Supporting information

Sequential C-H Arylation and Enantioselective Hydrogenation Enables Ideal Asymmetric Entry to the Indenopiperidine Core of an 11β-HSD-1 Inhibitor

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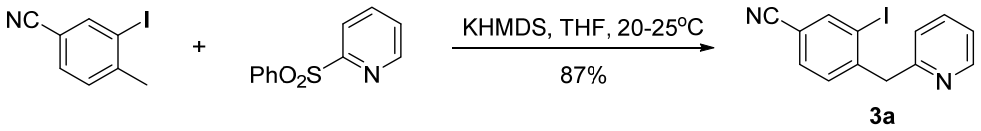
1. General Information

All reactions, unless specified otherwise, were performed in oven-dried glassware under argon or nitrogen atmosphere. All reagents and solvents were purchased from commercial sources (Aldrich or Fisher) and used as received, unless otherwise indicated. Palladium catalysts and $[Ir(COD)Cl]_2$ were purchased from Aldrich or Strem and used as received. HPLC analyses were performed on an Agilent 1100 quaternary pump HPLC system. Chiral HPLC analyses (either reverse phase or normal phase) were conducted on Agilent 1100 quaternary pump HPLC systems. LC-MS analyses were performed on an Agilent LC/MSD SL system. UPLC-MS analyses were conducted on a Waters Acquity Ultra Performance LC system. Flash Chromatography was performed on EMD 230-400 mesh silica gel eluted with hexanes and ethyl acetate. Melting points were obtained on a Fisher-Johns Melting Point Apparatus and are uncorrected. NMR spectra (^1H, ^{13}C, DEPT 135, COSY, NOESY, HMQC, HMBC, etc) were recorded on Bruker spectrometers: 400 MHz or 500 MHz for ^1H; 100 MHz or 125 MHz for ^{13}C. The NMR spectra were calibrated to the internal standard TMS or deuterated solvents: $CDCl_3$ (^1H NMR δ 7.26 ppm and ^{13}C NMR δ 77.0 ppm), DMSO-d_6 (^1H NMR δ 2.50 ppm and ^{13}C NMR δ 39.5 ppm), MeOH-d_4 (^1H NMR δ 2.50 ppm and ^{13}C NMR δ 39.5 ppm). Optical Rotations were performed on a Rudolph Research Autopol III polarimeter at 589 nm.

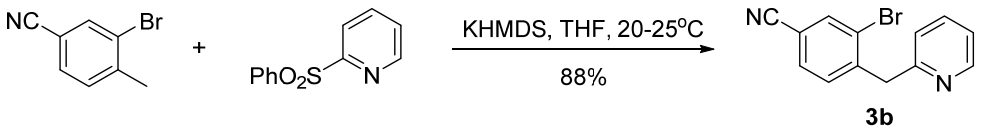
Synthesis of 3-iodo-4-(pyridin-2-ylmethyl)benzonitrile (3a)



3a

To a mixture of 2-(phenylsulfonyl)pyridine (43.85 g, 0.2 mol) and 3-iodo-4-methylbenzonitrile (51.04 g, 0.21 mol) in THF (100 mL) was added KHMDS (1.0 M solution in THF, 400 ml, 0.4 mol) slowly in 1 h at 20-25 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for another 2-4 hours until HPLC showed the starting material 3-iodo-4-methylbenzonitrile disappeared. Water (150 mL) was added, followed by phase cut to remove aqueous layer. Organic layer was washed with 10% aqueous $NaHCO_3$ (60 mL), then concentrated. Crude solid residue was purified by crystallization from isopropanol-water. Desired product **3a** was obtained as beige solid (55.6 g, 87% yield). M.p. 72-74 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 M Hz) δ 8.57 (d, *J* = 4.5 Hz, 1H), 8.128 (s, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 5.5, 7.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 4.33 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 M Hz) δ 157.9, 149.7, 148.0, 142.5, 136.7, 131.7, 130.8, 123.6, 121.8, 117.0, 112.0, 100.7, 49.1. HRMS-EI calcd for $C_{13}H_{10}IN_2$ $[M+H]^+$: 320.9883, Found: 320.9868.

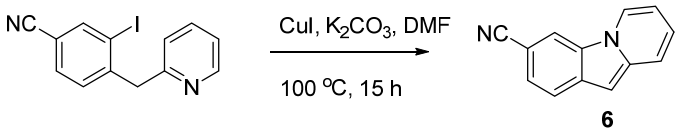
Synthesis of 3-bromo-4-(pyridin-2-ylmethyl)benzonitrile (3b)



3b

To a mixture of 2-(phenylsulfonyl)pyridine (32.89 g, 0.150 mol) and 3-bromo-4-methylbenzonitrile (30.88 g, 0.158 mol) in THF (75 mL) was added KHMDS (1.0 M solution in THF, 300 ml, 0.3 mol) slowly in 1 h at 20-25 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for another 2-4 hours until HPLC showed that the starting material 3-bromo-4-methylbenzonitrile was consumed. Water (110 mL) was added, followed by phase cut to remove aqueous layer. Organic layer was washed with 10% aqueous $NaHCO_3$ (45 mL), then concentrated. Crude solid residue was purified by crystallization from isopropanol-water. Desired product **3b** was obtained as beige solid (36.1 g, 88% yield). M.p. 55-57 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 M Hz) δ 8.55 (d, *J* = 4.5 Hz, 1H), 7.86 (d, *J* = 1.5 Hz, 1H), 7.63 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.55 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 5.0, 7.5 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.34 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 M Hz) δ 157.8, 149.7, 144.7, 136.7, 135.9, 131.9, 130.9, 125.1, 123.4, 121.8, 117.3, 112.0, 44.4. HRMS-EI calcd for $C_{13}H_9BrN_2$ $[M+H]^+$: 273.0022, Found: 273.0009.

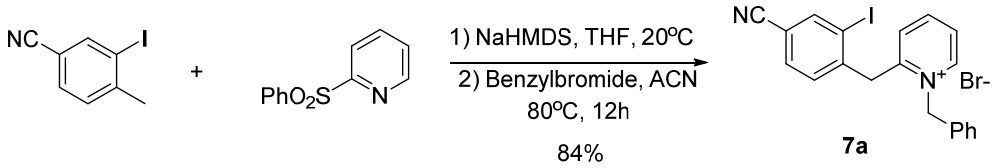
Synthesis of Pyrido[1,2-a]indole-3-carbonitrile (6)



6

A 25 ml flask was charged with starting material 3-iodo-4-(pyridin-2-ylmethyl)benzonitrile (273 mg, 1 mmol), K_2CO_3 (276 mg, 2 mmol) and DMF (2 mL). Reaction mixture was purged with argon, CuI (19.05 mg, 0.1 mmol) was then added. Reaction mixture was stirred at 100 °C and the reaction progress was monitored by LCMS. After 14 h, the reaction was quenched with water (5 mL) and extracted with MeTHF (15 mL). After removal of the organics, product was purified by chromatography through a short silica gel column to give product ca. 115 mg **6** was obtained as bright orange solid, 60% yield, m.p. 215-217 °C (decomp.). ^{1}H NMR ($CDCl_3$, 500 M Hz) δ 8.98 (d, *J* = 7.5 Hz, 1H), 8.86 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 9.5 Hz, 1H), 7.58 (d, *J* = 9.5 Hz, 1H), 7.16 (dd, *J* = 1.5, 9.0 Hz, 1H), 6.77-6.74 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 M Hz) δ 139.0, 130.9, 128.0, 126.1, 125.2, 124.6, 120.7, 120.7, 118.8, 117.0, 109.4, 99.4, 92.3. HRMS-EI calcd for $C_{13}H_9BN_2$ $[M+H]^+$: 193.0766, Found: 193.0757.

Synthesis of 1-benzyl-2-(4-cyano-2-iodobenzyl)pyridin-1-ium bromide (7a)

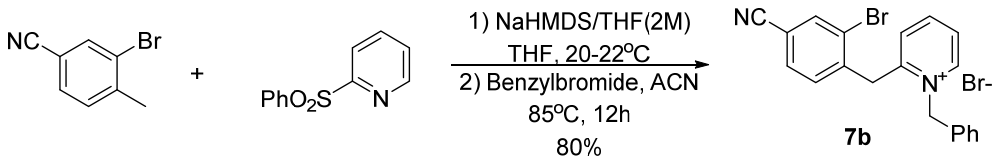


7a

To a mixture of 2-(phenylsulfonyl)pyridine (43.85 g, 0.2 mol) and 3-iodo-4-methylbenzonitrile (51.04 g, 0.21 mol) in THF (265 mL) was added NaHMDS (2.0 M solution in THF, 100 mL, 0.2 mol) slowly in 1 h at 20-25 °C. The reaction mixture was stirred at 25 °C for another 2-4 hours until HPLC showed starting material 3-iodo-4-methylbenzonitrile completely consumed. Water (118 mL) was added, followed by phase cut to remove aqueous layer. Organic layer was washed with 10% $NaHCO_3$ solution (60 mL), then concentrated. Acetonitrile (200 mL) was added, followed by distillation to a final volume of ~185 mL. A sample was taken to make sure water content was <1 wt% (Karl Fischer), otherwise additional acetonitrile was added for further azetropic distillation to water level at <1%. Benzylbromide (37.39 g, 0.22 mol) was added, and the reaction mixture was stirred at 80 °C for 12 h. After cooling to 20 °C, MeTHF (120 mL) was added. Desired product **7a** was isolated as white solid after filtration and drying in oven at 60 °C under vacuum (82.2 g, 84% isolated yield over two steps). M.p. 202-204 °C. ^{1}H NMR (CD_3OD, 500 M Hz) δ 9.20 (dd, *J* = 1.0, 5.0 Hz, 1H), 8.52 (t, *J* = 7.5 Hz, 1H), 8.29 (d, *J* = 1.5 Hz, 1H), 8.12 (t, *J* = 7.0 Hz, 1H), 7.79 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.50-7.40 (m, 5H),), 7.35 (d, *J* = 7.0 Hz, 1H), 6.05 (s, 2H). ^{13}C NMR (CD_3OD, 125 M Hz) δ 156.8, 148.6, 147.8, 144.4, 144.1, 134.0, 133.4, 133.1, 130.9, 130.8, 130.69, 130.68, 129.3, 128.0, 128.0, 117.7, 114.9, 102.1, 63.0. HRMS-EI calcd for $C_{20}H_{16}IN_2$ $[M]^+$: 411.0353, Found: 411.0360. Note: the two bridging

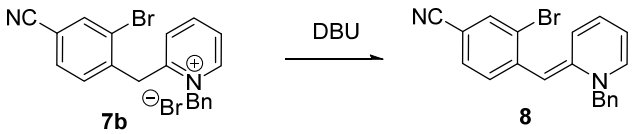
benzylic protons are exchangeable with deuterium in CD_3OD. The methylene protons appear in both ^1H and ^{13}C NMR spectra when CD_3OH was used as NMR solvent; ^1H NMR (CD_3OH, 500 M Hz) δ 9.20 (dd, *J* = 6.5 Hz, 1H), 8.50 (t, *J* = 7.5 Hz, 1H), 8.28 (s, 1H), 8.10 (t, *J* = 7.0 Hz, 1H), 7.77 (dd, *J* = 1.0, 7.5 Hz, 1H), 7.48-7.38 (m, 5H), 7.34 (d, *J* = 7.5 Hz, 1H), 6.04 (s, 2H), 4.72 (s, 2H). ^{13}C NMR (CD_3OH, 125 M Hz) δ 156.7, 148.5, 147.7, 144.3, 144.1, 133.9, 133.3, 133.0, 130.8, 130.6, 130.5, 129.2, 127.8, 117.6, 114.8, 102.1, 62.9, 44.9.

Synthesis of 1-benzyl-2-(4-cyano-2-iodobenzyl)pyridin-1-ium bromide (7b)



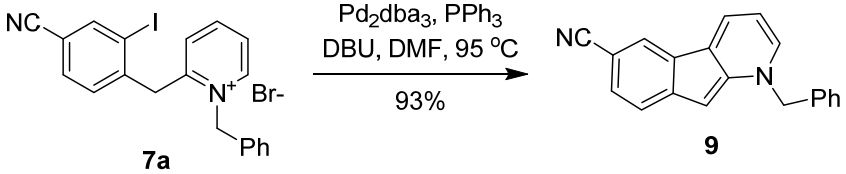
To a mixture of 2-(phenylsulfonyl)pyridine (32.89 g, 0.15 mol) and 3-bromo-4-methylbenzonitrile (30.88 g, 0.158 mol) in THF (165 mL) was added NaHMDS (2.0 M solution in THF, 150 ml, 0.3 mol) slowly in 1 h at 20-25 °C. The reaction mixture was stirred at 25 °C for another 2-4 hours until HPLC showed the starting material 3-bromo-4-methylbenzonitrile consumed. Water (89 mL) was added, followed by phase cut to remove aqueous layer. Organic layer was washed with 10% aqueous $NaHCO_3$ (45 mL), then concentrated. Acetonitrile (150 mL) was added, followed by distillation to a final volume of ~120 mL. A sample was taken to make sure water content was <1 wt% (Karl Fischer), otherwise additional acetonitrile was added for further azetropic distillation to water level at <1%. Benzylbromide (28.05 g, 0.165 mol) was added, and the reaction mixture was stirred at 80 °C for 12 ht. After cooling to 20 °C, MeTHF (86 mL) was added. Desired product **7b** was isolated as white solid after filtration and drying in oven at 60 °C under vacuum (53.4 g, 80% isolated yield over two steps). M.p. 193-195°C. ^1H NMR (CD_3OD, 500 M Hz) δ 9.19 (d, *J* = 6.0 Hz, 1H), 8.53 (dt, *J* = 1.0, 8.0 Hz, 1H), 8.11 (dt, *J* = 1.0, 7.0 Hz, 1H), 8.06 (d, *J* = 1.5 Hz, 1H), 7.76 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.54-7.40 (m, 5H),), 7.32 (d, *J* = 7.0 Hz, 1H), 6.06 (s, 2H). ^{13}C NMR (CD_3OD, 125 M Hz) δ 156.7, 148.6, 147.9, 140.7, 137.9, 134.1, 133.5, 133.4, 130.8, 130.7, 130.5, 129.1, 128.0, 126.5, 117.9, 115.2, 63.0. Note: the two bridging benzylic protons are exchangeable with deuterium in CD_3OD. The methylene protons appear in both ^1H and ^{13}C NMR spectra when CD_3OH is used as NMR solvent; ^1H NMR (CD_3OH, 500 M Hz) δ 9.18 (d, *J* = 6.0 Hz, 1H), 8.51 (t, *J* = 8.0 Hz, 1H), 8.10 (t, *J* = 7.0 Hz, 1H), 8.06 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.52-7.38 (m, 5H), 7.31 (d, *J* = 7.0 Hz, 1H), 6.04 (s, 2H), 4.72 (s, 2H). ^{13}C NMR δ (CD_3OH, 125 M Hz) 156.6, 148.5, 147.7, 140.6, 137.8, 134.0, 133.4, 133.3, 130.7, 130.6, 130.4, 129.0, 127.9, 126.4, 117.8, 115.1, 62.8, 40.3. HRMS-EI calcd for $C_{20}H_{16}BrN_2$ $[M]^+$: 363.0491, Found: 363.0494.

(*E*)-4-((1-benzylpyridin-2(1H)-ylidene)methyl)-3-bromobenzonitrile (8)



A 100 mL reactor was charged with 1.0 g (2.25 mmol) of 1-benzyl-2-(2-bromo-4-cyanobenzyl)pyridin-1-ium bromide (**7b**) under argon, 5 ml DMF and 0.67 mL (4.5 mmol) DBU were added. The mixture was sparged with Ar for 5 min before heating to 100 ^{o}C for 4 h. Then the mixture was cooled down to rt over 30 min. 10 mL water was added over 15 min, then cool down to 10 ^{o}C and hold for 30 min. The resulting bright red solid was filtered and washed with 10 mL water. The solid was dried in vacuum oven at 40 ^{o}C for 14 h. 0.82 g (2.16 mmol) red solid **8** was obtained, 96% yield. ^{1}H NMR (CD_3SOCD_3, 600 M Hz) δ 7.78 (d, *J* = 1.7 Hz, 1H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.43-7.48 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 9.5 Hz, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 5.92 (dt, *J* = 6.6 Hz, 1.2 Hz, 1H), 4.94 (s, 2H), 4.82 (s, 1H); ^{13}C NMR (CD_3SOCD_3, 150 M Hz) δ 145.9, 144.2, 141.5, 136.1, 135.9, 133.2, 131.3, 129.2, 127.9, 127.3, 124.2, 120.6, 119.2, 118.6, 105.5, 103.1, 89.7, 56.8. NMR analyses (attached) confirmed the *E*-configuration of the free base.

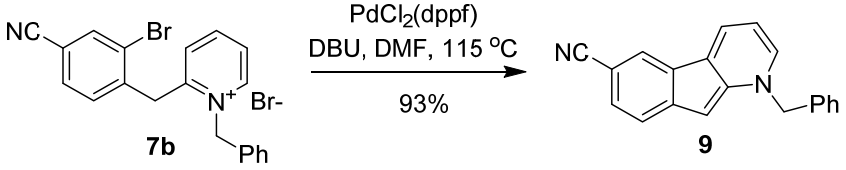
Synthesis of 1-benzyl-1H-indeno[2,1-b]pyridine-6-carbonitrile from 1-benzyl-2-(4-cyano-2-iodobenzyl)pyridin-1-ium bromide via Pd-catalyzed cyclization (9)



A 500 mL reactor was charged with 1-benzyl-2-(4-cyano-2-iodobenzyl)pyridin-1-ium bromide (33.72 g, 68.65 mmol), DMF (111.6 g) and DBU (31.36 g, 206 mmol). The mixture was purged with nitrogen for at least 30 minutes until O_2 level was < 0.5% (reaction is very sensitive to the oxygen; purge the reaction mixture thoroughly with nitrogen is necessary to achieve full conversion). A mixture of Pd_2dba_3 (0.64 g, 0.7 mmol) and DMF (8.5 mL) prepared in a separate flask under nitrogen was added, followed by a solution of PPh_3 (0.71 g, 2.71 mmol) in DMF (8.5 mL). The mixture was heated to 95-100^{o}C (maintain the N_2 bubbling until T = 70 ^{o}C.) and stirred at 95 ^{o}C for 12 to 18 hours. When a sample of HPLC analysis indicated a >99% conversion, the reaction mixture was cooled to 20-25 ^{o}C. Water (269.76 g) was added at such a flow rate that the batch temperature was maintained at <40 ^{o}C. The reaction was cooled and stirred at 20 ^{o}C for at least 1 hour before it was discharged to a filter. The wet cake was rinsed with water (85 mL) and dried overnight at ~ 50 ^{o}C under vacuum until water level was <0.5%. Desired product was isolated as a deep red crystalline solid (18.0 g, 93% isolated yield). M.p. 161-163 ^{o}C. ^{1}H NMR (CD_3SOCD_3, 500 M Hz) δ 8.68-8.66 (m, 2H), 8.37 (d, *J* = 6.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H),

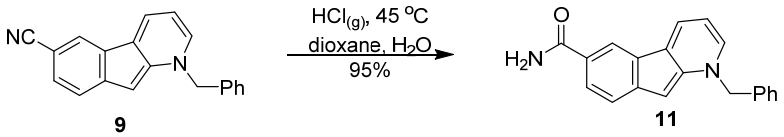
7.53 (d, J = 8.0 Hz, 1H), 7.36-7.34 (m, 4H), 7.31-7.28 (m, 1H), 6.91 (t, J = 7.0 Hz, 1H), 6.32 (s, 1H), 5.67 (s, 2H). ^{13}C NMR (CD_3SOCD_3, 125 M Hz) δ 142.4, 140.7, 136.5, 135.6, 128.8, 128.6, 127.9, 127.4, 127.4, 125.7, 125.7, 122.1, 121.7, 118.3, 105.4, 96.4, 86.5, 57.5. HRMS-EI calcd for $C_{20}H_{15}N_2$ $[M+H]^+$: 283.1229, Found: 283.1209.

Synthesis of 1-benzyl-1H-indeno[2,1-b]pyridine-6-carbonitrile from 1-benzyl-2-(4-cyano-2-bromobenzyl)pyridin-1-ium bromide (9)



A reactor was charged with 1-benzyl-2-(4-cyano-2-bromobenzyl)pyridin-1-ium bromide (22.2 g, 50.0 mmol), DMF (73.6 g) and DBU (22.8 g, 150 mmol). The mixture was purged with nitrogen for at least 30 minutes until O_2 level was < 0.5%**.** A mixture of $PdCl_2$(dppf) (0.51 g, 0.625 mol) and DMF (10.4 g) prepared in a separate flask under nitrogen was added. The mixture was heated to 115 °C (maintaining N_2 bubbling until T = 80 °C) and stirred at 115 °C for about 2 to 8 hours. When a sample of HPLC analysis indicated an >99% conversion, the reaction mixture was cooled to 20-25 °C. Water (178 g) was added at such a rate that the reaction temperature was maintained at <40 °C. The reaction was cooled and stirred at 20 °C for at least 1 hour before it was filtered. The wet cake was rinsed with water (60 mL) and dried overnight at ~ 50 °C under vacuum until water level was <0.5%. Desired product was isolated as red crystalline solid, 13.13 g, 46.5 mmol, 93% isolated yield.

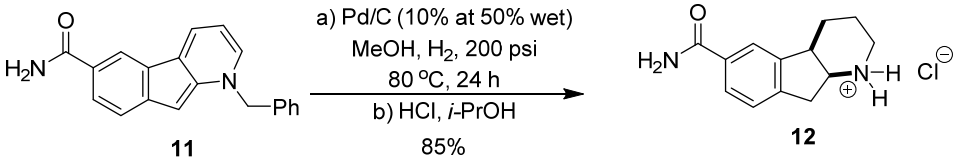
Synthesis of 1-benzyl-1H-indeno[2,1-b]pyridine-6-carboxamide (11)



To a 250 mL reactor was added 1-benzyl-1H-indeno[2,1-b]pyridine-6-carbonitrile (18.78 g, 66.50 mmol), 1,4-dioxane (167 mL) and water (3.6 mL). The reaction mixture was stirred under nitrogen, while HCl gas (24.2 g, 663 mmol) was bubbled in slowly for about 2-4 h. Reaction is exothermic; the addition rate was adjusted to keep the reaction temperature <40 °C. Afterwards, the reaction mixture was stirred at ~45 °C for 24-48 hours until a sample analysis by HPLC indicated an >99% conversion. At the end of the reaction, excess amount of HCl and part of the solvent 1,4-dioxane (total ~81 mL) were removed by rotavap, and water (36.6 mL) was added slowly keeping the reaction temperature at ~40 °C. A 20% NaOH solution (20 g, 200 mmol) was added slowly at 40 °C, which brought the pH >12. Additional water (97 g) was added over 1 hour, and the reaction mixture was cooled to 20 °C. After filtration, rinse with water (40 mL) and

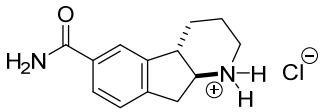
dry in the oven at 50 °C under vacuum, desired product **11** was isolated as a deep red crystalline solid. 18.97 g, 95% yield. M.p. 227-229 °C. ^{1}H NMR (CD_3SOCD_3, 500 M Hz) δ 8.77 (s, 1H), 8.44 (d, *J* = 7.0 Hz, 1H), 8.21 (d, *J* = 7.0 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.79 (br s, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.38-7.32 (m, 4 H), 7.32-7.25 (m, 1H), 7.03 (m, 1H), 6.76 (t, *J* = 7.0 Hz, 1H), 6.19 (s, 1H), 5.59 (s, 2H). ^{13}C NMR (CD_3SOCD_3, 125 M Hz) δ 169.0, 142.5, 140.7, 139.9, 135.9, 135.3, 128.6, 127.8, 127.4, 127.1, 126.6, 125.2, 122.1, 122.1, 120.8, 116.8, 104.0, 85.6, 57.2. HRMS-EI calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$: 301.1335, Found: 301.1343.

Synthesis of 1-benzyl-1H-indeno[2,1-b]pyridine-6-carboxamide (12)



11 **12**

A hydrogenation reactor was charged with 20.5 g Pd/C (10% at 50% wet, 0.96 mol), 1-benzyl-1H-indeno[2,1-b]pyridine-6-carboxamide (96 g, 319 mmol) and Na_2CO_3 (8.5 g, 80.2 mmol). Solvent MeOH (980 mL) was added, and the closed reactor was purged with nitrogen followed by hydrogen. The hydrogenation reaction was carried out at 80 °C under 220 psi hydrogen pressure for 24 hours. HPLC analysis showed the conversion was >99%. The reaction mixture was cooled to 20 °C, purged with nitrogen, and filtered through a closed filter pre-packed with Celite-545. The MeOH solution was transferred to a different reactor and distilled under vacuum to ~13 mL. Isopropanol (690 mL) was charged, and distillation was continued until 130 mL of total volume was reached. After addition of additional isopropanol (690 mL), 12 N HCl (16.2 g, 160 mmol) was added slowly for HCl salt formation. After addition of crystal seeds (0.8 g) the second portion of 12 N HCl (16.2 g, 160 mmol) was added, and the resulting slurry was cooled to 20 °C over a three hours period. After 1 h of additional stirring, the mixture was filtered. Both reactor and wet cake were rinsed with iso-propanol (14 mL). The wet cake was dried at 60 °C under vacuum for overnight to afford the desired product as white crystalline solid **12** containing ~3% water. 70.6 g (68.5 g pure product based on 97% wt, 3% water), 85% yield. M.p. 120-122 °C. ^{1}H NMR (CD_3SOCD_3, 500 M Hz) δ 9.20 (br, 2H), 8.01 (br, 1H), 7.83 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 3.95 (m, 1H), 3.40 (dd, *J* = 5.0, 10.0 Hz, 1H), 3.22 (dd, *J* = 6.0, 11.7 Hz, 1H), 3.00 (dd, *J* = 2.5, 17.0 Hz, 1H), 2.96 (m, 1H), 2.87 (dt, *J* = 2.5, 10.0 Hz, 1H), 2.16-2.09 (m, 1H), 2.02-1.92 (m, 1H), 1.73-1.63 (m, 1H), 1.50-1.38 (m, 1H). ^{13}C NMR (CD_3SOCD_3, 125 M Hz) δ 167.7, 143.3, 142.3, 133.3, 126.8, 125.1, 122.2, 56.7, 41.0, 40.9, 35.2, 22.0, 18.1. HRMS-EI calcd for $C_{13}H_{17}N_2O[M+H]^+$: 217.1335, Found: 217.1340.

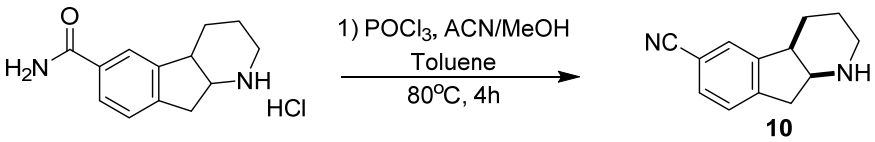


***trans*-12**

2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carboxamide (*trans*-12): A small sample of the *trans*-isomer was isoloated from mother liquor by preparative HPLC and characterized: ^{1}H NMR (CD_3SOCD_3, 500 M Hz) δ 10.08 (br, 1H), 9.90 (br, 1H), 8.50

(br, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.74 (s, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 3.39 (d, *J* = 12.0 Hz, 1H), 3.27 (t, *J* = 10.0 Hz, 1H), 3.22-3.10 (m, 2H), 3.09-2.90 (m, 2H), 2.44 (dd, *J* = 3.2, 12.4 Hz, 1H), 2.0-1.90 (m, 2H), 1.56 (ddd, *J* = 5.4, 12.0, 17.0 Hz, 1H). ^{13}C NMR (CD_3SOCD_3, 125 M Hz) δ 167.5, 141.9, 141.8, 133.1, 126.3, 124.1, 120.8, 62.1, 44.5, 44.2, 33.4, 24.7, 21.7. HRMS-EI calcd for $C_{13}H_{17}N_2O[M+H]^+$: 217.1335, Found: 217.1335.

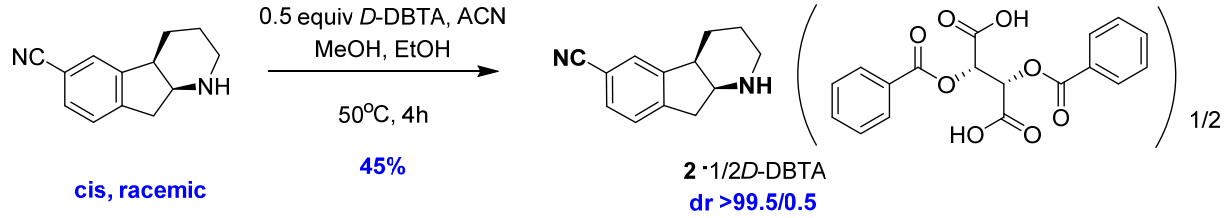
Synthesis of (±) 2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile



10

A 500 mL flask was charged with 1-benzyl-1H-indeno[2,1-b]pyridine-6-carboxamide (27.0 g, 97wt%, 103.6 mmol). Toluene (176 g, 200 mL) was added, followed by acetonitrile (53.2 g, 67.7 mL) and methanol (3.51 g, 4.4 mL, 110 mmol). $POCl_3$ (33.43 g, 218 mmol) was added and the mixture was heated to 80-85 ^oC. Reaction mixture was stirred at this temperature for 4 hours, and sample was taken for analysis by HPLC to make sure conversion was >99%. The batch was cooled to 55-60 ^oC, and distilled to remove ~154 mL of solvent mixture. (Caution: The distillate contains $POCl_3$. Keep this distillate separate from other waste streams). The mixture was cooled to 35-40 ^oC, and water (203 g) was added to quench the reaction mixture. (CAUTION: Exothermic! Adjust the charge rate to control the batch temperature at no more than 50 ^oC). The reaction was cooled to 30-35 ^oC and neutralized with 50% NaOH solution (46.9 g, 586 mmol) slowly to bring the pH to 9.5–10. (*Caution:* Exothermic! Adjust the charge rate to control the temperature at NMT 45 ^oC). The reaction was cooled to 30-35 ^oC, and agitation was stopped for a phase separation. The lower phase was discarded as waste. The organic phase was rinsed by H_2O (80 g). The organic layer was filtered through a celite pad, and additional amount of toluene (105 g, 120 mL) was used to rinse the filter. The filtrate was charged back into a clean reactor and concentrated under vacuum at 55-60 ^oC to remove toluene (~208 mL). The batch was cooled to 30-35 ^oC, and charged with crystal seeds (5 mg) as a suspension in heptane (0.5 mL) to make sure crystallization starts. Additional heptane (152 g, 220 mL) was added slowly, and the batch was stirred at 30-35 ^oC for 30 minutes then cooled to 10 ^oC. After stirring for another 3 hours, the batch was filtered. The wet cake was rinsed with a solvent mixture of toluene and heptane (V:V = 1:9). After drying overnight at 45 ^oC, the desired product *rac*-**10** (16.22 g, 79% yield) was obtained as white solid. M.p. 88-90 ^oC. ^{1}H NMR (CD_3SOCD_3, 500 M Hz) δ 7.63 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 3.52 (m, 1H), 3.00 (q, *J* = 4.5, 1H), 2.90 (dd, *J* = 5.0, 16.0 Hz, 1H), 2.66-2.61 (m, 2H), 2.47 (dd, *J* = 1.0, 1.5 Hz, 1H), 2.16 (dd, *J* = 14.0, 3.5 Hz, 1H), 1.92 (br s, 1H), 1.82-1.78 (m, 1H), 1.34-1.31 (m, 1H), 1.20-1.15 (m, 1H). ^{13}C NMR (CD_3SOCD_3, 125 M Hz) δ 150.2, 146.9, 130.3, 126.3, 126.0, 119.6, 108.5, 58.1, 43.7, 42.9, 39.2, 23.7, 21.8. HRMS-EI calcd for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230, Found: 199.1235.

Synthesis of (*4aR,9aS*)-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile *D*-DBTA salt (2· 0.5*D*-DBTA)

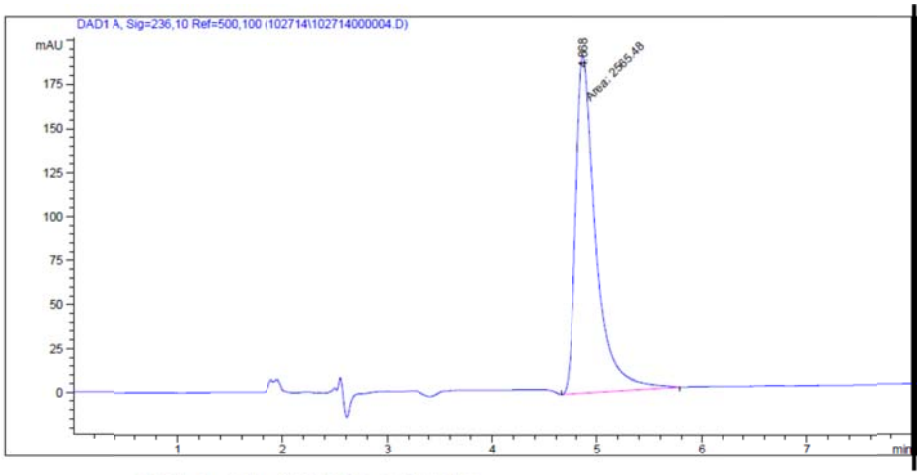


A 250 mL reactor was charged with **(±) 2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile** (16.18 g, 81.61 mmol) and acetonitrile (93.84 g, 119.2 mL). The mixture was heated to 50 °C, and a solution of *(D)*-dibenzoyl-tartaric acid (7.29 g, 20.35 mmol) in acetonitrile (75.98 mL) was added slowly. After ~10% of the dibenzoyl-tartaric acid solution was added over half an hour, seed crystals (32 mg) were added as a suspension in acetonitrile (0.32 g). The remaining dibenzoyl-tartaric acid solution was added in 4.5 hours, and the batch was cooled to 20 °C slowly over 4 hours. After stirring at 20 °C for 2 hours, a sample of the slurry was filtered and analyzed by chiral HPLC, which showed the solid was the chiral amine salt with ~95% de. The batch was filtered, and both the reactor and wet cake were rinsed with acetonitrile (53.23 g, 67.6 mL) and ethanol (17.80 g, 22.5 mL). The wet solid was charged back into the reactor. MeOH (29.29 g, 37.07 mL) and EtOH (78.80 g) were added, and the mixture was stirred at 50 °C for 2 hours. After cooling to 20 °C over 2 hours and stirring at 20 °C for another 2 hours, the slurry was filtered. After rinse with ethanol (20.30 g) the wet cake was dried under vacuum at 55-60 °C overnight. Product **2**· 0.5*D*-DBTA was isolated as white solid , 13.87 g, 45% isolated yield. M.p. 190-192 °C. $[\alpha]_D^{23}$ = + 138.8° (c 0.46, MeOH). ^{1}H NMR (CD_3SOCD_3, 500 M Hz) δ 7.99 (d, J = 7.5 Hz, 4H), 7.67-7.61 (m, 6H), 7.52 (t, *J* = 7.5 Hz, 4 H), 7.37 (d, *J* = 9.0 Hz, 2H), 5.62 (s, 2H), 3.80 (dd, *J* = 5.5, 8.5 Hz, 2 H), 3.20 (dd, *J* = 4.5, 10.0 Hz, 2H), 3.01 (dd, *J* = 5.5, 17.0 Hz, 2 H), 2.88 (dd, *J* = 2.5, 17.0 Hz), 2.84-2.75 (m, 2H), 2.69 (t, 1 *J* = 10.0 Hz, 2H), 2.05-1.96 (m, 2H), 1.83-1.74 (m, 2H), 1.50-1.42 (m, 2H), 1.32-1.22 (m, 2H). ^{13}C NMR (CD_3SOCD_3, 125 M Hz) δ 169.0, 164.9, 147.3, 144.9, 133.1, 131.0, 130.2, 129.2, 128.5, 126.7, 126.3, 119.2, 109.3, 73.7, 56.3, 41.3, 41.2, 36.2, 22.6, 19.1. HRMS-EI calcd for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230, Found: 199.1229.

Chiral HPLC of the product 2:

Method: Chiralpak IA, 80/20 heptane/1% Et_2NH in 1-PrOH, 1.5 mL/min, 25 °C, 220 nm. Major enantiomer: 4.80 min (100%); Minor enantiomer: 6.50 min (0%). Enantiomeric Excess: 100%.

Chiral HPLC spectrum of the isolated product:



Signal 1: DAD1 A, Sig=236,10 Ref=500,100

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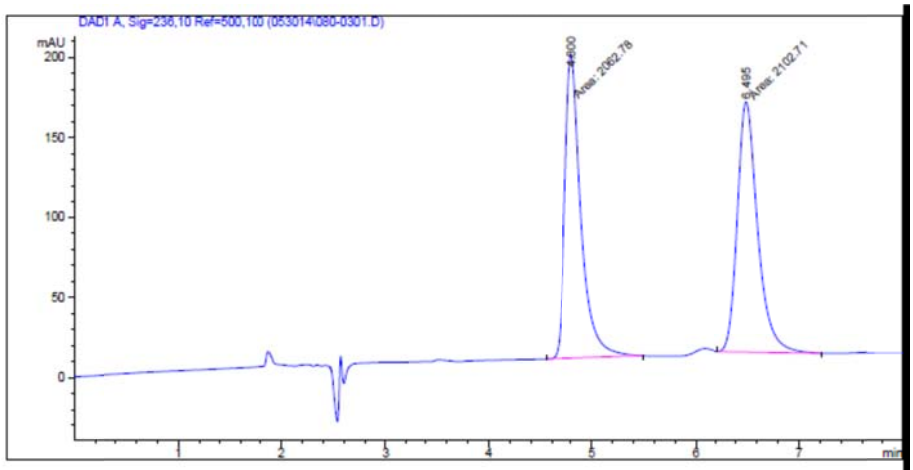
Totals :				2565.48438	190.83150	

Chiral HPLC spectrum of the racemic product



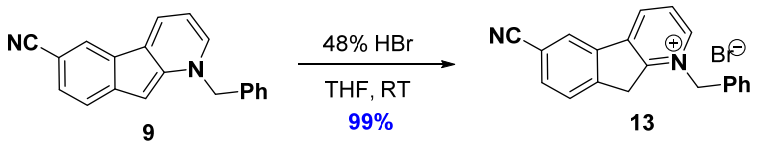
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=236,10 Ref=500,100

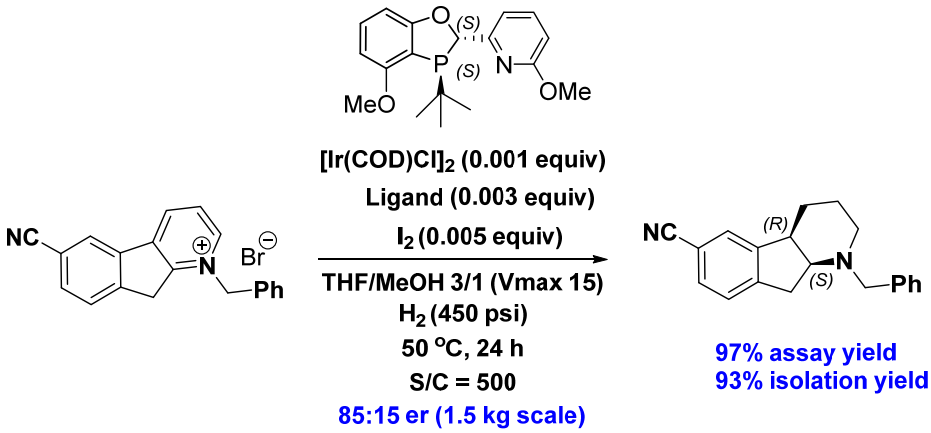
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.800	MM	0.1816	2062.77563	189.31041	49.5207
2	6.495	MM	0.2241	2102.70996	156.40251	50.4793
Totals :				4165.48560	345.71292	

Synthesis of 1-benzyl-6-cyano-9H-indeno[2,1-b]pyridin-1-ium bromide (13)



In a 2.0 L reactor with thermo couple and mechanical stirring, 1-benzyl-1H-indeno[2,1-b]pyridine-6-carbonitrile (100 g, 354.2 mmol) and THF (1.0 L) were added. The mixture was stirred at ~16 ^{o}C to obtain a solution. Hydrobromic acid (48 wt% aq., 48.1 mL, 1.2 eq) was slowly charged over 10-20 min. Exotherm was observed which brought reaction mixture to ~28 ^{o}C, and yellow precipitate formed instantly. After 1 h, the slurry was filtered. The cake was rinsed with THF (500 mL) and dried at 50 ^{o}C under vacuum for 20 h to give a light yellow solid **13** (127.4 g, 99% yield). M.p. 220-222^{o}C. ^{1}H NMR (CD_3OD, 500 M Hz) δ 9.08 (d, J = 8.0 Hz, 1H), 8.88 (d, J = 6.0 Hz, 1H), 8.56 (s, 1H), 8.16 (t, J = 7.0 Hz, 1H), 7.932 (s, 2H), 7.55-7.45 (m, 5H), 6.02 (s, 2H). ^{13}C NMR (CD_3OD, 125 M Hz) δ 161.3, 146.0, 143.5 (2C), 142.2, 138.5, 138.4, 135.1, 133.2, 131.1, 130.9 (2C), 130.2 (2C), 128.4, 127.9, 127.6, 119.3, 113.7, 63.1. Note: the two bridging benzylic protons are exchangeable with deuterium in CD_3OD. The methylene protons appear in both ^{1}H and ^{13}C NMR spectra when CD_3OH was used as NMR solvent; ^{1}H NMR (CD_3OH, 500 M Hz) δ 9.09 (d, J = 6.5 Hz, 1H), 8.89 (d, J = 5.5 Hz, 1H), 8.56 (s, 1H), 8.16 (t, J = 6.0 Hz, 1H), 7.93 (d, J = 7.0 Hz, 1H), 7.91 (d, J = 7.0 Hz, 1H), 7.55-7.45 (m, 5H), 6.03 (s, 2H), 4.67 (s, 2H). ^{13}C NMR (CD_3OH, 125 M Hz) δ 161.0, 145.8, 143.2, 141.9, 138.2, 138.1, 134.8, 132.9, 130.8, 130.6, 129.9, 128.1, 127.6, 127.3, 119.1, 113.3, 62.9, 38.2; HRMS-EI calcd for $C_{20}H_{15}N_2$ $[M+H]^+$: 283.1229, Found: 283.1235.

Synthesis of (4aR,9aS)-1-benzyl-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile (14) through Asymmetric hydrogenation

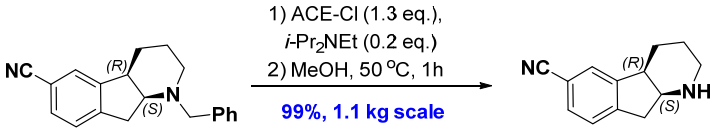


Catalyst preparation: The iridium complex $[Ir(COD)Cl]_2$ (2.8 g, 4.129 mmol) and chiral ligand **L5** (4.105 g, 12.388 mmol) were charged into a 1 L Schlenk flask with a stir bar under argon. Anhydrous degassed THF (200 mL) was added. The resulting clear yellow solution was stirred at

RT for 20 – 30 min. A solution of I_2 in anhydrous THF (100 mL) was charged. The resulting red-brown catalyst solution was stirred at room temperature for 5 min.

Asymmetric hydrogenation: Starting material 1-benzyl-6-cyano-9H-indeno[2,1-b]pyridin-1-ium bromide (1.50 Kg, 4.129 mol), THF (16.063 L) and MeOH (5.454 L) were charged into a 50 L hydrogenation reactor and sealed. Agitation was started. The reaction mixture was sparged with N_2 for 30-45 min. Then the catalyst solution was transferred into the reactor via Teflon tubing under N_2 pressure. The reaction mixture was then purged with 50 psi H_2 for 3 times, pressurized to 350 psi H_2, heated to 50 ^oC and finally pressurized to 450 psi H_2 and stir at this pressure and 50 °C for 24 h. A sample of the reaction mixture was taken, which was treated with Et_2NH and analyzed by HPLC, LC-MS & chiral HPLC to confirm >99.5% conversion and >85: 15 er of the product. The reaction mixture was cooled to 23 ^oC, vented, purged with N_2 and vented again. HPLC assay indicated ~98% yield. The reaction mixture, a red slurry with white solid on the bottom, was transferred into a 50 L reactor and rinsed with THF (10 L) and MeOH (4 L). N-Acetyl-L-cysteine solid (67.4 g, 0.413 mol) was charged. The mixture was stirred at room temperature for 5-10 min then concentrated under vacuum to minimum stirrable volume (~5 L). Dry toluene (9 L, 6 V) was charged, and the slurry was concentrated under vacuum to ~9 L to remove remaining THF and methanol. After more toluene (6 L) was charged, the mixture was cooled to 35-40 ^oC and treated with 10% NaOH (4.955 Kg, 3 eq) with agitation for 15-30 min so that all the white solid was dissolved. The mixture was cooled to 25 ^oC and the layers were separated. The bottom aq. layer was drained. The organic layer was rinsed with water (6.0 L), and concentrated at ~50 ^oC under vacuum to ~5 L. The isolated yield is ~93% (1.107 Kg, 3.84 mol) after assay of the solution in toluene, which was used in next step, debenzylation, without further purification. M.p. 50-52 ^oC. ^1H NMR (CD_3Cl_3, 500 M Hz) δ 7.44 (d, J = 7.5 Hz, 1H), 7.42 (s, 1H), 7.32-7.21 (m, 6H), 3.78 (d, J = 14.0 Hz, 1H), 3.53 (d, J = 14.0 Hz, 1H), 3.43-3.40 (m, 1H), 3.15-3.09 (m, 2H), 2.80 (dd, J = 6.0, 16.0 Hz, 1H), 2.52-2.49 (m, 1H), 2.43-2.39 (m, 1H), 1.85-1.81 (m, 1H), 1.65-1.46 (m, 3H). ^{13}C NMR (CD_3Cl_3, 125 M Hz) δ 148.0, 147.6, 138.8, 130.6, 128.6, 128.2, 126.9, 126.4, 126.0, 119.6, 109.9, 63.6, 59.7, 48.7, 43.5, 32.0, 26.2, 22.8. HRMS-EI calcd for $C_{20}H_{21}N_2$ $[M+H]^+$: 289.1699, Found: 289.1718.

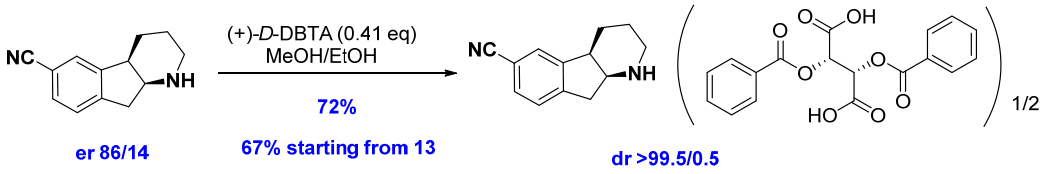
Synthesis of (*4aR,9aS*)-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile (19)



To a solution of the crude *(4aR,9aS)*-1-benzyl-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile (1.107 Kg, 3.84 mol, 1 equiv) in toluene (~5 L) was added dry MeCN (7.7 L). The mixture was heated to 60 ^oC with stirring. *N,N*-Diisopropylethylamine (133.8 mL, 0.2 eq) was charged, followed by 1-chloroethyl chloroformate (549.6 mL, 4.99 mol, 1.3 equiv) slowly over 10 min. The mixture was stirred at 60 ^oC for 1 h. A sample was taken and analyzed by HPLC & LC-MS, indicating 99.1% conversion to the chloroethyl carbamate. The mixture was

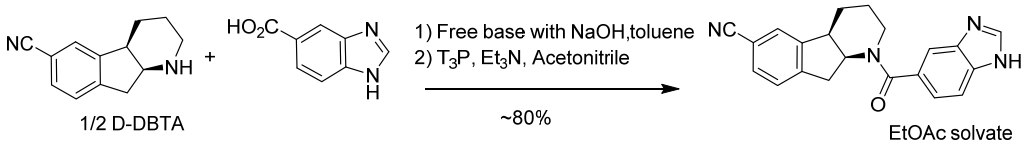
concentrated to ~ 5.0 L at 50-60 °C under vacuum. MeOH (5.5 L) was added, and the mixture was stirred at 50-55 °C for 1 h. A sample was taken and analyzed by HPLC & LC-MS indicating 100% conversion. The mixture was concentrated under vacuum at 50-60 °C to distill off MeOH/toluene (~7.8 L), during which dry toluene (9.24 L) was fed in portions to maintain reaction mixture volume ~8 L. The slurry was cooled to 25 °C and filtered. The reactor was rinsed with a mixture of toluene (2.6 L) & IPA (0.7 L) and the rinse was used to wash the wet cake. HPLC of the wet cake showed 99.6% product, 0.2% BnCl, and 0.2% SM. HPLC of the filtrate showed BnCl and toluene as major components with small amount of product present. The wet cake was charge back into the reactor, followed by addition of water (5.5 L), toluene (11.0 L) and 50% NaOH (1.23 kg, 4 eq). The mixture was stirred at ~40 °C for ~40 minutes and then cooled to 25 °C. The layers were separated. The bottom aq. layer was drained. The purple organic layer was concentrated under vacuum at 45-50 °C to 5 L and azeotroped with EtOH (denatured with 0.5% toluene) to give a dark purple solution (~8 L) with <500 ppm water content using Karl-Fischer titration. If target (<500 ppm) is not reached, use more dry EtOH to azeotrope water out and recheck. The solution was drained into a pre-weighed clean and dry container under N_2. A sample of this solution was taken and analyzed by HPLC & ^{1}H NMR assay, showing the yield is ~99% (757 g pure product). The solution (6.44 kg, ~8 L) was used in the next step without further purification.

Synthesis of (*4aR,9aS*)-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile (2) *D*-DBTA salt



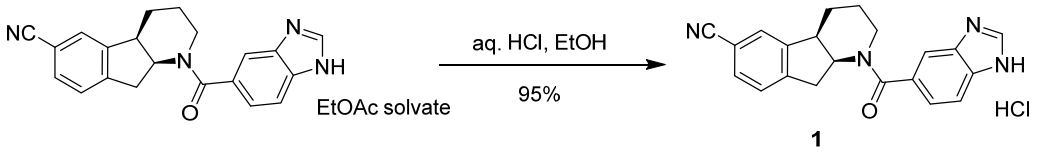
The crude **(*4aR,9aS*)-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile** (6.44 Kg solution in EtOH, 0.757 Kg pure, 3.818 mol) was charged to a 50 L reactor. The mixture was heated to 60 °C. A solution of dibenzoyl-*D*-tartaric acid (0.59 Kg, 1.565 mol, 0.41 eq) in dry MeOH (2.2 L) was slowly charged over 30 min. Precipitate formed after about 25% of the dibenzoyl-*D*-tartaric acid solution was charged. The mixture was stirred at 60 °C for 3 h, then cooled to 20 °C over 2 h, and held at 20 °C for 4 hours. A sample of the mixture (~10 mL) was filtered and analyzed by chiral HPLC, which showed the dr was ~99/1. The mixture was filtered, rinsed with EtOH (2 L), and the wet cake (~1.962 Kg) was charged back to the reactor. Dry MeOH (1.8 L) and dry EtOH (4.8 L) were charged. The mixture was stirred at 60 °C for 3 h, cooled to 20 °C over 2 h, and held at 20 °C for 4 h. The batch was filtered, rinsed with EtOH (2 L, 3 V), and the wet cake (1.41 kg) was dried under vacuum at 50 °C with a bleed of N_2 to give product as white solid, 1.037 kg, 72% isolated yield, and 66.5% total isolated yield starting from pyridinium salt **13**.

Synthesis of (4aR,9aS)-1-(1H-benzo[d]imidazole-5-carbonyl)-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile (1 – EtOAc solvate)



(*4aR,9aS*)-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile *D*-DBTA salt (56.04 g, 145 mmol) was charged to a 1 L reactor. Toluene (210 mL) and 10% aq. NaOH (116 g, 290 mmol) were added, and the mixture was stirred at 20 ^{o}C for 30 minutes followed by phase cut to remove aqueous layer. Another portion of 10% aq. NaOH (116 g, 2 eq) was charged, and the reaction mixture was stirred at 20 ^{o}C for 30 min. for a second phase cut. Again lower aqueous layer was drained. Organic layer was concentrated under vacuum, followed by addition of 1H-benzo[d]imidazole-5-carboxylic acid (25.99 g, 160 mmol) and acetonitrile (374 mL). The mixture was distilled at atmospheric pressure to remove most toluene and water. After additional acetonitrile (144 mL) was added, a sample was taken for analysis by HPLC and Karl Fischer titration to make sure toluene was <5% and water was <700 ppm. Triethylamine (80.8 mL, 4.0 eq) was charged, followed by slow addition of T_3P (115.3 g, 50% solution in THF, 181 mmol, 1.25 eq) at internal temperature < 0 ^{o}C. Reaction mixture was stirred at 0 ^{o}C for overnight, and a sample was taken for HPLC analysis to confirm conversion was >99%. DI water (144 mL) was added to quench the reaction slowly, followed by addition of NaOH solution (37.9 mL, 50 wt%, 5.0 eq.). The mixture was concentrated to 250 mL (2/5 of total volume) under vacuum to remove acetonitrile, followed by addition of MeTHF (632.5 mL, 22 vol) and adjust pH to 6-7 with 6 N HCl (65.2 mL, d= 1.1, 2.7 eq) and 50% NaOH (12.1 mL, 1.6 eq) keeping internal temperature at 30-40 ^{o}C. After phase cut at 35 ^{o}C, the organic layer was rinsed with 2% $NaHCO_3$ (144 mL) once, then concentrated under atmosphere pressure to 350 mL. For crystallization, EtOAc (500 mL, 1.0 vol) was added slowly at 65-70 ^{o}C, then product seed crystals suspension in EtOAc (0.5 g in 2 mL EtOAc) was added. To the slurry more EtOAc (150 mL) was added at 65-70 ^{o}C in 2 h, and the mixture was cooled to 30 ^{o}C in 2 h. The slurry was filtered and the wet cake was rinsed with small amount of EtOAc/MeTHF (100 mL, 2/3). After drying under vacuum at 60 ^{o}C for 6 h, 44.0 g white solid was obtained (80% isolated yield, as ~0.5 EtOAc solvate). HPLC showed >99.2% purity, and GC showed 10% wt EtOAc within the solid. M.p. 170-175^{o}C. ^{1}H NMR (CD_3SOCD_3, 500 M Hz) δ 8.30 (s, 1H), 7.70 (br, 1H), 7.66-7.58 (m, 3H), 7.45 (br, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 0.7 H EtOAc), 3.27 (br, 1H), 3.11 (br, 1H), 3.00 (br, 2H), 2.01 (s, 1 H, EtOAc), 1.74 (br, 1H), 1.52 (q, *J* = 12.5 Hz, 1H), 1.30 (dq, *J* = 3.0, 13.0 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 1 H, EtOAc). ^{13}C NMR (CD_3SOCD_3, 125 M Hz) δ 170.8, 170.3, 147.5, 145.8, 143.5, 138.4, 138.1, 130.9, 129.9, 127.1, 126.2, 120.6, 119.1, 114.9, 114.2, 109.2, 59.7, 41.2, 32.6, 32.1, 27.8, 23.1, 20.8, 20.7, 14.0. HRMS-EI calcd for $C_{21}H_{19}N_4O$ $[M+H]^+$: 343.1553, Found: 343.1544.

Synthesis of (4aR,9aS)-1-(1H-benzo[d]imidazole-5-carbonyl)-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile hydrochloride salt (1)



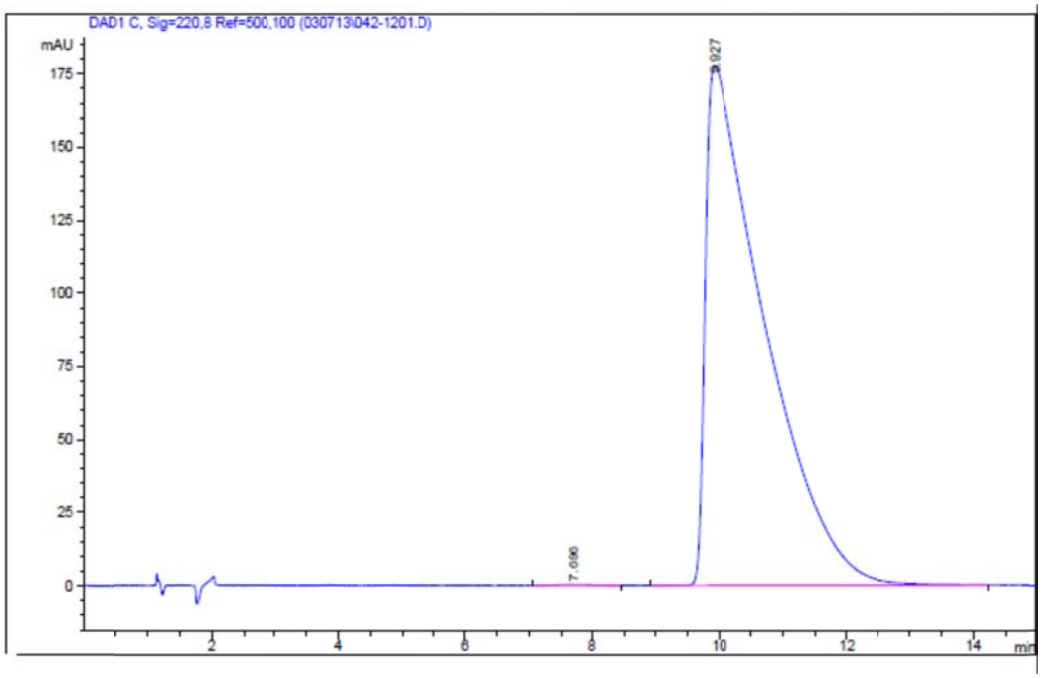
1

To a 1 L reactor was added (4aR,9aS)-1-(1H-benzo[d]imidazole-5-carbonyl)-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine-6-carbonitrile EtOAc solvate (42.0 g, 85.85 wt%) and 200 proof absolute EtOH (151.2 g). The mixture was heated up to 50-60 ^{o}C for dissolution, and the solution was filtered to remove insoluble impurities and rinsed with EtOH (16.9 g). The concentration was determined by HPLC analysis, and based on calculation, 35.7 g pure compound was in the 210 g solution. The solution was heated to 60 ^{o}C, then aq HCl (3.52 g, 32.37 wt% by titration) was added slowly. Crystal seed (0.84 g) was added as suspension in EtOH (3.36 g). After 30 minutes, additional aq. HCl (8.81 g, 32.37%) was added slowly over 2 hours. The mixture was cooled to 5-10 ^{o}C over 2 hours and stirred for another 4 hours. The mixture was filtered, and the wet cake was rinsed with EtOH (84.0 g). After drying at 65-70 ^{o}C under vacuum for 12 hours, desired product was obtained as white solid (39.5 g, 95% yield). M.p. 245-248 ^{o}C. $[\alpha]_D^{23}$ = + 63.5^{o} (c 0.82, MeOH). ^{1}H NMR (CD_3SOCD_3, 500 M Hz, 353 K) δ 13.85 (br, 2H), 9.41 (s, 1H), 7.89 (d, *J* = 6.2 Hz, 1H), 7.88 (s, 1H), 7.65 (s, 1H), 7.57 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.55 (dd, *J* = 6.2, 1.1 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 4.77 (br, 1H), 4.01 (m, 1H), 3.27 (dd, *J* = 16.3, 10.4 Hz, 1H), 3.18 (m, 1H), 3.03 (dd, *J* = 16.3, 10.4 Hz, 1H), 3.03 (m, br, 1H), 2.03 (m, 1H), 1.64 (m, 1H), 1.53 (m, 1H), 1.35 (m, 1H). ^{13}C NMR (CD_3SOCD_3, 125 M Hz, 353 K) δ 167.0, 147.0, 145.3, 141.0, 133.5, 131.7, 131.1, 130.4, 126.6, 125.7, 123.5, 118.5, 114.4, 112.7, 109.1, 54.8, 41.0, 39.7 (br), 32.2, 27.2, 22.3. HRMS-EI calcd for $C_{21}H_{19}N_4O$ $[M+H]^+$: 343.1553, Found: 343.1551.

Chiral HPLC of **the product**:

Method: Chiralpak AGP, 95/5 0.1% AcOH in water/MeCN, 1.2 mL/min, 30 ^{o}C, 220 nm. Major enantiomer: 9.93 min (99.9%); Minor enantiomer: 7.70 min (0.1%). Enantiomeric Excess: 99.8%.

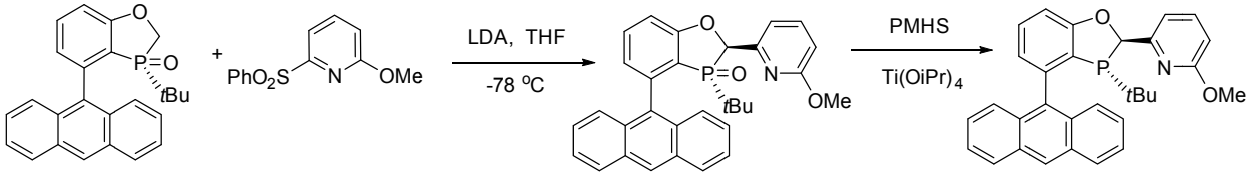
*Chiral HPLC spectrum of the isolated product **1**:*



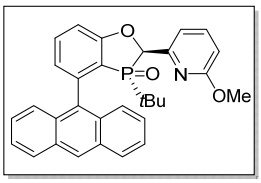
Signal 1: DAD1 C, Sig=220,8 Ref=500,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.696	MM	0.5614	11.31167	3.61642e-1	0.0978
2	9.927	MM	1.0817	1.15545e4	178.03818	99.9022
Totals :				1.15658e4	178.39982	

General procedure for the Synthesis of Ligands

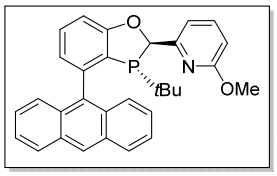


A 250 mL 3-neck round bottom flask equipped with a magnetic stir bar was charged with phosphine oxide (1.35 g, 3.493 mmol), 2-methoxy-6-(phenylsulfonyl)pyridine (0.87 g, 3.493 mmol) and THF (50 mL). The mixture was cooled down to -78 ^{o}C with a dry ice/acetone bath. LDA (5.3 mL, 2.0 M in THF/ethyl benzene, 10.48 mmol) was added slowly and the internal temperature was kept under -60 ^{o}C. After 2 h, a sample was taken and completed conversion was indicated from LC-MS. The mixture was quenched with methanol (5 mL) and sat Na_2CO_3 solution (10 mL) was added; the mixture was further warmed to 50 °C and stir for 2 h. The crude mixture was concentrated under reduced pressure, worked up with DCM (50 mL x 2) and dried over Na_2SO_4 and purified using column chromatography with 80% EtOAc/hexanes to get the desired product as a white solid after drying.

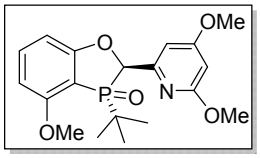


(2*R*,3*S*)-4-(anthracen-9-yl)-3-(tert-butyl)-2-(6-methoxypyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-oxide 1.12 g, 65% yield, m.p: 226.0–228.0 °C; $[\alpha]_D^{23}$ = + 10.7° (c 0.05, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.82 (s, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.65 (m, 1H), 7.60 (t, *J* = 8.2 Hz, 2H), 7.43 (dt, *J* = 7.6 Hz, 1H), 7.40 (m, 1H), 7.35 (m, 1H), 7.31 (m, 1H), 7.13 (m, 2H), 6.65 (d, *J* = 8.2 Hz, 1H), 5.53(d, *J* = 8.2 Hz, 1H), 3.79 (s, 3H), 0.53 (d, *J* = 16.2 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.0 (d, $J_{C–P}$ = 17.5 Hz), 163.6 (d, $J_{C–P}$ = 1.4 Hz), 151.9 (d, $J_{C–P}$ = 4.3 Hz), 142.9 (d, $J_{C–P}$ = 5.9 Hz), 139.3 (d, $J_{C–P}$ = 1.9 Hz),134.8 (d, $J_{C–P}$ = 1.7 Hz), 134.3 (d, $J_{C–P}$ = 1.9 Hz), 131.3 (d, $J_{C–P}$ = 22.5 Hz), 130.5 (d, $J_{C–P}$ = 8.9 Hz), 128.7 (d, $J_{C–P}$ = 60.3 Hz), 127.8 (d, $J_{C–P}$ = 64.4 Hz), 126.6 (d, $J_{C–P}$ = 8.1 Hz), 126.1 (d, $J_{C–P}$ = 39.5 Hz), 125.8 (d, $J_{C–P}$ = 25.5 Hz), 125.0, 116.1 (d, $J_{C–P}$ = 83.9 Hz), 114.4 (d, $J_{C–P}$ = 3.0 Hz), 113.4 (d, $J_{C–P}$ = 5.2 Hz), 110.3 (d, $J_{C–P}$ = 2.1 Hz), 77.8 (d, $J_{C–P}$ = 55.0 Hz), 53.5, 33.8 (d, $J_{C–P}$ = 71.2 Hz), 24.2 (d, $J_{C–P}$ = 0.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 60.4; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{31}H_{29}NO_3P]^+$ is 494.1880, found 494.1883.

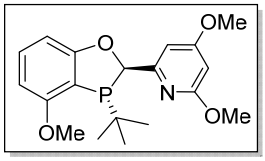
An oven dried 100 mL Schlenk flask equipped with a magnetic stir bar was charged with phosphine oxide (500 mg, 1.012 mmol) and THF (20 mL) and the solution was thoroughly degassed by vacuum *purge-and-refill* with argon. The mixture was then added polymethylhydrosiloxane (1.50 g). To this solution at rt added titanium tetraisopropoxide (575 mg, 2.024 mmol). Reaction mixture was stirred at 60 °C for 14 h under argon atmosphere. The reaction was quenched with degassed 30% aqueous NaOH (10 mL) over 10 min. The resulting mixture was stirred at 60 °C for 1 h. Then the mixture was cooled to room temperature and the layers were separated under argon. The aqueous layer was further washed twice with degassed MTBE. The combined organic layers was dried over $MgSO_4$, loaded on to a short plug of basic alumina, and eluted with MTBE. The product was obtained as a white solid after dryness.



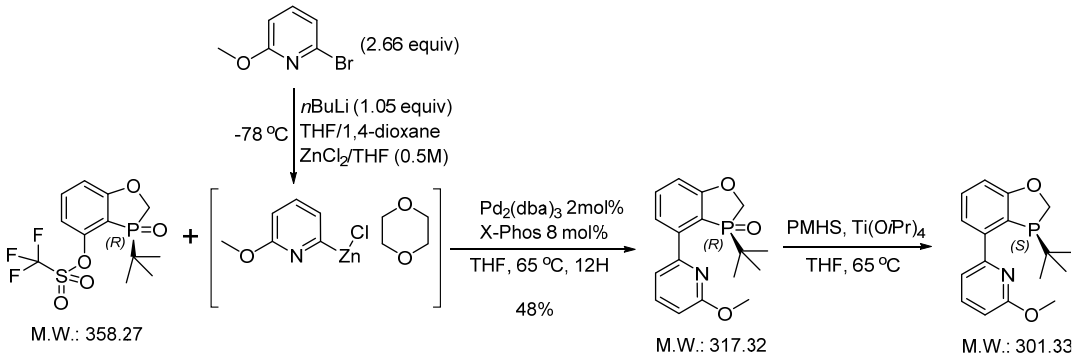
2-((2*R*,3*R*)-4-(anthracen-9-yl)-3-(tert-butyl)-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)-6-methoxypyridine 367 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 9.4 Hz, 2H), 7.54 (m, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.41 (dt, *J* = 6.9 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* =8.1 Hz, 1H), 7.05 (m, 2H), 6.85 (d, *J* = 6.7Hz, 1H), 6.61(d, *J* = 8.1 Hz, 1H), 5.89 (s, 1H), 3.81(s, 3H), 0.59 (d, *J* = 12.3 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.2, 163.9 (d, $J_{C–P}$ = 1.9 Hz), 158.8 (d, $J_{C–P}$ = 14.9 Hz), 142.7 (d, $J_{C–P}$ = 16.6 Hz), 139.1 (d, $J_{C–P}$ = 1.5 Hz), 136.3 (d, $J_{C–P}$ = 0.8 Hz), 131.5 (d, $J_{C–P}$ = 19.7 Hz), 131.4, 130.8, 128.9 (d, $J_{C–P}$ = 0.9 Hz), 128.6 (d, $J_{C–P}$ = 45.4 Hz), 127.66 (d, $J_{C–P}$ = 18.5 Hz), 127.65 (d, $J_{C–P}$ = 4.0 Hz), 125.7,125.6, 125.5 (d, $J_{C–P}$ = 7.0 Hz), 125.19 (d, $J_{C–P}$ = 21.6 Hz), 125.1, 111.6 (d, $J_{C–P}$ = 4.2 Hz), 110.3, 109.3 (d, $J_{C–P}$ = 2.5 Hz), 85.9 (d, $J_{C–P}$ = 27.7 Hz), 53.3, 31.7 (d, $J_{C–P}$ = 23.8 Hz), 27.1 (d, $J_{C–P}$ = 14.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$): δ 16.3; HRMS (ESI) $[M+H]^+$ *m*/*z* calcd for $[C_{31}H_{29}NO_2P]^+$ is 478.1930, found 478.1920.



(2*S*,3*R*)-3-(tert-butyl)-2-(4,6-dimethoxypyridin-2-yl)-4-methoxy-2H-benzo[d][1,3]oxaphosphole 3-oxide; glassy white solid, 49% yield; ^{1}H NMR (600 MHz, D_6-DMSO) δ 7.56 (t, *J* = 8.3 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.8 Hz, 1H), 6.71 (dd, *J* = 8.3, 4.1 Hz, 1H), 6.43 (s, 1H), 6.27 (s, 1H), 5.73 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 1.28 (d, *J* = 16.4 Hz, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 164.8, 164.6 (d, $J_{C–P}$ = 15.5 Hz), 160.8, 153.3 ($J_{C–P}$ = 4.4 Hz), 136.8, 105.8 (d, $J_{C–P}$ = 5.2 Hz), 104.0 (d, $J_{C–P}$ = 5.4 Hz), 102.6 (d, $J_{C–P}$ = 2.4 Hz), 102.0 (d, $J_{C–P}$ = 87.5 Hz), 92.4, 77.0 (d, $J_{C–P}$ = 52.8 Hz), 55.7, 55.5, 53.2, 33.7 (d, $J_{C–P}$ = 73.8 Hz), 24.5; ^{31}P NMR (242 MHz, $CDCl_3$) δ 61.6; HRMS (ESI) $[M + H]^+$ *m*/*z* calcd for $C_{19}H_{25}NO_5P$ 378.1465, found 378.1469.



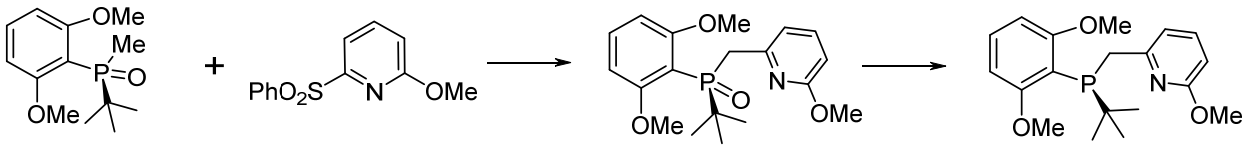
2-((2*S*,3*S*)-3-(tert-butyl)-4-methoxy-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)-4,6-dimethoxypyridine: white solid, 78% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.2 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 6.40 (dd, *J* = 8.3, 3.7 Hz, 1H), 6.29 (s, 1H), 5.91 (s, 1H), 5.79 (s, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.64 (s, 3H), 1.05 (d, *J* = 12.3 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4 (d, $J_{C–P}$ = 1.1 Hz), 164.4 (d, $J_{C–P}$ = 2.0 Hz), 164.3, 161.1 ($J_{C–P}$ = 11.8 Hz), 158.6 (d, $J_{C–P}$ = 14.6 Hz), 131.3, 108.6 (d, $J_{C–P}$ = 17.5 Hz), 103.2, 102.1 (d, $J_{C–P}$ = 2.0 Hz), 99.9 (d, $J_{C–P}$ = 3.8 Hz), 90.5 (d, $J_{C–P}$ = 2.4 Hz), 84.6 (d, $J_{C–P}$ = 27.0 Hz), 54.3, 54.1, 52.4, 31.3 (d, $J_{C–P}$ = 22.4 Hz), 26.2 (d, $J_{C–P}$ = 14.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.4; HRMS (ESI) $[M + H]^+$ *m*/*z* calcd for $C_{19}H_{25}NO_4P$ 362.1516, found 362.1523.



Preparation of pyridylzinc chloride dioxane solution[1]: Charged 2-bromo-6-methoxypyridine (700 mg, 3.723 mmol, 2.66 equiv to triflate) to a 25 mL Schlenk tube under argon. Evacuated and refilled the tube with argon three times. Charged dry THF (5.2 mL) and then cooled the mixture to -78 °C using dry ice/acetone bath. Charged *n*-BuLi (2.5M in hexanes, 1.56 mL, 3.909 mmol, 1.05 equiv to bromide) at -78 °C and stirred for 15 min. Charged 0.5M $ZnCl_2$ in THF (8.94 mL, 4.47 mmol, 1.2 equiv to bromide) to above mixture and then warmed up to RT and stirred for additional 1h. Charged 1,4-dioxane (0.76 g, 8.57 mmol, 2.3 equiv to bromide) to above mixture and stirred for additional 15 min at RT.

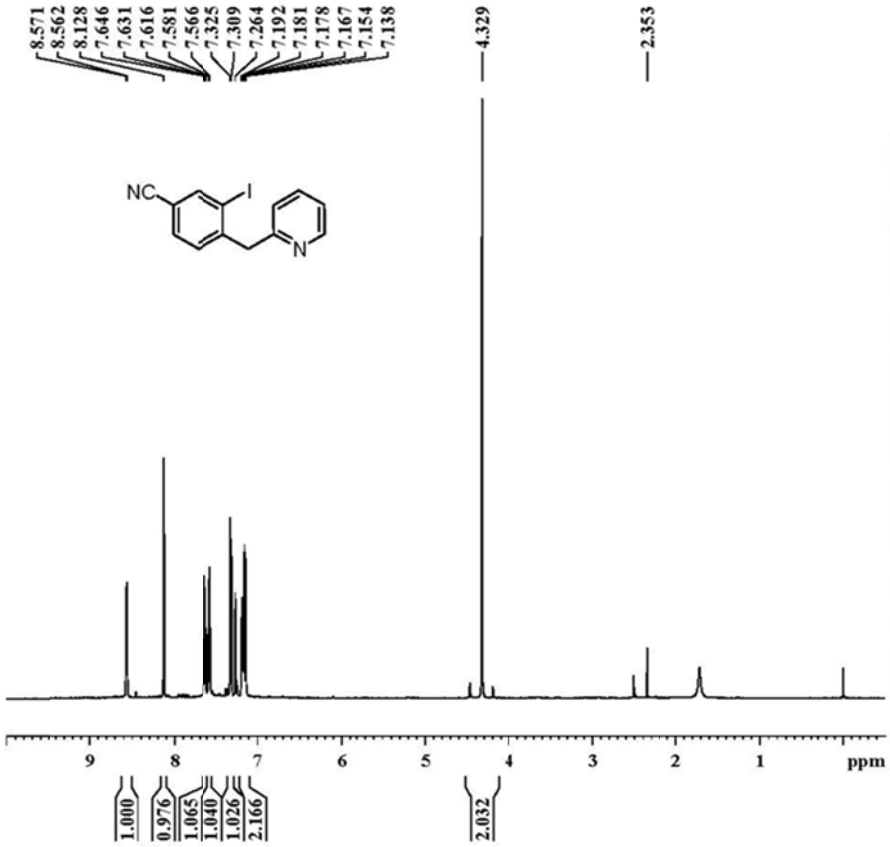
(*R*)-3-(tert-butyl)-4-(6-methoxypyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-oxide: Charged $Pd_2(dba)_3$ (2 mol%), X-Phos (8 mol%) to a Schlenk tube flushed with Ar line. Evacuated and refilled the tube with argon three times. Charged dry THF to the tube followed by pyridylzinc chloride dioxane solution to above solution at RT. Charged triflate (0.5 g, 1.4 mmol) in dry THF (4.5 mL) solution to above mixture and stirred at 65 ^oC for 15 h. The reaction mixture was quenched with 3 mL of 1N HCl and diluted with ethyl acetate (15 mL). Extracted the aqueous layer with ethyl acetate (15 mL) and combined both organic layers. Dried the organics over sodium sulfate and filtered through a short celite pad. Collected the filtrate and concentrated to dryness to give oil. Purified the oil by column chromatography (Rf = 0.25 in pure EtOAc, silica, 0-100% EtOAc in hexanes) to afford 210 mg of off-white to tan solid in 47% yield; M.P. 148-150 ^oC; $[\alpha]_D^{23}$ = - 119.90^o (c = 0.25, EtOH). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.70 (t, *J* = 8 Hz, 1H), 7.58-7.51 (m, 2H), 6.98 (ddd, *J* = 7.6, 3.2, 1.6 Hz, 1H), 6.76 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.63 (dd, *J* = 13.6, 1.0 Hz, 1H), 4.50 (dd, *J* = 13.6, 10.4 Hz, 1H), 4.04 (s, 3H), 0.89 (d, J = 16.0 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, *J* = 19.0 Hz), 163.8, 154.6 (d, *J* = 2.0 Hz), 145.1 (d, *J* = 5.0 Hz), 139.3, 134.8 (d, *J* = 2.0 Hz), 123.8 (d, *J* = 8.0 Hz), 118.5, 113.8 (d, *J* = 5.0 Hz), 111.7, 110.8, 110.3, 65.4 (d, *J* = 63.0 Hz), 53.5, 34.5 (d, *J* = 70.0 Hz), 23.9; ^{31}P NMR (160 MHz, $CDCl_3$) δ 65.26; HRMS (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{21}NO_3P$, 318.1254, found 318.1272.

(*S*)-2-(3-(tert-butyl)-2,3-dihydrobenzo[d][1,3]oxaphosphol-4-yl)-6-methoxypyridine
Charged (*R*)-3-(tert-butyl)-4-(6-methoxypyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-oxide (100 mg, 0.315 mmol) to a Schlenk tube under Argon. Charged degassed and dry THF (2 mL) to above tube. Charged PMHS (513 mg) to above tube followed by $Ti(OiPr)_4$ (179.15 mg, 0.63mmol, 2 equiv) at RT. The mixture was stirred at 65 ^oC for 15 h until ^{31}P NMR showed complete conversion. Concentrated the reaction mixture via reduced pressure under argon to dryness. Cooled to 0 ^oC and carefully added degassed 30% NaOH solution (4 mL). Gas was generated during addition. The resulting mixture was further stirred at 60 ^oC for 1 h. The aqueous layer was extracted with MTBE (5 mL x 4) under argon. The MTBE solution was passed through a pad of neutral alumina/$MgSO_4$/sand under argon and rinsed with degassed MTBE (3 mL). The MTBE layer was dried under vacuum under argon to afford 80.7 mg of thick oil in 85% yield. ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.54 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.29 (m, 2H), 6.87 (m, 1H), 6.6 (d, *J* = 8.0 Hz, 1H), 4.76 (dd, *J* = 12.5, 2.0 Hz, 1H), 4.55 (dd, *J* = 26.5, 12.5 Hz, 1H), 3.97 (s, 3H), 0.60 (d, J = 11.5 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 163.6, 156.6 (d, *J* = 2.0 Hz), 143.7 (d, *J* = 12.0 Hz), 138.9, 131.2 (d, *J* = 1.0 Hz), 121.8 (d, *J* = 20.0 Hz), 116.2 (d, *J* = 7.0 Hz), 111.3 (d, *J* = 1.0 Hz), 109.3, 69.9 (d, *J* = 27.0 Hz), 54.1 (d, *J* = 5.0 Hz), 31.8 (d, *J* = 21.0 Hz), 26.7 (d, *J* = 14.0 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ -9.65; HRMS (ESI) m/z $[M+H]^+$, $C_{17}H_{21}NO_2P$, 302.1304, found 302.1309.



(*R*)-tert-butyl(2,6-dimethoxyphenyl)((6-methoxypyridin-2-yl)methyl)phosphine oxide: (*R*)-tert-butyl(2,6-dimethoxyphenyl)(methyl)phosphine oxide (0.50 g, 1.95 mmol), 2-methoxy-6-(phenylsulfonyl)pyridine (0.535 g, 2.15 mmol, 1.1 eq), THF (10 mL) were added to a dry flask with agitation under nitrogen and the solution was cooled to -70 °C. LDA (2 M in THF, 0.98 mL, 1.95 mmol, 1.0 eq) was added to the flask dropwise. The mixture was warmed up to 20 °C. LDA (2 M in THF, 0.98 mL, 1.95 mmol, 1.0 eq) was added to the flask dropwise. After stir 1 h, the reaction is quenched with methanol (1.5 mL) at -45 °C. The solvent was removed under vacuum and ethyl acetate (30 mL) and saturated ammonium chloride aqueous solution (15 mL) were added. Layers were separated. The organic layer was dried over sodium sulfate and concentrated and purified by silica gel chromatography eluted with 25% ethanol in ethyl acetate to yield (*R*)-tert-butyl(2,6-dimethoxyphenyl)((6-methoxypyridin-2-yl)methyl)phosphine oxide (0.30 g) as a dense light yellow oil in 42% yield; $[\alpha]_D^{23}$ = - 42.2° (c 0.23, EtOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20 (d, *J* = 15.0 Hz, 9H), 3.69 (t, *J* = 14.8 Hz, 1H), 3.77 (s, 6H), 3.78 (s, 3H), 3.84 (dd, *J* = 14.8, 12.0 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 1H), 6.50 (d, *J* = 3.8 Hz, 1H), 6.52 (d, *J* = 3.8 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 163.1, 152.7 (d, *J* = 6.7 Hz), 138.5 (d, *J* = 1.7 Hz), 133.5 (d, *J* = 1.4 Hz), 117.8 (d, *J* = 4.1 Hz), 107.6 (d, *J* = 2.1 Hz), 107.4 (d, *J* = 81.1 Hz), 104.3 (d, *J* = 5.9 Hz), 55.7, 53.1, 38.7 (d, *J* = 62.3 Hz), 36.0 (d, *J* = 70.8 Hz), 24.9 (d, *J* = 1.3 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 49.79; HRMS (ESI) m/z $[M+H]^+$: $C_{19}H_{26}NO_4P$, 364.1681, found 364.1672.

(S)-2-((tert-butyl(2,6-dimethoxyphenyl)phosphanyl)methyl)-6-methoxypyridine (*R*)-tert-butyl(2,6-dimethoxyphenyl)((6-methoxypyridin-2-yl)methyl)phosphine oxide (0.50 g, 1.38 mmol), THF (5 mL), polymethyldydrosiloxane (1.40 mL, 5.50 mmol, 4.0 eq), titanium (IV) isopropoxide (1.21 mL, 4.13 mmol, 3.0 eq) were added to a dry flask with agitation under nitrogen and heated at 65°C for 16 h. The reaction mixture is cooled to 20 °C. 6 N sodium hydroxide aqueous solution (6 mL) is slowly charged to the flask. The mixture is heated up to 65 °C and agitated for 1 h. The mixture is then cooled to 20 °C and extracted with tert-butyl methyl ether (12 mL). The extract is filtered through a neutral alumina and magnesium sulfate pad and concentrated to yield (*S*)-2-((tert-butyl(2,6-dimethoxyphenyl)phosphanyl)methyl)-6-methoxypyridine, which solidified as white solid upon sitting, 0.25 g, 53% yield. NMR (500 MHz, $CDCl_3$) δ 1.13(d, *J* = 12.2 Hz, 9H), 3.35 (dd, *J* = 14.2, 2.0 Hz, 1H), 3.78 (s, 9H), 3.79–3.82 (m, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 8.3, 2.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.3 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0 (d, *J* = 6.9 Hz), 163.1 (d, *J* = 0.9 Hz), 159.4, 138.4, 131.2, 116.2 (d, *J* = 7.6 Hz), 106.7, 103.9 (d, *J* = 1.1 Hz), 55.4, 53.1, 31.9 (d, *J* = 13.8 Hz), 31.4, 28.6 (d, *J* = 14.5 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ -2.10; HRMS (ESI) m/z [M + H^+]), $C_{19}H_{26}NO_3P$, 348.1732, found 348.1723.



BRUKER

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Current Data Parameters
NAME          103178-097
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
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Time               16.39
INSTRUM            spect
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PULPROG             zg10
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             7500.000 Hz
FIDRES          0.228882 Hz
AQ              2.1845334 sec
RG                   406
DW                66.667 usec
DE                 6.50 usec
TE                299.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.90 usec
PL1                 2.10 dB
PL1W         18.43091774 W
SFO1         500.1325007 MHz

F2 - Processing parameters
SI                 16384
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WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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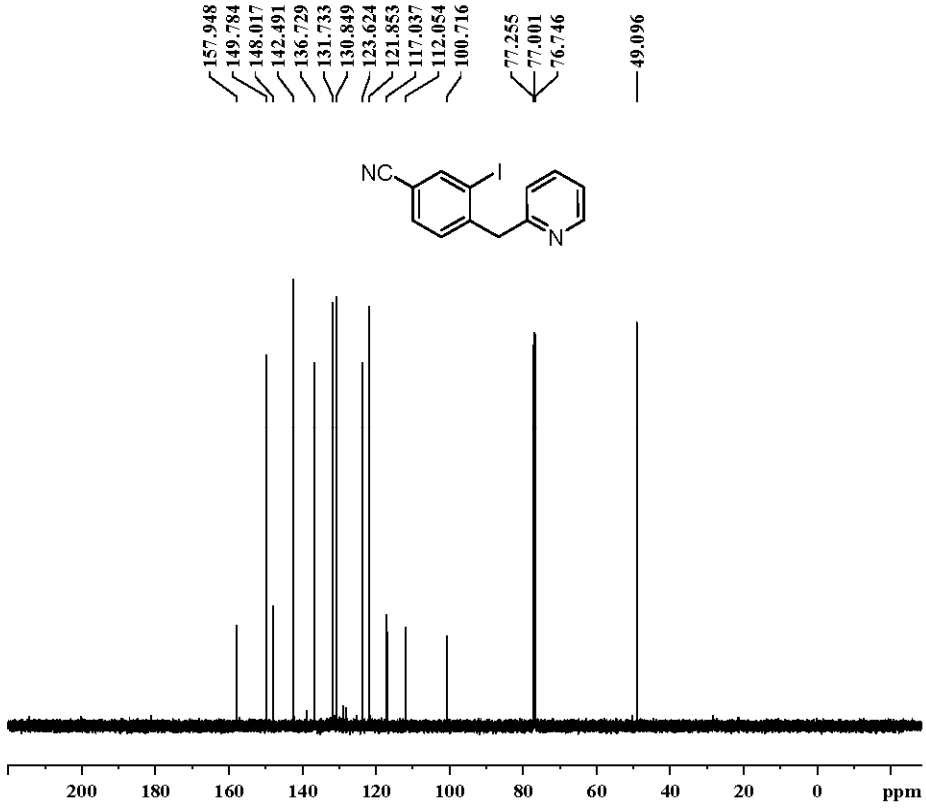


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Current Data Parameters
NAME          103178-097
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
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Time              17.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg
TD              262144
SOLVENT           CDCl3
NS                  256
DS                    0
SWH           31250.000 Hz
FIDRES         0.119209 Hz
AQ            4.1943040 sec
RG                 2050
DW               16.000 usec
DE                6.50 usec
TE               299.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                    1
SFO1        125.7698617 MHz
NUC1                13C
P1                10.64 usec
PLW1        -1.00000000 W
SFO2        500.1325007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        -1.00000000 W
PLW12       -1.00000000 W
PLW13       -1.00000000 W

F2 - Processing parameters
SI                131072
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WDW                 EM
SSB       0
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PC                 1.40
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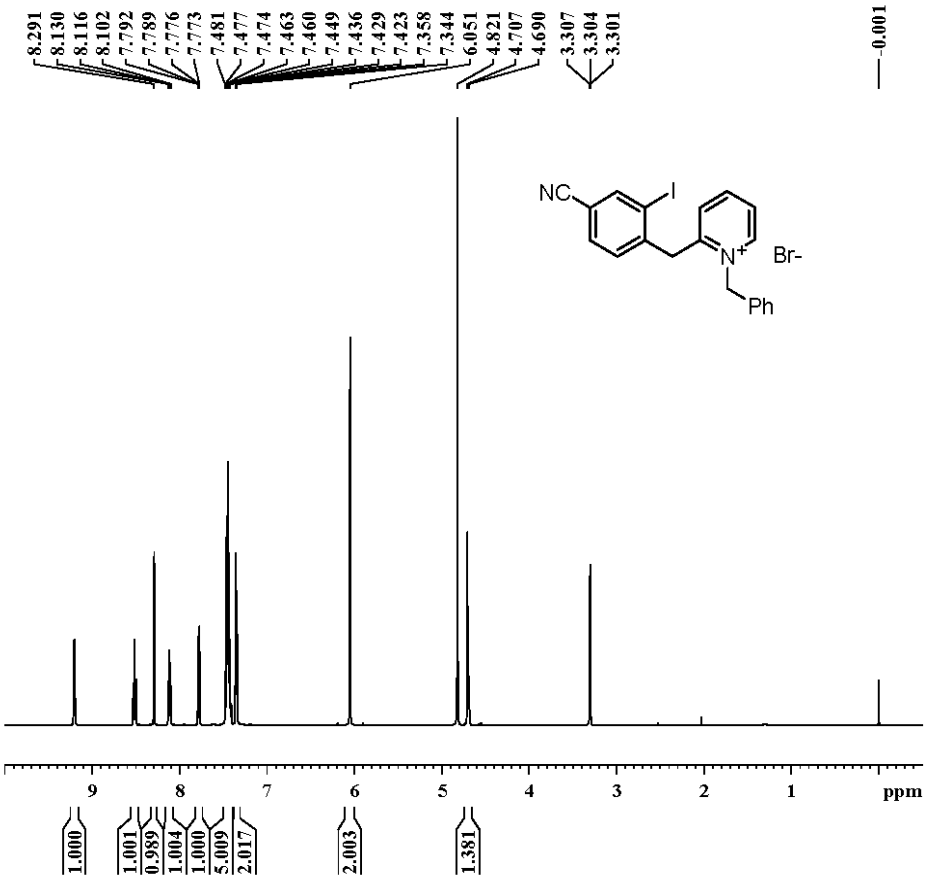

BRUKER

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Current Data Parameters
NAME          103790-066
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160404
Time               17.02
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg10
TD                 32768
SOLVENT             MeOD
NS                    32
DS                     0
SWH             7500.000 Hz
FIDRES          0.228882 Hz
AQ              2.1845334 sec
RG                   362
DW                66.667 usec
DE                 6.50 usec
TE                299.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.1325007 MHz
NUC1                  1H
P1                 11.75 usec
PLW1         18.39999962 W

F2 - Processing parameters
SI                 16384
SF            500.1300123 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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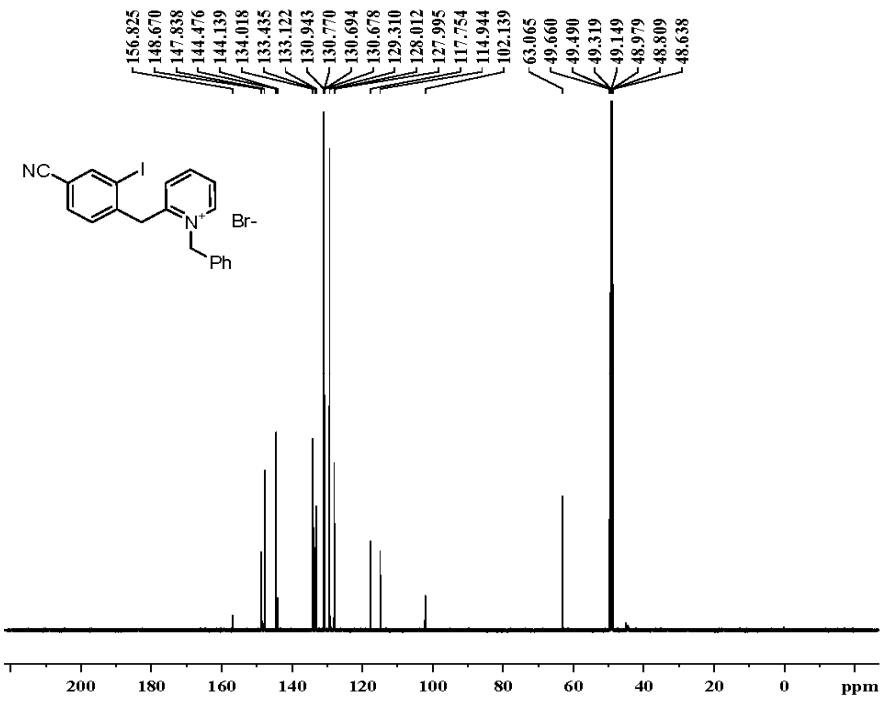

BRUKER

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Current Data Parameters
NAME          103790-066
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
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Time               19.23
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg
TD                262144
SOLVENT             MeOD
NS                  1600
DS                     0
SWH            31250.000 Hz
FIDRES         0.119209 Hz
AQ             4.1943040 sec
RG                  2050
DW                16.000 usec
DE                 6.50 usec
TE                299.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7698617 MHz
NUC1               13C
P1                9.75 usec
PLW1       126.00000000 W

======== CHANNEL f2 ========
SFO2         500.1325007 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         18.39999962 W
PLW12         0.41056001 W
PLW13         0.20651001 W

F2 - Processing parameters
SI                131072
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WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.40
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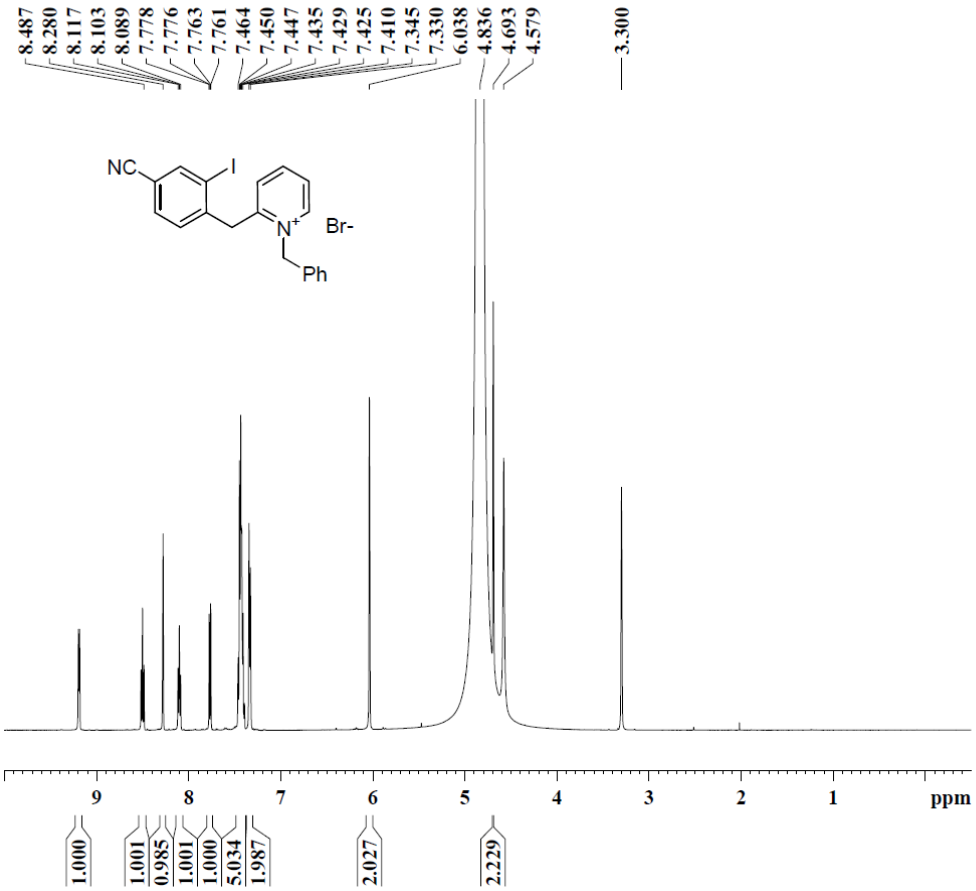
Sample in CD3OH

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Current Data Parameters
NAME          xze1-00025
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
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Time              17.11
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg10
TD                32768
SOLVENT            MeOD
NS                   256
DS                     0
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ            1.6384000 sec
RG                    36
DW               50.000 usec
DE                6.50 usec
TE               299.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        500.1325007 MHz
NUC1                   1H
P1                14.00 usec
PLW1        18.79999924 W

F2 - Processing parameters
SI                 16384
SF            500.1300139 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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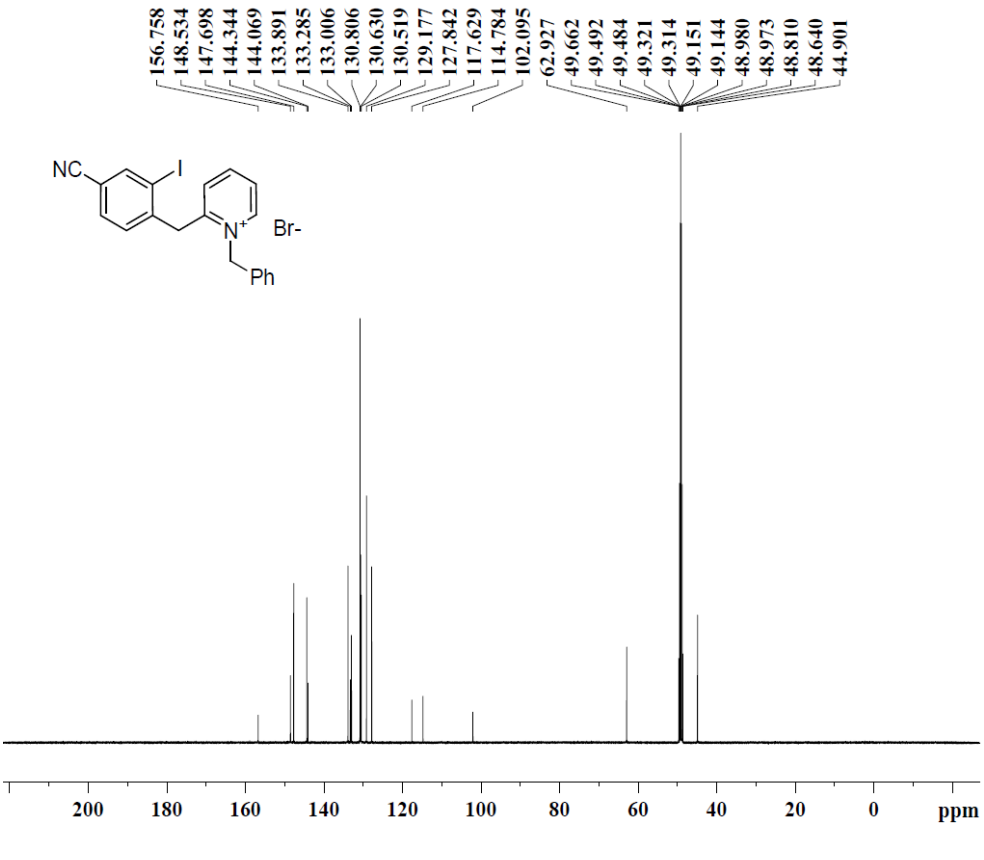
Sample in CD3OH

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Current Data Parameters
NAME          xze1-00025
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161024
Time               21.53
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg
TD                262144
SOLVENT             MeOD
NS                  3200
DS                     0
SWH            31250.000 Hz
FIDRES         0.119209 Hz
AQ             4.1943040 sec
RG                  2050
DW               16.000 usec
DE                6.50 usec
TE                299.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7698617 MHz
NUC1                 13C
P1                10.00 usec
PLW1         99.50000000 W

======== CHANNEL f2 ========
SFO2         500.1325007 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             80.00 usec
PLW2         18.79999924 W
PLW12         0.57574999 W
PLW13         0.28960001 W

F2 - Processing parameters
SI                131072
SF           125.7576133 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
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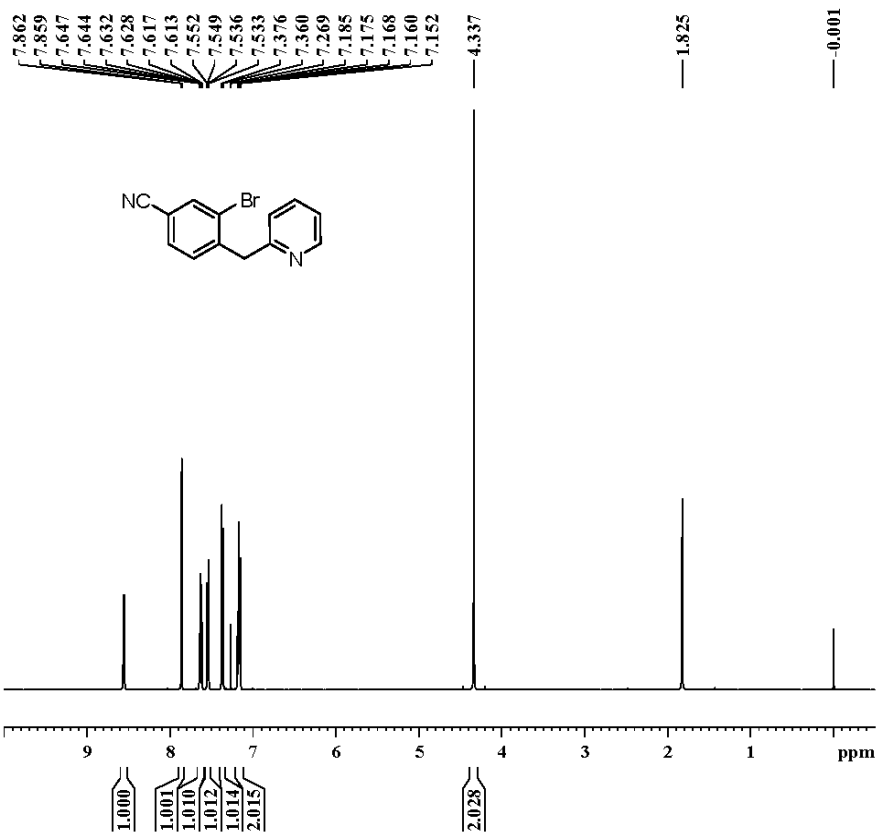


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Current Data Parameters
NAME          103790-067
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160404
Time              19.29
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            7500.000 Hz
FIDRES         0.228882 Hz
AQ             2.1845334 sec
RG                 322
DW              66.667 usec
DE               6.50 usec
TE               299.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1325007 MHz
NUC1               1H
P1              11.75 usec
PLW1        18.39999962 W

F2 - Processing parameters
SI                 16384
SF           500.1300075 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC                 1.00
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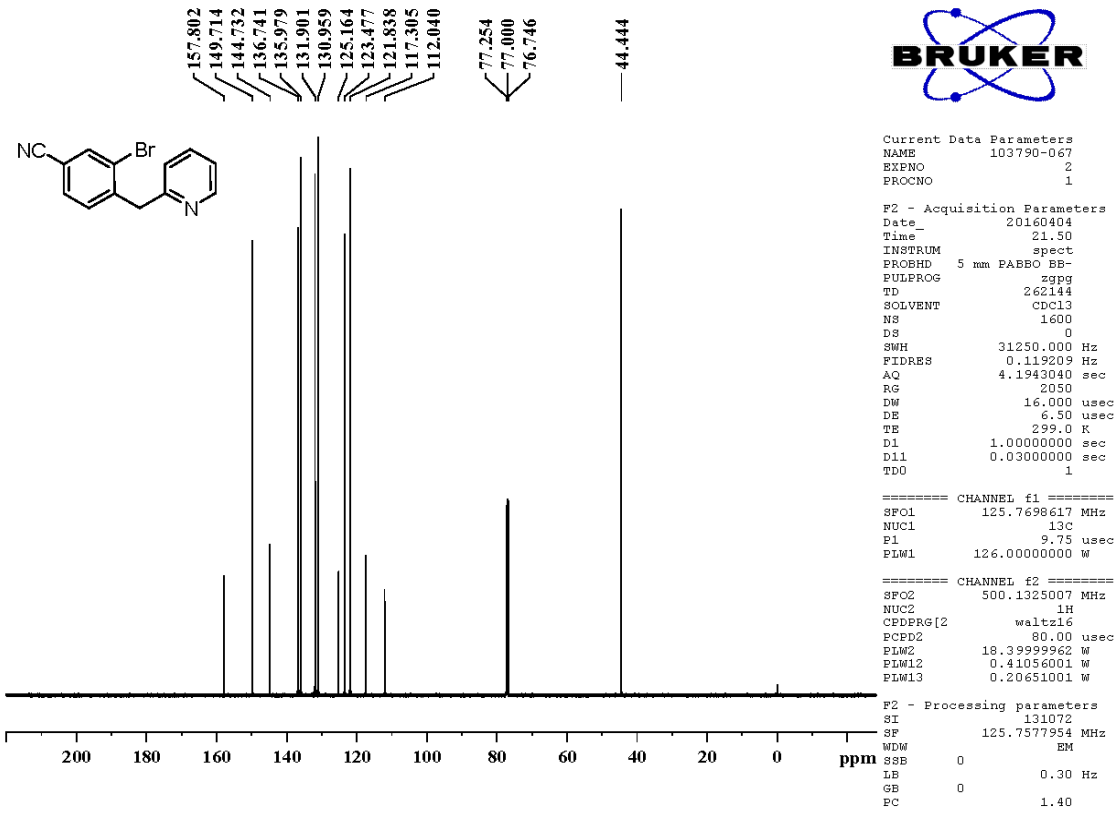
157.802
149.714
144.732
136.741
135.979
131.901
130.959
125.164
123.477
121.838
117.305
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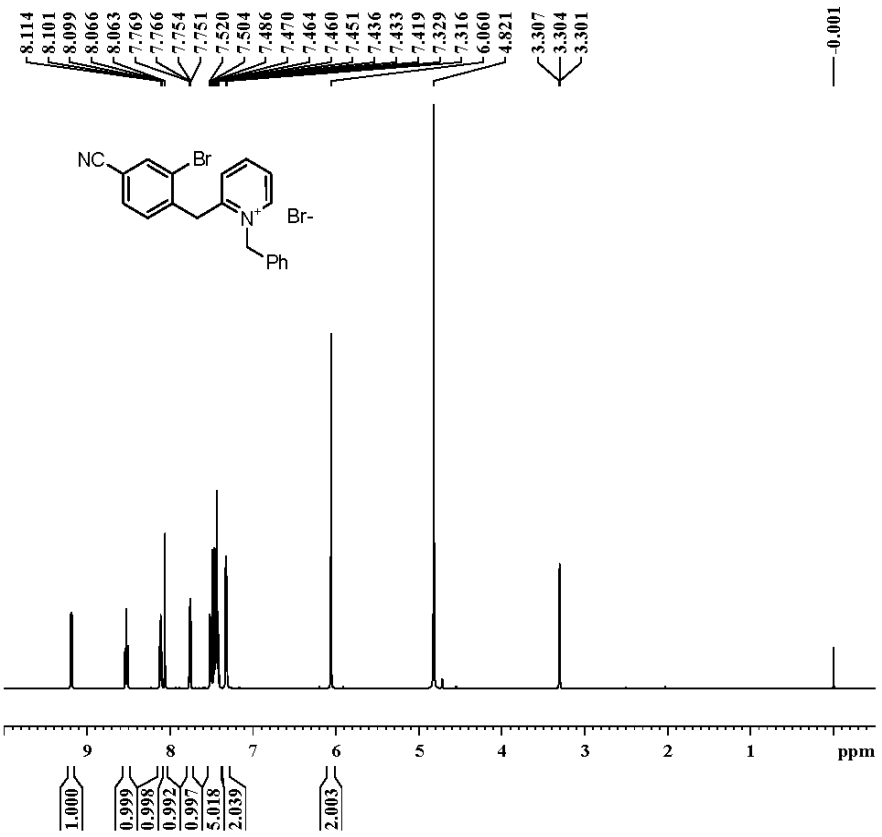
77.254
77.000
76.746
44.444
NC
Br
N
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME 103790-067
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160404
Time 21.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 262144
SOLVENT CDCl3
NS 1600
DS 0
SWH 31250.000 Hz
FIDRES 0.119209 Hz
AQ 4.1943040 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7698617 MHz
NUC1 13C
P1 9.75 usec
PLW1 126.00000000 W
======== CHANNEL f2 ========
SFO2 500.1325007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 18.39999962 W
PLW12 0.41056001 W
PLW13 0.20651001 W
F2 - Processing parameters
SI 131072
SF 125.7577954 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

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Current Data Parameters
NAME          103790-068
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160404
Time              21.55
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT            MeOD
NS                   32
DS                    0
SWH            7500.000 Hz
FIDRES         0.228882 Hz
AQ             2.1845334 sec
RG                  362
DW               66.667 usec
DE                6.50 usec
TE                299.0 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         500.1325007 MHz
NUC1               1H
P1                11.75 usec
PLW1        18.39999962 W

F2 - Processing parameters
SI                16384
SF           500.1300123 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
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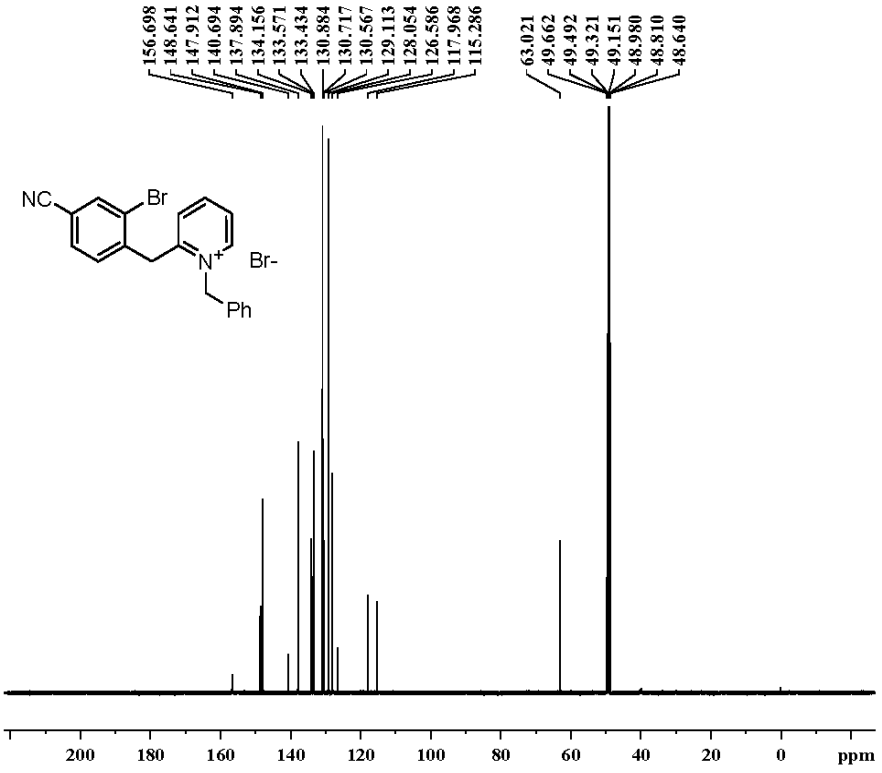
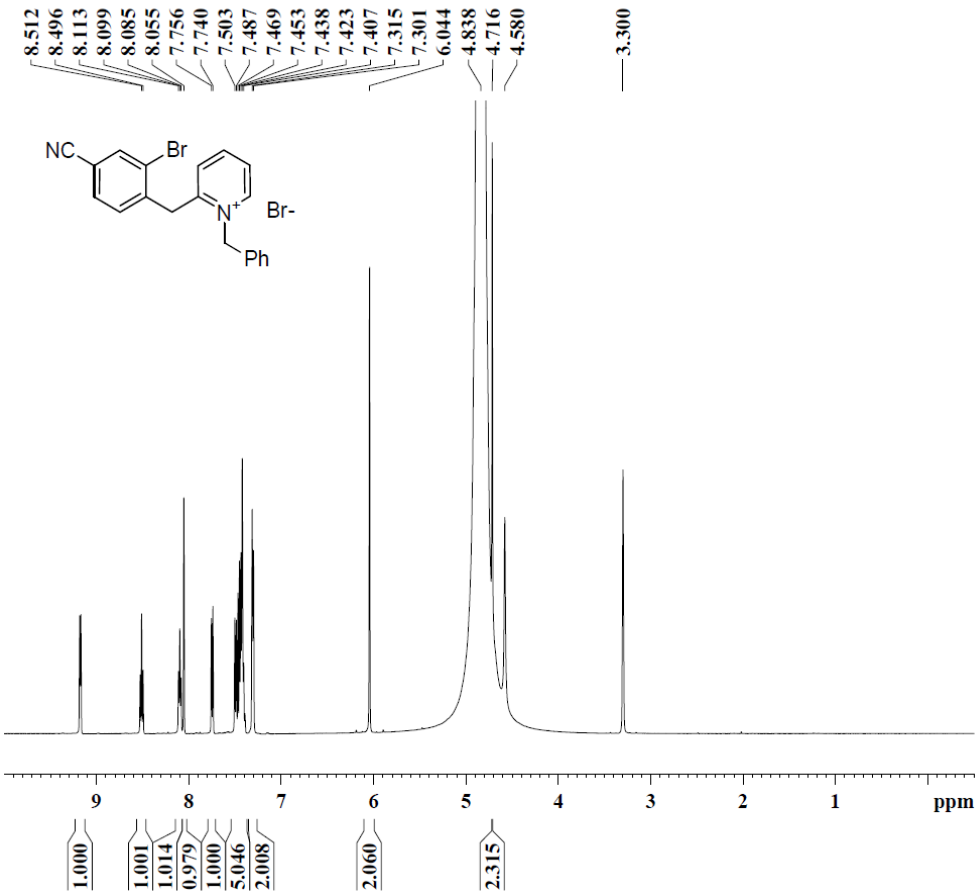


BRUKER

```
Current Data Parameters
NAME                 103790-068
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_               20160405
Time                     0.16
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg
TD                    262144
SOLVENT                 MeOD
NS                      1600
DS                         0
SWH                31250.000 Hz
FIDRES             0.119209 Hz
AQ                 4.1943040 sec
RG                      2050
DW                    16.000 usec
DE                     6.50 usec
TE                    299.0 K
D1                 1.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             125.7698617 MHz
NUC1                     13C
P1                      9.75 usec
PLW1            126.00000000 W

======== CHANNEL f2 ========
SFO2             500.1325007 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                  80.00 usec
PLW2             18.39999962 W
PLW12             0.41056001 W
PLW13             0.20651001 W

F2 - Processing parameters
SI                      131072
SF               125.7575964 MHz
WDW                        EM
SSB       0
LB                      0.30 Hz
GB        0
PC                      1.40
```

Sample in CD3OH

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Current Data Parameters
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EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161021
Time              18.43
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg10
TD               32768
SOLVENT           MeOD
NS                 256
DS                   0
SWH          10000.000 Hz
FIDRES         0.305176 Hz
AQ           1.6384000 sec
RG                  36
DW             50.000 usec
DE              6.50 usec
TE              299.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.1325007 MHz
NUC1                1H
P1                14.00 usec
PLW1        18.79999924 W

F2 - Processing parameters
SI                 16384
SF          500.1300135 MHz
WDW                  EM
SSB       0
LB              0.30 Hz
GB        0
PC                 1.00
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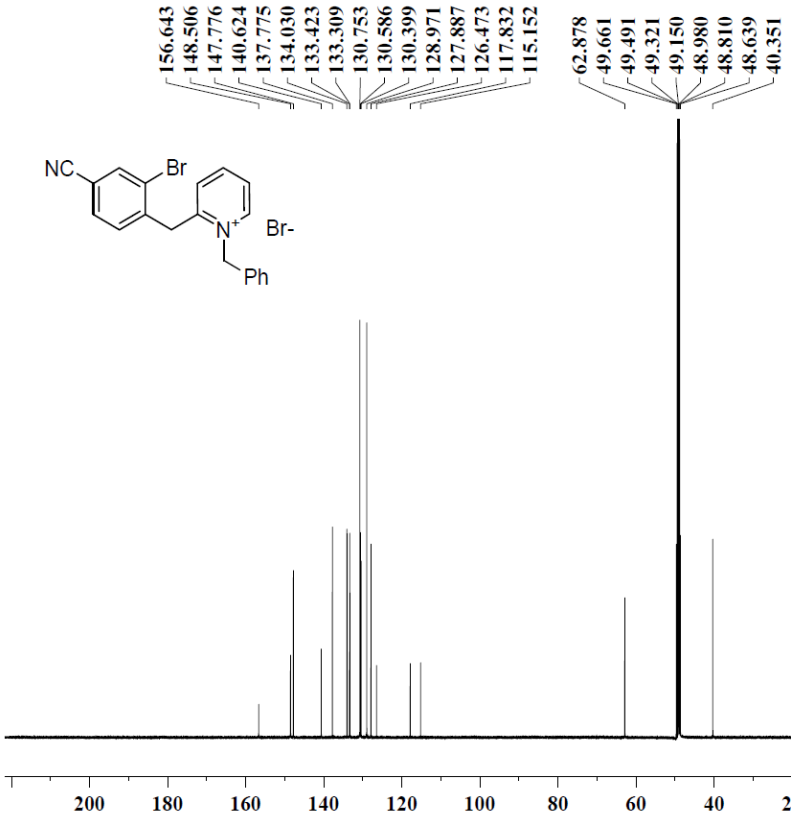
Sample in CD3OH




```
Current Data Parameters
NAME          xze1-00024
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
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Time              23.25
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg
TD              262144
SOLVENT           MeOD
NS                3200
DS                   0
SWH           31250.000 Hz
FIDRES        0.119209 Hz
AQ            4.1943040 sec
RG                2050
DW              16.000 usec
DE                6.50 usec
TE                299.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         125.7698617 MHz
NUC1               13C
P1               10.00 usec
PLW1         99.50000000 W

======== CHANNEL f2 ========
SFO2         500.1325007 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         18.79999924 W
PLW12         0.57574999 W
PLW13         0.28960001 W

F2 - Processing parameters
SI               131072
SF          125.7576122 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
```
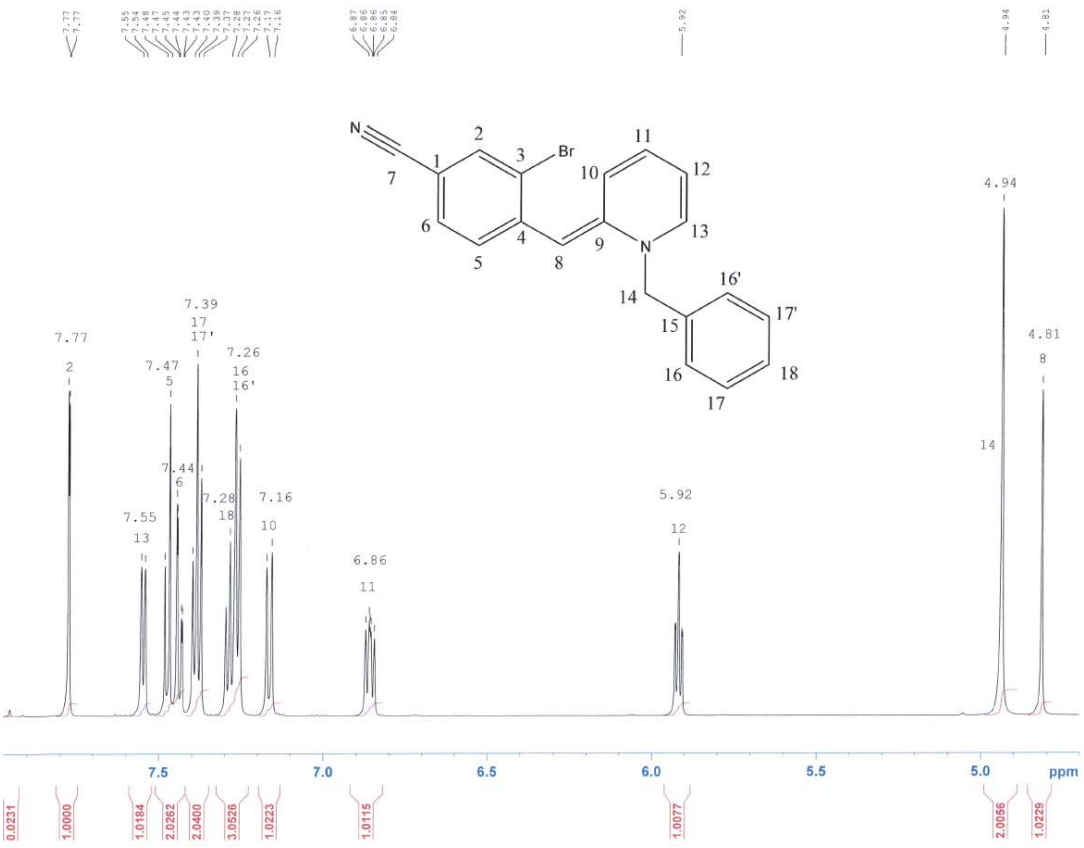
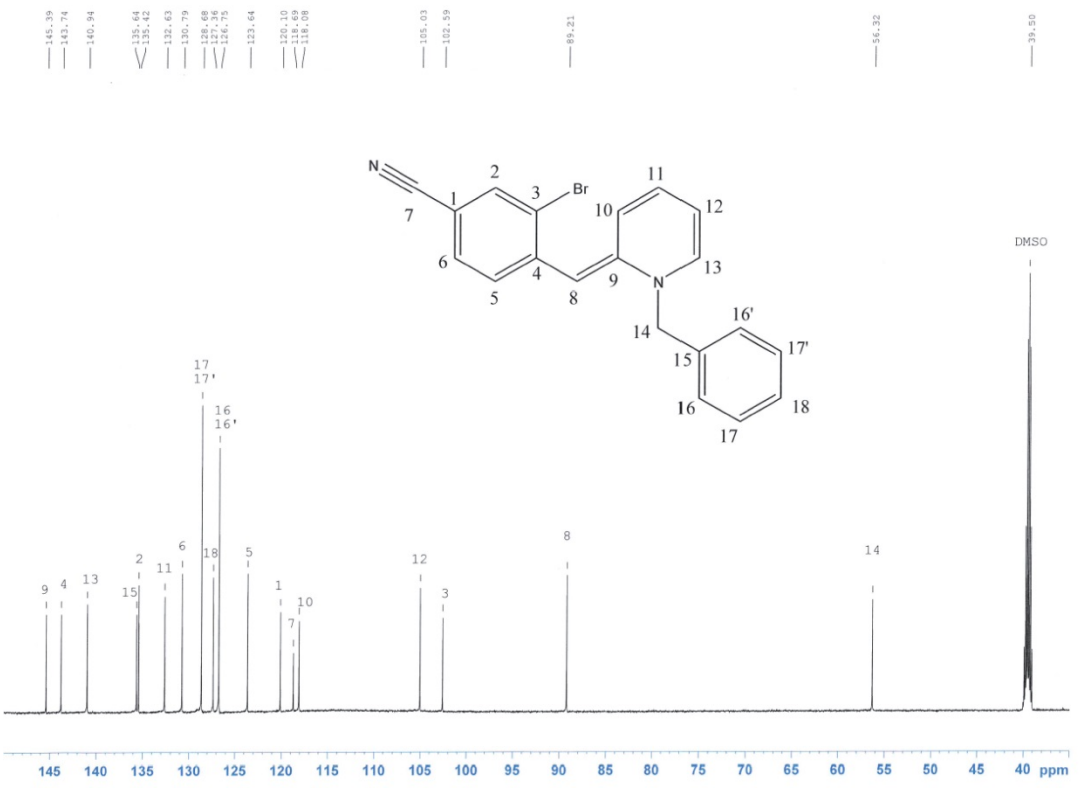
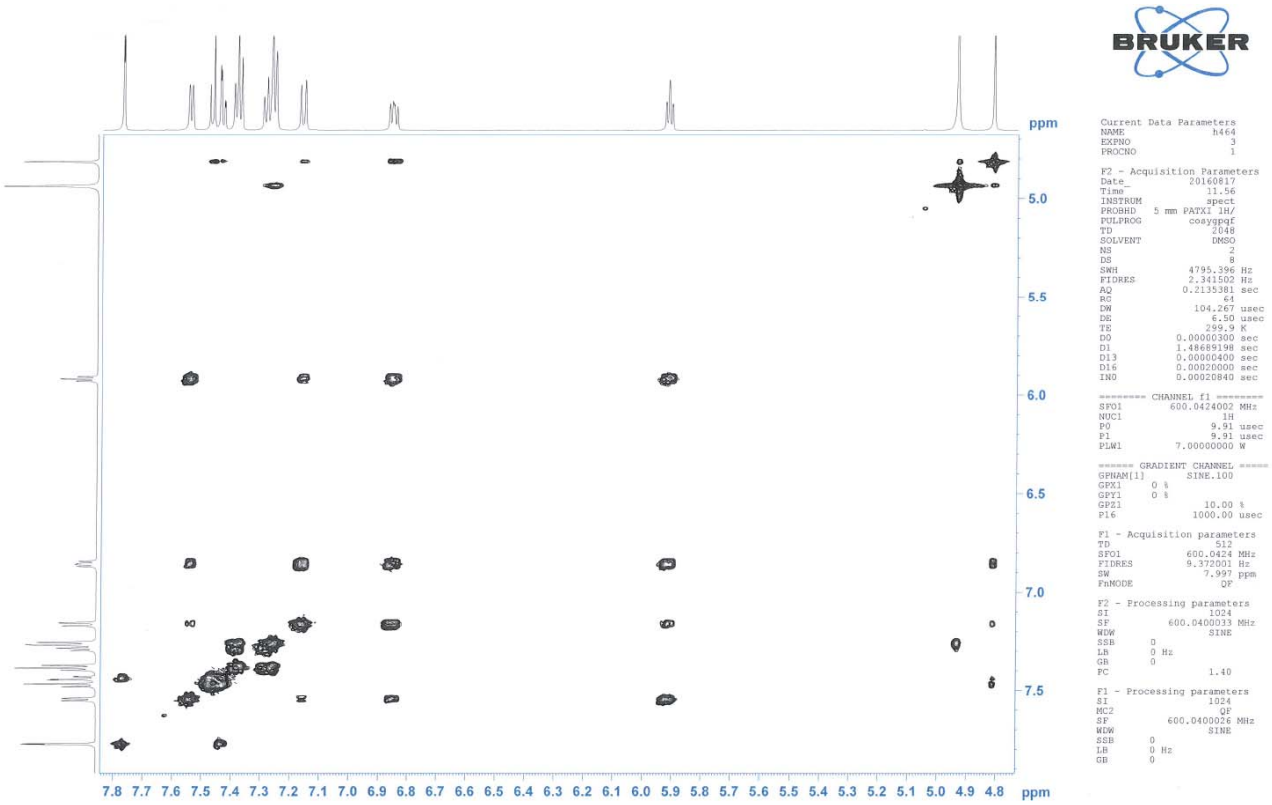





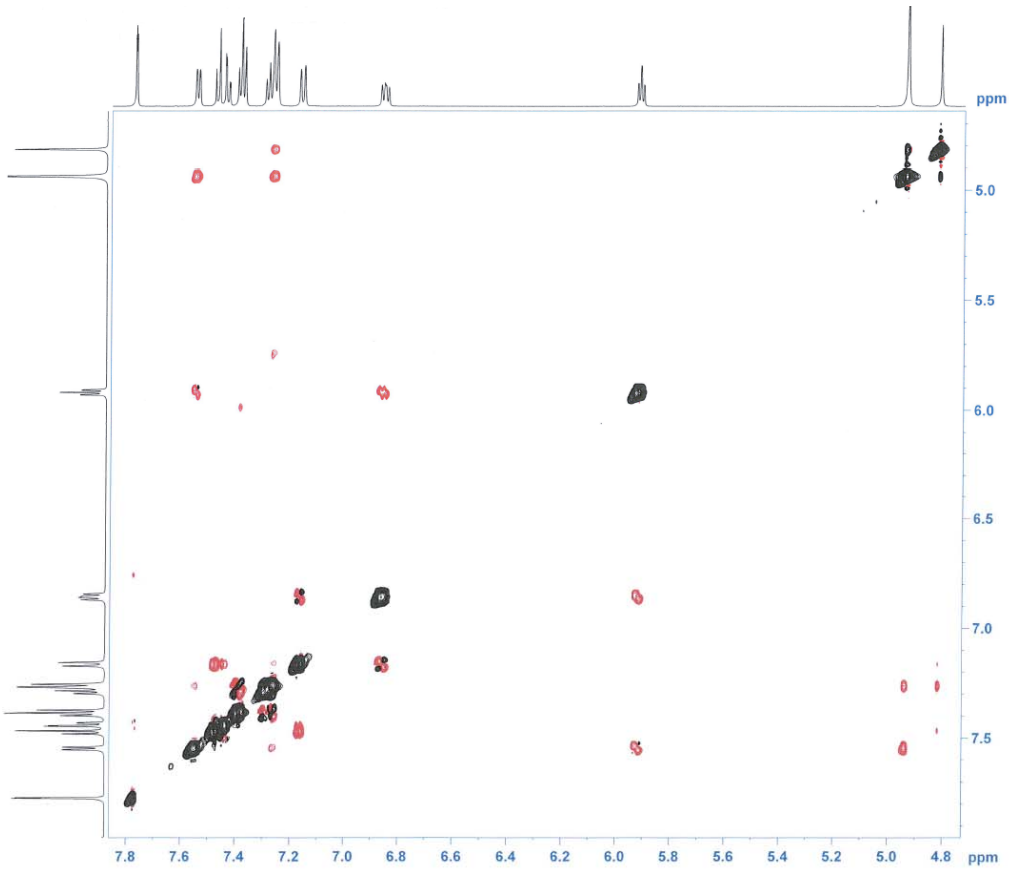

```
Current Data Parameters
NAME                  h464
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20160817
Time                 10.13
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG              zg10
TD                  32768
SOLVENT              DMSO
NS                     128
DS                       2
SWH              7211.539 Hz
FIDRES           0.220079 Hz
AQ               2.2719147 sec
RG                     144
DW                69.333 usec
DE                 6.50 usec
TE                 300.0 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            600.0428802 MHz
NUC1                    1H
P1                    9.91 usec
PLW1            7.00000000 W

F2 - Processing parameters
SI                   32768
SF              600.0400041 MHz
WDW                     EM
SSB                  0
LB                    0.30 Hz
GB                   0
PC                    1.00
```

```
Current Data Parameters
NAME                  h464
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20160817
Time                 11.55
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                    3200
DS                       4
SWH             27173.912 Hz
FIDRES           0.414641 Hz
AQ               1.2058624 sec
RG                     362
DW                18.400 usec
DE                 6.50 usec
TE                 300.0 K
D1              0.50000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            150.8930028 MHz
NUC1                   13C
P1                   14.00 usec
PLW1           177.00000000 W

======== CHANNEL f2 ========
SFO2            600.0424002 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2                70.00 usec
PLW2            7.00000000 W
PLW12           0.14030001 W
PLW13           0.07056900 W

F2 - Processing parameters
SI                   32768
SF              150.8802575 MHz
WDW                     EM
SSB                  0
LB                    1.00 Hz
GB                   0
PC                    1.40
```

COSY spectra of free base **8**



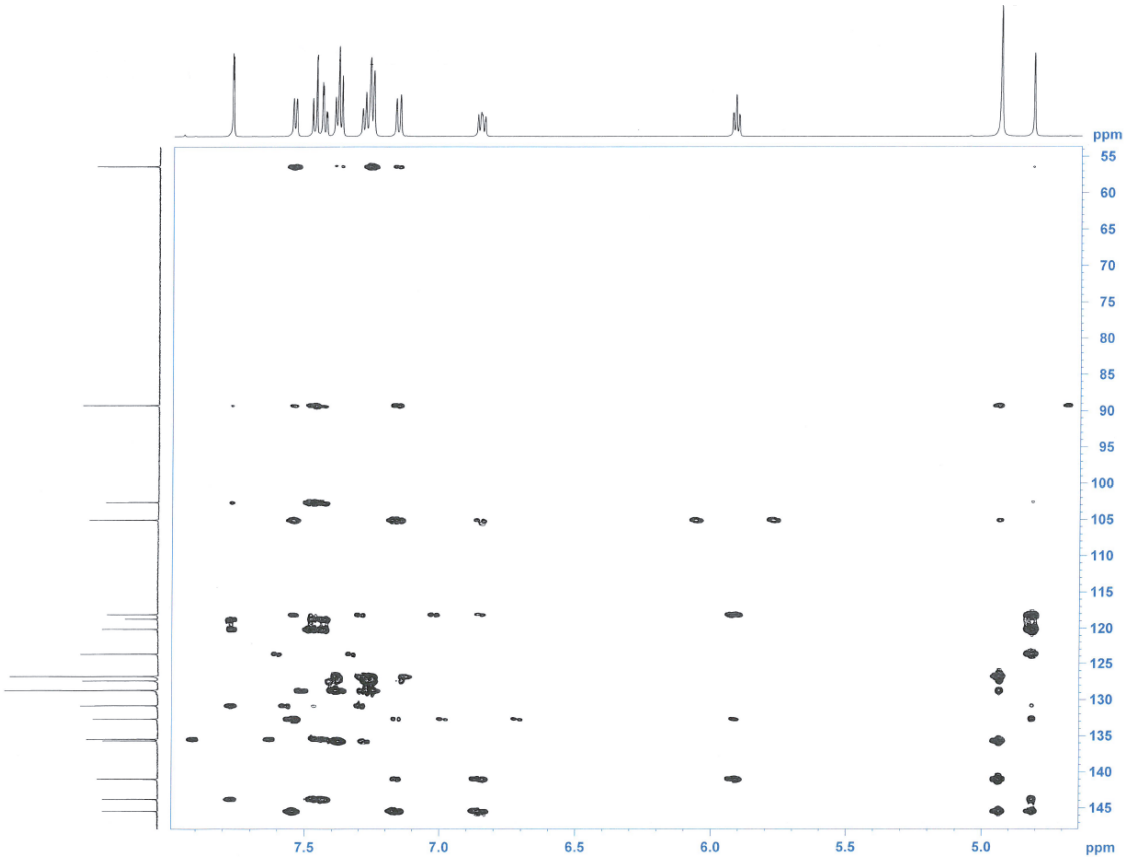
ROESY spectra of free base **8**



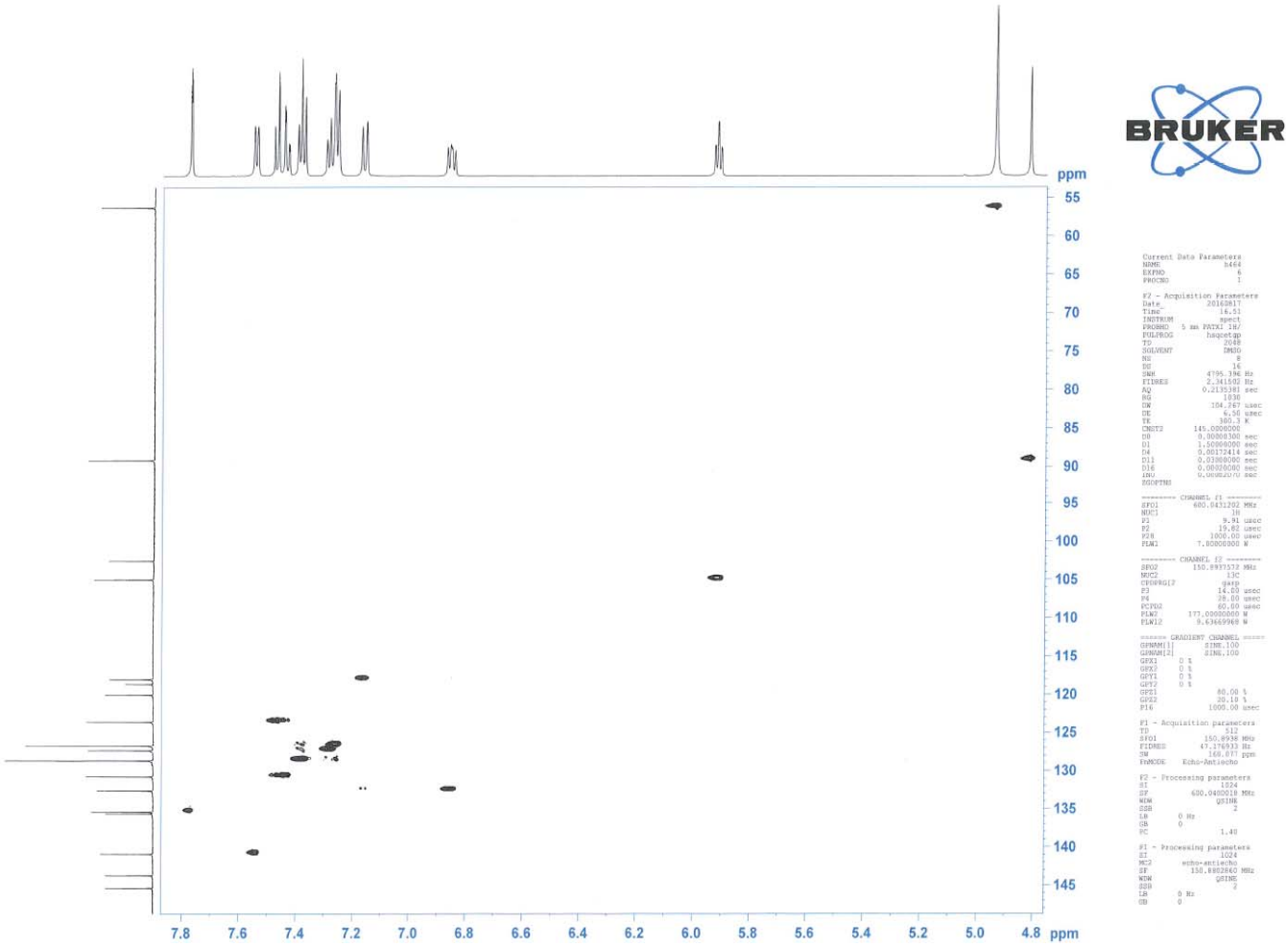
BRUKER

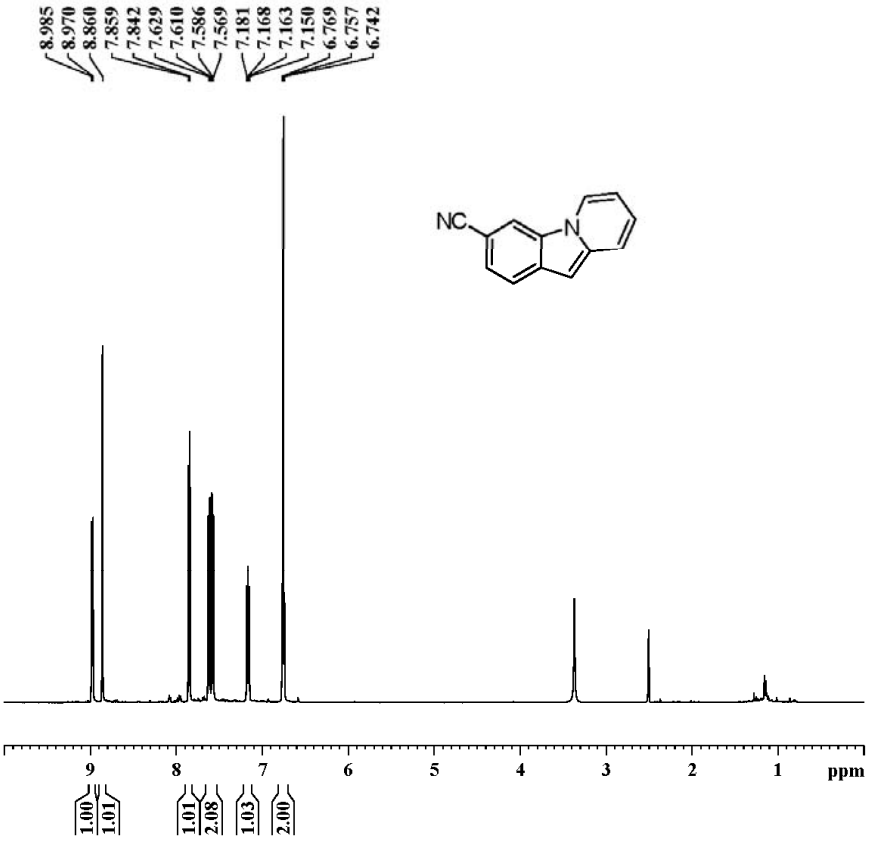
```
Current Data Parameters
NAME                  h464
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_              20160817
Time                 13.56
INSTRUM              spect
PROBHD    5 mm PATXI 1H/
PULPROG           roesyph
TD                   2048
SOLVENT               DMSO
NS                      8
DS                     16
SWH               4795.396 Hz
FIDRES            2.341502 Hz
AQ                0.2135381 sec
RG                     80.6
DW                 104.267 usec
DE                    6.50 usec
TE                   300.0 K
D0                0.00009389 sec
D1                2.00000000 sec
D12               0.00002000 sec
IN0               0.00020840 sec

======== CHANNEL f1 ========
SFO1            600.0428802 MHz
NUC1                    1H
P1                    9.91 usec
P15                300000.00 usec
PLW1              7.00000000 W
PLW11             0.08487100 W

F1 - Acquisition parameters
TD                      512
SFO1              600.0429 MHz
FIDRES            9.372001 Hz
SW                    7.997 ppm
FnMODE          States-TPPI

F2 - Processing parameters
SI                      1024
SF              600.0400010 MHz
WDW                   QSINE
SSB                       2
LB          0 Hz
GB          0
PC                     1.00

F1 - Processing parameters
SI                      1024
MC2             States-TPPI
SF              600.0400018 MHz
WDW                   QSINE
SSB                       2
LB          0 Hz
GB          0
```

HMBS spectra of **8**



HSQC spectra of **8**



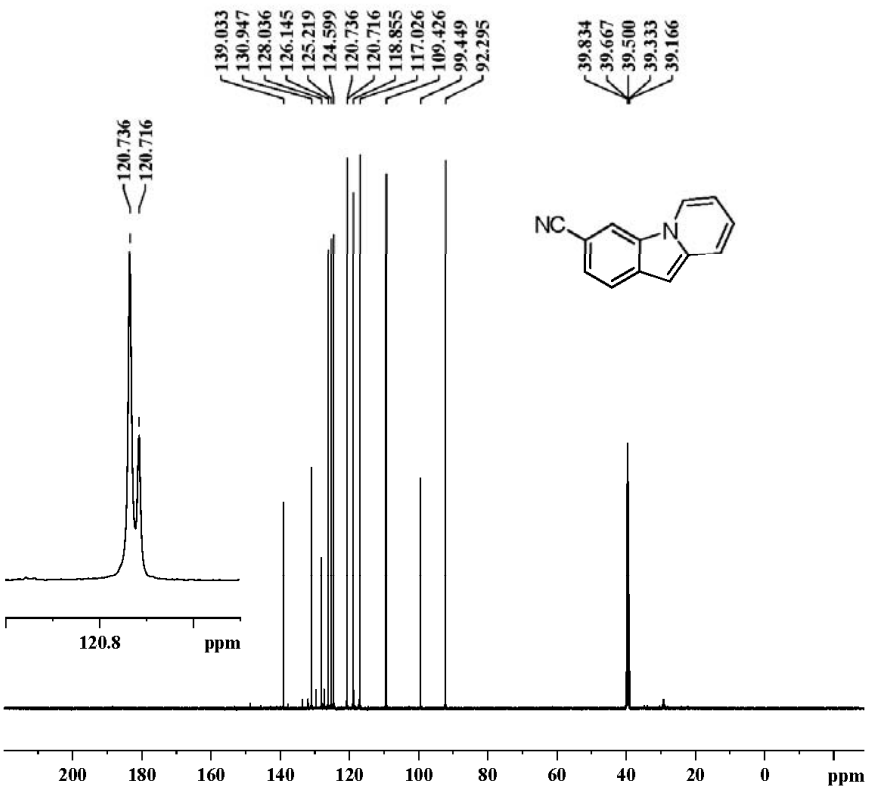


Current Data Parameters
NAME 103904-016
EXPNO 1
PROCNO 1

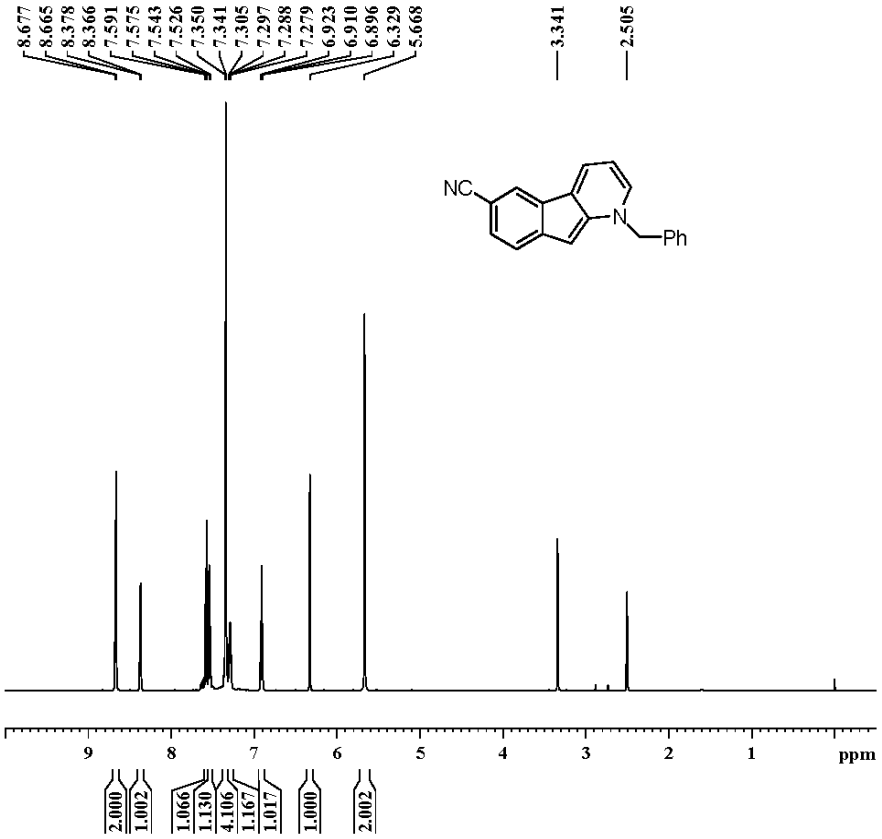
F2 - Acquisition Parameters
Date_ 20160609
Time 2.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg10
TD 32768
SOLVENT DMSO
NS 32
DS 0
SWH 7500.000 Hz
FIDRES 0.228882 Hz
AQ 2.1845334 sec
RG 144
DW 66.667 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1325007 MHz
NUC1 1H
P1 11.75 usec
PLW1 18.39999962 W

F2 - Processing parameters
SI 16384
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



```
Current Data Parameters
NAME                103904-016
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20160609
Time                      4.58
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zgpg
TD                     262144
SOLVENT                   DMSO
NS                        1600
DS                           0
SWH                31250.000 Hz
FIDRES             0.119209 Hz
AQ                 4.1943040 sec
RG                        2050
DW                   16.000 usec
DE                    6.50 usec
TE                    299.0 K
D1                 1.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1             125.7698617 MHz
NUC1                      13C
P1                     9.75 usec
PLW1            126.00000000 W

======== CHANNEL f2 ========
SFO2             500.1325007 MHz
NUC2                       1H
CPDPRG[2               waltz16
PCPD2                 80.00 usec
PLW2             18.39999962 W
PLW12             0.41056001 W
PLW13             0.20651001 W

F2 - Processing parameters
SI                       131072
SF               125.7578526 MHz
WDW                        EM
SSB          0
LB                     0.30 Hz
GB           0
PC                        1.40
```



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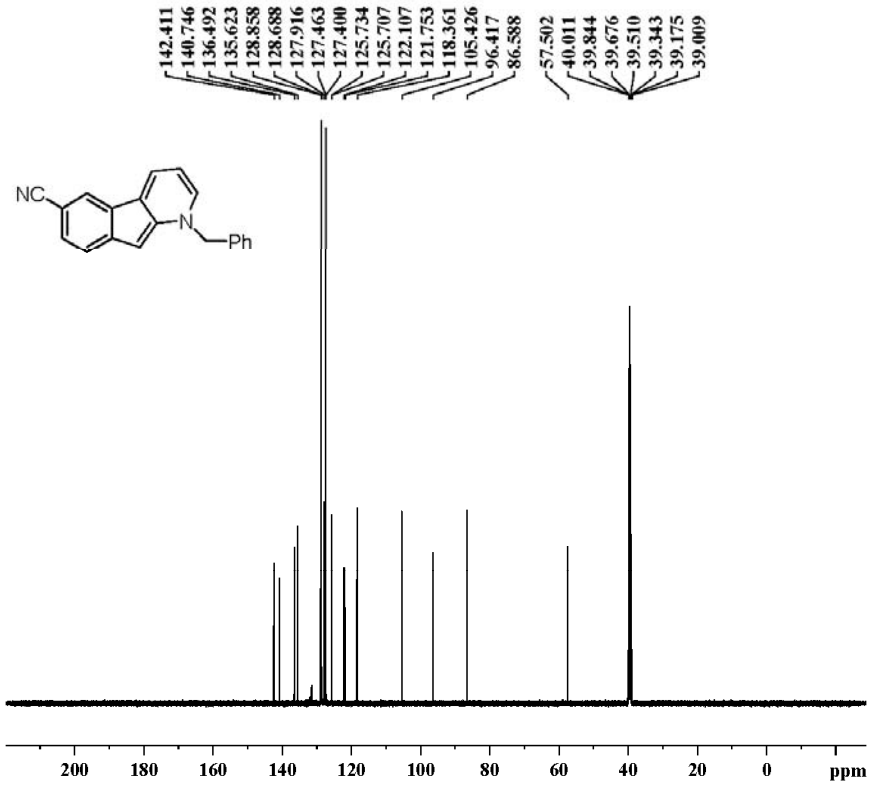
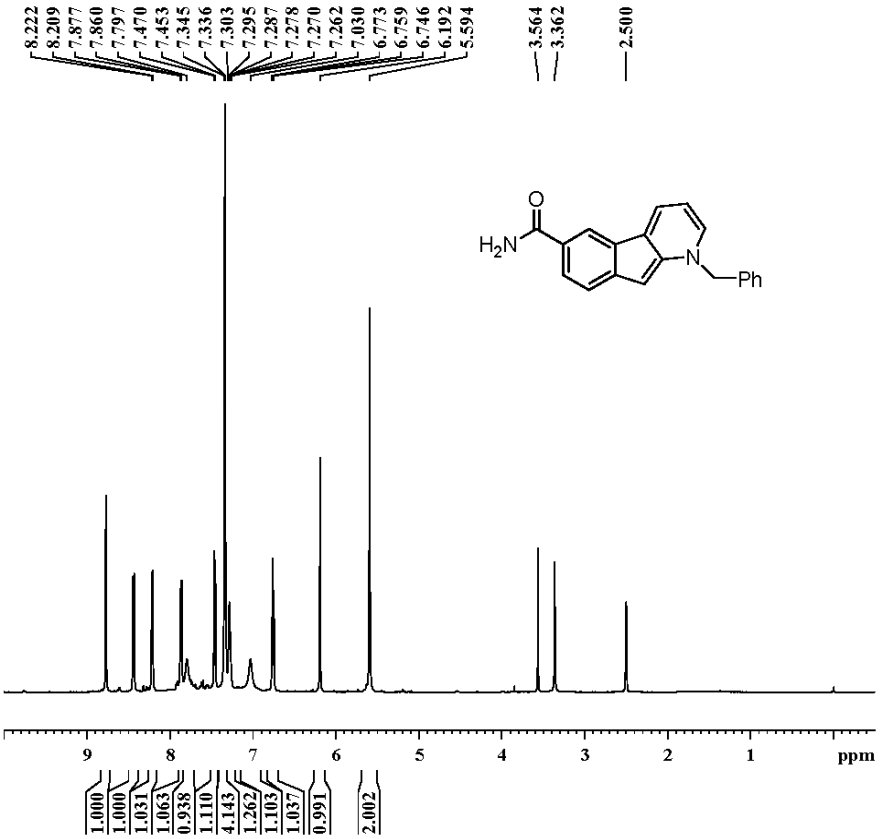
```
Current Data Parameters
NAME          102862-089-sm
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20130418
Time                 18.04
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg10
TD                  32768
SOLVENT              DMSO
NS                     32
DS                      0
SWH              7500.000 Hz
FIDRES           0.228882 Hz
AQ               2.1845334 sec
RG                     322
DW                66.667 usec
DE                 6.50 usec
TE                 299.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 11.70 usec
PL1                 2.10 dB
PL1W          18.43091774 W
SFO1          500.1325007 MHz

F2 - Processing parameters
SI                  16384
SF            500.1300015 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



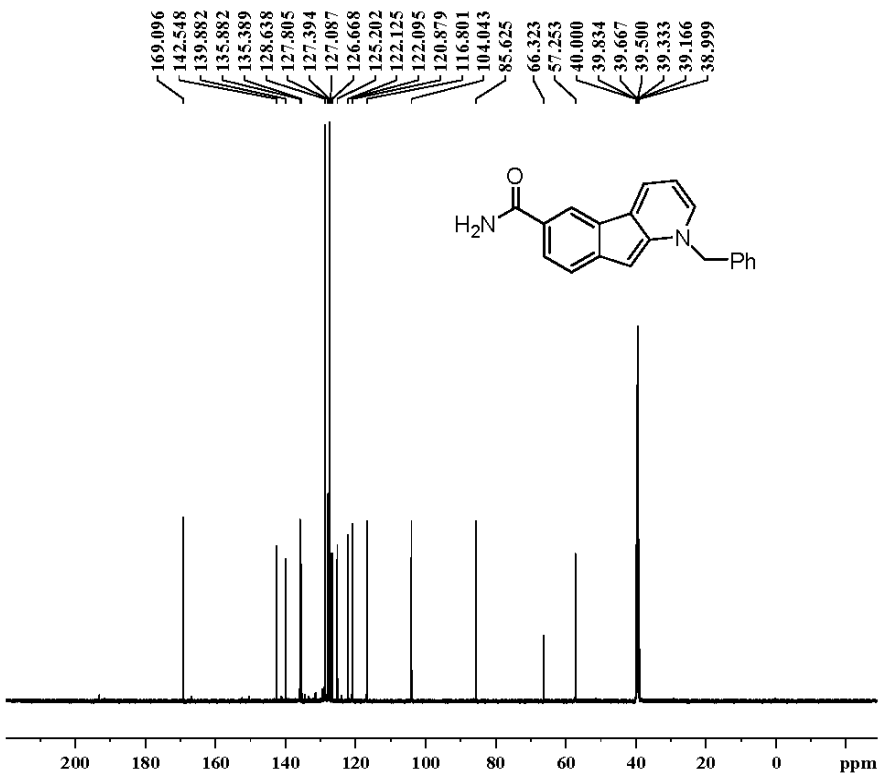
Current Data Parameters
NAME 102862-089-sm
EXPNO 2
PROCNO 1

F2 - Processing parameters
SI 131072
SF 125.7578528 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



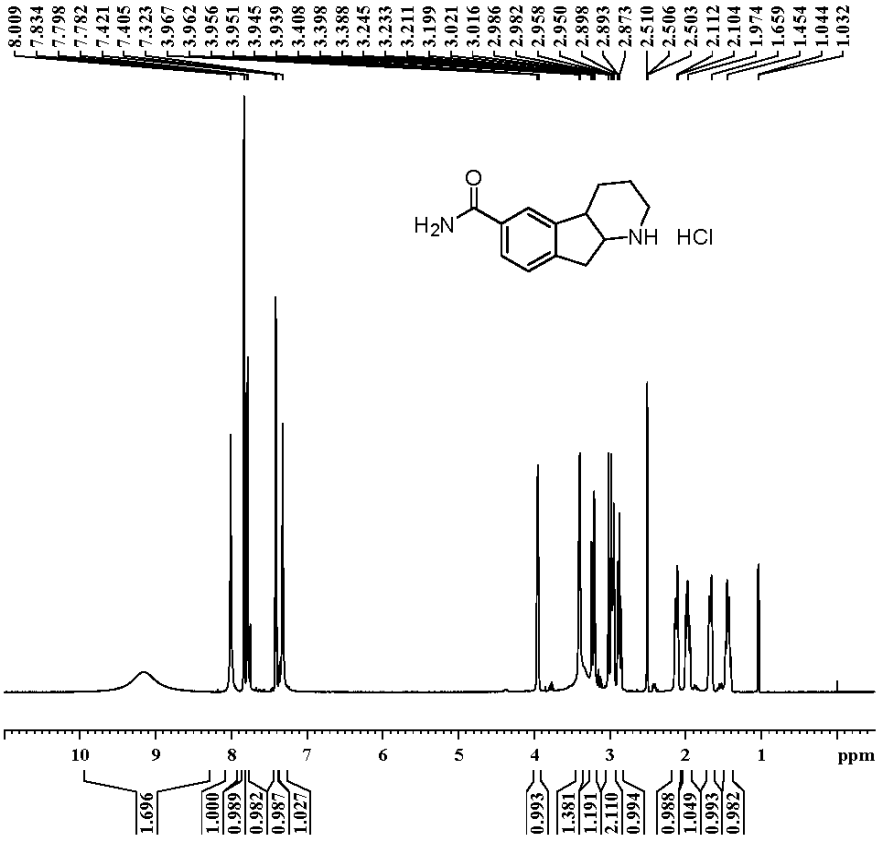
BRUKER

```
Current Data Parameters
NAME                  103904-013
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20160608
Time                       16.59
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                    zg10
TD                        32768
SOLVENT                    DMSO
NS                           32
DS                            0
SWH                    7500.000 Hz
FIDRES                 0.228882 Hz
AQ                     2.1845334 sec
RG                          228
DW                       66.667 usec
DE                         6.50 usec
TE                        299.0 K
D1                    1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 500.1325007 MHz
NUC1                         1H
P1                        11.75 usec
PLW1                 18.39999962 W

F2 - Processing parameters
SI                           16384
SF                   500.1300023 MHz
WDW                             EM
SSB                 0
LB                             0.30 Hz
GB                  0
PC                             1.00
```

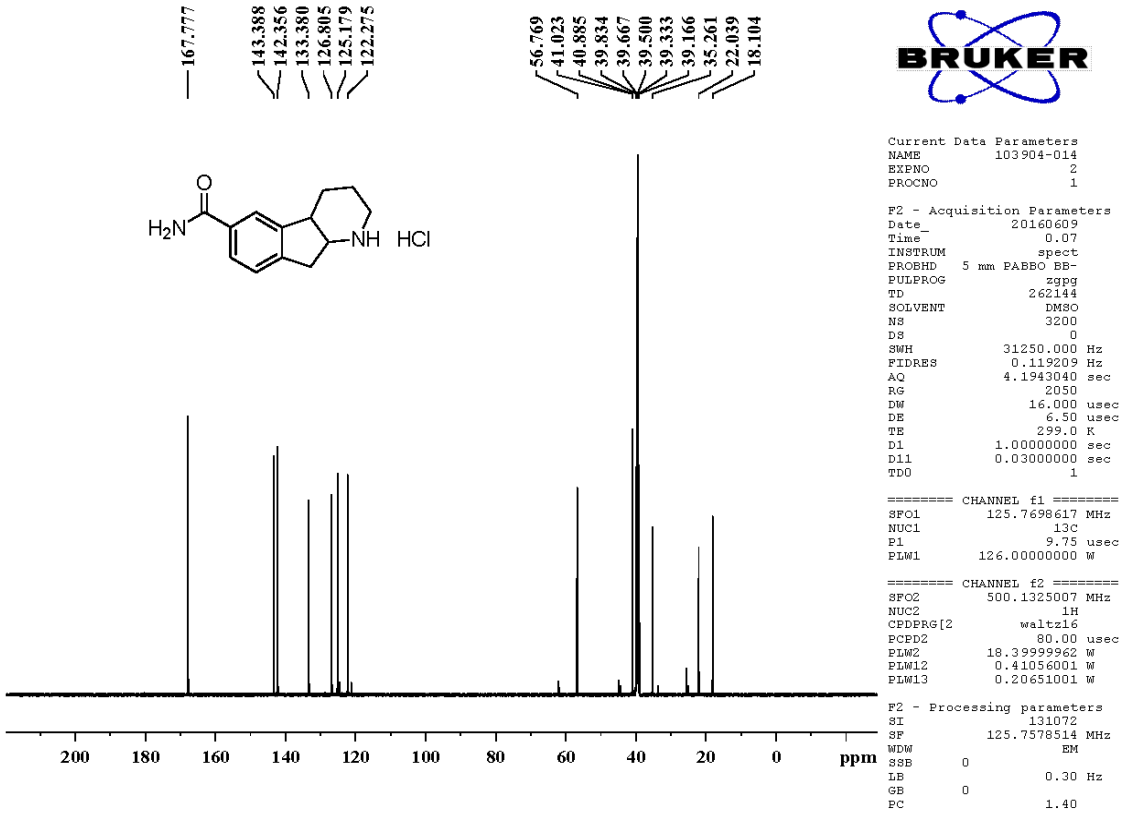


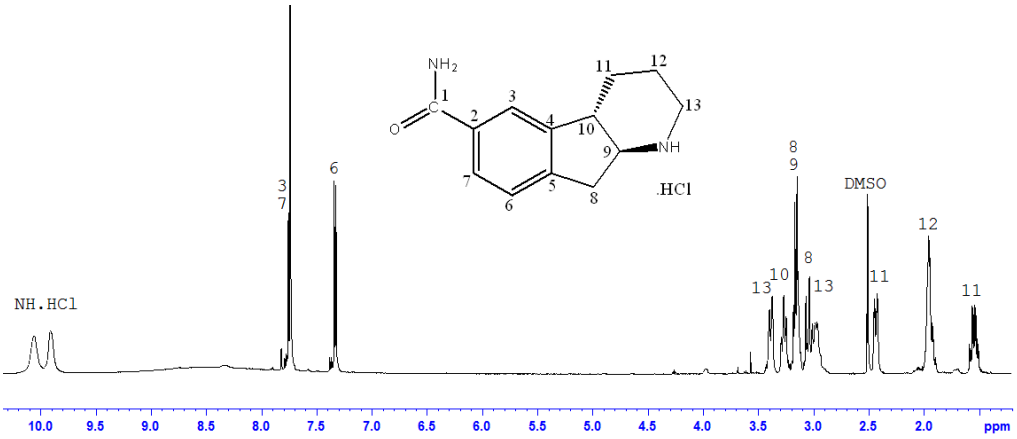
BRUKER

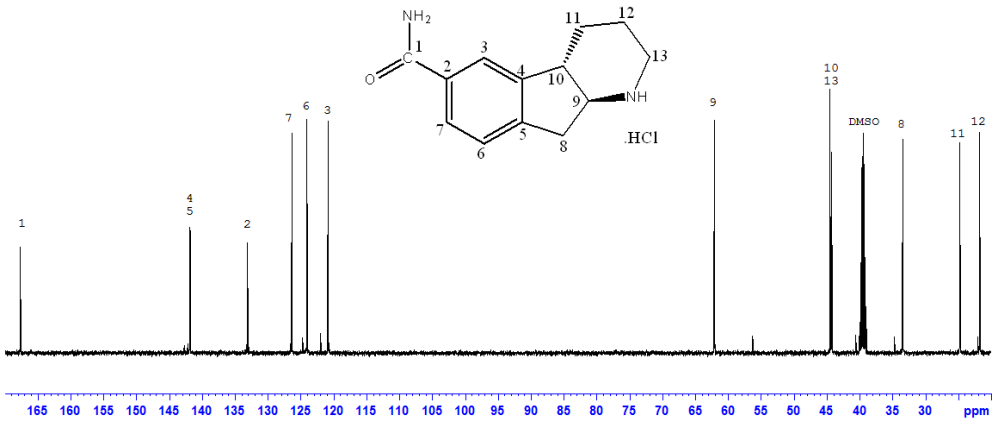
```
Current Data Parameters
NAME                  103904-013
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20160608
Time                       19.21
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                    zgpg
TD                       262144
SOLVENT                   DMSO
NS                          1600
DS                             0
SWH                   31250.000 Hz
FIDRES                0.119209 Hz
AQ                    4.1943040 sec
RG                          2050
DW                     16.000 usec
DE                      6.50 usec
TE                      299.0 K
D1                    1.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                125.7698617 MHz
NUC1                        13C
P1                       9.75 usec
PLW1               126.00000000 W

======== CHANNEL f2 ========
SFO2                500.1325007 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                   80.00 usec
PLW2                18.39999962 W
PLW12                0.41056001 W
PLW13                0.20651001 W

F2 - Processing parameters
SI                         131072
SF                  125.7578521 MHz
WDW                           EM
SSB       0
LB                       0.30 Hz
GB        0
PC                        1.40
```

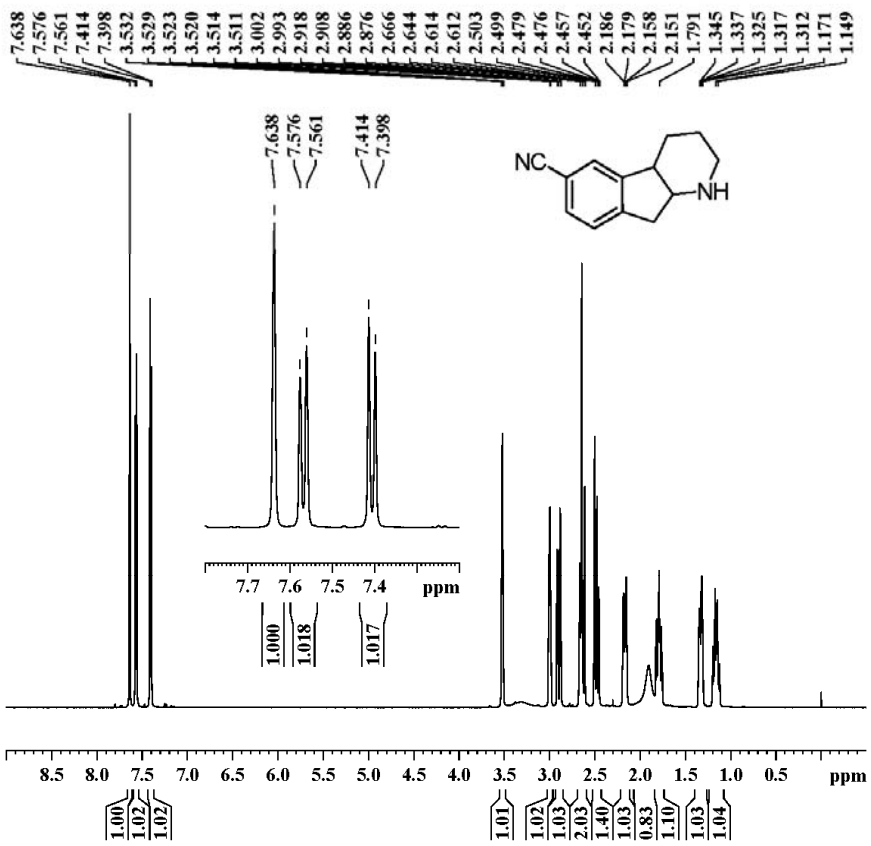



```
Current Data Parameters
NAME          103904-014
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160608
Time_              19.25
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg10
TD                 32768
SOLVENT             DMSO
NS                    32
DS                     0
SWH             7500.000 Hz
FIDRES             0.228882 Hz
AQ              2.1845334 sec
RG                   256
DW                66.667 usec
DE                 6.50 usec
TE                299.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.1325007 MHz
NUC1                  1H
P1                 11.75 usec
PLW1          18.39999962 W

F2 - Processing parameters
SI                 16384
SF            500.1299997 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

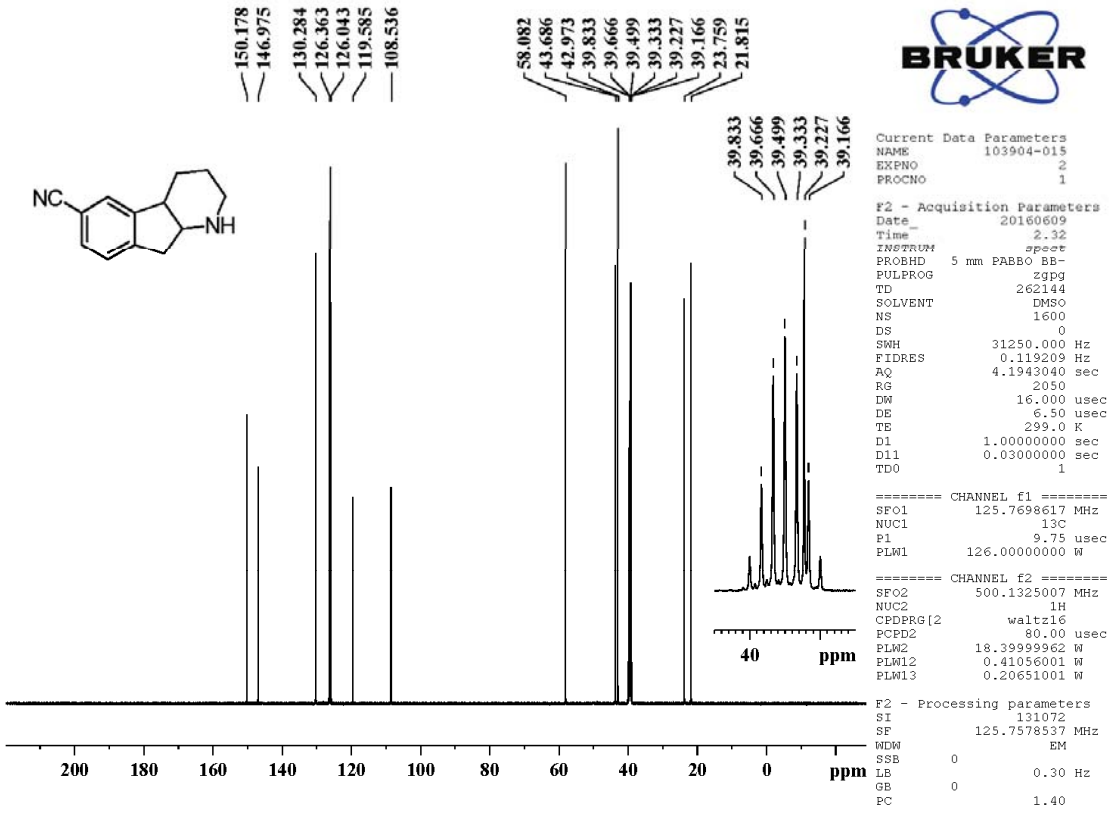

167.777
143.388
142.356
133.380
126.805
125.179
122.275
56.769
41.023
40.885
39.834
39.667
39.500
39.333
39.166
35.261
22.039
18.104
BRUKER
Current Data Parameters
NAME 103904-014
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160609
Time 0.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 262144
SOLVENT DMSO
NS 3200
DS 0
SWH 31250.000 Hz
FIDRES 0.119209 Hz
AQ 4.1943040 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7698617 MHz
NUC1 13C
P1 9.75 usec
PLW1 126.00000000 W
======== CHANNEL f2 ========
SFO2 500.1325007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 18.39999962 W
PLW12 0.41056001 W
PLW13 0.20651001 W
F2 - Processing parameters
SI 131072
SF 125.7578514 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

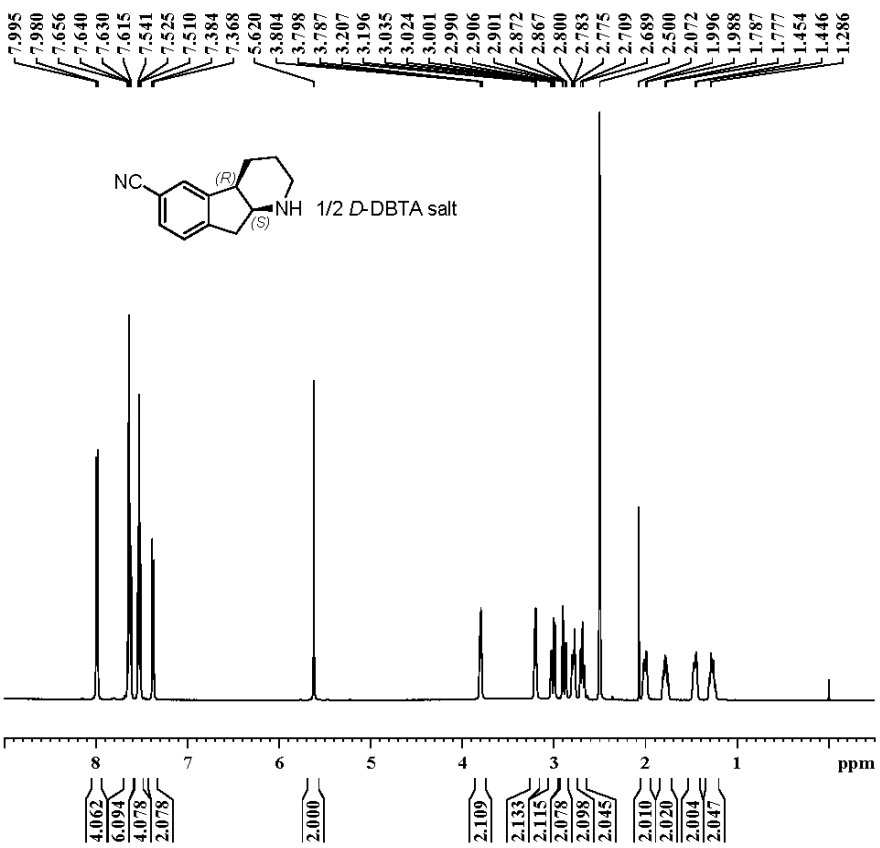

NH.HCl
3
7
6
13
10
8
9
13
DMSO
11
12
11
.HCl
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm


NH2
C
O
1
2
3
4
5
6
7
8
9
10
11
12
13
NH
.HCl
DMSO
ppm

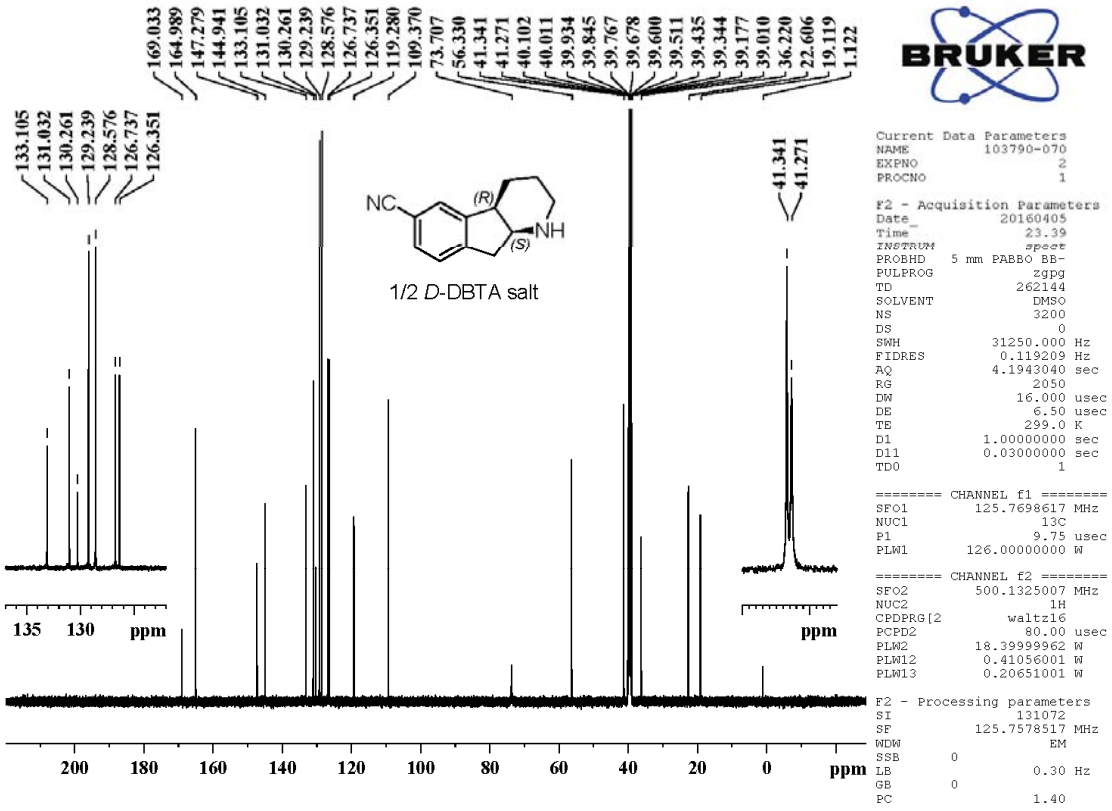


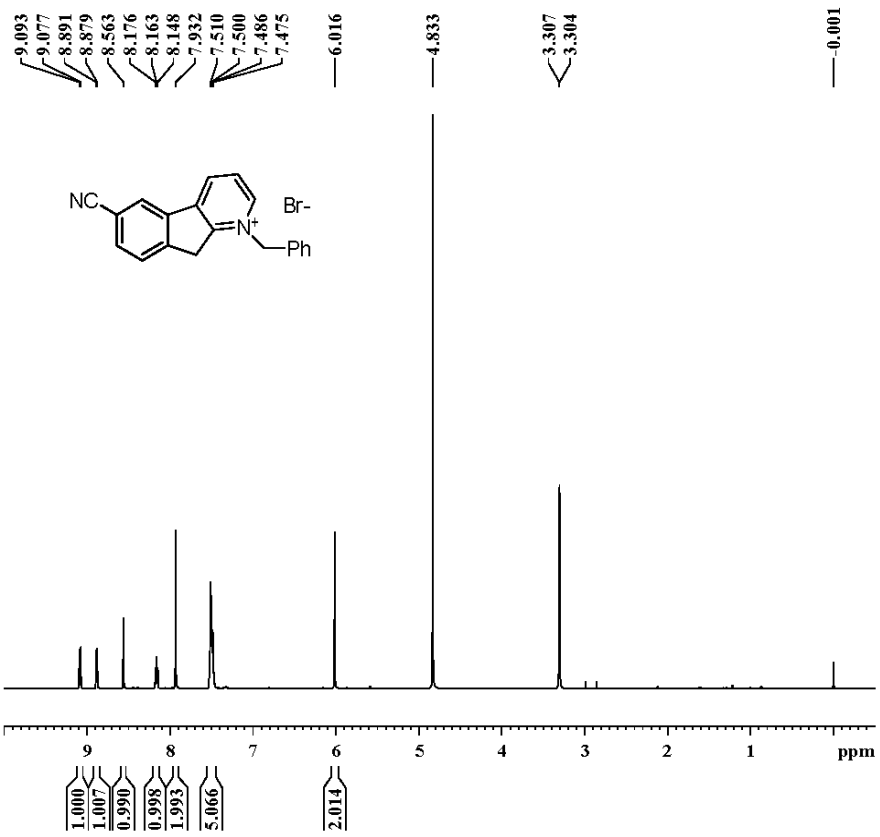

```
Current Data Parameters
NAME                  103904-015
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20160609
Time                        0.11
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                     zg10
TD                         32768
SOLVENT                     DMSO
NS                            32
DS                             0
SWH                    7500.000 Hz
FIDRES                 0.228882 Hz
AQ                     2.1845334 sec
RG                           144
DW                        66.667 usec
DE                         6.50 usec
TE                        299.0 K
D1                     1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                 500.1325007 MHz
NUC1                         1H
P1                        11.75 usec
PLW1                18.39999962 W

F2 - Processing parameters
SI                         16384
SF                   500.1300012 MHz
WDW                           EM
SSB                0
LB                         0.30 Hz
GB                 0
PC                         1.00
```


150.178
146.975
130.284
126.363
126.043
119.585
108.536
58.082
43.686
42.973
39.833
39.666
39.499
39.333
39.227
39.166
23.759
21.815
NC
NH
200
180
160
140
120
100
80
60
40
20
0
ppm
40
ppm
Current Data Parameters
NAME 103904-015
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160609
Time 2.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 262144
SOLVENT DMSO
NS 1600
DS 0
SWH 31250.000 Hz
FIDRES 0.119209 Hz
AQ 4.1943040 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7698617 MHz
NUC1 13C
P1 9.75 usec
PLW1 126.00000000 W
======== CHANNEL f2 ========
SFO2 500.1325007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 18.39999962 W
PLW12 0.41056001 W
PLW13 0.20651001 W
F2 - Processing parameters
SI 131072
SF 125.7578537 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



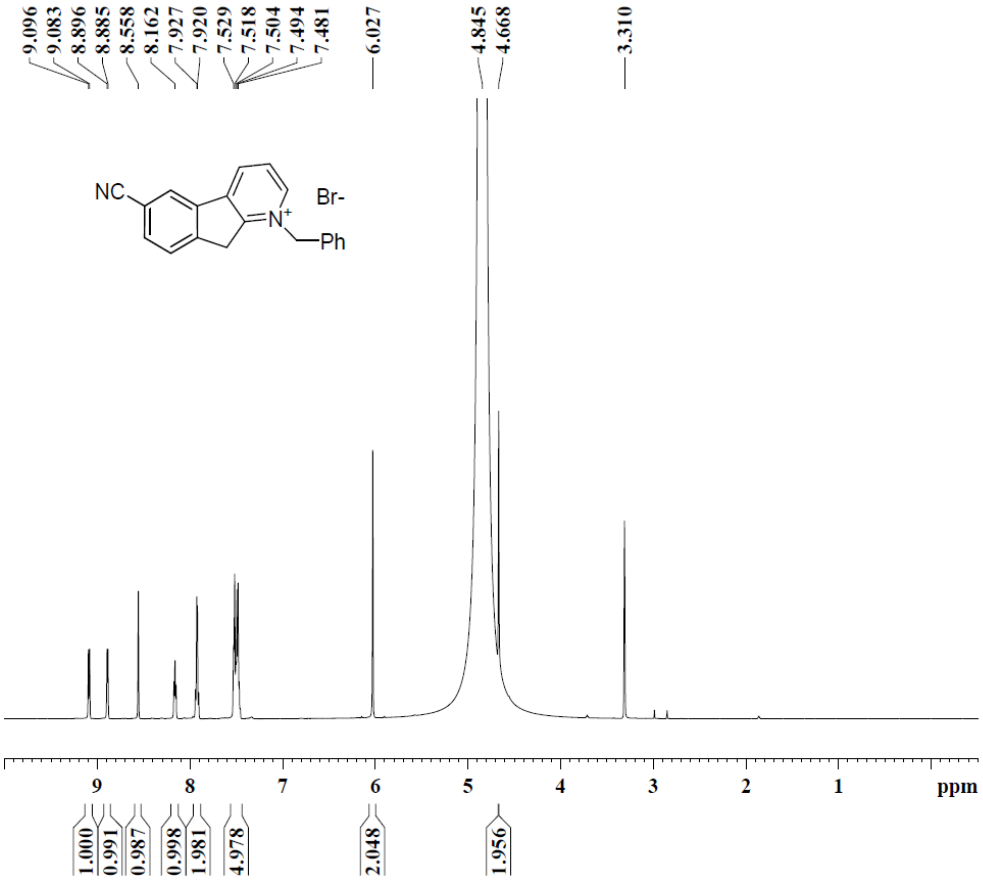

```
Current Data Parameters
NAME          103790-070
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160405
Time              18.58
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg10
TD               32768
SOLVENT           DMSO
NS                  32
DS                   0
SWH           15000.000 Hz
FIDRES            0.457764 Hz
AQ                1.0922667 sec
RG                 362
DW                33.333 usec
DE                 6.50 usec
TE                299.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.1325007 MHz
NUC1                  1H
P1                 11.75 usec
PLW1          18.39999962 W

F2 - Processing parameters
SI                 16384
SF            500.1300037 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```


169.033
164.989
147.279
144.941
133.105
131.032
130.261
129.239
128.576
126.737
126.351
119.280
109.370
73.707
56.330
41.341
41.271
40.102
40.011
39.934
39.845
39.767
39.678
39.600
39.511
39.435
39.344
39.177
39.010
36.220
22.606
19.119
1.122
133.105
131.032
130.261
129.239
128.576
126.737
126.351
41.341
41.271
NC
(R)
NH
(S)
1/2 D-DBTA salt
135
130
ppm
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm
Current Data Parameters
NAME 103790-070
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160405
Time 23.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 262144
SOLVENT DMSO
NS 3200
DS 0
SWH 31250.000 Hz
FIDRES 0.119209 Hz
AQ 4.1943040 sec
RG 2050
DW 16.000 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7698617 MHz
NUC1 13C
P1 9.75 usec
PLW1 126.00000000 W
======== CHANNEL f2 ========
SFO2 500.1325007 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 18.39999962 W
PLW12 0.41056001 W
PLW13 0.20651001 W
F2 - Processing parameters
SI 131072
SF 125.7578517 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

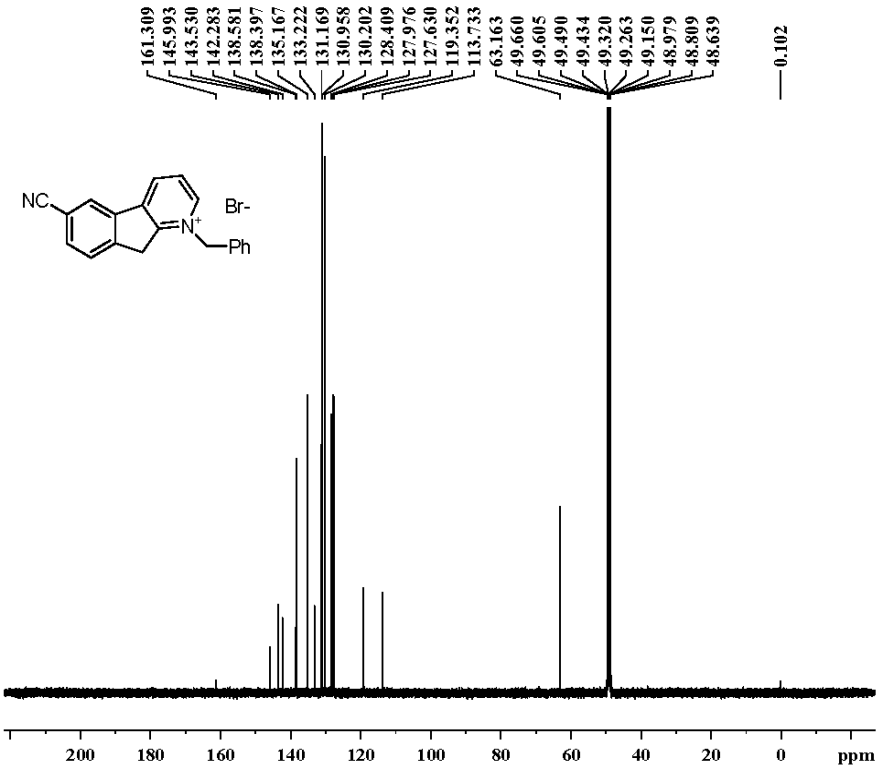



```
Current Data Parameters
NAME          102992-091
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131107
Time              16.22
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT            MeOD
NS                   32
DS                    0
SWH            7500.000 Hz
FIDRES            0.228882 Hz
AQ             2.1845334 sec
RG                  512
DW                66.667 usec
DE                 6.50 usec
TE                299.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.90 usec
PL1                2.10 dB
PL1W         18.43091774 W
SFO1         500.1325007 MHz

F2 - Processing parameters
SI                 16384
SF           500.1300129 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

Sample in CD3OH

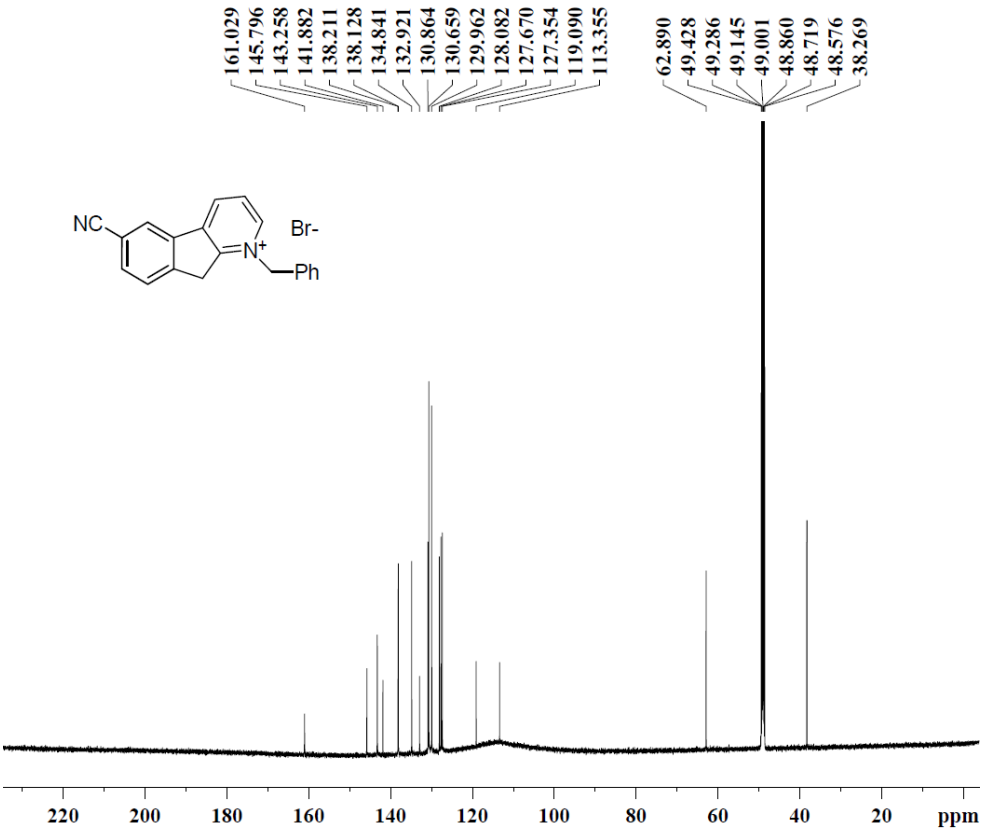



```
Current Data Parameters
NAME                  h223
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20141023
Time              15.48
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG           zg10
TD               32768
SOLVENT           MeOD
NS                 256
DS                   2
SWH          12335.526 Hz
FIDRES        0.376450 Hz
AQ            1.3281963 sec
RG                20.2
DW              40.533 usec
DE               6.50 usec
TE              300.8 K
D1           2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1                8.41 dB
PL1W         6.99129009 W
SFO1        600.0437055 MHz

F2 - Processing parameters
SI               32768
SF          600.0400110 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```



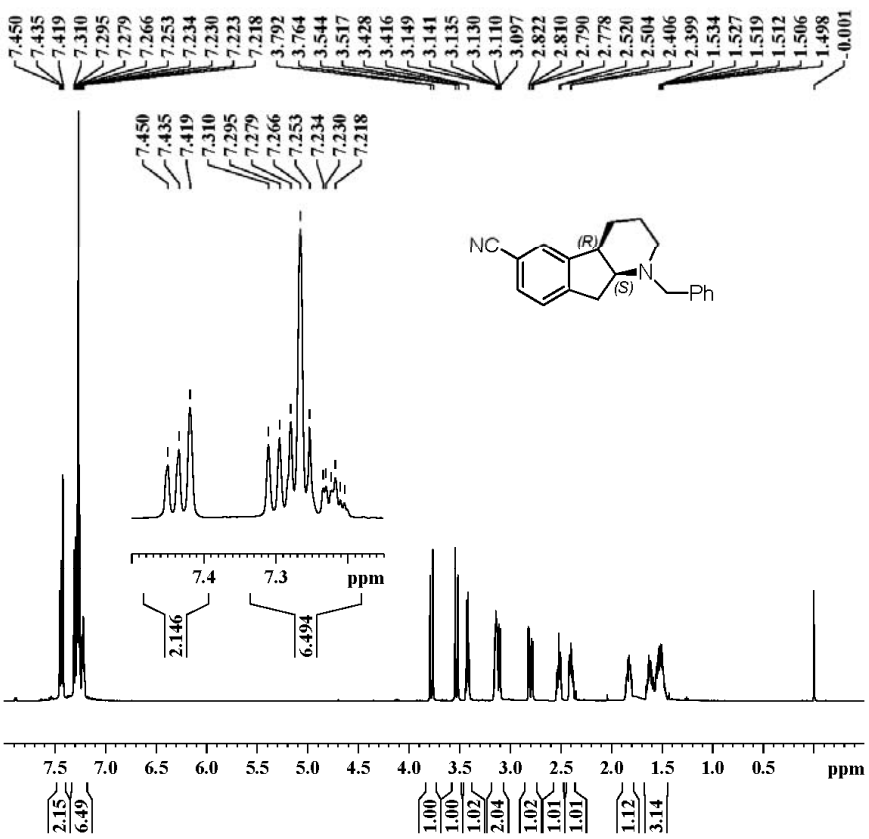

```
Current Data Parameters
NAME                 102992-091
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_               20131107
Time                   23.43
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg
TD                   262144
SOLVENT                MeOD
NS                     3200
DS                        0
SWH                31250.000 Hz
FIDRES             0.119209 Hz
AQ                 4.1943040 sec
RG                      2050
DW                    16.000 usec
DE                     6.50 usec
TE                    299.0 K
D1                 1.00000000 sec
d11                0.03000000 sec
DELTA              0.89999998 sec
TD0                        1
SFO1             125.7698617 MHz
NUC1                     13C
P1                    10.64 usec
PLW1              -1.00000000 W
SFO2             500.1325007 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                 80.00 usec
PLW2              -1.00000000 W
PLW12             -1.00000000 W
PLW13             -1.00000000 W

F2 - Processing parameters
SI                      131072
SF               125.7575940 MHz
WDW                        EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.40
```

Sample in CD3OH



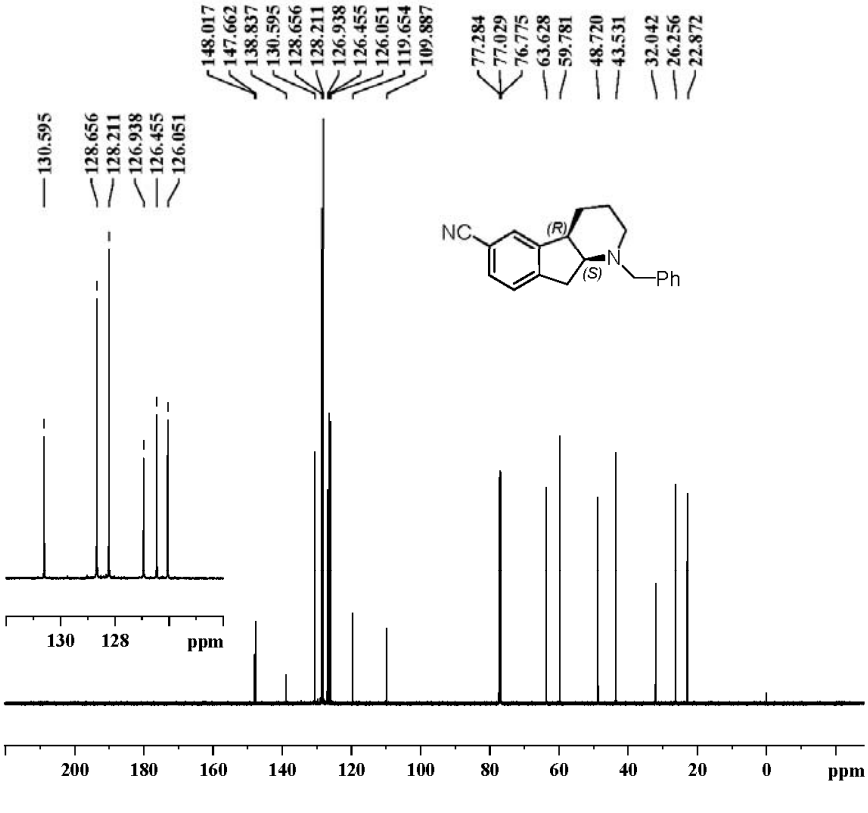
Current Data Parameters
NAME h223
EXPNO 2
PROCNO 1

F2 - Processing parameters
SI 32768
SF 150.8799875 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



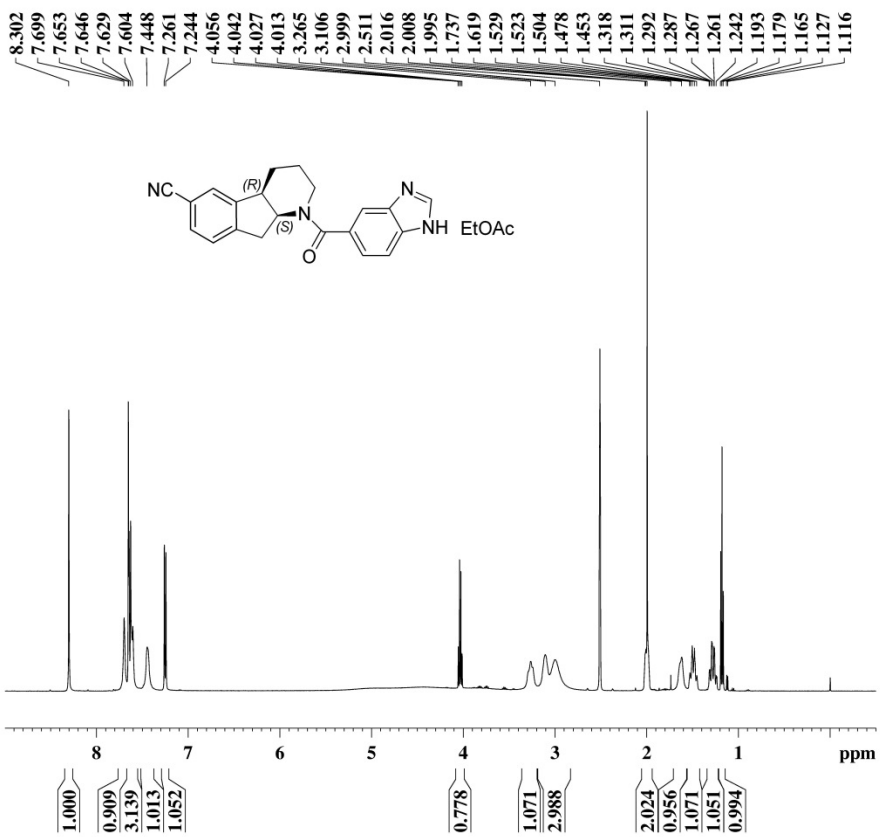
BRUKER

```
Current Data Parameters
NAME              103790-069
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160405
Time                  16.33
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg10
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        0
SWH                7500.000 Hz
FIDRES                0.228882 Hz
AQ                 2.1845334 sec
RG                      287
DW                   66.667 usec
DE                    6.50 usec
TE                   299.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1             500.1325007 MHz
NUC1                     1H
P1                    11.75 usec
PLW1            18.39999962 W

F2 - Processing parameters
SI                       16384
SF               500.1300153 MHz
WDW                      EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```

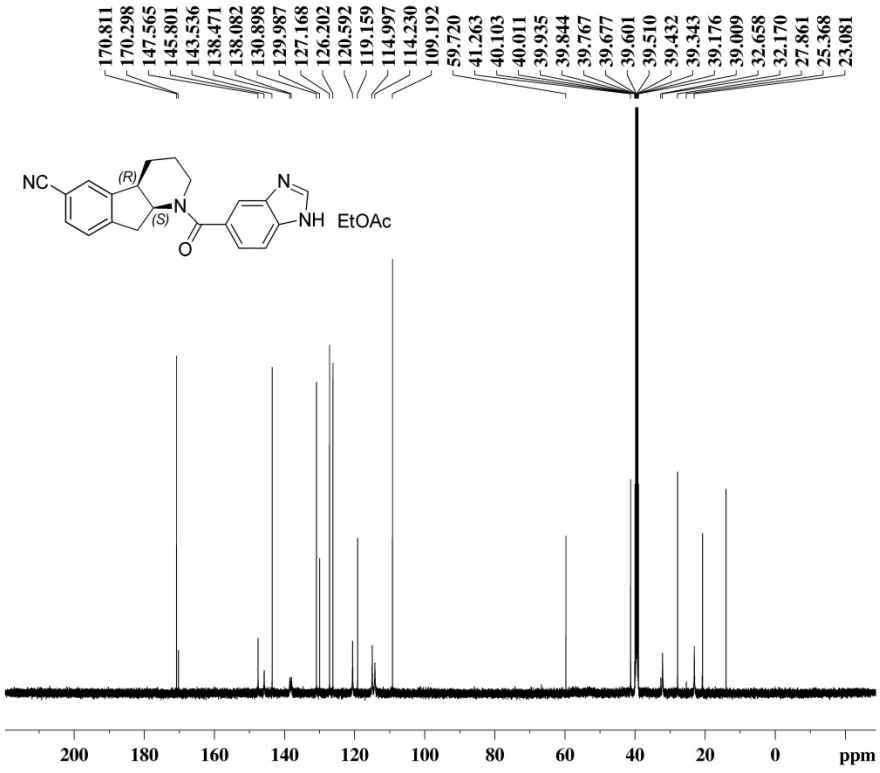


BRUKER

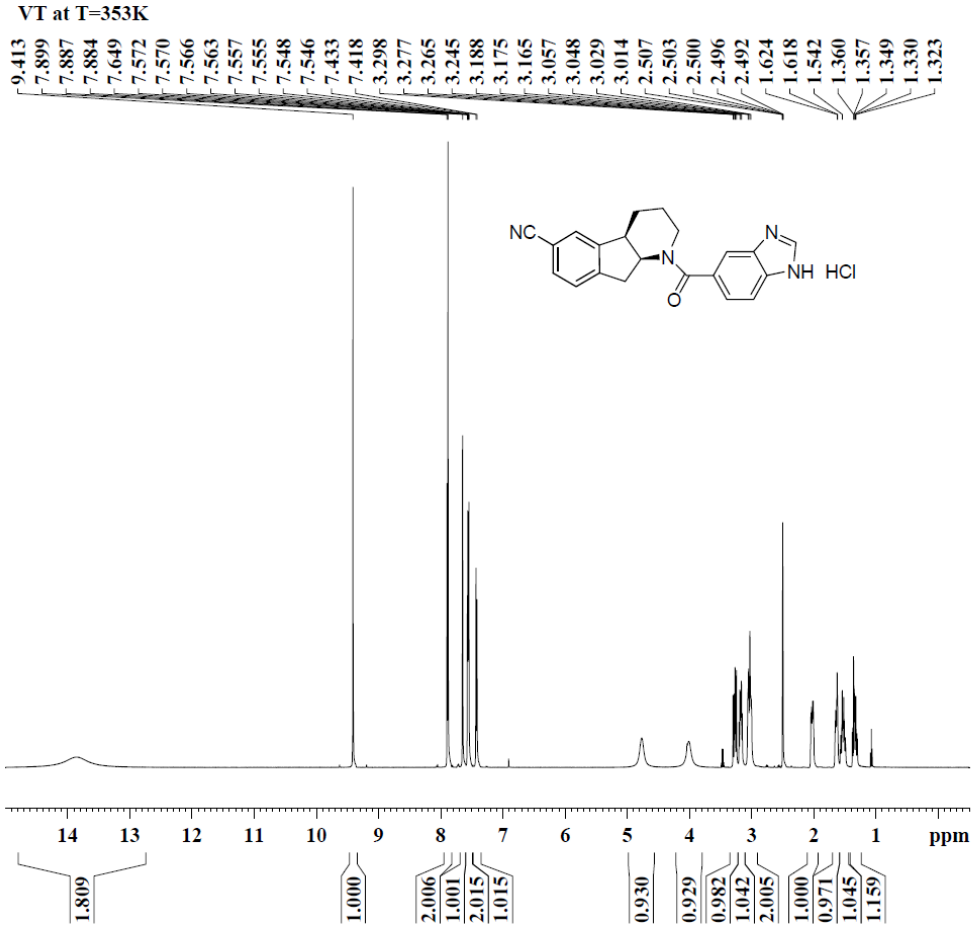
```
Current Data Parameters
NAME                  103790-069
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20160405
Time                       18.54
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                     zgpg
TD                        262144
SOLVENT                   CDCl3
NS                         1600
DS                            0
SWH                   31250.000 Hz
FIDRES                0.119209 Hz
AQ                    4.1943040 sec
RG                         1820
DW                       16.000 usec
DE                        6.50 usec
TE                       299.0 K
D1                    1.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1                125.7698617 MHz
NUC1                        13C
P1                         9.75 usec
PLW1               126.00000000 W

======== CHANNEL f2 ========
SFO2                500.1325007 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     80.00 usec
PLW2                18.39999962 W
PLW12                0.41056001 W
PLW13                0.20651001 W

F2 - Processing parameters
SI                        131072
SF                  125.7577903 MHz
WDW                           EM
SSB                0
LB                            0.30 Hz
GB                 0
PC                         1.40
```




```
Current Data Parameters
NAME          103790-071
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160406
Time                4.29
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg10
TD                 32768
SOLVENT             DMSO
NS                    32
DS                     0
SWH           15000.000 Hz
FIDRES         0.457764 Hz
AQ             1.0922667 sec
RG                   287
DW              33.333 usec
DE                6.50 usec
TE                299.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1325007 MHz
NUC1                   1H
P1                 11.75 usec
PLW1        18.39999962 W

F2 - Processing parameters
SI                 16384
SF           500.1299982 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

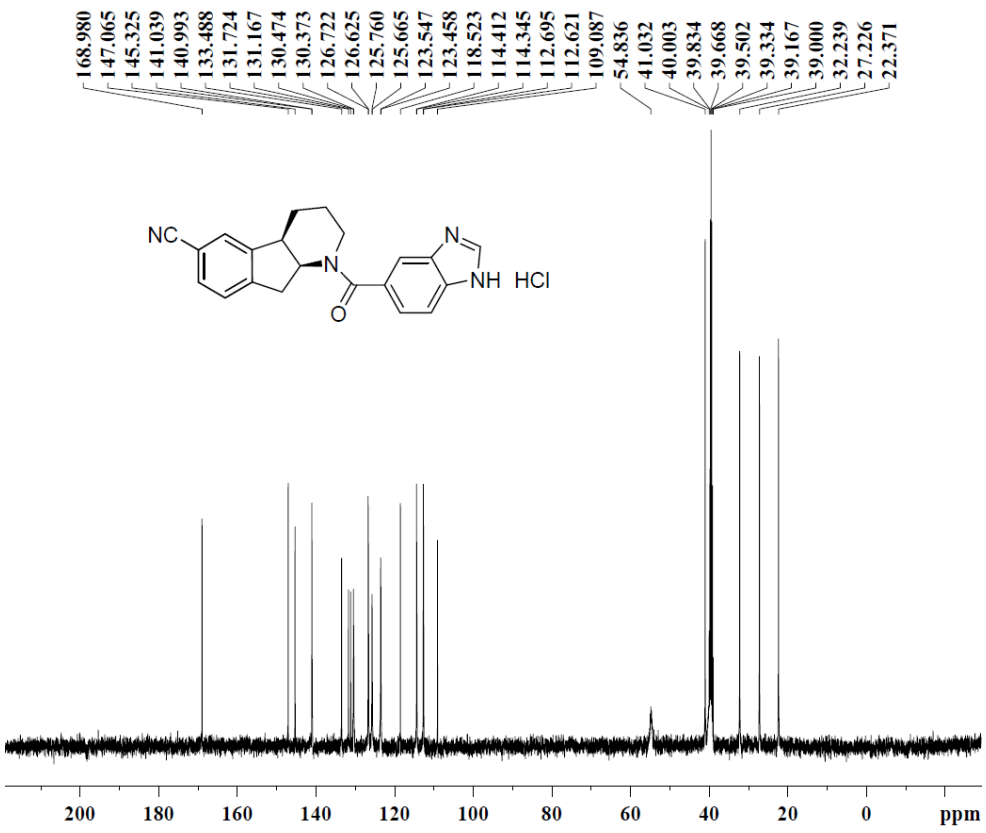



```
Current Data Parameters
NAME          103790-071
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160406
Time                6.50
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg
TD                262144
SOLVENT              DMSO
NS                   1600
DS                      0
SWH            31250.000 Hz
FIDRES          0.119209 Hz
AQ             4.1943040 sec
RG                   2050
DW              16.000 usec
DE               6.50 usec
TE                299.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7698617 MHz
NUC1                  13C
P1                   9.75 usec
PLW1        126.00000000 W

======== CHANNEL f2 ========
SFO2         500.1325007 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         18.39999962 W
PLW12         0.41056001 W
PLW13         0.20651001 W

F2 - Processing parameters
SI                  131072
SF           125.7578512 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.40
```



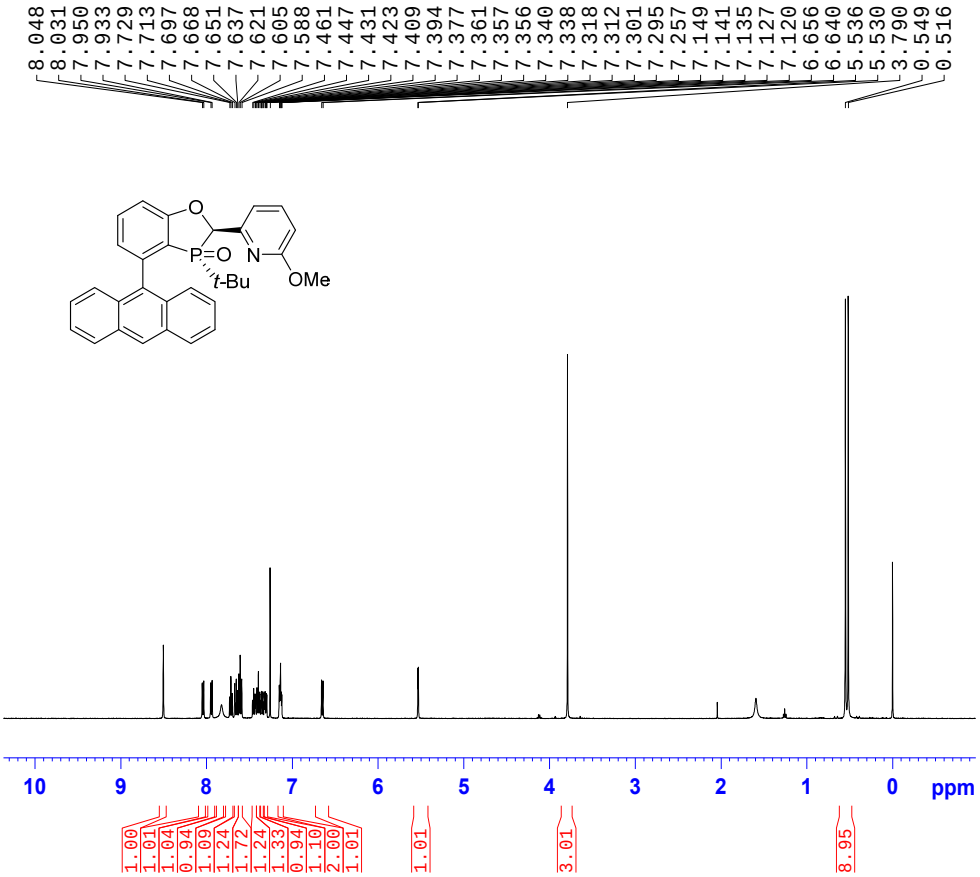

```
Current Data Parameters
NAME                  A8633
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130424
Time                   8.15
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              q_zg10
TD                    32768
SOLVENT                DMSO
NS                      128
DS                        0
SWH               9014.423 Hz
FIDRES            0.275098 Hz
AQ                1.8175317 sec
RG                      322
DW                   55.467 usec
DE                    6.50 usec
TE                   353.1 K
D1             2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.70 usec
PL1                   2.10 dB
PL1W          18.43091774 W
SFO1          500.1334009 MHz

F2 - Processing parameters
SI                    16384
SF            500.1300051 MHz
WDW                      EM
SSB         0
LB                    0.10 Hz
GB          0
PC                    1.00
```

VT at T=353K

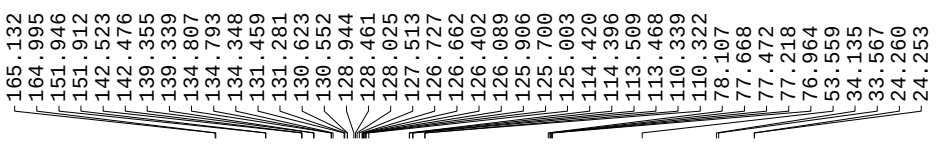


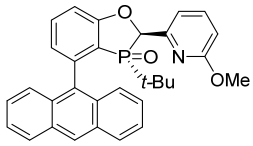
Current Data Parameters
NAME A8633
EXPNO 2
PROCNO 1

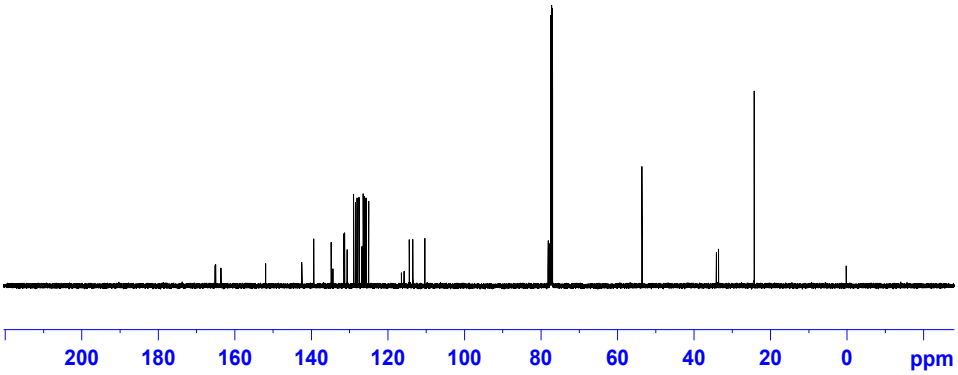
F2 - Processing parameters
SI 131072
SF 125.7579035 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40



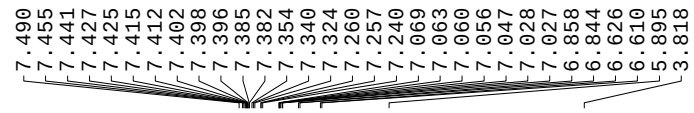

```
Current Data Parameters
NAME          10889-180
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160531
Time              22.22
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7500.000 Hz
FIDRES         0.228882 Hz
AQ            2.1845334 sec
RG                  456
DW               66.667 usec
DE                6.50 usec
TE               299.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.1325007 MHz
NUC1                   1H
P1                11.75 usec
PLW1        18.39999962 W

F2 - Processing parameters
SI                 16384
SF          500.1300128 MHz
WDW                   EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

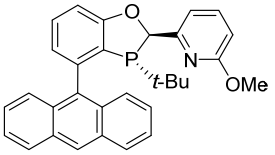


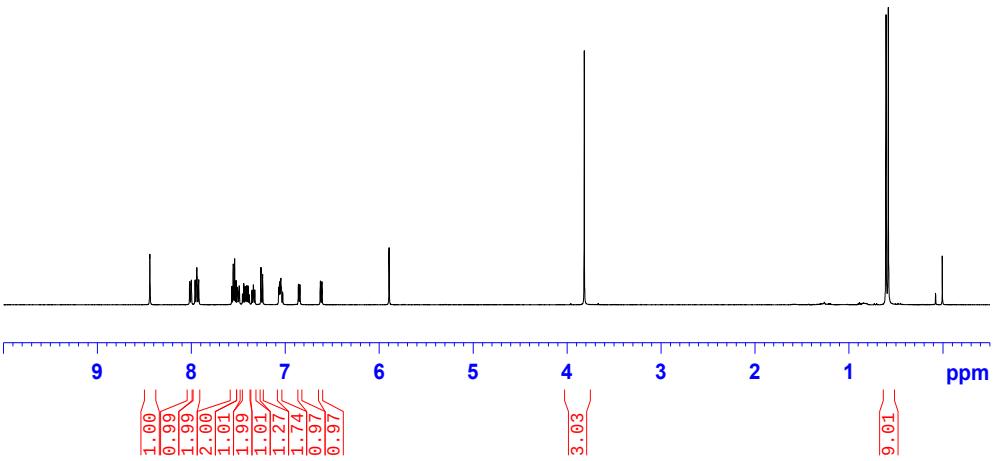




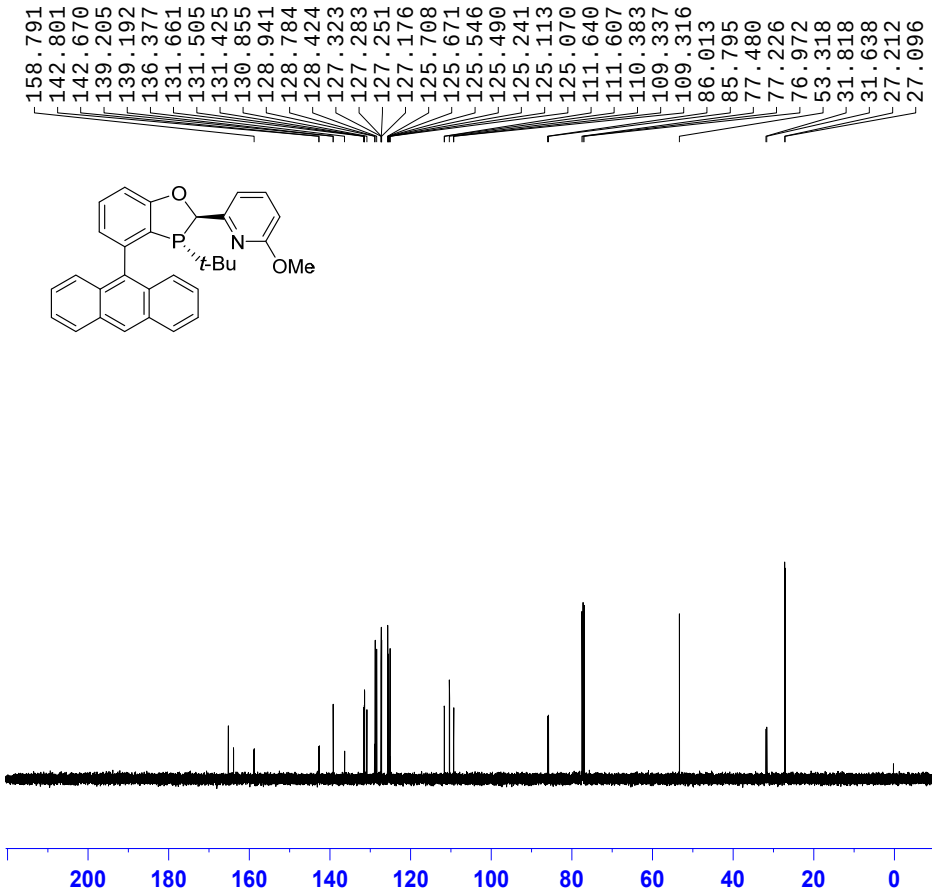

```
Current Data Parameters
NAME          10889-180
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20160531
Time              23.56
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg
TD                262144
SOLVENT            CDCl3
NS                  1024
DS                     0
SWH           31250.000 Hz
FIDRES         0.119209 Hz
AQ            4.1943040 sec
RG                  2050
DW               16.000 usec
DE                6.50 usec
TE                299.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7698617 MHz
NUC1                13C
P1                9.75 usec
PLW1       126.00000000 W

======== CHANNEL f2 ========
SFO2        500.1325007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        18.39999962 W
PLW12        0.41056001 W
PLW13        0.20651001 W

F2 - Processing parameters
SI                131072
SF          125.7577641 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.40
```



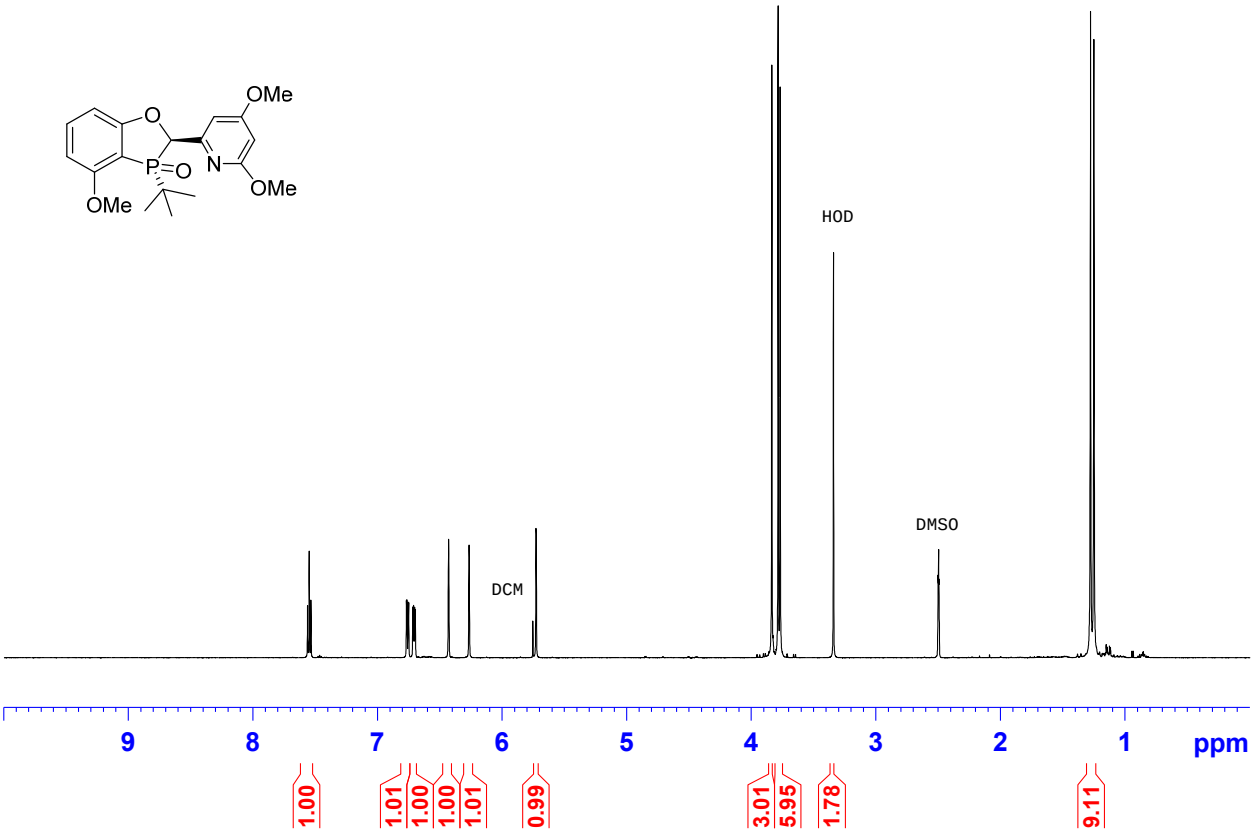


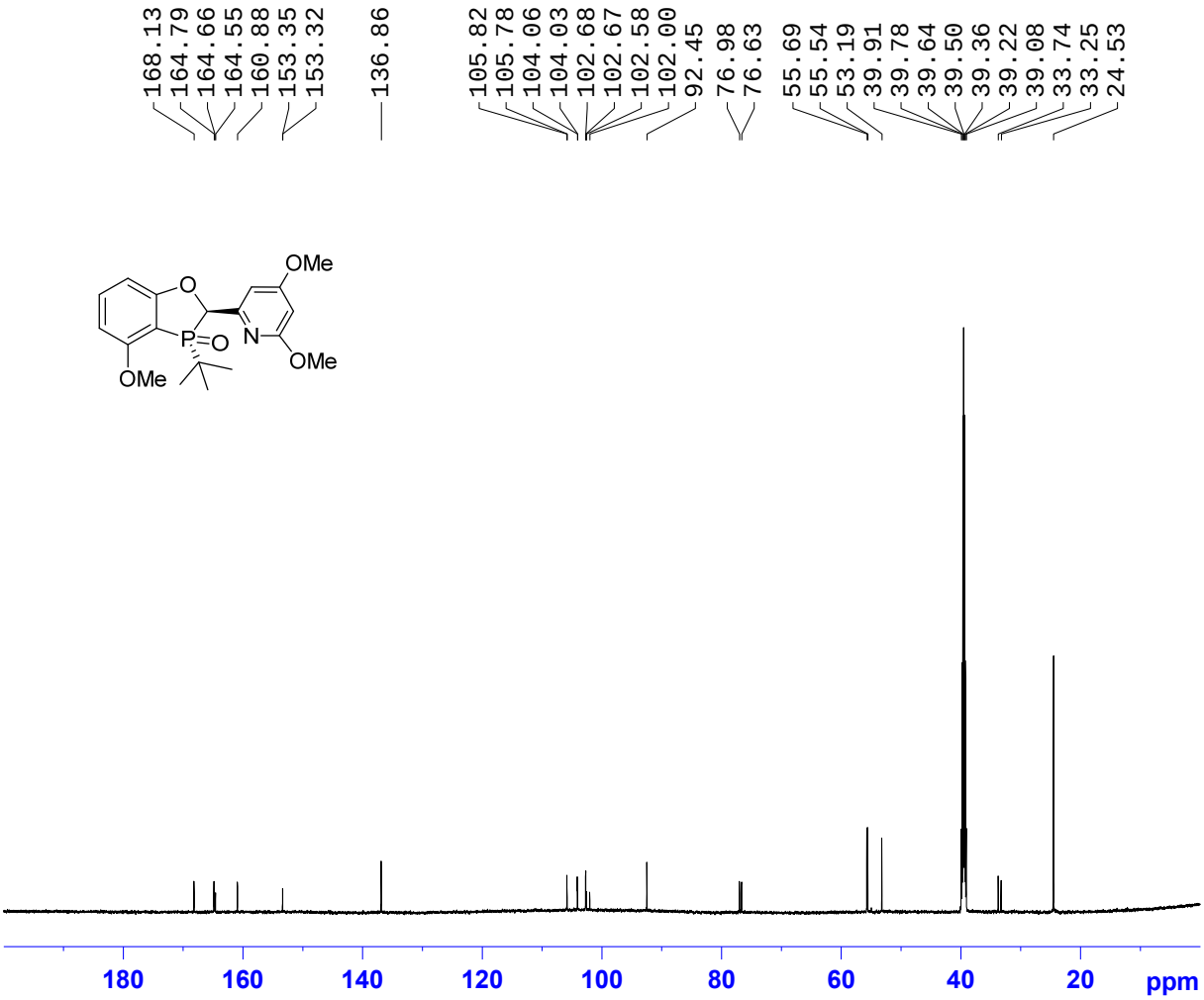


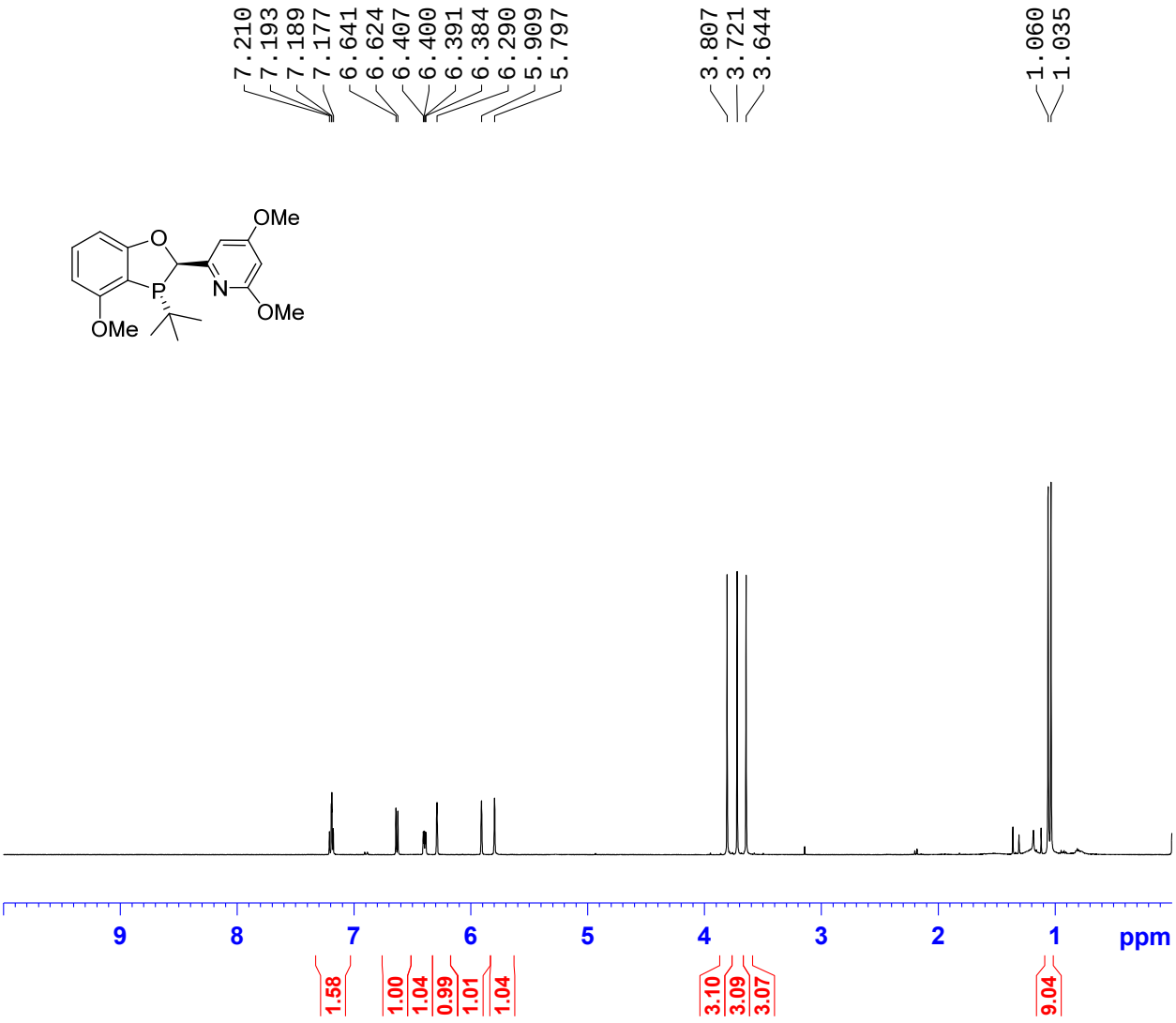

```
Current Data Parameters
NAME          10889-187
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20160527
Time              11.20
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg10
TD                32768
SOLVENT            CDCl3
NS                   16
DS                    0
SWH            7500.000 Hz
FIDRES         0.228882 Hz
AQ            2.1845334 sec
RG                  406
DW               66.667 usec
DE                6.50 usec
TE                299.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.1325007 MHz
NUC1                1H
P1               11.75 usec
PLW1        18.39999962 W

F2 - Processing parameters
SI                16384
SF          500.1300111 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

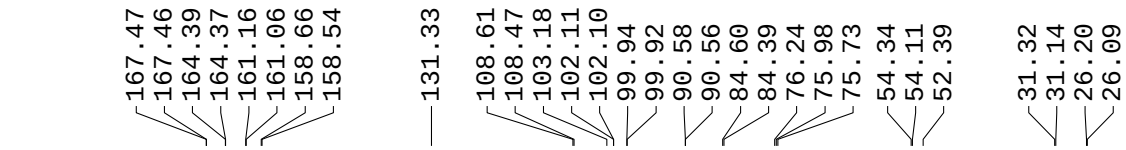


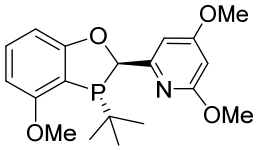

```
Current Data Parameters
NAME          10889-187
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20160527
Time              11.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg
TD               262144
SOLVENT           CDCl3
NS                  250
DS                    0
SWH           31250.000 Hz
FIDRES            0.119209 Hz
AQ             4.1943040 sec
RG                 2050
DW                16.000 usec
DE                 6.50 usec
TE                299.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7698617 MHz
NUC1                13C
P1                 9.75 usec
PLW1       126.00000000 W

======== CHANNEL f2 ========
SFO2        500.1325007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2        18.39999962 W
PLW12        0.41056001 W
PLW13        0.20651001 W

F2 - Processing parameters
SI                131072
SF          125.7577612 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.40
```

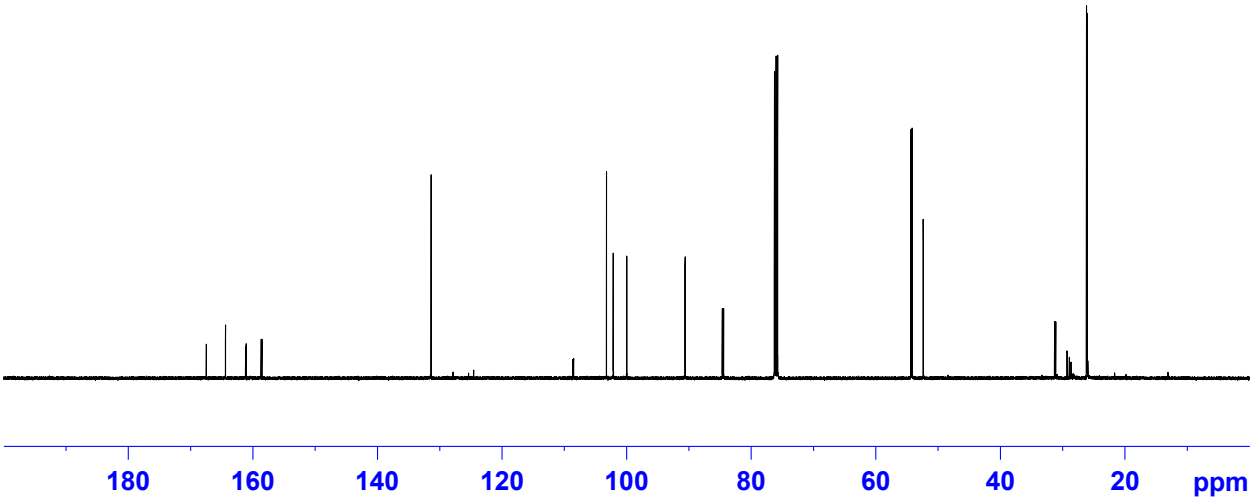

OMe
O
P
O
N
OMe
OMe
OMe
HOD
DMSO
DCM
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.00
1.00
1.01
0.99
3.01
5.95
1.78
9.11

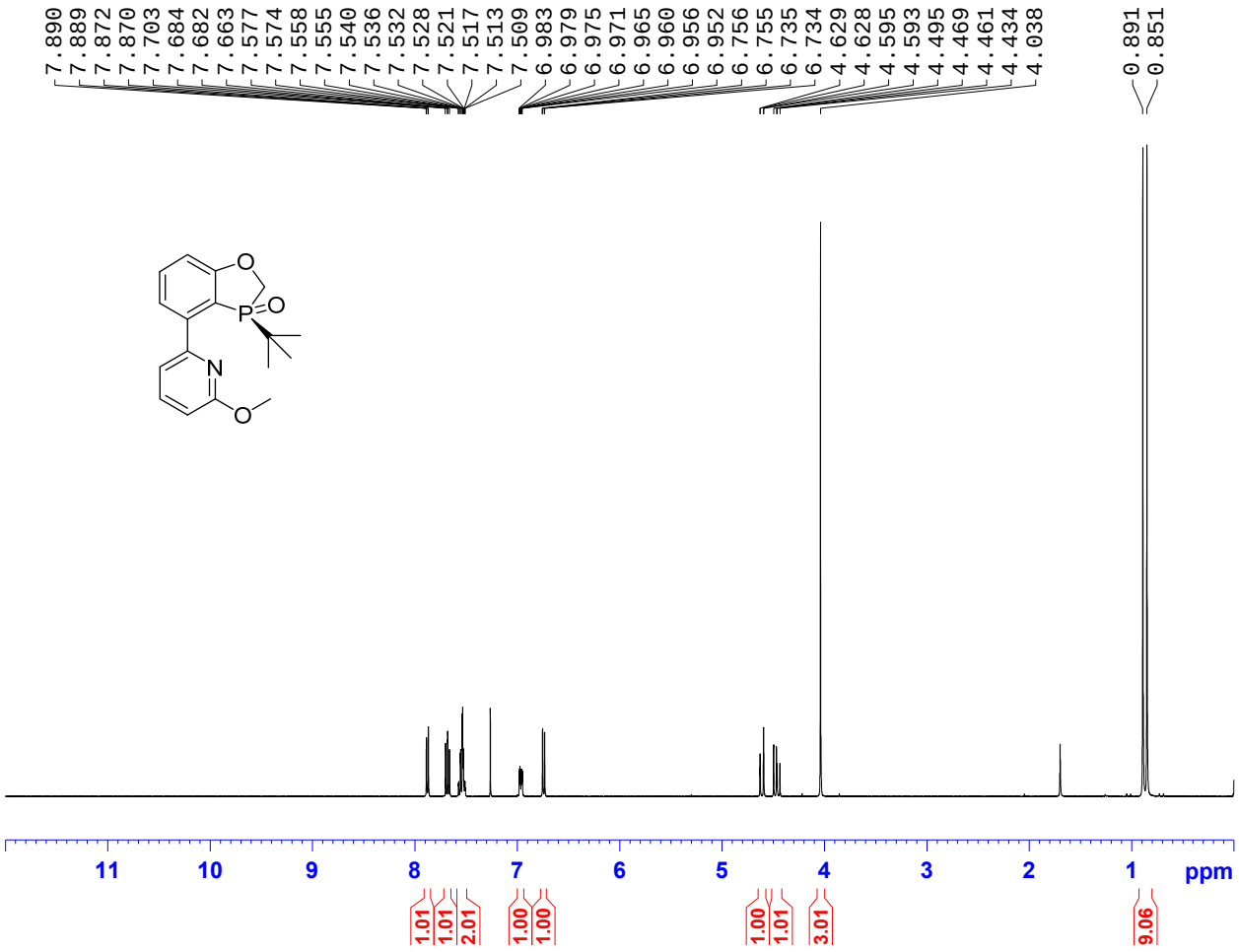

168.13
164.79
164.66
164.55
160.88
153.35
153.32
136.86
105.82
105.78
104.06
104.03
102.68
102.67
102.58
102.00
92.45
76.98
76.63
55.69
55.54
53.19
39.91
39.78
39.64
39.50
39.36
39.22
39.08
33.74
33.25
24.53
OMe
O
N
P
O
OMe
OMe
180
160
140
120
100
80
60
40
20
ppm


7.210
7.193
7.189
7.177
6.641
6.624
6.407
6.400
6.391
6.384
6.290
5.909
5.797
3.807
3.721
3.644
1.060
1.035
OMe
O
P
N
OMe
OMe
9
8
7
6
5
4
3
2
1
ppm
1.58
1.00
1.04
0.99
1.01
1.04
3.10
3.09
3.07
9.04


167.47
167.46
164.39
164.37
161.16
161.06
158.66
158.54
131.33
108.61
108.47
103.18
102.11
102.10
99.94
99.92
90.58
90.56
84.60
84.39
76.24
75.98
75.73
54.34
54.11
52.39
31.32
31.14
26.20
26.09


OMe
O
P
N
OMe
OMe


180
160
140
120
100
80
60
40
20
ppm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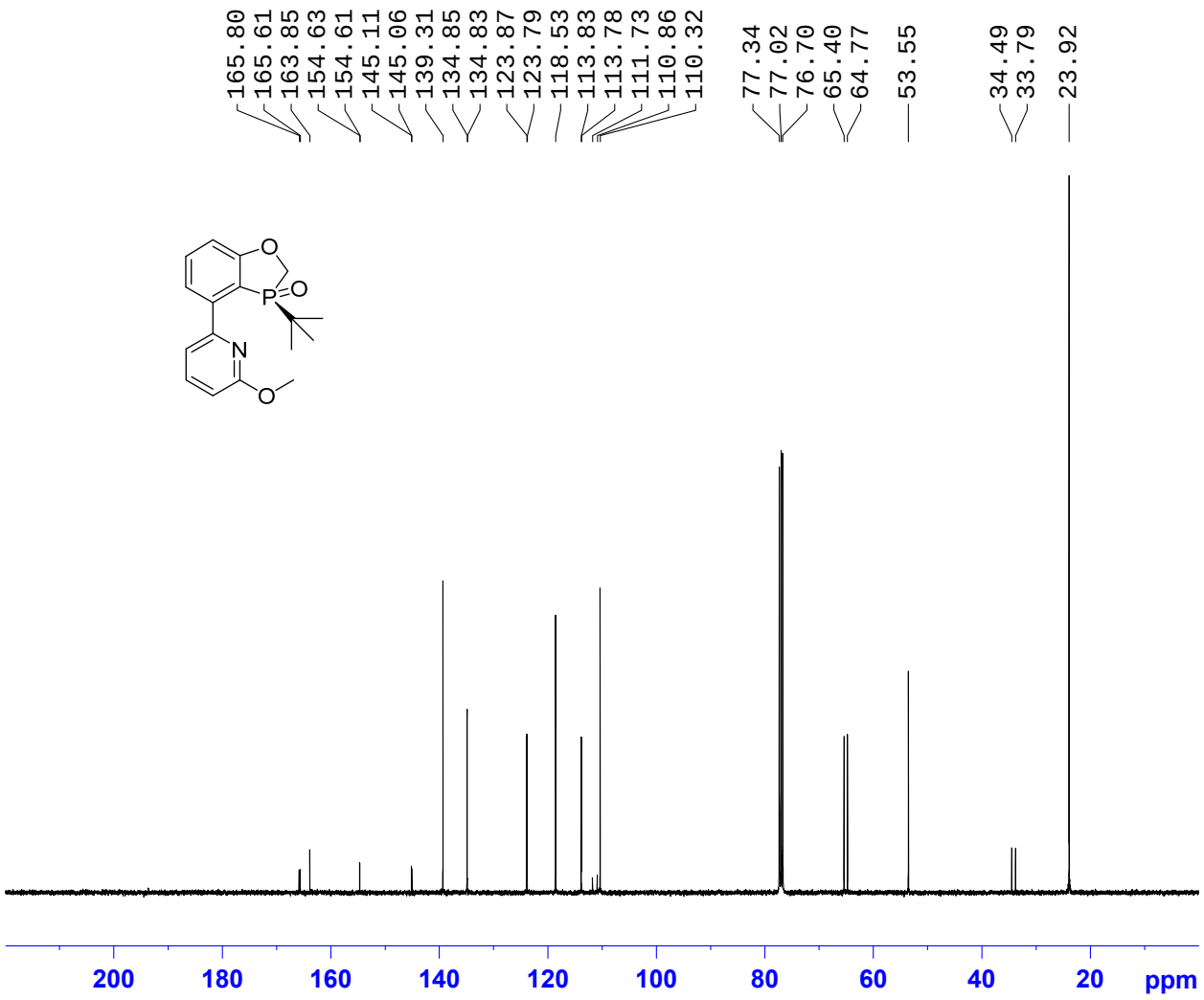
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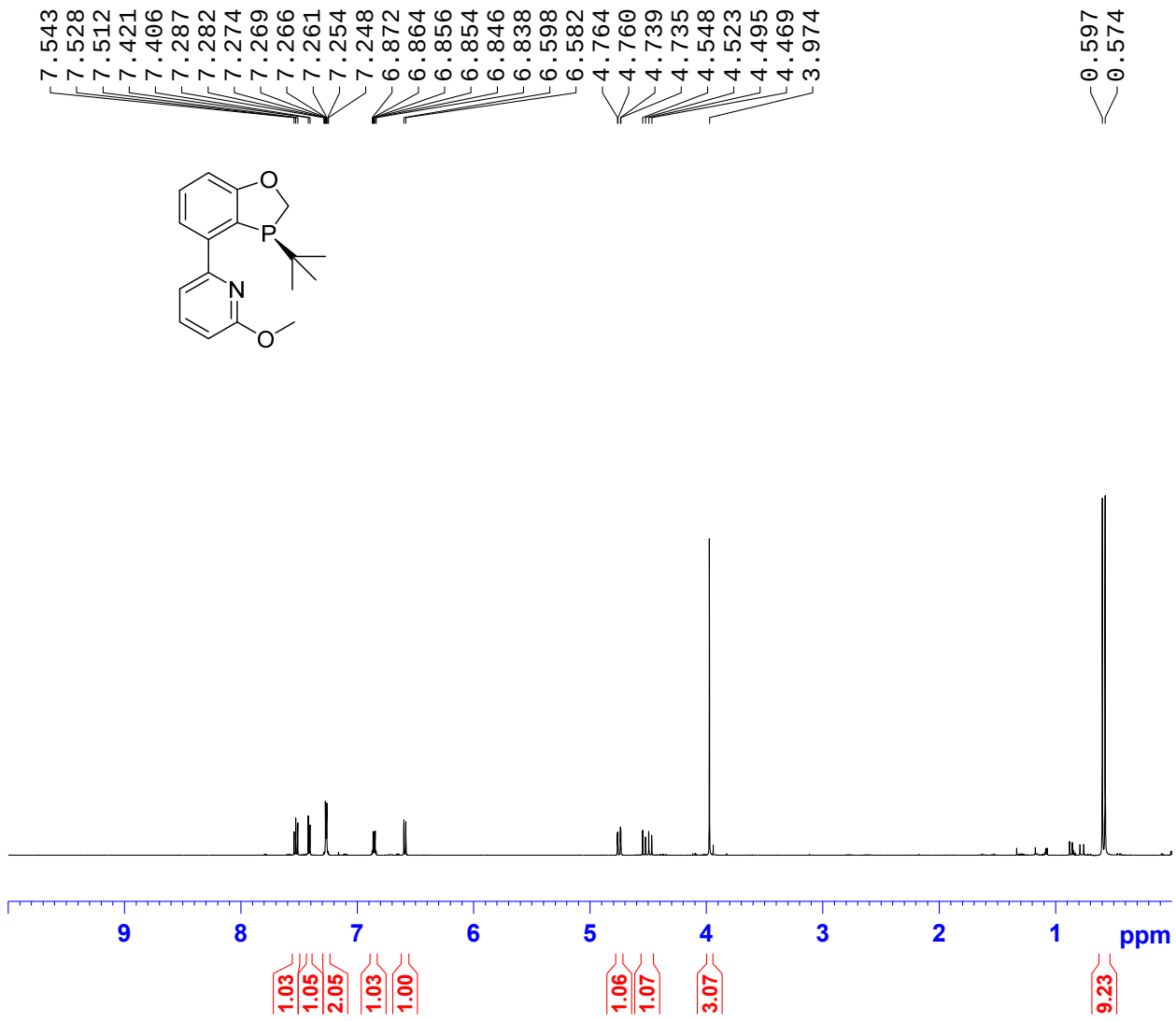
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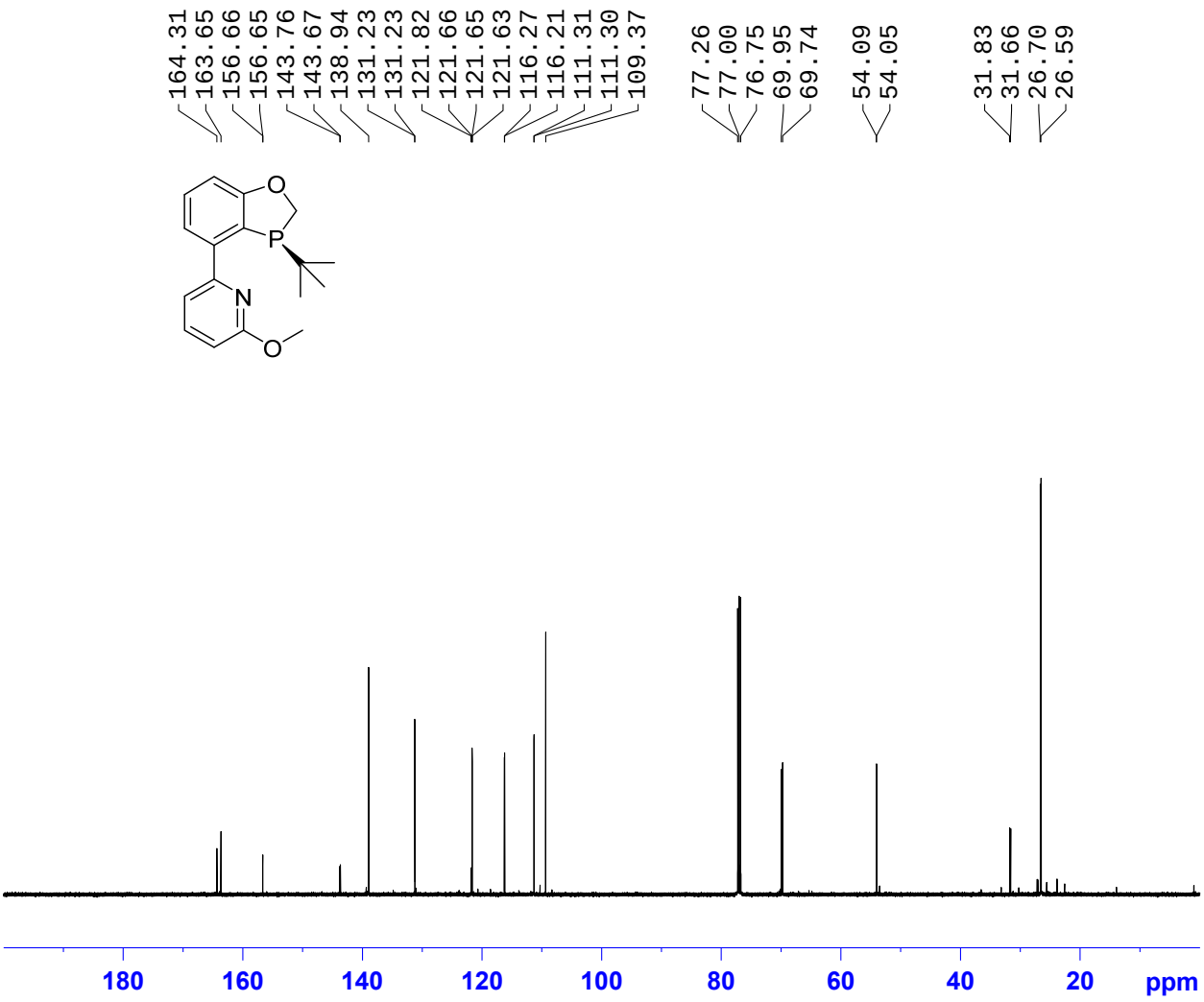
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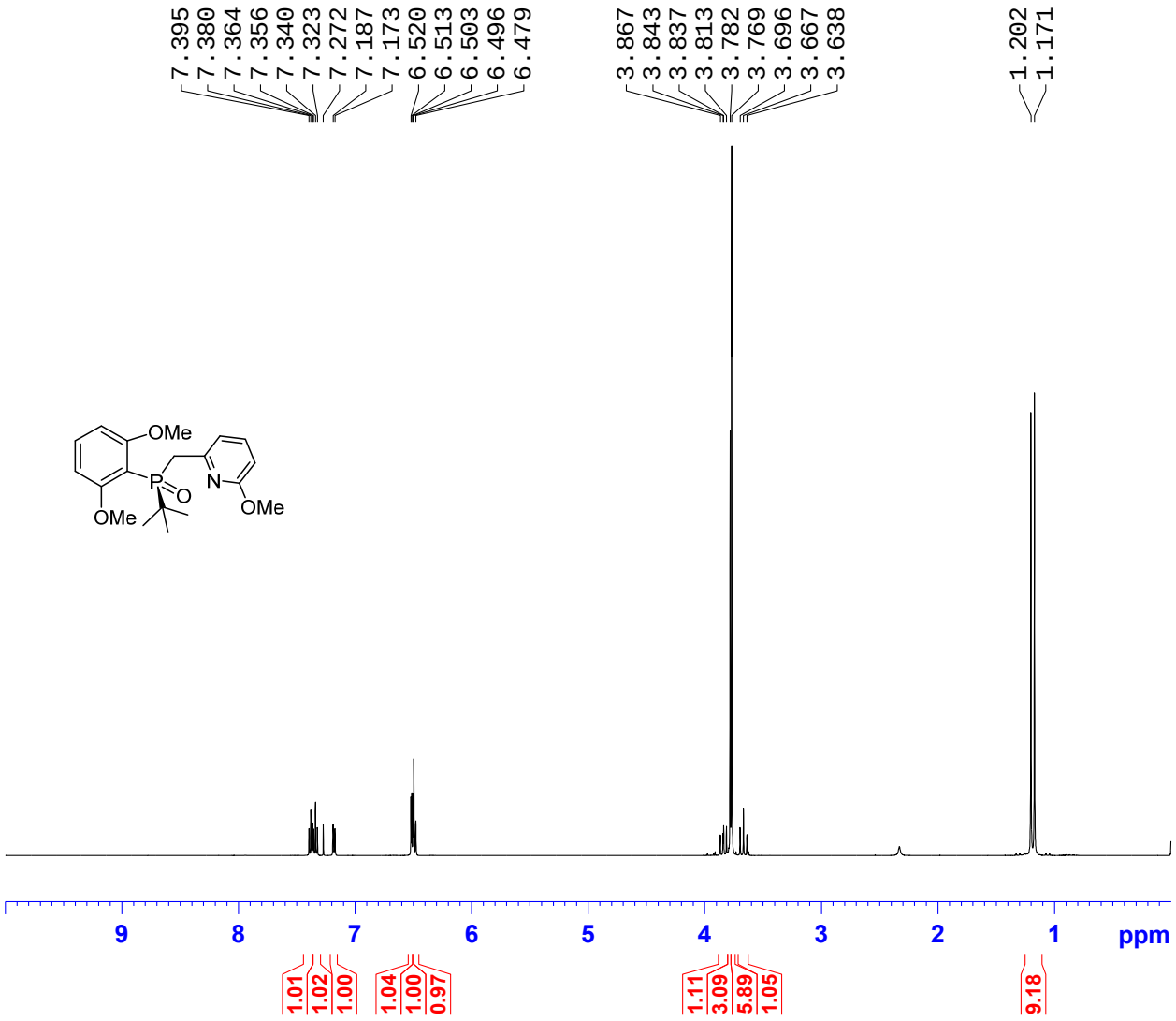
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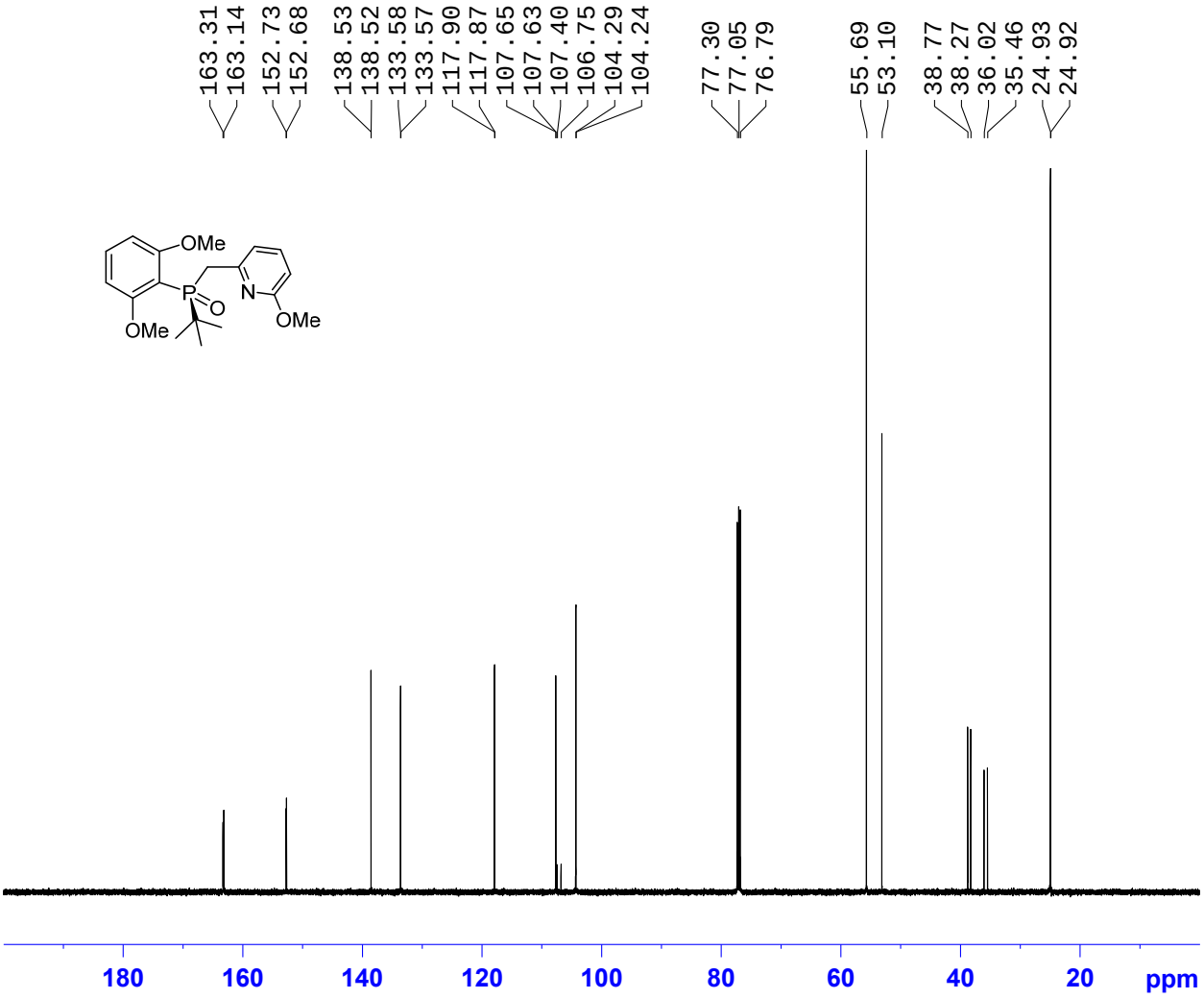
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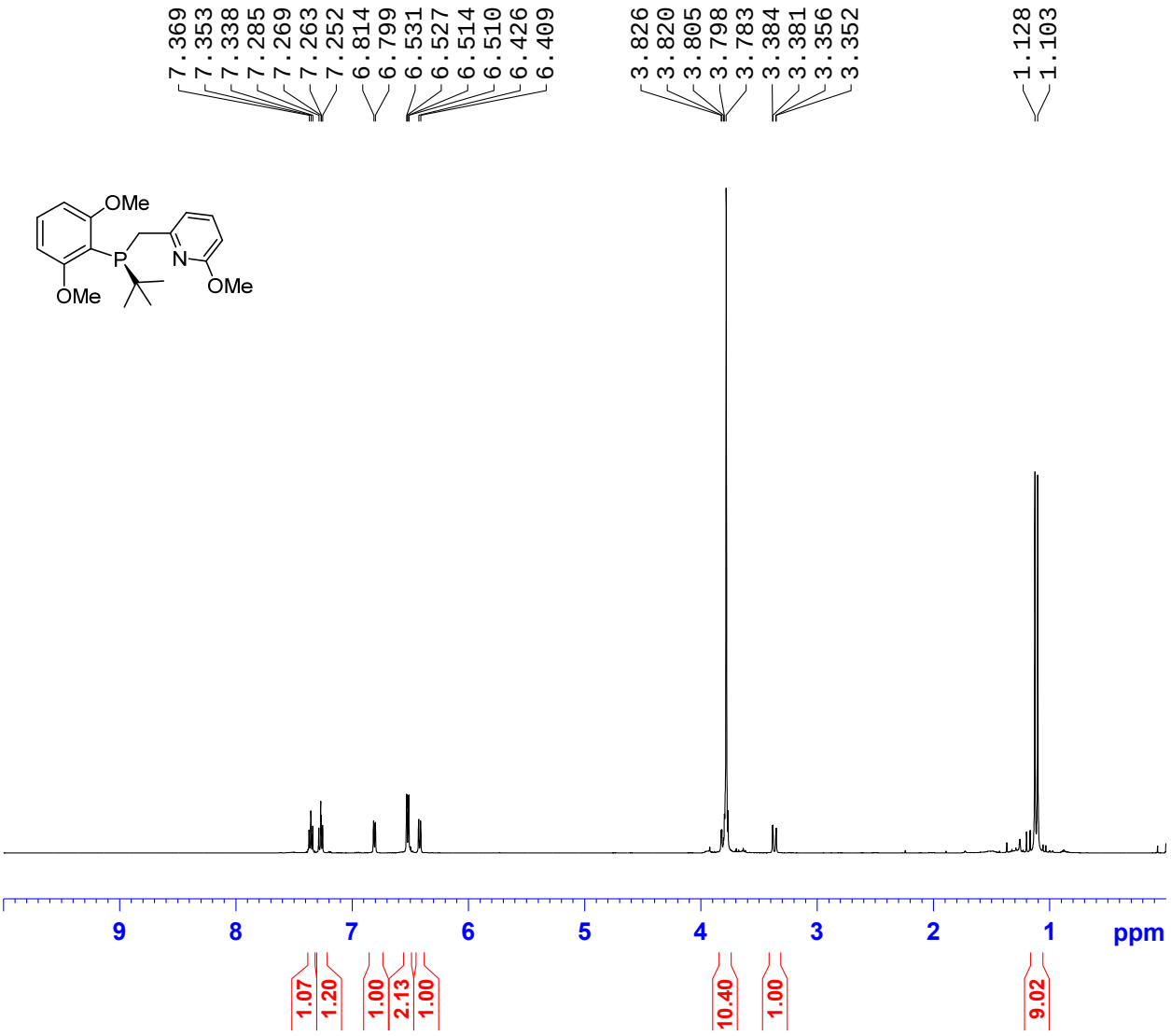
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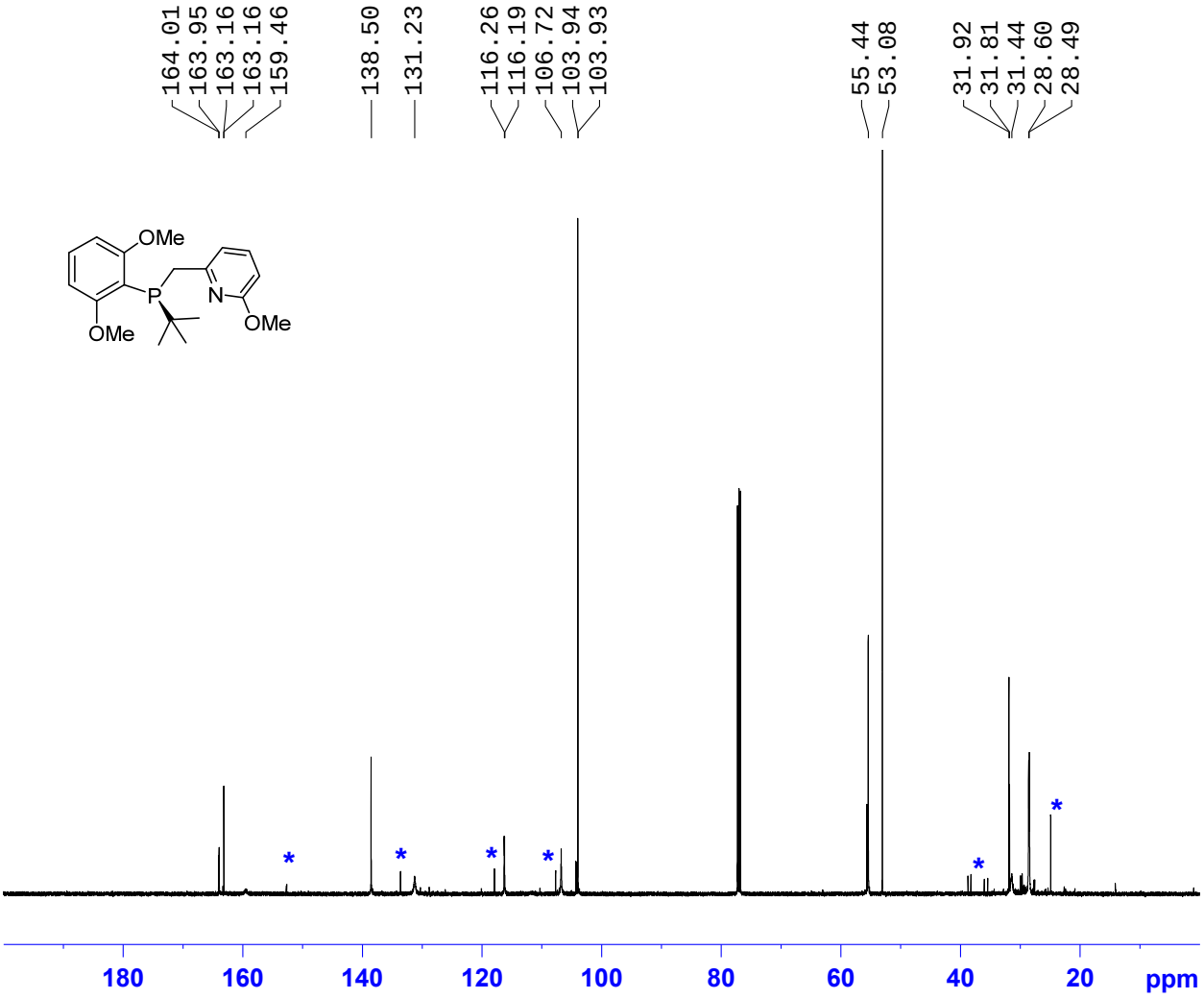


* Phosphine oxide

Kinetics studies of the intramolecular C-H arylation of 7b using catalyst $PdCl_2$(dppf)

General information:

Reactions were carried out in an Insight Omnical Super CRC reaction calorimeter. The system operates as a differential scanning calorimeter by comparing the heat released or consumed in sample vessels compared to a reference compartment. The sample vessel is a 16 ml septum-cap vial equipped with a stirring bar.

The reaction was monitored by measuring the heat flow compared to the reference heat flow every 2-6 seconds. When the heat flow signal returned to the baseline at the end of the reaction, the system was calibrated by switching on a 23 mW heat source for *ca* 30 minutes. A mathematical correction was applied to allow compensation for the time lag of heat through the reactor walls. The same correction was applied to the heat profile from the reaction.

An energy balance around the reaction vessel demonstrates that for the case of a single reaction occurring, the reaction heat flow, q, is proportional to the reaction rate, r, where H_{rxn} is the heat of the reaction and V is the reaction volume.

$$\mathbf{q = \Delta H_{rxn}\, V\, r}$$

If the units of reaction heat flow are given in watts ($mJ.s^{-1}$), the heat of the reaction in $J.mol^{-1}$, and the reaction volume in l, the reaction rate will be given in $M.s^{-1}$.

The heat of the reaction from integration of the observed heat flow *vs.* time gave an average value of 58 kcal/mole +/- 5% at a reaction temperature of 115 ^{o}C. The observed heat flow profiles can be used to obtain the fractional conversion of bromobenzene by calculation of the fractional area under the temporal heat flow curve as given below, where the numerator represents the area under the heat flow to any time point t and the denominator represents the total area under the heat flow curve.

$$\textit{fractional conversion} = \frac{\int_0^t q.dt}{\int_0^{t_f} q.dt}$$

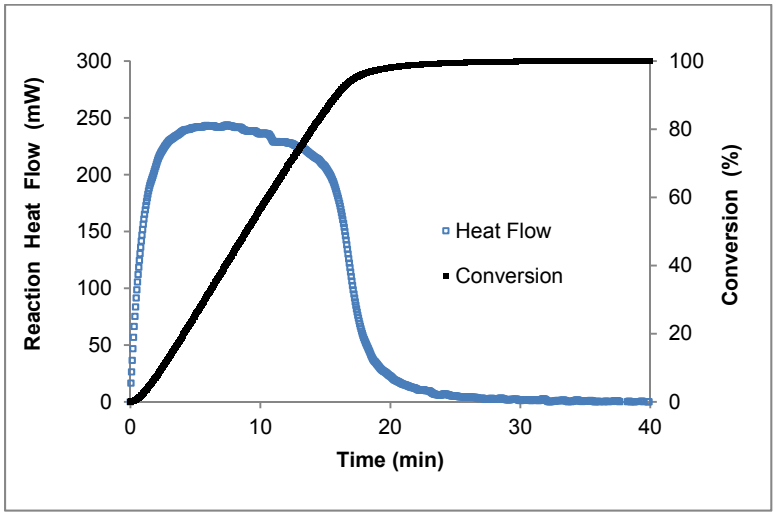
Conversion determined from heat flow was compared to the conversion by LC measurement to ascertain that no side reaction contributed to the observed heat flow and that this represents an accurate measure of rate of the reaction under study.

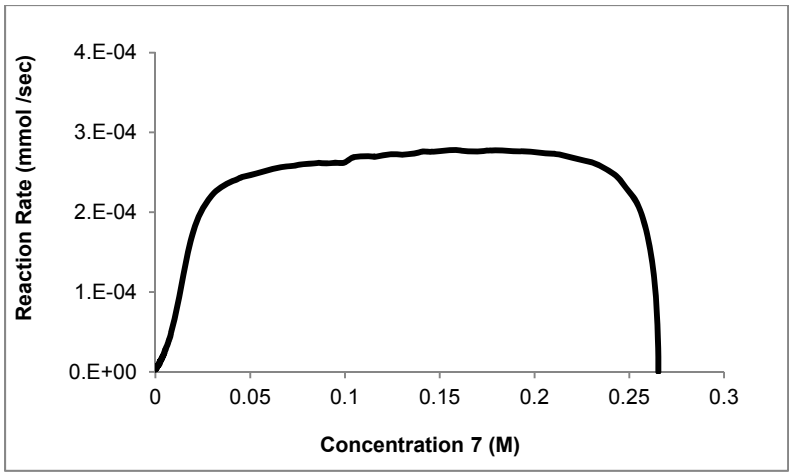
Procedure for reaction calorimetry

A solution of pyridinium **7b** (444 mg, 1.00 mmol) and DBU (457 mg, 3 mmol, 3 equiv.) in DMF (2.5 mL) was equilibrated thermally in a septum-cap vial at 110 °C. After thermal equilibration, a solution of $PdCl_2$.ddpf (14.6 mg, 0.02 mmol, 2 mol%) or $Pd_2(dba)_3$ (18.3 mg, 0.02 mmol, 2 mol%) in DMF (0.5 mL) was added in the reaction solution, while 0.5 mL of DMF was added in the reference compartment (2.8 ml DMF) to compensate the heat of mixing. A positive heat flow was detected over time as an exothermic heat was observed and the reaction was stopped when the no more heat flow was detected. The reaction solution was worked-up using the regular procedure and the reaction conversion was analyzed by HPLC.

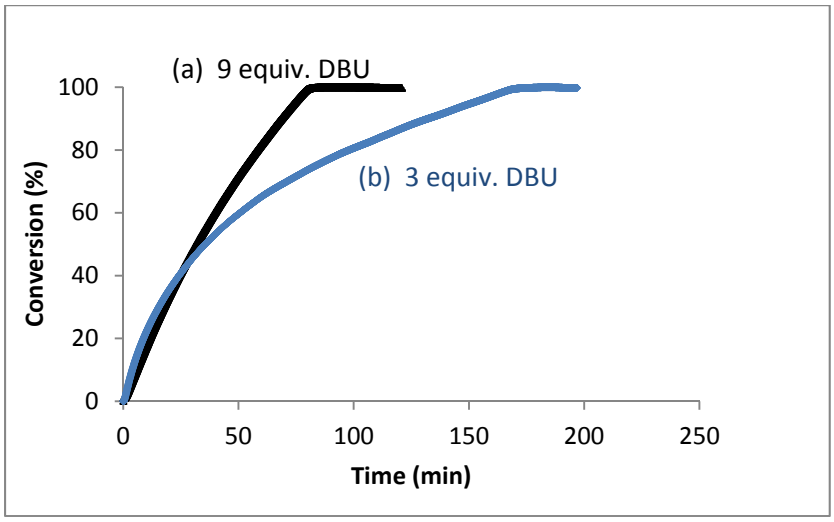
Typical Graph

Figure x show the kinetic profile for the reaction using $Pd_2(dba)_3$ (2 mol%) and excess of DBU (9 equiv.). The reaction rate graph show that the rate is constant over the consumption of the pyridinium **7b**, that would result in a zero order reaction in pyrimidine **7b** (ref : Blackmond, D.G, *Angew. Chem., Int. Ed.* **2005**, *44*, 4302.)



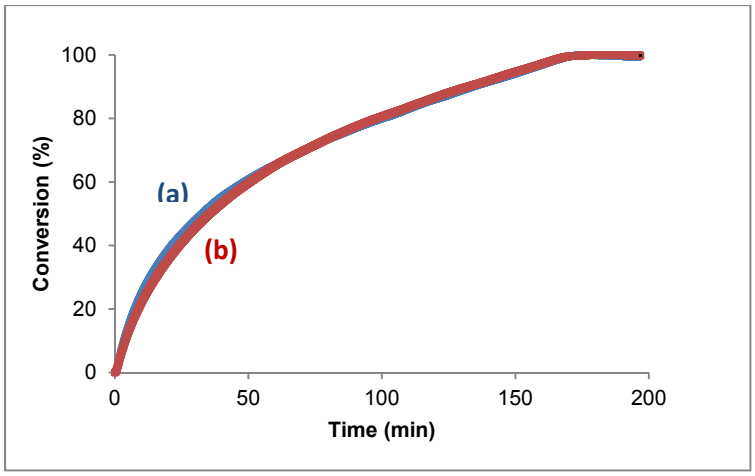


Using $PdCl_2$.ddpf (14.6 mg, 0.02 mmol, 2 mol%) and 9 equiv. of DBU, it was observed that the conversion is linear vs time, suggesting a zero order reaction in substrate. With 3 equiv. of DBU, and same amount of catalyst, the kinetic profile is different suggesting a more complex reaction mechanism.

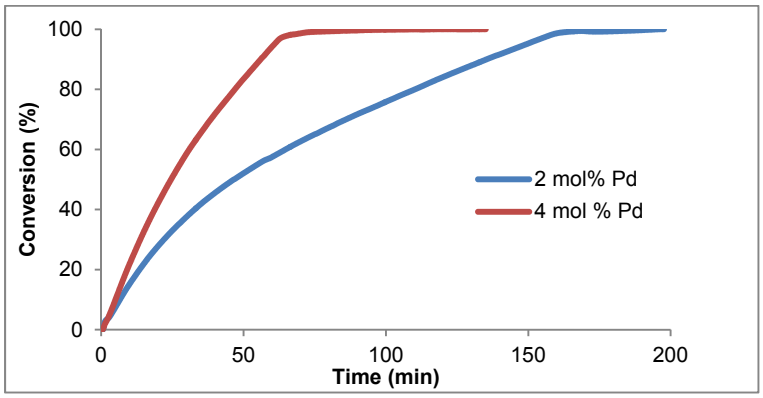


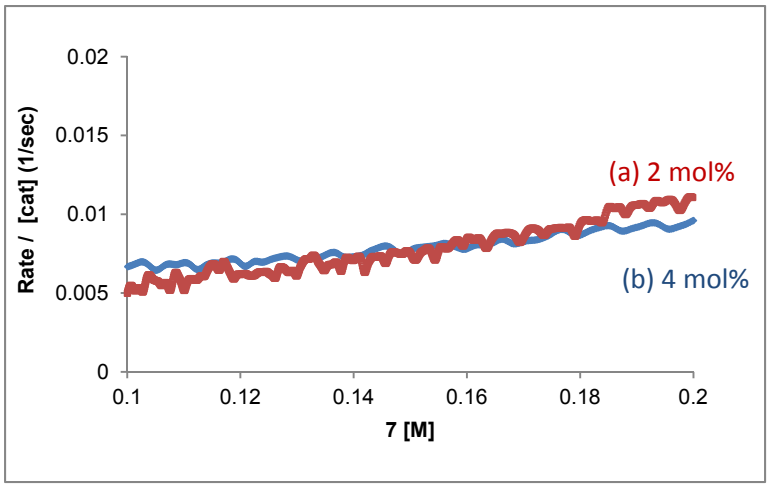
Reproducibility of kinetic experiments with $PdCl_2$.dppf

The reproducibility of the calorimetric experiments was controlled by repeating various experiments at least one time. This was done with different sources or lots of $PdCl_2$.dppf ((a) MatrixV09K and Aldrich 0619EU). Reaction with $PdCl_2$.ddpf (14.6 mg, 0.02 mmol, 2 mol%) and 3 equiv. DBU.



Catalyst order: Reaction with $PdCl_2$.ddpf (14.6 mg, 0.02 mmol, 2 mol%) *vs*. $PdCl_2$.ddpf (30 mg, 0.04 mmol, 4 mol%). The reaction with 4 mol % showed a zero order kinetic in pyridinium **7b**, the conversion is linear over time and rate is constant over time. With 2 mol%, the initial conversion profile suggested a different profile, however after 30 % of conversion the reaction exhibits a zero order kinetic in substrate 7. The curves Rate / [cat] overlays for 2 mol % and 4 mol %, indicating that the reaction is first order in catalyst.





S1. Details of Computational Studies for the C-H arylative cyclization

Optimizations for Ni species were performed using Gaussian 09[2]software with

a) spin-unrestricted DFT at the UB3LYP[3]/6-31G(d) level

and

b) spin-restricted DFT at the RB3LYP/6-31G(d)/Ni: lanl2dz[4] level in the gas phase.

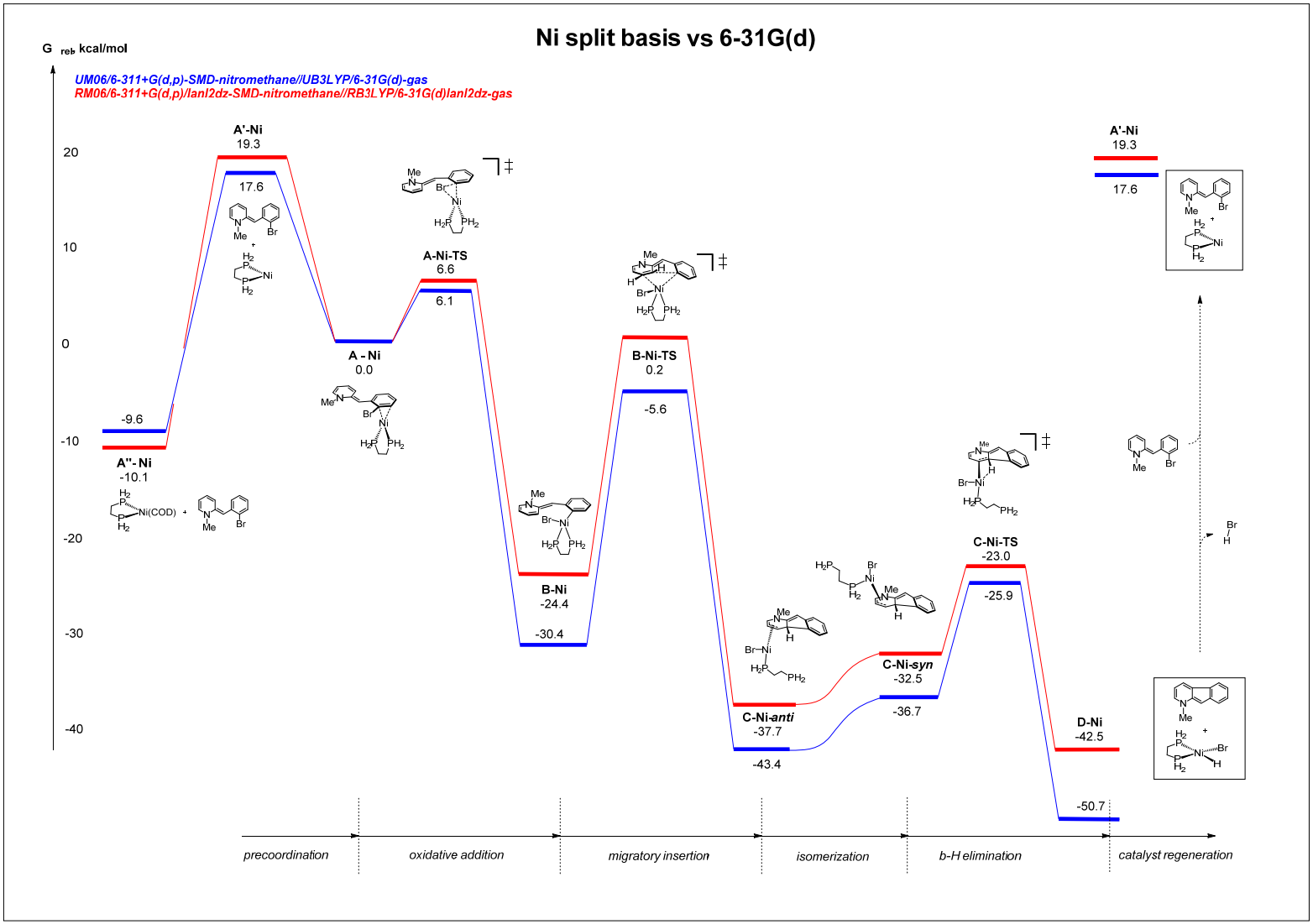
Optimizations for Pd species were performed using spin-restricted DFT at the RB3LYP/6-31G(d)/Pd: lanl2dz level in the gas phase.

For all species, vibrational frequencies were also computed at the specified level of theory to obtain thermal Gibbs Free Energy corrections (at 298 K) and to characterize the stationary points as transition states (one and only one imaginary frequency) or minima (zero imaginary frequencies). Single point energy calculations were performed on optimized geometries in nitromethane solvent [nitromethane (ε=36.562)], which resembles the dielectric properties of the solvent used in experiments (dimethylformamide ε=37.219) using the SMD[5] -solvation model and UM06[6] functional.

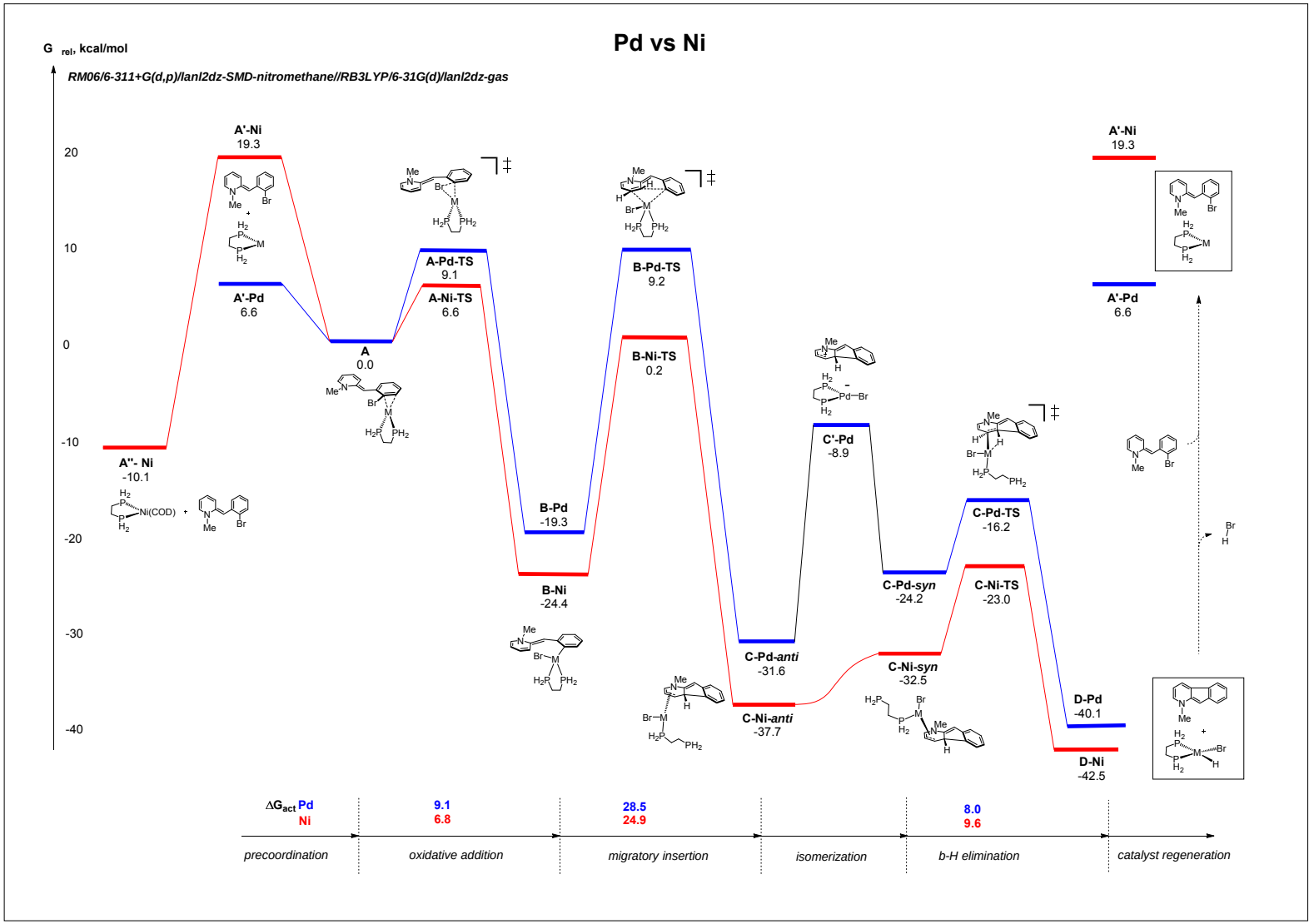
For Pd and Ni species optimized at RB3LYP/6-31G(d)/Ni: lanl2dz level of theory, the 6-311+G(d,p)/lanl2dz basis set was used for single point calculations.

For Ni species optimized at UB3LYP/6-31G(d) level of theory, the 6-311+G(d,p) basis set was used for single point calculations.

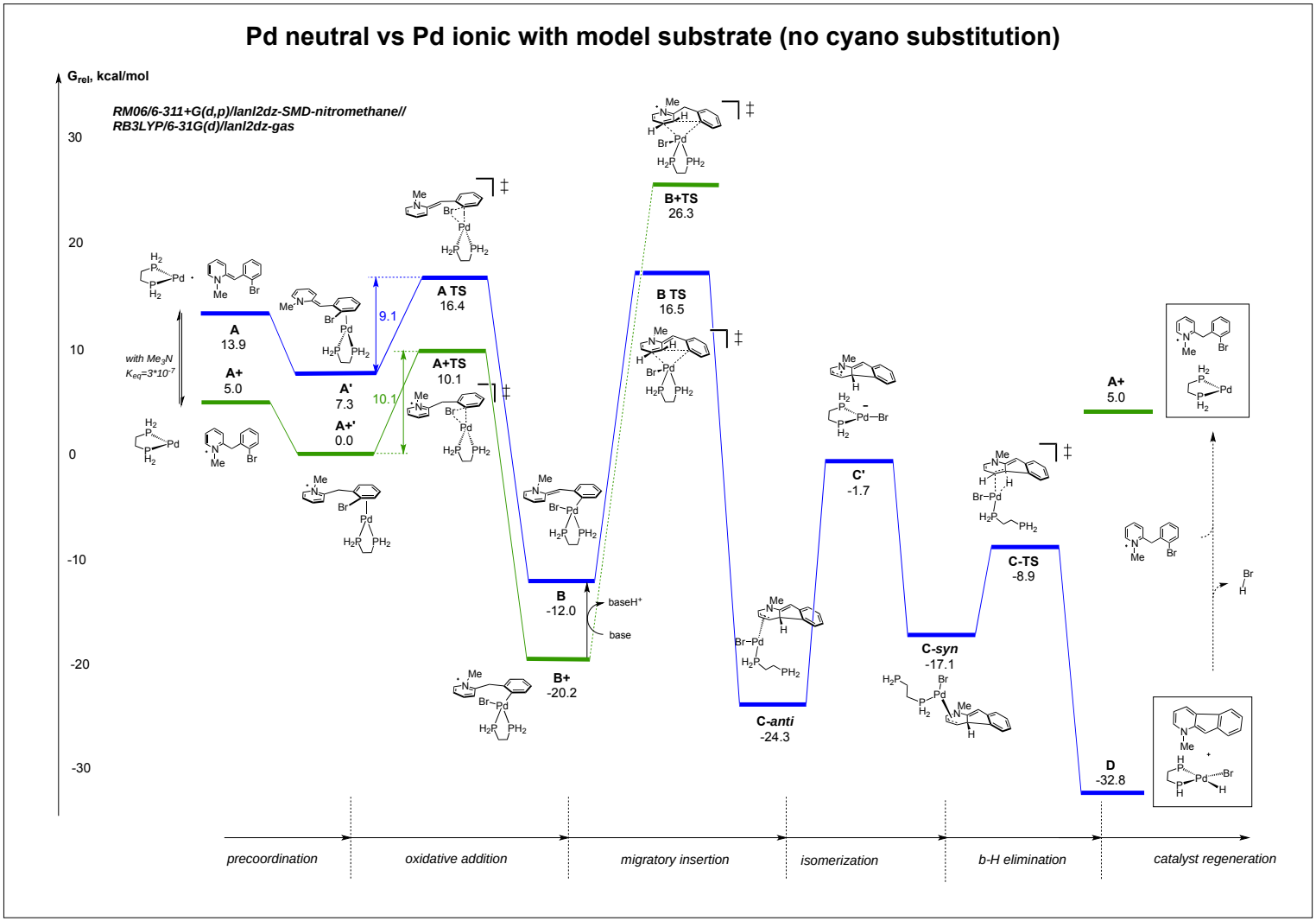
S2. Main computational results



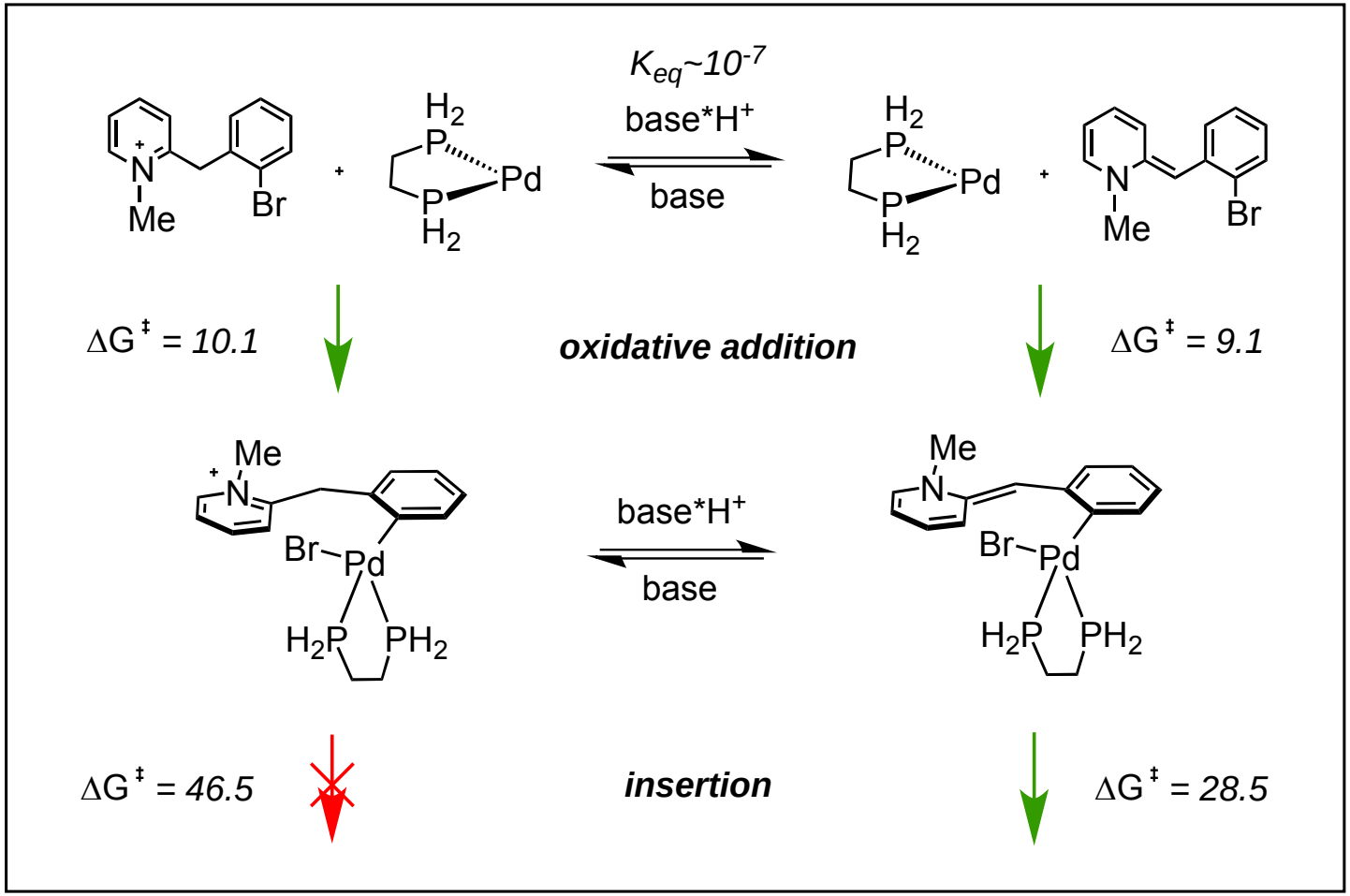
Scheme S2.1. Comparison of computational methods for Ni system


Pd vs Ni
G rel, kcal/mol
RM06/6-311+G(d,p)/lanl2dz-SMD-nitromethane//RB3LYP/6-31G(d)/lanl2dz-gas
20
10
0
-10
-20
-30
-40
A'-Ni
19.3
A'-Pd
6.6
A
0.0
A-Pd-TS
9.1
A-Ni-TS
6.6
A''- Ni
-10.1
B-Pd
-19.3
B-Ni
-24.4
B-Pd-TS
9.2
B-Ni-TS
0.2
C-Pd-anti
-31.6
C-Ni-anti
-37.7
C'-Pd
-8.9
C-Pd-syn
-24.2
C-Ni-syn
-32.5
C-Pd-TS
-16.2
C-Ni-TS
-23.0
D-Pd
-40.1
D-Ni
-42.5
A'-Ni
19.3
A'-Pd
6.6
ΔGact Pd
Ni
9.1
6.8
28.5
24.9
8.0
9.6
precoordination
oxidative addition
migratory insertion
isomerization
b-H elimination
catalyst regeneration

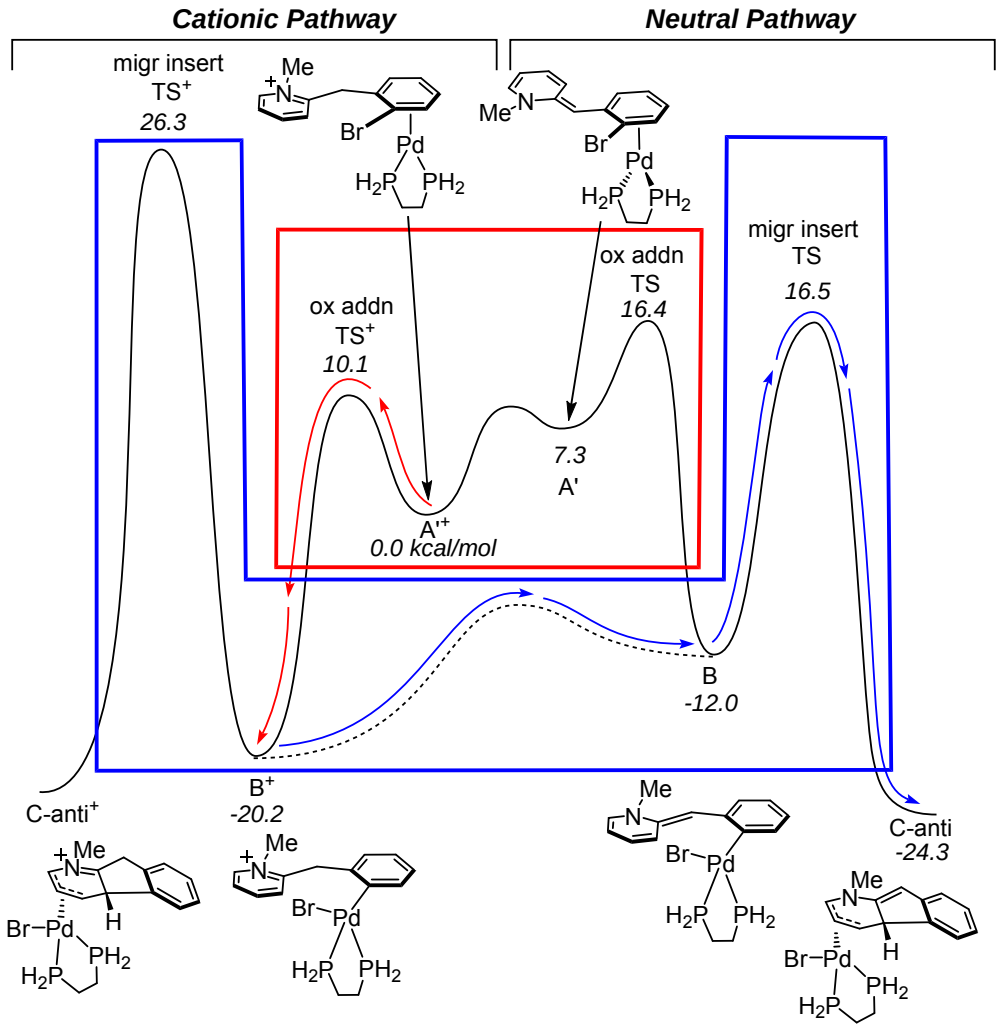
Scheme S2.2. Energetics profiles for Pd and Ni-catalyzed reaction



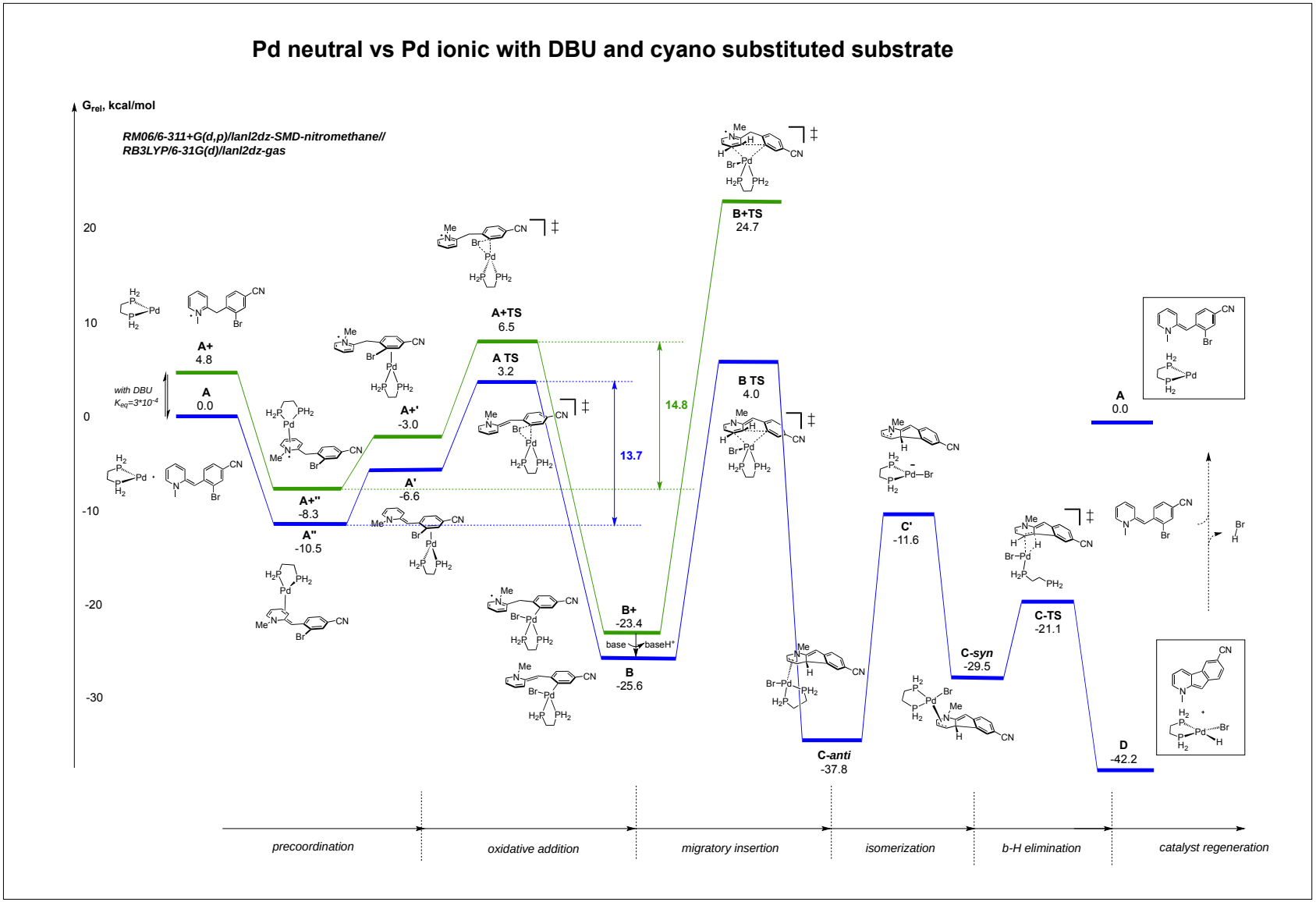
Scheme S2.3. Energetics profiles for Pd-catalyzed reaction of cationic and neutral starting materials using a model substrate



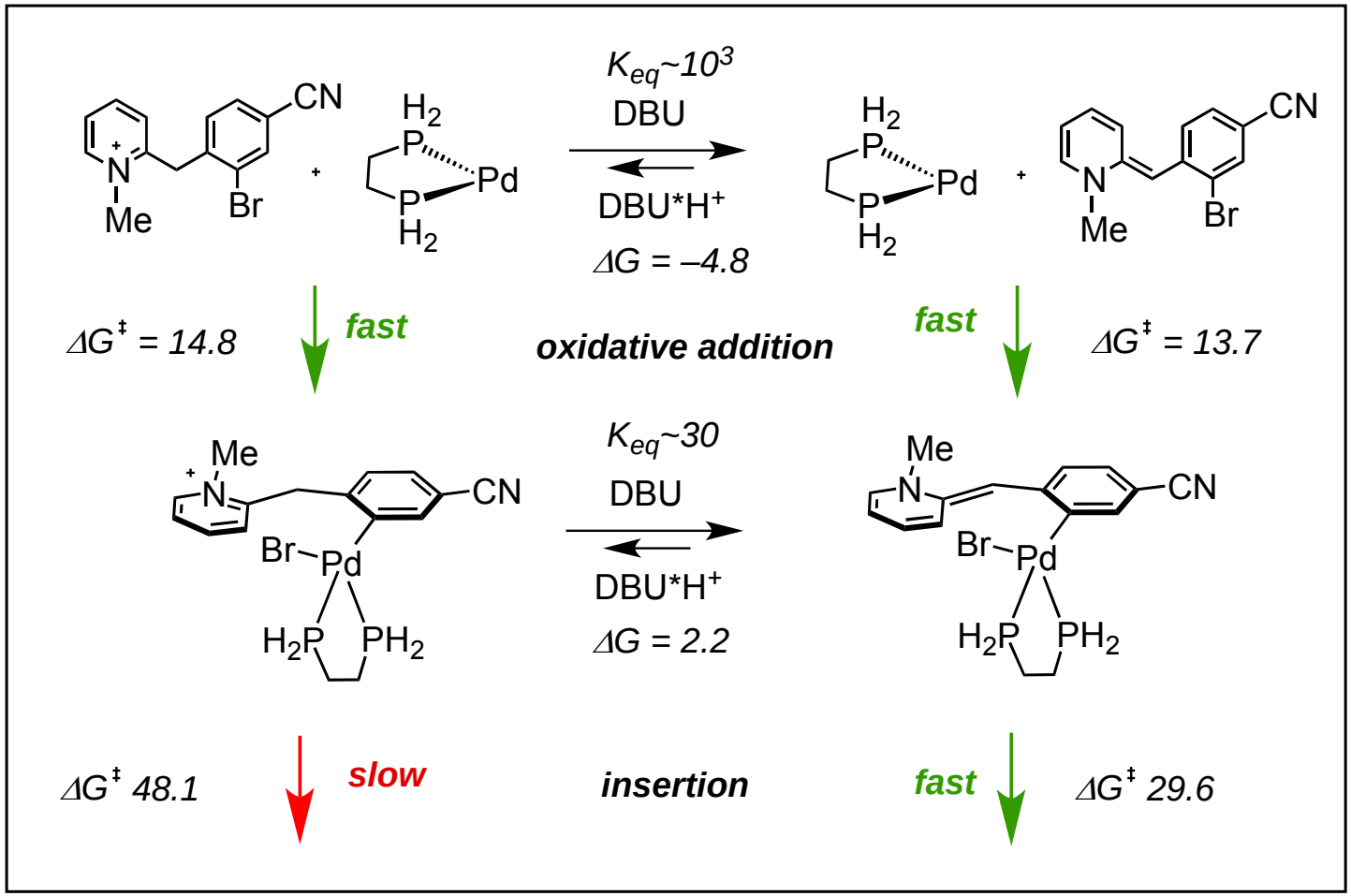
Scheme S2.4. Proposed partition for Pd-catalyzed reaction of model substrate



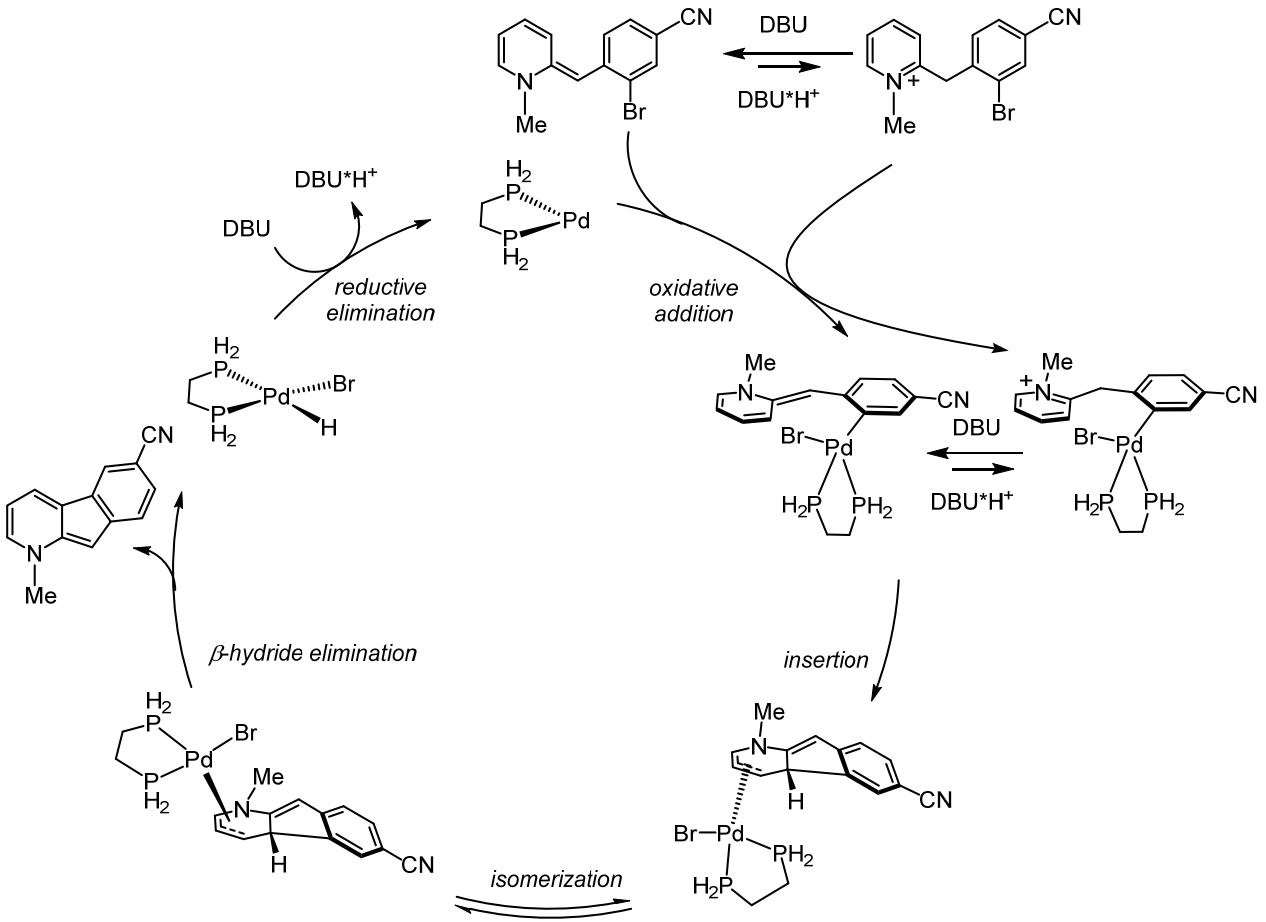
Scheme S2.5. Curtin-Hammett control elements (reaction follows course defined by the arrows) for Pd-catalyzed reaction of model substrate.



Scheme S2.6. Energetics profiles for Pd-catalyzed reaction of cationic and neutral starting materials using DBU and a cyano-substituted substrate.

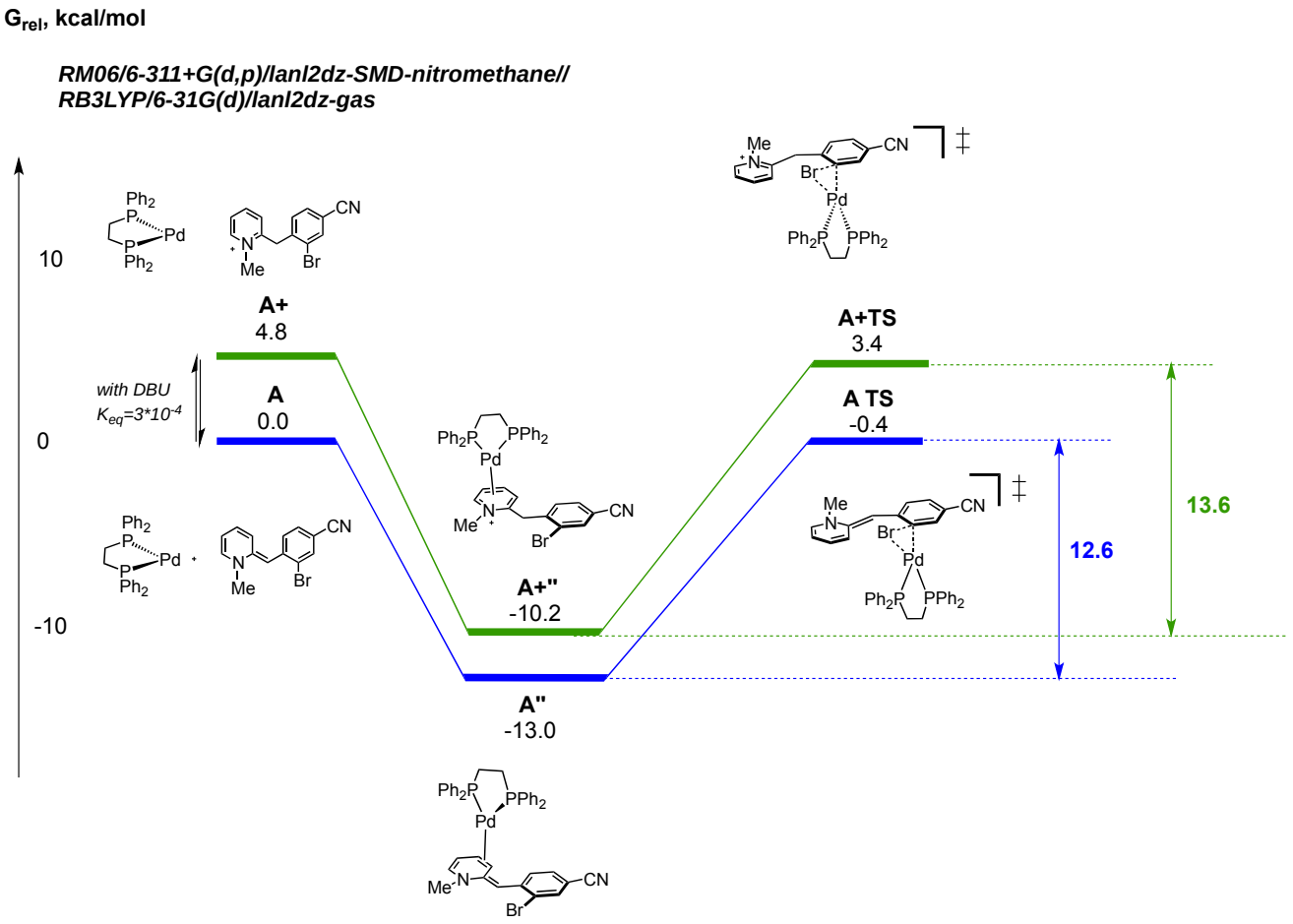


Scheme S2.7. Proposed partition for Pd-catalyzed reaction of DBU and a cyano-substituted substrate.



Scheme S2.8. Catalytic cycle for DBU and a cyano-substituted substrate.

Pd neutral vs Pd ionic with DBU and cyano substituted substrate and with dppe vs model ligand



Scheme S2.9. Energetics with dppe in place of model ligand used in Scheme S2.6.

S3. Brief discussion of the main computational results

Scheme S2.1 provides a comparison of the computational method used in this study (denoted in red) with one that was used in the recently published study of a similar system using diamine ligands (denoted in blue).[7] This scheme establishes that both methods provide very similar energetic profiles. However, the unrestricted method tends to over-stabilize Ni(II) species by ca. 5 kcal/mol. This outcome suggests that the results presented here can be qualitatively compared with the Ni-diamine systems, keeping in mind this consistent difference in free energies of the intermediates.

Scheme S2.2 compares the energetic profiles for Ni-diphosphine and Pd-diphosphine catalyzed reactions. In line with literature precedent,[8] the oxidative addition and migratory insertion paths are lower in energy for the Ni system than for the Pd system. For the Ni-catalyzed reaction, the rate limiting step is the troublesome reduction of the penultimate Ni(II) species back to Ni(0) (ca. 60kcal/mol uphill). For the Pd-catalyzed reaction, corresponding catalyst regeneration is less problematic and oxidative addition or migratory insertion is likely rate limiting. Both steps have low activation energies (ca. 9 kcal/mol) which provide an explanation for the superior reactivity of Pd over Ni in catalyzing this reaction.

Scheme S2.3 looks at the neutral vs cationic pathways for Pd with a model substrate lacking a cyano subsituent on the aryl bromide ring system and employing trimethylamine as the base. Similar to previously published results,[7] oxidative addition to the cationic species is lower in energy than the corresponding neutral species. This result arises mainly from to the difference in the acidities of the pyridinium and the neutral compound, as the barriers from the cationic or neutral Pd adducts to the oxidative addition transition state are about the same (ca. 10 kcal/mol). The aromaticity of pyridinium renders it more stable than corresponding neutral compound. These energetic differences set up the first of two Curtin-Hammett partitions where the overall oxidative addition barrier is lower from the cationic species. However, the following migratory insertion is very high energy for the cationic species, as aromaticity must be lost. Since the neutral and cationic oxidative addition adducts can interconvert by deprotonation, we now have the second Curtin-Hammett partition, where the reaction barrier is smaller from the higher energy ground state. Scheme S2.4 shows this partitioning and scheme S2.5 summarizes the salient Curtin-Hammett control elements.

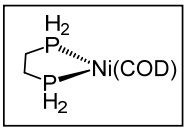
Scheme S2.6 looks at the same pathways as SchemS2.3 except a cyano subsituent is present on the aryl bromide ring and DBU is used as the base. Under these conditions, all intermediates and reaction steps are lower from the neutral form of the substrate, although reaction from the charged pyridinium substrate is viable until migratory insertion, which is very high in energy due the reacting double bond be part of a stable aromatic ring system. The corresponding partitioning diagram and catalytic cycle are shown in Scheme S2.6 and S2.7, respectively.

Scheme S2.9 shows the effect of the use of a complete ligand (dppe) in place of the model systems used in all prior calculations. Even though the phenyl groups of the diphosphine are in close proximity to the reacting centers, the relative energetics do not change in a significant way.

S4. Coordinates and thermochemical data for computed intermediates and transition states

Ni species from Scheme S2.1

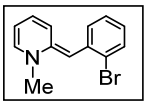
A''-Ni: LNi(cod)



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.276982 (Hartree/Particle)
Thermal correction to Energy= 0.292539
Thermal correction to Enthalpy= 0.293483
Thermal correction to Gibbs Free Energy= 0.234910
Sum of electronic and zero-point Energies= -1244.809895
Sum of electronic and thermal Energies= -1244.794338
Sum of electronic and thermal Enthalpies= -1244.793394
Sum of electronic and thermal Free Energies= -1244.851967
Electronic energy (RM06) -1244.91825008

C	3.28686500	0.73215200	0.23467100
H	4.13250000	1.28460600	-0.18898000
H	3.37977800	0.77702500	1.32689100
C	3.28747800	-0.73181600	-0.23287500
H	3.38242000	-0.77665500	-1.32492400
H	4.13249200	-1.28405800	0.19228100
P	1.63735400	1.54259100	-0.19047100
P	1.63742900	-1.54283100	0.18931800
H	1.98738100	2.15363300	-1.43281800
H	1.78981300	2.74094500	0.56808600
H	1.79103600	-2.74029400	-0.57042200
H	1.98583500	-2.15531500	1.43140800
C	-2.15017100	-1.80674900	-0.64893500
H	-3.06947400	-2.05052100	-1.20848100
H	-1.59263100	-2.74767700	-0.56475900
C	-2.52796700	-1.32878900	0.77718400
H	-3.44495100	-0.73092200	0.74060900
H	-2.77625700	-2.20890800	1.38354600
C	-1.43042900	-0.53923000	1.47715800
H	-0.88661700	-1.06785600	2.25742500
C	-1.28691800	-0.83451800	-1.43255900
H	-0.66023500	-1.29285100	-2.19639000
C	-1.43145600	0.53929300	-1.47685900
H	-0.88819200	1.06770400	-2.25765400
C	-1.28553200	0.83452500	1.43279400
H	-0.65808700	1.29266100	2.19612100
C	-2.52816900	1.32920700	-0.77597900
H	-2.77667600	2.20941400	-1.38212200
H	-3.44531800	0.73163900	-0.73864600
C	-2.14905100	1.80704500	0.64983100
H	-3.06780500	2.05119200	1.21011500
H	-1.59120600	2.74774800	0.56517600
Ni	0.08737700	-0.00016500	-0.00056300

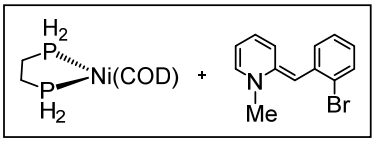
A''- Ni: Starting material



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.217074 (Hartree/Particle)
Thermal correction to Energy= 0.230064
Thermal correction to Enthalpy= 0.231009
Thermal correction to Gibbs Free Energy= 0.176015
Sum of electronic and zero-point Energies= -3128.820128
Sum of electronic and thermal Energies= -3128.807138
Sum of electronic and thermal Enthalpies= -3128.806194
Sum of electronic and thermal Free Energies= -3128.861187
Electronic energy (RM06) -3131.06727480

C	-3.12567100	1.01668700	-0.06071500
C	-3.00854400	2.38585700	0.17791100
C	-1.75828000	2.91361100	0.50464400
C	-0.64398600	2.08458900	0.58081800
C	-0.70814900	0.69651200	0.31076200
C	-1.99845600	0.20408500	0.00633100
H	-4.08642900	0.57686500	-0.30577400
H	-3.88612400	3.02315800	0.12018000
H	-1.65240400	3.97299500	0.72352600
H	0.30542000	2.50446500	0.89713600
C	0.44262100	-0.19176200	0.41561400
H	0.20067500	-1.19366800	0.74243100
C	1.74854500	0.09496700	0.09204100
C	2.20454400	1.28964000	-0.59102900
C	3.51218200	1.50929600	-0.89139200
H	1.44728500	1.99748100	-0.90233800
C	4.09058700	-0.59885200	0.06745800
C	4.50810600	0.54499000	-0.53525500
H	4.77679000	-1.39150000	0.34455400
H	5.55871200	0.69573200	-0.75100400
Br	-2.25599300	-1.67129700	-0.34622800
C	2.41880300	-2.10180300	1.01271300
H	1.75459200	-2.69264500	0.37114500
H	3.32585000	-2.67568300	1.20819900
H	1.90120600	-1.91062000	1.95992000
N	2.77437000	-0.84411000	0.37088900
H	3.79977000	2.41069000	-1.42561100

A''-Ni



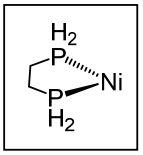
ub3lyp/6-31G(d)
Zero-point correction= 0.495950 (Hartree/Particle)
Thermal correction to Energy= 0.526286
Thermal correction to Enthalpy= 0.527230
Thermal correction to Gibbs Free Energy= 0.417448
Sum of electronic and zero-point Energies= -5712.485445
Sum of electronic and thermal Energies= -5712.455110

Sum of electronic and thermal Enthalpies= -5712.454165
Sum of electronic and thermal Free Energies= -5712.563947
Electronic energy (UM06) -5714.86571616

C	25.72303100	-3.07589200	1.19535600
C	26.67141900	-3.03892100	2.21731500
C	27.45749700	-1.89596900	2.37326300
C	27.28883900	-0.80652800	1.52505800
C	26.31536600	-0.78539500	0.49762600
C	25.55808100	-1.97227100	0.36444400
H	25.10527500	-3.95453900	1.04383500
H	26.79783400	-3.89721900	2.87074000
H	28.22185100	-1.85936200	3.14516600
H	27.95191200	0.04693800	1.62359800
C	26.14852600	0.33433600	-0.42057400
H	25.84221200	0.04914600	-1.41756100
C	26.27932700	1.67332000	-0.13348000
C	26.43080300	2.23978600	1.19233600
C	26.54059200	3.57723100	1.41051500
H	26.40697000	1.55079000	2.02668600
C	26.33069400	3.98091200	-0.93308100
C	26.51074900	4.49425800	0.31190000
H	26.27013400	4.60856100	-1.81531800
H	26.60547300	5.56401100	0.45229300
C	-27.12507600	1.75285800	1.51957200
H	-27.41668100	2.26952100	2.44002100
H	-27.49972800	2.34408100	0.67504200
C	-27.69600700	0.32891100	1.46052400
H	-27.50548200	-0.19301900	2.40627800
H	-28.77879000	0.33192900	1.29695900
P	-25.25361200	1.67270000	1.32488900
P	-26.78912700	-0.64100100	0.12491600
Br	24.22009300	-2.11235500	-1.01265000
C	26.01773900	2.17523600	-2.54218600
H	25.04894600	1.67423300	-2.65354000
H	26.05468000	3.03060200	-3.21843800
H	26.80590900	1.46435600	-2.81606800
N	26.20945100	2.63488900	-1.17400600
H	-24.86385500	1.72377500	2.69767200
H	-24.99914300	3.05027600	1.06789000
H	-27.21623400	-1.95362000	0.47581400
H	-27.71134000	-0.48922600	-0.95450400
H	26.62781500	3.95365600	2.42602600
C	-23.57821600	-2.45618300	-0.93414300
H	-22.72118100	-3.15013700	-0.92378100
H	-24.47204500	-3.08550100	-1.03106500
C	-23.49405500	-1.52234400	-2.16792400
H	-22.44778000	-1.30533200	-2.41031200
H	-23.89604300	-2.04777700	-3.04275100
C	-24.26222100	-0.21846300	-1.97031300
H	-25.16135800	-0.11641800	-2.57598900
C	-23.68577200	-1.70393900	0.38178500
H	-24.14284300	-2.27281000	1.19117800
C	-22.91296500	-0.59830800	0.74139900
H	-22.84873400	-0.37989300	1.80624200
C	-23.69982500	0.96758500	-1.49405300
H	-24.18904700	1.89773300	-1.78234100
C	-21.78466400	-0.02019100	-0.10796600
H	-20.99208600	0.35373500	0.55165400
H	-21.32186000	-0.81535900	-0.70313300
C	-22.26268900	1.13023600	-1.02901700

H	-21.57943900	1.23728800	-1.88811600
H	-22.19628200	2.07521800	-0.47496500
Ni	-24.74765800	0.03376800	0.02408500

A'-Ni: LNi



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.094519 (Hartree/Particle)
Thermal correction to Energy= 0.101790
Thermal correction to Enthalpy= 0.102735
Thermal correction to Gibbs Free Energy= 0.062638
Sum of electronic and zero-point Energies= -932.909826
Sum of electronic and thermal Energies= -932.902554
Sum of electronic and thermal Enthalpies= -932.901610
Sum of electronic and thermal Free Energies= -932.941707
Electronic energy (RM06) -932.98756522

C	0.70643800	-1.72400000	0.30881800
H	1.27786200	-2.59418000	-0.03469500
H	0.63570000	-1.79124000	1.40144500
C	-0.70643600	-1.72400100	-0.30881700
H	-0.63569800	-1.79124100	-1.40144500
H	-1.27785900	-2.59418100	0.03469300
P	1.62866200	-0.11018100	-0.05679800
P	-1.62866300	-0.11018300	0.05679800
H	2.28238700	-0.47837000	-1.27057100
H	2.76920700	-0.34297700	0.76989000
H	-2.76920700	-0.34298000	-0.76988900
H	-2.28238600	-0.47837300	1.27057300
Ni	-0.00000100	1.22882100	0.00000000

A'-Ni: COD

rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.181147 (Hartree/Particle)
Thermal correction to Energy= 0.188572
Thermal correction to Enthalpy= 0.189516
Thermal correction to Gibbs Free Energy= 0.149621
Sum of electronic and zero-point Energies= -311.849253
Sum of electronic and thermal Energies= -311.841829
Sum of electronic and thermal Enthalpies= -311.840884
Sum of electronic and thermal Free Energies= -311.880779
Electronic energy (RM06) -311.86128629

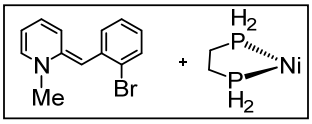
C	-1.08303000	1.10789900	0.66507000
H	-0.66660000	0.72449700	1.59997600
H	-1.77130600	1.91037700	0.95870600
C	-1.92326800	0.01155200	-0.02475300
H	-2.74176500	-0.28214200	0.65244600
H	-2.42443100	0.45634200	-0.89738800
C	-1.21563000	-1.23582300	-0.49481300
H	-1.82281600	-1.84174400	-1.16973500
C	-0.00728300	1.70477100	-0.21768000
H	-0.28995600	2.63556700	-0.71064400
C	1.21562000	1.23582600	-0.49482200

H	1.82279000	1.84174900	-1.16975700
C	0.00727900	-1.70477000	-0.21769900
H	0.28993800	-2.63556600	-0.71067100
C	1.92327000	-0.01154600	-0.02477200
H	2.42444200	-0.45632300	-0.89740900
H	2.74176100	0.28214900	0.65243500
C	1.08304100	-1.10790700	0.66504000
H	0.66662300	-0.72452200	1.59995800
H	1.77132300	-1.91038900	0.95865300

ub3lyp/6-31G(d)
Zero-point correction= 0.181147 (Hartree/Particle)
Thermal correction to Energy= 0.188572
Thermal correction to Enthalpy= 0.189516
Thermal correction to Gibbs Free Energy= 0.149621
Sum of electronic and zero-point Energies= -311.849253
Sum of electronic and thermal Energies= -311.841829
Sum of electronic and thermal Enthalpies= -311.840884
Sum of electronic and thermal Free Energies= -311.880779
Electronic energy (UM06) -311.86128629

C	1.08303000	-1.10789900	0.66507000
H	0.66660000	-0.72449700	1.59997600
H	1.77130600	-1.91037600	0.95870600
C	1.92326800	-0.01155100	-0.02475300
H	2.74176500	0.28214300	0.65244600
H	2.42443100	-0.45634100	-0.89738800
C	1.21563000	1.23582300	-0.49481300
H	1.82281500	1.84174500	-1.16973500
C	0.00728300	-1.70477100	-0.21768000
H	0.28995700	-2.63556700	-0.71064400
C	-1.21562000	-1.23582600	-0.49482200
H	-1.82279000	-1.84174900	-1.16975700
C	-0.00727900	1.70477000	-0.21769900
H	-0.28993900	2.63556600	-0.71067100
C	-1.92327000	0.01154600	-0.02477200
H	-2.42444200	0.45632300	-0.89740900
H	-2.74176100	-0.28215000	0.65243500
C	-1.08304100	1.10790700	0.66504000
H	-0.66662300	0.72452200	1.59995800
H	-1.77132400	1.91038900	0.95865300

A'-Ni

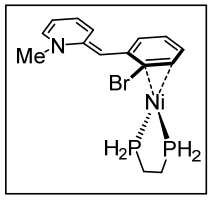


ub3lyp/6-31G(d)
Zero-point correction= 0.312523 (Hartree/Particle)
Thermal correction to Energy= 0.335154
Thermal correction to Enthalpy= 0.336098
Thermal correction to Gibbs Free Energy= 0.241218
Sum of electronic and zero-point Energies= -5400.530669
Sum of electronic and thermal Energies= -5400.508038
Sum of electronic and thermal Enthalpies= -5400.507094
Sum of electronic and thermal Free Energies= -5400.601974
Electronic energy (UM06) -5402.93434952

C	14.03510400	-3.19945500	0.80699100
C	14.98770700	-3.23353400	1.82518700

C	15.72051700	-2.07978200	2.10883800
C	15.49573900	-0.91048200	1.38970000
C	14.51567200	-0.81943800	0.37258300
C	13.81328700	-2.01771600	0.10714200
H	13.45816100	-4.08360900	0.55775400
H	15.15862500	-4.15337100	2.37683800
H	16.48729800	-2.09484000	2.87904400
H	16.11813400	-0.04282800	1.58382300
C	14.29001200	0.38792400	-0.41248900
H	13.99526500	0.20279400	-1.43633100
C	14.35081900	1.68973300	0.02755900
C	14.47601700	2.10582200	1.41071000
C	14.51072900	3.41283100	1.78331100
H	14.49400500	1.32453300	2.15948600
C	14.27147300	4.07394000	-0.49808700
C	14.42539400	4.44833200	0.79879700
H	14.17362300	4.79541000	-1.30172500
H	14.46005400	5.49812000	1.06300200
C	-25.34738100	0.39982000	0.72553900
H	-26.20956400	0.10426400	1.33425900
H	-25.42039300	1.48240500	0.56291600
C	-25.34738900	-0.33174900	-0.63058400
H	-25.41912900	-1.41441400	-0.46792700
H	-26.21025400	-0.03712700	-1.23878900
P	-23.72166700	0.11997600	1.64527700
P	-23.72252600	-0.05010100	-1.55128500
Br	12.47203500	-2.06168900	-1.27369200
C	14.05483800	2.45315100	-2.30735900
H	13.11352600	1.91798200	-2.47939900
H	14.04458500	3.38200500	-2.87961700
H	14.87863300	1.82153600	-2.65954800
N	14.22604300	2.76033400	-0.89446300
H	-24.07531500	-1.00695000	2.44331300
H	-23.89750900	1.10868200	2.65687200
H	-23.89783800	-1.03899800	-2.56278300
H	-24.07792600	1.07642600	-2.34911600
Ni	-22.48965200	0.03562000	0.04662500
H	14.58041800	3.67289400	2.83596900

A-Ni



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.311596 (Hartree/Particle)
Thermal correction to Energy= 0.333824
Thermal correction to Enthalpy= 0.334768
Thermal correction to Gibbs Free Energy= 0.257966
Sum of electronic and zero-point Energies= -4061.450103
Sum of electronic and thermal Energies= -4061.427875
Sum of electronic and thermal Enthalpies= -4061.426931
Sum of electronic and thermal Free Energies= -4061.503732
Electronic energy (RM06) -4064.10486223

C	-1.64313900	-1.69778700	1.21082700
C	-1.52820400	-1.51473000	2.62237600

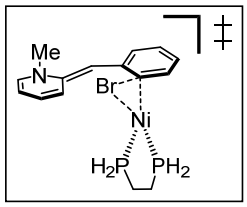
C	-0.33730000	-1.09200400	3.16816900
C	0.79036500	-0.85056900	2.34712800
C	0.76487900	-1.00215300	0.96094500
C	-0.50561800	-1.41162900	0.38893300
H	-2.45103200	-2.30944600	0.82102700
H	-2.37728600	-1.75960200	3.25571700
H	-0.23843500	-0.97938200	4.24494000
H	1.73024600	-0.58363700	2.82031000
C	1.92673900	-0.79697200	0.10617000
H	1.96557800	-1.44974800	-0.75522900
C	2.91092500	0.15464900	0.24909300
C	2.88711400	1.25654600	1.19241000
C	3.88002900	2.18228800	1.26692000
H	2.01089800	1.33952400	1.82238900
C	5.04248300	1.08346400	-0.50759500
C	5.01843100	2.09387500	0.40041100
H	5.85726300	0.95828700	-1.21242700
H	5.83247200	2.80706400	0.44454300
C	-2.43103700	2.85413000	-1.48585300
H	-2.10142700	3.87208800	-1.71850700
H	-2.89763800	2.44665900	-2.39168900
C	-3.44700400	2.85420400	-0.32954700
H	-3.03914500	3.40386400	0.52812200
H	-4.37874300	3.34956400	-0.62230000
P	-0.97973500	1.71869300	-1.07933700
P	-3.75016000	1.08992200	0.26720500
Br	-0.51129800	-2.31298300	-1.38112300
C	4.15765600	-0.90526300	-1.60884800
H	3.34523100	-0.83612000	-2.34253400
H	5.11302100	-0.80858600	-2.12748000
H	4.10315900	-1.89113500	-1.13225800
N	4.04570400	0.14409700	-0.60697300
H	-0.09721300	2.65913400	-0.47926900
H	-0.33998200	1.70774300	-2.34812500
H	-4.54980500	1.37332600	1.40907800
H	-4.83762400	0.73433400	-0.57970000
Ni	-1.81591000	0.05466900	0.11678700
H	3.80196800	3.00353700	1.97422700

ub3lyp/6-31G(d)
Zero-point correction= 0.312701 (Hartree/Particle)
Thermal correction to Energy= 0.334454
Thermal correction to Enthalpy= 0.335398
Thermal correction to Gibbs Free Energy= 0.259290
Sum of electronic and zero-point Energies= -5400.607831
Sum of electronic and thermal Energies= -5400.586078
Sum of electronic and thermal Enthalpies= -5400.585134
Sum of electronic and thermal Free Energies= -5400.661242
Electronic energy (UM06) -5402.98051554

C	-1.67694600	-1.46849800	1.32576000
C	-1.52266800	-1.21592800	2.73092000
C	-0.31990500	-0.78733700	3.23423000
C	0.81496800	-0.63604500	2.39334700
C	0.77330100	-0.86650700	1.02350500
C	-0.52710600	-1.22179200	0.48655500
H	-2.40234600	-2.22600700	1.03894500
H	-2.35550200	-1.42601800	3.39835700
H	-0.20445200	-0.61886500	4.30221900
H	1.76622100	-0.37841300	2.84876600
C	1.92485100	-0.76091000	0.13860100

H	1.90840600	-1.45372600	-0.69205400
C	2.96622100	0.13471400	0.21810100
C	3.02767300	1.28011600	1.10544600
C	4.07612700	2.14486600	1.11848100
H	2.16846100	1.44905300	1.74177100
C	5.13428100	0.89399700	-0.61966200
C	5.19040500	1.94434900	0.23983900
H	5.92573900	0.68576200	-1.33149000
H	6.04794400	2.60608700	0.23716100
C	-2.38079000	2.90183400	-1.37787600
H	-2.00525700	3.92783100	-1.44727000
H	-2.80754300	2.64071300	-2.35443000
C	-3.45820100	2.77240000	-0.28727600
H	-3.09534000	3.20789700	0.65206100
H	-4.37711300	3.29992500	-0.56306200
P	-0.99885400	1.66156200	-1.05132300
P	-3.77481600	0.95043500	0.06840400
Br	-0.59204900	-2.28836500	-1.22144800
C	4.10555400	-1.08193900	-1.61225800
H	3.28502000	-0.99302700	-2.33464500
H	5.05484300	-1.07029400	-2.15032400
H	3.99759700	-2.04010000	-1.09058600
N	4.07983800	0.01556000	-0.65760800
H	-0.07506800	2.49081000	-0.36324400
H	-0.35625100	1.69126600	-2.31749800
H	-4.58274100	1.07509600	1.22801100
H	-4.82544900	0.69119100	-0.85626200
Ni	-1.86168200	0.00148200	-0.01213000
H	4.06124500	3.00329900	1.78463700

A-Ni-TS



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.310944 (Hartree/Particle)
Thermal correction to Energy= 0.332854
Thermal correction to Enthalpy= 0.333798
Thermal correction to Gibbs Free Energy= 0.257415
Sum of electronic and zero-point Energies= -4061.445060
Sum of electronic and thermal Energies= -4061.423150
Sum of electronic and thermal Enthalpies= -4061.422206
Sum of electronic and thermal Free Energies= -4061.498589
Electronic energy (RM06) -4064.09378277

C	-1.50556100	-2.10770300	1.01184600
C	-1.15005100	-2.56845000	2.29527900
C	0.16417900	-2.43931800	2.72208000
C	1.13331300	-1.84898800	1.89450400
C	0.83212400	-1.31389800	0.63130800
C	-0.54483200	-1.41925700	0.24303400
H	-2.47170900	-2.35721700	0.58807700
H	-1.88827700	-3.07893600	2.90820900
H	0.46637800	-2.83961700	3.68645000
H	2.16482200	-1.83218100	2.23240600
C	1.79978200	-0.70586100	-0.26653300

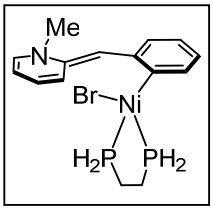
H	1.53848900	-0.80852400	-1.31121300
C	2.94008100	-0.00375100	0.05638600
C	3.31082400	0.44582100	1.38395800
C	4.44538900	1.15426400	1.63051100
H	2.61472700	0.23456800	2.18515900
C	4.98781100	1.09942500	-0.69479000
C	5.33869200	1.48412000	0.56075100
H	5.59663100	1.33043500	-1.56205100
H	6.25609600	2.03569400	0.72590700
C	-2.12610900	3.29640600	0.03367000
H	-1.83607600	4.26410400	0.45629500
H	-2.28057100	3.44389100	-1.04266300
C	-3.42561500	2.78502100	0.68053500
H	-3.31940700	2.76602300	1.77243400
H	-4.26844300	3.44357400	0.44501700
P	-0.74408000	2.01993500	0.19678200
P	-3.76081900	1.00826600	0.15245300
Br	-1.04855000	-1.46793100	-1.86570500
C	3.55291900	0.01764200	-2.34339200
H	2.62775100	0.49115100	-2.69295400
H	4.37756700	0.33394900	-2.98425600
H	3.42979900	-1.06878600	-2.42139400
N	3.84287300	0.39295400	-0.96661800
H	-0.12557900	2.49048900	1.39027500
H	0.19565100	2.62664500	-0.68131000
H	-4.84466400	0.71471200	1.02382500
H	-4.56302600	1.23833100	-0.99947200
Ni	-1.76713400	0.03689200	0.05119100
H	4.66452500	1.48977900	2.64049700

ub3lyp/6-31G(d)
Zero-point correction= 0.311887 (Hartree/Particle)
Thermal correction to Energy= 0.333188
Thermal correction to Enthalpy= 0.334132
Thermal correction to Gibbs Free Energy= 0.259720
Sum of electronic and zero-point Energies= -5400.606449
Sum of electronic and thermal Energies= -5400.585149
Sum of electronic and thermal Enthalpies= -5400.584205
Sum of electronic and thermal Free Energies= -5400.658617
Electronic energy (UM06) -5402.97122077

C	-1.57575700	-1.58897700	1.38091900
C	-1.31331100	-1.60139600	2.77656400
C	-0.03981200	-1.33012200	3.23791800
C	1.01776300	-1.06738200	2.33985300
C	0.83364000	-0.98661300	0.95602000
C	-0.52117800	-1.16887400	0.52396700
H	-2.42003500	-2.16056400	1.01369100
H	-2.09357300	-1.91441900	3.46624900
H	0.17718300	-1.38286200	4.30176200
H	2.01867900	-0.94422300	2.74155700
C	1.86930500	-0.71380400	-0.02646900
H	1.65800400	-1.14171900	-0.99734500
C	3.01673900	0.03310500	0.11925300
C	3.34428100	0.87104900	1.25542800
C	4.49363900	1.59354700	1.33012400
H	2.60374000	0.94125200	2.04121000
C	5.13704700	0.79685400	-0.82687500
C	5.44755000	1.54639200	0.26318600
H	5.79264300	0.72930400	-1.68823200
H	6.37926200	2.09759300	0.29866800

C	-2.31509700	3.14158400	-0.66438200
H	-2.01765600	4.15942700	-0.39186700
H	-2.55427500	3.14477800	-1.73518700
C	-3.54225100	2.68598500	0.14269600
H	-3.36517800	2.84442300	1.21374400
H	-4.43876700	3.25150300	-0.13246100
P	-0.90238600	1.91178900	-0.43725600
P	-3.78825400	0.83344300	-0.07305200
Br	-0.92536600	-1.88946700	-1.48051500
C	3.72500800	-0.69810200	-2.13781700
H	2.82743500	-0.33357900	-2.65143500
H	4.58080100	-0.60590400	-2.80837700
H	3.57069500	-1.75481400	-1.89080100
N	3.97693100	0.07070200	-0.92759500
H	-0.15776400	2.57522800	0.57572300
H	-0.08591900	2.32562700	-1.52545400
H	-4.74985900	0.60871200	0.94520300
H	-4.69449600	0.82060700	-1.17093300
Ni	-1.79524700	-0.00386400	-0.06628500
H	4.67946400	2.22632000	2.19372600

B-Ni



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.312824 (Hartree/Particle)
Thermal correction to Energy= 0.335164
Thermal correction to Enthalpy= 0.336108
Thermal correction to Gibbs Free Energy= 0.258606
Sum of electronic and zero-point Energies= -4061.487289
Sum of electronic and thermal Energies= -4061.464949
Sum of electronic and thermal Enthalpies= -4061.464004
Sum of electronic and thermal Free Energies= -4061.541507
Electronic energy (RM06) -4064.14435644

C	-1.05639900	2.68851900	-0.99264200
C	-0.30524400	3.84264000	-1.24567800
C	1.05354600	3.85993900	-0.92826800
C	1.65194600	2.73509700	-0.36122900
C	0.91706000	1.55683500	-0.11189500
C	-0.46290200	1.55597800	-0.42804100
H	-2.11870600	2.68457000	-1.22976200
H	-0.78196200	4.71958400	-1.67757600
H	1.64578200	4.75486700	-1.10404700
H	2.69830100	2.77678800	-0.06880300
C	1.50236500	0.37432200	0.54034400
H	0.86509000	-0.06026100	1.30180300
C	2.73880800	-0.17431300	0.30206600
C	3.62627400	0.21241700	-0.78082700
C	4.82545200	-0.38845800	-0.99733500
H	3.27516200	0.99639000	-1.44070100
C	4.44976800	-1.82400400	0.87784200
C	5.27136900	-1.44596000	-0.13622500
H	4.71063800	-2.61869400	1.56867300

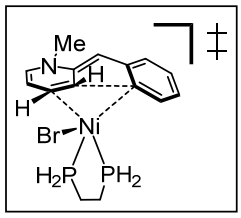
H	6.22601300	-1.93803100	-0.27705300
C	-1.41949600	-2.37053500	-2.43777200
H	-1.47832400	-2.57262800	-3.51253100
H	-0.61298100	-2.99328800	-2.03160400
C	-2.75017800	-2.69579700	-1.72971100
H	-3.58330100	-2.21345900	-2.25557600
H	-2.94580000	-3.77262800	-1.72912400
P	-0.93754900	-0.58766400	-2.08768100
P	-2.72135900	-1.96767800	0.00367200
Br	-2.07670100	0.60897600	2.11533900
C	2.42244100	-1.68914700	2.23132900
H	1.47761900	-2.12377900	1.88017500
H	2.97396300	-2.44460400	2.79385600
H	2.17922300	-0.85002400	2.89323800
N	3.23307400	-1.23270000	1.11375100
H	-1.53959600	0.11044400	-3.16067700
H	0.40749200	-0.53062400	-2.50185500
H	-4.07599200	-2.04603300	0.39379900
H	-2.23157100	-3.04725700	0.77720500
Ni	-1.51388700	-0.01914500	-0.07753600
H	5.44553900	-0.07558400	-1.83317900

ub3lyp/6-31G(d)
Zero-point correction= 0.313646 (Hartree/Particle)
Thermal correction to Energy= 0.335545
Thermal correction to Enthalpy= 0.336489
Thermal correction to Gibbs Free Energy= 0.260267
Sum of electronic and zero-point Energies= -5400.662581
Sum of electronic and thermal Energies= -5400.640682
Sum of electronic and thermal Enthalpies= -5400.639737
Sum of electronic and thermal Free Energies= -5400.715960
Electronic energy (UM06) -5403.02996675

C	-1.11319100	2.74081900	-0.81448000
C	-0.37968100	3.91843600	-0.99613600
C	0.98460100	3.92895400	-0.70696700
C	1.60250100	2.77193900	-0.23306800
C	0.87749900	1.57823900	-0.05526100
C	-0.50999900	1.56710000	-0.34833200
H	-2.17986900	2.74900200	-1.03547800
H	-0.87432900	4.81898500	-1.35269300
H	1.56534900	4.84008700	-0.83033100
H	2.65384000	2.80034500	0.04283300
C	1.47097200	0.35621800	0.51061600
H	0.84633300	-0.11489400	1.25952000
C	2.70528500	-0.18054000	0.24354500
C	3.60202400	0.26962300	-0.80547000
C	4.79911500	-0.32343100	-1.05128500
H	3.26013500	1.09783600	-1.41427000
C	4.39969700	-1.87654500	0.72282900
C	5.23095300	-1.43822400	-0.25818200
H	4.65011000	-2.71686200	1.36164300
H	6.18311100	-1.92716800	-0.42451300
C	-1.49566600	-2.12606700	-2.59214900
H	-1.62762800	-2.20875700	-3.67619700
H	-0.64887200	-2.76553100	-2.31427800
C	-2.76137800	-2.55825800	-1.82938700
H	-3.64371300	-2.06558200	-2.25588800
H	-2.92622400	-3.63840100	-1.89082900

P	-1.03529100	-0.38005300	-2.06978900
P	-2.61661000	-1.95023900	-0.06057300
Br	-1.94199700	0.40476100	2.15376800
C	2.36057100	-1.81510600	2.06556600
H	1.40366400	-2.19092000	1.68057100
H	2.88917200	-2.62899200	2.56489700
H	2.13750400	-1.02605200	2.79309100
N	3.18584600	-1.29304600	0.98822700
H	-1.69879500	0.40121800	-3.04453500
H	0.29424200	-0.28766600	-2.52355200
H	-3.94157600	-2.05895700	0.41414700
H	-2.05947300	-3.06967600	0.60359700
Ni	-1.49657600	-0.03884900	-0.05549100
H	5.42881600	0.03989000	-1.85905600

B-Ni-TS



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.310417 (Hartree/Particle)
Thermal correction to Energy= 0.332635
Thermal correction to Enthalpy= 0.333579
Thermal correction to Gibbs Free Energy= 0.256094
Sum of electronic and zero-point Energies= -4061.456474
Sum of electronic and thermal Energies= -4061.434256
Sum of electronic and thermal Enthalpies= -4061.433312
Sum of electronic and thermal Free Energies= -4061.510797
Electronic energy (RM06) -4064.10267966

C	1.85748100	1.87109600	-1.72570000
C	2.22813600	3.22080900	-1.65950100
C	2.57268100	3.79893200	-0.43303300
C	2.59372900	3.02395300	0.72793500
C	2.21339300	1.67391500	0.68177000
C	1.75059500	1.12934900	-0.54478700
H	1.57955300	1.43283500	-2.68161600
H	2.23238600	3.82100400	-2.56569800
H	2.86281400	4.84523600	-0.38928100
H	2.94310600	3.45177500	1.66503200
C	2.34715300	0.70520700	1.75956000
H	2.43499200	0.99687100	2.79983200
C	2.34222800	-0.57935800	1.30783700
C	2.34911100	-0.74044900	-0.17582500
C	1.65573300	-1.85390500	-0.73867000
H	3.25884300	-0.41164200	-0.67353700
C	1.55512500	-2.82471700	1.49664500
C	1.20764700	-2.88469100	0.19142300
H	1.31628900	-3.61747500	2.19724600
H	0.65050700	-3.73515200	-0.18045500
C	2.35717300	-1.64342900	3.50313200
H	2.36351500	-2.64452400	3.93967400
H	1.51705400	-1.07291200	3.92879000
H	3.29047200	-1.14018600	3.77399200

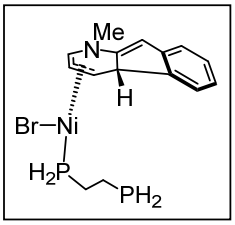
N	2.25852300	-1.74951500	2.05724900
Br	-1.27653000	-1.68748400	-1.89766900
C	-3.96704700	1.49811400	0.80139800
C	-2.79329900	0.52022400	0.67207400
H	-3.64494500	2.43695100	1.26368500
H	-4.35810200	1.74120300	-0.19377900
H	-3.09064400	-0.40795000	0.17252500
H	-2.40483100	0.23721900	1.65895800
P	-5.39591200	0.72786100	1.77004400
H	-6.14616200	1.92736400	1.94899400
H	-4.79312400	0.81657400	3.06025200
P	-1.33687300	1.15506700	-0.29432300
H	-1.05542700	2.36095900	0.40123700
H	-1.97794700	1.72838600	-1.41697600
Ni	0.33533500	-0.32300300	-0.79467100
H	1.87388500	-2.14811700	-1.76175900

ub3lyp/6-31G(d)
Zero-point correction= 0.311009 (Hartree/Particle)
Thermal correction to Energy= 0.332876
Thermal correction to Enthalpy= 0.333821
Thermal correction to Gibbs Free Energy= 0.257404
Sum of electronic and zero-point Energies= -5400.635145
Sum of electronic and thermal Energies= -5400.613277
Sum of electronic and thermal Enthalpies= -5400.612333
Sum of electronic and thermal Free Energies= -5400.688749
Electronic energy (UM06) -5402.98756556

C	2.14726900	1.69386700	-1.64209300
C	2.55396700	3.03155300	-1.57217300
C	2.73556000	3.65294800	-0.33253700
C	2.55562400	2.92970400	0.84850300
C	2.13607000	1.59478300	0.79520500
C	1.82696000	1.00675900	-0.46329100
H	2.00428300	1.22162700	-2.61127500
H	2.71943600	3.58896400	-2.49037000
H	3.05682000	4.69004600	-0.28774100
H	2.78040100	3.38555700	1.81011200
C	2.06850100	0.65875200	1.90761500
H	2.04212900	0.97564800	2.94381200
C	2.05522200	-0.63569600	1.47874900
C	2.23891400	-0.79343800	0.00355400
C	1.57936400	-1.89100600	-0.66200300
H	3.24885200	-0.56746900	-0.33678500
C	1.23056600	-2.87551300	1.55733700
C	1.05903900	-2.93895600	0.21979100
H	0.91043700	-3.67146200	2.22071400
H	0.56901500	-3.80478100	-0.20938500
C	1.71179300	-1.67300000	3.65454400
H	1.64042200	-2.66977500	4.09512200
H	0.81959600	-1.09270500	3.93701400
H	2.59456700	-1.17396200	4.06603300
N	1.84214300	-1.79209500	2.21226400
Br	-1.14273300	-1.50648300	-2.06088300
C	-3.82511800	1.59138400	0.73046500
C	-2.73254600	0.53451200	0.53281900
H	-3.45565900	2.42653000	1.33442000
H	-4.12499700	2.00033500	-0.24180500
H	-3.07653000	-0.29162800	-0.09884000

H	-2.43095200	0.09232400	1.49099800
P	-5.37783900	0.83862800	1.50134800
H	-6.03249800	2.06959200	1.80113200
H	-4.86062300	0.69809600	2.82368000
P	-1.17438500	1.15613400	-0.26541300
H	-0.86399800	2.25313600	0.57985800
H	-1.70120500	1.88835500	-1.35596300
Ni	0.41101500	-0.34906800	-0.78880900
H	1.98898200	-2.21430400	-1.61694200

C-Ni-anti



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.313105 (Hartree/Particle)
Thermal correction to Energy= 0.335442
Thermal correction to Enthalpy= 0.336386
Thermal correction to Gibbs Free Energy= 0.258039
Sum of electronic and zero-point Energies= -4061.517384
Sum of electronic and thermal Energies= -4061.495047
Sum of electronic and thermal Enthalpies= -4061.494103
Sum of electronic and thermal Free Energies= -4061.572449
Electronic energy (RM06) -4064.16495752

C	-2.29817200	2.87789500	1.06945800
C	-2.48919700	4.02806100	0.28852400
C	-2.89200600	3.91797600	-1.04599000
C	-3.10617100	2.66594500	-1.63196400
C	-2.90009900	1.51798300	-0.86227200
C	-2.49369000	1.63305300	0.48907100
H	-1.99840400	2.96824600	2.11125000
H	-2.32641100	5.00962900	0.72503700
H	-3.04240200	4.81785400	-1.63684400
H	-3.42216700	2.59076700	-2.66936600
C	-2.99574300	0.10239800	-1.21304800
H	-3.21171200	-0.26925400	-2.20730600
C	-2.67267800	-0.63563700	-0.12133900
C	-2.42884400	0.24688500	1.09430300
C	-1.19986100	-0.22171600	1.86303100
H	-3.30469100	0.14344200	1.76376000
C	-1.61244400	-2.44989100	0.98511900
C	-1.13612000	-1.64907700	2.02151600
H	-1.40519900	-3.51294800	0.96693400
H	-0.58160000	-2.12543100	2.82400100
C	-2.61933200	-2.83272300	-1.20704500
H	-1.82032600	-2.62495700	-1.92977400
H	-2.57563100	-3.88625600	-0.92350600
H	-3.59401800	-2.62901700	-1.65799000
N	-2.46256400	-2.00812100	-0.01046300
Br	1.38740700	-2.42149600	-0.76817400
C	3.14214200	0.76136500	0.24244200
C	3.90996500	1.96362700	-0.31940300
H	3.33967000	0.63174900	1.31418400

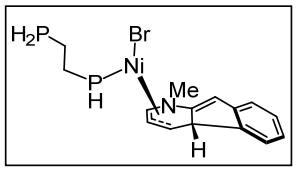
H	3.43378300	-0.17617200	-0.24344600
H	3.71790600	2.05761000	-1.39500700
H	3.57856200	2.89406300	0.15342800
P	1.29526600	0.85829000	0.06214800
H	1.03252700	2.12296000	0.64561000
H	1.16119900	1.24088200	-1.29254300
P	5.77634400	1.73747700	-0.12211900
H	6.14111100	3.07894800	-0.43980900
H	5.82680000	1.97059100	1.28438200
Ni	0.18906300	-0.94250400	0.63767500
H	-0.88472400	0.40326700	2.69659000

ub3lyp/6-31G(d)
Zero-point correction= 0.313795 (Hartree/Particle)
Thermal correction to Energy= 0.335769
Thermal correction to Enthalpy= 0.336713
Thermal correction to Gibbs Free Energy= 0.259137
Sum of electronic and zero-point Energies= -5400.691070
Sum of electronic and thermal Energies= -5400.669096
Sum of electronic and thermal Enthalpies= -5400.668152
Sum of electronic and thermal Free Energies= -5400.745728
Electronic energy (UM06) -5403.04952581

C	-2.40623900	2.77912000	1.11984300
C	-2.61463900	3.95561600	0.38360400
C	-2.95045600	3.88903400	-0.97126100
C	-3.07879700	2.65736100	-1.62235200
C	-2.85451600	1.48432600	-0.89750500
C	-2.51726400	1.55568700	0.47631600
H	-2.16017300	2.83349100	2.17825100
H	-2.51822100	4.92187100	0.87104300
H	-3.11576500	4.80770300	-1.52850800
H	-3.34303500	2.61762200	-2.67614400
C	-2.86198600	0.08386200	-1.31644700
H	-3.00588700	-0.24985900	-2.33679300
C	-2.54934600	-0.68959000	-0.24516400
C	-2.42129100	0.14648300	1.02058500
C	-1.21753000	-0.30510100	1.83687300
H	-3.32468800	-0.03403200	1.63177600
C	-1.38108800	-2.46743000	0.83068500
C	-1.12301200	-1.72593900	1.99180800
H	-1.14311300	-3.52330700	0.79699400
H	-0.63051500	-2.20881300	2.83115000
C	-2.30832100	-2.81920800	-1.41210600
H	-1.49978300	-2.51991300	-2.09201100
H	-2.19568900	-3.87970700	-1.17758500
H	-3.27526800	-2.66687100	-1.89937200
N	-2.27580800	-2.04995500	-0.17193500
Br	1.48497700	-2.36597600	-0.68205800
C	3.04044800	0.81984700	0.21019100
C	3.67693600	2.14304800	-0.22850600
H	3.35408200	0.54724800	1.22591200
H	3.33522300	-0.01426200	-0.43559400
H	3.35635600	2.39168400	-1.24741900
H	3.35671600	2.96362800	0.42185300
P	1.18467800	0.81154400	0.22211500
H	0.92064400	1.98274300	0.97228200
H	0.88755100	1.33341200	-1.05825900

P	5.56201400	2.01412900	-0.27329100
H	5.82261800	3.41042900	-0.39890700
H	5.76648700	2.01936800	1.13845800
Ni	0.16124300	-1.04710700	0.67427400
H	-0.94366100	0.31760600	2.68706000

C-Ni-syn



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.312495 (Hartree/Particle)
Thermal correction to Energy= 0.334935
Thermal correction to Enthalpy= 0.335879
Thermal correction to Gibbs Free Energy= 0.257283
Sum of electronic and zero-point Energies= -4061.508153
Sum of electronic and thermal Energies= -4061.485713
Sum of electronic and thermal Enthalpies= -4061.484769
Sum of electronic and thermal Free Energies= -4061.563365
Electronic energy (RM06) -4064.15594113

C	-4.08781300	-1.85001000	0.30999500
C	-5.46622900	-2.06944200	0.16535000
C	-6.30673100	-1.03683200	-0.26020600
C	-5.79724900	0.23469200	-0.54585500
C	-4.42823300	0.46268200	-0.38807700
C	-3.58256300	-0.58732100	0.04347900
H	-3.43343400	-2.65909700	0.62574300
H	-5.88088100	-3.05007900	0.38175800
H	-7.37172000	-1.22369300	-0.37232100
H	-6.45916300	1.03094300	-0.87749200
C	-3.63380000	1.67992900	-0.55563500
H	-4.04395700	2.65247200	-0.80188800
C	-2.34199800	1.39732200	-0.25368100
C	-2.15139700	-0.08141000	0.02981400
C	-1.23622700	-0.29809600	1.22950500
H	-1.66993300	-0.53874700	-0.85160800
C	-0.35400800	1.91239400	0.94183700
C	-0.61389500	0.81905900	1.81270100
H	0.26734400	2.73981700	1.26733800
H	-0.09347200	0.75467700	2.76377400
C	-1.35655200	3.62622500	-0.52346600
H	-2.02703400	4.20353000	0.13158300
H	-0.36650700	4.08939900	-0.51331900
H	-1.74755600	3.66318600	-1.54388200
N	-1.24602800	2.23769300	-0.10233600
Br	1.07077700	-2.04637200	-0.39427000
C	4.07112800	0.11389000	0.15660300
C	5.35591900	0.51840100	-0.57498100
H	4.13484700	0.34550900	1.22755500
H	3.87639700	-0.96110700	0.07826100
H	5.27719000	0.25407100	-1.63632000
H	5.51418600	1.60046200	-0.51836500
P	2.52059400	0.93132100	-0.46149300
H	2.90126300	2.30034700	-0.38819400

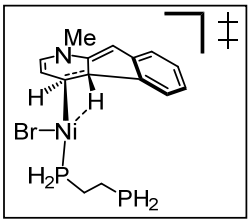
H	2.65905500	0.78110700	-1.86011000
P	6.85160500	-0.41768600	0.10411300
H	7.84737500	0.36486800	-0.55095000
H	6.96615000	0.31101800	1.32536200
Ni	0.61432600	0.13495000	0.38174200
H	-1.31136900	-1.23151800	1.77649300

ub3lyp/6-31G(d)
Zero-point correction= 0.313587 (Hartree/Particle)
Thermal correction to Energy= 0.335515
Thermal correction to Enthalpy= 0.336459
Thermal correction to Gibbs Free Energy= 0.259008
Sum of electronic and zero-point Energies= -5400.683859
Sum of electronic and thermal Energies= -5400.661931
Sum of electronic and thermal Enthalpies= -5400.660987
Sum of electronic and thermal Free Energies= -5400.738437
Electronic energy (UM06) -5403.038739

C	-4.06875100	-1.82499800	0.24547300
C	-5.45310200	-2.01783500	0.12387000
C	-6.28268600	-0.95985000	-0.25662200
C	-5.75579200	0.30901200	-0.52050500
C	-4.38003700	0.50840800	-0.38713600
C	-3.54475200	-0.56612300	0.00047800
H	-3.42284500	-2.65335700	0.52727700
H	-5.88043100	-2.99671900	0.32310600
H	-7.35319700	-1.12434300	-0.35081700
H	-6.40981300	1.12547500	-0.81702800
C	-3.56612300	1.71308400	-0.54426500
H	-3.96184400	2.69877000	-0.75943200
C	-2.27300600	1.39908000	-0.27993900
C	-2.10711700	-0.08641200	-0.01717300
C	-1.21037900	-0.33037400	1.19487100
H	-1.63138700	-0.54131000	-0.90194600
C	-0.24644900	1.81963600	0.88572000
C	-0.59153500	0.77800700	1.80205700
H	0.37568700	2.63858300	1.23433700
H	-0.12854900	0.72396600	2.78386300
C	-1.28022600	3.62422300	-0.44848300
H	-1.91221600	4.15124000	0.28374500
H	-0.28857500	4.08429900	-0.45610500
H	-1.72373800	3.74151400	-1.44105500
N	-1.15487700	2.20765400	-0.14375700
Br	1.03610500	-2.03644200	-0.36454600
C	4.02850700	0.07314000	0.14596900
C	5.29116100	0.55899200	-0.57390000
H	4.09524100	0.24976600	1.22709100
H	3.87035300	-1.00250700	0.01311000
H	5.20820600	0.35448400	-1.64798100
H	5.41567200	1.64049000	-0.45638200
P	2.45072800	0.87371300	-0.41712000
H	2.80356500	2.24542700	-0.29459000
H	2.57109100	0.77578000	-1.82234900
P	6.82277100	-0.36730400	0.03461000
H	7.78648400	0.48348900	-0.58185600
H	6.92769700	0.29044500	1.29615100

Ni	0.58422200	0.09309100	0.40617000
H	-1.33994600	-1.25420800	1.74866600

C-Ni-TS



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.307731 (Hartree/Particle)
Thermal correction to Energy= 0.330087
Thermal correction to Enthalpy= 0.331031
Thermal correction to Gibbs Free Energy= 0.252751
Sum of electronic and zero-point Energies= -4061.493950
Sum of electronic and thermal Energies= -4061.471594
Sum of electronic and thermal Enthalpies= -4061.470650
Sum of electronic and thermal Free Energies= -4061.548930
Electronic energy (RM06) -4064.13629103

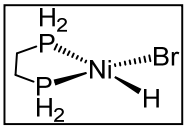
C	-1.32816500	2.15404400	-1.60688800
C	-1.61649500	3.51424600	-1.73872600
C	-2.57010900	4.12013800	-0.90514900
C	-3.25698100	3.38901500	0.06388100
C	-2.98741200	2.01993100	0.19984900
C	-2.01571200	1.41699600	-0.64589000
H	-0.58004900	1.68056300	-2.23812700
H	-1.09890800	4.10666300	-2.48760100
H	-2.77734900	5.18145000	-1.01765400
H	-3.99338900	3.87408500	0.69962800
C	-3.56337100	1.01475800	1.07735200
H	-4.35934000	1.19353900	1.78881000
C	-2.96822000	-0.18422800	0.79496200
C	-1.91977400	-0.00601400	-0.26267000
C	-1.56483300	-1.13835400	-1.06190200
H	-0.79111400	0.04968700	0.82172100
C	-2.67105700	-2.54303100	0.60786600
C	-1.92173000	-2.43142500	-0.52812100
H	-2.91439000	-3.50564700	1.04273900
H	-1.56138100	-3.32834000	-1.01687200
C	-4.19077000	-1.62632400	2.33100300
H	-5.19164800	-1.32669200	1.99456900
H	-4.21582100	-2.67385700	2.63639600
H	-3.91306500	-1.00846100	3.19186400
N	-3.21674400	-1.45473700	1.26298600
Br	1.56595700	-1.84764500	-1.59882400
C	3.20324000	0.65201700	0.64561800
C	4.44649800	0.74253200	1.53751300
H	3.42600200	0.18537800	-0.32004100
H	2.79385500	1.64691800	0.43073800
H	4.18922200	1.18423600	2.50798800
H	4.85314500	-0.25572900	1.72875400
P	1.80905300	-0.35473000	1.34563400
H	2.48045000	-1.50926300	1.80652400
H	1.62083900	0.27697600	2.60111800
P	5.75481200	1.86659500	0.76384600

H	6.82109200	1.51166500	1.64086600
H	6.17602400	0.96440200	-0.25525800
Ni	0.14671000	-0.77183100	-0.03688700
H	-1.27196700	-1.02934900	-2.09975800

ub3lyp/6-31G(d)
Zero-point correction= 0.308878 (Hartree/Particle)
Thermal correction to Energy= 0.330296
Thermal correction to Enthalpy= 0.331240
Thermal correction to Gibbs Free Energy= 0.257651
Sum of electronic and zero-point Energies= -5400.657737
Sum of electronic and thermal Energies= -5400.636320
Sum of electronic and thermal Enthalpies= -5400.635375
Sum of electronic and thermal Free Energies= -5400.708964
Electronic energy (UM06) -5403.02018321

C	1.89420800	-2.19224500	-0.70063400
C	2.85354200	-3.16810400	-0.41610600
C	4.01340800	-2.83520500	0.29852100
C	4.24245100	-1.52979900	0.73274400
C	3.29676400	-0.53892600	0.43761200
C	2.12437500	-0.88243000	-0.28769100
H	0.98242700	-2.45465800	-1.23184500
H	2.69574200	-4.19135100	-0.74518600
H	4.74525900	-3.60818000	0.52028100
H	5.14483100	-1.28436500	1.28757100
C	3.29395800	0.88669100	0.71595000
H	4.10827700	1.42803200	1.18082000
C	2.15457900	1.42191600	0.18426400
C	1.29016700	0.34121300	-0.40441200
C	0.42685900	0.72459800	-1.49355700
H	0.39705300	0.31490900	0.82932900
C	0.85025700	3.07324600	-0.94250300
C	0.23392400	2.14383700	-1.71584700
H	0.66846800	4.13648000	-1.05252200
H	-0.46606000	2.46917200	-2.47755000
C	2.62564000	3.76750500	0.62370500
H	3.61235000	3.78929400	0.14038200
H	2.14935300	4.74307400	0.50676200
H	2.76624600	3.56698700	1.69064700
N	1.77574600	2.74117200	0.03990200
C	-2.69140100	-0.75828500	2.53207300
C	-3.48916500	0.29264700	1.73743400
H	-3.35295000	-1.53592400	2.92717000
H	-2.19758100	-0.28484800	3.38981600
H	-4.07300400	-0.19573000	0.95112400
H	-4.18416100	0.82354500	2.39515900
P	-1.32166500	-1.50762400	1.48912600
H	-0.47783300	-1.99094300	2.51772800
H	-1.88125400	-2.73634300	1.07652600
P	-2.32833400	1.48330200	0.86098600
H	-3.26003500	2.16604100	0.04302500
H	-2.22068000	2.47775900	1.87728300
Br	-2.32641500	-0.86534000	-1.58448200
Ni	-0.72926400	-0.02484800	-0.04934200
H	0.28981100	0.04634600	-2.32838000

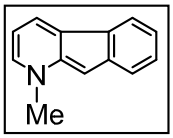
D-Ni: LNiHBr



rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.103664 (Hartree/Particle)
Thermal correction to Energy= 0.113467
Thermal correction to Enthalpy= 0.114411
Thermal correction to Gibbs Free Energy= 0.066909
Sum of electronic and zero-point Energies= -3504.969093
Sum of electronic and thermal Energies= -3504.959290
Sum of electronic and thermal Enthalpies= -3504.958345
Sum of electronic and thermal Free Energies= -3505.005848
Electronic energy (RM06) -3507.68181984

C	-2.60890100	1.29644500	-0.28723800
H	-3.21888100	2.12014000	0.09594900
H	-2.72717200	1.28121100	-1.37741800
C	-3.06221600	-0.04906600	0.31287200
H	-3.12184500	0.02617800	1.40543400
H	-4.05472900	-0.33515100	-0.04997500
P	-0.77711600	1.55060600	0.04838100
P	-1.78478000	-1.37821200	-0.05152400
H	-0.79368300	2.26754900	1.26865900
H	-0.45974300	2.62865500	-0.80688200
H	-2.17671600	-2.42246300	0.81355800
H	-2.24579500	-1.93249900	-1.26902300
H	0.65862900	-1.93098800	-0.06208300
Br	2.42461900	0.08609600	0.01026400
Ni	0.20476500	-0.52807700	-0.01729000

D-Ni: Product

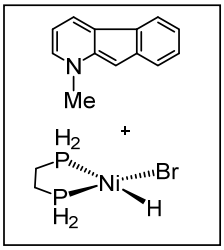


rb3lyp/6-31G(d)/Ni: lanl2dz
Zero-point correction= 0.204921 (Hartree/Particle)
Thermal correction to Energy= 0.215345
Thermal correction to Enthalpy= 0.216289
Thermal correction to Gibbs Free Energy= 0.169151
Sum of electronic and zero-point Energies= -556.544879
Sum of electronic and thermal Energies= -556.534455
Sum of electronic and thermal Enthalpies= -556.533511
Sum of electronic and thermal Free Energies= -556.580649
Electronic energy (RM06) -556.46886803

C	2.22153200	1.37914500	0.00005600
C	3.49643600	0.82080500	0.00017200
C	3.65850200	-0.57745900	0.00011300
C	2.56167500	-1.43403800	-0.00003000
C	1.26675800	-0.89065500	-0.00018800
C	1.10737500	0.53323200	-0.00019000
H	2.09653300	2.46001600	0.00002600
H	4.37142000	1.46499000	0.00028500
H	4.66233500	-0.99580900	0.00025500
H	2.70713800	-2.51180600	-0.00007100

C	-0.03328800	-1.52301800	-0.00007400
H	-0.21391100	-2.58986800	0.00005300
C	-0.96694300	-0.51132400	-0.00025600
C	-0.31316500	0.80183000	-0.00014600
C	-1.07247100	1.94233300	0.00007600
C	-3.08131000	0.59419400	-0.00002200
C	-2.49075800	1.83287600	0.00011100
H	-4.15744200	0.46279200	-0.00006300
H	-3.11966900	2.71546300	0.00015900
C	-2.99268600	-1.86769400	0.00034800
H	-2.69005400	-2.43159200	0.88989900
H	-4.07706100	-1.74562900	-0.00034900
H	-2.68908900	-2.43287800	-0.88803300
N	-2.35021300	-0.56036100	-0.00030600
H	-0.60864700	2.92548600	0.00015500

D-Ni



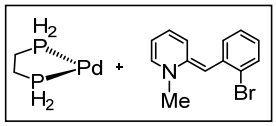
ub3lyp/6-31G(d)
Zero-point correction= 0.309921 (Hartree/Particle)
Thermal correction to Energy= 0.332412
Thermal correction to Enthalpy= 0.333357
Thermal correction to Gibbs Free Energy= 0.237631
Sum of electronic and zero-point Energies= -5400.662291
Sum of electronic and thermal Energies= -5400.639800
Sum of electronic and thermal Enthalpies= -5400.638856
Sum of electronic and thermal Free Energies= -5400.734581
Electronic energy (UM06) -5403.03970515

C	-28.64258100	1.68589500	0.01057000
C	-28.77307700	3.06745800	0.11747900
C	-30.04766300	3.65196000	0.24132100
C	-31.20233400	2.87529900	0.26038400
C	-31.09224800	1.47936600	0.15374300
C	-29.79257900	0.88945700	0.02812300
H	-27.65727100	1.23426900	-0.08512600
H	-27.88906000	3.69907300	0.10544500
H	-30.13051800	4.73320800	0.32367000
H	-32.17823700	3.34547700	0.35705800
C	-32.09782100	0.44077400	0.14505100
H	-33.16535500	0.59833200	0.22484100
C	-31.43093400	-0.75684400	0.01750500
C	-29.98193000	-0.54110300	-0.06084100
C	-29.13849500	-1.61308300	-0.19081900
C	-31.04449800	-3.10337800	-0.17273600
C	-29.68600700	-2.92494300	-0.24794500
H	-31.50529900	-4.08385900	-0.21191500
H	-29.04627100	-3.79372100	-0.35029900
C	-33.34994900	-2.25947400	0.03530700
H	-33.84657900	-1.73507900	-0.78883400
H	-33.57468200	-3.32565400	-0.02516400
H	-33.73279500	-1.85948600	0.98098400
N	-31.91001600	-2.05390500	-0.04286300

H	-28.06171200	-1.47609400	-0.25044300
C	28.32781900	0.26231700	1.35159800
H	29.24461800	0.85925300	1.33071200
H	28.02596800	0.15758000	2.40059600
C	28.54136300	-1.12638500	0.72297700
H	29.06326400	-1.03095600	-0.23682900
H	29.14524000	-1.77612800	1.36441000
P	26.90413700	1.11451100	0.47411300
P	26.86547500	-1.87996700	0.33662400
H	27.56773600	1.88696300	-0.50714400
H	26.56971700	2.13549800	1.38897500
H	27.21064500	-2.89982300	-0.57610500
H	26.61354200	-2.68007600	1.47764500
H	24.68462000	-1.59038400	-0.53411600
Br	23.78238900	0.93753400	-0.80492100
Ni	25.48465600	-0.41131500	-0.16240900

Pd species from Schemes S2.2 and S2.3

A’



Zero-point correction= 0.311590 (Hartree/Particle)
Thermal correction to Energy= 0.334886
Thermal correction to Enthalpy= 0.335830
Thermal correction to Gibbs Free Energy= 0.240333
Sum of electronic and zero-point Energies= -4018.897901
Sum of electronic and thermal Energies= -4018.874605
Sum of electronic and thermal Enthalpies= -4018.873661 Sum of electronic and thermal Free Energies= -4018.969158
Electronic energy (RM06) -4021.50974327

C	0.07805500	3.06288700	-0.95937100
C	-0.90658500	3.98006800	-1.32673500
C	-2.20318100	3.52329700	-1.57073300
C	-2.50718900	2.17214600	-1.43962700
C	-1.54931200	1.21110800	-1.03489100
C	-0.24544100	1.71617400	-0.81959800
H	1.09572200	3.38890000	-0.77356100
H	-0.65600200	5.03176400	-1.43047600
H	-2.97748500	4.21777100	-1.88622400
H	-3.50502600	1.82815800	-1.69244100
C	-1.85087400	-0.21135500	-0.92641500
H	-1.02697200	-0.86380400	-1.18110000
C	-3.02369900	-0.77906700	-0.48368800
C	-4.12092300	-0.06445000	0.13928500
C	-5.24895600	-0.68673300	0.57455400
H	-3.99019800	0.99891400	0.29291000
C	-4.36170100	-2.79108500	-0.12278400
C	-5.39664100	-2.10322000	0.42709500
H	-4.38303100	-3.86814100	-0.24693000
H	-6.28633500	-2.62642300	0.75535300
Pd	15.20412900	-3.68032800	31.49824100
C	15.87873400	-3.80771500	34.61811000
H	16.18599300	-3.32828500	35.55453000
H	15.13514700	-4.57224500	34.87563400

C	17.09850800	-4.46982700	33.94640400
H	17.87174600	-3.71599600	33.75266600
H	17.53520300	-5.21422000	34.62190300
P	14.98354800	-2.56423700	33.50582100
P	16.70500300	-5.25484400	32.26880300
Br	1.17986000	0.53298000	-0.29903800
C	-2.15568200	-3.00127000	-1.14139400
H	-1.24403900	-2.95157300	-0.53422400
H	-2.49041100	-4.03850900	-1.19330800
H	-1.91556000	-2.64840900	-2.15115400
N	-3.21147300	-2.18299000	-0.56191500
H	15.75627800	-1.40526800	33.79976100
H	13.93326500	-2.23871600	34.41341200
H	18.02937000	-5.68180900	31.95798300
H	16.27142400	-6.53431300	32.71779100
H	-6.03216100	-0.10942500	1.05813300

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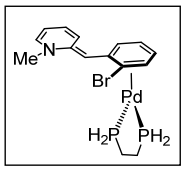

Zero-point correction= 0.310802 (Hartree/Particle)
Thermal correction to Energy= 0.333785
Thermal correction to Enthalpy= 0.334729
Thermal correction to Gibbs Free Energy= 0.254496
Sum of electronic and zero-point Energies= -4018.910105
Sum of electronic and thermal Energies= -4018.887122
Sum of electronic and thermal Enthalpies= -4018.886177
Sum of electronic and thermal Free Energies= -4018.966411
Electronic energy (RM06) -4021.53443461

C	1.24002400	1.74447500	-1.42276900
C	0.60556100	2.99391600	-1.21703700
C	-0.76846200	3.04818200	-1.06236800
C	-1.54148600	1.87547700	-1.10710500
C	-0.98082500	0.60215800	-1.28487600
C	0.45175200	0.56566600	-1.42814800
H	2.26757100	1.70714400	-1.76604200
H	1.20580900	3.89933900	-1.22498300
H	-1.26614600	4.00682800	-0.94066900
H	-2.62237200	1.95794100	-1.05204400
C	-1.77887100	-0.61202300	-1.38490600
H	-1.38119800	-1.35576600	-2.06173400
C	-2.91768300	-0.91337700	-0.67383400
C	-3.43755100	-0.14829500	0.44345200
C	-4.56323100	-0.50501200	1.11730200
H	-2.86122900	0.71325600	0.75557900
C	-4.79991900	-2.42366600	-0.28613900
C	-5.29481700	-1.67640800	0.73502100
H	-5.27917500	-3.33711500	-0.62092900
H	-6.20177300	-1.98012200	1.24337900
Pd	1.52188600	0.59078600	0.62043700
C	2.19292800	-1.05578600	3.48466600
H	1.85457400	-1.50066900	4.42658800
H	2.97025200	-1.71385500	3.07569000
C	2.77569000	0.34602300	3.73637400
H	2.02890600	0.97745300	4.23448300

H	3.64365600	0.28387700	4.40158200
P	0.80100100	-1.02800300	2.20992700
P	3.22181000	1.22585900	2.12602100
Br	1.29701300	-1.01665500	-2.21448300
C	-3.20211100	-2.94829800	-2.05322900
H	-2.21794600	-3.37438600	-1.82376900
H	-3.91647200	-3.76125500	-2.19342300
H	-3.11806100	-2.37644000	-2.98495500
N	-3.65951200	-2.08651800	-0.97347300
H	-0.29196600	-0.77534800	3.08655700
H	0.58002200	-2.43242500	2.13747400
H	3.62910200	2.46736500	2.69365900
H	4.54388800	0.72532700	1.96173100
H	-4.89811500	0.08871200	1.96351700

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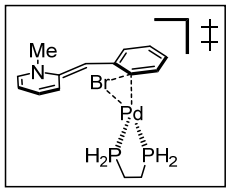
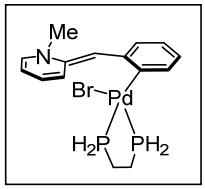


Zero-point correction= 0.310274 (Hartree/Particle)
Thermal correction to Energy= 0.332765
Thermal correction to Enthalpy= 0.333709
Thermal correction to Gibbs Free Energy= 0.254956
Sum of electronic and zero-point Energies= -4018.898072
Sum of electronic and thermal Energies= -4018.875580
Sum of electronic and thermal Enthalpies= -4018.874636
Sum of electronic and thermal Free Energies= -4018.953389
Electronic energy (RM06) -4021.52040836

C	0.70306800	2.53820100	-1.25644200
C	-0.12682500	3.66549600	-1.20907800
C	-1.50670600	3.49233400	-1.12769100
C	-2.05642100	2.20802200	-1.07778300
C	-1.26667000	1.04012300	-1.06079200
C	0.14243300	1.26130600	-1.10980400
H	1.77124700	2.64367500	-1.41604800
H	0.30791700	4.65850300	-1.28548000
H	-2.16826100	4.35447900	-1.14759800
H	-3.13689700	2.10027100	-1.08981200
C	-1.80394000	-0.31085100	-1.03335800
H	-1.17704600	-1.03427800	-1.53780600
C	-2.95226400	-0.75104500	-0.41596200
C	-3.76664900	0.02016800	0.50377400
C	-4.87886100	-0.48429800	1.10223000
H	-3.42705300	1.02079600	0.73786700
C	-4.52899800	-2.57297800	-0.00247600
C	-5.29951400	-1.82682200	0.83255400
H	-4.76584500	-3.60422800	-0.24075500
H	-6.18793300	-2.25320900	1.28203900
Pd	1.47449000	0.45032500	0.35402300
C	1.41797300	-0.95574100	3.47818600
H	1.00391100	-1.01371200	4.49033700
H	1.61450700	-1.98405900	3.14931100
C	2.72788400	-0.14854700	3.48520100
H	2.54502000	0.85580100	3.88749400

H	3.47005500	-0.62756500	4.13255900
P	0.15343800	-0.24592500	2.27245500
P	3.40272200	0.09763300	1.74531400
Br	1.37496100	-0.25754600	-2.20931800
C	-2.63565800	-2.95901200	-1.49120100
H	-1.62683300	-3.13177600	-1.09742800
H	-3.15015000	-3.91693800	-1.58373400
H	-2.54003600	-2.50192800	-2.48284700
N	-3.39710900	-2.08750600	-0.60776500
H	-0.46931800	0.70091600	3.13320300
H	-0.84977000	-1.24003100	2.43398200
H	4.46886200	0.98461000	2.05303700
H	4.21464000	-1.06331400	1.63294400
H	-5.44033900	0.12743100	1.80316200

B

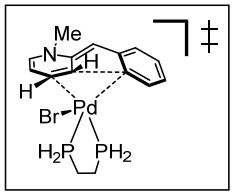


Zero-point correction= 0.312531 (Hartree/Particle)
Thermal correction to Energy= 0.335117
Thermal correction to Enthalpy= 0.336062
Thermal correction to Gibbs Free Energy= 0.257363
Sum of electronic and zero-point Energies= -4018.937821
Sum of electronic and thermal Energies= -4018.915235
Sum of electronic and thermal Enthalpies= -4018.914291
Sum of electronic and thermal Free Energies= -4018.992989
Electronic energy (RM06) -4021.56804238

C	0.28240200	3.02432100	-0.93834500
C	-0.67866600	3.99111400	-1.26049100
C	-2.00460800	3.60203900	-1.45048200
C	-2.36331900	2.26062600	-1.32553100
C	-1.41830900	1.26781500	-0.98560800
C	-0.07942800	1.68386900	-0.80536900
H	1.31842200	3.32575400	-0.80350100
H	-0.38629400	5.03283200	-1.36890300
H	-2.75867300	4.33842300	-1.71789900
H	-3.38749800	1.96083800	-1.53208300
C	-1.75722200	-0.16134200	-0.91004500
H	-1.01637800	-0.80558400	-1.36783300
C	-2.88622500	-0.71707700	-0.36207600
C	-3.88255800	0.00440400	0.41084500
C	-4.96948900	-0.60179000	0.95570600
H	-3.70763400	1.06246700	0.56279900
C	-4.24808900	-2.70189700	0.06883500
C	-5.17920800	-2.00996400	0.77641400
H	-4.32833400	-3.77001600	-0.10305900
H	-6.04135400	-2.52009800	1.18842700
Pd	1.35078400	0.31052100	-0.27665600
C	1.66347400	-0.46347100	3.02403500
H	1.72401400	-0.09713000	4.05441200
H	0.99916500	-1.33630300	3.02695200
C	3.05813300	-0.85711300	2.49768500
H	3.75247800	-0.01561300	2.61158600
H	3.46486500	-1.69350300	3.07484500

P	0.85721500	0.80478300	1.90311300
P	2.99100500	-1.24128600	0.65813000
Br	1.80021600	-0.25854700	-2.67701700
C	-2.19584800	-2.92659300	-1.23475400
H	-1.21038900	-2.92880000	-0.75151500
H	-2.56785800	-3.95120400	-1.29069700
H	-2.07015100	-2.53075800	-2.24915100
N	-3.13956800	-2.11176400	-0.48574500
H	1.30649500	2.03021400	2.44862500
H	-0.47380800	0.83555300	2.36703000
H	4.36498200	-1.30908300	0.33303900
H	2.72894500	-2.63301500	0.66353100
H	-5.67766600	-0.02101400	1.54074400

B TS

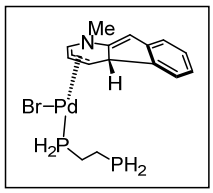


Zero-point correction= 0.310421 (Hartree/Particle)
Thermal correction to Energy= 0.332788
Thermal correction to Enthalpy= 0.333732
Thermal correction to Gibbs Free Energy= 0.255726
Sum of electronic and zero-point Energies= -4018.896292
Sum of electronic and thermal Energies= -4018.873925
Sum of electronic and thermal Enthalpies= -4018.872981
Sum of electronic and thermal Free Energies= -4018.950987
Electronic energy (RM06) -4021.52105763

C	-0.42637600	2.24816000	0.06925600
C	-0.50792200	3.56518400	0.53485100
C	0.59493300	4.16748600	1.14914900
C	1.79867100	3.47554500	1.26063800
C	1.89710000	2.14882600	0.80778000
C	0.73842300	1.51611600	0.30013300
H	-1.29953500	1.78181700	-0.37728500
H	-1.44535500	4.10736900	0.44370700
H	0.52365300	5.19011500	1.50953100
H	2.68166900	3.97032700	1.65860000
C	3.13668200	1.40079800	0.69148000
H	4.01813900	1.65660500	1.26784000
C	3.06042900	0.36374300	-0.18211500
C	1.79473300	0.24810600	-0.95492500
C	1.33618300	-1.06604400	-1.30618300
H	1.59452300	1.04984300	-1.66015800
C	3.56972300	-1.90358500	-0.77301400
C	2.30377700	-2.15735900	-1.17575800
H	4.33179600	-2.67524300	-0.74840500
H	2.03638000	-3.15959500	-1.49092900
C	5.30235600	-0.50323800	0.27202100
H	5.76098200	0.44805000	-0.01599000
H	5.95869800	-1.31635600	-0.04547400
H	5.20676100	-0.52685800	1.36771500
N	4.01060900	-0.64478700	-0.37910500
Br	-0.90857100	-0.18709200	2.78267600
C	-3.01216300	-4.33341200	1.34040100
C	-2.52792100	-2.94048900	0.91993900

H	-2.64080800	-5.10207600	0.65437000
H	-2.62775200	-4.57128900	2.33927600
H	-2.83863000	-2.16818000	1.63118700
H	-2.93129400	-2.65782100	-0.06089800
P	-4.89818900	-4.39377300	1.45790400
H	-5.01174500	-5.81050500	1.57444800
H	-5.15275800	-4.40815700	0.05407300
P	-0.68317300	-2.77199000	0.79601200
H	-0.38187600	-3.82169700	-0.11486300
H	-0.24559700	-3.40722100	1.97666000
Pd	0.21269200	-0.63068700	0.49424700
H	0.61489100	-1.14368300	-2.11852000

C-anti

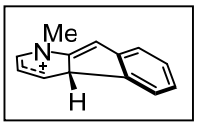


Zero-point correction= 0.313591 (Hartree/Particle)
Thermal correction to Energy= 0.335423
Thermal correction to Enthalpy= 0.336367
Thermal correction to Gibbs Free Energy= 0.260643
Sum of electronic and zero-point Energies= -4018.957186
Sum of electronic and thermal Energies= -4018.935353
Sum of electronic and thermal Enthalpies= -4018.934409
Sum of electronic and thermal Free Energies= -4019.010133
Electronic energy (RM06) -4021.59093412

C	0.57867300	2.05648900	-1.50664800
C	0.74436600	3.35867600	-1.00998400
C	1.83553600	3.66958800	-0.19223100
C	2.77623900	2.69408600	0.15628800
C	2.60913500	1.39098400	-0.32525100
C	1.50558400	1.08370200	-1.16168800
H	-0.26707700	1.81558800	-2.14598500
H	0.02130000	4.12870200	-1.26448000
H	1.95561400	4.68439000	0.17935400
H	3.62116500	2.94788500	0.79236700
C	3.37946600	0.17396000	-0.08103300
H	4.25368600	0.11534300	0.55715800
C	2.78491300	-0.85394400	-0.75427700
C	1.61991100	-0.36060400	-1.59469200
C	0.43426500	-1.32216200	-1.61175400
H	1.99650200	-0.35013500	-2.63772900
C	2.14834800	-3.08587300	-1.30819400
C	0.90085300	-2.71132100	-1.68928700
H	2.48803100	-4.11449300	-1.36377200
H	0.21808000	-3.46916900	-2.05845400
C	4.29282200	-2.67210500	-0.13182100
H	4.19247000	-2.61592900	0.96225600
H	4.47481300	-3.71189600	-0.41280800
H	5.15798100	-2.06941400	-0.42903600
N	3.10048000	-2.19067100	-0.80645100
Br	-2.76299300	-2.02044200	-1.70577700
C	-0.63911400	-0.39152000	3.24320000
C	-1.77348900	-1.41982700	3.40184400

H	-0.02298200	-0.34454900	4.14771900
H	-1.05653700	0.61011400	3.08203900
H	-1.35973600	-2.39478000	3.68767700
H	-2.46614300	-1.11504600	4.19289800
P	0.42978000	-0.75044000	1.74232900
H	1.29556800	0.35986400	1.75900900
H	1.31787400	-1.72140600	2.26655400
P	-2.63769400	-1.66429500	1.75465300
H	-3.41789400	-2.81751300	1.99784300
H	-3.67736400	-0.70736300	1.81961500
Pd	-0.96782900	-1.40844800	0.00756200
H	-0.28140400	-1.06721100	-2.39175600

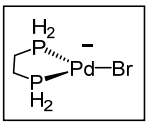
C': allyl cation



Zero-point correction= 0.217297 (Hartree/Particle)
Thermal correction to Energy= 0.227973
Thermal correction to Enthalpy= 0.228918
Thermal correction to Gibbs Free Energy= 0.181054
Sum of electronic and zero-point Energies= -556.886908
Sum of electronic and thermal Energies= -556.876232
Sum of electronic and thermal Enthalpies= -556.875288
Sum of electronic and thermal Free Energies= -556.923151
Electronic energy (RM06) -556.88129527

C	-2.26770600	1.33078100	0.23898600
C	-3.51964700	0.74177500	0.01444200
C	-3.64232100	-0.63496500	-0.22031600
C	-2.51808700	-1.45785300	-0.24689500
C	-1.26208700	-0.87268000	-0.04370400
C	-1.14501000	0.52013800	0.19364300
H	-2.19347900	2.39766200	0.43105800
H	-4.40947600	1.36372900	0.02150300
H	-4.62641600	-1.06398600	-0.38058300
H	-2.61515000	-2.52591900	-0.41739000
C	0.05953200	-1.47100200	-0.05694300
H	0.25697500	-2.51980000	-0.24708300
C	0.97662200	-0.49461500	0.17488900
C	0.31363300	0.83585600	0.46206700
C	1.06754300	1.95711400	-0.18770500
H	0.37015500	1.04038600	1.55203900
C	3.04691100	0.55773200	-0.15754900
C	2.40000800	1.81422200	-0.39391400
H	4.12529500	0.46428600	-0.22430200
H	3.01582100	2.63240200	-0.75085200
C	3.04205500	-1.86781300	0.12818100
H	2.74902000	-2.45264400	-0.74743600
H	4.12148400	-1.71878600	0.12039400
H	2.74357700	-2.38945600	1.03928400
N	2.36944300	-0.55407700	0.08154500
H	0.56743100	2.89852600	-0.39853000

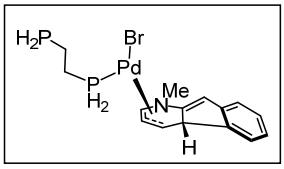
C': anion



Zero-point correction= 0.092931 (Hartree/Particle)
Thermal correction to Energy= 0.103122
Thermal correction to Enthalpy= 0.104067
Thermal correction to Gibbs Free Energy= 0.053845
Sum of electronic and zero-point Energies= -3461.902898
Sum of electronic and thermal Energies= -3461.892707
Sum of electronic and thermal Enthalpies= -3461.891763
Sum of electronic and thermal Free Energies= -3461.941985
Electronic energy (RM06) -3464.64779574

C	-3.10034500	-0.70374900	0.30675000
H	-3.97186400	-1.27425400	-0.03852400
H	-3.17333300	-0.62881000	1.40040100
C	-3.10013800	0.70343900	-0.30774400
H	-3.17206300	0.62847800	-1.40147200
H	-3.97210600	1.27381600	0.03663800
P	-1.47926600	-1.64002700	-0.04697500
P	-1.47958100	1.64007900	0.04719400
H	-1.88196200	-2.19721800	-1.30634700
H	-1.88531800	-2.82350000	0.67254100
H	-1.88554400	2.82356200	-0.67236300
H	-1.88317800	2.19696300	1.30642200
Pd	0.13881500	0.00003100	0.00029000
Br	2.77215600	0.00001800	-0.00022800

C-syn

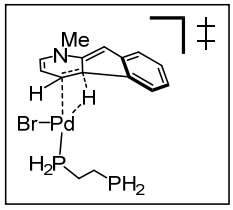


Zero-point correction= 0.313708 (Hartree/Particle)
Thermal correction to Energy= 0.335555
Thermal correction to Enthalpy= 0.336499
Thermal correction to Gibbs Free Energy= 0.260941
Sum of electronic and zero-point Energies= -4018.946794
Sum of electronic and thermal Energies= -4018.924947
Sum of electronic and thermal Enthalpies= -4018.924003
Sum of electronic and thermal Free Energies= -4018.999561
Electronic energy (RM06) -4021.57966574

C	-0.67473200	2.31714400	0.88526300
C	-0.75366700	3.69996800	1.10453200
C	0.33231600	4.53004300	0.80820700
C	1.52069900	4.00040300	0.29635000
C	1.61091400	2.62072300	0.09609200
C	0.50663500	1.78363500	0.39112400
H	-1.52829900	1.67954800	1.10447600
H	-1.66769400	4.13001400	1.50498100
H	0.25159300	5.60064500	0.97737600
H	2.35988800	4.65185500	0.06559100
C	2.72641100	1.79371000	-0.36083300
H	3.71278900	2.17107900	-0.60590300
C	2.32859300	0.50095400	-0.35462300

C	0.85881300	0.37227400	-0.02315200
C	0.58631100	-0.82572700	0.88208300
H	0.36974700	0.19288600	-1.00046900
C	2.73119200	-1.75199500	0.19926200
C	1.65623600	-1.72936700	1.12014300
H	3.41751200	-2.59087700	0.16113200
H	1.63083200	-2.46314900	1.91855000
C	4.05815400	-0.76454800	-1.61978800
H	4.68500300	0.13040500	-1.63524100
H	4.69461600	-1.63789800	-1.45474400
H	3.51838300	-0.86825600	-2.56745300
N	3.08529000	-0.66775600	-0.53055000
C	-1.08693500	-5.01253700	-2.39776400
C	-1.96233000	-3.76991300	-2.62427900
H	-1.00475700	-5.59567600	-3.32075600
H	-1.53844500	-5.66566700	-1.64031400
H	-1.56403500	-3.17307200	-3.45018100
H	-2.99307200	-4.05992000	-2.85488600
P	0.62154100	-4.56953900	-1.74904700
H	1.03002000	-5.86093900	-1.31322900
H	1.39738200	-4.51393500	-2.92432100
P	-1.90649800	-2.62860600	-1.14311700
H	-2.55970800	-1.48082200	-1.64018800
H	-2.98423600	-3.13431300	-0.36276600
Pd	0.36933700	-2.56827700	-0.45272600
Br	0.63007500	-1.33755900	-3.23851500
H	-0.20971000	-0.74475100	1.61609400

C-TS

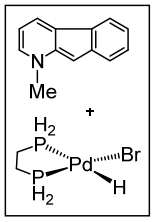


Zero-point correction= 0.306723 (Hartree/Particle)
Thermal correction to Energy= 0.329497
Thermal correction to Enthalpy= 0.330441
Thermal correction to Gibbs Free Energy= 0.250076
Sum of electronic and zero-point Energies= -4018.939116
Sum of electronic and thermal Energies= -4018.916343
Sum of electronic and thermal Enthalpies= -4018.915399
Sum of electronic and thermal Free Energies= -4018.995763
Electronic energy (RM06) -4021.55586957

C	-0.23336300	2.36614300	-0.31833900
C	-0.17856200	3.70280800	-0.71839300
C	1.04281300	4.27805600	-1.10422500
C	2.22711500	3.54200300	-1.09120200
C	2.19020500	2.20314000	-0.67729300
C	0.94765000	1.62900500	-0.29330000
H	-1.17954200	1.90941000	-0.03842700
H	-1.08615500	4.29907800	-0.73562300
H	1.06506300	5.31789000	-1.42049200
H	3.16471200	4.00221200	-1.39240700
C	3.25181900	1.22296200	-0.52236100
H	4.30244900	1.41190500	-0.70125900
C	2.69425800	0.06566000	-0.05341700
C	1.20535700	0.21385600	0.05676800

C	0.51560200	-0.63431800	0.99471200
H	0.92274500	-0.43835700	-1.27915500
C	2.53445900	-2.00504100	1.11942500
C	1.23366200	-1.78564300	1.47647600
H	3.07234900	-2.89220400	1.43300300
H	0.72111400	-2.51219100	2.09465300
C	4.71203900	-1.27248800	0.21198600
H	5.25524800	-0.53263900	0.81387600
H	5.00313300	-2.27533500	0.52890800
H	4.98459700	-1.13523400	-0.83968300
N	3.27382700	-1.10991100	0.37424000
Br	-2.34761300	-2.55966900	0.22866100
C	-2.72132600	-1.75712900	-3.47850300
C	-3.21295200	-2.46592100	-4.74554800
H	-3.33389600	-2.00674800	-2.60480200
H	-2.75904700	-0.66648500	-3.59008200
H	-2.55925800	-2.22948300	-5.59425400
H	-3.19178600	-3.55180400	-4.60793800
P	-0.98636000	-2.17790300	-2.97129100
H	-0.98117500	-3.58531700	-3.09753500
H	-0.26841000	-1.87641200	-4.15603600
P	-4.94561500	-1.87917400	-5.22220100
H	-5.20392700	-2.88883700	-6.19492700
H	-5.65116000	-2.56649400	-4.19289800
Pd	-0.34113200	-1.41295900	-0.87546700
H	-0.37640100	-0.29072600	1.50850300

D

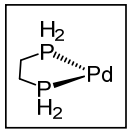


Zero-point correction= 0.309016 (Hartree/Particle)
Thermal correction to Energy= 0.332073
Thermal correction to Enthalpy= 0.333017
Thermal correction to Gibbs Free Energy= 0.237067
Sum of electronic and zero-point Energies= -4018.959553
Sum of electronic and thermal Energies= -4018.936496
Sum of electronic and thermal Enthalpies= -4018.935552
Sum of electronic and thermal Free Energies= -4019.031501
Electronic energy (RM06) -4021.58182072

C	5.32433600	-0.56093600	-12.74970900
C	5.45997900	0.63875200	-13.44294300
C	6.64080800	0.91525700	-14.15828500
C	7.69606500	0.00808100	-14.19371300
C	7.57908800	-1.20809700	-13.50069000
C	6.37515200	-1.48453700	-12.77409900
H	4.41183700	-0.77430200	-12.19679800
H	4.65272500	1.36593500	-13.43330500
H	6.72902400	1.85761300	-14.69391200
H	8.60021900	0.23969500	-14.75192200
C	8.49450400	-2.31862200	-13.36083300
H	9.47978800	-2.38141400	-13.80359600
C	7.86707900	-3.25295900	-12.56743200
C	6.53443100	-2.78754300	-12.16774600

C	5.74575500	-3.57706300	-11.37224600
C	7.48610000	-5.25789300	-11.33049300
C	6.23599400	-4.84249500	-10.94459100
H	7.90039100	-6.21340000	-11.02915600
H	5.63716200	-5.49048500	-10.31528500
C	9.61983500	-4.94725800	-12.52273300
H	10.37925400	-4.24189300	-12.16666500
H	9.81411100	-5.93405400	-12.09918600
H	9.68195600	-5.00088000	-13.61554500
N	8.29479600	-4.49244000	-12.12326000
H	4.75519600	-3.25170800	-11.06461600
C	-50.59666600	0.41921100	0.00398400
H	-51.50801400	0.98850000	0.21175500
H	-50.56286500	0.24207400	-1.07779100
C	-50.61907800	-0.92386700	0.75856500
H	-50.78206800	-0.75347800	1.82958300
H	-51.43554500	-1.56018300	0.40119400
P	-49.05135000	1.40128700	0.43177900
P	-48.97267300	-1.81107200	0.61578800
H	-49.49076100	2.15873900	1.54387400
H	-49.09814400	2.43454800	-0.53127700
H	-49.11867900	-2.85989300	1.54925700
H	-49.13219600	-2.56657800	-0.56930200
Pd	-47.27853500	-0.27868600	0.71886200
H	-46.24906400	-1.43977200	0.91587100
Br	-45.30453400	1.20742800	0.85828800

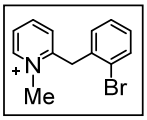
A+: Pd



Zero-point correction= 0.094271 (Hartree/Particle)
Thermal correction to Energy= 0.101909
Thermal correction to Enthalpy= 0.102853
Thermal correction to Gibbs Free Energy= 0.061238
Sum of electronic and zero-point Energies= -890.391673
Sum of electronic and thermal Energies= -890.384035
Sum of electronic and thermal Enthalpies= -890.383091
Sum of electronic and thermal Free Energies= -890.424706
Electronic energy (RM06) -890.44253923

Pd	15.20412900	-3.68032800	31.49824100
C	15.87873400	-3.80771500	34.61811000
H	16.18599300	-3.32828500	35.55453000
H	15.13514700	-4.57224500	34.87563400
C	17.09850800	-4.46982700	33.94640400
H	17.87174600	-3.71599600	33.75266600
H	17.53520300	-5.21422000	34.62190300
P	14.98354800	-2.56423700	33.50582100
P	16.70500300	-5.25484400	32.26880300
H	15.75627800	-1.40526800	33.79976100
H	13.93326500	-2.23871600	34.41341200
H	18.02937000	-5.68180900	31.95798300
H	16.27142400	-6.53431300	32.71779100

A+: pyridinium



Zero-point correction= 0.231051 (Hartree/Particle)
Thermal correction to Energy= 0.244034
Thermal correction to Enthalpy= 0.244978
Thermal correction to Gibbs Free Energy= 0.189939
Sum of electronic and zero-point Energies= -3129.226642
Sum of electronic and thermal Energies= -3129.213659
Sum of electronic and thermal Enthalpies= -3129.212715
Sum of electronic and thermal Free Energies= -3129.267754
Electronic energy (RM06) -3131.54458993

C	2.94270000	0.26791700	-0.68956100
C	3.74866200	-0.85387000	-0.48619600
C	3.29918300	-1.90395100	0.31399000
C	2.04065300	-1.83243800	0.91179500
C	1.21115400	-0.71920900	0.72336200
C	1.69008700	0.32043200	-0.08617300
H	3.28431700	1.09295000	-1.30464800
H	4.72817500	-0.89808600	-0.95220200
H	3.92665300	-2.77397200	0.47937900
H	1.69884800	-2.64627000	1.54677400
C	-1.30976700	-0.74337900	0.43845800
C	-1.28467100	-1.64769000	-0.62431100
C	-2.37339900	-1.78713000	-1.47582200
H	-0.38401000	-2.23257400	-0.77050200
C	-3.51020800	-0.11691900	-0.20589400
C	-3.50945200	-1.00180400	-1.26258800
H	-4.35536400	0.52312200	0.01340800
H	-4.38266600	-1.06927300	-1.90110500
Br	0.60592200	1.87895200	-0.37854000
C	-2.51431700	1.00695400	1.71521900
H	-1.75048100	1.76817300	1.54184000
H	-3.50077300	1.46718400	1.69518200
H	-2.36361300	0.52383600	2.68138700
N	-2.43905600	0.00234500	0.62491500
H	-2.33876000	-2.49654700	-2.29661400
C	-0.14136800	-0.63483800	1.40155000
H	-0.19740400	0.29273400	1.97264000
H	-0.23435000	-1.45545400	2.12598700

For equilibrium constant:

Me_3NH+

Zero-point correction= 0.136794 (Hartree/Particle)
Thermal correction to Energy= 0.142400
Thermal correction to Enthalpy= 0.143344
Thermal correction to Gibbs Free Energy= 0.109155
Sum of electronic and zero-point Energies= -174.714269
Sum of electronic and thermal Energies= -174.708663
Sum of electronic and thermal Enthalpies= -174.707718
Sum of electronic and thermal Free Energies= -174.741908
Electronic energy (RM06) -174.85091861

C	0.71505100	1.25127200	0.10360500
H	1.73404300	1.23145900	-0.28526300
H	0.17942400	2.11925400	-0.28321700
H	0.72796900	1.27128300	1.19447300

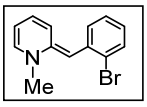
C	-1.44124300	-0.00648300	0.10364100
H	-1.93334200	0.88678700	-0.28348900
H	-1.92574100	-0.90326400	-0.28497100
H	-1.46501900	-0.00749200	1.19451600
C	0.72625500	-1.24480000	0.10360100
H	0.19922400	-2.11763600	-0.28412000
H	1.74540200	-1.21536500	-0.28428600
H	0.73828900	-1.26513100	1.19445700
H	-0.00008300	0.00007200	-1.36576500
N	-0.00007700	0.00001400	-0.33963100

Me_3N

Zero-point correction= 0.121119 (Hartree/Particle)
Thermal correction to Energy= 0.126535
Thermal correction to Enthalpy= 0.127480
Thermal correction to Gibbs Free Energy= 0.093826
Sum of electronic and zero-point Energies= -174.353281
Sum of electronic and thermal Energies= -174.347865
Sum of electronic and thermal Enthalpies= -174.346920
Sum of electronic and thermal Free Energies= -174.380574
Electronic energy (RM06) -174.38632433

N	-0.00007600	0.00015600	-0.37151400
C	1.10008800	0.84815800	0.06099200
H	2.04531300	0.45839700	-0.33314600
H	0.96161800	1.86235300	-0.33005000
H	1.19307900	0.91740500	1.16428100
C	-1.28475400	0.52837100	0.06100200
H	-1.41903200	1.54250700	-0.33160100
H	-2.09369900	-0.09779200	-0.33170500
H	-1.39223900	0.57223900	1.16425900
C	0.18471300	-1.37661300	0.06091400
H	-0.62659200	-2.00005300	-0.33125300
H	1.13132600	-1.76435800	-0.33186200
H	0.20047900	-1.49128100	1.16423100

Starting material



Zero-point correction= 0.217074 (Hartree/Particle)
Thermal correction to Energy= 0.230064
Thermal correction to Enthalpy= 0.231009
Thermal correction to Gibbs Free Energy= 0.176015
Sum of electronic and zero-point Energies= -3128.820128
Sum of electronic and thermal Energies= -3128.807138
Sum of electronic and thermal Enthalpies= -3128.806194
Sum of electronic and thermal Free Energies= -3128.861187
Electronic energy (RM06) -3131.06727480

C	-3.12567100	1.01668700	-0.06071500
C	-3.00854400	2.38585700	0.17791100
C	-1.75828000	2.91361100	0.50464400
C	-0.64398600	2.08458900	0.58081800
C	-0.70814900	0.69651200	0.31076200
C	-1.99845600	0.20408500	0.00633100
H	-4.08642900	0.57686500	-0.30577400
H	-3.88612400	3.02315800	0.12018000

H	-1.65240400	3.97299500	0.72352600
H	0.30542000	2.50446500	0.89713600
C	0.44262100	-0.19176200	0.41561400
H	0.20067500	-1.19366800	0.74243100
C	1.74854500	0.09496700	0.09204100
C	2.20454400	1.28964000	-0.59102900
C	3.51218200	1.50929600	-0.89139200
H	1.44728500	1.99748100	-0.90233800
C	4.09058700	-0.59885200	0.06745800
C	4.50810600	0.54499000	-0.53525500
H	4.77679000	-1.39150000	0.34455400
H	5.55871200	0.69573200	-0.75100400
Br	-2.25599300	-1.67129700	-0.34622800
C	2.41880300	-2.10180300	1.01271300
H	1.75459200	-2.69264500	0.37114500
H	3.32585000	-2.67568300	1.20819900
H	1.90120600	-1.91062000	1.95992000
N	2.77437000	-0.84411000	0.37088900
H	3.79977000	2.41069000	-1.42561100

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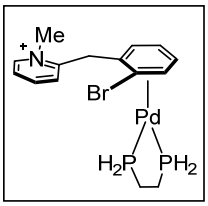

Zero-point correction= 0.325243 (Hartree/Particle)
Thermal correction to Energy= 0.348033
Thermal correction to Enthalpy= 0.348977
Thermal correction to Gibbs Free Energy= 0.269554
Sum of electronic and zero-point Energies= -4019.322291
Sum of electronic and thermal Energies= -4019.299501
Sum of electronic and thermal Enthalpies= -4019.298557
Sum of electronic and thermal Free Energies= -4019.377980
Electronic energy (RM06) -4022.01352165

C	-0.92235000	-2.35515100	0.01974300
C	-1.25223000	-2.95242500	1.27035700
C	-0.39358500	-2.86862700	2.34585700
C	0.85649800	-2.22504500	2.20183500
C	1.24041300	-1.64000900	1.00619000
C	0.30916100	-1.63764300	-0.08343800
H	-1.44267900	-2.67524000	-0.87691400
H	-2.17859800	-3.51462500	1.34607300
H	-0.64876500	-3.33745700	3.29089400
H	1.54932800	-2.21793100	3.04019500
C	2.74228600	0.41125500	0.74422600
C	1.99388600	1.23335300	1.59149000
C	2.15777000	2.61275600	1.57978000
H	1.28911500	0.75342700	2.26058800
C	3.77389400	2.35421800	-0.15887200
C	3.06418100	3.18453500	0.68108100
H	4.48745100	2.73060200	-0.88046900
H	3.22228200	4.25556000	0.62829600
Pd	-1.47058000	-0.18261700	0.01987100
C	-2.93390500	2.81392100	-0.61048000
H	-3.04111100	3.88204000	-0.39732200

H	-2.94477900	2.69650900	-1.70110800
C	-4.09101000	2.01968100	0.01974600
H	-4.13768500	2.21192000	1.09865100
H	-5.04629000	2.33917600	-0.40785600
P	-1.25888300	2.18541200	-0.02837300
P	-3.84967700	0.16615700	-0.18578200
Br	1.00551200	-1.34627900	-1.89444200
C	4.43388000	0.18422400	-1.05541200
H	3.76445300	-0.39439800	-1.69484700
H	5.03451700	0.85601700	-1.66658500
H	5.09454600	-0.47850000	-0.49392900
N	3.62062600	1.00081400	-0.11891500
H	-1.12362800	2.95038900	1.16452000
H	-0.42251900	3.01960000	-0.81972600
H	-4.92864600	-0.30230500	0.60550800
H	-4.47713600	-0.03199100	-1.44204000
H	1.58657100	3.23794400	2.25874200
C	2.64580300	-1.09769900	0.84839100
H	3.12009200	-1.57521500	-0.01003200
H	3.23309600	-1.38866700	1.73054000

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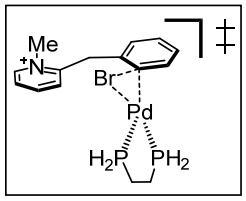

Zero-point correction= 0.324553 (Hartree/Particle)
Thermal correction to Energy= 0.346963
Thermal correction to Enthalpy= 0.347907
Thermal correction to Gibbs Free Energy= 0.270017
Sum of electronic and zero-point Energies= -4019.309189
Sum of electronic and thermal Energies= -4019.286779
Sum of electronic and thermal Enthalpies= -4019.285835
Sum of electronic and thermal Free Energies= -4019.363725
Electronic energy (RM06) -4021.99782723

C	-0.67537600	-2.52611300	1.05064300
C	-0.40419700	-2.94463600	2.35695000
C	0.83510600	-2.68051000	2.93713300
C	1.81156700	-2.00429500	2.19655200
C	1.56559900	-1.54126400	0.90133500
C	0.27332600	-1.74956100	0.36126800
H	-1.60503000	-2.80436300	0.56593400
H	-1.15443100	-3.51394100	2.89820700
H	1.06334300	-3.03712000	3.93636100
H	2.79879100	-1.85225400	2.62942300
C	2.64105700	0.64444700	0.11373200
C	2.56643000	1.34598200	1.32055200
C	2.64571400	2.73109500	1.35650000
H	2.44905400	0.76834700	2.23035300
C	2.83354700	2.72342600	-1.02312900
C	2.77690800	3.43531900	0.15482100
H	2.93570500	3.20554400	-1.98687500
H	2.83733700	4.51717300	0.12650600
Pd	-1.15198100	-0.11776500	-0.22232300
C	-2.69140300	2.72614800	0.88637900
H	-3.01323600	3.34012100	1.73336800

H	-2.33815200	3.41106600	0.10521000
C	-3.86843000	1.88720500	0.36052100
H	-4.29059100	1.28197000	1.17181400
H	-4.66601300	2.54180300	-0.00426900
P	-1.21233100	1.66702800	1.37493800
P	-3.32522900	0.68139600	-0.97208700
Br	0.11180600	-1.89232200	-1.75316600
C	2.86426200	0.68377700	-2.35946500
H	1.97853900	0.06192900	-2.50366700
H	2.90764300	1.44695800	-3.13492500
H	3.76911800	0.07480900	-2.40394200
N	2.77924100	1.36179700	-1.03978300
H	-1.60935100	1.28596400	2.68325900
H	-0.35351200	2.72365700	1.80096500
H	-4.52998600	-0.04234300	-1.14883300
H	-3.45554200	1.49310900	-2.12787000
H	2.60542700	3.25874600	2.30422900
C	2.67003100	-0.87282500	0.10646300
H	2.65529400	-1.25873700	-0.91278800
H	3.63737500	-1.16208200	0.53939700

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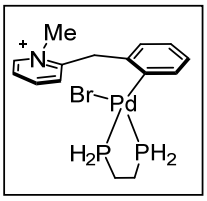
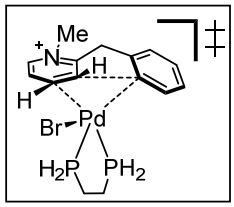


Zero-point correction= 0.326992 (Hartree/Particle)
Thermal correction to Energy= 0.349325
Thermal correction to Enthalpy= 0.350269
Thermal correction to Gibbs Free Energy= 0.273014
Sum of electronic and zero-point Energies= -4019.358623
Sum of electronic and thermal Energies= -4019.336290
Sum of electronic and thermal Enthalpies= -4019.335345
Sum of electronic and thermal Free Energies= -4019.412600
Electronic energy (RM06) -4022.04910639

C	-0.21697700	2.98452900	-0.59353600
C	0.58374300	4.10630400	-0.83714600
C	1.96451800	4.01921100	-0.68140700
C	2.52475000	2.81639600	-0.25301200
C	1.72945700	1.69020300	0.01242600
C	0.33291100	1.76325300	-0.17678700
H	-1.29285900	3.08635900	-0.71038400
H	0.12238200	5.04048900	-1.14591400
H	2.59943500	4.87930200	-0.87172200
H	3.59961000	2.75576400	-0.09273100
C	2.48207700	-0.74459200	-0.26976800
C	2.53994800	-0.64976200	-1.66399600
C	2.69780000	-1.77958900	-2.45520500
H	2.46539400	0.34069000	-2.09765700
C	2.72157600	-3.10382100	-0.46866000
C	2.78258200	-3.03554300	-1.84406000
H	2.78847600	-4.04081700	0.06973900
H	2.90377800	-3.94695100	-2.41806900
Pd	-1.02806800	0.23558800	0.16016800
C	-2.94645800	-1.04305400	-2.37714400
H	-3.51959800	-0.81496000	-3.28160100

H	-2.38647300	-1.96595900	-2.57105300
C	-3.87589600	-1.22514100	-1.16237200
H	-4.53070200	-0.35294100	-1.05100700
H	-4.51970200	-2.09946200	-1.29735900
P	-1.67760600	0.29410700	-2.05312600
P	-2.86562200	-1.34036900	0.41138500
Br	-0.47207800	0.02164500	2.60793800
C	2.54127200	-2.14506900	1.77229300
H	1.58260700	-1.77696900	2.15228800
H	2.65895100	-3.20196100	2.00755900
H	3.36011200	-1.58060100	2.22196300
N	2.58264400	-1.98627700	0.29490700
H	-2.31453500	1.47594600	-2.48882600
H	-0.76268400	0.13256400	-3.11492900
H	-3.82671200	-1.19114500	1.43071700
H	-2.62721300	-2.72853300	0.53559700
H	2.76056900	-1.68837100	-3.53533900
C	2.39518000	0.46947700	0.61891600
H	1.85849800	0.22156200	1.53804200
H	3.42553300	0.72247200	0.91367100

B+TS



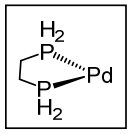
Zero-point correction= 0.324784 (Hartree/Particle)
Thermal correction to Energy= 0.346421
Thermal correction to Enthalpy= 0.347365
Thermal correction to Gibbs Free Energy= 0.273513
Sum of electronic and zero-point Energies= -4019.274380
Sum of electronic and thermal Energies= -4019.252743
Sum of electronic and thermal Enthalpies= -4019.251799
Sum of electronic and thermal Free Energies= -4019.325652
Electronic energy (RM06) -4021.97557681

C	0.64168000	2.50958800	-0.77553700
C	1.15401900	3.75161700	-0.39028100
C	2.29624200	3.83319900	0.41236000
C	2.96272900	2.66970800	0.80381500
C	2.46170800	1.42060300	0.43094400
C	1.26811500	1.34810000	-0.30776900
H	-0.26123500	2.44347800	-1.37476000
H	0.65225300	4.65720900	-0.71905100
H	2.68977100	4.80284200	0.70209600
H	3.89155500	2.73645300	1.36525600
C	2.53411000	-0.88285300	-0.23708900
C	1.69246800	-0.32838500	-1.30184900
C	0.63157800	-1.20775400	-1.75899400
H	2.16196000	0.33055200	-2.02949400
C	1.81090500	-3.09295600	-0.74253600
C	0.80232300	-2.61790900	-1.52074600
H	2.00739100	-4.14278400	-0.57583100
H	0.14401600	-3.32154500	-2.02009000
C	3.52514700	-2.74945000	0.98835200
H	3.05452400	-2.65648100	1.97227500
H	3.70317100	-3.80289500	0.77313600

H	4.47924300	-2.22214200	0.98241600
N	2.63462200	-2.20209200	-0.05384400
Br	-2.39906100	0.77243500	-1.46491400
C	-2.95319100	-1.30613400	1.95806200
C	-2.94604100	0.22545100	2.08228400
H	-3.97461600	-1.68157500	1.84229200
H	-2.53509600	-1.77115000	2.85833800
H	-3.49648500	0.67639700	1.25150300
H	-3.40330100	0.54093600	3.02528700
P	-1.90130200	-1.90050100	0.52889700
H	-1.54198100	-3.20290400	0.95478300
H	-2.79366400	-2.21740200	-0.50812900
P	-1.20830000	0.87360800	1.92963100
H	-1.36514100	2.26752000	1.81723800
H	-0.70792600	0.80147900	3.25366300
Pd	-0.27920900	-0.25761800	0.00532200
H	0.01880200	-0.89371500	-2.59762600
C	3.23905600	0.13046700	0.62246100
H	4.28530200	0.26270800	0.30201500
H	3.27875600	-0.19349400	1.67001300

Pd species from Scheme S2.6

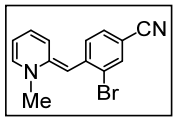
A+ and A: Pd



Zero-point correction= 0.094271 (Hartree/Particle)
Thermal correction to Energy= 0.101909
Thermal correction to Enthalpy= 0.102853
Thermal correction to Gibbs Free Energy= 0.061238
Sum of electronic and zero-point Energies= -890.391673
Sum of electronic and thermal Energies= -890.384035
Sum of electronic and thermal Enthalpies= -890.383091
Sum of electronic and thermal Free Energies= -890.424706
Electronic energy (RM06) -890.44253923

Pd	15.20412900	-3.68032800	31.49824100
C	15.87873400	-3.80771500	34.61811000
H	16.18599300	-3.32828500	35.55453000
H	15.13514700	-4.57224500	34.87563400
C	17.09850800	-4.46982700	33.94640400
H	17.87174600	-3.71599600	33.75266600
H	17.53520300	-5.21422000	34.62190300
P	14.98354800	-2.56423700	33.50582100
P	16.70500300	-5.25484400	32.26880300
H	15.75627800	-1.40526800	33.79976100
H	13.93326500	-2.23871600	34.41341200
H	18.02937000	-5.68180900	31.95798300
H	16.27142400	-6.53431300	32.71779100

A: neutral base

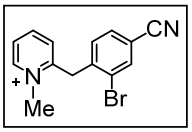


Zero-point correction= 0.215739 (Hartree/Particle)
Thermal correction to Energy= 0.230557
Thermal correction to Enthalpy= 0.231501

Thermal correction to Gibbs Free Energy= 0.172127
Sum of electronic and zero-point Energies= -3221.067300
Sum of electronic and thermal Energies= -3221.052483 Sum of electronic and thermal Enthalpies= -3221.051539
Sum of electronic and thermal Free Energies= -3221.110912
Electronic energy (RM06) -3223.28418904

C	2.82316500	0.01753300	-0.06288900
C	3.05801000	-1.35064900	0.15522100
C	1.96658600	-2.18656500	0.44994200
C	0.68497100	-1.66595700	0.50601400
C	0.39607500	-0.29881000	0.25402000
C	1.53111100	0.51376300	-0.00940300
H	3.65048300	0.68268900	-0.28051000
H	2.13701100	-3.23839700	0.65644700
H	-0.12716400	-2.32130300	0.80017800
C	-0.93221000	0.26711000	0.33821300
H	-0.95092900	1.31550000	0.60004300
C	-2.13614000	-0.35613200	0.06815700
C	-2.29405800	-1.63883200	-0.57924300
C	-3.51470000	-2.18302700	-0.84104000
H	-1.39458500	-2.14177400	-0.90861600
C	-4.57206000	-0.26291500	0.10011000
C	-4.70663400	-1.48773200	-0.47550800
H	-5.42660200	0.34144400	0.38230400
H	-5.69200900	-1.89611700	-0.66294300
Br	1.31853000	2.39600200	-0.32841700
C	-3.30620800	1.61972000	0.99231200
H	-2.84824400	2.35445900	0.32058300
H	-4.32187500	1.93975600	1.22802900
H	-2.71698000	1.57802800	1.91476800
N	-3.35078900	0.30214300	0.36748900
H	-3.58104900	-3.13838400	-1.35380500
C	4.38672700	-1.87350800	0.09258000
N	5.46729800	-2.30499400	0.04211000

A+: pyridinium



Zero-point correction= 0.229332 (Hartree/Particle)
Thermal correction to Energy= 0.244207
Thermal correction to Enthalpy= 0.245151
Thermal correction to Gibbs Free Energy= 0.185565
Sum of electronic and zero-point Energies= -3221.460140
Sum of electronic and thermal Energies= -3221.445266
Sum of electronic and thermal Enthalpies= -3221.444322
Sum of electronic and thermal Free Energies= -3221.503908
Electronic energy (RM06) -3223.75513806

C	2.47830100	0.52891600	-0.35421700
C	3.35183500	-0.51328500	-0.00328000
C	2.90529100	-1.55484000	0.82331200
C	1.59312900	-1.55034500	1.28761000
C	0.70080000	-0.52512100	0.94731000
C	1.17434000	0.50728200	0.12315800
H	2.82108500	1.33951100	-0.98643900
H	3.58420300	-2.35419400	1.09912900
H	1.25711000	-2.35417700	1.93718700

C	-1.76887100	-0.78171400	0.41760300
C	-1.56036700	-1.72769300	-0.58636000
C	-2.54295700	-2.00374300	-1.52975500
H	-0.60473700	-2.23809700	-0.61514700
C	-3.93970900	-0.38777400	-0.46559800
C	-3.75713900	-1.31582100	-1.46872400
H	-4.85485700	0.18136300	-0.36234100
H	-4.55337800	-1.49136100	-2.18288000
Br	0.01228800	1.94829100	-0.36672400
C	-3.24414600	0.90508500	1.48094800
H	-2.54164300	1.72928400	1.34045000
H	-4.26210900	1.26680300	1.34619200
H	-3.14459500	0.48076400	2.48086000
N	-2.97124200	-0.13386400	0.45576400
H	-2.36574500	-2.74409200	-2.30349600
C	-0.71717100	-0.52148400	1.48222700
H	-0.90284600	0.42919700	1.98414200
H	-0.81801600	-1.30426100	2.24606100
C	4.69868400	-0.50505200	-0.49562700
N	5.78886100	-0.50290300	-0.89862400

For equilibrium constant:

DBU*H+

Zero-point correction= 0.262161 (Hartree/Particle)
Thermal correction to Energy= 0.272130
Thermal correction to Enthalpy= 0.273075
Thermal correction to Gibbs Free Energy= 0.226936
Sum of electronic and zero-point Energies= -462.245820
Sum of electronic and thermal Energies= -462.235851
Sum of electronic and thermal Enthalpies= -462.234906
Sum of electronic and thermal Free Energies= -462.281045
Electronic energy (RM06) -462.35360677

C	-0.27016400	0.71619100	-0.40897100
C	2.08651000	-0.05951400	1.09699500
C	2.03915400	-1.34582800	0.25601600
C	1.01040100	-1.30016600	-0.89049000
H	1.21155400	-0.03060800	1.75992200
H	1.82150900	-2.19154400	0.91812700
H	2.95485800	-0.10721300	1.76237200
H	3.01794700	-1.54855800	-0.19451300
H	0.72981600	-2.30550000	-1.21182500
H	1.42475000	-0.80016400	-1.76949000
C	-1.43487100	-1.43364300	-0.21327200
H	-1.08130800	-2.36498100	0.23622000
H	-1.92856300	-1.68603000	-1.15954000
C	-2.38655400	-0.70894800	0.73673900
H	-3.32129300	-1.27074600	0.81400200
H	-1.94678400	-0.65920700	1.73885300
C	-2.66745800	0.70250600	0.22747400
H	-3.28261200	0.68660100	-0.67999400
H	-3.18790800	1.30132100	0.97874900
N	-0.24398500	-0.60706400	-0.51346100
C	2.15629800	1.25697800	0.30511700
H	3.08982300	1.30710600	-0.26504300
H	2.18889300	2.08223400	1.02316300
C	0.97646600	1.51874400	-0.68772600
H	1.28412200	1.29208700	-1.71454700
H	0.71448800	2.58082900	-0.68523800
H	-1.33980600	2.36886300	-0.02062900

N	-1.38575400	1.35957500	-0.06680800

DBU

Zero-point correction= 0.247318 (Hartree/Particle)
Thermal correction to Energy= 0.257186
Thermal correction to Enthalpy= 0.258130
Thermal correction to Gibbs Free Energy= 0.211823
Sum of electronic and zero-point Energies= -461.841935
Sum of electronic and thermal Energies= -461.832067
Sum of electronic and thermal Enthalpies= -461.831123
Sum of electronic and thermal Free Energies= -461.877431
Electronic energy (RM06) -461.87327751

C	-0.32539300	-0.78608600	0.39941300
C	2.03561400	0.07821900	-1.09615300
C	1.98795100	1.35530700	-0.24275500
C	0.95450100	1.28024300	0.90425900
H	1.13706700	0.04314500	-1.72459400
H	1.75550500	2.20479500	-0.89868800
H	2.88495400	0.14489800	-1.78815900
H	2.97337800	1.56350900	0.19673200
H	0.68946500	2.28852600	1.24049800
H	1.40334900	0.78622800	1.77233400
C	-1.44498200	1.41081500	0.19013600
H	-1.09392300	2.33470900	-0.28711500
H	-1.99141300	1.70820100	1.09939800
C	-2.37163100	0.64496500	-0.75323400
H	-3.31710400	1.18780100	-0.86923600
H	-1.90754500	0.57601700	-1.74540900
C	-2.59695500	-0.76855200	-0.20545500
H	-3.19240200	-0.71605600	0.72063700
H	-3.18909800	-1.36011100	-0.91470100
N	-0.28333500	0.59464300	0.54635900
N	-1.35409000	-1.48355500	0.05966000
C	2.13184400	-1.24404500	-0.31562900
H	3.08772000	-1.28905200	0.22298400
H	2.15810900	-2.05673100	-1.05103000
C	0.97098900	-1.52391900	0.68630700
H	1.29619700	-1.28999000	1.70779400
H	0.71608100	-2.58518600	0.67507900

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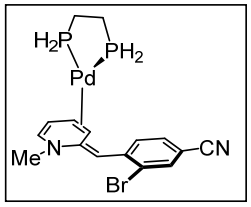

Zero-point correction= 0.310417 (Hartree/Particle)
Thermal correction to Energy= 0.334784
Thermal correction to Enthalpy= 0.335728
Thermal correction to Gibbs Free Energy= 0.252038
Sum of electronic and zero-point Energies= -4111.168004
Sum of electronic and thermal Energies= -4111.143637
Sum of electronic and thermal Enthalpies= -4111.142693
Sum of electronic and thermal Free Energies= -4111.226383

Electronic energy (RM06) -4113.76218812

C	-4.08836500	-0.85998400	-0.06650600
C	-4.15947800	-1.21377900	-1.42520700
C	-3.27781700	-0.59616100	-2.33104400
C	-2.35139000	0.32895100	-1.88128400
C	-2.21437000	0.68717400	-0.51285400
C	-3.14544200	0.06101200	0.36054100
H	-4.76434600	-1.31557600	0.64750500
H	-3.34550000	-0.82963600	-3.38894600
H	-1.73704500	0.84290700	-2.61194900
C	-1.27256300	1.67471000	-0.03656000
H	-1.60461700	2.21345300	0.83975500
C	0.01008800	1.92241800	-0.49423700
C	0.73644200	1.09480600	-1.45742800
C	2.02558600	1.43681400	-1.91496000
H	0.15747900	0.36382200	-2.00330000
C	2.00156000	3.33388800	-0.42723700
C	2.65928000	2.61309700	-1.36581100
H	2.43118900	4.21730400	0.03007500
H	3.64801000	2.91864800	-1.68797300
Pd	2.22957400	-0.26225200	-0.45209300
C	2.77669600	-3.07535400	1.37774200
H	2.66238700	-3.63228800	2.31350000
H	2.65199700	-3.79173800	0.55605000
C	4.17223100	-2.43012900	1.30485700
H	4.33498000	-1.79111600	2.18197300
H	4.95134700	-3.19944400	1.31440300
P	1.40851700	-1.79521400	1.17791000
P	4.34539600	-1.31097300	-0.20311200
Br	-3.12383800	0.45370500	2.24194900
C	0.09931600	3.88624800	1.00140000
H	-0.10024900	3.34574200	1.93442200
H	0.76780500	4.72093600	1.21699800
H	-0.85008100	4.27877400	0.61960700
N	0.72641000	3.01528900	0.01562700
H	1.24401200	-1.40668000	2.53408500
H	0.29002000	-2.66698300	1.13898000
H	5.63810800	-0.78601800	0.06967200
H	4.78482000	-2.26902000	-1.15665300
H	2.40582400	1.00624400	-2.83641800
C	-5.11989000	-2.17285300	-1.87166300
N	-5.89958500	-2.95639400	-2.23908500

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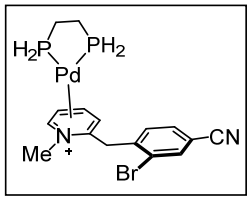

Zero-point correction= 0.324573 (Hartree/Particle)
Thermal correction to Energy= 0.348898
Thermal correction to Enthalpy= 0.349842
Thermal correction to Gibbs Free Energy= 0.266162
Sum of electronic and zero-point Energies= -4111.580751
Sum of electronic and thermal Energies= -4111.556427

Sum of electronic and thermal Enthalpies= -4111.555482
Sum of electronic and thermal Free Energies= -4111.639162
Electronic energy (RM06) -4114.23802944

C	5.36342100	0.13423000	-0.10606400
C	5.55205400	-1.25135200	-0.20746300
C	4.45420000	-2.08569600	-0.46891900
C	3.19062700	-1.52728800	-0.61983100
C	2.97052700	-0.14455900	-0.51999900
C	4.08691200	0.66962500	-0.26224400
H	6.20658000	0.78488100	0.09283200
H	4.59804000	-3.15733700	-0.55385100
H	2.34719300	-2.18002600	-0.82645100
C	0.43995300	-0.38460700	-0.16578800
C	-0.41114800	-1.11789000	-0.94913400
C	-1.49332600	-1.89440000	-0.41192800
H	-0.24495800	-1.11606600	-2.02159100
C	-0.72760800	-1.13662900	1.77652400
C	-1.59973500	-1.92473300	1.02372100
H	-0.78687100	-1.11803200	2.85886900
H	-2.20367500	-2.66022000	1.54488600
Pd	-3.14539800	-0.57215400	0.11289700
C	-6.01001000	0.75245100	-1.19283100
H	-6.50330700	1.33860400	-1.97417600
H	-6.66569900	-0.09510400	-0.96006100
C	-5.78484200	1.61495000	0.06230200
H	-5.22217700	2.52054300	-0.19445900
H	-6.74429200	1.93713500	0.47804000
P	-4.40566100	0.02234100	-1.83380100
P	-4.77541800	0.70995000	1.36018000
Br	3.92132100	2.57072000	-0.11594600
C	1.09589700	0.44096800	2.09914700
H	0.89765400	1.49910000	1.90831100
H	0.85878300	0.21492400	3.13853600
H	2.15081900	0.23114700	1.91938400
N	0.25536300	-0.40019600	1.22582600
H	-3.93907700	1.05429300	-2.68308200
H	-4.88317300	-0.84647900	-2.84161300
H	-4.58138100	1.74057300	2.30972800
H	-5.78403200	0.00515700	2.05920500
H	-1.90831600	-2.69797000	-1.01179000
C	1.57362000	0.42801700	-0.74292800
H	1.39530500	0.50886300	-1.82189400
H	1.53915600	1.45447800	-0.36644200
C	6.86317000	-1.80770100	-0.04050600
N	7.92312300	-2.26426700	0.09851400

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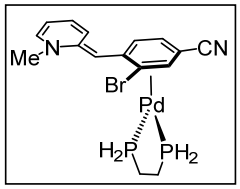

Zero-point correction= 0.309867 (Hartree/Particle)
Thermal correction to Energy= 0.334526
Thermal correction to Enthalpy= 0.335470
Thermal correction to Gibbs Free Energy= 0.251711

Sum of electronic and zero-point Energies= -4111.157485
Sum of electronic and thermal Energies= -4111.132825
Sum of electronic and thermal Enthalpies= -4111.131881
Sum of electronic and thermal Free Energies= -4111.215640
Electronic energy (RM06) -4113.75566737

C	1.31338100	-1.94682000	-0.02316400
C	1.34449200	-2.39601900	-1.38327400
C	0.20570400	-2.26370500	-2.17396900
C	-0.96530500	-1.70125700	-1.65577300
C	-1.07289500	-1.23278400	-0.33299400
C	0.11628200	-1.36949100	0.47957100
H	2.08242600	-2.28639500	0.66039200
H	0.21911700	-2.63125100	-3.19538900
H	-1.84849000	-1.68296200	-2.28441200
C	-2.29795300	-0.71080400	0.23203800
H	-2.39518000	-0.85915600	1.29811800
C	-3.29272600	-0.00528300	-0.41745300
C	-3.20154000	0.54659800	-1.75172000
C	-4.21007100	1.26345600	-2.32016100
H	-2.26529400	0.41221000	-2.27733600
C	-5.51071200	1.00944200	-0.33479100
C	-5.42363600	1.49632900	-1.60163400
H	-6.38689000	1.16216000	0.28539500
H	-6.24789000	2.05414000	-2.02881900
Pd	1.55811900	0.32729200	0.13050800
C	2.32911400	3.62543200	0.33661000
H	2.10652000	4.66743700	0.08383400
H	2.69389200	3.61342500	1.37160200
C	3.40967800	3.06566400	-0.60563000
H	3.08343600	3.16258400	-1.64881700
H	4.33863000	3.63620200	-0.50158700
P	0.76161500	2.57538000	0.31706400
P	3.70911700	1.22729100	-0.31389600
Br	-0.05120700	-1.35904800	2.43155400
C	-4.69131500	-0.20112600	1.61630500
H	-3.97596800	0.26548000	2.30368300
H	-5.70437000	0.03359800	1.94615900
H	-4.54227800	-1.28604100	1.64862900
N	-4.50324000	0.28902500	0.25627800
H	0.08944700	3.19430800	-0.77307000
H	0.04063200	3.26916100	1.32803900
H	4.63317200	0.99115100	-1.36597600
H	4.68533800	1.31163800	0.71545900
H	-4.08220500	1.68002200	-3.31536600
C	2.53116900	-2.99739000	-1.89766100
N	3.50778000	-3.47902200	-2.31393800

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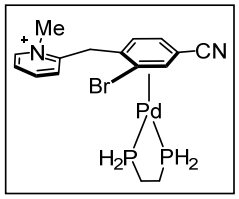

Zero-point correction= 0.323740 (Hartree/Particle)
Thermal correction to Energy= 0.348357
Thermal correction to Enthalpy= 0.349301

Thermal correction to Gibbs Free Energy= 0.265828
Sum of electronic and zero-point Energies= -4111.558928
Sum of electronic and thermal Energies= -4111.534311
Sum of electronic and thermal Enthalpies= -4111.533367
Sum of electronic and thermal Free Energies= -4111.616840
Electronic energy (RM06) -4114.22925518

C	1.25778200	-1.83572500	0.31595800
C	1.81476500	-2.46591600	-0.85186400
C	1.03625800	-2.70502600	-1.97120300
C	-0.33542100	-2.37379200	-1.95647700
C	-0.93613100	-1.79046900	-0.85293100
C	-0.12348500	-1.45460000	0.28121000
H	1.76625100	-1.96890200	1.26497900
H	1.47142500	-3.18067000	-2.84323100
H	-0.94053200	-2.61312500	-2.82693100
C	-2.91419900	-0.16869400	-0.85317500
C	-2.32203600	0.76426800	-1.70788100
C	-2.82438600	2.05516700	-1.81773200
H	-1.46387600	0.44283500	-2.28649200
C	-4.47568500	1.49578200	-0.18636000
C	-3.92128100	2.42927400	-1.03552600
H	-5.32358900	1.71950600	0.44828200
H	-4.34550400	3.42573400	-1.08031200
Pd	1.24058100	0.34748900	0.11858100
C	2.05174000	3.63237800	0.49108700
H	1.93506200	4.68029000	0.19802600
H	2.08593500	3.60267200	1.58703700
C	3.34811200	3.04790600	-0.09743800
H	3.35321000	3.16092600	-1.18838500
H	4.21639500	3.59119400	0.28770000
P	0.54307300	2.63194800	-0.01676300
P	3.49755900	1.20856200	0.25329900
Br	-1.01000500	-1.23802900	2.01686300
C	-4.65556600	-0.71477300	0.82802500
H	-3.92856900	-1.06130300	1.56515900
H	-5.46286600	-0.18573900	1.33195000
H	-5.07011800	-1.55817600	0.27334100
N	-3.98733600	0.22651900	-0.10680400
H	0.24671900	3.25389000	-1.26114300
H	-0.45305600	3.31681600	0.72842400
H	4.61299700	0.88160900	-0.55237200
H	4.17750300	1.22708800	1.49550100
H	-2.36871400	2.76333900	-2.50257900
C	-2.43996000	-1.60791200	-0.82786800
H	-2.84458600	-2.13302200	0.03839200
H	-2.86654700	-2.09606100	-1.71503400
C	3.19372700	-2.84862800	-0.81999900
N	4.32319800	-3.12444300	-0.77637400

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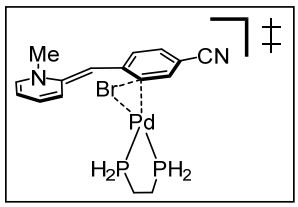
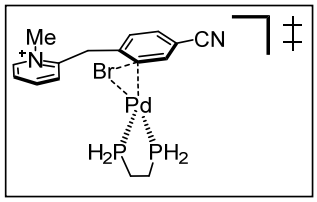


Zero-point correction= 0.309097 (Hartree/Particle)
Thermal correction to Energy= 0.333405

Thermal correction to Enthalpy= 0.334349
Thermal correction to Gibbs Free Energy= 0.251078
Sum of electronic and zero-point Energies= -4111.144457
Sum of electronic and thermal Energies= -4111.120150
Sum of electronic and thermal Enthalpies= -4111.119206
Sum of electronic and thermal Free Energies= -4111.202476
Electronic energy (RM06) -4113.73926422

C	-1.39977300	2.18105900	-0.01932600
C	-1.09232500	3.16149400	-0.98589700
C	0.23456600	3.29501700	-1.42268200
C	1.22469800	2.45569600	-0.92163200
C	0.96144100	1.41410300	-0.00322100
C	-0.40831300	1.28890000	0.40038000
H	-2.39785500	2.12745900	0.40049200
H	0.49301700	4.08400500	-2.12159500
H	2.25169500	2.63655300	-1.22070800
C	1.96720500	0.53660200	0.55022800
H	1.70436900	0.14031500	1.52158000
C	3.15567100	0.12585900	-0.02274900
C	3.53662300	0.31088900	-1.40622900
C	4.71144000	-0.15466800	-1.91404400
H	2.82043900	0.79787000	-2.05464200
C	5.27423400	-1.06067400	0.22147700
C	5.63245900	-0.85440900	-1.07462200
H	5.90652400	-1.60087900	0.91718900
H	6.57896400	-1.22883400	-1.44463800
Pd	-1.49481200	-0.54904800	0.17238500
C	-1.40355800	-3.48368600	-1.58730500
H	-1.18579300	-4.03512900	-2.50789900
H	-1.09050100	-4.11730100	-0.74785600
C	-2.91083200	-3.18852000	-1.48896700
H	-3.23975500	-2.62512900	-2.37108400
H	-3.48219200	-4.12243400	-1.46889900
P	-0.36355200	-1.91501900	-1.48390200
P	-3.31513700	-2.11436100	0.00164400
Br	-0.79761500	0.60838500	2.46582500
C	3.80140500	-0.86254500	2.15443700
H	2.92438000	-1.51182600	2.25918400
H	4.66150500	-1.34939800	2.61633600
H	3.59482200	0.07923700	2.67437600
N	4.09357500	-0.60389400	0.74930900
H	-0.38185300	-1.54030700	-2.85575600
H	0.92076900	-2.52362200	-1.53463000
H	-4.68801600	-1.87259500	-0.26521100
H	-3.53089200	-3.12038500	0.98080200
H	4.93896400	-0.01260700	-2.96682400
C	-2.11355100	4.03650700	-1.47080200
N	-2.94624800	4.74514000	-1.87276800

A+TS

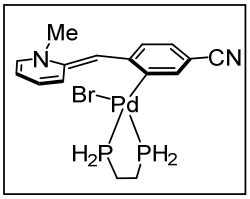


Zero-point correction= 0.322990 (Hartree/Particle)
Thermal correction to Energy= 0.347248

Thermal correction to Enthalpy= 0.348192
Thermal correction to Gibbs Free Energy= 0.265817
Sum of electronic and zero-point Energies= -4111.550033
Sum of electronic and thermal Energies= -4111.525775
Sum of electronic and thermal Enthalpies= -4111.524831
Sum of electronic and thermal Free Energies= -4111.607206
Electronic energy (RM06) -4114.21399383

C	0.42941600	2.08547000	-0.59083100
C	0.44526400	3.24916700	0.20492900
C	-0.24873300	3.28494800	1.42024600
C	-0.97180600	2.15821200	1.83086700
C	-1.00134200	0.98719800	1.07571900
C	-0.21468400	0.93324400	-0.10407700
H	0.89252000	2.08997200	-1.57075900
H	-0.24331200	4.18615500	2.02272200
H	-1.51123100	2.19339600	2.77501000
C	-3.10818300	-0.39151900	0.80119700
C	-3.92003300	0.71013100	0.52200300
C	-5.15348300	0.55655600	-0.09760000
H	-3.54929700	1.69260900	0.78921800
C	-4.77126400	-1.79810200	-0.15239400
C	-5.58693900	-0.72641700	-0.44496700
H	-5.04364800	-2.81710000	-0.39618500
H	-6.53868800	-0.89897400	-0.93389500
Pd	1.50018100	-0.35029000	-0.31144300
C	3.85497500	-2.09716800	1.46113500
H	4.47988100	-2.19692500	2.35397700
H	3.50824400	-3.10283100	1.19323600
C	4.67077000	-1.49022600	0.30645900
H	5.09109600	-0.52348100	0.60873400
H	5.51114000	-2.14392100	0.05316700
P	2.31540300	-1.09086600	1.85585700
P	3.60585700	-1.15588400	-1.20142100
Br	-0.86339600	-0.38294300	-1.65557200
C	-2.73554900	-2.83805900	0.69257600
H	-2.49310300	-2.92823300	1.75219600
H	-3.30075400	-3.71456200	0.37947000
H	-1.82508900	-2.75484300	0.09433100
N	-3.56824600	-1.63247600	0.46241300
H	2.87173200	-0.10225800	2.70707600
H	1.79310300	-1.89862700	2.90364300
H	4.52657200	-0.44870000	-2.00987000
H	3.69617500	-2.39622100	-1.88017000
H	-5.77029800	1.42399500	-0.31034800
C	-1.78326600	-0.22568300	1.52764400
H	-2.00884300	-0.14001700	2.60014300
H	-1.15554300	-1.11074600	1.40584200
C	1.15145900	4.40775600	-0.26019500
N	1.72844400	5.34331000	-0.63940200

B



Zero-point correction= 0.311420 (Hartree/Particle)

Thermal correction to Energy= 0.335778
Thermal correction to Enthalpy= 0.336722
Thermal correction to Gibbs Free Energy= 0.253959
Sum of electronic and zero-point Energies= -4111.185446
Sum of electronic and thermal Energies= -4111.161088
Sum of electronic and thermal Enthalpies= -4111.160144
Sum of electronic and thermal Free Energies= -4111.242908
Electronic energy (RM06) -4113.78805917

C	-0.92914200	2.55334300	-0.07081100
C	-0.21651200	3.77210500	-0.09825500
C	1.18112700	3.74727600	0.03517800
C	1.84005700	2.53540400	0.18800500
C	1.15126500	1.29800400	0.19456100
C	-0.26302500	1.34318700	0.07414500
H	-2.01104600	2.58232400	-0.16235700
H	1.73810400	4.67922100	0.03947900
H	2.91324100	2.54166900	0.35285200
C	1.81882100	0.01848900	0.41322200
H	1.23151700	-0.67461200	1.00203700
C	3.07487400	-0.35988000	-0.00703900
C	3.89399000	0.36175800	-0.96048200
C	5.11180200	-0.08603300	-1.36900600
H	3.47707800	1.26994400	-1.37727400
C	4.87535700	-2.00841800	0.03014000
C	5.63987200	-1.31295500	-0.85356100
H	5.19819300	-2.95143800	0.45752600
H	6.60913500	-1.69259900	-1.15275900
Pd	-1.37205100	-0.38562600	0.03918400
C	-2.05048100	-1.85969900	-2.95928700
H	-2.36926900	-1.71972700	-3.99754600
H	-1.22342200	-2.58006800	-2.96633300
C	-3.21030900	-2.38852000	-2.09281800
H	-4.08252800	-1.73086700	-2.19033700
H	-3.51641400	-3.38495700	-2.42662600
P	-1.35592900	-0.26843800	-2.25132600
P	-2.73538600	-2.37443600	-0.27484400
Br	-1.35445000	-0.53205700	2.53992900
C	2.90394000	-2.37295800	1.42219600
H	1.97419800	-2.75773600	0.98535600
H	3.52135400	-3.21366600	1.74278400
H	2.63915400	-1.76336200	2.29286000
N	3.64478000	-1.57445200	0.45430200
H	-2.14117500	0.72751200	-2.87564600
H	-0.16152100	-0.09226700	-2.98037500
H	-3.97473400	-2.62013900	0.35586100
H	-2.16955300	-3.66130900	-0.10812200
H	5.67875600	0.48053900	-2.10262000
C	-0.91361200	5.00901900	-0.26813700
N	-1.48612200	6.01226600	-0.42065900

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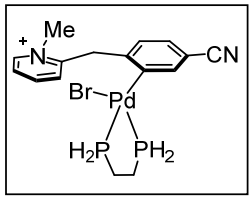
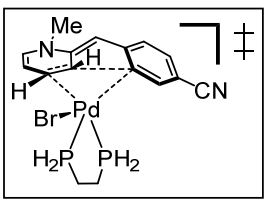


Zero-point correction= 0.325574 (Hartree/Particle)

Thermal correction to Energy= 0.349745
Thermal correction to Enthalpy= 0.350689
Thermal correction to Gibbs Free Energy= 0.269144
Sum of electronic and zero-point Energies= -4111.595388
Sum of electronic and thermal Energies= -4111.571217
Sum of electronic and thermal Enthalpies= -4111.570273
Sum of electronic and thermal Free Energies= -4111.651818
Electronic energy (RM06) -4114.26497370

C	2.72825400	-0.24541900	-0.02018500
C	3.74125200	-1.22262400	-0.07074800
C	3.40792700	-2.57640200	0.05389900
C	2.07507000	-2.92230600	0.25144900
C	1.06098800	-1.95304600	0.31537100
C	1.38304000	-0.58612800	0.15850600
H	3.02998400	0.79391700	-0.10418300
H	4.18014500	-3.33682800	0.01076200
H	1.81860200	-3.97102100	0.38371400
C	-1.37255200	-2.31307600	-0.41598500
C	-1.04141100	-2.37683300	-1.77251200
C	-2.02445500	-2.36187300	-2.75372600
H	0.00941700	-2.44872000	-2.02762000
C	-3.66868600	-2.20436100	-1.02995800
C	-3.36723100	-2.26643900	-2.37412400
H	-4.68614200	-2.13770800	-0.66568200
H	-4.17046600	-2.25055300	-3.10172700
Pd	0.06404700	1.01654300	0.22638000
C	-0.38202100	3.12411800	-2.44268500
H	0.10628500	3.65688300	-3.26497400
H	-1.32618600	2.72265000	-2.83002300
C	-0.64641000	4.06435600	-1.25177700
H	0.27742600	4.57621000	-0.95800200
H	-1.37260600	4.83621600	-1.52390100
P	0.64865100	1.65392000	-1.91727200
P	-1.20867700	3.07676500	0.23643300
Br	-0.70578200	0.52895300	2.57195600
C	-3.10643900	-2.17339700	1.34819500
H	-2.68782700	-1.27318900	1.80961200
H	-4.19426600	-2.14791800	1.39220500
H	-2.74404100	-3.06155100	1.86876800
N	-2.69607700	-2.23304600	-0.07955600
H	1.97967700	2.08842400	-2.09416100
H	0.55149200	0.77611100	-3.01729700
H	-1.10074100	3.98615800	1.30610800
H	-2.61511000	3.05066300	0.09997000
H	-1.75291900	-2.43073000	-3.80272900
C	-0.33963700	-2.40884800	0.67789200
H	-0.65981000	-1.82286600	1.54354600
H	-0.31114300	-3.46076400	1.00113800
C	5.10274400	-0.81765500	-0.26868400
N	6.19925300	-0.47272800	-0.44537000

B TS



Zero-point correction= 0.309000 (Hartree/Particle)
Thermal correction to Energy= 0.333246
Thermal correction to Enthalpy= 0.334190
Thermal correction to Gibbs Free Energy= 0.251454
Sum of electronic and zero-point Energies= -4111.139959
Sum of electronic and thermal Energies= -4111.115713
Sum of electronic and thermal Enthalpies= -4111.114769
Sum of electronic and thermal Free Energies= -4111.197506
Electronic energy (RM06) -4113.73843856

C	1.56995100	1.96565300	-0.97763900
C	2.37454700	3.06918500	-0.62726100
C	3.46374900	2.89964800	0.24811500
C	3.78154900	1.63427200	0.72357900
C	2.98967600	0.52356900	0.38155500
C	1.82096900	0.73058200	-0.39176200
H	0.72015400	2.12003200	-1.63413600
H	4.07282400	3.75737700	0.51400900
H	4.67184200	1.49126700	1.33033700
C	3.33025400	-0.85808400	0.65488400
H	4.03488200	-1.13456900	1.43007600
C	2.66644000	-1.74117700	-0.13991900
C	1.83583500	-1.14985500	-1.22536700
C	0.64286300	-1.84658600	-1.61875100
H	2.38445600	-0.62699800	-2.00438700
C	1.50376200	-3.81403100	-0.45156500
C	0.51829000	-3.23572200	-1.17426900
H	1.48041600	-4.86336700	-0.17897400
H	-0.32387300	-3.83505400	-1.50097000
C	3.52192600	-3.74983100	0.96007400
H	4.55640200	-3.45734000	0.75504800
H	3.44441400	-4.83568800	0.87637100
H	3.26946400	-3.45012700	1.98744000
N	2.63206600	-3.12798400	-0.00881900
Br	-0.82698900	1.18057200	1.70900900
C	-5.06247600	-0.60088800	-0.02239800
C	-3.67392400	-0.02381600	-0.32270500
H	-5.24781400	-1.50481700	-0.61226600
H	-5.12633000	-0.88038500	1.03596900
H	-3.45111100	0.85244100	0.29510200
H	-3.59168500	0.29336100	-1.37000100
P	-6.41479600	0.68663400	-0.32325900
H	-7.51683400	-0.21484900	-0.24607700
H	-6.37288000	0.64152000	-1.74853900
P	-2.27124300	-1.20025700	-0.02200900
H	-2.68045500	-2.31862100	-0.79720000
H	-2.57593900	-1.71948600	1.25309900
Pd	-0.09007900	-0.37698500	-0.20263100
H	0.21750200	-1.60090000	-2.59047800
C	2.07234800	4.36490000	-1.15627500
N	1.83634800	5.41440100	-1.60138700

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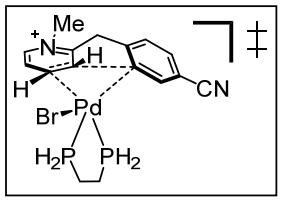

Zero-point correction= 0.323186 (Hartree/Particle)
Thermal correction to Energy= 0.346660
Thermal correction to Enthalpy= 0.347604
Thermal correction to Gibbs Free Energy= 0.269427
Sum of electronic and zero-point Energies= -4111.506097
Sum of electronic and thermal Energies= -4111.482623
Sum of electronic and thermal Enthalpies= -4111.481679
Sum of electronic and thermal Free Energies= -4111.559857
Electronic energy (RM06) -4114.18867959

C	-2.32558400	0.42711000	-0.52979500
C	-3.58065200	0.82009800	-0.03177500
C	-3.70085900	1.96326100	0.77942500
C	-2.57660500	2.73595000	1.05964600
C	-1.32357500	2.35446700	0.57390000
C	-1.19590900	1.16633400	-0.16823300
H	-2.23456000	-0.47066300	-1.13403900
H	-4.67640700	2.25585000	1.15297200
H	-2.68429300	3.65641500	1.62749900
C	0.89894800	2.63089600	-0.28042400
C	0.33758600	1.72235700	-1.28610700
C	1.27243400	0.73990500	-1.80825300
H	-0.40968200	2.12400300	-1.96902300
C	3.11732400	2.10172200	-0.95757600
C	2.67537400	1.04273300	-1.68698000
H	4.15469700	2.39534500	-0.87912600
H	3.39372300	0.44383700	-2.23759700
C	2.76061100	3.80686900	0.77879800
H	2.80427000	3.34062700	1.76822500
H	3.76722300	4.08548800	0.46762000
H	2.14282500	4.70407100	0.81702100
N	2.21311700	2.85276800	-0.20641600
Br	-0.38124700	-2.41833400	-1.39913900
C	2.00453200	-2.82730800	1.84251400
C	0.49304800	-2.97064000	2.07637100
H	2.46666900	-3.80468300	1.67268600
H	2.49235300	-2.38280000	2.71771900
H	0.03365000	-3.54763900	1.26847400
H	0.29206800	-3.47006100	3.02923000
P	2.38560300	-1.69697400	0.40195600
H	3.67281200	-1.21148900	0.73752000
H	2.70707200	-2.53109400	-0.68097000
P	-0.32438300	-1.30044500	2.01498400
H	-1.70252500	-1.58600700	2.00797800
H	-0.19082700	-0.81207200	3.33838100
Pd	0.56084700	-0.24310100	0.02484600
H	0.94880800	0.09281100	-2.61694200
C	-0.10330700	3.25426700	0.65169400
H	-0.36316000	4.27669100	0.33261400
H	0.29525900	3.34346600	1.66999400
C	-4.74409200	0.04015400	-0.34321200
N	-5.69015200	-0.59069900	-0.58463400

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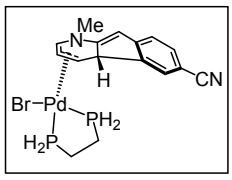

Zero-point correction= 0.312063 (Hartree/Particle)
Thermal correction to Energy= 0.335813
Thermal correction to Enthalpy= 0.336757
Thermal correction to Gibbs Free Energy= 0.256231
Sum of electronic and zero-point Energies= -4111.202793
Sum of electronic and thermal Energies= -4111.179043
Sum of electronic and thermal Enthalpies= -4111.178099
Sum of electronic and thermal Free Energies= -4111.258625
Electronic energy (RM06) -4113.80975582

C	-2.38667100	-1.37369700	-1.07645900
C	-3.37097000	-2.20103000	-0.48713700
C	-4.27954100	-1.66556100	0.44714400
C	-4.21653100	-0.32474200	0.81809300
C	-3.23070100	0.49543200	0.25090300
C	-2.32702000	-0.04476500	-0.70458300
H	-1.69306700	-1.79074500	-1.80048500
H	-5.03315600	-2.31596300	0.88045500
H	-4.92358000	0.07307800	1.54124100
C	-2.89366300	1.88648500	0.49973800
H	-3.39803200	2.52467300	1.21545100
C	-1.82139400	2.21653400	-0.28552700
C	-1.44268300	1.07194300	-1.20865400
C	0.06335700	0.91816900	-1.40365200
H	-1.83794300	1.36170000	-2.20349800
C	0.12752000	3.36890000	-1.03578600
C	0.69769900	2.23759900	-1.51793000
H	0.59979800	4.34142500	-1.11788400
H	1.66691900	2.30565500	-2.00017800
C	-1.53594100	4.54608600	0.38439400
H	-1.37374300	4.40518400	1.46265500
H	-0.96856200	5.41978700	0.05674000
H	-2.60154500	4.73432200	0.21614000
N	-1.11288200	3.38278800	-0.37828600
Br	2.80812300	-0.77527300	-1.88797200
C	0.74078300	-0.73484700	3.33911200
C	2.27696500	-0.82191800	3.30271500
H	0.39028400	-0.37724800	4.31323700
H	0.30169800	-1.72728700	3.17944700
H	2.71604300	0.14090900	3.59167700
H	2.63957800	-1.57236200	4.01233700
P	0.07146800	0.35521700	1.96533400
H	-1.31686400	0.19166000	2.14144500
H	0.20690000	1.64079400	2.54411300
P	2.84621500	-1.16904200	1.55017700
H	4.23454000	-0.92095700	1.62647300
H	2.89209800	-2.58151700	1.51971500
Pd	1.30020700	-0.07309400	0.04112400
H	0.29318800	0.26449200	-2.24380900
C	-3.44695800	-3.58697300	-0.83426800
N	-3.51271100	-4.71693800	-1.10875200

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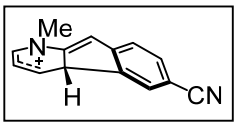
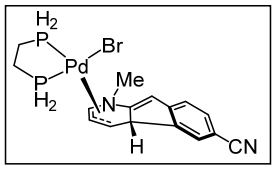


Zero-point correction= 0.215630 (Hartree/Particle)
Thermal correction to Energy= 0.228176
Thermal correction to Enthalpy= 0.229121

Thermal correction to Gibbs Free Energy= 0.176687
Sum of electronic and zero-point Energies= -649.120841
Sum of electronic and thermal Energies= -649.108295
Sum of electronic and thermal Enthalpies= -649.107351
Sum of electronic and thermal Free Energies= -649.159784
Electronic energy (RM06) -649.09455379

C	1.84642800	-0.81023100	0.23363800
C	2.98797300	-0.01357300	0.00526500
C	2.87079300	1.37206100	-0.22859400
C	1.62195600	1.98354900	-0.24957900
C	0.48486200	1.19257700	-0.04520100
C	0.60776100	-0.19969600	0.19100900
H	1.96418200	-1.87228800	0.42488500
H	3.76953500	1.95718400	-0.39066300
H	1.53773500	3.05246500	-0.41910800
C	-0.92090300	1.55684600	-0.05583100
H	-1.29475400	2.55646900	-0.24428800
C	-1.65400200	0.43669200	0.17427500
C	-0.77419300	-0.76121100	0.46052800
C	-1.32224900	-1.99733100	-0.18779600
H	-0.79541900	-0.97195500	1.55065000
C	-3.51118900	-0.95608500	-0.16098800
C	-2.65867900	-2.08343900	-0.39853500
H	-4.58960900	-1.05069900	-0.22951800
H	-3.12521200	-2.99491200	-0.75564900
C	-3.92808300	1.43337300	0.13823600
H	-3.74141300	2.06429800	-0.73448000
H	-4.96540300	1.09966600	0.13024900
H	-3.72269200	1.99280300	1.05264300
N	-3.03815800	0.25518400	0.08343600
H	-0.66826600	-2.84090500	-0.39173400
C	4.28219800	-0.62717700	0.01008800
N	5.32891200	-1.13379300	0.01483800

C-syn

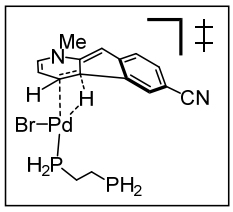


Zero-point correction= 0.312079 (Hartree/Particle)
Thermal correction to Energy= 0.335838
Thermal correction to Enthalpy= 0.336782
Thermal correction to Gibbs Free Energy= 0.256699
Sum of electronic and zero-point Energies= -4111.191857
Sum of electronic and thermal Energies= -4111.168098
Sum of electronic and thermal Enthalpies= -4111.167153
Sum of electronic and thermal Free Energies= -4111.247236
Electronic energy (RM06) -4113.79712573

C	3.58180500	-1.14294900	-0.26749200
C	4.95651400	-1.15082400	0.05757800
C	5.58610400	0.02189800	0.51754400
C	4.86968200	1.20915000	0.64764700
C	3.51369100	1.22760100	0.30193500
C	2.87950200	0.04055300	-0.15038600
H	3.10536600	-2.05919800	-0.60396000
H	6.64123700	-0.01016100	0.76976100

H	5.36515900	2.10731800	1.00547700
C	2.55488500	2.32304700	0.27581800
H	2.78970700	3.35145800	0.52349400
C	1.36923500	1.84153100	-0.17613800
C	1.40928200	0.33690500	-0.32867300
C	0.62148100	-0.13888300	-1.54197400
H	0.90539500	-0.03666700	0.58604800
C	-0.54887000	1.97725000	-1.54830600
C	-0.14025800	0.81711100	-2.25520000
H	-1.32720800	2.62242700	-1.93963100
H	-0.53368200	0.62721200	-3.24762500
C	-0.29222400	3.63298600	0.25997300
H	0.52939100	4.30921800	0.50832200
H	-1.03766700	4.18726800	-0.31645000
H	-0.74542200	3.23879500	1.17634300
N	0.21014000	2.52132000	-0.54713200
C	-4.55549600	-1.41075000	0.15059300
C	-3.52361700	-2.26388900	0.90544100
H	-5.43806600	-1.23463300	0.77397800
H	-4.89420400	-1.93076500	-0.75427200
H	-3.24820100	-1.77923600	1.84703000
H	-3.92627800	-3.25979800	1.11823900
P	-3.82797600	0.22143100	-0.42974700
H	-4.84095200	0.60868200	-1.34918000
H	-4.16782200	1.10660900	0.61308900
P	-1.92415400	-2.38021100	-0.05412600
H	-1.06753300	-3.00200400	0.87797300
H	-2.17137300	-3.51384200	-0.87727900
Pd	-1.50522000	-0.16793500	-0.85745000
Br	-1.28717900	0.33718800	2.07577500
H	0.94276700	-1.04606200	-2.04429400
C	5.71180600	-2.35895400	-0.08124500
N	6.32294300	-3.34305800	-0.19874100

C-TS

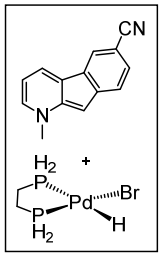


Zero-point correction= 0.305462 (Hartree/Particle)
Thermal correction to Energy= 0.330032
Thermal correction to Enthalpy= 0.330976
Thermal correction to Gibbs Free Energy= 0.246675
Sum of electronic and zero-point Energies= -4111.182954
Sum of electronic and thermal Energies= -4111.158384
Sum of electronic and thermal Enthalpies= -4111.157440
Sum of electronic and thermal Free Energies= -4111.241741
Electronic energy (RM06) -4113.77370477

C	1.92566200	2.12497100	0.81830900
C	2.51023000	3.38495900	0.59423800
C	3.55422200	3.52754700	-0.34957500
C	4.02892400	2.43655500	-1.06459100
C	3.46586500	1.16957400	-0.83829400
C	2.41133300	1.03695300	0.11066400
H	1.10996500	2.02175200	1.52793700
H	3.98309300	4.51178700	-0.50957400
H	4.83162900	2.56499400	-1.78518800

C	3.79021900	-0.12421100	-1.39475300
H	4.58601400	-0.31446100	-2.10278400
C	2.96908400	-1.05503600	-0.80999300
C	1.99703200	-0.38595300	0.11300400
C	1.44987900	-1.17111700	1.19207300
H	0.88256900	-0.32228000	-0.88933700
C	2.26667700	-3.16648400	0.04317900
C	1.58041400	-2.59996100	1.07953400
H	2.32964700	-4.24060400	-0.08454300
H	1.08705700	-3.23616600	1.80375900
C	3.87105900	-3.07142700	-1.83502800
H	4.91572200	-2.87893800	-1.56059700
H	3.69246900	-4.14772400	-1.83109900
H	3.69457300	-2.68230300	-2.84289100
N	2.96612600	-2.42637800	-0.89074300
Br	-1.98531100	-1.49503700	1.91125100
C	-3.45106300	0.74145900	-0.82477600
C	-4.72147500	0.78983600	-1.68148100
H	-3.66448300	0.44256600	0.20765200
H	-2.96409800	1.72322700	-0.77594500
H	-4.47266400	1.04436200	-2.71910500
H	-5.21189900	-0.18886500	-1.69225400
P	-2.16512900	-0.46021600	-1.41243800
H	-2.93508300	-1.61609700	-1.66928000
H	-1.98133700	-0.04375500	-2.75446800
P	-5.90307000	2.13282300	-1.06841700
H	-7.02880000	1.72806800	-1.84354400
H	-6.35080100	1.44978300	0.09901200
Pd	-0.38741100	-0.82906600	0.03730800
H	1.19909700	-0.71648500	2.14513800
C	2.04551600	4.52976800	1.31622100
N	1.67182500	5.46506000	1.90040000

D



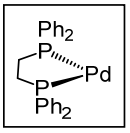
Zero-point correction= 0.307794 (Hartree/Particle)
Thermal correction to Energy= 0.331737
Thermal correction to Enthalpy= 0.332681
Thermal correction to Gibbs Free Energy= 0.241634
Sum of electronic and zero-point Energies= -4111.207245
Sum of electronic and thermal Energies= -4111.183302
Sum of electronic and thermal Enthalpies= -4111.182358
Sum of electronic and thermal Free Energies= -4111.273405
Electronic energy (RM06) -4113.80227377

C	27.78983800	-0.78599700	-0.44132300
C	28.90625700	0.01708700	-0.71838900
C	28.80149400	1.43096100	-0.65296500
C	27.60649200	2.04585400	-0.31706500
C	26.47489500	1.25675500	-0.03544400
C	26.58630000	-0.17412400	-0.10358600
H	27.87988400	-1.86731700	-0.49399900

H	29.68037200	2.02945100	-0.87211000
H	27.54767500	3.13008100	-0.27251000
C	25.13385900	1.61885100	0.33261900
H	24.76549400	2.62811100	0.45782700
C	24.43117200	0.43864800	0.48830600
C	25.28779800	-0.71727700	0.22832400
C	24.77684900	-1.98640600	0.32933000
C	22.62726400	-1.05380000	0.92763700
C	23.41300200	-2.15478100	0.68798400
H	21.58223800	-1.13505400	1.20350300
H	22.97608900	-3.14232000	0.77703700
C	22.26227600	1.37775600	1.09197900
H	22.22040600	2.01375200	0.20118200
H	21.25533000	1.04499600	1.34808900
H	22.67443500	1.96340000	1.92075900
N	23.11181300	0.21977300	0.83368600
H	25.39661100	-2.85887300	0.13991700
C	30.15362400	-0.58923300	-1.06767600
N	31.16969900	-1.08302700	-1.35212400
C	-24.27916500	-0.30296800	0.61632900
H	-25.18939500	-0.87571400	0.41323500
H	-24.24790700	-0.11319100	1.69603400
C	-24.30161500	1.03123100	-0.15395400
H	-24.46244100	0.84808800	-1.22319900
H	-25.11947500	1.67076000	0.19436900
P	-22.73180100	-1.28795300	0.20309100
P	-22.65650500	1.92208000	-0.01871800
H	-23.16795300	-2.05827300	-0.90140000
H	-22.77936400	-2.31036400	1.17760900
H	-22.80138400	2.95827400	-0.96636900
H	-22.81961200	2.69306100	1.15586000
Pd	-20.96032900	0.39066000	-0.09848200
H	-19.93172800	1.55080200	-0.30569200
Br	-18.98434800	-1.09498600	-0.21511800

Pd species from scheme 2.9

A+ and A: Pd

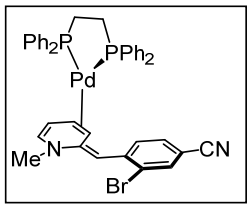


Zero-point correction= 0.424896 (Hartree/Particle)
Thermal correction to Energy= 0.451963
Thermal correction to Enthalpy= 0.452907
Thermal correction to Gibbs Free Energy= 0.361974
Sum of electronic and zero-point Energies= -1814.261653
Sum of electronic and thermal Energies= -1814.234586
Sum of electronic and thermal Enthalpies= -1814.233642
Sum of electronic and thermal Free Energies= -1814.324575
Electronic energy (RM06) -1814.17569916

Pd	-0.00015900	-0.06189200	1.70892000
C	-0.68426300	0.32921700	-1.35442500
H	-1.24022000	0.07226900	-2.26432200
H	-0.51249800	1.41098400	-1.38208000
C	0.66399200	-0.41878500	-1.33896100
H	0.49321500	-1.50097100	-1.29118300
H	1.20927000	-0.23610400	-2.27359100

P	-1.74763000	-0.01112600	0.17713600
P	1.73369100	-0.03138500	0.16837800
C	-3.08471500	1.25084300	-0.05438400
C	-2.72301200	2.61015900	-0.09006100
C	-4.45037200	0.92674700	-0.07673900
C	-3.69214200	3.60797100	-0.17846800
H	-1.67482300	2.89483100	-0.03404400
C	-5.42120800	1.92812600	-0.15616700
H	-4.76268000	-0.11176700	-0.03326500
C	-5.04791700	3.27098600	-0.21383100
H	-3.38789700	4.65108900	-0.21227600
H	-6.47295500	1.65326400	-0.17464200
H	-5.80426300	4.04866300	-0.27766400
C	-2.55923000	-1.61110000	-0.28320600
C	-3.19471600	-1.82703300	-1.51841900
C	-2.51112100	-2.66722000	0.63839900
C	-3.76339200	-3.06432700	-1.82114500
H	-3.26059700	-1.02105200	-2.24458000
C	-3.07969700	-3.90752100	0.33740400
H	-2.01942300	-2.50847300	1.59514700
C	-3.70566600	-4.10811100	-0.89324700
H	-4.25236100	-3.21435100	-2.78036200
H	-3.03189600	-4.71448900	1.06386800
H	-4.14779500	-5.07227300	-1.13042600
C	3.12745100	-1.22327500	-0.11251000
C	4.22207800	-0.96413100	-0.95173200
C	3.06681400	-2.45647000	0.55563300
C	5.22552700	-1.91956800	-1.12346100
H	4.29786400	-0.01064400	-1.46645400
C	4.06310400	-3.41662100	0.37389900
H	2.23554500	-2.65475600	1.22895700
C	5.14677000	-3.14883100	-0.46524500
H	6.07027600	-1.70274500	-1.77263400
H	3.99920900	-4.36743900	0.89681500
H	5.92964300	-3.89070300	-0.59975200
C	2.48810300	1.61323800	-0.22869300
C	2.54001100	2.17984100	-1.51256800
C	3.02291900	2.34715200	0.84410700
C	3.11557300	3.43657400	-1.71790500
H	2.13172000	1.64689000	-2.36593600
C	3.61007500	3.59539600	0.63903900
H	2.96637900	1.93404800	1.84831500
C	3.65572900	4.14555300	-0.64425000
H	3.14186700	3.85926900	-2.71913900
H	4.02158300	4.14337300	1.48264000
H	4.10306100	5.12291100	-0.80479800

A''



Zero-point correction= 0.641456 (Hartree/Particle)
Thermal correction to Energy= 0.685052
Thermal correction to Enthalpy= 0.685996
Thermal correction to Gibbs Free Energy= 0.557068

Sum of electronic and zero-point Energies= -5035.041965
Sum of electronic and thermal Energies= -5034.998369
Sum of electronic and thermal Enthalpies= -5034.997425
Sum of electronic and thermal Free Energies= -5035.126353
Electronic energy (RM06) -5037.50355013

C	5.40160800	0.87020000	-0.79162300
C	5.17466900	1.99904600	-1.59938200
C	4.11551400	1.95914400	-2.52520600
C	3.29830800	0.84562400	-2.60607900
C	3.44803300	-0.29527000	-1.76707300
C	4.56876800	-0.23100700	-0.88905500
H	6.22278500	0.86730900	-0.08472800
H	3.95685600	2.79910600	-3.19460100
H	2.54444500	0.81927100	-3.38349300
C	2.60859300	-1.46464000	-1.83017700
H	3.09482400	-2.36546200	-1.48554500
C	1.26641200	-1.56386400	-2.17907600
C	0.36409100	-0.44215300	-2.41802400
C	-0.96825700	-0.62773400	-2.86828300
H	0.81991900	0.52932100	-2.53218900
C	-0.63266700	-3.01055700	-2.68836700
C	-1.45425300	-1.98207000	-3.00278900
H	-0.95135900	-4.04435500	-2.74763400
H	-2.46679200	-2.18255300	-3.33402100
Pd	-1.07538300	-0.05119700	-0.73411600
C	-1.76289400	1.05092400	2.38357700
H	-1.63647000	1.01273100	3.47222600
H	-1.78234100	2.11270100	2.10946300
C	-3.08098400	0.37996000	1.96147800
H	-3.09851300	-0.66769700	2.28155800
H	-3.93316400	0.87730200	2.43902600
P	-0.27086800	0.34330300	1.48964600
P	-3.28013600	0.38208600	0.08733700
Br	4.99181600	-1.71254000	0.26441400
C	1.48639400	-4.02201000	-2.02058000
H	1.82308600	-4.04532700	-0.97757100
H	0.88004200	-4.90861700	-2.21061700
H	2.36778700	-4.04855400	-2.67154600
N	0.68474500	-2.83333200	-2.28347500
H	-1.47866600	0.17259500	-3.39659200
C	6.00920000	3.15180400	-1.48438300
N	6.68055800	4.09945500	-1.38846200
C	-4.71443000	-0.75795700	-0.14297700
C	-4.60060300	-2.08013900	0.32471700
C	-5.86480000	-0.40280500	-0.86469300
C	-5.62023800	-3.00553100	0.10790600
H	-3.70399100	-2.39553400	0.85289800
C	-6.88145600	-1.33430500	-1.08913600
H	-5.97350700	0.60532100	-1.25171400
C	-6.76740500	-2.63535800	-0.59899400
H	-5.51551600	-4.01918000	0.48612600
H	-7.76574600	-1.03727700	-1.64718400
H	-7.56077900	-3.35755400	-0.77141100
C	-3.96513100	2.06987700	-0.21812100
C	-5.08886400	2.57468000	0.45943200
C	-3.30837700	2.89620800	-1.14168400
C	-5.54183300	3.87115000	0.21635900
H	-5.62143400	1.94992100	1.17181700
C	-3.75976800	4.19618200	-1.38393800
H	-2.43503000	2.51159400	-1.66265000

C	-4.87658800	4.68477200	-0.70554300
H	-6.41280200	4.24759700	0.74645600
H	-3.23766500	4.82485000	-2.10022900
H	-5.22906200	5.69572400	-0.89197900
C	1.04445000	1.55221900	1.95320000
C	1.62613500	2.33530300	0.94644500
C	1.47206800	1.72139200	3.28065000
C	2.60913700	3.27781800	1.25879500
H	1.31664500	2.19237100	-0.08527300
C	2.45210900	2.66301400	3.59190500
H	1.04981700	1.10597500	4.07094300
C	3.02115200	3.44373700	2.58135500
H	3.06092000	3.87017800	0.46821000
H	2.77752600	2.78379100	4.62198100
H	3.79047800	4.17186900	2.82392300
C	0.19052700	-1.15493300	2.46750400
C	-0.53866800	-1.63923600	3.56372000
C	1.32855800	-1.86861900	2.04971400
C	-0.14148900	-2.80459400	4.22670800
H	-1.42113100	-1.11434000	3.91637500
C	1.73181000	-3.02083200	2.72134800
H	1.90725100	-1.51951100	1.19838500
C	0.99507400	-3.49669900	3.81023300
H	-0.72062400	-3.16465100	5.07333100
H	2.62461300	-3.54562400	2.39157800
H	1.30615500	-4.39946400	4.32918700

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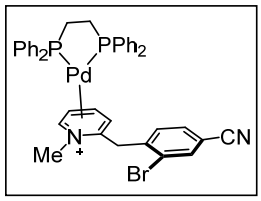

Zero-point correction= 0.654799 (Hartree/Particle)
Thermal correction to Energy= 0.698609
Thermal correction to Enthalpy= 0.699553
Thermal correction to Gibbs Free Energy= 0.568000
Sum of electronic and zero-point Energies= -5035.467829
Sum of electronic and thermal Energies= -5035.424020
Sum of electronic and thermal Enthalpies= -5035.423075
Sum of electronic and thermal Free Energies= -5035.554628
Electronic energy (RM06) -5037.97523761

C	7.12746800	0.02897200	-0.42521300
C	7.26348500	0.37804100	-1.77685400
C	6.12776900	0.73081800	-2.52109800
C	4.87808500	0.72447400	-1.91151000
C	4.70988400	0.37265700	-0.56364000
C	5.86497100	0.03107800	0.16094000
H	7.99977200	-0.23995700	0.15845700
H	6.23090800	1.00791200	-3.56466400
H	4.00512700	1.00575000	-2.49313000
C	2.15832400	0.19792500	-0.83122200
C	1.32174000	1.21318100	-1.20061900
C	0.17638100	1.02008300	-2.05687500
H	1.53227100	2.20664800	-0.81861800
C	0.88577900	-1.31801200	-2.16858200

C	0.03017800	-0.30964000	-2.60223700
H	0.77489800	-2.33512100	-2.52743500
H	-0.63071500	-0.52314900	-3.43583800
Pd	-1.35559500	0.04739400	-0.87089100
C	-3.71116600	0.69873700	1.45434600
H	-4.02901100	1.24982700	2.34702000
H	-4.58759500	0.62828800	0.79946300
C	-3.22036400	-0.71258600	1.82342200
H	-2.38381500	-0.66327800	2.52871400
H	-4.02195500	-1.27546200	2.31415600
P	-2.45162700	1.68731300	0.47787200
P	-2.60375300	-1.64268300	0.31301000
Br	5.76427800	-0.43874600	2.01333900
C	2.69298400	-2.24883900	-0.83462500
H	2.39540100	-2.49440300	0.18981800
H	2.49086500	-3.10814000	-1.47470400
H	3.76072800	-2.03058200	-0.86746200
N	1.92043600	-1.09782100	-1.32998800
H	-0.22975400	1.87652800	-2.58513000
C	3.33254000	0.41205300	0.09081000
H	3.19833600	1.39051500	0.56809700
H	3.30717500	-0.30982800	0.91364400
C	8.56022500	0.37099900	-2.38908700
N	9.60900400	0.36329100	-2.89064200
C	-4.13364900	-2.31830300	-0.44147600
C	-4.38288000	-2.06664100	-1.79922600
C	-5.07641200	-3.05306100	0.29965200
C	-5.54926200	-2.53720600	-2.40647600
H	-3.66062500	-1.49552100	-2.37724800
C	-6.24019700	-3.52253100	-0.30793900
H	-4.89878300	-3.27128200	1.34943800
C	-6.47827200	-3.26411000	-1.66122200
H	-5.73151300	-2.33463100	-3.45798700
H	-6.96137800	-4.08987000	0.27334600
H	-7.38664400	-3.62956200	-2.13144000
C	-1.69679600	-3.07506400	1.03103900
C	-0.61804900	-2.82154000	1.89811000
C	-1.97844200	-4.40233500	0.67507000
C	0.14194500	-3.87073600	2.41368300
H	-0.36883700	-1.80000700	2.17681200
C	-1.20867300	-5.45114400	1.18577000
H	-2.80220100	-4.62375000	0.00423200
C	-0.15122200	-5.19078200	2.05735500
H	0.95839100	-3.65956600	3.09925300
H	-1.44405200	-6.47375900	0.90456300
H	0.43960000	-6.00855200	2.45966400
C	-3.45484000	3.01068800	-0.30298400
C	-3.95062800	4.09962000	0.43367400
C	-3.76931400	2.90541400	-1.66651900
C	-4.74948900	5.06002600	-0.18643700
H	-3.70650600	4.20350700	1.48709900
C	-4.57265000	3.86632600	-2.28318400
H	-3.38192100	2.06831600	-2.24264800
C	-5.06197100	4.94441200	-1.54373700
H	-5.12768900	5.89963700	0.38973700
H	-4.80998500	3.77628600	-3.33943000
H	-5.68254000	5.69571900	-2.02362000
C	-1.41498900	2.56140500	1.71778900
C	-0.56288200	3.58669000	1.26736900
C	-1.38707200	2.21113200	3.07605600
C	0.28286500	4.24956600	2.15478200

H	-0.58128100	3.88464600	0.22186700
C	-0.53149900	2.87107900	3.96245500
H	-2.03702400	1.43133000	3.46028000
C	0.30399100	3.89024200	3.50587700
H	0.92039100	5.05225200	1.79447600
H	-0.52816500	2.59216000	5.01239600
H	0.96301600	4.40682700	4.19750600

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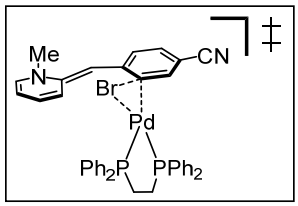

Zero-point correction= 0.640218 (Hartree/Particle)
Thermal correction to Energy= 0.683690
Thermal correction to Enthalpy= 0.684634
Thermal correction to Gibbs Free Energy= 0.556466
Sum of electronic and zero-point Energies= -5035.018761
Sum of electronic and thermal Energies= -5034.975290
Sum of electronic and thermal Enthalpies= -5034.974345
Sum of electronic and thermal Free Energies= -5035.102513
Electronic energy (RM06) -5037.48285224

C	0.36223000	2.71984900	-1.60061300
C	-0.06233800	4.00336300	-1.18952200
C	-1.41751300	4.20246300	-0.88741500
C	-2.32073300	3.14675400	-0.97900600
C	-1.93875300	1.82745500	-1.31771000
C	-0.53826000	1.64754500	-1.57378000
H	1.37569200	2.57648600	-1.95812200
H	-1.76965000	5.19646200	-0.63007500
H	-3.37248100	3.35934800	-0.82139100
C	-2.85195500	0.72043000	-1.46200900
H	-2.47805500	-0.06063900	-2.10989900
C	-4.09543300	0.54989500	-0.88016200
C	-4.61985100	1.31248400	0.23081800
C	-5.84826900	1.07545100	0.77112500
H	-3.96743300	2.05229200	0.67462800
C	-6.17761200	-0.71203500	-0.77491000
C	-6.67909700	0.04110700	0.24246100
H	-6.73191000	-1.53494300	-1.21173100
H	-7.66590200	-0.16509700	0.63856900
Pd	0.75147200	0.33139600	-0.55821400
C	0.87480400	-1.86948500	2.01686100
H	0.55468500	-2.20368000	3.01027200
H	0.99007300	-2.76800400	1.40027600
C	2.21704300	-1.12754400	2.11291900
H	2.11463600	-0.23627900	2.74407200
H	2.96555100	-1.78062100	2.57754900
P	-0.47969000	-0.82545900	1.21736000
P	2.77307000	-0.53938200	0.42392300
Br	0.03758200	0.15999300	-3.17927300
C	-4.49074600	-1.35679000	-2.41084400
H	-3.62554000	-1.94998400	-2.09658500
H	-5.30100300	-2.03163200	-2.69071300
H	-4.20643000	-0.75212700	-3.27857200
N	-4.94415600	-0.49045700	-1.32720200

H	-6.18446000	1.65796200	1.62440200
C	-1.75954500	-2.13397800	0.94047900
C	-1.43461400	-3.20048000	0.08086200
C	-3.05631600	-2.08022100	1.47369300
C	-2.36391800	-4.19993700	-0.20377900
H	-0.45040400	-3.24675500	-0.37916300
C	-3.99003800	-3.07784900	1.18033300
H	-3.34541900	-1.25694900	2.11819300
C	-3.64720600	-4.14469200	0.34876100
H	-2.08639500	-5.02073200	-0.86026500
H	-4.98824700	-3.01540300	1.60596500
H	-4.37169000	-4.92452200	0.12887900
C	-1.10105800	0.14714200	2.66159000
C	-1.15917000	1.54395000	2.54137600
C	-1.46556000	-0.44022400	3.88617900
C	-1.57175900	2.33530000	3.61719400
H	-0.87419500	2.01089900	1.60300400
C	-1.87818100	0.34917100	4.95937300
H	-1.43651000	-1.52064400	4.00188500
C	-1.93102200	1.73989700	4.82653100
H	-1.60532700	3.41592900	3.50789000
H	-2.15606600	-0.11981400	5.89982700
H	-2.24838400	2.35451700	5.66486700
C	3.50315000	-2.07258400	-0.31121600
C	2.90247000	-2.60751200	-1.46083100
C	4.61996800	-2.72280700	0.23823200
C	3.40094300	-3.77738800	-2.04122700
H	2.05222800	-2.09485800	-1.90490300
C	5.11710700	-3.88899500	-0.34239500
H	5.11485600	-2.30924400	1.11327400
C	4.50597600	-4.41997500	-1.48233500
H	2.92867600	-4.17926500	-2.93382700
H	5.98444200	-4.38124600	0.09000900
H	4.89661100	-5.32725400	-1.93575100
C	4.23548200	0.52197200	0.78933700
C	4.95533300	0.47541200	1.99426400
C	4.63620600	1.43671200	-0.19844700
C	6.05060000	1.31698600	2.20081500
H	4.66464300	-0.21142600	2.78372600
C	5.73580500	2.27008200	0.00431900
H	4.07317600	1.50234900	-1.12619600
C	6.44518400	2.21276100	1.20605300
H	6.59353800	1.27232900	3.14142300
H	6.02856800	2.97377300	-0.76995100
H	7.29533800	2.86943900	1.36956900
C	0.86622200	5.08849400	-1.14693000
N	1.62580700	5.97115500	-1.10432400

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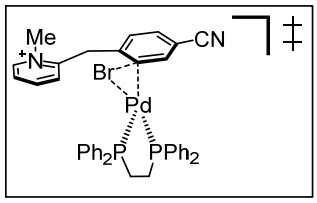

Zero-point correction= 0.653770 (Hartree/Particle)
Thermal correction to Energy= 0.697340

Thermal correction to Enthalpy= 0.698284
Thermal correction to Gibbs Free Energy= 0.569035
Sum of electronic and zero-point Energies= -5035.435488
Sum of electronic and thermal Energies= -5035.391918
Sum of electronic and thermal Enthalpies= -5035.390974
Sum of electronic and thermal Free Energies= -5035.520223
Electronic energy (RM06) -5037.48285224

C	-0.27579000	2.57972200	-1.21686800
C	-0.44329300	3.84926400	-0.62012900
C	-1.52515300	4.09324500	0.23223100
C	-2.45075800	3.06729000	0.47666300
C	-2.30533400	1.79745100	-0.07499100
C	-1.14565700	1.52916900	-0.85100100
H	0.48615900	2.43433400	-1.97472000
H	-1.65978500	5.07390900	0.67444400
H	-3.29176000	3.26405800	1.13844600
C	-4.28612900	0.49273100	-0.95183000
C	-4.83938400	1.58005000	-1.63305600
C	-5.77272000	1.39625300	-2.64381000
H	-4.50077500	2.57241600	-1.36000200
C	-5.61016400	-0.95741800	-2.28897300
C	-6.16472100	0.09721300	-2.98114400
H	-5.86544000	-1.98781400	-2.50086200
H	-6.88572800	-0.10012700	-3.76585600
Pd	0.46489300	0.27966800	-0.35220400
C	1.66518400	-1.85228700	2.00270500
H	1.77723100	-2.14298600	3.05304700
H	1.53265500	-2.77228800	1.42279900
C	2.91297700	-1.09943700	1.51429800
H	3.05079800	-0.17353700	2.08492800
H	3.81143400	-1.70501300	1.67596600
P	0.10843400	-0.81573800	1.80211200
P	2.73519200	-0.57798300	-0.27361900
Br	-1.36292400	0.07014700	-2.48122700
C	-4.11938200	-1.95821500	-0.63950200
H	-4.26540400	-1.91403100	0.44019300
H	-4.61844300	-2.84261800	-1.03262800
H	-3.05404400	-2.00172000	-0.87482200
N	-4.70319600	-0.76131300	-1.29404000
H	-6.18907400	2.25171500	-3.16629000
C	-3.30608900	0.69630200	0.19042900
H	-3.89566100	0.93587400	1.08676300
H	-2.76507400	-0.22536400	0.40730300
C	0.49235000	4.89388300	-0.92149100
N	1.26750600	5.72883900	-1.15556200
C	4.17595900	0.53143500	-0.54972000
C	3.98329400	1.91033200	-0.36345700
C	5.44470300	0.06520600	-0.92727800
C	5.04135400	2.80391800	-0.53097900
H	2.99806200	2.28597600	-0.09691100
C	6.49970200	0.96204300	-1.10159200
H	5.60985800	-0.99389200	-1.09929900
C	6.30168700	2.32994000	-0.90098500
H	4.87554100	3.86791200	-0.38792500
H	7.47667000	0.59089000	-1.39859100
H	7.12449700	3.02501800	-1.04204400
C	3.06433300	-2.10440100	-1.24701300
C	2.41305700	-2.23536000	-2.48526700
C	3.92442200	-3.13224500	-0.82477800
C	2.62958100	-3.35590400	-3.28831000

H	1.73100700	-1.45618200	-2.81628100
C	4.13264800	-4.25728100	-1.62497200
H	4.44321600	-3.06335400	0.12708500
C	3.48878000	-4.36943700	-2.85901700
H	2.12427900	-3.43832100	-4.24659600
H	4.80120400	-5.04343800	-1.28523000
H	3.65520300	-5.24393700	-3.48169400
C	0.16290000	0.25878100	3.29790800
C	0.18776500	1.65085500	3.12473300
C	0.24156100	-0.26546800	4.60124200
C	0.29054900	2.50243400	4.22796500
H	0.13664300	2.06497300	2.12147400
C	0.33998400	0.58545600	5.70116400
H	0.21827600	-1.34034800	4.76097300
C	0.36608600	1.97121400	5.51557000
H	0.31544600	3.57821000	4.07880800
H	0.40086300	0.16863000	6.70258000
H	0.44798200	2.63216100	6.37379700
C	-1.22625100	-2.04835000	2.14885900
C	-2.27766500	-1.78749600	3.04482600
C	-1.25941100	-3.24958000	1.41430900
C	-3.31547300	-2.70846900	3.21772000
H	-2.27698800	-0.87256200	3.62917500
C	-2.28945700	-4.17321900	1.59675400
H	-0.47480800	-3.47352300	0.69601800
C	-3.32248800	-3.90751200	2.50128400
H	-4.10700800	-2.49549100	3.93153900
H	-2.27836900	-5.10653000	1.03989200
H	-4.11726400	-4.63238000	2.65367900

Transition State Computational Studies for the Asymmetric Hydrogenation Reaction

All optimizations and transition state searches were performed with the Gaussian 09 program[2] on a Unix HPC platform. All structures were optimized at the B3LYP[3] level of theory employing the LANL2DZ basis set with ECP for Ir[4] and D95v for the remaining atoms.[9] All optimized structures were subjected to a frequency test to verify a single imaginary frequency was found (Transition states) and that the imaginary vibrational mode corresponds with the expected reaction pathway. All stable structures were subjected to a frequency test to verify no imaginary frequencies. The resulting transition state structures was subjected to an IRC calculation (B3LYP/LANL2DZ) to verify a clean reaction pathway from the starting material to the respected product. An outer-sphere dissociated mechanism[10] similar to the DFT computed Ir-hydrogenation mechanism of imines[11] and quinolines[12] was used as the basis for the computational studies of the asymmetric Ir-hydrogenation of the enamine intermediate (Figure 1). An iodo-Ir complex was found to be a viable catalyst for the sequential protonation and hydride delivery pathway for the enamine hydrogenation with a maximum energy barrier of 26 kcal/mol. A second hydrogenation pathway with an associated immonium intermediate was shown to be energetically infeasible.

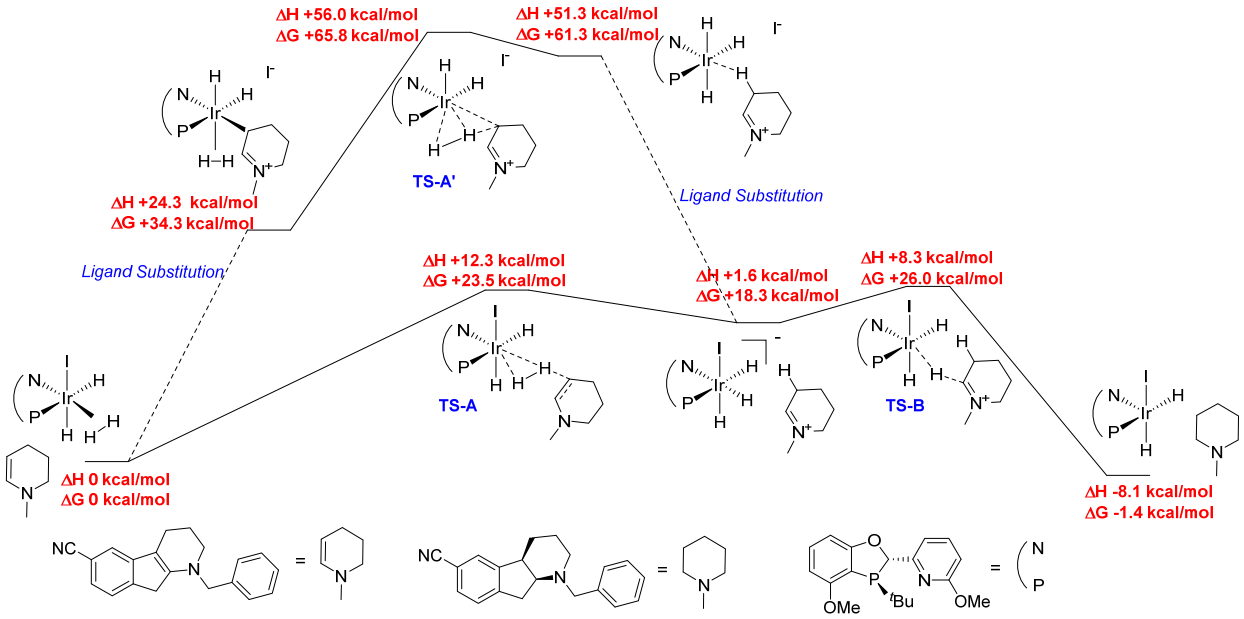

Figure. Reaction pathways for the Ir-BI-Ligand Asymmetric Hydrogenation (B3LYP/LANL2DZ CPCM=THF, 323.15 K, 1 atm).

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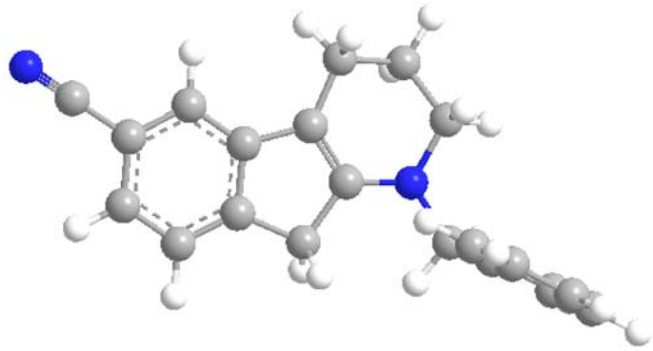
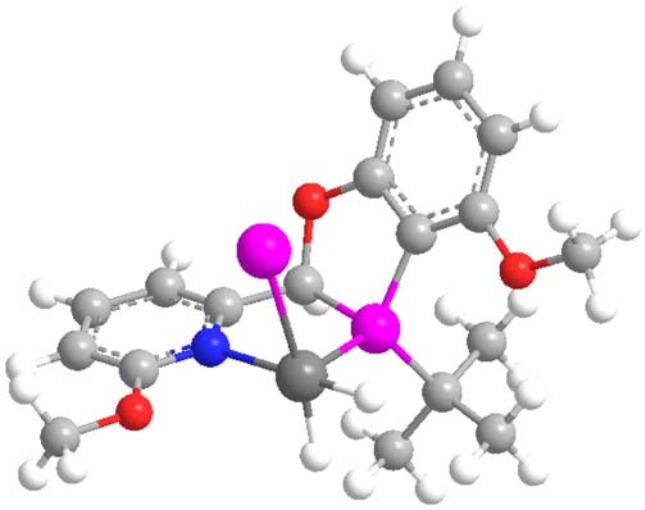


SCF Done: E(RB3LYP) = -882.325543886 A.U.
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.332478 (Hartree/Particle)
Zero-point correction= 0.332478 (Hartree/Particle)
Thermal correction to Energy= 0.350185
Thermal correction to Enthalpy= 0.351129
Thermal correction to Gibbs Free Energy= 0.284661
Sum of electronic and zero-point Energies= -881.993066
Sum of electronic and thermal Energies= -881.975359
Sum of electronic and thermal Enthalpies= -881.974415
Sum of electronic and thermal Free Energies= -882.040883

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.332478 (Hartree/Particle)
Thermal correction to Energy= 0.353120
Thermal correction to Enthalpy= 0.354143
Thermal correction to Gibbs Free Energy= 0.278966

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.912518043502	-9.449334683573	-2.607063805684
C	4.638238808500	-8.314718035112	-2.173560597918
C	4.276215436728	-7.688105753906	-0.982829426523
C	3.184352392712	-8.166925273679	-0.189194319710
C	2.455832497188	-9.293892167828	-0.612898414895
C	2.831163884583	-9.928549235229	-1.827760450092
H	4.177954596277	-9.954033817477	-3.530905713817
H	5.467022531558	-7.944349805790	-2.771500312950
H	1.623590441264	-9.681134061730	-0.032327226328
C	3.038723164789	-7.321312109579	0.987653929112
C	1.999198797431	-7.394271298319	2.080461958400
C	4.011668572013	-6.336592372749	0.948820343065
C	1.907713584882	-6.014458867863	2.782845060787
H	1.016044620837	-7.662059540116	1.667110381745
C	3.307016255041	-5.452329481334	3.118892468282
H	1.386892928722	-5.304861846954	2.125950766558
H	3.790447869761	-6.091752161833	3.874767197085
C	4.876318502161	-6.468202940239	-0.301368452344
H	5.939184287583	-6.613901975192	-0.063849735227
H	4.813726195841	-5.578197616068	-0.943334588254
H	3.215959435309	-4.447148564398	3.548700722471
H	1.328972322033	-6.093129196027	3.711581702304
H	2.245467397665	-8.175204439876	2.817141735744
N	4.162623616202	-5.360724693232	1.911933239206
C	2.099182336886	-11.083266127541	-2.278216792131
N	1.495659927355	-12.033200887651	-2.647431317011
C	5.246493858585	-4.372203003280	1.904152152893
H	4.826401982791	-3.378237476730	2.112776219555
H	5.666114856282	-4.323950122992	0.892748266428
C	6.375368070384	-4.649620781804	2.904201949514
C	7.049554085665	-3.571415401569	3.517053262862
C	6.784767077269	-5.967760147440	3.201942370992

B



SCF Done: E(RB3LYP) = -1103.29465932
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.390330 (Hartree/Particle)
Thermal correction to Energy= 0.417522
Thermal correction to Enthalpy= 0.418466
Thermal correction to Gibbs Free Energy= 0.331744
Sum of electronic and zero-point Energies= -1102.904329
Sum of electronic and thermal Energies= -1102.877137
Sum of electronic and thermal Enthalpies= -1102.876193
Sum of electronic and thermal Free Energies= -1102.962915

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.390330 (Hartree/Particle)
Thermal correction to Energy= 0.421711
Thermal correction to Enthalpy= 0.422734
Thermal correction to Gibbs Free Energy= 0.324301

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-9.629203015655	9.426970111035	3.102639345095
C	-8.770168061647	10.014148900830	2.149654171053
C	-8.600882831592	9.403449140794	0.891399715684
C	-9.283545327242	8.208096669312	0.609788796267
C	-10.145124078856	7.599779742616	1.534899797214
C	-10.302640408459	8.229732073697	2.781608329951
H	-9.777520295106	9.880580972412	4.075739439105
H	-10.657919821812	6.676734560158	1.288412215372
H	-10.960839335405	7.782945605492	3.521937410465
O	-8.052423901974	11.185946212940	2.353063404586
C	-8.134359430811	11.857056474342	3.655563852264
H	-7.782011629814	11.195165581296	4.455008045560
H	-7.476097031944	12.722733859319	3.571359399468
H	-9.160424629072	12.185198322957	3.859895482595
O	-9.065202220030	7.613156580860	-0.643728331748
C	-8.208923162929	8.425944256709	-1.548466880761
P	-7.483607982180	9.879794162226	-0.501197855788
C	-8.071001092458	11.537361425196	-1.330576069172
C	-7.398213749867	12.718354464537	-0.590830064431
H	-7.720374656950	13.655233516470	-1.064982673609
H	-7.681642333184	12.745859849367	0.465994982042
H	-6.306244714605	12.657346575225	-0.656715074323
C	-9.611684179224	11.632040682383	-1.226469706912
H	-9.938524492267	12.547303741828	-1.737572335657
H	-10.119040319822	10.786285248306	-1.707764348423
H	-9.945707693246	11.688089779622	-0.184852393940
C	-7.620722760455	11.515513303928	-2.812392168162
H	-6.536105477124	11.388843610878	-2.903494466086
H	-8.115738828903	10.726625367210	-3.392105946793
H	-7.889528369091	12.476652406809	-3.269392299843
C	-7.130488510452	7.548514669984	-2.148185917569
C	-7.478755566534	6.534179622134	-3.050719781256
C	-6.463082159401	5.726670553955	-3.596296810912
H	-8.518836518991	6.380953487791	-3.314415311594
C	-4.848134461248	7.016005687719	-2.350770101698
C	-5.126952827379	5.967162282365	-3.250511499449
H	-6.707733987289	4.927870213836	-4.289153352272
N	-5.825995104449	7.775517182594	-1.791129841859
Ir	-5.294848017088	9.327146352755	-0.339587266642
O	-3.587139969153	7.389710786875	-1.956329707971
C	-2.420950467355	6.618679178328	-2.415855600942
H	-2.327739003241	6.676857544898	-3.506001966879

H	-2.496817290608	5.575602031911	-2.089431704271
H	-1.565253385657	7.098421113106	-1.941085500882
H	-5.067902094983	10.420149917351	-1.473145150543
I	-5.095471417734	7.378223218293	1.788051819586
H	-4.936171784350	10.484610536786	0.709833853108
H	-4.330045068633	5.367047901972	-3.671233776206
H	-8.871236573729	8.803558248591	-2.333484732821

Iodide

SCF Done: E(RB3LYP) = -11.5603193090 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016848
Sum of electronic and zero-point Energies= -11.560319
Sum of electronic and thermal Energies= -11.558903
Sum of electronic and thermal Enthalpies= -11.557959
Sum of electronic and thermal Free Energies= -11.577168

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001535
Thermal correction to Enthalpy= 0.002558
Thermal correction to Gibbs Free Energy= -0.018467

Atomic Type	Coordinates (Angstroms) X	Y	Z
I	0.381558050000	1.359300460000	0.000000000000

Hydrogen

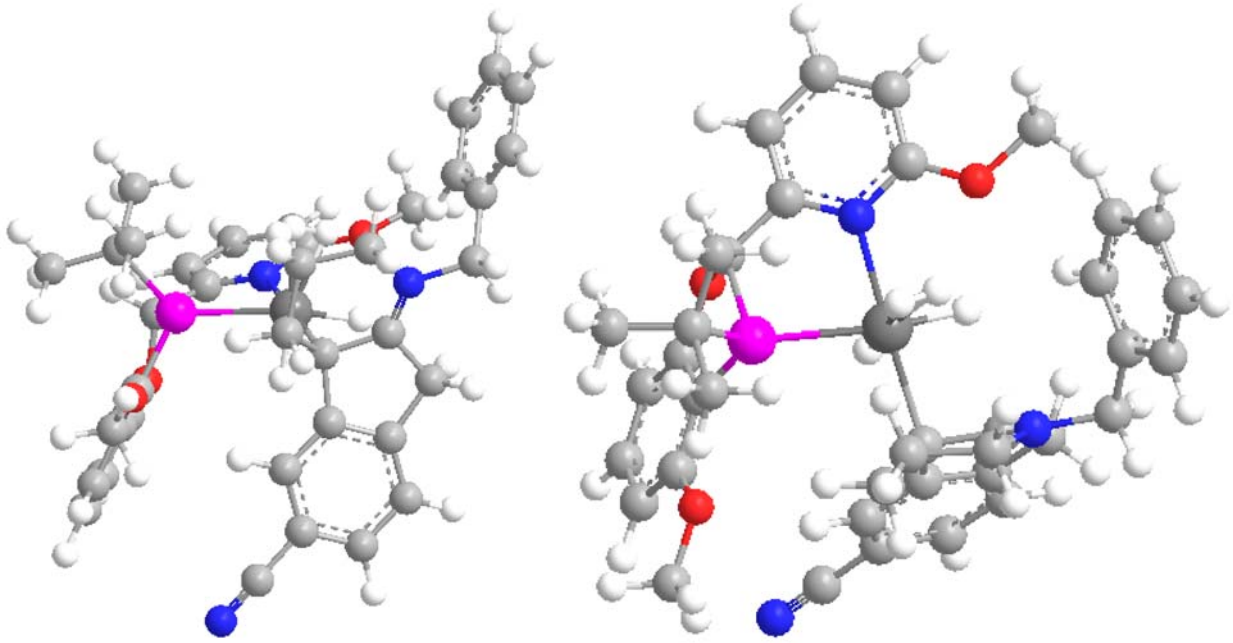
SCF Done: E(RB3LYP) = -1.17449948 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.010144 (Hartree/Particle)
Thermal correction to Energy= 0.012504
Thermal correction to Enthalpy= 0.013449
Thermal correction to Gibbs Free Energy= -0.001346
Sum of electronic and zero-point Energies= -1.164356
Sum of electronic and thermal Energies= -1.161995
Sum of electronic and thermal Enthalpies= -1.161051
Sum of electronic and thermal Free Energies= -1.175845

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
ero-point correction= 0.010144 (Hartree/Particle)
Thermal correction to Energy= 0.012702
Thermal correction to Enthalpy= 0.013726
Thermal correction to Gibbs Free Energy= -0.002598

Atomic Type	Coordinates (Angstroms) X	Y	Z
H	0.000000000000	0.000000000000	0.371854993324
H	0.000000000000	0.000000000000	-0.371854993324

c



SCF Done: E(RB3LYP) = -1975.20915297

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.741726 (Hartree/Particle)
Thermal correction to Energy= 0.786682
Thermal correction to Enthalpy= 0.787626
Thermal correction to Gibbs Free Energy= 0.662167
Sum of electronic and zero-point Energies= -1974.467427
Sum of electronic and thermal Energies= -1974.422471
Sum of electronic and thermal Enthalpies= -1974.421527
Sum of electronic and thermal Free Energies= -1974.546986

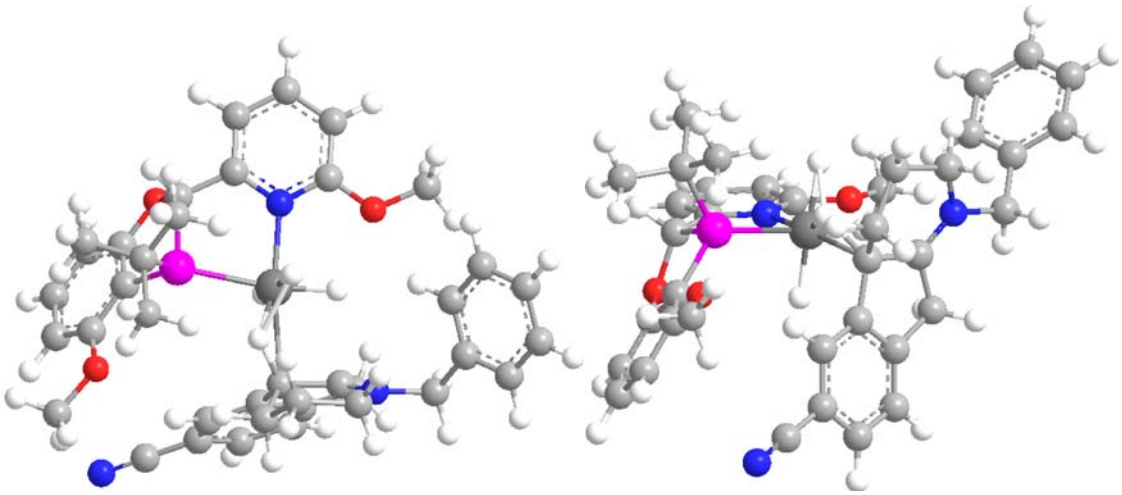
Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.741726 (Hartree/Particle)
Thermal correction to Energy= 0.793959
Thermal correction to Enthalpy= 0.794983
Thermal correction to Gibbs Free Energy= 0.651350

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.291255674602	-0.857548919735	0.359346526646
C	-4.039076332522	-0.562490614186	0.941322923831
C	-3.284371460804	0.529760508979	0.474807452764
C	-3.793070373996	1.297805351179	-0.588166514066
C	-5.024983367868	1.025096499045	-1.199542153175
C	-5.764879864929	-0.063738395282	-0.704784152585
H	-5.889768152891	-1.688502992965	0.714201291028
H	-5.385030755713	1.640375218782	-2.016784688222
H	-6.726800829746	-0.300660258364	-1.150884320622
O	-3.462260590435	-1.304281692899	1.972964614606
C	-4.221062524167	-2.414253814797	2.563234500020
H	-3.579655612224	-2.810933898740	3.351513408542
H	-5.163081091163	-2.053817438569	2.992570166775
H	-4.420606409004	-3.192807178178	1.817675676502
O	-2.990096924542	2.359333061779	-1.042407967980

C	-1.934946655194	2.712673089367	-0.051782909166
H	-2.360483358607	3.499150987115	0.579823979500
P	-1.590925859098	1.125153569079	0.983992109498
C	-1.694475541099	1.781020905027	2.832364431099
C	-1.386558668492	0.607334069181	3.793241367500
H	-2.099086185158	-0.213145040598	3.664695350562
H	-0.372408394881	0.220881744807	3.647164740059
H	-1.457827439583	0.971857251678	4.827111528581
C	-3.097065738888	2.352460380999	3.138268819285
H	-3.380044059552	3.174513250780	2.469817722833
H	-3.869331734375	1.578118368023	3.075726262122
H	-3.098423648512	2.749511864872	4.162778837664
C	-0.607306411892	2.875772384833	2.980117961282
H	-0.823897623478	3.767690794015	2.379372800190
H	-0.565055192736	3.191316228212	4.030972477159
H	0.387773844654	2.503877098378	2.704224269707
C	-0.733450421057	3.258838745663	-0.776729184582
C	-0.790466838880	4.578681599570	-1.239096828955
C	0.321469317907	5.129783262962	-1.898156893659
H	-1.692547926231	5.158360755095	-1.081959520235
C	1.480800556491	3.032339093280	-1.539773557823
C	1.472359941318	4.353205760460	-2.041400922705
H	0.296977656693	6.146624562414	-2.275947181131
H	2.352111642216	4.762221974392	-2.520041136368
N	0.384389194118	2.468112331636	-0.944124825328
Ir	0.366397751283	0.380062188607	-0.385692351361
O	2.591776222161	2.232605183485	-1.599602439379
C	3.794353923907	2.714878774256	-2.302549975829
H	4.216329750448	3.588601605992	-1.794043994748
H	4.493725315338	1.880607417226	-2.256118396043
H	3.562517250668	2.949457638223	-3.346845287590
C	-1.632420702773	-3.593955986191	-3.423449433555
C	-0.244681617778	-3.361724516689	-3.369647052208
C	0.308210133835	-2.818642437673	-2.205013194701
C	-0.501867181407	-2.461026330064	-1.098271862614
C	-1.877661951005	-2.712641188988	-1.130683043931
C	-2.440097068714	-3.285325486369	-2.301087920867
H	-2.084482283470	-4.026490324590	-4.310716989655
H	0.382103288975	-3.624881903158	-4.217314995107
H	-2.510276356506	-2.476663381334	-0.282792830218
C	0.330325573692	-1.841999481788	0.001307504471
C	0.009268859347	-2.251986797323	1.451112745085
C	1.706525753469	-2.179722647321	-0.407815387000
C	1.160105773629	-1.855653570112	2.397249794839
H	-0.927707146755	-1.802171745181	1.789310968487
C	2.531097770445	-2.366104052120	1.920822271804
H	1.192939472224	-0.767485944385	2.498553645126
H	2.673177952288	-3.417885944889	2.204868820653
C	1.772096416942	-2.580977529669	-1.882494281130
H	2.362714727348	-3.495906208578	-2.012926253642
H	2.227005826376	-1.806559098937	-2.510366594172
H	3.335867791068	-1.787224109270	2.383558038811
H	0.984075760348	-2.265059217567	3.399421127000
H	-0.129507552743	-3.345783892311	1.489495250706
N	2.726039421898	-2.315805714434	0.432861895977
C	-3.850564533653	-3.567112138615	-2.353788170265
N	-5.009583655801	-3.803842773614	-2.398965463651
C	4.121309351860	-2.610982636689	-0.014997773436
H	4.132916977826	-2.644392223993	-1.105821471259
H	4.388186309232	-3.608029936000	0.355554367526
C	5.133590899792	-1.584922498549	0.482003753051

C	5.001343313469	-0.219742297426	0.141730253679
C	6.235198840481	-1.996694626316	1.259741185035
C	5.955215097408	0.717025192058	0.578193175475
H	4.156803839569	0.109402748861	-0.460171913849
C	7.195798673521	-1.060409134179	1.691939918301
H	6.345920037098	-3.045186305226	1.528603047994
C	7.056817469916	0.299296345666	1.353815576966
H	5.845694614396	1.766426978870	0.316401155616
H	8.042046494125	-1.389635123343	2.289281802973
H	7.794976838082	1.023603835659	1.688374278176
H	1.393577417258	0.105277274943	-1.575048122907
H	2.009406143363	0.673199580026	0.454860668613
H	1.512953924501	0.739995836172	1.092249221157
H	-0.721094418059	0.120594135555	-1.502990729557

D



SCF Done: E(RB3LYP) = -1975.15880201
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.739599 (Hartree/Particle)
Thermal correction to Energy= 0.783946
Thermal correction to Enthalpy= 0.784890
Thermal correction to Gibbs Free Energy= 0.661670
Sum of electronic and zero-point Energies= -1974.419203
Sum of electronic and thermal Energies= -1974.374856
Sum of electronic and thermal Enthalpies= -1974.373912
Sum of electronic and thermal Free Energies= -1974.497132

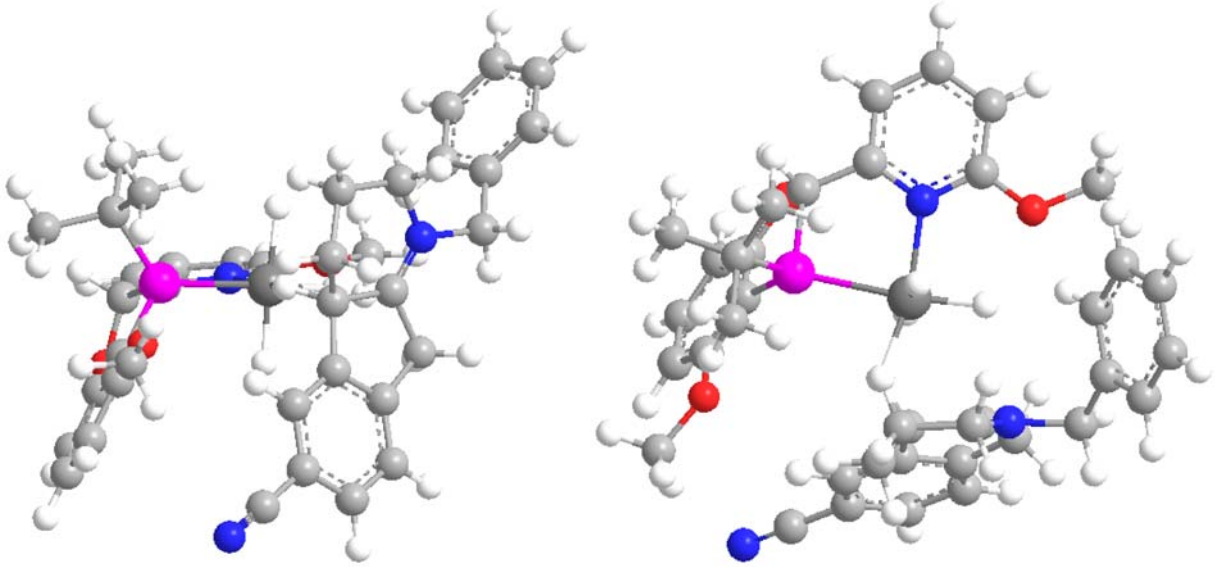
Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.739599 (Hartree/Particle)
Thermal correction to Energy= 0.791143
Thermal correction to Enthalpy= 0.792167
Thermal correction to Gibbs Free Energy= 0.651045

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.446261010190	0.373118795751	0.473524843938
C	4.207919114916	0.184504407526	1.125337649380
C	3.325497227205	-0.817839058249	0.681567382452
C	3.702912191283	-1.616415098322	-0.413469003302
C	4.918614341288	-1.449374749029	-1.090522371340
C	5.781862436990	-0.439748906582	-0.627427868944

H	6.139660218949	1.137647738508	0.803942020300
H	5.176337645299	-2.084722637557	-1.930768208119
H	6.735021564628	-0.284603964216	-1.125412152723
O	3.776307299423	0.946153763116	2.213482069027
C	4.721172467202	1.879114958079	2.844989688732
H	4.183231392692	2.295067060915	3.698191166944
H	5.615634313332	1.346721254567	3.188337770862
H	5.002685835652	2.680826536221	2.153172942123
O	2.787672496444	-2.603634445066	-0.823211388116
C	1.744194110218	-2.857651278906	0.213445993018
H	2.105306299275	-3.698115888312	0.814826692602
P	1.615531103469	-1.269659848807	1.270444421808
C	1.720351408599	-1.893974423497	3.119936676891
C	1.448357772351	-0.682280760661	4.044509758449
H	2.184821392600	0.112269334752	3.887528121179
H	0.442923925189	-0.274195441772	3.882698921139
H	1.509796764957	-1.012776234950	5.090226061120
C	3.111062439064	-2.496295082468	3.418717560092
H	3.364267501273	-3.325738649398	2.746647472672
H	3.900255322681	-1.740640760128	3.345543928969
H	3.112131079533	-2.891008866261	4.443949954950
C	0.606872498316	-2.955407262530	3.310355944302
H	0.807387059513	-3.877564344079	2.750450468454
H	0.556784011116	-3.223664466599	4.373916670153
H	-0.374840119821	-2.569551058049	3.010508525420
C	0.469803756055	-3.251823176776	-0.486623906879
C	0.412169824274	-4.548390002040	-1.006487689705
C	-0.727871596431	-4.967006997953	-1.711039702657
H	1.256553706609	-5.211845452422	-0.862389437267
C	-1.682592601793	-2.771074120143	-1.311877182975
C	-1.780338201993	-4.068026427155	-1.866768006982
H	-0.793238846437	-5.967500274996	-2.125336842983
H	-2.673429436023	-4.361626692526	-2.401253013697
N	-0.572859765636	-2.351154772171	-0.619405282274
Ir	-0.449477795646	-0.396893655463	0.234585367386
O	-2.697568916307	-1.864131080534	-1.439943695364
C	-3.881972312263	-2.200930380100	-2.252850631463
H	-4.434357239279	-3.033350412833	-1.804020007405
H	-4.489745079380	-1.297145818997	-2.234767793303
H	-3.589284815433	-2.436960926388	-3.281349821908
C	2.023590620475	3.833237653267	-2.131844883092
C	0.660578007261	3.563465016887	-2.357035902175
C	-0.083758305804	2.945486894585	-1.347496922541
C	0.519313539557	2.563127159599	-0.126238936810
C	1.866199494124	2.837273769505	0.120138329531
C	2.618357750294	3.481955599274	-0.895369132171
H	2.619233183916	4.323885657528	-2.895346459448
H	0.198276924471	3.850096512663	-3.297070093885
H	2.339828053817	2.551438196905	1.053600558638
C	-0.498253321002	1.939325782525	0.799324960075
C	-0.528671492547	2.510206586411	2.250094364630
C	-1.799197781659	2.181406637316	0.096377713252
C	-1.780058869361	1.998156307652	2.985695667393
H	0.378110669011	2.230706808521	2.795833922228
C	-3.079484927046	2.317454002463	2.226094150814
H	-1.701833863074	0.916319151071	3.135118535715
H	-3.435932256673	3.327176416973	2.468547619001
C	-1.565050725331	2.617883365614	-1.349784508461
H	-2.173828816223	3.494187177111	-1.599268445773
H	-1.812798462790	1.827036855661	-2.066361972889
H	-3.866449919907	1.612319086862	2.503426904393

H	-1.847983887283	2.459900544121	3.976538090281
H	-0.541010933538	3.606582142491	2.177437441241
N	-2.952476988077	2.297381745388	0.726966926500
C	4.002642903739	3.799078390137	-0.663479948997
N	5.138558480240	4.062400453822	-0.461233317513
C	-4.234586355646	2.570933570023	-0.002921737560
H	-4.039774019895	2.478219633299	-1.072987997252
H	-4.519747847065	3.609433091920	0.203197676097
C	-5.361875812759	1.628496306058	0.398236740984
C	-5.188773791465	0.227554979280	0.336784239603
C	-6.609094343013	2.155161425578	0.790494734944
C	-6.251547393549	-0.631709013406	0.668446804614
H	-4.227939666402	-0.189263656349	0.042889453783
C	-7.676815418974	1.294363686827	1.114253441362
H	-6.750127740970	3.232566063980	0.844634949659
C	-7.499975171702	-0.101346391623	1.055463517144
H	-6.109529707654	-1.708615394895	0.625349617507
H	-8.635253657238	1.710375623731	1.413587168512
H	-8.321096935536	-0.766869585492	1.308914296105
H	-1.791398087798	-0.075766533769	-0.558661246971
H	-1.492133842943	-0.915120029133	1.451979719026
H	-0.379453559506	0.628347394012	1.484693488081
H	0.429111731386	-0.008608777893	-1.135737190531

E



SCF Done: E(RB3LYP) = -1975.16624100

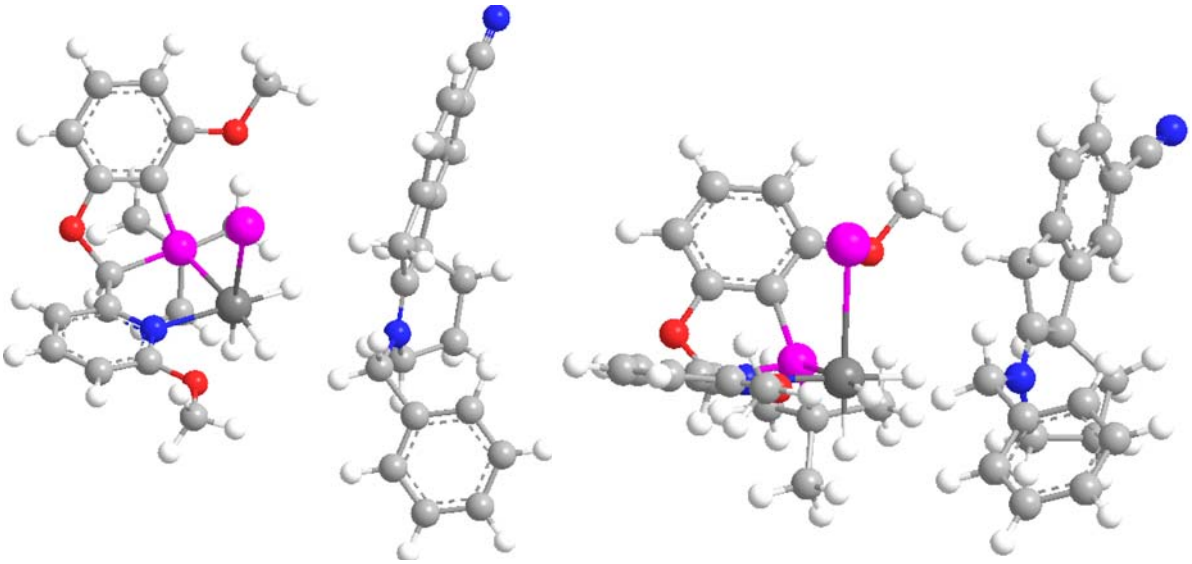
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.742301 (Hartree/Particle)
Thermal correction to Energy= 0.787163
Thermal correction to Enthalpy= 0.788107
Thermal correction to Gibbs Free Energy= 0.662211
Sum of electronic and zero-point Energies= -1974.423940
Sum of electronic and thermal Energies= -1974.379078
Sum of electronic and thermal Enthalpies= -1974.378134
Sum of electronic and thermal Free Energies= -1974.504030

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.742301 (Hartree/Particle)
Thermal correction to Energy= 0.794377
Thermal correction to Enthalpy= 0.795400
Thermal correction to Gibbs Free Energy= 0.651361

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.417130668596	-0.515221127798	-0.112810213524
C	-4.207176203196	-0.330272962494	0.591988286072
C	-3.375778716440	0.764255106828	0.289168795309
C	-3.770314678620	1.650987795255	-0.728867207391
C	-4.959664107231	1.493251548605	-1.454412336738
C	-5.775198442589	0.395064433466	-1.127415679599
H	-6.072919834591	-1.348218650813	0.112816842606
H	-5.231477167156	2.199226465940	-2.231502979811
H	-6.706346617481	0.243846300412	-1.666630972310
O	-3.755794067918	-1.188010511033	1.598378191731
C	-4.665606616304	-2.224916625703	2.104508090995
H	-4.127632626148	-2.701134272396	2.925655862136
H	-5.594523588488	-1.776061229124	2.474768582423
H	-4.892093376816	-2.964830159739	1.327969307769
O	-2.899386257379	2.716172151313	-1.018147173599
C	-1.852027367057	2.893455741974	0.030950064575
H	-2.213395441741	3.685095939094	0.694666853072
P	-1.699309735392	1.228928697536	0.960598872961
C	-1.887878725075	1.708635726573	2.847011275455
C	-1.674223954591	0.427085069015	3.689198498771
H	-2.409751498002	-0.344139442044	3.439828720034
H	-0.667951389070	0.016645663351	3.541608253839
H	-1.779135839371	0.679850776343	4.753171855330
C	-3.283316672417	2.309120439290	3.125434786322
H	-3.483779222708	3.202496181076	2.520673589076
H	-4.080908491394	1.581974934639	2.938081457919
H	-3.336562233287	2.607840348398	4.181387880835
C	-0.770504380932	2.733185612657	3.168429331623
H	-0.927863181969	3.696096545312	2.666196374611
H	-0.768555515440	2.925066012474	4.249663347555
H	0.218212136802	2.349810422248	2.888619091354
C	-0.581262983480	3.350915453037	-0.639472481965
C	-0.531396786233	4.688952510891	-1.040165267318
C	0.597990815346	5.179111586849	-1.713501614991
H	-1.379149878734	5.330075872362	-0.829321736183
C	1.574131187799	2.961945952231	-1.519456961330
C	1.654188209529	4.303792461209	-1.954613005435
H	0.653128218100	6.212786747949	-2.037682734897
H	2.541845981704	4.650241437089	-2.465947527440
N	0.467932425255	2.467984208910	-0.861599791570
Ir	0.344670952166	0.506114390958	-0.220073940694
O	2.602166186008	2.085458581184	-1.730199971469
C	3.779809581791	2.513222673552	-2.508887670548
H	4.316855287398	3.314237375628	-1.989710299136
H	4.404281134138	1.622300234261	-2.567418920579
H	3.483629517307	2.830984139531	-3.514207604182
C	-1.762132993411	-3.977785519887	-2.935229928255
C	-0.406041058314	-3.618769958073	-3.028710165219
C	0.217766246153	-3.032050488383	-1.919654485624
C	-0.501253514028	-2.798163461036	-0.729956829452
C	-1.849086809155	-3.144150914364	-0.618759735245

C	-2.480699462610	-3.744105436009	-1.735662119555
H	-2.265405819221	-4.437105348057	-3.780342702185
H	0.141468341419	-3.799174448355	-3.948778642714
H	-2.409374321359	-2.944470990527	0.288799283813
C	0.375220337163	-2.143493240434	0.317841587844
C	0.418391920475	-2.780267899333	1.733484106311
C	1.752931387059	-2.177677964714	-0.321672684786
C	1.507312096297	-2.065517345913	2.550431973974
H	-0.555343961356	-2.682182519318	2.222822019731
C	2.892353539117	-2.144594544917	1.884746523206
H	1.228472256745	-1.014106109855	2.673300576742
H	3.425043598846	-3.056355249550	2.182012645960
C	1.659539293826	-2.578588471285	-1.792303940525
H	2.363475507211	-3.383298964699	-2.032270698059
H	1.884447799649	-1.733881348200	-2.453816173985
H	3.506105095537	-1.289460727960	2.177325700087
H	1.586660670281	-2.508966475815	3.548602278460
H	0.634174895189	-3.851609687908	1.627810739516
N	2.860355716444	-2.184991040004	0.380757868029
C	-3.867663963988	-4.119267698582	-1.653338627823
N	-5.007664222235	-4.426395812178	-1.576755413514
C	4.210981001329	-2.347366418245	-0.268868021477
H	4.080228893174	-2.216443760818	-1.344014773527
H	4.535653896004	-3.377779534084	-0.083448272933
C	5.249190133832	-1.363705909118	0.248915454452
C	5.050715041538	0.029242228945	0.117648668031
C	6.444420020344	-1.843348878711	0.821727761497
C	6.037708641103	0.927489534883	0.560877267054
H	4.129328438656	0.409560134558	-0.317702863856
C	7.437195531320	-0.943374266657	1.257369504831
H	6.603992903340	-2.914360221274	0.927058428000
C	7.234913617717	0.444258202729	1.129340628889
H	5.877412294986	1.998130474850	0.463085907779
H	8.357113470358	-1.322622119159	1.694362492739
H	7.998055679831	1.140353783988	1.467649069543
H	1.634011678215	0.221348429683	-1.107440212222
H	1.362837808895	0.825132354831	1.094016796574
H	-0.054108931663	-1.095179263940	0.603406551899
H	-0.587281062209	0.144584336601	-1.573174665668

F



SCF Done: E(RB3LYP) = -1986.804797 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.744093 (Hartree/Particle)
Thermal correction to Energy= 0.791857
Thermal correction to Enthalpy= 0.792801
Thermal correction to Gibbs Free Energy= 0.654503
Sum of electronic and zero-point Energies= -1986.060704
Sum of electronic and thermal Energies= -1986.012939
Sum of electronic and thermal Enthalpies= -1986.011995
Sum of electronic and thermal Free Energies= -1986.150294

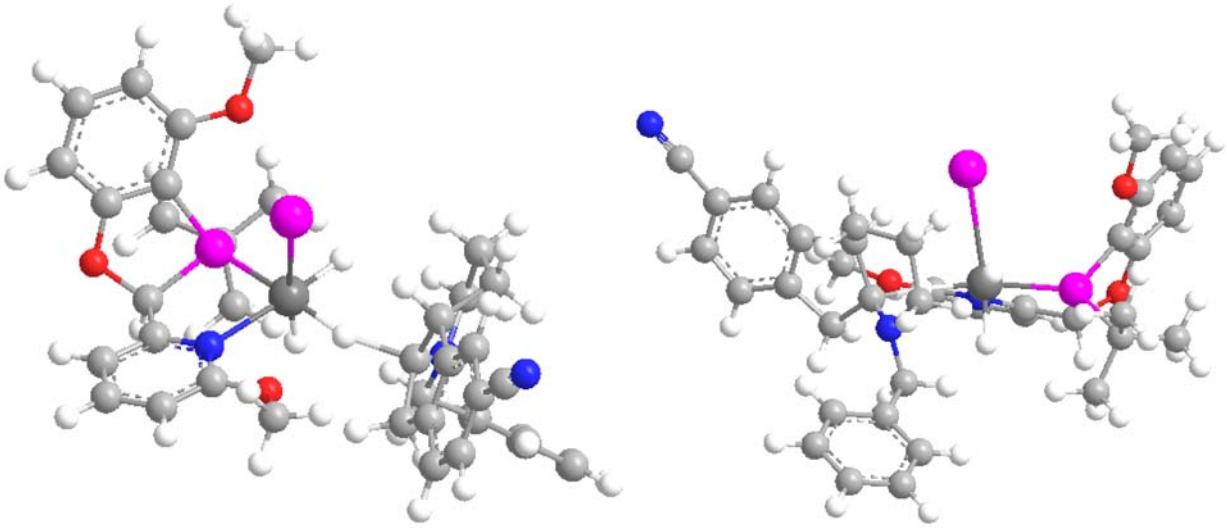
Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.744093 (Hartree/Particle)
Thermal correction to Energy= 0.799303
Thermal correction to Enthalpy= 0.800326
Thermal correction to Gibbs Free Energy= 0.642603

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.430102087318	-5.389664079541	0.771080699480
C	-2.744106455106	-4.135997033277	1.324202632651
C	-2.843619099820	-3.023957414676	0.475923576573
C	-2.625453138627	-3.152498750779	-0.915076664765
C	-2.308170394139	-4.390991149537	-1.478431792409
C	-2.213819347065	-5.518860249730	-0.623923745389
H	-2.350623524060	-6.264519086929	1.409082663699
H	-2.905875641298	-4.039353708983	2.393602081814
H	-2.134704695182	-4.501216141375	-2.544569547926
C	-2.768731654429	-1.811323626312	-1.614226859499
C	-3.746214521211	-1.738057408762	-2.831682622349
C	-3.214819303738	-0.902457242936	-0.489106175789
C	-4.218022560026	-0.276370567639	-3.103008557354
H	-3.235661880577	-2.150327073662	-3.707211945396
C	-3.535499816754	0.762488783902	-2.182724806790
H	-5.302415945264	-0.205119734548	-2.965227322506

H	-4.029418438988	1.732108358607	-2.254744573834
C	-3.151962363835	-1.586264434316	0.853319940196
H	-4.072237575860	-1.475034573179	1.439388210130
H	-2.330159151119	-1.145577833101	1.451015757290
H	-2.476375238661	0.888654033700	-2.435706763134
H	-4.001127792652	0.011635489449	-4.137024492804
H	-4.610442389224	-2.378419926095	-2.625577895374
N	-3.593802153333	0.317311682138	-0.753114043599
C	-1.893296401252	-6.808755872725	-1.175382478418
N	-1.630016107164	-7.869552868270	-1.629008644472
C	-3.967317905769	1.325006851453	0.291128018609
H	-3.162410824799	2.068882688809	0.292078063916
H	-3.953116534850	0.819844769124	1.259990329607
C	-5.318128328237	1.972725615671	0.028003883171
C	-6.497954761161	1.196631842085	-0.021631167424
C	-5.406261137678	3.371224516157	-0.133728950321
C	-7.745158903877	1.811055438594	-0.234246639549
H	-6.447719646615	0.117529613292	0.107574367236
C	-6.655520809774	3.989166518016	-0.339989686815
H	-4.503407073514	3.977184131715	-0.097749722219
C	-7.827456705246	3.210163280797	-0.392990628898
H	-8.647323596366	1.205939227647	-0.271989366991
H	-6.712062307991	5.067706663711	-0.461182729172
H	-8.791882911756	3.684828603807	-0.554637011122
H	-1.784764249564	-1.447093413413	-1.954649135309
C	4.769565670977	-2.335056482165	0.629282808822
C	3.775881039238	-1.633524553440	-0.091085430110
C	3.832079083353	-0.229424734246	-0.186837168466
C	4.897229988101	0.445309598871	0.432560135339
C	5.906618826588	-0.218176261889	1.148096875579
C	5.820579497064	-1.618686732807	1.237840648817
H	4.737284248361	-3.414910953967	0.719292668246
H	6.713253759140	0.338902139404	1.612504293882
H	6.581194503377	-2.165089889427	1.789694083456
O	2.716999050155	-2.252424223979	-0.754670370205
C	2.561246101687	-3.704222031321	-0.638065486452
H	2.422483551468	-3.999683618868	0.408961668500
H	1.665385056834	-3.943641954720	-1.213097012741
H	3.426621548194	-4.226981513916	-1.063792512360
O	4.941914072451	1.842736093463	0.287048265927
C	3.689986799882	2.395694334827	-0.293883178226
P	2.647671507989	0.953524758122	-1.026778173929
C	3.190569079449	0.905921018108	-2.910170019137
C	2.458958822817	-0.293041631029	-3.565141585563
H	2.748312304662	-0.357186451042	-4.623826572494
H	2.717653251400	-1.239172615680	-3.076592709389
H	1.370042880385	-0.169167423434	-3.516010171085
C	4.720507315048	0.738202756963	-3.059550010774
H	4.978352221560	0.754211213291	-4.128135956612
H	5.276839047753	1.548606179068	-2.571857087515
H	5.067426055799	-0.214137894366	-2.643102084876
C	2.734945488273	2.223265203617	-3.584421371124
H	1.663565140167	2.399993562127	-3.439393898690
H	3.281325967545	3.096113311775	-3.203641774183
H	2.933495791615	2.156840744047	-4.663354262005
C	2.956147757801	3.195330331528	0.775916873516
C	3.734939355673	4.018897126332	1.605845957566
C	3.104811351940	4.816501864425	2.571556300579
H	4.811469980075	4.017102242874	1.488872787158
C	0.982306307726	3.943006299125	1.797638965902
C	1.709779931012	4.787145690829	2.664897870171

H	3.684245360698	5.456174931559	3.230169543437
N	1.583577620505	3.126605637866	0.875104604645
Ir	0.429743488285	1.617052499708	-0.330134597140
O	-0.391445907083	3.895046543384	1.817357285924
C	-1.126116877549	4.698099406896	2.802216795346
H	-0.945104776812	5.769370660713	2.652924366869
H	-0.858749682425	4.405526722415	3.824375691122
H	-2.176262217983	4.471254784554	2.614623141956
H	-1.004219858276	2.241666319826	0.056501809634
H	0.338857180299	2.567297220057	-1.599367516229
I	0.305209333403	-0.141740103289	2.139507595471
H	-0.391705316987	0.537136687397	-1.194183872214
H	1.197920977125	5.404873371865	3.391015992749
H	4.008364675139	3.074533705663	-1.091278853839

G



SCF Done: E(RB3LYP) = -1986.79514445 A.U.
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.743419 (Hartree/Particle)
Thermal correction to Energy= 0.790205
Thermal correction to Enthalpy= 0.791149
Thermal correction to Gibbs Free Energy= 0.656798
Sum of electronic and zero-point Energies= -1986.051725
Sum of electronic and thermal Energies= -1986.004940
Sum of electronic and thermal Enthalpies= -1986.003996
Sum of electronic and thermal Free Energies= -1986.138347

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.

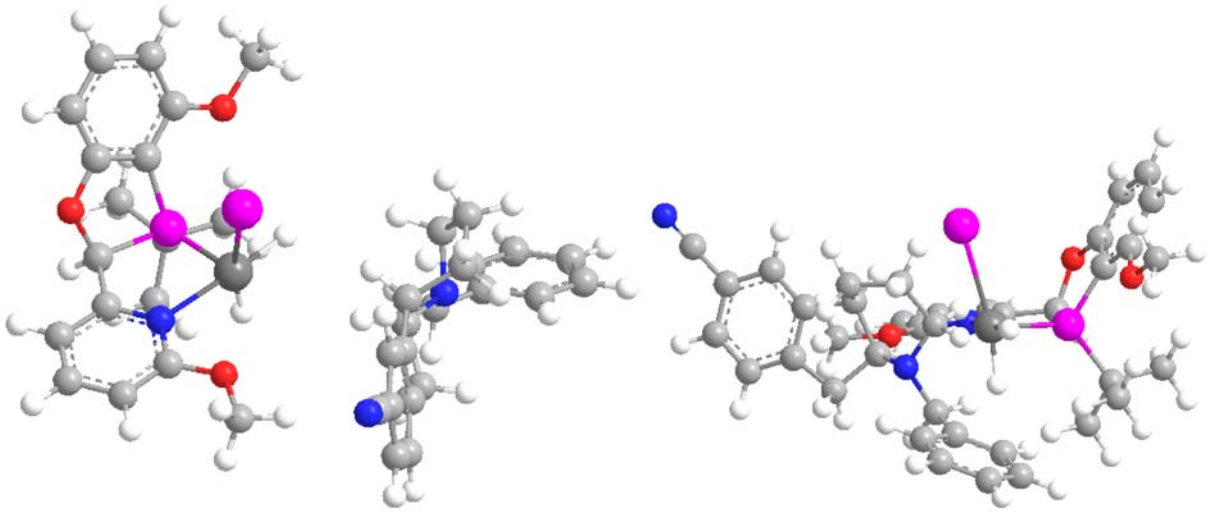
Zero-point correction= 0.743419 (Hartree/Particle)
Thermal correction to Energy= 0.797571
Thermal correction to Enthalpy= 0.798594
Thermal correction to Gibbs Free Energy= 0.645232

Atomic Coordinates (Angstroms)
Type X Y Z

C	6.189387135585	-3.010405112868	0.078096383555
C	5.522249231623	-2.110784308951	-0.770766912937
C	4.585009457397	-1.219634092777	-0.223698053035
C	4.314302196361	-1.215203088749	1.160676539168
C	4.965358372905	-2.109833880938	2.017240275331
C	5.910781077865	-3.012652401915	1.468494173191
H	6.919315746470	-3.706217483912	-0.324406708595
H	5.736089144804	-2.111087013189	-1.835856161577
H	4.760404855885	-2.120698381600	3.083609766646
C	3.280051764577	-0.165623993343	1.530085936846
C	3.680369171334	0.798492798872	2.669129875680
C	3.070824984268	0.588369070135	0.195956821191
C	2.640657394497	1.930559964113	2.717255728053
H	3.695211163801	0.256543839598	3.621367552359
C	2.617270748548	2.724089132843	1.396783776638
H	2.856719938878	2.626871620161	3.535356268951
H	3.309230158818	3.572241951545	1.439886696260
C	3.759473452208	-0.177147205561	-0.954948925456
H	4.390619236461	0.478458992567	-1.564534856695
H	3.020498033003	-0.643086997532	-1.613291252736
H	1.608760972182	3.117589778948	1.211683374245
H	1.651711841573	1.497364643043	2.904966404403
H	4.688460824466	1.200107110610	2.497758924615
N	3.004246578580	1.927846651219	0.193021461255
C	6.598556912413	-3.939976203103	2.327300408520
N	7.165154589932	-4.702485222388	3.033198038926
C	2.908216376733	2.698665398137	-1.075786425936
H	1.875132603918	3.061658961498	-1.156728669461
H	3.061621721260	2.015843755884	-1.913785852389
C	3.886986237186	3.864197648308	-1.157553351627
C	5.264084887055	3.677526078172	-0.902115783823
C	3.428560019951	5.140802502294	-1.543636182683
C	6.165731721220	4.749714773095	-1.031842845470
H	5.632074843548	2.700384165106	-0.596342437094
C	4.330048110010	6.215374974396	-1.678938953208
H	2.369387025768	5.297245033047	-1.737878058365
C	5.701560814897	6.022756703268	-1.423118418203
H	7.223088116827	4.595144097949	-0.831543715871
H	3.964030359121	7.194541771079	-1.977322186513
H	6.398390801181	6.850956068337	-1.524536939053
H	2.336221800219	-0.651716351729	1.814813811889
C	-5.606804995274	-0.516304680874	2.077623530958
C	-4.435973569822	0.163195252460	1.670628921749
C	-4.008865101495	0.086332621395	0.330949142047
C	-4.781685319653	-0.645759985904	-0.586049395272
C	-5.956288092145	-1.320553776575	-0.220543679458
C	-6.349651834916	-1.247097678872	1.127835577930
H	-5.945009936821	-0.479260796744	3.106993672919
H	-6.526372902822	-1.878298869056	-0.955642866141
H	-7.249551999639	-1.765522369907	1.448546562590
O	-3.660025896408	0.951625519208	2.515652886870
C	-3.957236543678	0.961550380722	3.950875987509
H	-3.900857136131	-0.051813183475	4.365771743652
H	-3.184990096761	1.589204418851	4.398065998413
H	-4.946730936772	1.393943348171	4.143345022825
O	-4.348131512652	-0.653316014518	-1.925218957527
C	-2.964116958413	-0.134252255266	-2.070525033166
P	-2.503413739968	0.839747059933	-0.482197235317
C	-3.021782082763	2.691406697269	-0.850967692185
C	-2.685112474696	3.522274661809	0.412749131509
H	-2.977300511492	4.567971234988	0.241685981736

H	-3.221255134437	3.152385893561	1.293855280189
H	-1.610554050059	3.496647958036	0.629605227341
C	-4.532962892115	2.787309866149	-1.165863615856
H	-4.776490245267	3.829301918597	-1.416208968081
H	-4.818308616445	2.162215150206	-2.020923517991
H	-5.146243973631	2.494568327367	-0.306632722852
C	-2.199287234178	3.213175162798	-2.054250913260
H	-1.122852803315	3.103590837553	-1.886336181246
H	-2.457067126798	2.699820822584	-2.989673602585
H	-2.421487646851	4.280149039522	-2.194208963680
C	-2.020589270593	-1.301677088280	-2.338356480179
C	-2.475853908348	-2.306770128128	-3.206803518529
C	-1.638215757093	-3.392174420403	-3.502136376778
H	-3.471767760222	-2.230845667314	-3.624712127111
C	0.038138296282	-2.385510732990	-2.074931717337
C	-0.361978663119	-3.433210424936	-2.933260271296
H	-1.967072068799	-4.184519738296	-4.167304279180
N	-0.774330745897	-1.335042967685	-1.752478107032
Ir	-0.223563087094	0.244868096388	-0.203570025685
O	1.294349202617	-2.351710159465	-1.514112798907
C	2.113439949070	-3.573986705864	-1.558205045945
H	2.443206188652	-3.788910567227	-2.581450600611
H	1.557711081695	-4.424439802744	-1.148016986711
H	2.975779117717	-3.356508969628	-0.930641248886
H	1.443052828915	0.055484109018	-0.162885639643
H	0.099347203799	1.328851249579	-1.320175985933
I	-0.446695476878	-1.764992200048	1.980780822504
H	0.069493237697	1.383891289236	0.871921606270
H	0.310164167592	-4.251181989970	-3.156412955167
H	-2.984185603901	0.530668013103	-2.938636244458

H



SCF Done: E(RB3LYP) = -1986.81971991 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.746754 (Hartree/Particle)
Thermal correction to Energy= 0.794531
Thermal correction to Enthalpy= 0.795476
Thermal correction to Gibbs Free Energy= 0.654945

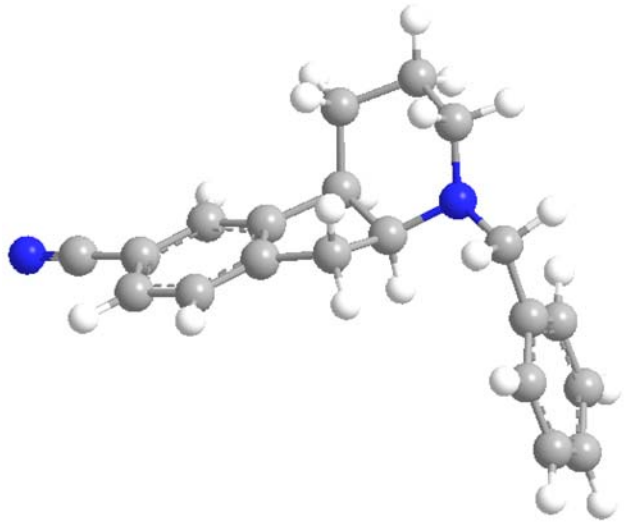
Sum of electronic and zero-point Energies= -1986.072965
Sum of electronic and thermal Energies= -1986.025189
Sum of electronic and thermal Enthalpies= -1986.024244
Sum of electronic and thermal Free Energies= -1986.164775

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.746754 (Hartree/Particle)
Thermal correction to Energy= 0.801926
Thermal correction to Enthalpy= 0.802949
Thermal correction to Gibbs Free Energy= 0.642860

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.767578670858	4.748377840353	-0.654431918071
C	0.690984865798	6.084880577617	-1.085384701819
C	0.035882494406	7.033144176517	-0.281007633534
C	-0.544811722087	6.653769101033	0.951658613245
C	-0.475271267978	5.327393529152	1.392473280086
C	0.185550359464	4.368272524989	0.581541549935
H	1.268149279701	4.001583024461	-1.263901558540
H	1.135200122018	6.372985383531	-2.034498685531
H	-0.921562494260	5.023944330343	2.335523090637
C	-1.174194985241	7.842138531235	1.655949948448
C	-0.363145421235	8.322534963935	2.884815469721
C	-1.210043794308	8.947919309121	0.539093243786
C	-1.014454020110	9.590245081654	3.494203057756
H	-0.308851196425	7.523660363481	3.636360872325
C	-1.633868498945	10.494004890490	2.395372192116
H	-0.255112717429	10.148749665268	4.056807939803
H	-1.542198114078	11.546799519128	2.681144929075
C	-0.155871313424	8.516276444431	-0.531060371836
H	0.784236288600	9.061680529262	-0.364196669612
H	-0.477303733166	8.724492475468	-1.558139383308
H	-2.716740917101	10.282383189114	2.288234976878
H	-1.800991009425	9.305308825593	4.206041336860
H	0.665260840624	8.544505432736	2.572335254219
N	-0.940396885622	10.297272025444	1.096199445204
C	0.265104207844	2.997614925360	1.010563849365
N	0.330908264362	1.869431331532	1.363960711688
C	-1.228860304008	11.369802877325	0.114806290454
H	-2.320291832201	11.484551738824	-0.044590629406
H	-0.806426449259	11.055855855957	-0.849004242690
C	-0.632086776406	12.722176045938	0.489262436328
C	0.688000412660	12.820709038062	0.984404365973
C	-1.374056537574	13.907426420907	0.297439852729
C	1.253068172937	14.075707074453	1.278475335535
H	1.258226027985	11.909788987125	1.145504814355
C	-0.810953572074	15.167142394750	0.586868008908
H	-2.394894914678	13.846846201235	-0.076048574306
C	0.506201766571	15.255898004049	1.078582946933
H	2.269818968909	14.135782227748	1.660485597288
H	-1.397191986668	16.070421617223	0.434222625387
H	0.942518006825	16.225838276056	1.305312624752
H	-2.193149983211	7.603364958804	1.989544052736
C	-9.749557602388	10.225069126595	2.931942498210
C	-8.814337312603	10.533713586808	1.921247329612
C	-8.756059361084	9.740990264738	0.757976548221
C	-9.628475326080	8.647346813728	0.626434418828
C	-10.569421458080	8.314682282864	1.612265924456
C	-10.610836639279	9.120548209014	2.763307612514

H	-9.815392043562	10.823001006552	3.833487552388
H	-11.229343000387	7.464239211133	1.481874452415
H	-11.327205023216	8.888873795747	3.546917647009
O	-7.917827170091	11.593675581539	1.975757883848
C	-7.881841765763	12.437877383618	3.175835580459
H	-7.632212288136	11.841902237466	4.061287660720
H	-7.095542150660	13.169535756332	2.985489142615
H	-8.841327343919	12.948408139316	3.320666592794
O	-9.522484044708	7.867128488262	-0.536345908606
C	-8.572266440844	8.419258583367	-1.540173237277
P	-7.588690800210	9.836455183086	-0.672093067386
C	-7.876410278543	11.461009665899	-1.701700406926
C	-6.983443044183	12.578144800816	-1.110598722646
H	-7.137790096588	13.493580019706	-1.697669596125
H	-7.238051949266	12.784829659900	-0.066519343675
H	-5.922514265606	12.309866248227	-1.164902939196
C	-9.370294649463	11.853422266203	-1.617157516261
H	-9.527321913425	12.751940978212	-2.228482532453
H	-10.034629208958	11.070639685363	-2.004898506748
H	-9.670734828819	12.084947908090	-0.589784834738
C	-7.466095908759	11.174581302500	-3.167722683461
H	-6.426529565994	10.835286784096	-3.238382425981
H	-8.111906151787	10.428820869265	-3.647574227200
H	-7.558194914525	12.106589901687	-3.740412930712
C	-7.675323207040	7.306969275748	-2.038767058368
C	-8.213069785123	6.287879594420	-2.836779214070
C	-7.372241520592	5.248343074141	-3.276661368756
H	-9.264215654206	6.307402374759	-3.100395020780
C	-5.538860875991	6.331100011087	-2.140266835180
C	-6.015611658194	5.263898981067	-2.929659085896
H	-7.766396604928	4.442540076453	-3.887670401544
N	-6.349826050815	7.321974379521	-1.686456112506
Ir	-5.532209493577	8.924160223633	-0.416240569171
O	-4.229077063562	6.490158531688	-1.762336380867
C	-3.245276624352	5.446074327554	-2.093102795399
H	-3.126113030091	5.361790748297	-3.179134300751
H	-3.546339874352	4.485006106155	-1.661831069928
H	-2.314826475751	5.785227086928	-1.638994123653
H	-2.218797480178	8.921489483900	0.073294298818
H	-5.139016687772	9.817571877847	-1.671696984204
I	-5.593698503973	7.261573352958	1.934839027628
H	-4.981805787020	10.121738337868	0.489673800199
H	-5.349178354836	4.480430871124	-3.267420051201
H	-9.185229113369	8.810976515017	-2.357481822943

I



SCF Done: E(RB3LYP) = -883.526510298 A.U.

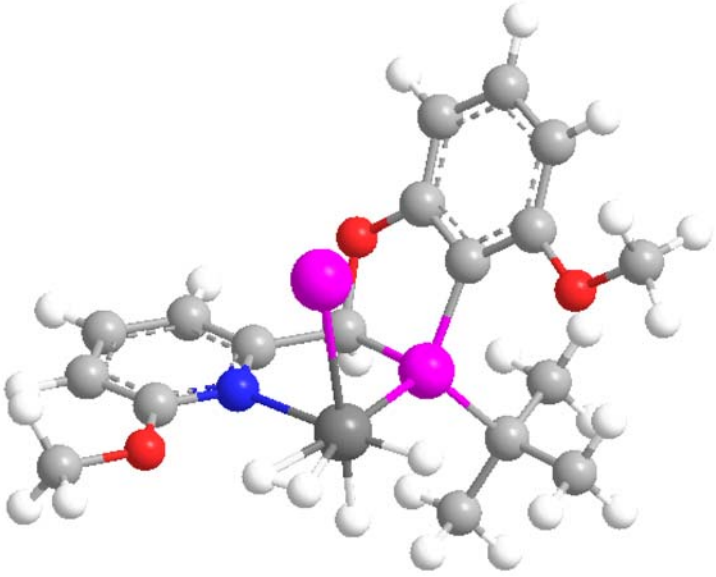
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.356383 (Hartree/Particle)
Thermal correction to Energy= 0.374055
Thermal correction to Enthalpy= 0.374999
Thermal correction to Gibbs Free Energy= 0.309080
Sum of electronic and zero-point Energies= -883.170127
Sum of electronic and thermal Energies= -883.152456
Sum of electronic and thermal Enthalpies= -883.151511
Sum of electronic and thermal Free Energies= -883.217430

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.356383 (Hartree/Particle)
Thermal correction to Energy= 0.377026
Thermal correction to Enthalpy= 0.378050
Thermal correction to Gibbs Free Energy= 0.303430

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.590073182202	2.219940823669	-0.193165358468
C	-2.316533905198	2.195917393160	-0.791566860134
C	-1.537994113259	1.030648102662	-0.708431007392
C	-2.024440253966	-0.112676871394	-0.023914712232
C	-3.288141431914	-0.102951355812	0.572550972061
C	-4.076224600852	1.075720410268	0.487598036719
H	-4.205023347049	3.113746971152	-0.245315403618
H	-1.945356016861	3.077246593959	-1.307750317636
H	-3.669293515652	-0.973067528460	1.100036935800
C	-1.019758838106	-1.250153246153	-0.110662184521
C	-1.392300065695	-2.237158424773	-1.255205998211
C	0.309899457722	-0.475419523992	-0.400065431881
C	-0.185040250154	-3.109278468599	-1.650186289820
H	-2.238840061403	-2.859499404244	-0.935882290323
C	1.004446989347	-2.219145447583	-2.048009775699
H	0.110482733433	-3.750299461894	-0.807557807723
H	0.742823738269	-1.651946975858	-2.965732359551
C	-0.150104728050	0.763584227420	-1.261101842656
H	-0.199085065574	0.509195337849	-2.330427685083

H	0.518664414569	1.625605354060	-1.160484128362
H	1.873650915640	-2.842246414784	-2.294463242150
H	-0.451158290877	-3.764476003745	-2.490737447237
H	-1.729985602013	-1.670787005074	-2.136008886985
N	1.387213604484	-1.330495948850	-0.928182803165
C	-5.377028986026	1.114026666571	1.100378073730
N	-6.447886503166	1.143230961725	1.604927377312
C	2.670127257200	-0.624592209773	-1.148952769747
H	2.572621780234	0.201038862088	-1.879665456752
H	3.358371894866	-1.354756458286	-1.598637780941
C	3.299248235057	-0.081969399508	0.130853963323
C	3.386601081689	-0.885661296674	1.290438561803
C	3.853344096880	1.215488512198	0.161846164146
C	4.016649003698	-0.403643917390	2.452427945279
H	2.950818109687	-1.881617204253	1.274465493477
C	4.488234602057	1.702280098146	1.323253519749
H	3.789296220340	1.848035276185	-0.721890719614
C	4.572351338129	0.893436353979	2.473217401240
H	4.076911880304	-1.033452818998	3.337213323490
H	4.909702143807	2.704846268326	1.330459151087
H	5.059861721217	1.266195559584	3.370926461478
H	-0.938126187910	-1.815997153638	0.825605066685
H	0.664073727297	-0.070891233268	0.557800112522

J



SCF Done: E(RB3LYP) = -1104.48278058 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.406320 (Hartree/Particle)
Thermal correction to Energy= 0.434508
Thermal correction to Enthalpy= 0.435452
Thermal correction to Gibbs Free Energy= 0.345711
Sum of electronic and zero-point Energies= -1104.076461
Sum of electronic and thermal Energies= -1104.048273
Sum of electronic and thermal Enthalpies= -1104.047328
Sum of electronic and thermal Free Energies= -1104.137070

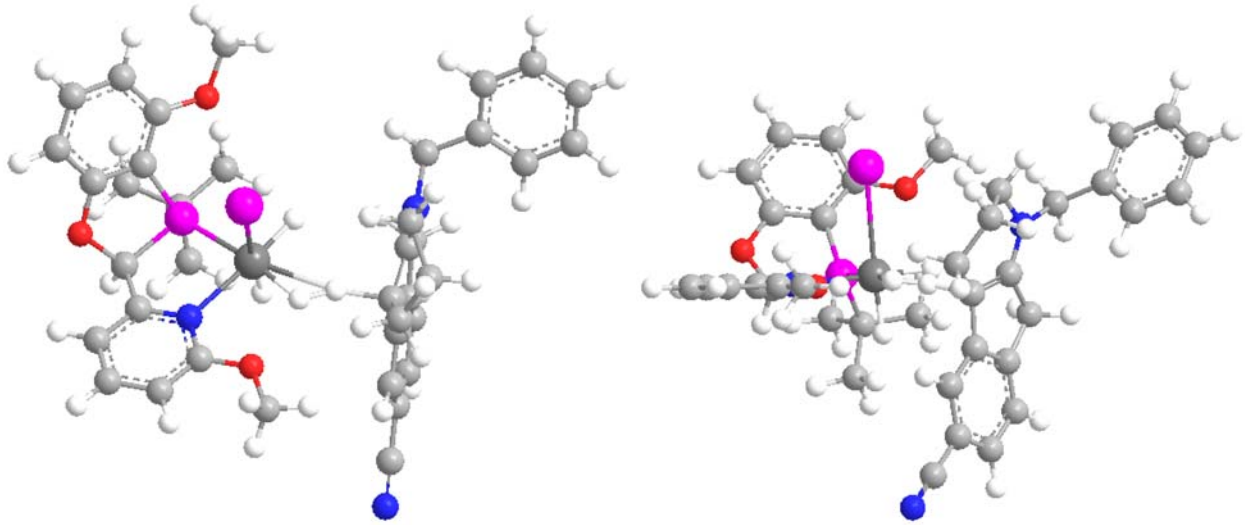
Temperature 323.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.406320 (Hartree/Particle)
Thermal correction to Energy= 0.438879
Thermal correction to Enthalpy= 0.439902
Thermal correction to Gibbs Free Energy= 0.338006

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.960099544396	-1.372795389568	1.366443938687
C	3.204116183566	-0.696142969907	0.384874580152
C	2.185127534306	0.192564256616	0.778053924929
C	1.929714903089	0.381605130402	2.145302602188
C	2.663666772868	-0.272773276580	3.146180760983
C	3.679861049293	-1.150979220486	2.730691211412
H	4.749924640762	-2.060264739113	1.086832693822
H	2.441648324622	-0.105079958340	4.194239381209
H	4.265484685932	-1.676917172138	3.479998645238
O	3.392921867982	-0.833302671254	-0.984811012055
C	4.390131535430	-1.791501447014	-1.474606061699
H	4.151135198288	-2.806588883645	-1.136925523299
H	4.327435802149	-1.736863307987	-2.562263876607
H	5.396608003983	-1.509566603446	-1.142855352374
O	0.894686272424	1.265249980661	2.494850483768
C	0.184231302206	1.843505788517	1.322691760941
P	1.008184538440	1.160155734285	-0.271055371463
C	1.968458015423	2.652388181532	-1.071190080427
C	2.640512456659	2.148342374998	-2.372182352934
H	3.173183615702	2.987586792433	-2.839492357943
H	3.359667186241	1.347741176738	-2.170846403202
H	1.897652394504	1.773895722467	-3.085774913318
C	3.034321815800	3.170458902614	-0.076992340171
H	3.555675694304	4.020774974880	-0.536228286190
H	2.594529530806	3.524351169488	0.864214215371
H	3.779837319489	2.402995779024	0.157097010725
C	0.947822492747	3.768874787115	-1.402576387560
H	0.169988277427	3.415692896558	-2.088210144006
H	0.462371009693	4.177012329910	-0.507053844053
H	1.483198839699	4.593854718233	-1.890696002202
C	-1.294787619765	1.516593380455	1.424604259374
C	-1.982989553579	1.934495626344	2.573053460424
C	-3.353688807785	1.652371877817	2.693165439668
H	-1.448604830126	2.464794592627	3.352293852842
C	-3.255804580710	0.589905217102	0.525825159005
C	-4.004493735159	0.975034763426	1.656427457103
H	-3.907148037861	1.960512503012	3.574365187828
N	-1.919480620477	0.838989661534	0.406217463777
Ir	-0.774623717011	0.137005187293	-1.376946558976
O	-3.808240770499	-0.063621517984	-0.548429389393
C	-5.230097313229	-0.443940538554	-0.527931010342
H	-5.865949717802	0.446433602841	-0.475743507410
H	-5.434721394506	-1.117383330103	0.311145940367
H	-5.390140909080	-0.963542115482	-1.472661079594
H	-1.000041888949	1.513026786814	-2.144575925110
I	-0.499131451161	-2.510298258535	-0.172083574505
H	0.179696896725	-0.288918348613	-2.584819504609
H	-5.062061859659	0.754461652328	1.720810139833
H	0.326011095478	2.925901053613	1.394787405606

H	-2.377317125965	-0.417732586043	-1.938693929179
H	-1.841836787110	-0.612114596881	-2.564479796633

K



SCF Done: E(RB3LYP) = -1986.78877245 A.U.

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.737718 (Hartree/Particle)
Thermal correction to Energy= 0.785228
Thermal correction to Enthalpy= 0.786172
Thermal correction to Gibbs Free Energy= 0.648239
Sum of electronic and zero-point Energies= -1986.051054
Sum of electronic and thermal Energies= -1986.003544
Sum of electronic and thermal Enthalpies= -1986.002600
Sum of electronic and thermal Free Energies= -1986.140533

Temperature 323.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.737718 (Hartree/Particle)
Thermal correction to Energy= 0.792657
Thermal correction to Enthalpy= 0.793681
Thermal correction to Gibbs Free Energy= 0.636371

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.041936309200	-5.503981883454	-1.201073520464
C	-2.122761697111	-4.987180514386	0.109265869250
C	-2.422716916229	-3.634905690900	0.288197256152
C	-2.640767941979	-2.774460918517	-0.823386288837
C	-2.550886582372	-3.272032169078	-2.129035681827
C	-2.255998206249	-4.650210303379	-2.310304558014
H	-1.817962769421	-6.553604386342	-1.364922508571
H	-1.958914439980	-5.642063235902	0.960614515085
H	-2.704036541020	-2.630886378930	-2.992034880779
C	-2.867529790626	-1.387862314623	-0.343677366955
C	-3.592961848982	-0.286839480078	-1.121307629409
C	-3.008762873111	-1.477682763529	1.075925054004
C	-4.516213571666	0.517254373767	-0.172453636027
H	-2.870455870675	0.393069928087	-1.592936241989
C	-3.829071886250	0.810311535673	1.175984897907

H	-5.440085912850	-0.045634031475	0.015587989448
H	-4.513655062361	1.331857347971	1.851424270264
C	-2.580103489215	-2.847398202278	1.578950060495
H	-3.315639678546	-3.295647929601	2.258116927323
H	-1.629120434804	-2.780024233021	2.127179292214
H	-2.937366570552	1.437241994616	1.032159550170
H	-4.796474001348	1.470569774580	-0.635199201242
H	-4.190877009498	-0.728684434479	-1.929044553693
N	-3.413688076218	-0.457573590400	1.843425251469
C	-2.170026227621	-5.189293819808	-3.641967374327
N	-2.100116134274	-5.631171888230	-4.738173982870
C	-3.388491651883	-0.473666940716	3.324325746948
H	-2.762551100849	0.361105639307	3.663432855737
H	-2.894317897132	-1.393721322310	3.650154806174
C	-4.773828292961	-0.366268935143	3.958361221682
C	-5.847669984552	-1.163274149346	3.503442907212
C	-4.982648613618	0.510292106619	5.043507780944
C	-7.106508371203	-1.088463229783	4.127718493029
H	-5.706145390148	-1.836321956741	2.660841361093
C	-6.241094756489	0.584407648636	5.673101742804
H	-4.165558386140	1.136593645685	5.396183892574
C	-7.306886804188	-0.215511190285	5.217083563749
H	-7.926097609782	-1.706117006635	3.768788208691
H	-6.389339258531	1.264580890563	6.508097873485
H	-8.279376396873	-0.157655897556	5.699495396120
H	-1.480346079898	-0.894291535753	-0.382646388945
C	4.093143566004	2.374249117045	3.783834092304
C	3.392701260024	1.268210110565	3.253272635743
C	3.688681043498	0.805260519508	1.956565442646
C	4.689224550785	1.455499005159	1.216103071284
C	5.409645450764	2.552265636238	1.714257073008
C	5.090699079918	2.999956469840	3.007989319692
H	3.876338855110	2.748260973387	4.777872080388
H	6.175073993509	3.030343874573	1.112774917966
H	5.624631776928	3.850743759345	3.423169249011
O	2.408000906404	0.566512149166	3.942683605473
C	1.985832625385	1.046226099089	5.261672934472
H	1.600551470248	2.070708634157	5.197715577345
H	1.189139457640	0.367886352841	5.570744126410
H	2.814359571164	0.999082085478	5.978830861542
O	4.971184683051	0.955316229662	-0.066594614760
C	4.023676780320	-0.104238402814	-0.502302847194
P	2.905072026362	-0.575752809266	0.985267598201
C	3.658885004865	-2.237238021035	1.679011704765
C	2.811910563901	-2.662193508497	2.904546873573
H	3.221818473037	-3.596580696129	3.312720053226
H	2.829585335570	-1.901223399901	3.692085406446
H	1.767585761192	-2.841092522354	2.622417142998
C	5.134710802710	-2.028187857590	2.092292505333
H	5.541749782802	-2.986357984737	2.443488570090
H	5.759185005805	-1.691177822780	1.255056284210
H	5.229895003642	-1.301218587746	2.906371700335
C	3.559633650231	-3.318859771882	0.575253978790
H	2.529494419064	-3.442725687813	0.224018982956
H	4.196073726512	-3.094490406529	-0.290376110532
H	3.899275491719	-4.276762467671	0.991983385707
C	3.243192922727	0.386139036152	-1.713218561086
C	3.979950518164	0.946958167904	-2.768134709822
C	3.308307041833	1.379201961014	-3.921661433853
H	5.054797788877	1.041696938582	-2.672539975666
C	1.240450892790	0.635677548005	-2.907578651918

C	1.921622094728	1.215580602817	-3.999648792213
H	3.853294315596	1.823898012278	-4.748410525506
N	1.875640800502	0.245332433098	-1.761246837488
Ir	0.748743826636	-0.484084929817	0.047355196599
O	-0.115502255002	0.412609783908	-2.922553406359
C	-0.901074824915	0.836575421308	-4.090225206636
H	-0.574118793692	0.310173929272	-4.994255186594
H	-0.832829504527	1.921253908848	-4.231332724263
H	-1.926811119250	0.556958308055	-3.849775089823
H	-0.711010369849	-0.469606824506	-0.810094184067
H	0.914187085822	-2.009904906007	-0.370765810491
I	0.144792469050	2.318799950508	0.760369612475
H	0.033670325277	-1.014150762474	1.376861818955
H	1.382914449120	1.526470345601	-4.884979890925
H	4.647560684347	-0.953381946674	-0.796798472818

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