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Supporting Information

CAAC–IPr*: Easily Accessible, Highly Sterically-Hindered Cyclic (Alkyl)(Amino)Carbenes

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Table of Contents

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Additional Information Referred to from the Main Manuscript

HOMO and LUMO Energy: To gain insight into the electronic properties of IPr*–CAACs, HOMO and LUMO energy levels were determined at the B3LYP 6-311++g(d,p) level (Figure 4). Most importantly, the HOMO of IPr*–CAAC^{Me} (-5.49 eV) is significantly higher than IPr (-6.01 eV), which is a model for σ-donating NHCs. This value can be compared with Dipp–CAAC^{Me} (-5.33 eV) and IPr* (-6.12 eV). Furthermore, the LUMO of IPr*–CAAC^{Me} (-0.90 eV) can be compared with Dipp–CAAC^{Me} (-5.33 eV) and IPr* (-6.12 eV). Furthermore, the LUMO of IPr*–CAAC^{Me} (-0.90 eV) can be compared with IPr (-0.48 eV, LUMO+1 due to required symmetry), Dipp–CAAC^{Me} (-0.51 eV) and IPr* (-0.90 eV). Thus, the strong σ-donation of IPr*–CAACs in combination with variable bulk makes this class of NHCs well-suited for catalysis. Note the enhancement of π-acceptance of CAAC–IPr* as a result of ortho-benzhydryl substitutents.

Steric Impact: Furthermore, to eliminate impact from steric packing, the percent buried volume (%V_{bur}) was calculated from the optimized structures of [Cu(CAAC)Cl] complexes **6a**–**6d** at the B3LYP 6-311++g(d,p) level (see pages S24-S26). These studies determined the %V_{bur} of NHC in [Cu(IPr*-CAAC^{Me})Cl] (**6a**) as 47.1% (SW, 31.8%; NW, 34.7%; NE, 62.3%; SE, 59.7%); [Cu(IPr*^{MeO}-CAAC^{Me})Cl] (**6b**) as 47.1% (SW, 31.8%; NW, 35.0%; NE, 61.9%; SE, 59.6%); [Cu(IPr*-CAAC^{Cy})Cl] (**6c**) as 47.3% (SW, 32.1%; NW, 34.9%; NE, 62.5%; SE, 59.8%); and in [Cu(IPr*^{MeO}-CAAC^{Cy})Cl] (**6d**) as 47.3% (SW, 32.1%; NW, 35.4%; NE, 62.0%; SE, 59.8%). The unsymmetrical geometry rendered by the quaternary carbon provides unique steric environment of these strongly σ-donating NHC ligands.

Selected Parameters, X-ray Crystal Structures, 6a and 6b: Selected bond lengths [Å] and angles [°]: **6a**: Cu–C1, 2.0835(9); Cu–C1, 1.864(2); N1–C1, 1.300(3); N1–C9, 1.459(4); C1–C2, 1.512(4); C1–Cu–Cl, 174.45(8); C1–N1–C4, 115.4(2); C1–N1–C9, 122.7(2); C4–N1–C9, 121.8(2); Cu–C1–C2, 122.4(2); Cu–C1–N1, 128.6(2); N1–C1–C2, 122.4(2). **6b**: Cu–C1, 2.1142(5); Cu–C1, 1.882(1); N1–C1, 1.305(2); N1–C9, 1.457(2); C1–C2, 1.519(2); C1–Cu–Cl, 176.06(5); C1–N1–C4, 115.3(1); C1–N1–C9, 121.6(1); C4–N1–C9, 123.1(1); Cu–C1–C2, 122.5(1); Cu–C1–N1, 128.2(1); N1–C1–C2, 122.5(1).

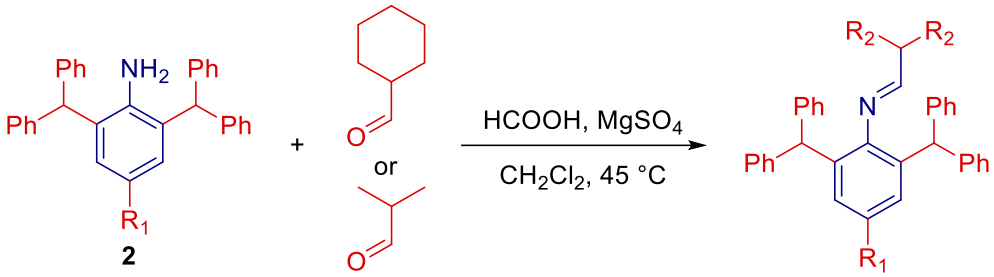
List of Known Compounds/General Methods

All starting materials reported in the manuscript have been previously described in literature and prepared by the method reported previously unless stated otherwise. All experiments were performed using standard Schlenk techniques under nitrogen or argon unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 500 (^{1}H NMR) and 125 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.26 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5973A inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 22.0 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument. All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm UV lamp or aqueous potassium permanganate. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental for characterization purposes. ^{1}H NMR, ^{13}C NMR, and HRMS data are given for all new compounds.

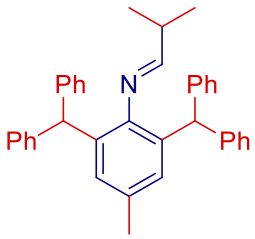
Experimental Procedures and Characterization Data

Compounds **2a**[1] and **2b**[2] have been previously reported. Spectroscopic properties matched literature.

1. General Procedure for the Synthesis of Imines 3a–3d.



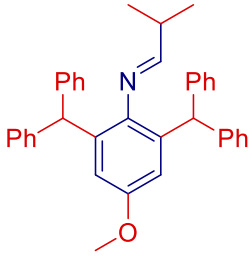
An oven-dried 250 mL round-bottomed flask equipped with a stir bar was charged with aniline **2** (10 mmol, 1.0 equiv), aldehyde (15 mmol, 1.5 equiv), formic acid (23.01 mg, 0.5 mmol, 0.05 equiv) and anhydrous $MgSO_4$ (5.95 g, 50 mmol, 5 equiv). Dichloromethane (20 mL) was added and the reaction mixture was heated at 45 °C until the reaction was completed (monitored by ^1H NMR, typically 24 h). The reaction mixture was then cooled down to room temperature, filtered and washed with CH_2Cl_2 until the filter cake was white. The solution was collected and concentrated to give the crude solid which was further washed with a minimum amount of EtOAc to afford the imine product.[3]



3a

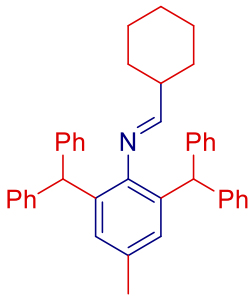
(*E*)-*N*-(2,6-Dibenzhydryl-4-methylphenyl)-2-methylpropan-1-imine (3a). White solid. Yield 70% (3.46 g). ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.4 Hz, 8H), 7.17 (t, *J* = 7.3 Hz, 4H), 7.03 (d, *J* = 7.2 Hz, 8H), 6.55 (s, 2H), 6.35 (d, *J* = 4.3 Hz, 1H), 5.45 (s, 2H), 2.10 (s, 3H), 2.00 (dtd, *J* = 13.6, 6.8, 4.5 Hz, 1H), 0.67 (d, *J* = 6.9 Hz, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 148.1,

144.5, 133.1, 132.1, 124.0, 129.2, 128.3 (d, J = 15.4 Hz), 126.3, 51.7, 34.4, 21.5, 18.6. HRMS calcd for $C_{37}H_{36}N$ (M^+ + H): 494.2842, found: 494.2824.



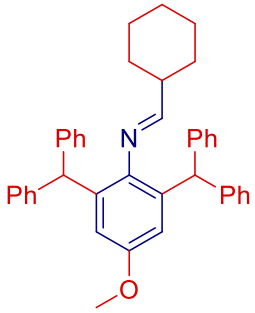
3b

(*E*)-*N*-(2,6-Dibenzhydryl-4-methoxyphenyl)-2-methylpropan-1-imine (3b). White solid. Yield 73% (3.72 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, J = 7.4 Hz, 8H), 7.17 (t, J = 7.3 Hz, 4H), 7.04 (d, J = 7.4 Hz, 8H), 6.37 (d, J = 4.3 Hz, 1H), 6.33 (s, 2H), 5.47 (s, 2H), 3.49 (s, 3H), 2.05 – 1.95 (m, 1H), 0.66 (d, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 155.3, 144.2 (d, J = 8.2 Hz), 134.6, 129.9, 129.7, 128.7, 128.3, 126.4, 114.3, 55.2, 51.9, 34.4, 18.6. HRMS calcd for $C_{37}H_{36}NO$ (M^+ + H): 510.2791, found: 510.2771.



3c

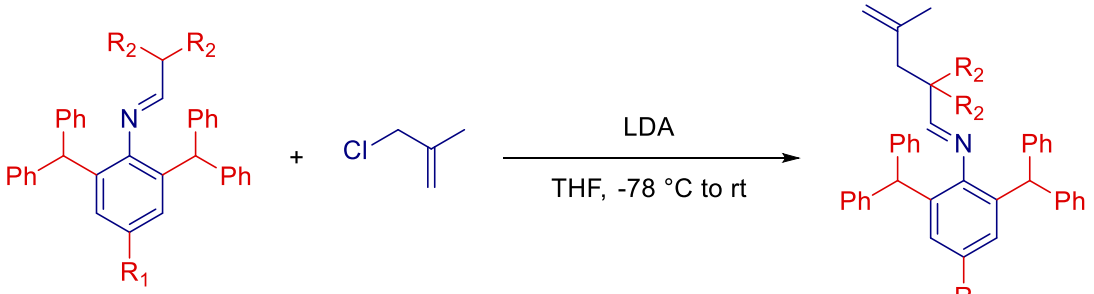
(*E*)-1-Cyclohexyl-*N*-(2,6-dibenzhydryl-4-methylphenyl)methanimine (3c). White solid. Yield 65% (3.48 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, J = 7.4 Hz, 8H), 7.17 (t, J = 7.2 Hz, 4H), 7.03 (d, J = 7.5 Hz, 8H), 6.55 (s, 2H), 6.38 (d, J = 4.6 Hz, 1H), 5.46 (s, 2H), 2.10 (s, 3H), 1.78 (ddd, J = 15.3, 7.7, 4.0 Hz, 1H), 1.56 (d, J = 9.3 Hz, 3H), 1.39 (d, J = 11.8 Hz, 2H), 1.17 – 1.08 (m, 2H), 1.01 (m, 1H), 0.73 (td, J = 14.5, 2.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 148.3, 144.5, 133.1, 132.1, 130.0, 129.2, 128.3 (d, J = 16.1 Hz), 126.2, 51.6, 43.9, 29.0, 26.1, 25.6, 21.5. HRMS calcd for $C_{40}H_{40}N$ (M^+ + H): 534.3155, found: 534.3133.



3d

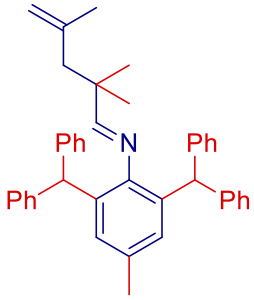
(*E*)-1-Cyclohexyl-*N*-(2,6-dibenzhydryl-4-methoxyphenyl)methanimine (3d). White solid. Yield 61% (3.35 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.4 Hz, 9H), 7.16 (t, *J* = 7.2 Hz, 4H), 7.03 (d, *J* = 7.5 Hz, 9H), 6.38 (d, *J* = 4.6 Hz, 1H), 6.32 (s, 2H), 5.47 (s, 2H), 3.49 (s, 3H), 1.77 (ddd, *J* = 15.2, 7.7, 4.0 Hz, 1H), 1.56 (d, *J* = 9.4 Hz, 3H), 1.36 (d, *J* = 11.9 Hz, 2H), 1.16 – 1.08 (m, 2H), 1.03 (m, 1H), 0.71 (dt, *J* = 14.3, 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 155.3, 144.4, 144.2, 134.6, 129.9, 128.3, 126.4, 114.3, 55.2, 51.8, 43.9, 29.0, 26.1, 25.6. HRMS calcd for $C_{40}H_{40}NO$ (M^+ + H): 550.3104, found: 550.3094.

2. General Procedure for the Synthesis of Imines 4a–4d.



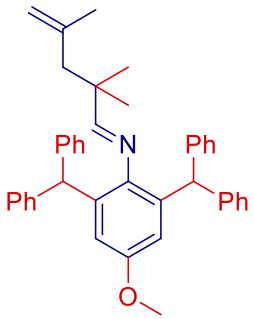
An oven-dried vial equipped with a stir bar was charged with imine **3** (1 mmol, 1 equiv) and THF (2 mL), and cooled down to -78 °C. LDA in THF (1.0 M, 3.6 mL, 3.6 mmol, 3.6 equiv) was cooled to -78 °C and added slowly to the solution of imine. After 15 min, the reaction mixture was warmed up slowly to room temperature and the stirring was continued for additional 3 hours. The reaction mixture was cooled to -78 °C, 3-chloro-2-methylprop-1-ene (1.086 g, 6 mmol, 6 equiv) was added. The reaction mixture was stirred at -78 °C for 15 min, warmed up slowly to room temperature and the stirring was continued for additional 20 h. After the indicated time, the reaction mixture was

concentrated under vacuum. Extraction with hexanes afforded the crude product. Purification by chromatography on silica gel(hexane/diethyl ether = 100:1-60:1) afforded the title product.[4]



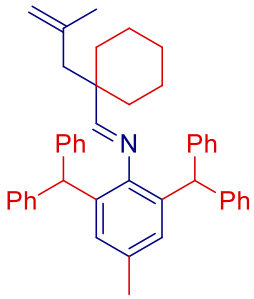
4a

(*E*)-*N*-(2,6-Dibenzhydryl-4-methylphenyl)-2,2,4-trimethylpent-4-en-1-imine (4a). Yellow oil. Yield 85% (465 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.6 Hz, 8H), 7.09 (t, *J* = 7.1 Hz, 4H), 6.94 (d, *J* = 7.2 Hz, 8H), 6.65 (s, 1H), 6.47 (s, 2H), 5.41 (s, 2H), 4.66 (s, 1H), 4.38 (s, 1H), 2.01 (s, 3H), 1.59 (s, 2H), 1.50 (s, 3H), 0.64 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 147.9, 144.7, 142.4, 132.7, 132.1, 130.0, 129.5, 128.2, 126.2, 115.0, 51.3, 46.3, 40.0, 25.3, 24.4, 21.5. HRMS calcd for $C_{41}H_{42}N$ (M^+ + H): 548.3312, found: 548.3289.



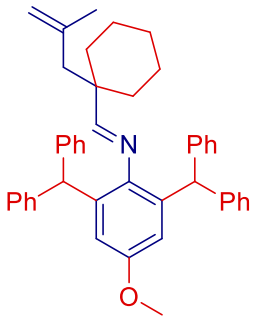
4b

(*E*)-*N*-(2,6-Dibenzhydryl-4-methoxyphenyl)-2,2,4-trimethylpent-4-en-1-imine (4b). Yellow oil. Yield 82% (462 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.3 Hz, 8H), 7.04 (t, *J* = 6.9 Hz, 4H), 6.91 (d, *J* = 7.2 Hz, 8H), 6.61 (s, 1H), 6.20 (s, 2H), 5.38 (s, 2H), 4.61 (s, 1H), 4.33 (s, 1H), 3.35 (s, 3H), 1.52 (s, 2H), 1.44 (s, 3H), 0.59 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 155.3, 144.4, 144.0, 142.4, 134.3, 130.0, 128.3, 126.4, 115.0, 114.5, 55.2, 51.6, 46.2, 39.9, 25.3, 24.4. HRMS calcd for $C_{41}H_{42}NO$ (M^+ + H): 564.3261, found: 564.3242.



4c

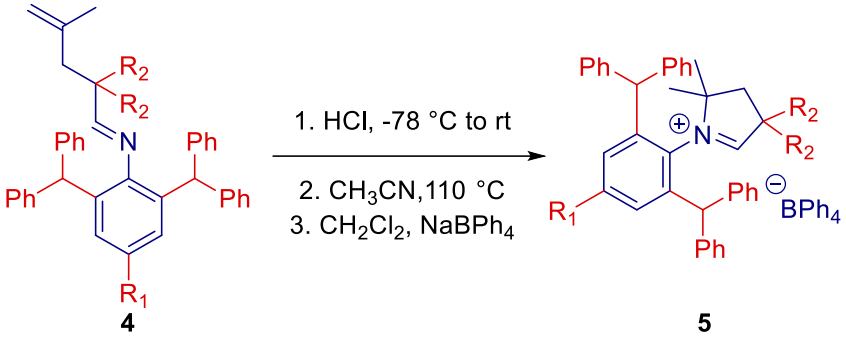
(*E*)-*N*-(2,6-Dibenzhydryl-4-methylphenyl)-1-(1-(2-methylallyl)cyclohexyl)methanimine (4c). Yellow oil. Yield 75 % (440 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.5 Hz, 9H), 7.08 (t, *J* = 7.2 Hz, 4H), 6.98 (s, 1H), 6.95 (d, *J* = 7.5 Hz, 8H), 6.51 (s, 2H), 5.53 (s, 2H), 4.61 (s, 1H), 4.36 (s, 1H), 2.01 (s, 3H), 1.72 (s, 2H), 1.41 (s, 3H), 1.35 – 1.30 (m, 2H), 1.25 – 1.20 (m, 3H), 1.18 – 1.05 (m, 5H), 0.78 (dd, *J* = 11.0, 7.4 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 148.2, 144.8, 142.4, 132.7, 132.2, 130.0, 129.7, 128.6, 128.2, 126.2, 115.2, 51.1, 44.8, 43.7, 33.1, 25.9, 25.5, 22.4, 21.5, 1.2. HRMS calcd for $C_{44}H_{46}N$ (M^+ + H): 588.3625, found: 588.3596.



4d

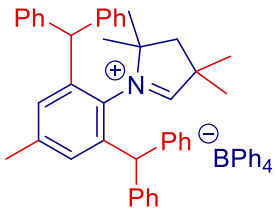
(*E*)-*N*-(2,6-Dibenzhydryl-4-methoxyphenyl)-1-(1-(2-methylallyl)cyclohexyl)methanimine (4d). Yellow oil. Yield 72% (434 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.5 Hz, 8H), 7.17 (t, *J* = 7.1 Hz, 4H), 7.04 (m, 9H, containing H-C=N), 6.37 (s, 2H), 5.63 (s, 2H), 4.69 (s, 1H), 4.44 (s, 1H), 3.49 (s, 3H), 1.78 (s, 2H), 1.48 (s, 3H), 1.40 (d, *J* = 13.3 Hz, 2H), 1.33 – 1.10 (m, 8H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 155.3, 144.6, 144.3, 142.4, 134.3, 129.9, 128.3, 126.3, 115.2, 114.7, 55.2, 51.3, 44.9, 43.7, 33.1, 25.9, 25.5, 22.4. HRMS calcd for $C_{44}H_{46}NO$ (M^+ + H): 604.3574, found: 604.3539.

3. General Procedure for the Synthesis of CAAC–IPr* Salts 5a-5d.



4 **5**

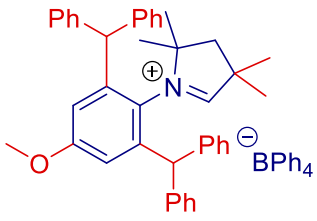
Imine **4** (1 mmol, 1 equiv) was dissolved in 5 mL hexane, and cooled to -78 °C. HCl in diethyl ether solution (2 M, 0.55 mL, 1.1 mmol, 1.1 equiv) was added slowly. Precipitation of a white powder was immediately observed. The reaction mixture was stirred for 15 min at -78 °C, and then slowly warmed to room temperature over 15 min. The precipitate was filtered, washed with hexanes (2 x 10 mL), and dried under vacuum to afford the corresponding alkenyl iminium salt. The alkenyl iminium salt was dissolved in CH_3CN (2 mL) and heated at 110 °C for 24 h. After the indicated time, the reaction mixture was cooled down to room temperature, filtered and concentrated. Diethyl ether (5 mL) was added to the crude reaction to afford the chloride salt. The chloride salt was dissolved in dichloromethane (5 mL), $NaBPh_4$ (5 mmol, 5 equiv) was added, and the reaction mixture was stirred for 15 h. After the indicated time, the reaction mixture was filtered and concentrated. Purification by chromatography on silica gel (dichloromethane/MeOH = 25:1-15:1) afforded the title product.[4]



5a

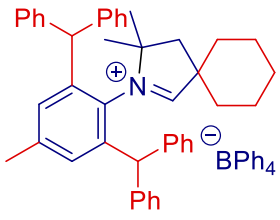
1-(2,6-Dibenzhydryl-4-methylphenyl)-2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-1-ium tetraphenylborate (IPr*–CAAC^{Me}HBPh$_4$, 5a). Brown solid. Yield 65% (564 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 8H), 7.35 (d, *J* = 7.2 Hz, 6H), 7.24 (s, 6H), 7.04 (t, *J* = 7.3 Hz, 8H), 6.89 (dt, *J* = 14.3, 6.9 Hz, 8H), 6.78 (s, 2H), 6.69 – 6.60 (m, 4H), 5.76 (s, 1H), 5.35 (s, 2H), 2.24 (s, 3H), 1.74 (s, 2H), 1.58 (s, 6H), 0.74 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 191.1, 164.9, 164.6,

164.2, 163.8, 142.3, 141.4, 140.7, 140.4, 136.5, 133.9, 131.8, 129.8, 129.6, 129.3 (dd, *J* = 21.0, 3.5 Hz), 128.8, 128.4, 128.3, 128.0, 127.7, 125.8, 125.4, 122.0, 86.3, 66.2, 52.0, 51.0, 47.8, 47.2, 29.6, 26.9, 21.9. HRMS calcd for $C_{41}H_{42}N$ (M^+ – BPh_4): 548.3312, found: 548.3290.



5b

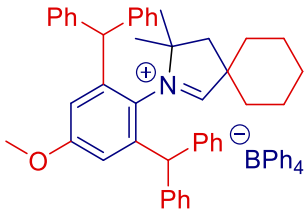
1-(2,6-Dibenzhydryl-4-methoxyphenyl)-2,2,4,4-tetramethyl-3,4-dihydro-2*H*-pyrrol-1-ium tetraphenylborate (IPr*^{MeO}–CAAC^{Me}HBPh$_4$, 5b). Brown solid. Yield 61% (539 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 8H), 7.34 (dd, *J* = 16.1, 7.2 Hz, 6H), 7.25 (d, *J* = 4.8 Hz, 6H), 7.06 (t, *J* = 7.3 Hz, 8H), 6.91 (dt, *J* = 14.3, 7.3 Hz, 8H), 6.70 (d, *J* = 4.8 Hz, 4H), 6.49 (s, 2H), 5.76 (s, 1H), 5.35 (s, 2H), 3.54 (s, 3H), 1.72 (s, 2H), 1.57 (s, 6H), 0.72 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 165.0, 164.6, 164.2, 163.8, 161.1, 142.7, 141.0, 140.3, 136.5, 129.4, 129.3, 129.2, 129.1, 128.5, 128.1, 125.7, 124.0, 121.9, 116.5, 86.0, 55.6, 52.2, 47.8, 47.0, 29.6, 26.9. HRMS calcd for $C_{41}H_{42}NO$ (M^+ – BPh_4): 564.3261, found: 564.3242.



5c

2-(2,6-Dibenzhydryl-4-methylphenyl)-3,3-dimethyl-2-azaspiro[4.5]dec-1-en-2-ium tetraphenylborate (IPr*–CAAC^{Cy}HBPh$_4$, 5c). Brown solid. Yield 71% (644 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 8H), 7.34 (t, *J* = 7.1 Hz, 6H), 7.24 (d, *J* = 3.5 Hz, 7H), 7.05 (t, *J* = 7.3 Hz, 8H), 6.89 (dd, *J* = 15.1, 7.4 Hz, 8H), 6.79 (s, 2H), 6.70 – 6.65 (m, 4H), 6.12 (s, 1H), 5.40 (s, 2H), 2.24 (s, 3H), 1.84 (s, 2H), 1.62 (s, 6H), 1.40 – 1.32 (m, 1H), 1.26 – 1.15 (m, 4H), 1.09 – 0.97 (m, 1H), 0.94 – 0.83 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 165.0, 164.2, 142.2, 141.6, 140.7, 140.5, 136.6, 131.8, 129.4, 129.4, 129.2, 129.1, 128.3, 128.0, 127.4, 125.8, 125.8, 125.7, 125.7,

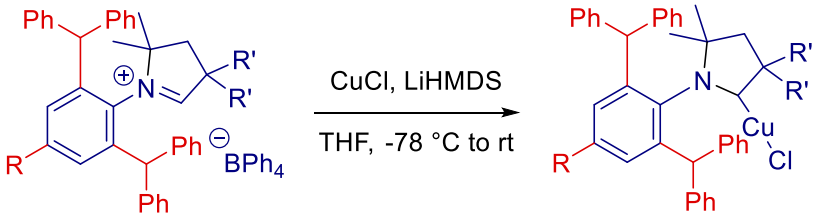
121.9, 85.5, 52.4, 51.8, 35.5, 30.1, 24.1, 21.9, 21.7. HRMS calcd for $C_{44}H_{46}N$ (M^+ – BPh_4): 588.3625, found: 588.3596.



5d

2-(2,6-Dibenzhydryl-4-methoxyphenyl)-3,3-dimethyl-2-azaspiro[4.5]dec-1-en-2-ium tetraphenylborate (IPr*^{MeO}–CAAC^{Cy}HBPh$_4$, 5d). Brown solid. Yield 74% (683 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 8H), 7.38 – 7.31 (m, 7H), 7.26 (s, 16H), 7.05 (t, *J* = 7.4 Hz, 8H), 6.89 (dd, *J* = 14.9, 7.3 Hz, 8H), 6.72 (d, *J* = 3.9 Hz, 4H), 6.48 (s, 2H), 6.12 (s, 1H), 5.40 (s, 2H), 3.53 (s, 3H), 1.82 (s, 2H), 1.60 (s, 6H), 1.42 – 1.31 (m, 1H), 1.26 – 1.16 (m, 4H), 1.09 – 0.97 (m, 1H), 0.95 – 0.84 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.08, 160.98, 142.77, 141.48 (d, *J* = 9.0 Hz), 140.81, 136.57, 134.94, 134.44, 131.26, 130.29, 129.51 (dd, *J* = 18.0, 11.5 Hz), 129.2, 129.0, 128.7, 128.5, 128.5 – 127.8 (m), 127.8 – 127.3 (m), 127.0, 125.8, 122.0, 116.6, 115.8, 67.3, 55.6, 52.0, 35.7, 30.8, 24.2, 21.8, 14.4, 1.2. HRMS calcd for $C_{44}H_{46}NO$ (M^+ – BPh_4): 604.3574, found: 604.3541.

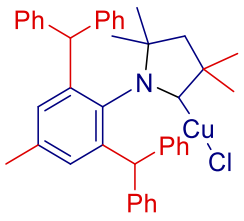
4. General Procedure for the Synthesis of [Cu(IPr*–CAAC)Cl] 6a-6d.



5 **6**

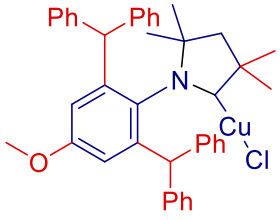
An oven-dried vial was equipped with a stirring bar and charged with IPr*–CAAC salt **5** (0.2 mmol, 1 equiv) and CuCl (60 mg, 0.6 mmol, 3 equiv), subjected to three evacuation/backfilling cycles under high vacuum, freshly distilled THF (1 mL) was added, and the reaction mixture was cooled down to -78 °C. LiHMDS (1.0 M in hexane, 0.6 mL, 0.6 mmol, 3 equiv) was added slowly at -78 °C, the reaction mixture was stirred for 15 min at -78 °C, slowly warmed up to room temperature and stirred for additional 20 h. After the indicated time, the reaction mixture was

filtered through a short pad of silica and concentrated. Purification by chromatography on silica gel (hexane/diethyl ether = 5:1-1:1) afforded the title product.



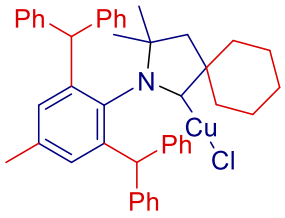
6a

(1-(2,6-Dibenzhydryl-4-methylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene)copper(I) chloride, [Cu(IPr*–CAAC^{Me})Cl] (6a). Yellow solid. Yield 84% (108 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.1 Hz, 8H), 7.28 – 7.22 (m, 4H), 7.17 (d, *J* = 7.2 Hz, 4H), 7.12 (d, *J* = 7.2 Hz, 4H), 7.04 (s, 2H), 5.56 (s, 2H), 2.26 (s, 3H), 2.01 (s, 2H), 1.45 (s, 6H), 1.32 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 253.8, 143.6, 142.9, 139.7, 138.2, 136.6, 132.6, 129.7, 129.5, 129.4, 128.5, 127.3, 126.7, 82.7, 54.7, 51.7, 50.78, 30.7, 28.8, 21.7. HRMS calcd for $C_{41}H_{41}CuN$ (M^+ – Cl): 610.2535, found: 610.2512.



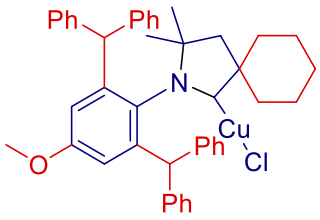
6b

(1-(2,6-Dibenzhydryl-4-methoxyphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene)copper(I) chloride, [Cu(IPr*^{MeO}–CAAC^{Me})Cl] (6b). Yellow solid. Yield 82% (108 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 15.1, 7.5 Hz, 8H), 7.24 (t, *J* = 7.3 Hz, 4H), 7.18 (d, *J* = 7.7 Hz, 4H), 7.12 (d, *J* = 7.6 Hz, 4H), 6.74 (s, 2H), 5.56 (s, 2H), 3.62 (s, 3H), 1.99 (s, 2H), 1.42 (s, 6H), 1.31 (s, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 254.5, 158.4, 143.5, 142.7, 141.6, 133.4, 132.2, 129.6, 129.5 (d, *J* = 6.8 Hz), 128.6, 128.5, 127.6, 127.4, 126.8, 125.8, 117.3, 82.6, 55.3, 54.6, 52.0, 50.8, 30.7, 28.8. HRMS calcd for $C_{41}H_{41}CuNO$ (M^+ – Cl): 626.2479, found: 626.2449.



6c

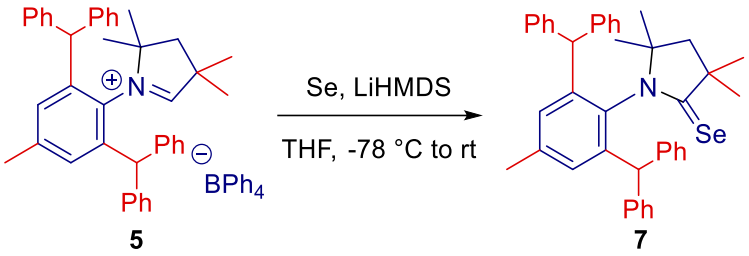
(2-(2,6-Dibenzhydryl-4-methylphenyl)-3,3-dimethyl-2-azaspiro[4.5]decan-1-ylidene) copper(I) chloride, [Cu(IPr*–CAAC^{Cy})Cl] (6c). Yellow solid. Yield 77% (105 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 8H), 7.23 (dd, *J* = 14.3, 7.2 Hz, 4H), 7.15 (d, *J* = 7.4 Hz, 4H), 7.11 (d, *J* = 7.5 Hz, 4H), 7.05 (s, 2H), 5.54 (s, 2H), 2.27 (s, 3H), 2.15 (t, *J* = 12.6 Hz, 2H), 2.03 (s, 2H), 1.84 (d, *J* = 12.7 Hz, 2H), 1.69 (d, *J* = 11.8 Hz, 1H), 1.54 (s, 1H), 1.49 – 1.33 (m, 4H), 1.30 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 253.9, 143.7, 143.0, 139.7, 138.1, 136.8, 132.6, 129.7, 129.5, 129.4, 128.5, 128.4, 128.2, 127.3, 126.7, 81.7, 60.1, 51.8, 47.0, 36.4, 31.3, 25.2, 22.2, 21.7, 8.0. HRMS calcd for $C_{44}H_{45}CuN$ (M^+ – Cl): 650.2843, found: 650.2808.



6d

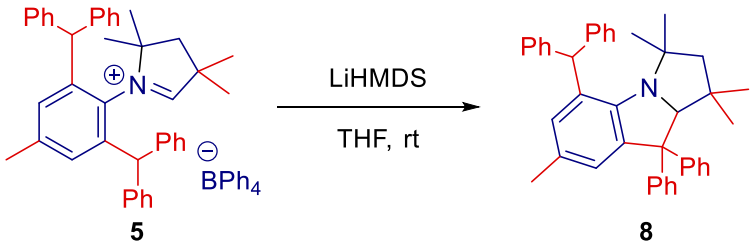
(2-(2,6-Dibenzhydryl-4-methoxyphenyl)-3,3-dimethyl-2-azaspiro[4.5]decan-1-ylidene) copper(I) chloride, [Cu(IPr*^{MeO}–CAAC^{Cy})Cl] (6d). Yellow solid. Yield 69% (96 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 13.7, 7.2 Hz, 8H), 7.25 – 7.20 (m, 5H), 7.16 (d, *J* = 7.6 Hz, 4H), 7.11 (d, *J* = 7.5 Hz, 4H), 6.75 (s, 2H), 5.55 (s, 2H), 3.62 (s, 3H), 2.12 (t, *J* = 11.3 Hz, 2H), 2.01 (s, 2H), 1.82 (d, *J* = 12.6 Hz, 2H), 1.67 (d, *J* = 10.7 Hz, 1H), 1.52 (d, *J* = 13.3 Hz, 2H), 1.36 (m, 3H), 1.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 254.6, 158.3, 143.6, 142.9, 141.5, 132.4, 129.8, 129.6, 129.5, 128.6, 127.4, 126.8, 117.3, 115.5, 59.9, 55.3, 52.0, 46.9, 36.3, 31.3, 29.9, 25.2, 22.1. HRMS calcd for $C_{44}H_{45}CuNO$ (M^+ – Cl): 666.2792, found: 666.2744.

5. General Procedure for the Synthesis of [Se(IPr*–CAAC^{Me})] 7.



1-(2,6-Dibenzhydryl-4-methylphenyl)-3,3,5,5-tetramethylpyrrolidine-2-selenone, [Se(IPr*–CAAC^{Me})] (7). An oven-dried vial equipped with a stirring bar was charged with salt **5** (0.5 mmol, 1 equiv) and Se (1.5 mmol, 3 equiv), subjected to three evacuation/backfilling cycles under high vacuum, freshly distilled THF (1 mL) was added, and the reaction mixture was cooled down to -78 °C. LiHMDS (1.0 M in hexane, 1.5 mL, 1.5 mmol, 3 equiv) was added slowly at -78 °C, the reaction mixture was stirred for 15 min at -78 °C, slowly warmed up to room temperature and stirred for additional 20 h. After the indicated time, the reaction mixture was filtered through a short pad of silica and concentrated. Purification by chromatography on silica gel (hexane/diethyl ether = 20:1) afforded the title product. Yellow solid. Yield 84% (263 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.21 (d, *J* = 7.3 Hz, 2H), 7.20 – 7.14 (m, 9H), 7.12 – 7.08 (m, 4H), 5.39 (s, 2H), 2.23 (s, 3H), 2.01 (s, 2H), 1.62 (s, 6H), 0.67 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.5, 145.5, 144.4, 140.8, 137.2 (d, *J* = 14.2 Hz), 133.1, 130.8, 129.8, 128.6, 128.0, 126.4 (d, *J* = 10.6 Hz), 53.7, 52.0 (d, *J* = 11.3 Hz), 32.2, 29.9, 29.7, 22.9, 21.8. ^{77}Se NMR (95 MHz, $CDCl_3$) δ 532.45. HRMS calcd for $C_{41}H_{42}NSe$ (M^+ + H): 628.2481, found: 628.2448.

6. General Procedure for C–H Activation.

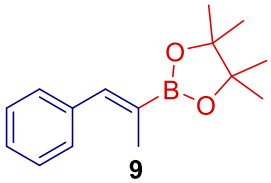


5-Benzhydryl-1,1,3,3,7-pentamethyl-9,9-diphenyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (8). An oven-dried vial equipped with a stirring bar was charged with salt **5** (0.2 mmol, 1 equiv), subjected to three evacuation/backfilling cycles under high vacuum, freshly distilled THF

(0.5 mL) was added. LiHMDS (1.0 M in hexane, 0.6 mL, 0.6 mmol, 3 equiv) was added slowly, and the reaction mixture was stirred at room temperature for 15 h. After the indicated time, the reaction mixture was filtered through a short pad of silica and concentrated. Purification by chromatography on silica gel (hexane/diethyl ether) afforded the title product. White solid. Yield 87% (95 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.6 Hz, 2H), 7.24 – 7.11 (m, 10H), 7.00 (dd, *J* = 9.9, 6.8 Hz, 6H), 6.77 (s, 1H), 6.53 (d, *J* = 7.0 Hz, 2H), 6.30 (s, 1H), 5.94 (s, 1H), 4.40 (s, 1H), 1.98 (s, 3H), 1.86 (d, *J* = 12.6 Hz, 1H), 1.57 (d, *J* = 12.6 Hz, 1H), 1.49 (s, 6H), 0.51 (d, *J* = 16.6 Hz, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 146.1, 144.8, 144.2, 140.6, 137.3, 132.6, 130.9, 130.1, 129.4, 128.3, 128.0 (d, *J* = 9.8 Hz), 127.8, 127.0 – 126.8 (m), 126.7, 126.2, 125.8, 125.6, 125.2, 84.9, 64.1, 59.6, 58.1, 52.6, 40.4, 33.0, 31.8, 28.1, 26.6, 23.4, 22.9, 21.3, 14.3, 1.2. HRMS calcd for $C_{41}H_{42}N$ (M^+ + H): 548.3312, found: 548.3287.

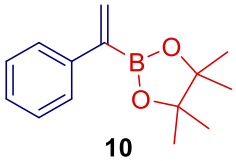
7. General Procedure for Borylation of Alkynes.

An oven dried vial equipped with a stir bar was charged with *t*BuONa (9.61 mg, 0.10 mmol, 0.5 equiv), B_2Pin_2 (1.1-1.5 equiv) and [Cu(CAAC)Cl] (0.01 mmol, 5 mol%), subjected to three evacuation/backfilling cycles under high vacuum, freshly distilled THF (1.0 M), alkyne (0.2 mmol) and MeOH (51 mg, 1.6 mmol, 8 equiv) were added at room temperature. The reaction mixture was stirred at 50 °C for 12 h. After the indicated time, the sample was analyzed by ^{1}HNMR ($CDCl_3$, 500 MHz) and GC-MS to obtain conversion, selectivity and yield using internal standard. Purification by chromatography on silica gel (hexane/EtOAc) afforded the title product.



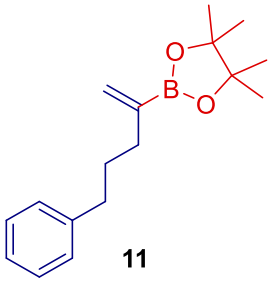
9

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (9). Colorless oil. Eluent (hexane/EtOAc = 40:1-20:1) Yield 88% (42 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.0 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.26 (s, 1H), 2.01 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 138.1, 129.6, 128.2, 127.3, 83.7, 67.3, 25.0, 16.1. Spectroscopic data matched literature values.[5]



10

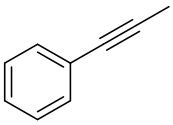
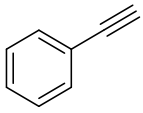
4,4,5,5-Tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (10). White solid, Eluent (hexane/EtOAc = 40:1-20:1). Yield 90% (41 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.22 (m, 1H), 6.11 – 6.05 (m, 2H), 1.33 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 131.1, 128.4, 127.4, 127.2, 84.0, 25.0. Spectroscopic data matched literature values.[6]

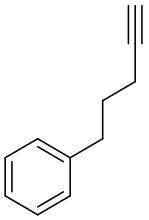


11

4,4,5,5-Tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (11). Colorless oil. Eluent (hexane/Et_2O = 60:1). Yield 90% (49 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 4.5 Hz, 2H), 7.18 (d, *J* = 6.7 Hz, 3H), 5.80 (s, 1H), 5.62 (s, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.20 (d, *J* = 7.1 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.27 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0, 129.5, 128.6, 128.4, 125.7, 83.5, 35.7, 35.3, 31.1, 25.0. Spectroscopic data matched literature values.[7]

8. Optimization of the Reaction Conditions[a]

Alkyne	Cat.	B_2Pin_2 (equiv)	*t*BuONa (equiv)	MeOH (equiv)	*T* (°C)	Yield	Selectivity (β/α)[b]
	**6a**	1.1	0.5	3	50	47%	82:18
	6a	1.1	0.8	3	50	39%	90:10
	6a	1.1	1.0	3	50	29%	>99:1
	6a	1.1	0.5	3	50	47%	82:18
	6a	1.1	0.5	6	50	52%	87:13
	6a	1.1	0.5	8	50	67%	80:20
	6a	1.1	0.5	3	80	46%	87:13
	6a	1.1	0.5	3	100	56%	82:18
	6a	1.1	0.5	3	120	44%	77:23
	6a	1.5	0.5	8	50	98%	83:17
	6b	1.5	0.5	8	50	99%	85:15
	6c	**1.5**	**0.5**	**8**	**50**	**93%**	**96:4**
	6d	1.5	0.5	8	50	99%	90:10
	^{Me}CAAC	1.5	0.5	8	50	33%	90:10
	**6a**	1.1	0.5	8	50	70%	23:77
	6b	**1.1**	**0.5**	**8**	**50**	**95%**	**14:86**
	6c	1.1	0.5	8	50	52%	30:70
	6d	1.1	0.5	8	50	52%	19:81
	^{Me}CAAC	1.1	0.5	8	50	Trace	nd
	6a	1.1	0.5	8	50	95%	16:84
	6b	1.1	0.5	8	50	80%	10:90
	6c	**1.1**	**0.5**	**8**	**50**	**95%**	**4:96**

	**6d**	1.1	0.5	8	50	92%	10:90
	^{Me}CAAC	1.1	0.5	8	50	40%	64:36

[a][Cu(CAAC)Cl] (5 mol%), *t*BuONa (0.5-1 equiv), B_2Pin_2 (1.1-1.5 equiv), alkyne (0.2 mmol), MeOH (8 equiv), THF (1.0 M), 50 °C, 12 h. [b]Determined by ^{1}HNMR.

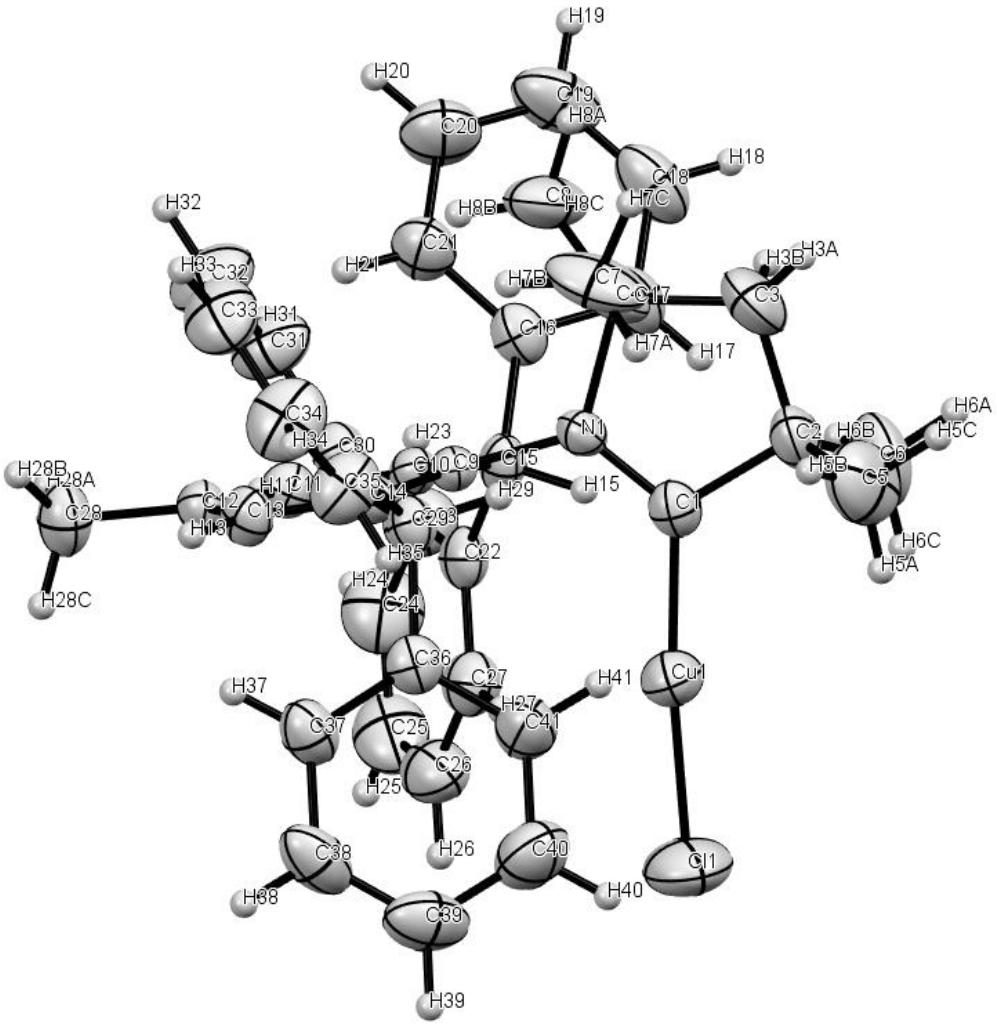
Table S1. *Crystal Data and Structure Refinement Summaries for* **6a** *and* **6b**.

Compound	**6a**	**6b**
Chemical formula	$C_{41}H_{41}ClCuN$	$C_{41}H_{41}ClCuNO$
M_r	646.74	662.74
Crystal system, space group	Triclinic, *P*	Monoclinic, $P2_1/c$
Temperature (K)	293	100
a, *b*, *c* (Å)	10.4977 (3), 13.2850 (5), 14.4578 (5)	18.9464 (2), 10.4063 (1), 17.4414 (2)
β (°)		100.363 (1)
α, β, γ (°)	99.161 (4), 95.616 (5), 116.579 (3), 91.872 (2), 107.172 (3)	
V (Å^3)	1690.51 (11)	3382.69 (6)
Z	2	4
Radiation type	Mo *K*α	Cu *K*α
μ (mm^{-1})	0.75	1.88
Crystal size (mm)	0.4 × 0.25 × 0.1	0.35 × 0.30 × 0.25
Diffractometer	Xcalibur	XtaLAB Synergy R, DW system, HyPix-Arc 150
Absorption correction	Multi-scan	Multi-scan SCALE3 ABSPACK (Rigaku Oxford Diffraction, 2015).
T_{min}, T_{max}	0.998, 1.000	0.529, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11647, 6542, 3724	22019, 6106, 5770
R_{int}	0.029	0.016
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617	0.599
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.079, 0.87	0.027, 0.073, 1.04
No. of reflections	6542	6106
No. of parameters	402	411
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.31	0.26, −0.39

Computer programs: *CrysAlis CCD* (Oxford Diffraction Ltd., 2008), *SHELXS2014*/7 (Sheldrick, 2014), *SHELXL2014*/7 (Sheldrick, 2014), *SHELXTL* (Sheldrick, 2008).

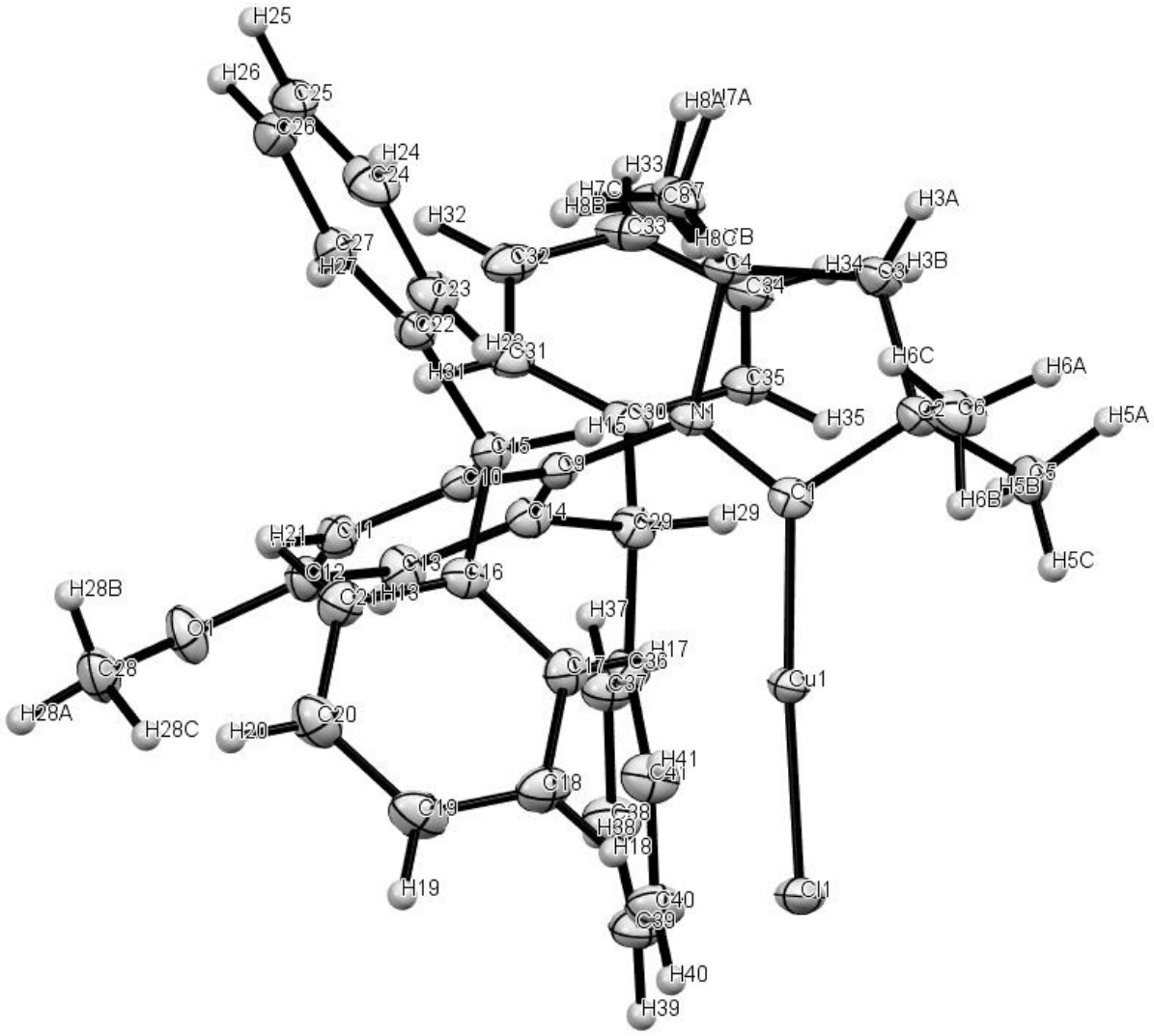
ORTEP Structures of 6a and 6c (Figures S1-S2)

Figure S1. *ORTEP Structure of* **6a** *(50% ellipsoids).* (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2209831).



Selected bond lengths [Å] and angles [°], **6a**: Cu–C1, 2.0835(9); Cu–C1, 1.864(2); N1-C1, 1.300(3); N1-C9, 1.459(4); C1-C2, 1.512(4); C1–Cu–Cl, 174.45(8); C1–N1–C4, 115.4(2); C1–N1–C9, 122.7(2); C4–N1–C9, 121.8(2); Cu–C1–C2, 122.4(2); Cu–C1–N1, 128.6(2); N1–C1–C2, 122.4(2).

Figure S2. *ORTEP Structure of* **6b** *(50% ellipsoids).* (Crystallographic data has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 2209832).



Selected bond lengths [Å] and angles [°], **6b**: Cu–C1, 2.1142(5); Cu–C1, 1.882(1); N1-C1, 1.305(2); N1-C9, 1.457(2); C1-C2, 1.519(2); C1–Cu–Cl, 176.06(5); C1–N1–C4, 115.3(1); C1–N1–C9, 121.6(1); C4–N1–C9, 123.1(1); Cu–C1–C2, 122.5(1); Cu–C1–N1, 128.2(1); N1–C1–C2, 122.5(1).

Computational Methods

Computational Methods. All of the calculations were performed using Gaussian 09 suite of programs. All of the geometry optimizations were performed at the B3LYP level of theory in the gas phase with the 6-311++G(d,p) basis. For geometry optimizations, we employed the X-ray structures of [Cu(IPr*–CAAC^{Me})Cl], [Cu(IPr*^{MeO}–CAAC^{Me})Cl], [Cu(IPr–CAAC)Cl], [Cu(IPr–CAAC^{Cy})Cl] as the starting geometry and performed full optimization. The absence of imaginary frequencies was used to characterize the structures as minima on the potential energy surface. All of the optimized geometries were verified as minima (no imaginary frequencies). Energetic parameters were calculated under standard conditions (298.15 K and 1 atm). Structural representations were generated using CYLview software (Legault, C. Y. CYLview version 1.0 BETA, University of Sherbrooke). All other representations were generated using GaussView (GaussView, version 5, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission, KS, 2009) or ChemCraft software (Andrienko, G. L. ChemCraft version b562a, https://www.chemcraftprog.com).

Full Reference for Gaussian 09

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table S2. HOMO and LUMO Energy Levels Calculated at the B3LYP 6-311++g(d,p) Level

entry	Compound	orbital	E [au]	E [eV]	E [kcal/mol]	ΔE [eV]
1	IPr*–CAAC^{Me}	HOMO	-0.2017	-5.49	-126.57	
2	IPr*–CAAC^{Me}	LUMO	-0.033	-0.90	-20.71	-4.59
3	IPr*^{MeO}–CAAC^{Me}	HOMO	-0.2007	-5.46	-125.94	
4	IPr*^{MeO}–CAAC^{Me}	LUMO	-0.0335	-0.91	-21.021	-4.55
5	IPr*–CAAC^{Cy}	HOMO	-0.2005	-5.46	-125.81	
6	IPr*–CAAC^{Cy}	LUMO	-0.0325	-0.88	-20.39	-4.57
7	IPr*^{MeO}–CAAC^{Cy}	HOMO	-0.1995	-5.43	-125.19	
8	IPr*^{MeO}–CAAC^{Cy}	LUMO	-0.033	-0.90	-20.71	-4.53

Table S3. %V_{bur} and Quadrant Distribution for Linear [Cu(IPr*–CAAC)Cl] Complexes at the B3LYP 6-311++g(d,p) Level (Falivene, L. et al. *Nat. Chem.* 2019*, 11,* 872)

entry	Compound	%V_{bur}	SW	NW	NE	SE
1	[Cu(IPr*–CAAC^{Me})Cl]	47.1	31.8	34.7	62.3	59.7
2	[Cu(IPr*^{MeO}–CAAC^{Me})Cl]	47.1	31.8	35.0	61.9	59.6
3	[Cu(IPr*–CAAC^{Cy})Cl]	47.3	32.1	34.9	62.5	59.8
4	[Cu(IPr*^{MeO}–CAAC^{Cy})Cl]	47.3	32.1	35.4	62.0	59.8
5[a]	[Cu(IPr*–CAAC^{Me})Cl]	49.5	35.2	34.4	63.7	64.9
6[a]	[Cu(IPr*^{MeO}–CAAC^{Me})Cl]	49.4	32.6	34.4	68.8	61.9

[a]%V_{bur} and quadrant distribution of [Cu(IPr*–CAAC)Cl] complexes **6a** and **6b** are shown for comparison (x-ray data). For further comparison of %V_{bur} , see Figures S3-S4.

Figure S3. (A-D) Topographical steric maps of [Cu(IPr*–CAAC^{Me})Cl] **6a**, [Cu(IPr*^{MeO}–CAAC^{Me})Cl] **6b**, [Cu(IPr*–CAAC^{cy})Cl] **6c**, [Cu(IPr*^{MeO}–CAAC^{cy})Cl] **6d** showing %V_{bur} per quadrant at the B3LYP 6-311++g(d,p) level.

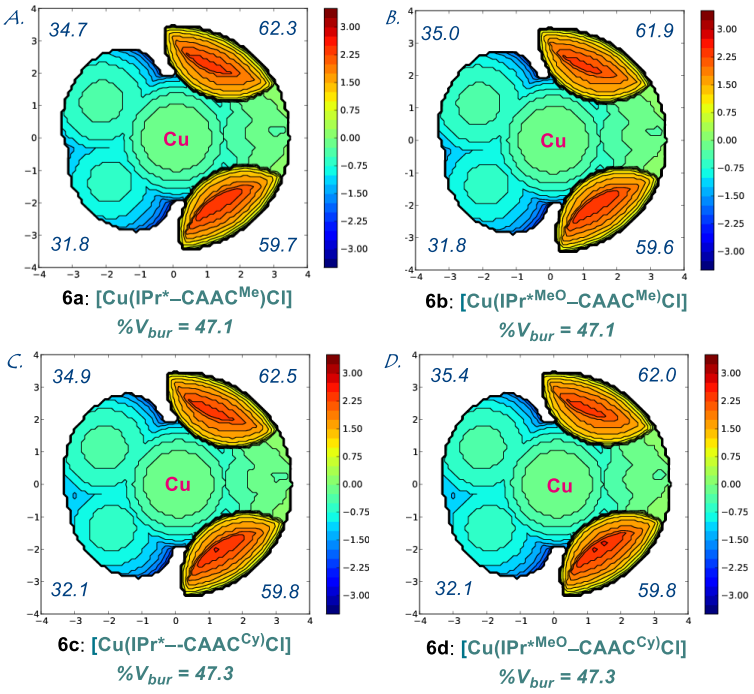
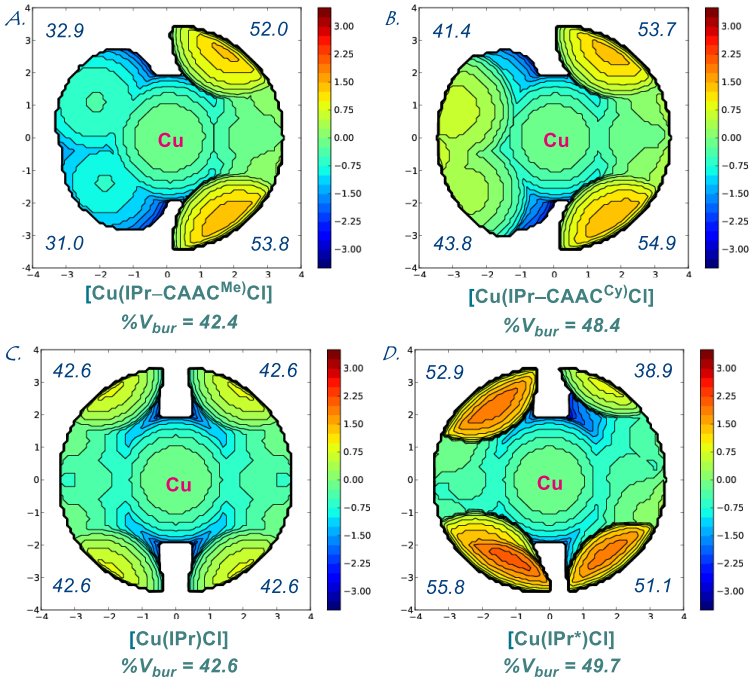


Figure S4. (A-D) Topographical steric maps of [Cu(IPr–CAAC^{Me})Cl], [Cu(IPr–CAAC^{Cy})Cl], [Cu(IPr)Cl] and [Cu(IPr*)Cl] showing %V_{bur} per quadrant at the B3LYP 6-311++g(d,p) level.



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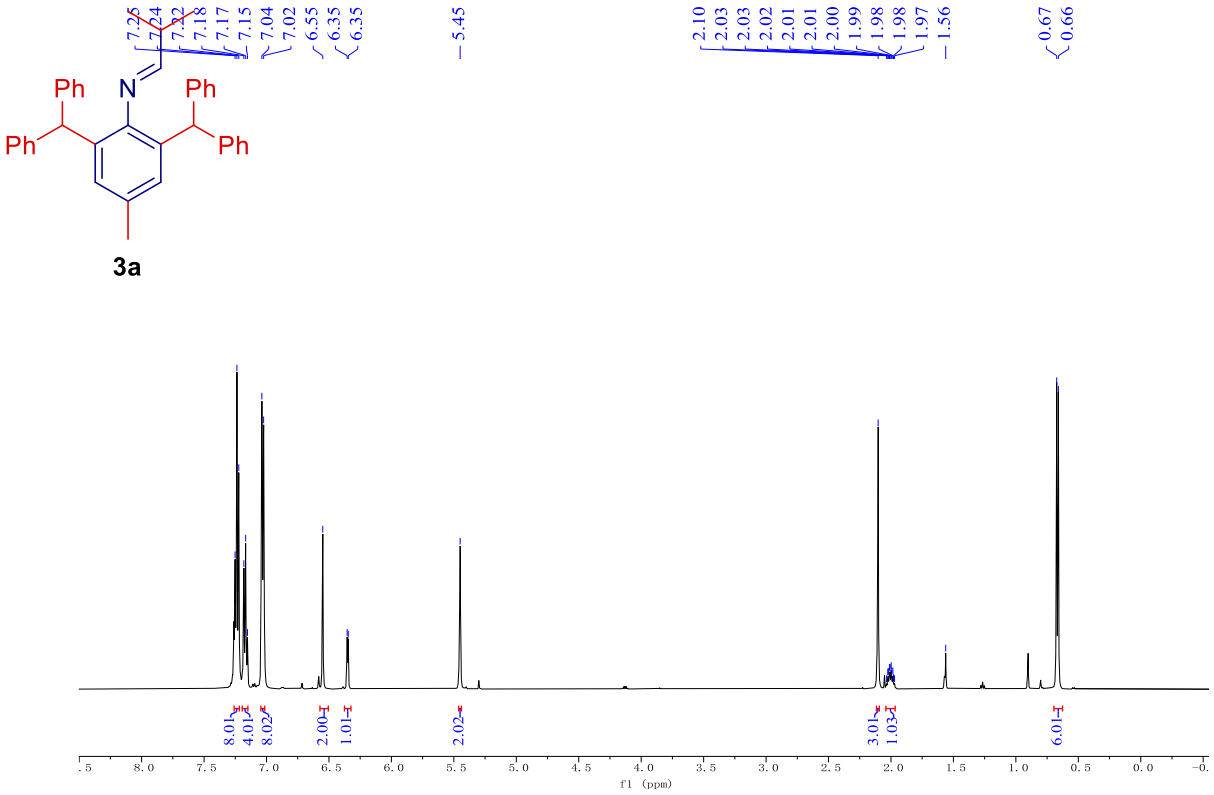
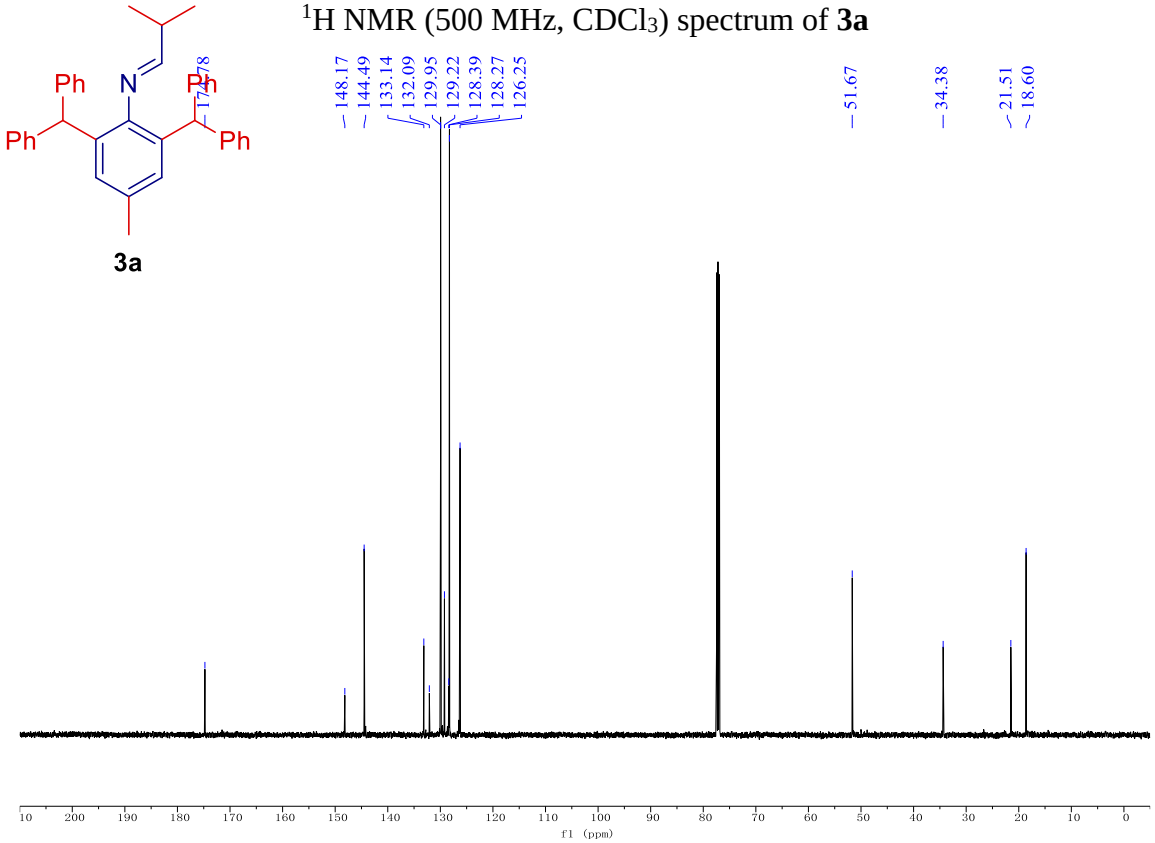
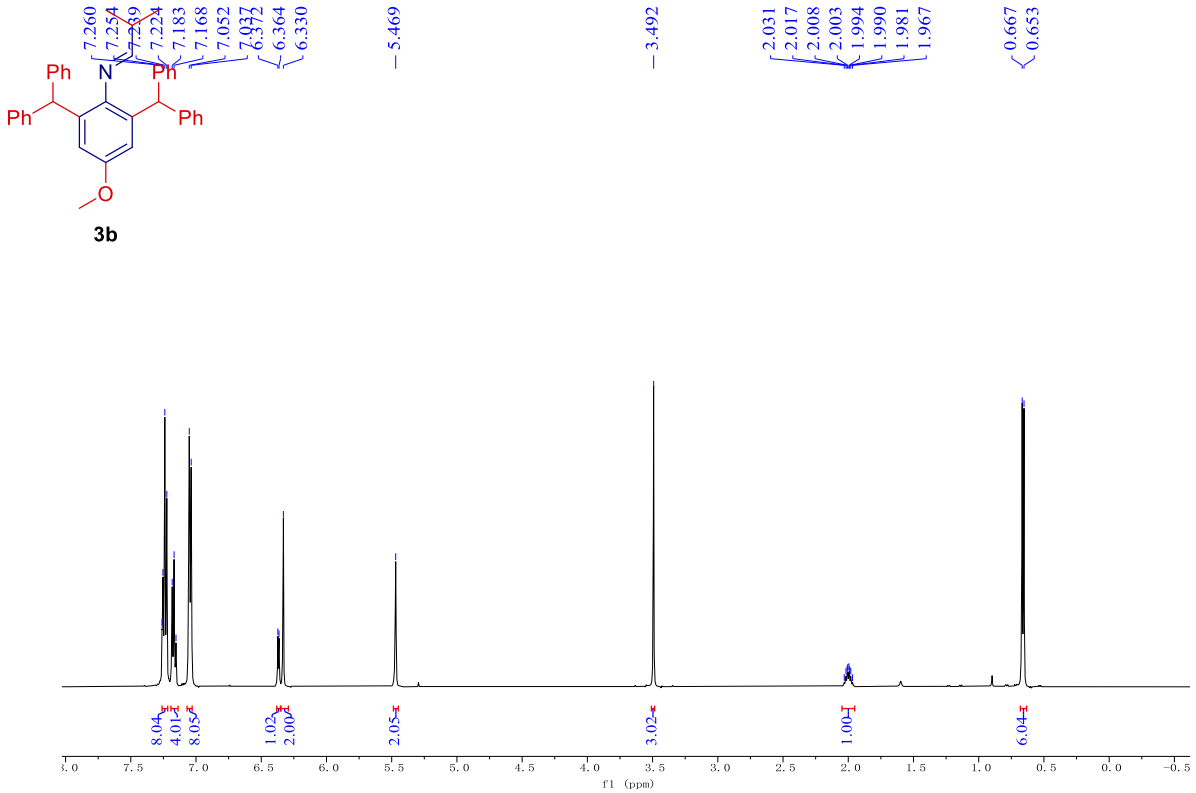


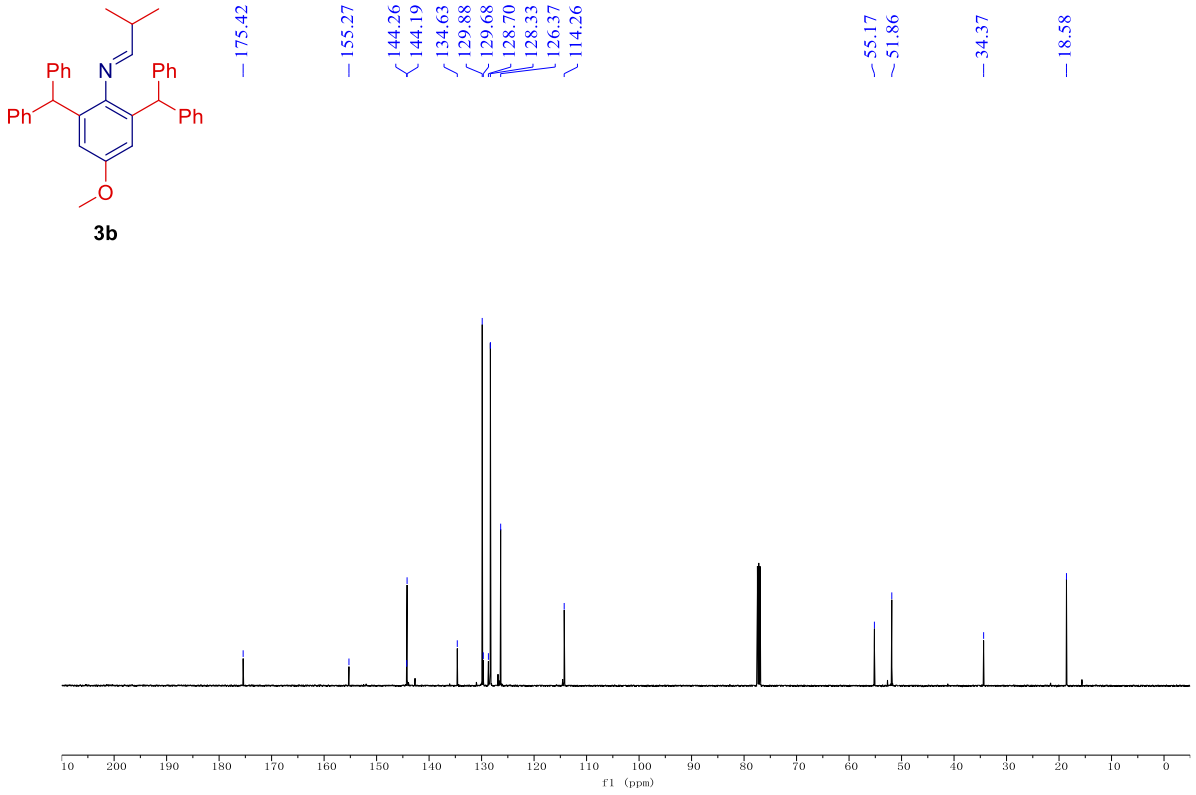
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3a**



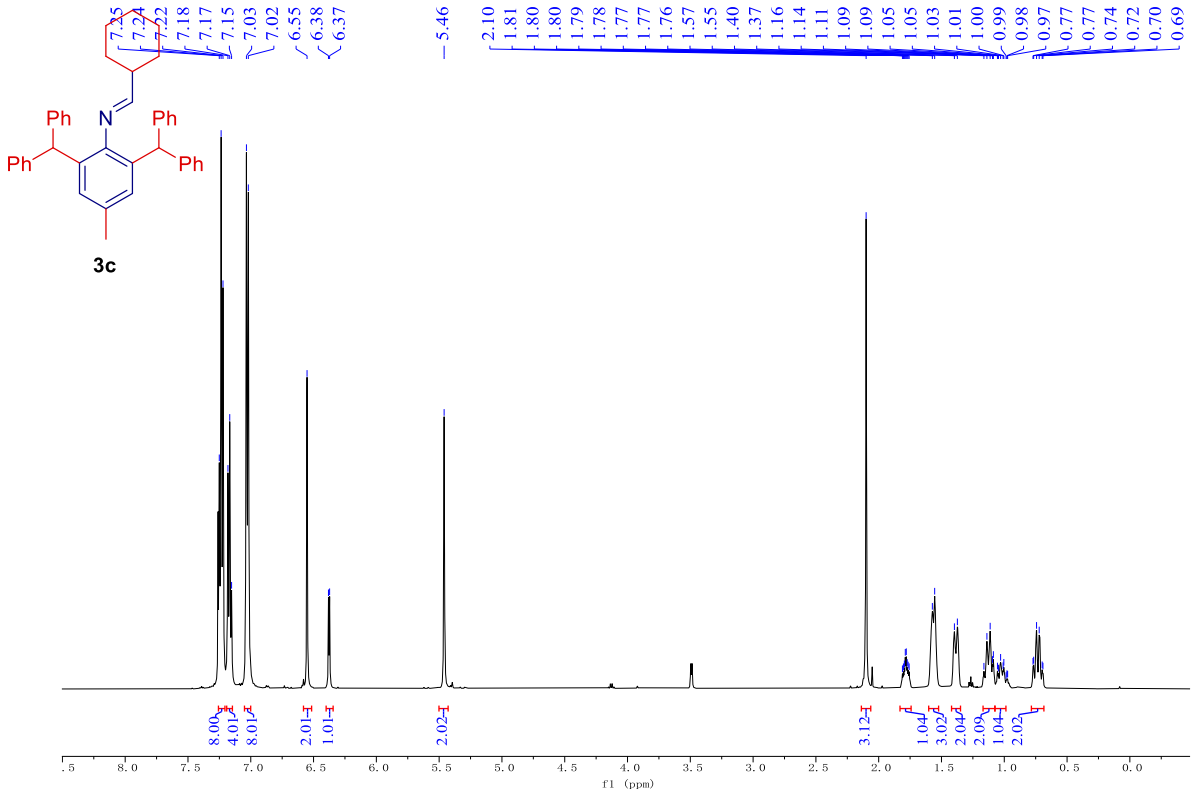
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3a**



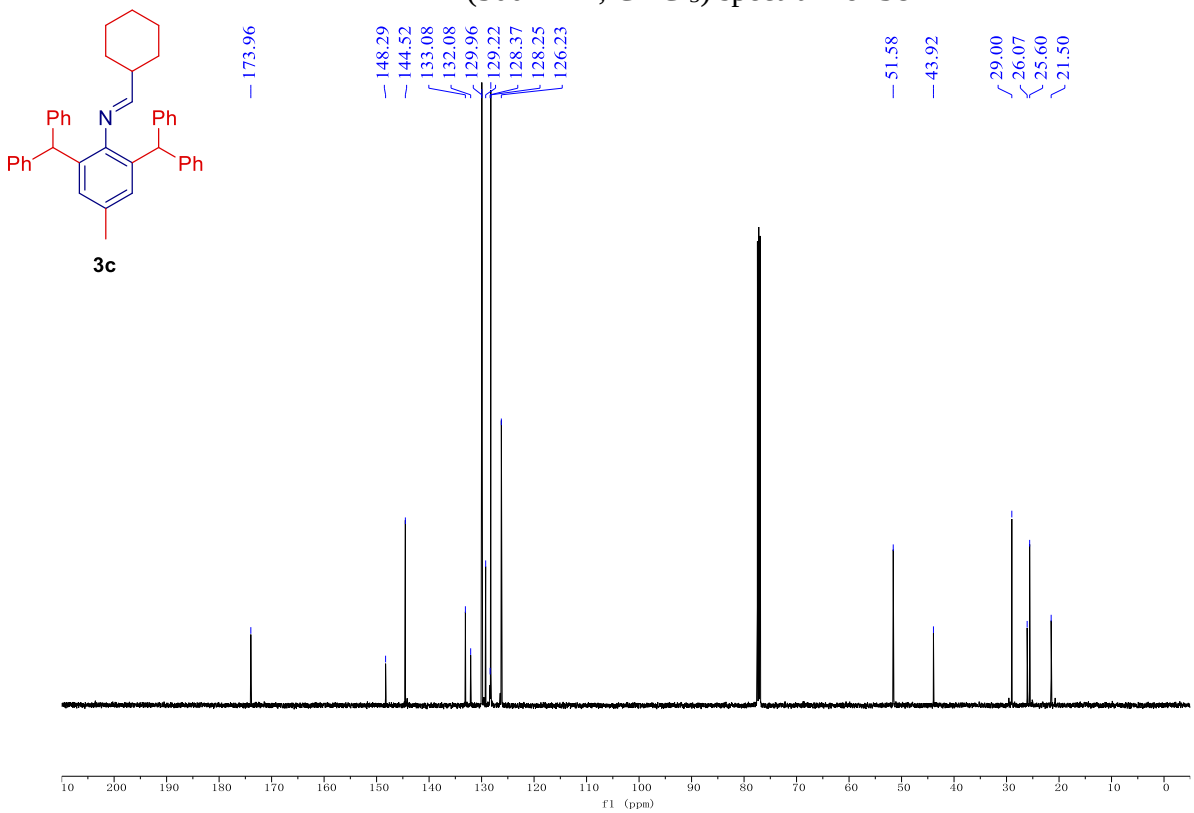
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3b**



^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3b**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3c**



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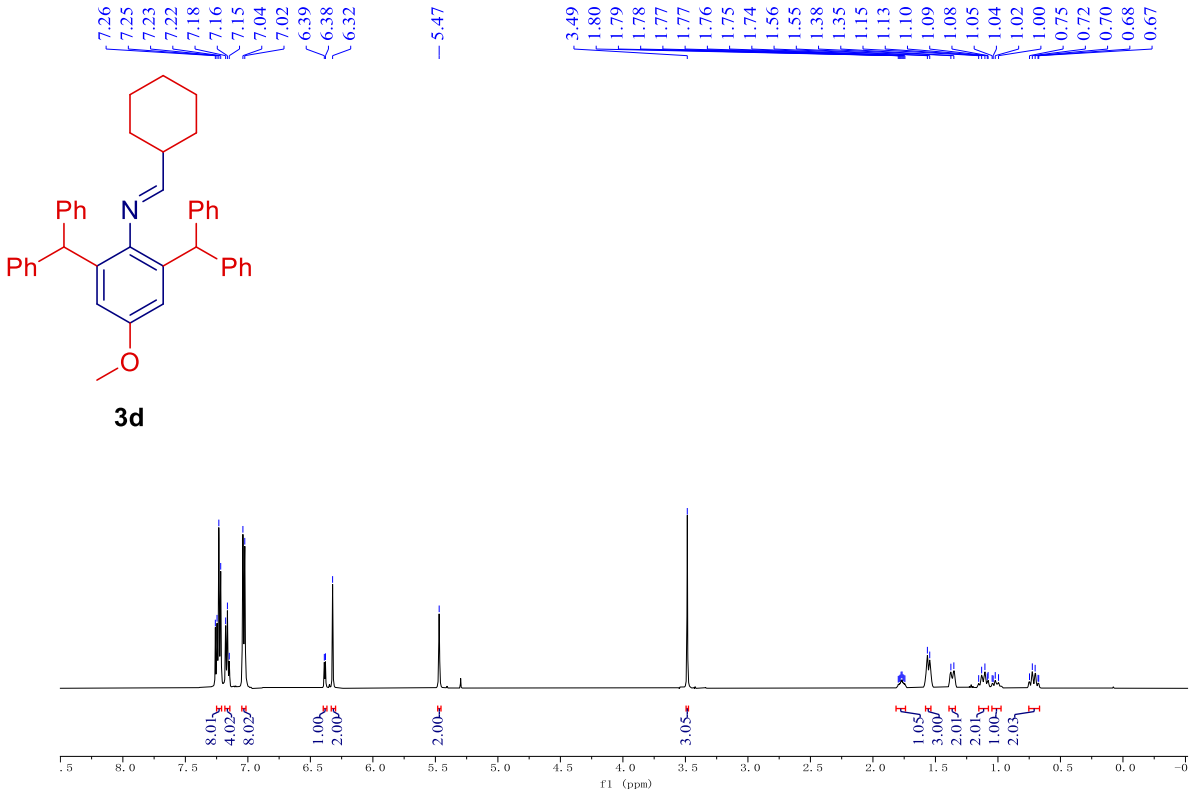
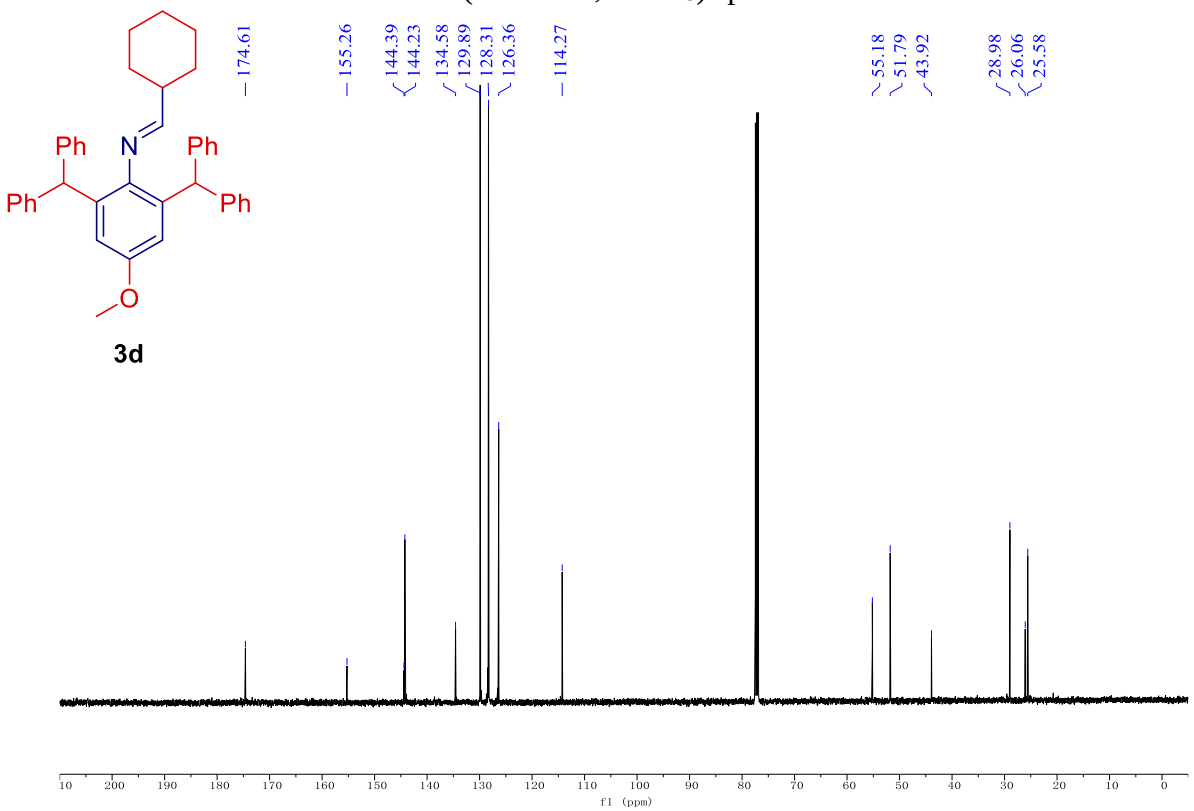
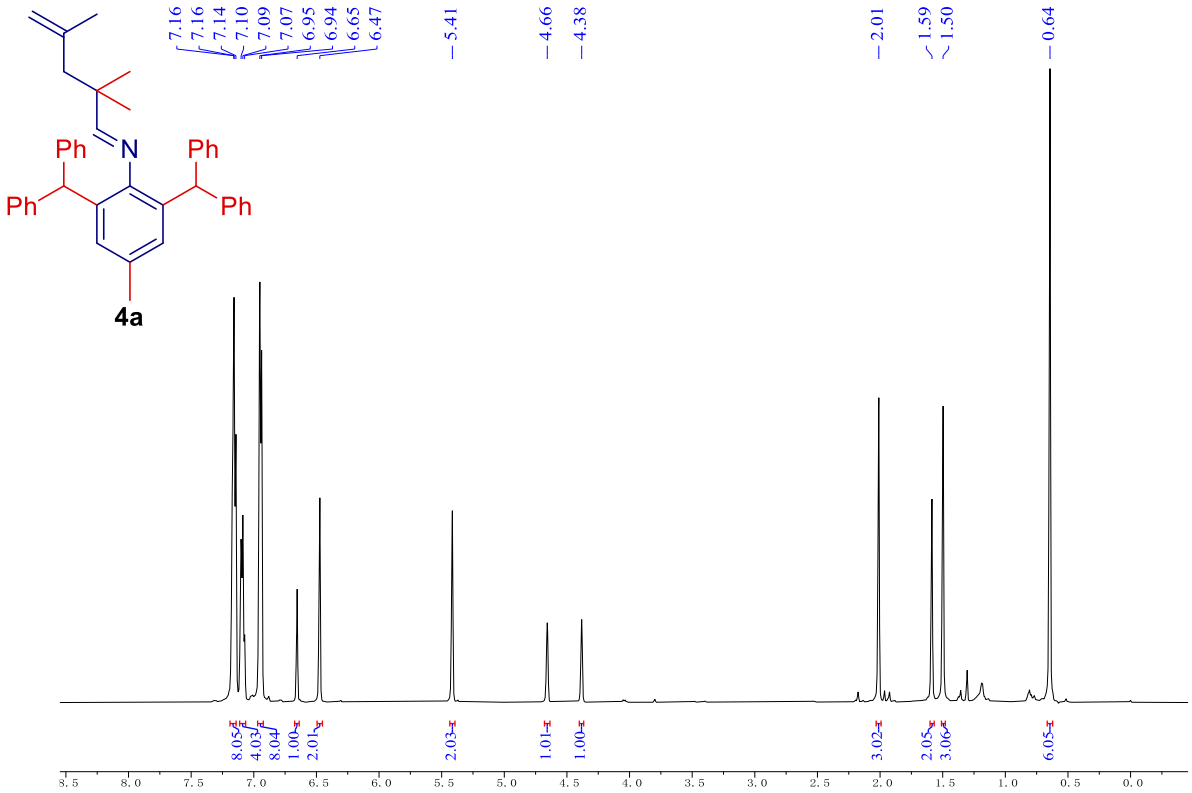


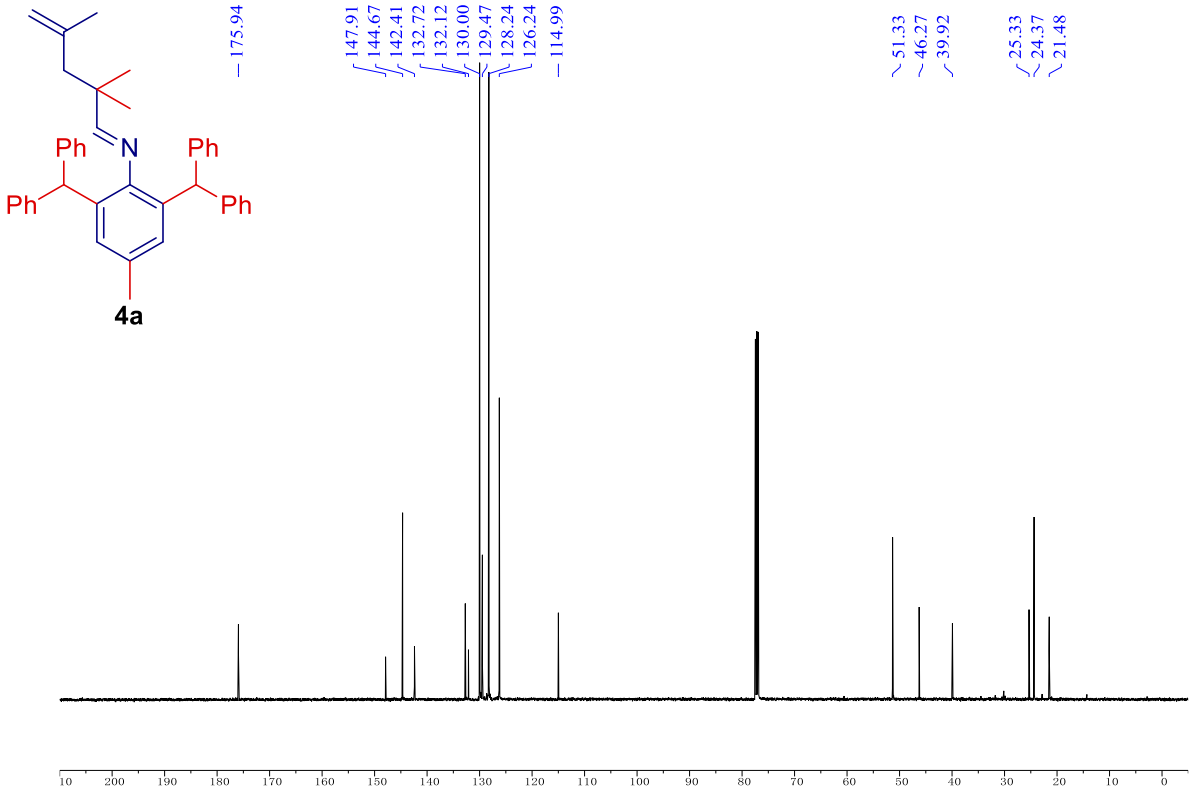
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3d**



^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **3d**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4a**



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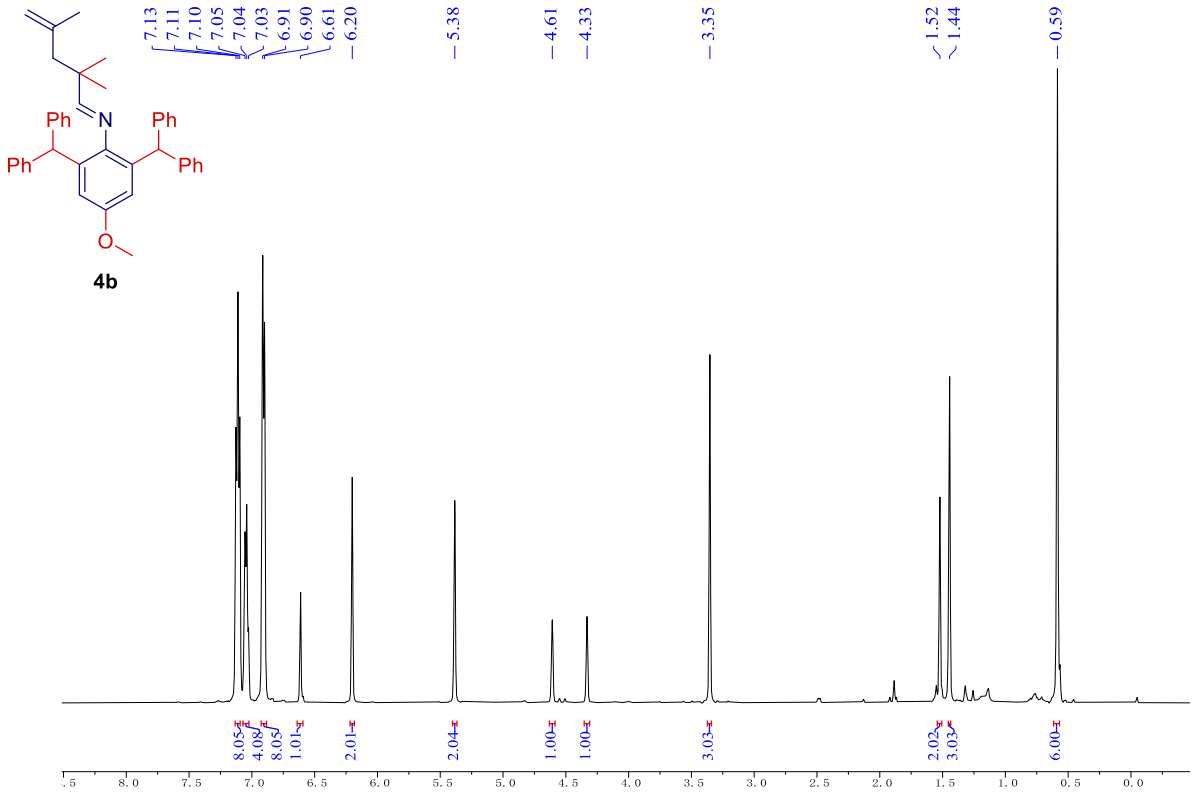

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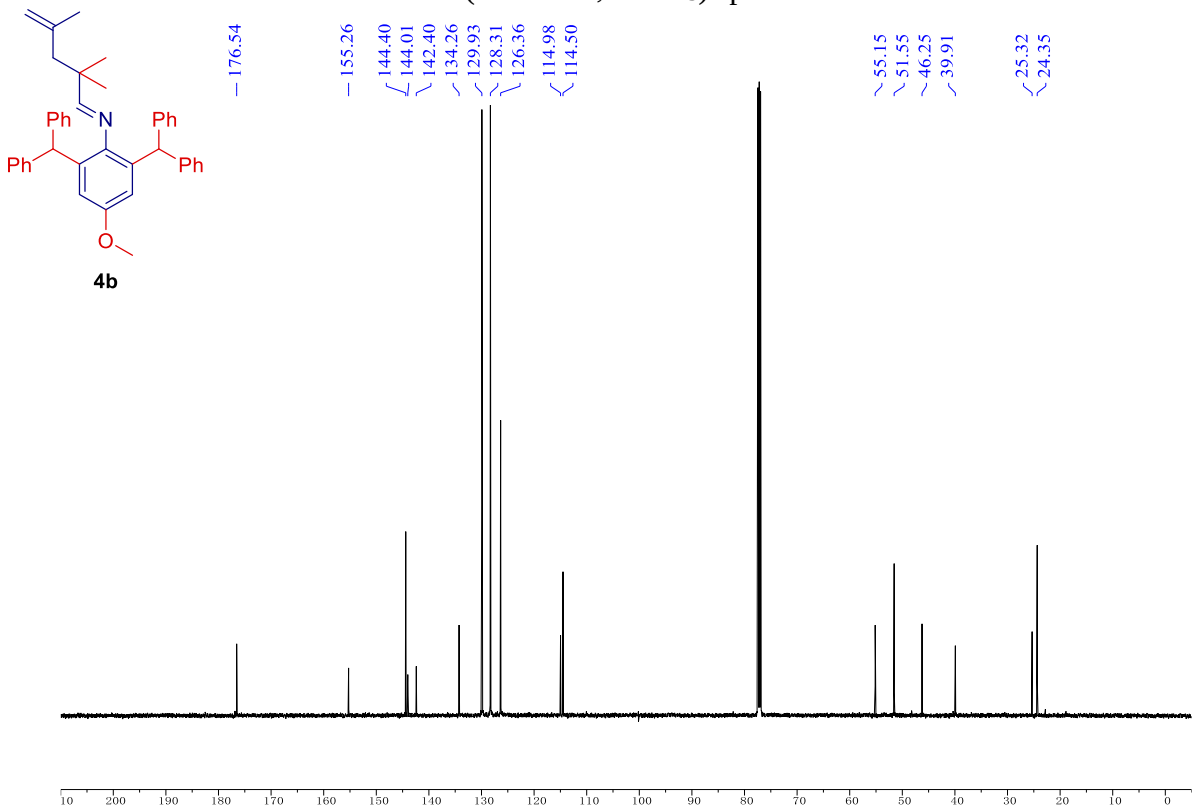

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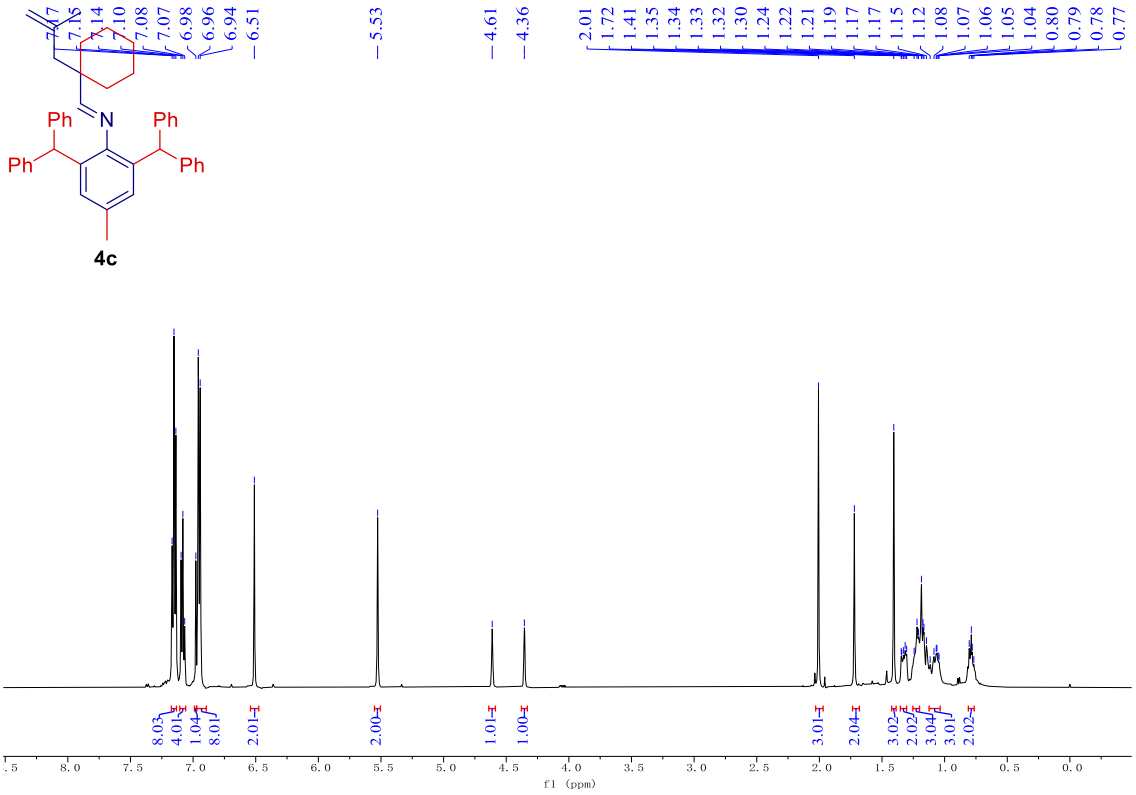

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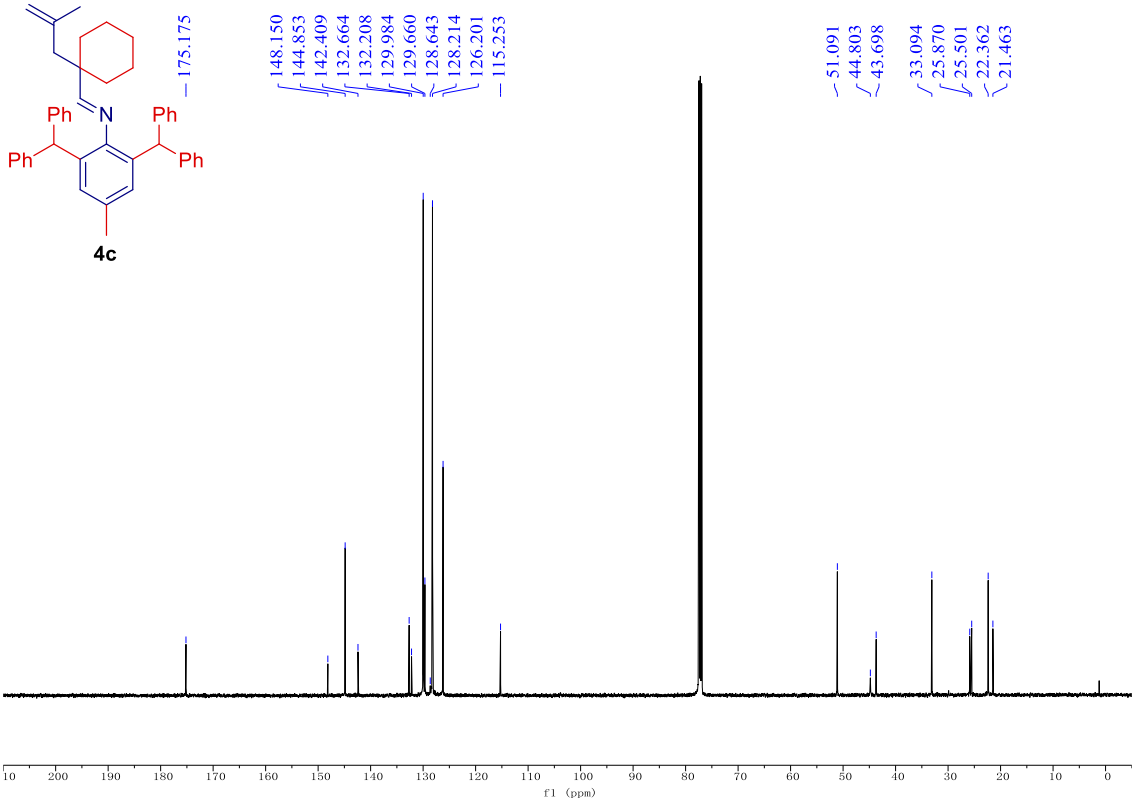

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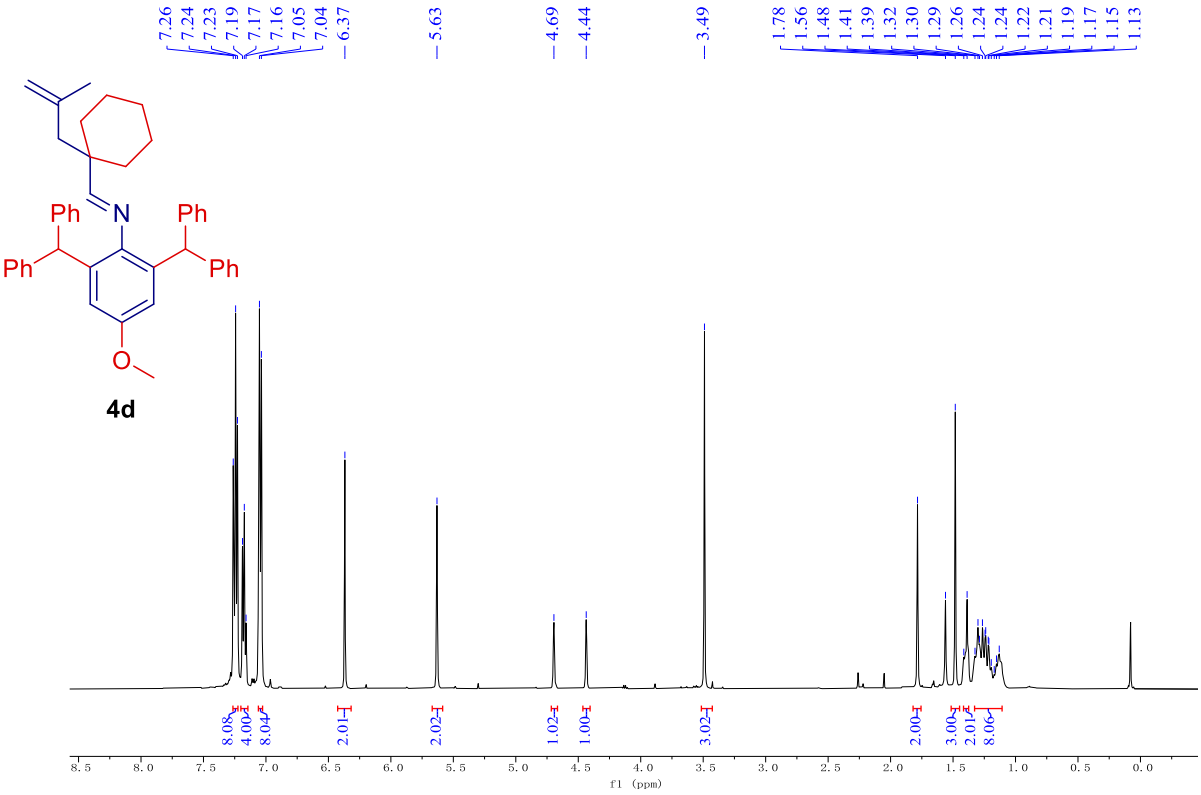

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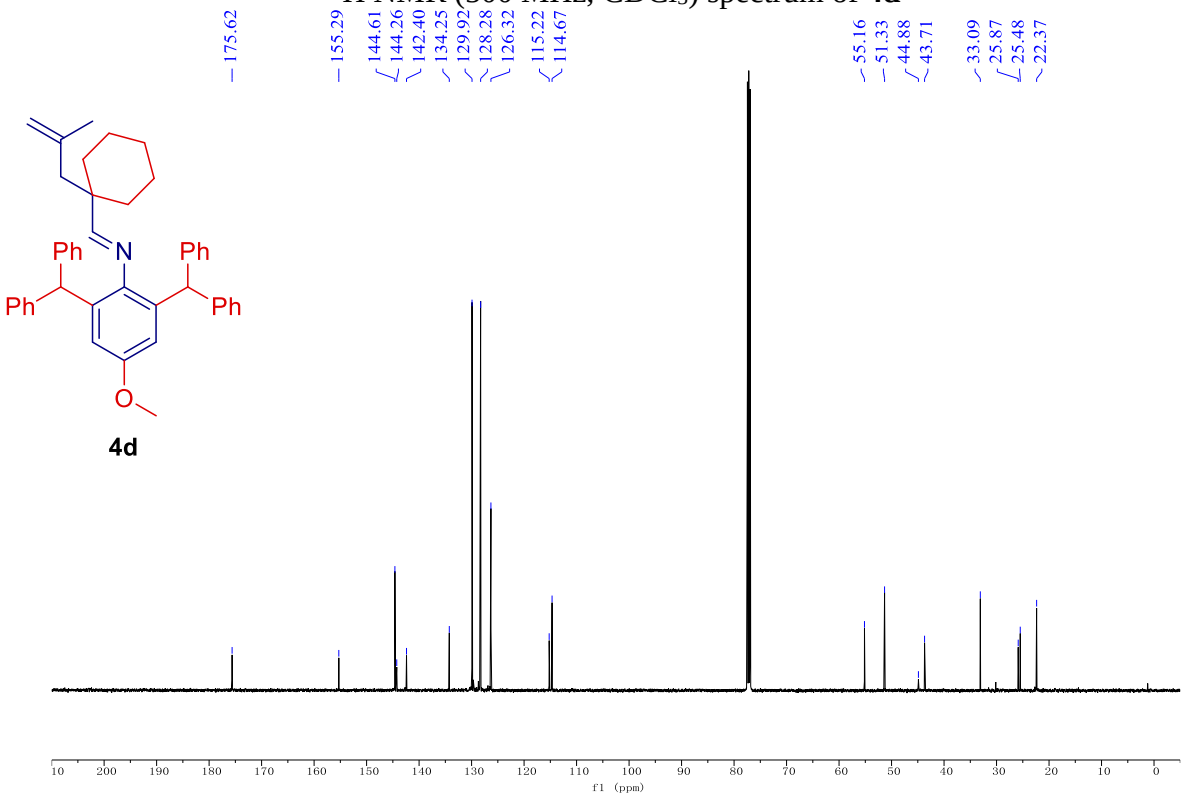

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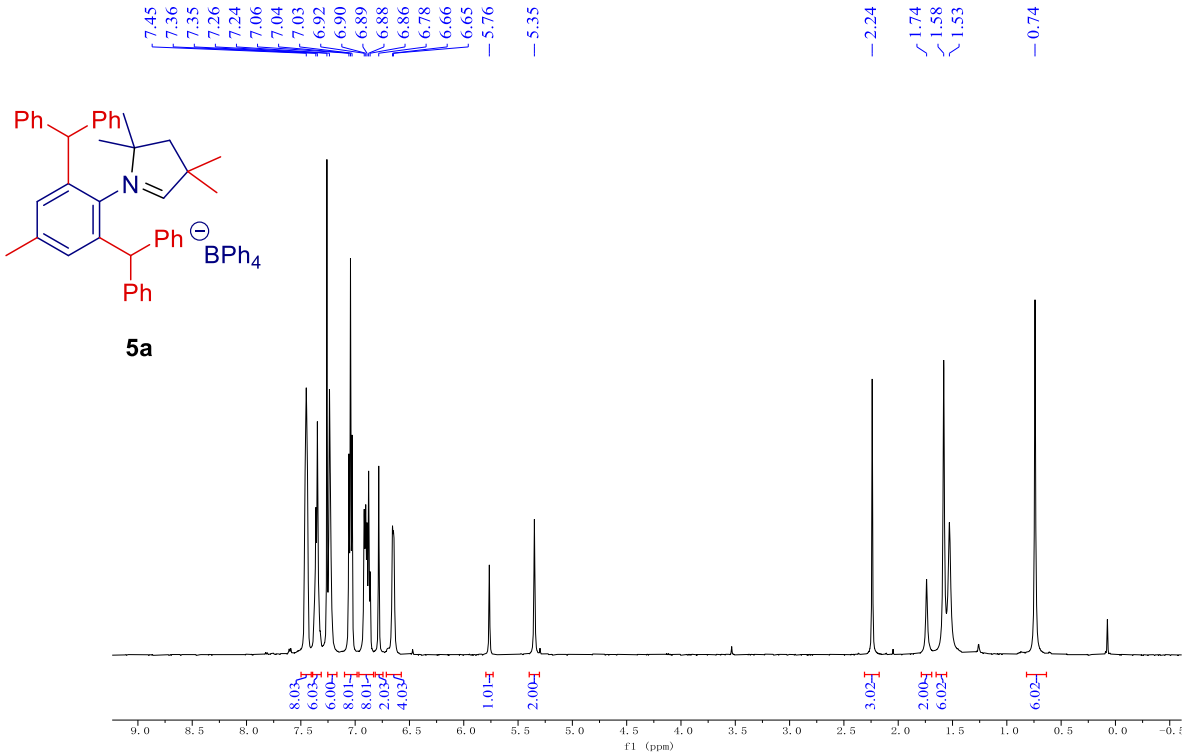
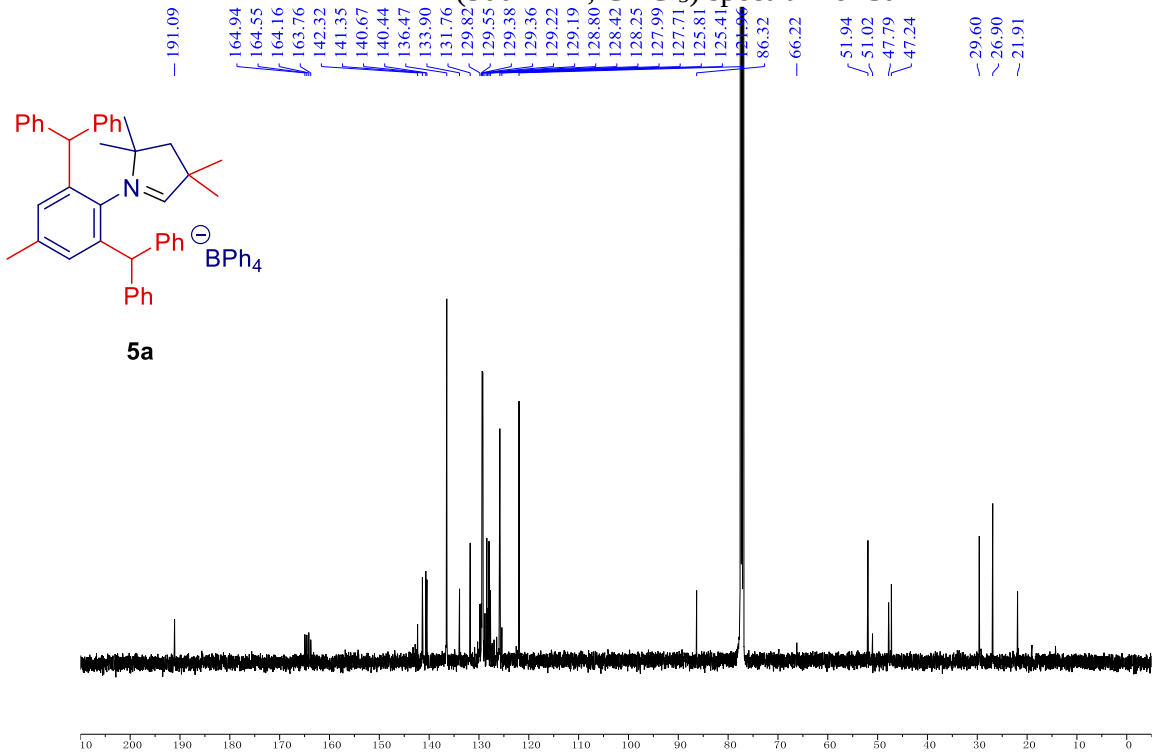


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5a**



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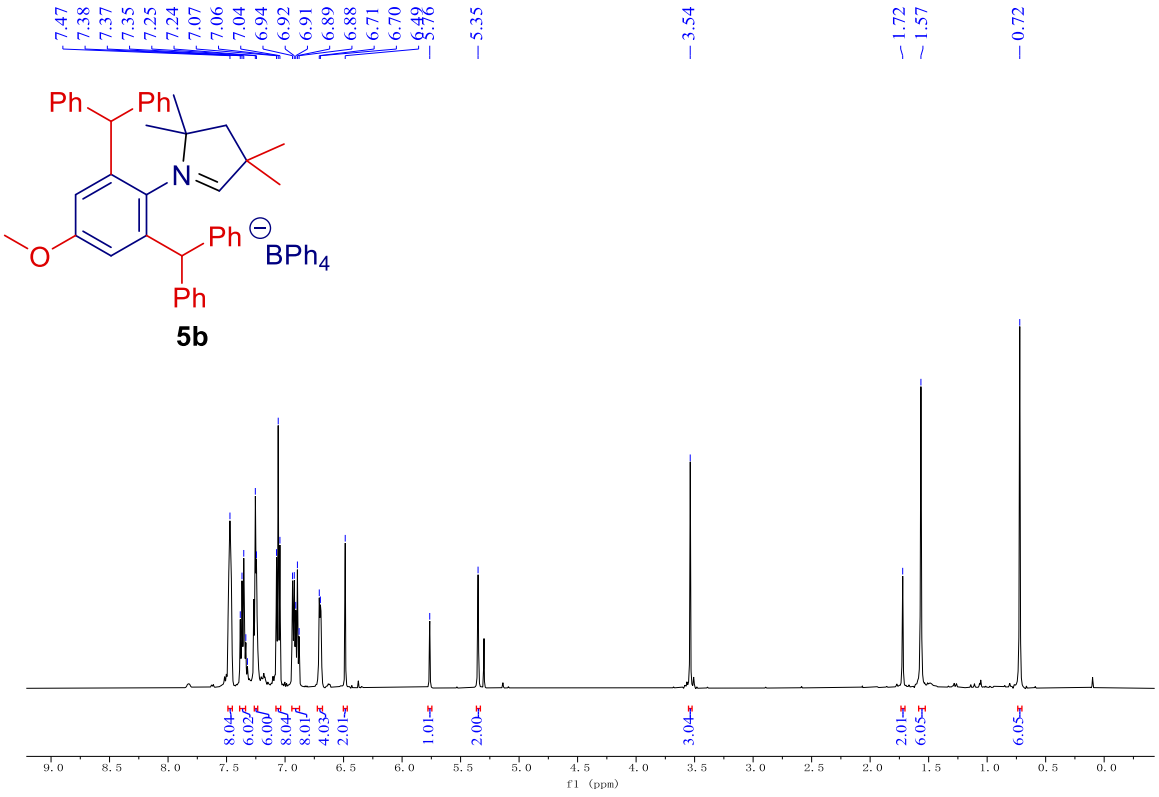

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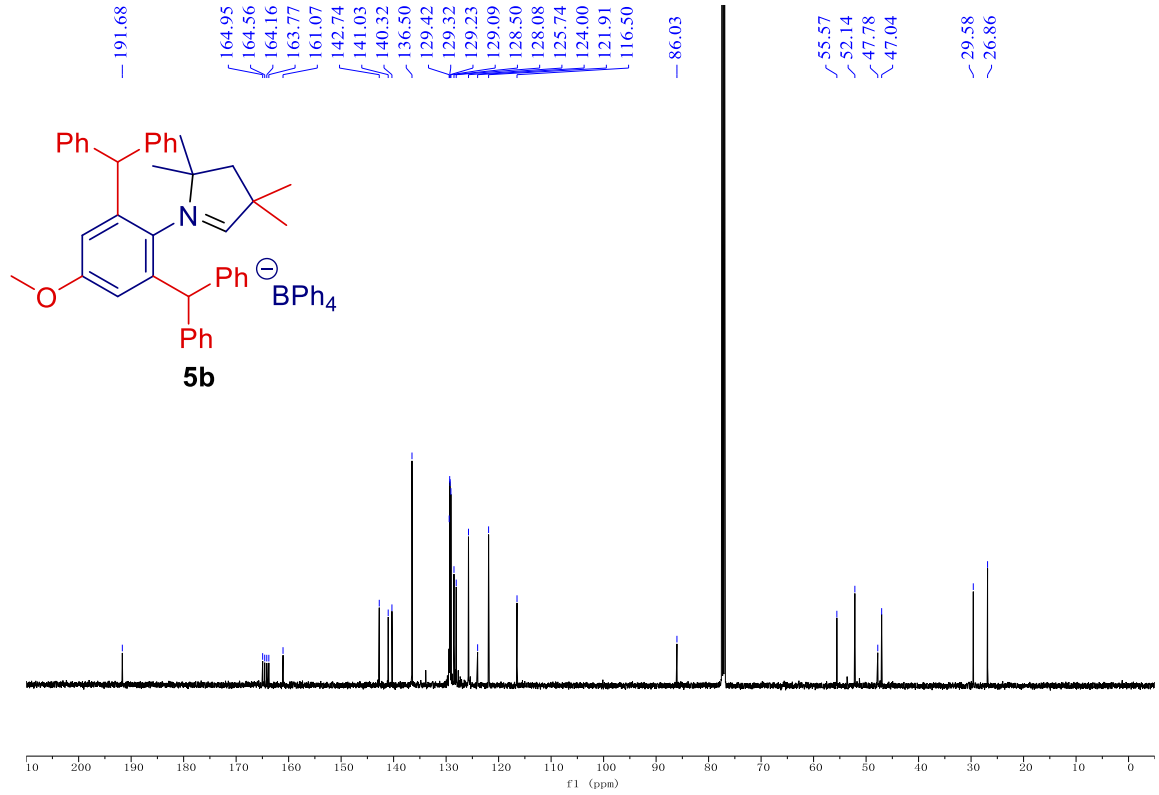

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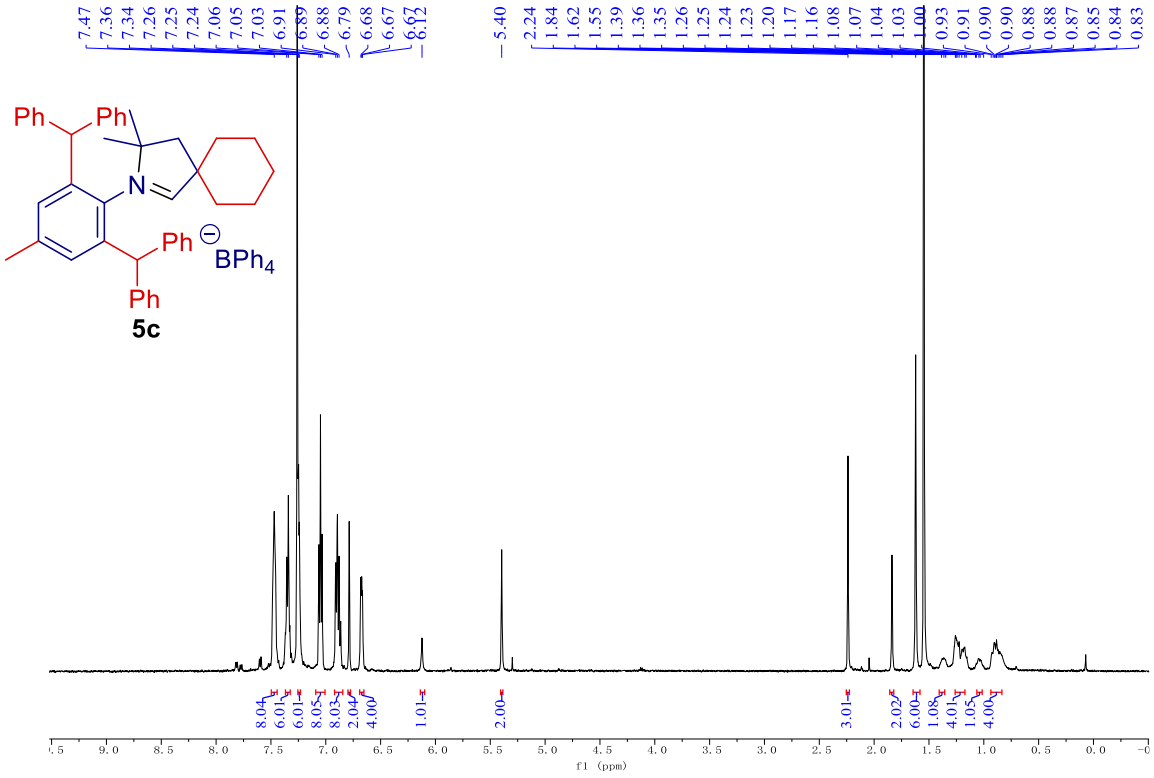
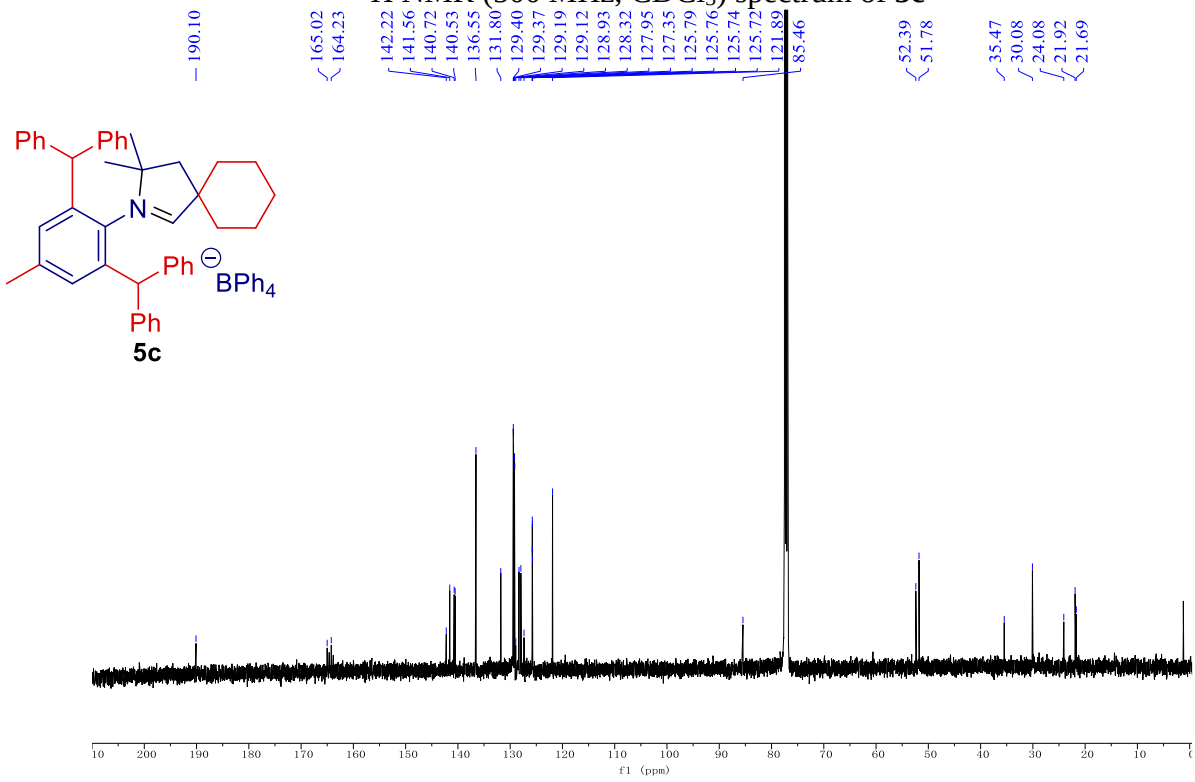
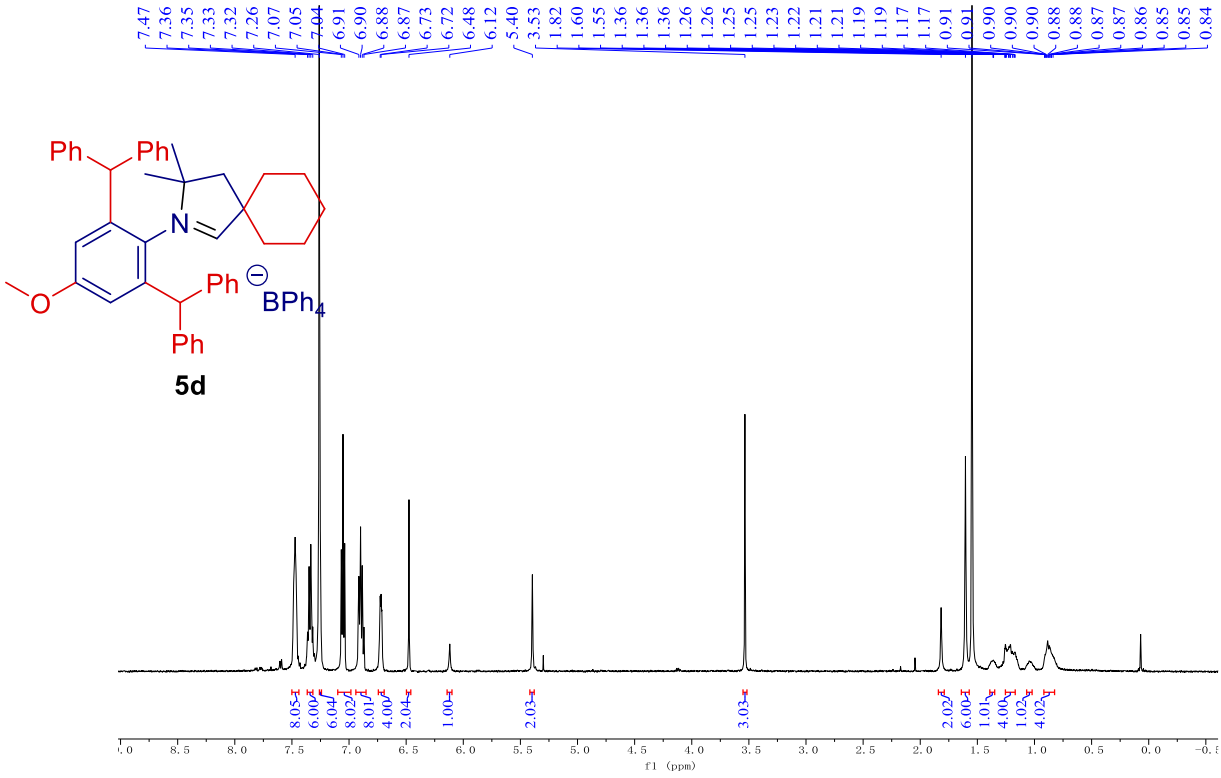


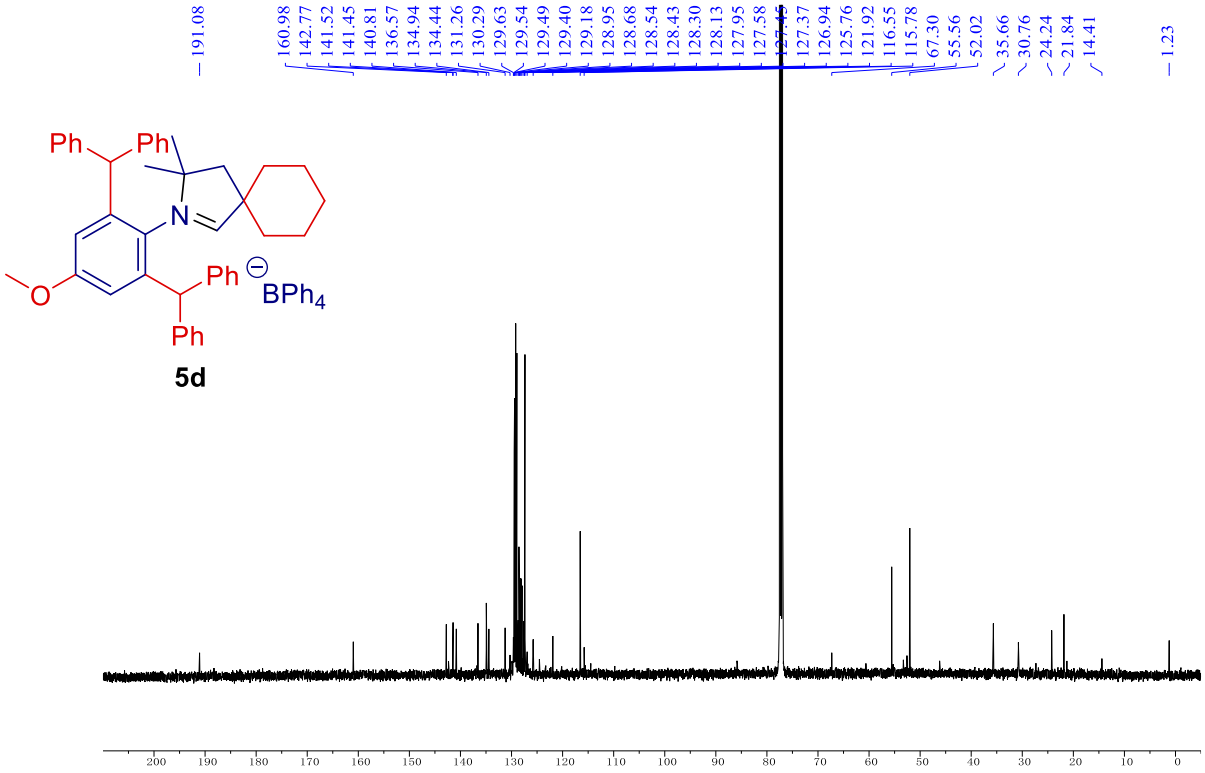
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5c**



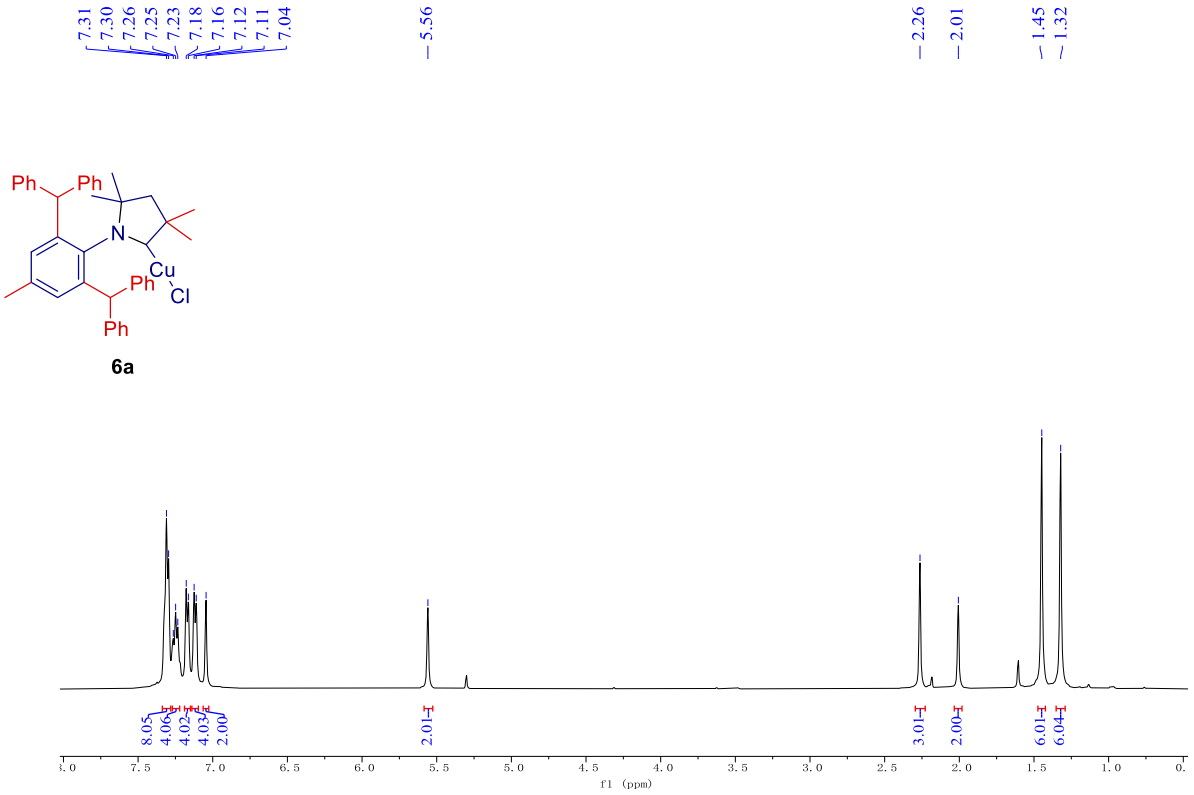
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **5c**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5d**

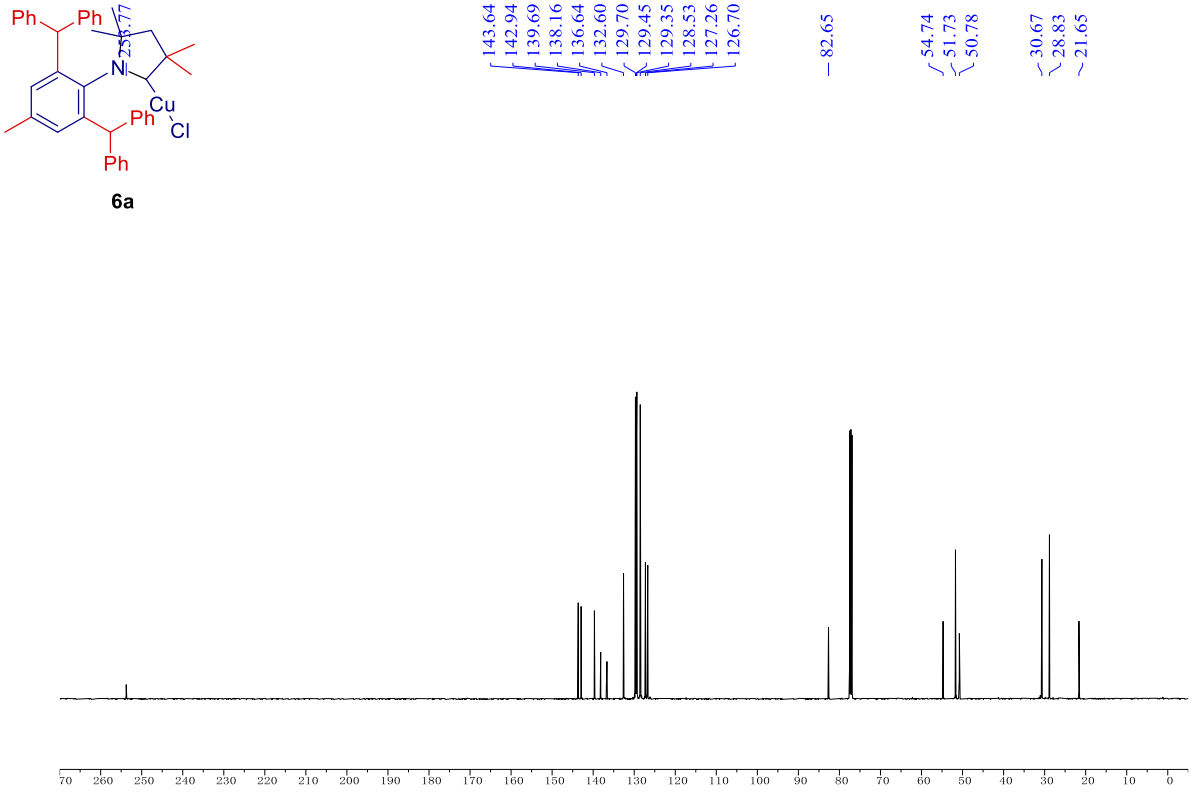


^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **5d**



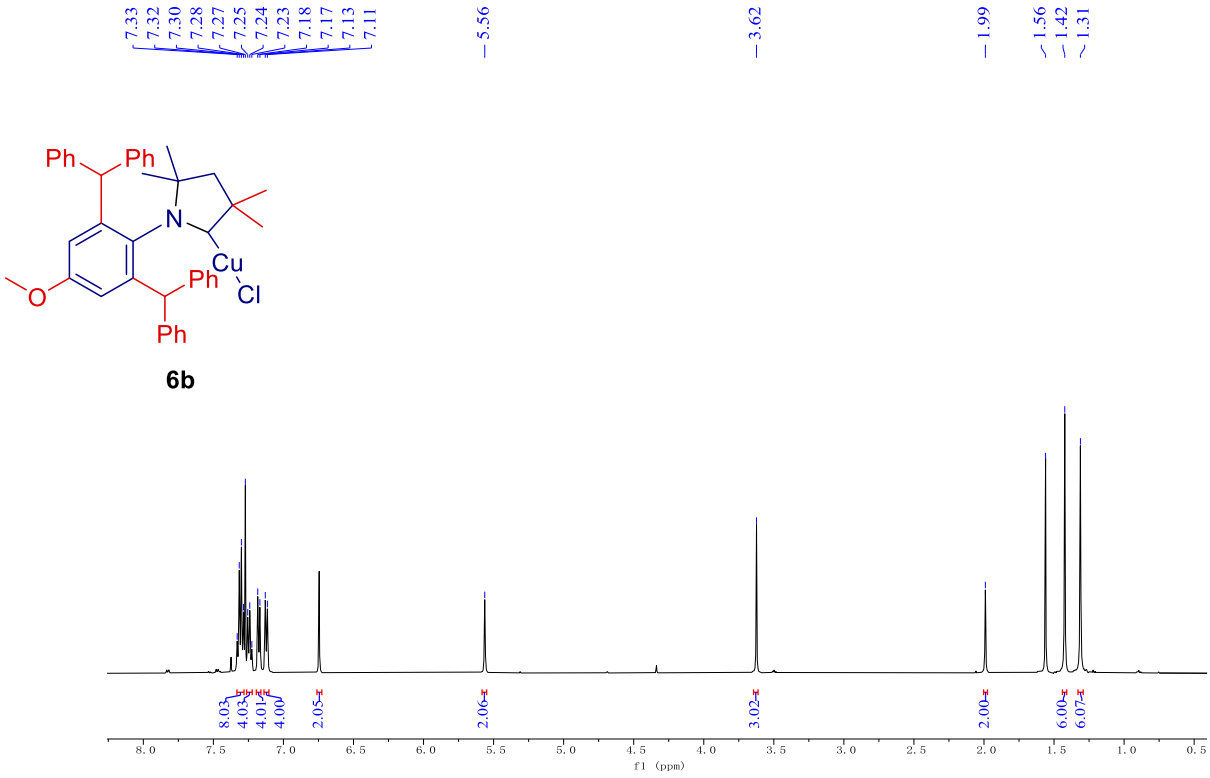
6a

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **6a**



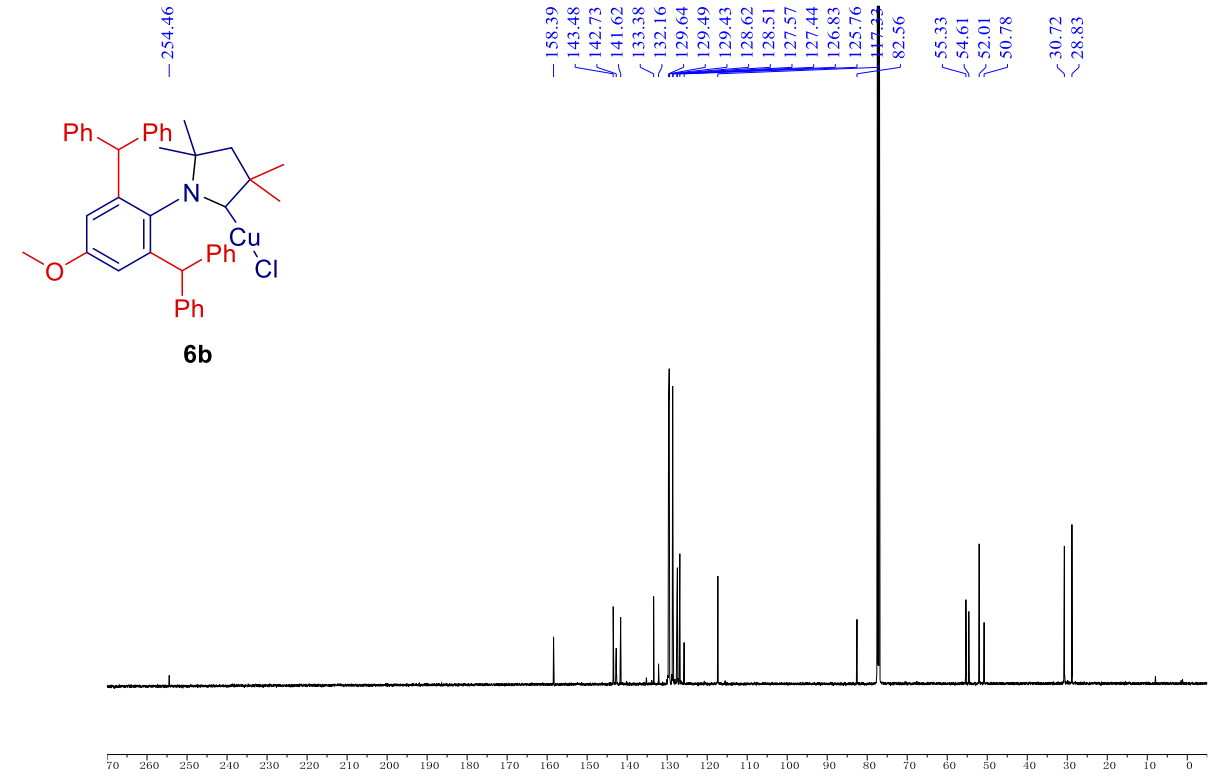
6a

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **6a**



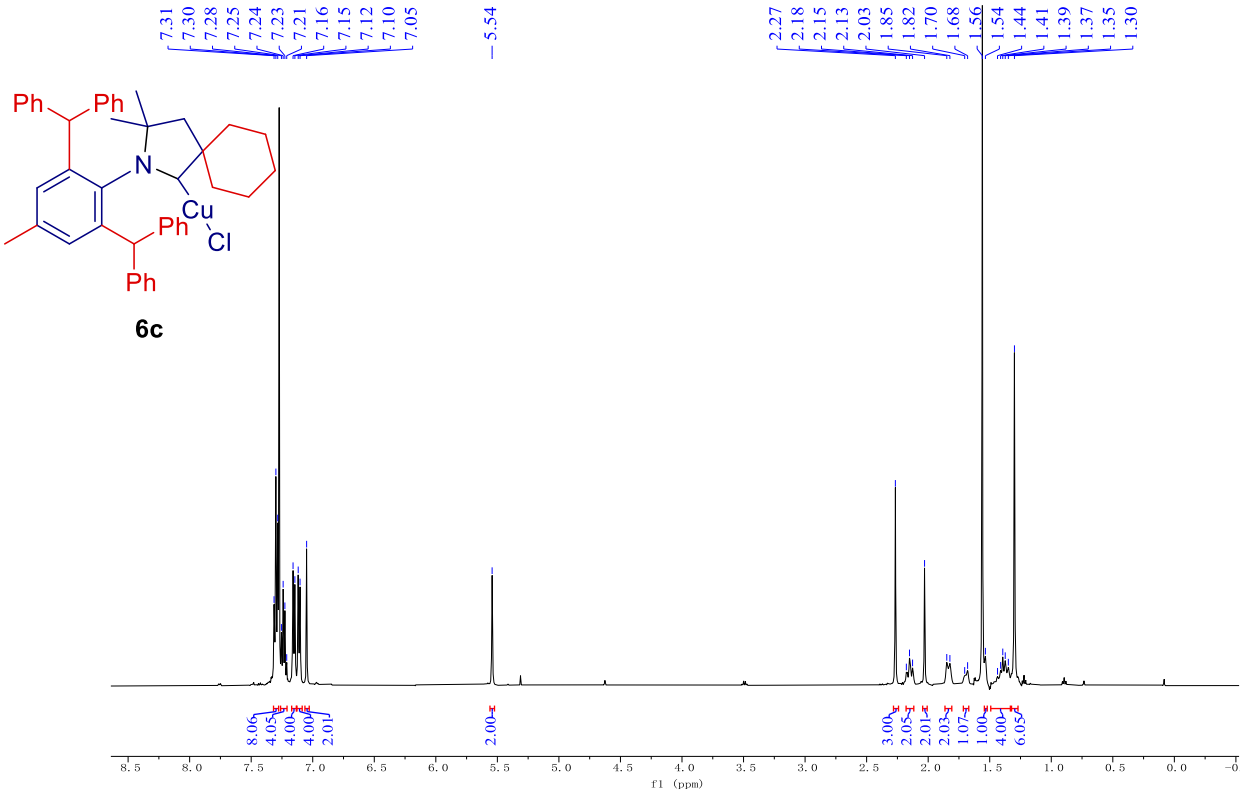
6b

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **6b**



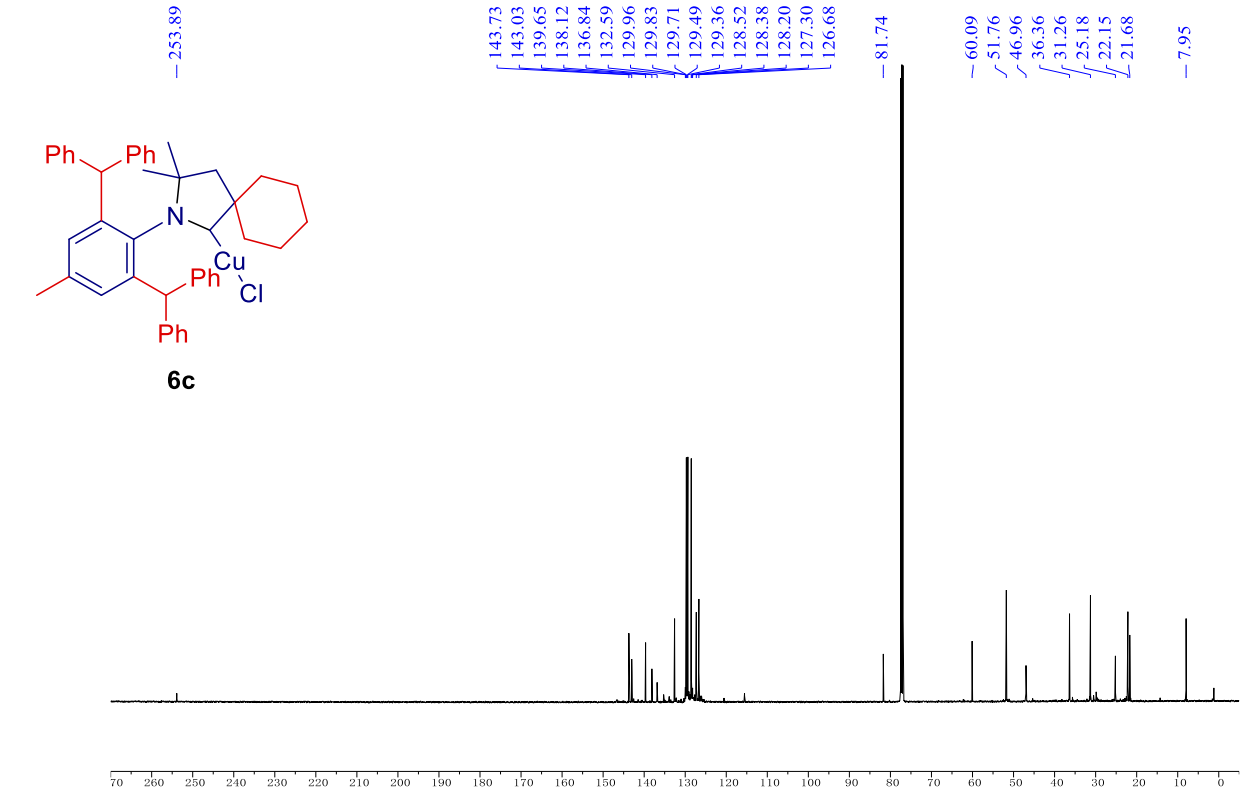
6b

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **6b**



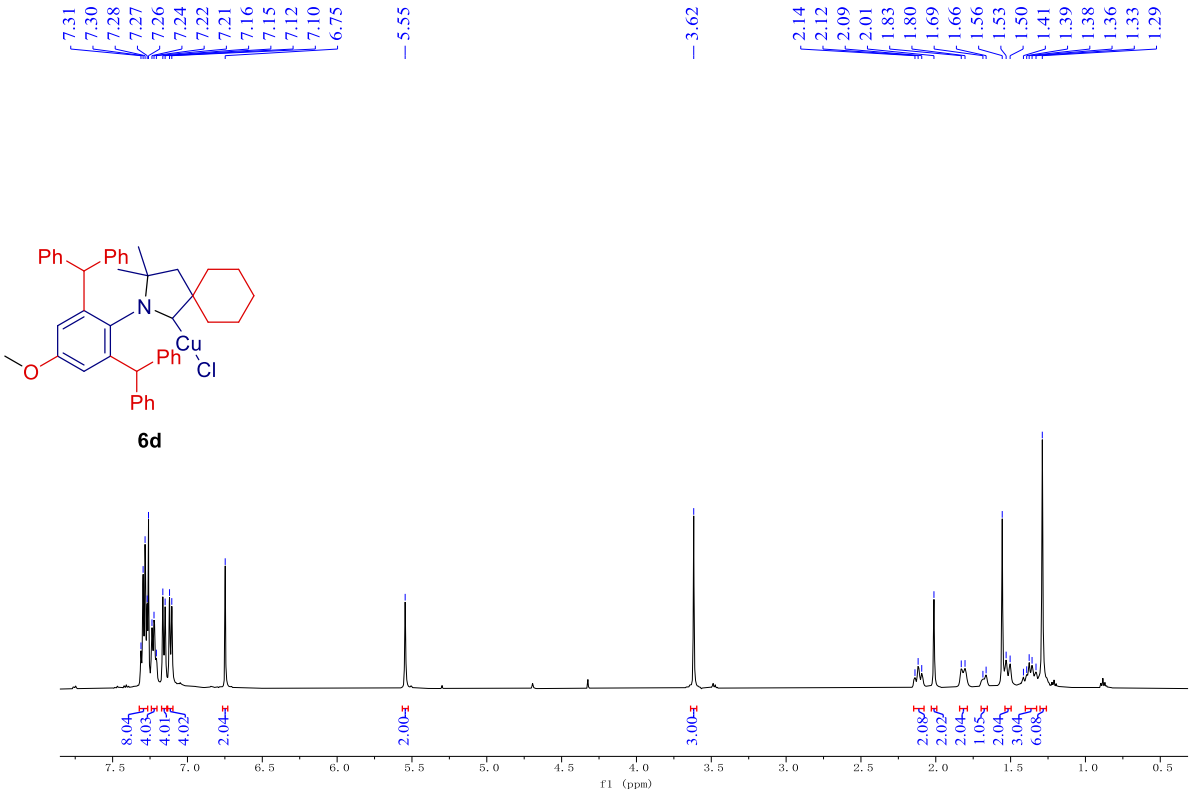
6c

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **6c**



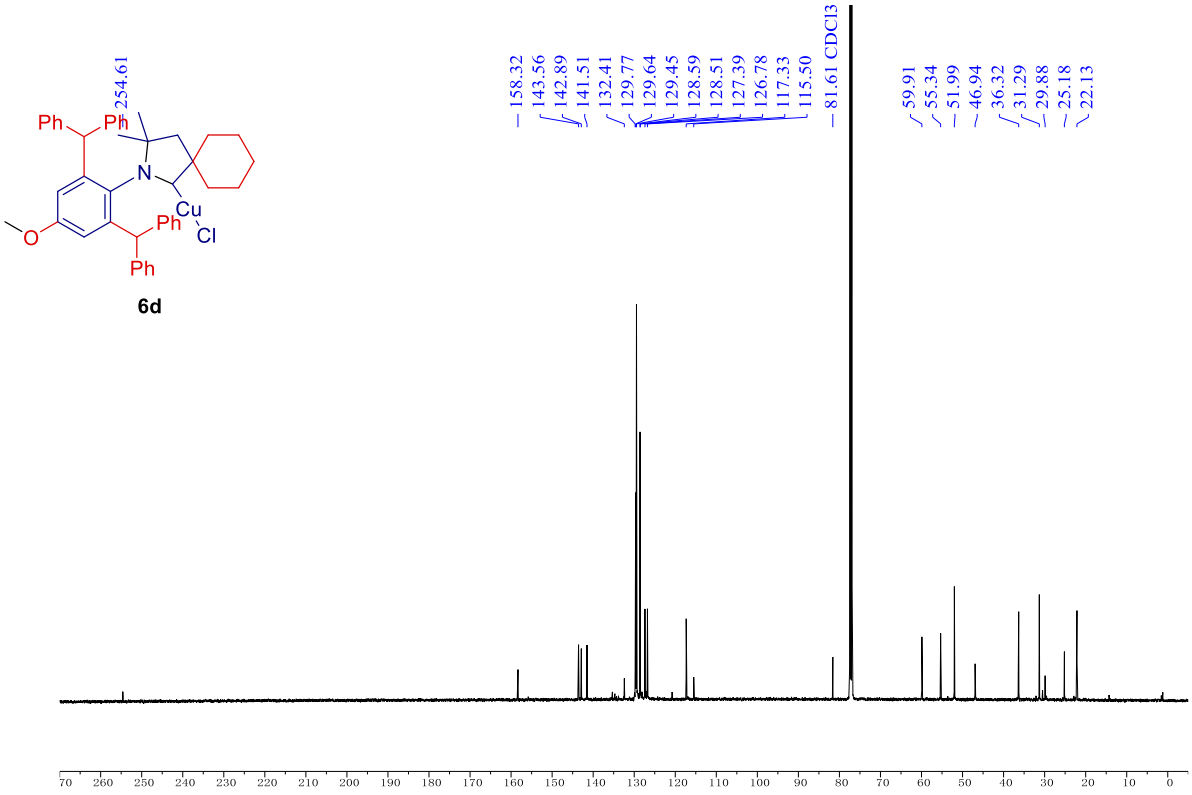
6c

^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **6c**



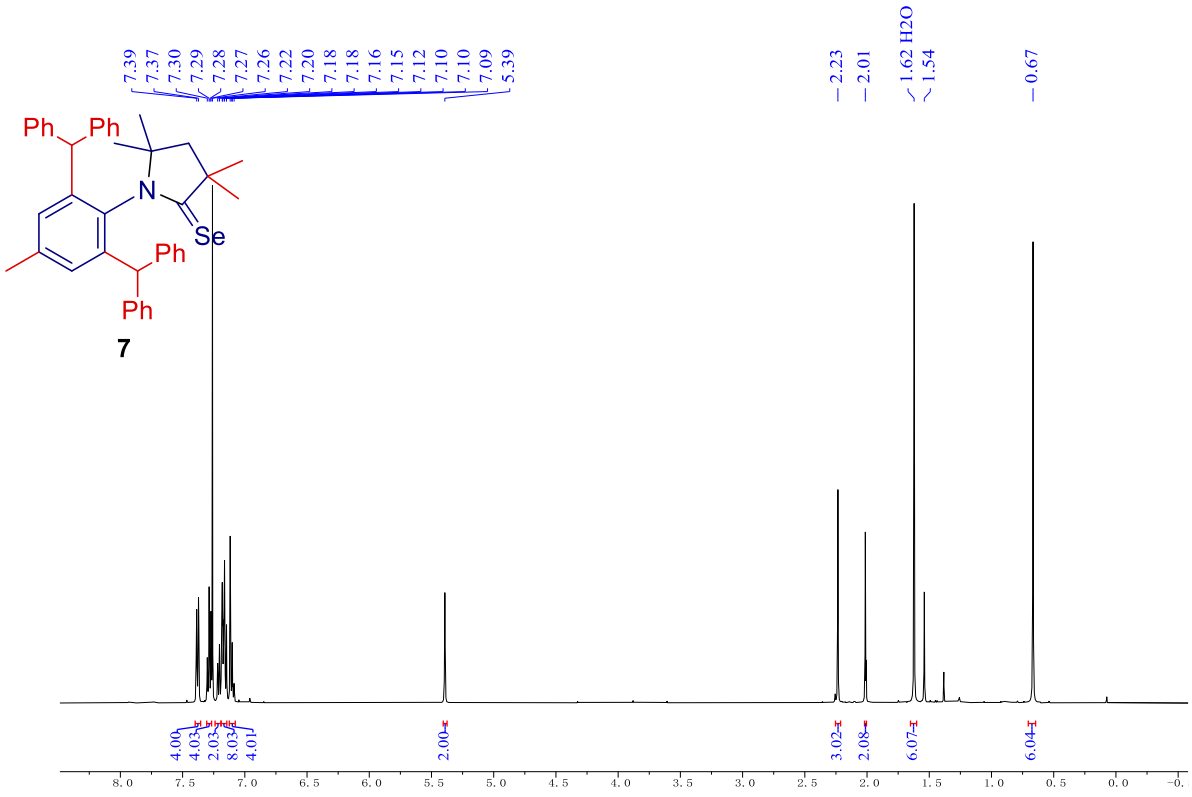
6d

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **6d**

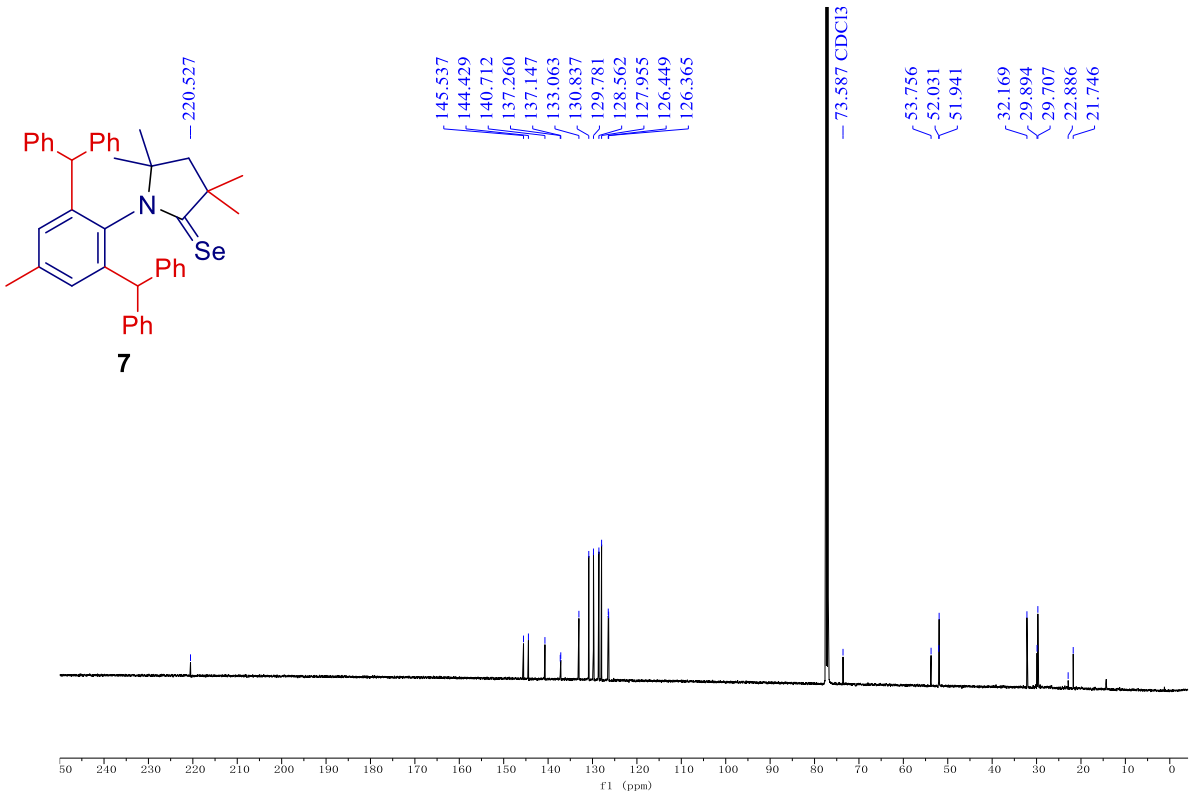


6d

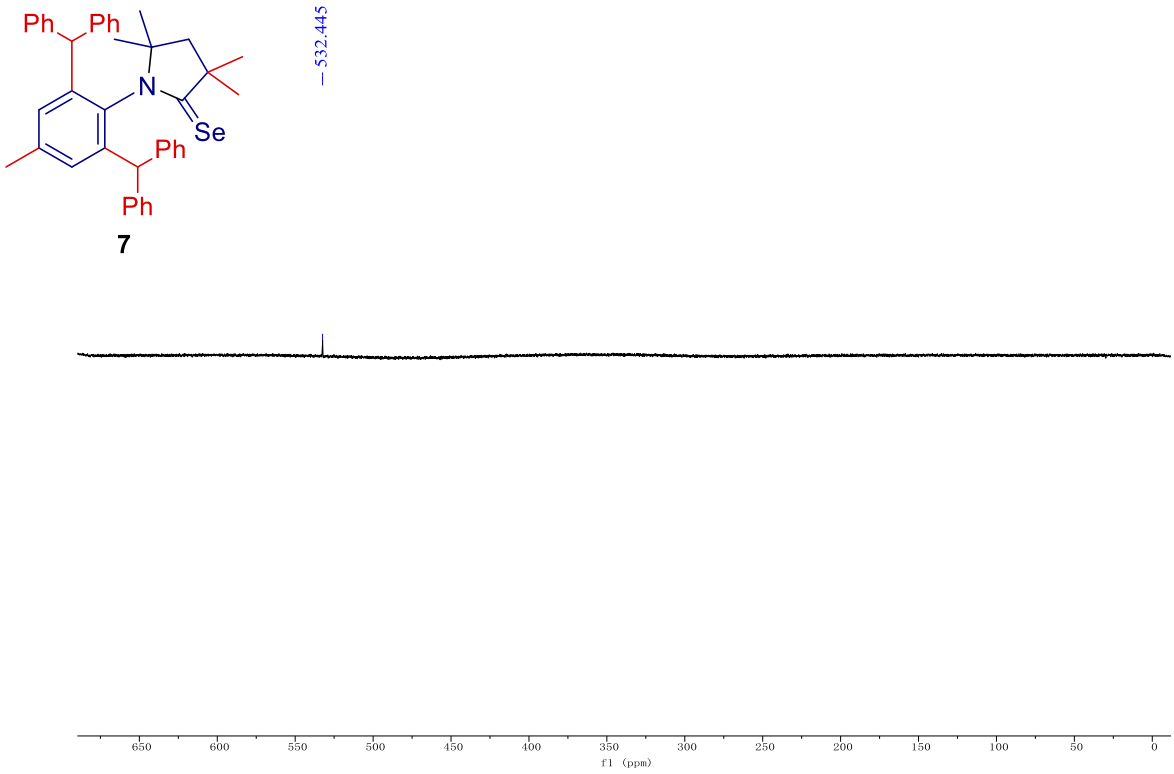
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **6d**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7**

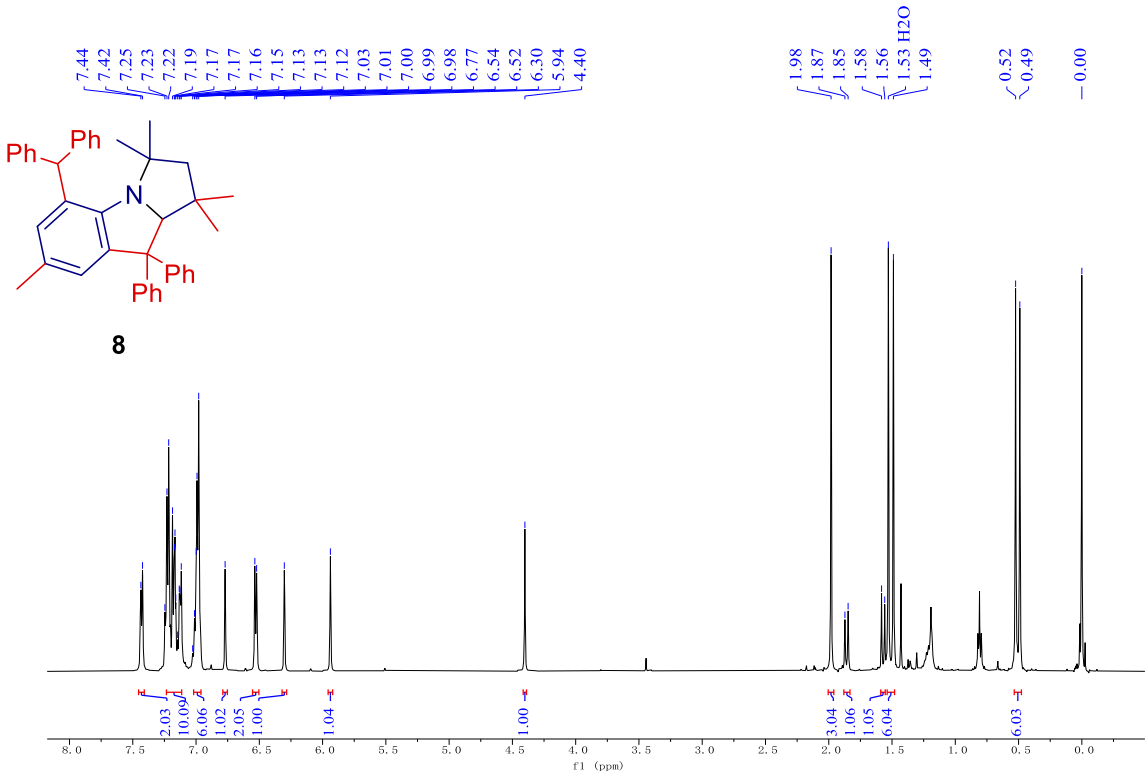


^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **7**

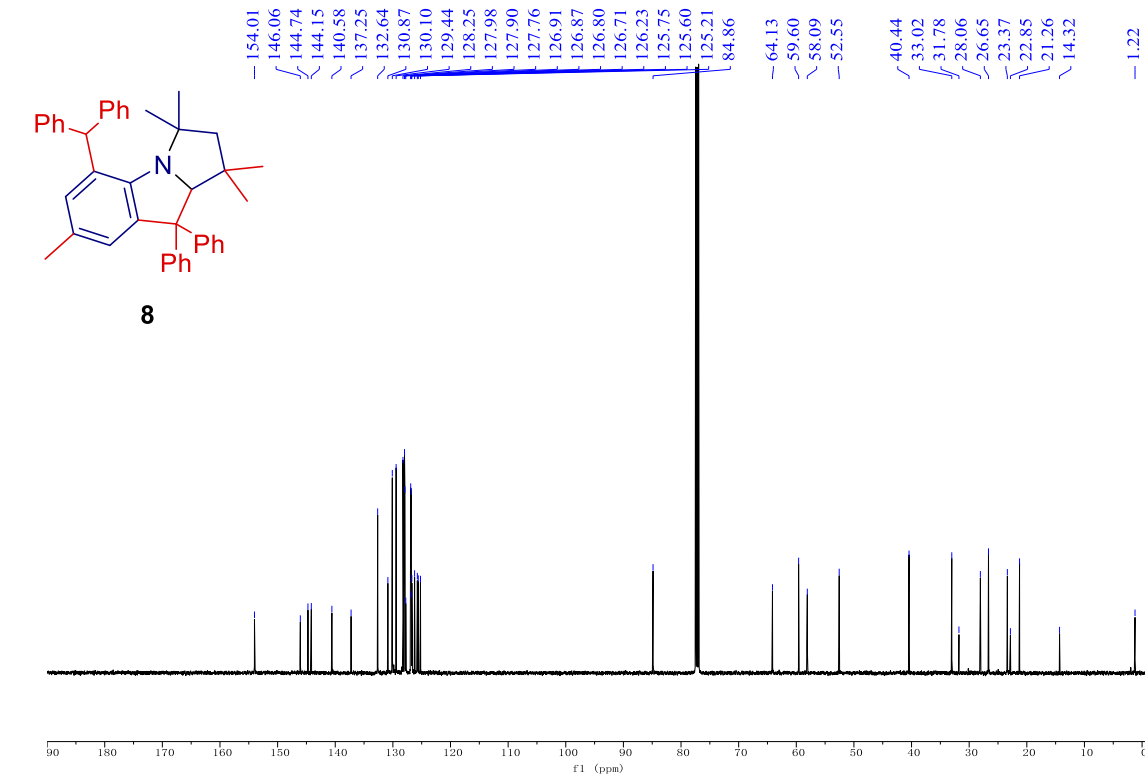


7

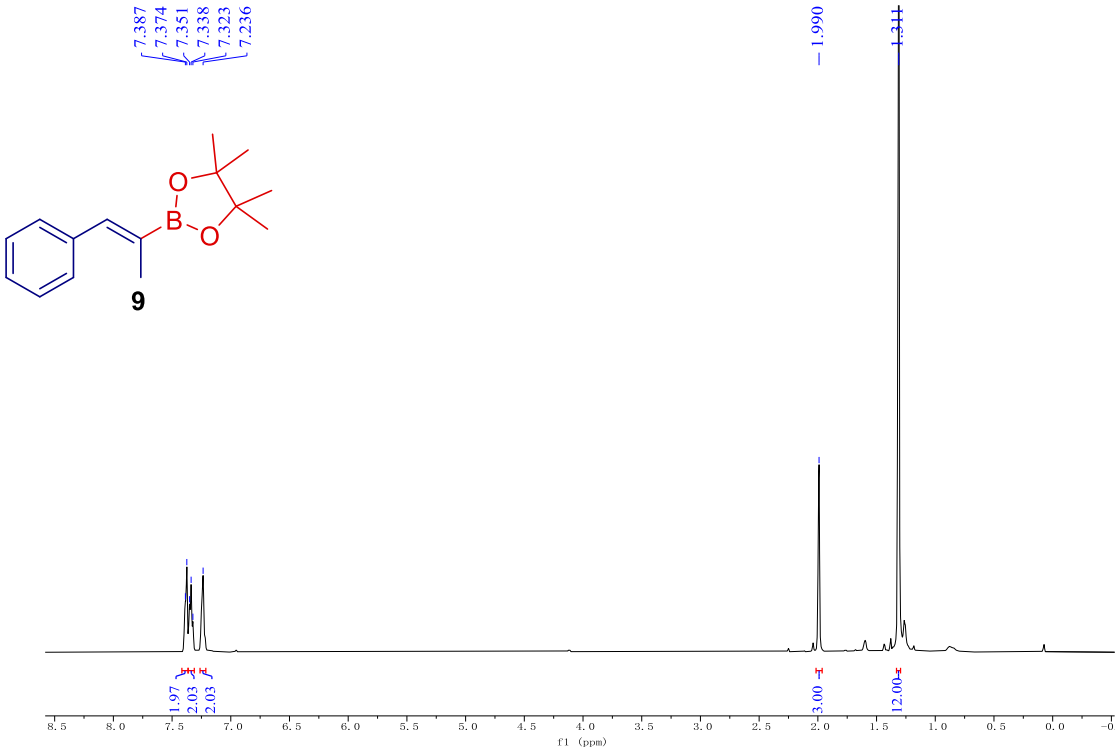
^{77}Se NMR (95 MHz, $CDCl_3$) spectrum of **7**



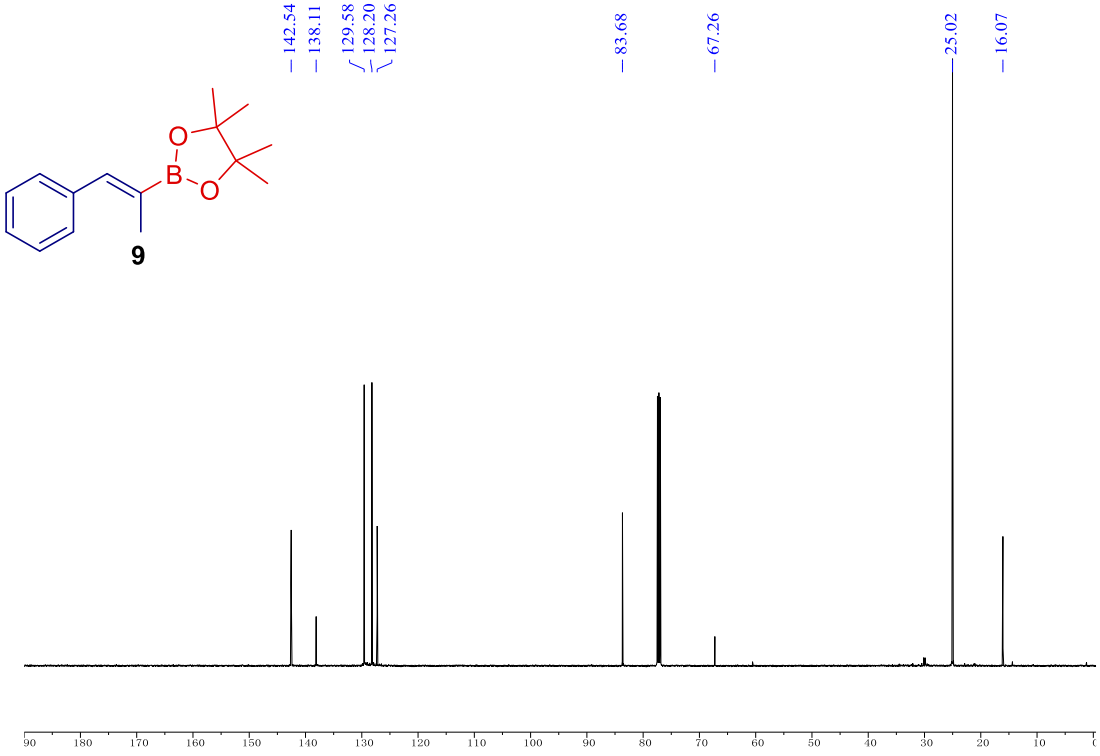
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8**



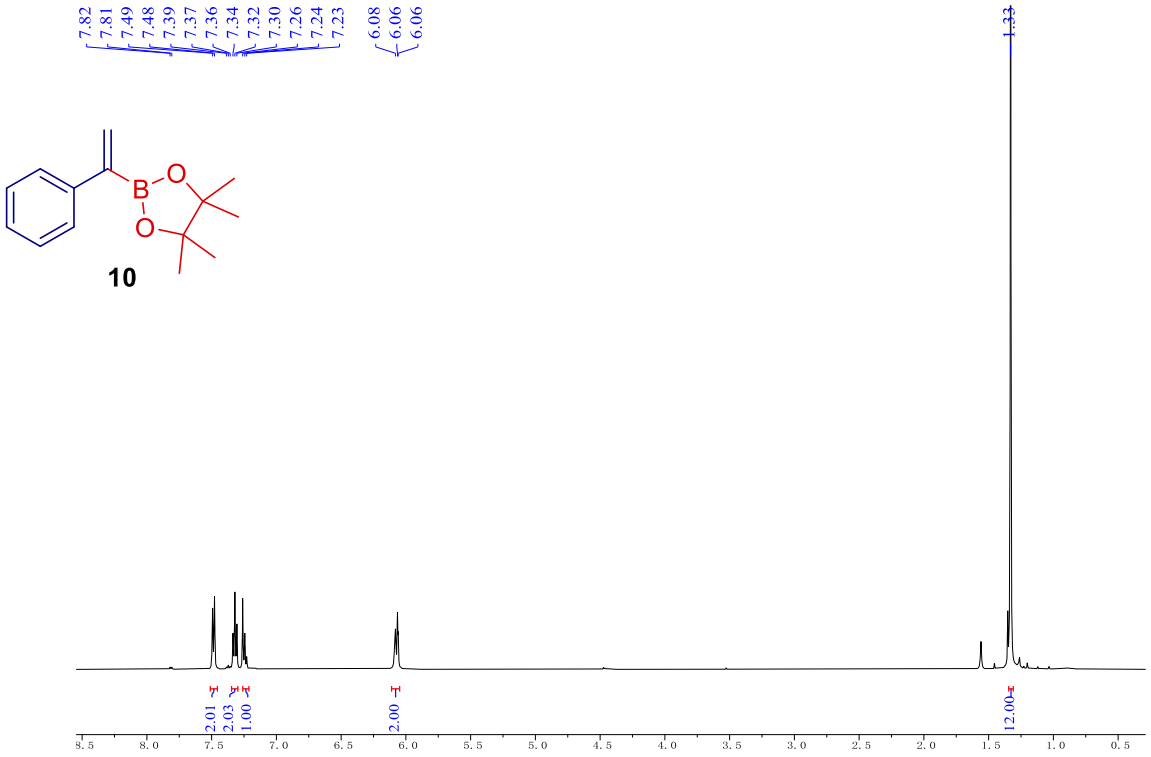
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **8**



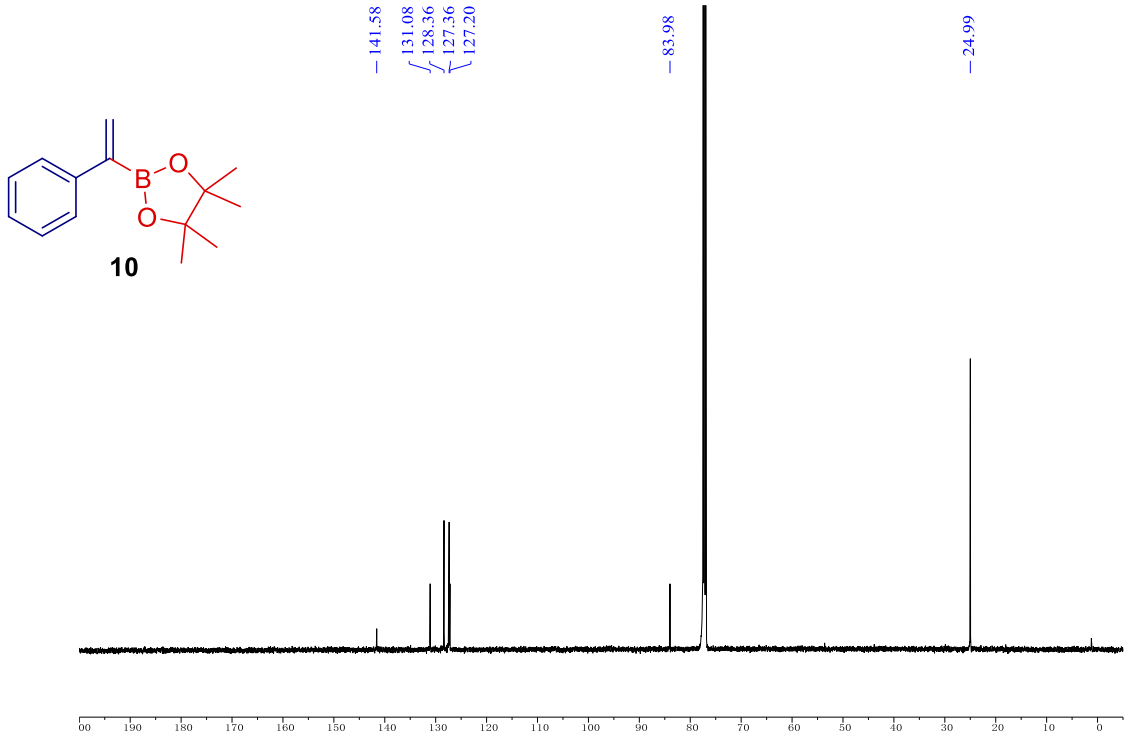
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **9**



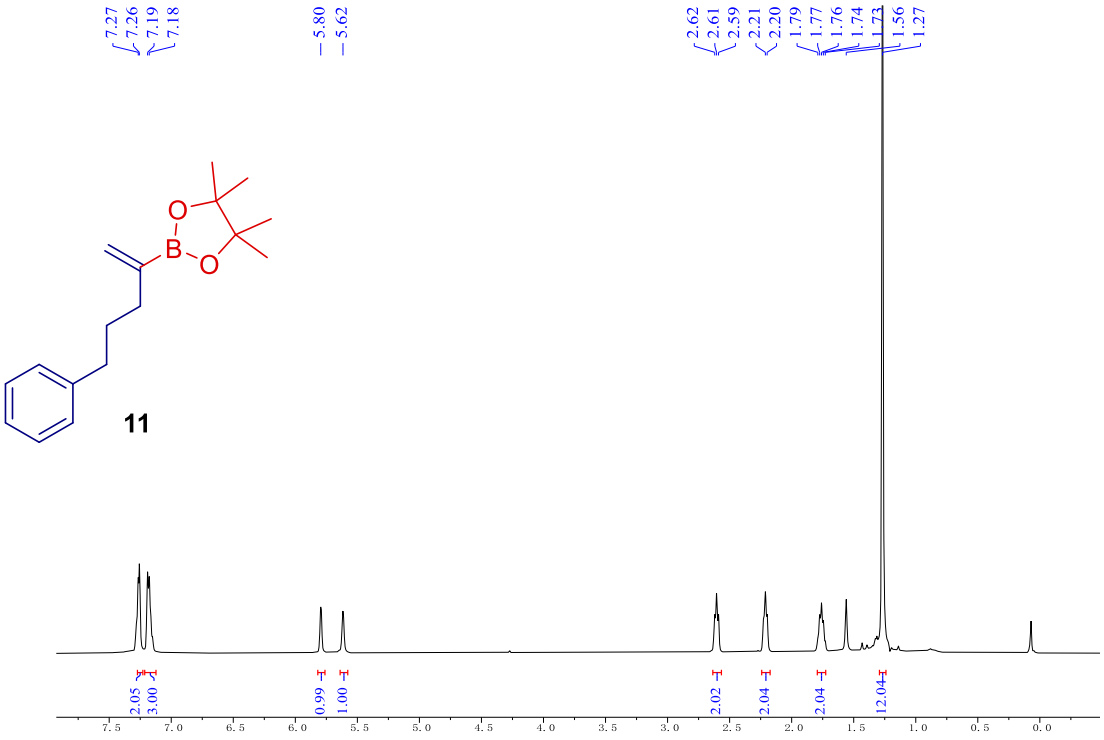
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **9**



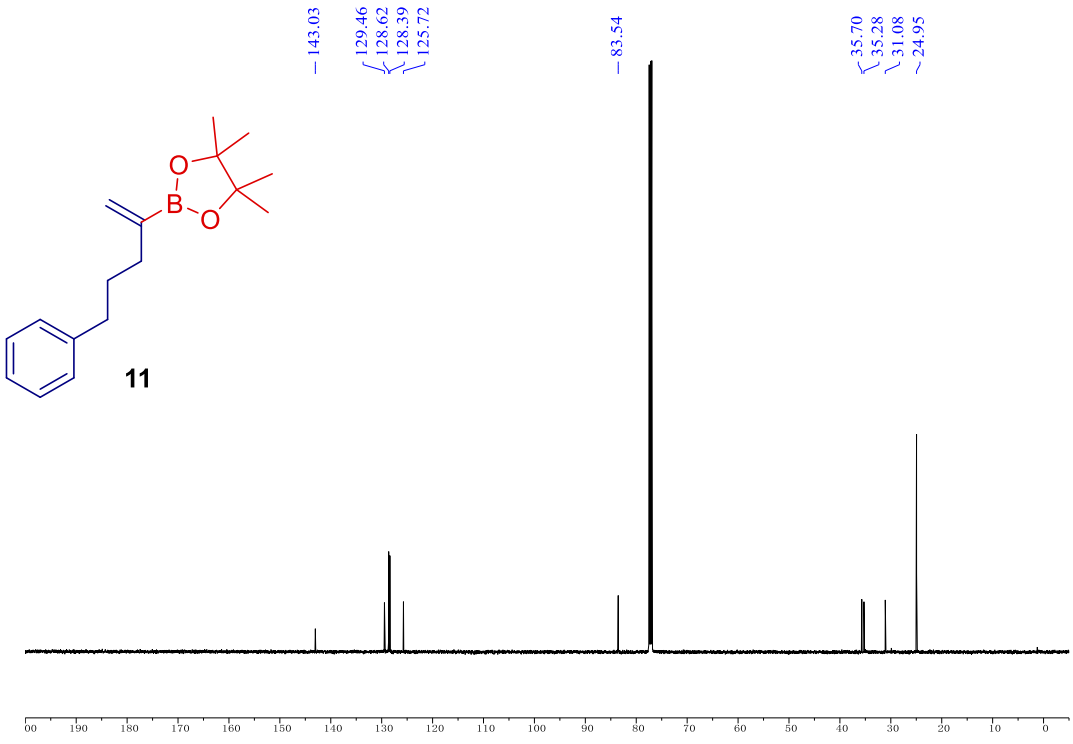
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10**



^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **10**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **11**



^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of **11**

IPr*–CAAC^{Me}

Energy: -1642.161545 au

Sum of electronic and thermal Energies: -1641.421838 au

Geometry:

N	-0.01144200	-0.84046600	1.11769300
C	-0.01396600	-0.14239200	2.22834700
C	-0.04859500	-1.13155700	3.38663000
C	-0.32538200	-2.52241400	2.74544800
H	0.26525400	-3.31992400	3.20225700
H	-1.37870400	-2.78612100	2.87504700
C	-0.00917600	-2.38328000	1.24304200
C	-1.15482700	-0.72807100	4.37724000
H	-1.20795200	-1.44575300	5.20298500
H	-2.13451600	-0.70037200	3.89171100
H	-0.95891100	0.26337400	4.79200700
C	1.31411200	-1.07127500	4.11099400
H	1.30743300	-1.74201400	4.97613600
H	1.51671400	-0.05717600	4.46302200
H	2.14028100	-1.37113000	3.46157600
C	1.36616400	-2.95431800	0.87800800
H	1.34996000	-4.03807200	1.02324400
H	2.16323900	-2.54744600	1.50112400
H	1.61777500	-2.76599800	-0.16620700
C	-1.06822500	-3.03417300	0.35370200
H	-1.04067700	-4.11711300	0.50503100
H	-0.87999700	-2.84373600	-0.70506700

H	-2.07437500	-2.69174400	0.59259200
C	0.00008200	-0.16473400	-0.17350200
C	1.22143200	0.21584400	-0.77026600
C	1.18799900	0.87529100	-2.00210100
H	2.12471200	1.20202100	-2.44001200
C	-0.00220400	1.18611300	-2.65254600
C	-1.19246600	0.87474200	-2.00059300
H	-2.12959300	1.20277500	-2.43675300
C	-1.22370400	0.21352500	-0.77086500
C	2.57396700	0.08182400	-0.06231600
H	2.37081800	-0.30408600	0.93668300
C	3.17146500	1.48383000	0.15765600
C	2.61212400	2.30167200	1.14856300
H	1.78061000	1.92650200	1.73871300
C	3.10051000	3.58692600	1.36712200
H	2.65699200	4.20453000	2.14072900
C	4.15318600	4.08115300	0.59625400
H	4.53350500	5.08227200	0.76670500
C	4.71291900	3.27637400	-0.39249000
H	5.53373300	3.64791200	-0.99654400
C	4.22717700	1.98573500	-0.60813400
H	4.68546000	1.36614200	-1.37028500
C	3.57263600	-0.89326300	-0.69582800
C	4.70947300	-1.24126200	0.04934200
H	4.85517500	-0.80118000	1.03074200
C	5.65588900	-2.13040100	-0.44815600

H	6.52462500	-2.38230400	0.15031800
C	5.48820600	-2.69728600	-1.71264600
H	6.22388600	-3.39084400	-2.10409600
C	4.36456800	-2.36503100	-2.46184200
H	4.21778300	-2.80105900	-3.44412000
C	3.41527800	-1.47232200	-1.95689400
H	2.54287500	-1.23904800	-2.55382400
C	-2.57555100	0.07160300	-0.06173800
H	-2.36922900	-0.31098400	0.93829700
C	-3.57033200	-0.91183300	-0.68894200
C	-3.43682300	-1.46315400	-1.96481500
H	-2.58274700	-1.20617800	-2.57808300
C	-4.38543000	-2.35986600	-2.46305400
H	-4.25723200	-2.77494700	-3.45694500
C	-5.48470500	-2.72410200	-1.69245800
H	-6.21947900	-3.42132600	-2.07905900
C	-5.62863700	-2.18496100	-0.41319400
H	-6.47797600	-2.46167100	0.20190700
C	-4.68278500	-1.29121400	0.07766300
H	-4.80938500	-0.87281200	1.07119300
C	-3.18393000	1.46945400	0.15545000
C	-4.25202800	1.95619400	-0.60279500
H	-4.71122800	1.32767200	-1.35700900
C	-4.74858800	3.24322300	-0.38984700
H	-5.57884700	3.60298800	-0.98808800
C	-4.18770900	4.05918300	0.58895100

H	-4.57642400	5.05741000	0.75738700
C	-3.12292500	3.57989100	1.35267000
H	-2.67860800	4.20612000	2.11882600
C	-2.62361800	2.29849400	1.13655900
H	-1.78343400	1.93520200	1.72181500
C	-0.00365800	1.87544900	-3.99502300
H	-0.02262200	1.14539200	-4.81197800
H	-0.87974200	2.51778900	-4.11066100
H	0.88941200	2.49053000	-4.12673100

IPr*–CAAC^{Me}–CuCl

Energy: -3743.024102 au

Sum of electronic and thermal Energies: -3742.277293 au

Geometry:

N	-0.01050600	-0.63235000	1.19166200
C	-0.16731200	0.40814900	1.97874300
C	-0.34816200	-0.06189200	3.41822900
C	-0.53692100	-1.59321800	3.28826900
H	-0.06171800	-2.14415500	4.10206700
H	-1.60330200	-1.83327700	3.30920800
C	0.05132800	-1.99429900	1.92321800
C	-1.58865300	0.60877900	4.03992800
H	-1.74987600	0.21914100	5.05002100
H	-2.48989900	0.40882200	3.45444100
H	-1.46223700	1.69180600	4.10670000
C	0.89380000	0.33785000	4.24706100

H	0.76222700	0.01039400	5.28247100
H	1.02402900	1.42252500	4.24724800
H	1.81350800	-0.11004800	3.86651100
C	1.50113400	-2.47839500	2.05040100
H	1.51154600	-3.36500400	2.68966900
H	2.15496600	-1.73353600	2.50368300
H	1.91891600	-2.76425000	1.08738700
C	-0.76359700	-3.07337900	1.21665200
H	-0.66516500	-4.00518300	1.78021700
H	-0.39478000	-3.25801000	0.20562800
H	-1.82065100	-2.82461900	1.16262100
C	0.05126300	-0.50091700	-0.26503700
C	1.29087800	-0.40225400	-0.93762500
C	1.28265700	-0.30155400	-2.33242000
H	2.23091400	-0.18735700	-2.84428600
C	0.11138700	-0.28160800	-3.07943600
C	-1.09453600	-0.30474700	-2.38438200
H	-2.01936600	-0.18940900	-2.93771300
C	-1.16321800	-0.40463100	-0.99408500
C	2.65517600	-0.28772700	-0.24043100
H	2.46504700	-0.14279000	0.82474500
C	3.38718400	0.98405000	-0.71264500
C	2.98253600	2.22712700	-0.21629600
H	2.17333500	2.28765400	0.50402400
C	3.58688100	3.40585800	-0.64316400
H	3.23925500	4.35240600	-0.24548500

C	4.61994900	3.36010100	-1.57824600
H	5.09484700	4.27535600	-1.91359100
C	5.03831500	2.12832500	-2.07653000
H	5.84485700	2.07962300	-2.80021300
C	4.42820900	0.94957100	-1.64656500
H	4.77776400	0.00011900	-2.03494000
C	3.55407600	-1.52630100	-0.35406700
C	4.67258600	-1.60340600	0.48896300
H	4.87175500	-0.79223300	1.18199300
C	5.53439300	-2.69360500	0.44621300
H	6.39091000	-2.72889900	1.11048700
C	5.29934300	-3.73837100	-0.44954000
H	5.96974400	-4.58956700	-0.48603000
C	4.19573400	-3.67456100	-1.29337900
H	3.99984500	-4.47891200	-1.99409300
C	3.33043100	-2.57795800	-1.24513500
H	2.47226300	-2.55529300	-1.90478900
C	-2.55807000	-0.30656100	-0.35145300
H	-2.41364300	-0.04579600	0.69814800
C	-3.37475600	-1.60289700	-0.35937100
C	-3.21876000	-2.61340400	-1.31117700
H	-2.45799300	-2.52162200	-2.07635800
C	-4.02131600	-3.75526200	-1.28162800
H	-3.87963500	-4.52824000	-2.02913900
C	-4.99583700	-3.90676300	-0.29894700
H	-5.61694100	-4.79499000	-0.27523800

C	-5.16490000	-2.90329400	0.65529100
H	-5.92155300	-3.00598700	1.42536100
C	-4.36363800	-1.76571500	0.62050800
H	-4.51144400	-0.98546800	1.36067400
C	-3.35958300	0.86263400	-0.96064500
C	-4.44075600	0.66607800	-1.82549400
H	-4.76288100	-0.33815700	-2.07291300
C	-5.12537100	1.75390900	-2.37032000
H	-5.96162400	1.57824000	-3.03844200
C	-4.74457900	3.05523900	-2.05444800
H	-5.27923900	3.89947600	-2.47529200
C	-3.67150700	3.26290800	-1.18800200
H	-3.35792500	4.26699900	-0.92607900
C	-2.98921600	2.17617000	-0.65041200
H	-2.15151600	2.36423200	0.01322000
C	0.14226300	-0.19655100	-4.58519300
H	0.08030500	-1.19361900	-5.03524800
H	-0.69902400	0.38671300	-4.96627300
H	1.06618800	0.26641100	-4.93781000
Cu	-0.14865500	2.26483200	1.55303900
Cl	-0.10060600	4.38399900	1.26607200

IPr*^{MeO}–CAAC^{Me}

Energy: -1717.390439 au

Sum of electronic and thermal Energies: -1716.644917 au

Geometry:

N	-0.08057500	-1.20578800	0.92951300
O	-0.02820900	2.74297000	-3.07471300
C	-0.09641400	-0.84968000	2.19238700
C	-0.17655700	-2.12388300	3.02374300
C	-0.46304100	-3.27077200	2.01152000
H	0.10105400	-4.17913500	2.23572300
H	-1.52397600	-3.53416600	2.04184600
C	-0.10706000	-2.72147000	0.61600700
C	-1.29902800	-1.98881600	4.06767800
H	-1.38554000	-2.90862300	4.65609600
H	-2.26589600	-1.80117800	3.59205600
H	-1.09500100	-1.15958200	4.74896100
C	1.16877800	-2.30299300	3.76083400
H	1.12930500	-3.19073000	4.40019700
H	1.37998600	-1.43494700	4.38955900
H	2.00555100	-2.42617200	3.06882000
C	1.26815300	-3.19747600	0.13299100
H	1.23202500	-4.27806900	-0.03100500
H	2.05533200	-2.99804800	0.86090300
H	1.54834900	-2.73045000	-0.81168600
C	-1.15253500	-3.07271700	-0.44209900
H	-1.14277000	-4.15438500	-0.60444000
H	-0.93636400	-2.59310800	-1.39913200
H	-2.15973500	-2.79305800	-0.13564100
C	-0.02901200	-0.19567900	-0.11906500
C	1.20576500	0.31737500	-0.55945700

C	1.22463000	1.30336900	-1.55492400
H	2.17795500	1.71653500	-1.85273300
C	0.04343600	1.79357400	-2.09731300
C	-1.17529100	1.34156300	-1.59511800
H	-2.07975300	1.81760200	-1.95236800
C	-1.23675700	0.36300900	-0.60975400
C	2.54114700	-0.04039500	0.10231100
H	2.30900200	-0.68805000	0.94776300
C	3.15575400	1.22961800	0.71895200
C	2.57577600	1.75626400	1.88091200
H	1.71859000	1.25341300	2.32020000
C	3.07738300	2.91854800	2.46011200
H	2.61740300	3.30989300	3.36111800
C	4.16435700	3.57941300	1.88683200
H	4.55508700	4.48441100	2.33875100
C	4.74534100	3.06440100	0.73111100
H	5.59380700	3.56627800	0.27837300
C	4.24594000	1.89605100	0.15288700
H	4.72155200	1.49824000	-0.73618900
C	3.53555300	-0.81946700	-0.76571700
C	4.65750400	-1.37824100	-0.13497400
H	4.79676700	-1.22720900	0.93074500
C	5.59710600	-2.11356100	-0.84933300
H	6.45419100	-2.53512500	-0.33553300
C	5.43724900	-2.30979300	-2.22203600
H	6.16750000	-2.88276300	-2.78230000

C	4.32770800	-1.76635100	-2.86065900
H	4.18602100	-1.91603800	-3.92558800
C	3.38526300	-1.02940900	-2.13831100
H	2.52237500	-0.62872200	-2.65482400
C	1.18104700	3.32305200	-3.54851800
H	0.88474600	4.05286100	-4.30018900
H	1.83163800	2.57214400	-4.00998700
H	1.72276900	3.83004500	-2.74334900
C	-2.60653400	0.04816400	0.00312700
H	-2.42678600	-0.60954000	0.85395600
C	-3.59747900	-0.69626700	-0.89919200
C	-3.44539600	-0.85425400	-2.27812400
H	-2.57906200	-0.44081700	-2.77810000
C	-4.39326800	-1.55367700	-3.02952500
H	-4.25100900	-1.66257200	-4.09928400
C	-5.50985400	-2.11052400	-2.41474800
H	-6.24402900	-2.65435700	-2.99847700
C	-5.67262100	-1.96432800	-1.03632400
H	-6.53602400	-2.39519100	-0.54114500
C	-4.72759200	-1.26563000	-0.29268000
H	-4.86881400	-1.15178000	0.77751900
C	-3.20420200	1.33437300	0.60228300
C	-4.24544400	2.03916000	-0.00712900
H	-4.68929000	1.66532100	-0.92249200
C	-4.73392900	3.21789700	0.55854400
H	-5.54252800	3.75128200	0.07047000

C	-4.19196300	3.70456800	1.74505800
H	-4.57447700	4.61815900	2.18662500
C	-3.15387400	3.00537400	2.36159300
H	-2.72434800	3.37454900	3.28671400
C	-2.66233800	1.83280400	1.79458400
H	-1.84211100	1.30067800	2.26841700

IPr*^{MeO}–CAAC^{Me}-CuCl

Energy: -3818.253390 au

Sum of electronic and thermal Energies: -3817.500757 au

Geometry:

N	0.08536000	-0.61436400	-1.31177600
O	-0.13958100	-0.20752600	4.29584400
C	0.26450300	0.43464500	-2.08313000
C	0.50168900	-0.01964600	-3.51937000
C	0.69394800	-1.55126200	-3.39767800
H	0.25355800	-2.09647000	-4.23462700
H	1.76169200	-1.78556700	-3.38001800
C	0.05618200	-1.96828900	-2.06006700
C	1.76122400	0.66390500	-4.08644300
H	1.96331500	0.28518500	-5.09334400
H	2.64052700	0.46311400	-3.46877100
H	1.63118400	1.74685200	-4.14750200
C	-0.70986800	0.38220500	-4.39100000
H	-0.53666300	0.06705700	-5.42410900
H	-0.84667800	1.46605300	-4.38430700

H	-1.64073300	-0.07523900	-4.05106600
C	-1.38660800	-2.45422800	-2.24725700
H	-1.37116300	-3.33228600	-2.89813000
H	-2.02554000	-1.70489100	-2.71435700
H	-1.83823700	-2.75379500	-1.30397200
C	0.84625000	-3.05320900	-1.33470800
H	0.76996000	-3.97980200	-1.91020200
H	0.44099400	-3.24757600	-0.33962100
H	1.90030400	-2.80410100	-1.23941300
C	-0.02457700	-0.49701600	0.14244500
C	-1.28055800	-0.40005100	0.77739800
C	-1.33163100	-0.30285100	2.17413000
H	-2.29777500	-0.18752600	2.64337700
C	-0.17316400	-0.28785500	2.93826700
C	1.06354700	-0.31098900	2.29668500
H	1.95203200	-0.19348000	2.90345800
C	1.16908100	-0.40525100	0.91503000
C	-2.62403500	-0.29249200	0.03890100
H	-2.40056800	-0.13419700	-1.01788100
C	-3.38557500	0.96554600	0.50110000
C	-2.96999400	2.21989200	0.04346000
H	-2.13197100	2.29898600	-0.64112200
C	-3.60033100	3.38675600	0.46521700
H	-3.24385700	4.34224700	0.09793100
C	-4.67066300	3.31799400	1.35610200
H	-5.16617200	4.22408100	1.68650200

C	-5.10018800	2.07495300	1.81537100
H	-5.93666400	2.00814900	2.50280000
C	-4.46400500	0.90785600	1.39059300
H	-4.82348500	-0.05067800	1.74640200
C	-3.51037400	-1.54318000	0.11120700
C	-4.60637700	-1.62102900	-0.76081800
H	-4.79854700	-0.80190500	-1.44638100
C	-5.45458300	-2.72269800	-0.75666600
H	-6.29361700	-2.75837600	-1.44285300
C	-5.22799200	-3.77876900	0.12794500
H	-5.88764500	-4.63906500	0.13394100
C	-4.14605600	-3.71492200	0.99942400
H	-3.95590000	-4.52882200	1.69063500
C	-3.29448700	-2.60658700	0.99027700
H	-2.45172600	-2.58432100	1.66952500
C	-1.36792700	-0.05960700	5.00182100
H	-1.09673400	0.00887100	6.05374900
H	-2.02143300	-0.92549800	4.85146000
H	-1.89191800	0.85263400	4.70024800
C	2.58388300	-0.30930400	0.31683300
H	2.47161500	-0.05131500	-0.73726200
C	3.39791500	-1.60705900	0.35344200
C	3.20664000	-2.61859800	1.29758400
H	2.42040000	-2.52653600	2.03643400
C	4.00878800	-3.76123000	1.29470200
H	3.83996700	-4.53469400	2.03602300

C	5.01761900	-3.91232600	0.34732300
H	5.63844000	-4.80108500	0.34460900
C	5.22211700	-2.90737900	-0.59847700
H	6.00606400	-3.00947300	-1.34084100
C	4.42138000	-1.76905000	-0.59050700
H	4.59680200	-0.98748500	-1.32323600
C	3.36759100	0.85974900	0.94765000
C	4.40485100	0.66328300	1.86453700
H	4.70466700	-0.34089700	2.13884100
C	5.07341300	1.75114700	2.42842900
H	5.87465100	1.57589200	3.13819200
C	4.72039000	3.05201000	2.08012300
H	5.24210100	3.89623500	2.51692200
C	3.69139200	3.25941500	1.16183500
H	3.39913400	4.26333500	0.87570500
C	3.02503800	2.17257400	0.60480900
H	2.22047100	2.35948700	-0.09906400
Cu	0.21507100	2.28614900	-1.63760700
Cl	0.12944500	4.40100000	-1.32714900

IPr*–CAAC^{Cy}

Energy: -1758.924452 au

Sum of electronic and thermal Energies: -1758.116855 au

Geometry:

N	0.00842000	0.94014600	-0.37149000
C	-0.00000500	1.66037000	0.72530300

C	0.01741700	3.12522200	0.31305600
C	0.27853700	3.12789300	-1.22226100
H	-0.33726800	3.85066200	-1.76091500
H	1.32203600	3.38767800	-1.42217400
C	-0.00216700	1.69421800	-1.71876200
C	1.12919300	3.85947100	1.10259400
H	2.10683100	3.45362600	0.82022500
H	0.99536700	3.63302200	2.16605700
C	-1.35287200	3.74872800	0.70146800
H	-1.54866200	3.50318900	1.75110700
H	-2.15554500	3.28284000	0.12087300
C	0.01528600	-0.51492600	-0.29179200
C	-1.19731500	-1.23088900	-0.19180900
C	-1.14659400	-2.62462500	-0.10072000
H	-2.07658500	-3.17002300	0.01609200
C	0.05240200	-3.33071800	-0.08720300
C	1.23360200	-2.59370900	-0.10203100
H	2.17736000	-3.11493000	0.01508500
C	1.24757200	-1.20030500	-0.19528700
C	-2.55866500	-0.54807000	-0.02099300
H	-2.36915600	0.52359300	0.04156600
C	-3.15159600	-0.93597900	1.34612600
C	-2.59543600	-0.37002100	2.50117500
H	-1.76994400	0.32967500	2.40385900
C	-3.07938200	-0.70952000	3.76157900
H	-2.63833400	-0.25908500	4.64431600

C	-4.12447000	-1.62466500	3.89205100
H	-4.50128100	-1.88897900	4.87394200
C	-4.68106000	-2.19393400	2.74983000
H	-5.49599900	-2.90444600	2.83768600
C	-4.19970400	-1.84965800	1.48567300
H	-4.65559800	-2.28893400	0.60592300
C	-3.55442400	-0.73349000	-1.17140600
C	-4.70014900	0.07648200	-1.18164600
H	-4.85394000	0.78747500	-0.37610100
C	-5.64507100	-0.02017500	-2.19732800
H	-6.52088700	0.61935900	-2.18031300
C	-5.46671100	-0.93608700	-3.23543400
H	-6.20109700	-1.01447900	-4.02917500
C	-4.33408600	-1.74318100	-3.24136800
H	-4.17895300	-2.45620900	-4.04390300
C	-3.38649900	-1.64133000	-2.21924900
H	-2.50701200	-2.27158900	-2.25266800
C	2.59104800	-0.47981000	-0.03231100
H	2.37245800	0.58666700	0.03118500
C	3.58728000	-0.63486400	-1.18713000
C	3.45947000	-1.56613600	-2.21960600
H	2.60967600	-2.23618400	-2.24097800
C	4.40822700	-1.63974100	-3.24266300
H	4.28451600	-2.37147300	-4.03375000
C	5.50190600	-0.78032800	-3.25342200
H	6.23683900	-0.83684200	-4.04851200

C	5.63998800	0.15939300	-2.23077800
H	6.48487800	0.83943500	-2.22667100
C	4.69404300	0.22750100	-1.21347200
H	4.81609300	0.95761200	-0.41961300
C	3.20321400	-0.85123200	1.33095200
C	4.28176100	-1.72997700	1.46244400
H	4.74697000	-2.15197600	0.57913700
C	4.78116300	-2.06122300	2.72310000
H	5.61958400	-2.74464600	2.80465000
C	4.21254000	-1.51327800	3.86976700
H	4.60328500	-1.76733400	4.84891100
C	3.13720300	-0.63269200	3.74734600
H	2.68664600	-0.19885800	4.63356900
C	2.63523300	-0.30655000	2.49050900
H	1.78688700	0.36619800	2.40014200
C	1.07388500	1.18108600	-2.67567700
C	-1.37133900	1.57123700	-2.39802200
H	2.07562300	1.27440300	-2.25787300
H	-1.60257500	0.53784700	-2.65854200
H	-2.17838600	1.95625800	-1.77356300
H	0.90859200	0.13653300	-2.94811200
C	0.07247200	-4.83798200	-0.01464500
H	0.95310300	-5.19805200	0.52233700
H	-0.81587800	-5.22322200	0.49100500
H	0.09682700	-5.27980000	-1.01712800
C	-1.39430100	5.27328400	0.51833900

C	1.10440500	5.38010500	0.89638600
C	-0.25895300	5.96980700	1.27935800
H	-2.36534200	5.65162100	0.85486100
H	-1.32130400	5.52416500	-0.54727500
H	1.89882900	5.84354300	1.49066600
H	1.32430700	5.62049800	-0.15180900
H	-0.41551500	5.84134200	2.35824000
H	-0.27820300	7.04752500	1.08652800
H	1.04065300	1.77198500	-3.59554000
H	-1.36113200	2.15107500	-3.32515400

IPr*–CAAC^{Cy}–CuCl

Energy: -3859.787293 au

Sum of electronic and thermal Energies: -3858.972523 au

Geometry:

N	0.01893500	0.67385600	-0.81425200
C	0.22644700	1.65114400	0.04006800
C	0.48548400	2.94873000	-0.71367400
C	0.64544300	2.49647200	-2.18741300
H	0.20090500	3.19163400	-2.90045600
H	1.70792500	2.41701200	-2.43356500
C	-0.01172000	1.10773700	-2.29564200
C	1.77496500	3.61761900	-0.16773600
H	2.63123600	2.95714400	-0.34031200
H	1.67988000	3.72760600	0.91840700
C	-0.70530700	3.92300200	-0.47560900

H	-0.85463500	4.01732800	0.60589600
H	-1.62946400	3.49965800	-0.87839700
C	-0.12207000	-0.71780900	-0.38313200
C	-1.39627100	-1.28656300	-0.15445600
C	-1.46402900	-2.62870100	0.23235300
H	-2.43826300	-3.05304900	0.44457800
C	-0.33553400	-3.41892900	0.41253100
C	0.90654000	-2.81102500	0.25310100
H	1.80031000	-3.37853800	0.48534000
C	1.05082900	-1.47712100	-0.13118700
C	-2.71978600	-0.50710900	-0.19357200
H	-2.47074700	0.55282300	-0.27218500
C	-3.46788400	-0.66389800	1.14508600
C	-3.03004100	0.05926200	2.25886000
H	-2.18333600	0.73209900	2.17132900
C	-3.64857400	-0.07931100	3.49784100
H	-3.27415400	0.48815100	4.34208900
C	-4.72969100	-0.94742600	3.64350100
H	-5.21572500	-1.05872400	4.60635100
C	-5.18144600	-1.66932900	2.54102900
H	-6.02529200	-2.34356900	2.64071900
C	-4.55697600	-1.52798600	1.30143800
H	-4.93260500	-2.08701300	0.45238100
C	-3.63250000	-0.82609300	-1.38524600
C	-4.70384100	0.04267100	-1.64061800
H	-4.85849200	0.89926300	-0.99232300

C	-5.57495700	-0.17843400	-2.70146300
H	-6.39419900	0.51003600	-2.87755700
C	-5.39707600	-1.28336100	-3.53613400
H	-6.07484700	-1.45910400	-4.36381600
C	-4.34060200	-2.15470000	-3.29383000
H	-4.18920100	-3.01694900	-3.93412100
C	-3.46581000	-1.92722800	-2.22774200
H	-2.64476100	-2.61396000	-2.06519100
C	2.47946900	-0.90583100	-0.15842700
H	2.39467800	0.18137400	-0.12053000
C	3.28836600	-1.22565200	-1.41961300
C	3.07579600	-2.35551500	-2.21305500
H	2.27451400	-3.04242100	-1.97053700
C	3.87368100	-2.60625900	-3.33075500
H	3.68760300	-3.48825100	-3.93393100
C	4.90027800	-1.73098300	-3.67474900
H	5.51790300	-1.92522600	-4.54429500
C	5.12611500	-0.60096700	-2.88848700
H	5.92375000	0.08852100	-3.14244900
C	4.32899000	-0.35614500	-1.77403800
H	4.52041700	0.51989600	-1.16216900
C	3.25105300	-1.30446300	1.11701100
C	4.29049200	-2.23986900	1.10901500
H	4.60075600	-2.69953000	0.17849500
C	4.94857600	-2.58516300	2.29088900
H	5.75245000	-3.31283500	2.26135700

C	4.58274700	-1.99653500	3.49828300
H	5.09689900	-2.26277000	4.41507000
C	3.55128600	-1.05779600	3.51695300
H	3.24994100	-0.58477400	4.44463900
C	2.89507000	-0.71972800	2.33777100
H	2.08893500	0.00540100	2.38044500
C	0.76127800	0.15271700	-3.20057000
C	-1.45512800	1.20599700	-2.80496900
H	1.81516000	0.09726700	-2.93893000
H	-1.92556600	0.22811000	-2.88269600
H	-2.07882800	1.84173300	-2.17639500
H	0.34039200	-0.85454900	-3.17486200
C	-0.44901400	-4.87057600	0.80663900
H	0.37776900	-5.17103300	1.45418100
H	-1.38464700	-5.06658200	1.33441600
H	-0.42636700	-5.51915700	-0.07619400
C	-0.46301400	5.31664100	-1.07403100
C	2.02990500	4.99586300	-0.79317400
C	0.84242700	5.93866700	-0.56279700
H	-1.31281800	5.96168000	-0.82948200
H	-0.43185000	5.25393600	-2.16880000
H	2.94240600	5.42227400	-0.36518600
H	2.21381100	4.89187400	-1.87009200
H	0.74914800	6.14320500	0.51097400
H	1.01935300	6.90202600	-1.05130100
H	0.68817600	0.51577200	-4.22935800

H	-1.43610600	1.64229100	-3.80704800
Cu	0.19326100	1.61417600	1.94671300
Cl	0.14039100	1.76151300	4.08112200

IPr*^{MeO}–CAAC^{Cy}

Energy: -1834.153350 au

Sum of electronic and thermal Energies: -1833.339889 au

Geometry:

N	0.08495800	1.06964300	-0.36476200
O	-0.03365100	-4.54426700	-0.04854300
C	0.11349200	1.78277600	0.73676700
C	0.21513700	3.24698400	0.33436700
C	0.47880500	3.24519600	-1.20053500
H	-0.09295000	4.00618800	-1.73513700
H	1.53598900	3.44533100	-1.39714800
C	0.11651800	1.83360100	-1.70629800
C	1.36711100	3.90922500	1.13010200
H	2.31949100	3.44817500	0.84626400
H	1.21858000	3.68433200	2.19194300
C	-1.11651800	3.94731000	0.72583900
H	-1.32755500	3.70666600	1.77368500
H	-1.94453800	3.53342300	0.14135500
C	0.01618600	-0.38391800	-0.29784700
C	-1.22621800	-1.03879700	-0.20029000
C	-1.26145100	-2.43725000	-0.11886400
H	-2.22026600	-2.92249800	-0.00300900

C	-0.08907500	-3.18233000	-0.11348400
C	1.13756600	-2.52132100	-0.12338500
H	2.03533200	-3.11491100	-0.00517700
C	1.21528700	-1.13581500	-0.20590900
C	-2.55217600	-0.28985800	-0.02580800
H	-2.30736600	0.76995500	0.04524800
C	-3.16437100	-0.65844000	1.33806200
C	-2.57492400	-0.13731600	2.49770800
H	-1.71232500	0.51692300	2.40548000
C	-3.07374300	-0.46433100	3.75559800
H	-2.60618100	-0.04926800	4.64198100
C	-4.16757600	-1.32174400	3.87905900
H	-4.55615100	-1.57570400	4.85908600
C	-4.75810000	-1.84579400	2.73223500
H	-5.61194500	-2.50981300	2.81462500
C	-4.26132100	-1.51419300	1.47049600
H	-4.74430900	-1.91593600	0.58716700
C	-3.55396300	-0.41558700	-1.17900000
C	-4.66727100	0.43848700	-1.17523300
H	-4.79489800	1.13969900	-0.35672800
C	-5.61305200	0.39803400	-2.19394500
H	-6.46324800	1.07085900	-2.16585200
C	-5.46823600	-0.50379100	-3.24946500
H	-6.20340400	-0.53810500	-4.04559400
C	-4.36719300	-1.35322000	-3.27012000
H	-4.23704600	-2.05462200	-4.08722500

C	-3.41853600	-1.30787200	-2.24491400
H	-2.56239200	-1.96878600	-2.29066700
C	-1.25172000	-5.26867300	0.07241300
H	-0.96826600	-6.31881500	0.12039400
H	-1.90084600	-5.10832700	-0.79535800
H	-1.78969900	-4.99536800	0.98603500
C	2.59325200	-0.48398800	-0.03973600
H	2.42632400	0.59128300	0.02910000
C	3.58005100	-0.68128600	-1.19627300
C	3.41498500	-1.60942300	-2.22624400
H	2.54063600	-2.24704000	-2.24528500
C	4.36011000	-1.72258700	-3.24909200
H	4.20765900	-2.45139400	-4.03781700
C	5.48696300	-0.90722400	-3.26198400
H	6.21904700	-0.99485600	-4.05690000
C	5.66277400	0.02828300	-2.24126800
H	6.53429900	0.67385800	-2.23839300
C	4.72036000	0.13614100	-1.22418500
H	4.87163600	0.86220200	-0.43160200
C	3.18829100	-0.89088600	1.32071000
C	4.21759600	-1.82743700	1.44601900
H	4.65426600	-2.27379900	0.56016500
C	4.70357800	-2.18706100	2.70399800
H	5.50287100	-2.91627400	2.78103900
C	4.17099400	-1.61020600	3.85378400
H	4.55150600	-1.88677900	4.83086300

C	3.14485800	-0.67205500	3.73736300
H	2.72267900	-0.21545000	4.62614800
C	2.65588100	-0.31734200	2.48311600
H	1.84497800	0.40066300	2.39726800
C	1.15918000	1.26646000	-2.66953400
C	-1.25886100	1.79431600	-2.38317200
H	2.16627700	1.30433700	-2.25602400
H	-1.54763400	0.77816000	-2.65363500
H	-2.04182300	2.21755800	-1.75257900
H	0.93657200	0.23307300	-2.94383300
C	-1.06800400	5.47297100	0.55322100
C	1.43234900	5.42981300	0.93344000
C	0.10571200	6.09629300	1.31953100
H	-2.01538200	5.90554800	0.89191400
H	-0.97942900	5.72656300	-0.51057800
H	2.25220900	5.84199700	1.53091000
H	1.66675400	5.66311000	-0.11318700
H	-0.05912900	5.96999200	2.39744300
H	0.15008900	7.17455000	1.13396200
H	-1.21836700	2.38210200	-3.30446500
H	1.15410400	1.86097300	-3.58766300

IPr*^{MeO}–CAAC^{Cy}-CuCl

Energy: -3935.016620 au

Sum of electronic and thermal Energies: -3934.195979 au

Geometry:

N	0.12424600	0.84398300	-0.76770600
O	-0.66088100	-4.59856100	0.42574600
C	0.39368200	1.73161100	0.16412200
C	0.78330000	3.05538700	-0.47992300
C	0.93347100	2.70715100	-1.98273100
H	0.56696800	3.49291700	-2.64426000
H	1.98960300	2.55208200	-2.22016700
C	0.15847300	1.39569400	-2.20916400
C	2.11706400	3.55393300	0.13737300
H	2.91171700	2.83104700	-0.07509600
H	2.00813400	3.58606800	1.22729300
C	-0.31622900	4.11610400	-0.18142800
H	-0.48057000	4.13795300	0.90180700
H	-1.26656600	3.81602300	-0.63133000
C	-0.13134100	-0.56042300	-0.44814700
C	-1.44381400	-1.04533000	-0.26813100
C	-1.63427100	-2.40203000	0.02535900
H	-2.64154300	-2.75015500	0.20190300
C	-0.55855100	-3.26953300	0.15335900
C	0.73614700	-2.76630600	0.04382400
H	1.56023400	-3.43739300	0.24864200
C	0.97927400	-1.42953700	-0.24426200
C	-2.70515500	-0.16717500	-0.27286200
H	-2.37496200	0.87332700	-0.26369000
C	-3.49874600	-0.36840200	1.03316000
C	-3.03006100	0.21937600	2.21221900

H	-2.12778100	0.82176400	2.19818400
C	-3.68946100	0.03198200	3.42336000
H	-3.29040000	0.49385200	4.31911200
C	-4.84297600	-0.74946800	3.47538000
H	-5.36125000	-0.89747700	4.41622700
C	-5.32583800	-1.33571300	2.30755400
H	-6.22661100	-1.93956900	2.33402600
C	-4.66032300	-1.14587200	1.09582100
H	-5.06106500	-1.59657700	0.19531900
C	-3.60522600	-0.32511400	-1.50574300
C	-4.60887300	0.63305900	-1.71151600
H	-4.72365100	1.44305500	-0.99835500
C	-5.46320500	0.55907600	-2.80591800
H	-6.22948000	1.31426800	-2.94240000
C	-5.33618900	-0.48380900	-3.72540500
H	-6.00098000	-0.54463800	-4.57960600
C	-4.34657100	-1.44196400	-3.53367400
H	-4.23419800	-2.25660700	-4.24086100
C	-3.48826400	-1.36241200	-2.43337500
H	-2.71769200	-2.11296100	-2.31085300
C	-1.95223700	-5.14835000	0.66872000
H	-1.78756600	-6.20179600	0.88770800
H	-2.59688500	-5.05757700	-0.21199700
H	-2.43314700	-4.66846700	1.52670000
C	2.44836400	-0.97098700	-0.22993500
H	2.44694200	0.11505200	-0.12612300

C	3.23990600	-1.27540000	-1.50629400
C	2.94118900	-2.32799400	-2.37461600
H	2.08371300	-2.96058900	-2.18196800
C	3.72717000	-2.57011000	-3.50277200
H	3.47439900	-3.39182500	-4.16398900
C	4.82691800	-1.76365000	-3.78246700
H	5.43525000	-1.95126500	-4.66000700
C	5.13872300	-0.71150400	-2.92101900
H	5.99409800	-0.07653000	-3.12417400
C	4.35358000	-0.47514800	-1.79645000
H	4.61175700	0.33874400	-1.12605900
C	3.17728000	-1.50508500	1.02004000
C	4.11689400	-2.53887300	0.95996400
H	4.37773200	-2.98125800	0.00615100
C	4.73776300	-3.00624600	2.11950800
H	5.46318200	-3.80962100	2.04997800
C	4.43405400	-2.44394400	3.35633700
H	4.91870900	-2.80622600	4.25609900
C	3.50264500	-1.40827700	3.42715900
H	3.24983900	-0.95554900	4.37915300
C	2.88355200	-0.94760600	2.26958400
H	2.15392100	-0.14844900	2.35149000
C	0.85752400	0.45057800	-3.18173600
C	-1.26258300	1.66409800	-2.72098800
H	1.89817100	0.27982300	-2.91694300
H	-1.81545300	0.74169500	-2.88535700

H	-1.83784600	2.29769100	-2.04556900
H	0.34843100	-0.51362800	-3.24055400
C	0.06877200	5.52367400	-0.66114600
C	2.51390300	4.94695900	-0.37022100
C	1.41467700	5.97676600	-0.08187100
H	-0.72241300	6.22505700	-0.37800400
H	0.11863300	5.54514800	-1.75682500
H	3.45224400	5.24938600	0.10488100
H	2.71190500	4.91194300	-1.44910400
H	1.31685700	6.10351000	1.00343800
H	1.69145200	6.95472800	-0.48809300
H	-1.18985900	2.17955500	-3.68220000
H	0.83298700	0.89933200	-4.17853400
Cu	0.30856100	1.54748000	2.06032800
Cl	0.20386000	1.53780800	4.19800900