Supporting Information for:

The Roles of Iron Complexes in Catalytic Radical Alkene Cross-Coupling: A Computational and Mechanistic Study

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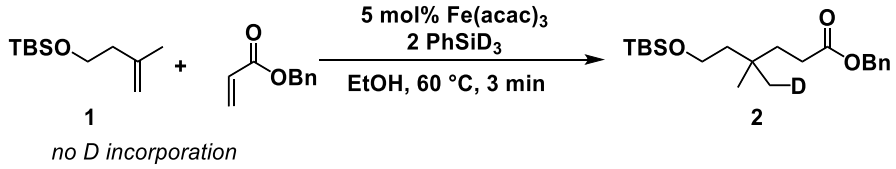
Contents

1. General considerations and experimental data

1.A General considerations. Unless otherwise noted, all manipulations were performed under an N_2 atmosphere in an M. Braun glovebox maintained at or below 1 ppm of O_2. Glassware was dried at 150 °C at least 12 hours before use and Celite was dried at 200 °C under vacuum. Solvents were dried by passage through activated alumina and Q5 columns from Glass Contour Co. with the exception of THF, which was distilled under Ar from potassium benzophenone ketyl. All solvents were stored over activated 4 Å molecular sieves. Benzene-d_6 was dried over sodium benzophenone ketyl and stored over activated alumina and filtered before use. $PhSiD_3$, **1,** and $Fe(acac)_2$ were prepared according to published methods.[1-2] Benzyl acrylate was purchased from Alfa Aesar, degassed with three freeze-pump-thaw cycles, and stored with 4 Å molecular sieves in the dark under an N_2 atmosphere. Iron(III) acetylacetonate, $Fe(acac)_3$, was purchased from Strem Chemicals. Azobisisobutyronitrile, AIBN, was purified by recrystallization from methanol before use and stored at -38 °C under dark. Absolute ethanol was purchased from Decon labs Inc. Ethanol-OD and ethanol-d_6 were purchased from Sigma-Aldrich. ^{1}H NMR and ^{13}C NMR spectroscopic data were recorded on a Bruker Avance 400 spectrometer (400 MHz). All resonances in the ^{1}H NMR spectra are referenced to residual C_6D_5H (δ 7.16 ppm). Gas chromatography (GC) was performed on a Shimadzu GC-2010 Plus chromatograph equipped with a flame ionization detector and a Shimadzu SHRXI-5MS column (30 m, 250 μm inner diameter, 0.25 μm average thickness). Gas chromatography-Mass spectrometry (GC-MS) was performed using Agilent 5973 inert GC/MS system using electron impact (EI) ionization after analytes passed through HP-5MS column (30 m, 250 μm inner diameter, 0.25 μm average thickness). Mössbauer samples were frozen in Delrin sample cups and recorded on a SEECo Mössbauer spectrometer with alternating constant acceleration; isomer shifts are relative to α-iron metal at 298 K. The sample temperature was maintained at 80 K in a Janis Research Company Inc. cryostat. The zero-field spectra were simulated using Lorentzian doublets using WMoss (SeeCo).



1.B Test for reversible hydrogen atom transfer from Fe-H to alkene. In an N_2-filled glove box, compound **1** (40 mg, 0.20 mmol, 1.0 equiv), benzyl acrylate (30 µL, 0.20 mmol, 1.0 equiv), $PhSiD_3$ (68 mg of 65% solution in diethyl ether, 0.40 mmol, 2.0 equiv) and $Fe(acac)_3$ (3.5 mg, 0.010 mmol, 0.050 equiv) were added to a Schlenk flask with 1.0 mL EtOH. The resulting red solution was stirred at 60 °C for 3 min before removing the solvents under vacuum. The resulting residue was then filtered through a plug of silica (3.0 cm) in a pipette, eluting with 4.0 mL of hexanes:EtOAc (4:1). After removing the solvents from the filtrate, the crude reaction mixture was dissolved in $CDCl_3$ and analyzed using ^1H and ^{13}C NMR spectroscopy (**Figure S1 and S2**). A GCMS sample was prepared by dissolving the crude mixture in 2.0 mL of EtOAc (**Figure S3 – S5**).

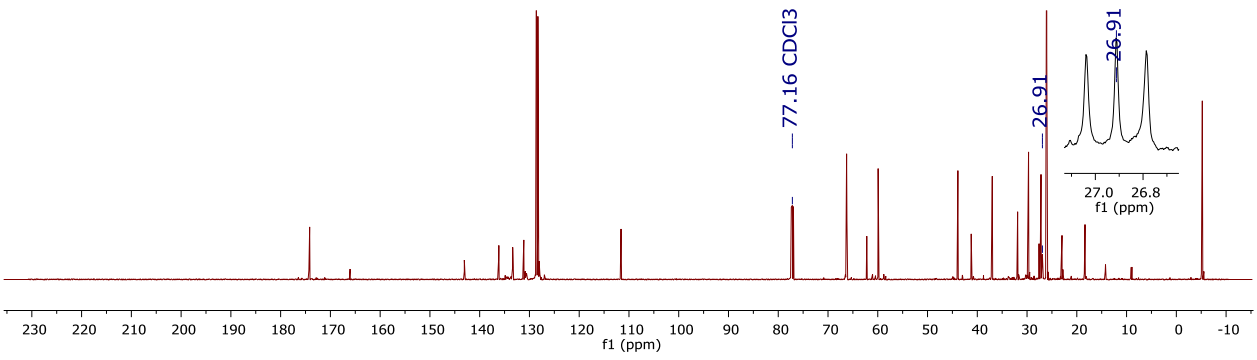


Figure S1. $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture in $CDCl_3$ after filtering through a plug of silica.

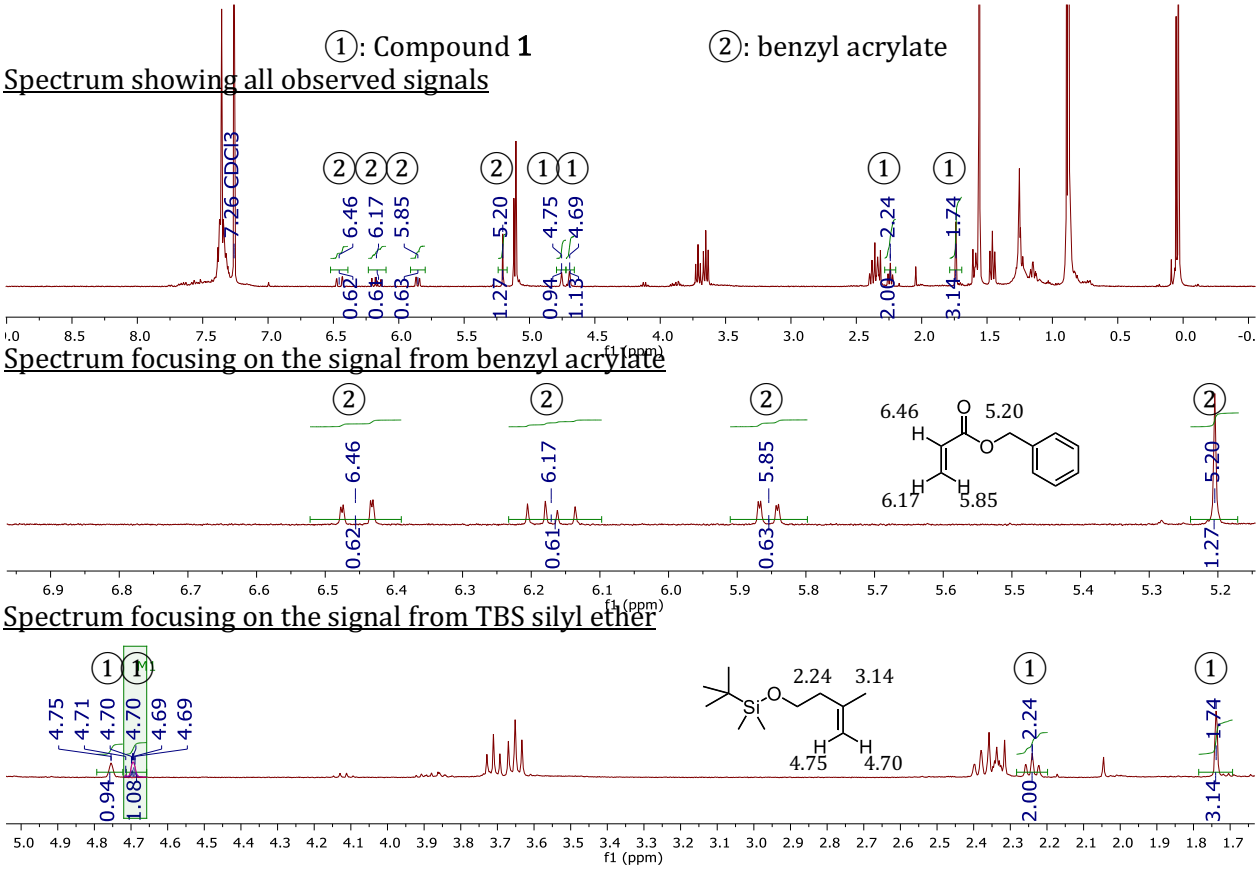
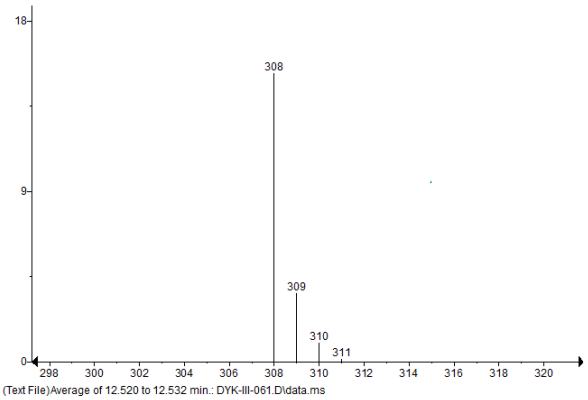


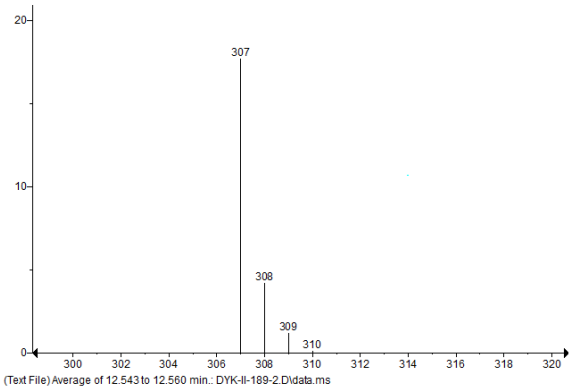
Figure S2. ^{1}H NMR spectrum of the reaction mixture in $CDCl_3$ after filtering through a plug of silica. Figure shows integrations and chemical shifts from starting materials.

m/z of product from the experiment



m/z observed: 308 (100%), 309 (23.7%), 310 (6.4%)

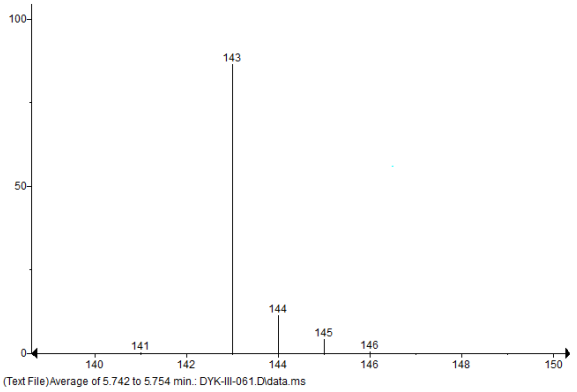
natural abundance product



m/z observed: 307 (100%), 309 (23.6%), 310 (6.6%)

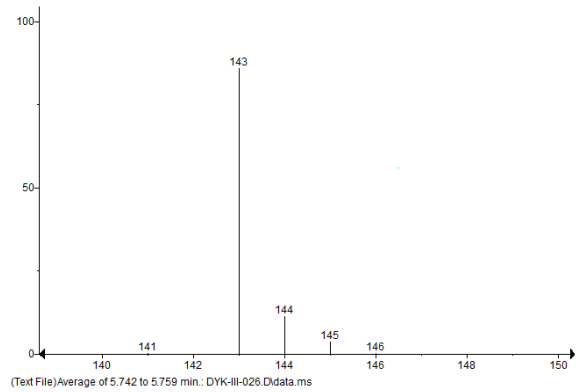
Figure S3. Mass spectra of the products obtained from experiments in EtOD (left) and EtOH (right). The molecular ion of the product, $C_{21}H_{36}O_3Si^+$, was not observed; rather, the observed *m/z* is consistent with fragmentation and loss of the tBu group to form $C_{17}H_{27}O_3Si^+$.

m/z of TBS-silyl ether from the experiment



m/z observed: 143 (100%), 144 (12.9%), 145 (4.9%), 146 (0.3%)

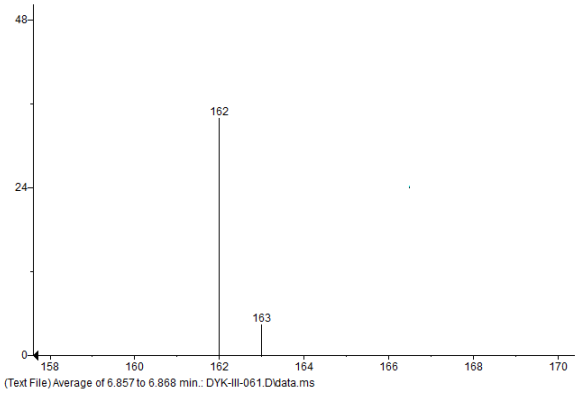
natural abundance compound 1



m/z observed: 143 (100%), 144 (13.0%), 145 (4.3%), 146 (0.2%)

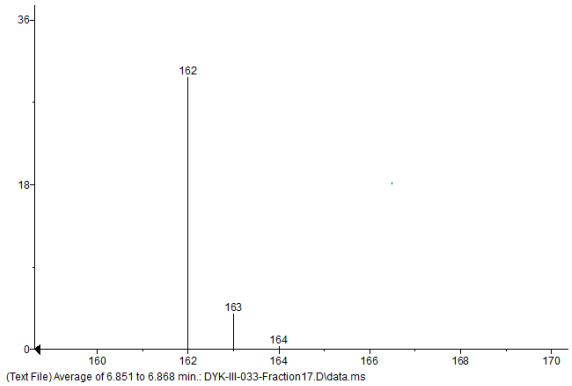
Figure S4. Mass spectra of the donor olefin (compound **1**). (Left) Material recovered from reaction in EtOD. (Right) Independently prepared material. The molecular ion of the product, $C_{11}H_{24}OSi^+$, was not observed; rather, the observed m/z is consistent with fragmentation and loss of the tBu group to form $C_7H_{15}OSi^+$.

m/z of benzyl acrylate from the experiment



m/z observed: 162 (100%), 163 (12.7%)

natural abundance benzyl acrylate



m/z observed: 162 (100%), 163 (13.0%)

Figure S5. Mass spectra of the acceptor olefin (benzyl acrylate). (Left) Material recovered from reaction in EtOD. (Right) Commercially obtained benzyl acrylate.

1.C $Fe^{3+/2+}$ reduction/oxidation of $Fe(acac)_2$ in EtOH by cyclic voltammetry. In an N_2-filled glove box, tetrabutylammonium tetrafluoroborate, $TBABF_4$ (170 mg, 0.50 mmol) was dissolved in 5.0 mL of EtOH to give a 0.10 M $TBABF_4$ solution. After scanning the solvent window to ensure the absence of any possible impurities, $Fe(acac)_2$ (3.8 mg, 0.015 mmol) was added to the above solution to give a 3.0 mM $Fe(acac)_2$ solution for cyclic voltammetry.

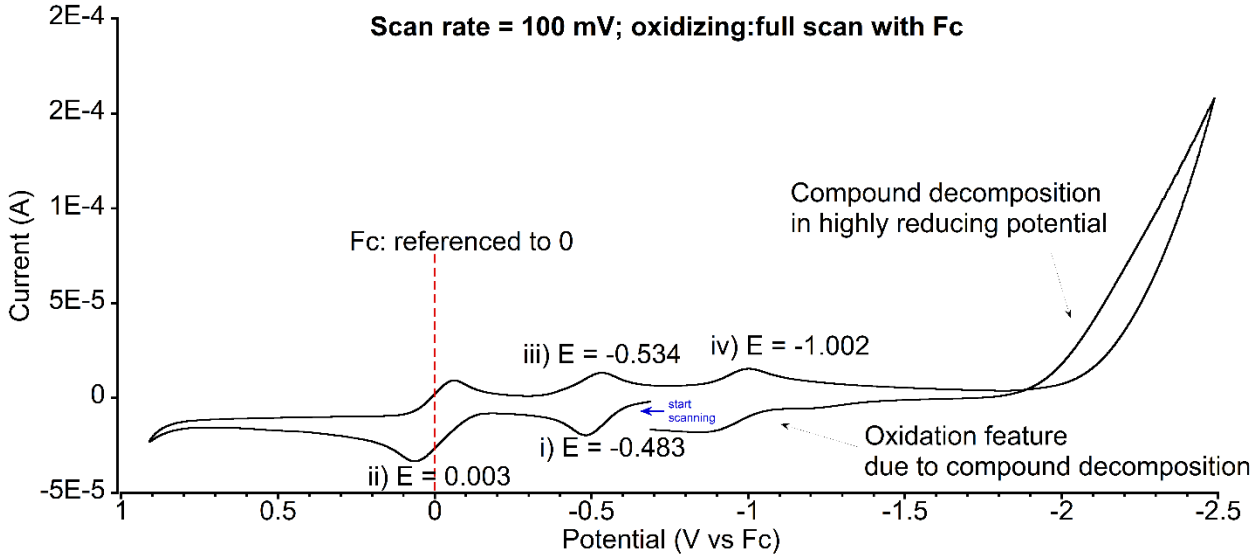


Figure S6. Cyclic voltammogram of $Fe(acac)_2$ showing all observed oxidation and reduction events.

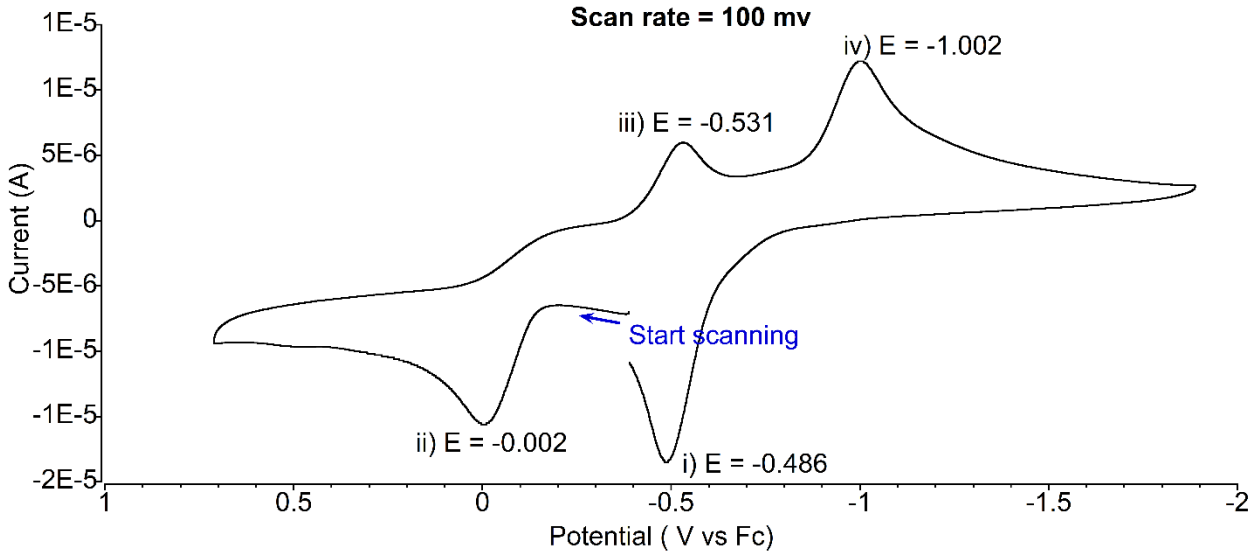


Figure S7. Cyclic voltammogram of $Fe(acac)_2$ showing all observed oxidation and reduction events within the window where no compound decomposition is observed.

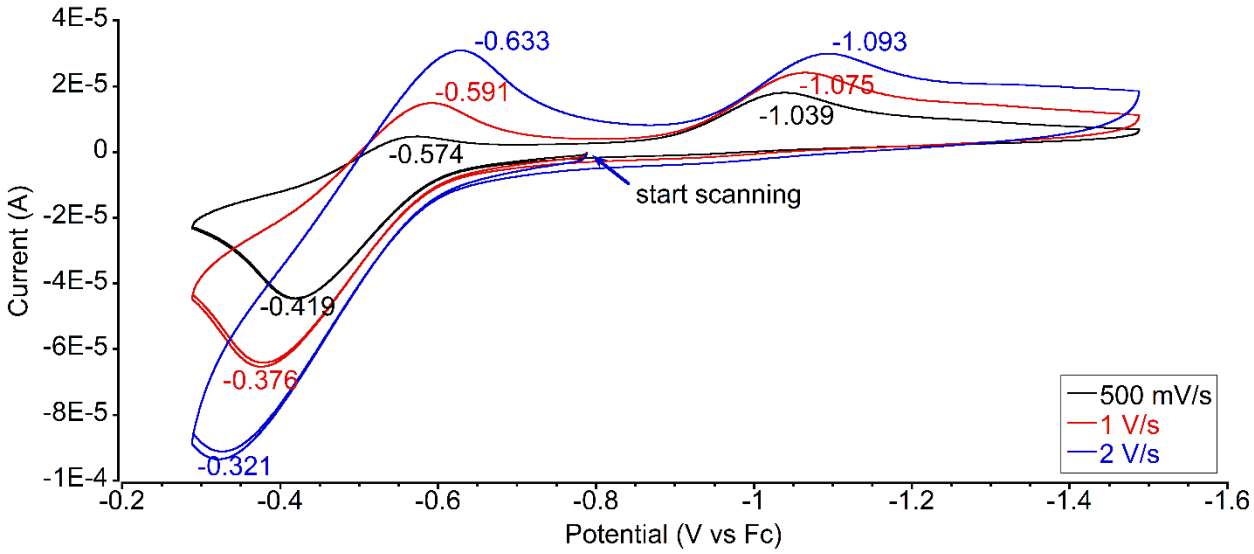


Figure S8. Cyclic voltammogram of $Fe(acac)_2$ in EtOH at various scan rates.

1.D Kinetic isotope effect (KIE) for olefin coupling in EtOH and EtOD. In a N_2-filled glove box, compound **1** (120 mg, 0.60 mmol, 1.0 equiv), benzyl acrylate (140 μL, 0.90 mmol, 1.5 equiv), $Fe(acac)_3$ (21 mg, 0.060 mmol, 0.10 equiv) and 1,3,5-trimethoxybenzene (100 mg, 0.60 mmol, 1.0 equiv) were added to a Schlenk flask with 3 mL of EtOH. The flask was then taken out of the glovebox and stirred at room temperature for 1 minute to make a homogenous reaction solution. Under a flow of N_2, $PhSiH_3$ (110 μL, 0.90 mmol, 1.5 equiv) was injected into the solution, and the reaction was heated to 40 °C in an oil bath. The reaction was monitored by taking aliquots of the reaction mixture at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 min and immediately filtering each reaction aliquot through a silica plug with EtOAc. The product formation at each time point was analyzed by gas chromatography. An analogous reaction in EtOD used the same amounts. These parallel experiments were analyzed using the method of initial rates.

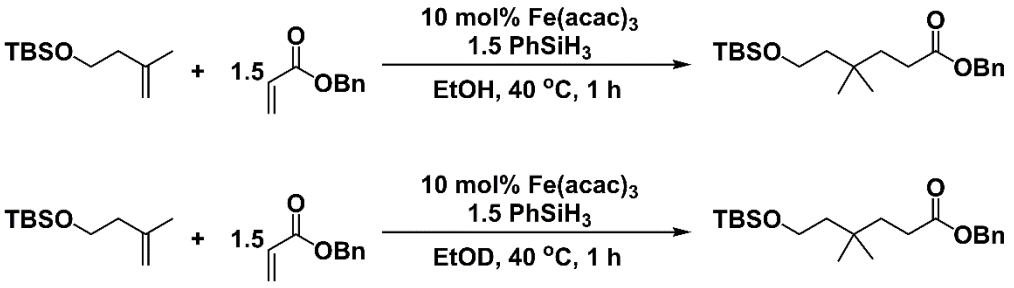
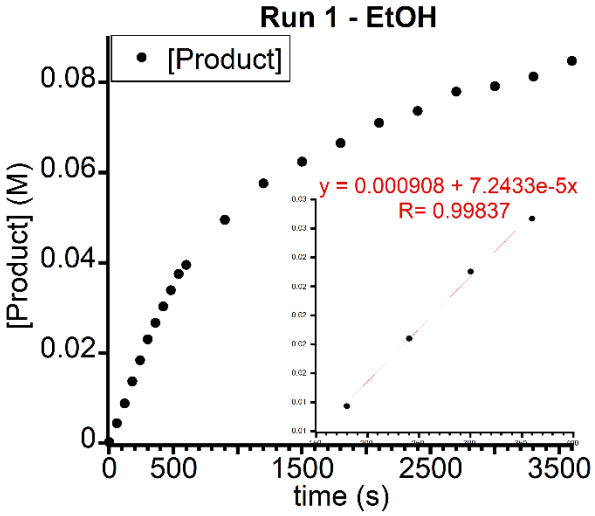
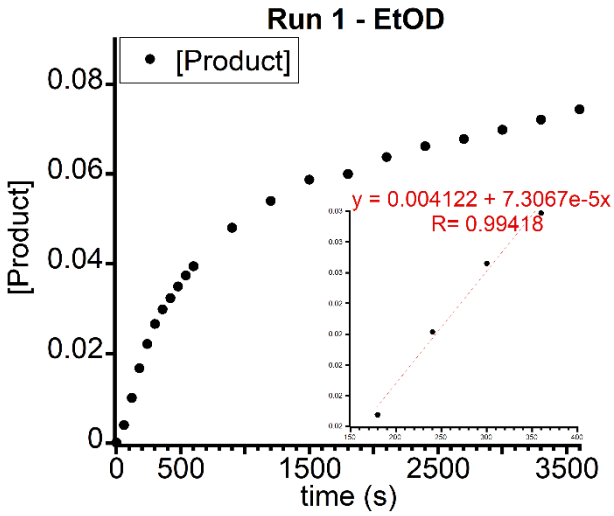
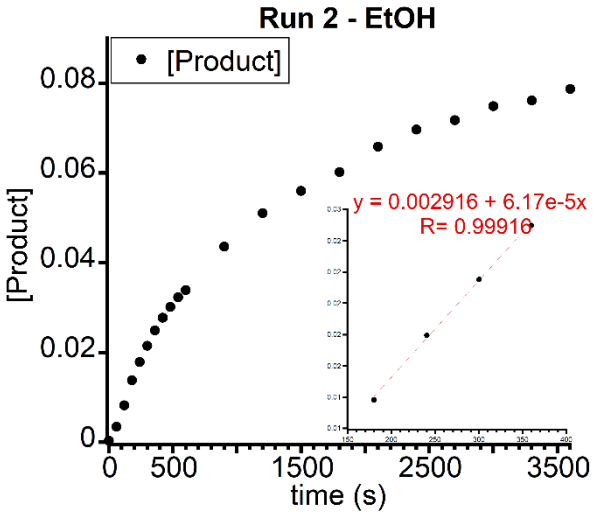


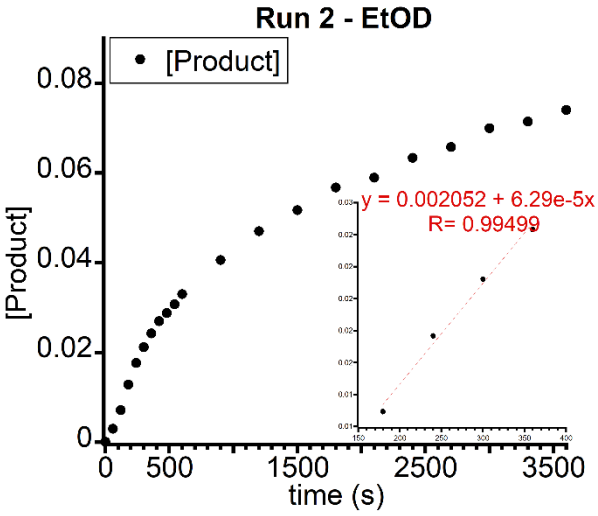
Table S1. KIE experiment in EtOH and EtOD

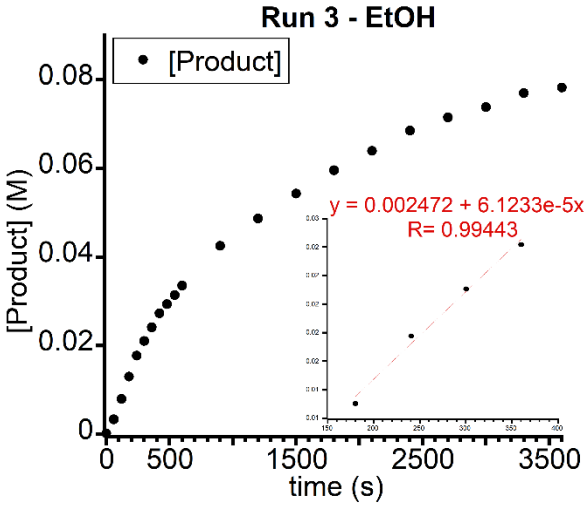
Run	Rate in EtOH	Rate in EtOD
1	7.2×10^{-5}	7.3×10^{-5}
2	6.2×10^{-5}	6.3×10^{-5}
3	6.1×10^{-5}	5.0×10^{-5}
Overall KIE = 1.1 ± 0.3		

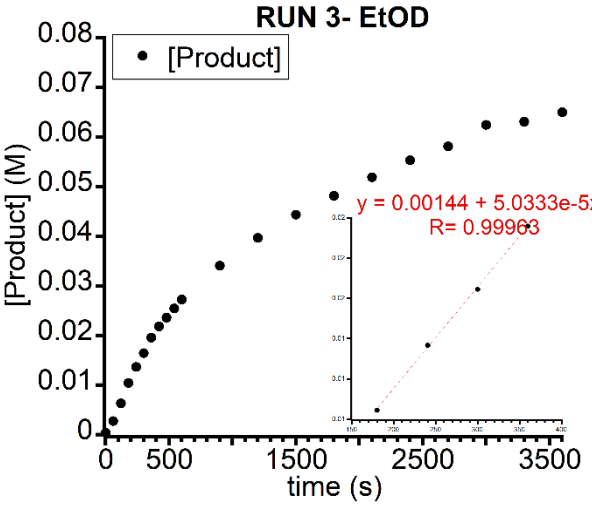

Run 1 - EtOH
[Product]
y = 0.000908 + 7.2433e-5x
R= 0.99837
[Product] (M)
time (s)

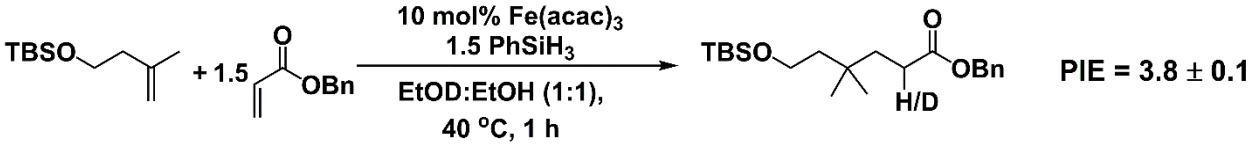

Run 1 - EtOD
[Product]
y = 0.004122 + 7.3067e-5x
R= 0.99418
[Product]
time (s)


Run 2 - EtOH
[Product]
y = 0.002916 + 6.17e-5x
R= 0.99916
[Product]
time (s)


Run 2 - EtOD
[Product]
y = 0.002052 + 6.29e-5x
R= 0.99499
[Product]
time (s)


Run 3 - EtOH
[Product]
y = 0.002472 + 6.1233e-5x
R= 0.99443
[Product] (M)
time (s)


RUN 3- EtOD
[Product]
y = 0.00144 + 5.0333e-5x
R= 0.99903
[Product] (M)
time (s)



1.E Product isotope effect (PIE) determination for olefin coupling in 1:1 EtOH/EtOD solution. To minimize error in this experiment, a stock solution was prepared in EtOH containing compound **1** (0.40 M), benzyl acrylate (0.60 M) and $Fe(acac)_3$ (0.040 M). Separately, a second stock solution was prepared containing 0.60 M $PhSiH_3$ in EtOD. In a N_2 filled glove box, a 4.0 mL vial was charged with a stir bar and 0.50 mL of each stock solution. The resulting mixture was then stirred at 40 °C for 1 h. The ratio of H/D incorporation in the cross-coupling product was determined by mass spectrometry (**Figure S9 – S11**). The molecular ion of the product, $C_{21}H_{36}O_3Si^+$, was not observed; rather, the observed m/z is consistent with fragmentation and loss of the tBu group to form $C_{17}H_{27}O_3Si^+$.The experiment was repeated three times.

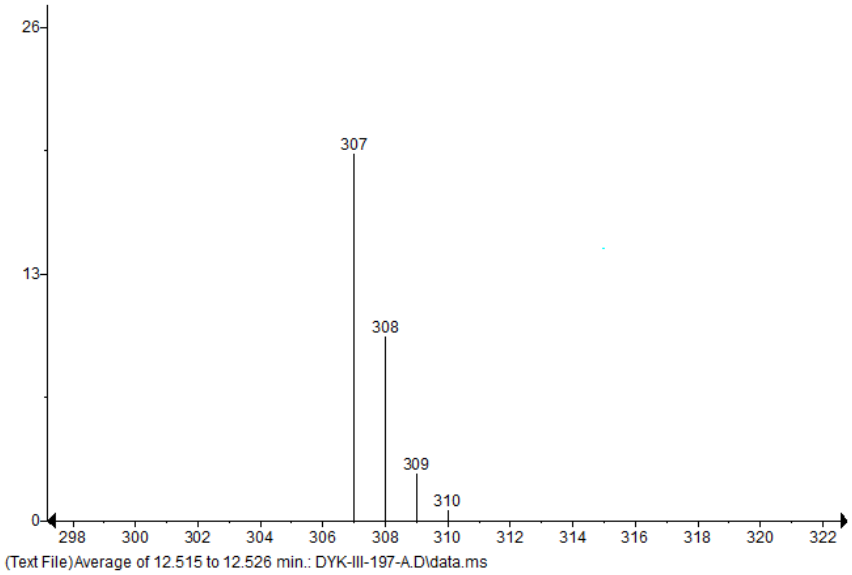


Figure S9. Mass spectrum of H/D product mixture from the reaction. Observed peaks correspond to loss of the tBu group to form $C_{17}H_{27}O_3Si^+$ at m/z 307 (100%), 308 (49.8%), 309 (12.8%) and 310 (2.5%). From these, the ratio of H/D product was calculated to be 3.9:1 (H:D).

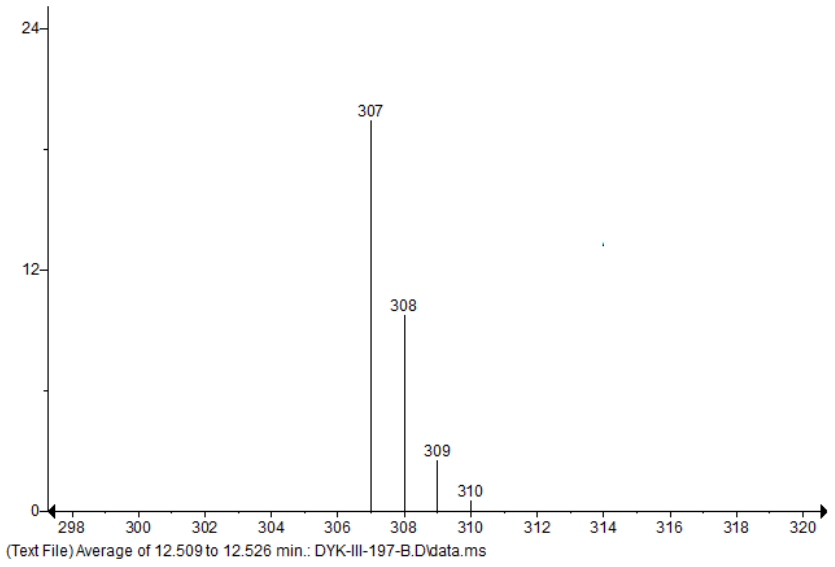


Figure S10. Mass spectrum of H/D product mixture from the reaction. Observed peaks correspond to loss of the tBu group to form $C_{17}H_{27}O_3Si^+$ at m/z 307 (100%), 308 (50.0%), 309 (12.9%) and 310 (2.5%). From these, the ratio of H/D product was calculated to be 3.9:1 (H:D).

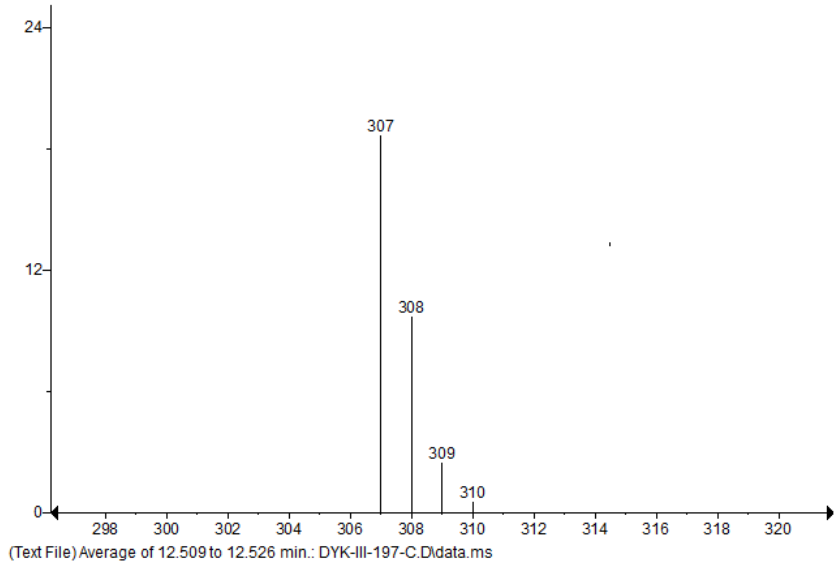


Figure S11. Mass spectrum of H/D product mixture from the reaction. Observed peaks correspond to loss of the tBu group to form $C_{17}H_{27}O_3Si^+$ at m/z 307 (100%), 308 (51.8%), 309 (13.0%) and 310 (2.6%). From these, the ratio of H/D product was calculated to be 3.7:1 (H:D).

1.F Reaction between $Fe(acac)_2$ and 0.5 equiv AIBN with 20 equiv EtOH. In an N_2-filled glovebox, $Fe(acac)_2$ (10 mg, 0.040 mmol, 1.0 equiv) and EtOH (48 μL, 0.80 mmol, 20 equiv) were mixed in 0.9 mL of CD_3CN. This resulting solution was then transferred to a J. Young tube containing azobisisobutyronitrile, AIBN (0.10 mL of 0.20 M solution in CD_3CN, 0.020 mmol, 0.50 equiv). After heating the J. Young tube at 80 °C for 2 h, all volatile materials were vacuum transferred to another J. Young tube containing 1,3,5-trimethoxybenzene (0.10 mL of 0.40 M solution in CD_3CN, 0.040 mmol, 1.0 equiv) as an internal standard. The amount of isobutyronitrile was determined by ^1H NMR spectroscopy (**Figure S12**).

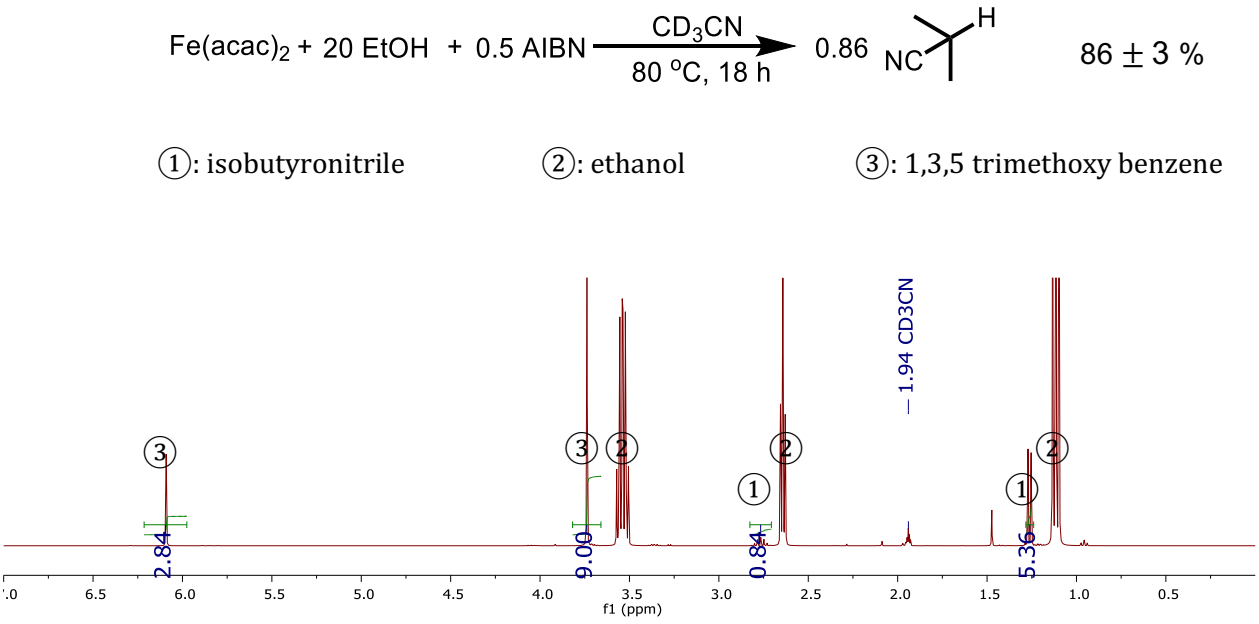
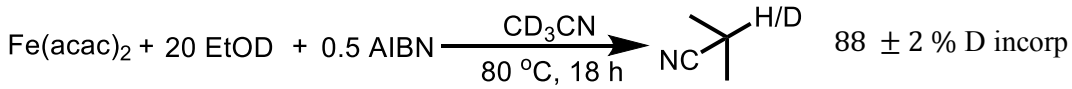


Figure S12. ^1H NMR of vacuum transferred reaction solution containing isobutyronitrile and ethanol. Integrations of α and β hydrogens to nitrile group of isobutyronitrile respect to the integrations of 1,3,5-trimethoxybenzene were used to quantify the formation of isobutyronitrile.

1.G Reaction between $Fe(acac)_2$ and 0.5 equiv AIBN with 20 equiv EtOD. In an N_2-filled glovebox, $Fe(acac)_2$ (0.80 mL of 0.050 M solution in CD_3CN, 0.040 mmol, 1.0 equiv) and EtOD (48 μL, 0.80 mmol, 20 equiv) were mixed. The orange solution was then transferred to a J. Young tube containing azobisisobutyronitrile, AIBN, (0.20 mL of 0.10 M solution in CD_3CN, 0.020 mmol, 0.50 equiv). After heating the J. Young tube at 80 °C for 2 h, all volatile materials were vacuum transferred to another J. Young tube containing 1,3,5-trimethoxybenzene (0.10 mL of 0.40 M solution in CD_3CN, 0.040 mmol, 1.0 equiv) as an internal standard. The deuteration of isobutyronitrile was determined by ^1H NMR spectroscopy (**Figure S13**).



①: isobutylronitrile ②: ethanol

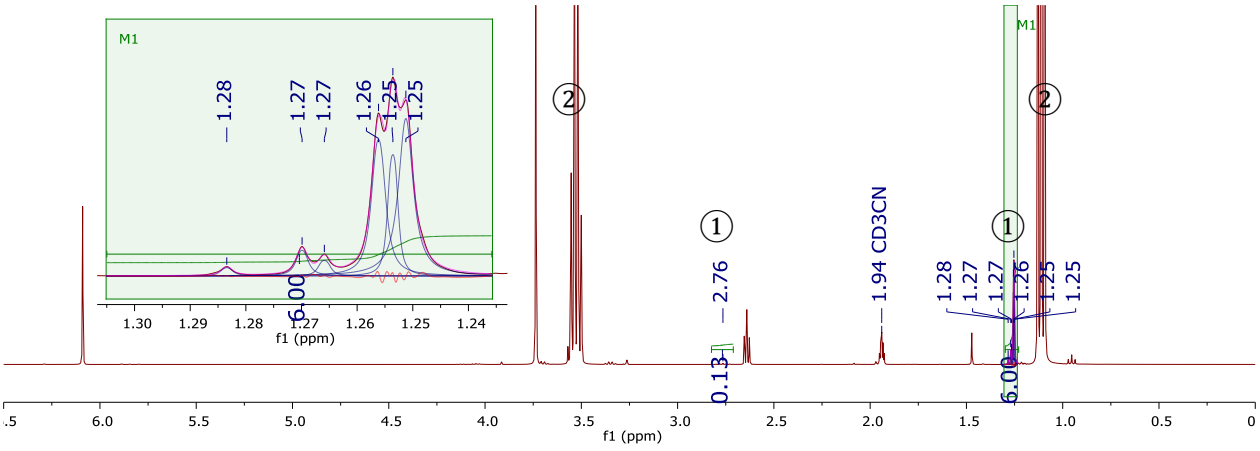


Figure S13. ^1H NMR of vacuum transferred reaction solution containing isobutyronitrile and ethanol. Deuterium incorporation to the product was examined by the change in the splitting pattern of hydrogens β to the nitrile group of isobutyronitrile and the decrease in signal intensity from the hydrogen α to the nitrile group of isobutyronitrile.

1.H Reaction between $Fe(acac)_2$ and 0.5 equiv AIBN with 20 equiv CD_3CD_2OD. In an N_2-filled glovebox, $Fe(acac)_2$ (0.80 mL of 0.050 M solution in CD_3CN, 0.040 mmol, 1.0 equiv) and CD_3CD_2OD (48 μL, 0.80 mmol, 20 equiv) were mixed. The orange solution was then transferred to a J. Young tube containing azobisisobutyronitrile, AIBN, (0.20 mL of 0.10 M solution in CD_3CN, 0.020 mmol, 0.50 equiv). After heating the J. Young tube at 80 °C for 2 h, all volatile materials were vacuum transferred to another J. Young tube containing 1,3,5-trimethoxybenzene (0.10 mL of 0.40 M solution in CD_3CN, 0.040 mmol, 1.0 equiv) as an internal standard. The deuteration of isobutyronitrile was determined by ^1H NMR spectroscopy (**Figure S14**).

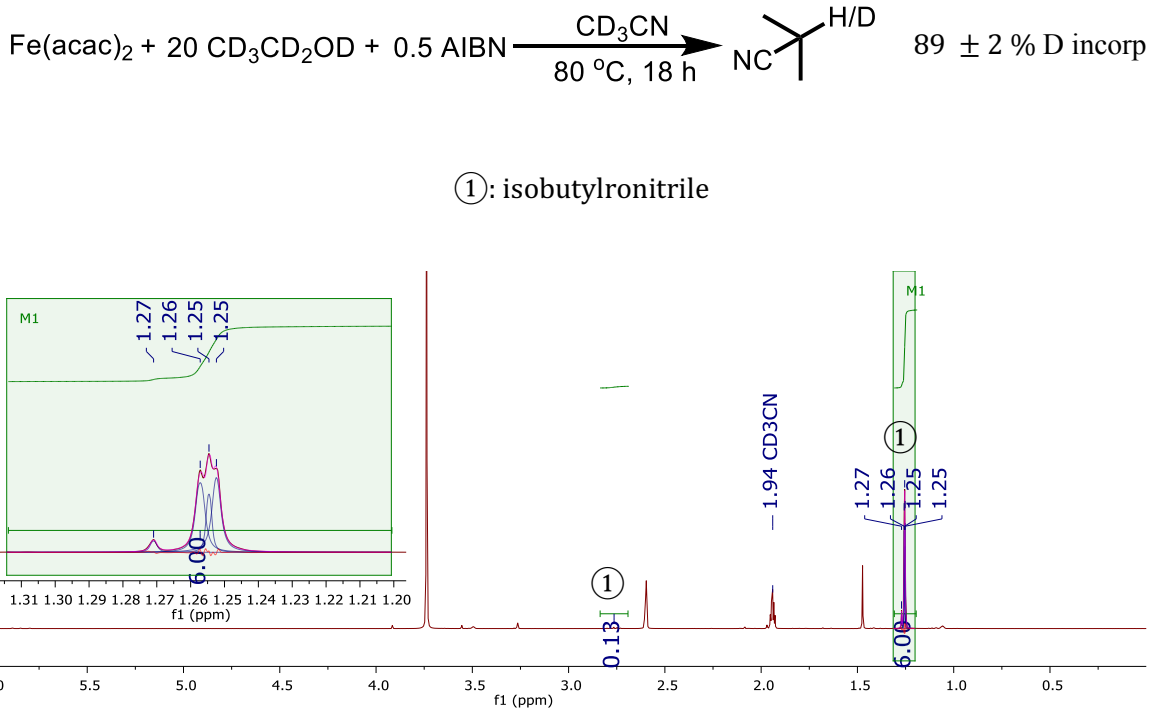
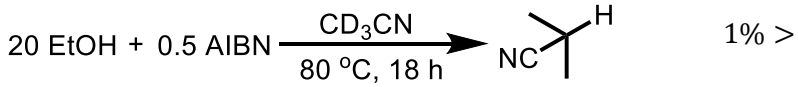
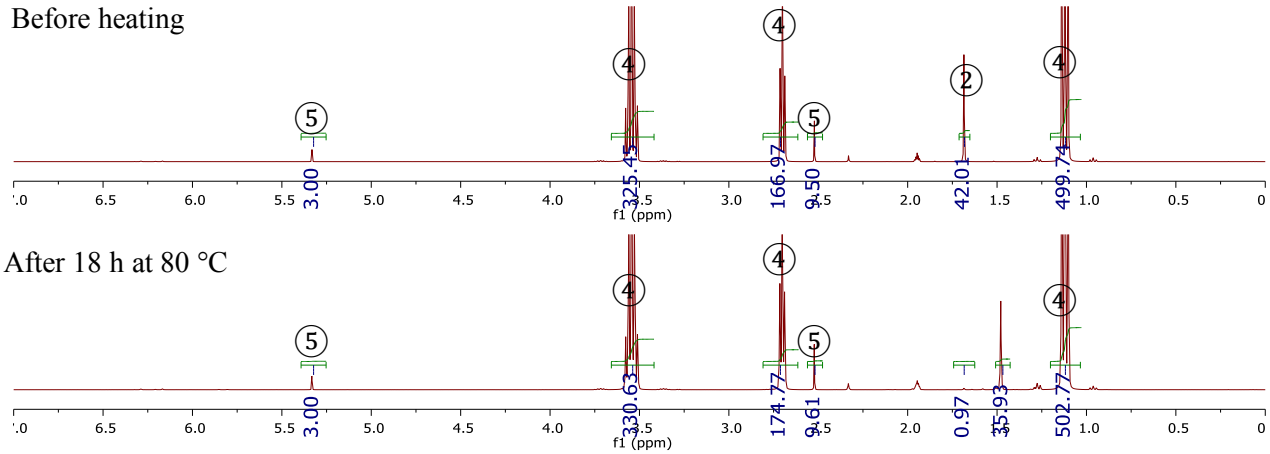


Figure S14. ^1H NMR of vacuum transferred reaction solution containing isobutyronitrile and ethanol. Deuterium incorporation to the product was examined by the change in the splitting pattern of hydrogens β to the nitrile group of isobutyronitrile and the decrease in signal intensity from the hydrogen α to the nitrile group of isobutyronitrile.

1.I Reaction between AIBN and 20 equiv EtOH. In an N_2-filled glovebox, azobisisobutyronitrile, AIBN (0.10 mL of 0.20 M solution in CD_3CN, 0.020 mmol, 0.50 equiv) and 0.9 mL of CD_3CN containing ethanol (48 μL, 0.40 mmol, 20 equiv) were transferred to a J.Young tube containing an internal capillary with [4.8 mM] solution of 1,3,5-trimethoxybenzene in toluene-d_6. The ^{1}H NMR spectrum was recorded immediately to quantify the initial concentration of ethanol and AIBN in the solution (**Figure S15**, top). After heating the solution at 80 °C for 18 hours, the ^{1}H NMR spectrum was recorded to quantify the final concentration of starting materials and products (**Figure S15**, bottom).



①: isobutylronitrile (IBN) ②: azobisisobutyronitrile (AIBN)
③: tetramethylsuccinonitrile(TMSN) ④: ethanol ⑤: internal standard



	[EtOH]	[AIBN]	[TMSN]	[IBN]
Before heating	793 ± 12 mM	16 ± 1 mM	-	-
After 12 h at 80 °C	812 ± 29 mM	-	14 ± 1 mM	-

Figure S15. ^{1}H NMR spectra of the reaction before and after heating at 80 °C. The table shows the concentrations of starting materials and products calculated using the internal capillary.

1.J Mössbauer spectroscopic characterization of Fe(acac)$_2$. Fe(acac)$_2$ was prepared by a previously reported method.[2] The zero-field Mössbauer spectrum of solid Fe(acac)$_2$ was recorded at 80 K (**Figure S16**). The observation of two unique iron sites with different isomer shifts and quadrupole splittings is consistent with previously reported characterization of the compound.[3] X-ray crystallographic characterization of the compound showed a dimeric form where one iron site was in a distorted octahedral environment while the other was in a distorted square-pyramidal coordination. Previous Mössbauer characterization of the compound at 95 K showed two quadrupole doublets (one with δ = 1.22 mm/s ΔE_Q = 2.47 mm/s and the other with δ = 1.20 mm/s, ΔE_Q = 2.17 mm/s).[3]

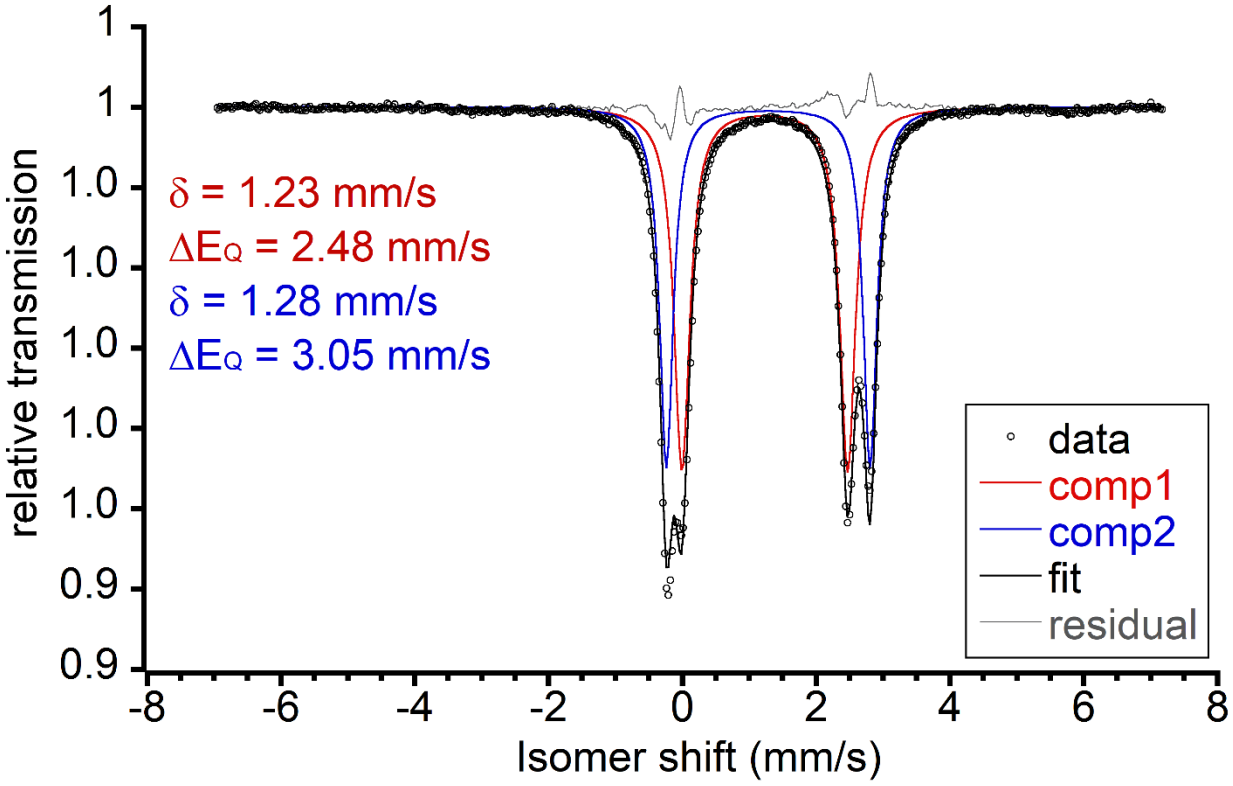


Figure S16. Zero-field Mössabauer spectrum of solid Fe(acac)$_2$. The black circles represent the data, the red line is a simulation with fit parameters (δ = 1.23 mm/s, ΔE_Q = 2.48 mm/s), the blue line is a simulation with fit parameters (δ = 1.28 mm/s, ΔE_Q = 3.05 mm/s), the black line is the sum of the red and blue simulations, and the gray line is the residual.

1.K Monitoring reaction between $Fe(acac)_2(EtOH)_2$ and 0.5 equiv AIBN by Mössbauer spectroscopy. In an N_2-filled glovebox, $Fe(acac)_2$ (80 mg, 0.32 mmol, 1.0 equiv.) and EtOH (370 µL, 6.3 mmol, 20 equiv.) were mixed in a 50 mL resealable vessel with 6 mL of C_6H_6. To this orange solution, azobisisobutyronitrile (AIBN, 26 mg, 0.16 mmol, 0.50 equiv) in 2 mL C_6H_6 was added. The resulting reaction mixture was heated at 80 °C for 2 h. After removing the solvents under vacuum, the crude material was analyzed by Mössbauer spectroscopy at 80 K (**Figure S17**).

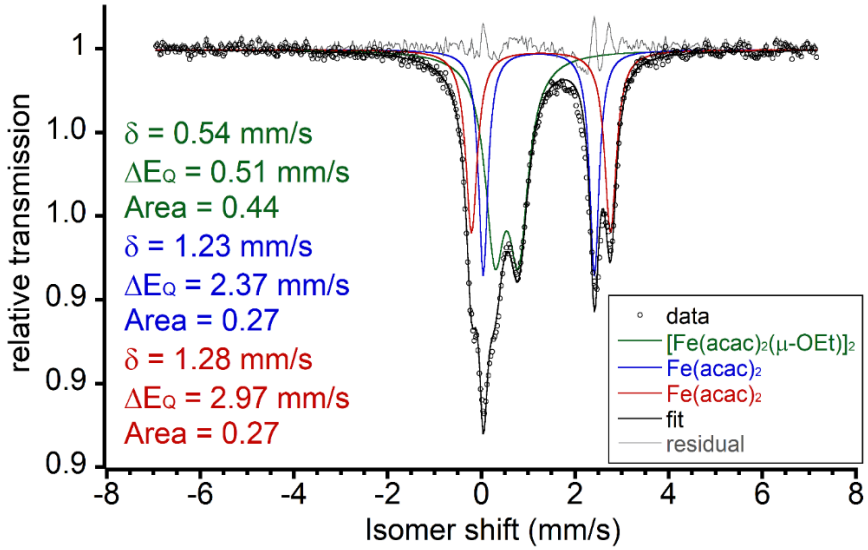


Figure S17. Zero-field Mössabauer spectrum of concentrated crude reaction mixture. The black circles represent the data, the red line is a simulation with fit parameters (δ = 1.28 mm/s, ΔE_Q = 2.97 mm/s), the blue line is a simulation with fit parameters (δ = 1.23 mm/s, ΔE_Q = 2.37 mm/s), the green line is a simulation with fit parameters (δ = 0.54 mm/s, ΔE_Q = 0.51 mm/s) the black line is the sum of green, red and blue simulations and the gray line is the residual.

1.L Monitoring reaction between $Fe(acac)_2(EtOH)_2$ and 2.0 equiv AIBN by Mössbauer spectroscopy. In an N_2-filled glovebox, $Fe(acac)_2$ (100 mg, 0.40 mmol, 1.0 equiv.) and EtOH (450 μL, 8.0 mmol, 20 equiv.) were mixed in a 50 mL resealable vessel with 6 mL of C_6H_6. To this orange solution, azobisisobutyronitrile (AIBN, 130 mg, 0.80 mmol, 2.0 equiv.) in 2 mL C_6H_6 was added. The resulting reaction mixture was heated at 80 °C for 2 h. After removing the solvents, resulting mixture of reaction was used to record the Mössbauer spectrum **(Figure S18).** Crystals suitable for X-ray diffraction were obtained by concentrating a solution of this material in EtOH at -20 °C.

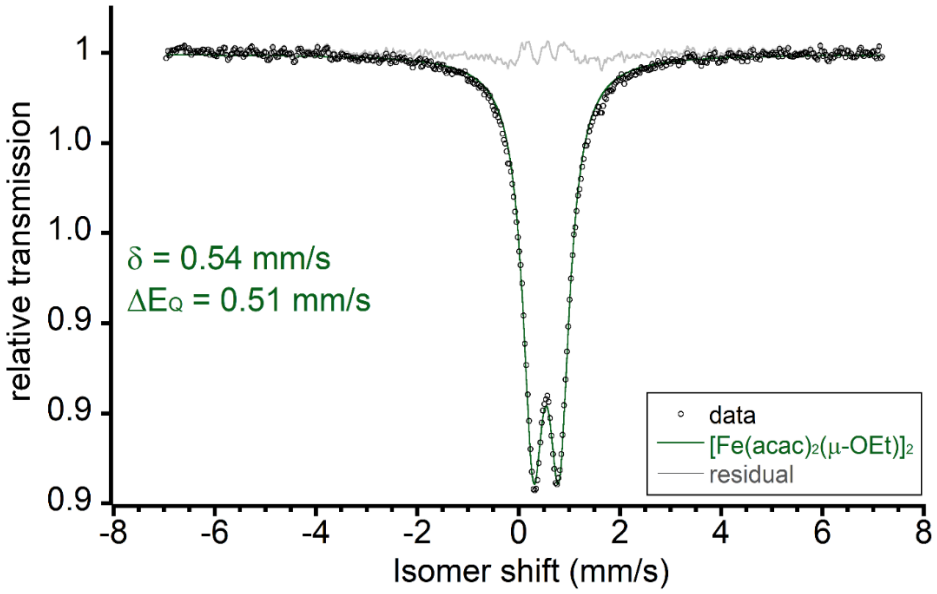


Figure S18. Zero-field Mössbauer spectrum of the crude reaction mixture with 2.0 equiv of AIBN. The black circles are the data, the green line is a simulation with fit parameters δ = 0.54 mm/s, ΔE_Q = 0.51 m/s. The gray line is the residual.

Crystal structure of $[Fe(acac)_2(\mu\text{-}OEt)]_2$

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structure of $[Fe(acac)_2(\mu\text{-}OEt)]_2$. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compound $[Fe(acac)_2(\mu\text{-}OEt)]_2$ can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1829492 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

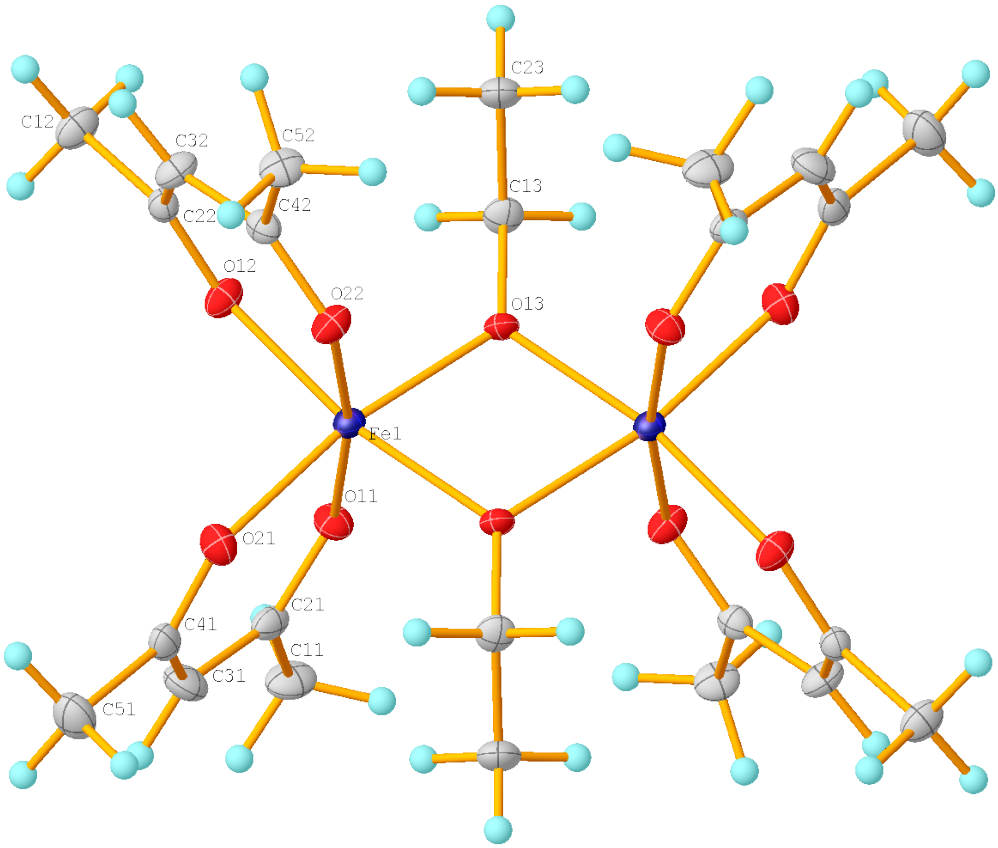
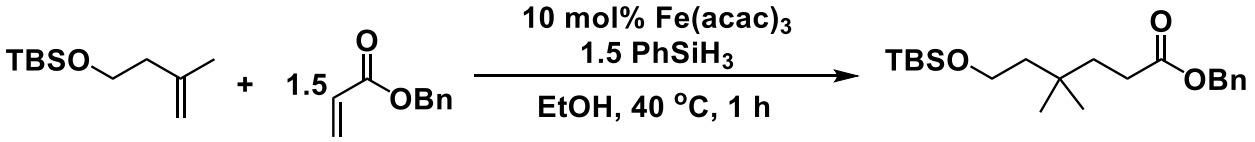


Figure S19. The complete numbering scheme of $[Fe(acac)_2(\mu\text{-}OEt)]_2$ with 50% thermal ellipsoid probability levels. Only the asymmetric unit is number. The hydrogen atoms are shown as circles for clarity.

Table 2. Crystal data and structure refinement for of $[Fe(acac)_2(\mu\text{-}OEt)]_2$.

Identification code	007c-17053	
Empirical formula	C24 H38 Fe2 O10	
Formula weight	598.24	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.3679(2) Å	α= 68.047(4)°.
	b = 9.3117(4) Å	β= 81.979(3)°.
	c = 10.5715(4) Å	γ = 65.376(3)°.
Volume	694.39(5) $Å^3$	
Z	1	
Density (calculated)	1.431 g/cm^3	
Absorption coefficient	1.095 mm^{-1}	
F(000)	314	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Crystal color and habit	Red Block	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	2.883 to 27.473°.	
Index ranges	-10<=h<=10, -12<=k<=12, -13<=l<=13	
Reflections collected	16738	
Independent reflections	3186 [R(int) = 0.0241]	
Observed reflections (I > 2sigma(I))	3012	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.91116	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3186 / 0 / 168	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0229, wR2 = 0.0618	
R indices (all data)	R1 = 0.0244, wR2 = 0.0623	
Largest diff. peak and hole	0.352 and -0.376 $e.Å^{-3}$	



1.L Determination of overall barrier for the catalytic reaction. The overall rate constant for the catalytic reaction was determined by measuring the rate of formation of coupling product and assuming the reaction orders determined previously.[2]

$$\text{rate of reaction} = k\frac{[\text{Fe(acac)}_3]^{0.5}[\text{compound } \mathbf{1}]^{0.5}[\text{PhSiH}_3]^1}{[\text{benzyl acrylate}]^1}$$

Table S3. Determination of $\Delta G^{\ddagger}$ for the catalytic reaction

Run	Rate of reaction	k	$\Delta G^{\ddagger}$
1	7.2×10^{-5} M s^{-1}	1.1×10^{-3} s^{-1}	22.6 kcal/mol
2	6.2×10^{-5} M s^{-1}	9.8×10^{-4} s^{-1}	22.7 kcal/mol
3	6.1×10^{-5} M s^{-1}	9.6×10^{-4} s^{-1}	22.7 kcal/mol

1.M Determination of association constant between $Fe(acac)_2$ and EtOH. The association constant for $Fe(acac)_2$ and EtOH was determined by titration experiments at 80 °C using the following equation.[4]

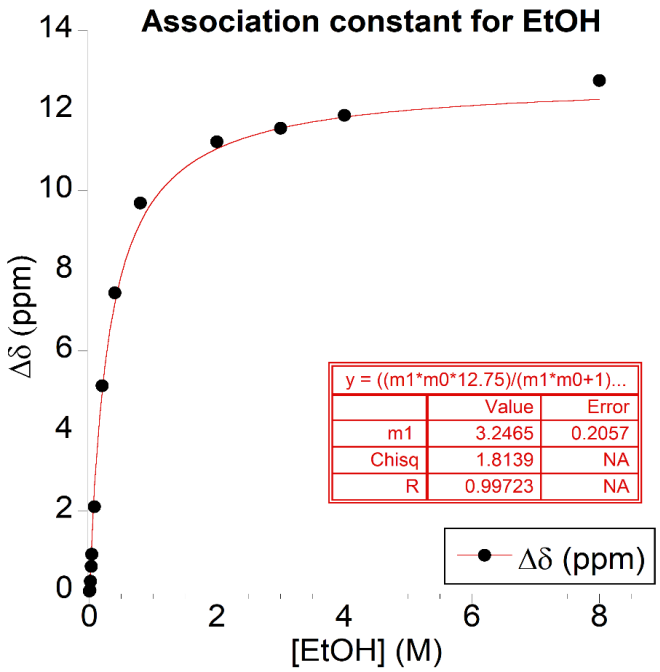
$$\Delta\delta = \frac{K_{eq} \cdot \delta_{\Delta HG} \cdot [\mathrm{EtOH}]}{1 + K_{eq} \cdot [\mathrm{EtOH}]}$$

$$\Delta\delta = \delta_{\mathrm{Fe(acac)_2}} - \delta_{\mathrm{observed}};\ \delta_{\Delta HG} = \text{largest } \Delta\delta \text{ observed in the experiement}$$

Samples were prepared by mixing 0.40 mL of 0.050 M $Fe(acac)_2$ in C_6D_6 with 0, 10, 20, 30, 40, 80 μL of 0.50 M EtOH solution in C_6D_6 and diluting to 0.50 mL C_6D_6. Entries 6 to 13 were prepared by using 6, 12, 24, 60, 90, 120, 240 μL of absolute EtOH. All ^{1}H NMR samples were then taken to an NMR spectrometer that was preheated at 80 °C; the samples were kept in the instrument for 5 minutes before the data collection for temperature equilibration.

Table S4. Concentration of [EtOH] and Δδ used for determining association constant.

Entry	$[Fe(acac)_2]$	[EtOH] (mM)	δ observed (ppm)	$\Delta\delta$ ($\delta_{Fe(acac)2}$-δ_{obs})
1	40 mM	0	39.45	-
2	40 mM	10	39.43	0.02
3	40 mM	20	39.20	0.25
4	40 mM	30	38.83	0.62
5	40 mM	40	38.53	0.92
6	40 mM	80	37.34	2.11
7	40 mM	200	34.32	5.13
8	40 mM	400	32.00	7.45
9	40 mM	800	29.76	9.69
10	40 mM	2000	28.23	11.22
11	40 mM	3000	27.89	11.56
12	40 mM	4000	27.57	11.88
13	40 mM	8000	26.70	12.75



$\mathbf{K_{eq}} = 3.2 \pm 0.2\ M^{-1}$

$\mathbf{\Delta G} = -0.8 \pm 0.1$ kcal/mol

Figure S20. Data used for calculation of K_{eq}. The fit for weak binding does not specify the number of EtOH molecules that bind. The observation of one K_{eq} is reasonable if the first EtOH binding constant is weaker than the binding constant of the second EtOH, as indicated by the DFT computations given in the text.

1.N Monitoring product distribution and starting material consumption of olefin coupling. In a N_2-filled glove box, compound **1** (120 mg, 0.60 mmol, 1.0 equiv.), benzyl acrylate (90 μL, 0.60 mmol, 1.0 equiv.), $Fe(acac)_3$ (11 mg, 0.030 mmol, 0.050 equiv.) and 1,3,5-trimethoxybenzene (100 mg, 0.60 mmol, 1.0 equiv.) were added to a Schlenk flask with 3 mL of EtOH. The flask was then taken out of the glovebox and stirred at room temperature for 1 minute to make a homogenous reaction solution. Under a flow of N_2, $PhSiH_3$ (150 μL, 1.20 mmol, 2.0 equiv) was injected into the solution, and the reaction was heated to 40 °C in an oil bath. The reaction was monitored by taking aliquots of the reaction mixture at 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20 min and immediately filtering each reaction aliquot through a silica plug with EtOAc. The product formation and starting material consumption at each time point were analyzed by gas chromatography.

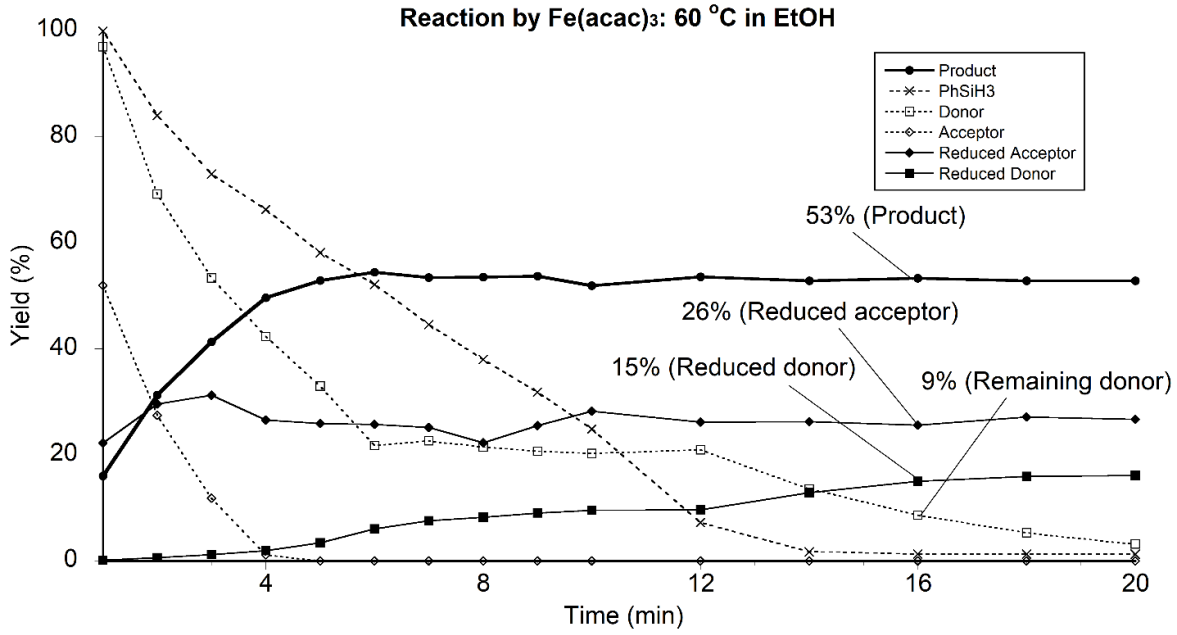
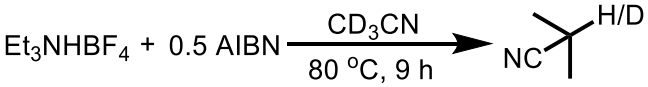


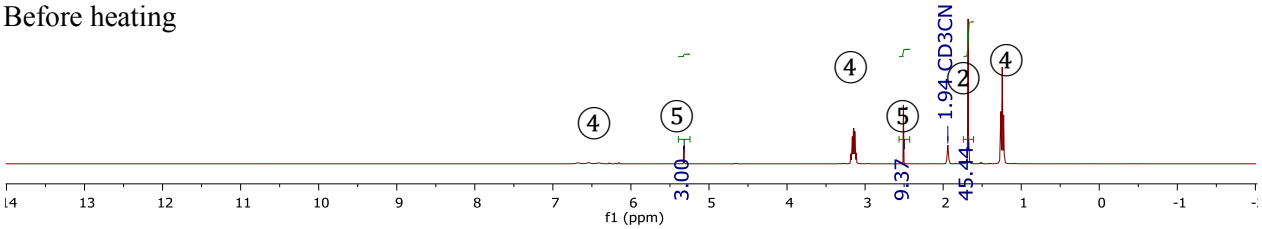
Figure S21. Product distribution of olefin coupling reaction.

1.O Reaction between AIBN and Et_3NHBF_4. In an N_2-filled glovebox, azobisisobutyronitrile, AIBN (3.3 mg, 0.020 mmol, 1.0 equiv) and triethylammonium tetrafluoroborate (8 mg, 0.040 mmol, 2.0 equiv) were mixed in 1 mL of CD_3CN. The solution was transferred to a J.Young tube containing an internal capillary with [4.8 mM] solution of 1,3,5-trimethoxybenzene in toluene-d_6. The ^1H NMR spectrum was recorded immediately to quantify the initial concentration AIBN in the solution (**Figure S22**, top). After heating the solution at 80 °C for 9 hours, the ^1H NMR spectrum was recorded to quantify the final concentration of starting materials and products (**Figure S22**, bottom).

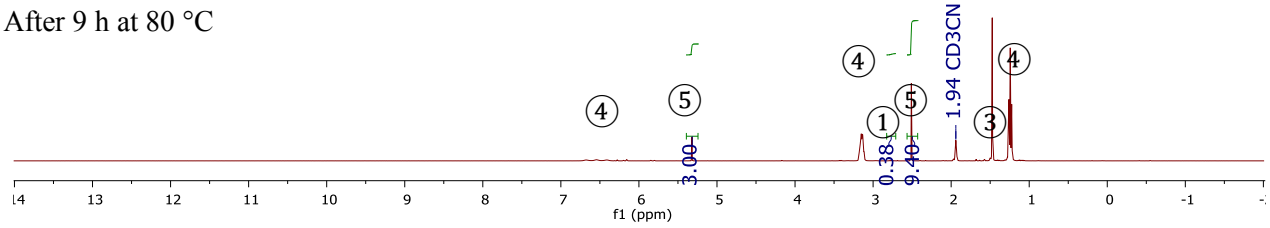


①: isobutyronitrile (IBN) ②: azobisisobutyronitrile (AIBN)
③: tetramethylsuccinonitrile(TMSN) ④: Et_3NHBF_4 ⑤: internal standard

Before heating



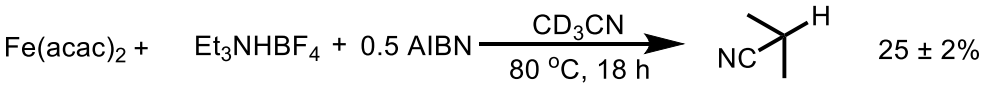
After 9 h at 80 °C



	[AIBN]	[IBN]
Before heating	17 ± 1 mM	-
After 12 h at 80 °C	-	0.3 mM

Figure S22. ^1H NMR spectra of the reaction before and after heating at 80 °C. The table shows the concentrations of starting materials and products calculated using the internal capillary.

1.P Reaction between $Fe(acac)_2$ and 0.5 equiv AIBN with 1 equiv Et_3NHBF_4. In an N_2-filled glovebox, $Fe(acac)_2$ (10 mg, 0.040 mmol, 1.0 equiv) and triethylammonium tetrafluoroborate (8 mg, 0.040 mmol, 1.0 equiv) were mixed in 0.5 mL of CD_3CN. The solution was transferred to a J.Young tube containing azobisisobutyronitrile (AIBN, 3.3 mg, 0.020 mmol, 0.50 equiv) in 0.5 mL of CD_3CN. After heating the J. Young tube at 80 °C for 18 h, all volatile materials were vacuum transferred to another J. Young tube containing 1,3,5-trimethoxybenzene (6.7 mg, 0.040 mmol, 1.0 equiv.) as an internal standard. The amount of isobutyronitrile was determined by ^{1}H NMR spectroscopy (**Figure S23**)



①: isobutyronitrile ②: triethylamine ③: 1,3,5 trimethoxy benzene ④*: diethyl ether

*residual diethyl ether from Et_3NHBF_4

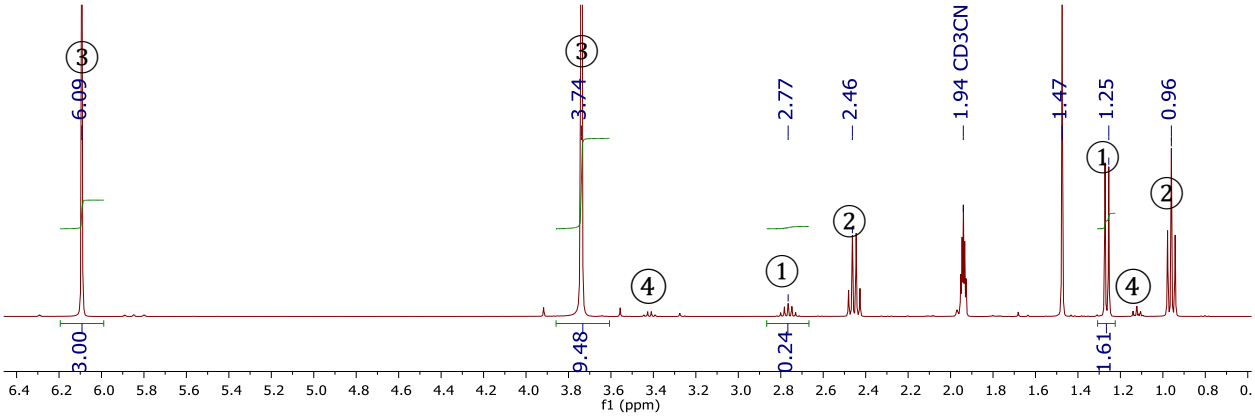
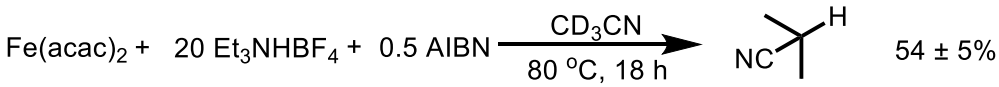


Figure S23. ^{1}H NMR of vacuum transferred reaction solution containing isobutyronitrile and ethanol. Integrations of α and β hydrogens to nitrile group of isobutyronitrile respect to the integrations of 1,3,5-trimethoxybenzene were used to quantify the formation of isobutyronitrile.

1.Q Reaction between $Fe(acac)_2$ and 0.5 equiv AIBN with 20 equiv Et_3NHBF_4. In an N_2-filled glovebox, $Fe(acac)_2$ (10 mg, 0.040 mmol, 1.0 equiv) and triethylammonium tetrafluoroborate (160 mg, 0.80 mmol, 20.0 equiv) were mixed in 0.5 mL of CD_3CN. The solution was transferred to a J.Young tube containing azobisisobutyronitrile (AIBN, 3.3 mg, 0.020 mmol, 0.50 equiv) in 0.5 mL of CD_3CN. After heating the J. Young tube at 80 °C for 18 h, all volatile materials were vacuum transferred to another J. Young tube containing 1,3,5-trimethoxybenzene (6.7 mg, 0.040 mmol, 1.0 equiv.) as an internal standard. The amount of isobutyronitrile was determined by ^{1}H NMR spectroscopy (**Figure S24**)



①: isobutyronitrile ②: triethylamine ③: 1,3,5 trimethoxybenzene ④*: diethyl ether

*residual diethyl ether from Et_3NHBF_4

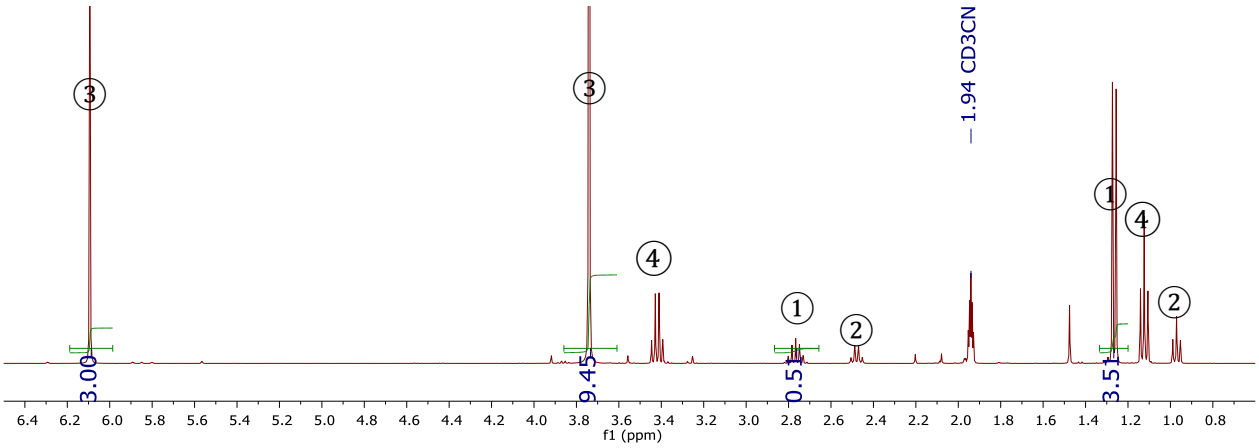
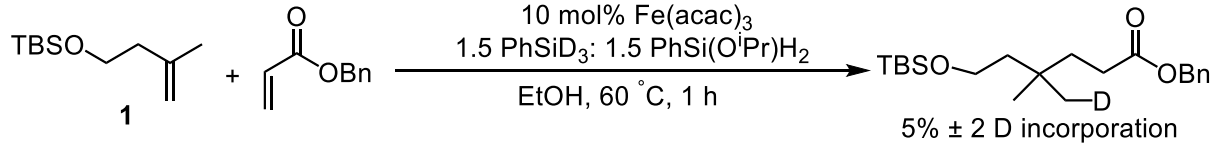
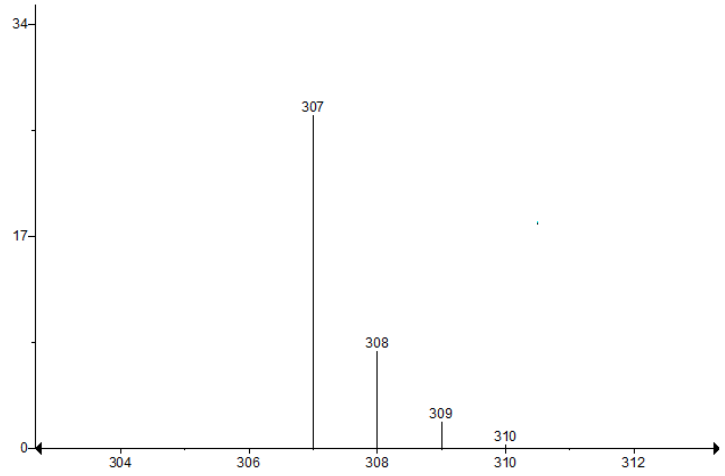


Figure S24. ^{1}H NMR of vacuum transferred reaction solution containing isobutyronitrile and ethanol. Integrations of α and β hydrogens to nitrile group of isobutyronitrile respect to the integrations of 1,3,5-trimethoxybenzene were used to quantify the formation of isobutyronitrile.

1.R Competition reaction between $PhSiD_3$ and $PhSi(O^iPr)H_2$. In an N_2-filled glove box, compound **1** (20 mg, 0.10 mmol, 1.0 equiv) and benzyl acrylate (15 µL, 0.10 mmol, 1.0 equiv) and $Fe(acac)_3$ (3.5 mg, 0.010 mmol, 0.10 equiv) were added to a vial. $PhSiD_3$ (21 mg of 65% solution in diethyl ether, 0.15 mmol, 1.5 equiv) and $PhSi(O^iPr)H_2$ (25 mg, 0.15 mmol, 1.5 equiv) in 0.5 mL of EtOH were added to the reaction vial. The reaction vial was then placed immediately to preheated oil bath at 60 °C. After stirring the reaction for an hour, 0.3 mL of reaction aliquot was taken out and filtrated through a plug of silica (3.0 cm) in a pipette with 2.0 mL of hexanes:EtOAc (4:1). From this eluent, the ratio of H/D incorporation in the cross-coupling product was determined by mass spectrometry (**Figure S25**).





	307	308	309	310
Observed (%)	100	28.9(3)	7.7(9)	1.1
Calculated (%)	100	28.9(8)	7.5(0)	0.8
Error	0	0.05	0.2	0.3

Figure S25. Mass spectrum of H/D product mixture from the reaction. Observed peaks correspond to loss of the tBu group to form $C_{17}H_{27}O_3Si^+$ at m/z 307 (100%), 308 (28.9%), 309 (7.7%) and 310 (1.1%). From these, the ratio of H/D product was calculated to be 21.5:1 (H:D).

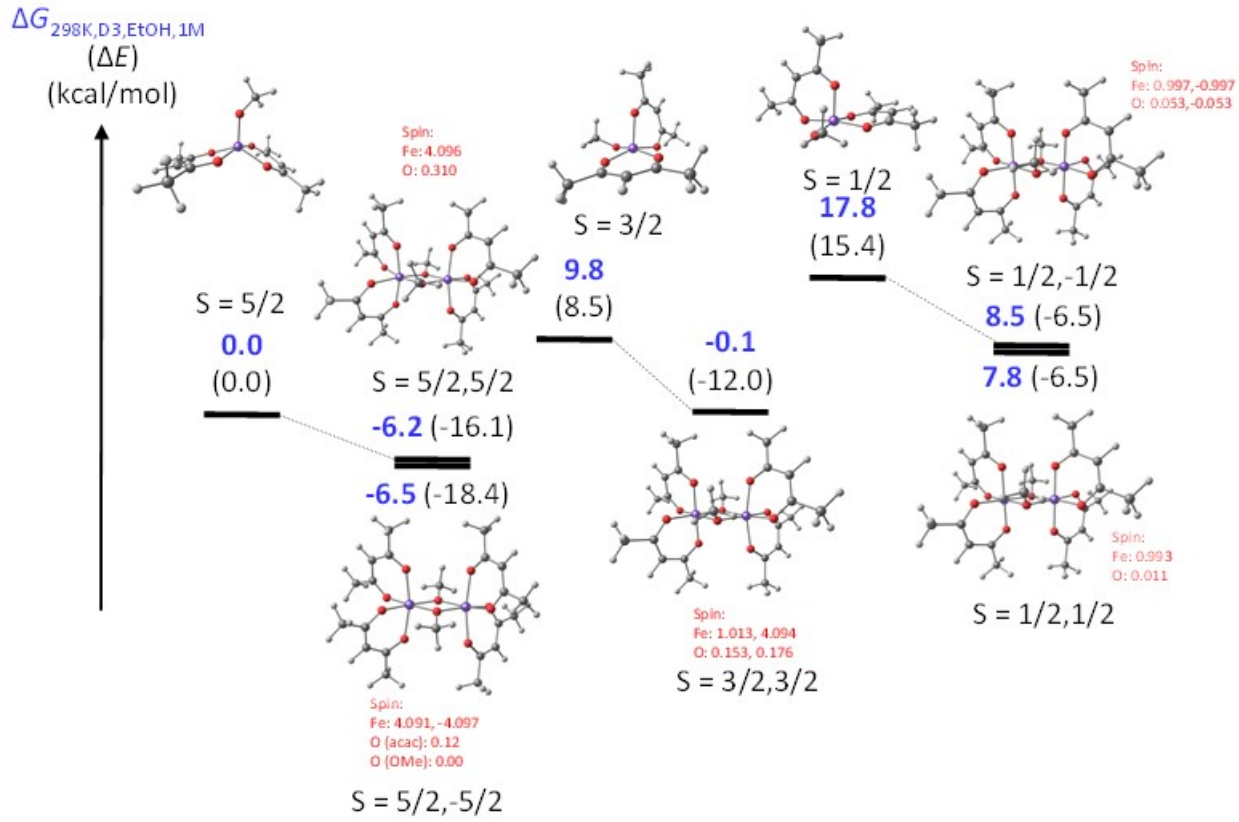
2. Computational Procedures and Data

Computational Details. The computational work was carried out using the Gaussian09 suite of programs.[5] Gas-phase geometry optimizations were performed without any symmetry constraint using the BPW91* functional, which is a reparametrized version of B3PW91 with the same parameters previously optimized for B3LYP,[6] and the 6-31G(d,p) basis functions for all light atoms (H, C, O, Si), whereas the Fe, atom was treated with the LANL2DZ basis set augmented by an f polarization function ($\alpha = 2.462$).[7] The unrestricted formulation was used for open-shell molecules, which typically yielded only minor spin contamination for all mononuclear systems ($<S^2>$ at convergence was very close to the expected values, namely 0.75 for doublet states, 2 for triplet states, 3.75 for quartet states, 6 for quintet states and 8.75 for sextet states). Significant spin contaminations were found in the dinuclear structures with an open-shell singlet state, with the strongest discrepancy for the antiferromagnetic (S = 5/2,5/2) $[Fe(acac)_2(OMe)]_2$, for which $<S^2> = 4.95$ vs. a theoretical value of 0 (the corresponding ferromagnetic dimer with S = 5 yields $<S^2> = 30.01$ vs. a theoretical value of 30). Some of the O-bound enolate complexes also had large values of $<S^2>$, and showed significant spin density on the alpha-carbon atom. We presume that this corresponds to a second resonance structure Fe^{2+}–O=C(OR)–C•HR being important, meaning that a single-determinant model is not ideal. Please see the individual computational results below, which each give the value of $<S^2>$.

All final geometries were characterized as local minima by verifying that all second derivatives of the energy were positive. Thermochemical corrections were obtained at 298.15 K on the basis of frequency calculations, using the standard approximations (ideal gas, rigid rotor and harmonic oscillator). Corrections for dispersion were carried out at the fixed BPW91* optimized geometries using Grimme's D3 empirical method (BPW91*-D3), using SR6 and S8 parameters identical to those optimized for B3PW91.[8] Solvation effects in ethanol solution were taken into account by treating the solvent medium as a polarizable continuum with the SMD approach,[9] using the standard parameters and the dielectric constant ($\varepsilon = 24.852$) of the Gaussian program package. A further correction of 1.95 kcal/mol was applied to bring the *G* values from the gas phase (1 atm) to the solution (1 mol/L) standard state.[10]

2.A $(acac)_2Fe^{III}$ methoxides

A1. Energy diagram and views of the optimized geometries



A2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

$Fe(acac)_2(OMe)$ S = 5/2

E = -928.28484578

$G_{298K,D3,EtOH,1M}$ = -928.136367

$\langle S^2 \rangle$ = 8.762

26	0.045704000	0.009496000	0.412557000
8	-1.155265000	1.453178000	-0.235616000
8	-1.470766000	-1.246149000	-0.024373000
6	-2.340282000	1.418445000	-0.712593000
6	-3.095325000	0.250075000	-0.885098000
1	-4.092264000	0.333754000	-1.305793000
6	-2.620051000	-1.022859000	-0.527097000
8	1.539778000	1.318547000	0.151729000
8	1.226655000	-1.334375000	-0.452586000
6	2.753826000	1.114212000	-0.173157000
6	3.264965000	-0.123531000	-0.600741000
1	4.315318000	-0.186355000	-0.866654000
6	2.473260000	-1.272329000	-0.729607000
6	-3.491380000	-2.237045000	-0.730622000
1	-4.466040000	-1.990031000	-1.160652000
1	-2.973046000	-2.944896000	-1.388469000
1	-3.637129000	-2.744011000	0.230735000
6	-2.918096000	2.755830000	-1.099819000
1	-3.931334000	2.675877000	-1.503324000
1	-2.927620000	3.412584000	-0.221631000
1	-2.266485000	3.228924000	-1.844175000
6	3.082341000	-2.555726000	-1.234930000
1	4.144935000	-2.453043000	-1.471915000
1	2.953484000	-3.337805000	-0.477017000
1	2.540625000	-2.885583000	-2.129482000
6	3.661988000	2.315100000	-0.087905000
1	4.687537000	2.091293000	-0.394502000
1	3.260161000	3.117472000	-0.718038000
1	3.665149000	2.689403000	0.942870000
8	0.081875000	-0.192918000	2.209064000
6	-0.895113000	-0.534188000	3.141858000

1	-1.405025000	0.364147000	3.528778000
1	-1.658593000	-1.200727000	2.708162000
1	-0.432990000	-1.052079000	3.997148000

$[Fe(acac)_2(OMe)]_2$ S = 5/2,5/2 (overall S = 5)
E = -1856.59531473
$G_{298K,D3,EtOH,1M}$ = -1856.282663
$\langle S^2 \rangle$ = 30.015

26	-1.552409000	0.079721000	0.058342000
8	-2.875010000	-0.218298000	1.560743000
8	-1.722708000	-1.928240000	-0.264172000
6	-3.646069000	-1.210039000	1.787294000
6	-3.583309000	-2.440081000	1.118545000
1	-4.289324000	-3.216233000	1.397175000
6	-2.610204000	-2.738092000	0.146430000
8	-1.813159000	2.059636000	0.303108000
8	-3.002508000	0.226682000	-1.375812000
6	-2.668145000	2.857960000	-0.193555000
6	-3.632055000	2.506259000	-1.154146000
1	-4.311347000	3.274820000	-1.509515000
6	-3.735580000	1.217946000	-1.699502000
6	-2.575483000	-4.114979000	-0.473422000
1	-3.331456000	-4.786368000	-0.056183000
1	-2.730935000	-4.024296000	-1.555388000
1	-1.580995000	-4.552456000	-0.327705000
6	-4.672611000	-0.999009000	2.873881000
1	-5.297115000	-1.881234000	3.041069000
1	-4.162952000	-0.734137000	3.808175000
1	-5.311487000	-0.148509000	2.606801000
6	-4.775697000	0.938021000	-2.758466000
1	-5.373246000	1.819695000	-3.007448000
1	-4.279255000	0.570483000	-3.664708000
1	-5.439752000	0.137487000	-2.410585000
6	-2.598985000	4.278981000	0.311337000
1	-3.351976000	4.927334000	-0.145839000
1	-2.729746000	4.280458000	1.400065000
1	-1.600276000	4.682929000	0.107848000
8	0.039223000	0.100039000	1.263377000
8	-0.054424000	0.097716000	-1.254320000
26	1.537658000	0.070304000	-0.040893000
6	0.127696000	-0.310106000	2.604667000
1	-0.876403000	-0.348743000	3.046126000
1	0.591389000	-1.305621000	2.668146000
1	0.745138000	0.395511000	3.178704000
6	-0.123799000	-0.487282000	-2.531944000
1	0.818222000	-0.315883000	-3.069026000
1	-0.303752000	-1.569384000	-2.449901000
1	-0.952331000	-0.043517000	-3.100739000
8	1.682911000	-1.942540000	0.258914000
8	2.871970000	-0.225203000	-1.534607000
8	1.826339000	2.044923000	-0.280639000
6	2.555143000	-2.762709000	-0.163927000
6	3.621092000	-1.228928000	-1.779797000
6	2.736438000	2.810471000	0.168255000
6	4.651686000	-1.020583000	-2.863145000
1	4.147192000	-0.729824000	-3.792516000
1	5.307706000	-0.187787000	-2.582208000
1	5.258178000	-1.912322000	-3.045538000
6	2.494840000	-4.147246000	0.436541000
1	2.650037000	-4.074476000	1.519874000
1	1.492580000	-4.564097000	0.283836000
1	3.239063000	-4.826431000	0.010845000
6	3.533129000	-2.468976000	-1.132352000
1	4.223485000	-3.254415000	-1.423913000
8	2.976368000	0.194355000	1.406135000
6	3.767340000	1.154516000	1.682914000
6	4.816207000	0.852435000	2.727033000
1	4.322877000	0.537241000	3.654423000
1	5.430605000	0.009159000	2.389048000
1	5.463231000	1.709175000	2.936305000
6	2.715905000	4.223788000	-0.361857000
1	2.802697000	4.198672000	-1.454657000
1	1.747365000	4.681245000	-0.127786000
1	3.517389000	4.842204000	0.052286000
6	3.715096000	2.431379000	1.103077000
1	4.440879000	3.173733000	1.420266000

$[Fe(acac)_2(OMe)]_2$ S = 5/2,-5/2 (overall S = 0)
E = -1856.59900167
$G_{298K,D3,EtOH,1M}$ = -1856.283126
$\langle S^2 \rangle$ = 4.945

26	-1.664609000	-0.000052000	0.000300000
8	-2.993673000	-0.279894000	1.499493000
8	-1.866940000	-1.992575000	-0.336436000
6	-3.619460000	-1.326007000	1.876398000
6	-3.476041000	-2.595455000	1.300424000
1	-4.059259000	-3.416434000	1.705527000
6	-2.602449000	-2.859219000	0.230375000
8	-1.865723000	1.992838000	0.337196000
8	-2.993242000	0.280735000	-1.499019000
6	-2.599398000	2.860174000	-0.230856000
6	-3.472327000	2.597116000	-1.301662000
1	-4.054007000	3.418736000	-1.707678000
6	-3.617207000	1.327581000	-1.876996000
6	-2.498118000	-4.261436000	-0.319774000
1	-3.140528000	-4.971935000	0.208225000
1	-2.765946000	-4.251861000	-1.383233000
1	-1.455873000	-4.594799000	-0.253173000
6	-4.571228000	-1.130675000	3.031912000
1	-5.084371000	-2.053680000	3.316560000
1	-4.017383000	-0.743965000	3.895974000
1	-5.314879000	-0.370960000	2.762726000
6	-4.568537000	1.132921000	-3.032982000
1	-5.080254000	2.056471000	-3.318433000

1	-4.014689000	0.745013000	-3.896505000
1	-5.313385000	0.374358000	-2.763856000
6	-2.493674000	4.262570000	0.318618000
1	-3.134771000	4.973619000	-0.210235000
1	-2.762265000	4.253917000	1.381890000
1	-1.450946000	4.594538000	0.252576000
8	-0.096063000	0.035597000	1.233773000
8	-0.096117000	-0.036202000	-1.233259000
26	1.459790000	-0.000355000	0.000194000
6	-0.114438000	0.645339000	2.502948000
1	-0.958002000	0.255515000	3.088649000
1	0.825245000	0.431099000	3.028646000
1	-0.237054000	1.733673000	2.404604000
6	-0.114536000	-0.646610000	-2.502133000
1	0.824893000	-0.432154000	-3.028172000
1	-0.236594000	-1.734953000	-2.403197000
1	-0.958485000	-0.257502000	-3.087750000
8	1.700941000	-2.003396000	0.046673000
8	2.856742000	-0.026725000	-1.490766000
8	1.700974000	2.002758000	-0.046260000
6	2.683857000	-2.698659000	-0.361451000
6	3.716665000	-0.932763000	-1.747595000
6	2.683882000	2.698023000	0.361861000
6	4.792284000	-0.546781000	-2.734959000
1	4.323992000	-0.245295000	-3.679811000
1	5.334399000	0.327093000	-2.354170000
1	5.501489000	-1.357078000	-2.927194000
6	2.697382000	-4.138258000	0.093571000
1	2.698255000	-4.167386000	1.189689000
1	1.776368000	-4.631390000	-0.239430000
1	3.560366000	-4.693212000	-0.285501000
6	3.708083000	-2.225545000	-1.200938000
1	4.491052000	-2.916730000	-1.497283000
8	2.857425000	0.025790000	1.490490000
6	3.717238000	0.931926000	1.747359000
6	4.793207000	0.545833000	2.734308000
1	4.325236000	0.244061000	3.679228000
1	5.335300000	-0.327884000	2.353131000
1	5.502372000	1.356168000	2.926527000
6	2.697274000	4.137691000	-0.092975000
1	2.699412000	4.166919000	-1.189097000
1	1.775652000	4.630368000	0.238989000
1	3.559601000	4.692984000	0.287091000
6	3.708294000	2.224862000	1.201097000
1	4.491218000	2.916086000	1.497468000

$Fe(acac)_2(OMe)$ S = 3/2
E = -928.271325462
$G_{298K,D3,EtOH,1M}$ = -928.120782
$\langle S^2 \rangle$ = 3.813

26	0.050582000	-0.238101000	-0.490360000
8	0.880212000	1.492389000	-0.217325000
8	1.762555000	-1.085763000	-0.348584000
6	2.068148000	1.749100000	0.158344000
6	3.078662000	0.783761000	0.316210000
1	4.067313000	1.107534000	0.624416000
6	2.876353000	-0.566078000	0.027136000
8	-1.448593000	0.685775000	-1.246255000
6	-0.381104000	-2.964132000	-0.450532000
1	-0.811539000	-3.780354000	-1.051245000
1	0.697469000	-3.151235000	-0.333518000
1	-0.848776000	-2.989142000	0.548127000

$[Fe(acac)_2(OMe)]_2$ S = 3/2,3/2 (overall S = 3)
E = -1856.58883102
$G_{298K,D3,EtOH,1M}$ = -1856.272921
$\langle S^2 \rangle$ = 12.064

26	-1.441907000	0.049683000	0.010509000
8	-2.775530000	-0.180549000	1.527509000
8	-1.603702000	-1.987419000	-0.186607000
6	-3.552157000	-1.155343000	1.797731000
6	-3.487603000	-2.419118000	1.194037000
1	-4.200216000	-3.177564000	1.503198000
6	-2.501104000	-2.769936000	0.253866000
8	-1.760989000	2.026847000	0.193279000
8	-2.873334000	0.099289000	-1.448000000
6	-2.696606000	2.751689000	-0.267271000
6	-3.669345000	2.322721000	-1.187841000
1	-4.415526000	3.038348000	-1.518927000
6	-3.686261000	1.035400000	-1.744729000
6	-2.461746000	-4.180341000	-0.287581000
1	-3.242040000	-4.818718000	0.136910000
1	-2.573607000	-4.148937000	-1.378094000
1	-1.480221000	-4.621277000	-0.077304000
6	-4.588886000	-0.885765000	2.862282000
1	-5.215238000	-1.757624000	3.072247000
1	-4.087496000	-0.569495000	3.784967000
1	-5.225476000	-0.051532000	2.543309000
6	-4.721827000	0.688961000	-2.788610000
1	-5.400047000	1.519803000	-3.003741000
1	-4.215044000	0.389177000	-3.714013000
1	-5.304234000	-0.175526000	-2.447929000
6	-2.713538000	4.181498000	0.219260000
1	-3.581701000	4.739964000	-0.142648000
1	-2.702465000	4.190003000	1.315196000
1	-1.799679000	4.686064000	-0.117628000
8	0.163374000	0.073947000	1.236832000
8	0.048424000	0.015148000	-1.255820000
26	1.565698000	0.055048000	-0.033441000
6	0.259267000	-0.681364000	2.422335000
1	-0.683351000	-0.579716000	2.975070000
1	0.440983000	-1.742635000	2.202889000
1	1.084519000	-0.305537000	3.041807000
6	0.085420000	-0.721238000	-2.450791000

1	0.897127000	-0.349321000	-3.091522000
1	0.238786000	-1.792775000	-2.253578000
1	-0.873168000	-0.598849000	-2.972491000
8	1.643209000	-1.845359000	0.091500000
8	2.873003000	0.114592000	-1.418170000
8	1.438593000	1.938345000	-0.212315000
6	2.630971000	-2.551752000	-0.291455000
6	3.724009000	-0.811197000	-1.649671000
6	2.237972000	2.763430000	0.331108000
6	4.798623000	-0.446422000	-2.642754000
1	4.332913000	-0.166021000	-3.595167000
1	5.344060000	0.433509000	-2.281640000
1	5.503522000	-1.264567000	-2.814719000
6	2.582787000	-3.997190000	0.136885000
1	2.574358000	-4.049460000	1.232191000
1	1.648074000	-4.448812000	-0.215226000
1	3.429239000	-4.574742000	-0.244714000
6	3.690738000	-2.094571000	-1.091881000
1	4.464400000	-2.801254000	-1.374896000
8	2.944551000	0.079056000	1.272932000
6	3.568559000	1.135342000	1.636583000
6	4.674266000	0.894686000	2.635084000
1	4.253601000	0.445272000	3.542873000
1	5.389673000	0.174147000	2.221444000
1	5.201070000	1.814613000	2.903203000
6	1.975258000	4.209260000	-0.010796000
1	1.987716000	4.331727000	-1.099878000
1	0.969814000	4.477128000	0.334133000
1	2.704989000	4.886782000	0.441303000
6	3.291142000	2.435917000	1.204189000
1	3.895670000	3.245672000	1.600589000

$Fe(acac)_2(OMe)$ S = 1/2
E = -928.26038061
$G_{298K,D3,EtOH,1M}$ = -928.107934
$\langle S^2 \rangle$ = 1.093

26	-0.036238000	-0.358223000	-0.639093000
8	0.596089000	1.460982000	-0.651280000
8	1.737647000	-0.999546000	-0.325014000
6	1.695115000	1.888149000	-0.159077000
6	2.736085000	1.067763000	0.293394000
1	3.634332000	1.533696000	0.685605000
6	2.720234000	-0.325521000	0.131151000
8	-1.686055000	0.320474000	-1.236502000
8	-0.410162000	-0.395419000	1.187303000
6	-2.672319000	0.549097000	-0.467826000
6	-2.663188000	0.367237000	0.929479000
1	-3.573089000	0.595451000	1.475160000
6	-1.562404000	-0.081071000	1.663178000
6	3.946290000	-1.137736000	0.462855000
1	4.770659000	-0.520167000	0.829589000
1	3.689806000	-1.887380000	1.220858000
1	4.273234000	-1.682807000	-0.430664000
6	1.843513000	3.387670000	-0.127114000
1	2.786641000	3.706394000	0.325357000
1	1.785191000	3.778839000	-1.150133000
1	1.006141000	3.823975000	0.430195000
6	-1.663519000	-0.232736000	3.159608000
1	-2.647085000	0.055833000	3.539381000
1	-1.462584000	-1.275127000	3.434177000
1	-0.894470000	0.381806000	3.642309000
6	-3.917906000	1.049614000	-1.152373000
1	-4.723196000	1.269164000	-0.446361000
1	-3.679551000	1.953467000	-1.724858000
1	-4.261921000	0.294646000	-1.869368000
8	-0.538184000	-1.971535000	-1.145375000
6	-0.055124000	-3.137554000	-0.541240000
1	-0.582718000	-3.998278000	-0.979509000
1	1.026266000	-3.267977000	-0.696672000
1	-0.240815000	-3.136833000	0.546080000

$[Fe(acac)_2(OMe)]_2$ S = 1/2,1/2 (overall S = 1)
E = -1856.58004998
$G_{298K,D3,EtOH,1M}$ = -1856.260270
$\langle S^2 \rangle$ = 2.114

26	-1.468055000	0.034379000	0.021661000
8	-2.771038000	0.078851000	1.424200000
8	-1.506723000	-1.875473000	-0.055621000
6	-3.608030000	-0.855559000	1.667044000
6	-3.557655000	-2.143017000	1.119480000
1	-4.321381000	-2.858699000	1.407036000
6	-2.487247000	-2.590733000	0.328157000
8	-1.438258000	1.925794000	0.183328000
8	-2.849613000	-0.024640000	-1.282646000
6	-2.282725000	2.699310000	-0.364587000
6	-3.310221000	2.312084000	-1.245197000
1	-3.954613000	3.086726000	-1.649177000
6	-3.518279000	0.996458000	-1.667266000
6	-2.416351000	-4.040524000	-0.084255000
1	-3.263666000	-4.622910000	0.288176000
1	-2.387463000	-4.103888000	-1.178560000
1	-1.484334000	-4.479852000	0.290264000
6	-4.685731000	-0.498434000	2.660186000
1	-5.377568000	-1.325658000	2.842050000
1	-4.221736000	-0.201718000	3.608506000
1	-5.245634000	0.369587000	2.292401000
6	-4.602255000	0.690947000	-2.672125000
1	-5.172417000	1.580722000	-2.953337000
1	-4.152022000	0.255599000	-3.572606000
1	-5.284049000	-0.060923000	-2.257464000
6	-2.111230000	4.161849000	-0.030712000
1	-2.956518000	4.768772000	-0.367756000
1	-1.983991000	4.275104000	1.051205000
1	-1.197029000	4.532431000	-0.510372000

8	0.074079000	0.071469000	1.235209000
8	-0.074132000	0.071733000	-1.235281000
26	1.468000000	0.034361000	-0.021678000
6	0.099586000	-0.805621000	2.338057000
1	-0.746171000	-0.560299000	2.994208000
1	0.032368000	-1.856820000	2.026730000
1	1.038750000	-0.662747000	2.887988000
6	-0.099519000	-0.805598000	-2.337974000
1	0.746221000	-0.560290000	-2.994148000
1	-0.032193000	-1.856718000	-2.026437000
1	-1.038693000	-0.662922000	-2.887940000
8	1.506791000	-1.875491000	0.055438000
8	2.770939000	0.079027000	-1.424202000
8	1.438132000	1.925776000	-0.183002000
6	2.487354000	-2.590658000	-0.328417000
6	3.608031000	-0.855277000	-1.667122000
6	2.282633000	2.699251000	0.364938000
6	4.685790000	-0.497903000	-2.660106000
1	4.221858000	-0.200656000	-3.608288000
1	5.245853000	0.369842000	-2.291906000
1	5.377487000	-1.325164000	-2.842335000
6	2.416578000	-4.040477000	0.083910000
1	2.387329000	-4.103895000	1.178200000
1	1.484772000	-4.479969000	-0.290949000
1	3.264120000	-4.622695000	-0.288272000
6	3.557716000	-2.142807000	-1.119729000
1	4.321501000	-2.858407000	-1.407333000
8	2.849641000	-0.024803000	1.282587000
6	3.518205000	0.996265000	1.667419000
6	4.602129000	0.690678000	2.672317000
1	4.151788000	0.255687000	3.572920000
1	5.283693000	-0.061488000	2.257826000
1	5.172537000	1.580364000	2.953316000
6	2.111390000	4.161710000	0.030625000
1	1.990549000	4.275148000	-1.052043000
1	1.193748000	4.530915000	0.504669000
1	2.953922000	4.769581000	0.372786000
6	3.310075000	2.311968000	1.245570000
1	3.954421000	3.086567000	1.649693000

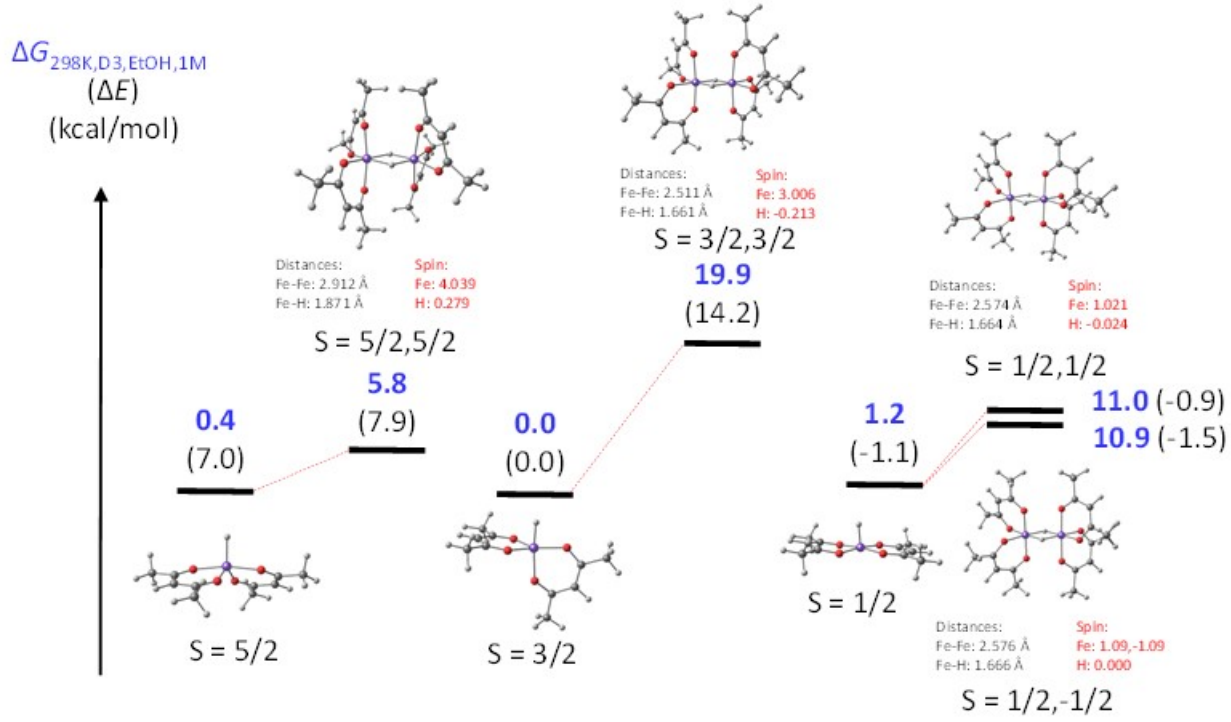
$[Fe(acac)_2(OMe)]_2$ S = 1/2,-1/2 (overall S = 0)
E = -1856.58004925
$G_{298K,D3,EtOH,1M}$ = -1856.259205
$\langle S^2 \rangle$ = 1.123

26	1.468345000	0.033951000	-0.020602000
8	2.774034000	0.078399000	-1.421599000
8	1.509371000	-1.876747000	0.057816000
6	3.612448000	-0.855161000	-1.662241000
6	3.562572000	-2.142399000	-1.113859000
1	4.327570000	-2.857373000	-1.399810000
6	2.491380000	-2.590988000	-0.324160000
8	1.436926000	1.925769000	-0.183245000
8	2.847346000	-0.021744000	1.285301000
6	2.284078000	2.699917000	0.359581000
6	3.313410000	2.313744000	1.238499000
1	3.960006000	3.088466000	1.638779000
6	3.518822000	0.999274000	1.665368000
6	2.421611000	-4.040703000	0.088823000
1	3.270180000	-4.622296000	-0.282006000
1	2.391067000	-4.103587000	1.183112000
1	1.490665000	-4.481286000	-0.286896000
6	4.691528000	-0.497681000	-2.653822000
1	5.384312000	-1.324450000	-2.834157000
1	4.228840000	-0.201789000	-3.603034000
1	5.250163000	0.370943000	-2.285533000
6	4.602547000	0.695008000	2.670831000
1	5.174869000	1.584540000	2.948385000
1	4.151691000	0.264155000	3.573155000
1	5.282390000	-0.060022000	2.258722000
6	2.113394000	4.161687000	0.022030000
1	2.959391000	4.768888000	0.356781000
1	1.985431000	4.272143000	-1.060103000
1	1.199786000	4.534235000	0.501280000
8	-0.070448000	0.067582000	-1.234504000
8	0.070458000	0.067595000	1.234450000
26	-1.468333000	0.033939000	0.020579000
6	-0.095132000	-0.810415000	-2.336657000
1	0.749355000	-0.563640000	-2.993939000
1	-0.025152000	-1.861156000	-2.024536000
1	-1.035128000	-0.669854000	-2.885734000
6	0.095154000	-0.810254000	2.336715000
1	-0.749355000	-0.563427000	2.993949000
1	0.025217000	-1.861040000	2.024725000
1	1.035135000	-0.669591000	2.885790000
8	-1.509342000	-1.876759000	-0.057747000
8	-2.774034000	0.078429000	1.421569000
8	-1.436922000	1.925758000	0.183161000
6	-2.491355000	-2.590993000	0.324235000
6	-3.612444000	-0.855126000	1.662241000
6	-2.284104000	2.699884000	-0.359651000
6	-4.691529000	-0.497619000	2.653808000
1	-4.228845000	-0.201751000	3.603030000
1	-5.250130000	0.371026000	2.285519000
1	-5.384340000	-1.324368000	2.834128000
6	-2.421574000	-4.040720000	-0.088704000
1	-2.391045000	-4.103636000	-1.182992000
1	-1.490617000	-4.481280000	0.287014000
1	-3.270131000	-4.622311000	0.282154000
6	-3.562560000	-2.142382000	1.113902000
1	-4.327559000	-2.857350000	1.399869000
8	-2.847334000	-0.021798000	-1.285320000
6	-3.518835000	0.999200000	-1.665395000
6	-4.602572000	0.694896000	-2.670832000
1	-4.151740000	0.263916000	-3.573106000

1	-5.282467000	-0.060046000	-2.258645000	1	-1.199384000	4.534009000	-0.500486000
1	-5.174840000	1.584434000	-2.948481000	1	-2.959096000	4.768970000	-0.357519000
6	-2.113481000	4.161646000	-0.022037000	6	-3.313439000	2.313682000	-1.238551000
1	-1.986433000	4.272129000	1.060207000	1	-3.960053000	3.088385000	-1.638837000

2.B FeH(acac)$_2$ (monomers vs. dimers)

B1. Energy diagram and views of the optimized geometries



B2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

FeH(acac)$_2$ S = ½
E = -813.823991991
$G_{298K,D3,EtOH,1M}$ = -813.689331
<S^2> = 0.790

26	0.001647000	-0.000044000	0.039614000	8	1.275477000	1.367510000	0.013952000
8	1.275570000	-1.367524000	0.013841000	6	2.548536000	1.230073000	-0.010780000
6	2.548623000	-1.229992000	-0.010535000	6	3.323998000	2.521448000	-0.023221000
6	3.324190000	-2.521311000	-0.022203000	6	3.219225000	0.000064000	-0.020423000
8	-1.276242000	1.360803000	-0.131030000	1	2.998136000	3.135161000	-0.871288000
6	-2.543190000	1.228239000	-0.004878000	1	-2.972122000	3.173405000	0.768198000
6	-3.206965000	-0.000045000	0.113281000	1	-3.127371000	3.037954000	-0.982323000
6	-2.543181000	-1.228246000	-0.005454000	1	4.403365000	2.358818000	-0.087821000
8	-1.276251000	-1.360672000	-0.132166000	1	-4.398679000	2.356185000	0.068927000
6	-3.322335000	2.516907000	-0.037224000	1	3.099182000	3.089268000	0.887820000
6	-3.322208000	-2.516979000	-0.037685000	1	4.304605000	0.000101000	-0.029630000
				1	-4.288705000	-0.000071000	0.202760000
				1	2.999335000	-3.134977000	-0.870695000
				1	-4.398589000	-2.356334000	0.068207000
				1	4.403617000	-2.358605000	-0.085599000

1	-3.126955000	-3.038272000	-0.982581000
1	3.098375000	-3.089225000	0.888529000
1	-2.972125000	-3.173215000	0.768017000
1	-0.213470000	-0.000957000	1.465491000

$FeH(acac)_2$ S = 3/2
E = -813.822212133
$G_{298K,D3,EtOH,1M}$ = -813.691295
$\langle S^2 \rangle$ = 3.879

26	-0.041408000	-0.631042000	-0.001393000
8	-1.786635000	-1.388792000	-0.002610000
6	-2.926095000	-0.782044000	-0.001184000
6	-4.111678000	-1.710730000	-0.002938000
8	1.258583000	-0.296114000	-1.400791000
6	2.497203000	-0.025846000	-1.241937000
6	3.139609000	0.100830000	0.000465000
6	2.496839000	-0.030490000	1.242200000
8	1.258237000	-0.301637000	1.399660000
6	3.279981000	0.168548000	-2.516202000
6	3.279096000	0.159707000	2.517420000
8	-0.824969000	1.189632000	0.001952000
6	-2.046436000	1.524010000	0.002828000
6	-2.334855000	3.004564000	0.004832000
6	-3.113704000	0.598068000	0.001556000
1	-1.866203000	3.462877000	0.883807000
1	3.218503000	-0.743304000	-3.122369000
1	2.823603000	0.975057000	-3.102500000
1	-3.405879000	3.225446000	0.010322000
1	4.330673000	0.408091000	-2.330873000
1	-1.875632000	3.463284000	-0.878973000
1	-4.130044000	0.978772000	0.002530000
1	4.200257000	0.331794000	0.001050000
1	-4.061844000	-2.364693000	0.876046000
1	4.330315000	0.397902000	2.333340000
1	-5.063818000	-1.173280000	-0.000411000
1	2.823748000	0.965812000	3.105102000
1	-4.063522000	-2.359116000	-0.886161000
1	3.215546000	-0.753296000	3.121602000
1	0.399407000	-2.072651000	-0.004221000

$FeH(acac)_2$ S = 5/2
E = -813.810985212
$G_{298K,D3,EtOH,1M}$ = -813.690720
$\langle S^2 \rangle$ = 8.759

1	-0.001879000	0.000445000	-2.322085000
26	-0.000114000	0.000025000	-0.649398000
8	-1.540442000	-1.266401000	-0.459832000
6	-2.746322000	-1.041246000	-0.117615000
6	-3.689808000	-2.210822000	-0.230076000
8	1.540574000	1.265911000	-0.461035000
6	2.746323000	1.041210000	-0.117974000
6	3.216256000	-0.201225000	0.345408000
6	2.396716000	-1.329550000	0.471048000
8	1.149549000	-1.361898000	0.179832000
6	3.689475000	2.211079000	-0.229995000
6	2.966894000	-2.626870000	0.982060000
8	-1.148956000	1.361356000	0.181577000
6	-2.396516000	1.329543000	0.471329000
6	-2.966713000	2.627123000	0.981640000
6	-3.216287000	0.201500000	0.345011000
1	-2.409401000	2.941420000	1.872225000
1	3.717691000	2.549303000	-1.272883000
1	3.301575000	3.045779000	0.365819000
1	-4.029764000	2.552248000	1.226280000
1	4.703754000	1.969108000	0.099187000
1	-2.822379000	3.406379000	0.223605000
1	-4.261617000	0.289134000	0.623257000
1	4.261379000	-0.288517000	0.624534000
1	-3.301071000	-3.046581000	0.363666000
1	4.029757000	-2.551675000	1.227416000
1	-4.703569000	-1.969235000	0.100977000
1	2.409059000	-2.941036000	1.872366000
1	-3.719714000	-2.547217000	-1.273528000
1	2.823244000	-3.406384000	0.224163000

$[FeH(acac)_2]_2$ S = 1/2,1/2 (overall S = 1)
E = -1627.64584795
$G_{298K,D3,EtOH,1M}$ = -1627.365047
$\langle S^2 \rangle$ = 2.103

26	-1.287207000	-0.000019000	0.000009000
8	-2.618375000	0.089256000	-1.350358000
8	-1.302211000	1.870900000	0.307612000
6	-3.403540000	1.079483000	-1.541649000
6	-3.316477000	2.311567000	-0.885489000
1	-4.046221000	3.078383000	-1.125990000
6	-2.253428000	2.645279000	-0.029545000
8	-1.302245000	-1.870938000	-0.307588000
8	-2.618361000	-0.089272000	1.350391000
6	-2.253468000	-2.645303000	0.029590000
6	-3.316545000	-2.311546000	0.885480000
1	-4.046381000	-3.078305000	1.125882000
6	-3.403535000	-1.079489000	1.541698000
6	-2.152443000	4.047475000	0.519011000
1	-3.057353000	4.633006000	0.332533000
1	-1.957677000	4.003205000	1.595976000
1	-1.300325000	4.557466000	0.053080000
6	-4.461206000	0.851542000	-2.592662000
1	-5.135275000	1.706606000	-2.694864000
1	-3.976846000	0.659784000	-3.557815000
1	-5.042078000	-0.043072000	-2.339831000
6	-4.461300000	-0.851473000	2.592595000
1	-5.135437000	-1.706491000	2.694732000
1	-3.977021000	-0.659742000	3.557792000
1	-5.042093000	0.043178000	2.339705000

6	-2.152647000	-4.047439000	-0.519148000
1	-3.057619000	-4.632896000	-0.332738000
1	-1.957880000	-4.003067000	-1.596111000
1	-1.300582000	-4.557568000	-0.053277000
26	1.287207000	-0.000017000	-0.000013000
8	1.302218000	1.870890000	-0.307685000
8	2.618377000	0.089303000	1.350349000
8	1.302237000	-1.870924000	0.307658000
6	2.253436000	2.645280000	0.029444000
6	3.403546000	1.079534000	1.541603000
6	2.253453000	-2.645308000	-0.029499000
6	4.461208000	0.851630000	2.592629000
1	3.976845000	0.659901000	3.557786000
1	5.042084000	-0.042990000	2.339828000
1	5.135274000	1.706699000	2.694806000
6	2.152447000	4.047459000	-0.519151000
1	1.957682000	4.003157000	-1.596115000
1	1.300327000	4.557461000	-0.053236000
1	3.057355000	4.632998000	-0.332689000
6	3.316483000	2.311597000	0.885403000
1	4.046225000	3.078422000	1.125882000
8	2.618358000	-0.089327000	-1.350393000
6	3.403523000	-1.079558000	-1.541669000
6	4.461309000	-0.851575000	-2.592553000
1	3.977045000	-0.659876000	-3.557764000
1	5.042097000	0.043084000	-2.339683000
1	5.135447000	-1.706597000	-2.694650000
6	2.152644000	-4.047415000	0.519316000
1	1.957861000	-4.002988000	1.596274000
1	1.300593000	-4.557579000	0.053459000
1	3.057626000	-4.632870000	0.332950000
6	3.316534000	-2.311585000	-0.885397000
1	4.046378000	-3.078350000	-1.125757000
1	0.000008000	-0.000008000	1.054801000
1	-0.000008000	-0.000046000	-1.054806000

$[FeH(acac)_2]_2$ S = 1/2,-1/2 (overall S = 0)
E = -1627.64681213
$G_{298K,D3,EtOH,1M}$ = -1627.365163
$\langle S^2 \rangle$ = 1.265

26	-1.288047000	0.000046000	-0.000022000
8	-2.620225000	0.069395000	-1.358775000
8	-1.306695000	1.872123000	0.282037000
6	-3.403378000	1.057691000	-1.565140000
6	-3.317684000	2.297702000	-0.922947000
1	-4.046230000	3.062064000	-1.174644000
6	-2.257960000	2.641601000	-0.067414000
8	-1.306555000	-1.872033000	-0.282077000
8	-2.620273000	-0.069393000	1.358679000
6	-2.257780000	-2.641577000	0.067336000
6	-3.317549000	-2.297758000	0.922845000
1	-4.046029000	-3.062182000	1.174547000
6	-3.403367000	-1.057742000	1.565015000
6	-2.159000000	4.049826000	0.465650000
1	-3.062521000	4.633612000	0.267522000
1	-1.970359000	4.017728000	1.544145000
1	-1.303931000	4.553739000	-0.001474000
6	-4.458050000	0.819555000	-2.617039000
1	-5.132283000	1.673181000	-2.729783000
1	-3.970579000	0.618652000	-3.578778000
1	-5.039219000	-0.072923000	-2.357439000
6	-4.458066000	-0.819691000	2.616905000
1	-5.132230000	-1.673372000	2.729645000
1	-3.970622000	-0.618745000	3.578649000
1	-5.039305000	0.072739000	2.357297000
6	-2.158657000	-4.049815000	-0.465662000
1	-3.062122000	-4.633687000	-0.267533000
1	-1.969994000	-4.017740000	-1.544154000
1	-1.303546000	-4.553623000	0.001501000
26	1.288049000	0.000045000	0.000026000
8	1.306697000	1.872111000	-0.282107000
8	2.620228000	0.069445000	1.358775000
8	1.306555000	-1.872023000	0.282154000
6	2.257963000	2.641602000	0.067314000
6	3.403381000	1.057749000	1.565101000
6	2.257776000	-2.641583000	-0.067234000
6	4.458057000	0.819653000	2.617005000
1	3.970589000	0.618783000	3.578753000
1	5.039227000	-0.072834000	2.357435000
1	5.132290000	1.673283000	2.729716000
6	2.159006000	4.049806000	-0.465806000
1	1.970364000	4.017665000	-1.544300000
1	1.303939000	4.553740000	0.001299000
1	3.062529000	4.633598000	-0.267704000
6	3.317688000	2.297735000	0.922859000
1	4.046236000	3.062105000	1.174525000
8	2.620273000	-0.069448000	-1.358674000
6	3.403364000	-1.057807000	-1.564975000
6	4.458057000	-0.819800000	-2.616881000
1	3.970608000	-0.618883000	-3.578629000
1	5.039304000	0.072635000	-2.357307000
1	5.132214000	-1.673489000	-2.729596000
6	2.158645000	-4.049804000	0.465809000
1	1.969974000	-4.017693000	1.544298000
1	1.303536000	-4.553624000	-0.001344000
1	3.062110000	-4.633685000	0.267704000
6	3.317542000	-2.297800000	-0.922762000
1	4.046014000	-3.062238000	-1.174443000
1	-0.000020000	0.000099000	1.057445000
1	0.000022000	0.000059000	-1.057441000

$[FeH(acac)_2]_2$ S = 3/2,3/2 (overall S = 3)
E = -1627.6217793
$G_{298K,D3,EtOH,1M}$ = -1627.350935

<S^2> = 12.313

26	1.255600000	0.000027000	-0.000030000
8	2.547163000	0.047750000	-1.516644000
8	1.372433000	-1.948106000	0.000384000
6	3.125519000	-0.921265000	-2.100602000
6	2.953367000	-2.272910000	-1.755607000
1	3.506409000	-3.024638000	-2.309729000
6	2.103012000	-2.699938000	-0.727493000
8	1.372473000	1.948154000	-0.000417000
8	2.547208000	-0.047742000	1.516584000
6	2.103034000	2.699969000	0.727500000
6	2.953378000	2.272918000	1.755611000
1	3.506421000	3.024634000	2.309747000
6	3.125540000	0.921264000	2.100573000
6	1.996251000	-4.173803000	-0.418697000
1	2.740341000	-4.766539000	-0.958397000
1	2.116051000	-4.328355000	0.659436000
1	0.994436000	-4.525802000	-0.692836000
6	4.051998000	-0.547031000	-3.232539000
1	4.526426000	-1.417740000	-3.694253000
1	3.485845000	0.002600000	-3.994087000
1	4.827487000	0.131266000	-2.857186000
6	4.052013000	0.547016000	3.232513000
1	4.526635000	1.417701000	3.694074000
1	3.485789000	-0.002379000	3.994181000
1	4.827340000	-0.131498000	2.857223000
6	1.996314000	4.173838000	0.418707000
1	2.740384000	4.766558000	0.958452000
1	2.116181000	4.328397000	-0.659418000
1	0.994490000	4.525850000	0.692790000
26	-1.255647000	0.000014000	0.000018000
8	-1.372466000	-1.948117000	-0.000506000
8	-2.547199000	0.047631000	1.516647000
8	-1.372543000	1.948139000	0.000520000
6	-2.102962000	-2.700010000	0.727391000
6	-3.125477000	-0.921428000	2.100608000
6	-2.103063000	2.699996000	-0.727394000
6	-4.051919000	-0.547268000	3.232600000
1	-3.485748000	0.002338000	3.994153000
1	-4.827438000	0.131029000	2.857312000
1	-4.526309000	-1.418010000	3.694293000
6	-1.996154000	-4.173858000	0.418534000
1	-2.116023000	-4.328377000	-0.659596000
1	-0.994303000	-4.525819000	0.692587000
1	-2.740178000	-4.766649000	0.958264000
6	-2.953271000	-2.273055000	1.755573000
1	-3.506246000	-3.024826000	2.309704000
8	-2.547245000	-0.047674000	-1.516606000
6	-3.125547000	0.921363000	-2.100574000
6	-4.052003000	0.547171000	-3.232546000
1	-3.485793000	-0.002281000	-3.994183000
1	-4.827398000	-0.131277000	-2.857276000
1	-4.526542000	1.417885000	-3.694137000
6	-1.996338000	4.173849000	-0.418529000
1	-2.116247000	4.328361000	0.659598000
1	-0.994497000	4.525860000	-0.692553000
1	-2.740377000	4.766604000	-0.958278000
6	-2.953370000	2.273001000	-1.755559000
1	-3.506381000	3.024749000	-2.309685000
1	0.000036000	0.000018000	1.087981000
1	-0.000079000	0.000082000	-1.087994000

[FeH(acac)$_2$]$_2$ S = 5/2,5/2 (overall S = 5)

E = -1627.62473863

$G_{298K,D3,EtOH,1M}$ = -1627.374175

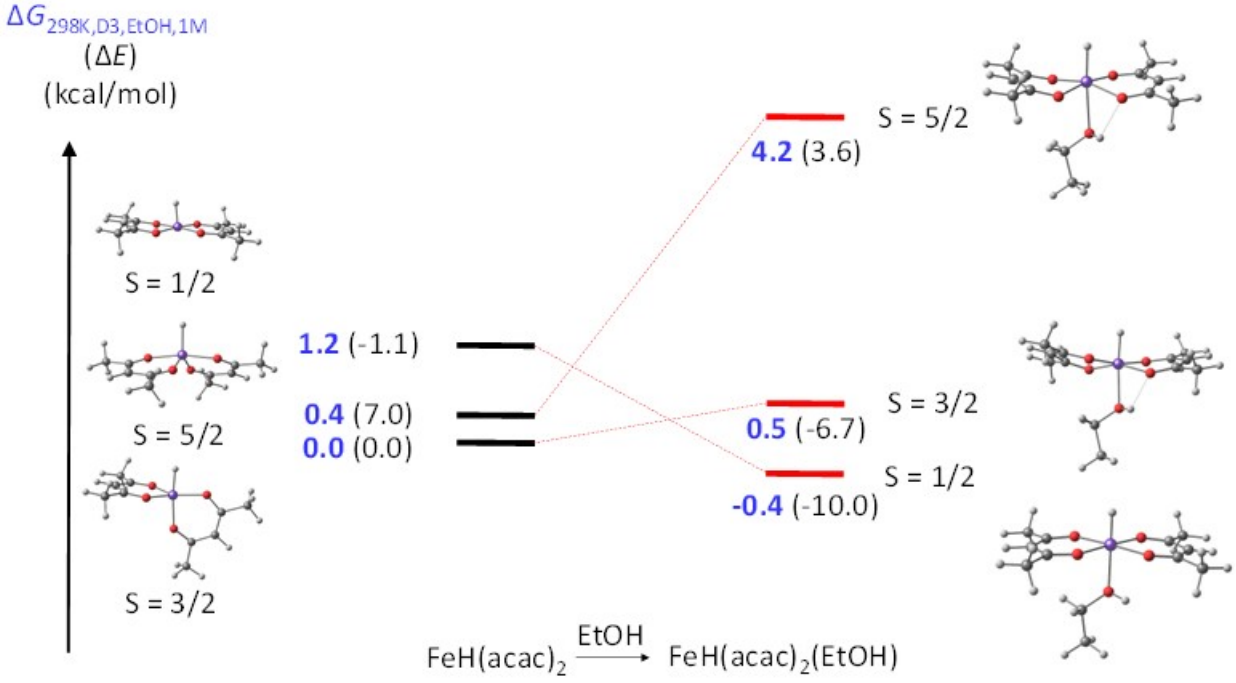
<S^2> = 30.021

26	-1.456190000	-0.001914000	-0.000033000
8	-2.610385000	-1.611114000	0.202415000
8	-1.603416000	-0.279203000	-1.977732000
6	-2.762460000	-2.569834000	-0.628410000
6	-2.358338000	-2.529019000	-1.970121000
1	-2.532168000	-3.404536000	-2.587740000
6	-1.817391000	-1.382409000	-2.578621000
8	-1.605085000	0.274702000	1.977598000
8	-2.615287000	1.603671000	-0.202833000
6	-1.823549000	1.376879000	2.578728000
6	-2.368328000	2.521692000	1.970255000
1	-2.545840000	3.396345000	2.588052000
6	-2.771499000	2.561531000	0.628227000
6	-1.473254000	-1.408499000	-4.045651000
1	-1.771110000	-2.341146000	-4.532962000
1	-1.955671000	-0.562461000	-4.548801000
1	-0.389298000	-1.277417000	-4.149228000
6	-3.440721000	-3.799634000	-0.080185000
1	-3.575906000	-4.578829000	-0.835636000
1	-2.843718000	-4.197595000	0.749328000
1	-4.417294000	-3.520455000	0.332915000
6	-3.453621000	3.789114000	0.079834000
1	-3.592886000	4.567289000	0.835597000
1	-2.856900000	4.189919000	-0.748519000
1	-4.428494000	3.506488000	-0.334921000
6	-1.480554000	1.403632000	4.046019000
1	-1.781945000	2.335068000	4.533472000
1	-1.960430000	0.555751000	4.548497000
1	-0.396235000	1.276210000	4.150360000
26	1.456025000	0.001908000	-0.000020000
8	1.603299000	0.279445000	-1.977701000
8	2.610181000	1.611066000	0.202701000
8	1.604744000	-0.274976000	1.977646000
6	1.817540000	1.382661000	-2.578469000
6	2.762557000	2.569803000	-0.628053000
6	1.823472000	-1.377148000	2.578672000
6	3.440869000	3.799484000	-0.079630000
1	2.843608000	4.197639000	0.749608000

1	4.417202000	3.520109000	0.333899000	1	2.857722000	-4.189325000	-0.749334000
1	3.576533000	4.578604000	-0.835071000	1	4.429088000	-3.506137000	-0.334474000
6	1.473518000	1.408959000	-4.045525000	1	3.592736000	-4.567369000	0.835091000
1	1.955461000	0.562640000	-4.548648000	6	1.480516000	-1.404117000	4.045973000
1	0.389485000	1.278523000	-4.149165000	1	1.959864000	-0.555937000	4.548443000
1	1.771932000	2.341439000	-4.532812000	1	0.396113000	-1.277381000	4.150337000
6	2.358625000	2.529131000	-1.969822000	1	1.782476000	-2.335373000	4.533417000
1	2.532683000	3.404658000	-2.587362000	6	2.368424000	-2.521827000	1.970087000
8	2.615149000	-1.603600000	-0.202935000	1	2.546117000	-3.396491000	2.587815000
6	2.771545000	-2.561502000	0.628046000	1	-0.001749000	1.174579000	0.000353000
6	3.453938000	-3.788892000	0.079555000	1	0.001592000	-1.174600000	0.000164000

2.C EtOH adducts of $FeH(acac)_2$

C1. Energy diagram and views of the optimized geometries



C2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

$FeH(acac)_2(EtOH)$ S = 1/2
E = -968.72715008
$G_{298K,D3,EtOH,1M}$ = -968.536197
$\langle S^2 \rangle$ = 0.790

1	-0.277705000	0.288683000	-2.011239000	6	-2.906298000	1.274223000	-0.085051000
26	-0.162670000	0.107126000	-0.587370000	6	-3.550398000	0.022757000	-0.162978000
8	0.009410000	-0.165606000	1.548422000	6	-2.884469000	-1.196429000	-0.402107000
8	-1.661319000	1.467903000	-0.250561000	8	-1.636674000	-1.320351000	-0.608420000
				6	-3.733157000	2.507623000	0.214046000
				6	-3.689044000	-2.479589000	-0.425910000
				8	1.342961000	-1.263636000	-0.841813000
				6	2.602095000	-1.092212000	-0.830817000

6	3.250605000	0.151873000	-0.694000000
6	2.579627000	1.378451000	-0.514094000
6	3.395700000	2.643153000	-0.343885000
8	1.317621000	1.524546000	-0.484093000
6	3.441025000	-2.344194000	-0.982955000
1	-3.581110000	3.249210000	-0.579512000
1	-3.379408000	2.964383000	1.146823000
1	-4.802031000	2.292235000	0.307338000
1	-4.624977000	-0.006957000	-0.005394000
1	-4.761333000	-2.313353000	-0.283960000
1	-3.525610000	-2.994241000	-1.380489000
1	-3.325534000	-3.150648000	0.362373000
1	3.173830000	3.089610000	0.633506000
1	4.473476000	2.468502000	-0.417936000
1	3.094590000	3.375641000	-1.102564000
1	4.336971000	0.163144000	-0.704878000
1	3.151768000	-2.866788000	-1.902755000
1	4.515357000	-2.137331000	-1.007526000
1	3.228940000	-3.026714000	-0.150475000
1	-0.658100000	-0.842019000	1.684419000
6	1.246443000	-0.525139000	2.169217000
1	1.605615000	-1.471678000	1.747826000
1	2.007042000	0.228525000	1.932592000
6	1.131537000	-0.664104000	3.697605000
1	0.400791000	-1.433395000	3.967241000
1	0.804425000	0.276158000	4.153024000
1	2.094441000	-0.939580000	4.140493000

FeH(acac)$_2$(EtOH) S = 3/2
E = -968.721910476
$G_{298K,D3,EtOH,1M}$ = -968.534730
$\langle S^2 \rangle$ = 3.905

1	-0.215478000	0.941113000	-1.670412000
26	-0.090128000	0.251572000	-0.311146000
8	-0.104719000	-0.978486000	1.483367000
8	-1.390912000	1.527852000	0.272900000
6	-2.662303000	1.495888000	0.095770000
6	-3.413560000	0.416548000	-0.380835000
6	-2.899711000	-0.867910000	-0.669491000
8	-1.680536000	-1.203106000	-0.567844000
6	-3.362296000	2.778226000	0.473188000
6	-3.855497000	-1.949497000	-1.122295000
8	1.190140000	-0.863586000	-1.206825000
6	2.435566000	-0.603482000	-1.413388000
6	3.168656000	0.439013000	-0.849467000
6	2.664949000	1.356842000	0.109128000
6	3.592934000	2.423245000	0.649082000
8	1.488301000	1.352994000	0.568252000
6	3.107475000	-1.562682000	-2.364868000
1	-2.962400000	3.600085000	-0.132973000
1	-3.138309000	3.016292000	1.519916000
1	-4.446170000	2.721988000	0.339304000
1	-4.483362000	0.566576000	-0.492333000
1	-4.898948000	-1.621867000	-1.136603000
1	-3.568607000	-2.279091000	-2.128496000
1	-3.758585000	-2.820576000	-0.463041000
1	3.596400000	2.380728000	1.744544000
1	4.617372000	2.329923000	0.276995000
1	3.199069000	3.408651000	0.371179000
1	4.208858000	0.537133000	-1.145914000
1	2.618392000	-1.500980000	-3.344847000
1	4.175779000	-1.359945000	-2.481412000
1	2.970349000	-2.589681000	-2.005749000
1	-0.699222000	-1.663021000	1.127415000
6	1.079478000	-1.570726000	2.033355000
1	1.580910000	-2.178802000	1.267219000
1	1.730717000	-0.724311000	2.270495000
6	0.765792000	-2.387753000	3.273324000
1	0.113082000	-3.238375000	3.038019000
1	0.266978000	-1.769772000	4.028005000
1	1.689430000	-2.788553000	3.708669000

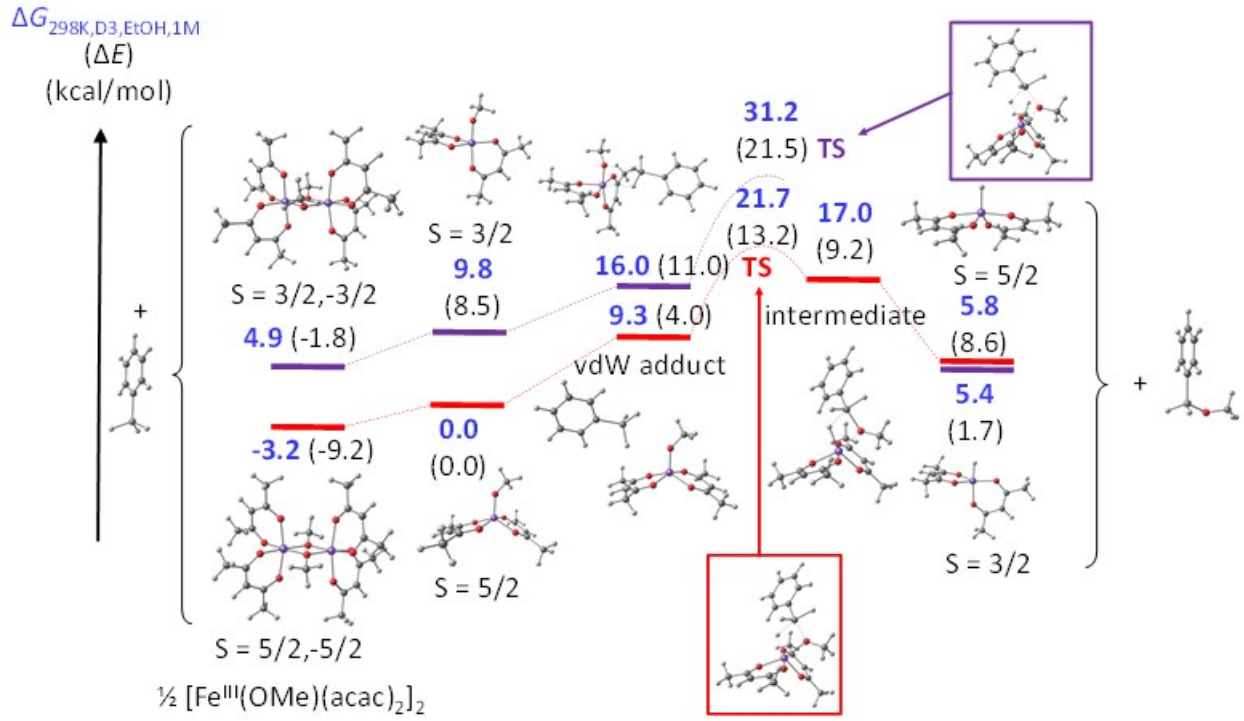
FeH(acac)$_2$(EtOH) S = 5/2
E = -968.705443892
$G_{298K,D3,EtOH,1M}$ = -968.528839
$\langle S^2 \rangle$ = 8.757

1	-0.165254000	1.130522000	-1.972516000
26	-0.104134000	0.381368000	-0.445043000
8	-0.143324000	-1.028642000	1.569519000
8	-1.561906000	1.453465000	0.375994000
6	-2.819063000	1.329204000	0.209585000
6	-3.440993000	0.222246000	-0.396409000
6	-2.751551000	-0.913900000	-0.843655000
8	-1.482288000	-1.071511000	-0.786012000
6	-3.658921000	2.469199000	0.726989000
6	-3.519745000	-2.069968000	-1.433675000
8	1.338637000	-0.922782000	-1.010244000
6	2.560774000	-0.628386000	-1.227407000
6	3.198531000	0.534604000	-0.759153000
6	2.564352000	1.501178000	0.036980000
6	3.344702000	2.686041000	0.546227000
8	1.336767000	1.459343000	0.392643000
6	3.340346000	-1.631454000	-2.040775000
1	-3.357891000	3.394349000	0.220833000
1	-3.455438000	2.608868000	1.795410000
1	-4.730240000	2.307220000	0.579320000
1	-4.522843000	0.230468000	-0.484989000
1	-4.601576000	-1.911511000	-1.418118000
1	-3.192100000	-2.223780000	-2.469125000
1	-3.279425000	-2.988036000	-0.883894000
1	3.257207000	2.736396000	1.638047000
1	4.401063000	2.648972000	0.265927000
1	2.897279000	3.605115000	0.148337000
1	4.249164000	0.673578000	-0.994144000

1	2.918192000	-1.670783000	-3.052802000
1	4.404523000	-1.388218000	-2.107119000
1	3.218145000	-2.629930000	-1.605374000
1	-0.501411000	-1.764508000	1.047862000
6	1.048991000	-1.451676000	2.228563000
1	1.796639000	-1.778668000	1.490713000
1	1.440077000	-0.552304000	2.716574000
6	0.780234000	-2.544308000	3.250233000
1	0.401819000	-3.455413000	2.767912000
1	0.038403000	-2.213244000	3.985572000
1	1.702129000	-2.810321000	3.782465000

2.D Silane activation of $Fe(OMe)(acac)_2$

D1. Energy diagram and views of the optimized geometries



$PhSiH_3$
E = -522.5619520
$G_{298K,D3,EtOH,1M}$ = -522.492697
(restricted closed-shell system, S = 0)

6	-2.350031000	0.001733000	0.008509000
6	-1.651621000	-1.206585000	0.002718000
6	-1.649446000	1.207408000	0.002500000
1	-2.194243000	-2.150328000	0.003091000
1	-2.189417000	2.152660000	0.002508000
6	-0.257639000	-1.206142000	-0.007782000
6	-0.254203000	1.203574000	-0.007878000
1	0.270876000	-2.159445000	-0.018528000
1	0.278899000	2.153856000	-0.018419000
6	0.467106000	-0.001745000	-0.009872000
1	-3.438556000	0.002647000	0.014350000
14	2.345267000	-0.000023000	0.004735000
1	2.879410000	-1.029412000	-0.934481000
1	2.843776000	1.344600000	-0.405749000
1	2.890514000	-0.303707000	1.361760000

$[Fe(OMe)(acac)_2]\cdots PhSiH_3$ (vdW adduct, S = 5/2)
E = -1450.84048913
$G_{298K,D3,EtOH,1M}$ = -1450.614230
$\langle S^2 \rangle$ = 8.762

26	-1.786716000	-0.035241000	-0.013338000
8	-3.100523000	-0.393718000	1.442034000
8	-3.360147000	-0.164532000	-1.258864000
6	-4.349589000	-0.656550000	1.406599000
6	-5.122587000	-0.691040000	0.236815000
1	-6.181033000	-0.916231000	0.319513000
6	-4.584756000	-0.440942000	-1.035984000
8	-0.662923000	0.796148000	1.416386000

8	-1.187810000	1.463713000	-1.182080000
6	0.145246000	1.780034000	1.369261000
6	0.353225000	2.583090000	0.235580000
1	1.061905000	3.402429000	0.302824000
6	-0.325675000	2.382375000	-0.975054000
6	-5.474404000	-0.485333000	-2.252907000
1	-6.510870000	-0.734247000	-2.008613000
1	-5.443976000	0.488507000	-2.756172000
1	-5.081310000	-1.222769000	-2.962853000
6	-4.988685000	-0.934810000	2.743371000
1	-6.058202000	-1.148304000	2.663064000
1	-4.482747000	-1.785981000	3.214647000
1	-4.838855000	-0.071050000	3.402104000
6	-0.058099000	3.291059000	-2.148483000
1	0.679099000	4.066142000	-1.921136000
1	0.295875000	2.690466000	-2.995007000
1	-0.996685000	3.763246000	-2.462367000
6	0.899564000	2.063117000	2.643597000
1	1.584826000	2.910137000	2.549047000
1	0.183480000	2.264592000	3.449425000
1	1.464547000	1.169328000	2.933202000
8	-0.876256000	-1.536646000	-0.454084000
6	-1.295159000	-2.781916000	-0.920028000
1	-1.519050000	-3.463421000	-0.082218000
1	-2.198590000	-2.702040000	-1.546602000
1	-0.499075000	-3.243188000	-1.524779000
14	3.061516000	-1.380494000	-0.450357000
1	2.133003000	-0.374156000	0.128578000
1	2.840832000	-2.708847000	0.191635000
1	2.761936000	-1.514410000	-1.907564000
6	4.848972000	-0.857059000	-0.177754000
6	5.851474000	-1.813644000	0.058703000
6	5.228696000	0.494882000	-0.231391000
6	7.184342000	-1.436377000	0.225486000
6	6.560045000	0.877561000	-0.065285000
6	7.540865000	-0.088738000	0.162183000
1	5.587558000	-2.869521000	0.118362000
1	4.473936000	1.263187000	-0.401059000
1	7.944831000	-2.193845000	0.408665000
1	6.832320000	1.930976000	-0.110084000
1	8.580065000	0.208191000	0.293767000

[Fe(OMe)(acac)$_2$]···PhSiH$_3$ (vdW adduct, S = 3/2)
E = -1450.82930312
$G_{298K,D3,EtOH,1M}$ = -1450.603485
$\langle S^2 \rangle$ = 3.813

26	1.207788000	0.059068000	-0.138867000
8	1.347159000	0.976961000	1.560154000
8	0.720887000	1.697303000	-1.000941000
6	1.323231000	2.229743000	1.783556000
6	1.051547000	3.207208000	0.810493000
1	1.035564000	4.250310000	1.108564000
6	0.738439000	2.884712000	-0.510517000
8	1.219250000	-1.586302000	0.834061000
8	3.197353000	-0.033416000	-0.425382000
6	2.136048000	-2.475927000	0.796890000
6	3.415098000	-2.302338000	0.249164000
1	4.102820000	-3.140577000	0.300953000
6	3.886793000	-1.096765000	-0.302737000
6	0.364794000	3.966484000	-1.489084000
1	0.391288000	4.962724000	-1.039782000
1	1.050669000	3.935354000	-2.344100000
1	-0.641921000	3.770310000	-1.877158000
6	1.589458000	2.635279000	3.210059000
1	1.570400000	3.719690000	3.347966000
1	0.839594000	2.173579000	3.863369000
1	2.566892000	2.245862000	3.518241000
6	5.317641000	-1.005742000	-0.777228000
1	5.861991000	-1.947128000	-0.660882000
1	5.331432000	-0.707975000	-1.832407000
1	5.835226000	-0.218750000	-0.215446000
6	1.763467000	-3.791182000	1.433230000
1	2.592887000	-4.503723000	1.437706000
1	1.429268000	-3.616026000	2.462501000
1	0.916626000	-4.225535000	0.888221000
8	0.696469000	-0.849571000	-1.595545000
6	1.077754000	-0.411850000	-2.870042000
1	0.597009000	-1.068369000	-3.611354000
1	0.761786000	0.624324000	-3.063259000
1	2.169269000	-0.473841000	-3.010256000
14	-2.264457000	-0.767756000	-0.778872000
1	-1.887113000	-2.204699000	-0.859852000
1	-1.388199000	-0.085201000	0.221828000
1	-2.152939000	-0.115205000	-2.112076000
6	-4.055839000	-0.590509000	-0.213580000
6	-4.448056000	-0.923909000	1.095294000
6	-5.046056000	-0.126864000	-1.095895000
6	-5.775301000	-0.802744000	1.505334000
6	-6.376903000	-0.004556000	-0.692011000
6	-6.743550000	-0.342675000	0.610454000
1	-3.705591000	-1.282166000	1.809320000
1	-4.774197000	0.145747000	-2.115785000
1	-6.055890000	-1.066082000	2.524110000
1	-7.127003000	0.356971000	-1.393882000
1	-7.780286000	-0.246770000	0.929172000

[Fe(acac)$_2$·· (H)(OMe) · SiPhH$_2$] (TS, S = 5/2)
E = -1450.82578558
$G_{298K,D3,EtOH,1M}$ = -1450.594510
$\langle S^2 \rangle$ = 8.760

26	0.971572000	0.028137000	-0.138162000
8	2.832553000	-0.501629000	-0.474537000
8	0.788270000	-1.682522000	0.909063000
6	3.492045000	-1.540344000	-0.106852000

6	2.967972000	-2.580850000	0.663315000
1	3.616290000	-3.414117000	0.914401000
6	1.637215000	-2.601123000	1.129873000
8	1.291359000	1.823543000	-0.986678000
8	0.899479000	1.004619000	1.578215000
6	1.185186000	2.995488000	-0.498183000
6	0.948797000	3.265048000	0.861508000
1	0.882048000	4.300065000	1.180708000
6	0.835821000	2.258568000	1.828192000
6	1.144660000	-3.765409000	1.949726000
1	1.914998000	-4.524212000	2.112012000
1	0.786408000	-3.396012000	2.917936000
1	0.284619000	-4.221255000	1.444905000
6	4.925158000	-1.582223000	-0.568289000
1	5.445091000	-2.485948000	-0.239198000
1	4.955974000	-1.523457000	-1.662940000
1	5.453575000	-0.700312000	-0.186454000
6	0.636736000	2.615964000	3.277705000
1	0.601566000	3.696208000	3.442827000
1	-0.295825000	2.163161000	3.635331000
1	1.450352000	2.183574000	3.872336000
6	1.341761000	4.129955000	-1.477017000
1	1.290076000	5.110783000	-0.996707000
1	2.300959000	4.028183000	-1.998158000
1	0.553600000	4.058119000	-2.236300000
8	0.103542000	-0.565621000	-1.788973000
6	0.621245000	-0.553712000	-3.102929000
1	1.568989000	-1.104485000	-3.134011000
1	-0.101568000	-1.035893000	-3.776803000
1	0.795630000	0.478155000	-3.439170000
14	-1.737644000	-0.169717000	-1.417107000
1	-1.760948000	1.191897000	-2.042586000
1	-2.048200000	-1.197745000	-2.485146000
1	-0.995318000	0.067132000	-0.023461000
6	-3.401694000	-0.348979000	-0.467817000
6	-4.482892000	-1.003435000	-1.078620000
6	-3.605352000	0.191157000	0.811231000
6	-5.728013000	-1.091633000	-0.452476000
6	-4.844694000	0.108865000	1.446961000
6	-5.911206000	-0.532661000	0.813082000
1	-4.345077000	-1.455023000	-2.062674000
1	-2.772952000	0.679910000	1.321159000
1	-6.553324000	-1.602778000	-0.947262000
1	-4.980378000	0.538037000	2.439339000
1	-6.878553000	-0.604676000	1.308453000

[Fe(acac)$_2$·· (H)(OMe) · SiPhH$_2$] (TS, S = 3/2)
E = -1450.81254994
$G_{298K,D3,EtOH,1M}$ = -1450.579294
$\langle S^2 \rangle$ = 3.810

26	0.837488000	0.046893000	-0.093179000
8	1.482361000	0.651100000	1.615448000
8	1.434548000	1.616055000	-0.941373000
6	2.176764000	1.692550000	1.856805000
6	2.523505000	2.660361000	0.900146000
1	3.100488000	3.523074000	1.215261000
6	2.115874000	2.579216000	-0.431176000
8	0.118594000	-1.475392000	0.748190000
8	2.508715000	-1.019005000	-0.569509000
6	0.570125000	-2.675178000	0.799732000
6	1.796406000	-3.107096000	0.288160000
1	2.060508000	-4.151898000	0.415448000
6	2.713125000	-2.254668000	-0.357912000
6	2.451422000	3.675581000	-1.404476000
1	3.034397000	4.476181000	-0.942239000
1	3.013595000	3.254432000	-2.246308000
1	1.521439000	4.089487000	-1.812080000
6	2.611250000	1.851535000	3.289605000
1	1.724284000	1.895153000	3.932622000
1	3.185072000	0.967939000	3.592666000
1	3.215456000	2.749086000	3.444839000
6	4.035318000	-2.802918000	-0.837147000
1	4.144014000	-3.873490000	-0.642350000
1	4.136340000	-2.618646000	-1.913256000
1	4.850687000	-2.261823000	-0.341982000
6	-0.349306000	-3.643773000	1.496680000
1	-1.307683000	-3.677860000	0.965164000
1	0.073593000	-4.650573000	1.548954000
1	-0.557539000	-3.281953000	2.510266000
8	-0.193025000	-0.301442000	-1.674040000
6	0.369049000	-0.358970000	-2.973872000
1	-0.450462000	-0.387750000	-3.704038000
1	0.994601000	0.523565000	-3.161246000
1	0.975759000	-1.266512000	-3.070994000
14	-1.813660000	0.625546000	-1.302820000
1	-2.305267000	-0.039710000	-2.585179000
1	-0.998303000	0.774885000	0.075246000
1	-1.626672000	2.052928000	-1.734817000
6	-3.445127000	0.394278000	-0.328769000
6	-3.545366000	0.672744000	1.043314000
6	-4.604559000	-0.034870000	-0.994618000
6	-4.758965000	0.554842000	1.721580000
6	-5.823899000	-0.156893000	-0.325720000
6	-5.902857000	0.140124000	1.035854000
1	-2.651614000	0.982916000	1.587307000
1	-4.545780000	-0.278870000	-2.056395000
1	-4.814458000	0.779759000	2.786328000
1	-6.711332000	-0.489484000	-0.863348000
1	-6.850664000	0.040570000	1.563416000

[FeH(acac)$_2$]···PhSi(OMe)H$_2$ (intermediate, S = 5/2)
E = -1450.83208165
$G_{298K,D3,EtOH,1M}$ = -1450.601975
$\langle S^2 \rangle$ = 8.760

26	-0.873896000	0.093699000	0.029412000
8	-1.701051000	1.743710000	-0.705661000
8	0.338244000	1.320375000	1.072899000
6	-1.336828000	2.967507000	-0.618063000
6	-0.243145000	3.417924000	0.131008000
1	-0.013885000	4.478794000	0.123438000
6	0.531344000	2.572425000	0.947928000
8	-2.214066000	-1.096767000	-0.887545000
8	-1.749247000	-0.432320000	1.717873000
6	-3.047379000	-1.925263000	-0.394651000
6	-3.283677000	-2.085318000	0.981956000
1	-4.019878000	-2.816933000	1.298898000
6	-2.631832000	-1.326831000	1.962199000
6	1.655193000	3.144618000	1.773125000
1	1.810364000	4.212027000	1.593281000
1	1.437476000	2.985579000	2.836471000
1	2.577035000	2.595379000	1.548921000
6	-2.186850000	3.951503000	-1.381433000
1	-1.819758000	4.978125000	-1.297585000
1	-2.220833000	3.662362000	-2.438589000
1	-3.216184000	3.905281000	-1.005268000
6	-2.957081000	-1.529399000	3.418798000
1	-3.731068000	-2.285700000	3.575525000
1	-2.046058000	-1.826677000	3.952195000
1	-3.285118000	-0.577169000	3.852412000
6	-3.810836000	-2.758508000	-1.391727000
1	-4.528657000	-3.432504000	-0.916436000
1	-4.339577000	-2.095451000	-2.086878000
1	-3.101173000	-3.346916000	-1.985804000
8	0.257565000	-0.115333000	-1.740659000
6	-0.162654000	0.204205000	-3.063394000
1	-0.189189000	1.293398000	-3.173509000
1	0.541407000	-0.220835000	-3.788804000
1	-1.165273000	-0.204068000	-3.236881000
14	1.332815000	-1.447274000	-1.329003000
1	0.715400000	-2.805787000	-1.162063000
1	1.896934000	-1.566750000	-2.737034000
1	0.452726000	-1.085765000	0.188736000
6	2.940003000	-1.133534000	-0.376836000
6	4.155924000	-1.253727000	-1.072723000
6	2.993353000	-0.829784000	0.993927000
6	5.380961000	-1.094822000	-0.422710000
6	4.215112000	-0.667337000	1.647883000
6	5.412037000	-0.802188000	0.941041000
1	4.140319000	-1.476922000	-2.139504000
1	2.062204000	-0.704138000	1.544300000
1	6.310720000	-1.196070000	-0.980986000
1	4.234630000	-0.434955000	2.712023000
1	6.365892000	-0.674781000	1.451240000

PhSi(OMe)H_2

E = -637.022084664

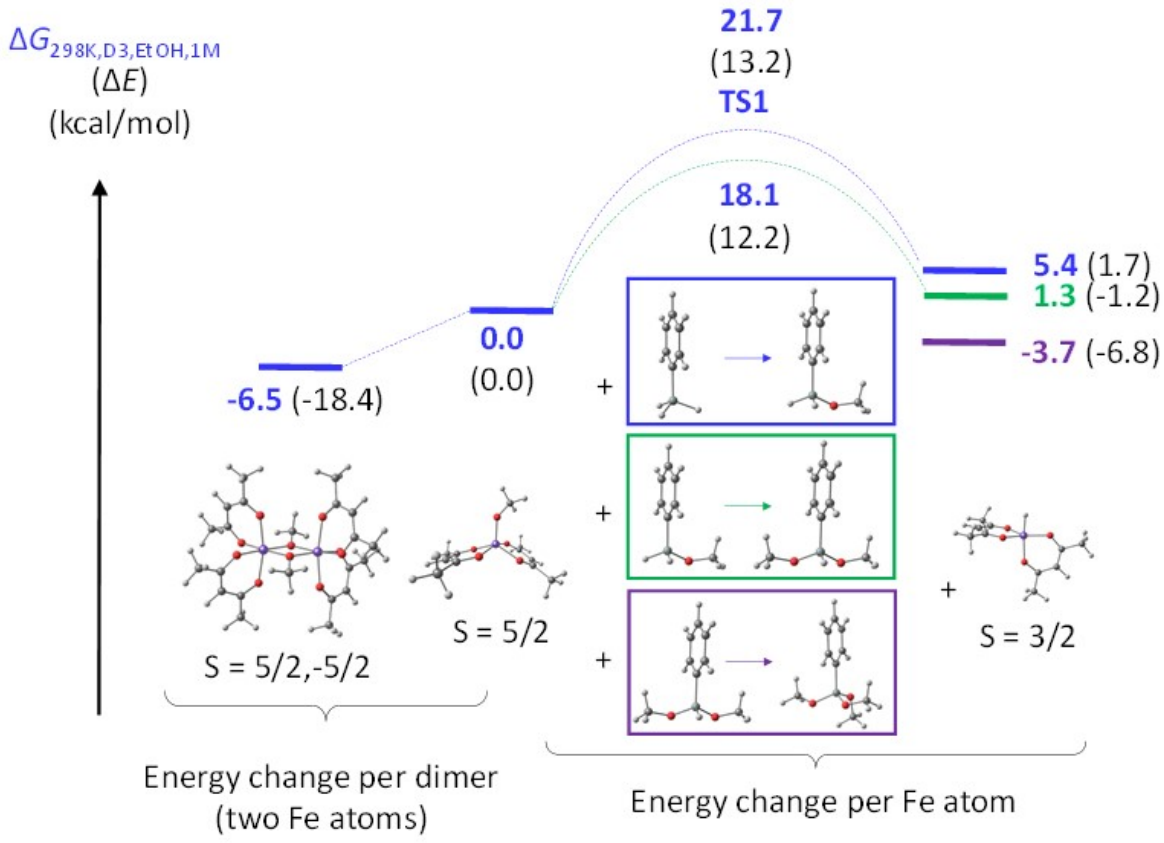
$G_{298K,D3,EtOH,1M}$ = -636.929137

(restricted closed-shell system, S = 0)

6	-2.974628000	0.054748000	-0.430485000
6	-2.320378000	1.219626000	-0.030317000
6	-2.296841000	-1.165852000	-0.414351000
1	-2.847350000	2.172179000	-0.039062000
1	-2.807382000	-2.076588000	-0.722681000
6	-0.989119000	1.161566000	0.383337000
6	-0.967571000	-1.218424000	0.001167000
1	-0.489631000	2.077861000	0.698595000
1	-0.453114000	-2.179364000	0.012934000
6	-0.286994000	-0.055560000	0.405997000
1	-4.013692000	0.096194000	-0.752704000
14	1.503220000	-0.118601000	0.958346000
1	1.806990000	1.196550000	1.608076000
1	1.726595000	-1.243246000	1.904529000
8	2.570533000	-0.416284000	-0.286436000
6	2.704124000	0.474124000	-1.379645000
1	1.769850000	0.559052000	-1.954301000
1	3.002703000	1.482193000	-1.051712000
1	3.484126000	0.084497000	-2.043244000

2.E Comparison of different silanes as activators

E1. Energy diagram and views of the optimized geometries



E2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

$PhSiH(OMe)_2$
E = -751.486638191
$G_{298K,D3,EtOH,1M}$ = -751.372166
(restricted closed-shell system, S = 0)

6	3.339951000	0.049073000	-0.187515000
6	2.792396000	-0.300647000	1.046782000
6	2.501505000	0.376310000	-1.255323000
1	3.444484000	-0.552284000	1.881463000
1	2.928701000	0.653227000	-2.217686000
6	1.406773000	-0.323122000	1.209688000
6	1.118015000	0.350408000	-1.087819000
1	0.989019000	-0.590368000	2.181129000
1	0.472305000	0.612498000	-1.925630000
6	0.544905000	-0.002961000	0.147756000
1	4.420624000	0.069798000	-0.317904000
14	-1.310957000	-0.047034000	0.381826000
1	-1.576404000	-0.162776000	1.852246000
8	-2.031927000	-1.282199000	-0.448770000
6	-1.641740000	-2.634280000	-0.300085000
1	-0.576798000	-2.782380000	-0.532394000
1	-1.830483000	-3.005512000	0.718959000
1	-2.234770000	-3.236256000	-0.997327000
8	-2.033586000	1.294252000	-0.260836000
6	-1.747819000	2.597921000	0.210212000
1	-1.988751000	2.711205000	1.278376000
1	-0.690299000	2.863240000	0.063306000
1	-2.364044000	3.305443000	-0.355428000

$PhSi(OMe)_3$
E = -865.960189226
$G_{298K,D3,EtOH,1M}$ = -865.823076
(restricted closed-shell system, S = 0)

6	3.705223000	-0.121988000	0.314154000
6	2.885172000	-0.671872000	1.300191000

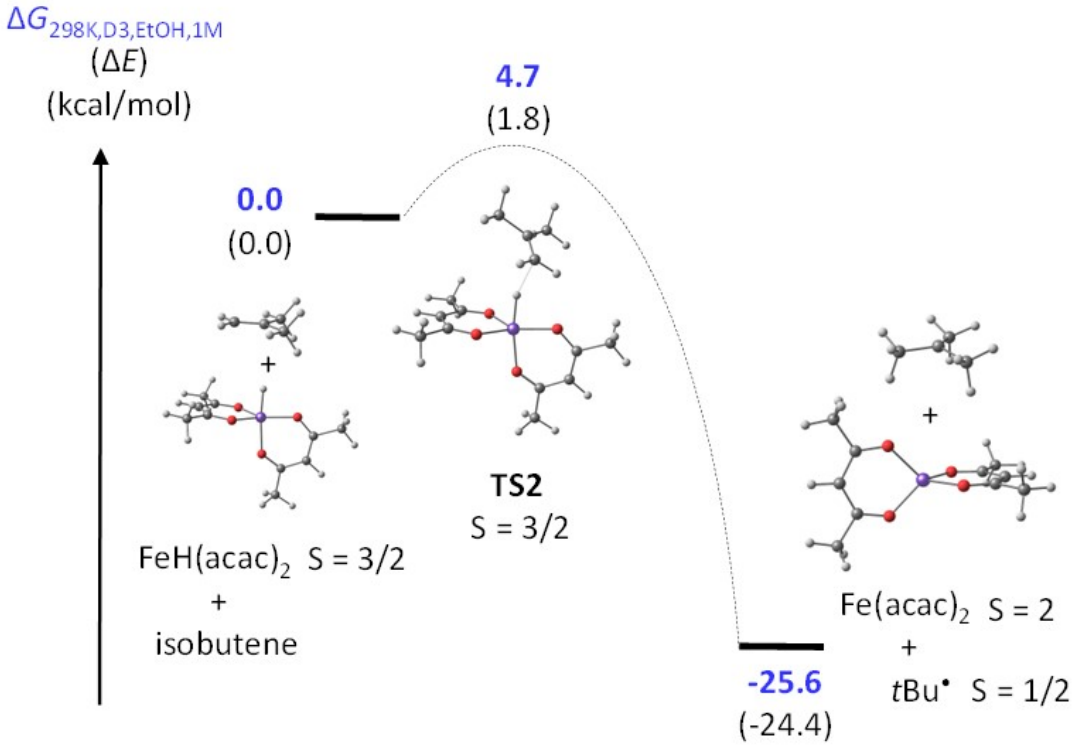
6	3.135659000	0.486675000	-0.805176000
1	3.327569000	-1.142993000	2.176389000
1	3.773024000	0.919994000	-1.574097000
6	1.498059000	-0.615046000	1.165835000
6	1.748542000	0.541685000	-0.936852000
1	0.861339000	-1.035902000	1.941967000
1	1.314279000	1.024276000	-1.812196000
6	0.904995000	-0.010037000	0.044541000
1	4.788078000	-0.165176000	0.418920000
14	-0.942718000	0.064134000	-0.175226000
8	-1.514867000	-0.934940000	-1.360187000
6	-1.153721000	-2.301385000	-1.457732000
1	-0.067473000	-2.447847000	-1.369463000
1	-1.648818000	-2.907339000	-0.684960000
1	-1.473206000	-2.667573000	-2.439785000
8	-1.440231000	1.540770000	-0.722223000
6	-1.142342000	2.745120000	-0.038131000
1	-1.712657000	2.832095000	0.897797000
1	-0.071973000	2.827712000	0.200431000
1	-1.418014000	3.582207000	-0.689235000
8	-1.567619000	-0.325513000	1.309170000
6	-2.962255000	-0.462188000	1.536951000
1	-3.459937000	0.517186000	1.556722000
1	-3.442731000	-1.077566000	0.763925000
1	-3.105685000	-0.945272000	2.509968000

[Fe(acac)$_2$·· (H)(OMe)·SiPh(OMe)H] (TS, S = 5/2)
E = -1565.28746082
$G_{298K,D3,EtOH,1M}$ = -1565.036698
$\langle S^2 \rangle$ = 8.860

26	1.161053000	0.067916000	-0.014959000
8	3.014745000	-0.246761000	-0.592117000
8	1.185387000	-1.827544000	0.681888000
6	3.774667000	-1.274428000	-0.478980000
6	3.390695000	-2.482141000	0.109356000
1	4.113566000	-3.290668000	0.148413000
6	2.110003000	-2.698483000	0.657556000
8	1.303846000	2.005585000	-0.494880000
8	1.108490000	0.677284000	1.860769000
6	0.962349000	3.025314000	0.186135000
6	0.708576000	2.996655000	1.570854000
1	0.456336000	3.925965000	2.071354000
6	0.832553000	1.834102000	2.339019000
6	1.769630000	-4.032549000	1.270696000
1	2.598965000	-4.743609000	1.223250000
1	1.477390000	-3.882255000	2.316772000
1	0.898884000	-4.453335000	0.753992000
6	5.164384000	-1.107338000	-1.035813000
1	5.770774000	-2.010581000	-0.926743000
1	5.100802000	-0.837910000	-2.096916000
1	5.660386000	-0.273523000	-0.524374000
6	0.655205000	1.885191000	3.833789000
1	0.422231000	2.890744000	4.194598000
1	-0.147184000	1.197586000	4.126679000
1	1.572679000	1.530212000	4.318571000
6	0.853249000	4.316685000	-0.579157000
1	0.638392000	5.173422000	0.065362000
1	1.783761000	4.494287000	-1.130501000
1	0.052271000	4.209075000	-1.320665000
8	0.236915000	-0.272078000	-1.742432000
6	0.679087000	-0.026622000	-3.066011000
1	1.684343000	-0.443406000	-3.194233000
1	-0.012150000	-0.512300000	-3.768948000
1	0.700099000	1.051587000	-3.264597000
14	-1.542730000	-0.225448000	-1.251286000
1	-1.817459000	-1.173580000	-2.404703000
1	-0.742476000	-0.119668000	0.151426000
6	-3.074210000	-0.756583000	-0.212297000
6	-4.069505000	-1.551492000	-0.801870000
6	-3.262443000	-0.358438000	1.120931000
6	-5.218367000	-1.920636000	-0.098366000
6	-4.408860000	-0.714709000	1.831614000
6	-5.390698000	-1.498606000	1.220535000
1	-3.937407000	-1.890991000	-1.830810000
1	-2.489305000	0.235467000	1.611926000
1	-5.976755000	-2.540482000	-0.575680000
1	-4.536445000	-0.391011000	2.864206000
1	-6.283026000	-1.786742000	1.774685000
8	-1.796345000	1.368570000	-1.740018000
6	-3.089501000	1.899561000	-1.942138000
1	-3.657399000	1.333486000	-2.697233000
1	-3.683144000	1.914666000	-1.016434000
1	-2.982476000	2.930690000	-2.303268000

2.F H atom transfer from $FeH(acac)_2$ to isobutene

F1. Energy diagram and views of the optimized geometries



F2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

isobutene
E = -157.060349441
$G_{298K,D3,EtOH,1M}$ = -156.986544
(restricted closed-shell system, S = 0)

6	-0.000014000	1.458999000	-0.000006000
6	-0.000001000	0.121173000	0.000019000
1	0.927266000	2.029552000	0.000045000
1	-0.927305000	2.029535000	-0.000040000
6	-1.274186000	-0.677749000	0.000004000
1	-1.327377000	-1.334852000	0.880040000
1	-2.160202000	-0.034456000	0.000313000
1	-1.327636000	-1.334362000	-0.880381000
6	1.274198000	-0.677728000	0.000002000
1	1.327394000	-1.334880000	0.879996000
1	1.327673000	-1.334288000	-0.880425000
1	2.160203000	-0.034419000	0.000345000

TS1
E = -970.879727691
$G_{298K,D3,EtOH,1M}$ = -970.670294
$<S^2>$ = 4.005

26	-0.338070000	-0.119499000	-0.087294000
8	-1.353921000	1.519981000	-0.276123000
6	-2.629037000	1.693428000	-0.185184000
6	-3.074514000	3.118064000	-0.400604000
8	0.726464000	-0.892169000	1.351293000
6	1.546437000	-1.866227000	1.249280000
6	1.852970000	-2.542649000	0.056561000
6	1.275875000	-2.258051000	-1.193130000
8	0.420515000	-1.335891000	-1.412797000
6	2.205245000	-2.290667000	2.539434000
6	1.658367000	-3.083893000	-2.397419000
8	-2.060392000	-1.105676000	0.267036000
6	-3.241220000	-0.654587000	0.299423000
6	-4.337542000	-1.653221000	0.585627000
6	-3.572108000	0.704125000	0.085267000
1	-4.314918000	-2.442118000	-0.175731000
1	2.742414000	-1.438366000	2.972802000
1	1.432617000	-2.582128000	3.261207000
1	-5.331878000	-1.197651000	0.602466000

1	2.900928000	-3.123444000	2.403136000
1	-4.144560000	-2.134770000	1.551740000
1	-4.617068000	0.994399000	0.133555000
1	2.571427000	-3.355144000	0.107285000
1	-2.747445000	3.456197000	-1.391521000
1	2.406319000	-3.846915000	-2.164105000
1	-4.158873000	3.235277000	-0.321022000
1	0.762343000	-3.570869000	-2.801178000
1	-2.587365000	3.767685000	0.336931000
1	2.046461000	-2.425217000	-3.183611000
1	0.836837000	0.858740000	-0.370572000
6	1.699179000	2.393836000	-1.019221000
1	0.710657000	2.830028000	-0.886872000
1	1.890880000	1.889607000	-1.965429000
6	2.702512000	2.631282000	-0.142725000
6	4.090458000	2.104914000	-0.361949000
1	4.829146000	2.919625000	-0.342603000
1	4.376508000	1.409043000	0.440799000
1	4.183579000	1.578909000	-1.317653000
6	2.469852000	3.381638000	1.135633000
1	3.147204000	4.244334000	1.217174000
1	1.439066000	3.740911000	1.215657000
1	2.675378000	2.740926000	2.005962000

$Fe(acac)_2$ S = 2
E = -813.288650469
$G_{298K,D3,EtOH,1M}$ = -813.165701
$<S^2>$ = 6.023

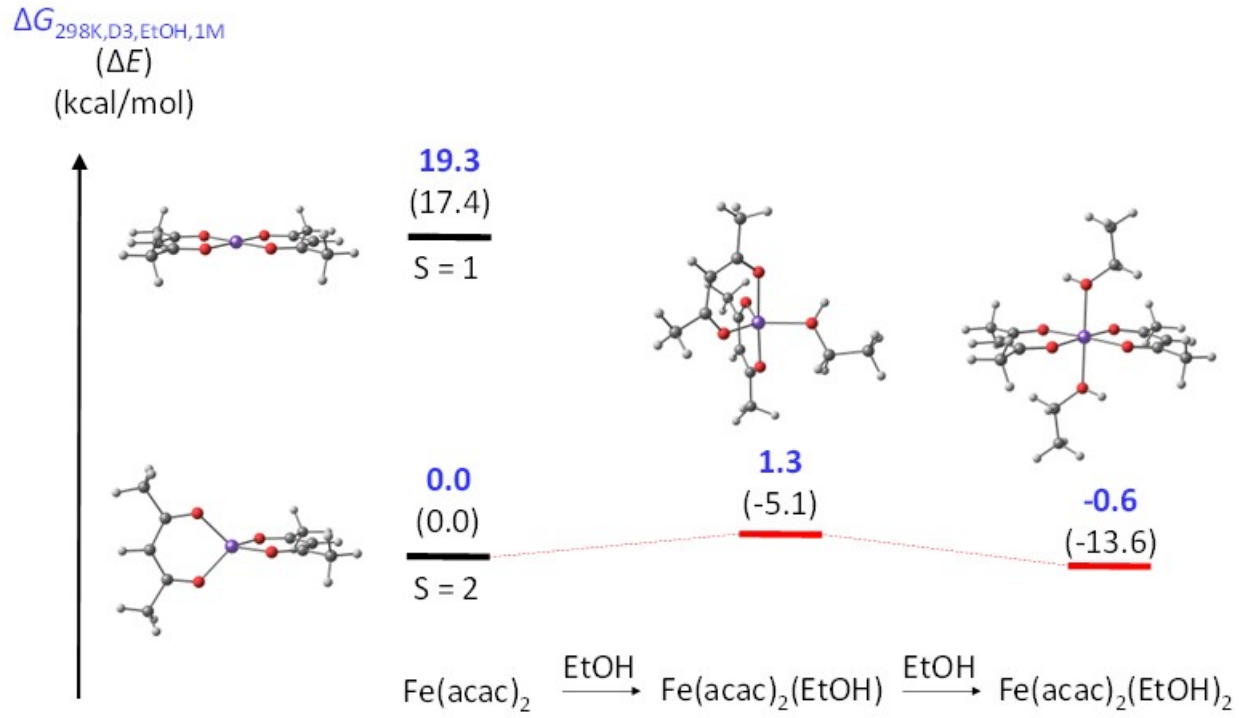
6	3.442438000	1.779416000	1.780519000
6	2.633102000	0.880340000	0.880213000
6	3.286717000	0.000395000	0.000345000
6	2.633895000	-0.879696000	-0.879922000
6	3.443996000	-1.778796000	-1.779507000
8	1.362953000	0.990922000	0.990821000
26	0.000000000	-0.000158000	-0.000660000
8	-1.363633000	0.990888000	-0.991022000
6	-2.633727000	0.879930000	-0.879893000
6	-3.443660000	1.780039000	-1.778620000
8	1.363820000	-0.990860000	-0.991087000
8	-1.363140000	-0.991372000	0.990407000
6	-2.633269000	-0.880493000	0.879856000
6	-3.442773000	-1.780103000	1.779477000
6	-3.286717000	-0.000201000	0.000213000
1	3.179893000	1.577309000	2.826093000
1	4.520249000	1.649528000	1.648942000
1	3.178141000	2.825105000	1.581488000
1	4.372447000	0.000507000	0.000713000
1	3.179822000	-2.824511000	-1.580432000
1	4.521694000	-1.648638000	-1.647273000
1	3.182056000	-1.576960000	-2.825282000
1	-3.179483000	-2.825764000	1.578890000
1	-3.179379000	-1.579600000	2.825130000
1	-4.520561000	-1.649208000	1.648703000
1	-4.372447000	-0.000059000	0.000630000
1	-3.180373000	2.825612000	-1.577531000
1	-4.521384000	1.649017000	-1.647451000
1	-3.180674000	1.580167000	-2.824490000

***tert*-butyl radical**
E = -157.632783362
$G_{298K,D3,EtOH,1M}$ = -157.552909
$<S^2>$ = 0.754

6	0.000002000	-0.000041000	-0.142150000
6	-0.001639000	1.484857000	0.014322000
6	1.286843000	-0.741016000	0.014321000
6	-1.285210000	-0.743831000	0.014323000
1	1.239256000	-1.740373000	-0.438651000
1	2.126864000	-0.199372000	-0.440835000
1	1.555056000	-0.893979000	1.077822000
1	0.887094000	1.943366000	-0.439691000
1	-0.001934000	1.793636000	1.077824000
1	-0.891332000	1.941425000	-0.439756000
1	-1.235420000	-1.743199000	-0.438422000
1	-1.553197000	-0.897220000	1.077825000
1	-2.126360000	-0.204096000	-0.441012000

2.G $Fe(acac)_2$ and EtOH adducts

G1. Energy diagram and views of the optimized geometries



G2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

$Fe(acac)_2$ S = 1
E = -813.26093563
$G_{298K,D3,EtOH,1M}$ = -813.134945
$\langle S^2 \rangle$ = 2.014

6	3.366069000	2.516864000	0.000166000
6	2.574918000	1.234209000	0.000032000
6	3.242396000	0.000000000	-0.000029000
6	2.574918000	-1.234209000	-0.000050000
6	3.366069000	-2.516864000	-0.000144000
8	1.306626000	1.385058000	0.000051000
26	0.000000000	0.000000000	-0.000010000
8	-1.306626000	-1.385057000	0.000154000
6	-2.574918000	-1.234209000	0.000097000
6	-3.366069000	-2.516864000	0.000012000
8	1.306625000	-1.385058000	0.000009000
8	-1.306626000	1.385057000	-0.000250000
6	-2.574918000	1.234209000	-0.000093000
6	-3.366069000	2.516864000	0.000019000
6	-3.242397000	0.000000000	0.000043000
1	3.093078000	3.109914000	0.881277000
1	4.445821000	2.345043000	-0.000219000
1	3.092495000	3.110465000	-0.880387000
1	4.327696000	0.000000000	-0.000042000
1	3.092496000	-3.110442000	0.880424000
1	4.445821000	-2.345043000	0.000235000
1	3.093077000	-3.109937000	-0.881240000
1	-3.092875000	3.110058000	0.880970000
1	-3.092697000	3.110321000	-0.880694000
1	-4.445820000	2.345044000	-0.000097000
1	-4.327697000	0.000000000	0.000090000
1	-3.092951000	-3.110028000	-0.880984000
1	-4.445820000	-2.345044000	0.000227000
1	-3.092620000	-3.110352000	0.880680000

EtOH
E = -154.888989006
$G_{298K,D3,EtOH,1M}$ = -154.844242
(restricted closed-shell system, S = 0)

8	-0.027152000	1.971259000	-0.796728000
1	-0.861659000	1.943185000	-1.293313000
6	0.028174000	3.121693000	0.059153000
1	-0.873064000	3.164296000	0.688958000
1	0.882544000	2.934236000	0.716967000
6	0.205894000	4.402037000	-0.735191000
1	-0.653022000	4.588276000	-1.392707000
1	1.107802000	4.349500000	-1.354757000
1	0.299195000	5.259856000	-0.057941000

$Fe(acac)_2(EtOH)$ S = 2
E = -968.185759582
$G_{298K,D3,EtOH,1M}$ = -968.007871
$\langle S^2 \rangle$ = 6.013

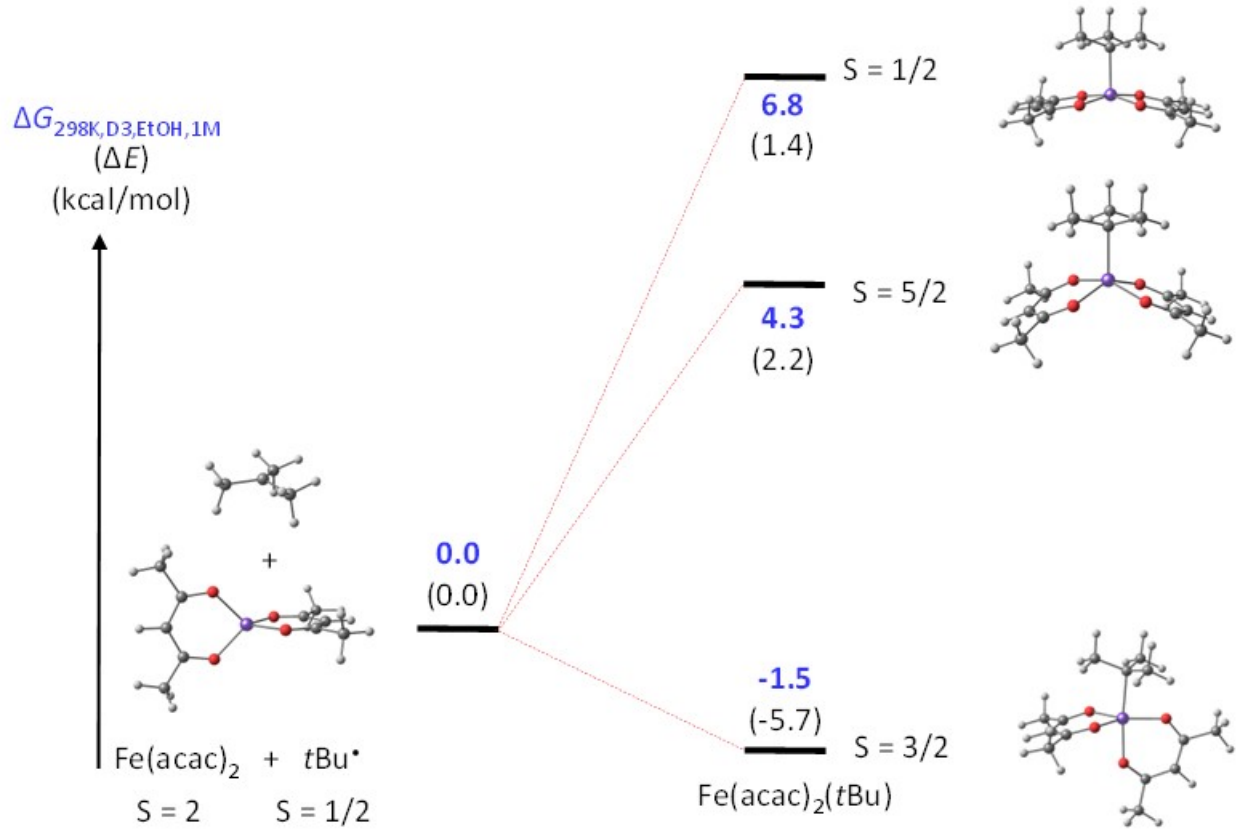
8	0.253532000	2.169588000	-0.828045000
26	0.019108000	0.169287000	-0.032439000
8	0.676705000	-1.326043000	-1.190433000
6	1.761867000	-1.971755000	-1.021988000
6	1.961854000	-3.151104000	-1.954772000
6	2.760538000	-1.678713000	-0.070252000
6	2.726056000	-0.601648000	0.831635000
8	1.781124000	0.251749000	0.931044000
6	3.890953000	-0.394030000	1.779787000
8	-1.761332000	0.083413000	-1.197521000
6	-2.898866000	-0.309397000	-0.807547000
6	-3.242111000	-0.619607000	0.529142000
6	-2.361307000	-0.508052000	1.610673000
6	-2.855671000	-0.813826000	3.010134000
8	-1.131817000	-0.156970000	1.537935000
6	-3.963536000	-0.442869000	-1.883561000
1	1.126724000	-3.849090000	-1.834935000
1	-4.066608000	0.509852000	-2.414233000
1	-3.637734000	-1.185893000	-2.619109000
1	2.900960000	-3.679815000	-1.778324000
1	-4.937571000	-0.736088000	-1.485810000
1	1.935959000	-2.798047000	-2.991039000
1	3.630883000	-2.323568000	-0.045250000
1	-4.256999000	-0.939807000	0.732246000
1	3.525979000	-0.430872000	2.811666000
1	-3.908327000	-1.103929000	3.033394000
1	4.679814000	-1.138150000	1.651728000
1	-2.249609000	-1.618851000	3.439040000
1	4.313317000	0.604841000	1.625079000
1	-2.710361000	0.066862000	3.644912000
1	-0.139156000	2.398966000	-1.673493000
6	0.993279000	3.148855000	-0.094076000
1	0.541114000	3.282466000	0.895978000
1	2.013216000	2.784222000	0.077049000
6	1.056982000	4.510684000	-0.808114000
1	0.053012000	4.917667000	-0.965943000
1	1.533208000	4.416682000	-1.789375000
1	1.629433000	5.235995000	-0.220367000

$Fe(acac)_2(EtOH)_2$ S = 2
E = -1123.08835008
$G_{298K,D3,EtOH,1M}$ = -1122.855087
$\langle S^2 \rangle$ = 6.018

8	-0.698224000	2.097592000	-0.352979000
26	-0.024438000	0.073808000	-0.012522000
8	0.648907000	-1.950186000	0.327558000
8	-1.474128000	-0.213906000	1.411108000
6	-2.635670000	-0.715315000	1.291581000
6	-3.214204000	-1.143101000	0.079392000
6	-2.558573000	-1.103116000	-1.167848000
8	-1.387120000	-0.651514000	-1.364493000
6	-3.434610000	-0.845097000	2.571925000
6	-3.278924000	-1.627937000	-2.392619000
8	1.451528000	0.283698000	-1.422532000
6	2.668638000	0.617903000	-1.274627000
6	3.265406000	0.989842000	-0.052923000
6	2.590842000	1.005867000	1.184727000
6	3.357049000	1.391941000	2.433043000
8	1.363817000	0.721251000	1.352972000
6	3.514124000	0.608524000	-2.531398000
1	-3.508324000	0.136145000	3.056213000
1	-2.899867000	-1.503004000	3.268380000
1	-4.440528000	-1.243815000	2.408404000
1	-4.220547000	-1.551309000	0.112214000
1	-4.296866000	-1.966471000	-2.176338000
1	-3.313113000	-0.843988000	-3.158813000
1	-2.709130000	-2.463139000	-2.818790000
1	3.343266000	0.553989000	3.141202000
1	4.396399000	1.666206000	2.227818000
1	2.851503000	2.231394000	2.925530000
1	4.317952000	1.259096000	-0.062106000
1	3.048472000	1.251209000	-3.288321000
1	4.541618000	0.942170000	-2.356694000
1	3.535380000	-0.406652000	-2.947093000
1	-0.116496000	2.570116000	0.246949000
1	0.066891000	-2.422499000	-0.272256000
6	-2.062159000	2.483908000	-0.164982000
1	-2.707089000	1.874220000	-0.809077000
1	-2.363732000	2.270585000	0.867519000
6	-2.310073000	3.972638000	-0.466162000
1	-2.047824000	4.211825000	-1.501785000
1	-1.702580000	4.610370000	0.184031000
1	-3.362231000	4.234569000	-0.312610000
6	2.012689000	-2.336843000	0.139154000
1	2.314037000	-2.123501000	-0.893409000
1	2.657955000	-1.727386000	0.783131000
6	2.260292000	-3.825666000	0.440124000
1	1.652454000	-4.463176000	-0.209964000
1	1.998263000	-4.064884000	1.475796000
1	3.312339000	-4.087860000	0.286261000

2.H *t*Bu• trapping by Fe(acac)$_2$

H1. Energy diagram and views of the optimized geometries



H2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

Fe(acac)$_2$(*t*Bu) S = 1/2
E = -970.91921492
G$_{298K,D3,EtOH,1M}$ = -970.707712
<S^2> = 0.882

26	-0.017945000	0.033945000	-0.172487000
8	-1.277352000	1.436875000	-0.278487000
6	-2.524971000	1.323063000	-0.538607000
6	-3.277010000	2.626540000	-0.627665000
8	1.267528000	-1.298066000	-0.565249000
6	2.520867000	-1.133477000	-0.762888000
6	3.182832000	0.102072000	-0.734751000
6	2.509076000	1.318424000	-0.551297000
8	1.257390000	1.429966000	-0.317442000
6	3.285902000	-2.394990000	-1.074845000
6	3.259705000	2.622618000	-0.644370000
8	-1.300722000	-1.311776000	-0.495160000
6	-2.548523000	-1.136163000	-0.721836000
6	-3.327091000	-2.397671000	-0.997025000
6	-3.195668000	0.107604000	-0.738384000
1	-2.874354000	-2.927709000	-1.843357000
1	3.179003000	-3.104135000	-0.245004000
1	2.852407000	-2.873760000	-1.961032000
1	-4.379785000	-2.199111000	-1.216798000
1	4.348567000	-2.206234000	-1.251198000
1	-3.261386000	-3.065886000	-0.129687000
1	-4.259895000	0.133161000	-0.951701000
1	4.249682000	0.123587000	-0.934743000
1	-2.793176000	3.276087000	-1.366540000
1	4.317468000	2.481094000	-0.883382000
1	-4.326695000	2.486729000	-0.900715000
1	2.796602000	3.255066000	-1.410963000
1	-3.223603000	3.145487000	0.337307000

1	3.175079000	3.160817000	0.307601000
6	0.052341000	-0.273464000	1.851165000
6	-1.241263000	0.307205000	2.403981000
6	1.263223000	0.459711000	2.402568000
1	2.200111000	0.101810000	1.959630000
1	1.193038000	1.540725000	2.246534000
1	1.325604000	0.277272000	3.489697000
1	-1.292440000	1.391793000	2.266759000
1	-1.288220000	0.100265000	3.487218000
1	-2.131154000	-0.144566000	1.950172000
6	0.140225000	-1.770047000	2.105395000
1	1.073057000	-2.194936000	1.724135000
1	0.102919000	-1.954177000	3.193184000
1	-0.688872000	-2.310476000	1.639608000

Fe(acac)$_2$(*t*Bu) S = 3/2
E = -970.930552924
$G_{298K,D3,EtOH,1M}$ = -970.721069
$\langle S^2 \rangle$ = 4.183

26	0.101423000	0.282979000	0.000393000
8	1.975684000	0.806097000	0.000856000
6	3.046300000	0.085575000	0.000043000
6	4.328222000	0.880233000	-0.000437000
8	-1.197454000	-0.121103000	-1.421542000
6	-2.261230000	-0.807723000	-1.248537000
6	-2.807564000	-1.155815000	-0.000511000
6	-2.262343000	-0.806991000	1.247786000
8	-1.198649000	-0.120360000	1.421302000
6	-2.956242000	-1.250069000	-2.513580000
6	-2.958488000	-1.248493000	2.512493000
8	0.754469000	-1.677720000	0.001483000
6	1.934079000	-2.123311000	0.000618000
6	2.090458000	-3.627127000	0.000732000
6	3.091239000	-1.304708000	-0.000268000
1	1.588191000	-4.041990000	0.882805000
1	-3.171492000	-0.374914000	-3.138283000
1	-2.280207000	-1.894895000	-3.088531000
1	3.136885000	-3.945925000	-0.000344000
1	-3.886269000	-1.791256000	-2.317915000
1	1.586223000	-4.042349000	-0.880043000
1	4.064876000	-1.784861000	-0.000938000
1	-3.723507000	-1.738892000	-0.000753000
1	4.353883000	1.532477000	0.881216000
1	-3.888300000	-1.789879000	2.316350000
1	5.216691000	0.242658000	-0.000917000
1	-2.282942000	-1.892855000	3.088535000
1	4.353102000	1.532699000	-0.881949000
1	-3.174387000	-0.372905000	3.136365000
6	-0.377340000	2.392553000	-0.000321000
6	0.265632000	2.884419000	-1.277877000
6	0.264577000	2.884697000	1.277670000
1	-0.174937000	2.396365000	2.156598000
1	1.345627000	2.713679000	1.277829000
1	0.092884000	3.970464000	1.386678000
1	1.346689000	2.713462000	-1.277080000
1	0.093954000	3.970146000	-1.387296000
1	-0.173093000	2.395858000	-2.157077000
6	-1.883812000	2.528090000	-0.000958000
1	-2.335336000	2.080632000	0.889811000
1	-2.144238000	3.601436000	-0.001386000
1	-2.334644000	2.080100000	-0.891809000

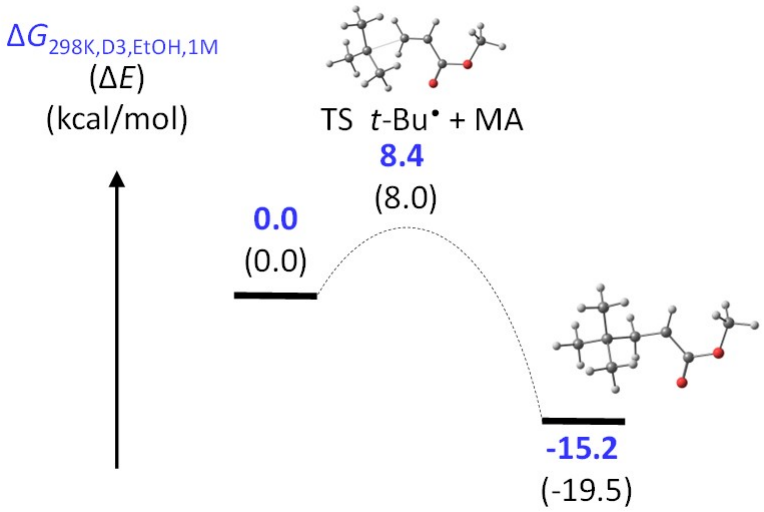
Fe(acac)$_2$(*t*Bu) S = 5/2
E = -970.917939319
$G_{298K,D3,EtOH,1M}$ = -970.711792
$\langle S^2 \rangle$ = 8.758

26	-0.002563000	-0.019360000	0.141332000
8	-1.427934000	1.397235000	-0.008255000
6	-2.592832000	1.348360000	-0.522132000
6	-3.386306000	2.630302000	-0.461832000
8	1.453052000	-1.232708000	-0.547155000
6	2.605922000	-0.957498000	-1.018155000
6	3.146647000	0.335797000	-1.100157000
6	2.472455000	1.480416000	-0.643984000
8	1.301331000	1.481573000	-0.139407000
6	3.410650000	-2.138856000	-1.501249000
6	3.142551000	2.829475000	-0.730436000
8	-1.315557000	-1.248466000	-0.744088000
6	-2.493007000	-1.028758000	-1.185636000
6	-3.180222000	-2.215424000	-1.814625000
6	-3.156765000	0.205646000	-1.114911000
1	-2.575619000	-2.578845000	-2.654324000
1	3.540306000	-2.850087000	-0.676582000
1	2.849134000	-2.660359000	-2.285767000
1	-4.188135000	-1.981780000	-2.168917000
1	4.392408000	-1.852241000	-1.888608000
1	-3.232828000	-3.031656000	-1.084071000
1	-4.159287000	0.277184000	-1.524824000
1	4.141513000	0.454226000	-1.517780000
1	-2.828476000	3.423295000	-0.974288000
1	4.141721000	2.778729000	-1.172178000
1	-4.378273000	2.536209000	-0.912638000
1	2.516337000	3.505324000	-1.325137000
1	-3.492022000	2.940470000	0.584726000
1	3.212877000	3.262565000	0.274659000
6	-0.000789000	-0.561520000	2.250516000
6	-1.227712000	0.071048000	2.878283000
6	1.302178000	-0.011877000	2.800581000
1	2.174854000	-0.427754000	2.280619000
1	1.351762000	1.081581000	2.725096000
1	1.408076000	-0.271785000	3.870851000
1	-1.214360000	1.164867000	2.798528000
1	-1.280369000	-0.180672000	3.954399000
1	-2.156301000	-0.289958000	2.417538000

6	-0.051112000	-2.077859000	2.231115000	1	-0.024908000	-2.476534000	3.262809000
1	0.800273000	-2.506500000	1.688910000	1	-0.969137000	-2.449499000	1.759301000

2.I *t*Bu• addition to methyl acrylate

I1. Energy diagram and views of the optimized geometries



I2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

Methyl acrylate
E = -306.168903475
$G_{298K,D3,EtOH,1M}$ = -306.114831
(restricted closed-shell system, S = 0)

6	0.011509000	0.488734000	0.000095000
6	1.494207000	0.384684000	0.000100000
8	-0.593443000	1.548943000	-0.000112000
8	-0.603519000	-0.730174000	0.000196000
6	-2.049689000	-0.673309000	-0.000097000
1	-2.415680000	-0.145478000	-0.893274000
1	-2.380699000	-1.718537000	-0.003494000
1	-2.416181000	-0.151408000	0.896397000
1	1.994300000	1.356592000	0.000224000
6	2.184457000	-0.765400000	-0.000117000
1	1.673742000	-1.730556000	-0.000248000
1	3.277312000	-0.769019000	-0.000153000

$Me_3C\cdots CH_2$=CHCOOMe (TS3)
E = -463.788969776
$G_{298K,D3,EtOH,1M}$ = -463.654306
$\langle S^2 \rangle$ = 0.763

6	-2.218770000	0.125269000	0.253280000
6	-2.552836000	1.583869000	0.233255000
1	-2.906313000	1.914880000	-0.751557000
1	-3.360571000	1.812395000	0.952695000
1	-1.691669000	2.200140000	0.520865000
6	-1.512007000	-0.404354000	1.458246000
1	-2.217074000	-0.534765000	2.299585000
1	-1.044490000	-1.376226000	1.264457000
1	-0.729159000	0.283594000	1.799885000
6	-3.132687000	-0.802884000	-0.482690000
1	-2.710404000	-1.811563000	-0.565710000
1	-4.097953000	-0.905067000	0.046631000
1	-3.367581000	-0.437277000	-1.491006000
6	0.867450000	0.447693000	-0.774069000
1	1.176449000	1.489311000	-0.754931000
6	1.691381000	-0.589151000	-0.124685000
8	2.911616000	-0.240793000	0.376203000
8	1.346241000	-1.750187000	-0.008425000
6	3.415846000	1.079960000	0.230269000
1	3.483915000	1.380815000	-0.823347000
1	2.813132000	1.814091000	0.782117000
1	4.422052000	1.062310000	0.657380000
6	-0.294356000	0.091242000	-1.371687000
1	-0.538985000	-0.963150000	-1.469087000
1	-0.878339000	0.808487000	-1.941712000

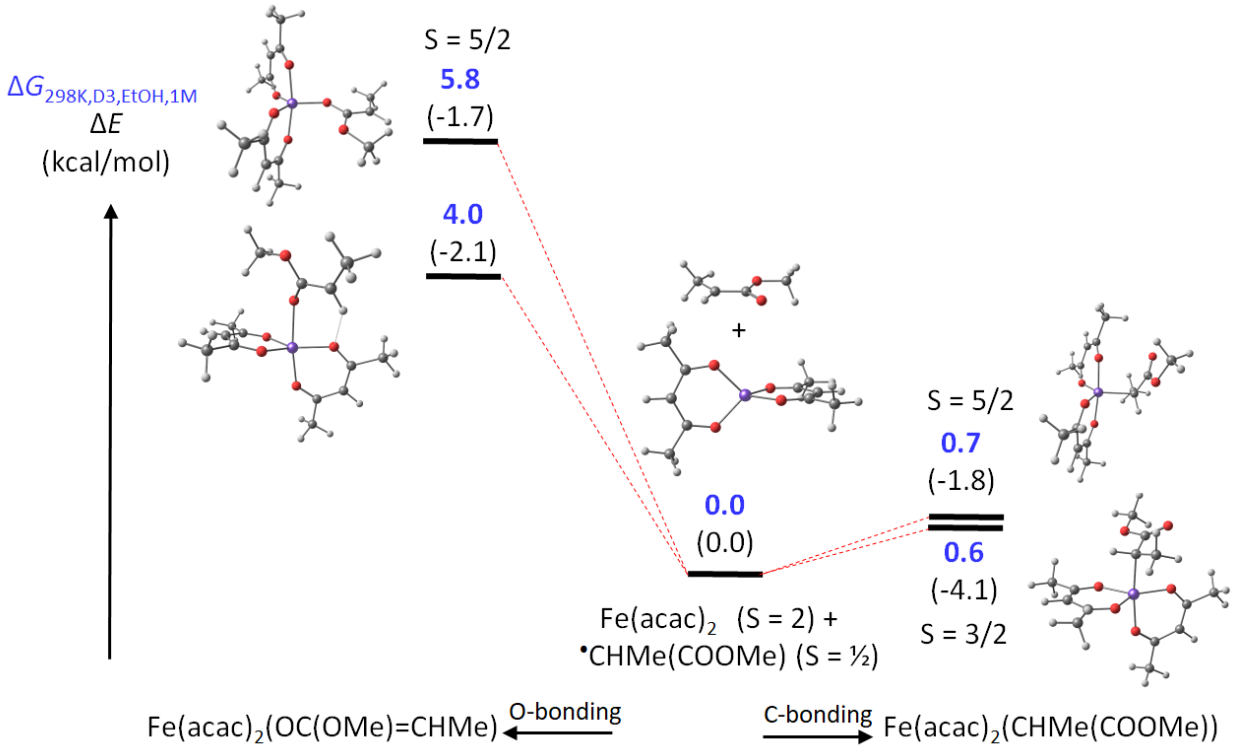
Me_3C-$CH_2CH^{\bullet}COOMe$

E = -463.832774967
$G_{298K,D3,EtOH,1M}$ = -463.691982
$\langle S^2 \rangle$ = 0.758

6	-2.020541541	0.121763975	0.085896732
6	-2.354607541	1.580363975	0.065871732
1	-2.708084541	1.911374975	-0.918940268
1	-3.162342541	1.808889975	0.785311732
1	-1.493440541	2.196634975	0.353481732
6	-1.313778541	-0.407859025	1.290862732
1	-2.018845541	-0.538270025	2.132201732
1	-0.846261541	-1.379731025	1.097073732
1	-0.530930541	0.280088975	1.632501732
6	-2.934458541	-0.806389025	-0.650073268
1	-2.512175541	-1.815068025	-0.733093268
1	-3.899724541	-0.908572025	-0.120752268
1	-3.169352541	-0.440782025	-1.658389268
6	0.669221541	0.451198025	-0.606685732
1	0.978220541	1.492816025	-0.587547732
6	1.493152541	-0.585645975	0.042698268
8	2.713387541	-0.237287975	0.543586268
8	1.148012541	-1.746681975	0.158958268
6	3.217617541	1.083465025	0.397652268
1	3.285686541	1.384320025	-0.655963732
1	2.614903541	1.817596025	0.949500268
1	4.223823541	1.065815025	0.824763268
6	-0.492584459	0.094747025	-1.204303732
1	-0.737213459	-0.959644975	-1.301703732
1	-1.076567459	0.811992025	-1.774328732

2.J Me•CH(COOMe) trapping by $Fe(acac)_2$

J1. Energy diagram and views of the optimized geometries



J2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

•CHMeCOOMe
E = -306.750548945
$G_{298K,D3,EtOH,1M}$ = -306.691179
$\langle S^2 \rangle$ = 0.757

6	-0.077502000	0.518816000	0.000108000
6	1.370456000	0.517017000	-0.000014000
8	-0.764290000	1.532794000	-0.000002000
8	-0.609917000	-0.734258000	0.000014000

6	-2.036890000	-0.768854000	-0.000046000
1	-2.439767000	-0.269726000	-0.888289000
1	-2.309531000	-1.826436000	-0.000137000
1	-2.439836000	-0.269860000	0.888241000
1	1.819457000	1.507644000	-0.000075000
6	2.232089000	-0.688536000	-0.000018000
1	1.641907000	-1.607777000	-0.000200000
1	2.896399000	-0.696294000	-0.877977000
1	2.896114000	-0.696497000	0.878161000

$Fe(acac)_2(CHMeCOOMe)$ S = 3/2
E = -1120.04576948
$G_{298K,D3,EtOH,1M}$ = -1119.855942
$\langle S^2 \rangle$ = 4.016

26	-0.107089000	0.031460000	-0.311072000
8	1.585151000	0.970355000	-0.514313000
6	1.904562000	2.190009000	-0.239009000
6	3.339710000	2.538965000	-0.544601000
8	-0.930338000	-0.985246000	1.158906000
6	-2.184175000	-1.208757000	1.263464000
6	-3.131729000	-1.005399000	0.244638000
6	-2.844562000	-0.518309000	-1.042789000
8	-1.682400000	-0.198844000	-1.467449000
6	-2.635018000	-1.740832000	2.602375000
6	-3.964574000	-0.350761000	-2.041051000
8	-0.878990000	1.796072000	0.438009000
6	-0.305828000	2.906319000	0.607920000
6	-1.147652000	4.022508000	1.183569000
6	1.054104000	3.153260000	0.293696000
1	-2.008883000	4.199566000	0.528307000
1	-2.070113000	-2.648973000	2.844542000
1	-2.402045000	-1.002528000	3.379565000
1	-0.590536000	4.956022000	1.305289000
1	-3.705408000	-1.963574000	2.630124000
1	-1.544430000	3.709985000	2.156875000
1	1.455794000	4.145018000	0.476935000
1	-4.166709000	-1.244641000	0.469381000
1	3.539541000	2.363481000	-1.608868000
1	-4.931337000	-0.681787000	-1.651294000
1	3.579548000	3.577753000	-0.301133000
1	-4.035990000	0.705824000	-2.327266000
1	4.005308000	1.874239000	0.019768000
1	-3.729996000	-0.913671000	-2.952417000
6	0.885751000	-1.712977000	-1.117747000
6	1.326275000	-1.247246000	-2.487622000
1	0.464743000	-0.978608000	-3.111923000
1	2.002064000	-0.388678000	-2.423688000
1	1.862576000	-2.063364000	-3.003940000
1	0.334913000	-2.634407000	-1.235834000
6	1.962314000	-2.127826000	-0.097692000
8	2.852225000	-2.927507000	-0.310777000
8	1.829944000	-1.504158000	1.101208000
6	2.896922000	-2.001387000	1.913132000
1	3.793573000	-1.378248000	1.819199000
1	2.617065000	-2.019483000	2.972594000
1	3.173301000	-3.022663000	1.627267000

$Fe(acac)_2(CHMeCOOMe)$ S = 5/2
E = -1120.04215532
$G_{298K,D3,EtOH,1M}$ = -1119.855716
$\langle S^2 \rangle$ = 8.760

26	0.273186000	0.278721000	-0.033523000
8	-1.342506000	-0.156369000	-1.117011000
6	-2.427868000	0.509864000	-1.199784000
6	-3.628917000	-0.253150000	-1.683451000
8	1.425321000	-0.665133000	-1.309104000
6	2.699598000	-0.778543000	-1.357028000
6	3.588275000	-0.180860000	-0.453257000
6	3.171364000	0.614936000	0.628795000
8	1.954191000	0.875109000	0.902158000
6	3.224592000	-1.625896000	-2.486337000
6	4.195324000	1.222589000	1.553474000
8	-0.297472000	2.164485000	-0.116668000
6	-1.462664000	2.631187000	-0.379152000
6	-1.630849000	4.107325000	-0.129030000
6	-2.535074000	1.873189000	-0.865210000
1	-1.399292000	4.325927000	0.920311000
1	2.803326000	-2.635056000	-2.404221000
1	2.877146000	-1.211728000	-3.440422000
1	-2.639478000	4.461081000	-0.359364000
1	4.316164000	-1.688224000	-2.493680000
1	-0.905352000	4.660428000	-0.737860000
1	-3.488502000	2.368067000	-1.019751000
1	4.652082000	-0.342126000	-0.595303000
1	-3.863649000	-1.008265000	-0.922138000
1	5.220403000	0.952987000	1.284825000
1	-4.500967000	0.386483000	-1.844823000
1	4.091466000	2.314259000	1.536234000
1	-3.380730000	-0.783429000	-2.609912000
1	3.992020000	0.898783000	2.581224000
6	-0.412083000	-0.779897000	1.720735000
6	-0.989944000	0.286905000	2.623222000
1	-0.285007000	1.113652000	2.769246000
1	-1.924393000	0.682462000	2.209728000
1	-1.229855000	-0.120859000	3.618119000
1	0.551699000	-1.192917000	2.034344000
6	-1.349710000	-1.811933000	1.266545000
8	-2.570741000	-1.740718000	1.288125000
8	-0.692679000	-2.899726000	0.770972000
6	-1.537860000	-3.906621000	0.221276000
1	-2.080219000	-3.524180000	-0.651265000
1	-0.876112000	-4.723733000	-0.076510000
1	-2.267611000	-4.256111000	0.960242000

$Fe(acac)_2[O(MeO)C=CHMe]$ S = 3/2
E = -1120.04254694
$G_{298K,D3,EtOH,1M}$ = -1119.850568
$<S^2>$ = 4.758

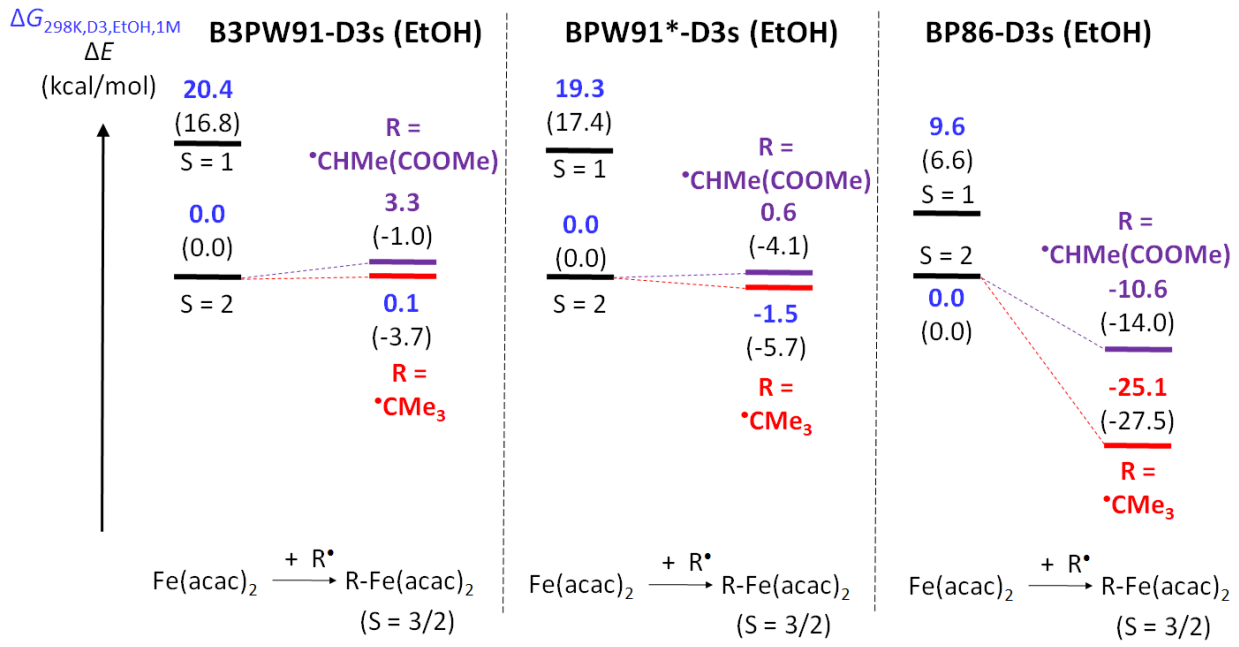
26	0.496253000	0.333725000	0.165568000
8	2.227566000	1.293401000	-0.287761000
8	1.583159000	-1.319743000	0.416150000
6	3.416239000	0.858067000	-0.282984000
6	3.776891000	-0.474993000	0.021881000
1	4.829921000	-0.739086000	-0.002620000
6	2.856993000	-1.476051000	0.340625000
8	-0.635104000	0.773116000	-1.408540000
8	-0.353810000	1.748222000	1.262153000
6	-1.558240000	1.652600000	-1.441652000
6	-1.940118000	2.474121000	-0.364207000
1	-2.744017000	3.183775000	-0.538115000
6	-1.318547000	2.496343000	0.901167000
6	3.348173000	-2.875790000	0.624390000
1	4.438929000	-2.953475000	0.600417000
1	2.984609000	-3.197574000	1.607825000
1	2.928803000	-3.568948000	-0.116266000
6	4.495058000	1.856424000	-0.635300000
1	5.499937000	1.425204000	-0.603523000
1	4.305422000	2.253594000	-1.639898000
1	4.443421000	2.704018000	0.058502000
6	-1.797101000	3.485908000	1.938768000
1	-2.650981000	4.079362000	1.599073000
1	-2.069746000	2.948536000	2.855011000
1	-0.973066000	4.161620000	2.198947000
6	-2.266435000	1.801925000	-2.769183000
1	-3.080174000	2.532249000	-2.735993000
1	-1.540508000	2.111928000	-3.531048000
1	-2.664341000	0.830028000	-3.085103000
8	-1.256096000	-0.937877000	0.860636000
6	-1.792604000	-1.920741000	0.331628000
8	-3.132364000	-2.068499000	0.317774000
6	-3.870076000	-1.009294000	0.937677000
1	-3.645975000	-0.961452000	2.009137000
1	-3.620213000	-0.044221000	0.484129000
1	-4.922576000	-1.253693000	0.779762000
6	-1.066581000	-2.993352000	-0.296387000
1	0.014552000	-2.872478000	-0.254737000
6	-1.685545000	-4.168191000	-0.951538000
1	-1.305446000	-5.103357000	-0.512898000
1	-2.775362000	-4.158575000	-0.872433000
1	-1.411228000	-4.205113000	-2.017555000

$Fe(acac)_2[O(MeO)C=CHMe]$ S = 5/2
E = -1120.04192241
$G_{298K,D3,EtOH,1M}$ = -1119.847568
$<S^2>$ = 8.776

26	0.297710000	0.171968000	-0.042848000
8	1.731783000	-0.247694000	1.331340000
6	2.994764000	-0.227944000	1.217396000
6	3.776022000	-0.617570000	2.449018000
8	-0.498806000	1.398555000	1.265515000
6	-1.463965000	2.235250000	1.154925000
6	-2.176421000	2.485649000	-0.020703000
6	-1.903316000	1.833274000	-1.241469000
8	-1.002504000	0.955329000	-1.399478000
6	-1.807949000	2.979434000	2.420528000
6	-2.714599000	2.176193000	-2.468103000
8	1.761901000	0.566514000	-1.294040000
6	3.033841000	0.501210000	-1.142526000
6	3.838618000	0.869452000	-2.363174000
6	3.682083000	0.126147000	0.037414000
1	3.555301000	0.211919000	-3.193895000
1	-2.056832000	2.257272000	3.207464000
1	-0.927042000	3.534368000	2.765494000
1	4.916639000	0.796002000	-2.194520000
1	-2.642388000	3.673839000	2.287708000
1	3.588000000	1.893018000	-2.667147000
1	4.767421000	0.110461000	0.046627000
1	-2.971530000	3.224354000	0.004974000
1	3.517526000	-1.646168000	2.728457000
1	-3.460986000	2.952989000	-2.278799000
1	4.857718000	-0.545372000	2.304387000
1	-2.039043000	2.507889000	-3.265447000
1	3.476273000	0.025874000	3.284548000
1	-3.217619000	1.272095000	-2.831837000
8	-0.261538000	-1.627198000	-0.259641000
6	-1.378816000	-2.210795000	0.015167000
6	-1.630563000	-3.529547000	-0.286056000
8	-2.269183000	-1.383840000	0.634760000
6	-3.534935000	-1.901495000	0.998172000
1	-3.441080000	-2.732918000	1.711354000
1	-4.074316000	-1.078197000	1.473131000
1	-4.098217000	-2.243661000	0.118094000
1	-2.593997000	-3.959501000	-0.026973000
6	-0.629481000	-4.402108000	-0.963239000
1	-0.373428000	-5.276074000	-0.345146000
1	-1.017658000	-4.797630000	-1.914044000
1	0.289887000	-3.847950000	-1.172135000

2.K Testing of other functionals

K1. Energy diagram



K2. Discussion

Because the computed energetics of reactions involving a change of oxidation state and spin state such as those in Figure 4 and S.2J.1 are highly functional-dependent, we used this opportunity to test the suitability of the BPW91* functional versus other popular functionals. Additional exploration of the propionate and *tert*-butyl radical trapping by $Fe(acac)_2$ was carried out with BP86, a pure functional known to have a bias in favor of lower spin states, and with B3PW91, a classical hybrid functional known to have a bias in favor of the higher spin states. The results in section S.2K.1 are in line with these expected biases and indicate that the observed cross-coupling selectivity, which implies PRE for the *tert*-butyl radical but not for the acrylate radical, is consistent only with the results obtained using the BPW91* functional.

K3. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

BP86 calculations

$Fe(acac)_2$ S = 2 BP86
E = -814.031250293
$G_{298K,D3,EtOH,1M}$ = -813.909734
$\langle S^2 \rangle$ = 6.036

6	3.434305000	1.840473000	1.745399000
6	2.623565000	0.869892000	0.902842000
6	3.276990000	0.000058000	0.000168000
6	2.623823000	-0.869970000	-0.902488000
6	3.434807000	-1.840091000	-1.745282000
8	1.338610000	0.905348000	1.089441000
26	0.000000000	-0.000079000	-0.000201000
8	-1.338802000	1.089484000	-0.905372000
6	-2.623742000	0.902838000	-0.869712000
6	-3.434647000	1.745384000	-1.840154000
8	1.338892000	-0.905426000	-1.089451000
8	-1.338700000	-1.089579000	0.905232000
6	-2.623645000	-0.902615000	0.870027000
6	-3.434465000	-1.745583000	1.840123000
6	-3.276990000	0.000059000	0.000135000
1	3.196225000	1.693765000	2.817142000
1	4.518664000	1.723026000	1.598268000
1	3.148229000	2.875352000	1.491133000
1	4.369723000	0.000242000	0.000138000
1	3.149001000	-2.875077000	-1.491247000
1	4.519129000	-1.722379000	-1.598122000
1	3.196687000	-1.693225000	-2.816988000
1	-3.195948000	-2.817227000	1.693452000
1	-3.148900000	-1.491304000	2.875125000
1	-4.518812000	-1.598800000	1.722230000
1	-4.369723000	-0.000062000	0.000070000
1	-3.196371000	2.817118000	-1.693663000
1	-4.518981000	1.598390000	-1.722369000

1	-3.148923000	1.490949000	-2.875092000

$Fe(acac)_2$ S = 1 BP86
E = -814.020818532
$G_{298K,D3,EtOH,1M}$ = -813.894431
$<S^2>$ = 2.020

6	-3.399006000	2.414494000	-0.668879000
6	-2.583979000	1.186887000	-0.314194000
6	-3.217686000	-0.028733000	0.008103000
6	-2.523131000	-1.208782000	0.358201000
6	-3.298804000	-2.479062000	0.651084000
8	-1.299235000	1.359991000	-0.361552000
26	-0.000035000	0.053094000	-0.000002000
8	1.299259000	1.359955000	0.361460000
6	2.584005000	1.186877000	0.314181000
6	3.398991000	2.414487000	0.668935000
8	-1.237549000	-1.324960000	0.454611000
8	1.237579000	-1.324921000	-0.454531000
6	2.523162000	-1.208764000	-0.358199000
6	3.298796000	-2.479052000	-0.651121000
6	3.217742000	-0.028730000	-0.008102000
1	-3.107187000	2.774549000	-1.669360000
1	-4.481159000	2.217772000	-0.655191000
1	-3.172815000	3.231184000	0.040805000
1	-4.310581000	-0.064303000	-0.028189000
1	-3.017031000	-3.253082000	-0.082897000
1	-4.388365000	-2.325022000	0.614524000
1	-3.016645000	-2.860437000	1.648217000
1	3.016994000	-3.253097000	0.082819000
1	3.016638000	-2.860369000	-1.648277000
1	4.388363000	-2.325041000	-0.614555000
1	4.310637000	-0.064301000	0.028201000
1	3.172789000	3.231208000	-0.040707000
1	4.481150000	2.217791000	0.655261000
1	3.107154000	2.774477000	1.669436000

•CHMeCOOMe BP86
E = -307.052449413
$G_{298K,D3,EtOH,1M}$ = -306.995549
$<S^2>$ = 0.754

6	-0.074782000	0.524804000	0.000007000
6	1.377922000	0.519694000	-0.000005000
8	-0.771703000	1.546224000	0.000028000
8	-0.609719000	-0.747806000	-0.000018000
6	-2.051363000	-0.773272000	-0.000014000
1	-2.452873000	-0.267377000	-0.893565000
1	-2.328031000	-1.836621000	-0.000043000
1	-2.452867000	-0.267427000	0.893567000
1	1.830956000	1.515884000	0.000021000
6	2.243913000	-0.690943000	-0.000004000
1	1.651074000	-1.616093000	-0.000249000
1	2.914677000	-0.698573000	-0.882295000
1	2.914298000	-0.698836000	0.882579000

$Fe(acac)_2$(CHMeCOOMe) S = 3/2 BP86
E = -1121.10608971
$G_{298K,D3,EtOH,1M}$ = -1120.922159
$<S^2>$ = 3.857

26	-0.006517000	-0.254788000	0.192904000
8	1.859243000	-0.048565000	0.520056000
6	2.852017000	-0.827446000	0.196413000
6	4.207988000	-0.279371000	0.586942000
8	-1.239641000	0.168718000	-1.236019000
6	-2.523123000	0.036428000	-1.213094000
6	-3.262130000	-0.461990000	-0.115895000
6	-2.695300000	-0.935481000	1.089523000
8	-1.433528000	-0.925975000	1.361232000
6	-3.235991000	0.455183000	-2.484833000
6	-3.587325000	-1.518752000	2.170186000
8	0.351838000	-2.063843000	-0.578425000
6	1.475794000	-2.640213000	-0.782673000
6	1.414949000	-4.013885000	-1.425818000
6	2.729792000	-2.069772000	-0.438671000
1	0.815640000	-4.689672000	-0.792211000
1	-3.010218000	1.513482000	-2.699172000
1	-2.851639000	-0.135654000	-3.333737000
1	2.413348000	-4.451228000	-1.576614000
1	-4.326207000	0.322437000	-2.417562000
1	0.899578000	-3.942364000	-2.398655000
1	3.639503000	-2.633947000	-0.655147000
1	-4.347946000	-0.519667000	-0.221863000
1	4.282548000	-0.233419000	1.687601000
1	-4.652742000	-1.487440000	1.896919000
1	5.033637000	-0.893700000	0.197734000
1	-3.295378000	-2.565693000	2.361347000
1	4.301290000	0.755691000	0.219556000
1	-3.438623000	-0.965903000	3.113317000
6	-0.206474000	1.608616000	1.053917000
6	0.191452000	1.512182000	2.514816000
1	-0.369510000	0.710565000	3.021496000
1	1.271632000	1.318022000	2.602695000
1	-0.015323000	2.462791000	3.045058000
1	-1.284245000	1.752573000	0.876105000
6	0.616384000	2.564666000	0.257516000
8	1.731645000	2.982967000	0.561459000
8	-0.022625000	2.944128000	-0.903292000
6	0.745372000	3.843429000	-1.727442000
1	1.677402000	3.364362000	-2.071556000
1	0.100258000	4.083986000	-2.584290000
1	1.010557000	4.758264000	-1.171925000

•CMe_3 BP86
E = -157.774370206
$G_{298K,D3,EtOH,1M}$ = -157.696749

$\langle S^2 \rangle$ = 0.754

6	0.000043000	-0.000031000	-0.135294000
6	1.238893000	0.831586000	0.013414000
6	0.100758000	-1.488614000	0.013421000
6	-1.339669000	0.657043000	0.013407000
1	-0.759549000	-2.005379000	-0.444046000
1	1.022242000	-1.885200000	-0.444940000
1	0.122903000	-1.807541000	1.079187000
1	2.116501000	0.345314000	-0.444604000
1	1.504343000	1.009680000	1.079191000
1	1.121330000	1.828045000	-0.444443000
1	-2.143626000	0.057285000	-0.445213000
1	-1.627254000	0.797384000	1.079120000
1	-1.357038000	1.660512000	-0.443936000

$Fe(acac)_2(CMe_3)$ S = 3/2 BP86
E = -971.849395442
$G_{298K,D3,EtOH,1M}$ = -971.646466
$\langle S^2 \rangle$ = 3.898

26	-0.098429000	0.302181000	-0.000157000
8	-1.973937000	0.787207000	-0.000388000
6	-3.039270000	0.036046000	-0.000295000
6	-4.341281000	0.813921000	-0.000121000
8	1.169865000	-0.104421000	1.424508000
6	2.262836000	-0.773824000	1.255638000
6	2.822186000	-1.104997000	0.000470000
6	2.263572000	-0.773375000	-1.254907000
8	1.170694000	-0.103923000	-1.424188000
6	2.958904000	-1.206488000	2.533293000
6	2.960407000	-1.205554000	-2.532308000
8	-0.692982000	-1.669979000	-0.000773000
6	-1.870784000	-2.156003000	-0.000696000
6	-1.981666000	-3.672582000	-0.001020000
6	-3.053003000	-1.362977000	-0.000394000
1	-1.465881000	-4.078088000	-0.888063000
1	3.164046000	-0.324093000	3.163187000
1	2.288207000	-1.865221000	3.111658000
1	-3.025769000	-4.020851000	-0.000665000
1	3.902694000	-1.737908000	2.338509000
1	-1.465098000	-4.078535000	0.885358000
1	-4.021271000	-1.868746000	-0.000334000
1	3.758131000	-1.668911000	0.000644000
1	-4.381116000	1.469926000	-0.886795000
1	3.904051000	-1.737100000	-2.337158000
1	-5.221955000	0.154300000	-0.000063000
1	2.290035000	-1.864012000	-3.111361000
1	-4.380935000	1.469843000	0.886623000
1	3.165988000	-0.322909000	-3.161709000
6	0.314508000	2.343798000	0.000315000
6	-0.323576000	2.877053000	1.280416000
6	-0.323208000	2.877526000	-1.279775000
1	0.119867000	2.404590000	-2.173931000
1	-1.411590000	2.708059000	-1.290473000
1	-0.148856000	3.971760000	-1.365148000
1	-1.411948000	2.707499000	1.290773000
1	-0.149335000	3.971273000	1.366200000
1	0.119297000	2.403850000	2.174531000
6	1.830638000	2.533799000	0.000569000
1	2.300997000	2.099302000	-0.895426000
1	2.058130000	3.621392000	0.000949000
1	2.300774000	2.098724000	0.896399000

B3PW91 calculations

$Fe(acac)_2$ S = 2 B3PW91
E = -813.739506624
$G_{298K,D3,EtOH,1M}$ = -813.615985
$\langle S^2 \rangle$ = 6.018

6	-3.453539000	-1.744396000	1.811426000
6	-2.642067000	-0.883524000	0.875137000
6	-3.295361000	-0.000062000	0.000071000
6	-2.642206000	0.883410000	-0.875083000
6	-3.453814000	1.744290000	-1.811240000
8	-1.375147000	-1.042732000	0.939775000
26	0.000000000	0.000037000	-0.000099000
8	1.375260000	-0.939771000	-1.042758000
6	2.642168000	-0.875089000	-0.883450000
6	3.453740000	-1.811380000	-1.744229000
8	-1.375301000	1.042681000	-0.939856000
8	1.375189000	0.939907000	1.042607000
6	2.642104000	0.875174000	0.883442000
6	3.453613000	1.811371000	1.744373000
6	3.295361000	0.000015000	0.000046000
1	-3.175984000	-1.514766000	2.846351000
1	-4.529266000	-1.601667000	1.691609000
1	-3.205025000	-2.796784000	1.639780000
1	-4.378975000	-0.000072000	0.000145000
1	-3.205312000	2.796681000	-1.639586000
1	-4.529522000	1.601521000	-1.691298000
1	-3.176375000	1.514707000	-2.846203000
1	3.176141000	2.846321000	1.514766000
1	3.205050000	1.639711000	2.796746000
1	4.529335000	1.691477000	1.601676000
1	4.378975000	-0.000029000	0.000129000
1	3.176197000	-2.846307000	-1.514594000
1	4.529453000	-1.691529000	-1.601412000
1	3.205308000	-1.639767000	-2.796644000

$Fe(acac)_2$ S = 1 B3PW91
E = -813.712648955
$G_{298K,D3,EtOH,1M}$ = -813.583418
$\langle S^2 \rangle$ = 2.014

6	-3.363644000	2.514393000	-0.001154000
6	-2.574260000	1.231378000	-0.000410000

6	-3.242477000	-0.000014000	0.000023000
6	-2.574231000	-1.231390000	0.000403000
6	-3.363584000	-2.514426000	0.001192000
8	-1.306674000	1.382326000	-0.000542000
26	-0.000015000	0.000026000	-0.000015000
8	1.306688000	1.382297000	0.000891000
6	2.574270000	1.231373000	0.000572000
6	3.363638000	2.514400000	0.001046000
8	-1.306640000	-1.382308000	0.000477000
8	1.306654000	-1.382278000	-0.000880000
6	2.574242000	-1.231384000	-0.000576000
6	3.363578000	-2.514433000	-0.001011000
6	3.242503000	-0.000014000	-0.000005000
1	-3.091508000	3.103147000	-0.883049000
1	-4.441926000	2.345330000	0.002472000
1	-3.085930000	3.107712000	0.875864000
1	-4.325834000	-0.000029000	0.000057000
1	-3.085909000	-3.107734000	-0.875847000
1	-4.441871000	-2.345391000	-0.002367000
1	-3.091379000	-3.103178000	0.883067000
1	3.088385000	-3.105884000	0.878093000
1	3.088870000	-3.105037000	-0.880837000
1	4.441872000	-2.345403000	-0.000640000
1	4.325860000	-0.000029000	-0.000001000
1	3.088421000	3.105907000	-0.878012000
1	4.441927000	2.345343000	0.000624000
1	3.088982000	3.104962000	0.880918000

˙CHMeCOOMe B3PW91
E = -306.939152848
$G_{298K,D3,EtOH,1M}$ = -306.879092
$\langle S^2 \rangle$ = 0.758

6	-0.078324000	0.518132000	-0.000048000
6	1.369945000	0.515962000	-0.000001000
8	-0.761227000	1.531704000	0.000042000
8	-0.611803000	-0.731006000	-0.000033000
6	-2.037475000	-0.768262000	0.000004000
1	-2.440227000	-0.271668000	-0.887122000
1	-2.307433000	-1.824538000	0.000009000
1	-2.440183000	-0.271672000	0.887151000
1	1.818181000	1.504716000	0.000073000
6	2.232597000	-0.689488000	0.000005000
1	1.644205000	-1.607599000	-0.000278000
1	2.894833000	-0.696295000	-0.876942000
1	2.894404000	-0.696591000	0.877278000

$Fe(acac)_2$(CHMeCOOMe) S = 3/2 B3PW91
E = -1120.68025649
$G_{298K,D3,EtOH,1M}$ = -1120.489776
$\langle S^2 \rangle$ = 4.150

26	0.072906000	0.216494000	0.180601000
8	-1.818381000	0.309696000	0.494432000
6	-2.654816000	1.253851000	0.231740000
6	-4.078182000	0.932621000	0.601673000
8	1.267570000	-0.368688000	-1.259614000
6	2.540703000	-0.382137000	-1.251158000
6	3.345016000	-0.021057000	-0.157004000
6	2.852843000	0.444133000	1.073189000
8	1.619267000	0.564184000	1.369954000
6	3.188688000	-0.824544000	-2.539565000
6	3.821383000	0.849945000	2.156818000
8	-0.003462000	2.114127000	-0.518597000
6	-1.011524000	2.858501000	-0.669406000
6	-0.749893000	4.229343000	-1.244790000
6	-2.332380000	2.484239000	-0.330327000
1	-0.066557000	4.771469000	-0.583223000
1	2.824283000	-1.822670000	-2.802048000
1	2.882667000	-0.149060000	-3.344995000
1	-1.662546000	4.814134000	-1.375436000
1	4.278607000	-0.840583000	-2.479495000
1	-0.245593000	4.123796000	-2.210348000
1	-3.131281000	3.196035000	-0.499470000
1	4.419858000	-0.081430000	-0.279911000
1	-4.145347000	0.793793000	1.686008000
1	4.863553000	0.706859000	1.865066000
1	-4.776136000	1.714502000	0.296608000
1	3.659614000	1.903907000	2.405407000
1	-4.363453000	-0.019377000	0.144333000
1	3.617382000	0.271908000	3.063750000
6	-0.057069000	-1.745466000	1.006659000
6	-0.338328000	-1.594803000	2.473080000
1	0.398675000	-0.942053000	2.946222000
1	-1.342747000	-1.194570000	2.629702000
1	-0.299253000	-2.574195000	2.971433000
1	0.957006000	-2.040487000	0.732088000
6	-1.101619000	-2.461119000	0.232885000
8	-2.190734000	-2.784602000	0.663725000
8	-0.700614000	-2.733308000	-1.030688000
6	-1.666208000	-3.411393000	-1.831747000
1	-2.582168000	-2.820523000	-1.920859000
1	-1.202154000	-3.542035000	-2.809621000
1	-1.920816000	-4.382216000	-1.396808000

˙CMe_3 B3PW91
E = -157.754113094
$G_{298K,D3,EtOH,1M}$ = -157.673402
$\langle S^2 \rangle$ = 0.755

6	-0.000051000	0.000120000	-0.144657000
6	-1.480485000	-0.116005000	0.014973000
6	0.639796000	1.340088000	0.014713000
6	0.840683000	-1.224087000	0.014693000
1	1.638323000	1.369372000	-0.436883000
1	0.036916000	2.135042000	-0.439780000
1	0.769472000	1.615635000	1.077079000

1	-2.005660000	0.733224000	-0.437627000
1	-1.784066000	-0.140339000	1.077347000
1	-1.866837000	-1.036324000	-0.438457000
1	1.830669000	-1.098851000	-0.439338000
1	1.014181000	-1.475020000	1.076952000
1	0.367343000	-2.103431000	-0.437627000

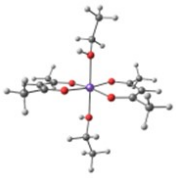
$Fe(acac)_2(CMe_3)$ S = 3/2 B3PW91
E = -971.499484946
$G_{298K,D3,EtOH,1M}$ = -971.289174
$<S^2>$ = 4.367

26	-0.103148000	0.244204000	-0.000121000
8	-1.970359000	0.834383000	-0.000053000
6	-3.061900000	0.151164000	0.000071000
6	-4.319213000	0.984376000	0.000220000
8	1.215416000	-0.160380000	1.422017000
6	2.274927000	-0.847786000	1.247574000
6	2.818998000	-1.199019000	0.000198000
6	2.275191000	-0.847772000	-1.247289000
8	1.215709000	-0.160375000	-1.421958000
6	2.972948000	-1.290841000	2.510742000
6	2.973468000	-1.290835000	-2.510312000
8	-0.832983000	-1.697667000	-0.000275000
6	-2.026920000	-2.096248000	-0.000134000
6	-2.240624000	-3.592830000	-0.000247000
6	-3.153056000	-1.236340000	0.000043000
1	-1.754093000	-4.024902000	-0.880545000
1	3.188587000	-0.416790000	3.133523000
1	2.298233000	-1.934200000	3.085249000
1	-3.296331000	-3.872186000	0.000081000
1	3.900919000	-1.831428000	2.314219000
1	-1.753462000	-4.025126000	0.879587000
1	-4.140896000	-1.681742000	0.000135000
1	3.731349000	-1.783932000	0.000290000
1	-4.324227000	1.635753000	-0.880106000
1	3.901375000	-1.831462000	-2.313596000
1	-5.225623000	0.375922000	0.000290000
1	2.298855000	-1.934155000	-3.084983000
1	-4.324054000	1.635696000	0.880590000
1	3.189281000	-0.416779000	-3.133027000
6	0.446534000	2.446268000	-0.000059000
6	-0.198859000	2.915147000	1.280042000
6	-0.199116000	2.915294000	-1.279977000
1	0.235316000	2.414656000	-2.151764000
1	-1.278362000	2.746495000	-1.272056000
1	-0.026794000	3.997549000	-1.405947000
1	-1.278098000	2.746288000	1.272344000
1	-0.026573000	3.997402000	1.406066000
1	0.235790000	2.414452000	2.151685000
6	1.952096000	2.524020000	-0.000206000
1	2.383869000	2.059667000	-0.889549000
1	2.253619000	3.584860000	-0.000066000
1	2.384058000	2.059387000	0.888899000

2.L Redox properties and electron transfer from $Fe(acac)_2$ to the acrylate radical

L1. Cartesian coordinates, energies (E and D3-corrected G in EtOH at 298 K, in hartrees) and views of the optimized geometries.

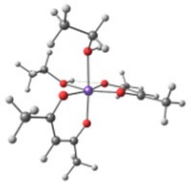
***trans*-$[Fe(acac)_2(EtOH)_2]^+$**
E = -1122.86569436
$G_{298K,D3,EtOH,1M}$ = -1122.683182
$<S^2>$ = 8.757



26	0.011863000	0.000855000	-0.000079000
8	1.436593000	0.390373000	1.319992000
8	1.437412000	-0.382177000	-1.321676000
6	2.714935000	0.366230000	1.186154000
6	3.373246000	0.001062000	0.000672000
1	4.458288000	-0.000073000	0.001316000
6	2.715576000	-0.361076000	-1.186163000
8	-1.383368000	0.643439000	1.209915000
8	-1.381351000	-0.647275000	-1.209169000
6	-2.661548000	0.556040000	1.106044000
6	-3.319134000	-0.004894000	0.000289000
1	-4.404090000	-0.006573000	0.000315000
6	-2.659837000	-0.563943000	-1.105355000
6	3.505223000	-0.752674000	-2.401892000
1	4.583854000	-0.679890000	-2.244743000
1	3.250239000	-1.782111000	-2.682761000
1	3.216427000	-0.118115000	-3.248433000
6	3.503862000	0.758858000	2.402013000
1	4.582425000	0.678728000	2.247970000
1	3.254792000	1.791441000	2.676730000
1	3.208777000	0.130720000	3.251121000
6	-3.443186000	-1.116023000	-2.259996000
1	-4.522454000	-1.032952000	-2.112951000
1	-3.160293000	-0.581352000	-3.175138000
1	-3.177786000	-2.168773000	-2.415327000
6	-3.446674000	1.105166000	2.260900000
1	-4.525686000	1.019661000	2.113373000
1	-3.162895000	0.570219000	3.175616000
1	-3.183772000	2.158358000	2.417410000
6	-0.360909000	4.375331000	-0.992601000
1	-0.352443000	5.298332000	-0.401325000

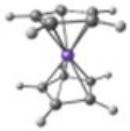
1	0.318770000	4.523758000	-1.841147000
1	-1.374134000	4.222979000	-1.378804000
6	0.072708000	3.212267000	-0.126589000
1	-0.604551000	3.053142000	0.716246000
1	1.085453000	3.354935000	0.272986000
8	0.027897000	1.965228000	-0.866982000
1	0.638391000	2.003848000	-1.618385000
8	0.037785000	-1.963789000	0.865688000
1	0.648471000	-2.001353000	1.616951000
6	0.083363000	-3.211177000	0.126018000
1	-0.595045000	-3.053410000	-0.716144000
1	1.095867000	-3.352745000	-0.274566000
6	-0.347721000	-4.374356000	0.993142000
1	-0.338334000	-5.297716000	0.402445000
1	0.332949000	-4.521224000	1.841173000
1	-1.360830000	-4.223332000	1.380164000

***cis*-[Fe(acac)$_2$(EtOH)$_2$]$^+$**
E = -1122.86938432
$G_{298K,D3,EtOH,1M}$ = -1122.682342
$\langle S^2 \rangle$ = 8.758



26	0.077827000	-0.093094000	0.030212000
8	1.419586000	0.223436000	-1.346087000
8	1.582710000	-0.672722000	1.236281000
6	2.683627000	0.425424000	-1.219401000
6	3.394703000	0.190632000	-0.033228000
1	4.459178000	0.399719000	-0.030100000
6	2.826750000	-0.354711000	1.127708000
8	-1.582110000	0.234211000	-0.940499000
8	0.039522000	1.751605000	0.646166000
6	-2.302208000	1.301230000	-0.999883000
6	-1.994857000	2.487491000	-0.321410000
1	-2.672931000	3.327436000	-0.428878000
6	-0.847695000	2.662737000	0.468769000
6	3.676435000	-0.619770000	2.335927000
1	4.732348000	-0.399231000	2.163708000
1	3.314981000	-0.004717000	3.169976000
1	3.569420000	-1.667423000	2.641838000
6	3.384460000	0.927740000	-2.447013000
1	4.462436000	1.026823000	-2.301006000
1	3.190311000	0.247941000	-3.285124000
1	2.966705000	1.903041000	-2.726283000
6	-0.582698000	3.968944000	1.156553000
1	-1.366909000	4.706155000	0.970199000
1	-0.493531000	3.798110000	2.236279000
1	0.380376000	4.369050000	0.816941000
6	-3.524268000	1.213800000	-1.865883000
1	-4.109276000	2.136267000	-1.857680000
1	-3.221000000	0.990367000	-2.896345000
1	-4.155670000	0.381815000	-1.531189000
6	-1.616828000	-2.901046000	-2.299904000
1	-1.742365000	-3.158081000	-3.358036000
1	-1.937804000	-3.758351000	-1.698640000
1	-2.258925000	-2.044116000	-2.075632000
6	-0.170315000	-2.558078000	-2.033547000
1	0.170950000	-1.717444000	-2.649313000
1	0.483600000	-3.416953000	-2.225696000
8	-0.011746000	-2.181770000	-0.630552000
1	0.825563000	-2.538098000	-0.300634000
8	-0.954289000	-0.807083000	1.759634000
1	-0.256391000	-1.099059000	2.369136000
6	-2.085560000	-1.709360000	1.810506000
1	-2.780599000	-1.322365000	1.060592000
1	-1.761494000	-2.706457000	1.486409000
6	-2.702938000	-1.731446000	3.192456000
1	-3.578159000	-2.391387000	3.195725000
1	-1.999935000	-2.115352000	3.942350000
1	-3.025432000	-0.730163000	3.496468000

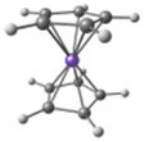
Cp_2Fe
E = -510.14907138
$G_{298K,D3,EtOH,1M}$ = -510.050152



(restricted closed-shell system, S = 0)

26	0.000057000	0.000057000	-0.000418000
6	-1.639964000	-1.052171000	0.608511000
1	-1.608375000	-1.990043000	1.150794000
6	1.640069000	1.208932000	0.126606000
1	1.608957000	2.286488000	0.239171000
6	-1.640046000	1.208936000	0.126349000
1	-1.609195000	2.286522000	0.238720000
6	1.639522000	0.253332000	1.188951000
1	1.607505000	0.478811000	2.248504000
6	-1.640753000	0.493544000	-1.110585000
1	-1.610036000	0.933535000	-2.100588000
6	1.639756000	-1.052296000	0.608426000
1	1.608422000	-1.990258000	1.150523000
6	1.640771000	0.493732000	-1.110435000
6	-1.639745000	0.253502000	1.188831000
1	-1.607667000	0.479170000	2.248369000
6	-1.640588000	-0.903857000	-0.812523000
1	-1.609793000	-1.709566000	-1.536664000
1	1.610463000	0.933813000	-2.100435000
6	1.640737000	-0.903744000	-0.812575000
1	1.609683000	-1.709409000	-1.536858000

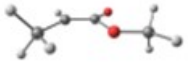
$[Cp_2Fe]^+$
E = -509.888421561
$G_{298K,D3,EtOH,1M}$ = -509.862895
$\langle S^2 \rangle$ = 0.774



26	-0.000004000	-0.000448000	-0.000310000
6	1.675254000	1.041882000	-0.628716000
1	1.643432000	1.969684000	-1.188636000

6	-1.675367000	-0.472791000	1.121029000
1	-1.643274000	-0.894075000	2.119477000
6	1.675369000	-0.472949000	1.120964000
1	1.643277000	-0.894381000	2.119348000
6	-1.675087000	0.920230000	0.796287000
1	-1.642901000	1.739622000	1.505434000
6	1.676007000	-1.212142000	-0.103385000
1	1.644911000	-2.291845000	-0.195562000
6	-1.675256000	1.041787000	-0.628868000
1	-1.643435000	1.969509000	-1.188923000
6	-1.675996000	-1.212162000	-0.103214000
6	1.675080000	0.920118000	0.796422000
1	1.642890000	1.739410000	1.505685000
6	1.675606000	-0.276023000	-1.184730000
1	1.644423000	-0.522284000	-2.240093000
1	-1.644893000	-2.291879000	-0.195234000
6	-1.675597000	-0.276199000	-1.184693000
1	-1.644404000	-0.522613000	-2.240021000

[MeCH(COOMe)]$^-$
E = -306.77699757
$G_{298K,D3,EtOH,1M}$ = -306.807310
(restricted closed-shell system, S = 0)



6	-0.026576000	0.561643000	-0.006027000
6	1.355695000	0.555186000	0.012509000
8	-0.843238000	1.512241000	-0.005856000
8	-0.592007000	-0.778969000	-0.033282000
6	-1.989206000	-0.782492000	0.017445000
1	-2.445030000	-0.049965000	-0.713189000
1	-2.303968000	-1.835949000	-0.229176000
1	-2.398884000	-0.511883000	1.044990000
1	1.825554000	1.538702000	0.022372000
6	2.226220000	-0.660414000	0.005099000
1	1.605469000	-1.565100000	0.042169000
1	2.873407000	-0.761668000	-0.895053000
1	2.928605000	-0.723846000	0.866828000

L2. Calculations of Redox Potential

$[Fe^{II}(acac)_2(EtOH)_2]/[Fe^{III}(acac)_2(EtOH)_2]^+$ redox potential:

$[Fe^{II}(acac)_2(EtOH)_2] + Cp_2Fe^+$
E = -1632.976772
$G_{298K,D3,EtOH,1M}$ = -1632.717983

$[Fe^{III}(acac)_2(EtOH)_2]^+ + Cp_2Fe$
E = -1633.014766
$G_{298K,D3,EtOH,1M}$ = -1632.733333

$[Fe^{III}(acac)_2(EtOH)_2]^+ + Cp_2Fe \rightarrow [Fe^{II}(acac)_2(EtOH)_2] + Cp_2Fe^+$

ΔE = 23.84 kcal/mol

$\Delta G_{298K,D3,EtOH,1M}$ = 9.63 kcal/mol = 40294 J/mol

$\rightarrow \Delta E_{1/2}$ ($[Fe^{II}(acac)_2(EtOH)_2]/[Fe^{III}(acac)_2(EtOH)_2]^+$) = -0.418 V vs. Cp_2Fe/Cp_2Fe^+

$[Fe^{II}(acac)_2(EtOH)_2] + {}^{\bullet}CHMe(COOMe)$
E = -1429.838899
$G_{298K,D3,EtOH,1M}$ = -1429.546266

$[Fe^{III}(acac)_2(EtOH)_2]^+ + {}^{-}CHMe(COOMe)$
E = -1429.642692
$G_{298K,D3,EtOH,1M}$ = -1429.490492

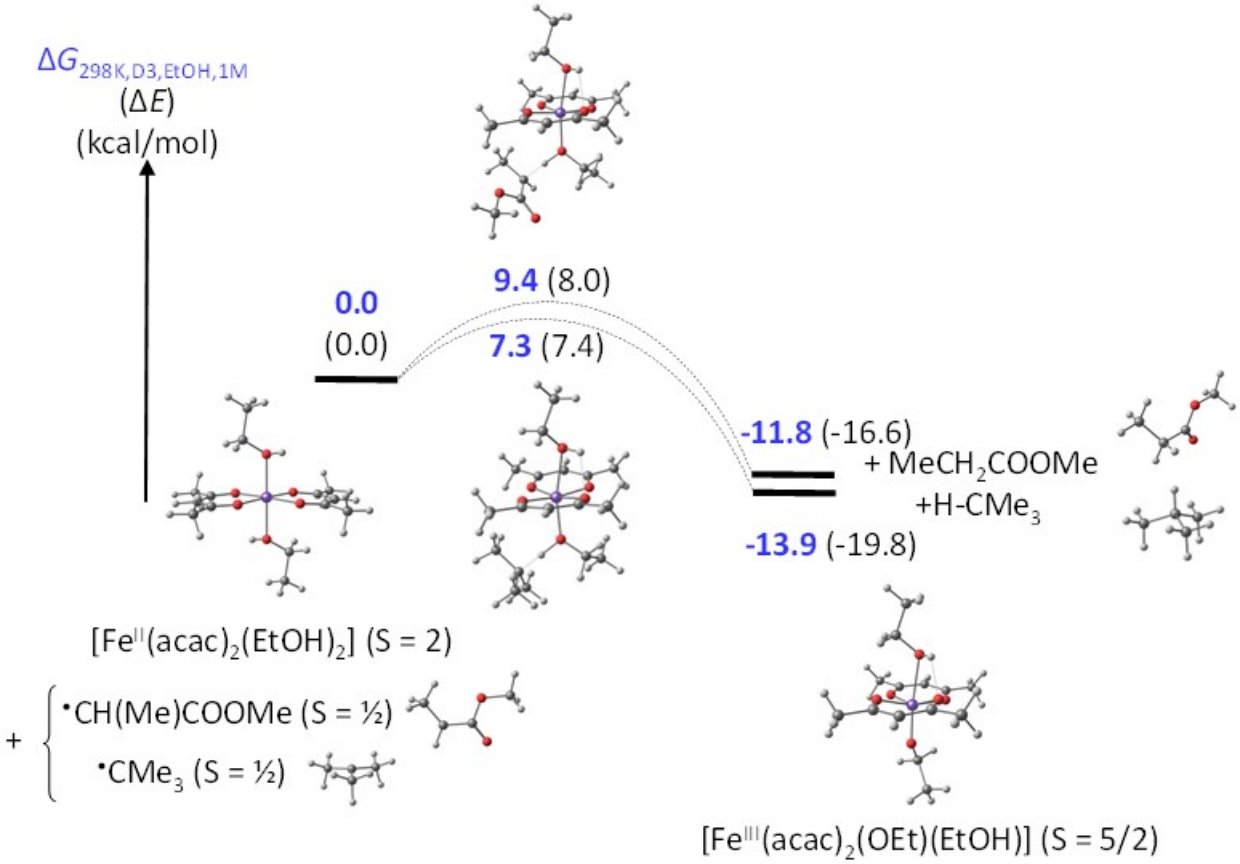
$[Fe^{III}(acac)_2(EtOH)_2]^+ + {}^{\bullet}CHMe(COOMe) \rightarrow [Fe^{II}(acac)_2(EtOH)_2]^+ + {}^{-}CHMe(COOMe)$

ΔE = 123.12 kcal/mol

$\Delta G_{298K,D3,EtOH,1M}$ = 35.00 kcal/mol

2.M Concerted proton-electron transfers to the acrylate and *t*Bu radicals

M1. Energy diagram and views of the optimized geometries



J2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

[Fe(acac)$_2$(EtOH)(EtO-H···CH(Me)COOMe)] TS
E = -1429.82619829
$G_{298K,D3,EtOH,1M}$ = -1429.531329
<S^2> = 8.772

26	0.782415000	0.098048000	0.093449000
8	0.484068000	1.513463000	1.586224000
8	-0.405921000	1.250009000	-1.063226000
6	-0.454514000	2.380081000	1.641813000
6	-1.320686000	2.701682000	0.585110000
1	-2.078906000	3.458426000	0.763100000
6	-1.252065000	2.131728000	-0.700887000
8	2.138774000	-0.851326000	1.266289000
8	1.449500000	-0.981089000	-1.443721000
6	3.085337000	-1.618638000	0.901460000
6	3.283923000	-2.089220000	-0.410939000
1	4.121062000	-2.756844000	-0.590725000
6	2.459598000	-1.762083000	-1.497361000
6	-2.237446000	2.565575000	-1.757215000
1	-2.802303000	3.457179000	-1.469063000
1	-1.709758000	2.750275000	-2.699437000
1	-2.939587000	1.739483000	-1.930579000
6	-0.603884000	3.095902000	2.964155000
1	-1.369670000	3.876440000	2.940233000
1	-0.862402000	2.366058000	3.741468000
1	0.356911000	3.538605000	3.253149000
6	2.746758000	-2.356983000	-2.855363000
1	3.633181000	-2.997701000	-2.857571000
1	1.880007000	-2.942832000	-3.185275000
1	2.881131000	-1.549937000	-3.585665000
6	4.042152000	-2.042534000	1.991529000
1	4.818517000	-2.724754000	1.633459000
1	4.516386000	-1.150918000	2.419672000
1	3.482224000	-2.525426000	2.801362000
6	-0.545063000	-2.806699000	2.400872000

1	-0.789671000	-3.062645000	3.439856000
1	-1.004302000	-3.561415000	1.751864000
1	0.541342000	-2.850298000	2.276060000
6	-1.057829000	-1.415668000	2.072839000
1	-0.595440000	-0.665806000	2.726291000
1	-2.147783000	-1.361283000	2.198625000
8	-0.743093000	-1.025030000	0.732133000
1	-1.558333000	-1.420488000	0.047836000
8	2.531596000	1.556284000	-0.198700000
1	2.308199000	2.071663000	0.594211000
6	2.585190000	2.425983000	-1.335706000
1	2.672540000	1.759112000	-2.199496000
1	1.636841000	2.971253000	-1.439961000
6	3.766140000	3.377048000	-1.257758000
1	3.818699000	3.995854000	-2.162105000
1	3.678498000	4.053480000	-0.397359000
1	4.706044000	2.822059000	-1.162375000
6	-3.805609000	-1.357459000	-0.237216000
8	-4.238546000	-0.316157000	-1.007134000
6	-2.609442000	-2.008396000	-0.770995000
1	-2.525856000	-3.030700000	-0.393716000
8	-4.367040000	-1.659689000	0.808679000
6	-2.151147000	-1.776265000	-2.183622000
1	-1.159414000	-2.213091000	-2.344718000
1	-2.840357000	-2.230907000	-2.914051000
1	-2.083556000	-0.708992000	-2.415055000
6	-5.382425000	0.361564000	-0.487237000
1	-5.630316000	1.135065000	-1.218405000
1	-6.223538000	-0.329142000	-0.363060000
1	-5.161821000	0.813545000	0.486525000

[Fe(acac)$_2$(EtOH)(EtO-H···CMe$_3$)] TS
E = -1280.70939472
$G_{298K,D3,EtOH,1M}$ = -1280.396322
$\langle S^2 \rangle$ = 8.774

26	0.343580000	-0.081805000	0.054023000
8	0.852052000	1.374735000	1.468302000
8	-0.112456000	1.481798000	-1.181224000
6	0.693787000	2.638565000	1.398134000
6	0.206857000	3.335326000	0.278280000
1	0.122291000	4.415694000	0.351385000
6	-0.164068000	2.728683000	-0.938171000
8	1.116207000	-1.529842000	1.275946000
8	0.279345000	-1.445640000	-1.409677000
6	1.527881000	-2.685256000	0.940893000
6	1.389177000	-3.258000000	-0.337837000
1	1.778397000	-4.260392000	-0.490169000
6	0.778560000	-2.618954000	-1.428729000
6	-0.659632000	3.599638000	-2.071584000
1	-0.627886000	4.667023000	-1.833966000
1	-0.056424000	3.408699000	-2.967125000
1	-1.691363000	3.320622000	-2.319681000
6	1.073427000	3.417048000	2.638877000
1	0.974847000	4.498901000	2.510085000
1	0.437697000	3.098040000	3.474242000
1	2.106464000	3.179203000	2.920381000
6	0.681235000	-3.344929000	-2.751523000
1	1.135958000	-4.339564000	-2.724451000
1	-0.373340000	-3.440899000	-3.037942000
1	1.169142000	-2.746109000	-3.530182000
6	2.209066000	-3.481934000	2.032143000
1	2.557467000	-4.460634000	1.689163000
1	3.062480000	-2.910824000	2.417361000
1	1.515072000	-3.622503000	2.869991000
6	-2.028044000	-1.574649000	2.832815000
1	-2.293903000	-1.471162000	3.893192000
1	-2.802853000	-2.174871000	2.341500000
1	-1.075549000	-2.108754000	2.760234000
6	-1.895591000	-0.207367000	2.181968000
1	-1.117359000	0.384591000	2.682127000
1	-2.838263000	0.357352000	2.263642000
8	-1.527169000	-0.300976000	0.813112000
1	-2.518932000	-0.267575000	0.131274000
8	2.636531000	0.233240000	-0.295203000
1	2.724890000	0.621879000	0.590378000
6	3.164045000	1.151039000	-1.257177000
1	2.871175000	0.748121000	-2.232357000
1	2.685444000	2.135120000	-1.148004000
6	4.675489000	1.266970000	-1.152463000
1	5.065058000	1.933277000	-1.932372000
1	4.976791000	1.680525000	-0.180986000
1	5.148252000	0.285133000	-1.267164000
6	-3.620961000	-0.178032000	-0.655803000
6	-3.000687000	-0.326788000	-2.026816000
1	-2.528836000	-1.307647000	-2.151429000
1	-3.771735000	-0.221013000	-2.810419000
1	-2.229282000	0.431717000	-2.203062000
6	-4.183945000	1.195925000	-0.367575000
1	-5.042273000	1.408640000	-1.028697000
1	-4.546200000	1.285338000	0.664590000
1	-3.437342000	1.980371000	-0.538456000
6	-4.512633000	-1.325346000	-0.236731000
1	-4.859670000	-1.220262000	0.799124000
1	-5.412393000	-1.368667000	-0.875169000
1	-4.000769000	-2.290578000	-0.333892000

Fe(acac)$_2$(OEt)(EtOH)
E = -1122.46004922
$G_{298K,D3,EtOH,1M}$ = -1122.232209
$\langle S^2 \rangle$ = 8.762

26	0.018011000	0.272699000	-0.102276000
8	-1.437442000	-0.201698000	-1.393810000
8	-1.415047000	0.602419000	1.271139000
6	-2.685686000	-0.347493000	-1.176896000

6	-3.322498000	-0.123321000	0.053777000
1	-4.393233000	-0.291727000	0.113562000
6	-2.659375000	0.339685000	1.203167000
8	1.431570000	-0.534104000	-1.312512000
8	1.394120000	0.008674000	1.404806000
6	2.684860000	-0.342940000	-1.185713000
6	3.325067000	0.009600000	0.017738000
1	4.403616000	0.132919000	0.006077000
6	2.658530000	0.132603000	1.245394000
6	-3.441801000	0.569682000	2.473433000
1	-4.513112000	0.387326000	2.350024000
1	-3.052165000	-0.091341000	3.257344000
1	-3.284065000	1.598968000	2.816308000
6	-3.502625000	-0.781167000	-2.370466000
1	-4.556913000	-0.938703000	-2.125908000
1	-3.425818000	-0.018563000	-3.155208000
1	-3.082141000	-1.705513000	-2.783745000
6	3.446286000	0.414679000	2.500722000
1	4.525819000	0.438060000	2.327190000
1	3.126293000	1.380532000	2.910892000
1	3.215093000	-0.344253000	3.257732000
6	3.505494000	-0.541490000	-2.436354000
1	4.580426000	-0.446799000	-2.258507000
1	3.290396000	-1.528984000	-2.861279000
1	3.197377000	0.201065000	-3.182790000
8	0.362205000	2.014060000	-0.516309000
6	-0.474516000	3.127933000	-0.605960000
1	-0.911839000	3.175185000	-1.620073000
1	-1.317651000	3.030247000	0.100262000
6	0.296759000	4.410821000	-0.320189000
1	1.127952000	4.523850000	-1.025744000
1	-0.358446000	5.287026000	-0.410380000
1	0.710260000	4.389447000	0.694736000
8	-0.317033000	-1.964792000	0.716529000
1	0.413282000	-1.803953000	1.338379000
6	-0.006852000	-3.101003000	-0.092335000
1	-0.813457000	-3.157207000	-0.830964000
1	0.926396000	-2.928070000	-0.646586000
6	0.063629000	-4.377089000	0.729332000
1	-0.874248000	-4.543341000	1.271324000
1	0.247845000	-5.242703000	0.080829000
1	0.879433000	-4.333103000	1.463065000

$MeCH_2COOMe$

E = -307.405250263

$G_{298K,D3,EtOH,1M}$ = -307.332905

(restricted closed-shell system, S = 0)

6	0.084008000	0.505606000	-0.063031000
6	-1.393201000	0.426792000	-0.378033000
8	0.680552000	1.508089000	0.267631000
8	0.685979000	-0.695572000	-0.217784000
6	2.093400000	-0.700241000	0.043155000
1	2.298416000	-0.381285000	1.070431000
1	2.420934000	-1.730479000	-0.110644000
1	2.617045000	-0.025106000	-0.641986000
1	-1.487831000	0.334076000	-1.469762000
6	-2.121762000	-0.733521000	0.301913000
1	-1.694390000	-1.695092000	0.002030000
1	-2.054552000	-0.658737000	1.393446000
1	-3.183411000	-0.728665000	0.031156000
1	-1.823126000	1.393341000	-0.097468000

Me_3CH

E = -158.292724054

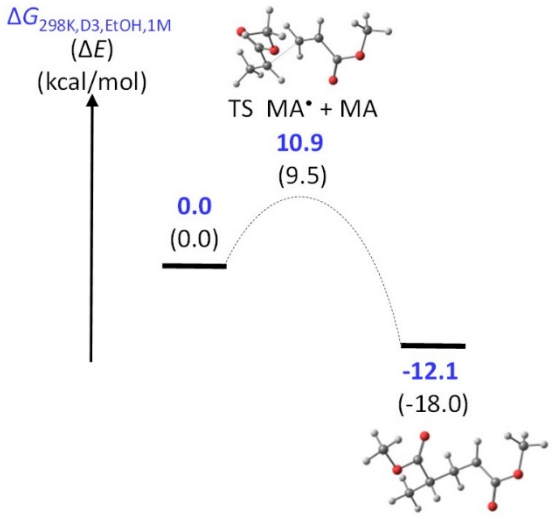
$G_{298K,D3,EtOH,1M}$ = -158.197875

(restricted closed-shell system, S = 0)

1	-0.000190000	-0.000183000	-1.474955000
6	-0.000117000	-0.000150000	-0.372895000
6	1.086888000	-0.970273000	0.095433000
1	2.077916000	-0.667113000	-0.265268000
1	1.130262000	-1.006689000	1.192918000
1	0.896747000	-1.989896000	-0.262788000
6	-1.383945000	-0.455831000	0.095491000
1	-1.438151000	-0.472723000	1.192983000
1	-2.171672000	0.217862000	-0.264757000
1	-1.616701000	-1.466367000	-0.263363000
6	0.297099000	1.426169000	0.095395000
1	-0.461997000	2.132801000	-0.263091000
1	0.309951000	1.481321000	1.192864000
1	1.274288000	1.771492000	-0.265086000

2.N Acrylate radical homopropagation

N1. Energy diagram and views of the optimized geometries



N2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

MeOOC(Me)C···CH_2=CHCOOMe TS
E = -612.904336956
$G_{298K,D3,EtOH,1M}$ = -612.788627
$<S^2>$ = 0.772

6	1.562643000	-0.995790000	-0.443575000
6	1.998525000	0.347144000	-0.072936000
6	2.447164000	-2.146176000	-0.119577000
1	1.887949000	-3.084747000	-0.035615000
1	3.186816000	-2.290537000	-0.924255000
1	3.007613000	-1.959313000	0.801952000
6	-1.136799000	-0.339142000	0.846110000
1	-1.158318000	0.616835000	1.361784000
6	-2.082083000	-0.619692000	-0.254026000
8	-3.159324000	0.191269000	-0.419166000
8	-1.931309000	-1.541786000	-1.033152000
6	-3.438105000	1.232026000	0.510828000
1	-3.497904000	0.857004000	1.540330000
1	-2.694858000	2.038459000	0.454807000
1	-4.413038000	1.633081000	0.222604000
6	-0.172585000	-1.253930000	1.133612000
1	-0.248822000	-2.248584000	0.701518000
1	0.508104000	-1.108910000	1.968798000
1	0.825857000	-1.084742000	-1.238776000
8	1.257220000	1.305315000	-0.685766000
8	2.905184000	0.602613000	0.707343000
6	1.631997000	2.644505000	-0.359360000
1	2.672851000	2.837854000	-0.640887000
1	0.958579000	3.289354000	-0.928169000
1	1.526451000	2.831287000	0.715368000

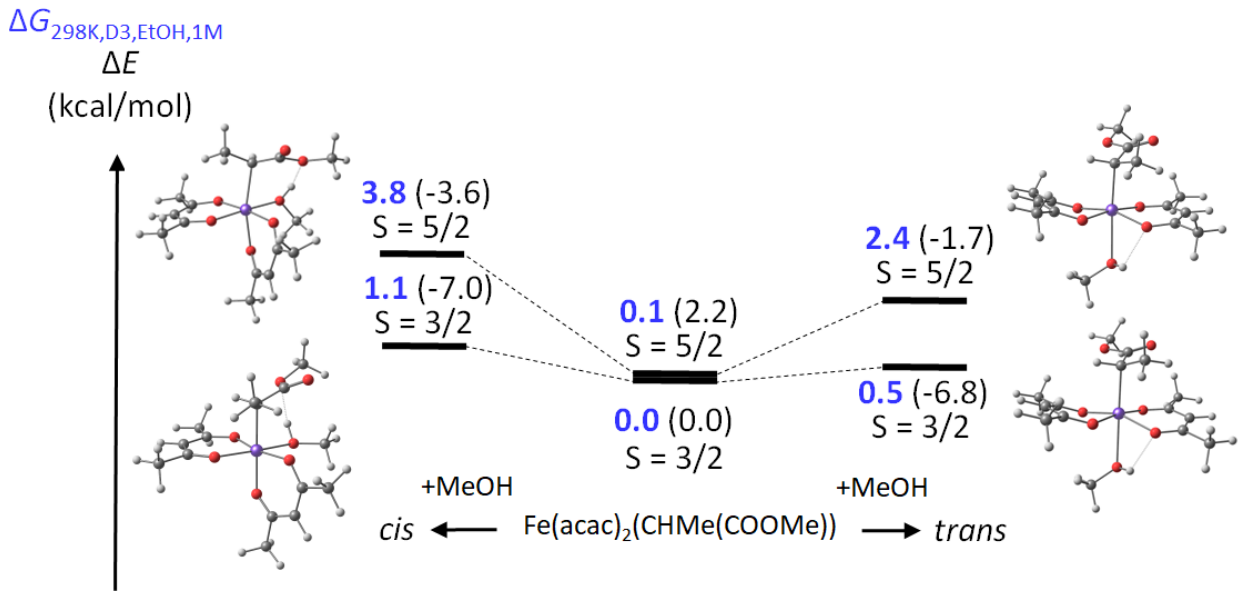
MeOOC(Me)C-CH_2C•(COOMe)
E = -612.948121087
$G_{298K,D3,EtOH,1M}$ = -612.825343
$<S^2>$ = 0.758

6	1.430587601	-1.015435131	-0.323546936
6	1.866469601	0.327498869	0.047092064
6	2.315108601	-2.165821131	0.000451064
1	1.755893601	-3.104392131	0.084413064
1	3.054760601	-2.310182131	-0.804226936
1	2.875557601	-1.978958131	0.921980064
6	-1.004743601	-0.319496869	0.726081936
1	-1.026262601	0.636480131	1.241755936
6	-1.950027601	-0.600046869	-0.374054064
8	-3.027268601	0.210914131	-0.539194064
8	-1.799253601	-1.522140869	-1.153180064
6	-3.306049601	1.251671131	0.390799936
1	-3.365848601	0.876649131	1.420301936
1	-2.562802601	2.058104131	0.334778936
1	-4.280982601	1.652726131	0.102575936
6	-0.040529601	-1.234284869	1.013583936
1	-0.116766601	-2.228938869	0.581489936
1	0.640159399	-1.089264869	1.848769936
1	0.693801601	-1.104387131	-1.118747936
8	1.125164601	1.285669869	-0.565737936
8	2.773128601	0.582967869	0.827371064
6	1.499941601	2.624859869	-0.239331936
1	2.540795601	2.818208869	-0.520858936
1	0.826523601	3.269708869	-0.808140936

1 1.394395601 2.811641869 0.835396064

2.O MeOH adducts of $(acac)_2Fe^{III}(CHMeCOOMe)$

O1. Energy diagram and views of the optimized geometries



O2. Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

MeOH
E = -115.609711214
$G_{298K,D3,EtOH,1M}$ = -115.586844s
(restricted closed-shell system, S = 0)

8	-0.747348000	0.122005000	-0.000001000
1	-1.129605000	-0.764244000	0.000025000
6	0.658234000	-0.019463000	-0.000003000
1	1.081083000	0.990720000	-0.000164000
1	1.038974000	-0.542720000	0.893218000
1	1.038925000	-0.543024000	-0.893054000

***trans*-Fe(acac)$_2$(CHMeCOOMe)(MeOH) S = 3/2**
E = -1235.66640182
$G_{298K,D3,EtOH,1M}$ = -1235.442055
$\langle S^2 \rangle$ = 4.116

26	-0.117679000	-0.374128000	-0.137102000
8	-0.473060000	-2.157266000	-1.841289000
8	1.437190000	0.259929000	-1.180102000
6	2.671077000	-0.010359000	-1.000024000
6	3.138574000	-1.127671000	-0.281025000
6	2.300954000	-2.057660000	0.343648000
8	1.020006000	-1.979708000	0.388190000
6	3.647752000	0.960015000	-1.601799000
6	2.896052000	-3.259841000	1.032263000
8	-1.658902000	-1.293211000	0.820005000
6	-2.824216000	-0.800835000	0.991469000
6	-3.336771000	0.306413000	0.292484000
6	-2.650902000	0.959873000	-0.746949000
6	-3.300996000	2.108445000	-1.472180000
8	-1.480266000	0.647378000	-1.149635000
6	-3.681663000	-1.494477000	2.021390000
1	3.604333000	1.874214000	-0.995121000
1	3.336130000	1.216591000	-2.619968000
1	4.673279000	0.580340000	-1.607575000
1	4.211064000	-1.284431000	-0.225016000
1	3.985595000	-3.297653000	0.948873000
1	2.614468000	-3.243763000	2.092207000
1	2.469452000	-4.174827000	0.603145000
1	-3.257604000	1.930773000	-2.552783000
1	-4.338166000	2.270899000	-1.166206000
1	-2.717788000	3.015351000	-1.270874000
1	-4.341006000	0.642595000	0.531137000
1	-3.184957000	-1.441745000	2.997854000
1	-4.681926000	-1.060046000	2.102277000
1	-3.767313000	-2.557367000	1.765626000
1	-0.124110000	-2.777026000	-1.181169000
6	-1.765141000	-2.574467000	-2.253393000
1	-2.458467000	-2.666171000	-1.405963000
1	-2.144173000	-1.806311000	-2.933095000
1	-1.725986000	-3.531138000	-2.794878000

6	0.147620000	1.026633000	1.535281000
1	-0.912929000	1.251104000	1.690988000
6	0.823817000	0.273831000	2.659717000
1	0.785534000	0.845436000	3.600960000
1	0.344657000	-0.694852000	2.841110000
1	1.881229000	0.108019000	2.428146000
6	0.886333000	2.175706000	1.008605000
8	2.096857000	2.352946000	1.074439000
8	0.061579000	3.072432000	0.389214000
6	0.732171000	4.171399000	-0.220726000
1	1.386264000	4.681797000	0.494764000
1	1.339416000	3.835444000	-1.069813000
1	-0.052531000	4.848072000	-0.569132000

***trans*-Fe(acac)$_2$(CHMeCOOMe)(MeOH) S = 5/2**
E = -1235.65820741
$G_{298K,D3,EtOH,1M}$ = -1235.438996
$\langle S^2 \rangle$ = 8.758

26	-0.117679000	-0.374128000	-0.137102000
8	-0.473060000	-2.157266000	-1.841289000
8	1.437190000	0.259929000	-1.180102000
6	2.671077000	-0.010359000	-1.000024000
6	3.138574000	-1.127671000	-0.281025000
6	2.300954000	-2.057660000	0.343648000
8	1.020006000	-1.979708000	0.388190000
6	3.647752000	0.960015000	-1.601799000
6	2.896052000	-3.259841000	1.032263000
8	-1.658902000	-1.293211000	0.820005000
6	-2.824216000	-0.800835000	0.991469000
6	-3.336771000	0.306413000	0.292484000
6	-2.650902000	0.959873000	-0.746949000
6	-3.300996000	2.108445000	-1.472180000
8	-1.480266000	0.647378000	-1.149635000
6	-3.681663000	-1.494477000	2.021390000
1	3.604333000	1.874214000	-0.995121000
1	3.336130000	1.216591000	-2.619968000
1	4.673279000	0.580340000	-1.607575000
1	4.211064000	-1.284431000	-0.225016000
1	3.985595000	-3.297653000	0.948873000
1	2.614468000	-3.243763000	2.092207000
1	2.469452000	-4.174827000	0.603145000
1	-3.257604000	1.930773000	-2.552783000
1	-4.338166000	2.270899000	-1.166206000
1	-2.717788000	3.015351000	-1.270874000
1	-4.341006000	0.642595000	0.531137000
1	-3.184957000	-1.441745000	2.997854000
1	-4.681926000	-1.060046000	2.102277000
1	-3.767313000	-2.557367000	1.765626000
1	-0.124110000	-2.777026000	-1.181169000
6	-1.765141000	-2.574467000	-2.253393000
1	-2.458467000	-2.666171000	-1.405963000
1	-2.144173000	-1.806311000	-2.933095000
1	-1.725986000	-3.531138000	-2.794878000
6	0.147620000	1.026633000	1.535281000
1	-0.912929000	1.251104000	1.690988000
6	0.823817000	0.273831000	2.659717000
1	0.785534000	0.845436000	3.600960000
1	0.344657000	-0.694852000	2.841110000
1	1.881229000	0.108019000	2.428146000
6	0.886333000	2.175706000	1.008605000
8	2.096857000	2.352946000	1.074439000
8	0.061579000	3.072432000	0.389214000
6	0.732171000	4.171399000	-0.220726000
1	1.386264000	4.681797000	0.494764000
1	1.339416000	3.835444000	-1.069813000
1	-0.052531000	4.848072000	-0.569132000

***cis*-Fe(acac)$_2$(CHMeCOOMe)(MeOH) S = 3/2**
E = -1235.66660484
$G_{298K,D3,EtOH,1M}$ = -1235.441036
$\langle S^2 \rangle$ = 4.011

26	0.204770000	0.057267000	0.037572000
8	-0.494049000	1.686703000	0.819429000
6	-0.097995000	2.895667000	0.627149000
6	-0.821895000	3.924603000	1.458568000
8	0.483453000	-1.563270000	-1.036916000
6	1.394238000	-2.454842000	-0.926108000
6	2.367679000	-2.500408000	0.079406000
6	2.495500000	-1.539501000	1.104480000
8	1.731478000	-0.537767000	1.256594000
6	1.371677000	-3.519386000	-1.996312000
6	3.613930000	-1.678166000	2.111749000
8	1.481699000	1.136208000	-1.058067000
6	1.651956000	2.388388000	-1.046956000
6	2.737606000	2.917021000	-1.954944000
6	0.906096000	3.292350000	-0.254960000
1	3.694343000	2.459820000	-1.675664000
1	0.393065000	-4.014470000	-1.997493000
1	1.493121000	-3.045003000	-2.977698000
1	2.832341000	4.005732000	-1.910759000
1	2.155396000	-4.270166000	-1.860793000
1	2.525439000	2.612779000	-2.986658000
1	1.139721000	4.350143000	-0.323389000
1	3.082387000	-3.317294000	0.056173000
1	-0.640447000	3.720803000	2.521096000
1	4.228835000	-2.566483000	1.940743000
1	-0.505742000	4.946424000	1.230978000
1	4.250573000	-0.786172000	2.068035000
1	-1.902133000	3.830067000	1.296752000
1	3.191327000	-1.720524000	3.122758000
6	-1.129311000	-1.012683000	1.282284000
6	-1.007239000	-0.502674000	2.694014000
1	0.040548000	-0.491019000	3.007265000
1	-1.418151000	0.506997000	2.774908000

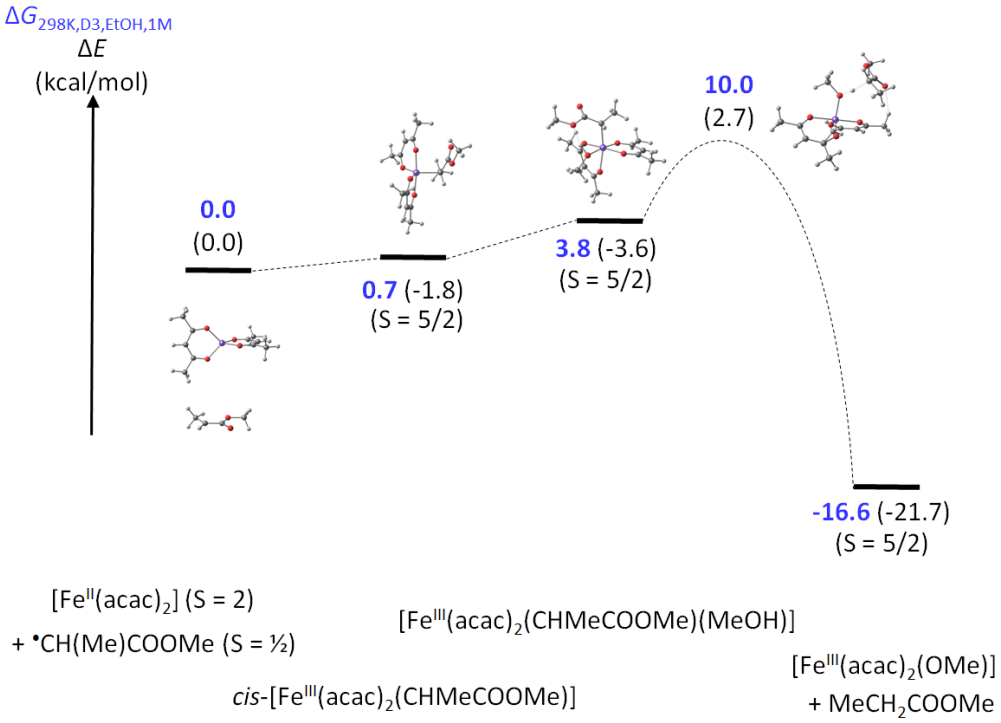
1	-1.569974000	-1.149630000	3.385200000
1	-0.671063000	-1.986923000	1.095084000
6	-2.497659000	-0.937984000	0.732287000
8	-3.417303000	-0.273666000	1.173922000
8	-2.669838000	-1.744490000	-0.373507000
6	-4.023993000	-1.839281000	-0.829032000
1	-4.413131000	-0.862607000	-1.137250000
1	-4.004157000	-2.528652000	-1.676445000
1	-4.669841000	-2.230556000	-0.035679000
8	-1.279677000	0.322264000	-1.730929000
1	-1.696904000	-0.554282000	-1.663571000
6	-2.285189000	1.328155000	-1.784283000
1	-1.767265000	2.289419000	-1.842173000
1	-2.905651000	1.213266000	-2.684682000
1	-2.925155000	1.323978000	-0.891883000

cis-Fe(acac)$_2$(CHMeCOOMe)(MeOH) S = 5/2
E = -1235.66117678
$G_{298K,D3,EtOH,1M}$ = -1235.436776
$\langle S^2 \rangle$ = 8.759

26	-0.113303000	-0.179637000	0.215596000
8	1.150022000	1.019007000	-0.755447000
6	0.972157000	2.242166000	-1.090593000
6	1.864128000	2.742515000	-2.198259000
8	-1.512504000	-1.250379000	1.172159000
6	-2.704335000	-1.534372000	0.824417000
6	-3.280344000	-1.183912000	-0.409756000
6	-2.597126000	-0.476800000	-1.410901000
8	-1.393456000	-0.061291000	-1.317432000
6	-3.513165000	-2.306325000	1.836665000
6	-3.288708000	-0.166353000	-2.714627000
8	-0.820361000	1.582105000	1.115614000
6	-0.789509000	2.734110000	0.583231000
6	-1.711964000	3.767785000	1.188917000
6	0.040876000	3.102672000	-0.497097000
1	-2.747766000	3.416057000	1.109135000
1	-2.992263000	-3.240317000	2.079255000
1	-3.574826000	-1.725232000	2.764664000
1	-1.626925000	4.747030000	0.709055000
1	-4.523113000	-2.535562000	1.485594000
1	-1.491915000	3.869622000	2.258481000
1	-0.015111000	4.124186000	-0.860696000
1	-4.304915000	-1.486072000	-0.602709000
1	1.695856000	2.133230000	-3.094403000
1	-4.322668000	-0.521554000	-2.739236000
1	1.692470000	3.796113000	-2.436439000
1	-3.271672000	0.916988000	-2.883332000
1	2.913581000	2.600516000	-1.913717000
1	-2.728587000	-0.626301000	-3.537829000
6	1.067772000	-2.017707000	-0.224005000
6	0.336234000	-2.723594000	-1.345691000
1	-0.722554000	-2.869002000	-1.103353000
1	0.405541000	-2.155889000	-2.279450000
1	0.770341000	-3.717464000	-1.539473000
1	0.948023000	-2.472765000	0.763949000
6	2.444827000	-1.661295000	-0.527005000
8	2.995486000	-1.623616000	-1.610804000
8	3.151589000	-1.318600000	0.632855000
6	4.485566000	-0.863708000	0.403891000
1	4.487564000	0.068201000	-0.172662000
1	4.924990000	-0.702801000	1.391894000
1	5.056412000	-1.616378000	-0.148662000
8	1.145043000	-0.251648000	2.038133000
1	1.998799000	-0.602825000	1.689604000
6	1.393414000	0.856866000	2.895074000
1	0.426555000	1.217428000	3.249629000
1	2.002162000	0.541348000	3.753376000
1	1.900398000	1.675097000	2.365624000

2.P Intramolecular acrylate protonation (Part 1: to the C-bound enolate)

P1. Freely optimized transition state (sextet):



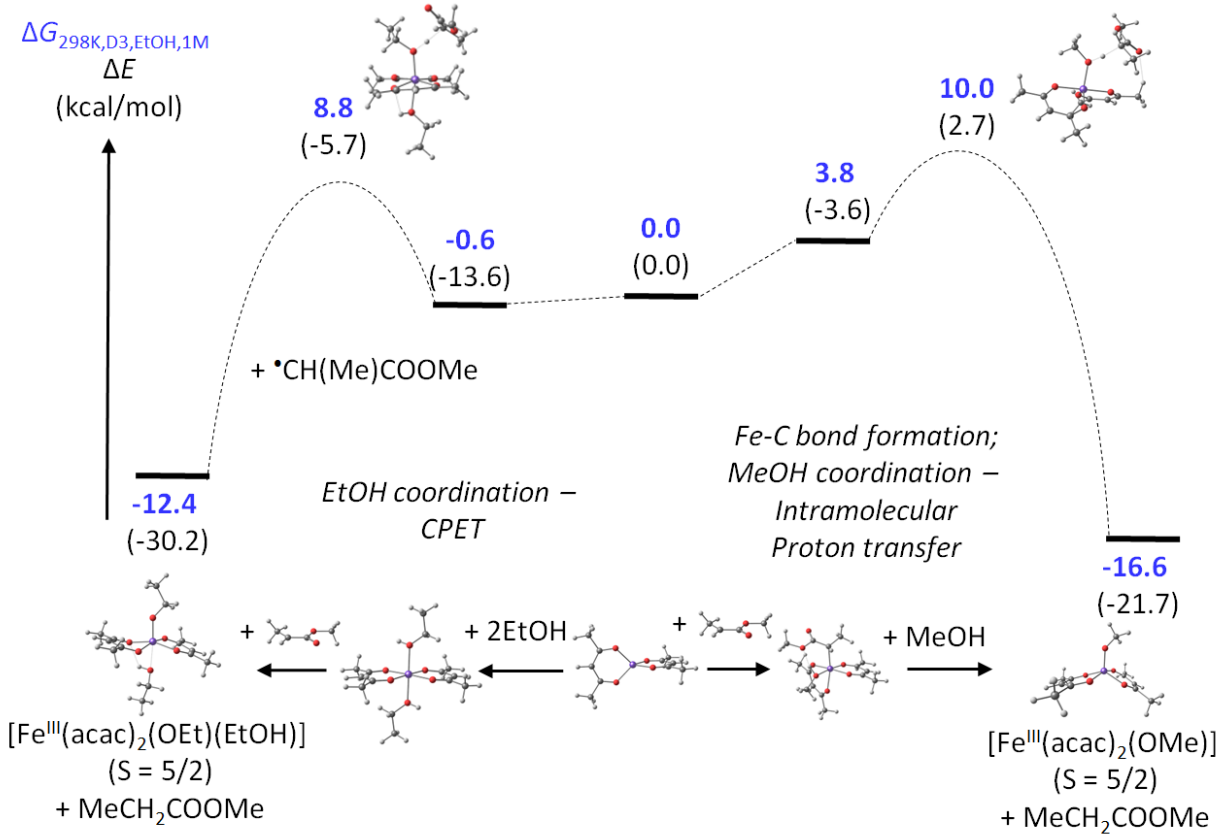
Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries.

Intramolecular proton transfer TS S = 5/2
E = -1235.65113656
$G_{298K,D3,EtOH,1M}$ = -1235.426910
$<S^2>$ = 8.768

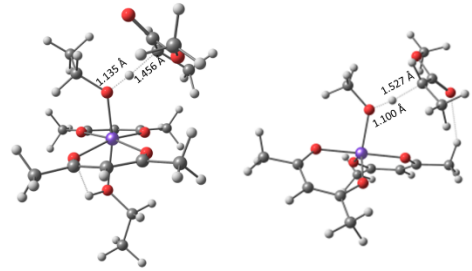
26	0.866522000	0.171552000	-0.048180000
8	-0.601999000	0.768528000	1.201955000
6	-1.224314000	1.877526000	1.245855000
6	-2.304069000	1.990924000	2.286773000
8	2.350034000	-0.387074000	-1.323184000
6	3.547157000	-0.726282000	-1.055774000
6	4.059995000	-0.877763000	0.247144000
6	3.301570000	-0.677276000	1.407695000
8	2.071674000	-0.318766000	1.426777000
6	4.444205000	-0.977416000	-2.243722000
6	3.928461000	-0.887261000	2.762619000
8	0.723263000	1.920803000	-0.940197000
6	-0.019723000	2.927376000	-0.649488000
6	0.184586000	4.139431000	-1.523138000
6	-0.965829000	2.961086000	0.378326000
1	1.230143000	4.463411000	-1.452674000
1	4.017122000	-1.777200000	-2.861032000
1	4.476874000	-0.075642000	-2.866915000
1	-0.470145000	4.971661000	-1.250159000
1	5.462125000	-1.253583000	-1.954543000
1	0.006282000	3.865492000	-2.570091000
1	-1.542822000	3.870782000	0.512438000
1	5.097864000	-1.175562000	0.359182000
1	-1.898629000	1.703865000	3.264069000
1	4.977924000	-1.188433000	2.700401000
1	-2.728571000	2.997137000	2.347056000
1	3.850585000	0.039017000	3.344534000
1	-3.095129000	1.272352000	2.032010000
1	3.363490000	-1.653315000	3.307552000
6	-2.495450000	-2.198315000	0.469209000
6	-2.185983000	-2.267174000	1.933893000
1	-1.270350000	-2.841578000	2.116824000
1	-2.055407000	-1.264922000	2.351926000
1	-2.998504000	-2.759241000	2.493876000
1	-2.463893000	-3.134227000	-0.095141000
6	-3.527373000	-1.271533000	0.018952000
8	-4.046022000	-0.379427000	0.678374000
8	-3.855991000	-1.487124000	-1.289095000

6	-4.829292000	-0.585981000	-1.813172000	1	-1.261043000	-1.565833000	-0.168733000
1	-4.475530000	0.450170000	-1.758669000	6	-0.215907000	-2.074074000	-1.865047000
1	-4.980513000	-0.881253000	-2.854380000	1	-0.042990000	-3.123372000	-1.589359000
1	-5.771254000	-0.657672000	-1.257530000	1	-1.121196000	-2.004776000	-2.480692000
8	-0.349978000	-1.260949000	-0.703857000	1	0.647941000	-1.705166000	-2.424205000

P2. The geometry of the optimized sextet TS involves full rupture of the Fe-C bond, adoption of a tbp geometry with equatorial methanol (like in optimized [Fe(acac)$_2$(EtOH)]), and location of the H proton still quite close to the methanol O atom (1.100 Å) but also not far from the methyl acrylate radical C atom (1.527 Å). The relative geometry of the alcohol OH bond and acrylate radical is rather close to that of the TS previously obtained for the CPET pathway (optimized in the presence of two EtOH molecule). The two pathways (CPET and intramolecular proton transfer for the alkyl adduct), with the energies and geometries of the two TS's, are compared below.



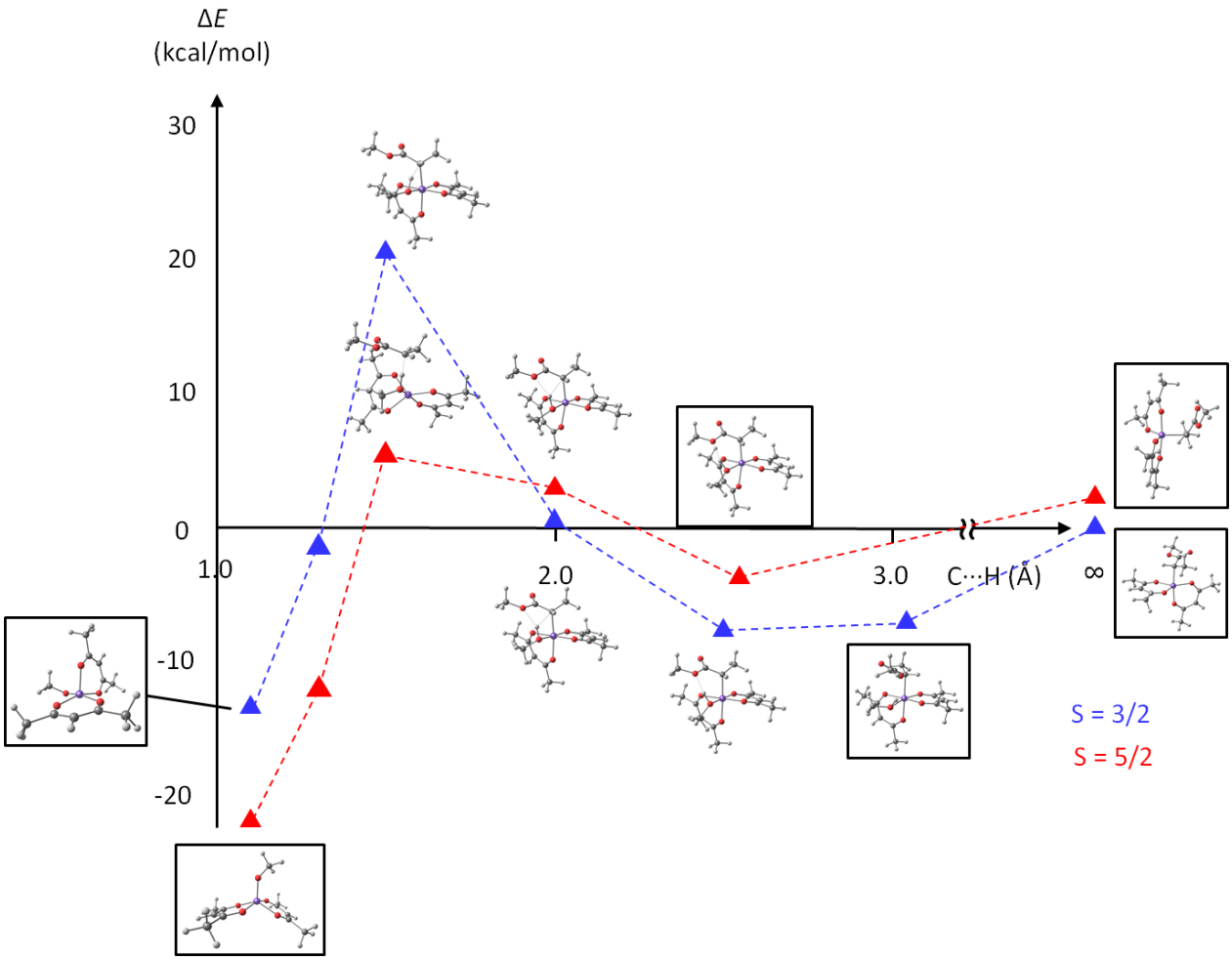
P3. The next figure compares the two TS geometries in closer detail.



We conclude that this pathway corresponds to another CPET transition state. The slight energy difference is due to the coordination of one extra alcohol molecule and to the minor difference between MeOH and EtOH. Therefore, bond formation does not help proton transfer.

An attempt to free optimize the transition state for the intramolecular proton transfer in the quartet state failed.

P4. Relaxed scan along the C···H parameter



At infinite distance, we start from $Fe(acac)_2(CHMeCOOMe)$ (section H) plus methanol. The other geometries shown in black frames at intermediate C···H distances are the fully optimized adducts, $Fe(acac)_2(CHMeCOOMe)(MeOH)$ already described above (section M). The other points correspond to partially optimized geometries at fixed C···H, except the last ones on the left at C-H = 1.099 Å, which correspond to the energies of the sum of fully optimized CH_3CH_2COOMe (section K) plus $Fe(acac)_2(OMe)$ (section N) in each spin state. The y axis values are uncorrected electronic energies. The relative G values of the fully optimized structures are above in the corresponding sections.

Proton transfer is easier on the sextet PES. The highest point at C-H = 1.5 Å is at 5.3 kcal/mol. The Fe-C bond has already broken (3.94 A) and the two acac ligands have rearranged from the perpendicular arrangement of the cis-octahedral environment, with the acac ligand parallel to the Fe-C bond axis of the leaving alkyl group swinging on its way to the relative configuration in the final sextet $Fe(acac)_2(OMe)$. For comparison, the TS for the process on the sextet surface, which corresponds to the CPET, on the same energy scale (relative to quartet $Fe(acac)_2(CHMeCOMe)$ plus methanol) has E = 2.7 kcal/mol (G = 10.0 kcal/mol), hence easier. It is therefore evident that a direct proton transfer path is less favorable than CPET (the TS must be higher than the highest point on the PES explored by the relaxed scan).

Along the quartet PES, there is still a Fe-C bond for C-H = 1.5 Å. The coordination geometry is octahedral, and the energy is much higher. An intramolecular proton transfer via the quartet surface can be discarded.

Cartesian coordinates and energies (gas-phase E in hartrees) of the partially optimized geometries along the relaxed scan.

$Fe(CHMeCOOMe)(acac)_2(MeOH)$ S = 5/2 (C-H = 2.0 A)
E = -1235.65057313
$\langle S^2 \rangle$ = 8.760

26	-0.224013000	-0.149614000	0.217421000
8	1.069267000	1.026714000	-0.744977000
6	0.920390000	2.259043000	-1.059761000
6	1.820814000	2.757094000	-2.161115000
8	-1.626426000	-1.251968000	1.128583000
6	-2.803455000	-1.558014000	0.748932000
6	-3.348773000	-1.224037000	-0.503306000
6	-2.650600000	-0.502992000	-1.484333000
8	-1.460338000	-0.059990000	-1.353272000
6	-3.627514000	-2.337487000	1.742724000
6	-3.308865000	-0.207851000	-2.808712000
8	-0.883503000	1.589807000	1.128053000
6	-0.823882000	2.755770000	0.626806000
6	-1.714477000	3.794583000	1.268324000
6	0.011414000	3.129964000	-0.446572000
1	-2.759289000	3.470137000	1.191619000
1	-3.099578000	-3.262370000	2.004338000
1	-3.722223000	-1.752860000	2.665671000
1	-1.609867000	4.783214000	0.812328000
1	-4.624138000	-2.583423000	1.365786000
1	-1.480311000	3.862970000	2.337528000
1	-0.019931000	4.160732000	-0.786013000
1	-4.361022000	-1.546683000	-0.725847000
1	1.628873000	2.173211000	-3.069373000
1	-4.329872000	-0.594914000	-2.868415000
1	1.679381000	3.820315000	-2.375054000
1	-3.321066000	0.876404000	-2.972371000
1	2.866884000	2.576392000	-1.886619000
1	-2.708102000	-0.645473000	-3.615216000
6	1.094954000	-1.943685000	-0.048627000
6	0.355080000	-2.692545000	-1.146419000
1	-0.696759000	-2.855511000	-0.886863000
1	0.402109000	-2.144469000	-2.093332000
1	0.807712000	-3.680835000	-1.325700000
1	1.017659000	-2.444413000	0.922414000
6	2.465754000	-1.597519000	-0.425417000
8	2.947944000	-1.542929000	-1.540392000
8	3.217252000	-1.300518000	0.699517000
6	4.544599000	-0.847021000	0.438575000
1	4.532125000	0.099583000	-0.113659000
1	5.016951000	-0.712449000	1.414740000
1	5.093564000	-1.587083000	-0.152858000
8	0.982036000	-0.315281000	2.047916000
1	1.619947000	-0.890481000	1.568514000
6	1.661775000	0.795220000	2.622908000
1	0.900859000	1.434324000	3.075405000
1	2.358086000	0.451415000	3.398722000
1	2.208909000	1.369604000	1.864666000

$Fe(CHMeCOOMe)(acac)_2(MeOH)$ S = 5/2 (C-H = 1.5 A)
E = -1235.64705748

$<S^2>$ = 8.775

26	-1.137523000	0.402385000	0.269693000
8	0.169555000	0.774977000	-1.152413000
6	0.802875000	1.867403000	-1.351573000
6	1.820486000	1.829289000	-2.460415000
8	-1.857946000	-1.434747000	0.518578000
6	-2.987533000	-1.939643000	0.179906000
6	-4.020016000	-1.241153000	-0.453740000
6	-3.926239000	0.117963000	-0.820959000
8	-2.909974000	0.847812000	-0.609235000
6	-3.163476000	-3.400253000	0.514056000
6	-5.088833000	0.784006000	-1.517697000
8	-0.962345000	2.249102000	0.989736000
6	-0.255282000	3.186773000	0.485033000
6	-0.396999000	4.533542000	1.153300000
6	0.617313000	3.048376000	-0.608203000
1	-1.437467000	4.869357000	1.063109000
1	-2.398514000	-3.987552000	-0.009171000
1	-3.000975000	-3.548940000	1.588385000
1	0.261458000	5.292631000	0.721738000
1	-4.152324000	-3.780156000	0.241864000
1	-0.185417000	4.436450000	2.224945000
1	1.188010000	3.921912000	-0.908571000
1	-4.936648000	-1.775409000	-0.683919000
1	1.352930000	1.443175000	-3.373645000
1	-5.936394000	0.108940000	-1.667204000
1	2.263286000	2.808805000	-2.662263000
1	-5.415188000	1.649584000	-0.928843000
1	2.610964000	1.123235000	-2.173106000
1	-4.755852000	1.165983000	-2.490344000
6	2.107000000	-1.856019000	0.723425000
6	1.360204000	-2.344939000	-0.473036000
1	0.316346000	-2.570359000	-0.220916000
1	1.379010000	-1.594619000	-1.268845000
1	1.811996000	-3.271349000	-0.865476000
1	2.128582000	-2.484419000	1.617246000
6	3.289310000	-1.020287000	0.525961000
8	3.639809000	-0.502475000	-0.525393000
8	3.978303000	-0.850544000	1.689459000
6	5.142488000	-0.032364000	1.576617000
1	4.884215000	0.971076000	1.219394000
1	5.570705000	0.018117000	2.580366000
1	5.862781000	-0.471637000	0.877255000
8	0.332815000	-0.250145000	1.657807000
1	1.091441000	-0.894528000	1.265803000
6	0.940244000	0.584348000	2.636664000
1	0.141022000	1.147108000	3.126704000
1	1.467738000	-0.024341000	3.382260000
1	1.645026000	1.298267000	2.189225000

Fe(CHMeCOOMe)(acac)$_2$(MeOH) S = 5/2 (C-H = 1.3 A)

E = -1235.67437939

$<S^2>$ = 8.762

26	-0.983943000	0.911325000	0.452452000
8	-0.609805000	2.128069000	-1.068253000
6	-0.531037000	3.402873000	-1.131570000
6	-0.165702000	3.958576000	-2.483763000
8	-2.595968000	0.230390000	1.389080000
6	-3.315424000	-0.800681000	1.158387000
6	-3.158021000	-1.653395000	0.057346000
6	-2.182630000	-1.451605000	-0.933506000
8	-1.342656000	-0.492855000	-0.933351000
6	-4.398639000	-1.067543000	2.172081000
6	-2.088569000	-2.400844000	-2.100979000
8	-1.231107000	2.581579000	1.544102000
6	-1.100359000	3.810099000	1.230997000
6	-1.341374000	4.797048000	2.344935000
6	-0.758712000	4.267958000	-0.052828000
1	-2.361048000	4.665954000	2.726614000
1	-3.941498000	-1.198591000	3.160258000
1	-5.056101000	-0.192401000	2.238008000
1	-1.204610000	5.834143000	2.026349000
1	-4.994633000	-1.951455000	1.928853000
1	-0.659618000	4.579096000	3.175605000
1	-0.671823000	5.337080000	-0.217783000
1	-3.830076000	-2.499689000	-0.041890000
1	-0.891863000	3.608291000	-3.226908000
1	-2.839884000	-3.194305000	-2.060615000
1	-0.133051000	5.051461000	-2.494680000
1	-2.204129000	-1.837506000	-3.034632000
1	0.812677000	3.563720000	-2.783182000
1	-1.088524000	-2.850016000	-2.120024000
6	2.269365000	-1.877581000	-0.731200000
6	2.475161000	-0.921424000	-1.894283000
1	1.512913000	-0.646768000	-2.337417000
1	2.973523000	-0.009241000	-1.551654000
1	3.103450000	-1.370873000	-2.674425000
1	1.830933000	-2.836612000	-1.024130000
6	3.502247000	-2.100193000	0.094210000
8	4.388508000	-1.287617000	0.279601000
8	3.507648000	-3.330334000	0.659198000
6	4.618006000	-3.588030000	1.521716000
1	4.629816000	-2.885786000	2.362757000
1	4.484809000	-4.610679000	1.881954000
1	5.564311000	-3.493138000	0.978196000
8	0.520785000	0.237893000	1.217509000
1	1.417338000	-1.344033000	0.093043000
6	1.607182000	0.878775000	1.827487000
1	1.577404000	1.970771000	1.688896000
1	1.609511000	0.672002000	2.909507000
1	2.551048000	0.500957000	1.406232000

Fe(CHMeCOOMe)(acac)$_2$(MeOH) S = 3/2 (C-H = 2.5 A)
E = -1235.66766868
<S^2> = 3.998

26	-0.064293000	-0.305398000	-0.270762000
8	-0.986182000	1.313218000	0.386311000
6	-0.452554000	2.476571000	0.464230000
6	-1.186549000	3.450777000	1.351487000
8	0.750783000	-1.923444000	-0.981666000
6	1.894944000	-2.427069000	-0.699365000
6	2.737963000	-2.005906000	0.334844000
6	2.438423000	-0.951479000	1.227296000
8	1.379460000	-0.258309000	1.193640000
6	2.314080000	-3.574771000	-1.585999000
6	3.423311000	-0.611386000	2.323394000
8	1.098005000	0.870684000	-1.407993000
6	1.373831000	2.085005000	-1.158850000
6	2.501913000	2.679981000	-1.968645000
6	0.693577000	2.889964000	-0.222889000
1	3.409273000	2.084283000	-1.813527000
1	1.555709000	-4.365801000	-1.542470000
1	2.356767000	-3.229683000	-2.626175000
1	2.704156000	3.722948000	-1.708877000
1	3.285788000	-3.990293000	-1.304204000
1	2.256971000	2.616282000	-3.035825000
1	1.028461000	3.913556000	-0.086976000
1	3.678412000	-2.532652000	0.465632000
1	-1.308687000	3.005899000	2.345688000
1	4.339269000	-1.207274000	2.271319000
1	-0.670581000	4.411070000	1.438507000
1	3.678513000	0.453112000	2.263326000
1	-2.193942000	3.623451000	0.952055000
1	2.947393000	-0.771295000	3.298713000
6	-1.428991000	-1.533986000	0.757329000
6	-0.737137000	-2.243810000	1.895880000
1	0.161124000	-2.764570000	1.552284000
1	-0.460783000	-1.537743000	2.683745000
1	-1.411297000	-2.991907000	2.342151000
1	-1.679504000	-2.183765000	-0.087505000
6	-2.577646000	-0.715204000	1.200053000
8	-2.813642000	-0.321218000	2.321416000
8	-3.433239000	-0.445143000	0.149413000
6	-4.529569000	0.415523000	0.470793000
1	-4.163757000	1.397760000	0.786954000
1	-5.124214000	0.500182000	-0.441692000
1	-5.127547000	-0.016799000	1.278851000
8	-1.606174000	-0.423355000	-1.853178000
1	-2.394626000	-0.428249000	-1.266256000
6	-1.716520000	0.634572000	-2.797403000
1	-0.792379000	0.642239000	-3.379747000
1	-2.566347000	0.463528000	-3.472522000
1	-1.828518000	1.609267000	-2.303319000

Fe(CHMeCOOMe)(acac)$_2$(MeOH) S = 3/2 (C-H = 2.0 A)
E = -1235.6543992
<S^2> = 3.958

26	0.017380000	-0.294581000	-0.297596000
8	-0.917185000	1.328061000	0.330658000
6	-0.381254000	2.490115000	0.403495000
6	-1.134941000	3.478502000	1.257774000
8	0.848041000	-1.910422000	-0.989574000
6	1.981237000	-2.416545000	-0.675590000
6	2.787921000	-2.004350000	0.392471000
6	2.454760000	-0.959091000	1.280320000
8	1.398872000	-0.260234000	1.206713000
6	2.430724000	-3.556321000	-1.557366000
6	3.391068000	-0.628894000	2.420120000
8	1.195032000	0.859080000	-1.420998000
6	1.471693000	2.075503000	-1.179132000
6	2.614791000	2.655093000	-1.978082000
6	0.781934000	2.891649000	-0.261818000
1	3.521260000	2.068707000	-1.785958000
1	1.671553000	-4.347633000	-1.547858000
1	2.509886000	-3.201259000	-2.591970000
1	2.805990000	3.705580000	-1.741439000
1	3.391967000	-3.974459000	-1.245203000
1	2.394408000	2.560163000	-3.048104000
1	1.118206000	3.915365000	-0.130668000
1	3.722388000	-2.533060000	0.554060000
1	-1.299444000	3.040495000	2.248743000
1	4.300662000	-1.236531000	2.411622000
1	-0.610766000	4.433064000	1.357421000
1	3.662846000	0.432118000	2.369963000
1	-2.124363000	3.660860000	0.819405000
1	2.867829000	-0.779634000	3.372328000
6	-1.447356000	-1.481638000	0.610193000
6	-0.782037000	-2.264447000	1.728660000
1	0.091957000	-2.812977000	1.366902000
1	-0.475058000	-1.596004000	2.537378000
1	-1.488166000	-2.995880000	2.151794000
1	-1.745658000	-2.149893000	-0.206907000
6	-2.567567000	-0.654191000	1.129437000
8	-2.720719000	-0.253424000	2.262619000
8	-3.478498000	-0.399163000	0.136267000
6	-4.568221000	0.446313000	0.511161000
1	-4.200819000	1.431681000	0.815927000
1	-5.204215000	0.528768000	-0.372972000
1	-5.125192000	0.004879000	1.343949000
8	-1.515579000	-0.508337000	-1.857380000
1	-2.124319000	-0.776035000	-1.134469000
6	-2.051201000	0.601692000	-2.566663000
1	-1.255118000	0.978200000	-3.214306000
1	-2.901078000	0.287508000	-3.187216000

1	-2.367077000	1.399825000	-1.883933000

Fe(CHMeCOOMe)(acac)$_2$(MeOH) S = 3/2 (C-H = 1.5 A)
E = -1235.62305684
<S^2> = 3.923

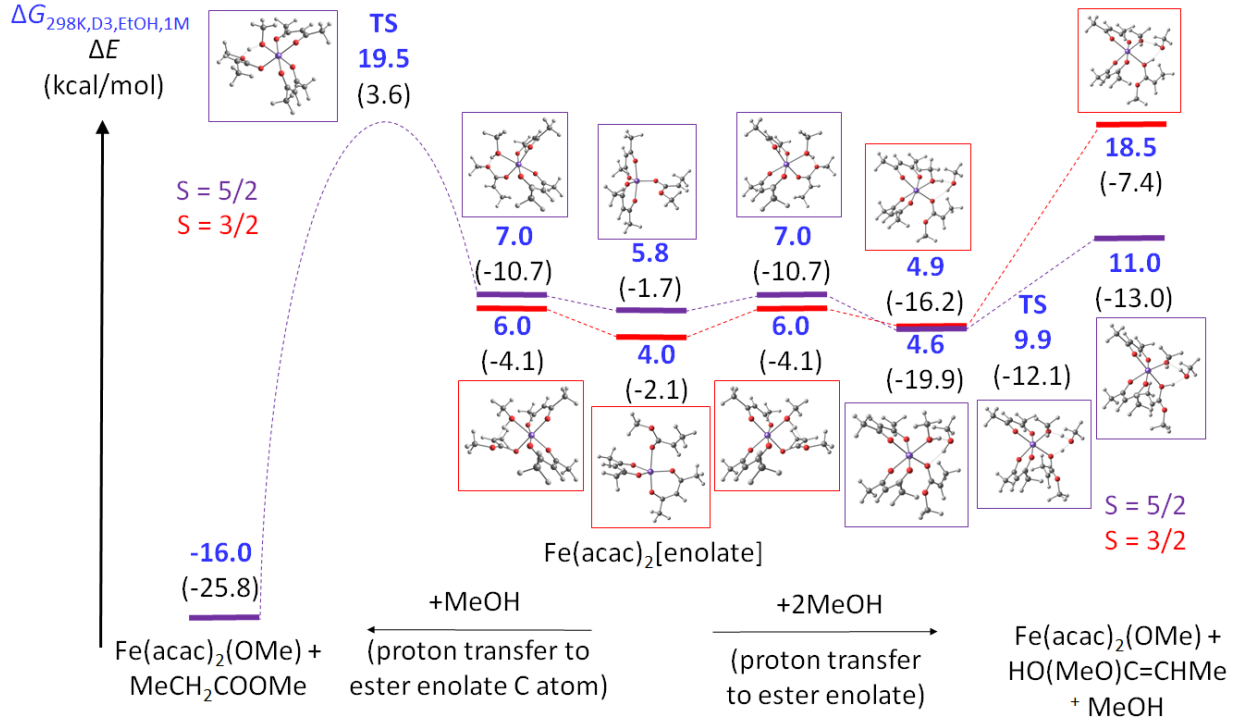
26	0.089826000	-0.266150000	-0.328980000
8	-0.840202000	1.345417000	0.276459000
6	-0.308808000	2.509363000	0.341817000
6	-1.101413000	3.513991000	1.138470000
8	0.920792000	-1.877007000	-0.995587000
6	2.061474000	-2.361482000	-0.675519000
6	2.839543000	-1.955313000	0.416189000
6	2.459260000	-0.947535000	1.325627000
8	1.388846000	-0.268919000	1.242146000
6	2.547810000	-3.472225000	-1.573507000
6	3.352032000	-0.633550000	2.503084000
8	1.340245000	0.837433000	-1.376191000
6	1.608032000	2.060342000	-1.147788000
6	2.785560000	2.615391000	-1.911083000
6	0.882491000	2.896979000	-0.281313000
1	3.675688000	2.016175000	-1.685982000
1	1.806128000	-4.279682000	-1.591768000
1	2.633578000	-3.093421000	-2.599021000
1	2.983744000	3.664588000	-1.675209000
1	3.513190000	-3.875436000	-1.254897000
1	2.596929000	2.516291000	-2.986784000
1	1.213727000	3.923253000	-0.159299000
1	3.781887000	-2.467417000	0.584490000
1	-1.318722000	3.092831000	2.126415000
1	4.273117000	-1.223516000	2.505919000
1	-0.579077000	4.468366000	1.247810000
1	3.603818000	0.433524000	2.492748000
1	-2.065450000	3.690455000	0.644823000
1	2.801782000	-0.822155000	3.433047000
6	-1.533022000	-1.430700000	0.428664000
6	-0.858760000	-2.262201000	1.524825000
1	-0.033091000	-2.854337000	1.122366000
1	-0.483677000	-1.614644000	2.320850000
1	-1.587187000	-2.954558000	1.972844000
1	-1.946416000	-2.154024000	-0.294075000
6	-2.611750000	-0.591412000	1.042021000
8	-2.630772000	-0.172477000	2.180491000
8	-3.624968000	-0.364169000	0.162071000
6	-4.687574000	0.444606000	0.670086000
1	-4.315653000	1.431179000	0.966328000
1	-5.410636000	0.535319000	-0.143673000
1	-5.151180000	-0.028556000	1.542430000
8	-1.437863000	-0.564571000	-1.896145000
1	-1.723638000	-0.957642000	-0.981968000
6	-2.286658000	0.449017000	-2.404789000
1	-1.818685000	0.835793000	-3.317073000
1	-3.273972000	0.040660000	-2.658315000
1	-2.414510000	1.273942000	-1.692709000

Fe(CHMeCOOMe)(acac)$_2$(MeOH) S = 3/2 (C-H = 1.3 A)
E = -1235.65863976
<S^2> = 3.800

26	0.358050000	-0.114056000	-0.712958000
8	-0.612680000	1.389488000	-0.098902000
6	-0.100353000	2.565354000	0.026302000
6	-0.904953000	3.485332000	0.908534000
8	1.207293000	-1.774430000	-1.123301000
6	2.273910000	-2.259112000	-0.623137000
6	2.938029000	-1.735268000	0.499388000
6	2.407166000	-0.673168000	1.232174000
8	1.347660000	-0.027655000	0.903075000
6	2.794237000	-3.497089000	-1.306409000
6	3.046192000	-0.225689000	2.518854000
8	1.664206000	1.080773000	-1.805345000
6	1.853092000	2.294256000	-1.499523000
6	3.007868000	2.982118000	-2.191349000
6	1.061618000	3.034119000	-0.586619000
1	3.928229000	2.416378000	-2.004766000
1	2.020165000	-4.273120000	-1.288954000
1	2.996652000	-3.268572000	-2.359304000
1	3.145053000	4.017575000	-1.866906000
1	3.702958000	-3.880714000	-0.835142000
1	2.835988000	2.963990000	-3.274349000
1	1.342947000	4.064827000	-0.393214000
1	3.835896000	-2.227539000	0.856906000
1	-1.014582000	3.026396000	1.898209000
1	3.949684000	-0.794330000	2.754577000
1	-0.445877000	4.472288000	1.010428000
1	3.292777000	0.840415000	2.450340000
1	-1.913486000	3.599554000	0.492392000
1	2.324203000	-0.336144000	3.336955000
6	-2.656534000	-2.135945000	0.446012000
6	-1.659643000	-3.102225000	1.057398000
1	-1.277585000	-3.793639000	0.298591000
1	-0.815212000	-2.561745000	1.497021000
1	-2.120529000	-3.692628000	1.859143000
1	-3.519565000	-2.623816000	-0.018036000
6	-3.122836000	-1.065886000	1.389425000
8	-2.595020000	-0.761140000	2.441019000
8	-4.226854000	-0.437855000	0.913043000
6	-4.705474000	0.629887000	1.732395000
1	-3.950696000	1.418454000	1.824337000
1	-5.597901000	1.013003000	1.231739000
1	-4.955657000	0.270864000	2.736894000
8	-0.868695000	-0.487853000	-1.940004000
1	-2.069741000	-1.494441000	-0.520501000
6	-1.609412000	0.489609000	-2.623821000

1	-0.956323000	1.251453000	-3.076019000	1	-2.333645000	0.989560000	-1.964459000
1	-2.159386000	-0.012890000	-3.433705000				

2.Q Intramolecular acrylate protonation (Part 2: to the O-bound enolate)



Observations:

1. The O-bound enolate Fe^{III} complex, like the C-bound one, is more stable in the quartet state, even though $[(acac)_2Fe^{III}(OMe)]$ prefers a sextet state (see section N). The possible reason is that the π delocalization of the donor O lone pair makes this donor "softer" than the O donor of methoxide. This idea seems to agree with the observation that the quartet-sextet gap is reduced upon partial disruption of this π delocalization by introduction of one and then two H-bonded MeOH molecules. The final conversion to the enol-bonded methoxide complex, where the enol O donor atom is much less longer involved in the π-delocalized system, reverts this energy trend to yield a more stable sextet state for the $[(acac)_2Fe^{III}(OMe)(HOC(OMe)=CHMe)]$ product at 11.0 kcal/mol relative to $[Fe^{II}(acac)_2]$ + MeOH + acrylate radical, whereas the corresponding quartet product is located at 18.5 kcal/mol.
2. The transition state for the intramolecular proton transfer in the sextet state is found at a barely higher gas-phase electronic energy (-12.1 kcal/mol) than that of the final product (-13.0 kcal/mol). However, the thermal and solvation correction actually yield a lower energy for the TS (9.9 kcal/mol) than for final product (11.0 kcal/mol). This phenomenon is related to the inevitable problem that the stationary points (local minima and transition states) can only be optimized on the electronic energy surface; they are only approximations of the real stationary points. We can only conclude that the proton transfer process occurs with a very small overbarrier relative to the thermodynamic energy difference between alcohol-enolate and alcoholate-enol.
3. Given the high energy of the final product of proton transfer, the methoxide-enol complex, in the quartet state, the transition state leading to this product, which would necessarily have even higher energy, was not optimized.

Cartesian coordinates and energies (gas-phase E and D3-corrected G in EtOH at 298 K, in hartrees) of the optimized geometries

[Fe(acac)$_2$(OC(OMe)=CHMe)(MeOH)] S = 3/2
E = -1235.65542687
$G_{298K,D3,EtOH,1M}$ = -1235.655427
$\langle S^2 \rangle$ = 4.638

26	0.296154000	0.073753000	0.075442000
8	-0.857697000	1.505879000	0.685648000
6	-0.754612000	2.766569000	0.450153000
6	-1.789600000	3.613784000	1.146591000
8	1.072252000	-1.467584000	-0.862793000
6	2.158805000	-2.095956000	-0.615284000
6	3.007273000	-1.853489000	0.471930000
6	2.790575000	-0.849754000	1.439409000
8	1.791905000	-0.067053000	1.458850000
6	2.507047000	-3.175288000	-1.611711000
6	3.801573000	-0.660758000	2.547050000
8	1.371188000	1.392946000	-0.972947000
6	1.225525000	2.647034000	-1.028717000
6	2.232968000	3.393752000	-1.871334000
6	0.204138000	3.366250000	-0.365232000
1	3.239806000	3.203927000	-1.480670000
1	1.685905000	-3.900268000	-1.665750000
1	2.605828000	-2.726651000	-2.607640000
1	2.051477000	4.472141000	-1.890140000
1	3.433929000	-3.698468000	-1.359871000
1	2.207164000	3.003482000	-2.895558000
1	0.175468000	4.445026000	-0.481886000
1	3.899888000	-2.464523000	0.564265000
1	-1.671273000	3.506350000	2.231893000
1	4.630448000	-1.372089000	2.488461000
1	-1.713854000	4.671954000	0.881244000
1	4.199763000	0.360118000	2.500834000
1	-2.791289000	3.243898000	0.897917000
1	3.303029000	-0.766192000	3.518062000
8	-0.851171000	-1.244955000	1.266461000
6	-2.133268000	-1.539753000	0.595809000
6	-3.392040000	-1.046106000	0.958861000
8	-1.989272000	-2.408692000	-0.465835000
6	-3.225406000	-2.859897000	-1.030291000
1	-3.810267000	-2.026164000	-1.434205000
1	-2.951172000	-3.556568000	-1.826017000
1	-3.831253000	-3.367891000	-0.272322000
8	-1.022272000	-0.116682000	-1.828998000
1	-1.215147000	-1.066438000	-1.741197000
6	-2.234087000	0.600778000	-2.035087000
1	-1.965982000	1.658179000	-2.110238000
1	-2.713328000	0.296316000	-2.976640000
1	-2.939639000	0.472667000	-1.203380000
1	-4.274165000	-1.374626000	0.429400000
6	-3.518843000	-0.034650000	2.113191000
1	-4.534927000	-0.023037000	2.523734000
1	-2.834105000	-0.277655000	2.933672000
1	-3.286062000	0.982961000	1.779438000

[Fe(acac)$_2$(OC(OMe)=CHMe)(MeOH)] S = 5/2
E = -1235.66591872
$G_{298K,D3,EtOH,1M}$ = -1235.432612
$\langle S^2 \rangle$ = 8.770

26	0.158902000	-0.026367000	-0.282937000
8	-0.305927000	1.639440000	0.830163000
6	0.503791000	2.498425000	1.306002000
6	-0.049478000	3.381251000	2.400458000
8	0.769272000	-1.566918000	-1.411204000
6	1.445550000	-2.591054000	-1.080644000
6	1.929105000	-2.849617000	0.215270000
6	1.720244000	-1.996223000	1.308451000
8	1.079780000	-0.893273000	1.266087000
6	1.723504000	-3.576554000	-2.190443000
6	2.276308000	-2.365848000	2.662802000
8	1.832461000	1.010249000	-0.811995000
6	2.413713000	1.941258000	-0.164503000
6	3.827874000	2.251830000	-0.596476000
6	1.832312000	2.677003000	0.880825000
1	4.451690000	1.361518000	-0.449692000
1	0.771743000	-3.932683000	-2.602840000
1	2.252700000	-3.064503000	-3.002986000
1	4.264700000	3.090585000	-0.046744000
1	2.315098000	-4.433729000	-1.856424000
1	3.840844000	2.475235000	-1.670022000
1	2.425994000	3.450753000	1.358194000
1	2.495472000	-3.761398000	0.378226000
1	-0.327438000	2.754536000	3.256797000
1	2.825708000	-3.311484000	2.650420000
1	0.660971000	4.144838000	2.730453000
1	2.939983000	-1.565765000	3.012265000
1	-0.967907000	3.865950000	2.048555000
1	1.452875000	-2.435620000	3.383875000
8	-1.578892000	-0.768423000	0.105660000
6	-2.830039000	-0.480846000	0.136064000
6	-3.773319000	-1.171243000	0.849559000
8	-3.145923000	0.612114000	-0.661398000
6	-4.498685000	1.021626000	-0.759474000
1	-4.889386000	1.329470000	0.219699000
1	-4.514159000	1.878252000	-1.438746000
1	-5.130619000	0.220749000	-1.167735000

8	-0.814640000	0.894031000	-2.031122000
1	-1.743715000	0.898311000	-1.712699000
6	-0.451587000	2.197364000	-2.474212000
1	0.590575000	2.147030000	-2.795525000
1	-1.077294000	2.500297000	-3.324710000
1	-0.538761000	2.936448000	-1.666844000
1	-4.811630000	-0.854430000	0.818411000
6	-3.421188000	-2.345817000	1.699565000
1	-3.989560000	-3.241175000	1.406285000
1	-2.354206000	-2.572290000	1.619252000
1	-3.652821000	-2.162455000	2.759903000

Intramolecular proton transfer to C, TS S = 5/2
E = -1235.64322319
$G_{298K,D3,EtOH,1M}$ = -1235.412578
$\langle S^2 \rangle$ = 8.759

26	-0.138803000	0.052729000	-0.277127000
8	-0.393664000	-1.928939000	0.348534000
6	-1.543738000	-2.423944000	0.535034000
6	-1.612493000	-3.632709000	1.439752000
8	0.031162000	2.010239000	-0.883522000
6	-0.192178000	3.023619000	-0.154355000
6	-0.772639000	2.973596000	1.129468000
6	-1.229626000	1.795418000	1.723967000
8	-1.173064000	0.624761000	1.206930000
6	0.194437000	4.361142000	-0.740487000
6	-1.883318000	1.836694000	3.082615000
8	-1.747932000	-0.196911000	-1.352576000
6	-2.762055000	-0.892544000	-0.984809000
6	-4.056288000	-0.527090000	-1.669593000
6	-2.732033000	-1.938085000	-0.059009000
1	-4.319938000	0.506943000	-1.415235000
1	1.279962000	4.384722000	-0.897305000
1	-0.274304000	4.473157000	-1.724987000
1	-4.880182000	-1.188901000	-1.387653000
1	-0.091793000	5.202300000	-0.102621000
1	-3.917944000	-0.563076000	-2.756707000
1	-3.663092000	-2.452514000	0.158819000
1	-0.911227000	3.903713000	1.671204000
1	-1.293107000	-3.338324000	2.447069000
1	-1.986860000	2.856864000	3.462315000
1	-2.614344000	-4.068795000	1.493713000
1	-2.871371000	1.365093000	3.028986000
1	-0.902625000	-4.390694000	1.088746000
1	-1.281193000	1.248807000	3.786030000
8	1.501943000	0.232948000	0.877045000
6	2.564087000	-0.397223000	0.574235000
6	3.297576000	-0.163229000	-0.614886000
8	2.843055000	-1.415289000	1.417906000
6	4.048190000	-2.148914000	1.258009000
1	4.923958000	-1.487981000	1.218984000
1	4.121291000	-2.797749000	2.134696000
1	4.022976000	-2.771605000	0.353566000
8	0.986864000	-0.564160000	-1.682711000
1	2.095880000	-0.590325000	-1.332096000
6	0.607363000	-1.522220000	-2.655321000
1	-0.342432000	-1.211641000	-3.100904000
1	1.376661000	-1.557648000	-3.437997000
1	0.490440000	-2.518611000	-2.207774000
1	4.174000000	-0.787685000	-0.783082000
6	3.383196000	1.239818000	-1.185466000
1	3.674631000	1.208100000	-2.242150000
1	2.417424000	1.750102000	-1.121520000
1	4.132279000	1.847649000	-0.656549000

[Fe(acac)$_2$(OC(OMe)=CHMe)(MeOH)···MeOH]
S = 3/2
E = -1351.28449409
$G_{298K,D3,EtOH,1M}$ = -1351.022758
$\langle S^2 \rangle$ = 4.489

26	0.298970000	-0.009367000	0.277550000
8	0.885335000	-1.478156000	-0.828675000
6	2.027678000	-1.690716000	-1.522841000
6	2.055896000	-2.747965000	-2.602200000
8	-0.002180000	1.531752000	1.450520000
6	-0.008793000	2.799082000	1.185997000
6	0.126229000	3.329400000	-0.108289000
6	0.253275000	2.541058000	-1.264280000
8	0.284052000	1.283929000	-1.300032000
6	-0.175807000	3.733573000	2.360647000
6	0.357451000	3.211324000	-2.614485000
8	2.235115000	0.319867000	0.529240000
6	3.277841000	0.001556000	-0.224477000
6	4.600513000	0.681576000	0.046004000
6	3.185775000	-0.941686000	-1.263563000
1	4.474240000	1.766694000	-0.050743000
1	-1.107656000	3.489941000	2.884825000
1	0.642686000	3.568156000	3.071693000
1	5.394468000	0.349338000	-0.629210000
1	-0.189303000	4.787121000	2.066527000
1	4.904069000	0.487204000	1.081882000
1	4.071589000	-1.142039000	-1.858639000
1	0.113595000	4.409068000	-0.223594000
1	1.254361000	-2.547200000	-3.322940000
1	0.327878000	4.302833000	-2.548259000
1	3.013998000	-2.789750000	-3.128334000
1	1.291789000	2.904068000	-3.099619000
1	1.850368000	-3.730473000	-2.158957000
1	-0.462919000	2.865584000	-3.254962000
8	-1.654986000	-0.719752000	-0.082324000
6	-2.774154000	-0.108570000	-0.327408000
6	-3.867632000	-0.732861000	-0.878558000
8	-2.748385000	1.207250000	0.012972000
6	-3.871522000	2.008317000	-0.296039000

1	-4.760616000	1.697048000	0.271561000
1	-3.600529000	3.028110000	-0.011477000
1	-4.103715000	1.978956000	-1.370372000
8	0.320308000	-1.331317000	2.183958000
1	-0.284550000	-2.118191000	2.065105000
6	1.458960000	-1.658815000	2.963768000
1	2.097725000	-0.773546000	2.997145000
1	1.158183000	-1.929205000	3.985171000
1	2.030890000	-2.488431000	2.523527000
1	-4.786213000	-0.169741000	-1.012852000
6	-3.858564000	-2.164001000	-1.304048000
1	-2.835411000	-2.520923000	-1.463204000
1	-4.335793000	-2.826005000	-0.563155000
1	-4.410974000	-2.298009000	-2.243736000
1	-1.673993000	-2.402668000	0.826843000
8	-1.430376000	-3.124296000	1.452766000
6	-0.900022000	-4.205100000	0.695437000
1	-1.688052000	-4.707834000	0.116091000
1	-0.110821000	-3.866736000	0.010593000
1	-0.482331000	-4.931066000	1.401395000

[Fe(acac)$_2$(OMe)(HO(MeO)C=CHMe)···MeOH]
S = 3/2
E = -1351.27045376
$G_{298K,D3,EtOH,1M}$ = -1351.001117
$\langle S^2 \rangle$ = 3.808

26	0.516506000	-0.047289000	0.363256000
8	0.928299000	-1.555507000	-0.765820000
6	2.033471000	-1.814272000	-1.353900000
6	1.969553000	-2.965709000	-2.328428000
8	-0.019773000	1.419835000	1.461673000
6	-0.089906000	2.647227000	1.104767000
6	0.104879000	3.126235000	-0.193848000
6	0.299142000	2.278375000	-1.295578000
8	0.385544000	1.009448000	-1.237984000
6	-0.437261000	3.600130000	2.218367000
6	0.392563000	2.857614000	-2.684450000
8	2.522997000	0.406576000	0.491278000
6	3.435081000	-0.092662000	-0.236228000
6	4.814081000	0.504339000	-0.068837000
6	3.247388000	-1.145228000	-1.154091000
1	4.765947000	1.584805000	-0.249152000
1	-1.425190000	3.337735000	2.615820000
1	0.281912000	3.481466000	3.037059000
1	5.553679000	0.058086000	-0.739909000
1	-0.445712000	4.642756000	1.889379000
1	5.142913000	0.367297000	0.968545000
1	4.107410000	-1.484189000	-1.723251000
1	0.031852000	4.194807000	-0.368017000
1	1.185880000	-2.770388000	-3.069713000
1	0.329646000	3.949223000	-2.688103000
1	2.921273000	-3.131406000	-2.840986000
1	1.338356000	2.545824000	-3.142819000
1	1.688198000	-3.881314000	-1.793957000
1	-0.414482000	2.445491000	-3.301620000
8	-1.733445000	-0.687324000	0.009507000
6	-2.867512000	-0.083317000	-0.400069000
6	-3.971060000	-0.716837000	-0.839914000
8	-2.693371000	1.261753000	-0.316644000
6	-3.699865000	2.075178000	-0.880130000
1	-4.642024000	2.002192000	-0.316663000
1	-3.326724000	3.101464000	-0.826771000
1	-3.893121000	1.802417000	-1.927997000
8	0.504968000	-1.149729000	1.822805000
1	-0.737397000	-2.162307000	1.836413000
6	1.066243000	-0.695068000	3.028459000
1	0.495125000	0.141371000	3.457762000
1	1.064618000	-1.528861000	3.746974000
1	2.104623000	-0.365437000	2.877750000
1	-4.847549000	-0.122217000	-1.080021000
6	-4.077479000	-2.204127000	-0.995362000
1	-3.087472000	-2.671649000	-1.047813000
1	-4.625181000	-2.681980000	-0.168700000
1	-4.608994000	-2.463736000	-1.920781000
1	-1.883019000	-1.532229000	0.554082000
8	-1.573471000	-2.664110000	1.590835000
6	-1.184662000	-3.907749000	1.028388000
1	-2.085846000	-4.411408000	0.661816000
1	-0.483818000	-3.775797000	0.191666000
1	-0.715989000	-4.554819000	1.784273000

[Fe(acac)$_2$(OC(OMe)=CHMe)(MeOH)···MeOH]
S = 5/2
E = -1351.29035085
$G_{298K,D3,EtOH,1M}$ = -1351.023308
$\langle S^2 \rangle$ = 8.771

26	-0.266472000	0.016658000	-0.301463000
8	-1.119406000	-1.487842000	0.802808000
6	-2.239815000	-1.476335000	1.411331000
6	-2.431570000	-2.561445000	2.445426000
8	0.274109000	1.573653000	-1.426432000
6	0.444086000	2.788262000	-1.089307000
6	0.365102000	3.280154000	0.224636000
6	0.111908000	2.471872000	1.345579000
8	-0.096685000	1.216875000	1.309640000
6	0.757542000	3.736276000	-2.222438000
6	0.082174000	3.095662000	2.721502000
8	-2.213562000	0.649785000	-0.568020000
6	-3.221795000	0.424947000	0.173073000
6	-4.432329000	1.293899000	-0.081054000
6	-3.277934000	-0.562625000	1.172789000
1	-4.157200000	2.345869000	0.061952000
1	1.653969000	3.385567000	-2.747684000
1	-0.065298000	3.715745000	-2.947277000

1	-5.274920000	1.049528000	0.572386000
1	0.913650000	4.764938000	-1.884594000
1	-4.744520000	1.185518000	-1.126883000
1	-4.191854000	-0.660443000	1.750807000
1	0.526680000	4.341919000	0.384907000
1	-1.620729000	-2.503954000	3.181266000
1	0.264894000	4.174016000	2.701056000
1	-3.393884000	-2.489504000	2.960500000
1	-0.893075000	2.903274000	3.184779000
1	-2.358672000	-3.544569000	1.963574000
1	0.836536000	2.613050000	3.354571000
8	1.451980000	-0.913990000	0.025328000
6	2.641747000	-0.475988000	0.305964000
6	3.628942000	-1.268891000	0.840710000
8	2.805106000	0.842987000	0.020443000
6	4.024366000	1.465737000	0.372892000
1	4.869665000	1.055839000	-0.198947000
1	3.902751000	2.523988000	0.128549000
1	4.234078000	1.361240000	1.447168000
8	-0.430162000	-1.118184000	-2.111646000
1	0.057018000	-1.986182000	-2.020083000
6	-1.591596000	-1.251445000	-2.914890000
1	-2.099884000	-0.284763000	-2.917271000
1	-1.316280000	-1.520316000	-3.943846000
1	-2.280315000	-2.009619000	-2.514870000
1	4.615055000	-0.845899000	1.006805000
6	3.413712000	-2.700471000	1.206140000
1	2.348470000	-2.916528000	1.340849000
1	3.804836000	-3.392710000	0.442761000
1	3.927865000	-2.948003000	2.144491000
1	1.374421000	-2.511822000	-0.781970000
8	1.041799000	-3.166602000	-1.439618000
6	0.354416000	-4.191774000	-0.732874000
1	1.055746000	-4.822730000	-0.167716000
1	-0.389951000	-3.773754000	-0.041848000
1	-0.149963000	-4.823250000	-1.472272000

Intramolecular proton transfer to O, TS S = 5/2
E = -1351.2779576
$G_{298K,D3,EtOH,1M}$ = -1351.015296
$\langle S^2 \rangle$ = 8.758

26	0.485983000	-0.052784000	-0.391632000
8	1.596070000	1.201083000	0.742818000
6	2.752450000	1.017615000	1.243947000
6	3.227524000	2.090467000	2.193270000
8	-0.592942000	-1.444312000	-1.378914000
6	-1.361157000	-2.359963000	-0.938138000
6	-1.530597000	-2.676831000	0.418650000
6	-0.861396000	-2.003443000	1.453527000
8	-0.034350000	-1.051052000	1.278814000
6	-2.120722000	-3.130744000	-1.989120000
6	-1.113725000	-2.393809000	2.888155000
8	2.161386000	-1.164800000	-0.597446000
6	3.257112000	-1.091775000	0.049851000
6	4.248894000	-2.194663000	-0.230430000
6	3.585781000	-0.078317000	0.963833000
1	3.792910000	-3.160481000	0.018797000
1	-2.786538000	-2.441819000	-2.523113000
1	-1.415027000	-3.532875000	-2.725391000
1	5.179071000	-2.078742000	0.332844000
1	-2.712262000	-3.948617000	-1.567868000
1	4.474907000	-2.214855000	-1.303258000
1	4.554687000	-0.122663000	1.451210000
1	-2.208158000	-3.483682000	0.679933000
1	2.522615000	2.168383000	3.029701000
1	-1.727940000	-3.294380000	2.979135000
1	4.230588000	1.895818000	2.582976000
1	-0.156932000	-2.547932000	3.399572000
1	3.221594000	3.058437000	1.677943000
1	-1.621224000	-1.561289000	3.391043000
8	-1.123390000	1.274200000	-0.053500000
6	-2.289588000	1.046848000	0.572952000
6	-2.493785000	1.286806000	1.883648000
8	-3.213598000	0.569190000	-0.312084000
6	-4.514412000	0.332984000	0.182270000
1	-4.957987000	1.248577000	0.601407000
1	-5.112377000	-0.003534000	-0.669138000
1	-4.513109000	-0.447583000	0.957801000
8	0.774563000	0.886338000	-2.083654000
1	-0.061506000	1.896299000	-2.187747000
6	1.105058000	0.217660000	-3.279915000
1	0.308229000	-0.479366000	-3.578754000
1	1.262852000	0.947533000	-4.087719000
1	2.029268000	-0.360105000	-3.143503000
1	-3.469783000	1.072067000	2.310924000
6	-1.440140000	1.849803000	2.786964000
1	-0.503923000	2.000125000	2.241173000
1	-1.751233000	2.813391000	3.218819000
1	-1.227738000	1.180280000	3.633387000
1	-1.151652000	2.030909000	-0.987797000
8	-0.838932000	2.659395000	-1.966253000
6	-0.205299000	3.872143000	-1.564832000
1	-0.970951000	4.571586000	-1.211549000
1	0.522253000	3.697813000	-0.760251000
1	0.307382000	4.320068000	-2.424190000

[Fe(acac)$_2$(OMe)(HO(MeO)C=CHMe)···MeOH]
S = 5/2
E = -1351.28013368
$G_{298K,D3,EtOH,1M}$ = -1351.012992
$\langle S^2 \rangle$ = 8.758

26	-0.527105000	0.058744000	-0.443500000
8	-1.534885000	-1.235673000	0.743357000
6	-2.690719000	-1.096269000	1.257820000

6	-3.105296000	-2.174837000	2.229128000
8	0.559651000	1.461310000	-1.411357000
6	1.266854000	2.427245000	-0.973510000
6	1.395776000	2.773414000	0.379395000
6	0.748765000	2.075238000	1.413854000
8	-0.013445000	1.071935000	1.241028000
6	1.996746000	3.224420000	-2.026268000
6	0.951640000	2.506288000	2.845665000
8	-2.234337000	1.101796000	-0.618398000
6	-3.314274000	0.977448000	0.049560000
6	-4.363680000	2.027058000	-0.224289000
6	-3.578050000	-0.042493000	0.976097000
1	-3.951052000	3.017206000	0.003973000
1	2.688000000	2.561725000	-2.560967000
1	1.275265000	3.597773000	-2.762667000
1	-5.276317000	1.872859000	0.358075000
1	2.555535000	4.066251000	-1.607316000
1	-4.610332000	2.021655000	-1.292759000
1	-4.540926000	-0.038840000	1.477182000
1	2.021882000	3.621355000	0.639150000
1	-2.392661000	-2.201589000	3.062311000
1	1.521107000	3.436393000	2.930838000
1	-4.114441000	-2.024726000	2.622795000
1	-0.023049000	2.627277000	3.331806000
1	-3.052803000	-3.150196000	1.730839000
1	1.484091000	1.710091000	3.380299000
8	1.206639000	-1.264406000	0.005558000
6	2.386564000	-0.984133000	0.614123000
6	2.572347000	-1.127496000	1.937383000
8	3.294207000	-0.558133000	-0.303783000
6	4.600093000	-0.291551000	0.165617000
1	5.040208000	-1.176866000	0.647753000
1	5.192815000	-0.019841000	-0.711599000
1	4.603257000	0.543405000	0.881696000
8	-0.729439000	-0.886719000	-2.071744000
1	0.236570000	-2.119304000	-2.181453000
6	-1.062828000	-0.269279000	-3.288586000
1	-2.039014000	0.233888000	-3.213156000
1	-0.313213000	0.488314000	-3.564565000
1	-1.118416000	-1.020110000	-4.091582000
1	3.534883000	-0.849980000	2.359455000
6	1.522722000	-1.655771000	2.866064000
1	0.594136000	-1.861382000	2.325991000
1	1.854646000	-2.581389000	3.359845000
1	1.290628000	-0.937501000	3.665196000
1	1.296554000	-1.931272000	-0.785492000
8	0.944789000	-2.804027000	-1.943770000
6	0.281456000	-3.972897000	-1.478144000
1	1.041547000	-4.671469000	-1.111960000
1	-0.417598000	-3.747300000	-0.659923000
1	-0.270705000	-4.460746000	-2.293328000

2.R Bond strength calculations (all energies are in hartrees)

R1. Fe-H bond in $FeH(acac)_2$

H atom	$Fe(acac)_2$ (S = 2)	$FeH(acac)_2$ (S = 3/2)
E = -0.499935773744	E = -813.288650469	E = -813.822212133
E-D3 = -0.499589719405	E-D3 = -813.345258118	E-D3 = -813.875909871
H = -0.497575	H = -813.045524	H = -813.570726
$G_{298K, gas,1atm}$ = -0.510590	$G_{298K, gas,1atm}$ = -813.112200	$G_{298K, gas,1atm}$ = -813.640705
$G_{298K,D3,EtOH,1M}$ = -0.507136	$G_{298K,D3,EtOH,1M}$ = -813.165701	$G_{298K,D3,EtOH,1M}$ = -813.691295

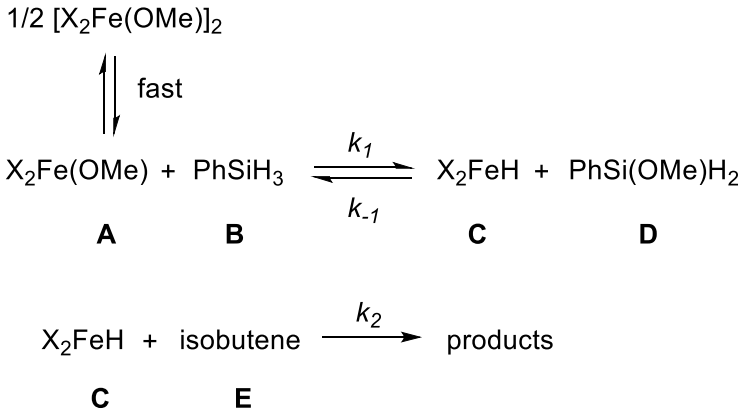
R2. C-H bond in $MeCH_2(COOMe)$

H atom	$MeC\dot{H}(COOMe)$	$MeCH_2COOMe$
E = -0.499935773744	E = -306.750548945	E = -307.405250263
E-D3 = -0.499589719405	E-D3 = -306.765994664	E-D3 = -307.422234539
H = -0.497575	H = -306.637742	H = -307.278578
$G_{298K, gas,1atm}$ = -0.510590	$G_{298K, gas,1atm}$ = -306.678841	$G_{298K, gas,1atm}$ = -307.319028
$G_{298K,D3,EtOH,1M}$ = -0.507136	$G_{298K,D3,EtOH,1M}$ = -306.691179	$G_{298K,D3,EtOH,1M}$ = -307.332905

R3. O-H bond in $Fe(acac)_2(EtOH)_2$

H atom	$Fe(acac)_2(OEt)(EtOH)$ S = 5/2	$Fe(acac)_2(EtOH)_2$ S = 2
E = -0.499935773744		
E-D3 = -0.499589719405	E = -1122.46004922	E = -1123.08835008
H = -0.497575	E-D3 = -1122.54590513	E-D3 = -1123.17824487
$G_{298K, gas,1atm}$ = -0.510590	H = -1122.054198	H = -1122.669822
$G_{298K,D3,EtOH,1M}$ = -0.507136	$G_{298K, gas,1atm}$ = -1122.149460	$G_{298K, gas,1atm}$ = -1122.768300
	$G_{298K,D3,EtOH,1M}$ = -1122.232209	$G_{298K,D3,EtOH,1M}$ = -1122.855087

2.S Estimation of the expected steady-state concentration of the hydride complex



This yields the steady-state concentration of **C** as:

$$[C] = \frac{k_1[A][B]}{(k_{-1}[D] + k_2[E])}$$

The experimental conditions are $[Fe]_{total} = 0.02$ M, $[B]_{initial} = 0.4$ M, $[E]_{initial} = 0.2$ M.

The computational barriers and rates (at RT) are:

$\Delta G^{\ddagger}_1 = 24.9$ kcal/mol → $k_1 = 3.53 \cdot 10^{-6}$ s^{-1} M^{-1};

$\Delta G^{\ddagger}_{-1} = 16.3$ kcal/mol → $k_{-1} = 7.07$ s^{-1} M^{-1};

$\Delta G^{\ddagger}_2 = 4.7$ kcal/mol → $k_2 = 2.2 \cdot 10^{9}$ s^{-1} M^{-1}.

Since k_{-1} is much smaller than k_2, and [D] is smaller than [E], this reduces to

$$[C] = \frac{k_1[A][B]}{k_2[E]}$$

Using the above numbers, and [A] < 0.02 M, we calculate an upper limit for the concentration of the hydride complex as **[C] < 6 • 10^{-17} M**. Even though this value is rough (it is calculated for room temperature and using estimated numbers and is therefore only a rough estimation), it is evident that the steady-state concentration of the hydride is expected to be undetectably small.

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