-H(19)	121.1
N(2)-C(20)-C(19)	126.5(6)

N(2)-C(20)-Br(1)	115.3(5)
C(19)-C(20)-Br(1)	118.1(5)

Table 4. Anisotropic Displacement Parameters (A^2 x 10^3) for **4-C-Br**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Rh(1)	33(1)	22(1)	26(1)	-11(1)	-2(1)	-2(1)
Br(1)	203(2)	70(1)	30(1)	-14(1)	-21(1)	-7(1)
Cl(1)	37(1)	37(1)	42(1)	-10(1)	-3(1)	2(1)
N(1)	39(3)	24(2)	28(2)	-13(2)	-4(2)	-1(2)
N(2)	57(4)	43(3)	27(2)	-13(2)	-9(2)	1(3)
C(1)	42(4)	42(4)	33(3)	-16(3)	0(3)	-1(3)
C(2)	41(3)	36(3)	26(3)	-12(2)	0(2)	-10(3)
C(3)	39(3)	26(3)	36(3)	-5(2)	1(2)	-8(2)
C(4)	54(4)	33(4)	44(3)	-21(3)	9(3)	-16(3)
C(5)	26(3)	45(4)	48(3)	-18(3)	0(3)	-15(3)
C(6)	43(4)	66(5)	63(5)	-30(4)	0(3)	7(4)
C(7)	56(4)	55(4)	34(3)	-22(3)	8(3)	-18(3)
C(8)	54(5)	37(4)	49(4)	-2(3)	-6(3)	1(3)
C(9)	90(6)	44(5)	69(5)	-36(4)	13(5)	-20(4)
C(10)	54(5)	102(7)	54(4)	-39(5)	-11(4)	-26(4)
C(11)	55(4)	35(4)	33(3)	-16(3)	-2(3)	-9(3)
C(12)	56(4)	41(4)	41(3)	-23(3)	0(3)	-10(3)
C(13)	67(5)	23(3)	50(4)	-17(3)	1(3)	-7(3)
C(14)	49(4)	29(3)	35(3)	-11(2)	-7(3)	0(3)
C(15)	39(3)	25(3)	29(3)	-11(2)	-3(2)	1(2)
C(16)	37(3)	29(3)	29(3)	-10(2)	-7(2)	4(2)
C(17)	35(3)	29(3)	30(3)	-13(2)	2(2)	-3(2)
C(18)	59(4)	36(4)	36(3)	-19(3)	2(3)	-6(3)
C(19)	77(5)	52(5)	35(3)	-28(3)	0(3)	-7(4)
C(20)	81(5)	46(4)	24(3)	-11(3)	-8(3)	-5(4)

Table 5. Hydrogen Coordinates (x 10^4) and Isotropic Displacement Parameters (A^2 x 10^3) for **4-C-Br**.

	x	y	z	U(eq)
H(6A)	6373	2643	1822	87
H(6B)	5093	1914	1684	87
H(6C)	5428	1803	3068	87
H(7A)	2242	4216	-621	69
H(7B)	3264	2871	140	69
H(7C)	4007	4128	-828	69
H(8A)	895	5970	-349	79
H(8B)	1570	7150	-284	79
H(8C)	350	6438	779	79
H(9A)	2673	6245	3516	95
H(9B)	1378	6814	2516	95
H(9C)	2983	7278	2079	95
H(10A)	4568	3969	4570	97
H(10B)	5657	4906	3538	97
H(10C)	5908	3372	3876	97
H(11)	1394	1674	1658	48
H(12)	1230	-534	2250	52
H(13)	1545	-2032	4431	56
H(14)	1997	-1235	5936	46
H(18)	1889	4328	5377	51
H(19)	2052	3053	7635	62

Table 6. Torsion Angles [deg] for **4-C-Br**.

C(5)-C(1)-C(2)-C(3)	-5.2(7)
C(6)-C(1)-C(2)-C(3)	-178.3(7)
Rh(1)-C(1)-C(2)-C(3)	59.5(5)
C(5)-C(1)-C(2)-C(7)	171.6(6)
C(6)-C(1)-C(2)-C(7)	-1.5(11)
Rh(1)-C(1)-C(2)-C(7)	-123.7(6)
C(5)-C(1)-C(2)-Rh(1)	-64.7(4)
C(6)-C(1)-C(2)-Rh(1)	122.2(8)
C(1)-C(2)-C(3)-C(4)	1.2(7)
C(7)-C(2)-C(3)-C(4)	-175.5(6)
Rh(1)-C(2)-C(3)-C(4)	57.6(4)
C(1)-C(2)-C(3)-C(8)	-178.2(6)
C(7)-C(2)-C(3)-C(8)	5.0(11)
Rh(1)-C(2)-C(3)-C(8)	-121.9(7)
C(1)-C(2)-C(3)-Rh(1)	-56.3(4)
C(7)-C(2)-C(3)-Rh(1)	126.9(7)
C(2)-C(3)-C(4)-C(5)	3.1(7)
C(8)-C(3)-C(4)-C(5)	-177.4(6)
Rh(1)-C(3)-C(4)-C(5)	64.2(4)
C(2)-C(3)-C(4)-C(9)	172.8(7)
C(8)-C(3)-C(4)-C(9)	-7.7(11)
Rh(1)-C(3)-C(4)-C(9)	-126.1(8)
C(2)-C(3)-C(4)-Rh(1)	-61.1(5)
C(8)-C(3)-C(4)-Rh(1)	118.4(6)
C(2)-C(1)-C(5)-C(4)	7.1(7)
C(6)-C(1)-C(5)-C(4)	-179.8(7)
Rh(1)-C(1)-C(5)-C(4)	-60.4(4)
C(2)-C(1)-C(5)-C(10)	-171.4(7)
C(6)-C(1)-C(5)-C(10)	1.7(12)
Rh(1)-C(1)-C(5)-C(10)	121.0(7)
C(2)-C(1)-C(5)-Rh(1)	67.6(5)
C(6)-C(1)-C(5)-Rh(1)	-119.3(7)
C(3)-C(4)-C(5)-C(1)	-6.3(7)

C(9)-C(4)-C(5)-C(1)	-175.8(7)
Rh(1)-C(4)-C(5)-C(1)	60.3(4)
C(3)-C(4)-C(5)-C(10)	172.2(7)
C(9)-C(4)-C(5)-C(10)	2.7(11)
Rh(1)-C(4)-C(5)-C(10)	-121.2(7)
C(3)-C(4)-C(5)-Rh(1)	-66.6(4)
C(9)-C(4)-C(5)-Rh(1)	123.9(7)
C(15)-N(1)-C(11)-C(12)	-2.5(10)
Rh(1)-N(1)-C(11)-C(12)	178.6(5)
N(1)-C(11)-C(12)-C(13)	1.1(11)
C(11)-C(12)-C(13)-C(14)	0.5(11)
C(12)-C(13)-C(14)-C(15)	-0.6(11)
C(11)-N(1)-C(15)-C(14)	2.3(9)
Rh(1)-N(1)-C(15)-C(14)	-178.7(5)
C(11)-N(1)-C(15)-C(16)	-173.5(5)
Rh(1)-N(1)-C(15)-C(16)	5.5(7)
C(13)-C(14)-C(15)-N(1)	-0.8(10)
C(13)-C(14)-C(15)-C(16)	174.4(7)
C(20)-N(2)-C(16)-C(17)	1.2(10)
C(20)-N(2)-C(16)-C(15)	-174.8(6)
N(1)-C(15)-C(16)-N(2)	178.9(6)
C(14)-C(15)-C(16)-N(2)	3.4(10)
N(1)-C(15)-C(16)-C(17)	2.5(8)
C(14)-C(15)-C(16)-C(17)	-173.0(6)
N(2)-C(16)-C(17)-C(18)	-4.3(10)
C(15)-C(16)-C(17)-C(18)	171.8(6)
N(2)-C(16)-C(17)-Rh(1)	174.3(5)
C(15)-C(16)-C(17)-Rh(1)	-9.6(7)
C(16)-C(17)-C(18)-C(19)	2.9(10)
Rh(1)-C(17)-C(18)-C(19)	-175.4(6)
C(17)-C(18)-C(19)-C(20)	1.0(12)
C(16)-N(2)-C(20)-C(19)	3.6(12)
C(16)-N(2)-C(20)-Br(1)	-178.5(5)
C(18)-C(19)-C(20)-N(2)	-4.7(14)
C(18)-C(19)-C(20)-Br(1)	177.4(6)

X-Ray Crystallographic Data of **4-D-Br**

Table 1. Crystal Data and Structure Refinement for **4-D-Br**.

Identification code	**4-D-Br**
Empirical formula	$C_{34}H_{31}BrClN_2Rh$
Formula weight	685.88
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	11.4817(8)
b/Å	20.8558(13)
c/Å	14.9780(10)
α/°	90
β/°	111.615(8)
γ/°	90
Volume/Å3	3334.4(4)
Z	4
ρcalcg/cm3	1.366
μ/mm^{-1}	1.814
F(000)	1384.0
Crystal size/mm3	0.18×0.15×0.14
Radiation	MoKα (λ=0.71073)
2Θ range for data collection/°	5.462 to 50.012
Index ranges	-13≤h≤13, -16≤k≤24, -
Reflections collected	14848
Independent reflections	5875 [Rint=0.0459,
Data/restraints/parameters	5875/30/345
Goodness-of-fit on F2	1.020
Final R indexes [I>=2σ (I)]	R1=0.0429, wR2=0.0922
Final R indexes [all data]	R1=0.0655, wR2=0.1055
Largest diff. peak/hole/e Å-3	1.02/-1.04

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4-D-Br**. U (eq) is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U (eq)
Rh1	8388.9(3)	6950.5(2)	3050.1(2)	32.23(12)
Br1	2459.1(6)	5608.3(4)	1715.7(6)	92.9(3)
Cl1	10137.3(11)	7266.3(7)	2612.4(8)	50.7(3)
N2	7625(3)	6431.1(18)	1727(2)	35.6(8)
N1	4548(4)	6120(2)	1516(3)	47.6(10)
C28	7403(4)	7740(2)	2342(3)	35.1(10)
C29	8138(4)	8342(2)	2392(3)	34.5(10)
C17	5291(4)	7209(2)	1812(3)	37.9(11)
C12	8455(4)	6136(2)	1430(3)	41.3(11)
C21	6149(4)	7751(2)	1859(3)	37.1(10)
C18	4223(4)	7352(3)	2021(3)	48.2(12)
C4	9334(4)	7107(3)	4576(3)	45.0(12)
C11	6399(4)	6321(2)	1234(3)	39.5(11)
C22	5461(3)	8354.1(14)	1386(2)	44.3(12)
C23	5519(3)	8914.4(18)	1903.0(19)	68.8(16)
C24	4875(4)	9457.6(15)	1441(3)	92(2)
C25	4172(3)	9440.5(16)	462(3)	83.8(19)
C26	4114(3)	8880(2)	-55.7(19)	72.5(17)
C27	4758(3)	8336.9(16)	406(2)	57.6(14)
C5	8004(4)	7095(2)	4353(3)	37.6(11)
C1	7579(4)	6476(2)	3973(3)	36.2(10)
C16	5408(4)	6582(2)	1561(3)	39.3(11)
C2	8657(5)	6098(2)	4025(3)	44.7(12)
C20	3587(5)	6283(3)	1732(4)	54.8(13)
C19	3365(5)	6891(3)	1991(4)	54.4(13)
C15	6015(5)	5929(3)	419(3)	53.3(13)
C32	9398(5)	9508(3)	2473(4)	58.8(14)
C3	9706(5)	6472(3)	4395(3)	51.0(13)
C13	8105(5)	5739(3)	634(3)	58.0(14)
C7	8570(5)	5403(3)	3743(4)	65.2(15)

C30	8624(4)	8695(2)	3231(3)	48.1(12)
C6	6311(4)	6210(3)	3803(3)	52.7(13)
C33	8930(5)	9159(3)	1641(3)	65.3(16)
C34	8325(5)	8589(3)	1607(3)	52.7(14)
C10	7200(5)	7607(2)	4535(3)	54.0(13)
C14	6864(6)	5638(3)	119(3)	63.6(16)
C9	10237(5)	7626(3)	5094(3)	68.8(17)
C8	11034(5)	6279(4)	4595(4)	85(2)
C31	9238(5)	9266(3)	3271(3)	52.8(13)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4-D-Br**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
Rh1	36.6(2)	31.1(2)	32.35(19)	0.61(14)	16.58(15)	1.34(17)
Br1	78.2(5)	65.5(5)	149.9(6)	-17.5(4)	59.7(4)	-34.4(4)
Cl1	46.7(7)	52.8(8)	63.4(7)	-0.7(6)	32.9(6)	-3.0(6)
N2	43(2)	30(2)	36.6(19)	-0.4(16)	17.7(17)	3.8(19)
N1	44(2)	39(3)	59(2)	-9.0(19)	17.2(19)	-11(2)
C28	46(3)	30(3)	37(2)	-2.2(19)	24(2)	3(2)
C29	39(2)	24(2)	41(2)	-1.1(19)	15.1(19)	-1(2)
C17	40(3)	32(3)	41(2)	1(2)	16(2)	-2(2)
C12	45(3)	37(3)	47(3)	-2(2)	22(2)	10(2)
C21	43(3)	29(3)	46(2)	-2(2)	25(2)	0(2)
C18	45(3)	37(3)	71(3)	5(2)	31(2)	4(3)
C4	51(3)	51(3)	34(2)	3(2)	16(2)	-6(3)
C11	49(3)	28(3)	41(2)	1.2(19)	16(2)	-2(2)
C22	34(3)	39(3)	65(3)	8(2)	24(2)	1(2)
C23	62(3)	45(3)	91(3)	0(3)	17(2)	5(3)
C24	82(4)	62(4)	127(4)	-4(3)	31(3)	9(3)
C25	66(3)	70(4)	121(4)	28(3)	41(3)	9(3)
C26	57(3)	92(4)	75(3)	27(3)	32(2)	8(3)
C27	44(3)	66(4)	66(3)	15(3)	25(3)	12(3)
C5	48(3)	38(3)	33(2)	-1.0(19)	21(2)	-5(2)
C1	51(3)	35(3)	30(2)	1.4(19)	22.8(19)	0(2)
C16	42(3)	34(3)	39(2)	0(2)	11(2)	-1(2)
C2	69(3)	32(3)	45(3)	9(2)	35(2)	16(3)
C20	42(3)	48(4)	73(3)	1(3)	20(2)	-7(3)
C19	43(3)	46(4)	81(3)	6(3)	31(3)	1(3)
C15	58(3)	49(3)	46(3)	-13(2)	12(2)	0(3)
C32	74(4)	40(3)	75(3)	-7(3)	43(3)	-19(3)
C3	51(3)	65(4)	40(3)	17(2)	20(2)	15(3)
C13	77(4)	51(4)	57(3)	-12(3)	37(3)	13(3)
C7	90(3)	48(3)	69(3)	7(2)	43(2)	15(3)
C30	61(3)	39(3)	46(3)	-4(2)	23(2)	-11(3)

C6	60(3)	56(4)	51(3)	8(2)	30(2)	-12(3)
C33	93(4)	60(4)	52(3)	3(3)	37(3)	-26(4)
C34	75(4)	48(3)	41(3)	-3(2)	29(2)	-21(3)
C10	79(4)	41(3)	57(3)	-6(2)	42(3)	0(3)
C14	86(4)	51(4)	53(3)	-21(3)	25(3)	6(3)
C9	66(4)	89(5)	43(3)	-4(3)	11(2)	-23(4)
C8	52(3)	124(7)	77(4)	31(4)	21(3)	23(4)
C31	65(3)	38(3)	59(3)	-16(2)	27(3)	-14(3)

Table 4. Bond Lengths for **4-D-Br**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rh1	Cl1	2.4214(12)	C4	C3	1.447(7)
Rh1	N2	2.142(3)	C4	C9	1.503(7)
Rh1	C28	2.057(4)	C11	C16	1.497(6)
Rh1	C4	2.163(4)	C11	C15	1.399(6)
Rh1	C5	2.175(4)	C22	C23	1.3900
Rh1	C1	2.168(4)	C22	C27	1.3900
Rh1	C2	2.249(4)	C23	C24	1.3900
Rh1	C3	2.258(4)	C24	C25	1.3900
Br1	C20	1.906(5)	C25	C26	1.3900
N2	C12	1.342(5)	C26	C27	1.3900
N2	C11	1.346(5)	C5	C1	1.423(6)
N1	C16	1.364(6)	C5	C10	1.499(6)
N1	C20	1.305(6)	C1	C2	1.445(6)
C28	C29	1.500(6)	C1	C6	1.490(6)
C28	C21	1.353(6)	C2	C3	1.368(7)
C29	C30	1.384(6)	C2	C7	1.502(7)
C29	C34	1.371(6)	C20	C19	1.377(7)
C17	C21	1.482(6)	C15	C14	1.357(7)
C17	C18	1.406(6)	C32	C33	1.370(7)
C17	C16	1.381(6)	C32	C31	1.371(6)
C12	C13	1.384(6)	C3	C8	1.498(7)
C21	C22	1.516(5)	C13	C14	1.363(7)
C18	C19	1.365(7)	C30	C31	1.375(7)
C4	C5	1.438(6)	C33	C34	1.368(7)

Table 5. Bond Angles for **4-D-Br**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Rh1	Cl1	89.14(10)	C9	C4	Rh1	129.5(3)
N2	Rh1	C4	158.21(17)	N2	C11	C16	121.7(4)
N2	Rh1	C5	138.66(15)	N2	C11	C15	120.6(4)
N2	Rh1	C1	103.48(15)	C15	C11	C16	117.7(4)
N2	Rh1	C2	96.45(16)	C23	C22	C21	121.8(3)
N2	Rh1	C3	120.88(18)	C23	C22	C27	120.0
C28	Rh1	Cl1	89.79(12)	C27	C22	C21	118.2(3)
C28	Rh1	N2	88.15(14)	C22	C23	C24	120.0
C28	Rh1	C4	113.00(18)	C23	C24	C25	120.0
C28	Rh1	C5	95.53(16)	C26	C25	C24	120.0
C28	Rh1	C1	114.23(16)	C25	C26	C27	120.0
C28	Rh1	C2	152.29(17)	C26	C27	C22	120.0
C28	Rh1	C3	150.97(19)	C4	C5	Rh1	70.2(2)
C4	Rh1	Cl1	95.85(13)	C4	C5	C10	128.2(4)
C4	Rh1	C5	38.72(16)	C1	C5	Rh1	70.6(2)
C4	Rh1	C1	63.97(16)	C1	C5	C4	106.6(4)
C4	Rh1	C2	62.45(18)	C1	C5	C10	125.1(4)
C4	Rh1	C3	38.14(18)	C10	C5	Rh1	127.2(3)
C5	Rh1	Cl1	131.91(12)	C5	C1	Rh1	71.2(2)
C5	Rh1	C2	63.36(16)	C5	C1	C2	108.3(4)
C5	Rh1	C3	63.35(17)	C5	C1	C6	125.1(4)
C1	Rh1	Cl1	152.83(12)	C2	C1	Rh1	74.0(2)
C1	Rh1	C5	38.26(16)	C2	C1	C6	124.8(4)
C1	Rh1	C2	38.14(16)	C6	C1	Rh1	133.0(3)
C1	Rh1	C3	62.14(17)	N1	C16	C17	122.8(4)
C2	Rh1	Cl1	117.51(13)	N1	C16	C11	110.5(4)
C2	Rh1	C3	35.35(18)	C17	C16	C11	126.5(4)
C3	Rh1	Cl1	90.71(13)	C1	C2	Rh1	67.9(2)
C12	N2	Rh1	116.1(3)	C1	C2	C7	122.9(5)
C12	N2	C11	117.8(4)	C3	C2	Rh1	72.7(3)
C11	N2	Rh1	125.7(3)	C3	C2	C1	108.6(4)
C20	N1	C16	117.9(4)	C3	C2	C7	128.4(5)

C29	C28	Rh1	116.9(3)	C7	C2	Rh1	127.0(3)
C21	C28	Rh1	124.3(3)	N1	C20	Br1	116.0(4)
C21	C28	C29	118.8(4)	N1	C20	C19	124.8(5)
C30	C29	C28	121.4(4)	C19	C20	Br1	119.2(4)
C34	C29	C28	122.4(4)	C18	C19	C20	116.9(5)
C34	C29	C30	116.2(4)	C14	C15	C11	121.0(5)
C18	C17	C21	116.6(4)	C33	C32	C31	117.7(5)
C16	C17	C21	127.2(4)	C4	C3	Rh1	67.4(2)
C16	C17	C18	116.2(4)	C4	C3	C8	123.9(6)
N2	C12	C13	122.9(4)	C2	C3	Rh1	72.0(3)
C28	C21	C17	124.8(4)	C2	C3	C4	108.7(4)
C28	C21	C22	122.2(4)	C2	C3	C8	127.4(6)
C17	C21	C22	112.8(4)	C8	C3	Rh1	126.5(3)
C19	C18	C17	121.5(5)	C14	C13	C12	119.4(5)
C5	C4	Rh1	71.1(2)	C31	C30	C29	121.9(4)
C5	C4	C3	107.6(4)	C34	C33	C32	121.2(5)
C5	C4	C9	127.1(5)	C33	C34	C29	122.2(4)
C3	C4	Rh1	74.5(3)	C15	C14	C13	118.2(5)
C3	C4	C9	124.1(5)	C32	C31	C30	120.8(4)

Table 6. Torsion Angles for **4-D-Br**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Rh1	N2	C12	C13	174.5(4)	C11	N2	C12	C13	1.4(7)
Rh1	N2	C11	C16	2.2(6)	C11	C15	C14	C13	0.0(8)
Rh1	N2	C11	C15	-174.6(3)	C22	C23	C24	C25	0.0
Rh1	C28	C29	C30	-71.6(5)	C23	C22	C27	C26	0.0
Rh1	C28	C29	C34	111.1(4)	C23	C24	C25	C26	0.0
Rh1	C28	C21	C17	3.5(6)	C24	C25	C26	C27	0.0
Rh1	C28	C21	C22	177.2(3)	C25	C26	C27	C22	0.0
Rh1	C4	C5	C1	61.6(3)	C27	C22	C23	C24	0.0
Rh1	C4	C5	C10	-122.2(4)	C5	C4	C3	Rh1	63.8(3)
Rh1	C4	C3	C2	-60.3(3)	C5	C4	C3	C2	3.5(5)
Rh1	C4	C3	C8	119.8(4)	C5	C4	C3	C8	-176.4(4)
Rh1	C5	C1	C2	65.2(3)	C5	C1	C2	Rh1	-63.3(3)
Rh1	C5	C1	C6	-129.9(4)	C5	C1	C2	C3	-1.8(5)
Rh1	C1	C2	C3	61.6(3)	C5	C1	C2	C7	176.0(4)
Rh1	C1	C2	C7	-120.7(4)	C1	C2	C3	Rh1	-58.6(3)
Rh1	C2	C3	C4	57.5(3)	C1	C2	C3	C4	-1.1(5)
Rh1	C2	C3	C8	-122.6(5)	C1	C2	C3	C8	178.8(4)
Br1	C20	C19	C18	178.0(3)	C16	N1	C20	Br1	-177.1(3)
N2	C12	C13	C14	0.1(8)	C16	N1	C20	C19	1.0(7)
N2	C11	C16	N1	-134.1(4)	C16	C17	C21	C28	-51.7(6)
N2	C11	C16	C17	50.3(6)	C16	C17	C21	C22	134.1(4)
N2	C11	C15	C14	1.6(8)	C16	C17	C18	C19	1.0(7)
N1	C20	C19	C18	-0.1(8)	C16	C11	C15	C14	-175.3(5)
C28	C29	C30	C31	-176.3(4)	C20	N1	C16	C17	-0.9(6)
C28	C29	C34	C33	175.9(5)	C20	N1	C16	C11	-176.6(4)
C28	C21	C22	C23	-57.2(5)	C15	C11	C16	N1	42.7(5)
C28	C21	C22	C27	122.7(4)	C15	C11	C16	C17	-132.8(5)
C29	C28	C21	C17	-175.1(4)	C32	C33	C34	C29	1.0(9)
C29	C28	C21	C22	-1.4(6)	C3	C4	C5	Rh1	-66.1(3)
C29	C30	C31	C32	-0.4(8)	C3	C4	C5	C1	-4.5(4)
C17	C21	C22	C23	117.1(3)	C3	C4	C5	C10	171.7(4)
C17	C21	C22	C27	-62.9(4)	C7	C2	C3	Rh1	123.8(5)

C17	C18	C19	C20	-0.9(7)	C7	C2	C3	C4	-178.7(4)
C12	N2	C11	C16	174.6(4)	C7	C2	C3	C8	1.2(7)
C12	N2	C11	C15	-2.2(6)	C30	C29	C34	C33	-1.5(8)
C12	C13	C14	C15	-0.8(8)	C6	C1	C2	Rh1	131.7(4)
C21	C28	C29	C30	107.1(5)	C6	C1	C2	C3	-166.8(4)
C21	C28	C29	C34	-70.2(6)	C6	C1	C2	C7	11.0(6)
C21	C17	C18	C19	179.4(4)	C33	C32	C31	C30	-0.2(8)
C21	C17	C16	N1	-178.3(4)	C34	C29	C30	C31	1.2(7)
C21	C17	C16	C11	-3.3(7)	C10	C5	C1	Rh1	122.3(4)
C21	C22	C23	C24	179.9(3)	C10	C5	C1	C2	-172.5(4)
C21	C22	C27	C26	-179.9(3)	C10	C5	C1	C6	-7.5(6)
C18	C17	C21	C28	130.1(5)	C9	C4	C5	Rh1	125.8(5)
C18	C17	C21	C22	-44.1(5)	C9	C4	C5	C1	-172.7(4)
C18	C17	C16	N1	-0.1(6)	C9	C4	C5	C10	3.5(7)
C18	C17	C16	C11	175.0(4)	C9	C4	C3	Rh1	-127.6(4)
C4	C5	C1	Rh1	-61.3(3)	C9	C4	C3	C2	172.1(4)
C4	C5	C1	C2	3.9(4)	C9	C4	C3	C8	-7.7(7)
C4	C5	C1	C6	168.8(4)	C31	C32	C33	C34	-0.1(9)

Table 7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4-D-Br**.

	x	y	z	U(eq)
H12	9305	6201	1774	50
H18	4098	7770	2184	58
H23	5990	8926	2558	83
H24	4915	9832	1787	111
H25	3742	9804	153	101
H26	3643	8869	-711	87
H27	4718	7962	60	69
H19	2664	6983	2139	65
H15	5164	5867	77	64
H32	9811	9895	2495	71
H13	8710	5542	452	70
H7A	7918	5349	3124	98
H7B	8382	5151	4210	98
H7C	9354	5266	3716	98
H30	8533	8540	3784	58
H6A	5700	6547	3588	79
H6B	6296	6032	4389	79
H6C	6119	5882	3321	79
H33	9025	9313	1089	78
H34	8031	8362	1033	63
H10A	7654	8004	4676	81
H10B	6980	7485	5071	81
H10C	6452	7658	3975	81
H14	6606	5378	-422	76
H9A	10829	7694	4787	103
H9B	10675	7501	5750	103
H9C	9785	8016	5077	103
H8A	11047	5915	4206	128
H8B	11434	6168	5261	128
H8C	11475	6629	4446	128
H31	9549	9492	3846	63

Table 8. Solvent Masks Information for **4-D-Br**.

Number	X	Y	Z	Volume	Electron count
1	0.283	0.868	0.343	134	58
2	0.283	0.631	0.843	134	58
3	0.717	0.369	0.157	135	58
4	0.717	0.131	0.657	135	58