

# Supporting Information

## **RuBisCO-inspired CO<sub>2</sub> Activation and Transformation at two Cooperating Nucleophilic Sites in an Iridium(I) Complex**

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## Miscellaneous figures

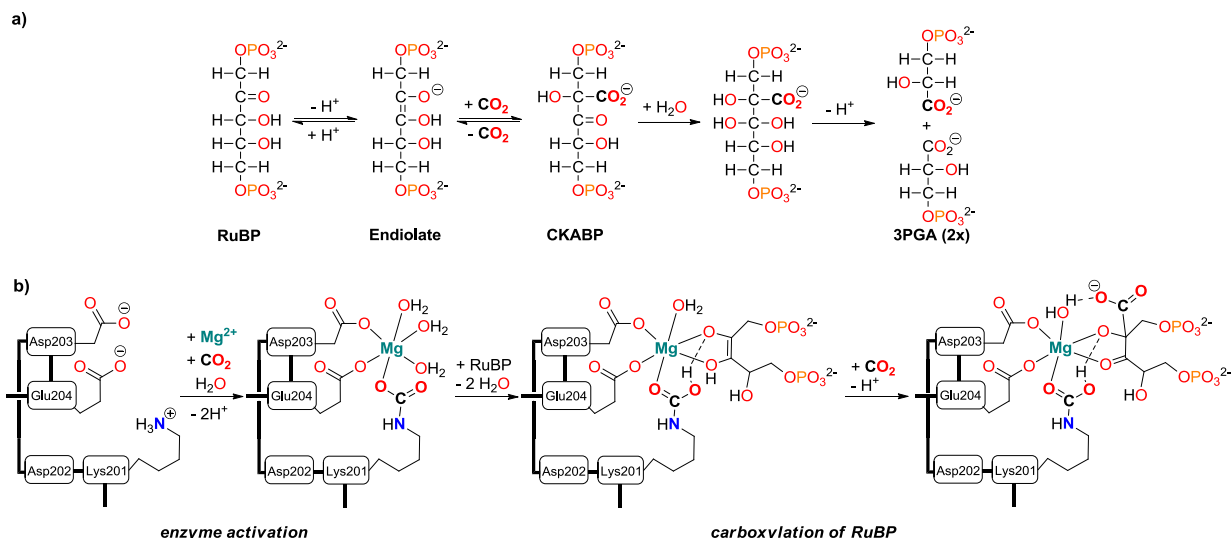


Figure S1. a) Reaction cascade observed in the enzymatic carboxylation of ribulose-bisphosphate (RuBP) by RuBisCO; b) Simplified schematic representation of the active center during enzyme activation, substrate binding and carboxylation (— protein backbone, the amino acid sequence numbers correspond to spinach RuBisCO).

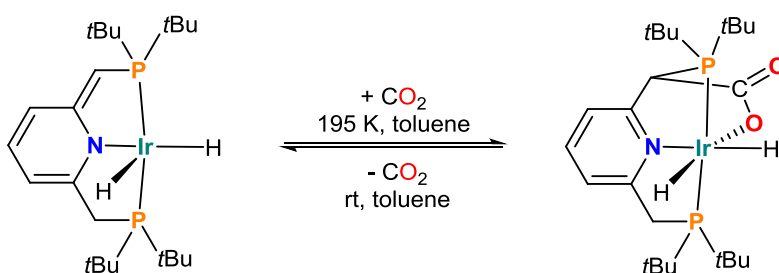


Figure S2. Metal ligand cooperation (MLC) in  $CO_2$  binding by a iridium(III) complex, containing an enamido phosphine ligand.<sup>[S1]</sup>

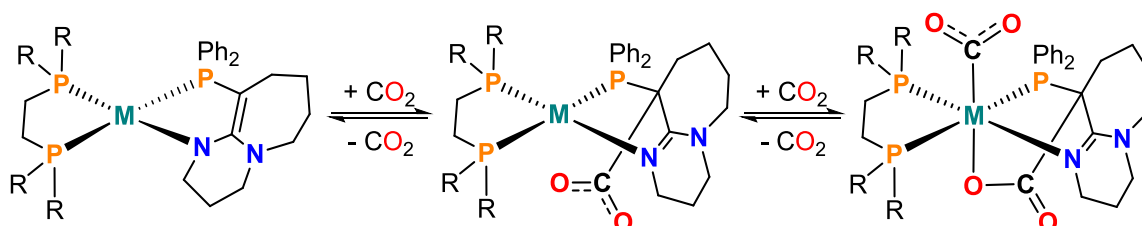
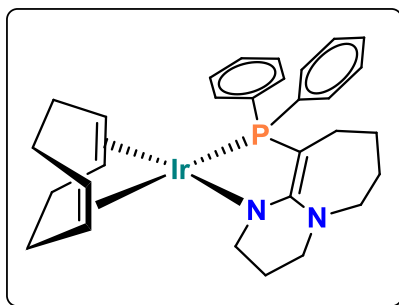


Figure S3.  $CO_2$  fixation by **2a** (R = Et, M = Ir), **2b** (R = Ph, M = Ir) and **4** (R = Et, M = Rh) at low temperatures (203 K).

## Experimental Section

**General remarks.** All experiments were carried out under an inert nitrogen atmosphere in a glove box (MBraun, Labmaster SP) or by using standard *Schlenk* techniques. THP was dried over molecular sieves (3Å) and distilled from sodium afterwards. Benzene, diethyl ether, *n*-pentane, *n*-hexane and toluene were degassed with nitrogen, dried over activated aluminum oxide (Innovative Technology, Pure Solv 400-4-MD, Solvent Purification System) and stored under an inert N<sub>2</sub> atmosphere. Deuterated solvents were purchased from Deutero GmbH and Euriso-top, degassed by three freeze-pump-thaw cycles and dried over molecular sieves (3Å). Carbon dioxide (N55; 99.9995% CO<sub>2</sub>) was purchased from Air Liquide.

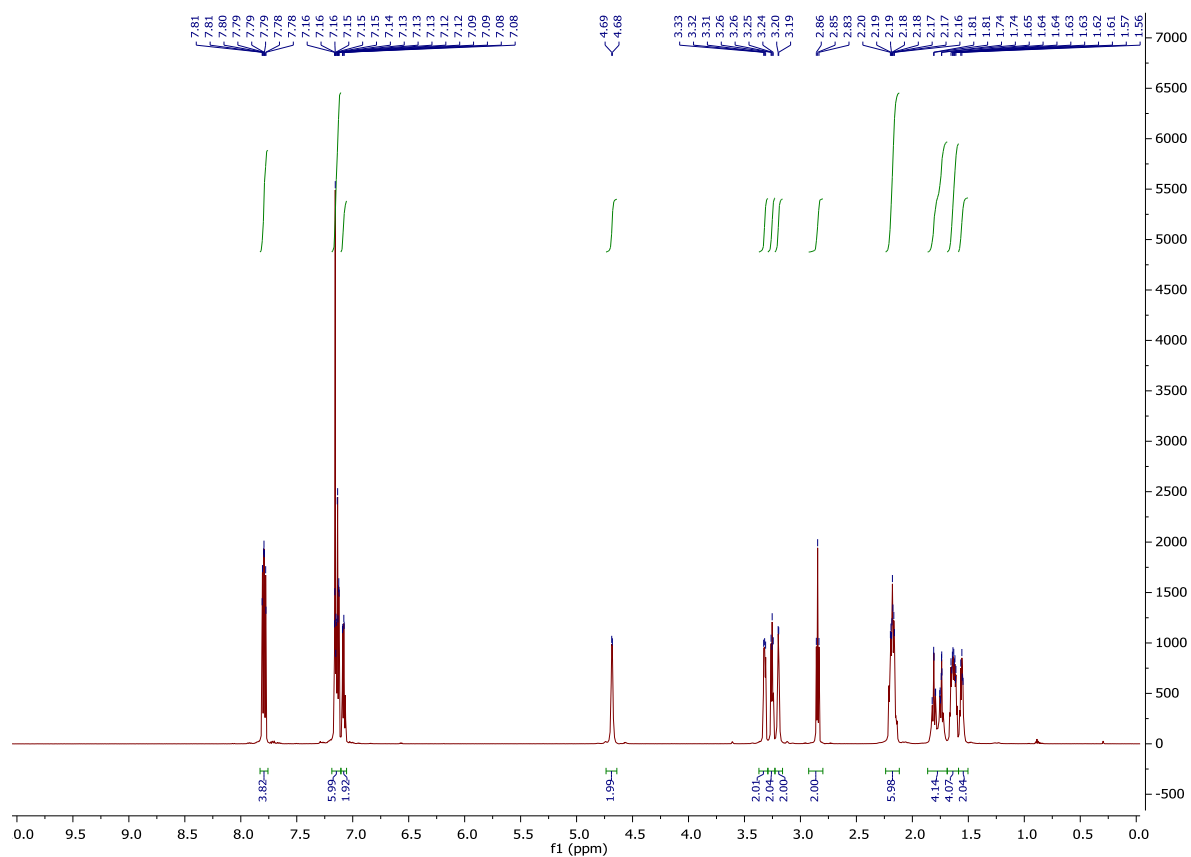
<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR data was recorded with a Bruker Avance III HD 400 MHz or a Bruker Avance III HD 600 MHz spectrometer. Chemical shifts of the <sup>1</sup>H and <sup>13</sup>C NMR spectra are reported in parts per million (ppm) relative to Me<sub>4</sub>Si as an external standard, while the residual signals of the deuterated solvents were used as internal standard. <sup>31</sup>P NMR shifts are referenced to 85% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O as external standard. Coupling constants are given in Hertz. Infrared spectra were recorded with a Bruker Alpha FT-IR spectrometer. UHR-ESI MS measurements of THF solutions were performed on a UHR-TOF Bruker Daltonik (Bremen, Germany) maXis 5G, an ESI-TOF MS capable of resolution of at least 60 000 FWHM. Detection was in positive-ion mode, with a source voltage of 4.5 kV. The flow rates were 250 µL per hour. The machine was calibrated prior to every experiment via direct infusion of the Agilent ESI-TOF low concentration tuning mixture, which provided an *m/z* range of singly charged peaks up to 2700 Da in both ion modes. Elemental analyses were obtained on an Euro Vector EA3000 Elemental Analyzer. Melting and decomposition points were determined in sealed glass capillaries with a Stuart Melting Point Apparatus SMP10. [Li(dbuP)(Et<sub>2</sub>O)]<sub>2</sub>, [Rh(cod)(dbuP)] and [IrCl(cod)]<sub>2</sub> were synthesized according to known procedures.<sup>[S2,S3]</sup>



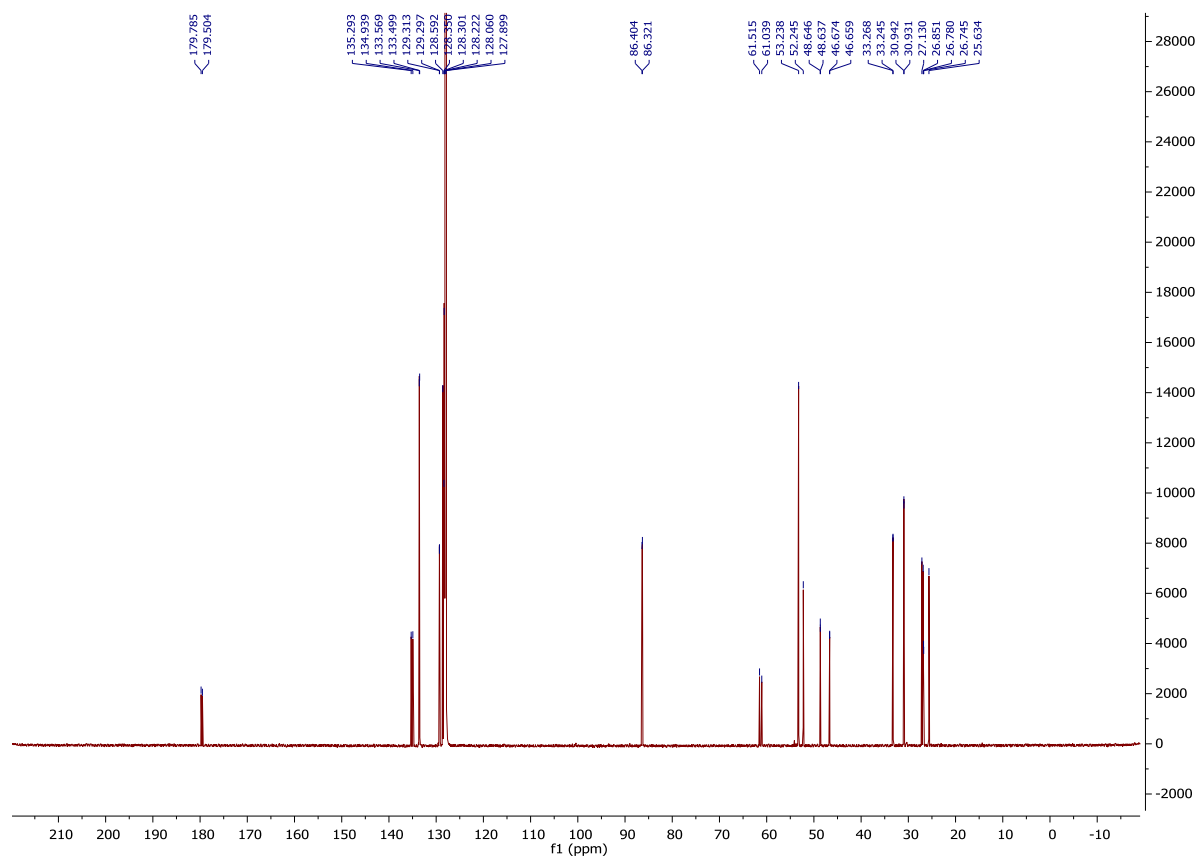
### Synthesis of [Ir(cod)(dbuP)] (1)

[{Li(dbuP)(Et<sub>2</sub>O)}<sub>2</sub>] (400 mg, 0.48 mmol) and [IrCl(cod)]<sub>2</sub> (320 mg, 0.48 mmol) were dissolved together in benzene (10 mL). The resulting red reaction mixture was stirred for 5 hours at ambient temperature.

Afterwards, the dark red suspension was filtered to remove precipitated LiCl. The solid residue was extracted with benzene (2 x 2 mL) and discarded. The combined benzene solutions were reduced to a volume of 6 mL in vacuum, layered with *n*-hexane (20 mL) and stored overnight at 5 °C. Afterwards, the resulting red crystals of 1·0.5Benzene were isolated by decantation, washed with *n*-hexane (5 mL) and briefly dried in a dynamic vacuum. Storage of the mother liquor at -20 °C resulted in a second crop of crystals, which was treated as described above. Combined yield: 475 mg (0.70 mmol, 74%) red crystals; m.p.: 219-220°C (dec., earlier loss of benzene without melting); <sup>1</sup>H NMR (600MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 1.56 (2H, m, CH<sub>2</sub> dbuP), 1.63 (4H, m, CH<sub>2</sub> dbuP), 1.70-1.86 (4H, m, CH<sub>2</sub> cod), 2.12-2.23 (6H, m, 2xCH<sub>2</sub> cod + CH<sub>2</sub> dbuP), 2.85 (2H, t, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, NCH<sub>2</sub> dbuP), 3.20 (2H, m, CH cod), 3.25 (2H, m, NCH<sub>2</sub> dbuP), 3.32 (2H, m, NCH<sub>2</sub> dbuP), 4.68 (2H, m, CH cod), 7.08 (2H, m, *p*-CH Ph), 7.11-7.17 (7H, m, *m*-CH Ph+0.5C<sub>6</sub>H<sub>6</sub>), 7.79 (4H, m, *o*-CH Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (151MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 25.6 (1C, s, CH<sub>2</sub> dbuP), 26.8 (1C, d, <sup>2</sup>J<sub>C-P</sub> = 5.2 Hz, CH<sub>2</sub> dbuP), 26.9 (1C, s, CH<sub>2</sub> dbuP), 27.1 (1C, s, CH<sub>2</sub> dbuP), 30.9 (2C, d, <sup>3</sup>J<sub>C-P</sub> = 1.6 Hz, CH<sub>2</sub> cod), 33.3 (2C, d, <sup>3</sup>J<sub>C-P</sub> = 3.5 Hz, CH<sub>2</sub> cod), 46.7 (1C, d, J<sub>C-P</sub> = 2.3 Hz, N-CH<sub>2</sub> dbuP), 48.6 (1C, d, J<sub>C-P</sub> = 1.4 Hz, NCH<sub>2</sub> dbuP), 52.2 (1C, s, NCH<sub>2</sub> dbuP), 53.2 (2C, s, CH cod), 61.3 (1C, d, <sup>1</sup>J<sub>C-P</sub> = 71.9 Hz, =C-P dbuP), 86.36 (2C, d, <sup>2</sup>J<sub>C-P</sub> = 12.6 Hz, CH cod), 128.3 (4C, d, <sup>3</sup>J<sub>C-P</sub> = 9.9 Hz, *m*-CH Ph), 128.6 (3C, s, CH Benzene), 129.3 (2C, d, <sup>4</sup>J<sub>C-P</sub> = 2.4 Hz, *p*-CH Ph), 133.5 (4C, d, <sup>2</sup>J<sub>C-P</sub> = 10.6 Hz, *o*-CH Ph), 135.1 (d, 2C, <sup>1</sup>J<sub>C-P</sub> = 53.4 Hz, *i*-C Ph), 179.6 (1C, d, <sup>2</sup>J<sub>C-P</sub> = 42.3 Hz, N<sub>2</sub>C= dbuP); <sup>31</sup>P{<sup>1</sup>H} NMR (242.9MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 24.6 (1P, s, dbuP); Anal. calcd. for C<sub>32</sub>H<sub>39</sub>IrN<sub>2</sub>P: C 56.95%, H 5.82 %, N 4.15 %; found: C 57.08 %, H 5.70 %, N 3.99%.

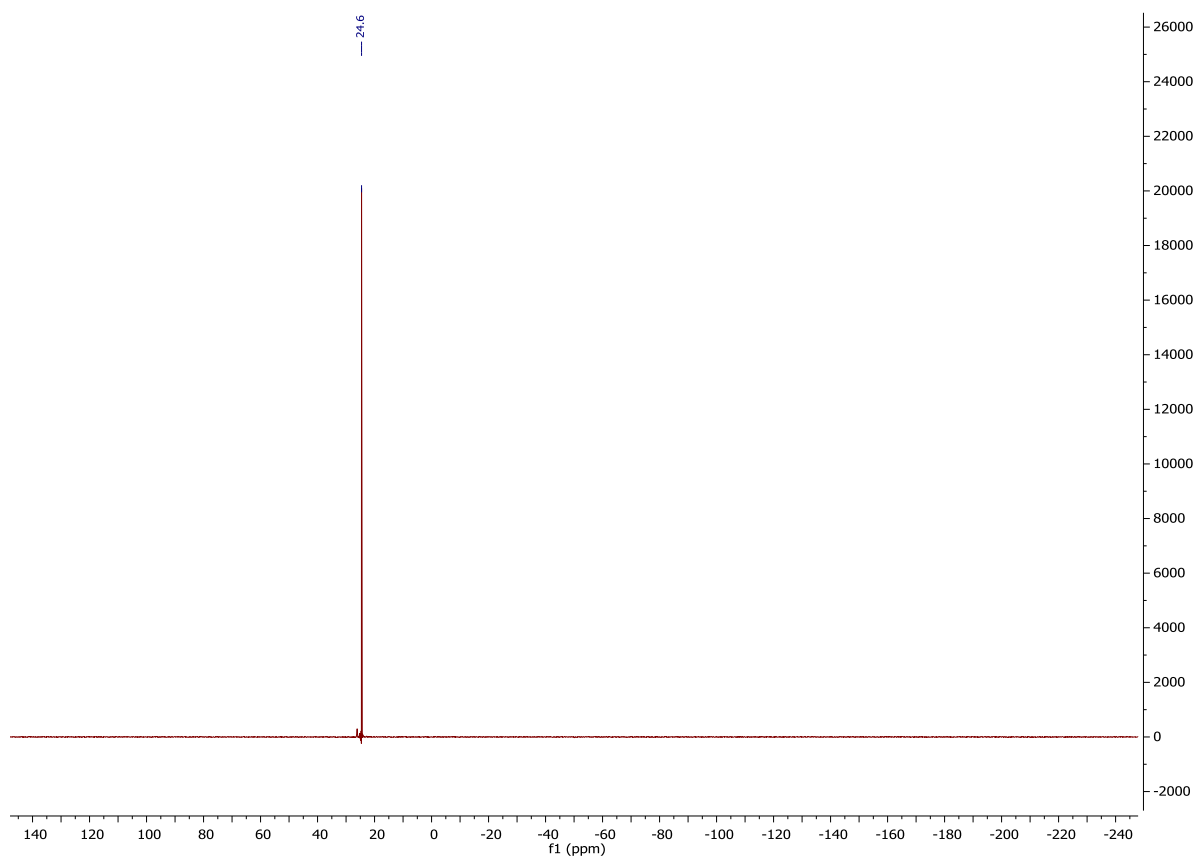


Spectrum S1: <sup>1</sup>H NMR spectrum of [Ir(cod)(dbuP)]·0.5Benzene (C<sub>6</sub>D<sub>6</sub>, 600.1 MHz, 298 K).

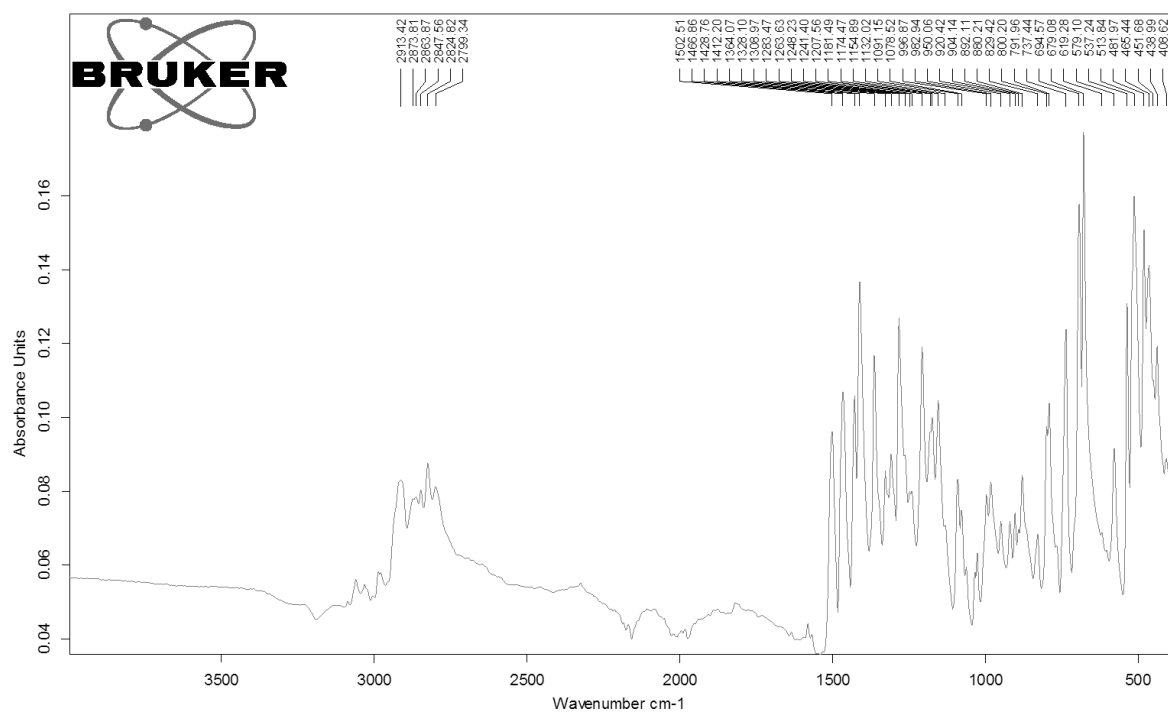


Spectrum S2: <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [Ir(cod)(dbuP)]·0.5Benzene (C<sub>6</sub>D<sub>6</sub>, 150.9 MHz, 298 K).

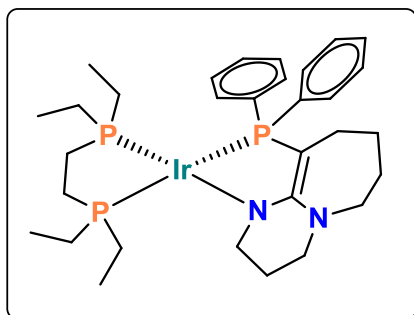




Spectrum S3: <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of [Ir(cod)(dbuP)]·0.5Benzene (C<sub>6</sub>D<sub>6</sub>, 242.9 MHz, 298 K).



Spectrum S4: ATR-FTIR spectrum of [Ir(cod)(dbuP)]·0.5Benzene.



### Synthesis of [Ir(depe)(dbuP)] (2a)

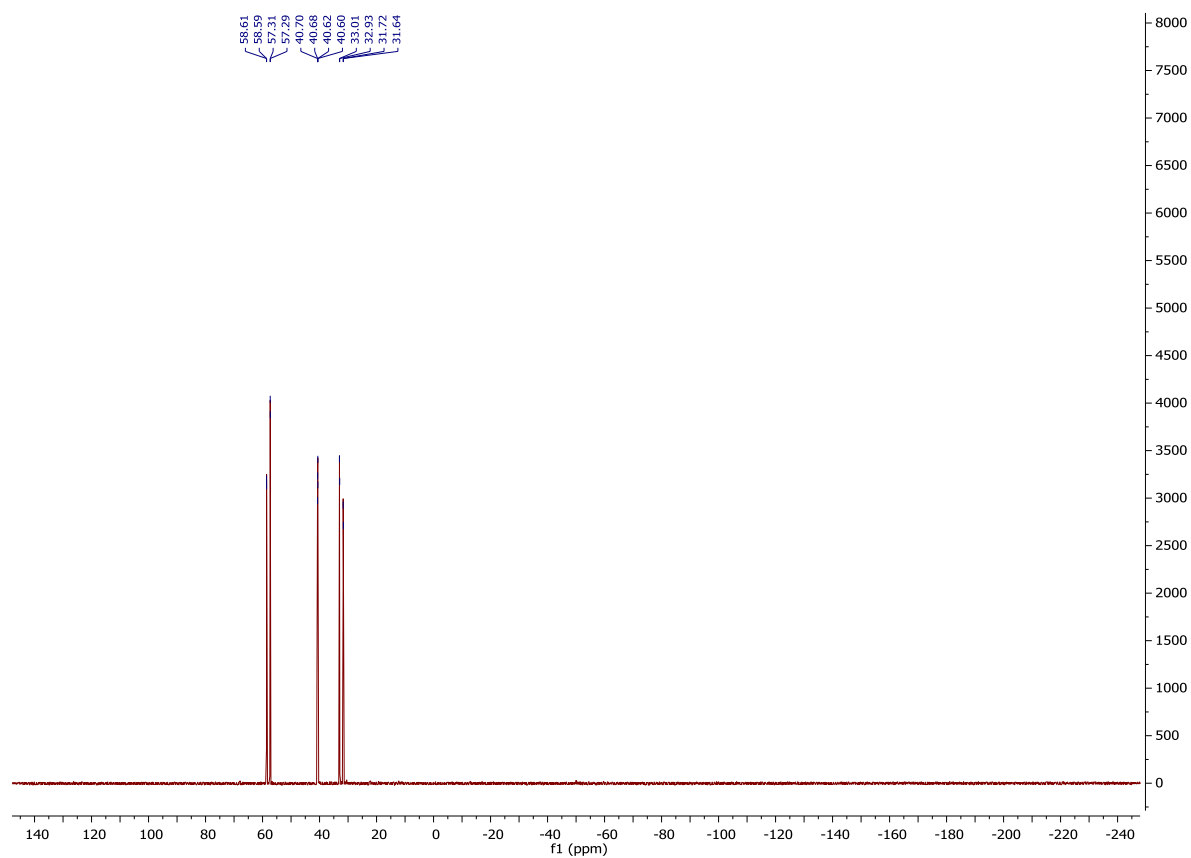
[Ir(cod)(dbuP)]·0.5Benzene (**1**) (50 mg, 0.074 mmol) was suspended in benzene (0.6 mL) in a NMR tube with a Teflon screw cap. Addition of 1,2-bis(diethylphosphino)ethane (depe; 18.5  $\mu$ L, 0.079 mmol) to the reaction mixture led to a color change of the solution from red to yellow. Afterwards, the sealed NMR tube was shaken until all of the red iridium starting material had dissolved. The obtained yellow solution was then heated to 80 °C for 1 day. The resulting red solution was afterwards concentrated in vacuum until a viscous red oil was obtained, which was rapidly taken up in *n*-hexane (1.5 mL). Crystallization of the product started almost immediately and was completed by storing the reaction mixture for 1 day at -20 °C. Then the red crystals were isolated by decantation, washed with cold *n*-hexane (0.3 mL) and dried in a vacuum. Yield: 39 mg (0.053 mmol, 72%); m.p.: 189-191 °C.  $^1\text{H}$  NMR (600MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta$  = 0.73 (6H, dt,  $^3J_{\text{H-P}}$  = 15.1 Hz,  $^3J_{\text{H-H}}$  = 7.5 Hz,  $\text{CH}_3$  depe), 1.04 (4H, m,  $\text{CH}_2$  depe), 1.12 (2H, m,  $\text{CH}_2$  depe), 1.17 (6H, dt,  $^3J_{\text{H-P}}$  = 15.4,  $^3J_{\text{H-H}}$  = 7.7 Hz,  $\text{CH}_3$  depe), 1.28 (2H, m,  $\text{CH}_2$  depe), 1.53 (2H, m,  $\text{CH}_2$  depe), 1.63 (2H, m,  $\text{CH}_2$  dbuP), 1.69-1.78 (4H, m,  $\text{CH}_2$  depe +  $\text{CH}_2$  dbuP), 1.89 (2H, m,  $\text{CH}_2$  dbuP), 2.27 (2H, m,  $\text{CH}_2$  dbuP), 3.06 (2H, t,  $^3J_{\text{H-H}}$  = 7.0 Hz,  $\text{NCH}_2$  dbuP), 3.25 (2H, m,  $\text{NCH}_2$  dbuP), 4.08 (2H, m,  $\text{NCH}_2$  dbuP), 7.11 (2H, m, *p*-CH Ph), 7.17 (4H, m, *m*-CH Ph), 8.12 (4H, m, *o*-CH Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR (151MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta$  = 9.7 (2C, s,  $\text{CH}_3$  depe), 10.4 (2C, d,  $^2J_{\text{C-P}}$  = 1.7 Hz,  $\text{CH}_3$  depe), 21.8 (2C, dd,  $^1J_{\text{C-P}}$  = 23.5 Hz,  $^3J_{\text{C-P}}$  = 3.1 Hz,  $\text{CH}_2$  depe), 22.5 (2C, d,  $^1J_{\text{C-P}}$  = 32.3 Hz,  $\text{CH}_2$  depe), 27.0 (1C, d,  $J_{\text{C-P}}$  = 2.2 Hz,  $\text{CH}_2$  dbuP), 27.2 (1C, d,  $J_{\text{C-P}}$  = 4.4 Hz,  $\text{CH}_2$  dbuP), 27.3 (1C, ddd,  $^1J_{\text{C-P}}$  = 29.9 Hz,  $^2J_{\text{C-P}}$  = 16.1 Hz,  $^3J_{\text{C-P}}$  = 5.8 Hz,  $\text{CH}_2$  depe), 28.0 (1C, s,  $\text{CH}_2$  dbuP), 28.0 (1C, dd,  $^1J_{\text{C-P}}$  = 33.2 Hz,  $^2J_{\text{C-P}}$  = 14.2 Hz,  $\text{CH}_2$  depe), 28.4 (1C, s,  $\text{CH}_2$  dbuP), 48.9 (1C, s,  $\text{N-CH}_2$  dbuP), 52.8 (1C, s,  $\text{N-CH}_2$  dbuP), 58.5 (1C, m,  $\text{N-CH}_2$  dbuP), 62.3 (1C, dd,  $^1J_{\text{C-P}}$  = 66.5 Hz,  $^3J_{\text{C-P}}$  = 3.4 Hz,  $=\text{C-P}$  dbuP), 127.5 (4C, d,  $^3J_{\text{C-P}}$  = 9.3 Hz, *m*-CH Ph), 128.2 (2C, d,  $^4J_{\text{C-P}}$  = 2.1 Hz, *p*-CH Ph), 134.0 (4C, d,  $^2J_{\text{C-P}}$  = 11.3 Hz, *o*-CH Ph), 139.4 (2C, dd,  $^1J_{\text{C-P}}$  = 48.1 Hz,  $^3J_{\text{C-P}}$  = 1.6 Hz, *i*-C Ph), 177.4 (1C, apparent dt,  $^2J_{\text{C-P}}$  = 44.8 Hz,  $^3J_{\text{C-P}}$  =  $^3J_{\text{C-P'}}$  = 2.4 Hz,  $\text{N}_2\text{C=}$  dbuP);  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta$  = 32.3 (1P, dd,  $^2J_{\text{P-P,trans}}$  = 315.0,  $^2J_{\text{P-P,cis}}$  = 20.0 Hz, dbuP), 40.6 (dd,  $^2J_{\text{P-P,cis}}$  = 20.0,  $^2J_{\text{P-P,cis}}$  = 5.0 Hz, depe), 58.0 (1P, dd,  $^2J_{\text{P-P,trans}}$  = 315.0,  $^2J_{\text{P-P,cis}}$  = 5.0 Hz, depe); MS (ESI in

<sup>1</sup>H NMR spectrum of compound 10a in CDCl<sub>3</sub>. The x-axis represents the chemical shift in ppm (f1) from 10.0 to 0.0. The y-axis represents intensity from 0 to 5000. The spectrum shows several peaks with integration values below them: 3.86, 4.84, 2.00, 1.96, 2.01, 1.98, 2.06, 2.02, 4.03, 2.06, 2.15, 2.28, 8.05, 4.13, and 6.08. A list of chemical shifts (δ) is provided on the right side of the spectrum, ranging from 8.13 to 0.70 ppm.

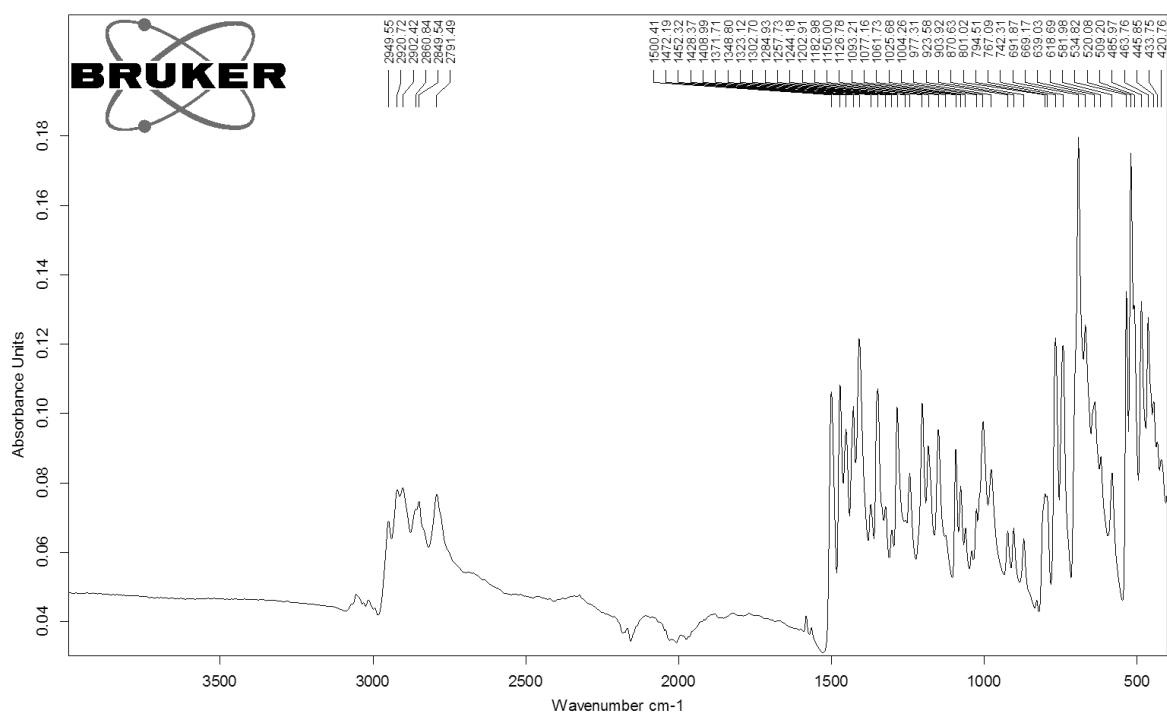
<sup>13</sup>C NMR spectrum (f1 (ppm)) of compound 10. The spectrum shows a small peak at 177.60 ppm and a large cluster of peaks between 10 and 60 ppm. Numerous peaks are labeled with their chemical shift values.

Chemical Shift (ppm)
177.60
177.58
177.56
177.38
177.27
139.52
139.51
139.20
139.19
134.04
133.96
127.45
62.56
62.54
62.12
62.10
58.51
58.47
58.42
52.85
48.89
28.40
28.16
28.07
27.98
27.94
27.85
27.52
27.48
27.41
27.37
27.32
27.28
27.20
27.17
26.96
26.85
22.62
22.40
21.84
21.82
21.69
21.67
18.44
10.43
9.72

Spectrum S6:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(\text{depe})(\text{dbuP})]$  ( $\text{C}_6\text{D}_6$ , 150.9 MHz, 298 K).



Spectrum S7:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(\text{depe})(\text{dbuP})]$  ( $\text{C}_6\text{D}_6$ , 242.9 MHz, 298 K).



Spectrum S8: ATR-FTIR spectrum of  $[\text{Ir}(\text{depe})(\text{dbuP})]$ .

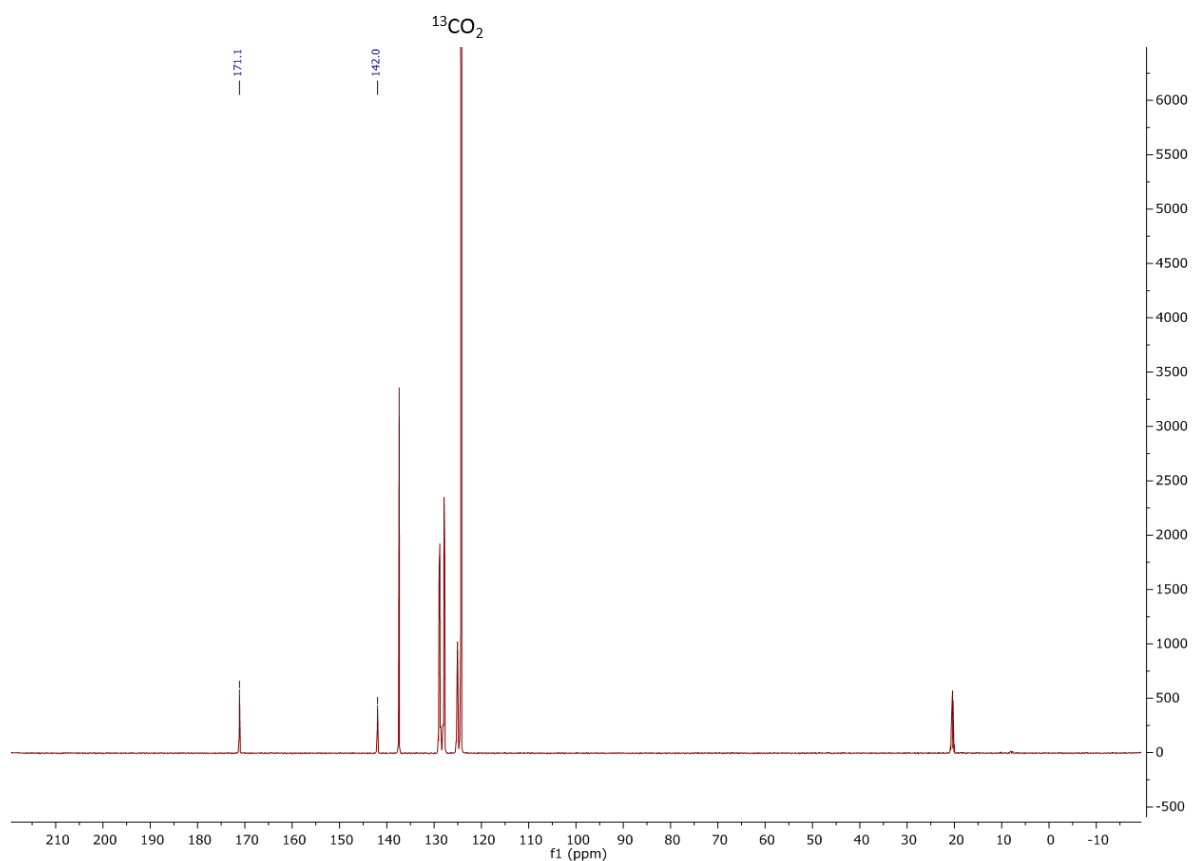
### Low temperature CO<sub>2</sub> uptake by [Ir(depe)(dbuP)] (2a)

In a Young tube, approximately 10 mg of red complex **2a** were dissolved in toluene-*d*<sub>8</sub> at ambient temperature. Afterwards, the sample was cooled to -90°C (183K) in an ethanol bath by addition of liquid nitrogen. After 10 min, the N<sub>2</sub> atmosphere was replaced by a <sup>13</sup>CO<sub>2</sub> atmosphere, while keeping the bath temperature constant (-90°C). Then the NMR tube was carefully shaken. During this procedure, the solution should not come in contact with those parts of the tube, which are not cooled to -90°C. The gentle shaking was stopped after the discoloration (red to very pale yellow) was complete.

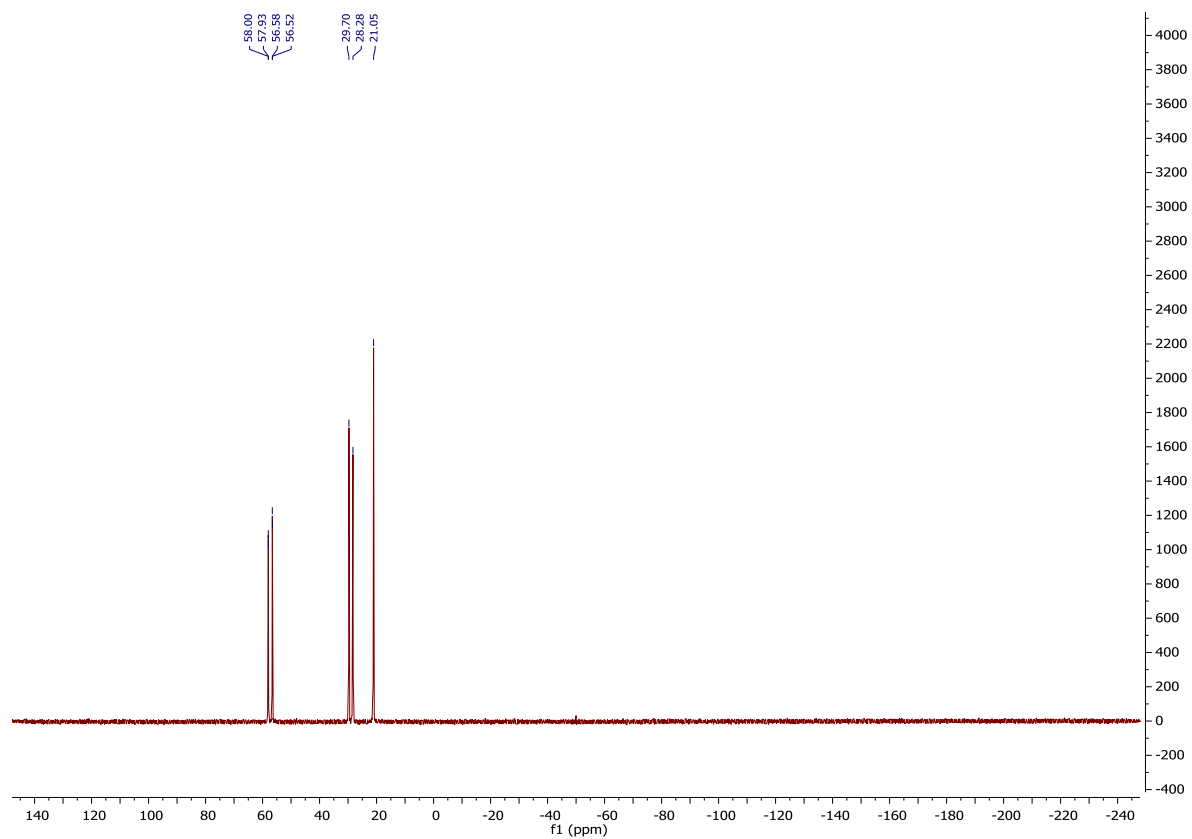
Afterwards the cooled sample was transferred into the precooled NMR spectrometer (-90°C) as fast as possible. For the following measurements, the sample was then warmed to -70°C (203 K). At this temperature, the formation of a single species [Ir(<sup>13</sup>CO<sub>2</sub>)(depe)(dbuP<sup>13</sup>CO<sub>2</sub>)] (**2a**·2(<sup>13</sup>CO<sub>2</sub>), intermediate **I**<sub>2</sub> in the calculations) was confirmed by <sup>13</sup>C{<sup>1</sup>H} NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.

When slowly warmed up, this new compound started to transform into complex **3** at approximately -50°C (223 K) without formation of detectable intermediates or reformation of **2a**.

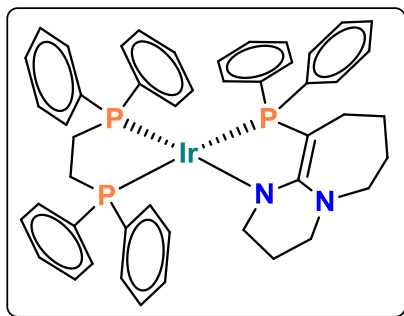
**[Ir(<sup>13</sup>CO<sub>2</sub>)(depe)(dbuP<sup>13</sup>CO<sub>2</sub>)]**: <sup>13</sup>C{<sup>1</sup>H} NMR (151MHz, toluene-*d*<sub>8</sub>, 203 K, <sup>13</sup>CO<sub>2</sub> atmosphere): δ = 142.0 (s, Ir-<sup>13</sup>CO<sub>2</sub>), 171.1 (s, dbuP<sup>13</sup>CO<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (242.9 MHz, toluene-*d*<sub>8</sub>, 203 K, <sup>13</sup>CO<sub>2</sub> atmosphere): δ = 21.0 (1P, s, <sup>2</sup>J<sub>P-P,cis</sub> not resolved), 29.0 (1P, d, <sup>2</sup>J<sub>P-P,trans</sub> = 344 Hz, <sup>2</sup>J<sub>P-P,cis</sub> not resolved), 57.3 (1P, dd, <sup>2</sup>J<sub>P-P,trans</sub> = 344 Hz, <sup>2</sup>J<sub>P-P,cis</sub> = 16 Hz).



Spectrum S9: Partial  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(^{13}\text{CO}_2)(\text{depe})(\text{dbuP}^{13}\text{CO}_2)]$  (toluene- $d_8$ , 150.9 MHz, 203 K,  $^{13}\text{CO}_2$  atmosphere).



Spectrum S10:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(^{13}\text{CO}_2)(\text{depe})(\text{dbuP}^{13}\text{CO}_2)]$  (toluene- $d_8$ , 242.9 MHz, 203 K,  $^{13}\text{CO}_2$  atmosphere).

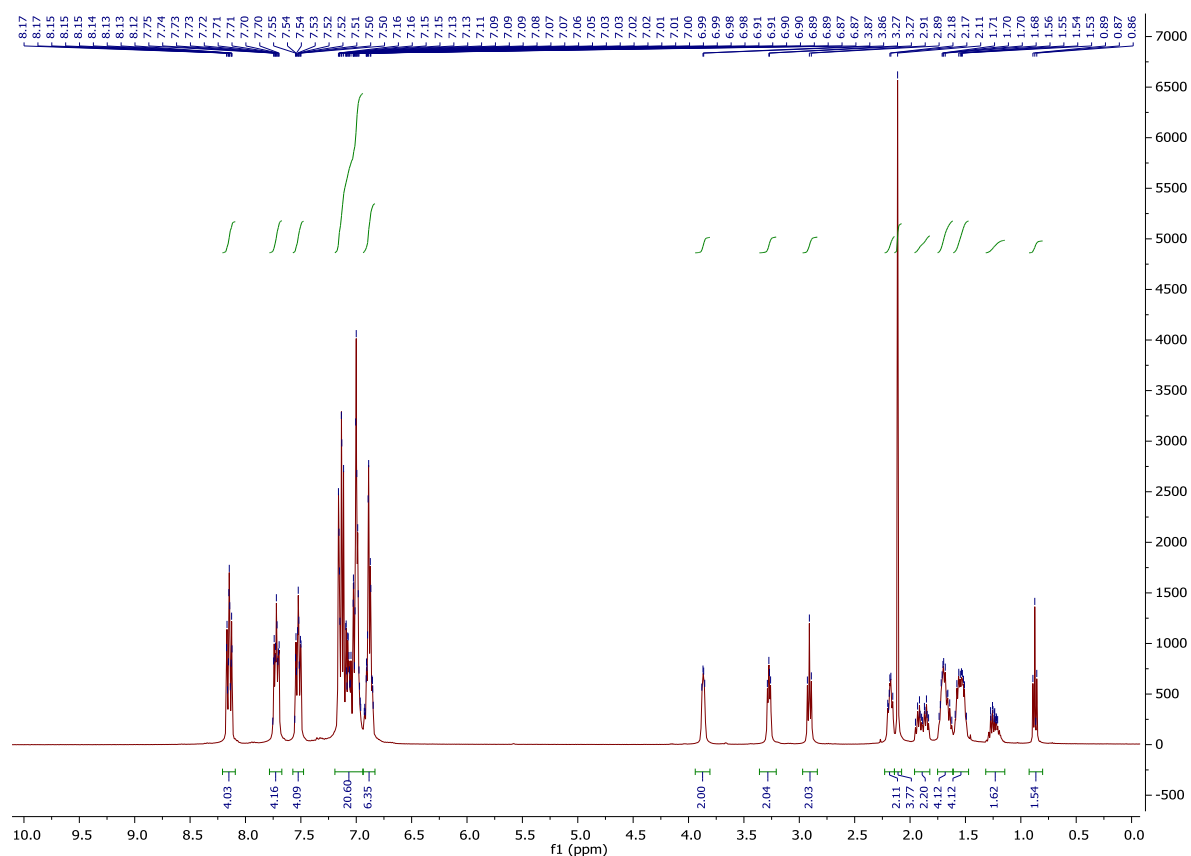


### Synthesis of [Ir(dppe)(dbuP)] (2b)

[Ir(cod)(dbuP)]·0.5Benzene (**1**) (50 mg, 0.074 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe; 30 mg 0.075 mmol) were suspended together in toluene (0.6 mL) in a NMR tube with a Teflon screw cap. Afterwards, the sealed NMR tube was shaken until all

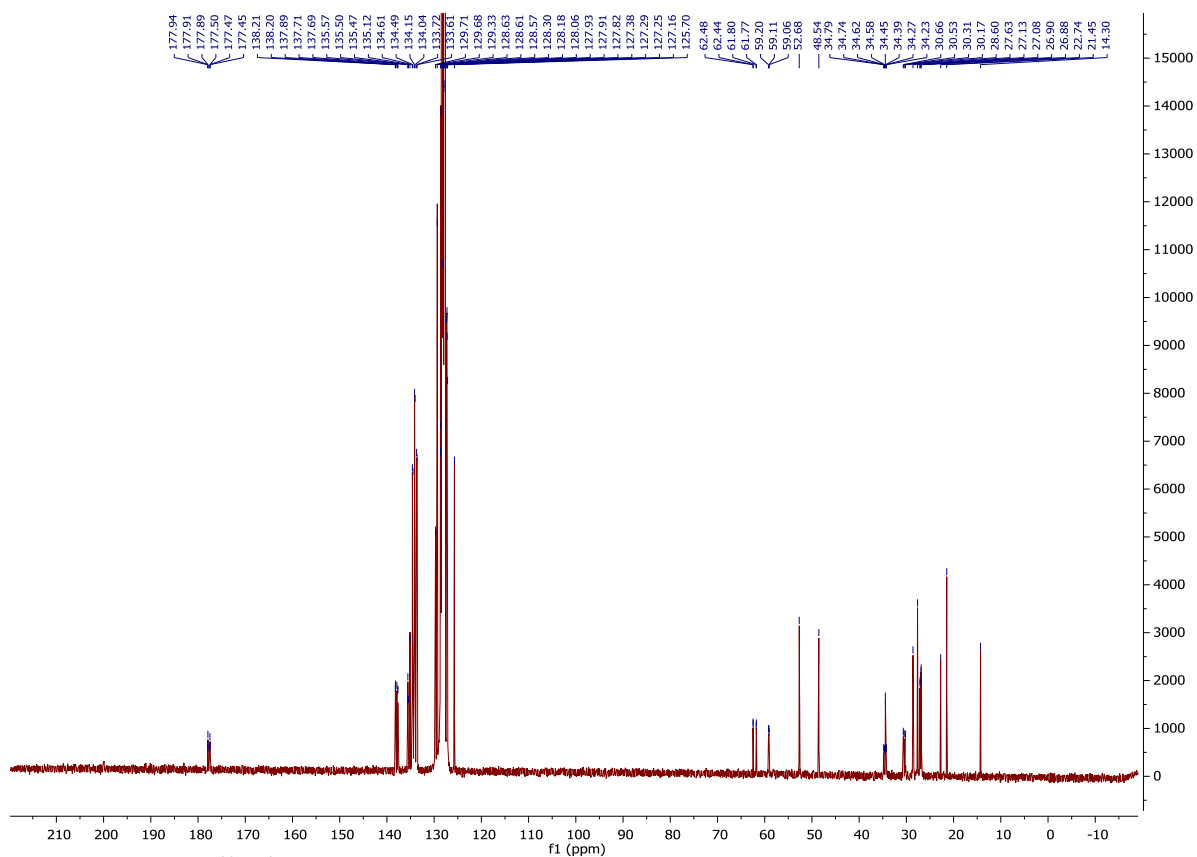
of the red iridium starting material had dissolved. The obtained yellowish orange solution was then heated to 80 °C for 1 day. Afterwards, the resulting red solution was transferred into a small vial and pentane (3 mL) was allowed to diffuse into the reaction mixture over 3 days via the gas phase. Afterwards, a small amount of an amorphous precipitate was removed by decantation and the red mother liquor was stored for 1 week at -25°C. Then the red crystals formed were isolated by decantation, washed with cold *n*-pentane (0.3 mL) and briefly dried in a vacuum. Yield: 52 mg (0.049 mmol, 66 %) red crystals of **2b**·1.25(toluene)·0.25(*n*-pentane) (Note that the content of toluene and pentane and the ratio between them slightly varies between different crops). <sup>1</sup>H NMR (400MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 0.87 (t, <sup>3</sup>J<sub>H-H</sub> = 7.0 Hz, CH<sub>3</sub> pentane); 1.15-1.32 (m, CH<sub>2</sub> pentane), 1.47-1.61 (4H, m, CH<sub>2</sub> dbuP), 1.61-1.76 (4H, m, CH<sub>2</sub> dppe + CH<sub>2</sub> dbuP), 1.89 (2H, m, CH<sub>2</sub> dppe), 2.11 (s, CH<sub>3</sub> toluene), 2.18 (2H, m, CH<sub>2</sub> dbuP), 2.91 (2H, t, <sup>3</sup>J<sub>H-H</sub> = 7.1 Hz, NCH<sub>2</sub> dbuP), 3.27 (2H, m, NCH<sub>2</sub> dbuP), 3.87 (2H, m, NCH<sub>2</sub> dbuP), 6.84-6.94 (6H, m, *m*-CH + *p*-CH Ph dppe), 6.95-7.18 (12H, m, *m*-CH + *p*-CH Ph dppe + dbuP (+ CH toluene)), 7.52 (4H, m, *o*-CH Ph dppe), 7.72 (4H, m, *o*-CH Ph dppe), 8.15 (4H, m, *o*-CH Ph dbuP); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, 298K): δ = 14.3 (s, CH<sub>3</sub> pentane), 21.4 (s, CH<sub>3</sub> toluene), 22.7 (s, CH<sub>2</sub> pentane), 26.9 (1C, d, J<sub>C-P</sub> = 2.5 Hz, CH<sub>2</sub> dbuP), 27.1 (1C, d, J<sub>C-P</sub> = 4.9 Hz, CH<sub>2</sub> dbuP), 27.6 (1C, s, CH<sub>2</sub> dbuP), 28.6 (1C, s, CH<sub>2</sub> dbuP), 30.4 (1C, dd, <sup>1</sup>J<sub>C-P</sub> = 35.6 Hz, <sup>2</sup>J<sub>C-P</sub> = 13.6 Hz, CH<sub>2</sub> dppe), 34.45 (CH<sub>2</sub> pentane), 34.5 (1C, ddd, <sup>1</sup>J<sub>C-P</sub> = 35.1 Hz, <sup>2</sup>J<sub>C-P</sub> = 16.5 Hz, <sup>3</sup>J<sub>C-P</sub> = 4.2 Hz, CH<sub>2</sub> dppe), 48.5 (1C, s, N-CH<sub>2</sub> dbuP), 52.7 (1C, s, N-CH<sub>2</sub> dbuP), 59.1 (1C, m, N-CH<sub>2</sub> dbuP), 62.1 (1C, dd, <sup>1</sup>J<sub>C-P</sub> = 67.8 Hz, <sup>3</sup>J<sub>C-P</sub> = 3.4 Hz, =C-P dbuP), 125.7 (*p*-CH toluene), 127.2 (4C, d, <sup>3</sup>J<sub>C-P</sub> = 9.3 Hz, *m*-CH Ph dppe), 127.3 (4C, d, <sup>3</sup>J<sub>C-P</sub> = 9.6 Hz, *m*-CH Ph dppe), 127.9 (2C, d, <sup>3</sup>J<sub>C-P</sub> = 2.2 Hz, *p*-CH Ph dppe), 128.3 (4C, d, <sup>3</sup>J<sub>C-P</sub> = 9.4 Hz, *m*-CH dbuP), 128.6 (s, *m*-CH toluene), 128.6 (2C, d, <sup>4</sup>J<sub>C-P</sub> = 1.7 Hz, *p*-CH Ph dppe), 129.3 (s, *o*-CH Ph), 129.7 (2C, d, <sup>4</sup>J<sub>C-P</sub> = 1.7 Hz, *p*-CH Ph dbuP), 133.7 (4C, d, <sup>2</sup>J<sub>C-P</sub> = 11.1 Hz, *o*-CH Ph dppe), 134.1 (4C, d, <sup>2</sup>J<sub>C-P</sub> = 10.8 Hz, *o*-CH Ph dppe), 134.6 (4C, d, <sup>2</sup>J<sub>C-P</sub> = 12.1 Hz, *o*-CH Ph dbuP),

135.31 (2C, dd,  $^1J_{C-P} = 36.2$  Hz,  $^3J_{C-P} = 2.6$  Hz, *i*-C Ph dppe), 135.34 (2C, d,  $^1J_{C-P} = 45.8$  Hz, *i*-C Ph dppe), 137.9 (s, *i*-C toluene), 138.0 (2C, dd,  $^1J_{C-P} = 50.7$  Hz,  $^3J_{C-P} = 1.6$  Hz, *i*-C Ph dbuP), 177.7 (1C, apparent dt,  $^2J_{C-P} = 43.8$  Hz,  $^3J_{C-P} = ^3J_{C-P'} = 2.6$  Hz, N<sub>2</sub>C= dbuP);  $^{31}P\{^1H\}$  NMR (162.0 MHz, C<sub>6</sub>D<sub>6</sub>, 298K):  $\delta = 32.3$  (1P, dd,  $^2J_{P-P,trans} = 313.8$ ,  $^2J_{P-P,cis} = 21.0$  Hz, dbuP), 41.9 (1P, dd,  $^2J_{P-P,cis} = 20.7$ ,  $^2J_{P-P,cis} = 3.8$  Hz, dppe), 56.9 (1P, dd,  $^2J_{P-P,trans} = 314.0$ ,  $^2J_{P-P,cis} = 3.9$  Hz, dppe); Anal. calcd. for C<sub>57</sub>H<sub>61</sub>IrN<sub>2</sub>P<sub>3</sub>: C 64.63 %, H 5.80 %, N 2.64 %; found: C 64.69 %, H 5.49 %, N 2.59 %.

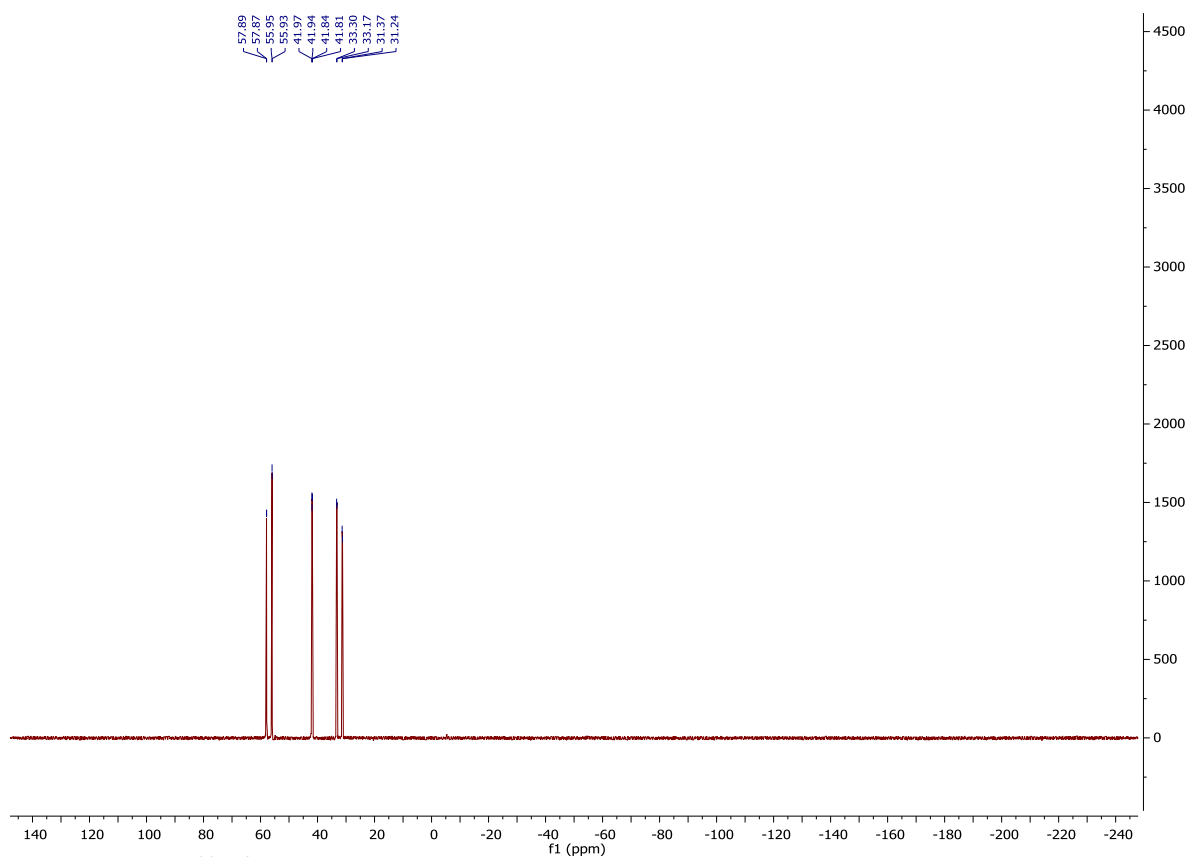


Spectrum S11:  $^1H$  NMR spectrum of  $[Ir(dppe)(dbuP)] \cdot 1.25(toluene) \cdot 0.25(n\text{-pentane})$  (C<sub>6</sub>D<sub>6</sub>, 600.1 MHz, 298 K).

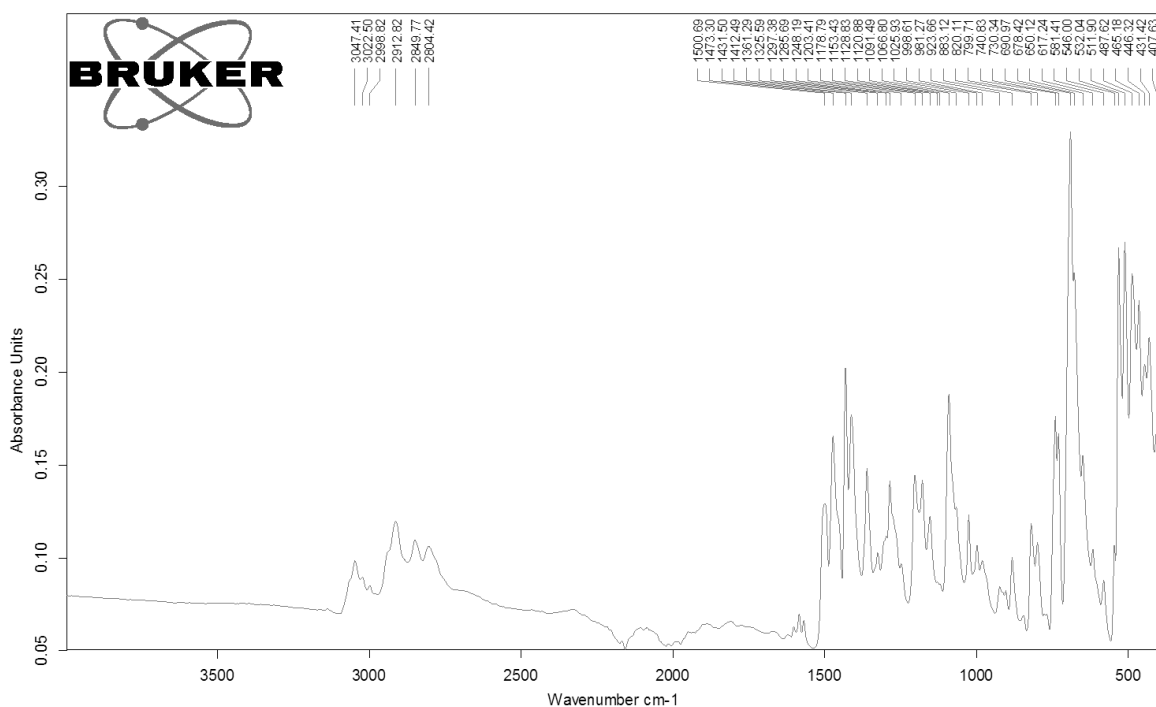




Spectrum S12:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(\text{dppe})(\text{dbuP})] \cdot 1.25(\text{toluene}) \cdot 0.25(n\text{-pentane})$  ( $\text{C}_6\text{D}_6$ , 150.9 MHz, 298 K).



Spectrum S13:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(\text{dppe})(\text{dbuP})] \cdot 1.25(\text{toluene}) \cdot 0.25(n\text{-pentane})$  ( $\text{C}_6\text{D}_6$ , 162.0 MHz, 298 K).



Spectrum S14: ATR-FTIR spectrum of  $[\text{Ir}(\text{dppe})(\text{dbuP})] \cdot 1.25(\text{toluene}) \cdot 0.25(n\text{-pentane})$ .

### Low temperature $\text{CO}_2$ uptake by $[\text{Ir}(\text{dppe})(\text{dbuP})]$ (**2b**)

In a Young tube, 15 mg of red complex **2b** were dissolved in toluene- $d_8$  at ambient temperature. Replacement of the  $\text{N}_2$  atmosphere by a  $^{13}\text{CO}_2$  atmosphere, followed by shaking of the reaction mixture for 3 min did not lead to a noticeable color change.  $^{31}\text{P}$  NMR spectroscopy showed a barely noticeably broadening of the signals of complex **2b** at ambient temperature. At 223 K, a new intermediate compound  $[\text{Ir}(\text{dppe})(\text{dbuP}^{13}\text{CO}_2)]$  (**2b**· $^{13}\text{CO}_2$ ) is formed in equilibrium via C-C bond formation between the  $\text{dbuP}^-$  ligand and  $^{13}\text{CO}_2$  (see Figures S4 and S5). At 203 K, the formation of a second species  $[\text{Ir}(^{13}\text{CO}_2)(\text{dppe})(\text{dbuP}^{13}\text{CO}_2)]$  (**2b**· $2(^{13}\text{CO}_2)$ ) was confirmed by  $^{13}\text{C}\{^1\text{H}\}$  NMR and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. This iridium(III) compound forms by  $^{13}\text{CO}_2$  coordination to the iridium center of **2b**· $^{13}\text{CO}_2$  and simultaneous formation of an Ir-O bond to the carboxylated  $\text{dbuP}$  ligand.

**$[\text{Ir}(\text{dppe})(\text{dbuP}^{13}\text{CO}_2)]$ :**  $^{13}\text{C}\{^1\text{H}\}$  NMR (151MHz, toluene- $d_8$ , 203 K,  $^{13}\text{CO}_2$  atmosphere):  $\delta = 165.3$  (br,  $\text{dbuP}^{13}\text{CO}_2$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9 MHz, toluene- $d_8$ , 203 K,  $^{13}\text{CO}_2$  atmosphere):  $\delta = 46.2$  (1P, br. s), 54.2 (1P, br. d,  $^2J_{\text{P-P,trans}} = 337$  Hz), 70.9 (1P, br. d,  $^2J_{\text{P-P,trans}} = 337$  Hz).

**$[Ir(^{13}CO_2)(dppe)(dbuP^{13}CO_2)]$** :  $^{13}C\{^1H\}$  NMR (151MHz, toluene- $d_8$ , 203 K,  $^{13}CO_2$  atmosphere):  $\delta$  = 140.8 (br, Ir- $^{13}CO_2$ ), 169.5 (dbuP $^{13}CO_2$ );  $^{31}P\{^1H\}$  NMR (242.9 MHz, toluene- $d_8$ , 203 K,  $^{13}CO_2$  atmosphere):  $\delta$  = 35.0 (1P, br. d,  $^2J_{P-P}$  = 351 Hz), 37.7 (1P, br. s), 53.5 (1P, br. d,  $^2J_{P-P}$  = 351 Hz).

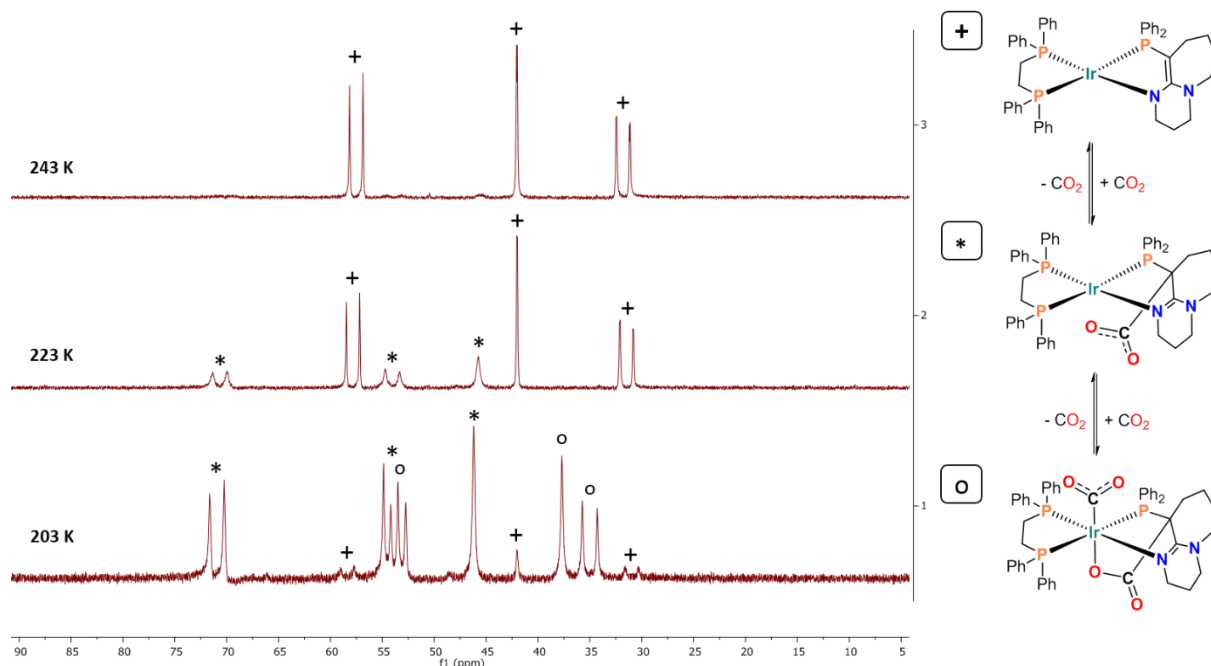


Figure S4: Temperature dependent  $^{13}CO_2$  fixation of **2b**, followed by  $^{31}P\{^1H\}$  NMR spectroscopy (toluene- $d_8$ , 242.9 MHz,  $^{13}CO_2$  atmosphere) (left) and underlying equilibria (right).

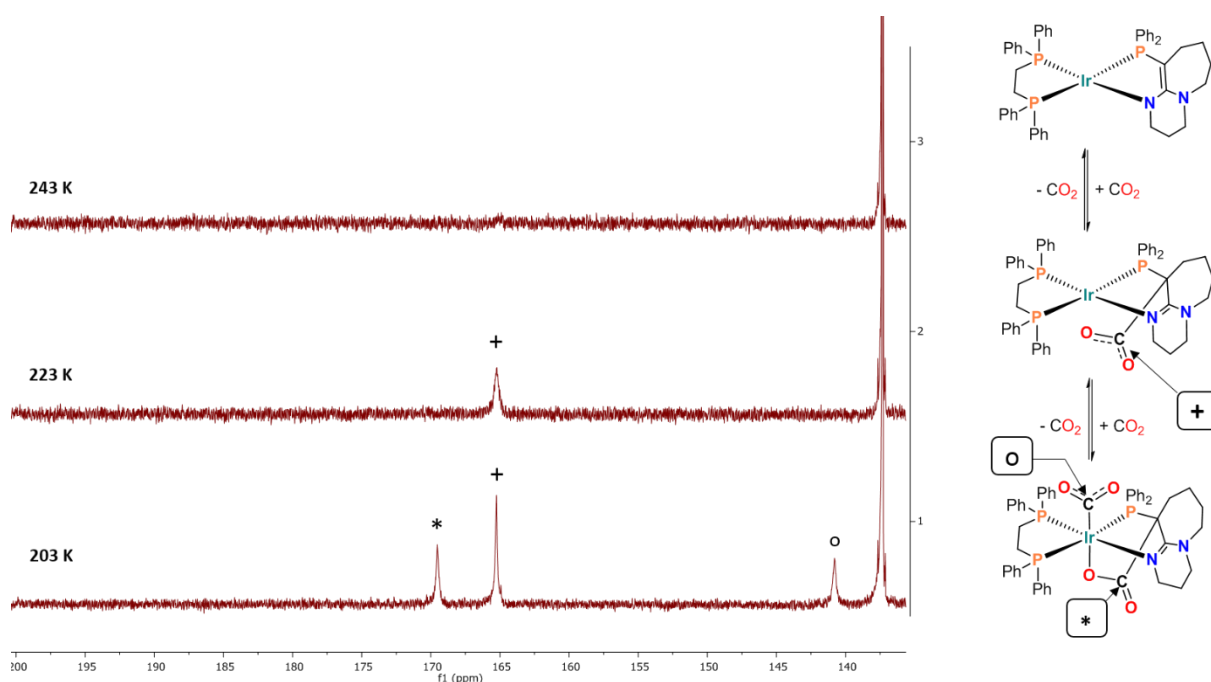
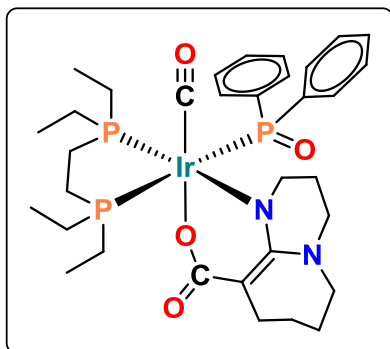


Figure S5: Temperature dependent  $^{13}CO_2$  fixation of **2b**, followed by  $^{13}C\{^1H\}$  NMR spectroscopy (toluene- $d_8$ , 150.9 MHz,  $^{13}CO_2$  atmosphere) (left) and underlying equilibria (right).

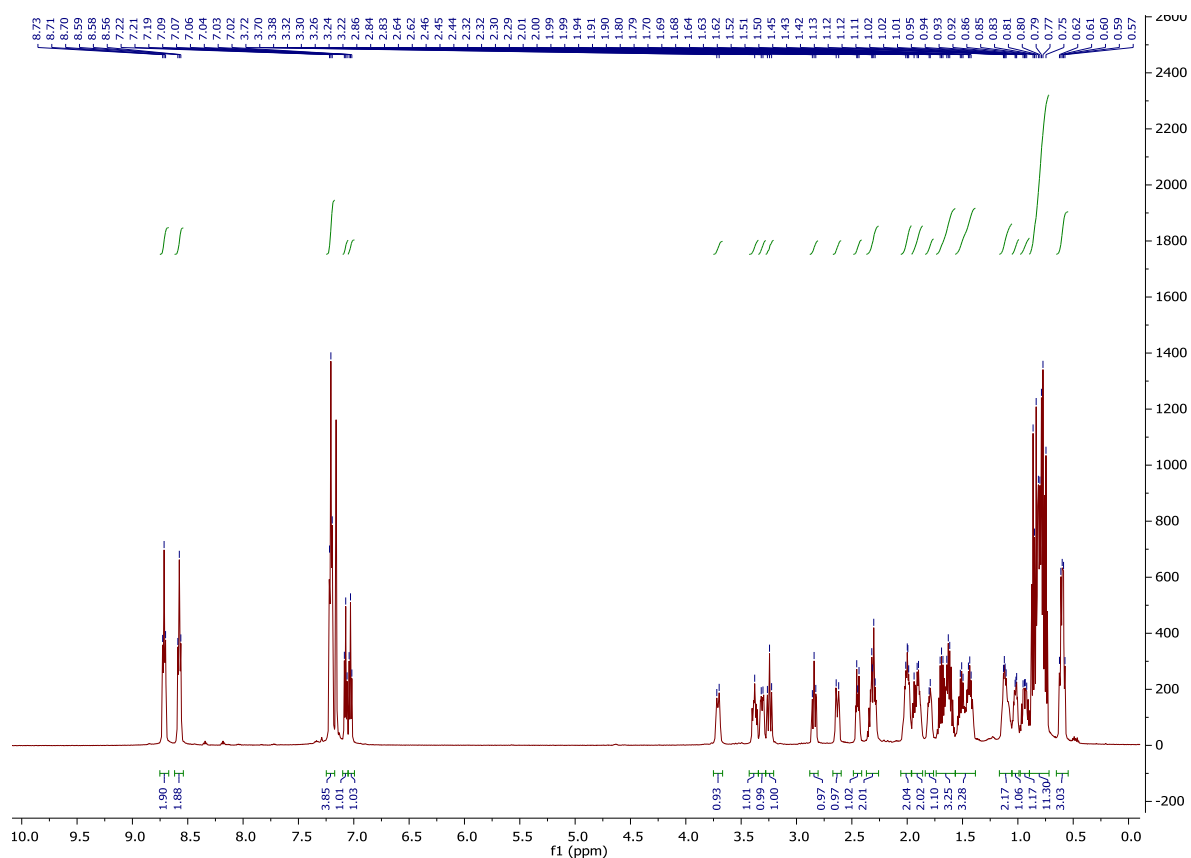


### Synthesis of $[\text{Ir}(\text{depe})(\text{CO})(\text{Ph}_2\text{PO})(\text{dbuCO}_2)]$ (3)

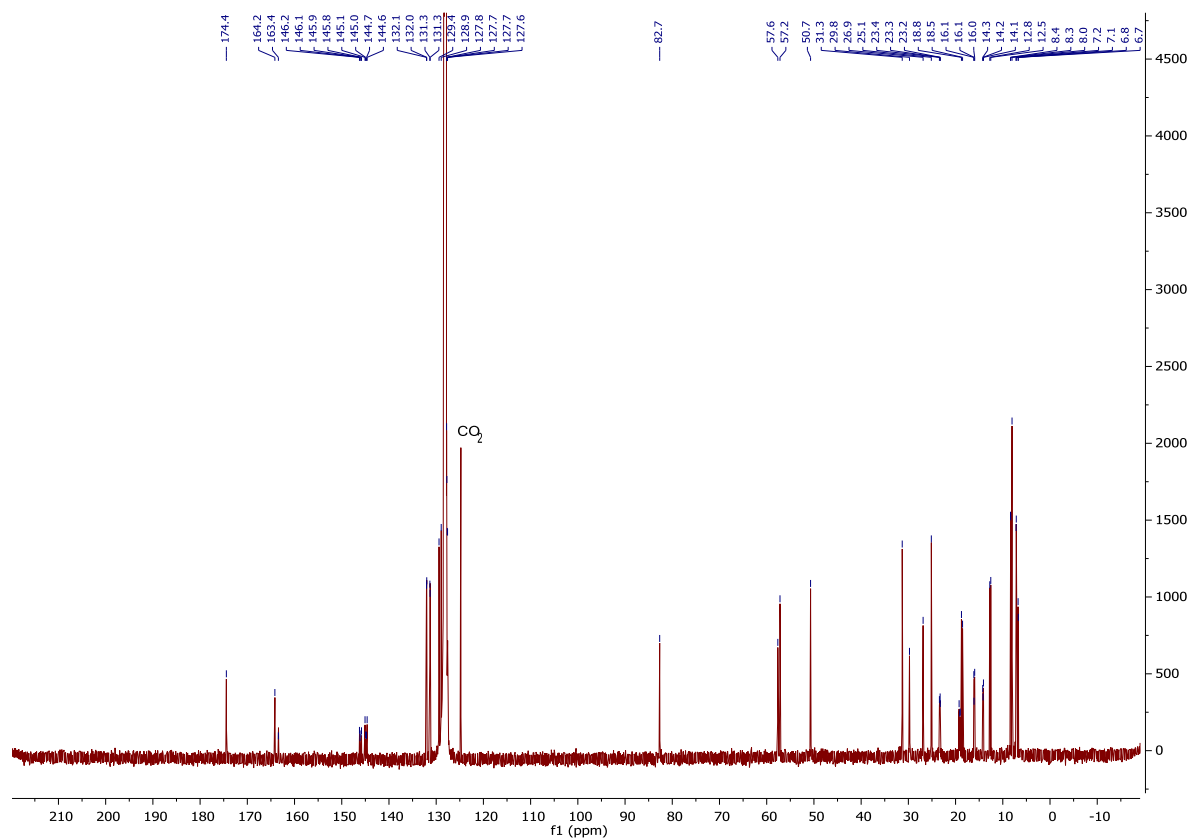
$[\text{Ir}(\text{depe})(\text{dbuP})]$  (2a) (25 mg, 0.034 mmol) was suspended in diethyl ether (3 ml). Afterwards, the reaction mixture was pressurized with  $\text{CO}_2$  (0.2 bar overpressure) with rapid stirring. The stirring was continued until the reddish color of the starting material had completely vanished and a pale yellow suspension

had formed (typically 2-3 min). Thereafter, the solvent was rapidly evaporated in vacuum. The resulting yellow amorphous solid was dried in a dynamic vacuum. Yield: 28 mg (0.034 mmol, quantitative);  $^1\text{H}$  NMR (600MHz,  $\text{C}_6\text{D}_6$ , 298K,  $\text{CO}_2$  atmosphere):  $\delta$  = 0.60 (3H, dt,  $^3J_{\text{H-P}}$  = 14.9, 7.6 Hz,  $\text{CH}_3$  depe), 0.72-0.89 (11H, m, 3 x  $\text{CH}_3$  depe +  $\text{CHH}'$  depe +  $\text{CHH}'$  dbuCO<sub>2</sub>), 0.94 (1H, m,  $\text{CHH}'$  depe), 1.02 (1H, m,  $\text{CHH}'$  depe), 1.05-1.16 (2H, m,  $\text{CHH}'$  depe +  $\text{CHH}'$  dbuCO<sub>2</sub>), 1.38-1.57 (3H, m,  $\text{CHH}'$  + 2 x  $\text{CHH}'$  depe), 1.57-1.74 (3H, m, 2 x  $\text{CHH}'$  depe +  $\text{CHH}'$  dbuCO<sub>2</sub>), 1.80 (1H, m,  $\text{CHH}'$  dbuCO<sub>2</sub>), 1.86-1.96 (2H, m,  $\text{CHH}'$  depe +  $\text{CHH}'$  dbuCO<sub>2</sub>), 1.96-2.05 (2H, m,  $\text{CHH}'$  depe +  $\text{CHH}'$  dbuCO<sub>2</sub>), 2.26-2.37 (2H, m,  $\text{CHH}'$  depe +  $\text{CHH}'$  dbuCO<sub>2</sub>), 2.45 (1H, m,  $\text{NCHH}'$  dbuCO<sub>2</sub>), 2.63 (1H, m,  $\text{NCHH}'$  dbuCO<sub>2</sub>), 2.84 (1H, m,  $\text{NCHH}'$  dbuCO<sub>2</sub>), 3.24 (1H, m,  $\text{NCHH}'$  dbuCO<sub>2</sub>), 3.31 (1H, m,  $\text{CHH}'$  dbuCO<sub>2</sub>), 3.38 (1H, m,  $\text{NCHH}'$  dbuCO<sub>2</sub>), 3.71 (1H, m,  $\text{NCHH}'$  dbuCO<sub>2</sub>), 7.03 (1H, app. t, *p*-CH Ph), 7.07 (1H, app. t, *p*-CH Ph), 7.21 (4H, app. t, *m*-CH Ph), 8.58 (2H, app. t, *o*-CH Ph), 8.71 (2H, app. t, *o*-CH Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR (151MHz,  $\text{C}_6\text{D}_6$ , 298K,  $\text{CO}_2$  atmosphere):  $\delta$  = 6.7 (1C, d,  $^2J_{\text{C-P}}$  = 6.3 Hz,  $\text{CH}_3$  depe), 7.2 (1C, d,  $^2J_{\text{C-P}}$  = 6.6 Hz,  $\text{CH}_3$  depe), 8.0 (1C, s,  $\text{CH}_3$  depe), 8.3 (1C, d,  $^2J_{\text{C-P}}$  = 5.4 Hz,  $\text{CH}_3$  depe), 12.65 (1C, d,  $^1J_{\text{C-P}}$  = 31.6 Hz,  $\text{CH}_2$  depe), 14.2 (1C, m,  $\text{CH}_2$  depe), 16.0 (1C, m,  $\text{CH}_2$  depe), 18.64 (1C, d,  $^1J_{\text{C-P}}$  = 34.6 Hz,  $\text{CH}_2$  depe), 19.2 (1C, m,  $\text{CH}_2$  depe), 23.3 (1C, m,  $\text{CH}_2$  depe), 25.1 (1C, s,  $\text{CH}_2$  dbuCO<sub>2</sub>), 26.9 (1C, s,  $\text{CH}_2$  dbuCO<sub>2</sub>), 29.8 (1C, s,  $\text{CH}_2$  dbuCO<sub>2</sub>), 31.3 (1C, s,  $\text{CH}_2$  dbuCO<sub>2</sub>), 50.7 (1C, s,  $\text{NCH}_2$  dbuCO<sub>2</sub>), 57.2 (1C, s,  $\text{NCH}_2$  dbuCO<sub>2</sub>), 57.6 (1C, s,  $\text{NCH}_2$  dbuCO<sub>2</sub>), 82.7 (1C, s,  $>\text{C}=\text{dbuCO}_2$ ), 127.6 (2C, d,  $^3J_{\text{C-P}}$  = 9.1 Hz, *m*-CH Ph), 127.8 (2C, d,  $^3J_{\text{C-P}}$  = 8.9 Hz, *m*-CH Ph), 128.9 (1C, s, *p*-CH Ph), 129.4 (1C, s, *p*-CH Ph), 131.3 (2C, d,  $^2J_{\text{C-P}}$  = 7.6 Hz, *o*-CH Ph), 132.0 (2C, d,  $^2J_{\text{C-P}}$  = 7.6 Hz, *o*-CH Ph), 144.85 (1C, m, *i*-C Ph), 146.0 (1C, m, *i*-C Ph), 163.4 (1C, m, Ir-CO), 164.2 (1C, s,  $\text{N}_2\text{C}=\text{dbuCO}_2$ ), 174.4 (1C, s, -COIr);  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9MHz,  $\text{C}_6\text{D}_6$ , 298K,  $\text{CO}_2$  atmosphere):  $\delta$   $\approx$  13.6 (3P, m, ABC spin system), calculated parameters:  $\delta$  = 12.25 (A), 13.38 (B), 14.21 (C);  $J_{\text{AB}}$  = 17.00 Hz,  $J_{\text{AC}}$  = 402.05 Hz,  $J_{\text{BC}}$  = -3.75 Hz; line width = 14 Hz (A); 9 Hz (B), 9 Hz (C);

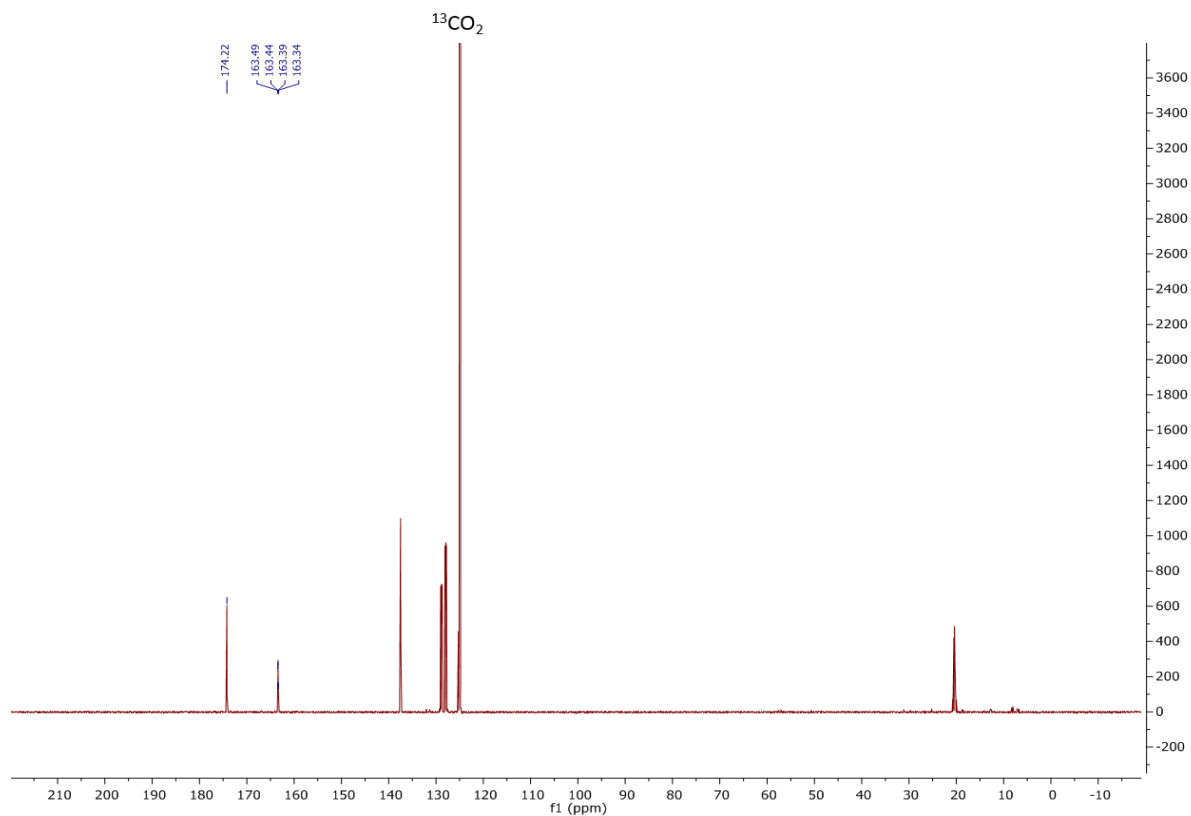
MS (ESI in THF):  $m/z$ : 823.2481  $[M+H]^+$  (calculated for  $C_{33}H_{49}IrN_2O_4P_3$ : 823.2531);  
 Anal. calcd. for  $C_{33}H_{48}IrN_2O_4P_3$ : C 48.23%, H 5.89 %, N 3.41 %; found: C 48.14 %, H 6.01 %, N 3.29%. Suitable crystals for XRD analysis were obtained from a saturated solution in THP at  $-25^\circ\text{C}$ .



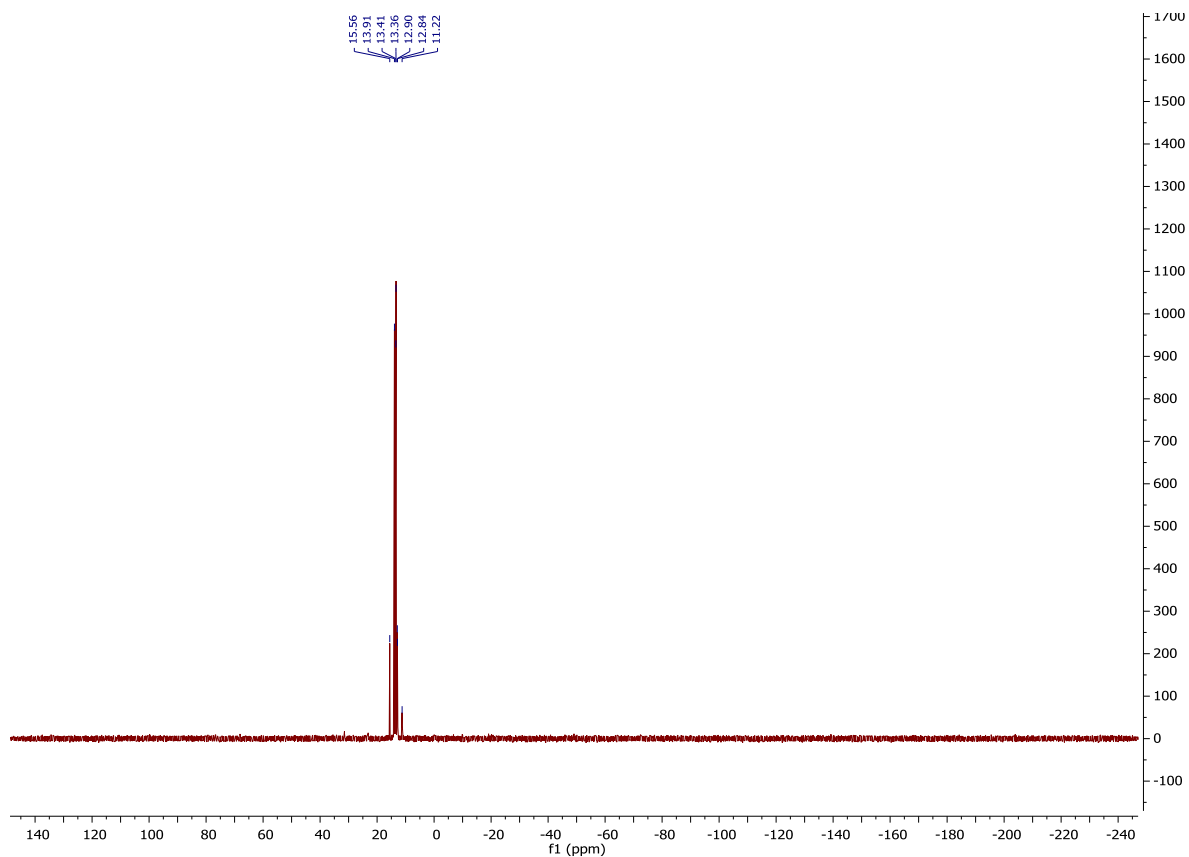
Spectrum S15:  $^1\text{H}$  NMR spectrum of  $[\text{Ir}(\text{depe})(\text{CO})(\text{Ph}_2\text{PO})(\text{dbuCO}_2)]$  ( $\text{C}_6\text{D}_6$ , 600.1 MHz, 298 K,  $\text{CO}_2$  atmosphere).



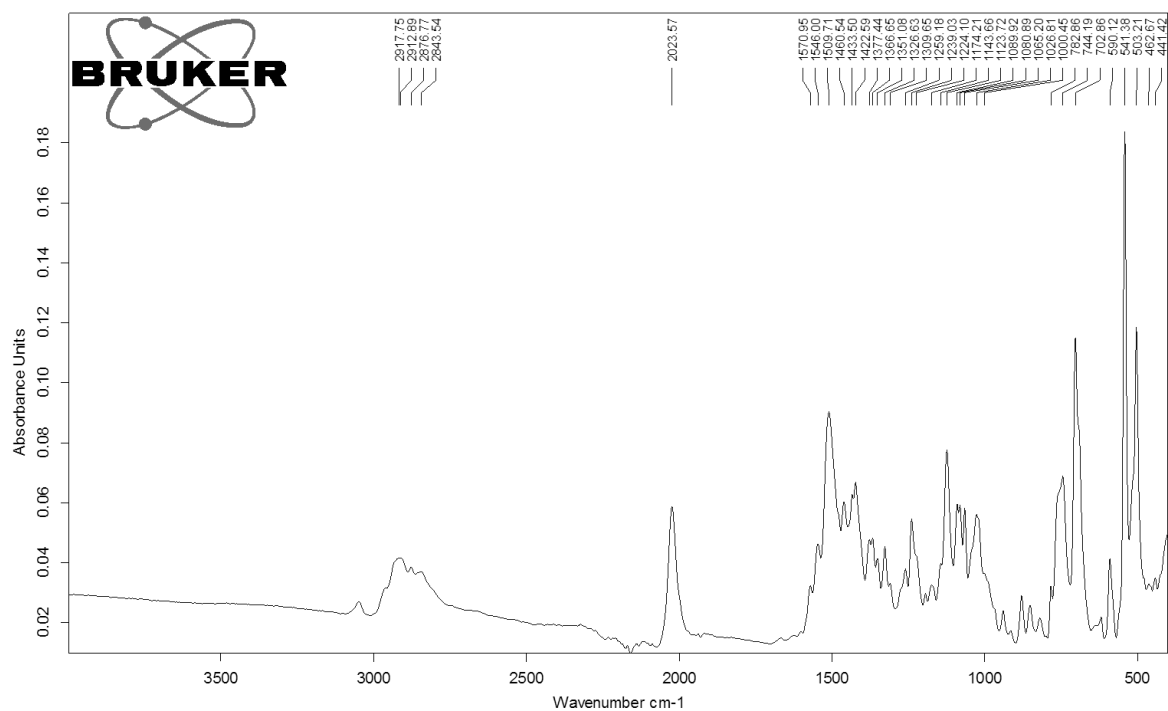
Spectrum S16:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(\text{depe})(\text{CO})(\text{Ph}_2\text{PO})(\text{dbuCO}_2)]$  ( $\text{C}_6\text{D}_6$ , 150.9 MHz, 298 K,  $\text{CO}_2$  atmosphere).



Spectrum S17: Partial  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(\text{depe})(^{13}\text{CO})(\text{Ph}_2\text{PO})(\text{dbu}^{13}\text{CO}_2)]$  (toluene- $d_8$ , 242.9 MHz, 298 K,  $^{13}\text{CO}_2$  atmosphere).



Spectrum S18:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ir}(\text{depe})(\text{CO})(\text{Ph}_2\text{PO})(\text{dbuCO}_2)]$  ( $\text{C}_6\text{D}_6$ , 242.9 MHz, 298 K,  $\text{CO}_2$  atmosphere).



Spectrum S19: ATR-FTIR spectrum of  $[\text{Ir}(\text{depe})(\text{CO})(\text{Ph}_2\text{PO})(\text{dbuCO}_2)]$ .

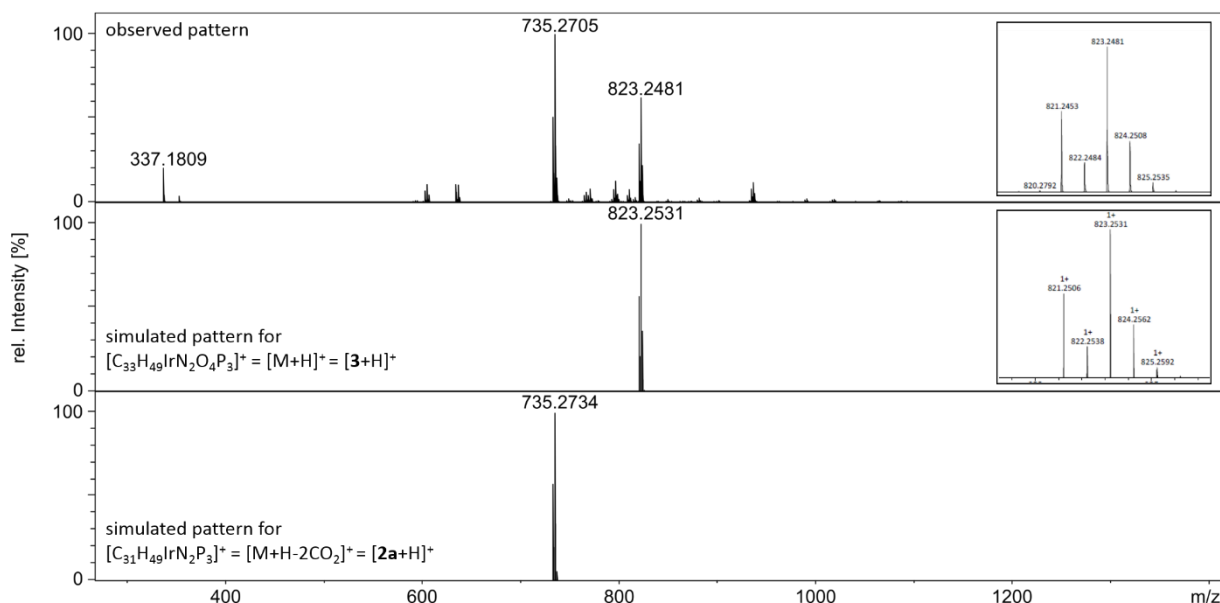
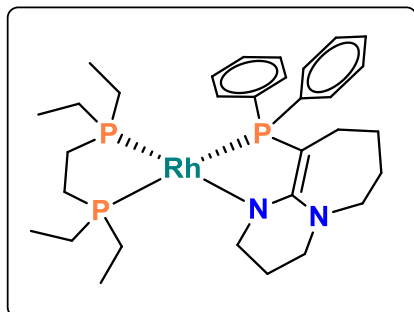


Figure S6: Mass spectroscopic investigation of a diluted solution ( $\approx 1 \cdot 10^{-5} \text{M}$ ) of  $[\text{Ir}(\text{depe})(\text{CO})(\text{Ph}_2\text{PO})(\text{dbuCO}_2)]$  in THF (electron spray ionization mass spectroscopy, positive ionization mode); magnified observed and calculated isotopic pattern of  $[3+\text{H}]^+$  are shown in frames at the right.

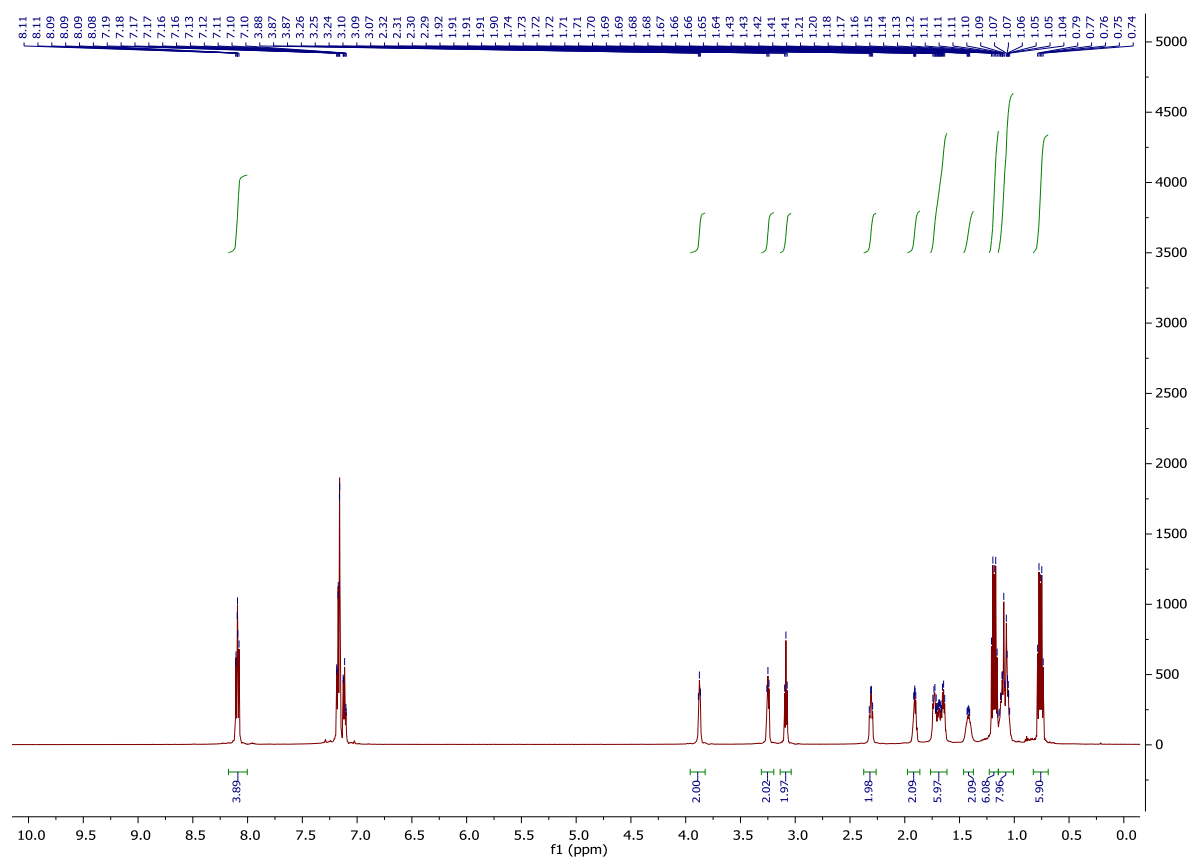


### Synthesis of $[\text{Rh}(\text{depe})(\text{dbuP})]$ (4)

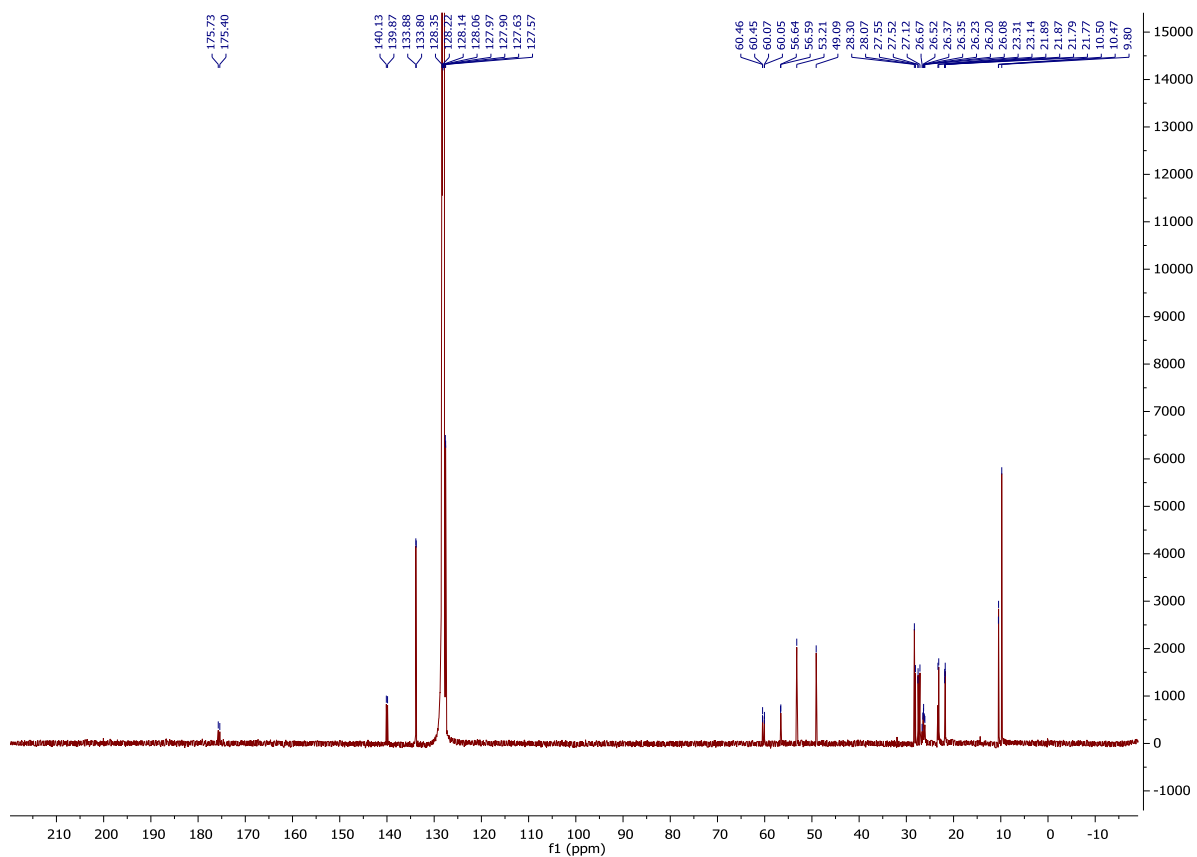
Crystalline  $[\text{Rh}(\text{cod})(\text{dbuP})] \cdot 0.5\text{C}_6\text{H}_6 \cdot 0.17\text{Hexane}$  <sup>[S2]</sup> (52 mg, 0.087 mmol) was suspended in benzene (1.2 mL) in a vial. Addition of 1,2-bis(diethylphosphino)ethane (depe; 21  $\mu\text{L}$ , 0.090 mmol) and subsequent stirring led to the formation of an orange solution. Stirring was continued overnight and the solvent was removed afterwards in a vacuum until a viscous reddish orange oil was obtained, which was rapidly taken up in *n*-hexane (2.0 mL). Crystallization of the product started almost immediately and was completed by storing the reaction mixture for 2 days at  $-20^\circ\text{C}$ . Then the orange crystals were isolated by decantation, washed with cold *n*-hexane (0.3 mL) and dried in a vacuum. Yield: 44 mg (0.068 mmol, 78%); m.p.:  $184\text{--}186^\circ\text{C}$ .  $^1\text{H}$  NMR (600MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta$  = 0.76 (6H, dt,  $^3J_{\text{H-P}} = 15.2$  Hz,  $^3J_{\text{H-H}} = 7.6$  Hz,  $\text{CH}_3$  depe), 1.02–1.15 (8H, m,  $\text{CH}_2$  depe), 1.18 (6H, dt,  $^3J_{\text{H-P}} = 15.4$ ,  $^3J_{\text{H-H}} = 7.6$  Hz,  $\text{CH}_3$  depe), 1.42 (2H, m,  $\text{CH}_2$  depe), 1.61–1.76 (6H, m,  $\text{CH}_2$  depe +  $2 \times \text{CH}_2$  dbuP), 1.91 (2H, m,  $\text{CH}_2$  dbuP), 2.30 (2H, m,  $\text{CH}_2$  dbuP), 3.08 (2H, t,  $^3J_{\text{H-H}} = 6.9$  Hz,  $\text{NCH}_2$  dbuP), 3.25 (2H, m,  $\text{NCH}_2$  dbuP), 3.87 (2H, m,  $\text{NCH}_2$  dbuP), 7.11 (2H,



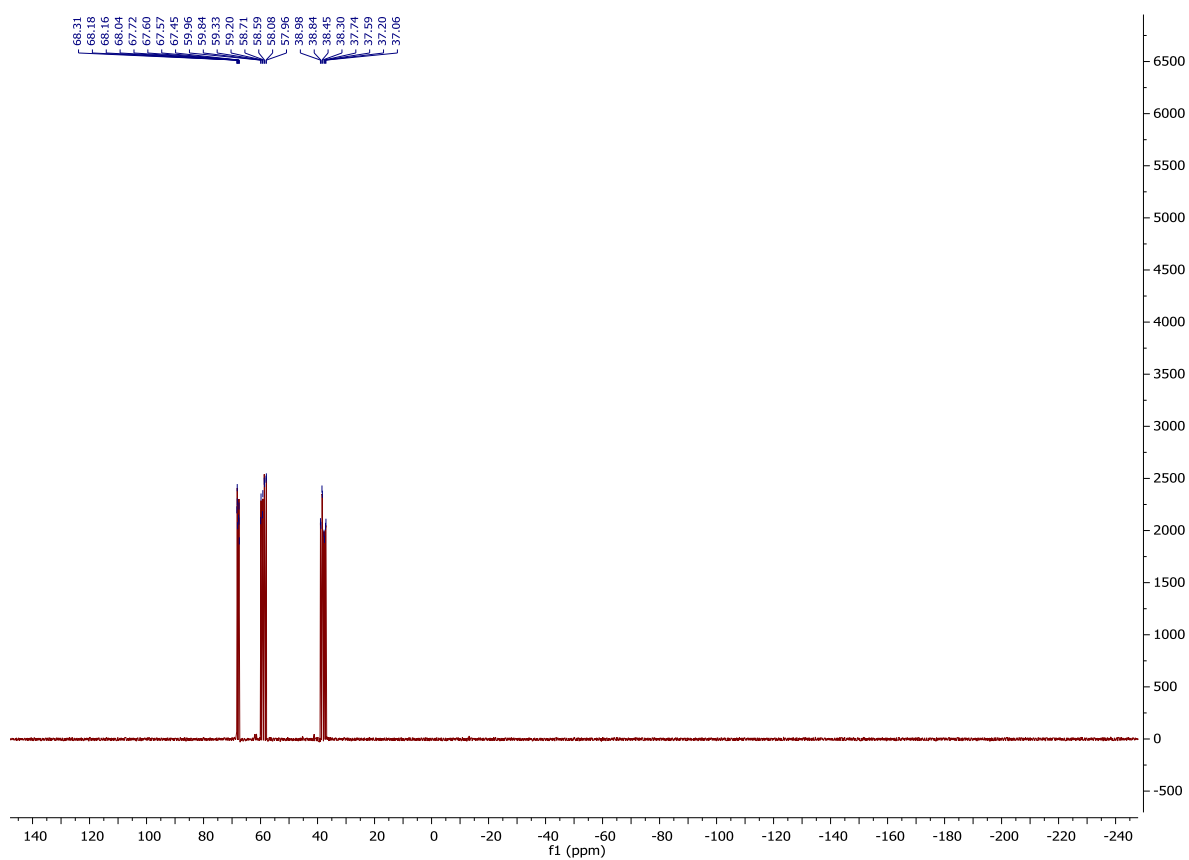
m, *p*-CH Ph), 7.17 (4H, m, *m*-CH Ph), 8.09 (4H, m, *o*-CH Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR (151MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta$  = 9.8 (2C, s,  $\text{CH}_3$  depe), 10.5 (2C, d,  $^2J_{\text{C-P}} = 4.0$  Hz,  $\text{CH}_3$  depe), 21.8 (2C, dd,  $^1J_{\text{C-P}} = 16.0$  Hz,  $^3J_{\text{C-P}} = 3.3$  Hz,  $\text{CH}_2$  depe), 23.2 (2C, d,  $^1J_{\text{C-P}} = 25.0$  Hz,  $\text{CH}_2$  depe), 26.2 (1C, ddd,  $^1J_{\text{C-P}} = 25.9$ ,  $^2J_{\text{C-P}} = 17.9$ ,  $J = 3.6$  Hz,  $\text{CH}_2$  depe), 26.5 (1C, m,  $\text{CH}_2$  depe), 27.1 (1C, s,  $\text{CH}_2$  dbuP), 27.5 (1C, d,  $J_{\text{C-P}} = 4.4$  Hz,  $\text{CH}_2$  dbuP), 28.1 (1C, s,  $\text{CH}_2$  dbuP), 28.3 (1C, s,  $\text{CH}_2$  dbuP), 49.1 (1C, s, N- $\text{CH}_2$  dbuP), 53.2 (1C, s, N- $\text{CH}_2$  dbuP), 56.6 (1C, dd,  $J = 9.5$  Hz,  $J = 3.1$  Hz, N- $\text{CH}_2$  dbuP), 60.3 (1C, dd,  $^1J_{\text{C-P}} = 59.5$  Hz,  $^3J_{\text{C-P}} = 2.6$  Hz, =C-P dbuP), 127.6 (4C, d,  $^3J_{\text{C-P}} = 9.0$  Hz, *m*-CH Ph), 128.0 (2C, d,  $^4J_{\text{C-P}} = 1.9$  Hz, *p*-CH Ph), 133.8 (4C, d,  $^2J_{\text{C-P}} = 12.0$  Hz, *o*-CH Ph), 140.0 (2C, d,  $^1J_{\text{C-P}} = 38.6$  Hz, *i*-C Ph), 175.6 (1C, d,  $^2J_{\text{C-P}} = 50.3$  Hz,  $\text{N}_2\text{C}=\text{dbuP}$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (242.9MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta$  = 38.0 (ddd,  $^2J_{\text{P-P,trans}} = 302.2$  Hz,  $^1J_{\text{P-Rh}} = 129.4$  Hz,  $^2J_{\text{P-P,cis}} = 35.3$  Hz), 59.0 (ddd,  $^2J_{\text{P-P,trans}} = 302.2$  Hz,  $^1J_{\text{P-Rh}} = 154.0$  Hz,  $^2J_{\text{P-P,cis}} = 30.1$  Hz), 67.9 (ddd,  $^1J_{\text{P-Rh}} = 143.0$  Hz,  $^2J_{\text{P-P,cis}} = 35.3$  Hz,  $^2J_{\text{P-P,cis}} = 30.3$  Hz); Anal. calcd. for  $\text{C}_{31}\text{H}_{48}\text{RhN}_2\text{P}_3$ : C 57.77%, H 7.51 %, N 4.35 %; found: C 57.75 %, H 7.50 %, N 4.10 %.



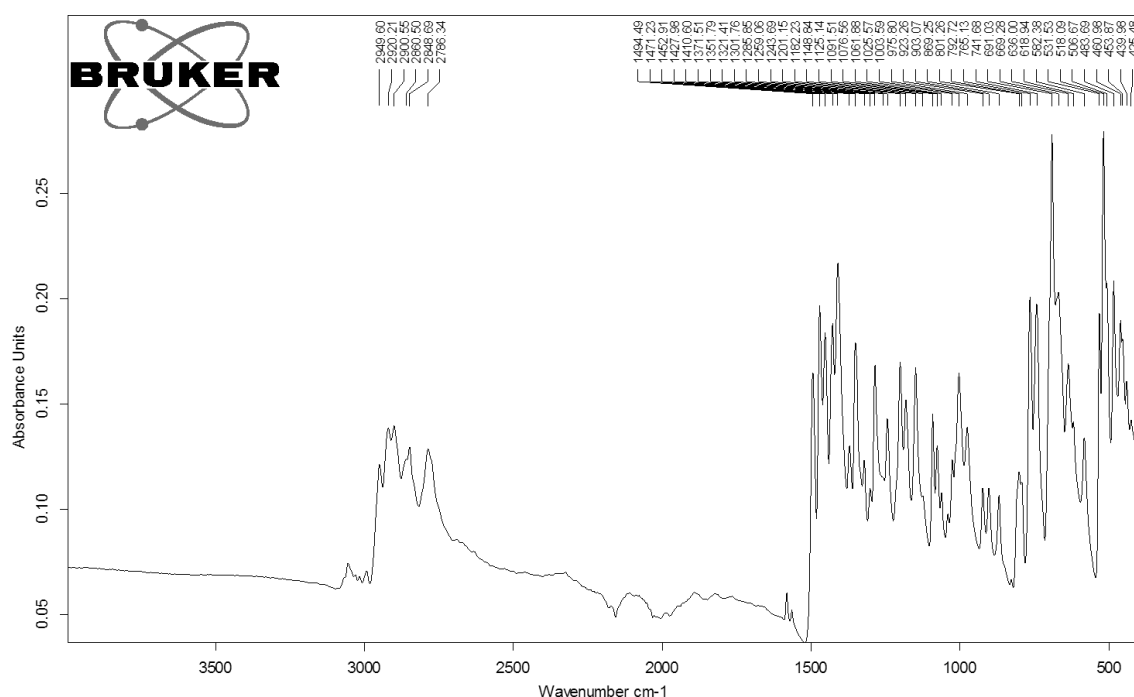
Spectrum S20:  $^1\text{H}$  NMR spectrum of  $[\text{Rh}(\text{depe})(\text{dbuP})]$  ( $\text{C}_6\text{D}_6$ , 600.1 MHz, 298 K).



Spectrum S21:  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Rh}(\text{depe})(\text{dbuP})]$  ( $\text{C}_6\text{D}_6$ , 150.9 MHz, 298 K).



Spectrum S22:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Rh}(\text{depe})(\text{dbuP})]$  ( $\text{C}_6\text{D}_6$ , 242.9 MHz, 298 K).



Spectrum S23: ATR-FTIR spectrum of [Rh(depe)(dbuP)].

### Low temperature CO<sub>2</sub> uptake by complex **4**

In a Young tube, 15 mg of orange complex **4** were dissolved in toluene-*d*<sub>8</sub>. Replacement of the N<sub>2</sub> atmosphere by a <sup>13</sup>CO<sub>2</sub> atmosphere, followed by shaking of the reaction mixture for 3 min did not lead to a noticeable color change, however <sup>31</sup>P NMR spectroscopy showed a broadening of the signals of complex **4** (see Figure S7, middle). Since this is an indication for <sup>13</sup>CO<sub>2</sub> uptake in equilibrium at ambient temperature, the system was further studied at low temperature. At 243 K, the new intermediate compound [Rh(depe)(dbuP<sup>13</sup>CO<sub>2</sub>)] (**4**·<sup>13</sup>CO<sub>2</sub>) is the dominant species in solution. At 203 K, the selective formation of the new phosphorous containing species [Rh(<sup>13</sup>CO<sub>2</sub>)(depe)(dbuP<sup>13</sup>CO<sub>2</sub>)] (**4**·2(<sup>13</sup>CO<sub>2</sub>)) was confirmed (see Figure S7, bottom).

When the <sup>13</sup>CO<sub>2</sub> atmosphere was replaced at ambient temperature by an N<sub>2</sub> atmosphere by reducing the volume of the reaction solution by 20 % under vacuum and refilling the Young tube with N<sub>2</sub>, quantitative reformation of **4** was observed.

**[Rh(depe)(dbuP<sup>13</sup>CO<sub>2</sub>)]:** <sup>13</sup>C{<sup>1</sup>H} NMR (151MHz, toluene-*d*<sub>8</sub>, 243 K, <sup>13</sup>CO<sub>2</sub> atmosphere):  $\delta$  = 166.3 (br. s, dbuP<sup>13</sup>CO<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (242.9 MHz, toluene-*d*<sub>8</sub>, 243 K, <sup>13</sup>CO<sub>2</sub> atmosphere):  $\delta$  = 58.0-65.0 (1P, br), 78.0-83.0 (2P, br).

**[Rh(<sup>13</sup>CO<sub>2</sub>)(depe)(dbuP<sup>13</sup>CO<sub>2</sub>)]:** <sup>13</sup>C{<sup>1</sup>H} NMR (151MHz, toluene-*d*<sub>8</sub>, 203 K, <sup>13</sup>CO<sub>2</sub> atmosphere):  $\delta$  = 159.9 (d, <sup>1</sup>J<sub>C-Rh</sub> = 18.8 Hz, Rh-<sup>13</sup>CO<sub>2</sub>), 169.3 (s, dbuP<sup>13</sup>CO<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (242.9 MHz, toluene-*d*<sub>8</sub>, 203 K, <sup>13</sup>CO<sub>2</sub> atmosphere):  $\delta$  = 53.6 (1P, ddd, <sup>2</sup>J<sub>P-P,trans</sub> = 351 Hz, <sup>1</sup>J<sub>P-Rh</sub> = 130 Hz, <sup>2</sup>J<sub>P-P,cis</sub> = 26 Hz), 60.6 (1P, m), 74.1 (1P, ddd, <sup>2</sup>J<sub>P-P,trans</sub> = 352 Hz, <sup>1</sup>J<sub>P-Rh</sub> = 115 Hz, <sup>2</sup>J<sub>P-P,cis</sub> = 15 Hz).

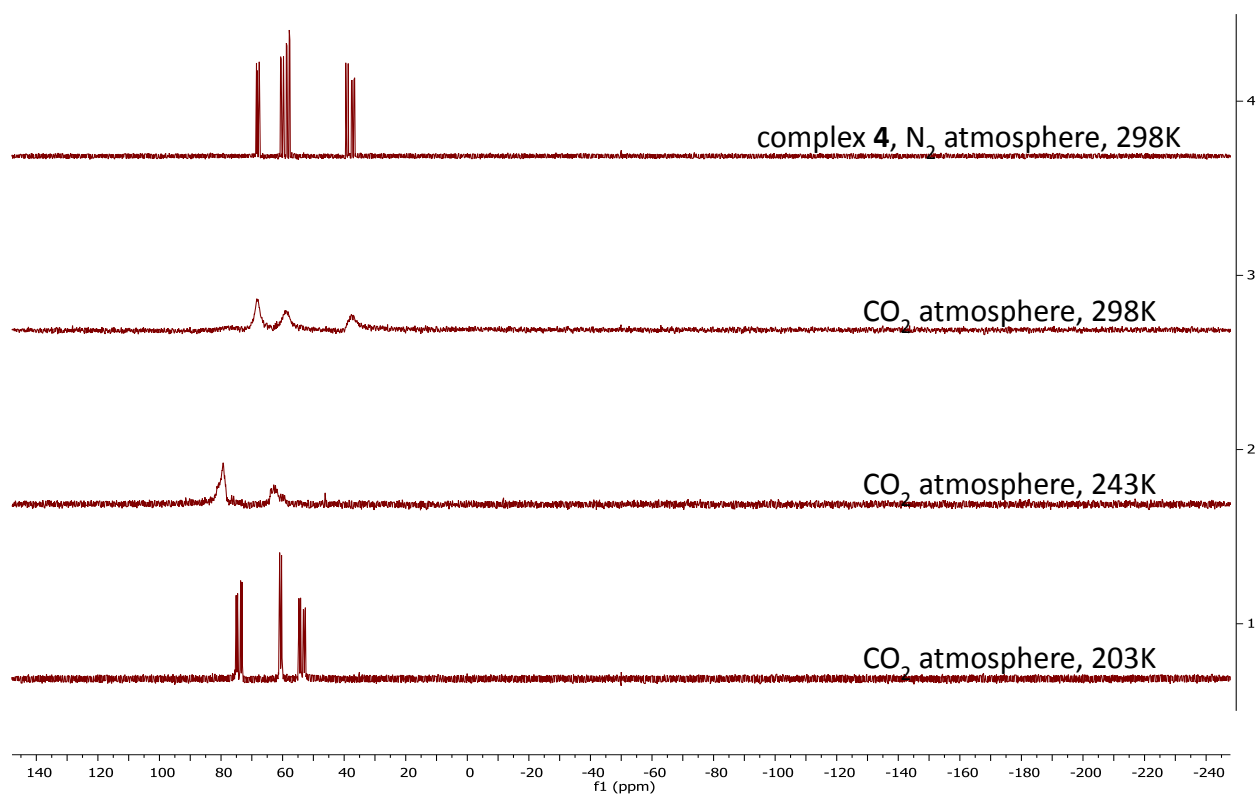
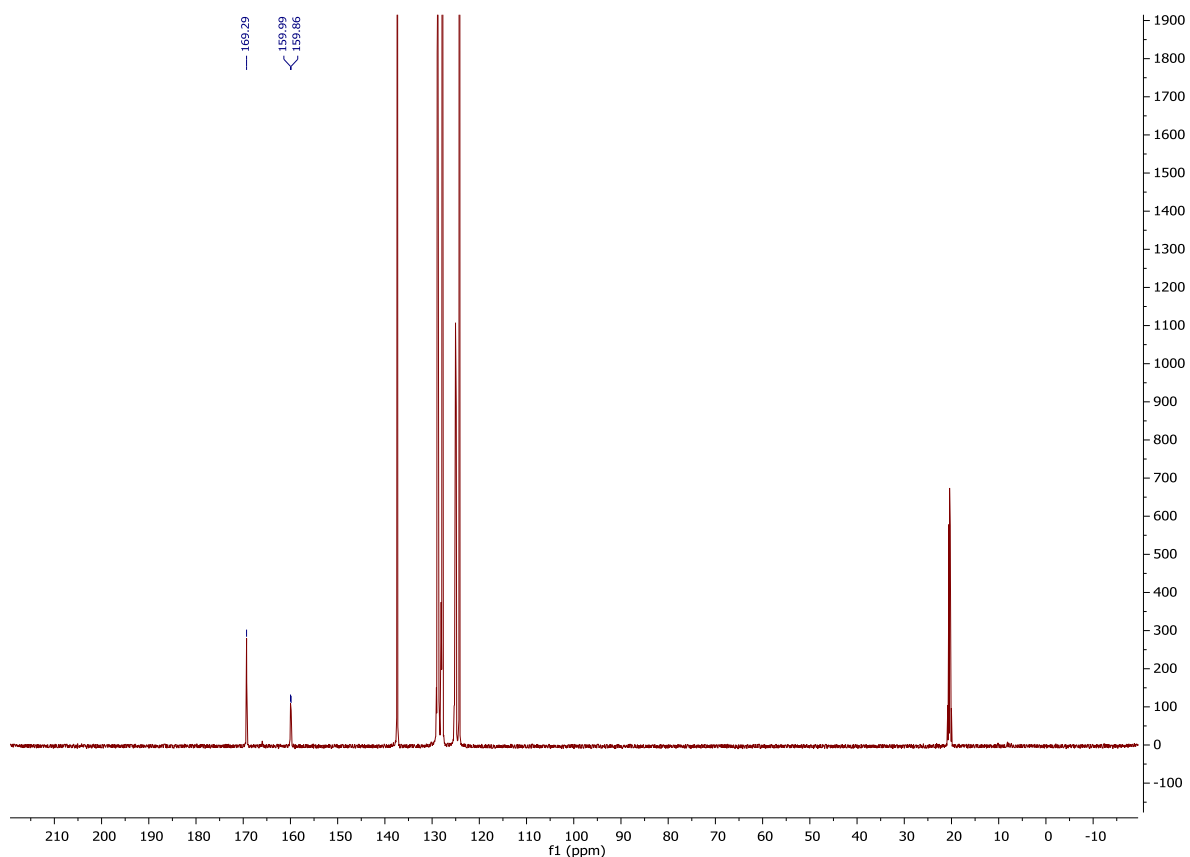
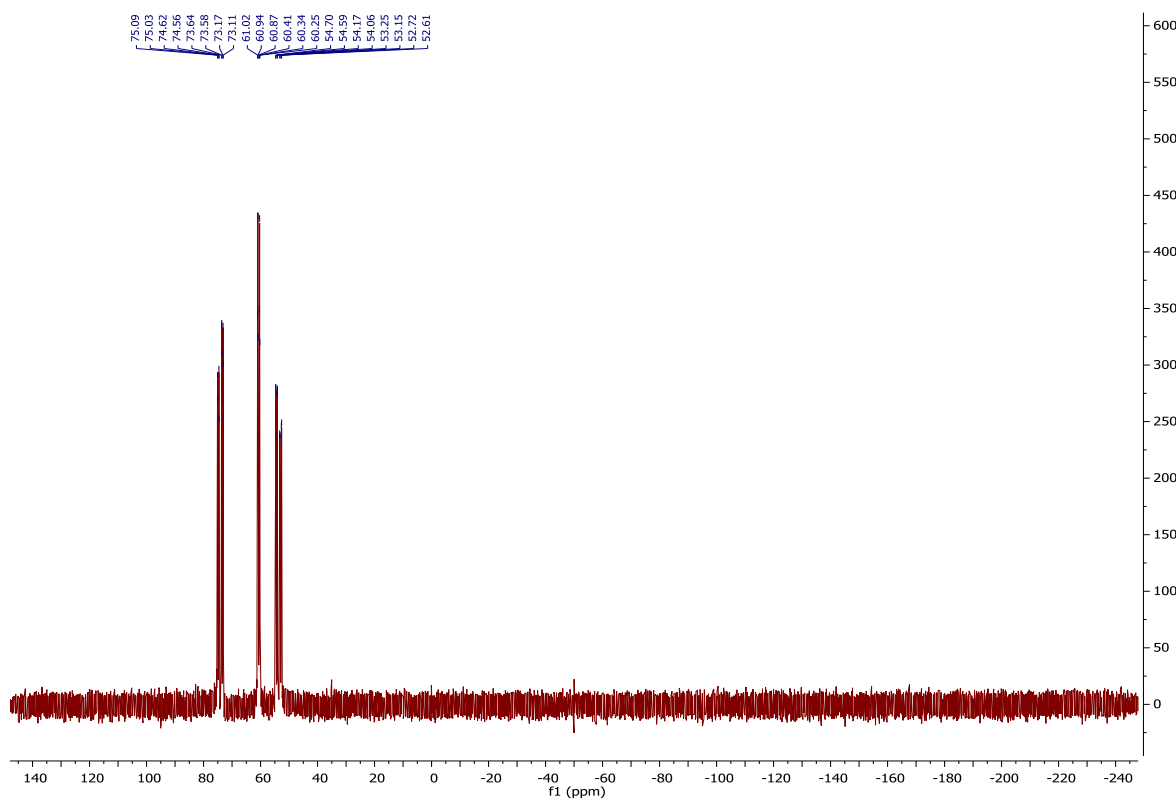


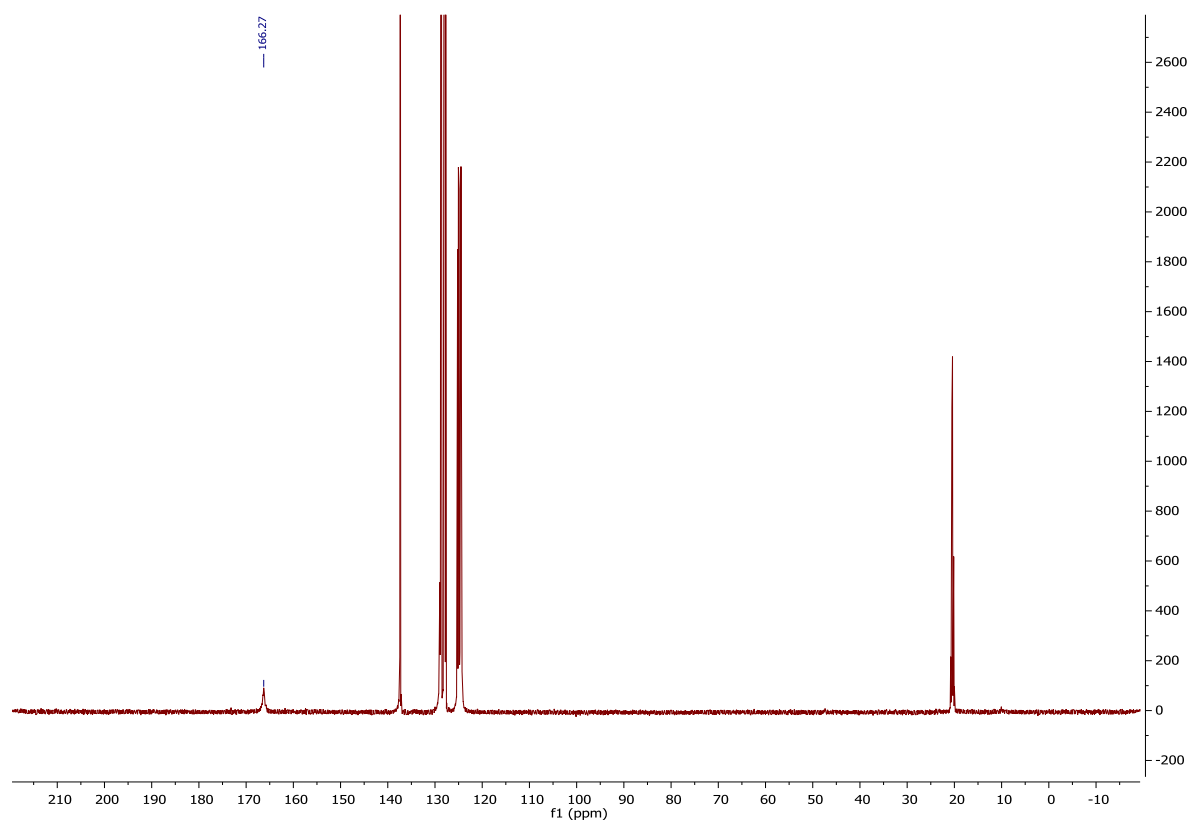
Figure S7: Comparison of the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of [Rh(depe)(dbuP)] (**4**) in absence (top) and presence of CO<sub>2</sub> at 298 K, 243 K and 203 K (bottom) (toluene-*d*<sub>8</sub>, 242.9 MHz).



Spectrum S24: Partial  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Rh}(^{13}\text{CO}_2)(\text{depe})(\text{dbuP}^{13}\text{CO}_2)]$  (toluene- $d_8$ , 150.9 MHz, 203 K,  $^{13}\text{CO}_2$  atmosphere).



Spectrum S25:  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Rh}(\text{CO}_2)(\text{depe})(\text{dbuPCO}_2)]$  (toluene- $d_8$ , 242.9 MHz, 203K,  $\text{CO}_2$  atmosphere).



Spectrum S26: Partial  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of intermediate  $[\text{Rh}(\text{depe})(\text{dbuP}^{13}\text{CO}_2)]$  (toluene- $d_8$ , 150.9 MHz, 243K,  $^{13}\text{CO}_2$  atmosphere).

## Crystallographic Data

### Structure determination of 1-4

All crystals were embedded in inert perfluoropolyalkylether (viscosity 1800 cSt; ABCR GmbH) and mounted using a Hampton Research CryoLoop. The selected crystal was then flash cooled at 100 K in a nitrogen gas stream. The crystal structures of **1-4** were measured on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The measured data was processed with the CrysAlisPro (v38.46) software package.<sup>[S4]</sup> Using Olex2,<sup>[S5]</sup> the structures were solved by Direct Methods (ShelXT)<sup>[S6]</sup> and refined with ShelXL<sup>[S7]</sup> using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise mentioned. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

While compound **1** usually crystallized with 0.5 molecules of benzene per asymmetric unit (see experimental section and Table S1), in one case a few crystals of a solvent-free form were obtained from a solution in a *n*-hexane/benzene mixture, which contained only a small amount of benzene. The crystals were of low quality and insufficient to obtain a complete dataset. However, a partial low resolution data set (0.99 Å) was measured in order to determine the unit cell and space group of this form. This additional information is also given in Table S1.

The crystal of **2b** suffered from twinning (twin law -1, 0, 0 / 0, 1, 0 / 0, 0, -1). The fractional contributions of the two domains of the measured specimen were refined to 0.631 and 0.369, respectively. Additionally, disorder of two of the three symmetry-independent co-crystallized toluene molecules and within the 7-membered ring of dbuP<sup>-</sup> was observed. A suitable disorder model was built, applying SIMU, RIGU<sup>[S8]</sup> and ISOR restraints. The carbon atoms of the disordered toluene molecules were refined with isotropic displacement parameters

The crystal of **3** contained solvent-accessible voids filled with 2.5 THP molecules per molecule of the iridium complex. The structural model was refined with contributions from the disordered solvate molecules accounted for through use of the solvent mask

subroutine<sup>[S9,S10]</sup> in Olex2.<sup>[S5]</sup> The contribution of 397.7 electrons in solvent-accessible voids (1674.1 Å<sup>3</sup>/cell, 34.7% of the cell volume) was masked.

ORTEP-3<sup>[S11]</sup> and POV-RAY<sup>[S12]</sup> were used for structure representations. Crystallographic data (excluding structure factors) of **1-4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1579346-1579350. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).



Table S1: Crystal data and structure refinement details of **1-4**.

Compound	[Ir(cod)(dbuP)]·0.5C <sub>6</sub> H <sub>6</sub> ( <b>1</b> )	[Ir(cod)(dbuP)]
Empirical formula	C <sub>32</sub> H <sub>39</sub> IrN <sub>2</sub> P	C <sub>29</sub> H <sub>36</sub> IrN <sub>2</sub> P
Formula weight	674.82	635.77
Temperature/K	100.0(1)	100.0(1)
Crystal system	orthorhombic	monoclinic
Space group	Pbca	I2/a
a/Å	13.1571(3)	11.1697(5)
b/Å	11.22081(19)	13.4133(4)
c/Å	36.0309(7)	32.8080(10)
α/°	90	90
β/°	90	96.415(4)
γ/°	90	90
Volume/Å <sup>3</sup>	5319.37(19)	4884.6(3)
Z	8	8
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.685	1.729
μ/mm <sup>-1</sup>	5.105	11.343
F(000)	2696.0	2528.0
Crystal size/mm <sup>3</sup>	0.254 × 0.1561 × 0.0852	n.d.
Crystal color	red	red
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2θ range for data collection/°	5.854 to 52.082	19.892 to 101.812
Index ranges	-10 ≤ h ≤ 16, -10 ≤ k ≤ 13, -34 ≤ l ≤ 44	-9 ≤ h ≤ 11, -11 ≤ k ≤ 13, -32 ≤ l ≤ 17
Reflections collected	14382	4227
Independent reflections	5234 [R <sub>int</sub> = 0.0316, R <sub>sigma</sub> = 0.0357]	2347 [R <sub>int</sub> = 0.1591, R <sub>sigma</sub> = 0.1222]
Data/restraints/parameters	5234/0/325	2347/0/299
Goodness-of-fit on F <sup>2</sup>	1.105	0.897
Final R indexes [I > 2σ (I)]	R <sub>1</sub> = 0.0306, wR <sub>2</sub> = 0.0775	R <sub>1</sub> = 0.0890, wR <sub>2</sub> = 0.2142
Final R indexes [all data]	R <sub>1</sub> = 0.0350, wR <sub>2</sub> = 0.0808	R <sub>1</sub> = 0.0977, wR <sub>2</sub> = 0.2208
Largest diff. peak/hole / e Å <sup>-3</sup>	1.61/-1.25	2.79/-7.01
CCDC number	1579347	motif

Table S1: Crystal data and structure refinement details of **1-4**.

Compound	[Ir(depe)(dbuP)] (2a)	[Ir(dppe)(dbuP)]·1.5Toluene (2b)
Empirical formula	C <sub>31</sub> H <sub>48</sub> IrN <sub>2</sub> P <sub>3</sub>	C <sub>57.5</sub> H <sub>60</sub> IrN <sub>2</sub> P <sub>3</sub>
Formula weight	733.82	1064.18
Temperature/K	100.0(1)	100.0(3)
Crystal system	orthorhombic	monoclinic
Space group	Pbca	Pn
a/Å	9.3846(2)	11.3856(3)
b/Å	19.2478(4)	27.0609(7)
c/Å	34.1465(8)	15.7760(5)
α/°	90	90
β/°	90	93.751(3)
γ/°	90	90
Volume/Å <sup>3</sup>	6168.0(2)	4850.2(2)
Z	8	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.580	1.457
μ/mm <sup>-1</sup>	4.508	2.892
F(000)	2960.0	2164.0
Crystal size/mm <sup>3</sup>	0.1865 × 0.0945 × 0.0765	0.094 × 0.075 × 0.065
Crystal color	orangeish red	orangeish red
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.18 to 52.744	4.682 to 52.742
Index ranges	-11 ≤ h ≤ 11, -24 ≤ k ≤ 23, -41 ≤ l ≤ 42	-14 ≤ h ≤ 14, -33 ≤ k ≤ 33, -19 ≤ l ≤ 19
Reflections collected	28862	74552
Independent reflections	6303 [R <sub>int</sub> = 0.0460, R <sub>sigma</sub> = 0.0407]	19724 [R <sub>int</sub> = 0.0649, R <sub>sigma</sub> = 0.0661]
Data/restraints/parameters	6303/0/338	19724/110/1109
Goodness-of-fit on F <sup>2</sup>	1.071	1.104
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0301, wR <sub>2</sub> = 0.0499	R <sub>1</sub> = 0.0518, wR <sub>2</sub> = 0.1089
Final R indexes [all data]	R <sub>1</sub> = 0.0431, wR <sub>2</sub> = 0.0544	R <sub>1</sub> = 0.0593, wR <sub>2</sub> = 0.1124
Largest diff. peak/hole / e Å <sup>-3</sup>	1.47/-1.14	2.93/-1.56
CCDC number	1579349	1579350

Table S1. Crystal data and structure refinement details of **1-4** (continued).

Compound	[Ir(depe)(CO)(Ph <sub>2</sub> PO)(dbuCO <sub>2</sub> )]·2.5THP·(3)	[Rh(depe)(dbuP)] (4)
Empirical formula	C <sub>33</sub> H <sub>48</sub> IrN <sub>2</sub> O <sub>4</sub> P <sub>3</sub> [+ disordered solvent]	C <sub>31</sub> H <sub>48</sub> N <sub>2</sub> P <sub>3</sub> Rh
Formula weight	821.84	644.53
Temperature/K	100.0(1)	100.0(1)
Crystal system	triclinic	orthorhombic
Space group	P-1	Pbca
a/Å	14.9965(4)	9.37453(18)
b/Å	16.3592(5)	19.2645(4)
c/Å	20.1638(6)	34.2534(6)
α/°	66.734(3)	90
β/°	79.605(3)	90
γ/°	89.097(2)	90
Volume/Å <sup>3</sup>	4461.5(2)	6186.01(19)
Z	4	8
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.224	1.384
μ/mm <sup>-1</sup>	3.130	6.092
F(000)	1656.0	2704.0
Crystal size/mm <sup>3</sup>	0.103 × 0.082 × 0.074	0.196 × 0.09 × 0.057
Crystal color	yellow	orange
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2θ range for data collection/°	4.798 to 52.744	9.182 to 147.768
Index ranges	-17 ≤ h ≤ 18, -20 ≤ k ≤ 20, -25 ≤ l ≤ 25	-7 ≤ h ≤ 11, -23 ≤ k ≤ 22, -42 ≤ l ≤ 36
Reflections collected	53609	23963
Independent reflections	18212 [R <sub>int</sub> = 0.0588, R <sub>sigma</sub> = 0.0775]	6043 [R <sub>int</sub> = 0.0565, R <sub>sigma</sub> = 0.0353]
Data/restraints/parameters	18212/0/783	6043/0/338
Goodness-of-fit on F <sup>2</sup>	1.041	1.073
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0506, wR <sub>2</sub> = 0.1130	R <sub>1</sub> = 0.0384, wR <sub>2</sub> = 0.1032
Final R indexes [all data]	R <sub>1</sub> = 0.0760, wR <sub>2</sub> = 0.1221	R <sub>1</sub> = 0.0424, wR <sub>2</sub> = 0.1063
Largest diff. peak/hole / e Å <sup>-3</sup>	4.08/-2.02	1.47/-1.28
CCDC number	1579346	1579348

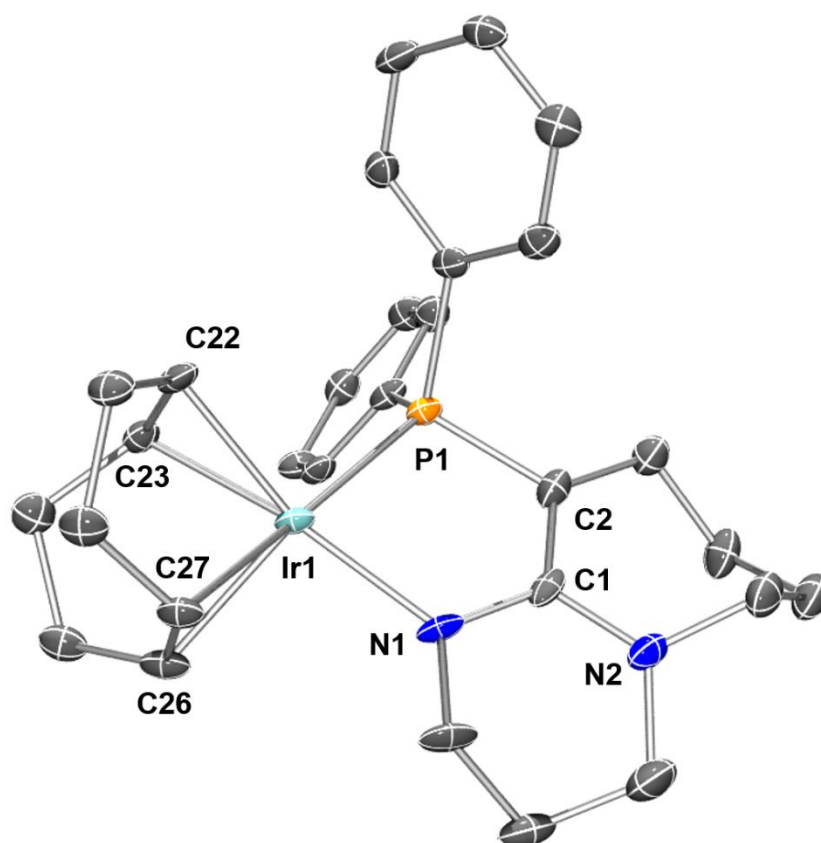


Figure S8: ORTEP plot of compound **1**·0.5Benzene with ellipsoids drawn at the 50% probability level. Hydrogen atoms and co-crystallized solvent are omitted for clarity.

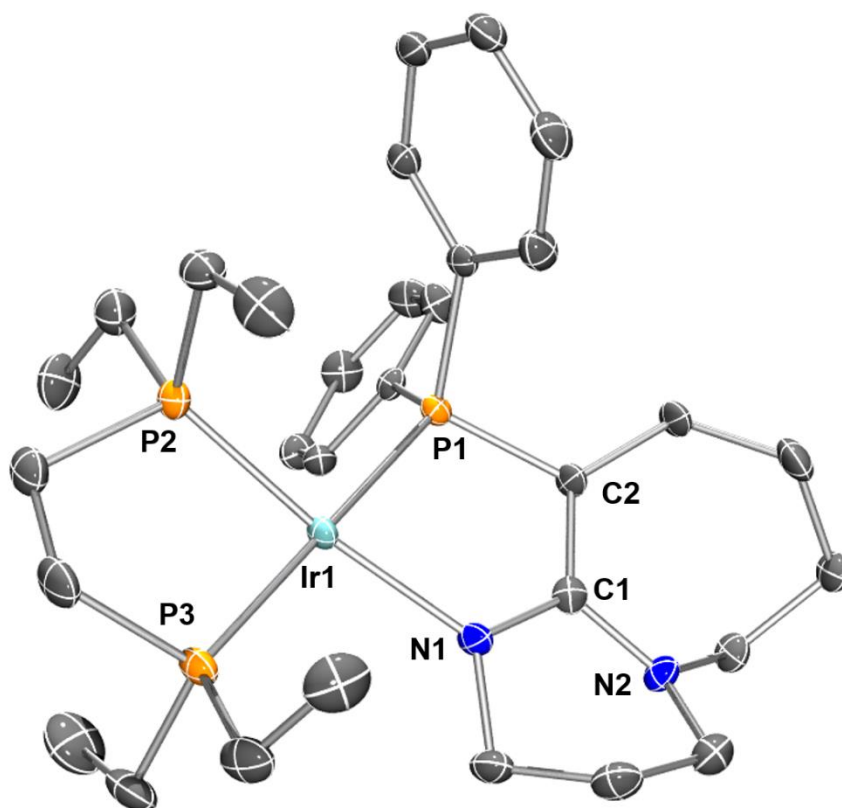


Figure S9: ORTEP plot of compound **2a** with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

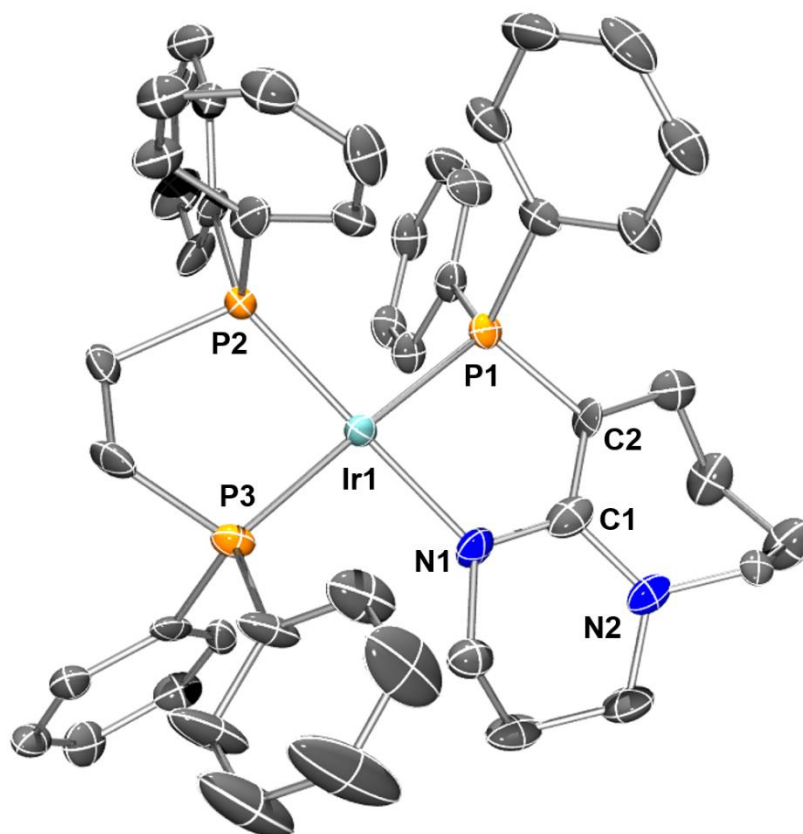


Figure S10: ORTEP plot of compound **2b**·1.5Toluene with ellipsoids drawn at the 50% probability level (Molecule A of two symmetry-independent molecules). Hydrogen atoms and co-crystallized toluene are omitted for clarity.

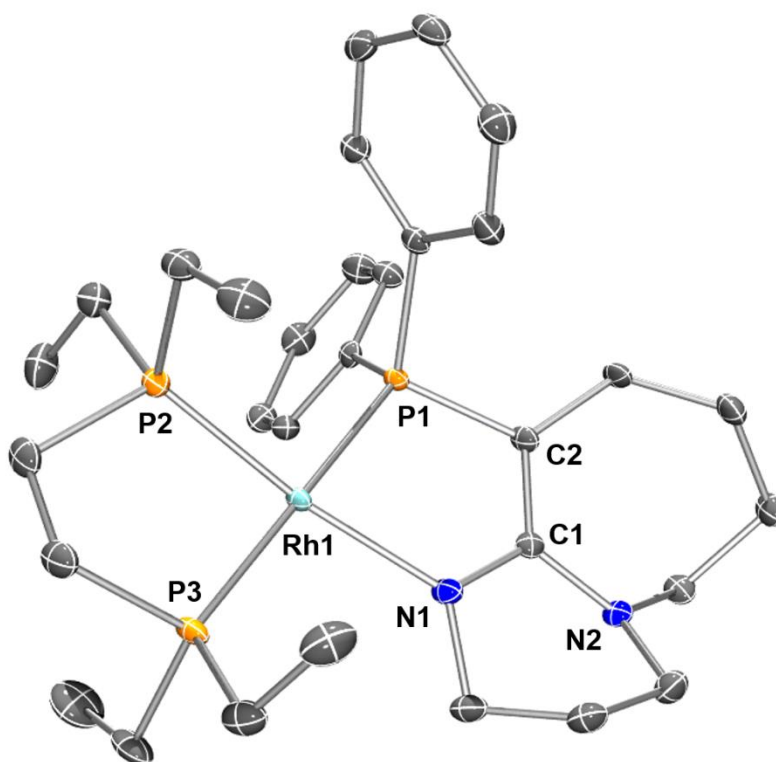


Figure S11: ORTEP plot of compound **4** with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S2: Comparison of selected bond lengths [Å] and angles [°] of the complexes [M(L)(dbuP)] (1-4).

Compound	1 (M = Ir, L = cod)	2a (M = Ir, L = depe)	2b (M = Ir, L = dppe) <sup>a)</sup>	4 (M = Rh, L = depe)
<i>Bond lengths</i>				
M1-P1	2.2859(10)	2.2749(9)	2.285(4)	2.2788(6)
M1-P2	-	2.2060(10)	2.204(3)	2.2058(7)
M1-P3	-	2.2703(10)	2.263(4)	2.2844(7)
M1-N1	2.043(3)	2.072(3)	2.085(11)	2.095(2)
N1-C1	1.385(5)	1.367(4)	1.364(18)	1.362(3)
N2-C1	1.381(5)	1.394(5)	1.406(17)	1.400(3)
C1-C2	1.375(6)	1.398(5)	1.38(2)	1.391(4)
C2-C3	1.529(6)	1.517(5)	1.526(17)	1.528(3)
C2-P1	1.756(4)	1.744(4)	1.754(13)	1.751(3)
<i>Angles</i>				
P1-M1-N1	81.56(9)	80.49(8)	80.7(3)	80.62(6)
P2-M1-N1	-	172.12(9)	178.7(4)	171.57(7)
P3-M1-N1	-	99.42(9)	97.0(3)	99.37(6)
P1-M1-P2	-	95.58(4)	98.69(11)	95.47(2)
P1-M1-P3	-	178.01(4)	176.93(15)	178.23(3)
P2-M1-P3	-	84.74(4)	83.60(14)	84.78(3)
N1-C1-N2	116.3(4)	116.5(3)	115.0(12)	116.1(2)
N1-C1-C2	122.5(3)	122.0(3)	122.9(12)	122.4(2)
N2-C1-C2	121.2(4)	121.5(3)	122.1(12)	121.4(2)
Sum of valence angles around C1	360.0	360.0	360.0	359.9
C1-C2-P1	112.5(3)	111.7(3)	112.3(9)	112.27(19)
C1-C2-C3	127.2(4)	126.1(3)	125.6(12)	126.4(2)
P1-C2-C3	119.8(3)	122.0(3)	121.5(11)	121.1(2)
Sum of valence angles around C2	359.5	359.8	359.4	359.8

a) Data for molecule A of two independent molecules is given.

## Computational Analysis

### Details of DFT calculations

In the present study, we apply density functional theory (DFT) as an electronic structure method to examine the structure and relative stabilities of possible reaction intermediates and relevant transition states. The DFT calculations were performed by using the dispersion-corrected, range-separated hybrid  $\omega$ B97X-D exchange-correlation functional<sup>[S13,S14]</sup> along with a basis set that includes the SDD effective core potential set for the metal atoms extended by *f* polarization functions and the 6-31G(d,p) set for the lighter atoms. For each optimized structure, additional single-point energy calculation was carried out using the same functional but with a larger basis set (two *f* and one *g* functions for metal atoms, and the 6-311++G(2d,p) basis set for lighter atoms).<sup>[S15]</sup> All DFT calculations were carried out with the *Gaussian09* package.<sup>[S16]</sup>

For each located structure, we performed vibrational normal mode analysis to verify the nature of the obtained stationary point (energy minimum or transition state). From transition state structures, we followed intrinsic reaction coordinate (IRC) pathways in both forward and reverse directions, and we identified the related intermediates accordingly. The thermal and entropic contributions were estimated within the ideal gas - rigid rotor - harmonic oscillator (RRHO) approximation usually for  $T = 298.15$  K and  $c = 1$  mol/dm<sup>3</sup> conditions, but in some cases, for lower temperature as well. The solvent effects were taken into account by computing the solvation free energies (using the smaller basis set) via the integral equation formalism variant of the polarizable continuum model (IEFPCM).<sup>[S17]</sup> The atomic radii and non-electrostatic terms in the IEFPCM calculations were those of the SMD solvation model.<sup>[S18]</sup> We used benzene, toluene and diethyl ether as solvents in PCM calculations to model the solvent media used in experiments (benzene and toluene in NMR measurements, diethyl ether in the synthetic reactions). The energetics reported in the paper refers to relative solution-phase standard Gibbs free energies ( $T = 298.15$  K,  $c = 1$  mol/L) with diethyl ether as a solvent. Data obtained for benzene and toluene are given in section "*Free energy data for reaction **2a** + 2CO<sub>2</sub> → **3***" below.

We note that although for the reaction **2a** + 2CO<sub>2</sub> → **3** the present computational approach gives thermodynamic and kinetic data that are in reasonable agreement

with the experimental observations (reversibility, reaction rate, etc.), the computed free energy data by no means can be regarded as accurate predictions.

### Conformational analysis

The conformational space of the species examined in our work is fairly complex (see below), so the identification of the most relevant conformers required special attention. Our conformational analysis thus involved an initial Monte Carlo sampling using the OPLS\_2005 force fields as implemented in the *MacroModel* software.<sup>[S19]</sup> In these calculations, the metal-ligand bond distances were fixed at arbitrarily chosen values since no force field parameters exist for the Ir atom. The Monte Carlo screening was applied not only for reaction intermediates, but also for transition states. Several, at least twenty, structurally distinct conformers were selected for DFT geometry optimizations.

For the **2a** complex, the conformational space was explored via systematic potential energy scan calculations as well. In these calculations, the most stable isomer of **2a** emerging from the conformational search described above was used as an initial structure and various dihedral angles corresponding to different isomerization pathways were varied to map the energy barriers. For each located energy maximum, a transition state was identified computationally. The free energy barriers computed for different types of conformational changes are given in Figure S12.

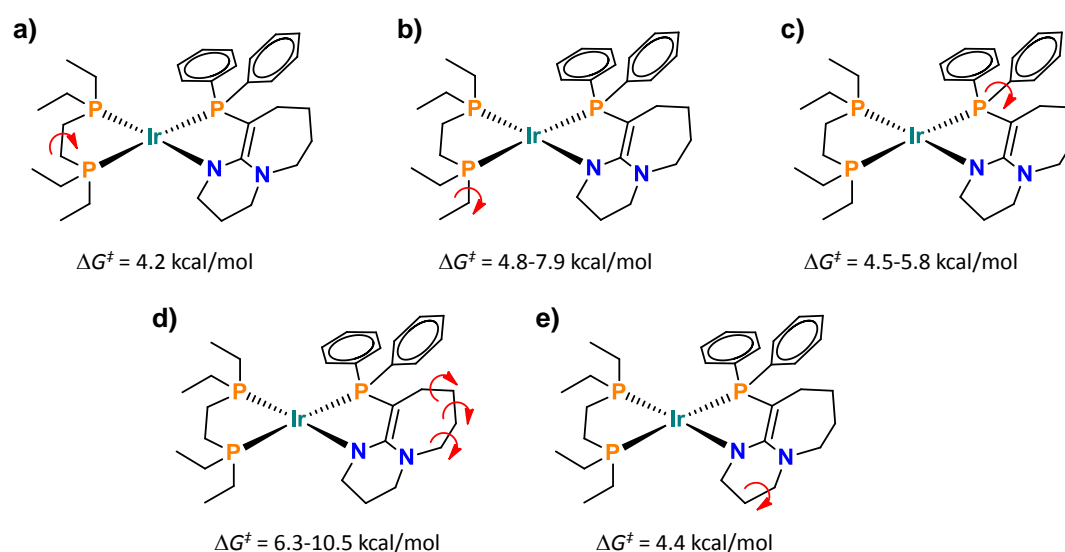


Figure S12: Computed free energy barriers of various conformational changes in complex **2a**: a) rotation along the C-C bond of depe, b) rotation of ethyl groups in depe, c) phenyl rotations in dbuP, d) ring puckering changes in the seven-membered ring, e) ring puckering in the six-membered ring. The barriers are computed with respect to the most stable form of **2a** and the values refer to benzene as a solvent. Dihedral angles varied in the potential energy calculations are indicated by red arrows.



The obtained barriers are all significantly lower than those computed for the mechanistically relevant steps of the reaction cascade revealed for **2a** + 2CO<sub>2</sub> → **3** (see Figure 4 of the paper) suggesting that the conformers of complex **2a** are likely in fast equilibrium in solution. Our calculations suggest that the conformational space becomes more restricted after the uptake of the CO<sub>2</sub> molecules, nevertheless, we carried out extensive conformational analysis for the species involved in the later phase of the reaction as well. In our discussion, we consider only the most stable forms of these species when characterizing the relative stabilities and deriving the entire free energy profile.

The extensive conformational analysis (Monte Carlo screening followed by DFT optimizations) indeed revealed a large number of energetically close lying conformers for each species identified computationally along the reaction pathway. For complex **2a** for instance, we find 9 different isomers within a 2 kcal/mol free energy window that show variations not only in the orientation of the ethyl groups of depe, but also in other structural parameters. For illustration, the first three most stable structures having very similar stabilities are depicted in Figure S13.

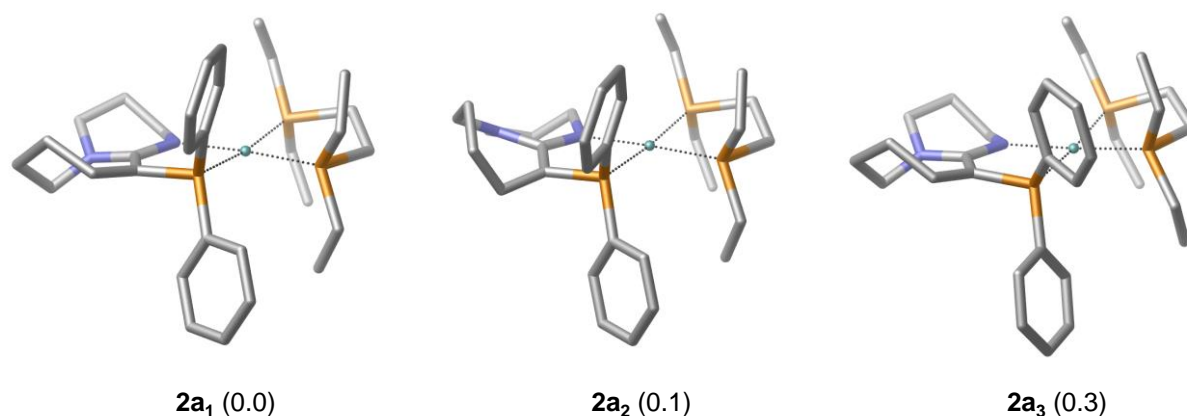


Figure S13: The three most stable forms of complex **2a**. Relative stabilities are shown in parentheses (in kcal/mol).

It is interesting to note that the most stable forms of complex **2a** and the reaction product **3** do not correspond to the X-ray structures. In the case of **2a**, isomer **2a<sub>3</sub>** shown in Figure S13 is analogous to the solid state structure. For product **3**, computations predict the most stable form to be favored by 4.5 kcal/mol suggesting that crystal forces provide substantial stabilization in the solid state. As illustrated in

Figure S14, the two structures differ in the orientation of the coordinated phosphinite anion  $[\text{Ph}_2\text{PO}]^-$ .

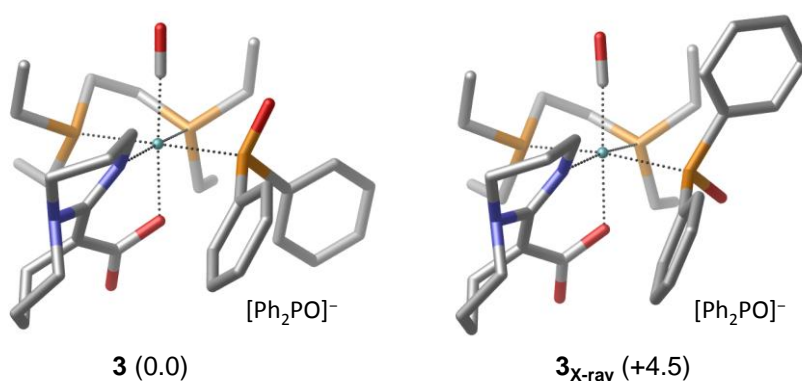


Figure S14: The most stable form of product **3** as obtained from DFT calculations and the optimized structure corresponding to X-ray measurements. Relative stabilities are shown in parentheses (in kcal/mol).

### Free energy data for reaction $2\mathbf{a} + 2\text{CO}_2 \rightarrow \mathbf{3}$

In this section we summarize the results of our test calculations regarding the solvent effects and the variation of temperature (see Table S3). The structures of the most stable forms of reaction intermediates and transition states are shown in Figure S15.

Table S3: Relative Gibbs free energies of species involved in the  $2\mathbf{a} + 2\text{CO}_2 \rightarrow \mathbf{3}$  reaction when using different solvents in PCM calculations.<sup>a</sup>

	benzene	toluene	diethyl ether
<b>2a</b>	0.0 (0.0)	0.0	0.0 (0.0)
<b>TS<sub>1</sub></b>	15.1 (12.3)	15.1	15.7 (13.0)
<b>I<sub>1</sub></b>	3.9 (0.4)	3.7	2.9 (-0.5)
<b>TS<sub>2</sub></b>	14.8 (8.3)	14.6	14.9 (8.4)
<b>I<sub>2</sub></b>	2.8 (-4.0)	2.5	1.9 (-4.9)
<b>TS<sub>3</sub></b>	21.9 (14.5)	21.7	21.9 (14.5)
<b>I<sub>3</sub></b>	16.6 (10.0)	16.4	16.5 (9.9)
<b>TS<sub>4</sub></b>	18.3 (11.7)	18.1	18.1 (11.6)
<b>3</b>	0.2 (-6.4)	0.0	-0.3 (-6.8)

<sup>a</sup> Data refer to T = 298.15 K except for those shown in parentheses, which were obtained for T = 203 K.

It is apparent from these data that the solvent effects are not significant for the solvents used in experiments. On the other hand, the variation of the temperature has a large effect on the relative stabilities of reaction intermediates. Importantly, the

formation of intermediates **I**<sub>1</sub> and **I**<sub>2</sub> become thermodynamically feasible at low temperature (but not at room temperature).

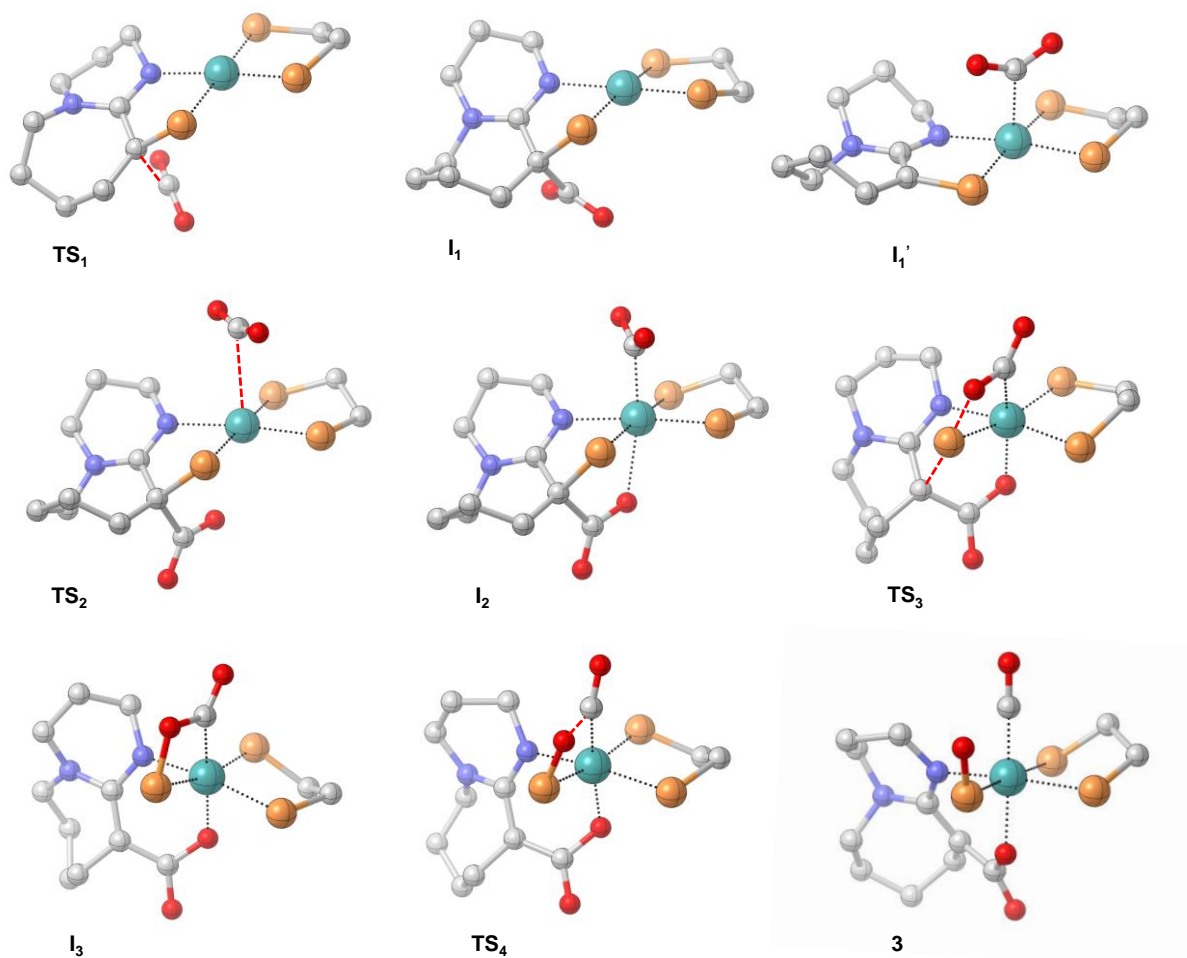


Figure S15: The most stable forms of reaction intermediates and related transition states identified computationally for reaction **2a** + 2CO<sub>2</sub> → **3**.

### Cooperativity of CO<sub>2</sub> molecules

As mentioned in the main text, the fixation of the second CO<sub>2</sub> molecule (that leads to intermediate **I**<sub>2</sub> is found to be thermodynamically favored with respect to both **I**<sub>1</sub> and **I**<sub>1'</sub> species and these data suggest a high degree of cooperativity between the CO<sub>2</sub> molecules (the formation of both **I**<sub>1</sub> and **I**<sub>1'</sub> intermediates is endergonic). The structural changes (bond shortening) observed upon the coordination of the second CO<sub>2</sub> molecule either to **I**<sub>1</sub> or **I**<sub>1'</sub> confirm the cooperativity (the binding with the first CO<sub>2</sub> molecule becomes stronger, see structural data in Figure 4).

To provide further support for the beneficial interaction between the two CO<sub>2</sub> molecules, we performed potential energy scan calculations as illustrated in Figure S16.

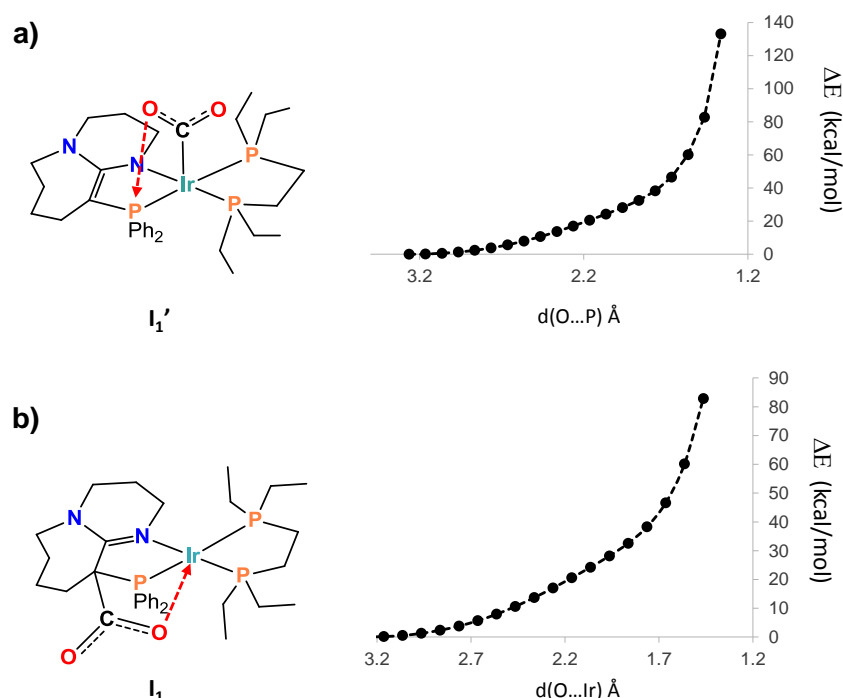


Figure S16: Potential energy scans carried out for complexes **I<sub>1</sub>** and **I<sub>1</sub>'**: a) approach of the CO<sub>2</sub>'s oxygen to the P atom of dbuP<sup>−</sup> in **I<sub>1</sub>'**, b) approach of the CO<sub>2</sub>'s oxygen to the Ir center in **I<sub>1</sub>**. Scanned parameters are indicated by dashed arrows on the schematic views (left); the variation of the electronic energy as a function of bond distances is shown on the right.

The energy profile shown in Figure S16a indicates that the Ir-coordinated CO<sub>2</sub> molecule in **I<sub>1</sub>'** is unable to initiate a nucleophilic substitution at the neighboring Ph<sub>2</sub>P group, because this process requires the assistance of the carboxylate group (as in **I<sub>2</sub>**). On the other hand, the carboxylate group in **I<sub>1</sub>** cannot interact favorably with the Ir center, which lacks the  $\eta^1_{\text{C}}$ -coordinated CO<sub>2</sub>. These results underline the importance of preactivation of the metal complex via the carboxylation of the chelating dbuP<sup>−</sup> moiety, which is then able to bind the second CO<sub>2</sub> and cleave the substrate molecule.

### Results for the reactions of CO<sub>2</sub> with complexes **2b** and **4**

DFT calculations were carried out for the intermediates analogues to **I<sub>2</sub>** in the original reaction and for the product species (analogous to **3**) envisioned for the reactions of CO<sub>2</sub> with [Ir(dppe)(dbuP)] (**2b**) and [Rh(depe)(dbuP)] (**4**) complexes (see Figure S3). For species derived from **2b**, we carried out conformational analysis as described

above, however, for intermediates and the product formed with **4** we assumed structures (isomers) analogous to that obtained with complex **2a**.<sup>[S20]</sup> All these structures were reoptimized and the free energies were derived at the same level of DFT as described in the computational details. The results are collected in Table S4 below. The free energies refer to benzene as a solvent, which was used in NMR measurements at ambient temperature.

Table S4: Relative Gibbs free energies of selected species involved in the reactions of CO<sub>2</sub> with complexes **2a**, **2b** and **4**.<sup>a</sup>

Complex	I <sub>2</sub> type complex		product of <b>3</b> type	
	RT	203 K	RT	203 K
<b>2a</b>	2.8	-4.0	0.2	-6.4
<b>2b</b>	11.0	4.1	9.0	1.8
<b>4</b>	7.0	0.2	19.1	12.3

<sup>a</sup> Relative stabilities are given in kcal/mol with respect to the reactant states of the reactions (e.g. **2a** + 2CO<sub>2</sub>, etc.).

The computations suggest that at room temperature (RT) the product formation is thermodynamically feasible for complex **2a** (close to equilibrium), but for the other two complexes (**2b** and **4**), the overall process is clearly endergonic. At low temperature, the first process becomes exergonic for **2a**, which is not true for the others. The entropic penalty of CO<sub>2</sub> uptake is significantly reduced at low temperature, so the formation of the I<sub>2</sub> type intermediate becomes thermodynamically feasible not only for **2a**, but for **2b** and **4** as well. Considering the uncertainty of free energy predictions by the present computational approach, the computed free energy data are in reasonable agreement with the experimental observations and they reflect the trend in the CO<sub>2</sub> affinity found experimentally (**2b** < **4** < **2a**, see main text).

### Total energy data of the calculated structures

The energy data computed for the geometry optimized structures discussed in the manuscript and the Supporting Information are listed in Table S5 and Table S6. Structure labelling corresponds to that used in the paper and in the present document.

Table S5: Energy data (in a.u.) computed for optimized structures.<sup>a</sup>

<i>structures</i>	$E_0$	$E'_0$	$G_{298.15\text{ K}}^0$	$G_{203\text{ K}}^0$	$G_{\text{benzene}}^{\text{solv}}$	$G_{\text{diethylether}}^{\text{solv}}$
<i>reaction with 2a</i>						
<b>2a</b>	-2447.9398	-2448.3332	-2447.2680	-2447.2353	-2447.9704	-2447.9731
<b>TS<sub>1</sub></b>	-2636.4552	-2636.9103	-2635.7748	-2635.7401	-2636.4844	-2636.4874
<b>I<sub>1</sub></b>	-2636.4766	-2636.9290	-2635.7898	-2635.7562	-2636.5114	-2636.5169
<b>I<sub>1</sub>'</b>	-2636.4660	-2636.9164	-2635.7810	-2635.7474	-2636.5001	-2636.5049
<b>TS<sub>2</sub></b>	-2825.0023	-2825.5160	-2824.3039	-2824.2689	-2825.0351	-2825.0401
<b>I<sub>2</sub></b>	-2825.0251	-2825.5333	-2824.3239	-2824.2894	-2825.0625	-2825.0691
<b>TS<sub>3</sub></b>	-2824.9967	-2825.5066	-2824.2944	-2824.2609	-2825.0314	-2825.0366
<b>I<sub>3</sub></b>	-2824.9976	-2825.5105	-2824.2993	-2824.2645	-2825.0329	-2825.0384
<b>TS<sub>4</sub></b>	-2824.9907	-2825.5061	-2824.2944	-2824.2596	-2825.0257	-2825.0311
<b>3</b>	-2825.0201	-2825.5369	-2824.3214	-2824.2866	-2825.0555	-2825.0615
<i>reaction with 2b</i>						
<b>2b</b>	-3057.4074	-3057.9484	-3056.6468	-3056.6088	-3057.4537	-3057.4566
<b>I<sub>2</sub> (2b)</b>	-3434.4838	-3435.1392	-3433.6927	-3433.6531	-3434.5340	-3434.5391
<b>3 (2b)</b>	-3434.4811	-3435.1444	-3433.6901	-3433.6510	-3434.5293	-3434.5346
<i>reaction with 4</i>						
<b>4</b>	-2454.0888	-2454.4800	-2453.4174	-2453.3847	-2454.1187	-2454.1210
<b>I<sub>2</sub> (4)</b>	-2831.1675	-2831.6745	-2830.4662	-2830.4319	-2831.2033	-2831.2092
<b>3 (4)</b>	-2831.1385	-2831.6547	-2830.4390	-2830.4045	-2831.1732	-2831.1789

<sup>a</sup> Notation:  $E_0$  and  $E'_0$  refer to electronic energies computed with the smaller and the larger basis sets, respectively;  $G_{298.15\text{ K}}^0$  and  $G_{203\text{ K}}^0$  denote gas-phase Gibbs free energies at room temperature and at 203 K, respectively;  $G_{\text{benzene}}^{\text{solv}}$  and  $G_{\text{diethylether}}^{\text{solv}}$  represent solution-phase Gibbs free energies.

Table S6: Free energy data (in a.u.) computed for optimized structures.<sup>a</sup>

<i>structures</i>	$G_{298.15\text{ K}}^{\text{benzene}}$	$G_{203\text{ K}}^{\text{benzene}}$	$G_{298.15\text{ K}}^{\text{diethylether}}$	$G_{203\text{ K}}^{\text{diethylether}}$
<i>reaction with 2a</i>				
<b>2a</b>	-2447.6891	-2447.6576	-2447.6918	-2447.6602
<b>TS<sub>1</sub></b>	-2636.2559	-2636.2225	-2636.2589	-2636.2255
<b>I<sub>1</sub></b>	-2636.2738	-2636.2415	-2636.2793	-2636.2470
<b>I<sub>1</sub>'</b>	-2636.2625	-2636.2300	-2636.2673	-2636.2348
<b>TS<sub>2</sub></b>	-2824.8474	-2824.8136	-2824.8523	-2824.8186
<b>I<sub>2</sub></b>	-2824.8665	-2824.8332	-2824.8731	-2824.8398
<b>TS<sub>3</sub></b>	-2824.8360	-2824.8037	-2824.8413	-2824.8090
<b>I<sub>3</sub></b>	-2824.8445	-2824.8108	-2824.8499	-2824.8163
<b>TS<sub>4</sub></b>	-2824.8418	-2824.8082	-2824.8472	-2824.8136
<b>3</b>	-2824.8705	-2824.8369	-2824.8766	-2824.8429
<i>reaction with 2b</i>				
<b>2b</b>	-3057.2311	-3057.1943	-3057.2340	-3057.1972
<b>I<sub>2</sub> (2b)</b>	-3434.3953	-3434.3569	-3434.4005	-3434.3621
<b>3 (2b)</b>	-3434.3986	-3434.3607	-3434.4038	-3434.3659
<i>reaction with 4</i>				

<b>4</b>	-2453.8355	-2453.8040	-2453.8378	-2453.8063
<b>I<sub>2</sub> (4)</b>	-2831.0061	-2830.9730	-2831.0120	-2830.9789
<b>3 (4)</b>	-2830.9869	-2830.9537	-2830.9926	-2830.9594

<sup>a</sup> Notation: All the columns are obtained as  $G_{\text{TEMP}}^{\text{solv}} = E_0' + (G_{\text{TEMP}}^0 - E_0) + (G^{\text{sol}} - E_0) + \Delta G_{\text{conc}}^{\text{TEMP}}$ , where TEMP denotes the temperature: 298.15 K, or 203 K. The relative stabilities discussed in the manuscript and in the SI are obtained from these values. The value  $\Delta G_{\text{conc}}^{\text{TEMP}}$  corresponds to concentration correction to the free energy when switching from  $p = 1$  atm (ideal gas standard state) to  $c = 1$  mol/dm<sup>3</sup> calculated at the given temperature (standard concentration in solution phase, where  $\Delta G_{\text{conc}}^{298.15\text{K}} = 0.00302$  a.u. and  $\Delta G_{\text{conc}}^{203\text{K}} = 0.00181$ ).

## Cartesian coordinates of the calculated structures

Cartesian coordinates of optimized geometries are given below in standard XYZ format (units are in Å). First line indicates total number of atoms, second line is molecule name (as defined above, see also Table S5).

85

**2a<sub>1</sub>**

```

Ir 0.866686 0.245780 -0.099608
P -1.295735 -0.580312 0.012430
P 2.957600 1.161322 0.069207
P 1.934499 -1.725028 -0.049222
N -0.225659 2.039156 -0.252066
N -2.217528 3.200575 -0.674507
C -1.816629 -1.794694 -1.270828
C -2.327525 0.835284 -0.149326
C -1.586132 2.005633 -0.336943
C 4.190446 -0.165203 0.502946
H 5.198400 0.142159 0.202819
H 4.182200 -0.243666 1.595415
C -1.747474 -1.398062 1.598136
C 0.344622 3.329537 -0.593963
H 0.208706 3.570438 -1.662521
H 1.415060 3.306229 -0.406082
C 3.274185 2.405498 1.404985
H 4.357183 2.469360 1.567402
H 2.953252 3.384588 1.034371
C -2.251927 -1.292295 -2.500559
H -2.356260 -0.216081 -2.614035
C -1.020098 -1.032643 2.737198
H -0.188010 -0.343117 2.617409
C 3.746876 1.994469 -1.385403
H 3.173846 2.908076 -1.574726
H 4.764636 2.301741 -1.115029
C 1.694520 -2.954547 -1.412268
H 2.527803 -3.667815 -1.375603
H 0.784821 -3.516698 -1.187283
C 1.721166 -2.831365 1.421254
H 0.643121 -2.999729 1.520063
H 2.190143 -3.801642 1.216382
C 3.786007 -1.498354 -0.122119
H 4.292053 -2.343861 0.356682
H 4.056991 -1.518177 -1.182967
C -3.813490 0.745212 0.149237
H -3.964471 -0.073693 0.862545
H -4.402598 0.460341 -0.739252
C -1.692577 -3.178364 -1.117487
H -1.366121 -3.590672 -0.166365
C -2.542056 -2.150237 -3.556070
H -2.875991 -1.743629 -4.505951
C -1.784123 4.473160 -0.120070
H -2.400056 4.760512 0.746912
H -1.945397 5.237534 -0.892240
C 2.269096 -2.228833 2.714214

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H	1.906466	-1.204860	2.844922
H	3.364060	-2.201704	2.708554
H	1.955490	-2.814496	3.583070
C	-0.304851	4.415402	0.257510
H	-0.180460	4.137886	1.309325
H	0.163558	5.394081	0.107903
C	2.535193	2.075323	2.701776
H	2.741580	2.827452	3.469313
H	2.837557	1.100069	3.097655
H	1.457273	2.035402	2.520828
C	-2.414238	-2.433217	4.118547
H	-2.668553	-2.840302	5.092522
C	-2.827531	-2.274089	1.745528
H	-3.414799	-2.561578	0.878544
C	-3.536506	3.181174	-1.272213
H	-3.577774	2.317703	-1.942461
H	-3.633501	4.076567	-1.900063
C	-1.346653	-1.547333	3.986362
H	-0.764837	-1.259649	4.857042
C	-3.156039	-2.790977	2.997235
H	-3.995360	-3.473057	3.094049
C	1.569508	-2.315129	-2.792899
H	0.723736	-1.622581	-2.814062
H	1.412339	-3.079428	-3.559854
H	2.468722	-1.748639	-3.058007
C	-1.987148	-4.039712	-2.171320
H	-1.886982	-5.112396	-2.034673
C	-2.407988	-3.527363	-3.395188
H	-2.636052	-4.198322	-4.217662
C	-4.686822	3.108237	-0.266854
H	-5.613582	2.905756	-0.818184
H	-4.825199	4.074748	0.232667
C	-4.428471	2.008514	0.768062
H	-5.368110	1.757484	1.273022
H	-3.745632	2.379301	1.541583
C	3.747994	1.122637	-2.641116
H	2.737249	0.760729	-2.854067
H	4.400887	0.251862	-2.523579
H	4.106647	1.686900	-3.506900

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**2a<sub>2</sub>**

Ir	-0.900386	0.144752	0.036911
P	1.348976	-0.394151	0.175147
P	-3.078307	0.79225	-0.255468
P	-1.661873	-1.920624	-0.38994
N	-0.096728	2.041625	0.49543
N	1.763788	3.503826	0.627268
C	1.83102	-1.609234	1.468057
C	2.128604	1.118684	0.580019
C	1.257057	2.206874	0.568348
C	-4.060044	-0.610924	-0.986233
H	-5.124495	-0.48407	-0.759494
H	-3.943978	-0.529579	-2.07231
C	2.178197	-1.016793	-1.346359
C	-0.869103	3.265691	0.580437
H	-1.906113	3.009112	0.789017
H	-0.858433	3.8374	-0.366333
C	-3.47098	2.159475	-1.440955
H	-4.534207	2.095916	-1.703061
H	-3.329529	3.107763	-0.913625
C	2.010112	-2.972177	1.219323
H	1.970822	-3.346437	0.199893
C	3.438945	-1.623061	-1.333867
H	3.9236	-1.844717	-0.387379
C	-4.09887	1.28723	1.209769
H	-3.684848	2.230768	1.581032
H	-5.123615	1.49541	0.878193
C	-1.37032	-3.295408	0.814201
H	-2.049005	-4.119569	0.559999
H	-0.352633	-3.658728	0.648027
C	-1.156704	-2.76614	-1.958597



H	-0.062083	-2.802451	-1.945375
H	-1.520365	-3.800922	-1.944744
C	-3.524678	-1.955445	-0.500506
H	-3.850611	-2.78015	-1.143767
H	-3.891396	-2.168836	0.508741
C	3.605689	1.241773	0.844789
H	4.014432	0.268574	1.142895
H	3.768644	1.898636	1.711022
C	1.90105	-1.15104	2.787782
H	1.768068	-0.089086	2.977641
C	2.241211	-3.860832	2.266862
H	2.377574	-4.917478	2.056732
C	1.067353	4.574284	1.316451
H	1.008251	5.442145	0.640778
H	1.644516	4.89991	2.196854
C	-1.637682	-2.042537	-3.215785
H	-1.405336	-0.974287	-3.159611
H	-2.720804	-2.143644	-3.343565
H	-1.159146	-2.450562	-4.1108
C	-0.335987	4.144494	1.704602
H	-0.96371	5.025976	1.87137
H	-0.32566	3.553339	2.626524
C	-2.587872	2.12202	-2.688162
H	-2.833853	2.946549	-3.364082
H	-2.715474	1.18567	-3.241398
H	-1.53305	2.193543	-2.407069
C	3.47851	-1.655773	-3.747388
H	3.9813	-1.907749	-4.676148
C	1.586801	-0.722548	-2.57937
H	0.614269	-0.237109	-2.582424
C	3.04674	3.922466	0.071018
H	3.777278	4.115014	0.874843
H	2.863291	4.895715	-0.406886
C	4.0828	-1.943151	-2.526032
H	5.060372	-2.415214	-2.500187
C	2.229063	-1.041079	-3.771434
H	1.752288	-0.810012	-4.719463
C	-1.52993	-2.874854	2.273064
H	-2.5475	-2.528512	2.48376
H	-0.845106	-2.056435	2.509835
H	-1.312505	-3.71259	2.942239
C	2.131862	-2.036597	3.834462
H	2.181558	-1.665854	4.85382
C	2.298675	-3.395777	3.577142
H	2.478082	-4.088211	4.393876
C	3.655715	2.983913	-0.970186
H	4.341399	3.567839	-1.593912
H	2.856046	2.62766	-1.627588
C	4.394309	1.793527	-0.351382
H	5.398201	2.099329	-0.027761
H	4.523216	1.014833	-1.110932
C	-4.080435	0.245669	2.328712
H	-3.04996	-0.012756	2.591442
H	-4.592867	-0.673533	2.027502
H	-4.585248	0.624809	3.222042

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**2a<sub>3</sub>**

Ir	0.857542	0.218866	-0.169924
P	-1.324772	-0.548879	-0.065645
P	2.969847	1.095066	-0.120978
P	1.867614	-1.737626	0.2497
N	-0.197284	2.028165	-0.381954
N	-2.172767	3.27834	-0.455444
C	-2.000853	-1.551418	-1.450121
C	-2.296219	0.910642	0.076403
C	-1.552651	2.052651	-0.234052
C	4.175957	-0.183848	0.496749
H	5.182528	0.038181	0.125234
H	4.201344	-0.080355	1.586353
C	-1.678201	-1.581632	1.412541
C	0.348516	3.272528	-0.890574

H	-0.014181	3.48983	-1.90949
H	1.43164	3.191833	-0.952988
C	3.329708	2.519972	1.005124
H	4.41628	2.603977	1.130192
H	2.99746	3.432629	0.499358
C	-1.243509	-1.692013	-2.615304
H	-0.251422	-1.250624	-2.642827
C	-1.879764	-2.962862	1.369029
H	-1.938349	-3.473331	0.412695
C	3.75617	1.67509	-1.694215
H	3.197005	2.558569	-2.020235
H	4.781375	2.002297	-1.481315
C	1.494296	-3.231845	-0.77892
H	1.920036	-4.124954	-0.306718
H	0.404031	-3.336432	-0.743299
C	1.659948	-2.455634	1.946109
H	0.628368	-2.811834	2.010539
H	2.31056	-3.334511	2.035289
C	3.722927	-1.592238	0.109192
H	4.216207	-2.357212	0.718362
H	3.980361	-1.789974	-0.935351
C	-3.731787	0.86248	0.563354
H	-3.825362	0.013794	1.253183
H	-4.449975	0.651841	-0.247521
C	-3.294376	-2.087153	-1.416206
H	-3.90043	-1.978905	-0.520749
C	-1.755302	-2.371195	-3.718102
H	-1.152357	-2.475569	-4.615309
C	-1.576488	4.521042	0.010762
H	-1.968425	4.805581	1.000215
H	-1.884084	5.308172	-0.68985
C	1.926676	-1.459618	3.073196
H	1.345394	-0.546593	2.914275
H	2.985679	-1.184217	3.12699
H	1.64439	-1.886968	4.039871
C	-0.048347	4.414504	0.039632
H	0.307299	4.170447	1.045963
H	0.404714	5.367116	-0.256289
C	2.621257	2.38847	2.353603
H	2.828591	3.255533	2.988088
H	2.945508	1.492444	2.892483
H	1.540885	2.304082	2.203715
C	-1.913131	-3.061652	3.781216
H	-2.000039	-3.635486	4.698716
C	-1.608752	-0.948627	2.659038
H	-1.454039	0.127207	2.69008
C	-3.574571	3.328132	-0.816542
H	-3.767579	2.484929	-1.485654
H	-3.73803	4.242257	-1.401702
C	-1.996467	-3.698822	2.547728
H	-2.149415	-4.772687	2.498252
C	-1.723836	-1.680888	3.833598
H	-1.661952	-1.176155	4.792975
C	1.959387	-3.113599	-2.231306
H	1.753659	-2.114734	-2.627887
H	1.446212	-3.841721	-2.865638
H	3.034851	-3.2931	-2.323737
C	-3.806748	-2.765879	-2.516532
H	-4.809631	-3.180372	-2.476501
C	-3.036146	-2.912808	-3.668863
H	-3.43698	-3.444935	-4.526315
C	-4.540397	3.277878	0.368341
H	-5.557085	3.151232	-0.024388
H	-4.532063	4.229534	0.913434
C	-4.18612	2.123324	1.313144
H	-5.051268	1.893721	1.945375
H	-3.376531	2.430481	1.986154
C	3.733053	0.617652	-2.797752
H	2.711527	0.259127	-2.957127
H	4.356102	-0.244628	-2.540128
H	4.111057	1.028064	-3.738646

TS<sub>1</sub>

Ir	0.958165	-0.254348	0.184630
P	-1.054129	0.861493	0.054334
P	2.868176	-1.518290	0.143645
P	2.329971	1.503681	-0.015042
N	-0.455673	-1.836913	0.299634
N	-2.658426	-2.609276	0.170256
C	-1.889372	1.151890	1.672764
C	-2.088135	-0.398024	-0.724933
C	-1.724772	-1.624845	-0.058861
C	4.299863	-0.456613	-0.393069
H	5.244241	-0.890100	-0.045982
H	4.309546	-0.486170	-1.487522
C	-1.188999	2.493100	-0.761621
C	-0.209772	-3.123256	0.929352
H	-0.642132	-3.155771	1.943374
H	0.864488	-3.263943	1.036597
C	2.988226	-2.955475	-1.009649
H	4.029102	-3.302412	-1.025937
H	2.389130	-3.763762	-0.575272
C	-1.385869	0.506828	2.808159
H	-0.455262	-0.049275	2.721947
C	-1.043891	3.654303	0.009264
H	-0.987640	3.582260	1.091508
C	3.481727	-2.282148	1.716683
H	2.779482	-3.083071	1.972371
H	4.450509	-2.759049	1.523892
C	2.283988	2.886938	1.212178
H	3.177878	3.507193	1.070695
H	1.422569	3.507445	0.945825
C	2.260591	2.468025	-1.591944
H	1.360997	3.089320	-1.538666
H	3.119418	3.149884	-1.622891
C	4.119926	0.982559	0.090041
H	4.750027	1.678825	-0.473341
H	4.407004	1.067199	1.143382
C	-3.498963	-0.028623	-1.162299
H	-3.392595	0.750357	-1.924996
H	-4.090218	0.429173	-0.352110
C	-3.088751	1.867501	1.780257
H	-3.486366	2.388936	0.914329
C	-2.066857	0.571497	4.021074
H	-1.661880	0.068304	4.894004
C	-2.330741	-4.025296	0.083929
H	-2.790764	-4.467160	-0.811070
H	-2.766570	-4.527852	0.958616
C	2.203706	1.587324	-2.838883
H	1.347183	0.908812	-2.788237
H	3.106413	0.975669	-2.943466
H	2.109049	2.199589	-3.740581
C	-0.819884	-4.227444	0.072649
H	-0.426914	-4.128739	-0.942667
H	-0.573025	-5.225133	0.449340
C	2.480481	-2.635236	-2.415192
H	2.586350	-3.506452	-3.068333
H	3.039839	-1.810966	-2.869833
H	1.426710	-2.349354	-2.386433
C	-1.045986	5.014136	-1.982510
H	-0.986953	5.989040	-2.456577
C	-1.271192	2.612928	-2.151532
H	-1.372051	1.725286	-2.764192
C	-4.030516	-2.254781	0.490879
H	-4.009134	-1.324589	1.066727
H	-4.419763	-3.025349	1.167090
C	-0.968812	4.904377	-0.596143
H	-0.851538	5.792640	0.017123
C	-1.203942	3.866987	-2.754061
H	-1.269927	3.941714	-3.835090
C	2.162636	2.410720	2.657991
H	3.007086	1.776455	2.947295
H	1.250117	1.821880	2.787861

H	2.131973	3.259946	3.347378
C	-3.768420	1.931633	2.992550
H	-4.696126	2.491692	3.061298
C	-3.259960	1.281793	4.115283
H	-3.791079	1.333692	5.060839
C	-4.948229	-2.093097	-0.718146
H	-5.896699	-1.668723	-0.365829
H	-5.183749	-3.070057	-1.156115
C	-4.309870	-1.181885	-1.773039
H	-5.090779	-0.775795	-2.424221
H	-3.655942	-1.780979	-2.414471
C	3.576977	-1.293430	2.878324
H	2.626560	-0.767465	3.011839
H	4.353213	-0.542425	2.701203
H	3.826571	-1.809670	3.809951
C	-1.278360	-1.094016	-2.780919
O	-1.521275	-0.168669	-3.489927
O	-0.901173	-2.207130	-2.609064

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I<sub>1</sub>

Ir	1.008884	-0.240632	0.254842
P	-1.024039	0.784416	0.012599
P	2.890584	-1.499457	-0.054497
P	2.424121	1.492796	0.355774
N	-0.406477	-1.846970	0.166993
N	-2.359585	-2.786159	-0.737445
C	-2.155202	0.590706	1.460630
C	-1.716913	-0.424844	-1.272677
C	-1.483328	-1.764784	-0.582639
C	4.418730	-0.445157	0.081635
H	4.754939	-0.512208	1.122074
H	5.216485	-0.857258	-0.545715
C	-1.332583	2.540090	-0.417242
C	-0.144001	-3.105268	0.851712
H	0.404129	-3.779892	0.176876
H	0.498835	-2.896549	1.707837
C	2.949386	-2.242069	-1.739739
H	3.840169	-2.878128	-1.821217
H	2.064884	-2.885492	-1.807201
C	-1.723611	-0.153852	2.563121
H	-0.716798	-0.563289	2.553862
C	-1.398521	3.026547	-1.724960
H	-1.300747	2.324466	-2.547252
C	3.342633	-2.935322	1.021639
H	2.644082	-3.744036	0.784845
H	4.341064	-3.287512	0.735782
C	2.805356	2.128349	2.050814
H	3.267204	1.297627	2.596350
H	3.551515	2.928658	1.972806
C	2.101230	3.044282	-0.585298
H	1.179724	3.474546	-0.181842
H	2.911229	3.750561	-0.362440
C	4.105807	1.007371	-0.276168
H	4.064846	1.122316	-1.362659
H	4.872182	1.693477	0.100312
C	-3.154169	-0.046832	-1.740856
H	-3.222242	-0.206473	-2.823122
H	-3.264557	1.033520	-1.613231
C	-3.438261	1.149088	1.489413
H	-3.783675	1.754271	0.656718
C	-2.563260	-0.360078	3.655002
H	-2.211213	-0.938828	4.503691
C	-2.289652	-3.995365	0.069833
H	-1.867771	-4.814662	-0.529876
H	-3.312827	-4.279988	0.342257
C	1.952836	2.824314	-2.092202
H	1.231258	2.032456	-2.316400
H	2.907382	2.554990	-2.555915
H	1.605138	3.744924	-2.569813
C	-1.439987	-3.761044	1.301727
H	-1.246371	-4.708616	1.811756

H	-1.958117	-3.094761	2.000472
C	2.898425	-1.205942	-2.864953
H	2.013783	-0.568747	-2.777368
H	2.844283	-1.709608	-3.833049
H	3.794842	-0.575850	-2.866720
C	-1.551700	5.292801	-0.890980
H	-1.632786	6.359428	-1.077208
C	-1.379320	3.449159	0.651196
H	-1.330320	3.089820	1.674492
C	-3.244588	-2.853640	-1.898315
H	-3.398180	-3.913146	-2.125145
H	-2.700800	-2.430610	-2.745966
C	-1.515908	4.396461	-1.953116
H	-1.564792	4.760531	-2.974718
C	-1.481549	4.814616	0.416166
H	-1.509302	5.503964	1.254441
C	1.560570	2.613027	2.794432
H	1.096701	3.460969	2.280759
H	1.811069	2.933836	3.809977
H	0.818145	1.811067	2.856128
C	-4.277924	0.944037	2.578758
H	-5.271881	1.380466	2.581945
C	-3.844186	0.183516	3.662317
H	-4.499591	0.025464	4.513303
C	-4.574465	-2.147188	-1.656457
H	-5.215537	-2.737183	-0.990667
H	-5.096943	-2.067116	-2.617179
C	-4.331396	-0.759282	-1.061313
H	-4.143737	-0.850785	0.011733
H	-5.234878	-0.148585	-1.164453
C	3.287080	-2.605745	2.513937
H	2.317128	-2.175745	2.783403
H	4.050861	-1.872786	2.792078
H	3.454942	-3.500800	3.119991
C	-0.759713	-0.475908	-2.560027
O	-0.610413	-1.623654	-3.016648
O	-0.325368	0.614061	-2.976465

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I<sub>1</sub>'

Ir	-0.814330	0.230218	-0.001930
P	1.373113	-0.583429	-0.111862
P	-2.987974	1.085807	-0.285817
P	-1.885604	-1.797294	0.071305
N	0.253510	2.000368	-0.285346
N	2.224983	3.256479	-0.381760
C	1.953030	-1.792678	1.129688
C	2.374209	0.856882	-0.027458
C	1.621873	2.011618	-0.210976
C	-4.145516	-0.353661	-0.489094
H	-5.166018	-0.039671	-0.246833
H	-4.135813	-0.644313	-1.546665
C	1.769279	-1.368288	-1.730441
C	-0.326130	3.322290	-0.442272
H	-1.403953	3.246981	-0.346052
H	-0.112752	3.742240	-1.440251
C	-3.292503	2.038957	-1.842496
H	-4.357063	1.950747	-2.089733
H	-3.104674	3.097235	-1.636508
C	2.316590	-1.323321	2.396608
H	2.289913	-0.256896	2.590746
C	2.977691	-2.041120	-1.947369
H	3.653041	-2.218867	-1.115389
C	-3.892550	2.057745	0.997515
H	-4.859350	2.343899	0.564407
H	-4.072595	1.342847	1.803233
C	-1.455433	-3.172086	1.223389
H	-2.286461	-3.886364	1.183630
H	-0.586136	-3.674997	0.787555
C	-1.862029	-2.674025	-1.560037
H	-0.807698	-2.889342	-1.763953
H	-2.157838	-1.933028	-2.311692

C	-3.681773	-1.513667	0.389603
H	-4.269771	-2.420017	0.218176
H	-3.751088	-1.242960	1.447301
C	3.866105	0.765885	0.223689
H	4.444232	0.642331	-0.707493
H	4.057386	-0.148354	0.796713
C	1.948674	-3.169492	0.888989
H	1.680414	-3.549158	-0.093000
C	2.661276	-2.219378	3.402570
H	2.933400	-1.843652	4.383716
C	1.725892	4.419060	0.338706
H	1.891861	5.296157	-0.301599
H	2.290204	4.585793	1.269359
C	-2.703480	-3.942068	-1.698326
H	-3.766942	-3.746484	-1.531027
H	-2.388747	-4.715851	-0.992893
H	-2.601093	-4.355352	-2.706041
C	0.235326	4.252699	0.627624
H	-0.264835	5.226856	0.634878
H	0.078497	3.778118	1.601068
C	-2.412401	1.565875	-2.999658
H	-2.556968	0.498286	-3.201250
H	-1.354693	1.717944	-2.763086
H	-2.645672	2.112995	-3.917557
C	2.470799	-2.257122	-4.297296
H	2.741013	-2.606299	-5.289084
C	0.930073	-1.130542	-2.824442
H	-0.000553	-0.589256	-2.671778
C	3.575015	3.348199	-0.898202
H	3.672185	4.318531	-1.402571
H	3.680787	2.581899	-1.671350
C	3.322004	-2.487692	-3.219015
H	4.260066	-3.013362	-3.369290
C	1.275887	-1.571809	-4.098226
H	0.610538	-1.380334	-4.934757
C	-1.152551	-2.785435	2.669122
H	-0.922616	-3.685645	3.246560
H	-1.992153	-2.269434	3.138025
H	-0.288018	-2.121730	2.726517
C	2.288871	-4.064631	1.899310
H	2.278034	-5.131902	1.700107
C	2.644542	-3.590377	3.158597
H	2.909113	-4.287686	3.947579
C	4.680127	3.185537	0.147131
H	4.752409	4.081991	0.774302
H	5.637403	3.097450	-0.381912
C	4.436606	1.948578	1.020115
H	3.728316	2.191141	1.820785
H	5.375067	1.657397	1.505110
C	-3.164866	3.272650	1.566431
H	-3.019471	4.058366	0.818375
H	-2.189765	2.985373	1.966742
H	-3.748024	3.703386	2.385047
C	-0.988540	0.398241	2.133857
O	0.095344	0.705207	2.601263
O	-2.128938	0.216180	2.557488

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**TS<sub>2</sub>**

Ir	-0.900690	-0.203728	0.113540
P	1.153944	0.791876	0.067298
P	-2.883557	-1.357724	-0.143230
P	-2.225875	1.623695	0.058372
N	0.492592	-1.841520	0.005630
N	2.385421	-2.783960	-1.010312
C	1.365357	2.517862	-0.485333
C	2.033296	-0.335270	-1.149558
C	1.612835	-1.719677	-0.676562
C	-4.288571	-0.248918	0.337043
H	-5.242549	-0.636205	-0.034407
H	-4.329525	-0.251876	1.432662
C	2.248703	0.681442	1.547291

C	0.118605	-3.172899	0.466565
H	-0.441708	-3.686217	-0.328562
H	-0.539553	-3.051606	1.325884
C	-3.285368	-2.935161	0.732224
H	-2.601353	-3.693964	0.342208
H	-3.006428	-2.781482	1.778707
C	1.081805	3.524028	0.449252
H	0.886223	3.258591	1.484721
C	3.310063	1.565045	1.766997
H	3.463225	2.408144	1.101146
C	-3.224984	-1.733375	-1.917979
H	-4.255496	-2.090751	-2.030624
H	-3.143051	-0.778063	-2.446680
C	-1.986228	2.819161	-1.330848
H	-2.808834	3.542851	-1.293540
H	-1.066886	3.374090	-1.126364
C	-2.300563	2.719652	1.548150
H	-2.840158	2.147240	2.309300
H	-1.279284	2.802611	1.924365
C	-4.016059	1.158214	-0.189860
H	-4.669245	1.899305	0.281565
H	-4.213435	1.196213	-1.265926
C	3.547829	-0.004393	-1.197557
H	3.686321	1.006939	-0.806461
H	3.813456	0.060094	-2.256606
C	1.635822	2.871623	-1.809575
H	1.874314	2.116638	-2.552365
C	1.047829	4.858479	0.064776
H	0.824332	5.626161	0.799015
C	2.228764	-4.091743	-0.385129
H	3.226055	-4.462835	-0.121238
H	1.797442	-4.793887	-1.111718
C	-2.919551	4.103906	1.361981
H	-3.012317	4.608805	2.328213
H	-3.920424	4.055706	0.919659
H	-2.298712	4.731687	0.716676
C	1.345579	-3.988006	0.840494
H	1.882953	-3.484612	1.652185
H	1.063217	-4.984621	1.189502
C	-4.728873	-3.426094	0.614613
H	-4.842918	-4.387076	1.124749
H	-5.026336	-3.570838	-0.428281
H	-5.433734	-2.726957	1.072977
C	4.008193	0.301491	3.701136
H	4.689418	0.155306	4.533564
C	2.078932	-0.390667	2.431243
H	1.263639	-1.086149	2.270416
C	3.487844	-2.677188	-1.962320
H	3.199694	-1.992409	-2.763375
H	3.611627	-3.663018	-2.421167
C	4.181728	1.376851	2.836126
H	4.999919	2.073651	2.989171
C	2.951980	-0.582054	3.495932
H	2.800609	-1.419696	4.169852
C	-1.905999	2.160998	-2.707591
H	-2.854707	1.685109	-2.982349
H	-1.127283	1.394014	-2.746833
H	-1.692755	2.917196	-3.469118
C	1.596153	4.212149	-2.190373
H	1.800166	4.475154	-3.223283
C	1.296034	5.204171	-1.262974
H	1.261397	6.244891	-1.569747
C	4.776202	-2.208864	-1.288465
H	5.510834	-1.995965	-2.073438
H	5.198912	-3.001909	-0.659901
C	4.501224	-0.949837	-0.460018
H	5.441837	-0.429400	-0.254262
H	4.087301	-1.222034	0.517586
C	-2.216321	-2.717472	-2.513435
H	-2.251587	-3.688061	-2.005184
H	-1.206893	-2.300820	-2.446799
H	-2.437514	-2.892184	-3.569920

C	1.333303	-0.193173	-2.620529
O	2.108722	0.045679	-3.555329
O	0.099052	-0.368098	-2.617843
C	-1.108004	-0.439343	3.012750
O	-1.264300	-1.609340	3.050690
O	-0.961744	0.672297	3.363337

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I<sub>3</sub>

Ir	-0.860690	-0.228947	0.194757
P	1.180164	0.825004	0.109363
P	-2.826750	-1.476388	-0.047415
P	-2.288745	1.581422	0.147419
N	0.557478	-1.831722	0.111361
N	2.433983	-2.728433	-0.958292
C	1.269347	2.543184	-0.479202
C	1.897315	-0.301470	-1.215310
C	1.619245	-1.692115	-0.644628
C	-4.223477	-0.405071	0.506800
H	-5.188518	-0.830089	0.214834
H	-4.174435	-0.389323	1.601558
C	2.413785	0.735929	1.453798
C	0.291548	-3.139303	0.697519
H	-0.260181	-3.750727	-0.032202
H	-0.340763	-2.969711	1.571553
C	-3.113773	-3.064199	0.829309
H	-2.389935	-3.781244	0.433923
H	-2.818344	-2.860453	1.862302
C	1.047004	3.539975	0.481297
H	0.958831	3.266147	1.529606
C	3.530165	1.578634	1.461453
H	3.618649	2.374119	0.728251
C	-3.180949	-1.825454	-1.820369
H	-4.231321	-2.115356	-1.940028
H	-3.023236	-0.883578	-2.355764
C	-2.135356	2.812734	-1.216442
H	-2.962293	3.521389	-1.095565
H	-1.214054	3.372218	-1.035024
C	-2.370642	2.625075	1.662350
H	-2.831004	1.995330	2.429178
H	-1.342938	2.747465	2.005749
C	-4.041811	0.997635	-0.069620
H	-4.727486	1.713885	0.393565
H	-4.259464	0.992419	-1.142434
C	3.355286	0.082714	-1.561892
H	3.490810	1.135380	-1.298846
H	3.444018	0.045222	-2.651926
C	1.379593	2.894288	-1.827083
H	1.543488	2.139738	-2.590009
C	0.929193	4.869809	0.095959
H	0.753905	5.634423	0.846000
C	2.421336	-3.978310	-0.203489
H	3.459683	-4.243488	0.029005
H	2.010093	-4.777086	-0.835653
C	-3.091280	3.965059	1.530563
H	-3.189942	4.427977	2.516508
H	-4.100335	3.864267	1.115400
H	-2.534642	4.658998	0.894170
C	1.597529	-3.827324	1.060755
H	2.135008	-3.217885	1.795201
H	1.412740	-4.807275	1.507536
C	-4.529103	-3.630932	0.720123
H	-4.583745	-4.596905	1.230080
H	-4.830272	-3.790660	-0.320431
H	-5.266251	-2.974121	1.189950
C	4.435761	0.393016	3.354049
H	5.220380	0.258705	4.092238
C	2.307491	-0.266066	2.424452
H	1.427836	-0.896045	2.462920
C	3.382186	-2.659814	-2.065848
H	2.930131	-2.082367	-2.876501
H	3.510442	-3.679562	-2.441806



C	4.536415	1.407119	2.406564
H	5.397894	2.067310	2.400809
C	3.318288	-0.437523	3.363656
H	3.218802	-1.211756	4.117601
C	-2.134974	2.233055	-2.630023
H	-3.097587	1.771527	-2.876957
H	-1.360879	1.473370	-2.753325
H	-1.965922	3.034263	-3.355507
C	1.260929	4.230140	-2.205546
H	1.343400	4.495074	-3.254612
C	1.031989	5.216115	-1.250886
H	0.935152	6.253938	-1.553755
C	4.715963	-2.048604	-1.645108
H	5.309084	-1.871162	-2.549568
H	5.284349	-2.746614	-1.019639
C	4.470147	-0.734863	-0.898785
H	5.389989	-0.142565	-0.877586
H	4.218601	-0.937979	0.147671
C	-2.239017	-2.886890	-2.393242
H	-2.391205	-3.861470	-1.917461
H	-1.199909	-2.574965	-2.258796
H	-2.412467	-3.008611	-3.465516
C	0.914515	-0.217432	-2.472139
O	1.426048	-0.130459	-3.587614
O	-0.315749	-0.280441	-2.172409
C	-0.967575	-0.302911	2.279718
O	-1.336555	-1.411289	2.728028
O	-0.590713	0.712201	2.882312

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**TS<sub>3</sub>**

Ir	0.897620	-0.219868	-0.141746
P	-1.015652	0.942172	-0.704856
P	2.856018	-1.495971	-0.052375
P	2.350555	1.553146	0.158270
N	-0.523314	-1.780047	-0.162079
N	-2.649619	-2.480593	0.584052
C	-1.394744	2.655372	-0.240254
C	-1.729579	-0.376711	1.394844
C	-1.589293	-1.594161	0.623895
C	4.321315	-0.361581	0.084072
H	4.565870	-0.265378	1.147398
H	5.192869	-0.803098	-0.407001
C	-2.543596	0.332949	-1.504517
C	-0.347733	-2.972595	-0.980091
H	0.656067	-3.365980	-0.813496
H	-0.394219	-2.673328	-2.036032
C	3.229314	-2.487173	-1.556689
H	2.333847	-3.063140	-1.800072
H	3.315399	-1.745320	-2.358811
C	-1.462520	3.042932	1.099994
H	-1.327003	2.318330	1.897563
C	-3.794989	0.765008	-1.062118
H	-3.863429	1.455903	-0.228603
C	3.051060	-2.586288	1.413705
H	4.062816	-3.007799	1.425086
H	2.954991	-1.908505	2.268754
C	2.743892	1.965317	1.907101
H	2.885107	1.009658	2.420435
H	3.705962	2.492266	1.896820
C	2.014560	3.153421	-0.674054
H	1.824397	2.919495	-1.726161
H	1.065513	3.519172	-0.272626
C	3.982940	1.007499	-0.511124
H	3.867486	0.938757	-1.598521
H	4.766445	1.738413	-0.290507
C	-3.101735	-0.116045	1.987841
H	-3.855885	-0.356155	1.231842
H	-3.200786	0.950107	2.215473
C	-1.571078	3.604539	-1.254112
H	-1.504823	3.298563	-2.293340
C	-1.691256	4.380009	1.418711

H	-1.736115	4.677484	2.461505
C	-2.716311	-3.397464	-0.544891
H	-2.979499	-2.842810	-1.450583
H	-3.518013	-4.115249	-0.357113
C	3.103135	4.215724	-0.524254
H	4.051079	3.895763	-0.966301
H	3.282925	4.464916	0.525813
H	2.797232	5.134048	-1.032589
C	-1.365084	-4.071400	-0.709368
H	-1.359082	-4.795683	-1.529703
H	-1.114884	-4.607227	0.214846
C	4.446467	-3.406533	-1.473840
H	4.615106	-3.896223	-2.436849
H	5.361697	-2.862772	-1.220467
H	4.305967	-4.190236	-0.723095
C	-4.871637	-0.547291	-2.775282
H	-5.776339	-0.889329	-3.268356
C	-2.465179	-0.519688	-2.607794
H	-1.496257	-0.820280	-2.990278
C	-3.274334	-3.019058	1.803003
H	-3.008040	-4.085679	1.864135
H	-4.364914	-2.970600	1.676385
C	-4.953696	0.323164	-1.691914
H	-5.921055	0.665859	-1.338687
C	-3.625153	-0.960659	-3.237489
H	-3.552273	-1.621601	-4.095803
C	1.678547	2.773936	2.648453
H	0.808935	2.151165	2.871632
H	1.359505	3.656245	2.084373
H	2.086818	3.121838	3.601835
C	-1.798671	4.935695	-0.926692
H	-1.927735	5.670690	-1.714992
C	-1.855704	5.325133	0.410915
H	-2.029404	6.366337	0.665299
C	-2.883471	-2.359168	3.119018
H	-1.792838	-2.379077	3.223683
H	-3.280841	-2.985546	3.925607
C	-3.395996	-0.927568	3.259008
H	-2.906349	-0.453446	4.111822
H	-4.476925	-0.936313	3.449797
C	1.984900	-3.675558	1.519242
H	2.041573	-4.383744	0.685291
H	0.989334	-3.222886	1.534554
H	2.116099	-4.243057	2.444350
C	-0.597462	-0.006377	2.302156
O	-0.822534	0.637395	3.335075
O	0.612853	-0.366991	1.964004
C	0.907754	0.299273	-2.084217
O	1.635974	0.114232	-3.037451
O	-0.176828	1.170573	-2.230233

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I<sub>3</sub>

Ir	0.342656	-0.746731	-0.140815
P	0.896149	1.494464	-0.573652
P	-0.175667	-3.005666	-0.256166
P	2.310468	-1.459160	0.899136
N	-1.598471	-0.242698	-0.698219
N	-3.665989	0.723189	-0.374974
C	2.404203	2.374841	-0.053534
C	-2.180243	0.575803	1.539560
C	-2.450468	0.334852	0.192271
C	0.858273	-3.818186	1.036665
H	0.427068	-3.519976	1.997564
H	0.808300	-4.907699	0.950783
C	-0.294726	2.845208	-0.795247
C	-2.158538	-0.547306	-2.002886
H	-2.988566	-1.270289	-1.922213
H	-1.387336	-0.997485	-2.625296
C	0.224228	-3.973550	-1.767839
H	1.257043	-3.724387	-2.030555
H	0.197496	-5.031600	-1.481173

C	3.593544	2.206513	-0.765521
H	3.601293	1.587270	-1.656319
C	-1.033182	3.310921	0.293890
H	-0.960210	2.811740	1.254215
C	-1.911180	-3.379495	0.182930
H	-2.079767	-2.809973	1.102023
H	-2.536435	-2.913387	-0.583222
C	2.355633	-1.064198	2.692333
H	1.460245	-1.522374	3.118847
H	3.247496	-1.550307	3.106915
C	4.004321	-1.040002	0.323949
H	4.142284	0.028301	0.516618
H	4.704120	-1.573561	0.978535
C	2.298467	-3.312648	0.910271
H	2.747091	-3.663111	-0.025712
H	2.924075	-3.677190	1.731261
C	-3.079449	1.513261	2.309595
H	-3.354923	2.369427	1.679615
H	-2.523309	1.903130	3.166038
C	2.384699	3.197949	1.075958
H	1.462753	3.346296	1.630343
C	4.757616	2.840030	-0.337252
H	5.678669	2.706874	-0.895939
C	-3.674374	1.378281	-1.679596
H	-3.475086	2.455392	-1.575731
H	-4.692542	1.280629	-2.073135
C	4.289682	-1.352487	-1.144061
H	4.194073	-2.420884	-1.360092
H	5.311299	-1.056418	-1.398347
H	3.606763	-0.825562	-1.812612
C	-2.675664	0.729222	-2.650277
H	-1.828026	1.392685	-2.833922
H	-3.146295	0.516977	-3.616624
C	-0.681429	-3.716019	-2.971485
H	-0.471645	-4.448427	-3.755665
H	-0.488111	-2.724502	-3.381602
H	-1.742286	-3.796796	-2.714795
C	-2.055596	4.977835	-1.118441
H	-2.747160	5.804807	-1.246444
C	-0.430858	3.453856	-2.045672
H	0.143322	3.083778	-2.889140
C	-4.944212	0.795222	0.327544
H	-5.694355	0.371812	-0.356014
H	-5.239065	1.845756	0.489791
C	-1.909093	4.380222	0.130038
H	-2.486621	4.732159	0.978636
C	-1.317930	4.513009	-2.205915
H	-1.432719	4.976232	-3.180688
C	2.335426	0.427679	3.009535
H	1.391216	0.864601	2.677249
H	3.166373	0.967020	2.545226
H	2.395701	0.575293	4.090559
C	3.548487	3.827067	1.500955
H	3.526803	4.460194	2.381912
C	4.738103	3.644148	0.798367
H	5.646429	4.135540	1.132388
C	-5.007945	0.044449	1.655420
H	-4.520929	-0.928475	1.530898
H	-6.061140	-0.157949	1.880168
C	-4.355980	0.824336	2.802610
H	-4.102320	0.144101	3.621479
H	-5.061104	1.567045	3.198957
C	-2.244887	-4.861287	0.345795
H	-1.648377	-5.326023	1.136347
H	-2.077708	-5.420893	-0.580110
H	-3.297137	-4.980219	0.617536
C	-1.225753	-0.169188	2.355817
O	-1.163751	-0.011684	3.578577
O	-0.430366	-1.064867	1.780247
C	1.047809	-0.429734	-1.997539
O	1.290465	-1.074725	-2.983542
O	1.272625	1.004664	-2.111864

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TS<sub>4</sub>

Ir	0.479887	-0.666777	-0.276335
P	0.670657	1.570598	-0.952955
P	0.335782	-3.010240	-0.015026
P	2.713229	-0.934590	0.380798
N	-1.598918	-0.549029	-0.495974
N	-3.756929	-0.295534	0.396313
C	1.581008	2.840558	-0.029887
C	-1.931260	0.467947	1.714731
C	-2.379838	-0.139411	0.531696
C	1.843714	-3.504871	0.928399
H	1.680437	-3.218096	1.972363
H	1.991737	-4.588426	0.893559
C	-0.856721	2.425261	-1.468951
C	-2.277033	-1.057097	-1.674020
H	-2.639522	-2.092507	-1.534753
H	-1.565201	-1.076918	-2.501223
C	0.443720	-4.132842	-1.471499
H	1.366690	-3.866767	-1.997302
H	0.575479	-5.149888	-1.083922
C	2.704824	3.427962	-0.615029
H	3.005071	3.116986	-1.611823
C	-1.774752	2.939877	-0.551878
H	-1.594582	2.842968	0.511770
C	-1.118335	-3.527248	0.964559
H	-1.107135	-2.852731	1.827307
H	-1.996762	-3.241246	0.376224
C	3.119930	-0.552902	2.127307
H	2.385433	-1.097649	2.725601
H	4.109920	-0.990540	2.303485
C	4.019537	-0.162465	-0.647034
H	3.844455	-0.498545	-1.674220
H	3.805643	0.910593	-0.650716
C	3.052541	-2.757558	0.344867
H	3.228891	-3.053637	-0.695862
H	3.962164	-2.983997	0.909081
C	-2.818380	1.464778	2.433133
H	-3.297481	2.136195	1.704272
H	-2.151327	2.071178	3.051768
C	1.172179	3.228893	1.249308
H	0.344212	2.729770	1.747421
C	3.421390	4.399261	0.079291
H	4.297453	4.852735	-0.374144
C	-4.449325	-0.233222	-0.879979
H	-5.138704	0.623069	-0.904397
H	-5.061486	-1.140802	-0.992081
C	5.457136	-0.431497	-0.204743
H	5.683811	-1.501924	-0.175772
H	5.654632	-0.014738	0.786683
H	6.156736	0.034297	-0.903826
C	-3.454005	-0.157160	-2.023835
H	-3.088253	0.862652	-2.156362
H	-3.931638	-0.468664	-2.958218
C	-0.733860	-4.078060	-2.440806
H	-0.607893	-4.831067	-3.223190
H	-0.797343	-3.101839	-2.923050
H	-1.684173	-4.276767	-1.935998
C	-3.189383	3.664195	-2.367624
H	-4.099891	4.142489	-2.715672
C	-1.104748	2.543320	-2.837862
H	-0.378666	2.146070	-3.539945
C	-4.528819	-0.782677	1.532677
H	-3.904771	-1.489514	2.094271
H	-5.373049	-1.350385	1.121799
C	-2.940398	3.549468	-1.000446
H	-3.654746	3.935221	-0.279627
C	-2.267619	3.167506	-3.284763
H	-2.454650	3.259749	-4.350214
C	3.073555	0.920293	2.518513
H	2.033488	1.226438	2.637041

H	3.569238	1.572985	1.792260
H	3.569769	1.055852	3.483604
C	1.884406	4.209071	1.931217
H	1.572478	4.498520	2.929411
C	3.008381	4.792349	1.349905
H	3.566798	5.550057	1.891092
C	-5.053005	0.280105	2.498195
H	-5.802930	-0.181883	3.152491
H	-5.568310	1.059352	1.920618
C	-3.931015	0.899595	3.324012
H	-3.501665	0.145799	3.996063
H	-4.341260	1.696233	3.956738
C	-1.167046	-4.998532	1.369806
H	-0.296761	-5.280253	1.970360
H	-1.206499	-5.660467	0.498900
H	-2.058086	-5.193850	1.972425
C	-0.625967	0.239379	2.292087
O	-0.213395	0.842725	3.290631
O	0.141062	-0.719236	1.752875
C	0.986100	-0.623790	-2.163766
O	1.203212	-1.130371	-3.190990
O	1.449291	1.216658	-2.280839

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**3**

Ir	0.343509	-0.411004	-0.545112
P	2.448465	-1.287420	0.061802
P	1.068540	1.857663	-0.748226
P	-0.310612	-2.745222	-0.271291
O	1.632372	2.182705	-2.120288
O	0.047791	-0.043567	1.426396
O	0.809674	-0.802431	-3.499288
O	-0.876956	-0.858439	3.255388
N	-1.639635	0.154286	-0.841387
C	2.321762	2.284911	0.524400
N	-3.906141	0.126758	-0.147394
C	0.650373	-0.635696	-2.372773
C	4.001080	-0.666224	-0.693937
H	4.243369	0.265535	-0.173301
H	4.786990	-1.389926	-0.449134
C	2.434531	-3.117144	-0.346211
H	3.306607	-3.346295	-0.965516
H	2.569226	-3.652604	0.599420
C	-1.012639	-0.551557	2.068801
C	-2.551855	-0.128425	0.109774
C	2.754786	-1.205935	1.866238
H	2.777996	-0.140074	2.104713
H	1.857335	-1.580604	2.365514
C	-0.297802	3.017947	-0.346592
C	1.145567	-3.594727	-1.033573
H	1.058120	-4.683744	-0.976738
H	1.159363	-3.323390	-2.093692
C	-1.800297	-3.356312	-1.149285
H	-1.858131	-4.442093	-1.011985
H	-2.640903	-2.909146	-0.607731
C	-0.461494	-3.511434	1.398249
H	0.123872	-2.923344	2.108875
H	-1.500549	-3.341409	1.691242
C	3.551083	2.749961	0.049944
H	3.690700	2.836955	-1.024004
C	4.028205	-1.895237	2.354274
H	4.926254	-1.423720	1.945604
H	4.058718	-2.959509	2.098706
H	4.085892	-1.821193	3.443237
C	-1.959925	0.880915	-2.070596
H	-1.866367	0.183594	-2.918863
H	-1.220371	1.665585	-2.241556
C	3.916618	-0.424003	-2.200057
H	4.903538	-0.157991	-2.588028
H	3.232270	0.400515	-2.423339
H	3.582715	-1.317386	-2.739523
C	-0.500817	4.075624	-1.235753

H	0.140490	4.151056	-2.109080
C	-2.266938	-0.715051	1.354737
C	-0.114875	-4.997581	1.483548
H	0.950013	-5.185014	1.315667
H	-0.679190	-5.596838	0.761758
H	-0.357865	-5.371333	2.481638
C	-1.121975	2.890988	0.775151
H	-0.991893	2.052103	1.449263
C	4.349925	2.988324	2.313177
H	5.137386	3.259575	3.009998
C	2.105989	2.189477	1.903557
H	1.165925	1.800352	2.278707
C	-3.359016	1.467279	-2.092151
H	-3.622386	1.754037	-3.114815
H	-3.412245	2.362379	-1.461115
C	4.564251	3.095215	0.941588
H	5.517282	3.454637	0.564998
C	-4.269813	0.387192	-1.532718
H	-5.328060	0.654722	-1.569186
H	-4.153067	-0.536065	-2.116362
C	-4.355703	-0.526325	2.879239
H	-4.933476	-1.127911	3.591483
H	-3.783626	0.202073	3.466473
C	-2.327884	4.878721	0.118717
H	-3.116259	5.602527	0.302687
C	-1.516468	5.000390	-1.005954
H	-1.670931	5.817842	-1.703781
C	-1.864762	-2.984999	-2.628451
H	-1.019234	-3.388368	-3.193690
H	-1.872737	-1.900374	-2.753140
H	-2.780077	-3.380585	-3.076487
C	-3.362219	-1.421441	2.127396
H	-3.933802	-2.076034	1.451920
H	-2.864280	-2.055608	2.866231
C	-5.314901	0.192522	1.936734
H	-5.982311	-0.534873	1.456372
H	-5.948675	0.889181	2.499415
C	-2.125528	3.825963	1.009212
H	-2.754666	3.729000	1.889141
C	-4.589295	0.973865	0.845944
H	-3.865534	1.657151	1.305000
H	-5.309079	1.596008	0.303981
C	3.119405	2.541123	2.791087
H	2.946745	2.459201	3.859874

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**2b**

Ir	-0.411852	-0.105128	-0.145715
P	1.445697	1.274068	-0.320414
P	0.617893	-2.029038	0.354066
P	-2.321825	-1.294853	0.232766
N	-1.342926	1.702137	-0.621364
N	-1.326030	3.985645	-1.105928
C	-0.611864	2.847747	-0.741920
C	0.771091	2.883163	-0.552656
C	1.634494	4.120338	-0.388764
H	2.116537	4.428017	-1.331417
H	2.464796	3.865973	0.282073
C	0.904422	5.328267	0.217853
H	0.277434	4.970050	1.043576
H	1.628887	6.026071	0.653077
C	0.035328	6.071774	-0.803389
H	0.650888	6.754293	-1.402762
H	-0.707232	6.692338	-0.287302
C	-0.651580	5.090463	-1.754582
H	-1.389978	5.616678	-2.373436
H	0.086869	4.663244	-2.438941
C	-2.624021	4.269721	-0.508667
H	-3.197164	4.844465	-1.247803
H	-2.521016	4.909821	0.382127
C	-3.361071	2.969527	-0.167297
H	-3.235732	2.703355	0.887157

H	-4.433981	3.074504	-0.360408
C	-2.735256	1.861215	-1.004731
H	-3.270990	0.927571	-0.850064
H	-2.830295	2.111466	-2.074784
C	2.445686	1.341623	1.221634
C	1.949576	2.090832	2.293714
H	1.042348	2.672572	2.148871
C	2.603057	2.090358	3.520716
H	2.209141	2.681674	4.342222
C	3.761655	1.335513	3.695678
H	4.270777	1.331095	4.654634
C	4.263371	0.588508	2.635101
H	5.164547	-0.003213	2.763908
C	3.610934	0.594625	1.404899
H	4.015626	0.018532	0.578723
C	2.697693	0.967943	-1.626643
C	2.370663	0.113145	-2.681722
H	1.416436	-0.404778	-2.659861
C	3.258894	-0.083171	-3.734480
H	2.996724	-0.763568	-4.538643
C	4.484480	0.575665	-3.745166
H	5.181374	0.418494	-4.563088
C	4.815989	1.438848	-2.702939
H	5.768870	1.959771	-2.709198
C	3.926728	1.636671	-1.651869
H	4.194148	2.307835	-0.840411
C	-0.620081	-3.427398	0.423190
H	-0.843996	-3.748411	-0.599228
H	-0.207461	-4.282647	0.965163
C	-1.884567	-2.885596	1.087751
H	-1.690011	-2.641910	2.138029
H	-2.708683	-3.603264	1.053936
C	1.902999	-2.677288	-0.789365
C	1.505019	-3.145803	-2.046584
H	0.449302	-3.185073	-2.301599
C	2.447965	-3.528324	-2.993149
H	2.121272	-3.894480	-3.961781
C	3.807316	-3.425940	-2.706215
H	4.544792	-3.710996	-3.449891
C	4.214248	-2.946017	-1.466493
H	5.271383	-2.852082	-1.238634
C	3.268365	-2.579979	-0.512579
H	3.597029	-2.214343	0.454829
C	1.371794	-2.219202	2.025065
C	1.135082	-1.224497	2.975025
H	0.585788	-0.337462	2.672363
C	1.618306	-1.356205	4.274200
H	1.441489	-0.564268	4.994784
C	2.343010	-2.486379	4.636066
H	2.726504	-2.588074	5.646861
C	2.578655	-3.490108	3.697605
H	3.142008	-4.375436	3.976606
C	2.091401	-3.359349	2.402156
H	2.283547	-4.144344	1.675136
C	-3.278776	-1.878556	-1.221533
C	-2.898017	-1.414432	-2.484447
H	-2.071173	-0.710811	-2.554009
C	-3.562450	-1.853964	-3.626687
H	-3.258472	-1.486356	-4.601759
C	-4.610603	-2.762796	-3.517350
H	-5.128025	-3.106742	-4.407687
C	-4.995645	-3.233779	-2.263491
H	-5.812342	-3.943528	-2.175238
C	-4.332007	-2.795256	-1.122586
H	-4.645388	-3.162496	-0.148718
C	-3.548110	-0.511520	1.351200
C	-3.047766	0.008869	2.551434
H	-1.990327	-0.099891	2.778982
C	-3.882307	0.691892	3.427528
H	-3.481286	1.089695	4.354530
C	-5.224856	0.882934	3.105961
H	-5.874961	1.427444	3.783709

C	-5.726011	0.383388	1.908769
H	-6.768291	0.538238	1.647506
C	-4.893168	-0.313506	1.035598
H	-5.293246	-0.685109	0.097639

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**l<sub>2</sub> (2b)**

Ir	-0.240707	0.138549	-0.320966
P	2.018371	0.125670	0.145138
P	-2.589787	0.290293	-0.648284
P	-0.707843	-2.082966	-0.790680
N	0.174854	2.163745	0.216767
N	1.208671	3.641952	1.707740
C	2.872739	-1.403212	0.638833
C	1.905559	1.244796	1.654345
C	1.059125	2.415402	1.150159
C	-3.128049	-1.165792	-1.700191
H	-3.793932	-1.775917	-1.084155
H	-3.704704	-0.793347	-2.549912
C	3.234449	1.002346	-0.907291
C	-0.636828	3.266956	-0.287415
H	-1.521893	3.384509	0.353442
H	-0.954245	2.986176	-1.291050
C	-3.334475	1.734693	-1.496959
C	3.476794	-2.156917	-0.375706
H	3.439261	-1.812183	-1.404478
C	2.795966	1.990040	-1.796299
H	1.737301	2.142033	-1.975628
C	-3.627080	0.159485	0.854017
C	-1.683005	-2.972181	0.493527
C	0.512840	-3.356888	-1.284360
C	-1.938509	-2.012389	-2.168069
H	-1.416091	-1.550241	-3.007225
H	-2.264174	-3.011168	-2.468692
C	3.300781	1.534555	2.255463
H	3.966975	0.723536	1.950161
H	3.207544	1.434567	3.341116
C	2.898902	-1.873948	1.954874
H	2.446993	-1.309422	2.763161
C	4.126175	-3.345762	-0.071924
H	4.587298	-3.920633	-0.867433
C	0.654063	4.844786	1.093683
H	1.434364	5.615382	1.096773
H	-0.176935	5.213170	1.710765
C	0.176164	4.549210	-0.313395
H	1.029481	4.416927	-0.987470
H	-0.424706	5.380602	-0.689833
C	5.085977	2.577507	-2.295017
H	5.803552	3.189064	-2.833399
C	4.610007	0.801602	-0.736132
H	4.970810	0.030763	-0.063574
C	1.914196	3.840915	2.970260
H	1.702542	2.993536	3.627463
H	1.475138	4.723176	3.445986
C	3.721218	2.771579	-2.482058
H	3.365088	3.525265	-3.177094
C	5.528746	1.585223	-1.424888
H	6.591423	1.418356	-1.279842
C	3.538877	-3.075735	2.248320
H	3.558643	-3.430459	3.273787
C	4.158283	-3.807579	1.241226
H	4.661834	-4.739995	1.477209
C	3.417858	4.008006	2.769783
H	3.896620	3.987608	3.755646
H	3.644799	4.982211	2.321576
C	3.951678	2.873860	1.891011
H	5.036769	2.792894	2.006682
H	3.777605	3.102971	0.834395
C	0.930150	0.519688	2.672999
O	1.206977	0.550576	3.870107
O	-0.083849	-0.004790	2.116789
C	0.059778	0.482977	-2.358598



O	-0.272298	1.619096	-2.741877
O	0.587886	-0.440538	-3.004062
C	-4.044746	2.699305	-0.776107
C	-4.562650	3.818609	-1.420142
C	-4.380699	3.981389	-2.790270
C	-3.677286	3.022312	-3.513632
C	-3.152277	1.905941	-2.872465
H	-4.196670	2.579028	0.291738
H	-5.113261	4.559914	-0.849396
H	-4.785469	4.854144	-3.293474
H	-3.521572	3.147268	-4.580175
H	-2.560469	1.197108	-3.439453
C	-4.971872	-0.219774	0.766763
C	-5.754461	-0.299421	1.911597
C	-5.204487	0.011426	3.154351
C	-3.874449	0.405644	3.244642
C	-3.084794	0.481596	2.099033
H	-5.417472	-0.443013	-0.198578
H	-6.794221	-0.601383	1.834740
H	-5.815862	-0.054512	4.049195
H	-3.436588	0.642672	4.209070
H	-2.033464	0.737295	2.183978
C	0.814239	-4.407777	-0.411641
C	1.678879	-5.422802	-0.806871
C	2.251037	-5.399187	-2.074792
C	1.973675	-4.342262	-2.937667
C	1.113288	-3.320126	-2.548355
H	0.373419	-4.441291	0.578470
H	1.905763	-6.230551	-0.118261
H	2.918252	-6.197566	-2.386306
H	2.427542	-4.309073	-3.923387
H	0.923995	-2.473621	-3.198319
C	-2.441137	-4.097244	0.136041
C	-3.229404	-4.747090	1.075886
C	-3.267649	-4.285484	2.391602
C	-2.503120	-3.185923	2.758180
C	-1.708919	-2.531018	1.816800
H	-2.407132	-4.481022	-0.879390
H	-3.813995	-5.613861	0.783332
H	-3.890409	-4.788184	3.125392
H	-2.523955	-2.818676	3.779204
H	-1.120198	-1.669915	2.116880

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### 3 (2b)

Ir	0.102268	-0.079953	-0.524907
P	1.990546	-1.428453	0.048631
P	1.334758	1.917686	-0.949782
P	-1.197629	-2.143322	-0.173121
O	1.798684	2.002524	-2.395805
O	0.004553	0.540311	1.395694
O	0.287030	-0.862821	-3.435219
O	-1.025823	0.467237	3.334757
N	-1.646052	0.989808	-0.858682
C	2.782307	2.082692	0.158412
N	-3.794624	1.716157	-0.153647
C	0.241206	-0.551243	-2.331076
C	3.210825	-1.731320	-1.281398
C	1.290870	-3.113769	0.416175
H	2.067100	-3.875281	0.321226
H	0.991558	-3.104830	1.468699
C	-1.132367	0.537648	2.105784
C	-2.562996	1.103363	0.121972
C	2.971856	-1.086051	1.549684
C	0.325472	3.399392	-0.558311
C	0.093715	-3.436134	-0.482510
H	-0.301309	-4.433748	-0.271336
H	0.399381	-3.399881	-1.533844
C	-2.483620	-2.347024	-1.443099
C	-1.959524	-2.746456	1.373112
C	4.032318	2.176448	-0.458115
H	4.084564	2.139562	-1.541759

C	-1.823503	1.575426	-2.187872
H	-2.052572	0.759237	-2.892274
H	-0.884568	2.024723	-2.522180
C	0.225497	4.357368	-1.569777
H	0.729268	4.170180	-2.513399
C	-2.407842	0.615785	1.429628
C	-0.316338	3.618690	0.663643
H	-0.265815	2.872730	1.446828
C	5.086338	2.423438	1.694551
H	5.981364	2.554200	2.295685
C	2.691716	2.152700	1.552500
H	1.732248	2.028888	2.041525
C	-2.946733	2.591597	-2.255074
H	-3.162644	2.830825	-3.301028
H	-2.662594	3.517524	-1.741247
C	5.182545	2.339819	0.309358
H	6.150841	2.412492	-0.176834
C	-4.128929	1.947515	-1.553422
H	-5.035098	2.555472	-1.594878
H	-4.360819	0.990904	-2.036798
C	-4.302532	1.524042	2.946387
H	-5.002169	1.181355	3.718657
H	-3.535075	2.122612	3.451559
C	-1.145334	5.738765	-0.145544
H	-1.717035	6.647444	0.017934
C	-0.511300	5.521580	-1.365364
H	-0.586006	6.259543	-2.158385
C	-3.617676	0.319973	2.290624
H	-4.370111	-0.221475	1.697736
H	-3.283036	-0.360288	3.077735
C	-5.053147	2.377694	1.930041
H	-5.909319	1.818212	1.530371
H	-5.453630	3.278702	2.411440
C	-1.040763	4.788214	0.868273
H	-1.530458	4.953214	1.823390
C	-4.170390	2.809392	0.762510
H	-3.264592	3.289800	1.147876
H	-4.697383	3.562945	0.168485
C	3.841212	2.331406	2.312483
H	3.765319	2.376256	3.394013
C	4.368001	-1.093881	1.522048
C	5.089873	-0.923771	2.699717
C	4.426484	-0.743151	3.908072
C	3.034741	-0.702429	3.934314
C	2.305828	-0.864468	2.763033
H	4.899241	-1.218188	0.585407
H	6.174578	-0.925281	2.665641
H	4.992801	-0.613540	4.825284
H	2.506121	-0.521977	4.864604
H	1.229707	-0.734972	2.789529
C	4.007149	-2.885785	-1.274229
C	4.953645	-3.098954	-2.268392
C	5.122664	-2.158315	-3.282485
C	4.347448	-1.005235	-3.289413
C	3.396190	-0.786550	-2.295405
H	3.915974	-3.616950	-0.477463
H	5.561676	-3.997703	-2.248345
H	5.860643	-2.325709	-4.060773
H	4.472629	-0.262073	-4.069916
H	2.815442	0.132712	-2.333725
C	-1.353250	-2.457612	2.597984
C	-1.886137	-2.952547	3.782698
C	-3.028535	-3.744943	3.756085
C	-3.635819	-4.042472	2.538851
C	-3.105349	-3.550140	1.351630
H	-0.495537	-1.801404	2.646271
H	-1.417156	-2.688550	4.724115
H	-3.451970	-4.122113	4.681566
H	-4.529887	-4.657256	2.510889
H	-3.592048	-3.787193	0.411687
C	-2.280731	-3.095962	-2.604360
C	-3.268792	-3.154660	-3.584234

C	-4.468298	-2.473905	-3.407855
C	-4.678375	-1.729675	-2.248802
C	-3.690777	-1.656239	-1.274086
H	-1.355453	-3.640143	-2.759903
H	-3.098136	-3.737474	-4.483504
H	-5.239135	-2.523630	-4.170206
H	-5.613468	-1.198553	-2.101532
H	-3.857069	-1.064886	-0.378493

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Rh	0.943263	0.287333	-0.125749
P	-1.194594	-0.577701	0.010489
P	3.021834	1.230945	0.057736
P	2.037627	-1.669959	-0.121545
N	-0.178001	2.071436	-0.230943
N	-2.195319	3.181693	-0.682446
C	-1.733124	-1.814433	-1.245484
C	-2.249837	0.819396	-0.140645
C	-1.531156	2.008040	-0.330524
C	4.268261	-0.089782	0.472236
H	5.277901	0.233022	0.193817
H	4.247167	-0.196757	1.562444
C	-1.596363	-1.390574	1.614015
C	0.370606	3.366182	-0.586331
H	0.249286	3.589889	-1.661433
H	1.438845	3.368776	-0.379735
C	3.310008	2.450690	1.422360
H	4.387126	2.506329	1.622576
H	3.005586	3.437696	1.058790
C	-2.225166	-1.334636	-2.463031
H	-2.359015	-0.262060	-2.580996
C	-0.852016	-0.990304	2.730394
H	-0.043899	-0.277317	2.583646
C	3.811637	2.104448	-1.372665
H	3.232320	3.018413	-1.540294
H	4.826554	2.412418	-1.092225
C	1.803438	-2.855968	-1.521843
H	2.645155	-3.560207	-1.519672
H	0.901290	-3.435110	-1.309805
C	1.844060	-2.815290	1.320747
H	0.768302	-2.991938	1.427827
H	2.315996	-3.776860	1.083648
C	3.884899	-1.411929	-0.191251
H	4.408567	-2.262600	0.259368
H	4.152678	-1.395013	-1.253104
C	-3.729947	0.701067	0.181204
H	-3.853059	-0.109543	0.909764
H	-4.325575	0.388452	-0.693892
C	-1.573810	-3.194640	-1.086226
H	-1.204146	-3.591835	-0.144412
C	-2.536116	-2.208757	-3.499496
H	-2.915080	-1.818183	-4.439221
C	-1.786782	4.477682	-0.165147
H	-2.418850	4.783706	0.683745
H	-1.948051	5.215490	-0.963154
C	2.404106	-2.249995	2.625575
H	2.027034	-1.238698	2.803982
H	3.498164	-2.205432	2.604343
H	2.112802	-2.872626	3.476161
C	-0.313226	4.455297	0.234969
H	-0.200519	4.199545	1.293707
H	0.137646	5.440676	0.075045
C	2.524273	2.100844	2.686454
H	2.706348	2.837236	3.475155
H	2.808955	1.117012	3.074920
H	1.453063	2.071366	2.466096
C	-2.170707	-2.409720	4.165112
H	-2.389051	-2.810414	5.150380
C	-2.647605	-2.293817	1.801192
H	-3.248628	-2.608429	0.953253
C	-3.515690	3.120925	-1.274059

H	-3.539813	2.244097	-1.927687
H	-3.637386	4.002638	-1.916899
C	-1.132031	-1.496471	3.994356
H	-0.536908	-1.180990	4.846291
C	-2.930182	-2.802404	3.067508
H	-3.748088	-3.505297	3.194578
C	1.657560	-2.166835	-2.876799
H	0.805077	-1.481874	-2.863636
H	1.497044	-2.903842	-3.669234
H	2.549633	-1.584821	-3.132185
C	-1.889562	-4.072290	-2.120235
H	-1.762162	-5.141333	-1.977434
C	-2.366944	-3.581102	-3.332167
H	-2.612087	-4.264694	-4.139205
C	-4.658404	3.037391	-0.260719
H	-5.583717	2.805037	-0.802686
H	-4.816005	4.007815	0.225429
C	-4.367087	1.959262	0.787957
H	-5.296551	1.694864	1.304904
H	-3.686112	2.356783	1.549779
C	3.824108	1.266779	-2.651412
H	2.817117	0.904746	-2.881444
H	4.482594	0.397579	-2.555408
H	4.182642	1.856791	-3.499909

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**I<sub>2</sub> (4)**

Rh	-0.924337	-0.266739	0.245011
P	1.083457	0.827392	0.128659
P	-2.859579	-1.559531	-0.002472
P	-2.400474	1.514896	0.144592
N	0.541195	-1.834333	0.167688
N	2.388572	-2.705555	-0.973740
C	1.144763	2.546560	-0.465404
C	1.820251	-0.284336	-1.193660
C	1.573884	-1.679299	-0.621790
C	-4.297671	-0.511112	0.489701
H	-5.245684	-0.964014	0.182950
H	-4.282735	-0.465401	1.584737
C	2.332280	0.768517	1.464959
C	0.304118	-3.153797	0.734162
H	-0.251444	-3.763106	0.004828
H	-0.317860	-3.014884	1.620012
H	-2.372529	-3.838343	0.552864
H	-2.911939	-2.916190	1.936931
C	0.896755	3.542454	0.490514
H	0.804494	3.269615	1.538869
C	3.422557	1.644858	1.477915
H	3.485511	2.447884	0.750402
C	-3.160680	-1.943709	-1.778250
H	-4.203056	-2.251186	-1.923407
H	-2.998752	-1.009137	-2.324816
C	-2.249892	2.751861	-1.215835
H	-3.090603	3.445770	-1.103746
H	-1.340867	3.326214	-1.019912
C	-2.554786	2.562541	1.653588
H	-2.998712	1.917242	2.417568
H	-1.538296	2.737486	2.008439
C	-4.130018	0.880580	-0.117021
H	-4.851769	1.590844	0.298743
H	-4.305954	0.840690	-1.196734
C	3.272199	0.128111	-1.537610
H	3.396655	1.177119	-1.255677
H	3.355874	0.110833	-2.628620
C	1.259094	2.898327	-1.813062
H	1.441390	2.145549	-2.573691
C	0.759680	4.869541	0.102271
H	0.565812	5.632350	0.849686
C	2.419959	-3.958949	-0.225278
H	3.468600	-4.205186	-0.019066
H	2.009855	-4.762887	-0.851621
C	-3.332543	3.869352	1.508382

H	-3.469610	4.327074	2.492226
H	-4.328087	3.723621	1.074812
H	-2.795665	4.587740	0.882552
C	1.625613	-3.832843	1.060829
H	2.174318	-3.225321	1.788764
H	1.463887	-4.820414	1.500118
C	-4.528116	-3.762192	0.719313
H	-4.580154	-4.714471	1.254878
H	-4.759242	-3.962442	-0.331880
H	-5.315195	-3.119096	1.122743
C	4.369361	0.475592	3.361430
H	5.159521	0.360761	4.096973
C	2.262276	-0.243055	2.429201
H	1.407900	-0.907672	2.456676
C	3.326044	-2.605797	-2.087649
H	2.860604	-2.019485	-2.884195
H	3.464268	-3.617157	-2.482608
C	4.435643	1.498184	2.420283
H	5.276374	2.184696	2.416717
C	3.278700	-0.389921	3.366341
H	3.206469	-1.174184	4.113146
C	-2.222418	2.180529	-2.632815
H	-3.179901	1.719613	-2.899905
H	-1.444271	1.423538	-2.748105
H	-2.042752	2.988167	-3.348637
C	1.119375	4.231398	-2.194894
H	1.204697	4.495434	-3.244017
C	0.866529	5.215455	-1.244438
H	0.754179	6.250908	-1.550143
C	4.655967	-1.985415	-1.666054
H	5.239779	-1.784798	-2.571748
H	5.238348	-2.686994	-1.057440
C	4.400861	-0.687077	-0.895654
H	5.314390	-0.085056	-0.871209
H	4.158723	-0.909603	0.149404
C	-2.186883	-2.998846	-2.307421
H	-2.333693	-3.967589	-1.817703
H	-1.157203	-2.665527	-2.153128
H	-2.331186	-3.142516	-3.381310
C	0.835158	-0.217253	-2.455672
O	1.353817	-0.112513	-3.568549
O	-0.388544	-0.305904	-2.155261
C	-1.023043	-0.308154	2.335541
O	-1.355273	-1.423737	2.759376
O	-0.683226	0.737225	2.886339

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### 3 (4)

Rh	0.360270	-0.426876	-0.590504
P	2.453086	-1.341644	0.005085
P	1.092993	1.813658	-0.779475
P	-0.316032	-2.766729	-0.342153
O	1.629446	2.134898	-2.163263
O	0.099125	-0.063646	1.368711
O	0.815265	-0.773368	-3.558046
O	-0.798545	-0.936109	3.182419
N	-1.610817	0.131912	-0.897491
C	2.374316	2.220222	0.469289
N	-3.865056	0.134552	-0.165481
C	0.663098	-0.626137	-2.433755
C	4.023719	-0.735046	-0.730028
H	4.280008	0.184223	-0.194353
H	4.797031	-1.475300	-0.494440
C	2.421444	-3.162871	-0.437931
H	3.292488	-3.388103	-1.060476
H	2.550825	-3.716656	0.497758
C	-0.949297	-0.595972	2.004423
C	-2.508894	-0.140622	0.067649
C	2.749352	-1.290051	1.812822
H	2.810251	-0.227236	2.058612
H	1.833757	-1.631480	2.303060
C	-0.261838	2.975224	-0.349748

C	1.127924	-3.614442	-1.132370
H	1.033136	-4.704173	-1.102819
H	1.141836	-3.318025	-2.185858
C	-1.811002	-3.359299	-1.227617
H	-1.879928	-4.445910	-1.101213
H	-2.649289	-2.909575	-0.684654
C	-0.464659	-3.578963	1.307466
H	0.121698	-3.010851	2.033571
H	-1.503064	-3.411610	1.605141
C	3.598288	2.678006	-0.026896
H	3.720536	2.768167	-1.102541
C	3.993421	-2.028128	2.305781
H	4.911502	-1.594910	1.898838
H	3.981679	-3.093604	2.054171
H	4.050269	-1.953310	3.394832
C	-1.936849	0.879486	-2.110509
H	-1.869064	0.192651	-2.970275
H	-1.187092	1.654148	-2.284354
C	3.950837	-0.468492	-2.232660
H	4.941693	-0.204717	-2.612252
H	3.274261	0.364398	-2.448722
H	3.613043	-1.351244	-2.787456
C	-0.476394	4.035229	-1.234083
H	0.146416	4.108881	-2.120741
C	-2.213352	-0.743247	1.303795
C	-0.126342	-5.068650	1.357176
H	0.937109	-5.258834	1.182825
H	-0.695283	-5.647200	0.622178
H	-0.369474	-5.465154	2.346577
C	-1.062466	2.851715	0.789055
H	-0.923161	2.009230	1.456474
C	4.439893	2.902228	2.222211
H	5.242040	3.165299	2.905236
C	2.182848	2.120975	1.851816
H	1.246473	1.737599	2.241484
C	-3.326785	1.489724	-2.103577
H	-3.602353	1.793201	-3.118324
H	-3.355434	2.377733	-1.460832
C	4.629614	3.013279	0.847234
H	5.577846	3.367880	0.454423
C	-4.245867	0.417362	-1.541767
H	-5.300083	0.702312	-1.558806
H	-4.153011	-0.500438	-2.138300
C	-4.281838	-0.555961	2.857944
H	-4.856231	-1.162208	3.569065
H	-3.696734	0.159714	3.448153
C	-2.267761	4.849226	0.160831
H	-3.046875	5.578264	0.362579
C	-1.480196	4.966735	-0.981123
H	-1.643745	5.786111	-1.674550
C	-1.870129	-2.974825	-2.703618
H	-1.030234	-3.386085	-3.272007
H	-1.863817	-1.889019	-2.818799
H	-2.790482	-3.353771	-3.156029
C	-3.304906	-1.449291	2.082458
H	-3.890553	-2.092620	1.408045
H	-2.801475	-2.094401	2.807932
C	-5.245913	0.184346	1.937248
H	-5.925611	-0.530237	1.454866
H	-5.866582	0.878838	2.517104
C	-2.053809	3.793824	1.045357
H	-2.665177	3.699472	1.937928
C	-4.525592	0.974030	0.848900
H	-3.788514	1.641858	1.309255
H	-5.245055	1.612723	0.325961
C	3.215480	2.461703	2.721238
H	3.062238	2.376769	3.792706

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