Methane Conversion to Ethylene Using an Ir Complex and Phosphorus Ylide as a Methylene Transfer Reagent

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General Procedures

All operations were performed in an M. Braun glove box or using standard Schlenk techniques under a nitrogen atmosphere unless otherwise stated. Anhydrous hydrocarbon solvents were purchased from Fisher Scientific. All anhydrous hydrocarbon solvents (pentane, hexanes, toluene, benzene) and were purified and dried by passage through two columns of activated alumina and Q-5 drying agent in a Grubbs-type solvent system. Dichloromethane was purified and dried by passage through two columns of activated alumina. Stabilizer-free ethereal solvents (Et_2O and THF) were purchased from Alfa Aesar and dried by passage through two columns of activated alumina. All bulk solvents were kept over sodium and 4 Å molecular sieves. THF-d_8 and benzene-d_6 (Cambridge Isotope Laboratories) were dried and degassed over a potassium mirror prior to use. Celite and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. Cp*(Me_3P)Ir(CH_3)$_2$ [1], Cp*(Me_3P)Ir(CD_3)$_2$ [1]and Cp*(Me_3P)Ir(OTf)$_2$[2] were synthesized according to literature procedures. [$H_3{}^{13}CPPh_3$][I] was prepared from $^{13}CH_3I$ (Sigma-Aldrich, 99 atom % ^{13}C) and PPh_3 in THF. All other chemicals were purchased from commercial sources and degassed before being used. ^1H, ^2H, ^{13}C, ^{31}P, ^{19}F, HSQC and COSY NMR spectra were recorded on Bruker AV-II 500 MHz, DRX 500 MHz or AV-III 400 MHz spectrometers. ^1H, ^2H and ^{13}C NMR chemical shifts are reported referenced to the internal residual proton, deuterium or carbon resonances of THF-d_8 (δ = 3.58 ppm or 67.21 ppm) or benzene-d_6 (δ = 7.15 ppm). ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (δ 0.0 ppm). ^{19}F NMR chemical shifts are reported with respect to external CF_3CO_2H (δ –78.5 ppm). Elemental analyses were performed by Midwest Microlab, Inc (Indianapolis, Indiana, USA)

Syntheses

Cp*(Me_3P)Ir(CH_3)(OTf): Cp*(Me_3P)Ir(CH_3)$_2$ (118 mg, 272 µmol) and Cp*(Me_3P)Ir(OTf)$_2$ (191 mg, 272 µmol) were placed into a vial with a stir bar. While stirring vigorously, dichloromethane (10 mL) was added yielding an amber-coloured solution. This solution was stirred for 4 hours at room temperature. Subsequently, the solution was concentrated by vacuum to a fifth of its original volume and layered carefully with diethyl ether and placed into a freezer at –35°C overnight which precipitates a dark brown solid, which is filtered away. The filtrate is concentrated to saturation and then layered with hexanes and placed into a freezer at –35°C overnight, yielding orange crystals. The crystals are washed with cold ether and dried under vacuum, providing the product (190 mg, 335 µmol, 61.5 %). The NMR spectra of this product are concurrent with those found in reference [3].

Cp*(Me_3P)Ir(CD_3)(OTf): Produced as above using Cp*(Me_3P)Ir(CD_3)$_2$ (89 mg, 202 µmol) as a starting material with Cp*(Me_3P)Ir(OTf)$_2$ (142 mg, 202 µmol). Yield: 214 mg, 93.4%.

Cp*(Me_3P)Ir(C_6H_5)(OTf): Cp*(Me_3P)Ir(CH_3)(OTf) (100 mg, 146 µmol) was dissolved and stirred in 5 mL of benzene for 16 hours at room temperature. The solvent was removed by vacuum and the residues were redissolved in the minimum amount of 50:50 dichloromethane/benzene solution required to completely dissolve the orange solids. This solution was then filtered through glass fiber and layered with an equal volume of hexanes and cooled at –35°C overnight. Removing the supernatant and washing with 3 mL of cold hexanes yields an orange crystalline product (85 mg, 135 µmol, 76.6 %). The NMR spectra of this product are concurrent with those found in reference [3].

H_2CPPh_3: Methyltriphenylphosphonium bromide (1 g, 2.80 mmol) was suspended in THF (60 mL) with a stir bar. While stirring vigorously, a THF solution of sodium hexamethyldisilazide (0.51 g, 2.80 mmol, in 20 mL of THF) was added dropwise at room temperature and allowed to stir for 4 hours. The solvent was evacuated, and the yellow product was extracted into toluene (80 mL) and filtered through Celite, which was washed with additional toluene (20 mL) until all yellow residue was washed into the filtrate.

The filtrate was then concentrated to saturation, layered with an equal volume of hexanes, and placed into a –35°C freezer. After overnight at –35°C, yellow crystals were obtained, which where washed with 5 mL of cold hexanes and then dried under vacuum, providing the product (0.67 g, 2.42 mmol, 87%).

$H_2{}^{13}CPPh_3$: Prepared as above. ^{13}C-Methyltriphenylphosphonium bromide (1.69 g, 4.17 mmol) and sodium hexamethyldisilazide (0.765 g, 4.17 mmol) were used to produce 0.257 g (0.93 mmol, 22.2%) of crystalline $H_2{}^{13}CPPh_3$.

$PhHCPMe_3$: Benzyltrimethylphosphonium bromide (0.482 g, 1.95 mmol) was suspended in THF (15 mL) in a Schlenk bomb and a 15 mL solution of 0.36 g (1.95 mmol) of sodium hexamethyldisilazide in THF were added. The mixture was then stirred at 70°C for 16 hours then cooled to room temperature. The solution was filtered through Celite, which was washed with toluene (20 mL) then evacuated leaving a yellow film. This was then dissolved in a 15 mL solution of 1:2 hexanes:toluene and filtered through glass fibre to remove any remaining solids and the solvent was evacuated leaving a yellow oil which was placed in a freezer at -35°C overnight. The pale-yellow solid was then placed under vacuum for 3 hours yielding the product as a pale-yellow dense foam that remained solid at room temperature (0.302 g, 1.82 mmol, 93.2 %). ^{1}H NMR (400 MHz, benzene-d_6, 300 K): δ 7.24 (apparent t, $^3J_{HH}$ = 7.6 Hz; 2H, *m*-Ph), 6.82 (d, $^3J_{HH}$ = 7.7 Hz; 2H, *o*-Ph), 6.72 (t, $^3J_{HH}$ = 7.2 Hz; 1H, *p*-Ph), 2.16 (d, $^2J_{HP}$ = 20.8 Hz; 1H, Ph*H*CPMe$_3$), 0.82 (d, $^2J_{HP}$ = 12.5 Hz; 9H, PhHCP*Me*$_3$); ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K): δ -12.92.

Synthesis of [Cp*(Me$_3$P)Ir(H)(η^2-CH$_2$CH$_2$)][B(C$_6$F$_5$)$_4$] (2-B(C$_6$F$_6$)$_4$): Cp*(Me$_3$P)Ir(CH$_3$)$_2$ (90 mg, 207 µmol) was dissolved in 10 mL of dichloromethane and placed in a freezer to cool to -35°C. Once cooled, the solution was stirred vigorously and solid [CPh$_3$][B(C$_6$F$_5$)$_4$] (191 mg, 207 µmol) was added in one portion at which point the solution changed colour from colourless to beige. This mixture was allowed to warm to room temperature and stir for 1 hour, and was subsequently evacuated to remove the solvent leaving a glossy residue. This was redissolved in benzene (2 mL) and a beige solid could be precipitated and suspended by addition of 5 mL of pentane. This suspension was then filtered through a frit, collecting the beige solid, which was washed with 50 mL of pentane and dried under vacuum. Yield: 180 mg (162 µmol, 77.9 %). ^{1}H NMR (400 MHz, THF-d_8, 300 K): δ 2.78 (br, [Ir]-C*H$_2$*CH$_2$), 2.17 (br, [Ir]-CH$_2$C*H$_2$*), 2.03 (d, $^4J_{HP}$ = 0.7 Hz; 15H, Cp*), 1.56 (d, $^2J_{HP}$ = 11.1 Hz; 9H, P*Me$_3$*), -16.49 (d, $^2J_{HP}$ = 31.9 Hz; 1H, [Ir]-*H*); ^{11}B NMR (128 MHz, THF-d_8, 300 K): δ -17.09; ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, 300 K): δ 148.98 (dm, $^1J_{CF}$ = 247.8 Hz; *o*-B(C$_6$*F$_5$*)$_4$), 138.94 (dm, $^1J_{CF}$ = 244.7 Hz; *p*-B(C$_6$*F$_5$*)$_4$), 136.92 (dm, $^1J_{CF}$ = 242.0 Hz; *m*-B(C$_6$*F$_5$*)$_4$), 124.9 (br, *i*-B(C$_6$*F$_5$*)$_4$), 100.54 (d, $^2J_{CP}$ = 2.2 Hz; *C*$_5$(CH$_3$)$_5$), 33.52 (br, [Ir]-*C*H$_2$CH$_2$), 29.95 (br, [Ir]-CH$_2$*C*H$_2$), 15.79 (d, $^2J_{CP}$ = 43.0 Hz; P*Me*$_3$), 8.96 (s, C$_5$(*C*H$_3$)$_5$); ^{19}F NMR (376 MHz, THF-d_8, 300 K): δ -132.70 (apparent singlet, 8F, *o*-B(C$_6$*F$_5$*)$_4$), 166.03 (t, $^3J_{FF}$ = 19.8 Hz; 4H, *p*-B(C$_6$*F$_5$*)$_4$), 168.50 (t, $^3J_{FF}$ = 19.8 Hz, 8H, *m*-B(C$_6$*F$_5$*)$_4$); ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, 300 K): δ -35.50 (s, $^2J_{PP}$ = 18.3 Hz)[this peak in **2** appears as a doublet of varying coupling values if the ^{1}H decoupling range (only 20 ppm at 400 MHz on this instrument) is not set properly over the hydride].

Synthesis of [Cp*(Me$_3$P)(Ph$_3$P)Ir(CH$_2$CH$_3$)][B(C$_6$F$_5$)$_4$] (1-B(C$_6$F$_6$)$_4$) from 2-B(C$_6$F$_6$)$_4$: A 166 mg (149 µmol) sample of the obtained **2-**B(C$_6$F$_6$)$_4$ and 39 mg (149 µmol) of triphenyl phosphine were dissolved in 3 mL of THF. This solution was allowed to stir for 4 days at 50°C whereupon a colour change from beige to pale yellow occurred. The solvent was removed under vacuum yielding a yellow oil, which was redissolved in 5 mL of toluene, filtered through glass fibre and then evacuated to remove the solvent once more forming an oil. This oil was suspended in pentane (10 mL) forming an emulsion and evacuated to dryness leaving a foamy yellow solid. This was crushed into a powder, washed with 30 mL of pentane over a frit and dried under vacuum for 8 hours. While the solid was >90% pure (by NMR) with respect to contents of other iridium containing by-products, about half an equivalent of pentane seemed to be trapped with the solid despite attempts to remove it under vacuum and thus should constitute about 2.5% of the mass of the material. The mass of solid obtained was 98 mg (47% yield with pentane considered). ^{1}H NMR (400 MHz, THF-d_8, 300 K): δ 7.58-7.46 (m, 9H, *o*- and *p*-P*Ph*$_3$), 7.40 (t, $^{3}J_{HH}$ = 9.1 Hz; 6H, *m*-P*Ph*$_3$) 2.07 (m, 1H, [Ir]-C*H$_2$*CH$_3$), 1.70 (m, 1H, [Ir]-C*H$_2$*CH$_3$), 1.57 (s, 15H, Cp*), 1.28 (d, $^{2}J_{HP}$ = 10.0 Hz; 9H, PMe$_3$), 1.21 (t, $^{3}J_{HH}$ = 7.5 Hz; 3H, [Ir]-CH$_2$C*H$_3$*); ^{11}B NMR (128 MHz, THF-d_8, 300 K): δ -17.07; ^{13}C{^{1}H} NMR (126 MHz, THF-d_8, 300 K): δ 148.99 (dm, $^{1}J_{CF}$ = 241.8 Hz; *o*-B(C$_6$*F$_5$*)$_4$), 138.95 (dm, $^{1}J_{CF}$ = 245.2 Hz; *p*-B(C$_6$*F$_5$*)$_4$), 136.96 (dm, $^{1}J_{CF}$ = 245.3 Hz; *m*-B(C$_6$*F$_5$*)$_4$), 135.49 (br, *o*-P*Ph*$_3$), 131.96 (s, *p*-P*Ph*$_3$), 129.26 (d, $^{3}J_{CP}$ = 10.2 Hz; *m*-P*Ph*$_3$), 125.05 (br, *i*-B(C$_6$*F$_5$*)$_4$), 100.30 (virtual t, $^{2}J_{CP}$ = 2.4 Hz; *C*$_5$(CH$_3$)$_5$), 18.99 (virtual t, $^{2}J_{CP}$ = 4.6 Hz; [Ir]-CH$_2$*C*H$_3$), 16.38 (d, $^{2}J_{CP}$ = 38.7 Hz; P*Me*$_3$), 9.28 (s, C$_5$(*C*H$_3$)$_5$), -11.12 (virtual t, $^{2}J_{HP}$ = 8.0 Hz; [Ir]-*C*H$_2$CH$_3$); ^{19}F NMR (376 MHz, THF-d_8, 300 K): δ -132.64 (apparent singlet, 8F, *o*-B(C$_6$*F$_5$*)$_4$), 164.93 (t, $^{3}J_{FF}$ = 19.8 Hz; 4H, *p*-B(C$_6$*F$_5$*)$_4$), 168.39 (t, $^{3}J_{FF}$ = 19.8 Hz, 8H, *m*-B(C$_6$*F$_5$*)$_4$); ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, 300 K): δ -4.10 (d, $^{2}J_{PP}$ = 18.3 Hz; *P*Ph$_3$), -54.20 (d, $^{2}J_{PP}$ = 18.3 Hz; *P*Me$_3$).

Crystallization of [Cp*(Me$_3$P)(Ph$_3$P)Ir(CH$_2$CH$_3$)][OTf] (1-OTf) sample for single crystal X-ray diffractometry: Contents from the reaction in dichloromethane were filtered through glass fibre into a small vial. This vial was placed into a larger vial, and into the larger vial, outside the inner vial, pentane was added until it reached the same level as the solution in the inner vial. The large vial was capped and then set aside at room temperature overnight. After this period, dichloromethane had evaporated from the inner vial to the out vial, leaving small, pale yellow crystals of **1**-OTf.

Crystallization of [Cp*(Me$_3$P)(Ph$_3$P)Ir(CH$_2$C$_6$H$_5$)][OTf] (3-OTf) sample for single crystal X-ray diffractometry: Contents from the reaction in dichloromethane were evacuated to remove the solvent and dissolved in as little THF as was necessary to dissolve the solids completely. The THF solution was then filtered through glass fibre into a small vial. This vial was placed into a larger vial, and into the inter-vial space toluene was added up to the level of the solution of the inner vial. The larger vial was capped and set aside at room temperature. Following diffusion of some THF to the outer solution the formation of colourless crystals was observed, the yellow supernatant was then collected and filtered through glass fibre into a new small vial placed into a larger vial containing toluene. Pale yellow crystals of **3**-OTf we obtained therein.

Upscaled Synthesis of Analytically Pure 1-OTf: Cp*(Me$_3$P)Ir(CH$_3$)(OTf) (56 mg, 98.6 µmol) and H$_2$CPPh$_3$ (27 mg, 98.6 µmol) were dissolved in 3 mL of THF and transferred to a Schlenk bomb and heated with stirring for 4 days at 50°C. The solvent was then removed by vacuum and the solid washed with 10 mL of toluene and 10 mL of pentane and dried under vacuum for 3 hours giving a pale off-white solid (71 mg, 84.1 µmol, 85.5 %) Anal. Calcd. for C$_{34}$H$_{44}$F$_3$IrO$_3$P$_2$S: C, 48.39, H, 5.26. Found: C, 47.79, H, 5.17.

Upscaled Synthesis of Analytically Pure 1-OTf: Cp*(Me$_3$)Ir(C$_6$H$_5$)(OTf) (84 mg, 133 µmol) and H$_2$CPPh$_3$ (36.9 mg, 133 µmol) were dissolved in 3 mL of THF and transferred to a Schlenk bomb and stirred at 50°C for 15 hours, then cooled to room temperature. The solvent was removed under vacuum and the solid was suspended in toluene and collected on a glass frit and washed with 10 mL of toluene and 15 mL of hexanes and then dried for 3 hours under vacuum yielding an off-white powder (98.6 mg, 109 µmol, 81.5 %) Anal. Calcd. for C$_{39}$H$_{46}$F$_3$IrO$_3$P$_2$S: C, 51.70, H, 5.12. Found: C, 51.53, H, 4.92.

NMR Spectral Data for 2-B(C_6F_6)$_4$

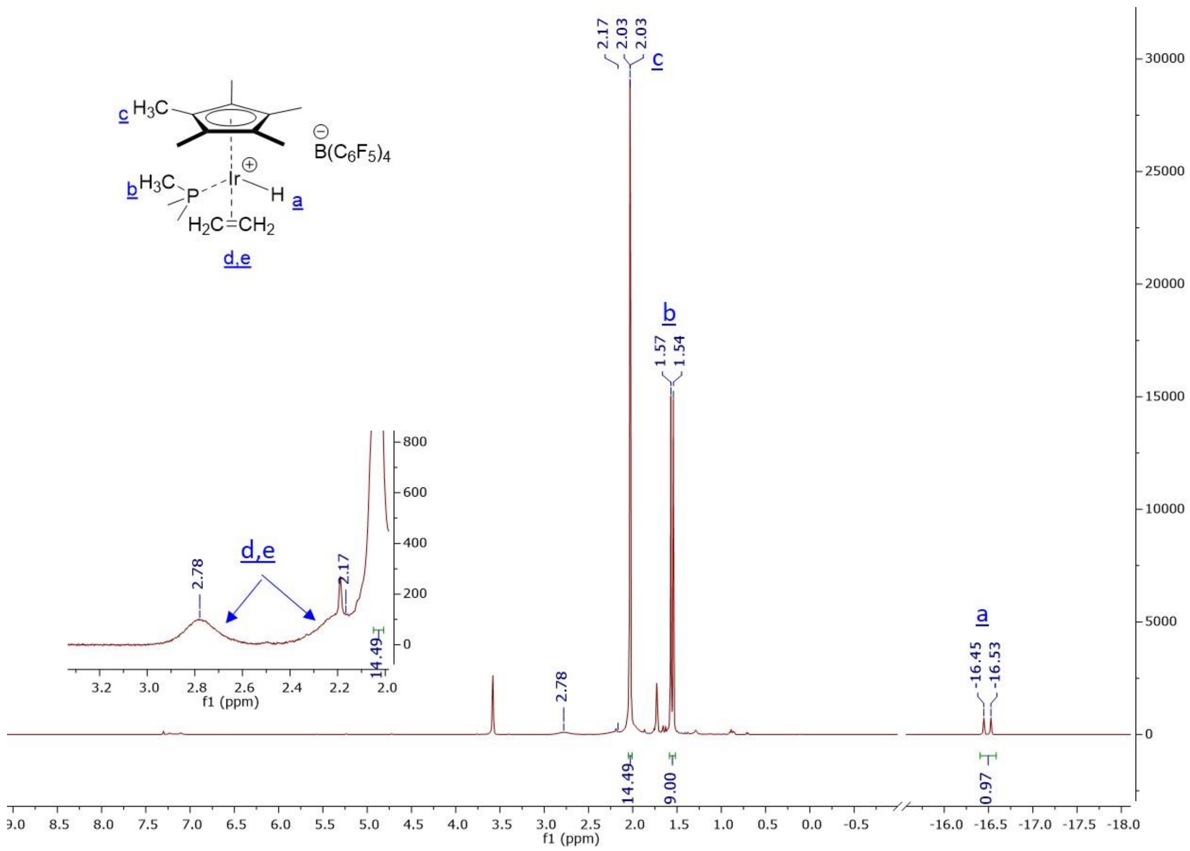


Figure S1. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of **2**-B(C_6F_6)$_4$.

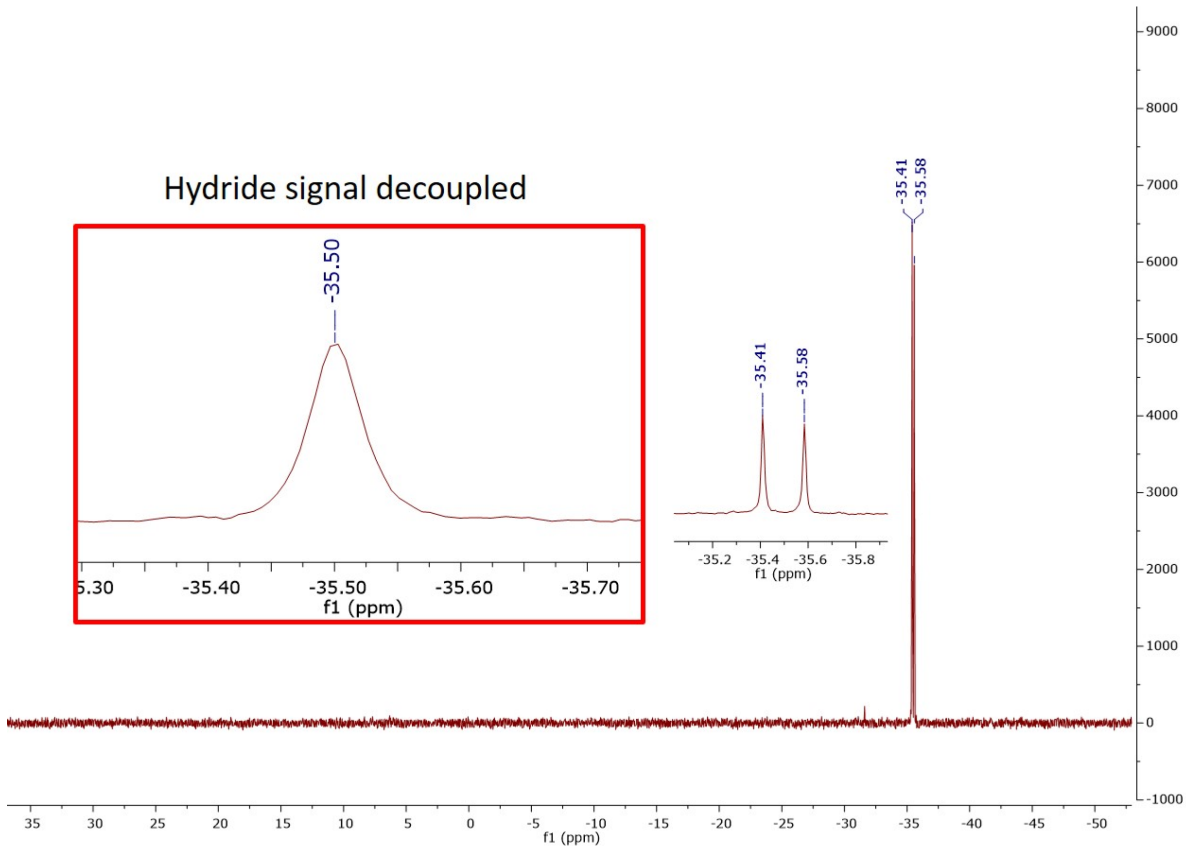


Figure S2. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of **2**-$B(C_6F_6)_4$ with irradiation of frequencies corresponding to 16 to -4 ppm of a ^1H spectrum at 400 MHz. The expansion bordered in red was taken with the range set to 1 to -19 ppm.

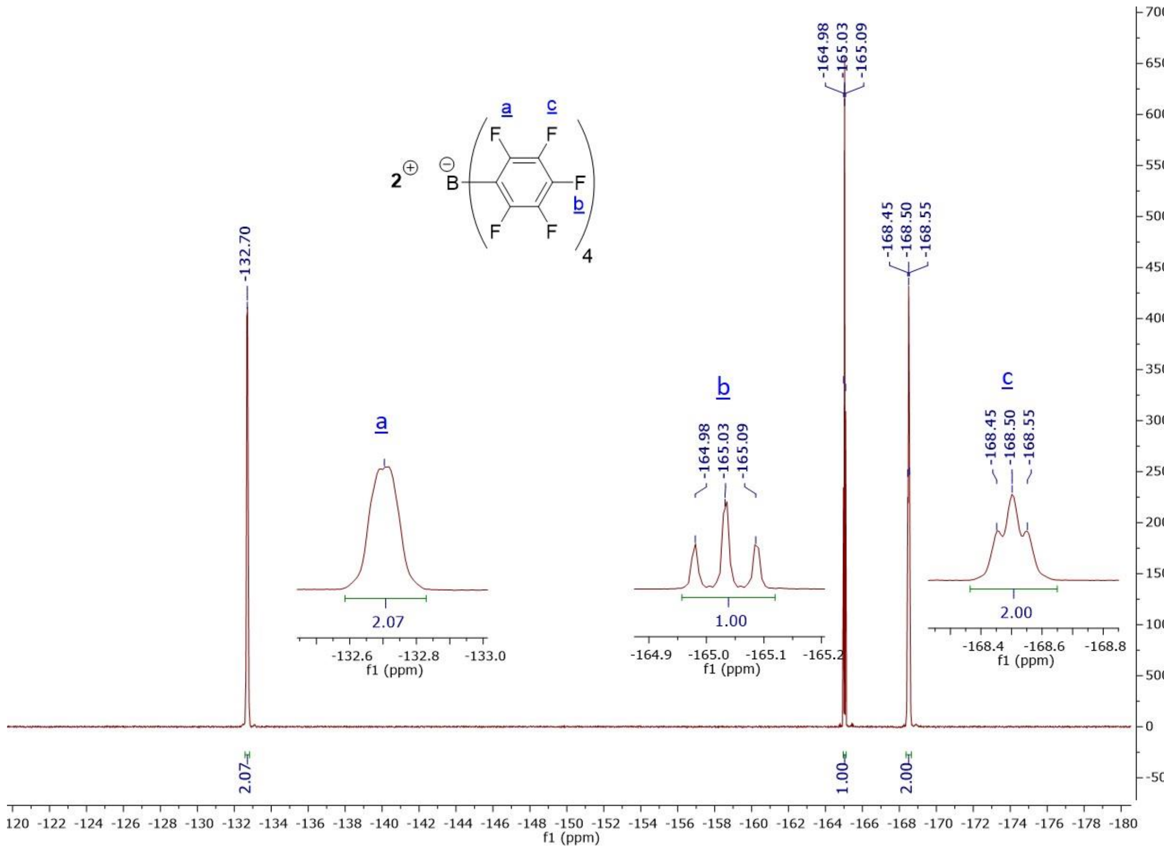


Figure S3. $^{19}F\{^1H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of **2**-$B(C_6F_6)_4$.

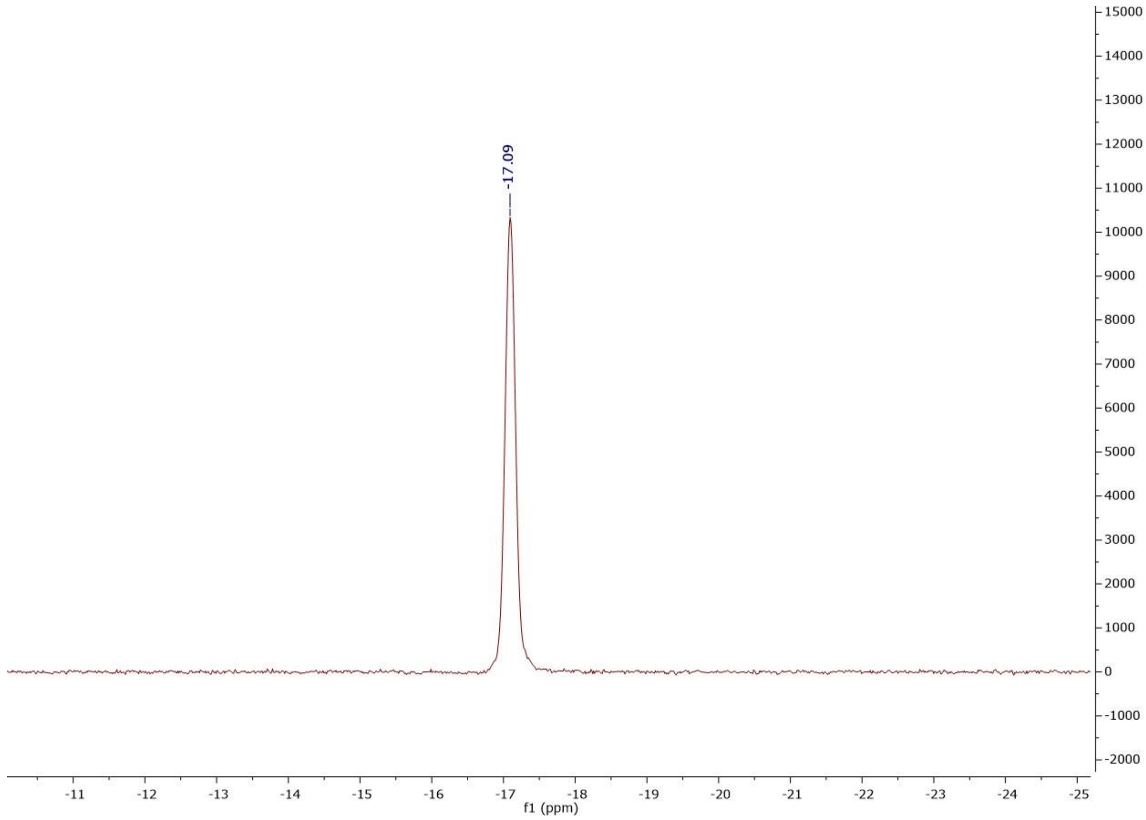


Figure S4. $^{11}B\{^1H\}$ NMR spectrum (128 MHz, THF-d_8, 300 K) of **2**-$B(C_6F_6)_4$.

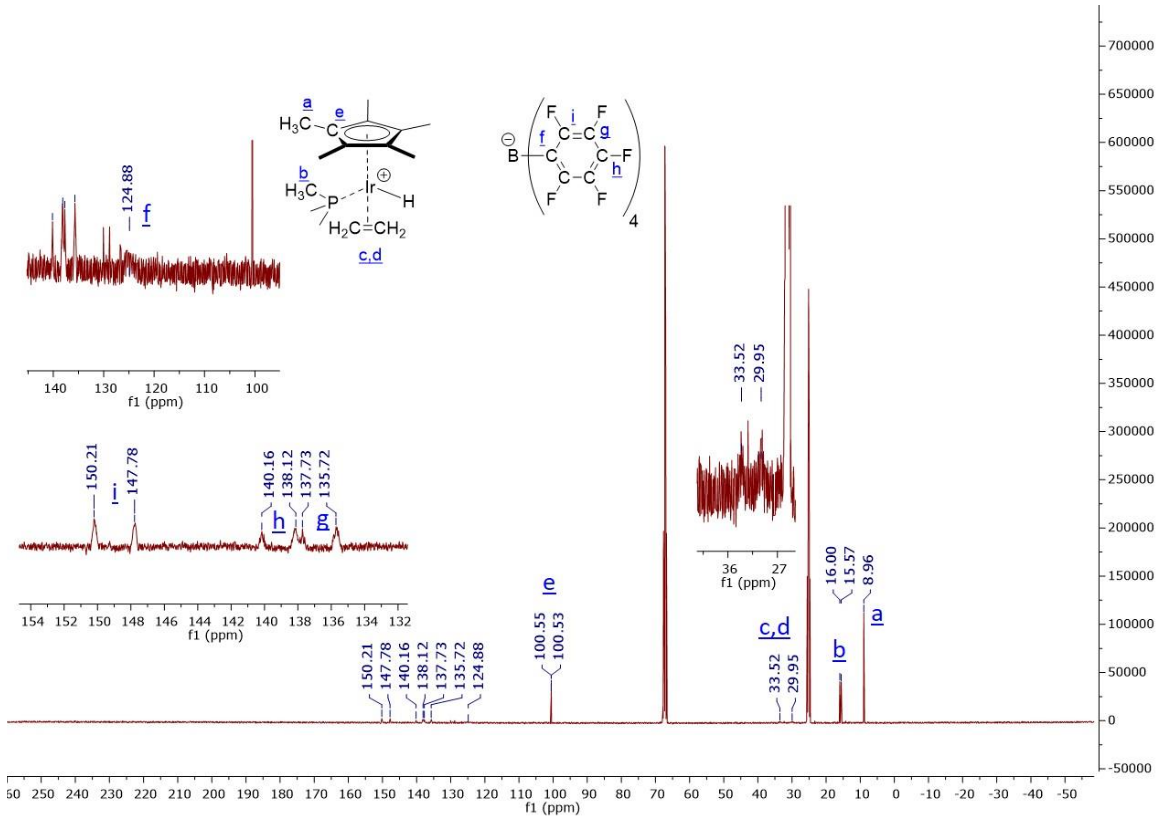


Figure S5. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, THF-d_8, 300 K) of **2**-$B(C_6F_6)_4$.

NMR Spectra of 1-B(C_6F_6)$_4$

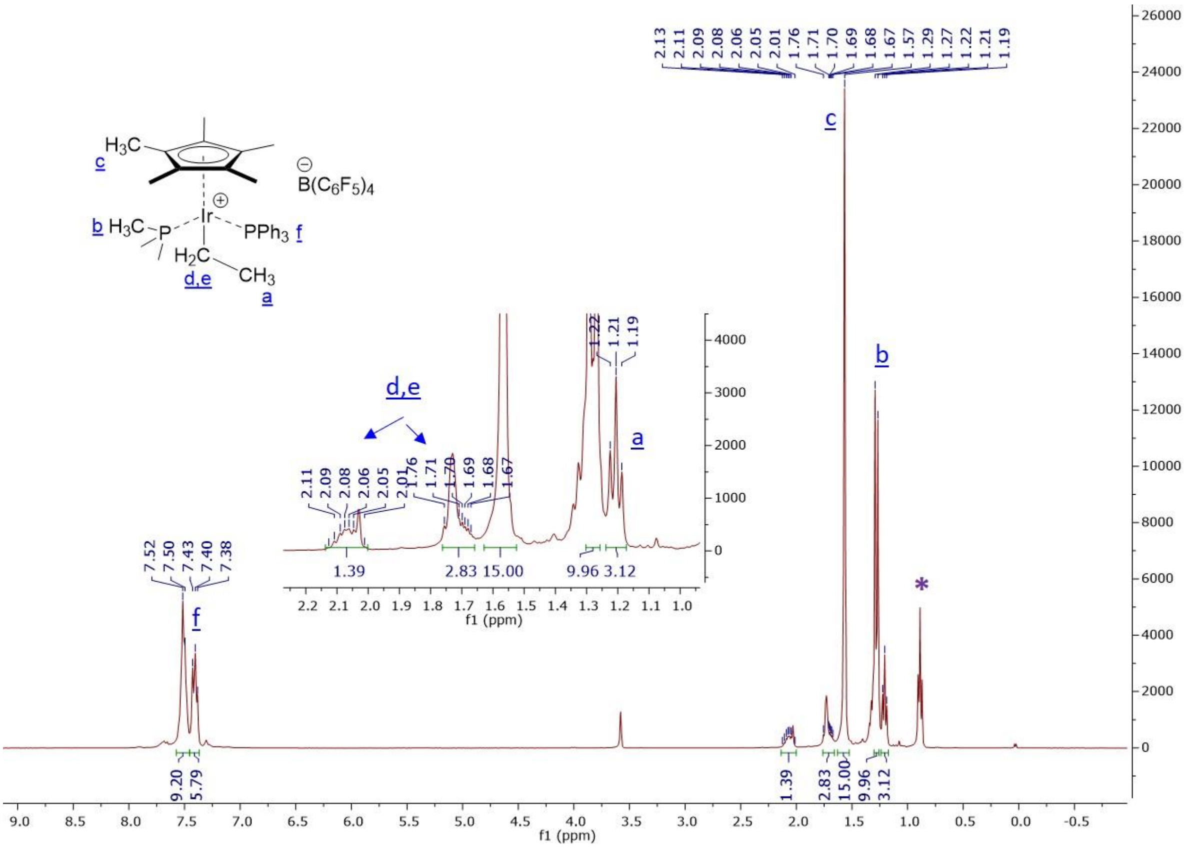


Figure S6. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of **1**-B(C_6F_6)$_4$. Resonances labeled with "*" represent residual pentane.

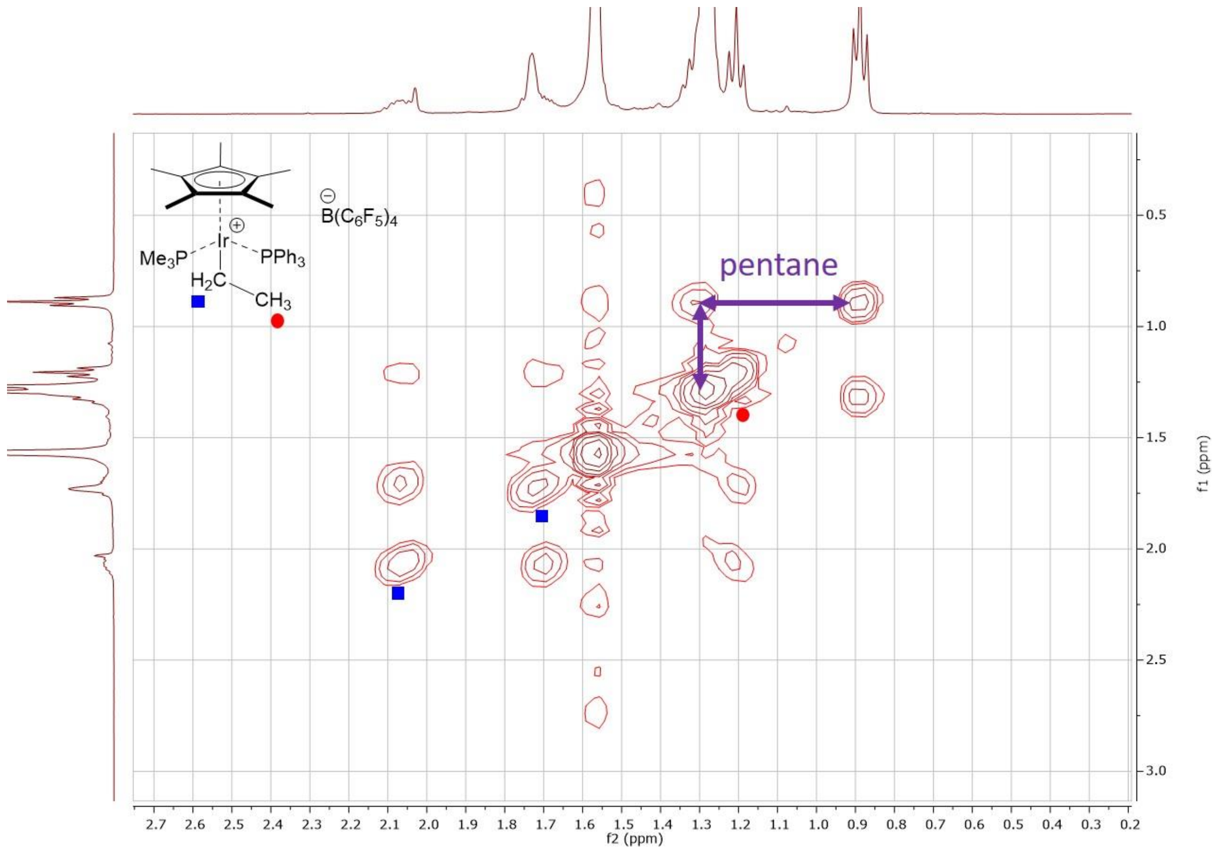


Figure S7. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, THF-d_8, 300 K) in aliphatic signal region of the sample of **1-**B(C_6F_5).

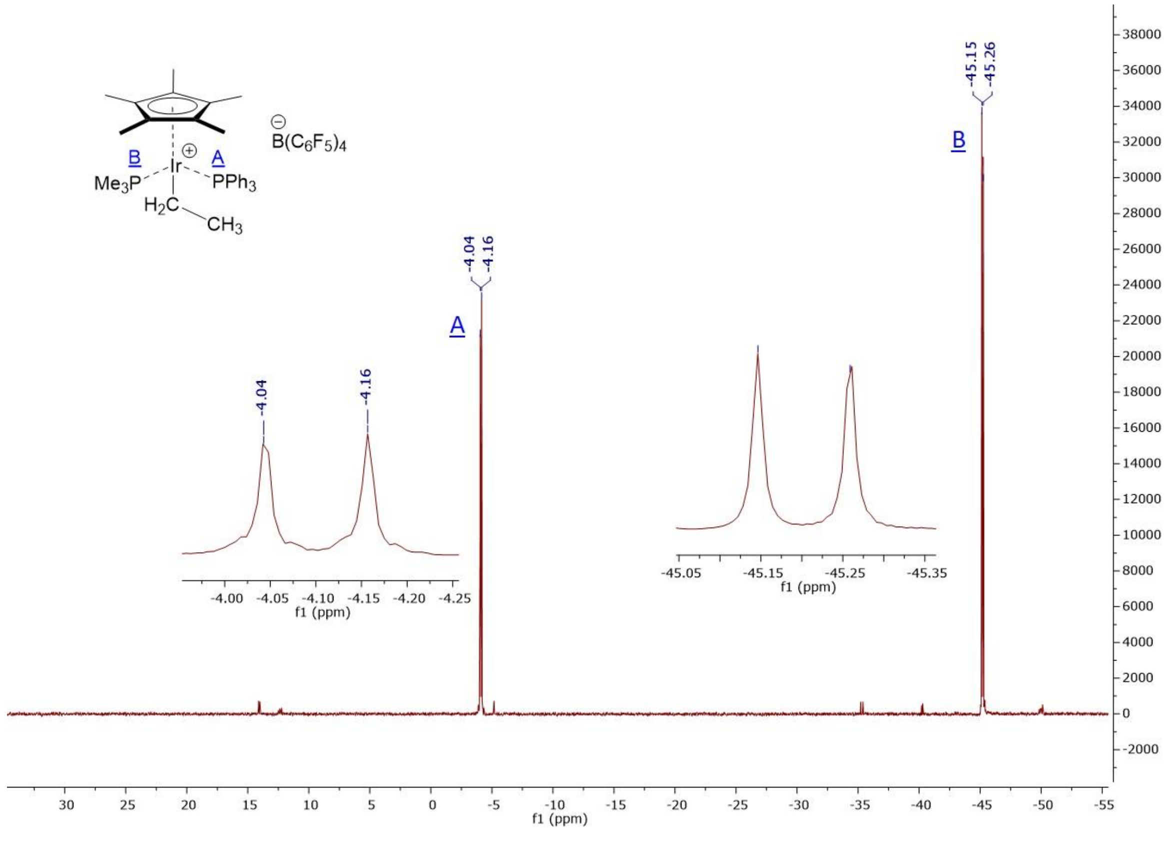


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of **1-**B(C_6F_5)**.**

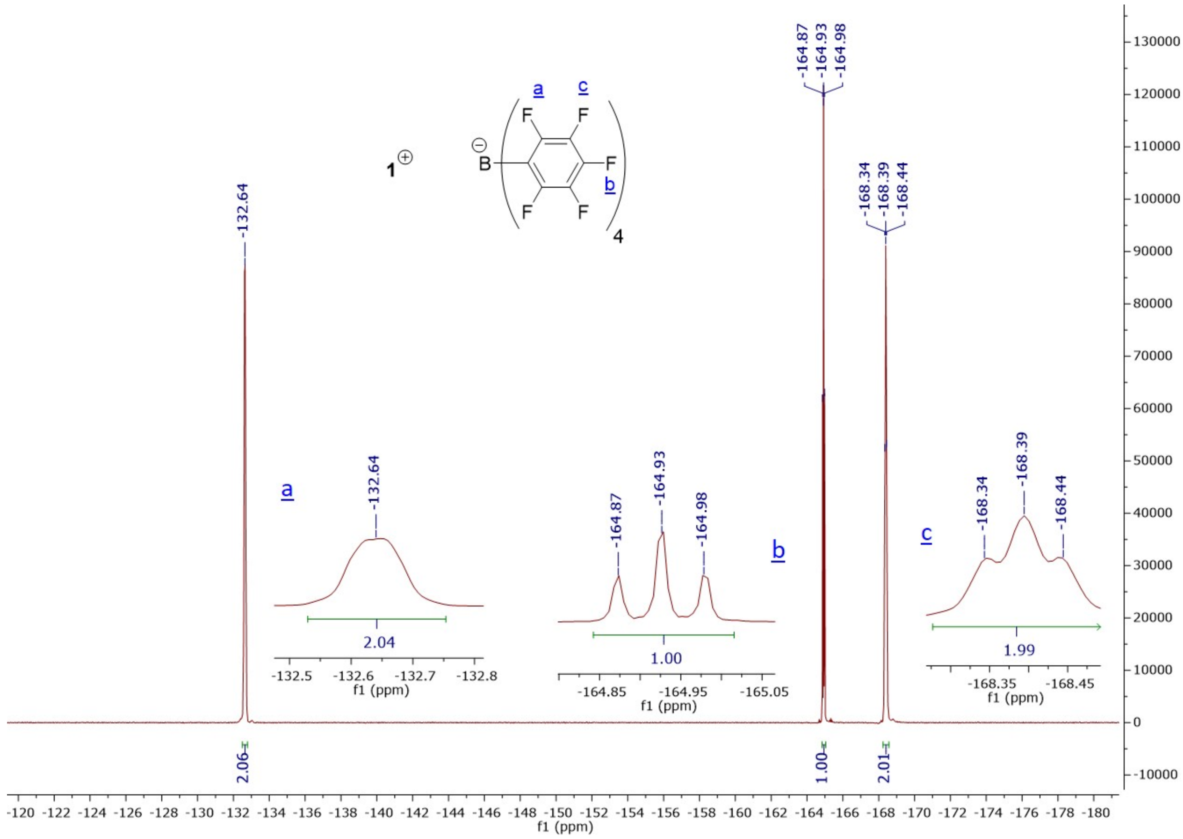


Figure S9. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of **1**-$B(C_6F_5)$.

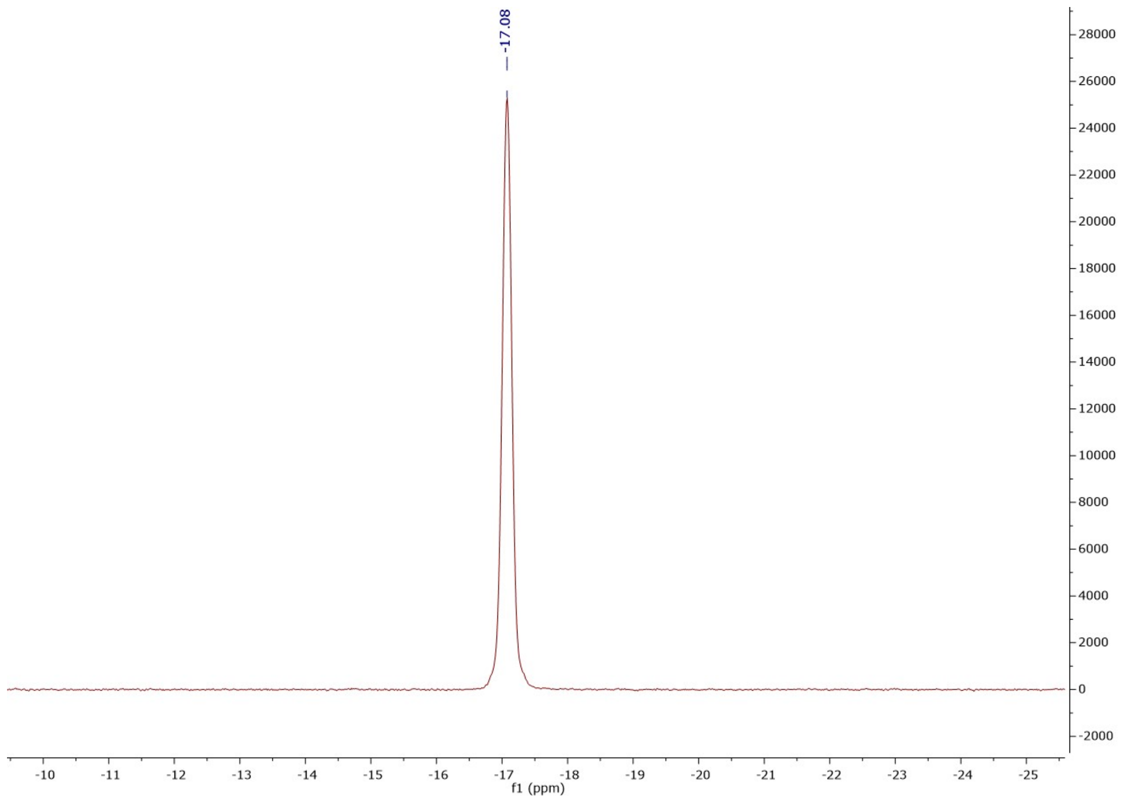


Figure S10. $^{11}B\{^{1}H\}$ NMR spectrum (128 MHz, THF-d_8, 300 K) of **1**-$B(C_6F_6)_4$.

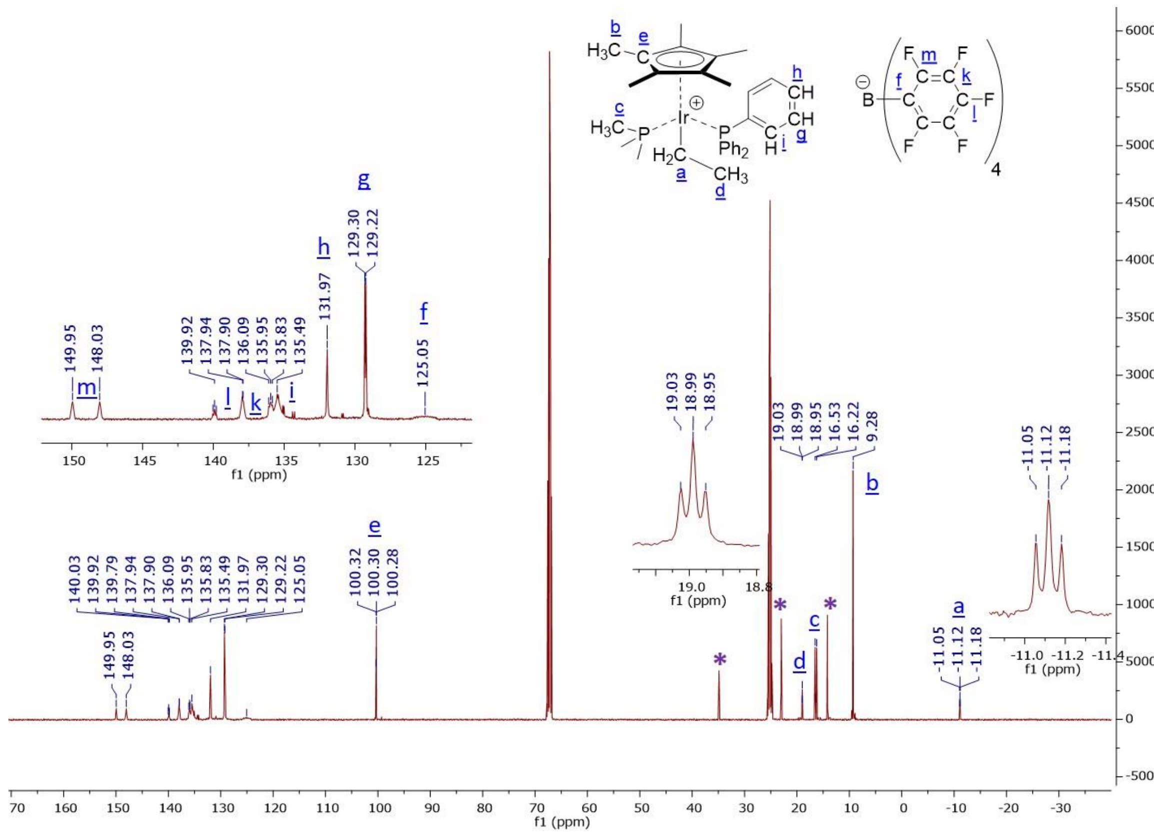
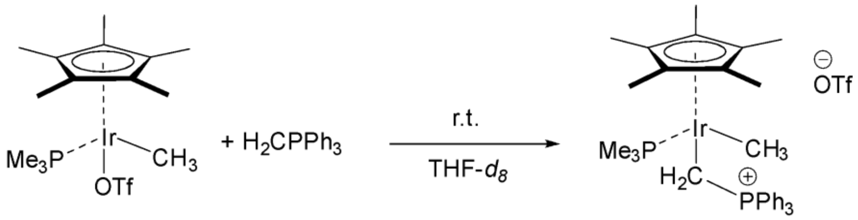


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, THF-d_8, 300 K) of **1**-$B(C_6F_5)$. Peaks labeled with "*" belong to pentane which could not be removed from the sample.

NMR Monitoring Reactions

Reaction of Cp*(Me$_3$P)Ir(CH$_3$)(OTf) with H$_2$CPPh$_3$: Crystals of Cp*(Me$_3$P)Ir(CH$_3$)(OTf) (18.5 mg, 32.6 µmol) and H$_2$CPPh$_3$ (9.0 mg, 32.6 µmol) were placed into a single vial, crushed into powder, and mixed thoroughly together. Half a millilitre of THF-d_8 was then used to dissolve the contents, which were shaken/swirled quickly to promote mixing. The resulting yellow solution was then transferred to a J-Young NMR tube. NMR spectra were obtained within an hour after mixing, and then the tube and its contents were placed an oil bath at 50°C for 8 hours after which further NMR spectra of the sample were obtained.



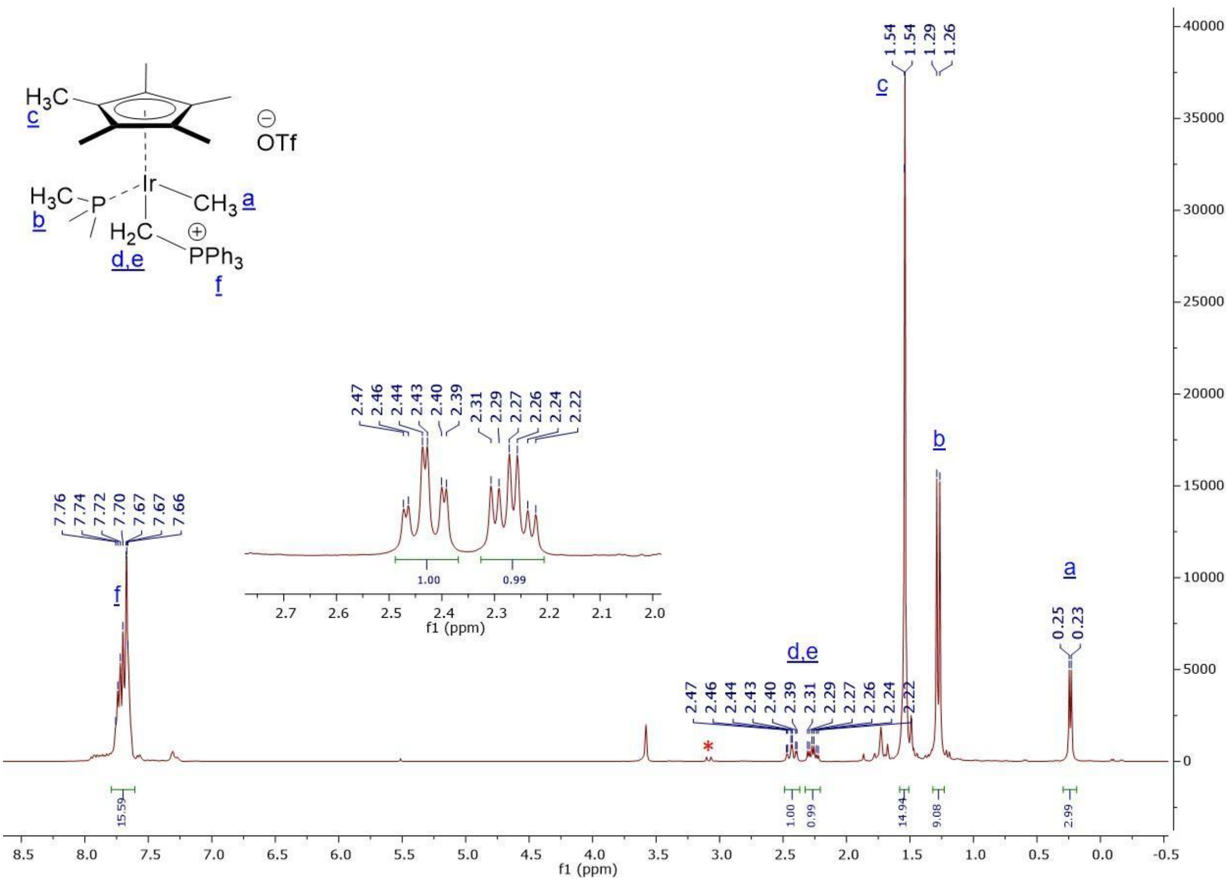


Figure S12. [1]H NMR spectrum (400 MHz, THF-d_8, 300 K) of [Cp*(Me$_3$P)(H$_2$CPPh$_3$)Ir(CH$_3$)][OTf] formed *in situ* from Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and H$_2$CPPh$_3$. Peaks labeled with "*" belong to the phosphonium by protonation of H$_2$CPPh$_3$. All other unlabeled signals belong to unidentified side-products.

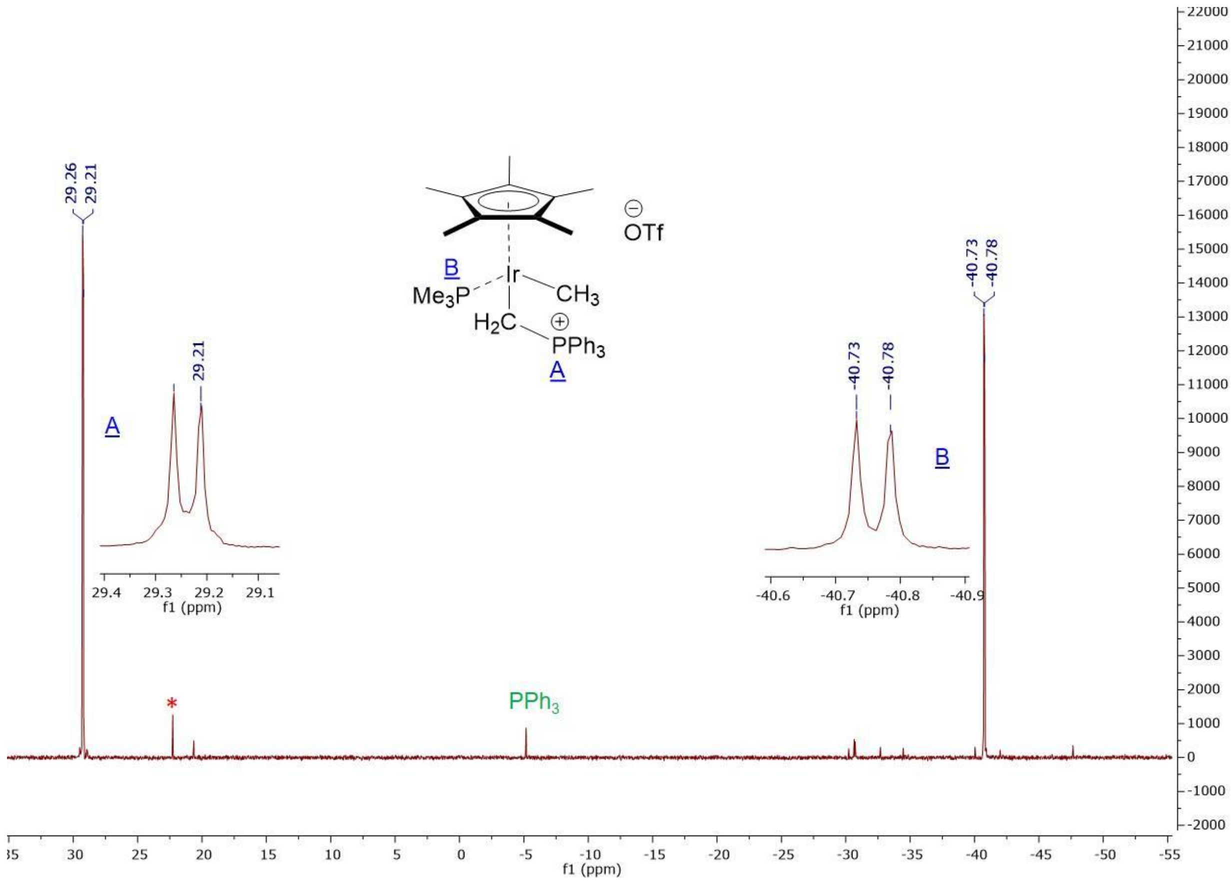


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)(H_2CPPh_3)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and H_2CPPh_3. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. All other unlabelled peaks belong to unidentified side-products.

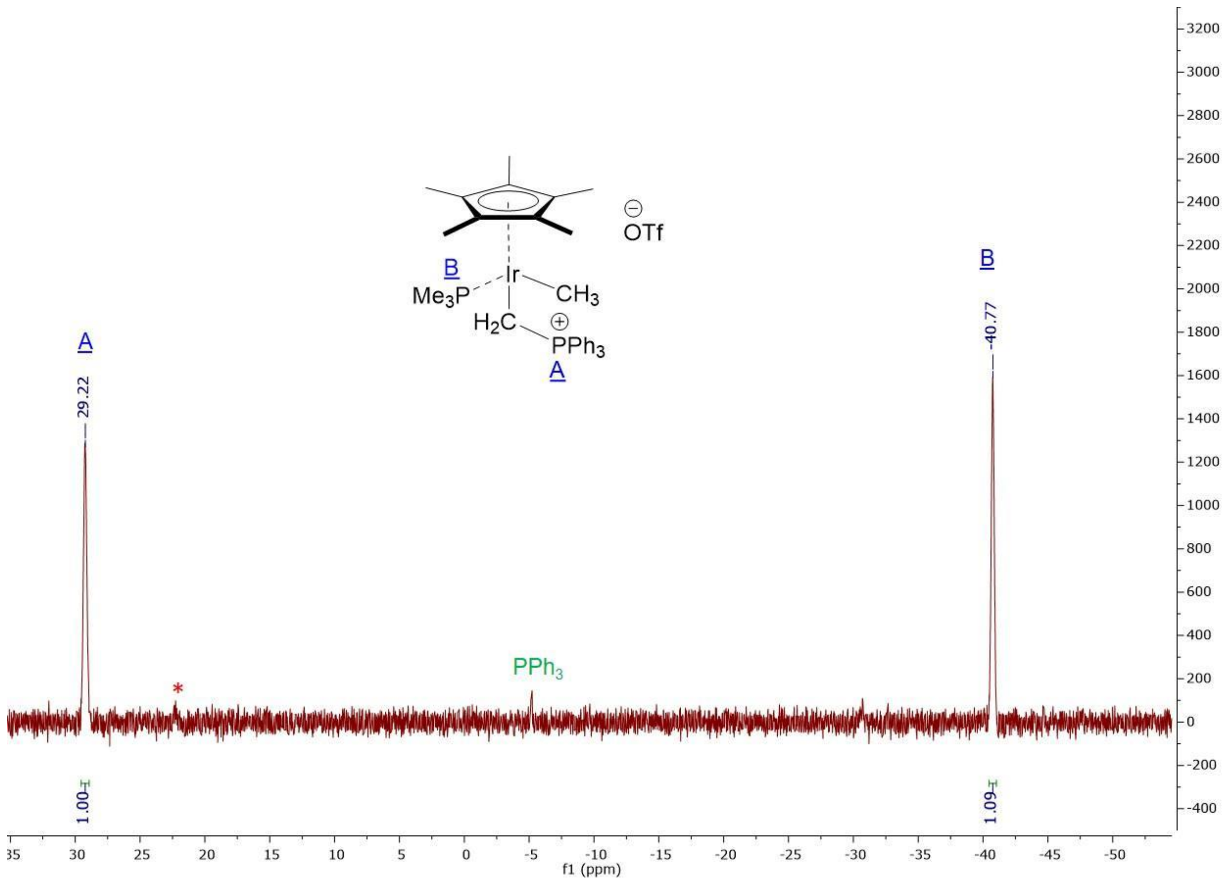


Figure S14. [31]P NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)(H_2CPPh_3)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and H_2CPPh_3. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. All other unlabelled peaks belong to unidentified side-products.

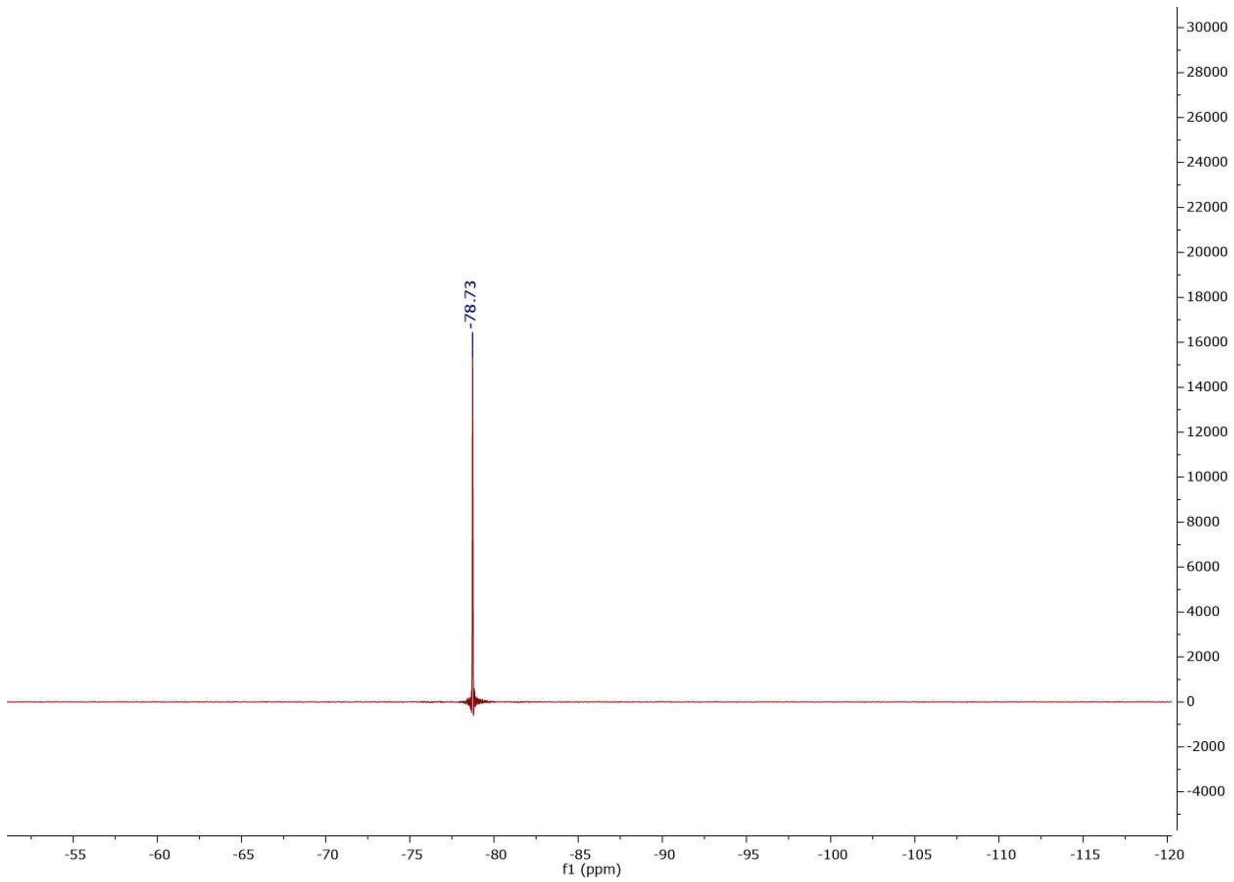


Figure S15. $^{19}F\{^1H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)(H_2CPPh_3)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and H_2CPPh_3.

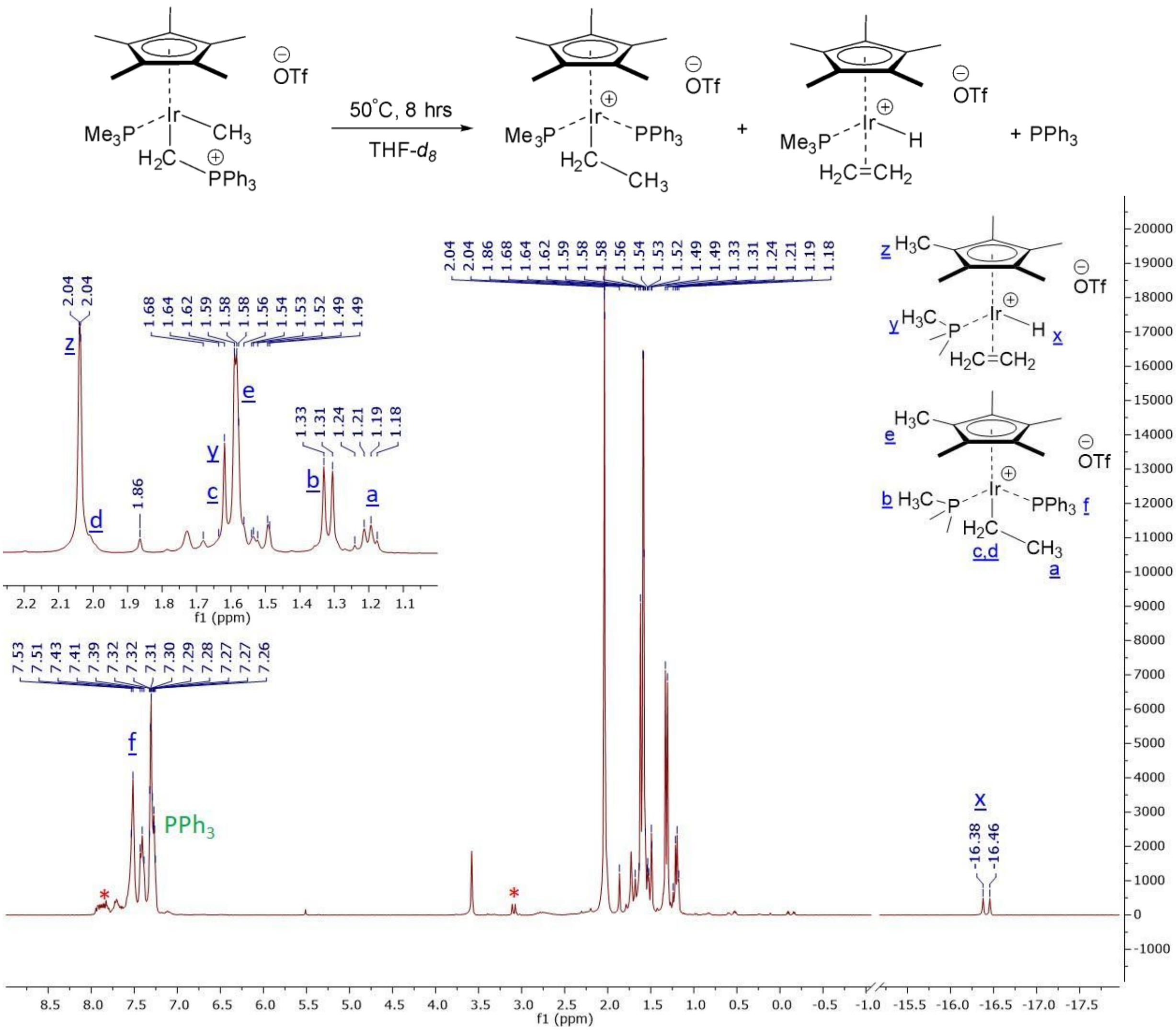


Figure S16. [1]H NMR spectrum (400 MHz, THF-d_8, 300 K) of **1**-OTf and **2**-OTf formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and H_2CPPh_3 and heating at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. All other unlabeled signals belong to unidentified side-products.

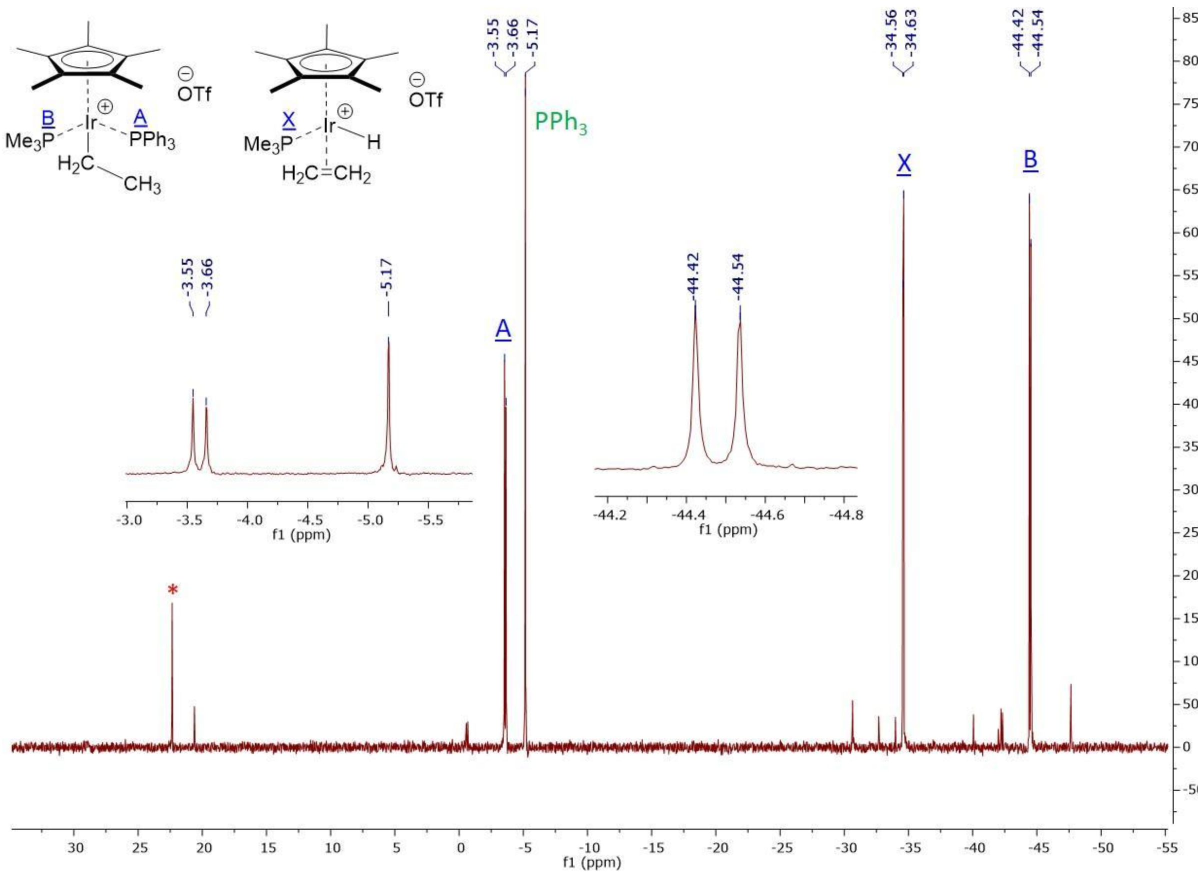


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of **1**-OTf and **2**-OTf formed *in situ* from Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and H_2CPPh_3 and heating at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. All other unlabelled peaks belong to unidentified side-products.

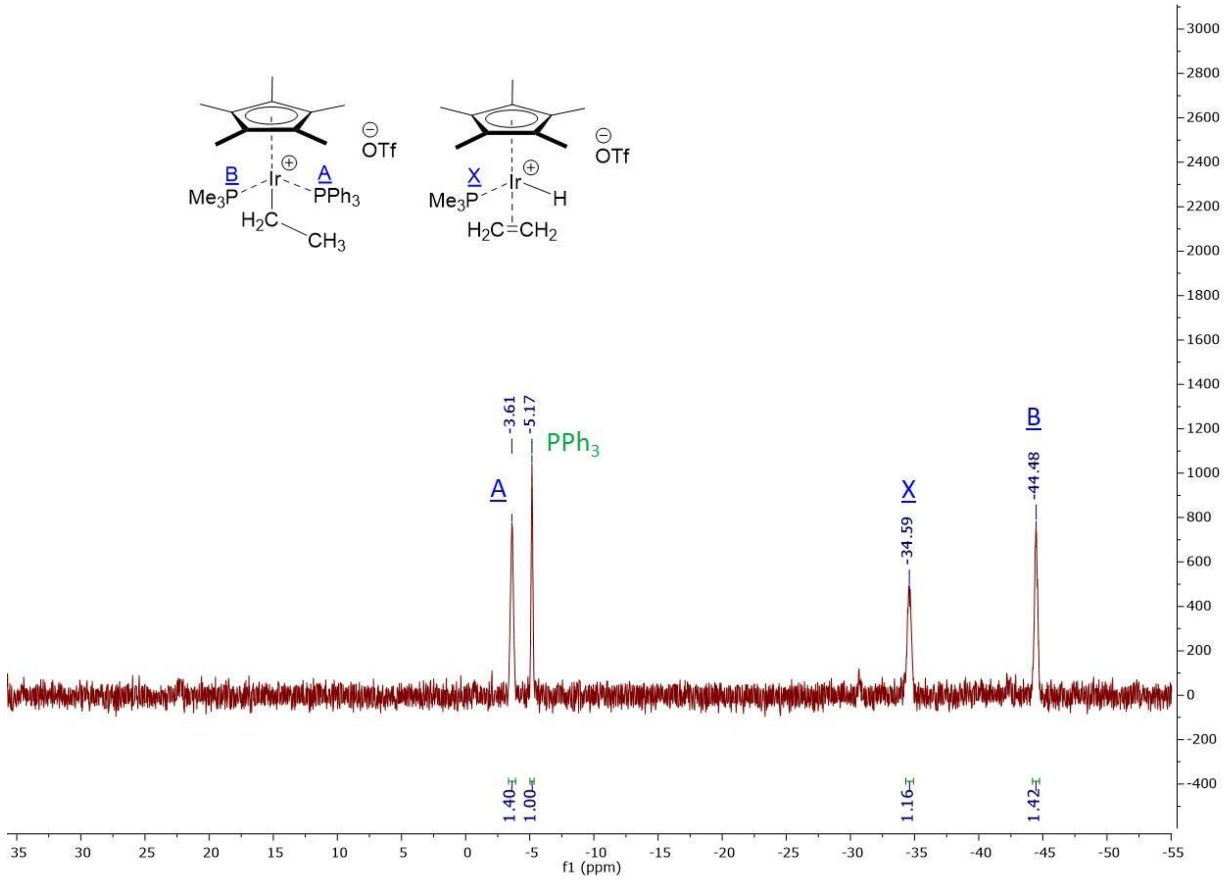


Figure S18. [31]P NMR spectrum (162 MHz, THF-d_8, 300 K) of **1**-OTf and **2**-OTf formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and H_2CPPh_3 and heating at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. All other unlabelled peaks belong to unidentified side-products.

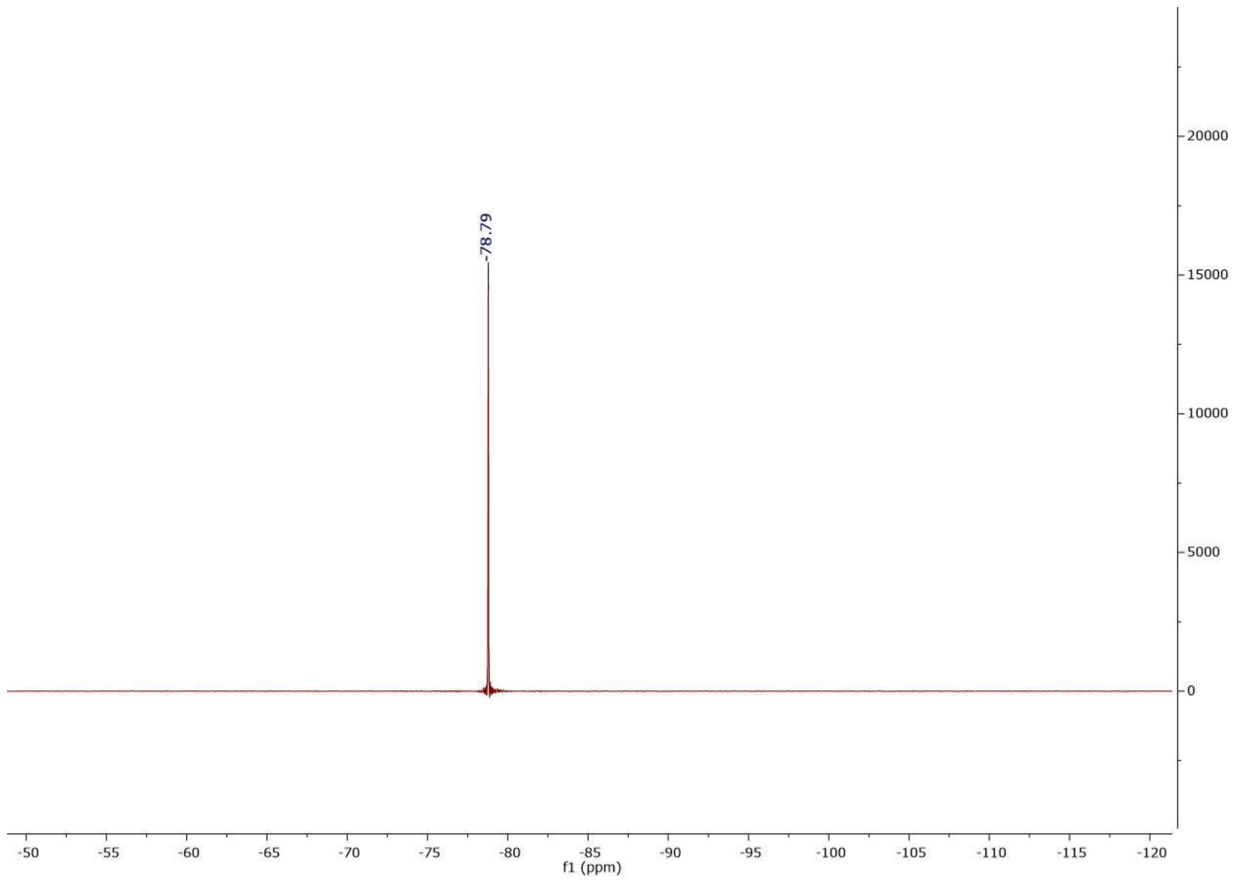
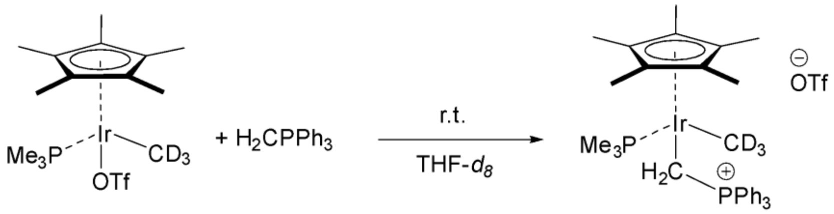


Figure S19. $^{19}F\{^1H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of **1**-OTf and **2**-OTf formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and H_2CPPh_3 and heating at 50 °C.

Reaction of Cp*(Me$_3$P)Ir(CD$_3$)(OTf) with H$_2$CPPh$_3$: Performed as described above using Cp*(Me$_3$P)Ir(CD$_3$)(OTf) in THF-d_8. A similar experiment was reproduced in THF to obtain a ^{2}H NMR spectrum.



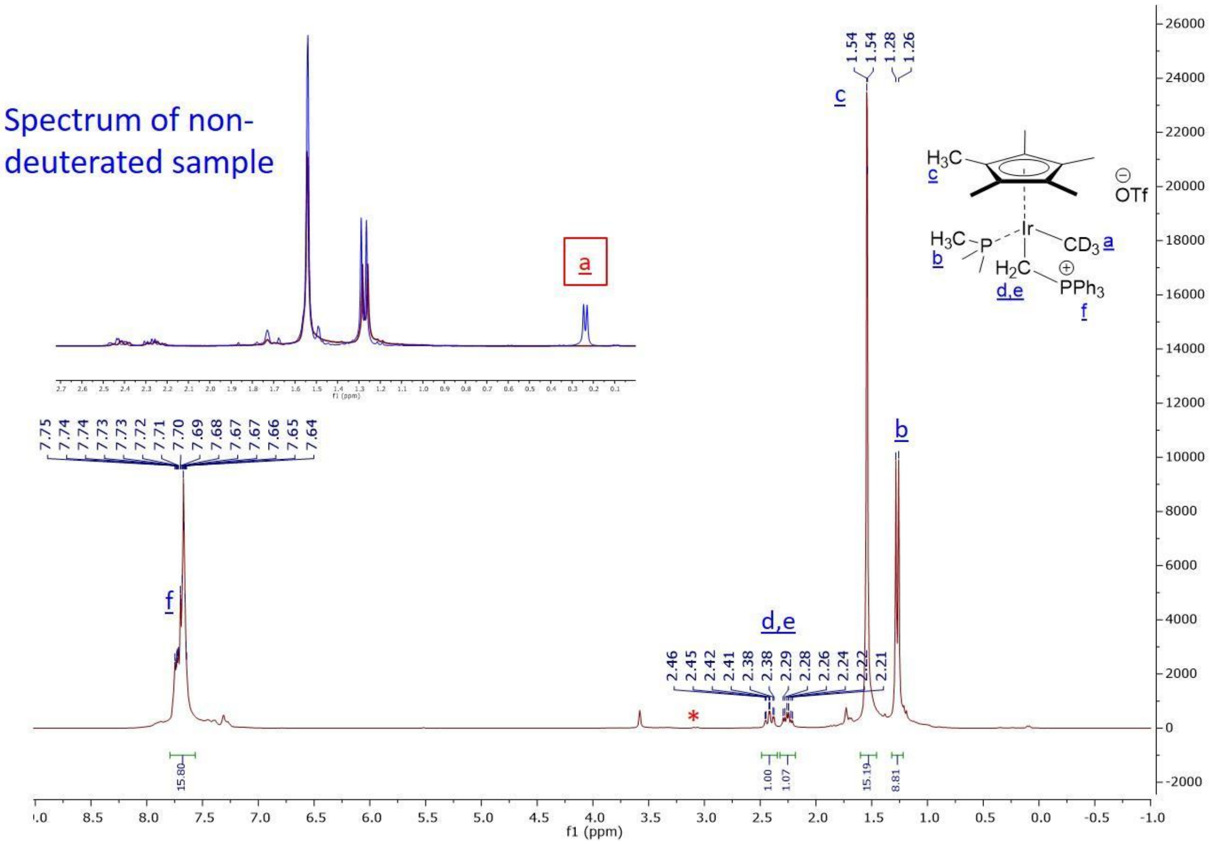


Figure S20. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of [Cp*(Me$_3$P)(H$_2$CPPh$_3$)Ir(CD$_3$)][OTf] formed *in situ* from Cp*(Me$_3$P)Ir(CD$_3$)(OTf) and H$_2$CPPh$_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of H$_2$CPPh$_3$. All other unlabeled signals belong to unidentified side-products.

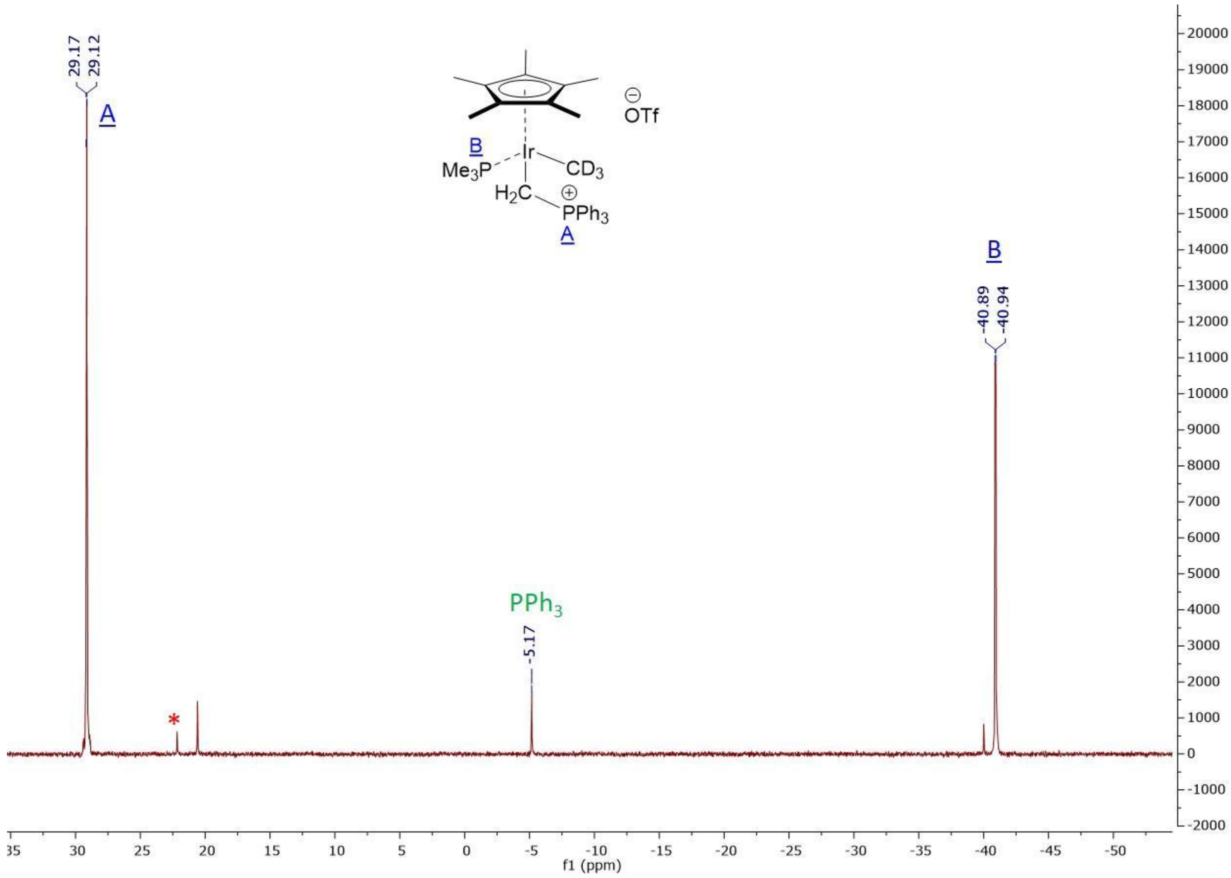


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)(H_2CPPh_3)Ir(CD_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CD_3)(OTf) and H_2CPPh_3. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. All other unlabelled peaks belong to unidentified side-products.

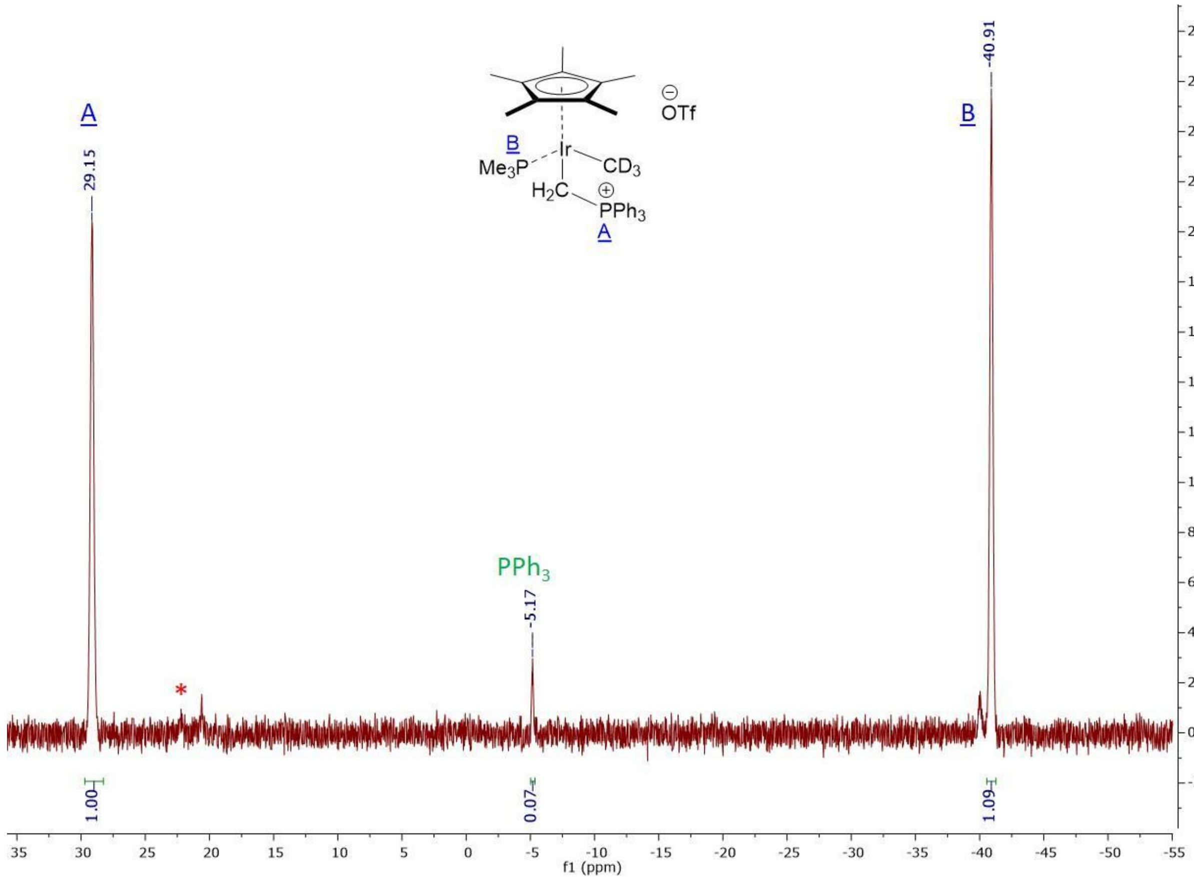


Figure S22. ^{31}P NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me$_3$P)(H$_2$CPPh$_3$)Ir(CD$_3$)][OTf] formed *in situ* from Cp*(Me$_3$P)Ir(CD$_3$)(OTf) and H$_2$CPPh$_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of H$_2$CPPh$_3$. All other unlabelled peaks belong to unidentified side-products.

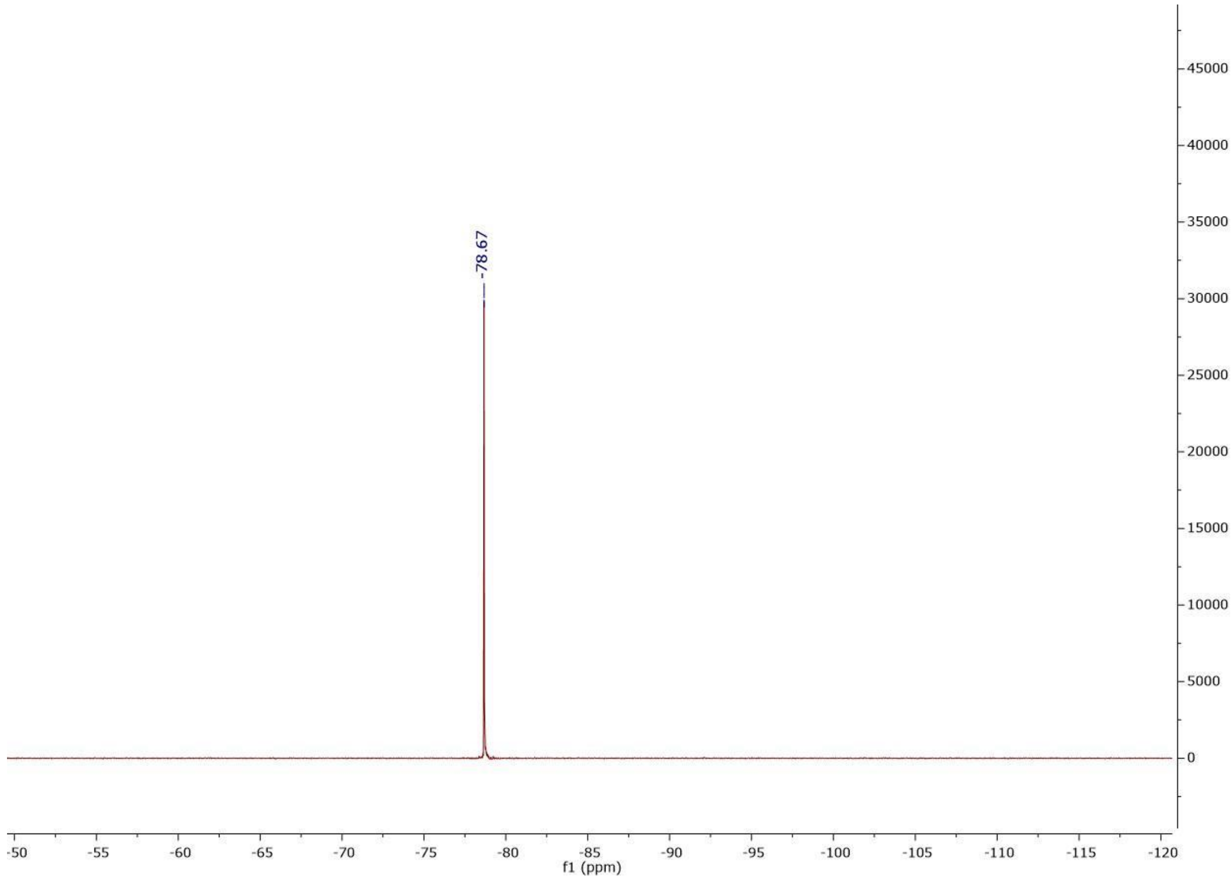
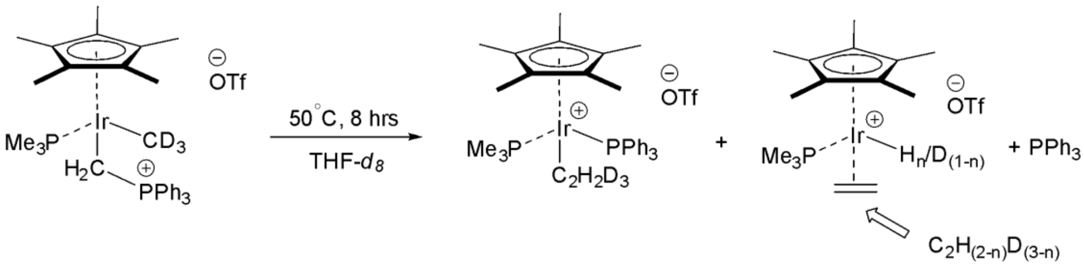


Figure S23. $^{19}F\{^1H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)(H_2CPPh_3)Ir(CD_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CD_3)(OTf) and H_2CPPh_3.



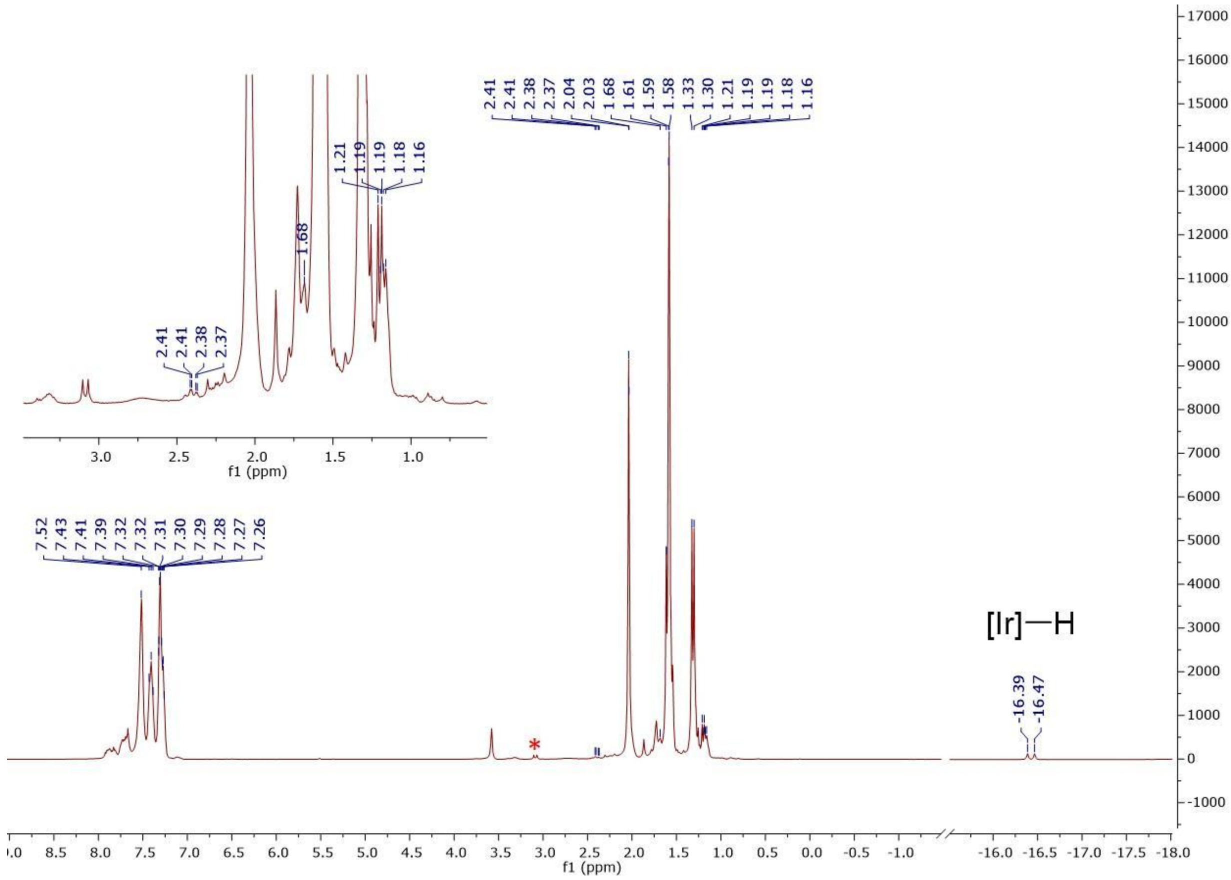


Figure S24. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of **1-*d₃*** and **2-*d₃*** formed *in situ* from Cp*(Me$_3$P)Ir(CD$_3$)(OTf) and H$_2$CPPh$_3$ and heating at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H$_2$CPPh$_3$. All other unlabeled signals belong to unidentified side-products.

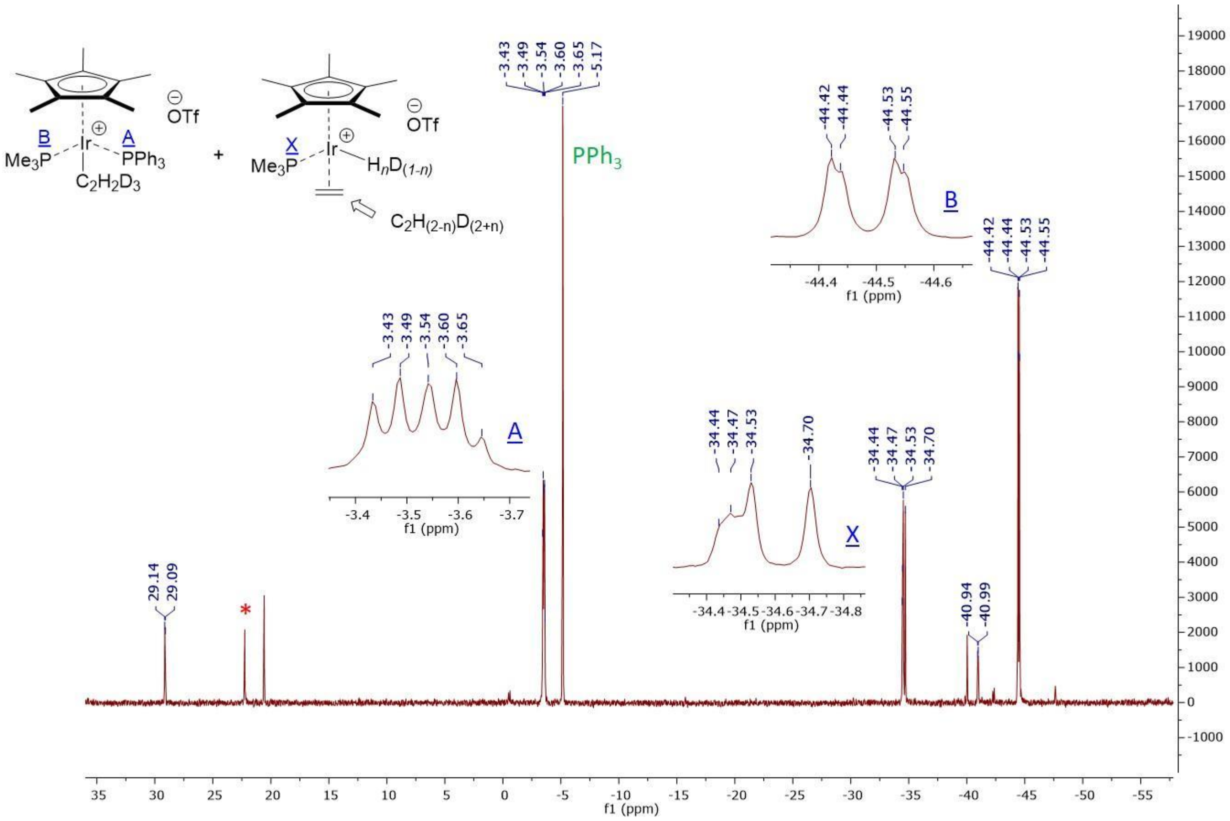


Figure S25. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of **1**-OTf-d_3 and **2**-OTf-d_3 formed *in situ* from Cp*(Me_3P)Ir(CD_3)(OTf) and H_2CPPh_3 and heating at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. All other unlabelled peaks belong to unidentified side-products.

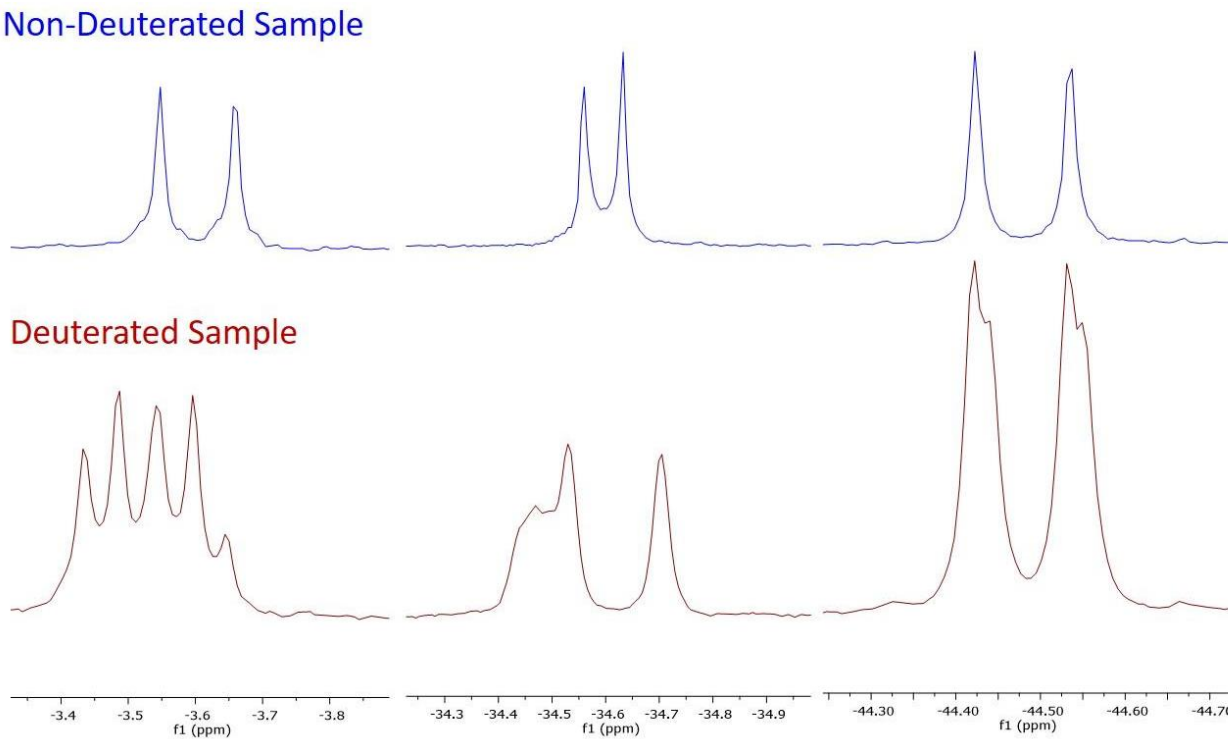


Figure S26. Comparison of $^{31}P\{^1H\}$ NMR spectroscopic signals of **1**-OTf and **2**-OTf (blue)with **1**-OTf-d_3 and **2**-OTf-d_3 (maroon).

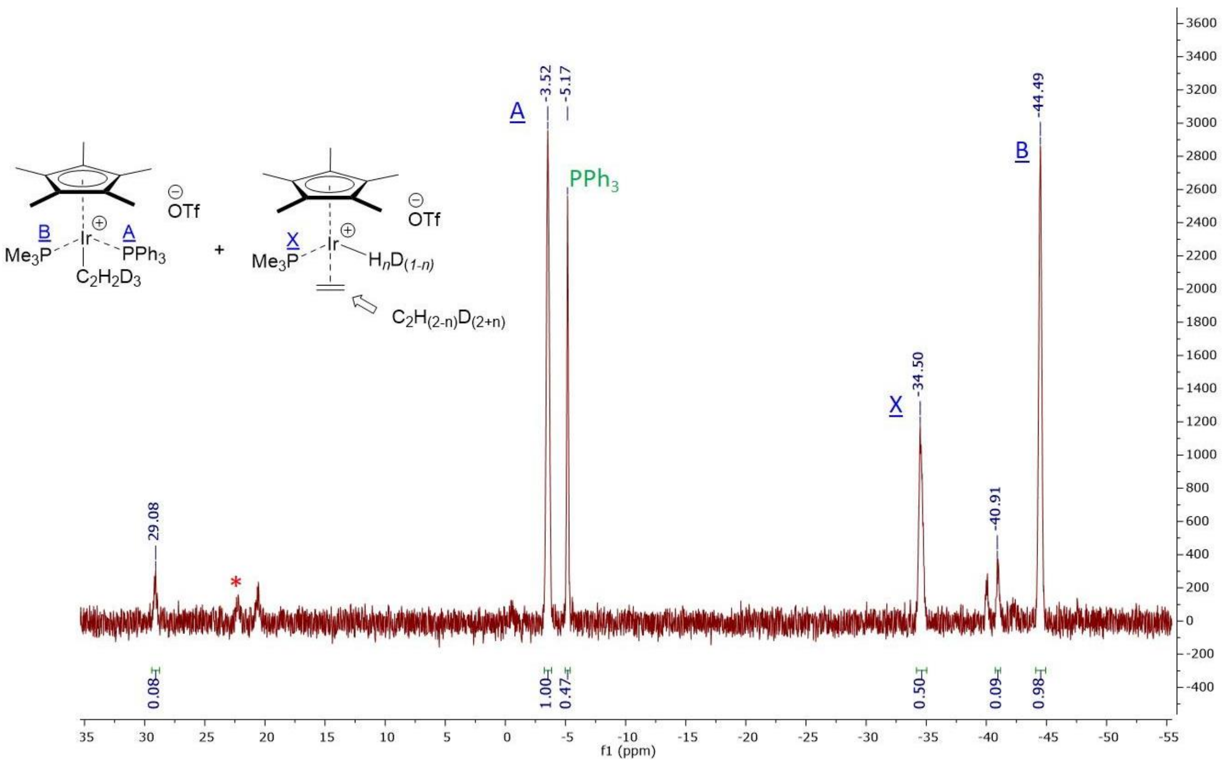


Figure S27. ^{31}P NMR spectrum (162 MHz, THF-d_8, 300 K) of **1**-OTf-d_3 and **2**-OTf-d_3 formed *in situ* from Cp*(Me_3P)Ir(CD_3)(OTf) and H_2CPPh_3 and heating at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. All other unlabelled peaks belong to unidentified side-products.

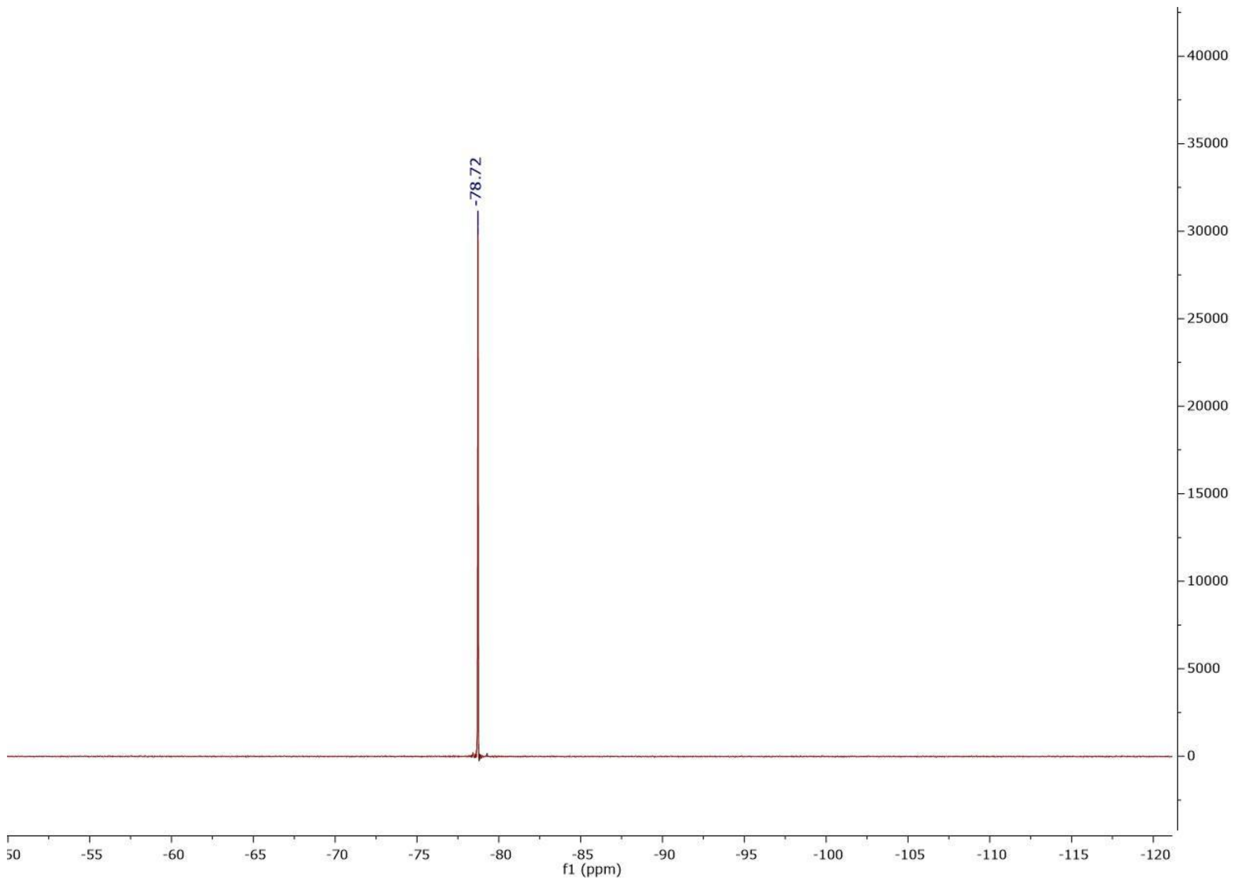


Figure S28. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of **1**-OTf-d_3 and **2**-OTf-d_3 formed *in situ* from Cp*(Me_3P)Ir(CD_3)(OTf) and H_2CPPh_3 and heating at 50 °C.

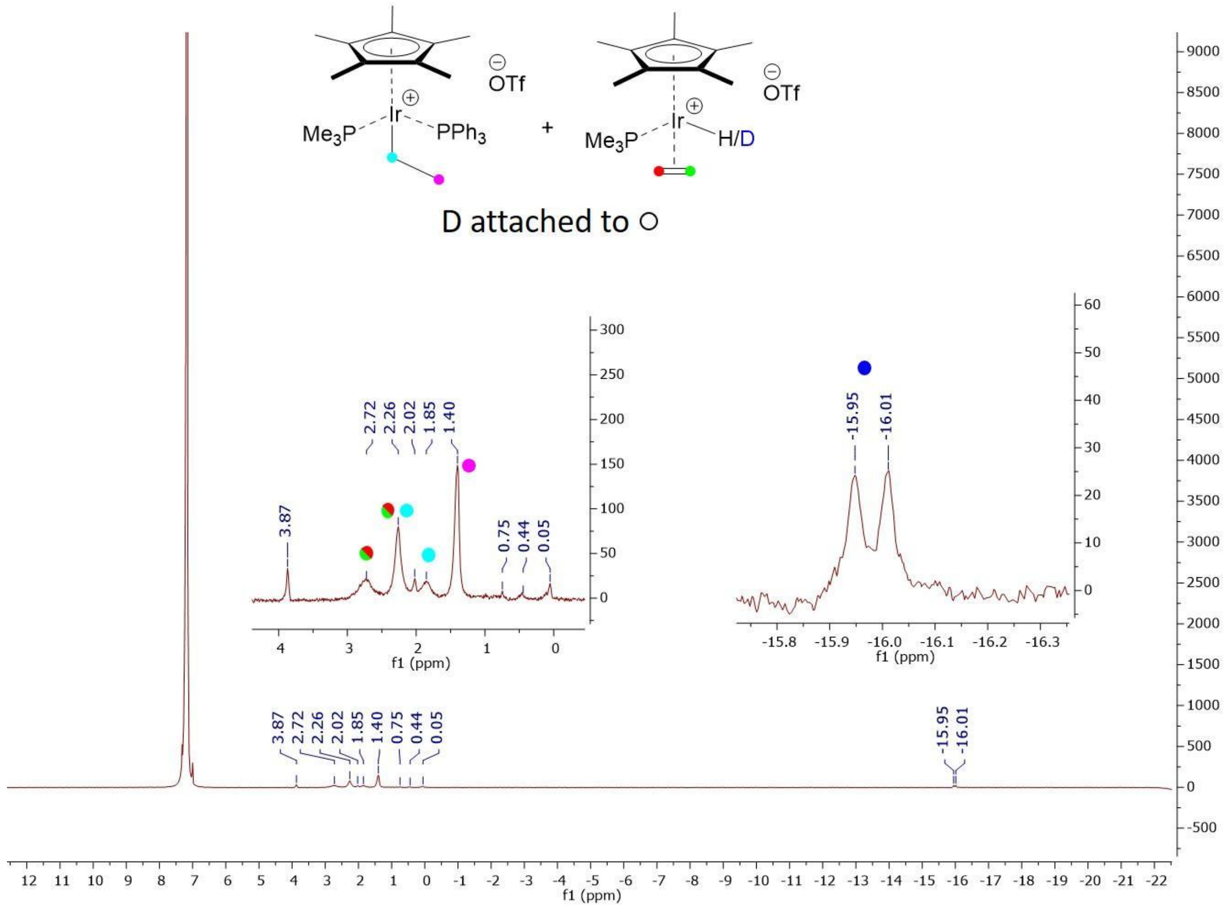
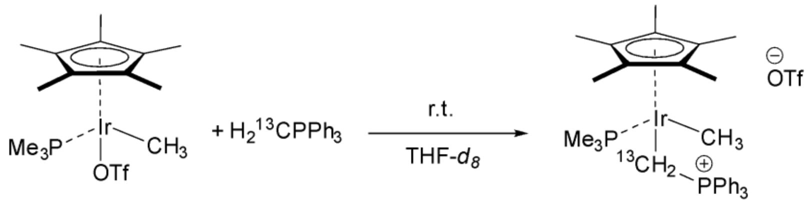


Figure S29. ^{2}H NMR spectrum (76.7 MHz, THF, 300 K) of **1**-OTf-d_3 and **2**-OTf-d_3 and H_2CPPh_3 at 50 °C for 12 hours. Signals were referenced against at C_6D_6 capillary whose signal was set as 7.16 ppm.

Reaction of Cp*(Me$_3$P)Ir(CH$_3$)(OTf) with H$_2$^{13}CPPh$_3$: Performed as described above for the unlabeled sample using the ^{13}C-enriched ylide H$_2$^{13}CPPh$_3$ and heated for 7 hours.



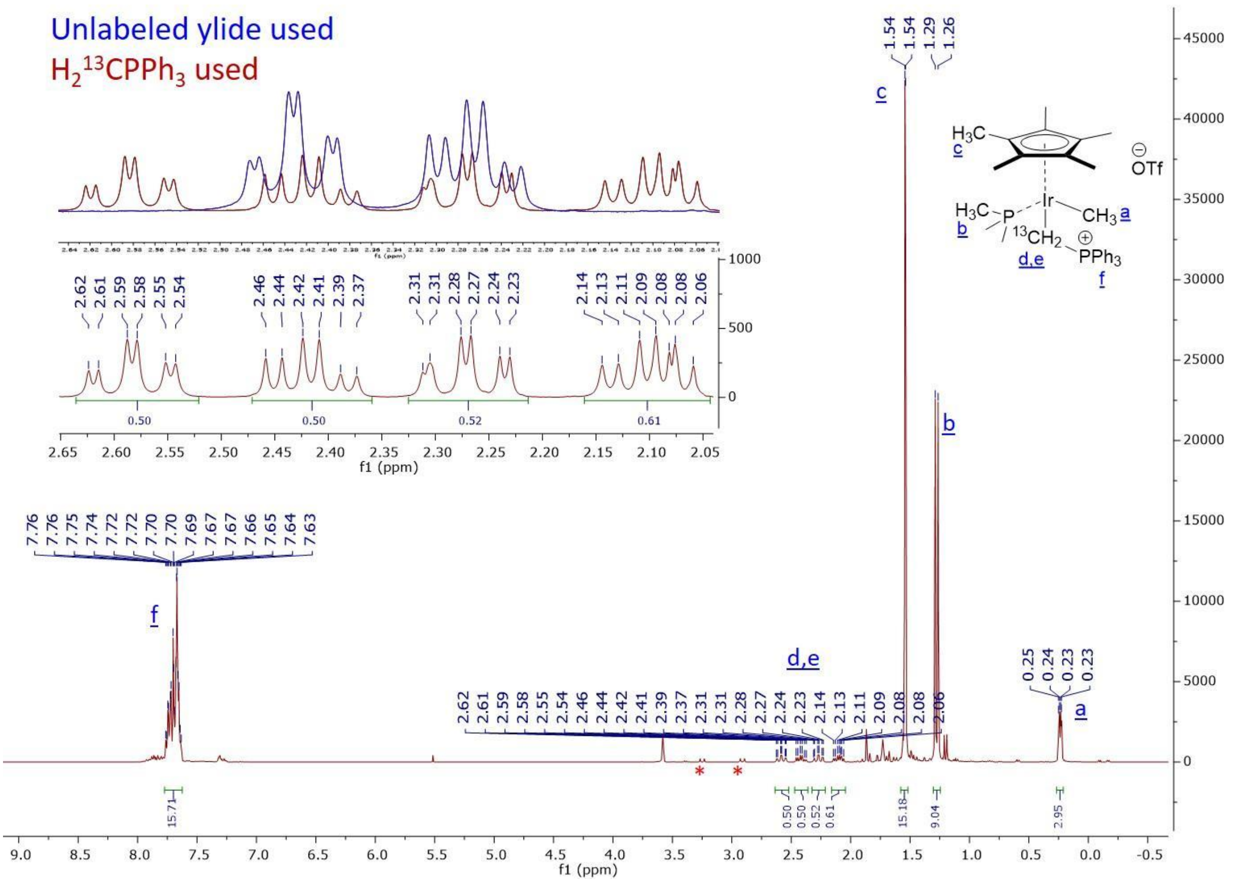


Figure S30. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of [Cp*(Me$_3$P)(H$_2$^{13}CPPh$_3$)Ir(CH$_3$)][OTf] formed *in situ* from Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and H$_2$^{13}CPPh$_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of H$_2$^{13}CPPh$_3$. All other unlabeled signals belong to unidentified side-products.

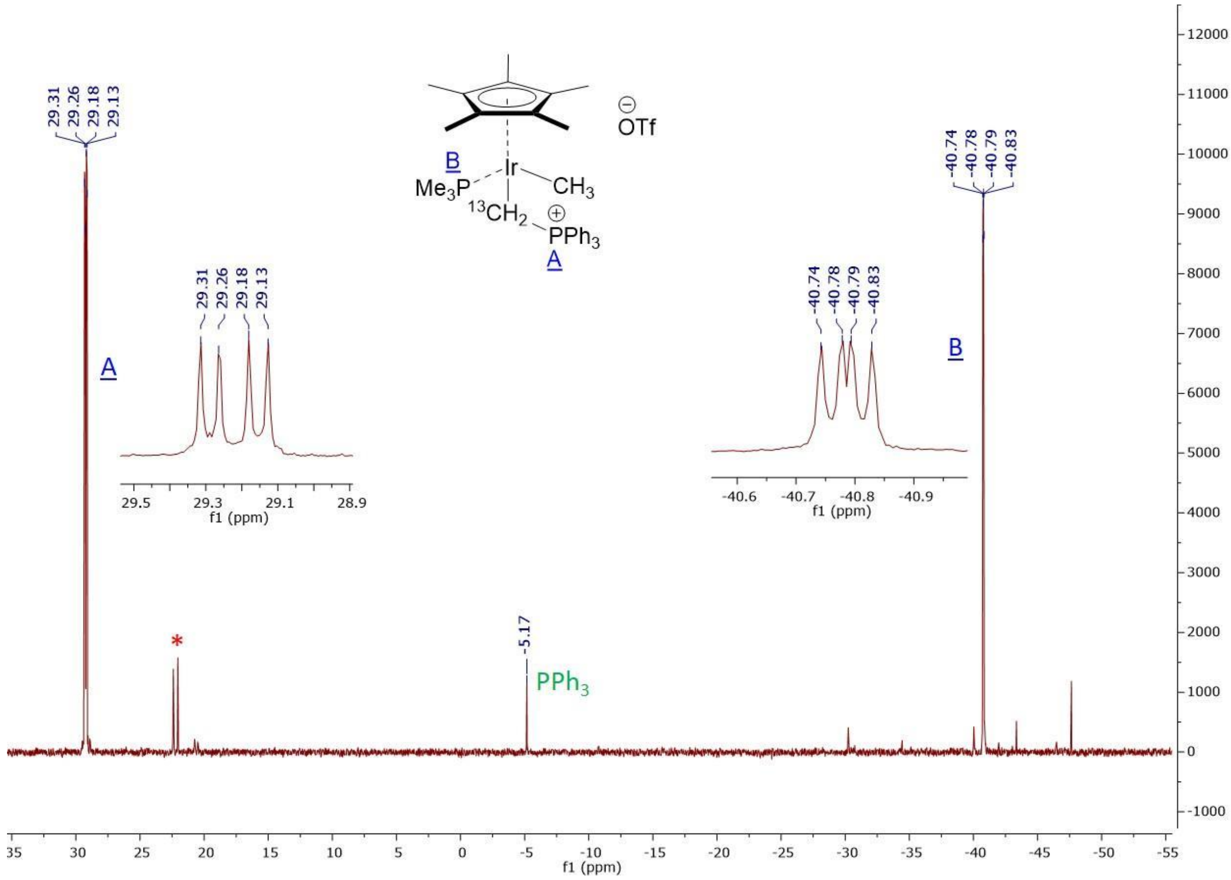


Figure S31. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me$_3$P)(H$_2$^{13}CPPh$_3$)Ir(CH$_3$)][OTf] formed *in situ* from Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and H$_2$^{13}CPPh$_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of H$_2$^{13}CPPh$_3$. All other unlabelled peaks belong to unidentified side-products.

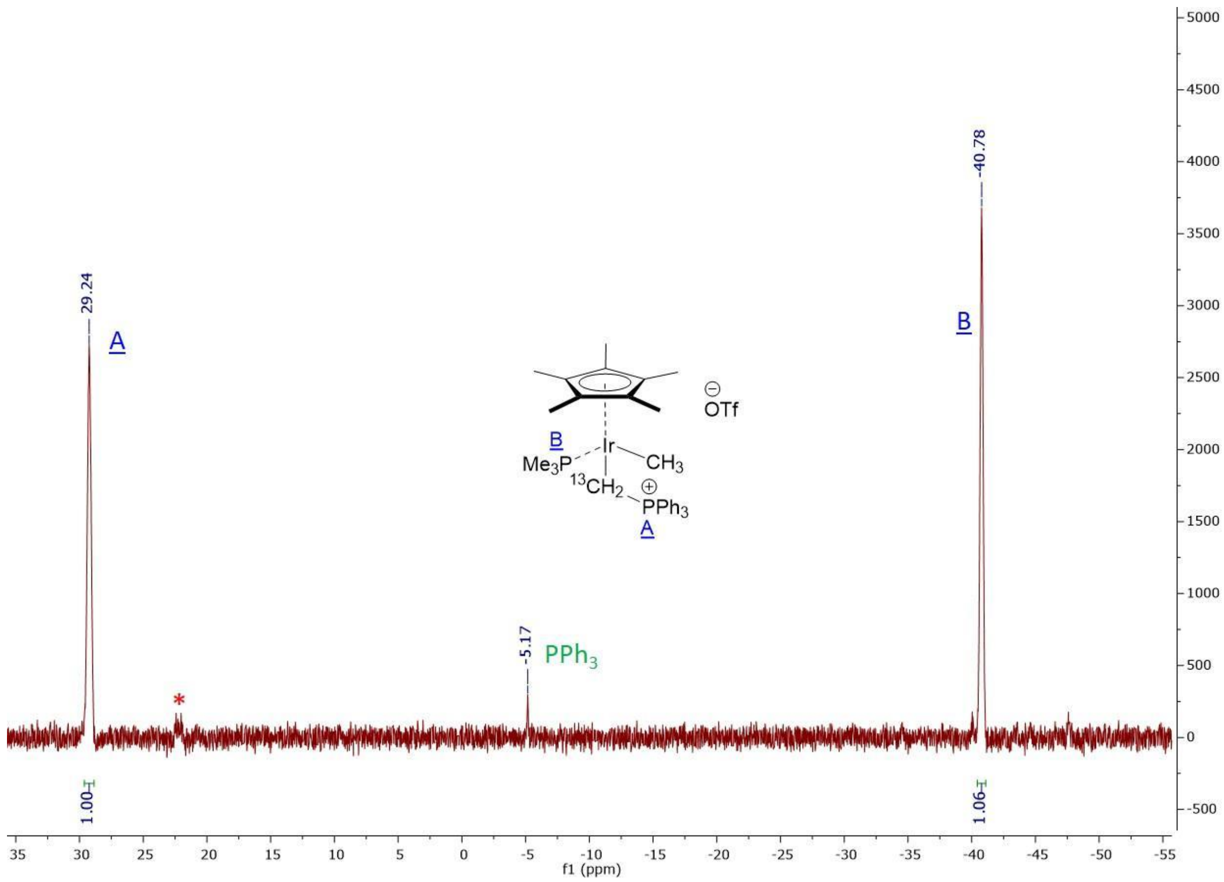


Figure S32. ^{31}P NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)($H_2{}^{13}CPPh_3$)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. All other unlabelled peaks belong to unidentified side-products.

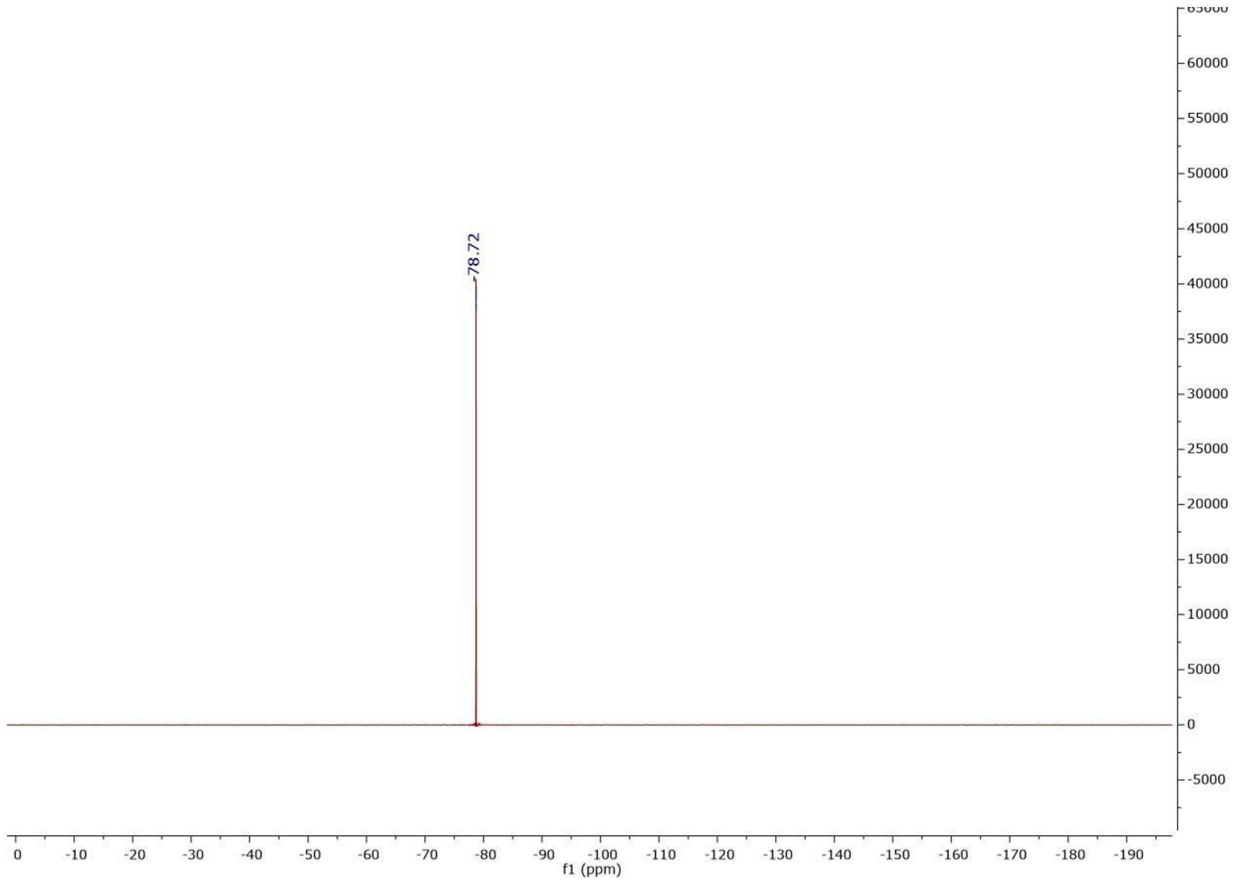


Figure S33. $^{19}F\{^1H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)($H_2{}^{13}CPPh_3$)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$.

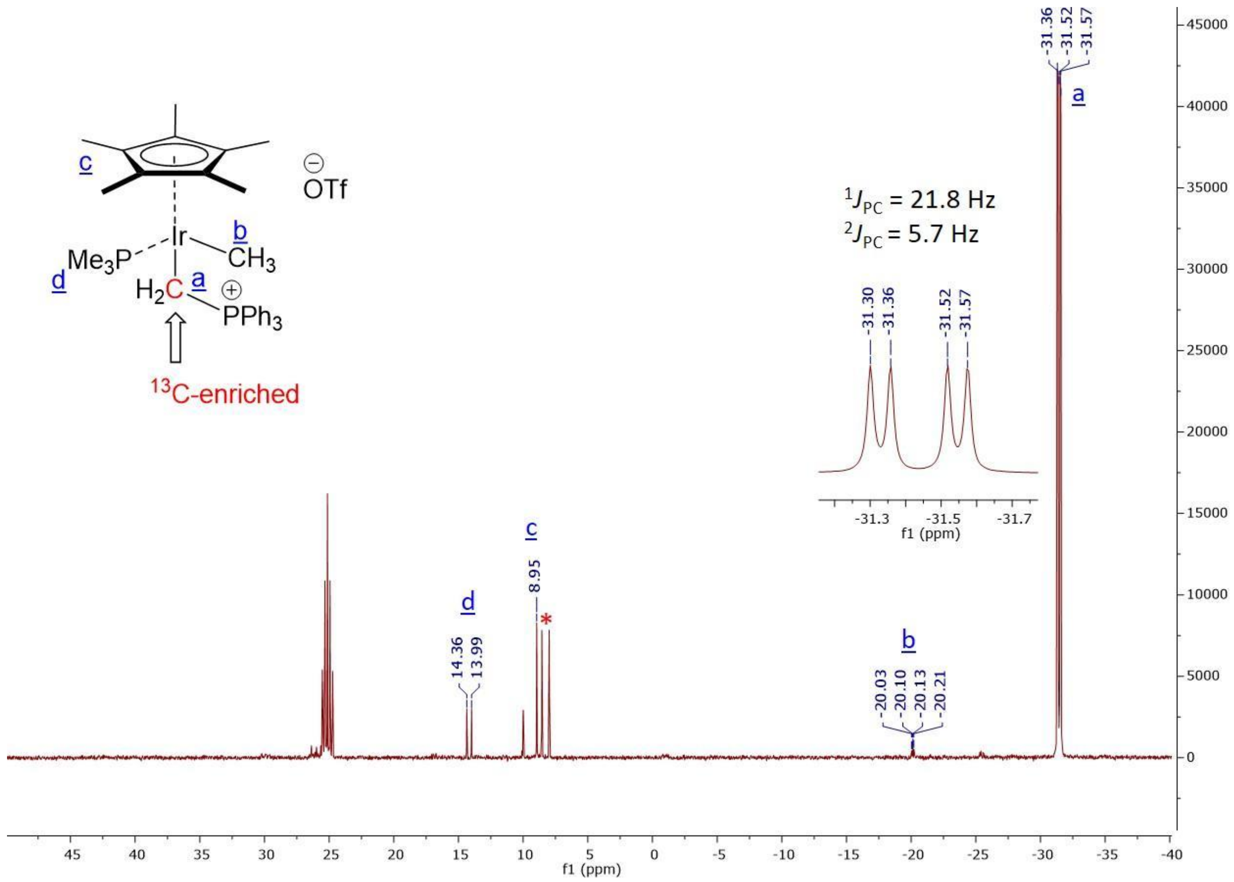


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, THF-d_8, 300 K) in the aliphatic region of [Cp*(Me$_3$P)(H$_2{}^{13}$CPPh$_3$)Ir(CH$_3$)][OTf] formed *in situ* from Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and H$_2{}^{13}$CPPh$_3$. Peaks labeled with "*" belong to the phosphonium salt with adventitious moisture. Other unlabelled peaks belong to unidentified side-products.

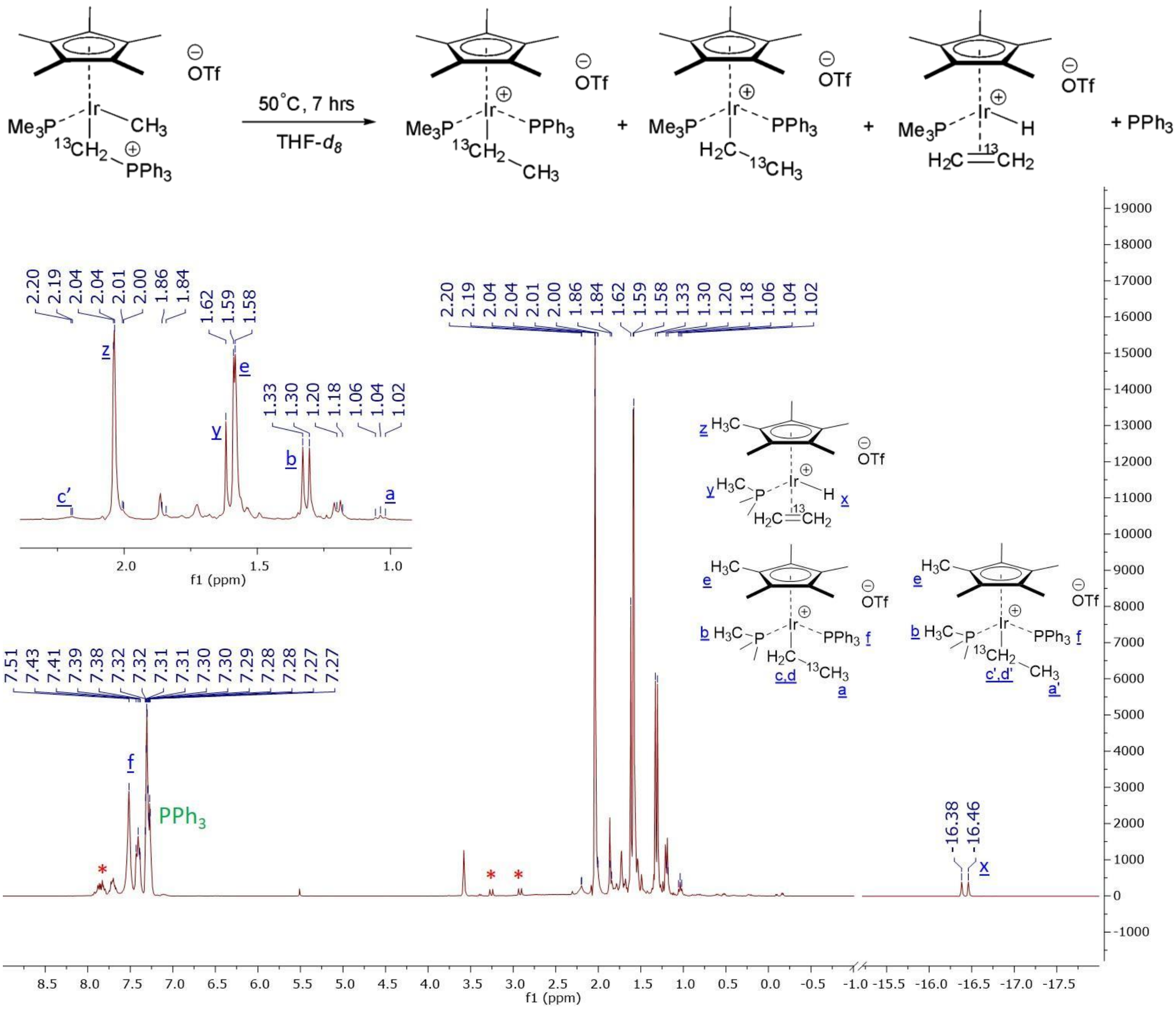


Figure S35. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-13C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$ and heating at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. All other unlabeled signals belong to unidentified side-products. Note that not all protons could be matched with signals due to overlap of peaks.

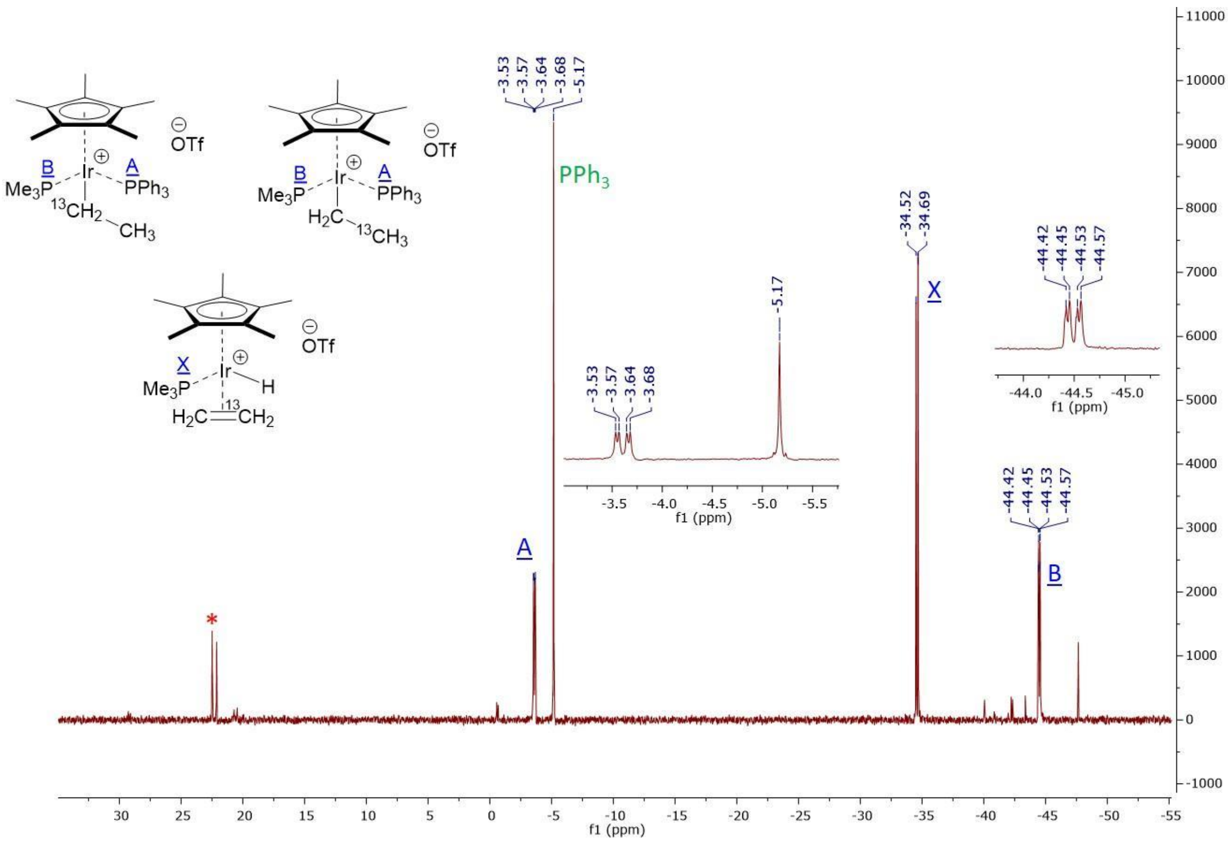


Figure S36. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and $H_2{}^{13}CPPh_3$ and heating at 50°C. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. All other unlabelled peaks belong to unidentified side-products.

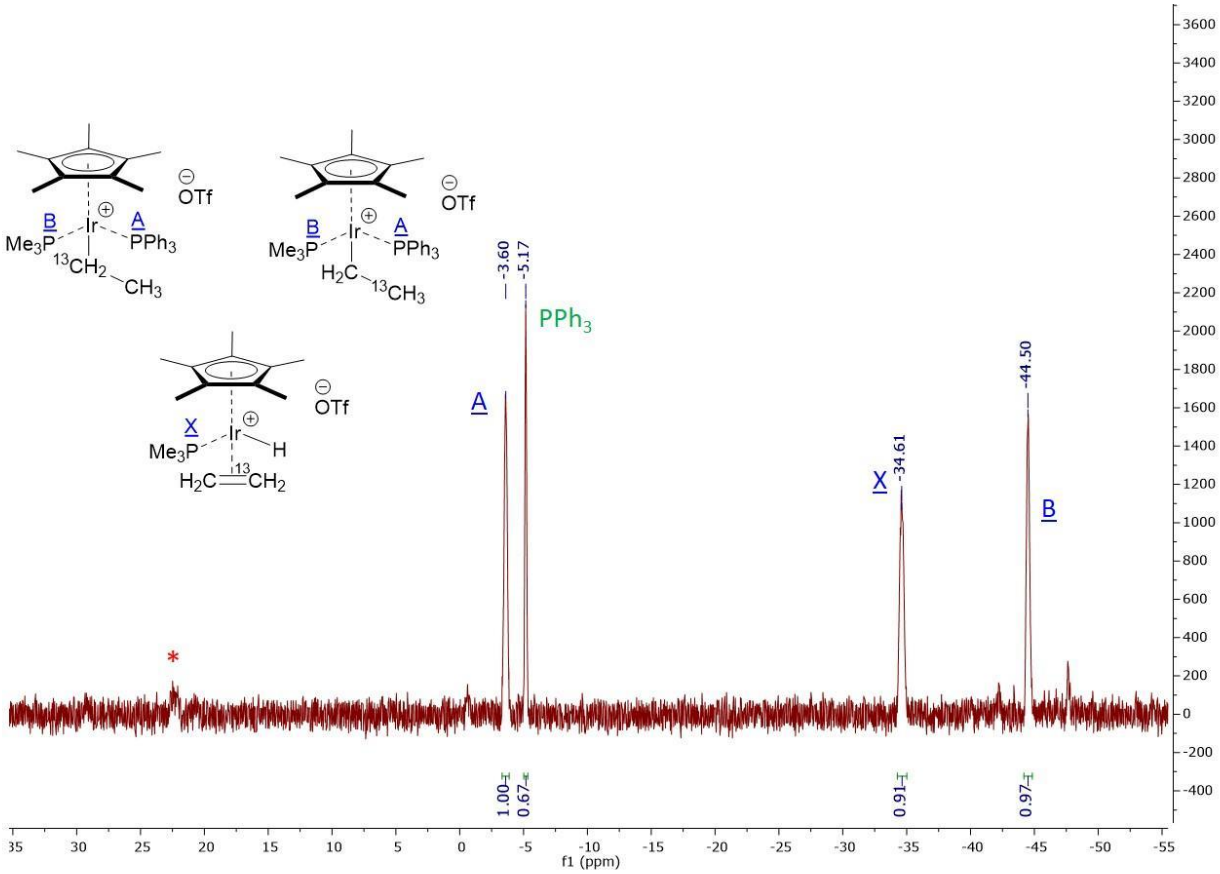


Figure S37. ^{31}P NMR spectrum (162 MHz, THF-d_8, 300 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$ and heating at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. All other unlabelled peaks belong to unidentified side-products.

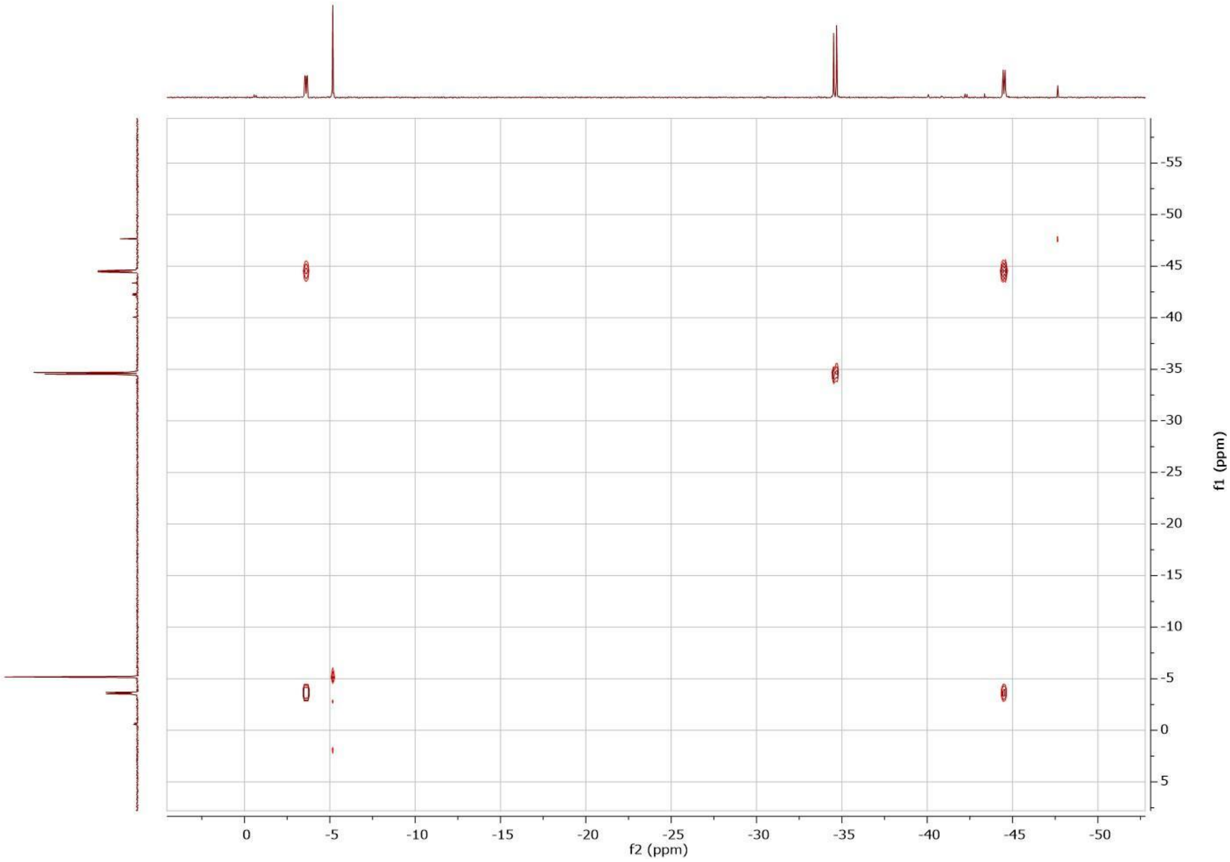


Figure S38. ^{31}P COSY NMR spectrum (162 MHz, THF-d_8, 300 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$ and heating at 50 °C, including only the region of the spectrum with signals corresponding to Ir-containing species for clarity.

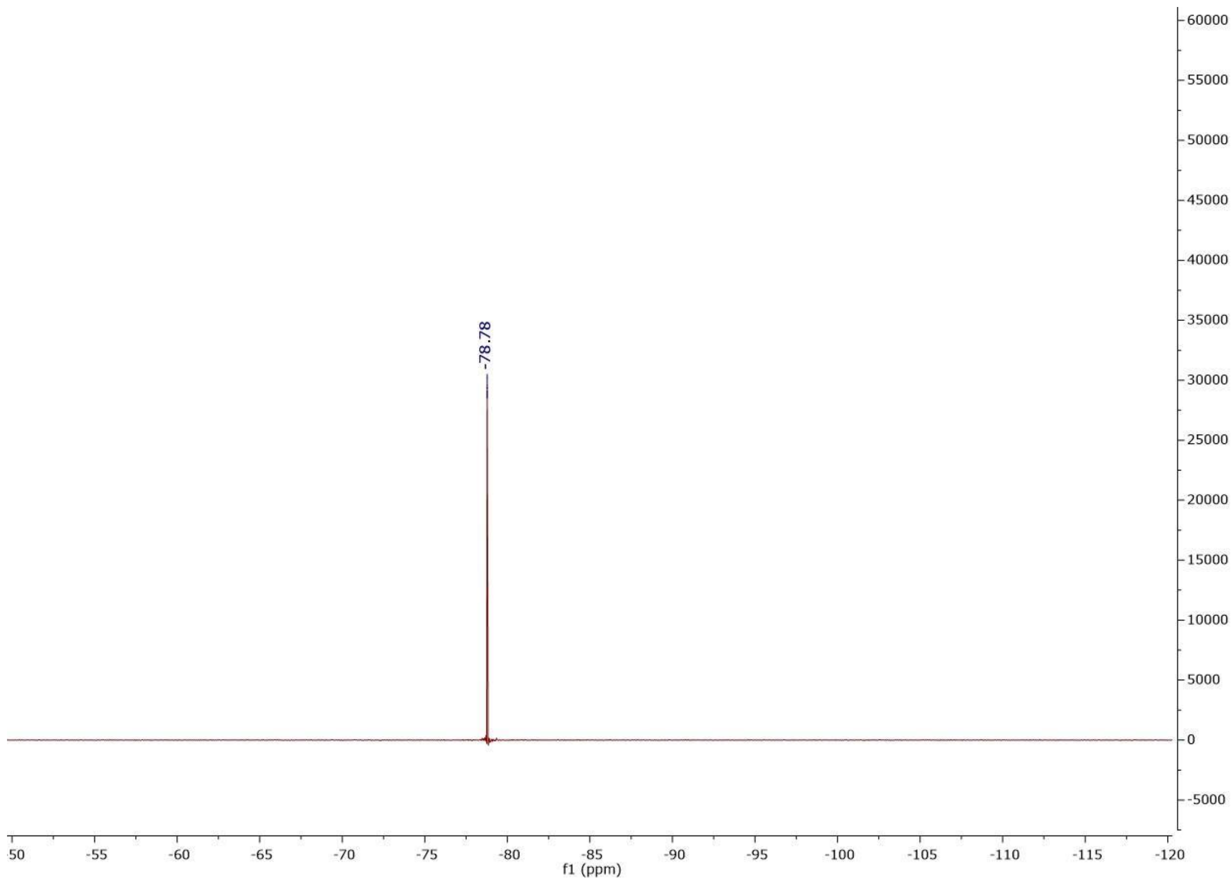


Figure S39. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of **1**-OTf-$^{13}CH_2CH_3$**,** **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$ and heating at 50 °C.

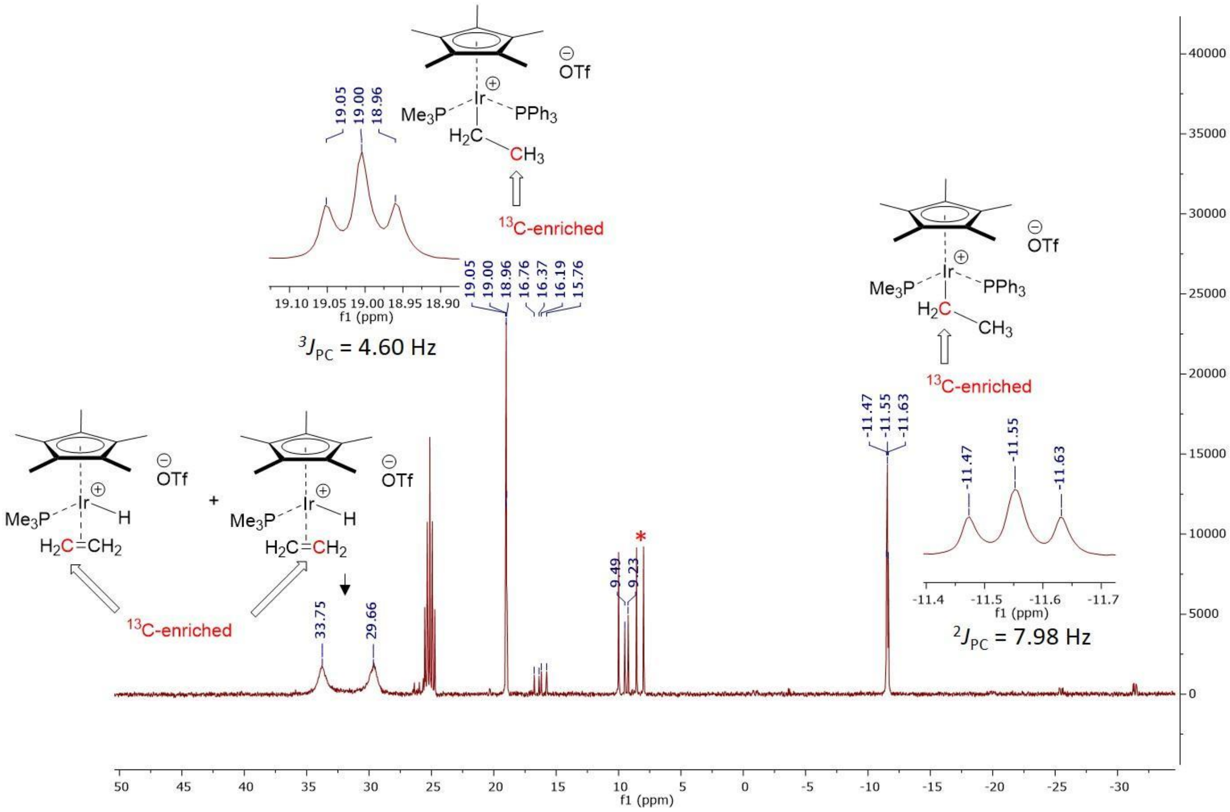


Figure S40. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, THF-d_8, 300 K) in the aliphatic region of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and $H_2{}^{13}CPPh_3$ after heating in a 50 °C bath for 7 hours. The other labelled peaks correspond to the methyl groups of Cp* ligand and the methyl groups of PMe$_3$ ligand. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. Other unlabelled peaks belong to unidentified side-products.

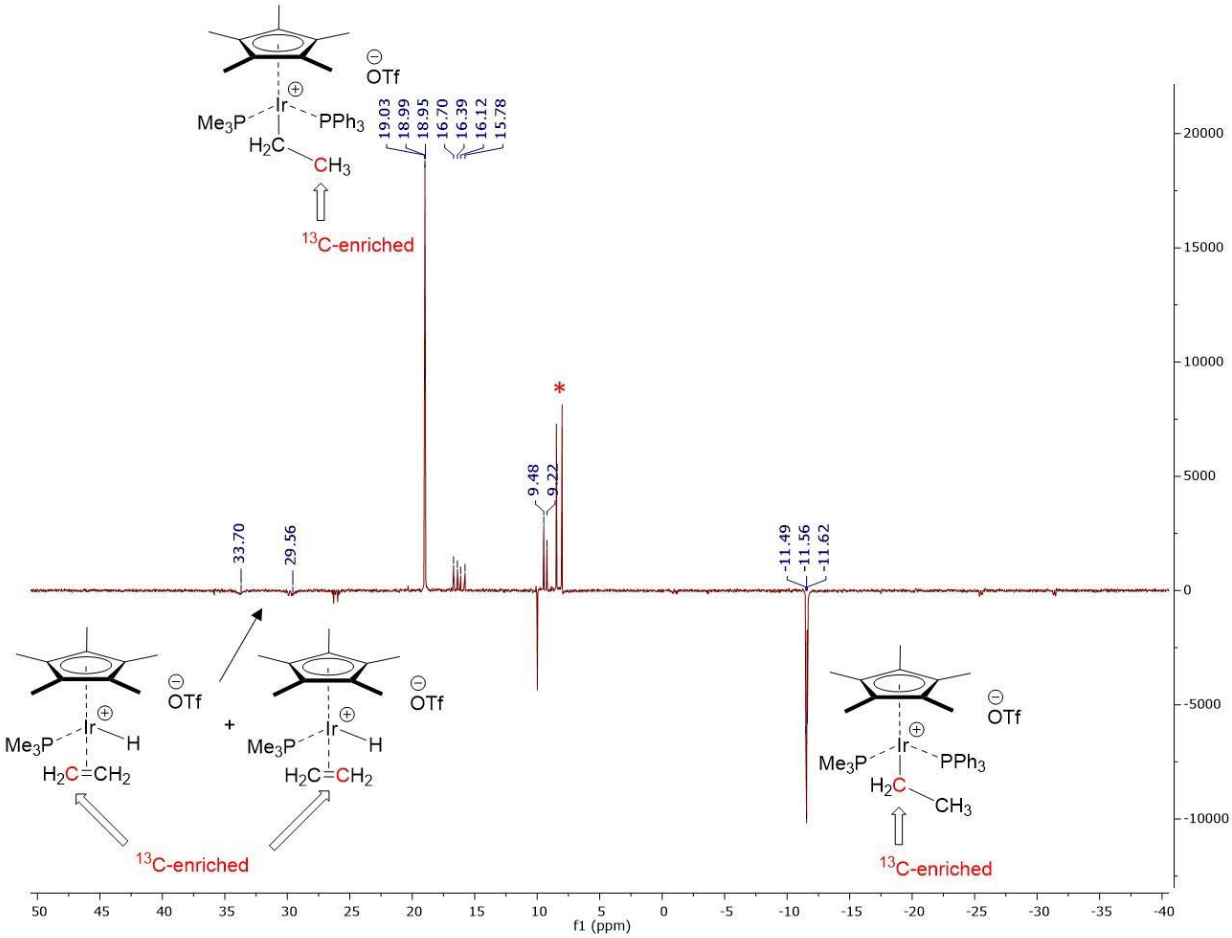


Figure S41. ^{13}C DEPT135 NMR spectrum (126 MHz, THF-d_8, 300 K) in the aliphatic region of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and$H_2{}^{13}CPPh_3$ after heating in a 50 °C bath for 7 hours. The other labelled peaks correspond to the methyl groups of Cp* ligand and the methyl groups of PMe_3 ligand. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. Other unlabelled peaks belong to unidentified side-products.

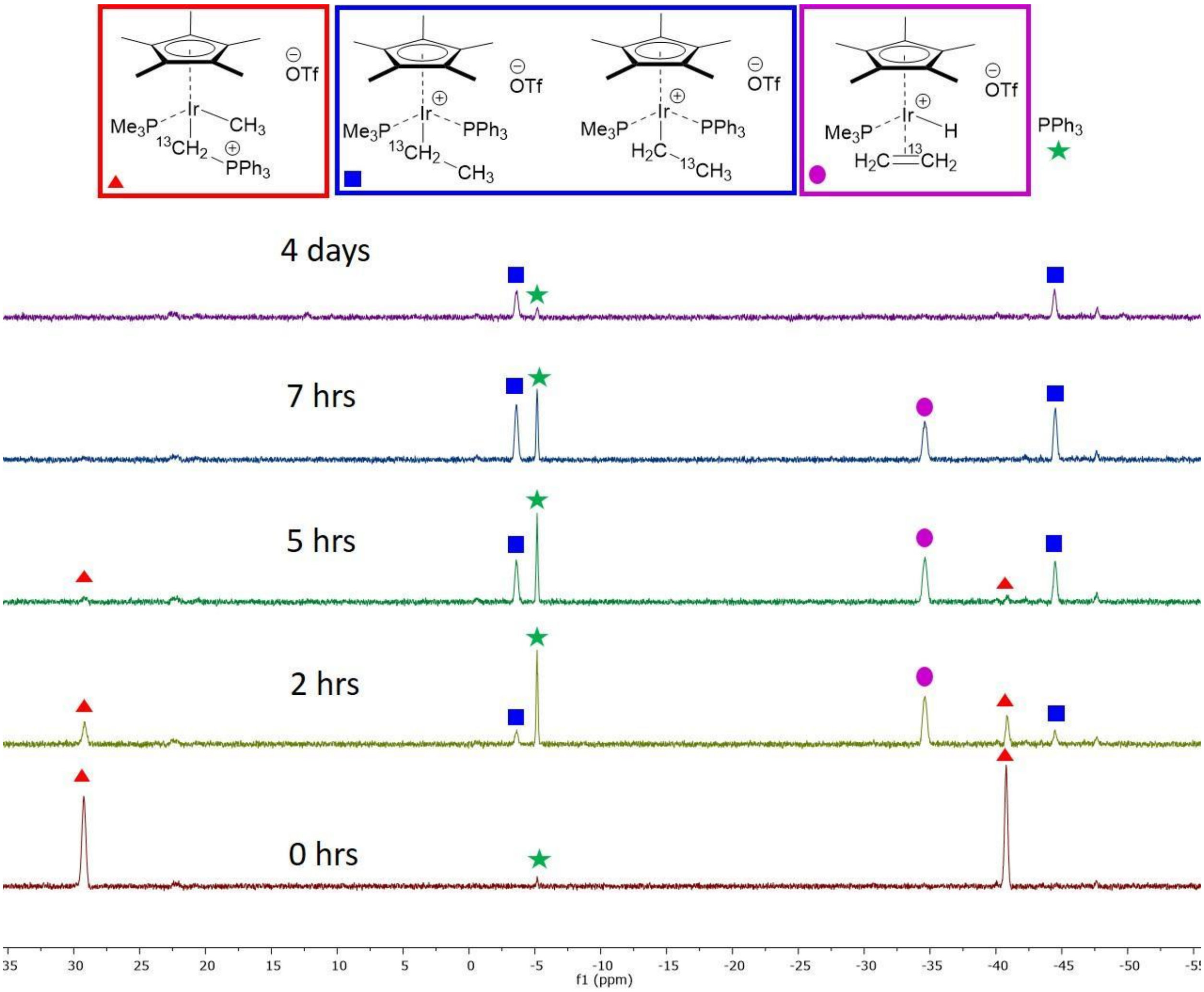


Figure S42. ^{31}P NMR spectra (162 MHz, THF-d_8, 300 K) of the reaction between Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and H$_2$^{13}CPPh$_3$ after heating in a 50 °C bath at various time intervals.

Low Temperature NMR Experiments: Spectra were collected at 223 K of the contents of the reaction between Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$ following heating at 50 °C for 7 hrs and then 12 hrs at room temperature. A concurrent reaction between Cp*(Me_3P)Ir(CH_3)(OTf) and unlabeled H_2CPPh_3 was subject to similar conditions.

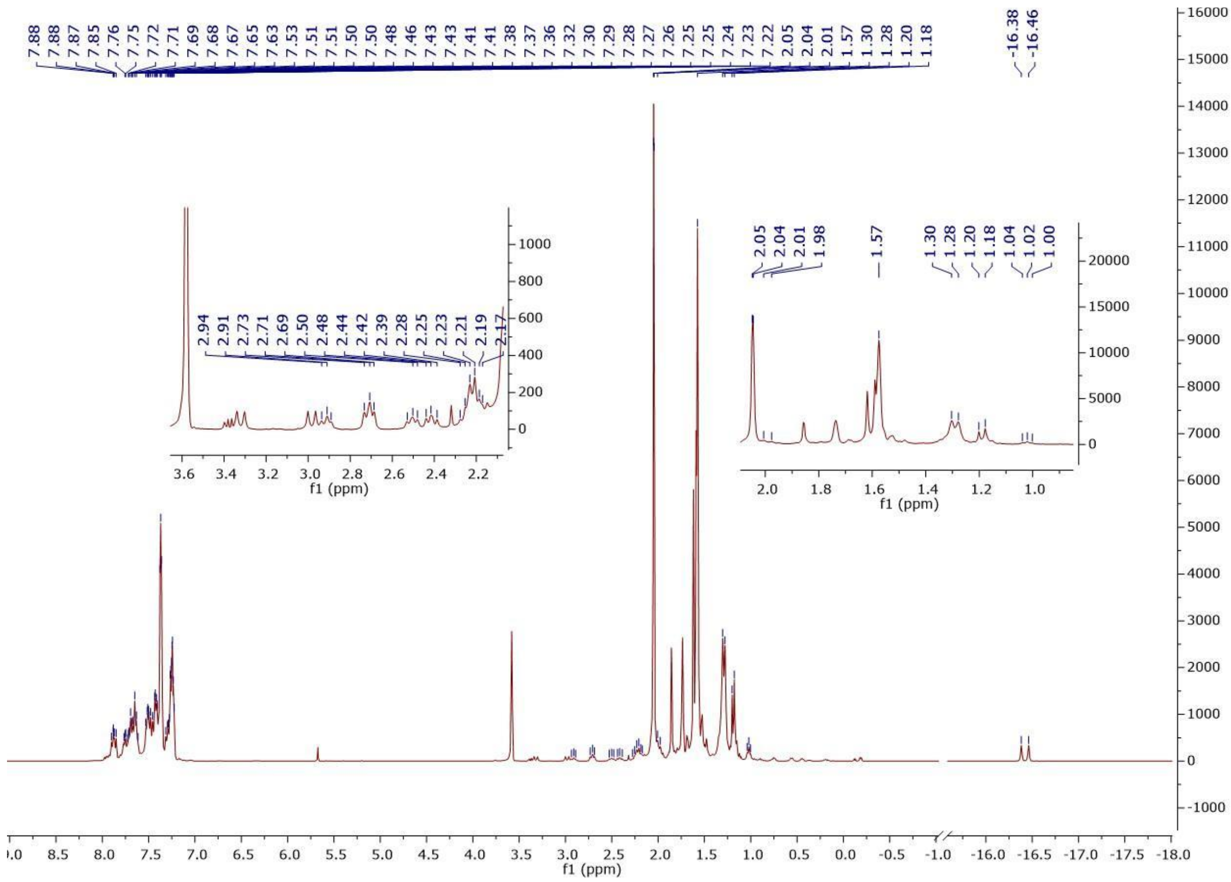


Figure S43. ^{1}H NMR spectrum (400 MHz, THF-d_8, 223 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$ following the procedure noted above.

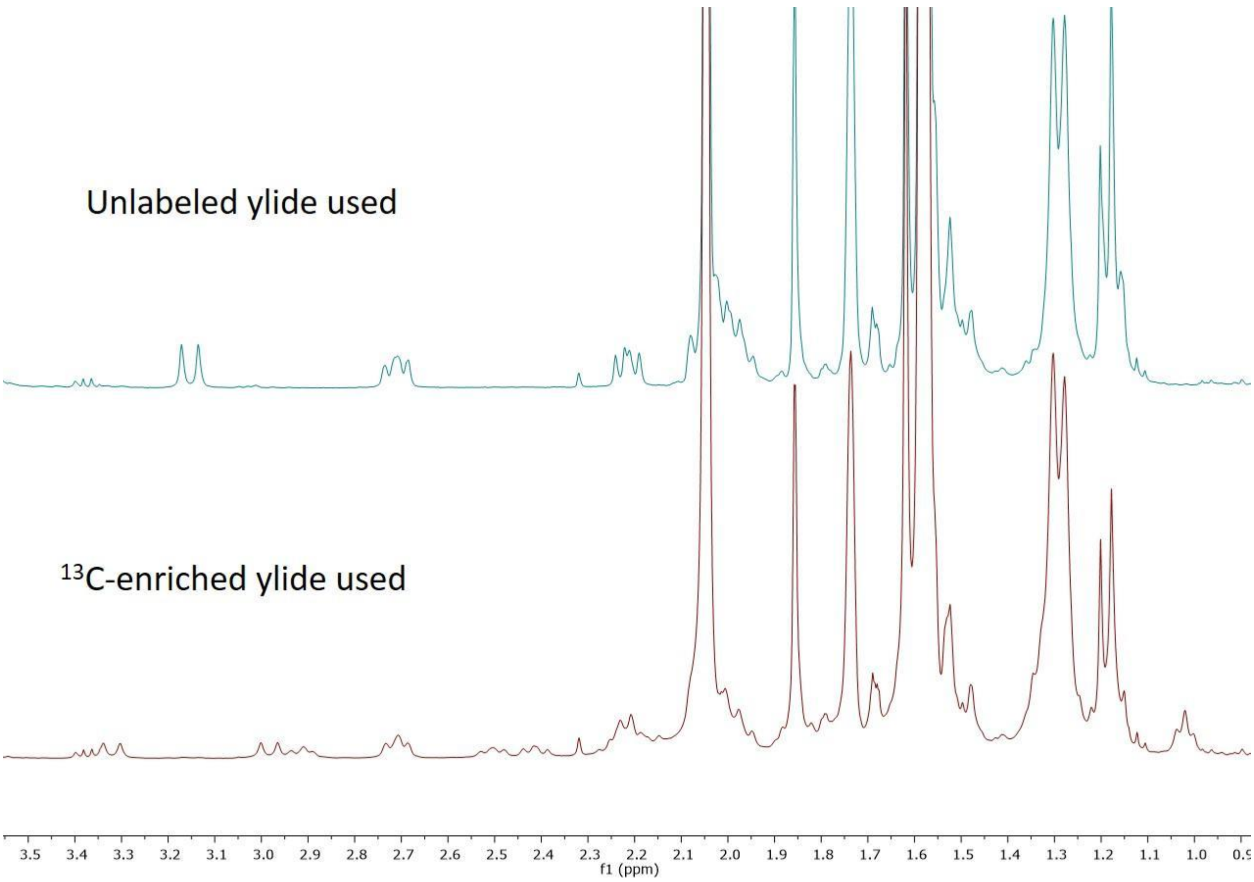


Figure S44. ^{1}H NMR spectra (400 MHz, THF-d_8, 223 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and H_2CPPh_3 (upper) or $H_2{}^{13}CPPh_3$ (lower) following the procedure noted above.

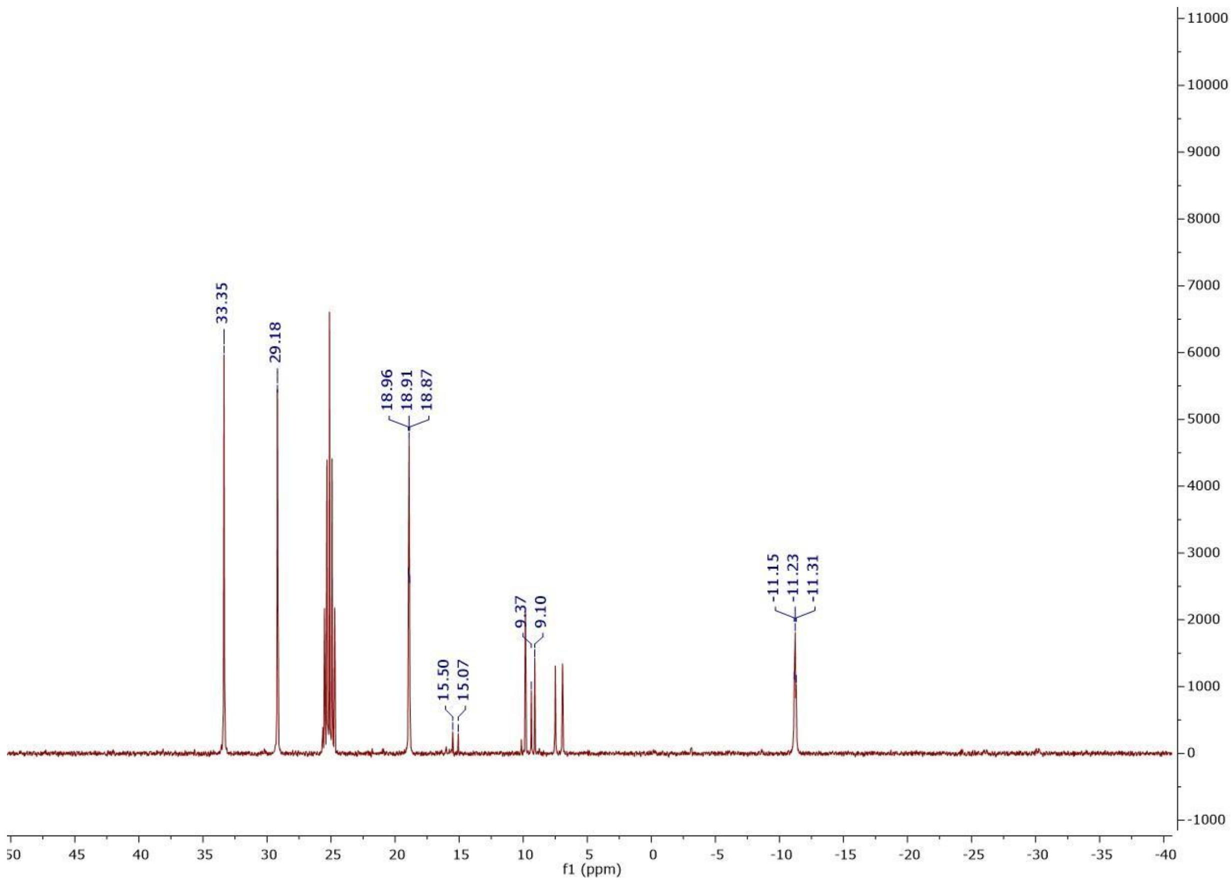


Figure S45. $^{13}C\{^1H\}$ NMR spectrum (101 MHz, THF-d_8, 223 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$ following the procedure noted above.

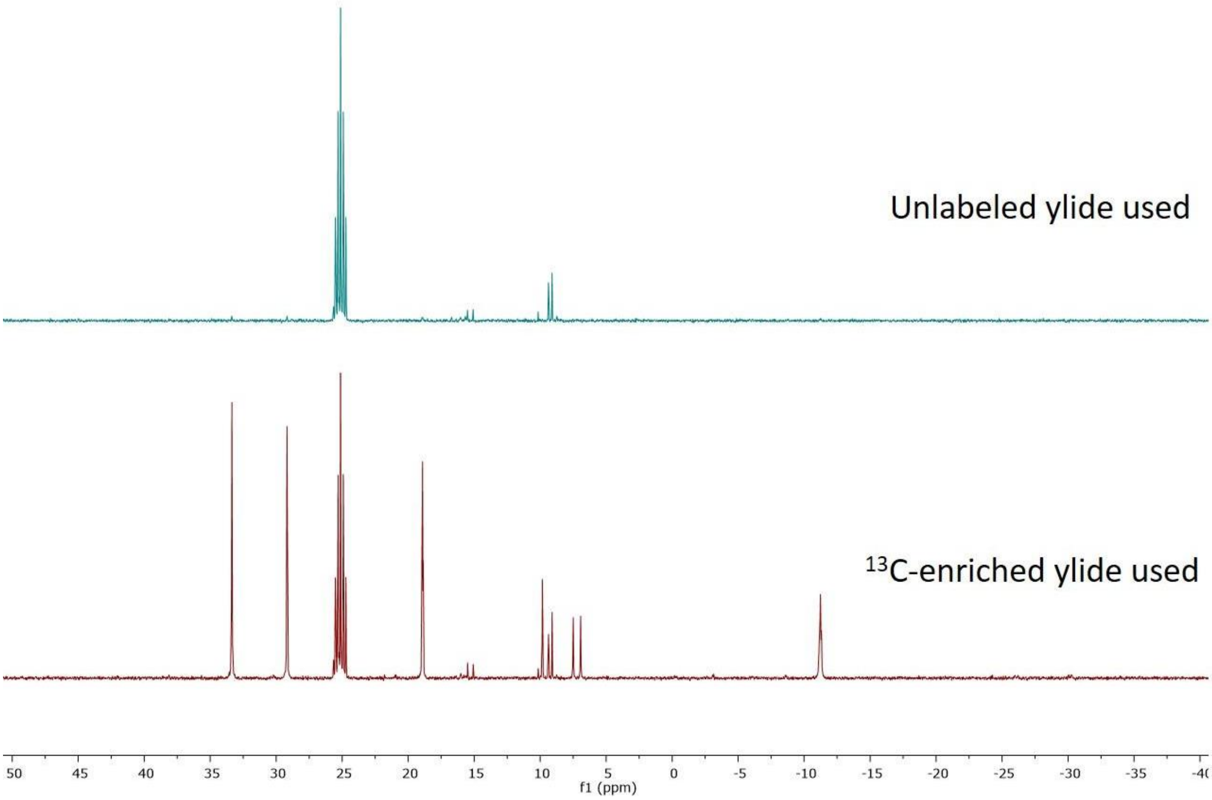


Figure S46. $^{13}C\{^1H\}$ NMR spectra (101 MHz, THF-d_8, 223 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and H_2CPPh_3 (upper) or $H_2{}^{13}CPPh_3$ (lower) following the procedure noted above.

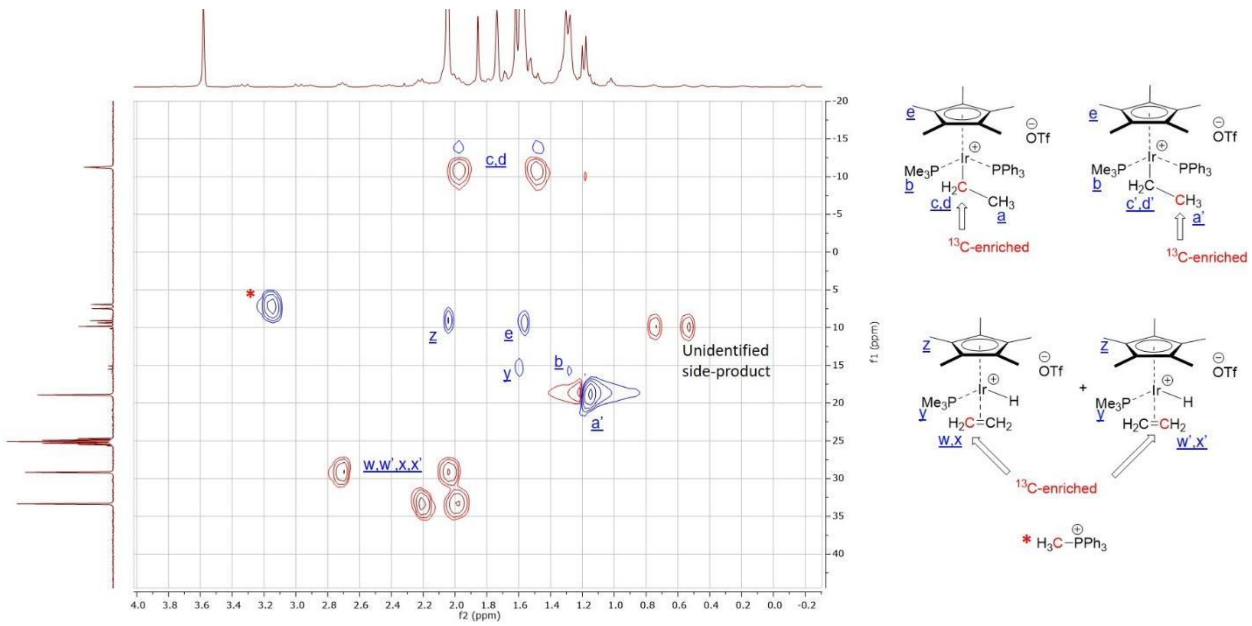


Figure S47. Decoupled ^1H-^{13}C HSQC NMR spectrum (400 MHz, THF-d_8, 223 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $H_2{}^{13}CPPh_3$ following the procedure noted above.

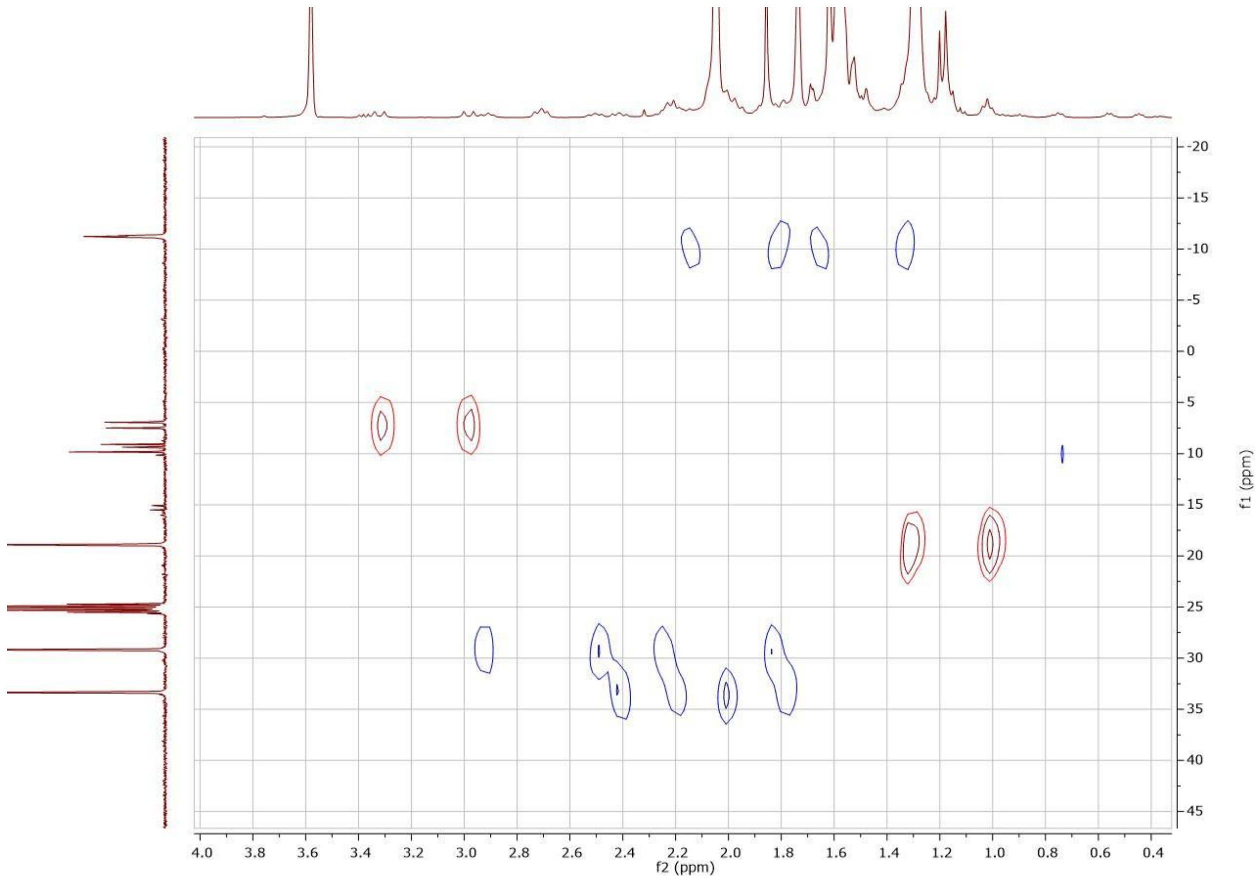
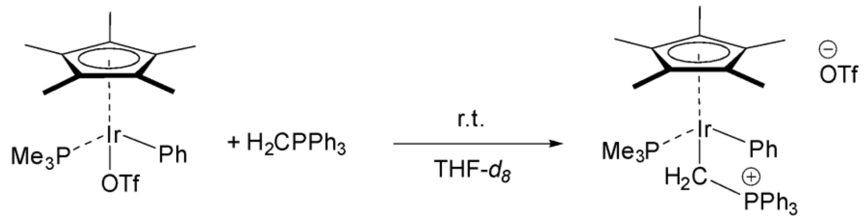


Figure S48. Non-decoupled ^{1}H-^{13}C HSQC NMR spectrum (400 MHz, THF-d_8, 223 K) of **1**-OTf-$^{13}CH_2CH_3$, **1**-OTf-$CH_2{}^{13}CH_3$ and **2**-OTf-^{13}C formed *in situ* from Cp*$(Me_3P)Ir(CH_3)(OTf)$ and $H_2{}^{13}CPPh_3$ following the procedure noted above.

Reaction of Cp*(Me$_3$P)Ir(C$_6$H$_5$)(OTf) with H$_2$CPPh$_3$: Crystals of Cp*(Me$_3$P)Ir(C$_6$H$_5$)(OTf) (15.4 mg, 24.4 µmol) and H$_2$CPPh$_3$ (6.7 mg, 24.4 µmol) were placed into a single vial, crushed into powder and mixed thoroughly together. Half a millilitre of THF-*d*$_8$ was then used to dissolve the contents, which were shaken/swirled quickly to promote mixing. The resulting yellow solution was then transferred to a J-Young NMR tube. NMR spectra were obtained within an hour after mixing, and then the tube and its contents were placed an oil bath at 50 °C for 5 hours after which further NMR spectra of the sample were obtained.



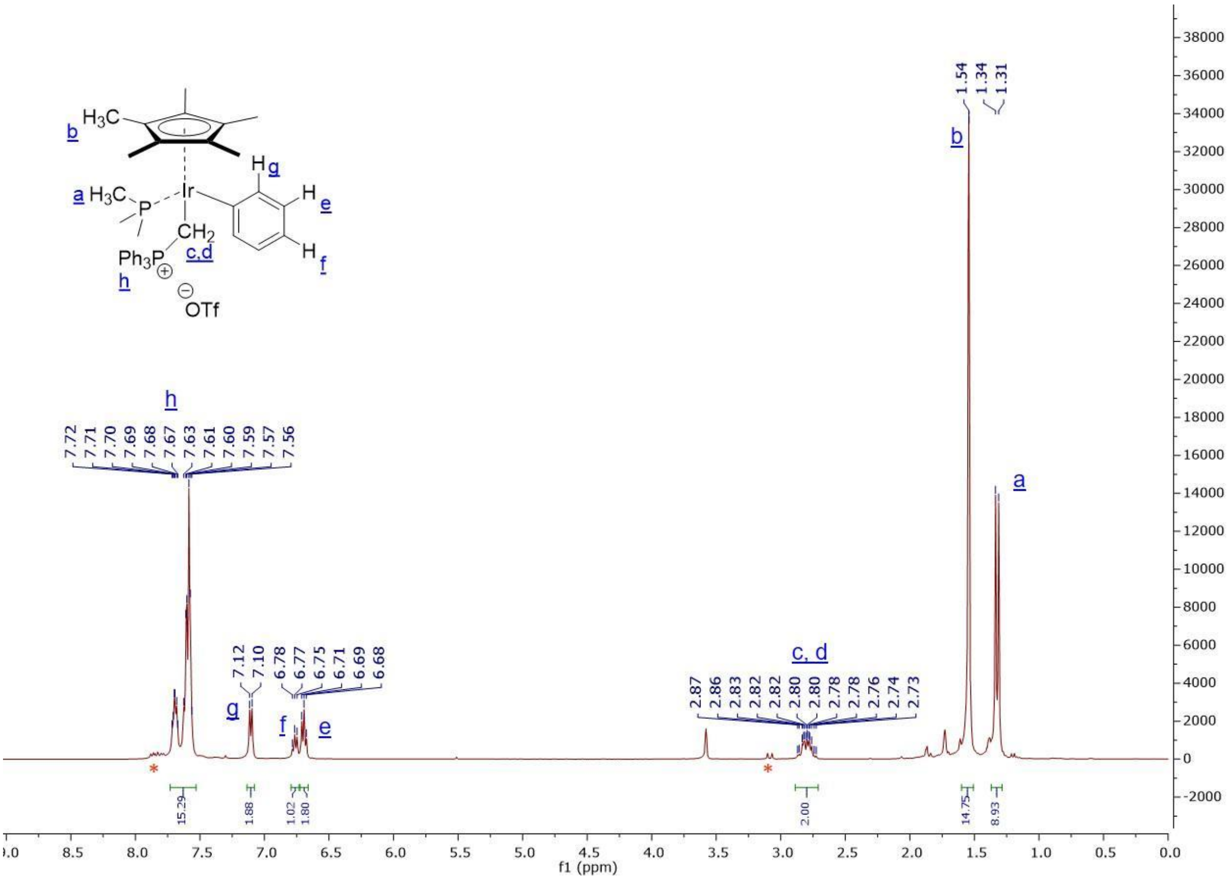


Figure S49. ^{1}H NMR spectrum (400 MHz, THF-*d*$_8$, 300 K) of [Cp*(Me$_3$P)(H$_2$CPPh$_3$)Ir(C$_6$H$_5$)][OTf] formed *in situ* from Cp*(Me$_3$P)Ir(C$_6$H$_5$)(OTf) and H$_2$CPPh$_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of H$_2$CPPh$_3$. All other unlabeled signals belong to unidentified side-products.

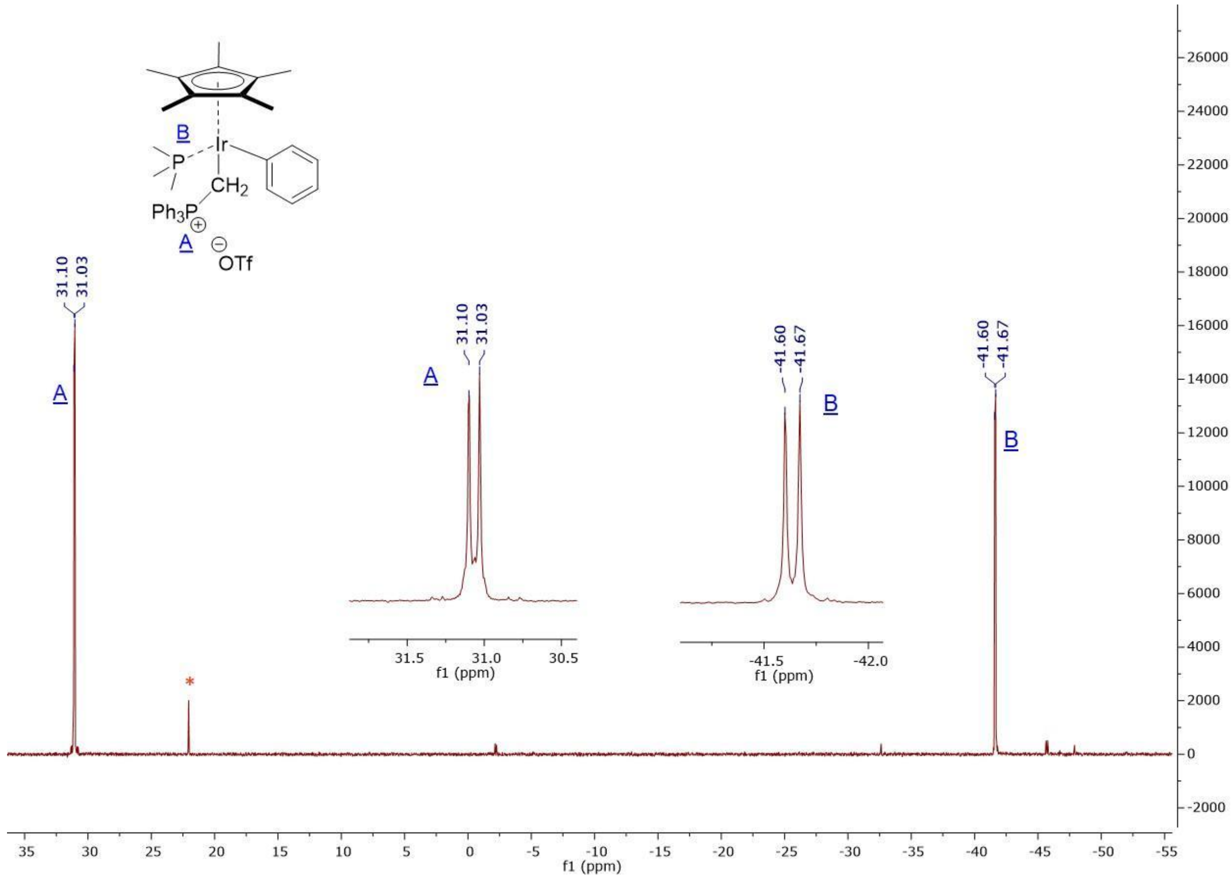


Figure S50. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)(H_2CPPh_3)Ir(C_6H_5)][OTf] formed *in situ* from Cp*(Me_3P)Ir(C_6H_5)(OTf) and H_2CPPh_3. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. Unlabeled peaks belong to unidentified side-products.

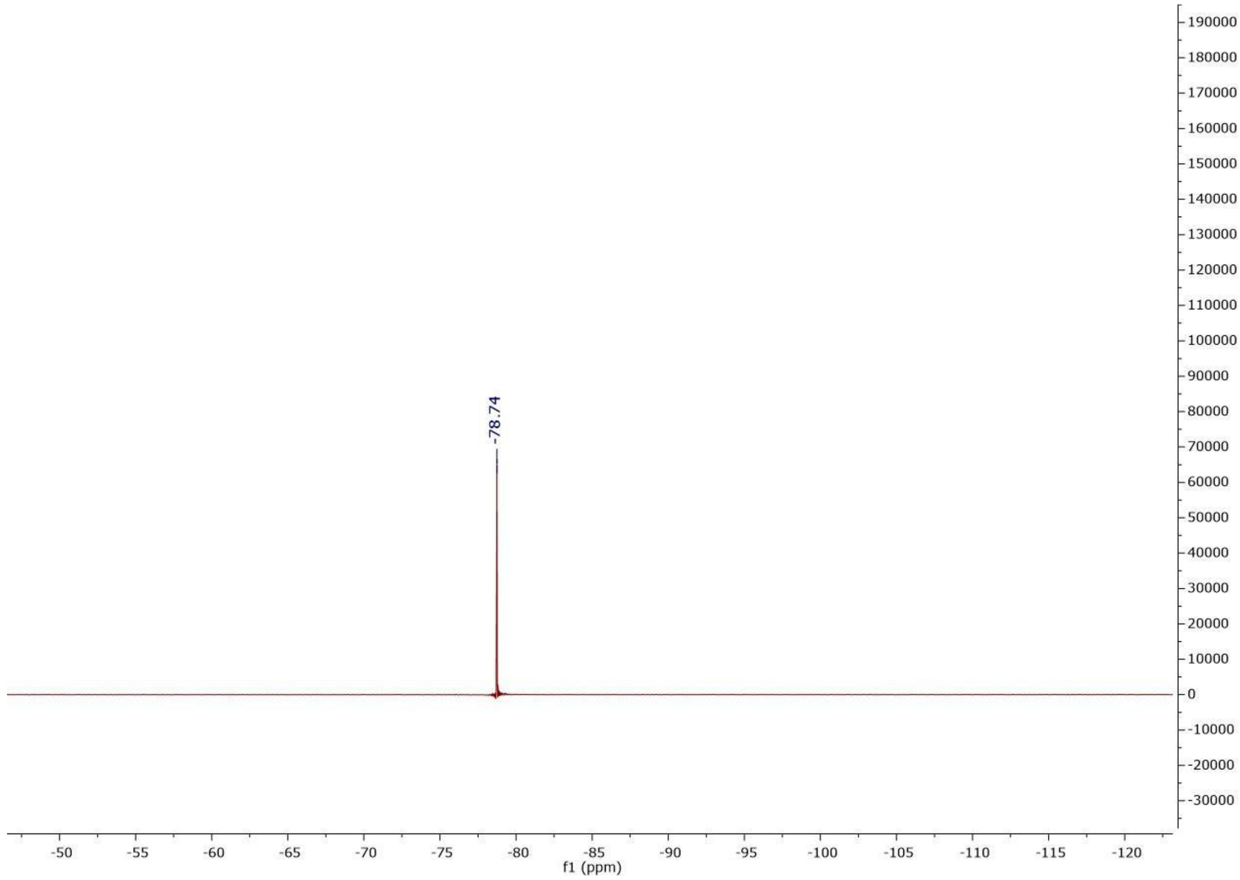


Figure S51. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)(H_2CPPh_3)Ir(C_6H_5)][OTf] formed *in situ* from Cp*(Me_3P)Ir(C_6H_5)(OTf) and H_2CPPh_3.

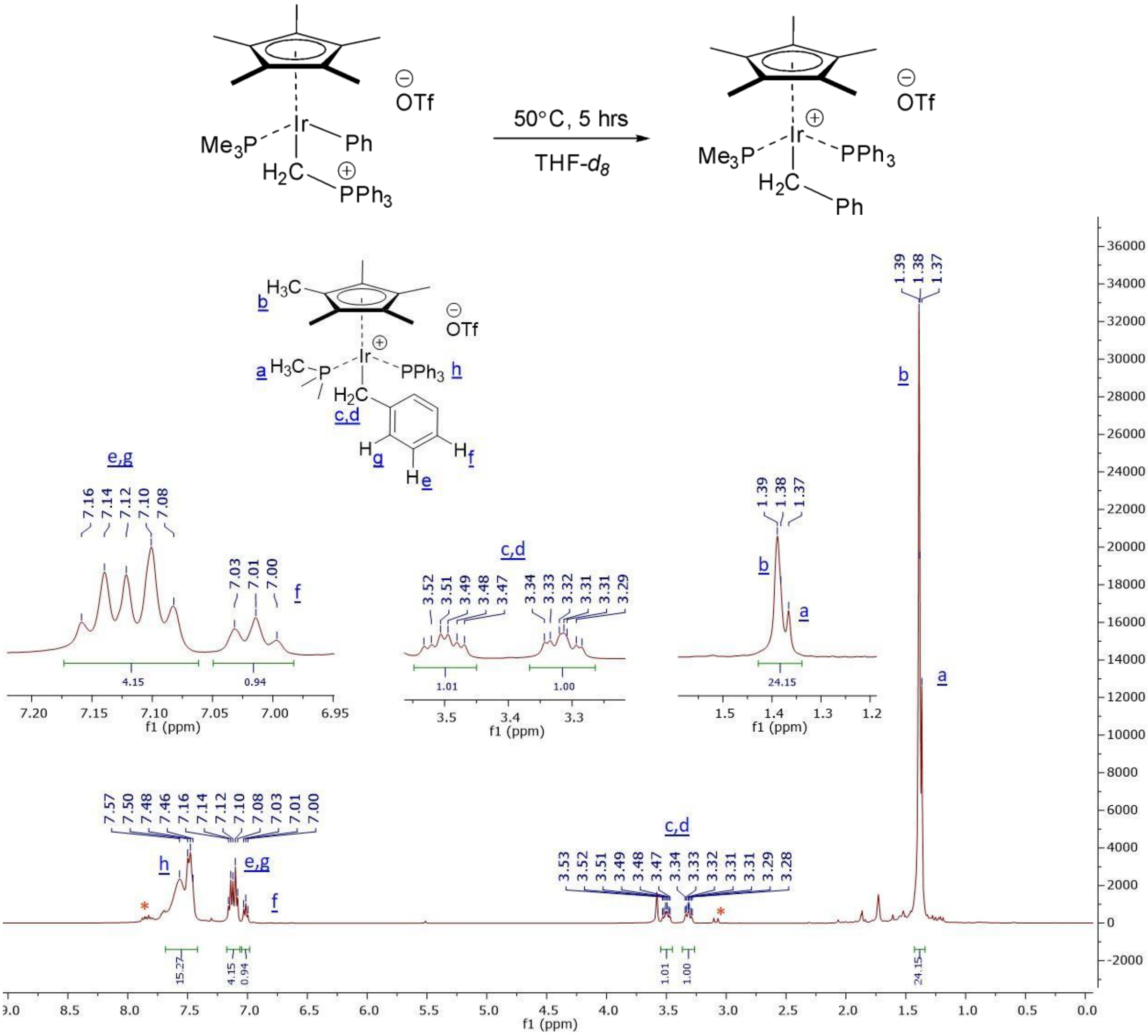


Figure S52. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of **3**-OTf formed *in situ* from Cp*(Me_3P)Ir(C_6H_5)(OTf) and H_2CPPh_3 and heating for 5 hrs at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. Unlabeled peaks belong to unidentified side-products.

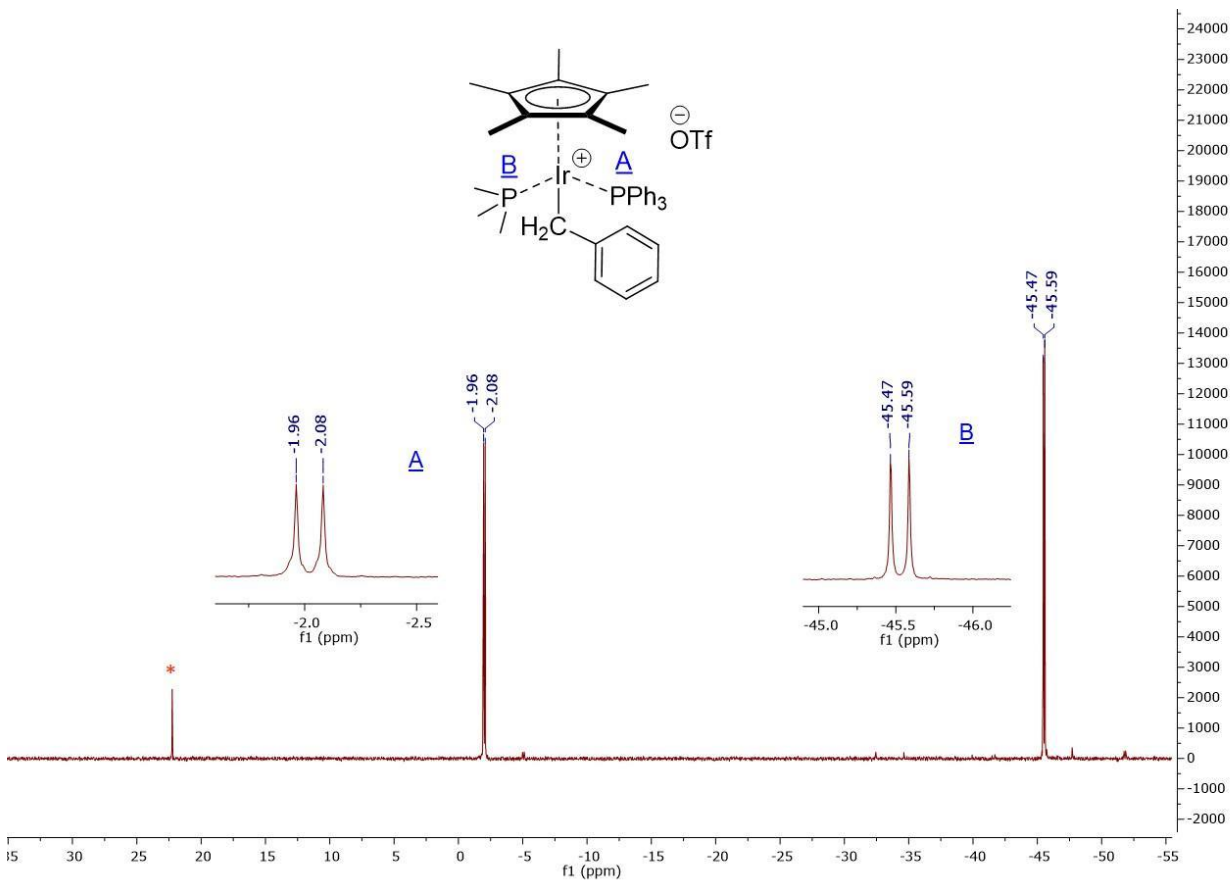


Figure S53. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of **3**-OTf formed *in situ* from Cp*(Me_3P)Ir(C_6H_5)(OTf) and H_2CPPh_3 and heating for 5 hrs at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H_2CPPh_3. Unlabeled peaks belong to unidentified side-products.

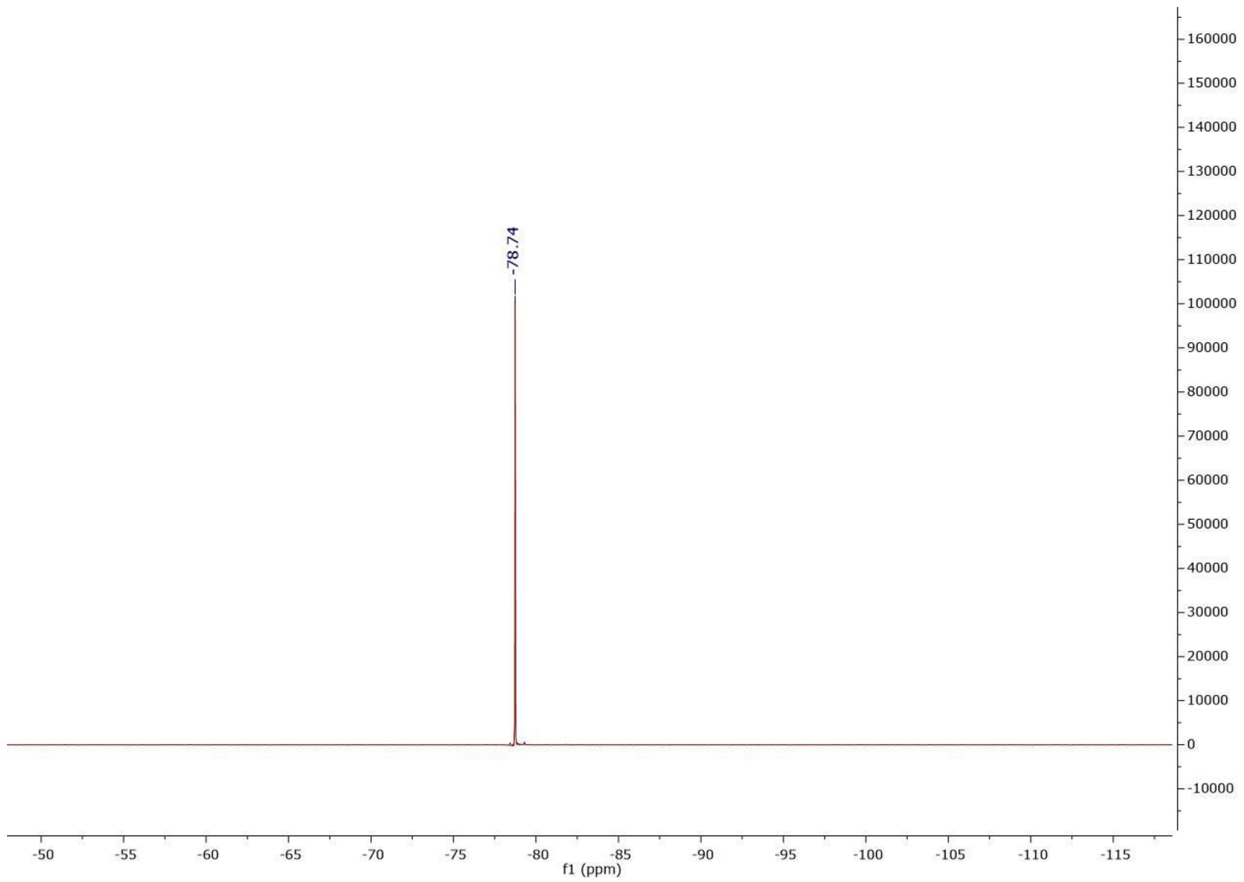
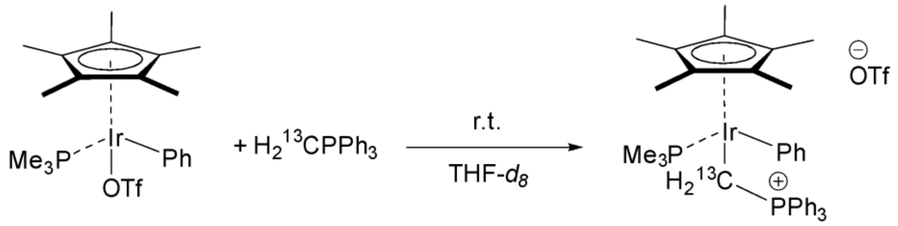


Figure S54. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of **3**-OTf formed *in situ* from $Cp^*(Me_3P)Ir(C_6H_5)(OTf)$ and H_2CPPh_3 and heating for 5 hrs at 50 °C.

Reaction of Cp*(Me₃P)Ir(C₆H₅)(OTf) with $H_2{}^{13}CPPh_3$: Performed as described above for Cp*(Me₃P)Ir(CH₃)(OTf), and using the ^{13}C-enriched ylide $H_2{}^{13}CPPh_3$; the sample was subject to heating for 15 hours rather than 5.



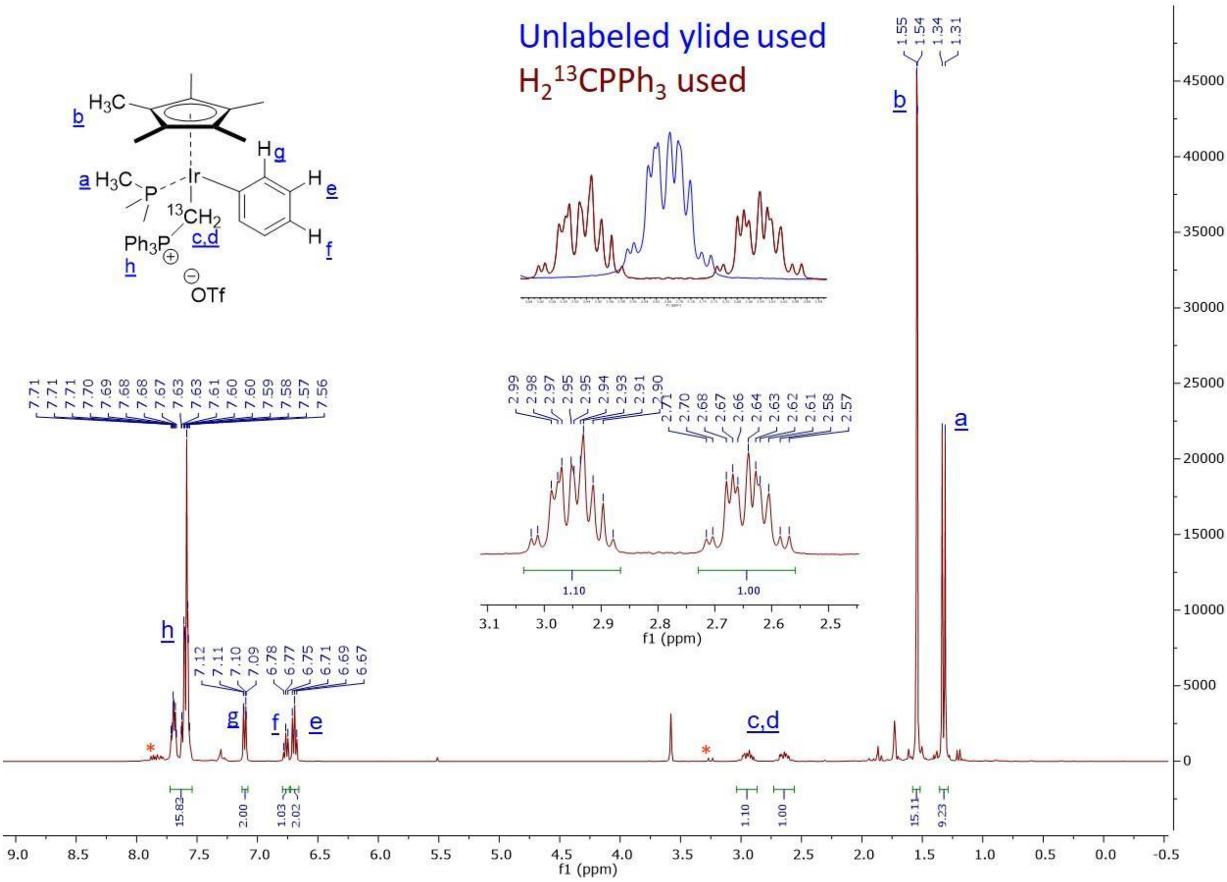


Figure S55. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of $[Cp^*(Me_3P)(H_2{}^{13}CPPh_3)Ir(C_6H_5)][OTf]$ formed *in situ* from Cp*(Me₃P)Ir(C₆H₅)(OTf) and $H_2{}^{13}CPPh_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. Unlabeled peaks belong to unidentified side-products.

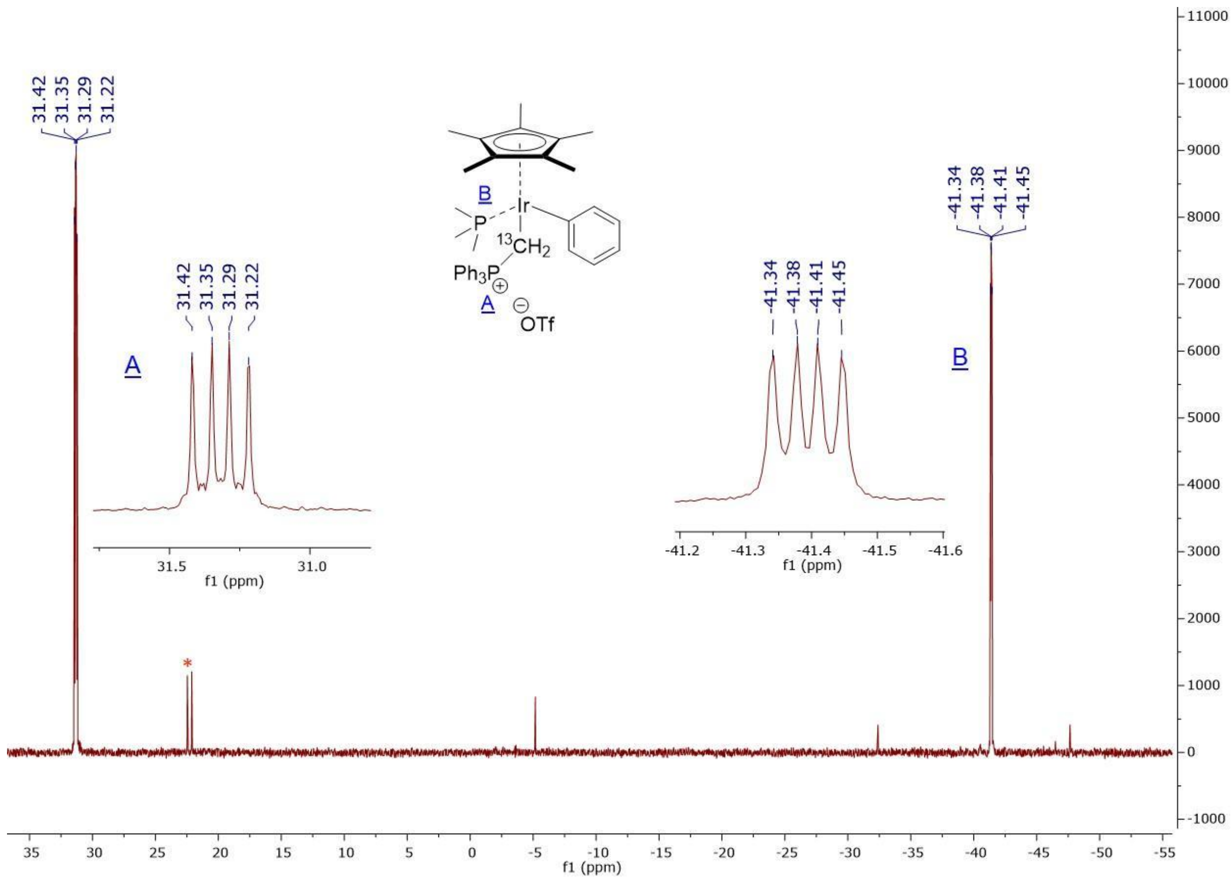


Figure S56. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)($H_2{}^{13}CPPh_3$)Ir(C_6H_5)][OTf] formed *in situ* from Cp*(Me_3P)Ir(C_6H_5)(OTf) and $H_2{}^{13}CPPh_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. Unlabeled peaks belong to unidentified side-products.

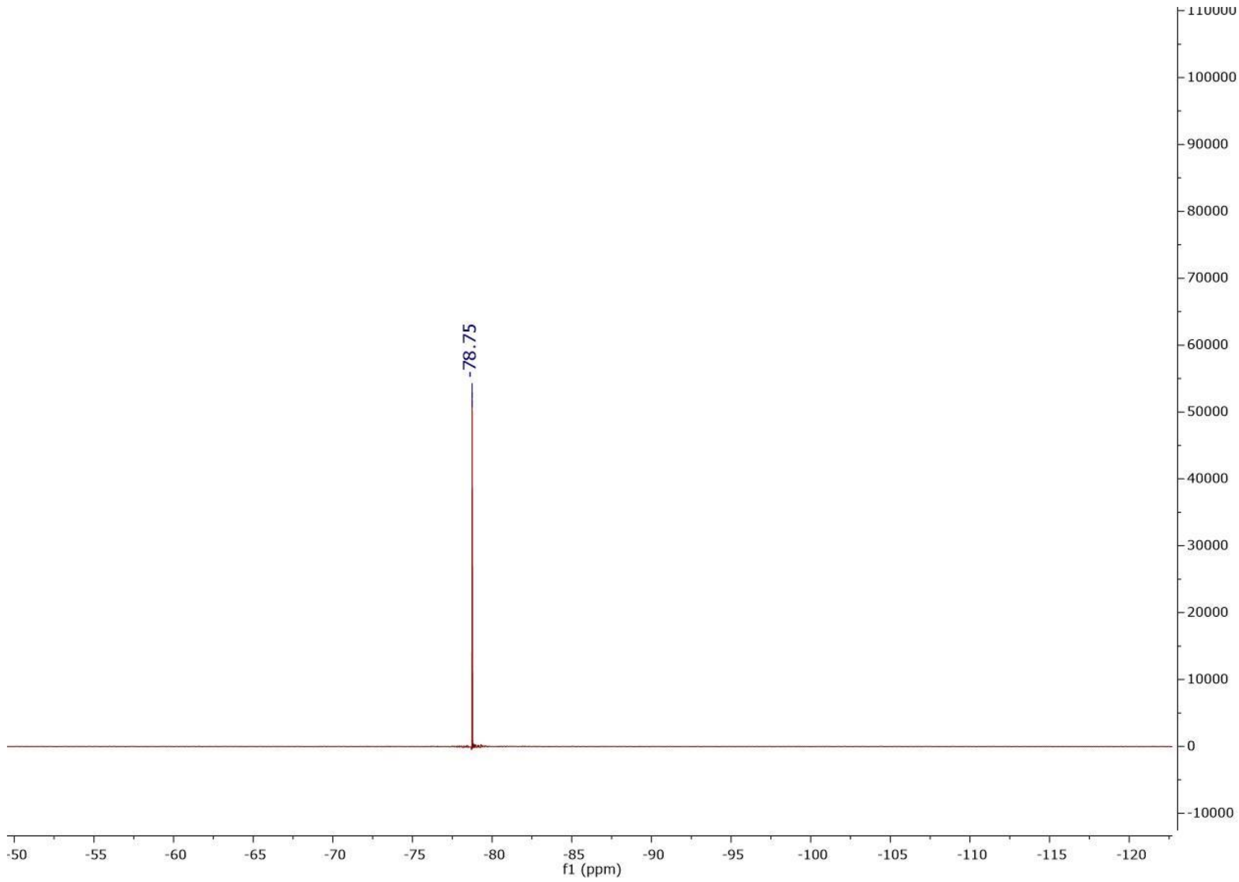


Figure S57. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)(H_2CPPh_3)Ir(C_6H_5)][OTf] formed *in situ* from Cp*(Me_3P)Ir(C_6H_5)(OTf) and $H_2{}^{13}CPPh_3$.

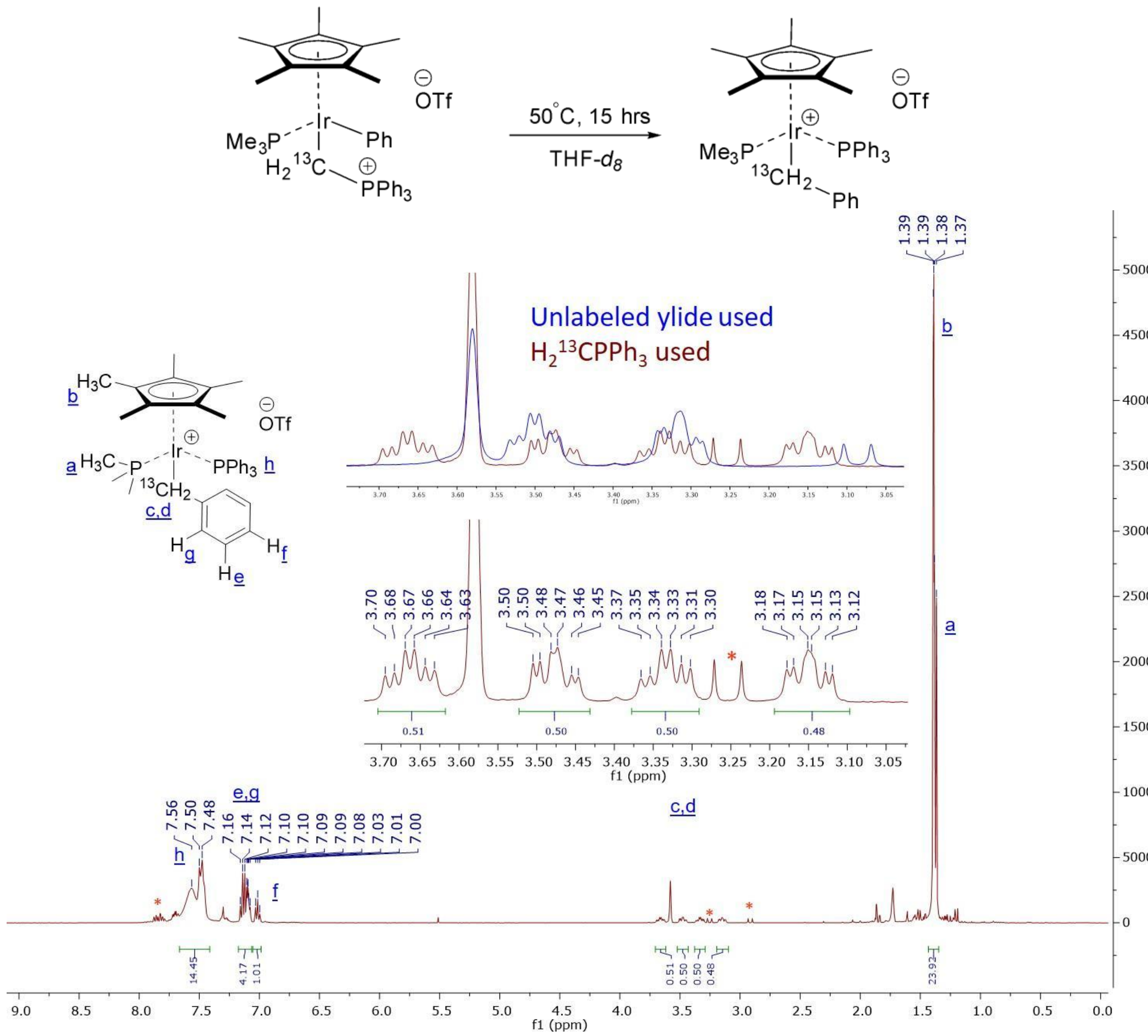


Figure S58. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of **3**-OTf-^{13}C formed *in situ* from Cp*(Me$_3$P)Ir(C$_6$H$_5$)(OTf) and H$_2$^{13}CPPh$_3$ and heating for 15 hrs at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of H$_2$^{13}CPPh$_3$. Unlabeled peaks belong to unidentified side-products.

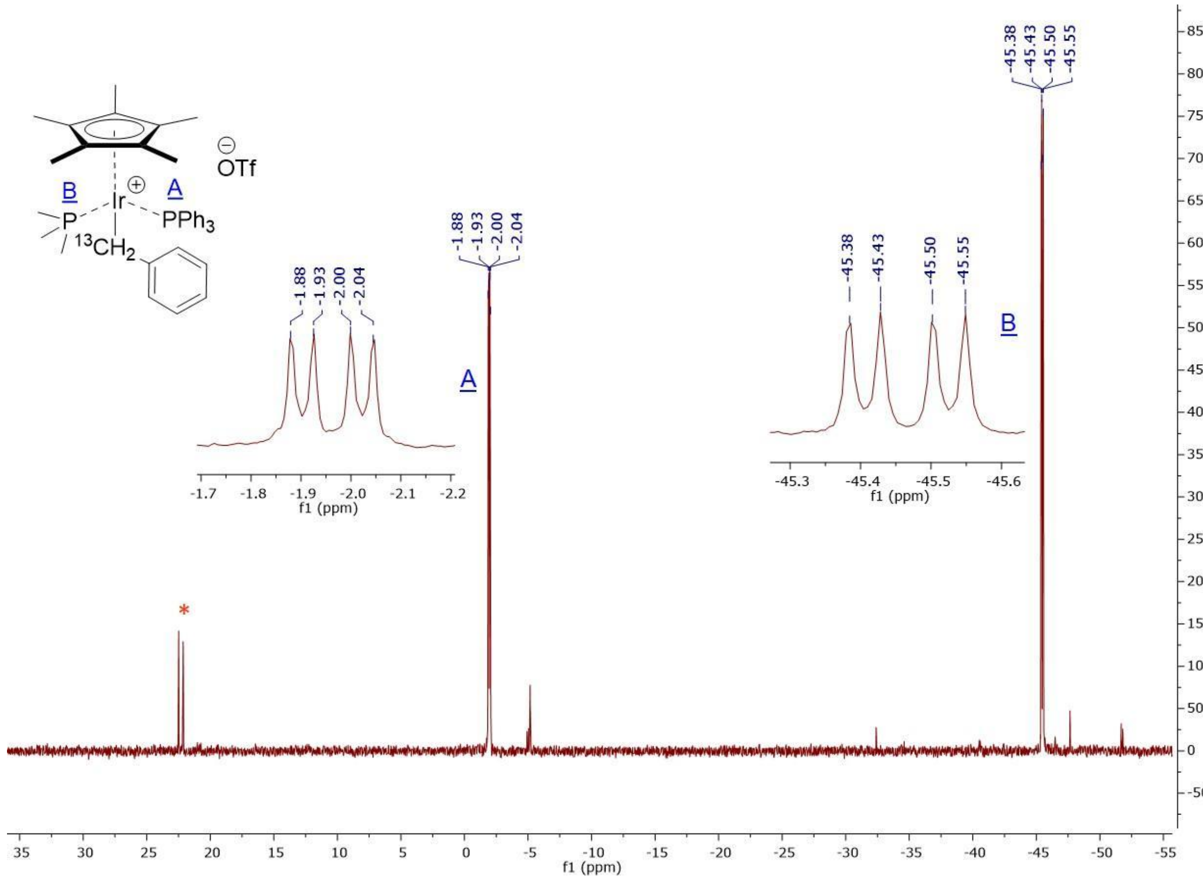


Figure S59. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of **3**-OTf-^{13}C formed *in situ* from Cp*$(Me_3P)Ir(C_6H_5)(OTf)$ and $H_2{}^{13}CPPh_3$ and heating for 15 hrs at 50 °C. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$. Unlabelled peaks belong to unidentified side-products.

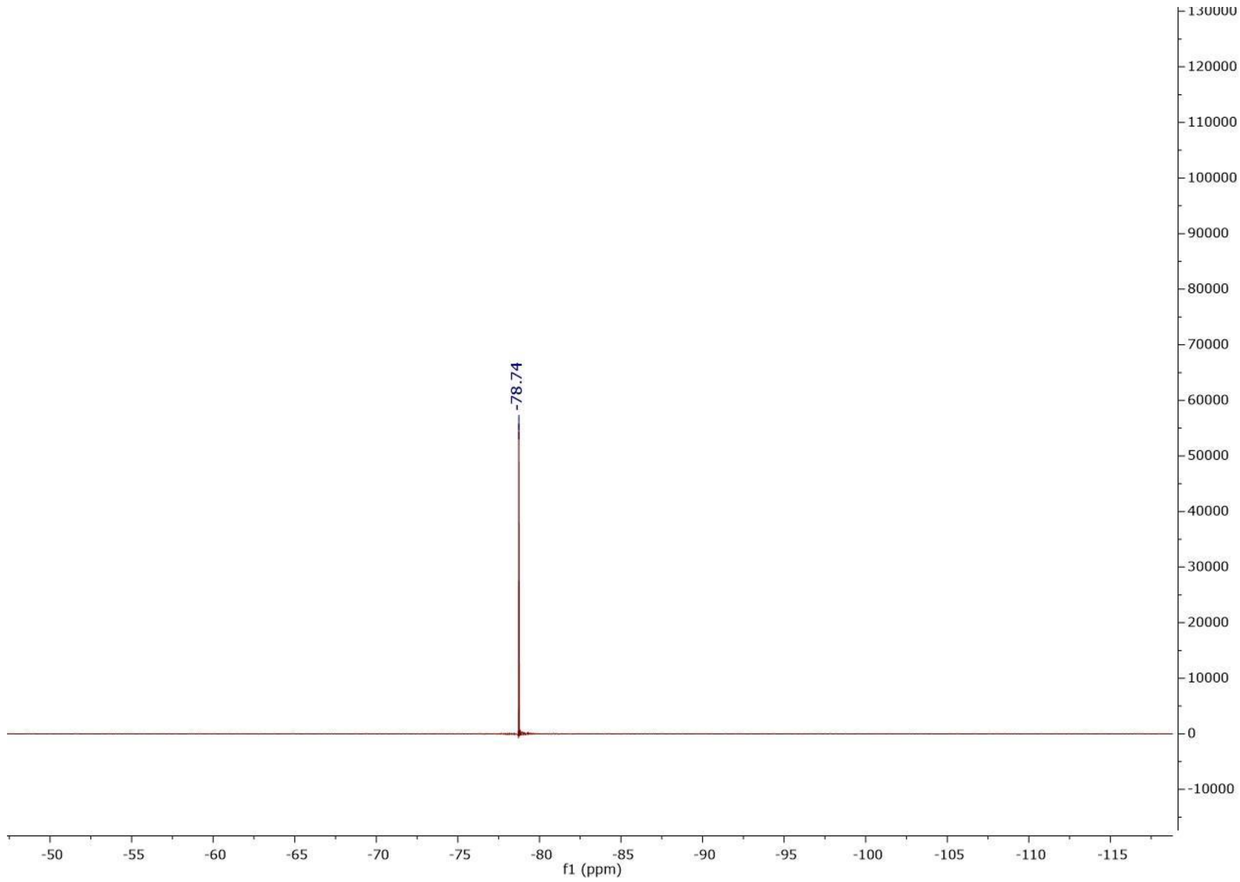


Figure S60. $^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, THF-d_8, 300 K) of **3**-OTf-^{13}C formed *in situ* from Cp*$(Me_3P)Ir(C_6H_5)(OTf)$ and $H_2{}^{13}CPPh_3$ and heating for 15 hrs at 50 °C.

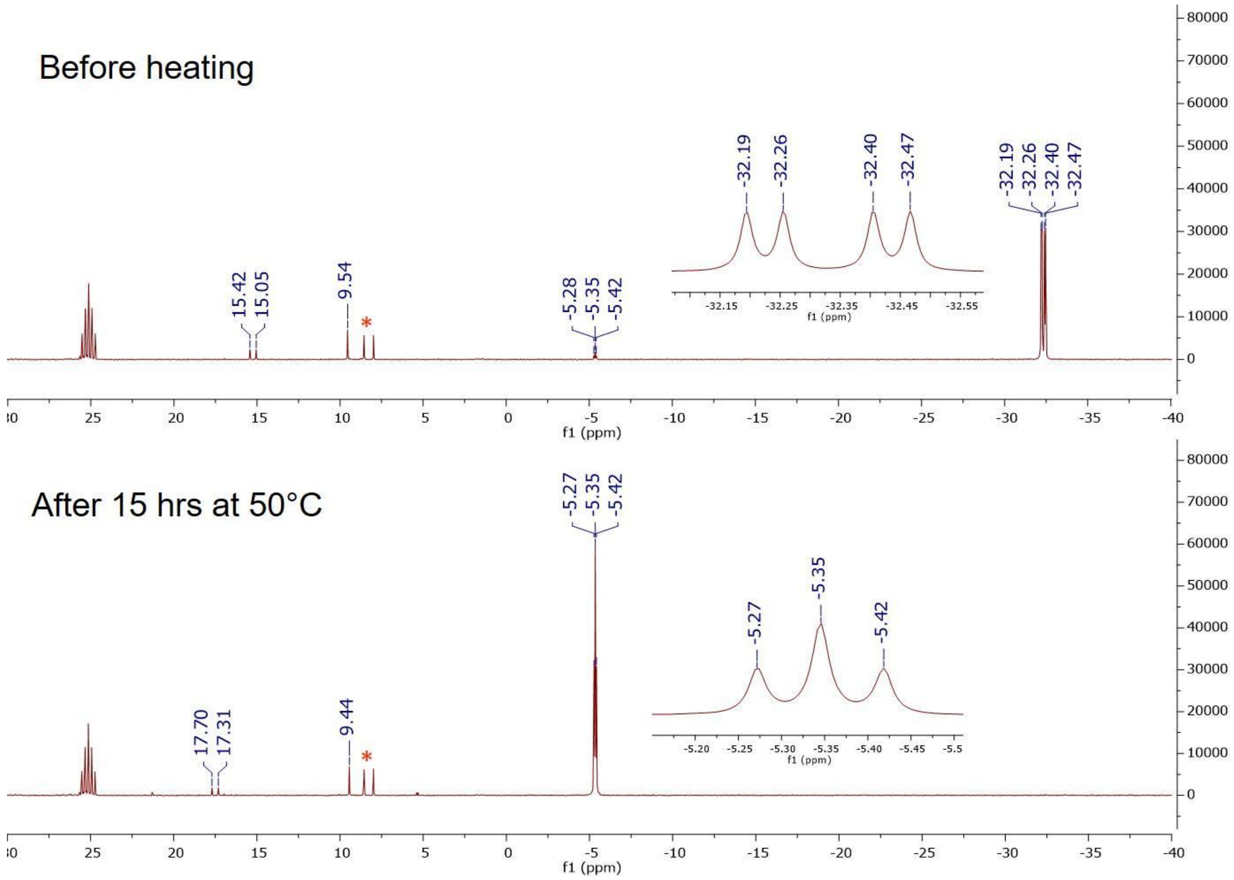


Figure S61. Two $^{13}C\{^{1}H\}$ NMR spectra (101 MHz, THF-d_8, 300 K) in the aliphatic region of the contents of the reaction between Cp*(Me_3P)Ir(C_6H_5)(OTf) and $H_2{}^{13}CPPh_3$ before heating the sample and after heating overnight (15 hrs) in a 50 °C bath. Note that by the time the first spectrum was recorded, some conversion to the final product is already observed. The other labelled peaks correspond to the methyl groups of Cp* ligand and the methyl groups of PMe_3 ligand. Peaks labeled with "*" belong to the phosphonium salt by protonation of $H_2{}^{13}CPPh_3$.

Reaction of Cp*(Me$_3$P)Ir(CH$_3$)(OTf) with PhHCPMe$_3$: Crystals of the iridium complex (26.4 mg, 46.5 µmol) and the ylide (8.1 mg, 48.7 µmol) were added into on vial then crushed into a powder together then dissolved in THF-d_8 and placed into a J-Young NMR tube. This resulted in the formation of a pair of diastereomers of the ylide adduct in an approximately 7:10 ratio. The minor of these two has slightly broadened signals in the ^{1}H NMR spectrum, and the Ir-bound methyl group and Ir-bound ylide carbon could not be located in the ^{13}C{^{1}H} spectrum. Interestingly, it appears that the configuration of the major diastereomer in solution situates the phosphorus atoms in such a way that coupling is not observed between them, i.e. the dihedral angle is such that ^3J-coupling is minimized. It was not clear from the experiments conducted which signals belong to which diastereomer.

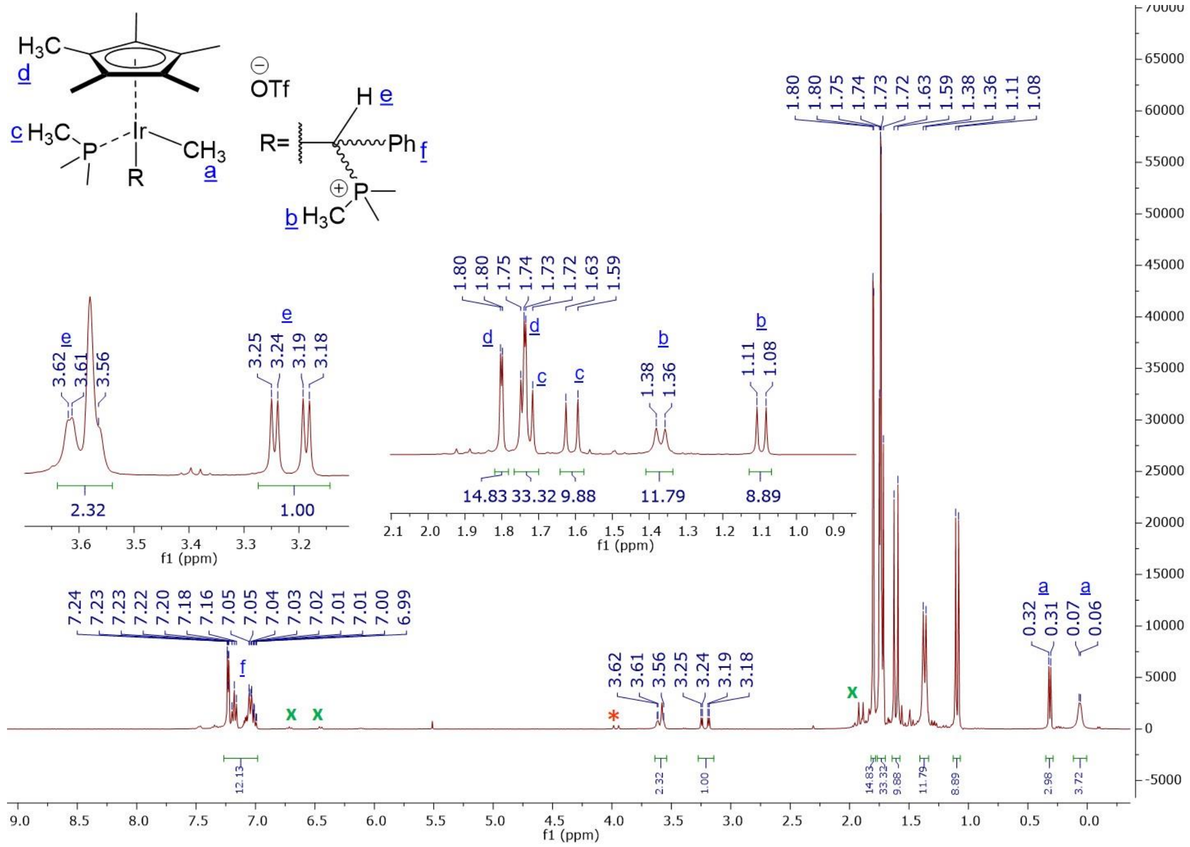


Figure S62. ^{1}H NMR spectrum (400 MHz, THF-d_8, 300 K) of [Cp*(Me$_3$P)(PhHCPMe$_3$)Ir(CH$_3$)][OTf] formed *in situ* from Cp*(Me$_3$P)Ir(CH$_3$)(OTf) and PhHCPMe$_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of PhHCPMe$_3$. Peaks labeled with "x" belong to excessive ylide. All other unlabeled signals belong to unidentified side-products.

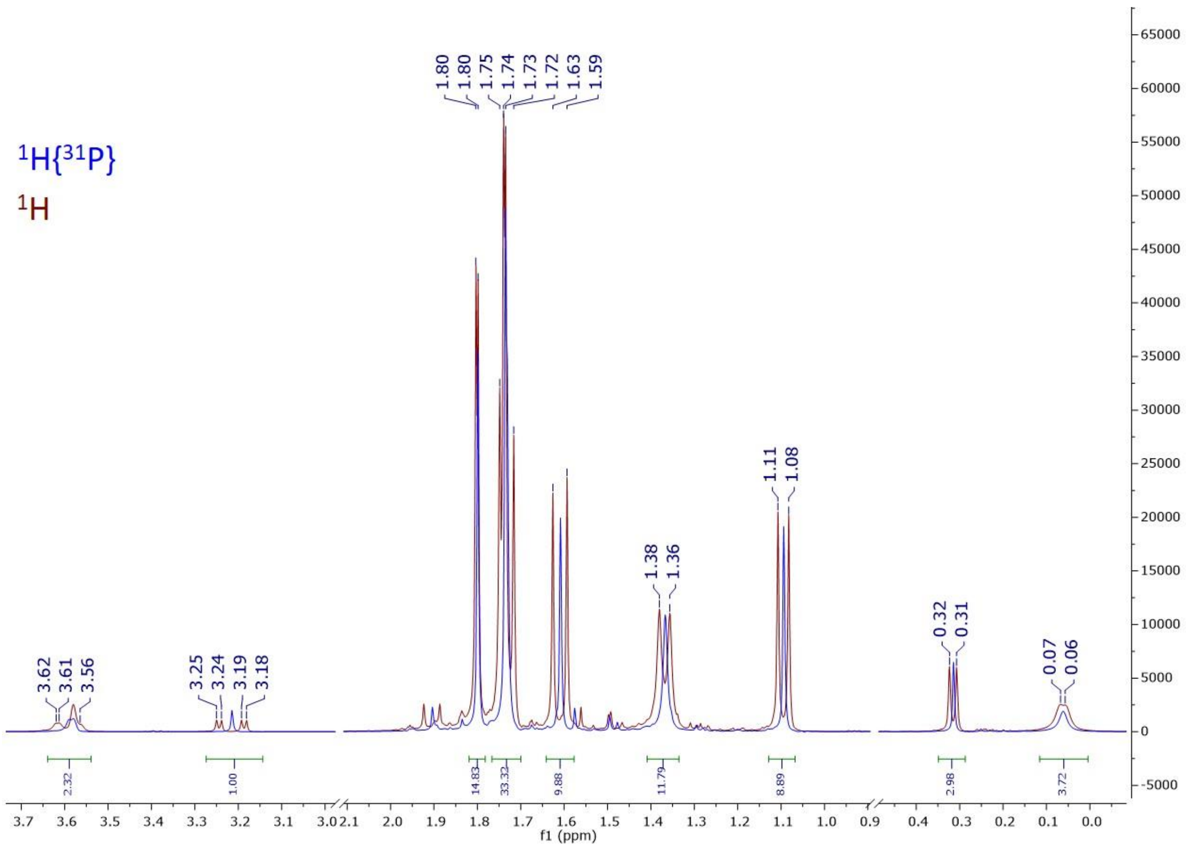


Figure S63. Inserts from the $^1H\{^{31}P\}$ NMR spectrum (400 MHz, THF-d_8, 300 K)(blue) of [Cp*(Me_3P)($PhHCPMe_3$)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $PhHCPMe_3$ in the aliphatic region overlaid onto the ^1H spectrum (maroon) of the same chemical shift range.

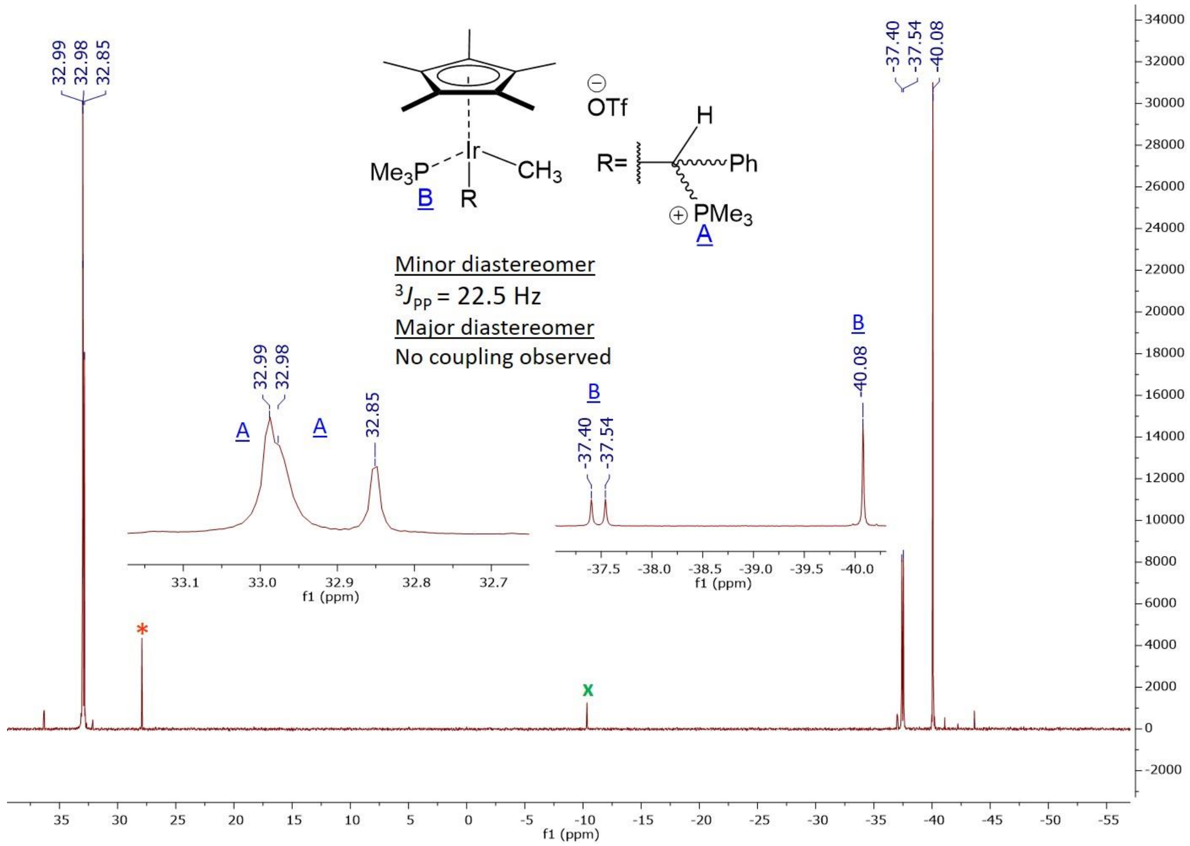


Figure S64. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)($PhHCPMe_3$)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $PhHCPMe_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of $PhHCPMe_3$. Peaks labeled with "**x**" belong to excessive ylide. All other unlabeled signals belong to unidentified side-products.

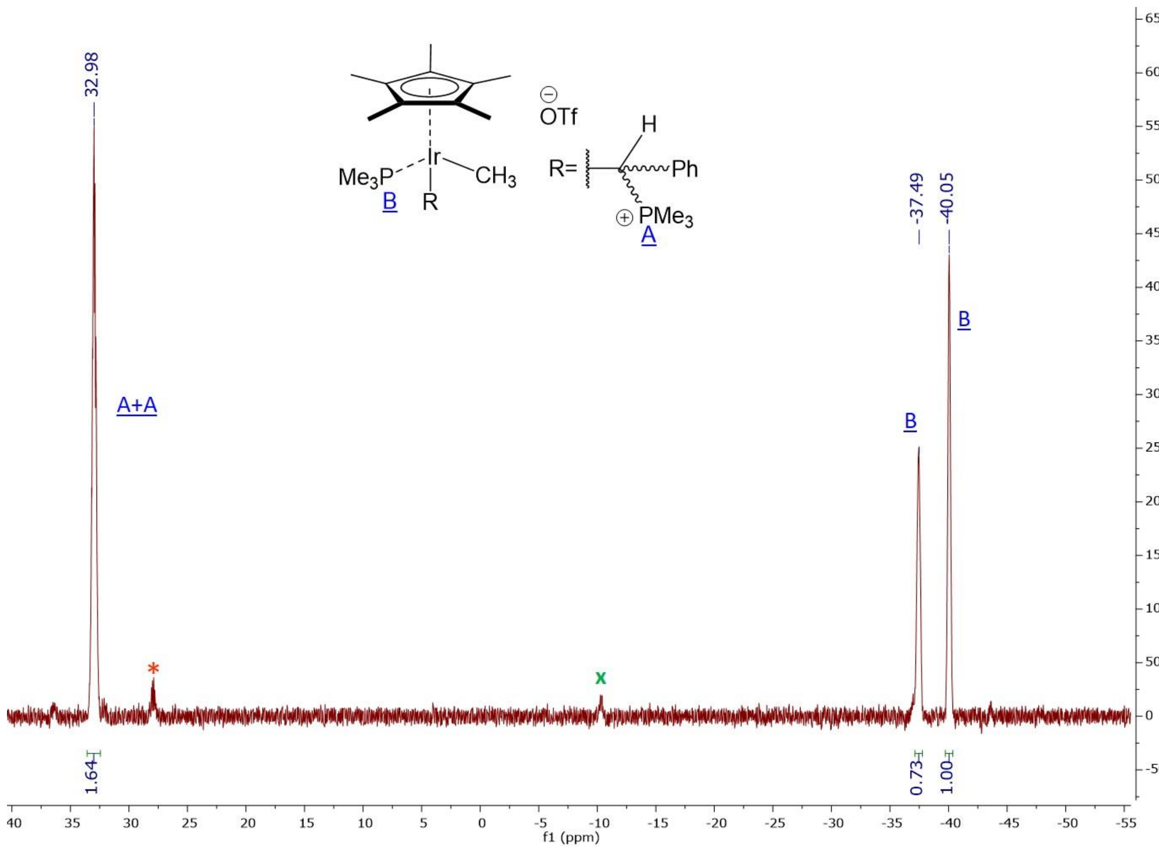


Figure S65. ${}^{31}P$ NMR spectrum (162 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)($PhHCPMe_3$)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $PhHCPMe_3$. Peaks labeled with "*" belong to the phosphonium salt by protonation of $PhHCPMe_3$. Peaks labeled with "**x**" belong to excessive ylide. All other unlabeled signals belong to unidentified side-products.

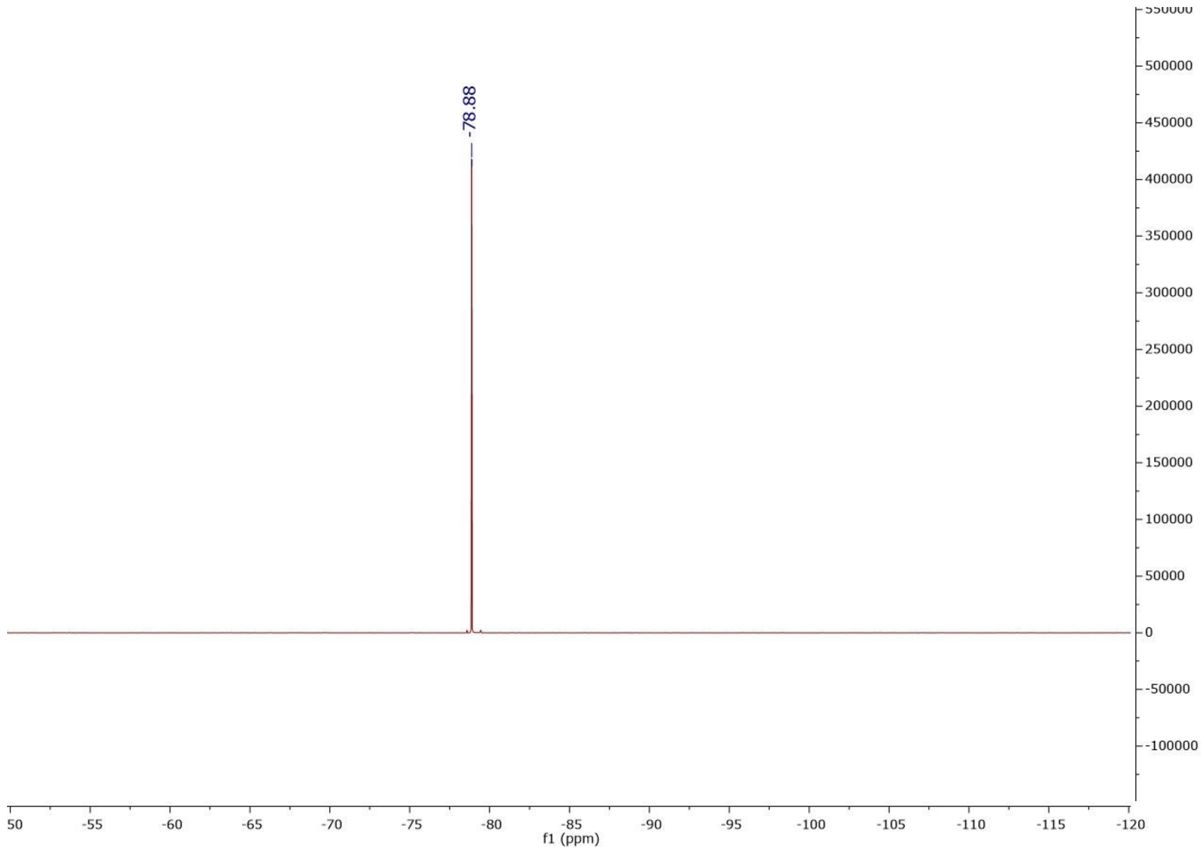


Figure S66. ^{19}F NMR spectrum (376 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)($PhHCPMe_3$)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $PhHCPMe_3$.

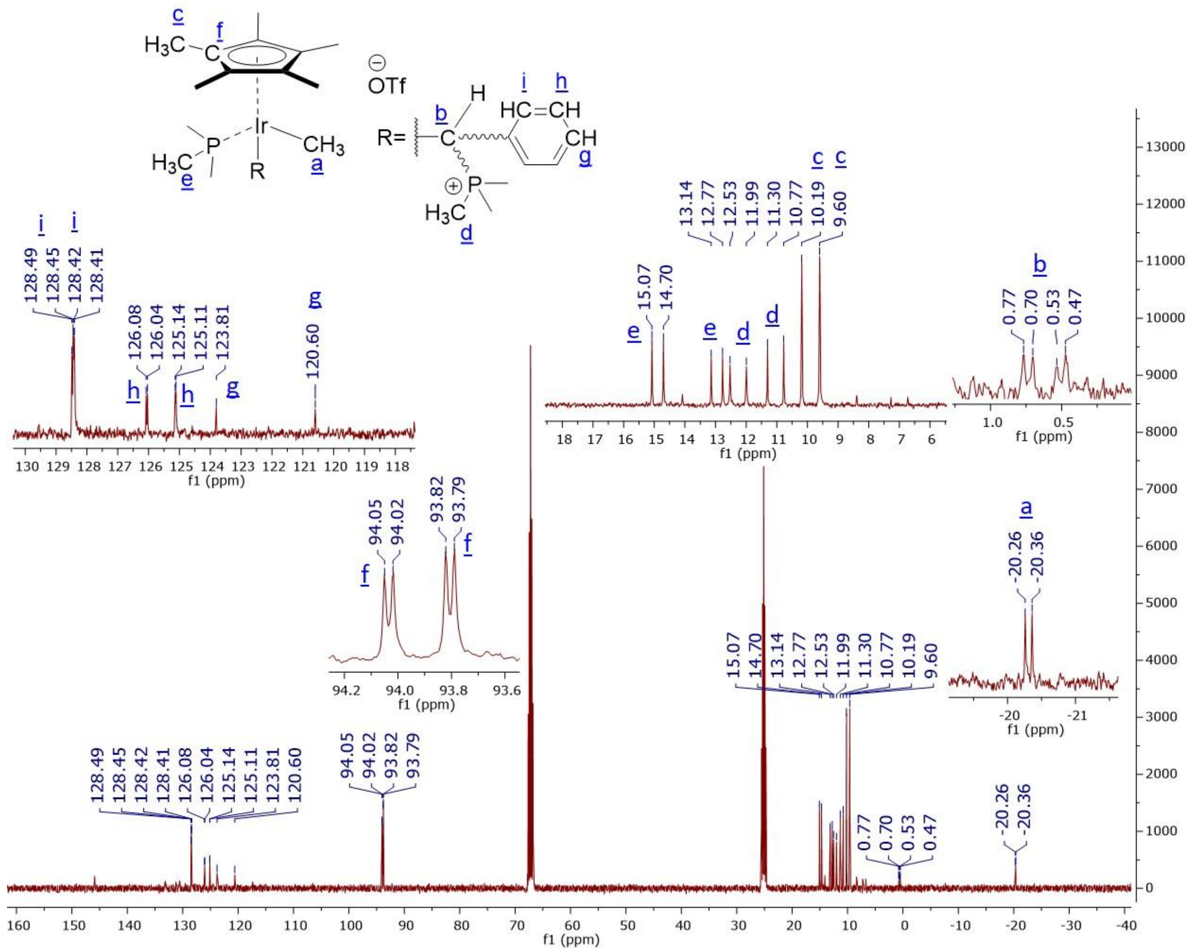


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, THF-d_8, 300 K) of [Cp*(Me_3P)($PhHCPMe_3$)Ir(CH_3)][OTf] formed *in situ* from Cp*(Me_3P)Ir(CH_3)(OTf) and $PhHCPMe_3$. The *ipso* carbon's signal of the phenyl group could not be located as well as the Ir-bound carbon signals for the minor diastereomer as noted above.

X-ray Crystallographic Data

Crystallographic data are summarized Table S1-S2. Suitable crystals for X-ray analysis of **1**-OTf and **3**-OTf were placed on the end of a Cryoloop coated in NVH oil. The X-ray intensity data collection was carried out on a Bruker D8QUEST CMOS area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K. Preliminary indexing was performed from a series of twenty-four 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,[4] producing a listing of non-averaged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[5] The initial structures were determined by SHELXT.[6,7 6–8] The further structure determination was performed by Fourier transform method and refined by least squares method on SHELXL.[8,‡] All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using riding models. For **3**, there were two independent but chemically equivalent [Cp*(Me_3P)(Ph_3P)Ir(CH_2Ph)][OTf] ion pairs in the asymmetric unit and one of the $^-$OTf anions was disordered. The thermal ellipsoids were fixed by SHELXL restraints, RIGU and SIMU, and the bond lengths were fixed by DFIX.

These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the disordered groups and crystal solvents and a Q peak that is unrealistically close to an Ir centre.

Table S1. Summary of Structural Determination of 1-OTf

Empirical formula	$C_{34}H_{44}F_3IrO_3P_2S$
Formula weight	843.89
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a	13.1294(7)Å
b	18.0745(9)Å
c	13.8835(8)Å
β	92.213(2)°
Volume	3292.2(3)Å^3
Z	4
d_{calc}	1.703 g/cm^3
μ	4.267 mm^{-1}
F(000)	1688.0
Crystal size, mm	0.13 × 0.07 × 0.05
2θ range for data collection	5.874 - 55.248°
Index ranges	-17 ≤ h ≤ 17, -23 ≤ k ≤ 22, -18 ≤ l ≤ 18
Reflections collected	69602
Independent reflections	7595[R(int) = 0.0819]
Data/restraints/parameters	7595/0/407
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0662, wR_2 = 0.1567
Final R indexes [all data]	R_1 = 0.0885, wR_2 = 0.1706
Largest diff. peak/hole	7.73/-2.63 eÅ^{-3}

Table S2. Summary of Structural Determination of 3-OTf

Empirical formula	$C_{39}H_{46}F_3IrO_3P_2S$
Formula weight	905.96
Temperature/K	100
Crystal system	triclinic
Space group	P
a	10.6431(4)Å
b	18.1825(7)Å
c	19.2066(8)Å
α	87.071(2)°
β	79.140(2)°
γ	84.124(2)°
Volume	3629.2(2)$Å^3$
Z	4
d_{calc}	1.658 g/cm^3
μ	3.878 mm^{-1}
F(000)	1816.0
Crystal size, mm	0.29 × 0.11 × 0.01
2θ range for data collection	5.764 - 55.102°
Index ranges	-13 ≤ h ≤ 13, -23 ≤ k ≤ 23, -24 ≤ l ≤ 24
Reflections collected	118384
Independent reflections	16716[R(int) = 0.0650]
Data/restraints/parameters	16716/263/932
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0390, wR_2 = 0.0741
Final R indexes [all data]	R_1 = 0.0576, wR_2 = 0.0808
Largest diff. peak/hole	2.08/-2.22 e$Å^{-3}$

Computational Studies

Computational Details

All geometry optimizations and frequency calculations were performed using DFT[9] as implemented in the Jaguar 9.1[10] suite of ab initio quantum chemistry programs. Geometry optimizations were carried out with the B3LYP[11–13] functional and the 6-31G** basis set[14–18] with D3 dispersion correction.[19] Iridium was represented using the Los Alamos LACVP** basis[20,21] that includes Los Alamos effective core potentials. The energies of the optimized structures were re-evaluated by additional single-point calculations on each optimized geometry using Dunning's correlation consistent triple-ζ basis set cc-pVTZ(-f)[22–24] that includes a double set of polarization functions. For Ir, a modified version of LACVP, designated LACV3P, in which the exponents were decontracted to match the effective core potential with triple-ζ quality. Analytical vibrational frequencies within the harmonic approximation were computed with the 6-31G**/LACVP** basis to confirm proper convergence to well-defined minima on the potential energy surface. Solvation energies were evaluated by a self-consistent reaction field (SCRF) approach based on accurate numerical solutions of the Poisson−Boltzmann equation.[25,26] In the results reported, solvation calculations were carried out with the 6-31G**/LACVP** basis at the optimized gas-phase geometry employing the dielectric constant of $\varepsilon = 7.60$ for THF. As is the case for all continuum models, the solvation energies are subject to empirical parametrization of the atomic radii that are used to generate the solute surface. The free energy in solution-phase G(sol) has been calculated as follows:

$$G(sol) = G(gas) + \Delta G^{solv} \quad (1)$$

$$G(gas) = H(gas) - TS(gas) \quad (2)$$

$$H(gas) = E(SCF) + ZPE \quad (3)$$

$$\Delta E(SCF) = \Sigma E(SCF) \text{ for products} - \Sigma E(SCF) \text{ for reactants} \quad (4)$$

$$\Delta G(sol) = \Sigma G(sol) \text{ for products} - \Sigma G(sol) \text{ for reactants} \quad (5)$$

G(gas) is the free energy in the gas phase; G(sol) is the free energy of solvation as computed using the continuum solvation model; H(gas) is the enthalpy in gas phase; T is the temperature (298.15K); S(gas) is the entropy in the gas phase; E(SCF) is the self-consistent field energy, i.e., raw electronic energy as computed from the SCF procedure; and ZPE is the zero-point energy. Note that by entropy here we refer specifically to the vibrational/rotational/translational entropy of the solute(s); the entropy of the solvent is incorporated implicitly in the continuum solvation model. Transition state structures were obtained from the quadratic synchronous transit search methods (QST)[27] and transition state optimization.

Mechanistic Study

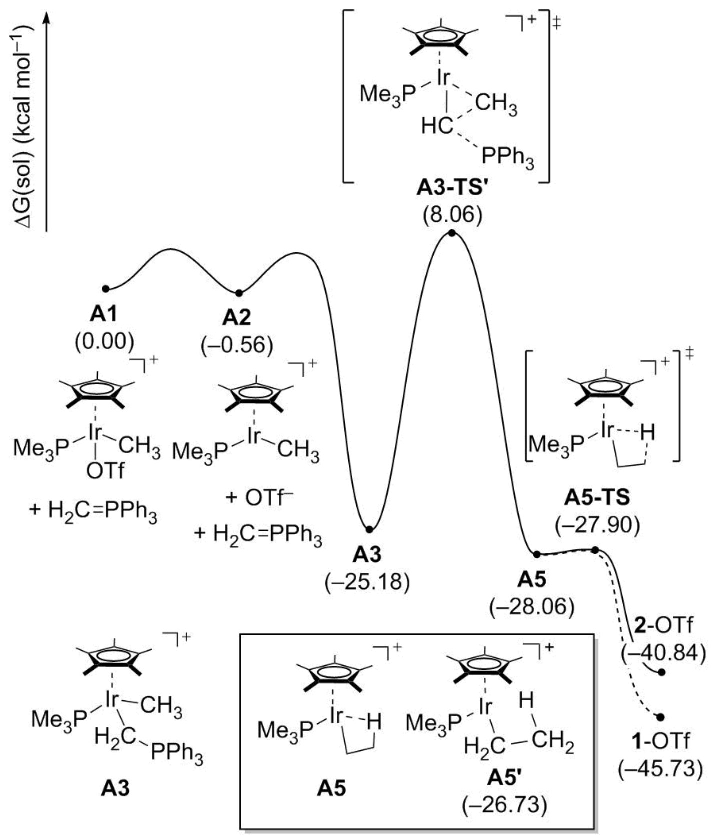


Figure S68. Calculated energy profile via the concerted pathway.

Fig. S62 displays the calculated energy profile *via* the concerted pathway. The reaction follows the same pathway before reaching intermediate **A3** as shown in Fig. 1. In contrast with the stepwise pathway, the intermediate **A5** is generated *via* a concerted mechanism at **A3-TS’** with a barrier of 33.2 kcal mol^{-1}. Compared to **A3-TS**, the barrier of this transition state is 9.7 kcal mol^{-1} higher, which indicates that this pathway is unfavorable at the given conditions. Two conformers **A5** and **A5'** were obtained, the latter intermediate does not contain Ir–(H–C) interaction. This **A5'** intermediate was located at –26.7 kcal mol^{-1} which is slightly higher than **A5** by 1.3 kcal mol^{-1}. In addition, for **B1**, we investigated the concerted pathway and this transition state **B3-TS’** has a higher barrier than **B4-TS** (Table S4). Based on the computed results, we ruled out the concerted pathway and conclude the stepwise mechanism in Fig. 1 and Fig. 2 as appropriate.

Structural Analysis

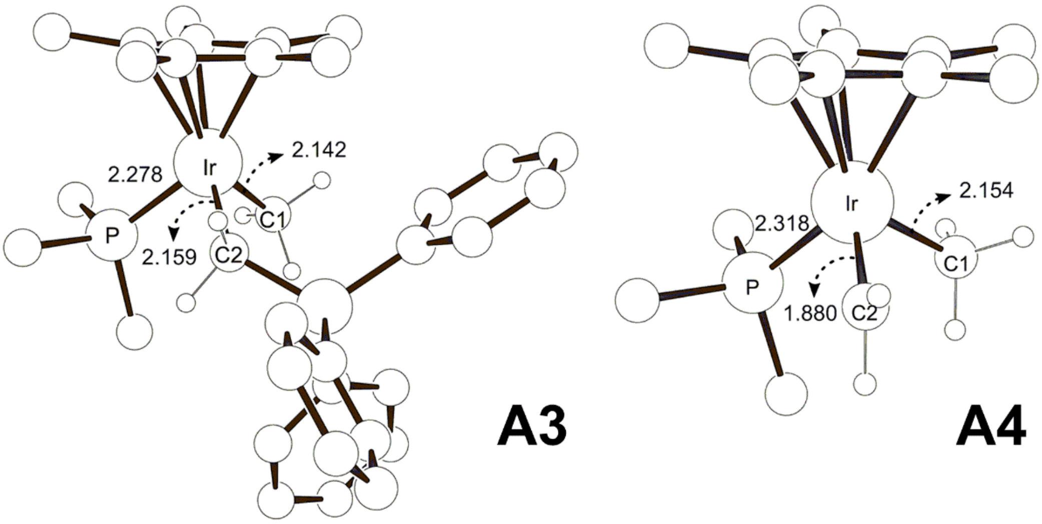


Figure S69. Selected bond lengths of **A3** and **A4**.

Table S3. Selected bond orders of **A3** and **A4**.

	Mayer[28,29]/Wiberg Bond Order[30]		
	Ir–P	Ir–C1	Ir–C2
A3	1.100/0.658	0.960/0.646	0.845/0.532
A4	1.027/0.604	0.946/0.612	1.534/1.218

Molecular Orbital Analysis

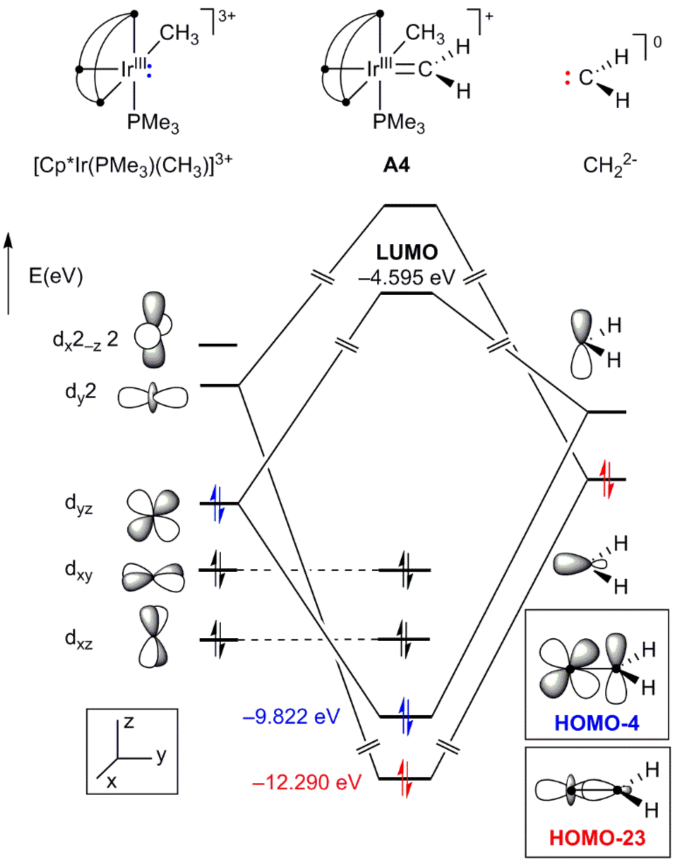


Figure S70. Quantitative MO-diagram comparing the Ir−methylidene (**A4**) bond.

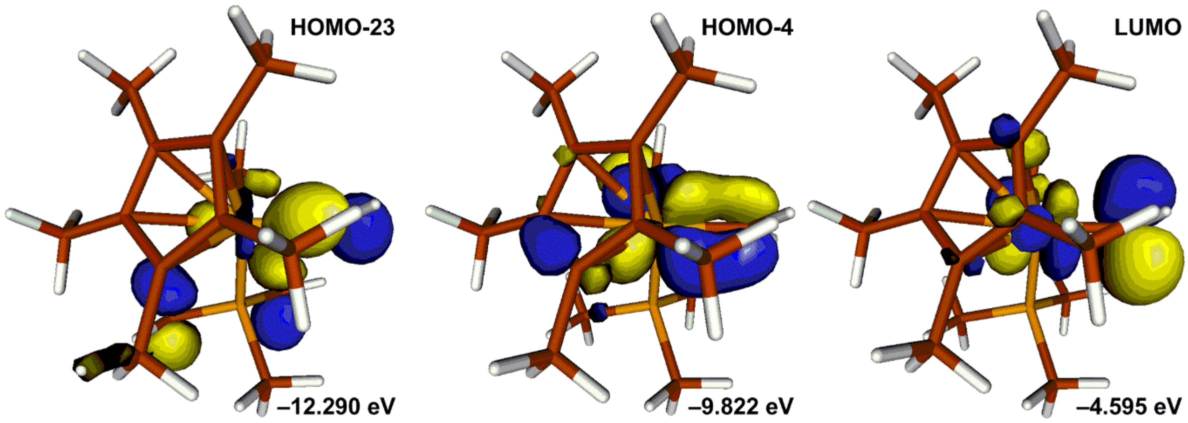


Figure S71. Kohn−Sham orbital plots (isodensity value: 0.05 au) of σ, π and π* orbitals of **A4**.

Computed energy components of all DFT-computed structures

Table S4. Computed energy components of all DFT-computed structures.

	E(SCF)/(eV)	ZPE/(kcal/mol)	S(gas)/(cal/mol·K)	G(solv)/(kcal/mol)
	cc-pVTZ(-f)/ LACV3P**	6-31G**/LACVP**	6-31G**/LACVP**	6-31G**/LACVP**
Methane	-1103.085	28.24	49.41	-0.32
OTF⁻	-26171.497	17.11	85.53	-53.75
PPh_3	-28206.578	172.02	132.46	-5.75
$H_2C{=}PPh_3$	-29275.350	188.09	136.68	-7.07
A1	-53277.038	254.65	196.13	-11.00
A2	-27101.298	235.27	162.39	-36.65
A3	-56379.234	427.51	240.43	-31.81
A3-TS	-56378.105	425.89	239.54	-32.95
A3-TS'	-56377.477	425.26	253.23	-34.66
A4	-56377.369	424.43	288.87	-41.96
A4-TS	-28170.361	252.12	162.18	-36.00
A5	-28171.504	253.49	159.98	-36.70
A5′	-28171.412	253.84	165.98	-35.90
A5-TS	-28171.498	252.25	158.34	-35.97
1^+	-56380.293	429.94	234.18	-32.38
2^+	-28172.086	253.12	158.05	-36.31
B1	-58496.504	288.50	212.03	-10.05
B2	-32320.516	269.22	178.85	-36.70
B3	-61598.516	461.55	254.04	-32.20
B3-TS	-61597.398	459.80	255.868	-33.04
B3-TS'	-61596.969	459.78	254.35	-33.02
B4	-33390.070	286.32	179.46	-36.15
B4-TS	-33389.641	286.49	174.35	-35.44
B5	-33391.090	288.17	172.51	-35.36
B6	-61599.594	463.51	247.38	-33.10
3^+	-61599.594	463.51	247.38	-33.10

Cartesian coordinates of the optimized geometries

Table S5. Cartesian coordinates of the optimized geometries.

==============================

Methane

==============================

C 3.273129463 -2.437929153 -1.990829587
H 3.943516970 -2.099319220 -2.783367395
H 2.248855114 -2.471172810 -2.366722584
H 3.330340624 -1.746174932 -1.147462010
H 3.573076963 -3.434991598 -1.660695910

==============================

OTf⁻

==============================

O 1.154517055 -0.695410430 -3.001827478
S 2.522758722 -1.261016488 -2.997672796
O 3.148710728 -1.402745128 -1.663334012
O 3.416322470 -0.777619958 -4.074698448
C 2.225597143 -3.033476591 -3.495768785
F 1.649205327 -3.119859934 -4.716548920
F 3.376030445 -3.741808653 -3.551570177
F 1.409931183 -3.674518108 -2.628141880

==============================

PPh_3

==============================

P 2.047825098 -3.427883625 0.765788972
C 2.453516245 -3.391863585 2.571159363
C 2.592527390 -4.532318115 3.375992060
C 2.651361704 -2.128733873 3.153244734
C 2.928109646 -4.410610199 4.725729942
C 3.000949860 -2.008560419 4.497397423
C 3.137955189 -3.151097775 5.288575172
H 2.447091103 -5.518492222 2.947237968
H 2.539520025 -1.234351516 2.544902325
H 3.031334639 -5.303509235 5.336439133
H 3.158113003 -1.024361730 4.929973125
H 3.403086662 -3.058915138 6.338106632
C 1.597273111 -5.206399918 0.525238752
C 0.250213832 -5.558666229 0.704429269
C 2.519076347 -6.214601517 0.202888116
C -0.163741067 -6.885318756 0.584071636
C 2.102911711 -7.540100098 0.071675681
C 0.762749493 -7.879974842 0.265319288
H -0.478528619 -4.787821770 0.943712592
H 3.564908266 -5.963620186 0.058586955
H -1.209169626 -7.141346455 0.732606351
H 2.828345537 -8.309967041 -0.177460745
H 0.441572517 -8.913112640 0.165820986
C 3.738753796 -3.382845640 0.014332201
C 4.929627895 -3.519721508 0.742541373
C 3.814904928 -3.218637228 -1.378519535
C 6.164656639 -3.499685287 0.090884879
C 5.047357559 -3.211550713 -2.029794216
C 6.227357864 -3.350656033 -1.295239687
H 4.893585205 -3.648011446 1.819527268
H 2.901413918 -3.100519896 -1.956475496
H 7.078888416 -3.608938456 0.668306947
H 5.087998390 -3.091821671 -3.108960152
H 7.189105988 -3.340164900 -1.800536275

==============================

$H_2C{=}PPh_3$

==============================

P 2.453108072 0.073635116 -1.709339857
C 1.423507452 0.311190873 -0.404812425
H 0.787376046 -0.515591264 -0.103730351
H 1.077209353 1.319560409 -0.209220707
C 3.741074085 1.374656916 -1.758503079
C 4.957392216 1.187677264 -1.088466167
C 3.488597393 2.598783016 -2.394489050
C 5.909748554 2.205675840 -1.063235044
C 4.437847614 3.620818615 -2.356399298
C 5.651144981 3.424133062 -1.695118427
H 5.160131454 0.243474364 -0.592429399
H 2.556191921 2.751384497 -2.929155588
H 6.854474545 2.047311783 -0.550792217
H 4.231333733 4.567042828 -2.848709345
H 6.393696308 4.216936111 -1.672966003
C 3.279586792 -1.555225611 -1.546889544
C 3.531213760 -2.030309439 -0.250065953
C 3.698755980 -2.317224979 -2.647084951

C 4.193349361 -3.243478537 -0.060194727
C 4.365373611 -3.527178049 -2.452633858
C 4.616154671 -3.992650270 -1.160324216
H 3.191534519 -1.439161658 0.594923675
H 3.496548653 -1.976783752 -3.656675816
H 4.379747868 -3.602362394 0.948156238
H 4.684002399 -4.109133720 -3.313004732
H 5.134267807 -4.936057568 -1.012366533
C 1.837164879 0.078161255 -3.467567921
C 2.660730124 0.275267273 -4.588139057
C 0.465357959 -0.116615631 -3.657625437
C 2.119639635 0.259337127 -5.873555660
C -0.077609643 -0.135921970 -4.943783760
C 0.749255180 0.050391056 -6.052624702
H 3.725390911 0.449446201 -4.456054688
H -0.169584796 -0.237340331 -2.782429218
H 2.763940811 0.413696498 -6.735080242
H -1.144747257 -0.288793027 -5.079957008
H 0.328015506 0.041691575 -7.054185867

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A1

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Ir -0.362017304 0.210799262 -1.186659098
C 0.020172987 1.539864063 0.584473252
C -1.165983081 1.937965512 -0.154628158
C 1.143453002 1.665470600 -0.281629056
C -0.714030564 2.472522020 -1.446495891
C 0.680338979 2.258641005 -1.541226029
C -0.501154602 -1.532476306 0.011847219
H -0.170118243 -2.407792568 -0.551851988
H 0.180394217 -1.414952278 0.857785106
H -1.513173342 -1.710339665 0.397476941
C -2.529040337 2.128996134 0.442319155
H -3.307887793 2.106187820 -0.323503017
H -2.751668453 1.342397928 1.167321682
H -2.598573208 3.095310688 0.958860815
C 0.046454489 1.091137409 2.012340069
H -0.836489797 0.496666223 2.259229183
H 0.930407584 0.484758735 2.220196009
H 0.068306483 1.962009311 2.679322720
C -1.594313622 3.157281876 -2.448218584
H -1.167669535 3.117300749 -3.453019142
H -2.589999914 2.706775665 -2.484975338
H -1.727071404 4.214118004 -2.184410810
C 1.578302264 2.569599152 -2.700475216
H 2.215470076 3.433578253 -2.474193335
H 2.229225636 1.719603658 -2.923807621
H 1.001752734 2.801630497 -3.598572493
C 2.575841665 1.394549251 0.069118567
H 2.668421984 0.499734372 0.685927987
H 3.176317692 1.222647429 -0.825608075
H 3.000984669 2.248157740 0.612484336
P -1.974827051 -0.686855435 -2.551628590
C -3.728684425 -0.309045970 -2.145431280
H -4.411288738 -0.816763580 -2.833672762
H -3.933491707 -0.634326935 -1.122256517
H -3.898430586 0.768554211 -2.206448078
C -1.782627940 -0.138867408 -4.296643257
H -0.762702405 -0.389771044 -4.599478245
H -2.501891613 -0.630604148 -4.959309578
H -1.909622788 0.944445372 -4.358772278
C -1.954106092 -2.516918898 -2.704088688
H -2.640643120 -2.848292589 -3.488841772
H -0.933519840 -2.825631142 -2.939221621
H -2.241241932 -2.967800379 -1.752010345
O 0.883357942 -0.989260852 -2.549928665
S 2.326679230 -1.353927016 -2.180527925
O 2.517094612 -1.680582881 -0.764316678
O 3.307067156 -0.465628535 -2.823127985
C 2.414722681 -2.975495815 -3.089239597
F 2.244370461 -2.789329529 -4.404443741
F 3.596293449 -3.562662125 -2.880801439
F 1.441869974 -3.794307947 -2.646831751

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A2

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Ir -0.486716777 0.231939614 -0.961812317
C -0.004483463 1.715827107 0.632447183
C -1.057500601 2.218096495 -0.271353722
C 1.156473160 1.524284244 -0.150287613
C -0.473424286 2.483613253 -1.563787580
C 0.845676720 1.954571962 -1.530508399

C -0.326730192 -1.560410023 0.081331603
H 0.401771516 -2.170194387 -0.478872061
H 0.064138360 -1.403289437 1.090825081
H -1.247750998 -2.151409388 0.147273660
C -2.433240414 2.600414276 0.168397874
H -3.134091377 2.612078905 -0.668836594
H -2.811455488 1.911687016 0.926991463
H -2.414346933 3.606146812 0.607197940
C -0.166041166 1.494815707 2.102529049
H -1.152413368 1.087443113 2.336780548
H 0.585346103 0.804575920 2.489868402
H -0.059666801 2.446471214 2.636754513
C -1.132232904 3.191057920 -2.707522869
H -0.769406974 2.830837727 -3.672173023
H -2.217956066 3.073278666 -2.685145617
H -0.920216799 4.265367985 -2.653441191
C 1.836618662 1.952807188 -2.649140835
H 2.512356758 2.811228991 -2.547976017
H 2.448819876 1.047682762 -2.634166479
H 1.346914768 2.021948576 -3.622165918
C 2.496526480 1.045733571 0.310076267
H 2.419550180 0.457948983 1.226297736
H 2.980903864 0.427749634 -0.449681848
H 3.150580883 1.903092146 0.509827733
P -1.826979876 -0.808179080 -2.561060190
C -3.515313148 -1.167543530 -1.933276653
H -4.108011246 -1.670753598 -2.703315258
H -3.446181774 -1.808186412 -1.051094532
H -4.006052017 -0.233497545 -1.649018168
C -2.108335257 0.118116297 -4.119534969
H -1.147677779 0.343857557 -4.589186192
H -2.713747978 -0.477345496 -4.809131145
H -2.625637770 1.055646777 -3.908815384
C -1.198324561 -2.438451529 -3.126209974
H -1.895313144 -2.886902332 -3.840122223
H -0.224293038 -2.310450554 -3.605056763
H -1.081589222 -3.103014708 -2.267534494

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A3

==============================

Ir -0.107196555 -0.387977242 -0.786395490
C 0.124656804 1.466366887 0.591522932
C -0.830328584 1.786730647 -0.418100804
C 1.397480965 1.218537807 -0.067681812
C -0.187327206 1.682986617 -1.711869836
C 1.206852555 1.383286119 -1.473711014
C -2.219838142 2.295719385 -0.175655499
H -2.915214300 1.989432931 -0.959535122
H -2.615248203 1.961658835 0.786057115
H -2.213091850 3.392022371 -0.163317755
C -0.074568085 1.531159163 2.075930834
H -1.119346261 1.367939353 2.352194548
H 0.526778817 0.775166750 2.590789318
H 0.230106130 2.506589890 2.474316835
C -0.772001863 2.077543497 -3.036145926
H -0.387061715 1.443359494 -3.838953257
H -1.860405326 1.986345410 -3.035018682
H -0.527094007 3.117793560 -3.284161568
C 2.262223959 1.370108247 -2.534471989
H 2.540172100 2.397595644 -2.796837568
H 3.162057161 0.853484631 -2.201078176
H 1.907192588 0.885569453 -3.448402405
C 2.693555593 1.033071041 0.662183642
H 2.603677034 0.295130074 1.464263558
H 3.494229317 0.703185201 0.000976901
H 3.001302958 1.978939295 1.125038266
P -2.153954029 -1.370714068 -0.965681255
C -3.233867168 -1.216689229 0.519748032
H -4.191726685 -1.724059939 0.368102163
H -2.725953817 -1.656624675 1.382485390
H -3.418076277 -0.161242589 0.730002880
C -3.215059280 -0.729408383 -2.326704502
H -2.677492857 -0.828825593 -3.272974491
H -4.154724121 -1.287276864 -2.383897543
H -3.438525915 0.326528966 -2.164983034
C -2.200023413 -3.180586815 -1.295532942
H -3.235811234 -3.530155182 -1.337158084
H -1.709298611 -3.393561840 -2.246845961
H -1.669947863 -3.724684238 -0.514071345
C 0.397298932 -1.595377803 -2.482071638
H 1.279182434 -1.168347955 -2.971220493
H 0.610476971 -2.642289639 -2.246740103
H -0.389420539 -1.593410730 -3.247777939

P 1.852233410 -2.959135532 0.706899464
C 0.431825727 -1.828021526 0.728984058
H -0.376443923 -2.514489174 1.017650008
H 0.610308409 -1.211717129 1.616521120
C 2.158041954 -3.577254772 2.398913860
C 2.666420937 -4.871663094 2.597278357
C 1.950151801 -2.743268728 3.510143042
C 2.950246334 -5.323923588 3.885019302
C 2.236523867 -3.201539516 4.795721054
C 2.735486746 -4.491754532 4.985906124
H 2.834786415 -5.528172493 1.749430299
H 1.567152977 -1.736063004 3.383247375
H 3.340572357 -6.327101707 4.027424335
H 2.068567753 -2.549966097 5.647901058
H 2.956802368 -4.847008228 5.987710953
C 1.469396353 -4.437656403 -0.279134780
C 0.383388370 -5.227537632 0.136948258
C 2.215198994 -4.824435711 -1.399485946
C 0.035152007 -6.371711254 -0.575648785
C 1.859357357 -5.970812798 -2.111135960
C 0.769273877 -6.740674496 -1.705824375
H -0.175996348 -4.964452744 1.030817986
H 3.072106838 -4.242326736 -1.718694568
H -0.803981245 -6.977280140 -0.246936455
H 2.440528870 -6.262683868 -2.980535030
H 0.497411579 -7.632773399 -2.262026787
C 3.419861794 -2.247189045 0.135401830
C 4.513915062 -2.158728838 1.011563540
C 3.557501554 -1.796800256 -1.188007832
C 5.722014904 -1.619712114 0.569965124
C 4.776741505 -1.281135440 -1.627494335
C 5.859114170 -1.185097218 -0.749590516
H 4.428090572 -2.505439281 2.035491943
H 2.720385313 -1.844354391 -1.869477749
H 6.559099197 -1.548284411 1.257665753
H 4.876933575 -0.950864077 -2.657245874
H 6.804341793 -0.775803387 -1.093275905

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A3-TS

==============================

Ir -0.473886907 -0.683912814 0.315298885
C -0.304325491 1.437803507 1.293180108
C -0.855161965 1.638108373 -0.025604792
C 1.015550375 0.881763041 1.133344412
C 0.096600145 1.183176517 -0.993563235
C 1.263075948 0.717543840 -0.273095489
C -2.135977030 2.359592438 -0.326023132
H -2.644948959 1.959648371 -1.212528110
H -2.831689596 2.323407412 0.521466494
H -1.921032310 3.420405626 -0.524688423
C -0.924563587 1.889404297 2.584503651
H -2.013930798 1.804157138 2.558051586
H -0.566093147 1.292395234 3.426661730
H -0.678806663 2.938409328 2.792243719
C -0.025668297 1.289829493 -2.485108852
H 0.453436971 0.442481339 -2.984493256
H -1.072360158 1.316340446 -2.800422907
H 0.454409122 2.204637051 -2.853786707
C 2.564356565 0.307695985 -0.888558805
H 3.191089392 1.191564083 -1.059694290
H 3.117673635 -0.375646651 -0.243639618
H 2.414758682 -0.185805038 -1.851846933
C 2.000037909 0.639401257 2.236710310
H 1.497131586 0.354257405 3.166399956
H 2.710623503 -0.147784248 1.975427985
H 2.568605661 1.554132581 2.444193125
P -2.624200344 -1.406191111 -0.049914144
C -3.893884182 -0.646563709 1.044227600
H -4.888689041 -1.045767307 0.822353184
H -3.641156912 -0.862440348 2.086253643
H -3.905858278 0.436329514 0.905891180
C -3.243969917 -1.072563529 -1.748431325
H -2.623596430 -1.614159584 -2.467367649
H -4.284393311 -1.396254897 -1.851335645
H -3.177749634 -0.004622322 -1.967698812
C -2.979954243 -3.200892687 0.139241800
H -4.024946213 -3.394852400 -0.119925775
H -2.334698200 -3.781599998 -0.522561848
H -2.813608408 -3.518212557 1.171516418
C 0.112547010 -2.103215456 -1.167295575
H 1.202814579 -2.122465849 -1.186471224
H -0.233408406 -3.117956877 -0.961205602
H -0.246476531 -1.800158978 -2.157274723

P 1.526703358 -3.761607647 1.630124331
C -0.286713243 -1.908275127 1.812592030
H -0.943267107 -2.737855196 2.079838276
H 0.332063258 -1.601231575 2.658551455
C 1.980579495 -4.425081253 3.288244724
C 3.006555080 -5.379690170 3.440586567
C 1.303534389 -3.953322172 4.427200794
C 3.346768379 -5.843410015 4.708222866
C 1.646145821 -4.417827129 5.699196815
C 2.669003725 -5.361372471 5.839785576
H 3.541419744 -5.758977890 2.569402218
H 0.500493228 -3.228507757 4.315588951
H 4.141903877 -6.580997944 4.816172600
H 1.114613891 -4.043225765 6.574741840
H 2.939387798 -5.723702431 6.827346802
C 1.178154945 -5.268317699 0.636080682
C -0.165460229 -5.631739140 0.463216335
C 2.177077055 -6.086895943 0.082968749
C -0.508129716 -6.784245014 -0.244057477
C 1.832790494 -7.235866547 -0.629054189
C 0.491326749 -7.587438583 -0.796267927
H -0.946851969 -5.016426563 0.897140086
H 3.224601984 -5.826252460 0.194495797
H -1.553539276 -7.055086613 -0.362257659
H 2.615821123 -7.858047485 -1.053187370
H 0.228049457 -8.482060432 -1.352401972
C 3.128004789 -3.117748260 1.008305907
C 3.980408669 -2.446523905 1.902919173
C 3.491380453 -3.187222242 -0.346819162
C 5.161382198 -1.858002901 1.451883078
C 4.683162212 -2.613088846 -0.790997386
C 5.515791416 -1.938394785 0.103443593
H 3.731761456 -2.402253389 2.959516048
H 2.855330706 -3.705948353 -1.056362629
H 5.809737682 -1.345927238 2.157173157
H 4.955745220 -2.687262297 -1.839854360
H 6.438950062 -1.485430598 -0.245844662

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A3-TS’

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Ir 0.227857277 0.037667599 -0.226329103
C 0.325459570 2.184287786 0.469257176
C -1.038194299 1.872941732 0.083927982
C 1.152863503 2.051502228 -0.694223523
C -1.060955167 1.653558969 -1.351001620
C 0.281640530 1.727331877 -1.815986514
C -2.234840631 2.051975965 0.971341670
H -3.109282494 1.528092623 0.582353294
H -2.041480780 1.688346863 1.983214378
H -2.496612072 3.114307404 1.040877223
C 0.762123704 2.638111830 1.829481125
H 0.161941320 2.176243067 2.616265059
H 1.811020136 2.399302006 2.016383171
H 0.645843208 3.725985765 1.911953330
C -2.279569864 1.500928283 -2.212862730
H -2.124436617 0.772343397 -3.012876749
H -3.148294449 1.187039971 -1.633500934
H -2.529832125 2.459289312 -2.683736563
C 0.735316038 1.579476833 -3.234690189
H 0.879748166 2.568713188 -3.684367895
H 1.688097239 1.048003793 -3.300235510
H 0.001764362 1.041268349 -3.837738037
C 2.621569633 2.338470697 -0.785719633
H 3.126352787 2.145279408 0.164257884
H 3.101920128 1.724862099 -1.552637577
H 2.796853065 3.387962341 -1.048083067
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C -1.437438607 -2.170847893 1.916635513
H -2.157751083 -2.986057043 2.032154322
H -0.475118756 -2.484945059 2.326038122
H -1.784763694 -1.296435118 2.473242044
C -2.973818541 -1.437197804 -0.406297207
H -2.994009733 -1.234425068 -1.478915095
H -3.575831652 -2.326611280 -0.198266417
H -3.406304121 -0.587984741 0.125601068
C -0.822571754 -3.312231302 -0.661781788
H -1.566122890 -4.071553230 -0.400885671
H -0.806311488 -3.181973696 -1.747170806
H 0.164837718 -3.649443150 -0.334850520
C 1.667945266 -1.267523050 -1.451096535
H 2.550548077 -0.675682545 -1.688133121
H 1.946906805 -2.278798580 -1.156972170
H 1.001566172 -1.333726883 -2.311248302

P 2.643278837 -4.464591980 0.722285569
C 1.606687069 -0.926516950 0.676746845
H 1.564252496 -1.960922122 1.011362076
H 2.580549955 -0.469898850 0.886037230
C 1.813508630 -4.382788658 2.377346516
C 0.814653337 -5.309664249 2.717567921
C 2.047548056 -3.304151773 3.250472069
C 0.079333670 -5.166290760 3.894174337
C 1.311416388 -3.164616823 4.429117680
C 0.322069854 -4.093729496 4.754263878
H 0.621059597 -6.159438610 2.069382906
H 2.827927589 -2.582558393 3.025534630
H -0.679892123 -5.902088165 4.144259453
H 1.519781590 -2.332742214 5.096659184
H -0.247850806 -3.988157749 5.672611713
C 2.825774908 -6.276676655 0.444598615
C 1.807923675 -6.908566952 -0.289616466
C 3.897551298 -7.049715042 0.916372240
C 1.842139959 -8.284770966 -0.519259155
C 3.937309742 -8.422635078 0.672676682
C 2.908699512 -9.045132637 -0.038557343
H 0.981425285 -6.320315838 -0.682322383
H 4.707339764 -6.581780434 1.466561437
H 1.043289065 -8.758958817 -1.082131982
H 4.774365902 -9.008424759 1.041649580
H 2.943221092 -10.114518166 -0.223294586
C 4.336607933 -3.838531256 1.075119853
C 5.039432049 -4.087058067 2.267502546
C 4.949473858 -3.055570602 0.083253123
C 6.321331024 -3.571476460 2.455197573
C 6.235049248 -2.543124914 0.270724148
C 6.922951221 -2.799650908 1.457653880
H 4.574645996 -4.671607018 3.056132317
H 4.416960239 -2.850544453 -0.842997432
H 6.851684093 -3.772428274 3.381527424
H 6.697573662 -1.944603682 -0.509142280
H 7.921314716 -2.399573565 1.606782675

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A4

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Ir -0.223420218 0.052494898 -1.107485533
C -0.088983342 1.093196869 0.957477868
C -1.277336240 1.577550173 0.291769654
C 1.047688961 1.496767402 0.175296307
C -0.865963459 2.331305504 -0.874322832
C 0.557744801 2.274070501 -0.946195126
C -2.671194553 1.509711862 0.843844235
H -3.424657106 1.529289007 0.052863866
H -2.824596882 0.609830260 1.443482518
H -2.859045029 2.373550653 1.492835164
C -0.036324233 0.378853589 2.275258541
H -0.957267463 -0.173956513 2.472189426
H 0.797261953 -0.326765239 2.316585302
H 0.104557119 1.098948479 3.090119839
C -1.739704967 3.169585705 -1.762362003
H -1.468155861 3.061252832 -2.816341877
H -2.795189381 2.913398504 -1.656288028
H -1.636167049 4.230216503 -1.504937530
C 1.409414291 2.997741699 -1.941301942
H 1.600412011 4.016876698 -1.584397912
H 2.376618862 2.511666298 -2.082674026
H 0.918798923 3.071685553 -2.914416075
C 2.488389969 1.302169323 0.544548392
H 2.631568909 0.395639747 1.137670875
H 3.121584654 1.228316426 -0.342502654
H 2.845963717 2.149819851 1.142290235
P -2.049826145 -0.942752361 -2.130813122
C -3.190356970 -1.743994594 -0.936936617
H -4.062508106 -2.155930042 -1.454298258
H -2.660853148 -2.548283339 -0.419855237
H -3.522829056 -1.013672709 -0.196735948
C -3.119313955 0.208146438 -3.076256990
H -2.515718460 0.758692384 -3.802108526
H -3.899027586 -0.350912362 -3.602874756
H -3.591077805 0.921057522 -2.397598267
C -1.698544264 -2.275700569 -3.341881514
H -2.639166355 -2.749128103 -3.637206078
H -1.216580033 -1.860916018 -4.229173660
H -1.042878389 -3.032066822 -2.905551195
C 0.709053814 0.017989948 -3.048357964
H 1.736342311 0.368136734 -2.930041790
H 0.740164876 -0.977499306 -3.489705801
H 0.172384501 0.699827969 -3.716083527

C	0.523370326	-1.614842892	-0.665785491
H	0.487933695	-2.537413359	-1.254725218
H	1.102219462	-1.739539266	0.258783549

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A4-TS

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Ir	-0.447026461	-0.342930406	-0.571285546
C	-0.339824468	1.168539524	1.108079076
C	-1.315379262	1.604983449	0.125330806
C	0.941697657	1.124689221	0.466230959
C	-0.602594733	1.940990806	-1.095553041
C	0.767059326	1.612828612	-0.895802975
C	-2.751515865	1.923687100	0.420699060
H	-3.372594595	1.862872362	-0.475673825
H	-3.165380239	1.242364764	1.167228699
H	-2.840971947	2.943674803	0.812829375
C	-0.622583628	0.885813475	2.552047253
H	-1.621307969	0.467309147	2.691186666
H	0.101699039	0.187638387	2.975724220
H	-0.565273285	1.817966819	3.127403021
C	-1.169541478	2.635316372	-2.298260450
H	-0.744285583	2.253455877	-3.229590416
H	-2.253812551	2.535332918	-2.354380608
H	-0.944737315	3.707127571	-2.247653961
C	1.874221444	1.809741259	-1.883689284
H	2.385782242	2.758604288	-1.682967901
H	2.621727467	1.015729070	-1.817713499
H	1.499211550	1.842536330	-2.908405066
C	2.254057884	0.795546174	1.112311959
H	2.130046606	0.082250863	1.930809736
H	2.957990170	0.366295755	0.394722402
H	2.718391895	1.697831631	1.526710153
P	-2.209519148	-1.289303660	-1.744221926
C	-3.597845316	-1.826336622	-0.667668581
H	-4.415474415	-2.248555899	-1.259795070
H	-3.236251593	-2.575093508	0.041420743
H	-3.966067791	-0.966369033	-0.102392711
C	-3.029889345	-0.211660072	-2.984366179
H	-2.293812513	0.170832619	-3.694806814
H	-3.793174505	-0.779417455	-3.524715900
H	-3.509835005	0.632326007	-2.485711575
C	-1.816250801	-2.794701815	-2.724299669
H	-2.721705437	-3.177423954	-3.203750849
H	-1.079642534	-2.551891804	-3.493973255
H	-1.404853702	-3.577379465	-2.082652569
C	1.143340349	-1.604030609	-1.639438868
H	2.107769489	-1.320999742	-1.223113060
H	1.090729237	-2.684345484	-1.767462134
H	0.989178777	-1.146843314	-2.616880417
C	0.017302604	-2.046101332	0.161274880
H	-0.388405055	-3.020730019	-0.117336020
H	0.792887866	-2.138801336	0.929285824

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A5

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Ir	-0.365840703	-0.206827283	-0.828102767
C	-0.193166018	0.942211688	1.083037376
C	-1.353280902	1.353890419	0.310099423
C	0.967505455	1.239285588	0.301119447
C	-0.872556388	2.060762167	-0.884580016
C	0.536885142	1.948144436	-0.903923988
C	-2.764879942	1.371676564	0.814066589
H	-3.484786749	1.343821287	-0.007202023
H	-2.962941408	0.522175729	1.470613599
H	-2.950608730	2.289816141	1.383978248
C	-0.224555016	0.338050872	2.452458858
H	-1.110380411	-0.284457296	2.593016863
H	0.656766236	-0.277645677	2.643253565
H	-0.245313644	1.132207990	3.208308935
C	-1.708730340	2.863147020	-1.835215807
H	-1.362854600	2.767138243	-2.866966248
H	-2.759396315	2.573494196	-1.799556017
H	-1.657668114	3.924743891	-1.564327121
C	1.459770679	2.523675203	-1.933654189
H	1.841404080	3.493247509	-1.591258407
H	2.322204590	1.876738667	-2.110134602
H	0.950390995	2.681355238	-2.886120081
C	2.394574642	1.003758311	0.697614133
H	2.488301516	0.146378770	1.368109941
H	3.027352333	0.822361171	-0.174865797
H	2.798178673	1.879254460	1.219616294
P	-2.125629663	-1.195185065	-1.969835997

C	-3.397240639	-1.939086795	-0.871388137
H	-4.193311214	-2.407890797	-1.457559466
H	-2.929456234	-2.689382076	-0.229780778
H	-3.828273296	-1.162206411	-0.236002743
C	-3.110525846	-0.104620852	-3.071731567
H	-2.452920198	0.397573888	-3.784803867
H	-3.855948448	-0.692050874	-3.615807772
H	-3.627726555	0.651783466	-2.478508234
C	-1.664600492	-2.589803934	-3.077647448
H	-2.556653976	-2.991693974	-3.566252708
H	-0.964365125	-2.243392467	-3.842237949
H	-1.194392443	-3.390233755	-2.501421213
C	1.158426404	-1.964734674	-1.302817345
H	2.193470240	-1.752140284	-1.034963250
H	1.091954112	-2.754035473	-2.054047346
H	0.860577226	-1.037839770	-2.002533436
C	0.212975636	-2.101312637	-0.136733487
H	-0.482953787	-2.937331200	-0.194003478
H	0.681477666	-2.059435129	0.845727146

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A5'

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Ir	-0.507642031	-0.189118102	-0.581682980
C	-0.125637904	1.194785357	1.123121858
C	-1.310168147	1.583965421	0.334898502
C	0.987219930	1.281818390	0.256313503
C	-0.861149192	2.098944902	-0.950481832
C	0.518994153	1.815482855	-1.040954709
C	-2.695542574	1.690419078	0.886659622
H	-3.446065664	1.645774722	0.094167106
H	-2.897435665	0.888013303	1.599542499
H	-2.816993952	2.647023201	1.410604119
C	-0.140354529	0.813892722	2.569776535
H	-1.005407333	0.189992696	2.808033943
H	0.760212958	0.265443027	2.851953983
H	-0.194643140	1.715500355	3.191334248
C	-1.709156036	2.797586679	-1.968300343
H	-1.384730101	2.580909967	-2.988058805
H	-2.761710882	2.520540953	-1.877012610
H	-1.647261500	3.882473946	-1.823539376
C	1.421245813	2.091187239	-2.200807810
H	2.006280899	3.000079393	-2.013922930
H	2.129041910	1.272269368	-2.354001760
H	0.858548284	2.236588240	-3.124552011
C	2.416686535	0.981650054	0.577717960
H	2.504020929	0.314257383	1.436786413
H	2.924400568	0.514375806	-0.269857496
H	2.951977491	1.909429908	0.813055217
P	-1.949407578	-1.244228125	-2.074637890
C	-3.513137102	-1.765801191	-1.263374329
H	-4.167053699	-2.270946741	-1.980560064
H	-3.286462545	-2.443110466	-0.436842650
H	-4.023458958	-0.886207283	-0.863014460
C	-2.507120132	-0.254680783	-3.518166065
H	-1.639655471	0.085217670	-4.089175701
H	-3.150162697	-0.857707977	-4.166397095
H	-3.067121267	0.617969871	-3.177629232
C	-1.309104323	-2.787904501	-2.839880228
H	-2.075790882	-3.233229876	-3.480410099
H	-0.425506145	-2.564193010	-3.442937374
H	-1.031286478	-3.502802134	-2.062770128
C	1.170943618	-2.569061041	-0.191563576
H	2.020330429	-1.917675853	0.035479780
H	1.389361858	-3.553821802	0.241616175
H	1.146063089	-2.705339909	-1.279553294
C	-0.150921792	-2.011413574	0.386464000
H	-0.947736204	-2.754863977	0.272327662
H	-0.033616696	-1.830031157	1.459479570

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A5-TS

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Ir	-0.550142884	-0.201095894	-0.703831792
C	-0.116699345	0.887872219	1.260613441
C	-1.413852572	1.253428698	0.751474619
C	0.871095359	1.284005284	0.295845538
C	-1.200317025	1.955141068	-0.512801826
C	0.202059239	1.971457243	-0.793360472
C	-2.705407143	1.181997657	1.509712219
H	-3.567536831	1.204805970	0.840812266
H	-2.768448353	0.270989686	2.108298779
H	-2.793594837	2.039210796	2.188416004
C	0.149692997	0.251309752	2.589562178

H	-0.677030325	-0.392169327	2.897885084
H	1.064480186	-0.345961601	2.580189228
H	0.272557080	1.027464867	3.354216576
C	-2.259013414	2.710652590	-1.256022215
H	-1.980906248	2.884473324	-2.296922445
H	-3.223501682	2.197974920	-1.230986118
H	-2.401537180	3.689544439	-0.783493161
C	0.876604736	2.673281431	-1.934089661
H	1.140472412	3.698166132	-1.646438956
H	1.796276212	2.164707661	-2.230877399
H	0.227139920	2.728132963	-2.810073376
C	2.354701996	1.119989038	0.438884944
H	2.607059479	0.237813979	1.032372594
H	2.842502832	1.027125001	-0.534232557
H	2.786978960	1.991306901	0.944648564
P	-2.244608402	-0.980687737	-2.076538086
C	-3.880728245	-1.140981674	-1.258073449
H	-4.624102116	-1.548942208	-1.949259520
H	-3.787738323	-1.797734857	-0.389754266
H	-4.216056824	-0.159951627	-0.914243281
C	-2.596264601	0.033382218	-3.568548203
H	-1.685022712	0.119405806	-4.165607929
H	-3.379584551	-0.438406199	-4.169585705
H	-2.924553633	1.033485174	-3.284832478
C	-1.976870298	-2.642300367	-2.821007729
H	-2.850515604	-2.920875311	-3.416912317
H	-1.102685690	-2.616354227	-3.476982355
H	-1.823458910	-3.401998281	-2.052018881
C	0.772342861	-2.030280352	-0.970779479
H	1.799305916	-1.835191846	-0.667656302
H	0.704371095	-2.710621595	-1.818974614
H	0.527246892	-0.925726771	-1.806085348
C	-0.237957180	-2.164395332	0.081281237
H	-1.013253212	-2.913190126	-0.053898018
H	0.111092515	-2.105904341	1.108879924

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Ir	-0.637722492	0.060511682	0.047397818
C	-0.360649467	1.378643870	1.929520249
C	-1.031797051	2.154108763	0.926957965
C	0.946890354	1.045256257	1.439120889
C	-0.089999996	2.391202927	-0.159350485
C	1.113104701	1.711931109	0.158733070
C	-2.330793142	2.879272223	1.126947165
H	-2.876634836	3.026758671	0.192521006
H	-2.984508753	2.347232580	1.821145415
H	-2.141499996	3.872599125	1.551103711
C	-0.863895059	1.098083854	3.311404705
H	-1.954712272	1.087002873	3.361074686
H	-0.497291595	0.142598271	3.689280510
H	-0.509410560	1.882156253	3.990891457
C	-0.252428442	3.385999441	-1.274271846
H	-0.096630454	2.952502012	-2.265735626
H	-1.242279530	3.844398499	-1.262082458
H	0.478404880	4.193957329	-1.156187296
C	2.410735846	1.854478598	-0.575179696
H	2.979772091	2.684092522	-0.135670453
H	3.027090311	0.958900034	-0.503564060
H	2.263064146	2.084016562	-1.632837176
C	2.062404394	0.489420176	2.270741701
H	1.715345860	-0.294139653	2.946943998
H	2.857997179	0.074210815	1.654163480
H	2.496700287	1.287243605	2.886859655
P	-2.566670656	0.001808355	-1.256166101
C	-4.117501736	0.103120238	-0.267360359
H	-4.987071514	0.106848471	-0.930880189
H	-4.181634903	-0.757315099	0.401545733
H	-4.124661922	1.011144280	0.335936755
C	-2.752548218	1.399449110	-2.438345671
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H	-3.704399109	1.308293700	-2.969880819
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H	-2.139660597	-1.636119723	-3.037720919
H	-3.200214624	-2.309095144	-1.783227205
C	-0.643903136	-2.288022757	2.136882782
H	0.128848732	-1.718177795	2.660515070
H	-1.198135614	-2.859074831	2.894611835
H	-0.139368132	-3.015336037	1.495744228
C	-1.582199693	-1.383996487	1.339623570
H	-2.302341461	-2.010753393	0.807222486

H	-2.182935715	-0.775465727	2.023289680
P	0.516829073	-1.534731746	-1.226978540
C	0.154254302	-3.350022793	-1.204582214
C	1.160016537	-4.258325100	-1.587636352
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C	-1.374027610	-5.228401184	-0.955956876
C	-0.372486085	-6.117276192	-1.346026182
H	2.153514385	-3.901718855	-1.835900903
H	-1.891782284	-3.192184448	-0.560558319
H	1.687061548	-6.306212902	-1.960303307
H	-2.361746550	-5.597480297	-0.695710063
H	-0.574619412	-7.182770729	-1.398537517
C	0.436332077	-1.123543501	-3.029319048
C	0.511580586	0.228680328	-3.397957802
C	0.337827951	-2.093100548	-4.037908554
C	0.492452592	0.607191920	-4.739092350
C	0.299804777	-1.711257577	-5.381313324
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H	0.560962081	1.658325553	-5.005795956
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C	2.330743551	-1.587094545	-0.905224085
C	2.771162987	-2.084298372	0.331952900
C	3.280666113	-1.244076967	-1.877671361
C	4.132910728	-2.224585533	0.593762755
C	4.645674229	-1.377383828	-1.607934237
C	5.076028824	-1.866129637	-0.374236554
H	2.048152447	-2.368387461	1.089529753
H	2.964354515	-0.877194524	-2.847965002
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C	0.900926352	1.099947929	0.393867016
C	-0.931389987	2.052044153	-0.681752026
C	0.517413139	1.939626694	-0.703217506
C	-2.824494600	1.354075432	0.990163565
H	-3.547992468	1.338440657	0.172041610
H	-3.028875589	0.509624958	1.651245952
H	-3.005086660	2.272148848	1.561997890
C	-0.310224324	-0.012197830	2.435729980
H	-1.253826022	-0.541034520	2.584793329
H	0.499633700	-0.743324876	2.490321159
H	-0.177041918	0.680547237	3.275552988
C	-1.745279551	2.982230902	-1.532520771
H	-1.336059809	3.059772491	-2.541557789
H	-2.782414675	2.651790142	-1.614358902
H	-1.751754642	3.986693144	-1.092890739
C	1.437410355	2.669384003	-1.635953188
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H	2.370155096	2.123791218	-1.791585684
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C	2.300345659	0.749345541	0.798131883
H	2.384688854	-0.294875115	1.112049222
H	3.006933451	0.917985976	-0.016051261
H	2.612850428	1.369844198	1.645622849
P	-2.282780647	-1.199668765	-1.840876579
C	-3.281375885	-2.047410488	-0.553400755
H	-4.133612633	-2.566228867	-1.002178311
H	-2.658307314	-2.770180941	-0.021716824
H	-3.648478270	-1.310938597	0.164526001
C	-3.492043734	-0.126470208	-2.706467152
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H	-4.315644741	-0.723984122	-3.108244658
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C	-1.924562097	-2.510395765	-3.074138403
H	-2.850872755	-2.998953819	-3.389625549
H	-1.439042926	-2.060869932	-3.943821907
H	-1.256119251	-3.263813734	-2.651235104
C	1.145928860	-1.572724581	-1.550598264
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H 0.777025163 -1.971851587 0.551878035

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B1

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C -2.460838556 -0.651722848 -7.562981606
C -3.725058079 -0.338288099 -6.979527950
C -5.372452259 -1.496381640 -5.265765667
H -6.265391350 -1.590344071 -5.894207478
H -5.349749565 -2.361319780 -4.593103886
H -5.497022629 -0.600336075 -4.647143841
C -3.020067930 -3.717569113 -5.382158279
H -4.031314373 -4.079231739 -5.163779736
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C -0.732386589 -2.646781445 -7.407216072
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C -1.670905709 0.236189380 -8.542378426
H -0.694466650 0.514583349 -8.129858971
H -1.492803812 -0.278956026 -9.493173599
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C -4.538623810 0.947175562 -7.218889236
H -4.560937405 1.213155866 -8.281840324
H -5.576253414 0.830479205 -6.886001587
H -4.111074448 1.797098041 -6.674883842
S -2.625360966 -2.941557884 -2.146370649
O -2.019067049 -2.287769794 -3.857074976
O -2.130220175 -4.195782661 -2.224876404
O -1.532196164 -1.954749107 -1.206930757
C -3.832645416 -2.988678217 -1.191465378
F -4.238818169 -4.271396637 -1.076917887
F -4.875185013 -2.276561975 -1.670490026
F -3.572285652 -2.535168648 0.053526498
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C 1.616411567 -0.405897558 -5.596374989
H 2.348102331 -0.698904276 -4.834873676
H 1.286995530 -1.318504095 -6.106023788
H 2.138211727 0.214155540 -6.334187508
C 0.367078096 2.270148993 -5.299103737
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H 0.458066374 2.400207758 -6.383499146
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C 0.645366788 0.669565380 -3.073759079
H -0.218178988 0.488000840 -2.423811913
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H 1.017911673 1.676558852 -2.854025364
C -2.905365229 1.228020549 -4.280224800
C -2.778985977 2.483912230 -4.897553921
C -3.599815845 1.156555772 -3.060813904
C -3.326833010 3.626579523 -4.317038059
C -4.147883415 2.298866272 -2.479804277
C -4.013979435 3.539476871 -3.105238914
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H -4.440912247 4.429631233 -2.652745724

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B2

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C -4.081217289 -1.443388224 -6.113562584
C -2.483388662 -0.618172824 -7.548471451
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C -5.345942497 -1.561641693 -5.251265526
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H -5.303079605 -2.443289757 -4.590933800
H -5.484872818 -0.679856062 -4.607483864
C -2.972417831 -3.748829126 -5.446048260
H -3.993584394 -4.101071835 -5.233439922
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C	1.610721588	-0.455977559	-5.545515060
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H	1.278969765	2.688966513	-4.860661507
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C	0.618406773	0.695335388	-3.054358959
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B3

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C	-2.460838556	-0.651722848	-7.562981606
C	-3.725058079	-0.338288099	-6.979527950
C	-5.372452259	-1.496381640	-5.265765667
H	-6.265391350	-1.590344071	-5.894207478
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H	-5.497022629	-0.600336075	-4.647143841
C	-3.020067930	-3.717569113	-5.382158279
H	-4.031314373	-4.079231739	-5.163779736
H	-2.502889633	-4.503159046	-5.944725513
H	-2.498372555	-3.598583937	-4.425714016
C	-0.732386589	-2.646781445	-7.407216072
H	-0.102376513	-2.774062634	-6.519525051
H	-0.922567487	-3.642981768	-7.822575569
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H	-4.560937405	1.213155866	-8.281840324
H	-5.576253414	0.830479205	-6.886001587
H	-4.111074448	1.797098041	-6.674883842
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C	1.616411567	-0.405897558	-5.596374989
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C -3.165101051 1.265951037 -4.780673504
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B3-TS

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P 0.016968967 -1.095060706 -4.202576637
C 0.594562471 -2.784299612 -4.649021149
H 1.610256553 -2.954129457 -4.278974056
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C 1.396532774 -0.045063749 -4.815477371
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H -0.643207788 -3.447242737 1.272183061
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C -1.919267654 2.845772982 -2.337629795
C -3.251278877 2.988386631 -1.943253160
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H -0.495889366 1.731855035 -3.476962566
H -5.236468792 2.150084257 -2.105170727
H -1.172907829 3.562936306 -2.004923105
H -3.549290180 3.808718204 -1.297077656

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B4

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H -5.497022629 -0.600336075 -4.647143841
C -3.020067930 -3.717569113 -5.382158279
H -4.031314373 -4.079231739 -5.163779736
H -2.502889633 -4.503159046 -5.944725513
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H -0.694466650 0.514583349 -8.129858971
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C 1.616411567 -0.405897558 -5.596374989
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H 1.286995530 -1.318504095 -6.106023788
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B4-TS

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C -2.127785206 -0.725286126 -7.553847790
C -3.404407501 -0.302197009 -7.100925446
C -5.369598866 -1.429094434 -5.781145096
H -5.952032089 -1.918215513 -6.575304508
H -5.487542629 -2.028877497 -4.874540329
H -5.810029507 -0.445154160 -5.609839916
C -3.106136799 -3.654357433 -5.349033356
H -3.480619192 -4.426962852 -6.032038212
H -2.150465012 -3.998289824 -4.946100712
H -3.815041780 -3.569715261 -4.521181107
C -0.635152519 -2.860972404 -7.164285660
H -0.270956367 -3.363994837 -6.266170979
H -0.942258358 -3.633702278 -7.879303932
H 0.197134480 -2.319126844 -7.611994743
C -1.311190605 -0.092714176 -8.638256073
H -0.238541976 -0.184824333 -8.457035065
H -1.518817902 -0.592380166 -9.591610909
H -1.552190542 0.963994324 -8.762451172
C -4.160606384 0.916902423 -7.531737804
H -4.886080742 0.662864566 -8.314325333
H -4.705909252 1.353524804 -6.691397667
H -3.490812063 1.682357311 -7.928804874
P 0.034400236 0.630389035 -5.185622692
C 1.437095404 -0.394577324 -5.785569668
H 2.379255533 0.146176204 -5.651981831
H 1.471328497 -1.328588247 -5.220756054
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C 0.171090931 2.139188051 -6.231873989
H 1.164758205 2.586164236 -6.124896526
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H -5.629936218 3.966995239 -3.124561310

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B3-TS’

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C	-3.829149723	-2.117980957	-6.281223774
C	-1.905462384	-1.113272905	-7.136021614
C	-3.321598053	-1.013076901	-7.082535744
C	-5.259527683	-2.560462952	-6.188289165
H	-5.448899269	-3.349442959	-6.926621437
H	-5.490498066	-2.978053093	-5.203871727
H	-5.955327988	-1.745324016	-6.391488552
C	-2.801889896	-4.196646214	-5.104749203
H	-3.566402435	-4.161232948	-4.323934555
H	-3.075489759	-4.997951508	-5.803183079
H	-1.858320236	-4.464875698	-4.631785870
C	-0.138830081	-2.855803967	-6.281535149
H	0.049144775	-3.365031242	-5.335800171
H	-0.037597127	-3.596946239	-7.084280491
H	0.639881492	-2.106285095	-6.437998772
C	-0.997800350	-0.288482964	-7.999415874
H	0.037623338	-0.326268673	-7.653559208
H	-1.007277489	-0.671949923	-9.026955605
H	-1.309077740	0.758057714	-8.034079552
C	-4.168682098	-0.006196983	-7.799782753
H	-4.526347160	-0.423027754	-8.749081612
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H	-3.604643106	0.901823044	-8.022884369
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H	1.621191382	0.190293387	-3.529978752
H	0.637884378	-1.082222581	-2.780641556
H	1.058965206	-1.187919140	-4.507122517
C	-0.141392395	1.743339181	-5.221257687
H	0.625342369	2.352204084	-4.733348370
H	0.287071139	1.284258842	-6.113394737
H	-0.970634520	2.382760286	-5.531593800
C	-0.944196045	1.325962901	-2.478610516
H	-1.829836607	1.961889982	-2.466805220
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H	-0.059022039	1.947171926	-2.312389851
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H	-3.031050444	-0.227074236	-2.266272306
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P	-2.236520052	-2.941395283	-1.233784914
C	-1.066827297	-1.942996383	-0.209806249
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C	0.283606768	-2.256575584	0.015154088
C	-0.786316693	0.062504329	1.148493171
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C	0.561132789	-0.253046930	1.354454160
H	-2.633024693	-0.506474197	0.207790330
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C	-1.557458282	-5.697768211	-1.530877709
C	-0.142234415	-4.111421585	-2.680830240
C	-0.820922911	-6.747853279	-2.086309910
C	0.604919970	-5.160356998	-3.216238737
C	0.262519240	-6.486460209	-2.927200317
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H	0.120354258	-3.088005066	-2.930774212
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H	1.451549768	-4.943471432	-3.863378525
H	0.837124467	-7.305527210	-3.349730253
C	-3.342211485	-3.672600746	0.042589813
C	-4.676266193	-3.925640345	-0.312439024
C	-2.910634518	-3.988753319	1.341639757
C	-5.561122894	-4.493215084	0.606833756
C	-3.797388077	-4.548842907	2.260558128
C	-5.122802734	-4.803851604	1.895358562
H	-5.024928093	-3.677249670	-1.313085675
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H	-6.591248035	-4.685402393	0.319607615
H	-3.453987360	-4.788438320	3.263158798
H	-5.810887814	-5.239166737	2.614315510
C	-4.095187187	0.652397394	-4.345865726
C	-3.807867289	2.033416510	-4.301848412
C	-5.452883244	0.279043674	-4.419431686
C	-4.821910858	2.985796928	-4.383241653
C	-6.471491337	1.231999397	-4.480213642
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H	-2.786374092	2.383821964	-4.253216743
H	-5.723274231	-0.768797219	-4.410703659
H	-4.565128803	4.041598320	-4.379511356
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B5

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C -3.718168020 -0.337498099 -6.971107960
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H -0.149835527 -2.085711956 -8.148159981
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H -0.702816665 0.535653353 -8.128838539
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H -5.096178532 -2.426062584 1.023389101

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C -4.099226952 -1.406928301 -6.126002789
C -2.461098671 -0.653142869 -7.565831661
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H -5.372329712 -2.319529772 -4.594123840
H -5.488212585 -0.561146080 -4.661473751
C -3.021977901 -3.714259148 -5.389758110
H -4.104344368 -3.911961794 -4.667339802
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H -2.005582571 -3.777343988 -4.596333981
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H	-4.096964359	1.802327991	-6.680493832
P	0.071329966	0.740345418	-4.880154133
C	1.578879476	-0.010500006	-5.621516705
H	2.342706203	-0.208070040	-4.859110355
H	1.347957015	-0.962501407	-6.113642216
H	2.026814222	0.650916278	-6.374376297
C	0.044679951	2.516784430	-5.359823227
H	0.881197095	3.064261436	-4.910487652
H	0.117257491	2.637292385	-6.446932316
H	-0.881559730	3.004127264	-5.034501076
C	0.505109251	0.993592918	-3.110111713
H	-0.328359395	0.736284077	-2.455158234
H	1.358819008	0.356768727	-2.871719837
H	0.769900918	2.032746315	-2.909913540
C	-1.471614599	-1.451367497	-2.929116488
H	-1.081402898	-0.680980563	-2.271080971
P	-3.423532963	1.751258612	-3.226142645
C	-4.940900326	0.930841208	-2.530597210
C	-4.870948792	-0.350762904	-1.958819509
C	-6.189349174	1.574944973	-2.562164307
C	-6.008020878	-0.965710819	-1.437408566
C	-7.326705933	0.960374594	-2.041025639
C	-7.241461277	-0.313047826	-1.476172566
H	-3.916050196	-0.867387772	-1.923253417
H	-6.266611576	2.565498114	-2.999268532
H	-5.929744244	-1.957148433	-0.999557912
H	-8.281439781	1.477561831	-2.076479435
H	-8.127450943	-0.792150140	-1.070050240
C	-3.898840189	3.105467081	-4.409836292
C	-2.977440357	4.101308823	-4.776344299
C	-5.189457417	3.161751270	-4.962880611
C	-3.333185196	5.115948677	-5.663363934
C	-5.545856953	4.176038742	-5.850080013
C	-4.619289875	5.158111572	-6.204638004
H	-1.974443078	4.078050137	-4.361351490
H	-5.917882919	2.403139353	-4.693610191
H	-2.603874445	5.875027180	-5.932199001
H	-6.549616814	4.199023724	-6.265024185
H	-4.896719456	5.948472023	-6.895851135
C	-2.991204262	2.885267258	-1.817113161
C	-1.661087155	3.261671066	-1.572782159
C	-3.985355377	3.388970852	-0.966614366
C	-1.336901784	4.111012936	-0.516386569
C	-3.662405729	4.238697529	0.090184897
C	-2.336496353	4.603773117	0.320331365
H	-0.876247048	2.884087563	-2.217396498
H	-5.018969536	3.110752344	-1.137474298
H	-0.301339388	4.388309002	-0.346653104
H	-4.448071003	4.616155148	0.734981000
H	-2.084464788	5.265635967	1.143631697
H	-2.374423981	-1.861251593	-2.524262428
C	-0.373713344	-2.516458988	-3.053274155
C	0.268291116	-3.020112753	-1.910586119
C	0.016734511	-3.012492657	-4.309812069
C	1.258147836	-3.986507654	-2.018713474
C	1.004843116	-3.980567694	-4.418142796
C	1.630321026	-4.472993374	-3.271466970
H	-0.011992961	-2.648712873	-0.930274189
H	-0.452927887	-2.635882854	-5.214298248
H	1.739690781	-4.359911919	-1.121266603
H	1.286583543	-4.349681854	-5.402094364
H	2.400409460	-5.226779461	-3.354487181

Vibrational frequencies of the optimized geometries

Table S6. Vibrational frequencies (in cm^{-1}) of the optimized geometries.

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Methane

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1352.97 1354.52 1355.85 1575.86 1576.30 3047.02

3160.65 3163.26 3167.25

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OTf^{-}

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56.93 190.96 191.92 290.81 331.30 331.46

498.67 498.96 555.81 556.16 622.04 740.36

999.50 1178.75 1180.11 1228.04 1256.34 1257.01

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PPh_3

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23.64 27.30 42.00 54.31 54.70 67.60

188.66 205.29 208.35 250.20 260.83 264.05

407.28 408.03 412.60 417.10 430.41 433.29

506.67 509.43 520.72 631.45 631.55 631.82

693.58 705.67 706.44 711.88 712.29 713.38

762.51 763.11 763.72 865.24 865.87 868.22

933.19 934.24 935.99 981.63 982.27 983.59

1003.91 1004.24 1004.89 1013.48 1013.65 1013.90

1052.11 1052.37 1052.79 1109.66 1110.18 1110.58

1111.49 1111.76 1118.47 1196.13 1196.53 1196.76

1221.31 1221.54 1222.83 1323.26 1327.24 1328.58

1362.44 1362.79 1363.19 1474.49 1475.57 1476.03

1524.38 1525.29 1525.48 1627.58 1628.44 1628.68

1645.41 1645.66 1647.44 3169.42 3169.56 3169.75

3176.79 3177.31 3177.51 3187.94 3188.34 3188.58

3200.37 3200.57 3201.01 3207.50 3207.79 3208.89

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$H_2C=PPh_3$

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31.93 36.23 46.76 59.16 73.11 77.98

145.45 187.30 202.66 218.04 242.11 246.37

265.30 274.36 371.27 406.32 411.64 414.91

427.67 438.82 449.64 472.81 514.81 518.09

524.49 629.63 630.91 631.99 687.90 707.72

710.34 713.76 715.16 716.75 760.66 763.15

768.37 866.17 873.51 877.57 881.38 940.86

945.18 957.31 978.02 984.97 990.68 1000.97

1005.63 1009.25 1012.37 1014.62 1015.64 1017.15

1051.22 1052.45 1054.98 1102.44 1110.54 1113.28

1115.96 1121.55 1132.89 1195.70 1196.49 1198.27

1214.89 1220.96 1225.07 1326.51 1331.46 1335.40

1360.66 1363.14 1367.12 1391.33 1473.90 1476.44

1478.54 1522.22 1524.33 1529.49 1628.41 1629.79

1631.58 1645.65 1647.35 1649.63 3156.89 3167.29

3173.05 3176.22 3176.87 3182.46 3185.78 3187.20

3190.96 3195.63 3198.52 3202.02 3202.98 3205.68

3208.17 3215.75 3259.77

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A1

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26.91 34.18 44.79 48.50 52.09 80.31

99.28 108.57 118.22 129.77 142.64 146.37

154.79 161.44 164.04 166.71 169.53 174.15

178.79 186.50 198.11 202.37 206.92 208.78

213.67 216.39 231.46 231.64 249.33 260.04

262.10 271.03 297.46 306.03 309.50 312.94

314.08 320.18 331.33 350.19 362.23 383.95

399.80 440.13 492.44 499.92 525.95 532.83

539.57 552.30 560.91 565.59 590.08 606.33

616.69 619.57 668.06 730.04 734.65 755.84

805.59 806.13 810.50 851.79 868.17 873.29

882.72 933.23 966.04 972.01 975.49 980.68

991.93 1052.10 1056.31 1059.11 1062.01 1067.78

1099.63 1102.43 1130.25 1135.99 1178.10 1180.30

1204.57 1227.78 1247.96 1279.08 1302.12 1330.55

1333.71 1352.89 1386.51 1394.63 1418.95 1425.20

1430.80 1438.29 1442.40 1451.40 1459.97 1467.93

1470.15 1473.19 1474.83 1477.42 1480.92 1485.68

1488.19 1490.83 1496.04 1497.80 1503.28 1505.68

1508.22 1510.75 1515.33 1518.06 1528.66 1556.30

3020.29 3033.53 3036.23 3037.82 3039.60 3042.25

3050.85 3053.43 3059.48 3101.65 3108.86 3111.47

3114.61 3115.50 3131.48 3136.03 3139.38 3141.87

3142.56 3143.99 3144.78 3148.57 3151.42 3152.78

3157.99 3165.13 3171.53

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A2

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15.41 27.46 52.19 95.28 122.96 131.64

138.81 141.12 146.56 149.67 150.99 155.92

163.34 177.29 181.26 189.25 197.60 205.18

210.81 214.40 231.71 234.63 257.66 263.67

303.61 309.80 315.21 316.44 350.27 380.32

407.78 427.57 516.86 529.98 534.56 558.85

587.36 592.92 599.24 664.81 694.08 734.82

738.93 805.28 808.03 808.75 848.92 870.18

875.54 965.68 969.46 976.32 978.13 990.36
1038.49 1039.99 1045.50 1049.60 1051.65 1099.03
1101.81 1127.92 1175.15 1180.34 1258.21 1339.94
1340.82 1361.33 1379.59 1386.52 1413.30 1427.73
1430.33 1433.47 1437.30 1444.18 1447.86 1460.80
1464.91 1468.35 1468.51 1470.93 1474.80 1477.36
1478.79 1482.01 1487.34 1488.72 1490.72 1493.18
1502.79 1504.21 1507.75 1519.38 1529.78 1558.85
2991.48 3046.39 3047.90 3051.28 3052.18 3052.76
3056.95 3060.17 3062.17 3073.13 3117.82 3118.47
3120.73 3122.41 3123.01 3124.29 3147.48 3148.23
3148.67 3150.13 3151.94 3152.63 3154.72 3157.26
3159.36 3163.21 3167.87

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A3

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22.61 30.09 30.58 35.91 47.23 50.39
55.52 59.14 69.93 78.67 88.05 91.23
102.99 117.20 124.02 134.42 145.47 148.84
153.08 158.03 165.91 168.53 179.53 180.61
183.21 195.35 197.54 203.11 206.05 211.78
212.90 218.11 226.33 230.30 237.36 253.51
256.58 265.60 267.55 277.00 280.81 288.51
298.89 302.45 304.86 309.42 310.55 332.26
368.07 374.80 395.92 405.05 406.76 409.62
420.43 446.15 454.29 487.74 505.22 507.52
518.27 534.18 538.03 557.19 567.57 595.75
607.50 609.06 629.06 629.99 631.47 667.39
670.76 682.10 707.26 707.89 713.42 725.32
726.02 727.54 737.23 746.25 768.28 769.81
777.17 799.46 807.44 813.19 841.29 846.04
863.97 869.84 870.41 876.18 878.70 945.38
950.79 959.77 965.92 966.81 968.36 969.81
986.31 988.01 991.98 1001.08 1013.56 1014.44
1016.48 1021.67 1021.69 1024.09 1045.61 1048.42
1051.83 1052.83 1054.59 1055.04 1056.35 1056.83
1095.86 1098.63 1106.29 1116.17 1117.87 1121.71
1123.66 1126.59 1127.94 1140.14 1140.85 1179.85
1182.35 1204.34 1205.38 1205.96 1229.23 1229.34
1232.70 1286.81 1327.62 1333.32 1335.01 1336.78
1339.84 1357.98 1367.34 1370.21 1372.71 1400.24
1404.35 1419.09 1423.30 1427.04 1429.00 1441.96
1443.55 1459.21 1462.07 1464.67 1467.89 1468.77
1475.14 1476.63 1477.29 1477.63 1480.43 1482.00
1485.96 1487.94 1491.45 1493.96 1499.62 1503.11
1508.28 1510.12 1515.05 1517.67 1519.23 1526.67
1528.02 1530.15 1530.96 1541.36 1626.47 1627.19
1631.53 1644.20 1644.45 1647.53 3019.37 3026.94
3038.71 3041.06 3043.89 3050.96 3051.55 3054.72
3059.49 3069.19 3079.43 3091.59 3095.31 3104.57
3109.26 3110.97 3115.90 3121.58 3128.75 3139.02
3140.41 3145.63 3149.17 3157.43 3160.62 3164.58
3165.15 3171.31 3179.69 3183.19 3190.87 3191.57
3194.63 3196.31 3200.45 3204.14 3204.38 3210.23
3211.86 3214.37 3217.97 3220.69 3223.68 3264.78

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A3-TS

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-76.03 18.63 20.76 30.58 40.60 51.03
54.72 59.20 62.54 70.74 78.15 80.09
84.60 109.80 117.04 143.43 146.36 152.38
159.30 163.69 165.78 169.02 175.05 180.20
183.17 186.60 188.50 190.59 200.66 204.83
214.01 220.37 226.11 229.11 236.86 247.29
252.21 257.53 258.40 263.26 268.66 280.00
281.03 284.68 304.69 308.50 313.91 318.08
337.89 365.87 399.33 409.44 409.57 414.86
414.93 424.96 436.05 451.03 494.30 518.21
520.80 527.69 535.65 539.19 562.68 594.18
601.08 613.16 627.12 630.18 632.07 637.09
669.21 692.06 696.22 708.95 711.40 715.16
721.91 725.13 728.06 731.16 762.22 767.05
775.35 805.16 813.32 815.91 847.08 862.25
870.58 873.26 874.28 874.43 880.75 930.99
943.29 947.57 953.50 966.15 971.94 973.48
976.44 979.66 989.45 990.24 993.01 999.00
1007.13 1012.74 1015.61 1016.37 1019.28 1021.51
1039.93 1050.48 1051.59 1052.32 1053.95 1054.98
1055.61 1057.75 1099.65 1101.54 1106.57 1110.20
1115.46 1115.90 1117.64 1118.64 1133.44 1179.55
1183.46 1200.77 1201.16 1202.44 1222.82 1226.75
1229.68 1276.66 1312.10 1323.79 1333.34 1336.91
1337.75 1358.28 1361.28 1365.26 1369.35 1406.17
1407.28 1425.30 1429.24 1430.69 1442.16 1443.87
1452.64 1456.56 1461.38 1465.80 1467.83 1470.50
1472.03 1472.42 1475.63 1476.92 1479.53 1483.74
1487.78 1489.44 1491.32 1493.38 1497.81 1503.98
1504.40 1511.16 1516.02 1519.36 1520.45 1522.43
1524.86 1526.11 1527.41 1530.38 1612.14 1624.29
1627.31 1638.82 1643.32 1644.05 3012.56 3039.90
3040.69 3042.33 3044.02 3046.97 3054.22 3056.62
3060.44 3071.68 3085.19 3098.74 3100.81 3103.93
3108.44 3118.71 3130.17 3133.43 3136.36 3139.79
3143.72 3145.18 3145.46 3151.56 3154.06 3158.72

3162.08 3162.41 3165.75 3168.34 3168.85 3169.75
3182.05 3182.71 3185.30 3189.07 3191.60 3197.89
3203.84 3203.98 3206.72 3209.84 3213.13 3215.12

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A3-TS'

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-309.32 5.82 15.75 23.34 29.45 32.45
35.49 40.62 46.27 50.08 60.44 64.55
73.00 87.80 94.55 108.46 118.00 127.95
132.32 146.44 150.70 152.50 156.62 165.71
168.38 169.95 180.17 186.20 188.10 194.22
200.35 204.79 211.32 220.31 224.14 228.58
235.01 249.70 251.07 252.22 259.61 271.16
276.37 278.31 303.21 306.46 312.16 314.26
356.30 367.34 406.10 408.98 409.41 411.49
420.11 421.29 424.72 431.42 454.10 490.88
510.94 529.19 532.46 538.30 559.46 592.64
605.58 615.98 629.58 631.15 632.47 646.76
672.46 689.50 704.18 711.01 715.56 716.79
720.69 734.62 736.46 744.56 760.52 764.61
770.90 775.36 807.01 810.05 813.20 866.41
873.67 875.54 876.89 880.94 885.31 916.35
938.79 940.95 948.24 966.02 971.06 975.39
979.62 981.45 989.50 990.82 992.03 1008.80
1011.93 1012.52 1014.15 1014.63 1015.75 1047.52
1050.12 1050.82 1051.82 1051.95 1053.64 1053.88
1055.82 1082.73 1097.67 1100.02 1107.48 1108.93
1113.00 1114.31 1117.45 1119.64 1129.56 1178.81
1180.91 1199.65 1200.02 1200.60 1220.48 1224.68
1229.73 1247.79 1317.11 1326.16 1330.12 1338.72
1346.21 1360.96 1363.47 1364.75 1369.39 1398.64
1402.99 1423.56 1426.84 1430.18 1440.38 1441.74
1451.09 1457.85 1461.57 1464.35 1467.06 1470.10
1471.66 1473.97 1475.38 1476.77 1478.22 1479.72
1484.66 1487.41 1490.80 1494.03 1496.93 1502.45
1507.04 1508.99 1512.25 1513.98 1520.21 1521.31
1524.28 1525.84 1526.91 1537.30 1623.16 1626.15
1627.26 1642.48 1643.42 1645.02 3044.88 3046.56
3049.28 3050.28 3052.60 3053.87 3057.96 3064.39
3074.60 3078.54 3113.54 3113.96 3119.22 3119.76
3121.32 3135.88 3136.02 3144.49 3145.21 3150.10
3150.73 3151.60 3153.21 3161.08 3166.10 3167.41
3168.55 3170.12 3172.10 3176.52 3183.73 3185.21
3186.87 3191.81 3192.36 3195.36 3195.49 3198.30
3200.75 3201.47 3207.80 3209.10 3211.94 3214.29

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A4

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3.17 39.62 100.75 118.27 129.76 136.30
144.69 149.91 154.36 156.60 161.88 163.43
169.00 177.98 186.18 187.00 193.20 201.05
214.14 215.85 231.01 242.62 250.10 267.98
272.63 298.85 306.45 309.99 313.75 316.40
346.69 365.17 402.58 411.80 438.97 510.77
532.31 537.62 561.22 592.71 609.06 615.30
667.45 733.67 739.79 772.80 807.47 809.41
813.91 855.66 866.55 870.98 876.63 881.70
963.51 972.70 974.40 977.18 988.45 1017.29
1043.99 1047.70 1050.60 1053.83 1054.32 1096.84
1097.59 1130.21 1177.71 1180.04 1280.27 1341.23
1342.67 1362.90 1402.60 1405.14 1426.26 1427.67
1430.94 1439.87 1441.19 1451.33 1456.72 1458.41
1462.31 1466.49 1470.80 1473.19 1474.17 1480.72
1482.90 1487.58 1489.21 1494.56 1495.46 1501.26
1503.47 1509.61 1514.49 1515.46 1517.85 1522.00
1528.27 3045.91 3046.70 3048.98 3049.80 3050.71
3051.02 3053.14 3058.67 3060.03 3066.69 3110.14
3114.84 3115.41 3117.08 3122.47 3133.49 3142.45
3143.75 3144.57 3146.53 3147.30 3147.62 3149.45
3153.95 3154.44 3166.11 3166.85 3167.11 3174.26

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-315.61 27.55 36.83 96.45 105.07 110.16
127.43 133.64 145.23 148.33 153.21 158.78
162.15 163.55 171.33 173.88 187.12 200.40
204.01 210.59 213.77 226.98 236.28 246.34
265.58 273.90 304.34 308.84 309.92 314.07
356.59 367.50 409.68 424.11 429.06 531.30
537.16 559.29 592.36 604.49 614.92 647.38
670.24 732.21 734.32 738.03 772.50 803.46
806.75 812.01 856.90 873.36 875.64 896.08
965.50 969.61 971.61 973.97 987.14 1045.47
1048.18 1051.16 1052.03 1053.86 1080.58 1097.24
1099.57 1129.14 1178.50 1180.07 1241.78 1339.53
1341.34 1361.82 1398.06 1402.15 1423.66 1426.91
1430.37 1439.91 1440.92 1449.73 1458.84 1460.33
1464.02 1464.84 1467.36 1472.89 1475.41 1476.04
1481.70 1487.14 1487.95 1491.13 1492.93 1499.39
1501.07 1503.98 1511.22 1512.60 1518.55 1519.61
1536.36 3049.43 3051.01 3051.72 3052.88 3053.83
3055.04 3061.01 3063.10 3073.26 3089.09 3115.11

3118.02 3119.82 3120.77 3123.68 3139.05 3146.04
3146.31 3148.39 3150.62 3151.80 3154.30 3155.40
3155.77 3159.75 3160.07 3168.24 3175.67 3208.23

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A5

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28.71 53.98 98.93 106.35 128.76 131.18
135.17 140.58 143.61 155.41 159.16 166.86
167.56 177.08 187.74 194.46 203.03 206.17
221.08 223.30 237.60 240.15 268.68 276.49
279.19 308.27 309.63 312.41 314.09 357.17
367.35 408.26 446.81 485.56 502.46 536.46
539.95 558.80 589.43 611.58 620.54 670.04
731.02 736.20 803.58 805.46 808.88 832.89
872.54 875.22 895.35 954.28 968.77 971.58
972.28 979.63 988.38 1033.73 1043.84 1047.99
1051.52 1053.11 1054.68 1097.86 1099.84 1118.24
1128.67 1167.78 1177.17 1179.63 1339.29 1340.09
1345.76 1361.83 1391.11 1396.77 1419.67 1426.74
1429.21 1435.09 1439.23 1449.44 1456.51 1461.02
1463.31 1465.24 1470.99 1475.60 1478.42 1479.87
1485.87 1488.11 1490.91 1494.38 1500.66 1502.14
1507.90 1511.08 1514.87 1518.61 1522.42 1547.33
1616.39 2079.27 3049.72 3049.92 3051.16 3051.36
3052.68 3059.20 3060.44 3062.59 3098.79 3114.56
3115.93 3118.48 3119.94 3120.66 3123.51 3141.55
3147.42 3147.86 3149.39 3150.96 3152.38 3153.74
3155.04 3158.34 3161.98 3167.02 3171.84 3188.22

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A5′

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18.25 35.74 59.14 100.50 114.78 129.11
135.42 138.10 144.05 151.04 155.46 159.33
160.97 166.88 174.30 178.84 188.86 196.54
202.92 211.05 216.41 232.94 236.52 258.09
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A5-TS

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B1

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B2

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B3

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B4

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B5

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167.78 177.54 182.83 188.85 193.82 197.11
207.45 210.41 229.07 232.54 234.87 247.64
253.25 273.99 290.82 304.18 308.20 312.31
313.52 351.07 363.05 375.21 397.84 426.33
436.27 457.67 505.65 527.73 539.23 557.58
559.91 591.95 603.34 615.95 624.45 666.86
706.39 721.61 730.23 768.92 803.57 806.12
808.25 810.02 837.32 857.15 874.48 879.40
892.89 963.71 966.81 969.61 973.51 975.81
986.51 995.46 1001.94 1012.20 1035.94 1042.99
1043.73 1045.83 1051.20 1053.46 1056.60 1097.89
1100.85 1118.63 1130.21 1177.17 1182.32 1205.23
1211.22 1262.72 1334.54 1339.17 1343.47 1364.31
1386.71 1393.37 1401.98 1422.81 1425.95 1428.18
1434.76 1444.71 1454.20 1460.05 1464.03 1465.35
1468.06 1468.73 1474.85 1476.49 1483.73 1484.16
1486.00 1490.25 1496.70 1499.51 1502.26 1503.90
1505.75 1514.75 1516.71 1520.04 1521.39 1542.35
1578.47 1658.94 3045.63 3049.10 3050.30 3051.35
3053.64 3059.36 3063.24 3067.63 3109.03 3117.64
3121.41 3123.12 3130.20 3135.49 3147.21 3147.51
3147.93 3148.54 3152.63 3160.18 3161.06 3163.15
3167.92 3170.61 3181.79 3186.00 3192.17 3202.58
3213.41 3222.10 3243.68

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25.93 30.17 36.23 49.13 56.16 57.19
63.96 67.49 71.43 79.06 84.38 90.41
96.61 112.24 121.07 129.90 135.09 142.66
146.20 150.24 155.47 161.45 167.61 171.12
175.72 182.81 188.07 193.44 200.97 202.54
209.64 212.90 217.68 229.74 232.49 236.65
241.04 250.16 252.54 260.69 270.63 275.07
284.03 285.09 293.67 300.33 314.20 317.15
323.03 325.84 343.46 381.42 390.35 402.26
412.16 418.39 422.72 429.60 440.39 446.67
451.04 477.10 505.61 525.45 530.17 532.39
547.25 559.09 570.60 580.79 600.66 609.72
614.61 631.36 633.08 634.09 637.73 671.52
694.79 709.93 713.65 716.47 716.67 718.16
721.38 723.91 725.58 764.93 766.09 769.09
771.81 791.70 811.36 811.82 814.75 830.57
864.64 869.33 874.34 876.88 877.21 881.68
928.75 946.16 951.57 960.32 962.89 972.20
973.39 974.73 977.79 990.79 991.95 995.48
999.63 1003.68 1013.32 1015.95 1016.72 1016.97
1017.52 1019.47 1020.73 1040.53 1044.03 1046.94
1052.18 1052.58 1053.16 1053.95 1055.87 1058.47
1094.07 1095.74 1104.17 1110.13 1112.08 1113.06
1117.20 1118.43 1121.87 1128.45 1171.58 1178.57
1179.07 1196.07 1201.27 1201.73 1203.18 1213.55
1220.66 1225.36 1226.43 1233.73 1242.14 1322.77
1326.60 1334.01 1336.74 1339.15 1358.52 1360.37
1362.38 1364.64 1365.29 1369.66 1400.11 1404.80
1422.60 1428.80 1429.14 1440.18 1443.86 1455.93
1461.20 1464.63 1471.05 1473.65 1474.61 1476.55
1479.40 1480.37 1481.57 1484.17 1485.53 1489.28
1491.44 1494.90 1496.96 1500.98 1502.90 1506.72
1509.27 1512.09 1518.63 1525.80 1526.53 1527.26
1528.39 1537.17 1544.25 1623.96 1625.67 1629.35
1633.92 1642.31 1644.63 1646.26 1656.31 3036.35
3047.32 3048.84 3049.23 3052.95 3059.12 3065.63
3071.98 3100.41 3118.58 3119.04 3121.45 3124.72
3126.58 3141.35 3147.72 3152.80 3155.00 3161.62
3164.72 3164.88 3171.24 3171.81 3172.81 3173.55
3181.36 3186.46 3187.17 3188.45 3188.67 3191.08
3192.71 3195.65 3196.25 3203.01 3207.19 3209.97
3211.80 3213.86 3217.26 3219.90 3220.65 3234.59
3237.45 3241.65 3263.48

Notes and References:

‡R1 = $\Sigma||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{½}$, $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{½}$; where n = the number of reflections and p = the number of parameters refined.

1 J. M. Buchanan, J. M. Stryker and R. G. Bergman, *J. Am. Chem. Soc.*, 1986, **108**, 1537–1550.
2 P. J. Stang, Y. H. Huang and A. M. Arif, *Organometallics*, 1992, **11**, 231–237.
3 P. Burger and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 10462–10463.
4 *SAINT*, Bruker AXS Inc., Madison, WI, USA, 2009.
5 G. M. Sheldrick, *SADABS*, University of Gottingen, Germany, 2007.
6 *SHELXTL*, Bruker AXS Inc., Madison, WI, USA, 2009.
7 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.
8 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3–8.
9 R. G. Parr and Y. Weitao, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, 1994.
10 A. D. Bochevarov, E. Harder, T. F. Hughes, J. R. Greenwood, D. A. Braden, D. M. Philipp, D. Rinaldo, M. D. Halls, J. Zhang and R. A. Friesner, *Int. J. Quantum Chem.*, 2013, **113**, 2110–2142.
11 A. D. Becke, *Phys. Rev. A Gen. Phys.*, 1988, **38**, 3098–3100.
12 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
13 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B Condens. Matter*, 1988, **37**, 785–789.
14 R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724–728.
15 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.
16 J. S. Binkley, J. Stephen Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.*, 1980, **102**, 939–947.
17 M. M. Francl, W. J. Pietro, W. J. Hehre, J. Stephen Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654–3665.
18 V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern and L. A. Curtiss, *J. Comput. Chem.*, 2001, **22**, 976–984.
19 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
20 W. R. Wadt and P. Jeffrey Hay, *J. Chem. Phys.*, 1985, **82**, 284–298.
21 P. J. Hay, P. Jeffrey Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270–283.
22 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.
23 D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358–1371.
24 T. H. Dunning, K. A. Peterson and A. K. Wilson, *J. Chem. Phys.*, 2001, **114**, 9244–9253.
25 S. R. Edinger, C. Cortis, P. S. Shenkin and R. A. Friesner, *J. Phys. Chem. B*, 1997, **101**, 1190–1197.
26 M. Friedrichs, R. Zhou, S. R. Edinger and R. A. Friesner, *J. Phys. Chem. B*, 1999, **103**, 3057–3061.
27 C. Peng and H. Bernhard Schlegel, *Isr. J. Chem.*, 1993, **33**, 449–454.
28 I. Mayer, *Chem. Phys. Lett.*, 1985, **117**, 396–396.
29 I. Mayer, *Int. J. Quantum Chem.*, 1986, **29**, 73–84.
30 K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083–1096.