SUPPORTING INFORMATION

Activator-Free Single-Component Co(I)-Catalysts for Regio- and Enantioselective Heterodimerization and Hydroacylation Reactions of 1,3-Dienes. New Reduction Procedures for Synthesis of [L]Co(I)-Complexes and Comparison to *in-situ* Generated Catalysts

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General Methods

All manipulations of moisture- and oxygen-sensitive materials were conducted using standard Schlenk technique under an argon atmosphere or in a glovebox under nitrogen atmosphere maintained at <5 ppm O_2. The Schlenk line was equipped with a vacuum pump maintained between 0.2- and 0.01-mm Hg for all evacuation and drying of air sensitive compounds. All glassware was cleaned by soaking in a base bath overnight, rinsing with water, then soaking in an acid bath (1 h), then water again and finally acetone, then dried in an oven kept at 160 °C overnight. Glass vials used for reactions were purchased from VWR (8 mL, 17 x 60 mm [O.D. x H), screw-thread sample vials, PTFE-faced silicone septa), the caps were dried in a desiccator overnight while the vials were dried in an oven at 140 °C for 24 h before transferring into the glovebox. Gas chromatographic analysis of reaction mixtures was done on an Agilent 6850 Network G.C. equipped with an HP-1 methyl siloxane column (30 m, 0.32 mm I.D, 0.25 µm), H_2 carrier gas, FID at 300 °C or an HP 5890 GC equipped with HP-5MS column (30 m, 0.32 mm I.D, 0.25 µm) and hydrogen as carrier gas with FID-detector at 250 °C. GC-MSD analysis was performed on a 6850 GC-5975 MSD equipped with an EI-ionizer. Enantiomeric ratios of chiral compounds were determined by chiral gas chromatographic analyses which were performed on an Agilent 7850 A equipped with a cyclosil-B column, hydrogen carrier gas, using an FID detector at 250°C. Proton, fluorine, and phosphorous nuclear magnetic resonance spectra (^{1}H, ^{19}F and ^{31}P NMR) were recorded on a Bruker Avance III HD Ascend 600 MHz or 400 MHz. Solvent resonance was used as internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm, ^{13}C NMR, $CDCl_3$ at 77.16 ppm, C_6D_6 at 128.06 ppm). Solution state effective magnetic moment was obtained by Evans method (sealed capillary half-filled with 2% CH_2Cl_2 in CD_2Cl_2 was inserted in NMR-tube and ^{1}H NMR spectrum of given complex was recorded in CD_2Cl_2).

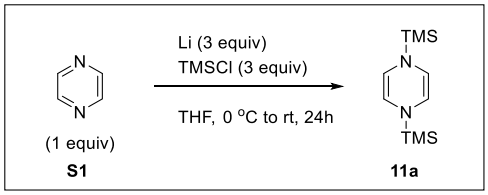
Methylene chloride was distilled over CaH_2 and stored in the glovebox over activated 4Å molecular sieves or used for reactions out of the box when freshly distilled. Et_2O, THF, and hexanes were distilled and stored over molecular sieves for prolonged used in the glovebox. Activated zinc dust was prepared by washing with dilute aqueous HCl (1 – 2 N), washing with distil water several times, and finally with copious amounts of acetone and the resulting solid transferred into a Schlenk flask and all volatiles removed under vacuum. The solid was further dried under vacuum at ca. 90 °C for at least 12 h, then allowed to cool to ambient temperature and transferred into the glovebox. Zinc dust for reactions were prepared by taking chunks of activated zinc and making a powder using a mortar and pistil inside the box. Sodium *tetrakis*-[3,5 *bis*(trifluoromethyl)phenyl]borate (NaBARF) was prepared using reported procedure.[1] All the ligands were obtained from commercial sources.

The single crystal X-ray diffraction studies were carried out on a Nonius Kappa diffractometer equipped with a Bruker APEX-II CCD and Mo K_α radiation (λ = 0.71073 Å). A desired single crystal suitable for X-ray diffraction were coated with polytoluene oil in a glovebox and was then quickly transferred and mounted on a MiTeGen Micromount with CHRISTO-LUBE MCG 1024 oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

Preparation of Organic Reductant via Reductive Silylation

All reducing agents were synthesized from commercially available starting materials by reported methods with some modification.[2]

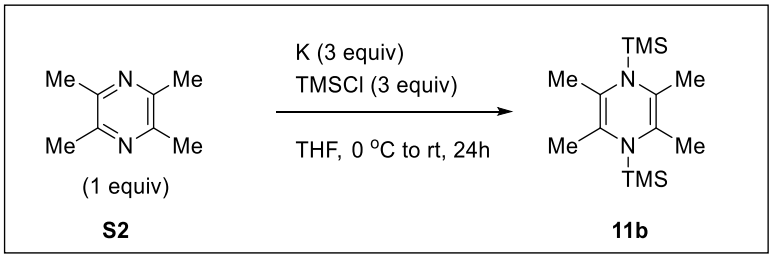
1,4-*Bis*(trimethylsilyl)-1,4-dihydropyrazine (11a)



At 0 °C, solution of Pyrazine (5 g, 62.5 mmol) in THF (20 mL) was added dropwise to a mixture of Li (3 equiv., 187.5 mmol, 1.3 g), TMSCl (3 equiv., 187.5 mmol, 24.8 mL) and THF (20 mL) over a period of 1 h. The resulting mixture allowed to come to room temperature and was stirred for 24 h at rt. Upon completion of reaction, the unreacted Li and precipitated LiCl were filtered off under inert atmosphere inside N_2-filled the glovebox. The filtrate was evacuated under high vacuum and solid yellow residue was recrystallized from diethyl ether at -35 °C to obtain the pure titled compound as yellow needles (11.6 g, 82% yield).

^{1}H NMR (600 MHz, C_6D_6): δ 4.70 (s, 4H), -0.03 (s, 18H); **^{13}C NMR (150 MHz, C_6D_6):** δ 115.5 (4xC), -1.7(6xC).

2,3,5,6-Tetramethyl-1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (11b)



At 0 °C, a solution of 2,3,5,6-tetramethylpyrazine (1g, 7.34 mmol) in THF (10 mL) was added dropwise to a mixture of K (0.86 g, 22 mmol), TMSCl (3 equiv., 22 mmol, 2.8 mL) and THF (10 mL) over a period of 30 min. The resulting mixture allowed to come to room temperature and was stirred for 24 h at rt. Upon completion of reaction, the unreacted K and precipitated KCl were filtered off under inert atmosphere inside N_2-filled the glovebox. The filtrate was evacuated

under high vacuum and solid residue was sublimed by using bulb-to-bulb distillation set up under reduced pressure to afford pure titled compound as a white solid (1.5 g, 72% yield).

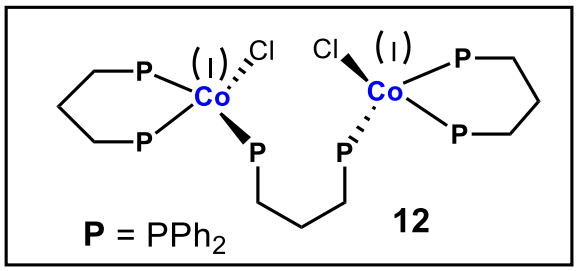
^{1}H NMR (400 MHz, C_6D_6): δ 1.69 (s, 12H), 0.23 (s, 18H); **^{13}C NMR (150 MHz, C_6D_6):** δ 127.0 (4xC), 19.1 (4xC), 1.8 (6xC).

Preparation of Cobalt(II)-Complexes

All cobalt(II)-complexes were prepared by following our previously reported procedures:[3] in the glovebox, anhydrous CoX_2 (0.95 eq) was dissolved in dry distilled THF. In another flask, the ligand (1.0 eq) was dissolved in dry distilled THF and added slowly to a stirring solution of the CoX_2. After the addition, the resultant mixture was stirred overnight (18 - 24 h), after which the complex may be precipitated. Stirring was stopped and hexanes added to the mixture, shaken thoroughly, and allowed to sit for ~ 10 min. The supernatant was decanted, and the resultant precipitate washed with diethyl ether until the supernatant was almost colorless. Solvent was stripped and the solid dried under high vacuum (~0.1 mm Hg) for 12 to 24 h to afford desired complex.

Preparation of Cobalt(I)-Complexes

Synthesis of [(dppp)(Cl)Co[μ-(dppp)]Co(Cl)(dppp)] (12) by using 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine



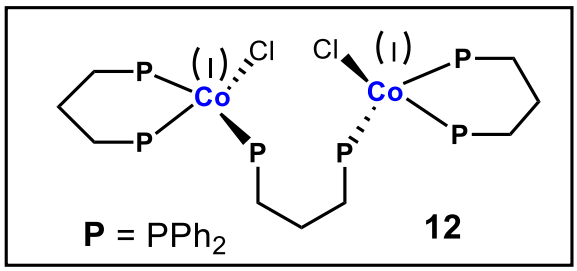
In the glovebox, a 25-mL Schlenk flask was charged with a magnetic stir bar, anhydrous $CoCl_2$ (200 mg, 1.54 mmol, 1 equiv.) and dry freshly distilled THF (0.5 M). The resulting mixture was stirred until all the $CoCl_2$ dissolved to afford a homogenous solution. In another flask, the ligand, dppp (992 mg, 2.38 mmol, 1.55 equiv.) was dissolved in dry distilled THF (0.5 M) and added slowly to a stirring solution of the $CoCl_2$. After

the addition, the resultant blue mixture was stirred for 15 minutes followed by the addition of 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (696 mg, 3.08 mmol, 2 equiv.). Upon which the color changed from blue to green. The resulting green solution stirred overnight. Stirring was stopped and solvent was stripped, washed with hexanes (1-2 mL), and the solid dried under high vacuum (~0.1 mm Hg) for 2-3 h to afford desired crude complex. The crude complex thus obtained was then dissolved in minimum amount of THF and filtered inside the glovebox. To the filtrate was then diffused hexanes (by slow evaporation of hexane into a THF solution placed in an atmosphere of hexane) to afford the green crystals (958 mg, 87% yield). The green crystal was then characterized by X-ray Crystallography (CCDC # 1873380). Solution state effective magnetic moment μ_{eff} (298 K) = 4.57 B.M.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 17.54 ($\Delta_{1/2}$ = 94 Hz), 15.47 ($\Delta_{1/2}$ = 11 Hz), 14.93 ($\Delta_{1/2}$ = 154 Hz), 14.46 ($\Delta_{1/2}$ = 120 Hz), 11.15 ($\Delta_{1/2}$ = 75 Hz), 10.16 ($\Delta_{1/2}$ = 149 Hz), 7.49 ($\Delta_{1/2}$ = 87 Hz), 7.41 ($\Delta_{1/2}$ = 69 Hz), 3.68 ($\Delta_{1/2}$ = 22 Hz), 3.28 ($\Delta_{1/2}$ = 54 Hz), 2.79 ($\Delta_{1/2}$ = 34 Hz), 2.43 ($\Delta_{1/2}$ = 80 Hz), 1.82 ($\Delta_{1/2}$ = 22 Hz), 1.27 ($\Delta_{1/2}$ = 74 Hz), 0.13 ($\Delta_{1/2}$ = 29 Hz), 0.09 ($\Delta_{1/2}$ = 20 Hz), -3.94 ($\Delta_{1/2}$ = 111 Hz), -4.95 ($\Delta_{1/2}$ = 56 Hz), -18.70 ($\Delta_{1/2}$ = 6 Hz).

Synthesis of [(dppp)(Cl)Co[μ-(dppp)]Co(Cl)(dppp)] (12) by using Li_3N

By following the same procedure as above with modification of reducing agent, it is prepared as follows:



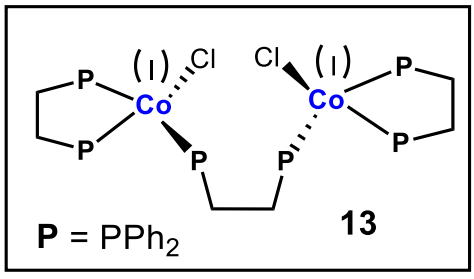
In the glovebox, a 25-mL Schlenk flask was charged with a magnetic stir bar, anhydrous $CoCl_2$ (100 mg, 0.77 mmol, 1 equiv.) and dry freshly distilled THF (0.5 M). The resulting mixture was stirred until all the $CoCl_2$ dissolved to afford a homogenous solution. In another flask, the ligand, dppp (496mg, 1.19 mmol, 1.55

equiv.) was dissolved in dry distilled THF (0.5 M) and added slowly to a stirring solution of the $CoCl_2$. After the addition, the resultant blue mixture was stirred for 15 minutes followed by the addition of Li_3N (14 mg, 0.4 mmol, 0.52 equiv.),upon which the color changed from blue to green. The resulting green solution stirred overnight. Stirring was stopped and mixture was filtered out with fret funnel over celite. The resulting filtrate was stripped, washed with hexanes (1-2 mL), and the solid dried under high vacuum (~0.1 mm Hg) for 2-3 h to afford desired crude complex (545 mg, 77% yield). Some portion of the crude complex was then dissolved in minimum amount of THF and filtered inside the glovebox. To the filtrate was then diffused hexanes (by slow evaporation of hexane into a THF solution placed in an atmosphere of hexane) to afford the green crystals. The green crystal was then characterized by X-ray Crystallography. This crystal structure has been previously reported by our group.[3]

The crystal was an olive-green rectangular rod. All work was done at 150 K. The initial unit cell was determined to be primitive triclinic with cell constants of a = 21.25 Ang., b = 21.49, c = 23.69, alpha = 66.38 deg., beta = 65.92 deg., and gamma = 71.77 deg. Since this cell matches that for our previously determined structure of the same compound (CCDC # 1873380), no data collection was done.

Synthesis of [(dppe)(Cl)Co[*μ*-(dppe)]Co(Cl)(dppe)] (13)

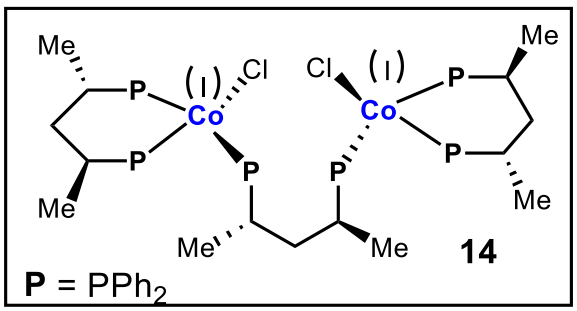
In the glovebox, a 20-mL scintillation vial was charged with a magnetic stir bar, anhydrous $CoCl_2$ (31 mg, 0.24 mmol, 1 equiv.) and dry freshly distilled THF (1 mL). The resulting mixture was stirred until all the $CoCl_2$ dissolved to afford a homogenous solution. In another vial, the ligand, dppe (147 mg, 0.37 mmol, 1.55 equiv.) was dissolved in dry distilled THF (3 mL) and added slowly to a stirring solution of the $CoCl_2$. After the addition, the resultant mixture was stirred for 15 minutes followed by the addition of 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (107



mg, 0.48 mmol, 2 equiv.) upon which the color changed from green to brownish yellow. The resulting brownish yellow solution stirred for 6 h. Stirring was stopped, solvent was stripped, washed with hexanes (1-2 mL), and the solid dried under high vacuum (~0.1 mm Hg) for 2-3 h to afford desired crude complex (crude 80% yield). The crude complex thus obtained was then dissolved in minimum amount of THF and filtered inside the glovebox. To the filtrate was then diffused hexanes (by slow evaporation of hexane into a THF solution placed in an atmosphere of hexane) to afford the yellowish green crystals (79 mg, 48% yield). The green crystal was then characterized by X-ray Crystallography (CCDC # 1966496). Solution state effective magnetic moment μ_{eff} (301 K) = 3.46 B.M.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 13.76 ($\Delta_{1/2}$ = 122 Hz), 11.75 ($\Delta_{1/2}$ = 141 Hz), 10.53 ($\Delta_{1/2}$ = 260 Hz), 3.27 ($\Delta_{1/2}$ = 145 Hz), 2.20 ($\Delta_{1/2}$ = 164 Hz), 1.41 ($\Delta_{1/2}$ = 65 Hz), 0.91 ($\Delta_{1/2}$ = 130 Hz), -4.22 ($\Delta_{1/2}$ = 187 Hz), -5.61 ($\Delta_{1/2}$ = 11 Hz).

Synthesis of [(S,S)-(BDPP)(Cl)Co[μ-[(S,S)-(BDPP)]]Co(Cl)(S,S)-(BDPP)] (14)

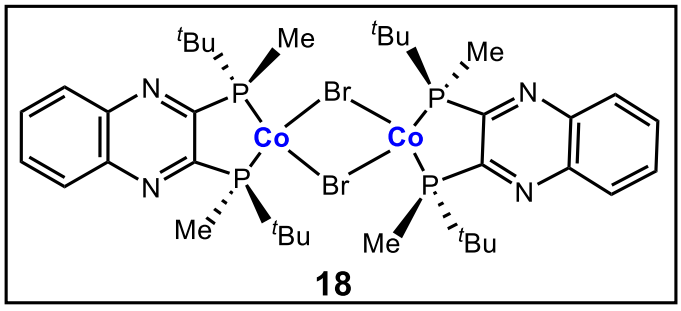


In the glovebox, a 20-mL scintillation vial was charged with a magnetic stir bar, anhydrous $CoCl_2$ (50 mg, 0.38 mmol, 1 equiv) and dry freshly distilled THF (0.5 M). The resulting mixture was stirred until all the $CoCl_2$ dissolved to afford a homogenous solution. In another vial, the ligand, (*S,S*)-BDPP (263 mg, 0.6 mmol, 1.55 equiv.) was dissolved in dry distilled THF (0.5 M) and added slowly to a stirring solution of the $CoCl_2$. After the addition, the resultant blue mixture was stirred for 15 minutes followed by the addition of 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (174 mg, 0.77 mmol, 2 equiv.). Upon which the color changed from blue to green. The resulting green solution stirred overnight. Stirring

was stopped, solvent was stripped, washed with hexanes (1-2 mL), and the solid dried under high vacuum (~0.1 mm Hg) for 2-3 h to afford desired crude complex (244 mg, 84% yield). The crude complex thus obtained was then dissolved in minimum amount of THF and filtered inside the glovebox. To the filtrate was then diffused hexanes (by slow evaporation of hexane into a THF solution placed in an atmosphere of hexane) to afford the green crystals (160 mg, 55% yield). The green crystal was then characterized by X-ray Crystallography. This crystal structure has been previously reported by our group.[3] Solution state effective magnetic moment μ_{eff} (301 K) = 5.25 B.M.

^{1}H NMR (600 MHz, C_6D_6): δ 17.55 ($\Delta_{1/2}$ = 62 Hz), 14.13 ($\Delta_{1/2}$ = 84 Hz), 10.74 ($\Delta_{1/2}$ = 6 Hz), 9.93 ($\Delta_{1/2}$ = 31 Hz), 7.82 ($\Delta_{1/2}$ = 73 Hz), 7.76 ($\Delta_{1/2}$ = 27 Hz), 7.47 ($\Delta_{1/2}$ = 25 Hz), 7.39 ($\Delta_{1/2}$ = 44 Hz), 6.72 ($\Delta_{1/2}$ = 67 Hz), 6.40 ($\Delta_{1/2}$ = 27 Hz), 6.21 ($\Delta_{1/2}$ = 62 Hz), 3.57 ($\Delta_{1/2}$ = 24 Hz), 3.42 ($\Delta_{1/2}$ = 80 Hz), 3.08 ($\Delta_{1/2}$ = 53 Hz), 2.99 ($\Delta_{1/2}$ = 36 Hz), 2.91 ($\Delta_{1/2}$ = 13 Hz), 1.91 ($\Delta_{1/2}$ = 24 Hz), 1.41 ($\Delta_{1/2}$ = 25 Hz), 1.22 ($\Delta_{1/2}$ = 78 Hz), 1.03 ($\Delta_{1/2}$ = 76 Hz), 0.95 ($\Delta_{1/2}$ = 40 Hz), 0.89 ($\Delta_{1/2}$ = 51 Hz), 0.12 ($\Delta_{1/2}$ = 51Hz), - 2.10 ($\Delta_{1/2}$ = 4 Hz), -4.23 ($\Delta_{1/2}$ = 6 Hz), -7.60 ($\Delta_{1/2}$ = 4 Hz), -11.84 ($\Delta_{1/2}$ = 4 Hz), -17.07 ($\Delta_{1/2}$ = 9 Hz), -17.29 ($\Delta_{1/2}$ = 4 Hz).

Synthesis of {[(*R,R*)-QuinoxP*]cobalt(μ-Br)}$_2$ (18)



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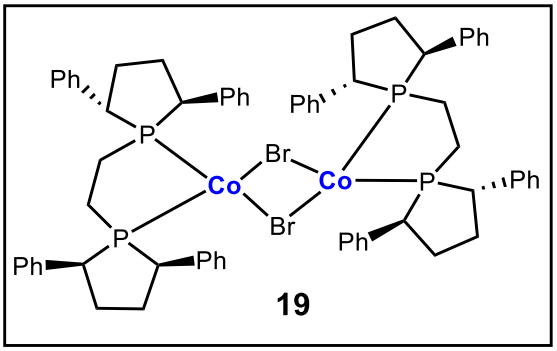
In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, anhydrous $CoBr_2$ (50 mg, 0.145 mmol, 1 equiv.) and dry freshly distilled THF (3 mL). The resulting mixture was stirred until all the $CoBr_2$ dissolved to afford a homogenous solution. In another vial, the ligand, R-QuinoxP* (50 mg, 0.145 mmol, 1.0 equiv.) was dissolved in dry distilled THF (2 mL) and added slowly to a stirring solution of the $CoBr_2$.

After the addition, the resultant green mixture was stirred for 3 h followed by the addition of 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (33 mg, 0.145 mmol, 1 equiv.). Upon which the color changed from green to deep green. The resulting green solution stirred overnight. Stirring was stopped and solvent was stripped and the solid dried under high vacuum (~0.1 mm Hg) for 2 to 3 h to afford desired crude complex (65 mg, crude yield 95%). The crude complex thus obtained was then dissolved in minimum amount of hexanes and filtered inside the glovebox. The filtrate was kept at -25 ^{o}C overnight to afford the green crystals (55 mg, 80% yield). The green crystal was then characterized by X-ray Crystallography (CCDC # 1966498). Solution state effective magnetic moment μ_{eff} (301 K) = 4.70 B.M.

^{1}H NMR (600 MHz, C_6D_6): δ 26.25 ($\Delta_{1/2}$ = 73 Hz), 9.71 ($\Delta_{1/2}$ = 13 Hz), 8.84 ($\Delta_{1/2}$ = 11Hz), 3.04 ($\Delta_{1/2}$ = 67 Hz), 0. 29 ($\Delta_{1/2}$ = 3 Hz), 0.12 ($\Delta_{1/2}$ = 33 Hz), 0.04 ($\Delta_{1/2}$ = 4 Hz).

Synthesis of {[(S,S)-Ph-BPE]cobalt(μ-Br)}$_2$ (19)

Method A, in situ generation of the precursor Co(II) complex: In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, anhydrous $CoBr_2$ (44 mg, 0.2 mmol, 1 equiv.) and dry freshly distilled THF (2 mL). The resulting mixture was stirred until all the $CoBr_2$ dissolved to afford a homogenous solution. In another vial, the ligand, (*S,S*)-Ph-BPE(106 mg, 0.21 mmol, 1.05 equiv.) was dissolved in dry distilled THF (3 mL) and added slowly to a stirring solution of the $CoBr_2$. After the addition, the resultant purple mixture was stirred for 2 h followed by the addition of 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (45.3 mg, 0.2 mmol, 1 equiv.). Upon which the color changed from purple to green. The resulting bluish green solution stirred overnight.



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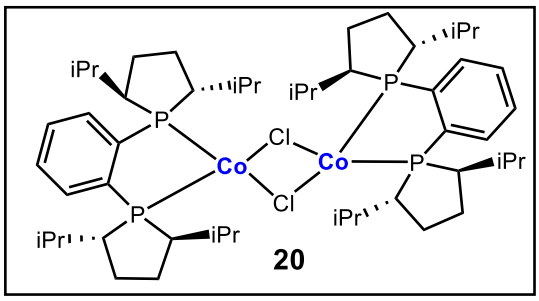
Stirring was stopped and solvent was stripped, washed with hexanes (3-4 mL), and the solid dried under high vacuum (~0.1 mm Hg) for 2 to 3 h to afford desired crude complex (132 mg, yield 94%). The crude complex thus obtained was then dissolved in minimum amount of THF and filtered inside the glovebox. To the filtrate was then diffused hexanes (by slow evaporation of hexane into a THF solution placed in an atmosphere of hexane) to afford the green crystals. The green crystal was then characterized by X-ray Crystallography (CCDC # 1966499).

Method B, Use of isolated Co(II) precursor: In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, isolated (Ph-BPE)$CoBr_2$ (15 mg, 0.021 mmol, 1 equiv.) and dry freshly distilled THF (1 mL). To the resultant solution, 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (13 mg, 0.058 mmol, 2 equiv.) was added, upon which the color changed from purple to green. The resulting bluish green solution stirred overnight. Stirring was stopped and solvent was stripped, washed with hexanes (1 mL), and the solid dried under high vacuum (~0.1 mm Hg) for 2 to 3 h to afford desired crude complex (crude yield 91%). The crude complex thus obtained was then dissolved in minimum amount of THF and filtered inside the glovebox. To the filtrate was then diffused hexanes (by slow evaporation of hexane into a THF solution placed in an atmosphere of hexane) to afford the green crystals (7.9 mg, 52% yield). Solution state effective magnetic moment μ_{eff} (301 K) = 3.85 B.M.

^{1}H NMR (600 MHz, C_6D_6): δ 67.86($\Delta_{1/2}$ = 33 Hz), 51.61($\Delta_{1/2}$ = 6 Hz), 10.83($\Delta_{1/2}$ = 107 Hz), 8.99 ($\Delta_{1/2}$ = 4 Hz), 7.35 ($\Delta_{1/2}$ = 22 Hz), 7.25($\Delta_{1/2}$ = 36 Hz), 7.10 ($\Delta_{1/2}$ = 36 Hz), 7.00 ($\Delta_{1/2}$ = 47 Hz), 6.91 ($\Delta_{1/2}$ = 49Hz), 4.71 ($\Delta_{1/2}$ = 113Hz), 4.45 ($\Delta_{1/2}$ = 6 Hz), 3.67 ($\Delta_{1/2}$ = 33Hz), 3.57 ($\Delta_{1/2}$ = 24 Hz), 3.33 ($\Delta_{1/2}$ = 24 Hz), 3.32 ($\Delta_{1/2}$ = 7 Hz), 3.23 ($\Delta_{1/2}$ = 58 Hz), 3.00 ($\Delta_{1/2}$ = 13 Hz), 2.99 ($\Delta_{1/2}$ = 9 Hz), 2.98 ($\Delta_{1/2}$ = 22Hz), 2.69 ($\Delta_{1/2}$ = 49 Hz), 2.10 ($\Delta_{1/2}$ = 60Hz), 1.90 ($\Delta_{1/2}$ = 67Hz), 1.76 ($\Delta_{1/2}$ = 44 Hz), 1.66 ($\Delta_{1/2}$ = 7 Hz), 1.65 ($\Delta_{1/2}$ = 9 Hz), 1.64 ($\Delta_{1/2}$ = 7 Hz), 1.54 ($\Delta_{1/2}$ = 82 Hz), 1.42 ($\Delta_{1/2}$ = 29 Hz), 1.26 ($\Delta_{1/2}$ = 7 Hz).

Synthesis of {[(*R,R*)-^{i}Pr-DuPhos]cobalt(μ-Cl)}$_2$ (20)[4]



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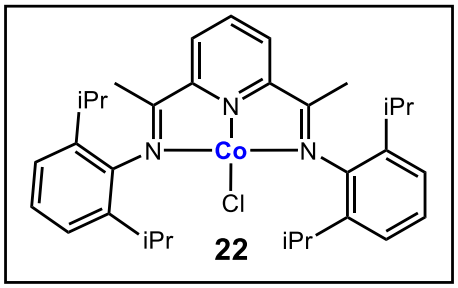
In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, anhydrous $CoCl_2$ (75 mg, 0.58 mmol, 1 equiv.) and dry freshly distilled THF (5 mL). The resulting mixture was stirred until all the $CoCl_2$ dissolved to afford a homogenous solution. In another vial, the ligand, ^{i}Pr-DuPhos (250 mg, 0.58 mmol, 1.0 equiv.) was dissolved in dry distilled THF (3 mL) and added slowly to a stirring solution of the $CoCl_2$. After the addition, the resultant green mixture was stirred for 2 h followed by the addition of 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (131 mg, 0.58 mmol, 1 equiv.), upon which the color changed from green to brownish orange. The resulting brown orange solution stirred overnight. Stirring was stopped, solvent was stripped, and the solid dried under high vacuum (~0.1 mm Hg) for 2 to 3 h to afford desired crude complex (280 mg, 94% yield). The crude complex thus obtained was then dissolved in minimum amount of diethyl ether and filtered inside the glovebox. The filtrate was kept at -25 ^{o}C overnight to afford the brown crystals (256 mg, 86% yield). The brown crystal was then characterized by X-ray Crystallography. Solution state effective magnetic moment μ_{eff} (301 K) = 3.93 B.M. This crystal structure has been reported in the literature by Chirik et al.[4]

^{1}H NMR (600 MHz, C_6D_6): δ 66.30 ($\Delta_{1/2}$ = 38 Hz), 57.24($\Delta_{1/2}$ = 51 Hz), 14.10 ($\Delta_{1/2}$ = 18 Hz), 9.19($\Delta_{1/2}$ = 24 Hz), 9.06($\Delta_{1/2}$ = 9 Hz), 2.35($\Delta_{1/2}$ = 31 Hz),, 1.02($\Delta_{1/2}$ = 25 Hz), 0.90($\Delta_{1/2}$ = 11 Hz), 0.73 ($\Delta_{1/2}$ = 18Hz), 0.72 ($\Delta_{1/2}$ = 35 Hz), 0.59 ($\Delta_{1/2}$ = 53 Hz), -1.04 ($\Delta_{1/2}$ = 44 Hz), -1.53($\Delta_{1/2}$ = 25 Hz),, -2.69 ($\Delta_{1/2}$ = 45 Hz),-3.96 ($\Delta_{1/2}$ = 45Hz)

NMR matches with the complex reported by Chirik et al.[4]

Synthesis of [bis(N-aryliminoethyl-κN,N')pyridine-κN]CoCl (22)



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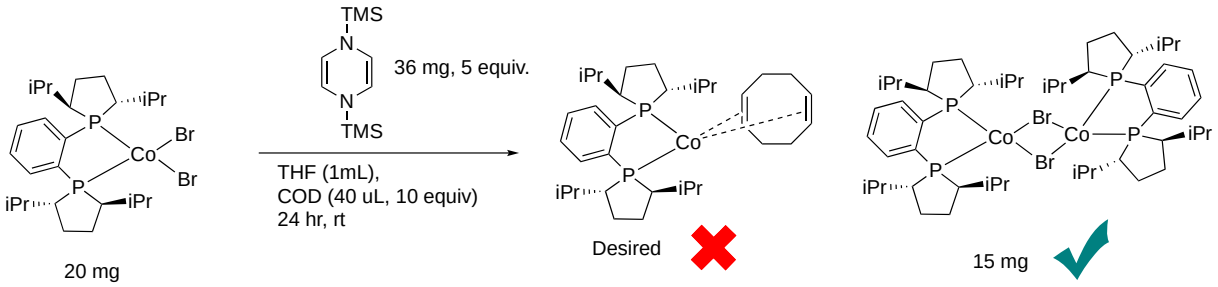
In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, isolated *Bis*(imino)pyridylCoCl$_2$ (150 mg, 0.24 mmol, 1 equiv.) and dry freshly distilled THF (3 mL). To the resultant yellow solution, 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine (30 mg, 0.132 mmol, 0.55 equiv) was added. Upon which the color changed from yellow to purple. The resulting purple solution stirred for 3 hr. Stirring was stopped and solvent was stripped, washed with hexanes (1-2 mL), and the solid dried under high vacuum (~0.1 mm Hg) for 2 to 3 h to afford desired crude complex (133 mg, 94% yield). The crude complex thus obtained was then dissolved in minimum amount of THF and filtered inside the glovebox. To the filtrate was then diffused hexanes (by slow evaporation of hexane into a THF solution placed in an atmosphere of hexane) and kept at -25 ^{o}C overnight to afford the purple crystals (115 mg, 81% yield). The purple crystal was then characterized by X-ray Crystallography (CCDC # 1966500).

^{1}H NMR (600 MHz, C_6D_6): δ 9.56 ($\Delta_{1/2}$ = 27 Hz), 8.49 ($\Delta_{1/2}$ = 33 Hz), 8.43 ($\Delta_{1/2}$ = 49 Hz), 7.44($\Delta_{1/2}$ = 25 Hz), 7.30 ($\Delta_{1/2}$ = 22 Hz), 7.15($\Delta_{1/2}$ = 13 Hz), 6.93($\Delta_{1/2}$ = 20 Hz), 3.56($\Delta_{1/2}$ = 25Hz), 3.35($\Delta_{1/2}$ = 29 Hz), 2.91($\Delta_{1/2}$ = 34Hz), 2.27 ($\Delta_{1/2}$ = 49 Hz), 1.41 ($\Delta_{1/2}$ = 24 Hz), 1.19 ($\Delta_{1/2}$ = 20 Hz), 1.08 ($\Delta_{1/2}$ = 20 Hz), 0.88 ($\Delta_{1/2}$ = 29 Hz), 0.84 ($\Delta_{1/2}$ = 20 Hz), 0.07 ($\Delta_{1/2}$ = 11 Hz), -1.18 ($\Delta_{1/2}$ = 44 Hz), -8.93 ($\Delta_{1/2}$ = 36 Hz), -17.83 ($\Delta_{1/2}$ = 7 Hz), -18.37 ($\Delta_{1/2}$ = 34 Hz).

^{13}C NMR (150 MHz, CD_2Cl_2): δ 167.86, 152.56, 150.63, 140.82, 126.39, 125.82, 123.32, 115.69, 28.65, 23.54, 23.09, 21.36.

NMR matches with the complex reported by Gal et al.[5]

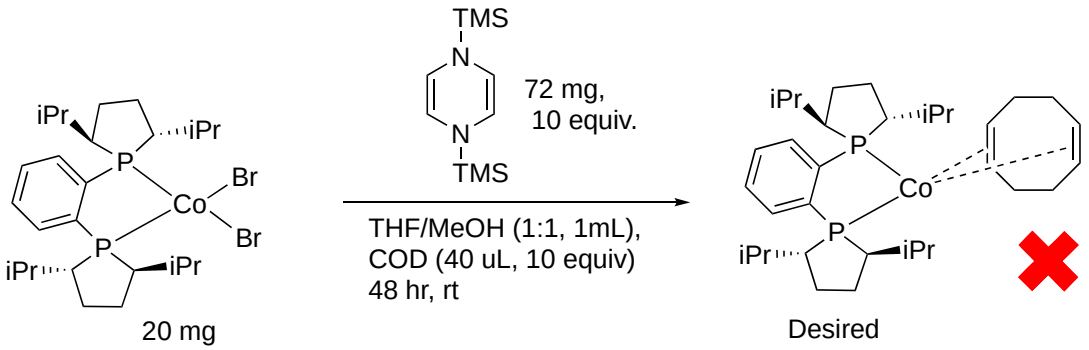
Attempts towards the synthesis of Co(0)-Complexes



In the N_2-filled glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, isolated (*R*)-iPr-DuPhosCoBr$_2$ (20 mg, 0.031 mmol, 1 equiv.) and 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine, **11a** (36 mg, 0.16 mmol, 5 equiv.) and dry freshly distilled THF (1 mL). Upon letting it stir for ca. 2 min, 1,5-cyclooctadiene (COD) (40 μL, 0.31 mmol, 10 equiv.) was added to the resulting solution via micro-syringe. The resulting brown solution stirred for 24 hr. Stirring was stopped, solvent was stripped, and the solid dried under high vacuum (~0.1 mm Hg) for 5 to 6 h to afford desired crude complex (15 mg, 86% yield). The ^{1}H-NMR recorded for crude solid in C_6D_6 and it did not show any peaks corresponding to ^{1}H-NMR spectrum of previously reported [(*R*)-iPr-DuPhosCo$^{(0)}$(COD)] complex by Chirik et al.[4] It showed the peaks analogues to [(*R*)-iPr-DuPhosCo$^{(I)}$(μCl)]$_2$ which suggests that there is only formation of [(*R*)-iPr-DuPhosCo$^{(I)}$(Br)]$_2$.

^{1}H NMR (600 MHz, C_6D_6): δ 63.41 ($\Delta_{1/2}$ = 107 Hz), 52.74($\Delta_{1/2}$ = 164 Hz), 14.04 ($\Delta_{1/2}$ = 27 Hz), 9.13 ($\Delta_{1/2}$ = 7 Hz), 8.74 ($\Delta_{1/2}$ = 27 Hz), 2.51 ($\Delta_{1/2}$ = 38 Hz), 1.40 ($\Delta_{1/2}$ = 23 Hz), 1.04 ($\Delta_{1/2}$ = 11 Hz), 0.88 ($\Delta_{1/2}$ = 0 Hz), -0.99 ($\Delta_{1/2}$ = 61 Hz), -1.38 ($\Delta_{1/2}$ = 38 Hz), -2.18 ($\Delta_{1/2}$ = 65 Hz), -4.24 ($\Delta_{1/2}$ = 137 Hz).

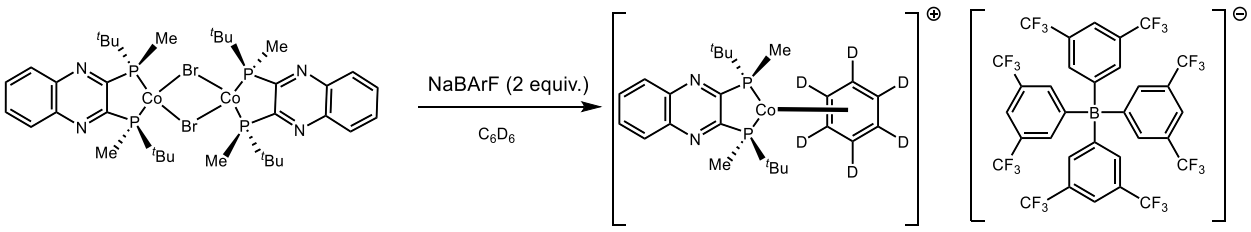
Using THF/MeOH solvent:



In the glovebox, a 20 mL scintillation vial was charged with a magnetic stir bar, isolated (R)-iPr-DuPhosCoBr$_2$ (20 mg, 0.031 mmol, 1 equiv.) and 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine, **11a** (72 mg, 0.31 mmol, 10 equiv.), dry freshly distilled THF (0.5 mL) and anhydrous MeOH (0.5 mL). Upon letting it stir for ca. 2 min, 1,5-cyclooctadiene (40 μL, 0.31 mmol, 10 equiv.) was added to the resulting solution via micro-syringe. The resulting brown solution stirred for 48 hr. Stirring was stopped, solvent was stripped, and the solid dried under high vacuum (~0.1 mm Hg) for 5 to 6 h to afford desired crude complex (32 mg). The crude solid remains insoluble in C_6D_6 as well as THF-D_8. ^{1}H-NMR recorded for crude solid in C_6D_6 and THF-D_8 only showed peak correspond to free ligand [(*R*)-iPr-DuPhos]. ^{31}P also showed peak corresponding to free ligand.

Preparation of Cationic Cobalt(I) Complexes

{[(*R,R*)-QuinoxP]cobalt(η^6 -C_6D_6)}$^+$ [BARF]$^-$ (23)



In N_2-filled glovebox, 20 mL scintillation vial was charged with a magnetic stir bar, {[(*R,R*)-QuinoxP*]cobalt(μ-Br)}$_2$ **18** (25 mg, 0.026 mmol, 1 equiv.), NaBARF(49 mg, 0.055 mmol, 2.1 equiv.), and 2 mL of C_6D_6. The color changed from green to purple. The resulting purple solution was stirred for 3 h at room temperature inside the glovebox. Upon letting it sit for 5 minutes, C_6D_6 was decanted. The crude complex then washed with 3 mL of hexanes and residual solvents were stripped down to obtain purple solid **23** (55 mg, 78% yield). The saturated solution of **23** in C_6D_6 leads to solid purple crystal at room temperature which was then characterized by X-ray crystallography (CCDC # 2016105)**.**

^{1}H NMR (600 MHz, C_6D_6): δ 11.45 (4H), 8.82 (2H), 8.34 (8H), 8.04 (2H), 7.84 (1H), 7.64 (4H), 7.58 (1H), 7.29 (1H), 7.03 (1H), 6.41 (1H), 5.63 (1H), 5.51 (3H), 3.57 (2H), 3.46(1H), 3.27 (2H), 3.07 (6H), 1.35 (12H), 1.21(4H), 0.89 (6H), 0.77 (1H), 0.56 (1H), 0.41 (9H), 0.29 (5H), 0.12 (7H), 0.03 (7H) ; **^{13}C NMR (150 MHz, C_6D_6):** δ 162.56 (q, $^1J_{B\text{-}C}$ = 49.6 Hz), 135.42, 133.04, 129.84, 129.78, 126.14, 124.33, 118.08, 34.98, 26.94, 26.39, 25.64; **^{31}P NMR (243 MHz, C_6D_6):** δ 58.19; **^{19}F NMR (565 MHz, C_6D_6):** δ -62.05.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 14.87 (bs, 2H), 8.21 (q, *J* = 3.3 Hz, 1H), 7.95 (q, *J*= 3.3 Hz, 1H), 7.69 (bs, 8H), 7.54 (bs, 4H), 4.20-3.40 (m, 9H), 1.95 (virtual coupling, t, J = 5.1 Hz, 6H), 1.00 (t, *J* = 7.4 Hz, 9H) ; **^{13}C NMR (150 MHz, CD_2Cl_2):** δ 162.12 (q, $^1J_{B\text{-}C}$ = 49.8 Hz), 155.28, 135.20, 133.26, 130.40, 129.25, (q, $^2J_{C\text{-}F}$ = 29.5 Hz), 124.99 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 117.87, 37.55, 27.89, 27.24, 12.47; **^{31}P NMR (243 MHz, C_6D_6):** δ 58.24.

Synthesis, isolation, and spectral properties of {[(*R,R*)-^{i}Pr-DuPhos]cobalt- η^4 -(2,3-dimethylbutadiene))}$^+$ [BARF]$^-$ (**25**) has been recently reported by our group.[6]

UV-Vis Spectroscopy of the Co(II) and Co(I) complexes

A background of THF was taken. All the samples were made inside the N_2-filled glovebox with appropriate concentration in THF and transferred to modified cuvette that allowed the preservation of air sensitive materials. The cuvette was placed in the in-situ UV- VIS and a wavelength scan was performed from 1100 nm to 190 nm.

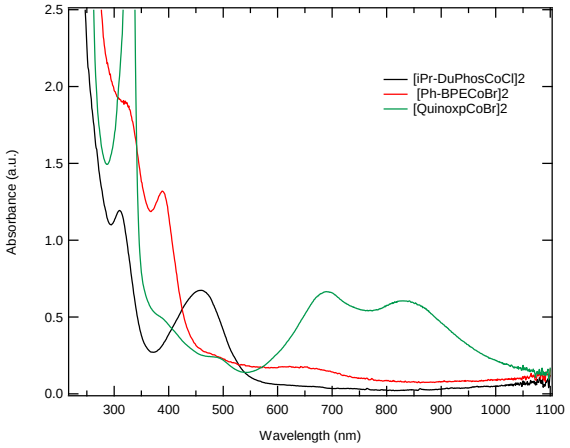
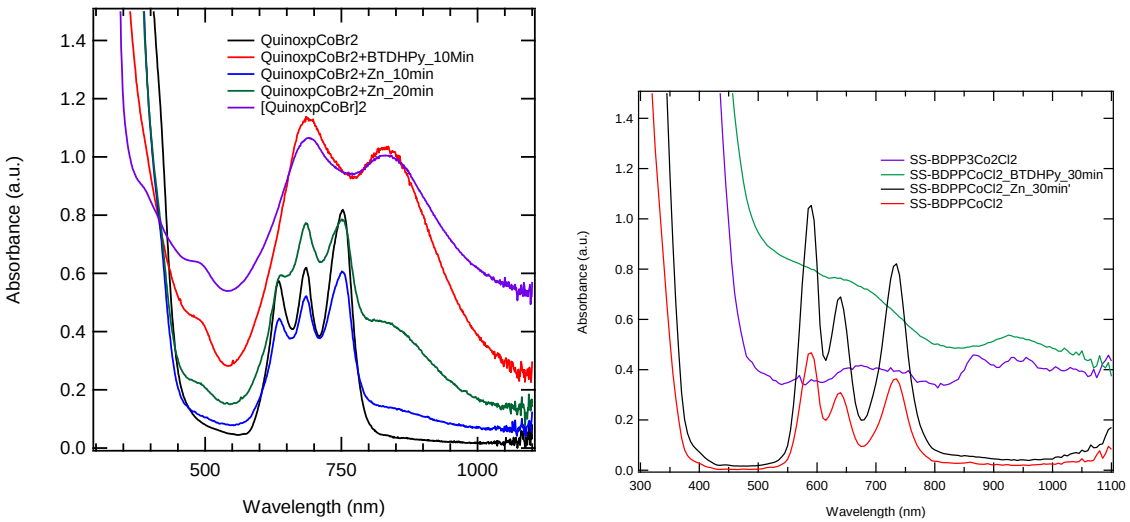


Figure S1. UV-Vis Spectra of 18, 19, and 20; Each of them showing two characteristic peaks in visible region (which are the characteristic for d^8 system).



a) b)

Figure S2. UV-Vis Spectra for relative rate of reduction; This study clearly shows that 11a is much better reductant as compared to Zn.

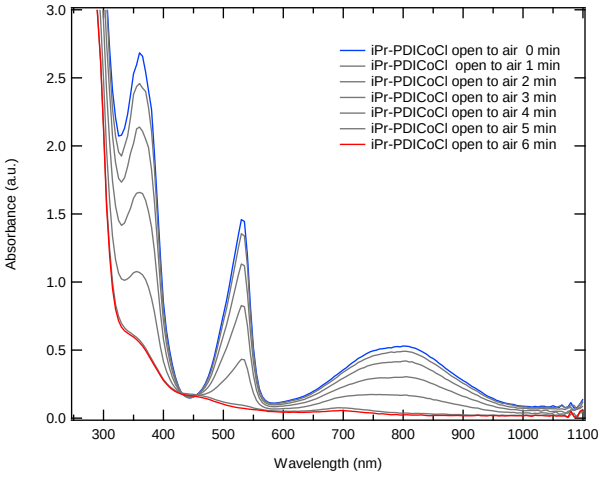


Figure S3. Sensitivity of the Co(I) complexes to oxidation. UV-Vis spectra of **22** while expose to air

Table S1. Effect of counter ion on the rate of heterodimerization: ZnBr2 vs NaBArF

	0 min (% conversion)	5 min (% conversion)	15 min (% conversion)	25 min (% conversion)
$ZnBr_2$ (average)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	5.3 ± 3.1
NaBArF (average)	0.0 ± 0.0	38.0 ± 7.3	70.0 ± 4.3	89.3 ± 3.3
$ZnBr_2$ (trial 1)	0.0	0.0	0.0	1.0
$ZnBr_2$ (trial 2)	0.0	0.0	0.0	7.0
$ZnBr_2$ (trial 3)	0.0	0.0	0.0	8.0
NaBArF (trial 1)	0.0	48.0	68.0	90.0
NaBArF (trial 2)	0.0	31.0	66.0	85.0
NaBArF (trial 3)	0.0	35.0	76.0	93.0

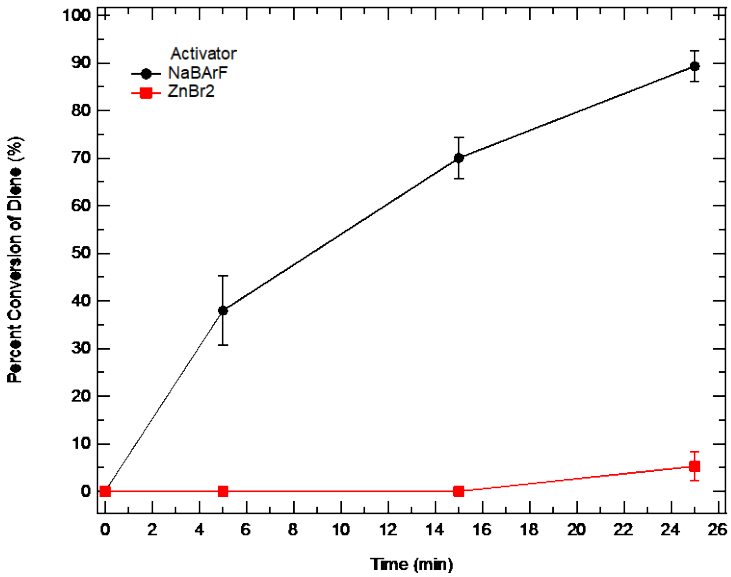


Figure S4. Graph showing effect of counter ion on heterodimerization

Adapted from Gray, M. et al. Mechanism of Cobalt-Catalyzed Heterodimerization of Acrylates and 1,3-Dienes. A Potential Role of Cationic Cobalt(I) Intermediates. ACS Catal. 10, 4337-4348 (2020).

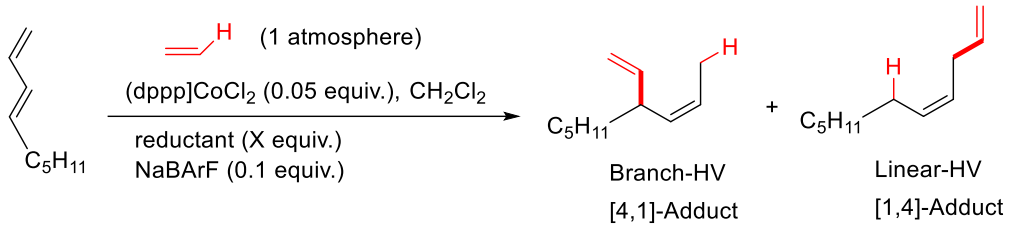
General procedures for catalytic reactions

Procedure A1. Typical procedure for checking the viability of reducing agents via hydrovinylation of linear diene [(*E*)-1,3-nonadiene].[7,8] (For Table 2 in the paper and Table S2)

In N_2 filled glovebox, a 25-mL Schenk flask was charged with a magnetic stir bar, [Co(dppp)Cl_2] (5.5 mg, 0.01 mmol, 0.05 equiv.), reductant (X equiv., as mentioned the in table S1) and NaBARF (18 mg, 0.02 mmol, 0.1equiv.). The flask was capped with rubber septum and taken outside of the box. It was then connected to a Schlenk line with argon and subjected to vacuum then refill (3 cycles). Freshly distilled methylene chloride (0.2M) was added via septum and the mixture stirred for 10 minutes. The flow control stopcock was closed, and an ethylene balloon inserted using a needle via the septum. A 50-mL syringe was used to evacuate the flask (3 x 25 mL) to remove residual argon. At the room temperature, (*E*)-1,3-nonadiene (25 mg, 0.2 mmol, 1 equiv.) was added neat via a microliter syringe. Progress of the reaction was monitored via GC-FID by taking an aliquot using a syringe and long needle, diluted with pentanes or hexanes and filtered through a shot pad of silica in a glass pipette. Upon completion of reaction, it was further concentrated on a rotary evaporator to afford crude product. The crude hydrovinylation product was subjected to column chromatography using pentane to obtain the product as a clear oil.

GC (methyl silicone, 80 ^{o}C, 3 min, 20 ^{o}C/min → 250 ^{o}C): Rt major [4,1-adduct, branch], 3.1 min (80%); minor [1,4-adduct, linear], 3.8 min (20%)

Table S2: Optimization of unconventional reducing agents via Co(I)-catalyzed hydrovinylation of diene[a]



Entry	Reductant (equiv)	Time (min)	Conversion (%)[b]	[4,1]:[1,4]
1	Zn (0.5)	30	100	78:22
2	**11a** (0.05)	75	100	79:20
3	**11b** (0.05)	45	100	80:20
4	**11c (**0.5)	24x60	4	-
5	Li_3N (0.10)	90	100	80:20

[a] **Procedure A1** was followed with some modification in reducing agent as mentioned.

[b] Conversion is based on GC analysis.

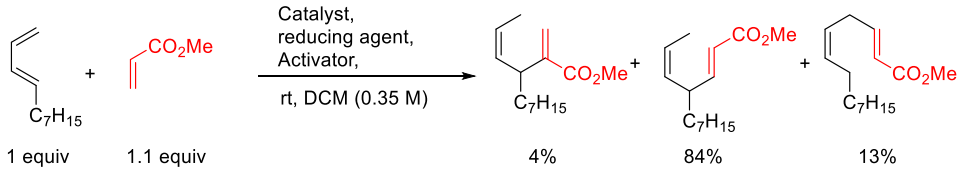
Procedure A2. Typical procedure for using lithium nitride as a reductant for Co(II) in heterodimerization of 1,3-diene and methyl acrylate.

In the N_2-filled glovebox, an 8-mL oven dried vial with a septum cap was charged with magnetic stir bar, isolated metal complex (0.05 equiv.), reducing agent (0.10 - 0.25 equiv.), activator (0.10 – 0.30 equiv.) and DCM (0.35 M). The vial was capped and while stirring the mixture, neat (E)-1,3-undecadiene (1.00 equiv.) followed by distilled methyl acrylate (1.10 equiv.) was added via micro-liter syringe. The resulting green solution was allowed to stir at room temperature and monitored via GC-FID by taking an aliquot with a glass pipette, removing from dry box atmosphere, adding 1:1 diethyl ether/hexanes, filtering through a short pad of silica in a glass pipette, and eluting with diethyl ether. Upon completion of the reaction, the mixture is diluted with 1:1 diethyl ether/hexane, filtered over a short pad of silica using a fritted glass funnel (I.D = 1 inch, height of silica pad ~1.5 inch), and concentrated.

For Table S2, entry 2

In the N_2-filled glovebox, an 8-mL oven dried vial with a septum cap was charged with magnetic stir bar, dpppCoCl$_2$ (0.05 eq.), Li_3N (1.14 mg, 0.03 mmol), $InBr_3$ (13 mg, 0.03 mmol) DCM (0.94 mL), (E)-1,3-undecadiene (50 mg, 0.3 mmol), and distilled methyl acrylate (31 mg, 0.36 mmol). Upon completion of the reaction (2 h), the mixture is exposed to air and diluted with 1:1 diethyl ether/hexane, filtered over a short pad of silica using a fritted glass funnel, and concentrated to afford the title compound (61mg, 79% yield) as a colorless oil.

Table S3: Optimization of reaction conditions for heterodimerization of diene and methyl acrylate: Li_3N as a reducing agent [a]



Entry	Catalyst	Reductant (0.10 equiv.)	Activator (0.10 equiv.)	Conv.[b] (%), time (h)	Isolated Yield (%)
1	dpppCoBr$_2$	Li_3N (0.25 eq.)	$InBr_3$	100, 7	65
2	**dpppCoBr$_2$**	**Li_3N**	**$InBr_3$**	**100, 2**	**79**
3	dpppCoBr$_2$	Li_3N	NaBARF	100, 2	52
4	dpppCoBr$_2$	Li_3N (0.25 eq.)	$InCl_3$ (0.30 eq.)	100, 2	83
5	**dpppCoCl$_2$**	**Li_3N**	**$InBr_3$**	**98, 0.25**	**91**
6	dpppCoCl$_2$	Li_3N	NaBARF	100, 24	70
7[c]	dpppCoCl$_2$	Li_3N	$InCl_3$	14, 12	-
8[d]	**(*S,S*)-BDPP)CoBr$_2$**	**Li_3N**	**$InBr_3$**	**100, 3**	**84 (99% ee)**

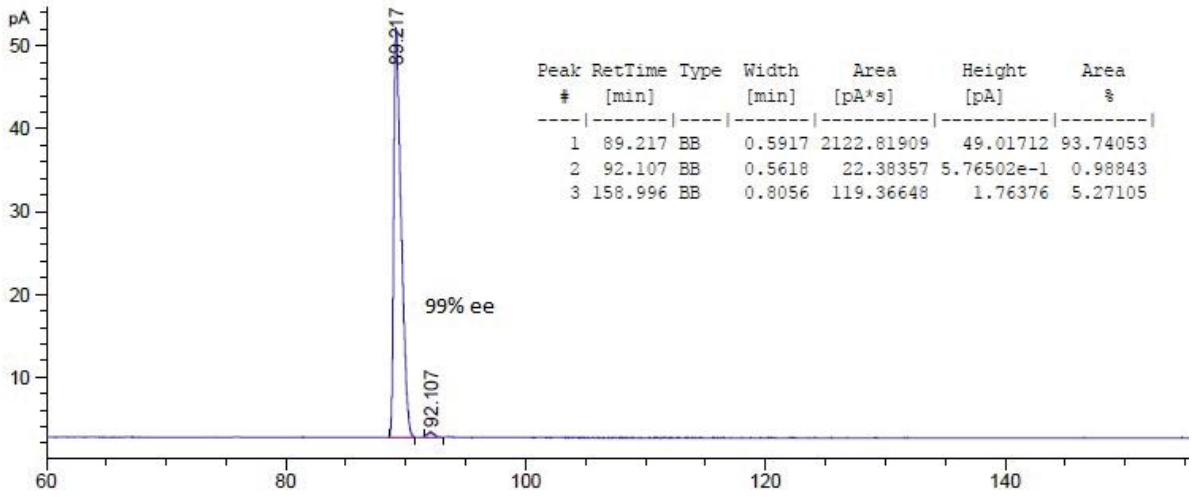
[a] **Procedure A2** followed with some modification in activators and reducing agent as mentioned. [b]Conversion is based on GC analysis. [c]0.5M DCM is used. [d](*S,S*)-BDPPCoBr$_2$ was synthesized in-situ as mentioned in the **procedure A3**.

Procedure A3. Typical procedure for in situ generation of metal complex for heterodimerization. (Table S3, Entry 8)

In N_2-filled glovebox, an 8 mL oven dried vial equipped with a septum cap was charged with a magnetic stir bar, (*S,S*)-BDPP (0.05 eq.), $CoBr_2$ (0.05 eq.) and DCM (0.35 M) and

allowed to stir for 15 min. Reducing agent (0.10 eq.) was then added and the solution was allowed to stir for another 15 minutes. $InBr_3$ (0.10 eq.), 1,3-(*E*)-undecadiene (50 mg, 0.3 mmol, 1.00 eq.), and distilled methyl acrylate (31 mg, 0.36 mmol, 1.10 eq.) were then added via micro-liter syringe. The mixture was stirred at room temperature and monitored by taking an aliquot using a glass pipette, diluting with mixture of diethyl ether/hexane (1:1) and filtered through a short pad of silica in a glass pipette eluting with diethyl ether and analyzed via GC. Upon completion of the reaction (0.25 h), the mixture is exposed to air and diluted with 1:1 diethyl ether/hexane, filtered over a short pad of silica using a fritted glass funnel (I.D = 1 inch, height of silica pad ~1.5 inch), and concentrated to afford the title compound as a colorless oil.

The product derived from in-situ generated catalyst [(S,S)-BDPP/$CoBr_2$/Li_3N/$InBr_3$] showed 99% ee. (See attached CSP-GC chromatogram below)



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	89.217	BB	0.5917	2122.81909	49.01712	93.74053
2	92.107	BB	0.5618	22.38357	5.76502e-1	0.98843
3	158.996	BB	0.8056	119.36648	1.76376	5.27105

Procedure A4. Typical procedure for heterodimerization of linear diene with methyl acrylate. (For Table 3, entry 3 in paper).

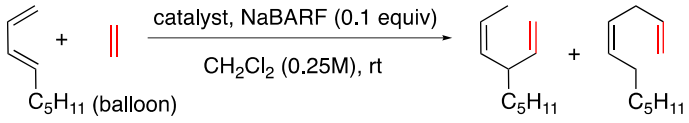
In N_2 filled glovebox, an 8-mL vial equipped with a septum screw cap was charged with a magnetic stir bar, (QuinoxP*)$CoBr_2$ (5 mol%), Zn (100 mol%) , NaBARF (10 mol%) and DCM (0.8 mL). The vial was capped and while stirring the mixture, (*E*)-1,3-nonadiene (25 mg, 0.2 mmol, 1 equiv.) was added neat using microliter syringe via the septum, followed by methyl

acrylate (19 mg, 0.22 mmol, 1.1 equiv.). The mixture was stirred at rt and monitored by taking an aliquot using a glass pipette, diluting with a mixture of *n*-pentane/Et_2O (1: 1) and filtered through a pad of silica in a glass pipette eluting with diethyl ether and analyzed via GC-FID. Upon completion of the reaction, the vial was taken out of the box and the reaction mixture worked-up and crude product was isolated via column chromatography.

For Table 3, entry 4 in paper, **Procedure C1** followed with some modification in reductant; **11a** (5 mol%) was used instead of Zn (100 mol%).

B1. Typical procedure for hydrovinylation of linear diene using isolated Co(I) complex 12.[7,8]

Hydrovinylation of 1,3-diene



entry	catalyst	time (min)	conver. (%)	% yield (% *rr*[+])
1.	(dppp)$CoCl_2$ (0.05 equiv) Zn (1 equiv.) (in situ)	30	100	95 (78:22)
2.	(dppp)$_3Co_2Cl_2$* (**12**, 0.02 equiv)	15	100	97 (77:23)

*isolated Co(I) complex. [+]*rr* regioisomeric ratio.

Figure S4: Hydrovinylation of linear diene using isolated Co(I) complex 12

In N_2 filled glovebox, a 25-mL Schlenk flask was charged with a magnetic stir bar, [Co_2(dppp)$_3Cl_2$] **(12)** (0.004 mmol, 0.02 equiv.), and NaBARF (0.008 mmol, 0.04equiv.). The flask was capped with rubber septum and taken outside of the box. It was then connected to a Schlenk line with argon and subjected to vacuum then refill (3 cycles). Freshly distilled methylene chloride (DCM) (0.25 M) was added via septum and the mixture stirred for a few minutes. The flow control stopcock was closed, and an ethylene balloon inserted using a

needle via the septum. A 50-mL syringe was used to evacuate the flask (3 x 25 mL) to remove residual argon. At the room temperature, (*E*)-1,3-nonadiene (25 mg, 0.2 mmol) was added neat via a microliter syringe. Progress of the reaction was monitored via GC-FID by taking an aliquot using a syringe and long needle, diluted with pentanes or hexanes, and filtered through a shot pad of silica in a glass pipette. Upon completion of reaction, it was further concentrated on a rotary evaporator to afford crude product. The crude hydrovinylation product was subjected to column chromatography using pentane to obtain the product as a clear oil.

GC (methyl silicone, 80 ^{o}C, 3 min, 20 ^{o}C/min → 250 ^{o}C): Rt major [4,1-adduct/branch], 3.1 min (80%); minor [1,4-adduct, linear], 3.8 min (20%)

For entry 1, i.e., in situ generation of the Co(I) complex, [$Co_2(dppp)_3Cl_2$] (**12**) was replaced by Co(dppp)Cl_2 (0.01 mmol, 0.05 equiv.), Zn (0.2 mmol, 1 equiv.).

Procedure B2. Use of isolated Co(I) complex (18) for heterodimerization of linear diene with methyl acrylate. (For Table 3, entry 2 in paper)

In N_2 filled glovebox, an 8-mL vial equipped with a septum screw cap was charged with a magnetic stir bar, Isolated {[(*R,R*)-QuinoxP*]cobalt(μ-Br)}$_2$ (**18**) (3.8 mg, 0.02 equiv.) , NaBARF (0.05 equiv., 8.9 mg) and DCM (0.8 mL). The vial was capped and while stirring the mixture, (*E*)-1,3-nonadiene (25 mg, 0.2 mmol, 1 equiv.) was added neat using microliter syringe via the septum, followed by methyl acrylate (19 mg, 0.22 mmol, 1.1 equiv.). The mixture was stirred at rt and monitored by taking an aliquot using a glass pipette, diluting with a mixture of *n*-pentane/Et_2O (1: 1) and filtered through a pad of silica in a glass pipette eluting with diethyl ether and analyzed via GC-FID. Upon completion of the reaction, the vial was taken out of the box and the reaction mixture worked-up and crude product was isolated via column chromatography.

Procedure B3. Use of isolated {[(R,R)-QuinoxP]Co(I)(η^6-C_6D_6)}+[BARF]-(23) for heterodimerization of linear diene with methyl acrylate. (For Table 3, entry 1 in paper)

In N_2 filled glovebox, an 8-mL vial equipped with a septum screw cap was charged with a magnetic stir bar, Isolated {[(*R,R*)-QuinoxP*]cobalt(η^6 -C_6D_6)}$^+$ [BARF]$^-$ (**23**) (0.01 equiv.,) and DCM (0.8 mL). The vial was capped and while stirring the mixture, (*E*)-1,3-nonadiene (25 mg, 0.2 mmol, 1 equiv.) was added neat using microliter syringe via the septum, followed by methyl acrylate (19 mg, 0.22 mmol, 1.1 equiv.). The mixture was stirred at rt and monitored by taking an aliquot using a glass pipette, diluting with a mixture of *n*-pentane/Et_2O (1: 1) and filtered through a pad of silica in a glass pipette eluting with diethyl ether and analyzed via GC-FID. Upon completion of the reaction, the vial was taken out of the box and the reaction mixture worked-up and crude product was isolated via column chromatography.

NMR data of compound 25 matched with the previously reported compound.[8]

GC (methyl silicone, 80 ^{o}C, 3 min, 20 ^{o}C/min → 250 ^{o}C): Rt major [4,1-adduct/branch], 7.24 min (>95%)

CSP-GC (cyclosil B, 125 °C, 60 min, 5^{o}C→ 175 ^{o}C)**:** Rt from dpppCoBr_2/Zn/NaBARF; [1,4 -adduct] 28.8 min (49.7%), 29.8 min (50.3%).

The product derived from (QuinoxP*)$CoBr_2$ / Zn/NaBARF; 28.8 min (96.8%), 29.8 min (3.2%); **93%ee**.

The product derived from (QuinoxP*)$CoBr_2$/**11a**/NaBARF; 28.7 min (96.6%), 29.7 min (3.4%); **93% ee.**

The product derived from Isolated {[(*R,R*)-QuinoxP*]cobalt(μ-Br)}$_2$ (**18**)/ NaBARF; 28.7 min (96.2%), 29.7 min (3.8%); **92% ee.**

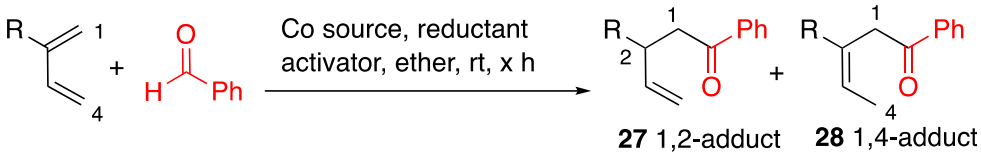
The product derived from Isolated {[(*R,R*)-QuinoxP*]cobalt(η^6 -C_6D_6)}$^+$ [BARF]$^-$ (**23**) in DCM; 28.7 min (97%), 29.7 min (3%); **94% ee.**

The product derived from Isolated {[(*R,R*)-QuinoxP*]cobalt(η^6 -C_6D_6)}$^+$ [BARF]$^-$ (**23**) in Benzene-D_6; 28.7 min (98%), 29.7 min (2%); **96% ee.**

Procedure C. Use of isolated {[(R,R)-iPr-DuPhos]Co(I)- η^4 -(2,3-dimethylbutadiene))}+ [BARF]– (25) for hydroacylation of isoprene/2-siloxy 1,3-diene (for Table 4, entry 1).

In N_2 filled glovebox, an 8-mL vial equipped with a septum screw cap was charged with a magnetic stir bar, Isolated {[(*R,R*)-^{i}Pr-DuPhos]cobalt- η^4 -(2,3-dimethylbutadiene))}$^+$ [BARF]$^-$ (**30**) (0.01 equiv.) and diethyl diethyl ether (0.8 mL). The vial was capped and while stirring the mixture, Benzaldehyde (0.2 mmol, 1.0 equiv.) was added neat using microliter syringe via the septum, followed by isoprene (0.6 mmol, 3 equiv.). The mixture was stirred at rt and monitored by taking an aliquot using a glass pipette, diluting with diethyl ether, and filtering through a pad of silica in a glass pipette eluting with diethyl ether. The mixture was analyzed via GC-FID. Upon completion of the reaction the vial was taken out of the box, exposed to air, and quenched with diethyl ether (5 mL) and the resulting mixture was filtered over a short pad of silica (using a fritted glass funnel, I.D = 1 inch, height of silica pad ~1.5 inch) eluting diethyl ether. It was further concentrated on a rotary evaporator to afford crude product. The crude hydroacylation product was subjected to column chromatography using 5% ethyl acetate-hexanes to obtain the desired products as a clear oil. NMR and CSP-GC data matched with previously reported compounds by our group.[6]

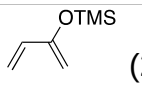
Table S4 . Activator-free, single-component (entries 1 and 5) and in situ generated [Co^{I}]$^{+}$-catalysts for hydroacylation of isoprene and 2-trimethylsilyloxy-1,3-butadiene[a]



27 1,2-adduct **28** 1,4-adduct

26a R = Me isoprene
26b R = OTMS. 2-trimethylsilyloxy-1,3-butadiene

a R = Me
b R = OTMS

no.	Co^{I}-source (equiv.)	reductant (equiv.)	activator (equiv.)	1,2:1,4 adduct	time (h)	Conversion, (% ee)[c]
				(isoprene)		
1.[b]	{[(*R,R*)-*i*-Pr-DUPHOS] Co^{I}[2,3-DMBD]}$^{+}$ [BARF]$^{-}$ (**25**, 0.01)	0	0	60:40	40	60 (96, *R*)
2.	**{**[(*R,R*)-*i*-Pr-DUPHOS] Co^{I}Cl}$_2$ (**20**, 0.025)	0	NaBARF (0.075)	60:40	24	100 (96, *R*)
3.	**{**[(*R,R*)-*i*-Pr-DUPHOS] Co^{I}Cl}$_2$ (**20**, 0.025)	0	0	N/A	24	0 (N/A)
4.	[(*R,R*)-*i*-Pr-DUPHOS] Co^{II}Br$_2$ (0.05)	Zn (0.5)	NaBARF (0.075)	60:40	24	93 (96, *R*)
5.	[(*R,R*)-*i*-Pr-DUPHOS] Co^{II}Br$_2$ (0.05)	Zn (0.5)	0	N/A	24	0 (N/A)
				(2-trimethylsilyloxy-1,3-butadiene)		
6[b]	{[(*R,R*)-*i*-Pr-DUPHOS] Co^{I}[2,3-DMBD]}$^{+}$ [BARF]$^{-}$ (**25**, 0.05)	0	0	35:65	30	90 (98, *R*)
7.	[(*R,R*)-*i*-Pr-DUPHOS] Co^{II}Br$_2$ **20** (0.05)	Zn (0.5)	NaBARF (0.075)	35:65	30	87 (98, *R*)
8.	[(*R,R*)-*i*-Pr-DUPHOS] Co^{II}Br$_2$ **20** (0.05)	Zn (0.5)	0	N/A	30	0 (N/A)

[a] Single-component catalyst (shaded entries). DMBD: 2,3-dimethyl-1,3-butadiene [b]Conversion is based on the consumption of benzaldehyde. [c] Regioselectivities and enantioselectivities were determined by GC and CSP-GC respectively.

Procedure D1. Use of isolated {[(R,R)-iPr-DuPhos]Co(I)-η^4 -(2,3-dimethylbutadiene))}+ [BARF]– (25) for hydroboration of 2,3-dimethylbuta-1,3-diene (for Table 5, entry 1 in the paper).

In N_2 filled glovebox, an 8-mL vial equipped with a septum screw cap was charged with a magnetic stir bar, Isolated {[(*R,R*)-^{i}Pr-DuPhos]cobalt- η^4 -(2,3-dimethylbutadiene))}$^+$ [BARF]$^-$ (**25**) (0.02 equiv.) and DCM (0.8 mL). The vial was capped and while stirring the mixture, HBPin (0.22 mmol, 1.05 equiv.) was added neat using microliter syringe via the septum, followed by 2,3-dimethylbuta-1,3-diene (0.2 mmol, 1 equiv.). The mixture was stirred at rt and monitored by taking an aliquot using a glass pipette, diluting with diethyl ether, and filtering through a pad of silica in a glass pipette eluting with diethyl ether. The mixture was analyzed via GC-FID. Upon completion of the reaction the vial was taken out of the box, exposed to air and quenched with diethyl ether (5 mL) and the resulting mixture was filtered over a short pad of silica (using a fritted glass funnel, I.D = 1 inch, height of silica pad ~1.5 inch) eluting diethyl ether. It was further concentrated on a rotary evaporator to afford crude product. The crude hydroboration product was subjected to column chromatography using 5% diethyl ether-pentane to obtain the hydroboration products as a clear oil.

Procedure D2. Use of in-situ generated Co(I) complex for hydroboration of 2,3-dimethylbuta-1,3-diene (for Table 5, entry 2 in the paper)

In N_2 filled glovebox, an 8-mL vial equipped with a septum screw cap was charged with a magnetic stir bar, [(*R,R*)-^{i}Pr-DuPhosCoBr$_2$] (0.05 equiv.), Zn (0.5 equiv.), and NaBARF (0.1 equiv.) and DCM (0.8 mL). The vial was capped and while stirring the mixture, HBPin (0.22 mmol, 1.05 equiv.) was added neat using microliter syringe via the septum, followed by 2,3-dimethylbuta-1,3-diene (0.2 mmol, 1 equiv.). The mixture was stirred at rt and monitored by taking an aliquot using a glass pipette, diluting with diethyl ether, and filtering through a pad of

silica in a glass pipette eluting with diethyl ether. The mixture was analyzed via GC-FID. Upon completion of the reaction the vial was taken out of the box, exposed to air and quenched with diethyl ether (5 mL) and the resulting mixture was filtered over a short pad of silica (using a fritted glass funnel, I.D = 1 inch, height of silica pad ~1.5 inch) eluting diethyl ether. It was further concentrated on a rotary evaporator to afford crude product. The crude hydroboration product was subjected to column chromatography using 5% diethyl ether-pentane to obtain the hydroboration product as a clear oil.

GC (methyl silicone, 50 ^{o}C, 5 min, 20 ^{o}C/min → 250 ^{o}C): Rt from dppp, major [1,2-adduct **29**], 8.9 min (66%); minor [1,4-adduct **30**], 9.1 min (34%); from {[(*R,R*)-^{i}Pr-DuPhos]cobalt- η^4 -(2,3-dimethylbutadiene))}$^{+}$ [BARF]$^{-}$ (**25**); major [1,2-adduct **29**], 8.9 min (53%); [1,4-adduct **30**], 9.1 min (33%); [Vinyl boronate **31**], 9.2 min (14%).

NMR of **29-31** matched with the previously reported data by our group.[3]
^{1}H NMR (600 MHz, C6D6) δ 4.9 (m, 1H), 4.75 (pent, J = 1.8 Hz, 1H), 2.68 – 2.61 (m, 1H), 1.70 (s, 3H), 1.16 (d, J = 6.8 Hz, 3H), 1.06 (s, 12H), 1.03 – 1.02 (m, 2H); **^{13}C NMR (150 MHz, C6D6)** δ 152.16, 108.40, 82.81, 37.43, 25.02, 24.94, 22.28, 20.04. Expected 9 C; observed 8 C (missing C-B).

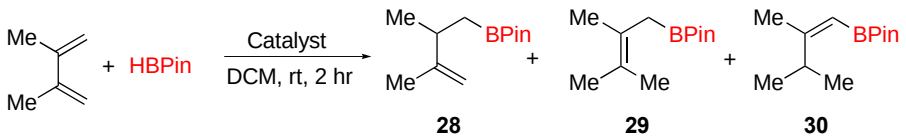
CSP-GC (cyclosil B, 90 °C, 60 min , 5 ^{o}C → 175 ^{o}C): Rt from dppp; [1,2 - adduct] 24.0 min (49.7%), 24.4 min (50.3%).

Using catalyst {[(*R,R*)-^{i}Pr-DuPhos]cobalt- η^4 -(2,3-dimethylbutadiene))}$^{+}$ [BARF]$^{-}$ (**25**)): major [1,2 -adduct] 24.0 min (10.7%), 24.4 min (89.3%); **79% *ee***

Using catalyst [(*R,R*)-^{i}Pr-DuPhosCoBr$_2$] (0.05 equiv.), Zn (0.5 equiv.), and NaBARF (0.1 equiv.): major [1,2 -adduct] 24.1 min (14.7%), 24.4 min (85.3%); **70% *ee***

HRMS (ESI-MS): m/z 233.1697 ([M+Na+]); exact mass calculated for [$C_{12}H_{23}BO_2Na$+] 233.1686.

Table S5: Catalytic activity of single-component catalyst {[(*R,R*)-^{i}Pr-DuPhos]cobalt- η^4-(2,3-dimethylbutadiene))}$^{+}$ [BARF]$^{-}$ (25) in an asymmetric hydroboration reaction[a]



no.	catalyst/additives (mol%)	conv.	**29** (% ee)	**30** (%)	**31** (%)
1[b]	**25** (2), no additives	100	53 (79)	33	14
2	**20** (5), Zn (50), NaBARF (10)	80	43 (70)	29	28

a. See procedure D1-D2 for experimental details. Conversion and relative ratios of **29**, **30** and **31** determined by GC. b. Single-component catalyst.

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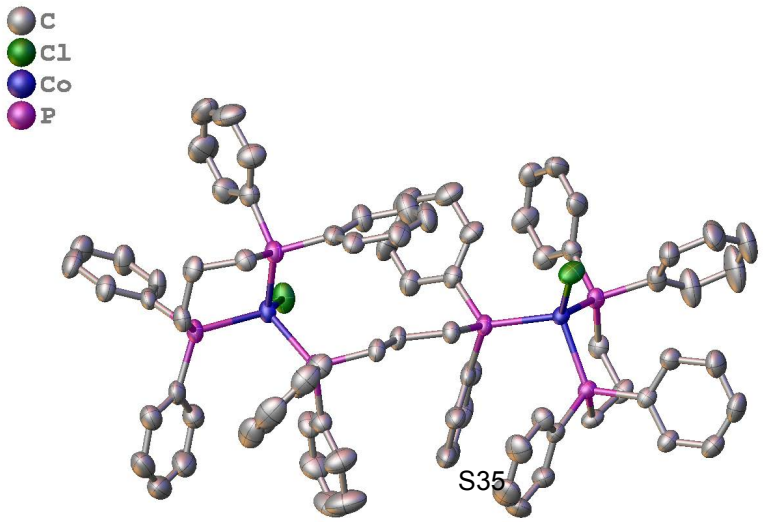
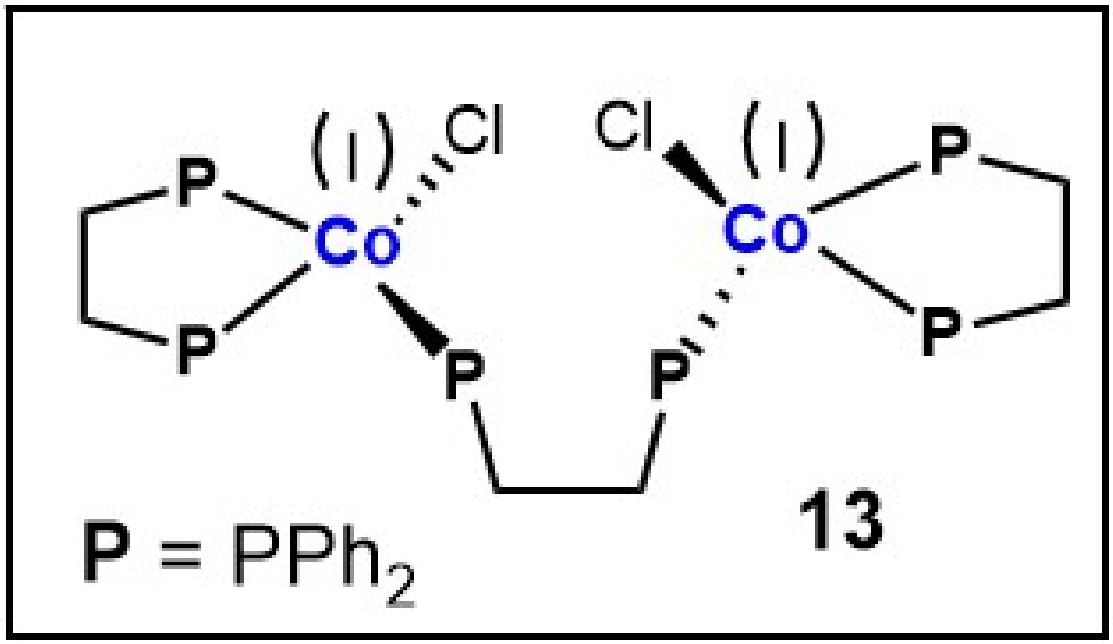
X-Ray Crystallographic Analysis of [(dppp)(Cl)Co[μ-(dppp)]Co(Cl)(dppp)] (**12**)

Table S6. Crystallographic details for RajanBabu 2160 (**12**)

Formula	C81 H78 Cl2 Co2 P6	
Formula weight	1426.01	
Temperature	210(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 21.4598(9) Å	α= 66.4390(10)°
	b = 21.5413(9) Å	β= 66.4010(10)°
	c = 23.7245(10) Å	γ = 71.7220(10)°
Volume	9056.8(7) $Å^3$	
Z	4	
Density (calculated)	1.046 Mg/m^3	
Absorption coefficient	0.566 mm^{-1}	
F(000)	2968	
Crystal size	0.04 x 0.15 x 0.35 mm^3	
Theta range for data collection	2.755 to 25.057°	
Index ranges	-25<=h<=25, -25<=k<=25, -28<=l<=28	
Reflections collected	242477	
Independent reflections	32006 [R(int) = 0.0625]	
Completeness to theta = 25.057°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	32006 / 0 / 1640	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1056	
R indices (all data)	R1 = 0.0644, wR2 = 0.1171	
Largest diff. peak and hole	0.343 and -0.523 $e/Å^3$	



X-Ray Crystallographic Analysis of [(dppe)(Cl)Co[μ-(dppe)]Co(Cl)(dppe)] (**13**)



Experimental Summary for 13

The single crystal X-ray diffraction studies were carried out on a Nonius Kappa diffractometer equipped with a Bruker APEX-II CCD and Mo K_α radiation (λ = 0.71073 Å). A 0.113 x 0.089 x 0.074 mm piece of a green block was mounted on a MiTeGen Micromount with CHRISTO-LUBE MCG 1024 oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm and exposure time was 60 seconds per frame using a scan width of 1.0°. Data collection was 100% complete to 25.00° in θ. A total of 56953 reflections were collected covering the indices, -17<=h<=17, -15<=k<=15, -23<=l<=23. 6870 reflections were found to be symmetry independent, with a R_{int} of 0.0910. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in **Table S7 .**

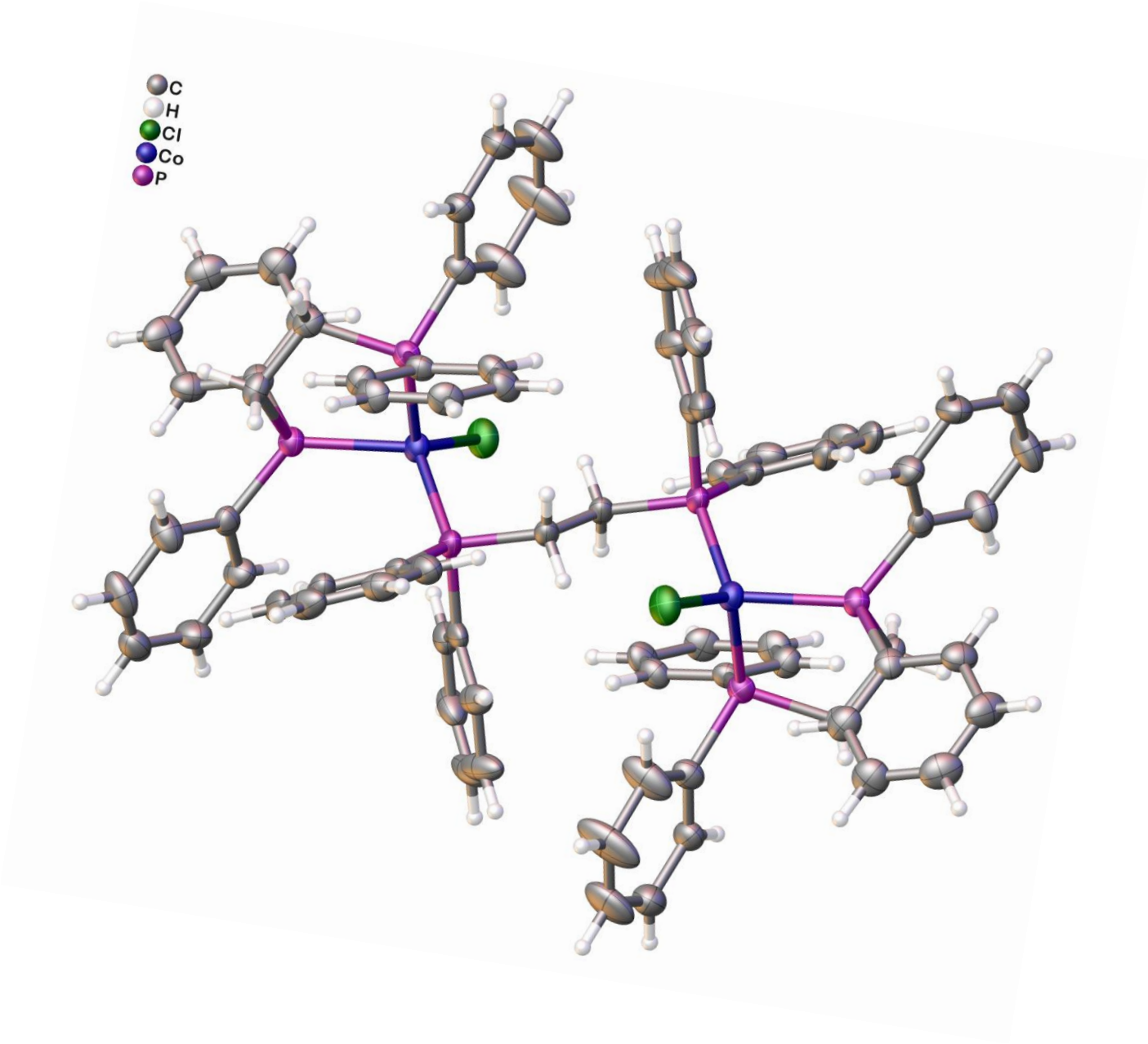
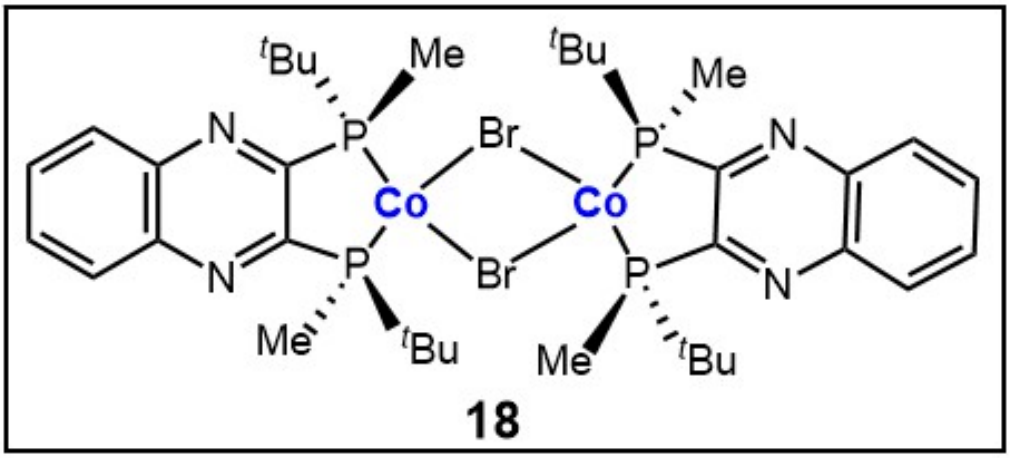

C
H
Cl
Co
P

Table S7. Crystal data and structure refinement for RBabu_MP-05-076.

Report date	2019-08-08	
Identification code	MP-05-076	
Empirical formula	C86 H88 Cl2 Co2 O2 P6	
Molecular formula	C78 H72 Cl2 Co2 P6, 2(C4 H8 O)	
Formula weight	1528.14	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 14.7933(14) Å	α= 90°.
	b = 13.2529(11) Å	β= 102.074(3)°.
	c = 19.5680(19) Å	γ = 90°.
Volume	3751.5(6) $Å^3$	
Z	2	
Density (calculated)	1.353 Mg/m^3	
Absorption coefficient	0.690 mm^{-1}	
F(000)	1596	
Crystal size	0.113 x 0.089 x 0.074 mm^3	
Crystal color, habit	Green Block	
Theta range for data collection	1.408 to 25.374°.	
Index ranges	-17<=h<=17, -15<=k<=15, -23<=l<=23	
Reflections collected	56953	
Independent reflections	6870 [R(int) = 0.0910, R(sigma) = 0.0726]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2590 and 0.2226	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6870 / 54 / 449	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1155	
R indices (all data)	R1 = 0.0974, wR2 = 0.1334	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.542 and -0.528 $e.Å^{-3}$	

X-Ray Crystallographic Analysis of {[(R,R)-QuinoxP]cobalt(I)(μ-Br)}2 (**18**)



18

Experimental Summary for 18

The single crystal X-ray diffraction studies were carried out on a Nonius Kappa diffractometer equipped with a Bruker APEX-II CCD and Mo K_α radiation (λ = 0.71073 Å). A 0.273x 0.254 x 0.216 mm piece of a green block was mounted on a MiTeGen Micromount with CHRISTO-LUBE MCG 1024 oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 80 mm and exposure time was 10 seconds per frame using a scan width of 0.75°. Data collection was 100% complete to 25.00° in θ. A total of 126335 reflections were collected covering the indices, -11<=h<=11, -11<=k<=11, -53<=l<=58. 4353 reflections were found to be symmetry independent, with a R_{int} of 0.0507. Indexing and unit cell refinement indicated a primitive, tetragonal lattice. The space group was found to be $P4_12_12$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. The absolute stereochemistry of the molecule was established by anomalous dispersion using the Parson's method with a Flack parameter of 0.009(2). Crystallographic data are summarized in **Table S8.**

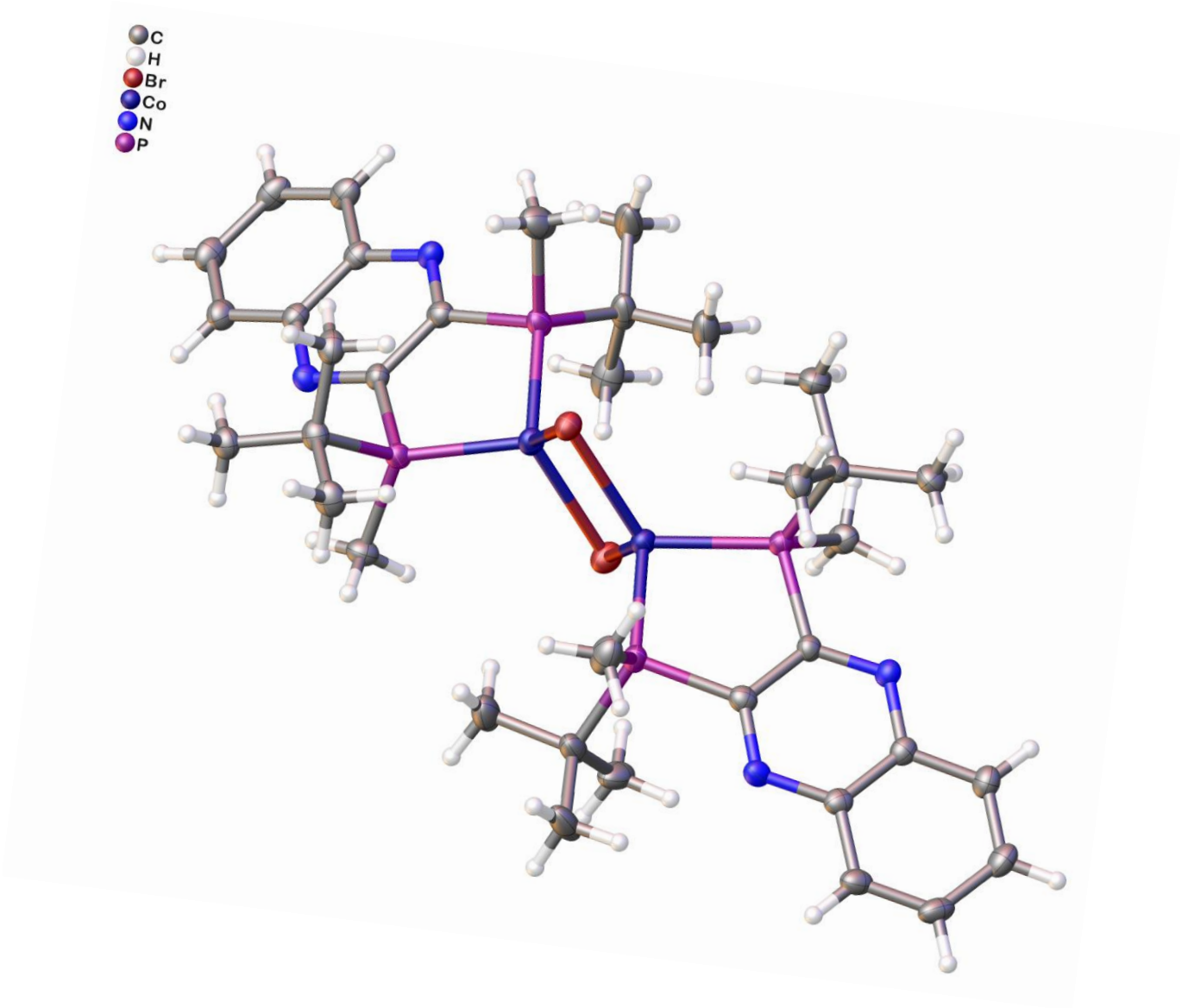
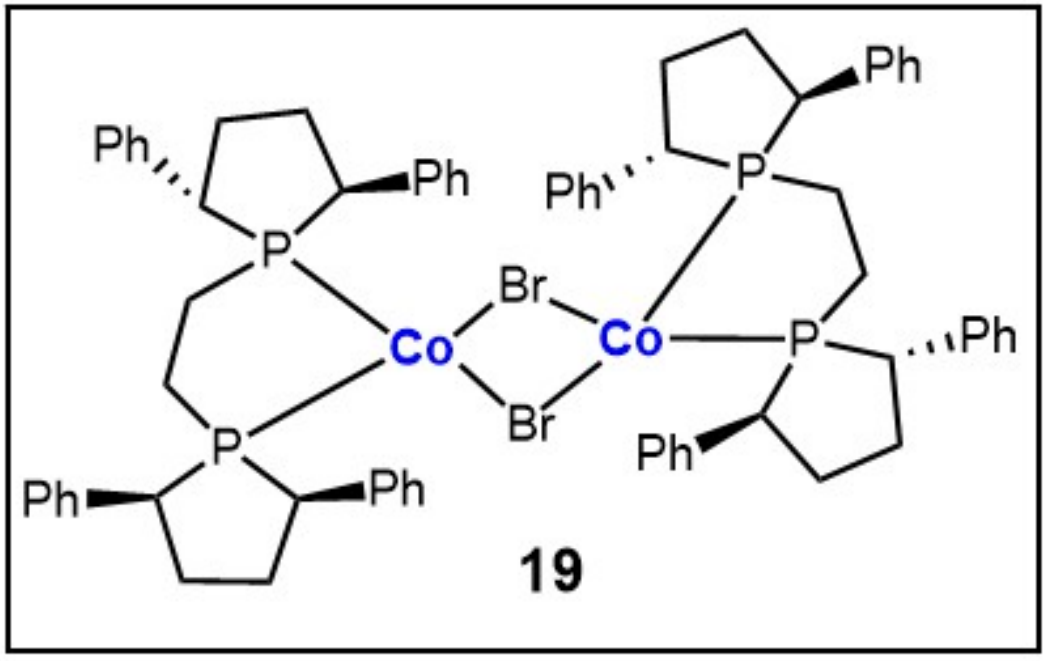

C
H
Br
Co
N
P

Table S8. Crystal data and structure refinement for RBabu_MP-05-065 (**18**).

Report date	2019-08-13	
Identification code	MP-05-065	
Empirical formula	C36 H56 Br2 Co2 N4 P4	
Molecular formula	C36 H56 Br2 Co2 N4 P4	
Formula weight	946.40	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_12_12$	
Unit cell dimensions	a = 9.5542(2) Å	α= 90°.
	b = 9.5542(2) Å	β= 90°.
	c = 46.3014(12) Å	γ = 90°.
Volume	4226.5(2) $Å^3$	
Z	4	
Density (calculated)	1.487 Mg/m^3	
Absorption coefficient	2.857 mm^{-1}	
F(000)	1936	
Crystal size	0.273 x 0.254 x 0.216 mm^3	
Crystal color, habit	Green Block	
Theta range for data collection	1.759 to 26.470°.	
Index ranges	-11<=h<=11, -11<=k<=11, -53<=l<=58	
Reflections collected	126335	
Independent reflections	4353 [R(int) = 0.0507, R(sigma) = 0.0213]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2602 and 0.2138	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4353 / 0 / 226	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0557	
R indices (all data)	R1 = 0.0267, wR2 = 0.0563	
Absolute structure parameter	0.009(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.467 and -0.199 $e.Å^{-3}$	

X-Ray Crystallographic Analysis of {[(S,S)-Ph-BPE]cobalt(I)(μ-Br)}2 (**19**)



19

Experimental Summary for 19

The single crystal X-ray diffraction studies were carried out on a Nonius Kappa diffractometer equipped with a Bruker APEX-II CCD and Mo K_α radiation (λ = 0.71073 Å). A 0.157 x 0.146 x 0.092 mm piece of a dark green block was mounted on a MiTeGen Micromount with CHRISTO-LUBE MCG 1024 oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 80 mm and exposure time was 30 seconds per frame using a scan width of 0.75°. Data collection was 99.8% complete to 23.291° in θ, 0.90Å. A total of 319126 reflections were collected covering the indices, -16<=h<=22, -23<=k<=23, -58<=l<=58. 17222 reflections were found to be symmetry independent, with a R_{int} of 0.1535. Indexing and unit cell refinement indicated a primitive, tetragonal lattice. The space group was found to be $P4_32_12$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. The absolute stereochemistry of the molecule was established by anomalous dispersion using the Parson's method with a Flack parameter of 0.006(5). Crystallographic data are summarized in **Table S9.**

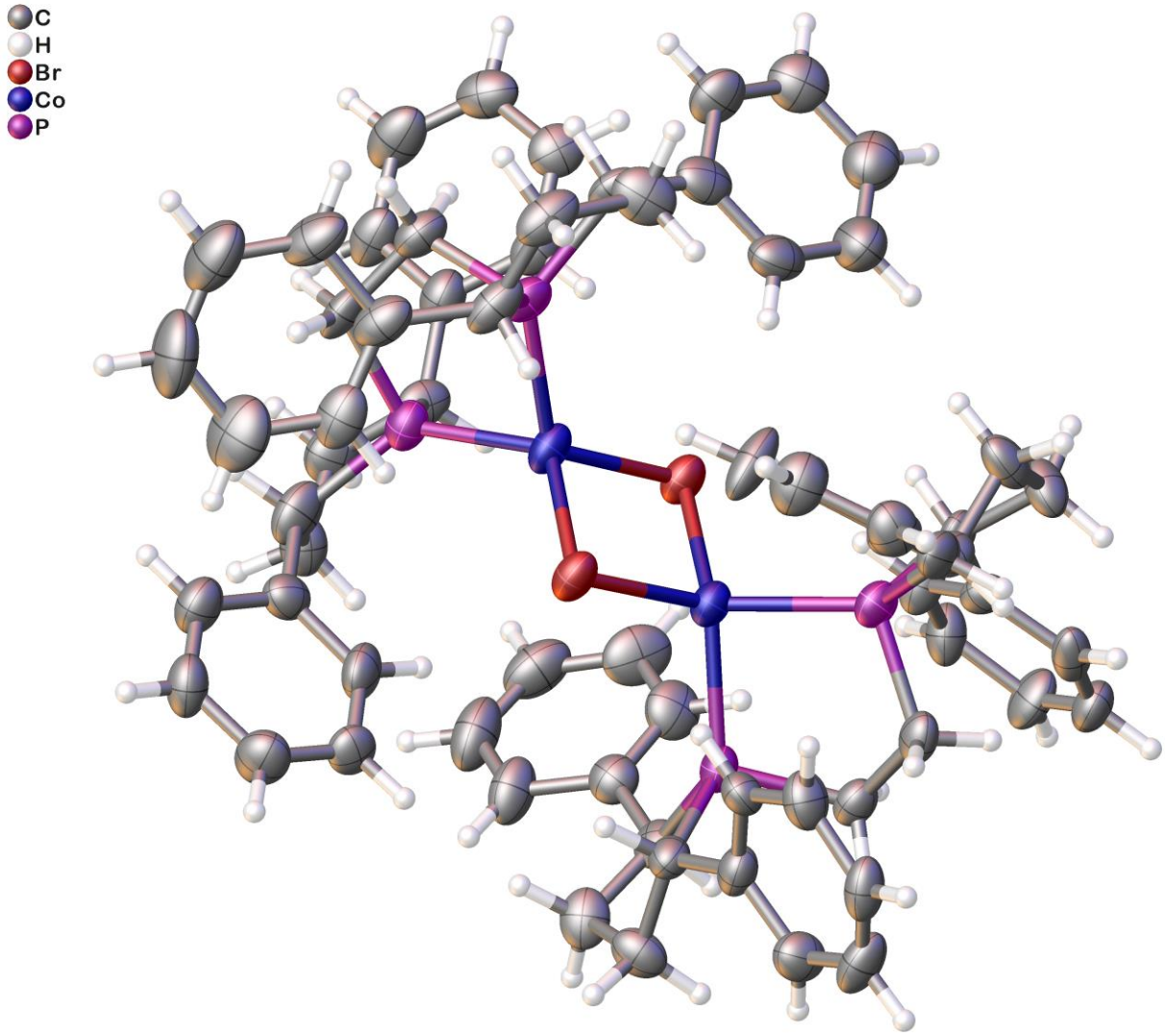
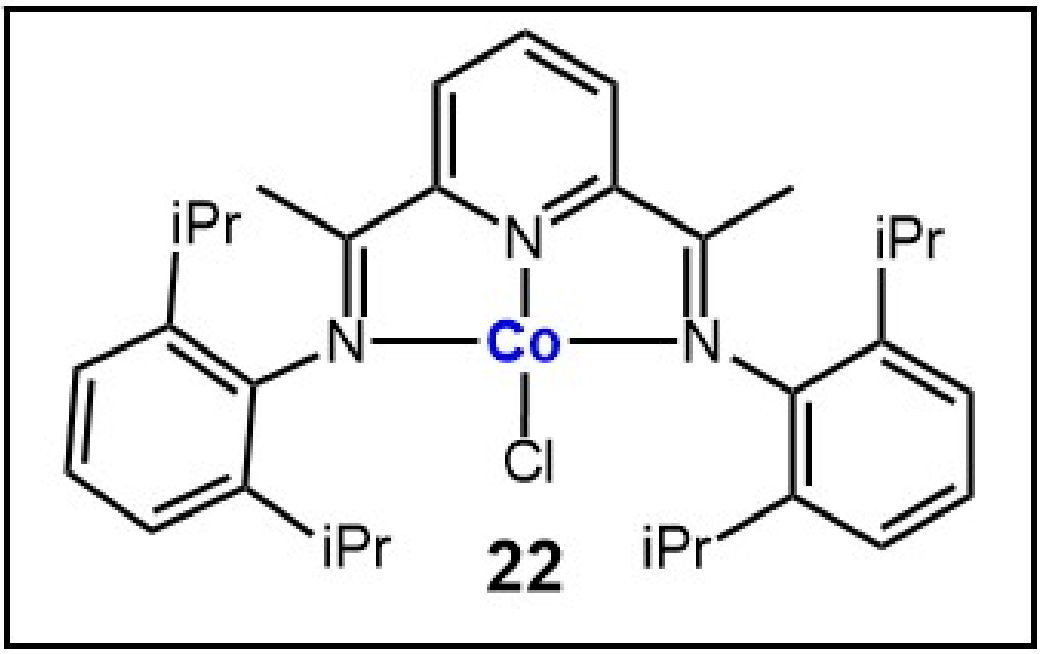

C
H
Br
Co
P

Table S9. Crystal data and structure refinement for RBabu_MP-05-066 (**19**).

Report date	2019-08-16	
Identification code	MP-05-066	
Empirical formula	C68 H72 Br2 Co2 P4	
Molecular formula	C68 H72 Br2 Co2 P4	
Formula weight	1290.81	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_32_12$	
Unit cell dimensions	a = 21.2718(9) Å	α= 90°.
	b = 21.2718(9) Å	β= 90°.
	c = 52.873(2) Å	γ = 90°.
Volume	23925(2) $Å^3$	
Z	16	
Density (calculated)	1.433 Mg/m^3	
Absorption coefficient	2.039 mm^{-1}	
F(000)	10624	
Crystal size	0.157 x 0.146 x 0.092 mm^3	
Crystal color, habit	Dark Green Block	
Theta range for data collection	1.032 to 23.291°.	
Index ranges	-16<=h<=22, -23<=k<=23, -58<=l<=58	
Reflections collected	319126	
Independent reflections	17222 [R(int) = 0.1535, R(sigma) = 0.0650]	
Completeness to theta = 23.291°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0243 and 0.0078	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17222 / 0 / 1369	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0693, wR2 = 0.1500	
R indices (all data)	R1 = 0.0982, wR2 = 0.1638	
Absolute structure parameter	0.006(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.797 and -0.525 $e.Å^{-3}$	

X-Ray Crystallographic Analysis of [bis(N-aryliminoethyl-kN,N’)pyridine-N]CoCl (**22**)



Experimental Summary for 22

The single crystal X-ray diffraction studies were carried out on a Nonius Kappa diffractometer equipped with a Bruker APEX-II CCD and Mo K_α radiation (λ = 0.71073 Å). A 0.286 x 0.274 x 0.209 mm piece of a purple block was mounted on a MiTeGen Micromount with CHRISTO-LUBE MCG 1024 oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm and exposure time was 5 seconds per frame using a scan width of 0.75°. Data collection was 100% complete to 25.00° in θ. A total of 21780 reflections were collected covering the indices, -10<=h<=10, -28<=k<=28, -11<=l<=19. 6221 reflections were found to be symmetry independent, with a R_{int} of 0.0475. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in **Table S10.**

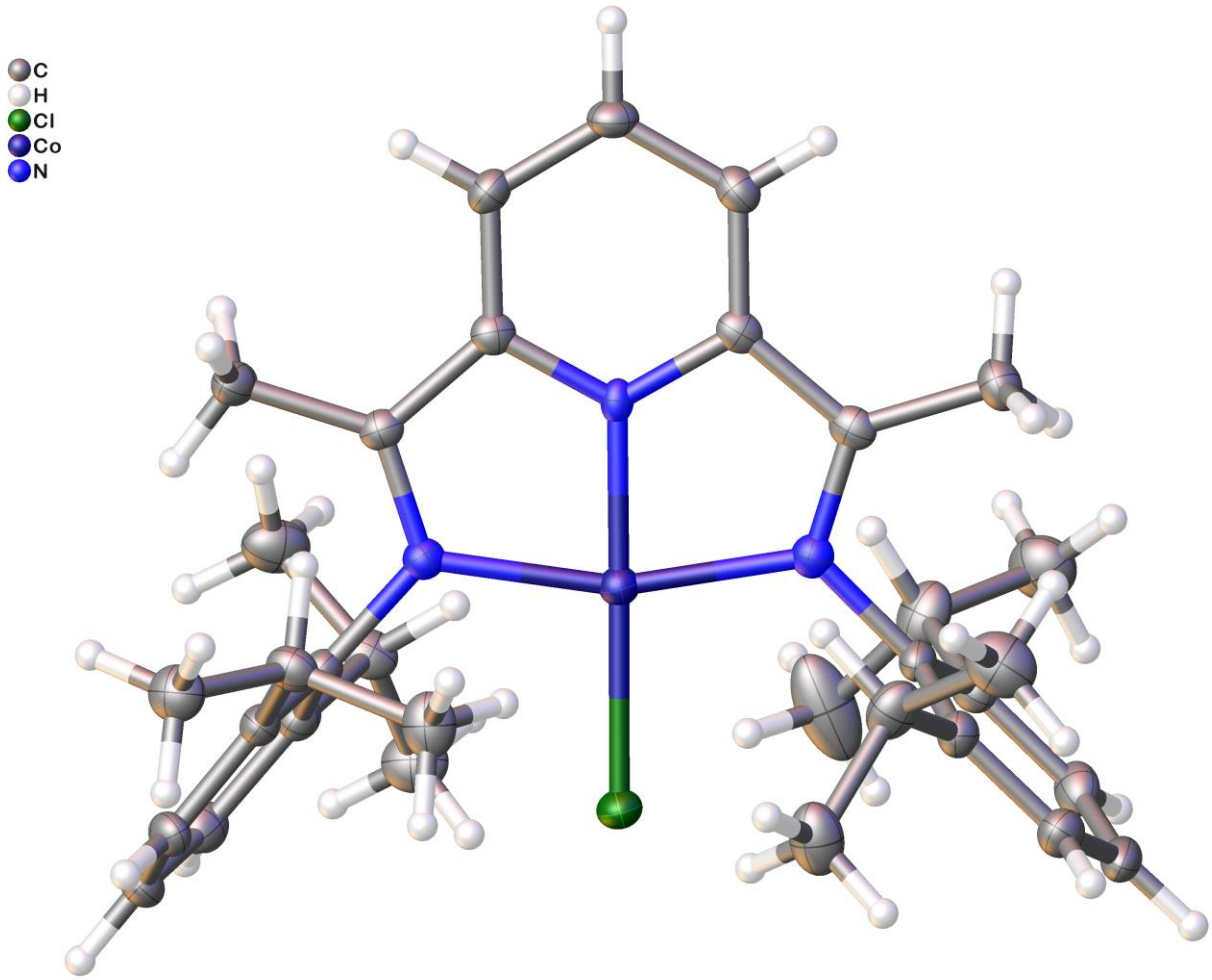
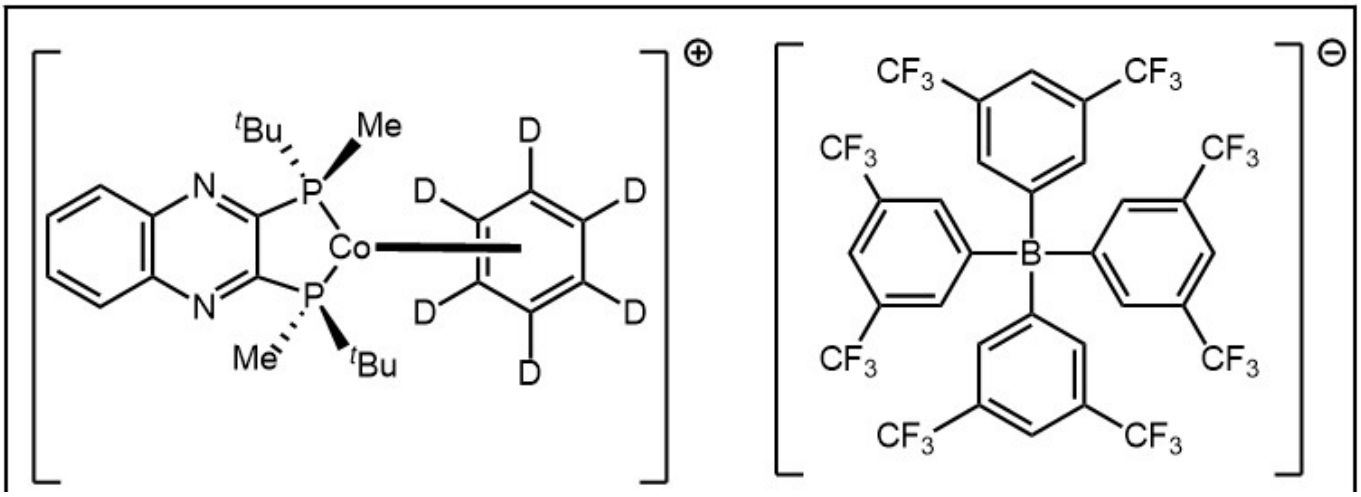

C
H
Cl
Co
N

Table S10. Crystal data and structure refinement for RBabu_MP-05-075.

Report date	2019-08-16	
Identification code	MP-05-075	
Empirical formula	C33 H43 Cl Co N3	
Molecular formula	C33 H43 Cl Co N3	
Formula weight	576.08	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.7386(6) Å	α= 90°.
	b = 22.8891(16) Å	β= 101.295(2)°.
	c = 15.5231(11) Å	γ = 90°.
Volume	3044.8(4) $Å^3$	
Z	4	
Density (calculated)	1.257 Mg/m^3	
Absorption coefficient	0.677 mm^{-1}	
F(000)	1224	
Crystal size	0.286 x 0.274 x 0.209 mm^3	
Crystal color, habit	Purple Block	
Theta range for data collection	1.607 to 26.396°.	
Index ranges	-10<=h<=10, -28<=k<=28, -11<=l<=19	
Reflections collected	21780	
Independent reflections	6221 [R(int) = 0.0475, R(sigma) = 0.0655]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2602 and 0.2116	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6221 / 0 / 353	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1027	
R indices (all data)	R1 = 0.0683, wR2 = 0.1108	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.938 and -0.298 e.$Å^{-3}$	

X-Ray Crystallographic Analysis of {[(R,R)-QuinoxP]cobalt(I)(eta-6 -C6D6)} +[BArF]⁻ (**23**)



Experimental Summary for 23

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa Photon II CPAD diffractometer equipped with Mo K_α radiation (λ = 0.71073 Å). A 0.315 x 0.228 x 0.154 mm piece of a purple block was mounted on a MiTeGen Micromount with Paratone 24EX oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 60 mm and exposure time was 10 seconds per frame using a scan width of 1.0°. Data collection was 99.8% complete to 25.00° in θ. A total of 124192 reflections were collected covering the indices, -17<=h<=17, -18<=k<=18, -21<=l<=21. 23621 reflections were found to be symmetry independent, with a R_{int} of 0.0381. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be *P*1. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model for refinement.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. The absolute stereochemistry of the molecule was established by anomalous dispersion using the Parson's method with a Flack parameter of 0.005(3). Crystallographic data are summarized in **Table S11.**

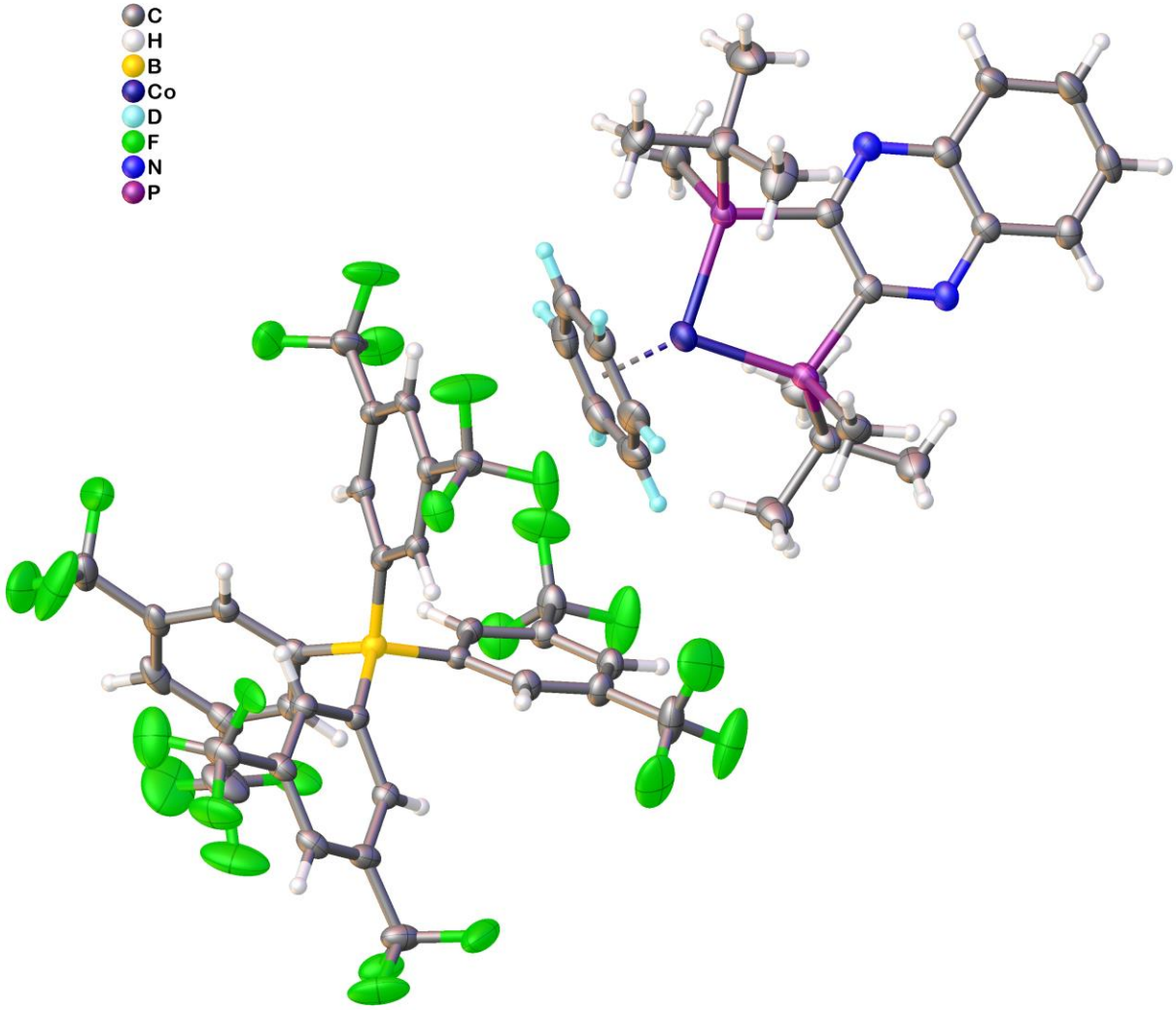
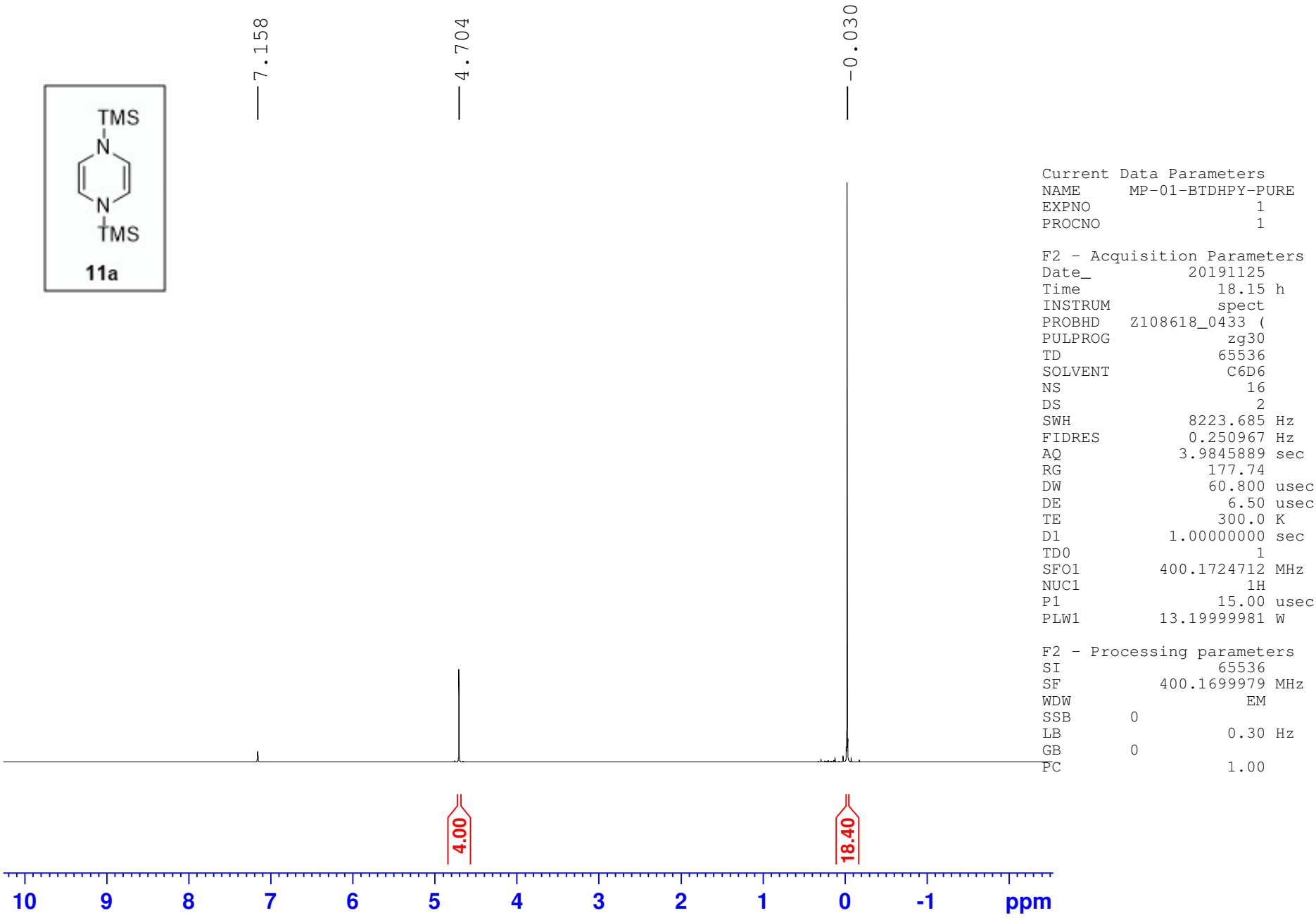

C
H
B
Co
D
F
N
P

Table S11. Crystal data and structure refinement for RBabu_MP-05-156 (**23**).

Report date	2020-07-13	
Identification code	MP-05-156	
Empirical formula	C56 H40 B Co D6 F24 N2 P2	
Molecular formula	C24 H28 Co D6 N2 P2, C32 H12 B F24	
Formula weight	1340.66	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 13.7516(7) Å	α= 106.052(2)°.
	b = 14.4882(7) Å	β= 102.166(2)°.
	c = 17.3962(9) Å	γ = 111.9630(10)°.
Volume	2890.8(3) $Å^3$	
Z	2	
Density (calculated)	1.540 Mg/m^3	
Absorption coefficient	0.469 mm^{-1}	
F(000)	1348	
Crystal size	0.315 x 0.228 x 0.154 mm^3	
Crystal color, habit	Purple Block	
Theta range for data collection	2.915 to 26.433°.	
Index ranges	-17<=h<=17, -18<=k<=18, -21<=l<=21	
Reflections collected	124192	
Independent reflections	23621 [R(int) = 0.0381, R(sigma) = 0.0363]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0932 and 0.0678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23621 / 156 / 1662	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0722	
R indices (all data)	R1 = 0.0419, wR2 = 0.0763	
Absolute structure parameter	0.005(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.469 and -0.291 $e.Å^{-3}$	

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PROCNO                   1

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PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                     16
DS                      2
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FIDRES          0.250967 Hz
AQ             3.9845889 sec
RG                177.74
DW                60.800 usec
DE                 6.50 usec
TE                300.0 K
D1           1.00000000 sec
TD0                     1
SFO1         400.1724712 MHz
NUC1                   1H
P1                15.00 usec
PLW1         13.19999981 W

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WDW                    EM
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PC                 1.00
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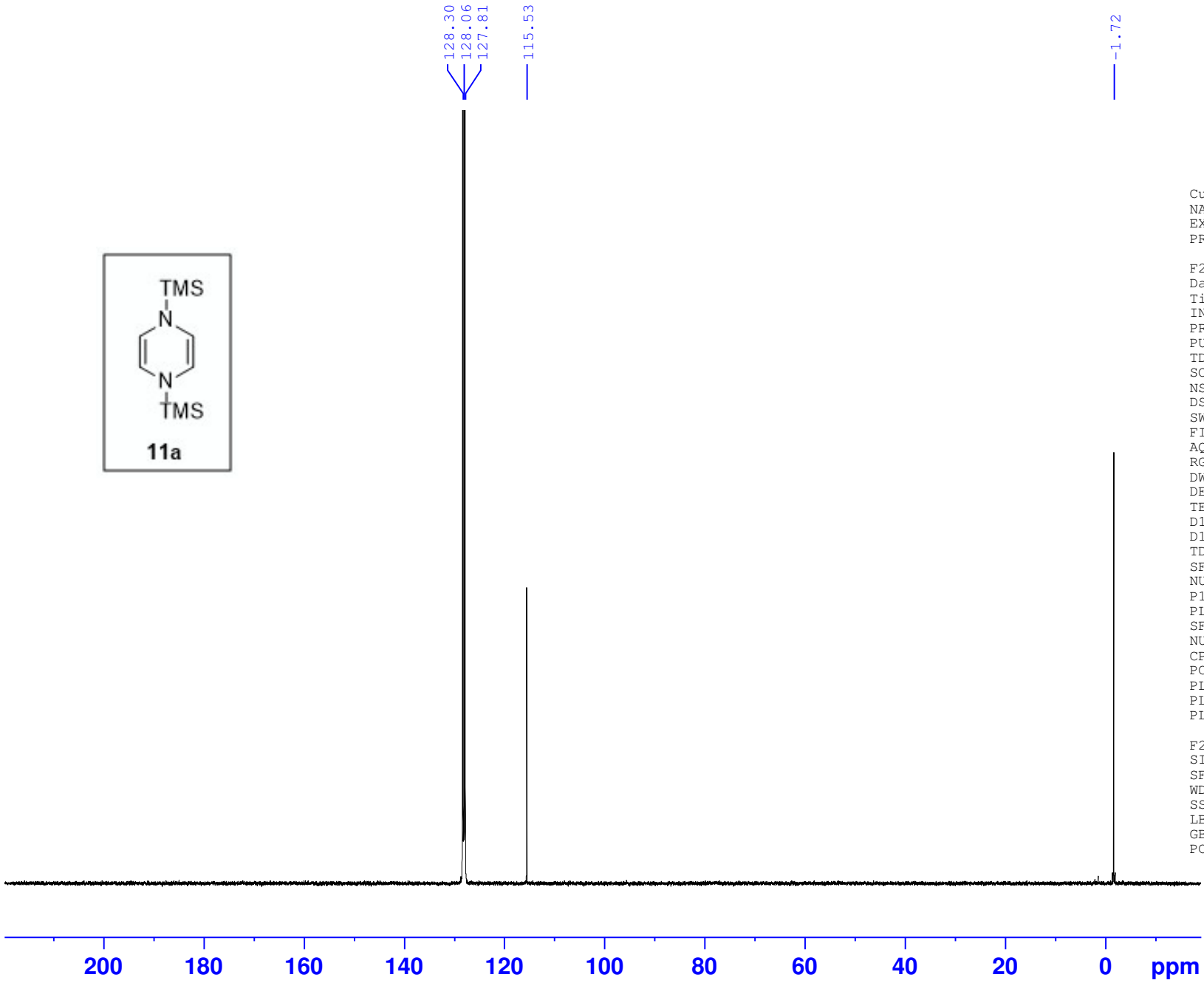


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PROCNO                   1

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PULPROG           zgpg30
TD                 65536
SOLVENT              C6D6
NS                   1024
DS                      4
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FIDRES          0.733596 Hz
AQ             1.3631488 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                     1
SFO1         100.6328888 MHz
NUC1                 13C
P1                 9.50 usec
PLW1         53.29999924 W
SFO2         400.1716007 MHz
NUC2                 1H
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PCPD2             90.00 usec
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PLW12         0.40555999 W
PLW13         0.20399000 W

F2 - Processing parameters
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GB        0
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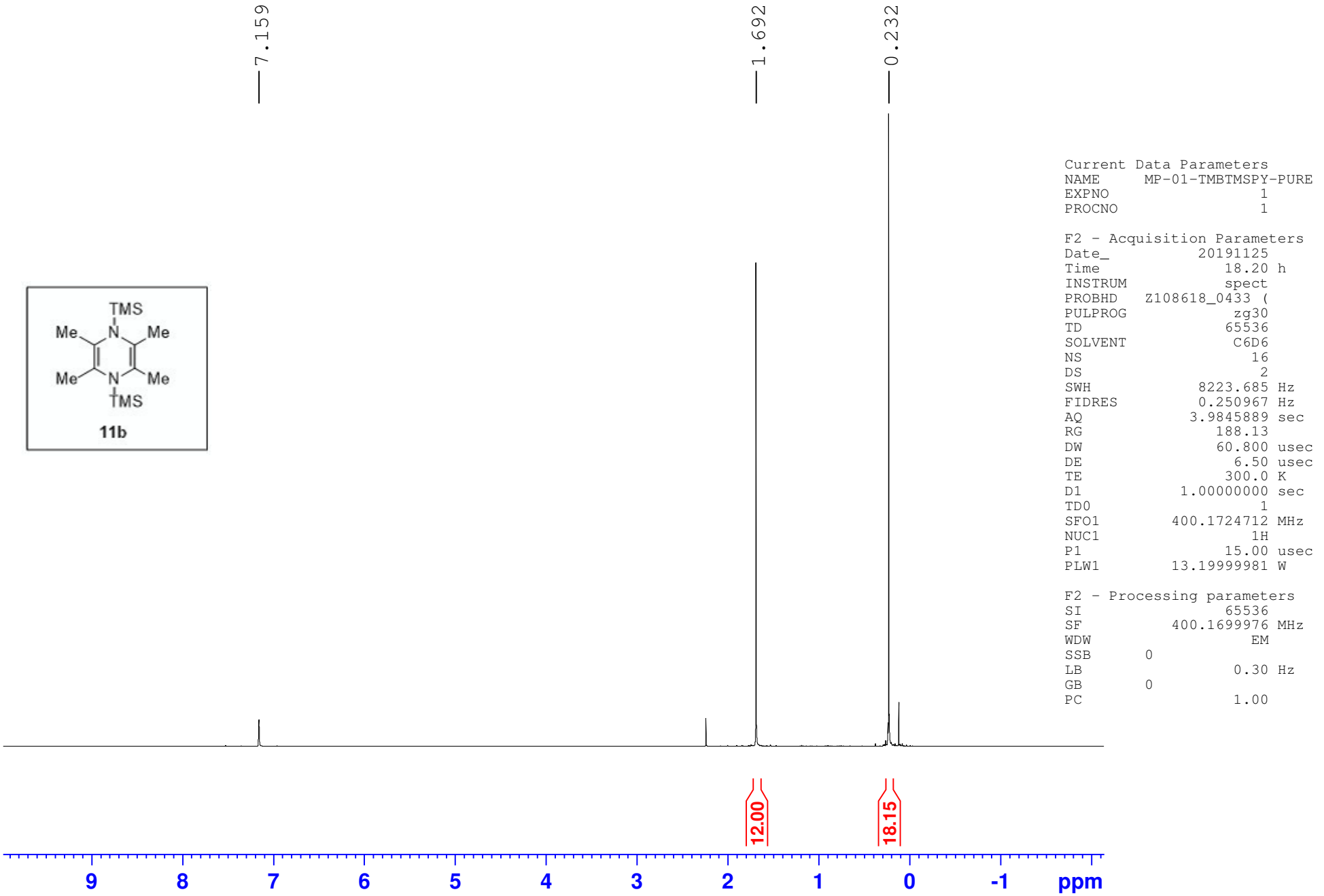


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EXPNO                      1
PROCNO                     1

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Time                18.20 h
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PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               3.9845889 sec
RG                  188.13
DW                  60.800 usec
DE                   6.50 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                     1
SFO1          400.1724712 MHz
NUC1                   1H
P1                  15.00 usec
PLW1          13.19999981 W

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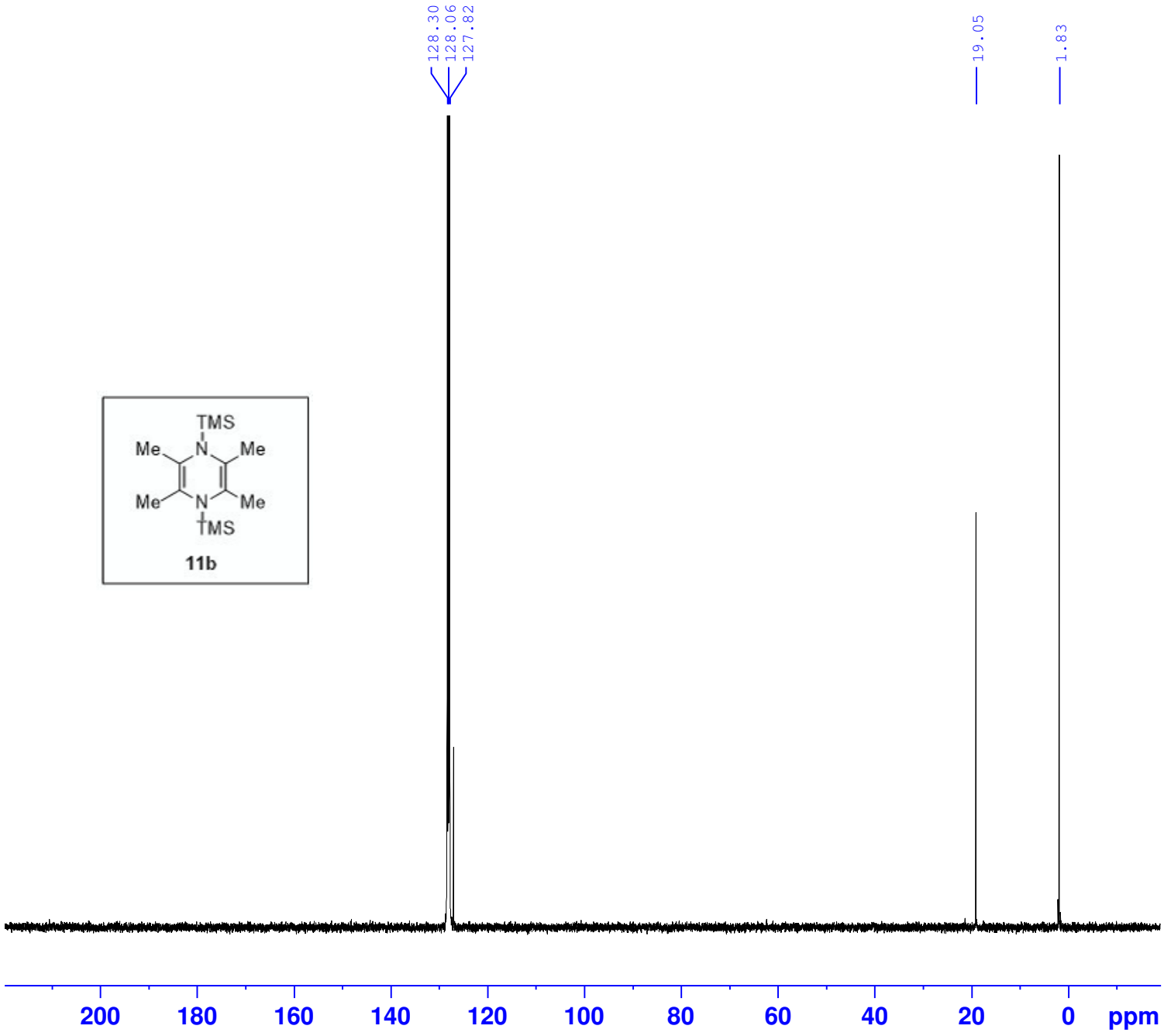


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PROCNO                     1

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TD                 65536
SOLVENT              C6D6
NS                   1024
DS                      4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ             1.3631488 sec
RG                   2050
DW                20.800 usec
DE                 6.50 usec
TE                 300.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1         100.6328888 MHz
NUC1                 13C
P1                 9.50 usec
PLW1         53.29999924 W
SFO2         400.1716007 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         14.60000038 W
PLW12         0.40555999 W
PLW13         0.20399000 W

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WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
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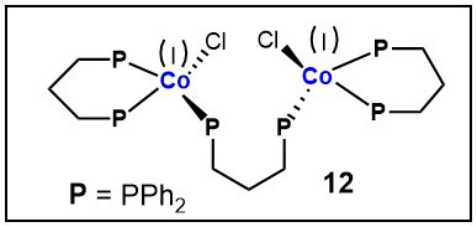

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11.152
10.162
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7.412
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2.790
2.431
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1.272
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PROCNO 1

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TD 96152
SOLVENT CD2Cl2
NS 512
DS 2
SWH 119047.617 Hz
FIDRES 2.476238 Hz
AQ 0.4038384 sec
RG 104.7
DW 4.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
SFO1 600.2040072 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
PLW1 25.10000038 W

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

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17.95
9.26
5.90
1.00
1.08
0.98
0.73
1.66
1.49
5.65
3.65

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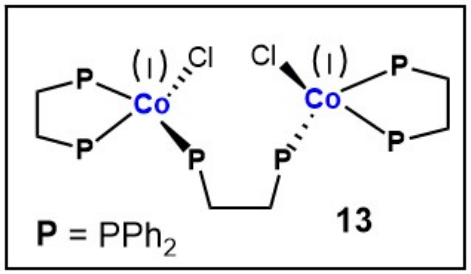

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10.534
3.572
3.265
2.204
1.414
0.911
-4.219
-5.612

0.01
4.78
6.03
6.31
3.54
5.02
2.87
3.61
2.91
2.79
6.26

20
15
10
5
0
-5
-10
ppm

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PROCNO                1

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TD0                  1
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P0                3.33 usec
P1               10.00 usec
PLW1        25.10000038 W

F2 - Processing parameters
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PC                1.00
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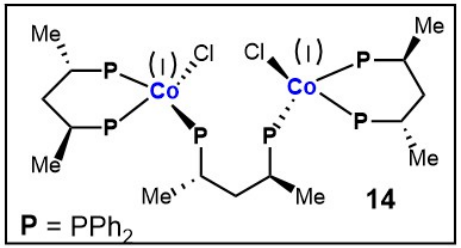


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Current Data Parameters
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PROCNO                 1

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PULPROG             zg30
TD                 84750
SOLVENT             C6D6
NS                   512
DS                     2
SWH           119047.617 Hz
FIDRES          2.809383 Hz
AQ             0.3559500 sec
RG                 104.7
DW                 4.200 usec
DE                 6.50 usec
TE                 300.2 K
D1            0.05900000 sec
TD0                    1
SFO1          600.1800000 MHz
NUC1                  1H
P0                 3.33 usec
P1                10.00 usec
PLW1         25.10000038 W

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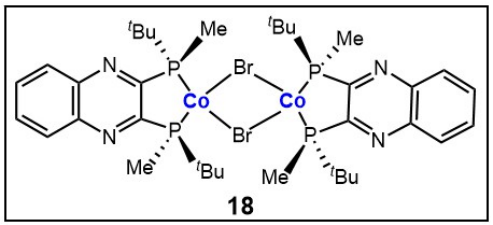

18


```
Current Data Parameters
NAME          MP-05-155
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
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TD               96152
SOLVENT           C6D6
NS                 256
DS                   2
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FIDRES         2.476238 Hz
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RG                104.7
DW                4.200 usec
DE                6.50 usec
TE                300.2 K
D1           1.00000000 sec
TD0                  1
SFO1         600.1828251 MHz
NUC1                1H
P0                3.33 usec
P1               10.00 usec
PLW1        25.10000038 W

F2 - Processing parameters
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SF           600.1799937 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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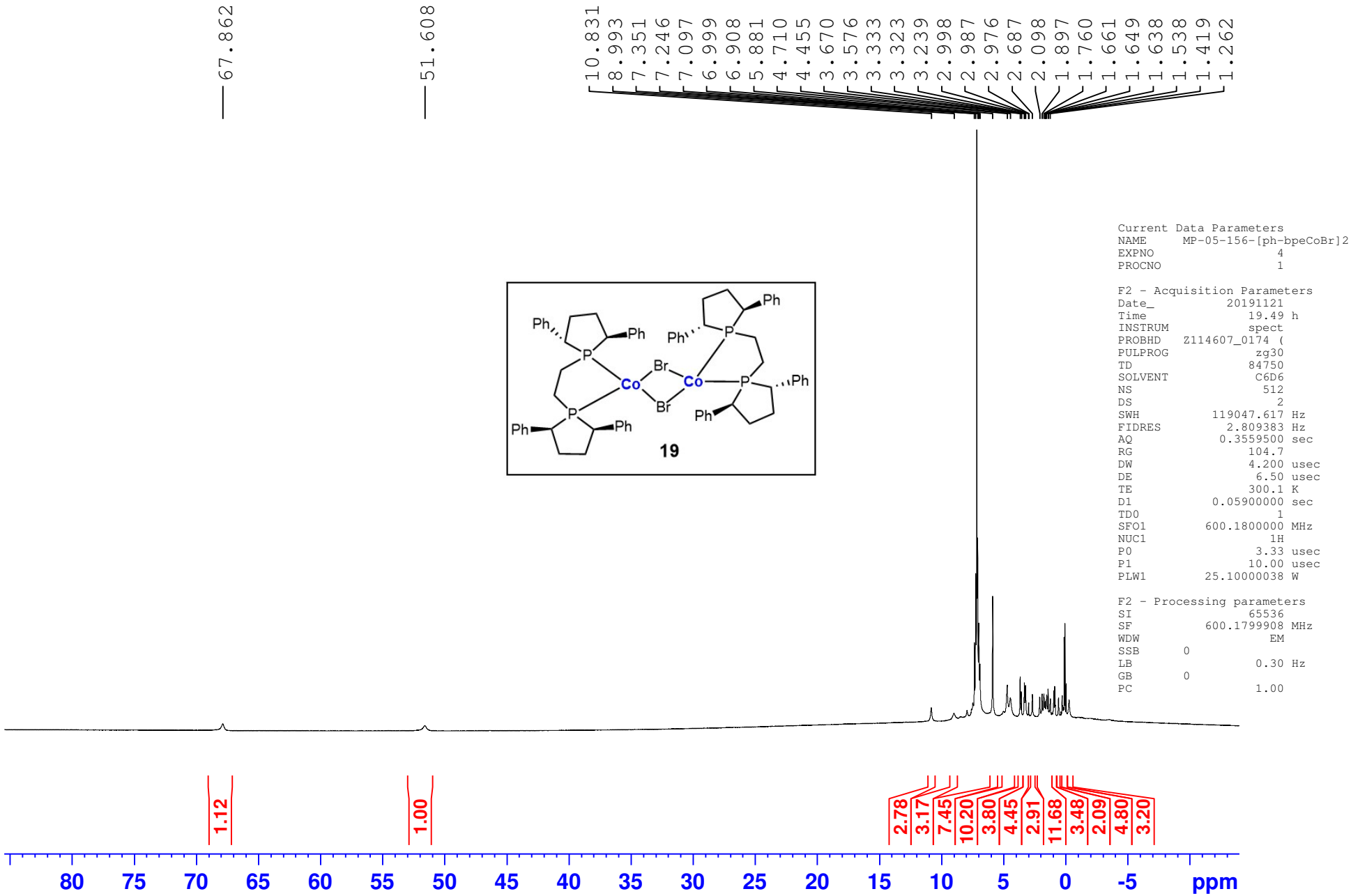
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8.993
7.351
7.246
7.097
6.999
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5.881
4.710
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3.323
3.239
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2.976
2.687
2.098
1.897
1.760
1.661
1.649
1.638
1.538
1.419
1.262
Current Data Parameters
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EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20191121
Time 19.49 h
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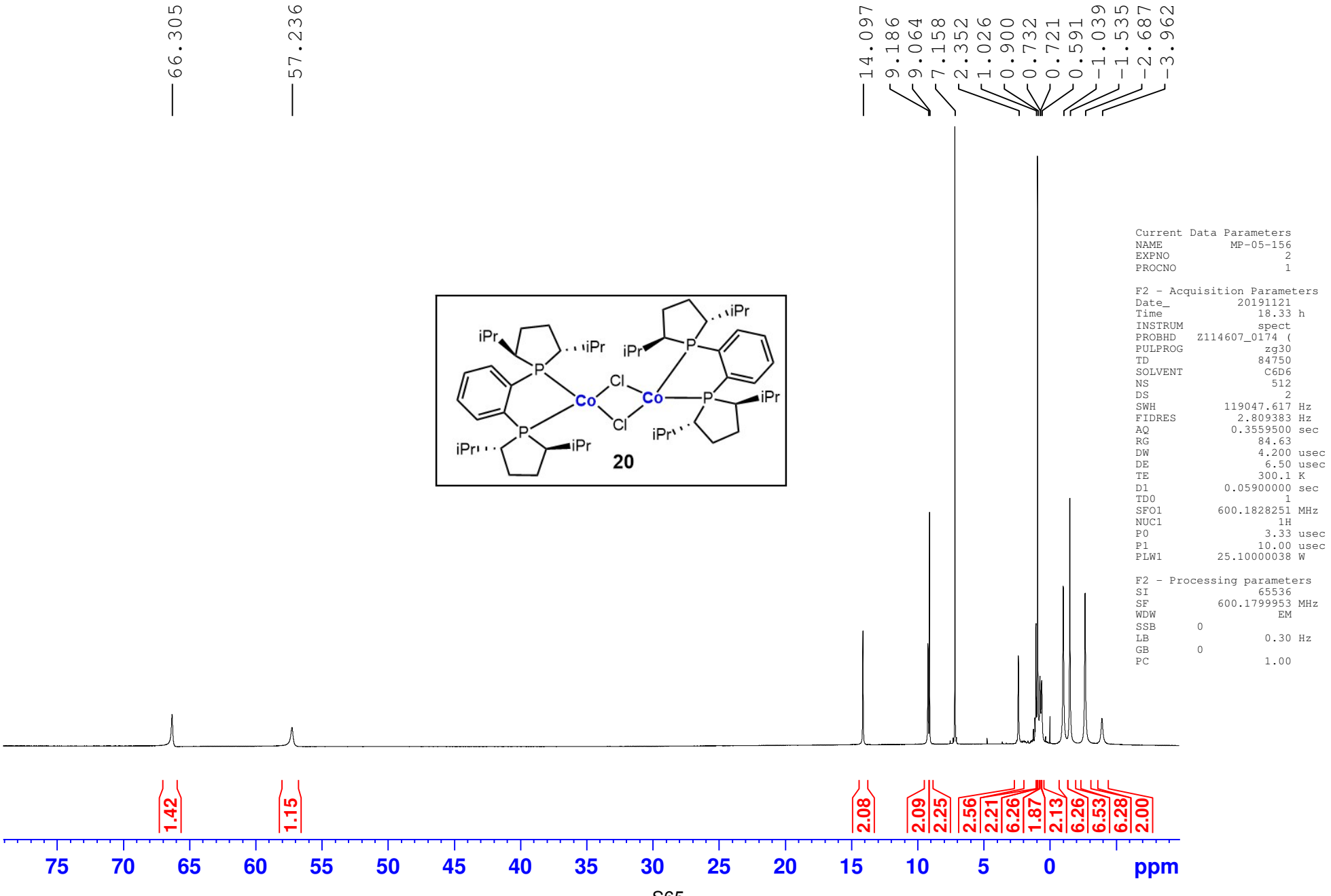
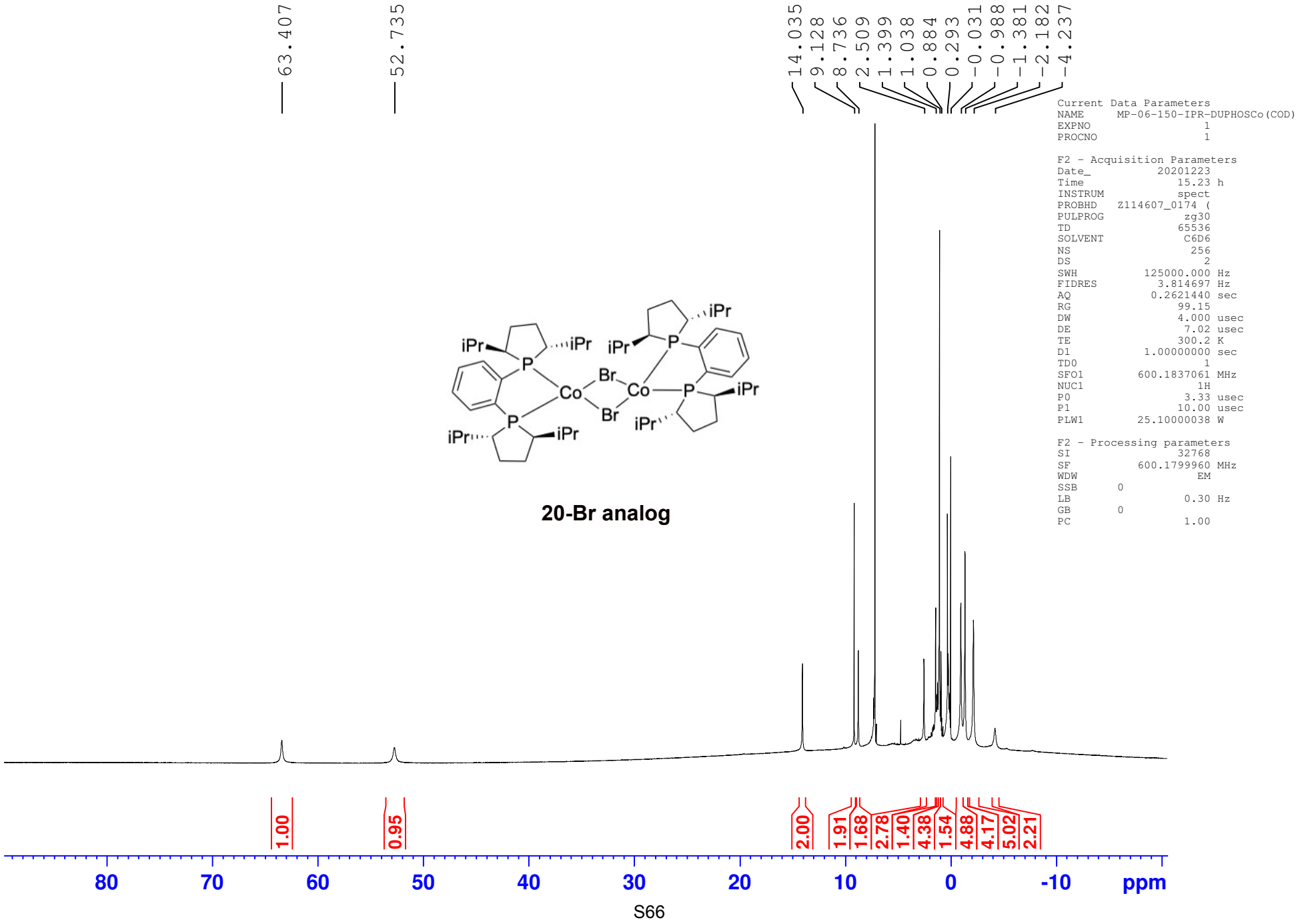
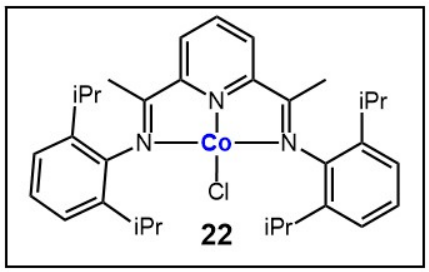
PROBHD Z114607_0174 (
PULPROG zg30
TD 84750
SOLVENT C6D6
NS 512
DS 2
SWH 119047.617 Hz
FIDRES 2.809383 Hz
AQ 0.3559500 sec
RG 104.7
DW 4.200 usec
DE 6.50 usec
TE 300.1 K
D1 0.05900000 sec
TD0 1
SFO1 600.1800000 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
PLW1 25.10000038 W
F2 - Processing parameters
SI 65536
SF 600.1799908 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
P
Co
Br
19
1.12
1.00
2.78
3.17
7.45
10.20
3.80
4.45
2.91
11.68
3.48
2.09
4.80
3.20
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
ppm

[ipr-duphosCoCl]2-1H-PARA




63.407
52.735
14.035
9.128
8.736
2.509
1.399
1.038
0.884
0.293
-0.031
-0.988
-1.381
-2.182
-4.237
Current Data Parameters
NAME MP-06-150-IPR-DUPHOSCo(COD)
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20201223
Time 15.23 h
INSTRUM spect
PROBHD Z114607_0174 (
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 256
DS 2
SWH 125000.000 Hz
FIDRES 3.814697 Hz
AQ 0.2621440 sec
RG 99.15
DW 4.000 usec
DE 7.02 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
SFO1 600.1837061 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
PLW1 25.10000038 W
F2 - Processing parameters
SI 32768
SF 600.1799960 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
iPr
P
Co
Br
20-Br analog
1.00
0.95
2.00
1.91
1.68
2.78
1.40
4.38
1.54
4.88
4.17
5.02
2.21
80
70
60
50
40
30
20
10
0
-10
ppm

Ipr-PDI-CoCl-1H

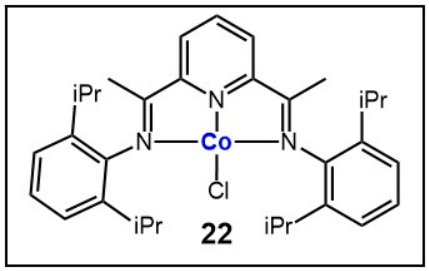



```
Current Data Parameters
NAME          MP-05-154
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20191120
Time              15.34 h
INSTRUM           spect
PROBHD   Z114607_0174 (
PULPROG           zg30
TD               96152
SOLVENT           C6D6
NS                 256
DS                   2
SWH          119047.617 Hz
FIDRES         2.476238 Hz
AQ           0.4038384 sec
RG                99.15
DW                4.200 usec
DE                6.50 usec
TE               300.1 K
D1           1.00000000 sec
TD0                  1
SFO1        600.1828251 MHz
NUC1                1H
P0                3.33 usec
P1               10.00 usec
PLW1        25.10000038 W

F2 - Processing parameters
SI                65536
SF          600.1799935 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

13C

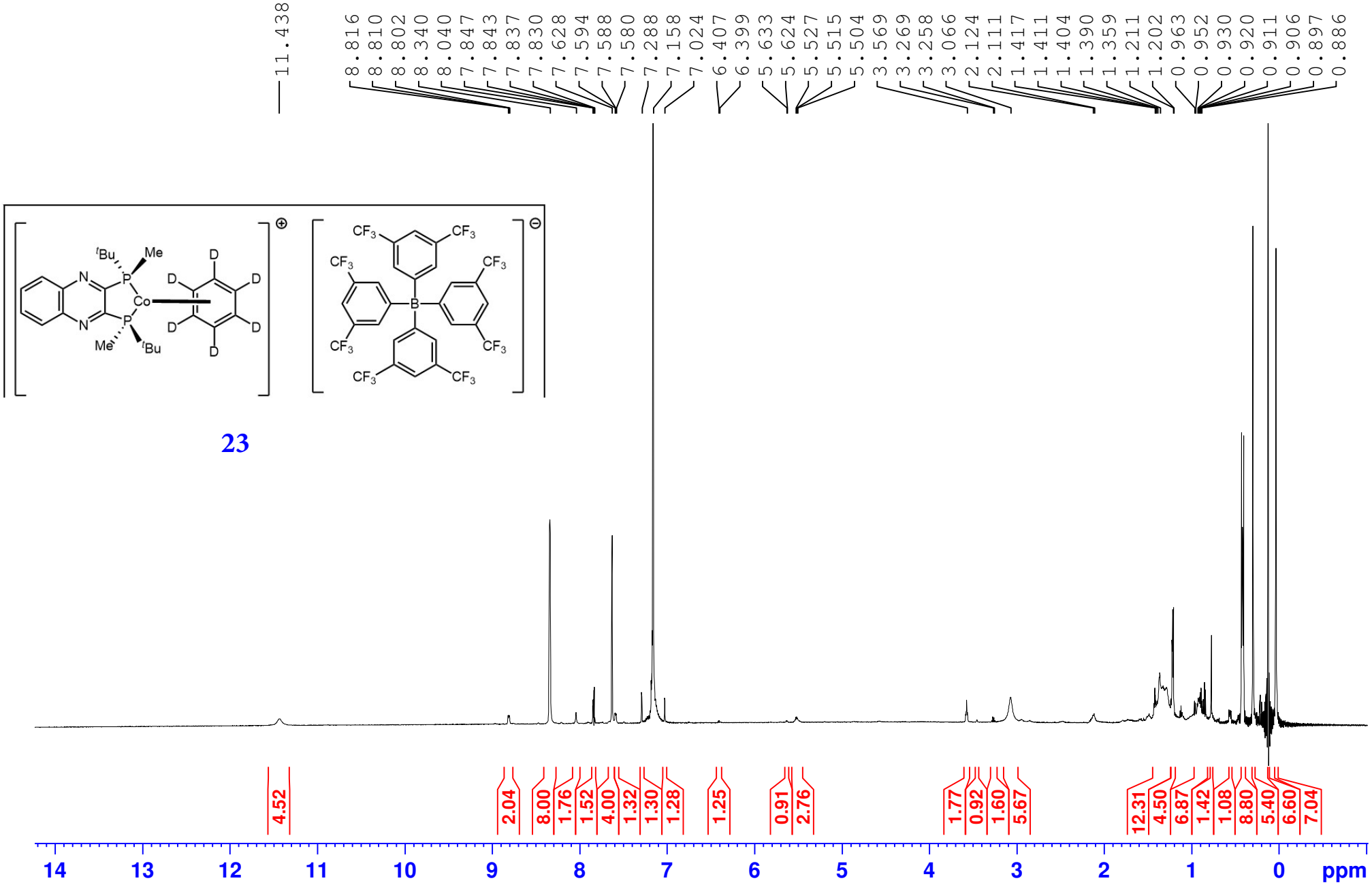



```
Current Data Parameters
NAME      MP-06-087-IPrPDICOCl
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_              20200916
Time                 18.58 h
INSTRUM              spect
PROBHD    Z114607_0174 (
PULPROG             zgpg30
TD                   65536
SOLVENT             CD2C12
NS                     1024
DS                        4
SWH              36231.883 Hz
FIDRES            1.105709 Hz
AQ                0.9043968 sec
RG                   189.17
DW                   13.800 usec
DE                    6.50 usec
TE                   300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1
SFO1          150.9304726 MHz
NUC1                   13C
P0                    4.00 usec
P1                   12.00 usec
PLW1          81.53399658 W
SFO2          600.1824007 MHz
NUC2                   1H
CPDPRG[2           waltz65
PCPD2                70.00 usec
PLW2          28.00000000 W
PLW12          0.57143003 W
PLW13          0.28742000 W

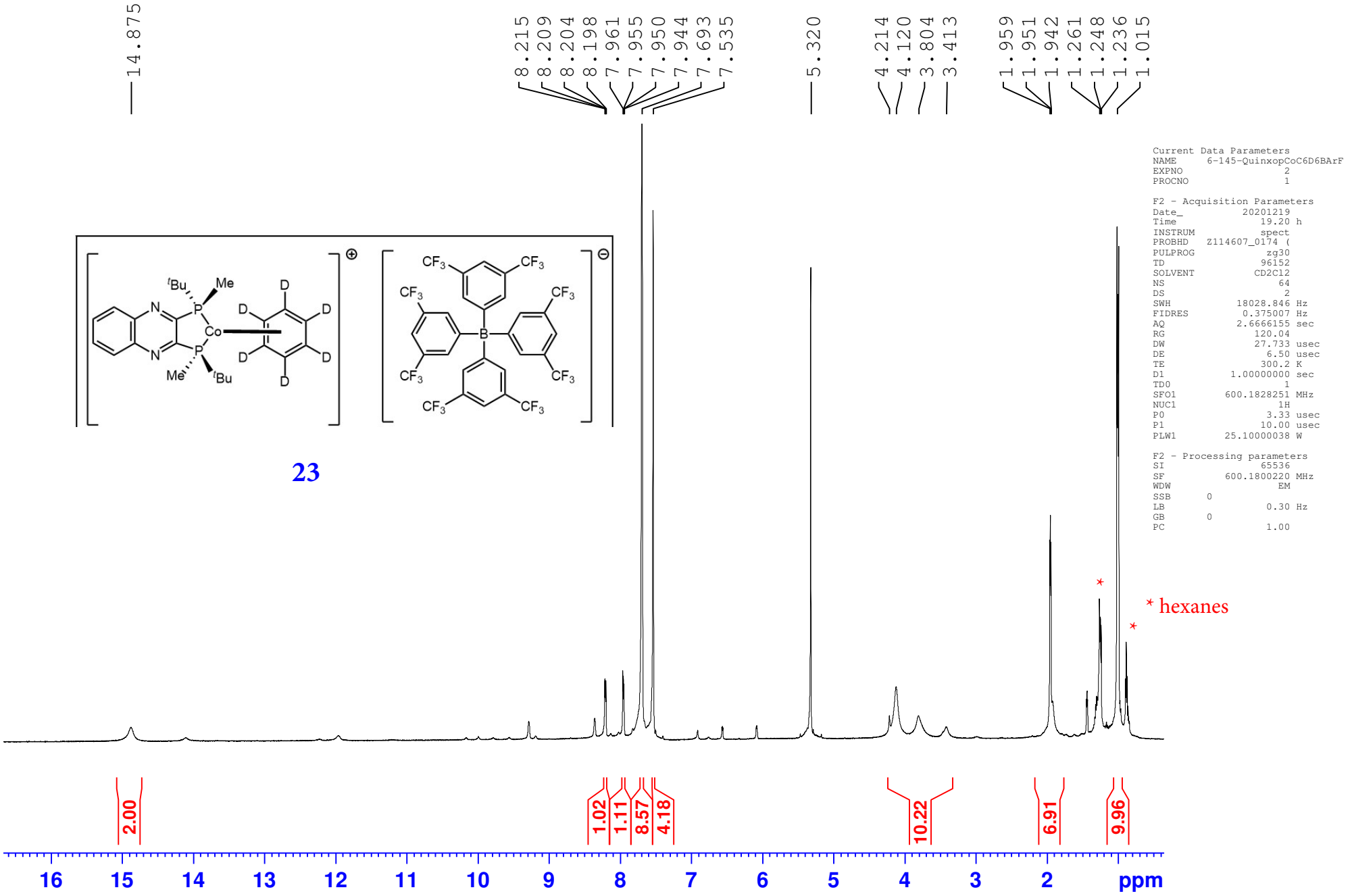
F2 - Processing parameters
SI                    32768
SF            150.9153719 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

MP-05-156-QUINOXPCo(C6D6)BARF; 1H NMR in C6D6

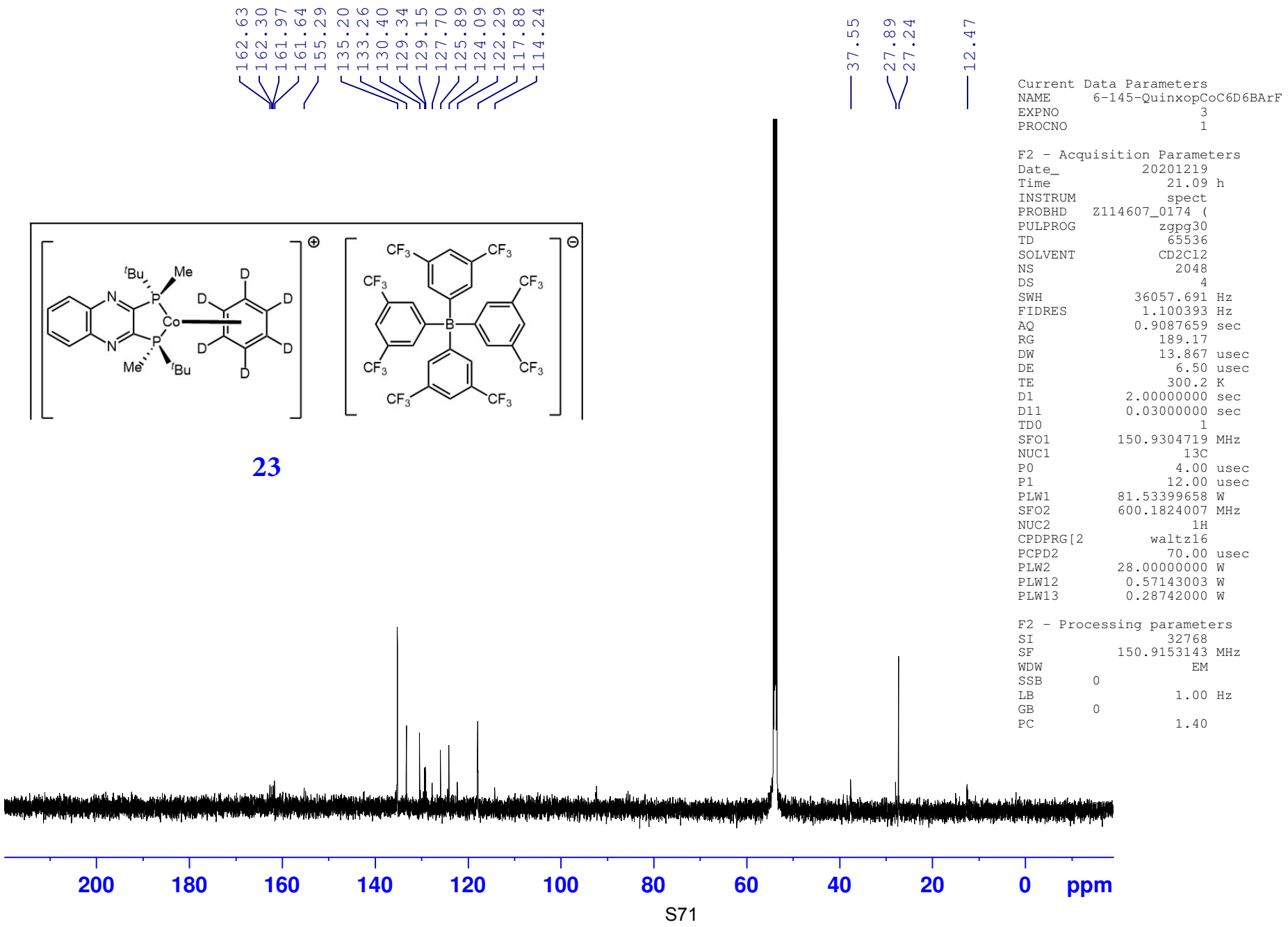


23

^{1}H NMR in CD_2Cl_2 (600 MHz)



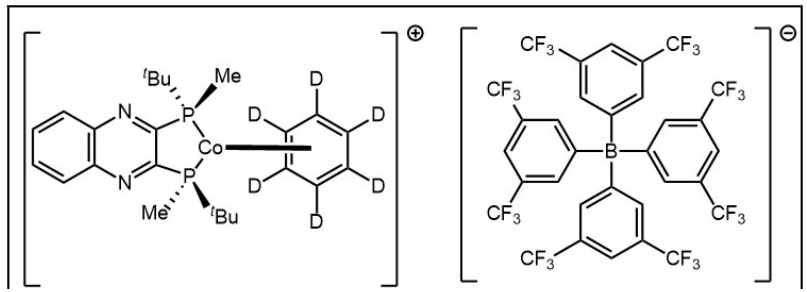
^{13}C NMR in CD2Cl2 (150 MHz)



23

MP-05-156-QUINOXPCo(C6D6)BARF-31P-rerun-2048 scans

58.19

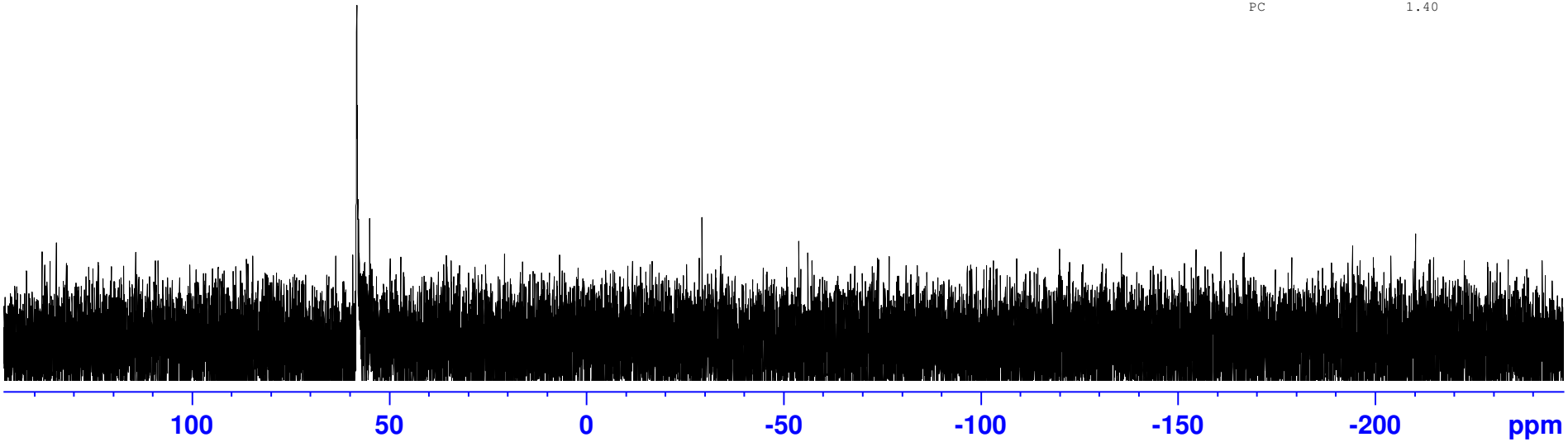


23

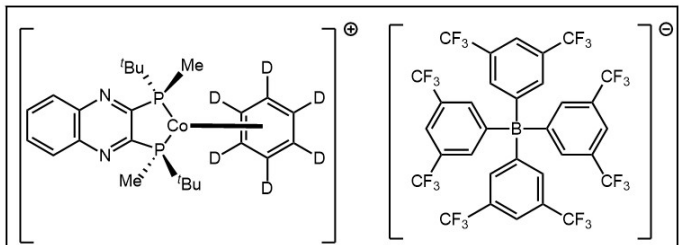
```
Current Data Parameters
NAME      MP-05-156-QUINOXPCo(C6D6)BARF
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20200713
Time              16.44 h
INSTRUM           spect
PROBHD   Z114607_0174 (
PULPROG           zg30
TD               65536
SOLVENT           C6D6
NS                2048
DS                   4
SWH           96153.844 Hz
FIDRES         2.934382 Hz
AQ             0.3407872 sec
RG               189.17
DW                5.200 usec
DE                6.50 usec
TE               300.1 K
D1            2.00000000 sec
TD0                  1
SFO1        242.9451695 MHz
NUC1               31P
P0                4.00 usec
P1               12.00 usec
PLW1        33.78099823 W

F2 - Processing parameters
SI               32768
SF          242.9573173 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



MP-05-156-QUINOXPCo(C6D6)BARF-19F



23

-62.05

```
Current Data Parameters
NAME      MP-05-156-QUINOXPCo(C6D6)BARF
EXPNO                  5
PROCNO                 1

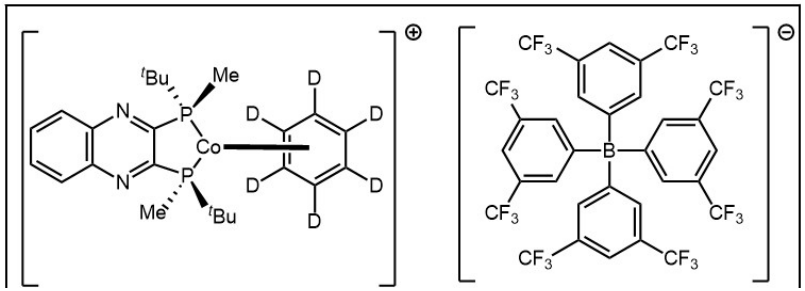
F2 - Acquisition Parameters
Date_           20200713
Time              16.54 h
INSTRUM            spect
PROBHD   Z114607_0174 (
PULPROG           zgflqn
TD                131072
SOLVENT             C6D6
NS                    128
DS                      4
SWH           133928.578 Hz
FIDRES          2.043588 Hz
AQ             0.4893355 sec
RG                189.17
DW                  3.733 usec
DE                  6.50 usec
TE                 300.2 K
D1            1.00000000 sec
TD0                    1
SFO1         564.6769619 MHz
NUC1                 19F
P1                 12.00 usec
PLW1         48.93199921 W

F2 - Processing parameters
SI                 65536
SF           564.7334352 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

^{19}F nmr in CD_2Cl_2

−62.79

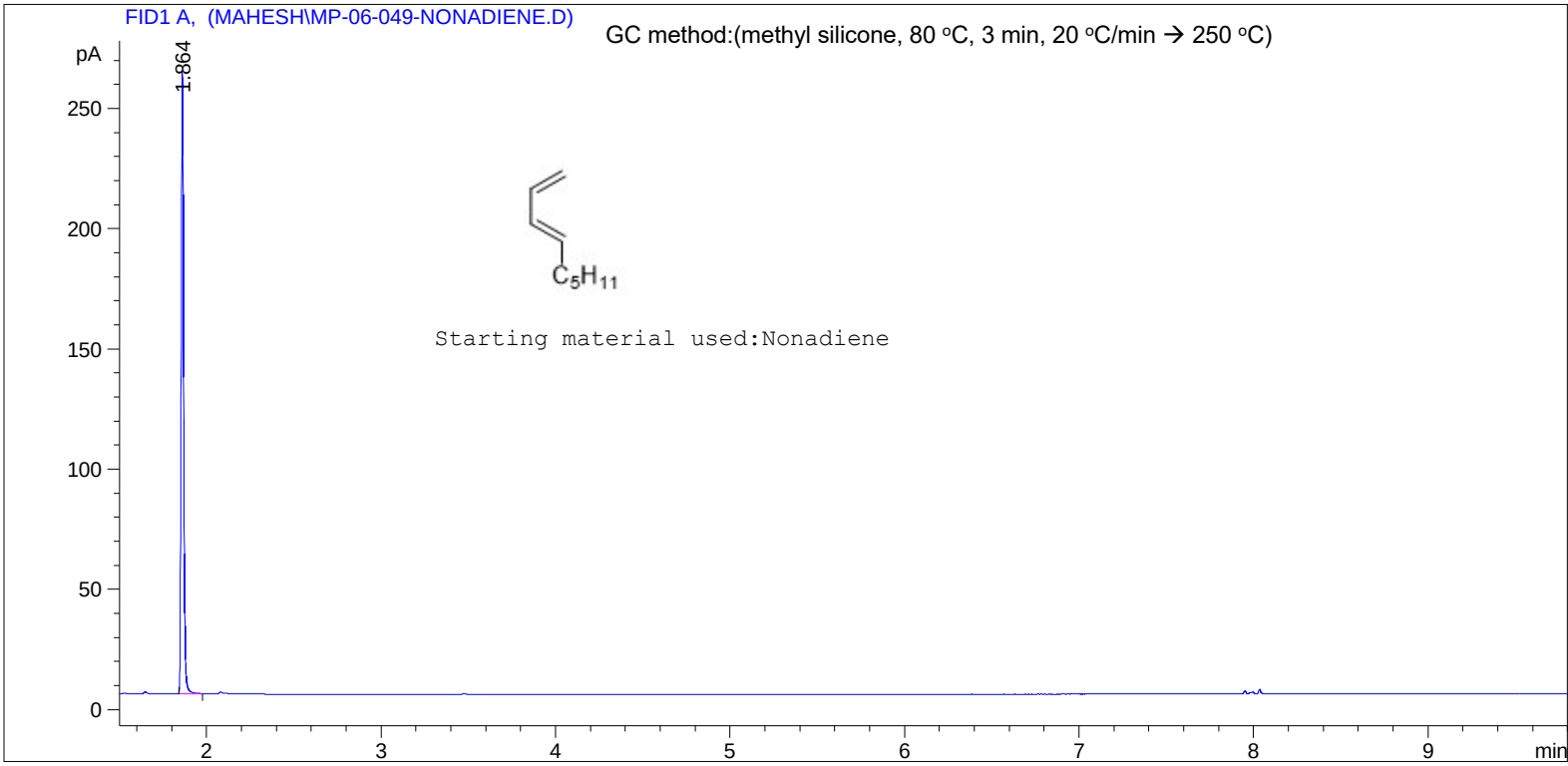


23

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-049-NONADIENE.D
Sample Name: MP-06-049-NONADIENE.D

```
==========================================================================
Acq. Operator   : MAHESH
Acq. Instrument : Instrument 1                    Location : Vial 5
Injection Date  : 7/22/2020 7:04:03 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 11/9/2018 7:49:41 PM by mahesh
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/22/2020 8:44:37 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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

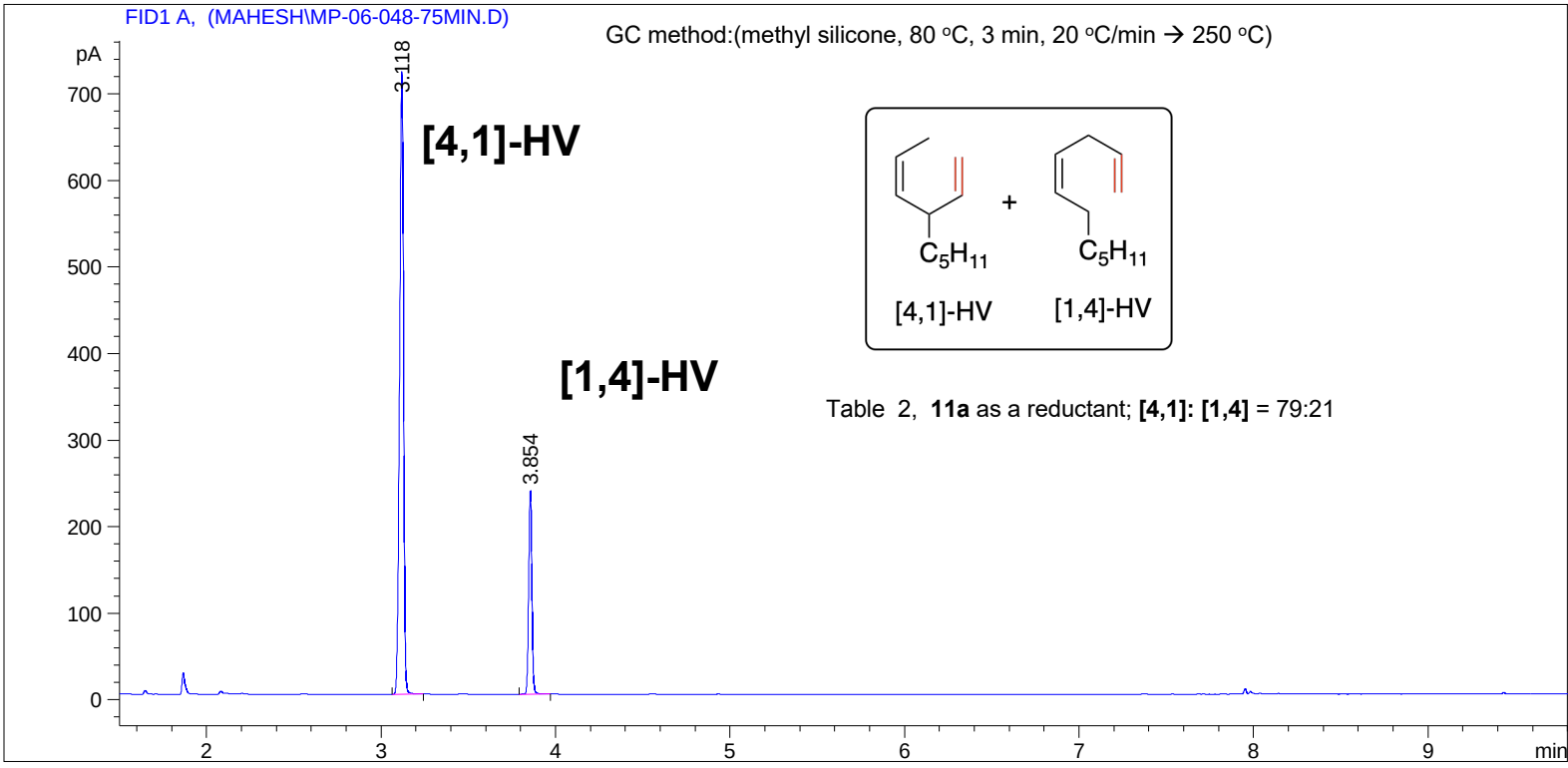

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   1.864 BB    0.0152  254.16351  258.91553 1.000e2
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-048-75MIN.D
Sample Name: MP-06-048-75MIN.D

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 4
Injection Date  : 7/22/2020 6:00:29 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 11/9/2018 7:49:41 PM by mahesh
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/22/2020 9:08:29 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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

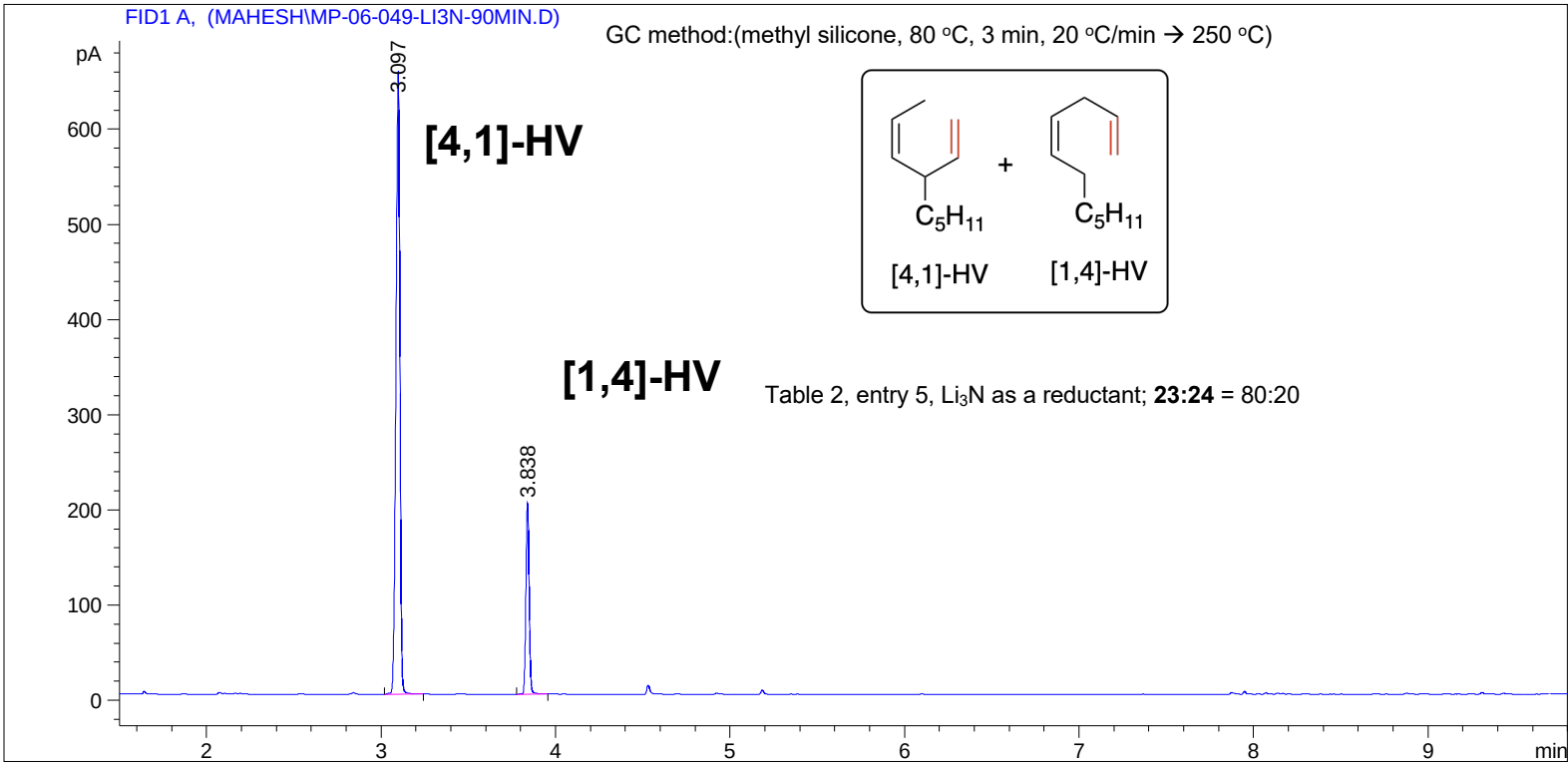

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   3.118 BB    0.0241 1130.81628  719.54199 78.91528
   2   3.854 BB    0.0202  302.13342  235.28177 21.08472
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-049-LI3N-90MIN.D
Sample Name: MP-06-049-LI3N-90MIN.D

```
==========================================================================
Acq. Operator   : MAHESH
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/22/2020 9:07:24 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/22/2020 9:03:55 PM by MAHESH
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/22/2020 9:19:08 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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

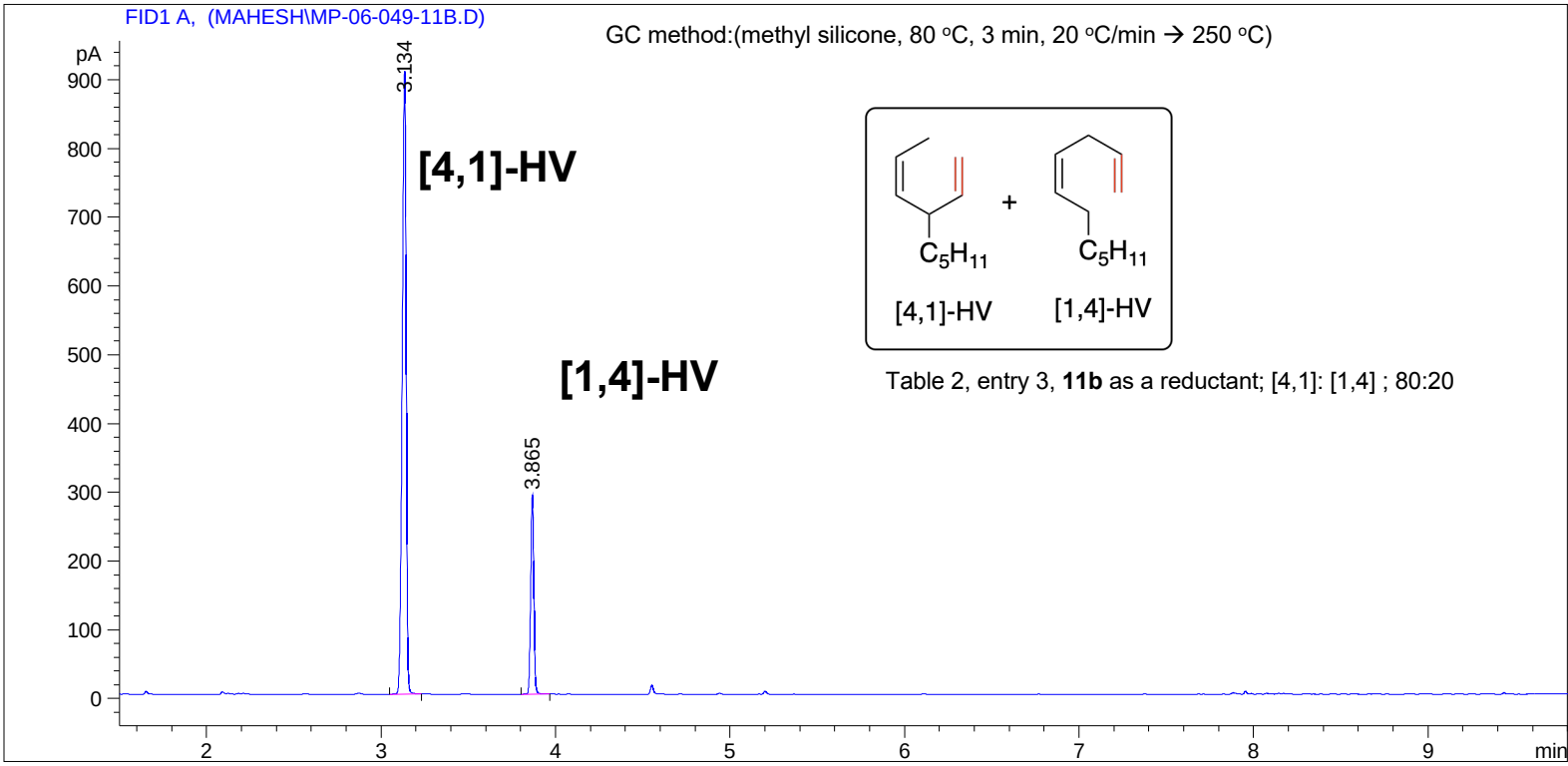

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   3.097 BB    0.0251 1043.61243  654.43933 79.92718
   2   3.838 BB    0.0204  262.09161  201.19478 20.07282
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-049-11B.D
Sample Name: MP-06-049-11B.D

```
==========================================================================
Acq. Operator   : MAHESH
Acq. Instrument : Instrument 1                    Location : Vial 4
Injection Date  : 7/22/2020 8:05:15 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/22/2020 7:20:34 PM by MAHESH
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/22/2020 9:08:29 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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

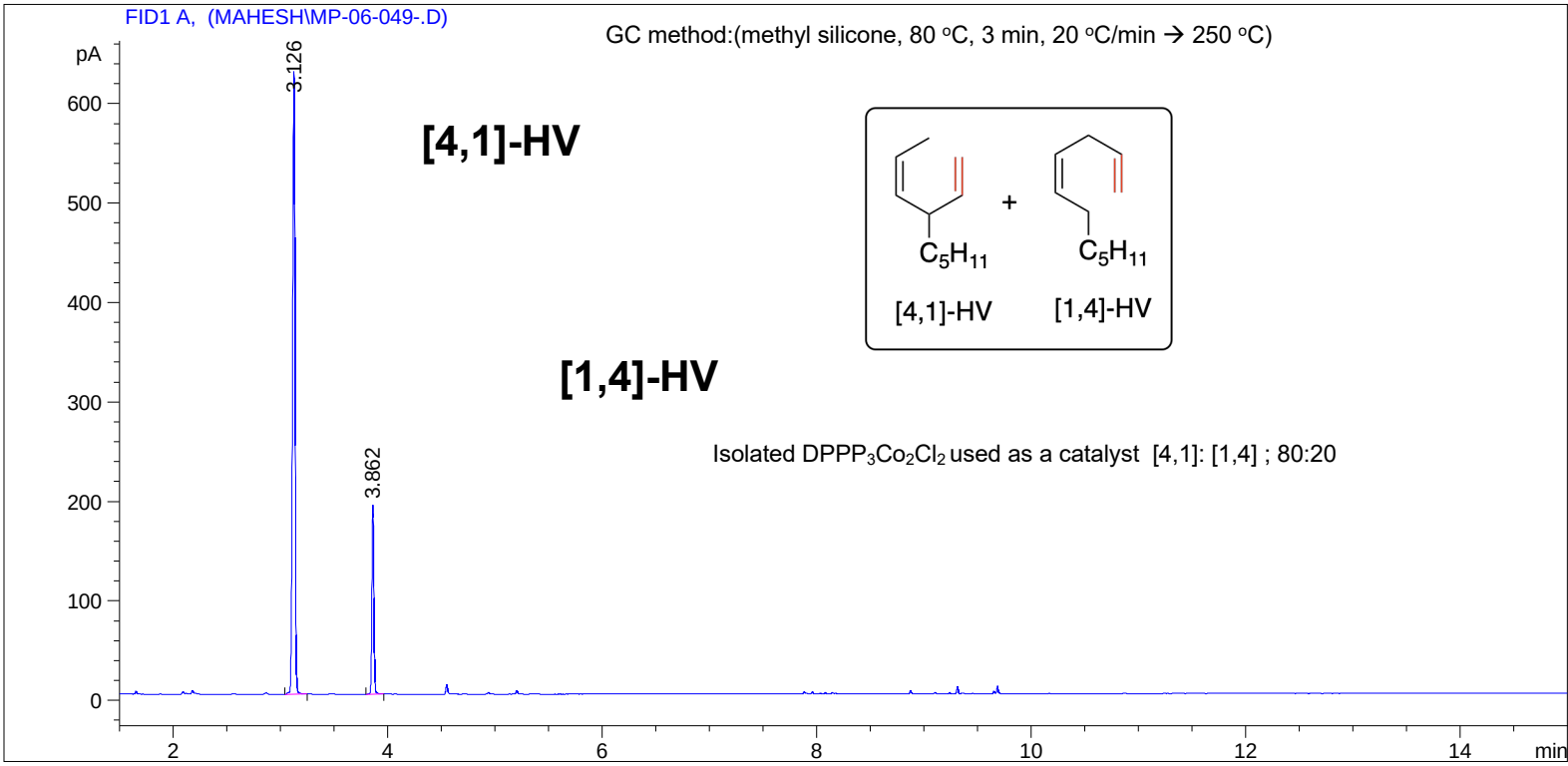

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   3.134 BB    0.0243 1422.05847  905.30200 79.62317
   2   3.865 BB    0.0197  363.92719  289.12943 20.37683
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-049-.D
Sample Name: MP-06-049-.D

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 5
Injection Date  : 7/22/2020 3:43:23 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 11/9/2018 7:49:41 PM by mahesh
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/22/2020 8:40:48 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: FID1 A,

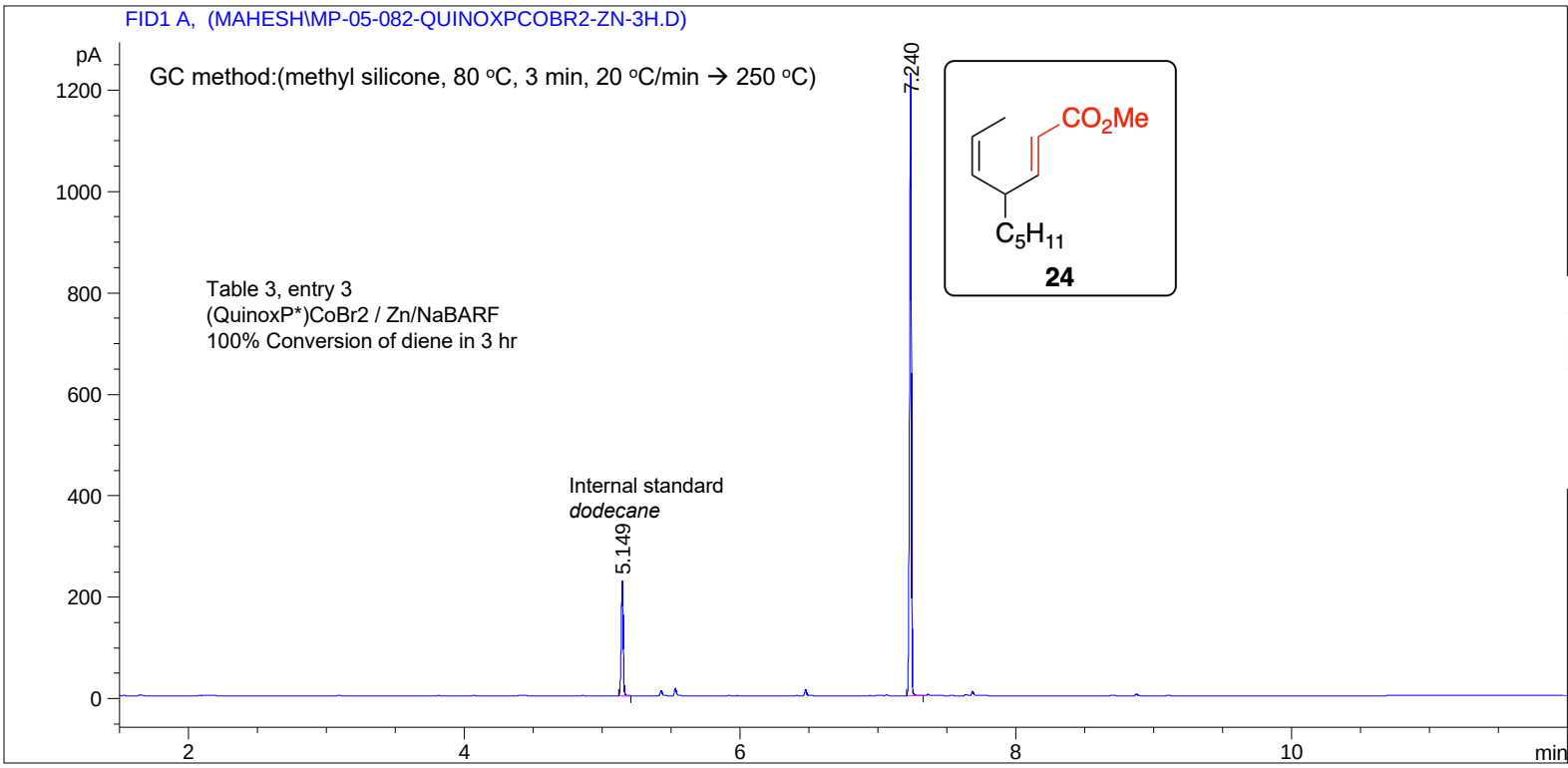
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   3.126 BB    0.0247  991.16547  626.02551 80.08844
   2   3.862 BB    0.0203  246.42316  190.48459 19.91156
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-05-082-QUINOXPCOBR2-ZN-3H.D
Sample Name: MP-05-082-QUINOXPCoBr2-Zn-3H.D

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 2
Injection Date  : 7/30/2019 9:21:08 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/30/2019 9:17:48 PM by MP
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/18/2020 1:24:31 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Sample Info     : dcm-3h-rt


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-05-082-QUINOXPCOBR2-ZN-3H.D
Sample Name: MP-05-082-QUINOXPCoBr2-Zn-3H.D

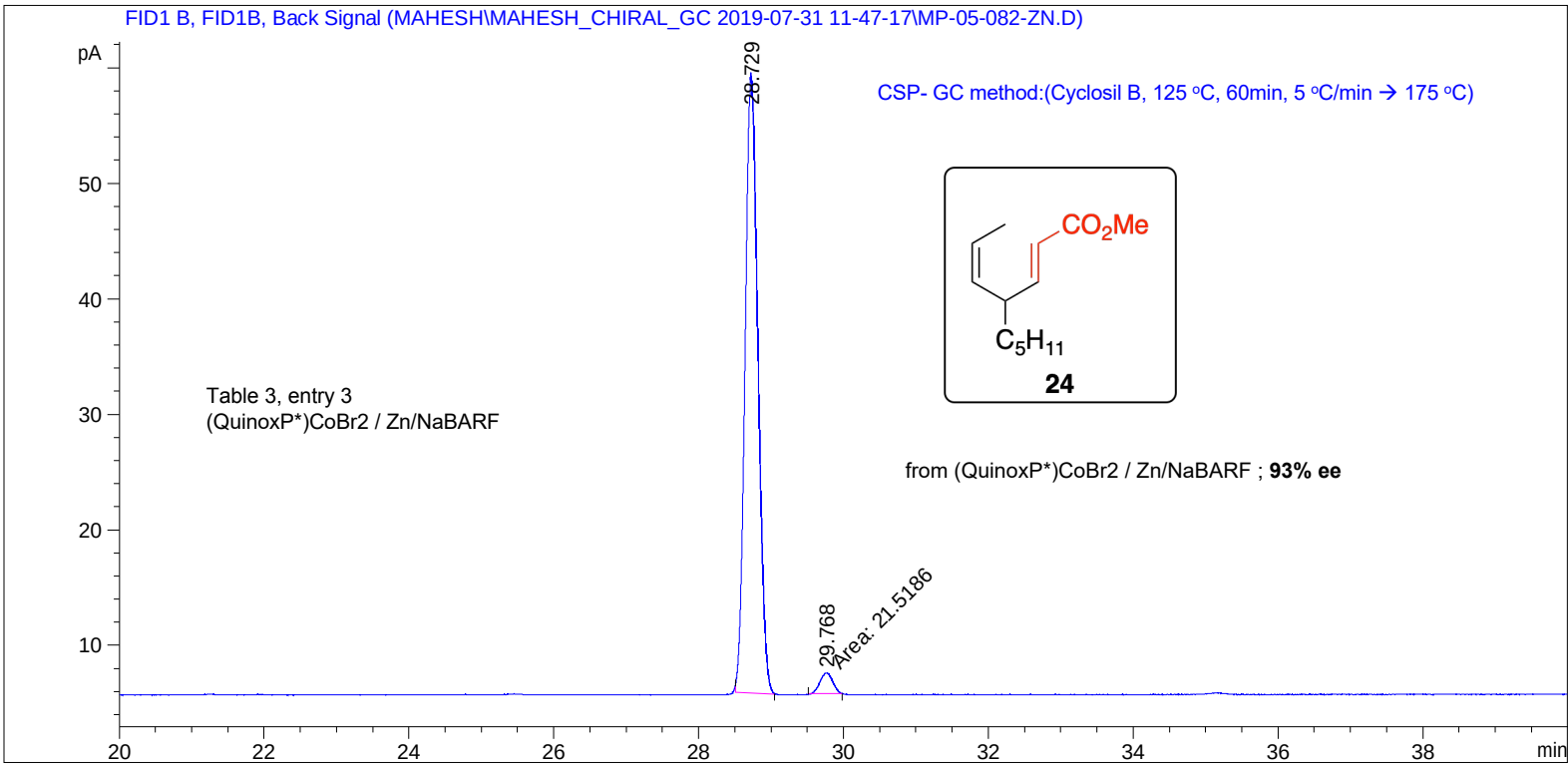
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.149	BB	0.0153	224.15259	226.86758	16.62074
2	7.240	BB	0.0142	1124.47925	1227.58936	83.37926
Totals :				1348.63184	1454.45694	

*** End of Report ***

Data File C:\CHEM32.NEW\1\DATA\MAHESH\MAHESH_CHIRAL_GC 2019-07-31 11-47-17\MP-05-082-ZN.D
Sample Name: MP-05-082-Zn

```
==========================================================================
Acq. Operator   : mp                                Seq. Line :   2
Acq. Instrument : Instrument 1                     Location : Vial 202
Injection Date  : 7/31/2019 1:11:23 PM                  Inj :   1
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\DATA\MAHESH\MAHESH_CHIRAL_GC 2019-07-31 11-47-17\MP-125-ISO-
                  CHIRAL-CYCLOSIL.M
Last changed    : 7/31/2019 12:41:21 PM by mp
                  (modified after loading)
Analysis Method : C:\CHEM32.NEW\1\METHODS\LI-90-ISO300-RAMP5-CYCLOSIL.M
Last changed    : 7/18/2020 2:10:01 PM by MP
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: FID1 B, FID1B, Back Signal

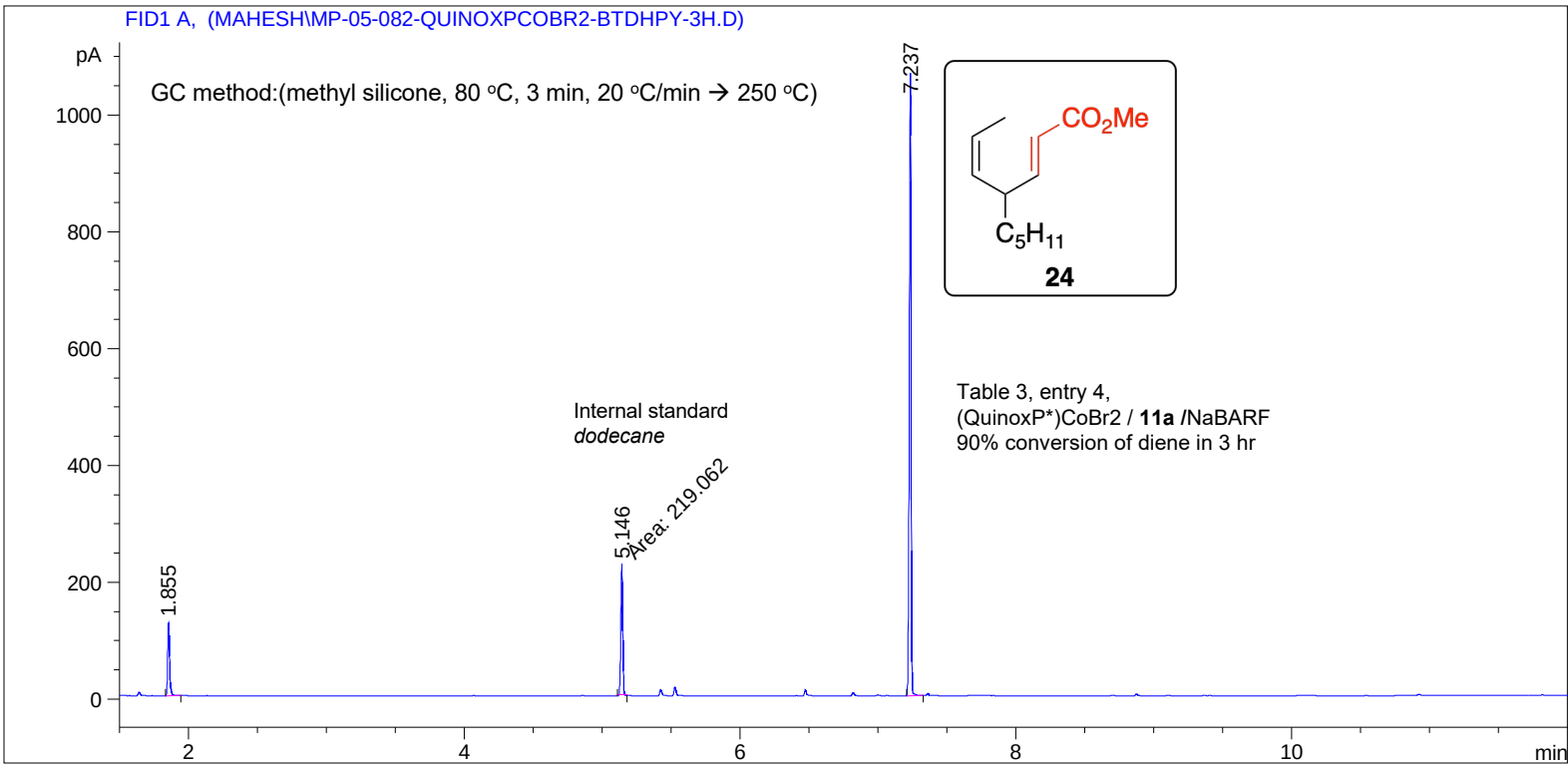
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  28.729 BB    0.1487  657.81714   53.63758 96.83241
   2  29.768 MM    0.2003   21.51856    1.79078  3.16759
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-05-082-QUINOXPCOBR2-BTDHPY-3H.D
Sample Name: MP-05-082-QUINOXPCOBR2-BTDHPY-3H.D

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 3
Injection Date  : 7/30/2019 9:37:37 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/30/2019 9:34:13 PM by MP
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/18/2020 1:26:37 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Sample Info     : dcm-3h-rt


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-05-082-QUINOXPCOBR2-BTDHPY-3H.D
Sample Name: MP-05-082-QUINOXPCOBR2-BTDHPY-3H.D

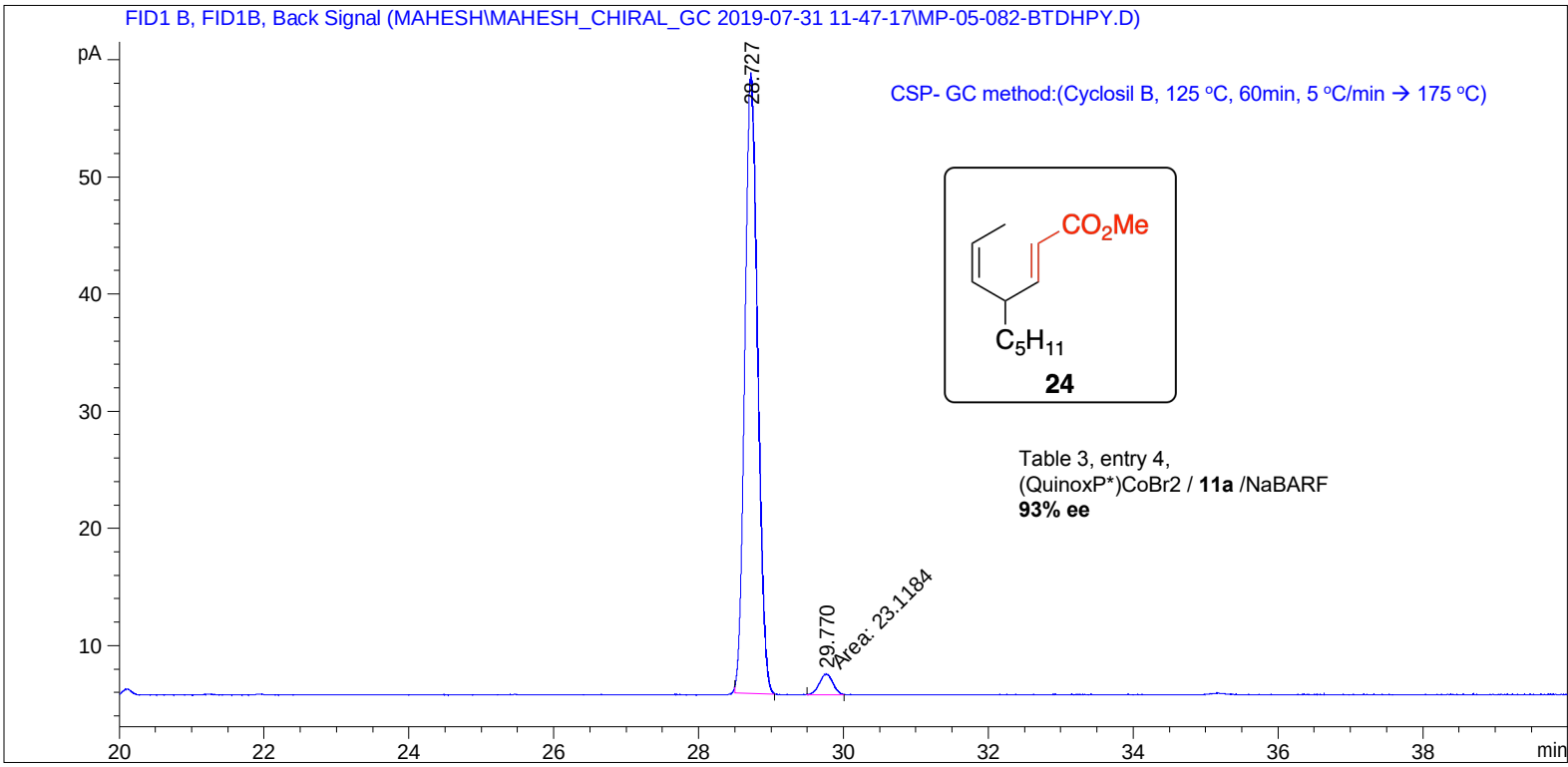
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.855	BB	0.0152	123.01768	125.06725	9.34019
2	5.146	MM	0.0163	219.06192	224.35565	16.63241
3	7.237	BB	0.0139	974.99933	1066.07556	74.02740
Totals :				1317.07893	1415.49846	

*** End of Report ***

Data File C:\CHEM32....DATA\MAHESH\MAHESH_CHIRAL_GC 2019-07-31 11-47-17\MP-05-082-BTDHPY.D
Sample Name: MP-05-082-btdhpy

```
==========================================================================
Acq. Operator   : mp                              Seq. Line :   3
Acq. Instrument : Instrument 1                    Location : Vial 203
Injection Date  : 7/31/2019 2:33:49 PM                 Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\DATA\MAHESH\MAHESH_CHIRAL_GC 2019-07-31 11-47-17\MP-125-ISO-
                  CHIRAL-CYCLOSIL.M
Last changed    : 7/31/2019 12:41:21 PM by mp
                  (modified after loading)
Analysis Method : C:\CHEM32.NEW\1\METHODS\LI-90-ISO300-RAMP5-CYCLOSIL.M
Last changed    : 7/18/2020 2:11:04 PM by MP
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: FID1 B, FID1B, Back Signal

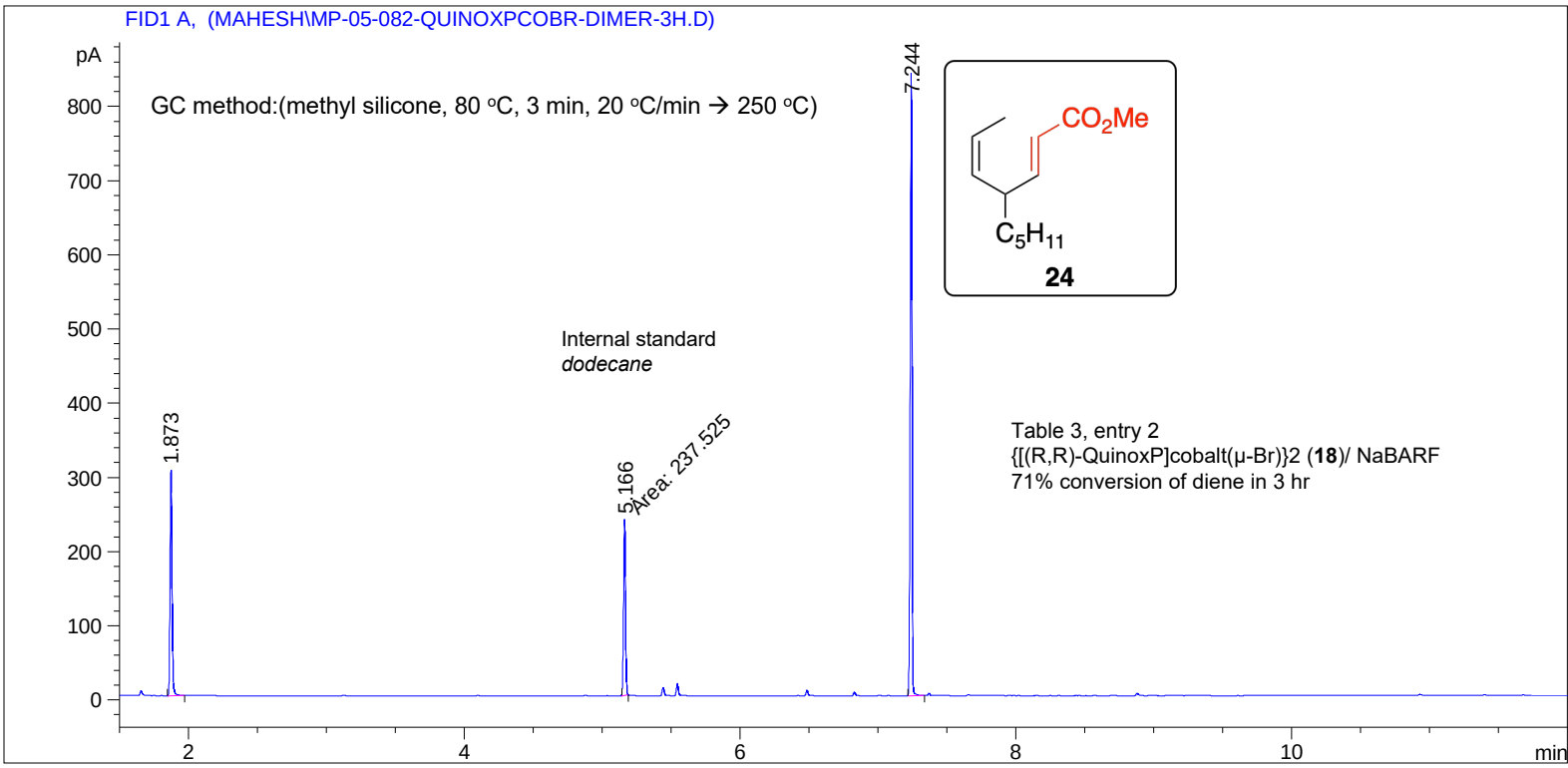
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  28.727 BB    0.1497  650.14160   52.92645 96.56620
   2  29.770 MM    0.2171   23.11838    1.77452  3.43380
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-05-082-QUINOXPCOBR-DIMER-3H.D
Sample Name: MP-05-082-QUINOXPCoBr-dimer-3H

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/30/2019 9:05:14 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 11/9/2018 7:49:41 PM by mahesh
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/18/2020 1:26:37 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Sample Info     : dcm-3h-rt


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-05-082-QUINOXPCOBR-DIMER-3H.D
Sample Name: MP-05-082-QUINOXPCoBr-dimer-3H

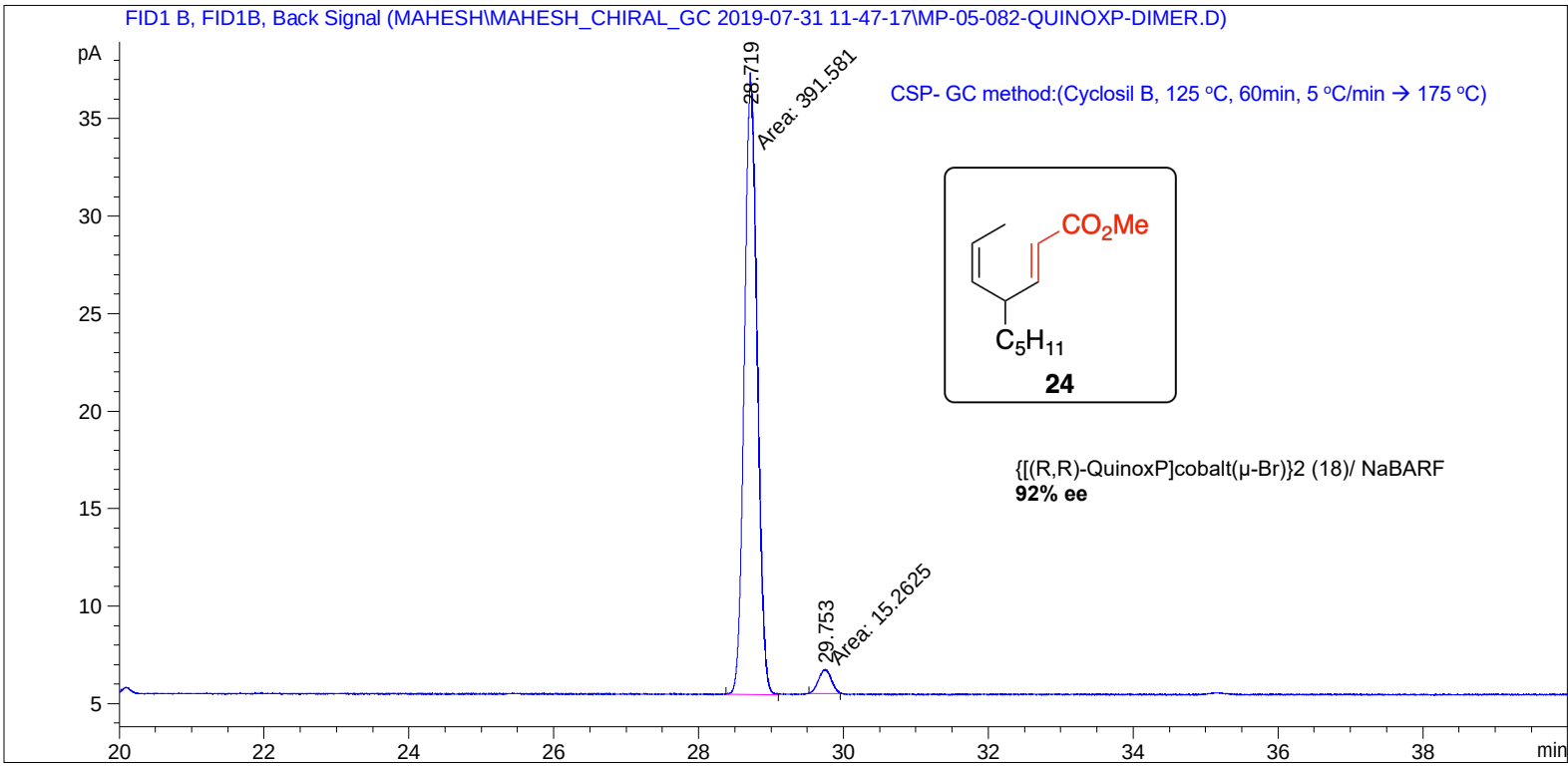
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.873	BB	0.0161	308.49216	304.28009	23.78464
2	5.166	MM	0.0167	237.52470	237.38588	18.31308
3	7.244	BB	0.0139	751.00549	839.08966	57.90228
Totals :				1297.02235	1380.75563	

*** End of Report ***

Data File C:\CHEM32....HESH\MAHESH_CHIRAL_GC 2019-07-31 11-47-17\MP-05-082-QUINOXP-DIMER.D
Sample Name: MP-05-082-QUINOXP-DIMER

```
==========================================================================
Acq. Operator   : mp                                Seq. Line :   1
Acq. Instrument : Instrument 1                       Location : Vial 201
Injection Date  : 7/31/2019 11:48:56 AM                  Inj :   1
                                                   Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\DATA\MAHESH\MAHESH_CHIRAL_GC 2019-07-31 11-47-17\MP-125-ISO-
                  CHIRAL-CYCLOSIL.M
Last changed    : 7/31/2019 12:41:21 PM by mp
                  (modified after loading)
Analysis Method : C:\CHEM32.NEW\1\METHODS\LI-90-ISO300-RAMP5-CYCLOSIL.M
Last changed    : 7/18/2020 2:07:49 PM by MP
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

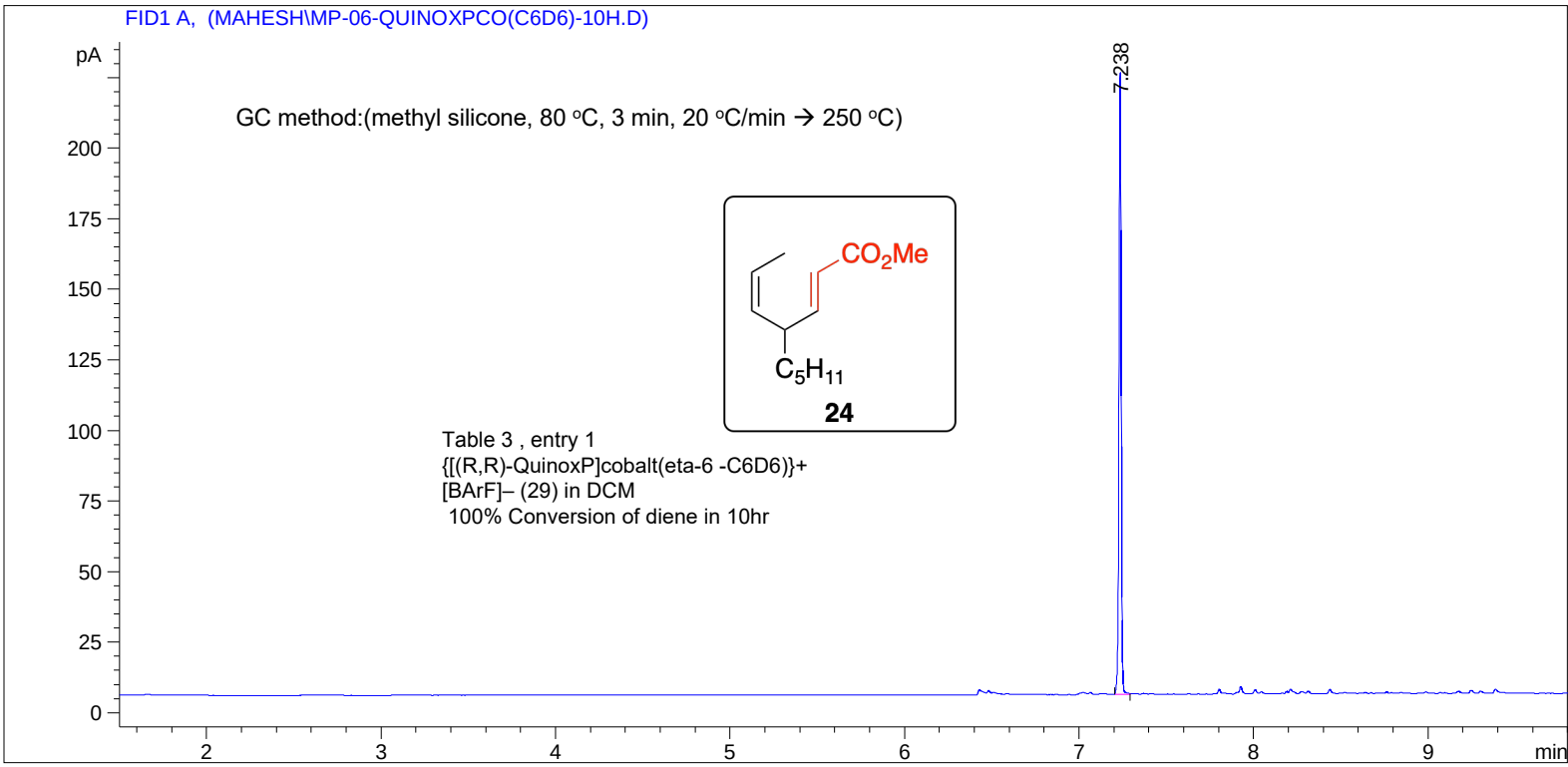
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, FID1B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  28.719 MM    0.2052  391.58096   31.80393 96.24855
   2  29.753 MM    0.2061   15.26251    1.23429  3.75145
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-QUINOXPCO(C6D6)-10H.D
Sample Name: MP-06-quinoxpCo(C6D6)-10H

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/21/2020 6:34:34 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 11/9/2018 7:49:41 PM by mahesh
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 7/22/2020 8:44:37 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min
```




```
==========================================================================
                        Area Percent Report
==========================================================================

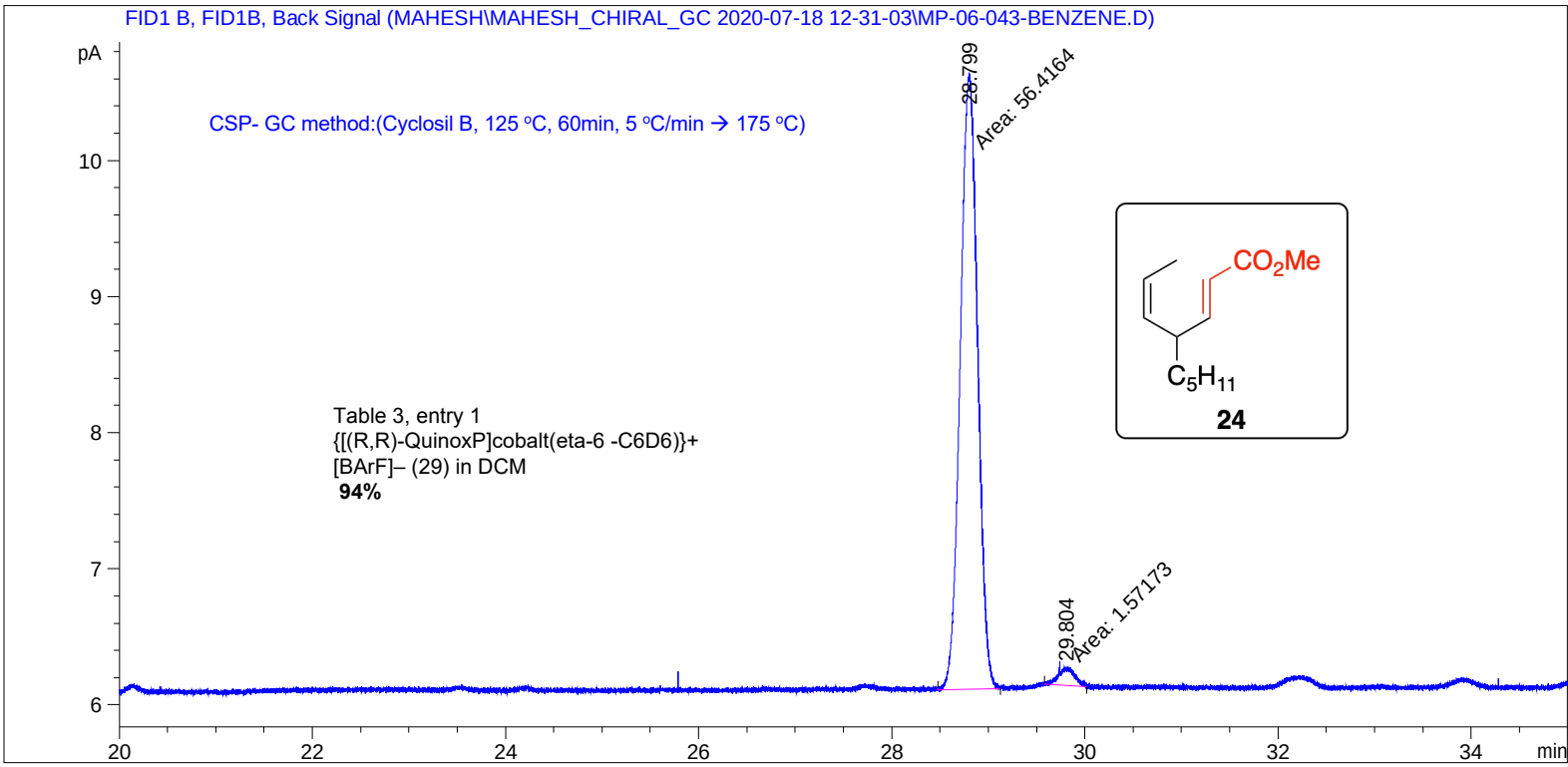
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   0.885 BB S  0.0123 6.27043e4  6.80424e4  99.49537
   2   1.174 BV    0.0177  121.58495  114.02174  0.19292
   3   7.238 BV    0.0139  196.44603  220.20207  0.31171
```

Data File C:\CHEM32....ATA\MAHESH\MAHESH_CHIRAL_GC 2020-07-18 12-31-03\MP-06-043-BENZENE.D
Sample Name: mp-06-043-benzene

```
==========================================================================
Acq. Operator   : MP                                 Seq. Line :   2
Acq. Instrument : Instrument 1                       Location : Vial 203
Injection Date  : 7/18/2020 8:15:04 PM                    Inj :   1
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\DATA\MAHESH\MAHESH_CHIRAL_GC 2020-07-18 12-31-03\MP-125-ISO-
                  CHIRAL-CYCLOSIL.M
Last changed    : 2/16/2020 6:29:57 PM by MP
Analysis Method : C:\CHEM32.NEW\1\METHODS\LI-90-ISO300-RAMP5-CYCLOSIL.M
Last changed    : 7/19/2020 6:47:53 PM by MP
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

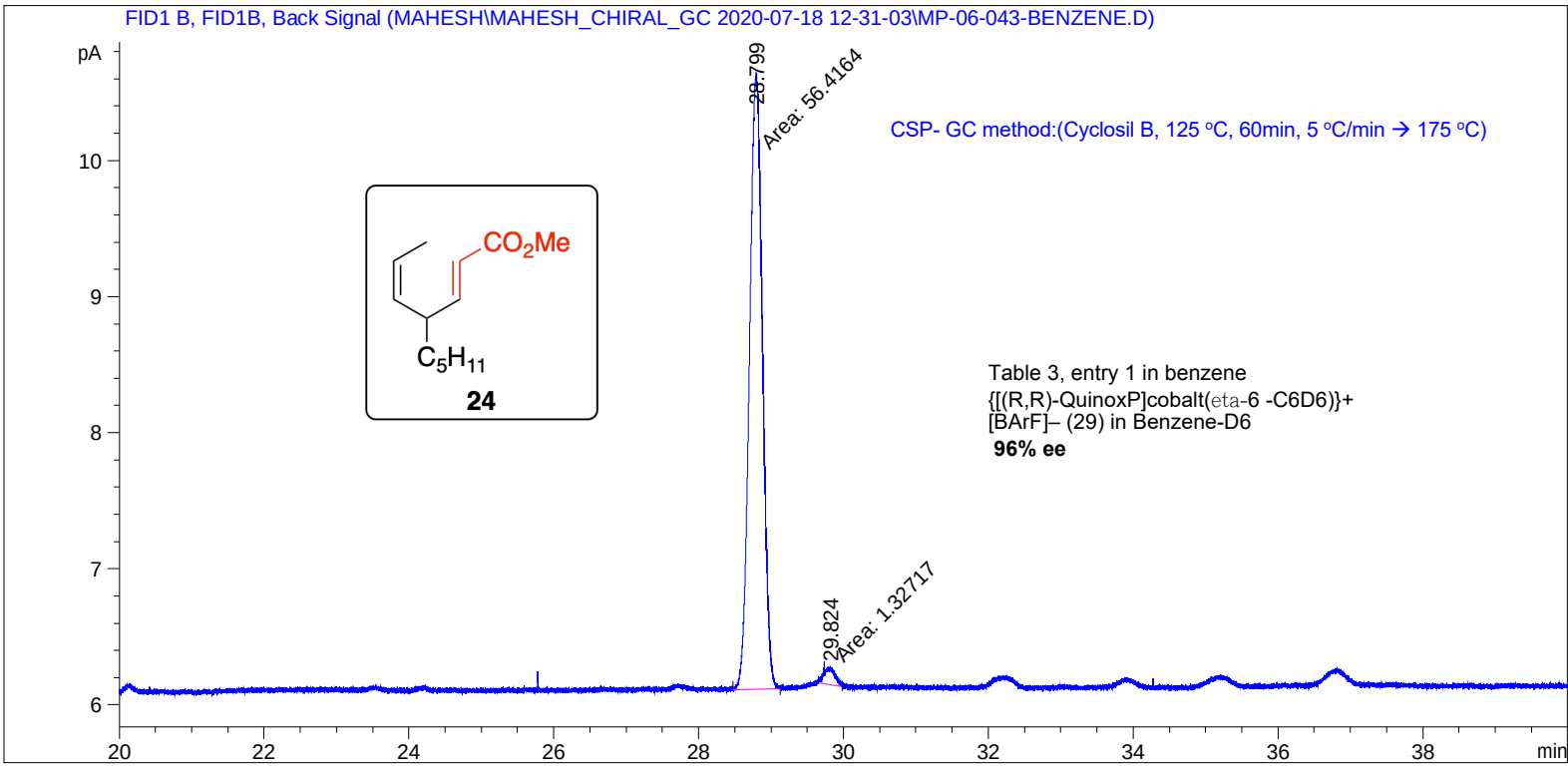
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, FID1B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  28.799 MM    0.2078   56.41642    4.52521 97.28958
   2  29.804 MM    0.1873    1.57173 1.39847e-1  2.71042
```

Data File C:\CHEM32....ATA\MAHESH\MAHESH_CHIRAL_GC 2020-07-18 12-31-03\MP-06-043-BENZENE.D
Sample Name: mp-06-043-benzene

```
==========================================================================
Acq. Operator   : MP                              Seq. Line :   2
Acq. Instrument : Instrument 1                    Location : Vial 203
Injection Date  : 7/18/2020 8:15:04 PM                 Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\DATA\MAHESH\MAHESH_CHIRAL_GC 2020-07-18 12-31-03\MP-125-ISO-
                  CHIRAL-CYCLOSIL.M
Last changed    : 2/16/2020 6:29:57 PM by MP
Analysis Method : C:\CHEM32.NEW\1\METHODS\LI-90-ISO300-RAMP5-CYCLOSIL.M
Last changed    : 7/21/2020 8:30:01 PM by MP
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

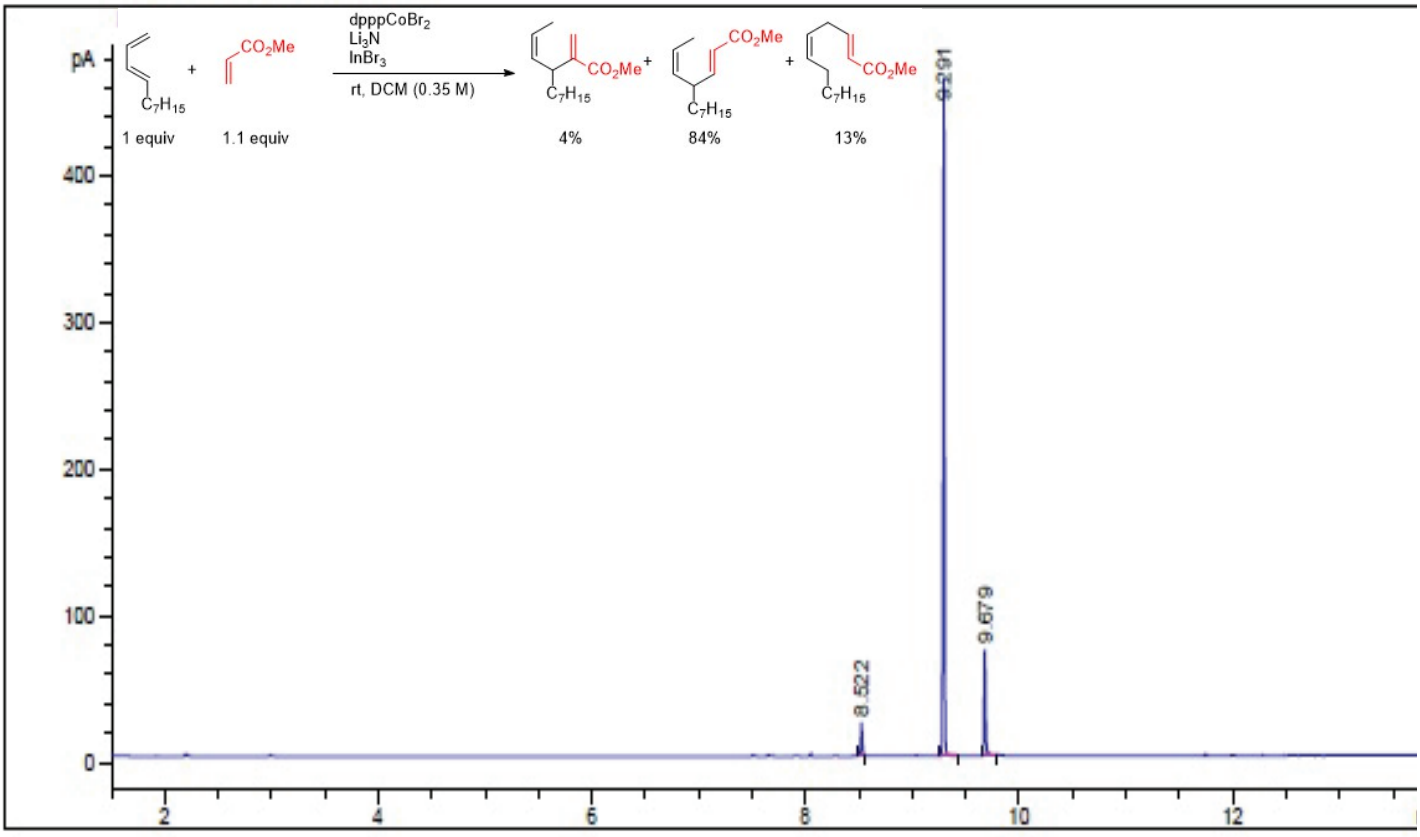
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, FID1B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  28.799 MM    0.2078   56.41642    4.52521 97.70162
   2  29.824 MM    0.1712    1.32717 1.29218e-1  2.29838
```

Table S2, Entry 2

GC Conditions: HP-5MS, 100°C, 5 min, 20°C/min to 250°C



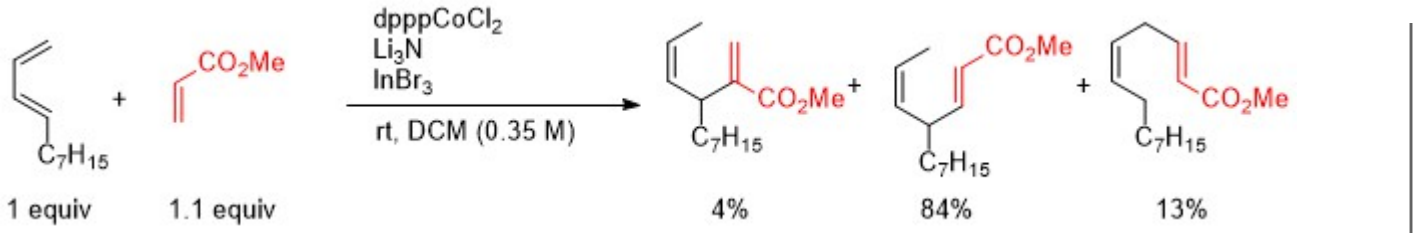

```
================================================================================
                          Area Percent Report
================================================================================

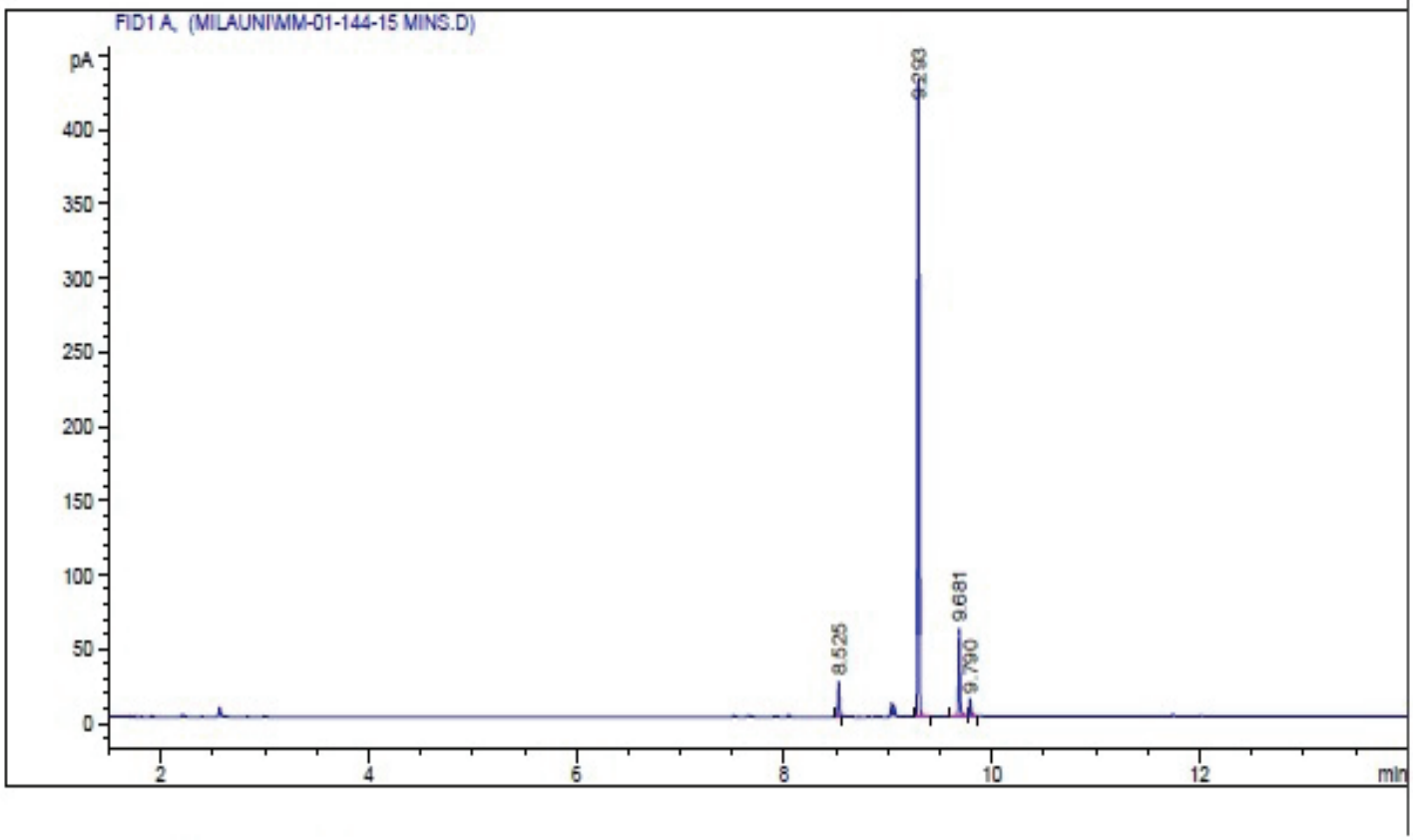
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   8.522 VV    0.0157   22.69189   22.68320  4.16608
   2   9.291 VB    0.0148  446.72842  459.56573 82.01640
   3   9.679 BV    0.0160   75.26148   72.93928 13.81751
```

Table S2, Entry 5
GC Conditions: HP-5MS, 100°C, 5 min, 20°C/min to 250°C





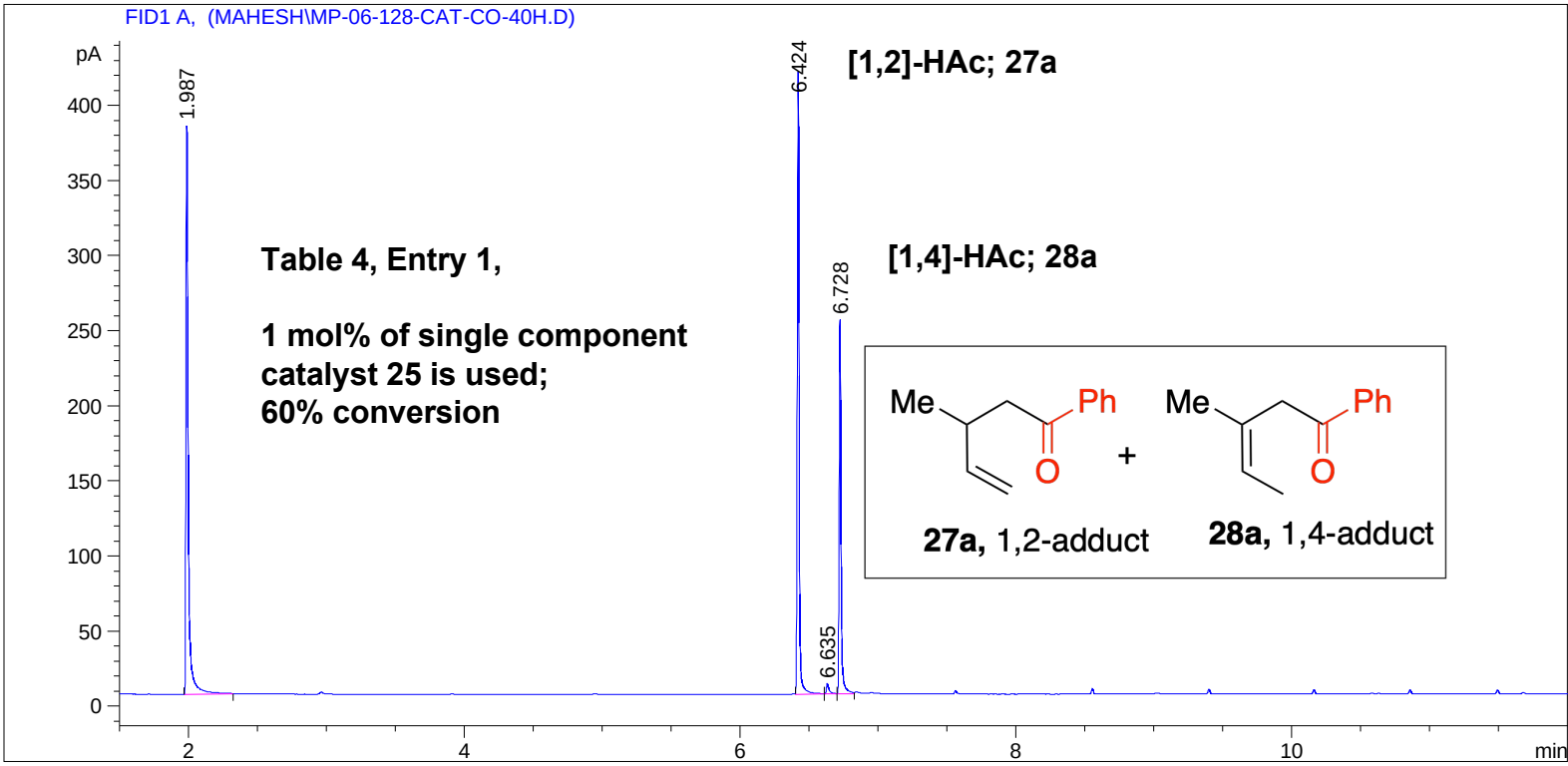
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.525	VV	0.0156	22.95272	23.15723	4.48849
2	9.293	VV	0.0152	411.92584	428.89218	80.55358
3	9.681	VV	0.0156	61.52719	59.30364	12.03186
4	9.790	VV	0.0187	14.96301	11.84402	2.92607
Totals :				511.36876	523.19708	

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-128-CAT-CO-40H.D
Sample Name: MP-06-128-CAT-CO-40H

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 16
Injection Date  : 11/12/2020 3:57:05 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 11/9/2018 7:49:41 PM by mahesh
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 3/24/2021 5:11:47 PM by Jon
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1   1.987 BB    0.0179  450.20267  378.57123 41.48139
   2   6.424 VV    0.0142  387.87872  414.54257 35.73890
```

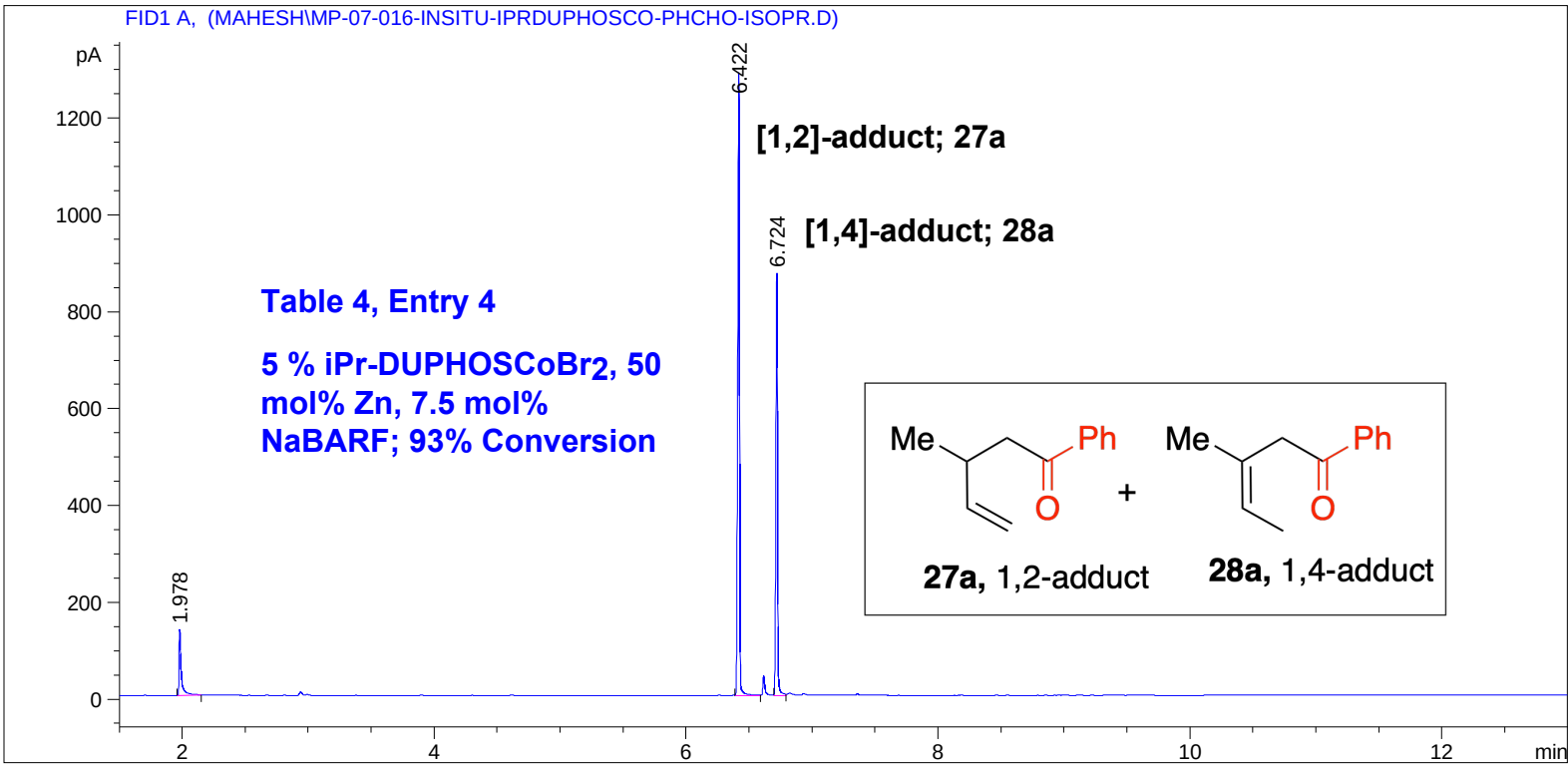
Data File C:\CHEM32\1\DATA\MAHESH\MP-06-128-CAT-CO-40H.D
Sample Name: MP-06-128-CAT-CO-40H

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
3	6.635	VV	0.0209	10.34493	7.13682	0.95318
4	6.728	VV	0.0143	236.88599	249.32899	21.82653
Totals :				1085.31231	1049.57961	

*** End of Report ***

Data File C:\CHEM32\1\DATA\MAHESH\MP-07-016-INSITU-IPRDUPHOSCO-PHCHO-ISOPR.D
Sample Name: MP-07-016-INSITU-IPRDUPHOSCO-PHCHO-ISOPR

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 15
Injection Date  : 3/30/2021 5:49:40 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 3/30/2021 5:46:01 PM by MP
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 3/30/2021 4:15:28 PM by MP
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min
```




```
==========================================================================
                        Area Percent Report
==========================================================================

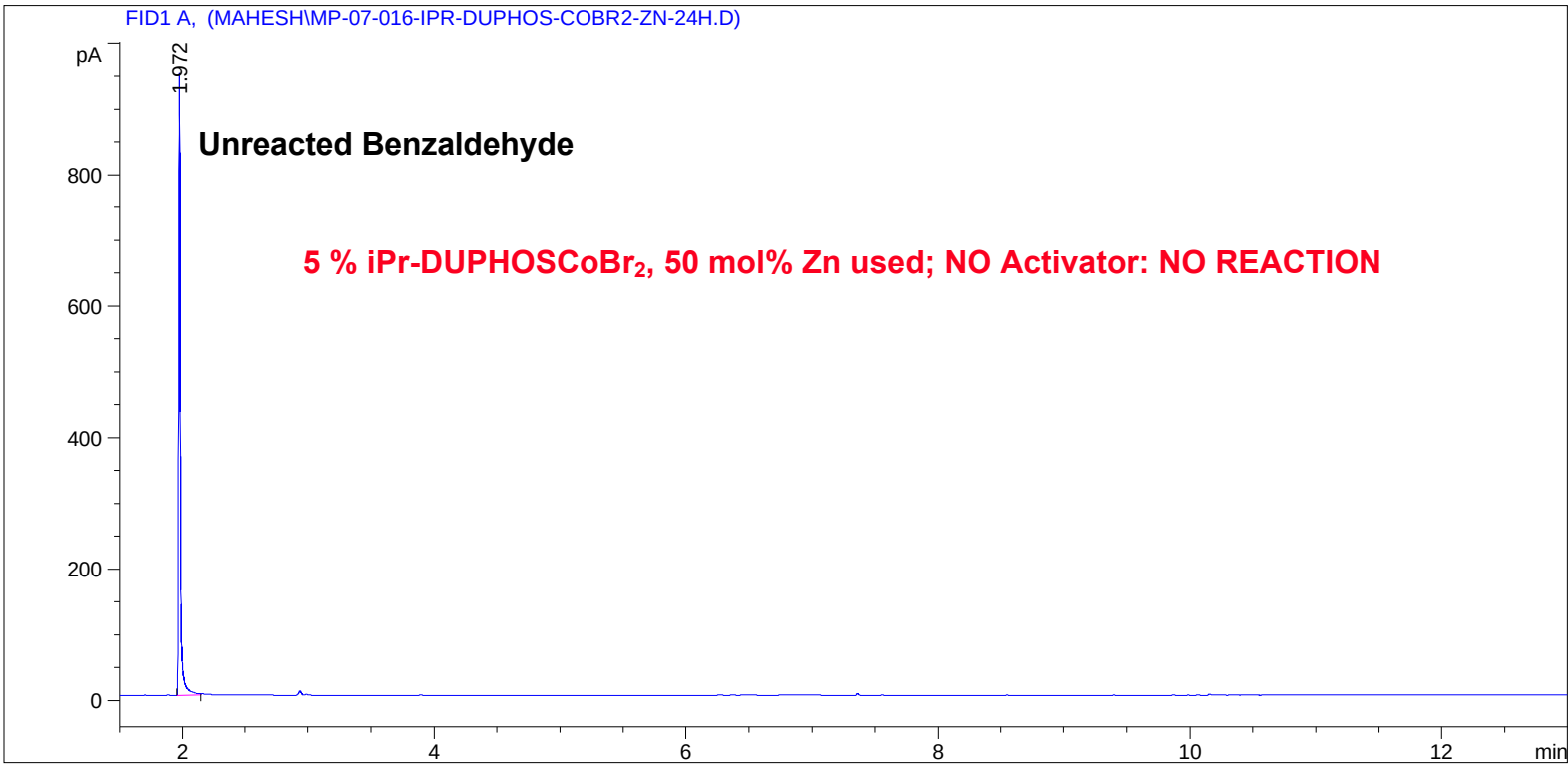
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   1.978 VV    0.0182  171.60773  136.51401  7.57846
   2   6.422 VV    0.0157 1286.15295 1287.02148 56.79845
   3   6.724 VV    0.0140  806.65472  872.00439 35.62309
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-07-016-IPR-DUPHOS-COBR2-ZN-24H.D
Sample Name: MP-07-016-IPR-DUPHOS-COBR2-ZN-24H

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 14
Injection Date  : 3/30/2021 6:08:39 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 3/30/2021 6:05:04 PM by MP
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 3/30/2021 4:15:28 PM by MP
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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

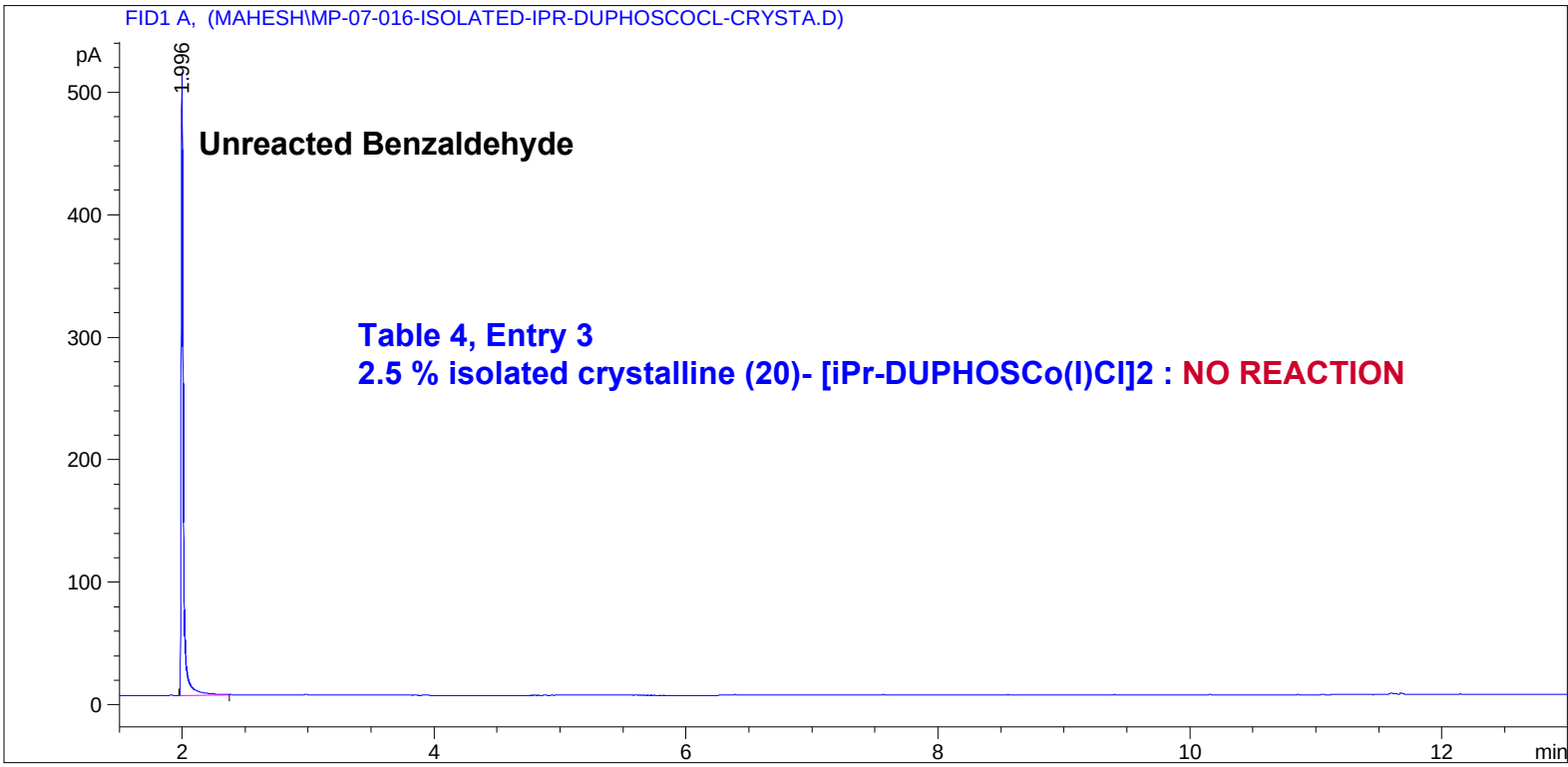

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   1.972 VV    0.0156  964.46014  948.07062 1.000e2

Totals :                   964.46014  948.07062
```

Data File C:\CHEM32\1\DATA\MAHESH\MP-07-016-ISOLATED-IPR-DUPHOSCOCL-CRYSTA.D
Sample Name: MP-07-016-ISOLATED-IPR-DUPHOSCOCL-CRYSTA

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 16
Injection Date  : 3/30/2021 5:29:31 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 3/30/2021 4:51:34 PM by DS
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed    : 3/30/2021 4:15:28 PM by MP
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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


Signal 1: FID1 A,

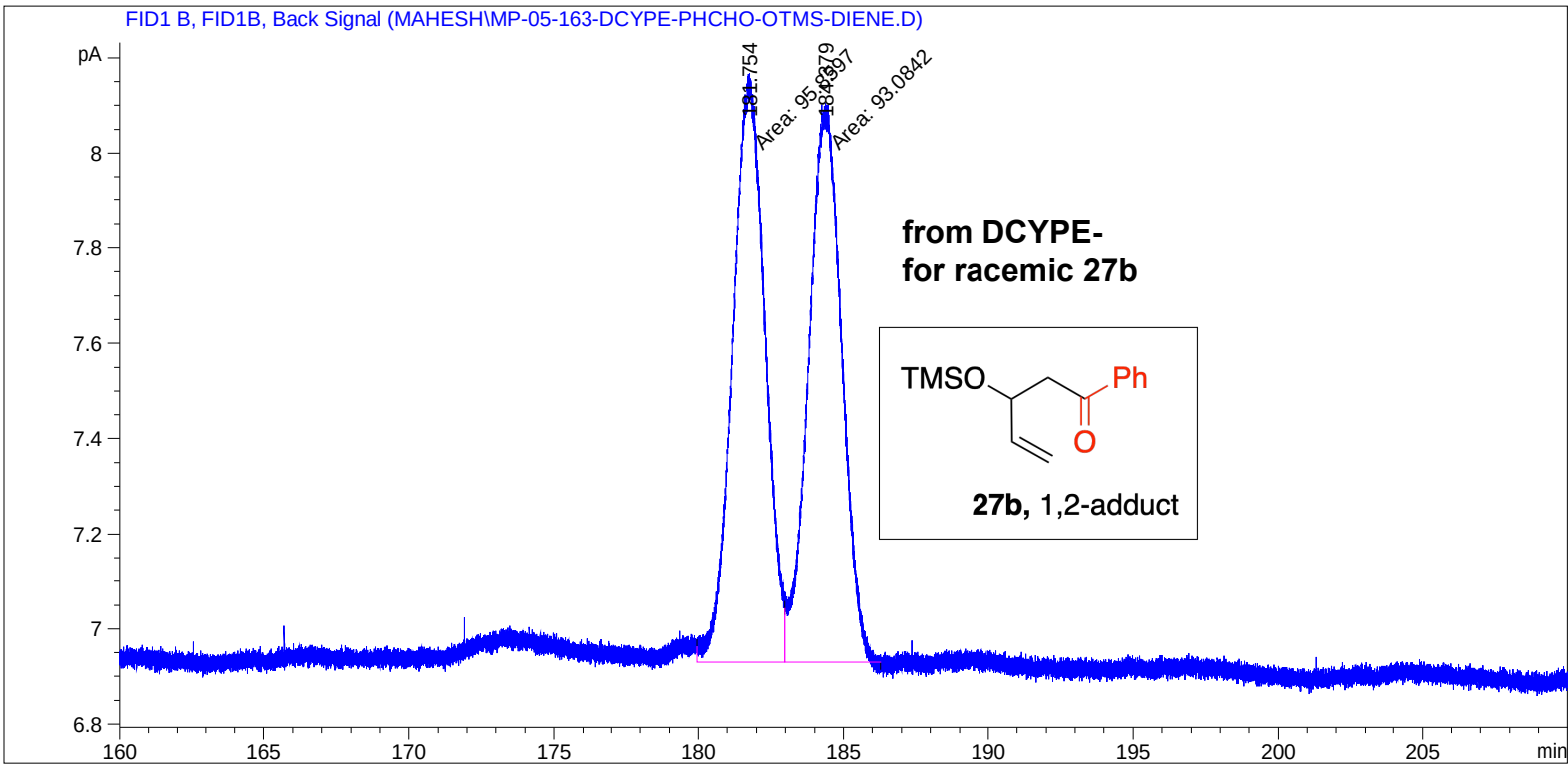
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   1.996 BB    0.0183  610.35071  508.30597 1.000e2

Totals :                   610.35071  508.30597
```

Data File C:\CHEM32.NEW\1\DATA\MAHESH\MP-05-163-DCYPE-PHCHO-OTMS-DIENE.D
Sample Name: MP-05-163-DCYPE-PHCHO-OTMS-DIENE

```
==========================================================================
Acq. Operator   : LI
Acq. Instrument : Instrument 1                    Location : Vial 202
Injection Date  : 3/12/2020 10:06:09 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\METHODS\MP-100-ISO300-CHIRAL.M
Last changed    : 3/12/2020 10:04:28 PM by LI
                  (modified after loading)
Analysis Method : C:\CHEM32.NEW\1\METHODS\LI-90-ISO300-RAMP5-CYCLOSIL.M
Last changed    : 8/19/2020 4:47:20 PM by MP
                  (modified after loading)
Sample Info     : 100-300-1-175-20


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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

Data File C:\CHEM32.NEW\1\DATA\MAHESH\MP-05-163-DCYPE-PHCHO-OTMS-DIENE.D
Sample Name: MP-05-163-DCYPE-PHCHO-OTMS-DIENE

Signal 1: FID1 B, FID1B, Back Signal

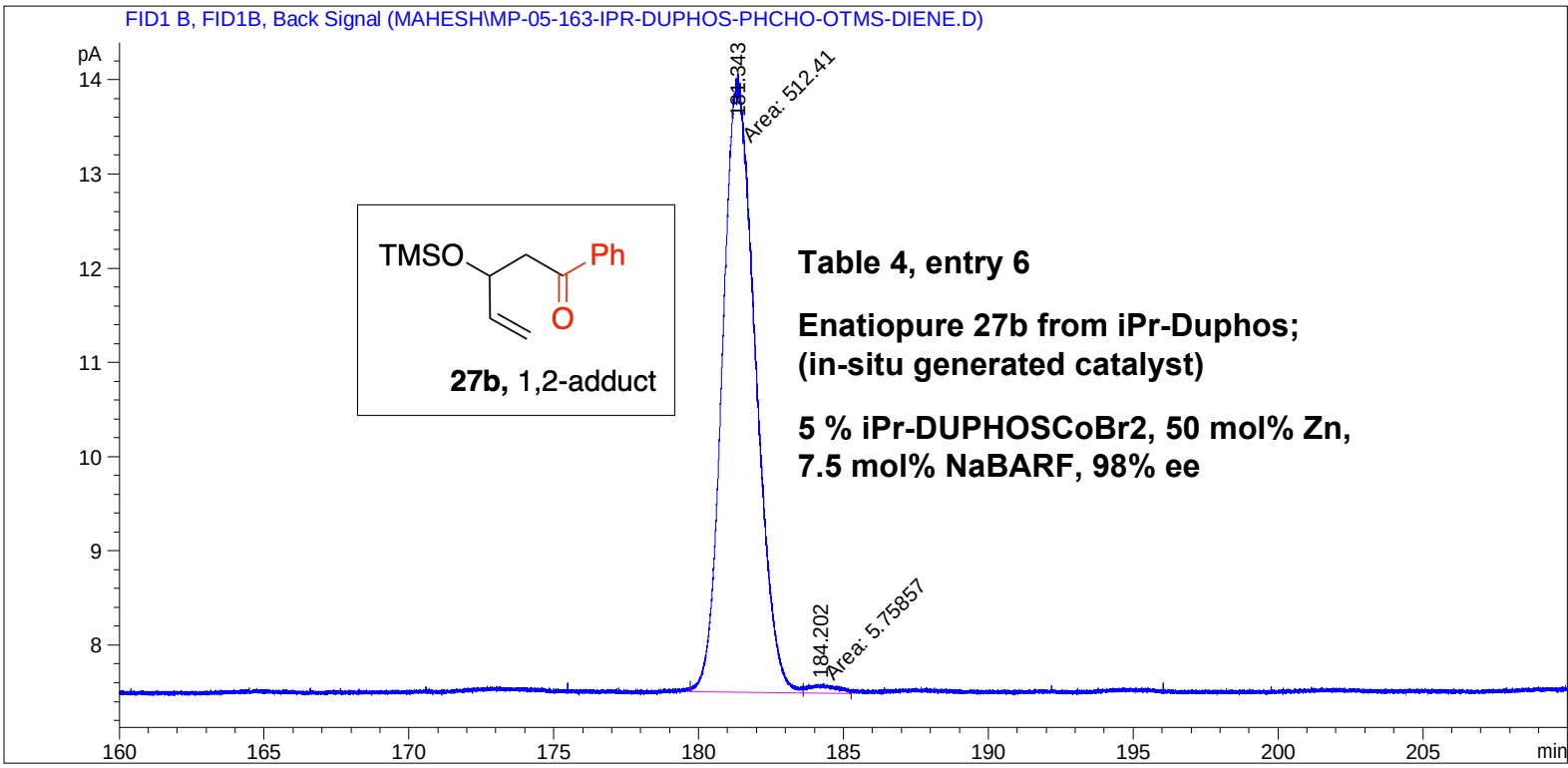
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	181.754	MF	1.3040	95.85970	1.22524	50.73448
2	184.379	FM	1.3261	93.08420	1.16987	49.26552
Totals :				188.94390	2.39511	

*** End of Report ***

Data File C:\CHEM32.NEW\1\DATA\MAHESH\MP-05-163-IPR-DUPHOS-PHCHO-OTMS-DIENE.D
Sample Name: MP-05-163-IPR-DUPHOS-PHCHO-OTMS-DIENE.D

```
==========================================================================
Acq. Operator   : LI
Acq. Instrument : Instrument 1                    Location : Vial 202
Injection Date  : 3/13/2020 12:00:37 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\METHODS\MP-100-ISO300-CHIRAL.M
Last changed    : 3/13/2020 4:18:32 PM by LI
                  (modified after loading)
Analysis Method : C:\CHEM32.NEW\1\METHODS\LI-90-ISO300-RAMP5-CYCLOSIL.M
Last changed    : 8/19/2020 4:47:20 PM by MP
                  (modified after loading)
Sample Info     : 100-300-1-175-20


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

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

Data File C:\CHEM32.NEW\1\DATA\MAHESH\MP-05-163-IPR-DUPHOS-PHCHO-OTMS-DIENE.D
Sample Name: MP-05-163-IPR-DUPHOS-PHCHO-OTMS-DIENE.D

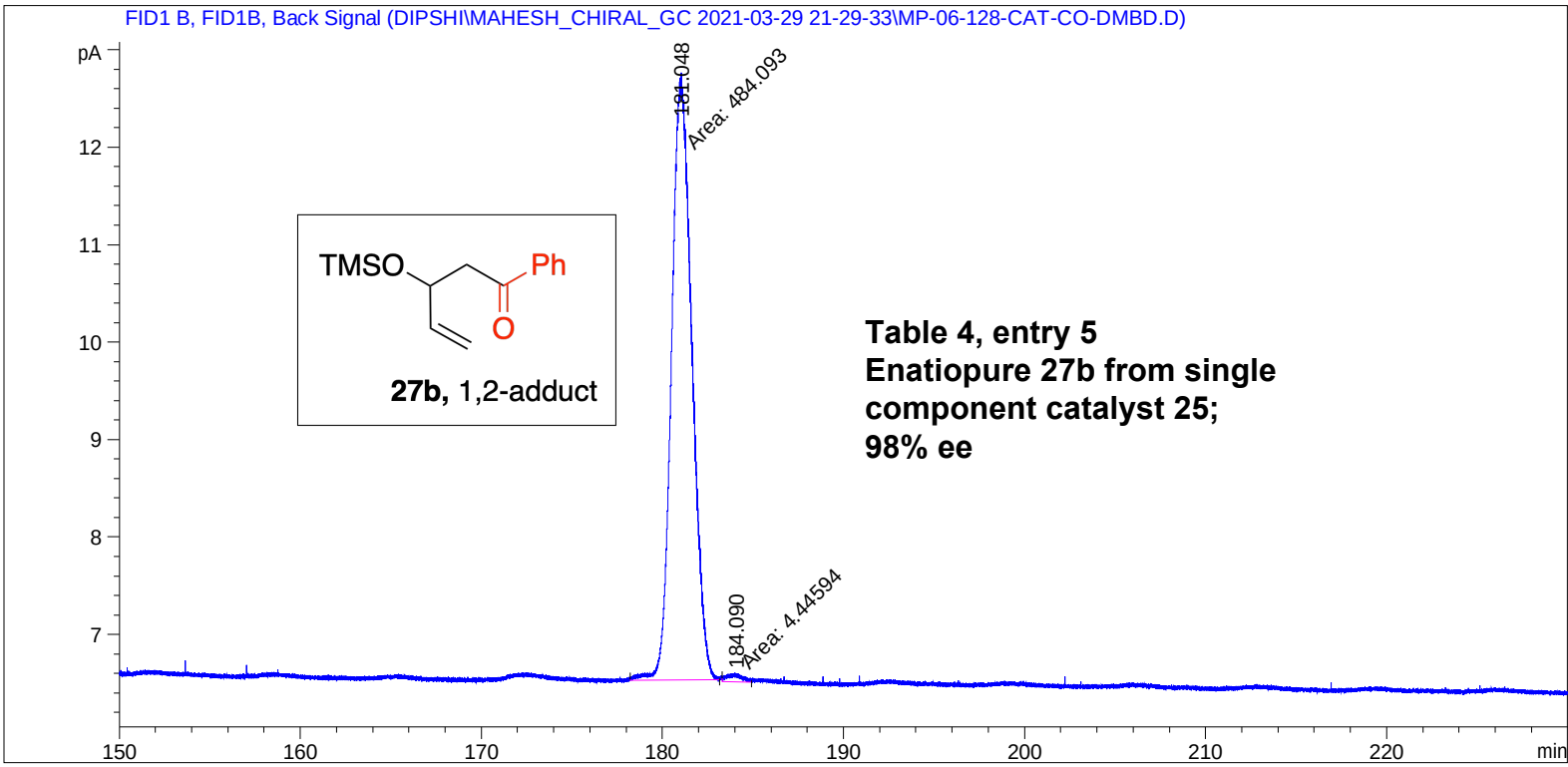
Signal 1: FID1 B, FID1B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	181.343	MF	1.2998	512.41040	6.57039	35.55996
2	184.202	FM	0.9961	5.75857	9.63546e-2	0.39963
3	239.486	MM	1.7411	922.80695	8.83366	64.04041
Totals :				1440.97592	15.50040	

*** End of Report ***

Data File C:\CHEM32....DIPSHI\MAHESH_CHIRAL_GC 2021-03-29 21-29-33\MP-06-128-CAT-CO-DMBD.D
Sample Name: MP-06-128-CAT-CO-DMBD

```
==========================================================================
Acq. Operator   : MP                                Seq. Line :   2
Acq. Instrument : Instrument 1                     Location : Vial 202
Injection Date  : 3/30/2021 5:13:28 AM                  Inj :   1
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\DATA\DIPSHI\MAHESH_CHIRAL_GC 2021-03-29 21-29-33\MP-100-
                  ISO300-CHIRAL.M
Last changed    : 7/28/2020 9:06:06 PM by MP
Analysis Method : C:\CHEM32.NEW\1\METHODS\LI-90-ISO300-RAMP5-CYCLOSIL.M
Last changed    : 3/30/2021 6:38:48 PM by Jon
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                          Area Percent Report
==========================================================================

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


Signal 1: FID1 B, FID1B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1 181.048 MM    1.2931  484.09302    6.23937 99.08995
   2 184.090 FM    0.8991    4.44594 8.24168e-2  0.91005
```

Totals :	488.53896	6.32178

==========

*** End of Report ***

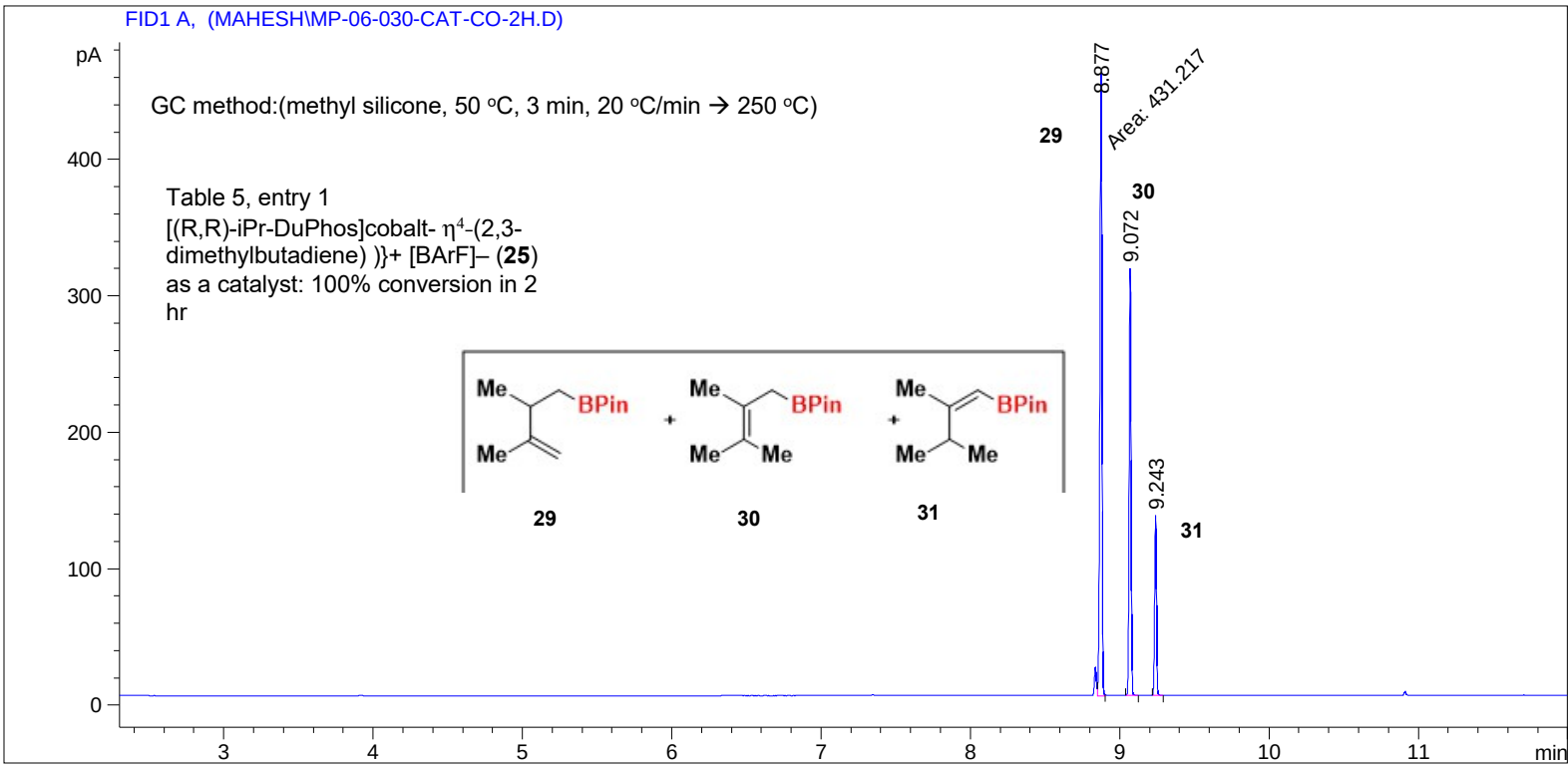
Data File C:\CHEM32\1\DATA\MAHESH\MP-06-030-CAT-CO-2H.D
Sample Name: MP-06-030-CAT-CO-2H.D

==========

Acq. Operator : mp
Acq. Instrument : Instrument 1 Location : Vial 2
Injection Date : 6/23/2020 5:28:26 PM
Inj Volume : 1 µl
Acq. Method : C:\CHEM32\1\METHODS\50-RAMP.M
Last changed : 3/5/2020 3:50:37 PM by MP
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed : 7/18/2020 2:32:42 PM by Jon
(modified after loading)
Method Info : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Sample Info : 2 MOL%

Additional Info : Peak(s) manually integrated



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Area Percent Report

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

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-030-CAT-CO-2H.D
Sample Name: MP-06-030-CAT-CO-2H.D

Signal 1: FID1 A,

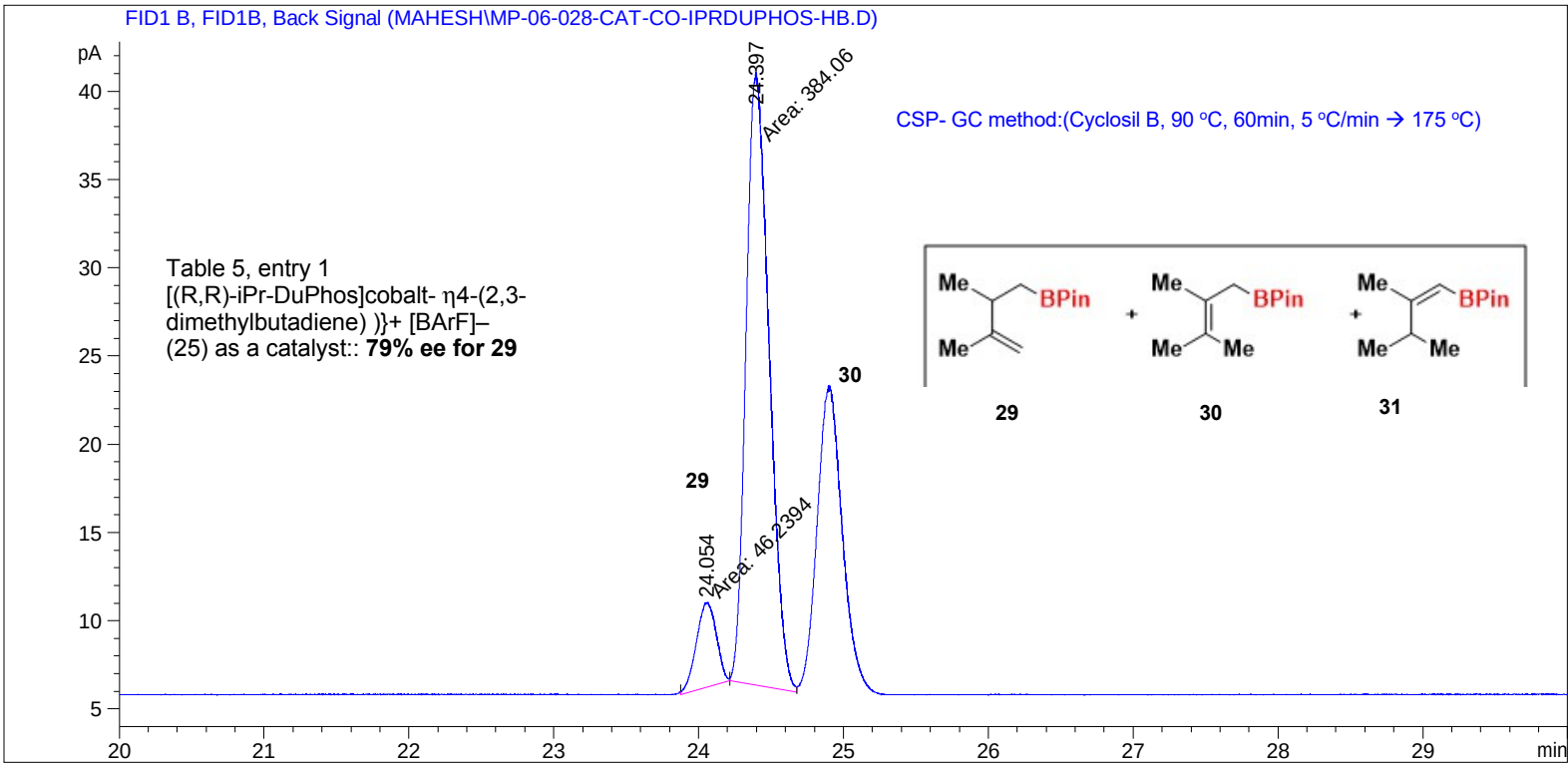
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.877	FM	0.0157	431.21741	457.18283	52.94511
2	9.072	BB	0.0133	270.53165	313.40701	33.21602
3	9.243	BB	0.0132	112.71218	132.18829	13.83886
Totals :				814.46124	902.77814	

*** End of Report ***

Data File C:\CHEM32.NEW\1\DATA\MAHESH\MP-06-028-CAT-CO-IPRDUPHOS-HB.D
Sample Name: MP-06-028-CAT-CO-IPRDUPHOS-HB

```
==========================================================================
Acq. Operator   : MP
Acq. Instrument : Instrument 1                    Location : Vial 201
Injection Date  : 6/23/2020 8:01:07 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32.NEW\1\METHODS\MP-90-30MIN-RAMP-CYCLOSIL.M
Last changed    : 6/19/2019 11:50:20 AM by MP
Analysis Method : C:\CHEM32.NEW\1\METHODS\MP-100-ISO300-CHIRAL.M
Last changed    : 7/7/2020 4:22:32 PM by MP
                  (modified after loading)
Sample Info     : 2.5HR


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs
```

Data File C:\CHEM32.NEW\1\DATA\MAHESH\MP-06-028-CAT-CO-IPRDUPHOS-HB.D
Sample Name: MP-06-028-CAT-CO-IPRDUPHOS-HB

Signal 1: FID1 B, FID1B, Back Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	24.054	MM	0.1600	46.23942	4.81647	10.74587
2	24.397	MM	0.1847	384.05994	34.65346	89.25413
Totals :				430.29936	39.46993	

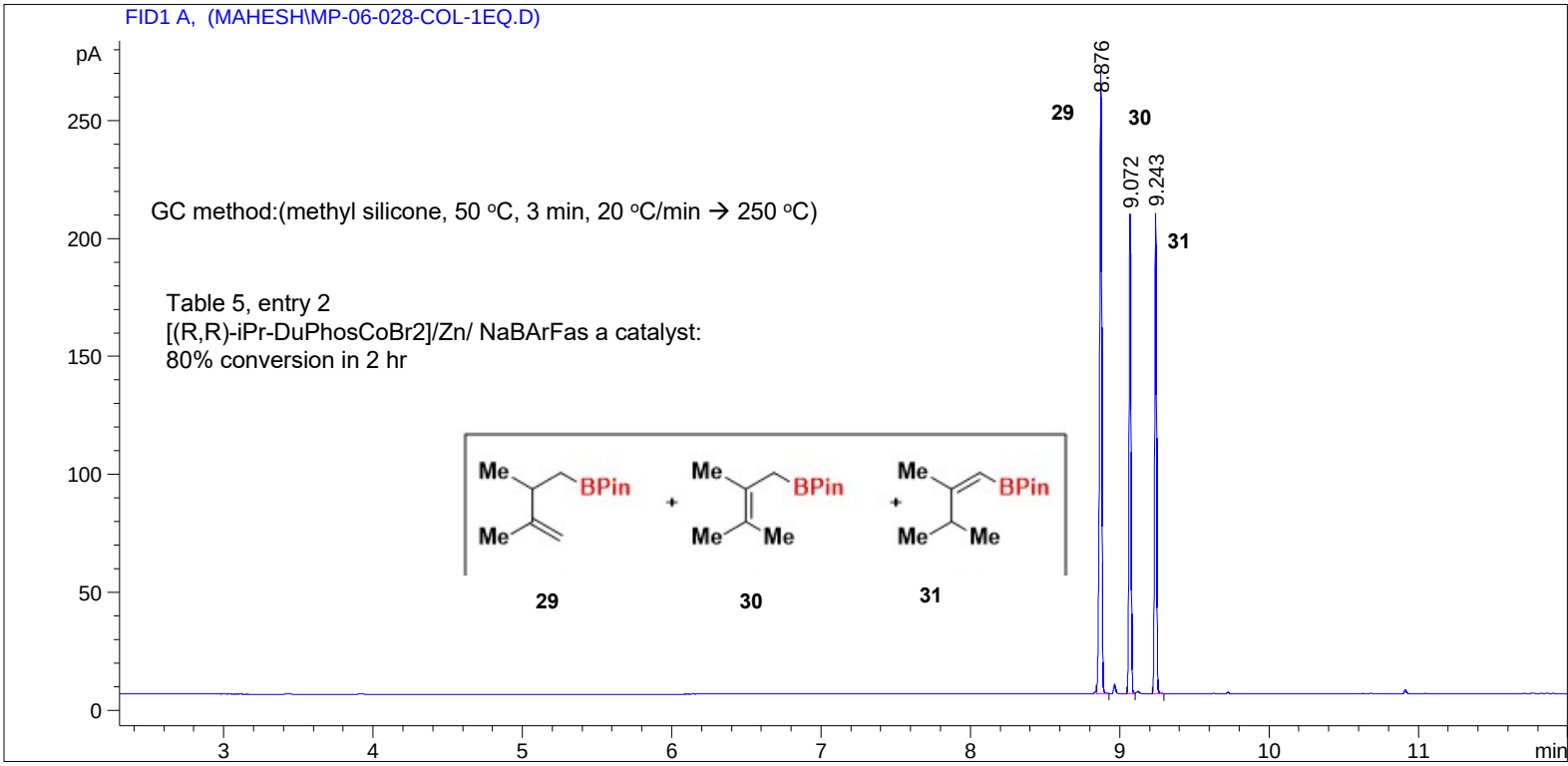
*** End of Report ***

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-028-COL-1EQ.D
Sample Name: MP-06-028-COL-1EQ.D

==========

Acq. Operator : mp
Acq. Instrument : Instrument 1 Location : Vial 3
Injection Date : 6/23/2020 5:53:05 PM
Inj Volume : 1 µl
Acq. Method : C:\CHEM32\1\METHODS\50-RAMP.M
Last changed : 6/23/2020 5:47:10 PM by mp
Analysis Method : C:\CHEM32\1\METHODS\MP-80-RAMP.M
Last changed : 7/18/2020 2:29:03 PM by Jon
(modified after loading)
Method Info : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Additional Info : Peak(s) manually integrated



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Area Percent Report

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.876	VB	0.0151	261.94107	263.63089	42.54850
2	9.072	BV	0.0137	177.83084	203.36923	28.88602

Data File C:\CHEM32\1\DATA\MAHESH\MP-06-028-COL-1EQ.D
Sample Name: MP-06-028-COL-1EQ.D

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
3	9.243	BB	0.0136	175.85747	204.12392	28.56548
Totals :				615.62938	671.12404	

*** End of Report ***