Peripheral mechanism of a carbonyl hydrosilylation catalysed by an SiNSi iron pincer complex

Toni T. Metsänen, Daniel Gallego, Tibor Szilvási, Matthias Driess,* and Martin Oestreich*

Institut für Chemie, Technische Universität Berlin,
Straße des 17. Juni 115, 10623 Berlin, Germany
and
Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4, 1111 Budapest, Hungary
martin.oestreich@tu-berlin.de;
matthias.driess@tu-berlin.de

Electronic Supplementary Information

Table of Contents

1 General Information S4
1.1 Experimental Details S4
1.2 Single-Crystal X-ray Structure Determinations S4
1.3 Computational Details S5
2 General Procedure for the Hydrosilylation of Ketones with Iron(0) Complex 2 (GP 1) S6
2.1 Optimisation with 4-Methoxyacetophenone (3a) S6
2.2 Substrate Scope S7
3 Identification of the Active Iron(II) Complex 7 S8
3.1 General Procedure for the Stoichiometric Reaction of Iron(0) Complex 2 with Hydrosilanes 4 S8
3.1.1 Si = (EtO)₃Si (7a) S8
3.1.2 Si = Me₂PhSi (7b) S9
3.1.3 Si = MePh₂Si (7c) S9
3.2 Crystallographic Data for 7b S10
4 Mechanistic Experiments S14
4.1 Kinetics: Iron(0) complex 2 vs. Iron(II) complex 7a S14
4.1.1 Iron(0) complex 2 S14
4.1.2 Iron(II) complex 7a S14
4.2 Scrambling at the Si–H Bond  
4.2.1 Hydrosilane Si–D/Fe–H Scrambling Using \( \text{Me}_2\text{PhSi–D} \) (4b–d)  
4.2.2 Deuteration Studies with \( \text{Me}_2\text{PhSi–D} \) (4b–d)  
4.3 Scrambling at the C–H Bond  
4.3.1 Scrambling Experiment with Deuterated Silyl Ether 8eb–d  
4.3.2 Racemisation Experiment with Enantiopure Silyl Ether (S)-8eb  
4.4 Phosphine Scrambling  
4.4.1 Synthesis of Trimethylphosphine-\( \text{d}_9 \) (6–d)  
4.4.2 Scrambling between Complex 7b and Trimethylphosphine-\( \text{d}_9 \) (6–d)  
4.5 Phosphine Dissociation  
4.5.1 Phosphine Dissociation in the Presence of Acetophenone (3e)  
4.6 Silyl Scrambling  
4.7 Silane Cross-over Experiment  
4.8 Hydrosilylation with Silicon-Stereogenic Hydrosilane  
4.8.1 Catalytic Reaction between Acetophenone (3e) with Enantioenriched Acyclic Hydrosilane (H–\( \text{Si}^{-}(\text{S})\text{-4d} \)  
4.8.2 Reductive Si–O Bond Cleavage of Silyl Ether 8ed  
4.9 Competition Experiment  
5 Cartesian Geometries at \( \omega \)B97X-D/6-31G(d)[Fe:cc-pVTZ] in Ångstrom [Å]  
5.1 Iron(II) Complex 7a  
5.2 Acetone (3o)  
5.3 Triethoxysilane (4a)  
5.4 Silyl Ether 8oa  
5.5 Tetrahydrofuran  
5.6 Benzene  
5.7 Transition State 9a\(^\ddagger\)  
5.8 Transition State 10oa\(^\ddagger\)  
5.9 Transition State 13a\(^\ddagger\)  
5.10 Intermediate \( \text{cis-14a} \)  
5.11 Transition State 15a\(^\ddagger\)  
5.12 Intermediate 11a  
5.13 Transition State 16a\(^\ddagger\)  
5.14 Intermediate 17a  
5.15 Transition State 18oa\(^\ddagger\)  
5.16 Intermediate 19oa  
5.17 Transition State 20oa\(^\ddagger\)  
5.18 Transition State 21a\(^\ddagger\)
5.19 Intermediate $trans$-14a  S90
5.20 Transition State 22oa‡  S94
5.21 Intermediate 23oa  S98
5.22 Transition State 24oa‡  S102
5.23 Intermediate 25oa  S107
5.24 Transition State 26oa‡  S111
5.25 Transition State 27oa‡  S116
5.26 Intermediate 28  S120
5.27 Intermediate 29  S124
5.28 Transition State 30oa‡  S128
5.29 Intermediate 31oa  S133
5.30 Transition State 32oa‡  S137
6 NMR Spectra  S143
7 Gibbs Free Energy Profile  S162
8 References  S163
1 General Information

1.1 Experimental Details

All experiments and manipulations were conducted under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun glovebox with an atmosphere of purified nitrogen or argon. Solvents were dried by standard methods and freshly distilled prior use. C₆D₆ and toluene-d₈ were dried over sodium and benzophenone, distilled and stored on 4 Å molecular sieves prior to use. Liquid ketones were degassed and stored on 4 Å molecular sieves prior to use. Triethoxysilane 4a, dimethylphenylsilane 4b, methylidiphenylsilane 4c, triethylsilane 4e, phenylsilane 4f, and diphenylsilane 4g were obtained from commercial sources and degassed, distilled, and stored under nitrogen atmosphere. PMHS 4h was obtained from commercial sources and used without further purification. Iron(0) complex 2, enantiomerically enriched hydrosilane (S-Si)-4d, silyl ether (S)-8eb, and tris(pentafluorophenyl)borane were prepared according to reported procedures. ¹H, ¹³C, ²⁹Si, and ³¹P NMR spectra were recorded on Bruker AV700, AV500, or AV400 instruments. The NMR chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as internal standard (¹H, C₆D₅H, 7.15 ppm; toluene-d₈, 2.09 ppm; CHCl₃, 7.26 ppm; ¹³C, C₆D₆, 128.0 ppm; toluene-d₈, 20.4 ppm; CDCl₃, 77.16 ppm) or an external standard (³¹P, 85% H₃PO₄, 0.0 ppm; ²⁹Si, TMS, 0.0 ppm). All signals were unambiguously assigned by a combination of 2D NMR ¹H−¹H COSY, HSQC, HMBC correlation spectroscopy. Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. Mass spectra were recorded using APCI or ESI as ionization source and a LTQ Orbitrap XL as analyser. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR. GC−MS measurements were conducted on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5ms column) linked to a Shimadzu GCMA-QP 2010 Plus mass spectrometer. Enantiomeric excesses were determined by analytical high pressure liquid chromatography (HPLC) analysis on an Agilent Technologies 1290 Infinity or an Agilent Technologies 1200 Infinity instrument with a chiral stationary phase using a Daicel Chiralcel OJ-RH column (MeCN/H₂O mixtures as solvent), a Daicel Chiralcel OJ-H column (n-heptane/iPrOH mixtures as solvent), or a Daicel Chiralpak IB column (n-heptane/iPrOH mixtures as solvent).

1.2 Single-Crystal X-ray Structure Determinations

The crystal was mounted on a glass capillary in perfluorinated oil and measured in a cold nitrogen flow. The data were collected on an Agilent Technologies SuperNova (single source) at 150 K (Cu Kα radiation, λ= 1.5418 Å). The structure was solved by direct methods...
and refined on $F_2$ with the SHELX-97 software package.\textsuperscript{[55]} The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model except the hydride on the iron centre which could be defined from the Fourier electron density map.

1.3 Computational Details

Due to the possible importance of zwitterionic and charge transfer resonance structures we intended to choose long-range corrected density functional which can correctly describe the physical interactions in such systems. Dispersion correction seemed necessary to provide realistic description of the problem, because of the large size of the reactants and the catalyst (over 100 atoms all together). Therefore, we chose $\omega$B97X-D density functional\textsuperscript{[56]} which satisfied these conditions and benchmark calculations showed that it had been able to provide accurate results for reaction energies, kinetics, as well as noncovalent interactions.\textsuperscript{[57]} For iron atoms, we employed the all-electron triple-$\zeta$ cc-pVTZ basis set\textsuperscript{[58]} which allows flexible description. For other atoms (H, C, N, O, Si, and P), we applied 6-31G(d) basis set.\textsuperscript{[59]} Frequency calculations (temperature = 343 K) were carried out to evaluate stationary points; minima no imaginary frequency, transition states with one imaginary frequency. All calculations were carried out with GAUSSIAN 09 program package.\textsuperscript{[60]} The structures were drawn using CYLview 1.0b.
2 General Procedure for the Hydrosilylation of Ketones with Iron(0) Complex 2 (GP 1)

A Schlenk flask equipped with a magnetic stirrer is charged with solution of ketone 3 (0.10 mmol, 1.0 equiv), hydrosilane 4, and iron(0) complex 2 in the indicated solvent (2 mL). The mixture is maintained at indicated temperature for 22 h and then quenched with 2 mL of a KOH solution (5% in H$_2$O). The reaction mixture is maintained for further 2 h at room temperature and subsequently extracted with diethyl ether (3 × 5.0 mL). The combined organic layers are dried over Na$_2$SO$_4$ and filtered. Anisole (internal standard) is added, and an aliquot is taken for GC-MS analysis.

2.1 Optimisation with 4-Methoxyacetophenone (3a)

According to GP 1, 4-methoxyacetophenone (3a, 15 mg, 0.10 mmol, 1.0 equiv) was hydrosilylated under various conditions (Table S1).

Table S1. Hydrosilylation of 4-methoxyacetophenone (3a) using iron(0) complex 2 as precatalyst.

| entry | solvent | temp. (°C) | hydrosilane 4 (equiv) | catalyst loading (mol %) | yield of 5a (%) |
|-------|---------|------------|-----------------------|--------------------------|-----------------|
| 1     | hexanes | 70         | (EtO)$_3$SiH (3)       | 2.5                      | 89              |
| 2     | toluene | 70         | (EtO)$_3$SiH (3)       | 2.5                      | 92              |
| 3     | THF     | 70         | (EtO)$_3$SiH (3)       | 2.5                      | 96              |
| 4     | dioxane | 70         | (EtO)$_3$SiH (3)       | 2.5                      | 85              |
| 5     | DMA     | 70         | (EtO)$_3$SiH (3)       | 2.5                      | 95              |
| 6     | THF     | 40         | (EtO)$_3$SiH (3)       | 2.5                      | 68              |
| 7     | THF     | 50         | (EtO)$_3$SiH (3)       | 2.5                      | 86              |
| 8     | THF     | 60         | (EtO)$_3$SiH (3)       | 2.5                      | 91              |
| 9     | THF     | 80         | (EtO)$_3$SiH (3)       | 2.5                      | 99              |
| 10    | THF     | 40         | PhSiH$_3$ (3)          | 2.5                      | 48              |
| 11    | THF     | 40         | Ph$_2$SiH$_2$ (3)      | 2.5                      | 40              |
| 12    | THF     | 40         | Me$_2$PhSiH (3)        | 2.5                      | 26              |
| 13    | THF     | 40         | Et$_3$SiH (3)          | 2.5                      | 1               |
| 14    | THF     | 40         | PMHS (3)               | 2.5                      | 62              |
| 15    | THF     | 70         | PMHS (3)               | 2.5                      | 43              |
| 16    | THF     | 70         | (EtO)$_3$SiH (1.1)     | 2.5                      | 73              |
| 17    | THF     | 70         | (EtO)$_3$SiH (1.5)     | 2.5                      | >99             |
| 18    | THF     | 70         | (EtO)$_3$SiH (2)       | 2.5                      | >99             |
| 19    | THF     | 70         | (EtO)$_3$SiH (2.5)     | 2.5                      | >99             |
| 20    | THF     | 70         | (EtO)$_3$SiH (4)       | 2.5                      | 98              |
| 21    | THF     | 70         | (EtO)$_3$SiH (1.5)     | 0                        | 0               |
| 22    | THF     | 70         | (EtO)$_3$SiH (1.5)     | 0.5                      | 77              |
| 23    | THF     | 70         | (EtO)$_3$SiH (1.5)     | 1.0                      | 88              |
2.2 Substrate Scope

According to GP 1, various ketones 3 (0.10 mmol, 1.0 equiv) were hydrosilylated with triethoxysilane (4a, 25 mg, 0.15 mmol, 1.5 equiv), and iron(0) complex 2 (2.2 mg, 2.5 µmol, 2.5 mol %).

Removal of diethyl ether and dissolution in CDCl₃ permitted the control also by NMR spectroscopy. The NMR spectra of the corresponding products were in accordance with the reported alcohols in the corresponding references (Table S2).

Table S2. Substrate scope for the hydrosilylation of ketones using iron(0) complex 2 as precatalyst.

| entry | 3     | R¹     | R²     | yield of 5 (%) | ref.    |
|-------|-------|--------|--------|----------------|---------|
| 1     | 3a    | X = OMe | Me     | >99 (5a)       | S1,S11  |
| 2     | 3b    | X = Et₂N | Me     | 40 (5b)        | S13     |
| 3     | 3c    | X = Me  | Me     | 82 (5c)        | S1,S14  |
| 4     | 3d    | X = Br  | Me     | >99 (5d)       | S1,S15  |
| 5     | 3e    | X = H   | Me     | 93 (5e)        | S1,S11  |
| 6    | 3f    | X = CF₃ | Me     | 95 (5f)        | S1,S11  |
| 7     | 3g    | X = OMe | Me     | 70 (5g)        | S14     |
| 8     | 3h    | X = Me  | Me     | 70 (5h)        | S16     |
| 9     | 3i    | X = Cl  | Me     | 49 (5i)        | S14     |
| 10    | 3j    | Mes    | Me     | 0 (5j)         | S14     |
| 11    | 3k    | Ph     | Ph     | 60 (5k)        | S16     |
| 12    | 3l    | Ph     | Et     | 18 (5l)        | S14     |
| 13    | 3m    | Ph     | i-Pr   | 16 (5m)        | S14     |
| 14    | 3n    | c-Pr   | Me     | >99 (5n)       | S20     |
| 15    | 3p    | 4-pyridyl | Me     | 92 (5p)        | S17     |
| 16    | 3q    | 2-tolyl | Ph     | 41 (5q)        | S14     |
| 17    | 3r    | 4-Br-C₆H₄ | Ph     | 72 (5r)        | S18     |
| 18    | 3s    | 2-furanyl | Me     | 84 (5s)        | S19     |
| 19    | 3t    | 2,6-Me₂-4-t-Bu-C₆H₂ | Me | 3 (5t)         | S3      |
| 20    | 3u    | 4-t-Bu-cyclohexanone | Me | 25 (cis-5u) (d.r. > 20:1) | S21 |

*In the presence of 25 mol % of PMe₃ (6).
3 Identification of the Active Iron(II) Complex 7

3.1 General Procedure for the Stoichiometric Reaction of Iron(0) complex 2 with Hydrosilanes 4

Complex 2 (44.5 mg, 50.0 µmol, 1.00 equiv) was weighed in a Schlenk flask with a magnetic stirrer. The hydrosilane 4 (0.15 mmol, 3 equiv) was weighed in a vial and dissolved in 2.0 mL of toluene (0.5 mL of C₆D₆ for NMR studies) and added into the Schlenk flask. The reaction mixture was heated in an oil bath at 70 °C changing the colour from dark purple to dark red. The time for completion (100% conversion by NMR) varied depending on the hydrosilane used: (EtO)₃SiH 12 h, Me₂PhSiH 6 days, and MePh₂SiH reached 90% conversion after 6 days. The reaction mixture was concentrated, and the product was obtained as a crude red oil. The crude product was dissolved in C₆H₆ and cold sublimation of the solvent in vacuo afforded the desired product as a red powder.

3.1.1 Si = (EtO)₃Si (7a)

¹H NMR (500 MHz, C₆D₆, 298 K): δ(ppm) = –14.83 (d, ²J,H-P = 3.2 Hz, ²J,H-Si = 19.3 Hz, 1H, Fe–H), 1.19 (s, 18H, NC(CH₃)₃), 1.41 (t, ³J,H-H = 7.0 Hz, 6H, NCH'H-CH₃), 1.47 (s, 18H, NC(CH₃)₃), 1.48 (d, ²J,H-P = 6.2 Hz, 9H, P(CH₃)₃), 1.58 (t, ³J,H-H = 7.1 Hz, 9H, SiOCH₂CH₃), 3.38 (dq, ²J,H-H = 14.0 Hz, ³J,H-H = 7.0 Hz, 2H, NCH'H–CH₃), 3.57 (dq, ²J,H-H = 14.0 Hz, ³J,H-H = 7.0 Hz, 2H, NCH'H–CH₃), 4.33 (q, ³J,H-H = 6.9 Hz, 6H, SiOCH₂CH₃), 5.91 (d, ³J,H-H = 8.1 Hz, 2H, 3,5-H py), 6.96-7.08 (m, 6H, C arom.H), 7.24 (t, ³J,H-H = 8.0 Hz, 1H, 4-H py), 7.23 (d, ³J,H-H = 7.2 Hz, 2H, C arom.H), 7.72 (d, ³J,H-H = 7.6 Hz, 2H, arom. CH). ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ(ppm) = 15.3 (NCH₂–CH₃), 19.8 (SiOCH₂CH₃), 25.9 (d, ¹J,C-P = 18.2 Hz, P(CH₃)₃), 31.9 (NC(CH₃)₃), 32.6 (NC(CH₃)₃), 38.9 (NCH₂–CH₃), 53.7 (NC(CH₃)₃), 54.1 (NC(CH₃)₃), 56.9 (SiOCH₂CH₃), 94.2 (3,5-C arom. py), 127.1(C arom.), 128.5 (C arom.), 129.0 (C arom.), 131.0 (4-C arom. py), 132.7 (C arom. quaternary Ph), 133.9 (C arom.), 168.1 (2,6-C arom. py), 171.7 (NCN). ²⁹Si{¹H} NMR (80 MHz, C₆D₆, 298 K): δ(ppm) = 33.7 (d, ²J,Si-P = 58.8 Hz, Si(OEt)₃), 79.2 (d, ²J,Si-P = 24.3 Hz, Si:→Fe). ³¹P{¹H} NMR (202 MHz, C₆D₆, 298 K): δ(ppm) = 16.8.
3.1.2 Si = Me$_2$PhSi (7b)

$^1$H NMR (500 MHz, C$_6$D$_6$, 298 K): $\delta$(ppm) = –13.95 (d, $^2$J$_{H-P}$ = 1.4 Hz, $^2$J$_{H-Si}$ = 19.7 Hz, 1H, Fe–H), 1.06 (s, 18H, NC(CH$_3$)$_2$), 1.08 (s, 6H, Si(CH$_3$)$_2$Ph), 1.28 (s, 18H, NC(CH$_3$)$_2$), 1.38 (t, $^3$J$_{H-H}$ = 7.0 Hz, 6H, NCH’H-CH$_3$), 1.44 (d, $^2$J$_{H-P}$ = 6.3 Hz, 9H, P(CH$_3$)$_3$), 3.33 (dq, $^2$J$_{H-H}$ = 13.2 Hz, $^3$J$_{H-H}$ = 6.6 Hz, 2H, NCH’H-CH$_3$), 5.90 (d, $^3$J$_{H-H}$ = 7.6 Hz, 2H, 3,5-H py), 6.93–7.02 (m, 8H, C arom.), 7.24 (t, $^3$J$_{H-H}$ = 7.6 Hz, 1H, 4-H py), 7.33 (t, $^3$J$_{H-H}$ = 7.1 Hz, 1H, 3-C arom. SiPh), 7.45 (m, 1H, C arom. SiPh), 7.50 (m, 2H, Carom. H SiPh), 7.76 (m, 2H, Carom. H Ph). 8.57 (d, $^3$J$_{H-H}$ = 7.1 Hz, 1H, 2-C arom. SiPh).

$^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$, 298 K): $\delta$(ppm) = 15.1 (NCH$_2$-C$_3$H$_3$), 16.3 (Si(CH$_3$)$_2$), 25.7 (d, $^1$J$_{C-P}$ = 16.5 Hz, P(CH$_3$)$_3$), 31.7 (NC(CH$_3$)$_3$), 32.5 (NC(CH$_3$)$_3$), 38.8 (NCH$_2$-CH$_3$), 53.6 (NC(CH$_3$)$_3$), 54.0 (NC(CH$_3$)$_3$), 94.3 (3,5-Carom. py), 125.0 (Carom. SiPh), 126.0 (Carom.), 126.1 (Carom. SiPh), 126.9 (Carom.), 128.4 (Carom.), 128.6 (Carom.), 129.6 (Carom.), 130.9 (Carom.), 132.8 (4-Carom. py), 133.3 (Carom.), 134.3 (Carom.), 136.4 (o-Carom. SiPh), 160.5 (Carom. quaternary SiPh) 168.3 (2,6-Carom. py), 171.8 (NCN). $^{29}$Si NMR, $^1$H–$^{29}$Si HMQC NMR (500 MHz / 99 MHz, C$_6$D$_6$, 298 K): $\delta$(ppm) = 31.1 (SiMe$_2$Ph), 77.2 (Si–→Fe). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$, 298 K): $\delta$(ppm) = 14.7.

IR (KBr pellet, cm$^{-1}$): $\nu$/cm$^{-1}$ = 2020. ESI-MS (m/z): calcd for [C$_{50}$H$_{79}$FeN$_7$PSi$_3$]$^+$ (M – H)$^+$ 948.47863; found 948.54423.

3.1.3 Si = MePh$_2$Si (7c)

$^1$H NMR (500 MHz, C$_6$D$_6$, 298 K): $\delta$(ppm) = –13.69 (br s, 1H, Fe–H), 1.06 (s, 18H, NC(CH$_3$)$_2$), 1.24 (s, 18H, NC(CH$_3$)$_2$), 1.34 (m, 6H, NCH’H-CH$_3$), 1.36 (m, 9H, P(CH$_3$)$_3$), 1.37 (m, 3H, SiCH$_2$Ph$_2$), 3.33 (dq, $^2$J$_{H-H}$ = 13.0 Hz, $^3$J$_{H-H}$ = 6.0 Hz, 2H, NCH’H-CH$_3$), 5.86 (d, $^3$J$_{H-H}$ = 7.8 Hz, 2H, 3,5-H py), 6.90–7.05 (m, 10H, C arom.), 7.24 (t, $^3$J$_{H-H}$ = 7.8 Hz, 1H, 4-H py), 7.34 (t, $^3$J$_{H-H}$ = 7.2 Hz, 4H, 3-Carom. H SiPh), 7.71 (d, $^3$J$_{H-H}$ = 6.7 Hz, 2H, Carom.H SiPh). 8.22 (d, $^3$J$_{H-H}$ = 6.7 Hz, 4H, 2-Carom.H SiPh).

$^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$, 298 K): $\delta$(ppm) = 15.0 (NCH$_2$-CH$_3$), 25.8 (d, $^1$J$_{C-P}$ = 16.7 Hz, P(CH$_3$)$_3$), 29.2 (SiCH$_2$Ph$_2$), 31.7 (NC(CH$_3$)$_3$), 32.4 (NC(CH$_3$)$_3$), 38.7 (NCH$_2$-CH$_3$), 53.7 (NC(CH$_3$)$_3$), 54.1 (NC(CH$_3$)$_3$), 94.3 (3,5-Carom. py), 125.0 (Carom. SiPh), 126.2 (Carom. SiPh), 126.8 (Carom.), 128.3 (Carom.), 129.1 (2xCarom. SiPh), 129.8 (Carom.), 130.7 (4-Carom. py), 133.2 (Carom.), 135.6 (Carom.), 136.4 (o-Carom. SiPh), 137.2 (Carom.), 159.8 (Carom. quaternary SiPh), 168.5 (2,6-Carom. py), 172.3 (NCN). $^{29}$Si NMR, $^1$H–$^{29}$Si HMQC (500 MHz / 99 MHz, C$_6$D$_6$, 298 K): $\delta$(ppm) = 34.4 (SiMePh$_2$), 76.3 (Si–→Fe). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$, 298 K): $\delta$(ppm) = 16.8.
3.2 Crystallographic Data for 7b

![Crystal structure diagram]

**Table S3.** Crystallographic data for compound 7b.

| Property                        | Value                      |
|--------------------------------|----------------------------|
| Empirical formula              | 2×(C₅₀H₈₀FeN₇PSi₃) • C₇H₈  |
| Mr                             | 1992.73                    |
| Space group                    | P-1                        |
| Crystal system                 | Triclinic                  |
| a [Å]                          | 11.5288(5)                 |
| b [Å]                          | 12.5203(5)                 |
| c [Å]                          | 21.1550(11)                |
| α [°]                          | 73.555(4)                  |
| β [°]                          | 75.604(4)                  |
| γ [°]                          | 74.650(4)                  |
| V [Å³]                         | 2774.0(2)                  |
| Z                              | 1                          |
| ρ<sub>calc</sub> [mg m⁻³]      | 1.193                      |
| Wavelength [Å]                 | 1.54184                    |
| μ (MoKα) [mm⁻¹]                | 3.379                      |
| crystal size [mm³]             | 0.45 × 0.12 × 0.04         |
| Θ limits [°]                   | 3.76 to 67.50              |
| completeness to Θ = 67.50° [%] | 99.9                       |
| reflns measured<sup>[a]</sup> | 18617                      |
| independent reflns             | 9988 [R(int) = 0.0490]     |
| parameters                     | 645                        |
| R₁ (R₁ all data)<sup>[b]</sup> | 0.0452 (0.0635)            |
| wR₂ (wR₂ all data)<sup>[c]</sup> | 0.1026 (0.1162)          |
| GOF                            | 1.020                      |
| max., min. peaks [eÅ⁻³]        | 0.475 and -0.389           |

<sup>[a]</sup> Observation criterion: I>2σ(I).  
<sup>[b]</sup> R₁ = Σ | |F₁| - |F₂| | / Σ |F₁|.  
<sup>[c]</sup> wR₂ = {Σ[w(F₁² - F₂²)²] / Σ[w(F₁²)]}¹/²
**Table S4.** Bond lengths [Å] and angles [°] for compound 7b.

| Bond                  | Length/Distance  | Angle                  |  |
|-----------------------|------------------|------------------------|------|
| Fe(1)-N(1)            | 2.063(2)         |                        | 1.489(3) |
| Fe(1)-Si(1)           | 2.1509(7)        |                        | 1.523(4) |
| Fe(1)-Si(2)           | 2.1715(7)        |                        | 1.500(3) |
| Fe(1)-P(1)            | 2.1975(8)        |                        | 1.515(4) |
| Fe(1)-Si(3)           | 2.2986(8)        |                        | 1.528(4) |
| Si(1)-N(2)            | 1.786(2)         |                        | 1.532(4) |
| Si(1)-N(5)            | 1.893(2)         |                        | 1.523(4) |
| Si(1)-N(4)            | 1.927(2)         |                        | 1.529(4) |
| Si(1)-C(10)           | 2.364(2)         |                        | 1.536(4) |
| Si(2)-N(3)            | 1.794(2)         |                        | 1.389(4) |
| Si(2)-N(6)            | 1.892(2)         |                        | 1.397(4) |
| Si(2)-N(7)            | 1.916(2)         |                        | 1.392(4) |
| Si(2)-C(25)           | 2.356(3)         |                        | 1.382(4) |
| Si(3)-C(43)           | 1.921(3)         |                        | 1.375(4) |
| Si(3)-C(44)           | 1.925(3)         |                        | 1.385(4) |
| Si(3)-C(45)           | 1.938(3)         |                        | 1.498(4) |
| P(1)-C(40)            | 1.839(3)         |                        | 1.519(4) |
| P(1)-C(41)            | 1.839(3)         |                        | 1.526(4) |
| P(1)-C(42)            | 1.839(3)         |                        | 1.531(4) |
| N(1)-C(1)             | 1.371(3)         |                        | 1.516(4) |
| N(1)-C(5)             | 1.376(3)         |                        | 1.519(5) |
| C(1)-N(2)             | 1.374(3)         |                        | 1.532(4) |
| C(1)-C(2)             | 1.402(4)         |                        | 1.379(4) |
| N(2)-C(6)             | 1.463(3)         |                        | 1.394(4) |
| C(2)-C(3)             | 1.371(4)         |                        | 1.390(4) |
| N(3)-C(5)             | 1.375(3)         |                        | 1.380(5) |
| N(3)-C(8)             | 1.467(3)         |                        | 1.372(5) |
| C(3)-C(4)             | 1.380(4)         |                        | 1.394(4) |
| N(4)-C(10)            | 1.321(3)         |                        | 1.385(4) |
| N(4)-C(11)            | 1.485(3)         |                        | 1.408(4) |
| C(4)-C(5)             | 1.401(4)         |                        | 1.393(4) |
| N(5)-C(10)            | 1.339(3)         |                        | 1.382(5) |
| N(5)-C(15)            | 1.489(3)         |                        | 1.379(5) |
| N(6)-C(25)            | 1.337(4)         |                        | 1.385(5) |
| N(6)-C(30)            | 1.488(3)         |                        | 1.525(18) |
| C(6)-C(7)             | 1.528(4)         |                        | 1.374(9) |
| N(7)-C(25)            | 1.327(3)         |                        | 1.389(10) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| C(53)-C(54)          | 1.386(10)    | C(44)-Si(3)-Fe(1)     | 116.23(9)    |
| C(54)-C(55)          | 1.362(10)    | C(45)-Si(3)-Fe(1)     | 117.61(10)   |
| C(55)-C(56)          | 1.373(9)     | C(40)-P(1)-C(41)      | 96.02(15)    |
| C(56)-C(57)          | 1.370(10)    | C(40)-P(1)-C(42)      | 95.81(15)    |
|                      |              | C(41)-P(1)-C(42)      | 99.13(15)    |
|                      |              |                       |              |
| N(1)-Fe(1)-Si(1)     | 82.72(6)     | C(40)-P(1)-Fe(1)      | 125.45(10)   |
| N(1)-Fe(1)-Si(2)     | 78.76(6)     | C(41)-P(1)-Fe(1)      | 120.69(11)   |
| Si(1)-Fe(1)-Si(2)    | 144.54(3)    | C(42)-P(1)-Fe(1)      | 114.18(10)   |
| N(1)-Fe(1)-P(1)      | 89.22(6)     | C(1)-N(1)-C(5)        | 117.8(2)     |
| Si(1)-Fe(1)-P(1)     | 105.82(3)    | C(1)-N(1)-Fe(1)       | 121.12(16)   |
| Si(2)-Fe(1)-P(1)     | 103.90(3)    | C(5)-N(1)-Fe(1)       | 120.92(16)   |
| N(1)-Fe(1)-Si(3)     | 176.87(6)    | N(1)-C(1)-N(2)        | 115.6(2)     |
| Si(1)-Fe(1)-Si(3)    | 95.53(3)     | N(1)-C(1)-C(2)        | 121.4(2)     |
| Si(2)-Fe(1)-Si(3)    | 101.41(3)    | N(2)-C(1)-C(2)        | 123.0(2)     |
| P(1)-Fe(1)-Si(3)     | 93.76(3)     | C(1)-N(2)-C(6)        | 118.7(2)     |
| N(2)-Si(1)-N(5)      | 102.79(10)   | C(1)-N(2)-Si(1)       | 115.61(16)   |
| N(2)-Si(1)-N(4)      | 98.58(9)     | C(6)-N(2)-Si(1)       | 125.60(17)   |
| N(5)-Si(1)-N(4)      | 68.26(9)     | C(3)-C(2)-C(1)        | 119.0(2)     |
| N(2)-Si(1)-Fe(1)     | 103.33(7)    | C(5)-N(3)-C(8)        | 118.1(2)     |
| N(5)-Si(1)-Fe(1)     | 133.05(7)    | C(5)-N(3)-Si(2)       | 112.63(17)   |
| N(4)-Si(1)-Fe(1)     | 142.90(8)    | C(8)-N(3)-Si(2)       | 125.58(18)   |
| N(2)-Si(1)-C(10)     | 105.36(9)    | C(2)-C(3)-C(4)        | 120.4(3)     |
| N(5)-Si(1)-C(10)     | 34.47(9)     | C(10)-N(4)-C(11)      | 130.2(2)     |
| N(4)-Si(1)-C(10)     | 33.94(9)     | C(10)-N(4)-Si(1)      | 91.49(16)    |
| Fe(1)-Si(1)-C(10)    | 151.06(7)    | C(11)-N(4)-Si(1)      | 138.31(17)   |
| N(3)-Si(2)-N(6)      | 103.59(10)   | C(3)-C(4)-C(5)        | 119.1(2)     |
| N(3)-Si(2)-N(7)      | 98.86(11)    | C(10)-N(5)-C(15)      | 127.9(2)     |
| N(6)-Si(2)-N(7)      | 68.64(9)     | C(10)-N(5)-Si(1)      | 92.40(17)    |
| N(3)-Si(2)-Fe(1)     | 102.13(7)    | C(15)-N(5)-Si(1)      | 137.99(16)   |
| N(6)-Si(2)-Fe(1)     | 145.31(8)    | N(3)-C(5)-N(1)        | 115.0(2)     |
| N(7)-Si(2)-Fe(1)     | 129.19(7)    | N(3)-C(5)-C(4)        | 123.9(2)     |
| N(3)-Si(2)-C(25)     | 106.27(10)   | N(1)-C(5)-C(4)        | 121.1(2)     |
| N(6)-Si(2)-C(25)     | 34.55(10)    | C(25)-N(6)-C(30)      | 128.0(2)     |
| N(7)-Si(2)-C(25)     | 34.28(9)     | C(25)-N(6)-Si(2)      | 92.07(16)    |
| Fe(1)-Si(2)-C(25)    | 149.13(7)    | C(30)-N(6)-Si(2)      | 137.62(18)   |
| C(43)-Si(3)-C(44)    | 98.63(14)    | N(2)-C(6)-C(7)        | 113.4(2)     |
| C(43)-Si(3)-C(45)    | 99.22(13)    | C(25)-N(7)-C(26)      | 129.5(2)     |
| C(44)-Si(3)-C(45)    | 99.58(13)    | C(25)-N(7)-Si(2)      | 91.35(17)    |
| C(43)-Si(3)-Fe(1)    | 121.55(10)   | C(26)-N(7)-Si(2)      | 138.81(17)   |
| Bond                  | Angle (°) 1 | Bond                  | Angle (°) 2 | Bond                  | Angle (°) 3 |
|-----------------------|------------|-----------------------|------------|-----------------------|------------|
| N(3)-C(8)-C(9)        | 113.4(3)   | C(27)-C(26)-C(29)     | 109.6(2)   |
| N(4)-C(10)-N(5)       | 107.4(2)   | N(7)-C(26)-C(28)      | 111.1(2)   |
| N(4)-C(10)-C(19)      | 125.1(2)   | C(27)-C(26)-C(28)     | 110.7(3)   |
| N(5)-C(10)-C(19)      | 127.5(2)   | C(29)-C(26)-C(28)     | 108.5(3)   |
| N(4)-C(10)-Si(1)      | 54.57(12)  | N(6)-C(30)-C(33)      | 105.4(2)   |
| N(5)-C(10)-Si(1)      | 53.13(13)  | N(6)-C(30)-C(31)      | 111.8(2)   |
| C(19)-C(10)-Si(1)     | 174.43(19) | C(33)-C(30)-C(31)     | 109.5(3)   |
| N(4)-C(11)-C(13)      | 106.6(2)   | N(6)-C(30)-C(32)      | 110.3(2)   |
| N(4)-C(11)-C(14)      | 112.7(2)   | C(33)-C(30)-C(32)     | 108.4(3)   |
| C(13)-C(11)-C(14)     | 108.2(2)   | C(31)-C(30)-C(32)     | 111.3(3)   |
| N(4)-C(11)-C(12)      | 110.5(2)   | C(35)-C(34)-C(39)     | 119.7(3)   |
| C(13)-C(11)-C(12)     | 110.0(2)   | C(35)-C(34)-C(25)     | 119.0(3)   |
| C(14)-C(11)-C(12)     | 108.8(2)   | C(39)-C(34)-C(25)     | 121.2(3)   |
| N(5)-C(15)-C(17)      | 110.4(2)   | C(34)-C(35)-C(36)     | 120.5(3)   |
| N(5)-C(15)-C(16)      | 107.9(2)   | C(37)-C(36)-C(35)     | 119.4(3)   |
| C(17)-C(15)-C(16)     | 109.7(2)   | C(38)-C(37)-C(36)     | 120.7(3)   |
| N(5)-C(15)-C(18)      | 111.4(2)   | C(37)-C(38)-C(39)     | 120.2(3)   |
| C(17)-C(15)-C(18)     | 110.5(3)   | C(34)-C(39)-C(38)     | 119.5(3)   |
| C(16)-C(15)-C(18)     | 106.8(3)   | C(46)-C(45)-C(50)     | 115.3(3)   |
| C(20)-C(19)-C(24)     | 119.4(2)   | C(46)-C(45)-Si(3)     | 123.7(2)   |
| C(20)-C(19)-C(10)     | 120.3(2)   | C(50)-C(45)-Si(3)     | 121.0(2)   |
| C(24)-C(19)-C(10)     | 120.2(2)   | C(45)-C(46)-C(47)     | 123.2(3)   |
| C(19)-C(20)-C(21)     | 119.8(3)   | C(48)-C(47)-C(46)     | 119.6(3)   |
| C(22)-C(21)-C(20)     | 120.3(3)   | C(49)-C(48)-C(47)     | 119.2(3)   |
| C(23)-C(22)-C(21)     | 120.0(3)   | C(48)-C(49)-C(50)     | 120.2(3)   |
| C(22)-C(23)-C(24)     | 120.3(3)   | C(49)-C(50)-C(45)     | 122.4(3)   |
| C(23)-C(24)-C(19)     | 120.1(3)   | C(53)-C(52)-C(57)     | 119.3(7)   |
| N(7)-C(25)-N(6)       | 107.4(2)   | C(53)-C(52)-C(51)     | 123.4(11)  |
| N(7)-C(25)-C(34)      | 126.8(3)   | C(57)-C(52)-C(51)     | 117.2(11)  |
| N(6)-C(25)-C(34)      | 125.7(2)   | C(52)-C(53)-C(54)     | 120.1(7)   |
| N(7)-C(25)-Si(2)      | 54.37(14)  | C(55)-C(54)-C(53)     | 120.3(7)   |
| N(6)-C(25)-Si(2)      | 53.39(13)  | C(54)-C(55)-C(56)     | 119.6(7)   |
| C(34)-C(25)-Si(2)     | 172.0(2)   | C(57)-C(56)-C(55)     | 120.9(7)   |
| N(7)-C(26)-C(27)      | 111.1(2)   | C(56)-C(57)-C(52)     | 119.7(7)   |
| N(7)-C(26)-C(29)      | 105.7(2)   |                           |            |
4 Mechanistic Experiments

4.1 Kinetics: Iron(0) complex 2 vs. Iron(II) complex 7a

4.1.1 Iron(0) complex 2

Iron(0) complex 2 (5 mg, 0.005 mmol, 2 mol%) was weighed in a Schlenk flask together with silane 4a (55 mg, 0.33 mmol, 1.5 equiv) and ketone 3a (34 mg, 0.22 mmol, 1.0 equiv). 2.0 mL of THF were added through a syringe and the mixture was heated to 70 °C. Aliquots were taken during the course of the reaction, hydrolysed and analysed by GC-MS (red squares).

4.1.2 Iron(II) complex 7a

Iron(0) complex 2 (5 mg, 0.005 mmol, 2 mol%) was weighed in a Schlenk flask together with silane 4a (55 mg, 0.33 mmol, 1.5 equiv). 2.0 mL of THF was added through a syringe and the mixture was heated to 70 °C for 30 min while the colour changed from dark purple to clear orange. Ketone 3a (34 mg, 0.22 mmol, 1.0 equiv) was added into the reaction mixture and the heating was continued at 70 °C. Aliquots were taken during the course of the reaction, hydrolysed and analysed by GC-MS (blue diamonds).
4.2 Scrambling at the Si–H Bond

4.2.1 Hydrosilane Si–D/Fe–H Scrambling Using Me₂PhSi–D (4b-d₁)

Complex 7b (54 mg, 0.057 mmol, 1.0 equiv) was mixed in a Schlenk flask with deuterated dimethylphenylsilane (4b-d₁, 9.5 mg, 0.069 mmol, 1.2 equiv) in 2.0 mL of THF. The reaction mixture was heated at 70 °C in an oil bath. The course of the reaction was followed by analysis of an aliquot (0.1 mL) by GC-MS. The deuterated dimethylphenylsilane/dimethylphenylsilane ratio (Si–D/Si–H, blue diamonds) was calculated according to the intensity of peaks at 122/121 [M–CH₃]⁺ in the mass spectrum for the GC peak corresponding to the dimethylphenylsilane 4b.

![Diagram](image-url)

- DH ratio of 4b vs. Time (min)
4.2.2 Deuteration Studies with Me₂PhSi–D (4b-d₁)

Complex 7b (49 mg, 0.051 mmol, 0.88 equiv) was mixed in a Schlenk flask with acetophenone (3e, 9.2 mg, 0.077 mmol, 1.3 equiv) and deuterated dimethylphenylsilane (4b-d₁, 8.0 mg, 0.058 mmol, 1.0 equiv) in 2.0 mL of THF. The reaction mixture was heated at 70 °C in an oil bath. The course of the reaction was followed by analysis of aliquots (0.1 mL) by GC-MS. The D/H ratio on the product was calculated according to the intensity of peaks at 242/241 [M–CH₃]+ in the mass spectrum for the GC peak corresponding to the silyl ether product 8eb.

![Diagram of reaction]

4.3 Scrambling at the C–H Bond

4.3.1 Scrambling Experiment with Deuterated Silyl Ether (8eb-d₁)

According to a literature procedure,[S21] a 2-mL vial was charged with acetophenone (3e, 100 mg, 0.84 mmol, 1.0 equiv), deuterated dimethylphenylsilane (4b-d₁, 120 mg, 0.87 mmol, 1.0 equiv), and B(C₆F₅)₃ (2 mg, 3 µmol, 0.5 mol %) in toluene (0.5 mL). The reaction mixture was stirred at room temperature for 2 h and then subjected directly to flash column chromatography on silica gel using cyclohexane/ethyl acetate (30:1) as eluent, yielding the silyl ether 8eb-d₁ (180 mg, 0.71 mmol, 84%, >95% D) as a colourless oil.
\[ \text{H NMR (500 MHz, CDCl}_3, 298 \text{ K): } \delta (\text{ppm}) = 0.29 (s, 3H, Si-Me), 0.34 (s, 3H, Si-Me), 1.42 (s, 3H, C-Me), 7.21-7.39 (m, 8H, Ar), 7.55-7.57 (m, 2H, Ar). \]
\[ \text{C^{13}(H) NMR (126 MHz, CDCl}_3, 298 \text{ K): } \delta (\text{ppm}) = -1.2, -0.7, 26.8, 70.8 \ (t, J_{C-D} = 21.7 \text{ Hz}), 127.9, 129.7, 133.1, 138.3, 146.3. \]

\[ \text{Si DEPT NMR (99 MHz, CDCl}_3, 298 \text{ K): } \delta (\text{ppm}) = 6.6. \]

\[ \text{R}_f = 0.5 \ \text{(cyclohexane:ethyl acetate 30:1).} \]
\[ \text{IR (ATR): } \tilde{\nu}/\text{cm}^{-1}= 3066 \ \text{(w)}, 3023 \ \text{(w)}, 2970 \ \text{(m)}, 2924 \ \text{(w)}, 2130 \ \text{(w)}, 1427 \ \text{(m)}, 1368 \ \text{(m)}, 1251 \ \text{(s)}, 1137 \ \text{(s)}, 1115 \ \text{(s)}, 1095 \ \text{(m)}, 1010 \ \text{(s)}, 861 \ \text{(m)}, 820 \ \text{(s)}, 783 \ \text{(s)}, 695 \ \text{(s).} \]
\[ \text{HRMS (APCI) for C}_{16}\text{H}_{20}\text{DOSi \ [(M+H)^+]: calcd}} 258.1419, \ \text{found} 258.1462. \]

Deuterated silyl ether 8eb-d$_1$ (13 mg, 0.049 mmol, 1.1 equiv) and iron hydride complex 7b (43 mg, 0.045 mmol, 1.0 equiv) were dissolved in THF (2.0 mL), stirred at 70 °C, and the reaction was followed by analysis of an aliquot (0.1 mL) by GC-MS. The H/D ratio on the product was calculated according to the intensity of peaks at 242/241 [M–CH$_3$]$^+$ in the mass spectrum for the GC peak corresponding to the silyl ether product 8eb.
4.3.2 Racemisation Experiment with Enantiopure Silyl Ether (S)-8eb

The enantiomerically enriched silyl ether product (S)-8eb (49 mg, 0.19 mmol, 1.0 equiv, e.r. > 99:1) was subjected to the catalytic conditions in the presence of the dimethylphenylsilane (4b, 13 mg, 90 µmol, 0.47 equiv) and the iron hydride complex 7b (4.8 mg, 5.0 µmol, 2.5 mol %). The reaction mixture was heated up for 6 days at 70 °C, and aliquots passed through a short plug of silica gel and analysed by chiral HPLC analysis showed no racemization during the course of the reaction.

4.4 Phosphine Scrambling

4.4.1 Synthesis of Trimethylphosphine-d₉ (6-d₉)

According to a literature procedure,[S23] in a 100 mL Schlenk flask magnesium turnings (2.3 g, 90 mmol, 3.8 equiv) were thermally and mechanically activated under vacuum. Freshly degassed di-n-butyl ether (15 mL) was added followed by rapid addition of methyl iodide-d₃ (0.36 mL, 5.6 mmol, 0.30 equiv) under nitrogen atmosphere at room temperature. After the initiation of the reaction (colour change to dark brown and heat formation), the solution was cooled to 0 °C and the rest of methyl iodide-d₃ (3.3 mL, 50 mmol, 3.0 equiv) was added dropwise. The solution was allowed to warm to rt and stirred for additional 3 h. The solution was cooled to 0 °C and a solution of triphenylphosphite (5.0 g, 15 mmol, 1.0 equiv) in di-n-butyl ether (40 mL) was added slowly over 2 h. The solution was warmed to rt and stirred for 30 min. The dropping funnel was replaced by a distillation apparatus equipped with a Vigreux column (10 cm) and the desired deuterated phosphine 6-d₉ (560 mg, 6.6 mmol, 44%) was distilled at 160 °C (oil bath).

bp 38 °C. ²H NMR (77 MHz, C₆D₆/C₆H₆, 298 K): δ(ppm) = 0.72. ¹³C{¹H} NMR (176 MHz, C₆D₆/C₆H₆, 298 K): δ(ppm) = 15.4 (dsept, J_{C-P} = 6.7, J_{C-D} = 16.4 Hz). ³¹P NMR (202 MHz, C₆D₆/C₆H₆, 298 K): δ(ppm) = -65.5.
4.4.2 Scrambling between Complex 7b and Trimethylphosphine-\textit{d}_9 (6-\textit{d}_9)

Complex \textit{7b} (10 mg, 0.011 mmol 1.0 equiv) was mixed with trimethylphosphine-\textit{d}_9 (6-\textit{d}_9, 2.5 mg, 0.029 mmol, 2.7 equiv) in C_6D_6. The sample was closed under nitrogen in a Young NMR tube, heated to 70 °C, and monitored by \textsuperscript{1}H and \textsuperscript{2}H NMR spectroscopy. Slow formation of 7b-\textit{d}_9 was observed.

Selected NMR data for 7b-\textit{d}_9

\textbf{\textsuperscript{1}H,\textsuperscript{31}P HMQC NMR} (500 MHz / 203 MHz, C_6H_6/C_6D_6, 298 K): \( \delta(\textsuperscript{1}H) = -13.9 / \delta(\textsuperscript{31}P) = 12.4 \) ppm.

4.5 Phosphine Dissociation

Complex \textit{7b} (5 mg, 0.005 mmol) was dissolved in THF (2.0 mL). The closed system was heated up to 70 °C for a period of 2 h. The sample was frozen and the gas phase was changed by 3 purge-cycles with N\textsubscript{2} while thawing the sample. This procedure was repeated 3 times with the same period of time between each other. After 8 h, all volatiles were removed \textit{in vacuo} and the sample was dissolved in 0.5 mL of C_6D_6 for \textsuperscript{1}H and \textsuperscript{31}P(\textsuperscript{1}H) NMR analyses.
4.5.1 Phosphine Dissociation in the Presence of Acetophenone (3e)

Complex 7b (5 mg, 0.005 mmol, 1 equiv) was dissolved in THF (2.0 mL). Acetophenone (3e, 2.0 mg, 0.02 mmol, 4 equiv) was added and the closed system was heated up to 70 °C for a period of 2 h. The sample was frozen and the gas phase was changed by 3 purge-cycles with N₂ while thawing the sample. This procedure was repeated 3 times with the same period of time between each other. After 8 h, all volatiles were removed in vacuo and the sample was dissolved in 0.5 mL of C₆D₆ for ¹H and ³¹P{¹H} NMR analyses.
4.6 Silyl Scrambling

Complex 7b (10 mg, 0.011 mmol 1.0 equiv) was mixed with methyldiphenylsilane 4c (4.0 mg, 0.020 mmol, 1.8 equiv) in C₆D₆. The sample was closed under nitrogen in a Young NMR tube, heated to 70 °C, and monitored by ¹H spectroscopy.

Selected NMR data for 11b-d₆:

¹H NMR (500 MHz, C₆D₆, 298 K): δ = –15.69 (s, ²J_H-Si = 23.8 Hz, 1H, Fe–H) ppm. ¹H-²⁹Si HMQC NMR (500 MHz / 99 MHz, C₆D₆, 298 K): δ(¹H) = –15.7 / δ(²⁹Si) = 22.2 (SiMe₂Ph), δ(¹H) = –15.7 / δ(²⁹Si) = 84.5 (Si→Fe) ppm.

Selected NMR data for 11c-d₆:

¹H NMR (500 MHz, C₆D₆, 298 K): δ = –15.50 (s, ²J_H-Si = 23.7 Hz, 1H, Fe–H) ppm. ¹H-²⁹Si HMQC NMR (500 MHz / 99 MHz, C₆D₆, 298 K): δ(¹H) = –15.5 / δ(²⁹Si) = 27.7 (SiMe₂Ph), δ(¹H) = –15.5 / δ(²⁹Si) = 83.0 (Si→Fe) ppm.
Iron Hydride Product Distribution

| Time (h) | 7b | 7c | 11c-\(d_6\) | 11b-\(d_6\) |
|----------|----|----|------------|------------|
| 0        | 96 | -  | -          | 4          |
| 1        | 91 | -  | -          | 9          |
| 2        | 85 | 1  | <1         | 13         |
| 4        | 79 | 3  | 2          | 16         |
| 8        | 68 | 10 | 5          | 17         |
| 24       | 44 | 25 | 12         | 19         |

4.7 Silane Cross-over Experiment

Complex 7b (48 mg, 0.050 mmol, 1.00 equiv) was mixed in a Schlenk flask with acetophenone (3e, 8.8 mg, 0.073 mmol, 1.5 equiv), and methyldiphenylsilane (4c, 11 mg, 0.053 mmol, 1.1 equiv) in 2.0 mL of THF. The reaction mixture was heated at 70 °C with an oil bath. The course of the reaction was followed by analysis of aliquots (0.1 mL) by GC-MS.
4.8 Hydrosilylation with Silicon-Stereogenic Hydrosilane

4.8.1 Catalytic Reaction between Acetophenone (3e) with Enantioenriched Acyclic Hydrosilane $^{(SiS)}$-4d

Acetophenone (3e, 60 mg, 0.50 mmol, 1.0 equiv), $^{(SiS)}$-isopropylmethylphenylsilane [$^{(SiS)}$-4d, 82 mg, 0.50 mmol, 1.0 equiv, e.r. > 95:5], and the iron hydride complex 7b (49 mg, 0.052 mmol, 10 mol %) were dissolved in 3 mL of toluene. The reaction mixture was maintained at 70 °C in an oil bath for 6 days reaching ca. 60% conversion. Purification by flash column chromatography using $n$-pentane:diethyl ether (100:1) as eluting solvent mixture gave silyl ether 8ed (44 mg, 0.15 mmol, 31% yield, d.r. = 56:44) and unreacted hydrosilane $^{(SiS)}$-4d (10 mg, 0.07 mmol, 15%, e.r. > 95:5). [S24]
4.8.2 Reductive Si–O Bond Cleavage of Silyl Ether 8ed

A Schlenk tube equipped with a magnetic stirrer and a reflux condenser was charged with a solution of the silyl ether 8ed (25 mg, 0.089 mmol, 1.0 equiv) in n-heptane (1.0 mL). DIBAL−H (0.5 mL, 0.5 mmol, 6 equiv, 1.0 M in n-hexane) was added in one portion at room temperature, and the resulting reaction mixture was heated to reflux and maintained at this temperature for 20 h. The reaction mixture was allowed to cool to room temperature and quenched by careful addition of aqueous HCl (1 M, 5 mL). The organic layer was separated, and the aqueous phase was extracted with tert-butyl methyl ether (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, filtered, and the volatiles were evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using n-pentane/diethyl ether mixtures (100:0→10:1) as eluent affording the analytically pure hydrosilane (SiS)-4d (9.3 mg, 0.057 mmol, 64%, e.r. > 95:5) as colourless oil.[S24]

4.9 Competition Experiment

In a nitrogen-filled glove box, iron(0) complex 2 (4.4 mg, 2.5 mol %, 5.0 μmol), 4-methoxyacetophenone (3a, 30 mg, 0.20 mmol, 1.0 equiv, red square), 4-trifluoromethylacetophenone (3f, 38 mg, 0.20 mmol, 1.0 equiv, blue diamond), and triethoxysilane (4a, 53 mg, 0.32 mmol, 1.6 equiv) were weighed in a Schlenk flask containing a magnetic stirrer and dissolved in 4 mL of THF. A sample (ca. 0.3 mL) was taken after mixing the reaction mixture (2 min) and quenched with a KOH solution (5% in H₂O). The flask was taken out of the glove box, stirred and heated to 70 °C with an oil bath. Samples of ca. 0.3 mL were taken every 5 minutes, quenched, and hydrolysed with 1 mL of KOH solution (5% in H₂O) for 1 h. The mixture was extracted with diethyl ether (2 × 1 mL). The combined organic layers were dried with anhydrous Na₂SO₄ and filtered. The sample was analysed by GC-MS. Integration of the peaks for the ketones and the respective alcohols permitted the evaluation of the conversion for each ketone.
Conversion (%) vs Time (min)

X = OMe (3a)
CF₃ (3f)

X = OMe (5a, ●)
CF₃ (6f, ▲)

2 (2.5 mol %)
4a (1.5 equiv)
THF, 70 °C
then
KOH (5% in H₂O)
5 Cartesian Geometries at ωB97X-D/6-31G(d)[Fe:cc-pVTZ] in Ångström [Å]

5.1 Iron(II) Complex 7a

C 5.078283 -2.422990 -1.821078
C 5.170447 -1.740584 -0.595460
C 6.344834 -1.833764 0.168246
C 7.418988 -2.602213 -0.290359
C 7.329255 -3.278457 -1.516092
C 6.157654 -3.187787 -2.279384
C 4.025198 -0.914503 -0.128438
N 2.988076 -1.343686 0.594893
C 2.790386 -2.604194 1.332259
C 1.545203 -2.394496 2.219895
Si 2.059498 0.340764 0.439762
N 3.825089 0.397898 -0.377674
C 4.592059 1.333048 -1.230328
C 3.931620 2.714602 -1.026920
Fe -0.028991 0.769723 0.196241
P -0.116212 2.937611 0.482472
C -1.302226 3.986007 -0.521396
Si -1.959808 -0.012548 0.588097
N -1.966958 -0.330477 2.389113
C -3.033567 -1.008387 3.130094
C -2.615741 -2.390280 3.656950
N -2.911095 -1.555775 -0.072287
C -2.587349 -2.837279 -0.736440
C -3.569926 -3.968682 -0.355002
C -4.078999 -0.886507 -0.108913
C  3.992802 -2.919593  2.249193
H  6.548538  2.265035 -1.300100
H  4.434355  3.466468 -1.658794
H -0.180292 -0.725658 -0.127063
H -1.708262 -0.052781  5.089284
H  0.348919  0.811099  6.198117
H  2.372675  1.336450  4.822463
H -3.885730 -1.126290  2.448935
H -3.392247 -0.372181  3.962044
H -2.329803 -3.033199  2.811773
H -3.450028 -2.869545  4.200127
H -1.753534 -2.303064  4.335894
H  4.523955  0.643151  2.036253
H  3.828882  0.410796  3.651675
H  4.223345  3.110321  2.196200
H  5.202789  2.507755  3.568967
H  3.478327  2.939337  3.805500
H -3.822709  1.697125  2.735798
H -0.438901 -2.501523 -0.544903
H -0.912955 -4.207803 -0.801178
H -1.146242 -3.439249  0.795242
H -2.298802 -3.545771 -2.788343
H -1.842071 -1.825876 -2.516051
H -3.674328 -4.032235  0.740231
H -3.158102 -4.924209 -0.721678
H -4.563037 -3.831579 -0.805706
H  1.727601 -3.541242 -0.328310
H  2.302893 -4.689020  0.916436
H  3.462859 -3.969409 -0.243253
H  4.876657 -3.232781  1.673535
H  3.717455 -3.738814  2.935642
H  4.245117 -2.031918  2.850898
H  1.768229 -1.685994  3.032553
H  1.248560 -3.358923  2.663073
H  0.711224 -1.987451  1.636052
H  5.082338  0.067525 -2.964041
H  4.873419  1.802627 -3.33712
| H  | 3.438139 | 0.795779 | -3.004554 |
|    | 6.136964 | 1.569263 | 0.295735  |
|    | 6.627906 | 0.498960 | -1.058150 |
|    | 2.864282 | 2.673529 | -1.300121 |
|    | 4.014880 | 3.031824 | 0.022312  |
|    | 4.163173 | -2.343162 | -2.412939 |
|    | 6.410593 | -1.299602 | 1.119465  |
|    | 1.782677 | 4.121694 | -0.578273 |
|    | 2.157497 | 3.601857 | 1.100970  |
|    | 1.137947 | 5.060439 | 0.819669  |
|    | 0.183179 | 3.211954 | 2.911635  |
|    | -1.511535 | 2.870956 | 2.553072  |
|    | -0.860297 | 4.525362 | 2.260927  |
|    | -4.447643 | 2.667223 | -0.840022 |
|    | -5.993078 | 3.006425 | -0.001018 |
|    | -5.860787 | 1.592775 | -1.093933 |
|    | -3.213251 | 2.645717 | 1.346948  |
|    | -6.756461 | 0.226550 | 0.819148  |
|    | -5.781079 | 0.022967 | 2.309703  |
|    | -3.571281 | -2.294406 | -2.612059 |
|    | -5.135730 | -0.352437 | -2.539068 |
|    | -7.384234 | -1.034270 | -3.382997 |
|    | -8.885787 | -2.438382 | -1.960261 |
|    | -8.125610 | -3.167542 | 0.309938  |
|    | -5.884750 | -2.469686 | 1.154321  |
|    | -1.249224 | 5.047193 | -0.212927 |
|    | -2.328575 | 3.614798 | -0.370173 |
|    | -1.039669 | 3.883624 | -1.584948 |
|    | 6.079623 | -3.714425 | -3.234689 |
|    | 8.173089 | -3.872432 | -1.876263 |
|    | 8.329158 | -2.672937 | 0.311114  |
|    | -4.761310 | 3.098578 | 2.113332  |
|    | -6.658754 | 1.550797 | 2.010321  |
|    | -3.949111 | 1.004072 | -2.635445 |
|    | -3.045484 | 0.478648 | -4.061213 |
|    | 1.658698 | 2.773667 | -4.370631 |
|    | 0.140315 | 3.631125 | -4.014973 |
### 5.2 Acetone (3o)

|   | Atom | X        | Y        | Z        |
|---|------|----------|----------|----------|
| H | 2.355894 | -0.997935 | -2.146663 |
| H | 1.020233  | -1.820593 | -1.348902 |
| H | 2.229941  | -3.404713 | -2.835088 |
| H | 0.568630  | -3.140084 | -3.424859 |
| H | 1.933712  | -2.330266 | -4.241387 |
| H | -3.822072 | 2.794201  | -4.348713 |
| H | -2.981742 | 3.305076  | -2.850834 |
| H | -2.035783 | 2.779478  | -4.262469 |
| H | 2.045317  | 5.125846  | -3.768440 |
| H | 1.241140  | 4.896955  | -2.186728 |
| H | 2.789659  | 4.070428  | -2.530040 |

|   | Atom | X        | Y        | Z        |
|---|------|----------|----------|----------|
| C | 1.274692 | -0.180094 | 2.058339 |
| C | 0.006395 | -0.005077 | 1.245844 |
| C | -1.277322 | 0.160314 | 2.035841 |
| O | 0.018038 | 0.002181  | 0.034788 |
| H | 1.149945 | -0.962026 | 2.815510 |
| H | 2.107293 | -0.428140 | 1.398141 |
| H | 1.501620 | 0.750993  | 2.591501 |
| H | -1.167230 | 0.933023 | 2.804659 |
| H | -2.097063 | 0.416455 | 1.362766 |
| H | -1.514415 | -0.777113 | 2.553228 |
5.3 Triethoxysilane (4a)

C   1.863680  0.000020  3.481743  
C   3.053391  -0.487545  2.671877  
O   2.739214  -1.701827  2.007982  
Si  2.365361  -1.767664  0.402031  
O   1.564050  -3.180525  0.175913  
C   0.626388  -3.755539  1.074126  
C   0.685087  -5.267091  0.953073  
H   1.604863  -0.560434  0.015863  
O   3.682417  -1.765679  -0.574082  
C   4.666593  -2.793097  -0.544440  
C   5.731804  -2.482395  -1.577896  
H   3.909104  -0.684372  3.326703  
H   3.367023   0.285710  1.955920  
H   0.846885  -3.445991  2.102850  
H  -0.377797  -3.922874  0.818770  
H   5.109703  -2.849020  0.458885  
H   4.193893  -3.760157  -0.755925  
H  -0.052873  -5.732080  1.615464  
H   0.474894  -5.575334  -0.075383  
H   1.679423  -5.632343  1.227278  
H   6.504097  -3.258805  -1.575727  
H   5.289097  -2.433477  -2.577078  
H   6.203705  -1.518904  -1.363273  
H   2.119982  0.905999  4.041367  
H   1.018630  0.227049  2.823267  
H   1.548331  -0.771269  4.190898
5.4 Silyl Ether 8oa

C  0.131313  -0.235600  0.113836
H  -0.107137  -0.781265  1.041523
O  1.507446  -0.422557  -0.214361
C  -0.733010  -0.784265  -1.013598
C  -0.087724  1.249087  0.359710
H  -0.505231  -0.256303  -1.945301
H  -0.528324  -1.848658  -1.163351
H  -1.796977  -0.656117  -0.787026
H  0.171967  1.816946  -0.539530
H  -1.133560  1.450843  0.613685
H  0.545244  1.598502  1.181349
Si  2.341701  -1.727121  0.319473
O  3.698579  -1.742600  -0.588607
O  2.627229  -1.601979  1.937515
O  1.553287  -3.150641  0.119672
C  2.897139  -0.370115  2.590792
C  0.672742  -3.763000  1.048624
C  4.679201  -2.763446  -0.455442
C  1.828415  -0.924332  3.633702
H  3.881956  -0.448617  3.065093
H  2.939078  0.453381  1.866628
C  0.771799  -5.270194  0.904988
H  0.924723  -3.454869  2.070071
H  -0.352580  -3.428382  0.837663
C  5.694191  -2.617133  -1.572524
H  5.169955  -2.676966  0.523279
H  4.197312  -3.748478  -0.503106
5.5 Tetrahydrofuran
5.6 Benzene

C  -1.498017  2.748940  2.920399
C   -0.517801  1.759962  2.954130
C    0.801580  2.075912  2.638759
C    1.140564  3.381164  2.289622
C    0.160329  4.369941  2.255701
C   -1.159073  4.053921  2.571011
H     2.169575  3.627407  2.043678
H     0.424586  5.387751  1.983164
H   -1.923777  4.824789  2.544491
H   -2.527059  2.502746  3.166228
H   -0.782401  0.742062  3.226236
H    1.566177  1.304908  2.664720

5.7 Transition State 9a‡

C    7.096135 -0.429482  0.964932
C    6.148857 -0.223079 -0.054233
C    6.591801  0.064400 -1.359750
C  7.960599  0.178793 -1.633256  
C  8.903184 -0.015425 -0.608791  
C  4.681179 -0.283614  0.235431  
N  3.960527  0.671588  0.801627  
C  4.442415  2.056800  1.097504  
C  5.420268  2.658673  0.048029  
N  3.892057 -1.323535 -0.141236  
C  4.390441 -2.718436 -0.424415  
C  3.147916 -3.618793 -0.545190  
Si  2.152888 -0.540733  0.303245  
N  1.798069 -1.745960  1.687290  
C  2.777816 -1.980930  2.759456  
C  2.284452 -1.528236  4.140303  
C  0.709957 -2.574728  1.557999  
N -0.215683 -2.238928  0.585568  
C -1.188196 -3.168061  0.275062  
C -1.183099 -4.473528  0.812697  
C -0.312029 -4.744618  1.872730  
C  0.597509 -3.779920  2.300236  
N -2.195737 -2.697903 -0.541857  
Si -2.152500 -0.883451 -0.603054  
N -3.795694 -0.405015 -1.393541  
C -4.479359 -0.399953 -0.211346  
C -5.925582 -0.078546 -0.060490  
C -6.914364 -1.016879 -0.416138  
C -8.270281 -0.715281 -0.238177  
C -8.652017  0.530760  0.289041  
C -7.669547  1.470561  0.640893  
C -6.310932  1.165643  0.472871  
Fe -0.009533 -0.390451 -0.508865  
P  0.517043 -1.465889 -2.417727  
C  0.250193 -3.328945 -2.517393  
Si  0.240060  1.525100 -1.733846  
O  1.583469  1.741034 -2.803564  
C  2.897081  1.999654 -2.341348  
C  3.831302  2.183732 -3.541859
|   |   |   |   |
|---|---|---|---|
| H | -0.348083 | -5.715014 | 2.373426 |
| H | -1.905965 | -5.213150 | 0.478725 |
| H | 3.688761 | -1.429120 | 2.494007 |
| H | 3.051890 | -3.050367 | 2.798184 |
| H | 2.091258 | -0.449078 | 4.149902 |
| H | 3.045378 | -1.762667 | 4.905042 |
| H | 1.343041 | -2.021880 | 4.415161 |
| H | -4.201085 | -2.869542 | -1.064703 |
| H | -3.652574 | -4.088479 | 0.099525 |
| H | -3.005210 | -3.979378 | -2.918222 |
| H | -4.029896 | -5.182167 | -2.081417 |
| H | -2.262553 | -5.151445 | -1.798422 |
| H | 2.645216 | -3.757611 | 0.418810 |
| H | 2.594006 | 2.912311 | 0.257643 |
| H | 3.568858 | 4.029401 | 1.257804 |
| H | 2.589787 | 2.759582 | 2.023514 |
| H | 5.457855 | 3.750467 | 0.189886 |
| H | 5.066407 | 2.459638 | -0.972642 |
| H | 4.446345 | 1.603226 | 3.235096 |
| H | 5.353163 | 3.082154 | 2.795608 |
| H | 6.060910 | 1.476006 | 2.463692 |
| H | -3.744083 | 0.739055 | 3.060093 |
| H | -4.660651 | -0.414699 | 4.038649 |
| H | -5.455453 | 0.379460 | 2.654362 |
| H | -6.177544 | -1.810061 | 1.878488 |
| H | -5.258470 | -2.734476 | 3.086913 |
| H | -4.997044 | -3.047519 | 1.351519 |
| H | -2.624446 | -2.867753 | 2.279430 |
| H | -3.002058 | -2.058996 | 3.820680 |
| H | -1.928583 | -1.263344 | 2.657046 |
| H | -5.085622 | 2.063952 | -1.626652 |
| H | -4.562328 | 2.357740 | -3.302411 |
| H | -3.332920 | 2.205832 | -2.014207 |
| H | -5.626075 | -1.292092 | -3.162174 |
| H | -6.447635 | 0.192766 | -2.592404 |
| H | -2.193144 | 0.319218 | -3.343240 |
| H | -3.188349 | -1.064052 | -3.927580 |
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| H    | -5.542882| 1.886729 | 0.753867 |
| H    | -6.612473| -1.981676| -0.824812|
| H    | -0.263271| -0.032988| -4.297101|
| H    | -1.185828| -1.567633| -4.245556|
| H    | 0.479362 | -1.553056| -4.879046|
| H    | -0.802881| -3.500236| -2.769811|
| H    | 0.455484 | -3.839356| -1.569515|
| H    | 0.888433 | -3.756440| -3.308163|
| H    | 4.654604 | -2.348901| -2.592581|
| H    | 5.317981 | -3.889344| -1.997601|
| H    | 6.183304 | -2.374361| -1.671552|
| H    | 2.445069 | -3.176533| -1.253001|
| H    | 6.307374 | -2.824967| 0.656491 |
| H    | 4.877393 | -3.102832| 1.689276 |
| H    | 6.442944 | 2.275528 | 0.148068 |
| H    | 5.857614 | 0.208879 | -2.151124|
| H    | 8.292696 | 0.415783 | -2.646256|
| H    | 9.970533 | 0.071923 | -0.822284|
| H    | 9.194624 | -0.490502| 1.488154 |
| H    | 6.753559 | -0.674473| 1.971201 |
| H    | 2.539337 | -2.187500| -3.674735|
| H    | 3.012455 | -1.228775| -2.230710|
| H    | 2.333362 | -0.402887| -3.646786|
| H    | -7.958974| 2.440284 | 1.050850 |
| H    | -9.709371| 0.766660 | 0.425205 |
| H    | -9.028936| -1.451653| -0.511021|
| H    | 3.447396 | -4.607195| -0.926067|
| H    | 5.417511 | -4.359395| 0.548680 |
| H    | -1.144882| 1.678695 | -4.898877|
| H    | 0.167771 | 2.760590 | -4.366466|
| H    | 1.342714 | 4.606288 | -0.891046|
| H    | 0.201165 | 4.305389 | -2.225493|
| H    | 2.909310 | 2.911180 | -1.716184|
| H    | 3.264101 | 1.168416 | -1.710556|
| H    | 4.856372 | 2.414221 | -3.204779|
| H    | 3.860092 | 1.268995 | -4.155277|
| H    | 3.476275 | 3.012150 | -4.175984|
| Atoms | x    | y    | z    |
|-------|------|------|------|
| H     | -1.735937 | 4.054099 | -5.373379 |
| H     | -2.851602  | 3.382289  | -4.144472  |
| H     | -1.533714  | 4.472302  | -3.642576  |
| H     | -0.601068  | 6.147975  | -0.656249  |
| H     | -1.735304  | 4.755984  | -0.694515  |
| H     | -0.611420  | 4.956751  | 0.680491   |
| H     | -1.194788  | 2.103652  | 4.540576   |
| H     | -2.103818  | 0.638300  | 4.101402   |
| H     | -1.882707  | 3.359320  | 3.186247   |
| H     | -1.777941  | 3.669871  | 1.440208   |
| H     | -0.528644  | 3.603896  | 3.357169   |
| H     | 0.984182   | 2.742559  | 3.694685   |
| H     | -1.533367  | 0.651268  | 6.446071   |
| H     | -0.720516  | -0.675643 | 5.581751   |
| H     | 0.191761   | 0.784611  | 6.030298   |
| H     | -3.864754  | 4.467868  | 2.362740   |
| H     | -4.119857  | 3.152809  | 1.191564   |
| H     | -4.238964  | 2.825941  | 2.936430   |
| H     | 1.304298   | 5.136659  | 3.734123   |
| H     | 2.226136   | 4.373930  | 2.417446   |
| H     | 0.717894   | 5.245745  | 2.057473   |
| Si    | -0.494112  | 1.293582  | 1.978123   |
5.8 Transition State 10oa$^2$

![Diagram of molecular structure]

| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | -6.738987 | -1.357006 | 0.088629 |
| C       | -6.227574 | -0.087057 | -0.241705 |
| C       | -7.120846 | 0.962220 | -0.522114 |
| C       | -8.506596 | 0.750859 | -0.458676 |
| C       | -9.010324 | -0.512462 | -0.108491 |
| C       | -8.121564 | -1.566596 | 0.164383 |
| C       | -4.744760 | 0.132408 | -0.249102 |
| N       | -4.056330 | 0.724896 | 0.712145 |
| C       | -4.611384 | 1.124690 | 2.046263 |
| C       | -5.659529 | 0.148722 | 2.654430 |
| Si      | -2.185011 | -0.009503 | -0.459534 |
| N       | -3.947991 | -0.331525 | -1.252267 |
| C       | -4.430229 | -0.617163 | -2.654293 |
| C       | -3.179800 | -0.865033 | -3.516309 |
| Fe      | -0.111024 | -1.000386 | -2.530205 |
| Si      | -0.510646 | -2.110346 | 1.702501 |
| O       | -1.915380 | -3.105891 | 1.900999 |
| C       | -3.209099 | -2.549058 | 2.067318 |
| C       | -4.227224 | -3.676495 | 2.268320 |
| N       | 0.223189 | -0.045017 | -2.164813 |
| C       | -0.601950 | 1.006519 | -2.530205 |
| C       | -0.406971 | 1.680795 | -3.765503 |
| C       | 0.459835 | 1.126043 | -4.705058 |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | 1.222595 | -0.003197 | -4.388358 |
| C       | 1.168577  | -0.487105  | -3.063487 |
| N       | -1.665623 | 1.289981  | -1.701196 |
| C       | -2.517719 | 2.452902  | -1.992310 |
| C       | -1.870968 | 3.783747  | -1.588192 |
| N       | 2.088866  | -1.374148 | -2.541873 |
| Si      | 2.035469  | -1.342407 | -0.724786 |
| N       | 3.679893  | -0.126223 | -0.644670 |
| C       | 4.232278  | 1.149148  | -1.212061 |
| C       | 5.388598  | 0.918306  | -2.217392 |
| P       | -0.791765 | -2.919249 | -1.234170 |
| C       | -0.501336 | -3.156340 | -3.080681 |
| C       | -2.616639 | -3.372199 | -1.111175 |
| C       | -0.253993 | -4.663463 | -0.759707 |
| C       | 3.236487  | -1.792092 | -3.350957 |
| C       | 2.925113  | -2.970317 | -4.290862 |
| N       | 3.589799  | -2.262871 | -0.185494 |
| C       | 4.390601  | -1.157747 | -0.237555 |
| C       | 5.842314  | -1.137611 | 0.095278  |
| C       | 6.270726  | -0.573273 | 1.312296  |
| C       | 7.636484  | -0.528171 | 1.627856  |
| C       | 8.585623  | -1.033930 | 0.724671  |
| C       | 8.162408  | -1.591260 | -0.494662 |
| C       | 6.798164  | -1.646542 | -0.806115 |
| C       | 3.891703  | -3.492303 | 0.614116  |
| C       | 5.192737  | -4.194724 | 0.149313  |
| C       | 2.734746  | -4.458621 | 0.365320  |
| C       | 3.990594  | -3.147719 | 2.114872  |
| C       | 3.086859  | 1.845819  | 1.970654  |
| C       | 4.748952  | 2.070122  | -0.087778 |
| O       | 0.661723  | -3.245075 | 2.223216  |
| C       | 0.452420  | -4.522552 | 2.827223  |
| C       | 1.309740  | -4.667570 | 4.089360  |
| O       | -0.662110 | -1.033952 | 3.030318  |
| C       | -0.870017 | -1.448140 | 4.376414  |
| C       | 0.083431  | -0.675722 | 5.294830  |
| C       | -5.225808 | 0.562553  | -3.267081 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -5.338487 | -1.876651 | -2.753184 |
| C    | -5.233540  | 2.536002  | 1.912346  |
| C    | -3.446650  | 1.220568  | 3.056415  |
| H    | 0.358492   | 0.813087  | -0.091722 |
| H    | 5.192598   | -5.218373 | 0.557812  |
| H    | 2.866694   | -5.365223 | 0.975697  |
| H    | 1.383774   | -0.793818 | 0.644390  |
| H    | -0.980937  | 2.569896  | -4.008369 |
| H    | 0.549948   | 1.581911  | -5.693811 |
| H    | 1.914638   | -0.433323 | -5.107663 |
| H    | -3.451657  | 2.315550  | -1.431719 |
| H    | -2.786372  | 2.472570  | -3.063455 |
| H    | -1.685666  | 3.811197  | -0.507912 |
| H    | -2.536223  | 4.622003  | -1.859126 |
| H    | -0.900118  | 3.929361  | -2.079220 |
| H    | 4.037781   | -2.088922 | -2.661323 |
| H    | 3.612924   | -0.936136 | -3.938189 |
| H    | 2.688488   | -3.873145 | -3.706600 |
| H    | 3.798392   | -3.188042 | -4.929020 |
| H    | 2.064506   | -2.743759 | -4.937624 |
| H    | -2.596922  | 0.050006  | -3.668557 |
| H    | -2.851372  | 0.298090  | 3.076936  |
| H    | -3.859780  | 1.404108  | 4.061156  |
| H    | -2.790430  | 2.059203  | 2.808973  |
| H    | -5.755572  | 0.363484  | 3.730775  |
| H    | -5.329878  | -0.893810 | 2.542611  |
| H    | -4.501696  | 3.229558  | 1.468377  |
| H    | -5.514684  | 2.914886  | 2.909563  |
| H    | -6.135529  | 2.513457  | 1.285217  |
| H    | 3.978813   | 2.261057  | 0.663714  |
| H    | 5.017562   | 3.041000  | -0.527897 |
| H    | 5.643763   | 1.643347  | 0.386631  |
| H    | 6.326453   | 0.635078  | -1.724136 |
| H    | 5.562011   | 1.864402  | -2.754789 |
| H    | 5.122136   | 0.148695  | -2.954819 |
| H    | 2.869810   | 1.327380  | -2.913387 |
| H    | 3.391737   | 2.876952  | -2.206244 |
|   |   |   |
|---|---|---|
| H | 2.178487 | 1.900982 | -1.365048 |
| H | 4.844963 | -2.483208 | 2.305938 |
| H | 4.146075 | -4.073714 | 2.692640 |
| H | 3.061383 | -2.673111 | 2.455028 |
| H | 5.226073 | -4.262534 | -0.949915 |
| H | 6.099864 | -3.692561 | 0.504415 |
| H | 1.789772 | -3.981745 | 0.638244 |
| H | 2.721730 | -4.751726 | -0.695866 |
| H | 5.529849 | -0.171571 | 2.004351 |
| H | 6.465187 | -2.076953 | -1.750995 |
| H | -0.226555 | -4.772161 | 0.331340 |
| H | 0.726263 | -4.908610 | -1.182029 |
| H | -0.991544 | -5.372402 | -1.170257 |
| H | 0.526463 | -3.513811 | -3.211425 |
| H | -0.607690 | -2.226025 | -3.649998 |
| H | -1.201636 | -3.909960 | -3.476337 |
| H | -4.902725 | -2.744426 | -2.243528 |
| H | -5.456444 | -2.131771 | -3.819276 |
| H | -6.338365 | -1.690569 | -2.344017 |
| H | -2.548746 | -1.613882 | -3.035658 |
| H | -6.239054 | 0.626382 | -2.850563 |
| H | -4.714598 | 1.519048 | -3.111119 |
| H | -6.654544 | 0.255239 | 2.206515 |
| H | -6.046669 | -2.170455 | 0.299818 |
| H | -8.506149 | -2.552377 | 0.434690 |
| H | -10.088592 | -0.675521 | -0.051453 |
| H | -9.190697 | 1.572314 | -0.681655 |
| H | -6.726241 | 1.942251 | -0.792914 |
| H | -2.896729 | -4.030762 | -1.950464 |
| H | -3.263722 | -2.493209 | -1.096009 |
| H | -2.740874 | -3.912124 | -0.166066 |
| H | 7.958117 | -0.093526 | 2.576420 |
| H | 9.649249 | -0.993722 | 0.968080 |
| H | 8.895553 | -1.982886 | -1.202753 |
| H | -3.484338 | -1.248804 | -4.502043 |
| H | -5.319347 | 0.393807 | -4.352653 |
| H | 0.732508 | -5.304723 | 2.094744 |
H  -0.611444  -4.664804  3.073855  
H  -1.919126  -1.230840  4.657793  
H  -0.717528  -2.535510  4.493871  
H  -3.224876  -1.872946  2.941777  
H  -3.493487  -1.941561  1.188162  
H  -5.237987  -3.264033  2.428776  
H  -4.253959  -4.339265  1.388718  
H  -3.952706  -4.283020  3.146557  
H  1.173060  -5.672743  4.524989  
H  2.374869  -4.525275  3.857466  
H  1.018551  -3.915439  4.839615  
H  -0.124445  -0.894536  6.356749  
H  1.127887  -0.946616  5.072271  
H  -0.036181  0.407465  5.127560  
C  0.513390  1.512988  0.837410  
O  0.917098  2.785284  0.155185  
C  -0.761810  1.800194  1.586817  
C  1.634917  1.132464  1.806896  
Si  1.269803  4.274204  0.713920  
H  -0.587384  2.607189  2.312051  
H  -1.563827  2.128123  0.909360  
H  -1.063953  0.900917  2.117513  
H  1.833594  2.004989  2.452592  
H  1.325769  0.300369  2.450646  
H  2.553707  0.859650  1.274989  
O  0.548305  5.371749  -0.307320  
O  0.722706  4.644095  2.249401  
O  2.927304  4.459300  0.703484  
C  0.176067  6.694283  0.106176  
C  3.548340  5.739676  0.877213  
C  1.512577  4.553508  3.444207  
C  -0.627801  7.351143  -1.015423  
H  -0.415338  6.645653  1.036049  
H  1.083048  7.292759  0.315541  
C  0.751121  3.789626  4.529922  
H  2.480828  4.065003  3.236929  
H  1.728492  5.581512  3.783633
5.9 Transition State 13a‡

\[
\begin{aligned}
\text{C} & : 3.832835 \quad 6.397607 \quad -0.476426 \\
\text{H} & : 2.923943 \quad 6.409472 \quad 1.498341 \\
\text{H} & : 4.489965 \quad 5.564939 \quad 1.425360 \\
\text{H} & : 4.356380 \quad 7.358653 \quad -0.335911 \\
\text{H} & : 4.464335 \quad 5.737198 \quad -1.091216 \\
\text{H} & : 2.891753 \quad 6.755595 \quad -1.016605 \\
\text{H} & : 1.321484 \quad 3.808366 \quad 5.473854 \\
\text{H} & : -0.232825 \quad 4.253205 \quad 4.701883 \\
\text{H} & : 0.595912 \quad 2.741669 \quad 4.233769 \\
\text{H} & : -0.911076 \quad 8.377527 \quad -0.728405 \\
\text{H} & : -0.029777 \quad 7.394517 \quad -1.939524 \\
\text{H} & : -1.540697 \quad 6.771922 \quad -1.219979 \\
\end{aligned}
\]

\[
\begin{aligned}
\text{C} & : 0.844488 \quad 3.289843 \quad -0.260515 \\
\text{C} & : 0.751075 \quad 4.695657 \quad -0.417166 \\
\text{C} & : -0.426784 \quad 5.337769 \quad -0.040257 \\
\text{C} & : -1.524384 \quad 4.599170 \quad 0.411350 \\
\text{Fe} & : 0.043763 \quad 0.518826 \quad 0.696527 \\
\text{Si} & : 0.296858 \quad -1.667728 \quad 1.044809 \\
\text{O} & : -0.149950 \quad -2.801952 \quad -0.189135 \\
\end{aligned}
\]
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 6.253475| -0.362367 | -2.076218 |
| C       | 7.414548| -1.102532 | -2.341198 |
| C       | 7.588386| -2.371264 | -1.762947 |
| C       | 6.598325| -2.896510 | -0.916891 |
| C       | 5.438983| -2.155532 | -0.645002 |
| C       | 2.536925| -0.813049 | -2.821128 |
| C       | 2.475177| -2.321669 | -2.498184 |
| C       | 3.534193| -0.546729 | -3.974561 |
| C       | 1.144876| -0.346737 | -3.284806 |
| C       | 6.121236| 1.510587  | 0.748669  |
| C       | 5.109300| -0.311961 | 2.184747  |
| O       | 1.947196| -2.162650 | 1.229030  |
| C       | 2.334490| -3.477061 | 1.605277  |
| C       | 2.498486| -3.586245 | 3.128821  |
| O       | -0.552168| -2.283468 | 2.435656  |
| C       | -0.988753| -3.637580 | 2.560057  |
| C       | -1.648525| -3.838693 | 3.927711  |
| H       | -6.408715| -0.986529 | 2.616501  |
| H       | -4.230506| -1.326703 | 3.722356  |
| H       | 0.074637 | 0.118764  | -0.772491 |
| H       | 1.587353 | 5.266676  | -0.812372 |
| H       | -0.501234| 6.424861  | -0.122080 |
| H       | -2.456762| 5.094751  | 0.667492  |
| H       | 3.959591 | 2.586200  | -1.218038 |
| H       | 3.355319 | 4.182330  | -0.770332 |
| H       | 2.584422 | 2.567306  | -3.289441 |
| H       | 3.613756 | 4.033225  | -3.264471 |
| H       | 1.870933 | 4.149767  | -2.870055 |
| H       | -4.533107| 2.088435  | 0.547949  |
| H       | -3.981673| 3.698287  | 0.052542  |
| H       | -4.119432| 2.595138  | 2.941305  |
| H       | -5.194171| 3.847008  | 2.244390  |
| H       | -3.461035| 4.198105  | 2.526837  |
| H       | 3.906479 | 2.908140  | 1.543751  |
| H       | 0.387204 | -0.606886 | -2.538330 |
| H       | 0.896009 | -0.849176 | -4.232487 |
| H       | 1.122608 | 0.741473  | -3.445188 |
| H     | 2.094067 | -2.866064 | -3.379027 |
|-------|----------|-----------|-----------|
| H     | 1.805725 | -2.502854 | -1.646104 |
| H     | 3.660446 | 0.536888  | -4.132135 |
| H     | 3.133518 | -0.989007 | -4.901252 |
| H     | 4.515459 | -0.997484 | -3.781457 |
| H     | -1.656314| -0.663922 | -3.441142 |
| H     | -2.386917| 0.342235  | -4.723306 |
| H     | -3.400189| -0.805630 | -3.807060 |
| H     | -4.982621| 1.104960  | -3.294536 |
| H     | -3.931121| 2.318124  | -4.069891 |
| H     | -4.401521| 2.517863  | -2.356609 |
| H     | -1.936521| 2.887834  | -2.053718 |
| H     | -1.462826| 2.351255  | -3.690468 |
| H     | -0.787297| 1.542640  | -2.238488 |
| H     | -5.035649| -2.795829 | 0.383483  |
| H     | -4.992075| -3.073089 | 2.144696  |
| H     | -3.463517| -2.923503 | 1.237485  |
| H     | -5.946542| 0.575241  | 1.879886  |
| H     | -6.552119| -0.763599 | 0.854173  |
| H     | -2.701438| -1.126314 | 2.809364  |
| H     | -3.741748| 0.292075  | 3.148650  |
| H     | -3.919047| -2.629128 | -2.052132 |
| H     | -6.532329| 0.674450  | -1.120480 |
| H     | -1.424271| 0.001570  | 4.761062  |
| H     | -1.944677| 1.639464  | 4.248237  |
| H     | -0.789701| 1.447636  | 5.609721  |
| H     | -0.074260| 3.527434  | 3.527267  |
| H     | 1.619596 | 3.213014  | 3.101446  |
| H     | 1.083164 | 3.038653  | 4.810790  |
| H     | 4.179724 | -0.831594 | 2.453608  |
| H     | 5.636224 | -0.001885 | 3.102489  |
| H     | 5.751779 | -1.017284 | 1.639497  |
| H     | 3.163482 | 1.647657  | 2.557468  |
| H     | 6.717812 | 0.749180  | 0.229883  |
| H     | 5.907067 | 2.336391  | 0.051471  |
| H     | 3.474147 | -2.714541 | -2.264699 |
| H     | 4.660469 | -2.547757 | 0.007563  |
| H       | 6.726611 | -3.883178 | -0.467040 |
|---------|----------|-----------|-----------|
| H       | 8.492258 | -2.947366 | -1.971701 |
| H       | 8.182543 | -0.689401 | -2.998418 |
| H       | 6.110950 | 0.622902  | -2.522630 |
| H       | 1.640961 | 0.609180  | 5.463590  |
| H       | 2.500942 | 0.053789  | 3.984551  |
| H       | 1.112486 | -0.870168 | 4.581461  |
| H       | -5.771742| -3.753147 | -3.293128 |
| H       | -8.013334| -2.655104 | -3.452594 |
| H       | -8.390745| -0.435972 | -2.364192 |
| H       | 4.763734 | 2.303614  | 2.997378  |
| H       | 6.721160 | 1.907186  | 1.583738  |
| H       | 3.306040 | -3.700566 | 1.123619  |
| H       | 1.622875 | -4.232686 | 1.225169  |
| H       | -1.706828| -3.882386 | 1.754543  |
| H       | -0.147611| -4.344432 | 2.456554  |
| H       | -2.205151| -2.798842 | -0.540977 |
| H       | -1.276829| -1.572250 | -1.421355 |
| H       | -1.968631| -3.446862 | -2.944440 |
| H       | -0.187232| -3.378251 | -2.801659 |
| H       | -1.100621| -4.619741 | -1.901637 |
| H       | 2.807199 | -4.606769 | 3.415855  |
| H       | 3.264348 | -2.873854 | 3.477124  |
| H       | 1.552341 | -3.336650 | 3.630554  |
| H       | -1.995754| -4.880001 | 4.044103  |
| H       | -0.930075| -3.616127 | 4.733097  |
| H       | -2.511467| -3.165273 | 4.040181  |
5.10 Intermediate *cis*-14a

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| C       | -4.959676 | -2.107994 | -1.269533 |
| C       | -5.255469  | -0.787792  | -0.879638  |
| C       | -6.573973  | -0.305068  | -0.959465  |
| C       | -7.595818  | -1.140784  | -1.435315  |
| C       | -7.302628  | -2.457346  | -1.827498  |
| C       | -5.985072  | -2.39462   | -1.740757  |
| C       | -4.146769  | 0.081155   | -0.406222  |
| N       | -3.260894  | 0.728699   | -1.177748  |
| C       | -3.095408  | 0.820573   | -2.640954  |
| C       | -2.149190  | 2.018650   | -2.883772  |
| Si      | -2.133957  | 1.032882   | 0.295678   |
| N       | -3.781949  | 0.305999   | 0.872068   |
| C       | -4.293278  | -0.287817  | 2.128605   |
| C       | -3.309584  | 0.145639   | 3.236247   |
| Fe      | -0.037443  | 0.638077   | 0.486048   |
| N       | 0.045055   | 2.743072   | 0.472877   |
| C       | 1.242397   | 3.407500   | 0.270365   |
| C       | 1.326030   | 4.820517   | 0.319759   |
| C       | 0.164923   | 5.559552   | 0.545692   |
| C       | -1.065946  | 4.915337   | 0.676073   |
| C       | -1.107777  | 3.503904   | 0.595996   |
| N       | 2.347553   | 2.611745   | 0.013919   |
| C       | 3.628212   | 3.231198   | -0.341580  |
| C       | 3.651920   | 3.760123   | -1.787457  |
| N       | -2.302217  | 2.800974   | 0.590822   |
| C       | -3.583103  | 3.515469   | 0.557997   |
| C       | -4.043549  | 3.994018   | 1.947259   |
| Si      | 2.071781   | 0.820628   | 0.092849   |
N  3.736639  0.304873  0.885381
C  4.360000  0.429027  2.217882
C  5.766207  1.064194  2.133634
C  4.206678  -0.146884  -0.284217
N  3.289127  0.163697  -1.225795
C  3.137855  -0.407629  -1.020530
C  4.335831  -0.019511  -3.486833
C  5.497499  -0.859179  -0.491867
C  6.601898  -0.162407  -1.83728
C  7.965764  -2.166965  -0.827942
C  6.864299  -2.864836  -0.306453
C  5.634208  -2.213197  -0.133418
C  1.853706  0.203641  -3.187155
C  2.990116  -1.944931  -2.522292
C  4.442983  -0.951906  2.908268
C  3.432598  1.351681  3.040203
Si -0.347308  -1.569794  0.545651
O  -1.571276  -2.194447  -0.503445
C  -1.446044  -3.332053  -1.35596
O  0.878263  -2.748975  0.191345
C  2.009819  -2.870936  1.031245
O  -0.821621  -1.995889  2.150369
C  -1.025260  -3.331633  2.603937
C  -4.320577  -1.831194  2.061765
C  -5.702072  0.270567  2.427744
C  -2.445047  -0.474141  -3.177006
C  -4.440901  1.085366  -3.348996
H  -6.048849  -0.105840  3.404042
H  -3.685637  -0.197227  4.213075
H  -0.131441  0.549337  -0.990858
H  2.276494  5.326939  0.175244
H  0.217355  6.649501  0.602051
H  -1.977893  5.488546  0.819186
H  4.405182  2.464002  -0.224848
H  3.880597  4.035586  0.373401
H  3.463173  2.928138  -2.482737
|   |    |    |    |
|---|----|----|----|
| H | 4.633206 | 4.205944 | -2.025020 |
| H | 2.872926 | 4.522127 | -1.939260 |
| H | -4.329483 | 2.819060 | 0.147370  |
| H | -3.520645 | 4.368804 | -0.142223 |
| H | -4.182755 | 3.129574 | 2.613556  |
| H | -5.000155 | 4.538982 | 1.873346  |
| H | -3.295028 | 4.659030 | 2.403758  |
| H | 3.359616  | 2.345902 | 2.575537  |
| H | 0.974038  | -0.090237 | -2.598854 |
| H | 1.730718  | -0.153141 | -4.221707 |
| H | 1.912730  | 1.303586 | -3.195683 |
| H | 2.756459  | -2.337536 | -3.525895 |
| H | 2.180696  | -2.221567 | -1.830436 |
| H | 4.487711  | 1.071607 | -3.475687 |
| H | 4.123577  | -0.331907 | -4.522049 |
| H | 5.262216  | -0.512358 | -3.164012 |
| H | -1.553399 | -0.716013 | -2.583356 |
| H | -2.168520 | -0.342458 | -4.236505 |
| H | -3.149912 | -1.314772 | -3.099317 |
| H | -5.118096 | 0.224120  | -3.272948 |
| H | -4.248032 | 1.280910  | -4.416038 |
| H | -4.936741 | 1.969146  | -2.915572 |
| H | -2.597929 | 2.948325  | -2.499868 |
| H | -1.967871 | 2.128610  | -3.964628 |
| H | -1.186946 | 1.856454  | -2.374603 |
| H | -5.103589 | -2.192088 | 1.380897  |
| H | -4.525232 | -2.233750 | 3.067526  |
| H | -3.343349 | -2.195457 | 1.721738  |
| H | -5.680441 | 1.371395  | 2.463054  |
| H | -6.421476 | -0.049286 | 1.659560  |
| H | -2.323097 | -0.305532 | 3.055410  |
| H | -3.212286 | 1.242676  | 3.261760  |
| H | -3.936138 | -2.464100 | -1.168755 |
| H | -6.790755 | 0.722422  | -0.662082 |
| H | 3.444736  | -1.409714 | 2.962851  |
| H | 4.834792  | -0.829022 | 3.931362  |
| H | 5.115796  | -1.624842 | 2.357642  |
H 2.419723 0.921509 3.097793
H 6.477591 0.404564 1.618348
H 5.721244 2.027233 1.601546
H 3.927643 -2.410853 -2.183330
H 4.775635 -2.750494 0.265317
H 6.959569 -3.917904 -0.033951
H 8.923646 -2.674455 -0.958185
H 8.685471 -0.266725 -1.589744
H 6.489043 0.886782 -1.297846
H -5.755404 -3.965401 -2.036401
H -8.099289 -3.106514 -2.196981
H -8.618380 -0.763319 -1.500970
H 3.830449 1.457611 4.061217
H 6.140474 1.247112 3.153655
H 2.725522 -2.055079 0.828884
H 1.727046 -2.781218 2.098947
C 2.672319 -4.231802 0.789673
C -1.277260 -3.315730 4.114447
H -1.891238 -3.782723 2.084483
H -0.145967 -3.961937 2.370379
H -2.141789 -3.180247 -2.202125
H -0.426910 -3.400116 -1.771673
C -1.788644 -4.640544 -0.633023
H -1.442083 -4.339462 4.492667
H -0.414200 -2.877506 4.641627
H -2.165784 -2.706435 4.343820
H 3.558412 -4.356614 1.436962
H 1.961886 -5.044605 1.009627
H 2.983778 -4.324702 -0.263477
H -1.769047 -5.490077 -1.338946
H -1.056914 -4.825853 0.165923
H -2.793512 -4.580982 -0.181667
5.11 Transition State 15a‡

C  -0.527473  1.861621  2.868683
C   0.775473  2.233001  2.522584
C   1.054831  3.577897  2.196099
C   0.055253  4.525048  2.204899
C  -1.247789  4.163771  2.582904
C  -1.526768  2.856414  2.917030
Fe  -0.017688  0.790118  0.546070
Si  -2.108398  0.762741  0.044985
N  -2.897341  0.013512 -1.486726
C  -2.721066  0.068260 -2.945292
C  -2.348778 -1.308284 -3.514767
N  -0.165516  2.548601 -0.509389
C   0.913423  3.022479 -1.185282
C   0.894510  4.301474 -1.770616
C  -0.270847  5.042811 -1.700655
C  -1.417947  4.511704 -1.134193
C  -1.352734  3.217101 -0.594336
N   2.007046  2.186081 -1.279381
Si   1.962126  0.699853 -0.261671
N   2.826391 -0.664328 -1.276150
C   3.990233 -0.477710 -0.643561
C   5.207174 -1.335143 -0.739654
C   5.436826 -2.317536  0.224094
C   6.580306 -3.106603  0.160338
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 7.504287| -2.915181| -0.863426|
| C    | 7.279285| -1.934593| -1.826576|
| C    | 6.133369| -1.147440| -1.766410|
| N    | -2.470860| 2.506513| -0.219375|
| C    | -3.794251| 3.047203| -0.473249|
| C    | -4.285258| 4.001072| 0.614783|
| Si   | -0.162932| -1.282614| 1.383123|
| O    | 1.178588| -2.323696| 1.692872|
| C    | 2.264948| -1.855442| 2.438889|
| C    | 2.988832| -3.028370| 3.082357|
| O    | -0.941410| -1.324441| 2.918474|
| C    | -0.890958| -2.356646| 3.867883|
| C    | -0.495022| -1.796045| 5.226981|
| O    | -1.030627| -2.378826| 0.381464|
| C    | -0.802995| -3.759414| 0.225858|
| C    | -1.730173| -4.611352| 1.085300|
| C    | 3.039175| 2.474214| -2.262808|
| C    | 2.571377| 2.248166| -3.700576|
| N    | 3.866918| 0.589742| 0.132269|
| C    | 4.887883| 1.297424| 0.922135|
| C    | 5.325679| 0.480222| 2.148088|
| C    | 4.225374| 2.583201| 1.416684|
| C    | 6.112540| 1.674476| 0.073100|
| C    | 2.443813| -1.835645| -2.099905|
| C    | 0.979349| -1.674007| -2.506670|
| C    | 2.577772| -3.148301| -1.310787|
| C    | 3.289004| -1.878882| -3.383219|
| N    | -3.757964| -0.052543| 0.481516|
| C    | -3.846964| -0.554997| -0.757507|
| C    | -4.736057| -1.653995| -1.217193|
| C    | -4.177449| -2.931649| -1.289970|
| C    | -4.953680| -4.004001| -1.712331|
| C    | -6.283343| -3.799970| -2.077226|
| C    | -6.835936| -2.523223| -2.016170|
| C    | -6.064122| -1.447652| -1.583544|
| C    | -4.440755| -0.515255| 1.707141|
| C    | -4.150098| -1.990036| 2.010821|
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -5.951648 | -0.264631 | 1.591937 |
| C    | -3.891889 | 0.337484  | 2.849038 |
| C    | -4.004177 | 0.590788  | -3.610249 |
| C    | -1.592206 | 1.071225  | -3.223656 |
| H    | -6.426866 | -0.435992 | 2.563931 |
| H    | -4.379727 | 0.060295  | 3.789218 |
| H    | 0.101839  | 0.104659  | -0.798753 |
| H    | 1.769695  | 4.697936  | -2.267718 |
| H    | -0.297354 | 6.041629  | -2.128392 |
| H    | -2.344338 | 5.069366  | -1.138383 |
| H    | 3.875811  | 1.803077  | -2.053222 |
| H    | 3.434327  | 3.492263  | -2.136513 |
| H    | 2.228071  | 1.214773  | -3.814657 |
| H    | 3.387599  | 2.425229  | -4.410252 |
| H    | 1.739504  | 2.910063  | -3.959554 |
| H    | -4.483160 | 2.198155  | -0.532574 |
| H    | -3.826377 | 3.541021  | -1.456168 |
| H    | -4.308112 | 3.488461  | 1.581532 |
| H    | -5.294788 | 4.361474  | 0.387194 |
| H    | -3.623992 | 4.866625  | 0.716009 |
| H    | 3.791702  | 3.145792  | 0.584271 |
| H    | 0.312219  | -1.744278 | -1.644100 |
| H    | 0.720472  | -2.468707 | -3.214838 |
| H    | 0.810479  | -0.712440 | -3.001559 |
| H    | 2.057175  | -3.951534 | -1.844572 |
| H    | 2.120816  | -3.035785 | -0.321703 |
| H    | 3.226675  | -0.923360 | -3.915709 |
| H    | 2.909356  | -2.664807 | -4.045165 |
| H    | 4.338612  | -2.099513 | -3.179386 |
| H    | -1.545799 | -1.754148 | -2.924396 |
| H    | -2.008685 | -1.205421 | -4.551167 |
| H    | -3.202696 | -1.990771 | -3.506691 |
| H    | -4.827345 | -0.123763 | -3.520247 |
| H    | -3.825164 | 0.761753  | -4.677548 |
| H    | -4.307512 | 1.540346  | -3.155777 |
| H    | -1.895759 | 2.089172  | -2.958520 |
| H    | -1.346008 | 1.059247  | -4.290610 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -0.694288 | 0.828701 | -2.650646 |
| H    | -4.595957  | -2.656540 | 1.268116  |
| H    | -4.571337  | -2.250534 | 2.988601  |
| H    | -3.070360  | -2.152577 | 2.035117  |
| H    | -6.146053  | 0.772056  | 1.293536  |
| H    | -6.423851  | -0.935339 | 0.870240  |
| H    | -2.816335  | 0.175313  | 2.958677  |
| H    | -4.096861  | 1.394989  | 2.656689  |
| H    | -3.138792  | -3.060062 | -0.999695 |
| H    | -6.491551  | -0.450555 | -1.531619 |
| H    | 4.453632   | 0.190648  | 2.743371  |
| H    | 5.985205   | 1.086570  | 2.779207  |
| H    | 5.870527   | -0.422913 | 1.862727  |
| H    | 3.432861   | 2.337931  | 2.124616  |
| H    | 6.694471   | 0.800266  | -0.225223 |
| H    | 5.806470   | 2.219179  | -0.826490 |
| H    | 3.620709   | -3.453406 | -1.193153 |
| H    | 4.711002   | -2.470144 | 1.015761  |
| H    | 6.746735   | -3.871160 | 0.912765  |
| H    | 8.398640   | -3.528880 | -0.911558 |
| H    | 7.997320   | -1.780127 | -2.626014 |
| H    | 5.957255   | -0.378800 | -2.513446 |
| H    | -4.518116  | -4.997300 | -1.759054 |
| H    | -6.889763  | -4.636948 | -2.410164 |
| H    | -7.870775  | -2.362278 | -2.301953 |
| H    | 4.956440   | 3.213872  | 1.932548  |
| H    | 6.770440   | 2.327306  | 0.656745  |
| H    | 2.955425   | -1.294273 | 1.790918  |
| H    | 1.943878   | -1.149114 | 3.222798  |
| H    | -1.883035  | -2.830541 | 3.942335  |
| H    | -0.177758  | -3.134405 | 3.562102  |
| H    | -0.965346  | -4.002256 | -0.836964 |
| H    | 0.237088   | -4.009696 | 0.460221  |
| H    | -0.490422  | -2.580002 | 5.993336  |
| H    | 0.504438   | -1.350308 | 5.178173  |
| H    | -1.198695  | -1.014434 | 5.533053  |
| H    | 3.893925   | -2.695243 | 3.605100  |
5.12 Intermediate 11a
| Atoms | X        | Y        | Z        |
|-------|----------|----------|----------|
| N     | -2.501781| 2.517138 | -0.123082|
| C     | -3.848515| 3.042898 | -0.350445|
| C     | -4.341991| 3.951328 | 0.790445 |
| N     | 2.041763 | 2.344794 | -1.080363|
| C     | 3.124311 | 2.717266 | -1.999170|
| C     | 2.718353 | 2.588068 | -3.479432|
| Si    | 1.968000 | 0.767667 | -0.195556|
| N     | 3.869146 | 0.535324 | 0.236474 |
| C     | 4.945247 | 1.168023 | 1.041081 |
| C     | 4.327635 | 2.416181 | 1.688324 |
| N     | 2.821159 | -0.520181| -1.350560|
| C     | 2.406976 | -1.618365| -2.275691|
| C     | 2.562800 | -3.013964| -1.624827|
| C     | 3.980493 | -0.446314| -0.670041|
| C     | 5.167180 | -1.334826| -0.837302|
| C     | 5.379726 | -2.388721| 0.071700 |
| C     | 6.497636 | -3.223345| -0.066048|
| C     | 7.416135 | -3.006703| -1.106727|
| C     | 7.210199 | -1.953137| -2.012345|
| C     | 6.088406 | -1.121283| -1.879894|
| C     | 3.220815 | -1.538302| -3.589459|
| C     | 0.923289 | -1.413774| -2.621320|
| C     | 6.138813 | 1.612039 | 0.161619 |
| C     | 5.451590 | 0.235467 | 2.166808 |
| Si    | -2.099869| 0.766951 | 0.118670 |
| N     | -3.776757| -0.072919| 0.542582 |
| C     | -4.418634| -0.635616| 1.762814 |
| C     | -5.949981| -0.434527| 1.699042 |
| N     | -2.903106| 0.041052 | -1.438556|
| C     | -3.875358| -0.533713| -0.724285|
| C     | -4.784408| -1.598350| -1.230436|
| C     | -4.236504| -2.882294| -1.421975|
| C     | -5.043904| -3.922189| -1.902546|
| C     | -6.393761| -3.681273| -2.211675|
| C     | -6.936340| -2.397961| -2.033991|
| C     | -6.134884| -1.357578| -1.538766|
| C     | -2.782395| 0.217922 | -2.902908|
Electronic Supplementary Information (ESI) for Chemical Science

C   -4.099896  0.777047  -3.488879  
C   -1.663465  1.258761  -3.136341  
C   -2.428108 -1.117884  -3.595190  
C   -3.870453  0.168754   2.952336  
C   -4.069862 -2.126668   1.955503  
O   -0.978070 -2.341555   0.233998  
C   -0.772127 -3.730308  -0.018431  
C   -1.712735 -4.626292   0.800760  
O    1.289797 -2.338462   1.522020  
C    2.313456 -1.972558   2.432266  
C    3.007953 -3.236160   2.953134  
C    0.804430  2.007590   2.486441  
H   -6.386273 -0.698774   2.676060  
H   -4.319109 -0.207679   3.884696  
H    0.132958  0.176361  -0.721463  
H    1.756925  4.897992  -1.998604  
H   -0.360868  6.201867  -1.863631  
H   -2.423097  5.126021  -0.951703  
H    3.963306  2.039903  -1.793927  
H    3.485703  3.739374  -1.781829  
H    2.418928  1.549141  -3.685820  
H    3.561046  2.853196  -4.140573  
H    1.867550  3.245934  -3.710648  
H   -4.522490  2.177782  -0.438303  
H   -3.889442  3.583778  -1.315269  
H   -4.354420  3.389694   1.736938  
H   -5.361557  4.316895   0.580233  
H   -3.675488  4.816456   0.919258  
H    3.887427  3.068039   0.920332  
H    0.281265 -1.584557  -1.747359  
H    0.648397 -2.133574  -3.408180  
H    0.745393 -0.400208  -3.006357  
H    2.008446 -3.753230  -2.226019  
H    2.145862 -2.996009  -0.607863  
H    3.138904 -0.534224  -4.034418  
H    2.816049 -2.271554  -4.305283  
H    4.280054 -1.773724  -3.425550
|            |            |            |            |
|------------|------------|------------|------------|
| H -1.578191| -1.593556  | -3.091378  |
| H -2.160313| -0.927303  | -4.647416  |
| H -3.282123| -1.809121  | -3.575349  |
| H -4.917113| 0.046952   | -3.402338  |
| H -3.954293| 1.008634   | -4.556594  |
| H -4.384002| 1.702899   | -2.964797  |
| H -1.994095| 2.260746   | -2.828358  |
| H -1.409587| 1.286668   | -4.207550  |
| H -0.766173| 1.008934   | -2.556168  |
| H -4.545992| -2.749962  | 1.186211   |
| H -4.433258| -2.460497  | 2.941650   |
| H -2.982656| -2.258201  | 1.908668   |
| H -6.189100| 0.619549   | 1.482615   |
| H -6.413110| -1.073269  | 0.935733   |
| H -2.781380| 0.056556   | 3.013987   |
| H -4.138286| 1.230486   | 2.840899   |
| H -3.187025| -3.044096  | -1.179089  |
| H -6.550014| -0.359249  | -1.393220  |
| H 4.612039 | -0.096039  | 2.795542   |
| H 6.164007 | 0.789860   | 2.799683   |
| H 5.966314 | -0.645119  | 1.760879   |
| H 3.544530 | 2.121910   | 2.398397   |
| H 6.673493 | 0.754605   | -0.265684  |
| H 5.796569 | 2.267819   | -0.653265  |
| H 3.613425 | -3.331367  | -1.585506  |
| H 4.659629 | -2.556817  | 0.871148   |
| H 6.648918 | -4.043030  | 0.639236   |
| H 8.288013 | -3.655540  | -1.211892  |
| H 7.921686 | -1.777239  | -2.821660  |
| H 5.925958 | -0.297851  | -2.576755  |
| H -4.618108| -4.918560  | -2.037710  |
| H -7.020836| -4.490776  | -2.591137  |
| H -7.983243| -2.206177  | -2.277742  |
| H 5.103116 | 2.973715   | 2.235408   |
| H 6.847427 | 2.179035   | 0.786516   |
| H 3.045734 | -1.315936  | 1.927841   |
| H 1.905177 | -1.400518  | 3.288899   |
|   | X      | Y      | Z       |
|---|--------|--------|---------|
| H | -1.826785 | -3.121505 | 3.704527 |
| H | -0.103004  | -3.387618 | 3.325448 |
| H | -0.957744  | -3.895564 | -1.098362 |
| H | 0.272406   | -4.015848 | 0.184532 |
| H | -0.477028  | -3.120040 | 5.814447 |
| H | 0.564011   | -1.814595 | 5.162608 |
| H | -1.153763  | -1.486181 | 5.520446 |
| H | 3.864105   | -2.975952 | 3.599664 |
| H | 2.301224   | -3.850839 | 3.532717 |
| H | 3.372364   | -3.846604 | 2.109961 |
| H | -1.548113  | -5.686736 | 0.538866 |
| H | -1.524063  | -4.499693 | 1.876588 |
| H | -2.767356  | -4.376683 | 0.607894 |
| C | 1.139890   | 3.382075  | 2.244351 |
| C | 0.174043   | 4.370243  | 2.256961 |
| C | -1.175371  | 4.046674  | 2.572344 |
| C | -1.518788  | 2.735615  | 2.843651 |
| C | -0.554452  | 1.679915  | 2.782126 |
| H | 2.170232   | 3.665034  | 2.049220 |
| H | 0.451079   | 5.406348  | 2.050323 |
| H | -1.928725  | 4.835282  | 2.622825 |
| H | -2.539382  | 2.497709  | 3.136247 |
| H | -0.783680  | 0.724725  | 3.245944 |
| H | 1.588582   | 1.303885  | 2.761529 |
5.13 Transition State 16a‡

Electronic Supplementary Information (ESI) for Chemical Science
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| N       | -2.325153 | 2.576435 | -0.627990 |
| C       | -3.600168 | 3.259315 | -0.762545 |
| C       | -3.956744 | 4.111846 | 0.455971  |
| N       | 3.115968  | -0.584189 | -1.809160 |
| C       | 2.923637  | -1.581943 | -2.882703 |
| C       | 1.554992  | -1.301941 | -3.511616 |
| C       | 4.109897  | -0.504063 | -0.911107 |
| N       | 3.734439  | 0.370209  | 0.010221  |
| C       | 4.417460  | 0.955275  | 1.166953  |
| C       | 4.497905  | -0.054780 | 2.321288  |
| C       | 5.403080  | -1.242682 | -0.921197 |
| C       | 5.596479  | -2.348166 | -0.093964 |
| C       | 6.825610  | -2.999082 | -0.076516 |
| C       | 7.869373  | -2.544104 | -0.878147 |
| C       | 7.680123  | -1.438015 | -1.703464 |
| C       | 6.449663  | -0.789578 | -1.726993 |
| C       | 2.908413  | -3.011631 | -2.322562 |
| C       | 4.008742  | -1.426379 | -3.958356 |
| C       | 3.564698  | 2.160451  | 1.594523  |
| C       | 5.828647  | 1.448546  | 0.812869  |
| C       | 3.410442  | 2.599723  | -2.166772 |
| C       | 3.250559  | 2.649544  | -3.685959 |
| Si      | -0.398897 | -1.648176 | 0.319741  |
| O       | 0.858792  | -2.842127 | 0.373268  |
| C       | 1.912922  | -2.699995 | 1.277137  |
| C       | 2.623827  | -4.036429 | 1.441423  |
| O       | -1.107499 | -1.905219 | 1.864764  |
| C       | -1.293169 | -3.158009 | 2.469733  |
| C       | -1.607446 | -2.958679 | 3.945195  |
| O       | -1.441746 | -2.535336 | -0.726204 |
| C       | -1.120752 | -3.714755 | -1.421582 |
| C       | -1.378840 | -4.967955 | -0.595803 |
| N       | -3.777373 | 0.183015  | 0.140780  |
| C       | -4.339881 | -0.095724 | 1.469392  |
| C       | -4.502924 | -1.598995 | 1.732630  |
| C       | -5.688590 | 0.624788  | 1.605080  |
| C       | -3.339514 | 0.478877  | 2.480431  |
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -3.058 | 0.042  | -3.374 |
| C    | -2.385 | -1.297 | -3.689 |
| C    | -4.404 | 0.160  | -4.102 |
| C    | -2.146 | 1.196  | -3.819 |
| H    | -6.093 | 0.487  | 2.614  |
| H    | -3.749 | 0.367  | 3.496  |
| H    | -0.042 | 0.138  | -1.658 |
| H    | 2.138  | 4.788  | -2.139 |
| H    | 0.120  | 6.189  | -1.984 |
| H    | -2.029 | 5.195  | -1.281 |
| H    | 4.203  | 1.890  | -1.917 |
| H    | 3.749  | 3.571  | -1.780 |
| H    | 2.979  | 1.657  | -0.459 |
| H    | 4.185  | 2.959  | -4.166 |
| H    | 2.462  | 3.348  | -3.982 |
| H    | -4.367 | 2.489  | -0.891 |
| H    | -3.619 | 3.867  | -1.678 |
| H    | -4.032 | 3.479  | 1.347  |
| H    | -4.918 | 4.617  | 0.312  |
| H    | -3.194 | 4.872  | 0.652  |
| H    | 3.577  | 2.934  | 0.824  |
| H    | 0.758  | -1.472 | -2.785 |
| H    | 1.402  | -1.967 | -4.368 |
| H    | 1.474  | -0.264 | -3.856 |
| H    | 2.637  | -3.714 | -3.119 |
| H    | 2.165  | -3.090 | -1.521 |
| H    | 4.058  | -0.391 | -4.318 |
| H    | 3.774  | -2.069 | -4.813 |
| H    | 4.994  | -1.716 | -3.587 |
| H    | -1.461 | -1.390 | -3.115 |
| H    | -2.158 | -1.362 | -4.759 |
| H    | -3.041 | -2.132 | -3.425 |
| H    | -5.057 | -0.692 | -3.897 |
| H    | -4.231 | 0.199  | -5.183 |
| H    | -4.923 | 1.078  | -3.805 |
| H    | -2.608 | 2.165  | -3.590 |
| H    | -1.967 | 1.133  | -4.897 |
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | -1.181640 | 1.147940  | -3.302271 |
| H    | -5.347363 | -2.023158 | 1.184008  |
| H    | -4.680217 | -1.765289 | 2.801245  |
| H    | -3.586039 | -2.117730 | 1.445032  |
| H    | -5.571464 | 1.698531  | 1.421822  |
| H    | -6.419949 | 0.226915  | 0.894122  |
| H    | -2.388173 | -0.056112 | 2.409592  |
| H    | -3.169985 | 1.546040  | 2.295103  |
| H    | -3.687838 | -2.892817 | -1.191003 |
| H    | -6.772477 | 0.056112  | -1.555568 |
| H    | 3.504335  | -0.438201 | 2.572048  |
| H    | 4.920661  | 0.425134  | 3.210860  |
| H    | 5.137249  | -0.902434 | 2.057849  |
| H    | 2.522014  | 1.866275  | 1.750175  |
| H    | 6.512293  | 0.621754  | 0.603809  |
| H    | 5.799684  | 2.108522  | -0.060831 |
| H    | 3.888518  | -3.311264 | -1.939009 |
| H    | 4.780081  | -2.704062 | 0.523869  |
| H    | 6.965038  | -3.864221 | 0.564235  |
| H    | 8.829870  | -3.049902 | -0.859619 |
| H    | 8.490732  | -1.079271 | -2.330181 |
| H    | 6.296896  | 0.076032  | -2.365189 |
| H    | -5.350972 | -4.694027 | -1.702636 |
| H    | -7.727020 | -4.095253 | -2.112658 |
| H    | -8.438276 | -1.722511 | -2.030731 |
| H    | 3.955449  | 2.585173  | 2.525492  |
| H    | 6.237855  | 2.018208  | 1.654350  |
| H    | 2.621202  | -1.924907 | 0.938173  |
| H    | 1.548231  | -2.369267 | 2.265876  |
| H    | -2.118674 | -3.701498 | 1.983645  |
| H    | -0.398229 | -3.786841 | 2.357929  |
| H    | -1.743718 | -3.743717 | -2.327904 |
| H    | -0.074403 | -3.703959 | -1.752247 |
| H    | -1.797440 | -3.917113 | 4.442034  |
| H    | -0.768668 | -2.466982 | 4.451065  |
| H    | -2.492962 | -2.324162 | 4.059195  |
| H    | 3.447025  | -3.960486 | 2.163905  |
### 5.14 Intermediate 17a

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 1.920196 | -4.793611 | 1.801902 |
| H    | 3.025480 | -4.383967 | 0.482702 |
| H    | -1.210268 | -5.870079 | -1.196951 |
| H    | -0.709034 | -4.991261 | 0.267749 |
| H    | -2.413608 | -4.982279 | -0.232071 |
| H    | 0.412886  | 3.452094  | 2.248415  |
| H    | -1.287517 | 2.944186  | 2.159622  |
| H    | -1.355185 | 2.368838  | 4.499987  |
| H    | -0.188064 | 3.704696  | 4.585288  |
| H    | 0.572712  | 1.240511  | 5.487337  |
| H    | 1.699005  | 2.143921  | 4.452106  |
| H    | -0.229379 | -0.091199 | 3.612884  |
| H    | 1.442002  | 0.154316  | 3.083525  |

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 5.603242 | -2.186979 | 0.340851 |
| C    | 5.412895 | -1.087083 | -0.495755 |
| C    | 6.458482 | -0.646325 | -1.308731 |
| C    | 7.685436 | -1.301256 | -1.283539 |
| C    | 7.872314 | -2.401023 | -0.449171 |
| C    | 6.829500 | -2.843844 | 0.360302 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 4.118228  | -0.351884 | -0.493906 |
| N       | 3.119954  | -0.465070 | -1.381980 |
| C       | 2.940949  | -1.468338 | -2.451074 |
| C       | 3.013065  | -2.897255 | -1.893448 |
| N       | 3.742883  | 0.547339  | 0.403191  |
| C       | 4.434749  | 1.177307  | 1.529998  |
| C       | 3.552319  | 2.361089  | 1.956076  |
| Si      | 1.999511  | 0.662944  | -0.365641 |
| N       | 2.205827  | 2.281949  | -1.140093 |
| C       | 3.395726  | 2.701309  | -1.861026 |
| C       | 3.191726  | 2.757082  | -3.374934 |
| C       | 1.148982  | 3.149565  | -1.008978 |
| N       | 0.002977  | 2.641286  | -0.476996 |
| C       | -1.133327 | 3.397482  | -0.510805 |
| C       | -1.099590 | 4.754602  | -0.869823 |
| C       | 0.104404  | 5.291186  | -1.294562 |
| C       | 1.233036  | 4.500617  | -1.398827 |
| Fe      | -0.041905 | 0.668844  | 0.240095  |
| Si      | -0.356291 | -1.501847 | 0.689506  |
| O       | -1.099421 | -1.793040 | 2.217847  |
| C       | -1.287990 | -3.046125 | 2.818096  |
| C       | -1.569410 | -2.851755 | 4.300697  |
| N       | -2.306548 | 2.738772  | -0.214567 |
| C       | -3.579840 | 3.426788  | -0.344135 |
| C       | -3.936949 | 4.264676  | 0.883785  |
| Si      | -2.129030 | 0.948396  | -0.116525 |
| N       | -3.777683 | 0.349169  | 0.540806  |
| C       | -4.328401 | 0.039084  | 1.867699  |
| C       | -5.690029 | 0.731206  | 2.019643  |
| N       | -3.197125 | 0.354628  | -1.518585 |
| C       | -3.024083 | 0.227744  | -2.969094 |
| C       | -4.368895 | 0.350805  | -3.696500 |
| C       | -4.079430 | -0.150861 | -0.664757 |
| C       | -5.097721 | -1.186404 | -0.967385 |
| C       | -4.661224 | -2.510203 | -1.058248 |
| C       | -5.580076 | -3.515938 | -1.334440 |
| C       | -6.925408 | -3.203421 | -1.524132 |
| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | -7.35577 | -1.881777 | -1.432996 |
| C       | -6.441835 | -0.869767 | -1.151613 |
| C       | -2.118783 | 1.397705 | -3.385275 |
| C       | -2.336770 | -1.098477 | -3.313655 |
| C       | -3.334888 | 0.618121 | 2.883199 |
| C       | -4.461022 | -1.470659 | 2.111729 |
| C       | 5.816167 | 1.711244 | 1.123970 |
| C       | 4.576808 | 0.194121 | 2.701564 |
| C       | 3.989081 | -1.264383 | -3.55375 |
| C       | 1.544668 | -1.252412 | -3.043285 |
| O       | -1.349321 | -2.369090 | 0.415845 |
| C       | -1.043110 | -3.574817 | -1.070166 |
| C       | -1.406274 | -4.803714 | -0.246515 |
| O       | 0.918901 | -2.677085 | 0.754080 |
| C       | 1.934025 | -2.546634 | 1.704152 |
| C       | 2.643510 | -3.882180 | 1.878181 |
| H       | -6.084533 | 0.574436 | 3.029910 |
| H       | -3.726396 | 0.490500 | 3.898661 |
| H       | -0.042743 | 0.242465 | 1.234220 |
| H       | 2.156385 | 4.915576 | -1.778743 |
| H       | 0.156363 | 6.340130 | -1.574553 |
| H       | -1.992504 | 5.363484 | -0.841080 |
| H       | 4.181929 | 1.975086 | -1.639762 |
| H       | 3.767472 | 3.664617 | -1.482293 |
| H       | 2.864988 | 1.776704 | -3.736096 |
| H       | 4.124616 | 3.023864 | -3.884709 |
| H       | 2.425810 | 3.487449 | -3.651749 |
| H       | -4.348188 | 2.660396 | -0.486426 |
| H       | -3.593734 | 4.047634 | -1.251362 |
| H       | -4.006529 | 3.622604 | 1.768194 |
| H       | -4.900951 | 4.767648 | 0.747328 |
| H       | -3.176400 | 5.026347 | 1.084066 |
| H       | 3.509076 | 3.119289 | 1.167817 |
| H       | 0.772500 | -1.460199 | -2.299757 |
| H       | 1.402464 | -1.925097 | -3.895638 |
| H       | 1.409074 | -0.220743 | -3.386508 |
| H       | 2.743880 | -3.612553 | -2.679154 |
H 2.306234  -3.006641  -1.064214
H 3.980207  -0.228333  -3.911050
H 3.762016  -1.920123  -4.403037
H 4.997108  -1.507151  -3.209700
H -1.429729  -1.208653  -2.715569
H -2.080345  -1.124847  -4.379170
H -2.995402  -1.945247  -3.097919
H -5.017950  -0.508179  -3.507919
H -4.193911   0.409252  -4.776136
H -4.893176   1.261588  -3.384782
H -2.585798   2.358267  -3.141166
H -1.940530   1.362568  -4.465314
H -1.153707   1.340815  -2.871054
H -5.291490  -1.907723  1.551464
H -4.643585  -1.652649  3.176849
H -3.530369  -1.967274  1.827879
H -5.596082   1.809055  1.847288
H -6.417809   0.326797  1.308666
H -2.374889   0.099466  2.803716
H -3.182559   1.689563  2.707265
H -3.610209  -2.723014  -0.877580
H -6.767798   0.164593  -1.089746
H  3.601071  -0.210120  2.986645
H  5.009526   0.701619  3.571071
H  5.232263  -0.640741  2.436895
H  2.527627   2.031908  2.154813
H  6.522044   0.904871  0.909230
H  5.734106   2.350617  0.238328
H  4.020125  -3.149817  -1.548345
H  4.786073  -2.534158  0.964130
H  6.967425  -3.703359  1.008894
H  8.829783  -2.912544  -0.431155
H  8.495310  -0.952089  -1.916394
H  6.309042   0.214458  -1.954109
H -5.244070  -4.546499  -1.399480
H -7.640676  -3.990827  -1.742379
H -8.402890  -1.638100  -1.582898
| Atom | X  | Y  | Z  |
|------|----|----|----|
| H    | 3.958568 | 2.823045 | 2.862263 |
| H    | 6.231137 | 2.311858 | 1.940841 |
| H    | 2.654446 | -1.768861 | 1.399774 |
| H    | 1.528900 | -2.225735 | 2.678940 |
| H    | -2.130614 | -3.576278 | 2.346835 |
| H    | -0.402584 | -3.685276 | 2.685481 |
| H    | -1.610585 | -3.587808 | -2.013012 |
| H    | 0.020807 | -3.620774 | -1.334807 |
| H    | -1.753071 | -3.810960 | 4.798385 |
| H    | -0.716858 | -2.365758 | 4.788926 |
| H    | -2.448587 | -2.212801 | 4.437731 |
| H    | 3.447619 | -3.808546 | 2.621529 |
| H    | 1.933188 | -4.644999 | 2.213680 |
| H    | 3.071532 | -4.219909 | 0.927730 |
| H    | -1.253093 | -5.720585 | -0.829037 |
| H    | -0.781818 | -4.851866 | 0.649396 |
| H    | -2.457022 | -4.762836 | 0.065896 |
| O    | 0.089515 | 1.412537 | 2.253367 |
| C    | -0.323389 | 2.717808 | 2.657467 |
| C    | -0.411359 | 2.657332 | 4.178247 |
| C    | 0.685615 | 1.643133 | 4.516323 |
| C    | 0.549160 | 0.645889 | 3.370776 |
| H    | 0.423039 | 3.447506 | 2.316079 |
| H    | -1.274678 | 2.940028 | 2.169454 |
| H    | -1.389825 | 2.269825 | 4.483843 |
| H    | -0.263102 | 3.634214 | 4.646355 |
| H    | 0.553830 | 1.171932 | 5.494007 |
| H    | 1.669520 | 2.126346 | 4.495548 |
| H    | -0.180811 | -0.142282 | 3.573470 |
| H    | 1.489458 | 0.173294 | 3.075087 |
### 5.15 Transition State 18oa²

| Element | X       | Y       | Z       | Coordinates |
|---------|---------|---------|---------|-------------|
| C       | 5.637070| -2.130804| 0.453906|             |
| C       | 5.380239| -1.148907| -0.522687|             |
| C       | 6.367896| -0.841336| -1.478576|             |
| C       | 7.599600| -1.511465| -1.458915|             |
| C       | 7.850032| -2.496700| -0.489160|             |
| C       | 6.865663| -2.806328| 0.464384 |             |
| C       | 4.096815| -0.398551| -0.507549|             |
| N       | 3.061707| -0.514757| -1.369485|             |
| C       | 2.807280| -1.597410| -2.359294|             |
| C       | 3.756965| -1.441761| -3.569489|             |
| Si      | 1.983658| 0.668233 | -0.330136|             |
| N       | 3.746789| 0.517522 | 0.401009 |             |
| C       | 4.515971| 1.249595 | 1.418893 |             |
| C       | 5.891215| 1.708907 | 0.889051 |             |
| Fe      | -0.037479| 0.683675 | 0.342271 |             |
| O       | 0.073599| 1.310063 | 2.791788 |             |
| C       | 0.015352| 2.254485 | 3.577385 |             |
| C       | -0.020278| 3.697899 | 3.110257 |             |
| Si      | -2.118255| 0.957664 | -0.077362|             |
| N       | -2.331193| 2.750479 | -0.224206|             |
| C       | -3.622214| 3.420112 | -0.408089|             |
C -4.003530  4.310121  0.789407
N -3.114267  0.287762  -1.535597
C -2.887905  0.102739  -2.981585
C -1.835071  1.160895  -3.382274
C -4.051423  -0.193876  -0.711031
N -3.809782  0.345072  0.502181
C -4.397036  0.027459  1.819213
C -3.468277  0.706042  2.842319
C -5.055403  -1.241038  -1.031785
C -4.614613  -2.578463  -1.089420
C -5.532766  -3.599923  -1.368082
C -6.885351  -3.292328  -1.597467
C -7.321079  -1.958180  -1.543032
C -6.408145  -0.931099  -1.256243
C -2.338134  -1.312103  -3.275295
C -4.190727  0.357008  -3.770303
C -4.430524  -1.492726  2.093862
C -5.817514  0.627433  1.905214
Si -0.319672  -1.464973  0.884268
O -1.232195  -2.371027  -0.271606
C -0.969417  -3.689157  -0.744181
C -1.523996  -4.772096  0.190836
N -0.007541  2.654959  -0.446906
C -1.157769  3.417738  -0.526761
C -1.128201  4.771723  -0.927987
C  0.080772  5.306960  -1.381466
C  1.214931  4.499858  -1.474598
C  1.136277  3.154870  -1.033915
N  2.190410  2.266893  -1.162325
C  3.385332  2.659739  -1.914229
C  3.142097  2.694534  -3.434286
O  1.007856  -2.574772  1.064338
C  2.012288  -2.305462  2.028230
C  2.789226  -3.595366  2.316237
O  -1.117559  -1.645226  2.399893
C  -1.221397  -2.848430  3.147500
C  -1.410456  -2.502137  4.628953
| C   | 4.695289 | 0.381647 | 2.686658 |
|-----|----------|----------|----------|
| C   | 3.654826 | 2.480182 | 1.773380 |
| C   | 1.351676 | -1.439787| -2.842502|
| C   | 2.968339 | -2.996148| -1.722495|
| C   | 0.005521 | 1.989855 | 5.073956 |
| H   | -6.223677| 0.472402 | 2.918326 |
| H   | -3.829368| 0.508211 | 3.863637 |
| H   | -0.000999| 0.167590 | -1.065102|
| H   | 2.138477 | 4.893915 | -1.891140|
| H   | 0.129487 | 6.352346 | -1.695724|
| H   | -2.031373| 5.375916 | -0.910784|
| H   | 4.168330 | 1.922693 | -1.692588|
| H   | 3.767865 | 3.634991 | -1.558402|
| H   | 2.835028 | 1.694953 | -3.778635|
| H   | 4.060604 | 2.988134 | -3.970936|
| H   | 2.342525 | 3.406982 | -3.685790|
| H   | -4.381603| 2.634495 | -0.532271|
| H   | -3.614432| 4.014510 | -1.340886|
| H   | -4.110780| 3.693509 | 1.695275 |
| H   | -4.958844| 4.829694 | 0.602464 |
| H   | -3.225417| 5.065385 | 0.979481 |
| H   | 3.564805 | 3.159485 | 0.914511 |
| H   | 0.644296 | -1.617601| -2.023799|
| H   | 1.159962 | -2.169086| -3.644917|
| H   | 1.174724 | -0.426873| -3.236752|
| H   | 2.649606 | -3.762371| -2.448467|
| H   | 2.336626 | -3.067736| -0.825010|
| H   | 3.691626 | -0.422654| -3.982617|
| H   | 3.465248 | -2.158227| -4.354588|
| H   | 4.798788 | -1.649198| -3.289701|
| H   | -1.523642| -1.540606| -2.577516|
| H   | -1.966974| -1.357363| -4.312781|
| H   | -3.126154| -2.070015| -3.155997|
| H   | -4.955832| -0.396332| -3.535824|
| H   | -3.975497| 0.310571 | -4.850120 |
| H   | -4.589498| 1.357191 | -3.534610|
| H   | -2.209038| 2.175503 | -3.173943|
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -1.619728 | 1.073830 | -4.458920 |
| H    | -0.905185  | 1.009424 | -2.814243 |
| H    | -5.192739  | -1.997464 | 1.484475  |
| H    | -4.671043  | -1.662097 | 3.156282  |
| H    | -3.442262  | -1.918539 | 1.881006  |
| H    | -5.790159  | 1.709411  | 1.698350  |
| H    | -6.492276  | 0.141030  | 1.184775  |
| H    | -2.449693  | 0.305340  | 2.726614  |
| H    | -3.448635  | 1.795281  | 2.675116  |
| H    | -3.565353  | -2.791246 | -0.884601 |
| H    | -6.738089  | 0.108470  | -1.216359 |
| H    | 3.715983   | 0.030696  | 3.044808  |
| H    | 5.171180   | 0.979925  | 3.481286  |
| H    | 5.333349   | -0.489432 | 2.478692  |
| H    | 2.647740   | 2.131198  | 2.045431  |
| H    | 6.553810   | 0.857121  | 0.684274  |
| H    | 5.767126   | 2.295892  | -0.034395 |
| H    | 4.015280   | -3.197330 | -1.453653 |
| H    | 4.865251   | -2.373153 | 1.182815  |
| H    | 7.052463   | -3.575414 | 1.216713  |
| H    | 8.808086   | -3.020430 | -0.476794 |
| H    | 8.363238   | -1.263005 | -2.198853 |
| H    | 6.169837   | -0.067339 | -2.221264 |
| H    | -5.191864  | -4.637013 | -1.402229 |
| H    | -7.598237  | -4.090204 | -1.816432 |
| H    | -8.370654  | -1.715976 | -1.722655 |
| H    | 4.102674   | 3.019288  | 2.622576  |
| H    | 6.372011   | 2.348286  | 1.647040  |
| H    | 2.698607   | -1.520668 | 1.658547  |
| H    | 1.568090   | -1.923746 | 2.969103  |
| H    | -2.084968  | -3.443743 | 2.790616  |
| H    | -0.318572  | -3.472909 | 3.014137  |
| H    | -1.451862  | -3.773278 | -1.736767 |
| H    | 0.113711   | -3.844746 | -0.882723 |
| H    | -1.518110  | -3.417823 | 5.236156  |
| H    | -0.542993  | -1.930807 | 4.998508  |
| H    | -2.311591  | -1.881934 | 4.761048  |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| H       | 3.598106   | -3.410535  | 3.045418   |
| H       | 2.115735   | -4.364569  | 2.726958   |
| H       | 3.232102   | -3.991678  | 1.388062   |
| H       | -1.391711  | -5.773777  | -0.255690  |
| H       | -0.998500  | -4.743843  | 1.155679   |
| H       | -2.598877  | -4.608557  | 0.376736   |
| H       | 1.008895   | 4.024864   | 2.875670   |
| H       | -0.600826  | 3.779481   | 2.183657   |
| H       | -0.427724  | 4.369192   | 3.882486   |
| H       | -0.913960  | 2.405920   | 5.523932   |
| H       | 0.053305   | 0.909653   | 5.266849   |
| H       | 0.855230   | 2.500956   | 5.563479   |

5.16 Intermediate 19oa

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 6.330101   | -0.674130  | -1.561784  |
| C       | 5.344812   | -1.052253  | -0.629287  |
| C       | 5.576026   | -2.153109  | 0.217969   |
| C       | 6.770014   | -2.880246  | 0.118478   |
| C       | 7.749752   | -2.503495  | -0.815424  |
| C       | 7.529449   | -1.395977  | -1.650964  |
| C       | 4.074593   | -0.286072  | -0.522905  |
| N       | 3.723703   | 0.511393   | 0.495285   |
| C       | 4.523645   | 1.125518   | 1.575255   |
| C       | 5.833779   | 1.737589   | 1.029374   |
| N       | 3.047189   | -0.285880  | -1.402864  |
C  2.796032  -1.232330  -2.527240
C  3.697210  -0.868351  -3.729280
Si  1.968711   0.769036  -0.238497
N  2.180900   2.459620  -0.868912
C  3.372533   2.940601  -1.572684
C  3.118501   3.175761  -3.073309
Fe  -0.062174   0.711388   0.395009
Si  -0.301773  -1.472968   0.756866
O  -1.263654  -2.264979  -0.449278
C  -0.996024  -3.482489  -1.136219
C  -1.623329  -4.699507  -0.438822
Si  -2.155314   1.023377   0.034980
N  -2.350762   2.817594   0.129009
C  -3.639190   3.513976   0.079320
C  -3.983470   4.218776   1.404912
N  -3.190718   0.529502  -1.452072
C  -2.969190   0.494098  -2.910378
C  -1.989093   1.651376  -3.210904
C  -4.095718  -0.062988  -0.661192
N  -3.821848   0.334234   0.601611
C  -4.378658  -0.141537   1.889106
C  -3.439740   0.400414   2.989011
C  -5.088358  -1.085120  -1.081573
C  -6.453520  -0.785324  -1.227147
C  -7.349130  -1.790399  -1.625400
C  -6.883259  -3.092518  -1.872054
C  -5.518021  -3.390562  -1.720693
C  -4.618249  -2.390459  -1.329071
C  -2.324431  -0.847858  -3.324274
C  -4.288941   0.730079  -3.673339
C  -4.415471  -1.685114   1.970479
C  -5.794962   0.446533   2.078486
O  -0.086697   1.490864   2.216275
C  0.244739   1.325878   3.406783
C  -0.007983   2.443209   4.405415
N  -0.034806   2.755245  -0.168402
C  1.119511   3.325997  -0.644159
C  1.203733  4.720724  -0.884493
C  0.070222  5.506767  -0.668173
C  -1.137372  4.922453  -0.278054
C  -1.175049  3.520736  -0.082712
C  1.321163  -1.069951  -2.943460
C  3.021437  -2.703352  -2.108748
C  4.850546   0.093508  2.680242
C  3.650648   2.251127  2.175580
O  1.022315  -2.609801  0.737363
C  2.029531  -2.579975  1.730791
C  2.799240  -3.908355  1.721915
O  -1.051901  -1.876736  2.268697
C  -1.223851  -3.207060  2.745175
C  -1.396826  -3.184706  4.268822
C  0.918853   0.059452  3.863034
H  -6.189695   0.148196  3.063706
H  -3.863039   0.157197  3.976791
H  -0.018733   0.348861  -1.071415
H  2.131026   5.171601  -1.229204
H  0.122459   6.586648  -0.828037
H  -2.033352   5.525615  -0.154783
H  4.150730   2.174600  -1.456552
H  3.765031   3.859396  -1.097166
H  2.782519   2.236275  -3.538588
H  4.039793   3.513285  -3.578489
H  2.335246   3.933575  -3.223268
H  -4.407849   2.758770  -0.141512
H  -3.647192   4.241028  -0.754510
H  -4.066776   3.476448  2.213510
H  -4.941434   4.760278  1.323144
H  -3.195566   4.936065  1.680964
H  3.422003   3.012909  1.416731
H  0.651743  -1.380829  -2.133311
H  1.129640  -1.695733  -3.829181
H  1.091942  -0.022809  -3.193325
H  2.683788  -3.360923  -2.926810
H  2.431446  -2.925343  -1.207714
| H  | 3.569686 | 0.191820 | -3.998720 |
| H  | 3.413104 | -1.486579 | -4.596387 |
| H  | 4.756144 | -1.057667 | -3.507688 |
| H  | -1.495385 | -1.078338 | -2.644798 |
| H  | -1.951844 | -0.778127 | -4.359442 |
| H  | -3.059668 | -1.664616 | -3.272779 |
| H  | -4.997012 | -0.096564 | -3.522815 |
| H  | -4.071663 | 0.810353  | -4.751093 |
| H  | -4.759237 | 1.669388  | -3.339772 |
| H  | -2.429522 | 2.616474  | -2.915490 |
| H  | -1.769453 | 1.675066  | -4.290023 |
| H  | -1.049531 | 1.511154  | -2.654925 |
| H  | -5.208319 | -2.107265 | 1.337704  |
| H  | -4.607849 | -1.988764 | 3.013097  |
| H  | -3.443307 | -2.085408 | 1.658203  |
| H  | -5.765782 | 1.547176  | 2.028934  |
| H  | -6.480742 | 0.070271  | 1.304648  |
| H  | -2.448011 | -0.062346 | 2.897299  |
| H  | -3.340634 | 1.493822  | 2.906771  |
| H  | -3.559603 | -2.599047 | -1.180169 |
| H  | -6.806761 | 0.230555  | -1.041082 |
| H  | 3.928671  | -0.384928 | 3.042972  |
| H  | 5.338793  | 0.604006  | 3.526885  |
| H  | 5.531343  | -0.683370 | 2.305304  |
| H  | 2.698826  | 1.846128  | 2.546808  |
| H  | 6.501311  | 0.963419  | 0.627057  |
| H  | 5.611621  | 2.466687  | 0.236098  |
| H  | 4.082435  | -2.916418 | -1.918679 |
| H  | 4.808049  | -2.445178 | 0.931058  |
| H  | 6.931715  | -3.743050 | 0.767982  |
| H  | 8.680096  | -3.069903 | -0.891644 |
| H  | 8.290404  | -1.094165 | -2.373469 |
| H  | 6.154638  | 0.189200  | -2.204874 |
| H  | -5.152401 | -4.403373 | -1.904401 |
| H  | -7.582431 | -3.872956 | -2.180163 |
| H  | -8.408859 | -1.556168 | -1.743023 |
| H  | 4.187378  | 2.723386  | 3.013258  |
|   | 6.359416  | 2.258024  | 1.845974  |
|---|------------|------------|------------|
| H | 2.722899   | -1.726896  | 1.547366   |
| H | 1.593161   | -2.426257  | 2.734179   |
| H | -2.120207  | -3.661304  | 2.275754   |
| H | -0.356272  | -3.837333  | 2.465020   |
| H | -1.423683  | -3.380169  | -2.153689  |
| H | 0.090993   | -3.644893  | -1.244123  |
| H | -1.587000  | -4.203376  | 4.652105   |
| H | -0.494129  | -2.788007  | 4.757156   |
| H | -2.247053  | -2.543912  | 4.541466   |
| H | 3.601836   | -3.900424  | 2.481220   |
| H | 2.117603   | -4.734867  | 1.945014   |
| H | 3.245914   | -4.086423  | 0.731661   |
| H | -1.479639  | -5.609058  | -1.049622  |
| H | -1.155880  | -4.857458  | 0.544982   |
| H | -2.706332  | -4.545938  | -0.287010  |
| H | 0.224686   | -0.784439  | 3.733478   |
| H | 1.766686   | -0.139168  | 3.194381   |
| H | 1.260173   | 0.121353   | 4.903586   |
| H | 0.935189   | 2.733881   | 4.902938   |
| H | -0.441657  | 3.317155   | 3.894202   |
| H | -0.696353  | 2.106684   | 5.204754   |
5.17 Transition State 20oa$^2$

C  -6.163049  0.601169  1.620953
C  -5.796482  0.813869  0.278216
C  -6.756737  1.296092 -0.632774
C  -8.062034  1.575490 -0.204152
C  -8.420747  1.370200  1.138469
C  -7.467588  0.884935  2.049313
C  -4.438951  0.440282 -0.210422
N  -3.414513  1.277172 -0.474501
C  -3.353533  2.725856 -0.112424
C  -3.763518  2.965406  1.361521
N  -4.041488 -0.807709 -0.484213
C  -4.833535 -2.062042 -0.505713
C  -3.984210 -3.108625 -1.249235
N  -4.165959 -0.260561 -3.488687
C  -3.146740  1.024511 -4.327335
C  -0.906263 -0.814205 -3.112022
N  0.163595 -0.735888 -2.250904
C  1.441510 -0.895498 -2.749537
C  1.657900 -1.421173 -4.044113
C  0.548748 -1.603062 -4.879529
| Atom | X         | Y         | Z       |
|------|-----------|-----------|---------|
| C    | -0.732139 | -1.254523 | -4.448335 |
| Fe   | -0.110979 | -0.281385 | -0.270132 |
| Si   | -0.307292 | 0.235336  | 1.891930  |
| O    | 0.598838  | -0.739137 | 3.005367  |
| C    | 0.957958  | -0.222668 | 4.285904  |
| C    | 1.009841  | -1.363532 | 5.305375  |
| N    | 2.459648  | -0.385279 | -1.949802 |
| C    | 3.791260  | -0.210083 | -2.541102 |
| C    | 4.652968  | -1.480203 | -2.441673 |
| Si   | 1.769852  | 0.674955  | -0.621985 |
| N    | 3.284351  | 1.538233  | 0.184447  |
| C    | 4.035826  | 1.371570  | 1.460839  |
| C    | 5.547168  | 1.544122  | 1.184947  |
| N    | 2.031581  | 2.419993  | -1.354453 |
| C    | 1.611319  | 3.183112  | -2.550617 |
| C    | 2.825579  | 3.415617  | -3.481707 |
| C    | 2.995511  | 2.685206  | -0.464315 |
| C    | 3.567986  | 4.032403  | -0.187827 |
| C    | 2.821163  | 4.940618  | 0.588305  |
| C    | 3.338007  | 6.211830  | 0.870494  |
| C    | 4.596550  | 6.588703  | 0.370091  |
| C    | 5.340136  | 5.686839  | -0.407866 |
| C    | 4.830248  | 4.407765  | -0.681126 |
| C    | 0.580908  | 2.306771  | -3.294678 |
| C    | 0.964913  | 4.536532  | -2.172407 |
| C    | 3.773954  | -0.65622  | 1.931271  |
| C    | 3.562124  | 2.344274  | 2.560154  |
| C    | -6.178016 | -1.910080 | -1.259210 |
| C    | -5.092469 | -2.598738 | 0.921086  |
| C    | -4.257042 | 3.544141  | -1.066027 |
| C    | -1.906757 | 3.225090  | -0.290034 |
| O    | 0.196909  | 1.858416  | 2.276203  |
| C    | -0.477190 | 2.776398  | 3.129839  |
| C    | 0.517636  | 3.799839  | 3.691003  |
| O    | -1.879775 | 0.264768  | 2.649445  |
| C    | -2.398254 | -0.746710 | 3.494117  |
| C    | -2.797215 | -0.149920 | 4.852111  |
|   |  H  |  H  |  H  |
|-----|-----|-----|-----|
| H   | 6.115924 | 1.272848 | 2.089484 |
| H   | 4.342993  | -0.254477 | 2.856170 |
| H   | -0.670128 | 1.057664  | -0.645894 |
| H   | -1.581762 | -1.339634 | -5.121979 |
| H   | 0.692587  | -1.983401 | -5.893962 |
| H   | 2.665659  | -1.618466 | -4.401552 |
| H   | -4.178198 | -0.203944 | -2.865187 |
| H   | -3.405815 | -1.140757 | -4.145932 |
| H   | -3.070324 | 1.892018  | -3.654015 |
| H   | -4.025123 | 1.157679  | -4.982269 |
| H   | -2.241371 | 0.991167  | -4.951987 |
| H   | 4.288812  | 0.597356  | -1.982683 |
| H   | 3.702530  | 0.125744  | -3.592950 |
| H   | 4.784429  | -1.733942 | -1.382607 |
| H   | 5.642776  | -1.320671 | -2.903319 |
| H   | 4.161793  | -2.333961 | -2.932999 |
| H   | -3.682138 | -2.742765 | -2.240967 |
| H   | -1.214161 | 2.734619  | 0.405155 |
| H   | -1.893383 | 4.311409  | -0.102799 |
| H   | -1.558654 | 3.045697  | -1.316907 |
| H   | -3.493825 | 3.995931  | 1.645843 |
| H   | -3.230884 | 2.260035  | 2.014905 |
| H   | -3.973768 | 3.359120  | -2.114437 |
| H   | -4.129085 | 4.618450  | -0.853650 |
| H   | -5.317988 | 3.296959  | -0.932301 |
| H   | 0.186643  | 4.390745  | -1.410505 |
| H   | 0.501274  | 4.977692  | -3.069962 |
| H   | 1.711206  | 5.244702  | -1.787988 |
| H   | 3.559347  | 4.087993  | -3.013579 |
| H   | 2.485654  | 3.876544  | -4.423752 |
| H   | 3.312173  | 2.455874  | -3.715553 |
| H   | 1.060550  | 1.410599  | -3.711892 |
| H   | 0.145719  | 2.886350  | -4.123671 |
| H   | -0.219953 | 1.979172  | -2.618874 |
| H   | 3.855428  | 3.382211  | 2.354326 |
| H   | 4.018660  | 2.045805  | 3.518621 |
| H   | 2.469956  | 2.279824  | 2.651140 |
|   |   |   |   |
|---|---|---|---|
| H | 5.862932 | 0.882548 | 0.361556 |
| H | 5.791248 | 2.583816 | 0.923730 |
| H | 2.705804 | -0.229082 | 2.130837 |
| H | 4.099384 | -0.782365 | 1.170872 |
| H | 1.847719 | 4.633604 | 0.972303 |
| H | 5.404857 | 3.698239 | -1.278472 |
| H | -4.139080 | -2.714403 | 1.455492 |
| H | -5.579852 | -3.586489 | 0.859016 |
| H | -5.748384 | -1.927229 | 1.490061 |
| H | -3.087058 | -3.342734 | -0.669579 |
| H | -6.902686 | -1.304478 | -0.702821 |
| H | -6.016594 | -1.455580 | -2.249666 |
| H | -4.845306 | 2.851375 | 1.509260 |
| H | -5.413559 | 0.237540 | 2.324913 |
| H | -7.738356 | 0.727703 | 3.095464 |
| H | -9.437471 | 1.586393 | 1.472982 |
| H | -8.799375 | 1.945682 | -0.919464 |
| H | -6.478563 | 1.429213 | -1.679050 |
| H | 2.759222 | 6.907815 | 1.481194 |
| H | 4.996468 | 7.581309 | 0.587534 |
| H | 6.317433 | 5.975726 | -0.799968 |
| H | -4.569389 | -4.034010 | -1.368384 |
| H | -6.613265 | -2.911865 | -1.405544 |
| H | -3.288662 | -1.196161 | 3.015501 |
| H | -1.661131 | -1.553441 | 3.651455 |
| H | 1.950697 | 0.264066 | 4.220013 |
| H | 0.245051 | 0.547450 | 4.631015 |
| H | -1.269856 | 3.299384 | 2.564979 |
| H | -0.976500 | 2.252705 | 3.964676 |
| H | 1.359199 | -0.995467 | 6.285928 |
| H | 0.010596 | -1.809009 | 5.431876 |
| H | 1.697576 | -2.151387 | 4.960307 |
| H | -3.307120 | -0.900538 | 5.482106 |
| H | -1.901376 | 0.207728 | 5.386052 |
| H | -3.473539 | 0.709061 | 4.706078 |
| H | 0.001873 | 4.511956 | 4.358695 |
| H | 1.307613 | 3.287031 | 4.262723 |
|   |    |    |    |    |    |    |    |    |
|---|----|----|----|----|----|----|----|----|
| H | 1.000678 | 4.368345 | 2.879917 |
| O | 0.639809  | -2.298313 | 0.032803 |
| C | -0.155108 | -3.291225 | -0.000863 |
| C | -0.717999 | -3.625196 | -1.395473 |
| C | -1.150127 | -3.397624 | 1.157801 |
| H | -0.607271 | -3.321889 | 2.109016 |
| H | -1.836358 | -2.541744 | 1.080612 |
| H | -1.716038 | -4.341705 | 1.114836 |
| H | -1.266271 | -4.580602 | -1.386650 |
| H | -1.393749 | -2.826605 | -1.712641 |
| H | 0.114077  | -3.669497 | -2.110904 |
| Si| 2.197824  | -3.546001 | 0.358074 |
| O | 3.708409  | -2.902122 | 0.623433 |
| O | 1.867419  | -4.359038 | 1.778895 |
| O | 2.445205  | -4.386962 | -1.058744 |
| C | 4.875647  | -3.712499 | 0.374540 |
| C | 1.946744  | -5.693636 | -1.395363 |
| C | 2.676940  | -4.192719 | 2.968485 |
| C | 6.077085  | -3.023442 | 1.015765 |
| H | 4.739472  | -4.719715 | 0.811266 |
| H | 5.012445  | -3.831244 | -0.711034 |
| C | 2.151247  | -5.907154 | -2.892962 |
| H | 2.494261  | -6.448260 | -0.803690 |
| H | 0.876646  | -5.770904 | -1.140954 |
| C | 1.966842  | -4.903880 | 4.116717 |
| H | 3.679682  | -4.620276 | 2.795873 |
| H | 2.794294  | -3.120880 | 3.188566 |
| H | 6.983248  | -3.633067 | 0.865150 |
| H | 6.238309  | -2.032265 | 0.564716 |
| H | 5.910244  | -2.889534 | 2.095409 |
| H | 2.550791  | -4.793987 | 5.045470 |
| H | 0.970963  | -4.464391 | 4.273660 |
| H | 1.850000  | -5.976470 | 3.895267 |
| H | 1.787900  | -6.905648 | -3.186476 |
| H | 1.597465  | -5.143221 | -3.460212 |
| H | 3.219009  | -5.828239 | -3.150561 |
| H | 0.687009  | -4.161136 | 0.164993 |
5.18 Transition State 21a‡

|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| C | -0.777444 | -2.291954 | 2.169251  |
| N | 0.257393  | -1.439901 | 1.793272  |
| C | 1.454936  | -1.541156 | 2.502303  |
| C | 1.568979  | -2.354404 | 3.653414  |
| C | 0.496035  | -3.157893 | 4.037092  |
| C | -0.677468 | -3.151693 | 3.283218  |
| Fe| 0.026602  | -0.107321 | 0.312586  |
| Si| -0.452028 | 2.218692  | 0.515451  |
| O | 0.363080  | 3.134313  | -0.665342 |
| C | 0.192279  | 4.521889  | -0.942466 |
| C | -0.469730 | 4.691409  | -2.315135 |
| N | 2.531956  | -0.852385 | 1.977159  |
| C | 3.880468  | -1.120061 | 2.496112  |
| C | 4.244077  | -0.274116 | 3.728309  |
| N | -1.927311 | -2.226166 | 1.397616  |
| C | -2.949601 | -3.273238 | 1.492771  |
| C | -2.469162 | -4.621000 | 0.924471  |
| Si| -1.971354 | -0.867984 | 0.236281  |
| N | -3.739402 | -0.232138 | 0.411220  |
| C | -4.587092 | 0.276962  | 1.514028  |
| C | -5.652850 | -0.767390 | 1.910161  |
| N | -3.057712 | -1.499502 | -1.221428 |
| C | -2.685631 | -1.729453 | -2.649905 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -3.857866 | -2.28405  | -3.48376  |
| C       | -4.080479 | -0.713810 | -0.788694 |
| C       | -5.314417 | -0.342384 | -1.529170 |
| C       | -5.434471 | 0.960608  | -2.045338 |
| C       | -6.591104 | 1.334547  | -2.744244 |
| C       | -7.641249 | 0.416076  | -2.909503 |
| C       | -7.530228 | -0.880589 | -2.379062 |
| C       | -6.366193 | -1.262941 | -1.697103 |
| C       | -1.559990 | -2.784736 | -2.649273 |
| C       | -2.158096 | -0.409158 | -3.252967 |
| C       | -5.276031 | 1.60607   | 1.124798  |
| C       | -3.626799 | 0.527954  | 2.693087  |
| Si      | 2.196579  | -0.072350 | 0.377333  |
| N       | 3.853045  | 0.834687  | 0.044762  |
| C       | 4.188196  | 2.284544  | -0.042193 |
| C       | 3.516151  | 2.953388  | 1.174442  |
| N       | 3.343058  | -1.125248 | -0.733280 |
| C       | 3.348250  | -2.523281 | -1.211344 |
| C       | 2.467896  | -3.332319 | -0.228737 |
| C       | 4.244949  | -0.144797 | -0.809584 |
| C       | 5.445414  | -0.144106 | -1.686594 |
| C       | 5.302426  | 0.000838  | -3.079305 |
| C       | 6.431968  | -0.050026 | -3.909604 |
| C       | 7.705111  | -0.260317 | -3.354946 |
| C       | 7.848346  | -0.410133 | -1.964841 |
| C       | 6.723444  | -0.346932 | -1.132225 |
| O       | -2.099077 | 2.777942  | 0.481915  |
| C       | -2.574611 | 3.902901  | 1.229264  |
| C       | -3.386376 | 4.879960  | 0.373483  |
| O       | 0.113432  | 2.866730  | 2.005985  |
| C       | -0.053082 | 2.111373  | 3.206611  |
| C       | 1.243265  | 2.161463  | 4.019242  |
| C       | 3.625463  | 2.870422  | -1.353750 |
| C       | 5.713066  | 2.532556  | 0.040137  |
| C       | 2.719262  | -2.565315 | -2.622430 |
| C       | 4.762275  | -3.143938 | -1.230048 |
| H       | 5.880660  | 3.604313  | 0.234205  |
|     |         |         |          |
|-----|---------|---------|----------|
| H   | 3.607455| 4.047316| 1.081176 |
| H   | 0.158888| -1.269892| -0.619846|
| H   | -1.515321| -3.789159| 3.553670 |
| H   | 0.579061| -3.798004| 4.918135 |
| H   | 2.496793| -2.375090| 4.217798 |
| H   | -3.811468| -2.924554| 0.908254 |
| H   | -3.296060| -3.392017| 2.536218 |
| H   | -2.253732| -4.509175| -0.148820|
| H   | -3.242070| -5.397175| 1.055139 |
| H   | -1.549641| -4.948558| 1.431965 |
| H   | 4.593423| -0.886936| 1.693831 |
| H   | 3.989911| -2.197936| 2.716585 |
| H   | 4.268837| 0.791136| 3.453996 |
| H   | 5.238797| -0.561302| 4.110302 |
| H   | 3.506336| -0.399856| 4.534504 |
| H   | -3.070350| -0.388482| 2.943050 |
| H   | -0.688109| -2.416426| -2.095409|
| H   | -1.258615| -2.997389| -3.686886|
| H   | -1.904792| -3.721770| -2.184439|
| H   | -1.857859| -0.558463| -4.303706|
| H   | -1.285338| -0.059577| -2.677283|
| H   | -4.350176| -3.115738| -2.952577|
| H   | -3.450006| -2.682197| -4.433023|
| H   | -4.603506| -1.524497| -3.736588|
| H   | 1.709568| -2.128358| -2.592460|
| H   | 2.646881| -3.608852| -2.970977|
| H   | 3.335481| -1.997815| -3.336819|
| H   | 5.409572| -2.690018| -1.991888|
| H   | 4.667393| -4.218869| -1.452657|
| H   | 5.241805| -3.033850| -0.244162|
| H   | 2.922770| -3.350844| 0.772917 |
| H   | 2.376731| -4.367008| -0.595834|
| H   | 1.465450| -2.888384| -0.150281|
| H   | 4.062083| 2.346289| -2.219281|
| H   | 3.892985| 3.937709| -1.431010|
| H   | 2.531713| 2.768330| -1.368265|
| H   | 6.156124| 1.959595| 0.870030|
|   |   |   |   |
|---|---|---|---|
| H | 6.231538 | 2.270704 | -0.891413 |
| H | 2.446381 | 2.713111 | 1.235178 |
| H | 4.010684 | 2.642147 | 2.109952 |
| H | 4.308566 | 0.151860 | -3.503210 |
| H | 6.826410 | -0.450376 | -0.051176 |
| H | -4.549093 | 2.256196 | 0.619548 |
| H | -5.632374 | 2.108877 | 2.038675 |
| H | -6.141793 | 1.436353 | 0.467663 |
| H | -2.907233 | 1.306663 | 2.409371 |
| H | -6.345733 | -0.948346 | 1.073947 |
| H | -5.182846 | -1.715765 | 2.205308 |
| H | -2.939996 | 0.365315 | -3.219785 |
| H | -4.624034 | 1.669564 | -1.876021 |
| H | -6.675092 | 2.344561 | -3.150321 |
| H | -8.546688 | 0.710034 | -3.447815 |
| H | -8.346709 | -1.595181 | -2.501310 |
| H | -6.259700 | -2.274125 | -1.301127 |
| H | 6.316736 | 0.070479 | -4.988687 |
| H | 8.582733 | -0.306536 | -4.002911 |
| H | 8.836495 | -0.573209 | -1.529912 |
| H | -4.199083 | 0.850259 | 3.576275 |
| H | -6.234062 | -0.386216 | 2.765446 |
| H | 1.192144 | 4.994178 | -0.940143 |
| H | -0.407854 | 5.026768 | -0.166097 |
| H | -3.220296 | 3.526212 | 2.049440 |
| H | -1.740463 | 4.440730 | 1.713684 |
| H | -0.895699 | 2.525627 | 3.794487 |
| H | -0.293245 | 1.056082 | 2.970863 |
| H | 1.105423 | 1.690787 | 5.008138 |
| H | 2.036067 | 1.626773 | 3.478366 |
| H | 1.556527 | 3.208601 | 4.164504 |
| H | -0.583065 | 5.758910 | -2.575269 |
| H | 0.143986 | 4.202181 | -3.088757 |
| H | -1.460594 | 4.213538 | -2.307040 |
| H | -3.894760 | 5.611053 | 1.026077 |
| H | -2.742784 | 5.431048 | -0.325746 |
| H | -4.150958 | 4.348911 | -0.211728 |
5.19 Intermediate *trans*-14a

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -6.406478 | -2.243592 | -0.160531 |
| C    | -5.217966 | -1.984222 | -0.867832 |
| C    | -5.080758 | -2.430875 | -2.195505 |
| C    | -6.125530 | -3.138502 | -2.808362 |
| C    | -7.312986 | -3.393134 | -2.102419 |
| C    | -7.451530 | -2.943575 | -0.778111 |
| C    | -4.116847 | -1.213417 | -0.232281 |
| N    | -3.189062 | -1.684884 | 0.620296  |
| C    | -2.809752 | -3.089970 | 0.910493  |
| C    | -1.790709 | -3.036083 | 2.070470  |
| N    | -3.25948  | -1.684884 | 0.620296  |
| C    | -4.507725 | 1.113986  | -1.276883 |
| C    | -3.903200 | 1.094525  | -2.699716 |
| Si   | -2.130761 | -0.092400 | 0.373184  |
| Fe   | -0.027128 | 0.121680  | -0.067272 |
| Si   | 2.100816  | -0.058542 | 0.175564  |
| N    | 3.759973  | -0.056756 | -0.800786 |
| C    | 4.197362  | 0.667981  | -2.028704 |
| C    | 3.002542  | 0.719426  | -3.011752 |
| N    | 0.049990  | 0.891577  | 1.795332  |
| C    | -1.108379 | 1.151617  | 2.521590  |
| C    | -1.069754 | 1.801943  | 3.775039  |
| C    | 0.157361  | 2.197774  | 4.303219  |
| C    | 1.335243  | 1.912352  | 3.613955  |
| C    | 1.269297  | 1.230537  | 2.377707  |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| N       | -2.298121 | 0.745570  | 1.943051  |
| C       | -3.569025 | 0.884598  | 2.665217  |
| C       | -3.760725 | -0.163899 | 3.776180  |
| N       | 2.403927  | 0.835936  | 1.697252  |
| C       | 3.726265  | 0.991216  | 2.310621  |
| C       | 4.306814  | 2.407885  | 2.154951  |
| Si      | -0.014859 | 2.231024  | -0.895784 |
| O       | 1.520068  | 3.028584  | -0.821959 |
| C       | 1.733240  | 4.410484  | -1.111646 |
| C       | 2.531849  | 5.069122  | 0.019615  |
| O       | -1.059912 | 3.477933  | -0.326721 |
| C       | -0.839461 | 4.126994  | 0.925638  |
| C       | -2.179162 | 4.407228  | 1.611526  |
| O       | -0.446212 | 2.139232  | -2.550310 |
| C       | -0.269513 | 3.225006  | -3.461791 |
| C       | -0.937964 | 2.879607  | -4.795370 |
| N       | 3.098408  | -1.637994 | 0.524027  |
| C       | 4.033506  | -1.312287 | -0.372086 |
| C       | 5.156796  | -2.194980 | -0.784360 |
| C       | 6.460600  | -1.929354 | -0.326811 |
| C       | 7.511023  | -2.795290 | -0.660240 |
| C       | 7.266075  | -3.923122 | -1.461569 |
| C       | 5.966052  | -4.185223 | -1.925590 |
| C       | 4.911007  | -3.327198 | -1.582853 |
| C       | 2.932645  | -2.782344 | 1.442767  |
| C       | 2.140102  | -3.892625 | 0.713274  |
| C       | 4.276639  | -3.328922 | 1.971428  |
| C       | 2.096911  | -2.270719 | 2.641037  |
| C       | 5.403281  | 0.035745  | -2.751290 |
| C       | 4.572788  | 2.099705  | -1.592196 |
| C       | -2.137047 | -3.707023 | -0.338138 |
| C       | -4.016438 | -3.947629 | 1.349546  |
| C       | -4.205105 | 2.468782  | -0.604960 |
| C       | -6.038800 | 0.920457  | -1.337644 |
| H       | 5.637738  | 0.672763  | -3.618514 |
| H       | 4.816399  | 2.706135  | -2.479834 |
| H       | 0.066906  | -1.426928 | 0.201156  |
|   | H     | 5.452297 | 2.077101 | -0.928227 |
|---|-------|----------|----------|-----------|
| H | 3.897799 | -3.524634 | -1.936286 |
| H | 6.640438 | -1.050124 | 0.294592  |
| H | -2.819017 | 1.274890  | -2.655736 |
| H | -4.368120 | 1.885720  | -3.311689 |
| H | -4.095520 | 0.122796  | -3.182701 |
| H | -3.124828 | 2.644235  | -0.517100 |
| H | -6.332490 | 0.053923  | -1.944125 |
| H | -6.459182 | 0.803305  | -0.325881 |
| H | -2.853463 | -3.758530 | -1.173323 |
| H | -4.159902 | -2.18409  | -2.740597 |
| H | -6.013614 | -3.486021 | -3.837408 |
| H | -8.127875 | -3.938923 | -2.582299 |
| H | -8.373776 | -3.138181 | -0.226914 |
| H | -6.504138 | -1.893468 | 0.868221  |
| H | 5.773274  | -5.058425 | -2.552174 |
| H | 8.085456  | -4.595597 | -1.723636 |
| H | 8.519859  | -2.589897 | -0.296637 |
| H | -4.637476 | 3.278563  | -1.214330 |
| H | -6.477260 | 1.822787  | -1.792168 |
| H | 2.295364  | 4.493757  | -2.062715 |
| H | 0.772684  | 4.938023  | -1.248132 |
| H | -0.206551 | 3.518345  | 1.594499  |
| H | -0.304294 | 5.080128  | 0.750299  |
| H | -0.710774 | 4.149624  | -3.044317 |
| H | 0.810054  | 3.412983  | -3.619267 |
| H | -2.016785 | 4.940859  | 2.563449  |
| H | -2.822603 | 5.022339  | 0.961653  |
| H | -2.696224 | 3.460591  | 1.819322  |
| H | 2.706626  | 6.137442  | -0.197746 |
| H | 1.980216  | 4.984291  | 0.968449  |
| H | 3.506406  | 4.572740  | 0.144846  |
| H | -0.795259 | 3.696136  | -5.524205 |
| H | -0.503336 | 1.955527  | -5.210343 |
| H | -2.018057 | 2.719063  | -4.650835 |
5.20 Transition State 22oa

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 4.834674| -3.321014| -1.157686|
| C       | 5.149101| -2.204585| -0.359981|
| C       | 6.453064| -2.056846| 0.149553 |
| C       | 7.433185| -3.016773| -0.136676|
| C       | 7.118663| -4.128580| -0.936894|
| C       | 5.819092| -4.277815| -1.448033|
| C       | 4.093035| -1.210998| -0.019066|
| N       | 3.159604| -1.351749| 0.915679 |
| C       | 2.891163| -2.425392| 1.888989 |
| C       | 1.970471| -1.809619| 2.967081 |
| Si      | 2.167291| 0.167791 | 0.237276 |
| N       | 2.482468| 1.370694 | 1.540684 |
| C       | 3.770434| 1.996049 | 1.848229 |
| C       | 3.765410| 3.504290 | 1.535528 |
| Fe      | 0.012427| 0.247554 | 0.005280 |
| O       | -0.338995| -0.829760| -2.279528|
| C       | -0.150755| -0.588895| -3.483083|
| C       | -0.658271| -1.574310| -4.523929|
| Si      | -1.937357| -0.294686| 0.705524 |
| N       | -1.974160| 0.259727 | 2.400645 |
| C       | -3.132707| 0.121117 | 3.290199 |
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | -2.917385    | -0.912648    | 4.411147     |
| N       | -2.820199    | -1.993451    | 0.678273     |
| C       | -2.302974    | -3.382749    | 0.617660     |
| C       | -3.412239    | -4.455862    | 0.684479     |
| C       | -3.913562    | -1.451143    | 0.101356     |
| N       | -3.776740    | -0.122128    | 0.169588     |
| C       | -4.668247    | 0.974309     | -0.262111    |
| C       | -6.157992    | 0.672401     | 0.012482     |
| C       | -5.017561    | -2.181513    | -0.576887    |
| C       | -6.105921    | -2.687838    | 0.156938     |
| C       | -7.138827    | -3.368978    | -0.500232    |
| C       | -7.088243    | -3.551097    | -1.892984    |
| C       | -6.001292    | -3.048098    | -2.626739    |
| C       | -4.967522    | -2.361489    | -1.971809    |
| C       | -1.393260    | -3.569960    | 1.852081     |
| C       | -1.486391    | -3.562116    | -0.683764    |
| C       | -4.446467    | 1.225722     | -1.770906    |
| C       | -4.259865    | 2.215909     | 0.561187     |
| N       | 0.212640     | 0.977350     | 1.938137     |
| C       | -0.848284    | 0.943829     | 2.822076     |
| C       | -0.783044    | 1.573743     | 4.087829     |
| C       | 0.385051     | 2.238060     | 4.455349     |
| C       | 1.488624     | 2.235863     | 3.603057     |
| C       | 1.396167     | 1.558116     | 2.365605     |
| Si      | -0.301517    | 2.398786     | -0.653527    |
| O       | -1.360541    | 2.650966     | -2.012954    |
| C       | -2.190744    | 3.799980     | -2.157799    |
| C       | -2.673072    | 3.887004     | -3.609135    |
| N       | 3.865522     | -0.023728    | -0.639877    |
| C       | 4.395839     | 0.430695     | -1.946578    |
| C       | 3.916024     | 1.883660     | -2.122906    |
| C       | 3.838222     | -0.470322    | -3.075502    |
| C       | 5.941369     | 0.428334     | -1.988630    |
| O       | 1.097431     | 3.333767     | -1.097860    |
| C       | 1.034233     | 4.518028     | -1.884250    |
| C       | 2.432262     | 5.132503     | -2.018239    |
| O       | -1.040329    | 3.340434     | 0.578538     |
|    |        |        |        |
|----|--------|--------|--------|
| C  | -0.758718 | 4.681897 | 0.937656 |
| C  | -1.267636 | 4.937641 | 2.359960 |
| C  | 2.148868  | -3.575245 | 1.168025 |
| C  | 4.177999  | -2.948578 | 2.561797 |
| C  | 0.522874  | 0.663511  | -3.982966 |
| H  | 6.268920  | 0.962254  | -2.895513 |
| H  | 4.172742  | 2.235157  | -3.135068 |
| H  | -0.214906 | -1.189832 | 0.638540  |
| H  | -1.637301 | 1.550200  | 4.758115  |
| H  | 0.441713  | 2.747776  | 5.420116  |
| H  | 2.419130  | 2.712740  | 3.897543  |
| H  | -3.983555 | -0.188239 | 2.667070  |
| H  | -3.398726 | 1.106287  | 3.713901  |
| H  | -2.812014 | -1.916836 | 3.975907  |
| H  | -3.776399 | -0.914942 | 5.103910  |
| H  | -2.005520 | -0.686215 | 4.983377  |
| H  | 4.524101  | 1.495710  | 1.223775  |
| H  | 4.050478  | 1.814011  | 2.903582  |
| H  | 3.474728  | 3.657205  | 0.486808  |
| H  | 4.762245  | 3.942891  | 1.714493  |
| H  | 3.031143  | 4.031080  | 2.163610  |
| H  | -4.472197 | 2.048104  | 1.628749  |
| H  | -0.630828 | -2.783389 | 1.903871  |
| H  | -0.889154 | -4.547123 | 1.789747  |
| H  | -1.994826 | -3.544149 | 2.773891  |
| H  | -1.044574 | -4.572649 | -0.714590 |
| H  | -0.689562 | -2.808038 | -0.742943 |
| H  | -4.082749 | -4.274089 | 1.538863  |
| H  | -2.929792 | -5.436676 | 0.824351  |
| H  | -4.011675 | -4.499459 | -0.233689 |
| H  | 1.281635  | -3.166398 | 0.630499  |
| H  | 1.799895  | -4.320814 | 1.901157  |
| H  | 2.819832  | -4.075001 | 0.452807  |
| H  | 4.822404  | -3.491544 | 1.857587  |
| H  | 3.894299  | -3.638477 | 3.372902  |
| H  | 4.749509  | -2.113653 | 2.998147  |
| H  | 2.481737  | -0.987746 | 3.490974  |
|   |   |   |
|---|---|---|
| H | 1.697148 | -2.585346 | 3.699932 |
| H | 1.056394 | -1.411980 | 2.505367 |
| H | 4.262070 | -1.483131 | -3.002709 |
| H | 4.098578 | -0.052528 | -4.062157 |
| H | 2.745406 | -0.538392 | -2.991119 |
| H | 6.347652 | 0.955347  | -1.110734 |
| H | 6.356885 | -0.586852 | -2.021372 |
| H | 2.835093 | 1.994647  | -1.969303 |
| H | 4.416459 | 2.535609  | -1.390812 |
| H | 3.821509 | -3.433293 | -1.545959 |
| H | 6.689057 | -1.191051 | 0.770078  |
| H | -3.378223 | 1.387125  | -1.968864 |
| H | -5.010574 | 2.116470  | -2.092985 |
| H | -4.802819 | 0.359546  | -2.351296 |
| H | -3.193388 | 2.452632  | 0.453174  |
| H | -6.550096 | -0.118998 | -0.639009 |
| H | -6.308704 | 0.377164  | 1.063818  |
| H | -2.149120 | -3.443593 | -1.556440 |
| H | -4.117516 | -1.968830 | -2.532208 |
| H | -5.957982 | -3.188919 | -3.708775 |
| H | -7.893485 | -4.082754 | -2.404048 |
| H | -7.983208 | -3.757587 | 0.072798  |
| H | -6.137280 | -2.540799 | 1.237597  |
| H | 5.569877  | -5.139489 | -2.070776 |
| H | 7.883209  | -4.875576 | -1.159917 |
| H | 8.441753  | -2.897807 | 0.264425  |
| H | -4.849026 | 3.082600  | 0.221299  |
| H | -6.737825 | 1.590300  | -0.175580 |
| H | 0.968224  | 0.520508  | -4.979964 |
| H | -0.233841 | 1.467255  | -4.028407 |
| H | 1.277092  | 0.996864  | -3.258912 |
| H | 0.171001  | -1.924400 | -5.163683 |
| H | -1.139012 | -2.432953 | -4.034922 |
| H | -1.383649 | -1.075646 | -5.193569 |
| H | 0.619520  | 4.290154  | -2.885653 |
| H | 0.363921  | 5.265818  | -1.418697 |
| H | 0.328522  | 4.878121  | 0.885411  |
5.21 Intermediate 23oa

H  -1.251538  5.381723  0.229490
H  -3.057839  3.728531  -1.477435
H  -1.649701  4.725211  -1.892482
H  -1.055859  5.976756  2.668132
H  -2.356134  4.769191  2.410747
H  -0.777687  4.242909  3.058049
H   2.387980  6.063855  -2.609040
H   2.838332  5.368070  -1.021387
H   3.122201  4.433896  -2.515047
H  -3.348054  4.749472  -3.747267
H  -1.814000  3.999859  -4.291244
H  -3.215392  2.967842  -3.884490

C    6.461257  -1.964535  -0.089001
C    5.134794  -2.203880  -0.494359
C    4.829998  -3.367254  -1.225429
C    5.843806  -4.279434  -1.552356
C    7.165282  -4.038902  -1.143964
C    7.472017  -2.881582  -0.410788
C    4.047460  -1.251622  -0.128133
N    3.756364  -0.077201  -0.744156
C    4.252101   0.446965  -2.037854
C    3.581714   1.819721  -2.219366
N    3.147579  -1.418310   0.839409
C    3.048444  -2.387208   1.950976
C    1.979899  -1.837687   2.924159
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Si      | 2.134177| 0.096734| 0.232196|
| N       | 2.468352| 1.249382| 1.564388|
| C       | 3.795731| 1.683126| 1.999234|
| C       | 4.051518| 3.172520| 1.706836|
| Fe      | 0.000449| 0.226310| -0.005842|
| O       | -0.160337| -0.451318| -1.825975|
| C       | 0.110164| 0.420179| 0.059756|
| Si      | -1.974248| -0.33891| 0.653120|
| N       | -2.938008| 1.990124| 0.650811|
| C       | -2.587526| -3.428107| 0.706858|
| C       | -3.753832| -4.283408| 1.255157|
| N       | -3.782008| -0.083347| 0.077176|
| C       | -4.565859| 1.069229| 0.418811|
| C       | -6.090878| 0.828510| -0.384280|
| C       | -3.994100| -1.403892| 0.043583|
| C       | -5.128648| -2.082116| -0.645346|
| C       | -5.084620| -2.237664| -2.043807|
| C       | -6.171221| -2.806248| -2.724058|
| C       | -7.308774| -3.218497| -2.012380|
| C       | -7.353368| -3.067869| -0.616805|
| C       | -6.267124| -2.504549| 0.065743|
| C       | -4.097614| 1.373817| 1.860770|
| C       | -4.229588| 2.255443| 0.511097|
| N       | -2.025144| 0.226355| 2.346687|
| C       | -0.904864| 0.921911| 2.767806|
| N       | 0.169953| 0.932337| 1.895753|
| C       | 1.357459| 1.490577| 2.351856|
| C       | 1.429710| 2.201941| 3.568685|
| C       | 0.301456| 2.259009| 4.387391|
| C       | -0.862428| 1.593333| 4.011988|
| C       | -3.187803| 0.082961| 3.227270|
| C       | -2.966614| -0.926700| 4.368019|
| Si      | -0.164289| 2.410064| -0.689345|
| O       | -0.982703| 2.716947| -2.196970|
| O       | 1.271965| 3.377592| -0.795015|
| O       | -1.092742| 3.295443| 0.455471|
| Element | U | V | W |
|---------|---|---|---|
| C       | 2.593849 | -3.764066 | 1.415746 |
| C       | 4.392244 | -2.517012 | 2.702522 |
| C       | 3.853395 | -0.483911 | -3.206860 |
| C       | 5.784887 | 0.643144  | -1.997798 |
| C       | -1.391567 | -3.574605 | 1.670320 |
| C       | -2.173178 | -3.922477 | -0.695774 |
| C       | -0.006005 | -2.157098 | -3.480639 |
| H       | 6.104638  | 1.167349  | -2.911427 |
| H       | 3.890819  | 2.259440  | -3.178231 |
| H       | 0.071012  | -1.274908 | 0.428742 |
| H       | -1.732055 | 1.594633  | 4.661225 |
| H       | 0.338680  | 2.803595  | 5.331918 |
| H       | 2.356721  | 2.680770  | 3.866910 |
| H       | -4.029238 | -0.249137 | 2.603456 |
| H       | -3.473059 | 1.068797  | 3.633962 |
| H       | -2.753520 | -1.918915 | 3.945856 |
| H       | -3.866539 | -0.997801 | 5.000031 |
| H       | -2.116517 | -0.629287 | 4.997639 |
| H       | 4.530312  | 1.071409  | 1.455212 |
| H       | 3.931035  | 1.472970  | 3.075921 |
| H       | 3.941749  | 3.359365  | 0.631170 |
| H       | 5.062206  | 3.468346  | 2.032259 |
| H       | 3.312389  | 3.800168  | 2.223550 |
| H       | -4.584896 | 2.048625  | 1.532223 |
| H       | -0.531555 | -3.004865 | 1.300744 |
| H       | -1.118701 | -4.637537 | 1.749511 |
| H       | -1.648914 | -3.200639 | 2.671663 |
| H       | -1.847824 | -4.973778 | -0.648903 |
| H       | -1.339607 | -3.304865 | -1.055999 |
| H       | -4.132970 | -3.850536 | 2.193064 |
| H       | -3.386608 | -5.300182 | 1.463243 |
| H       | -4.578040 | -4.359957 | 0.537067 |
| H       | 1.645625  | -3.656751 | 0.870649 |
| H       | 2.440245  | -4.454643 | 2.259538 |
| H       | 3.350925  | -4.193898 | 0.746067 |
| H       | 5.159294  | -2.997634 | 2.081997 |
| H       | 4.243789  | -3.128281 | 3.605795 |
| H   | 4.749316 | -1.522332 | 3.008986 |
| H   | 2.320243 | -0.899364 | 3.383458 |
| H   | 1.800694 | -2.577780 | 3.717865 |
| H   | 1.039656 | -1.639898 | 2.392615 |
| H   | 4.375969 | -1.447559 | -3.145686 |
| H   | 4.114554 | -0.006915 | -4.164165 |
| H   | 2.767766 | -0.662332 | -3.191882 |
| H   | 6.061762 | 1.256625  | -1.127464 |
| H   | 6.316999 | -0.314686 | -1.946189 |
| H   | 2.489590 | 1.736443  | -2.188188 |
| H   | 3.865675 | 2.496220  | -1.406098 |
| H   | 3.802007 | -3.548674 | -1.537787 |
| H   | 6.691905 | -1.065005 | 0.480675  |
| H   | -3.007925 | 1.493584  | -1.873706 |
| H   | -4.566660 | 2.297662  | -2.232770 |
| H   | -4.378127 | 0.547318  | -2.530234 |
| H   | -3.151808 | 2.459665  | 0.537358  |
| H   | -6.418717 | 0.096312  | -1.131443 |
| H   | -6.408285 | 0.483358  | 0.611287  |
| H   | -3.015322 | -3.844184 | -1.397825 |
| H   | -4.201847 | -1.907204 | -2.590296 |
| H   | -6.130510 | -2.923598 | -3.807421 |
| H   | -8.155834 | -3.655718 | -2.541832 |
| H   | -8.236251 | -3.385112 | -0.060986 |
| H   | -6.299112 | -2.379447 | 1.147383  |
| H   | 5.601490  | -5.176350 | -2.123200 |
| H   | 7.952086  | -4.750958 | -1.394623 |
| H   | 8.496518  | -2.692123 | -0.089384 |
| H   | -4.742774 | 3.157294  | 0.141051  |
| H   | -6.592442 | 1.785626  | -0.595913 |
| H   | 0.165942  | 0.026932  | -5.085909 |
| H   | -0.730658 | 1.120059  | -3.948754 |
| H   | 1.009410  | 1.019345  | -3.848231 |
| H   | 0.148307  | -2.264377 | -4.564483 |
| H   | 0.800184  | -2.688335 | -2.943756 |
| H   | -0.951210 | -2.649385 | -3.203133 |
| C   | -0.913477 | 4.648942  | 0.827311  |
5.22 Transition State 24oa^2
| Elements | x       | y       | z       |
|----------|---------|---------|---------|
| N        | 0.070437| 1.054802| 1.802996|
| C        | 1.259967| 1.546769| 2.323475|
| C        | 1.293146| 2.426913| 3.427478|
| C        | 0.095284| 2.799591| 4.032589|
| N        | -2.277530| 0.936209| 1.889449|
| C        | -3.573697| 1.280037| 2.490489|
| C        | -3.869245| 0.535615| 3.806581|
| Fe       | 0.036409 | 0.160436| -0.176075|
| Si       | -0.094448| 2.311367| -0.793385|
| O        | -1.367612| 3.176508| -0.025604|
| C        | -1.321139| 4.546566| 0.355895|
| C        | -2.507463| 4.861881| 1.270664|
| N        | 2.418572 | 1.107835| 1.719059|
| C        | 3.732716 | 1.382746| 2.306041|
| C        | 4.312445 | 2.741395| 1.877172|
| Si       | 2.181469 | 0.140276| 0.250020|
| N        | 3.142554 | -1.440126| 0.767677|
| C        | 2.996919 | -2.460659| 1.823660|
| C        | 4.351589 | -2.963595| 2.369918|
| C        | 4.111851 | -1.180182| -0.114158|
| N        | 3.868803 | 0.057049 | -0.624393|
| C        | 4.341633 | 0.596034 | -1.935222|
| C        | 5.856337 | 0.896857 | -1.878976|
| C        | 5.212813 | -2.107460| -0.482230|
| C        | 6.538461 | -1.828376| -0.098518|
| C        | 7.559606 | -2.749220| -0.372650|
| C        | 7.264656 | -3.951801| -1.036040|
| C        | 5.943136 | -4.232263| -1.423531|
| C        | 4.918272 | -3.318729| -1.141001|
| C        | 3.582313 | 1.911853 | -2.179192|
| C        | 4.018536 | -0.376656| -3.089300|
| C        | 2.207614 | -1.802166| 2.980199|
| C        | 2.170339 | -3.642912| 1.267913|
| O        | 0.165669 | -0.418955| -2.029469|
| C        | 0.020388 | -1.710015| -1.597798|
| C        | -1.275190| -2.337750| -2.158163|
| Si       | -2.093294| 0.046691 | 0.352628|
| Atom Type | x-Coordinate | y-Coordinate | z-Coordinate |
|-----------|--------------|--------------|--------------|
| N         | -3.834471    | 0.044730     | -0.441026    |
| C         | -4.029800    | -1.244461    | -0.081813    |
| C         | -5.120217    | -2.149760    | -0.532708    |
| C         | -4.863745    | -3.132247    | -1.507726    |
| C         | -5.891528    | -3.994044    | -1.919848    |
| C         | -7.173510    | -3.884228    | -1.356445    |
| C         | -7.429384    | -2.904392    | -0.381827    |
| C         | -6.407732    | -2.036312    | 0.025923     |
| C         | 1.232943     | -2.607481    | -1.943678    |
| N         | -3.014644    | -1.580566    | 0.729203     |
| C         | -2.782870    | -2.764601    | 1.583094     |
| C         | -2.191056    | -3.932997    | 0.762716     |
| C         | -4.075057    | -3.236732    | 2.285371     |
| C         | -1.738928    | -2.337083    | 2.639214     |
| C         | -4.388351    | 0.839528     | -1.570597    |
| C         | -4.395966    | 2.304056     | -1.085064    |
| C         | -5.822758    | 0.433566     | -1.966296    |
| C         | -3.456501    | 0.694619     | -2.796559    |
| O         | -0.363700    | 2.520707     | -2.461689    |
| C         | -1.226228    | 3.507259     | -3.018739    |
| C         | -1.366877    | 3.247496     | -4.521010    |
| O         | 1.294941     | 3.257485     | -0.444485    |
| C         | 1.607020     | 4.439322     | -1.178997    |
| C         | 2.659678     | 5.247108     | -0.415558    |
| H         | 6.148435     | 1.442284     | -2.790678    |
| H         | 3.963079     | 2.377720     | -3.101608    |
| H         | -0.060160    | -1.736453    | -0.419828    |
| H         | -2.047196    | 2.579890     | 4.025471     |
| H         | 0.100879     | 3.483423     | 4.884538     |
| H         | 2.240970     | 2.825870     | 3.777959     |
| H         | -4.346336    | 1.028208     | 1.751220     |
| H         | -3.631989    | 2.371371     | 2.641410     |
| H         | -3.974342    | -0.542190    | 3.620026     |
| H         | -4.808775    | 0.905626     | 4.251368     |
| H         | -3.058299    | 0.677874     | 4.535527     |
| H         | 4.410689     | 0.578038     | 1.980834     |
| H         | 3.667327     | 1.318400     | 3.406561     |
|   |   |   |   |
|---|---|---|---|
| H | 4.427540 | 2.762322 | 0.784244 |
| H | 5.298225 | 2.909785 | 2.346433 |
| H | 3.637639 | 3.561826 | 2.159904 |
| H | -5.086326 | 2.421093 | -0.232894 |
| H | -0.831794 | -1.966967 | 2.136738 |
| H | -1.471641 | -3.203446 | 3.264516 |
| H | -2.122835 | -1.532062 | 3.280331 |
| H | -2.031151 | -4.801064 | 1.422888 |
| H | -1.225737 | -3.636357 | 0.331334 |
| H | -4.573964 | -2.399031 | 2.794991 |
| H | -3.811365 | -3.995923 | 3.039052 |
| H | -4.781996 | -3.685700 | 1.574908 |
| H | 1.201492 | -3.279284 | 0.895317 |
| H | 1.990466 | -4.381395 | 2.066598 |
| H | 2.702022 | -4.138527 | 0.442735 |
| H | 4.895347 | -3.575728 | 1.638499 |
| H | 4.161467 | -3.579419 | 3.263500 |
| H | 4.987317 | -2.112819 | 2.662379 |
| H | 2.797616 | -1.004041 | 3.452193 |
| H | 1.969928 | -2.567102 | 3.736239 |
| H | 1.269903 | -1.362358 | 2.611513 |
| H | 4.555466 | -1.329566 | -2.977019 |
| H | 4.319484 | 0.079059 | -4.047178 |
| H | 2.937199 | -0.566875 | -3.114877 |
| H | 6.087022 | 1.527830 | -1.005216 |
| H | 6.454466 | -0.022823 | -1.825534 |
| H | 2.504629 | 1.733809 | -2.292999 |
| H | 3.730197 | 2.604054 | -1.339445 |
| H | 3.891184 | -3.527609 | -1.439622 |
| H | 6.757448 | -0.896787 | 0.424938 |
| H | -2.414738 | 0.943613 | -2.548775 |
| H | -3.802414 | 1.369111 | -3.596975 |
| H | -3.487052 | -0.338378 | -3.177428 |
| H | -3.389238 | 2.617240 | -0.775344 |
| H | -5.865525 | -0.569875 | -2.411247 |
| H | -6.505011 | 0.465702 | -1.102709 |
| H | -2.871750 | -4.229668 | -0.047669 |
|   |   |   |   |
|---|---|---|---|
| H | -3.866951 | -3.205394 | -1.943364 |
| H | -5.690217 | -4.750014 | -2.681698 |
| H | -7.971509 | -4.557372 | -1.676625 |
| H | -8.424806 | -2.815971 | 0.058332  |
| H | -6.595866 | -1.273364 | 0.783091  |
| H |  5.710187 | -5.163334 | -1.944309 |
| H |  8.061111 | -4.667614 | -1.249738 |
| H |  8.584138 | -2.529577 | -0.065547 |
| H | -4.735578 |  2.957005 | -1.905125 |
| H | -6.178323 |  1.157085 | -2.716598 |
| H |  1.125903 | -3.629619 | -1.538429 |
| H |  1.314167 | -2.668080 | -3.041574 |
| H |  2.152151 | -2.162471 | -1.551264 |
| H | -1.433614 | -3.373457 | -1.819523 |
| H | -2.137642 | -1.721678 | -1.882559 |
| H | -1.184531 | -2.332386 | -3.256831 |
| H |  1.985052 |  4.167420 | -2.181822 |
| H |  0.711448 |  5.066857 | -1.332637 |
| H | -0.372690 |  4.758630 |  0.879962 |
| H | -1.363690 |  5.197692 | -0.540318 |
| H | -2.217487 |  3.473730 | -2.531886 |
| H | -0.817448 |  4.524572 | -2.855364 |
| H | -2.502986 |  5.929549 |  1.549944 |
| H | -3.458766 |  4.633437 |  0.763648 |
| H | -2.439497 |  4.257053 |  2.187237 |
| H |  2.906211 |  6.174863 | -0.959810 |
| H |  2.282322 |  5.510552 |  0.585792 |
| H |  3.579569 |  4.656219 | -0.290614 |
| H | -2.032127 |  3.997069 | -4.984157 |
| H | -0.380940 |  3.296618 | -5.010086 |
| H | -1.784871 |  2.243389 | -4.690159 |
### 5.23 Intermediate 25oa

|   | X   | Y   | Z   |   |   |   |
|---|-----|-----|-----|---|---|---|
| C | -6.055636 | -2.627143 | 0.012786 |
| C | -4.677157 | -2.486873 | 0.255436 |
| C | -3.965556 | -3.524928 | 0.890249 |
| C | -4.634760 | -4.691852 | 1.282503 |
| C | -6.012650 | -4.831853 | 1.040350 |
| C | -4.399134 | 0.273863 | 1.816820 |
| N | -3.796241 | -0.105928 | 0.510347 |
| C | -3.702667 | 1.574006 | 2.266314 |
| C | -3.143577 | -1.179533 | -1.247667 |
| C | -2.794693 | -2.142824 | -2.310451 |
| C | -2.128054 | -1.302506 | -3.424350 |
| Si | 2.028930 | 0.257914 | -0.480432 |
| N | 2.995063 | -1.239282 | -1.171922 |
| C | 2.656434 | -2.374910 | -2.055063 |
| C | 3.879653 | -2.819520 | -2.885006 |
| N | 3.729312 | 0.073377 | 0.377894 |
C 4.382571  0.709928  1.547362
C 5.824235  0.216775  1.796888
C 3.914979 -1.132199 -0.199069
C 4.837822 -2.200030  0.271606
C 4.448741 -3.002472  1.362463
C 5.314050 -3.994158  1.846045
C 6.571924 -4.185418  1.249351
C 6.960457 -3.385207  0.162110
C 6.095682 -2.395334 -0.326632
C 3.510751  0.461732  2.797596
C 4.429016  2.221715  1.239587
N 2.233411  1.487799 -1.756667
C 1.072010  2.089064 -2.209812
N -0.117891  1.602717 -1.682804
C -1.304911  2.153115 -2.159051
C -1.318575  3.214477 -3.088899
C -0.108748  3.701552 -3.583051
C 1.093116  3.132395 -3.163687
C 3.534078  1.857442 -2.327978
C 3.763906  1.299905 -3.745185
Si -0.038319  2.096279  1.088502
O 0.038320   1.823169  2.777887
O -1.371421  3.152305  0.860159
O 1.307126   3.121902  0.773381
C -1.789804 -3.194612 -1.785772
C -4.053619 -2.828766 -2.881548
C -4.186674 -0.790089  2.920507
C -5.899471 -3.543008  1.611800
C 1.554209 -1.859398 -3.005193
C 2.092509 -3.555208 -1.236974
C 0.003931 -3.543008  1.742195
H -6.343066  0.910127  2.549730
H -4.201699  1.945305  3.175472
H 2.038893   3.493480 -3.557549
H -0.102113  4.524023 -4.301666
H -2.262272  3.651229 -3.404682
H 4.303111   1.460056 -1.651194
| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| H    | 3.648223     | 2.955824     | -2.318721    |
| H    | 3.768996     | 0.200872     | -3.716113    |
| H    | 4.733600     | 1.646110     | -4.142120    |
| H    | 2.967965     | 1.623432     | -4.432803    |
| H    | -4.446213    | 1.070342     | -2.111737    |
| H    | -3.682367    | 2.065874     | -3.360977    |
| H    | -4.567314    | 3.001068     | -0.548906    |
| H    | -5.352611    | 3.442657     | -2.097612    |
| H    | -3.708926    | 4.043493     | -1.702327    |
| H    | 5.071204     | 2.412282     | 0.364569     |
| H    | 0.691727     | -1.506367    | -2.421329    |
| H    | 1.223592     | -2.676183    | -3.665703    |
| H    | 1.919245     | -1.023809    | -3.620033    |
| H    | 1.779282     | -4.366050    | -1.915049    |
| H    | 1.221461     | -3.210549    | -0.668255    |
| H    | 4.318651     | -1.958068    | -3.413033    |
| H    | 3.557466     | -3.561324    | -3.633658    |
| H    | 4.650041     | -3.281870    | -2.253419    |
| H    | -0.967181    | -2.693188    | -1.258468    |
| H    | -1.387680    | -3.780333    | -2.628815    |
| H    | -2.282729    | -3.884752    | -1.085860    |
| H    | -4.523501    | -3.495703    | -2.146527    |
| H    | -3.764907    | -3.429126    | -3.759212    |
| H    | -4.790192    | -2.073321    | -3.200339    |
| H    | -2.839900    | -0.567498    | -3.830245    |
| H    | -1.794425    | -1.965899    | -4.237503    |
| H    | -1.256286    | -0.759885    | -3.030938    |
| H    | -4.710664    | -1.727216    | 2.694751     |
| H    | -4.603439    | -0.391416    | 3.860527     |
| H    | -3.118921    | -1.003969    | 3.088760     |
| H    | -6.048241    | 1.296797     | 0.826389     |
| H    | -6.425586    | -0.382993    | 1.322623     |
| H    | -2.641136    | 1.403257     | 2.488496     |
| H    | -3.766705    | 2.342614     | 1.484958     |
| H    | -2.900709    | -3.394397    | 1.085256     |
| H    | -6.597333    | -1.826695    | -0.493381    |
| H    | 2.493159     | 0.837473     | 2.630003     |
| Element | X     | Y       | Z     |
|---------|-------|---------|-------|
| H       | 3.944439 | 0.979422 | 3.669175 |
| H       | 3.455637 | -0.616076 | 3.017517 |
| H       | 3.419419 | 2.600954 | 1.037813 |
| H       | 5.863081 | -0.812605 | 2.175174 |
| H       | 6.424947 | 0.279663 | 0.875919 |
| H       | 2.844731 | -3.953010 | -0.540313 |
| H       | 3.471651 | -2.841803 | 1.822494 |
| H       | 5.007240 | -4.615795 | 2.689861 |
| H       | 7.246963 | -4.954009 | 1.631259 |
| H       | 7.938145 | -3.528208 | -0.302566 |
| H       | 6.393327 | -1.765271 | -1.166326 |
| H       | -4.081281 | -5.490453 | 1.780991 |
| H       | -6.531605 | -5.742646 | 1.346184 |
| H       | -7.790579 | -3.904671 | 0.212677 |
| H       | 4.848187 | 2.759248 | 2.106017 |
| H       | 6.279012 | 0.876706 | 2.552511 |
| H       | 1.088156 | -2.032640 | 3.790330 |
| H       | 0.737489 | -0.414351 | 3.078304 |
| H       | -0.600712 | -1.504790 | 3.485811 |
| H       | 0.731445 | -4.159378 | 2.299137 |
| H       | -0.967437 | -3.604369 | 2.262208 |
| H       | -0.116994 | -3.967054 | 0.734406 |
| C       | 1.274347 | 4.533194 | 0.576781 |
| C       | -1.714521 | 4.154084 | 1.814082 |
| C       | 0.701816 | 2.691155 | 3.698772 |
| C       | -2.717707 | 5.124990 | 1.186008 |
| H       | -2.148404 | 3.682366 | 2.714670 |
| H       | -0.821773 | 4.717993 | 2.142223 |
| C       | 2.451286 | 4.976556 | -0.297716 |
| H       | 0.325822 | 4.828941 | 0.096739 |
| H       | 1.327431 | 5.046036 | 1.559218 |
| C       | 0.875986 | 1.962836 | 5.034574 |
| H       | 1.685122 | 2.995037 | 3.296213 |
| H       | 0.107838 | 3.612862 | 3.848063 |
| H       | 2.426022 | 6.071667 | -0.433708 |
| H       | 3.412067 | 4.703725 | 0.165231 |
| H       | 2.382257 | 4.497129 | -1.284637 |
H  -2.989195  5.918329  1.903388
H  -2.280372  5.591498  0.288401
H  -3.632515  4.593527  0.882943
H   1.363671  2.623045  5.772582
H  -0.104401  1.652705  5.429990
H   1.494161  1.061711  4.901881
H   1.503306 -2.024774  1.301952

5.24 Transition State 26oa

C   6.879304 -1.303275 -1.004918
C   5.823161 -1.236969 -0.078443
C   5.980860 -1.792392  1.204167
C   7.186343 -2.418944  1.553872
C   8.241402 -2.481024  0.628651
C   8.086993 -1.918680 -0.649996
C   4.533624 -0.584094 -0.440173
N   3.544232 -1.143624 -1.173030
C   4.903703  1.771324  0.505304
C   4.267017  2.169438  1.847164
Si  2.301502  0.275778 -0.688522
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Fe      | 0.131993| 0.276860| -0.064362|
| O       | 0.192691| -1.224573| 1.430373|
| Si      | -0.656295| -2.619548| 0.498032|
| O       | -0.653426| -3.515087| -0.959369|
| N       | 0.048447| 1.649566| -1.740962|
| C       | 1.181058| 1.977126| -3.422125|
| C       | 0.049898| 3.799186| -3.585986|
| C       | -1.101169| 3.502302| -2.862587|
| C       | -1.103541| 2.376554| -2.003541|
| N       | 2.317877| 1.243740| -2.193331|
| C       | 3.462284| 1.317384| -3.113039|
| C       | 3.186257| 0.633800| -4.462169|
| N       | -2.269242| 1.899196| -1.455888|
| Si      | -2.102382| 0.511911| -0.325158|
| N       | -3.712820| 0.495469| 0.742123|
| C       | -4.148960| 0.911005| 2.097568|
| C       | -4.636117| -0.269245| 2.973460|
| Si      | 0.276034| 2.328932| 1.020355|
| O       | -1.092823| 3.408149| 0.932585|
| C       | -1.287692| 4.398807| 1.948277|
| C       | -2.527438| 5.239828| 1.641585|
| O       | 1.529368| 3.352741| 0.389662|
| C       | 1.347657| 4.755848| 0.159585|
| C       | 2.382624| 5.326475| -0.813250|
| O       | 0.554698| 2.292009| 2.715658|
| C       | 1.302501| 3.244969| 3.471562|
| C       | 2.072288| 2.548602| 4.601933|
| C       | -3.541282| 2.457467| -1.932471|
| C       | -3.884482| 3.848570| -1.332846|
| N       | -3.510849| -0.486919| -1.176897|
| C       | -4.345389| -0.296739| -0.149161|
| C       | -5.804444| -0.649314| -0.151041|
| C       | -6.625790| 0.088218| -1.032588|
| C       | -8.007162| -0.139812| -1.090003|
| C       | -8.596886| -1.108771| -0.263239|
| C       | -7.794030| -1.832853| 0.630620|
| Element | x       | y       | z       |
|---------|---------|---------|---------|
| C       | -6.4127 | -1.5955 | 0.6961  |
| C       | -3.5902 | -1.3560 | -2.3807 |
| C       | -3.9364 | -2.8222 | -2.0307 |
| C       | -4.6354 | -0.7977 | -3.3815 |
| C       | -2.2029 | -1.2895 | -3.0563 |
| C       | -5.2653 | 1.9717  | 1.9669  |
| H       | -5.6119 | 2.2785  | 2.9674  |
| O       | 0.1273  | -3.7947 | 1.4727  |
| O       | -2.2874 | -2.4558 | 0.8574  |
| H       | -5.6119 | 2.2785  | 2.9674  |
| H       | -3.2139 | 2.0119  | 3.7155  |
| H       | 2.0869  | 3.2310  | -3.9930 |
| H       | 0.0611  | 4.6453  | -4.2769 |
| H       | -1.9972 | 4.1019  | -2.9831 |
| H       | 4.3083  | 0.8229  | -2.6227 |
| H       | 3.7668  | 2.3679  | -3.2612 |
| H       | 2.9773  | -0.4303 | -4.2997 |
| H       | 4.0615  | 0.7282  | -5.1273 |
| H       | 2.3158  | 1.0855  | -4.9609 |
| H       | -4.3197 | 1.7385  | -1.6670 |
| H       | -3.5149 | 2.5031  | -3.0359 |
| H       | -4.7370 | 3.7833  | -0.6393 |
| H       | -4.1416 | 4.5782  | -2.1188 |
| H       | -3.0213 | 4.2257  | -0.7734 |
| H       | 5.2549  | 2.6645  | -1.4546 |
| H       | 1.2886  | -2.2065 | -1.9758 |
| H       | 1.9169  | -3.7955 | -2.4682 |
| H       | 2.4454  | -2.3321 | -3.3405 |
| H       | 2.6826  | -4.3169 | -0.1898 |
| H       | 2.3294  | -2.7369 | 0.5463  |
H 4.920693 -2.670712 -2.921039
H 4.287572 -4.263103 -2.418394
H 5.431471 -3.398909 -1.367207
H -3.029876 -3.334461 -1.691157
H -4.325984 -3.329239 -2.929014
H -4.705574 -2.879105 -1.245882
H -5.661345 -0.934694 -3.014973
H -4.539985 -1.339920 -4.336141
H -4.456536 0.272380 -3.567533
H -1.980277 -0.261822 -3.83571
H -2.204141 -1.950332 -3.937635
H -1.416898 -1.629242 -2.372792
H -5.656433 -0.581674 2.722831
H -4.638150 0.056457 4.026260
H -3.946840 -1.120901 2.871636
H -4.883287 2.858647 1.439442
H -6.122371 1.566033 1.407134
H -2.181754 0.725910 3.018393
H -2.432437 2.229684 2.114762
H -5.819872 -2.106508 1.451069
H -6.176285 0.837327 -1.683013
H 3.206818 2.398493 1.710672
H 4.770999 3.070657 2.233516
H 4.381383 1.359213 2.581295
H 3.695915 3.112298 -0.698277
H 6.598443 0.770083 1.512937
H 6.917735 -3.383021 0.556661
H 3.996635 -3.383021 0.556661
H 5.158830 -1.730730 1.918981
H 7.302773 -2.854346 2.548472
H 9.181125 -2.964830 0.902865
H 8.905660 -1.963528 -1.371129
H 6.744869 -0.876463 -2.000162
H -8.242636 -2.572703 1.296563
H -9.672907 -1.288616 -0.306512
H -8.620984 0.445815 -1.777348
H 5.220096 3.841136 -0.106528
|    |    |    |    |
|----|----|----|----|
| C  | -3.200439 | -3.461313 | 1.295150 |
| C  | -0.350525 | -3.936612 | 2.827565 |
| C  | -0.206495 | -4.859560 | -1.110320 |
| H  | -4.199275 | -3.076481 | 1.081294 |
| C  | -3.073453 | -4.858902 | 0.674558 |
| H  | -3.115613 | -3.604122 | 2.383707 |
| C  | -0.594852 | -5.356135 | -2.504440 |
| H  | 0.879880 | -4.920963 | -0.953572 |
| H  | -0.653254 | -5.520454 | -0.351593 |
| C  | 0.741640 | -4.492246 | 3.736403 |
| H  | -0.784761 | -2.996653 | 3.179048 |
| H  | -1.195598 | -4.647136 | 2.847416 |
| H  | 0.347457 | -4.636203 | 4.756343 |
5.25 Transition State 27oa²

|  |  |  |  |
|---|---|---|---|
| H | 1.080192 | -5.465035 | 3.346409 |
| H | 1.616926 | -3.827544 | 3.793444 |
| H | -0.258357 | -6.397504 | -2.645873 |
| H | -1.690062 | -5.321442 | -2.625030 |
| H | -0.150183 | -4.731039 | -3.292647 |
| H | -3.866229 | -5.491270 | 1.112492 |
| H | -3.188488 | -4.853201 | -0.414625 |
| H | -2.110143 | -5.322332 | 0.933435 |
| C | 4.795187 | -2.652740 | -2.058100 |
| C | 5.197294 | -2.011293 | -0.869722 |
| C | 6.508825 | -2.184956 | -0.391272 |
| C | 7.412699 | -2.992761 | -1.095940 |
| C | 7.011505 | -3.630547 | -2.281720 |
| C | 5.700984 | -3.460720 | -2.759963 |
| C | 4.226570 | -1.134777 | -0.161291 |
| N | 3.384042 | -1.503336 | 0.815770 |
| C | 3.195666 | -2.788844 | 1.508766 |
| C | 2.140746 | -2.518686 | 2.606132 |
| Si | 2.282056 | 0.031806 | 0.489012 |
| N | 3.911388 | 0.139746 | -0.480447 |
| C | 4.389763 | 1.003393 | -1.586549 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 4.262871| 2.454425| -1.076396|
| Fe      | 0.080748| 0.079980| 0.157580 |
| Si      | -0.294312| 2.116414| -0.598521|
| O       | -1.518725| 2.487084| -1.758052|
| C       | -2.057174| 3.804138| -1.842959|
| C       | -2.609647| 4.026906| -3.255263|
| Si      | -2.010376| -0.160534| 0.653156 |
| N       | -2.111111| 0.083671| 2.410735 |
| C       | -3.301485| -0.180894| 3.226006 |
| C       | -3.142929| -1.396608| 4.156905 |
| N       | -2.876758| -1.863397| 0.334647 |
| C       | -2.355290| -3.219703| 0.047154 |
| C       | -2.696681| -4.143577| 1.239749 |
| C       | -3.977980| -1.235027| -0.119716|
| N       | -3.804540| 0.079689| 0.104483 |
| C       | -4.759257| 1.213006| 0.038833 |
| C       | -6.148843| 0.822753| 0.588434 |
| C       | -5.145994| -1.878067| -0.766887|
| C       | -5.967135| -2.739652| -0.013152|
| C       | -7.060446| -3.375074| -0.617905|
| C       | -7.330615| -3.163998| -1.980832|
| C       | -6.506419| -2.311692| -2.735641|
| C       | -5.418575| -1.665722| -2.132068|
| C       | -0.817856| -3.088430| -0.059008|
| C       | -2.884692| -3.856471| -1.259492|
| C       | -4.881205| 1.708539| -1.418588|
| C       | -4.168731| 2.339691| 0.914017 |
| N       | 0.192749 | 0.523858| 2.205557 |
| C       | -0.944140| 0.545721| 3.001607 |
| C       | -0.933299| 1.002292| 4.337498 |
| C       | 0.261240 | 1.451220| 4.895708 |
| C       | 1.421944 | 1.445088| 4.124090 |
| C       | 1.366571 | 0.992898| 2.787517 |
| N       | 2.507999 | 0.940997| 1.999893 |
| C       | 3.827046 | 1.223696| 2.581319 |
| C       | 4.129054 | 2.729000| 2.701369 |
| C       | 3.470849 | 0.770355| -2.805799|
C  5.864522  0.750177  -1.968630
O  1.076802  3.007665  -1.108285
C  1.267913  3.576562  -2.398152
C  1.577981  5.073613  -2.278261
O -0.839065  3.069160   0.742318
C -0.429170  4.387431  1.076997
C  0.771476  4.378328  2.029951
C  2.684840 -3.868602  0.528061
C  4.505974 -3.254216  2.181658
C -1.884647 -0.504682 -2.821200
C -0.380225 -0.196661 -2.912935
C -0.097316  0.694495  -4.137009
H  6.174190  1.549953  -2.659974
H  4.535515  3.152738  -1.883486
H -1.849325  1.008179   4.921395
H  0.288104  1.809139   5.927226
H  2.358927  1.795905   4.544914
H -4.131273 -0.361825   2.530235
H -3.573848  0.718230   3.808747
H -2.952278 -2.298758   3.558068
H -4.062810 -1.551421   4.746211
H -2.300936 -1.254052   4.850186
H  4.575628  0.762868   1.920247
H  3.920477  0.728925   3.566316
H  4.073215  3.199952   1.710046
H  5.142132  2.881341   3.111543
H  3.404356  3.237003   3.352807
H -4.142981  2.037822   1.970632
H  0.530818 -2.484902  -0.934587
H -0.364574 -4.088128  -0.146958
H -0.414989 -2.602969   0.845157
H -2.309220 -4.776763  -1.450118
H -2.749323 -3.178758  -2.113776
H -2.233641 -3.764759   2.163139
H -2.319170 -5.161620   1.048993
H -3.786873 -4.196000   1.384014
H  1.814642 -3.485945  -0.024001
|   | x     | y     | z     |
|---|-------|-------|-------|
| H | 2.381989 | -4.771353 | 1.084038 |
| H | 3.469483  | -4.145789  | -0.191323 |
| H | 5.275800  | -3.492695  | 1.435547  |
| H | 4.307803  | -4.161683  | 2.774766  |
| H | 4.887055  | -2.470339  | 2.855466  |
| H | 2.485351  | -1.721610  | 3.282156  |
| H | 1.968467  | -3.435405  | 3.191458  |
| H | 1.189622  | -2.189327  | 2.161861  |
| H | 3.633804  | -0.242655  | -3.209251 |
| H | 3.699264  | 1.500589   | -3.599676 |
| H | 2.415893  | 0.867694   | -2.510948 |
| H | 6.513789  | 0.791266   | -1.079548 |
| H | 6.014129  | -0.212327  | -2.473679 |
| H | 3.232992  | 2.669666   | -0.760379 |
| H | 4.948650  | 2.612833   | -0.229543 |
| H | 3.777080  | -2.511818  | -2.424593 |
| H | 6.816768  | -1.676972  | 0.524000  |
| H | -3.878362 | 1.879269   | -1.827281 |
| H | -5.447853 | 2.653714   | -1.444426 |
| H | -5.411318 | 0.971380   | -2.038755 |
| H | -3.145028 | 2.595254   | 0.606674  |
| H | -6.641203 | 0.065867   | -0.036681 |
| H | -6.066356 | 0.437369   | 1.617450  |
| H | -3.946381 | -4.126445  | -1.187883 |
| H | -4.756642 | -1.024832  | -2.714390 |
| H | -6.707380 | -2.155099  | -3.797436 |
| H | -8.178643 | -3.663875  | -2.453345 |
| H | -7.699281 | -4.035286  | -0.027723 |
| H | -5.746944 | -2.896658  | 1.044130  |
| H | 5.384736  | -3.955602  | -3.680556 |
| H | 7.717157  | -4.256665  | -2.831451 |
| H | 8.430732  | -3.120081  | -0.722265 |
| H | -4.804323 | 3.234401   | 0.821145  |
| H | -6.785300 | 1.721951   | 0.606887  |
| H | -2.218982 | -1.020951  | -3.739348 |
| H | -2.086686 | -1.158581  | -1.966202 |
| H | -2.449294 | 0.427492   | -2.697134 |
Electronic Supplementary Information (ESI) for Chemical Science

|      | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -0.396152 | 0.180209 | -5.067140 |
| H    | -0.668439 | 1.628719 | -4.041187 |
| H    | 2.121581  | 3.072824 | -2.885531 |
| H    | 0.973222  | 0.939536 | -4.196468 |
| H    | -0.167387 | 4.968089 | 0.174286 |
| H    | -1.291985 | 4.888310 | 1.556953 |
| H    | -2.856433 | 3.941369 | -1.092140 |
| H    | -1.285655 | 4.566232 | -1.634499 |
| H    | 1.039794  | 5.407269 | 2.331867 |
| H    | 0.541524  | 3.787587 | 2.929512 |
| H    | 1.632539  | 3.918665 | 1.525061 |
| H    | 1.791508  | 5.503290 | -3.272843 |
| H    | 0.728913  | 5.618185 | -1.835906 |
| H    | 2.457017  | 5.227572 | -1.631482 |
| H    | -3.052426 | 5.034031 | -3.341839 |
| H    | -1.802681 | 3.931467 | -3.999390 |
| H    | -3.384831 | 3.281639 | -3.493443 |
| H    | 0.149102  | -1.165802 | -3.058538 |
| O    | 0.178435  | 0.417094 | -1.761617 |

5.26 Intermediate 28

![Intermediate 28 molecule](image)

|      | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -4.885009 | -3.087245 | 0.140055 |
| C    | -5.190608 | -1.708690 | 0.120317 |
| C    | -6.537398 | -1.301456 | 0.014092 |
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -7.558751  | -2.255820  | -0.076906  |
| C    | -7.249567  | -3.627774  | -0.054456  |
| C    | -5.910025  | -4.039378  | 0.059624   |
| C    | -4.099179  | -0.708959  | 0.156747   |
| N    | -3.135848  | -0.561405  | -0.766674  |
| N    | -3.032547  | -1.000956  | -2.173613  |
| C    | -2.163850  | 0.050625   | -2.903656  |
| Si   | -2.096535  | 0.548396   | 0.371227   |
| N    | -3.813167  | 0.171424   | 1.154756   |
| C    | -3.187579  | 0.063264   | 2.588385   |
| C    | -3.452141  | 1.207608   | 3.320039   |
| Fe   | 0.004704   | 0.605883   | 0.857053   |
| N    | -0.005711  | 2.257905   | -0.235451  |
| C    | 1.180498   | 2.873238   | -0.650048  |
| C    | 1.188915   | 4.147062   | -1.260057  |
| C    | -0.018522  | 4.801495   | -1.505025  |
| C    | -1.223258  | 4.171692   | -1.189832  |
| C    | -1.201886  | 2.891206   | -0.594957  |
| N    | 2.345786   | 2.152789   | -0.43861   |
| C    | 3.605886   | 2.590313   | -1.047498  |
| C    | 3.647865   | 2.374314   | -2.572106  |
| N    | -2.359459  | 2.169117   | -0.365244  |
| C    | -3.650691  | 2.658104   | -0.850411  |
| C    | -4.309475  | 3.664989   | 0.110674   |
| Si   | 2.101556   | 0.559749   | 0.365112   |
| N    | 3.833868   | 0.217387   | 1.093401   |
| C    | 4.628623   | 0.724920   | 2.228548   |
| C    | 6.100742   | 0.971317   | 1.830549   |
| C    | 4.105915   | -0.708330  | 0.155967   |
| N    | 3.123461   | -0.625601  | -0.765467  |
| C    | 2.672229   | -1.646120  | -1.741580  |
| C    | 3.779595   | -1.995716  | -2.759711  |
| C    | 5.228685   | -1.681351  | 0.182485   |
| C    | 6.330455   | -1.516495  | -0.681414  |
| C    | 7.398984   | -2.422423  | -0.642599  |
| C    | 7.373487   | -3.506169  | 0.252559   |
| C    | 6.273711   | -3.678974  | 1.109543   |
| C  | 5.206952 | -2.768794 | 1.078941 |
|----|----------|-----------|----------|
| C  | 1.474022 | -1.021561 | -2.488676|
| C  | 2.199885 | -2.919569 | -1.002503|
| C  | 4.555901 | -0.263112 | 3.416373 |
| C  | 3.982381 | 2.064930  | 2.644293 |
| C  | -3.726808| -1.293612 | 3.169847 |
| C  | -5.707931| 0.245990  | 2.797249 |
| C  | -2.319849| -2.372858 | -2.237824|
| C  | -4.411756| -1.079165 | -2.862609|
| H  | -5.914443| 0.352484  | 3.874787 |
| H  | -3.676240| 1.158385  | 4.397228 |
| H  | 2.131181 | 4.609264  | -1.542931|
| H  | -0.021286| 5.794943  | -1.959332|
| H  | -2.172302| 4.655709  | -1.404682|
| H  | 4.407124 | 2.004625  | -0.574806|
| H  | 3.804338 | 3.648944  | -0.790017|
| H  | 3.537980 | 1.301265  | -2.787380|
| H  | 4.606338 | 2.726674  | -2.990971|
| H  | 2.827105 | 2.917525  | -3.064427|
| H  | -4.307919| 1.782581  | -0.960711|
| H  | -3.535690| 3.100670  | -1.857417|
| H  | -4.504859| 3.174529  | 1.076014 |
| H  | -5.266073| 4.030906  | -0.300849|
| H  | -3.649416| 4.527576  | 0.288581 |
| H  | 4.018199 | 2.786532  | 1.815256 |
| H  | 0.694893 | -0.731637 | -1.763348|
| H  | 1.055125 | -1.755307 | -3.195344|
| H  | 1.783396 | -0.125016 | -3.047612|
| H  | 1.798278 | -3.649693 | -1.724925|
| H  | 1.407469 | -2.653383 | -0.284331|
| H  | 4.194352 | -1.077667 | -3.205538|
| H  | 3.344054 | -2.608511 | -3.565774|
| H  | 4.595783 | -2.566946 | -2.297273|
| H  | -1.353226| -2.317276 | -1.715134|
| H  | -2.141032| -2.651935 | -3.289762|
| H  | -2.937944| -3.154071 | -1.771545|
| H  | -5.033674| -1.884583 | -2.449920|
| H   | -4.260636 | -1.271212 | -3.937009 |
|-----|----------|-----------|-----------|
| H   | -4.949365 | -0.123906 | -2.751430 |
| H   | -2.672426 | 1.025011  | -2.932992 |
| H   | -1.975550 | -0.286124 | -3.935416 |
| H   | -1.199139 | 0.178381  | -2.390830 |
| H   | -4.247857 | -2.127180 | 2.675163  |
| H   | -3.942660 | -1.338402 | 4.250252  |
| H   | -2.641265 | -1.411115 | 3.019680  |
| H   | -6.055973 | 1.156075  | 2.283193  |
| H   | -6.276408 | -0.615557 | 2.423306  |
| H   | -2.361959 | 1.121879  | 3.177366  |
| H   | -3.775953 | 2.186640  | 2.934995  |
| H   | -3.844097 | -3.399724 | 0.233499  |
| H   | -6.770447 | -0.235993 | -0.007693 |
| H   | 3.502925  | -0.471966 | 3.662651  |
| H   | 5.047783  | 0.175549  | 4.300514  |
| H   | 5.061761  | -1.207759 | 3.170621  |
| H   | 2.926790  | 1.910978  | 2.920137  |
| H   | 6.615506  | 0.033988  | 1.579511  |
| H   | 6.155941  | 1.649564  | 0.964171  |
| H   | 3.037304  | -3.388418 | -0.462944 |
| H   | 4.348345  | -2.899182 | 1.739071  |
| H   | 6.245110  | -4.523176 | 1.801728  |
| H   | 8.205481  | -4.212760 | 0.280370  |
| H   | 8.250809  | -2.284094 | -1.311740 |
| H   | 6.340892  | -0.676192 | -1.377377 |
| H   | -5.664005 | -5.103131 | 0.087373  |
| H   | -8.047064 | -4.370261 | -0.124515 |
| H   | -8.597105 | -1.929951 | -0.168044 |
| H   | 4.520643  | 2.481480  | 3.509961  |
| H   | 6.628560  | 1.442442  | 2.675381  |
5.27 Intermediate 29

![Chemical structure of Intermediate 29 with atom coordinates]

| Atom | C (x) | C (y) | C (z) |
|------|-------|-------|-------|
| C    | 4.816924 | 2.972828 | -1.476562 |
| C    | 5.025306 | 1.980192 | -0.499246 |
| C    | 6.240323 | 1.953793 | 0.214274 |
| C    | 7.233376 | 2.907359 | -0.047152 |
| C    | 7.021200 | 3.897579 | -1.022172 |
| C    | 5.812058 | 3.927180 | -1.736152 |
| C    | 3.963281 | 0.983784 | -0.187967 |
| N    | 2.957910 | 1.146551 | 0.675490 |
| C    | 2.521079 | 2.333670 | 1.434684 |
| C    | 1.852035 | 3.348533 | 0.475984 |
| N    | 3.800197 | -0.232015 | -0.760734 |
| C    | 4.517998 | -0.820599 | -1.909601 |
| C    | 4.024130 | -2.75598 | -2.028132 |
| Si   | 2.017965 | -0.422950 | -0.041605 |
| N    | 2.278387 | -1.585672 | 1.341076 |
| C    | 3.570919 | -1.867878 | 1.972484 |
| C    | 3.824879 | -1.055742 | 3.257434 |
| C    | 1.125299 | -2.140865 | 1.854750 |
| N    | -0.046282 | -1.821895 | 1.177905 |
| C    | -1.261434 | -2.201921 | 1.743069 |
| C    | -1.311158 | -3.078381 | 2.850763 |
| C    | -0.115867 | -3.479020 | 3.453586 |
| C    | 1.106464 | -2.992014 | 2.984936 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Fe      | 0.012065| -0.996600| -0.638531|
| Si      | -2.004629| -0.398483| -0.117378|
| N       | -2.378591| -1.648902| 1.159516 |
| C       | -3.707024| -1.908580| 1.712607 |
| C       | -4.305431| -3.238638| 1.219354 |
| N       | -2.985762| 1.070860 | 0.704693 |
| C       | -2.849732| 1.871758 | 1.937027 |
| C       | -4.208585| 2.304230 | 2.530452 |
| C       | -3.928517| 1.032676 | -0.235674|
| N       | -3.713089| -0.094033| -0.976658|
| C       | -4.063848| -0.259104| -2.413725|
| C       | -5.590303| -0.221980| -2.655048|
| C       | -4.965636| 2.070141 | -0.458842|
| C       | -4.591039| 3.367285 | -0.867490|
| C       | -5.560326| 4.369726 | -1.012518|
| C       | -6.910145| 4.091357 | -0.736928|
| C       | -7.287568| 2.800042 | -0.327158|
| C       | -6.322893| 1.793426 | -0.194055|
| C       | -2.123251| 0.979356 | 2.972603 |
| C       | -1.981489| 3.116152 | 1.634248 |
| C       | -3.542330| -1.645703| -2.836754|
| C       | -3.363800| 0.829779 | -3.260423|
| C       | 6.048584 | -0.831302| -1.695421|
| C       | 4.164908 | -0.062004| -3.211211|
| C       | 3.678902 | 3.007646 | 2.202681 |
| C       | 1.464573 | 1.827401 | 2.440370 |
| H       | -5.796524| -0.556280| -3.685157|
| H       | -3.746100| -1.807774| -3.907178|
| H       | 2.034069 | -3.251739| 3.488546 |
| H       | -0.139159| -4.151059| 4.314636 |
| H       | -2.269750| -3.416048| 3.236597 |
| H       | 4.348014 | -1.626255| 1.232353 |
| H       | 3.652867 | -2.950063| 2.180006 |
| H       | 3.842745 | 0.015930 | 3.014594 |
| H       | 4.793314 | -1.334830| 3.707835 |
| H       | 3.029302 | -1.232806| 3.997245 |
| H       | -4.357584| -1.080486| 1.396310 |
| H     | -3.677043 | -1.887571 | 2.818565  |
|-------|-----------|-----------|-----------|
| H     | -4.392020 | -3.220445 | 0.122416  |
| H     | -5.307178 | -3.400320 | 1.653441  |
| H     | -3.661255 | -4.086445 | 1.498066  |
| H     | 4.268203  | -2.840742 | -1.115317 |
| H     | 0.661473  | 1.311091  | 1.896290  |
| H     | 1.034072  | 2.678516  | 2.990041  |
| H     | 1.909396  | 1.123968  | 3.158582  |
| H     | 1.418362  | 4.183084  | 1.051998  |
| H     | 1.051518  | 2.845748  | -0.088913 |
| H     | 4.213752  | 2.269516  | 2.821090  |
| H     | 3.261290  | 3.780756  | 2.868201  |
| H     | 4.397760  | 3.488089  | 1.525660  |
| H     | -1.015957 | 2.809182  | 1.208956  |
| H     | -1.797778 | 3.681693  | 2.563236  |
| H     | -2.495920 | 3.776239  | 0.919601  |
| H     | -4.710788 | 3.060374  | 1.913018  |
| H     | -4.033663 | 2.732673  | 3.530543  |
| H     | -4.875645 | 1.434109  | 2.635559  |
| H     | -2.764821 | 0.142626  | 3.282459  |
| H     | -1.870749 | 1.581440  | 3.859817  |
| H     | -1.199288 | 0.561261  | 2.552726  |
| H     | -3.735266 | 1.829355  | -2.986973 |
| H     | -3.558006 | 0.667529  | -4.333861 |
| H     | -2.276540 | 0.793001  | -3.083793 |
| H     | -6.102564 | -0.904071 | -1.958092 |
| H     | -6.003366 | 0.787116  | -2.534052 |
| H     | -2.458858 | -1.716977 | -2.656054 |
| H     | -4.045715 | -2.435360 | -2.257164 |
| H     | -3.540783 | 3.577284  | -1.074708 |
| H     | -6.608284 | 0.789263  | 0.123183  |
| H     | 3.071183  | -0.040536 | -3.341476 |
| H     | 4.617900  | -0.566507 | -4.081025 |
| H     | 4.541483  | 0.970529  | -3.174516 |
| H     | 2.933408  | -2.291456 | -2.166119 |
| H     | 6.475086  | 0.179550  | -1.726479 |
| H     | 6.294325  | -1.290904 | -0.724580 |
| Atom | X  | Y  | Z    |
|------|----|----|------|
| H    | 2.588965 | 3.760334 | -0.230004 |
| H    | 3.876130  | 2.991598 | -2.028433 |
| H    | 5.642473  | 4.693151 | -2.495912 |
| H    | 7.794367  | 4.641738 | -1.224002 |
| H    | 8.171401  | 2.880123 | 0.511333  |
| H    | 6.395421  | 1.184789 | 0.972953  |
| H    | -5.262111 | 5.368592 | -1.338433 |
| H    | -7.663542 | 4.874854 | -0.841102 |
| H    | -8.334828 | 2.578756 | -0.110446 |
| H    | 4.505850  | -2.764981 | -2.889361 |
| H    | 6.518738  | -1.428950 | -2.493373 |
| P    | 0.008311  | -3.029955 | -1.423527 |
| C    | 0.270552  | -3.347128 | -3.261837 |
| C    | 1.250371  | -4.233567 | -0.682370 |
| C    | -1.494079 | -4.124385 | -1.127484 |
| H    | 1.159391  | -5.231582 | -1.145909 |
| H    | 2.275655  | -3.862402 | -0.797749 |
| H    | 1.037590  | -4.320570 | 0.394019  |
| H    | 0.244684  | -4.427373 | -3.489131 |
| H    | -0.521711 | -2.843707 | -3.839827 |
| H    | 1.243650  | -2.938323 | -3.577934 |
| H    | -1.313542 | -5.160396 | -1.465870 |
| H    | -1.700388 | -4.130007 | -0.047524 |
| H    | -2.373795 | -3.719034 | -1.642248 |
5.28 Transition State 30oa^2

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -6.107929 | -1.074556 | -2.106190 |
| C    | -5.344975 | -0.091666 | -1.444509 |
| C    | -5.866994 | 1.206921  | -1.306929 |
| C    | -7.135038 | 1.516924  | -1.823662 |
| C    | -7.893487 | 0.532408  | -2.474165 |
| C    | -7.374794 | -0.765519 | -2.616035 |
| C    | -4.025122 | -0.469998 | -0.856843 |
| N    | -2.852086 | -0.566026 | -1.509353 |
| C    | -2.520759 | -0.058981 | -2.860627 |
| C    | -1.113862 | -0.573606 | -3.222081 |
| N    | -3.812024 | -0.804471 | 0.418334  |
| C    | -4.766925 | -1.093986 | 1.506679  |
| C    | -5.230318 | 0.217955  | 2.181883  |
| Si   | -1.874169 | -0.983052 | 0.108743  |
| Fe   | 0.061049  | -0.449193 | 0.824232  |
| Si   | -0.172912 | 1.945977  | 0.627896  |
| O    | 0.703530  | 2.584878  | 1.960291  |
| C    | 0.874835  | 3.868890  | 2.537892  |
| C    | 1.567324  | 3.764295  | 3.903985  |
| N    | 0.323585  | -2.567848 | 0.861311  |
| C    | -0.719825 | -3.407631 | 0.556614  |
C -0.639494 -4.801407 0.803209
C 0.537187 -5.321639 1.337278
C 1.641687 -4.494305 1.559180
C 1.527770 -3.117832 1.249597
N -1.842351 -2.809291 0.017348
C -2.897814 -3.652324 -0.548160
C -2.480906 -4.320900 -1.870445
N 2.598197 -2.240197 1.272273
Si 2.155976 -0.659753 0.437091
N 3.895347 0.230934 0.379209
C 4.628761 1.249837 1.155014
C 4.466734 2.655460 0.524876
P -0.078762 -0.453562 3.025668
C 1.376153 -0.229931 4.186116
C -0.576632 -2.123202 3.744065
C -1.303071 0.676935 3.882686
C 3.951661 -2.782642 1.423726
C 4.355820 -2.977960 2.898112
N 3.091948 -0.977201 -1.228833
C 4.117624 -0.193761 -0.878438
C 5.261652 0.193361 -1.751420
C 6.459693 -0.44308 1.737986
C 7.528040 -0.166911 -2.562849
C 7.409973 0.952982 -3.402227
C 6.218369 1.694769 -3.412682
C 5.146423 1.317273 -2.590394
C 2.908638 -1.852028 -2.406352
C 2.663068 -1.004891 -3.676154
C 4.129374 -2.777442 2.614848
C 1.673752 -2.740349 -2.122474
C 6.122608 0.886934 1.291973
C 3.971290 1.270525 2.544423
O 0.450919 2.452710 0.896126
C 1.375668 1.790966 -1.729743
C 1.432238 2.514480 -3.082981
O -1.919082 2.036035 0.627184
C -3.017417 2.901197 0.815515
|   |   |   |   |
|---|---|---|---|
| C | -3.076247 | 3.591187 | 2.186968 |
| C | -2.490320 | 1.487790 | -2.816545 |
| C | -3.494077 | -0.557297 | -3.954523 |
| C | -3.995723 | -1.943237 | 2.535456 |
| C | -5.997575 | -1.899693 | 1.034057 |
| O | -0.580260 | 4.140049 | 0.512194 |
| C | -0.924018 | 5.094174 | -0.188283 |
| C | -1.189966 | 6.460655 | 0.447406 |
| C | -1.122386 | 5.044214 | -1.693615 |
| H | 6.587172 | 1.554971 | 2.036308 |
| H | 4.443215 | 2.040866 | 3.175643 |
| H | -0.078355 | -0.320815 | -0.694919 |
| H | -1.485177 | -5.451687 | 0.591762 |
| H | 0.603752 | -6.388285 | 1.567762 |
| H | 2.574438 | -4.904639 | 1.936774 |
| H | -3.769816 | -3.011418 | -0.729706 |
| H | -3.224192 | -4.414216 | 0.185681 |
| H | -2.230402 | -3.542896 | -2.608043 |
| H | -3.301738 | -4.940241 | -2.272505 |
| H | -1.595603 | -4.957721 | -1.723016 |
| H | 4.644387 | -2.065478 | 0.958776 |
| H | 4.050972 | -3.737979 | 0.873761 |
| H | 4.317383 | -2.014515 | 3.427421 |
| H | 5.382026 | -3.377931 | 2.973045 |
| H | 3.669095 | -3.670454 | 3.409154 |
| H | -3.697559 | -2.908001 | 2.098089 |
| H | -0.380010 | -0.233433 | -2.485507 |
| H | -0.835494 | -0.184803 | -4.214405 |
| H | -1.090964 | -1.673585 | -3.255672 |
| H | -2.193353 | 1.896120 | -3.798145 |
| H | -1.772788 | 1.810407 | -2.049349 |
| H | -3.616241 | -1.650574 | -3.890977 |
| H | -3.062772 | -0.312807 | -4.939311 |
| H | -4.480062 | -0.080764 | -3.890346 |
| H | 1.809977 | -0.330093 | -3.523084 |
| H | 2.437428 | -1.667604 | -4.528281 |
| H | 3.552442 | -0.405022 | -3.922573 |
H 5.007551  -2.225536  -2.977326
H 3.874723  -3.550129  -3.359084
H 4.381109  -3.279875  -1.667184
H 1.902257  -3.471088  -1.333399
H 1.402759  -3.286691  -3.039868
H 0.818399  -2.138795  -1.788131
H 5.022775  2.735794  -0.422234
H 4.854545  3.417265  1.222010
H 3.400879  2.861943  0.348868
H 6.231319  -0.152085  1.641827
H 6.658380  1.003640  0.339969
H 2.905467  1.500271  2.428872
H 4.074771  0.295709  3.039931
H 4.219512  1.889494  -2.590324
H 6.546379  -1.412260  -1.082318
H 1.750669  0.798187  4.137807
H 2.169215  -0.917697  3.860341
H 1.089246  -0.464750  5.226382
H 0.277651  -2.806065  3.637186
H -1.411508  -2.558725  3.184326
H -0.841157  -2.037670  4.813486
H -4.360375  0.779873  2.547043
H -5.888061  -0.016103  3.035093
H -5.788872  0.845963  1.470869
H -3.092753  -1.413434  2.849641
H -6.685962  -1.292016  0.433998
H -5.680553  -2.774082  0.444833
H -3.484727  1.883147  -2.558158
H -5.274039  1.974657  -0.812702
H -7.528884  2.530235  -1.715758
H -8.882255  0.773853  -2.870764
H -7.957242  -1.537118  -3.124728
H -5.698570  -2.080151  -2.213079
H -1.296337  0.538160  4.978886
H -2.314565  0.491471  3.499842
H -1.021553  1.706300  3.628535
H 6.119607  2.567963  -4.061861
| H     | 8.244852 | 1.247575 | -4.041867 |
|-------|---------|---------|-----------|
| H     | 8.453427 | -0.747197 | -2.549261 |
| H     | -4.624751 | -2.122660 | 3.421419 |
| H     | -6.543122 | -2.260877 | 1.921380 |
| H     | -3.909035 | 2.262498 | 0.727177 |
| H     | -3.102513 | 3.668550 | 0.012566 |
| H     | 1.467450 | 4.525450 | 1.870179 |
| H     | -0.101261 | 4.363094 | 2.690215 |
| H     | 2.380507 | 1.774586 | -1.272720 |
| H     | 1.086408 | 0.743083 | -1.886679 |
| H     | 2.127407 | 2.003411 | -3.767507 |
| H     | 0.434396 | 2.513437 | -3.549106 |
| H     | 1.753180 | 3.560569 | -2.954964 |
| H     | -4.000542 | 4.189116 | 2.275489 |
| H     | -3.062604 | 2.837949 | 2.984868 |
| H     | -2.211071 | 4.253068 | 2.325825 |
| H     | 1.672858 | 4.773297 | 4.340642 |
| H     | 0.961102 | 3.152751 | 4.587279 |
| H     | 2.567289 | 3.317385 | 3.816903 |
| H     | -1.030142 | 6.417539 | 1.531418 |
| H     | -0.520960 | 7.209588 | 2.007144 |
| H     | -2.220346 | 6.781144 | 0.225070 |
| H     | -0.913027 | 4.040567 | -2.066692 |
| H     | -2.148774 | 5.369962 | -1.927389 |
| H     | -0.442208 | 5.775709 | -2.161038 |
### 5.29 Intermediate 31oa

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -1.535524 | -3.013340 | -1.399260 |
| N       | -0.330793 | -2.481993 | -0.989906 |
| C       | 0.707922  | -3.340297 | -0.727645 |
| C       | 0.631610  | -4.714868 | -1.062575 |
| C       | -0.544984 | -5.204133 | -1.625604 |
| C       | -1.651982 | -4.366345 | -1.789200 |
| Fe      | -0.054318 | -0.355493 | -0.824618 |
| Si      | 0.201138  | 2.043950  | 0.535935  |
| O       | -0.514959 | 2.143989  | 1.053114  |
| C       | -1.583393 | 1.425708  | 1.609496  |
| C       | -1.680277 | 1.785149  | 3.098851  |
| N       | 1.824361  | -2.776690 | -0.141775 |
| C       | 2.872050  | -3.658079 | 0.380871  |
| C       | 2.440003  | -4.414855 | 1.648939  |
| N       | -2.609103 | -2.142571 | -1.356546 |
| C       | -3.956935 | -2.693664 | -1.522074 |
| C       | -4.380871 | -2.797973 | -2.999034 |
| Si      | -2.158130 | -0.614173 | -0.432209 |
| N       | -3.897055 | 0.260257  | -0.328310 |
| C       | -4.635688 | 1.318216  | -1.049282 |
| C       | -6.125557 | 0.945000  | -1.227891 |
| N       | -3.092216 | -1.036950 | 1.205701  |
| C       | -2.913636 | -1.983582 | 2.324474  |
| C       | -4.135230 | -2.919912 | 2.472251  |
| C       | -4.123285 | -0.242486 | 0.900763  |
| C       | -5.274297 | 0.082109  | 1.790228  |
C   -5.180660  1.161857  2.686556
C   -6.265969  1.487235  3.512277
C   -7.448452  0.734812  3.450401
C   -7.542652 -0.345839  2.558673
C   -6.461591 -0.669701  1.729432
C   -1.680420 -2.849353  1.982560
C   -2.676692 -1.219550  3.647659
C   -3.966308  1.425968 -2.429926
C   -4.503502  2.685899 -0.337240
P    0.052784 -0.260619 -3.025028
C    0.546531 -1.900977 -3.815142
Si   1.873878 -0.950584 -0.118479
N    3.806099 -0.756350 -0.432728
C    4.740541 -0.955845 -1.557369
C    3.940907 -1.685066 -2.652986
C    1.278518  0.874978 -3.876053
C   -1.429557 -0.054815 -4.152198
N    2.863819 -0.657719  1.516161
C    4.033508 -0.531813  0.862447
C    5.355965 -0.201912  1.464653
C    6.121915 -1.223716  2.060664
C    7.398248 -0.949140  2.564725
C    7.923507  0.351187  2.481266
C    7.160965  1.373554  1.897202
C    5.882690  1.099639  1.388907
C    2.578156 -0.270924  2.916544
C    2.608555  1.269851  3.022660
C    3.566441 -0.911187  3.920138
C    1.166349 -0.769256  3.273561
C    5.969902 -1.812425 -1.180976
C    5.212240  0.404806 -2.116539
O    1.981480  2.027073 -0.535879
C    3.074788  2.884201 -0.794489
C    3.101537  3.480234 -2.208518
O   -0.785901  2.429274 -1.941522
C   -1.058489  3.607776 -2.694367
C   -1.797993  3.234524 -3.982670
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| O       | 0.607601 | 3.926938 | -0.396113|
| C       | 0.970068 | 4.855575 | 0.359038 |
| C       | 1.295830 | 6.218333 | -0.229980|
| C       | 1.102160 | 4.734556 | 1.858601 |
| H       | -6.585597| 1.648516 | -1.942026|
| H       | -4.441966| 2.227905 | -3.017925|
| H       | 0.092115 | -0.301679| 0.699391 |
| H       | 1.479810 | -5.374530| -0.894141|
| H       | -0.608242| -6.253025| -1.926983|
| H       | -2.588227| -4.750746| -2.186995|
| H       | 3.743084 | -3.033113| 0.613431 |
| H       | 3.205842 | -4.370498| -0.397507|
| H       | 2.179725 | -3.691885| 2.436348 |
| H       | 3.257693 | -5.059743| 2.016315 |
| H       | 1.558268 | -5.041654| 1.447049 |
| H       | -4.656885| -2.029744| -0.996409|
| H       | -4.030483| -3.687594| -1.039351|
| H       | -4.367639| -1.802431| -3.466932|
| H       | -5.400065| -3.213764| -3.085374|
| H       | -3.688775| -3.444617| -3.561465|
| H       | 3.632427 | -2.687815| -2.318285|
| H       | 0.422563 | -0.338469| 2.596156 |
| H       | 0.929585 | -0.465585| 4.305759 |
| H       | 1.105714 | -1.864756| 3.206720 |
| H       | 2.357868 | 1.590221 | 4.048830 |
| H       | 1.875960 | 1.688721 | 2.317603 |
| H       | 3.639321 | -1.996689| 3.746086 |
| H       | 3.181854 | -0.747407| 4.940446 |
| H       | 4.569834 | -0.469110| 3.861299 |
| H       | -1.831385| -0.526904| 3.542412 |
| H       | -2.447071| -1.935112| 4.455200 |
| H       | -3.573237| -0.647061| 3.931338 |
| H       | -5.012224| -2.390855| 2.871316 |
| H       | -3.879801| -3.737631| 3.166771 |
| H       | -4.389639| -3.360404| 1.495162 |
| H       | -1.908044| -3.528563| 1.147944 |
| H       | -1.405732| -3.452940| 2.862268 |
| Atom | Coordinates   |         |         |
|------|---------------|---------|---------|
|      | X             | Y       | Z       |
| H    | -0.828291     | -2.224748| 1.687667|
| H    | -5.091864     | 2.711375 | 0.592644|
| H    | -4.874226     | 3.481560 | -1.004699|
| H    | -3.446894     | 2.890678 | -0.110613|
| H    | -6.215268     | -0.073832| -1.637551|
| H    | -6.680296     | 1.003115 | -0.281872|
| H    | -2.900397     | 1.656732 | -2.298771|
| H    | -4.061879     | 0.482348 | -2.983952|
| H    | -4.261487     | 1.745879 | 2.724059 |
| H    | -6.531456     | -1.504595| 1.029630 |
| H    | -1.834240     | 0.961053 | -4.066518|
| H    | -2.194628     | -0.780188| -3.841384|
| H    | -1.146557     | -0.246507| -5.202809|
| H    | -0.296417     | -2.600670| -3.726872|
| H    | 1.400959      | -2.349293| -3.297484|
| H    | 0.789186      | -1.762264| -4.885150|
| H    | 4.344070      | 1.009389 | -2.408628|
| H    | 5.851913      | 0.243589 | -3.00283 |
| H    | 5.793612      | 0.953731 | -1.359224|
| H    | 3.043646      | -1.104104| -2.893449|
| H    | 6.674021      | -1.266780| -0.539913|
| H    | 5.655215      | -2.733895| -0.666174|
| H    | 3.609031      | 1.652849 | 2.767944 |
| H    | 5.285432      | 1.897541 | 0.944821 |
| H    | 7.560132      | 2.388755 | 1.834396 |
| H    | 8.920814      | 0.565569 | 2.872411 |
| H    | 7.983516      | -1.750200| 3.022574 |
| H    | 5.712636      | -2.234024| 2.113619 |
| H    | 1.236278      | 0.753715 | -4.973915|
| H    | 2.294336      | 0.638689 | -3.525105|
| H    | 1.041369      | 1.911858 | -3.601968|
| H    | -6.184660     | 2.328918 | 4.204383 |
| H    | -8.295217     | 0.990765 | 4.091278 |
| H    | -8.459756     | -0.937331| 2.507795 |
| H    | 4.556003      | -1.779206| -3.561489|
| H    | 6.495871      | -2.094557| -2.107418|
| H    | 3.973199      | 2.258562 | -0.673019|
|   | x   | y   | z   |
|---|-----|-----|-----|
| H | 3.171503 | 3.707875 | -0.052774 |
| H | -1.644436 | 4.342240 | -2.110682 |
| H | -0.123859 | 4.109181 | -3.003111 |
| H | -2.533939 | 1.660288 | 1.102513 |
| H | -1.436647 | 0.342661 | 1.504036 |
| H | -2.490933 | 1.222120 | 3.587573 |
| H | 2.230303 | 4.127593 | -2.374047 |
| H | -0.736090 | 1.529703 | 3.604947 |
| H | -1.861709 | 2.864179 | 3.228761 |
| H | 4.018899 | 4.077959 | -2.350679 |
| H | 3.080018 | 2.679759 | -2.960854 |
| H | 1.165248 | 6.200627 | -1.317891 |
| H | 0.638510 | 6.982031 | 0.217158 |
| H | 2.329418 | 6.504514 | 0.023533 |
| H | 0.831888 | 3.725449 | 2.175987 |
| H | 2.130783 | 4.998110 | 2.152824 |
| H | 0.432812 | 5.467960 | 2.337795 |

5.30 Transition State 32oa$^+$

![Diagram of transition state 32oa]$^+$

|   | x   | y   | z   |
|---|-----|-----|-----|
| C | -0.537049 | -4.180558 | 1.158485 |
| N | -1.356764 | -3.147759 | 0.747720 |
C  -2.677758 -3.436257  0.495763
C  -3.227152 -4.717552  0.753310
C  -2.399125 -5.719379  1.258169
C  -1.039053 -5.468264  1.457711
Fe -0.677397 -1.114019  0.758602
Si  0.300400  1.399074  0.557193
O   1.040333  1.406319 -1.023597
C   1.670080  0.372147 -1.734806
C   1.936528  0.864991 -3.162679
N  -3.428961 -2.401182 -0.037477
C  -4.722594 -2.704181 -0.654217
C  -4.579690 -3.503849 -1.963219
N   0.806483 -3.867774  1.201550
C   1.778048 -4.943595  1.401389
C   1.994621 -5.275047  2.890775
Si  1.138778 -2.224799  0.445070
N   3.072898 -2.282405  0.478885
C   4.161622 -1.798180  1.355163
C   5.207725 -2.910495  1.600447
N   1.885831 -2.907434 -1.221121
C   1.372232 -3.594550 -2.424692
C   2.080457 -4.953423 -2.635067
C   3.134614 -2.681032 -0.808972
C   4.366755 -2.810695 -1.641732
C   4.733280 -1.765786 -2.512407
C   5.881734 -1.879445 -3.309682
C   6.669564 -3.040729 -3.249770
C   6.305546 -4.086845 -2.385277
C   5.160735 -3.971895 -1.583315
C  -0.128551 -3.862764 -2.172709
C   1.528193 -2.715917 -3.686419
C   3.511265 -1.416920  2.692150
C   4.840257 -0.543326  0.780644
P  -0.901452 -1.083498  2.958678
C  -2.117168 -2.366994  3.621389
Si  -2.663806 -0.749566  0.042694
N  -4.340670  0.245128  0.377588
C  -5.377316  0.290557  1.433310
C  -5.036822 -0.843902  2.420459
C  -1.521256  0.452126  3.836162
C   0.453708 -1.542534  4.174677
N  -3.403929  0.026173 -1.569397
C  -4.404604  0.633283 -0.903472
C  -5.410723  1.580184 -1.469018
C  -6.514507  1.089605 -2.195209
C  -7.490706  1.967452 -2.685097
C  -7.373815  3.349362 -2.459120
C  -6.274247  3.845681 -1.740538
C  -5.298493  2.966881 -1.246166
C  -2.954274  0.308053 -2.957129
C  -2.483761  1.773214 -3.056938
C  -4.074840  0.014186 -3.983048
C  -1.759223 -0.609812 -3.281522
C  -6.803780  0.037420  0.887104
C  -5.356319  1.642116  2.185668
O  -1.320436  1.978839  0.542814
C  -2.213856  2.993153  0.952393
C  -1.956292  3.534659  2.365916
O   1.158784  1.293355  2.057837
C   1.805889  2.256316  2.897828
C   1.929414  1.741177  4.335958
O   0.944966  3.231558  0.446833
C   0.452074  4.284455 -0.292369
C  -0.171234  5.453108  0.530670
C  -0.214397  4.060413 -1.649382
O   2.854404  4.674488  1.570599
C   3.361877  5.982254  1.885434
O   3.508437  2.537173 -0.183525
C   4.659415  2.345700 -1.034372
O   3.689067  5.078500 -0.873629
C   3.340053  5.663846 -2.132282
H   5.915504 -2.575617  2.376558
H   4.280731 -1.020951  3.374291
H  -0.738845 -0.887564 -0.746234
| X      | Y      | Z      | Value   |
|--------|--------|--------|---------|
| -4.27890 | -4.917060 | 0.562971 |
| -2.810246 | -6.707320 | 1.480179 |
| -0.377182 | -6.251125 | 1.819317 |
| -5.213727 | -1.748742 | -0.873106 |
| -5.385722 | -3.234324 | 0.055329 |
| -3.995225 | -2.914635 | -2.686640 |
| -5.569077 | -3.724935 | -2.400127 |
| -4.052461 | -4.452260 | -1.783000 |
| 2.732656  | -4.614814 | 0.968580 |
| 1.468580  | -5.851706 | 0.849146 |
| 2.395598  | -4.392943 | 3.413885 |
| 2.708115  | -6.108964 | 3.009822 |
| 1.045223  | -5.552487 | 3.373461 |
| -5.072946 | -1.819109 | 1.914316 |
| -0.906669 | -0.375844 | -2.635990 |
| -1.468664 | -0.453660 | -4.332907 |
| -2.023834 | -1.668123 | -3.142196 |
| -2.002429 | 1.956301  | -4.032566 |
| -1.758885 | 1.951915  | -2.254727 |
| -4.515399 | -0.977779 | -3.796581 |
| -3.642118 | 0.017977  | -4.996801 |
| -4.869067 | 0.770779  | -3.950253 |
| 0.953427  | -1.786417 | -3.578636 |
| 1.145870  | -3.263871 | -4.563709 |
| 2.583817  | -2.466392 | -3.866246 |
| 3.125789  | -4.826770 | -2.949063 |
| 1.550566  | -5.518969 | -3.418907 |
| 2.051509  | -5.539229 | -1.702825 |
| -0.259706 | -4.626277 | -1.392932 |
| -0.592874 | -4.226828 | -3.103279 |
| -0.637790 | -2.949038 | -1.839529 |
| 5.310451  | -0.749364 | -0.190939 |
| 5.626282  | -0.204949 | 1.475924 |
| 4.097770  | 0.257350  | 0.673714 |
| 4.711587  | -3.828040 | 1.954642 |
| 5.780607  | -3.139541 | 0.691792 |
| 2.744466  | -0.649302 | 2.526217 |
|   |   |   |   |
|---|---|---|---|
| H | 3.047377 | -2.294657 | 3.161890 |
| H | 4.115964 | -0.868183 | -2.554503 |
| H | 4.872264 | -4.781812 | -0.912182 |
| H | 1.253124 | -0.796927 | 4.165747 |
| H | 0.861261 | -2.515665 | 3.864581 |
| H | 0.048626 | -1.628938 | 5.198617 |
| H | -1.623535 | -3.349903 | 3.594384 |
| H | -3.017787 | -2.432734 | 3.000488 |
| H | -2.401292 | -2.140596 | 4.663804 |
| H | -4.385545 | 1.793992 | 2.679261 |
| H | -6.145510 | 1.649164 | 2.956070 |
| H | -5.540284 | 2.476370 | 1.493113 |
| H | -4.029372 | -0.711451 | 2.828357 |
| H | -7.185124 | 0.890016 | 0.310976 |
| H | -6.821290 | -0.861016 | 0.251723 |
| H | -3.327961 | 2.471125 | -2.948688 |
| H | -4.439945 | 3.351882 | -0.698144 |
| H | -6.174044 | 4.918868 | -1.563813 |
| H | -8.134324 | 4.033686 | -2.840849 |
| H | -8.342523 | 1.572600 | -3.242873 |
| H | -6.604741 | 0.016289 | -2.365584 |
| H | -1.574990 | 0.308591 | 4.929990 |
| H | -2.515273 | 0.727597 | 3.458124 |
| H | -0.827758 | 1.268383 | 3.599050 |
| H | 6.158160 | -1.062208 | -3.979597 |
| H | 7.561795 | -3.130811 | -3.872850 |
| H | 6.912526 | -4.993227 | -2.335107 |
| H | -5.758632 | -0.839497 | 3.252248 |
| H | -7.481506 | -0.128301 | 1.740235 |
| H | -3.210388 | 2.530158 | 0.925834 |
| H | -2.243317 | 3.817896 | 0.219102 |
| H | 2.820260 | 2.457271 | 2.518330 |
| H | 1.262049 | 3.214444 | 2.891228 |
| H | 2.626885 | 0.104541 | -1.244992 |
| H | 1.050772 | -0.535149 | -1.743330 |
| H | 2.456557 | 0.096749 | -3.758525 |
| H | 0.982662 | 1.102789 | -3.662055 |
H  2.553349  1.779698 -3.142414
H  -2.549845  4.447825  2.547185
H  -2.233561  2.784102  3.116486
H  -0.892652  3.772132  2.503261
H  2.408860  2.521057  4.954246
H   0.948913  1.502846  4.773095
H  2.556218  0.837762  4.378788
H  0.208938  5.411047  1.557781
H  0.133969  6.413674  0.080895
H  -1.267846  5.434986  0.543494
H  0.157446  3.140673 -2.110240
H  -1.303083  3.989803 -1.534172
H  -0.003060  4.932357 -2.291682
H   1.435889  4.874563 -0.549750
C   3.168334  6.206126  3.385503
H  4.426626  6.052181  1.607115
H  2.814939  6.745437  1.303561
C   4.464325  6.610117 -2.555114
H   3.193884  4.874497 -2.894630
H  2.385387  6.218293 -2.042174
H   4.628195  1.291799 -1.338952
H  4.568732  2.972842 -1.935407
C   5.952278  2.682977 -0.292130
Si  2.781074  3.985425  0.069645
H   3.548620  7.200136  3.673428
H  2.100319  6.143715  3.646725
H   3.710071  5.436993  3.957473
H  4.221498  7.083070 -3.520540
H  4.602389  7.397032 -1.797248
H  5.409565  6.054755 -2.658441
H  6.826025  2.429811 -0.916381
H  5.979470  3.759838 -0.061940
H  6.011775  2.110567  0.644249
6 NMR Spectra

Iron(II) complex 7a

$^1$H NMR (500 MHz, C$_6$D$_6$):
$^{13}$C NMR (126 MHz, C$_6$D$_6$):
$^{31}\text{P}^{(1)\text{H}}$ NMR (202 MHz, $\text{C}_{6}\text{D}_{6}$):
\(^1\text{H},^{29}\text{Si} \text{HMQC (500 MHz/99 MHz, C}_6\text{D}_6):\)
Iron(II) complex 7b

$^1$H NMR (500 MHz, C$_6$D$_6$):
$^{13}$C NMR (126 MHz, C$_6$D$_6$):
$^{31}$P($^1$H) NMR (202 MHz, $C_6D_6$):
$^1$H, $^{29}$Si HMQC (500 MHz/99 MHz, C$_6$D$_6$):

H, Si-HMQC 20 Hz 300 K
Iron(II) complex 7c

$^1$H NMR (500 MHz, C$_6$D$_6$):

![NMR Spectrum Diagram]
$^{13}$C NMR (126 MHz, CD$_3$OD):
$^{31}\text{P}^{1}(\text{H})$ NMR (202 MHz, C$_6$D$_6$):
$^1$H, $^{29}$Si HMQC (500 MHz/ 99 MHz, C₆D₆):
Trimethylphosphine-$d_9$ 6-$d_9$

$^1$H NMR (500 MHz, C$_6$D$_6$/C$_6$H$_6$):

P(CD$_3$)$_3$
$^2$H NMR (77 MHz, CD$_3$OD/CD$_3$HOD):
$^{13}$C NMR (176 MHz, C$_6$D$_6$/C$_6$H$_6$):
$^{31}\text{P NMR (202 MHz, C}_6\text{D}_6/C_6\text{H}_6)$:
Dimethyl(phenyl)(1-phenylethoxy-1-d) silane (8eb-d₁)

¹H NMR (500 MHz, CDCl₃):

- Me
- Me
- O
- Si
- Ph
- D
- Me

ppm

12 11 10 9 8 7 6 5 4 3 2 1

3.00 2.76 2.69 2.58 2.00 1.00
$^{13}$C NMR (126 MHz, C$_6$D$_6$):
$^{29}\text{Si DEPT NMR (99 MHz, CDCl}_3)$: 
7 Gibbs Free Energy Profile

Peripheral Mechanism

Outer and Inner Sphere Mechanisms

ΔG° (kcal/mol)

7a + 8oa

(-26.9)
8 References

[S1] D. Gallego, S. Inoue, B. Blom and M. Driess, *Organometallics*, 2014, **33**, 6885–6897.

[S2] (a) H. F. T. Klare, M. Oestreich, J.-i. Ito, H. Nishiyama, Y. Ohki and K. Tatsumi, *J. Am. Chem. Soc.*, 2011, **133**, 3312–3315; (b) H. F. T. Klare, Ph.D. Thesis, Westfälische Wilhelms-Universität Münster, Germany, 2011; (c) For an alternative preparation of (SiS)4d, see: P. Jankowski, E. Schaumann, J. Wicha, A. Zarecki, G. Adiwidjaja and M. Asztemborska, *Chem. Commun.*, 2000, 1029–1030.

[S3] M. Mewald, Ph.D. Thesis, Westfälische Wilhelms-Universität Münster, Germany, 2012.

[S4] C. Wang, G. Erker, G. Kehr, K. Wedeking and R. Fröhlich, *Organometallics*, 2005, **24**, 4760–4773.

[S5] G. M. Sheldrick, *SHELX-97: Program for Crystal Structure Refinement*: University of Göttingen, Göttingen, Germany, 1997.

[S6] J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.

[S7] L. Goerigk and S. Grimme, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6670–6688.

[S8] T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.

[S9] M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265–3269.

[S10] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[S11] C. Y. Legault, CYLview 1.0b; Université de Sherbrook: Sherbrook, QC, Canada, 2009. http://www.cylview.org.

[S12] P. Bhattacharya, J. A. Krause and H. Guan, Organometallics, 2011, 30, 4720–4729.

[S13] A. M. Tondreau, E. Lobkovsky and P. J. Chirik, Org. Lett., 2008, 10, 2789–2792.

[S14] N. S. Shaikh, S. Enthaler, K. Junge and M. Beller, Angew. Chem. Int., Ed., 2008, 47, 2497–2501.

[S15] H. Nishiyama and A. Furuta, Chem. Commun., 2007, 760–762.

[S16] Z. Zuo, H. Sun, L. Wang and X. Li, Dalton Trans., 2014, 43, 11716–11722.

[S17] A. J. Ruddy, C. M. Kelly, S. M. Crawford, C. A. Wheaton, O. L. Sydora, B. L. Small, M. Stradiotto and L. Turculet, Organometallics, 2013, 32, 5581–5588.

[S18] S. E. Denmark and Y. Ueki, Organometallics, 2013, 32, 6631–6634.

[S19] S.-F. Hsu and B. Plietker, Chem. – Eur. J., 2014, 20, 4242–4245.

[S20] R. Lopes, J. M. S. Cardoso, L. Postigo and B. Royo, Catal. Lett., 2013, 143, 1061–1066.

[S21] T. Taniguchi and D. P. Curran, Org. Lett., 2012, 14, 4540–4543.

[S22] J. Mohr, M. Durmaz, E. Irran and M. Oestreich, Organometallics, 2014, 33, 1108–1111.

[S23] (a) T. T. Wenzel and R. G. Bergman, J. Am. Soc. Chem., 1986, 108, 4856–4867; (b) A. Kornath, F. Neumann and H. Oberhammer, Inorg. Chem., 2003, 42, 2894–2901.

[S24] T. T. Metsänen, P. Hrobářík, H. F. T. Klare, M. Kaupp and M. Oestreich, J. Am. Chem. Soc., 2014, 136, 6912–6915.