SUPPORTING INFORMATION

For

Reactivity of a Unique Si(I)-Si(I)-based η^2-bis(silylene) Iron Complex

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General information

Unless otherwise stated, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques or in a Vigor glovebox maintained at or below 1 ppm of O_2 and H_2O. All new metal complexes were prepared and handled in the glovebox under N_2 atmosphere. Anhydrous $FeCl_2$ (98%) was purchased from Strem Chemicals. $PhC(N^tBu)_2SiHCl_2$,[S1] $LiN(SiMe_3)_2(Et_2O)$[S1] and $Fe(N(SiMe_3)_2)_2$[S2] and complex **1**, $FeCl_2\{PhC(N^tBu)_2SiCl\}_2$,[S3] were synthesized according to reported procedures. Other reagents were purchased from J&K Chemical and SCRC. Glassware was dried at 150 °C overnight. Celite and molecular sieves were dried at 200 °C under vacuum. Benzene, pentane, hexanes, and diethyl ether were degassed with nitrogen and dried over activated molecular sieves, and kept over 4 Å molecular sieves in a N_2-filled glovebox. NMR data were recorded either on a Bruker 400 or a 500 MHz spectrometer, and are internally referenced to residual proton solvent signals in C_6D_6 (7.16 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), IR data were recorded on a Thermo Scientific Nicolet iS5 FTIR and signal strength is represented as follows: VS=very strong, W=weak, S=strong, VW=very weak, m=middle, w=wide. UV-vis spectra were recorded using a StellarNet BLACK Comet C-SR diode array miniature spectrophotometer connected to deuterium and halogen lamp by optical fiber using 1 cm matched quartz cuvettes at room temperature. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).

X-ray crystallography:

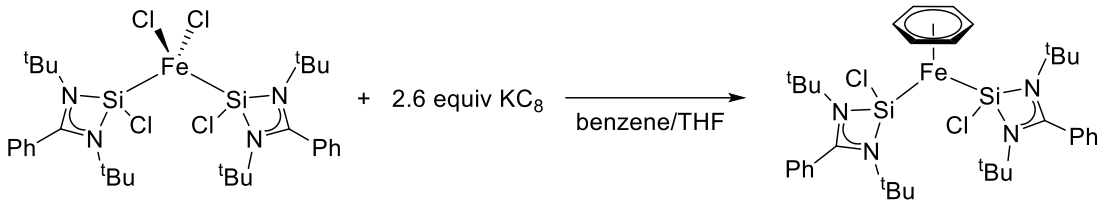
Crystals were coated with Paratone-N oil and mounted on a Bruker D8 Venture diffractometer equipped with an APEX-II CCD diffractometer. The crystal was kept at 150 K during data collection. Using Olex2,[S4] the structure was solved with the ShelXT[S5] structure solution program using Intrinsic Phasing and refined with the XL[S6] refinement package using least squares minimization. CCDC 2157512-2157516 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Mössbauer spectroscopy:

Mössbauer spectra were recorded with a ^{57}Co source in a Rh matrix using an alternating constant acceleration *Wissel* Mössbauer spectrometer operated in the transmission mode and equipped with a *Janis* closed-cycle helium cryostat. Isomer shifts are given relative to iron metal at ambient temperature.

Simulation of the experimental data was performed with the *Mfit* program (developed by Dr. E. Bill, Max-Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr, Germany) using *Lorentzian* line doublets.

Synthetic procedures of new compounds, including NMR, IR and UV-vis spectra



1 **2**

{PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (2).

A solution of **1** (110 mg, 0.153 mmol) in benzene (5 mL) was added dropwise to a solution of KC_8 (53.7 mg, 0.398 mmol) in THF (5 mL) in a vial whilst stirring. The color of the reaction mixture turned from yellow to dark red-brown. After stirring for 12 hours, volatile materials were removed under vacuum and compound **2** was extracted with pentane solution. The solid was crystallized in pentane solution in a –30 °C freezer for 2 days, and only crystalline material was used for subsequent reactions (Yield: 40 mg, 40%).

^{1}H NMR (500 MHz, benzene-d_6, ppm) δ 8.04 (m, 1H, Ar-H), 7.26 (d, 1H, Ar-H), 7.09 (d,1H, Ar-H), 7.00~6.9 (m, 6H, Ar-H), 6.86 (t, 1H, Ar-H), 5.15 (s, 6H, benzene-H), 1.52 (s, 18H, N^{t}Bu-H), 1.31 (s, 18H, N^{t}Bu-H).

^{13}C NMR (126 MHz, benzene-d_6, ppm) δ 171.84 (N*C*N), 170.75 (N*C*N), 132.55, 132.44, 129.80, 129.70, 129.47, 129.24, 129.02, 128.84, 128.55, 127.63, 127.36 (132.55 ~127.36: Ph), 80.23 (Fe-benzene), 54.24 (*C*Me$_3$), 53.64 (*C*Me$_3$), 31.86 (*C*H$_3$), 31.39 (*C*H$_3$).

^{29}Si NMR (99 MHz, benzene-d_6, ppm) δ 45.12, 42.45.

UV-Vis (THF, λ(nm) (ε, M^{-1}cm^{-1})): 410 (1604).

IR-ATR (cm^{-1}): 3059 (VW), 2970 (w), 2928 (VW), 2868 (VW), 1640 (VW), 1577 (VW), 1519 (VW), 1472 (m), 1443 (m), 1415.63 (S), 1389 (S), 1361 (S), 1272 (m), 1203 (S), 1085 (m), 1022 (m), 972 (VW), 926 (W), 882 (W), 789 (W), 753 (S), 726 (W), 708 (S), 636 (m), 617 (S).

Anal. Calcd for $C_{36}H_{52}Cl_2FeN_4Si_2$: C, 59.74; H, 7.24; N, 7.74. Found: C, 57.43; H, 7.29; N, 7.77. Due to the formation of silicon carbide the carbon values in the elemental analyses were consistently too low for the disilylene Fe compounds reported in this paper.

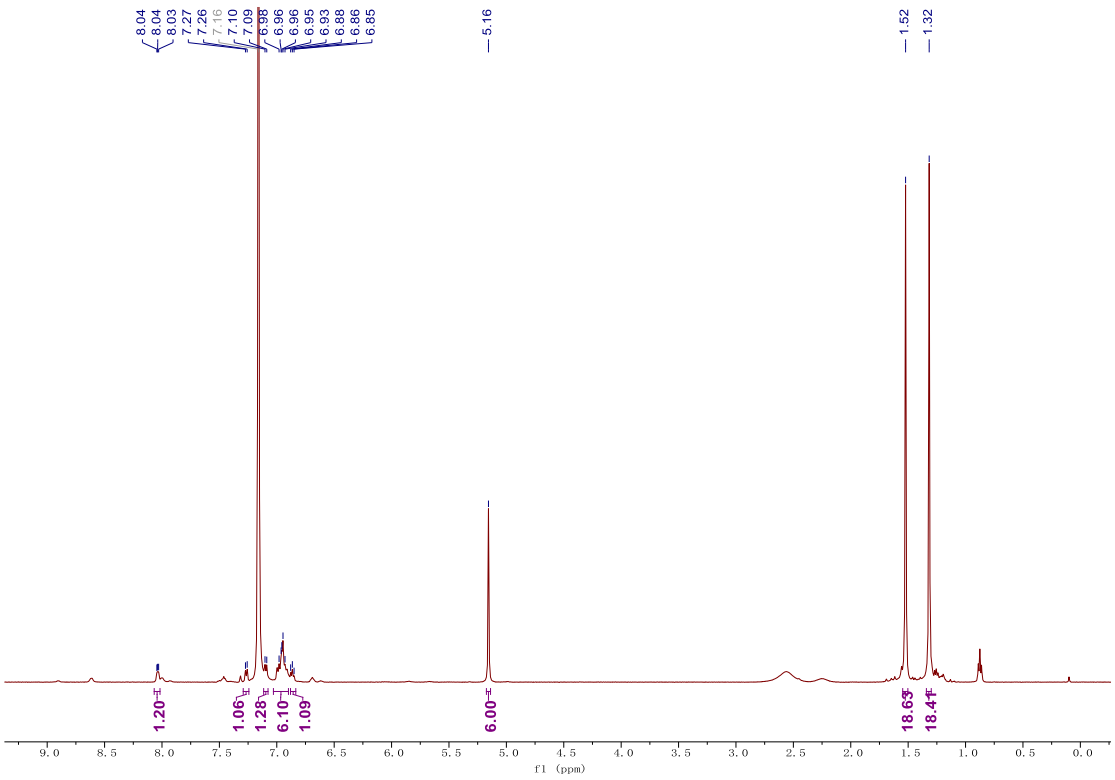


Figure S1. ^{1}H NMR spectrum of {PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (**2**) (500 MHz, C$_6$D$_6$).

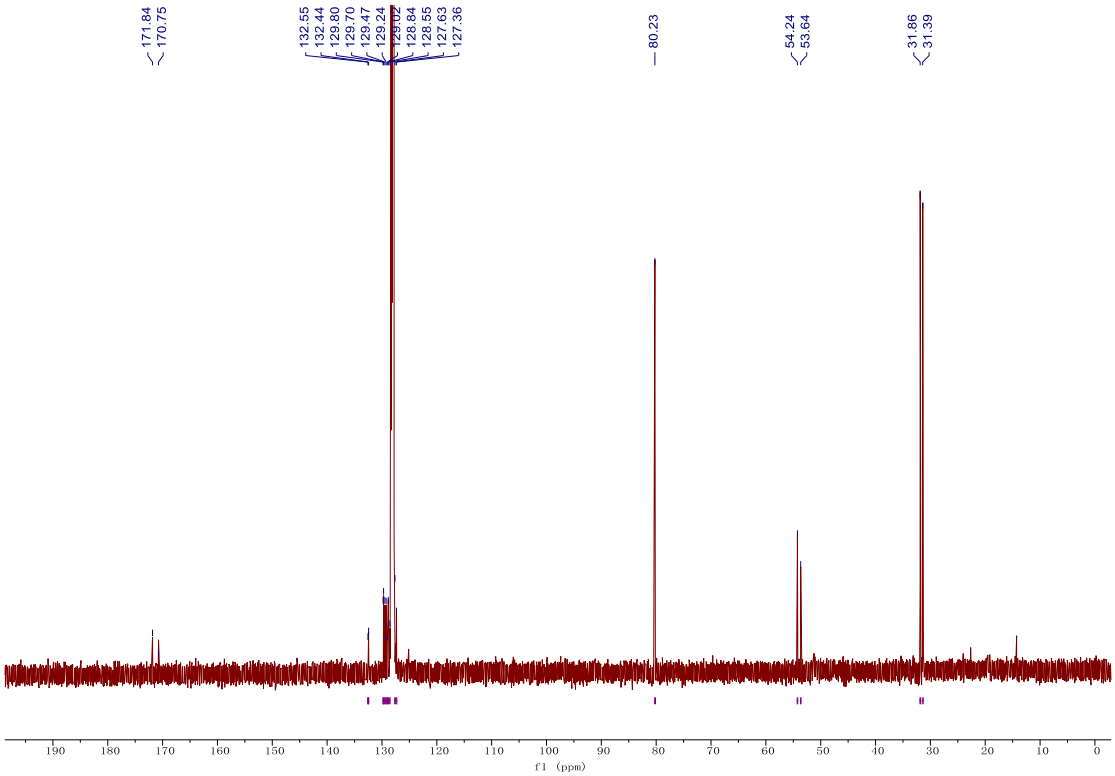


Figure S2. ^{13}C NMR spectrum of {PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (**2**) (126 MHz, C$_6$D$_6$).

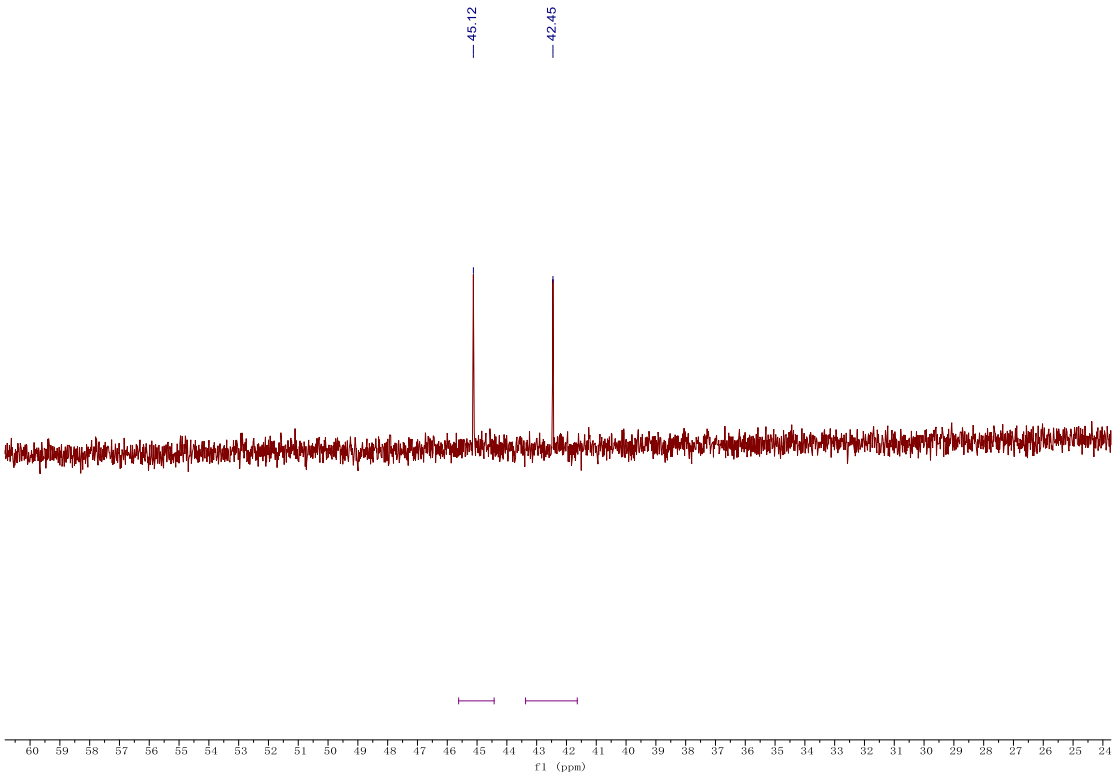


Figure S3. ^{29}Si NMR spectrum of {PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (**2**) (99 MHz, C$_6$D$_6$).

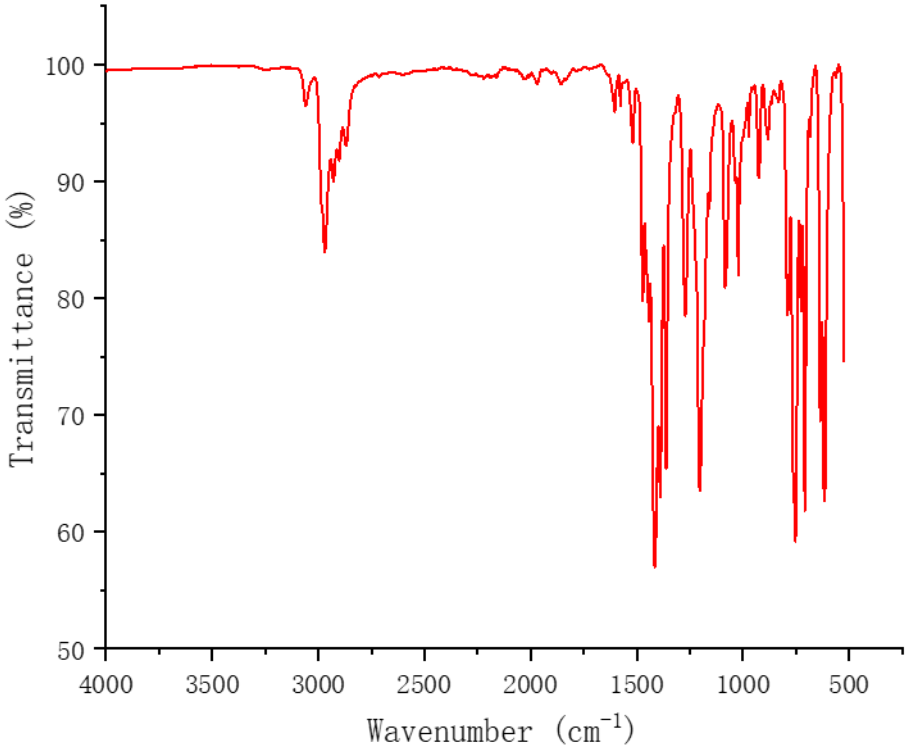


Figure S4. IR spectrum of {PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (**2**).

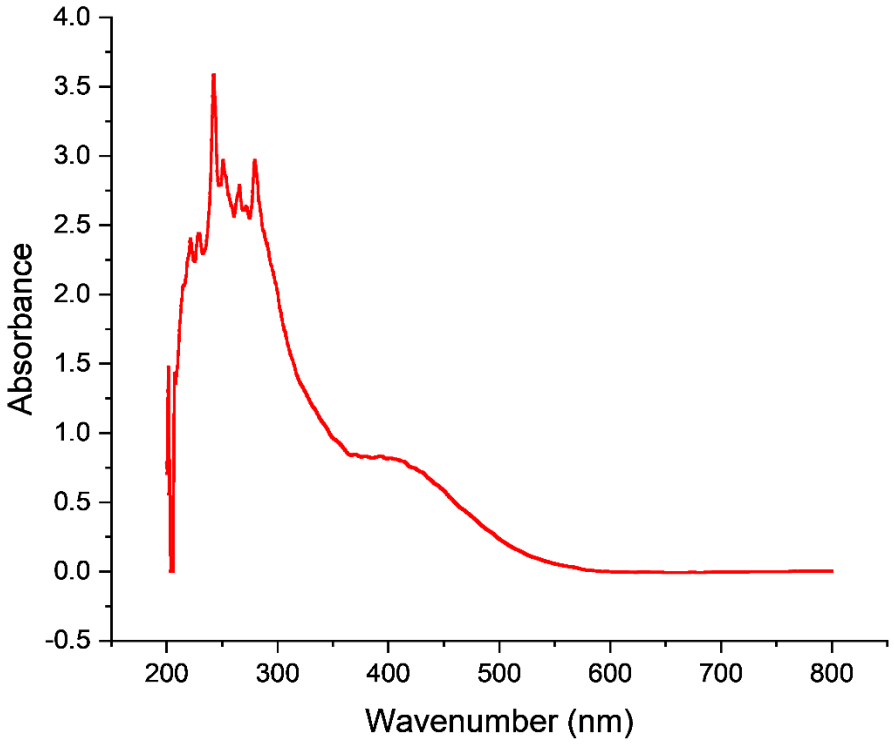
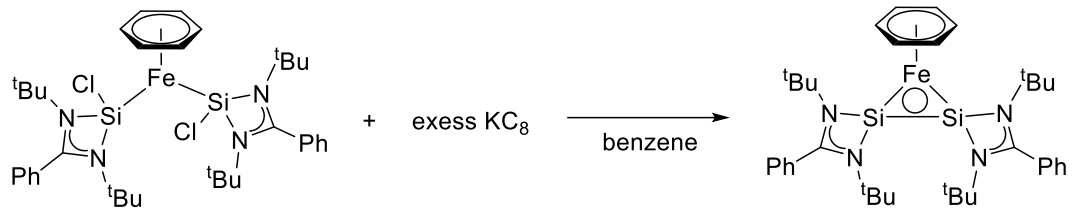


Figure S5. UV-vis spectrum of $\{PhC(N^tBu)_2SiCl\}_2Fe(C_6H_6)$ (**2**).



{PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$) (3).

A solution of {PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (37 mg, 0.051 mmol) in benzene (10 mL) was added dropwise to KC_8 (42 mg, 0.311 mmol) in a vial with stirring. About 20 mg KC_8 was added every three hours until all material was converted to {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$), which can be determined by ^{1}H NMR monitoring. The color of the reaction mixture turned from red-brown to black. Compound **3** (Yield: 29 mg, 89.3%) was collected by removing solvents and volatile materials under vacuum. The solid was stored in pentane solution in a −30 °C freezer for 1 month to give X-ray quality crystals.

^{1}H NMR (500 MHz, benzene-d_6) δ 7.14 (m, 2H, Ar-H), 7.00~6.9 (m, 6H, Ar-H), 6.80 (td, 2H, Ar-H), 5.34 s, 6H, benzene-H), 1.47 (s, 36H, N^{t}Bu-H).

^{13}C NMR (126 MHz, benzene-d_6, ppm) δ 162.70 (N*C*N), 135.72, 129.91, 128.98, 128.93, 127.77, 127.56 (135.72~127.56: Ph), 76.74 (Fe-benzene), 54.62 (*C*Me$_3$), 32.78 (*C*H$_3$).

^{29}Si NMR (99 MHz, benzene-d_6, ppm) δ 34.49.

UV-Vis (THF, λ(nm) (ε, M^{-1}cm^{-1})): 390 (4280).

IR-ATR (cm^{-1}): 3047 (W), 2961 (m), 2922 (m), 2855 (W), 1957 (VW), 1598 (W), 1442 (VW), 1403 (W), 1387 (VS), 1356 (S), 1266 (m), 1203 (S), 1071(m), 1029 (W), 965 (W), 925 (W), 889 (VW), 836 (VW), 791 (W), 752 (S), 704 (VS), 654 (VW), 610 (m), 560 (VW).

Anal. Calcd for $C_{36}H_{52}FeN_4Si_2$: C, 66.23; H, 8.03; N, 8.58. Found: C, 65.11; H, 8.17; N, 8.57. Due to the formation of silicon carbide the carbon values in the elemental analyses were consistently too low for the disilylene Fe compounds reported in this paper.

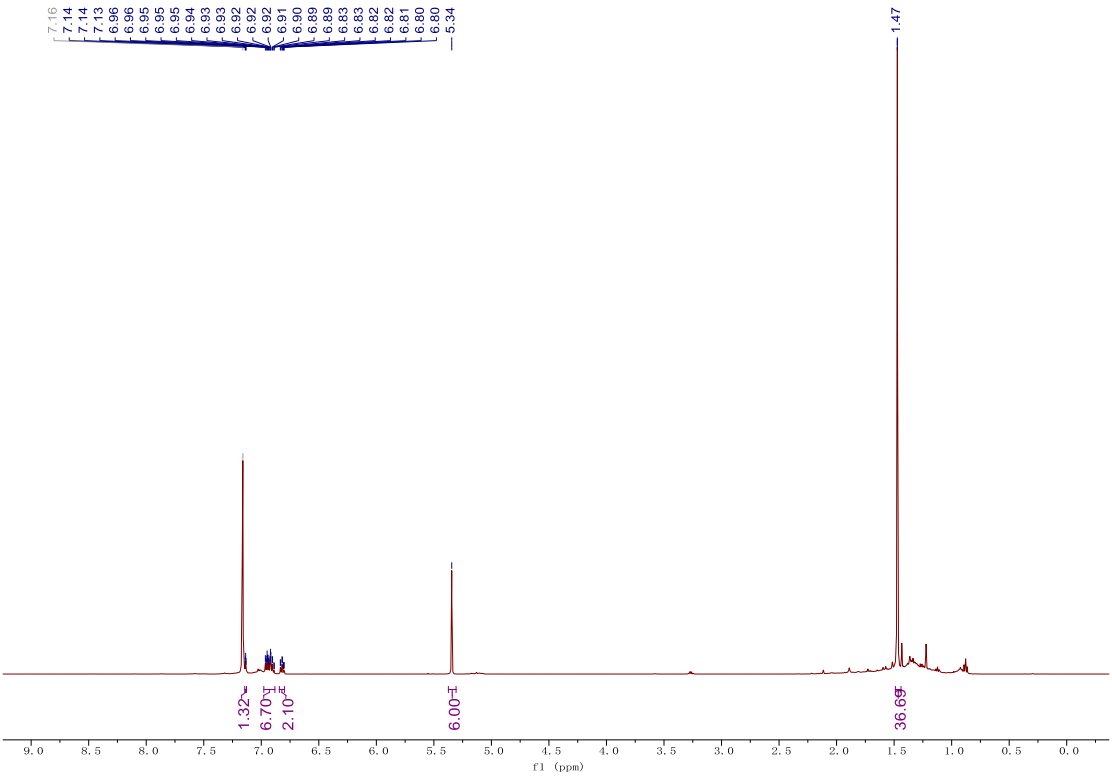


Figure S6. ^{1}H NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$) (**3**) (500 MHz, C$_6$D$_6$).

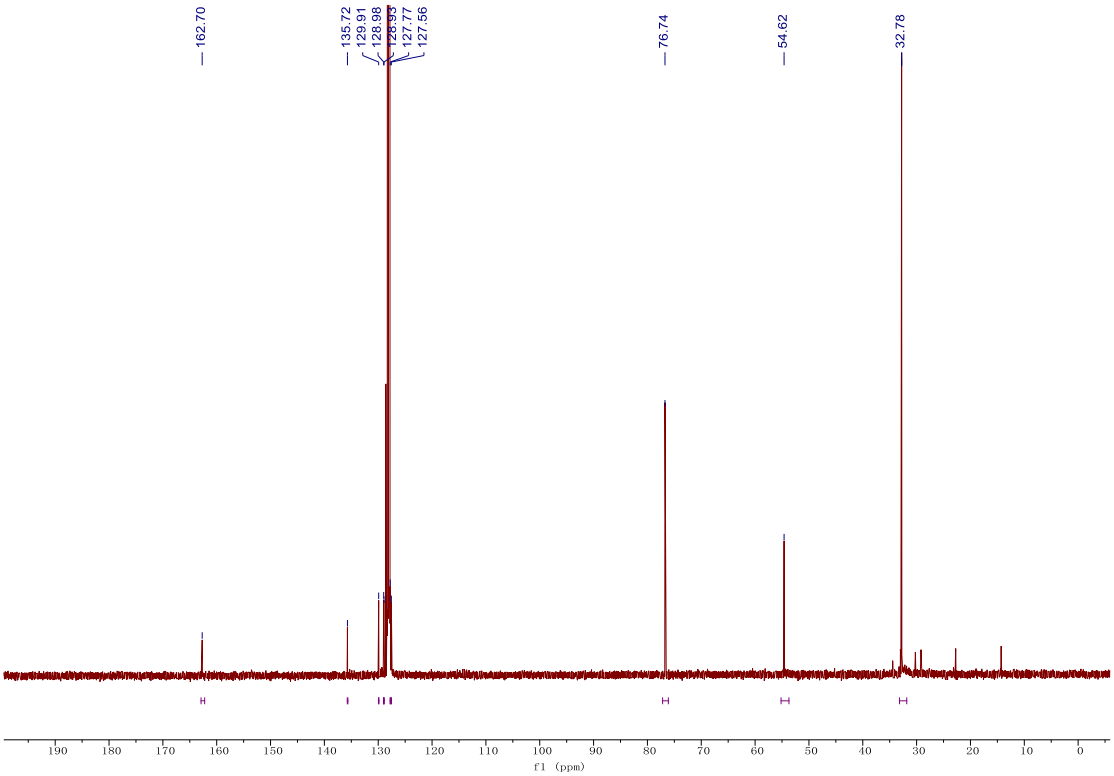


Figure S7. ^{13}C NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$) (**3**) (126 MHz, C$_6$D$_6$).

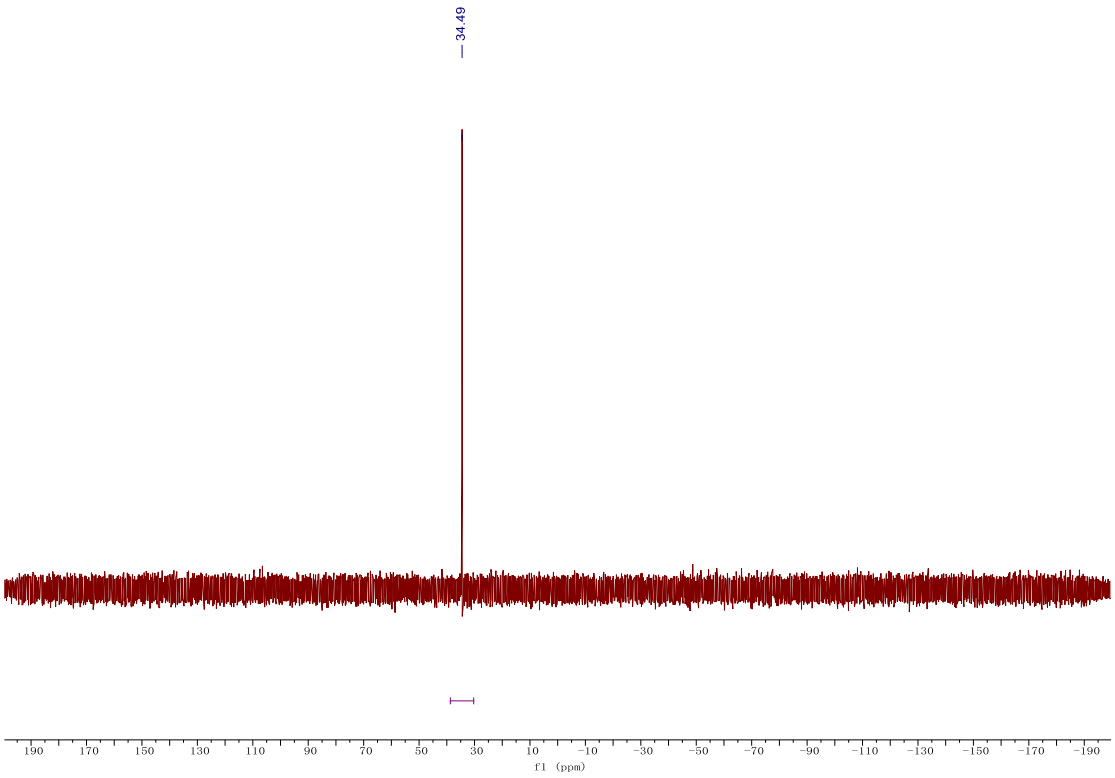


Figure S8. ^{29}Si NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$) (**3**) (99 MHz, C$_6$D$_6$).

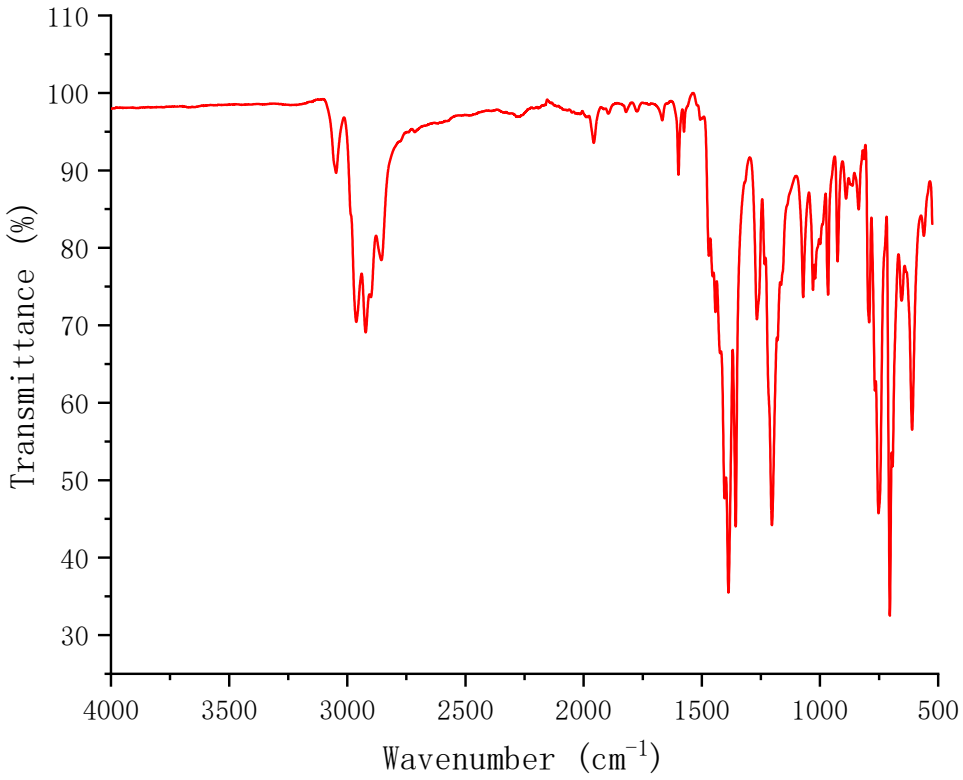


Figure S9. IR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$) (**3**).

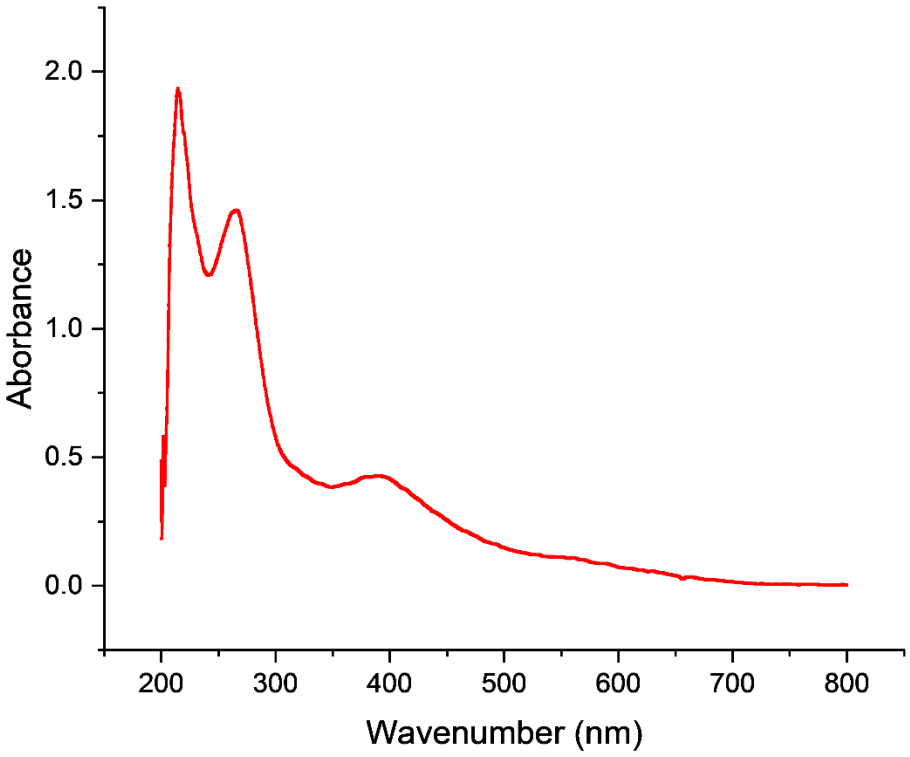
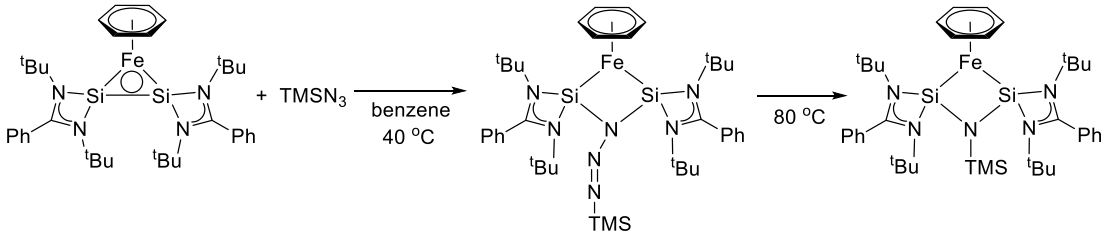


Figure S10. UV-vis spectrum of $\{PhC(N^tBu)_2Si\}_2Fe(C_6H_6)$ (**3**).



3 **4** **5**

{PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(N$_3$SiMe$_3$) (4).

Compound **4**, which is also formed during the formation of species **5** (*vide infra*), can be obtained as an isolable species upon reaction of **3** with $TMSN_3$ (7.5 µL, 0.153 mmol) for 1 hour at 40 °C in benzene solution in a J-Young tube (quantitative conversion). After 40 minutes of reaction, the solution was evaporated to dryness under vacuum and redissolved in pentane. X-ray quality crystals were grown from a pentane solution stored in a -30 °C freezer.

^{1}H NMR (500 MHz, benzene-d_6) δ 7.32 (dt, 2H, Ar-H), 7.22 (m, 1H, Ar-H), 7.11 (m, 2H, Ar-H), 7.04 (t, 2H, Ar-H), 7.00 (t, 2H, Ar-H), 6.97 (d, 1H, Ar-H), 5.26 (s, 6H, benzene-H), 1.33 (s, 36H, N^{t}Bu-H), 0.47 (s, 9H, Si(CH$_3$)$_3$).

^{13}C NMR (126 MHz, benzene-d_6, ppm) δ 159.33~127.76 (5 signals; 2 Ph), 76.66 (Fe-benzene), 53.68 (*C*Me$_3$), 32.04 (*C*H$_3$), –0.08 (Si(*C*H$_3$)$_3$), –1.23 (C: $TMSN_3$).

^{29}Si NMR (99 MHz, benzene-d_6, ppm) δ 15.41, 7.05.

UV-Vis (THF, λ(nm) (ε, M^{-1}cm^{-1})): 485 (2343).

IR-ATR (cm^{-1}): 3048 (VW), 2962 (W), 2033 (W), 1523 (VW), 1472 (W), 1422 (S), 1391 (W), 1358 (W), 1274 (W), 1237 (W), 1207 (S), 1148 (m), 1078 (W), 1021 (W), 989 (m), 966 (W), 923 (W), 832 (S), 789 (W), 751 (S), 724 (W), 704 (S), 641 (W), 609 (W).

Elemental analysis of this species did not yield satisfactory results, which are attributed to the demonstrated thermal instability of this complex with 'decomposition' to species **5**.

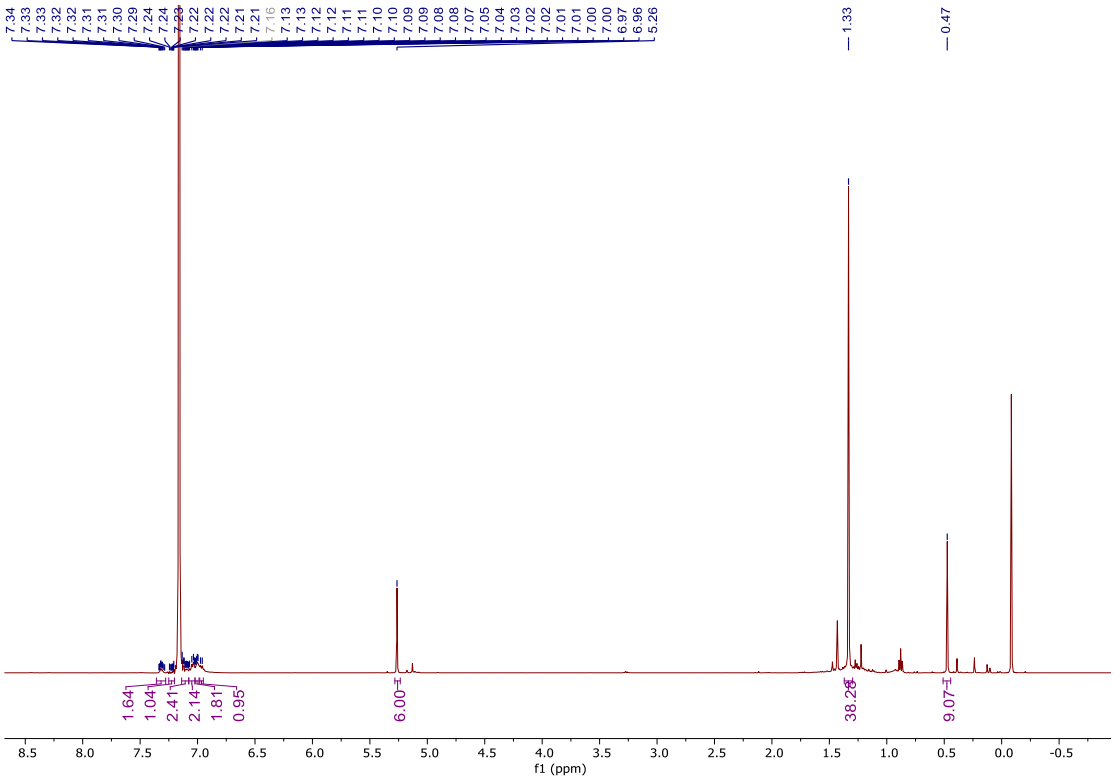


Figure S11. ^{1}H NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(N$_3$SiMe$_3$) (**4**) (500 MHz, C$_6$D$_6$).

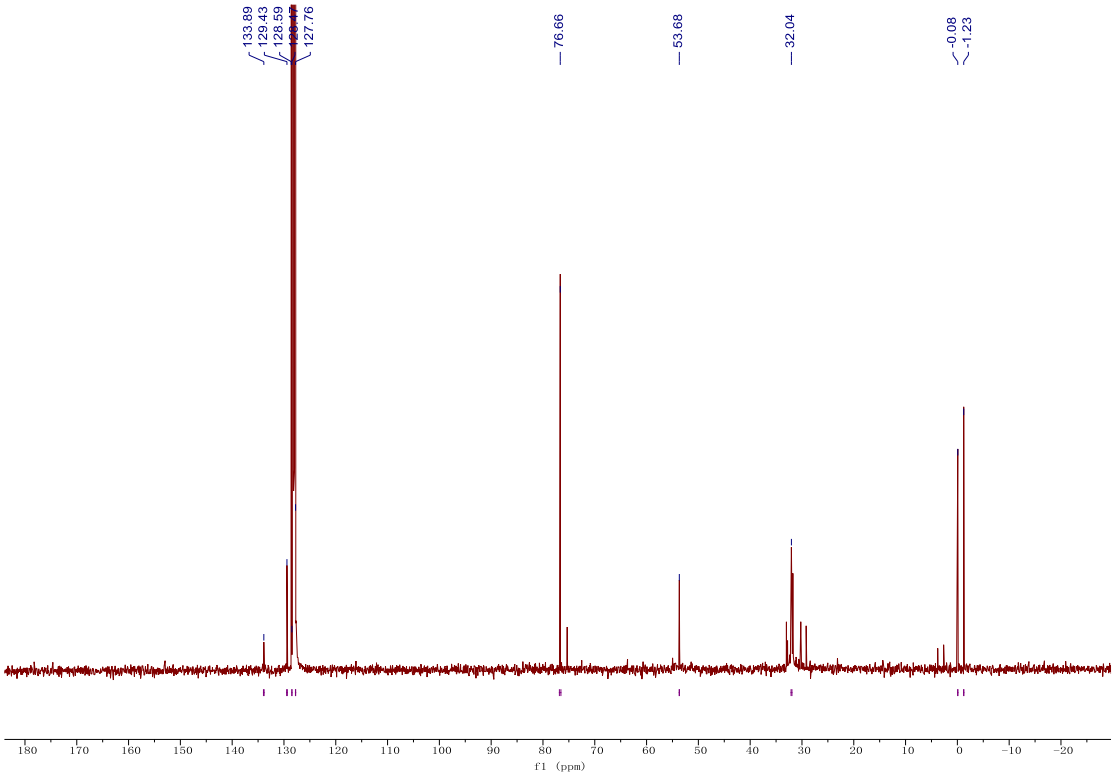


Figure S12. ^{13}C NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(N$_3$SiMe$_3$) (**4**) (126 MHz, C$_6$D$_6$).

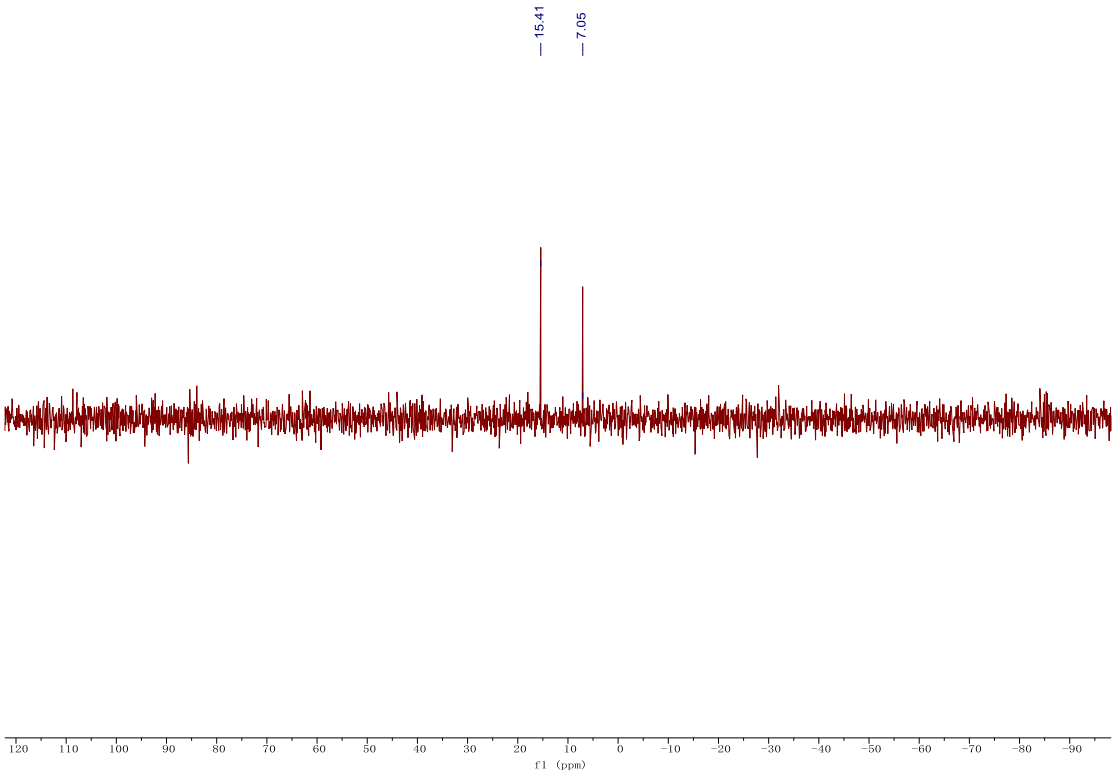


Figure S13. ^{29}Si NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(N$_3$SiMe$_3$) (**4**) (99 MHz, C$_6$D$_6$).

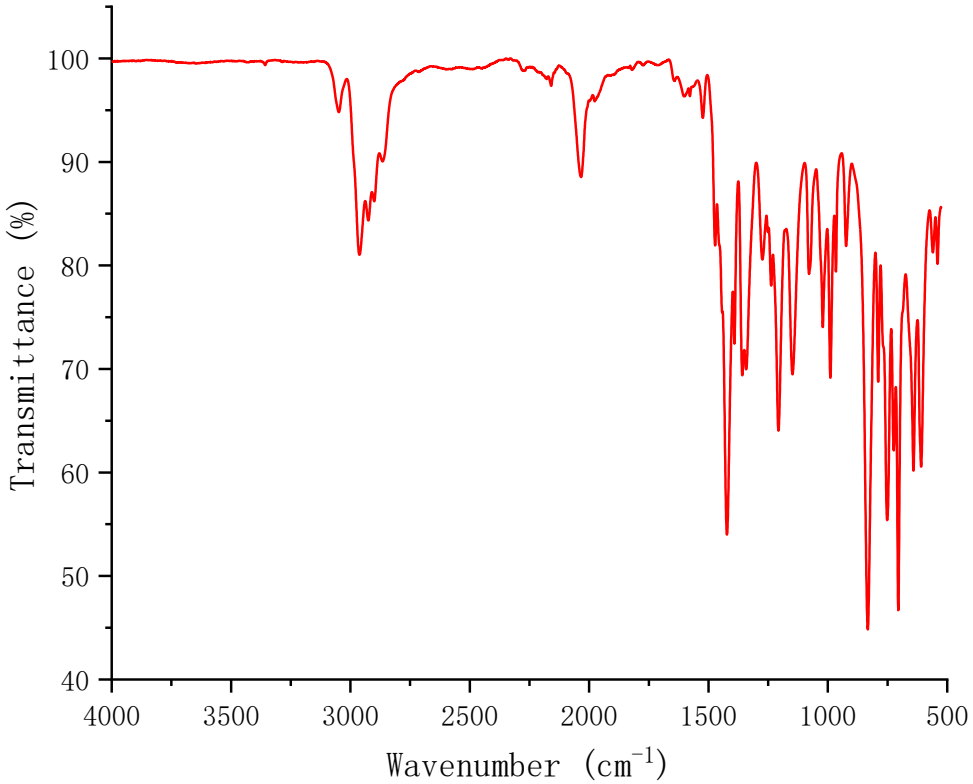


Figure S14. IR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(N$_3$SiMe$_3$) (**4**).

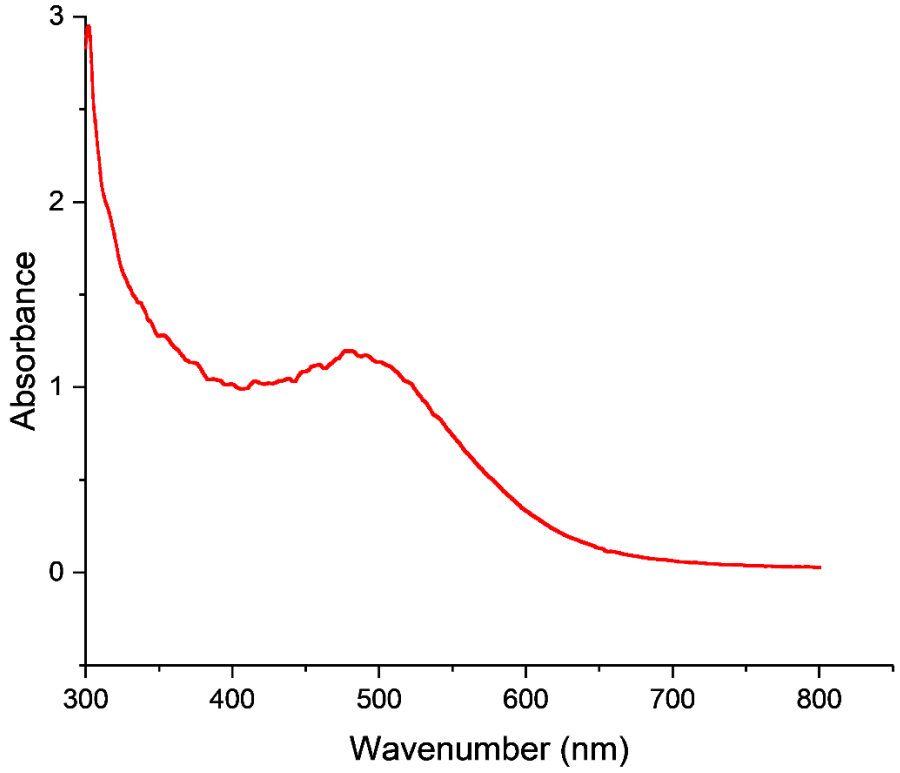


Figure S15. UV-vis spectrum of $\{PhC(N^tBu)_2Si\}_2Fe(C_6H_6)(N_3SiMe_3)$ (**4**).

{PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(NSiMe$_3$) (5).

$TMSN_3$ (7.5 μL, 0.153 mmol) was added by pipette to a solution of **3** {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$) (36 mg, 0.055 mmol) in a J-Young tube or Schlenk tube with stirring at 80 °C. After 90 minutes heating, the product was isolated (Yield: 20.3 mg, 50%) as purple-red solid by washing with cold pentane after removing all solvents and other volatile materials. At shorter reaction times, this product is accompanied by complex **4** {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(N$_3$SiMe$_3$), according to NMR spectroscopy. X-ray quality crystals were collected by dissolving the obtained solid in benzene solution and slow evaporation of the solution at room temperature.

^{1}H NMR (500 MHz, benzene-d_6) δ 7.36 (s, 1H, Ar-H), 7.31 (d, 3H, Ar-H), 7.01~6.99 (m, 4H, Ar-H), 6.96 (m, 2H, Ar-H), 5.12 (s, 6H, benzene-H), 1.43 (s, 36H, N^{t}Bu-H), 0.39 (s, 9H, Si(CH$_3$)$_3$).

^{13}C NMR (126 MHz, benzene-d_6, ppm) δ 169.61 (N*C*N), 133.69, 129.94, 128.47, 127.67 (133.69~127.67: Ph), 75.31 (Fe-benzene), 53.61 (*C*Me$_3$), 31.75 (*C*H$_3$), 3.79 (Si(*C*H$_3$)$_3$).

^{29}Si NMR (99 MHz, benzene-d_6, ppm) δ 7.42, –20.71.

UV-Vis (THF, λ(nm) (ε, M^{-1}cm^{-1})): 530 (592).

IR-ATR (cm^{-1}): 3357 (VW), 2961 (w), 2029 (S), 1597 (W), 1473 (VW), 1419 (S), 1392 (W), 1358 (m), 1237 (W), 1204 (S), 1074 (W), 1019 (S), 924(VW), 832 (S), 787 (VW), 746 (S), 704 (S), 649 (VW), 641 (VW), 609 (W).

Anal. Calcd for C$_{39}$H$_{61}$FeN$_5$Si$_3$: C, 63.30; H, 8.31; N, 9.46. Found: C, 60.19; H, 7.99; N, 8.82. Due to the formation of silicon carbide the carbon values in the elemental analyses were consistently too low for the disilylene Fe compounds reported in this paper.

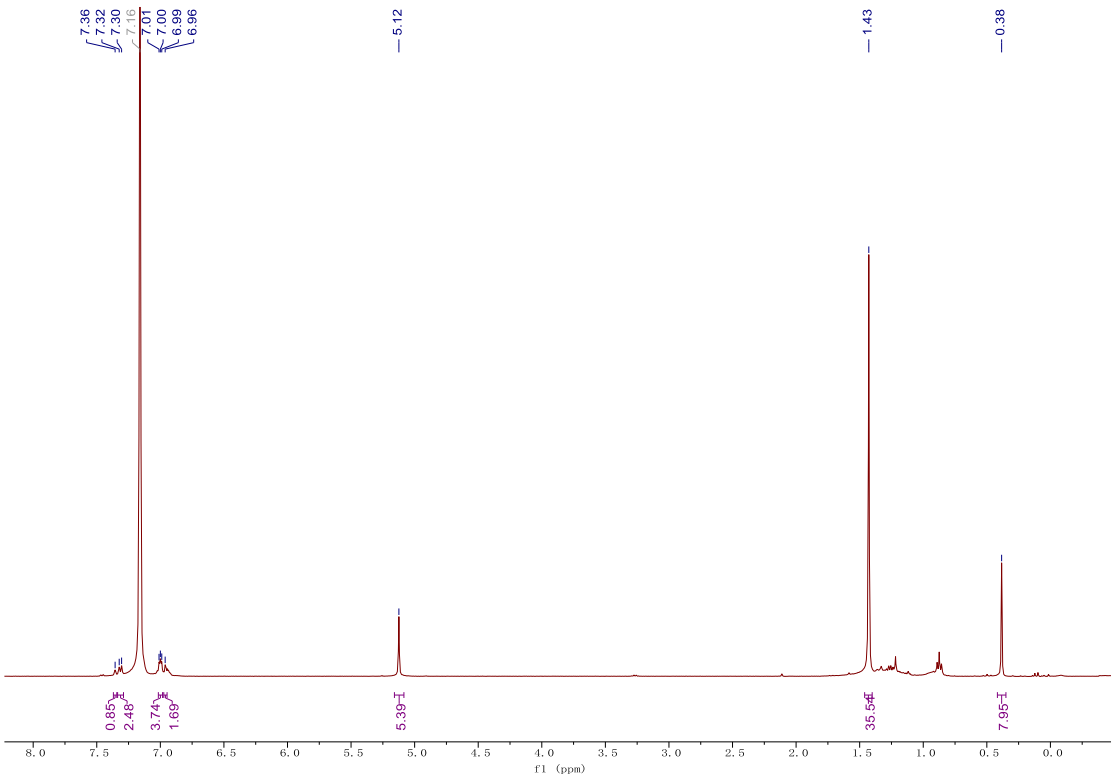


Figure S16. ^{1}H NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(NSiMe$_3$) (**5**) (500 MHz, C$_6$D$_6$).

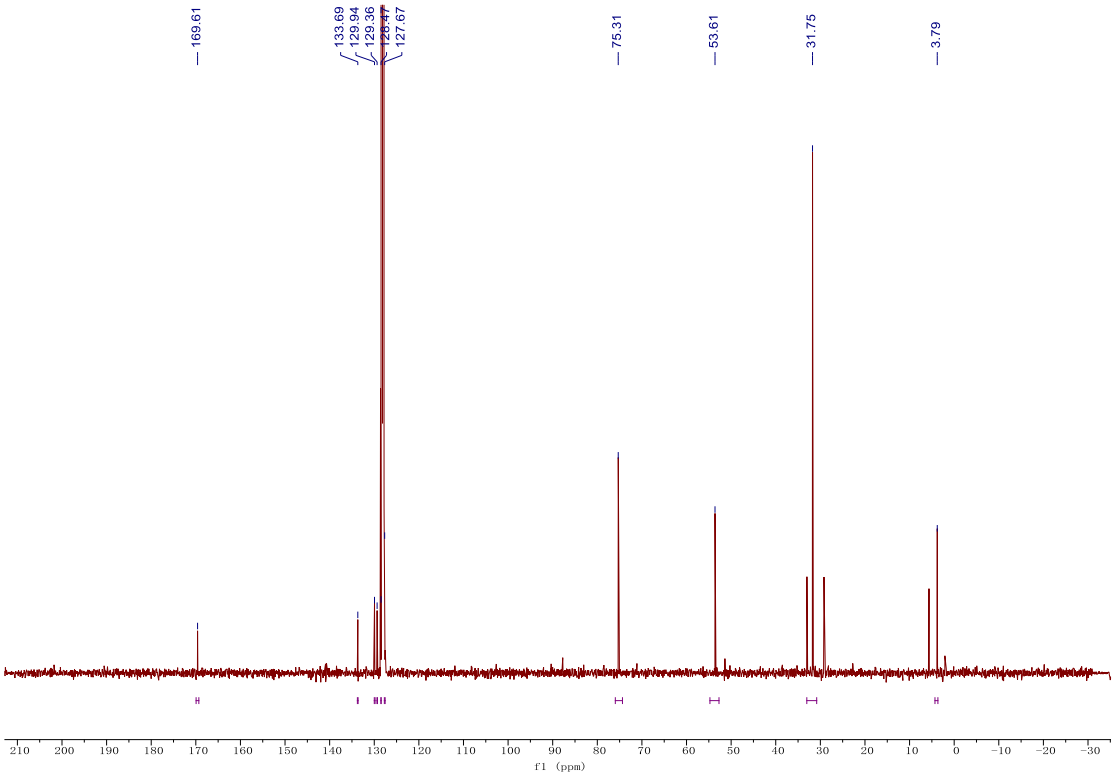


Figure S17. ^{13}C NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(NSiMe$_3$) (**5**) (126 MHz, C$_6$D$_6$).

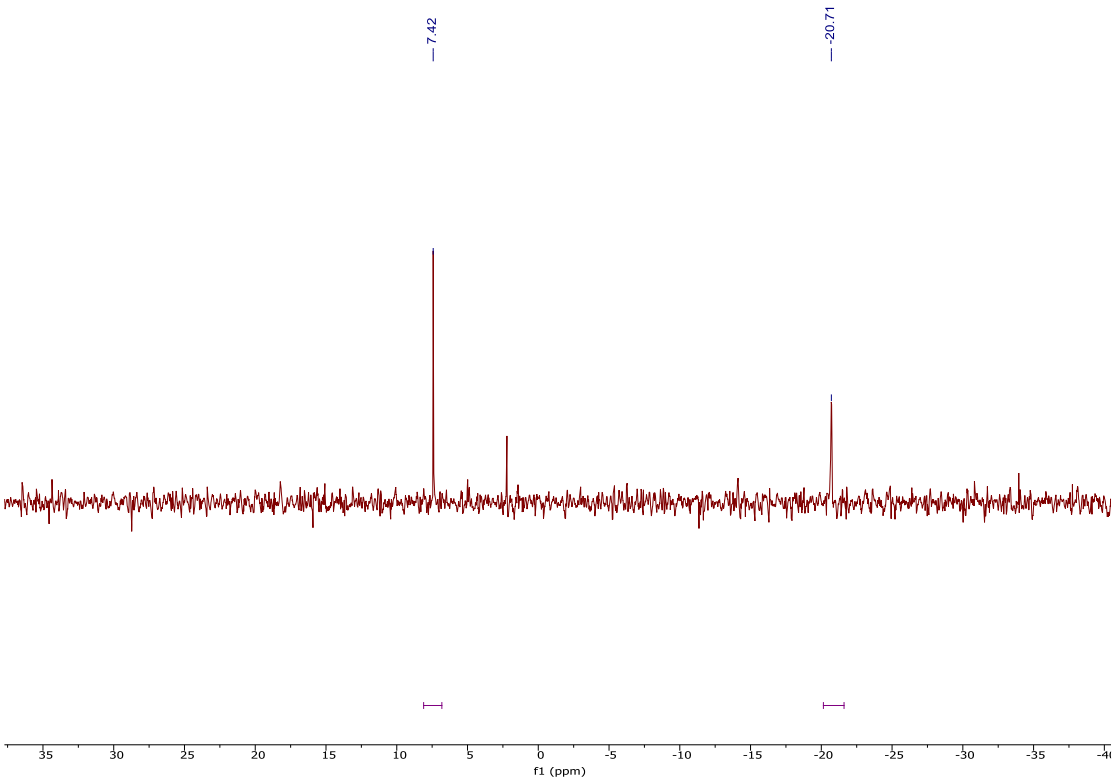


Figure S18. ^{29}Si NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(NSiMe$_3$) (**5**) (99 MHz, C$_6$D$_6$).

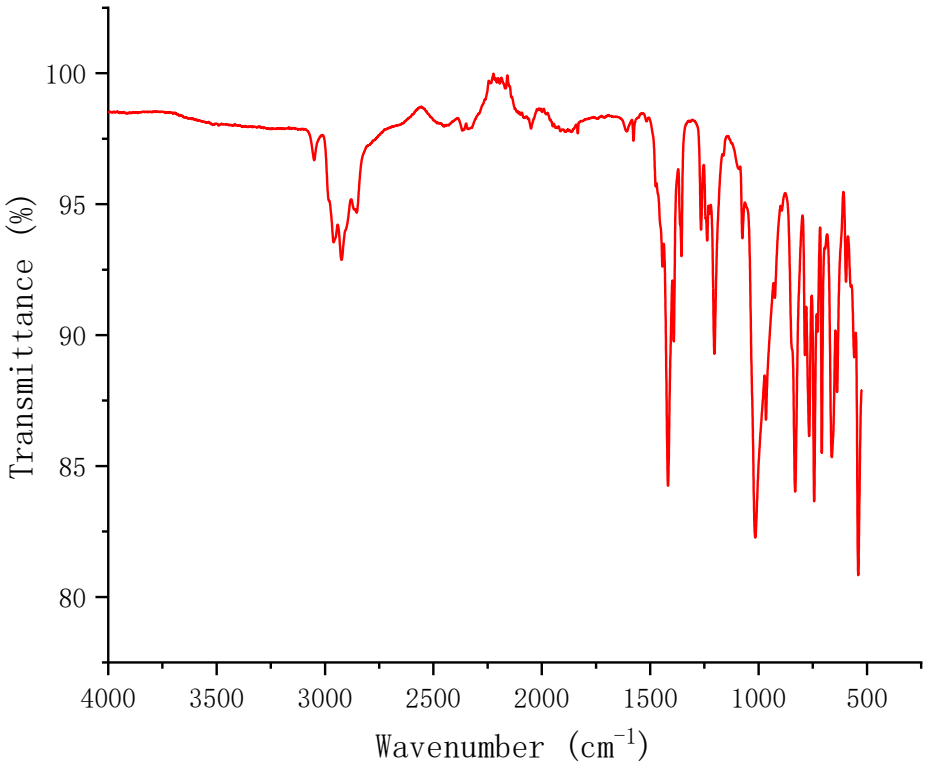


Figure S19. IR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(NSiMe$_3$) (**5**).

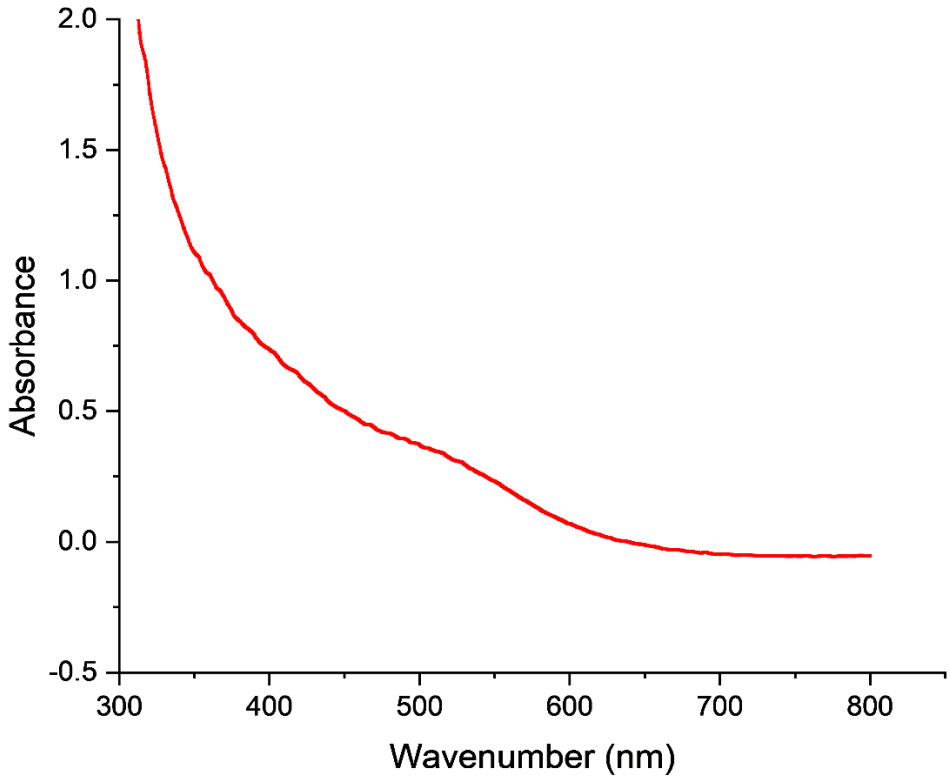
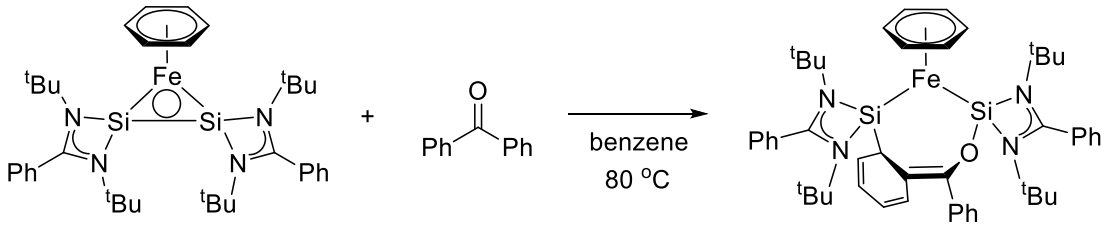


Figure S20. UV-vis spectrum of $\{PhC(N^tBu)_2Si\}_2Fe(C_6H_6)(NSiMe_3)$ (**5**).



3 **6**

{PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(Ph$_2$CO) (6).

Benzophenone (437 μL of a 100-mg-in-10-mL stock solution in benzene) was added dropwise to a solution of **3** (15.6 mg) in benzene (5 mL) in a J-Young tube or Schlenk tube at 80 °C with stirring. The product was isolated as dark greenish-black solid by washing with cold pentane after removing all solvents and other volatile materials. Yield: 12 mg, 60 %. X-ray quality crystals were collected by dissolving solid in diethyl ether solution and then placing the sample in a –30 °C freezer.

^{1}H NMR (500 MHz, benzene-d_6) δ 8.36 (d, 0.5H, Ar-H), 7.76 (d, 2H, Ar-H), 7.52 (d, 1H, Ar-H), 7.31 (d, 0.5H, Ar-H), 7.25 (t, 2H, Ar-H), 7.06~6.95 (m, 9H, Ar-H), 6.98(d,1H, de-ArCH), 6.17 (dd, 1H, de-ArCH), 5.86 (m, 1H, de-ArCH), 5.65 (dd, 1H, de-ArCH), 4.90 (d,1H, de-ArCH), 5.07 (s, 6H, benzene-H), 1.59/ 1.45/ 1.31/ 0.97 (s, 9H, N^{t}Bu-H).

^{13}C NMR (126 MHz, benzene-d_6, ppm) δ 170.46 (N*C*N), 167.56 (N*C*N), 159.33~122.22 (18 signals; 6 C + 18 C; CCCHCHCHCH + C of 3 Ph), 78.46 (Fe-benzene), 53.23 (*C*Me$_3$), 53.14 (*C*Me$_3$), 52.67 (*C*Me$_3$), 52.38 (*C*Me$_3$), 32.12 (*C*H$_3$), 32.01 (*C*H$_3$), 31.15 (*C*H$_3$), 31.09 (*C*H$_3$).

^{29}Si NMR (99 MHz, benzene-d_6, ppm) δ 65.57, 33.66.

UV-Vis (THF, λ(nm) (ε, M^{-1}cm^{-1})): 350 (4785), 435 (2782).

IR-ATR (cm^{-1}): 3052 (VW), 2965 (W), 2962 (VW). 1647 (VW), 1596 (VW), 1472 (W), 1421 (S), 1390 (m), 1358 (m), 1264 (m), 1204 (S), 1106 (VW), 1072 (W), 1009 (W), 970 (W), 923 (W), 865 (W), 790 (m), 745 (S), 722 (VW), 699 (VS), 607 (S), 544 (S).

Anal. Calcd for C$_{49}$H$_{62}$FeN$_4$OSi$_2$: C, 70.48; H, 7.48; N, 6.71. Found: C, 65.07; H,7.09; N, 6.15. Due to the formation of silicon carbide the carbon values in the elemental analyses were consistently too low for the disilylene Fe compounds reported in this paper.

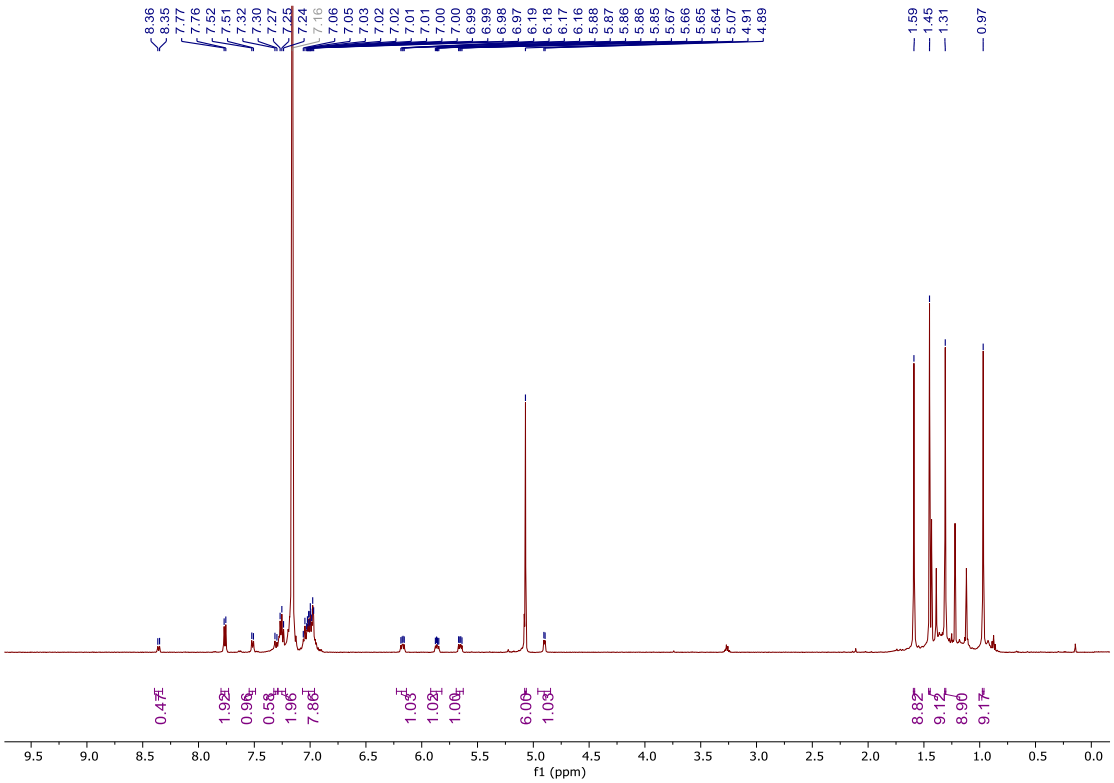


Figure S21. ^{1}H NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(Ph$_2$CO) (**6**) (500 MHz, C$_6$D$_6$).

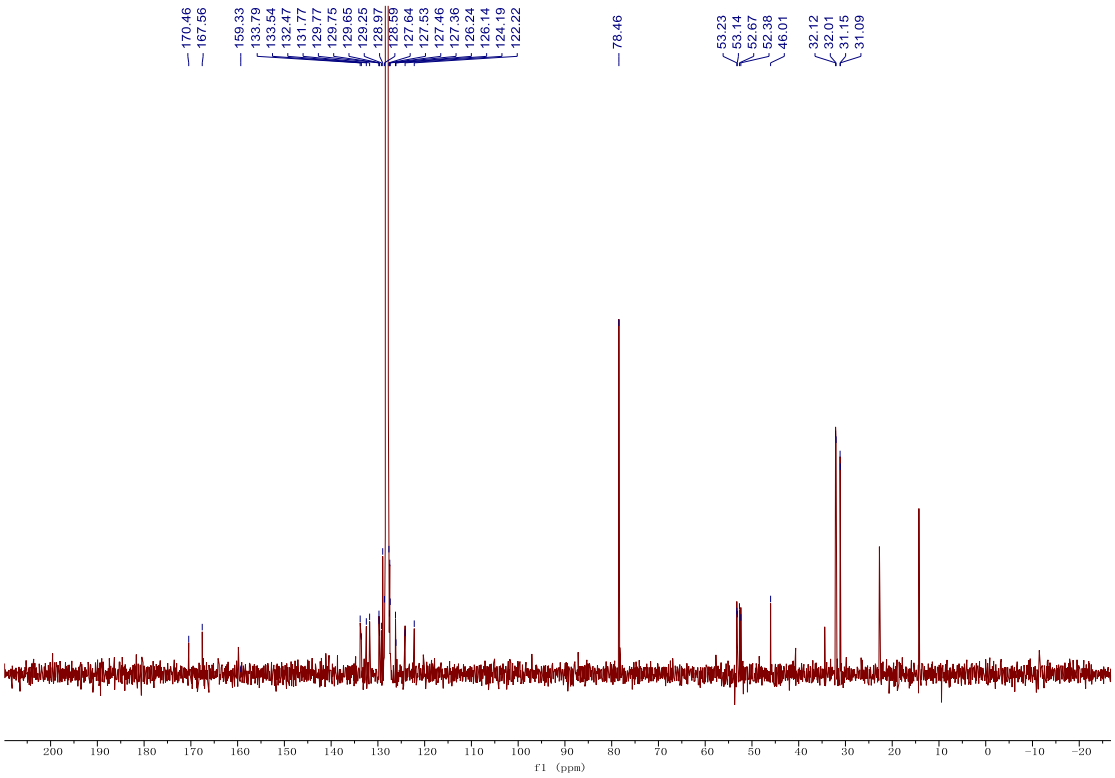


Figure S22. ^{13}C NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(Ph$_2$CO) (**6**) (126 MHz, C$_6$D$_6$).

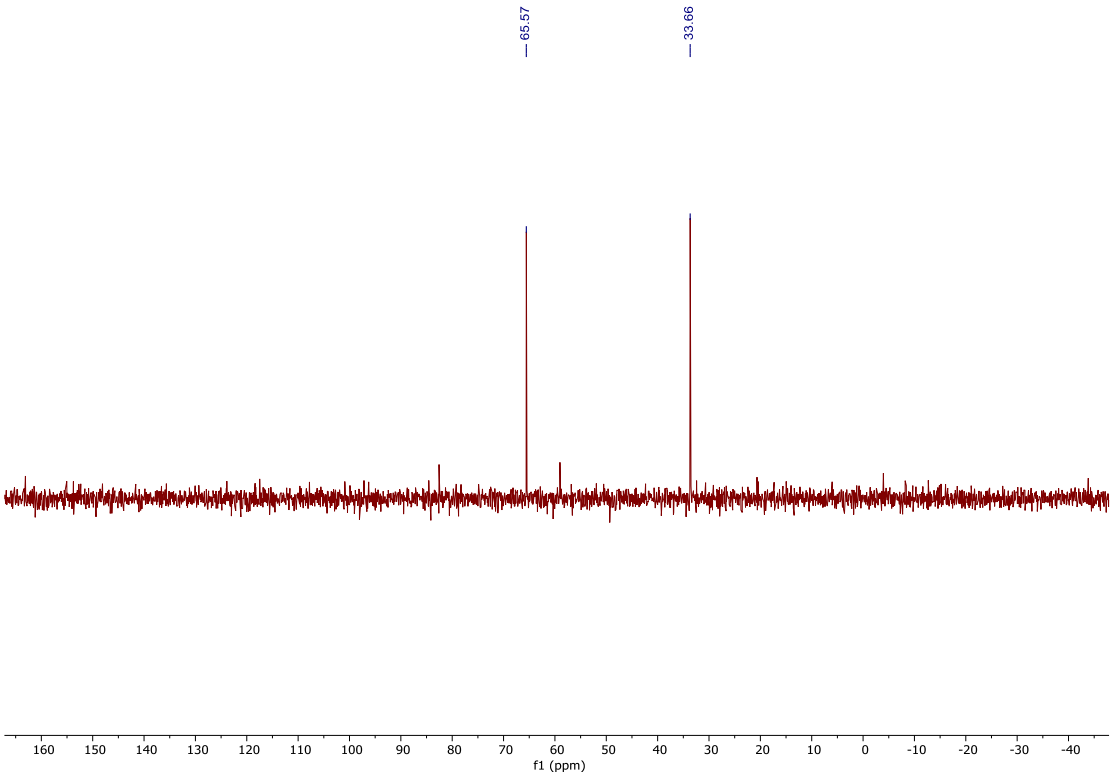


Figure S23. ^{29}Si NMR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(Ph$_2$CO) (**6**) (99 MHz, C$_6$D$_6$).

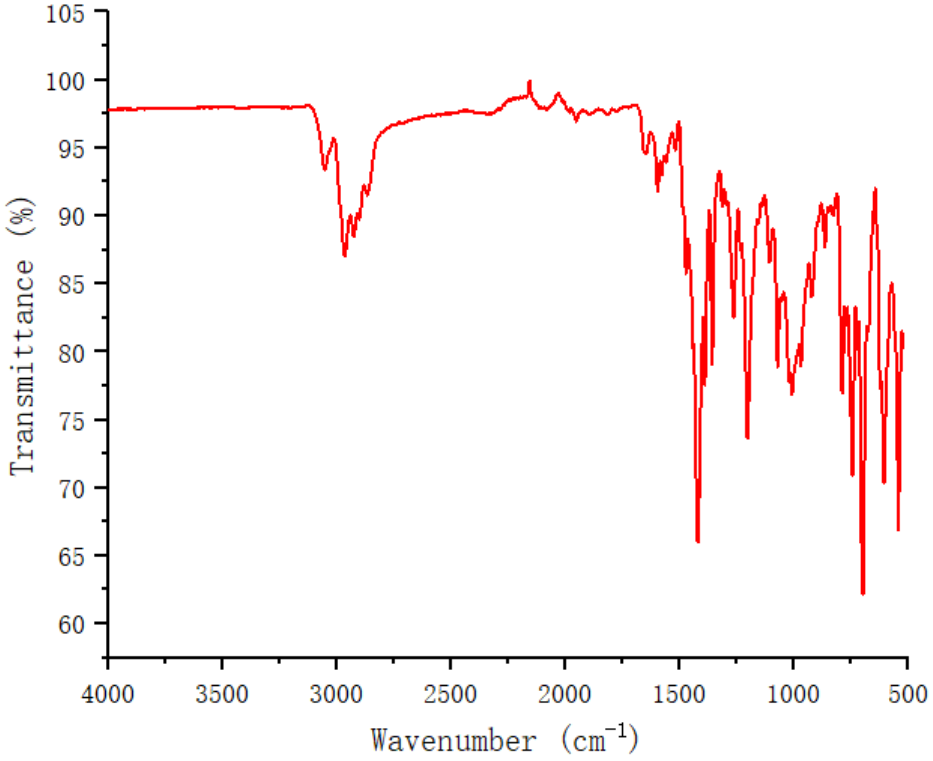


Figure S24. IR spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(Ph$_2$CO) (**6**).

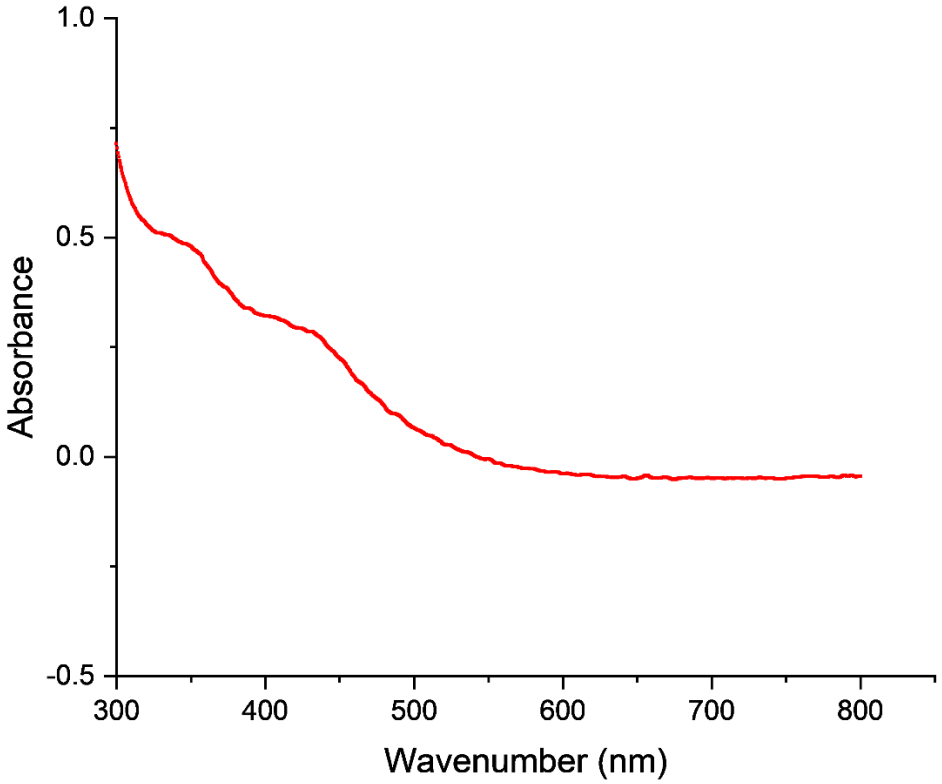


Figure S25. UV-vis spectrum of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(Ph$_2$CO) (**6**).

Reaction of 3 with TMS-azide followed by NMR

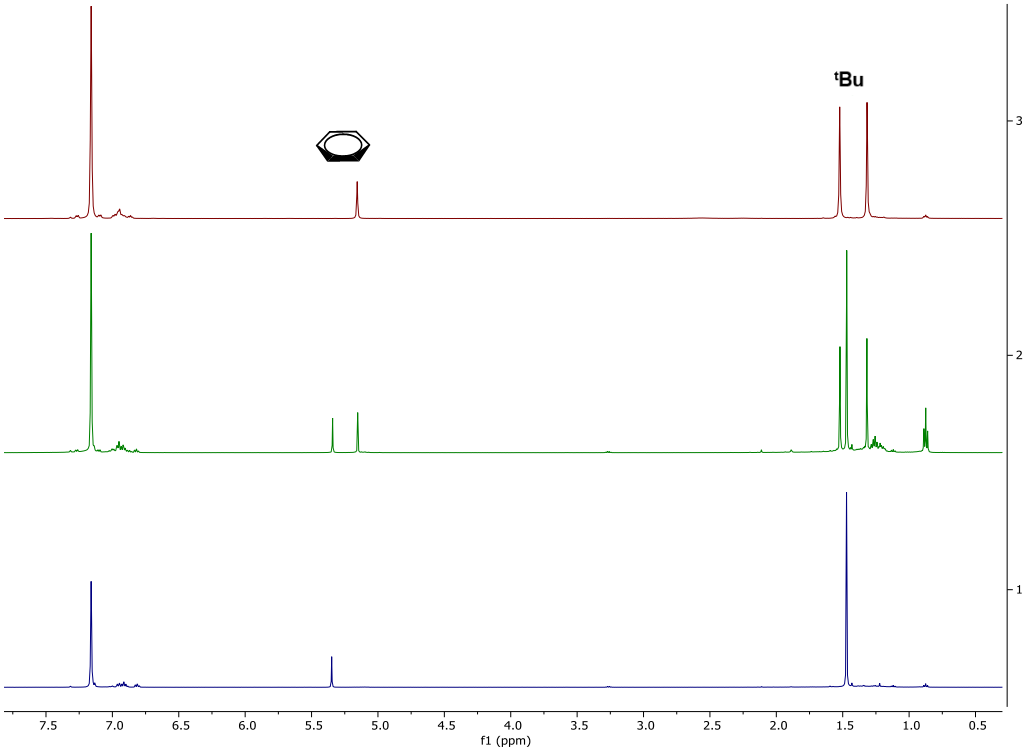


Figure S26. Reaction process of compound **3** under the ^{1}H NMR monitoring experiment.

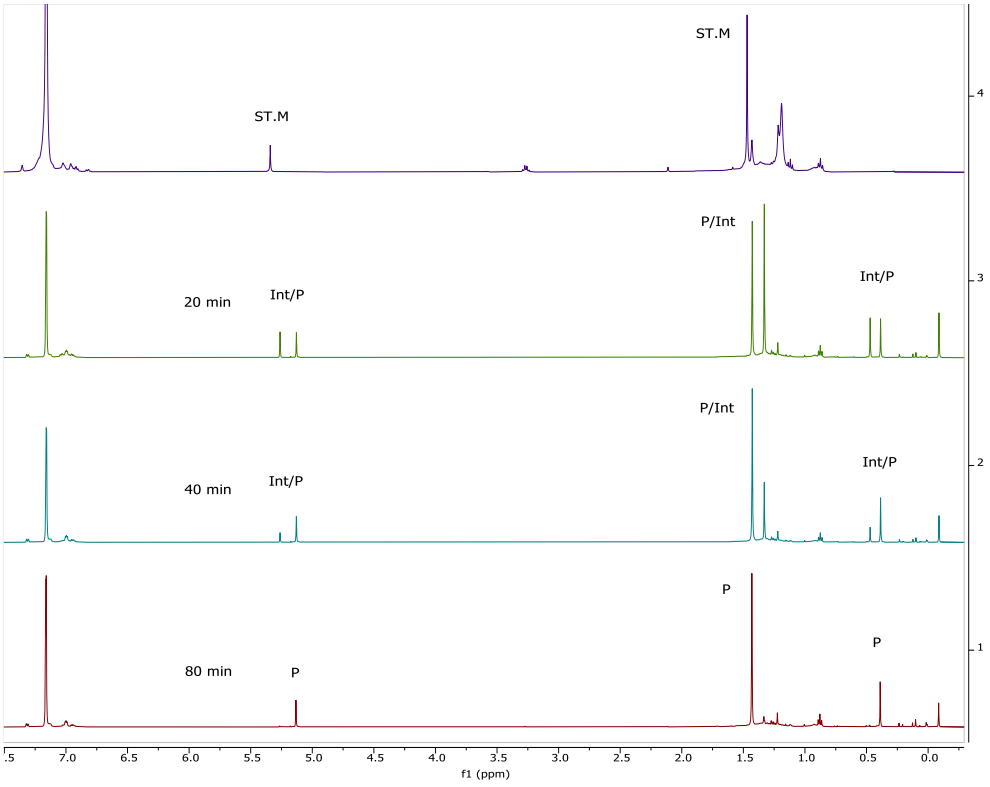


Figure S27. Reaction process of compound **3** with $TMSN_3$ to form compound **4** (Int) and compound **5** (P) via ^{1}H NMR monitoring.

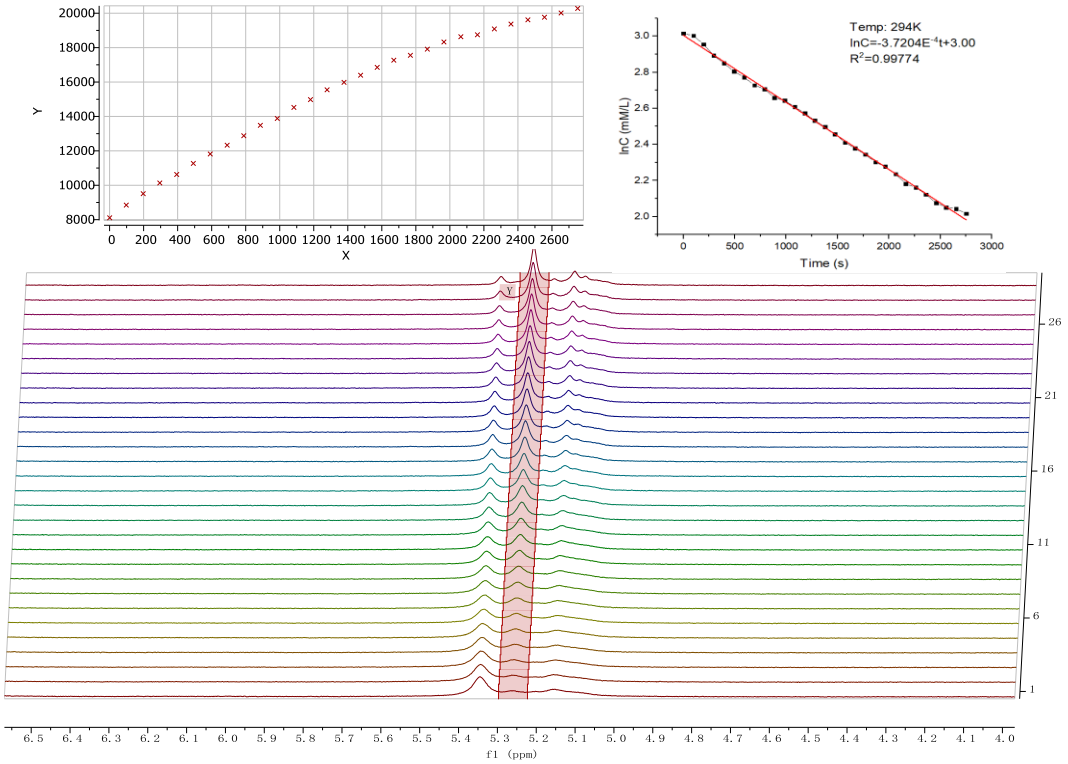


Figure S28. ^{1}H NMR monitoring of the reaction progress from **3** to **4** at 294 K.

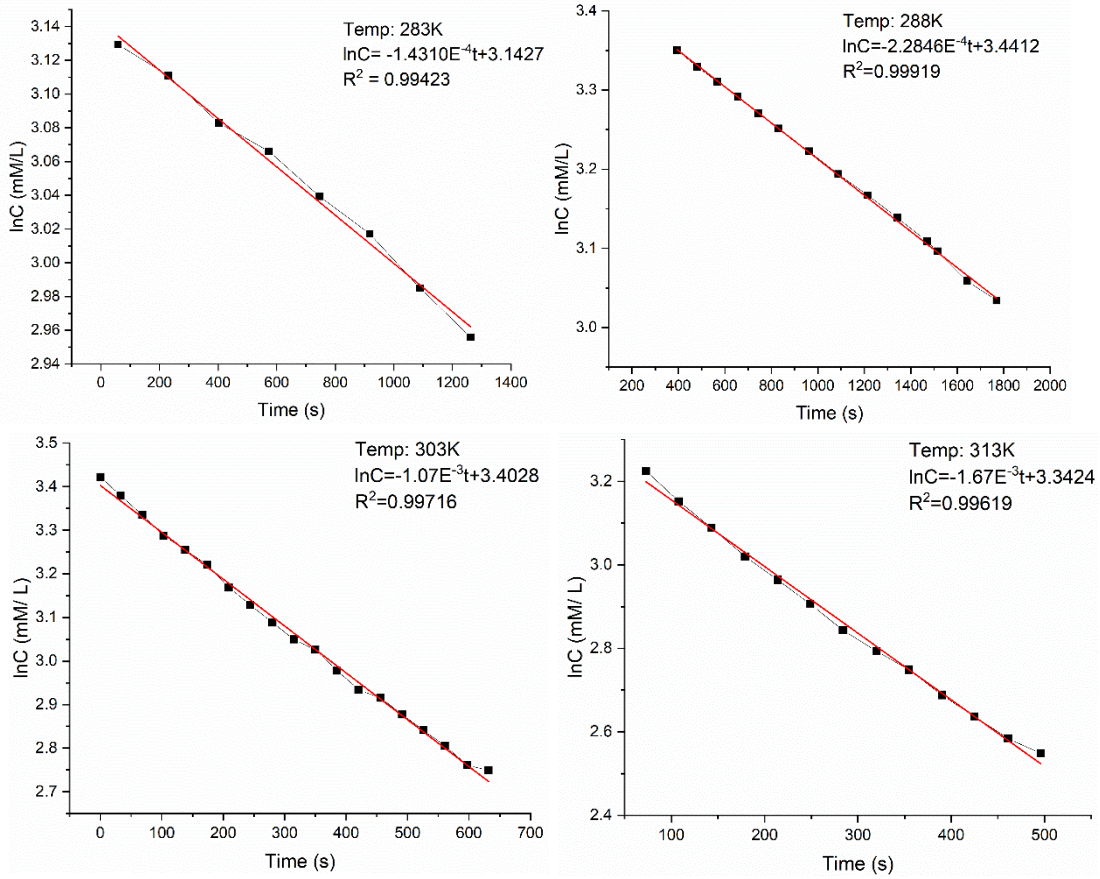


Figure S29. Reaction progress monitoring by ^{1}H NMR for conversion of **3** into intermediate **4** at different temperatures: 283 K (top left), 288 K (top right), 303 K (bottom left), 313 K (bottom right).

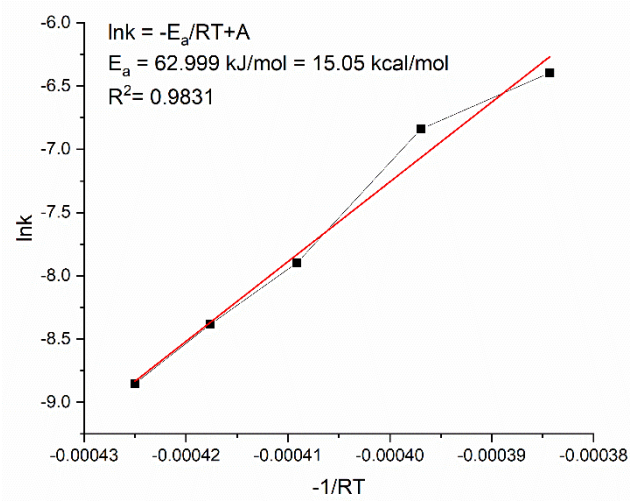


Figure S30. Arrhenius plot for conversion of compound **3** into intermediate **4**

EDA and DFT calculations

Computational details:

Geometries were fully optimized as minima or transition states using the Turbomole program package,[S7] coupled to the PQS Baker optimizer[S8] via the BOpt package.[S9] We used unrestricted ri-DFT-D3 calculations at the B3LYP level,[S10] in combination with the def2-TZVP basis set[S11] and a small (m4) grid size. Grimme's dispersion corrections[S12] (version 3, disp3, 'zero damping') were used to include Van der Waals interactions. All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by calculating the Hessian matrix. Thermochemical parameters such as the zero-point energy (ZPE), Gibbs free energy and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) were obtained from these analyses. The nature of the transition states was confirmed by following the intrinsic reaction coordinate (IRC). The relative free energies ($\Delta G°_{298K}$ in kcal·mol^{-1}) obtained from these calculations are reported in the main text. For every transition state, the imaginary eigenvalue was followed in both directions to confirm its connection to the relative reactant and product states. A separate archive file is provided, containing an Excel sheet with free energies ($\Delta G°_{298K}$) and negative eigenvalues of the transition states, and all optimized geometries. Optimized geometries of all stationary states and transition states are supplied in .pdb and .xyz format.

The energy decomposition analysis (EDA)[S13] has been performed on the TZ2P/OPBE[S14] optimized geometry constrained to C_{2v} symmetry (+3.9 kcal·mol^{-1}) since it is most informative if the orbital interactions can be dissected by different irreducible representation. The total bonding energy of –57.6 kcal mol^{-1} consists of the preparation energy of the fragments into the geometry and electronic state they possess in the complex as well as their orbital interactions and the steric interaction (+31.7 kcal·mol^{-1}), which is the balance between the Pauli repulsion of the electron densities of the interacting fragments and the attraction of the electron density of one fragment and the nuclei of the other and vice versa. The contribution of the orbital interaction is usually dominated by the stabilization of the high lying occupied orbitals of one fragment by the low-lying empty orbitals of the other fragment (donor-acceptor interaction) but also contains the mixing of occupied and empty orbitals at the same fragment (polarization).

The Fe(benzene) fragment (+42.3 kcal·mol^{-1}) has been calculated in the singlet state (Fe(0)-d^8) with a doubly occupied d_{yz} (perpendicular to the Si–Fe–Si plane) and an empty d_{xz} orbital. The electronic structure of the Si(I)–Si(I) fragment (+52.1 kcal·mol^{-1}) is best described as having a Si–Si single bond with a lone pair on each silicon and an empty π-orbital between them. The two lone pairs are forming a bonding (A1) and antibonding (B1) combination. The former donate electron density into the empty d_{xz} (A1: –30.3 kcal·mol^{-1}, 0.4 e; B1: –74.4 kcal·mol^{-1}, 0.8 e) orbital at iron. The metal itself donates charge density back from the occupied d_{yz} orbital into the empty π-symmetric orbital of the Si–Si bond (B2: –67.8 kcal·mol^{-1}, 0.9 e), giving rise to a considerable degree of π-backbonding.

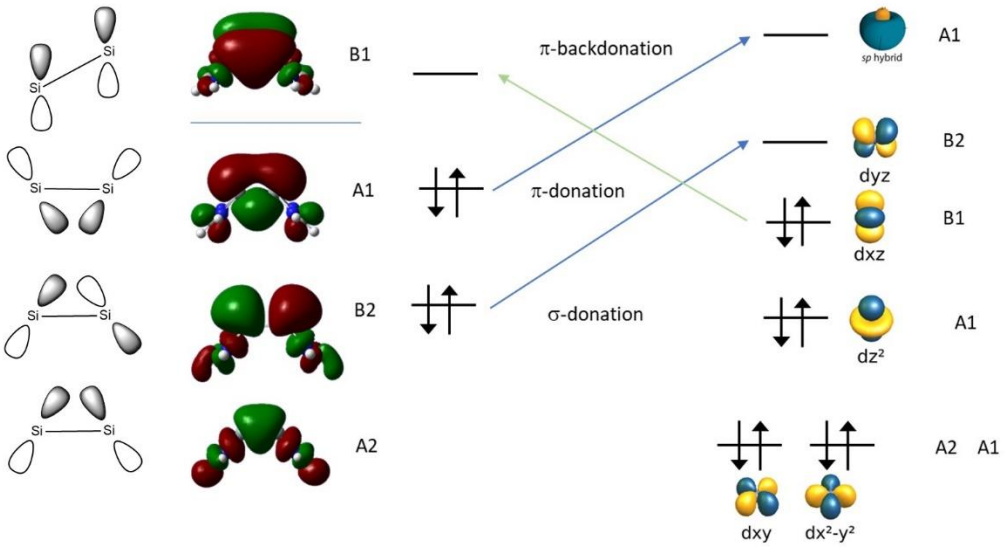


Figure S31. Results of the EDA analysis (interaction between Si(I)–Si(I) and Fe).

The Nucleus Independent Chemical Shift (NICS) [S15] was used as a diagnostic probe for quantitative measure for aromaticity at the B3LYP/6-11+G(d,p) level.[S16,S17] The NICS index is the negative value of the isotropic magnetic shielding computed at ring centers and points above and below[S18] in and around the molecule.[S19] We used the refined method by Stanger, following the out of plane component to the shielding tensor along a trajectory orthogonal to the plane of the ring ($NICS_{zz}$),[S20] as this can be used to characterize whether an inorganic system is aromatic, non-aromatic or anti-aromatic.[S22] A minimum in $NICS_{zz}$ (out of plane eigenvalue) at a nonzero r value is indicative of aromatic π-delocalization.[S23] Arguably, this is due to the π-electron density above (and below) the aromatic ring. A similar behaviour is calculated for the benzene ring in **3** (scanning the axis opposite to iron), again a minimum is found about 1 Å above the ring for the out of plane (zz) component (red line, left figure below). For the Fe–Si–Si ring in **3** (Figure S33), there is no real minimum for the out of plane component (red line) (note that the zz-eigenvalue of –60.4 at 0.2Å is slightly lower than that of –59.8 at the centre).

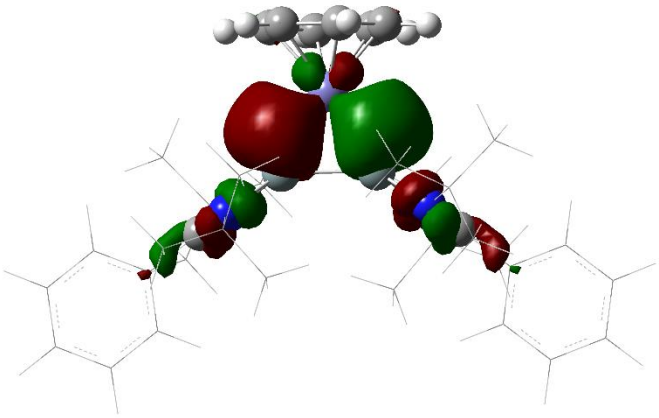


Figure S32. Representation of the HOMO-5 in complex **3**.

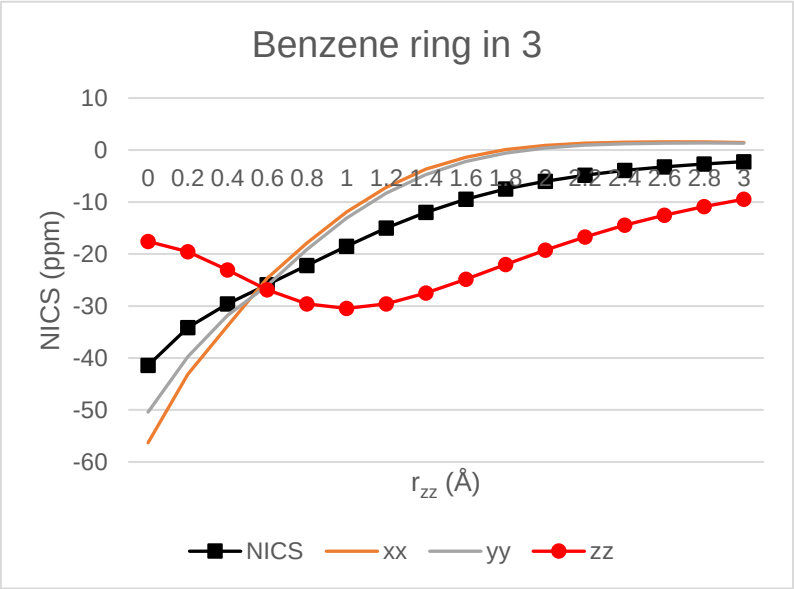


Figure S33. NICS perpendicular to the ring plane of the benzene ring in compound **3**.

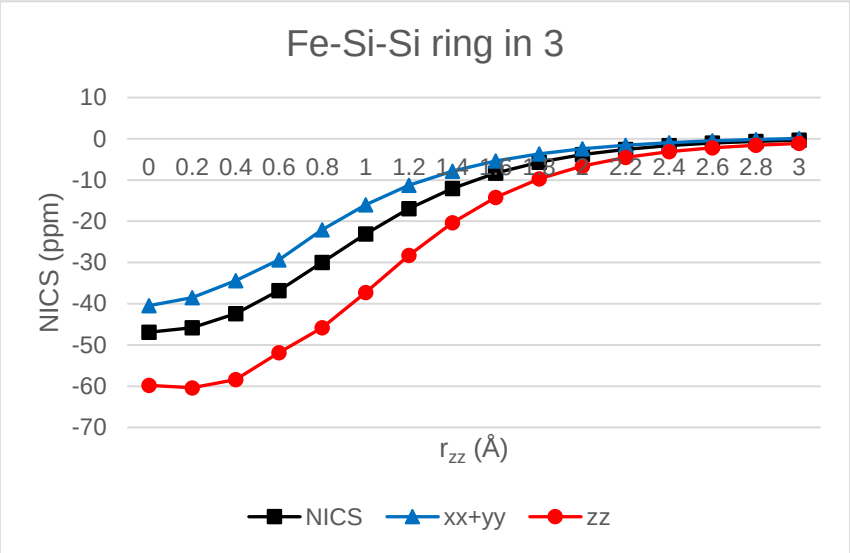


Figure S34. NICS perpendicular to the ring plane of the Fe-Si-Si ring in compound **3**.

Therefore we resorted to the CMO analysis of the NICS(0), which separates the total shieldings into contributions from canonical molecular orbitals.[S21] Indeed, there is a sizable contribution of −13.8 ppm from the Fe-d_{xy} orbital (HOMO-5) that is pointing toward the center of the three membered ring. More importantly, the major contribution of −16.6 ppm originates from the delocalized π-orbital shown in Fig. 3 (main text) proving definitely the 2π-aromaticity of the Si_2Fe-three-membered ring in complex **3**. It was also established that the shapes of the NICS-scan profiles provide a clear picture of the type of the ring current in aromatic and antiaromatic systems

Optimized coordinates

Compound **3**

95

E= 3463,66282

Fe	10.3351558	5.6647774	11.8737848
Si	9.2315091	3.7691544	11.7238373
N	8.2179792	2.8964234	10.3951047
N	8.1085331	2.4629532	12.4949055
C	7.6121262	2.1155942	11.3071703
C	7.6698782	3.3618082	9.1008354
C	6.4637921	4.2789570	9.3688814
C	7.2568080	2.2033103	8.1799861
C	8.7709090	4.1658316	8.3993657
C	8.1688582	1.7144469	13.7641206
C	8.4341272	2.7599946	14.8536881
C	6.8652141	0.9774390	14.1015066
C	9.3292312	0.7035906	13.7001415
C	6.6434094	1.0321192	11.0209545
C	5.2753247	1.2117313	11.2208302
C	4.3847454	0.1858481	10.9303274
C	4.8549927	-1.0308270	10.4456184
C	6.2201880	-1.2167970	10.2496354
C	7.1104600	-0.1886228	10.5317068
C	9.1397526	7.2256122	11.1238140
C	9.0917043	7.2189544	12.5365966
C	10.2861143	7.2025952	13.2938635
H	5.6624801	3.7307091	9.8668589
H	6.0687047	4.6790293	8.4324063
H	6.7605747	5.1131528	10.0067935
H	8.0692513	1.4808615	8.0863227
H	7.0358716	2.5996311	7.1865854
H	6.3708191	1.6806577	8.5346595
H	9.1953853	4.9147532	9.0693335
H	8.3593613	4.6640622	7.5194523
H	9.5746556	3.5084266	8.0701209
H	9.2879259	3.3802730	14.5892148
H	8.6328075	2.2710443	15.8095214
H	7.5695012	3.4159852	14.9702153
H	6.0086185	1.6499226	14.0382598
H	6.9297887	0.6047769	15.1258302
H	6.6849241	0.1266062	13.4476925
H	9.1646465	-0.0091984	12.8891201
H	9.3994037	0.1452273	14.6370367
H	10.2720226	1.2206076	13.5230106

H	4.9125164	2.1551735	11.6076975
H	3.3233036	0.3354458	11.0838220
H	4.1603660	-1.8304858	10.2209753
H	6.5911502	-2.1618286	9.8727517
H	8.1724239	-0.3233710	10.3690867
H	8.2215673	7.1597960	10.5569136
H	8.1379723	7.1353053	13.0378685
H	10.2471624	7.1515040	14.3731097
Si	11.4387734	3.7691333	12.0237883
N	12.4522738	2.8963836	13.3525329
N	12.5617060	2.4628549	11.2527562
C	13.0580890	2.1154973	12.4405000
C	13.0003941	3.3618148	14.6467716
C	14.2063528	4.2791123	14.3786763
C	13.4136648	2.2033741	15.5675937
C	11.8992651	4.1656795	15.3482891
C	12.5014079	1.7143558	9.9835078
C	12.2359681	2.7599474	8.8939911
C	13.8051492	0.9775570	9.6459830
C	11.3411527	0.7033136	10.0474787
C	14.0267808	1.0320138	12.7267514
C	15.3948620	1.2115326	12.5267869
C	16.2854074	0.1856285	12.8173187
C	15.8151291	-1.0309716	13.3021553
C	14.4499375	-1.2168433	13.4982373
C	13.5596995	-0.1886527	13.2161300
C	11.5305515	7.2256581	12.6236780
C	11.5786002	7.2189516	11.2108957
C	10.3841904	7.2025443	10.4536299
H	15.0076856	3.7309765	13.8806097
H	14.6014704	4.6791853	15.3151388
H	13.9094307	5.1133019	13.7408257
H	12.6013587	1.4807935	15.6613619
H	13.6346752	2.5997439	16.5609587
H	14.2997313	1.6808740	15.2128869
H	11.4748180	4.9146454	14.6783575
H	12.3108285	4.6638175	16.2282458
H	11.0956132	3.5080969	15.6773978
H	11.3821207	3.3801300	9.1585197
H	12.0373391	2.2710124	7.9381151
H	13.1005270	3.4160593	8.7774815
H	14.6616309	1.6501911	9.7092905
H	13.7405569	0.6050113	8.6216045
H	13.9855343	0.1266729	10.2997237

H	11.5059147	-0.0095532	10.8584126
H	11.2709160	0.1450943	9.1104896
H	10.3983258	1.2202172	10.2247749
H	15.7577027	2.1549192	12.1398347
H	17.3468488	0.3351425	12.6637528
H	16.5097219	-1.8306538	13.5268157
H	14.0789412	-2.1618181	13.8752109
H	12.4977367	-0.3233262	13.3788106
H	12.4487350	7.1599082	13.1905721
H	12.5323262	7.1353112	10.7096340
H	10.4231377	7.1514005	9.3743887

$TMSN_3$

16

E= -573,33931

Si	0.0478034	-0.0105189	1.5467950
C	-0.0963802	-0.0884830	-0.3187375
H	0.8927987	-0.1426692	-0.7815102
H	-0.6051191	0.7944088	-0.7117395
H	-0.6587082	-0.9706513	-0.6352391
C	0.8991746	-1.5426172	2.2063985
H	1.9105823	-1.6284123	1.7997715
H	0.3534382	-2.4484181	1.9302317
H	0.9746454	-1.5133137	3.2955377
C	0.8838015	1.5547942	2.1186729
H	1.9089249	1.6045670	1.7430985
H	0.9198639	1.6022840	3.2090921
H	0.3484756	2.4365151	1.7601224
N	-1.5800453	0.0777641	2.2391161
N	-2.4546883	-0.7546694	2.1034327
N	-3.3175673	-1.4815801	2.0239572

Compound TS**1**

111

E= -4036,97761

Fe	5.2058049	17.3971531	8.2093694
Si	3.8439645	16.9257711	9.8290533
Si	4.7902081	19.0143587	9.5274523
Si	3.5072936	18.7502000	14.8892969
N	2.7394025	18.4956017	12.4211176
N	3.7692948	18.6204712	13.1585886
C	5.1095038	18.1950092	15.6897653
H	5.9388320	18.8372834	15.3859618
H	5.3608551	17.1706451	15.4095352
H	5.0334632	18.2399477	16.7794351

C	3.1443946	20.5177122	15.4370989
H	2.8877323	20.5411074	16.5000618
H	2.3045670	20.9435460	14.8821719
H	4.0118560	21.1656202	15.2936671
C	2.0662751	17.6651993	15.4306765
H	1.8919616	17.7481755	16.5068072
H	2.2438954	16.6128523	15.1991370
H	1.1499709	17.9697268	14.9181052
N	3.8983534	15.6590238	11.1961087
N	2.3009422	15.8445029	9.7730212
N	5.7452462	20.2016482	10.6154054
N	3.8079005	20.5854311	9.7843691
N	2.3908181	18.2454417	11.3261450
C	2.7045053	15.1671540	10.8483794
C	1.9314096	14.1534492	11.6084702
C	1.1168840	14.6020737	12.6493186
H	1.0726489	15.6611844	12.8692805
C	0.3857939	13.6937505	13.4040948
H	-0.2407868	14.0495104	14.2123278
C	0.4638967	12.3324739	13.1256153
H	-0.1042561	11.6241299	13.7154250
C	1.2731905	11.8833118	12.0868537
H	1.3340755	10.8254724	11.8637614
C	2.0042078	12.7906533	11.3294356
H	2.6210952	12.4428874	10.5113600
C	4.9329500	15.0877681	12.0809527
C	4.4128475	14.8833539	13.5104733
H	3.9753111	15.8089843	13.8788142
H	5.2428557	14.6081702	14.1644624
H	3.6654466	14.0946743	13.5696678
C	6.0893199	16.0904161	12.1118973
H	6.4917364	16.2313787	11.1087045
H	6.8848178	15.7220030	12.7618290
H	5.7403168	17.0525558	12.4840480
C	5.4419996	13.7576012	11.5016491
H	4.6638983	12.9953924	11.5127110
H	6.2826556	13.3869312	12.0921527
H	5.7785367	13.8995325	10.4735446
C	1.0211514	15.8161193	9.0419312
C	-0.0613321	16.5906043	9.8107515
H	0.2617717	17.6080342	10.0191588
H	-0.2775617	16.1056811	10.7632397
H	-0.9844322	16.6204341	9.2273025
C	0.5390646	14.3794471	8.7798760

H	0.1890249	13.8877293	9.6846505
H	1.3382336	13.7779588	8.3421680
H	-0.2928552	14.4063122	8.0735532
C	1.2781310	16.4806465	7.6824663
H	0.3428569	16.5521773	7.1245281
H	1.9892002	15.8949272	7.0991081
H	1.6934204	17.4782302	7.7973424
C	4.7741025	21.1160773	10.5383418
C	4.7287716	22.4177584	11.2476829
C	5.1270886	23.6134262	10.6539029
H	5.5059398	23.6105927	9.6403712
C	5.0559726	24.8026313	11.3697958
H	5.3697919	25.7285185	10.9044420
C	4.5863469	24.8035933	12.6796664
H	4.5304075	25.7318510	13.2343097
C	4.1899902	23.6098274	13.2747733
H	3.8208601	23.6014121	14.2926199
C	4.2622792	22.4206269	12.5617600
H	3.9491795	21.4865344	13.0063433
C	7.0677072	20.2516760	11.2680520
C	7.8128988	21.5579438	10.9489163
H	8.8419685	21.4818376	11.3056139
H	7.3583084	22.4197518	11.4320194
H	7.8375473	21.7331631	9.8713527
C	7.8870101	19.0846544	10.7016972
H	8.0275034	19.1950486	9.6258035
H	7.3892421	18.1342795	10.8736020
H	8.8663831	19.0589571	11.1823656
C	6.9200830	20.0847503	12.7872623
H	6.3436811	19.1901211	13.0107115
H	6.4027969	20.9380721	13.2255096
H	7.9044896	20.0080093	13.2545199
C	2.5482470	21.1766144	9.2910514
C	1.6515984	21.6433164	10.4487352
H	1.4948917	20.8266637	11.1534200
H	0.6810717	21.9517727	10.0541843
H	2.0797770	22.4913822	10.9797440
C	1.8148440	20.0800974	8.5137447
H	2.4360324	19.6937381	7.7047735
H	0.8945883	20.4833623	8.0879898
H	1.5591091	19.2582860	9.1775826
C	2.8455390	22.3441423	8.3357063
H	3.3022065	23.1827297	8.8583150
H	1.9178420	22.6996247	7.8822183

H	3.5159025	22.0192435	7.5376892
C	4.7610852	16.9213033	6.2148939
H	3.8295624	17.0163381	5.6754609
C	5.0466458	15.7422023	6.9419374
H	4.3195064	14.9433340	6.9782371
C	6.2315563	15.6435210	7.7101978
H	6.4082369	14.7651541	8.3144242
C	7.1391821	16.7250395	7.7540109
H	8.0172767	16.6751070	8.3826923
C	6.8706805	17.8891342	6.9984265
H	7.5309083	18.7417301	7.0738964
C	5.6841848	17.9897032	6.2368273
H	5.4496092	18.9148031	5.7297503

Compound **4**

111

E= -4037,07239

Fe	5.1106086	17.4673073	8.2439896
Si	3.9901390	16.5198715	9.8357445
Si	4.6997841	18.9203676	9.8001544
Si	2.5728612	19.2303088	14.3332185
N	3.2246963	17.9823058	12.1612506
N	3.2674098	19.1229699	12.7275423
C	3.9598864	19.7387642	15.5006897
H	4.4329450	20.6661462	15.1684231
H	4.7342913	18.9684287	15.5385175
H	3.5900705	19.8964944	16.5175012
C	1.2733498	20.5916252	14.2980543
H	0.8646593	20.7741335	15.2956925
H	0.4445681	20.3228389	13.6386185
H	1.6943911	21.5305354	13.9311179
C	1.7975125	17.6202295	14.9231110
H	1.3788110	17.7277473	15.9272260
H	2.5420291	16.8216305	14.9485505
H	0.9934645	17.3119349	14.2509936
N	4.1828141	15.0324284	10.9986751
N	2.3574840	15.5709536	10.0073692
N	5.7662640	20.0780512	10.8244506
N	3.9369651	20.6379518	9.8618650
N	3.7835323	17.8993813	10.9668959
C	2.8836619	14.7590524	10.9199986
C	2.1428921	13.7754827	11.7480541
C	1.6184838	14.1960045	12.9686719

H	1.7622666	15.2207291	13.2837441
C	0.9186683	13.2996054	13.7681083
H	0.5134365	13.6314011	14.7157304
C	0.7414165	11.9844183	13.3513340
H	0.1964694	11.2864601	13.9743938
C	1.2659924	11.5658711	12.1313107
H	1.1298002	10.5427323	11.8042613
C	1.9652641	12.4584603	11.3302758
H	2.3743295	12.1366850	10.3812909
C	5.2397828	14.5439843	11.8988606
C	5.1824393	15.3224572	13.2242947
H	5.2400431	16.3947657	13.0445488
H	6.0092748	15.0266591	13.8738678
H	4.2460782	15.1221855	13.7460898
C	6.5710200	14.8231083	11.1859897
H	6.6429104	14.2347720	10.2694320
H	7.4065331	14.5600242	11.8369642
H	6.6567185	15.8722614	10.9088661
C	5.1456102	13.0369112	12.1779801
H	4.2962611	12.7831454	12.8085024
H	6.0519739	12.7151623	12.6944980
H	5.0670980	12.4737820	11.2462692
C	0.9678247	15.8260029	9.5965054
C	0.3117420	16.7958477	10.5944918
H	0.9027313	17.7045529	10.6966464
H	0.2361935	16.3362419	11.5807070
H	-0.6934338	17.0625910	10.2605583
C	0.1254131	14.5468002	9.4882230
H	-0.0930363	14.1092750	10.4599916
H	0.6330890	13.7986407	8.8768266
H	-0.8256436	14.7887369	9.0099584
C	1.0467381	16.4737066	8.2056771
H	0.0510827	16.7761881	7.8764312
H	1.4550785	15.7669048	7.4807737
H	1.6985357	17.3462336	8.2108827
C	4.9334296	21.0935736	10.6161084
C	5.0607194	22.4566933	11.1893922
C	5.7189369	23.4796136	10.5126671
H	6.1350788	23.2946629	9.5306334
C	5.8368639	24.7358241	11.0984626
H	6.3503736	25.5289314	10.5697100
C	5.2967923	24.9716278	12.3581035
H	5.3903547	25.9498345	12.8128297
C	4.6363778	23.9483970	13.0334749

H	4.2146992	24.1275305	14.0146009
C	4.5188982	22.6938068	12.4524257
H	4.0164115	21.8828726	12.9625309
C	7.1062386	20.0205435	11.4267453
C	7.1547187	20.6807398	12.8126097
H	8.1099287	20.4495321	13.2884500
H	6.3511488	20.2960796	13.4416111
H	7.0642796	21.7636647	12.7573498
C	8.1255674	20.6775605	10.4813949
H	7.9137737	21.7404950	10.3596012
H	8.0909166	20.2002292	9.5002774
H	9.1376108	20.5779054	10.8801028
C	7.4422732	18.5319491	11.5791857
H	7.3773512	18.0227536	10.6165226
H	6.7421232	18.0526549	12.2644648
H	8.4514879	18.4137336	11.9769252
C	2.6984110	21.2800577	9.3938801
C	1.8476411	21.7866714	10.5691306
H	1.7317311	20.9970407	11.3113990
H	0.8606654	22.0851463	10.2090491
H	2.3011414	22.6498956	11.0530151
C	1.9075474	20.1994966	8.6466826
H	2.5009158	19.7596470	7.8442969
H	0.9989807	20.6297808	8.2225979
H	1.6203606	19.3991893	9.3279880
C	3.0220571	22.4279555	8.4252034
H	3.5611825	23.2305187	8.9271485
H	2.0992404	22.8465979	8.0178149
H	3.6313995	22.0637477	7.5957421
C	4.5011048	17.2130532	6.2501723
H	3.5095496	17.1727665	5.8214790
C	5.1284095	16.0304352	6.7106369
H	4.5944453	15.0913357	6.6677550
C	6.4009729	16.0807318	7.3287739
H	6.8359338	15.1793227	7.7372829
C	7.0631964	17.3172564	7.4835595
H	8.0198365	17.3674525	7.9848614
C	6.4493049	18.4959447	6.9950098
H	6.9214868	19.4540974	7.1636515
C	5.1728687	18.4467611	6.3839506
H	4.6899862	19.3636396	6.0750775

Compound TS**2**

111

E= -4037,03353

Fe	5.1223520	17.5258050	9.3552989
Si	3.7872228	17.0733837	11.1232870
Si	4.5041266	19.4272478	10.1604310
Si	3.2753116	17.5431440	14.9234157
N	3.4327787	18.9948663	12.7355627
N	3.5422263	17.7800403	13.1887049
C	4.8377017	16.9403485	15.7770447
H	5.6705908	17.6164994	15.5686054
H	5.1364126	15.9379297	15.4713294
H	4.6826615	16.9239325	16.8598310
C	2.7458552	19.1623060	15.7086932
H	2.5333112	19.0206668	16.7721250
H	1.8489534	19.5566616	15.2274610
H	3.5290981	19.9167619	15.6127366
C	1.9014702	16.2702514	15.0819876
H	1.7258021	15.9916659	16.1243906
H	2.1476398	15.3658509	14.5253120
H	0.9702487	16.6696400	14.6731009
N	3.8269730	15.2119751	11.7985972
N	2.1026721	16.2160754	10.9920860
N	5.4905337	20.8473793	10.9504658
N	3.9413275	21.1016247	9.4852000
N	3.3797430	18.8949947	11.4352298
C	2.5894707	15.0281253	11.3779424
C	1.8931214	13.7183207	11.2558249
C	1.1689450	13.1819882	12.3183555
H	1.1048641	13.7269861	13.2507403
C	0.5144081	11.9647514	12.1761095
H	-0.0497442	11.5584807	13.0063039
C	0.5792376	11.2726283	10.9709402
H	0.0674007	10.3248879	10.8604074
C	1.3037092	11.8028656	9.9079407
H	1.3600666	11.2688881	8.9676129
C	1.9573882	13.0205138	10.0498162
H	2.5219843	13.4347769	9.2245928
C	4.8306212	14.2636583	12.3087386
C	4.3568863	13.5793264	13.6025048
H	4.0724971	14.3163044	14.3509695
H	5.1655568	12.9716026	14.0148568
H	3.5070905	12.9234983	13.4212552
C	6.0827110	15.0964901	12.6235355
H	6.4427708	15.6098205	11.7344427
H	6.8734519	14.4519244	13.0121047
H	5.8610850	15.8606360	13.3667142

C	5.1871095	13.1774148	11.2786672
H	4.3509394	12.5016022	11.1060493
H	6.0278204	12.5829544	11.6433763
H	5.4720420	13.6209587	10.3271839
C	0.8291922	16.5538662	10.3212205
C	0.4733852	17.9969221	10.7081366
H	1.2517246	18.6914352	10.4089761
H	0.3528996	18.0837692	11.7894775
H	-0.4617054	18.2895530	10.2267975
C	-0.3473799	15.6638958	10.7533970
H	-0.4251760	15.6217492	11.8410281
H	-0.2750208	14.6484002	10.3726308
H	-1.2707592	16.0964514	10.3637563
C	1.0221085	16.4632599	8.7980274
H	0.1218580	16.7940790	8.2743808
H	1.2320537	15.4344466	8.4994021
H	1.8645213	17.0845790	8.4939332
C	4.8592261	21.7485613	10.2089183
C	5.1397094	23.2056285	10.1647360
C	6.0240224	23.7200483	9.2184643
H	6.4972995	23.0527594	8.5096636
C	6.2878017	25.0834259	9.1811100
H	6.9767266	25.4777564	8.4447444
C	5.6660617	25.9395416	10.0848819
H	5.8708349	27.0022662	10.0540554
C	4.7813616	25.4271501	11.0287342
H	4.2970458	26.0893466	11.7352900
C	4.5198937	24.0633621	11.0713483
H	3.8433547	23.6588896	11.8131211
C	6.7756031	20.8945289	11.6709748
C	6.9405928	22.1713959	12.5062051
H	7.8238189	22.0691168	13.1397108
H	6.0736172	22.3227053	13.1514375
H	7.0732775	23.0590222	11.8903671
C	7.9263848	20.7649628	10.6588076
H	7.9380332	21.6154522	9.9744552
H	7.8098468	19.8488909	10.0782986
H	8.8881042	20.7315116	11.1756344
C	6.7807421	19.6809175	12.6125371
H	6.6301389	18.7569947	12.0504849
H	5.9792442	19.7655710	13.3470013
H	7.7357846	19.6204906	13.1376982
C	2.7471441	21.5886860	8.7764166
C	1.6627408	21.9496680	9.8064501

H	1.4672471	21.1038795	10.4661917
H	0.7328252	22.2258363	9.3043170
H	1.9814364	22.7950838	10.4183693
C	2.2597140	20.4290230	7.8964608
H	3.0117479	20.1711471	7.1495368
H	1.3393945	20.7127831	7.3831429
H	2.0637121	19.5352579	8.4873491
C	3.0391237	22.7951692	7.8716462
H	3.2755264	23.6924672	8.4397212
H	2.1578359	23.0079303	7.2632352
H	3.8734871	22.5808979	7.2014356
C	4.6248718	16.6472620	7.5254912
H	3.6604276	16.4830349	7.0669172
C	5.1937073	15.6686419	8.3741041
H	4.6410083	14.7669815	8.5971854
C	6.4375087	15.9025329	9.0029284
H	6.8395747	15.1709732	9.6871460
C	7.1227696	17.1204465	8.8054938
H	8.0551165	17.3123685	9.3184152
C	6.5749062	18.0818118	7.9264130
H	7.0644573	19.0375274	7.7989649
C	5.3341542	17.8450724	7.2909839
H	4.8888873	18.6223596	6.6859587

Compound Int**2**

111

E= -4037,03454

Fe	5.1437542	17.5423524	9.4868143
Si	3.8090572	17.0877811	11.3008491
Si	4.5042304	19.4700644	10.2050655
Si	3.3550789	17.4069500	14.8893492
N	3.5407877	19.0165274	12.7993458
N	3.6502196	17.7498117	13.1738540
C	4.8825981	16.7582324	15.7708335
H	5.7426109	17.3996722	15.5644889
H	5.1501726	15.7390443	15.4964839
H	4.7060789	16.7738684	16.8503179
C	2.8330767	19.0008387	15.7277721
H	2.5902629	18.8118826	16.7773441
H	1.9561158	19.4331794	15.2430998
H	3.6307995	19.7446698	15.6885481
C	1.9529542	16.1596796	14.9640157
H	1.7717676	15.8180109	15.9864869
H	2.1768757	15.2908110	14.3469025
H	1.0322766	16.6092771	14.5850904

N	3.8187419	15.1704415	11.9015690
N	2.1260996	16.2374831	11.0962202
N	5.4846561	20.9287138	10.9351463
N	3.9140518	21.1174298	9.4826275
N	3.4025001	18.9622733	11.5104766
C	2.5926739	15.0264462	11.4351174
C	1.8865981	13.7333556	11.2163177
C	1.1680179	13.1164903	12.2379477
H	1.1096723	13.5862926	13.2106467
C	0.5075897	11.9163489	12.0049622
H	-0.0530422	11.4483637	12.8044391
C	0.5619615	11.3206104	10.7491376
H	0.0463943	10.3858730	10.5681934
C	1.2809325	11.9310534	9.7261267
H	1.3297645	11.4724254	8.7464799
C	1.9386691	13.1321144	9.9585574
H	2.4985142	13.6077926	9.1641777
C	4.8004747	14.1673217	12.3520110
C	4.3239764	13.4412136	13.6227529
H	4.0715858	14.1499069	14.4088259
H	5.1189794	12.7912152	13.9952388
H	3.4525040	12.8197724	13.4243423
C	6.0816938	14.9473080	12.6841516
H	6.4443982	15.4898014	11.8144399
H	6.8587690	14.2637616	13.0312959
H	5.8962304	15.6831350	13.4636786
C	5.1161451	13.1102451	11.2786932
H	4.2636937	12.4591984	11.0933782
H	5.9465821	12.4845006	11.6129343
H	5.4017842	13.5770117	10.3391891
C	0.8490690	16.6189736	10.4539594
C	0.4992648	18.0401989	10.9211066
H	1.2737313	18.7512229	10.6526595
H	0.3887764	18.0679347	12.0068139
H	-0.4412566	18.3575181	10.4670078
C	-0.3317386	15.7152445	10.8466373
H	-0.4007670	15.6131031	11.9308725
H	-0.2730069	14.7223562	10.4091611
H	-1.2543483	16.1770086	10.4902969
C	1.0308157	16.6081323	8.9268732
H	0.1392114	16.9958771	8.4281597
H	1.2058751	15.5917328	8.5699360
H	1.8921877	17.2165868	8.6522319
C	4.8379112	21.7968942	10.1690852

C	5.1114123	23.2523315	10.0627523
C	5.9923373	23.7285564	9.0933561
H	6.4656554	23.0331039	8.4123042
C	6.2523338	25.0896529	8.9970841
H	6.9384447	25.4538101	8.2428321
C	5.6305673	25.9820514	9.8650021
H	5.8324314	27.0429556	9.7883707
C	4.7496650	25.5080458	10.8320301
H	4.2656160	26.1983703	11.5112355
C	4.4918400	24.1466646	10.9333173
H	3.8191691	23.7730584	11.6944149
C	6.7710446	21.0155563	11.6501371
C	6.9226556	22.3226562	12.4398676
H	7.8069083	22.2518956	13.0761264
H	6.0544959	22.4872746	13.0800346
H	7.0460157	23.1894094	11.7932403
C	7.9220716	20.8641130	10.6416542
H	7.9206716	21.6870430	9.9245720
H	7.8193449	19.9242522	10.0983050
H	8.8844089	20.8655001	11.1583027
C	6.7926485	19.8357288	12.6333555
H	6.6478367	18.8914465	12.1041563
H	5.9948006	19.9387963	13.3691200
H	7.7516342	19.8021999	13.1536746
C	2.7197620	21.5761666	8.7553299
C	1.6495338	22.0223295	9.7665507
H	1.4454523	21.2241614	10.4810072
H	0.7202121	22.2786285	9.2530162
H	1.9840256	22.9015359	10.3189658
C	2.2022689	20.3693731	7.9611894
H	2.9466930	20.0342790	7.2380657
H	1.2907273	20.6397220	7.4257213
H	1.9781525	19.5300483	8.6172889
C	3.0236363	22.7142755	7.7692895
H	3.2824832	23.6423552	8.2744688
H	2.1405702	22.9035101	7.1557720
H	3.8470259	22.4396427	7.1076668
C	4.6278758	16.6717215	7.6612236
H	3.6610385	16.5317782	7.1998344
C	5.1729283	15.6803496	8.5089858
H	4.6002166	14.7914194	8.7303852
C	6.4235376	15.8821318	9.1354932
H	6.8073180	15.1383790	9.8162173
C	7.1400354	17.0823873	8.9423974

H	8.0790245	17.2476411	9.4523992
C	6.6175445	18.0557550	8.0619716
H	7.1320943	18.9974247	7.9292586
C	5.3715664	17.8492401	7.4264110
H	4.9472123	18.6389346	6.8223070

Compound TS**3**

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E= -4037,02559

Fe	4.9930235	17.6909309	9.6815038
Si	3.7546262	17.0574926	11.4564102
Si	4.3711768	19.5639999	10.5255827
Si	3.2121701	17.1365752	14.9027955
N	3.4368720	19.0206972	13.0931139
N	3.5065662	17.6908752	13.2338157
C	4.7800315	16.5862501	15.7805115
H	5.5554760	17.3486442	15.6729679
H	5.1853250	15.6426320	15.4194496
H	4.5725637	16.4700233	16.8484004
C	2.4931108	18.5727674	15.8693316
H	2.2221476	18.2416524	16.8763430
H	1.5980553	18.9656886	15.3836611
H	3.2073204	19.3924331	15.9540175
C	1.9366540	15.7602895	14.8541709
H	1.7182009	15.4082664	15.8660708
H	2.2772501	14.9128348	14.2650242
H	1.0068116	16.1269625	14.4141068
N	3.8235302	15.1655727	11.9512211
N	2.0787068	16.1852759	11.2106059
N	5.4821513	21.0335090	11.0216157
N	3.8191069	21.1666216	9.6715737
N	3.2953729	19.3073729	11.8631711
C	2.5952300	14.9852112	11.4712454
C	1.9569305	13.6806514	11.1455126
C	1.3234028	12.9091149	12.1164997
H	1.2817925	13.2601338	13.1385446
C	0.7197466	11.7057928	11.7708326
H	0.2235441	11.1167810	12.5319115
C	0.7474580	11.2622129	10.4530506
H	0.2772242	10.3244255	10.1853097
C	1.3791018	12.0298654	9.4791015
H	1.4045936	11.6913464	8.4509462
C	1.9772656	13.2346302	9.8232265
H	2.4655884	13.8354119	9.0673751

C	4.8741051	14.1779177	12.2757616
C	4.4935616	13.3417601	13.5104525
H	4.2738853	13.9763626	14.3663001
H	5.3252810	12.6870999	13.7799924
H	3.6271029	12.7125206	13.3137343
C	6.1375421	14.9878177	12.6023284
H	6.4348958	15.6059666	11.7585417
H	6.9566456	14.3146523	12.8616458
H	5.9638804	15.6559841	13.4437288
C	5.1757846	13.2126077	11.1157952
H	4.3480507	12.5293134	10.9351116
H	6.0548304	12.6121983	11.3595147
H	5.3804298	13.7534441	10.1959377
C	0.7593281	16.5903072	10.6890026
C	0.3982406	17.9187003	11.3721884
H	1.1755463	18.6646442	11.2253091
H	0.2808297	17.7722711	12.4477173
H	-0.5420959	18.3019141	10.9712863
C	-0.3643343	15.5906740	11.0027640
H	-0.3834340	15.3439393	12.0654544
H	-0.2825164	14.6668306	10.4356248
H	-1.3189669	16.0534614	10.7458437
C	0.8704916	16.7946023	9.1696243
H	-0.0570684	17.2077109	8.7665249
H	1.0666138	15.8431252	8.6717235
H	1.6934758	17.4712851	8.9460174
C	4.8447340	21.8466245	10.1926086
C	5.2370013	23.2446572	9.8719585
C	6.1692943	23.4906494	8.8648772
H	6.5757124	22.6623955	8.2989241
C	6.5676668	24.7917502	8.5837981
H	7.2913164	24.9744660	7.7994414
C	6.0381079	25.8550792	9.3079012
H	6.3499984	26.8687293	9.0901308
C	5.1076604	25.6123355	10.3134941
H	4.6950672	26.4359451	10.8824181
C	4.7084256	24.3120448	10.5956116
H	3.9965103	24.1193939	11.3875900
C	6.7426318	21.1488028	11.7692671
C	6.9155666	22.5210056	12.4350220
H	7.7753427	22.4860281	13.1069299
H	6.0328365	22.7762458	13.0236751
H	7.0909773	23.3145388	11.7109322
C	7.9271261	20.8609274	10.8318138

H	7.9861689	21.6085981	10.0392478
H	7.8110387	19.8764062	10.3790303
H	8.8671812	20.8810246	11.3878630
C	6.6841998	20.0689849	12.8620258
H	6.5444775	19.0814161	12.4168892
H	5.8519633	20.2551391	13.5419103
H	7.6139949	20.0652466	13.4338908
C	2.7428263	21.5897957	8.7628750
C	1.8577449	22.6565489	9.4288327
H	1.5105747	22.3022310	10.4007038
H	0.9865700	22.8651025	8.8037091
H	2.3983013	23.5913198	9.5700400
C	1.8892368	20.3453857	8.4883718
H	2.4900416	19.5477468	8.0527270
H	1.0795535	20.5931177	7.8000295
H	1.4495013	19.9673452	9.4108109
C	3.2984168	22.1164354	7.4295644
H	3.8536938	23.0434981	7.5610154
H	2.4779149	22.3125761	6.7361002
H	3.9613980	21.3779333	6.9750999
C	4.4348927	16.9658330	7.8034521
H	3.4556106	16.8265296	7.3683362
C	5.0569820	15.9222215	8.5278919
H	4.5291193	14.9921529	8.6817065
C	6.3243576	16.1128746	9.1207746
H	6.7697575	15.3204758	9.7023562
C	6.9819070	17.3565937	9.0210586
H	7.9364345	17.5115885	9.5046800
C	6.3827173	18.3871957	8.2625296
H	6.8518904	19.3598379	8.2075213
C	5.1203451	18.1903044	7.6550595
H	4.6469781	19.0128658	7.1375566

Compound **5**

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E= -3927,6511

Fe	12.6087723	7.6362958	1.6459379
Si	11.6348270	7.0049179	3.4865382
Si	13.6951047	8.2621142	3.4220609
Si	12.7054092	7.7193873	6.4682643
N	15.5362652	8.1222526	3.9087926
N	9.8222077	7.1564502	4.0584340
N	10.9291894	5.3196372	4.0328158
N	14.4095653	9.9520347	3.9538068

N	12.7020522	7.6323633	4.7532898
C	8.4617608	5.0641414	4.4156757
C	7.7210307	4.5618344	3.3475912
H	8.0441063	4.7558672	2.3333645
C	9.7121956	5.8342597	4.1796118
C	8.0392669	4.8172697	5.7216203
H	8.6196786	5.1997638	6.5509249
C	8.7819937	8.1978760	3.9865755
C	13.9894304	11.3503984	3.7328298
C	15.6365913	9.4391896	4.0566213
C	11.3757695	3.9230176	3.8923997
C	6.5697845	3.8190714	3.5828719
H	6.0001705	3.4329180	2.7470074
C	6.1522636	3.5733450	4.8864561
H	5.2565789	2.9931957	5.0692412
C	6.8892717	4.0748941	5.9550831
H	6.5698719	3.8858302	6.9722032
C	12.8976153	3.9537953	4.0620186
H	13.3407240	4.6092392	3.3142909
H	13.3139561	2.9523319	3.9418878
H	13.1694598	4.3293390	5.0491790
C	9.5240700	9.5296988	3.8467075
H	10.1692388	9.7007291	4.7069737
H	8.8116537	10.3533280	3.7780796
H	10.1495871	9.5233041	2.9539787
C	16.5804406	7.0924591	3.7508785
C	15.8533975	5.7452045	3.7712924
H	15.3290078	5.6024243	4.7151970
H	16.5663726	4.9295153	3.6407194
H	15.1200928	5.7056385	2.9656306
C	16.8858060	10.2014470	4.3224084
C	17.2470135	10.4541026	5.6463620
H	16.6148772	10.0951058	6.4484122
C	18.4076255	11.1594096	5.9324523
H	18.6805322	11.3492891	6.9628002
C	19.2168578	11.6207535	4.8980988
H	20.1219737	12.1714537	5.1210857
C	18.8593542	11.3723931	3.5776530
H	19.4841214	11.7293386	2.7686351
C	17.6978537	10.6639932	3.2897702
H	17.4222393	10.4718460	2.2616542
C	10.7727034	2.9914794	4.9538268
H	10.9157668	3.3998904	5.9552814
H	11.2762131	2.0239419	4.9050280

H	9.7093784	2.8200565	4.8007692
C	11.0396309	3.4087635	2.4819726
H	9.9614079	3.3376589	2.3385725
H	11.4666170	2.4153199	2.3263427
H	11.4490519	4.0873211	1.7332926
C	12.4585315	11.3469392	3.7664692
H	12.0695736	10.6578711	3.0168920
H	12.0759042	12.3477631	3.5592231
H	12.0941524	11.0332062	4.7428348
C	7.8882894	7.9979961	2.7509686
H	8.5048752	7.9196793	1.8541923
H	7.2136699	8.8488546	2.6334061
H	7.2797871	7.0990765	2.8376167
C	14.4494160	11.8239421	2.3425507
H	15.5354699	11.8904571	2.2865970
H	14.0416640	12.8136738	2.1250583
H	14.0996891	11.1282857	1.5789777
C	7.9308167	8.2328411	5.2647336
H	7.3216693	7.3376213	5.3740356
H	7.2592974	9.0934488	5.2351502
H	8.5696137	8.3284945	6.1446159
C	11.4673457	6.4986672	7.1943099
H	10.4575006	6.7359540	6.8534812
H	11.4760482	6.5452963	8.2864926
H	11.6908812	5.4740975	6.8934677
C	14.5143278	12.3011519	4.8184453
H	14.2673298	11.9253333	5.8126408
H	14.0437067	13.2791239	4.6984989
H	15.5918526	12.4411052	4.7603473
C	12.6901186	6.2385696	0.0743398
H	12.7958726	5.1625609	0.0822202
C	11.4044665	6.8316070	0.1304015
H	10.5322714	6.2007290	0.2388828
C	13.8319304	7.0654384	0.0300590
H	14.8202797	6.6271107	0.0141815
C	11.2525789	8.2400983	0.1603613
H	10.2671088	8.6769655	0.2474314
C	13.6800337	8.4737352	0.0494031
H	14.5599670	9.1015127	0.0941554
C	12.3951817	9.0670122	0.1237092
H	12.2929862	10.1425853	0.1721426
C	17.2741571	7.2562950	2.3869252
H	16.5285379	7.2833709	1.5915828
H	17.9494249	6.4176480	2.2030913

H	17.8617819	8.1727524	2.3495639
C	17.6192019	7.1222016	4.8815286
H	18.2334571	8.0200131	4.8535051
H	18.2835551	6.2614980	4.7802838
H	17.1316109	7.0635898	5.8549413
C	14.4145182	7.3362172	7.1654150
H	14.7350982	6.3232103	6.9120316
H	14.4227560	7.4299683	8.2549606
H	15.1564051	8.0269146	6.7604424
C	12.2406517	9.4318474	7.1122475
H	12.9540370	10.1838528	6.7694316
H	12.2389762	9.4473150	8.2061218
H	11.2468251	9.7346047	6.7743653

N_2

2

E= -109,53461

N	0.0000000	0.0000000	0.9805221
N	0.0000000	0.0000000	-0.1105221

SM	-3463,66282	
azide	-573,33931	
combined	-4037,00213	0,0000
FeSi2TS1	-4036,97761	15,3865
FeSi2TMSN3-1	-4037,07239	-59,4754
FeSi2TMSN3-TS2-1	-4037,03353	24,3850
4_ring	-4037,03454	-0,6338
4_ring-TS3	-4037,02559	5,6162
FeSi2NTMS	-3927,6511	
N2	-109,53461	
FeSi2NTMS+N2	-4037,18571	-94,8607

Single crystal X-ray data diffraction

Table S1. X-ray data of {PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (**2**). CCDC 2157512.

	{PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (2)
chemical formula	$C_{36}H_{52}Cl_2FeN_4Si_2$
fw	723.74
***T* (K)**	300
***λ* (Å)**	1.54178
***a* (Å)**	9.7347(7)
***b* (Å)**	13.6577(8)
***c* (Å)**	18.8704(11)
***α* (°)**	99.845(4)
***β* (°)**	92.800(5)
***γ* (°)**	101.432(5)
***V* (Å^3)**	2413.99
space group	*P* -1
Z*, *Z'	2, 1
D$_{calc}$ (g/cm^3)	0.996
***μ* (mm^{-1})**	4.174
R1 (I > 2σ(I)), wR2[a]	0.0840, 0.2672

[a] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, wR2 = $(\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])c^{1/2}$

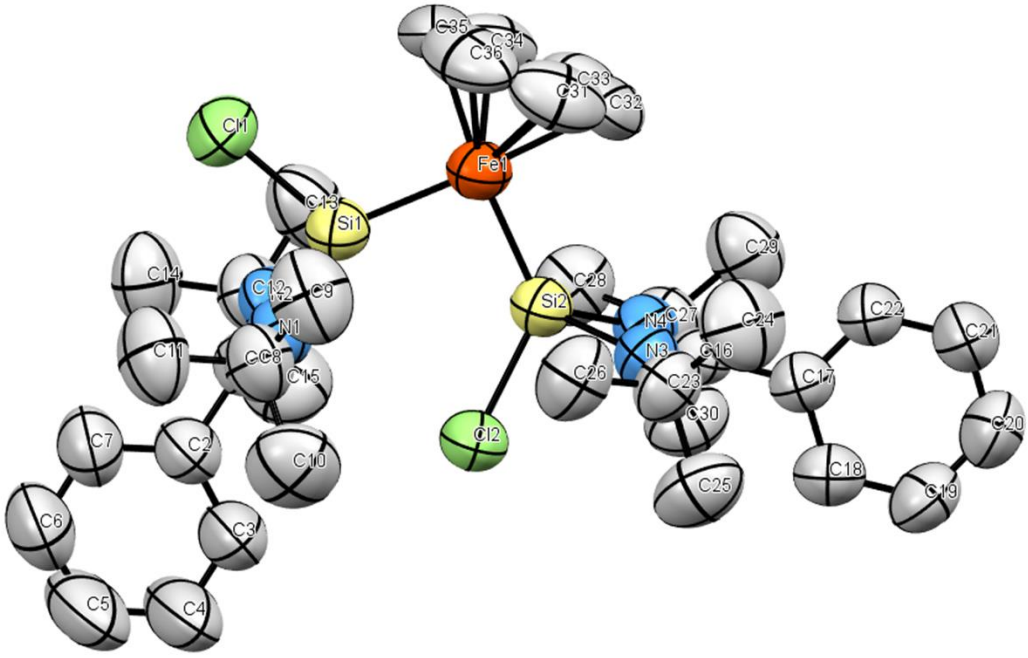

Figure S35. The full numbering scheme of {PhC(N^{t}Bu)$_2$SiCl}$_2$Fe(C$_6$H$_6$) (**2**). All atoms shown are depicted with 50% thermal contours. The hydrogen atoms have been removed for clarity.

Table S2. X-ray data of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$) (**3**). CCDC 2157514.

	{PhC(N^{t}Bu)$_2$Si}$_2$Fe((C$_6$H$_6$) (3)
chemical formula	$C_{36}H_{52}FeN_4Si_2$
fw	652.86
***T* (K)**	150
***λ* (Å)**	1.34138
***a* (Å)**	21.1980(9)
***b* (Å)**	10.2965(5)
***c* (Å)**	15.8356(6)
***α* (°)**	90
***β* (°)**	91.273(2)
***γ* (°)**	90
***V* (Å^3)**	3455.51
space group	*C 2/c*
Z*, *Z'	4, 0.5
D$_{calc}$ (g/cm^3)	1.255
***μ* (mm^{-1})**	2.995
R1 (I > 2σ(I)), wR2[a]	0.0418, 0.1035

[a] R1 = Σ||F_o| - |F_c||/Σ|F_o|, wR2 = (Σ[w(F_o^2 - F_c^2)^2]/Σ[w(F_o^2)^2])c$^{1/2}$

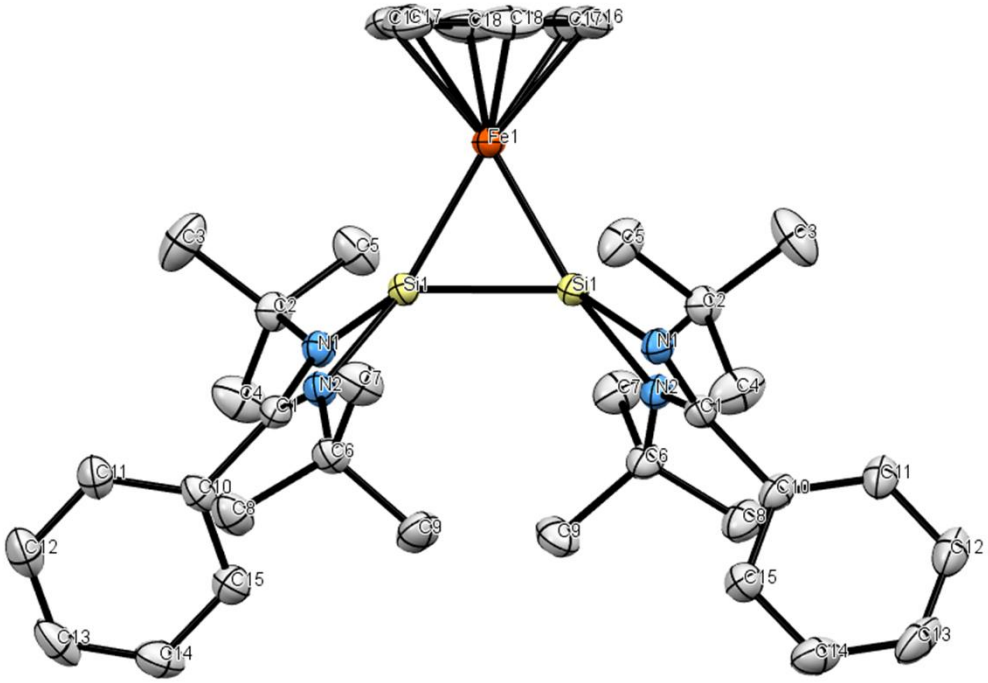

Figure S36. The full numbering scheme of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$) (**3**). All atoms shown are depicted with 50% thermal contours. The hydrogen atoms have been removed for clarity.

Table S3. X-ray data of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(N$_3$SiMe$_3$) (**4**). CCDC 2157515.

	{PhC(N^{t}Bu)$_2$Si}$_2$Fe((C$_6$H$_6$)(N$_3$SiMe$_3$) (4)
chemical formula	$C_{39}H_{61}FeN_7Si_3$
fw	768.06
***T* (K)**	150
***λ* (Å)**	1.34138
***a* (Å)**	9.8807(8)
***b* (Å)**	28.708(2)
***c* (Å)**	14.9418(13)
***α* (°)**	90
***β* (°)**	92.442(5)
***γ* (°)**	90
***V* (Å^3)**	4234.47
space group	*P* $2_1/n$
Z*, *Z'	4, 1
D_{calc} (g/cm^3)	1.205
***μ* (mm^{-1})**	2.676
R1 (I > 2σ(I)), wR2[a]	0.0515, 0.1454

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])c^{1/2}$

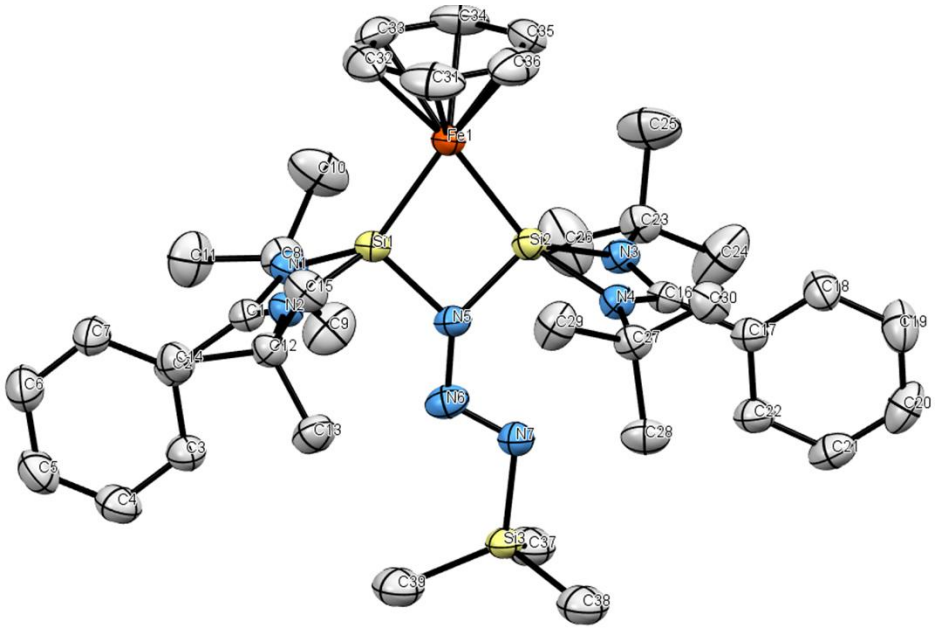

Figure S37. The full numbering scheme of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(N$_3$SiMe$_3$) (**4**). All atoms shown are depicted with 50% thermal contours. The hydrogen atoms have been removed for clarity.

Table S4. X-ray data of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(NSiMe$_3$) (**5**). CCDC 2157513.

	{PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(NSiMe$_3$) (5)
chemical formula	$C_{39}H_{61}FeN_5Si_3$
fw	740.05
***T* (K)**	150
***λ* (Å)**	1.34138
***a* (Å)**	13.2544(10)
***b* (Å)**	13.2778(10)
***c* (Å)**	16.7537(13)
***α* (°)**	76.065(3)
***β* (°)**	89.450(3)
***γ* (°)**	62.243(2)
***V* (Å^3)**	2514.29
space group	*P* -1
Z, Z'	2, 1
D_{calc} (g/cm^3)	0.978
***μ* (mm^{-1})**	2.187
R1 (I > 2σ(I)), wR2[a]	0.0833, 0.2473

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])c^{1/2}$

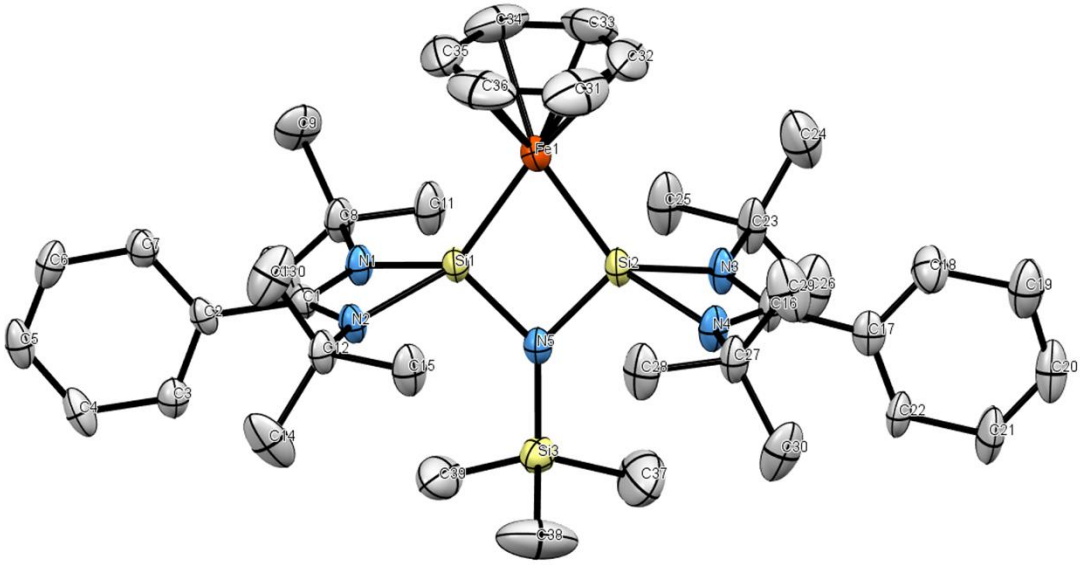

Figure S38. The full numbering scheme of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(NSiMe$_3$) (**5**). All atoms shown are depicted with 50% thermal contours. The hydrogen atoms have been removed for clarity.

Table S5. X-ray data of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$))(Ph$_2$O) (**6**). CCDC 2157516.

	{PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(Ph$_2$O) (6)
chemical formula	$C_{49}H_{62}FeN_4OSi_2$
fw	835.05
***T* (K)**	150
***λ* (Å)**	1.34138
***a* (Å)**	13.0002(10)
***b* (Å)**	13.7708(9)
***c* (Å)**	14.3396(11)
***α* (°)**	86.224(3)
***β* (°)**	68.025(3)
***γ* (°)**	70.234(3)
***V* (Å^3)**	2234.93
space group	*P* -1
Z, Z'	2, 1
D$_{calc}$ (g/cm^3)	1.241
***μ* (mm^{-1})**	2.347
R1 (I > 2σ(I)), wR2[a]	0.0537, 0.1579

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])c^{1/2}$

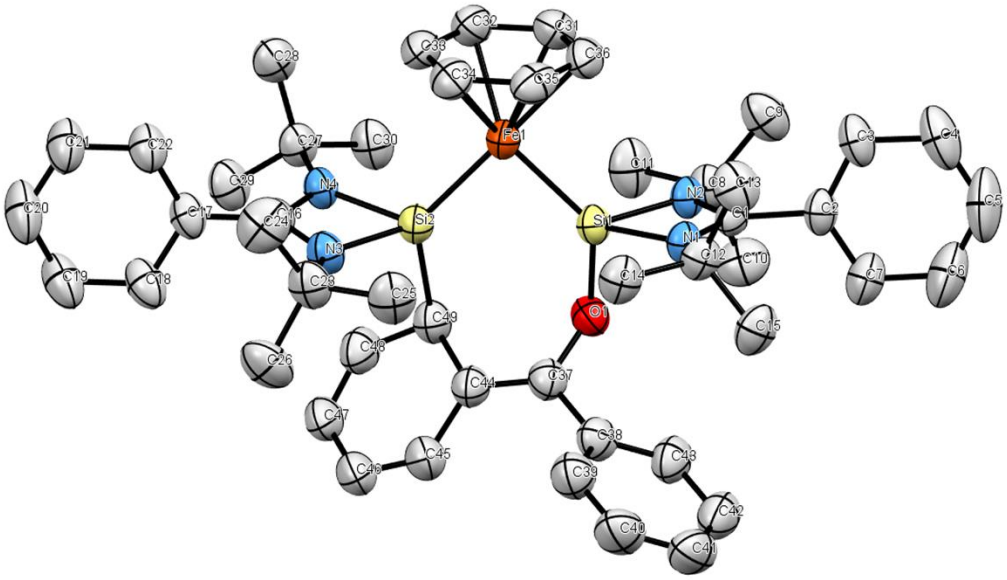

Figure S39. The full numbering scheme of {PhC(N^{t}Bu)$_2$Si}$_2$Fe(C$_6$H$_6$)(Ph$_2$O) (**6**). All atoms shown are depicted with 50% thermal contours. The hydrogen atoms have been removed for clarity.

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