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Supporting Information

Facile C=O Bond Splitting of Carbon Dioxide Induced by Metal–Ligand Cooperativity in a Phosphinine Iron(0) Complex

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The supporting information contains:

S1 Experimental Section

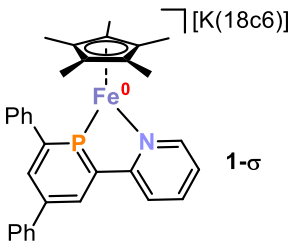
S1.1 General experimental details

All experiments were performed under an atmosphere of dry argon using standard glovebox and Schlenk line techniques. Tetrahydrofuran, toluene and *n*-hexane were purified, dried, and degassed using an MBraun SPS800 solvent purification system. 1,4-Dioxane and 1,2-dimethoxyethane were dried over potassium and distilled under inert gas atmosphere. Deuterated tetrahydrofurane was purchased from Sigma Aldrich and used as received. [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** were synthesized according to literature procedures.[1][2] CO_2 (purity 4.8) was purchased from Linde Gas and used as received.

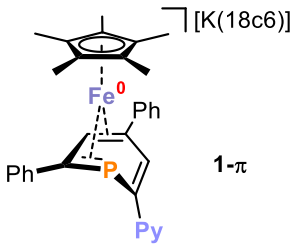
NMR spectra were recorded on Bruker Avance 300 and Avance 400 spectrometers at 300 K K and a Bruker Avance III HD 600 MHz spectrometer with a fluorine selective TBIF probe at 273 K. ^{1}H and $^{13}C\{^{1}H\}$ spectra were referenced internally to residual solvent resonances, while $^{31}P\{^{1}H\}$ and ^{31}P spectra were referenced externally to 85% $H_3PO_{4\,(aq.)}$. The assignment of ^{1}H and ^{13}C NMR signals was confirmed by two-dimensional (COSY, HSQC, and HMBC) experiments. Solid state ^{31}P MAS-NMR spectra were recorded with a Bruker 400 MHz spectrometer. UV/vis spectra were recorded using a Varian Cary 50 spectrometer. Elemental analyses were determined by the analytical department of the University of Regensburg. IR spectra were recorded using a Bruker ALPHA spectrometer equipped with a diamond ATR unit.

Single-crystal X-ray diffraction data were recorded on an Agilent Technologies SuperNova diffractometer with Cu-K_α radiation (λ = 1.54184 Å). Either semi-empirical multi-scan absorption corrections[3] or analytical ones[4] were applied to the data. The structures were solved with SHELXT[5] and least-square refinements on F^2 were carried out with SHELXL.[6] The hydrogen atoms were located in idealized positions and refined isotropically with a riding model. CCDC 1942537 (for **1-σ**), 1942538 (for **2**), 1942550 (for **3-σ**), and 1942542 (for **3-π**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

S1.2 Synthesis of 1



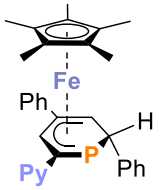
1-σ



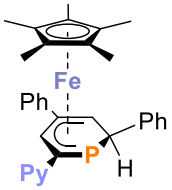
1-π

A solution of **L** (200 mg, 0.62 mmol, 1 eq.) in 1,2-dimethoxyethane (4 mL) was added dropwise to a solution of [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] (383 mg, 0.62 mmol, 1 eq.) in 1,2-dimethoxyethane (8 mL) at −35 °C. The orange/brown reaction mixture turned into a deep green suspension. After stirring overnight and warming up to room temperature a deep purple suspension was formed. The suspension was layered with *n*-hexane (16 mL) and stored at −35 °C over two days. Product **1** could be isolated as dark purple solid after decanting off the supernatant solution and drying under vacuum. Crystals suitable for single-crystal XRD were grown by slow diffusion of *n*-hexane into a 1,2-dimethoxyethane solution of **1**. Yield 350 mg, 68%. Elemental analysis calcd. for $C_{44}H_{55}FeKNO_6P$ (Mw = 819.84 g·mol^{-1}) C 64.46, H 6.76,

N 1.71; found C 63.27, H 6.69, N 1.54. UV-Vis: (THF, λ_{max} / nm, ε_{max} / L·mol^{-1}·cm^{-1}): 310 (sh, 16553), 500 (3708). ^{1}H NMR (400.13 MHz, 300 K, [D$_8$]THF): δ = 1.23 (s, 15H, C$_5$(C*H*$_3$)$_5$), 3.25 (s, 24H, [18]crown-6), 6.20−10.45 (m, 16H signals for **L** of **1-σ** and **1-π**). ^{13}C{^{1}H} NMR (100.61 MHz, 300 K, [D$_8$]THF): δ = 11.0 (s, C$_5$(*C*H$_3$)$_5$), 12.6 (s), 12.8 (s), 70.9 (bs, [18]crown-6), 72.6 (s), 78.7 (s), 80.9 (s, *C*$_5$(CH$_3$)$_5$), 105.3 (s), 109.6 (s), 111.7 (s), 116.1 (s), 117.0 (s), 122.1 (s), 123.5 (s), 125.00 (s), 125.3 (s), 125.7 (bs), 126.4 (s), 127.4 (s), 127.5 (s), 128.5 (s), 128.8 (s), 130.3 (d, *J* = 6 Hz), 132.0 (m), 133.8 (s), 144.1 (s), 147.5 (s), 148.7 (s), 158.5 (s).



endo-4

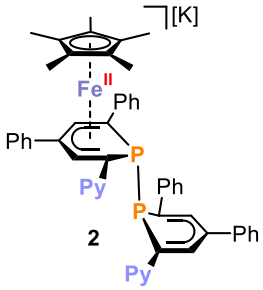


exo-4

^{31}P{^{1}H} NMR (161.98 MHz, 300 K, [D$_8$]THF): δ = 131.7 (s, **1-σ**), −44.8 (bs, **1-π**). ^{31}P NMR (161.98 MHz, 300 K, [D$_8$]THF): δ = 130.7 (t, $^{3}J_{PH}$ = 12 Hz, **1-σ**), −46.2 (bs, **1-π**).

NMR spectroscopy and elemental analysis consistently indicate the presence of persistent, minor impurities in samples of **1** prepared in the above manner. Specifically, ^{31}P{^{1}H} NMR analysis indicates the presence of side-products **endo-4** and **exo-4** (typically *ca.* 8%), which are presumed to arise from protonation of **1** by adventitious moisture.[7]

S1.3 Synthesis of 2



2

Py = pyridyl

A solution of **L** (100 mg, 0.31 mmol, 2 eq.) in toluene (2 mL) was added dropwise to a solution of [K([18]crown-6)][Cp*Fe(C$_{10}$H$_8$)] (96 mg, 0.15 mmol, 1 eq.) in tetrahydrofuran (0.5 mL) at −35 °C. A colour change from orange brown to wine red was observed. After stirring for 5 hours and warming to room temperature the brown reaction mixture was layered with *n*-hexane (6 mL) and stored at −35 °C overnight. Product **2** was isolated as a dark brown solid after decanting off the supernatant solution and drying under vacuum. Crystals suitable for single-crystal XRD were grown from slow diffusion of *n*-hexane into a 1,2-dimethoxyethane solution of **2**. Yield 126 mg, 72%. Elemental analysis calcd. for C$_{66}$H$_{71}$FeKN$_2$O$_6$P$_2$ (Mw = 1145.19g·mol^{-1}) C 69.22, H 6.25, N 2.45; found C 69.60, H 6.26, N 2.28. UV-Vis: (THF, λ_{max} / nm, ε_{max} / L·mol^{-1}·cm^{-1}): 250 (40598), 280 (39399), 510 (8023). ^{1}H NMR (400.13 MHz, 300 K, [D$_8$]THF): δ = 0.90 (s, 15H, C$_5$(C*H*$_3$)$_5$), 3.25 (s, 44H, [18]crown-6), 5.87 (m, 1H), 6.17 (m, 2H) 6.51 7.44 (m, 40H), 7.74 8.00 (m, 10H), 8.34 (m, 1H). ^{13}C{^{1}H} NMR (100.61 MHz, 300 K, [D$_8$]THF): δ = 8.9 (s, C$_5$(*C*H$_3$)$_5$), 71.6 (bs, [18]crown-6), 84.3 (d, 1.66 Hz), 85.2 (m), 85.6 (m), 94.74 (s), 94.7 (s), 112.6 (s) 113.5 (s), 113.9 (s), 117.8 (s), 119.4 (m), 120.6 (s), 120.8 (s), 122.5 (s), 122.6 (s), 123.7 (m), 125.0 (m), 125.2 (m), 125.4 (m), 125.5 (s), 125.9 (s), 126.4 (s), 126.7 (m), 127.5 (s), 127.7 (s), 128.5 (s), 128.5 (s), 128.6 (s), 128.8 (s), 129.3 (s), 129.5 (s), 131.8 (m), 133.3 (s), 133.6 (s), 133.8 (s), 134.5 (s), 134.8 (s), 135.0 (s), 138.3 (s), 143.0 (s), 143.2 (s), 146.1 (s), 148.4 (s), 148,5 (s), 162.5 (s), 162.8 (s), 164.9 (s), 165.2 (s). ^{31}P{^{1}H} NMR (161.98 MHz, 300 K, [D$_8$]THF): δ = −24.31 (AB, $^{1}J_{PP}$ = 262 Hz), −42.09 (AB, $^{1}J_{PP}$ = 262 Hz), −25.27 (AB, $^{1}J_{PP}$ = 257 Hz), −41.69 (AB, $^{1}J_{PP}$ = 257 Hz). ^{31}P NMR (161.98 MHz, 300 K, [D$_8$]THF): δ = −24.31 (AB, $^{1}J_{PP}$ = 262 Hz), −42.09 (AB, $^{1}J_{PP}$ = 262 Hz), −25.27 (AB, $^{1}J_{PP}$ = 257 Hz), −41.69 (AB, $^{1}J_{PP}$ = 257 Hz).

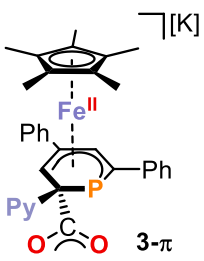
As for compound **1**, samples of **2** prepared in the above manner were found to contain trace impurities, and specifically side-products **endo-4** and **exo-4** (typically *ca.* 1%).[7]

S1.4 Synthesis of 3-σ and 3-π

*Stoichiometric conversion of **1** and CO_2 leads also to **3-σ** and **3-π**, but leads also to more hydrolysis side products **endo-4** and **exo-4**, due to opening of the reaction vessel and adding CO_2 via syringe. It is advisable to keep the reaction mixture in a closed system.*

A sealed vessel containing a solution of **1** (100 mg, 0.122 mmol) in tetrahydrofuran (3 mL) was charged with CO_2 (1 atm). An immediate colour change from purple to deep green was observed, and the reaction mixture was stirred for 30 minutes at room temperature. The solvent was removed under vacuum, and the resulting green oil was washed with *n*-hexane (3 x 2 mL). The remaining residue was extracted with toluene (3 mL), layered with *n*-hexane (6 mL), and stored at room temperature for 7 days. The mother liquor was then decanted from the resulting orange powder.

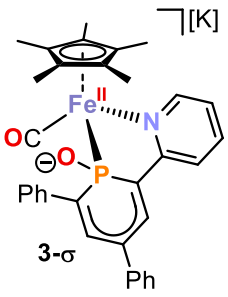
Isolation of 3-π: A small amount of orange powder was isolated and dried under vacuum to give **3-π**. This sample was used for spectroscopic characterization The ^{1}H NMR spectrum of **3-π** isolated in this manner shows minor impurities with signals at 1.13 ppm and 3.86 ppm, which is believed to account for deviations in the elemental analysis. Crystals suitable for single-crystal XRD were grown by slow diffusion of *n*-hexane into a 1,4-dioxane solution of **3-π**.



3-π

Elemental analysis calcd. for $C_{45}H_{55}FeKNO_8P$ (Mw = 863.85 g·mol^{-1}) C 62.57, H 6.42, N 1.62; found C 59.77, H 6.12, N 1.31. UV-Vis: (THF, λ_{max} / nm, ε_{max} / L·mol^{-1}·cm^{-1}): 334sh (9494). ^{1}H NMR (400.13 MHz, 300 K, [D$_8$]THF): δ = 1.28 (s, 15H, $C_5(CH_3)_5$), 3.29 (s, 24H, [18]crown-6), 6.62 (s, 1H, $PC_5H_2Ph_2Py$), 6.96−7.74 (m, 8H, $PC_5H_2Ph_2Py$), 7.91 (m, 2H, $PC_5H_2Ph_2Py$), 8.09 (m, 3H, $PC_5H_2Ph_2Py$), 8.52 (m, 1H, $PC_5H_2Ph_2Py$). ^{13}C{^{1}H} NMR (100.61 MHz, 300 K, [D$_8$]THF): δ = 9.5 (s, $C_5(CH_3)_5$), 70.7 (s, [18]crown-6), 90.9 (s, $C_5(CH_3)_5$), 111.8 (s), 115.7. (s), 121.3 (s), 123.0 (s), 123.7 (s), 125.6 (s), 127.8 (s), 127.8 (s), 128.0 (s), 131.2 (s), 133.6 (s), 157.2 (s). ^{31}P{^{1}H} NMR (161.98 MHz, 300 K, [D$_8$]THF): δ = −116.6 (s). ^{31}P NMR (161.98 MHz, 300 K, [D$_8$]THF): δ = −116.6 (s).

Isolation of 3-σ: The decanted mother liquor was evaporated to dryness, and the remaining residue was extracted into tetrahydrofuran (3 mL) and layered with *n*-hexane (6 mL). Dark green crystals of **3-σ** were isolated after standing at room temperature for 6 days, filtering, and drying under vacuum. Crystals suitable for single-crystal XRD were grown from slow diffusion of *n*-hexane into a 1,4-dioxane solution of **3-σ**. Yield: 16 mg, 15%.



Elemental analysis calcd. for $C_{45}H_{55}FeKNO_8P$ (Mw = 863.85 g·mol^{-1}) C 62.57, H 6.42, N 1.62; found C 62.57, H 6.31, N 1.60. UV-Vis: (THF, λ_{max} / nm, ε_{max} / L·mol^{-1}·cm^{-1}): 270 (sh, 16070), 340 (13458), 417 (15900), 620 (9617). ATR-IR: $\tilde{\nu}$ (CO) = 1876 cm^{-1}. ^{1}H NMR (400.13 MHz, 300 K, [D$_8$]THF): δ = 1.24 (s, 15H, $C_5(CH_3)_5$), 3.38 (s, 24H, [18]crown-6), 6.02 (m, 1H, pyridyl-*H*), 6.75 (m, 1H, pyridyl-*H*), 6.88 (m, 1H, pyridyl-*H*), 6.99 (m, 2H, phenyl-*H*), 7.12 (m, 4H, phenyl-*H*), 7.28 (m, 2H, phenyl-*H*), 7.40 (m, 2H, phenyl-*H*), 8.00 (bd, 1H, pyridyl-*H*, $^{4}J_{PH'}$ = 5 Hz), 8.23 (bd, 2H, $^{3,5}H$ of PC_5H_2, $^{3}J_{PH'}$ = 7 Hz). ^{13}C{^{1}H} NMR (100.61 MHz, 300 K, [D$_8$]THF): δ = 9.5 (s, $C_5(CH_3)_5$), 70.7 (s, [18]crown-6), 90.9 (s, $C_5(CH_3)_5$), 111.8 (s, pyridyl-*C*H), 115.7. (s,$^{2,6}C$ of PC_5H_2), 121.8 (s, pyridyl-*C*H), 123.0 (s, pyridyl-*C*H), 123.7 (s, phenyl-*C*H), 125.6 (s, phenyl-*C*H), 127.8 (s, $^{3,5}C$H of PC_5H_2), 127.8 (s, $^{3,5}C$H of PC_5H_2), 128.0 (s, phenyl-*C*H), 128.4 (s, phenyl-*C*H), 131.2 (s, phenyl-*C*H), 133.6 (s, phenyl-*C*H), 146.8 (s, phenyl-*C*), 147.8 (phenyl-*C*), 157.2 (s, pyridyl-*C*H), 170.7 (s, *C*O). ^{31}P{^{1}H} NMR (161.98 MHz, 300 K, [D$_8$]THF): δ = 97.9 (s). ^{31}P NMR (161.98 MHz, 300 K, [D$_8$]THF): δ = 96.9 (t, $^{3}J_{PH}$ = 17 Hz).

S2 NMR Spectra

S2.1 NMR spectra of compounds 1-σ and 1-π

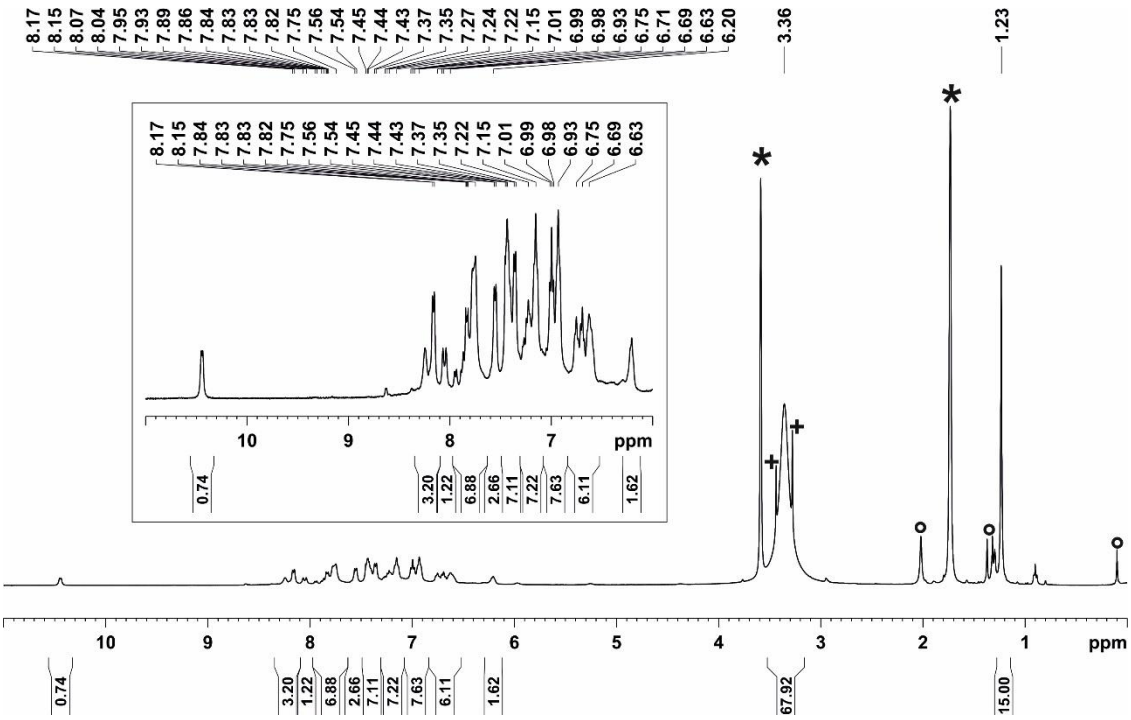


Figure S1 - ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of **1-σ** and **1-π** (* = [D_8]THF, + = 1,2-dimethoxy ethane, ° = unidentified impurities).

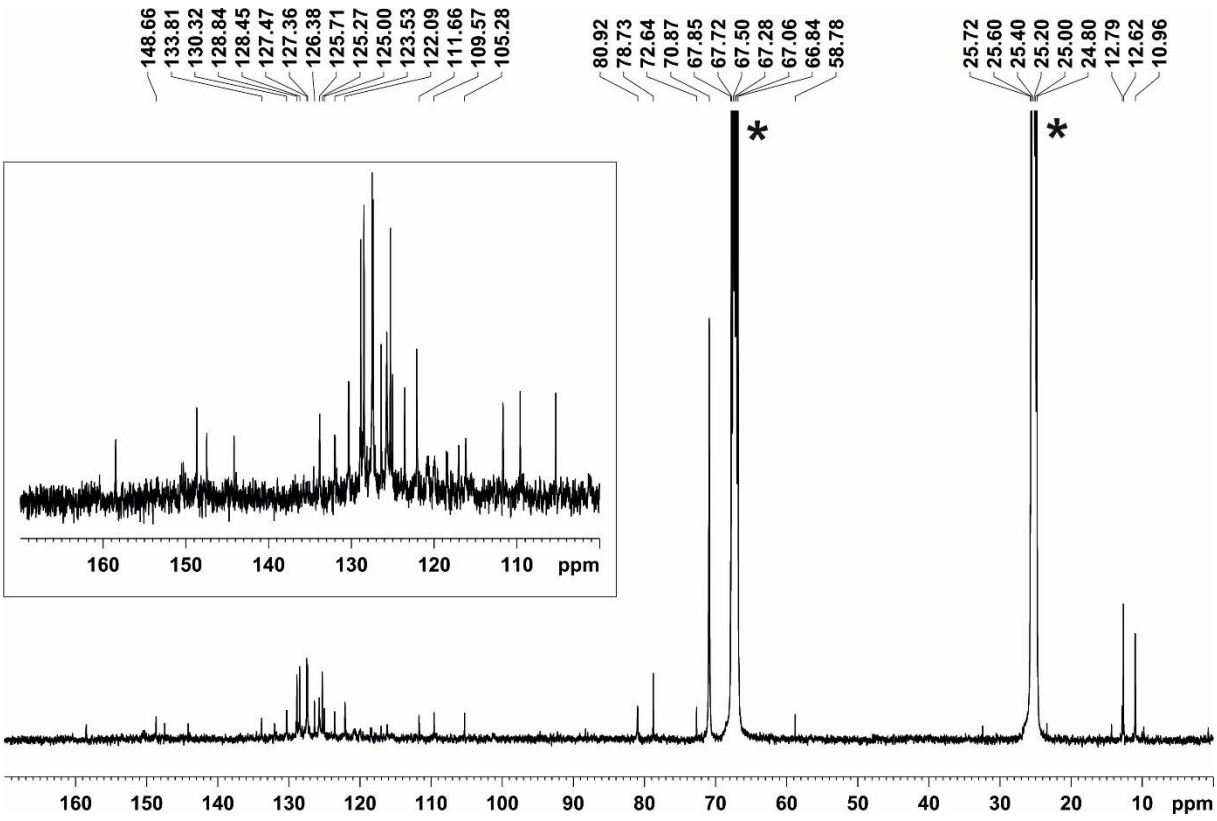


Figure S2 - ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of **1-σ** and **1-π** (* = [D_8]THF).

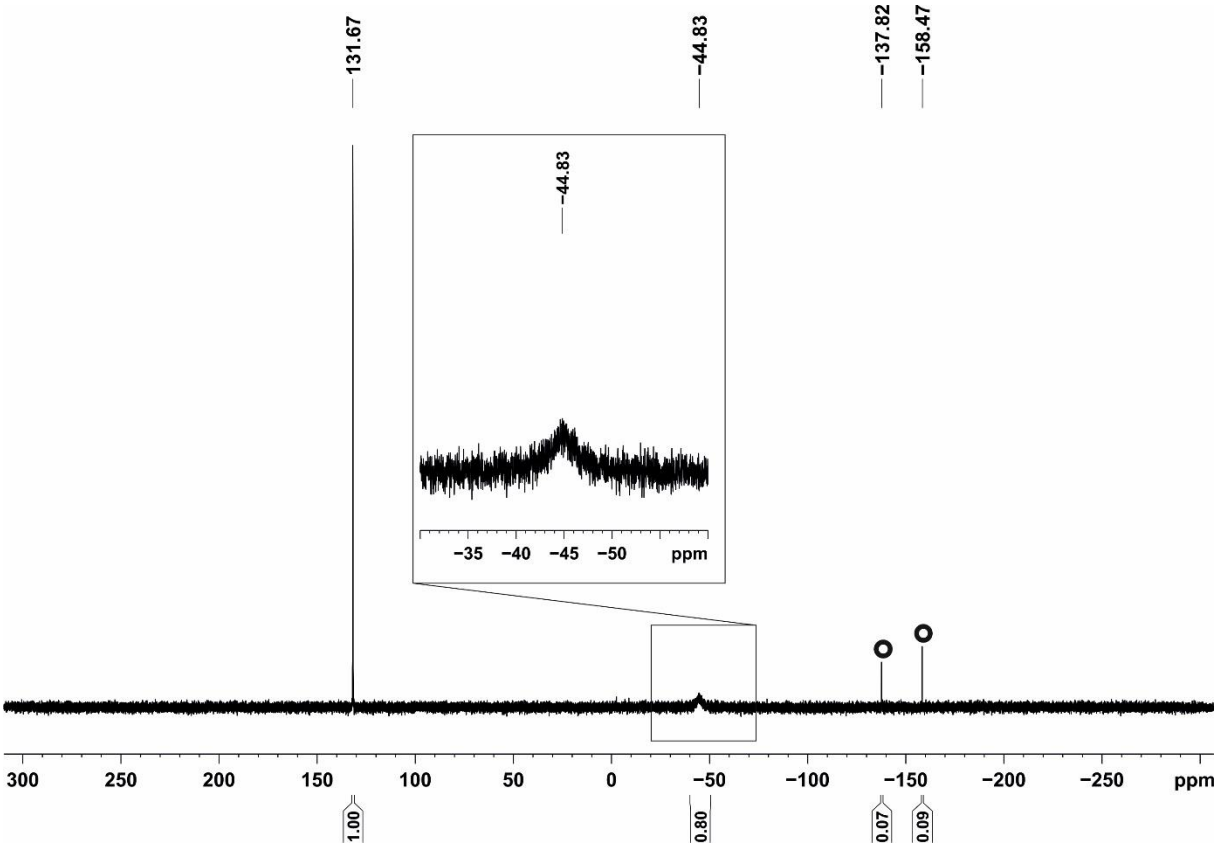


Figure S3 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **1-σ** and **1-π** (° = hydrophosphinine iron complexes **endo-4** and **exo-4**).

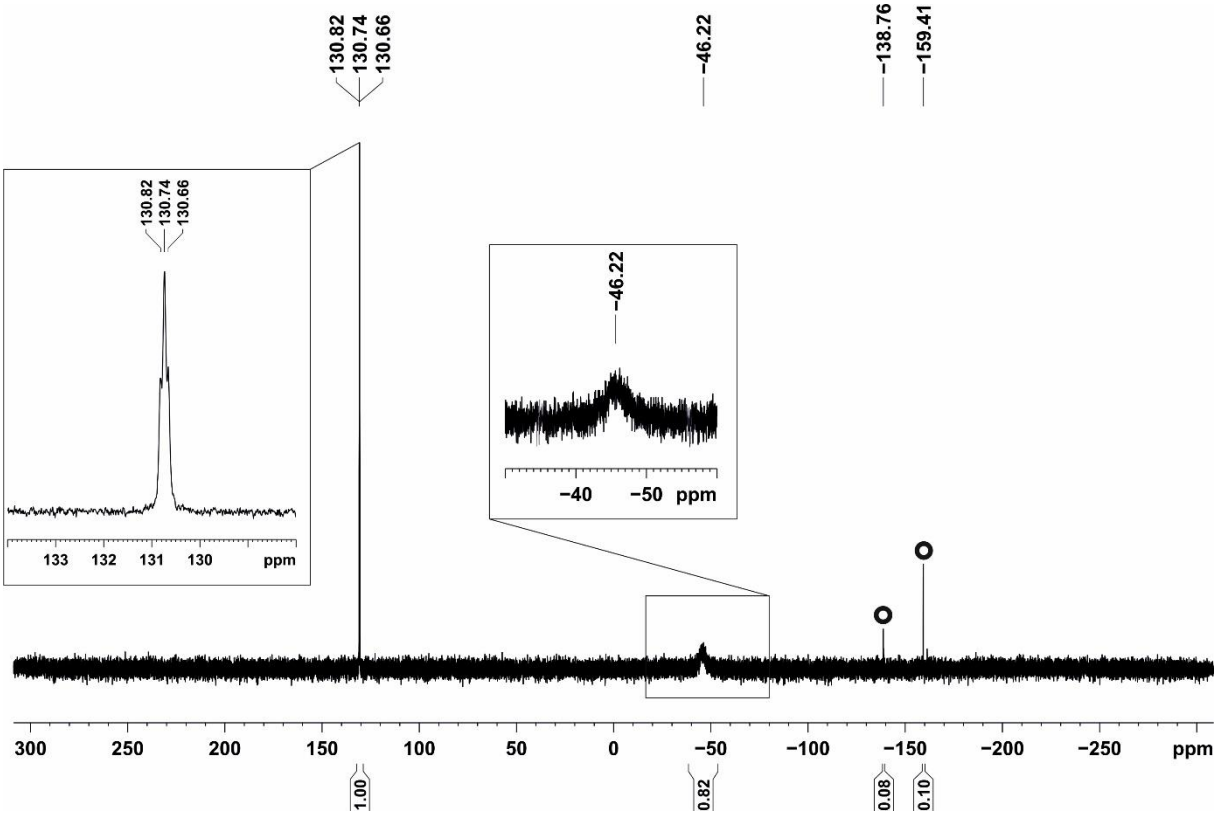


Figure S4 - ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **1-σ** and **1-π** (° = hydrophosphinine iron complexes **endo-4** and **exo-4**).

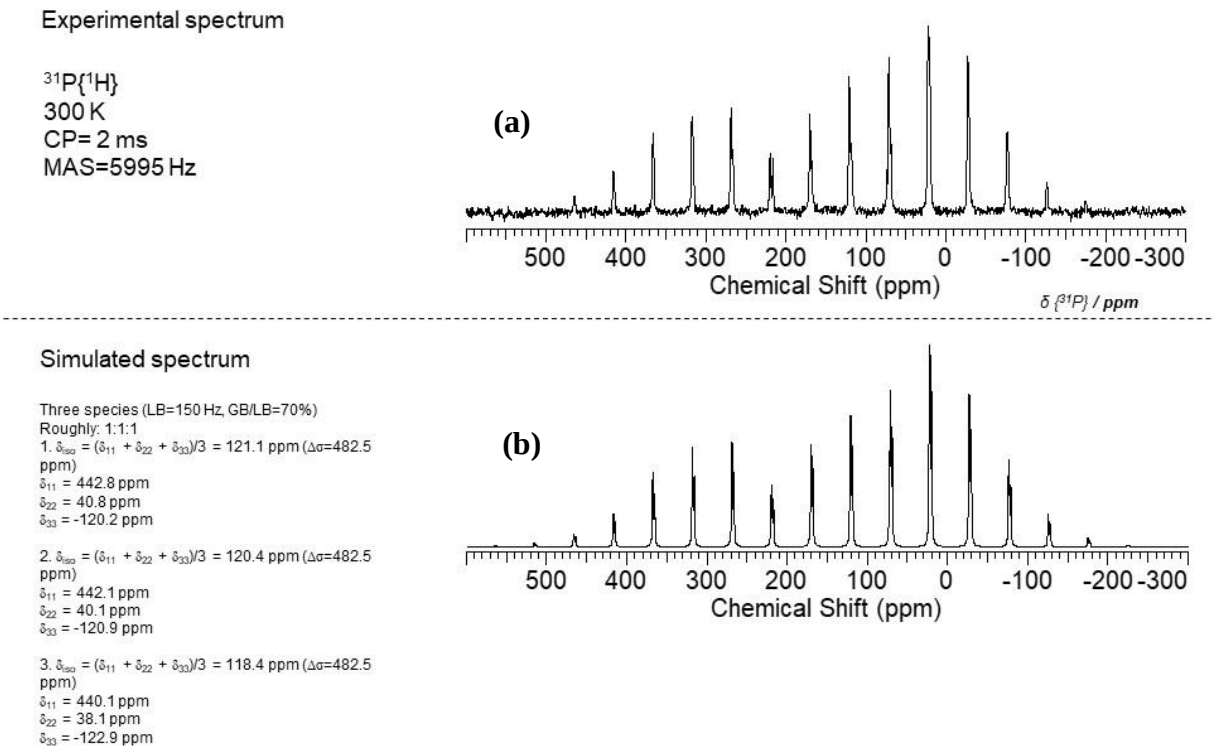


Figure S5. $^{31}P\{^{1}H\}$ CP MAS spectrum (6 kHz, 300 K) of **1-σ**; a) experimental spectrum (δ_{iso} = 121.1 ppm), b) simulated spectrum. The spectrum of **1-σ** indicates that there are three structurally similar species. These might arise from crystallographically different molecules.

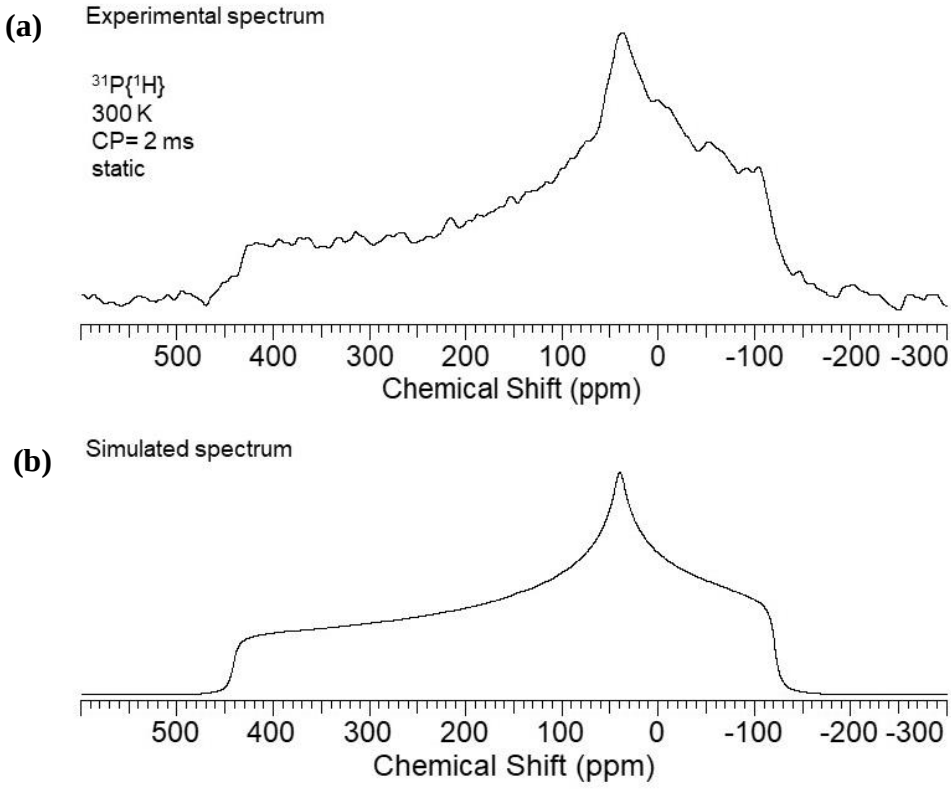


Figure S6 - ^{31}P CP MAS static spectrum (6 kHz, 300 K) of **1-σ**; a) experimental spectrum, b) simulated spectrum.

S2.2 NMR spectra of compound 2

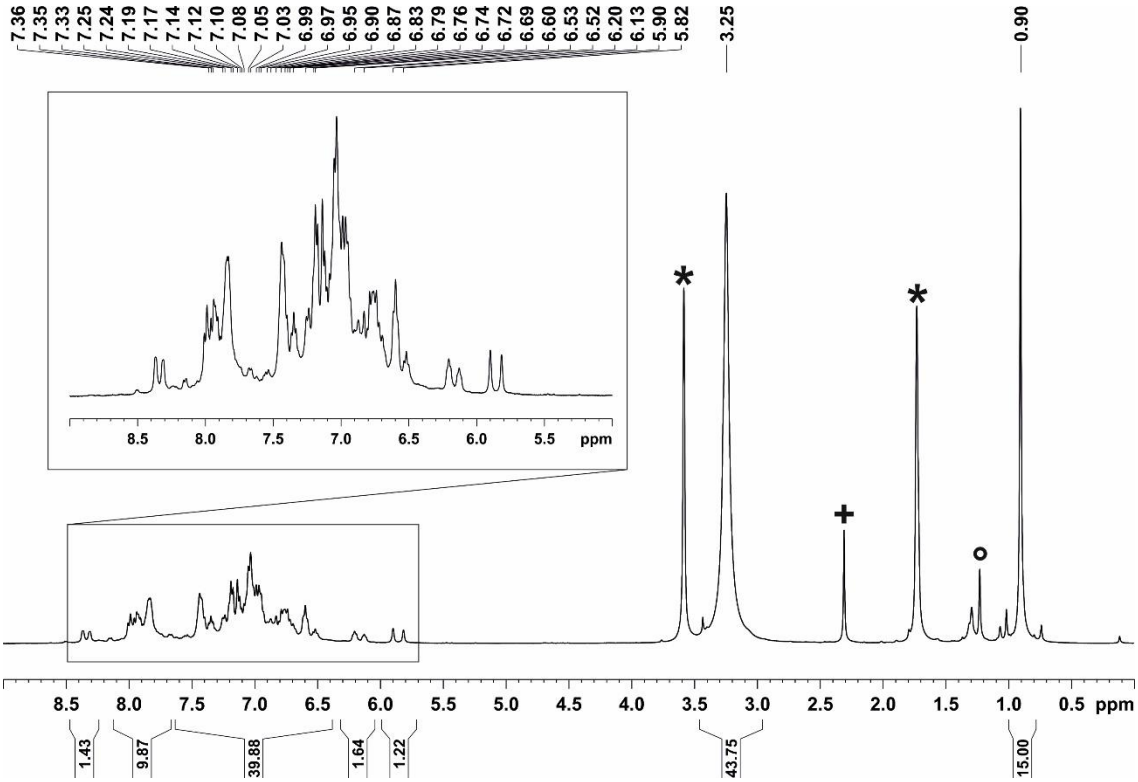


Figure S7 - ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of **2** (* = [D_8]THF, + = toluene, ° = unidentified impurity).

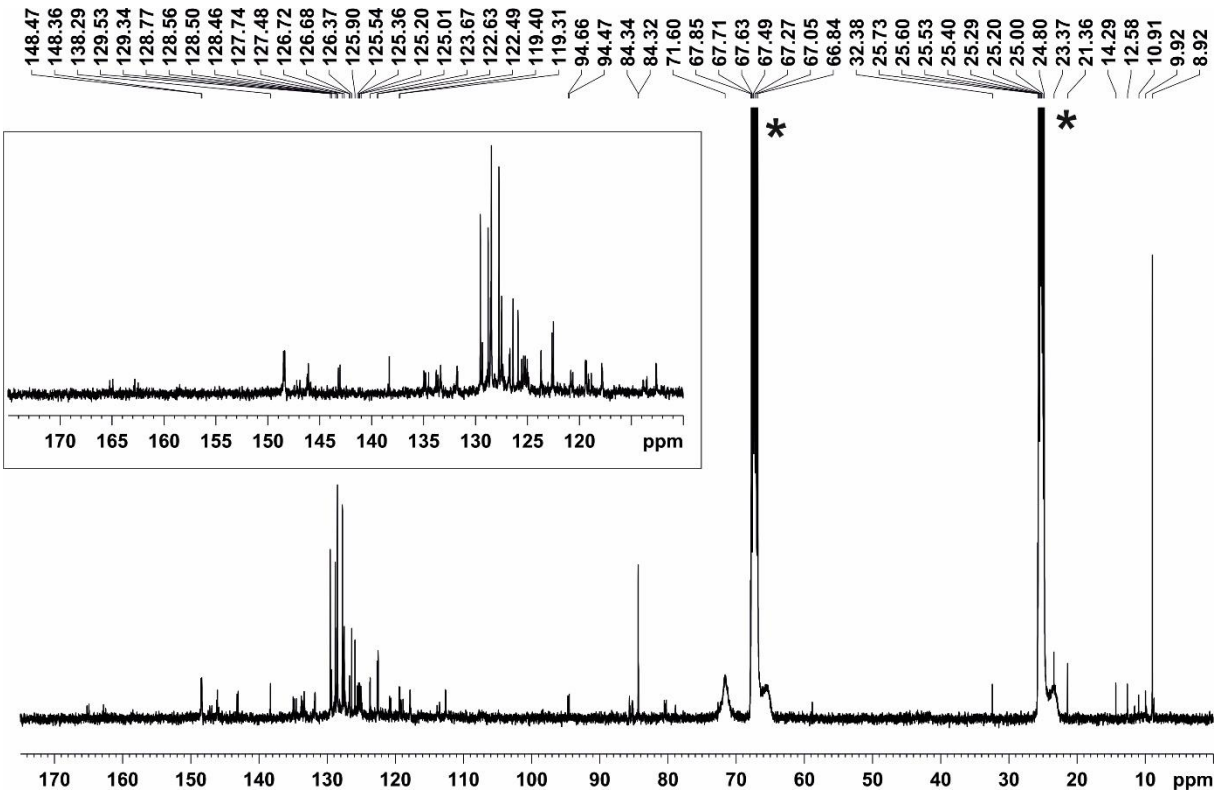


Figure S8 - ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of **2** (* = [D_8]THF).

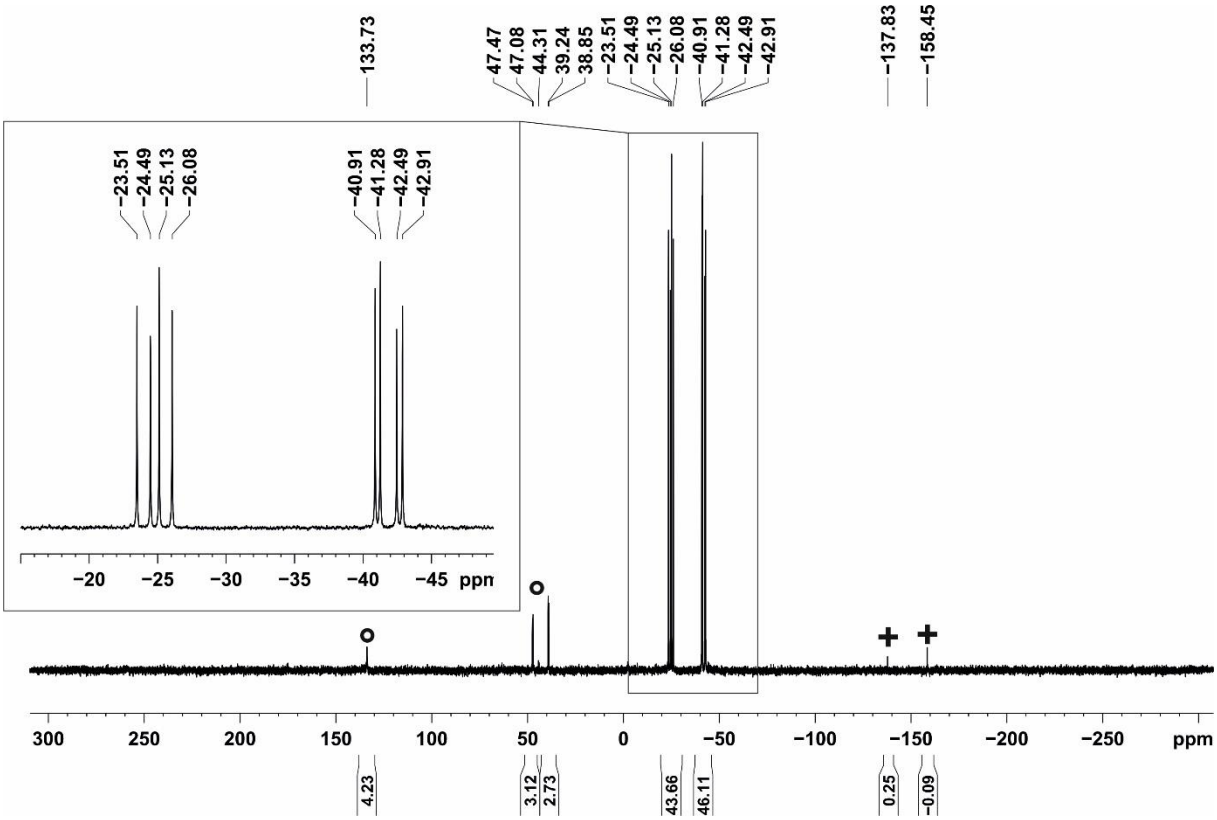


Figure S9 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of **2** (° = unidentified impurities, + = hydrophosphinines **endo-4** and **exo-4**).

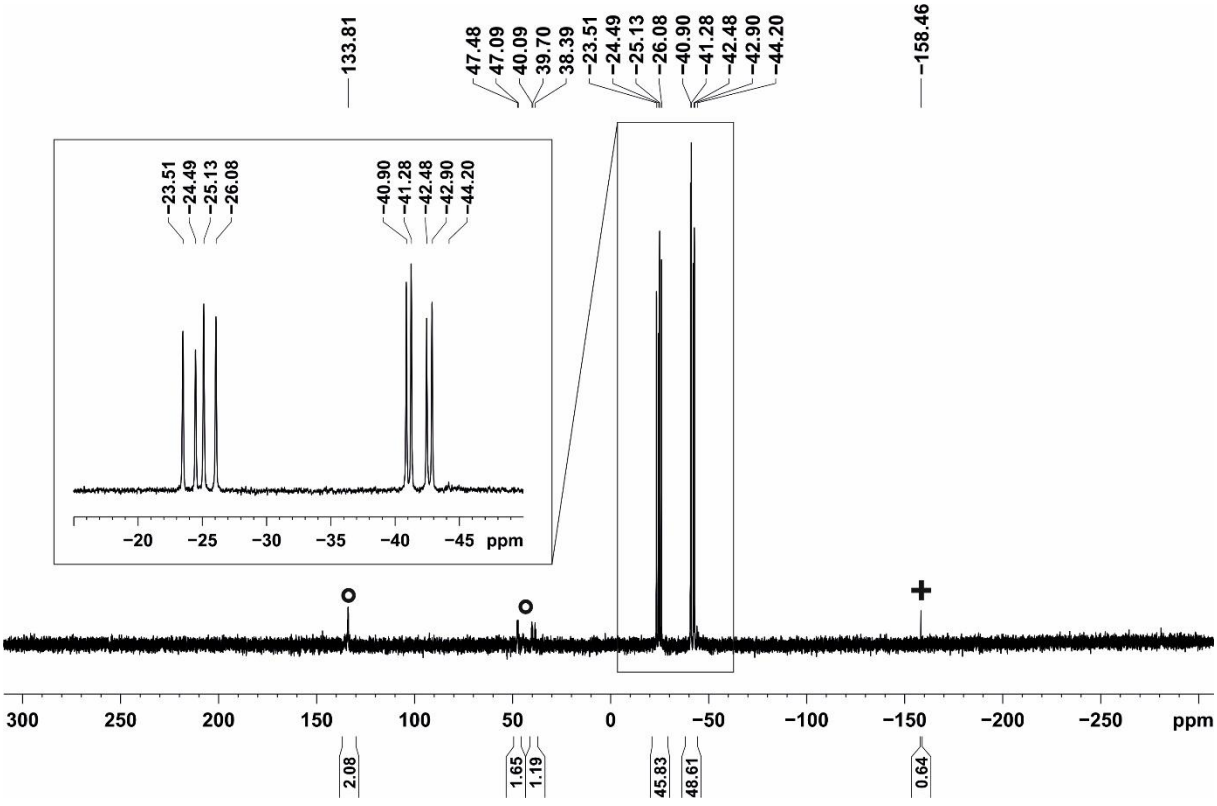


Figure S10 - ^{31}P NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of **2** (° = impurities, + = hydrophosphinines **endo-4** and **exo-4**).

S2.3 NMR spectra of compound 3-σ

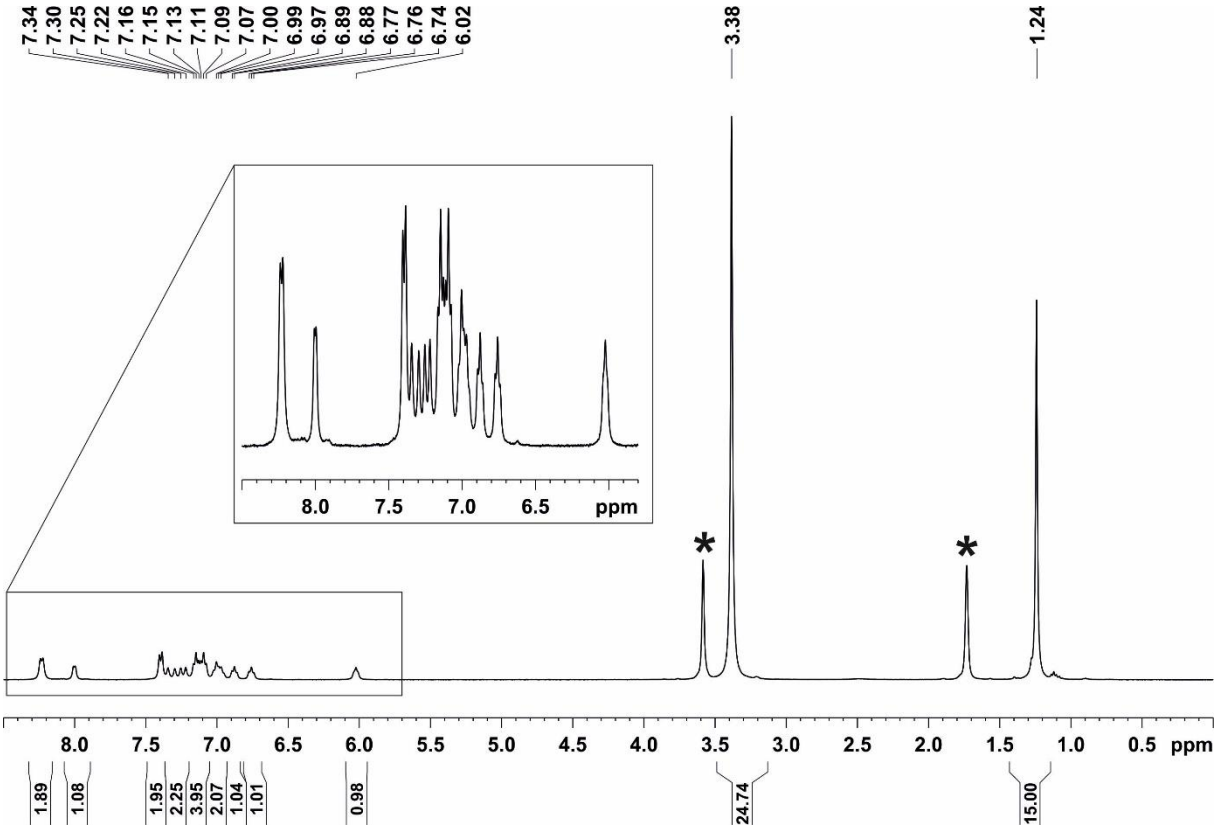


Figure S11 - ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of **3-σ** (* = [D_8]THF).

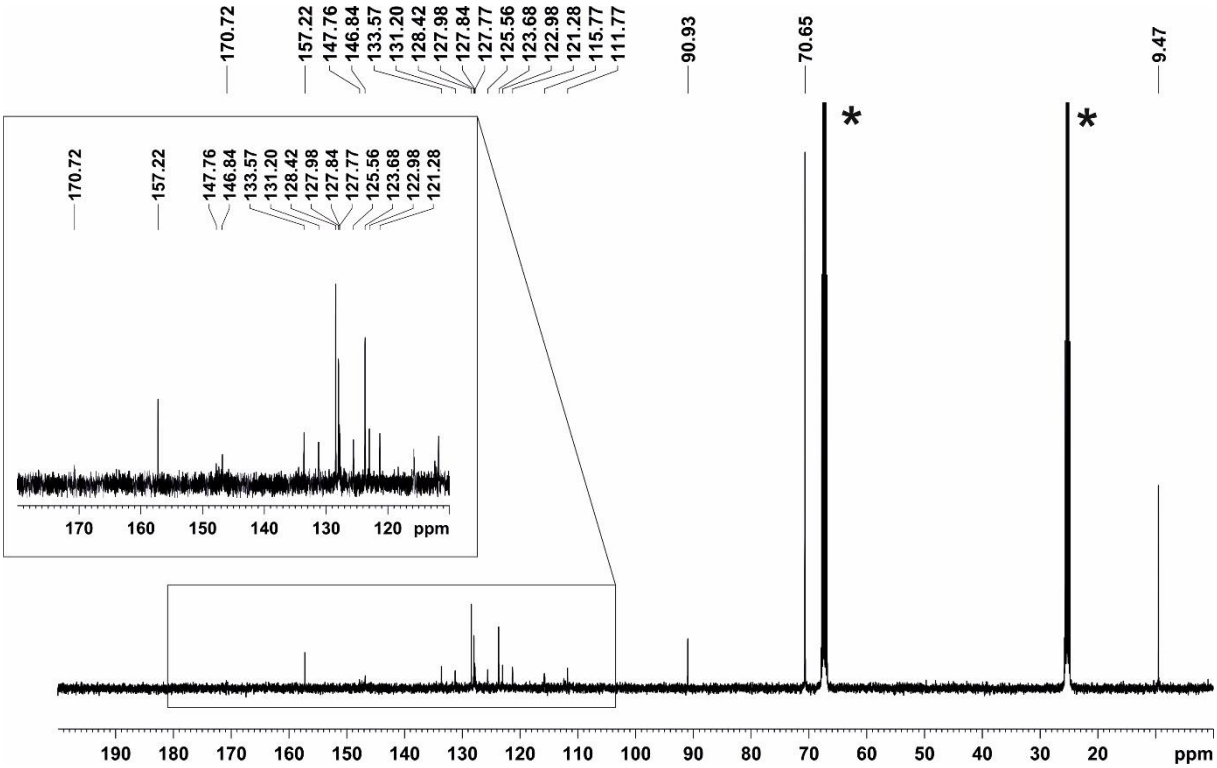


Figure S12 - ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of **3-σ** (* = [D_8]THF).

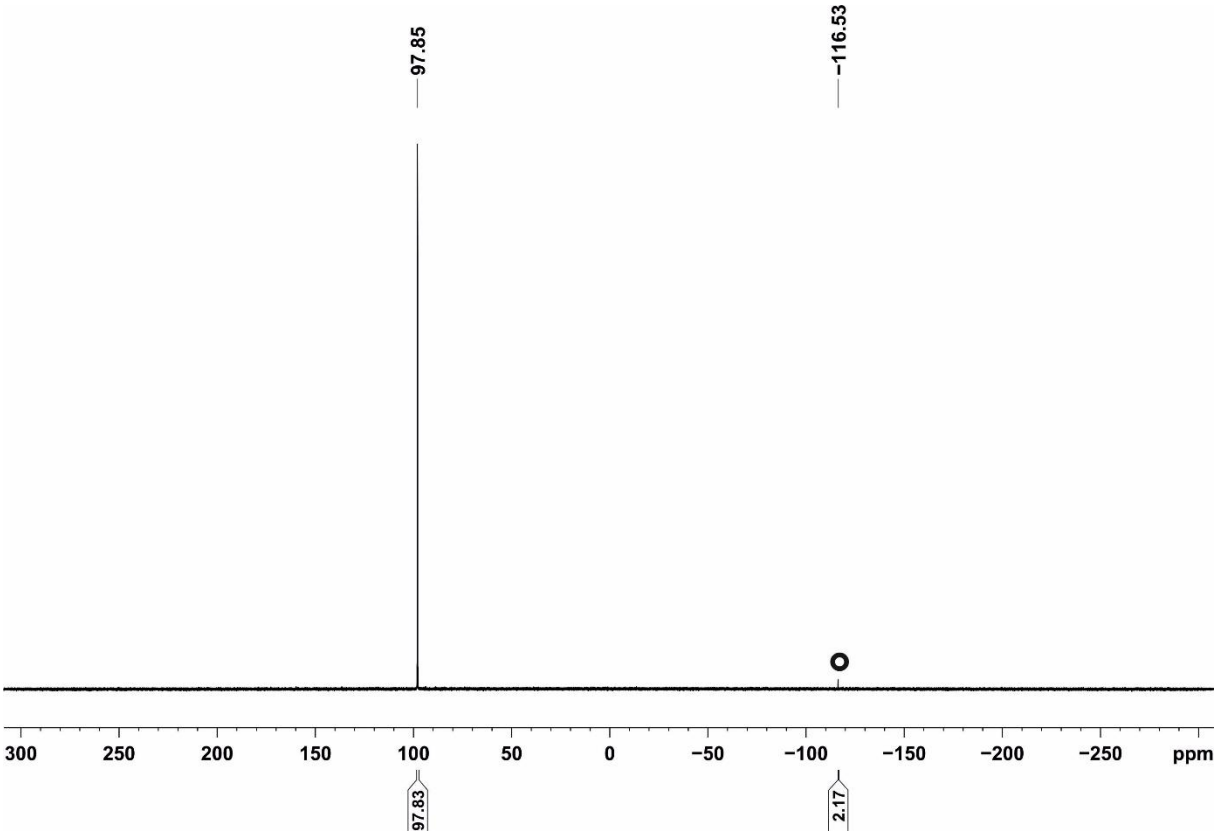


Figure S13 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **3-σ** (° = **3-π**).

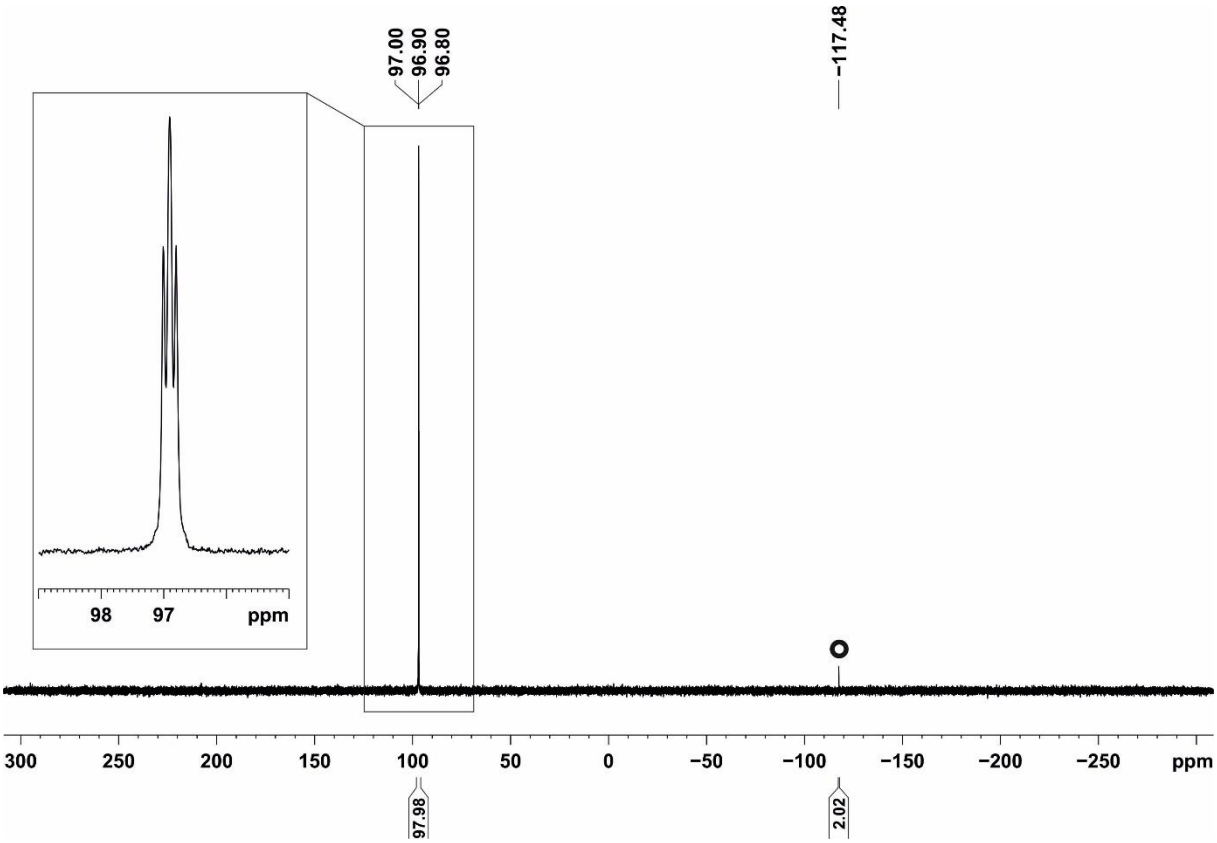


Figure S14 - ^{31}P NMR spectrum (161.98 MHz, 300 K, $[D_8]$THF) of **3-σ** (° = **3-π**).

S2.4 NMR Spectra of compound 3-π

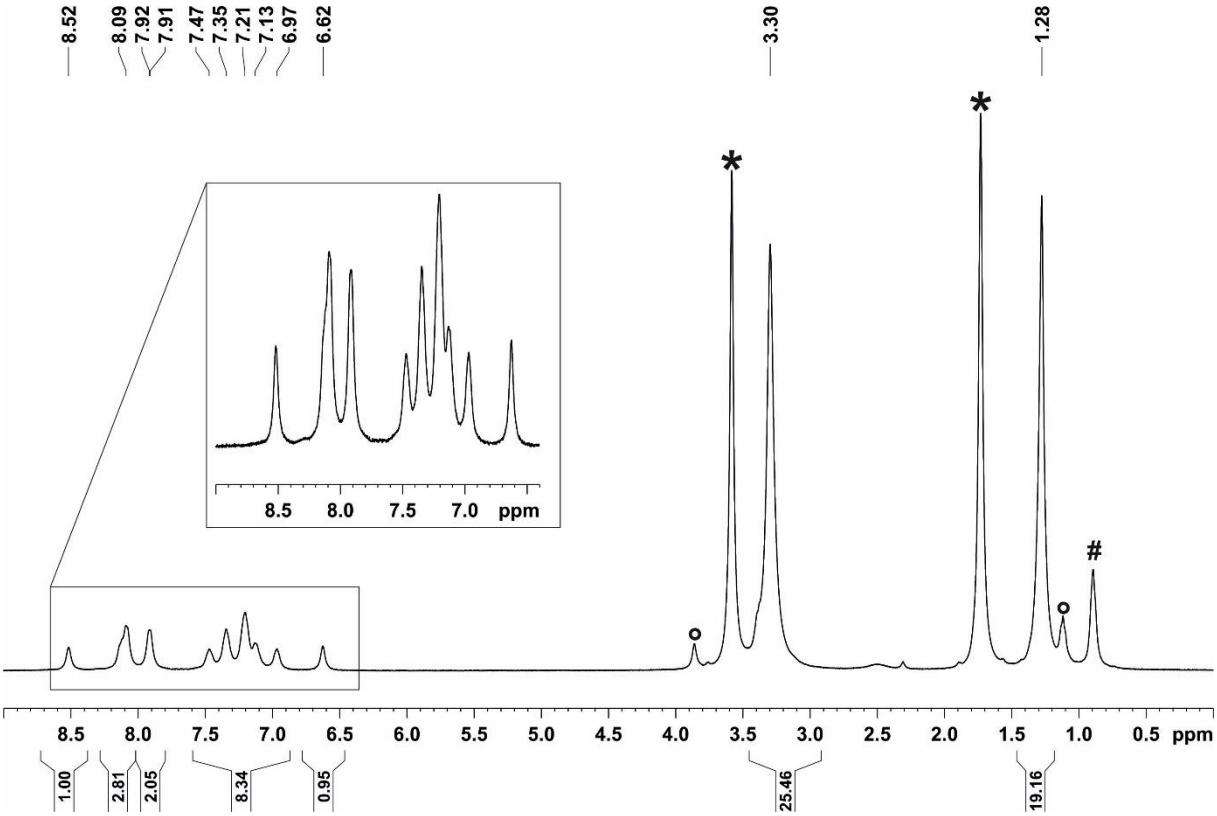


Figure S15 ^{1}H NMR spectrum (400.13 MHz, 300 K, [D_8]THF) of **3-π** (* = [D_8]THF, # = *n*-hexane, ° = unidentified impurities).

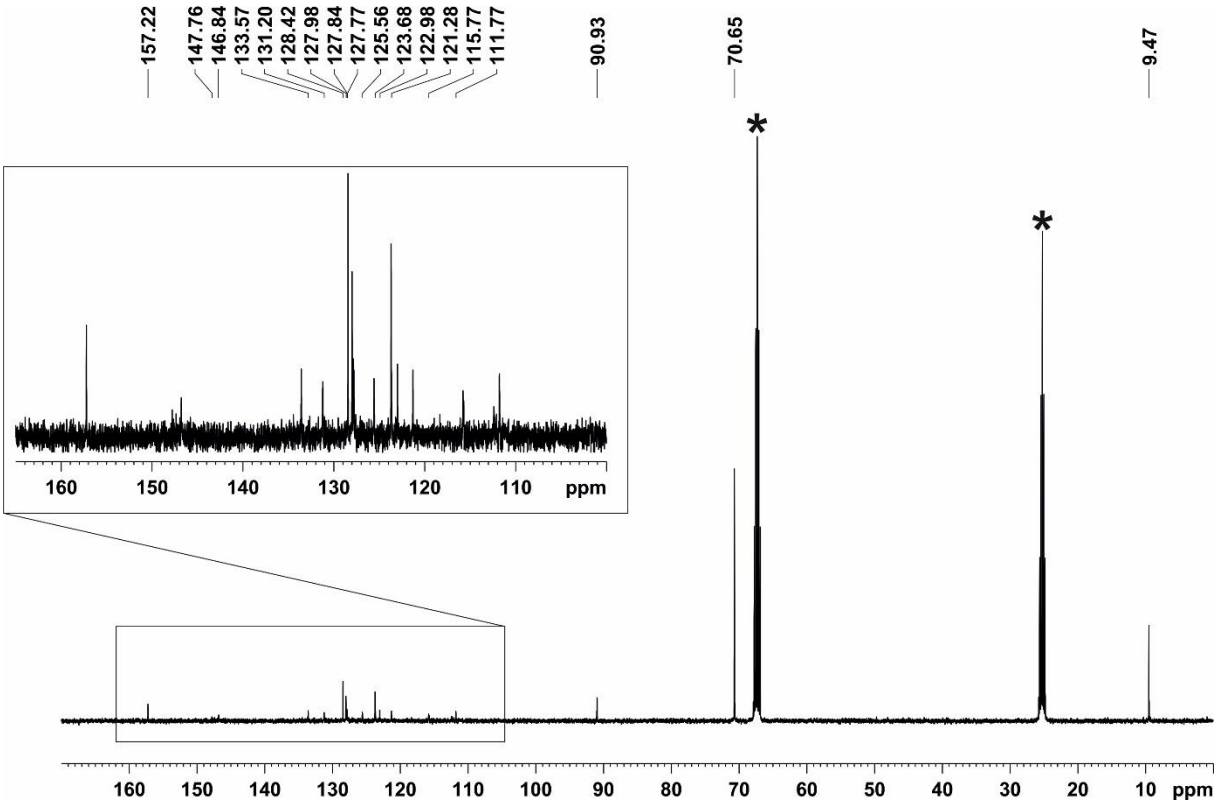


Figure S16 - ^{13}C{^{1}H} NMR spectrum (100.61 MHz, 300 K, [D_8]THF) of **3-π** (* = [D_8]THF).

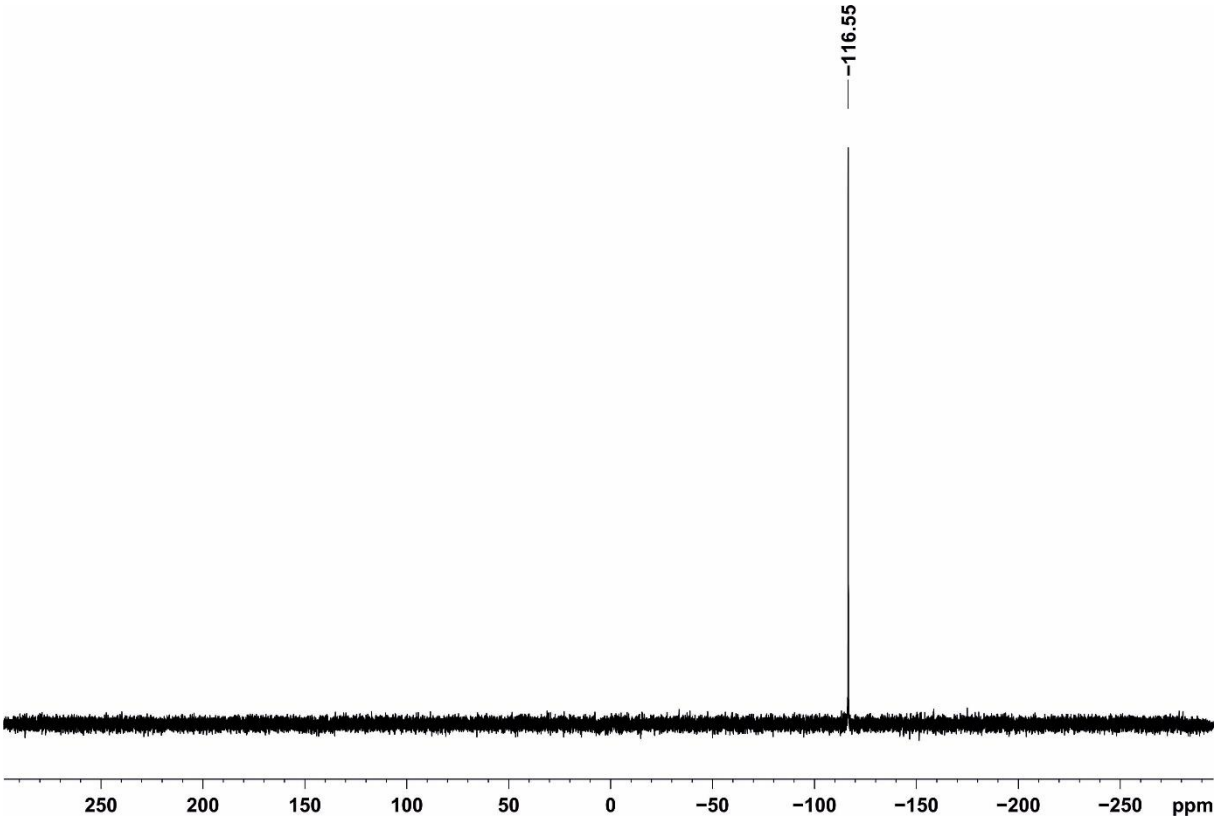


Figure S17 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of **3-π**.

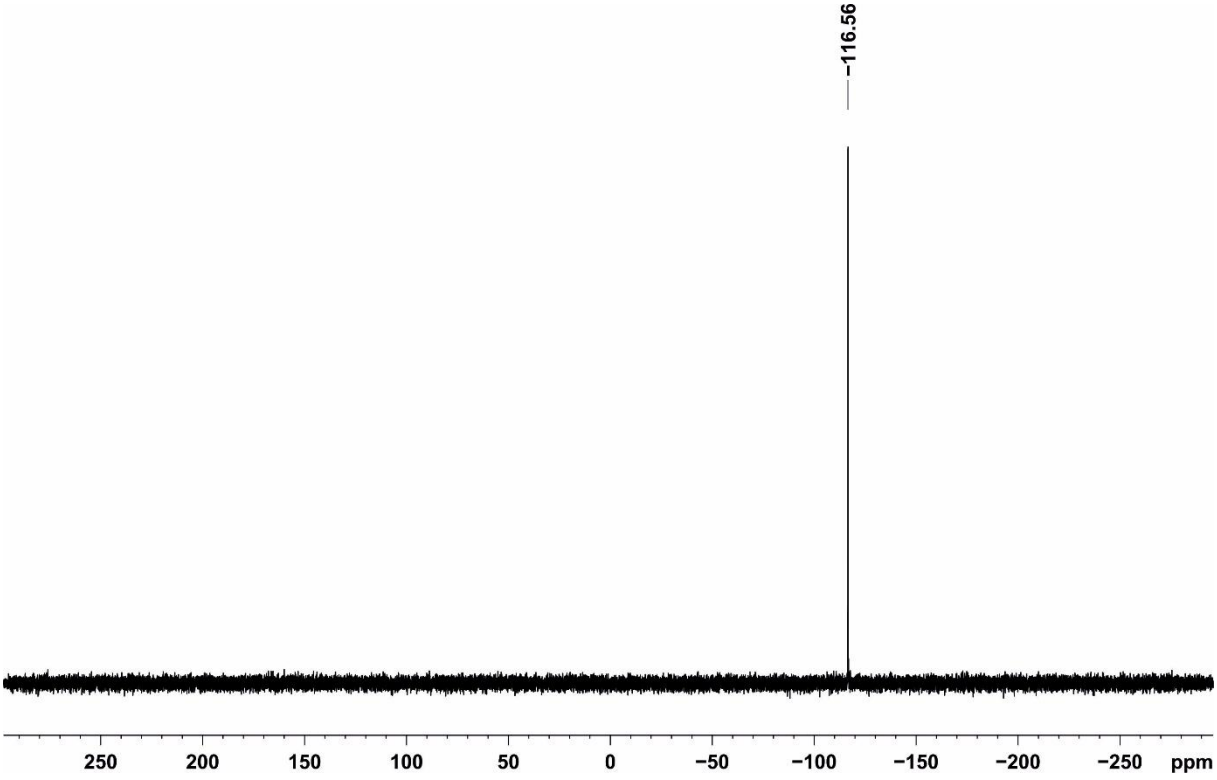


Figure S18 - ^{31}P NMR spectrum (161.98 MHz, 300 K, [D_8]THF) of **3-π**.

S2.5 Variable temperature $^{31}P\{^{1}H\}$ NMR spectra of compounds 1-σ and 1-π

[K([18]crown-6)][Cp*Fe($C_{10}H_8$)] (38 mg, 0.061 mmol) and **L** (20 mg, 0.061 mmol) were dissolved in [D_8]THF (0.5 mL) at room temperature. $^{31}P\{^{1}H\}$ NMR spectra were recorded at 300 K, 243 K and 333 K.

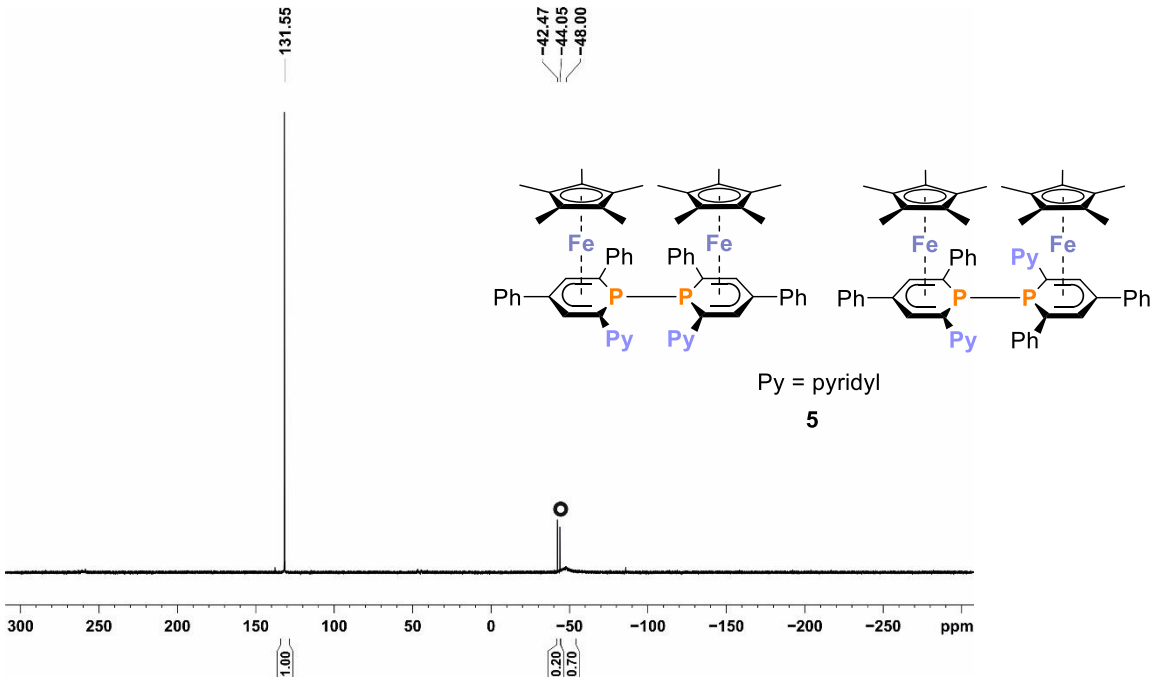


Figure S19 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, [D_8]THF) at 300 K (° = phosphinine iron dimers **5**).[8]

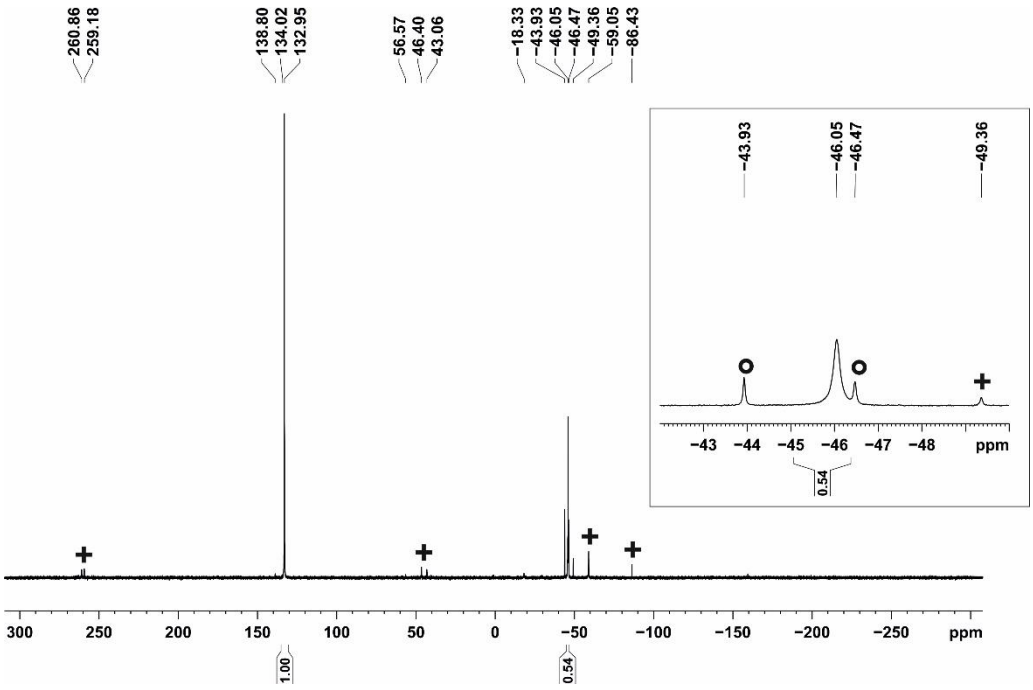


Figure S20 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, [D_8]THF) at 243 K (° = phosphinine iron dimers **5**, + = unidentified impurities).

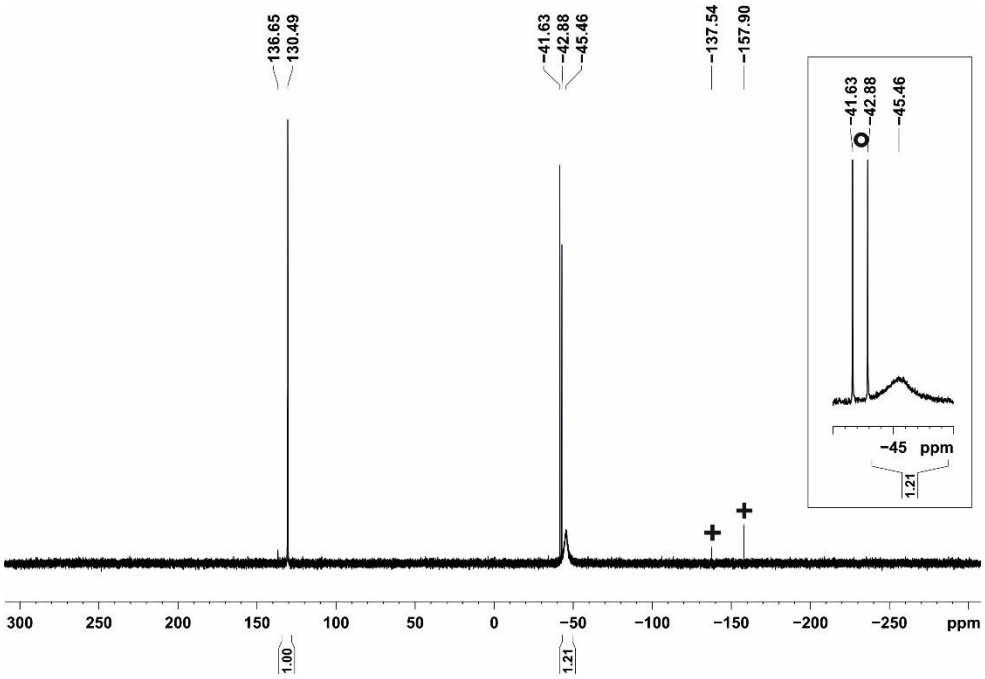


Figure S21 - $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, $[D_8]$THF) at 333 K (° = phosphinine iron dimers **5**, + = hydrophosphinine iron complexes **endo-4** and **exo-4**).

S2.6 $^{31}P\{^{1}H\}$ NMR monitoring of the formation of 1-σ and 1-π at 273 K

[K([18]crown-6)][Cp*Fe($C_{10}H_8$)] (38 mg, 0.061 mmol) and **L** (20 mg, 0.061 mmol) were dissolved in [D_8]THF (0.8 mL) cooled to −35 °C inside an NMR tube fitted with a screw cap. $^{31}P\{^{1}H\}$ NMR spectra were immediately recorded at a controlled temperature of 273 K, and recorded periodically while being maintained at the same temperature.

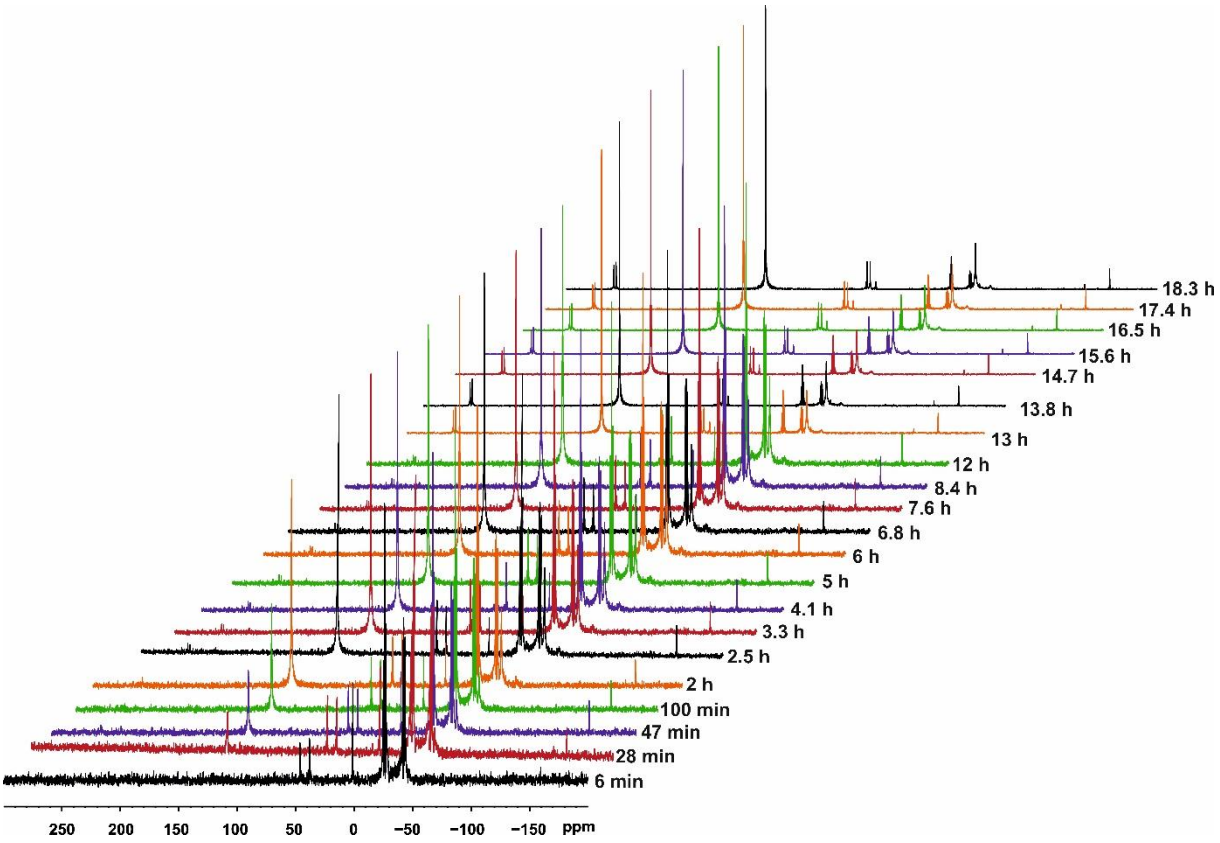


Figure S22 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, [D_8]THF) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of 300 ppm ≥ δ ≥ −200 ppm.

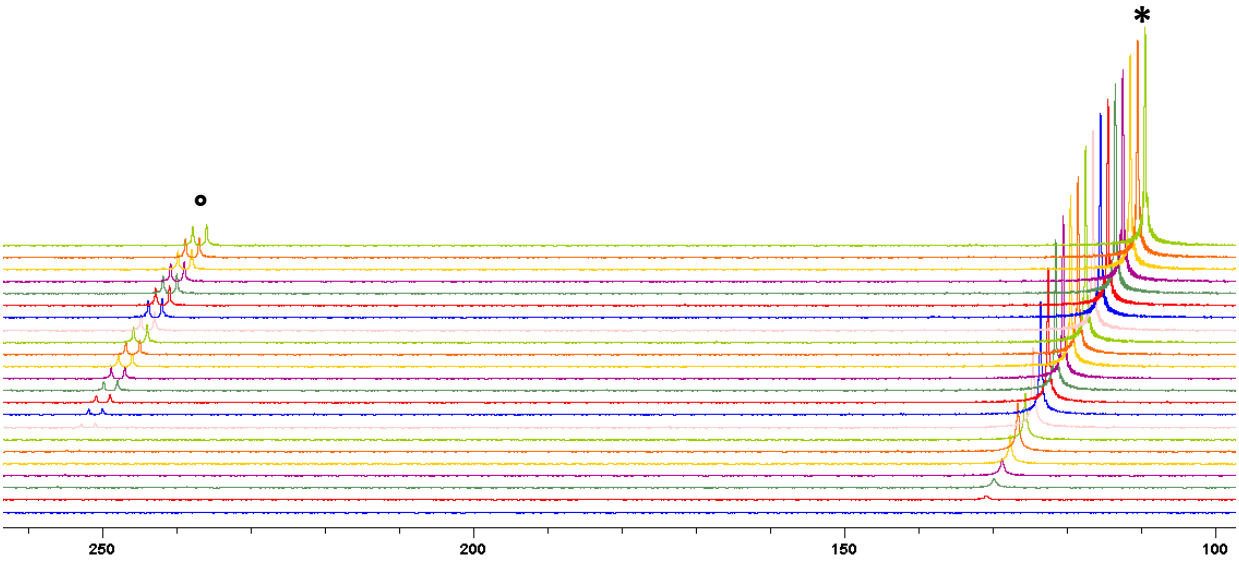


Figure S23 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, $[D_8]THF$) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of 260 ppm ≥ δ ≥ 130 ppm. * = **1-σ**, ° = unknown species.

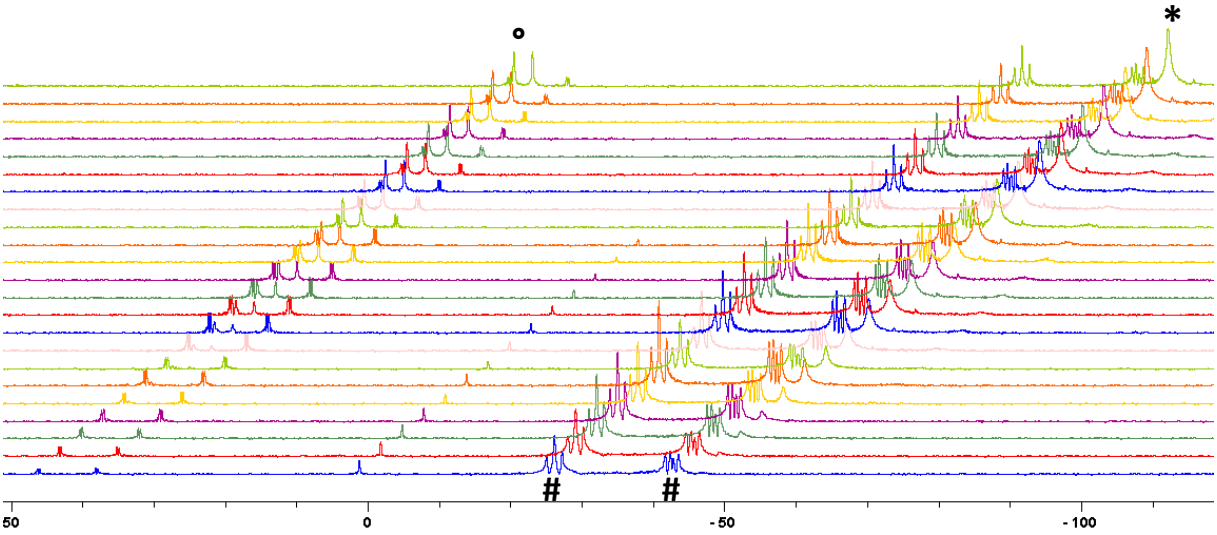


Figure S24 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, $[D_8]THF$) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of 50 ppm ≥ δ ≥ −50 ppm. * = **1-π**, ° = unknown species, # = **2**.

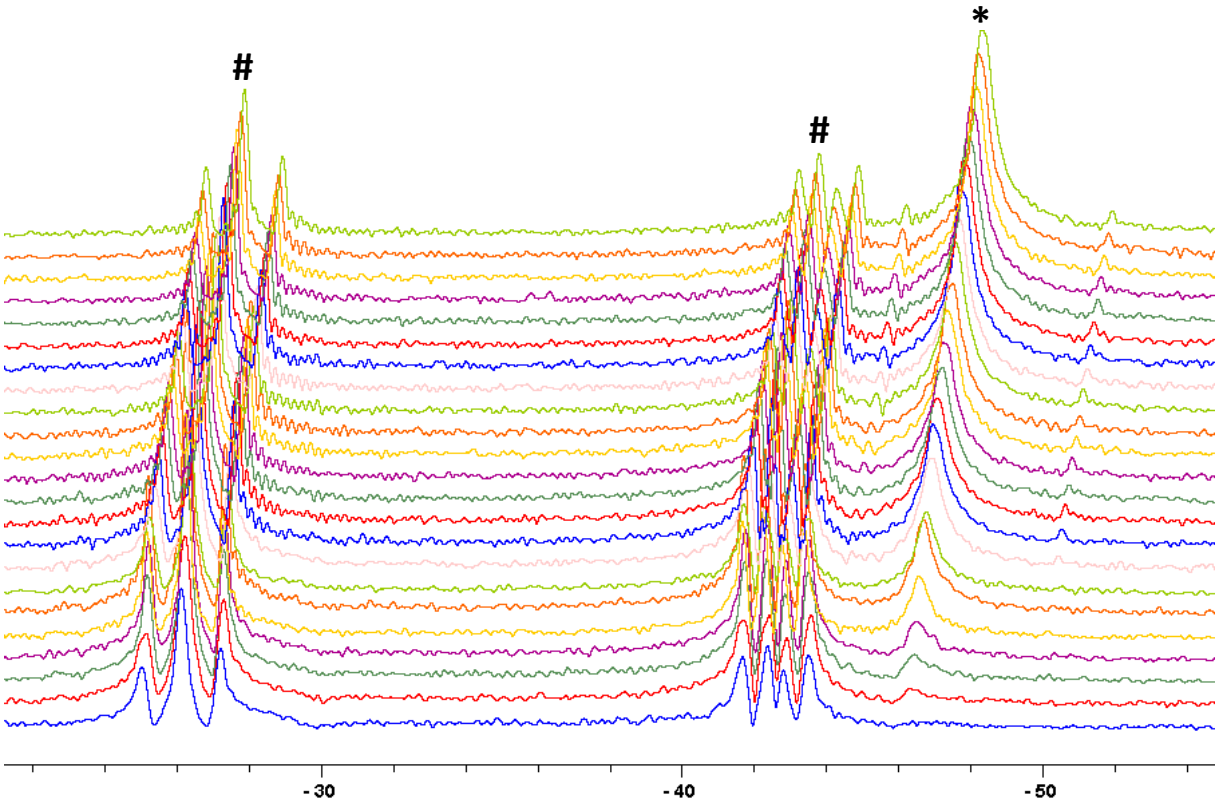


Figure S25 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, $[D_8]THF$) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of −20 ppm ≥ δ ≥ −50 ppm. * = **1-*π***, # = **2**.

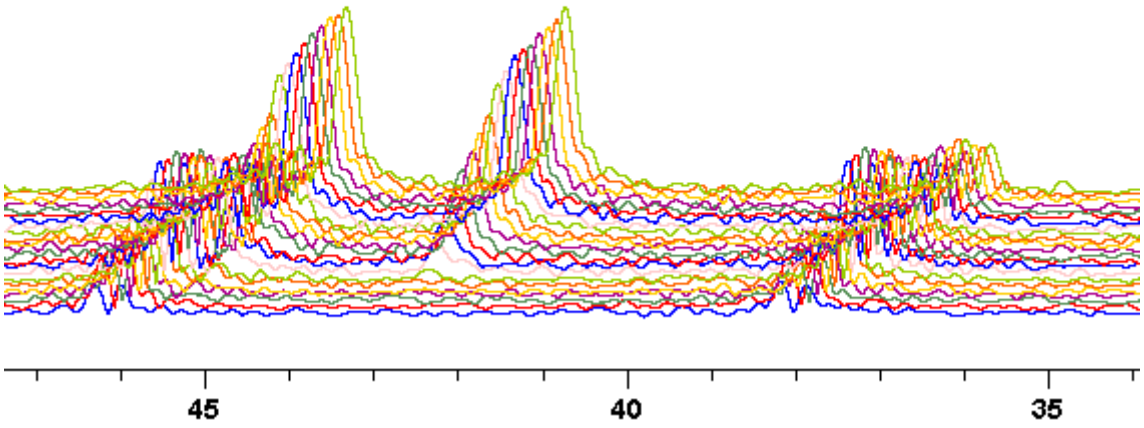


Figure S26 - $^{31}P\{^{1}H\}$ NMR monitoring (242.87 MHz, $[D_8]THF$) of the reaction between [K([18]crown-6)][Cp*Fe($C_{10}H_8$)] and **L** at 273 K; range of 50 ppm ≥ δ ≥ 35 ppm; unknown species.

S3 UV-vis Spectra

S3.1 UV-vis spectrum of 1-σ and 1-π

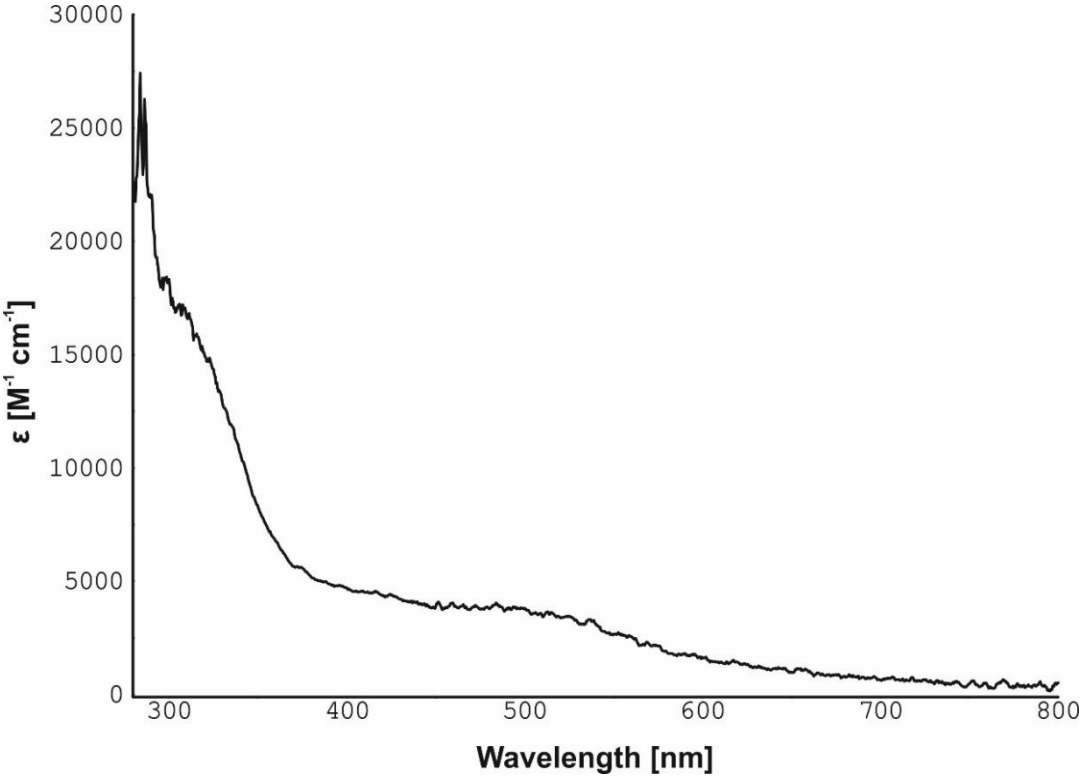


Figure S27 - UV/vis spectrum of **1-σ** and **1-π** in THF.

S3.2 UV-vis spectrum of 2

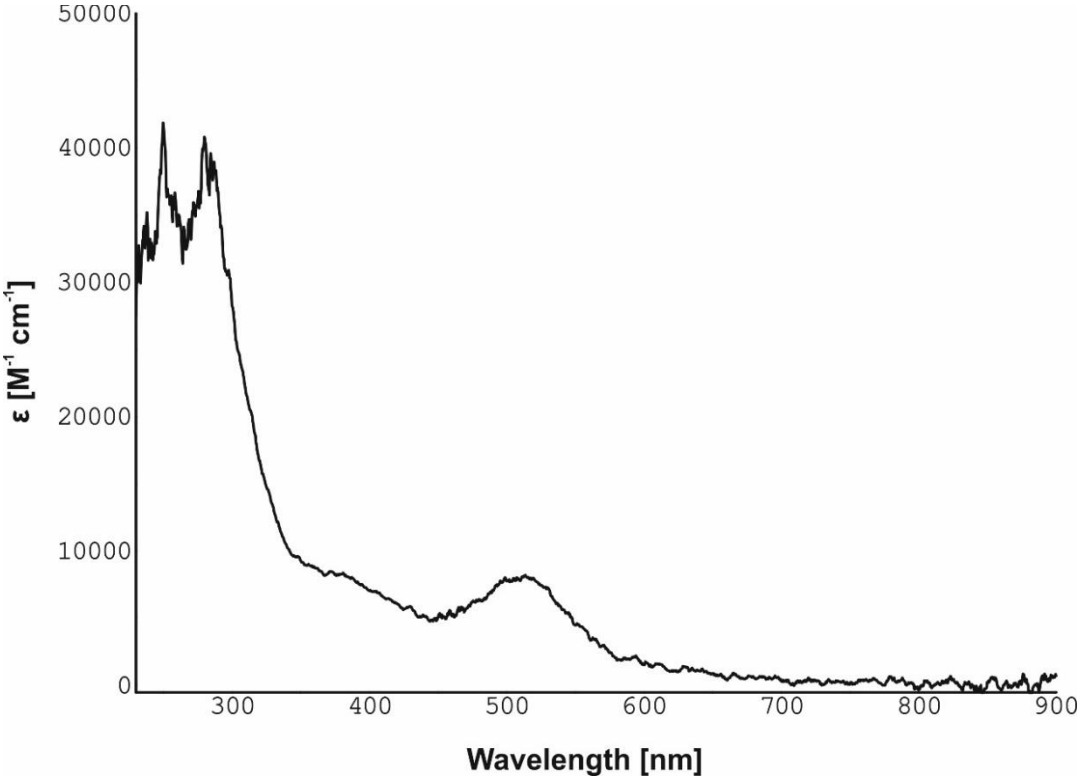


Figure S28 - UV/vis spectrum of **2** in THF.

S3.3 UV-vis spectrum of 3-σ

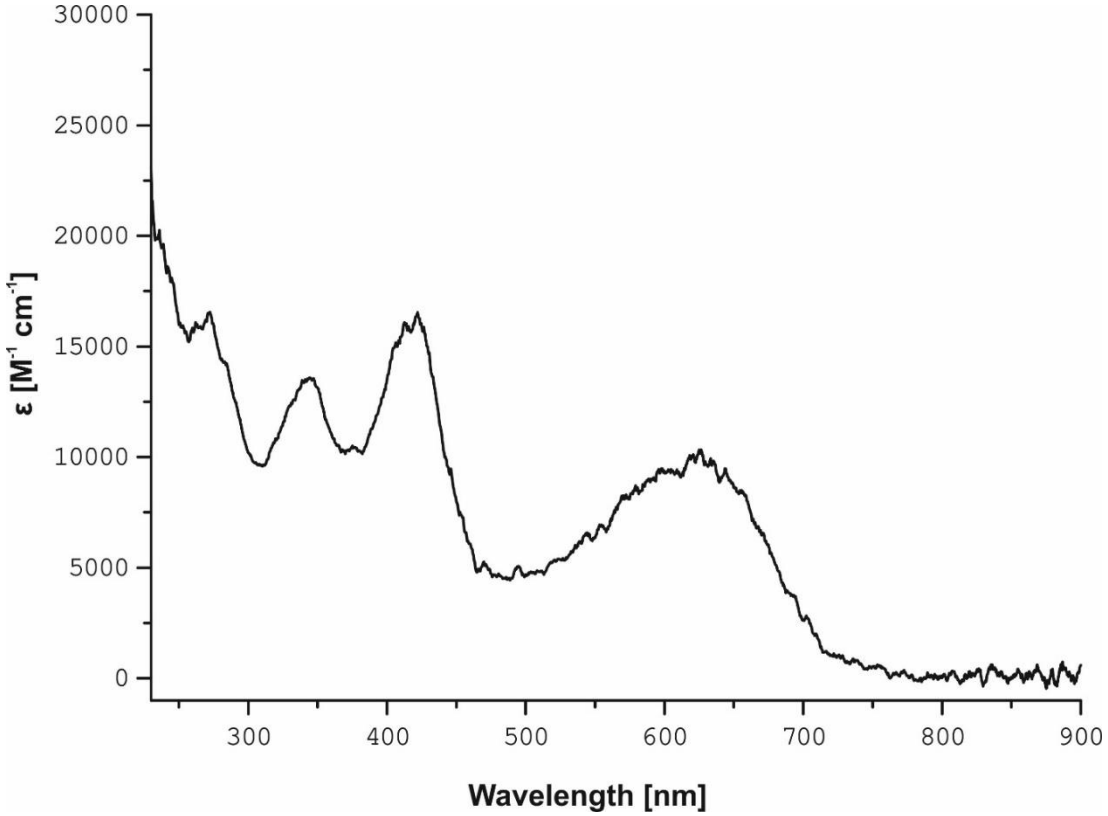


Figure S29 - UV/vis spectrum of **3-σ** in THF.

S3.4 UV-vis spectrum of 3-π

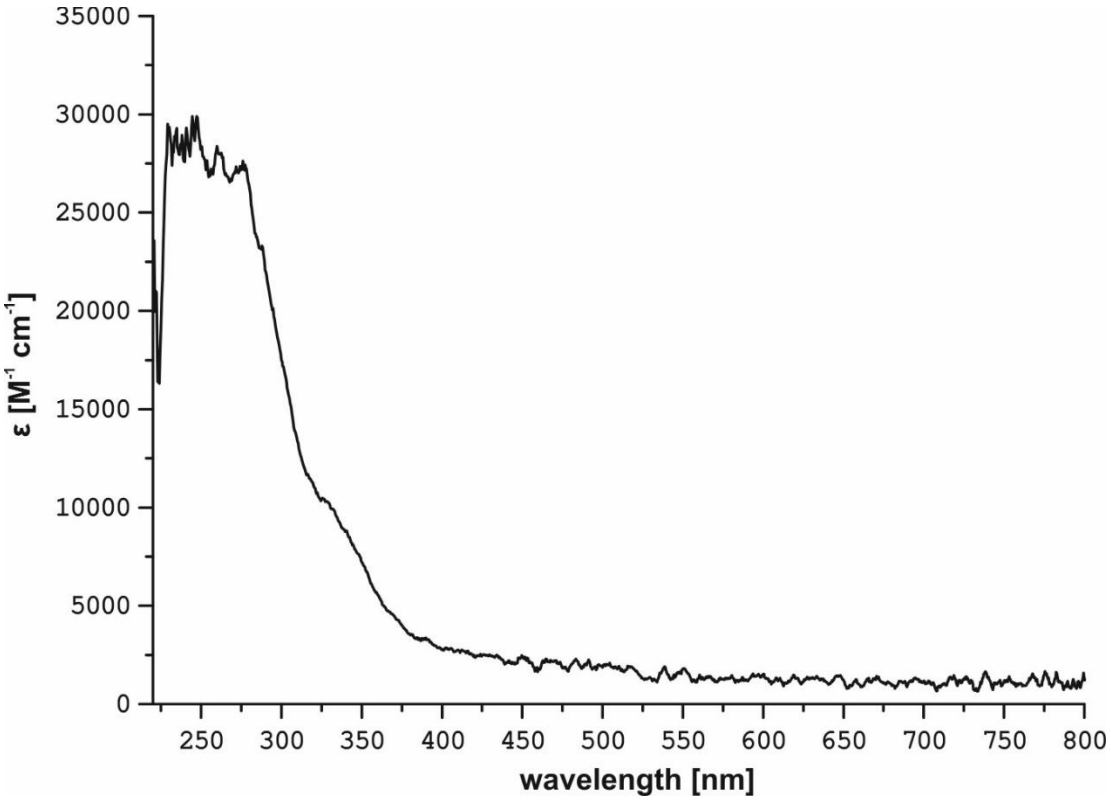


Figure S30 UV/vis spectrum of **3-π** in THF.

S4 IR Spectra

S4.1 IR spectrum of 3-σ

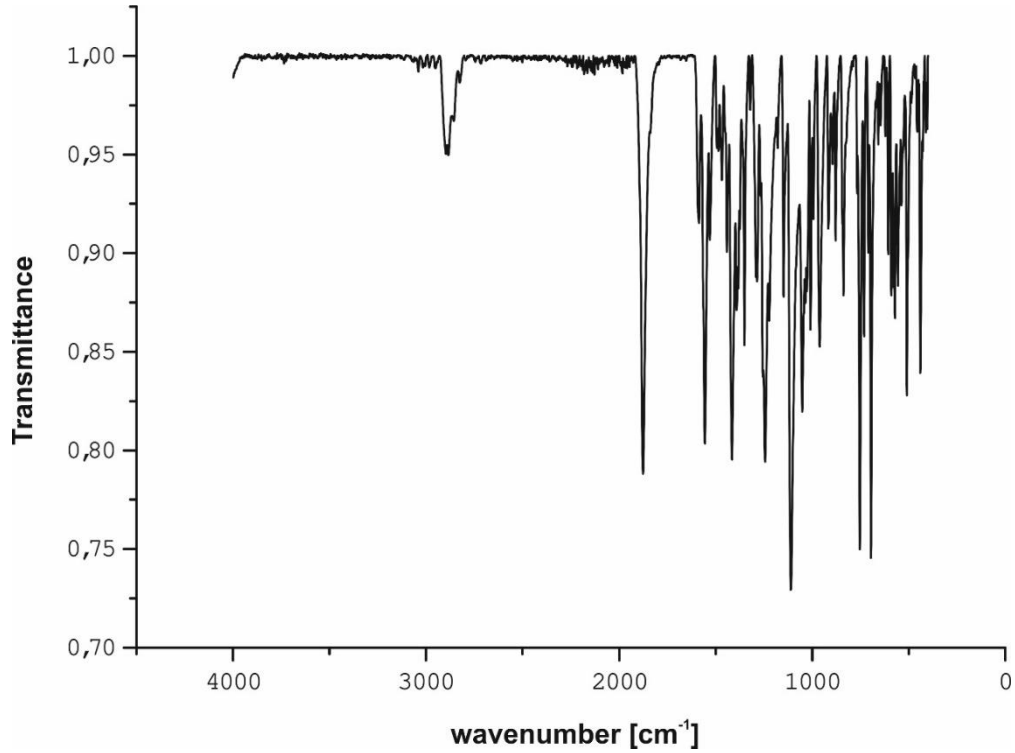


Figure S31 Solid state IR spectrum of **3-σ**.

S4.2 IR spectrum of 3-π

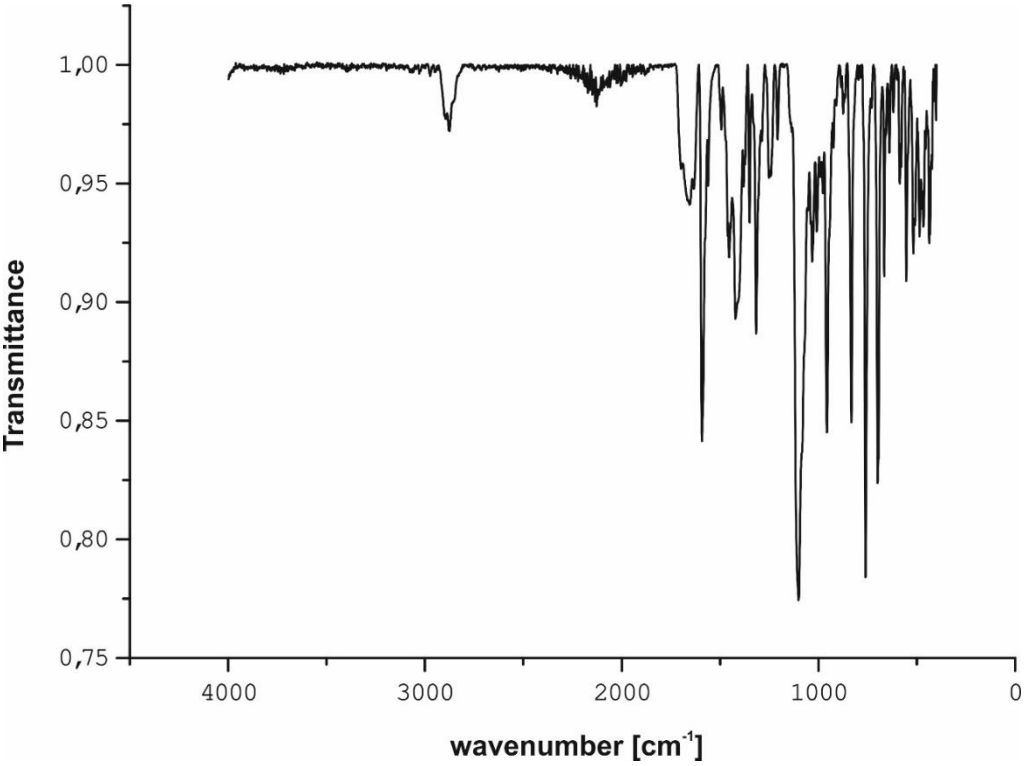


Figure S32 Solid state IR spectrum spectrum of **3-π**.

S5 X-ray Crystallographic Data

Table S1. Crystallographic data and structure refinement of **1-σ**, **2**, **3-σ** and **3-π**.

	1-σ	**2**	**3-σ**	**3-π**
Empirical formula	$C_{44}H_{55}FeKNO_6P$	$C_{66}H_{71}FeKN_2O_6P_2$	$C_{45}H_{55}FeKNO_8P$	$C_{45}H_{55}FeKNO_8P$
Formula weight / g·mol^{-1}	819.81	1145.13	863.82	863.82
Temperature / K	123.01(10)	123.00(10)	123.00(10)	123.00(10)
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/n$	Pbcn	P-1	P21/n
a / Å	15.3111(2)	13.8522(4)	12.0465(4)	16.9137(3)
b / Å	17.0781(2)	38.2033(10)	12.2446(5)	11.6932(2)
c / Å	16.7872(3)	23.0082(6)	15.7693(5)	21.2321(4)
α /°	90	90	108.340(3)	90
β /°	106.967(2)	90	95.737(3)	99.828(2)
γ /°	90	90	92.223(3)	90
V / Å^3	4198.53(11)	12175.9(6)	2190.75(14)	4137.56(13)
Z	4	8	2	4
ρ_{calc} / g cm^{-1}	1.297	1.249	1.310	1.387
μ / mm^{-1}	4.503	3.503	4.379	4.637
F(000)	1736.0	4832.0	912.0	1824.0
Crystal size / mm^3	0.369 × 0.172 × 0.122	0.376 × 0.305 × 0.186	0.385 × 0.243 × 0.125	0.739 × 0.222 × 0.072
Radiation / Å	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2*Θ* range for data collection /°	7.558 to 147.676	6.788 to 147.266	7.396 to 147.044	7.324 to 152.886
Diffractometer	SuperNova	SuperNova	SuperNova	SuperNova
Index ranges	-19 ≤ h ≤ 18, -20 ≤ k ≤ 21, -20 ≤ l ≤ 19	-15 ≤ h ≤ 16, -38 ≤ k ≤ 46, -19 ≤ l ≤ 28	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -19 ≤ l ≤ 17	-21 ≤ h ≤ 21, -12 ≤ k ≤ 14, -26 ≤ l ≤ 24
Reflections collected	33166	32483	16728	27823
Independent reflections	8388 [R_{int} = 0.0402, R_{sigma} = 0.0289]	11993 [R_{int} = 0.0520, R_{sigma} = 0.0493]	8612 [R_{int} = 0.0404, R_{sigma} = 0.0481]	8583 [Rint = 0.0310, Rsigma = 0.0267]
Data/restraints/parameters	8388/390/655	11993/1623/1076	8612/0/519	8583/46/538
Goodness-of-fit on F^2	1.029	1.052	1.037	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0796	R_1 = 0.0850, wR_2 = 0.2172	R_1 = 0.0411, wR_2 = 0.1034	R1 = 0.0782, wR2 = 0.1713
Final R indexes [all data]	R_1 = 0.0322, wR_2 = 0.0812	R_1 = 0.0998, wR_2 = 0.2290	R_1 = 0.0427, wR_2 = 0.1051	R1 = 0.0799, wR2 = 0.1722
Largest diff. peak/hole / e Å^{-3}	0.46/-0.40	0.78/-0.54	0.87/-0.51	1.23/-0.49

S6 DFT Calculations

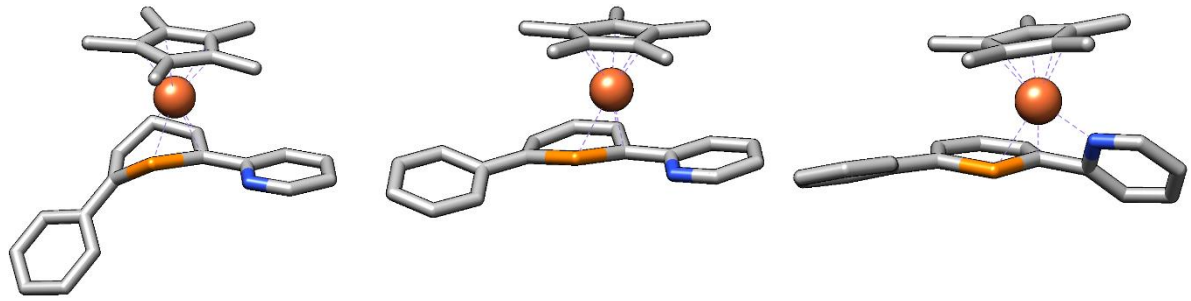
S6.1 General methods

All calculations were carried out with the ORCA program package.[9,10] All geometry optimisations were performed at the BP86-D3BJ/def2-TZVP[11–15] level of theory in the gas phase. Frequency calculations were carried out to confirm the nature of stationary points found by geometry optimisations. Density fitting techniques, also called resolution-of-identity approximation (RI),[16] were used for GGA calculations, whereas the RIJCOSX[17] approximation was used for TPSSh calculations. To save computational cost the phenyl groups at the 4-position of the phosphinine moiety of ligand **L** were replaced by hydrogen atoms, and $[K([18]crown-6)]^+$ countercations were omitted. Approximate transition states were generated using the nudged elastic band (NEB) method implemented in ORCA, followed by a saddle-point optimisation.

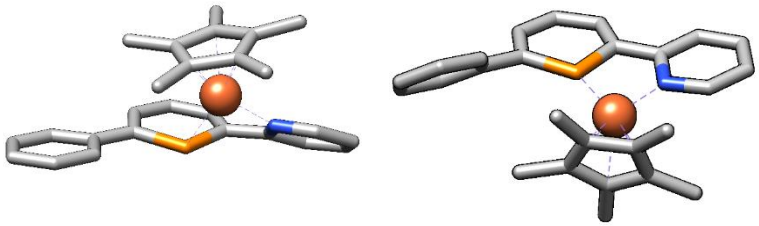
S6.2 Isomerisation of complex 1

Final single-point calculations on the BP86 geometries were conducted at the TPSSh-D3BJ/def2-TZVP level of theory and zero-point energies and thermal corrections at 298 K were added from the BP86 calculations. Additionally, final single-point calculations of the calculated minima and transition states were carried out with the CPCM[19] model for THF at the TPSSh-D3BJ/def2-TZVP level.

The isomerisation of **1-π** to **1-σ** proceeds *via* a two-step mechanism. First, the intermediate **1-int** is formed, in which the Cp*Fe moiety 'slips' from η^4 to η^2 coordination to the phosphinine moiety, with concomitant formation of a new Fe—N interaction. Subsequent reorientation of the phosphinine switches it from a π- to a σ-coordination mode, providing the final isomerised complex (Figure S33).



1-π (ΔE = 0.0 [0.0]) **TS-π-int** (ΔE = 25.2 [27.0]) **1-int** (ΔE = 7.5 [8.8])



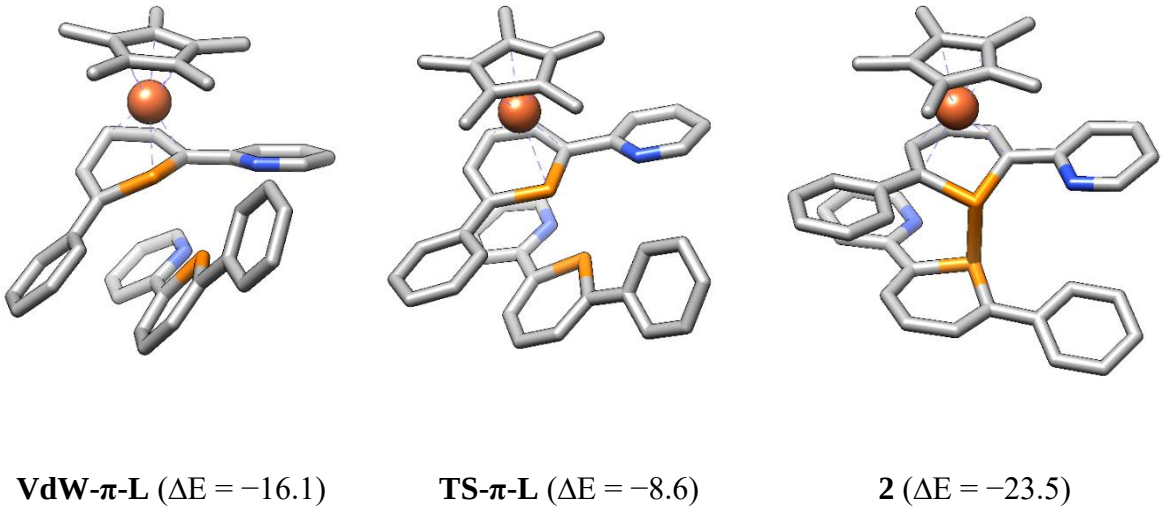
TS-σ-int (ΔE = 20.2 [23.0]) **1-σ** (ΔE = −1.4 [−0.9])

Figure S33 - Optimised structures for the isomerisation of **1-π to 1-σ**. Energies are given in kcal·mol^{-1} relative to the optimised structure of **1-π**. Energies in brackets correspond to electronic energies with solvent correction (TPSSh-D3BJ/def2-TZVP CPCM(THF)).

S6.3 Formation and electronic structure of compound 2

The reaction between **1-π** and **L** in the gas phase involves two steps (energies were obtained at the TPSSh-D3BJ/def2-TZVP[18] level of theory): the activation barrier-free formation of the Van-der-Waals complex **VdW-π-L**, and subsequent P−P bond formation yielding **2**. The respective transition state **TS-π-L** has a low energy (Figure S35), consistent with the experimental observation of rapid formation of **2** at room temperature.

The highest occupied molecular orbital (HOMO) of **2** strongly resembles the HOMO of the phosphacyclohexadienyl anion (Figure S35). Additionally, inspection of the molecular orbitals of **2** (Figure S36) revealed a $3d^6$ configuration at the iron center. Therefore, **2** can be described as an iron(II) complex with an η^6-coordinating, dianionic di(phosphacyclohexadienyl) ligand. Thus, the formation of **2** could formally be regarded as a redox reaction.



VdW-π-L (ΔE = −16.1) **TS-π-L** (ΔE = −8.6) **2** (ΔE = −23.5)

Figure S34 - Optimised key structures for the formation of **2** from **1-π** and **L**. Energies are given in kcal·mol^{-1} relative to the sum of the electronic energies of **1-π** and **L**.

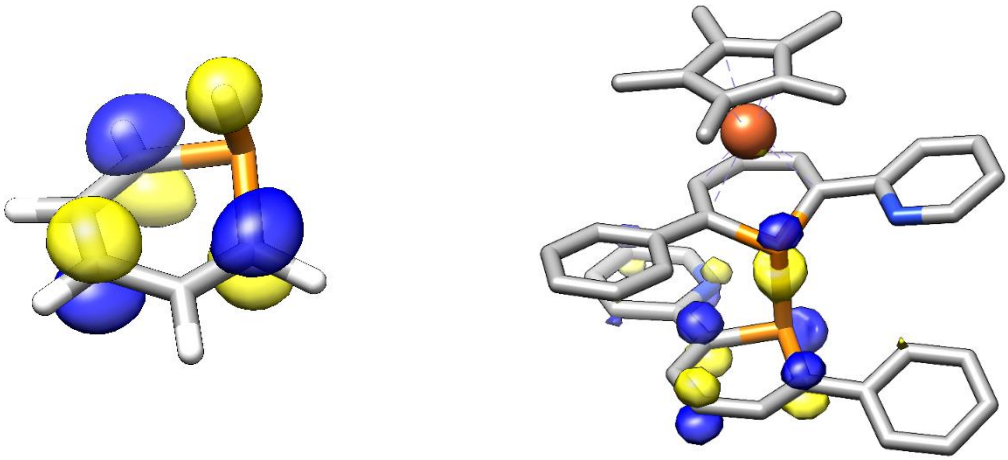
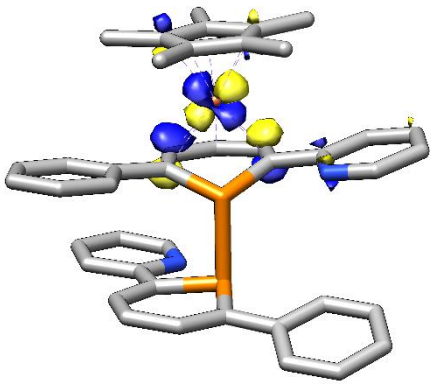
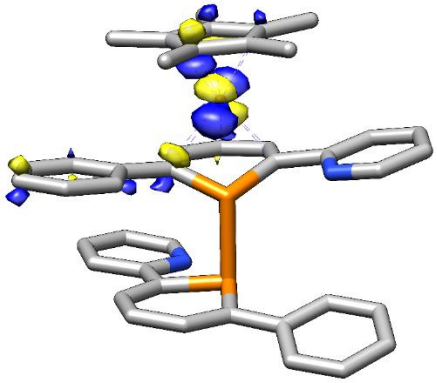


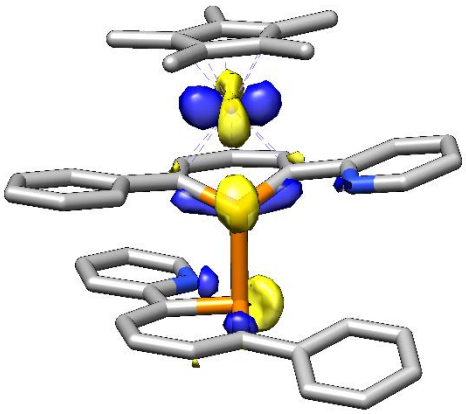
Figure S35 - Comparison of the HOMOs of the phosphacyclohexadienyl anion (left) and **2** (right), obtained at the BP86-D3BJ/def2-TZVP level. Hydrogen atoms of **2** have been omitted for claritiy. Surface isovalue = 0.06.



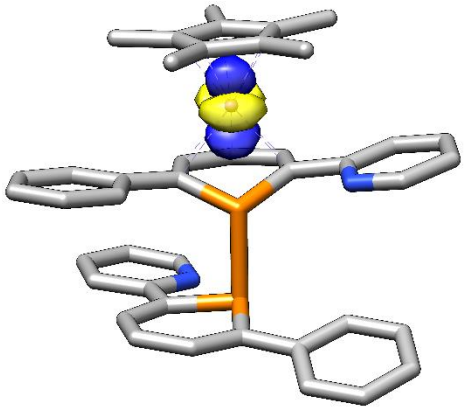
LUMO+3



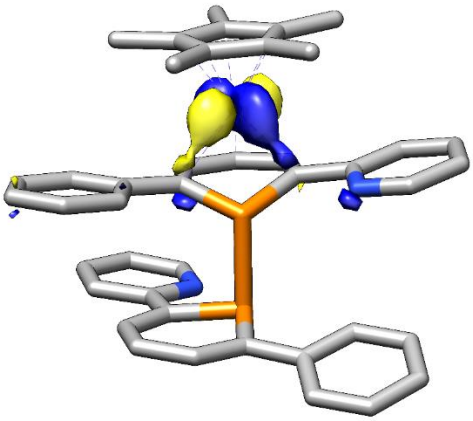
LUMO+1



HOMO−2



HOMO−3



HOMO−6

Figure S36 - Kohn-Sham orbitals of **2** with significant 3d character at iron (BP86-D3BJ/def2-TZVP level). Hydrogen atoms have been omitted for claritiy. Surface isovalue = 0.06.

S6.4 Reactions of 1-π and 1-σ with CO_2

To account for solvent effects, final single point calculations of the calculated minima and transition states were carried out with the CPCM[19] model for THF at the TPSSh-D3BJ/def2-TZVP level.

In the case of **1-π**, the first step of the mechanism involves the activation barrier-free formation of the van-der-Waals complex **VdW-π-CO_2**, followed by the exothermic formation of **3-π** *via* an energetically low-lying transition state **TS-π-CO_2** (+5.5 kcal·mol^{-1}, Figure S37). Note that for these calculations the [K([18]crown-6)]$^+$ countercation has been omitted for the sake of computational efficiency; they therefore do not account for any addition electrostatic stabilisation as a result of K···O—C interactions (as observed in the solid state for **3-π**).

In the case of **1-σ**, the first step involves the activation barrier-free coordination of CO_2 at the iron atom forming intermediate **VdW-σ-CO_2**. Subsequently, **VdW-σ-CO_2** undergoes CO_2 cleavage *via* transition state **TS-σ-CO_2** to form **3-σ** in a very strongly exothermic reaction. As for **1-π**, the activation barrier for this process is very small (+3.5 kcal·mol^{-1}, Figure S37), in agreement with the instantaneous reaction observed experimentally.

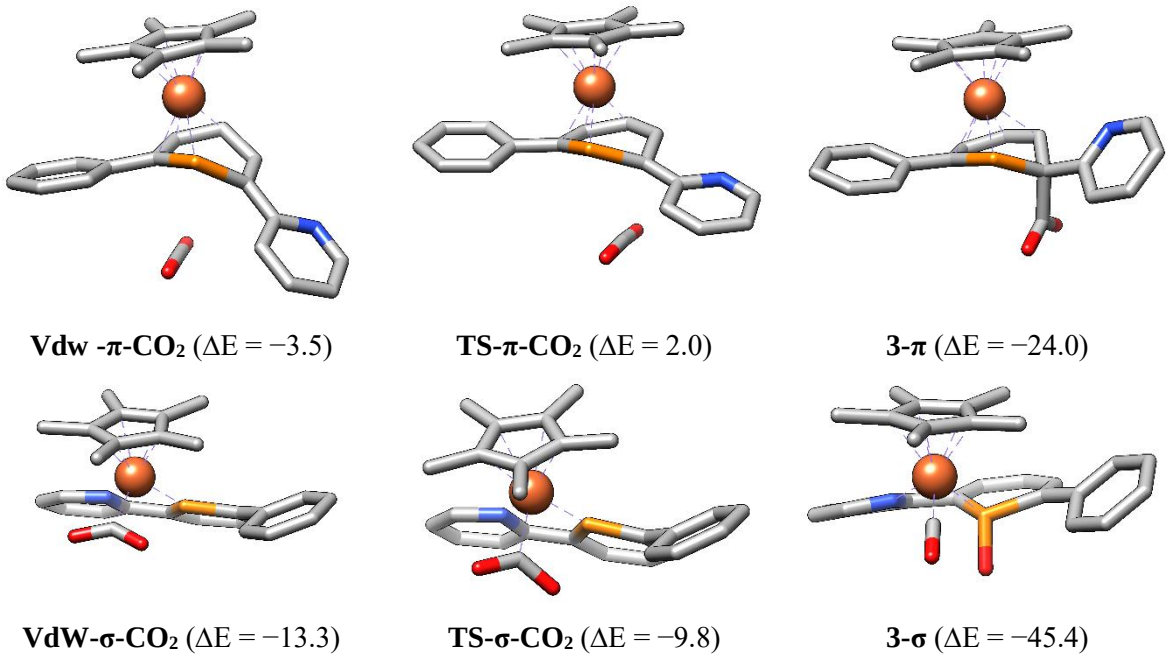


Figure S37 - Optimised key structures for the activation of CO_2 by **1-π** (top) and **1-σ** (bottom). Energies are given in kcal·mol^{-1} relative to the sum of the electronic energies of CO_2 and the relevant isomer of **1**.

S6.5 Electronic structure of 3-σ

Because the analysis of the Kohn-Sham orbitals of **3-σ** was not as straightforward as for **2**, CASSCF/def2-TZVP calculations with ten electrons in seven orbitals were carried out in order to obtain an insight into the electronic structure and bonding in **3-σ**. To aid convergence, the CASSCF calculation was carried out including six roots. The ground-state of **3-σ** is of dominant single-reference character (94% contribution of the ground-state configuration state function). Inspection of the natural orbitals of the active space reveals three lone pairs of electrons at the iron center (HOMO, HOMO−1 and HOMO−2, Figure S39) accounting for a $3d^6$ configuration and two metal-ligand bonding orbitals (HOMO−3 and HOMO−4) and their respective antibonding counterparts

(LUMO and LUMO+1). Additionally, the HOMO−5 resembles the HOMO of the phosphacyclohexadienyl anion, thus indicating the presence of a negative charge within the C_5P ring in **3-σ**. The bonding situation can therefore be described as an interaction of a cationic $[Fe^{II}(CO)(Cp^*)]^+$ fragment with a dianionic oxo-phosphacyclohexadiene ligand.

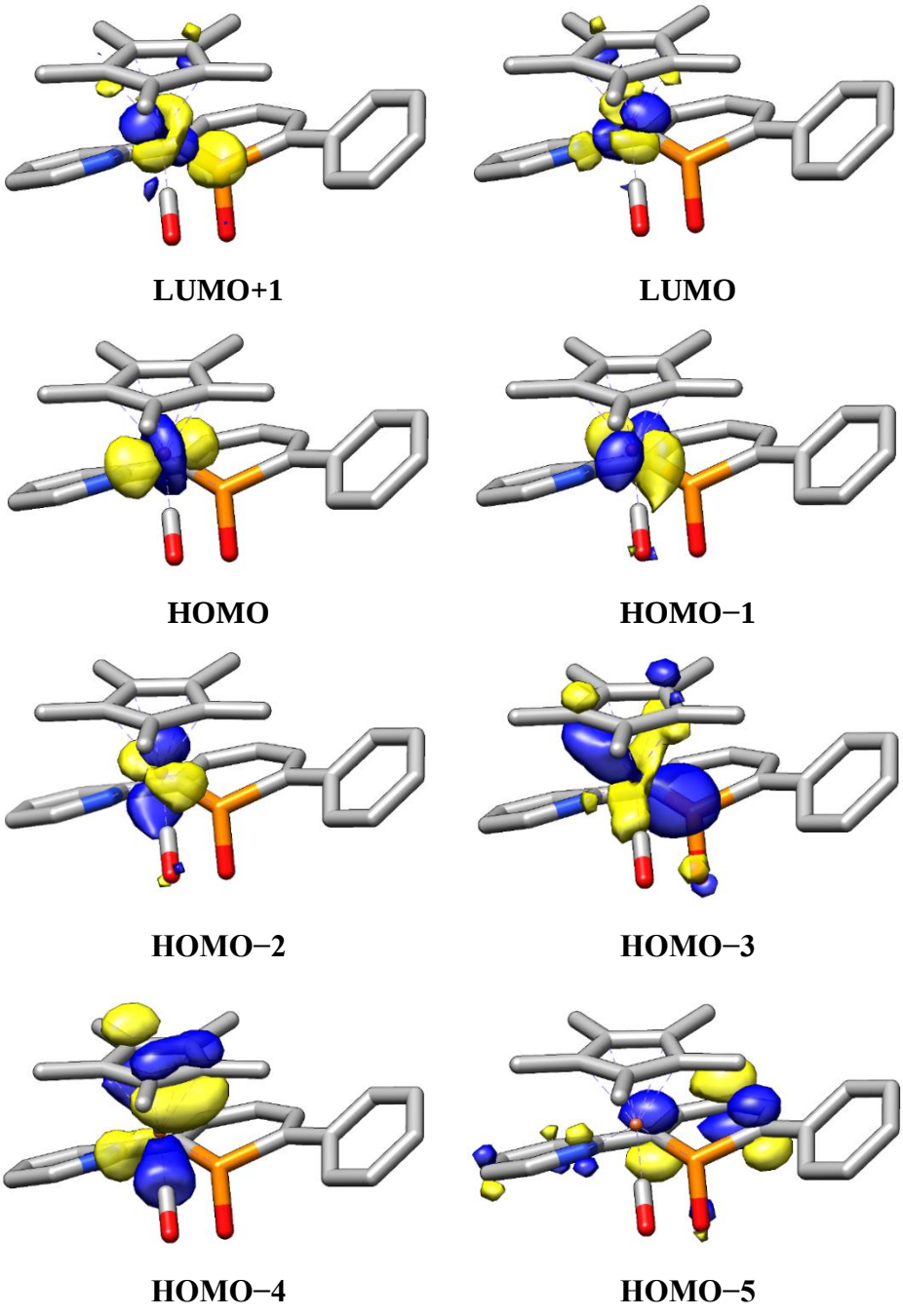


Figure S38 Selected molecular orbitals of 4-σ (CASSCF(10/7)/def2-TZVP level). Hydrogen atoms of the 4-σ have been omitted for claritiy. Surface isovalue = 0.06.

S6.6 Cartesian coordinates of optimised structures

$[C_5H_5P]^-$

C	-7.61943319559269	1.22409425547681	0.13533784859837
C	-7.64465161413261	2.59587319386719	0.30655806150595
C	-6.46424418962032	0.47009145181158	-0.19230249875865
C	-5.17738486014462	1.04326799732260	-0.03165911543904
C	-4.92836447320168	2.39473921664987	0.12075910803984
P	-6.23079634688711	3.61428255628433	-0.18313646659172
H	-8.53726116116016	0.65629539320926	0.35526367967173
H	-8.52398638132399	3.07923019770116	0.74215399853911
H	-4.33148673543528	0.34486561603294	0.06765676734310
H	-6.55098221652423	-0.61550683348109	-0.28501854811743
H	-3.93687915667162	2.73953775574318	0.42846629093591
H	-6.34139966930567	3.47491919938217	-1.64968912572718

L

P	6.04122337926595	24.63408168499444	10.97933198060370
C	6.08960118303451	26.38102873225077	10.75022889366670
C	5.86394350235381	27.01786074063859	9.52198000089409
H	5.94173500748529	28.10846159769303	9.48776660296668
C	5.58319435084327	26.34316947281555	8.33494039956308
C	5.49794456569007	24.95320382160534	8.25123074122980
H	5.30488939279188	24.51332433392341	7.26873401066420
C	5.68871142267727	24.09357247778719	9.33797204441012
C	5.57916845761728	22.62759068525408	9.15123071191018
C	4.72646922398813	22.05698178249720	8.18793551438395
H	4.09772039713966	22.69146888071547	7.56349075890103
C	4.67201228383245	20.67090387157797	8.06514324487574
H	4.01602743110801	20.20974644533032	7.32525654825285
C	5.45558524081305	19.88503800485405	8.91149915598559
H	5.44375709874828	18.79671836851895	8.85008926594723
C	6.25604186692401	20.53456912567334	9.85513931531024
C	6.36810393266843	27.20464479007647	11.95036446841172
H	5.44717675621914	26.92807203796902	7.42378818398789
C	5.66160778644344	28.39942471765804	12.18383860842483
C	5.91647771486721	29.17118253374181	13.31686695234687
C	6.88192929376833	28.76510071451661	14.24259996517816
C	7.58856340350576	27.57932192690138	14.02585573436544
C	7.33467792257424	26.80721372213552	12.89250019850521
H	7.90164320401353	25.89157814763470	12.71613940404032
N	6.32603590454227	21.86411741452478	9.97879964270533
H	6.87779545221354	19.95805821272706	10.54645969983165
H	4.88436086533311	28.70664610395373	11.48235146563765
H	5.35129726149673	30.08954095601434	13.48311094968027
H	7.08159905106075	29.36934419713680	15.12843577416666
H	8.34813664698058	27.25666449888003	14.73934976315279

1-σ

Fe	3.72592401196239	13.42136286396835	13.05841048003086
P	5.50741856996626	12.40791601565484	12.77336220237265
N	4.45241524290449	14.58019982644907	11.69500525801739
C	7.96462190229615	11.14102547354741	12.95606485756925
H	8.56915206010328	10.28075232362786	13.26636731763079
C	5.80641481923798	14.54496225852838	11.26442046771582
C	6.30886722935948	15.51378447711643	10.37749995200805
H	7.36328550097966	15.45172990411800	10.10107369759245
C	8.61257994180999	12.14895602150099	12.21596825323474
C	7.94006245125282	13.23602191264865	11.64947452229262
H	8.53515965993015	13.95662339415390	11.07573608031956
C	6.04969205736462	9.90197877564039	13.92441084653583
C	5.50499492078208	16.50825541721105	9.84398734262572
H	5.90390161046380	17.24814981645005	9.14910467590880
C	6.60301295011311	11.08955062401833	13.26070281068218
C	2.06852235235543	12.38475414999738	13.72796025904286
C	6.56911992103160	13.45528404035571	11.78893669337016
C	2.98081276905463	12.65666820618897	14.81297457402019
C	3.15405039715675	14.08461905644085	14.90286003940619
C	4.83456319370247	9.33506960098914	13.48305128108727
H	4.31361889190257	9.81972260698764	12.65523824027235
C	3.67656117724735	15.53917517058476	11.08757962846528
H	2.62314082720625	15.50252095239016	11.34565220829595
C	4.31144986189041	8.18986829728283	14.07885684681174
H	3.37135936815636	7.77312205640991	13.71040867036698
C	2.30985713851632	14.68902834537661	13.90626746829831
C	1.64324555980373	13.64169246323483	13.17061768004312
C	4.13596313835306	16.49196859562335	10.20490336036189
H	3.42638997780370	17.20825812544575	9.78736340357240
C	6.71017006174308	9.26860520477863	14.99909926502537
H	7.63453278865358	9.70764137059168	15.37903089264052
C	4.97964493548110	7.57430956223483	15.14498562727098
H	4.56431678037425	6.68346009548213	15.61936254361677
C	2.11383635004085	16.16705541338921	13.76137267678583
H	3.06235146947623	16.69551462891634	13.57668379258487
H	1.67072971472238	16.59054152389485	14.67931428666458
H	1.43629224333642	16.41405881993866	12.93252660351801
C	3.58157681527615	11.66108258655962	15.75583659653268
H	3.58984112836042	10.64899607456343	15.33469526972583
H	3.01723092338621	11.62411800589632	16.70577162028925
H	4.62376025244625	11.91323213049187	15.99862602858001
C	6.18396301654359	8.12388323293657	15.59808025445408
H	6.71052148874602	7.66448735273890	16.43799462637624
C	3.96119197469626	14.81723702801862	15.92748433455901
H	4.82076387435136	14.21610210308666	16.25397150416272
H	3.36429959773181	15.06391193851799	16.82811354696823
H	4.35593206491193	15.76005496209445	15.52276601974220
C	1.55142316545978	11.03854484229403	13.32953550274087
H	1.40274959551542	10.97051456401285	12.24164636164965
H	0.58195927042286	10.81344541188779	13.81368058140783
H	2.25163750959263	10.24466763738927	13.61942752165738
C	0.59863817538809	13.81063038573668	12.11381759495715
H	0.72122631804818	14.74995394836136	11.55356499138391
H	-0.42320135351064	13.82443949026823	12.53957132469791
H	0.63885161773648	12.99147387278839	11.38086274489048
H	9.68525271836241	12.04756704118894	12.03925876916626

1-π

C	3.61125486582820	9.03918688569993	27.68565513128886
C	3.83569963790186	8.87868373420748	29.08701205164057
H	4.35892737111890	9.63073639780870	29.68484927774780
C	3.33951778876598	7.66820746531041	29.73171538270757
C	2.01123064442944	7.16390603046133	29.44649065062213
H	1.37111885610258	6.82209476473519	30.26988569633945
C	1.52754999379959	7.17775317644029	28.17129466438196
C	4.17902427921395	10.15283487453821	26.91445660588487
C	5.02441339761459	11.12580525431114	27.49721257345247
H	5.25112062903747	11.06634353469987	28.56183789207276
C	5.59210805828843	12.14880232204174	26.73905450222963
H	6.24256599877326	12.87961647420594	27.22629102557377
C	5.34549844340157	12.24055611051254	25.36472125392829
H	5.79402174755969	13.03927165067001	24.77100295255508
C	4.50652497248837	11.29132287965869	24.76932659912789
H	4.29422308329745	11.34653506996670	23.69877312596449
C	3.92881866711998	10.27674669202870	25.53031800571930
C	6.54766619613959	7.46215079102878	27.18740790679346
C	6.73795837305055	7.48257915239320	28.60905806482385
C	6.11753747310611	6.30206654385060	29.15339893734285
C	5.54262332482801	5.53801189059696	28.06762681125098
C	5.81417722031901	6.26948349037433	26.85023331323779
C	7.03710614385524	8.48850287239565	26.21658359188551
H	8.05012209039953	8.24760598430484	25.84677669819766
H	7.07369096780055	9.48937141961007	26.66900135096448
C	7.46280776687605	8.53905577966933	29.38269506232281
H	8.53754908268238	8.30604903309117	29.49888790276883
H	7.04253638759369	8.65575111006754	30.39247800415420
H	7.38916909389704	9.51422521220043	28.88020554911778
C	6.10592904099172	5.90988662883733	30.59728703427114
H	7.00417208568400	5.32519869017604	30.86707633123483
H	5.22495570132331	5.29726937819093	30.83407650044078
H	6.07877557447794	6.79190017745350	31.25423151992198
C	4.88130900455148	4.20019045518585	28.17308792384076
H	5.60597610873259	3.36596765559566	28.09878201867071
H	4.13575358924854	4.06741353625465	27.37710731727004
H	4.34968992661270	4.09609969295551	29.12938847738430
C	5.45035460796757	5.83503312990096	25.46534088571024
H	6.26559421160988	5.25344051034710	24.99754909052807
H	5.23737000792554	6.69833934739815	24.81957089840732
H	4.54612710791980	5.21184322149256	25.47176895626531
H	6.37206990346448	8.56253381860202	25.34513433630705
C	0.15859846923210	6.84249591547721	27.82732610656442
C	-0.33036561042876	7.04136039754358	26.50864320510524
H	0.34767287327893	7.45727753802423	25.76133313959421
C	-1.63978230579314	6.70894145656353	26.19428100153755
H	-2.01830178088633	6.87010222160379	25.18163495944226
C	-1.90690740604016	5.99110774914719	28.45828744993659
H	-2.51660911748483	5.56411306885656	29.26518925950920
N	-0.65614129971411	6.31218111901965	28.79003554541147
Fe	4.69824576616723	7.38199706574192	28.15876673419968
C	-2.46629510269177	6.16476894236064	27.18654775284141
H	-3.50155532690195	5.88416064880012	26.98708225360933
P	2.81682056658736	7.58708804890620	26.89683759769819
H	3.69136504792863	7.52454772404499	30.75869674819384
H	3.26651580094814	9.54155526464030	25.06805637200694

VdW-π-L

P	0.49711555235886	10.61636542853112	26.83776075559199
P	2.16936279076416	8.60449430257576	27.60384033314439
C	3.44522299724362	9.78465068401888	28.20132369517420
C	4.07112283755185	9.43143034559252	29.42985968453436
H	4.91077633138880	10.00635606338555	29.83097961070587
C	3.61510570885541	8.22531789208598	30.08692908139276
C	2.19991346672340	7.90211025678621	30.20142623606057
H	1.85424001015765	7.42605767368927	31.12935495477637
C	1.32706604503570	8.11480211909985	29.18081744191446
C	3.88252965857899	10.89328807011530	27.36549741267833
C	4.64776674935856	11.96910245222644	27.86907133079094
H	4.89888000465057	12.00322604135567	28.92893241149860
C	5.07109273504993	12.97567681978939	27.00971693401019
H	5.66728294538504	13.80795113975535	27.39094458617448
C	4.71375097339717	12.91774478915427	25.65851997086862
H	5.01641890555527	13.69048545382692	24.95092266954224
C	3.93869914509011	11.83165682071324	25.24357803932552
H	3.61475441871584	11.74422314393263	24.20049010756221
N	3.54236137207733	10.84774512919366	26.05297971046353
C	6.02877319928328	8.07685539513139	26.96394175119096
C	6.32343172231325	7.44700217507229	28.22260524354126
C	5.47850646922049	6.28156891473190	28.34680085555718
C	4.66009013150021	6.18731109238386	27.17397400717873
C	4.99740781579732	7.30673793382676	26.31340132001462
C	6.69735200790049	9.29311086055484	26.40612630240128
H	7.61021115239678	9.03321894594030	25.84040526874349
H	6.98794019626113	9.99577209193131	27.20080126009962
C	7.33046615577773	7.90913763059800	29.22731796478942
H	8.31143217038343	7.41873690679997	29.08916449225793
H	6.99964254173955	7.69343222462345	30.25410110848010
H	7.49225748177251	8.99440776128242	29.15442853950052
C	5.47733317969230	5.32007876170581	29.49380735798895
H	6.20413071039328	4.50271790370325	29.33501552524084
H	4.48613987886918	4.86620224306927	29.62956408917092
H	5.74325948166598	5.81830674066527	30.43682089351860
C	3.67195874282299	5.10631830442801	26.86720175688858
H	4.14485441577168	4.25202751638427	26.34742266681351
H	2.86449174229678	5.48320110882488	26.22539827874690
H	3.20401122849227	4.72372243336558	27.78496306378821
C	4.40508685926055	7.59553639923325	24.97073646234446
H	4.99672903469775	7.14329971491825	24.15427691522955
H	4.34803654358461	8.67897939976458	24.79762055213735
H	3.37960525123744	7.20939077024882	24.89759223157736
H	6.02702405929022	9.83527529843775	25.72679339435221
C	-0.07684108570116	7.72432190879349	29.22287023451090
C	-0.74100222027560	7.31459642233350	28.04715360490012
H	-0.20613132073534	7.36722140256427	27.09733301563153
C	-2.05654249420576	6.86119934137657	28.07899631495702
H	-2.54171415077694	6.56261676908487	27.14782560215425
C	-2.12353944732911	7.21724678506520	30.46311207184397
H	-2.66478432914089	7.19567749479491	31.41243462176050
C	-0.80691602083796	7.67303747992098	30.43277666880154
H	-0.32864248573077	8.02171391719255	31.34894782047629
Fe	4.32336391909208	7.97448519765756	28.11788649659384
C	-2.76019697124184	6.80348288898467	29.28679356382442
H	-3.79507425609783	6.45709319756016	29.30970151838014
H	4.24546827154862	7.87266825803716	30.90921190171951
C	-0.66211839641078	9.97115691985447	25.63199573007212
C	-2.00203620201338	9.70769338182312	25.91442432849794

H	-2.62237570606283	9.28238964744869	25.11825935556124
C	-2.61807362991814	9.92023999969356	27.15215953587048
C	-1.92559061208095	10.39100148615935	28.26335984281686
H	-2.49185370983128	10.50445928578196	29.19197797638945
C	-0.56646966485557	10.71621891613624	28.26784943945103
C	0.10815622475899	11.12215196194840	29.50681632709908
C	-0.44169607009093	10.89769731727144	30.78992787985946
H	-1.41708592973719	10.42594070939499	30.89247322538149
C	0.30132593517683	11.21766155591457	31.91868001285393
H	-0.10376244962782	11.02191035352115	32.91402266171674
C	1.58031097081056	11.76211193341840	31.76509629929887
H	2.20552074988386	12.00925701115052	32.62393980503279
C	2.03846427944343	11.97584879022394	30.46320683211315
C	-0.12224476371229	9.71552741169307	24.28410213274723
H	-3.67393815726708	9.66910187596279	27.26153064770476
C	-0.94571608084070	9.67582113829348	23.13685265155387
C	-0.41831535887895	9.41771145100083	21.87316650613745
C	0.95459383472104	9.19653355072379	21.70996022938171
C	1.78690466116713	9.24693323488604	22.83157356349077
C	1.26233722700487	9.50346868375518	24.09859063086513
H	1.93801097872776	9.54792786022563	24.95620416381893
N	1.33770327948838	11.67715873632031	29.36967324267267
H	3.03045373753518	12.40475621000643	30.28798559974700
H	-2.01358854707542	9.87774411042299	23.23499538570116
H	-1.08194725031173	9.40053168241650	21.00548345817030
H	1.36814071713186	8.99544108067765	20.71977100038582
H	2.86032970393816	9.07674548705494	22.72726083229182

TS-π-L

P	-1.84025253592688	1.89966658445788	-0.64937669915608
P	-0.17810638971946	0.02296333809118	-0.32689675623801
C	1.22614304770461	1.01147888682122	0.30510774825981
C	1.71019996524247	0.95585298288477	1.64190424342553
H	2.55008962468559	1.57688714007989	1.95756408448759
C	1.19290392038820	0.00016364172709	2.55442386251500
C	-0.02949236931069	-0.70937949464310	2.36511963088646
H	-0.30070547574936	-1.39513510617964	3.17580212477697
C	-0.85692101134675	-0.66516340703832	1.25557985202312
C	1.82784734521874	1.91637540760485	-0.67433102914526
C	2.73641880820380	2.93789273984320	-0.31904458986509
H	2.99767886721995	3.09849585285796	0.72580635320839
C	3.27863208315214	3.75092574570667	-1.30625008560980
H	3.97999974730203	4.54397366172556	-1.03807721134293
C	2.90168681575002	3.55531756071013	-2.63940964341537
H	3.29164061594340	4.17988721710608	-3.44378539489234
C	1.97683023813809	2.54402839523621	-2.90460457059005
H	1.62168366687610	2.37013266916243	-3.92546299566279
N	1.45686762079382	1.74730217414327	-1.96709538662369
C	3.66372875932722	-1.13230121979826	-0.24752754483301
C	3.79676046181040	-1.57178722966353	1.12004458941577
C	2.82056623229272	-2.61102597676736	1.35200871369227
C	2.07123901356108	-2.79656507385008	0.14345057892906
C	2.59472973893957	-1.88432096751311	-0.85344081956950
C	4.50908720978601	-0.10738381070053	-0.93318187816255
H	5.42613585663187	-0.55725127103572	-1.35344355310999
H	4.81686825796444	0.69157684851898	-0.24333102124774
C	4.79695575530129	-1.06969752966020	2.11212288026164

H	5.71803722475090	-1.67986920620723	2.10984515831253
H	4.39252472425322	-1.08995685706595	3.13444886933246
H	5.08766240935270	-0.03301059448576	1.89077378812172
C	2.62548607183115	-3.36278015432289	2.63122765245574
H	3.25239359338121	-4.27197965353302	2.66529981347660
H	1.57957234117302	-3.67585018307939	2.75233852709372
H	2.89007578959846	-2.74686333737452	3.50220495755292
C	0.92754595983517	-3.74215219686597	-0.04739251789096
H	1.27295837597618	-4.73608053909739	-0.38450415436767
H	0.21900926430040	-3.35791618274989	-0.79211380838577
H	0.36182098604990	-3.88040459010008	0.88401902497657
C	2.12105724026222	-1.74512411687076	-2.26431400300757
H	2.77264199087238	-2.29803423503092	-2.96358710742642
H	2.09546247117041	-0.68954148645239	-2.57050843761744
H	1.09777954423565	-2.12478620069294	-2.37678645421374
H	3.96347369828061	0.36927055331820	-1.75798997398898
C	-2.04822082056521	-1.48918498846527	1.18964302966862
C	-2.61034337169049	-1.87853812080885	-0.05027795062624
H	-2.15814020820951	-1.51168533436097	-0.97296282516187
C	-3.72811571696103	-2.70560936736857	-0.11561301929010
H	-4.12955960897185	-2.97868196710248	-1.09399763624387
C	-3.83213684598372	-2.76335398823616	2.29022865128432
H	-4.32215213869709	-3.08157902129616	3.21402131307615
C	-2.71232964278108	-1.94262840916992	2.36132845086167
H	-2.35686895039074	-1.60808483207132	3.33733040086235
Fe	1.91794693866444	-0.84752349103311	0.77802635335870
C	-4.34763019462065	-3.16944161561181	1.04967778779078
H	-5.23315509722659	-3.80489009983582	0.99605425529605
H	1.70496598442521	-0.12354921570229	3.50988535898126
C	-3.04635403851182	1.20472181686447	-1.81275329167802
C	-4.26656452983946	0.67599250308431	-1.42311785253698
H	-4.91765846200895	0.26484855293403	-2.20264746022139
C	-4.71360527417937	0.56527011512823	-0.09365634090532
C	-3.96832594812503	1.00825672186765	0.99191378473848
H	-4.40959140102715	0.86728404880305	1.98251192119644
C	-2.70478650782430	1.60464393045225	0.91124874413548
C	-1.99192081366354	2.04454180018972	2.10166247149668
C	-2.37199797158421	1.69242125545472	3.42375553897772
H	-3.22173523902207	1.03061054852049	3.58985215964470
C	-1.63033653706320	2.15218143937866	4.49932405309679
H	-1.91114290962333	1.87022965835204	5.51687821053843
C	-0.50798856305367	2.96631325912040	4.26812921586939
H	0.10599084190963	3.34515795167522	5.08619841575707
C	-0.19256392496717	3.25389917764177	2.94055412040329
C	-2.68366446668895	1.22272615249953	-3.23764863841371
H	-5.67417573400061	0.08449034661940	0.09474754406395
C	-3.65744746336042	1.36082318611870	-4.25312631301453
C	-3.30895307358275	1.34224356924698	-5.60218990766841
C	-1.97084260719827	1.19192450928089	-5.98664286964511
C	-0.99251251803042	1.07007804637826	-4.99473894101357
C	-1.33662047826472	1.09046564159638	-3.64289129238327
H	-0.55361362600450	0.97974643931641	-2.88998168640168
N	-0.89332263953295	2.82231331224185	1.88967396794577
H	0.68620313802967	3.86543729666940	2.70317669355667
H	-4.70059813816776	1.51151466740943	-3.96966093096495
H	-4.08583531968528	1.45935145460788	-6.36161450297663
H	-1.69656217631557	1.17755908744389	-7.04330860287386
H	0.05554949889052	0.94187018295010	-5.27562919742235

2

Fe	10.21225277107162	22.22869978882484	10.63094430610991
P	8.30989992011892	24.09913469167970	11.50075351167609
P	5.95932602564988	24.09248808631658	11.43407342427005
C	8.73218054493100	23.61855385968920	9.77896359991731
C	8.63325830377453	22.29124847807736	9.29763145640670
H	8.70968060544747	22.08962753262971	8.22847892943161
C	8.52679224012926	21.15366274607740	10.13368376178608
C	8.65214652063285	21.24658668462587	11.53984182121186
H	8.74007945166115	20.30577929780162	12.08754441004464
C	8.80026934894637	22.49115672241850	12.21436965672426
C	8.93329644774081	24.72215921658984	8.82082616399602
C	9.08585543145161	26.05196332221342	9.27564577854108
H	9.05463484811524	26.23943868563548	10.34952516837905
C	9.25479909512739	27.11324634129383	8.39038048209008
H	9.36568432023122	28.12437858493951	8.78687973824632
C	9.25283234640063	26.89671418943704	7.00947937689258
H	9.36944117632271	27.72994539282321	6.31412105415316
C	9.06702752781027	25.59269161941697	6.53387575033555
H	9.03428510708204	25.40149348641463	5.45883015105550
C	8.91536157205639	24.52834696204324	7.41925645497677
H	8.75093851563316	23.53494435097977	7.00666601286090
C	9.07053840795360	22.50389496568550	13.66133072530653
C	9.26405880986509	21.33842273903535	14.43791051161527
H	9.22423091557399	20.35210581970403	13.97813426800092
C	9.50716661033480	21.44873061872756	15.80238693584608
H	9.66350218640004	20.55099412687363	16.40434864932149
C	9.54052376745691	22.71850610927545	16.39176957799339
H	9.71737669099700	22.85024190181528	17.45997322078617
C	9.30928405101337	23.81763053449816	15.56308718854112
H	9.28312955837372	24.83089609704156	15.97656576579391
N	9.08574416150338	23.72519934893959	14.24981422064261
C	11.96382221311670	22.64999516665483	11.67175019960462
C	11.85434571735393	21.23996080932407	11.38362654275908
C	11.76598598038297	21.08582538893437	9.95436653932992
C	11.81432002948907	22.39785929279085	9.36284811562439
C	11.93804749192795	23.36339854664834	10.43109081399851
C	12.11659577631018	23.28234677325228	13.01630693345565
H	13.16629739926072	23.57462527733222	13.19005311076951
H	11.81938036766481	22.60165511759273	13.82390820361410
H	11.49100387833699	24.18136668329550	13.10422429034861
C	11.91475567046268	20.13042037271973	12.38470045949007
H	11.58292605482239	20.46885196651073	13.37419719331796
H	12.94499439414535	19.74750588748704	12.48969600762222
H	11.27852422966795	19.28391020684581	12.08922211522126
C	11.68579441205569	19.78985899239584	9.21102500000490
H	11.19200213236942	19.01387105508910	9.81212492936632
H	12.68951728052344	19.41483881263131	8.94458689162407
H	11.11596180040122	19.90068360285624	8.27825534319063
C	11.82895103312372	22.70850949731388	7.90107731512687
H	11.27798344518522	21.95438508973933	7.32227439520180
H	12.86334147240442	22.73178395954218	7.51572027009964
H	11.37023192108382	23.68272414878007	7.69161973506697
C	12.06598730059051	24.84320385676144	10.28640162296955
H	13.12485599933686	25.15096583747630	10.33699516797297
H	11.52191664381611	25.36369312842289	11.08692148960892
H	11.65405037156468	25.19596609621826	9.33351300505838
C	5.76031473847259	25.76931639411443	12.15731436626220
C	5.83103905166302	26.91050760419562	11.37846706707288
H	5.81847492310239	27.88243490239997	11.88541910286908

C	5.92756756994553	26.94094648390844	9.97104105223004
C	5.86719241108673	25.79683405381315	9.17960602511351
H	5.86367880238836	25.95586605071662	8.09673700985306
C	5.80529625145249	24.48153214934067	9.65139459196476
C	5.64017942925432	25.84120982270031	13.61281437491146
C	5.95635627529247	24.72324640739773	14.42467215274081
H	6.26913861065388	23.79652221429527	13.94343255710898
C	5.88917935432005	24.78041771756591	15.81497111892917
H	6.15841758105518	23.89612808496447	16.39724204544693
C	5.50188340306142	25.95694199877469	16.46390278788694
H	5.45259067950195	26.00438843287855	17.55351042856136
C	5.16529925560141	27.07305817223115	15.68339967370428
H	4.83869721544852	27.99738439281107	16.16709969760085
C	5.22609218123100	27.01453165757917	14.29455543929988
H	4.92739584096762	27.89011271546727	13.71624316823920
C	5.71897787900715	23.34716612478292	8.76465021682519
C	5.82541693096659	23.44758213698386	7.34336432663197
H	5.94589147249910	24.42135310563240	6.87110031921298
C	5.81378816022658	22.30542096748010	6.56269985015036
H	5.91806113439616	22.38892878311615	5.47761649445213
C	5.67289796489128	21.04464966051523	7.17107340596703
H	5.65643552583169	20.12063656192512	6.59155763914159
C	5.54532657648237	21.02943452750353	8.56340552928381
H	5.42355003471721	20.07405671439476	9.09043024927284
N	5.57506815290018	22.11109840712871	9.33991694908458
H	6.00307432620971	27.91049205424665	9.47622171251203
H	8.48649797216979	20.16775383299674	9.66867288427009

CO_2

O	-6.60332940005156	1.90052897740132	-0.00000000264688
C	-5.43292683925670	1.85008065184282	0.00000000529375
O	-4.26252376069174	1.79964037075586	-0.00000000264686

VdW-σ-CO_2

Fe	2.91506937427901	12.03761676589542	11.71132815048738
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N	3.58101392353033	13.84104903516326	11.43908047222587
C	6.97384006045567	11.18768610200906	14.06755982454969
H	7.62842545684727	10.45741996695445	14.55623618101538
C	4.69185285488964	14.35965477588063	12.11218145065662
C	4.95400152694683	15.73745226523233	12.11167264842955
H	5.81913485359461	16.10233045040087	12.66730357574632
C	7.29613567266747	12.54467393568061	14.23035921630320
C	6.59651928730910	13.58156191744265	13.60299593533825
H	6.92002652444875	14.61011190536132	13.79911359286915
C	5.75415859857014	9.22142107951128	13.12328098317932
C	4.14141257870896	16.61977018906468	11.40923073710652
H	4.34279337611113	17.69194285421748	11.41424537622335
C	5.92965125458595	10.67428815012657	13.29075367436407
C	1.05051977710566	10.98932335395474	11.24600178807244
C	5.50333157296352	13.36272850201147	12.76733416541198
C	1.74658988421250	10.36213155422557	12.32588957670813
C	1.90091119181636	11.33402280850994	13.38400474222862

C	5.32527428530807	8.69456298135441	11.88626712304251
H	5.05815094490507	9.37151911694905	11.06756449656322
C	2.86568241249067	14.71082415048875	10.67050766612572
H	2.13609236398676	14.23850113657486	10.02059737949864
C	5.20424020007035	7.31792064038975	11.70643573855699
H	4.87101184284879	6.93895608290193	10.73845198480673
C	1.32544436924973	12.56812927947231	12.93165456402186
C	0.79551016943479	12.34978271029655	11.60255177332506
C	3.08826165244912	16.07761320174674	10.65141791618134
H	2.46128665598992	16.70629876494466	10.01756232954228
C	6.02193914603173	8.31811686614762	14.17295062813469
H	6.31120977075130	8.70904197492446	15.15048013516069
C	5.48948482514096	6.43086039480131	12.75014660950437
H	5.38536688744098	5.35374543548549	12.60556280811654
C	1.26478887981874	13.85226976550800	13.69603597977122
H	2.07767461124135	13.91141481686829	14.43329471350814
H	0.30872769218668	13.96246314877646	14.23845027269546
H	1.36792594935871	14.71924684482256	13.02665086445770
C	2.10790719256539	8.91469132761268	12.38526270679506
H	2.50420731980277	8.57509377145833	11.41967654577394
H	1.22649211035141	8.29467672417743	12.63095517546906
H	2.87771052483301	8.71626716294510	13.14116515142021
C	5.89293058573302	6.94128307666253	13.98852471217716
H	6.09641890102428	6.26309506362679	14.82049197655864
C	2.47695132691017	11.06329137309089	14.73947466750421
H	3.27358617158084	10.30781736879777	14.69357077144267
H	1.70289524277102	10.69114422009256	15.43441880753673
H	2.91511985255239	11.97052953510036	15.17827121507038
C	0.52502915135889	10.29692591394056	10.02835285493803
H	0.47299142138064	10.98332128441680	9.17391258160363
H	-0.48947588754974	9.90089553105803	10.21881318528188
H	1.17454906987997	9.46176641535396	9.73991560655683
C	-0.04075989678452	13.29562421371610	10.80104085311612
H	0.07076762371514	14.33153038219108	11.14742259228973
H	-1.11211957380265	13.03446049382925	10.87616006351614
H	0.23405671082369	13.25987837825828	9.73619977226587
H	8.15253505360587	12.79729971192003	14.85825359188132
C	3.20091851853001	11.47585559730916	9.66862498558332
O	2.80957746600907	12.35079709671019	8.88345476598036
O	3.68264249928746	10.34064242437345	9.54261506235651

TS-σ-CO2

Fe	-0.49718521136388	0.69118464090412	-0.26414529953450
P	1.13854470183591	-0.53977611292608	-0.49746368646056
N	0.45092743437057	1.80029275998367	-1.51930426620480
C	3.31993290291312	-2.19470182124939	-0.33911590426194
H	3.76313794323342	-3.14936353085290	-0.03407265910560
C	1.79240843694679	1.60213566993688	-1.86715908135270
C	2.46747965307120	2.52832039114831	-2.67025331514226
H	3.51927457929676	2.34884076130426	-2.89732375639593
C	4.14240336443287	-1.29209626796975	-1.02736385618489
C	3.67956038816052	-0.07363186362813	-1.53533697195728
H	4.38980136175576	0.55463297663249	-2.08447375090246
C	1.18655977134097	-3.11162987100933	0.57785931435764
C	1.81300423500351	3.64005178481300	-3.19528443348794
H	2.34204446297256	4.35613009890647	-3.82523294186827
C	1.96014254589585	-2.02336047618367	-0.04914480985311

C	-1.30973551125895	0.03621988379673	1.56969608474623
C	2.36978426922292	0.37098924079153	-1.36370832894926
C	-0.60655067618633	1.27885434460138	1.77930034813482
C	-1.23483281932159	2.27268412462745	0.96837974526377
C	-0.07285057442954	-3.47111959651078	0.05584898595611
H	-0.45311075537625	-2.91850596193579	-0.80915692120890
C	-0.19296852553633	2.83612729848063	-2.13247988556071
H	-1.26790868301084	2.85987987038839	-1.97958332531031
C	-0.80141155792306	-4.51367815764939	0.62790517332397
H	-1.77297966620491	-4.78039652742913	0.20649987937261
C	-2.32908444273281	1.66186689309975	0.25674032372367
C	-2.36509002488708	0.27094670505321	0.63005283414118
C	0.43987041178136	3.76962777448572	-2.93629756781297
H	-0.15079891259065	4.57359044727612	-3.37725172048806
C	1.68234554904233	-3.82511609437339	1.68531680411797
H	2.64482109018478	-3.53689501856240	2.11339939500082
C	-0.30202381502390	-5.21338509595002	1.73219661032194
H	-0.88100870653248	-6.02248491689699	2.18184872564400
C	-3.32455579410074	2.33708777868992	-0.63167724987470
H	-3.07686386932608	3.39858317915003	-0.77972971260638
H	-4.33976327502274	2.29866570297354	-0.19929637986542
H	-3.35120159015558	1.83524048536542	-1.61291037807434
C	0.54437541971835	1.48228511923889	2.71542505293360
H	1.13178545230088	0.56030908669787	2.82358981712371
H	0.20687598824767	1.78249210433105	3.72523901159996
H	1.22799133225480	2.26143738048757	2.34958541010425
C	0.94570062072724	-4.86364441452023	2.25775556740760
H	1.34230371823344	-5.39466758621399	3.12607792288743
C	-0.84826280238523	3.71599429956680	0.91998735964102
H	0.19498237091940	3.85721725603096	1.23441446591797
H	-1.48523515068378	4.32163838151033	1.58766886096318
H	-0.94009454316783	4.13597803591509	-0.09221663570264
C	-1.08419987365704	-1.21487760054279	2.35723278220987
H	-1.47698308485021	-2.09806036375177	1.84177429167790
H	-1.58627506893313	-1.14571862468210	3.33910115506432
H	-0.01796910976802	-1.40041879201622	2.54451685680522
C	-3.41201447427355	-0.71144640757476	0.20991814800905
H	-3.68190549167174	-0.55612893158281	-0.84266884851722
H	-4.32283080945922	-0.61074435895732	0.82828233735307
H	-3.04949854470611	-1.74320506431044	0.31255179456719
H	5.18218479063719	-1.57298430839313	-1.20325040267385
C	-1.13158937659014	-0.30191754921172	-1.94780934038847
O	-2.10425781362463	0.15304401214593	-2.57086873018150
O	-0.40720323974578	-1.31239517344901	-2.27358689844305

3-σ

Fe	3.06224880227793	13.63376368863445	12.66633579472992
P	4.94417997565082	12.48778618024030	12.19039644091891
N	3.90823031315052	14.85062955239089	11.33300552702012
C	7.15483730206376	11.86800649548408	13.75274340719305
H	7.71307768007056	11.15668818613633	14.37562039354153
C	5.29238168967496	14.99924972658188	11.37824305124658
C	5.87743848021579	16.10838759194239	10.71261786295936
H	6.95763255864843	16.24172112526299	10.77845858906782
C	7.86287345357895	13.02365260857137	13.34140035306659
C	7.29099596545121	14.03545877092082	12.57028327362768

H	7.88984569594440	14.93687383399069	12.38248470808490
C	5.20094615236106	10.35875635312195	14.02819330663885
C	5.10151263895140	16.97179136314238	9.96312508401464
H	5.56350665377522	17.81459695776789	9.44408799546864
C	5.84320597444965	11.53438708613444	13.45015612012388
C	2.42078339400496	13.08474123651810	14.59824317225480
C	5.97945458812168	13.97952814459456	12.08924533937765
C	3.55145142847345	13.95850317301839	14.75023703738949
C	3.23533510665128	15.20042533054524	14.12721659403768
C	4.17762700289758	9.66916951901130	13.33115807648762
H	3.92670601465927	10.00194026460454	12.32205051203635
C	3.17996098423776	15.66137673543455	10.54834765529707
H	2.11407332562768	15.43727622731211	10.51549269642594
C	3.52309758471230	8.58207356504359	13.90336294486907
H	2.73519896340214	8.07721530490018	13.33957851614477
C	1.88541189471500	15.13589737282319	13.61669981555304
C	1.38909254336086	13.82778256173248	13.90924656761846
C	3.71778880798917	16.73412951285123	9.84572633408725
H	3.07374745767908	17.36038481535809	9.22991610680531
C	5.53225134699276	9.88559872305070	15.32063548478155
H	6.28925506327262	10.41868187577341	15.89934868019718
C	3.86374569150206	8.13035374168871	15.18498698676991
H	3.34426546911585	7.28061474423624	15.63195839970229
C	1.11662923914606	16.27263632662169	13.02429012257877
H	1.77039349092114	16.95004442080966	12.45742405624767
H	0.62096019715547	16.87611464722479	13.80663405443931
H	0.33339157879523	15.91671851356124	12.33955708047649
C	4.80334286907281	13.68251474648200	15.51654761159176
H	4.90227014695567	12.61695107193268	15.74897511345753
H	4.79484027076293	14.24209309985050	16.46817922289731
H	5.69997534696981	13.97826857137563	14.95446495283383
C	4.87975596250675	8.79050081740472	15.88561614596367
H	5.15015584080190	8.46294544053321	16.89265829941275
C	4.14557142763844	16.38376721304843	14.05861761977828
H	5.19437096831770	16.06506671012024	13.99377908799813
H	4.03784208467519	17.01717063437719	14.95601230697821
H	3.93329390307226	17.01031679205638	13.18132182023270
C	2.23700056914072	11.74072916169182	15.22641242114314
H	1.66755032562286	11.06385898990139	14.57697521841057
H	1.68912628885111	11.83039576851574	16.18184095212951
H	3.19584020654315	11.25225773034084	15.43168992406067
C	-0.00080431825000	13.33607852588430	13.64940136176853
H	-0.43920885637432	13.81350258707559	12.76242163899170
H	-0.65812743785497	13.55223955404557	14.50910531151301
H	-0.01643558700861	12.25153496712694	13.48184018290999
H	8.89776174758339	13.13403090910028	13.67063553012828
C	2.19652886969382	12.60992434683899	11.57714154353527
O	4.92752045555454	11.70069550165734	10.88475990118654
O	1.52795440602684	11.92449058360323	10.89960569179834

VdW-π-CO_2

Fe	8.21324871075741	15.39579092730344	2.44799070725311
P	6.15870594528159	15.53124944418308	3.38179717801195
N	5.66337265380671	18.68303068680170	6.04985374551191
C	5.37199293708823	17.56371648694024	5.32031950120531
C	7.39456167688561	14.29378654294266	3.94813854390813
C	8.66253610118560	14.86519517568269	4.27848573335317
H	9.52693208906475	14.25018285615237	4.54284829632373
C	8.79538409688032	16.31503818978434	4.24710000119612

C	7.77057122619762	17.16313943133458	4.82093955446203
H	8.05868560644397	18.01154116078325	5.45430025854195
C	6.45043404612386	16.86709520222377	4.64250349131202
C	9.44598947631420	16.37673568550193	1.11810737229672
C	9.90837764815151	15.02122483823605	1.28870139642626
C	8.83407667044040	14.13999527945552	0.92859743836150
C	7.70725194551038	14.95035259099240	0.52874242457481
C	8.09200279438448	16.34387278834999	0.64007504492593
C	10.25221568252530	17.61259563421427	1.36973673747905
H	10.98852244235395	17.45500489944506	2.17050747861228
H	10.80719844495043	17.92432554358539	0.46603086728387
H	9.60919189573338	18.44931358825163	1.67526329319270
C	11.26387441821921	14.61140446409650	1.77138877636149
H	11.23017309930708	13.62190465488152	2.25001761086077
H	12.00090924747056	14.55557947750771	0.94902440768869
H	11.65694198082586	15.32197187688133	2.51377754727984
C	8.87833851631261	12.64495726166723	0.93133009054407
H	7.89052615738573	12.21518759779928	1.14617858271414
H	9.21616463136558	12.24471394220894	-0.04183228924401
H	9.56101464698289	12.26410926661003	1.70422061529175
C	6.39435504417096	14.43687203653835	0.02656413386393
H	5.57152718084803	15.10513286544642	0.31660977499422
H	6.38495333193445	14.34066168242148	-1.07469925915390
H	6.17111532982112	13.44748294473111	0.45000151582308
C	7.25368117267027	17.52434001313465	0.26226971010291
H	7.49478536492524	18.39787358069686	0.88392799693982
H	7.39788672956007	17.81351819738133	-0.79644541426853
H	6.18674106211096	17.30871946779488	0.40908344816180
C	4.03268894165827	17.10359956969381	5.21967007574792
H	3.83464145079649	16.20778310458543	4.62926763476776
C	3.01405943368218	17.78257558471170	5.87145754377966
H	1.98450628539934	17.42232430928397	5.80411234642605
C	3.32129284859198	18.93033612737707	6.61431826214974
H	2.55462454124975	19.49948112805925	7.14223212043469
C	4.66388601686235	19.32423655838865	6.65630182143519
H	4.95012817991247	20.21920396115014	7.22376129108510
C	7.17387946956917	12.84461020504298	3.86361407299068
C	8.14073634190495	11.90425022301838	4.28470372843340
H	9.07390164855380	12.25726159189223	4.72423156465710
C	7.93064531370477	10.53167069933266	4.14670022693215
H	8.70344660098011	9.83464452133185	4.48034772761041
C	6.74669977121450	10.04363300825196	3.58627752387055
H	6.58433100606161	8.96978216748255	3.47667994229877
C	5.76669262261597	10.96002968897164	3.18223986530764
H	4.82801119396161	10.60082807328079	2.75350167968148
C	5.97307015078134	12.32880589226570	3.32775803876490
H	5.20342628425424	13.04323348229278	3.02769802285861
H	9.82352139730059	16.68064322225909	4.33861745866367
O	7.38261720536468	14.67688085597441	7.30016100379112
O	5.21802973894519	14.17086383532841	6.56215648121860
C	6.30826155264433	14.43713990806245	6.89818725490211

TS-π-CO_2

Fe	0.79670071538316	0.01363206184289	-0.35012124231664
P	-1.30882085468482	0.06836820215528	0.57259868252842
N	-0.88445350799970	3.59287339157328	2.59286288090859
C	-1.52318644707243	2.46417188149576	2.11606683105039
C	-0.18264451841186	-1.31337798520023	0.89949004555332
C	1.14501678172539	-1.02123097141445	1.35057175255440

H	1.87447468851811	-1.82283705028734	1.48460944392848
C	1.56542829553060	0.32595386099750	1.56622082603012
C	0.69108988054554	1.43183171193418	1.60865089252885
H	1.14946104272063	2.42250759013272	1.71980641420759
C	-0.73035436357867	1.35339361722305	1.71535026164621
C	1.40966147562153	1.46747412181189	-1.69051944554577
C	2.44809917236379	0.47391376472313	-1.50446222386920
C	1.92774518289239	-0.80359950904994	-1.90686744691515
C	0.55973679951466	-0.61063659845339	-2.31027997311843
C	0.25107724010922	0.79817826024688	-2.19335509138705
C	1.53290665053038	2.93884036310102	-1.44681373560877
H	2.29800956604064	3.15579416345424	-0.68952746050326
H	1.81376640269623	3.47901597715106	-2.36989990469263
H	0.58787534184030	3.36256049866645	-1.08176058543732
C	3.84209647744093	0.74419352010321	-1.03371925814582
H	4.26303743630457	-0.12692310136152	-0.51061021923073
H	4.51846181420612	0.98408185466404	-1.87367632440188
H	3.87160525409873	1.59334862161483	-0.33620265331519
C	2.69792345619854	-2.08520715172896	-1.97711138809506
H	2.02850540826095	-2.95362799673464	-1.92295571760917
H	3.26833519444935	-2.16442047621018	-2.92060446093089
H	3.41972198335663	-2.16843334328070	-1.15108583286617
C	-0.37612717812908	-1.66538266325988	-2.80894731324272
H	-1.40912811740590	-1.45265099928308	-2.49963016911467
H	-0.36265423136718	-1.73339906910709	-3.91129746268530
H	-0.11958152062619	-2.65470673289943	-2.40616414986626
C	-1.03430483879538	1.45202094633795	-2.59232345900941
H	-1.23958866876389	2.33752905907884	-1.97594896409550
H	-1.00496231616927	1.77244913680255	-3.64964356091818
H	-1.88281893692428	0.76733500187608	-2.46641844288533
C	-2.95397862696901	2.44372306910137	2.03247968020750
H	-3.44497148079609	1.54597528366968	1.65248691911121
C	-3.69042135767594	3.53846912895833	2.43625645519586
H	-4.78225725170554	3.51204695658836	2.37850929665687
C	-3.02792793963750	4.68660973907957	2.91988421352532
H	-3.56968796077320	5.57304003914846	3.25212732444245
C	-1.63046172277658	4.63521638584846	2.96090845924953
H	-1.07029703632374	5.50708231804328	3.32734468153050
C	-0.54562724084417	-2.67430177841260	0.45359834307498
C	0.41720162899541	-3.68087795060713	0.22408850155002
H	1.47175161472223	-3.45750364913860	0.38162501742416
C	0.05411466328662	-4.94514251160793	-0.23646409973146
H	0.82758524614029	-5.69767086074426	-0.40763519679883
C	-1.28768534106305	-5.25030059408463	-0.49376916434095
H	-1.57104919619179	-6.23815705954076	-0.86161696686486
C	-2.25747373742610	-4.27053216701277	-0.26247590775310
H	-3.31136737061639	-4.49123488174096	-0.44624427046111
C	-1.89366080429198	-3.01108854972983	0.21444015591351
H	-2.65328195229453	-2.25213565089076	0.40942363765252
H	2.63687462435306	0.50427765474174	1.68304906288834
O	-0.08983661243988	-0.01750584273826	4.44973849351109
O	-2.33507905722843	-0.28852197189365	3.83371229581045
C	-1.19457384886347	-0.09450106575315	4.05225152307615

3-π

Fe	8.18925342341807	15.13213331472631	3.02970232795329
P	6.08151348982295	14.93746091350255	3.97610991279840
O	7.40015366972282	15.70515754922816	7.57402791173986
O	5.37752491743997	14.88451102565925	6.90662185782368

N	6.49365042097522	18.47173390031480	4.60900838960502
C	5.89722119732046	17.37753575118265	5.13577070464472
C	7.26935711550293	13.59687798164741	4.11013686624144
C	8.59231370257813	13.84333201491006	4.58873303067898
H	9.32445919800517	13.03374293034950	4.61279790216207
C	9.02012190989990	15.16200493343712	4.89473299132993
C	8.11490822692515	16.24611050475698	4.84609943841611
H	8.54058630466215	17.25057041974231	4.84382478183796
C	6.69339408878719	16.11707707260678	5.29857269104765
C	8.82149783822063	16.71684520613877	1.85201376164933
C	9.79578345391465	15.65857620811728	1.82727535885488
C	9.15748822648637	14.47265742993378	1.31907630244738
C	7.78211568215013	14.79636111851085	1.03946446684642
C	7.57608350845349	16.18814246153909	1.36964591324630
C	9.05608389372593	18.13357701340177	2.27023194503268
H	9.96241165458087	18.22308876680891	2.88515724762748
H	9.18890771116206	18.78485351395847	1.38869129753385
H	8.21500046433376	18.51100692161133	2.86969142481592
C	11.23489502355236	15.77373838307136	2.21995288751362
H	11.61512196594258	14.82503318451670	2.62487627717417
H	11.87015785499634	16.04439491946904	1.35807716319984
H	11.37932687912325	16.54349145619204	2.99033146288552
C	9.84060976723987	13.17620669510911	1.01694362604661
H	9.12927165479916	12.34109768479000	1.00828651960926
H	10.32993023569136	13.20811642670304	0.02703943280258
H	10.61867888221419	12.94664619280049	1.75939014843165
C	6.74625666276712	13.87337237421969	0.48103569616524
H	5.76338607039295	14.07072244449118	0.93205187429934
H	6.64756419542996	13.99159127801766	-0.61209362322857
H	6.98935053338526	12.82280938325081	0.68769869197969
C	6.31995196497399	16.97525684957441	1.16785184302494
H	6.22573565954990	17.76585617460693	1.92368977109157
H	6.30865659006426	17.44943809219208	0.16987004944201
H	5.43266690032905	16.33460016571744	1.25209633006203
C	4.53205619353477	17.39509395765084	5.50522660671391
H	4.11374706299728	16.48322916161553	5.93487611777661
C	3.79570484902887	18.55831057716882	5.34030972198471
H	2.74210586936317	18.58658929576990	5.62804296804166
C	4.41834287875502	19.69406008023166	4.80090400577187
H	3.87685827331392	20.62973966590566	4.65132662161530
C	5.76329696203824	19.58902201380606	4.45872449477658
H	6.29327824985525	20.44815240748361	4.03032106590432
C	6.90942585124124	12.27853767088643	3.54134710882202
C	7.87657760216179	11.32989144253721	3.15064204500351
H	8.93394942132795	11.56055571148840	3.27331004449577
C	7.51147513439335	10.11088904762364	2.58193684450482
H	8.28761651783668	9.40155172468649	2.28548522700414
C	6.16264363007521	9.79785052342401	2.37985842662638
H	5.87681547194889	8.84601182850347	1.92840313086433
C	5.18856154852114	10.71661654832596	2.77960163452432
H	4.12989086009293	10.48245221754801	2.64921998173048
C	5.55595099988878	11.92981889232870	3.36200288165964
H	4.79339762700265	12.63380366084509	3.69867625897627
C	6.46932631668566	15.49546455508166	6.77275900413619
H	10.08890774139760	15.33737036028270	5.03512113423429

S7 References

[1] E.-M. Schnöckelborg, R. Wolf, Chem. Commun. 2010, 46, 2832–2834.

[2] C. Müller, D. Wasserberg, J. J. M. Weemers, E. A. Pidko, S. Hoffmann, M. Lutz, A. L. Spek, S. C. J. Meskers, R. A. J. Janssen, R. A. van Santen, *Chem. – Eur. J.* **2007**, *13* (16), 4548–4559.

[3] a) SCALE3ABS, CrysAlisPro, Aglient Technologies Inc., Oxford, GB, **2012**; b) G. M. Sheldrick, SADABS, Bruker AXS, Madison, USA, **2007**.a) SCALE3ABS, CrysAlisPro, Aglient Technologies Inc., Oxford, GB, **2012**; b) G. M. Sheldrick, SADABS, Bruker AXS, Madison, USA, **2007**.

[4] R. C. Clark, J. S. Reid, *Acta Cryst.* **1995**, *51*, 887–897.

[5] G. M. Sheldrick, *Acta Cryst.* **2015**, *71*, 3–8.

[6] G. M. Sheldrick, *Acta Cryst.* **2008**, *64*, 112–122.

[7] C. M. Hoidn, R. Wolf, *Dalton Trans.* **2016**, *45*, 8875–8884.

[8] B. Rezaei Rad, U. Chakraborty, B. Mühldorf, J. A. W. Sklorz, M. Bodensteiner, C. Müller, R. Wolf, *Organometallics* **2015**, *34*, 622–635.

[9] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, DOI 10.1002/wcms.1327.

[10] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73–78.

[11] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[12] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[13] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[14] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[15] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[16] J. L. Whitten, *J. Chem. Phys.* **1973**, *58*, 4496–4501.

[17] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98–109.

[18] V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, *J. Chem. Phys.* **2003**, *119*, 12129–12137.

[19] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681.