Supporting Information Part A

Mechanism of Cobalt-Catalyzed Heterodimerization of Acrylates and 1,3-Dienes. A Potential Role of Cationic Cobalt(I) Intermediates

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1.1 General Methods

All use of moisture and oxygen sensitive materials were handled using standard Schlenk techniques under an argon atmosphere or in a glove-box under a nitrogen atmosphere maintained at less than 5 ppm oxygen. The Schlenk line was attached to a vacuum pump that was kept between 0.2 and 0.01 mm Hg for all evacuations and drying of air sensitive compounds. Before use, all glassware is washed by soaking it in an base bath (isopropanol and KOH) overnight (12 h), rinsing with water, then soaking in an acid bath overnight (12 h), then rinsed a second time with water and dried with acetone. The glassware was stored in an oven for 12 h that was set at 160 °C.

All gas chromatographic analysis of the reactions were performed on an Agilent 6850 G.C. with a HP-1 methyl siloxane column (30 m, 0.32 mm ID, 0.25 μm) and hydrogen carrier gas with FID-detector at 250 °C. The method of analysis: initial temperature 50 °C held for 5 min, ramp 10 °C/min to 70 °C, held for 15 min ramp 20 °C/min to 250 °C held for 5 min.

Proton and carbon nuclear magnetic resonance spectra (^{1}H and ^{13}C) were recorded on a Bruker Avance III HD Ascend 400 MHz SPX equipped with an inverse probe and for deuterium labeling experiments a Bruker Avance III HD Ascend 600 MHz SPX was used. Solvent resonance was used as an internal standard for the chemical shifts, $CDCl_3$ at 7.26 ppm for ^{1}H NMR and $CDCl_3$ at 77.16 ppm for ^{13}C NMR. NMR data are reported as the following: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet), coupling constants (Hz), and integration.

All UV-Vis spectra were collected on an Agilent Cary 60 spectrophotometer outfitted with stirring capabilities at room temperature (22 °C). All IR spectra were collected on a Mettler Toledo ReactIR 45m instrument.

2.1 Chemicals

The chemicals used for the experiments were as follows: Diethyl ether (Fischer Scientific, Anhydrous), tetrahydrofuran (Alfa Aesar, 99%), hexanes (Sigma Aldrich, ≥ 98.5%), pentanes (Sigma Aldrich, ≥ 99%), 1,2-dichloroethane (Sigma Aldrich, ≥ 99%), dichloromethane (Sigma Aldrich, ≥ 99.8%, 40-150 ppm amylene), methyl acrylate (Sigma Aldrich, 99%, ≤ 100 ppm monomethyl ether hydroquinone), 2,3-dimethyl-1,3-butadiene (Alfa Aesar, 98%, 100 ppm BHT), Zinc (Sigma Aldrich), $CoBr_2$ (Sigma Aldrich, 99%), $ZnBr_2$ (Sigma Aldrich, 98%, Anhydrous), and 1,3-Bis(diphenylphosphino)propane (Sigma Aldrich, 97%).

2.2 Purification methods

2.2.1 Purification of solvents and storage of purified chemicals

Diethyl ether, tetrahydrofuran, hexanes, and pentanes were freshly distilled prior to each reaction. They were distilled over Na metal and allowed to cool to room temperature before use. 1,2-Dichloroethane and dichloromethane were freshly distilled prior to each reaction. The solvents were distilled over CaH_2 and allowed to cool to room temperature before their use in reactions.

2.2.2 Distillation of methyl acrylate[1]

Methyl acrylate, (50.00 mL, 47.80 g, 0.555 moles), was added to a 100 mL beaker. The methyl acrylate was washed with 2 M NaOH (20 mL portions, 3 times) and then washed with distilled water (20

mL portions, 3 times) in order to get wash the methyl acrylate clean of the inhibitor monomethyl ether hydroquinone. The washed methyl acrylate is added to a 100 mL round bottom flask equipped with a magnetic stirrer and $CaCl_2$ (0.50 g, 0.0045 moles). A short-path distillation apparatus is attached to the round bottom flask, and the apparatus is added to an oil bath at 60 ºC. The fractional distillation is then carried out under reduced pressure (via a Schlenk line 0.2 to 0.01 mmHg). After distillation, the acrylate is partitioned into two 20 mL oven dried glass vials. The vials are then wrapped in black electrical tape and stored in a freezer, while not in use, set to -4 ºC. Before use, the methyl acrylate is taken out and allowed to warm to room temperature (23 ºC) in the dark. After use, the methyl acrylate is purged with dry nitrogen and stored again in the dark at -4 ºC.

2.2.3 Distillation of 2,3-dimethyl-1,3-butadiene[1]

2,3-Dimethyl-1,3-butadiene (Alfa Aesar, 98%, 25.00 mL, 18.15 g, 0.221 moles) was added to a 50 mL round bottom flask equipped with a magnetic stir bar and $NaBH_4$ (1.00 g, 0.026 moles). A short path distillation apparatus is attached to the round bottom flask and the flask is placed in an oil bath set to 50 ºC. The fractional distillation is carried out under reduced pressure (via a Schlenk line 0.2 to 0.01 mmHg). After distillation, the diene is split into 2 portions and stored in two 20 mL oven dried glass vials at -4 ºC when not in use. Before use, the 2,3-dimethyl-1,3-butadiene is allowed to warm to room temperature (23 ºC). After use, the 2,3-dimethyl-1,3-butadiene is purged with dried nitrogen and stored in a freezer at -4 ºC.

3.1 Synthesis of reagents

3.1.1 Activation of Zn[2]

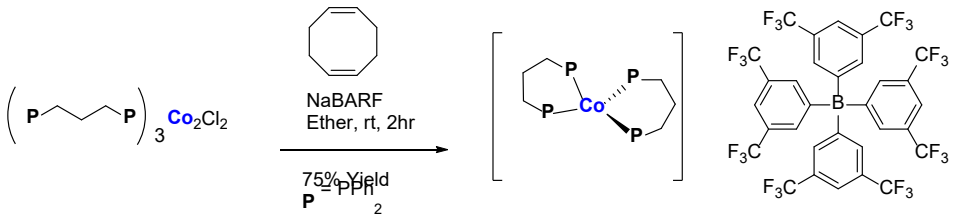
Zn (15.00 grams, 0.229 moles) was placed in a 250 mL beaker charged with a magnetic stir bar. HCl (2.00 M, 25 mL) was added to the beaker and the mixture was allowed to stir for 25 min. The stirring was stopped, and the liquid was decanted out of the beaker. The contents of the beaker was then washed with distilled water (20 mL portions, 3 times). Following the addition of each portion of distilled water, the mixture was stirred for 5 min, and the water is decanted off. The solution was then washed with acetone (20 mL portions, 3 times), and the acetone is decanted off. The Zn is then placed in a 50 mL round bottom flask stoppered with a flow control valve. The Zn is then dried under vacuum (via a Schlenk line 0.2 to 0.01 mmHg) while in an oil bath at 100 ºC. The flask was then filled with argon and brought into a glove-box. The zinc was then ground into a fine powder using a ceramic mortar and pestle. The resulting activated Zn powder is stored in a 20 mL oven dried glass vial in the glove-box.

3.1.2 Synthesis of (dppp)$CoBr_2$[2]

In a glove-box, anhydrous Co(II)Br_2 (3.46 grams, 0.0159 moles, 1.00 eq) is added to a 250 mL round bottom flask equipped with a magnetic stir bar. In a separate 250 mL round bottom flask is taken 1,3-bis(diphenylphosphino)propane (dppp) (6.86 grams, 0.0166 moles, 1.04 eq) with a magnetic stir bar. To the flask containing the Co(II)Br_2, freshly distilled THF (100 mL) is added, and the mixture is allowed to stir until all the Co(II)Br is dissolved. To the flask containing the dppp, a minimal amount of distilled THF (20 mL) is added, and the mixture is stirred until the majority of the dppp has dissolved. The stirring is stopped for the dppp flask and the undissolved dppp is allowed to settle to the bottom of the flask. The dissolved dppp solution is slowly added to the stirring Co(II)Br_2 solution, the undissolved dppp is dissolved in THF (5 mL), and the remainder of the solution is slowly added to the Co(II)Br_2

solution. The dppp and Co(II)Br_2 solution is allowed to stir in the glove-box for 12 hr. The stirring is then stopped, and freshly distilled hexanes/diethyl ether solution (1:1 by volume, 100 mL) was added to the solution. Immediate precipitation of the (dppp)Co(II)Br_2 complex was observed and the solution is allowed to stir for 5 min. The supernatant is then decanted to obtain a green mixture. The solution is allowed to sit undisturbed for 5 min. The mixture is then washed with diethyl ether (50 mL portions, 3 times), and the supernatant is decanted. The solid is then taken out of the box and put on a Schlenk line where it is dried via vacuum (0.2 to 0.01 mmHg) for 12 h. A green solid is obtained. The solid is then brought into the glove-box and made into a fine powder and is further dried via vacuum for an additional 12 hr. The yield of (dppp)Co(II)Br_2 is 5.6 grams, 0.00887 moles, 56%. The (dppp)Co(II)Br_2 is stored in the glove-box.

3.1.3 Synthesis of cationic cobalt complex



Scheme S1. Procedure for synthesizing the crystalline $Co(I)^+$ $BArF^-$ complex.

In the dry-box, an 8-mL vial was charged with a magnetic stir bar, recrystallized $dppp_3Co_2Cl_2$ (50 mg, 0.035 mmol, 1 equiv.) and NaBArF (62.2 mg, 0.07 mmol, 2 equiv.).[3] The vail was capped and a solution of cyclooctadiene (COD) (0.25 mL, 1.75 mmol, 50 equiv.) in ether (5 mL) was added via syringe. The resulting green mixture was stirred for 2 hr. Upon which the color changed from green to sea green. Stirring was stopped and solvent was evacuated under high vacuum (~0.1 mm Hg) for 2-3 h to afford crude solid. The crude solid thus obtained was then dissolved in minimum amount of ether and filtered inside the drybox. To the filtrate was then diffused hexanes (by slow evaporation of hexane into an ether solution placed in an atmosphere of hexane) to afford the sea green crystals (23 mg, 75% yield upon recrystalization). The sea green crystal was then characterized by X-ray Crystallography and the data deposited at the Cambridge Crystallographic Data Center (CCDC #1945796).

4.1 General procedure for in situ experiment

4.1.1 React IR set up

The ReactIR 45m (from Mettler Toledo) was filled with liquid N_2 and allowed to cool down for 1 h before use. The probe was attached, and the instrument was tuned to obtain optimal S/N. The readings were set to take one every 30 sec for a total of 8 hr. The instrument had the following specifications: ReactIR 45m; SN: 23553; Detector: MCT; Apodization: HappGenzel; Probe: DiComp (Diamond); SN: 23563; Interface: AgX 9.5mm x 1.5m Fiber (Silver Halide); Sampling: 3000 to 650 cm^{-1}; Resolution: 4; Scan option: AutoSelect; Gain: 1x.

4.1.2 Catalyst preparation

Before use, the glassware (see below) was cooled in a desiccator to room temperature (23 ºC), it was then pumped into the glove-box. To a modified Schlenk flask, **Figure S1**, a flow control switch and a magnetic stir bar were added. Using an analytical balance (dppp)$CoBr_2$ (the indicated amounts as seen in section **5.1**), Zn dust (the indicated amounts as seen in section **5.1**), and $ZnBr_2$ (the indicated amounts as seen in section **5.1**) were weighed out and placed in the modified Schlenk flask. After the solid reagents had been added, the flask was then sealed via a septum and electrical tape. Once sealed, the flask is taken out of the glove-box and immediately attached to a Schlenk line.

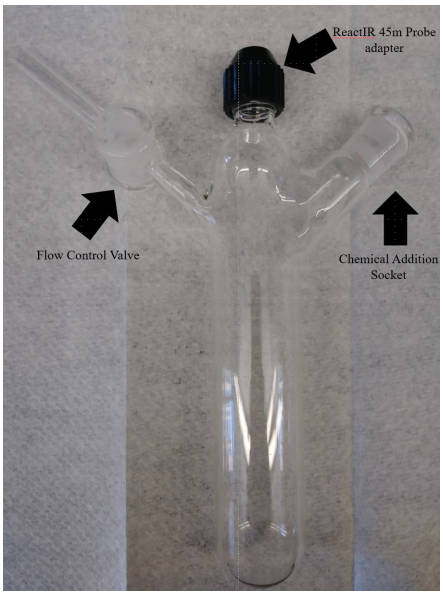


Figure S1. Modified Schlenk flask used for all procedures involving React IR.

4.1.3 Reaction set-up and analysis

The Schlenk flask attached to a Schlenk line was placed in a water bath set to 30 ºC with a stirring rate of 250 to 400 rpm. The Schlenk line was evacuated to 0.2 mmHg, and then filled with argon. This process was repeated two more times. After the line had been evacuated, the flask was open to the Schlenk line while under high argon flow. The flask itself was then evacuated to 0.2 mmHg and then filled with argon until it was at atmospheric pressure. This process was repeated 2 more times. After the third evacuation, the argon flow was turned on high, and the septa closing the top valve of the flask was removed and the ReactIR probe was placed into the neck and slid down until the tip of the probe is about 1 cm from the bottom of the flask. The probe was then sealed on and the flask was evacuated to 0.2 mmHg and then filled with argon. This process was repeated two more times for a total of three evacuations. A background scan (180 total scans) was performed while the probe was in the flask under argon. After the scan, DCE (2 mL) was added to the flask via a 3 mL syringe and a 6 inch needle. The solution was allowed to stir for 2 hr. A color change from blue/green to red/brown was observed after about 45 min of stirring. The solution was allowed to stir for 2 h under argon. A DCE (3 mL) solution of the indicated amounts as seen in section **5.1** of methyl acrylate, 2,3-dimethyl-1,3-butadiene, and dodecane (10 µL) was prepared by adding 3 mL of distilled DCE via a 10 mL syringe, 10 uL dodecane via a 10 µL syringe, methyl acrylate via a 100 µL syringe, and 2,3-dimethyl-1,3-butadiene via a 100 µL syringe. The vial was then wrapped in aluminum foil and stored at -4 ºC and taken out 30 min prior to addition in order to allow it to warm to room temperature. After the solution of (dppp)$CoBr_2$, Zn, and $ZnBr_2$ had been

stirring for 2 hr, 2 mL of the solution containg methyl acrylate and 2,3-dimethyl-1,3-butadiene was added to the solution via a 3 mL syringe and disposable needle. An immediate color change from red/brown to dark green was observed upon the addition of the solution. The solution was allowed to stir for an additional 2 h after the addition of the starting material solution. The remaining 1 mL of the 3 mL starting material solution was diluted using 1 mL adding 50:50 diethyl ether:hexane mixture. The resulting solution was used to obtain a GC spectra. After 2 hr, the reaction was stopped by using a 50:50 solution of diethyl ether:hexanes (4 mL) to the reaction vessel. The resulting solution was filtered through a short pad of silica gel using an additional 4 to 8 mL of the 50:50 diethyl ether:hexane mixture to rinse the reaction vessel. A small sample was then run on the GC to analyze the conversion of diene to product. This analysis is done by comparing the ratio of the diene peak area to that of the internal standard dodecane peak of the end reaction with the ratio of the starting material mixture, Equation S1.

$$Percent\ Conversion\ of\ Diene = 1 - \frac{Diene_{Post\ Area}/Dodecane_{Post\ Area}}{Diene_{Pre\ Area}/Dodecane_{Pre\ Area}} * 100$$

Equation S1. Equation used to calculate conversion of diene via G.C. analysis.

4.1.4 IR Analysis

A ReactIR probe was used to collect in-situ data on the reaction progress and provided an infra-red spectrum every 30 sec and records the wavenumbers from 3000 cm^{-1} to 650 cm^{-1}. The peaks that are monitored for this reaction are as follows: for the methyl acrylate, 1401 cm^{-1}, for the 2,3-dimethyl-1,3-butadiene, 896 cm^{-1}, and for the product, 896 cm^{-1}.[4,5,6] The resulting data was then converted to an excel file and a MATLAB script was run that was able to fit the experimental data to a curve, using the provided curve fitting functions. After which the data was deconvoluted to put it into its final form for analysis.

5.1 Specifics for IR experiments:

5.1.1 Same Excess

The general procedure is followed for these experiments with the following modifications

Table S1. Data for Same Excess Experiments

Excess Experiment	Diene (mg)	Diene (M)	Acrylate (mg)	Acrylate (M)	(dppp)$CoBr_2$ (mg)	(dppp)$CoBr_2$ (mmol)	Zn (mg)	Zn (mmol)	$ZnBr_2$ (mg)	$ZnBr_2$ (mmol)	Diene Conversion (%)[a]
Same Excess #1	32.9	0.100	89.5	0.26	96.1	0.152	99.5	1.52	356.0	1.58	90
Same Excess #2	40.1	0.122	95.4	0.28	95.8	0.152	100.0	1.53	355.4	1.58	91
Same Excess #3	49.6	0.151	106.4	0.31	95.6	0.152	99.6	1.52	354.4	1.57	98
Same Excess #4	66.0	0.201	124.3	0.36	95.9	0.152	99.6	1.52	354.9	1.58	89

[a] Determined by GC-FID analysis.

5.1.2 Different Excess

The general procedure is followed for these experiments with the following modifications

Table S2. Data for Different Excess Experiments

Excess Experiment	Diene (mg)	Diene (M)	Acrylate (mg)	Acrylate (M)	(dppp)$CoBr_2$ (mg)	(dppp)$CoBr_2$ (mmol)	Zn (mg)	Zn (mmol)	$ZnBr_2$ (mg)	$ZnBr_2$ (mmol)	Conversion of Diene (%)[a]
Different Excess #1	49.6	0.151	58.2	0.17	95.7	0.152	99.6	1.52	355.7	1.58	97
Different Excess #2	47.6	0.145	68.9	0.20	96.2	0.153	99.9	1.53	354.9	1.58	92
Different Excess #3	49.9	0.152	108.1	0.31	95.5	0.151	100.6	1.55	354.5	1.57	94
Different Excess #4	49.6	0.151	106.4	0.31	95.6	0.152	99.6	1.52	354.4	1.57	98
Different Excess #5	99.1	0.302	110.5	0.32	95.9	0.152	100.1	1.54	350.0	1.56	98

[a] Determined by GC-FID analysis.

5.1.3 Stir Test

The general procedure is followed for these experiments with the following modifications

Table S3. Data for Stir Test Experiments

Stir Time for Initial Catalyst Mixture	Diene (mg)	Diene (M)	Acrylate (mg)	Acrylate (M)	(dppp)$CoBr_2$ (mg)	(dppp)$CoBr_2$ (mmol)	Zn (mg)	Zn (mmol)	$ZnBr_2$ (mg)	$ZnBr_2$ (mmol)	Conversion of Diene (%)[a]
5 min	50.3	0.153	105.7	0.307	96.0	0.152	99.9	1.53	356.5	1.58	90
30 min	50.3	0.153	105.7	0.307	96.0	0.152	99.9	1.53	356.5	1.58	90
1 hr	50.3	0.153	105.7	0.307	95.8	0.152	100.3	1.53	354.6	1.57	90
2 hr	50.3	0.153	105.7	0.307	95.8	0.152	100.5	1.54	353.8	1.57	90
8 hr	50.3	0.153	105.7	0.307	95.6	0.152	99.6	1.52	354.6	1.57	96

[a] Determined by GC-FID analysis.

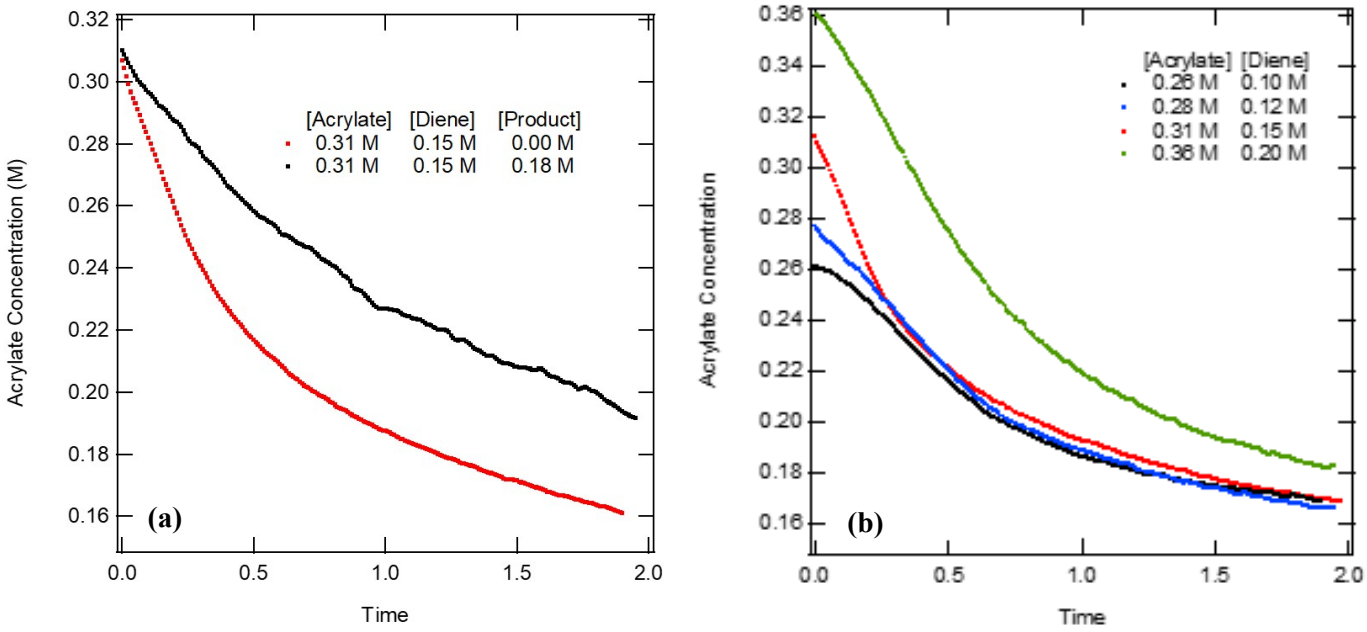


Figure S2. (a) Product inhibition. Red: acrylate 0.31 M; diene 0.15 M; product 0.0 M, reaction run for 2 h. Black: acrylate 0.31 M; diene 0.15 M; product 0.18 M, added together with the starting materials, reaction run for 2 h. See experimental details on p. S10. **(b) Same excess experiment.** Same excess experiments without time shift. Black: acrylate 0.26 M and diene 0.10 M. blue: acrylate 0.28 M and diene 0.12 M. Red: acrylate 0.31 M and diene 0.15 M. Green: acrylate 0.36 M and diene 0.20 M.

5.1.4 Catalyst Order Test

The general procedure is followed for these experiments with the following modifications

Table S4. Data for Catalyst Order Experiments

Catalyst Loading	Diene (mg)	Diene (M)	Acrylate (mg)	Acrylate (M)	(dppp)$CoBr_2$ (mg)	(dppp)$CoBr_2$ (mmol)	Zn (mg)	Zn (mmol)	$ZnBr_2$ (mg)	$ZnBr_2$ (mmol)	Conversion of Diene (%)
Normal	49.9	0.152	107.4	0.312	95.5	0.151	100.6	1.54	354.5	1.574	94
Half Catalyst Loading	49.6	0.151	107.8	0.313	47.9	0.076	50.5	0.77	178.7	0.794	98
Three Thirds Catalyst Loading	49.6	0.151	110.2	0.320	74.9	0.119	77.8	1.20	266.4	1.18	> 99

[a] Determined by GC-FID analysis.

5.1.5 Diene polymerization without catalyst Test

The general procedure is followed for these experiments with the following modifications

1. Diene amount: 0.152 M
2. Acrylate amount: 0.00
3. (dppp)$CoBr_2$ amount: 0
4. Zn amount: 0
5. $ZnBr_2$: 0
6. DCE used: 4 mL
7. Ligand amount: 0.00
8. Conversion: 0%

5.1.6 Diene polymerization with catalyst Test

The general procedure was followed for these experiments with the following modifications

1. Diene amount: 0.148 M
2. Acrylate amount: 0.00
3. (dppp)$CoBr_2$ amount: 0.151 mmol
4. Zn amount: 1.50 mmol
5. $ZnBr_2$: 1.55 mmol
6. DCE used: 4 mL
7. Ligand amount: 0.00
8. Conversion: 20%

5.1.7 Product Inhibition

The general procedure was followed for these experiments with the following modifications. The relative rates can be seen in the graphs below.

1. Diene amount: 0.151 M
2. Acrylate amount: 0.31 M
3. (dppp)$CoBr_2$ amount: 0.152 mmol
4. Zn amount: 1.54 mmol
5. $ZnBr_2$: 1.59 mmol
6. DCE used: 4 mL
7. Product added: 0.182 M
8. Conversion: 79%

6.1 Isotopic Labeling Experiments

6.1.1 Reversibility of β-hydride elimination

Inside a glove-box, to an oven-dried 8 mL screw cap vial equipped with a stir bar and screw septum cap, (dppp)Co(II)Br_2 (10.2 mg, 0.016 mmol), Zn (9.5 mg, 0.15 mmol), and $ZnBr_2$ (32.4 mg, 0.144 mmol) were added. Upon the starting of stirring, DCM (1 mL); stored with molecular sieves, was added to the vial. The solution was allowed to stir undisturbed for 2 hr. After the 2 hour period, methyl acrylate-d_3 (23.3 mg, 0.26 mmol) was added neat the solution via a 100 µL syringe. Directly after this addition 2,3-dimethyl-1,3-butadiene (20.3 mg, 0.25 mmol) was added to the solution via a 100 µL syringe. The reaction was allowed to react for three hr. After which the reaction was stopped with a 1:1 solution by volume of diethyl ether and pentanes. The reaction was purified by evaporating off all the solvents and starting materials to yield pure deuterated product (17.00 mg, 0. 099 mmol, 39.6 %yield).

7.1 Co(I) activity vs $Co(I)^+$ activity

Inside a glove-box, to an oven dried 8 mL screw cap vial equipped with a stir bar and screw septum cap, (dppp)3Co_2(I)Br_2 (5.5 mg, 0.009 mmol) was added. DCM (0.5 mL), that was stored with molecular sieves, was added to the vial. The solution was allowed to stir for 2 hr, after which, methyl acrylate (17.2 mg, 0.20 mmol) and 2,3-dimethyl-1,3-butadiene (14.5 mg, 0.18 mmol) in 0.5 mL DCM was added. The reaction was allowed to proceed for 2 hr. The reaction was then stopped with a 1:1 solution of diethyl ether and hexanes. The progress was monitored via gas chromatography. The G.C. showed no product formation. In a parallel reaction inside a glove-box, to an oven dried 8 mL screw cap vial equipped with a stir bar and screw septum cap, $(dppp)_3Co_2(I)Br_2$ (6.6 mg, 0.01 mmol) and $ZnBr_2$ (32.2 mg, 0.143 mmol) was added. DCM (0.5 mL), that was stored with molecular sieves, was added to the vial. The solution was allowed to stir for 2 hr, after which, methyl acrylate (17.2 mg, 0.20 mmol) and 2,3-dimethyl-1,3-butadiene (14.5 mg, 0.18 mmol) in 0.5 mL DCM was added. The reaction was allowed to proceed for 2 hr. The reaction was then stopped with a 1:1 solution of diethyl ether and hexanes. The progress was monitored via gas chromatography The G.C. showed 19.2% conversion of diene.

8.1 UV-Vis studies

8.1.1 Background

A background of DCE was taken. To a modified cuvette that allowed the preservation of air sensitive materials, 2 mL of freshly distilled DCE was added. The cuvette was placed in the in-situ UV-VIS and a wavelength scan was performed from 1100 nm to 190 nm. This reading was used as the background for the rest of the UV-Vis experiments.

8.1.2 $(dppp)_3Co^{(I)}{}_2Br_2$

To a clean 4 mL oven dried glass vial, 2.2 mg of $(dppp)_3Co(I)_2Br_2$[2] (recrystallized from THF upon diffusion with hexanes) and DCE (2 mL) were added to the vial. While in a glove-box, the solution was transferred to a modified cuvette. The cuvette was taken out of the glove-box and placed in the in-situ UV-Vis and a wavelength scan from 1100 nm to 190 nm was performed.

8.1.3 (dppp)$Co^{(II)}Br_2$

To a clean 4 mL oven dried glass vial, 2.5 mg of (dppp)$Co^{(II)}Br_2$ and DCE (2 mL) were added to the vial. While in a glove-box, the solution was transferred to a modified cuvette. The cuvette was taken out of the glove-box and placed in the in-situ UV-VIS and a wavelength scan from 1100 nm to 190 nm was performed.

8.1.4 $[(dppp)Co^{(I)}]^+$

While inside a glove-box, to a clean 20 mL oven dried glass vial, a magnetic stir bar, (dppp)$Co^{(II)}Br_2$ (48.00 mg, 0.0761 mmols, 1 eq), activate Zn dust (49.00 mg, 0.778 mmols, 10.22 eq) and $ZnBr_2$ (171.00 mg, 0.759 mmols, 9.98 eq) and DCE (2 mL) were added. The solution was allowed to stir for 2 hr inside the glove-box. After this period, the solution changed colors from a blue/green to a dark red/brown. After a 2 hour stirring period, 0.100 mL of the solution was transferred to a modified cuvette and then DCE (1.900 mL) was added to the cuvette to make a 0.002 M solution of $(dppp)Co(I)^+$. The cuvette was taken out of the glove-box and placed in the in-situ UV-VIS and a wavelength scan from 1100 nm to 190 nm was taken every minute for four min.

8.1.4 Diene Coordination

To a freshly prepared sample of $[(dppp)Co^{(I)}]^+$, prepared as described above at 0.002 M, 2,3-dimethyl-1,3-butadiene in DCE was added to the cuvette (0.176 molar, 0.044 mmols, 11 eq) and a wavelength scan from 1100 nm to 190 nm was taken every minute for five min.

8.1.5 Acrylate Coordination

To a freshly prepared sample of $[(dppp)Co^{(I)}]^+$, prepared as described above at 0.002 M, methyl acrylate in DCE was added to the cuvette (0.464 molar, 0.232 mmols, 58 eq) and a wavelength scan from 1100 nm to 190 nm was taken every minute for four min.

8.1.6 Diene vs Acrylate Competition Test

To a freshly prepared sample of $[(dppp)Co^{(I)}]^+$, prepared as described above at 0.002 M, methyl acrylate in DCE was added to the cuvette (0.464 molar, 0.232 mmols, 58 eq) and a wavelength scan from 1100 nm to 190 nm was taken every minute for four min. After this, 2,3-dimethyl-1,3-butadiene in DCE was added to the cuvette (0.176 molar, 0.044 mmols, 11 eq) and a wavelength scan from 1100 nm to 190 nm was taken every minute for five min.

8.1.7 Synthesis and UV-Vis Analysis of Cationic Cobalt(I) from $(dppp)_3Co_2^{(I)}Br_2$ crystal.

To a modified cuvette, crystalline $(dppp)_3Co_2{}^{(I)}Br_2$ (3.4 mg, 0.002 mmole) and NaBArF (3.9 mg, 0.004 mmole), and 2 mL of DCE were added. The solution was allowed to stir for 15 min after which, UV-Vis spectra was recorded with a wavelength scan from 1100 nm to 190 nm.

8.1.8 Stir Time Analysis UV-Vis

While inside a glove-box, to a clean 20 mL oven dried glass vial, a magnetic stir bar, (dppp)$Co^{(II)}Br_2$ (19.80 mg, 0.031 mmols, 1 eq), activate Zn dust (20.3 mg, 0.31 mmols, 10.00 eq) and $ZnBr_2$ (70.00 mg, 0.31 mmols, 10.00 eq) and DCE (2 mL) were added. The solution was allowed to stir for 2 hr inside the glove-box. After this period, the solution changed colors from a blue/green to a dark

red/brown. After a 120 min, 150 min, 240 min, and 270 min stirring period, 0.050 mL of the solution was transferred to a modified cuvette and then DCE (1.950 mL) was added to the cuvette to make a 0.002 M solution of (dppp)Co(I)$^{+}$. The cuvette was taken out of the glove-box and placed in the in-situ UV-VIS and a wavelength scan from 1100 nm to 190 nm was taken. The UV-Vis reading was performed.

8.1.9 Preparation of the Catalyst for Product Investigation:

While inside a glove-box, to a clean 20 mL oven dried glass vial, a magnetic stir bar, (dppp)Co(II)Br2 (47.5 mg, 0.075 mmols, 1 eq), activate Zn dust (47.4 mg, 0.729 mmols, 9.7 eq) and ZnBr2 (173.0 mg, 0.769 mmols, 10.3 eq) and DCE (2 mL) were added. The solution was allowed to stir for 2 hr inside the glove-box. After this period, the solution changed colors from a blue/green to a dark red/brown. After a 2 hour stirring period, 0.100 mL of the solution was transferred to a modified cuvette and then DCE (1.900 mL) was added to the cuvette to make a 0.0019 M solution of (DPPP)Co(I)+. The cuvette was taken out of the glove-box and placed in the in-situ UV-VIS and a wavelength scan from 1100 nm to 190 nm was taken every minute. To this cuvette product (17.94 mg, 0.11 mmole, 28.73 eq) in DCE (0.100 mL) was added to the catalyst three times and the UV-Vis was taken. This process was repeated two more times for a total addition of 53.82 mg, 0.32 mmole, and 86.19 eq of catalyst was added. After all the addition of the product, five UV-Vis scans were taken (across five minutes).

8.1.10 Preparation of the Catalyst for Product+Diene Investigation:

While inside a glove-box, to a clean 20 mL oven dried glass vial, a magnetic stir bar, (dppp)Co(II)Br2 (47.5 mg, 0.075 mmols, 1 eq), activate Zn dust (47.4 mg, 0.729 mmols, 9.7 eq) and ZnBr2 (173.0 mg, 0.769 mmols, 10.3 eq) and DCE (2 mL) were added. The solution was allowed to stir for 2 hr inside the glove-box. After this period, the solution changed colors from a blue/green to a dark red/brown. After a 2 hour stirring period, 0.100 mL of the solution was transferred to a modified cuvette and then DCE (1.900 mL) was added to the cuvette to make a 0.0019 M solution of (DPPP)Co(I)+. The cuvette was taken out of the glove-box and placed in the in-situ UV-VIS and a wavelength scan from 1100 nm to 190 nm was taken every minute. To this cuvette product (26.78 mg, 0.16 mmole, 43.24 eq) was added. UV-Vis readings were taken for two minutes. Diene (37.79 mg, 0.46 mmole, 124.2 eq) was added. UV-Vis readings were taken for three minutes.

8.1.11 Preparation of the Catalyst for Dilution Investigation:

While inside a glove-box, to a clean 20 mL oven dried glass vial, a magnetic stir bar, (dppp)Co(II)Br2 (47.5 mg, 0.075 mmols, 1 eq), activate Zn dust (47.4 mg, 0.729 mmols, 9.7 eq) and ZnBr2 (173.0 mg, 0.769 mmols, 10.3 eq) and DCE (2 mL) were added. The solution was allowed to stir for 2 hr inside the glove-box. After this period, the solution changed colors from a blue/green to a dark red/brown. After a 2 hour stirring period, 0.100 mL of the solution was transferred to a modified cuvette and then DCE (1.900 mL) was added to the cuvette to make a 0.0019 M solution of (DPPP)Co(I)+. The cuvette was taken out of the glove-box and placed in the in-situ UV-VIS and a wavelength scan from 1100 nm to 190 nm was taken every minute. To this solution, 0.15 mL, 0.10 mL, and 0.25 mL of DCE were added to make 0.0039 M, 0.0036 M, 0.0034 M, and 0.0031 M solutions of the cobalt complex. A separate solution of DPPPCo(I)+ was made following the procedure above. To this solution, 0.10, 0.20, 0.30, and 0.40 mL of DCE were added to make 0.0019, 0.0018, 0.0017, and 0.0016 M solutions of DPPPCo(I)+.

Table S5. Effect of Counter-ions on the Rate of Reaction

	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

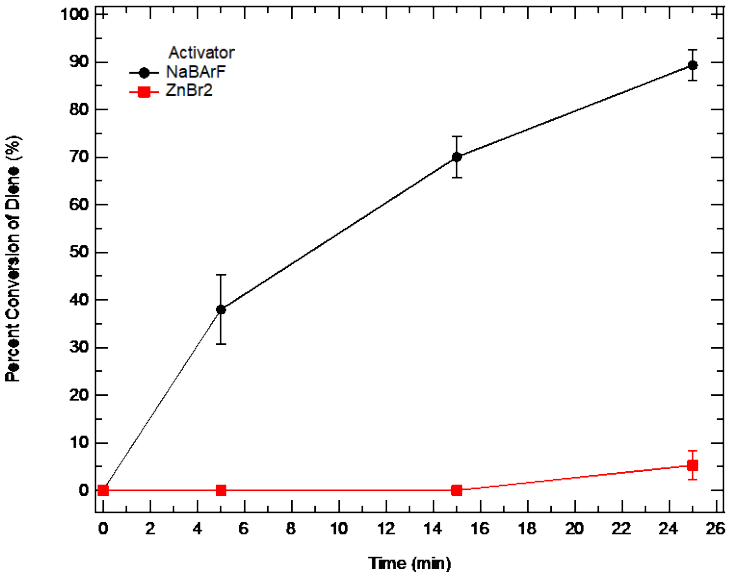


Figure S3. The average percent conversion (with standard deviation) of the test shown above. The red line represents the percent conversion using $ZnBr_2$ activation across twenty five minutes. The black line represents the percent conversion using NaBArF activation across twenty five minutes. The percent conversions was found using gas chromatography and an internal standard of dedecane.

9.1 Reaction Engineering

9.1.1 High Concentration Batch Reaction

While inside a glove-box, to an oven dried 50.00 mL Schlenk flask was charged with a magnetic stir bar, (dppp)$CoBr_2$ (96.2 mg, 0.152 mmol, 0.01 eq), Zn (95.8 mg, 1.47 mmol, 0.1 eq), and $ZnBr_2$ (345 mg, 1.53 mmol, 0.1 eq). The flask was then taken and attached to a Schlenk line. Once on the Schlenk line, the flask was evacuated to 0.2 mmHg, and then filled with argon. This process was repeated 2 more times. After the line has been evacuated, the Schlenk flask was open to the Schlenk line while under high argon flow. The flask itself was then evacuated to 0.2 mmHg and then filled with argon until it was at atmospheric pressure. This process was repeated 2 more times. To the flask DCE was added (2 mL) and the mixture was allowed to stir for 2 hr. After the 2 hr, methyl acrylate (1.6 mL, 17.8 mmol, 1.1 eq), 2,3-dimethyl-1,3-butadiene (1.8 mL, 15.9 mmol, 1.0 eq), and dodecane (30 µL), as an internal standard, were added to the flask. The reaction was allowed to react for eighteen hr after which it was stopped by adding a 1:1 mixture of pentane:diethyl ether. The resulting suspension was filtered through a short pad of silica and a small aliquot was analyzed via GC-FID to yield product in 48% conversion.

10.1 Stir Time Comparison

10.1.1 Stir Time Analysis of $ZnBr_2$ vs NaBArF

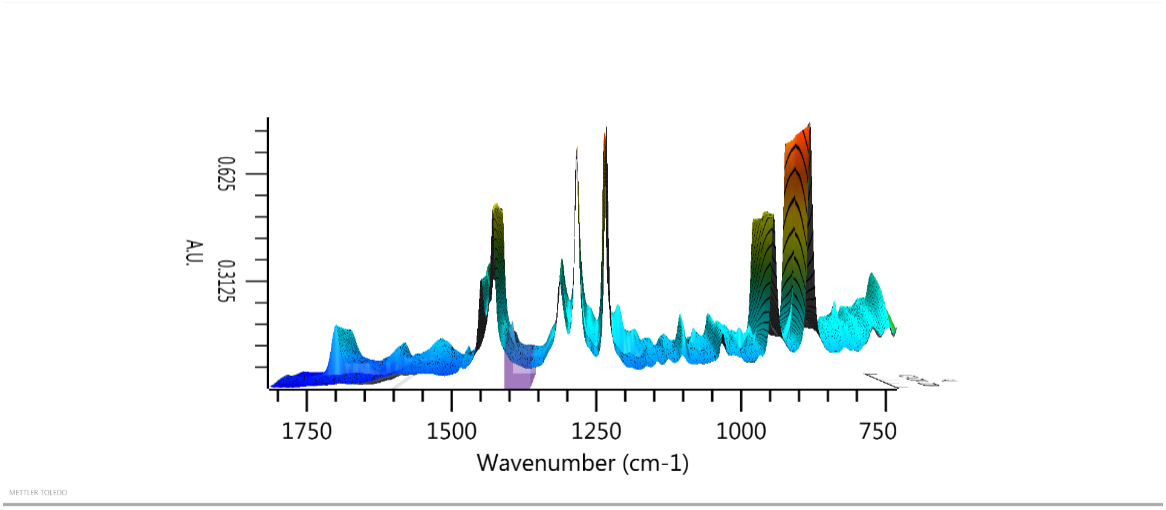
To an 8 mL vial, (dppp)$CoBr_2$ (9.5 mg, 0.015 mmole, 0.095 eq), Zn (11 mg, 0.17 mmole, 1.08 eq), and NaBArF (14.8 mg, 0.017, 0.108 eq) and a magnetic spin vane was added. To the 8 mL vial, DCM (0.50 mL) was added. The mixture was allowed to stir fir five minutes. After the 5 minute stir period, 2,3-dimethyl-1,3-butadiene (13 mg, 0.158 mmole, 1 eq), methyl acrylate (15 mg, 0.17 mmole, 1.08 eq), and DCM (0.5 mL) were added to the solution. The solution was allowed to stir for five minutes. After five minutes, the reaction progress was monitered by G.C. by taking out a small aliquot and diluting this with approximately 1 mL of 1:1 ether:hexanes mixture. The reaction was again monitered after 15 min and then again after 25 minutes. This procedure was repeated two additional times.

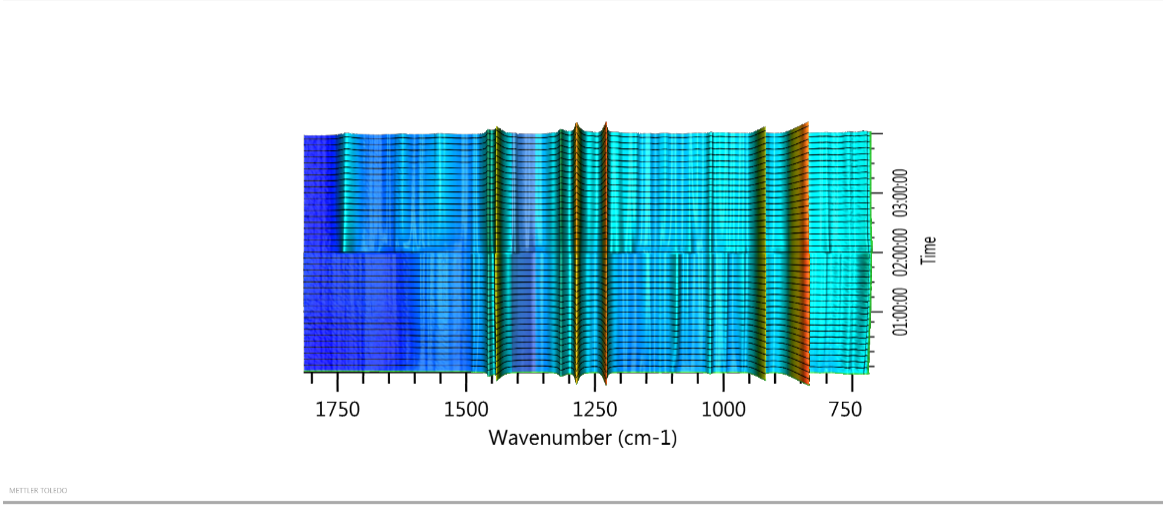
To an 8 mL vial, (dppp)$CoBr_2$ (9.5 mg, 0.015 mmole, 0.095 eq), Zn (11 mg, 0.17 mmole, 1.08 eq), and $ZnBr_2$ (5.5 mg, 0.024, 0.15 eq) and a magnetic spin vane was added. To the 8 mL vial, DCM (0.50 mL) was added. The mixture was allowed to stir fir five minutes. After the 5 minute stir period, 2,3-dimethyl-1,3-butadiene (13 mg, 0.158 mmole, 1 eq), methyl acrylate (15 mg, 0.17 mmole, 1.08 eq), and DCM (0.5 mL) were added to the solution. The solution was allowed to stir for five minutes. After five minutes, the reaction progress was monitered by G.C. by taking out a small aliquot and diluting this with approximately 1 mL of 1:1 ether:hexanes mixture. The reaction was again monitered after 15 min and then again after 25 minutes. This procedure was repeated two additional times.

The results for the above test can be seen in the table below. The conversion was calculated by using an internal standard of dodecane with gas chromatography.

11.1 Spectral Analysis

11.1.1 Typical In-Situ IR Spectrums





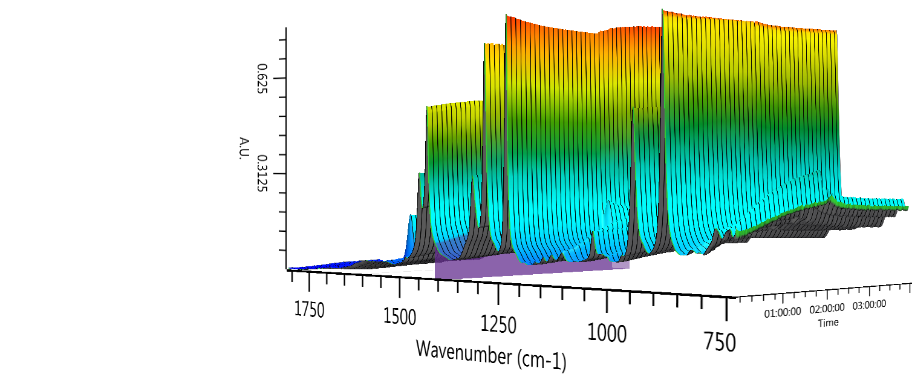


Figure S4: IR spectrum under standard reaction conditions (0.31 M methyl acrylate, 0.15 M 2,3-dimethyl-1,3-butadiene, 100 mg (dppp)$CoBr_2$, 100 mg Zn, 355 mg $ZnBr_2$, and 4 mL DCE) from 1800 cm^{-1} to 750 cm^{-1} from the start of the stirring of the (dppp)$CoBr_2$, Zn, and $ZnBr_2$ process (0 hr) to the end of the reaction (4 hr). Front view, aerial view, and side view respectively.

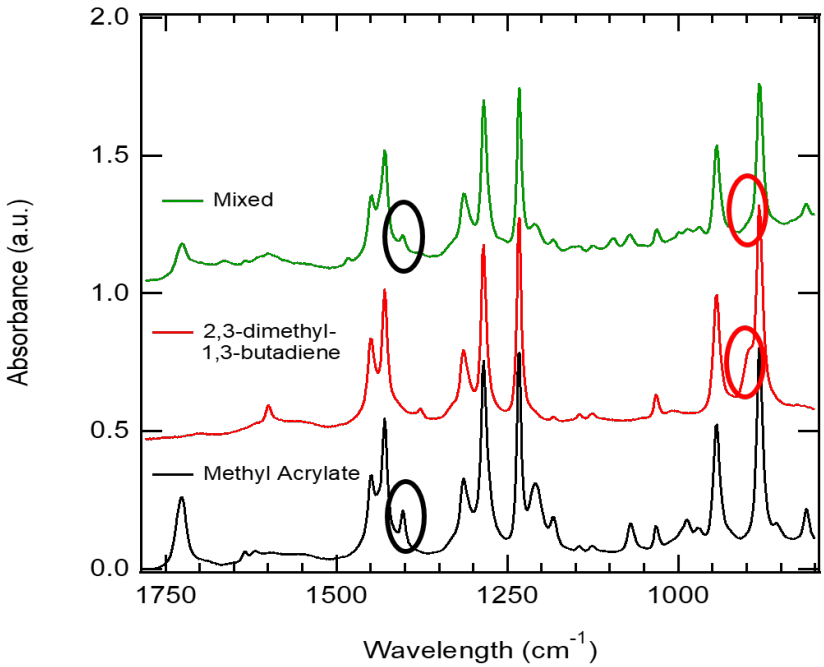


Figure S5. The IR spectrum of methyl acrylate (black), 2,3-dimethyl-1,3-butadiene (red), and a mixture of the 2 (green). Methyl acrylate has a characteristic peak at 1402 cm^{-1} and 2,3-dimethyl-1,3-butadiene has a characteristic peak at 896 cm^{-1}.

Analysis if the IR spectra shows a decrease in the intensities of the peaks that are attributed to methyl acrylate (1402 cm^{-1}) and 2,3-dimethyl-1,3-butadiene (896 cm^{-1}) when they were reacted with the cobalt catalyst (dppp)$CoBr_2$, Zn, and $ZnBr_2$). The frequency of 1402 cm^{-1} is attributed to the scissoring

vibration of the terminal $=CH_2$ group in the methyl acrylate.[5] This peak as can be seen in Figure S4 and S5 to have slight overlap with the DCE peak. However, this proved to not affect the data interpretation. The frequency at 896 cm^{-1} is attributed to the $=CH_2$ out of plane wagging in 2,3-dimethyl-1,3-butadiene.[6] Again this peak is seen to have overlap with a DCE peak, however, it proved to agree well with the decrease seen in 1402 cm^{-1} as the reaction proceeded and thus was used to monitor the 2,3-dimethyl-1,3-butadiene concentration.

11.1.2 UV-Vis Spectra

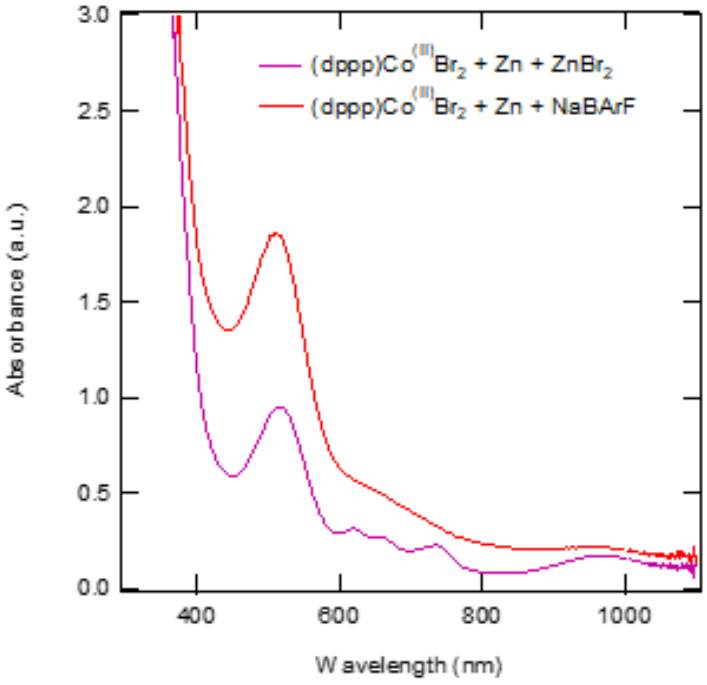


Figure S6. (dppp)Co(II)Br_2 activated with $ZnBr_2$ (purple) and (dppp)Co(II)Br_2 activated with NaBArF (Red) both stirred for 2 hr at the same concentration.

The peak attributed to the active catalyst (517 nm) can be seen in Figure S6. It is seen for the species activated by $ZnBr_2$ (purple) there are peaks present in the range of 600-750 nm. These peaks are attributed to the Co(II) species, and thus not full activation of the active catalyst is seen after the stir time used (ca. 2 hr). The red line represents the activation with NaBArF, the peaks between 600-750 nm are seen to completely go away. This suggest that the activation is complete after the allotted stir time (ca. 2 hr).

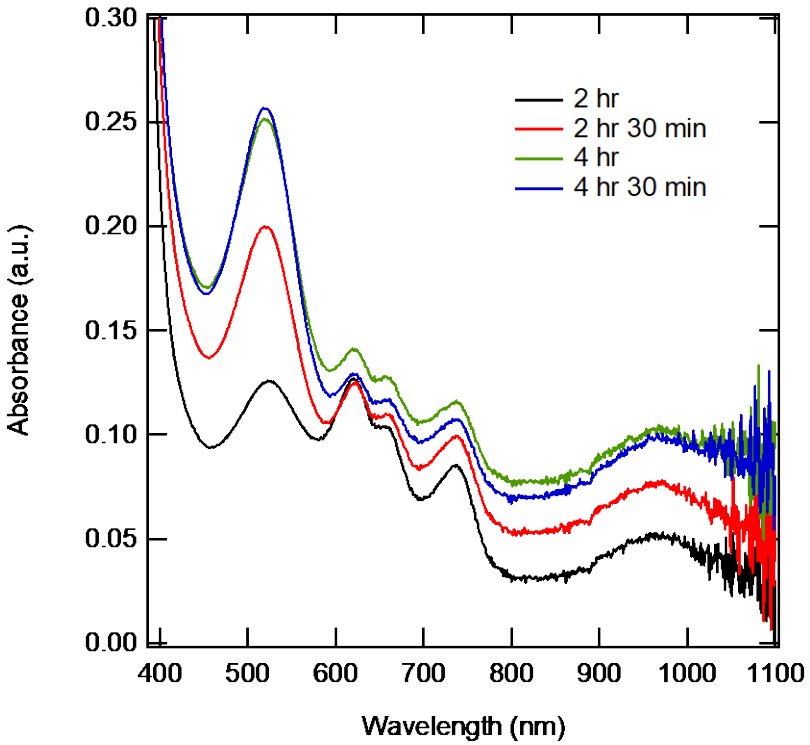


Figure S7. The supernatant of a reaction mixture of (dppp)Co(II)Br_2, Zn, and $ZnBr_2$ was mixed for 2 hr, 2 hr thirty min, four hr, and four hr and thirty min. The peak at 517 nm stops increasing at four hr and thirty min.

Figure S7 shows stir time analysis via UV-Vis. The peak at 517 nm (the peak attributed to the active catalyst) is seen to hit a maximum after ca. four hr. This suggest that after this amount of stirring, as much of the active catalyst has been formed as possible and the induction period is complete.

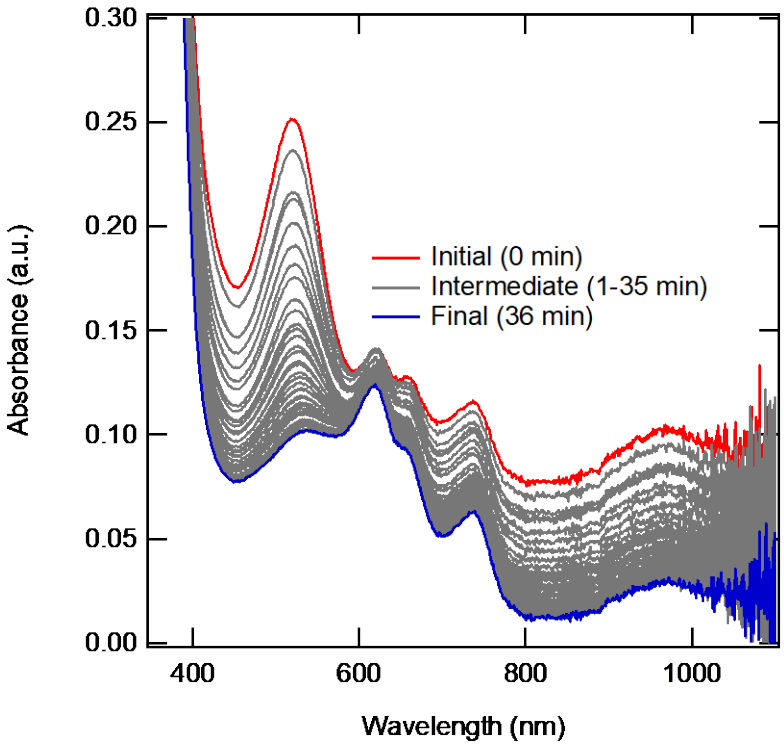


Figure S8. The supernatant of a reaction mixture of (dppp)Co(II)Br_2, Zn, and $ZnBr_2$ was mixed for 2 hr. The UV-Vis spectrum from 0 to 36 min, nonsmoothed. The initial intensity (0 min) is red with the final intensity (36 min) is blue, all intermediate intensities are gray.

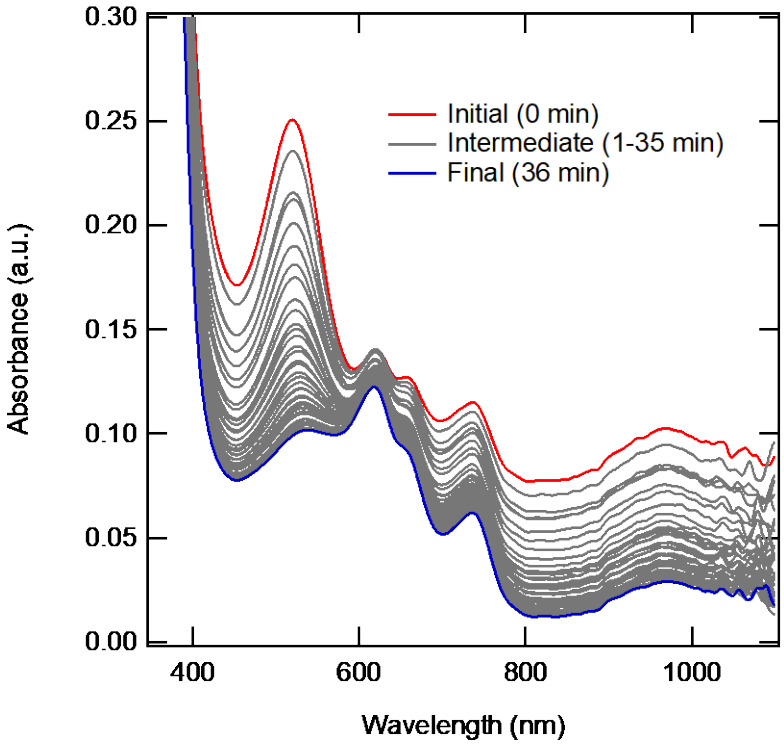
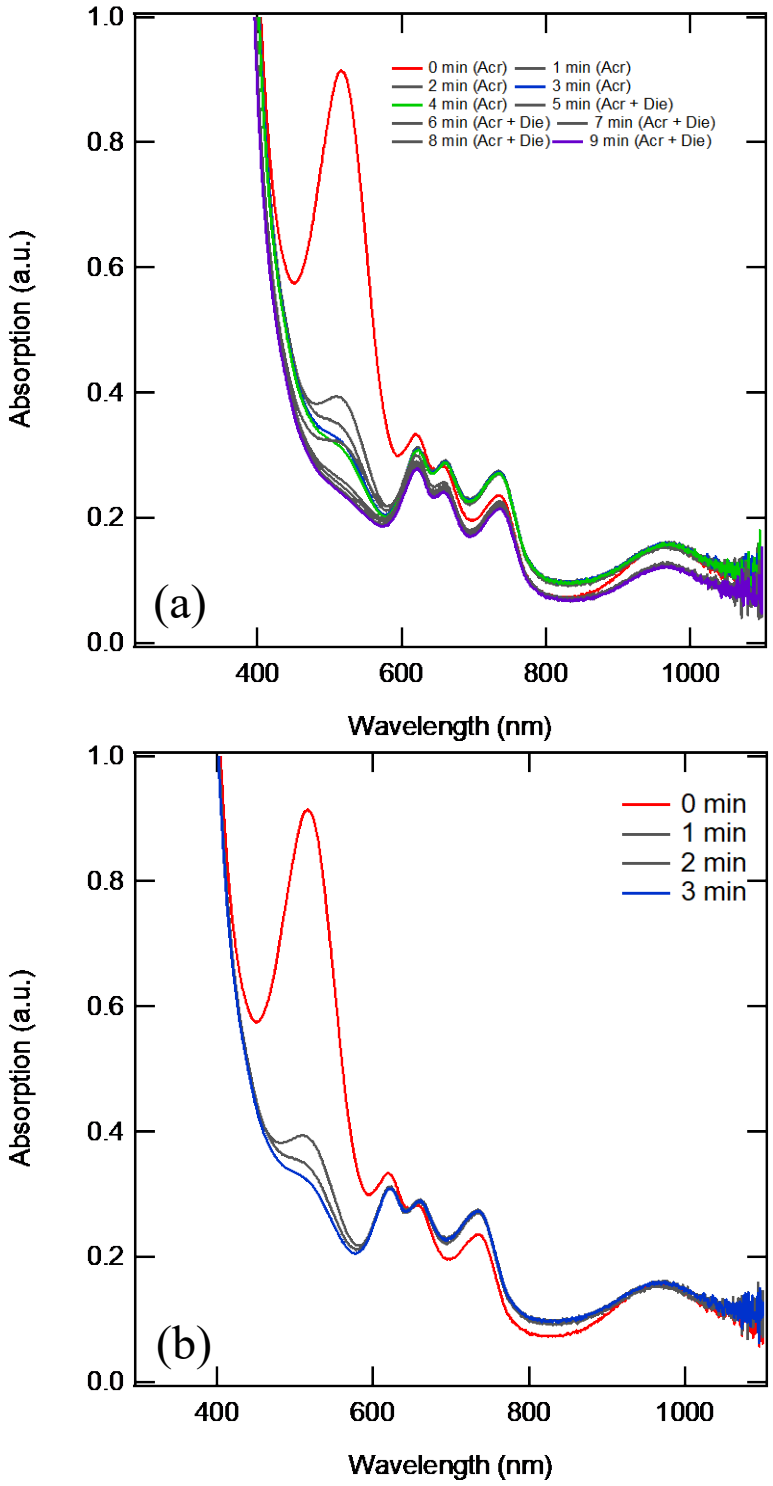


Figure S9. The supernatant of a reaction mixture of (dppp)Co(II)Br_2, Zn, and $ZnBr_2$ was mixed for 2 hr. The UV-Vis spectrum from 0 to 36 min, smoothed. The initial intensity (0 min) is red with the final intensity (36 min) is blue, all intermediate intensities are gray.

Figure S8 and S9 show the change in the active catalyst UV-Vis spectra with time (across a 36 minute duration). Most notably is the decrease in the 517 nm peak. This test was performed in anaerobic and moisture free conditions. This suggest that the active catalyst deactivates through disproportion pathways into most likely Co(II) and Co(0) species as can be seen in the decrease of the Co(I) signature peak at ca. 900 nm and the increase (relative) of the peaks attributed to the Co(II) species, the peaks between the 600-750 nm.[7,8,9,10,11]


0 min (Acr)
1 min (Acr)
2 min (Acr)
3 min (Acr)
4 min (Acr)
5 min (Acr + Die)
6 min (Acr + Die)
7 min (Acr + Die)
8 min (Acr + Die)
9 min (Acr + Die)
(a)
Absorption (a.u.)
Wavelength (nm)
0 min
1 min
2 min
3 min
(b)
Absorption (a.u.)
Wavelength (nm)

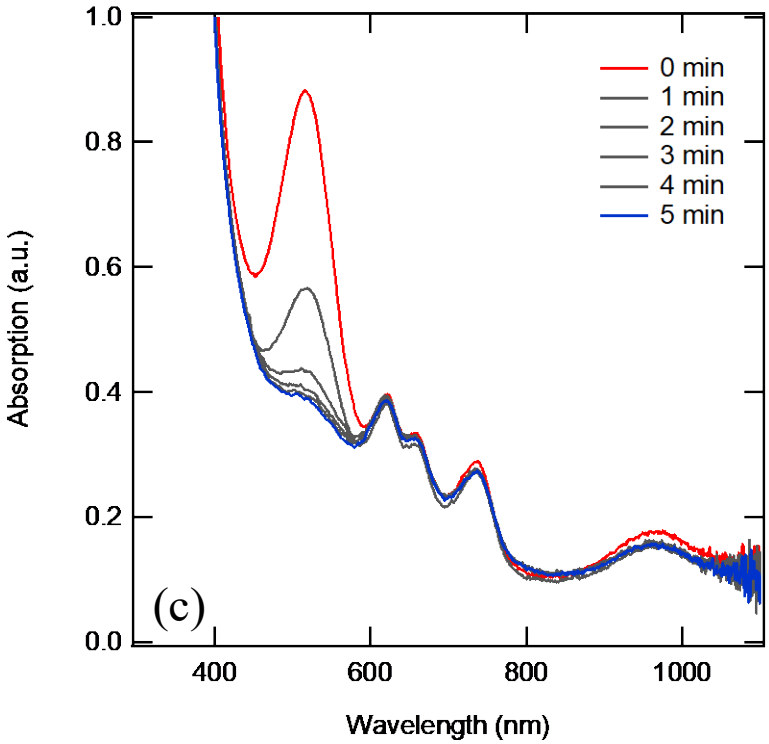


Figure S10. The supernatant of a reaction mixture of (dppp)Co(II)Br_2, Zn, and $ZnBr_2$ was mixed for two hours after which, the following additions were performed: (a) Methyl acrylate in DCE added (0.11 mmoles, 0.22 M, 58 eq with respect to cobalt species) added to $[(dppp)Co(I)]^+$ (0.0038 mmole, 1.9 mM), reading were taken for 4 minutes. 2,3-Dimethyl-1,3-butadiene in DCE added (0.044 mmoles, 0.044 M, 11.63 eq with respect to cobalt species) added to $(dppp)Co(I)^+$ (0.0038 mmole, 19 mM), readings were taken for 5 minutes. (b) Methyl acrylate in DCE added (0.11 mmoles, 0.22 M, 58 eq with respect to cobalt species) added to $[(dppp)Co(I)]^+$ (0.0038 mmole, 1.9 mM). (c) 2,3-Dimethyl-1,3-butadiene in DCE added (0.044 mmoles, 0.044 M, 11.63 eq with respect to cobalt species) added to $DPPPCo(I)^+$ (0.0038 mmole, 19 nM)

Figure S10 shows the affects that methyl acrylate or 2,3-dimethyl-1,3-butadiene have on the UV-Vis spectrum of the active catalyst. Methyl acrylate is shown to both decrease the peak of the active catalyst (517 nm) and increase the peak of the Co(II) species, 600-750 nm. 2,3-dimethyl-1,3-butadiene is shown to decrease the peak at 517 nm, but at a slower rate than the methyl acrylate, and it is decreases the peaks attributed to the Co(II) species, 600-750 nm. When both methyl acrylate and 2,3-dimethyl-1,3-butadiene are added, the change in the UV-Vis spectrum is shown to resemble that of the 2,3-dimethyl-1,3-butadiene more strongly than the change caused by the

methyl acrylate. This suggest that the 2,3-dimethyl-1,3-butadiene is coordinating to the active catalyst more quickly than the methyl acrylate.[7,8,9,10,11] The calculated time constants can be seen below.

Diene: The absorbance was considered to be equivalent to concentration. The data was fit to an exponential function of the form:
Abs=0.76e^(-0.17t)
The natural log was taken of this function in order to obtain a straight line and the function obtained was of the form:
Ln(Abs)=-0.17t-0.274
The rate constant, k, was calculated to be 0.17 Abs/min. The time constant was calculated to be **5.88 min/Abs**.
Acrylate: The absorbance was considered to be equivalent to concentration. The data was fit to an exponential function of the form:
Abs=0.79e^(-0.27t)
The natural log was taken of this function in order to obtain a straight line and the function obtained was of the form:
Ln(Abs)=-0.27t-0.233
The rate constant, k, was calculated to be 0.27 Abs/min. The time constant was calculated to be **3.7 min/Abs**.

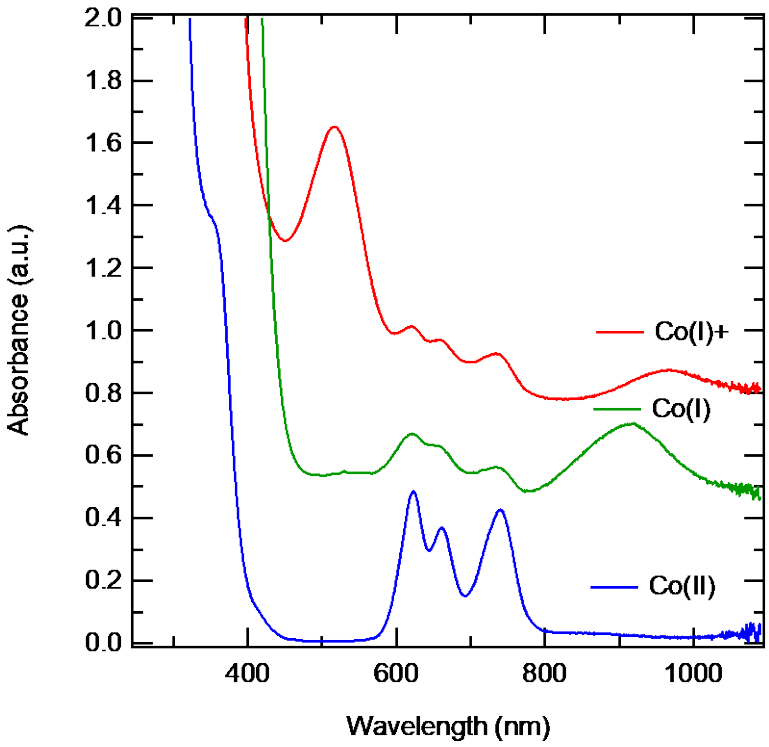


Figure S11. (dppp)$CoBr_2$ (Blue), (dppp)$_3Co_2{}^{I)}Br_2$ (Green), and [(dppp)$Co^{(I)}]^+$ (Red). (dppp)$CoBr_2$ (Blue) and (dppp)$_3Co_2Br_2$ (Green) were obtained from pure crystallized material of the named compound. [(dppp)$Co^{(I)}]^+$ (Red) was obtained by the following: the supernatant of a reaction mixture of (dppp)$CoBr_2$, Zn, and $ZnBr_2$ was mixed for 2 hr. The three spectra are offset (Y-axis) to allow for ease of reading.

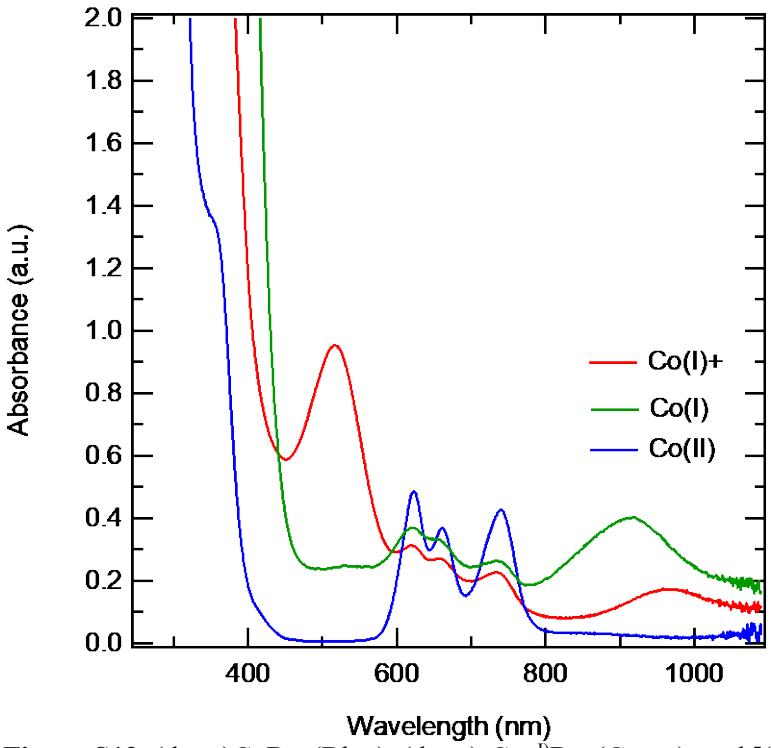


Figure S12. (dppp)$CoBr_2$ (Blue), (dppp)$_3Co_2{}^{I)}Br_2$ (Green), and [(dppp)$Co^{(I)}]^+$ (Red). (dppp)$CoBr_2$ (Blue) and (dppp)$_3Co_2Br_2$ (Green) were obtained from pure crystallized material of the named compound. [(dppp)$Co^{(I)}]^+$ (Red) was obtained by the following: the supernatant of a reaction mixture of (dppp)$CoBr_2$, Zn, and $ZnBr_2$ was mixed for 2 hr.

Figure S11 and S12 show the isolated spectra for (dppp)$CoBr_2$, (dppp)$_3Co_2^{(I)}Br_2$ crystals, and the active species [(dppp)$Co^{(I)}]^+$ species. The (dppp)$CoBr_2$ species shows three peaks between 600-700 nm which are indicative of a Co(II) d-d transitions. The (dppp)Co(I)Br crystals show both a merging of the peaks between 600-750 nm and the formation of a peak at 913 nm, that matches the reported spectra of different Co(I) species. The active species [(dppp)Co(I)]$^+$ shows both a shift in the 913 nm peak to ca. 960 nm and the formation of an intense peak at 517 nm. This matches reported spectra of other cationic cobalt species.[7,8,9,10,11]

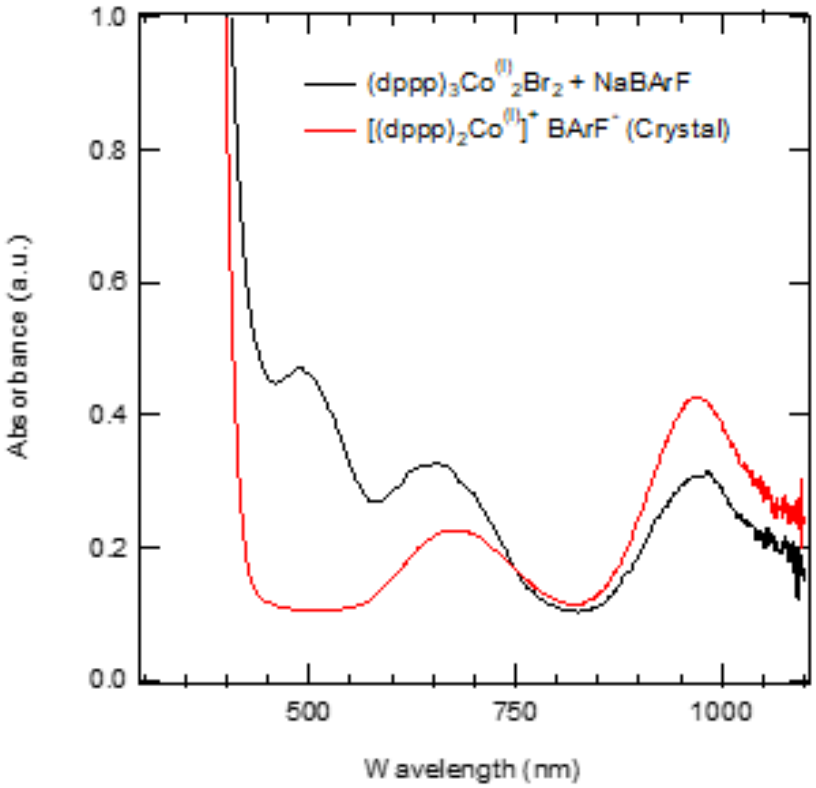


Figure S13. The UV-Vis spectrum of crystalline $(dppp)_3Co_2Br_2$ with the addition of NaBArF compared to the crystal structure of $[(dppp)_2Co(I)]^+$ $BArF^-$. The peak attributed to the active catalyst is at ca. 500 nm. This peak is not seen in the crystalline $[(dppp)_2Co^{(I)}]^+$ $BArF^-$.

Figure S13 shows a comparison of an isolated $[(dppp)_2Co^{(I)}]^+$ $BArF^-$ species to that of activated crystalline $(dppp)_3Co_2^{(1)}Br_2$ (activated using NaBArF). It can be seen that upon activation of the crystalline Co(I) complex with NaBArF, a peak at ca. 500 nm appears. This matches closely with the experimental spectra for the active catalyst that was achieved by reducing (dppp)Co(II)Br_2 with Zn and then activating it with $ZnBr_2$. This suggest that the cationic crystal structure $[(dppp)_2Co^{(I)}]^+$ $BArF^-$ obtained is not the active catalyst, but instead it is an inactive species.

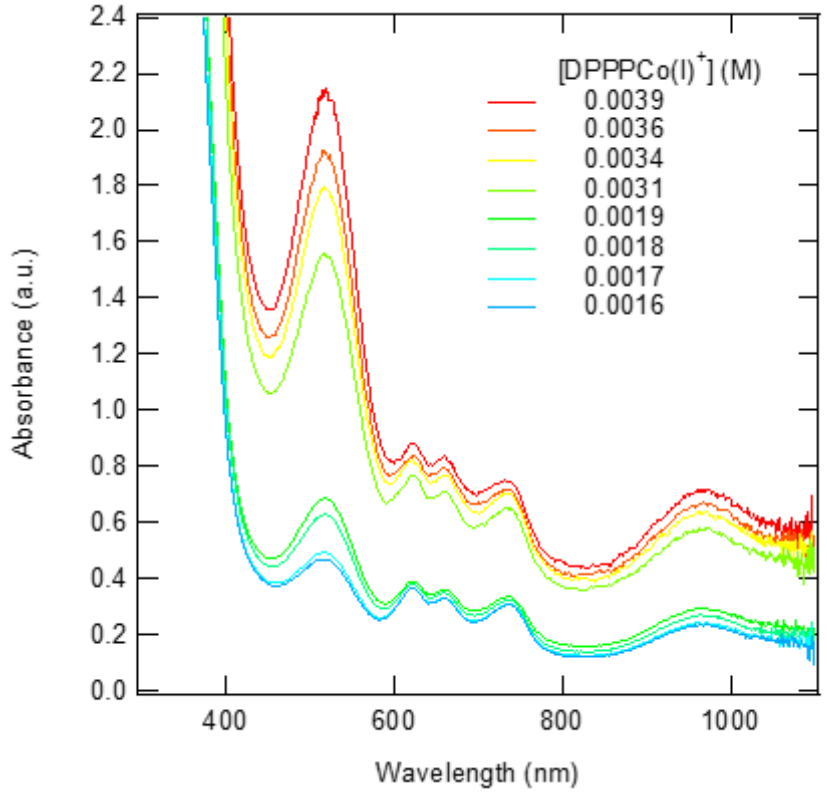


Figure S14. The supernatant of a reaction mixture of (dppp)Co(II)Br2, Zn, and ZnBr2 was mixed for two hours after which, the solution was diluted to make the following molariy solutions of (dppp)Co(II)Br2: 0.0039 M, 0.0036 M, 0.0034 M, 0.0031 M, 0.0019, 0.0018, 0.0017, and 0.0016 M

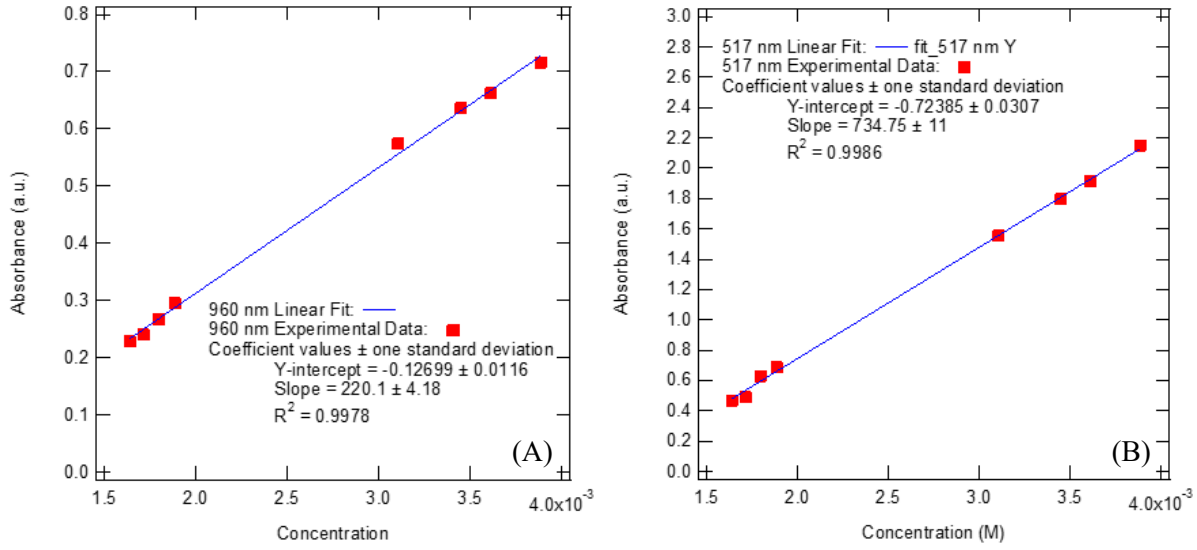


Figure S15. The absorbance values for 960 nm and 517 nm graphed agains the concentration.

Figure S14 shows the absorbance of the (dppp)Co(II)Br2 catalyst across multiple dilutions. Figure S15 shows the absorbance graphed against concentration. The absorbance is shown to have a linear relationship with concentration within the range shown.

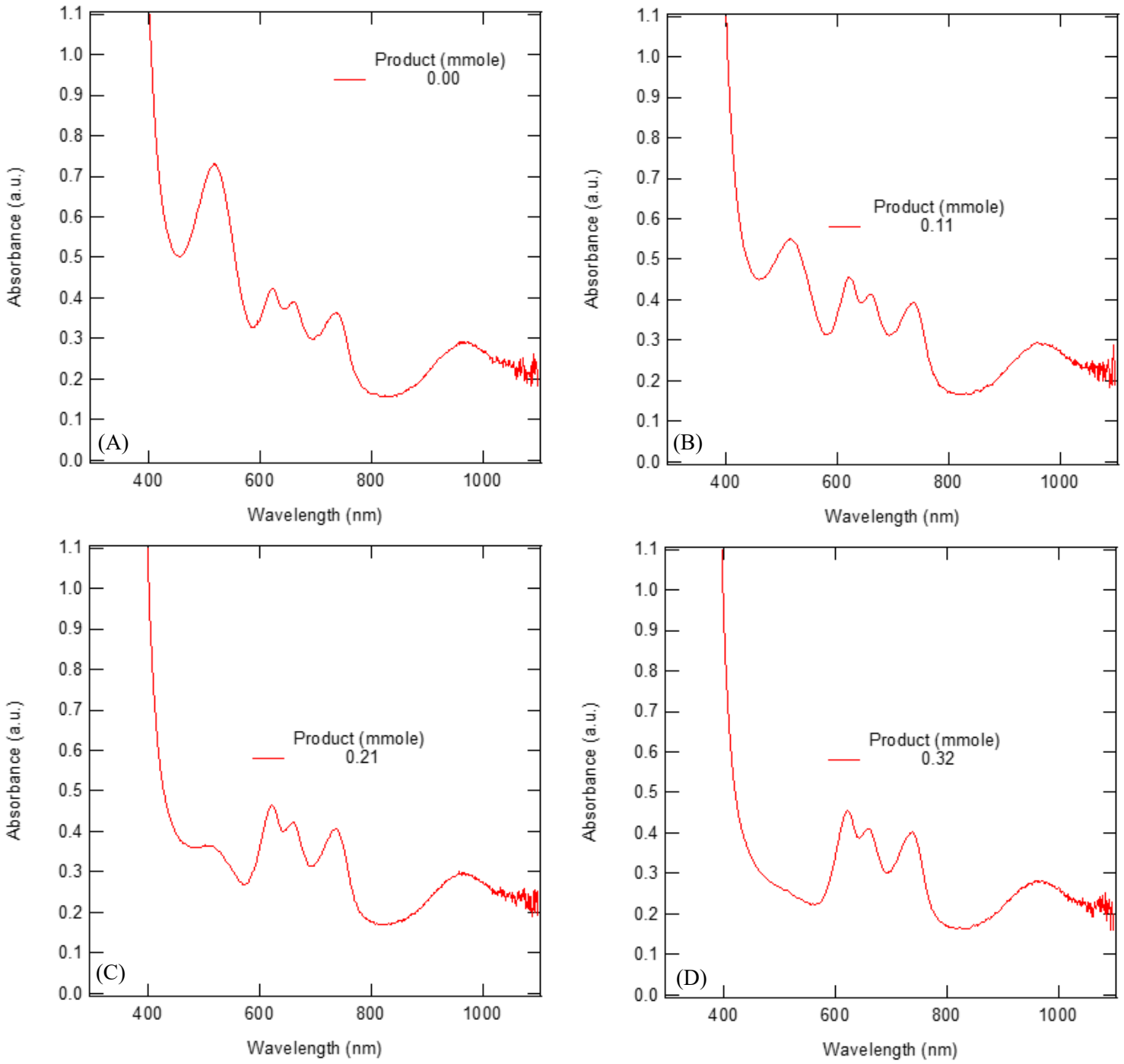


Figure S16. The supernatant of a reaction mixture of (dppp)Co(II)Br2, Zn, and ZnBr2 was mixed for two hoursas described in section 8.1.9. Product was added to the solution of 0.0019 M (dppp)Co(II)Br2 solution to obtain the following amount of product: 0.11 mmole (b) , 0.22 mmole (d), and 0.32 mmole (d).

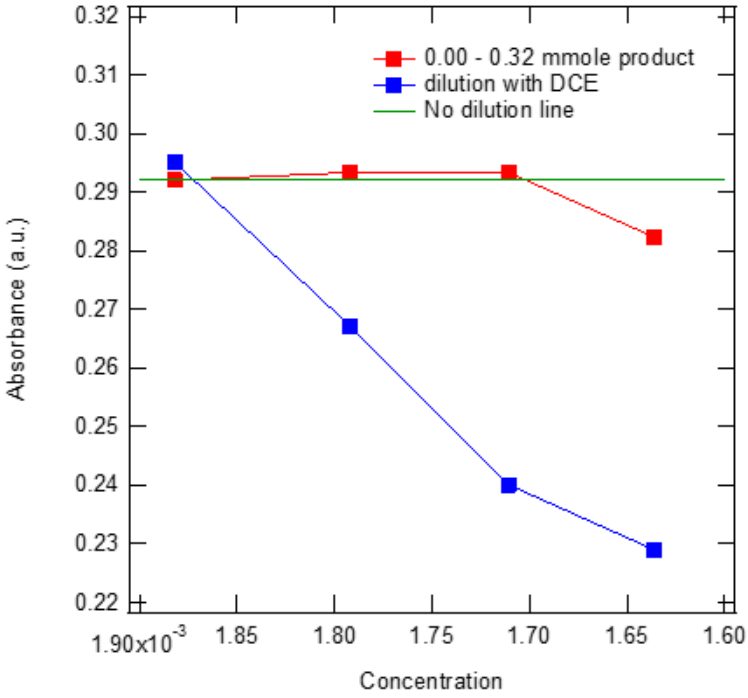


Figure S17. The profile of the absorbance at 960 nm from Figure S14 and S16. The blue line shows the effect of dilution with DCE on the absorbance spectra for (dppp)Co(I)+. The red line shows the effect of product being added (resulting in a concentration of (dppp)Co(I)+ that is the same as the concentration shown in the blue line) to the absorbance spectra of (dppp)Co(I)+.

Figure S17 shows that product is able to bind to the catalyst. As product is added, the absorbance at 960 nm is shown to stay approximately constant (red line). When the same dilution is made without product, the peak at 960 nm is shown to decrease (blue line). Figure S18 shows that diene binds to (dppp)Co(I)+ over the product when diene is in large enough concentrations. This is shown by the decrease in the peak at ca. 960 nm.

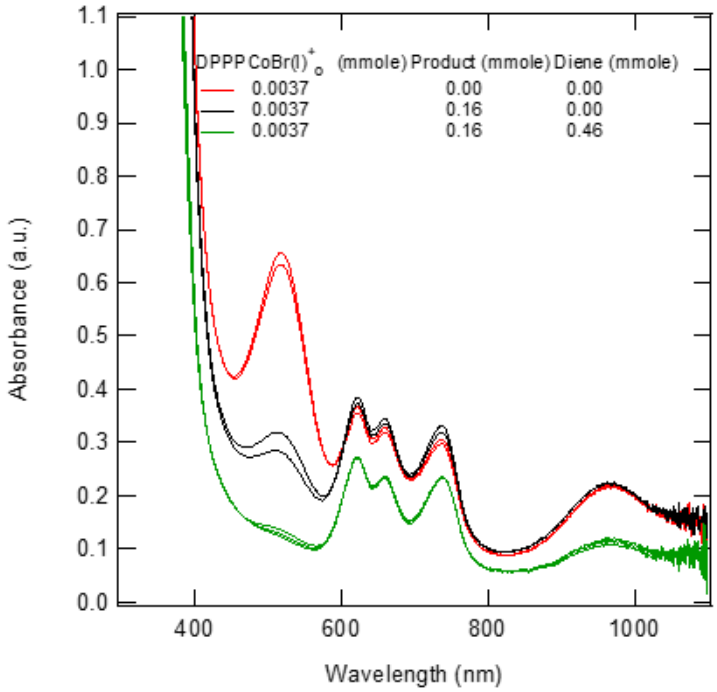
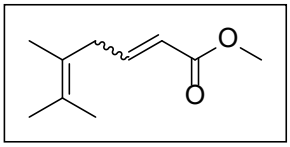


Figure S18. The supernatant of a reaction mixture of (dppp)Co(II)Br2, Zn, and ZnBr2 was mixed for two hoursas described in section 8.1.10. 0.0019 M solution of (DPPP)Co(I)+ was prepared. To this 0.16 mmole product was added. After two minutes 0.46 mmole diene was added to the solution.

11.1.3 ^{1}H and ^{13}C NMR of Pure product



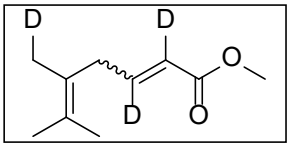
Methyl 5,6-dimethylhepta-2,5-dienoate: The reaction between 2.3-dimethyl-1,3-butadiene (145.20 mg, 1.77 mmol) and methyl acrylate (249.52, 2.90 mmol) in DCM and (dppp)$CoBr_2$ (153.00 mg, 0.24 mmol), zn (156 mg, 0.69 mmol), and $ZnBr_2$ (590 mg, 0.67 mmol) and were reacted for 4 hr. Upon completion, the reaction was filtered through a short pad of silica using 50:50 diethyl ether:hexanes (5 mL). The product was isolated by evaporating off the solvent to yield the titled compound as a colorless oil. 90% yield from G.C. analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (dt, , J = 15.66 Hz, 6.54, 1 H), 5.77 (dt, J = 15.46, 1.66, 1 H), 3.71 (s, 3 H), 2.89 (d, 6.60 , 2 H), 1.67 (s, 3 H), 1.63 (s, 6 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 167.58, 147.57, 127.65, 123.49, 51.69, 37.74, 20.90, 20.56, 18.94

11.1.4 NMR Analysis of (dppp)Co(m)Br_n Species

All the NMR samples were made inside the N_2- filled glove-box (Specific amount of each species is mentioned on the corresponding spectra). The NMR tube was capped which was wrapped by Teflon tape.

1. (dppp)$CoBr_2$ (10 mg dissolved in 0.6mL $CDCl_3$ in NMR tube) – no ^{31}P Signal
2. (dppp)$CoBr_2$ (10 mg, 0.0158 mmol, 1 equiv.) and Zn (10 mg, 0.158 mmol, 10 equiv.) dissolved in 0.6mL $CDCl_3$ in NMR tube. NMR took after 15 min – ^{31}P (243 MHz, $CDCl_3$) δ -21.87, 15.47.
3. (dppp)$CoBr_2$ (10 mg, 0.0158 mmol, 1 equiv.), Zn (10 mg, 10 equiv.), and $ZnBr_2$ (7mg, 2 equiv.) dissolved in 0.6 mL $CDCl_3$ in NMR tube. ^{31}P NMR took after 30 min. ^{31}P (243 MHz, $CDCl_3$) δ -21.89 (No peak at δ ~ 15.47)
4. (dppp)$CoBr_2$ (10 mg, 0.0158 mmol, 1 equiv.), Zn (10 mg, 10 equiv.), and NaBARF (18mg, 2 equiv.) dissolved in 0.6 mL $CDCl_3$ in NMR tube. 31P NMR took after 30 min. ^{31}P (243 MHz, $CDCl_3$) δ -21.29

11.1.5 ^{1}H and ^{13}C NMR of Deuterated product



d_3-Methyl 5,6-dimethylhepta-2,5-dienoate: The reaction between 2.3-dimethyl-1,3-butadiene (20.3 mg, 0.25 mmol) and d_3-methyl acrylate (23.3 mg, 0.26 mmol) in DCM and (dppp)$CoBr_2$ ((10.2 mg, 0.016 mmol), Zn (9.5 mg, 0.15 mmol), and $ZnBr_2$ (32.4 mg, 0.144 mmol) and were reacted for 3 hr. Upon completion, the reaction was filtered through a short pad of silica using 50:50 diethyl ether:pentanes (5 mL). The product was isolated by evaporating off the solvent to yield the titled compound as a colorless oil. 39.6 % yield by G.C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.71 (s, 3 H), 2.89 (s, 2 H), 1.67 (s, 3 H), 1.63 (s, 6 H). ^{13}C NMR (600 MHz, $CDCl_3$): δ 167.42, 147.57, 127.44, 123.32, 51.508, 37.4203, 20.70, 20.1 (t, 19.5 Hz, CDH_2), 18.75

^{1}H and ^{13}C NMR and Chromatograms

Data File C:\CHEM32\1\DATA\GRAY\MGMH_031ACR_015DIE_82818_POST.D
Sample Name: MGMH_031ACR_015DIE_82818_POST

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Injection Date  : 8/28/2018 6:30:12 PM
                                                  Inj Volume : 1 µl
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Last changed    : 7/16/2018 5:12:02 PM by Gray
Analysis Method : C:\CHEM32\1\DATA\JON\JG-02-119-COL.D\JG.M
Last changed    : 2/21/2019 3:44:48 PM by mp
                  (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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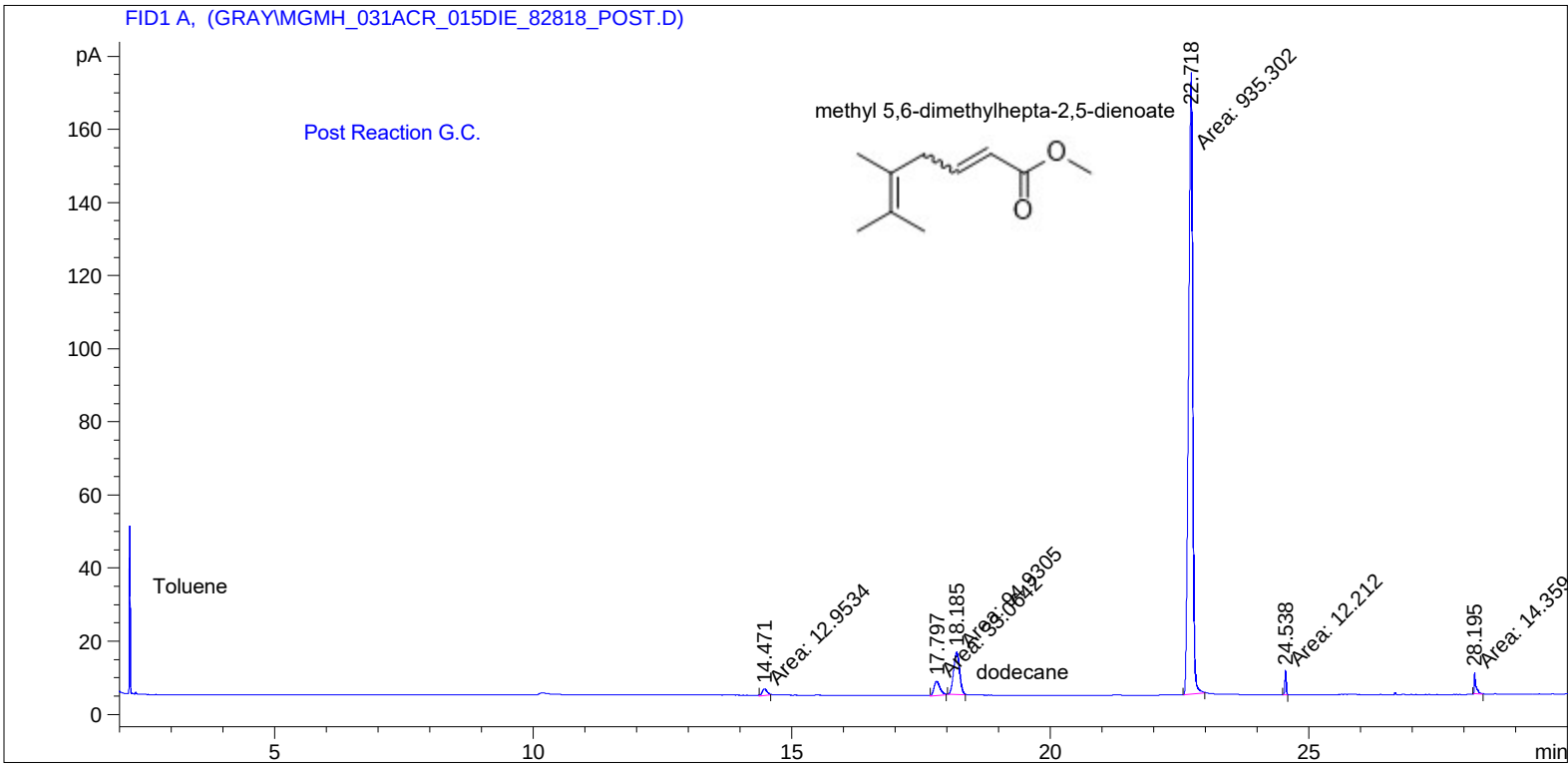


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Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1   1.183 VV    0.0101   47.14670   72.71666  4.09983 2,3-dimethyl-1,3-butadiene
   2  14.471 MM    0.1131   12.95340    1.90940  1.12641
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Data File C:\CHEM32\1\DATA\GRAY\MGMH_031ACR_015DIE_82818_POST.D
Sample Name: MGMH_031ACR_015DIE_82818_POST

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
3	17.797	MM	0.1391	33.06422	3.96246	2.87523	
4	18.185	MM	0.1360	94.93047	11.63571	8.25506	dodecane
5	22.718	MM	0.0917	935.30182	170.06023	81.33288	methyl 5,6-dimethylhepta-2,5-dienoate
6	24.538	MM	0.0304	12.21197	6.68881	1.06194	
7	28.195	MM	0.0412	14.35902	5.80433	1.24865	
Totals :				1149.96759	272.77760		

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*** End of Report ***

Data File C:\CHEM32\1\DATA\GRAY\MGMH_031ACR_015DIE_82818_PRE.D
Sample Name: mgmh_031acr_015die_82818_pRE

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Acq. Instrument : Instrument 1                    Location : Vial 1
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                                                  Inj Volume : 1 µl
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Last changed    : 7/16/2018 5:12:02 PM by Gray
Analysis Method : C:\CHEM32\1\DATA\JON\JG-02-119-COL.D\JG.M
Last changed    : 2/21/2019 3:48:57 PM by mp
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Sample Info     : MORE CONCENTRATED 50 RAMP


Additional Info : Peak(s) manually integrated
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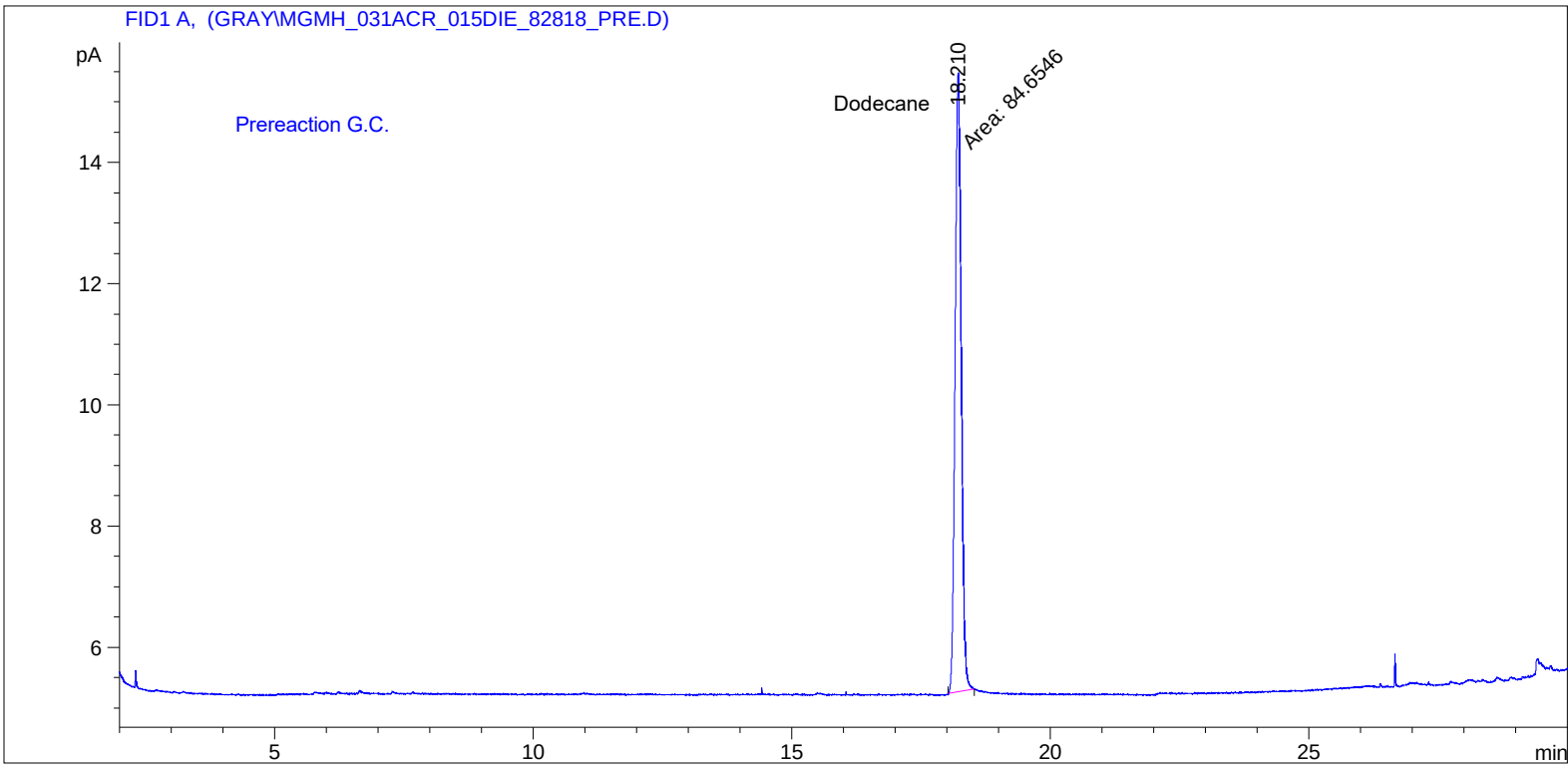


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Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs
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Data File C:\CHEM32\1\DATA\GRAY\MGMH_031ACR_015DIE_82818_PRE.D
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Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
1	1.182	VV S	9.10e-3	658.05780	1162.90784	88.60197	2,3-dimethyl-1,3-butadiene
2	18.210	MM	0.1382	84.65459	10.21097	11.39803	Dodecane

Totals : 742.71239 1173.11881

*** End of Report ***

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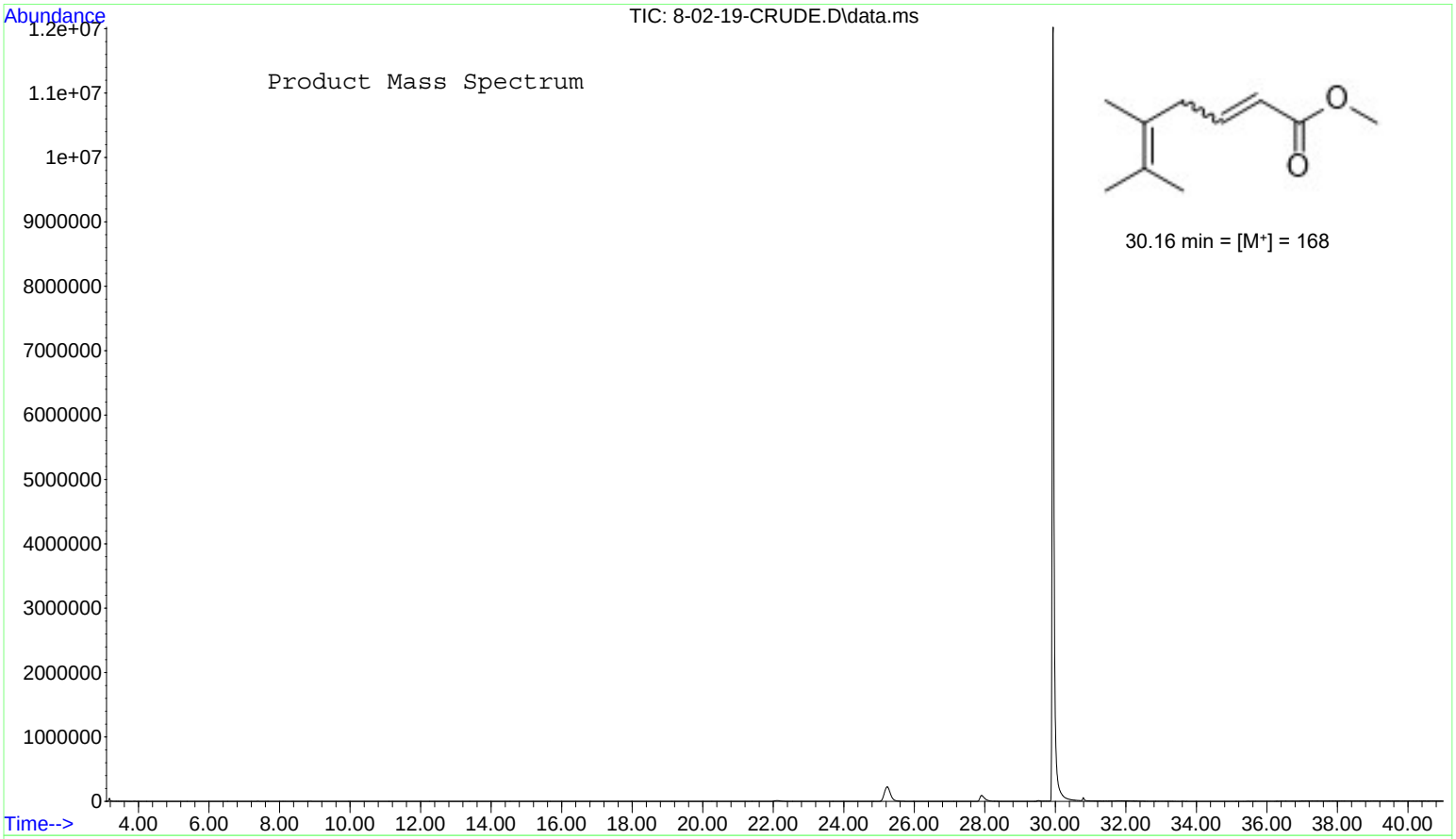
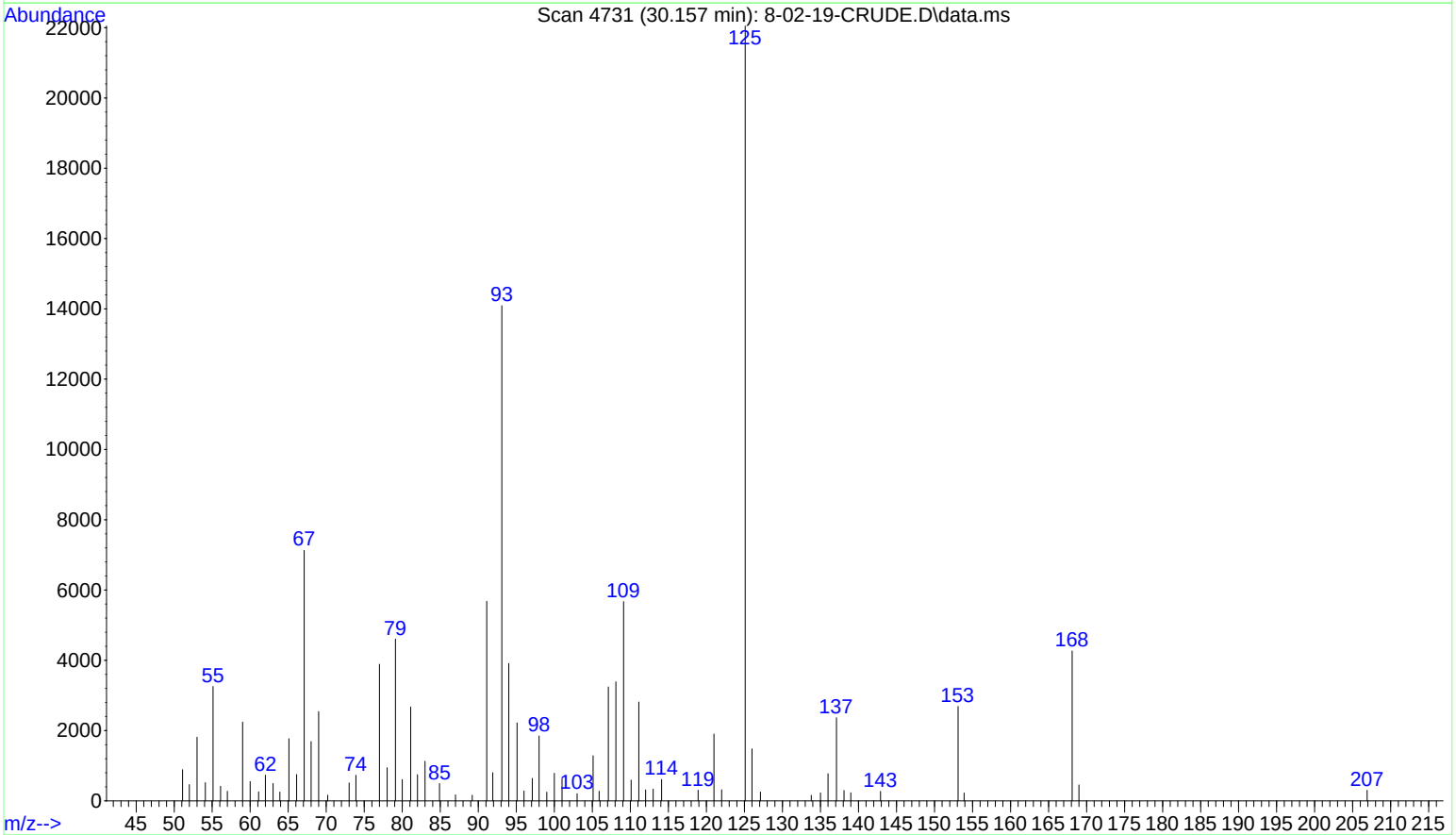
Instrument : GCMS
Sample Name: 8-02-18-Crude
Misc Info :
Vial Number: 2





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Acquired   :  6 Aug 2018  16:13     using AcqMethod MGMH_Method.M
Instrument :    GCMS
Sample Name: 8-02-18-Crude
Misc Info  :
Vial Number: 2
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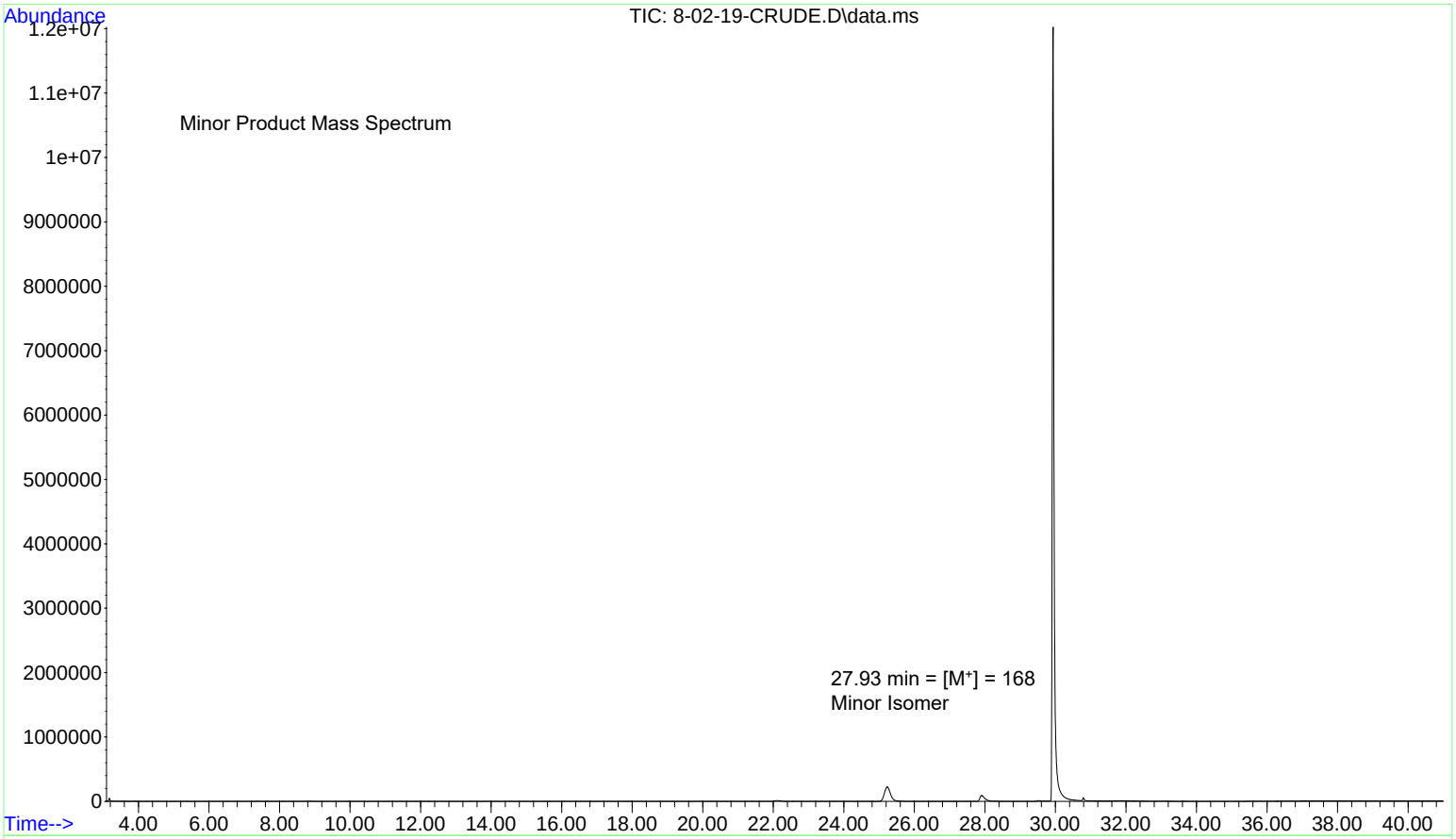

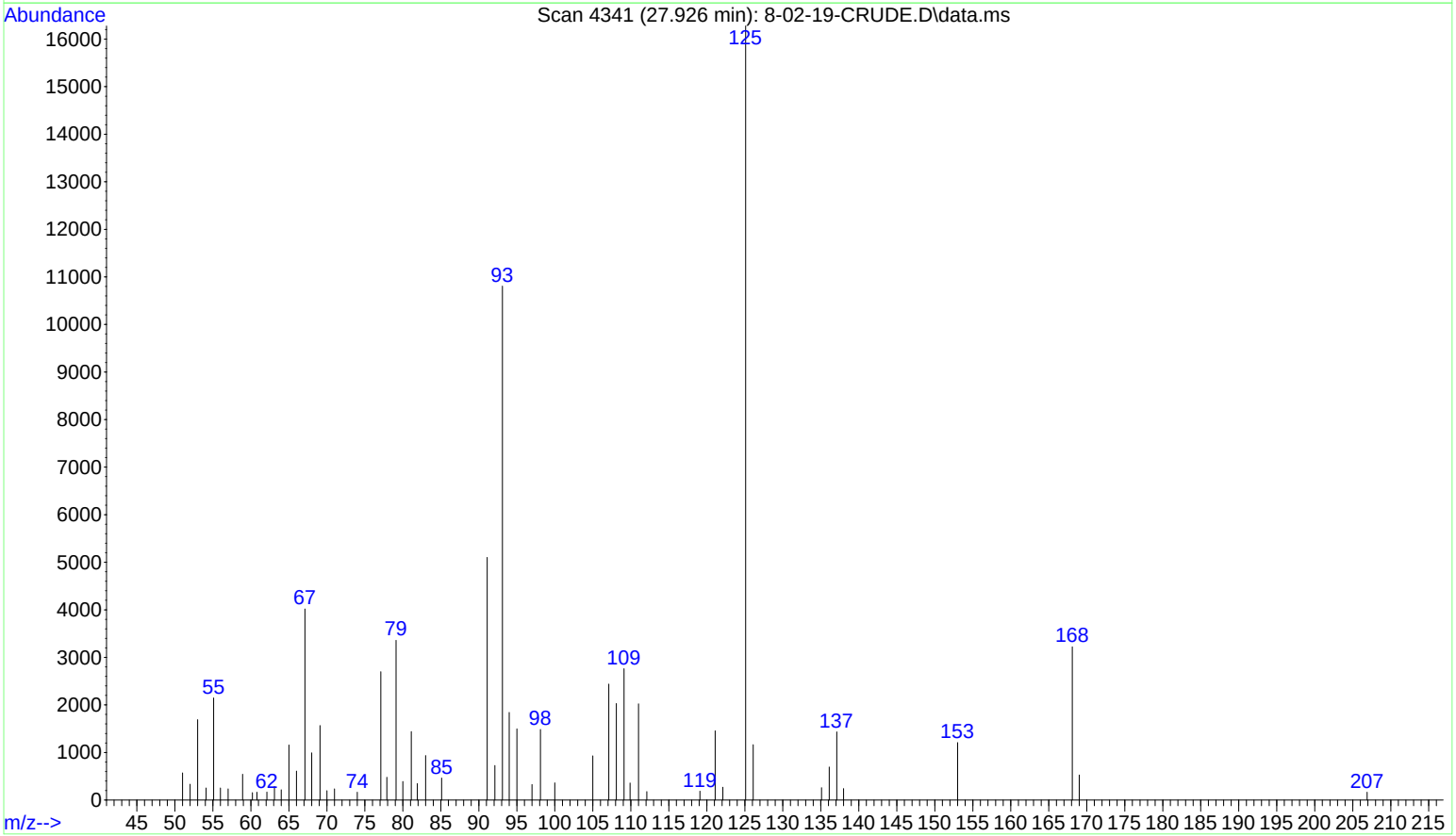

Data File C:\CHEM32\1\DATA\GRAY\04-06-19-YES-ZNBR2.D
Sample Name: 04-06-19-YES-ZNBR2

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Acq. Instrument : Instrument 1                    Location : Vial 11
Injection Date  : 4/6/2019 5:05:01 PM
                                                  Inj Volume : 1 µl
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Last changed    : 4/6/2019 4:57:56 PM by gRAY
Analysis Method : C:\CHEM32\1\DATA\JON\JG-02-119-COL.D\JG.M
Last changed    : 5/24/2019 4:08:43 PM by MP
                  (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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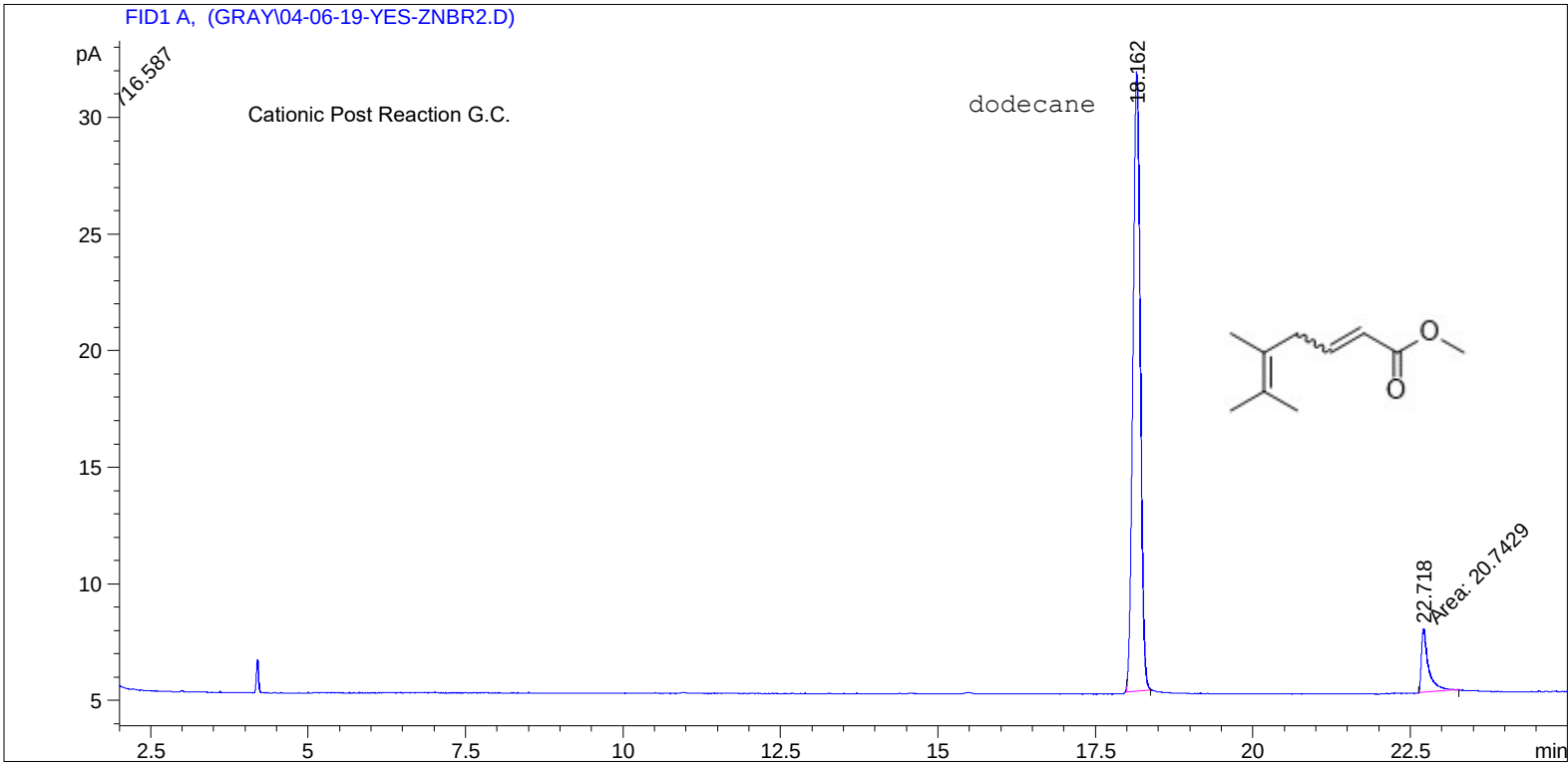


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Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,
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Data File C:\CHEM32\1\DATA\GRAY\04-06-19-YES-ZNBR2.D
Sample Name: 04-06-19-YES-ZNBR2

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1	1.182	MM	8.96e-3	716.58673	1332.75073	75.11813
2	18.162	BB	0.1223	216.61685	26.51304	22.70744
3	22.718	MM	0.1270	20.74292	2.72173	2.17443
Totals :				953.94650	1361.98551	

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*** End of Report ***

Data File C:\CHEM32\1\DATA\GRAY\04-06-19-NO-ZNBR2.D
Sample Name: 04-06-19-NO-ZNBR2

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Acq. Operator   : gRAY
Acq. Instrument : Instrument 1                    Location : Vial 10
Injection Date  : 4/6/2019 4:21:54 PM
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\MH_MG_50_5MIN_70_15_MIN_250_5MIN.M
Last changed    : 9/22/2018 5:50:10 PM by MAHESH
Analysis Method : C:\CHEM32\1\DATA\JON\JG-02-119-COL.D\JG.M
Last changed    : 5/24/2019 4:06:59 PM by MP
                  (modified after loading)
Method Info     : General Higher BP that correlates to Stambuli Group's GCMS - 30 min
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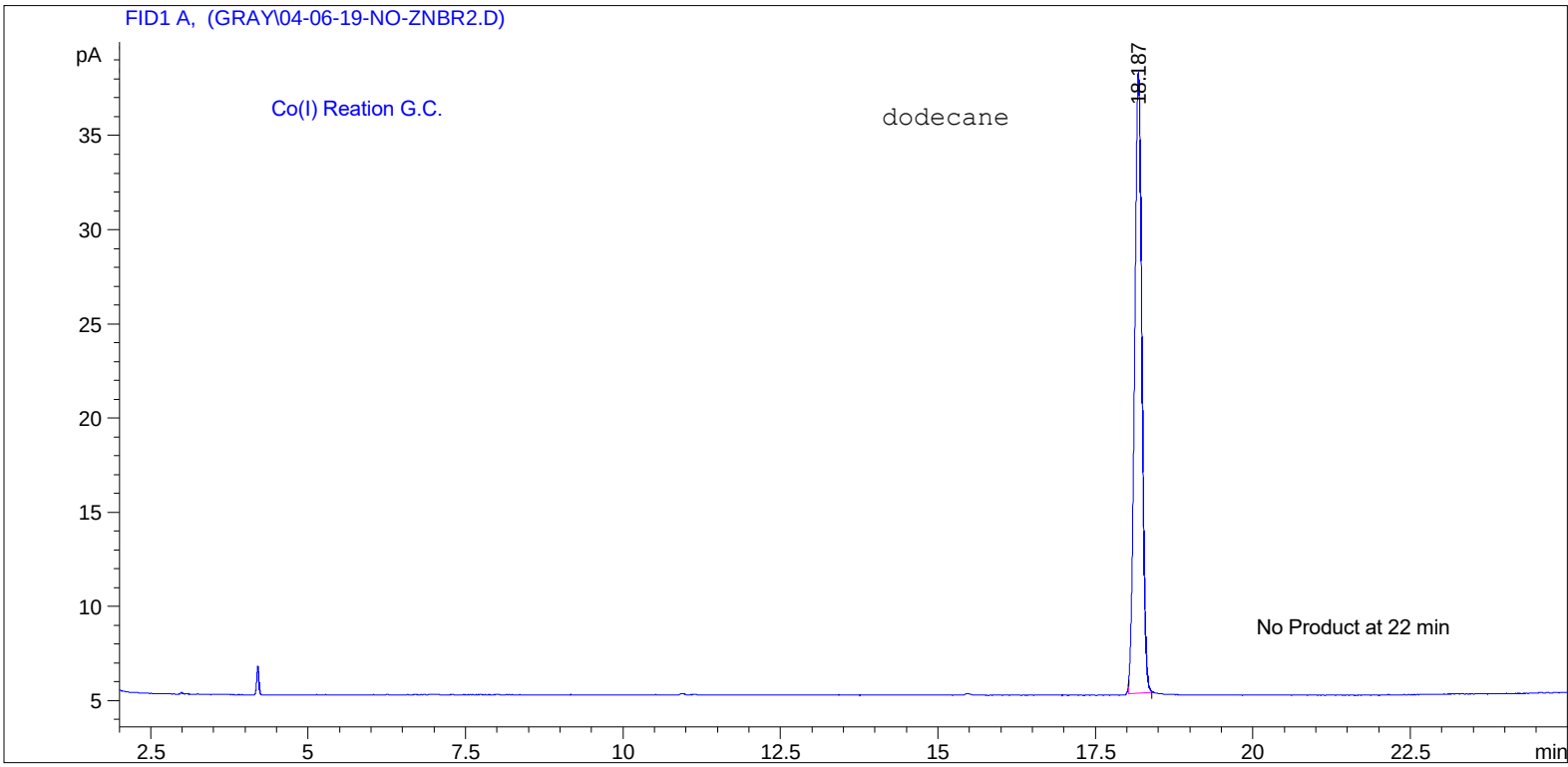


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Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   1.110 BV S  0.0111 1.03955e4  1.50564e4  13.21012
   2   1.147 VV S  0.0103 5.44367e4  8.83918e4  69.17587
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Data File C:\CHEM32\1\DATA\GRAY\04-06-19-NO-ZNBR2.D
Sample Name: 04-06-19-NO-ZNBR2

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
3	1.185	PV S	0.0107	971.59753	1518.90210	1.23467
4	1.218	PB S	0.0107	1.19648e4	1.86206e4	15.20436
5	1.326	BB	0.0114	550.08496	761.88428	0.69902
6	1.870	BB	0.0155	107.41399	109.34675	0.13650
7	18.187	BB	0.1221	267.13889	32.77401	0.33947
Totals :				7.86932e4	1.24492e5	

*** End of Report ***

Data File C:\CHEM32\1\DATA\GRAY\MG_02_35_CONC_3M_POST.D
Sample Name: MG_02_35_CONC_3M_POST

==========

Acq. Operator : GRAY
Acq. Instrument : Instrument 1 Location : Vial 12
Injection Date : 6/4/2019 8:53:48 AM
Inj Volume : 1 µl
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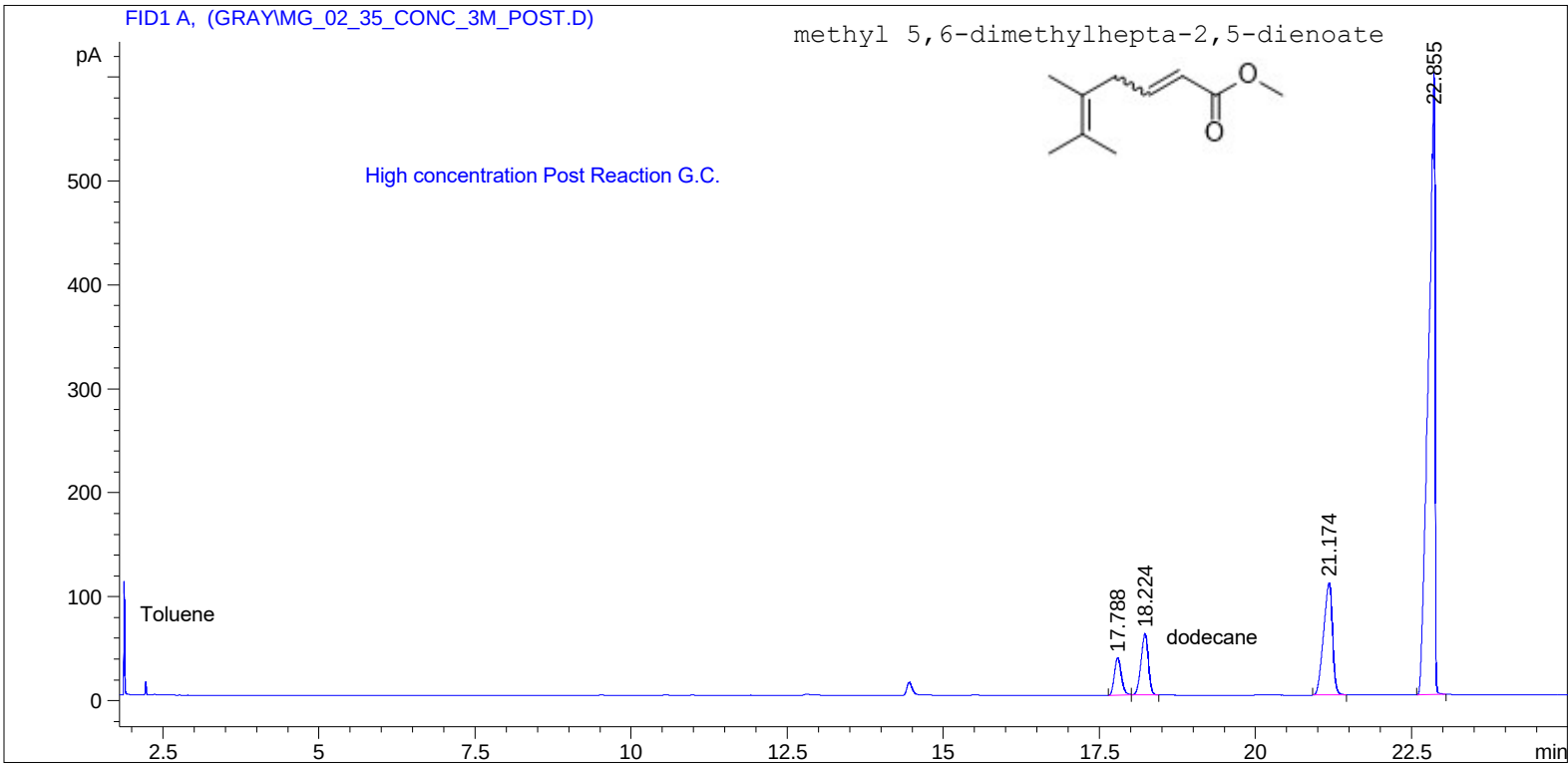
Last changed : 9/22/2018 5:50:10 PM by MAHESH
Analysis Method : C:\CHEM32\1\DATA\JON\JG-02-119-COL.D\JG.M
Last changed : 9/19/2019 12:47:42 PM by Jon
(modified after loading)
Method Info : General Higher BP that correlates to Stambuli Group's GCMS - 30 min

Additional Info : Peak(s) manually integrated



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Area Percent Report

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Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

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Sample Name: MG_02_35_CONC_3M_POST

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1	1.182	VV S	9.14e-3	1.53719e4	2.70155e4	71.09499
2	17.788	BV	0.0921	280.49377	36.20875	1.29728
3	18.224	VB	0.0972	485.05856	59.10673	2.24339
4	21.174	BB	0.1166	1076.78674	108.42671	4.98012
5	22.855	BB	0.0887	4407.41309	598.56598	20.38422
Totals :				2.16217e4	2.78178e4	

*** End of Report ***

Data File C:\CHEM32\1\DATA\GRAY\MG-02-035_BATCH_CONC_3M_PRE.D
Sample Name: MG-02-035_BATCH_CONC_3M_PRE

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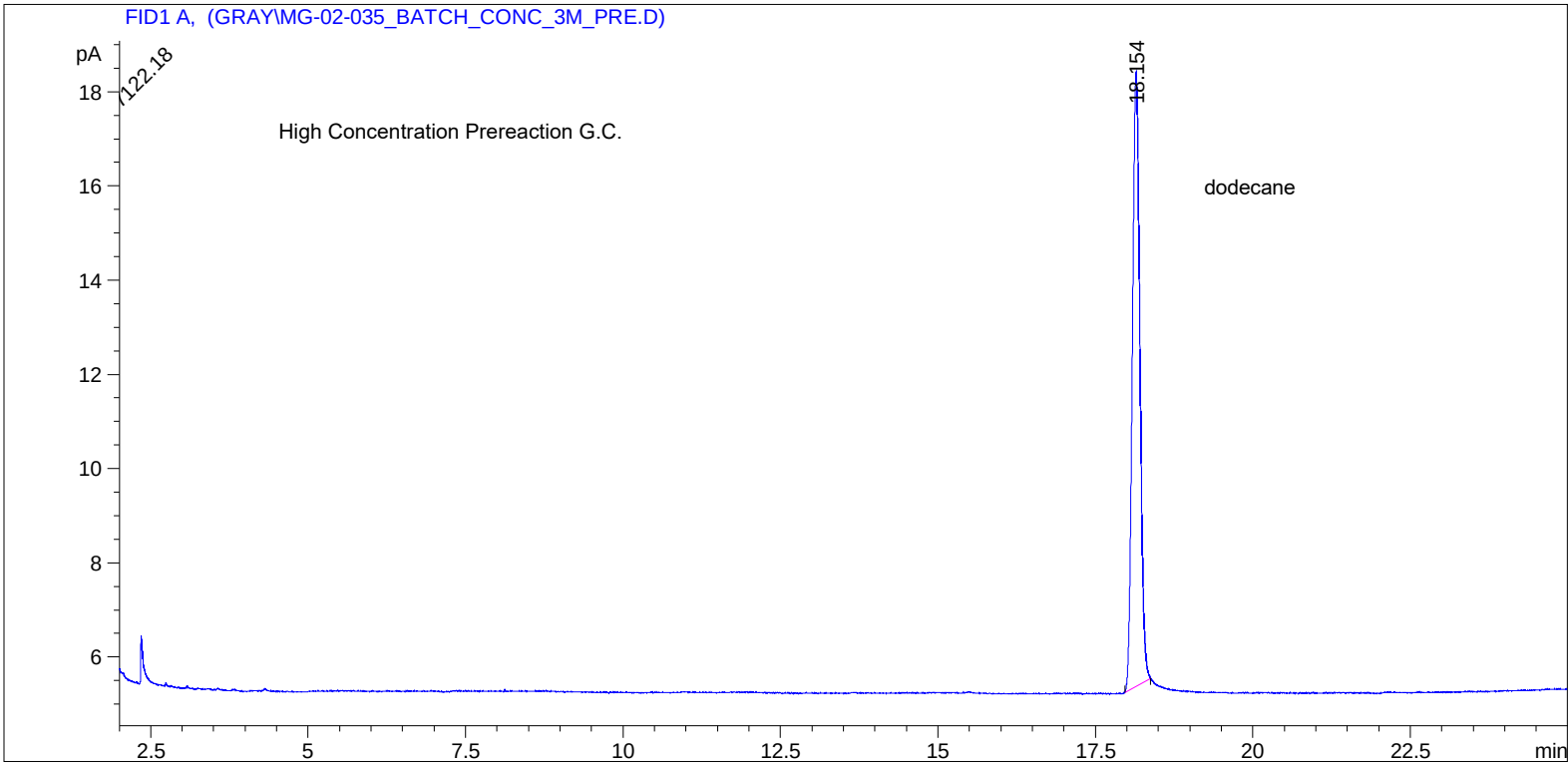
Acq. Operator : MG
Acq. Instrument : Instrument 1 Location : Vial 11
Injection Date : 6/3/2019 3:33:01 PM
Inj Volume : 1 µl
Acq. Method : C:\CHEM32\1\METHODS\MH_MG_50_5MIN_70_15_MIN_250_5MIN.M
Last changed : 6/3/2019 3:27:06 PM by ER
Analysis Method : C:\CHEM32\1\DATA\JON\JG-02-119-COL.D\JG.M
Last changed : 9/19/2019 12:49:21 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
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Data File C:\CHEM32\1\DATA\GRAY\MG-02-035_BATCH_CONC_3M_PRE.D
Sample Name: MG-02-035_BATCH_CONC_3M_PRE

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.179	MM	8.85e-3	7122.18066	1.34062e4	98.49684
2	18.154	BB	0.0982	108.69138	13.04811	1.50316
Totals :				7230.87204	1.34193e4	

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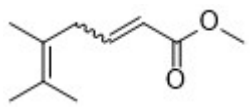
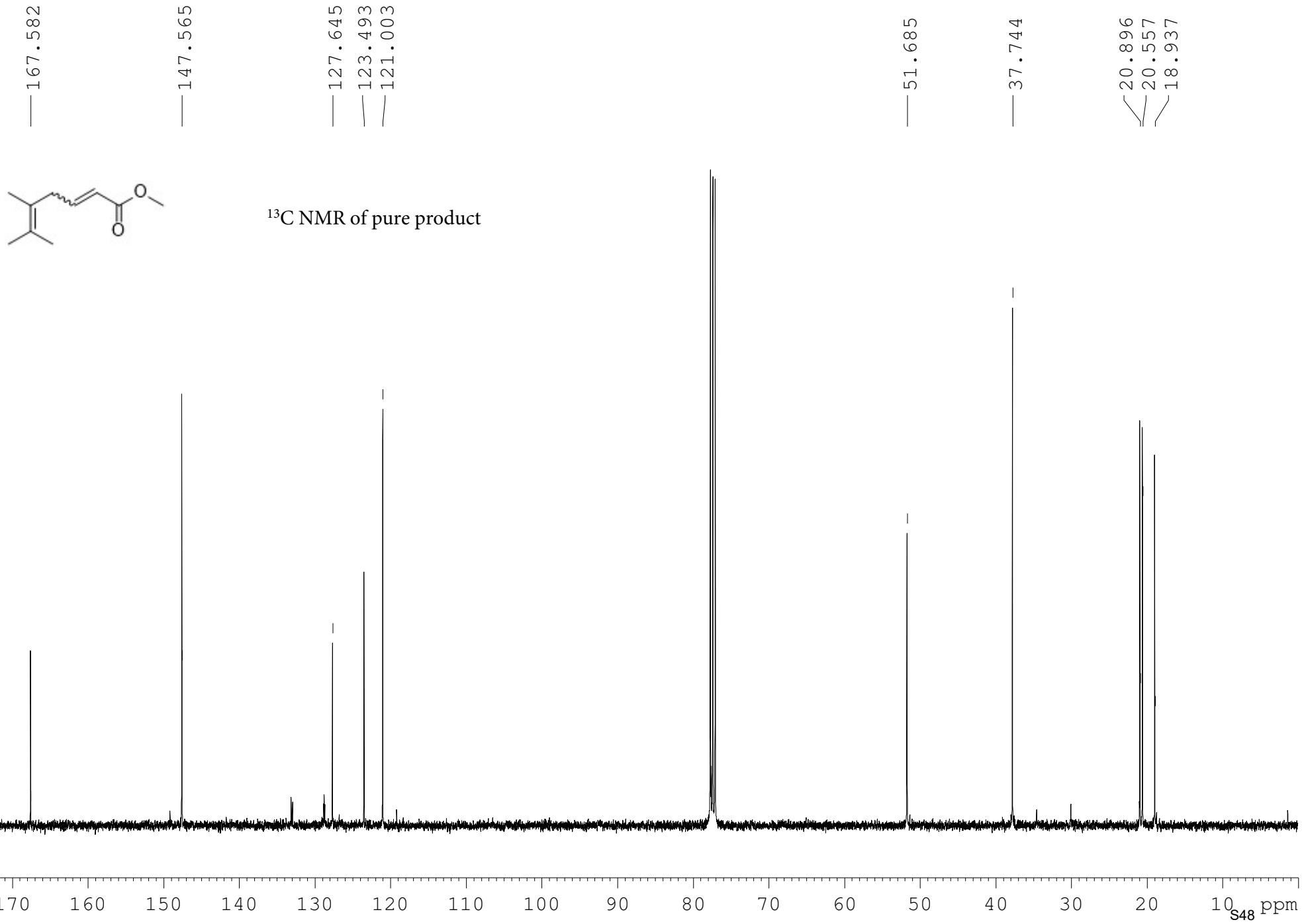
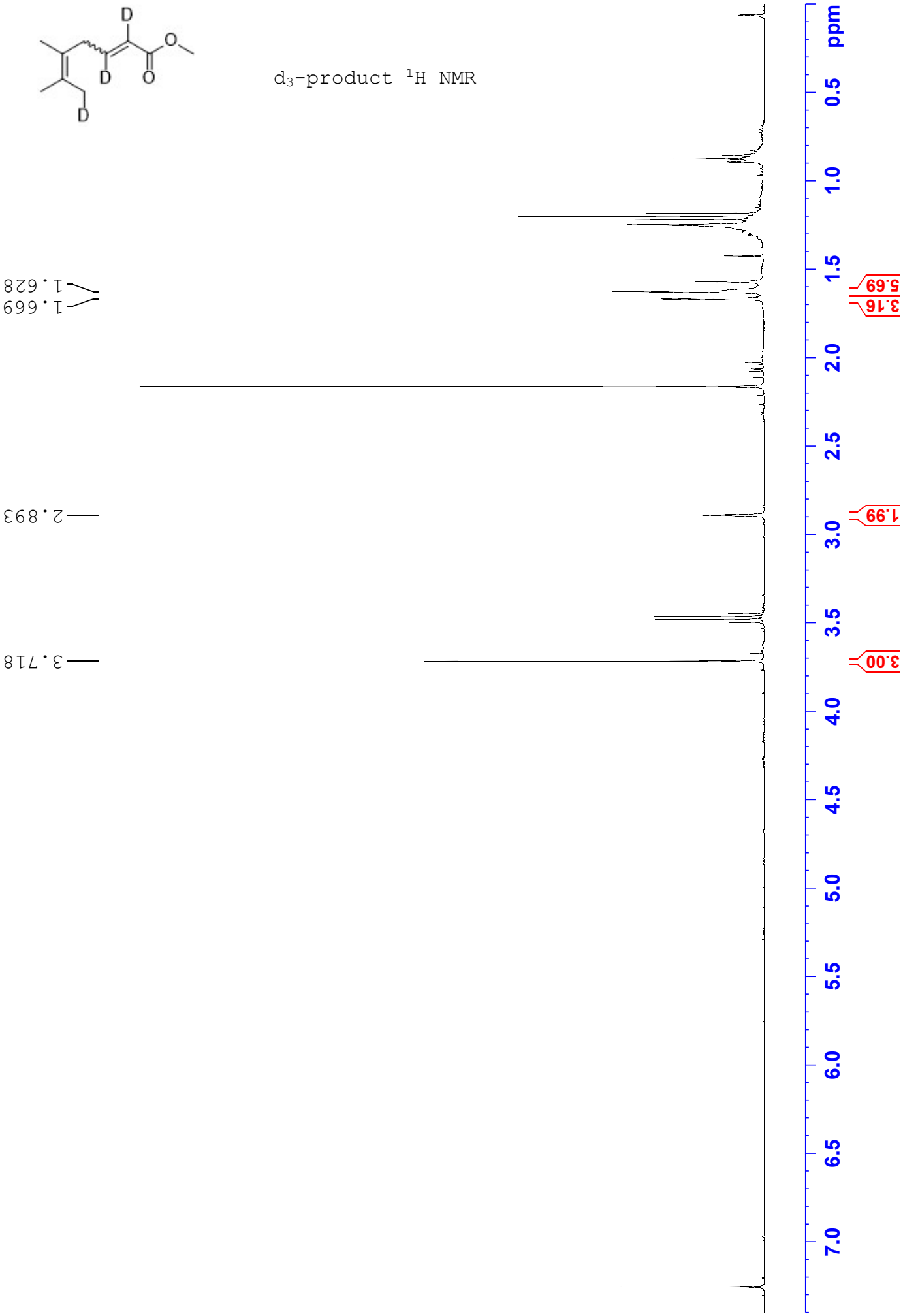
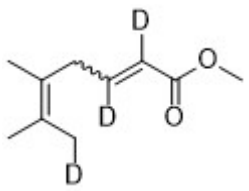


^{1}H NMR of pure product



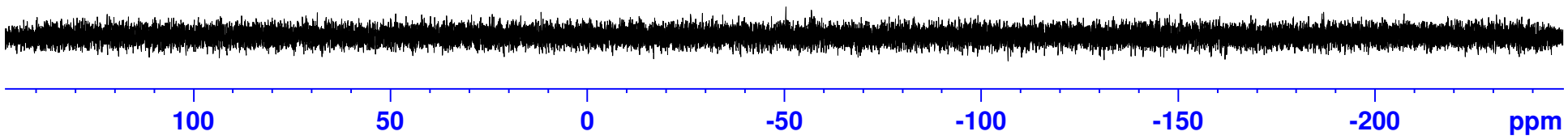
^{13}C NMR of pure product

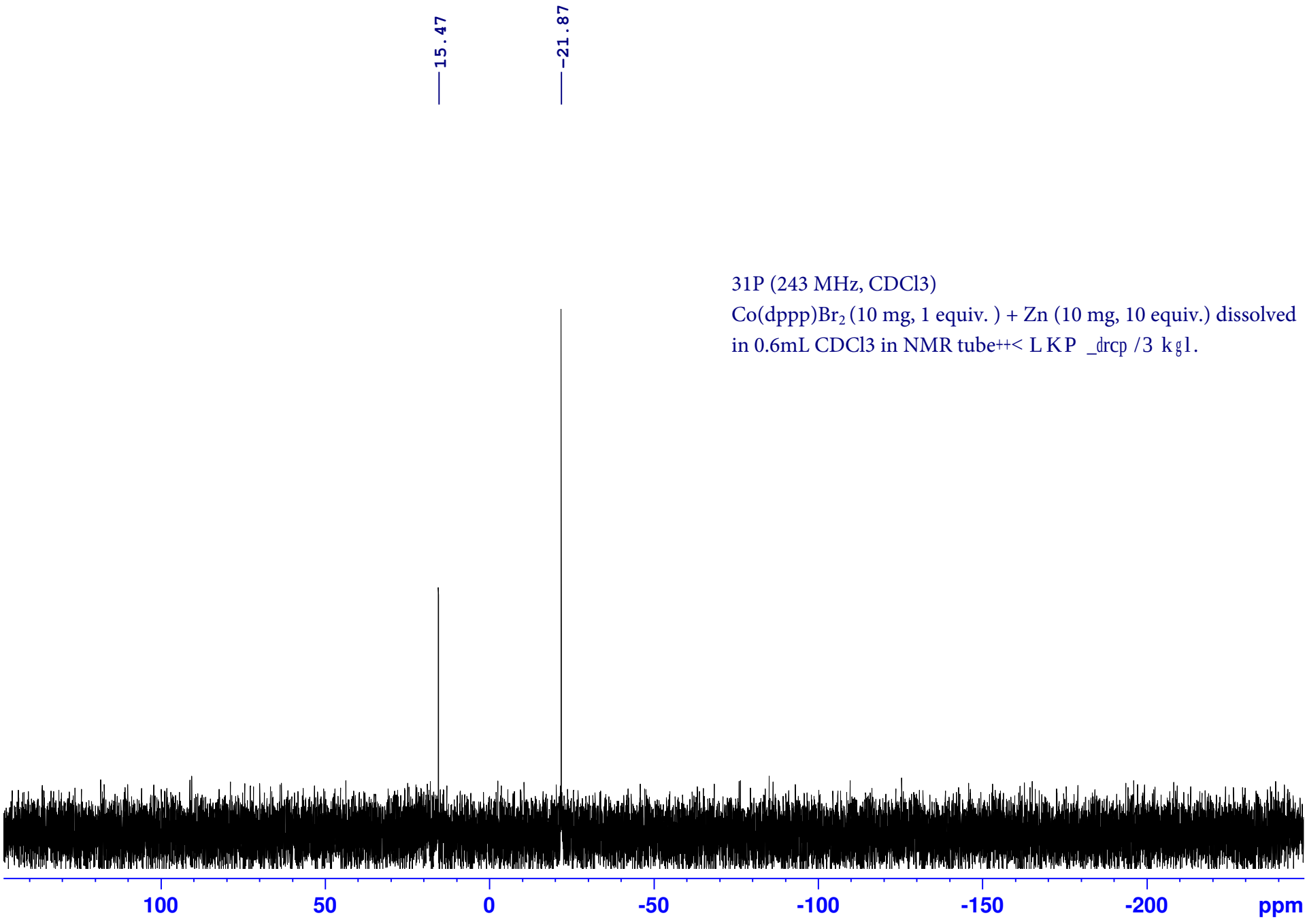

D
D
O
O
D
d3-product 1H NMR
1.628
1.669
2.893
3.718
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
5.69
3.16
1.99
3.00



d_3-product ^{13}C NMR (Selected Region)

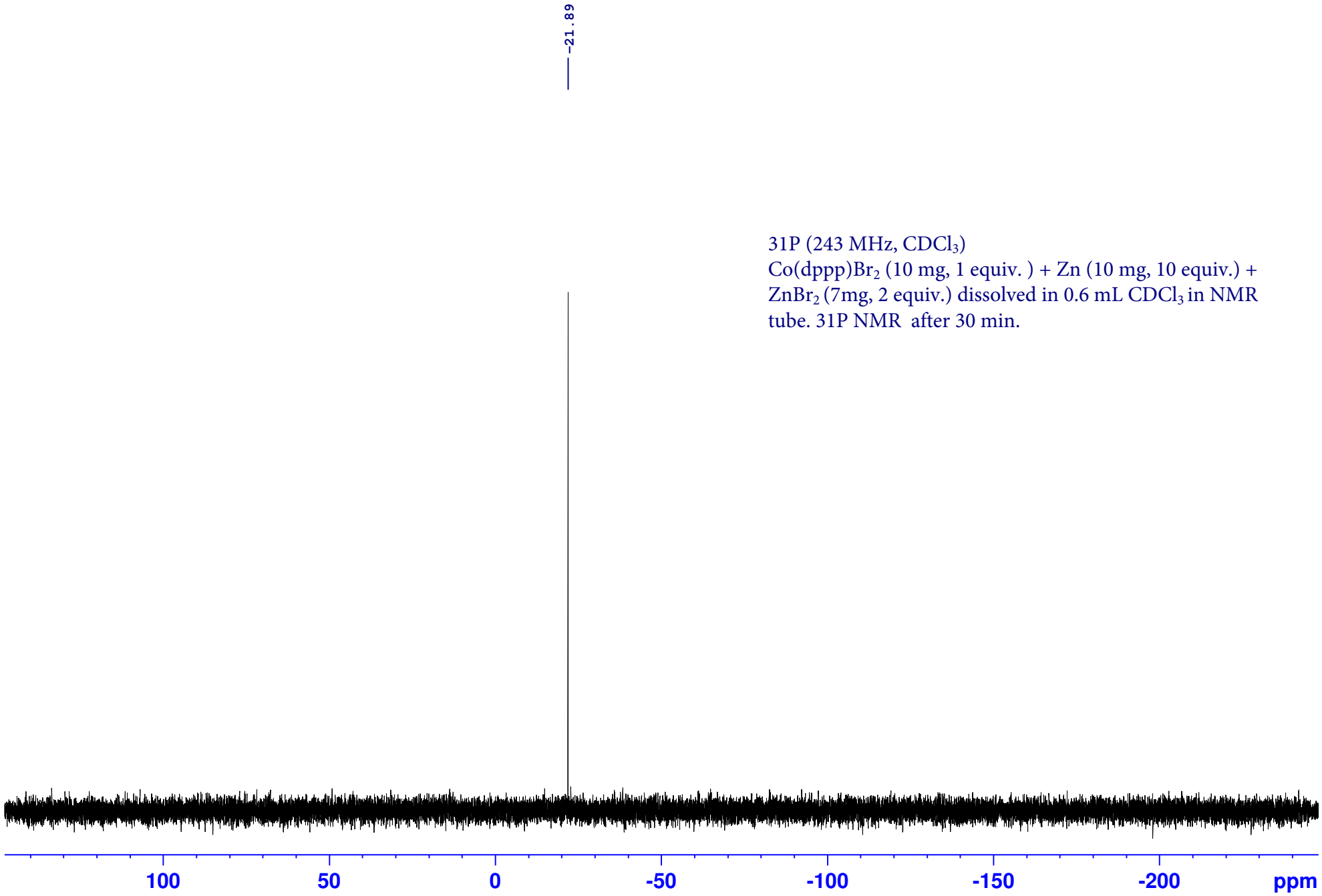
31P (243 MHz, CDCl3)
$Co(dppp)Br_2$ (10 mg dissolved in 0.6mL $CDCl_3$ in NMR tube)





31P (243 MHz, CDCl3)

Co(dppp)Br_2 (10 mg, 1 equiv.) + Zn (10 mg, 10 equiv.) dissolved in 0.6mL CDCl3 in NMR tube++< L K P _drcp /3 kg1.

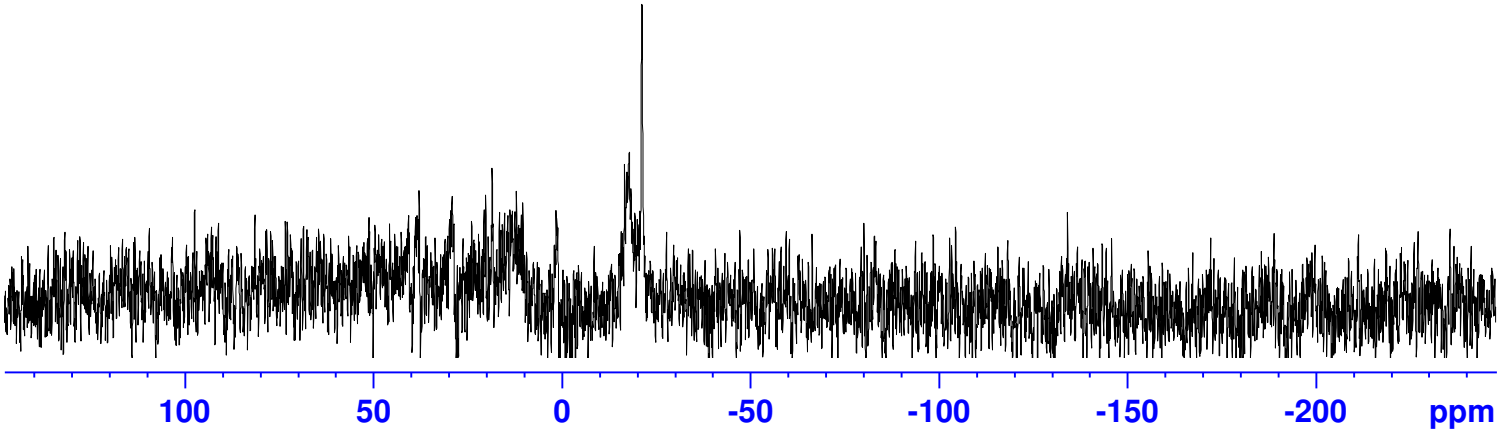


31P (243 MHz, $CDCl_3$)
$Co(dppp)Br_2$ (10 mg, 1 equiv.) + Zn (10 mg, 10 equiv.) + $ZnBr_2$ (7mg, 2 equiv.) dissolved in 0.6 mL $CDCl_3$ in NMR tube. 31P NMR after 30 min.

codpppbr2+Zn+NaBARF-dppp-31p

-21.29

31P (243 MHz, CDCl3)
Co(dppp)Br2 (10 mg, 1 equiv.), Zn (10 mg, 10 equiv.), and NaBARF (18mg, 2 equiv.) dissolved in 0.6 mL CDCl3 in NMR tube. 31P NMR after 30 min.

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EXPNO                         3
PROCNO                        1

F2 - Acquisition Parameters
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PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                          512
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                        300.0 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                        20.00 Hz
GB                0
PC                         1.40
```

13.1 VTNA Experiments

The graphs below show the VTNA analysis. The overlap of the functions means that the order of that component is equal to the value that is represented on the normalized time axis.[12] The experimental procedure is the exact same as that seen in section 5.1.2 and 5.1.4. The only difference is the data analysis. The x-axis is a normalized time axis that was calculated using the procedure used in the paper of Bures et al.[12]

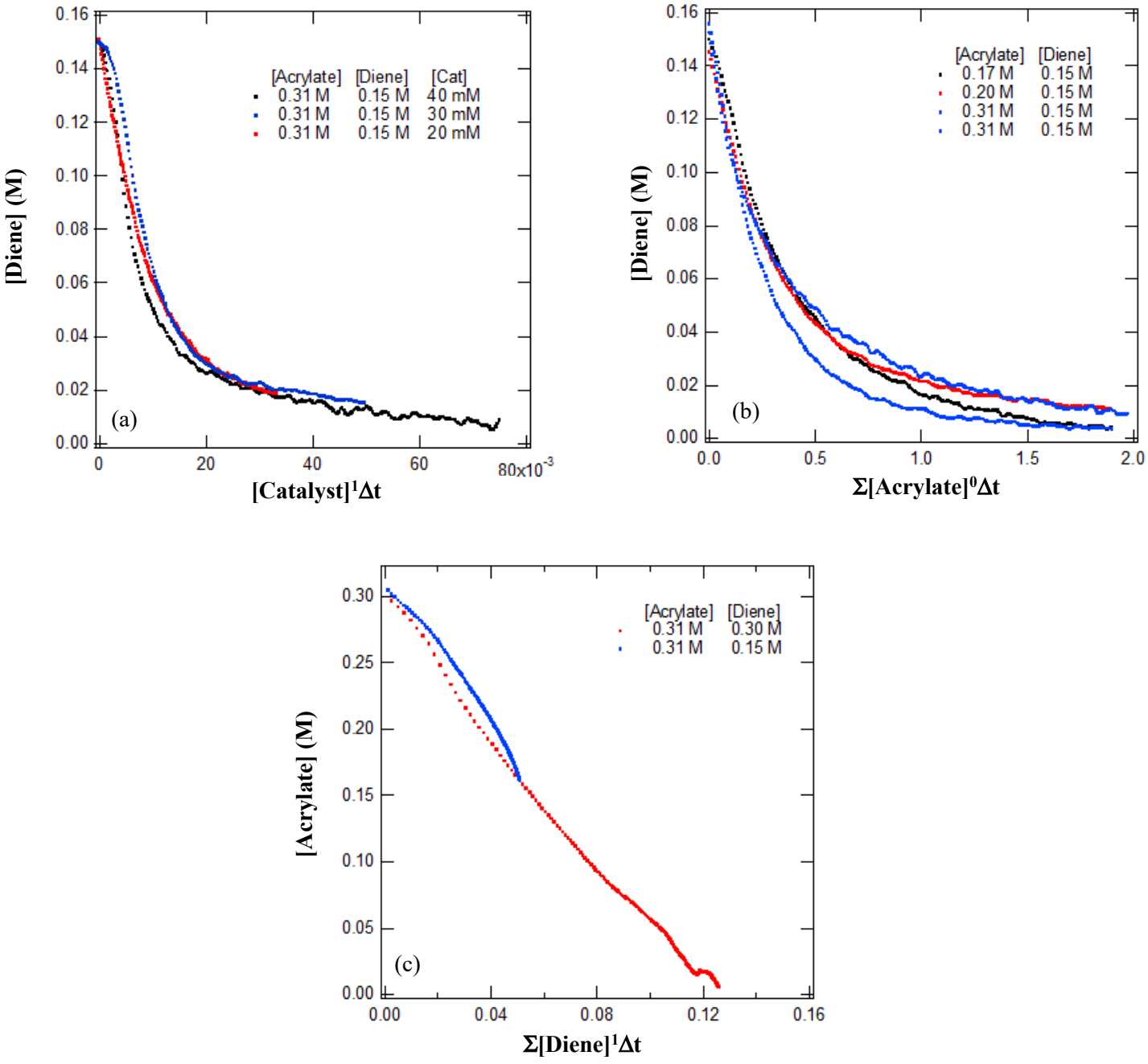


Figure S19. (a) The VTNA analysis of the catalyst order. The x-axis is time normalized to the catalyst to the first power. (b) The VTNA analysis of the acrylate order. The x-axis is time normalized to the acrylate to the zeroth power. (c) The VTNA analysis of the diene order. The x-axis is time normalized to the diene to the first power.

14.1.1 Model No Free Cobalt

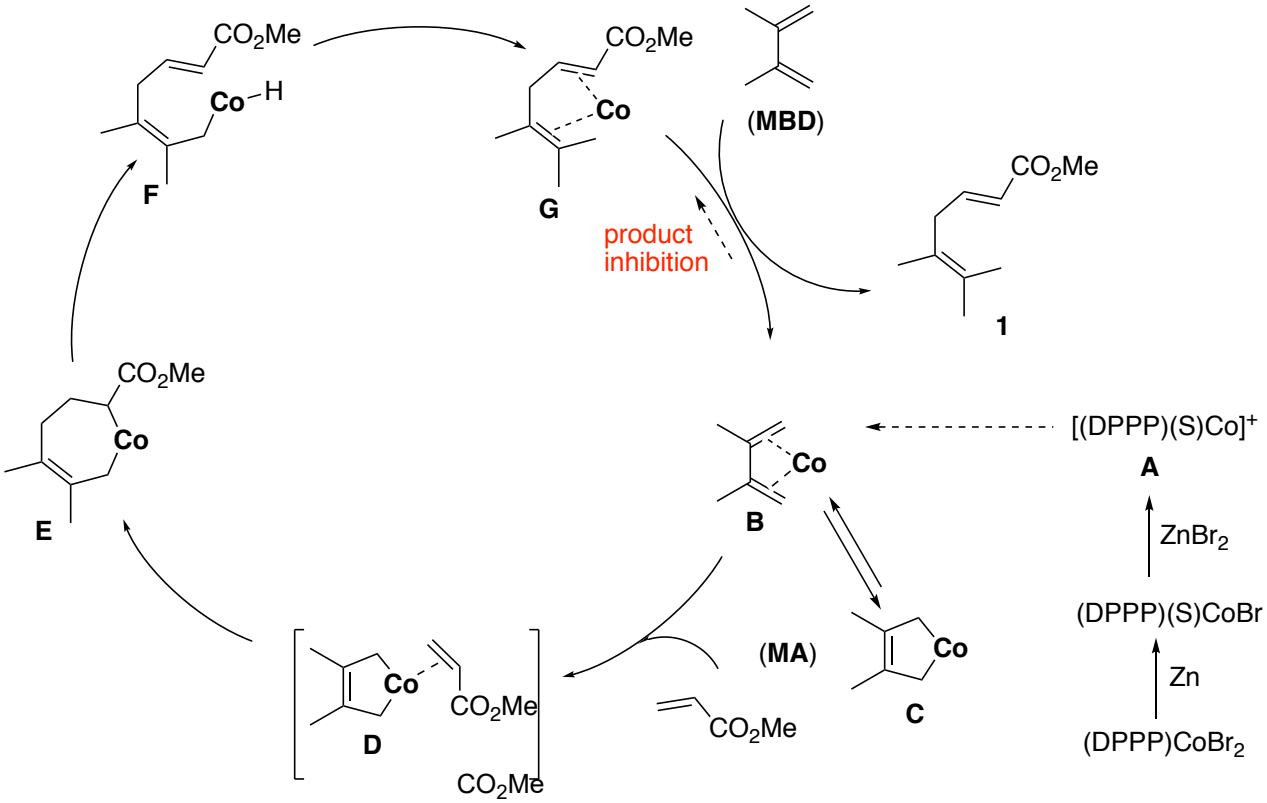
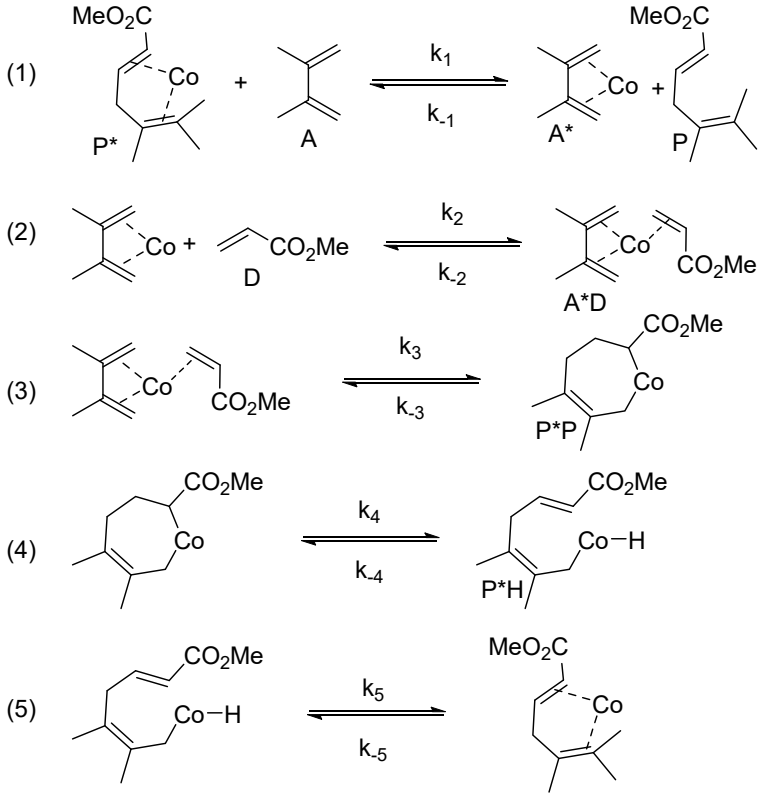


Figure S20. Proposed mechanism based off of experimental data without free cobalt. S is a solvent molecule.

14.1.1 Model No Free Cobalt(I)+



Reaction 1 is the slow step.

$$r_1 = k_1[P*][A] - k_{-1}[A*][P]$$

$$r_2 = k_2[A*][D] - k_{-2}[A*D]$$

$$\frac{r_2}{k_{-2}} = K_2[A*][D] - [A*D], \frac{r_2}{k_{-2}} \approx 0$$

$$[A*] = \frac{[A*D]}{K_2[D]}$$

$$r_1 = k_1[P*][A] - k_{-1}\frac{[A*D][P]}{K_2[D]}$$

$$r_3 = k_3[A*D] - k_{-3}[P*P]$$

$$\frac{r_3}{k_{-3}} = K_3[A*D] - [P*P], \frac{r_3}{k_{-3}} \approx 0$$

$$[A*D] = \frac{[P*P]}{K_3}$$

$$r_1 = k_1[P*][A] - k_{-1}\frac{[P*P][P]}{K_2K_3[D]}$$

$$r_4 = k_4[P*P] - k_{-4}[P*H]$$

$$\frac{r_4}{k_{-4}} = K_4[P*P] - [P*H], \frac{r_4}{k_{-4}} \approx 0$$

$$[P*P] = \frac{[P*H]}{K_4}$$

$$r_1 = k_1[P*][A] - k_{-1}\frac{[P*H][P]}{K_2K_3K_4[D]}$$

$$r_5 = k_5[P*H] - k_{-5}[P*]$$

$$\frac{r_5}{k_{-5}} = K_5[P*H] - [P*], \frac{r_5}{k_{-5}} \approx 0$$

$$[P*H] = \frac{[P*]}{K_5}$$

$$r_1 = k_1[P*][A] - k_{-1}\frac{[P*][P]}{K_2K_3K_4K_5[D]}$$

$$[*]_{total} = [P*] + [A*] + [A*D] + [P*P] + [P*H]$$

$$[*]_{total} = [P*] + \frac{[P*]}{K_2K_3K_4K_5[D]} + \frac{[P*]}{K_3K_4K_5} + \frac{[P*]}{K_4K_5} + \frac{[P*]}{K_5}$$

$$\frac{[*]_{total}}{1 + \frac{1}{K_2K_3K_4K_5[D]} + \frac{1}{K_3K_4K_5} + \frac{1}{K_4K_5} + \frac{1}{K_5}} = [P*]$$

$$r_1 = \frac{k_1[*]_{total}[A]}{1 + \frac{1}{K_2K_3K_4K_5[D]} + \frac{1}{K_3K_4K_5} + \frac{1}{K_4K_5} + \frac{1}{K_5}} - k_{-1}\frac{[P]}{K_2K_3K_4K_5[D]}\frac{[*]_{total}}{1 + \frac{1}{K_2K_3K_4K_5[D]} + \frac{1}{K_3K_4K_5} + \frac{1}{K_4K_5} + \frac{1}{K_5}}, K_5 \gg 1$$

$$r_1 = k_1[*]_{total}[A]$$

At High Concentrations of P

$$\boldsymbol{r_1 = k_1[*]_{total}[A] - k_{-1}\frac{[P]}{K_2K_3K_4K_5[D]}\frac{[*]_{total}}{C}}$$

$$\boldsymbol{C = 1 + \frac{1}{K_2K_3K_4K_5[D]} + \frac{1}{K_3K_4K_5} + \frac{1}{K_4K_5} + \frac{1}{K_5}}$$

This Suggest that at high concentrations of product, the reaction rate is hampered (through the subtraction of the term $k_{-1}\frac{[P]}{K_2K_3K_4K_5[D]}\frac{[*]_{total}}{C}$).

14.1.2 Model Free Cobalt(I)+

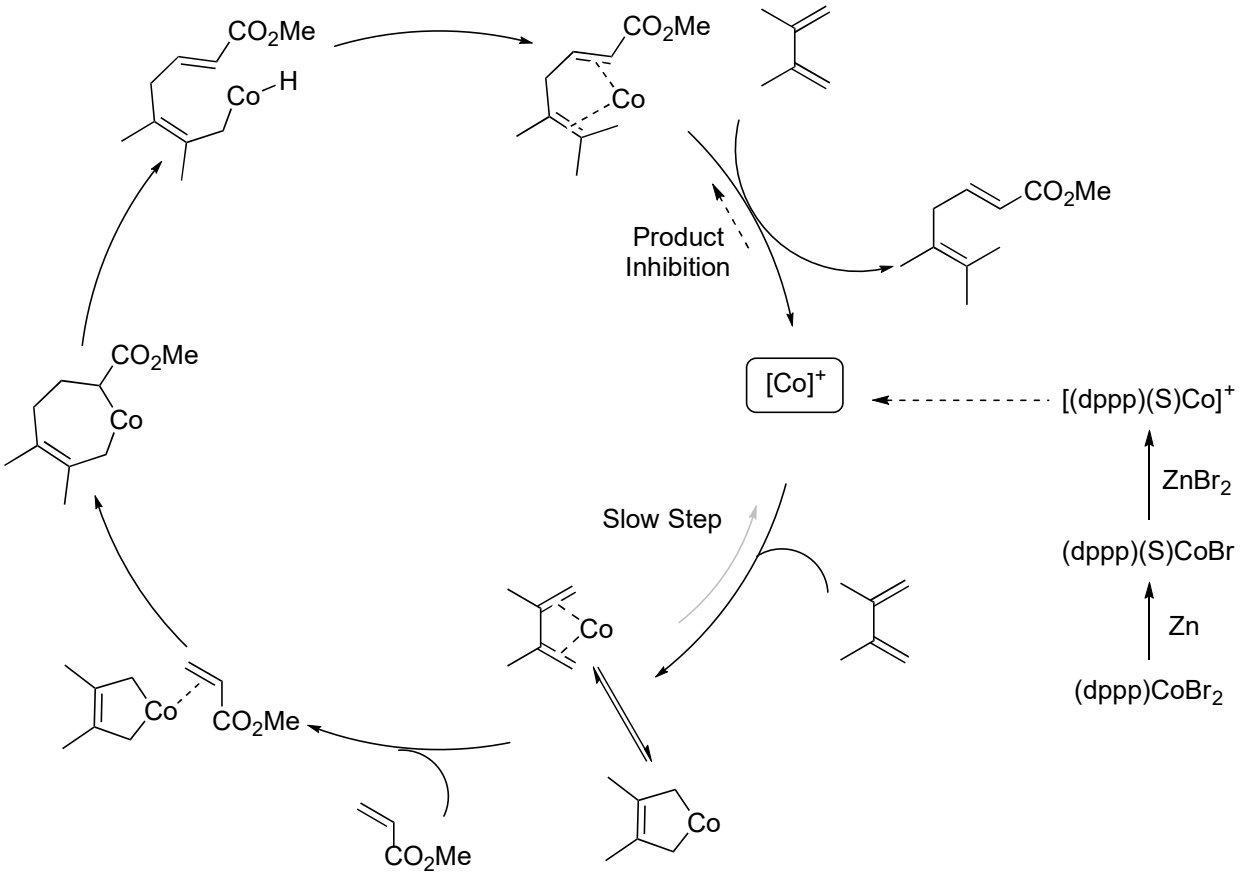
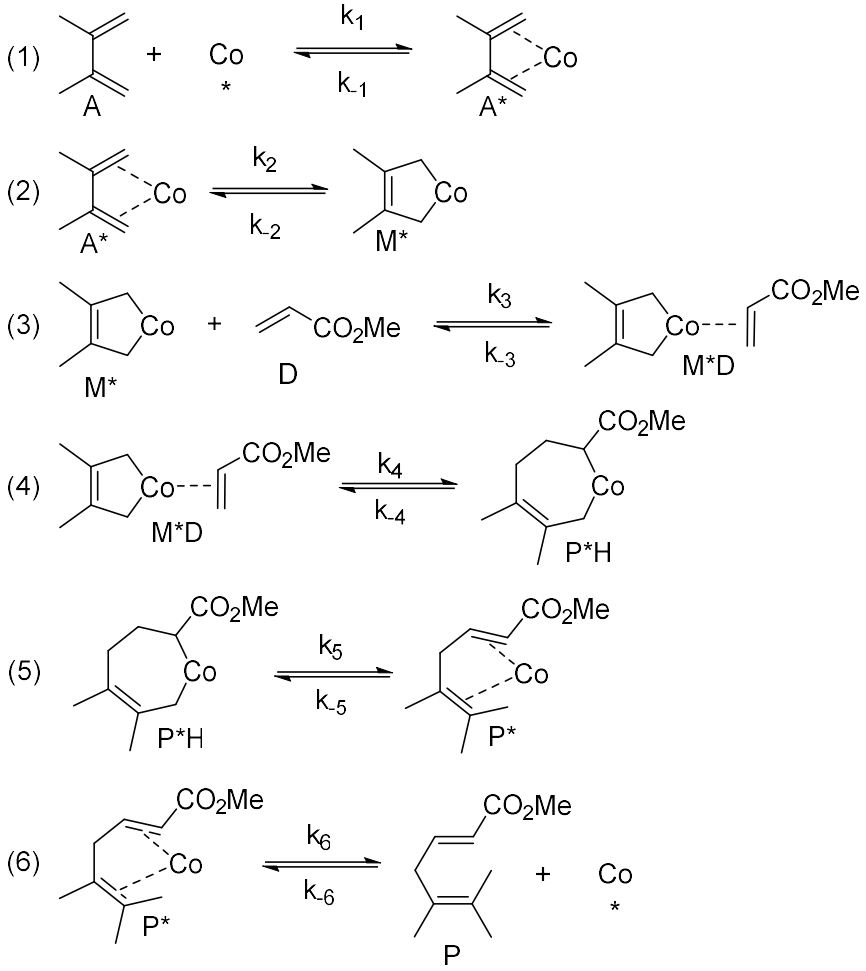


Figure S21. Proposed mechanism based off of experimental data including free cobalt. S is a solvent molecule.



Reaction 1 is the slow step.

$$\boldsymbol{r_1 = k_1[A][*] - k_{-1}[A*]}$$

$$r_2 = k_2[A*] - k_{-2}[M*]$$
$$\frac{r_2}{k_{-2}} = K_2[A*] - [M*], \frac{r_2}{k_{-2}} \approx 0$$
$$\frac{[M*]}{K_2} = [A*]$$

$$\boldsymbol{r_1 = k_1[A][*] - \frac{k_{-1}[M*]}{K_2}}$$

$$r_3 = k_3[M*][D] - k_{-3}[M*D]$$
$$\frac{r_3}{k_{-3}} = K_3[M*][D] - [M*D], \frac{r_3}{k_{-3}} \approx 0$$
$$\frac{[M*D]}{K_3[D]} = [M*]$$

$$\boldsymbol{r_1 = k_1[A][*] - \frac{k_{-1}[M*D]}{K_2K_3[D]}}$$

$$r_4 = k_4[M*D] - k_{-4}[P*H]$$

$$\frac{r_4}{k_{-4}} = K_4[M*D] - [P*H], \frac{r_4}{k_{-4}} \approx 0$$
$$\frac{[P*H]}{K_4} = [M*D]$$

$\boldsymbol{r_1 = k_1[A][*] - \frac{k_{-1}[P*H]}{K_2K_3K_4[D]}}$

$$r_5 = k_5[P*H] - k_{-5}[P*]$$
$$\frac{r_5}{k_{-5}} = K_5[P*H] - [P*], \frac{r_5}{k_{-5}} \approx 0$$
$$\frac{[P*]}{K_5} = [P*H]$$

$\boldsymbol{r_1 = k_1[A][*] - \frac{k_{-1}[P*H]}{K_2K_3K_4K_5[D]}}$

$$r_6 = k_6[P*] - k_{-6}[P][*]$$
$$\frac{r_6}{k_{-6}} = K_5[P*H] - [P][*], \frac{r_6}{k_{-6}} \approx 0$$
$$\frac{[P][*]}{K_6} = [P*H]$$

$\boldsymbol{r_1 = k_1[A][*] - \frac{k_{-1}[P][*]}{K_2K_3K_4K_5K_6[D]}}$

$$[*]_{total} = [*] + [A*] + [M*] + [M*D] + [P*H] + [P*]$$
$$[*]_{total} = [*] + \frac{[P][*]}{K_2K_3K_4K_5K_6[D]} + \frac{[P][*]}{K_3K_4K_5K_6[D]} + \frac{[P][*]}{K_4K_5K_6} + \frac{[P][*]}{K_5K_6} + \frac{[P][*]}{K_6}$$
$$\frac{[*]_{total}}{1 + \frac{[P]}{K_2K_3K_4K_5K_6[D]} + \frac{[P]}{K_3K_4K_5K_6[D]} + \frac{[P]}{K_4K_5K_6} + \frac{[P]}{K_5K_6} + \frac{[P]}{K_6}} = [*]$$

$\boldsymbol{r_1 = k_1[A]\frac{[*]_{total}}{1+\frac{[P]}{K_2K_3K_4K_5K_6[D]}+\frac{[P]}{K_3K_4K_5K_6[D]}+\frac{[P]}{K_4K_5K_6}+\frac{[P]}{K_5K_6}+\frac{[P]}{K_6}} - \frac{k_{-1}[P]}{K_2K_3K_4K_5K_6[D]}\frac{[*]_{total}}{1+\frac{[P]}{K_2K_3K_4K_5K_6[D]}+\frac{[P]}{K_3K_4K_5K_6[D]}+\frac{[P]}{K_4K_5K_6}+\frac{[P]}{K_5K_6}+\frac{[P]}{K_6}}}$

$$\boldsymbol{r_1 = \left(k_1[A] - \frac{k_{-1}[P]}{K_2K_3K_4K_5K_6[D]}\right)\left(\frac{[*]_{total}}{1 + \frac{[P]}{K_2K_3K_4K_5K_6[D]} + \frac{[P]}{K_3K_4K_5K_6[D]} + \frac{[P]}{K_4K_5K_6} + \frac{[P]}{K_5K_6} + \frac{[P]}{K_6}}\right)}$$

$$\boldsymbol{r_1 = \left(k_1[A] - \frac{k_{-1}[P]}{K_2K_3K_4K_5K_6[D]}\right)\left(\frac{[*]_{total}}{1 + \frac{[P]}{K_2K_3K_4K_5K_6[D]} + \frac{[P]}{K_3K_4K_5K_6[D]} + \frac{[P]}{K_4K_5K_6} + \frac{[P]}{K_5K_6} + \frac{[P]}{K_6}}\right), K_5 \gg 1}$$

$$\boldsymbol{r_1 = \frac{k_1[A][*]_{total}}{1 + \frac{[P]}{K_6}}}$$

$\boldsymbol{r_1 = k_1[A][*]_{total}$ (At low concentrations of P)
At high concentrations of P, the reaction is inhibited
This fits the experimental data obtained that shows the reaction is first order in the A (diene) and * (catalyst) and is inhibited by the product at high concentrations.

Reaction 4 is the slow step.

$\boldsymbol{r_4 = k_4[M*D] - k_{-4}[P*H]}$

$$r_3 = k_3[M*][D] - k_{-3}[M*D]$$
$$\frac{r_3}{k_{-3}} = K_3[M*][D] - [M*D], \frac{r_3}{k_{-3}} \approx 0$$
$$K_3[M*][D] = [M*D]$$

$\boldsymbol{r_4 = k_4K_3[M*][D] - k_{-4}[P*H]}$

$$r_2 = k_2[A*] - k_{-2}[M*]$$

$$\frac{r_2}{k_{-2}} = K_2[A*] - [M*], \frac{r_2}{k_{-2}} \approx 0$$
$$K_2[A*] = [M*]$$

$$\boldsymbol{r_4 = k_4K_3K_2[A*][D] - k_{-4}[P*H]}$$

$$r_1 = k_1[A][*] - k_{-1}[A*]$$
$$\frac{r_1}{k_{-1}} = K_1[A][*] - [A*], \frac{r_1}{k_{-1}} \approx 0$$
$$K_1[A][*] = [A*]$$

$$\boldsymbol{r_4 = k_4K_3K_2K_1[A][*][D] - k_{-4}[P*H]}$$

$$r_5 = k_5[P*H] - k_{-5}[P*]$$
$$\frac{r_5}{k_{-5}} = K_5[P*H] - [P*], \frac{r_5}{k_{-5}} \approx 0$$
$$\frac{[P*]}{K_5} = [P*H]$$

$$\boldsymbol{r_4 = k_4K_3K_2K_1[A][*][D] - \frac{k_{-4}[P*]}{K_5}}$$

$$r_6 = k_6[P*] - k_{-6}[P][*]$$
$$\frac{r_6}{k_{-6}} = K_5[P*H] - [P][*], \frac{r_6}{k_{-6}} \approx 0$$
$$\frac{[P][*]}{K_6} = [P*H]$$

$$\boldsymbol{4 = k_4K_3K_2K_1[A][*][D] - \frac{k_{-4}[P][*]}{K_5K_6}}$$

$$[*]_{total} = [*] + [A*] + [M*] + [M*D] + [P*H] + [P*]$$
$$[*]_{total} = [*] + K_1[A][*] + K_2K_1[A][*] + K_3K_2K_1[A][*][D] + \frac{[P][*]}{K_5K_6} + \frac{[P][*]}{K_6}$$
$$\frac{[*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A][D] + \frac{[P]}{K_5K_6} + \frac{[P]}{K_6}} = [*]$$

$$\boldsymbol{r_4 = k_4K_3K_2K_1[A]\frac{[*]_{total}}{1+K_1[A]+K_2K_1[A]+K_3K_2K_1[A][D]+\frac{[P]}{K_5K_6}+\frac{[P]}{K_6}} - \frac{k_{-4}[P][*]}{K_5K_6}\frac{[*]_{total}}{1+K_1[A]+K_2K_1[A]+K_3K_2K_1[A][D]+\frac{[P]}{K_5K_6}+\frac{[P]}{K_6}}}$$

$$\boldsymbol{r_4 = \left(k_4K_3K_2K_1[A] - \frac{k_{-4}[P][*]}{K_5K_6}\right)\left(\frac{[*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A][D] + \frac{[P]}{K_5K_6} + \frac{[P]}{K_6}}\right)}$$

$$\boldsymbol{r_4 = \left(k_4K_3K_2K_1[A] - \frac{k_{-4}[P][*]}{K_5K_6}\right)\left(\frac{[*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A][D] + \frac{[P]}{K_5K_6} + \frac{[P]}{K_6}}\right), K_5 \gg 1}$$

$$\boldsymbol{r_4 = \frac{k_4K_3K_2K_1[A][*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A][D] + \frac{[P]}{K_6}}}$$

Reaction 4 being the TOLS step does not fit the experimental data obtained that shows the reaction is first order in the A (diene) and * (catalyst) and is inhibited by the product at high concentrations. Instead, it shows that the reaction is inhibited by A (diene), acrylate (D) and P (product). Thus reaction 4 being the TOLS is not supported by the experimental data.

Reaction 6 is the slow step.

$$\boldsymbol{r_6 = k_6[P*] - k_{-6}[P][*]}$$

$$r_5 = k_5[P*H] - k_{-5}[P*]$$
$$\frac{r_5}{k_{-5}} = K_5[P*H] - [P*], \frac{r_5}{k_{-5}} \approx 0$$

$$K_5[P*H] = [P*]$$

$$\boldsymbol{r_6 = k_6 K_5 [P*H] - k_{-6}[P][*]}$$

$$r_4 = k_4[M*D] - k_{-4}[P*H]$$
$$\frac{r_4}{k_{-4}} = K_4[M*D] - [P*H], \frac{r_4}{k_{-4}} \approx 0$$
$$K_4[M*D] = [P*H]$$

$$\boldsymbol{r_6 = k_6 K_5 K_4 [M*D] - k_{-6}[P][*]}$$

$$r_3 = k_3[M*][D] - k_{-3}[M*D]$$
$$\frac{r_3}{k_{-3}} = K_3[M*][D] - [M*D], \frac{r_3}{k_{-3}} \approx 0$$
$$K_3[M*][D] = [M*D]$$

$$\boldsymbol{r_6 = k_6 K_5 K_4 K_3 [M*][D] - k_{-6}[P][*]}$$

$$r_2 = k_2[A*] - k_{-2}[M*]$$
$$\frac{r_2}{k_{-2}} = K_2[A*] - [M*], \frac{r_2}{k_{-2}} \approx 0$$
$$K_2[A*] = [M*]$$

$$\boldsymbol{r_6 = k_6 K_5 K_4 K_3 K_2 [A*][D] - k_{-6}[P][*]}$$

$$r_1 = k_1[A][*] - k_{-1}[A*]$$
$$\frac{r_1}{k_{-1}} = K_1[A][*] - [A*], \frac{r_1}{k_{-1}} \approx 0$$
$$K_1[A][*] = [A*]$$

$$\boldsymbol{r_6 = k_6 K_5 K_4 K_3 K_2 K_1 [A][*][D] - k_{-6}[P][*]}$$

$$[*]_{total} = [*] + [A*] + [M*] + [M*D] + [P*H] + [P*]$$
$$[*]_{total} = [*] + K_1[A][*] + K_2K_1[A][*] + K_3K_2K_1[A][*] + K_4K_3K_2K_1[A][*][D] + K_5K_4K_3K_2K_1[A][*][D]$$
$$\frac{[*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A] + K_4K_3K_2K_1[A][D] + K_5K_4K_3K_2K_1[A][D]} = [*]$$

$$\boldsymbol{r_6 = k_6 K_5 K_4 K_3 K_2 K_1 [A][D] \frac{[*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A] + K_4K_3K_2K_1[A][D] + K_5K_4K_3K_2K_1[A][D]}}$$
$$\boldsymbol{- \frac{k_{-1}[P]}{K_2K_3K_4K_5K_6[D]} \frac{[*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A] + K_4K_3K_2K_1[A][D] + K_5K_4K_3K_2K_1[A][D]}}$$

$$\boldsymbol{r_6 = (k_6 K_5 K_4 K_3 K_2 K_1 [A][D] - k_{-6}[P]) \left(\frac{[*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A] + K_4K_3K_2K_1[A][D] + K_5K_4K_3K_2K_1[A][D]} \right)}$$

$$\boldsymbol{r_6 = (k_6 K_5 K_4 K_3 K_2 K_1 [A][D] - k_{-6}[P]) \left(\frac{[*]_{total}}{1 + K_1[A] + K_2K_1[A] + K_3K_2K_1[A] + K_4K_3K_2K_1[A][D] + K_5K_4K_3K_2K_1[A][D]} \right), K_5 \gg 1}$$

$$\boldsymbol{r_6 = \frac{k_6 K_5 K_4 K_3 K_2 K_1 [A][D][*]_{total}}{K_5K_4K_3K_2K_1[A][D]} - \left(\frac{k_{-6}[P][*]_{total}}{K_5K_4K_3K_2K_1[A][D]} \right)}$$

Reaction 6 being the TOLS does not fit the experimental data. This would suggest that the reaction is inhibited by equilibrium (suggesting that quantitative conversion would not occur). However, it has been shown experimentally that quantitative conversion is obtained in this reaction.

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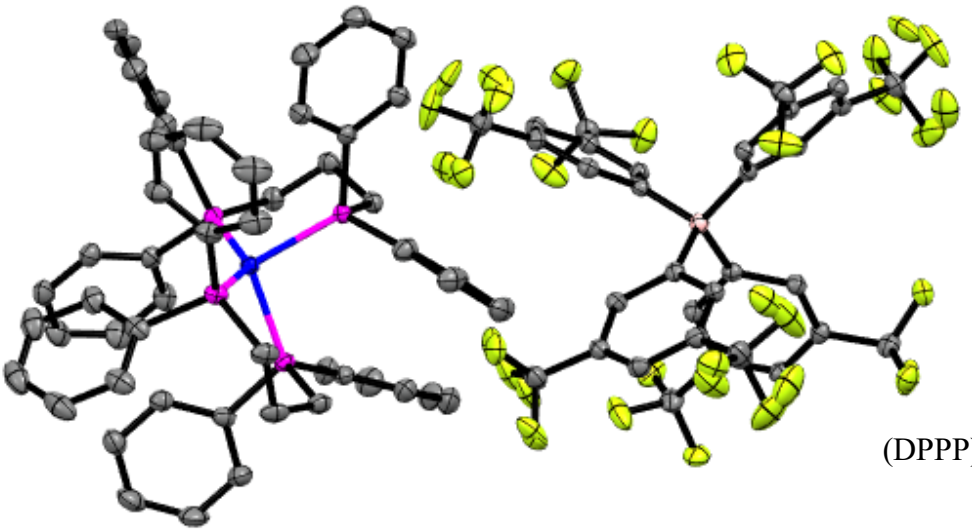
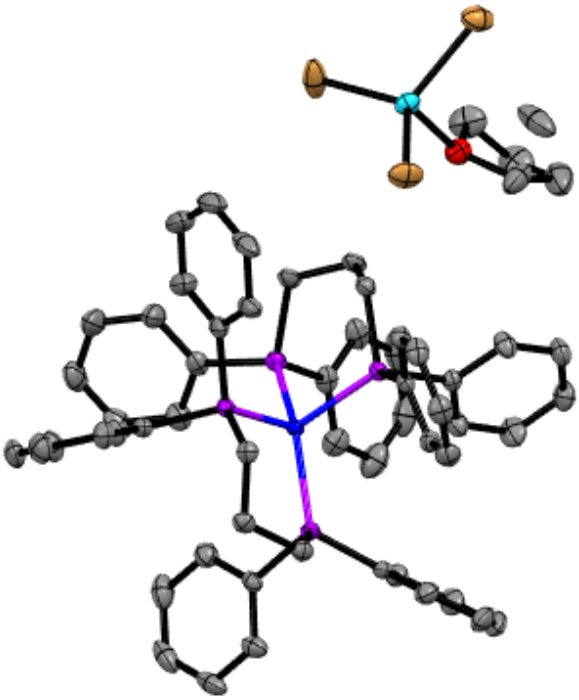
Experimental Summary of X-Ray Crystallography

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$_{\square}$ radiation ($\square$ = 0.71073 Å). A 0.357 x 0.313 x 0.268 mm piece of a dark bluish 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 $\square$ and $\square$ 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 $\square$. A total of 231454 reflections were collected covering the indices, -20<=h<=20, -15<=k<=15, -46<=l<=46. 15955 reflections were found to be symmetry independent, with a R_{int} of 0.0438. Indexing and unit cell refinement indicated a primitive, orthorhombic 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 1.



$(DPPP)_2Co(I)^+ BArF^-$



$(DPPP)_2Co(I)^+ ZnBr_3^-$

Table S6. Crystal data and structure refinement for RBabu_MP-05-007.

Report date	2019-08-06	
Identification code	MP-05-007	
Empirical formula	C86 H64 B Co F24 P4	
Molecular formula	C54 H52 Co P4, C32 H12 B F24	
Formula weight	1746.99	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 16.6366(7) Å	□= 90°.
	b = 12.7954(6) Å	□= 101.172(2)°.
	c = 37.4749(17) Å	□ = 90°.
Volume	7826.2(6) $Å^3$	
Z	4	
Density (calculated)	1.483 Mg/m^3	
Absorption coefficient	0.405 mm^{-1}	
F(000)	3552	
Crystal size	0.357 x 0.313 x 0.268 mm^3	
Crystal color, habit	Dark Bluish Green Block	
Theta range for data collection	1.248 to 26.379°.	
Index ranges	-20<=h<=20, -15<=k<=15, -46<=l<=46	
Reflections collected	231454	
Independent reflections	15955 [R(int) = 0.0438, R(sigma) = 0.0180]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2602 and 0.2187	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15955 / 144 / 1144	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0881	
R indices (all data)	R1 = 0.0421, wR2 = 0.0921	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.503 and -0.332 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for RBabu_MP-05-007. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	1677(1)	2941(1)	3692(1)	17(1)
P(1)	1478(1)	1588(1)	4052(1)	19(1)
P(2)	2990(1)	3235(1)	3973(1)	19(1)
P(3)	1067(1)	4379(1)	3882(1)	20(1)
P(4)	1437(1)	3382(1)	3091(1)	22(1)
C(1)	1985(1)	1712(1)	4530(1)	24(1)
C(2)	2903(1)	1948(1)	4577(1)	25(1)
C(3)	3104(1)	3059(1)	4467(1)	23(1)
C(4)	1493(1)	4785(1)	3010(1)	28(1)
C(5)	943(1)	5444(1)	3208(1)	29(1)
C(6)	1248(1)	5547(1)	3620(1)	27(1)
C(7)	412(1)	1289(1)	4065(1)	22(1)
C(8)	31(1)	1701(2)	4333(1)	29(1)
C(9)	-809(1)	1593(2)	4308(1)	35(1)
C(10)	-1274(1)	1075(2)	4016(1)	34(1)
C(11)	-894(1)	633(1)	3754(1)	31(1)
C(12)	-57(1)	737(1)	3778(1)	26(1)
C(13)	1839(1)	343(1)	3906(1)	23(1)
C(14)	1855(1)	-561(1)	4114(1)	32(1)
C(15)	2105(1)	-1494(2)	3987(1)	42(1)
C(16)	2340(1)	-1547(2)	3654(1)	41(1)
C(17)	2325(1)	-660(2)	3445(1)	37(1)
C(18)	2075(1)	283(2)	3572(1)	29(1)
C(19)	3823(1)	2434(1)	3864(1)	22(1)
C(20)	3713(1)	1878(1)	3542(1)	29(1)
C(21)	4355(1)	1311(2)	3447(1)	38(1)
C(22)	5112(1)	1306(2)	3674(1)	34(1)
C(23)	5234(1)	1871(1)	3993(1)	29(1)
C(24)	4597(1)	2430(1)	4089(1)	26(1)
C(25)	3416(1)	4534(1)	3925(1)	23(1)
C(26)	3610(1)	4792(1)	3591(1)	30(1)
C(27)	3887(1)	5782(2)	3526(1)	33(1)
C(28)	3979(1)	6526(2)	3799(1)	33(1)
C(29)	3807(1)	6276(2)	4133(1)	34(1)
C(30)	3529(1)	5279(1)	4198(1)	28(1)
C(31)	1301(1)	4880(1)	4350(1)	24(1)
C(32)	1788(1)	5757(1)	4447(1)	31(1)
C(33)	1944(1)	6121(2)	4801(1)	39(1)
C(34)	1616(1)	5623(2)	5064(1)	40(1)

C(35)	1124(1)	4753(2)	4972(1)	38(1)
C(36)	970(1)	4381(2)	4620(1)	32(1)
C(37)	-52(1)	4346(1)	3810(1)	23(1)
C(38)	-491(1)	5136(1)	3944(1)	32(1)
C(39)	-1337(1)	5097(2)	3886(1)	40(1)
C(40)	-1750(1)	4277(2)	3692(1)	39(1)
C(41)	-1327(1)	3495(2)	3556(1)	33(1)
C(42)	-476(1)	3526(1)	3619(1)	25(1)
C(43)	404(1)	3001(2)	2860(1)	26(1)
C(44)	-107(1)	3639(2)	2615(1)	33(1)
C(45)	-897(1)	3307(2)	2466(1)	43(1)
C(46)	-1177(1)	2347(2)	2554(1)	44(1)
C(47)	-672(1)	1702(2)	2792(1)	39(1)
C(48)	113(1)	2031(2)	2945(1)	31(1)
C(49)	2094(1)	2791(1)	2806(1)	26(1)
C(50)	1975(1)	1752(2)	2701(1)	31(1)
C(51)	2525(1)	1247(2)	2523(1)	38(1)
C(52)	3197(1)	1772(2)	2451(1)	44(1)
C(53)	3312(1)	2807(2)	2547(1)	46(1)
C(54)	2762(1)	3320(2)	2721(1)	37(1)
F(1)	7393(1)	11818(1)	4564(1)	33(1)
F(2)	8115(1)	10681(1)	4904(1)	32(1)
F(3)	7072(1)	11371(1)	5070(1)	41(1)
F(4)	4343(1)	10080(1)	4586(1)	32(1)
F(5)	4162(1)	8990(1)	4140(1)	50(1)
F(6)	4519(1)	8437(1)	4687(1)	40(1)
F(7)	6466(1)	5328(1)	4860(1)	40(1)
F(8)	5277(1)	4787(1)	4596(1)	50(1)
F(9)	6318(1)	3818(1)	4610(1)	40(1)
F(10)	5406(6)	3659(5)	3265(1)	60(1)
F(10B)	5194(12)	4830(30)	3040(6)	57(4)
F(11)	5322(3)	5102(4)	2974(2)	40(1)
F(11B)	5800(20)	3520(8)	3292(4)	55(4)
F(12)	6458(3)	4285(7)	3082(2)	51(1)
F(12B)	6417(15)	4570(20)	3032(7)	49(4)
F(13)	4000(1)	8019(4)	3066(1)	45(1)
F(13B)	3974(7)	8399(13)	3152(4)	45(1)
F(14)	3899(5)	9423(5)	2742(2)	36(1)
F(14B)	4326(10)	7792(14)	2682(7)	61(4)
F(15)	4389(2)	8015(2)	2552(1)	40(1)
F(15B)	3970(20)	9320(20)	2693(10)	37(4)
F(16)	6566(3)	11799(3)	3027(1)	61(1)
F(16B)	6943(3)	11666(4)	3101(2)	72(1)
F(17)	6663(4)	10938(8)	2550(2)	45(1)

F(17B)	6486(4)	11114(8)	2560(2)	49(1)
F(18)	7619(3)	10874(4)	3015(1)	78(1)
F(18B)	7615(2)	10549(4)	2868(1)	48(1)
F(19)	9101(1)	8708(1)	3024(1)	50(1)
F(20)	9295(1)	7064(1)	3052(1)	45(1)
F(21)	10253(1)	8081(1)	3299(1)	45(1)
F(22)	10666(1)	8119(2)	4583(1)	56(1)
F(22B)	10479(15)	7530(20)	4604(7)	49(4)
F(23)	9718(1)	8946(1)	4770(1)	67(1)
F(23B)	10205(16)	8981(19)	4622(6)	49(1)
F(24)	9797(1)	7308(1)	4821(1)	49(1)
F(24B)	9509(13)	7890(30)	4846(5)	50(5)
C(55)	6661(1)	8669(1)	4171(1)	19(1)
C(56)	7132(1)	9461(1)	4364(1)	20(1)
C(57)	6813(1)	10146(1)	4591(1)	21(1)
C(58)	6001(1)	10087(1)	4625(1)	22(1)
C(59)	5523(1)	9311(1)	4434(1)	22(1)
C(60)	5848(1)	8614(1)	4219(1)	21(1)
C(61)	7342(1)	10994(1)	4782(1)	25(1)
C(62)	4643(1)	9213(2)	4460(1)	29(1)
C(63)	6603(1)	6745(1)	3877(1)	19(1)
C(64)	6502(1)	6279(1)	4205(1)	21(1)
C(65)	6193(1)	5278(1)	4218(1)	22(1)
C(66)	5958(1)	4690(1)	3904(1)	23(1)
C(67)	6067(1)	5123(1)	3580(1)	22(1)
C(68)	6394(1)	6121(1)	3568(1)	21(1)
C(69)	6063(1)	4818(1)	4570(1)	28(1)
C(70)	5826(1)	4528(1)	3232(1)	30(1)
C(71)	6472(1)	8536(1)	3484(1)	19(1)
C(72)	5662(1)	8311(1)	3318(1)	20(1)
C(73)	5236(1)	8907(1)	3033(1)	22(1)
C(74)	5602(1)	9742(1)	2894(1)	24(1)
C(75)	6405(1)	9974(1)	3051(1)	24(1)
C(76)	6823(1)	9395(1)	3342(1)	21(1)
C(77)	4384(1)	8596(2)	2858(1)	29(1)
C(78)	6829(1)	10860(2)	2905(1)	36(1)
C(79)	7931(1)	7910(1)	3881(1)	19(1)
C(80)	8281(1)	7872(1)	3570(1)	20(1)
C(81)	9124(1)	7914(1)	3591(1)	22(1)
C(82)	9658(1)	7987(1)	3921(1)	22(1)
C(83)	9328(1)	7982(1)	4233(1)	21(1)
C(84)	8485(1)	7928(1)	4212(1)	20(1)
C(85)	9444(1)	7939(2)	3245(1)	28(1)
C(86)	9875(1)	8095(2)	4597(1)	27(1)

B(1)	6938(1)	7941(1)	3856(1)	18(1)

Table S8. Bond lengths [Å] and angles [°] for RBabu_MP-05-007.

Co(1)-P(1)	2.2575(5)	C(12)-H(12)	0.9500
Co(1)-P(2)	2.2633(5)	C(13)-C(14)	1.392(2)
Co(1)-P(3)	2.2811(5)	C(13)-C(18)	1.386(3)
Co(1)-P(4)	2.2823(5)	C(14)-H(14)	0.9500
P(1)-C(1)	1.8330(17)	C(14)-C(15)	1.379(3)
P(1)-C(7)	1.8237(17)	C(15)-H(15)	0.9500
P(1)-C(13)	1.8232(17)	C(15)-C(16)	1.379(3)
P(2)-C(3)	1.8388(17)	C(16)-H(16)	0.9500
P(2)-C(19)	1.8325(17)	C(16)-C(17)	1.376(3)
P(2)-C(25)	1.8299(17)	C(17)-H(17)	0.9500
P(3)-C(6)	1.8460(17)	C(17)-C(18)	1.389(3)
P(3)-C(31)	1.8343(18)	C(18)-H(18)	0.9500
P(3)-C(37)	1.8294(17)	C(19)-C(20)	1.383(2)
P(4)-C(4)	1.8264(18)	C(19)-C(24)	1.395(2)
P(4)-C(43)	1.8334(18)	C(20)-H(20)	0.9500
P(4)-C(49)	1.8323(18)	C(20)-C(21)	1.392(3)
C(1)-H(1A)	0.9900	C(21)-H(21)	0.9500
C(1)-H(1B)	0.9900	C(21)-C(22)	1.376(3)
C(1)-C(2)	1.533(2)	C(22)-H(22)	0.9500
C(2)-H(2A)	0.9900	C(22)-C(23)	1.380(3)
C(2)-H(2B)	0.9900	C(23)-H(23)	0.9500
C(2)-C(3)	1.535(2)	C(23)-C(24)	1.383(2)
C(3)-H(3A)	0.9900	C(24)-H(24)	0.9500
C(3)-H(3B)	0.9900	C(25)-C(26)	1.393(3)
C(4)-H(4A)	0.9900	C(25)-C(30)	1.385(2)
C(4)-H(4B)	0.9900	C(26)-H(26)	0.9500
C(4)-C(5)	1.536(2)	C(26)-C(27)	1.385(3)
C(5)-H(5A)	0.9900	C(27)-H(27)	0.9500
C(5)-H(5B)	0.9900	C(27)-C(28)	1.382(3)
C(5)-C(6)	1.534(3)	C(28)-H(28)	0.9500
C(6)-H(6A)	0.9900	C(28)-C(29)	1.374(3)
C(6)-H(6B)	0.9900	C(29)-H(29)	0.9500
C(7)-C(8)	1.390(2)	C(29)-C(30)	1.395(3)
C(7)-C(12)	1.394(2)	C(30)-H(30)	0.9500
C(8)-H(8)	0.9500	C(31)-C(32)	1.390(2)
C(8)-C(9)	1.388(3)	C(31)-C(36)	1.397(3)
C(9)-H(9)	0.9500	C(32)-H(32)	0.9500
C(9)-C(10)	1.381(3)	C(32)-C(33)	1.383(3)
C(10)-H(10)	0.9500	C(33)-H(33)	0.9500
C(10)-C(11)	1.385(3)	C(33)-C(34)	1.373(3)
C(11)-H(11)	0.9500	C(34)-H(34)	0.9500
C(11)-C(12)	1.384(2)	C(34)-C(35)	1.386(3)

C(35)-H(35)	0.9500	F(9)-C(69)	1.347(2)
C(35)-C(36)	1.381(3)	F(10)-C(70)	1.331(3)
C(36)-H(36)	0.9500	F(10B)-C(70)	1.219(15)
C(37)-C(38)	1.397(2)	F(11)-C(70)	1.365(4)
C(37)-C(42)	1.383(2)	F(11B)-C(70)	1.311(11)
C(38)-H(38)	0.9500	F(12)-C(70)	1.323(5)
C(38)-C(39)	1.383(3)	F(12B)-C(70)	1.349(18)
C(39)-H(39)	0.9500	F(13)-C(77)	1.325(3)
C(39)-C(40)	1.382(3)	F(13B)-C(77)	1.426(14)
C(40)-H(40)	0.9500	F(14)-C(77)	1.350(5)
C(40)-C(41)	1.379(3)	F(14B)-C(77)	1.216(12)
C(41)-H(41)	0.9500	F(15)-C(77)	1.366(3)
C(41)-C(42)	1.390(2)	F(15B)-C(77)	1.24(3)
C(42)-H(42)	0.9500	F(16)-C(78)	1.385(5)
C(43)-C(44)	1.388(3)	F(16B)-C(78)	1.258(5)
C(43)-C(48)	1.392(3)	F(17)-C(78)	1.308(6)
C(44)-H(44)	0.9500	F(17B)-C(78)	1.348(6)
C(44)-C(45)	1.393(3)	F(18)-C(78)	1.299(5)
C(45)-H(45)	0.9500	F(18B)-C(78)	1.399(4)
C(45)-C(46)	1.377(3)	F(19)-C(85)	1.340(2)
C(46)-H(46)	0.9500	F(20)-C(85)	1.329(2)
C(46)-C(47)	1.378(3)	F(21)-C(85)	1.334(2)
C(47)-H(47)	0.9500	F(22)-C(86)	1.326(2)
C(47)-C(48)	1.384(3)	F(22B)-C(86)	1.23(2)
C(48)-H(48)	0.9500	F(23)-C(86)	1.319(2)
C(49)-C(50)	1.390(3)	F(23B)-C(86)	1.26(2)
C(49)-C(54)	1.390(3)	F(24)-C(86)	1.334(2)
C(50)-H(50)	0.9500	F(24B)-C(86)	1.24(2)
C(50)-C(51)	1.392(3)	C(55)-C(56)	1.394(2)
C(51)-H(51)	0.9500	C(55)-C(60)	1.399(2)
C(51)-C(52)	1.375(3)	C(55)-B(1)	1.640(2)
C(52)-H(52)	0.9500	C(56)-H(56)	0.9500
C(52)-C(53)	1.376(3)	C(56)-C(57)	1.397(2)
C(53)-H(53)	0.9500	C(57)-C(58)	1.383(2)
C(53)-C(54)	1.390(3)	C(57)-C(61)	1.489(2)
C(54)-H(54)	0.9500	C(58)-H(58)	0.9500
F(1)-C(61)	1.346(2)	C(58)-C(59)	1.382(2)
F(2)-C(61)	1.339(2)	C(59)-C(60)	1.383(2)
F(3)-C(61)	1.3394(19)	C(59)-C(62)	1.491(2)
F(4)-C(62)	1.340(2)	C(60)-H(60)	0.9500
F(5)-C(62)	1.337(2)	C(63)-C(64)	1.403(2)
F(6)-C(62)	1.349(2)	C(63)-C(68)	1.396(2)
F(7)-C(69)	1.331(2)	C(63)-B(1)	1.635(2)
F(8)-C(69)	1.331(2)	C(64)-H(64)	0.9500

C(64)-C(65)	1.385(2)	C(13)-P(1)-C(7)	101.77(8)
C(65)-C(66)	1.388(2)	C(3)-P(2)-Co(1)	110.47(6)
C(65)-C(69)	1.497(2)	C(19)-P(2)-Co(1)	120.51(6)
C(66)-H(66)	0.9500	C(19)-P(2)-C(3)	102.73(8)
C(66)-C(67)	1.379(2)	C(25)-P(2)-Co(1)	117.54(5)
C(67)-C(68)	1.392(2)	C(25)-P(2)-C(3)	104.09(8)
C(67)-C(70)	1.494(2)	C(25)-P(2)-C(19)	99.32(7)
C(68)-H(68)	0.9500	C(6)-P(3)-Co(1)	110.97(6)
C(71)-C(72)	1.401(2)	C(31)-P(3)-Co(1)	123.74(6)
C(71)-C(76)	1.398(2)	C(31)-P(3)-C(6)	101.57(8)
C(71)-B(1)	1.643(2)	C(37)-P(3)-Co(1)	115.86(6)
C(72)-H(72)	0.9500	C(37)-P(3)-C(6)	101.84(8)
C(72)-C(73)	1.390(2)	C(37)-P(3)-C(31)	99.88(8)
C(73)-C(74)	1.382(2)	C(4)-P(4)-Co(1)	113.70(6)
C(73)-C(77)	1.496(2)	C(4)-P(4)-C(43)	104.85(9)
C(74)-H(74)	0.9500	C(4)-P(4)-C(49)	104.69(8)
C(74)-C(75)	1.383(2)	C(43)-P(4)-Co(1)	111.73(6)
C(75)-C(76)	1.389(2)	C(49)-P(4)-Co(1)	117.54(6)
C(75)-C(78)	1.494(2)	C(49)-P(4)-C(43)	103.02(8)
C(76)-H(76)	0.9500	P(1)-C(1)-H(1A)	109.0
C(79)-C(80)	1.400(2)	P(1)-C(1)-H(1B)	109.0
C(79)-C(84)	1.396(2)	H(1A)-C(1)-H(1B)	107.8
C(79)-B(1)	1.638(2)	C(2)-C(1)-P(1)	112.97(12)
C(80)-H(80)	0.9500	C(2)-C(1)-H(1A)	109.0
C(80)-C(81)	1.391(2)	C(2)-C(1)-H(1B)	109.0
C(81)-C(82)	1.379(2)	C(1)-C(2)-H(2A)	108.6
C(81)-C(85)	1.493(2)	C(1)-C(2)-H(2B)	108.6
C(82)-H(82)	0.9500	C(1)-C(2)-C(3)	114.55(14)
C(82)-C(83)	1.385(2)	H(2A)-C(2)-H(2B)	107.6
C(83)-C(84)	1.391(2)	C(3)-C(2)-H(2A)	108.6
C(83)-C(86)	1.493(2)	C(3)-C(2)-H(2B)	108.6
C(84)-H(84)	0.9500	P(2)-C(3)-H(3A)	108.9
		P(2)-C(3)-H(3B)	108.9
P(1)-Co(1)-P(2)	95.185(17)	C(2)-C(3)-P(2)	113.49(12)
P(1)-Co(1)-P(3)	107.853(17)	C(2)-C(3)-H(3A)	108.9
P(1)-Co(1)-P(4)	139.532(18)	C(2)-C(3)-H(3B)	108.9
P(2)-Co(1)-P(3)	99.716(17)	H(3A)-C(3)-H(3B)	107.7
P(2)-Co(1)-P(4)	112.730(18)	P(4)-C(4)-H(4A)	108.8
P(3)-Co(1)-P(4)	96.070(17)	P(4)-C(4)-H(4B)	108.8
C(1)-P(1)-Co(1)	115.05(6)	H(4A)-C(4)-H(4B)	107.7
C(7)-P(1)-Co(1)	115.67(5)	C(5)-C(4)-P(4)	113.87(12)
C(7)-P(1)-C(1)	104.90(8)	C(5)-C(4)-H(4A)	108.8
C(13)-P(1)-Co(1)	113.37(6)	C(5)-C(4)-H(4B)	108.8
C(13)-P(1)-C(1)	104.59(8)	C(4)-C(5)-H(5A)	108.5

C(4)-C(5)-H(5B)	108.5	C(13)-C(18)-C(17)	120.88(18)
H(5A)-C(5)-H(5B)	107.5	C(13)-C(18)-H(18)	119.6
C(6)-C(5)-C(4)	114.90(15)	C(17)-C(18)-H(18)	119.6
C(6)-C(5)-H(5A)	108.5	C(20)-C(19)-P(2)	120.25(13)
C(6)-C(5)-H(5B)	108.5	C(20)-C(19)-C(24)	118.50(16)
P(3)-C(6)-H(6A)	108.7	C(24)-C(19)-P(2)	121.08(13)
P(3)-C(6)-H(6B)	108.7	C(19)-C(20)-H(20)	119.6
C(5)-C(6)-P(3)	114.27(12)	C(19)-C(20)-C(21)	120.79(17)
C(5)-C(6)-H(6A)	108.7	C(21)-C(20)-H(20)	119.6
C(5)-C(6)-H(6B)	108.7	C(20)-C(21)-H(21)	119.9
H(6A)-C(6)-H(6B)	107.6	C(22)-C(21)-C(20)	120.10(18)
C(8)-C(7)-P(1)	121.54(13)	C(22)-C(21)-H(21)	119.9
C(8)-C(7)-C(12)	118.89(16)	C(21)-C(22)-H(22)	120.2
C(12)-C(7)-P(1)	119.16(13)	C(21)-C(22)-C(23)	119.66(17)
C(7)-C(8)-H(8)	119.8	C(23)-C(22)-H(22)	120.2
C(9)-C(8)-C(7)	120.49(17)	C(22)-C(23)-H(23)	119.8
C(9)-C(8)-H(8)	119.8	C(22)-C(23)-C(24)	120.43(17)
C(8)-C(9)-H(9)	119.9	C(24)-C(23)-H(23)	119.8
C(10)-C(9)-C(8)	120.24(18)	C(19)-C(24)-H(24)	119.7
C(10)-C(9)-H(9)	119.9	C(23)-C(24)-C(19)	120.50(17)
C(9)-C(10)-H(10)	120.2	C(23)-C(24)-H(24)	119.7
C(9)-C(10)-C(11)	119.58(17)	C(26)-C(25)-P(2)	117.75(13)
C(11)-C(10)-H(10)	120.2	C(30)-C(25)-P(2)	123.52(14)
C(10)-C(11)-H(11)	119.8	C(30)-C(25)-C(26)	118.70(16)
C(12)-C(11)-C(10)	120.43(18)	C(25)-C(26)-H(26)	119.5
C(12)-C(11)-H(11)	119.8	C(27)-C(26)-C(25)	121.10(18)
C(7)-C(12)-H(12)	119.8	C(27)-C(26)-H(26)	119.5
C(11)-C(12)-C(7)	120.30(17)	C(26)-C(27)-H(27)	120.2
C(11)-C(12)-H(12)	119.8	C(28)-C(27)-C(26)	119.57(18)
C(14)-C(13)-P(1)	122.05(14)	C(28)-C(27)-H(27)	120.2
C(18)-C(13)-P(1)	119.11(13)	C(27)-C(28)-H(28)	120.0
C(18)-C(13)-C(14)	118.79(17)	C(29)-C(28)-C(27)	119.99(17)
C(13)-C(14)-H(14)	120.0	C(29)-C(28)-H(28)	120.0
C(15)-C(14)-C(13)	120.02(19)	C(28)-C(29)-H(29)	119.7
C(15)-C(14)-H(14)	120.0	C(28)-C(29)-C(30)	120.53(18)
C(14)-C(15)-H(15)	119.6	C(30)-C(29)-H(29)	119.7
C(14)-C(15)-C(16)	120.81(19)	C(25)-C(30)-C(29)	120.07(18)
C(16)-C(15)-H(15)	119.6	C(25)-C(30)-H(30)	120.0
C(15)-C(16)-H(16)	120.1	C(29)-C(30)-H(30)	120.0
C(17)-C(16)-C(15)	119.76(18)	C(32)-C(31)-P(3)	122.43(14)
C(17)-C(16)-H(16)	120.1	C(32)-C(31)-C(36)	118.11(17)
C(16)-C(17)-H(17)	120.1	C(36)-C(31)-P(3)	119.46(13)
C(16)-C(17)-C(18)	119.74(19)	C(31)-C(32)-H(32)	119.5
C(18)-C(17)-H(17)	120.1	C(33)-C(32)-C(31)	120.92(18)

C(33)-C(32)-H(32)	119.5	C(46)-C(47)-C(48)	119.7(2)
C(32)-C(33)-H(33)	119.8	C(48)-C(47)-H(47)	120.2
C(34)-C(33)-C(32)	120.49(19)	C(43)-C(48)-H(48)	119.4
C(34)-C(33)-H(33)	119.8	C(47)-C(48)-C(43)	121.22(19)
C(33)-C(34)-H(34)	120.3	C(47)-C(48)-H(48)	119.4
C(33)-C(34)-C(35)	119.43(19)	C(50)-C(49)-P(4)	119.40(14)
C(35)-C(34)-H(34)	120.3	C(54)-C(49)-P(4)	121.75(15)
C(34)-C(35)-H(35)	119.8	C(54)-C(49)-C(50)	118.55(17)
C(36)-C(35)-C(34)	120.4(2)	C(49)-C(50)-H(50)	119.7
C(36)-C(35)-H(35)	119.8	C(49)-C(50)-C(51)	120.58(19)
C(31)-C(36)-H(36)	119.7	C(51)-C(50)-H(50)	119.7
C(35)-C(36)-C(31)	120.65(18)	C(50)-C(51)-H(51)	119.9
C(35)-C(36)-H(36)	119.7	C(52)-C(51)-C(50)	120.2(2)
C(38)-C(37)-P(3)	121.13(14)	C(52)-C(51)-H(51)	119.9
C(42)-C(37)-P(3)	119.80(13)	C(51)-C(52)-H(52)	120.1
C(42)-C(37)-C(38)	119.07(16)	C(51)-C(52)-C(53)	119.76(19)
C(37)-C(38)-H(38)	119.9	C(53)-C(52)-H(52)	120.1
C(39)-C(38)-C(37)	120.26(18)	C(52)-C(53)-H(53)	119.8
C(39)-C(38)-H(38)	119.9	C(52)-C(53)-C(54)	120.4(2)
C(38)-C(39)-H(39)	120.1	C(54)-C(53)-H(53)	119.8
C(40)-C(39)-C(38)	119.88(18)	C(49)-C(54)-H(54)	119.8
C(40)-C(39)-H(39)	120.1	C(53)-C(54)-C(49)	120.4(2)
C(39)-C(40)-H(40)	119.7	C(53)-C(54)-H(54)	119.8
C(41)-C(40)-C(39)	120.53(17)	C(56)-C(55)-C(60)	115.57(14)
C(41)-C(40)-H(40)	119.7	C(56)-C(55)-B(1)	125.28(14)
C(40)-C(41)-H(41)	120.2	C(60)-C(55)-B(1)	118.46(14)
C(40)-C(41)-C(42)	119.54(18)	C(55)-C(56)-H(56)	119.0
C(42)-C(41)-H(41)	120.2	C(55)-C(56)-C(57)	121.99(15)
C(37)-C(42)-C(41)	120.70(17)	C(57)-C(56)-H(56)	119.0
C(37)-C(42)-H(42)	119.7	C(56)-C(57)-C(61)	119.36(15)
C(41)-C(42)-H(42)	119.7	C(58)-C(57)-C(56)	120.97(15)
C(44)-C(43)-P(4)	123.59(15)	C(58)-C(57)-C(61)	119.56(15)
C(44)-C(43)-C(48)	118.68(17)	C(57)-C(58)-H(58)	121.1
C(48)-C(43)-P(4)	117.69(14)	C(59)-C(58)-C(57)	117.87(15)
C(43)-C(44)-H(44)	120.1	C(59)-C(58)-H(58)	121.1
C(43)-C(44)-C(45)	119.8(2)	C(58)-C(59)-C(60)	120.94(15)
C(45)-C(44)-H(44)	120.1	C(58)-C(59)-C(62)	120.17(15)
C(44)-C(45)-H(45)	119.6	C(60)-C(59)-C(62)	118.89(15)
C(46)-C(45)-C(44)	120.8(2)	C(55)-C(60)-H(60)	118.7
C(46)-C(45)-H(45)	119.6	C(59)-C(60)-C(55)	122.60(15)
C(45)-C(46)-H(46)	120.1	C(59)-C(60)-H(60)	118.7
C(45)-C(46)-C(47)	119.83(19)	F(1)-C(61)-C(57)	112.35(14)
C(47)-C(46)-H(46)	120.1	F(2)-C(61)-F(1)	105.84(13)
C(46)-C(47)-H(47)	120.2	F(2)-C(61)-F(3)	106.38(14)

F(2)-C(61)-C(57)	112.66(14)	F(12B)-C(70)-C(67)	111.2(12)
F(3)-C(61)-F(1)	106.17(14)	C(72)-C(71)-B(1)	122.43(14)
F(3)-C(61)-C(57)	112.89(14)	C(76)-C(71)-C(72)	115.40(15)
F(4)-C(62)-F(6)	105.92(14)	C(76)-C(71)-B(1)	121.66(14)
F(4)-C(62)-C(59)	112.96(15)	C(71)-C(72)-H(72)	118.9
F(5)-C(62)-F(4)	107.17(15)	C(73)-C(72)-C(71)	122.16(15)
F(5)-C(62)-F(6)	105.65(15)	C(73)-C(72)-H(72)	118.9
F(5)-C(62)-C(59)	112.64(14)	C(72)-C(73)-C(77)	119.36(15)
F(6)-C(62)-C(59)	111.97(15)	C(74)-C(73)-C(72)	121.21(15)
C(64)-C(63)-B(1)	122.68(14)	C(74)-C(73)-C(77)	119.30(15)
C(68)-C(63)-C(64)	115.54(15)	C(73)-C(74)-H(74)	121.1
C(68)-C(63)-B(1)	121.77(14)	C(73)-C(74)-C(75)	117.74(15)
C(63)-C(64)-H(64)	118.9	C(75)-C(74)-H(74)	121.1
C(65)-C(64)-C(63)	122.21(15)	C(74)-C(75)-C(76)	121.00(16)
C(65)-C(64)-H(64)	118.9	C(74)-C(75)-C(78)	119.54(16)
C(64)-C(65)-C(66)	121.03(15)	C(76)-C(75)-C(78)	119.46(16)
C(64)-C(65)-C(69)	120.95(15)	C(71)-C(76)-H(76)	118.8
C(66)-C(65)-C(69)	117.95(15)	C(75)-C(76)-C(71)	122.45(15)
C(65)-C(66)-H(66)	121.1	C(75)-C(76)-H(76)	118.8
C(67)-C(66)-C(65)	117.84(16)	F(13)-C(77)-F(14)	107.5(4)
C(67)-C(66)-H(66)	121.1	F(13)-C(77)-F(15)	105.8(2)
C(66)-C(67)-C(68)	121.03(15)	F(13)-C(77)-C(73)	114.40(18)
C(66)-C(67)-C(70)	120.28(15)	F(13B)-C(77)-C(73)	105.2(5)
C(68)-C(67)-C(70)	118.69(15)	F(14)-C(77)-F(15)	104.9(4)
C(63)-C(68)-H(68)	118.9	F(14)-C(77)-C(73)	112.9(4)
C(67)-C(68)-C(63)	122.25(15)	F(14B)-C(77)-F(13B)	105.7(9)
C(67)-C(68)-H(68)	118.9	F(14B)-C(77)-F(15B)	112.2(18)
F(7)-C(69)-F(8)	107.62(15)	F(14B)-C(77)-C(73)	115.6(8)
F(7)-C(69)-F(9)	106.10(14)	F(15)-C(77)-C(73)	110.8(2)
F(7)-C(69)-C(65)	112.90(15)	F(15B)-C(77)-F(13B)	102.2(17)
F(8)-C(69)-F(9)	104.83(15)	F(15B)-C(77)-C(73)	114(2)
F(8)-C(69)-C(65)	112.73(14)	F(16)-C(78)-C(75)	109.6(3)
F(9)-C(69)-C(65)	112.10(15)	F(16B)-C(78)-F(17B)	110.5(5)
F(10)-C(70)-F(11)	104.7(3)	F(16B)-C(78)-F(18B)	104.7(3)
F(10)-C(70)-C(67)	113.8(2)	F(16B)-C(78)-C(75)	115.9(3)
F(10B)-C(70)-F(11B)	111.5(10)	F(17)-C(78)-F(16)	104.6(4)
F(10B)-C(70)-F(12B)	107.2(12)	F(17)-C(78)-C(75)	114.1(5)
F(10B)-C(70)-C(67)	114.0(11)	F(17B)-C(78)-F(18B)	101.7(4)
F(11)-C(70)-C(67)	111.6(3)	F(17B)-C(78)-C(75)	113.1(5)
F(11B)-C(70)-F(12B)	100.5(11)	F(18)-C(78)-F(16)	104.4(3)
F(11B)-C(70)-C(67)	111.4(8)	F(18)-C(78)-F(17)	108.8(4)
F(12)-C(70)-F(10)	108.5(3)	F(18)-C(78)-C(75)	114.5(3)
F(12)-C(70)-F(11)	104.7(3)	F(18B)-C(78)-C(75)	109.7(3)
F(12)-C(70)-C(67)	112.8(3)	C(80)-C(79)-B(1)	122.06(14)

C(84)-C(79)-C(80)	115.58(14)
C(84)-C(79)-B(1)	122.36(14)
C(79)-C(80)-H(80)	119.0
C(81)-C(80)-C(79)	121.93(15)
C(81)-C(80)-H(80)	119.0
C(80)-C(81)-C(85)	118.48(15)
C(82)-C(81)-C(80)	121.36(15)
C(82)-C(81)-C(85)	120.07(15)
C(81)-C(82)-H(82)	121.1
C(81)-C(82)-C(83)	117.72(15)
C(83)-C(82)-H(82)	121.1
C(82)-C(83)-C(84)	120.90(15)
C(82)-C(83)-C(86)	119.96(15)
C(84)-C(83)-C(86)	119.05(15)
C(79)-C(84)-H(84)	118.8
C(83)-C(84)-C(79)	122.34(15)
C(83)-C(84)-H(84)	118.8
F(19)-C(85)-C(81)	111.71(14)
F(20)-C(85)-F(19)	105.74(15)
F(20)-C(85)-F(21)	105.97(14)
F(20)-C(85)-C(81)	113.10(15)
F(21)-C(85)-F(19)	106.91(15)
F(21)-C(85)-C(81)	112.88(14)
F(22)-C(86)-F(24)	105.11(17)
F(22)-C(86)-C(83)	113.64(15)
F(22B)-C(86)-F(23B)	100.7(18)
F(22B)-C(86)-F(24B)	112.0(17)
F(22B)-C(86)-C(83)	108.2(11)
F(23)-C(86)-F(22)	107.01(18)
F(23)-C(86)-F(24)	105.13(17)
F(23)-C(86)-C(83)	112.59(15)
F(23B)-C(86)-C(83)	109.6(8)
F(24)-C(86)-C(83)	112.68(15)
F(24B)-C(86)-F(23B)	114.2(18)
F(24B)-C(86)-C(83)	111.4(10)
C(55)-B(1)-C(71)	101.21(12)
C(63)-B(1)-C(55)	110.48(13)
C(63)-B(1)-C(71)	111.48(13)
C(63)-B(1)-C(79)	108.95(13)
C(79)-B(1)-C(55)	113.22(13)
C(79)-B(1)-C(71)	111.37(13)

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for RBabu_MP-05-007. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	17(1)	16(1)	19(1)	1(1)	4(1)	0(1)
P(1)	20(1)	18(1)	20(1)	2(1)	4(1)	-2(1)
P(2)	17(1)	18(1)	23(1)	0(1)	4(1)	-1(1)
P(3)	20(1)	16(1)	26(1)	1(1)	6(1)	0(1)
P(4)	22(1)	23(1)	21(1)	4(1)	6(1)	3(1)
C(1)	27(1)	26(1)	20(1)	2(1)	4(1)	-3(1)
C(2)	24(1)	26(1)	23(1)	3(1)	1(1)	1(1)
C(3)	20(1)	26(1)	22(1)	-2(1)	3(1)	-1(1)
C(4)	30(1)	25(1)	31(1)	10(1)	11(1)	4(1)
C(5)	33(1)	23(1)	33(1)	9(1)	12(1)	7(1)
C(6)	28(1)	18(1)	36(1)	4(1)	10(1)	2(1)
C(7)	23(1)	19(1)	25(1)	5(1)	6(1)	-3(1)
C(8)	29(1)	32(1)	26(1)	0(1)	9(1)	-6(1)
C(9)	31(1)	40(1)	37(1)	1(1)	16(1)	-6(1)
C(10)	23(1)	34(1)	45(1)	8(1)	11(1)	-5(1)
C(11)	27(1)	26(1)	38(1)	2(1)	2(1)	-6(1)
C(12)	27(1)	22(1)	30(1)	1(1)	6(1)	-3(1)
C(13)	20(1)	19(1)	29(1)	1(1)	1(1)	-2(1)
C(14)	34(1)	23(1)	38(1)	5(1)	2(1)	0(1)
C(15)	40(1)	21(1)	58(1)	5(1)	-4(1)	3(1)
C(16)	28(1)	27(1)	61(1)	-14(1)	-5(1)	7(1)
C(17)	31(1)	37(1)	42(1)	-13(1)	6(1)	2(1)
C(18)	29(1)	26(1)	31(1)	-2(1)	5(1)	1(1)
C(19)	20(1)	18(1)	27(1)	3(1)	5(1)	-1(1)
C(20)	24(1)	30(1)	33(1)	-5(1)	2(1)	2(1)
C(21)	36(1)	37(1)	40(1)	-10(1)	9(1)	7(1)
C(22)	29(1)	31(1)	44(1)	2(1)	13(1)	8(1)
C(23)	22(1)	30(1)	36(1)	9(1)	6(1)	3(1)
C(24)	24(1)	26(1)	27(1)	3(1)	4(1)	1(1)
C(25)	15(1)	21(1)	32(1)	1(1)	2(1)	0(1)
C(26)	30(1)	24(1)	38(1)	0(1)	13(1)	-1(1)
C(27)	30(1)	28(1)	45(1)	6(1)	15(1)	-1(1)
C(28)	23(1)	22(1)	51(1)	6(1)	5(1)	-4(1)
C(29)	33(1)	22(1)	42(1)	-2(1)	-2(1)	-2(1)
C(30)	26(1)	24(1)	32(1)	1(1)	0(1)	-1(1)
C(31)	21(1)	20(1)	30(1)	-2(1)	6(1)	2(1)
C(32)	30(1)	24(1)	36(1)	0(1)	1(1)	-2(1)
C(33)	40(1)	27(1)	43(1)	-6(1)	-6(1)	-3(1)
C(34)	45(1)	38(1)	33(1)	-10(1)	-2(1)	5(1)

C(35)	43(1)	43(1)	30(1)	-3(1)	10(1)	1(1)
C(36)	36(1)	28(1)	32(1)	-5(1)	10(1)	-6(1)
C(37)	22(1)	21(1)	27(1)	4(1)	7(1)	3(1)
C(38)	28(1)	23(1)	44(1)	-3(1)	8(1)	3(1)
C(39)	29(1)	32(1)	60(1)	1(1)	15(1)	11(1)
C(40)	20(1)	43(1)	53(1)	7(1)	6(1)	5(1)
C(41)	25(1)	36(1)	36(1)	2(1)	1(1)	-3(1)
C(42)	24(1)	25(1)	26(1)	1(1)	7(1)	2(1)
C(43)	25(1)	36(1)	18(1)	-2(1)	6(1)	2(1)
C(44)	30(1)	47(1)	23(1)	2(1)	9(1)	7(1)
C(45)	28(1)	72(2)	26(1)	-3(1)	2(1)	12(1)
C(46)	28(1)	71(2)	32(1)	-17(1)	6(1)	-5(1)
C(47)	36(1)	51(1)	32(1)	-13(1)	9(1)	-10(1)
C(48)	31(1)	38(1)	24(1)	-5(1)	6(1)	-2(1)
C(49)	28(1)	32(1)	19(1)	6(1)	6(1)	8(1)
C(50)	31(1)	37(1)	26(1)	0(1)	4(1)	7(1)
C(51)	45(1)	42(1)	28(1)	-3(1)	6(1)	15(1)
C(52)	53(1)	52(1)	31(1)	11(1)	22(1)	24(1)
C(53)	48(1)	51(1)	48(1)	17(1)	31(1)	13(1)
C(54)	41(1)	35(1)	41(1)	9(1)	23(1)	6(1)
F(1)	35(1)	21(1)	42(1)	2(1)	8(1)	-6(1)
F(2)	27(1)	33(1)	32(1)	-4(1)	-2(1)	-4(1)
F(3)	42(1)	48(1)	39(1)	-26(1)	22(1)	-18(1)
F(4)	26(1)	30(1)	44(1)	-5(1)	15(1)	4(1)
F(5)	20(1)	82(1)	46(1)	-28(1)	4(1)	-3(1)
F(6)	37(1)	28(1)	64(1)	-6(1)	32(1)	-6(1)
F(7)	62(1)	36(1)	19(1)	0(1)	4(1)	-11(1)
F(8)	33(1)	79(1)	41(1)	21(1)	16(1)	1(1)
F(9)	59(1)	27(1)	31(1)	8(1)	4(1)	0(1)
F(10)	100(3)	45(2)	32(1)	-9(1)	6(2)	-44(2)
F(10B)	52(5)	78(11)	35(7)	-13(5)	-11(4)	15(6)
F(11)	49(1)	43(2)	23(2)	-4(1)	-7(1)	3(1)
F(11B)	109(12)	21(3)	35(4)	-12(2)	12(7)	-18(4)
F(12)	44(1)	68(3)	37(2)	-27(2)	1(1)	13(2)
F(12B)	67(6)	51(9)	37(7)	-21(5)	31(6)	-15(5)
F(13)	24(1)	64(2)	44(1)	23(1)	-5(1)	-16(1)
F(13B)	24(1)	64(2)	44(1)	23(1)	-5(1)	-16(1)
F(14)	24(2)	35(1)	45(2)	0(1)	-6(1)	7(1)
F(14B)	36(5)	55(5)	82(8)	-34(6)	-16(7)	-3(5)
F(15)	39(1)	40(1)	37(1)	-13(1)	-5(1)	-5(1)
F(15B)	21(5)	52(7)	37(8)	18(7)	1(5)	4(6)
F(16)	104(3)	23(1)	62(2)	6(1)	30(2)	-11(2)
F(16B)	95(3)	43(2)	86(2)	-14(2)	35(2)	-32(2)
F(17)	51(3)	42(3)	45(1)	13(1)	14(1)	-2(2)

F(17B)	38(2)	54(4)	54(1)	34(2)	8(1)	0(2)
F(18)	33(1)	86(4)	107(3)	68(3)	-10(2)	-19(1)
F(18B)	31(1)	53(2)	60(2)	28(2)	11(1)	-4(1)
F(19)	56(1)	65(1)	36(1)	22(1)	27(1)	28(1)
F(20)	49(1)	56(1)	34(1)	-19(1)	17(1)	-3(1)
F(21)	22(1)	83(1)	33(1)	-5(1)	13(1)	-6(1)
F(22)	22(1)	112(2)	32(1)	7(1)	-4(1)	-14(1)
F(22B)	27(8)	73(6)	42(11)	-1(9)	-7(7)	18(7)
F(23)	87(1)	53(1)	44(1)	-27(1)	-31(1)	28(1)
F(23B)	57(1)	55(1)	28(1)	16(1)	-10(1)	-17(1)
F(24)	57(1)	55(1)	28(1)	16(1)	-10(1)	-17(1)
F(24B)	31(8)	92(14)	24(7)	17(9)	0(6)	-3(8)
C(55)	20(1)	20(1)	18(1)	1(1)	4(1)	1(1)
C(56)	19(1)	21(1)	21(1)	1(1)	5(1)	-1(1)
C(57)	24(1)	19(1)	19(1)	0(1)	4(1)	-1(1)
C(58)	26(1)	21(1)	22(1)	-2(1)	9(1)	1(1)
C(59)	21(1)	24(1)	22(1)	0(1)	5(1)	1(1)
C(60)	21(1)	22(1)	21(1)	-2(1)	5(1)	-3(1)
C(61)	28(1)	25(1)	26(1)	-4(1)	11(1)	-3(1)
C(62)	26(1)	32(1)	33(1)	-10(1)	11(1)	-1(1)
C(63)	15(1)	22(1)	21(1)	-1(1)	4(1)	2(1)
C(64)	20(1)	23(1)	19(1)	-2(1)	2(1)	1(1)
C(65)	19(1)	25(1)	21(1)	1(1)	2(1)	2(1)
C(66)	23(1)	22(1)	25(1)	1(1)	3(1)	-2(1)
C(67)	22(1)	22(1)	22(1)	-2(1)	2(1)	0(1)
C(68)	20(1)	22(1)	20(1)	1(1)	6(1)	1(1)
C(69)	30(1)	28(1)	25(1)	4(1)	3(1)	-2(1)
C(70)	38(1)	25(1)	26(1)	-3(1)	3(1)	-5(1)
C(71)	19(1)	21(1)	19(1)	-4(1)	6(1)	0(1)
C(72)	21(1)	20(1)	20(1)	0(1)	5(1)	0(1)
C(73)	20(1)	24(1)	20(1)	-2(1)	3(1)	1(1)
C(74)	26(1)	23(1)	23(1)	2(1)	3(1)	3(1)
C(75)	25(1)	21(1)	28(1)	1(1)	7(1)	1(1)
C(76)	18(1)	21(1)	24(1)	-2(1)	3(1)	-1(1)
C(77)	24(1)	29(1)	32(1)	4(1)	0(1)	-1(1)
C(78)	32(1)	29(1)	45(1)	12(1)	3(1)	-7(1)
C(79)	19(1)	16(1)	22(1)	-1(1)	4(1)	0(1)
C(80)	20(1)	21(1)	20(1)	-2(1)	3(1)	1(1)
C(81)	22(1)	21(1)	23(1)	-1(1)	6(1)	2(1)
C(82)	17(1)	21(1)	27(1)	0(1)	5(1)	1(1)
C(83)	21(1)	19(1)	22(1)	1(1)	1(1)	1(1)
C(84)	22(1)	19(1)	20(1)	0(1)	6(1)	1(1)
C(85)	21(1)	38(1)	25(1)	0(1)	7(1)	4(1)
C(86)	24(1)	32(1)	25(1)	1(1)	1(1)	-1(1)

B(1)	18(1)	20(1)	18(1)	-1(1)	4(1)	-1(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for RBabu_MP-05-007.

	x	y	z	U(eq)
H(1A)	1718	2279	4644	29
H(1B)	1912	1054	4658	29
H(2A)	3151	1443	4430	30
H(2B)	3162	1838	4835	30
H(3A)	3675	3228	4584	27
H(3B)	2739	3559	4560	27
H(4A)	2067	5017	3089	34
H(4B)	1334	4917	2745	34
H(5A)	891	6152	3100	35
H(5B)	389	5128	3164	35
H(6A)	972	6152	3708	32
H(6B)	1843	5695	3667	32
H(8)	347	2058	4534	34
H(9)	-1064	1876	4492	42
H(10)	-1851	1023	3994	40
H(11)	-1210	257	3557	37
H(12)	198	429	3598	31
H(14)	1694	-536	4344	39
H(15)	2115	-2108	4130	50
H(16)	2512	-2193	3569	49
H(17)	2484	-692	3215	44
H(18)	2066	894	3427	34
H(20)	3194	1884	3383	35
H(21)	4270	928	3226	45
H(22)	5550	915	3610	41
H(23)	5758	1875	4148	35
H(24)	4686	2814	4310	31
H(26)	3552	4281	3404	36
H(27)	4013	5950	3296	40
H(28)	4162	7209	3755	39
H(29)	3879	6785	4320	41
H(30)	3416	5111	4430	34
H(32)	2016	6111	4267	37
H(33)	2280	6719	4862	47
H(34)	1726	5873	5308	48
H(35)	890	4411	5153	46
H(36)	637	3779	4561	38
H(38)	-206	5704	4076	38

H(39)	-1633	5633	3980	47
H(40)	-2332	4252	3653	46
H(41)	-1614	2938	3420	39
H(42)	-182	2980	3530	30
H(44)	82	4300	2550	39
H(45)	-1248	3749	2301	51
H(46)	-1718	2129	2450	53
H(47)	-860	1036	2852	47
H(48)	458	1587	3111	37
H(50)	1513	1383	2751	38
H(51)	2436	538	2452	46
H(52)	3579	1421	2335	52
H(53)	3772	3173	2493	55
H(54)	2843	4038	2783	44
H(56)	7687	9536	4340	24
H(58)	5780	10565	4774	27
H(60)	5506	8075	4098	25
H(64)	6651	6664	4425	25
H(66)	5731	4012	3912	28
H(68)	6479	6386	3341	25
H(72)	5395	7732	3403	24
H(74)	5312	10144	2697	29
H(76)	7368	9590	3448	26
H(80)	7932	7816	3338	24
H(82)	10233	8039	3934	26
H(84)	8279	7903	4431	24

Table S11. Crystal data and structure refinement for RBabu2903.

Report date	2019-12-18	
Identification code	RBabu2903	
Empirical formula	C58 H60 Br3 Co O P4 Zn	
Molecular formula	C54 H52 Co P4, C4 H8 Br3 O Zn	
Formula weight	1260.97	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 14.1589(9) Å	α= 90°.
	b = 17.0352(10) Å	β= 100.025(3)°.
	c = 24.3773(14) Å	γ = 90°.
Volume	5790.0(6) $Å^3$	
Z	4	
Density (calculated)	1.447 Mg/m^3	
Absorption coefficient	2.919 mm^{-1}	
F(000)	2552	
Crystal size	0.19 x 0.12 x 0.08 mm^3	
Crystal color, habit	Bluish Green Plate	
Theta range for data collection	1.887 to 27.585°.	
Index ranges	-18<=h<=18, -22<=k<=22, -31<=l<=28	
Reflections collected	103708	
Independent reflections	13361 [R(int) = 0.0456, R(sigma) = 0.0354]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2616 and 0.2153	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13361 / 0 / 617	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0867	
R indices (all data)	R1 = 0.0537, wR2 = 0.0929	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.635 and -1.468 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for RBabu2903. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	3174(1)	7040(1)	6041(1)	16(1)
P(1)	3490(1)	8274(1)	5772(1)	18(1)
P(2)	1745(1)	6960(1)	5442(1)	21(1)
P(3)	4596(1)	6400(1)	6320(1)	19(1)
P(4)	2895(1)	7299(1)	6915(1)	19(1)
C(1)	2423(2)	8901(1)	5653(1)	23(1)
C(2)	1629(2)	8594(2)	5192(1)	28(1)
C(3)	1070(2)	7880(1)	5353(1)	27(1)
C(4)	5301(2)	6717(2)	6986(1)	23(1)
C(5)	4711(2)	6807(2)	7452(1)	24(1)
C(6)	4031(2)	7506(1)	7382(1)	22(1)
C(7)	4379(2)	8866(1)	6227(1)	19(1)
C(8)	5330(2)	8613(2)	6316(1)	24(1)
C(9)	6029(2)	9003(2)	6681(1)	31(1)
C(10)	5787(2)	9652(2)	6971(1)	31(1)
C(11)	4851(2)	9914(2)	6878(1)	30(1)
C(12)	4148(2)	9532(2)	6504(1)	25(1)
C(13)	3924(2)	8370(1)	5109(1)	21(1)
C(14)	4127(2)	7710(2)	4825(1)	30(1)
C(15)	4466(2)	7775(2)	4325(1)	39(1)
C(16)	4598(2)	8500(2)	4107(1)	34(1)
C(17)	4398(2)	9165(2)	4385(1)	34(1)
C(18)	4073(2)	9099(2)	4884(1)	30(1)
C(19)	1928(2)	6682(2)	4744(1)	27(1)
C(20)	1446(2)	7029(2)	4257(1)	35(1)
C(21)	1653(2)	6796(2)	3744(1)	46(1)
C(22)	2322(3)	6218(2)	3715(1)	50(1)
C(23)	2788(2)	5859(2)	4192(1)	47(1)
C(24)	2593(2)	6097(2)	4704(1)	35(1)

C(25)	879(2)	6230(2)	5593(1)	26(1)
C(26)	52(2)	6427(2)	5791(1)	39(1)
C(27)	-532(2)	5850(2)	5946(2)	49(1)
C(28)	-298(2)	5073(2)	5917(1)	42(1)
C(29)	502(2)	4866(2)	5715(1)	39(1)
C(30)	1089(2)	5441(2)	5552(1)	31(1)
C(31)	5484(2)	6360(1)	5860(1)	22(1)
C(32)	5231(2)	5983(2)	5348(1)	28(1)
C(33)	5848(2)	5960(2)	4967(1)	36(1)
C(34)	6732(2)	6315(2)	5090(1)	39(1)
C(35)	6998(2)	6688(2)	5595(1)	40(1)
C(36)	6386(2)	6710(2)	5982(1)	31(1)
C(37)	4410(2)	5352(1)	6431(1)	22(1)
C(38)	3488(2)	5054(2)	6353(1)	31(1)
C(39)	3319(2)	4261(2)	6416(1)	42(1)
C(40)	4089(3)	3758(2)	6555(1)	44(1)
C(41)	5005(2)	4046(2)	6631(1)	38(1)
C(42)	5176(2)	4834(2)	6575(1)	29(1)
C(43)	2365(2)	6557(1)	7314(1)	23(1)
C(44)	1808(2)	5961(2)	7042(1)	30(1)
C(45)	1379(2)	5410(2)	7338(1)	39(1)
C(46)	1492(2)	5453(2)	7907(1)	38(1)
C(47)	2041(2)	6045(2)	8187(1)	39(1)
C(48)	2469(2)	6598(2)	7894(1)	31(1)
C(49)	2159(2)	8152(2)	7024(1)	27(1)
C(50)	1169(2)	8090(2)	6888(1)	40(1)
C(51)	596(2)	8734(2)	6935(2)	54(1)
C(52)	1004(3)	9446(2)	7120(2)	54(1)
C(53)	1974(3)	9514(2)	7258(1)	45(1)
C(54)	2555(2)	8866(2)	7212(1)	31(1)
Br(1)	1321(1)	2786(1)	5568(1)	44(1)
Br(2)	154(1)	811(1)	6007(1)	55(1)
Br(3)	2883(1)	1431(1)	6688(1)	43(1)
Zn(1)	1556(1)	1511(1)	5953(1)	28(1)

O(1)	2052(1)	963(1)	5297(1)	33(1)
C(55)	2973(2)	1219(2)	5187(2)	49(1)
C(56)	2948(3)	1108(2)	4575(2)	64(1)
C(57)	2062(3)	629(3)	4379(2)	57(1)
C(57B)	1770(20)	1218(16)	4327(10)	57(1)
C(58)	1406(2)	878(2)	4766(1)	50(1)

Table S13. Bond lengths [Å] and angles [°] for RBabu2903.

Co(1)-P(1)	2.2703(7)
Co(1)-P(2)	2.2833(7)
Co(1)-P(3)	2.2866(7)
Co(1)-P(4)	2.2770(7)
P(1)-C(1)	1.831(2)
P(1)-C(7)	1.828(2)
P(1)-C(13)	1.833(2)
P(2)-C(3)	1.830(3)
P(2)-C(19)	1.829(3)
P(2)-C(25)	1.828(3)
P(3)-C(4)	1.833(2)
P(3)-C(31)	1.827(2)
P(3)-C(37)	1.831(2)
P(4)-C(6)	1.835(2)
P(4)-C(43)	1.833(2)
P(4)-C(49)	1.833(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(1)-C(2)	1.536(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(3)	1.537(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.530(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(5)-C(6)	1.522(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.394(3)

C(7)-C(12)	1.389(3)
C(8)-H(8)	0.9500
C(8)-C(9)	1.381(4)
C(9)-H(9)	0.9500
C(9)-C(10)	1.387(4)
C(10)-H(10)	0.9500
C(10)-C(11)	1.379(4)
C(11)-H(11)	0.9500
C(11)-C(12)	1.389(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.378(3)
C(13)-C(18)	1.389(3)
C(14)-H(14)	0.9500
C(14)-C(15)	1.389(4)
C(15)-H(15)	0.9500
C(15)-C(16)	1.370(4)
C(16)-H(16)	0.9500
C(16)-C(17)	1.375(4)
C(17)-H(17)	0.9500
C(17)-C(18)	1.378(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.394(4)
C(19)-C(24)	1.384(4)
C(20)-H(20)	0.9500
C(20)-C(21)	1.391(4)
C(21)-H(21)	0.9500
C(21)-C(22)	1.377(5)
C(22)-H(22)	0.9500
C(22)-C(23)	1.378(5)
C(23)-H(23)	0.9500
C(23)-C(24)	1.386(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.383(4)
C(25)-C(30)	1.383(4)
C(26)-H(26)	0.9500
C(26)-C(27)	1.380(4)

C(27)-H(27)	0.9500
C(27)-C(28)	1.370(4)
C(28)-H(28)	0.9500
C(28)-C(29)	1.358(4)
C(29)-H(29)	0.9500
C(29)-C(30)	1.387(4)
C(30)-H(30)	0.9500
C(31)-C(32)	1.394(4)
C(31)-C(36)	1.395(4)
C(32)-H(32)	0.9500
C(32)-C(33)	1.382(4)
C(33)-H(33)	0.9500
C(33)-C(34)	1.376(4)
C(34)-H(34)	0.9500
C(34)-C(35)	1.378(4)
C(35)-H(35)	0.9500
C(35)-C(36)	1.389(4)
C(36)-H(36)	0.9500
C(37)-C(38)	1.382(4)
C(37)-C(42)	1.395(4)
C(38)-H(38)	0.9500
C(38)-C(39)	1.386(4)
C(39)-H(39)	0.9500
C(39)-C(40)	1.381(5)
C(40)-H(40)	0.9500
C(40)-C(41)	1.369(5)
C(41)-H(41)	0.9500
C(41)-C(42)	1.376(4)
C(42)-H(42)	0.9500
C(43)-C(44)	1.381(4)
C(43)-C(48)	1.398(4)
C(44)-H(44)	0.9500
C(44)-C(45)	1.387(4)
C(45)-H(45)	0.9500
C(45)-C(46)	1.369(4)
C(46)-H(46)	0.9500

C(46)-C(47)	1.380(4)
C(47)-H(47)	0.9500
C(47)-C(48)	1.383(4)
C(48)-H(48)	0.9500
C(49)-C(50)	1.387(4)
C(49)-C(54)	1.384(4)
C(50)-H(50)	0.9500
C(50)-C(51)	1.382(4)
C(51)-H(51)	0.9500
C(51)-C(52)	1.385(5)
C(52)-H(52)	0.9500
C(52)-C(53)	1.361(5)
C(53)-H(53)	0.9500
C(53)-C(54)	1.393(4)
C(54)-H(54)	0.9500
Br(1)-Zn(1)	2.3660(5)
Br(2)-Zn(1)	2.3378(4)
Br(3)-Zn(1)	2.3642(4)
Zn(1)-O(1)	2.0785(19)
O(1)-C(55)	1.444(3)
O(1)-C(58)	1.456(4)
C(55)-H(55A)	0.9900
C(55)-H(55B)	0.9900
C(55)-C(56)	1.496(5)
C(56)-H(56A)	0.9900
C(56)-H(56B)	0.9900
C(56)-H(56C)	0.9900
C(56)-H(56D)	0.9900
C(56)-C(57)	1.504(6)
C(56)-C(57B)	1.69(3)
C(57)-H(57A)	0.9900
C(57)-H(57B)	0.9900
C(57)-C(58)	1.495(5)
C(57B)-H(57C)	0.9900
C(57B)-H(57D)	0.9900
C(57B)-C(58)	1.39(2)

C(58)-H(58A)	0.9900
C(58)-H(58B)	0.9900
C(58)-H(58C)	0.9900
C(58)-H(58D)	0.9900

P(1)-Co(1)-P(2)	93.87(2)
P(1)-Co(1)-P(3)	108.68(3)
P(1)-Co(1)-P(4)	99.56(2)
P(2)-Co(1)-P(3)	142.93(3)
P(4)-Co(1)-P(2)	109.35(3)
P(4)-Co(1)-P(3)	95.81(2)
C(1)-P(1)-Co(1)	112.78(8)
C(1)-P(1)-C(13)	101.70(11)
C(7)-P(1)-Co(1)	118.97(8)
C(7)-P(1)-C(1)	103.70(11)
C(7)-P(1)-C(13)	100.59(10)
C(13)-P(1)-Co(1)	116.78(8)
C(3)-P(2)-Co(1)	114.27(9)
C(19)-P(2)-Co(1)	110.93(9)
C(19)-P(2)-C(3)	105.50(12)
C(25)-P(2)-Co(1)	117.55(8)
C(25)-P(2)-C(3)	104.61(12)
C(25)-P(2)-C(19)	102.70(12)
C(4)-P(3)-Co(1)	116.00(8)
C(31)-P(3)-Co(1)	119.96(8)
C(31)-P(3)-C(4)	103.22(12)
C(31)-P(3)-C(37)	100.72(11)
C(37)-P(3)-Co(1)	111.53(8)
C(37)-P(3)-C(4)	103.12(11)
C(6)-P(4)-Co(1)	109.98(8)
C(43)-P(4)-Co(1)	121.08(8)
C(43)-P(4)-C(6)	101.51(11)
C(43)-P(4)-C(49)	100.03(11)
C(49)-P(4)-Co(1)	118.95(8)
C(49)-P(4)-C(6)	102.54(12)
P(1)-C(1)-H(1A)	108.9

P(1)-C(1)-H(1B)	108.9
H(1A)-C(1)-H(1B)	107.7
C(2)-C(1)-P(1)	113.31(17)
C(2)-C(1)-H(1A)	108.9
C(2)-C(1)-H(1B)	108.9
C(1)-C(2)-H(2A)	108.5
C(1)-C(2)-H(2B)	108.5
C(1)-C(2)-C(3)	115.2(2)
H(2A)-C(2)-H(2B)	107.5
C(3)-C(2)-H(2A)	108.5
C(3)-C(2)-H(2B)	108.5
P(2)-C(3)-H(3A)	108.5
P(2)-C(3)-H(3B)	108.5
C(2)-C(3)-P(2)	115.22(18)
C(2)-C(3)-H(3A)	108.5
C(2)-C(3)-H(3B)	108.5
H(3A)-C(3)-H(3B)	107.5
P(3)-C(4)-H(4A)	108.8
P(3)-C(4)-H(4B)	108.8
H(4A)-C(4)-H(4B)	107.7
C(5)-C(4)-P(3)	113.80(17)
C(5)-C(4)-H(4A)	108.8
C(5)-C(4)-H(4B)	108.8
C(4)-C(5)-H(5A)	108.7
C(4)-C(5)-H(5B)	108.7
H(5A)-C(5)-H(5B)	107.6
C(6)-C(5)-C(4)	114.4(2)
C(6)-C(5)-H(5A)	108.7
C(6)-C(5)-H(5B)	108.7
P(4)-C(6)-H(6A)	109.0
P(4)-C(6)-H(6B)	109.0
C(5)-C(6)-P(4)	112.84(17)
C(5)-C(6)-H(6A)	109.0
C(5)-C(6)-H(6B)	109.0
H(6A)-C(6)-H(6B)	107.8
C(8)-C(7)-P(1)	117.97(18)

C(12)-C(7)-P(1)	123.36(19)
C(12)-C(7)-C(8)	118.6(2)
C(7)-C(8)-H(8)	119.4
C(9)-C(8)-C(7)	121.1(2)
C(9)-C(8)-H(8)	119.4
C(8)-C(9)-H(9)	120.0
C(8)-C(9)-C(10)	120.0(3)
C(10)-C(9)-H(9)	120.0
C(9)-C(10)-H(10)	120.4
C(11)-C(10)-C(9)	119.3(2)
C(11)-C(10)-H(10)	120.4
C(10)-C(11)-H(11)	119.5
C(10)-C(11)-C(12)	121.0(2)
C(12)-C(11)-H(11)	119.5
C(7)-C(12)-H(12)	120.0
C(11)-C(12)-C(7)	120.0(2)
C(11)-C(12)-H(12)	120.0
C(14)-C(13)-P(1)	120.17(18)
C(14)-C(13)-C(18)	118.2(2)
C(18)-C(13)-P(1)	121.64(19)
C(13)-C(14)-H(14)	119.7
C(13)-C(14)-C(15)	120.7(2)
C(15)-C(14)-H(14)	119.7
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-C(14)	120.3(3)
C(16)-C(15)-H(15)	119.9
C(15)-C(16)-H(16)	120.1
C(15)-C(16)-C(17)	119.8(2)
C(17)-C(16)-H(16)	120.1
C(16)-C(17)-H(17)	120.1
C(16)-C(17)-C(18)	119.9(3)
C(18)-C(17)-H(17)	120.1
C(13)-C(18)-H(18)	119.4
C(17)-C(18)-C(13)	121.2(2)
C(17)-C(18)-H(18)	119.4
C(20)-C(19)-P(2)	123.7(2)

C(24)-C(19)-P(2)	117.3(2)
C(24)-C(19)-C(20)	119.0(3)
C(19)-C(20)-H(20)	120.2
C(21)-C(20)-C(19)	119.7(3)
C(21)-C(20)-H(20)	120.2
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-C(20)	120.3(3)
C(22)-C(21)-H(21)	119.8
C(21)-C(22)-H(22)	119.8
C(21)-C(22)-C(23)	120.5(3)
C(23)-C(22)-H(22)	119.8
C(22)-C(23)-H(23)	120.4
C(22)-C(23)-C(24)	119.3(3)
C(24)-C(23)-H(23)	120.4
C(19)-C(24)-C(23)	121.2(3)
C(19)-C(24)-H(24)	119.4
C(23)-C(24)-H(24)	119.4
C(26)-C(25)-P(2)	122.9(2)
C(30)-C(25)-P(2)	119.1(2)
C(30)-C(25)-C(26)	117.9(2)
C(25)-C(26)-H(26)	119.8
C(27)-C(26)-C(25)	120.5(3)
C(27)-C(26)-H(26)	119.8
C(26)-C(27)-H(27)	119.6
C(28)-C(27)-C(26)	120.8(3)
C(28)-C(27)-H(27)	119.6
C(27)-C(28)-H(28)	120.2
C(29)-C(28)-C(27)	119.6(3)
C(29)-C(28)-H(28)	120.2
C(28)-C(29)-H(29)	120.0
C(28)-C(29)-C(30)	120.0(3)
C(30)-C(29)-H(29)	120.0
C(25)-C(30)-C(29)	121.2(3)
C(25)-C(30)-H(30)	119.4
C(29)-C(30)-H(30)	119.4
C(32)-C(31)-P(3)	118.09(19)

C(32)-C(31)-C(36)	118.2(2)
C(36)-C(31)-P(3)	123.7(2)
C(31)-C(32)-H(32)	119.3
C(33)-C(32)-C(31)	121.4(3)
C(33)-C(32)-H(32)	119.3
C(32)-C(33)-H(33)	120.0
C(34)-C(33)-C(32)	119.9(3)
C(34)-C(33)-H(33)	120.0
C(33)-C(34)-H(34)	120.2
C(33)-C(34)-C(35)	119.6(3)
C(35)-C(34)-H(34)	120.2
C(34)-C(35)-H(35)	119.5
C(34)-C(35)-C(36)	120.9(3)
C(36)-C(35)-H(35)	119.5
C(31)-C(36)-H(36)	120.0
C(35)-C(36)-C(31)	119.9(3)
C(35)-C(36)-H(36)	120.0
C(38)-C(37)-P(3)	119.61(19)
C(38)-C(37)-C(42)	118.5(2)
C(42)-C(37)-P(3)	121.8(2)
C(37)-C(38)-H(38)	119.3
C(37)-C(38)-C(39)	121.4(3)
C(39)-C(38)-H(38)	119.3
C(38)-C(39)-H(39)	120.4
C(40)-C(39)-C(38)	119.1(3)
C(40)-C(39)-H(39)	120.4
C(39)-C(40)-H(40)	120.0
C(41)-C(40)-C(39)	120.1(3)
C(41)-C(40)-H(40)	120.0
C(40)-C(41)-H(41)	119.5
C(40)-C(41)-C(42)	121.0(3)
C(42)-C(41)-H(41)	119.5
C(37)-C(42)-H(42)	120.0
C(41)-C(42)-C(37)	120.0(3)
C(41)-C(42)-H(42)	120.0
C(44)-C(43)-P(4)	120.33(19)

C(44)-C(43)-C(48)	118.2(2)
C(48)-C(43)-P(4)	121.4(2)
C(43)-C(44)-H(44)	119.6
C(43)-C(44)-C(45)	120.9(3)
C(45)-C(44)-H(44)	119.6
C(44)-C(45)-H(45)	119.8
C(46)-C(45)-C(44)	120.4(3)
C(46)-C(45)-H(45)	119.8
C(45)-C(46)-H(46)	120.1
C(45)-C(46)-C(47)	119.8(3)
C(47)-C(46)-H(46)	120.1
C(46)-C(47)-H(47)	119.9
C(46)-C(47)-C(48)	120.1(3)
C(48)-C(47)-H(47)	119.9
C(43)-C(48)-H(48)	119.7
C(47)-C(48)-C(43)	120.6(3)
C(47)-C(48)-H(48)	119.7
C(50)-C(49)-P(4)	118.8(2)
C(54)-C(49)-P(4)	122.5(2)
C(54)-C(49)-C(50)	118.7(3)
C(49)-C(50)-H(50)	119.9
C(51)-C(50)-C(49)	120.3(3)
C(51)-C(50)-H(50)	119.9
C(50)-C(51)-H(51)	119.8
C(50)-C(51)-C(52)	120.3(3)
C(52)-C(51)-H(51)	119.8
C(51)-C(52)-H(52)	120.0
C(53)-C(52)-C(51)	120.1(3)
C(53)-C(52)-H(52)	120.0
C(52)-C(53)-H(53)	120.1
C(52)-C(53)-C(54)	119.8(3)
C(54)-C(53)-H(53)	120.1
C(49)-C(54)-C(53)	120.9(3)
C(49)-C(54)-H(54)	119.6
C(53)-C(54)-H(54)	119.6
Br(2)-Zn(1)-Br(1)	115.382(18)

Br(2)-Zn(1)-Br(3)	119.899(17)
Br(3)-Zn(1)-Br(1)	113.066(17)
O(1)-Zn(1)-Br(1)	98.60(5)
O(1)-Zn(1)-Br(2)	102.59(5)
O(1)-Zn(1)-Br(3)	103.12(5)
C(55)-O(1)-Zn(1)	116.40(17)
C(55)-O(1)-C(58)	108.2(2)
C(58)-O(1)-Zn(1)	118.98(17)
O(1)-C(55)-H(55A)	110.5
O(1)-C(55)-H(55B)	110.5
O(1)-C(55)-C(56)	106.3(3)
H(55A)-C(55)-H(55B)	108.7
C(56)-C(55)-H(55A)	110.5
C(56)-C(55)-H(55B)	110.5
C(55)-C(56)-H(56A)	110.7
C(55)-C(56)-H(56B)	110.7
C(55)-C(56)-H(56C)	111.6
C(55)-C(56)-H(56D)	111.6
C(55)-C(56)-C(57)	105.0(3)
C(55)-C(56)-C(57B)	101.1(8)
H(56A)-C(56)-H(56B)	108.8
H(56C)-C(56)-H(56D)	109.4
C(57)-C(56)-H(56A)	110.7
C(57)-C(56)-H(56B)	110.7
C(57B)-C(56)-H(56C)	111.6
C(57B)-C(56)-H(56D)	111.6
C(56)-C(57)-H(57A)	111.2
C(56)-C(57)-H(57B)	111.2
H(57A)-C(57)-H(57B)	109.1
C(58)-C(57)-C(56)	102.8(3)
C(58)-C(57)-H(57A)	111.2
C(58)-C(57)-H(57B)	111.2
C(56)-C(57B)-H(57C)	112.0
C(56)-C(57B)-H(57D)	112.0
H(57C)-C(57B)-H(57D)	109.7
C(58)-C(57B)-C(56)	98.7(15)

C(58)-C(57B)-H(57C)	112.0
C(58)-C(57B)-H(57D)	112.0
O(1)-C(58)-C(57)	103.0(3)
O(1)-C(58)-H(58A)	111.2
O(1)-C(58)-H(58B)	111.2
O(1)-C(58)-H(58C)	109.1
O(1)-C(58)-H(58D)	109.1
C(57)-C(58)-H(58A)	111.2
C(57)-C(58)-H(58B)	111.2
C(57B)-C(58)-O(1)	112.7(12)
C(57B)-C(58)-H(58C)	109.1
C(57B)-C(58)-H(58D)	109.1
H(58A)-C(58)-H(58B)	109.1
H(58C)-C(58)-H(58D)	107.8

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for RBabu2903. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	16(1)	17(1)	16(1)	1(1)	1(1)	0(1)
P(1)	20(1)	17(1)	18(1)	1(1)	2(1)	-1(1)
P(2)	19(1)	23(1)	21(1)	2(1)	-1(1)	-1(1)
P(3)	18(1)	19(1)	18(1)	1(1)	2(1)	3(1)
P(4)	21(1)	20(1)	17(1)	2(1)	4(1)	2(1)
C(1)	24(1)	18(1)	25(1)	3(1)	3(1)	0(1)
C(2)	22(1)	25(1)	32(1)	9(1)	-4(1)	1(1)
C(3)	19(1)	26(1)	33(1)	7(1)	-2(1)	2(1)
C(4)	19(1)	27(1)	21(1)	2(1)	0(1)	1(1)
C(5)	24(1)	28(1)	18(1)	2(1)	-1(1)	2(1)
C(6)	24(1)	23(1)	20(1)	-2(1)	3(1)	-1(1)
C(7)	23(1)	17(1)	17(1)	3(1)	4(1)	-1(1)
C(8)	23(1)	23(1)	24(1)	1(1)	4(1)	-1(1)
C(9)	24(1)	36(2)	31(1)	4(1)	-1(1)	-2(1)
C(10)	32(2)	33(2)	27(1)	-3(1)	0(1)	-10(1)
C(11)	40(2)	26(1)	26(1)	-6(1)	9(1)	-7(1)
C(12)	26(1)	25(1)	25(1)	0(1)	6(1)	-1(1)
C(13)	20(1)	22(1)	20(1)	0(1)	2(1)	-3(1)
C(14)	39(2)	23(1)	28(1)	1(1)	9(1)	-1(1)
C(15)	55(2)	35(2)	31(2)	-7(1)	19(1)	2(1)
C(16)	39(2)	43(2)	21(1)	-1(1)	11(1)	-4(1)
C(17)	44(2)	30(2)	30(1)	8(1)	12(1)	-5(1)
C(18)	44(2)	22(1)	26(1)	-1(1)	10(1)	-3(1)
C(19)	24(1)	32(2)	24(1)	-2(1)	0(1)	-10(1)
C(20)	32(2)	41(2)	29(1)	7(1)	-4(1)	-14(1)
C(21)	52(2)	59(2)	24(2)	4(1)	0(1)	-25(2)
C(22)	55(2)	70(2)	28(2)	-13(2)	16(2)	-27(2)
C(23)	43(2)	59(2)	42(2)	-15(2)	15(2)	-9(2)
C(24)	31(2)	43(2)	30(1)	-4(1)	4(1)	-4(1)

C(25)	22(1)	28(1)	27(1)	4(1)	-3(1)	-6(1)
C(26)	28(2)	30(2)	60(2)	8(1)	13(1)	0(1)
C(27)	25(2)	45(2)	78(2)	17(2)	14(2)	-2(1)
C(28)	35(2)	35(2)	54(2)	11(1)	3(1)	-13(1)
C(29)	46(2)	25(2)	42(2)	-1(1)	-2(1)	-9(1)
C(30)	35(2)	30(2)	29(1)	-3(1)	2(1)	-6(1)
C(31)	22(1)	21(1)	24(1)	5(1)	6(1)	7(1)
C(32)	30(2)	28(1)	28(1)	2(1)	7(1)	4(1)
C(33)	47(2)	34(2)	30(2)	-1(1)	16(1)	5(1)
C(34)	46(2)	34(2)	44(2)	5(1)	29(2)	9(1)
C(35)	26(2)	37(2)	62(2)	3(2)	20(1)	1(1)
C(36)	27(2)	29(2)	38(2)	-1(1)	9(1)	3(1)
C(37)	28(1)	20(1)	18(1)	2(1)	6(1)	2(1)
C(38)	35(2)	27(1)	33(2)	0(1)	10(1)	0(1)
C(39)	53(2)	35(2)	41(2)	-4(1)	19(2)	-16(2)
C(40)	80(3)	23(2)	31(2)	5(1)	18(2)	-2(2)
C(41)	60(2)	26(2)	29(2)	6(1)	6(1)	16(1)
C(42)	36(2)	26(1)	24(1)	3(1)	3(1)	6(1)
C(43)	21(1)	24(1)	24(1)	4(1)	6(1)	4(1)
C(44)	33(2)	32(2)	24(1)	1(1)	5(1)	-3(1)
C(45)	40(2)	34(2)	43(2)	4(1)	8(1)	-12(1)
C(46)	37(2)	40(2)	39(2)	17(1)	11(1)	-3(1)
C(47)	44(2)	50(2)	24(1)	8(1)	9(1)	-1(2)
C(48)	33(2)	35(2)	25(1)	1(1)	6(1)	-5(1)
C(49)	34(2)	26(1)	22(1)	8(1)	13(1)	8(1)
C(50)	34(2)	39(2)	49(2)	11(1)	13(1)	9(1)
C(51)	38(2)	58(2)	72(2)	24(2)	23(2)	23(2)
C(52)	66(2)	44(2)	60(2)	21(2)	32(2)	33(2)
C(53)	74(3)	26(2)	39(2)	9(1)	25(2)	18(2)
C(54)	43(2)	30(2)	24(1)	7(1)	11(1)	12(1)
Br(1)	37(1)	29(1)	64(1)	1(1)	0(1)	0(1)
Br(2)	34(1)	84(1)	42(1)	26(1)	-5(1)	-22(1)
Br(3)	30(1)	47(1)	45(1)	-3(1)	-11(1)	2(1)
Zn(1)	22(1)	33(1)	29(1)	-1(1)	0(1)	-1(1)

O(1)	32(1)	31(1)	36(1)	-5(1)	5(1)	-2(1)
C(55)	36(2)	45(2)	73(2)	-12(2)	27(2)	-4(2)
C(56)	87(3)	44(2)	74(3)	4(2)	51(2)	10(2)
C(57)	83(3)	51(3)	40(2)	-11(2)	15(2)	8(2)
C(57B)	83(3)	51(3)	40(2)	-11(2)	15(2)	8(2)
C(58)	52(2)	60(2)	34(2)	-14(2)	-3(2)	5(2)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for RBabu2903.

	x	y	z	U(eq)
H(1A)	2165	8943	6004	27
H(1B)	2611	9434	5551	27
H(2A)	1921	8450	4865	33
H(2B)	1169	9025	5076	33
H(3A)	497	7803	5062	32
H(3B)	843	8001	5706	32
H(4A)	5818	6330	7104	27
H(4B)	5608	7226	6931	27
H(5A)	4332	6322	7470	29
H(5B)	5156	6860	7811	29
H(6A)	4350	7955	7232	27
H(6B)	3894	7659	7752	27
H(8)	5499	8165	6123	28
H(9)	6675	8827	6733	37
H(10)	6262	9915	7230	38
H(11)	4684	10361	7073	36
H(12)	3509	9726	6438	30
H(14)	4034	7205	4971	35
H(15)	4607	7316	4134	47
H(16)	4828	8543	3764	40
H(17)	4484	9668	4234	41
H(18)	3948	9561	5078	36
H(20)	978	7424	4276	42
H(21)	1331	7038	3412	55
H(22)	2463	6066	3363	60
H(23)	3239	5452	4171	57
H(24)	2921	5855	5034	42
H(26)	-115	6964	5819	46
H(27)	-1104	5993	6076	59
H(28)	-694	4680	6037	50

H(29)	661	4328	5687	47
H(30)	1645	5291	5409	38
H(32)	4621	5737	5258	34
H(33)	5662	5698	4620	43
H(34)	7157	6304	4828	47
H(35)	7609	6933	5679	49
H(36)	6582	6964	6330	37
H(38)	2960	5400	6254	37
H(39)	2681	4065	6365	50
H(40)	3982	3213	6597	52
H(41)	5531	3695	6724	46
H(42)	5816	5026	6634	35
H(44)	1718	5928	6648	35
H(45)	1004	5000	7145	47
H(46)	1193	5077	8108	46
H(47)	2126	6074	8582	47
H(48)	2837	7009	8089	37
H(50)	885	7602	6763	48
H(51)	-82	8688	6841	65
H(52)	606	9888	7150	65
H(53)	2254	10003	7385	54
H(54)	3232	8915	7311	38
H(55A)	3494	902	5404	59
H(55B)	3082	1778	5290	59
H(56A)	3528	827	4506	77
H(56B)	2910	1621	4381	77
H(56C)	3177	580	4492	77
H(56D)	3334	1511	4423	77
H(57A)	1783	751	3987	69
H(57B)	2201	59	4413	69
H(57C)	1581	1777	4276	69
H(57D)	1563	930	3974	69
H(58A)	1087	1382	4646	60
H(58B)	911	474	4788	60
H(58C)	1290	313	4687	60
H(58D)	783	1124	4794	60