**Electronic Supplementary Information**

*for*

# Reduction of 2-*H*-substituted pyrrolinium cations: the carbon-carbon single bond in air stable 2,2'-bipyrrolidines as a two-electron-source

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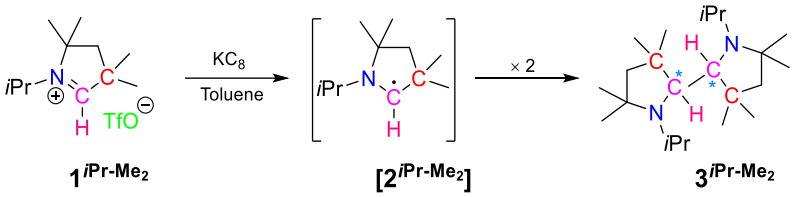
**General Considerations**

All experiments (unless otherwise stated) were carried out under an $N_2$ atmosphere using standard Schlenk techniques or in a PL-HE-2GB Innovative Technology GloveBox. Hexane, pentane, diethyl ether, THF, and toluene were dried with a PS-MD-5 Innovative Technology solvent purification system or common drying solvent technique. Compounds $\mathbf{1}^{i\text{Pr-Me}_2}$,[S1] $\mathbf{1}^{t\text{Bu-Me}_2}$,[S2] $KC_8$,[S3] **16**,[S4] **5**,[S5] **6**,[S6] **7**,[S7] $\mathbf{1}^{\text{Dip-Me}_2}$,[S8] and $\mathbf{1}^{\text{Dip-(CH}_2)_5}$,[S8] were prepared according to the literature procedures. Compound $\mathbf{1}^{\text{Dip-Et}_2}$ was prepared based on similar procedure as $\mathbf{1}^{\text{Dip-Me}_2}$ and $\mathbf{1}^{\text{Dip-(CH}_2)_5}$.[S8] Benzene-$d_6$ was dried and distilled over potassium under argon. Chloroform-$d_1$ and acetonitrile-$d_3$ were dried and distilled over $CaH_2$ under argon. NMR spectra were recorded on a BrukerNanoBay 300 MHz NMR spectrometer. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were referenced to the peaks of residual protons of the deuterated solvent ($^1H$) or the deuterated solvent itself ($^{13}C$). $^{19}F\{^1H\}$ NMR spectra were referenced to external tol-$CF_3$.

Elemental analyses were performed on a Perkin Elmer Analyser 240. HRMS of $\mathbf{3}^{i\text{Pr-Me}_2}$, $\mathbf{3}^{t\text{Bu-Me}_2}$, $\mathbf{3}^{\text{Dip-Me}_2}$, $\mathbf{3}^{\text{Dip-Et}_2}$, and $\mathbf{3}^{\text{Dip-(CH}_2)_5}$ were performed on a Waters Xevo G2-XS QTOF (Waters Corporation) using electrospray ionisation (ESI). Melting points were determined in closed NMR tubes under nitrogen atmosphere and are uncorrected. Cyclic voltammograms were recorded in 0.1 M $NBu_4PF_6/CH_3CN$ solutions using a three-electrode configuration (glassy carbon working, Pt wire counter electrodes, and Ag reference) with a Metrohm Autolab potentiostat. The ferrocene/ferrocenium ($Fc/Fc^+$) couple served as internal reference.

**Experimental Details and Analytical Data**

**Synthesis of $3^{iPr\text{-}Me_2}$**




$1^{iPr\text{-}Me_2}$ $[2^{iPr\text{-}Me_2}]$ $3^{iPr\text{-}Me_2}$

About 60 mL of toluene was added to the mixture of $\mathbf{1}^{iPr\text{-}Me_2}$ (2.00 g, 6.30 mmol) and $KC_8$ (1.28 g, 9.45 mmol) at room temperature and stirred for 12 hours. After that, the reaction mixture was filtered and all volatiles including solvent were removed under vacuum resulting in pure $\mathbf{3}^{iPr\text{-}Me_2}$. **Yield:** 965 mg (91 %). Subsequently, the two diastereomers (*meso*- and *d*/*l*-) were separated with silica gel column chromatography. First *meso*-$\mathbf{3}^{iPr\text{-}Me_2}$ (370 mg) was moved through the column with pure pentane as eluent. Then, using pure diethyl ether as an eluent two rotational isomers of *d*/*l*-$\mathbf{3}^{iPr\text{-}Me_2}$ (140 mg) were obtained in an approximate ratio of 1:0.17. $\mathbf{3}^{iPr\text{-}Me_2}$ is a colourless amorphous solid. **M. P.:** 67 °C.

**$^1$H NMR** of *meso*-$\mathbf{3}^{iPr\text{-}Me_2}$ ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 4.09 (br, 1H, *H*C($CH_3$)$_2$), 3.37 (br, 1H, C*H*), 3.18 (br, 1H, *H*C($CH_3$)$_2$), 3.09 (br, 1H, C*H*), 2.00 (br, 1H, C$H_2$), 1.60 (br, 3H, C$H_3$), 1.33 (br, 3H, C$H_2$), 1.31 (br, 3H, C$H_3$), 1.20 (d, 12H, $^3J_{H\text{-}H}$ = 6.4 Hz, HC(C$H_3$)$_2$), 1.06–1.27 (br, 18H, C$H_3$) ppm. **$^{13}$C{$^1$H} NMR** of *meso*-$\mathbf{3}^{iPr\text{-}Me_2}$ ($C_6D_6$, 25 °C, 75.4 MHz): $\delta$ = 74.9 (*C*H), 69.1 (*C*H), 60.2 (*C*($CH_3$)$_2$), 59.2 (*C*$H_2$), 58.9 (*C*$H_2$), 48.2 (H*C*($CH_3$)$_2$), 46.7 (H*C*($CH_3$)$_2$), 39.3 (C(*C*$H_3$)$_2$), 38.6 (C(*C*$H_3$)$_2$), 34.1 (*C*$H_3$), 33.2 (*C*$H_3$), 32.5 (*C*$H_3$), 30.6 (*C*$H_3$), 28.4 (*C*$H_3$), 27.5 (*C*$H_3$), 24.5 (*C*$H_3$), 23.3 (*C*$H_3$), 21.8 (*C*$H_3$), 19.1 (*C*$H_3$) ppm.

**$^1$H NMR** of major rotational-isomers of *d*/*l*-$\mathbf{3}^{iPr\text{-}Me_2}$ ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 4.18 (sept, 2H, $^3J_{H\text{-}H}$ = 7.0 Hz, *H*C($CH_3$)$_2$), 3.01 (s, 2H, C*H*), 1.43–1.60 (m, 4H, C$H_2$), 1.38 (d, 6H, $^3J_{H\text{-}H}$ = 7.2 Hz, HC(C$H_3$)$_2$), 1.31 (s, 6H, C$H_3$), 1.26 (s, 6H, C$H_3$), 1.17 (d, 6H, $^3J_{H\text{-}H}$ = 7.0 Hz, HC(C$H_3$)$_2$), 1.07 (s, 6H, C$H_3$), 1.04 (s, 6H, C$H_3$) ppm. **$^{13}$C{$^1$H} NMR** of major rotational-isomers of *d*/*l*-$\mathbf{3}^{iPr\text{-}Me_2}$ ($C_6D_6$, 25 °C, 75.4 MHz): $\delta$ = 69.4 (*C*H), 60.2 (*C*($CH_3$)$_2$), 59.6 (*C*$H_2$), 48.8 (H*C*($CH_3$)$_2$), 39.3 (*C*($CH_3$)$_2$), 34.4 (C(*C*$H_3$)$_2$), 31.2 (C(*C*$H_3$)$_2$), 30.8 (C(*C*$H_3$)$_2$), 27.0 (C(*C*$H_3$)$_2$), 24.3 (HC(*C*$H_3$)$_2$), 19.7 (HC(*C*$H_3$)$_2$) ppm.

**$^1$H NMR** of minor rotational-isomers of *d*/*l*-$\mathbf{3}^{iPr\text{-}Me_2}$ ($C_6D_6$, 25 °C, 300 MHz): (Some peaks overlapped with the major isomers indicated by integrations of peaks): $\delta$ = 3.36 (s, 2H, C*H*), 3.17 (sept, 2H, $^3J_{H\text{-}H}$ = 7.0 Hz, *H*C($CH_3$)$_2$), 2.02 (d, 2H, $^2J_{H\text{-}H}$ = 12.7 Hz, C$H_2$), 1.38 (d, $^3J_{H\text{-}H}$ = 6H, 7.2 Hz, HC(C$H_3$)$_2$), 1.31 (s, 6H, C$H_3$), 1.24 (s, 2H, C$H_2$), 1.21 (s, 6H, C$H_3$), 1.20 (d, 6H, $^3J_{H\text{-}H}$ = 7.0 Hz, HC(C$H_3$)$_2$), 1.18 (s, 6H, C$H_3$), 1.15 (s, 6H, C$H_3$) ppm. **$^{13}$C{$^1$H} NMR** of minor rotational-isomers of *d*/*l*-$\mathbf{3}^{iPr\text{-}Me_2}$ ($C_6D_6$, 25 °C, 75.4 MHz): $\delta$ = 70.5 (*C*H), 60.7 (*C*($CH_3$)$_2$), 57.3 (*C*$H_2$), 46.3 (H*C*($CH_3$)$_2$), 38.5 (*C*($CH_3$)$_2$), 36.5 (C(*C*$H_3$)$_2$), 31.3 (C(*C*$H_3$)$_2$), 28.2 (C(*C*$H_3$)$_2$), 28.1 (C(*C*$H_3$)$_2$), 25.7 (HC(*C*$H_3$)$_2$), 21.0 (HC(*C*$H_3$)$_2$) ppm.

**Elemental analysis:** calcd. (%) for $C_{22}H_{44}N_2$: C, 78.50; H, 13.18; N, 8.32; found: C, 78.45; H, 13.43; N, 8.16. **HRMS-ESI (m/z):** Calculated for $C_{22}H_{45}N_2$ $[M+H]^+$: 337.3578, Found: 337.3587.

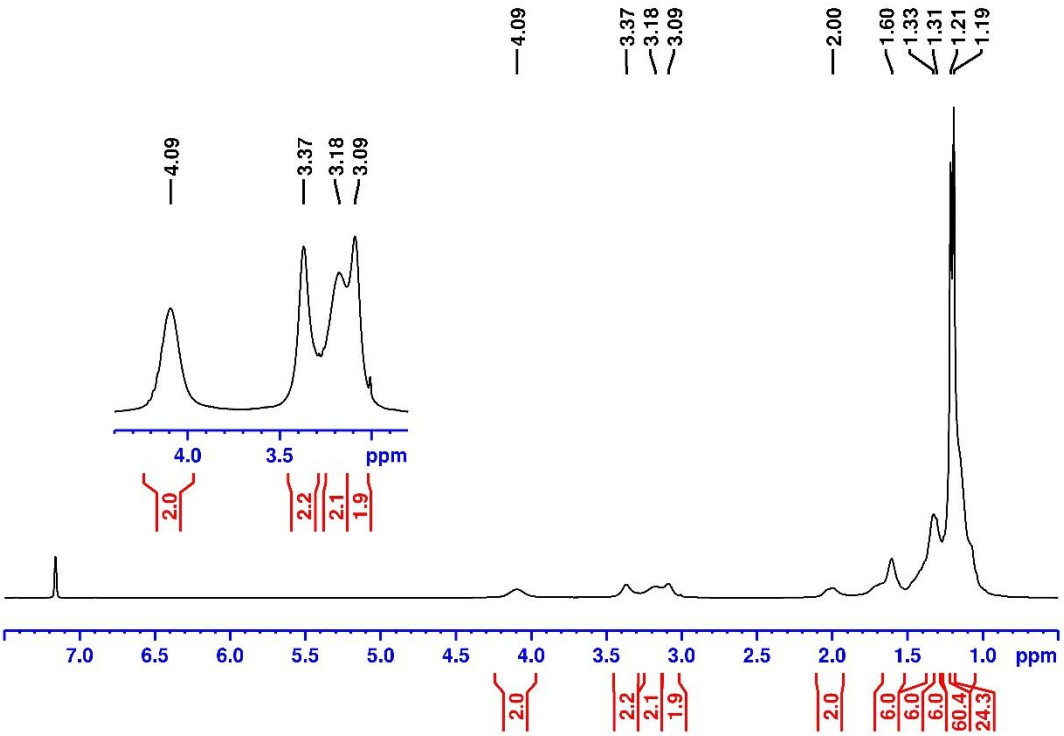



**Fig. S1** $^{1}$H NMR spectrum of *meso*-**3**$^{i\text{Pr-Me}_2}$ in $C_6D_6$ at room temperature.

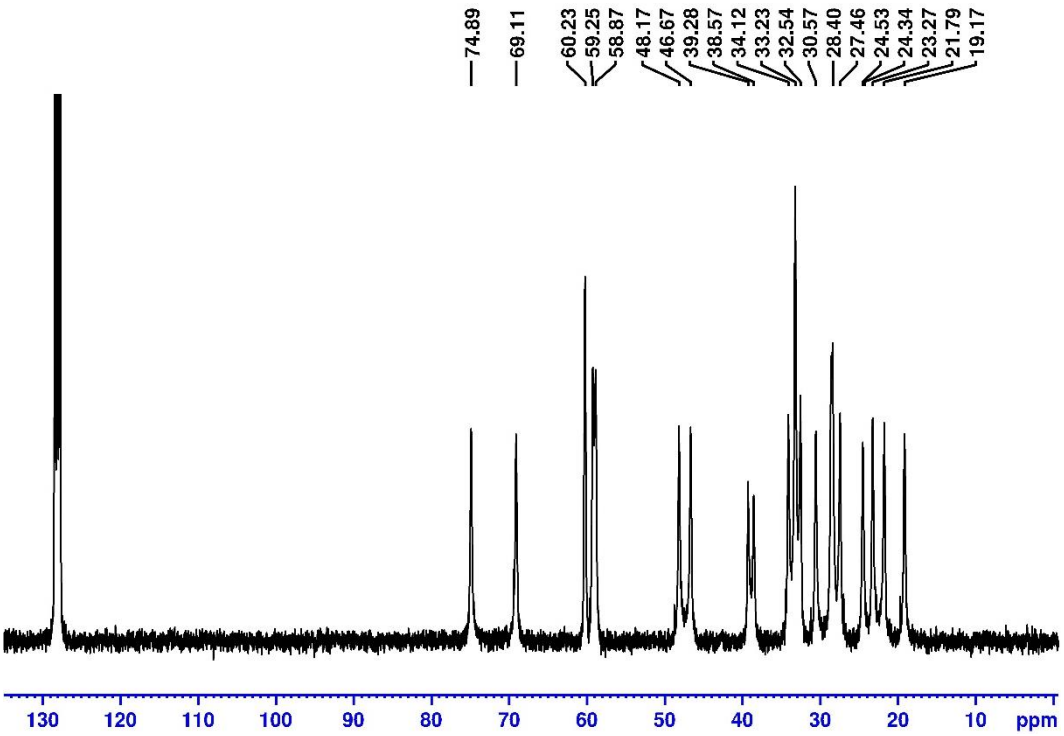



**Fig. S2** $^{13}$C{$^{1}$H} NMR spectrum of *meso*-**3**$^{i\text{Pr-Me}_2}$ in $C_6D_6$ at room temperature.

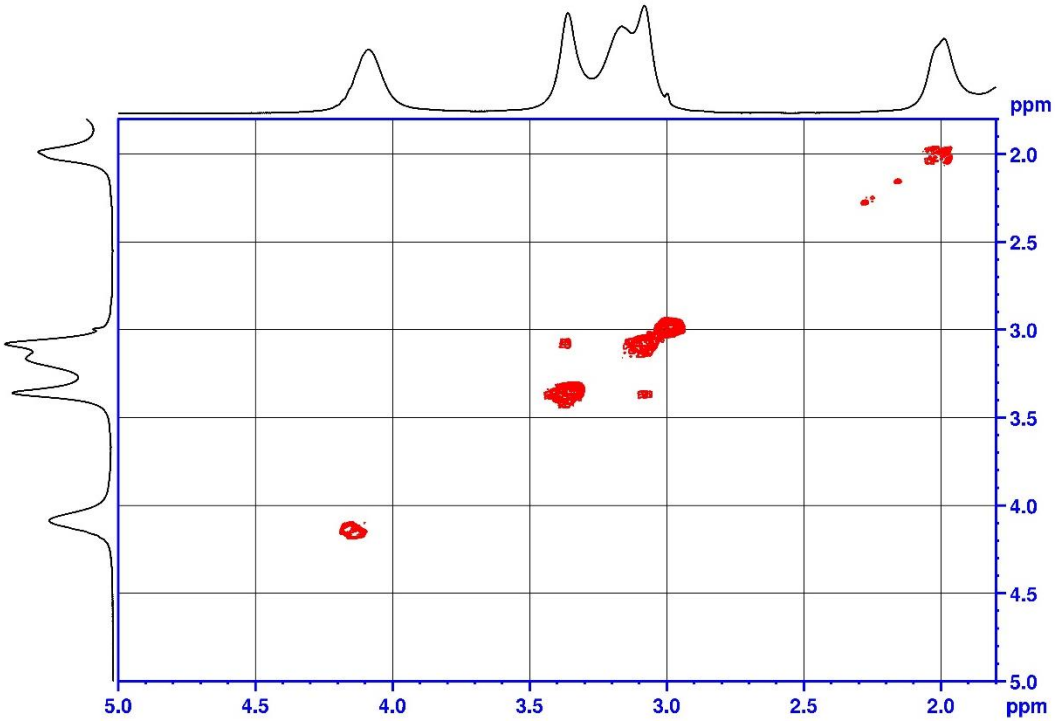



**Fig. S3** $^{1}$H-$^{1}$H 2D (COSY) NMR spectrum of *meso*-**3**$^{i\text{Pr-Me}_2}$ in $C_6D_6$ at room temperature.

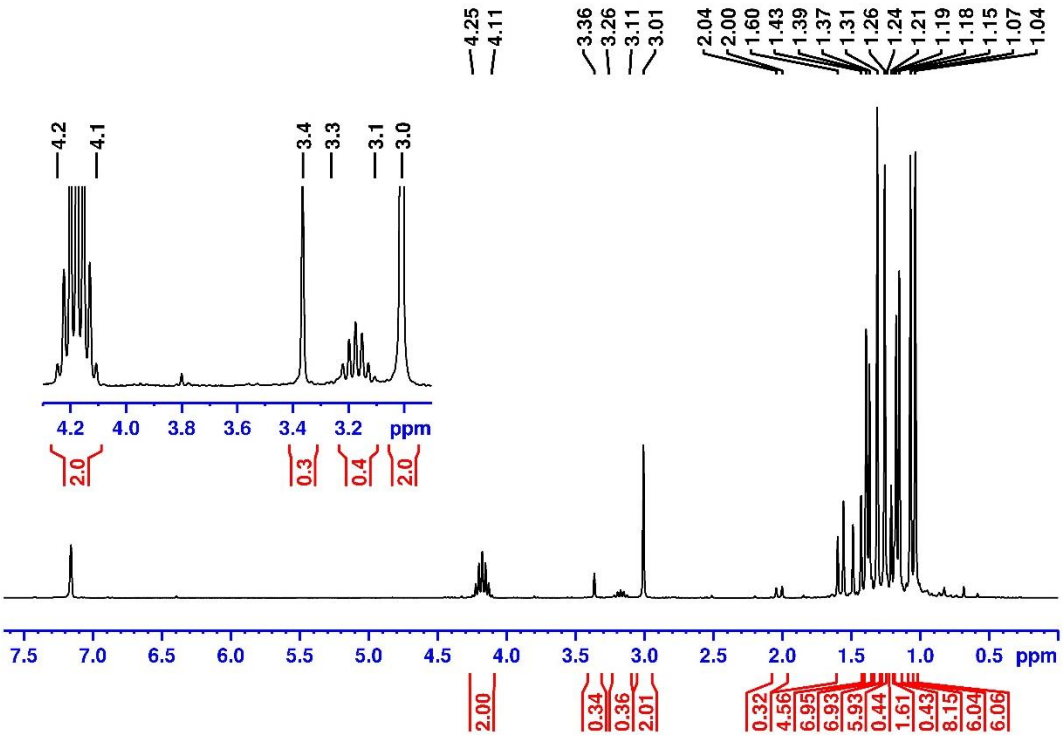



**Fig. S4** $^{1}$H NMR spectrum of *d*/*l*-**3**$^{i\text{Pr-Me}_2}$ (containing both rotational isomers) in $C_6D_6$ at room temperature.

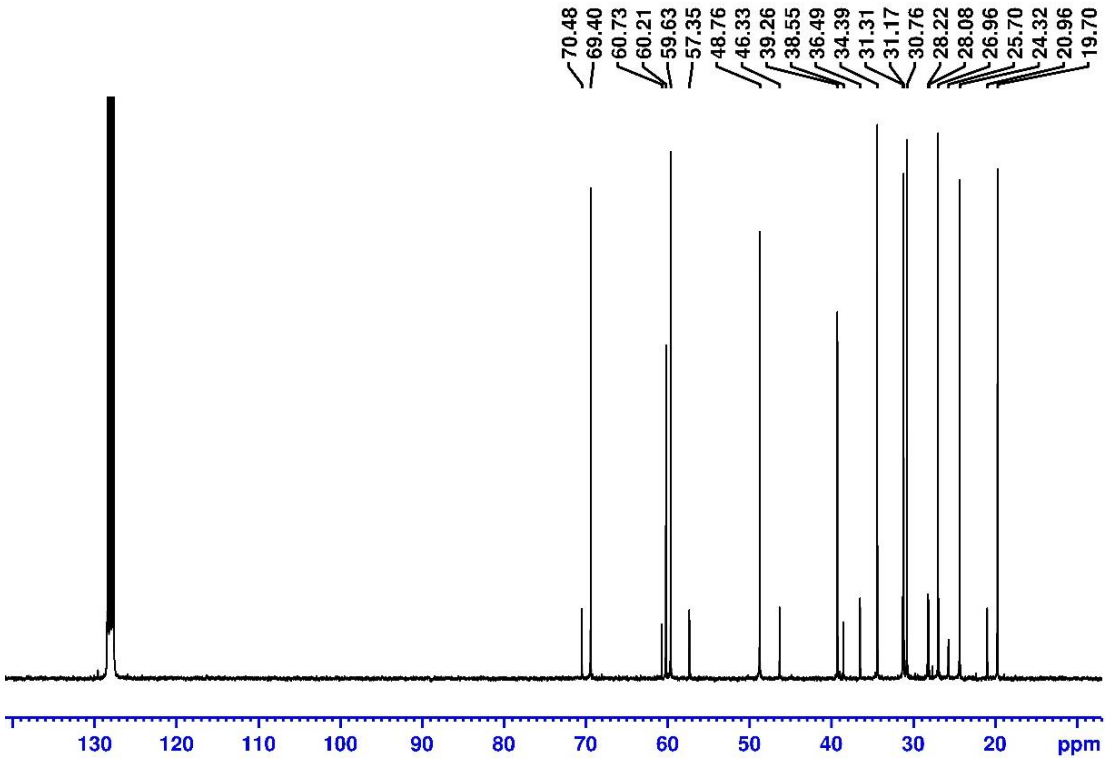



**Fig. S5** $^{13}C\{^{1}H\}$ NMR spectrum of *d*/*l*-**3**$^{iPr\text{-}Me_2}$ (containing both rotational isomers) in $C_6D_6$ at room temperature.

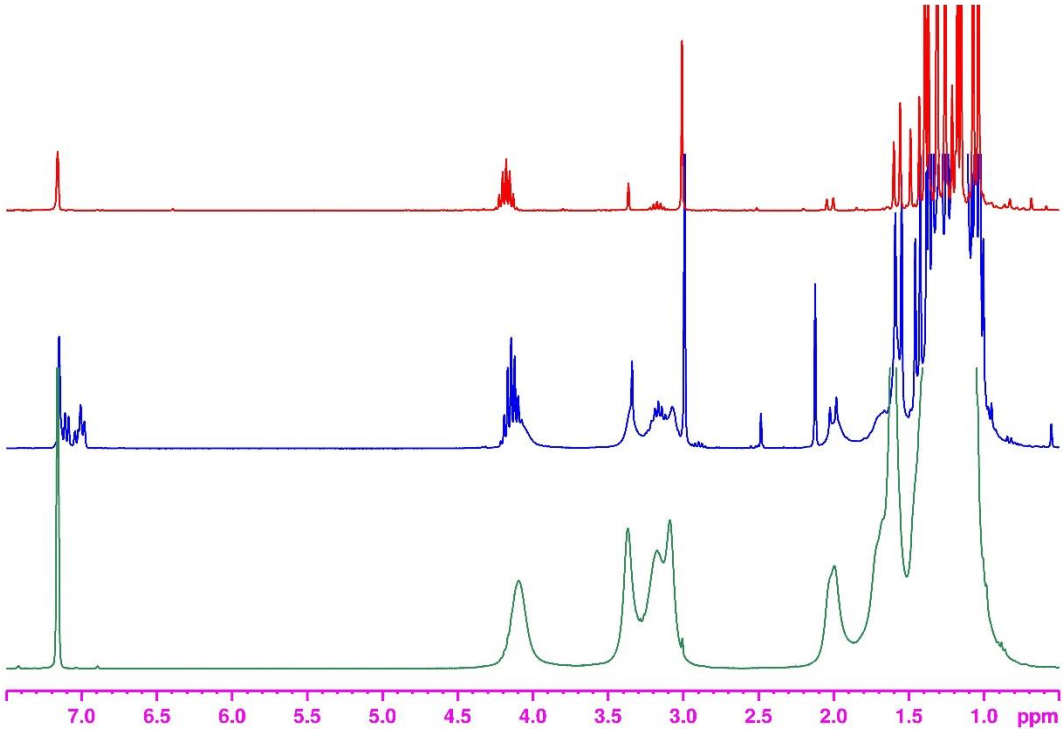



**Fig. S6** Overlay of $^{1}H$ NMR spectra of *meso*-**3**$^{iPr\text{-}Me_2}$ (green), **3**$^{iPr\text{-}Me_2}$ (blue), and *d*/*l*-**3**$^{iPr\text{-}Me_2}$ (red, containing two rotational isomers) in $C_6D_6$ at room temperature.

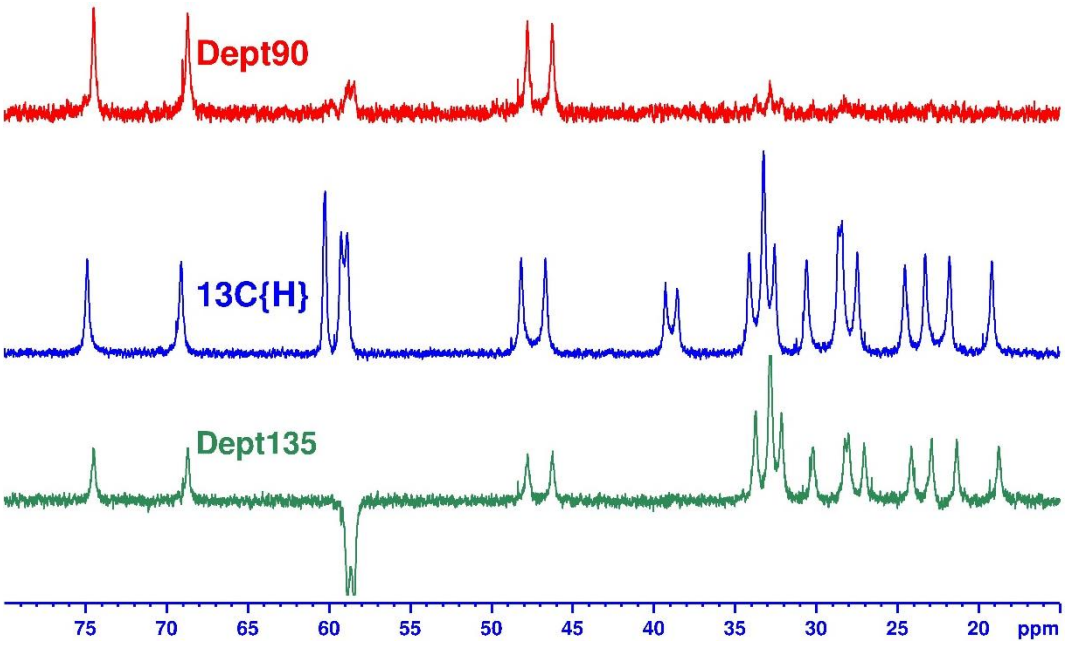



**Fig. S7** Overlay of $^{13}C\{^{1}H\}$-DEPT-135 (green), $^{13}C\{^{1}H\}$ (blue), $^{13}C\{^{1}H\}$-DEPT-90 (red) NMR spectra of *meso*-**3**$^{i\text{Pr-Me}_2}$ in $C_6D_6$ at room temperature.

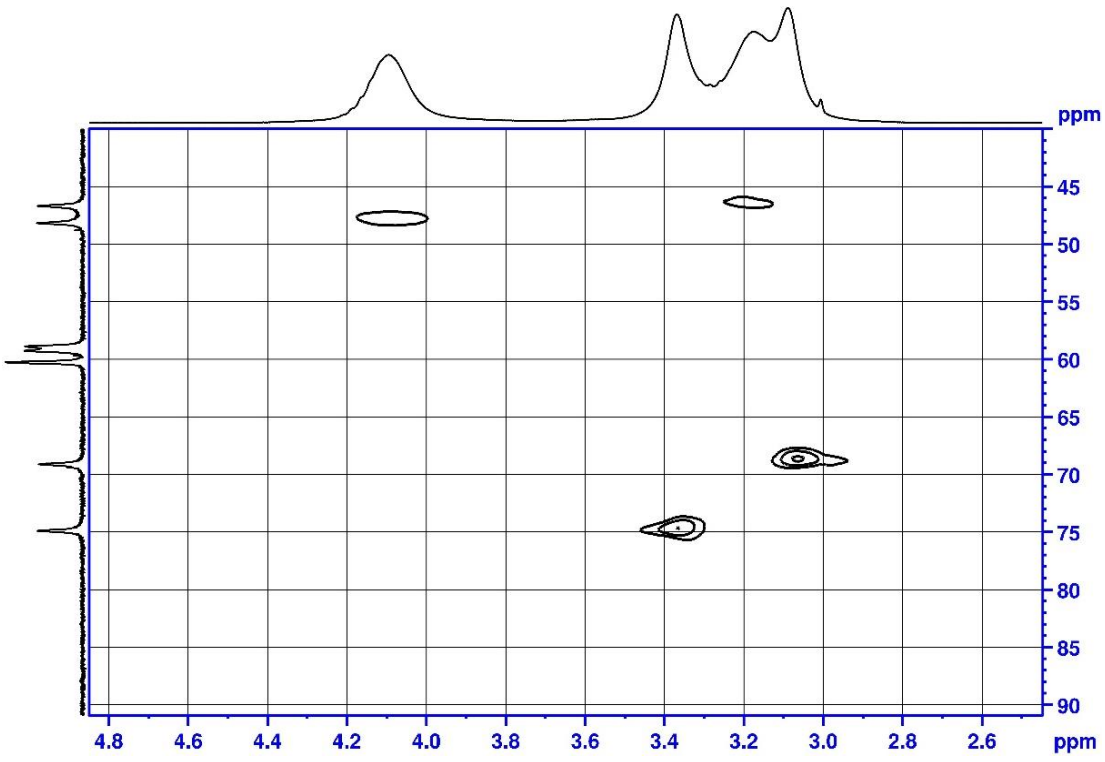



**Fig. S8** $^{13}C$-$^{1}H\{^{13}C\}$-2D (HMQC) NMR spectrum of *meso*-**3**$^{i\text{Pr-Me}_2}$ in $C_6D_6$ at room temperature.

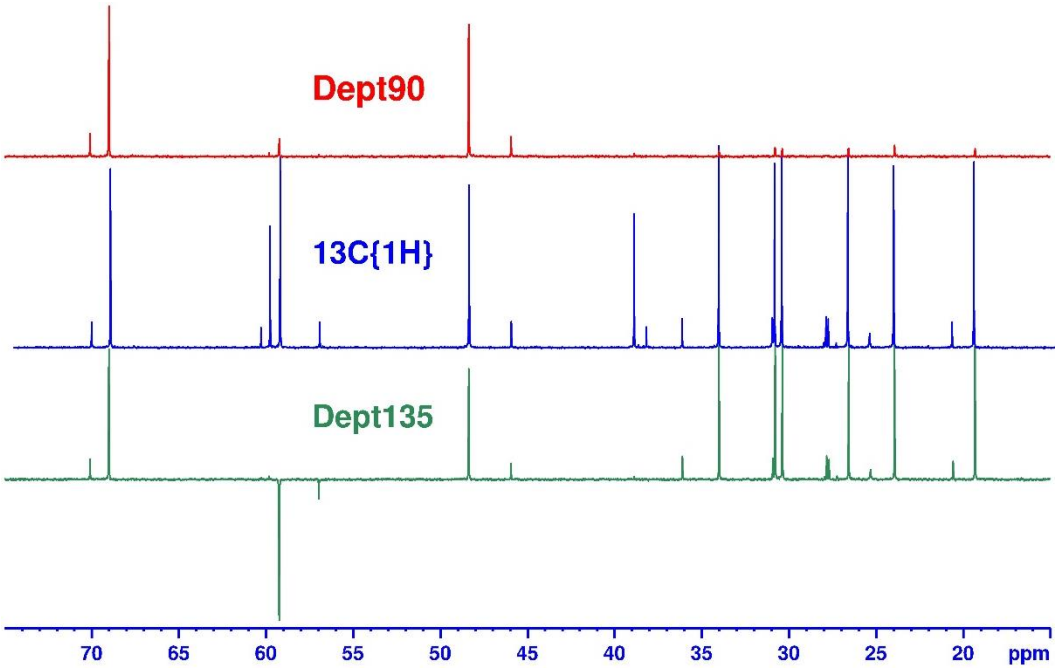



**Fig. S9** Overlay of $^{13}C\{^{1}H\}$-DEPT-135 (green), $^{13}C\{^{1}H\}$ (blue), $^{13}C\{^{1}H\}$-DEPT-90 (red) NMR spectra of *d*/*l*-**3**$^{iPr\text{-}Me_2}$ (containing two rotational isomers) in $C_6D_6$ at room temperature.

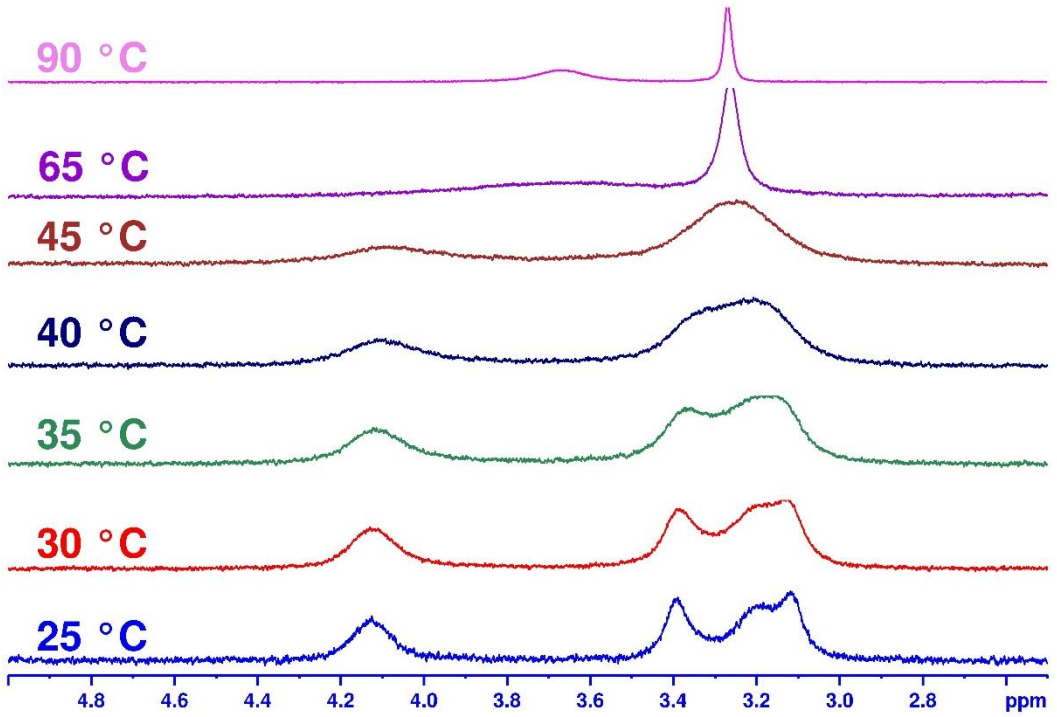



**Fig. S10** Overlay of VT-$^{1}H$ NMR spectra of *meso*-**3**$^{iPr\text{-}Me_2}$ (selected range: 2.6-5.0 ppm) in toluene-$d_8$.

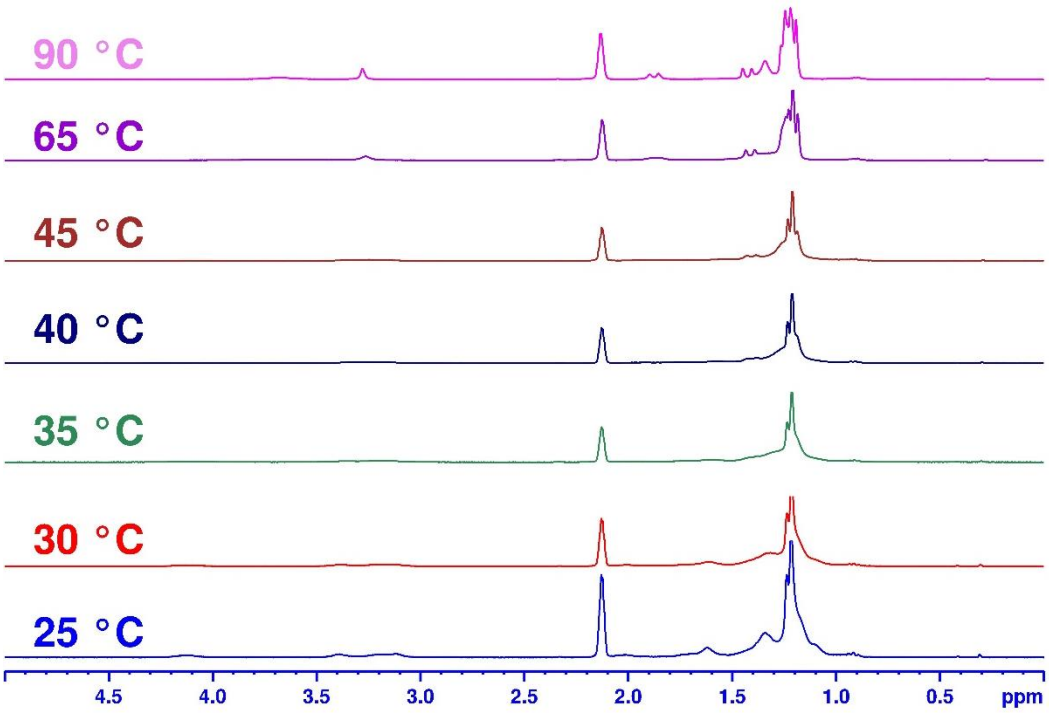



**Fig. S11** Overlay of VT-$^{1}$H NMR spectra of *meso*-**3**$^{iPr\text{-}Me_2}$ (selected range: 0.0-5.0 ppm) in toluene-$d_8$.

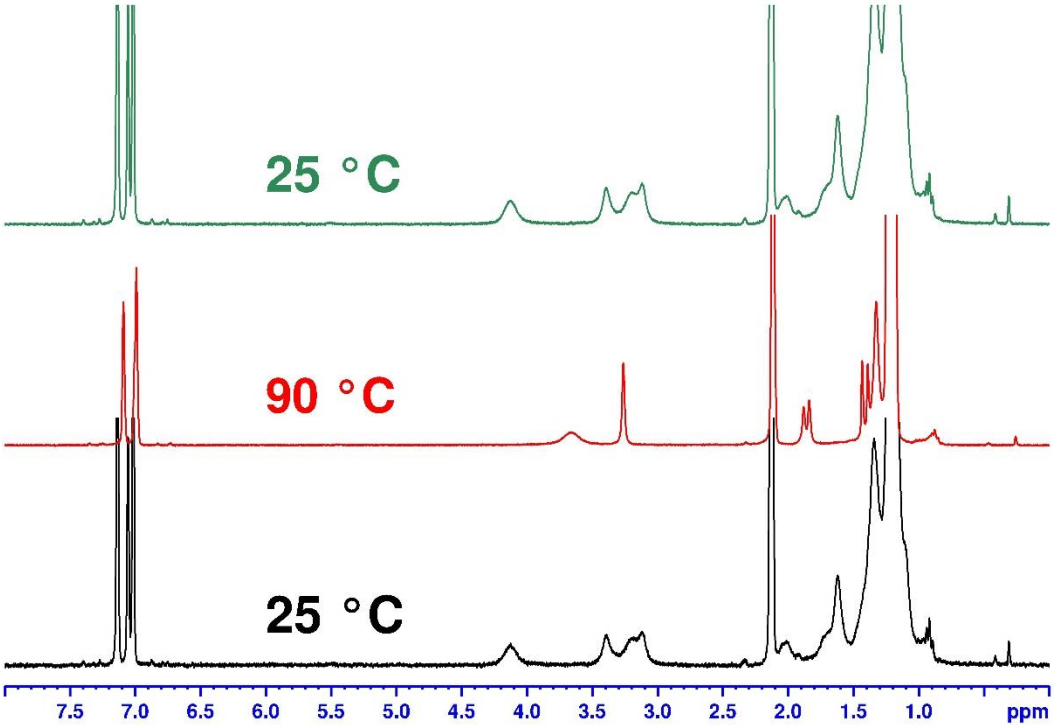



**Fig. S12** Overlay of VT-$^{1}$H NMR spectra of *meso*-**3**$^{iPr\text{-}Me_2}$ in toluene-$d_8$.

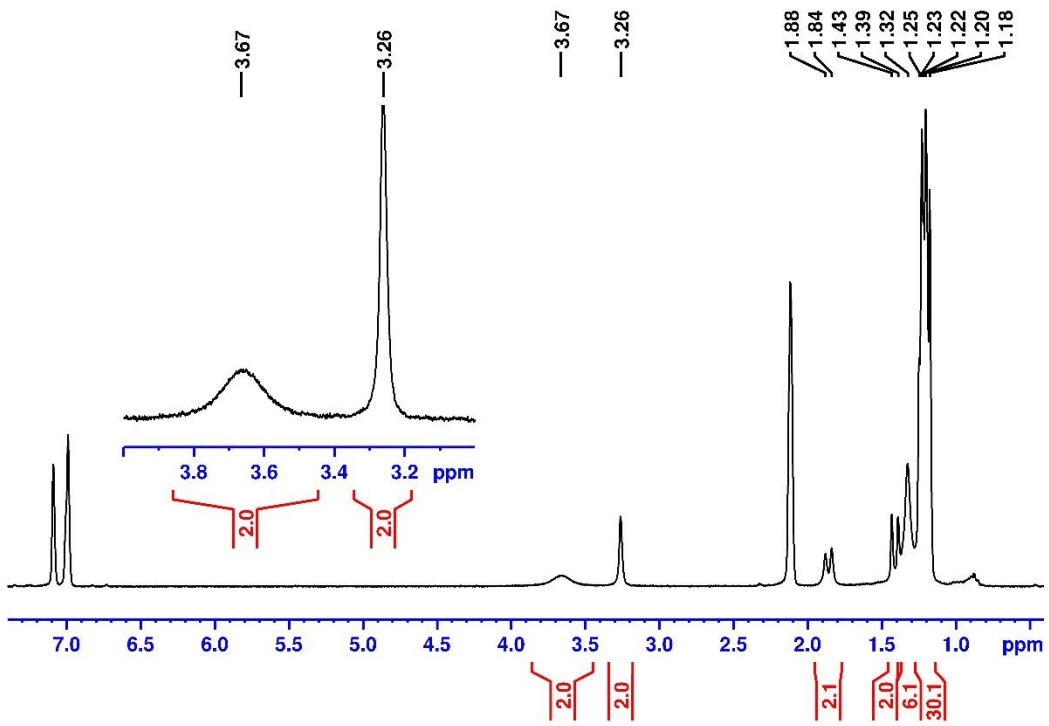



**Fig. S13** $^{1}$H NMR spectra of *meso*-**3**$^{iPr\text{-}Me_2}$ at 90 °C in toluene-d$_8$.

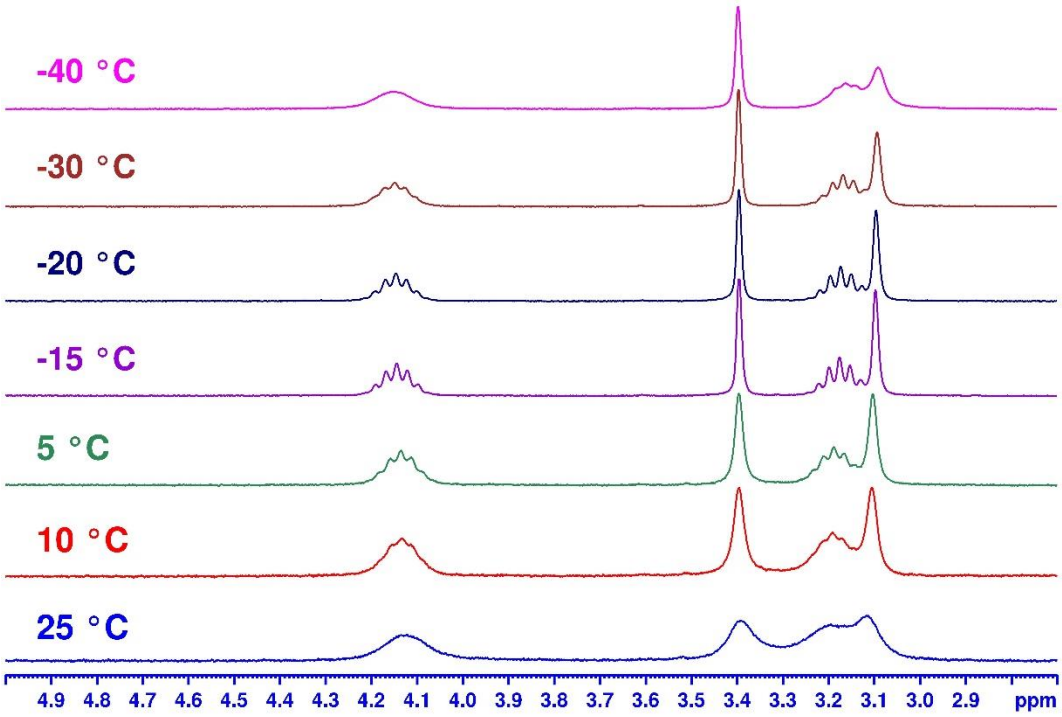



**Fig. S14** Overlay of VT-$^{1}$H NMR spectra of *meso*-**3**$^{iPr\text{-}Me_2}$ (selected range) in toluene-d$_8$.

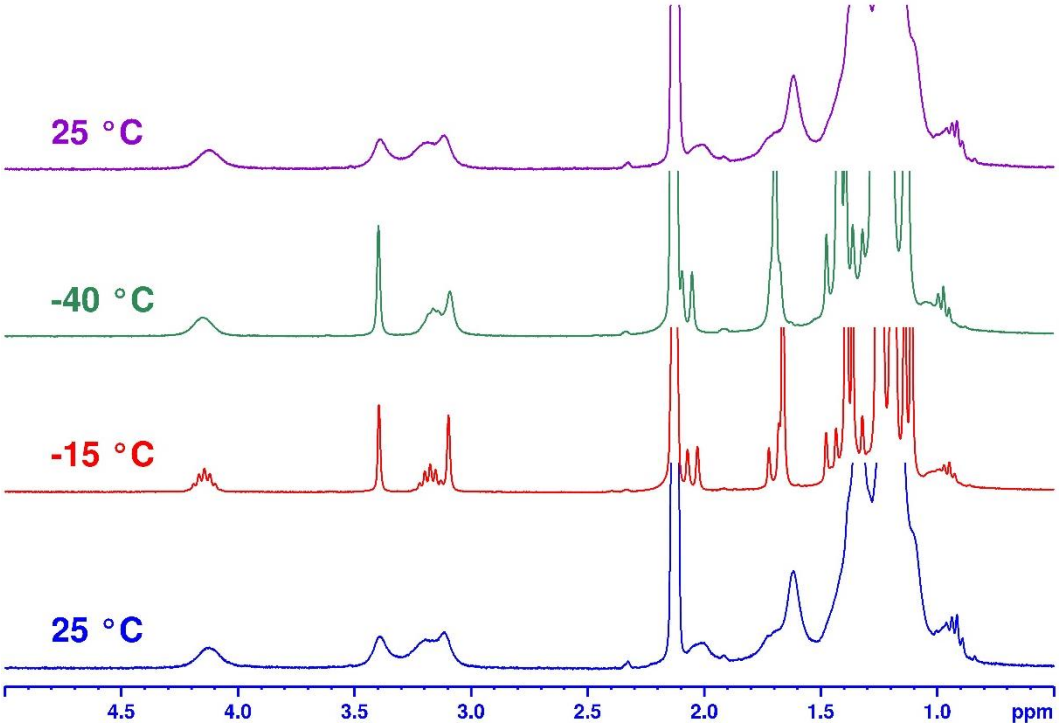



**Fig. S15** Overlay of VT-$^{1}$H NMR spectra of *meso*-**3**$^{iPr\text{-}Me_2}$ (selected range) in toluene-d$_8$.

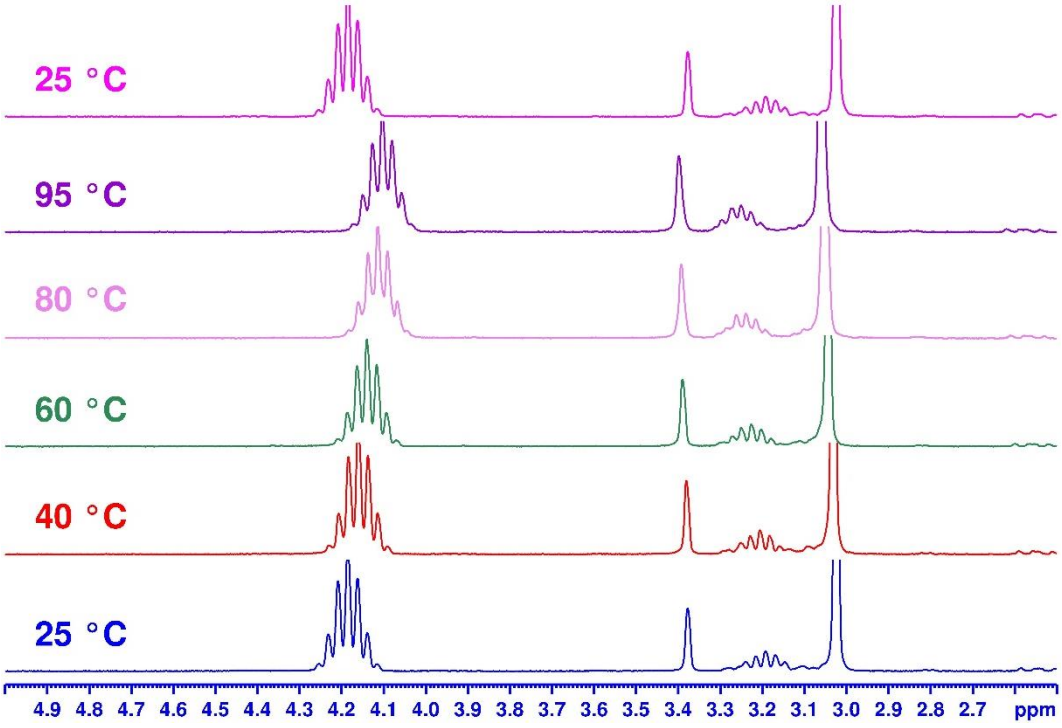



**Fig. S16** Overlay of VT-$^{1}$H NMR spectra of *d*/*l*-**3**$^{iPr\text{-}Me_2}$ (selected range: 2.6-5.0 ppm) in toluene-d$_8$.

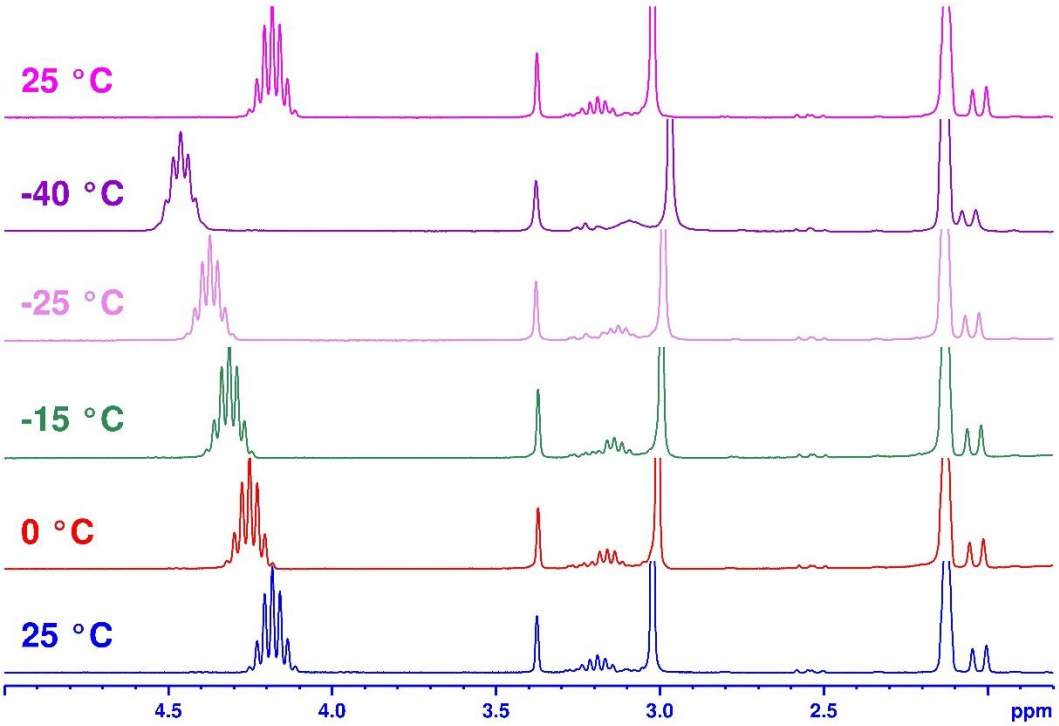



**Fig. S17** Overlay of VT-$^{1}$H NMR spectra of *d*/*l*-**3**$^{i\text{Pr-Me}_2}$ (selected range: 2.0-5.0 ppm) in toluene-$d_8$.

**Table S1.** Summary of C-*H* exchange rate of *meso*-**3**$^{i\text{Pr-Me}_2}$ at different temperatures (the fitted exchange rates reported here have an error of ±10 Hz; the reported rates (above 10 Hz) are, hence, rounded to the nearest decade).

| Entry No. | Temperature (°C) | Exchange Rate (Hz) | Entry No. | Temperature (°C) | Exchange Rate (Hz) |
|---|---|---|---|---|---|
| 1. | −10 | 2 | 12. | 45 | 510 |
| 2. | −5 | 4 | 13. | 50 | 700 |
| 3. | 0 | 9 | 14. | 55 | 980 |
| 4. | 5 | 20 | 15. | 60 | 1490 |
| 5. | 10 | 40 | 16. | 65 | 2080 |
| 6. | 15 | 60 | 17. | 70 | 2810 |
| 7. | 20 | 90 | 18. | 75 | 3740 |
| 8. | 25 | 120 | 19. | 80 | 4980 |
| 9. | 30 | 190 | 20. | 85 | 5500 |
| 10. | 35 | 280 | 21. | 90 | 8470 |
| 11. | 40 | 380 | | | |

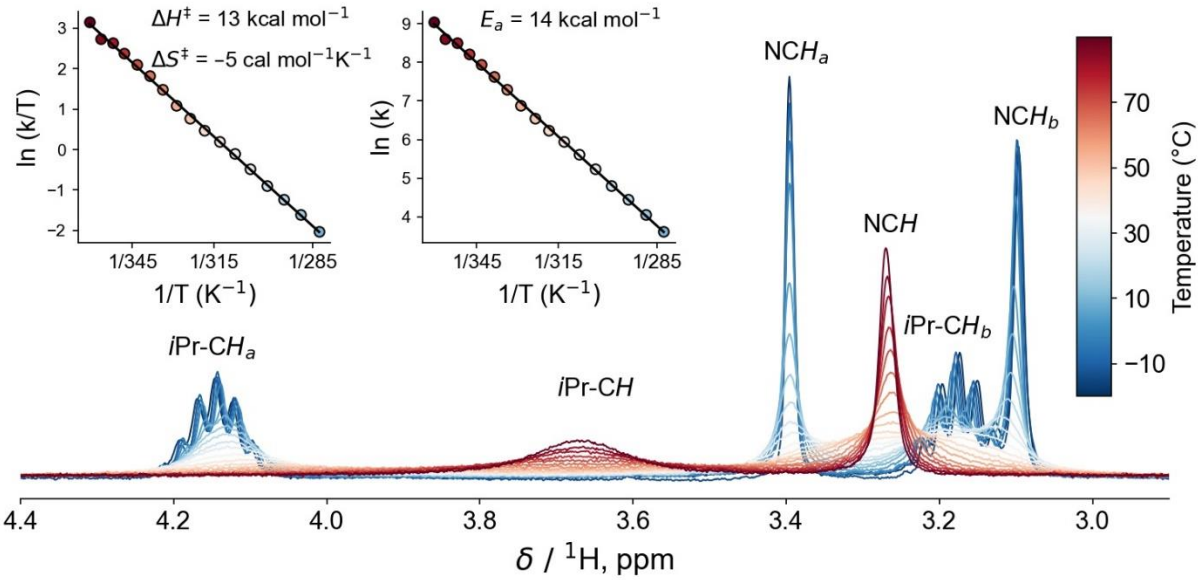
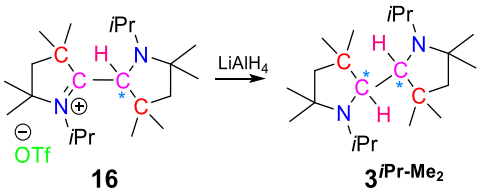



**Fig. S18** VT-$^1$H NMR spectra (selected range) of *meso*-**3**$^{i\text{Pr-Me}_2}$ showing coalescence at 60-65 °C for *i*Pr-C*H* at 45-50 °C for NC-*H* protons. Inset: Left: Eyring plot to determine the enthalpic and entropic contribution to the activation energy. Right: Arrhenius plot for determining the rotational barrier between the two gauche-conformers.

**Alternative Route for the Synthesis of $3^{iPr\text{-}Me_2}$**




**16** $3^{iPr\text{-}Me_2}$

THF (10 mL) was added to the mixture of **16** (230 mg, 0.474 mmol) and $LiAlH_4$ (25 mg, 0.66 mmol) at room temperature and stirred for 1 minute. After that, the solvent was evaporated and 3 mL water was added to the residue followed by 1 mL of 2 M NaOH and then 7 mL more water added. The resulting mixture was extracted with $Et_2O$ (2 × 10 mL). The combined collected $Et_2O$ phases were dried first over $MgSO_4$ and secondly under vacuum resulting in colourless sticky solid compound $\mathbf{3}^{iPr\text{-}Me_2}$. **Yield:** 120 mg (75 %).

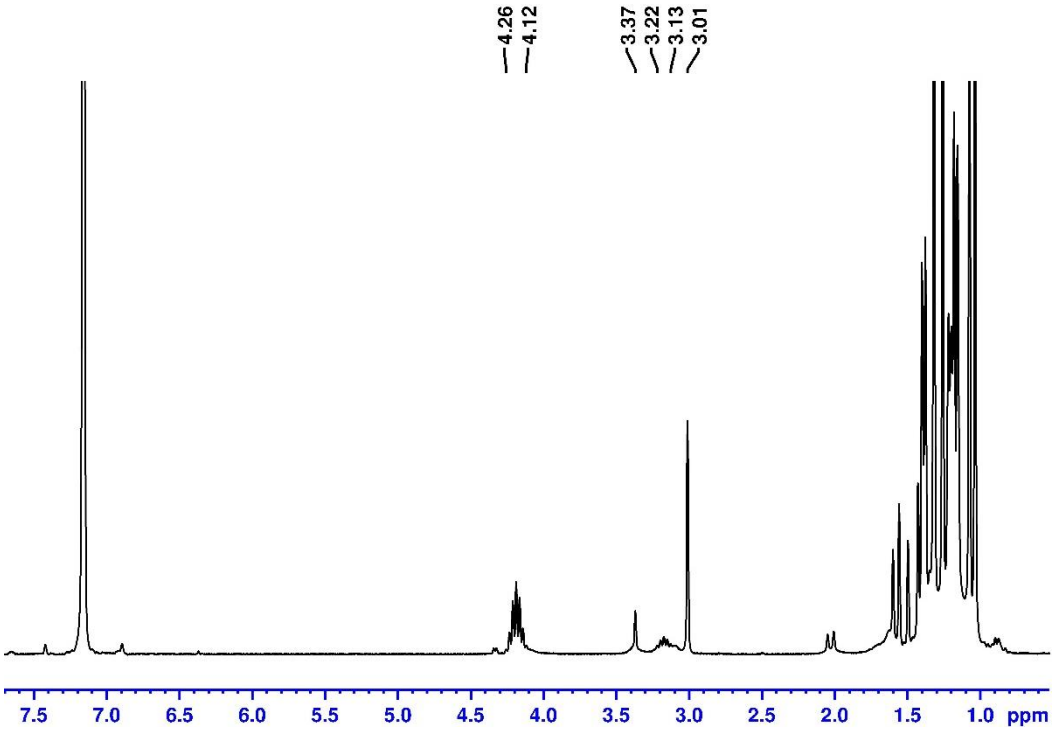
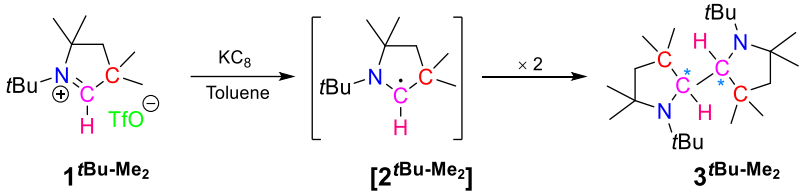



**Fig. S19** $^1H$ NMR spectrum of $\mathbf{3}^{iPr\text{-}Me_2}$ (synthesised from **16** using $LiAlH_4$) in $C_6D_6$ at room temperature.

**Synthesis of $3^{tBu\text{-}Me_2}$**




$1^{tBu\text{-}Me_2}$ $[2^{tBu\text{-}Me_2}]$ $3^{tBu\text{-}Me_2}$

About 60 mL of toluene was added to the mixture of $\mathbf{1}^{tBu\text{-}Me_2}$ (2.00 g, 6.03 mmol) and $KC_8$ (1.224 g, 9.055 mmol) at room temperature and stirred for 12 hours. After that the reaction mixture was filtered and all volatiles were evaporated under vacuum resulting in pure $\mathbf{3}^{tBu\text{-}Me_2}$. **Yield:** 1.004 g (91 %). Single crystals of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$ were obtained from saturated pentane solution at −30 °C after 7 days. It was possible to separate the minor rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$ using silica gel column chromatography. First, *meso*-$\mathbf{3}^{tBu\text{-}Me_2}$ was moved through the column using pentane as an eluent, followed by a mixture of the major rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$ along with the minor rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$ (still in pentane). Secondly, using diethyl ether as an eluent, the minor rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$ (50 mg) was obtained. $\mathbf{3}^{tBu\text{-}Me_2}$ is a colourless crystalline solid.

**M. P.** 79 °C.

**$^1$H NMR** of $\mathbf{3}^{tBu\text{-}Me_2}$ ($C_6D_6$, 25 °C, 300 MHz, Selected Resonances): $\delta$ = 3.71 (s, 2H, C*H* of major rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$), 3.59 (s, 1H, C*H* of *meso*), 3.40 (s, 1H, C*H* of *meso*-$\mathbf{3}^{tBu\text{-}Me_2}$), 3.21 (s, 2H, C*H* minor rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$), 2.28 (d, 1H, $^2J_{H\text{-}H}$ = 12.8 Hz, C$H_2$ of *meso*-$\mathbf{3}^{tBu\text{-}Me_2}$), 2.21 (d, 2H, $^2J_{H\text{-}H}$ = 13.0 Hz, C$H_2$ of major rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$), 2.08 (d, 1H, $^2J_{H\text{-}H}$ = 12.8 Hz, C$H_2$ of *meso*-$\mathbf{3}^{tBu\text{-}Me_2}$), 1.96 (d, 2H, $^2J_{H\text{-}H}$ = 12.8 Hz, C$H_2$ of minor rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$) ppm. **$^{13}$C{$^1$H} NMR** of $\mathbf{3}^{tBu\text{-}Me_2}$ ($C_6D_6$, 25 °C, 75.4 MHz, Selected Resonances): $\delta$ = 78.4 (*C*H of *meso*-$\mathbf{3}^{tBu\text{-}Me_2}$), 74.2 (*C*H of major rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$), 73.6 (*C*H of *meso*-$\mathbf{3}^{tBu\text{-}Me_2}$), 72.2 (*C*H of minor rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$), 61.2 (*C*$H_2$ of minor rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$), 61 (*C*$H_2$ of major rotational isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$), 60.6 (*C*$H_2$ of *meso*-$\mathbf{3}^{tBu\text{-}Me_2}$), 60.2 (*C*$H_2$ of *meso*-$\mathbf{3}^{tBu\text{-}Me_2}$) ppm.

**$^1$H NMR** of minor rotational-isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$ ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 3.21 (s, 2H, C*H*), 1.96 (d, 2H, $^2J_{H\text{-}H}$ = 12.9 Hz, C$H_2$), 1.43 (s, 6H, C$H_3$), 1.39 (s, 18H, C(C$H_3$)$_3$), 1.32 (s, 6H, C$H_3$), 1.23 (s, 2H, C$H_2$), 1.21 (s, 6H, C$H_3$), 1.03 (s, 6H, C$H_3$) ppm. **$^{13}$C{$^1$H} NMR** of minor rotational-isomer of *d*/*l*-$\mathbf{3}^{tBu\text{-}Me_2}$ ($C_6D_6$, 25 °C, 75.4 MHz): $\delta$ = 72.2 (*C*H), 62.0 (*C*(CH$_3$)$_2$), 61.1 (*C*H$_2$), 54.8 (*C*(CH$_3$)$_3$), 41 (*C*(CH$_3$)$_2$), 33.3 (C(*C*H$_3$)$_3$), 32.4 (C(*C*H$_3$)$_2$), 31.8 (C(*C*H$_3$)$_2$), 31.2 (C(*C*H$_3$)$_2$), 28.1 (C(*C*H$_3$)$_2$) ppm.

**Elemental analysis:** calcd. (%) for $C_{24}H_{48}N_2$: C, 79.05; H, 13.27; N, 7.68; found: C, 79.11; H, 13.68; N, 7.42. **HRMS-ESI (m/z):** Calculated for $C_{24}H_{49}N_2$ $[M+H]^+$: 365.3891, Found: 365.3898.

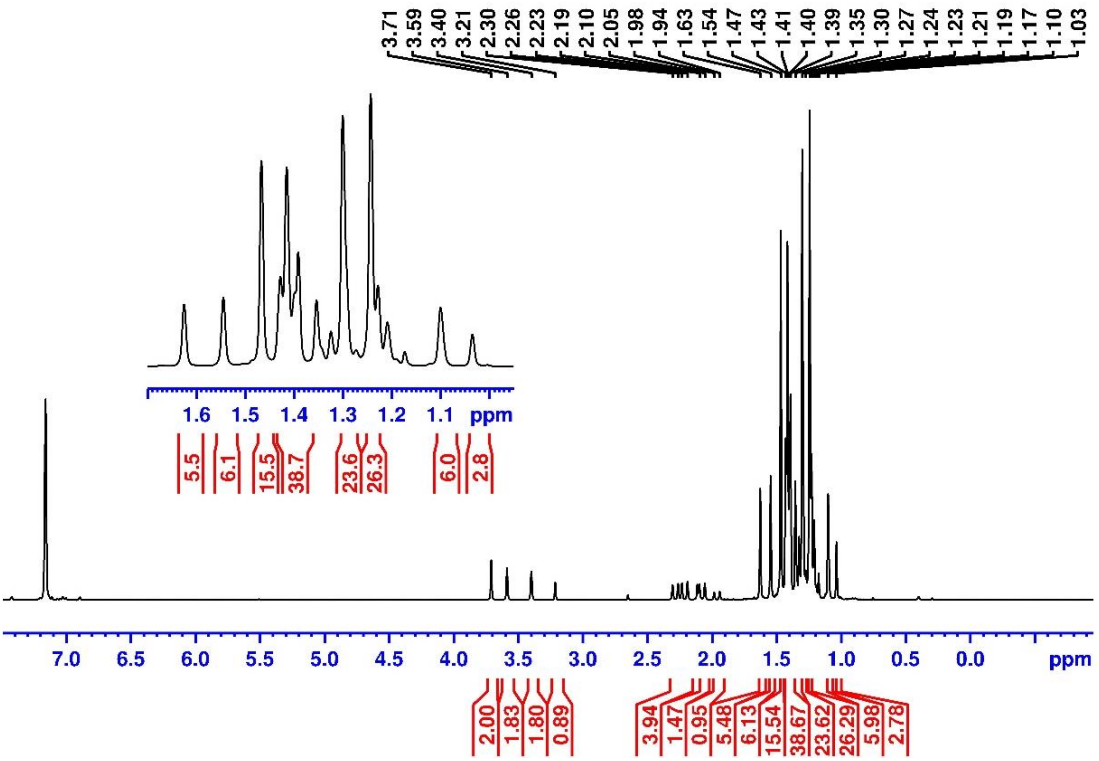



**Fig. S20** $^{1}H$ NMR spectrum of **3**$^{tBu\text{-}Me_2}$ in $C_6D_6$ at room temperature.

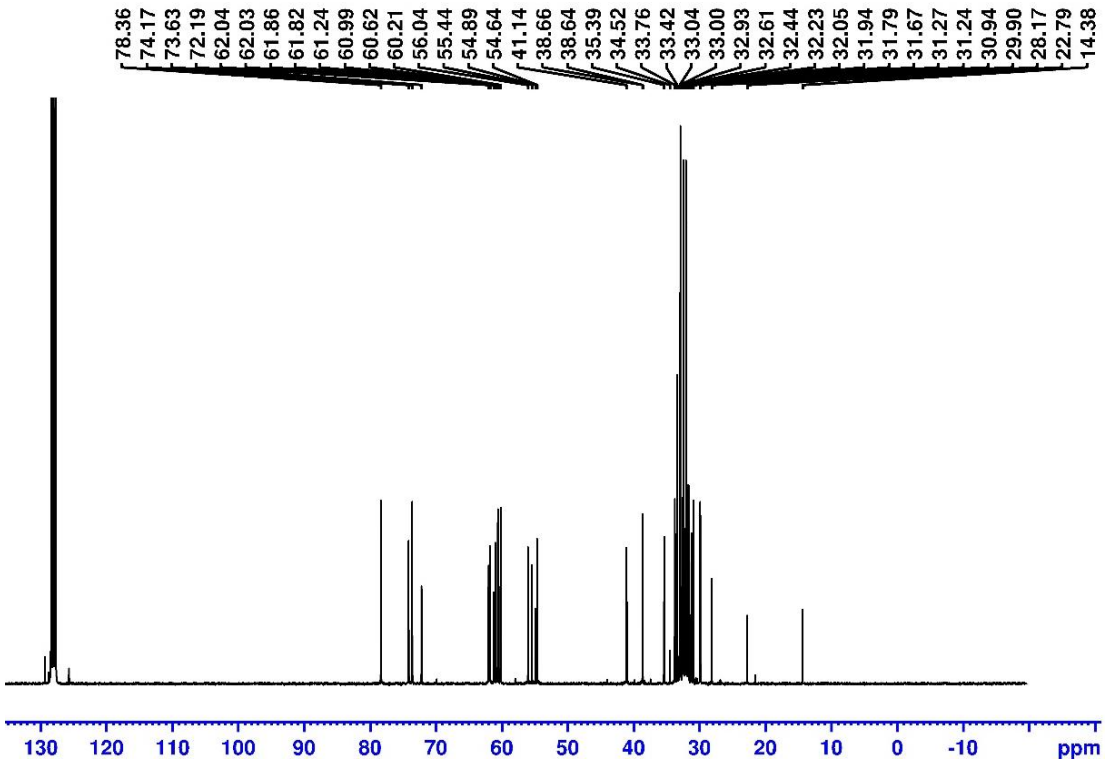



**Fig. S21** $^{13}C\{^{1}H\}$ NMR spectrum of **3**$^{tBu\text{-}Me_2}$ in $C_6D_6$ at room temperature.

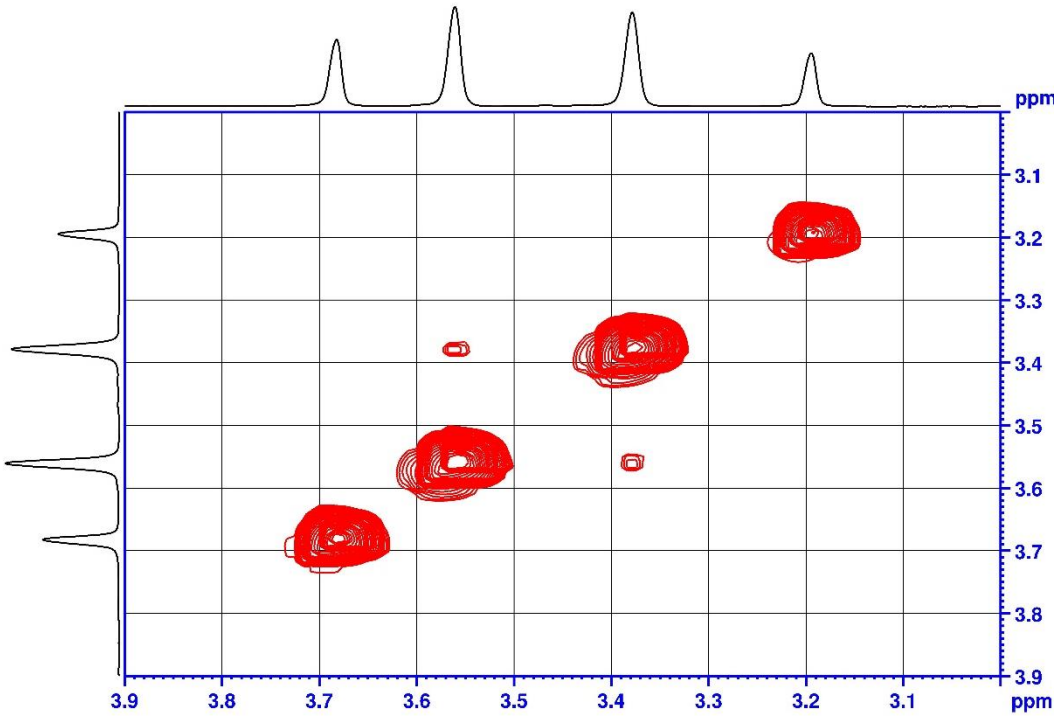



**Fig. S22** $^{1}$H-$^{1}$H 2D (COSY) NMR spectrum of **3**$^{t\text{Bu-Me}_2}$ in $C_6D_6$ at room temperature.

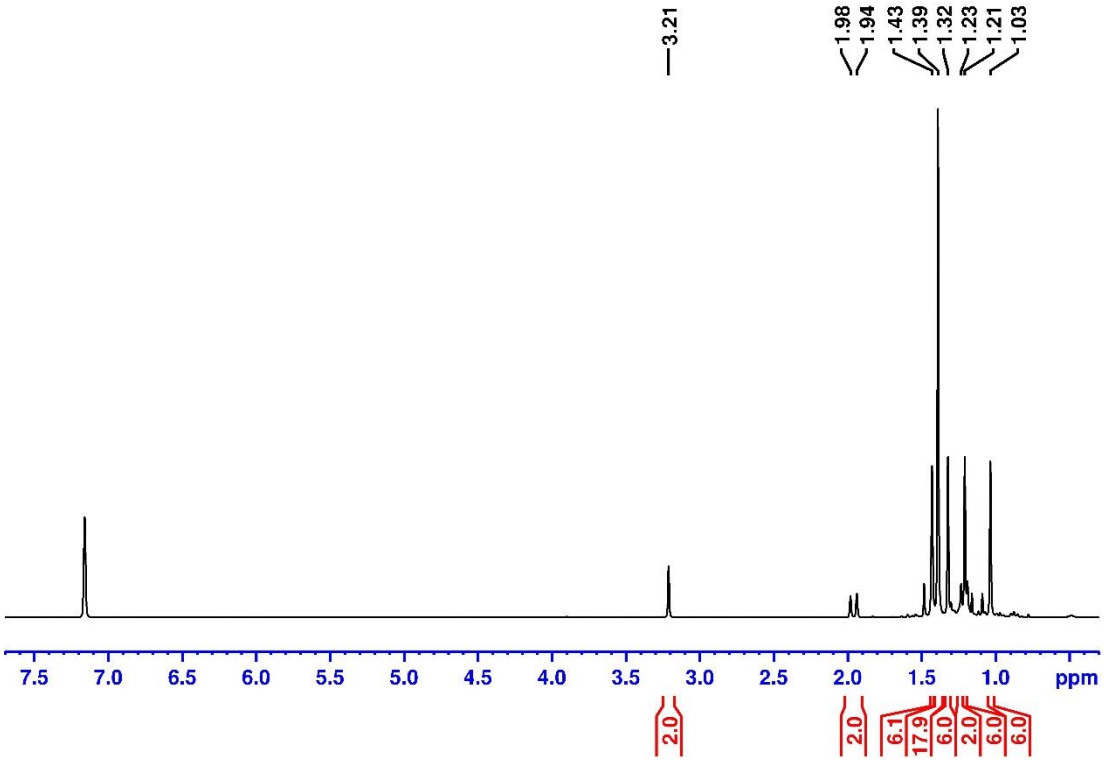



**Fig. S23** $^{1}$H NMR spectrum of minor rotational isomer of *d*/*l*-**3**$^{t\text{Bu-Me}_2}$ in $C_6D_6$ at room temperature.

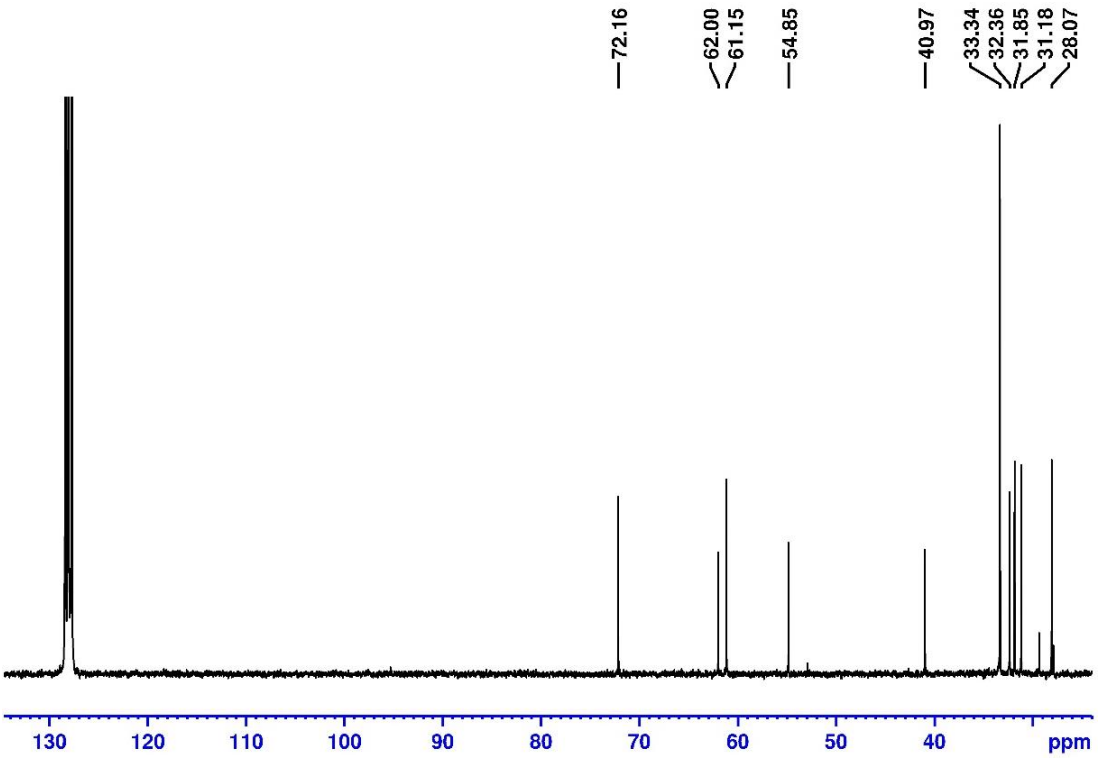



**Fig. S24** $^{13}C\{^{1}H\}$ NMR spectrum of minor rotational isomer of *d*/*l*-**3**$^{tBu\text{-}Me_2}$ in $C_6D_6$ at room temperature.

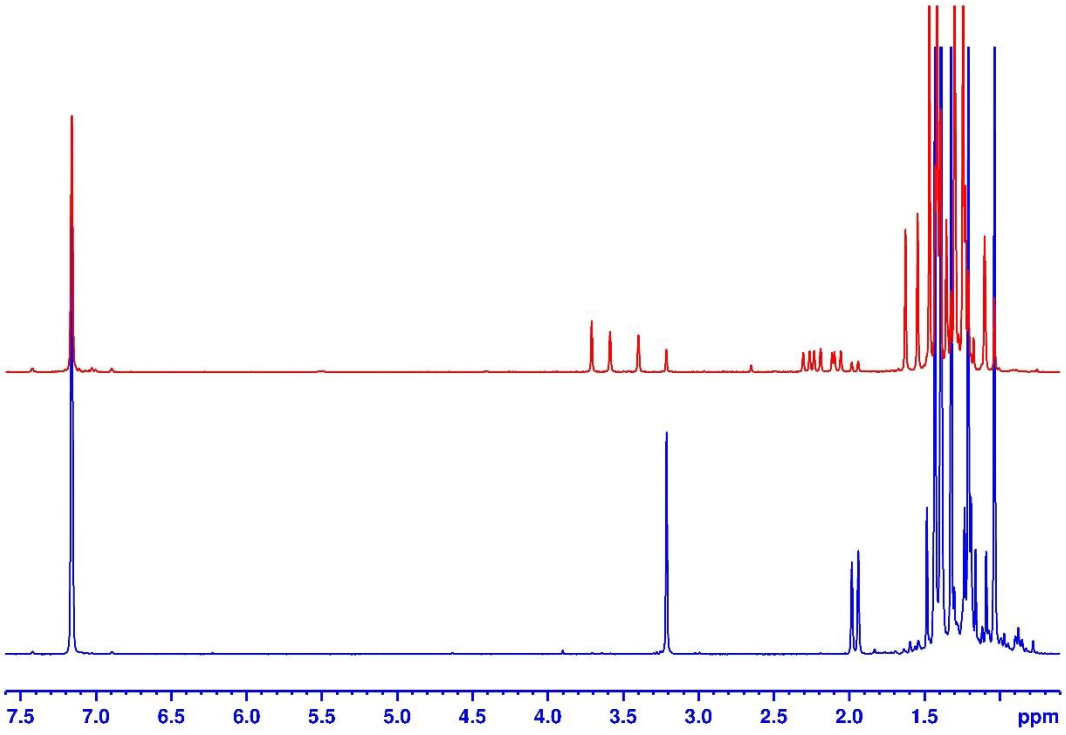



**Fig. S25** Overlay of $^{1}H$ NMR spectra of minor rotational isomer of *d*/*l*-**3**$^{tBu\text{-}Me_2}$ (blue) and **3**$^{tBu\text{-}Me_2}$ (red) in $C_6D_6$ at room temperature.

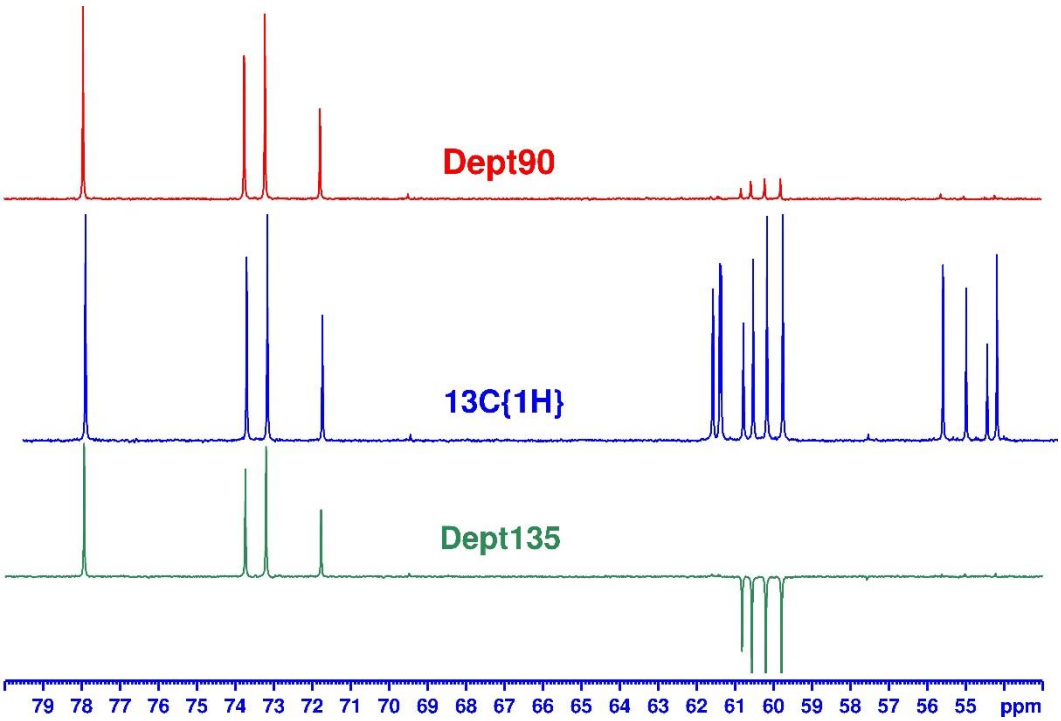



**Fig. S26** Overlay of $^{13}C\{^{1}H\}$-DEPT-135 (green), $^{13}C\{^{1}H\}$ (blue), $^{13}C\{^{1}H\}$-DEPT-90 (red) NMR spectra of **3**$^{tBu\text{-}Me_2}$ in $C_6D_6$ at room temperature.

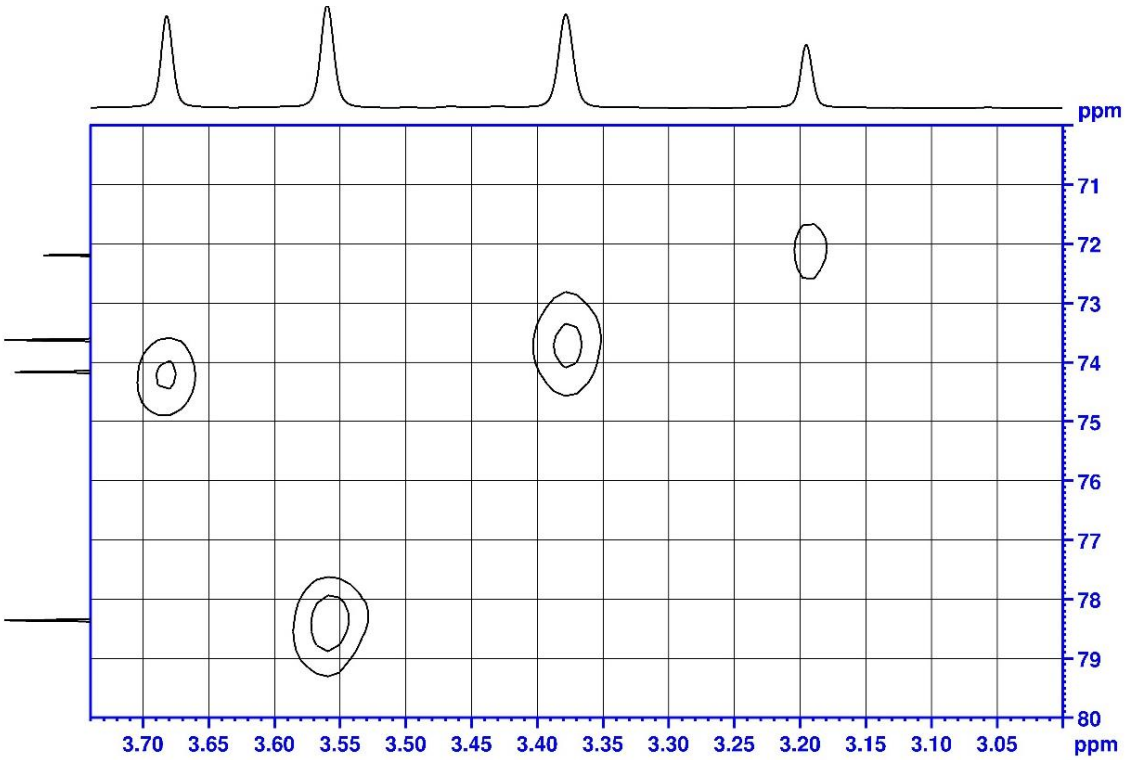



**Fig. S27** $^{13}C$-$^{1}H\{^{13}C\}$ 2D (HMQC) NMR spectrum of *meso*-**3**$^{tBu\text{-}Me_2}$ (showing correlation between C-*H* and *C*) in $C_6D_6$ at room temperature (projections on the X- and Y-axis are from the independently obtained 1-D experiments).

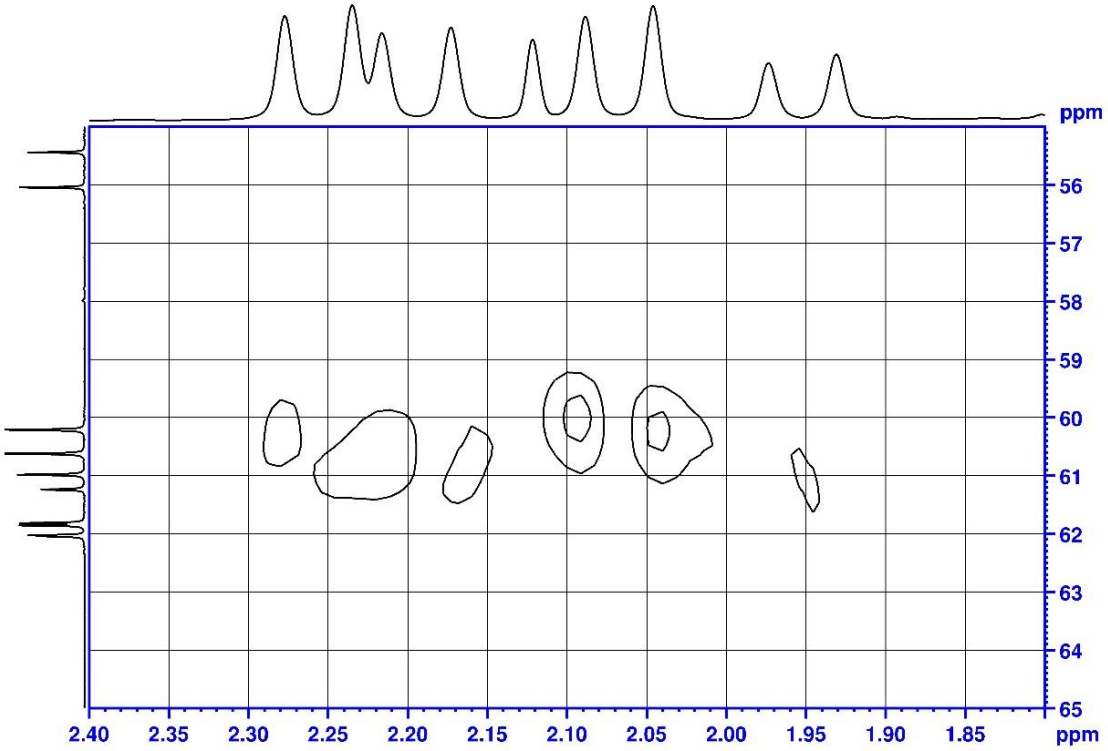
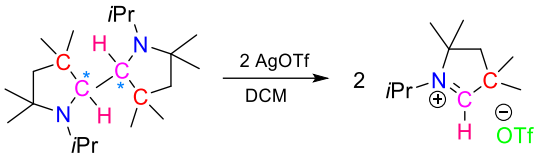



**Fig. S28** $^{13}C$-$^{1}H\{^{13}C\}$ 2D (HMQC) NMR spectrum of *meso*-**3**$^{t\text{Bu-Me}_2}$ (showing correlation between C-$H_2$ and *C*) in $C_6D_6$ at room temperature (projections on the X- and Y-axis are from the independently obtained 1-D experiments).

**1:2 Reaction of $3^{iPr\text{-}Me_2}$ and AgOTf**




$3^{iPr\text{-}Me_2}$ $1^{iPr\text{-}Me_2}$

About 20 mL DCM was added to the mixture of $3^{iPr\text{-}Me_2}$ (100 mg, 0.297 mmol) and AgOTf (153 mg, 0.595 mmol) at room temperature and stirred for 6 hours. Following this, the $^1$H NMR spectrum of the reaction mixture showed the formation of $1^{iPr\text{-}Me_2}$. Subsequently, the reaction mixture was filtered and after evaporation of the filtrate $1^{iPr\text{-}Me_2}$ was obtained.[S1] **Yield:** 179 mg (95 %).

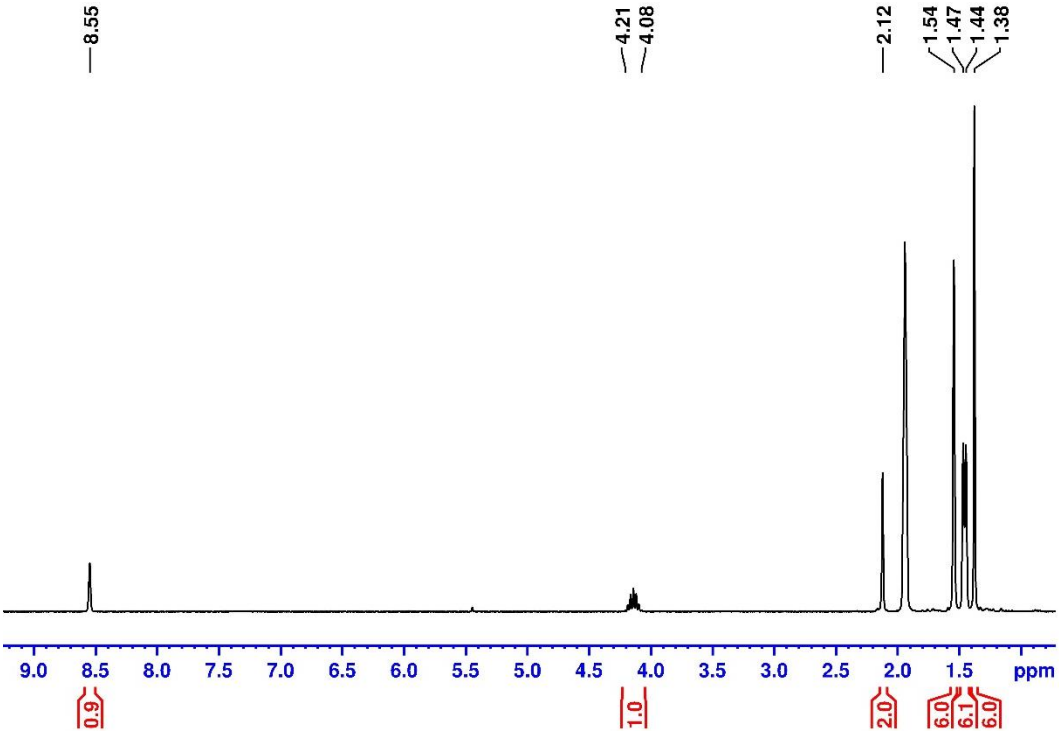
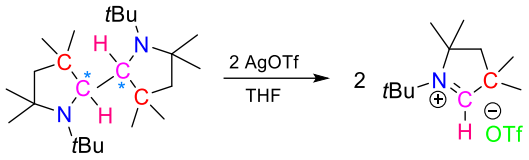



**Fig. S29** $^1$H NMR spectrum of $1^{iPr\text{-}Me_2}$ in $CD_3CN$ at room temperature.

**1:2 Reaction of $3^{tBu\text{-}Me_2}$ and AgOTf**




$3^{tBu\text{-}Me_2}$ $1^{tBu\text{-}Me_2}$

About 10 mL of THF was added to the mixture of $\mathbf{3}^{tBu\text{-}Me_2}$ (50 mg, 0.14 mmol) and AgOTf (72 mg, 0.28 mmol) at room temperature and stirred for 6 hours. Following this, the $^1$H NMR spectrum of the reaction mixture showed the formation of $\mathbf{1}^{tBu\text{-}Me_2}$. Subsequently, the reaction mixture was filtered and the resulting residue was extracted with DCM (10 mL). Evaporation of the filtrate leads to isolated $\mathbf{1}^{tBu\text{-}Me_2}$.[S2] **Yield:** 81 mg (89 %).

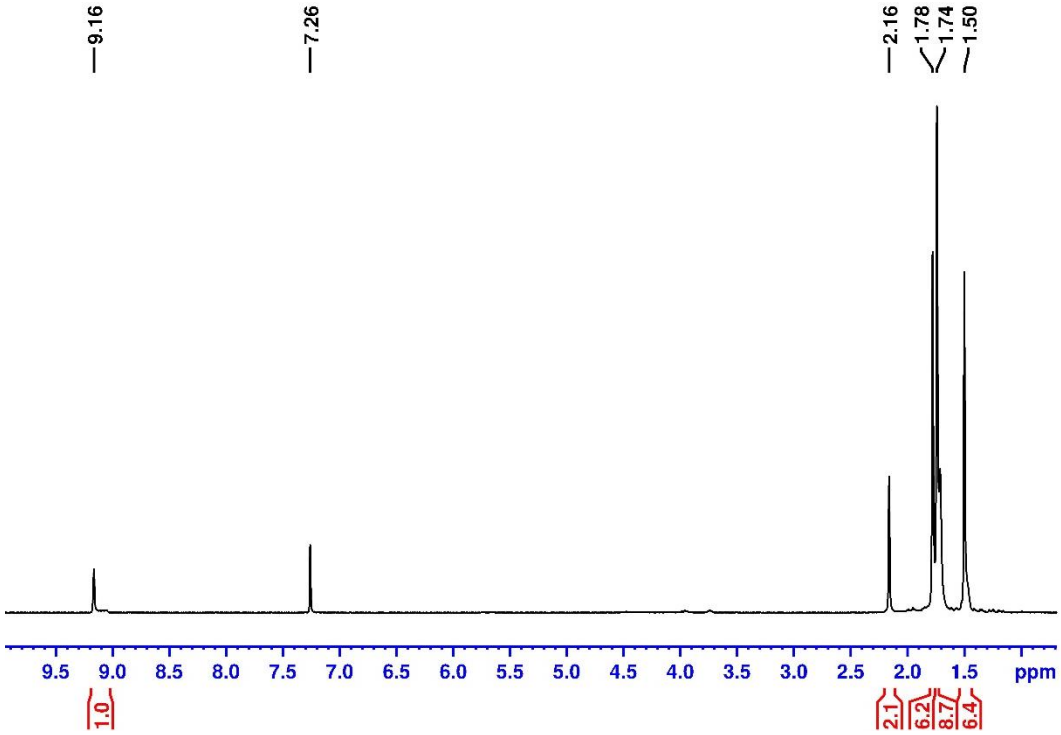
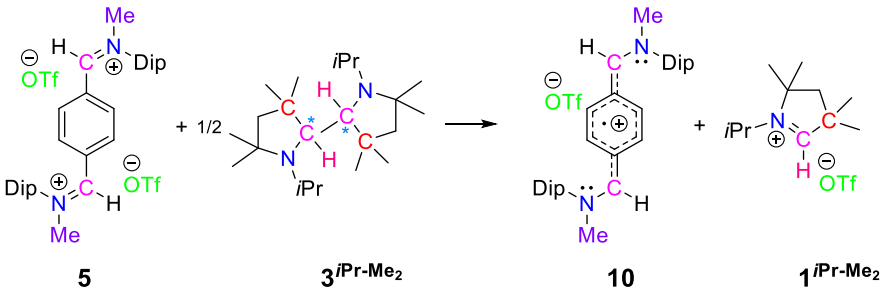



**Fig. S30** $^1$H NMR spectrum of $\mathbf{1}^{tBu\text{-}Me_2}$ in $CDCl_3$ at room temperature.

**Reaction of 5 and 3$^{i\text{Pr-Me}_2}$**




**5** **3$^{i\text{Pr-Me}_2}$** **10** **1$^{i\text{Pr-Me}_2}$**

Compound **3$^{i\text{Pr-Me}_2}$** (4 mg, 0.01 mmol) was added to a vial containing a colourless solution of **5** (20 mg, 0.026 mmol) in about 4 mL of $CH_3CN$ at room temperature. Immediately, an intense deep green colour appeared and the UV/Vis spectrum of the reaction solution confirms the formation of **10**.[S5]

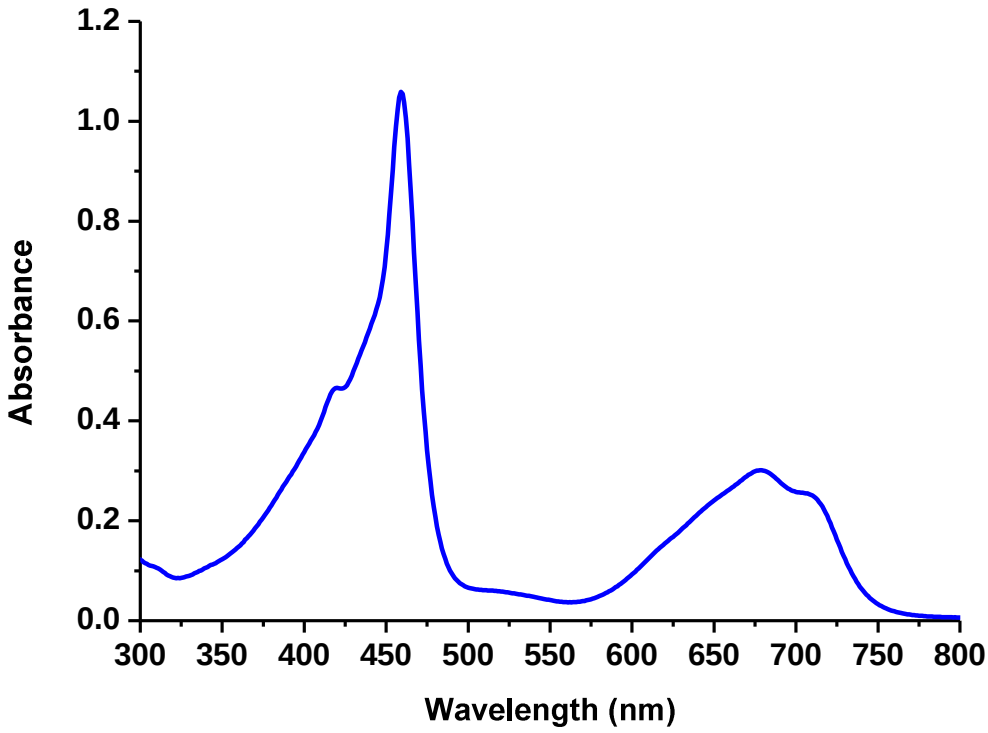
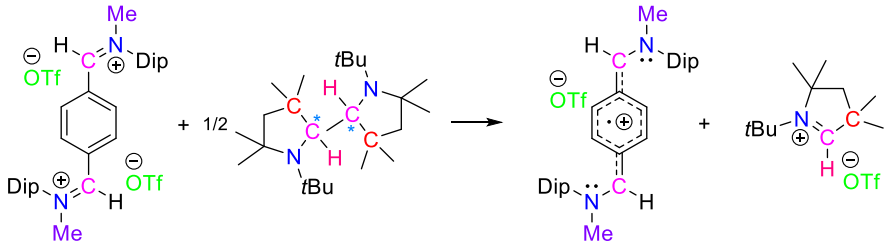



**Fig. S31** UV/Vis spectrum of **10**, obtained from the reaction between **5** and **3$^{i\text{Pr-Me}_2}$** in acetonitrile at room temperature.

**Reaction of 5 and $3^{tBu\text{-}Me_2}$**




**5** **$3^{tBu\text{-}Me_2}$** **10** **$1^{tBu\text{-}Me_2}$**

Compound **$3^{tBu\text{-}Me_2}$** (5 mg, 0.01 mmol) was added to a vial containing a colourless solution of **5** (20 mg, 0.026 mmol) in about 4 mL of $CH_3CN$ at room temperature. Immediately, an intense deep green colour appeared and the UV/Vis spectrum of the reaction solution confirms the formation of **10**.[S5]

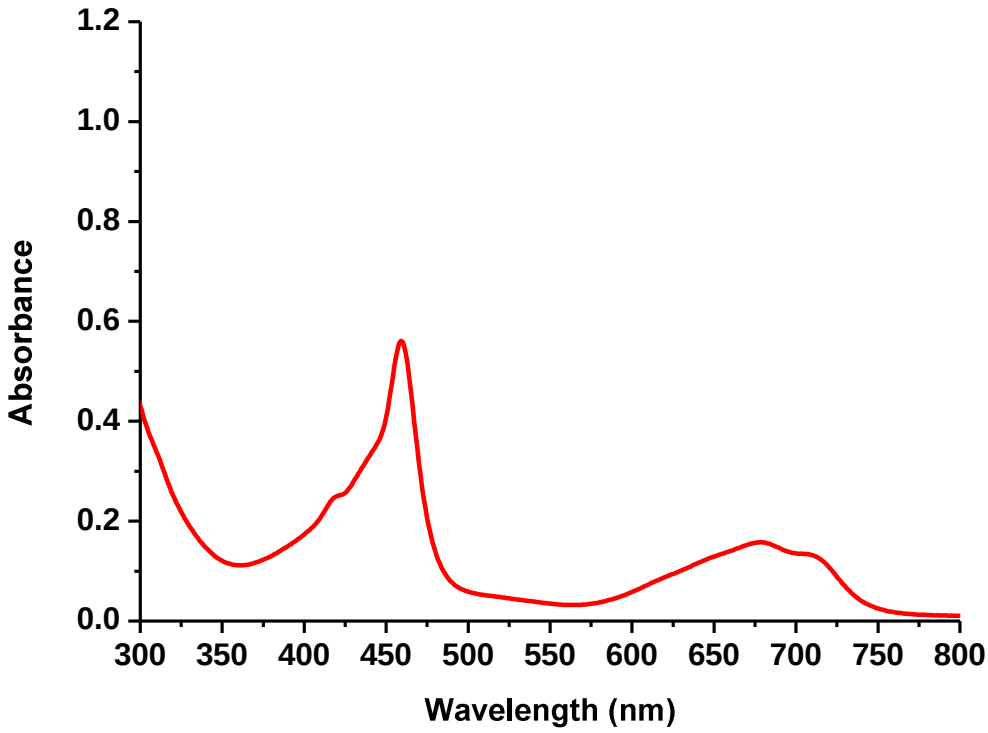
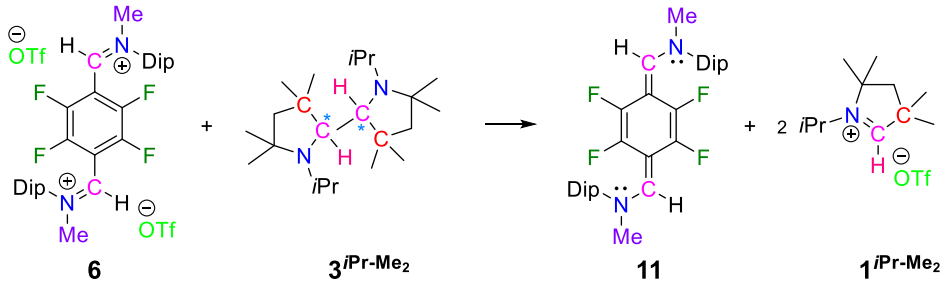



**Fig. S32** UV/Vis spectrum of **10**, obtained from the reaction between **5** and **$3^{tBu\text{-}Me_2}$** in acetonitrile at room temperature.

**Reaction of 6 and 3$^{i\text{Pr-Me}_2}$**




**6** **3$^{i\text{Pr-Me}_2}$** **11** **1$^{i\text{Pr-Me}_2}$**

About 1 mL of $CH_3CN$ was added to a vial containing a mixture of **6** (27 mg, 0.032 mmol) and **3$^{i\text{Pr-Me}_2}$** (12 mg, 0.036 mmol) at room temperature. The colour of the solution initially became intense deep green and changed to yellow after 15 minutes of sonication. The $^1$H NMR spectrum of the crude reaction mixture indicates the formation of **11**.[S6]

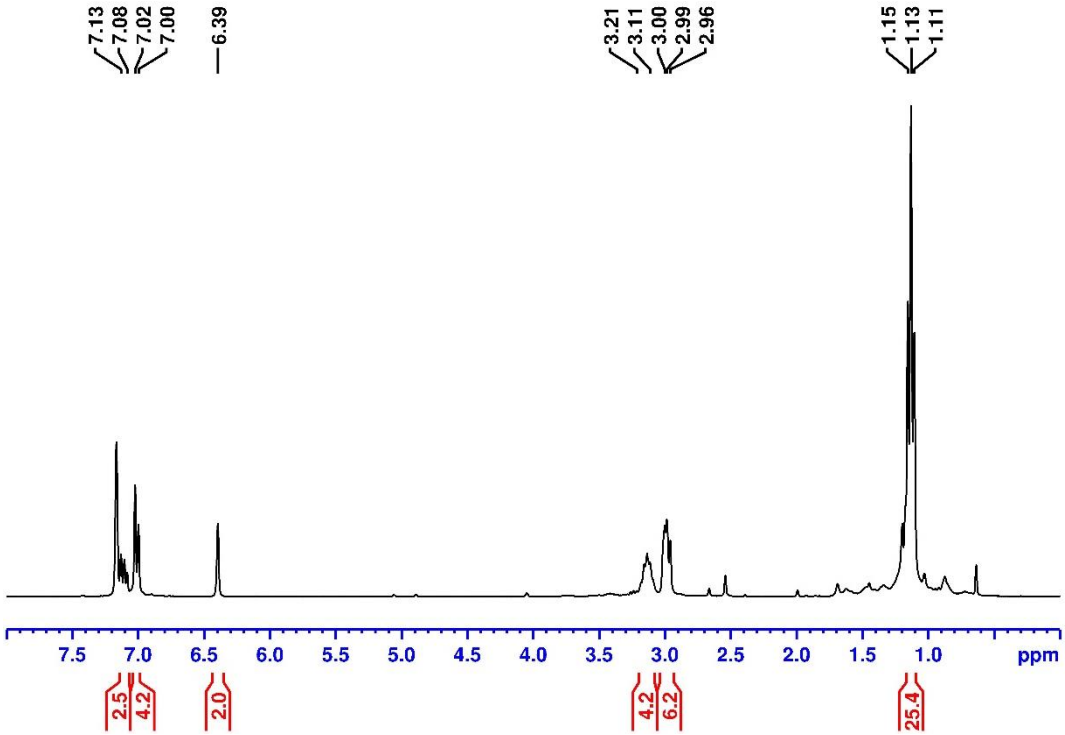
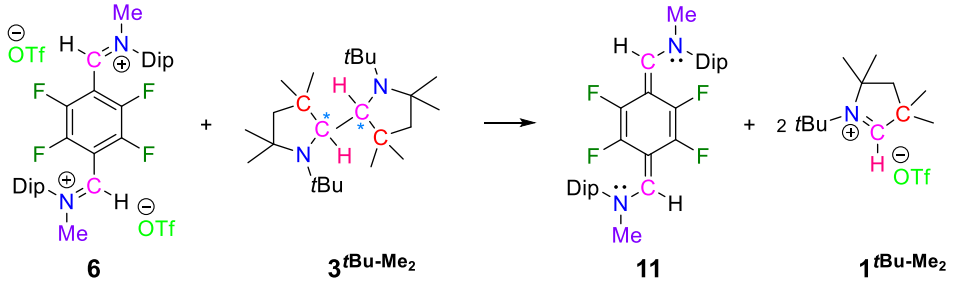



**Fig. S33** $^1$H NMR spectrum of **11** obtained from the crude reaction mixture between **6** and **3$^{i\text{Pr-Me}_2}$** in $C_6D_6$ at room temperature.

**Reaction of 6 and 3$^{tBu\text{-}Me_2}$**




**6** **3$^{tBu\text{-}Me_2}$** **11** **1$^{tBu\text{-}Me_2}$**

About 1 mL of $CH_3CN$ was added to a vial containing a mixture of **6** (27 mg, 0.032 mmol) and **3$^{tBu\text{-}Me_2}$** (13 mg, 0.036 mmol) at room temperature. The colour of the solution initially became intense deep green and changed to yellow after 15 minutes of sonication. The $^1$H NMR spectrum of the crude reaction mixture indicates the formation of **11**.[S6]

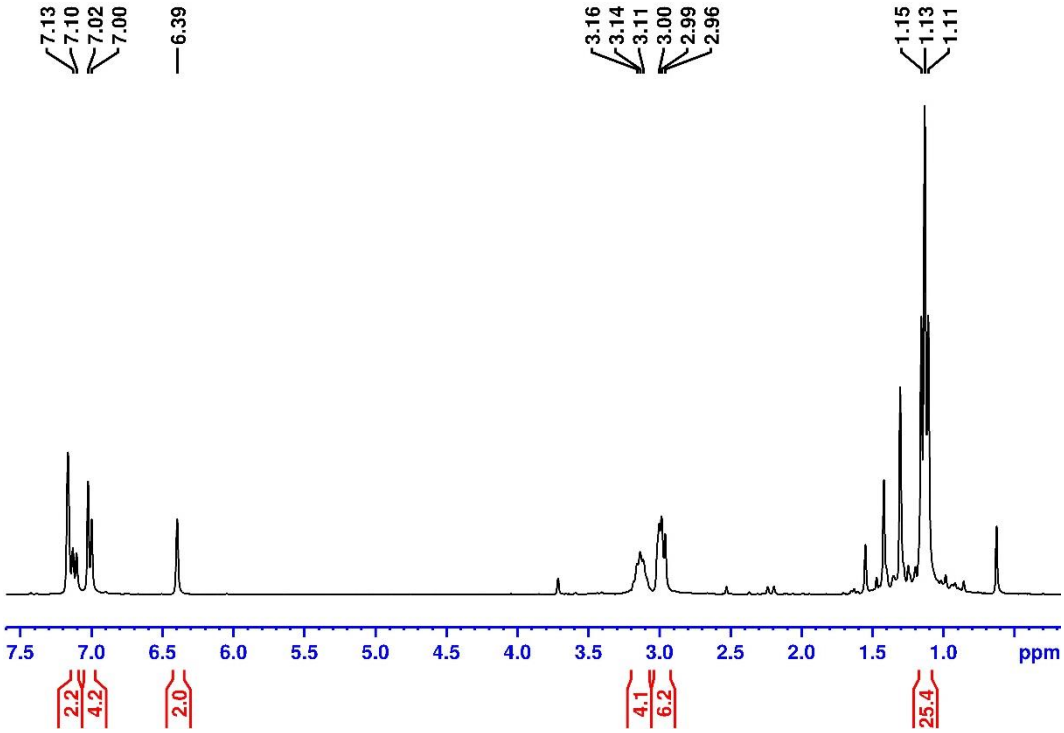
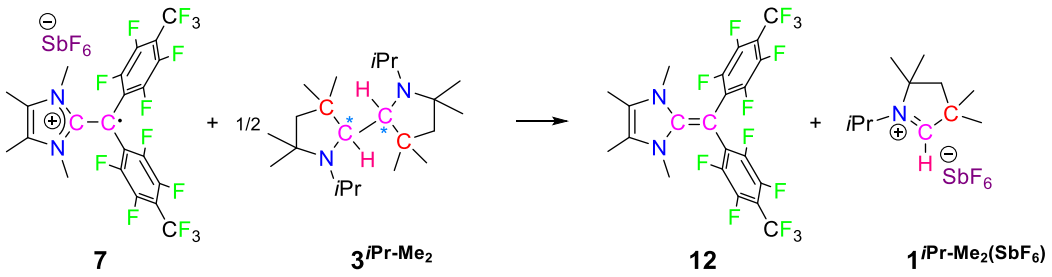



**Fig. S34** $^1$H NMR spectrum of **11** obtained from the crude reaction mixture between **6** and **3$^{tBu\text{-}Me_2}$** in $C_6D_6$ at room temperature.

**Reaction of 7 and 3$^{i\text{Pr-Me}_2}$**




**7** **3$^{i\text{Pr-Me}_2}$** **12** **1$^{i\text{Pr-Me}_2(SbF_6)}$**

About 1 mL $CH_3CN$ was added into the NMR tube containing radical cation **7** (24 mg, 0.030 mmol) and **3$^{i\text{Pr-Me}_2}$** (5 mg, 0.02 mmol) at room temperature. The solution became intense deep blue coloured and then the reaction mixture was shaken for 5 minutes. The colour of solution changed from intense deep blue to yellow coloured. The solvent was evaporated and a $^1$H NMR spectrum of the reaction mixture was measured which showed the formation of **12**.[S7]

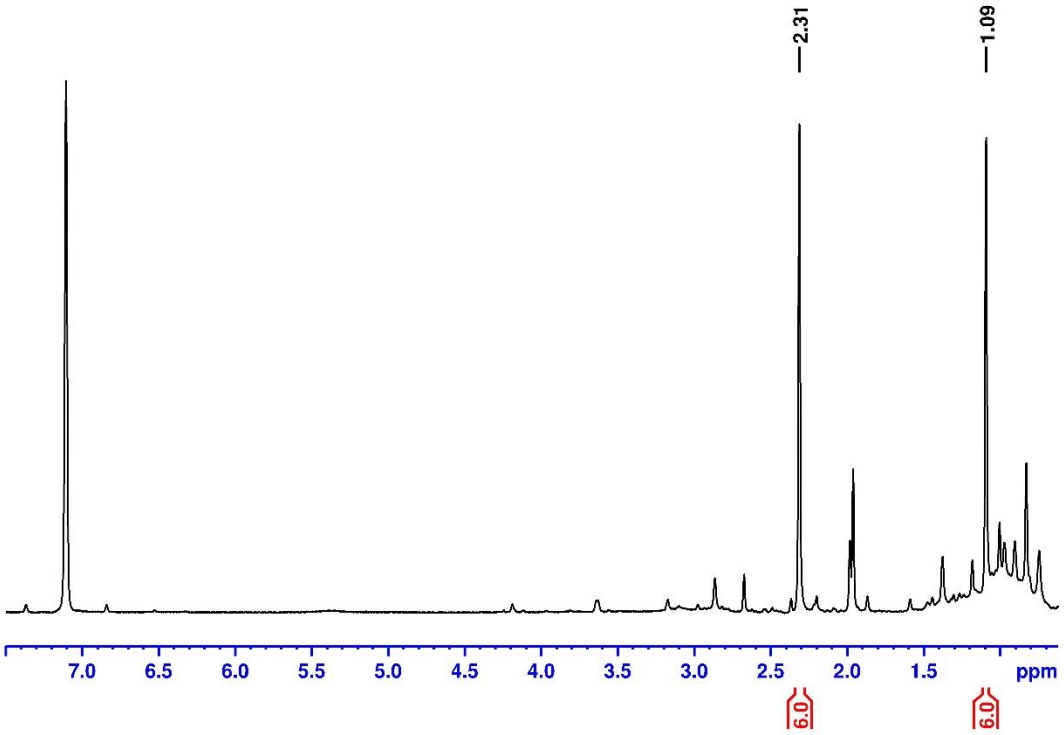
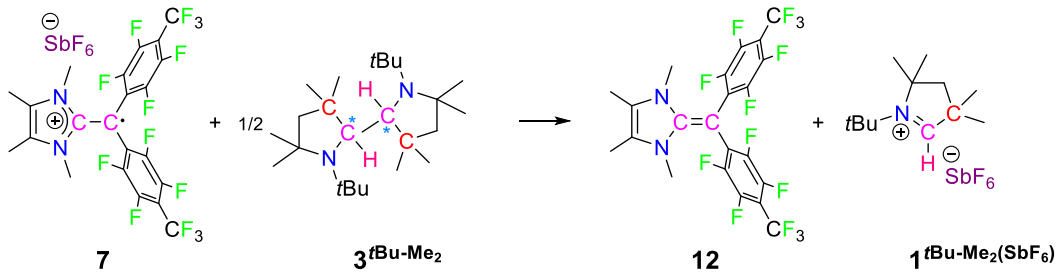



**Fig. S35** $^1$H NMR spectrum of the crude reaction mixture of **7** and **3$^{i\text{Pr-Me}_2}$** in $C_6D_6$ at room temperature showing the formation of **12**.

**Reaction of 7 and $3^{tBu\text{-}Me_2}$**




**7** $\quad$ $\mathbf{3}^{tBu\text{-}Me_2}$ $\quad$ **12** $\quad$ $\mathbf{1}^{tBu\text{-}Me_2(SbF_6)}$

About 1 mL $CH_3CN$ was added to the NMR tube containing radical cation **7** (24 mg, 0.030 mmol) and $\mathbf{3}^{tBu\text{-}Me_2}$ (6 mg, 0.02 mmol) at room temperature. The solution became intense deep blue coloured and then the reaction mixture was shaken for 5 minutes. The colour of solution changed from intense deep blue to yellow coloured. The solvent was evaporated and a $^1$H NMR spectrum of the reaction mixture was measured which showed the formation of **12**.[S7]

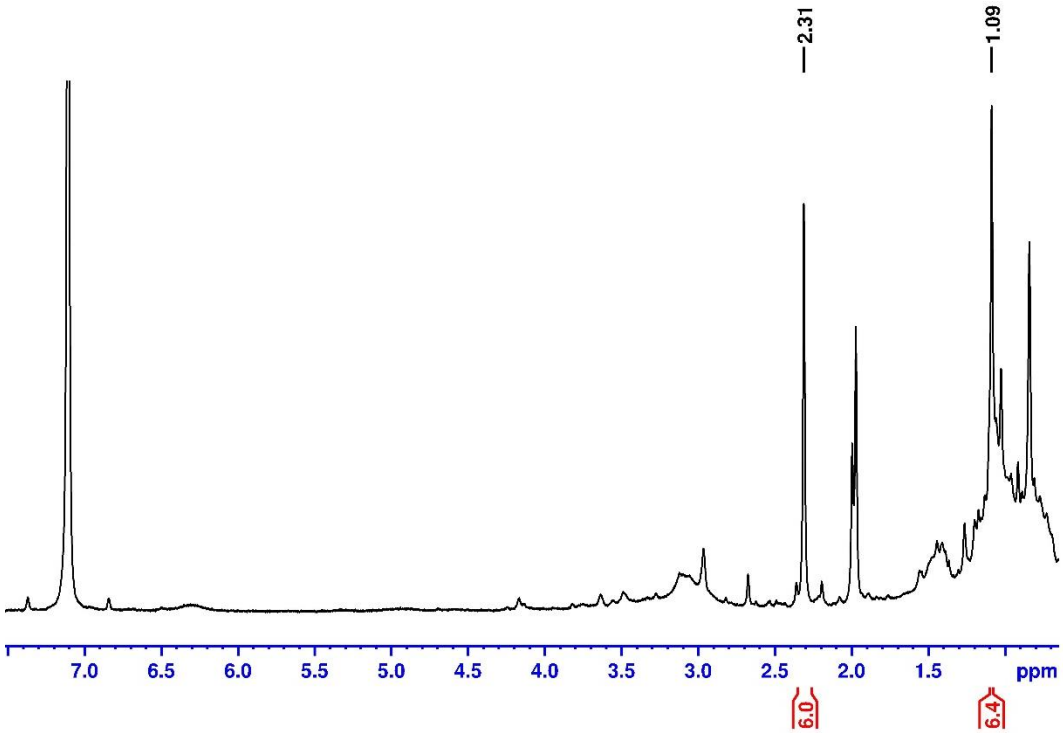
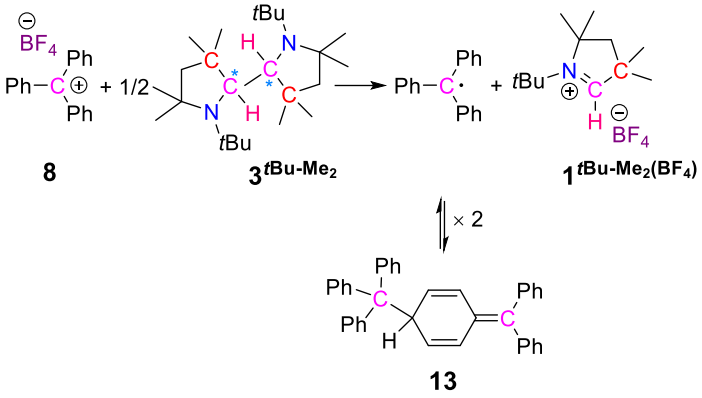



**Fig. S36** $^1$H NMR spectrum of the crude reaction mixture of **7** and $\mathbf{3}^{tBu\text{-}Me_2}$ in $C_6D_6$ at room temperature showing the formation of **12**.

**Reduction of 8 using 3$^{tBu\text{-}Me_2}$ under Inert Atmosphere**




About 2 mL of dry $CH_3CN$ was added to the mixture of **8** (50 mg, 0.15 mmol) and **3**$^{tBu\text{-}Me_2}$ (27 mg, 0.074 mmol) at room temperature. After stirring the reaction mixture at room temperature for 24 hours all volatiles were removed under vacuum and the $^1$H NMR of the residue was measured using $C_6D_6$, indicating the formation of **13**.[S9] Compound **13** was isolated from the residue by crystallisation using $CH_3CN$ at −30 °C (colourless crystals of **13** were obtained after 24 hrs. Due to the high solubility of **1**$^{tBu\text{-}Me_2\,(BF_4)}$ it remains in the mother liquor). **Yield of crystals:** 25 mg (69 %).

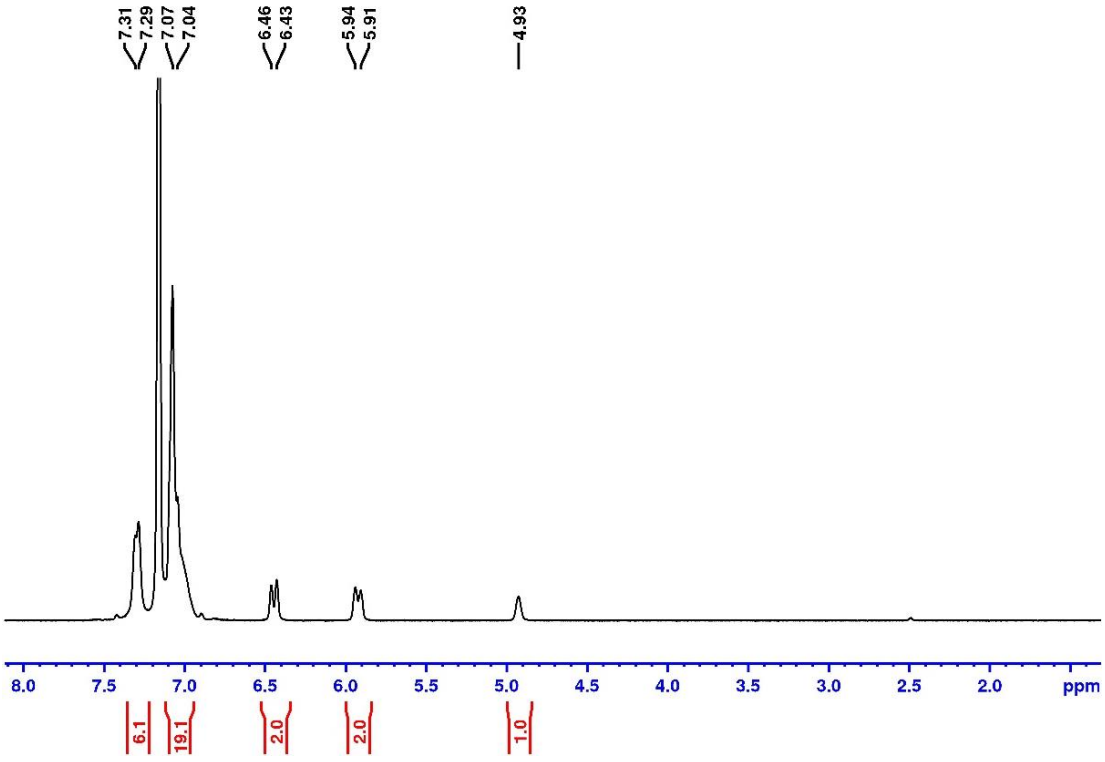



**Fig. S37** $^1$H NMR spectrum from crystalline sample of **13** in $C_6D_6$ at room temperature.

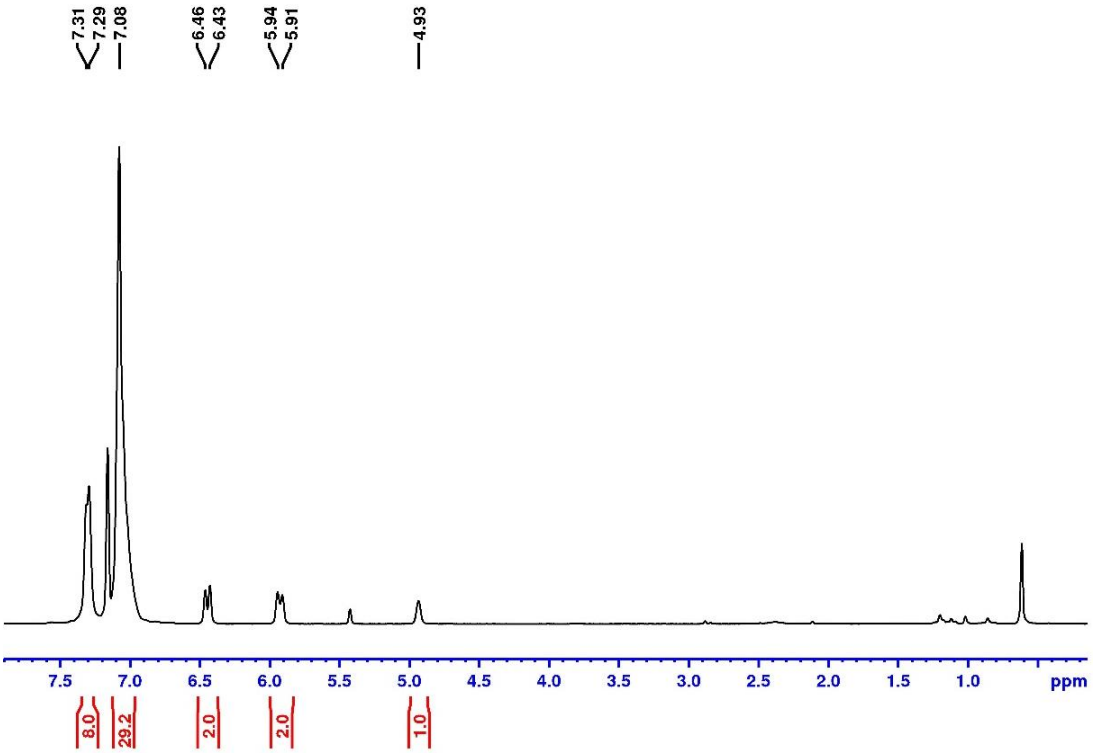
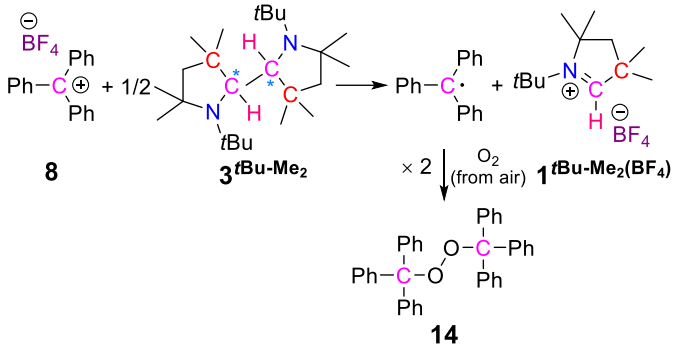



**Fig. S38** $^{1}$H NMR spectrum of **13** from the crude reaction mixture of **8** and **3**$^{t\text{Bu-Me}_2}$ in $C_6D_6$ at room temperature.

**Reduction of 8 using $3^{tBu\text{-}Me_2}$ under open atmosphere(!)**




**8** **$3^{tBu\text{-}Me_2}$** **$1^{tBu\text{-}Me_2(BF_4)}$** **14**

About 2 mL of dry $CH_3CN$ was added to the mixture of **8** (60 mg, 0.18 mmol) and **$3^{tBu\text{-}Me_2}$** (31 mg, 0.085 mmol) at room temperature. After 5 minutes, using a glass pipette, air was bubbled into the reaction solution; immediately colourless crystals of **14** started to appear. After 6 hours colourless crystals of **14** were collected. Single crystal X-ray diffraction data indicate the formation of **14**. Unit Cell Parameters: a = 8.8490(18), b = 9.0684(18), c = 10.784(2), α = 112.95(3), β = 91.52(3), ϒ = 115.49(3), and V = 699.4(4); this matched the previously reported crystal data[S10] and therefore we are not reporting the structure here. **Yield:** 30 mg (68 %). **$^1$H NMR ($C_6D_6$, 25 °C, 300 MHz):** $\delta$ = 7.36-7.38 (m, 12H), 7.02-7.03 (m, 18H) ppm.

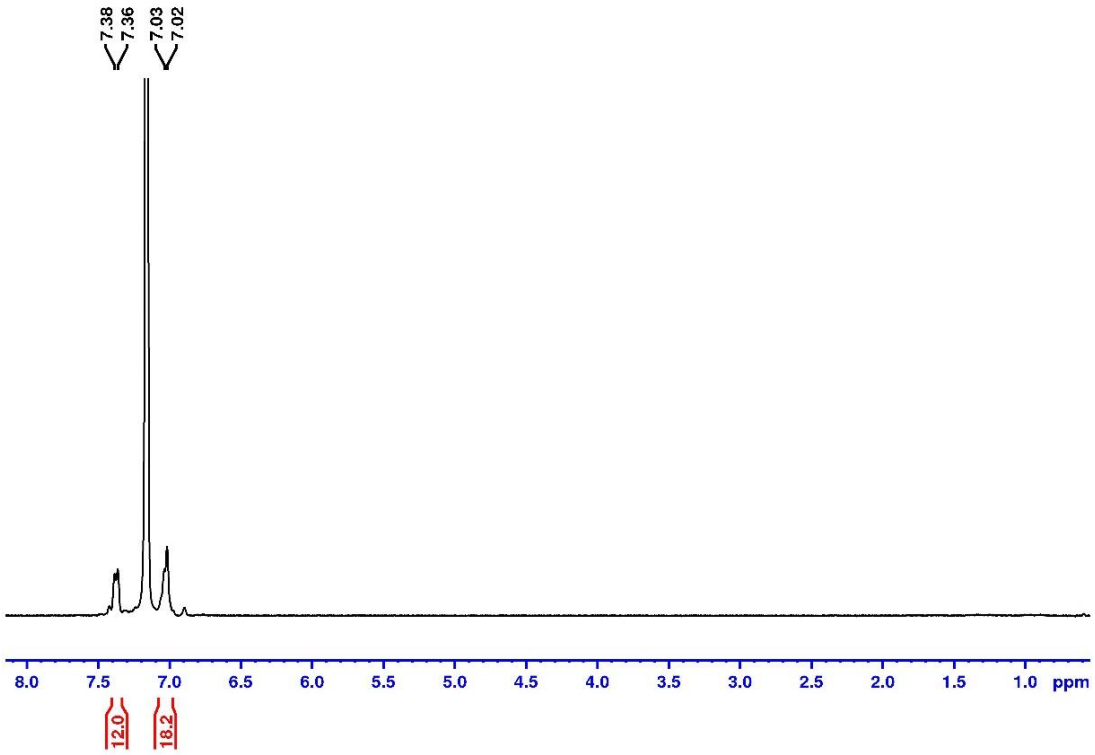



**Fig. S39** $^1$H NMR spectrum of **14** in $C_6D_6$ at room temperature.

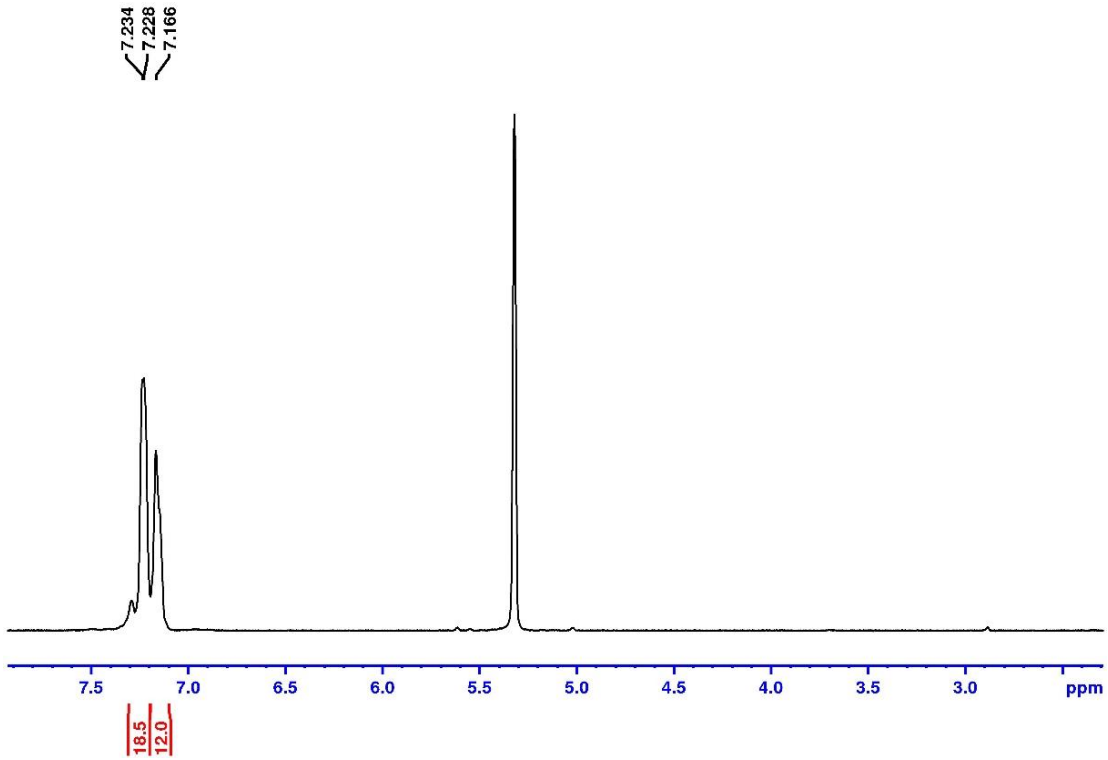
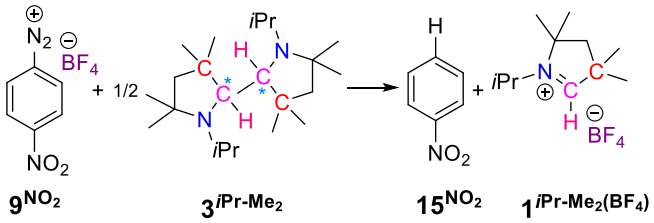



**Fig. S40** $^{1}$H NMR spectrum of **14** in $CD_2Cl_2$ at room temperature.

**Reduction of $9^{NO_2}$ using $3^{iPr\text{-}Me_2}$**




About 2 mL of dry $CH_3CN$ was added to the mixture of $\mathbf{9^{NO_2}}$ (25 mg, 0.11 mmol) and $\mathbf{3^{iPr\text{-}Me_2}}$ (20 mg, 0.059 mmol) at room temperature. The colour of the reaction mixture became red. The reaction mixture was sonicated for 5 minutes and subsequently stirred for 6 hrs. After that, all the volatiles were removed under vacuum and the $^1$H NMR spectrum of the crude reaction mixture indicates the formation of $\mathbf{15^{NO_2}}$.[S11] **$^1$H NMR** of reaction mixture ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 7.80 (d, 2H, $^3J_{H\text{-}H}$ = 7.6 Hz, Ar-*H*), 6.90 (t, 1H, $^3J_{H\text{-}H}$ = 7.2 Hz, Ar-*H*), 6.73 (t, 2H, $^3J_{H\text{-}H}$ = 7.6 Hz, Ar-*H*) ppm.

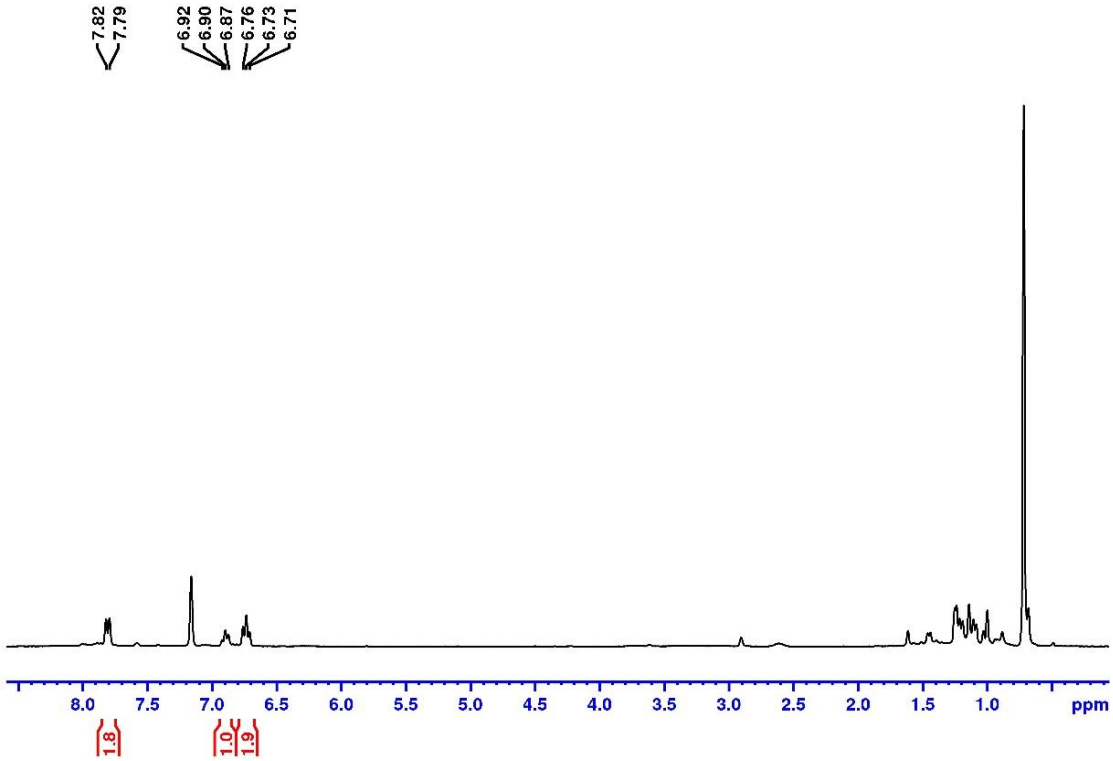
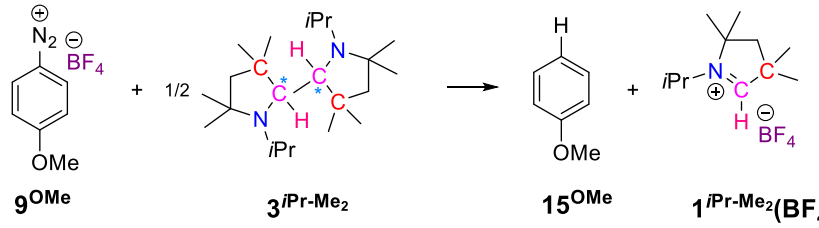



**Fig. S41** $^1$H NMR spectrum from the crude reaction mixture of **9** and $\mathbf{3^{iPr\text{-}Me_2}}$ in $C_6D_6$ at room temperature, indicating the formation $\mathbf{15^{NO_2}}$.

**Reduction of $9^{OMe}$ using $3^{iPr\text{-}Me_2}$**




$9^{OMe}$ $3^{iPr\text{-}Me_2}$ $15^{OMe}$ $1^{iPr\text{-}Me_2}(BF_4)$

About 2 mL of dry $CH_3CN$ was added to the mixture of $9^{OMe}$ (15 mg, 0.067 mmol) and $3^{iPr\text{-}Me_2}$ (10 mg, 0.030 mmol) at room temperature. The colour of the reaction mixture became red from colourless. The reaction mixture was sonicated for 2 minutes and subsequently stirred for 24 hrs at room temperature. After that all the volatiles were removed under vacuum and the $^1$H NMR spectrum of the crude reaction mixture indicates the formation of $15^{OM}$.[S12] **$^1$H NMR** of reaction mixture ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 7.10-7.12 (m, 2H, Ar-*H*), 6.79-6.90 (m, 3H, Ar-*H*), 3.30 (s, 3H, OC*H*$_3$) ppm.

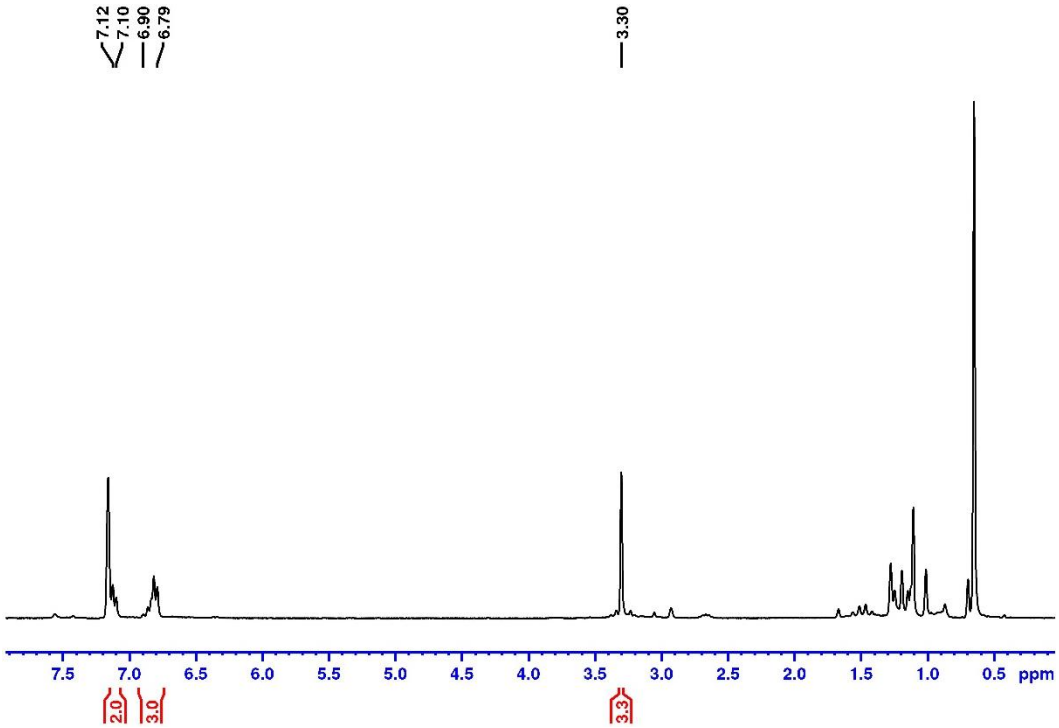
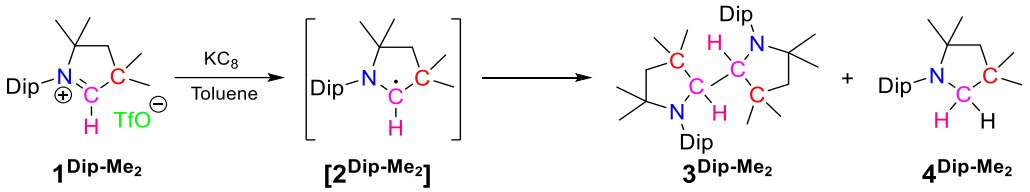



**Fig. S42** $^1$H NMR spectrum from the crude reaction mixture of $9^{OMe}$ and $3^{iPr\text{-}Me_2}$ in $C_6D_6$ at room temperature, indicating the formation $15^{OMe}$.

**Reduction of $1^{Dip\text{-}Me_2}$**




$1^{Dip\text{-}Me_2}$ $[2^{Dip\text{-}Me_2}]$ $3^{Dip\text{-}Me_2}$ $4^{Dip\text{-}Me_2}$

Toluene (40 mL) was added to a mixture of $\mathbf{1}^{Dip\text{-}Me_2}$ (1.000 g, 2.296 mmol) and $KC_8$ (466 mg, 3.45 mmol) at −78 °C (or at room temperature) and stirred for 12 hours at room temperature. The mixture was filtered and the volatiles were evaporated under reduced pressure to obtain the product as colourless solid compound. The $^1$H NMR spectrum of the crude residue in $C_6D_6$ shows the presence of two isomers of $\mathbf{3}^{Dip\text{-}Me_2}$ along with $\mathbf{4}^{Dip\text{-}Me_2}$ and some unidentified compounds. The compound was purified by fractional crystallisation. The solid compound was dissolved in hexane (4 mL) and then concentrated by evaporation and kept for crystallisation at room temperature for 2 days. Colourless crystals were obtained that were suitable for a single-crystal X-ray diffraction study. Then the obtained crystals were washed with a small amount (0.5 mL) of pentane. The $^1$H NMR spectrum of the resulting crystalline compounds in $C_6D_6$ show the presence of mainly two isomers of $\mathbf{3}^{Dip\text{-}Me_2}$ and some other unidentified compound in traces (< 5%). The ratios of isomers were different in different fractions of crystals. In the mother liquor there was $\mathbf{4}^{Dip\text{-}Me_2}$ present (subsequently we prepared $\mathbf{4}^{Dip\text{-}Me_2}$ as a pure compound in a different route from $\mathbf{1}^{Dip\text{-}Me_2}$ using $LiAlH_4$, please see below) and unidentified products as in the crude reaction mixture. **Yield** (Purity > 95%): 210 mg (32%). The pure compound $\mathbf{3}^{Dip\text{-}Me_2}$ was also crystallised by evaporating its pentane-methanol solution. The compound was dissolved in pentane and then methanol was added to it. This solution was exposed to air for slow evaporation. After 1 hour, colourless crystals of $\mathbf{3}^{Dip\text{-}Me_2}$ were obtained. $^1$H NMR signals of the isomers were assigned by considering 2-D and other NMR measurements along with peak integrations of crystals obtained in different fractions of crystallisation.

**$^1$H NMR** of major isomer ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 7.04–7.11 (m, 4H, Ar-*H*), 6.96–6.98 (m, 2H, Ar-*H*), 4.06 (s, 2H, C*H*), 3.82 (sep, 2H, $^3J_{H\text{-}H}$ = 6.5 Hz, C*H*($CH_3$)$_2$), 3.40 (sep, 2H, $^3J_{H\text{-}H}$ = 6.3 Hz, C*H*($CH_3$)$_2$), 2.47 (d, 2H, $^2J_{H\text{-}H}$ = 12.9 Hz, C*H*$_2$), 1.79 (s, 6H, C*H*$_3$), 1.75 (s, 6H, C*H*$_3$), 1.59 (d, 2H, $^2J_{H\text{-}H}$ = 12.9 Hz, C*H*$_2$), 1.42 (d, 6H, $^3J_{H\text{-}H}$ = 6.5 Hz, HC(C*H*$_3$)$_2$), 1.37 (d, 6H, $^3J_{H\text{-}H}$ = 6.6 Hz, HC(C*H*$_3$)$_2$), 1.25 (s, 6H, C*H*$_3$), 1.13 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz, HC(C*H*$_3$)$_2$), 0.98 (s, 6H, C*H*$_3$), 0.28 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz, HC(C*H*$_3$)$_2$) ppm. **$^1$H NMR** of minor isomer ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 7.60 (t, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, Ar-*H*), 7.09–7.11 (m, 4H, Ar-*H*), 4.38 (s, 2H, C*H*), 4.37 (sep, 2H, $^3J_{H\text{-}H}$ = 6.8 Hz, C*H*($CH_3$)$_2$), 3.60 (sep, 2H, $^3J_{H\text{-}H}$ = 6.7 Hz, C*H*($CH_3$)$_2$), 2.14 (d, 2H, $^2J_{H\text{-}H}$ = 13.0 Hz, C*H*$_2$), 1.66 (d, 6H, $^3J_{H\text{-}H}$ = 6.9 Hz, HC(C*H*$_3$)$_2$), 1.60 (d, 2H, $^2J_{H\text{-}H}$ = 13.0 Hz, C*H*$_2$), 1.45 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz, HC(C*H*$_3$)$_2$), 1.33 (d, 6H, $^3J_{H\text{-}H}$ = 6.8 Hz, HC(C*H*$_3$)$_2$), 1.16 (d, 6H, $^3J_{H\text{-}H}$ = 8.2 Hz, HC(C*H*$_3$)$_2$), 1.02 (s, 6H, C*H*$_3$), 0.98 (s, 6H, C*H*$_3$), 0.92 (s, 6H, C*H*$_3$), 0.72 (s, 6H, C*H*$_3$) ppm. **$^{13}$C{$^1$H} NMR** of the major and the minor isomers ($C_6D_6$, 25 °C, 75.4 MHz): $\delta$ = 154.2 (Ar-*C*), 151.5 (Ar-*C*), 151.1 (Ar-*C*), 150.6 (Ar-*C*), 150.2 (Ar-*C*), 147.8 (Ar-*C*), 147.2 (Ar-*C*), 140.8 (Ar-*C*), 140.4 (Ar-*C*), 129.6 (Ar-*C*), 126.4 (Ar-*C*), 126.2 (Ar-*C*), 126.1 (Ar-*C*), 125.9 (Ar-*C*), 125.8 (Ar-*C*), 125.3 (Ar-*C*), 125.0 (Ar-*C*), 123.7 (Ar-*C*), 87.1 (*C*H), 80.4 (*C*H), 65.6 (*C*($CH_3$)$_2$), 63.0 (*C*($CH_3$)$_2$), 62.1 (*C*($CH_3$)$_2$), 61.7 (*C*H$_2$), 56.0 (*C*H$_2$), 55.9 (*C*H$_2$), 47.2, 42.2, 39.6, 37.3, 37.0, 35.2, 34.9, 33.4, 32.0, 31.8, 31.4, 30.9, 30.6, 29.6, 29.5, 29.4, 29.0, 28.8, 28.1, 28.0, 27.8, 27.62, 27.56, 26.6, 26.4, 25.6, 25.3, 25.2, 24.9, 24.8, 22.7, 21.5 ppm.

**Elemental analysis** (samples prepared using the crystals of $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$)**:** calcd. (%) for $C_{40}H_{64}N_2$: C, 83.85; H, 11.26; N, 4.89; found: C, 83.59; H, 11.51; N, 4.64.

**HRMS-ESI (m/z)** (sample prepared using the crude reaction mixture)**:** Calculated for $C_{40}H_{65}N_2$ $[M+H]^+$: 573.5143, Found: 573.5152 (indicate the formation of $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$).

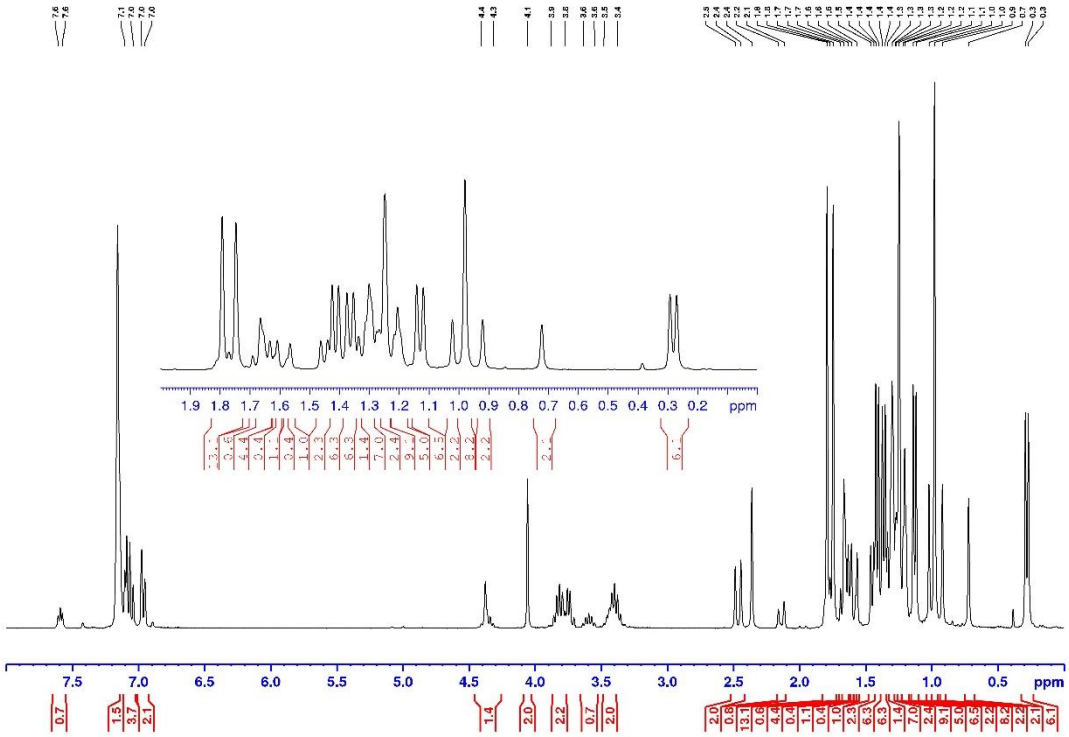



**Fig. S43** $^1$H NMR spectrum of $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$ containing both isomers in significant amounts in $C_6D_6$ at room temperature.

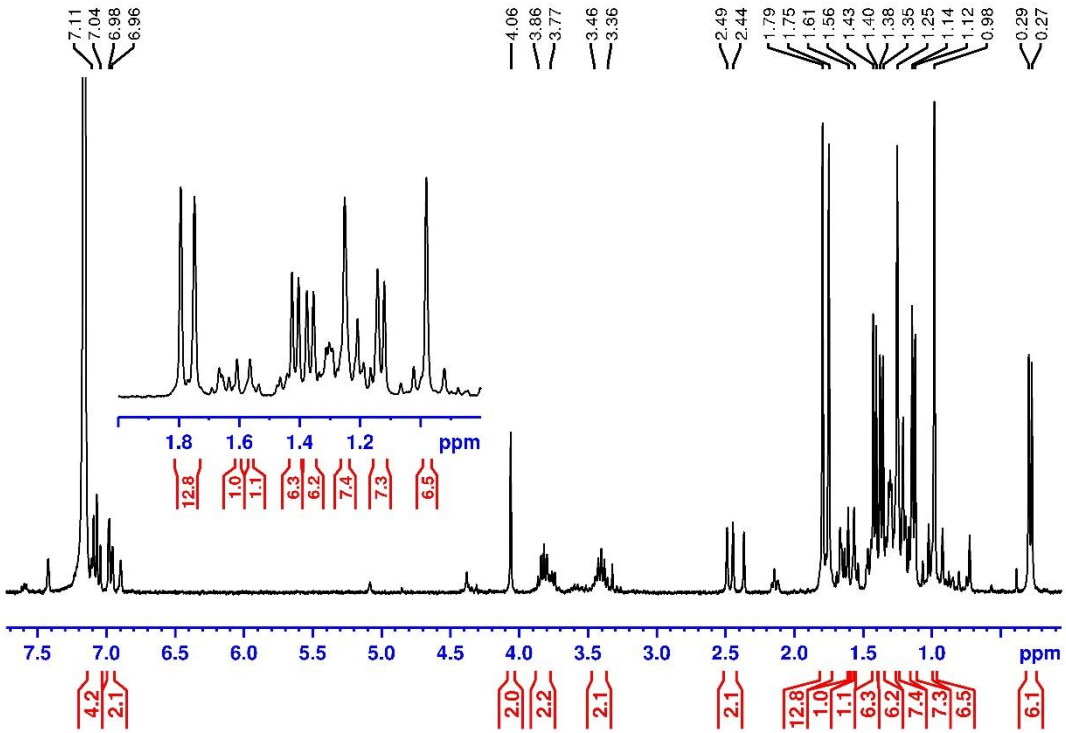


**Fig. S44** $^{1}$H NMR spectrum of $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$ containing significant amount of the major isomer in $C_6D_6$ at room temperature.

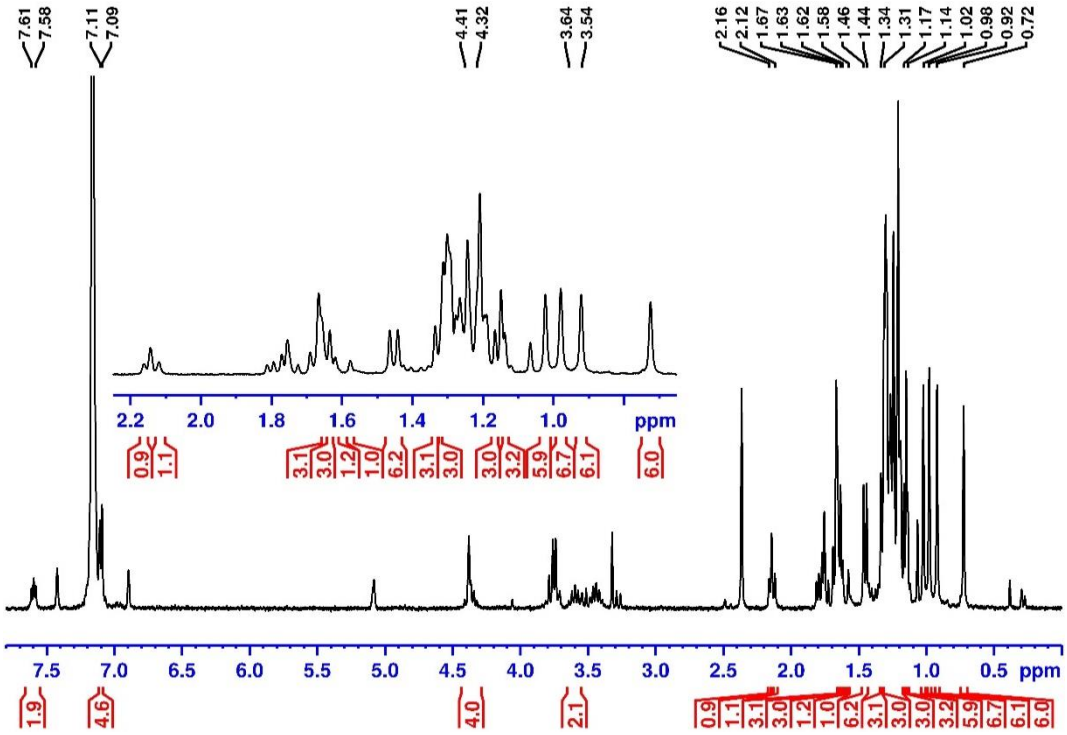


**Fig. S45** $^{1}$H NMR spectrum of $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$ containing significant amount of the minor isomer in $C_6D_6$ at room temperature.

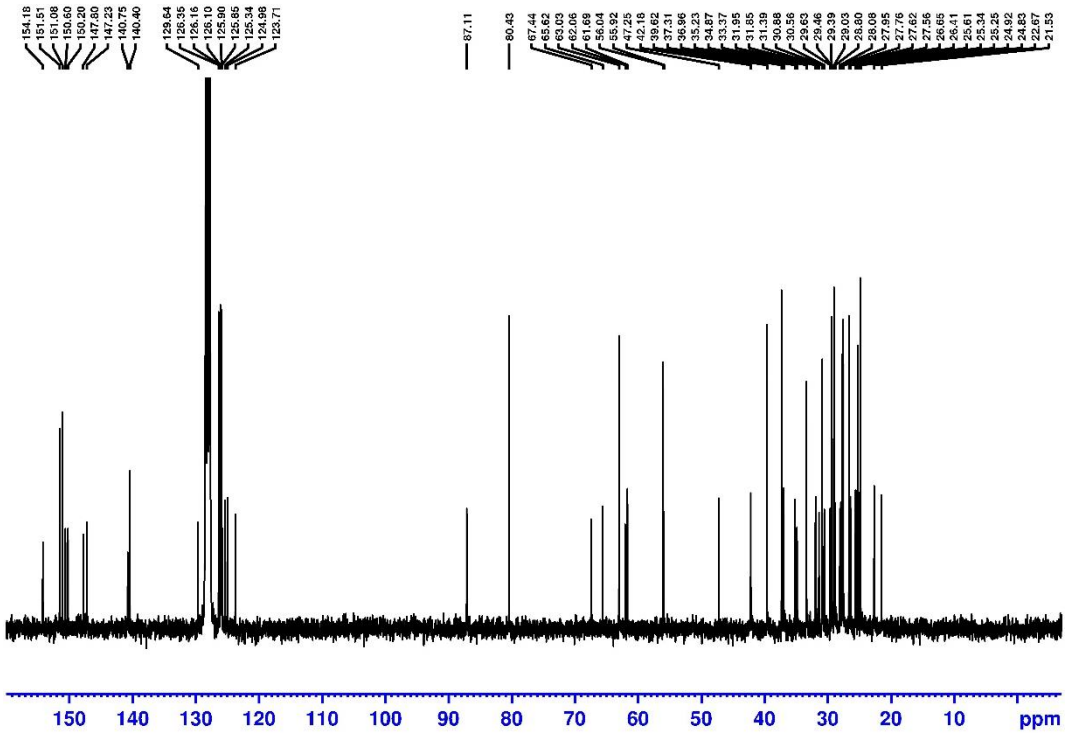



**Fig. S46** $^{13}C\{^{1}H\}$ NMR spectrum of **3**$^{Dip\text{-}Me_2}$ containing both major and minor isomers in $C_6D_6$ at room temperature.

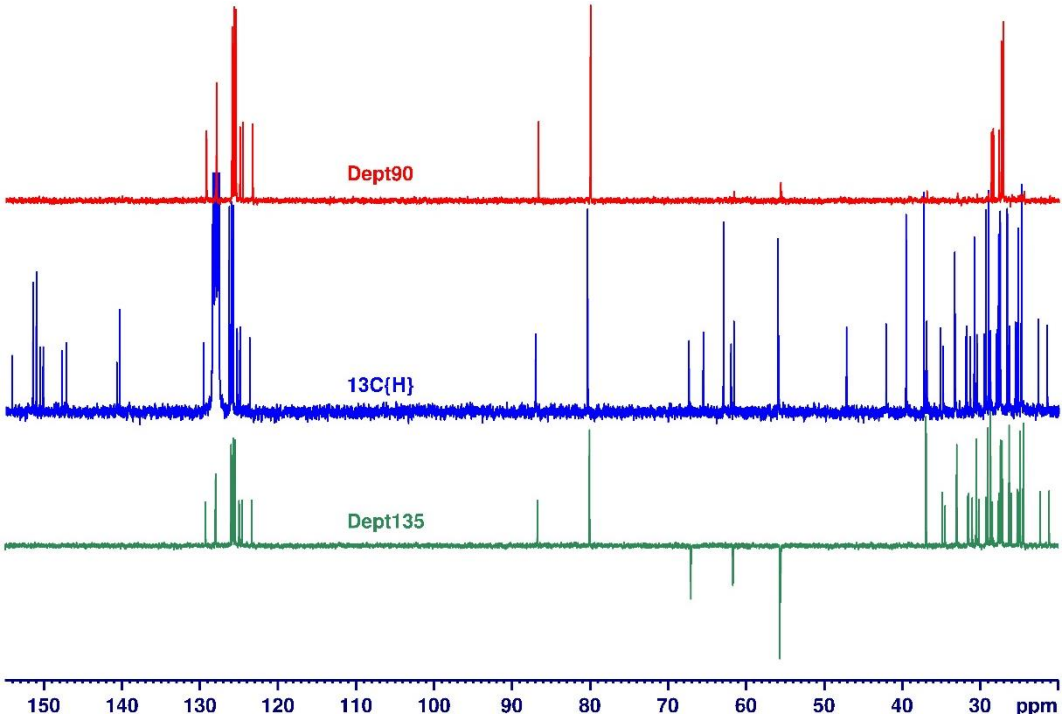



**Fig. S47** Overlap of the $^{13}C\{^{1}H\}$ NMR spectrum of **3**$^{Dip\text{-}Me_2}$ containing both major and minor isomers (blue) along with its corresponding Dept-90 (red) and Dept-135 (green) in $C_6D_6$ at room temperature.

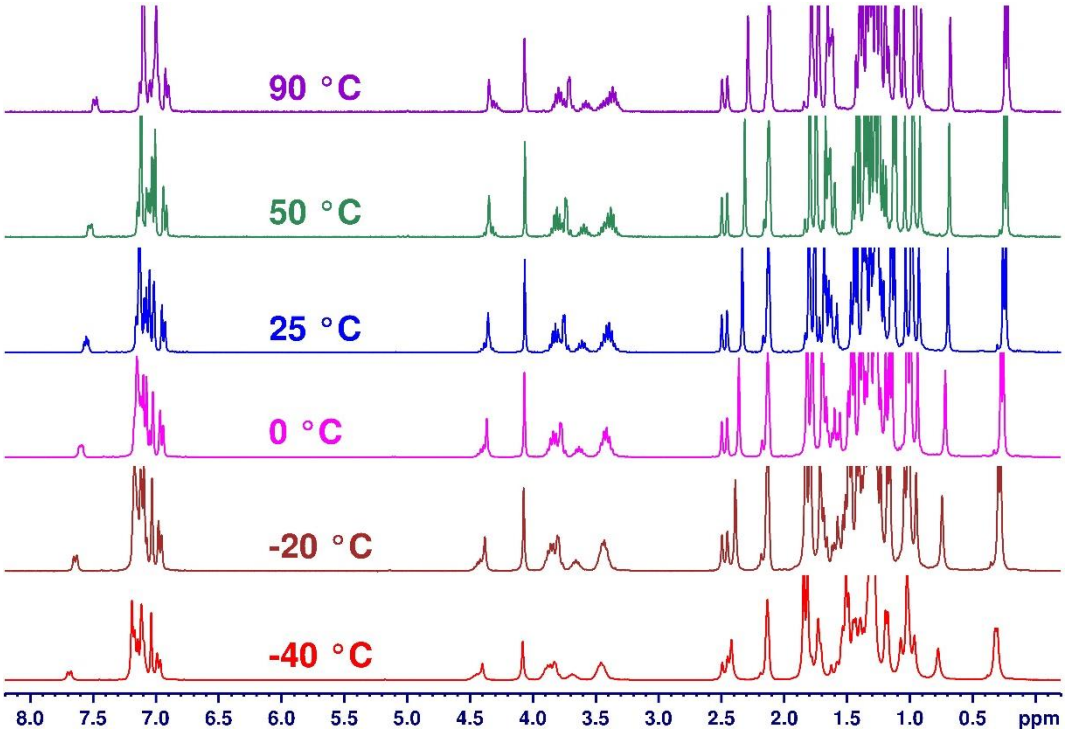



**Fig. S48** VT-$^{1}$H NMR spectra of **3**$^{\text{Dip-Me2}}$ containing both major and minor isomers in toluene-$D_8$.

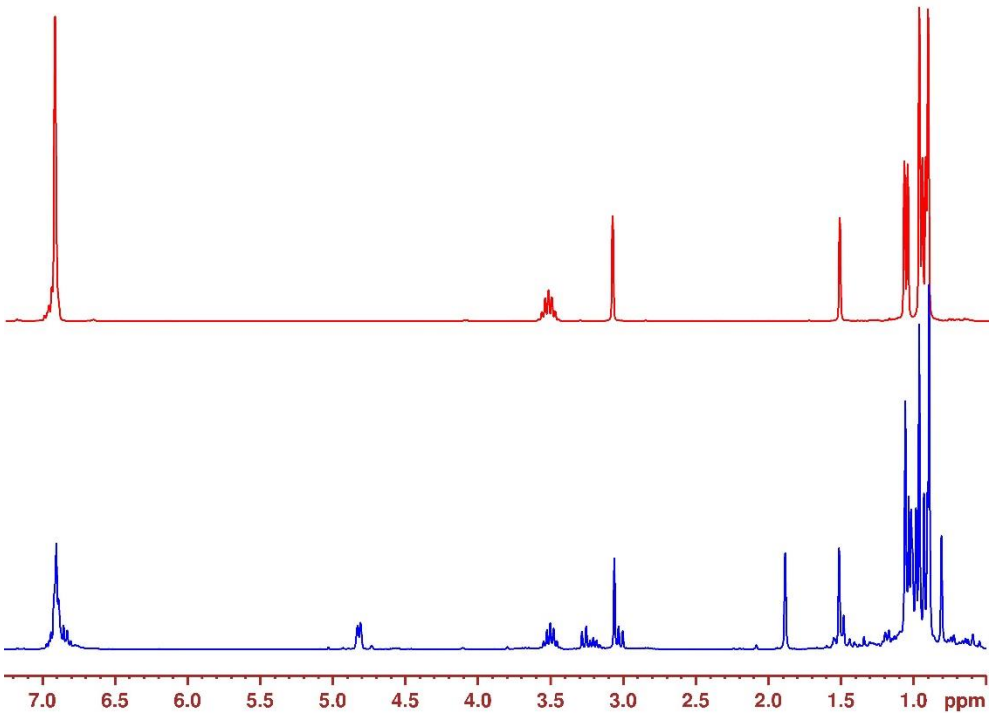



**Fig. S49** Overlap of $^{1}$H NMR spectra of **4**$^{\text{Dip-Me2}}$ of the mother liquor (blue) with hydrogenated product from **1**$^{\text{Dip-Me2}}$ (red) in $C_6D_6$ at room temperature.

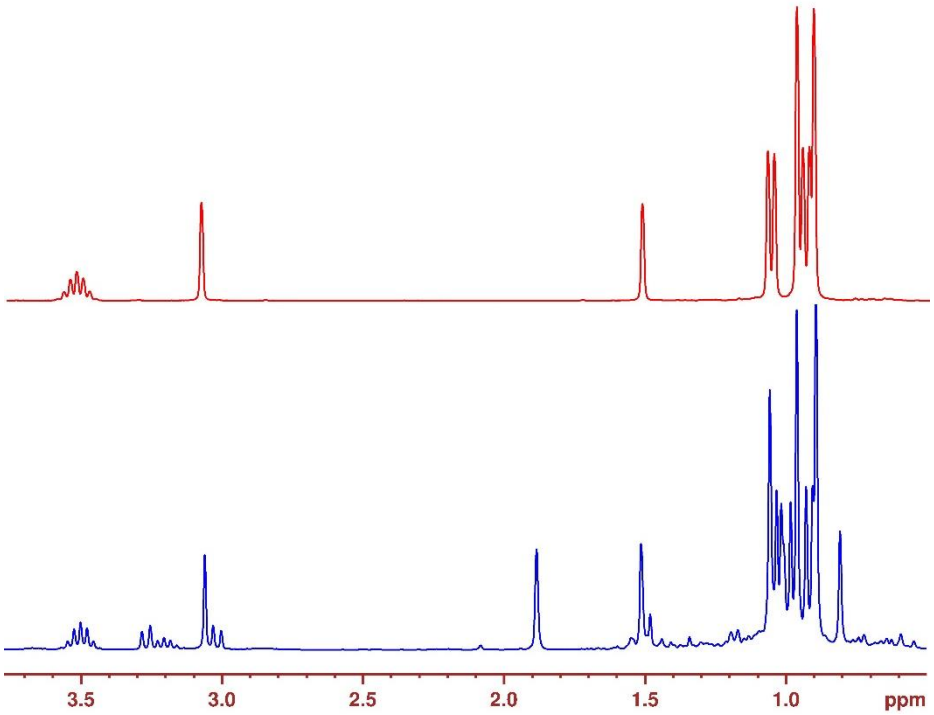



**Fig. S50** Overlap of $^{1}$H NMR spectra of **4**$^{\mathbf{Dip\text{-}Me_2}}$ of the mother liquor (blue) with hydrogenated product from **1**$^{\mathbf{Dip\text{-}Me_2}}$ (red) in $C_6D_6$ at room temperature.

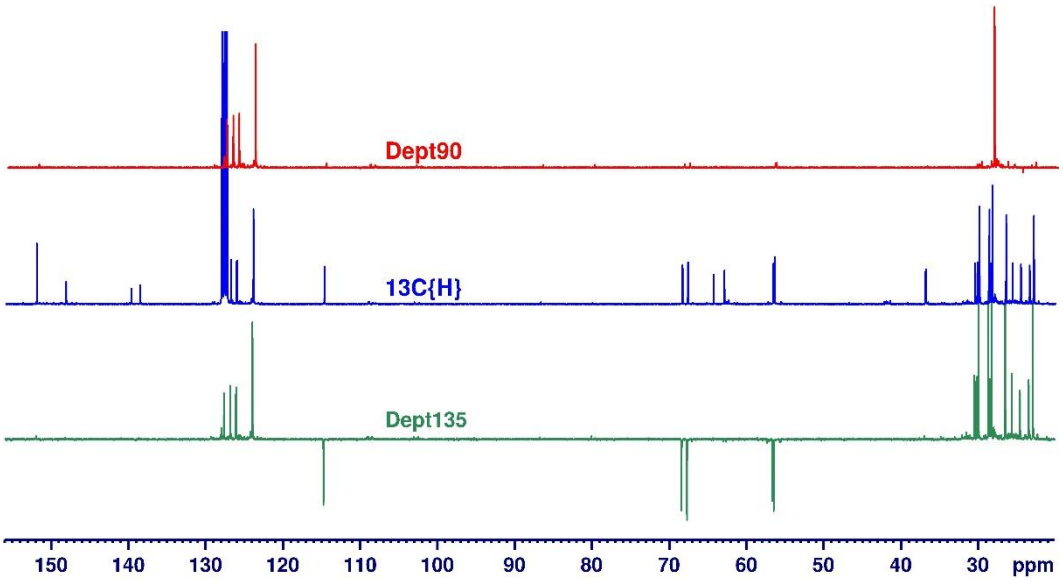



**Fig. S51** Overlap of the $^{13}C\{^{1}H\}$ NMR spectrum of **4**$^{\mathbf{Dip\text{-}Me_2}}$ of the mother liquor (blue) along with its corresponding Dept-90 (red) and Dept-135 (green) in $C_6D_6$ at room temperature.

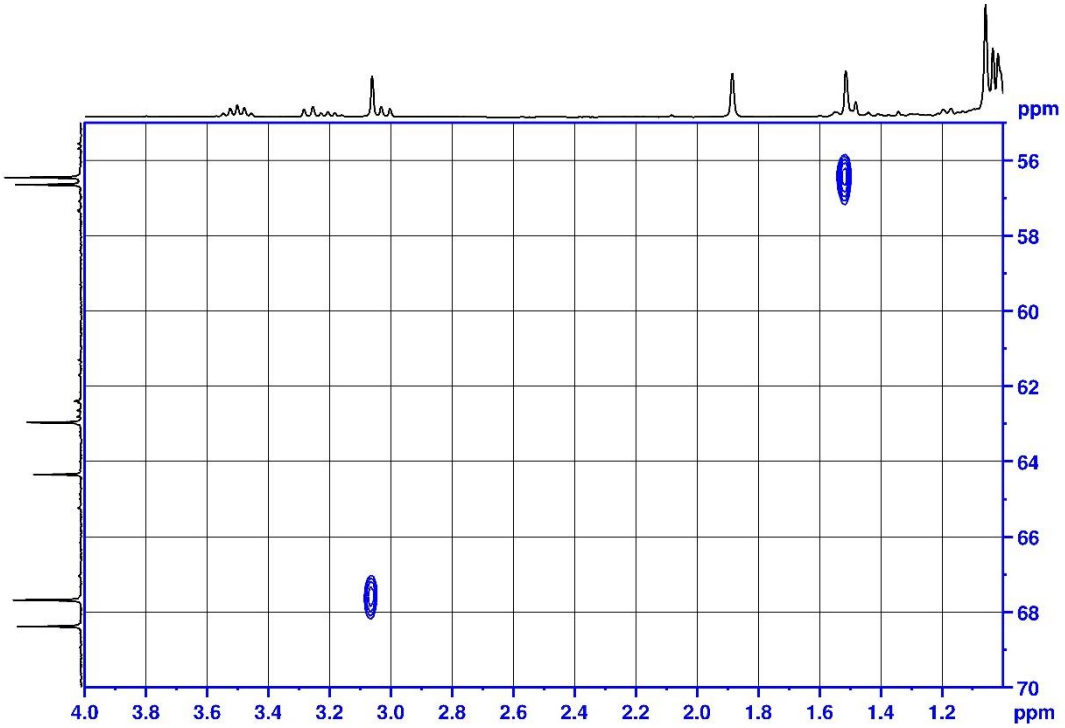
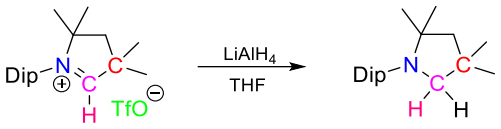



**Fig. S52** HMQC 2D-NMR spectrum of **4**$^{\text{Dip-Me}_2}$ of the mother liquor showing $CH_2$ correlation in $C_6D_6$ at room temperature.

**Direct Synthesis of $4^{Dip\text{-}Me_2}$**




$1^{Dip\text{-}Me_2}$ $4^{Dip\text{-}Me_2}$

THF (10 mL) was added to a mixture of $\mathbf{1}^{Dip\text{-}Me_2}$ (500 mg, 1.15 mmol) and powdered $LiAlH_4$ (65 mg, 1.7 mmol) at −78 °C and stirred for 10 minutes at room temperature. Then the volatiles were removed and 10 mL water was added to the residue at 0 °C followed by 5 mL of 2 M NaOH and then 20 mL more water. The resulting mixture was extracted with 40 mL of $Et_2O$ (2 × 20 mL). The combined $Et_2O$ phase was collected, pre-dried over $MgSO_4$ and dried under vacuum resulting in colourless solid compound $\mathbf{4}^{Dip\text{-}Me_2}$ as indicated by the $^1H$ NMR spectrum.[S13]

**Yield:** 300 mg (91%). **Elemental analysis:** calcd. (%) for $C_{20}H_{33}N$: C, 83.56; H, 11.57; N, 4.87; found: C, 83.73; H, 11.90; N, 4.79. **$^1H$ NMR** ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 7.12-7.23 (m, 3H, Ar-*H*), 3.76 (sep, 2H, $^3J_{H\text{-}H}$ = 6.8 Hz, C*H*$(CH_3)_2$), 3.32 (s, 2H, NC$H_2$), 1.76 (s, 2H, C$H_2$), 1.30 (d, 6H, $^3J_{H\text{-}H}$ = 6.9 Hz, CH(C$H_3$)$_2$), 1.21 (s, 6H, C(C$H_3$)$_2$), 1.17 (d, 6H, $^3J_{H\text{-}H}$ = 6.9 Hz, CH(C$H_3$)$_2$), 1.16 (s, 6H, C(C$H_3$)$_2$) ppm.

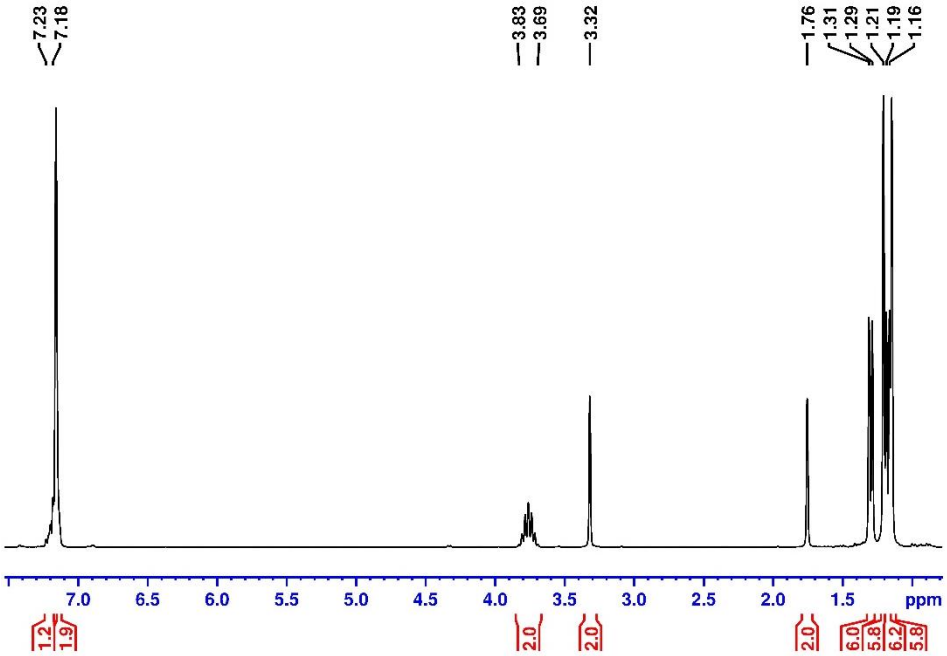
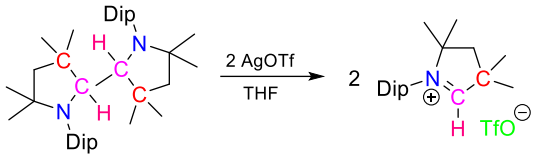



**Fig. S53** $^1H$ NMR spectrum of $\mathbf{4}^{Dip\text{-}Me_2}$ synthesised by using $LiAlH_4$ in $C_6D_6$ at room temperature.

**1:2 Reaction of $3^{Dip\text{-}Me_2}$ with AgOTf**




$3^{Dip\text{-}Me_2}$ $1^{Dip\text{-}Me_2}$

THF (10 mL) was added to a mixture of $\mathbf{3}^{Dip\text{-}Me_2}$ (50 mg, 0.087 mmol) and AgOTf (45 mg, 0.18 mmol) at room temperature and stirred for 12 hours. $^1$H NMR spectrum of the reaction mixture in $CD_3CN$ showed the formation of $\mathbf{1}^{Dip\text{-}Me_2}$. After that the reaction mixture was filtered and DCM (10 mL) was added to the residue and filtered again. The combined filtrates were evaporated. **Yield:** 64 mg (84%).

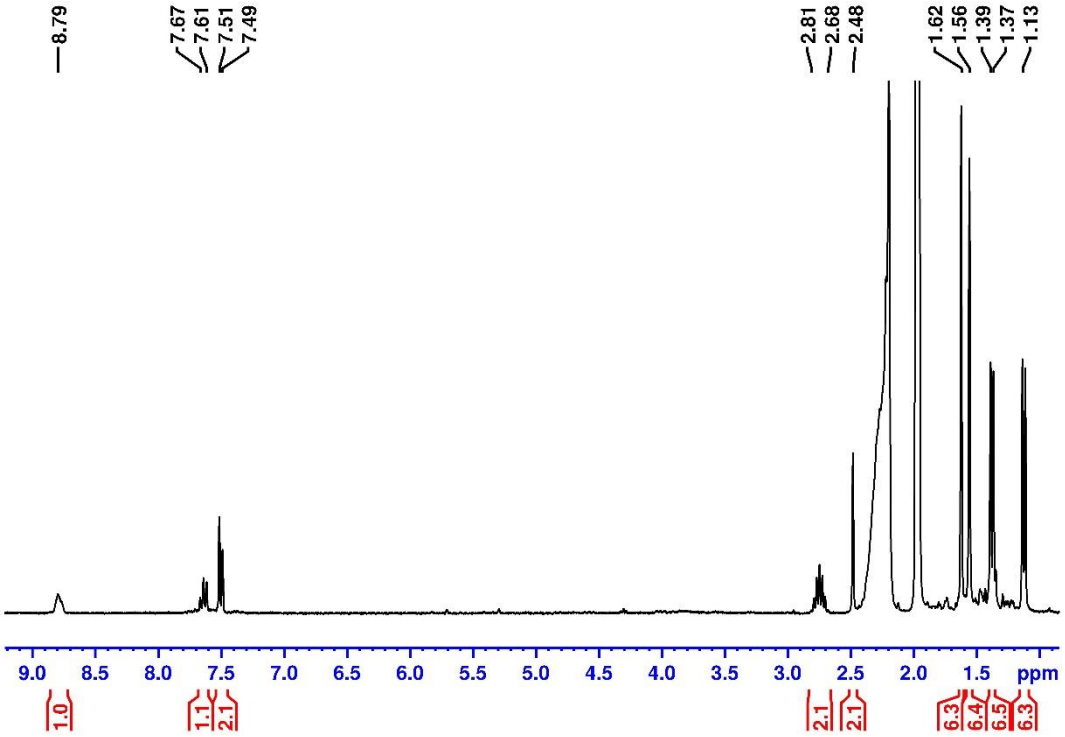
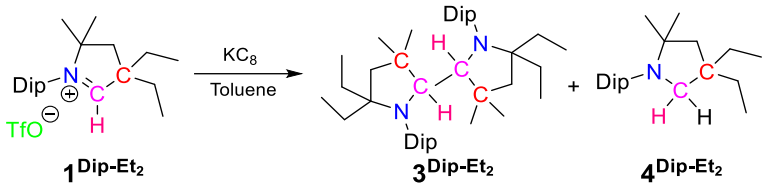



**Fig. S54** $^1$H NMR spectrum from the crude reaction mixture of $\mathbf{3}^{Dip\text{-}Me_2}$ and AgOTf in $CD_3CN$ at room temperature.

**Reduction of $1^{Dip\text{-}Et_2}$**




$1^{Dip\text{-}Et_2}$ $3^{Dip\text{-}Et_2}$ $4^{Dip\text{-}Et_2}$

Toluene (60 mL) was added to a mixture of $\mathbf{1}^{Dip\text{-}Et_2}$ (2.000 g, 4.314 mmol) and $KC_8$ (900 mg, 6.66 mmol) at room temperature and stirred for 12 hours. It was filtered and volatiles were evaporated under reduced pressure to obtain the product as colourless liquid compound. The $^1H$ NMR spectrum of the crude residue in $C_6D_6$ showed the presence of $\mathbf{4}^{Dip\text{-}Et_2}$ (subsequently we prepared $\mathbf{4}^{Dip\text{-}Et_2}$ as a pure compound in a different route from $\mathbf{1}^{Dip\text{-}Et_2}$ using $LiAlH_4$, please see below) along with some unidentified compounds. The HRMS spectrum also indicates the formation of $\mathbf{3}^{Dip\text{-}Et_2}$. **HRMS-ESI (m/z):** Calculated for $C_{44}H_{73}N_2$ $[M+H]^+$: 629.5769, Found: 629.5775 (this supports the formation of $\mathbf{3}^{Dip\text{-}Et_2}$).

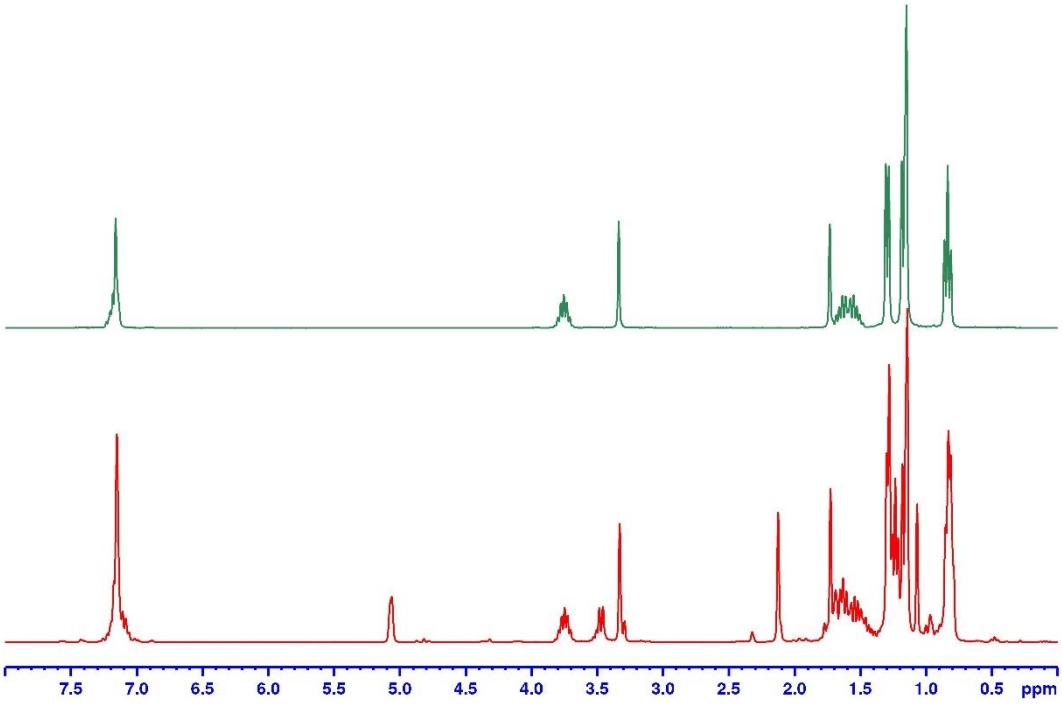
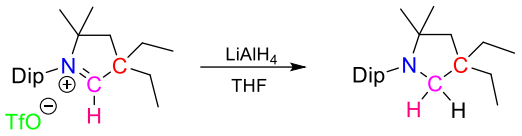



**Fig. S55** Overlay of $^1H$ NMR spectra of the crude reaction mixture from the $KC_8$ reduction of $\mathbf{1}^{Dip\text{-}Et_2}$ (red) along with pure $\mathbf{4}^{Dip\text{-}Et_2}$ (green) in $C_6D_6$ at room temperature.

**Direct Synthesis of $4^{Dip\text{-}Et_2}$**




$\mathbf{1}^{Dip\text{-}Et_2}$ $\mathbf{4}^{Dip\text{-}Et_2}$

THF (10 mL) was added to a mixture of $\mathbf{1}^{Dip\text{-}Et_2}$ (523 mg, 1.13 mmol) and powdered $LiAlH_4$ (65 mg, 1.7 mmol) at −78 °C and stirred for 10 minutes at room temperature. Then the volatiles were removed and 6 mL water was added to the residue followed by 4 mL of 2 M NaOH and then 30 mL more water. The resulting mixture was extracted with 40 mL of $Et_2O$ (2 × 20 mL). The combined $Et_2O$ phase was collected, pre-dried over $MgSO_4$ and dried under vacuum resulting in a colourless liquid $\mathbf{4}^{Dip\text{-}Et_2}$. **Yield:** 299 mg (84%). **$^1$H NMR** ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 7.11-7.24 (m, 3H, Ar-*H*), 3.75 (sep, 2H, $^3J_{H\text{-}H}$ = 6.8 Hz, C*H*$(CH_3)_2$), 3.34 (s, 2H, NC$H_2$), 1.73 (s, 2H, C$H_2$), 1.48-1.68 (m, 4H, C$H_2CH_3$), 1.30 (d, 6H, $^3J_{H\text{-}H}$ = 6.8 Hz, CH(C$H_3$)$_2$), 1.17 (d, 6H, $^3J_{H\text{-}H}$ = 7.0 Hz, CH(C$H_3$)$_2$), 1.15 (s, 6H, C(C$H_3$)$_2$), 0.83 (s, 6H, $CH_2CH_3$) ppm. **$^{13}$C{$^1$H} NMR** ($C_6D_6$, 25 °C, 75.4 MHz): $\delta$ = 152.4 (Ar-*C*), 139.1 (Ar-*C*), 127.2 (Ar-*C*H), 124.4 (Ar-*C*H), 64.9 (N$CH_2$), 62.6 (*C*$(CH_3)_2$), 53.5 (*C*$H_2$), 44.3 *C*$(CH_3)_2$, 30.8 (*C*$H_2CH_3$), 29.2 (C(*C*$H_3$)$_2$), 28.7 (*C*H$(CH_3)_2$), 26.8 (CH(*C*$H_3$)$_2$), 23.3 (CH(*C*$H_3$)$_2$), 9.4 ($CH_2$*C*$H_3$) ppm.

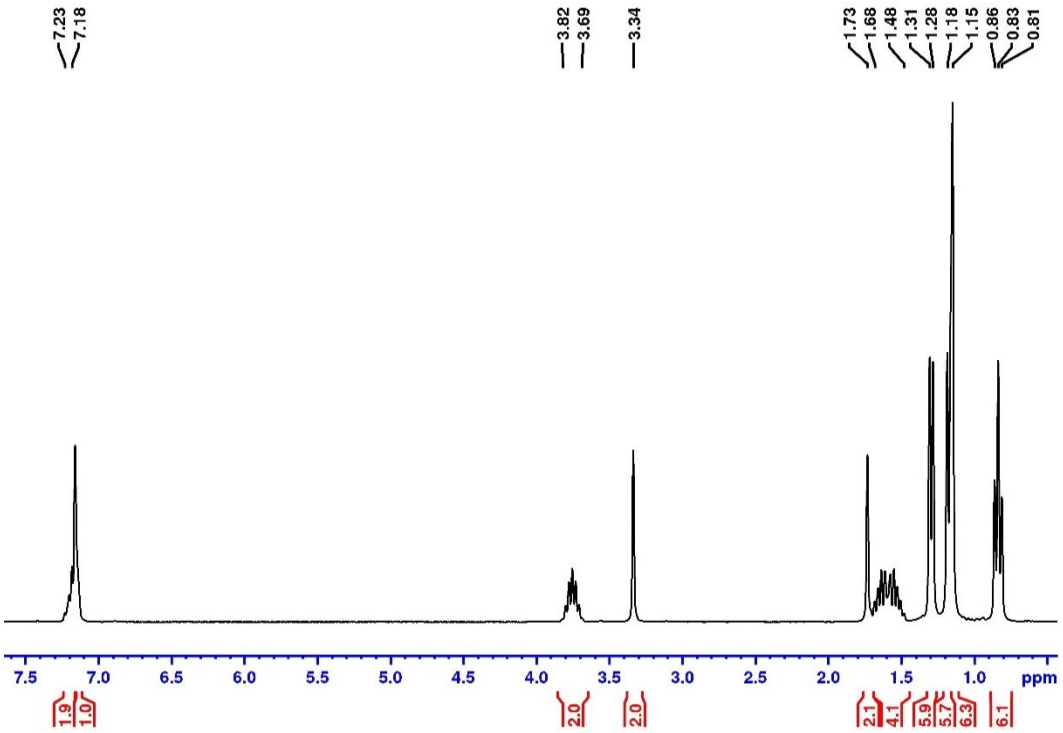



**Fig. S56** $^{1}H$ NMR spectra of $\mathbf{4}^{\mathbf{Dip\text{-}Et_2}}$ synthesised by using $LiAlH_4$ in $C_6D_6$ at room temperature.

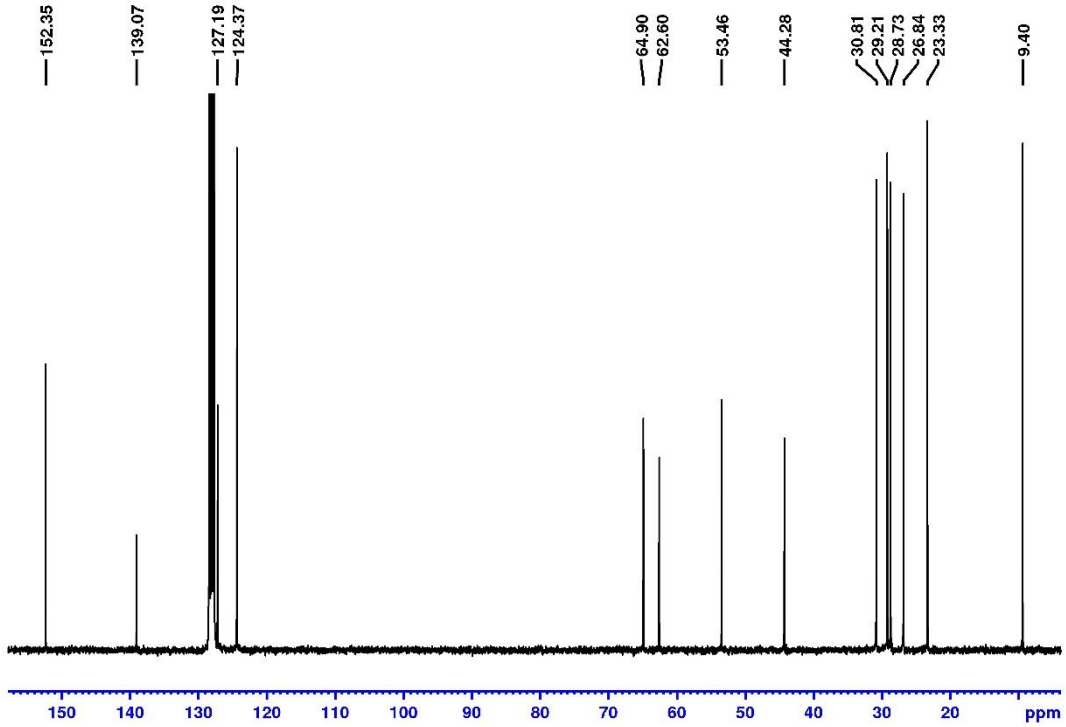
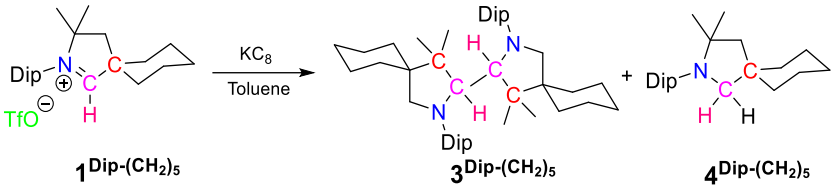



**Fig. S57** $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{4}^{\mathbf{Dip\text{-}Et_2}}$ synthesised by using $LiAlH_4$ in $C_6D_6$ at room temperature.

**Reduction of $\mathbf{1}^{\mathbf{Dip\text{-}(CH_2)_5}}$**




$\mathbf{1}^{\mathbf{Dip\text{-}(CH_2)_5}}$ $\mathbf{3}^{\mathbf{Dip\text{-}(CH_2)_5}}$ $\mathbf{4}^{\mathbf{Dip\text{-}(CH_2)_5}}$

Toluene (40 mL) was added to a mixture of $\mathbf{1}^{\mathbf{Dip\text{-}(CH_2)_5}}$ (780 mg, 1.64 mmol) and $KC_8$ (530 mg, 3.92 mmol) at room temperature and stirred for 12 hours. The mixture was filtered and the volatiles were evaporated from the filtrate under reduced pressure to obtain the product as colourless liquid compound. The $^1H$ NMR spectrum of the crude residue in $C_6D_6$ shows the presence of $\mathbf{4}^{\mathbf{Dip\text{-}(CH_2)_5}}$ (subsequently we prepared $\mathbf{4}^{\mathbf{Dip\text{-}(CH_2)_5}}$ as a pure compound in a different route from $\mathbf{1}^{\mathbf{Dip\text{-}(CH_2)_5}}$ using $LiAlH_4$, please see below) along with some unidentified compounds. The HRMS spectrum indicates the formation of $\mathbf{3}^{\mathbf{Dip\text{-}(CH_2)_5}}$. **HRMS-ESI (m/z):** Calculated for $C_{46}H_{73}N_2$ $[M+H]^+$: 653.5769, Found: 653.5779 (indicates the formation of $\mathbf{3}^{\mathbf{Dip\text{-}(CH_2)_5}}$).

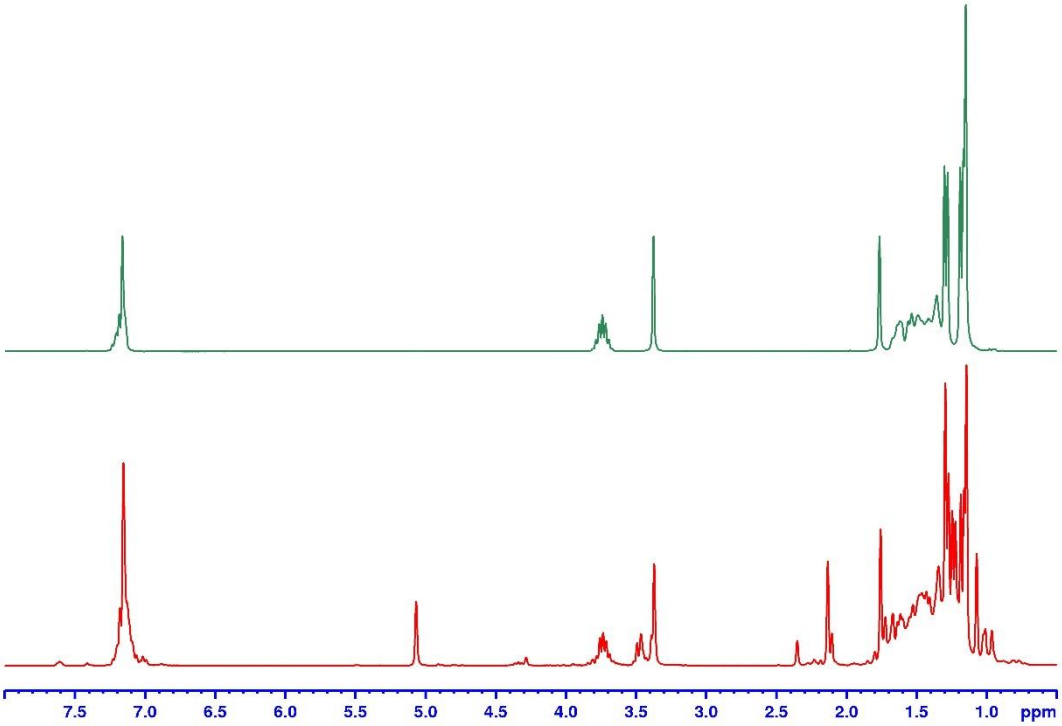
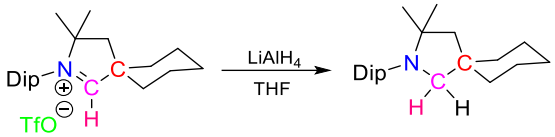



**Fig. S58** Overlay of $^1H$ NMR spectra of $\mathbf{4}^{\mathbf{Dip\text{-}(CH_2)_5}}$ in crude reaction mixture (red) with hydrogenated product from $\mathbf{1}^{\mathbf{Dip\text{-}(CH_2)_5}}$ (green) in $C_6D_6$ at room temperature.

**Direct Synthesis of $4^{Dip\text{-}(CH_2)_5}$**




$1^{Dip\text{-}(CH_2)_5}$ $4^{Dip\text{-}(CH_2)_5}$

THF (10 mL) was added to a mixture of $\mathbf{1}^{Dip\text{-}(CH_2)_5}$ (654 mg, 1.38 mmol) and powdered $LiAlH_4$ (75 mg, 2.0 mmol) at −78 °C and stirred for 10 minutes at room temperature. Then the volatiles were removed and 6 mL water was added to the residue followed by 4 mL of 2 M NaOH and then 30 mL more water. The resulting mixture was extracted with 40 mL of $Et_2O$ (2 × 20 mL). The combined $Et_2O$ phase was collected, pre-dried over $MgSO_4$ and dried under vacuum resulting in colourless solid compound $\mathbf{4}^{Dip\text{-}(CH_2)_5}$ as indicated by the $^1H$ NMR spectrum.[S14] **Yield:** 396 mg (88%). **Elemental analysis:** calcd. (%) for $C_{23}H_{37}N_1$: C, 84.34; H, 11.39; N, 4.28; found: C, 85.28; H, 11.24; N, 4.37. **$^1$H NMR** ($C_6D_6$, 25 °C, 300 MHz): $\delta$ = 7.12-7.24 (m, 3H, Ar-*H*), 3.74 (sep, 2H, $^3J_{H\text{-}H}$ = 6.9 Hz, C*H*$(CH_3)_2$), 3.37 (s, 2H, NC$H_2$), 1.76 (s, 2H, C$H_2$), 1.36-1.62 (m, 10H, $^{Cy\text{-}B}CH_2$), 1.29 (d, 6H, $^3J_{H\text{-}H}$ = 6.8 Hz, CH(C$H_3$)$_2$), 1.18 (d, 6H, $^3J_{H\text{-}H}$ = 7.0 Hz, CH(C$H_3$)$_2$), 1.15 (s, 6H, C(C$H_3$)$_2$) ppm. **$^{13}$C{$^1$H} NMR** ($C_6D_6$, 25 °C, 75.4 MHz): $\delta$ = 152.4 (Ar-*C*), 139.2 (Ar-*C*), 127.2 (Ar-*C*H), 124.3 (Ar-*C*H), 65.4 (N$CH_2$), 62.4 (*C*$(CH_3)_2$), 55.2 ($CH_2$), 41.6 (*C*$(CH_3)_2$), 39.6 ($^{Cy\text{-}B}CH_2$), 28.9 (C(*C*$H_3$)$_2$), 28.7 (*C*H$(CH_3)_2$), 26.8 (CH(*C*$H_3$)$_2$), 26.4 ($^{Cy\text{-}B}CH_2$), 24.4 ($^{Cy\text{-}B}CH_2$), 23.4 (CH(*C*$H_3$)$_2$) ppm.

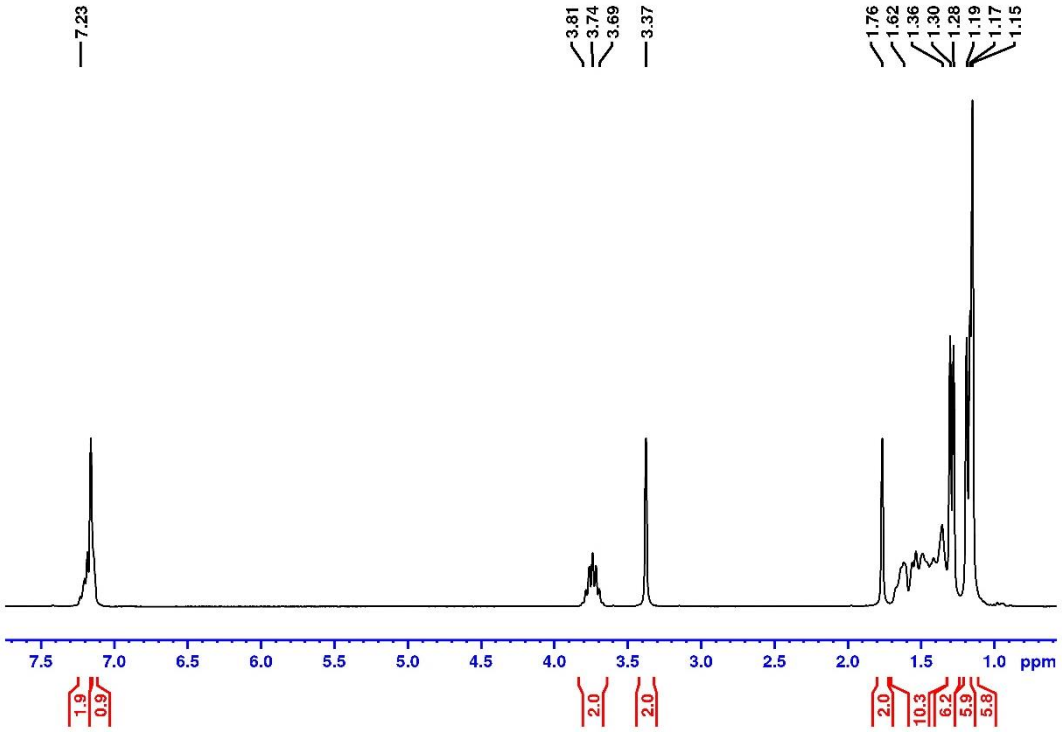



**Fig. S59** $^1$H NMR spectra of $\mathbf{4}^{Dip\text{-}(CH_2)_5}$ synthesised by using $LiAlH_4$ in $C_6D_6$ at room temperature.

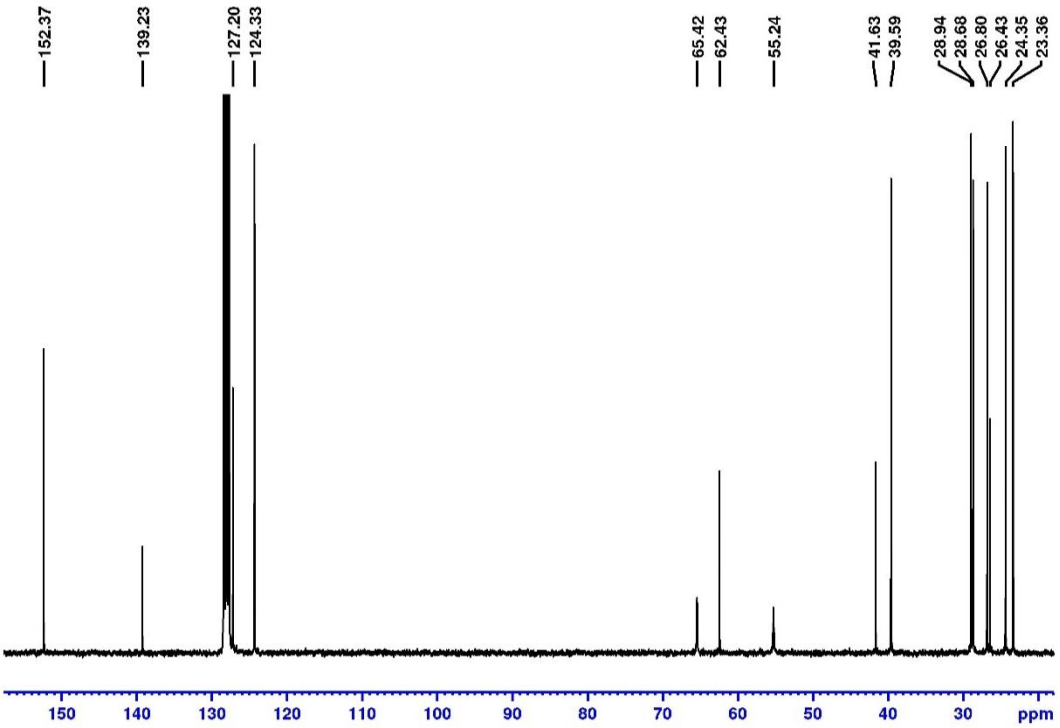



**Fig. S60** $^{13}C\{^{1}H\}$ NMR spectra of **4**$^{Dip\text{-}(CH_2)_5}$ synthesised by using $LiAlH_4$ in $C_6D_6$ at room temperature.

**Oxidation of $4^{Dip\text{-}Me_2}$**


$4^{Dip\text{-}Me_2}$ $1^{Dip\text{-}Me_2}(SbF_6)$

About 5 mL of acetonitrile was added to a mixture of $4^{Dip\text{-}Me_2}$ (100 mg, 0.348 mmol) and $NOSbF_6$ (102 mg, 0.384 mmol) at room temperature and stirred for 6 hours. The $^1H$ NMR spectrum of the reaction mixture in $CD_3CN$ showed the formation of $1^{Dip\text{-}Me_2}(SbF_6)$.[S8] The product was crystallised by diffusing its saturated solution in acetonitrile with $Et_2O$ at room temperature. **Yield:** 148 mg (81%). **$^1H$ NMR** of reaction mixture ($CD_3CN$, 25 °C, 300 MHz): $\delta$ = 8.70 (s, 1H, NC*H*), 7.61 (t, 1H, $^3J_{H\text{-}H}$ = 7.8 Hz, Ar-*H*), 7.47 (d, 2H, $^3J_{H\text{-}H}$ = 7.6 Hz, Ar-*H*), 2.72 (sep, 2H, $^3J_{H\text{-}H}$ = 6.6 Hz, C*H*$(CH_3)_2$), 2.46 (s, 2H, C$H_2$), 1.59 (s, 6H, C(C$H_3$)$_2$), 1.53 (s, 6H, C(C$H_3$)$_2$), 1.35 (d, 6H, $^3J_{H\text{-}H}$ = 6.4 Hz, CH(C$H_3$)$_2$), 1.10 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz, CH(C$H_3$)$_2$) ppm. **$^{19}F\{^1H\}$ NMR** ($CD_3CN$, 25 °C, 282.4 MHz,): $\delta$ = −123.7 (sextet, $^1J_{(^{121}Sb,\ ^{19}F)}$ = 1945.8 Hz), −123.8 (octet, $^1J_{(^{123}Sb,\ ^{19}F)}$ = 1055.4 Hz) ppm.

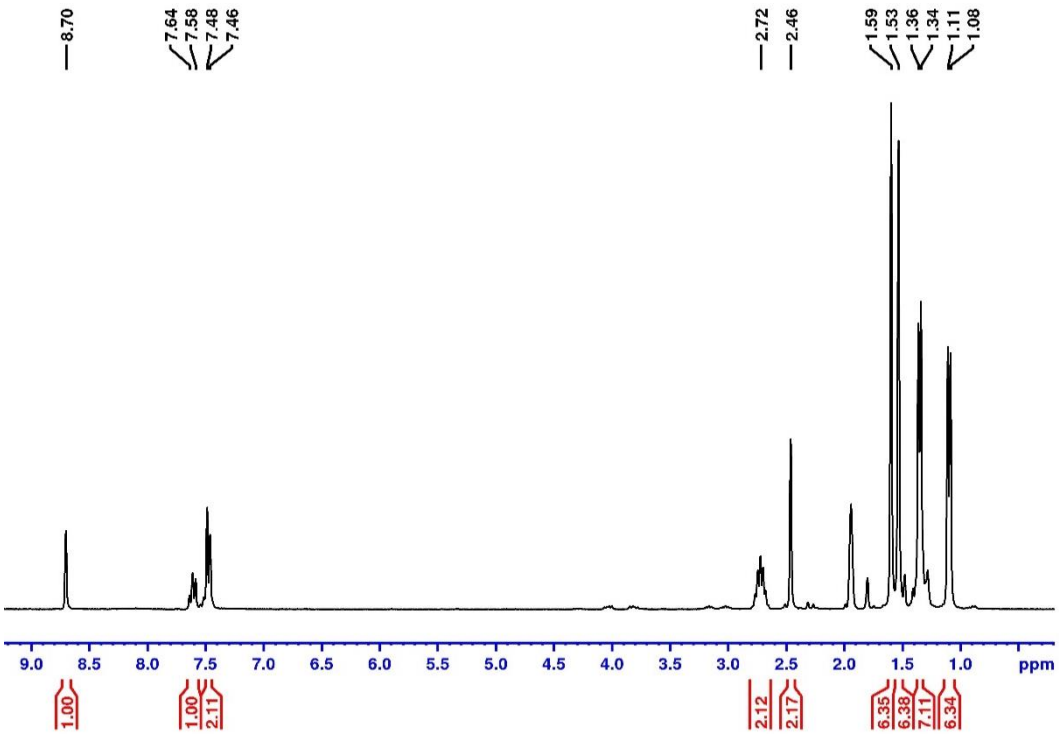



**Fig. S61** $^1H$ NMR spectrum from the crude reaction mixture of $4^{Dip\text{-}Me_2}$ and $NOSbF_6$ in $CD_3CN$ at room temperature.

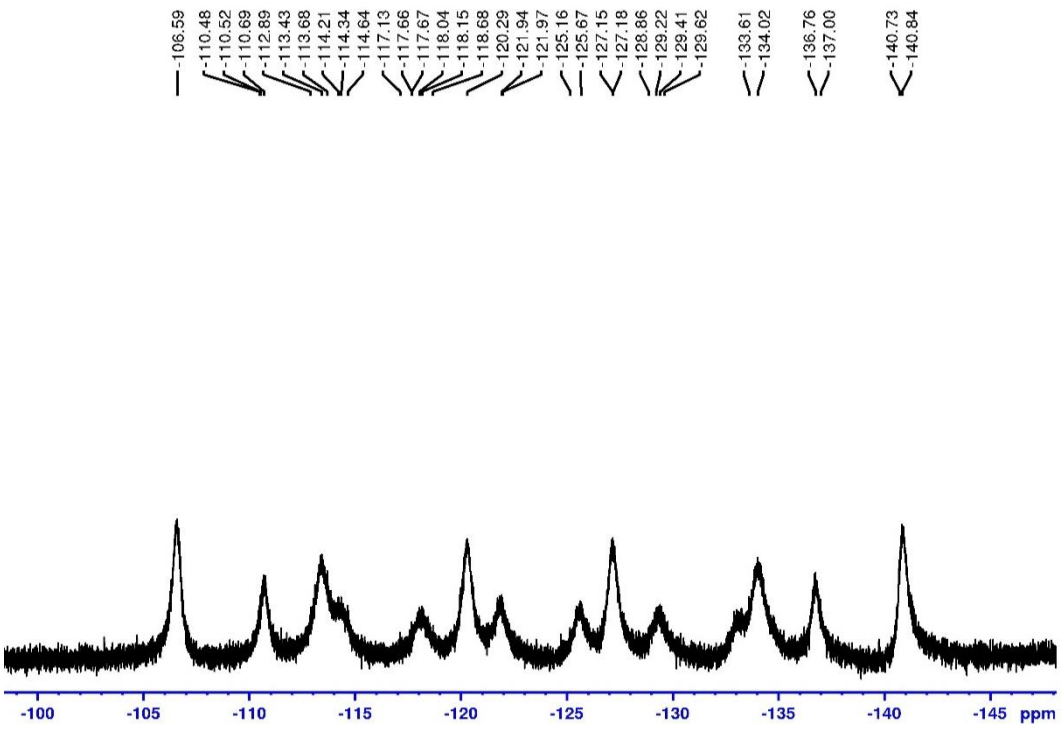
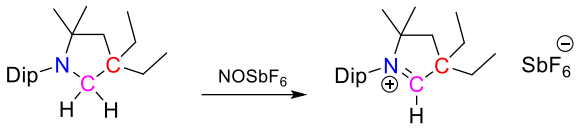



**Fig. S62** $^{19}F\{^{1}H\}$ NMR spectrum from the crude reaction mixture of $\mathbf{4}^{\mathbf{Dip\text{-}Me_2}}$ and $NOSbF_6$ in $CD_3CN$ at room temperature.

**Oxidation of $4^{Dip\text{-}Et_2}$**




$4^{Dip\text{-}Et_2}$ $1^{Dip\text{-}Et_2}(SbF_6)$

About 5 mL of acetonitrile was added to a mixture of $4^{Dip\text{-}Et_2}$ (100 mg, 0.317 mmol) and $NOSbF_6$ (92 mg, 0.35 mmol) at room temperature and stirred for 6 hours. Gas evolution was observed during the reaction. The $^1H$ NMR spectrum of the reaction mixture in $CD_3CN$ showed the formation of $\mathbf{1^{Dip\text{-}Et_2}(SbF_6)}$.[S8] The product was crystallised by diffusing its saturated solution in acetonitrile with $Et_2O$ at room temperature. **Yield:** 140 mg (80%). **$^1$H NMR** of reaction mixture ($CD_3CN$, 25 °C, 300 MHz): $\delta$ = 8.82 (s, 1H, NC*H*), 7.62 (t, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz, Ar-*H*), 7.48 (d, 2H, $^3J_{H\text{-}H}$ = 7.7 Hz, Ar-*H*), 2.71 (sep, 2H, $^3J_{H\text{-}H}$ = 6.6 Hz, C*H*$(CH_3)_2$), 2.40 (s, 2H, C$H_2$), 1.96-2.01 (m, 4H, C$H_2CH_3$), 1.54 (s, 6H, C(C$H_3$)$_2$), 1.36 (d, 6H, $^3J_{H\text{-}H}$ = 6.6 Hz, CH(C$H_3$)$_2$), 1.05-1.11 (m, CH(C$H_3$)$_2$, $CH_2CH_3$) ppm. **$^{19}$F{$^1$H} NMR** ($CD_3CN$, 25 °C, 282.4 MHz,): $\delta$ = −123.8 (sextet, $^1J_{(^{121}Sb,\,^{19}F)}$ = 1935.6 Hz), −123.8 (octet, $^1J_{(^{123}Sb,\,^{19}F)}$ = 1049.7 Hz) ppm.

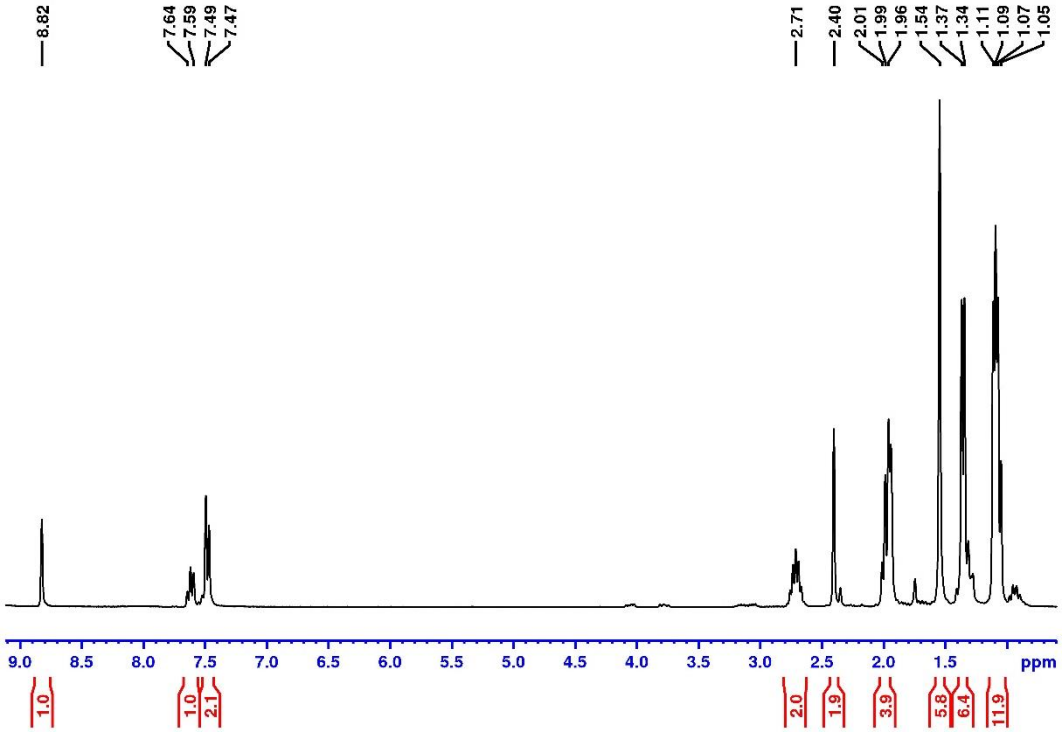



**Fig. S63** $^1$H NMR spectrum from the crude reaction mixture of $4^{Dip\text{-}Et_2}$ and $NOSbF_6$ in $CD_3CN$ at room temperature.

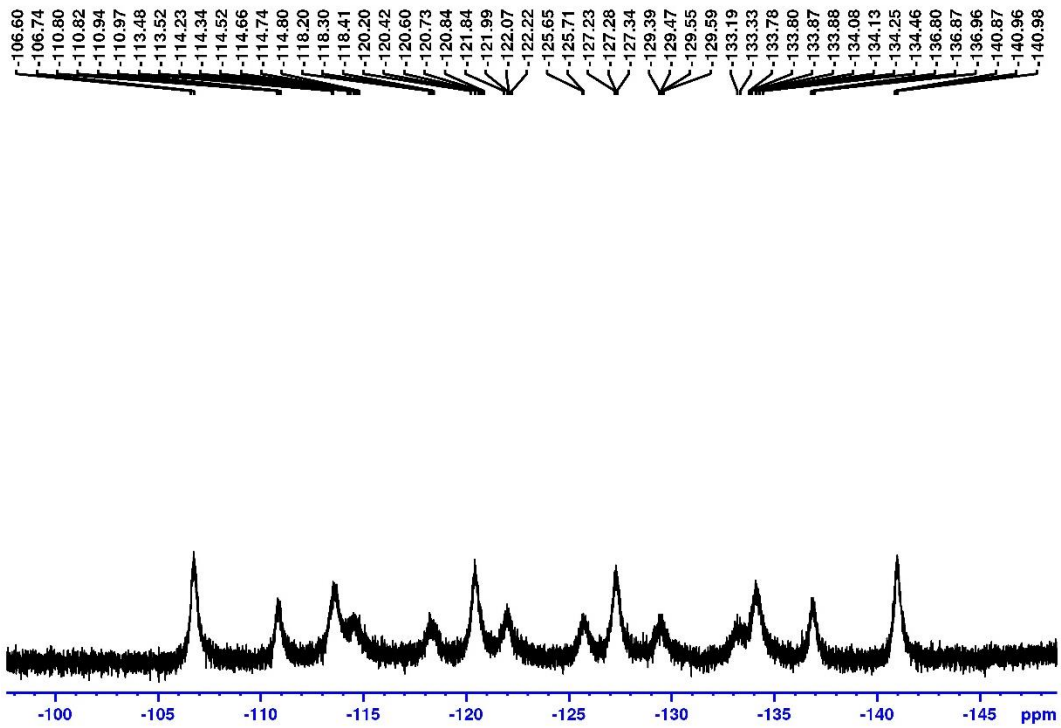
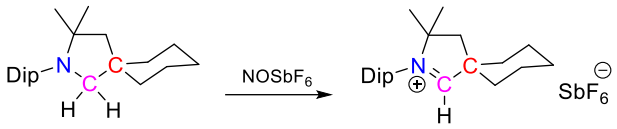



**Fig. S64** $^{19}F\{^{1}H\}$ NMR spectrum from the crude reaction mixture of $\mathbf{4^{Dip\text{-}Et_2}}$ and $NOSbF_6$ in $CD_3CN$ at room temperature.

**Oxidation of $4^{Dip\text{-}(CH_2)_5}$**




$4^{Dip\text{-}(CH_2)_5}$ $1^{Dip\text{-}(CH_2)_5}(SbF_6)$

About 5 mL of acetonitrile was added to a mixture of $4^{Dip\text{-}(CH_2)_5}$ (76 mg, 0.23 mmol) and $NOSbF_6$ (70 mg, 0.26 mmol) at room temperature and stirred for 6 hours. The $^1H$ NMR spectrum of the reaction mixture in $CD_3CN$ showed the formation of $\mathbf{1^{Dip\text{-}(CH_2)_5}(SbF_6)}$.[S8] The product was crystallised by diffusing its saturated solution in acetonitrile with $Et_2O$ at room temperature. **Yield:** 100 mg (77%). **$^1H$ NMR** of reaction mixture ($CD_3CN$, 25 °C, 300 MHz): $\delta$ = 8.78 (s, 1H, NC*H*), 7.61 (t, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz, Ar-*H*), 7.47 (d, 2H, $^3J_{H\text{-}H}$ = 7.6 Hz, Ar-*H*), 2.72 (sep, 2H, $^3J_{H\text{-}H}$ = 6.7 Hz, C*H*($CH_3$)$_2$), 2.47 (s, 2H, C$H_2$), 1.24-1.82 (m, 10H, $^{Cy\text{-}B}CH_2$), 1.53 (s, 6H, C(C$H_3$)$_2$), 1.34 (d, 6H, $^3J_{H\text{-}H}$ = 6.6 Hz, CH(C$H_3$)$_2$), 1.09 (d, 6H, $^3J_{H\text{-}H}$ = 6.7 Hz, CH(C$H_3$)$_2$) ppm. **$^{19}F\{^1H\}$ NMR** ($CD_3CN$, 25 °C, 282.4 MHz,): $\delta$ = −123.9 (sextet, $^1J_{(^{121}Sb,\ ^{19}F)}$ = 1929.4 Hz), −123.9 (octet, $^1J_{(^{123}Sb,\ ^{19}F)}$ = 1079.1 Hz) ppm.

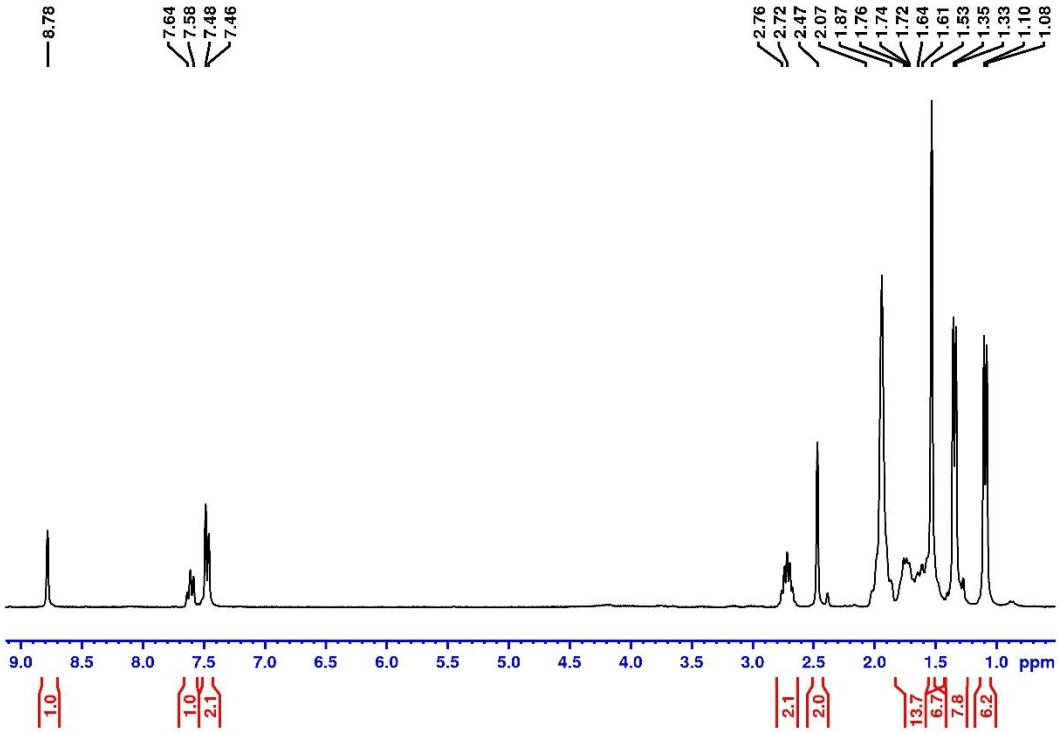



**Fig. S65** $^1H$ NMR spectrum from the crude reaction mixture of $4^{Dip\text{-}(CH_2)_5}$ and $NOSbF_6$ in $CD_3CN$ at room temperature.

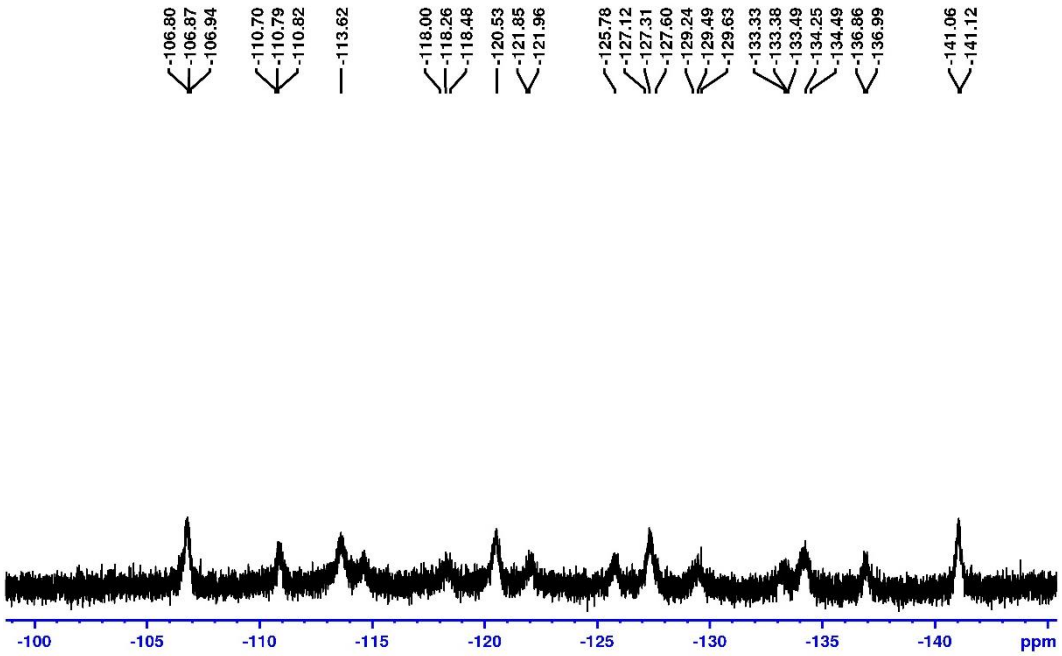



**Fig. S66** $^{19}F\{^{1}H\}$ NMR spectrum from the crude reaction mixture of **4**$^{Dip\text{-}(CH_2)_5}$ and $NOSbF_6$ in $CD_3CN$ at room temperature.

**Crystallographic Details**

Single-crystal X-ray diffraction data of $\mathbf{3}^{t\mathbf{Bu\text{-}Me_2}}$ and $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$ were collected at 298 K using a Rigaku diffractometer with graphite-monochromated molybdenum *Kα* radiation, $\lambda$ = 0.71073 Å. Data integration and reduction were processed with CrysAlisPro software.[S15] An empirical absorption correction was applied to the collected reflections with SCALE3 ABSPACK integrated with CrysAlisPro. The structure was solved by direct methods using the SHELXT[S16] programme and refined by full matrix least-squares method based on *F*2 using the SHELXL[S17] programme through the Olex2[S18] interface. All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*iso values constrained to 1.5 *U*eq of their pivot atoms for $sp^3$ carbon atoms and 1.2 times for aromatic and methylene and methine carbon atoms. In the case of $\mathbf{3}^{t\mathbf{Bu\text{-}Me_2}}$, the structure was refined as a non-merohedral twin with a hklf5 file and a BASF factor of 0.33947. The molecule is refined in S for the asymmetric unit. The symmetry-generated molecule (2-fold rotation axis) is the SS diastereomer and the unit cell is filled with a mix of two RR and two SS isomers. In the case of $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$, the molecule is refined in R for the asymmetric unit. The symmetry-generated molecule (2-fold rotation axis) is in RR diastereomer and the unit cell is filled with a mix of two RR and two SS isomers. Crystal data and structure refinement of all these compounds are summarised in Tables S2-S3.

**Table S2. Crystal data and structure refinement for $3^{tBu\text{-}Me_2}$** (CCDC 2056322)

| | |
|---|---|
| Identification code | aj1609_tw |
| Empirical formula | $C_{24}H_{48}N_2$ |
| Formula weight | 364.64 |
| Temperature/K | 298(2) |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 18.4911(16) |
| b/Å | 8.0630(7) |
| c/Å | 15.8001(11) |
| α/° | 90 |
| β/° | 96.727(7) |
| γ/° | 90 |
| Volume/Å$^3$ | 2339.5(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.035 |
| μ/mm$^{-1}$ | 0.059 |
| F(000) | 824.0 |
| Crystal size/mm$^3$ | 0.240 × 0.220 × 0.190 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.986 to 52.742 |
| Index ranges | -22 ≤ h ≤ 22, -10 ≤ k ≤ 10, -19 ≤ l ≤ 19 |
| Reflections collected | 2376 |
| Independent reflections | 2376 [$R_{int}$ = undetermined/hklf5, $R_{sigma}$ = 0.0571] |
| Data/restraints/parameters | 2376/0/126 |
| Goodness-of-fit on F$^2$ | 1.079 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0755, w$R_2$ = 0.1825 |
| Final R indexes [all data] | $R_1$ = 0.1189, w$R_2$ = 0.1996 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.17/-0.16 |

**Table S3. Crystal data and structure refinement for $3^{Dip\text{-}Me_2}$** (CCDC 2056323).

| | |
|---|---|
| Identification code | aj1598-1 |
| Empirical formula | $C_{40}H_{64}N_2$ |
| Formula weight | 572.93 |
| Temperature/K | 298(2) |
| Crystal system | monoclinic |
| Space group | *C*2/*c* |
| a/Å | 19.980(2) |
| b/Å | 9.5392(8) |
| c/Å | 20.618(3) |
| α/° | 90 |
| β/° | 115.474(15) |
| γ/° | 90 |
| Volume/Å$^3$ | 3547.5(8) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.073 |
| μ/mm$^{-1}$ | 0.061 |
| F(000) | 1272.0 |
| Crystal size/mm$^3$ | 0.210 × 0.190 × 0.150 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.83 to 50.054 |
| Index ranges | -23 ≤ h ≤ 23, -11 ≤ k ≤ 11, -22 ≤ l ≤ 24 |
| Reflections collected | 25298 |
| Independent reflections | 3124 [$R_{int}$ = 0.1445, $R_{sigma}$ = 0.0736] |
| Data/restraints/parameters | 3124/0/199 |
| Goodness-of-fit on F$^2$ | 1.036 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0598, w$R_2$ = 0.1539 |
| Final R indexes [all data] | $R_1$ = 0.0855, w$R_2$ = 0.1703 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.23/-0.21 |

**Cyclic Voltammetry**

All electrochemical measurements were carried out using an AUTOLAB PGSTA12 potentiostat/galvanostat controlled by the software NOVA. A glassy carbon electrode with a surface of around 1.6 $mm^2$ was used as working electrode. A platinum wire reference electrode and a platinum wire auxiliary electrode were used. All measurements were undertaken inside a glove box (argon atmosphere). For the measurements approximately $10^{-3}$ - $10^{-5}$ mol of the investigated compound was dissolved in 10 mL of electrolyte solution (0.1 mol $l^{-1}$ $Bu_4NPF_6$ in acetonitrile) in a double walled electrochemical cell. Cyclic voltammetry was performed using -0.00244 V/step up to 1000 mV/s, adjusted at faster scan rates. Differential pulse voltammetry was performed using modulation steps of +/− 0.005 V, modulation amplitude of 0.01 V, and a modulation time of 1 s as well as an interval time of 2 s. External referencing was performed by adding either ferrocene or decamethylferrocene while the potentials were in all cases calculated for the $Fc/Fc^+$ pair.

**Table S4.** Summary of the electrochemical data of $\mathbf{1}^{i\text{Pr-Me}_2}$, $\mathbf{3}^{i\text{Pr-Me}_2}$, $\mathbf{1}^{t\text{Bu-Me}_2}$, $\mathbf{3}^{t\text{Bu-Me}_2}$, $\mathbf{1}^{\text{Dip-Me}_2}$, $\mathbf{1}^{\text{Dip-Et}_2}$, $\mathbf{1}^{\text{Dip-(CH}_2)_5}$, $\mathbf{3}^{\text{Dip-Me}_2}$, $\mathbf{4}^{\text{Dip-Me}_2}$, $\mathbf{4}^{\text{Dip-Et}_2}$, and $\mathbf{4}^{\text{Dip-(CH}_2)_5}$, relative to the potential of $Fc/Fc^+$.

| **Compounds** | ***Epk / Epa*** **(100 mV/s)** **[V]** | ***Epk / Epa*** **(200 mV/s)** **[V]** | ***Epk / Epa*** **(300 mV/s)** **[V]** | ***Epk / Epa*** **(500 mV/s)** **[V]** | ***Epk / Epa*** **(1000 mV/s)** **[V]** | ***Epk / Epa*** **(2000 mV/s)** **[V]** | ***Epk / Epa*** **(3000 mV/s)** **[V]** | ***Epk / Epa*** **(5000 mV/s)** **[V]** |
|---|---|---|---|---|---|---|---|---|
| $\mathbf{1}^{i\text{Pr-Me}_2}$ | −1.96 / −0.25 | −1.97 −0.22 | −1.98 −0.20 | −1.99 −0.19 | −2.00 −0.17 | −2.03 −0.14 | −2.05 −0.12 | −2.06 −0.10 |
| $\mathbf{3}^{i\text{Pr-Me}_2}$ | −1.95 / −0.25 | −1.97 −0.24 | −1.97 −0.22 | −1.96 −0.19 | −1.96 −0.16 | −1.96 −0.13 | −1.97 −0.11 | −1.96 −0.08 |
| $\mathbf{1}^{t\text{Bu-Me}_2}$ | −1.97 / −0.27 | −1.99 −0.25 | −2.00 −0.23 | −2.02 −0.22 | −2.04 −0.19 | −2.06 −0.17 | −2.08 −0.15 | −2.11 −0.13 |
| $\mathbf{3}^{t\text{Bu-Me}_2}$ | −1.91 / −0.19 | −2.00 −0.24 | −2.00 −0.23 | −2.01 −0.21 | −2.02 −0.19 | −2.03 −0.17 | −2.03 −0.16 | −2.04 −0.14 |
| $\mathbf{1}^{\text{Dip-Me}_2}$ | −1.79 / 0.03 | −1.84 / 0.00 | −1.86 / 0.00 | −1.86 / −1.77, 0.03 | −1.87 / −1.79, 0.10 | −1.87 / −1.79, 0.10 | −1.88 / −1.78, 0.14 | −1.89 / −1.79, 0.15 |
| $\mathbf{1}^{\text{Dip-Et}_2}$ | −1.93 / 0.44 | −1.95 / - | - | −1.96 / −1.88 | −1.98 / −1.87 | −2.00 / −1.87 | - | −2.03 / --1.84 |
| $\mathbf{1}^{\text{Dip-(CH}_2)_5}$ | −1.92 / - | −1.92 / - | - | −1.92 / −1.84 | −1.92 / −1.84 | −1.93 / −1.83 | - | −1.93 / −1.83 |
| $\mathbf{3}^{\text{Dip-Me}_2}$ | −1.74 / 0.03 | −1.82 / −0.00 | −1.82 / −0.00 | −1.83 / 0.00 | −1.84 / 0.01 | −1.86 / 0.01 | −1.87 / 0.04 | −1.87 / 0.05 |
| $\mathbf{4}^{\text{Dip-Me}_2}$ | - / 0.80 | | | | | | | |
| $\mathbf{4}^{\text{Dip-Et}_2}$ | - / 0.74 | | | | | | | |
| $\mathbf{4}^{\text{Dip-(CH}_2)_5}$ | - / 0.76 | | | | | | | |

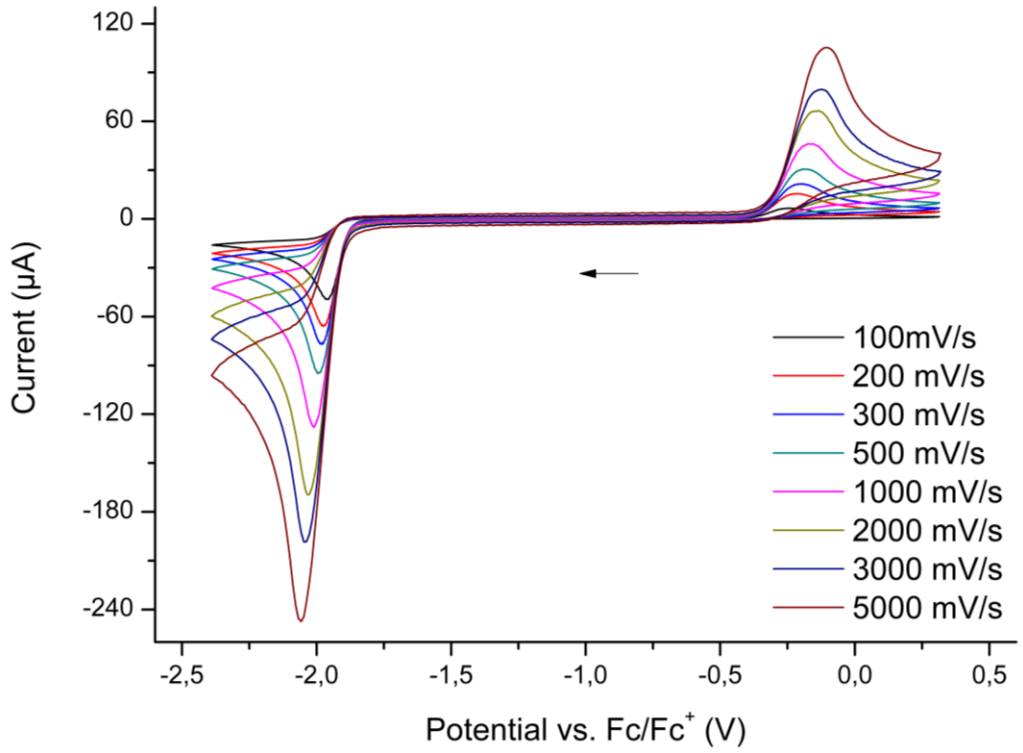



**Fig. S67** Cyclic voltammograms of **1**$^{i\text{Pr-Me}_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at different scan rates.

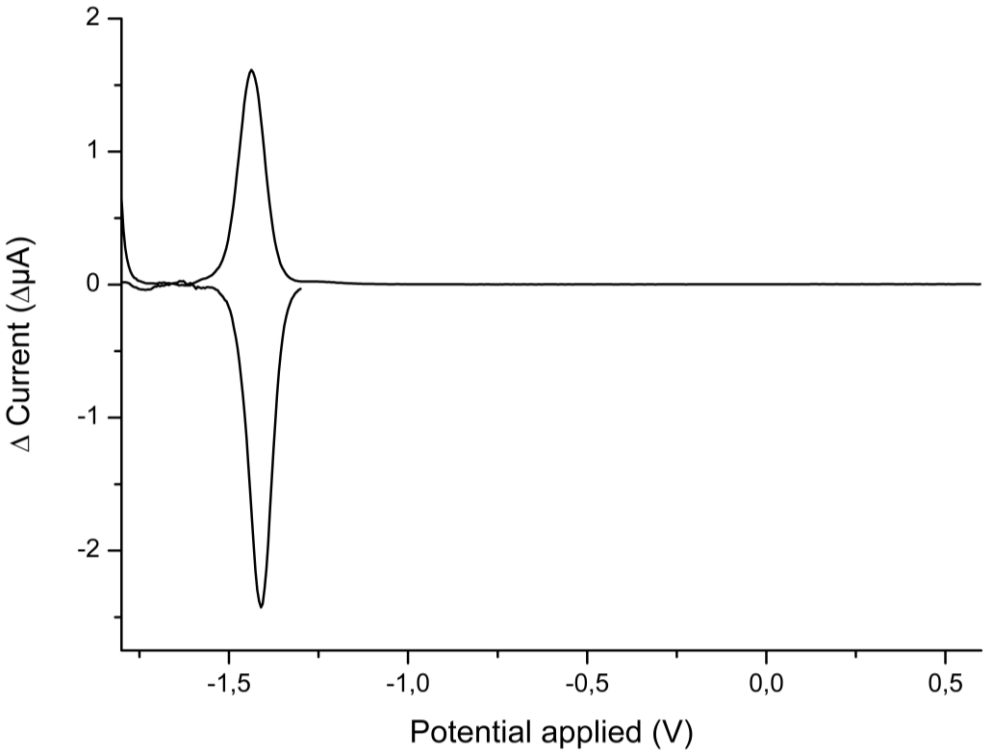



**Fig. S68** Differential pulse voltammogram (DPV) of **1**$^{i\text{Pr-Me}_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at room temperature.

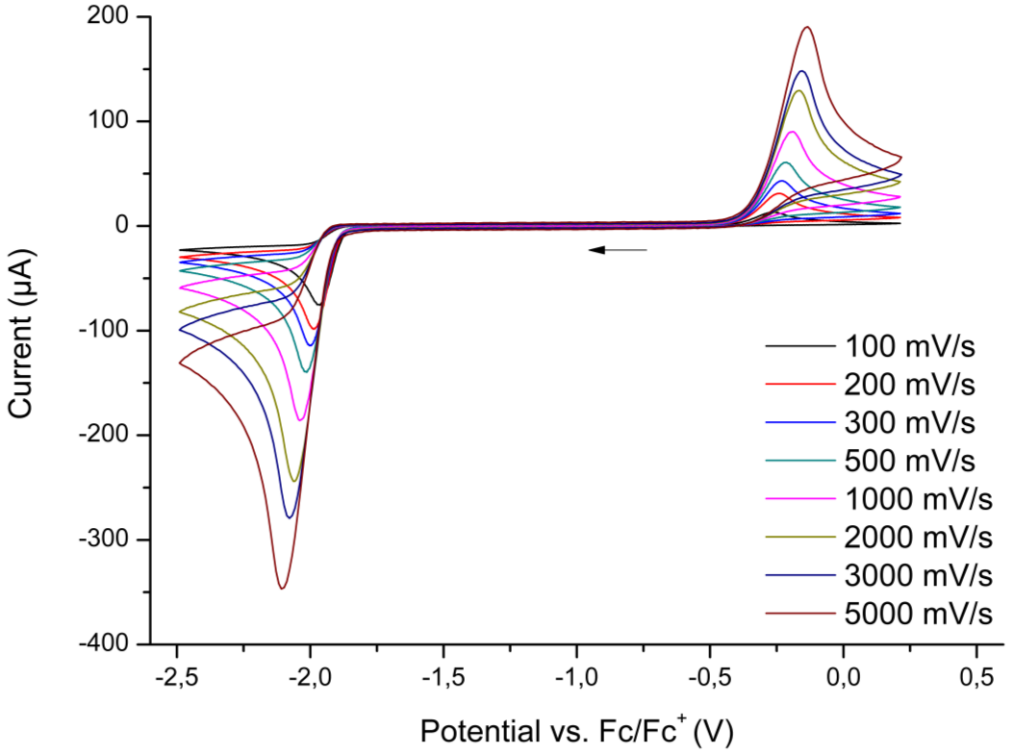



**Fig. S69** Cyclic voltammograms of **1**$^{tBu\text{-}Me_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at different scan rates.

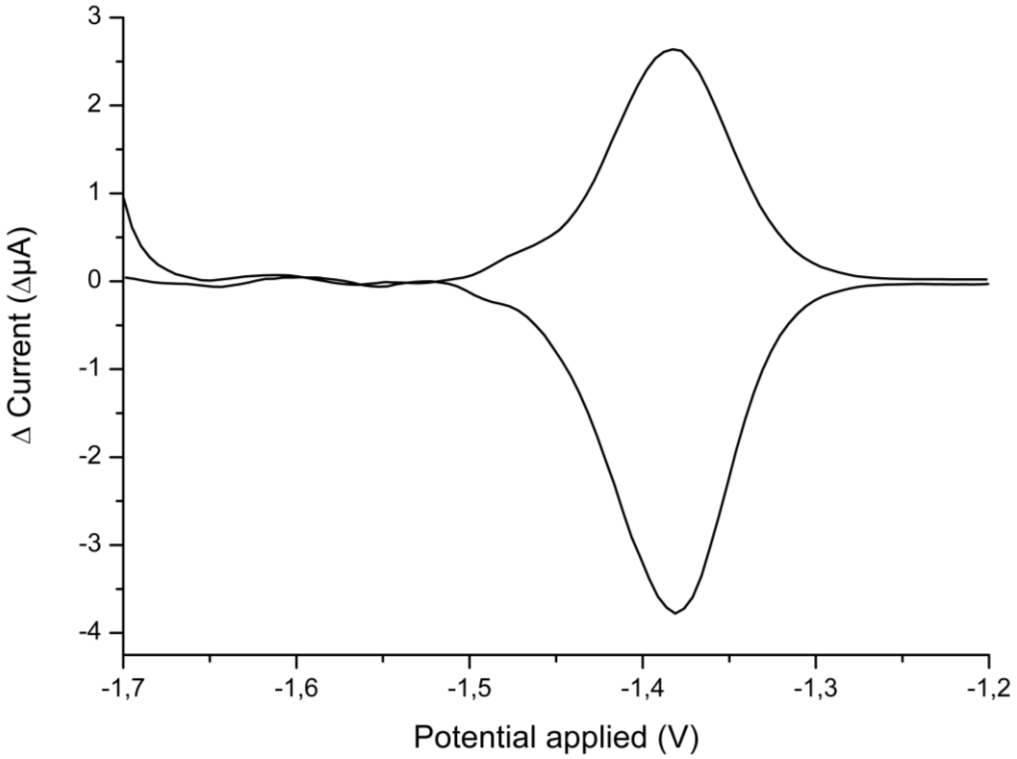



**Fig. S70** Differential pulse voltammogram (DPV) of **1**$^{tBu\text{-}Me_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at room temperature.

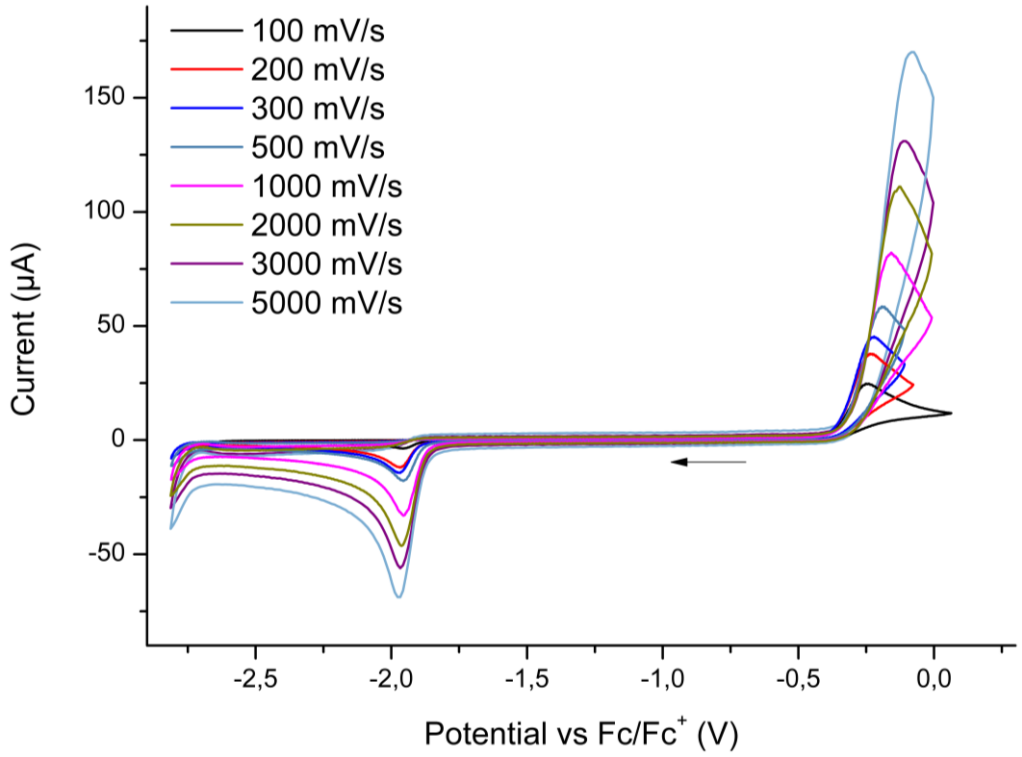



**Fig. S71** Cyclic voltammograms of **3**$^{i\text{Pr-Me}_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at different scan rates. NB: the second scans are shown since the reduction signal only appears after the first full cycle (see below).

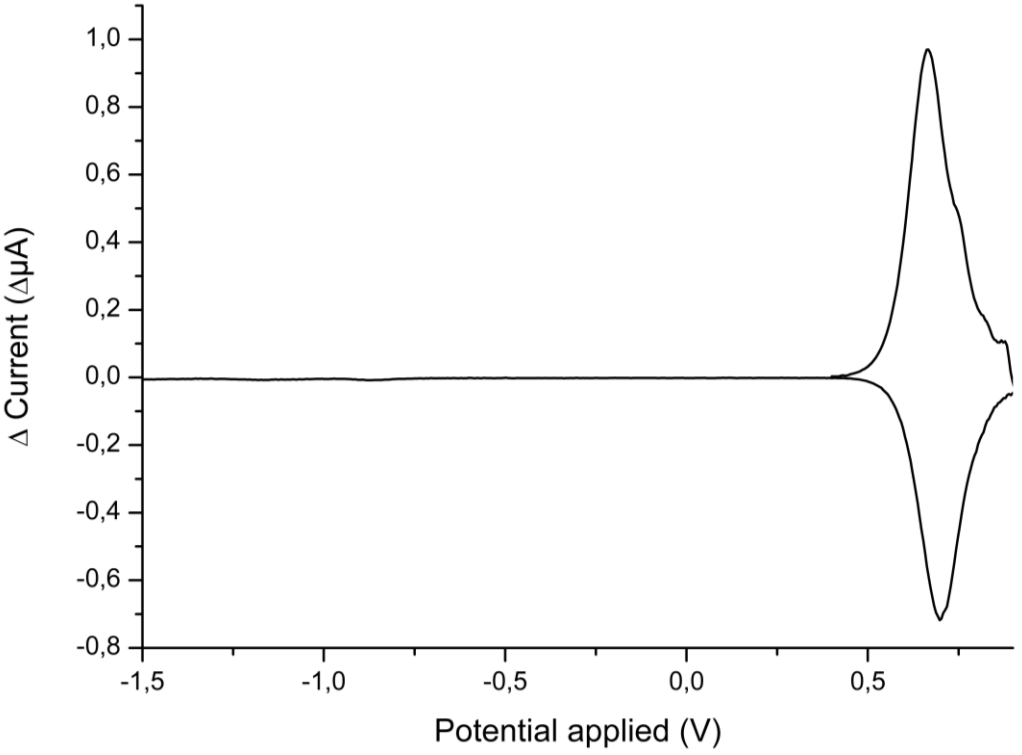



**Fig. S72** Differential pulse voltammogram (DPV) of **3**$^{i\text{Pr-Me}_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at room temperature.

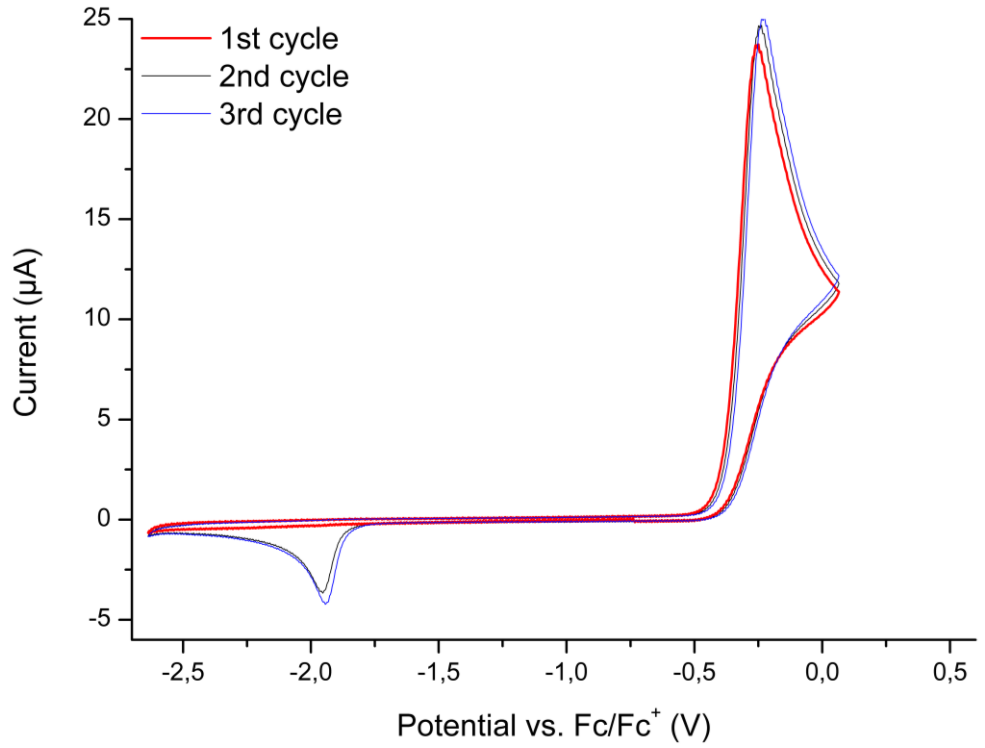



**Fig. S73** Cyclic voltammograms of $\mathbf{3}^{i\text{Pr-Me}_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ showing first three scans at 100 $mVs^{-1}$ scan rate.

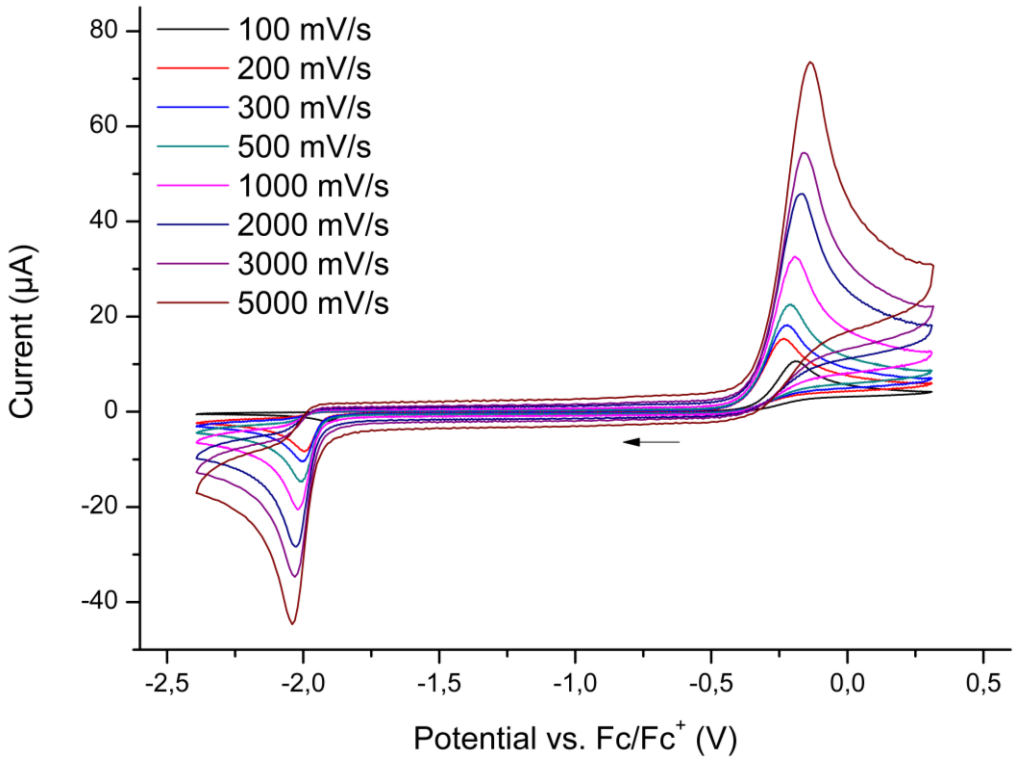



**Fig. S74** Cyclic voltammograms of $\mathbf{3}^{t\text{Bu-Me}_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at different scan rates. NB: the second scans are shown since the reduction signal only appears after the first full cycle (see below).

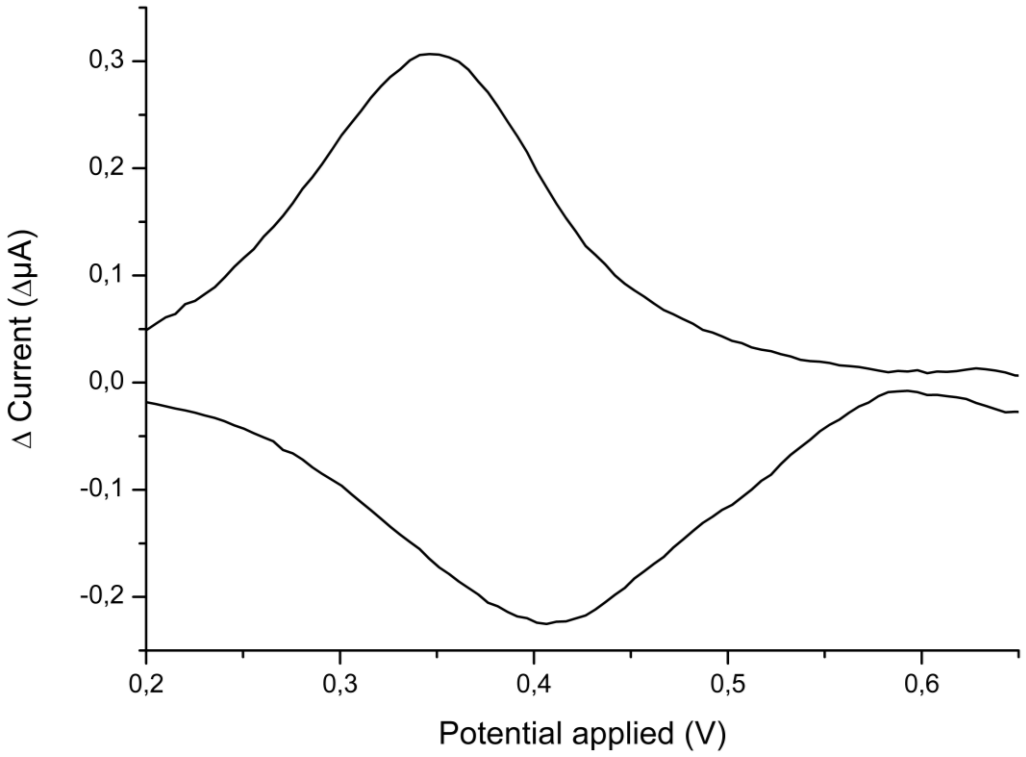



**Fig. S75** Differential pulse voltammogram (DPV) of **3**$^{t\text{Bu-Me}_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ at room temperature.

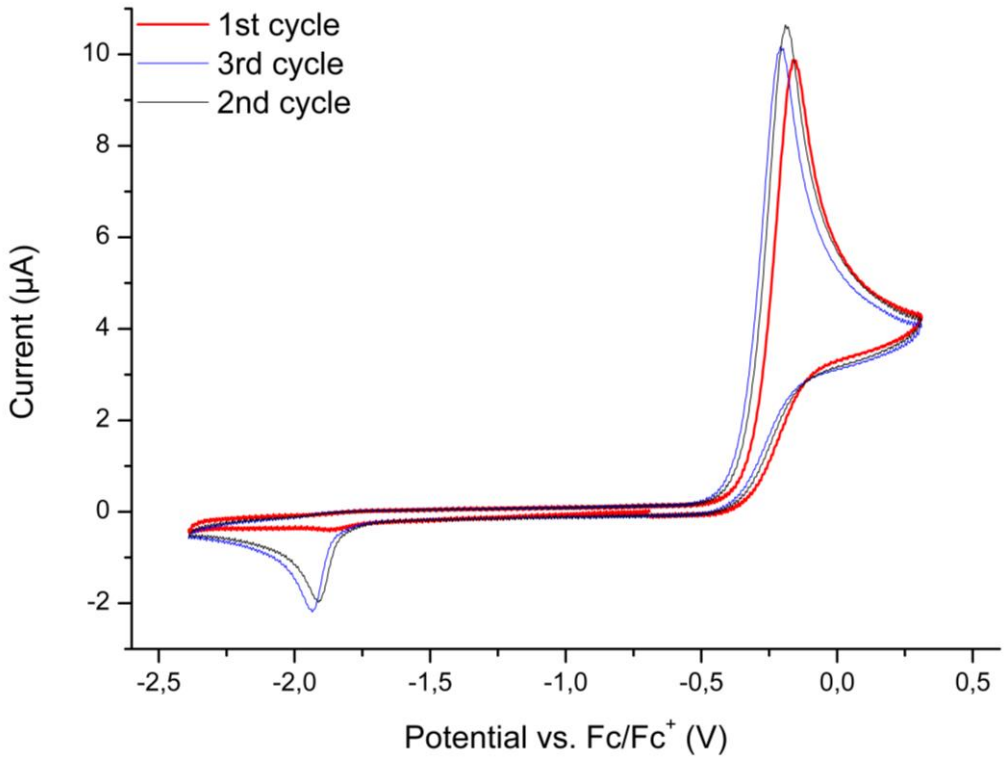



**Fig. S76** Cyclic voltammograms of **3**$^{t\text{Bu-Me}_2}$ in $CH_3CN$/0.1 M $Bu_4NPF_6$ showing the first three cycles at 100 $mVs^{-1}$ scan rate.

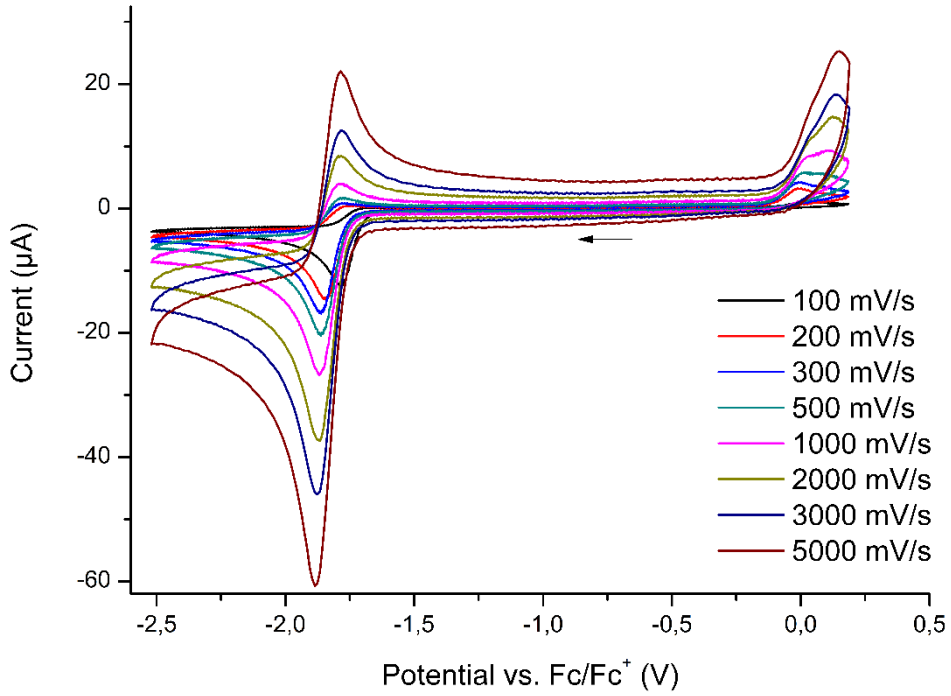



**Fig. S77** Cyclic voltammograms of $\mathbf{1}^{\mathbf{Dip\text{-}Me_2}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$]) at different scan rates.

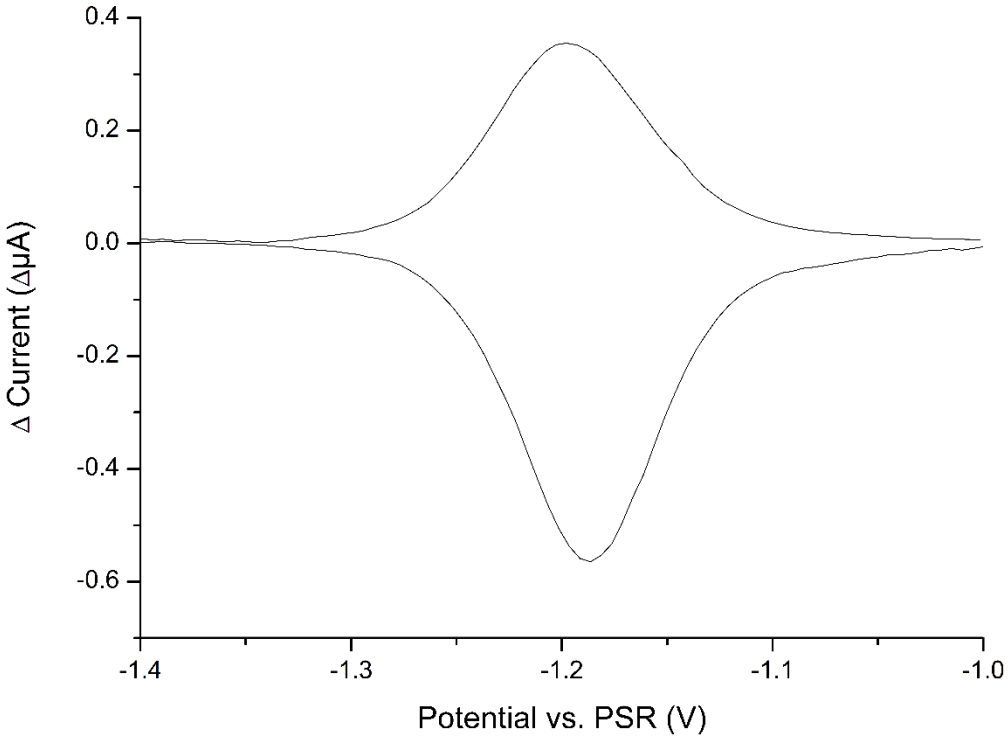



**Fig. S78** Differential pulse voltammogram (DPV) of $\mathbf{1}^{\mathbf{Dip\text{-}Me_2}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$] at 10 $mVs^{-1}$.

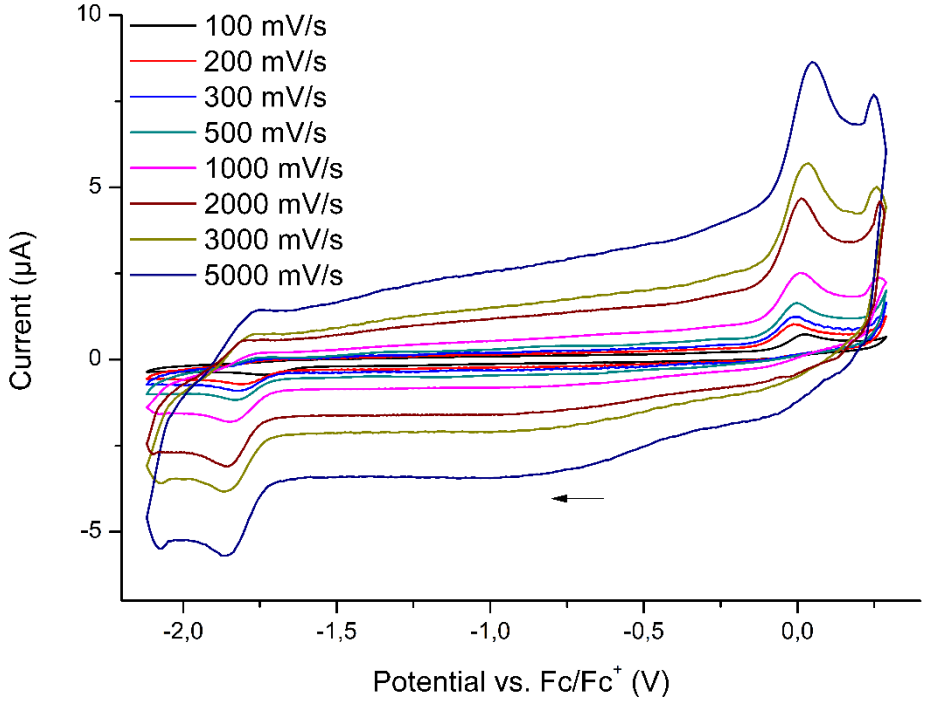



**Fig. S79** Cyclic voltammograms of $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$]) at different scan rates.

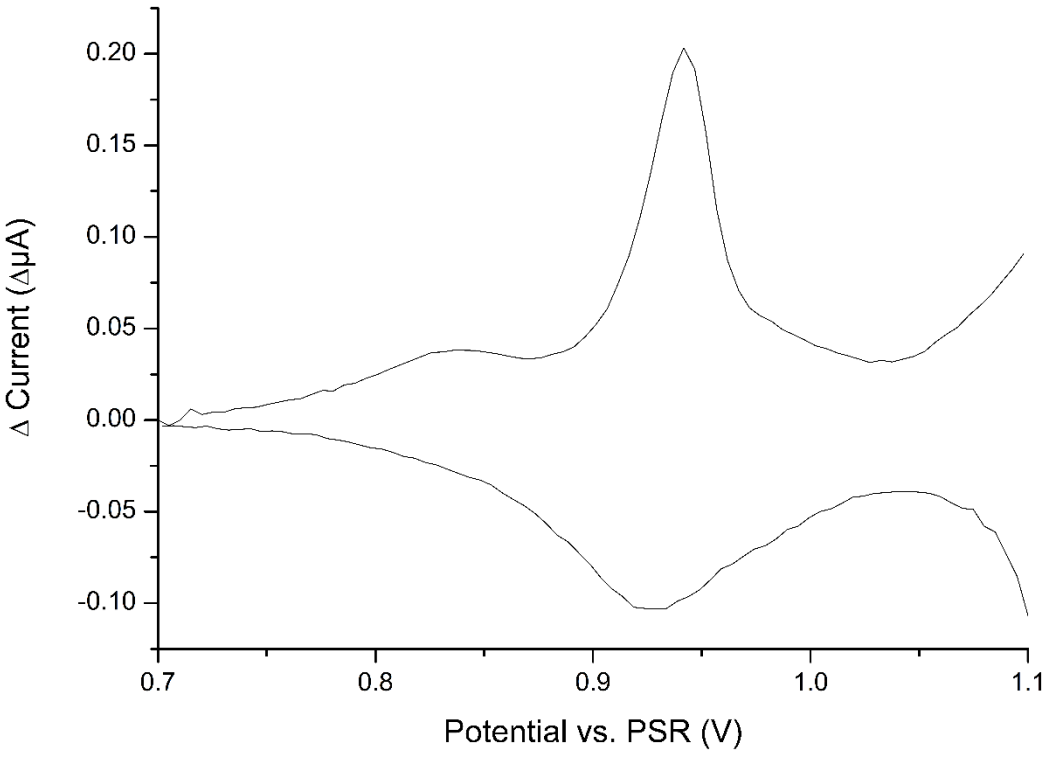



**Fig. S80** Differential pulse voltammogram (DPV) of $\mathbf{3}^{\mathbf{Dip\text{-}Me_2}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$]) at 10 $mVs^{-1}$.

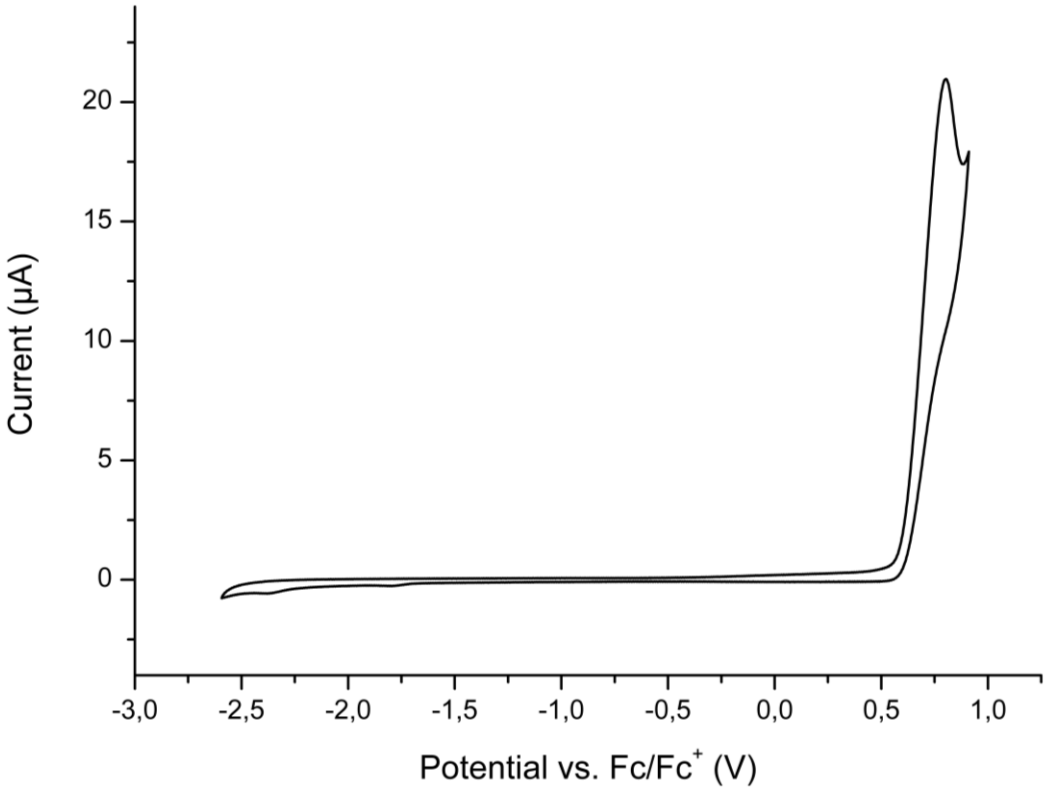



**Fig. S81** Cyclic voltammogram of **4**$^{\mathbf{Dip\text{-}Me_2}}$ in THF (0.1 M [$^{n}$Bu$_4$N][PF$_6$]) at 100 mVs$^{-1}$.

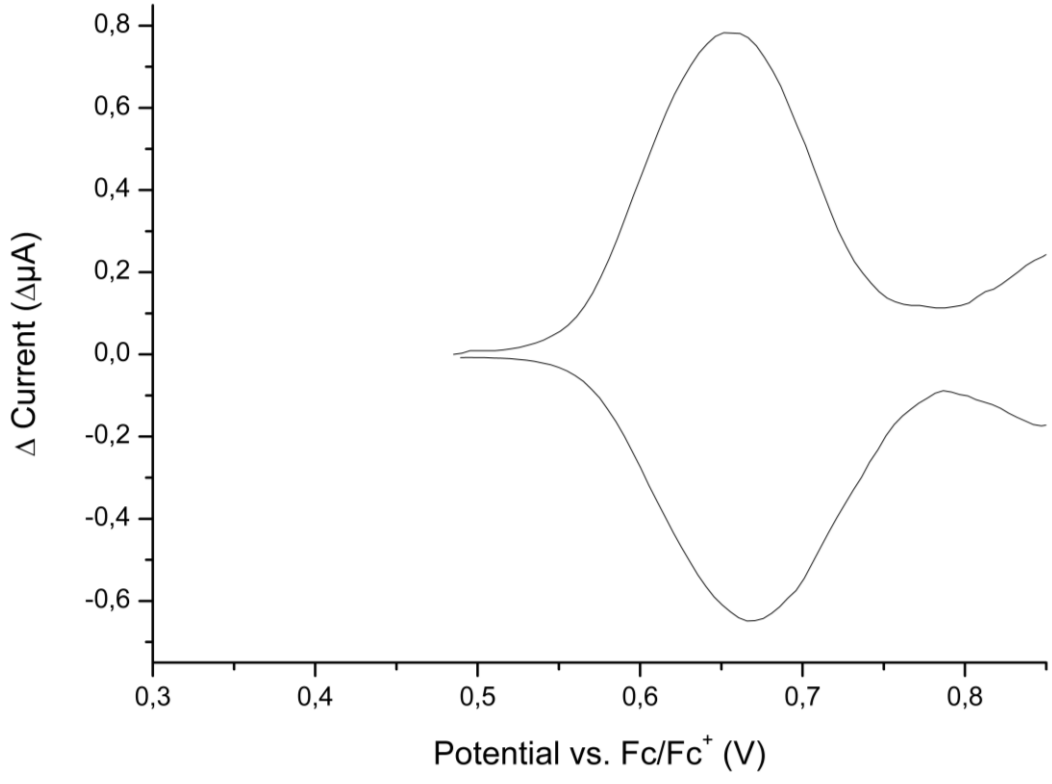



**Fig. S82** Differential pulse voltammogram (DPV) of **4**$^{\mathbf{Dip\text{-}Me_2}}$ in THF (0.1 M [$^{n}$Bu$_4$N][PF$_6$]) at 10 mVs$^{-1}$.

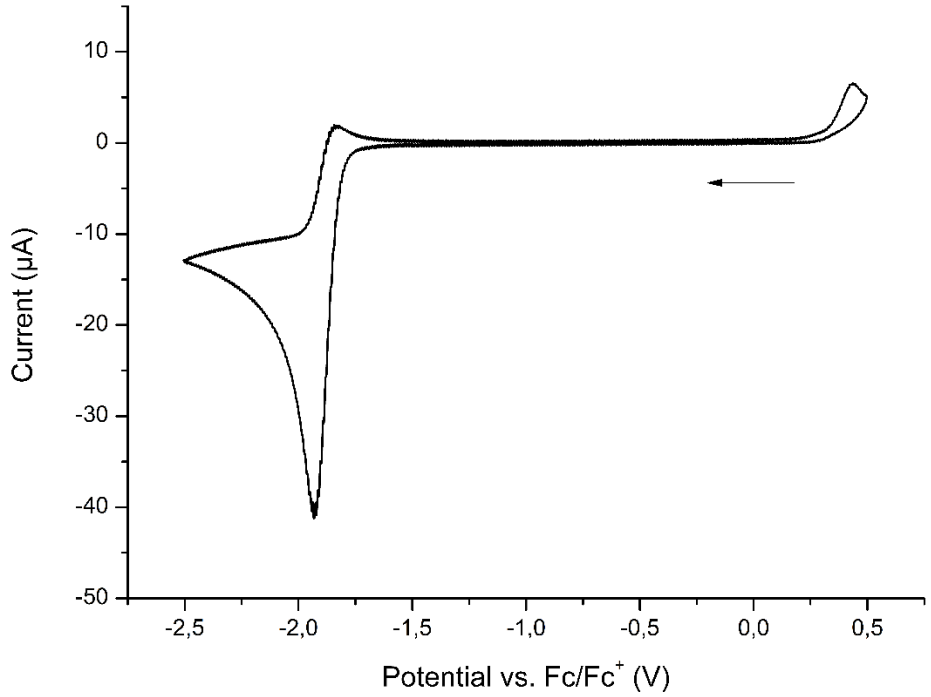



**Fig. S83** Cyclic voltammogram of $\mathbf{1}^{\mathbf{Dip\text{-}Et_2}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$]) at 100 $mVs^{-1}$.

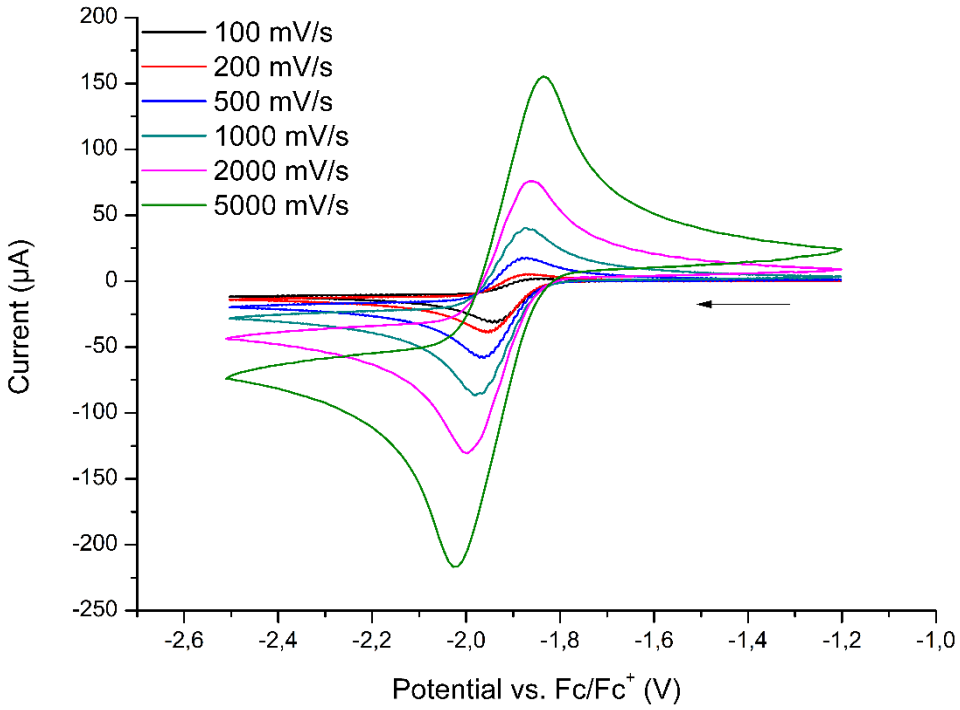



**Fig. S84** Cyclic voltammograms of $\mathbf{1}^{\mathbf{Dip\text{-}Et_2}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$]) at different scan rates.

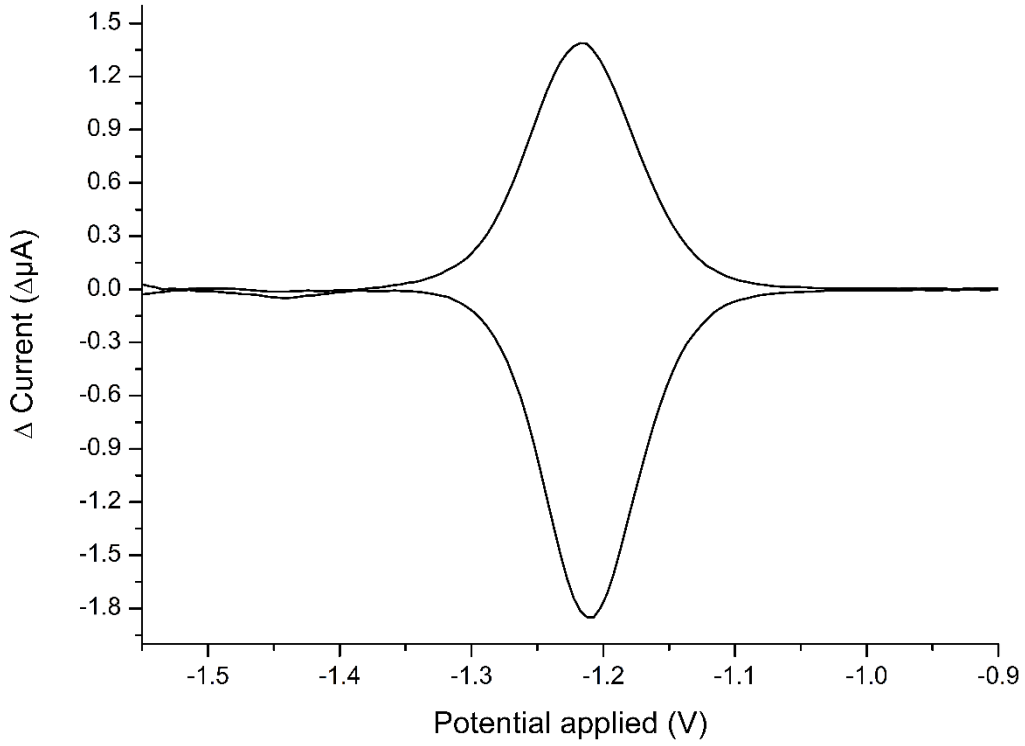



**Fig. S85** Differential pulse voltammogram (DPV) of $\mathbf{1}^{\mathbf{Dip\text{-}Et_2}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$]) at 10 mVs$^{-1}$.

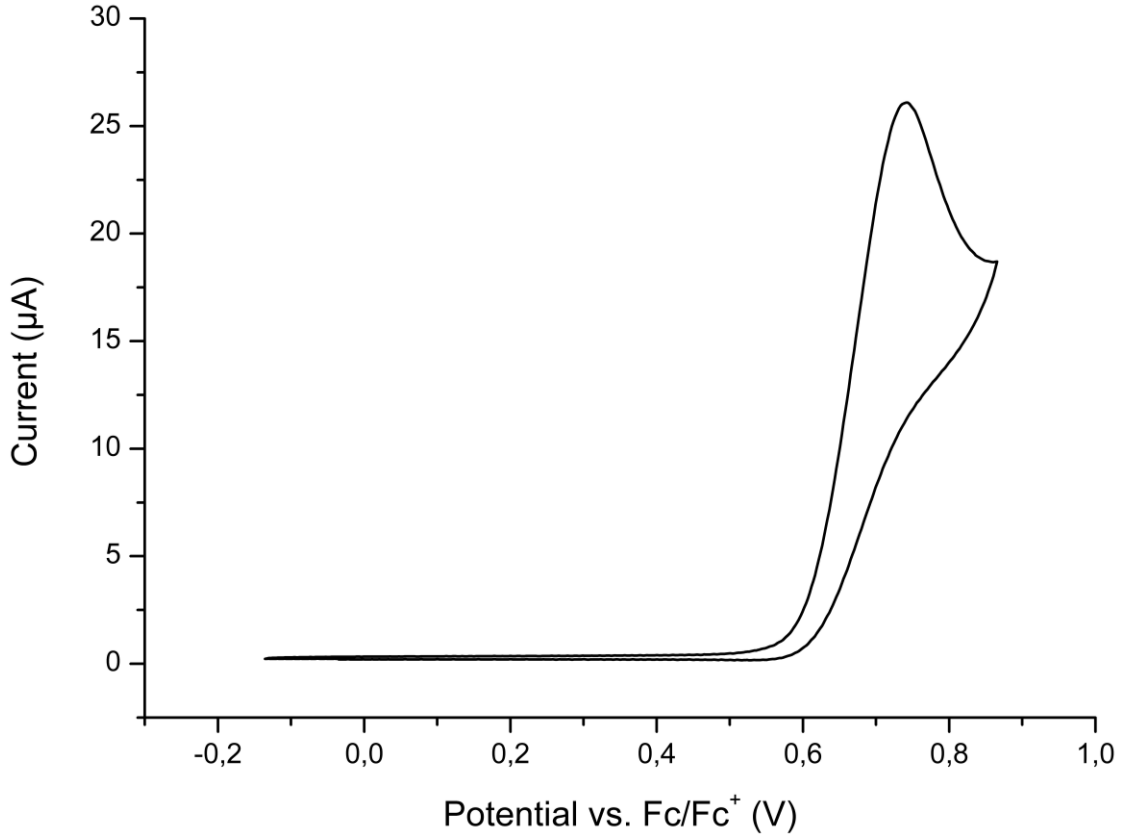



**Fig. S86** Cyclic voltammogram of $\mathbf{4}^{\mathbf{Dip\text{-}Et_2}}$ in THF (0.1 M [$^n$Bu$_4$N][$PF_6$]) at 100 mVs$^{-1}$.

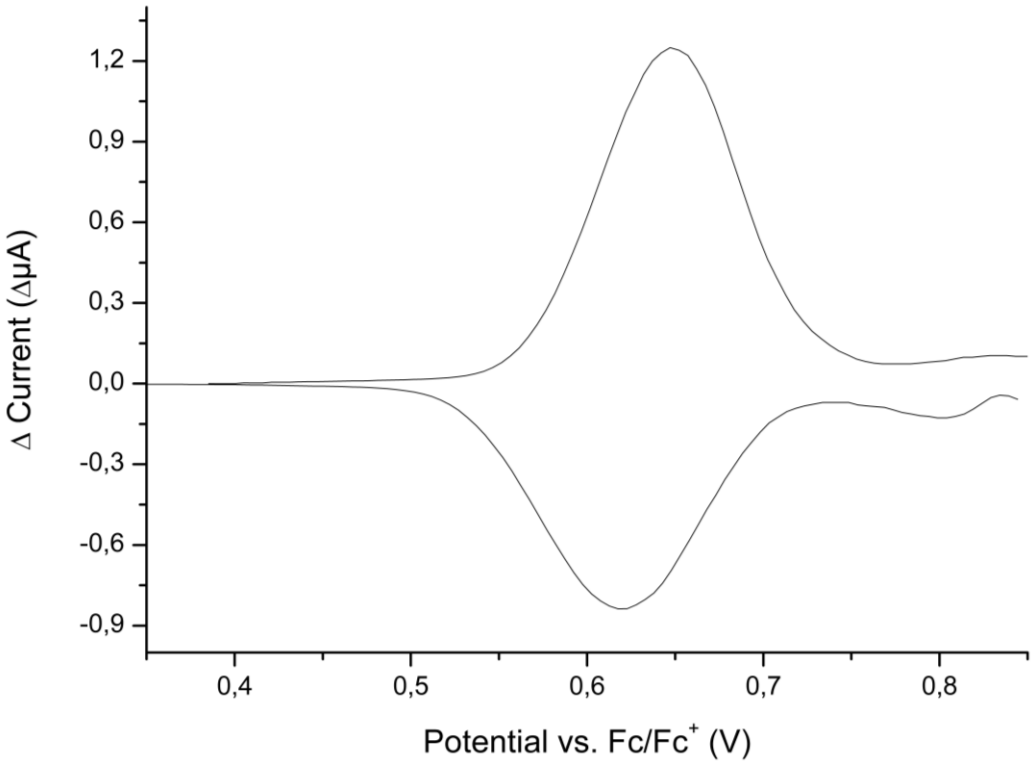



**Fig. S87** Differential pulse voltammogram (DPV) of $\mathbf{4}^{\mathbf{Dip\text{-}Et_2}}$ in THF (0.1 M [$^n$Bu$_4$N][PF$_6$]) at 10 mVs$^{-1}$.

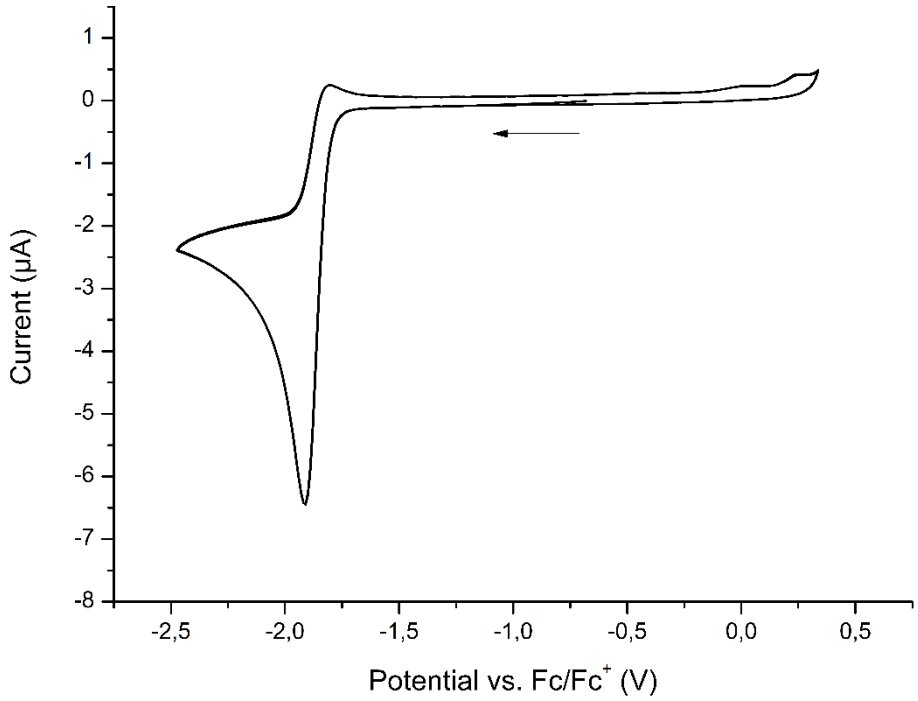



**Fig. S88** Cyclic voltammogram of $\mathbf{1}^{\mathbf{Dip\text{-}(CH_2)_5}}$ in CH$_3$CN (0.1 M [$^n$Bu$_4$N][PF$_6$]) at 100 mVs$^{-1}$.

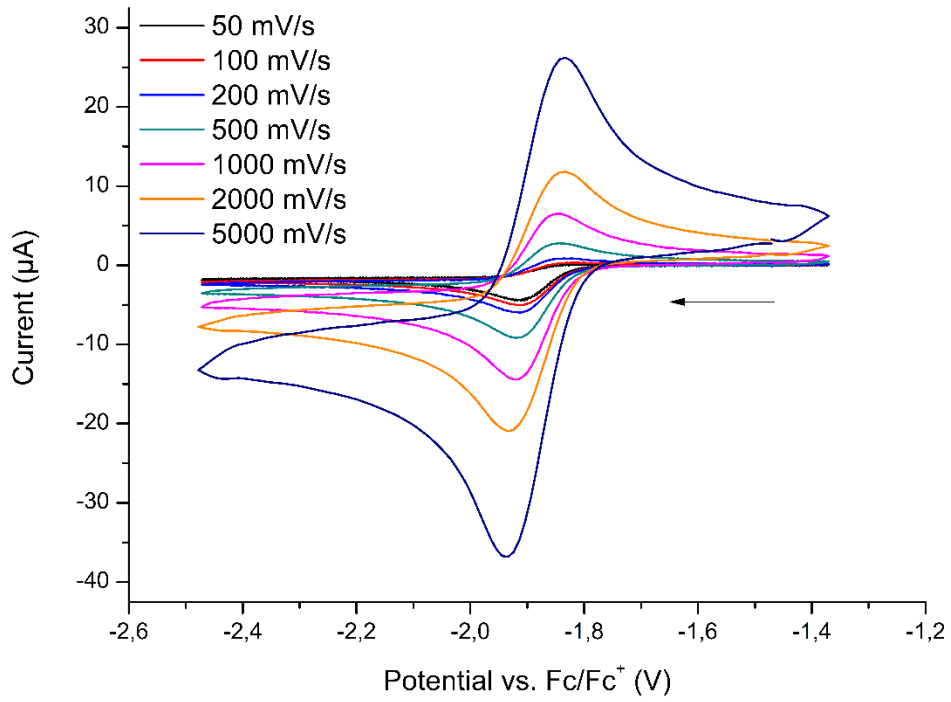



**Fig. S89** Cyclic voltammograms of $\mathbf{1}^{\mathbf{Dip\text{-}(CH_2)_5}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$]) at different scan rates.

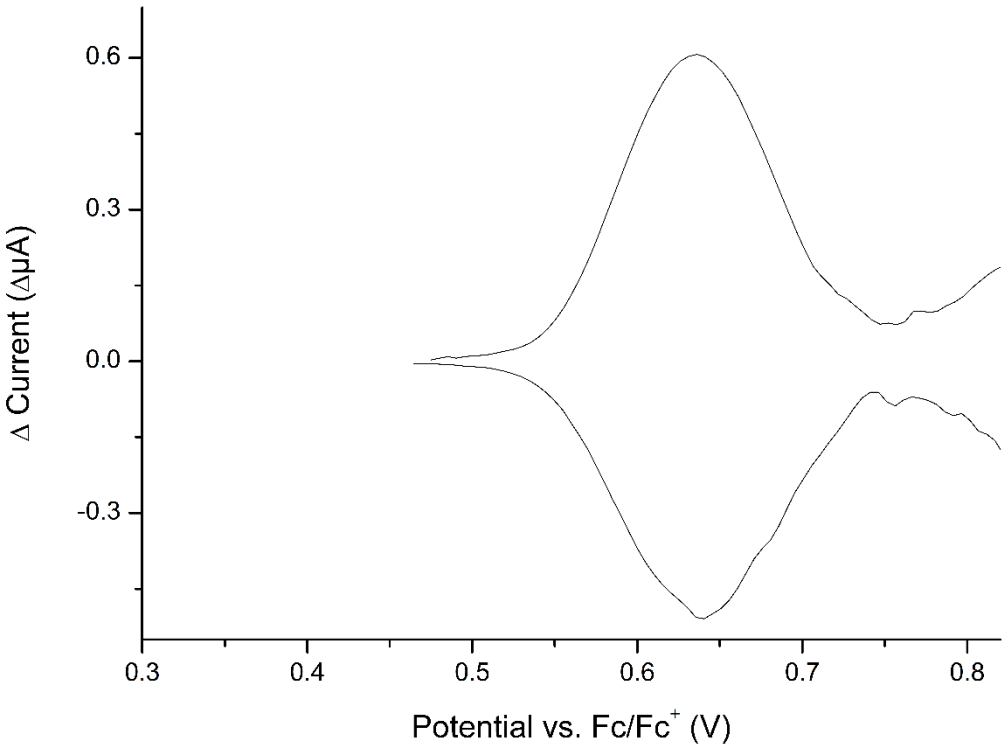



**Fig. S90** Differential pulse voltammogram (DPV) of $\mathbf{1}^{\mathbf{Dip\text{-}(CH_2)_5}}$ in $CH_3CN$ (0.1 M [$^n$Bu$_4$N][$PF_6$]) at 10 $mVs^{-1}$.

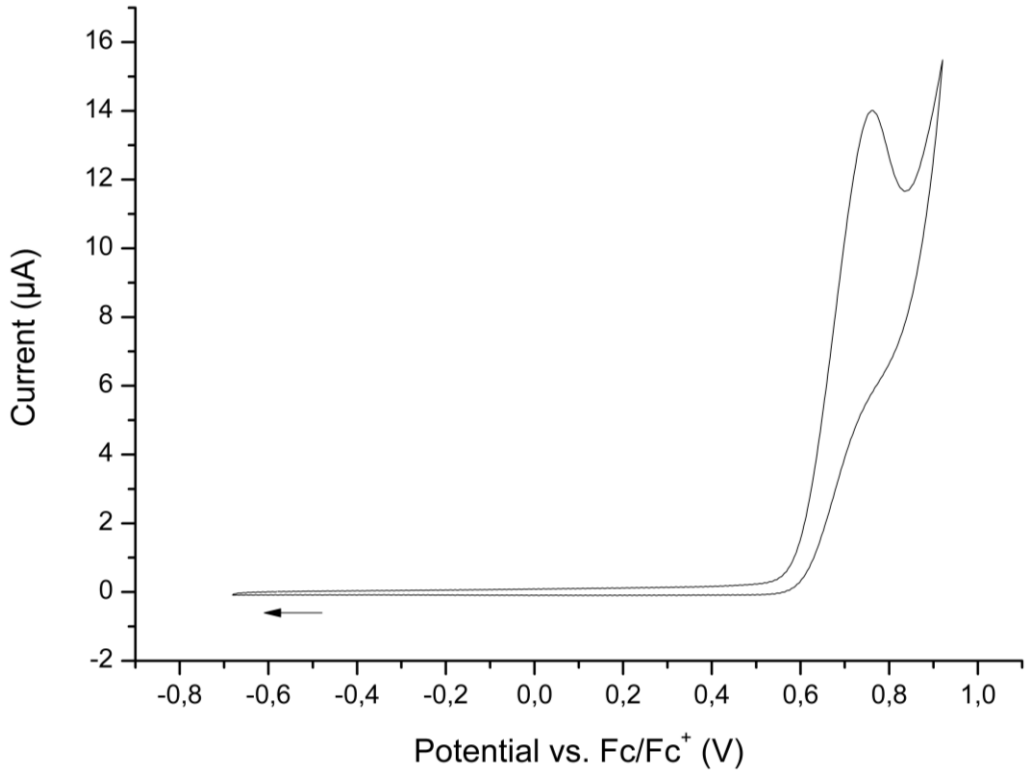



**Fig. S91** Cyclic voltammogram of **4**$^{\text{Dip-(CH}_2\text{)}_5}$ in THF (0.1 M [$^n$Bu$_4$N][PF$_6$]) at 100 mVs$^{-1}$.

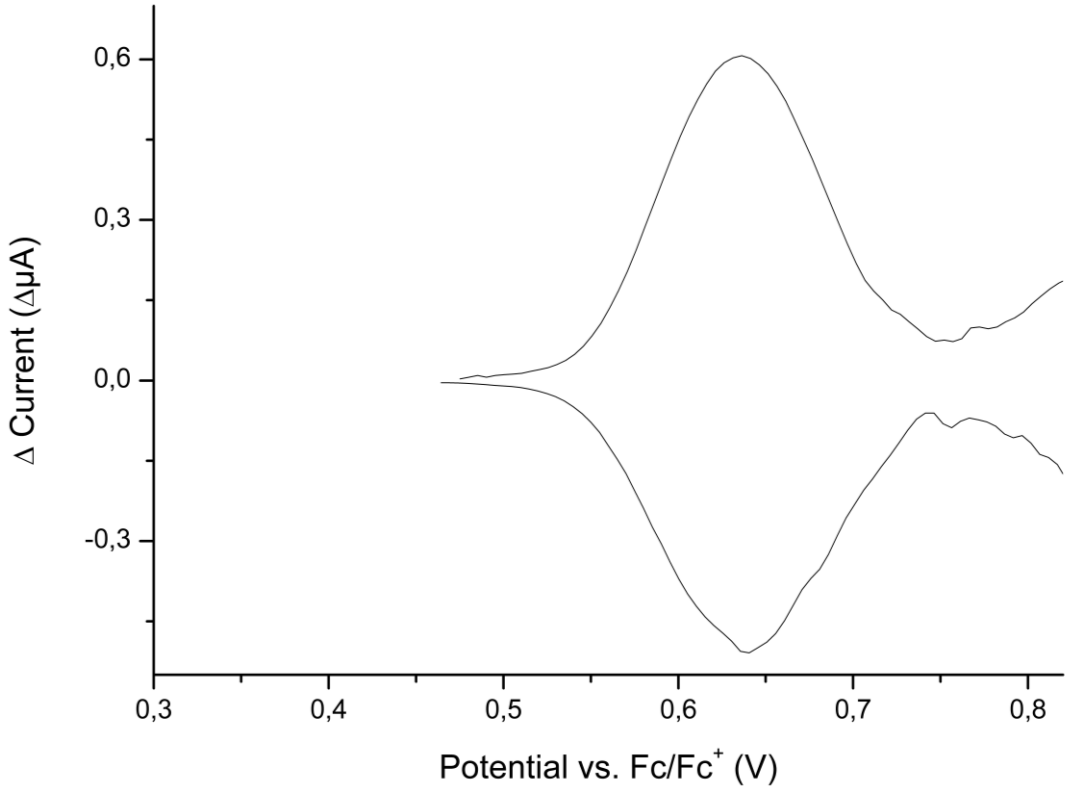



**Fig. S92** Differential pulse voltammogram (DPV) of **4**$^{\text{Dip-(CH}_2\text{)}_5}$ in THF (0.1 M [$^n$Bu$_4$N][PF$_6$]) at 10 mVs$^{-1}$.

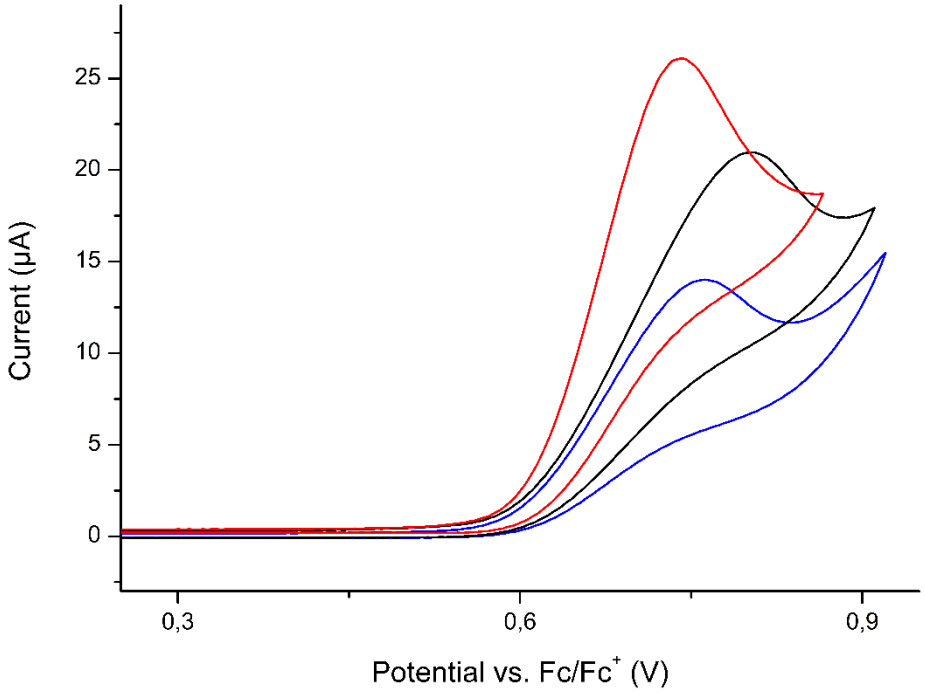



**Fig. S93** Cyclic voltammograms of $\mathbf{4}^{\mathbf{Dip\text{-}Me_2}}$ (black), $\mathbf{4}^{\mathbf{Dip\text{-}Et_2}}$ (red), and $\mathbf{4}^{\mathbf{Dip\text{-}(CH_2)_5}}$ (blue) in THF (0.1 M [$^n$Bu$_4$N][PF$_6$]) at 100 mVs$^{-1}$.

**HRMS Spectra of $3^{i\text{Pr-Me}_2}$, $3^{\text{Dip-Et}_2}$, and $3^{\text{Dip-(CH}_2)_5}$**

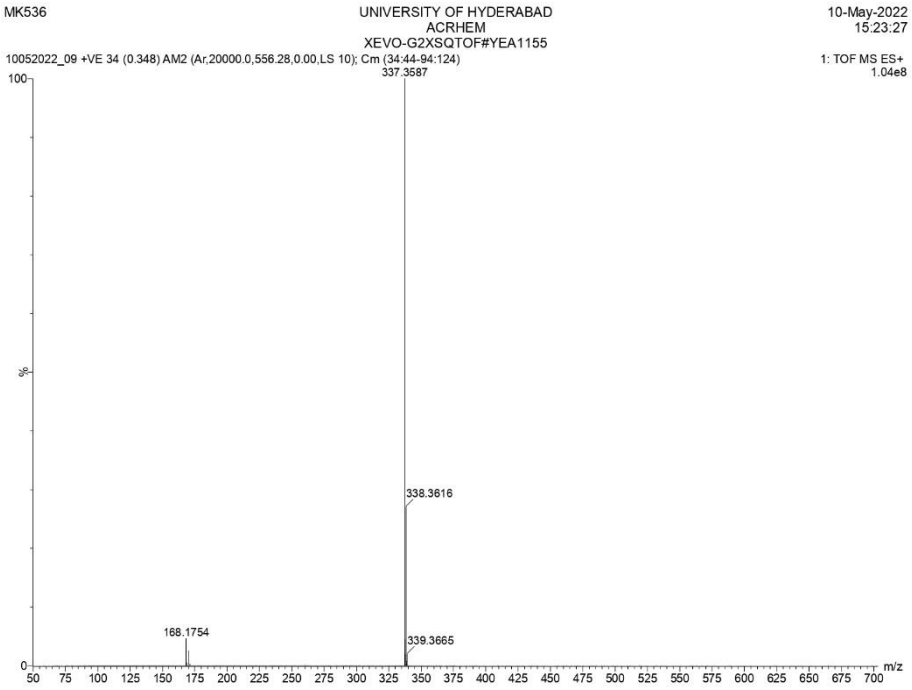



**Fig. S94** HRMS spectrum of $3^{i\text{Pr-Me}_2}$.

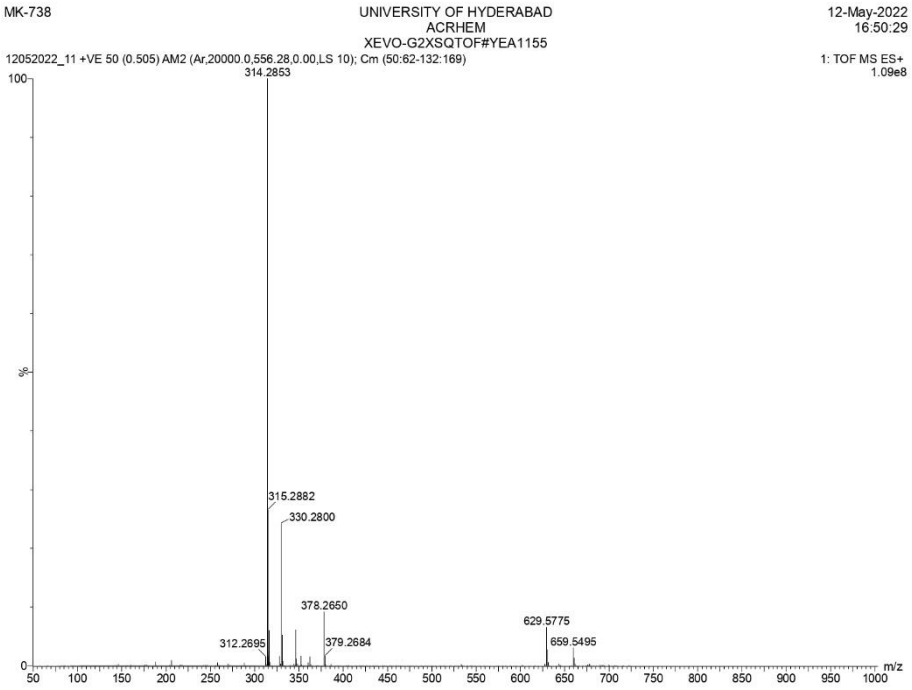



**Fig. S95** HRMS spectrum of the crude reaction mixture of $\mathbf{1}^{\text{Dip-Et}_2}$ and $KC_8$ showing the formation of $\mathbf{3}^{\text{Dip-Et}_2}$.

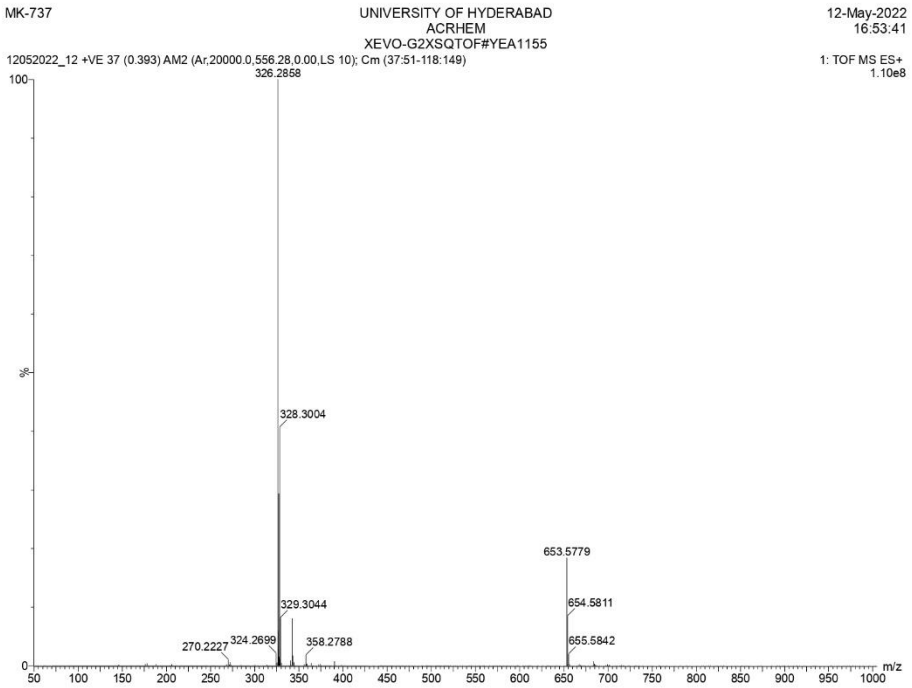
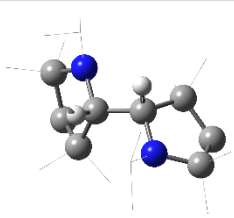
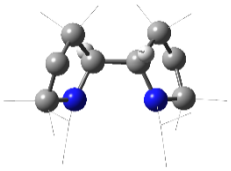
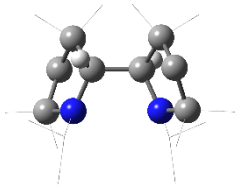
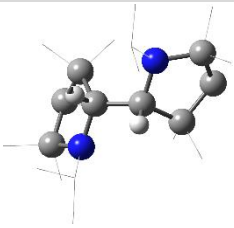
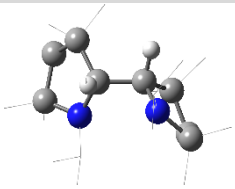
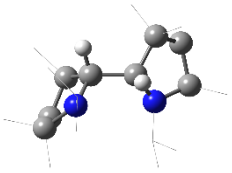
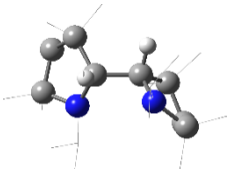
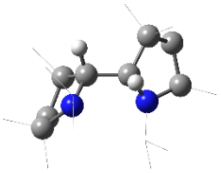



**Fig. S96** HRMS spectrum of the crude reaction mixture of $\mathbf{1}^{\mathbf{Dip\text{-}Cy}}$ and $KC_8$ showing the formation of $\mathbf{3}^{\mathbf{Dip\text{-}(CH_2)_5}}$.

**Quantum Chemical Calculations**

The quantum chemical calculations in this paper were performed with the Gaussian 16 (RevB.01) programme.[S19] Initially, possible geometries of *anti*- and *gauche*-rotamers of *(S/S)*, *(R/R)*, *(S/R)*, and *(R/S)* isomers of **3**$^{i\text{Pr-Me}_2}$ and **3**$^{t\text{Bu-Me}_2}$ were suggested from modification of the X-ray results of **3**$^{t\text{Bu-Me}_2}$ (*anti*-rotamer of *(R/R)* isomer). The scanning of H-C-C-H dihedral angles by semi-empirical methods (AM1 and PM3) was applied to define geometries. Eventually, the possible initial geometries from semi-empirical methods were re-optimised at the Becke-3-Lee−Yang−Parr (B3LYP) functional with 6-311G(d,p) basis set.[S20] For all the calculations, Grimme's empirical dispersion correction with BJ damping was applied.[S21,S22] Starting from possible initial geometries, the scanning of the H-C-C-H dihedral angles of *anti*- and *gauche*-rotamers of *(S/S)*, *(R/R)*, *(S/R)*, and *(R/S)* isomers of **3**$^{i\text{Pr-Me}_2}$ and **3**$^{t\text{Bu-Me}_2}$ was investigated by the modredundant method (10 degree; 36 step) at the B3LYP-(D3)BJ/6-311G(d,p) level of theory. For instance, for **3**$^{i\text{Pr-Me}_2}$ the scanning of the H-C-C-H dihedral angle of the *(R/R)* isomer was started from its *anti*-rotamer, whereas the *gauche*-rotamer was considered as initial geometry for the *(S/S)* configuration. The relative energies in kcal mol$^{-1}$ were determined from the optimised geometries of the corresponding points in scanning diagrams of **3**$^{i\text{Pr-Me}_2}$ and **3**$^{t\text{Bu-Me}_2}$. The GIAO approach was used to calculate the NMR chemical shifts at the B3LYP-(D3)BJ/6-311G(d,p)/CPCM=Benzene level of theory.[S23,S24] The chemical shifts were referenced to the values calculated for TMS (tetramethylsilane) at the same level of theory. The GaussView 5.0 programme was applied for all visualisations.[S25]

**Table S5.** Calculated relative energies, ∠H–C–C–H, and $\delta$ of NC-*H* of the optimised isomers of **3**$^{iPr\text{-}Me_2}$

| Diastereomers | *R*/*R* | | *S*/*S* | |
|---|---|---|---|---|
| Conformations | A | G | G | A |
| Optimised Geometry |  |  |  |  |
| $\Delta G_{rel}$ (kcal mol$^{-1}$) | +3.0 | 0 | 0 | +3.0 |
| ∠N–C–C–N | –178.6 | –24.6 | 24.6 | 178.6 |
| ∠H–C–C–H | 53.3 | –145.7 | 145.7 | –53.3 |
| $\delta_{cal}$ (ppm) of NC-*H* | 3.76 | 3.08 | 3.08 | 3.76 |
| $\delta_{obs}$ (ppm) of NC-*H* | 3.36 | 3.01 | 3.01 | 3.36 |
| Diastereomers | *R*/*S* | | *S*/*R* | |
| Conformations | G1 | G2 | G1 | G2 |
| Optimised Geometry |  |  |  |  |
| $\Delta G_{rel}$ (kcal mol$^{-1}$) | +0.2 | +0.2 | +0.2 | +0.2 |
| ∠N–C–C–N | –82.1 | 82.1 | –82.1 | 82.1 |
| ∠H–C–C–H | –79.0 | 79.0 | –79.0 | 79.0 |
| $\delta_{cal}$ (ppm) of NC-*H* | 3.42/2.91 | 2.91/3.42 | 2.91/3.42 | 3.42/2.91 |
| $\delta_{obs}$ (ppm) of NC-*H* | 3.37/3.09 | 3.09/3.37 | 3.09/3.37 | 3.37/3.09 |

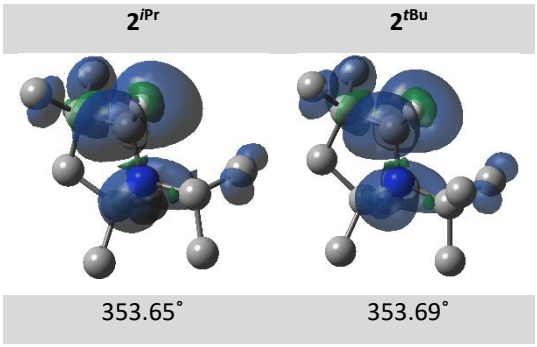
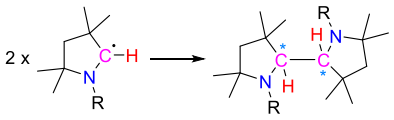



**Fig. S97** Spin density plots of the $\mathbf{2}^{i\text{Pr-Me}_2}$ and $\mathbf{2}^{t\text{Bu-Me}_2}$. Pyramidalisation angles (PA) of radical carbon centre for $\mathbf{2}^{i\text{Pr-Me}_2}$ and $\mathbf{2}^{t\text{Bu-Me}_2}$. Hydrogen atoms except for C-*H* omitted for clarity. Isovalue = 0.05.




R = *i*Pr –35.2 (RR Lowest Energy)
R = *t*Bu –15.8 (RR Crystal Structure)

**Scheme S1.** The calculated ΔG relative energies of $\mathbf{2}^{i\text{Pr-Me}_2}$ and $\mathbf{2}^{t\text{Bu-Me}_2}$ (left side) *vs* corresponding dimers $\mathbf{3}^{i\text{Pr-Me}_2}$ and $\mathbf{3}^{t\text{Bu-Me}_2}$ (right side) at the B3LYP-D3(BJ)/6-311G(d,p) level of theory.

**Table S6.** Relative energies, dihedral angles, and $^1$H-NMR data (*H*-C) of the optimised *(S,S)/(R,R)* and *(S,R)/(R,S)* isomers of $\mathbf{3}^{i\text{Pr-Me}_2}$ from computations at the B3LYP-D3(BJ)/6-311G(d,p) level of theory. (For NMR CPCM=benzene). All obtained data are from optimised geometries of the corresponding points (A = Anti; G = Gauche).

| | ***(R/R)*** | | ***(S/S)*** | | ***(R/S)*** | | ***(S/R)*** | |
|---|---|---|---|---|---|---|---|---|
| | **A** | **G** | **G** | **A** | **G1** | **G2** | **G1** | **G2** |
| **$\Delta G_{rel}$** | +3.0 | 0 | 0 | +3.0 | +0.2 | +0.2 | +0.2 | +0.2 |
| **Dihedral (NCCN)** | -178.6 | -24.6 | 24.6 | 178.6 | -82.1 | 82.1 | -82.1 | 82.1 |
| **Dihedral (HCCH)** | 53.3 | -145.7 | 145.7 | -53.3 | -79.0 | 79.0 | -79.0 | 79.0 |
| **NMR** | 3.76 | 3.08 | 3.08 | 3.76 | 3.42/2.91 | 2.91/3.42 | 2.91/3.42 | 3.42/2.91 |

**Table S7.** Relative energies, dihedral angles, and $^{1}$H-NMRs (*H*-C) of the optimised *(S/S)*, *(R/R)*, and *(S/R)/(R/S)* isomers of **3**$^{t\text{Bu-Me}_2}$ from computations at the B3LYP-D3(BJ)/6-311G(d,p) level of theory. (For NMR CPCM=benzene). All the obtained data are from optimised geometries of the corresponding points (A = Anti; G = Gauche).

| | *(R/R)* | | *(S/S)* | | *(R/S)* | | *(S/R)* | |
|---|---|---|---|---|---|---|---|---|
| | **A** | **G** | **A** | **G** | **G1** | **G2** | **G1** | **G2** |
| **$\Delta G_{rel}$** | +1.0 | +2.2 | +1.0 | +2.2 | 0 | +0.4 | 0 | +0.4 |
| **Dihedral (NCCN)** | 175.9 | -26.3 | 175.9 | 26.3 | -96.9 | 96.8 | -97.0 | 96.8 |
| **Dihedral (HCCH)** | 53.9 | -148.8 | -53.9 | +148.8 | -90.6 | 91.0 | -91.0 | 90.6 |
| **NMR** | 3.71 | 3.29 | 3.71 | 3.29 | 3.56/3.39 | 3.56/3.39 | 3.56/3.39 | 3.56/3.39 |

**Table S8.** Calculated C-C single bond lengths and HCCH dihedral angles (in parentheses) for neutral and radical cation states of **3**$^{i\text{Pr-Me}_2}$.

| | **(R/R) anti** | **(R/R) gauche** | **(S/S) anti** | **(S/S) gauche** | **(R/S)/(S/R) gauche1** | **(R/S)/(S/R) gauche2** |
|---|---|---|---|---|---|---|
| **3**$^{i\text{Pr-Me}_2}$ | 1.561 | 1.570 | 1.561 | 1.570 | 1.563 | 1.563 |
| **(Neutral)** | (53.3) | (-145.7) | (-53.3) | (145.7) | (-79.0) | (79.1) |
| **3**$^{i\text{Pr-Me}_2}$ | 1.699 | 1.670 | 1.702 | 1.670 | 1.669 | 1.669 |
| **(Radical-Cation)** | (51.8) | (-149.2) | (-51.8) | (149.2) | (-78.4) | (78.4) |

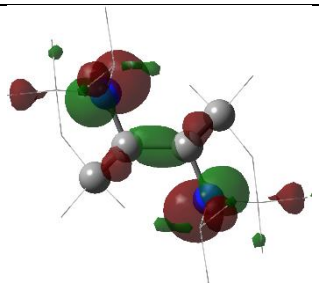
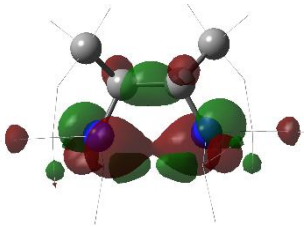
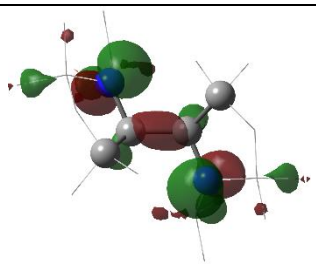
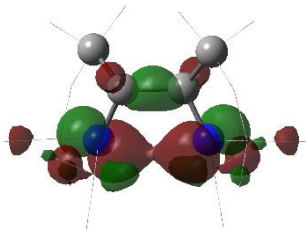
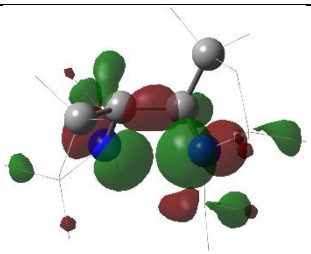
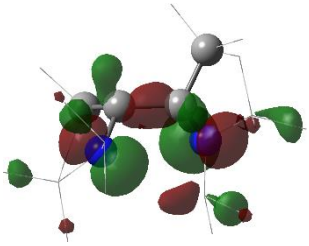
| $3^{i\text{Pr-Me}_2}$ | HOMO (IsoValue=0.05) | $3^{i\text{Pr-Me}_2}$ | HOMO (IsoValue=0.05) |
|---|---|---|---|
| ***S,S*** **(Anti)** |  | ***S,S*** **(Gauche)** |  |
| ***R,R*** **(Anti)** |  | ***R,R*** **(Gauche)** |  |
| ***R,S/S,R*** **(Gauche1)** |  | ***R,S/S,R*** **(Gauche2)** |  |

**Fig. S98** Highest occupied molecular orbital (HOMO) plots of the $\mathbf{3}^{i\text{Pr-Me}_2}$. All hydrogen atoms omitted for clarity. Isovalue = 0.05.

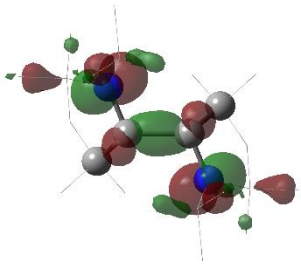
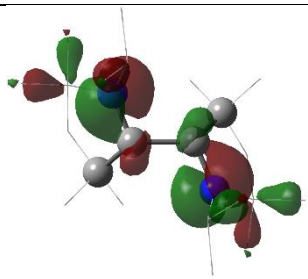
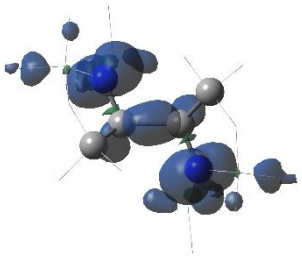
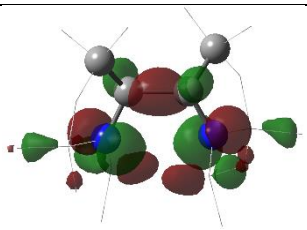
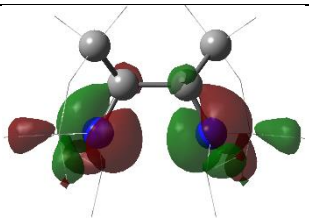
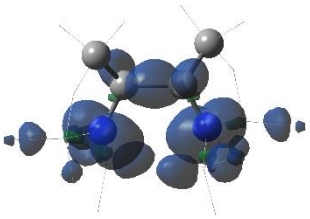
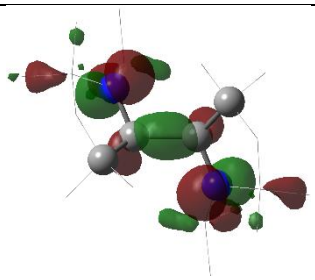
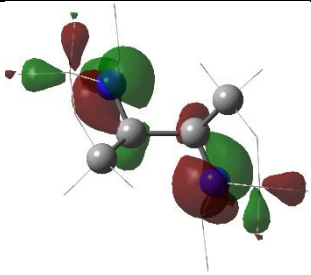
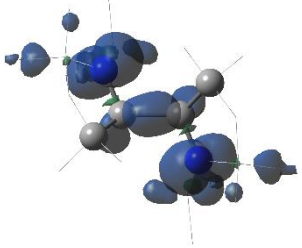
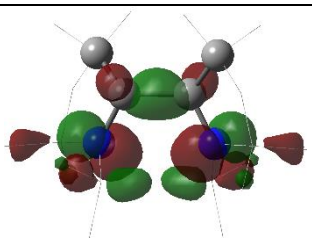
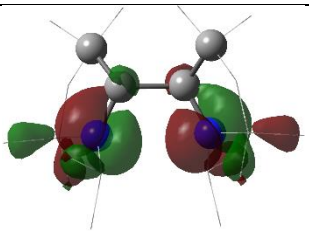
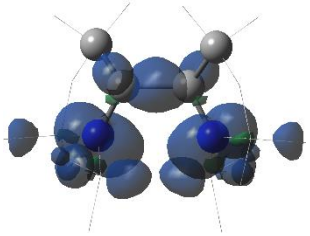
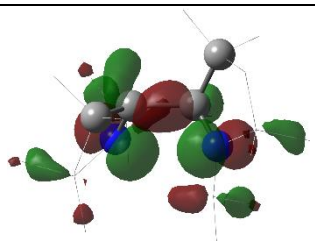
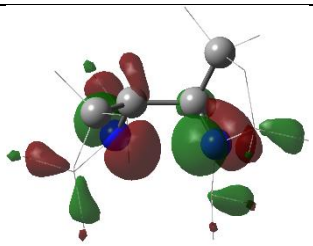
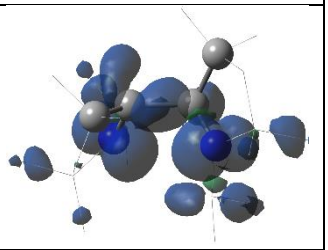
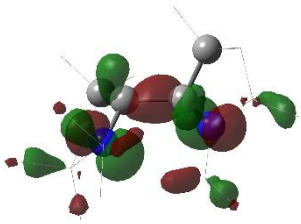
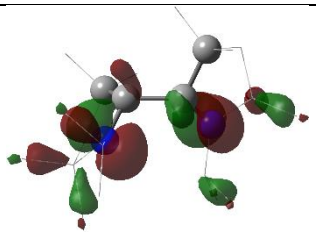
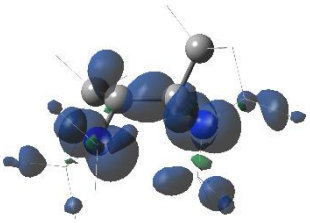
| $3^{i\text{Pr-Me}_2}$ (Radical-Cation) | SOMO-α (IsoValue=0.05) | SOMO-β (IsoValue=0.05) | Spin Density Plot (IsoValue=0.002) |
|---|---|---|---|
| ***S,S*** **(*anti*)** |  |  |  |
| ***S,S*** **(*gauche*)** |  |  |  |
| ***R,R*** **(*anti*)** |  |  |  |
| ***R,R*** **(*gauche*)** |  |  |  |
| ***R,S/S,R*** **(*gauche*-1)** |  |  |  |
| ***R,S/S,R*** **(*gauche*-2)** |  |  |  |

**Fig. S99** Highest occupied molecular orbital (HOMO) and spin density plots of the radical-cation of $\mathbf{3}^{i\text{Pr-Me}_2}$. All hydrogen atoms omitted for clarity. Isovalue = 0.05.

**Table S9.** Hybridisation of the Central C-C bond of **3**$^{i\text{Pr-Me}_2}$

| Diastereomers | ***R/R*** | | ***S/S*** | |
|---|---|---|---|---|
| Conformations | **A** | **G** | **G** | **A** |
| | C($sp^{2.52}$)-C($sp^{2.52}$) | C($sp^{2.59}$)-C($sp^{2.59}$) | C($sp^{2.59}$)-C($sp^{2.59}$) | C($sp^{2.52}$)-C($sp^{2.52}$) |
| Diastereomers | ***R/S*** | | ***S/R*** | |
| Conformations | **G1** | **G2** | **G1** | **G2** |
| | C($sp^{2.51}$)-C($sp^{2.53}$) | C($sp^{2.51}$)-C($sp^{2.53}$) | C($sp^{2.51}$)-C($sp^{2.53}$) | C($sp^{2.51}$)-C($sp^{2.53}$) |

**Table S10.** Hybridisation of the Central C-C bond of **3**$^{t\text{Bu-Me}_2}$

| Diastereomers | ***R/R*** | | ***S/S*** | |
|---|---|---|---|---|
| Conformations | **A** | **G** | **G** | **A** |
| | C($sp^{2.59}$)-C($sp^{2.59}$) | C($sp^{2.65}$)-C($sp^{2.65}$) | C($sp^{2.65}$)-C($sp^{2.65}$) | C($sp^{2.59}$)-C($sp^{2.59}$) |
| Diastereomers | ***R/S*** | | ***S/R*** | |
| Conformations | **G1** | **G2** | **G1** | **G2** |
| | C($sp^{2.62}$)-C($sp^{2.62}$) | C($sp^{2.62}$)-C($sp^{2.62}$) | C($sp^{2.62}$)-C($sp^{2.62}$) | C($sp^{2.62}$)-C($sp^{2.62}$) |

**Table S11.** Cartesian coordinates and energy values of **2**$^{i\text{Pr-Me}_2}$.

| | | | |
|---|---|---|---|
| N | 0.49462200 | -0.25731400 | -0.46305900 |
| C | -0.63590200 | -1.07201100 | -0.42311200 |
| C | -1.88782000 | -0.29200300 | -0.13927900 |
| C | 0.20622500 | 1.03728000 | 0.21158200 |
| C | -1.32684600 | 1.14579400 | 0.00165800 |
| H | -1.79747900 | 1.70518800 | 0.81316400 |
| H | -1.51223000 | 1.69485200 | -0.92473100 |
| C | 0.88633300 | 2.23184500 | -0.47175100 |
| H | 0.74891700 | 2.17695600 | -1.55331700 |
| H | 1.95256900 | 2.29159500 | -0.25703400 |
| H | 0.42697500 | 3.15751600 | -0.11326400 |
| C | -2.89900500 | -0.38148000 | -1.29793100 |
| H | -3.77404900 | 0.24956300 | -1.10816300 |
| H | -3.25099300 | -1.40959500 | -1.42535600 |
| H | -2.43988200 | -0.06119000 | -2.23647700 |
| C | 0.56708600 | 1.02606500 | 1.70809800 |
| H | 0.12982000 | 0.16413800 | 2.21301900 |
| H | 0.19386300 | 1.93450400 | 2.18900600 |
| H | 1.64871300 | 0.99604200 | 1.85423000 |
| C | -2.57886900 | -0.77066000 | 1.15586300 |
| H | -2.87843200 | -1.81825800 | 1.06353100 |
| H | -3.47661900 | -0.17689800 | 1.36206400 |
| H | -1.91040100 | -0.69159600 | 2.01484700 |
| C | 1.78670700 | -0.96314600 | -0.47683400 |
| C | 2.09062400 | -1.74216200 | 0.81606500 |
| C | 2.97201300 | -0.09129300 | -0.88690400 |
| H | 1.65762300 | -1.71026900 | -1.26931100 |
| H | 1.20569700 | -2.29572300 | 1.13589900 |
| H | 2.90228000 | -2.45436300 | 0.64173500 |
| H | 2.39660800 | -1.07948900 | 1.62748300 |
| H | 2.75761800 | 0.47131900 | -1.79664000 |
| H | 3.25488900 | 0.61037700 | -0.09966400 |
| H | 3.83679700 | -0.73214400 | -1.07557800 |
| H | -0.61792300 | -1.99069900 | -0.99875200 |

Zero-point correction= 0.310861 (Hartree/Particle)
Thermal correction to Energy= 0.325256
Thermal correction to Enthalpy= 0.326200
Thermal correction to Gibbs Free Energy= 0.271084
Sum of electronic and zero-point Energies= -487.005624
Sum of electronic and thermal Energies= -486.991228
Sum of electronic and thermal Enthalpies= -486.990284
Sum of electronic and thermal Free Energies= -487.045400

**Table S12.** Cartesian coordinates and energy values of **2**$^{t\text{Bu-Me}_2}$.

| | | | |
|---|---|---|---|
| N | 0.40278600 | -0.16548500 | -0.26350700 |
| C | -0.61763100 | -1.07053400 | 0.04380600 |
| C | -1.98118000 | -0.44873100 | -0.04298900 |
| C | 1.79894600 | -0.61019400 | 0.00715200 |
| C | -0.12212200 | 1.22390000 | -0.08852000 |
| C | -1.62654300 | 1.01317400 | -0.39967900 |
| H | -2.24268600 | 1.74209800 | 0.13141800 |
| H | -1.78334600 | 1.16959500 | -1.46966600 |
| C | 1.99702700 | -0.99301600 | 1.48953000 |
| H | 1.93332300 | -0.11894300 | 2.13879200 |
| H | 2.97927400 | -1.45108700 | 1.63426800 |
| H | 1.22975700 | -1.70345100 | 1.80154500 |
| C | 0.43719300 | 2.22910400 | -1.10646800 |
| H | 1.43427200 | 2.58738700 | -0.85792300 |
| H | -0.22341500 | 3.10022200 | -1.13938600 |
| H | 0.46169900 | 1.78172300 | -2.10205300 |
| C | -2.83649100 | -1.09656700 | -1.14953700 |
| H | -2.31764400 | -1.05635200 | -2.11050100 |
| H | -3.79963100 | -0.58529600 | -1.25515300 |
| H | -3.03997000 | -2.14615500 | -0.91676700 |
| C | 2.07190200 | -1.84732500 | -0.87322800 |
| H | 1.46965500 | -2.70604300 | -0.57545200 |

| | | | |
|---|---|---|---|
| H | 3.12198900 | -2.13708000 | -0.78878700 |
| H | 1.85350800 | -1.61890800 | -1.91845800 |
| C | 2.83460700 | 0.45258200 | -0.37759200 |
| H | 2.74403200 | 0.73804400 | -1.42644600 |
| H | 3.83207300 | 0.03437700 | -0.22614700 |
| H | 2.76165600 | 1.34751700 | 0.23965800 |
| C | 0.07210000 | 1.76058100 | 1.34125700 |
| H | -0.31194900 | 1.05563400 | 2.07917900 |
| H | -0.46048800 | 2.70834000 | 1.45944300 |
| H | 1.12493500 | 1.94504600 | 1.56238500 |
| C | -2.74631100 | -0.55404400 | 1.29357400 |
| H | -2.89222700 | -1.60261000 | 1.56768400 |
| H | -3.73266600 | -0.08274500 | 1.21683500 |
| H | -2.19829400 | -0.07261200 | 2.10507400 |
| H | -0.45234200 | -2.12388900 | -0.12882500 |

Zero-point correction= 0.338695 (Hartree/Particle)
Thermal correction to Energy= 0.354340
Thermal correction to Enthalpy= 0.355284
Thermal correction to Gibbs Free Energy= 0.298004
Sum of electronic and zero-point Energies= -526.306266
Sum of electronic and thermal Energies= -526.290621
Sum of electronic and thermal Enthalpies= -526.289677
Sum of electronic and thermal Free Energies= -526.346957

**Table S13.** Cartesian coordinates and energy values of **3**$^{i\text{Pr-Me}_2}$ for *anti-(R/R)*.

| | | | |
|---|---|---|---|
| N | -1.88809000 | 0.29937600 | -0.18956300 |
| C | -0.62369300 | -0.46988600 | -0.17299200 |
| H | -0.52420700 | -0.99668800 | -1.12977200 |
| C | -0.80862500 | -1.60884700 | 0.88927700 |
| C | -2.96291200 | -0.39569800 | 0.56046700 |
| C | -2.15155000 | -1.25317900 | 1.54979500 |
| H | -1.96626400 | -0.66604600 | 2.45166300 |
| H | -2.70608200 | -2.14340900 | 1.85670400 |
| C | -3.90603600 | -1.27232300 | -0.29446300 |
| H | -4.54837600 | -0.65841600 | -0.92832600 |
| H | -4.55794800 | -1.85712000 | 0.36060800 |
| H | -3.36404300 | -1.96525400 | -0.93613700 |
| C | -0.89431800 | -2.95908400 | 0.14771900 |
| H | -1.64058300 | -2.95003300 | -0.64749800 |
| H | -1.15235900 | -3.76364200 | 0.84268300 |
| H | 0.07105000 | -3.20455100 | -0.30364600 |
| C | -3.84004000 | 0.57691800 | 1.37381100 |
| H | -3.21838900 | 1.27498900 | 1.93479800 |
| H | -4.44389100 | 0.00775900 | 2.08717300 |
| H | -4.52652100 | 1.14761200 | 0.75016000 |
| C | 0.27810900 | -1.77359800 | 1.95818700 |
| H | 1.22573600 | -2.06153000 | 1.50999400 |
| H | -0.03254200 | -2.55439000 | 2.66045700 |
| H | 0.44379400 | -0.86455200 | 2.53205300 |
| N | 1.88808300 | -0.29931500 | -0.18973000 |
| C | 0.62371800 | 0.46999600 | -0.17303200 |
| H | 0.52416400 | 0.99682100 | -1.12979400 |
| C | 0.80875400 | 1.60892300 | 0.88925100 |
| C | 2.96297000 | 0.39549300 | 0.56047300 |
| C | 2.15171400 | 1.25322000 | 1.54968400 |
| H | 1.96642500 | 0.66622600 | 2.45164000 |
| H | 2.70634800 | 2.14343400 | 1.85645600 |
| C | 3.90655400 | 1.27180300 | -0.29427400 |
| H | 4.54906300 | 0.65766300 | -0.92773700 |
| H | 4.55829000 | 1.85664400 | 0.36093300 |
| H | 3.36493000 | 1.96467200 | -0.93632000 |
| C | 0.89436400 | 2.95919500 | 0.14774100 |
| H | 1.64047200 | 2.95016600 | -0.64761800 |
| H | 1.15256000 | 3.76370900 | 0.84269800 |
| H | -0.07108100 | 3.20471800 | -0.30342800 |
| C | 3.83965500 | -0.57735400 | 1.37401400 |
| H | 3.21768700 | -1.27529600 | 1.93481400 |
| H | 4.44344700 | -0.00835800 | 2.08755600 |
| H | 4.52616800 | -1.14819000 | 0.75053300 |

| | | | |
|---|---|---|---|
| C | -0.27789400 | 1.77365300 | 1.95824800 |
| H | -1.22554100 | 2.06164000 | 1.51013600 |
| H | 0.03283300 | 2.55440000 | 2.66053400 |
| H | -0.44356700 | 0.86458300 | 2.53208000 |
| C | 2.14018600 | -1.01055100 | -1.45270400 |
| C | 3.22963400 | -2.07989500 | -1.34564600 |
| C | 2.37157000 | -0.13866700 | -2.70823000 |
| H | 1.21589600 | -1.56117100 | -1.64284900 |
| H | 3.07318500 | -2.71360000 | -0.47127700 |
| H | 3.20374500 | -2.71132500 | -2.23764800 |
| H | 4.22975700 | -1.64684300 | -1.28564900 |
| H | 1.64886300 | 0.67721600 | -2.77547300 |
| H | 3.37236800 | 0.29244800 | -2.73336700 |
| H | 2.25214200 | -0.75361400 | -3.60508500 |
| C | -2.14031700 | 1.01072400 | -1.45244300 |
| C | -3.22956300 | 2.08024100 | -1.34506400 |
| C | -2.37220000 | 0.13891800 | -2.70792900 |
| H | -1.21597700 | 1.56119600 | -1.64278500 |
| H | -3.07273000 | 2.71394700 | -0.47076500 |
| H | -3.20386100 | 2.71164300 | -2.23709100 |
| H | -4.22973500 | 1.64734800 | -1.28472800 |
| H | -1.64960400 | -0.67704000 | -2.77544600 |
| H | -3.37305500 | -0.29209100 | -2.73274500 |
| H | -2.25300600 | 0.75388800 | -3.60480000 |

Zero-point correction= 0.631630 (Hartree/Particle)
Thermal correction to Energy= 0.659791
Thermal correction to Enthalpy= 0.660735
Thermal correction to Gibbs Free Energy= 0.578116
Sum of electronic and zero-point Energies= -974.088540
Sum of electronic and thermal Energies= -974.060380
Sum of electronic and thermal Enthalpies= -974.059436
Sum of electronic and thermal Free Energies= -974.142054

**Table S14.** Cartesian coordinates and energy values of **3**$^{iPr\text{-}Me_2}$ for *gauche-(R/R)*.

| | | | |
|---|---|---|---|
| N | -1.40788500 | -0.54107100 | 0.18322900 |
| C | -0.74229000 | 0.77175900 | 0.25625100 |
| H | -0.71102100 | 1.08023500 | 1.30292500 |
| C | -1.70121500 | 1.75718000 | -0.50318800 |
| C | -2.64978900 | -0.53454100 | -0.62125500 |
| C | -2.51708300 | 0.79379600 | -1.38212500 |
| H | -1.96383700 | 0.61447300 | -2.30926300 |
| H | -3.48910900 | 1.20772400 | -1.66178800 |
| C | -3.97511200 | -0.58737500 | 0.17341100 |
| H | -4.08842400 | -1.53779400 | 0.69639800 |
| H | -4.81499700 | -0.49742700 | -0.52136900 |
| H | -4.05952300 | 0.21312500 | 0.90504900 |
| C | -2.57780700 | 2.49480200 | 0.52555800 |
| H | -2.98274200 | 1.82012400 | 1.27899500 |
| H | -3.41544700 | 3.00077700 | 0.03609100 |
| H | -1.98952700 | 3.25257600 | 1.04991000 |
| C | -2.68270900 | -1.69389500 | -1.63924200 |
| H | -1.75418800 | -1.72702200 | -2.21123100 |
| H | -3.51121600 | -1.55119300 | -2.34018100 |
| H | -2.82171700 | -2.66108000 | -1.15682300 |
| C | -1.06922000 | 2.82208400 | -1.41484100 |
| H | -1.87147600 | 3.40164800 | -1.88193700 |
| H | -0.47721900 | 2.38616200 | -2.22064000 |
| H | -0.43853100 | 3.52594800 | -0.87187900 |
| N | 1.40789200 | -0.54110000 | -0.18319500 |
| C | 0.74231700 | 0.77174100 | -0.25623700 |
| H | 0.71104500 | 1.08018700 | -1.30291800 |
| C | 1.70126100 | 1.75717000 | 0.50316800 |
| C | 2.64984200 | -0.53455400 | 0.62122500 |
| C | 2.51717000 | 0.79379500 | 1.38208000 |
| H | 1.96396400 | 0.61448400 | 2.30924400 |
| H | 3.48920700 | 1.20772800 | 1.66169700 |
| C | 3.97513000 | -0.58740100 | -0.17349600 |
| H | 4.08842300 | -1.53783100 | -0.69646900 |
| H | 4.81504200 | -0.49743900 | 0.52124900 |

| | | | |
|---|---|---|---|
| H | 4.05951100 | 0.21308400 | -0.90515200 |
| C | 2.57780900 | 2.49479600 | -0.52561100 |
| H | 2.98272100 | 1.82012100 | -1.27906100 |
| H | 3.41546200 | 3.00077800 | -0.03617400 |
| H | 1.98950300 | 3.25256500 | -1.04994200 |
| C | 2.68281300 | -1.69388900 | 1.63923400 |
| H | 1.75433200 | -1.72699300 | 2.21128700 |
| H | 3.51137000 | -1.55118600 | 2.34011400 |
| H | 2.82177500 | -2.66108400 | 1.15682200 |
| C | 1.06929000 | 2.82207500 | 1.41483900 |
| H | 0.43857000 | 3.52592800 | 0.87189800 |
| H | 1.87155900 | 3.40165100 | 1.88189700 |
| H | 0.47732700 | 2.38615400 | 2.22066500 |
| C | 1.22633600 | -1.36417800 | -1.38405200 |
| C | 1.52283900 | -2.84901400 | -1.16313600 |
| C | 1.94143000 | -0.86473600 | -2.65935000 |
| H | 0.15482200 | -1.29624500 | -1.57238200 |
| H | 1.02387100 | -3.21997800 | -0.26883600 |
| H | 1.16175300 | -3.42257700 | -2.02112700 |
| H | 2.59204500 | -3.04988700 | -1.06788100 |
| H | 1.78690200 | 0.20536500 | -2.81578300 |
| H | 3.01567300 | -1.04985300 | -2.63126200 |
| H | 1.53769900 | -1.38377000 | -3.53416000 |
| C | -1.22642600 | -1.36409900 | 1.38413400 |
| C | -1.52293300 | -2.84894000 | 1.16326000 |
| C | -1.94162400 | -0.86459200 | 2.65934700 |
| H | -0.15492700 | -1.29617100 | 1.57254500 |
| H | -1.02389400 | -3.21995300 | 0.26901900 |
| H | -1.16192700 | -3.42246900 | 2.02130700 |
| H | -2.59213400 | -3.04980200 | 1.06792300 |
| H | -1.78708800 | 0.20551200 | 2.81575100 |
| H | -3.01586900 | -1.04968600 | 2.63116700 |
| H | -1.53798400 | -1.38360000 | 3.53421500 |

Zero-point correction= 0.631256 (Hartree/Particle)
Thermal correction to Energy= 0.659370
Thermal correction to Enthalpy= 0.660314
Thermal correction to Gibbs Free Energy= 0.578554
Sum of electronic and zero-point Energies= -974.094219
Sum of electronic and thermal Energies= -974.066105
Sum of electronic and thermal Enthalpies= -974.065161
Sum of electronic and thermal Free Energies= -974.146921

**Table S15.** Cartesian coordinates and energy values of **3**$^{iPr\text{-}Me_2}$ for *anti-(S/S)*.

| | | | |
|---|---|---|---|
| N | -1.88812500 | 0.29942400 | 0.18968000 |
| C | -0.62371700 | -0.46997800 | 0.17302000 |
| C | -0.80885000 | -1.60888000 | -0.88917300 |
| C | -2.96292300 | -0.39522800 | -0.56073700 |
| C | -2.15161000 | -1.25294300 | -1.54989200 |
| H | -2.70627100 | -2.14307600 | -1.85686000 |
| H | -1.96604400 | -0.66589800 | -2.45176100 |
| C | -3.83951200 | 0.57777400 | -1.37420200 |
| H | -4.52575600 | 1.14878800 | -0.75057800 |
| H | -4.44357800 | 0.00891500 | -2.08762900 |
| H | -3.21748800 | 1.27555300 | -1.93512700 |
| C | 0.27791400 | -1.77389500 | -1.95798800 |
| H | 0.44381800 | -0.86485200 | -2.53179900 |
| H | -0.03288700 | -2.55456600 | -2.66032300 |
| H | 1.22544400 | -2.06204700 | -1.50975900 |
| C | -3.90665000 | -1.27156000 | 0.29382500 |
| H | -3.36513700 | -1.96482900 | 0.93553400 |
| H | -4.55867400 | -1.85596000 | -0.36149200 |
| H | -4.54886200 | -0.65744800 | 0.92761200 |
| C | -0.89491200 | -2.95904000 | -0.14754400 |
| H | 0.07033600 | -3.20461000 | 0.30401600 |
| H | -1.15296900 | -3.76362300 | -0.84247300 |
| H | -1.64130500 | -2.94974800 | 0.64754500 |
| N | 1.88811800 | -0.29942900 | 0.18966000 |
| C | 0.62372100 | 0.46998900 | 0.17307000 |
| C | 0.80887900 | 1.60899900 | -0.88900500 |

| | | | |
|---|---|---|---|
| C | 2.96293400 | 0.39528200 | -0.56067200 |
| C | 2.15164600 | 1.25312200 | -1.54973900 |
| H | 2.70632200 | 2.14328300 | -1.85659800 |
| H | 1.96608700 | 0.66618100 | -2.45167700 |
| C | 3.83950700 | -0.57763800 | -1.37425100 |
| H | 3.21746900 | -1.27536400 | -1.93522800 |
| H | 4.52577000 | -1.14871200 | -0.75070200 |
| H | 4.44355300 | -0.00870800 | -2.08763700 |
| C | -0.27786300 | 1.77413700 | -1.95782200 |
| H | 0.03295200 | 2.55488600 | -2.66006400 |
| H | -1.22539800 | 2.06224100 | -1.50957400 |
| H | -0.44375800 | 0.86516000 | -2.53174000 |
| C | 3.90666900 | 1.27150200 | 0.29399600 |
| H | 3.36516100 | 1.96470600 | 0.93577900 |
| H | 4.55871100 | 1.85596700 | -0.36124500 |
| H | 4.54886300 | 0.65730600 | 0.92772100 |
| C | 0.89493900 | 2.95908400 | -0.14723500 |
| H | -0.07031300 | 3.20460900 | 0.30434000 |
| H | 1.15300800 | 3.76373700 | -0.84207800 |
| H | 1.64132300 | 2.94970400 | 0.64786100 |
| H | 0.52406200 | 0.99664400 | 1.12990300 |
| H | -0.52406200 | -0.99672900 | 1.12980000 |
| C | 2.14034800 | -1.01039100 | 1.45271900 |
| C | 2.37265100 | -0.13815400 | 2.70783700 |
| C | 3.22939900 | -2.08013300 | 1.34550500 |
| H | 1.21589200 | -1.56055500 | 1.64337200 |
| H | 1.65060300 | 0.67833600 | 2.77489700 |
| H | 2.25295600 | -0.75260500 | 3.60500000 |
| H | 3.37379100 | 0.29220100 | 2.73255600 |
| H | 3.07234800 | -2.71406100 | 0.47140700 |
| H | 4.22962800 | -1.64740200 | 1.28488800 |
| H | 3.20375600 | -2.71127000 | 2.23772600 |
| C | -2.14039000 | 1.01022700 | 1.45282000 |
| C | -2.37268900 | 0.13783700 | 2.70783200 |
| C | -3.22947500 | 2.07994500 | 1.34570300 |
| H | -1.21595100 | 1.56039200 | 1.64355200 |
| H | -1.65062900 | -0.67865100 | 2.77480000 |
| H | -2.25300600 | 0.75218600 | 3.60506700 |
| H | -3.37382300 | -0.29253400 | 2.73249700 |
| H | -3.07242900 | 2.71397000 | 0.47167300 |
| H | -4.22968800 | 1.64718700 | 1.28501900 |
| H | -3.20387200 | 2.71098800 | 2.23799100 |

| | |
|---|---|
| Zero-point correction= | 0.631633 (Hartree/Particle) |
| Thermal correction to Energy= | 0.659792 |
| Thermal correction to Enthalpy= | 0.660736 |
| Thermal correction to Gibbs Free Energy= | 0.578119 |
| Sum of electronic and zero-point Energies= | -974.088537 |
| Sum of electronic and thermal Energies= | -974.060378 |
| Sum of electronic and thermal Enthalpies= | -974.059434 |
| Sum of electronic and thermal Free Energies= | -974.142051 |

**Table S16.** Cartesian coordinates and energy values of $\mathbf{3}^{\mathbf{iPr\text{-}Me_2}}$ for *gauche-(S/S)*.

| | | | |
|---|---|---|---|
| N | 1.40791500 | -0.54108000 | 0.18321900 |
| C | 0.74234300 | 0.77175900 | 0.25620500 |
| C | 1.70123400 | 1.75714800 | -0.50331700 |
| C | 2.64993100 | -0.53453900 | -0.62109700 |
| C | 2.51729200 | 0.79376100 | -1.38205600 |
| H | 3.48934900 | 1.20769500 | -1.66161100 |
| H | 1.96419300 | 0.61434700 | -2.30927000 |
| C | 2.68308700 | -1.69392000 | -1.63903100 |
| H | 2.82188900 | -2.66110300 | -1.15654000 |
| H | 3.51182500 | -1.55128700 | -2.33970900 |
| H | 1.75474900 | -1.72701900 | -2.21131900 |
| C | 1.06916800 | 2.82188900 | -1.41510600 |
| H | 0.47745200 | 2.38580800 | -2.22103300 |
| H | 1.87135500 | 3.40167900 | -1.88203900 |
| H | 0.43815300 | 3.52557200 | -0.87228400 |
| C | 3.97513300 | -0.58731700 | 0.17377700 |
| H | 4.05944200 | 0.21325800 | 0.90534200 |

| | | | |
|---|---|---|---|
| H | 4.81514100 | -0.49748700 | -0.52087000 |
| H | 4.08831500 | -1.53768200 | 0.69689300 |
| C | 2.57764500 | 2.49500900 | 0.52540800 |
| H | 1.98926800 | 3.25291200 | 1.04946500 |
| H | 3.41537400 | 3.00085800 | 0.03596300 |
| H | 2.98243000 | 1.82051500 | 1.27908900 |
| N | -1.40791100 | -0.54109600 | -0.18320200 |
| C | -0.74235200 | 0.77174900 | -0.25619900 |
| C | -1.70125500 | 1.75713700 | 0.50330800 |
| C | -2.64994800 | -0.53454700 | 0.62108200 |
| C | -2.51731400 | 0.79375100 | 1.38204600 |
| H | -3.48937400 | 1.20768300 | 1.66159600 |
| H | -1.96421900 | 0.61433700 | 2.30926300 |
| C | -2.68314300 | -1.69393100 | 1.63901200 |
| H | -1.75482600 | -1.72703600 | 2.21133100 |
| H | -2.82193200 | -2.66111200 | 1.15651200 |
| H | -3.51190500 | -1.55129800 | 2.33966100 |
| C | -1.06920600 | 2.82189100 | 1.41509400 |
| H | -1.87140200 | 3.40167800 | 1.88201600 |
| H | -0.43819200 | 3.52557500 | 0.87227100 |
| H | -0.47749300 | 2.38582100 | 2.22103000 |
| C | -3.97512900 | -0.58730600 | -0.17382700 |
| H | -4.05941300 | 0.21328000 | -0.90538400 |
| H | -4.81515400 | -0.49747900 | 0.52079900 |
| H | -4.08830400 | -1.53766400 | -0.69695900 |
| C | -2.57766600 | 2.49498100 | -0.52543000 |
| H | -1.98928900 | 3.25287600 | -1.04949800 |
| H | -3.41539600 | 3.00083700 | -0.03599300 |
| H | -2.98244900 | 1.82047300 | -1.27909900 |
| H | -0.71113300 | 1.08033000 | -1.30284100 |
| H | 0.71112400 | 1.08035300 | 1.30284400 |
| C | -1.22626600 | -1.36415400 | -1.38404300 |
| C | -1.94135000 | -0.86471600 | -2.65935500 |
| C | -1.52275500 | -2.84899700 | -1.16314200 |
| H | -0.15474400 | -1.29618400 | -1.57233300 |
| H | -1.78687400 | 0.20539600 | -2.81576100 |
| H | -1.53759700 | -1.38372100 | -3.53417300 |
| H | -3.01558500 | -1.04988200 | -2.63125400 |
| H | -1.02380400 | -3.21996400 | -0.26882900 |
| H | -2.59196200 | -3.04988500 | -1.06790800 |
| H | -1.16163900 | -3.42255200 | -2.02112500 |
| C | 1.22631000 | -1.36411300 | 1.38408300 |
| C | 1.94141600 | -0.86463400 | 2.65936700 |
| C | 1.52281600 | -2.84895700 | 1.16321200 |
| H | 0.15479100 | -1.29615400 | 1.57239600 |
| H | 1.78692900 | 0.20548000 | 2.81575000 |
| H | 1.53769000 | -1.38362400 | 3.53420600 |
| H | 3.01565300 | -1.04978600 | 2.63124600 |
| H | 1.02385100 | -3.21995300 | 0.26891800 |
| H | 2.59202300 | -3.04983200 | 1.06796000 |
| H | 1.16172500 | -3.42249700 | 2.02121600 |

Zero-point correction= 0.631258 (Hartree/Particle)
Thermal correction to Energy= 0.659370
Thermal correction to Enthalpy= 0.660314
Thermal correction to Gibbs Free Energy= 0.578556
Sum of electronic and zero-point Energies= -974.094217
Sum of electronic and thermal Energies= -974.066105
Sum of electronic and thermal Enthalpies= -974.065160
Sum of electronic and thermal Free Energies= -974.146919

**Table S17.** Cartesian coordinates and energy values of **3**$^{iPr\text{-}Me_2}$ for *gauche1-(R/S)*.

| | | | |
|---|---|---|---|
| N | 1.49823900 | 0.56405800 | -0.18360200 |
| C | 0.72018600 | -0.45748100 | 0.54101400 |
| H | 0.45934200 | -0.06740700 | 1.53297400 |
| C | 1.70340800 | -1.65071800 | 0.80943700 |
| C | 2.94639100 | 0.24618600 | -0.21086800 |
| C | 2.93402700 | -1.28443400 | -0.03662100 |
| H | 2.84399200 | -1.74794700 | -1.02153200 |
| H | 3.86400800 | -1.64818700 | 0.40722400 |

| | | | |
|---|---|---|---|
| C | 3.80041000 | 0.92794200 | 0.88282500 |
| H | 3.89485100 | 1.99871600 | 0.69475100 |
| H | 4.80922000 | 0.50548000 | 0.87624500 |
| H | 3.38644400 | 0.79855000 | 1.88116700 |
| C | 2.03937900 | -1.69184800 | 2.31276100 |
| H | 2.40195400 | -0.73236800 | 2.68150900 |
| H | 2.80631600 | -2.44463300 | 2.51877000 |
| H | 1.14914200 | -1.95361600 | 2.89308300 |
| C | 3.59404100 | 0.58071100 | -1.56932400 |
| H | 3.01047300 | 0.16468700 | -2.39070600 |
| H | 4.59772300 | 0.14638500 | -1.61065400 |
| H | 3.69609700 | 1.65365800 | -1.72722800 |
| C | 1.20161900 | -3.05142800 | 0.42965000 |
| H | 0.35684600 | -3.36574900 | 1.04794900 |
| H | 2.00658400 | -3.77567900 | 0.58789000 |
| H | 0.90031400 | -3.11736800 | -0.61465800 |
| N | -1.69739300 | 0.17407000 | 0.37948300 |
| C | -0.68013200 | -0.82154700 | -0.05064200 |
| C | -0.91074800 | -1.00159000 | -1.58928100 |
| C | -2.55182200 | 0.65890400 | -0.72883500 |
| C | -1.70885600 | 0.26246800 | -1.95358100 |
| H | -2.32586600 | 0.11943600 | -2.84419500 |
| H | -1.00279600 | 1.06768300 | -2.17283600 |
| C | -2.72101100 | 2.19383300 | -0.71316400 |
| H | -3.36975800 | 2.52937900 | 0.09542500 |
| H | -3.17298400 | 2.52103300 | -1.65448600 |
| H | -1.75826100 | 2.69424000 | -0.60901100 |
| C | 0.32452600 | -1.08472700 | -2.49292400 |
| H | 0.94963300 | -0.20629700 | -2.37055900 |
| H | -0.00251600 | -1.15367400 | -3.53564000 |
| H | 0.93126100 | -1.96814100 | -2.28731100 |
| C | -3.97423100 | 0.05735100 | -0.80254000 |
| H | -3.97618700 | -1.03010600 | -0.80806700 |
| H | -4.46304300 | 0.39960900 | -1.71902400 |
| H | -4.58758400 | 0.39320600 | 0.03553700 |
| C | -1.73924500 | -2.28178100 | -1.81808900 |
| H | -1.12096000 | -3.16902900 | -1.65839100 |
| H | -2.11614600 | -2.31921300 | -2.84444400 |
| H | -2.59067800 | -2.35450300 | -1.14206600 |
| H | -0.92173200 | -1.78002800 | 0.42004100 |
| C | 0.98313500 | 1.92733400 | 0.01279600 |
| C | 1.43675400 | 2.91299400 | -1.06433700 |
| C | 1.15791200 | 2.54486900 | 1.41845100 |
| H | -0.08939100 | 1.80039500 | -0.10536200 |
| H | 1.31104100 | 2.48830700 | -2.06210500 |
| H | 0.83550800 | 3.82443400 | -1.00047100 |
| H | 2.48161600 | 3.20802800 | -0.94471300 |
| H | 0.93668900 | 1.82160700 | 2.20627900 |
| H | 2.16167100 | 2.93576300 | 1.58631700 |
| H | 0.45533100 | 3.37551600 | 1.53591400 |
| C | -2.18504600 | -0.03065100 | 1.74616000 |
| C | -3.10010600 | -1.25624800 | 1.96599900 |
| C | -2.80488400 | 1.22445500 | 2.36480800 |
| H | -1.28026800 | -0.22877200 | 2.33027300 |
| H | -2.70729400 | -2.14311200 | 1.46341000 |
| H | -3.16199100 | -1.48423500 | 3.03433700 |
| H | -4.11373600 | -1.08344300 | 1.60480100 |
| H | -2.14720900 | 2.08526500 | 2.23360100 |
| H | -3.77685400 | 1.46083800 | 1.92731800 |
| H | -2.96096800 | 1.06684500 | 3.43531500 |

| | |
|---|---|
| Zero-point correction= | 0.631262 (Hartree/Particle) |
| Thermal correction to Energy= | 0.659446 |
| Thermal correction to Enthalpy= | 0.660390 |
| Thermal correction to Gibbs Free Energy= | 0.578040 |
| Sum of electronic and zero-point Energies= | -974.093363 |
| Sum of electronic and thermal Energies= | -974.065180 |
| Sum of electronic and thermal Enthalpies= | -974.064236 |
| Sum of electronic and thermal Free Energies= | -974.146586 |

**Table S18.** Cartesian coordinates and energy values of **3**$^{\text{iPr-Me}_2}$ for *gauche2-(R/S)*.

| | | | |
|---|---|---|---|
| N | 1.69762000 | 0.17268400 | 0.38015200 |
| C | 0.68020200 | -0.82062000 | -0.05481400 |
| H | 0.92192500 | -1.78149700 | 0.41086300 |
| C | 0.91066800 | -0.99305900 | -1.59445300 |
| C | 2.55272400 | 0.66215500 | -0.72554900 |
| C | 1.71022800 | 0.27181700 | -1.95255700 |
| H | 1.00511700 | 1.07866100 | -2.16884100 |
| H | 2.32772700 | 0.13210400 | -2.84335400 |
| C | 3.97480300 | 0.06009200 | -0.80133900 |
| H | 4.58790900 | 0.39155900 | 0.03865100 |
| H | 4.46434400 | 0.40629200 | -1.71595000 |
| H | 3.97598300 | -1.02733800 | -0.81193500 |
| C | 1.73772000 | -2.27301400 | -1.82953500 |
| H | 2.58936300 | -2.34966800 | -1.15419100 |
| H | 2.11414000 | -2.30608200 | -2.85620800 |
| H | 1.11856400 | -3.16034300 | -1.67365200 |
| C | 2.72250300 | 2.19689400 | -0.70269500 |
| H | 1.75987000 | 2.69698500 | -0.59594900 |
| H | 3.17435900 | 2.52831900 | -1.64259100 |
| H | 3.37152200 | 2.52847000 | 0.10730400 |
| C | -0.32451200 | -1.07035200 | -2.49879000 |
| H | -0.93350700 | -1.95292800 | -2.29624400 |
| H | 0.00284300 | -1.13677700 | -3.54158900 |
| H | -0.94769800 | -0.19087900 | -2.37400400 |
| N | -1.49925500 | 0.56400200 | -0.18147800 |
| C | -0.71993100 | -0.45926000 | 0.53916700 |
| C | -1.70232300 | -1.65380800 | 0.80472700 |
| C | -2.94720200 | 0.24560000 | -0.20864000 |
| C | -2.93395000 | -1.28551700 | -0.03900600 |
| H | -3.86331600 | -1.65100500 | 0.40469700 |
| H | -2.84474900 | -1.74605900 | -1.02540300 |
| C | -3.59606100 | 0.58391700 | -1.56558800 |
| H | -3.69919500 | 1.65728300 | -1.71993400 |
| H | -4.59938400 | 0.14883000 | -1.60762400 |
| H | -3.01261700 | 0.17108100 | -2.38865700 |
| C | -1.20018200 | -3.05302100 | 0.42004300 |
| H | -0.89955000 | -3.11525200 | -0.62469200 |
| H | -2.00471400 | -3.77816000 | 0.57639000 |
| H | -0.35484000 | -3.36905000 | 1.03669400 |
| C | -3.80065300 | 0.92368700 | 0.88776600 |
| H | -3.38595400 | 0.79130100 | 1.88541500 |
| H | -4.80937600 | 0.50102300 | 0.88060100 |
| H | -3.89548800 | 1.99501700 | 0.70307500 |
| C | -2.03680800 | -1.69975800 | 2.30823500 |
| H | -1.14595800 | -1.96314900 | 2.88688000 |
| H | -2.80338100 | -2.45336100 | 2.51257600 |
| H | -2.39921700 | -0.74151700 | 2.68034400 |
| H | -0.45847700 | -0.07225300 | 1.53215400 |
| C | 2.18486800 | -0.03850500 | 1.74600500 |
| C | 2.80567700 | 1.21329500 | 2.37034500 |
| C | 3.09885800 | -1.26585600 | 1.96058800 |
| H | 1.27986800 | -0.23845600 | 2.32913400 |
| H | 2.14861400 | 2.07518200 | 2.24320900 |
| H | 2.96169400 | 1.05059200 | 3.44010200 |
| H | 3.77781100 | 1.45096700 | 1.93391500 |
| H | 2.70534400 | -2.15020900 | 1.45413900 |
| H | 4.11268000 | -1.09239100 | 1.60023400 |
| H | 3.16044900 | -1.49851000 | 3.02793900 |
| C | -0.98434600 | 1.92690900 | 0.01761300 |
| C | -1.15763000 | 2.54093300 | 1.42498200 |
| C | -1.43959900 | 2.91514100 | -1.05649900 |
| H | 0.08809500 | 1.80074200 | -0.10218300 |
| H | -0.93452500 | 1.81604700 | 2.21078400 |
| H | -0.45570300 | 3.37199800 | 1.54337800 |
| H | -2.16154200 | 2.93042100 | 1.59517400 |
| H | -1.31512900 | 2.49297500 | -2.05548600 |
| H | -2.48435200 | 3.20969900 | -0.93477800 |
| H | -0.83840800 | 3.82651200 | -0.99115800 |

Zero-point correction= 0.631243 (Hartree/Particle)
Thermal correction to Energy= 0.659435
Thermal correction to Enthalpy= 0.660379
Thermal correction to Gibbs Free Energy= 0.577993
Sum of electronic and zero-point Energies= -974.093382
Sum of electronic and thermal Energies= -974.065191
Sum of electronic and thermal Enthalpies= -974.064246
Sum of electronic and thermal Free Energies= -974.146632

**Table S19.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *anti-(R/R)*.

| | | | |
|---|---|---|---|
| N | 1.95312800 | 0.11879200 | -0.27903000 |
| C | 0.64930800 | 0.07063600 | 0.46663900 |
| H | 0.54360100 | 1.01687900 | 0.98398600 |
| C | 0.86473700 | -0.98409800 | 1.60356000 |
| C | 2.44990300 | 1.46700700 | -0.69089300 |
| C | 2.92895800 | -0.90228800 | 0.24627700 |
| C | 2.03080600 | -1.82675800 | 1.08141100 |
| H | 1.64436300 | -2.63340800 | 0.45721700 |
| H | 2.58986800 | -2.29930000 | 1.89249500 |
| C | 1.39303400 | 2.21877500 | -1.52576000 |
| H | 1.02472700 | 1.60162000 | -2.34453000 |
| H | 1.85340300 | 3.11242000 | -1.95308800 |
| H | 0.54856400 | 2.55712800 | -0.92681500 |
| C | 4.07793400 | -0.39667800 | 1.15880800 |
| H | 4.78704400 | 0.24273000 | 0.63599600 |
| H | 4.63623700 | -1.26935800 | 1.50788400 |
| H | 3.72312200 | 0.13511000 | 2.03741300 |
| C | 1.24381300 | -0.22872600 | 2.89738000 |
| H | 1.95632300 | 0.57612800 | 2.72356300 |
| H | 1.67486000 | -0.91356700 | 3.63361900 |
| H | 0.35144400 | 0.21721000 | 3.34393900 |
| C | 2.81291200 | 2.40232100 | 0.49126100 |
| H | 1.99096000 | 2.46602700 | 1.20767000 |
| H | 2.99838900 | 3.41427700 | 0.12047900 |
| H | 3.70334500 | 2.07943200 | 1.02413900 |
| C | 3.66278900 | 1.33528500 | -1.63103300 |
| H | 4.53964800 | 0.90810500 | -1.15228600 |
| H | 3.94369600 | 2.32822000 | -1.98965100 |
| H | 3.40703500 | 0.72018000 | -2.49590100 |
| C | 3.59872900 | -1.73154900 | -0.87151300 |
| H | 2.86671900 | -2.10598300 | -1.58190100 |
| H | 4.10379800 | -2.59216800 | -0.42199400 |
| H | 4.35067700 | -1.16664400 | -1.42001100 |
| C | -0.30279800 | -1.89557800 | 1.96964600 |
| H | -1.16215700 | -1.31592100 | 2.29579200 |
| H | 0.00479700 | -2.55978900 | 2.78447900 |
| H | -0.60768000 | -2.52267100 | 1.13480100 |
| N | -1.95313600 | 0.11877000 | 0.27904600 |
| C | -0.64931500 | 0.07066800 | -0.46662400 |
| H | -0.54361000 | 1.01694900 | -0.98390200 |
| C | -0.86474100 | -0.98397600 | -1.60362700 |
| C | -2.44990100 | 1.46696200 | 0.69099300 |
| C | -2.92896700 | -0.90227200 | -0.24633500 |
| C | -2.03081900 | -1.82667100 | -1.08155500 |
| H | -1.64438400 | -2.63338100 | -0.45743300 |
| H | -2.58988300 | -2.29913600 | -1.89268200 |
| C | -1.39301700 | 2.21867200 | 1.52589300 |
| H | -1.02471200 | 1.60146700 | 2.34462700 |
| H | -1.85337100 | 3.11229900 | 1.95327300 |
| H | -0.54854600 | 2.55704700 | 0.92696100 |
| C | -4.07795600 | -0.39658900 | -1.15881100 |
| H | -4.78704200 | 0.24280100 | -0.63594500 |
| H | -4.63628300 | -1.26924000 | -1.50792500 |
| H | -3.72315700 | 0.13524300 | -2.03739400 |
| C | -1.24379800 | -0.22849800 | -2.89739000 |
| H | -1.95629300 | 0.57635700 | -2.72351400 |
| H | -1.67485500 | -0.91327500 | -3.63368300 |
| H | -0.35141900 | 0.21745500 | -3.34391200 |
| C | -2.81290500 | 2.40234600 | -0.49110600 |
| H | -1.99095800 | 2.46608000 | -1.20751800 |

| | | | |
|---|---|---|---|
| H | -2.99836500 | 3.41428400 | -0.12026700 |
| H | -3.70334700 | 2.07949900 | -1.02399400 |
| C | -3.66278300 | 1.33520500 | 1.63113200 |
| H | -4.53965700 | 0.90808200 | 1.15236200 |
| H | -3.94366100 | 2.32812100 | 1.98982200 |
| H | -3.40703700 | 0.72003200 | 2.49595500 |
| C | -3.59872200 | -1.73163600 | 0.87138700 |
| H | -2.86670400 | -2.10611900 | 1.58174100 |
| H | -4.10378100 | -2.59222400 | 0.42179700 |
| H | -4.35067800 | -1.16679000 | 1.41993600 |
| C | 0.30279500 | -1.89543000 | -1.96977500 |
| H | 1.16216200 | -1.31574700 | -2.29585600 |
| H | -0.00479000 | -2.55956800 | -2.78467100 |
| H | 0.60766100 | -2.52259900 | -1.13498100 |

Zero-point correction= 0.689408 (Hartree/Particle)
Thermal correction to Energy= 0.719247
Thermal correction to Enthalpy= 0.720192
Thermal correction to Gibbs Free Energy= 0.636367
Sum of electronic and zero-point Energies= -1052.666038
Sum of electronic and thermal Energies= -1052.636199
Sum of electronic and thermal Enthalpies= -1052.635255
Sum of electronic and thermal Free Energies= -1052.719079

**Table S20.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *gauche-(R/R)*.

| | | | |
|---|---|---|---|
| N | -1.62198000 | -0.52403600 | 0.13453800 |
| C | -0.77981700 | 0.70741400 | 0.20800200 |
| H | -0.79343200 | 1.03353900 | 1.24472300 |
| C | -1.58777400 | 1.78061300 | -0.63370100 |
| C | -1.79037300 | -1.28202600 | 1.40756600 |
| C | -2.78448100 | -0.37178100 | -0.80459900 |
| C | -2.39708600 | 0.88764500 | -1.58041400 |
| H | -1.76569800 | 0.61194400 | -2.42935700 |
| H | -3.27076100 | 1.40276300 | -1.98693000 |
| C | -2.41521800 | -2.66370700 | 1.14566800 |
| H | -3.44343600 | -2.61548700 | 0.79390300 |
| H | -2.41927100 | -3.23309100 | 2.07824100 |
| H | -1.82364600 | -3.21610300 | 0.41317300 |
| C | -4.19019200 | -0.16484000 | -0.18001000 |
| H | -4.54584600 | -1.04870500 | 0.34738800 |
| H | -4.89518800 | 0.02364200 | -0.99396900 |
| H | -4.24264500 | 0.68048400 | 0.49926400 |
| C | -2.49067800 | 2.59717100 | 0.31347800 |
| H | -2.94179100 | 1.98289400 | 1.08967300 |
| H | -3.29453800 | 3.08804100 | -0.24318000 |
| H | -1.91375300 | 3.37635000 | 0.81538100 |
| C | -0.40838600 | -1.55936800 | 2.00197800 |
| H | 0.24111600 | -1.99733800 | 1.25096200 |
| H | -0.50135700 | -2.23391800 | 2.85706300 |
| H | 0.06644800 | -0.64476000 | 2.35457200 |
| C | -2.60987900 | -0.54580000 | 2.49835000 |
| H | -2.22137300 | 0.46142000 | 2.66659400 |
| H | -2.52484800 | -1.08562300 | 3.44562700 |
| H | -3.66729200 | -0.46887400 | 2.25811600 |
| C | -2.93744600 | -1.54473400 | -1.79871500 |
| H | -2.00991200 | -1.75223300 | -2.32323800 |
| H | -3.69258200 | -1.27868000 | -2.54490600 |
| H | -3.26976900 | -2.46139800 | -1.31420600 |
| C | -0.83708500 | 2.79768200 | -1.51269100 |
| H | -1.58435200 | 3.40390800 | -2.03440000 |
| H | -0.22114900 | 2.32603000 | -2.27924000 |
| H | -0.21135700 | 3.48376000 | -0.94598100 |
| N | 1.62195500 | -0.52404900 | -0.13453100 |
| C | 0.77980500 | 0.70741200 | -0.20796700 |
| H | 0.79342000 | 1.03355400 | -1.24468200 |
| C | 1.58778300 | 1.78058700 | 0.63374600 |
| C | 1.79036600 | -1.28197800 | -1.40759300 |
| C | 2.78446600 | -0.37181900 | 0.80459700 |
| C | 2.39708500 | 0.88759300 | 1.58044100 |
| H | 1.76569400 | 0.61187900 | 2.42937700 |

| | | | |
|---|---|---|---|
| H | 3.27076500 | 1.40269300 | 1.98696600 |
| C | 2.41522800 | -2.66366100 | -1.14575700 |
| H | 3.44344400 | -2.61544300 | -0.79398300 |
| H | 2.41929700 | -3.23299900 | -2.07835800 |
| H | 1.82366000 | -3.21610300 | -0.41329300 |
| C | 4.19016700 | -0.16487300 | 0.17999100 |
| H | 4.54580200 | -1.04872800 | -0.34743800 |
| H | 4.89518100 | 0.02358000 | 0.99394200 |
| H | 4.24261700 | 0.68046700 | -0.49926300 |
| C | 2.49069500 | 2.59713600 | -0.31343200 |
| H | 2.94178700 | 1.98285800 | -1.08963900 |
| H | 3.29457100 | 3.08798500 | 0.24322200 |
| H | 1.91378000 | 3.37633300 | -0.81532100 |
| C | 0.40838800 | -1.55930300 | -2.00203400 |
| H | -0.24111100 | -1.99733000 | -1.25104800 |
| H | 0.50137500 | -2.23379900 | -2.85716000 |
| H | -0.06646100 | -0.64468100 | -2.35457300 |
| C | 2.60987800 | -0.54568300 | -2.49832600 |
| H | 2.22136600 | 0.46154400 | -2.66651400 |
| H | 2.52486200 | -1.08545100 | -3.44563500 |
| H | 3.66728800 | -0.46876300 | -2.25807300 |
| C | 2.93743900 | -1.54479300 | 1.79868600 |
| H | 2.00991200 | -1.75230100 | 2.32321700 |
| H | 3.69258600 | -1.27875700 | 2.54487300 |
| H | 3.26975400 | -2.46144800 | 1.31415400 |
| C | 0.83712000 | 2.79766200 | 1.51275200 |
| H | 1.58440300 | 3.40387400 | 2.03445400 |
| H | 0.22118700 | 2.32601600 | 2.27930600 |
| H | 0.21139400 | 3.48375200 | 0.94605400 |

Zero-point correction= 0.688915 (Hartree/Particle)
Thermal correction to Energy= 0.718829
Thermal correction to Enthalpy= 0.719773
Thermal correction to Gibbs Free Energy= 0.636319
Sum of electronic and zero-point Energies= -1052.664638
Sum of electronic and thermal Energies= -1052.634725
Sum of electronic and thermal Enthalpies= -1052.633781
Sum of electronic and thermal Free Energies= -1052.717234

**Table S21.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *anti-(S/S)*.

| | | | |
|---|---|---|---|
| N | -1.95308000 | 0.11922400 | -0.27878500 |
| C | -0.64928500 | 0.07005600 | 0.46693000 |
| C | -0.86489100 | -0.98620700 | 1.60246400 |
| C | -2.44976000 | 1.46794800 | -0.68916900 |
| C | -2.92896400 | -0.90242800 | 0.24520700 |
| C | -2.03088300 | -1.82813200 | 1.07905800 |
| H | -2.59002000 | -2.30181800 | 1.88942200 |
| H | -1.64435400 | -2.63386000 | 0.45372300 |
| C | -2.81270300 | 2.40209000 | 0.49394200 |
| H | -3.70321400 | 2.07879100 | 1.02643900 |
| H | -2.99801800 | 3.41445300 | 0.12419200 |
| H | -1.99078100 | 2.46494800 | 1.21046100 |
| C | -3.59884000 | -1.73017400 | -0.87365400 |
| H | -4.35075400 | -1.16451000 | -1.42142200 |
| H | -4.10395100 | -2.59134500 | -0.42524700 |
| H | -2.86687500 | -2.10374700 | -1.58454900 |
| C | 0.30263500 | -1.89808400 | 1.96758000 |
| H | 0.60743300 | -2.52447000 | 1.13215000 |
| H | -0.00486800 | -2.56302300 | 2.78185000 |
| H | 1.16198200 | -1.31865000 | 2.29415600 |
| C | -1.39287600 | 2.22050900 | -1.52329400 |
| H | -0.54829200 | 2.55805900 | -0.92405900 |
| H | -1.85317400 | 3.11469700 | -1.94955500 |
| H | -1.02474600 | 1.60424800 | -2.34281800 |
| C | -3.66266700 | 1.33728700 | -1.62942500 |
| H | -3.40692200 | 0.72316800 | -2.49499900 |
| H | -3.94360700 | 2.33061900 | -1.98692300 |
| H | -4.53949300 | 0.90953600 | -1.15112200 |
| C | -4.07783800 | -0.39794800 | 1.15851000 |
| H | -3.72291500 | 0.13264500 | 2.03780400 |

| | | | |
|---|---|---|---|
| H | -4.63619000 | -1.27104000 | 1.50646800 |
| H | -4.78692700 | 0.24221700 | 0.63659600 |
| C | -1.24421100 | -0.23254000 | 2.89721200 |
| H | -0.35195200 | 0.21291300 | 3.34446500 |
| H | -1.67525700 | -0.91841000 | 3.63249000 |
| H | -1.95682000 | 0.57244400 | 2.72438500 |
| N | 1.95314900 | 0.11833900 | 0.27931800 |
| C | 0.64926200 | 0.07123100 | -0.46635800 |
| C | 0.86460100 | -0.98195000 | -1.60476600 |
| C | 2.45013100 | 1.46602400 | 0.69267900 |
| C | 2.92885900 | -0.90207600 | -0.24740000 |
| C | 2.03075300 | -1.82529600 | -1.08398000 |
| H | 2.58984600 | -2.29654100 | -1.89579700 |
| H | 1.64433600 | -2.63290400 | -0.46101700 |
| C | 3.66284700 | 1.33306600 | 1.63286000 |
| H | 3.40685200 | 0.71709200 | 2.49704000 |
| H | 3.94391300 | 2.32556100 | 1.99257500 |
| H | 4.53967500 | 0.90620500 | 1.15376600 |
| C | 3.59846500 | -1.73309900 | 0.86920600 |
| H | 2.86639300 | -2.10841200 | 1.57907600 |
| H | 4.35055000 | -1.16915900 | 1.41850400 |
| H | 4.10331300 | -2.59318500 | 0.41842800 |
| C | -0.30304200 | -1.89284900 | -1.97195700 |
| H | 0.00420300 | -2.55563500 | -2.78807700 |
| H | -1.16248700 | -1.31253900 | -2.29671500 |
| H | -0.60761500 | -2.52143000 | -1.13809500 |
| C | 2.81357900 | 2.40251100 | -0.48841200 |
| H | 3.70393300 | 2.07987700 | -1.02159000 |
| H | 2.99941900 | 3.41398200 | -0.11648700 |
| H | 1.99170900 | 2.46734400 | -1.20481800 |
| C | 1.39330400 | 2.21713600 | 1.52818500 |
| H | 0.54892900 | 2.55620100 | 0.92950300 |
| H | 1.85376900 | 3.11029200 | 1.95642500 |
| H | 1.02483400 | 1.59924500 | 2.34632200 |
| C | 4.07800400 | -0.39522800 | -1.15905600 |
| H | 3.72339200 | 0.13801000 | -2.03687000 |
| H | 4.63621300 | -1.26743700 | -1.50944900 |
| H | 4.78714300 | 0.24324600 | -0.63514300 |
| C | 1.24344800 | -0.22476300 | -2.89758600 |
| H | 0.35096800 | 0.22164700 | -3.34344600 |
| H | 1.67450700 | -0.90856300 | -3.63478300 |
| H | 1.95586900 | 0.57994800 | -2.72276800 |
| H | 0.54360400 | 1.01819800 | -0.98241500 |
| H | -0.54360000 | 1.01563400 | 0.98552500 |

Zero-point correction= 0.689409 (Hartree/Particle)
Thermal correction to Energy= 0.719247
Thermal correction to Enthalpy= 0.720191
Thermal correction to Gibbs Free Energy= 0.636369
Sum of electronic and zero-point Energies= -1052.666037
Sum of electronic and thermal Energies= -1052.636199
Sum of electronic and thermal Enthalpies= -1052.635255
Sum of electronic and thermal Free Energies= -1052.719078

**Table S22.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *gauche-(S/S)*.

| | | | |
|---|---|---|---|
| N | -1.62196500 | -0.52402400 | -0.13448700 |
| C | -0.77983200 | 0.70741500 | -0.20811000 |
| C | -1.58772600 | 1.78075600 | 0.63343100 |
| C | -1.79031800 | -1.28219700 | -1.40742200 |
| C | -2.78449900 | -0.37173900 | 0.80457700 |
| C | -2.39718600 | 0.88790400 | 1.58012400 |
| H | -3.27091400 | 1.40309500 | 1.98643900 |
| H | -1.76594300 | 0.61236000 | 2.42923600 |
| C | -2.41507100 | -2.66389500 | -1.14540300 |
| H | -1.82343000 | -3.21623300 | -0.41292000 |
| H | -2.41914600 | -3.23332600 | -2.07794800 |
| H | -3.44327200 | -2.61572200 | -0.79358200 |
| C | -2.93741700 | -1.54442800 | 1.79898200 |
| H | -3.26945100 | -2.46130400 | 1.31468000 |
| H | -3.69276800 | -1.27829300 | 2.54492900 |

| | | | |
|---|---|---|---|
| H | -2.00995800 | -1.75156800 | 2.32377300 |
| C | -0.83718100 | 2.79780900 | 1.51255300 |
| H | -0.22141700 | 2.32613800 | 2.27921200 |
| H | -1.58455600 | 3.40399700 | 2.03416600 |
| H | -0.21135500 | 3.48396300 | 0.94607200 |
| C | -2.60986400 | -0.54609000 | -2.49827100 |
| H | -3.66731500 | -0.46939800 | -2.25814100 |
| H | -2.52463600 | -1.08583300 | -3.44557700 |
| H | -2.22156500 | 0.46122800 | -2.66642500 |
| C | -0.40831500 | -1.55949900 | -2.00183900 |
| H | 0.06651000 | -0.64489200 | -2.35446400 |
| H | -0.50129500 | -2.23407200 | -2.85690500 |
| H | 0.24124300 | -1.99743000 | -1.25084700 |
| C | -4.19019600 | -0.16509500 | 0.17986900 |
| H | -4.24267300 | 0.68012400 | -0.49952300 |
| H | -4.89530500 | 0.02341100 | 0.99372600 |
| H | -4.54570500 | -1.04907000 | -0.34744800 |
| C | -2.49039800 | 2.59732800 | -0.31393100 |
| H | -1.91335300 | 3.37654600 | -0.81563400 |
| H | -3.29442100 | 3.08813600 | 0.24255500 |
| H | -2.94125800 | 1.98305500 | -1.09027500 |
| N | 1.62196200 | -0.52402600 | 0.13448300 |
| C | 0.77983700 | 0.70742000 | 0.20803700 |
| C | 1.58776300 | 1.78074400 | -0.63349700 |
| C | 1.79028900 | -1.28211500 | 1.40747100 |
| C | 2.78451800 | -0.37180600 | -0.80456400 |
| C | 2.39732000 | 0.88788100 | -1.58010200 |
| H | 3.27110300 | 1.40305600 | -1.98632100 |
| H | 1.76616000 | 0.61237200 | -2.42928600 |
| C | 0.40827100 | -1.55938000 | 2.00187200 |
| H | -0.06657100 | -0.64474900 | 2.35441200 |
| H | 0.50123200 | -2.23388600 | 2.85699300 |
| H | -0.24126500 | -1.99737600 | 1.25089700 |
| C | 2.93735300 | -1.54448000 | -1.79899900 |
| H | 2.00987900 | -1.75154700 | -2.32379400 |
| H | 3.26933000 | -2.46138900 | -1.31472400 |
| H | 3.69271900 | -1.27837400 | -2.54494200 |
| C | 0.83726500 | 2.79774800 | -1.51271600 |
| H | 1.58466800 | 3.40394100 | -2.03428300 |
| H | 0.21137100 | 3.48390300 | -0.94631100 |
| H | 0.22158100 | 2.32603800 | -2.27941500 |
| C | 2.41506200 | -2.66382500 | 1.14556500 |
| H | 1.82345300 | -3.21621500 | 0.41309500 |
| H | 2.41910700 | -3.23319400 | 2.07814700 |
| H | 3.44327700 | -2.61566400 | 0.79378100 |
| C | 2.60980400 | -0.54592400 | 2.49828600 |
| H | 3.66725800 | -0.46922800 | 2.25816600 |
| H | 2.52457100 | -1.08560900 | 3.44562500 |
| H | 2.22148400 | 0.46139800 | 2.66636800 |
| C | 4.19022800 | -0.16531700 | -0.17983200 |
| H | 4.24277700 | 0.67984500 | 0.49962200 |
| H | 4.89535900 | 0.02318600 | -0.99367000 |
| H | 4.54565700 | -1.04936100 | 0.34742300 |
| C | 2.49032100 | 2.59739000 | 0.31390600 |
| H | 1.91321500 | 3.37665900 | 0.81546100 |
| H | 3.29442200 | 3.08814200 | -0.24251800 |
| H | 2.94106800 | 1.98318800 | 1.09036800 |
| H | 0.79324300 | 1.03334800 | 1.24482000 |
| H | -0.79325700 | 1.03331400 | -1.24490000 |

Zero-point correction= 0.688915 (Hartree/Particle)
Thermal correction to Energy= 0.718828
Thermal correction to Enthalpy= 0.719773
Thermal correction to Gibbs Free Energy= 0.636319
Sum of electronic and zero-point Energies= -1052.664639
Sum of electronic and thermal Energies= -1052.634725
Sum of electronic and thermal Enthalpies= -1052.633781
Sum of electronic and thermal Free Energies= -1052.717235

**Table S23.** Cartesian coordinates and energy values of **3$^{tBu\text{-}Me_2}$** for *gauche1-(R/S)*.

| | | | |
|---|---|---|---|
| N | 1.76519000 | -0.50251700 | 0.00823500 |
| C | 0.70003600 | 0.51489100 | -0.27396200 |
| H | 0.43121300 | 0.41061600 | -1.31867500 |
| C | 1.43926100 | 1.90486500 | -0.12684600 |
| C | 1.80043900 | -1.68305100 | -0.90263800 |
| C | 3.05265900 | 0.13376000 | 0.45467800 |
| C | 2.61099400 | 1.56104200 | 0.79693500 |
| H | 2.27286700 | 1.60370400 | 1.83384600 |
| H | 3.43522400 | 2.27191300 | 0.70130200 |
| C | 2.77884900 | -2.75684100 | -0.39348700 |
| H | 2.54812500 | -3.01900300 | 0.64051500 |
| H | 3.82516200 | -2.46511700 | -0.45112900 |
| H | 2.66014500 | -3.65529300 | -1.00409000 |
| C | 4.21364900 | 0.21745800 | -0.57257200 |
| H | 4.60007400 | -0.75990900 | -0.85464100 |
| H | 5.03745200 | 0.76034300 | -0.10144200 |
| H | 3.94878900 | 0.75301100 | -1.47942900 |
| C | 1.91678100 | 2.37275100 | -1.51910100 |
| H | 2.30545500 | 1.55609600 | -2.12381900 |
| H | 2.69893300 | 3.13213200 | -1.42674400 |
| H | 1.08963400 | 2.81912500 | -2.07611700 |
| C | 0.42244700 | -2.34796900 | -0.89418700 |
| H | 0.20084500 | -2.73099900 | 0.10198700 |
| H | 0.41248500 | -3.19113600 | -1.59009400 |
| H | -0.36849600 | -1.65431400 | -1.17080300 |
| C | 2.13376900 | -1.34297500 | -2.37794500 |
| H | 1.44565200 | -0.59369700 | -2.77567400 |
| H | 2.02468000 | -2.23871900 | -2.99526700 |
| H | 3.14912500 | -0.97620400 | -2.50651500 |
| C | 3.64746400 | -0.53366000 | 1.71404000 |
| H | 2.90011000 | -0.65713200 | 2.49318100 |
| H | 4.44772600 | 0.09889400 | 2.11079400 |
| H | 4.08218800 | -1.50853500 | 1.49825000 |
| C | 0.66938700 | 3.08278100 | 0.49069500 |
| H | -0.19415400 | 3.38546000 | -0.10695000 |
| H | 1.34029500 | 3.94623300 | 0.54301200 |
| H | 0.32947200 | 2.87316000 | 1.50553000 |
| N | -1.84093000 | -0.15533100 | -0.32566400 |
| C | -0.73439300 | 0.50416700 | 0.45103200 |
| C | -0.91372100 | 0.00418600 | 1.92401200 |
| C | -2.53635700 | 0.69205800 | -1.34101400 |
| C | -2.64099100 | -1.09523900 | 0.53444700 |
| C | -1.71451200 | -1.28929200 | 1.74095500 |
| H | -2.27507500 | -1.55672900 | 2.64001600 |
| H | -1.01928200 | -2.10557300 | 1.54218400 |
| C | -3.32344900 | 1.88697200 | -0.74343400 |
| H | -4.19203200 | 1.57133500 | -0.17172400 |
| H | -3.67567300 | 2.53834200 | -1.54802300 |
| H | -2.68868700 | 2.49238200 | -0.09262300 |
| C | -2.89346500 | -2.46386500 | -0.13682500 |
| H | -3.68113500 | -2.42059500 | -0.88769800 |
| H | -3.21286100 | -3.18067600 | 0.62597200 |
| H | -1.99413800 | -2.85024700 | -0.60773600 |
| C | 0.34268000 | -0.31922000 | 2.73038600 |
| H | 0.94967600 | -1.05859500 | 2.21883300 |
| H | 0.04467500 | -0.70978300 | 3.70923400 |
| H | 0.95304900 | 0.56666100 | 2.90944000 |
| C | -1.52491200 | 1.29511400 | -2.33502800 |
| H | -0.85755100 | 2.01170500 | -1.86283400 |
| H | -2.07264800 | 1.83011100 | -3.11423200 |
| H | -0.92822800 | 0.51844000 | -2.81613900 |
| C | -3.48243400 | -0.16075600 | -2.20499200 |
| H | -2.93899200 | -0.99399600 | -2.65400200 |
| H | -3.88390500 | 0.45907100 | -3.01020100 |
| H | -4.33025000 | -0.55887200 | -1.65332500 |
| C | -4.02125700 | -0.60841400 | 1.04806200 |
| H | -3.96833700 | 0.31899700 | 1.61129100 |
| H | -4.41867700 | -1.37611600 | 1.71742400 |
| H | -4.74836400 | -0.48078900 | 0.24760200 |
| C | -1.69698000 | 1.06959200 | 2.72066400 |
| H | -1.03735900 | 1.90142300 | 2.98303000 |

| | | | |
|---|---|---|---|
| H | -2.08277400 | 0.64941600 | 3.65419500 |
| H | -2.53425600 | 1.48633300 | 2.16304900 |
| H | -0.97566900 | 1.56192100 | 0.46800500 |

Zero-point correction= 0.689296 (Hartree/Particle)
Thermal correction to Energy= 0.719063
Thermal correction to Enthalpy= 0.720007
Thermal correction to Gibbs Free Energy= 0.636511
Sum of electronic and zero-point Energies= -1052.667230
Sum of electronic and thermal Energies= -1052.637463
Sum of electronic and thermal Enthalpies= -1052.636519
Sum of electronic and thermal Free Energies= -1052.720015

**Table S24.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *gauche2-(R/S)*.

| | | | |
|---|---|---|---|
| N | 1.84088300 | -0.15497900 | -0.32573600 |
| C | 0.73433000 | 0.50386500 | 0.45146300 |
| H | 0.97561700 | 1.56159200 | 0.46930200 |
| C | 0.91352500 | 0.00255100 | 1.92403500 |
| C | 2.53625500 | 0.69323900 | -1.34037200 |
| C | 2.64096800 | -1.09557800 | 0.53361500 |
| C | 1.71443400 | -1.29068500 | 1.73991800 |
| H | 1.01925400 | -2.10683500 | 1.54044800 |
| H | 2.27497800 | -1.55883600 | 2.63877600 |
| C | 3.48247100 | -0.15884900 | -2.20492500 |
| H | 2.93920600 | -0.99198200 | -2.65435800 |
| H | 4.33042700 | -0.55707700 | -1.65356500 |
| H | 3.88372100 | 0.46154000 | -3.00981000 |
| C | 4.02122300 | -0.60918000 | 1.04766100 |
| H | 4.74832900 | -0.48081200 | 0.24732600 |
| H | 4.41866100 | -1.37750700 | 1.71630100 |
| H | 3.96832800 | 0.31769300 | 1.61176800 |
| C | 1.69659000 | 1.06726100 | 2.72182500 |
| H | 2.53377700 | 1.48474800 | 2.16464100 |
| H | 2.08247200 | 0.64617000 | 3.65490600 |
| H | 1.03681400 | 1.89868600 | 2.98508000 |
| C | 1.52474300 | 1.29694600 | -2.33393900 |
| H | 2.07243500 | 1.83286700 | -3.11253300 |
| H | 0.85705900 | 2.01286600 | -1.86116900 |
| H | 0.92838600 | 0.52055000 | -2.81589900 |
| C | 3.32315800 | 1.88775600 | -0.74176500 |
| H | 2.68825600 | 2.49251200 | -0.09048100 |
| H | 3.67534200 | 2.53984200 | -1.54579200 |
| H | 4.19174300 | 1.57176100 | -0.17025700 |
| C | 2.89351800 | -2.46361000 | -0.13885300 |
| H | 1.99413800 | -2.84978800 | -0.60981400 |
| H | 3.21331600 | -3.18098300 | 0.62324600 |
| H | 3.68095400 | -2.41952300 | -0.88992800 |
| C | -0.34300900 | -0.32170400 | 2.72987200 |
| H | -0.04517500 | -0.71332500 | 3.70835200 |
| H | -0.94994700 | -1.06050900 | 2.21742000 |
| H | -0.95339300 | 0.56399500 | 2.90978900 |
| N | -1.76516000 | -0.50249400 | 0.00783900 |
| C | -0.69996800 | 0.51507000 | -0.27367800 |
| C | -1.43916000 | 1.90493600 | -0.12571800 |
| C | -1.80031300 | -1.68244800 | -0.90380900 |
| C | -3.05261400 | 0.13351900 | 0.45477500 |
| C | -2.61085400 | 1.56055500 | 0.79791800 |
| H | -3.43505700 | 2.27153200 | 0.70283600 |
| H | -2.27262700 | 1.60250100 | 1.83482700 |
| C | -2.77866000 | -2.75667500 | -0.39547000 |
| H | -2.54798900 | -3.01954900 | 0.63836200 |
| H | -2.65984300 | -3.65468600 | -1.00669900 |
| H | -3.82499000 | -2.46499900 | -0.45296800 |
| C | -3.64730200 | -0.53469000 | 1.71375400 |
| H | -4.08220900 | -1.50934400 | 1.49733500 |
| H | -4.44740500 | 0.09769400 | 2.11110100 |
| H | -2.89982900 | -0.65883300 | 2.49267100 |
| C | -0.66925000 | 3.08243500 | 0.49254100 |
| H | -0.32951100 | 2.87225900 | 1.50731700 |
| H | -1.34008200 | 3.94592900 | 0.54522100 |

| | | | |
|---|---|---|---|
| H | 0.19440700 | 3.38534300 | -0.10481800 |
| C | -2.13345100 | -1.34146400 | -2.37892600 |
| H | -3.14894400 | -0.97509800 | -2.50750500 |
| H | -2.02377900 | -2.23673100 | -2.99684100 |
| H | -1.44557800 | -0.59159900 | -2.77596300 |
| C | -0.42226800 | -2.34722700 | -0.89568200 |
| H | 0.36859800 | -1.65319500 | -1.17155000 |
| H | -0.41208500 | -3.18977200 | -1.59234600 |
| H | -0.20079900 | -2.73110000 | 0.10019600 |
| C | -4.21371200 | 0.21798100 | -0.57228600 |
| H | -3.94893700 | 0.75418100 | -1.47877900 |
| H | -5.03743400 | 0.76056300 | -0.10066300 |
| H | -4.60022500 | -0.75916000 | -0.85500300 |
| C | -1.91663800 | 2.37371200 | -1.51770500 |
| H | -1.08940400 | 2.82026100 | -2.07445500 |
| H | -2.69863500 | 3.13319600 | -1.42489500 |
| H | -2.30546500 | 1.55749700 | -2.12292400 |
| H | -0.43101900 | 0.41147700 | -1.31841300 |

Zero-point correction= 0.689300 (Hartree/Particle)
Thermal correction to Energy= 0.719066
Thermal correction to Enthalpy= 0.720010
Thermal correction to Gibbs Free Energy= 0.636517
Sum of electronic and zero-point Energies= -1052.667226
Sum of electronic and thermal Energies= -1052.637460
Sum of electronic and thermal Enthalpies= -1052.636516
Sum of electronic and thermal Free Energies= -1052.720008

**Table S25.** Cartesian coordinates and energy values of **3**$^{iPr\text{-}Me_2}$ for *max1-(R/R)*.

| | | | |
|---|---|---|---|
| N | -1.71147700 | 0.51234200 | -0.00653700 |
| C | -0.62588400 | -0.30533900 | -0.52000700 |
| H | -0.17374400 | 0.02855100 | -1.45569400 |
| C | -1.44801600 | -1.55225200 | -1.01569200 |
| C | -2.70592100 | -0.31928600 | 0.70691200 |
| C | -2.42234200 | -1.75632600 | 0.15179200 |
| H | -1.97514900 | -2.37417100 | 0.93103900 |
| H | -3.34501200 | -2.25098100 | -0.16321100 |
| C | -4.16217600 | 0.09291800 | 0.43043800 |
| H | -4.37632900 | 1.09408400 | 0.80894100 |
| H | -4.83551100 | -0.59940500 | 0.94256000 |
| H | -4.39839300 | 0.06830000 | -0.63313800 |
| C | -2.25360800 | -1.08967700 | -2.25699700 |
| H | -2.87589500 | -0.22558400 | -2.04889700 |
| H | -2.89851600 | -1.90330900 | -2.60203500 |
| H | -1.57860700 | -0.83031800 | -3.07824500 |
| C | -2.50440100 | -0.32275600 | 2.24064700 |
| H | -1.48571500 | -0.61296900 | 2.50096300 |
| H | -3.18606400 | -1.04030600 | 2.70883700 |
| H | -2.70013700 | 0.65863700 | 2.67452800 |
| C | -0.68903400 | -2.78739000 | -1.51853900 |
| H | -0.14959500 | -2.53827100 | -2.43721600 |
| H | -1.40432900 | -3.57538500 | -1.77368700 |
| H | 0.03187300 | -3.20988000 | -0.83371000 |
| N | 1.71133600 | 0.51219700 | 0.00611400 |
| C | 0.62571700 | -0.30519300 | 0.52000700 |
| H | 0.17369700 | 0.02907600 | 1.45560800 |
| C | 1.44772200 | -1.55203800 | 1.01599400 |
| C | 2.70567400 | -0.31979700 | -0.70703400 |
| C | 2.42168700 | -1.75666800 | -0.15168700 |
| H | 1.97399500 | -2.37441200 | -0.93072400 |
| H | 3.34425100 | -2.25166200 | 0.16309500 |
| C | 4.16204300 | 0.09206200 | -0.43055700 |
| H | 4.37643700 | 1.09316900 | -0.80908600 |
| H | 4.83518800 | -0.60044400 | -0.94267800 |
| H | 4.39829900 | 0.06741000 | 0.63300700 |
| C | 2.25370600 | -1.08918300 | 2.25691500 |
| H | 2.87617400 | -0.22533100 | 2.04836700 |
| H | 2.89849500 | -1.90284100 | 2.60211900 |
| H | 1.57895200 | -0.82934700 | 3.07821100 |
| C | 2.50425200 | -0.32340500 | -2.24078500 |

| | | | |
|---|---|---|---|
| H | 1.48544000 | -0.61321200 | -2.50107000 |
| H | 3.18563500 | -1.04127500 | -2.70888900 |
| H | 2.70038500 | 0.65786800 | -2.67476000 |
| C | 0.68853600 | -2.78682700 | 1.51941600 |
| H | 0.14982200 | -2.53744100 | 2.43844500 |
| H | 1.40363000 | -3.57515900 | 1.77408900 |
| H | -0.03305200 | -3.20894600 | 0.83508400 |
| C | 1.74140100 | 1.95559800 | 0.19198800 |
| C | 1.89760400 | 2.75801700 | -1.10965000 |
| C | 2.73488700 | 2.46343500 | 1.25867400 |
| H | 0.75663800 | 2.19618600 | 0.59000500 |
| H | 1.16325300 | 2.44301300 | -1.85373300 |
| H | 1.75799200 | 3.82528500 | -0.91528100 |
| H | 2.89231700 | 2.63346100 | -1.54345400 |
| H | 2.59512700 | 1.92893000 | 2.19992200 |
| H | 3.77410900 | 2.34849800 | 0.94965900 |
| H | 2.56109800 | 3.52739000 | 1.44833500 |
| C | -1.74093900 | 1.95577900 | -0.19225500 |
| C | -1.89647000 | 2.75827300 | 1.10942400 |
| C | -2.73453000 | 2.46400600 | -1.25865500 |
| H | -0.75619300 | 2.19593500 | -0.59059000 |
| H | -1.16217600 | 2.44288700 | 1.85340000 |
| H | -1.75634100 | 3.82547200 | 0.91505000 |
| H | -2.89118100 | 2.63421900 | 1.54337100 |
| H | -2.59539300 | 1.92925900 | -2.19986000 |
| H | -3.77370400 | 2.34968300 | -0.94924900 |
| H | -2.56023300 | 3.52783700 | -1.44854100 |

Zero-point correction= 0.629885 (Hartree/Particle)
Thermal correction to Energy= 0.658613
Thermal correction to Enthalpy= 0.659557
Thermal correction to Gibbs Free Energy= 0.575359
Sum of electronic and zero-point Energies= -974.058073
Sum of electronic and thermal Energies= -974.029345
Sum of electronic and thermal Enthalpies= -974.028401
Sum of electronic and thermal Free Energies= -974.112599

**Table S26.** Cartesian coordinates and energy values of **3**$^{iPr\text{-}Me_2}$ for *max2-(R/R)*.

| | | | |
|---|---|---|---|
| N | 1.55121500 | -0.33454400 | 0.14875200 |
| C | 0.77440000 | 0.08368200 | -1.01173700 |
| H | 1.08282100 | 0.05505300 | -2.06755100 |
| C | 1.24671500 | 1.64465800 | -1.14429600 |
| C | 2.08127500 | 0.80494300 | 0.97562500 |
| C | 1.46683700 | 2.04796600 | 0.29852500 |
| H | 0.51047400 | 2.27927100 | 0.76948600 |
| H | 2.11349000 | 2.92295400 | 0.40967600 |
| C | 3.62530800 | 0.91123000 | 1.03395400 |
| H | 4.06682500 | 0.06251700 | 1.55603900 |
| H | 3.89426000 | 1.80802500 | 1.59831800 |
| H | 4.09257800 | 0.98452200 | 0.05650700 |
| C | 2.58917200 | 1.62632400 | -1.92303300 |
| H | 3.22449500 | 0.79057700 | -1.64360400 |
| H | 3.14503000 | 2.55364400 | -1.75834100 |
| H | 2.39879000 | 1.54344900 | -2.99755100 |
| C | 1.58897200 | 0.78805700 | 2.43477800 |
| H | 0.50424900 | 0.79743200 | 2.46178800 |
| H | 1.94698900 | 1.69055000 | 2.94024400 |
| H | 1.95175000 | -0.06897800 | 3.00012400 |
| C | 0.34718400 | 2.56435600 | -1.97695600 |
| H | 0.87469700 | 3.50302900 | -2.17388700 |
| H | -0.60344400 | 2.81991100 | -1.52298000 |
| H | 0.13159000 | 2.10719000 | -2.94767600 |
| N | -1.55171700 | 0.33468300 | 0.14849500 |
| C | -0.77475100 | -0.08335300 | -1.01183100 |
| H | -1.08329600 | -0.05502700 | -2.06761300 |
| C | -1.24660800 | -1.64451400 | -1.14426500 |
| C | -2.08059900 | -0.80489100 | 0.97598300 |
| C | -1.46620600 | -2.04787300 | 0.29865800 |
| H | -0.50979200 | -2.27918100 | 0.76945400 |
| H | -2.11279100 | -2.92290200 | 0.40992100 |

| | | | |
|---|---|---|---|
| C | -3.62451400 | -0.91174800 | 1.03561900 |
| H | -4.06593700 | -0.06290600 | 1.55757300 |
| H | -3.89264200 | -1.80832700 | 1.60071900 |
| H | -4.09252100 | -0.98581500 | 0.05857300 |
| C | -2.58944800 | -1.62678300 | -1.92230400 |
| H | -3.22524700 | -0.79168700 | -1.64204000 |
| H | -3.14451100 | -2.55460600 | -1.75775600 |
| H | -2.39977600 | -1.54322100 | -2.99688800 |
| C | -1.58697700 | -0.78734000 | 2.43465500 |
| H | -0.50223100 | -0.79592900 | 2.46045300 |
| H | -1.94387700 | -1.68993500 | 2.94073700 |
| H | -1.94979100 | 0.06963600 | 3.00008200 |
| C | -0.34692300 | -2.56353100 | -1.97750900 |
| H | -0.13448300 | -2.10714000 | -2.94929200 |
| H | -0.87290900 | -3.50355300 | -2.17210400 |
| H | 0.60534100 | -2.81630600 | -1.52545100 |
| C | -2.15175200 | 1.66917600 | 0.19346500 |
| C | -2.43726800 | 2.20240800 | 1.60279200 |
| C | -3.36617300 | 1.86407300 | -0.73310300 |
| H | -1.38078000 | 2.33435200 | -0.17831600 |
| H | -1.54666200 | 2.14386200 | 2.23020400 |
| H | -2.72669500 | 3.25388600 | 1.52597200 |
| H | -3.24975200 | 1.68126400 | 2.10896000 |
| H | -3.13147300 | 1.52993300 | -1.74625400 |
| H | -4.24196200 | 1.31431600 | -0.38517200 |
| H | -3.63551000 | 2.92381000 | -0.78650100 |
| C | 2.15052000 | -1.66941700 | 0.19394700 |
| C | 2.43739500 | -2.20193600 | 1.60326200 |
| C | 3.36379000 | -1.86546800 | -0.73385100 |
| H | 1.37872900 | -2.33450600 | -0.17636400 |
| H | 1.54752100 | -2.14275300 | 2.23165100 |
| H | 2.72628500 | -3.25357400 | 1.52663500 |
| H | 3.25066000 | -1.68089400 | 2.10825800 |
| H | 3.12818800 | -1.53172800 | -1.74692500 |
| H | 4.24020200 | -1.31593400 | -0.38713000 |
| H | 3.63255400 | -2.92536200 | -0.78697100 |

| | |
|---|---|
| Zero-point correction= | 0.630169 (Hartree/Particle) |
| Thermal correction to Energy= | 0.658555 |
| Thermal correction to Enthalpy= | 0.659499 |
| Thermal correction to Gibbs Free Energy= | 0.577238 |
| Sum of electronic and zero-point Energies= | -974.022707 |
| Sum of electronic and thermal Energies= | -973.994321 |
| Sum of electronic and thermal Enthalpies= | -973.993377 |
| Sum of electronic and thermal Free Energies= | -974.075638 |

**Table S27.** Cartesian coordinates and energy values of $\mathbf{3}^{\mathbf{iPr\text{-}Me_2}}$ for *max1-(S/S)*.

| | | | |
|---|---|---|---|
| N | 1.47398500 | -0.51297400 | -0.04581500 |
| C | 0.67684600 | 0.67020300 | 0.42971300 |
| C | 1.78095000 | 1.79128900 | 0.40763100 |
| C | 2.60889500 | -0.12876100 | -0.91350600 |
| C | 2.54335600 | 1.41014100 | -0.87225800 |
| H | 3.53616300 | 1.86560800 | -0.91121100 |
| H | 1.98282200 | 1.78527500 | -1.73483600 |
| C | 2.39661800 | -0.63297800 | -2.35637900 |
| H | 2.46881700 | -1.72065300 | -2.41159300 |
| H | 3.14975700 | -0.21185600 | -3.03074200 |
| H | 1.40904000 | -0.33870000 | -2.71707700 |
| C | 1.46846400 | 3.28703500 | 0.34507800 |
| H | 0.96500800 | 3.57776000 | -0.57058400 |
| H | 2.42120100 | 3.82517800 | 0.37190400 |
| H | 0.88779200 | 3.62980000 | 1.20238700 |
| C | 4.00745500 | -0.59418100 | -0.45200400 |
| H | 4.27786000 | -0.19456600 | 0.52340600 |
| H | 4.74825300 | -0.23611700 | -1.17217400 |
| H | 4.09333900 | -1.67912300 | -0.41522000 |
| C | 2.64800900 | 1.62198200 | 1.67224500 |
| H | 2.09176400 | 1.96124500 | 2.55150300 |
| H | 3.55134000 | 2.23400600 | 1.59445900 |
| H | 2.95049300 | 0.59712300 | 1.84713200 |

| | | | |
|---|---|---|---|
| N | -1.47401400 | -0.51295200 | 0.04577300 |
| C | -0.67686000 | 0.67019500 | -0.42976300 |
| C | -1.78093200 | 1.79130600 | -0.40766700 |
| C | -2.60884500 | -0.12870700 | 0.91355700 |
| C | -2.54331700 | 1.41020300 | 0.87224800 |
| H | -3.53612800 | 1.86566200 | 0.91118100 |
| H | -1.98279000 | 1.78537500 | 1.73481400 |
| C | -2.39643900 | -0.63286700 | 2.35643000 |
| H | -1.40883400 | -0.33857400 | 2.71704000 |
| H | -2.46862900 | -1.72054000 | 2.41168600 |
| H | -3.14952200 | -0.21172500 | 3.03084400 |
| C | -1.46837100 | 3.28703500 | -0.34516100 |
| H | -2.42107600 | 3.82523400 | -0.37198700 |
| H | -0.88768800 | 3.62974300 | -1.20248600 |
| H | -0.96488700 | 3.57775500 | 0.57048600 |
| C | -4.00743300 | -0.59415900 | 0.45219300 |
| H | -4.27790100 | -0.19462800 | -0.52323400 |
| H | -4.74818500 | -0.23603300 | 1.17238000 |
| H | -4.09331700 | -1.67910400 | 0.41551500 |
| C | -2.64806300 | 1.62201200 | -1.67223300 |
| H | -2.09183900 | 1.96118200 | -2.55154000 |
| H | -3.55133600 | 2.23411700 | -1.59442500 |
| H | -2.95064700 | 0.59717100 | -1.84704900 |
| H | -0.38644400 | 0.34799900 | -1.43099400 |
| H | 0.38644000 | 0.34801500 | 1.43094800 |
| C | -1.42053000 | -1.74067100 | -0.75625100 |
| C | -2.21821600 | -1.76981100 | -2.07877400 |
| C | -1.72365300 | -3.01619400 | 0.04561700 |
| H | -0.37546000 | -1.80343900 | -1.05223200 |
| H | -1.92385900 | -0.95475500 | -2.74165000 |
| H | -2.00513500 | -2.70610800 | -2.60421500 |
| H | -3.29666000 | -1.71770600 | -1.92211600 |
| H | -1.19516100 | -3.03236200 | 0.99814900 |
| H | -2.78818100 | -3.13850800 | 0.24988600 |
| H | -1.40561800 | -3.88858700 | -0.53070400 |
| C | 1.42044600 | -1.74068800 | 0.75621200 |
| C | 2.21811000 | -1.76985400 | 2.07875000 |
| C | 1.72353500 | -3.01620700 | -0.04567000 |
| H | 0.37537000 | -1.80342400 | 1.05218000 |
| H | 1.92376300 | -0.95478700 | 2.74161700 |
| H | 2.00498300 | -2.70614000 | 2.60419100 |
| H | 3.29655900 | -1.71778300 | 1.92211900 |
| H | 1.19495500 | -3.03239100 | -0.99815400 |
| H | 2.78804600 | -3.13849000 | -0.25004400 |
| H | 1.40557800 | -3.88860600 | 0.53068400 |

| | |
|---|---|
| Zero-point correction= | 0.631835 (Hartree/Particle) |
| Thermal correction to Energy= | 0.658746 |
| Thermal correction to Enthalpy= | 0.659691 |
| Thermal correction to Gibbs Free Energy= | 0.581457 |
| Sum of electronic and zero-point Energies= | -974.059536 |
| Sum of electronic and thermal Energies= | -974.032624 |
| Sum of electronic and thermal Enthalpies= | -974.031680 |
| Sum of electronic and thermal Free Energies= | -974.109914 |

**Table S28.** Cartesian coordinates and energy values of **3**$^{iPr\text{-}Me_2}$ for *max2-(S/S)*.

| | | | |
|---|---|---|---|
| N | 1.80768100 | 0.29021800 | -0.02141900 |
| C | 0.75160600 | -0.31475000 | -0.87423100 |
| C | 0.92780900 | -1.85517500 | -0.57156600 |
| C | 2.19072700 | -0.59536000 | 1.12119400 |
| C | 1.26543300 | -1.80996500 | 0.92319800 |
| H | 1.72658400 | -2.73553700 | 1.27761300 |
| H | 0.33354000 | -1.67323700 | 1.47336400 |
| C | 1.91933800 | 0.09875300 | 2.46860400 |
| H | 2.62707800 | 0.91093900 | 2.64460500 |
| H | 2.01756500 | -0.61433800 | 3.29351700 |
| H | 0.91544900 | 0.51492500 | 2.49552300 |
| C | -0.20657600 | -2.85084100 | -0.81013100 |
| H | -1.02094600 | -2.71166100 | -0.11268200 |
| H | 0.18679500 | -3.86147400 | -0.66162000 |

| | | | |
|---|---|---|---|
| H | -0.58383900 | -2.80709400 | -1.83509100 |
| C | 3.65728500 | -1.08658100 | 1.16953000 |
| H | 3.93127400 | -1.70450100 | 0.31853300 |
| H | 3.77483400 | -1.69924400 | 2.06724500 |
| H | 4.37109400 | -0.26810400 | 1.24746100 |
| C | 2.09792800 | -2.38861600 | -1.42427800 |
| H | 1.77882100 | -2.49025600 | -2.46648200 |
| H | 2.39707800 | -3.38032300 | -1.07236400 |
| H | 2.97180700 | -1.75099500 | -1.40982000 |
| N | -1.80771900 | -0.29017200 | -0.02147900 |
| C | -0.75162600 | 0.31480300 | -0.87425000 |
| C | -0.92782000 | 1.85520000 | -0.57151500 |
| C | -2.19067300 | 0.59531700 | 1.12122500 |
| C | -1.26531900 | 1.80989200 | 0.92327600 |
| H | -1.72638500 | 2.73545700 | 1.27781900 |
| H | -0.33337800 | 1.67304400 | 1.47333200 |
| C | -1.91925400 | -0.09892100 | 2.46856300 |
| H | -0.91539700 | -0.51517900 | 2.49536900 |
| H | -2.62704600 | -0.91106200 | 2.64455900 |
| H | -2.01735600 | 0.61411600 | 3.29353900 |
| C | 0.20653300 | 2.85086800 | -0.81019700 |
| H | -0.18685400 | 3.86151600 | -0.66183400 |
| H | 0.58380600 | 2.80697700 | -1.83514700 |
| H | 1.02090100 | 2.71182100 | -0.11271300 |
| C | -3.65720600 | 1.08661100 | 1.16967600 |
| H | -3.93121400 | 1.70461400 | 0.31874700 |
| H | -3.77468000 | 1.69919400 | 2.06745500 |
| H | -4.37104700 | 0.26815700 | 1.24757300 |
| C | -2.09803200 | 2.38866000 | -1.42410100 |
| H | -1.77899400 | 2.49045600 | -2.46631000 |
| H | -2.39722800 | 3.38030300 | -1.07204600 |
| H | -2.97185500 | 1.75096600 | -1.40966600 |
| H | -1.04063400 | 0.17670100 | -1.92275100 |
| H | 1.04064300 | -0.17660600 | -1.92272000 |
| C | -2.79911800 | -1.15873000 | -0.68453800 |
| C | -3.87727200 | -0.52145700 | -1.59057900 |
| C | -3.46008400 | -2.14701300 | 0.28947800 |
| H | -2.21394900 | -1.76321800 | -1.36966900 |
| H | -3.42980900 | 0.06489800 | -2.39385200 |
| H | -4.44716800 | -1.32748700 | -2.06343700 |
| H | -4.58539800 | 0.10670400 | -1.05210600 |
| H | -2.72378700 | -2.61389600 | 0.94424200 |
| H | -4.21132500 | -1.67152400 | 0.92095600 |
| H | -3.96516600 | -2.93536500 | -0.27484200 |
| C | 2.79908800 | 1.15877200 | -0.68449700 |
| C | 3.87717200 | 0.52150200 | -1.59061600 |
| C | 3.46009400 | 2.14701500 | 0.28952900 |
| H | 2.21391000 | 1.76329200 | -1.36958300 |
| H | 3.42963300 | -0.06485400 | -2.39384500 |
| H | 4.44702400 | 1.32753100 | -2.06352700 |
| H | 4.58535100 | -0.10665500 | -1.05221100 |
| H | 2.72381000 | 2.61388100 | 0.94431900 |
| H | 4.21135100 | 1.67151200 | 0.92097600 |
| H | 3.96516500 | 2.93538000 | -0.27478500 |

Zero-point correction= 0.633137 (Hartree/Particle)
Thermal correction to Energy= 0.660504
Thermal correction to Enthalpy= 0.661448
Thermal correction to Gibbs Free Energy= 0.581337
Sum of electronic and zero-point Energies= -974.055361
Sum of electronic and thermal Energies= -974.027995
Sum of electronic and thermal Enthalpies= -974.027050
Sum of electronic and thermal Free Energies= -974.107161

**Table S29.** Cartesian coordinates and energy values of **3**$^{iPr\text{-}Me_2}$ for *max1-(R/S)*.

| | | | |
|---|---|---|---|
| N | 1.40853000 | -0.60059500 | -0.08065100 |
| C | 0.87429300 | 0.52757200 | -0.81086600 |
| H | 1.01481800 | 0.64794000 | -1.89433300 |
| C | 2.03837200 | 1.61432500 | -0.53349700 |
| C | 2.32391000 | -0.21878300 | 1.03723600 |

| | | | |
|---|---|---|---|
| C | 2.41867000 | 1.31678200 | 0.90572400 |
| H | 1.70249600 | 1.79504200 | 1.58028700 |
| H | 3.41284100 | 1.68515700 | 1.17299600 |
| C | 3.73540300 | -0.84647500 | 0.96734000 |
| H | 3.70410800 | -1.93199400 | 1.05378300 |
| H | 4.32512200 | -0.47432800 | 1.80925900 |
| H | 4.26769300 | -0.59250900 | 0.05381300 |
| C | 3.18400800 | 1.20741600 | -1.50189000 |
| H | 3.33575000 | 0.13611600 | -1.56243000 |
| H | 4.12197300 | 1.67330400 | -1.18666000 |
| H | 2.96080100 | 1.56890500 | -2.51045300 |
| C | 1.74887800 | -0.54816300 | 2.42778500 |
| H | 0.77292700 | -0.08332600 | 2.55102500 |
| H | 2.41179200 | -0.14907000 | 3.20225500 |
| H | 1.64809700 | -1.61958100 | 2.59777200 |
| C | 1.84163800 | 3.10835900 | -0.83858600 |
| H | 1.16096200 | 3.26336400 | -1.68002200 |
| H | 2.80420600 | 3.53804600 | -1.12785300 |
| H | 1.48769100 | 3.68628800 | 0.00557600 |
| N | -1.47107200 | -0.44335400 | -0.15918600 |
| C | -0.75856100 | 0.79042400 | -0.70641800 |
| C | -1.51537800 | 1.94241200 | 0.04270000 |
| C | -2.26748900 | -0.18828000 | 1.06266300 |
| C | -1.86607100 | 1.25378300 | 1.37830500 |
| H | -2.64491300 | 1.79370600 | 1.92294500 |
| H | -0.96964900 | 1.25756200 | 2.00579000 |
| C | -1.86560700 | -1.14556200 | 2.20163100 |
| H | -2.27598900 | -2.14438200 | 2.04206300 |
| H | -2.24330600 | -0.78317800 | 3.16346600 |
| H | -0.78523000 | -1.22957600 | 2.25471200 |
| C | -0.85866500 | 3.27090700 | 0.41500200 |
| H | 0.00452200 | 3.13419800 | 1.06163900 |
| H | -1.59328700 | 3.85245200 | 0.98108800 |
| H | -0.57814900 | 3.86548000 | -0.45110700 |
| C | -3.81022300 | -0.27464700 | 0.94569000 |
| H | -4.23231800 | 0.43482500 | 0.23892700 |
| H | -4.23542700 | -0.05128800 | 1.92816100 |
| H | -4.14773200 | -1.27403600 | 0.67318100 |
| C | -2.75780500 | 2.32359200 | -0.78798100 |
| H | -2.45005000 | 2.92067600 | -1.65144300 |
| H | -3.44617300 | 2.92964200 | -0.19136800 |
| H | -3.30174800 | 1.46360700 | -1.16253700 |
| H | -1.07001000 | 0.58806900 | -1.73138200 |
| C | 1.34020400 | -1.94802500 | -0.64216100 |
| C | 1.24405500 | -3.06044200 | 0.40895900 |
| C | 2.42056800 | -2.28937500 | -1.69026900 |
| H | 0.39888300 | -1.97809400 | -1.17946700 |
| H | 0.45291100 | -2.84531400 | 1.12554200 |
| H | 1.01170300 | -4.00645400 | -0.08714800 |
| H | 2.17582300 | -3.20664500 | 0.95688400 |
| H | 2.43309600 | -1.54951700 | -2.49325400 |
| H | 3.42073700 | -2.34547100 | -1.25808500 |
| H | 2.19928900 | -3.26123900 | -2.14295600 |
| C | -1.94026700 | -1.38508200 | -1.19108100 |
| C | -3.12456900 | -0.95881300 | -2.09274900 |
| C | -2.18839200 | -2.79835200 | -0.65010700 |
| H | -1.10004000 | -1.47778400 | -1.88528100 |
| H | -2.94961300 | 0.00979300 | -2.56302800 |
| H | -3.23430700 | -1.69094100 | -2.89877000 |
| H | -4.07141500 | -0.91570800 | -1.55654600 |
| H | -1.35560300 | -3.13851600 | -0.03912300 |
| H | -3.09620000 | -2.85610500 | -0.04811100 |
| H | -2.31113300 | -3.49290900 | -1.48552800 |

Zero-point correction= 0.632273 (Hartree/Particle)
Thermal correction to Energy= 0.659889
Thermal correction to Enthalpy= 0.660833
Thermal correction to Gibbs Free Energy= 0.579893
Sum of electronic and zero-point Energies= -974.021823
Sum of electronic and thermal Energies= -973.994207
Sum of electronic and thermal Enthalpies= -973.993263

Sum of electronic and thermal Free Energies= -974.074204

**Table S30.** Cartesian coordinates and energy values of **3**$^{iPr\text{-}Me_2}$ for *max2-(R/S)*.

| | | | |
|---|---|---|---|
| N | -1.91275500 | -0.25294100 | -0.01562500 |
| C | -0.60595800 | 0.30665500 | 0.39618200 |
| H | -0.42916900 | 0.02799800 | 1.43715900 |
| C | -0.87465600 | 1.85258500 | 0.28571400 |
| C | -2.55970600 | 0.61627900 | -1.03457600 |
| C | -1.66963200 | 1.88837000 | -1.02872100 |
| H | -0.97338700 | 1.86725900 | -1.87253500 |
| H | -2.26357900 | 2.80006300 | -1.12875500 |
| C | -4.02004800 | 1.02279200 | -0.75329900 |
| H | -4.69092000 | 0.16687500 | -0.69966600 |
| H | -4.36533400 | 1.65234200 | -1.57748600 |
| H | -4.12125000 | 1.60068200 | 0.16342500 |
| C | -1.74779000 | 2.30218600 | 1.47390200 |
| H | -2.65169700 | 1.71982300 | 1.58730000 |
| H | -2.03996000 | 3.34769400 | 1.34097500 |
| H | -1.18053300 | 2.23338800 | 2.40758000 |
| C | -2.51869800 | -0.06569400 | -2.41613800 |
| H | -1.50099200 | -0.37817200 | -2.65576100 |
| H | -2.86418500 | 0.61615200 | -3.20032300 |
| H | -3.15630000 | -0.95236400 | -2.43320400 |
| C | 0.28751300 | 2.84346100 | 0.26084300 |
| H | 0.96261400 | 2.67968000 | 1.09897400 |
| H | -0.11300700 | 3.85857300 | 0.34299600 |
| H | 0.85912100 | 2.80967800 | -0.65974100 |
| N | 1.92650500 | 0.25356400 | 0.02036900 |
| C | 0.62190100 | -0.25869400 | -0.45374400 |
| C | 0.85304600 | -1.81569800 | -0.38756400 |
| C | 2.50136900 | -0.66250100 | 1.04479700 |
| C | 1.58330700 | -1.91294500 | 0.96011400 |
| H | 2.15336000 | -2.83988900 | 1.05944400 |
| H | 0.84948300 | -1.90114000 | 1.77169600 |
| C | 2.41866600 | -0.01671400 | 2.44214400 |
| H | 3.08716100 | 0.84412300 | 2.51286400 |
| H | 2.70336200 | -0.73190400 | 3.22110500 |
| H | 1.40401200 | 0.32897300 | 2.64564600 |
| C | -0.32564300 | -2.78579800 | -0.47097400 |
| H | -0.93378800 | -2.80579300 | 0.42466900 |
| H | 0.06377900 | -3.79959900 | -0.60727700 |
| H | -0.96656200 | -2.55588300 | -1.32105200 |
| C | 3.96236800 | -1.10103800 | 0.81820700 |
| H | 4.08750500 | -1.66575300 | -0.10375500 |
| H | 4.25579400 | -1.75338400 | 1.64479300 |
| H | 4.65672600 | -0.26228500 | 0.80842600 |
| C | 1.77627600 | -2.23244700 | -1.54989900 |
| H | 1.25046700 | -2.12987300 | -2.50468800 |
| H | 2.05590800 | -3.28387600 | -1.43909900 |
| H | 2.68676800 | -1.65295200 | -1.60574400 |
| H | 0.46418400 | 0.02972300 | -1.49635500 |
| C | -2.64336000 | -1.12998300 | 0.90825600 |
| C | -3.53957400 | -2.15238200 | 0.18732000 |
| C | -3.43639200 | -0.50958600 | 2.08289300 |
| H | -1.86031600 | -1.70468000 | 1.40344200 |
| H | -3.03642800 | -2.59270600 | -0.67087000 |
| H | -3.80567000 | -2.95729400 | 0.87775000 |
| H | -4.47437200 | -1.70796400 | -0.15680100 |
| H | -2.79292600 | 0.07223500 | 2.74256300 |
| H | -4.26473800 | 0.11961000 | 1.75651500 |
| H | -3.86006300 | -1.32288800 | 2.68053000 |
| C | 2.73084000 | 1.14201400 | -0.82898900 |
| C | 3.60106000 | 0.54398800 | -1.96070300 |
| C | 3.57911400 | 2.13345600 | -0.01428300 |
| H | 1.99407700 | 1.73806500 | -1.36438900 |
| H | 3.00089000 | -0.01379900 | -2.67907800 |
| H | 4.06960700 | 1.37000600 | -2.50502600 |
| H | 4.40132700 | -0.10058000 | -1.59736900 |
| H | 3.00199400 | 2.58086600 | 0.79222100 |
| H | 4.45936600 | 1.65961000 | 0.42245500 |

| | | | |
|---|---|---|---|
| H | 3.93740100 | 2.93516100 | -0.66566900 |

Zero-point correction= 0.631581 (Hartree/Particle)
Thermal correction to Energy= 0.658638
Thermal correction to Enthalpy= 0.659582
Thermal correction to Gibbs Free Energy= 0.581178
Sum of electronic and zero-point Energies= -974.069177
Sum of electronic and thermal Energies= -974.042120
Sum of electronic and thermal Enthalpies= -974.041175
Sum of electronic and thermal Free Energies= -974.119580

**Table S31.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *max1-(R/R)*.

| | | | |
|---|---|---|---|
| N | 1.89887400 | 0.30509800 | -0.14583000 |
| C | 0.63799500 | -0.16456800 | 0.48472300 |
| H | 0.19172400 | 0.16785400 | 1.42912500 |
| C | 1.16753200 | -1.46196300 | 1.28502500 |
| C | 2.20825300 | 1.74065200 | -0.40649100 |
| C | 3.00207900 | -0.71928600 | -0.12852500 |
| C | 2.32108500 | -1.97206200 | 0.44770800 |
| H | 1.95675800 | -2.60126800 | -0.35923800 |
| H | 3.02782500 | -2.57137900 | 1.02772700 |
| C | 1.10985200 | 2.40377500 | -1.26373100 |
| H | 1.10307500 | 1.95363800 | -2.25884600 |
| H | 1.32436800 | 3.47028000 | -1.37082400 |
| H | 0.11763700 | 2.30902900 | -0.86226400 |
| C | 4.23760600 | -0.40262400 | 0.75620100 |
| H | 4.81117600 | 0.45536200 | 0.41678700 |
| H | 4.90954200 | -1.26502200 | 0.72134100 |
| H | 3.97410500 | -0.23620500 | 1.79706800 |
| C | 1.67608400 | -0.90016300 | 2.64316100 |
| H | 2.18718000 | 0.05370200 | 2.53514900 |
| H | 2.35465000 | -1.60816600 | 3.12723100 |
| H | 0.82860400 | -0.73965800 | 3.31631300 |
| C | 2.43337600 | 2.49905900 | 0.92269900 |
| H | 1.64136500 | 2.30058400 | 1.64308700 |
| H | 2.48182100 | 3.57990300 | 0.76069800 |
| H | 3.37505200 | 2.18502100 | 1.37681900 |
| C | 3.46362000 | 1.97159200 | -1.28017200 |
| H | 4.39408500 | 1.62570700 | -0.84368700 |
| H | 3.56205300 | 3.05034600 | -1.42084200 |
| H | 3.34719700 | 1.52419400 | -2.26641300 |
| C | 3.51177800 | -1.06970200 | -1.54600600 |
| H | 2.67380200 | -1.12659200 | -2.24220600 |
| H | 4.00525800 | -2.04605300 | -1.52057000 |
| H | 4.23426900 | -0.35508400 | -1.93411600 |
| C | 0.17200300 | -2.55088000 | 1.68808400 |
| H | -0.71918700 | -2.11735200 | 2.14537800 |
| H | 0.64165800 | -3.19135500 | 2.44150600 |
| H | -0.13991300 | -3.19613100 | 0.87545700 |
| N | -1.89889300 | 0.30511000 | 0.14573600 |
| C | -0.63799600 | -0.16456700 | -0.48475200 |
| H | -0.19173000 | 0.16783300 | -1.42916500 |
| C | -1.16752400 | -1.46194900 | -1.28505900 |
| C | -2.20829500 | 1.74064000 | 0.40648800 |
| C | -3.00204100 | -0.71932900 | 0.12854400 |
| C | -2.32102500 | -1.97209900 | -0.44768900 |
| H | -1.95665200 | -2.60129400 | 0.35924300 |
| H | -3.02777100 | -2.57143500 | -1.02768200 |
| C | -1.10987600 | 2.40381300 | 1.26365000 |
| H | -1.10278500 | 1.95346200 | 2.25866400 |
| H | -1.32465100 | 3.47023800 | 1.37101400 |
| H | -0.11772800 | 2.30943600 | 0.86193200 |
| C | -4.23760200 | -0.40276200 | -0.75615800 |
| H | -4.81105900 | 0.45538100 | -0.41695300 |
| H | -4.90961900 | -1.26508800 | -0.72103600 |
| H | -3.97413500 | -0.23664900 | -1.79708200 |
| C | -1.67614400 | -0.90007000 | -2.64312700 |
| H | -2.18714700 | 0.05383900 | -2.53503200 |
| H | -2.35481900 | -1.60800400 | -3.12714400 |
| H | -0.82871400 | -0.73962400 | -3.31635700 |

| | | | |
|---|---|---|---|
| C | -2.43351100 | 2.49910600 | -0.92265500 |
| H | -1.64155200 | 2.30066600 | -1.64311500 |
| H | -2.48193700 | 3.57994300 | -0.76059800 |
| H | -3.37521700 | 2.18509500 | -1.37672700 |
| C | -3.46359400 | 1.97148500 | 1.28029900 |
| H | -4.39406500 | 1.62543500 | 0.84396100 |
| H | -3.56215200 | 3.05023700 | 1.42089400 |
| H | -3.34699800 | 1.52417900 | 2.26656300 |
| C | -3.51167300 | -1.06968200 | 1.54606300 |
| H | -2.67367800 | -1.12637300 | 2.24225800 |
| H | -4.00499800 | -2.04611200 | 1.52072400 |
| H | -4.23426800 | -0.35514000 | 1.93412100 |
| C | -0.17196100 | -2.55079800 | -1.68822600 |
| H | 0.71916400 | -2.11720500 | -2.14558600 |
| H | -0.64163400 | -3.19129200 | -2.44162000 |
| H | 0.14006400 | -3.19604000 | -0.87563400 |

Zero-point correction= 0.687750 (Hartree/Particle)
Thermal correction to Energy= 0.718146
Thermal correction to Enthalpy= 0.719091
Thermal correction to Gibbs Free Energy= 0.633740
Sum of electronic and zero-point Energies= -1052.602064
Sum of electronic and thermal Energies= -1052.571667
Sum of electronic and thermal Enthalpies= -1052.570723
Sum of electronic and thermal Free Energies= -1052.656074

**Table S32.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *max2-(R/R)*.

| | | | |
|---|---|---|---|
| N | -1.76114800 | -0.28172300 | -0.29840900 |
| C | -0.80596400 | 0.04545500 | 0.77441300 |
| H | -0.94885400 | -0.09813200 | 1.85134700 |
| C | -1.42614600 | 1.55678500 | 1.27565800 |
| C | -1.98776500 | -1.69350000 | -0.72621000 |
| C | -2.82221400 | 0.74582600 | -0.56993300 |
| C | -2.32493800 | 2.00948100 | 0.14415900 |
| H | -1.79209600 | 2.65099000 | -0.55381400 |
| H | -3.16872700 | 2.59766500 | 0.51389600 |
| C | -2.95413800 | -1.90377300 | -1.91448100 |
| H | -3.98710000 | -1.62881300 | -1.72193400 |
| H | -2.94654600 | -2.97632500 | -2.12652000 |
| H | -2.60992200 | -1.39725500 | -2.81378400 |
| C | -4.23332200 | 0.39814800 | -0.03031800 |
| H | -4.68667100 | -0.45058000 | -0.53554000 |
| H | -4.89262300 | 1.25587900 | -0.19234300 |
| H | -4.22564900 | 0.18286400 | 1.03558600 |
| C | -2.28941700 | 1.24419700 | 2.52970600 |
| H | -2.90425900 | 0.35355300 | 2.40637100 |
| H | -2.94740400 | 2.08627400 | 2.76068300 |
| H | -1.64726300 | 1.07845100 | 3.40107200 |
| C | -0.65634600 | -2.21700000 | -1.28226900 |
| H | -0.51452000 | -1.82932800 | -2.29302400 |
| H | -0.63066600 | -3.30965100 | -1.32538800 |
| H | 0.17048400 | -1.85988200 | -0.70194400 |
| C | -2.56443300 | -2.52357700 | 0.44395400 |
| H | -2.06389900 | -2.30372800 | 1.38195900 |
| H | -2.48267800 | -3.59761800 | 0.25217000 |
| H | -3.62290600 | -2.28878700 | 0.57375500 |
| C | -2.95121600 | 1.10334500 | -2.06993700 |
| H | -1.96182800 | 1.15543900 | -2.52648900 |
| H | -3.42233800 | 2.08674200 | -2.15873900 |
| H | -3.56441700 | 0.40615800 | -2.63464300 |
| C | -0.46381600 | 2.64883600 | 1.73600100 |
| H | -1.04586700 | 3.44354800 | 2.21508600 |
| H | 0.09922100 | 3.10327200 | 0.93029500 |
| H | 0.23776800 | 2.27221300 | 2.48343700 |
| N | 1.76097600 | 0.28151200 | -0.29883400 |
| C | 0.80596700 | -0.04529500 | 0.77429200 |
| H | 0.94909100 | 0.09887900 | 1.85110200 |
| C | 1.42605500 | -1.55633800 | 1.27598900 |
| C | 1.98783900 | 1.69328100 | -0.72653300 |
| C | 2.82222400 | -0.74600100 | -0.56979600 |

| | | | |
|---|---|---|---|
| C | 2.32492000 | -2.00942400 | 0.14467900 |
| H | 1.79211900 | -2.65116700 | -0.55311100 |
| H | 3.16867200 | -2.59749400 | 0.51467200 |
| C | 2.95421500 | 1.90340800 | -1.91480700 |
| H | 3.98718300 | 1.62852700 | -1.72218400 |
| H | 2.94658600 | 2.97591800 | -2.12706700 |
| H | 2.61003900 | 1.39668800 | -2.81401600 |
| C | 4.23325500 | -0.39803900 | -0.03014900 |
| H | 4.68680300 | 0.45021900 | -0.53598200 |
| H | 4.89249600 | -1.25596600 | -0.19136500 |
| H | 4.22539900 | -0.18190200 | 1.03558000 |
| C | 2.28929700 | -1.24350100 | 2.53001800 |
| H | 2.90416200 | -0.35288200 | 2.40655000 |
| H | 2.94726300 | -2.08553100 | 2.76122200 |
| H | 1.64709400 | -1.07755000 | 3.40131300 |
| C | 0.65646400 | 2.21686900 | -1.28254600 |
| H | 0.51446600 | 1.82902700 | -2.29321200 |
| H | 0.63094500 | 3.30952100 | -1.32584200 |
| H | -0.17031700 | 1.85998100 | -0.70202800 |
| C | 2.56442300 | 2.52325300 | 0.44371600 |
| H | 2.06375900 | 2.30332800 | 1.38164600 |
| H | 2.48269000 | 3.59731100 | 0.25202900 |
| H | 3.62288200 | 2.28847400 | 0.57362800 |
| C | 2.95147400 | -1.10400500 | -2.06965600 |
| H | 1.96215900 | -1.15653600 | -2.52630600 |
| H | 3.42290800 | -2.08728700 | -2.15807900 |
| H | 3.56452600 | -0.40680900 | -2.63452400 |
| C | 0.46368000 | -2.64826800 | 1.73650900 |
| H | 1.04566700 | -3.44290100 | 2.21580100 |
| H | -0.09926700 | -3.10282800 | 0.93082000 |
| H | -0.23795300 | -2.27147200 | 2.48380400 |

| | |
|---|---|
| Zero-point correction= | 0.687531 (Hartree/Particle) |
| Thermal correction to Energy= | 0.717958 |
| Thermal correction to Enthalpy= | 0.718902 |
| Thermal correction to Gibbs Free Energy= | 0.632461 |
| Sum of electronic and zero-point Energies= | -1052.552589 |
| Sum of electronic and thermal Energies= | -1052.522162 |
| Sum of electronic and thermal Enthalpies= | -1052.521218 |
| Sum of electronic and thermal Free Energies= | -1052.607659 |

**Table S33.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *max1-(S/S)*.

| | | | |
|---|---|---|---|
| N | -1.94976900 | -0.15518100 | 0.04243200 |
| C | -0.74268800 | 0.39716700 | -0.70271800 |
| C | -0.83553600 | 1.92300500 | -0.34007600 |
| C | -3.09309600 | -0.78770100 | -0.72683500 |
| C | -2.20549600 | 0.62869600 | 1.29260800 |
| C | -1.25101500 | 1.83025800 | 1.13912700 |
| H | -1.71527200 | 2.76227200 | 1.47094600 |
| H | -0.35403800 | 1.69670600 | 1.74122200 |
| C | -4.30631300 | 0.09701000 | -1.16112400 |
| H | -4.90646500 | 0.47507200 | -0.34195800 |
| H | -4.96304600 | -0.53287700 | -1.76748800 |
| H | -4.00395700 | 0.92691000 | -1.79596300 |
| C | -1.86788800 | -0.20839000 | 2.54055500 |
| H | -2.56440400 | -1.04211600 | 2.65020000 |
| H | -1.92717300 | 0.40434900 | 3.44607400 |
| H | -0.86534800 | -0.61706500 | 2.47890200 |
| C | 0.36778600 | 2.86420500 | -0.38724800 |
| H | 1.22828700 | 2.40965800 | 0.07944200 |
| H | 0.10644000 | 3.76864800 | 0.17198700 |
| H | 0.61295500 | 3.19091100 | -1.39799700 |
| C | -2.62567700 | -1.36410700 | -2.08622500 |
| H | -2.56844100 | -0.57977900 | -2.84485900 |
| H | -3.37159100 | -2.08451200 | -2.42950000 |
| H | -1.67194900 | -1.87016600 | -2.05235100 |
| C | -3.70001000 | -1.92386000 | 0.12936900 |
| H | -2.98387900 | -2.71236700 | 0.34886500 |
| H | -4.54509500 | -2.37567100 | -0.39702300 |
| H | -4.07483300 | -1.54271800 | 1.07875200 |

| | | | |
|---|---|---|---|
| C | -3.62150000 | 1.19514300 | 1.54002900 |
| H | -3.93515000 | 1.90875900 | 0.78102400 |
| H | -3.58672200 | 1.73141300 | 2.49159400 |
| H | -4.38280700 | 0.42217600 | 1.63928600 |
| C | -1.92507400 | 2.59843000 | -1.18977100 |
| H | -1.66064000 | 2.55878700 | -2.25088800 |
| H | -2.01096800 | 3.65207200 | -0.90753700 |
| H | -2.89925400 | 2.14538000 | -1.06510500 |
| N | 1.94972500 | 0.15518900 | 0.04258100 |
| C | 0.74250000 | -0.39686800 | -0.70269300 |
| C | 0.83531600 | -1.92287700 | -0.34077800 |
| C | 3.09281800 | 0.78830800 | -0.72664900 |
| C | 2.20603100 | -0.62950600 | 1.29214100 |
| C | 1.25183200 | -1.83119800 | 1.13821600 |
| H | 1.71660300 | -2.76337700 | 1.46884000 |
| H | 0.35529400 | -1.69853100 | 1.74115000 |
| C | 3.69955000 | 1.92432400 | 0.12987500 |
| H | 2.98326300 | 2.71252300 | 0.34994900 |
| H | 4.54439200 | 2.37661100 | -0.39651000 |
| H | 4.07470900 | 1.54282200 | 1.07898800 |
| C | 1.86876000 | 0.20657300 | 2.54087900 |
| H | 0.86587300 | 0.61458300 | 2.48038500 |
| H | 2.56479500 | 1.04069900 | 2.65049900 |
| H | 1.92920400 | -0.40673900 | 3.44593400 |
| C | -0.36820300 | -2.86388000 | -0.38750500 |
| H | -0.10663200 | -3.76854300 | 0.17127000 |
| H | -0.61408900 | -3.19027000 | -1.39817400 |
| H | -1.22836100 | -2.40931000 | 0.07983900 |
| C | 4.30634900 | -0.09582300 | -1.16124900 |
| H | 4.90741900 | -0.47275500 | -0.34223500 |
| H | 4.96215300 | 0.53412100 | -1.76856200 |
| H | 4.00421900 | -0.92645200 | -1.79523400 |
| C | 2.62512100 | 1.36486400 | -2.08587200 |
| H | 2.56817600 | 0.58066600 | -2.84466800 |
| H | 3.37077500 | 2.08561300 | -2.42899300 |
| H | 1.67121900 | 1.87057400 | -2.05191700 |
| C | 3.62225200 | -1.19581400 | 1.53861400 |
| H | 3.93586300 | -1.90853300 | 0.77876000 |
| H | 3.58787100 | -1.73306500 | 2.48963600 |
| H | 4.38336000 | -0.42272500 | 1.63847500 |
| C | 1.92417800 | -2.59795000 | -1.19164400 |
| H | 1.65884800 | -2.55789200 | -2.25252000 |
| H | 2.01042500 | -3.65169400 | -0.90989800 |
| H | 2.89841300 | -2.14481100 | -1.06759500 |
| H | 1.05624900 | -0.08731400 | -1.69307300 |
| H | -1.05637600 | 0.08785300 | -1.69320500 |

| | |
|---|---|
| Zero-point correction= | 0.689024 (Hartree/Particle) |
| Thermal correction to Energy= | 0.718212 |
| Thermal correction to Enthalpy= | 0.719156 |
| Thermal correction to Gibbs Free Energy= | 0.637201 |
| Sum of electronic and zero-point Energies= | -1052.598194 |
| Sum of electronic and thermal Energies= | -1052.569006 |
| Sum of electronic and thermal Enthalpies= | -1052.568062 |
| Sum of electronic and thermal Free Energies= | -1052.650017 |

**Table S34.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *max2-(S/S)*.

| | | | |
|---|---|---|---|
| N | 1.63340300 | -0.42530900 | -0.10693300 |
| C | 0.68398400 | 0.59309600 | 0.44426900 |
| C | 1.64821300 | 1.82885700 | 0.60785800 |
| C | 2.00791200 | -1.68791200 | 0.62531600 |
| C | 2.51879900 | 0.26704900 | -1.10152100 |
| C | 2.37801500 | 1.77919900 | -0.73853800 |
| H | 3.35062600 | 2.27705900 | -0.70209200 |
| H | 1.78286400 | 2.29553100 | -1.49670200 |
| C | 1.88345300 | -2.89675300 | -0.33029900 |
| H | 0.85772400 | -3.08415100 | -0.62775400 |
| H | 2.26292400 | -3.80166100 | 0.15273200 |
| H | 2.47372200 | -2.73333600 | -1.23429900 |
| C | 2.03403900 | 0.01913000 | -2.54759600 |

| | | | |
|---|---|---|---|
| H | 2.08166600 | -1.04302300 | -2.79651400 |
| H | 2.66523100 | 0.56337400 | -3.25751700 |
| H | 1.00878200 | 0.35461600 | -2.69801400 |
| C | 1.13371200 | 3.23447100 | 0.96761500 |
| H | 0.93993500 | 3.85132500 | 0.09952900 |
| H | 1.89585400 | 3.75438900 | 1.55218100 |
| H | 0.23476500 | 3.19717100 | 1.58615300 |
| C | 3.44023100 | -1.84016800 | 1.23774200 |
| H | 4.21130800 | -2.00701600 | 0.49164200 |
| H | 3.41836200 | -2.73077200 | 1.87075600 |
| H | 3.74796400 | -1.01614400 | 1.87681900 |
| C | 1.06461000 | -1.87789900 | 1.82449300 |
| H | 1.34274000 | -1.21570900 | 2.64831200 |
| H | 1.14901500 | -2.90511800 | 2.18657100 |
| H | 0.03047000 | -1.68442900 | 1.56552800 |
| C | 4.01125900 | -0.10095900 | -1.08429100 |
| H | 4.48482000 | 0.10682800 | -0.12683900 |
| H | 4.50999700 | 0.51293000 | -1.83808600 |
| H | 4.18680800 | -1.14307400 | -1.35288400 |
| C | 2.61202600 | 1.49590700 | 1.76661600 |
| H | 2.08232600 | 1.54038900 | 2.72365800 |
| H | 3.41956000 | 2.23249600 | 1.79979900 |
| H | 3.05702200 | 0.51879500 | 1.67187900 |
| N | -1.63360000 | -0.42537300 | 0.10617100 |
| C | -0.68454100 | 0.59312500 | -0.44505200 |
| C | -1.64869200 | 1.82900000 | -0.60734000 |
| C | -2.00729200 | -1.68833300 | -0.62555700 |
| C | -2.51888300 | 0.26639200 | 1.10123400 |
| C | -2.37689600 | 1.77888200 | 0.73992500 |
| H | -3.34900400 | 2.27785500 | 0.70530500 |
| H | -1.78022800 | 2.29362900 | 1.49797400 |
| C | -1.06158900 | -1.87961400 | -1.82262500 |
| H | -1.33873100 | -1.21863200 | -2.64776500 |
| H | -1.14469500 | -2.90733700 | -2.18356900 |
| H | -0.02810500 | -1.68497900 | -1.56203000 |
| C | -2.03495600 | 0.01661100 | 2.54723200 |
| H | -1.00935600 | 0.35077900 | 2.69823300 |
| H | -2.08386400 | -1.04571300 | 2.79517300 |
| H | -2.66578900 | 0.56090000 | 3.25744300 |
| C | -1.13362700 | 3.23421200 | -0.96774400 |
| H | -1.89551500 | 3.75438100 | -1.55239400 |
| H | -0.23476300 | 3.19617800 | -1.58637200 |
| H | -0.93928300 | 3.85131400 | -0.09997300 |
| C | -1.88561300 | -2.89577600 | 0.33206500 |
| H | -0.86104800 | -3.08066700 | 0.63510900 |
| H | -2.26093300 | -3.80203200 | -0.15168300 |
| H | -2.48085800 | -2.73233200 | 1.23280600 |
| C | -3.43807300 | -1.84043100 | -1.24149900 |
| H | -4.21224600 | -2.00127800 | -0.49734600 |
| H | -3.41628600 | -2.73443300 | -1.86973600 |
| H | -3.74103500 | -1.01904500 | -1.88628500 |
| C | -4.01155100 | -0.10077200 | 1.08269600 |
| H | -4.48428700 | 0.10822600 | 0.12510300 |
| H | -4.51058600 | 0.51251600 | 1.83679000 |
| H | -4.18770700 | -1.14311100 | 1.35004200 |
| C | -2.61451000 | 1.49653400 | -1.76456800 |
| H | -2.08589600 | 1.53829600 | -2.72233900 |
| H | -3.42034700 | 2.23496400 | -1.79786200 |
| H | -3.06178400 | 0.52068200 | -1.66765500 |
| H | -0.37523000 | 0.27078200 | -1.42675900 |
| H | 0.37428700 | 0.27027400 | 1.42569100 |

Zero-point correction= 0.689053 (Hartree/Particle)
Thermal correction to Energy= 0.718226
Thermal correction to Enthalpy= 0.719170
Thermal correction to Gibbs Free Energy= 0.636160
Sum of electronic and zero-point Energies= -1052.620325
Sum of electronic and thermal Energies= -1052.591152
Sum of electronic and thermal Enthalpies= -1052.590208
Sum of electronic and thermal Free Energies= -1052.673218

**Table S35.** Cartesian coordinates and energy values of $\mathbf{3}^{\mathbf{tBu\text{-}Me_2}}$ for *max1-(R/S)*.

| | | | |
|---|---|---|---|
| N | 1.54604300 | -0.53044300 | 0.04573700 |
| C | 0.84122800 | 0.37950500 | -0.86446000 |
| H | 0.97438100 | 0.41643900 | -1.95079400 |
| C | 1.89294600 | 1.62164100 | -0.87980100 |
| C | 1.85339300 | -1.95158700 | -0.29618500 |
| C | 2.42614400 | 0.23078700 | 1.03395400 |
| C | 2.30970700 | 1.70633300 | 0.57704700 |
| H | 1.55347000 | 2.21613700 | 1.17260400 |
| H | 3.25174000 | 2.24197300 | 0.72384200 |
| C | 1.87218300 | -2.82444500 | 0.97463900 |
| H | 0.91698900 | -2.76412800 | 1.49582300 |
| H | 2.66094500 | -2.54773200 | 1.67180400 |
| H | 2.04119900 | -3.86708200 | 0.69330800 |
| C | 3.92659700 | -0.15985800 | 1.09540400 |
| H | 4.07840200 | -1.18239100 | 1.43718000 |
| H | 4.39944300 | 0.49248200 | 1.83315000 |
| H | 4.46228200 | -0.02436800 | 0.16136100 |
| C | 3.10479200 | 1.15630000 | -1.73028000 |
| H | 3.51245000 | 0.20290100 | -1.43088000 |
| H | 3.89902000 | 1.90615700 | -1.66616000 |
| H | 2.81614500 | 1.07444700 | -2.78253900 |
| C | 0.73110200 | -2.47766500 | -1.17691200 |
| H | 0.80323300 | -3.56241100 | -1.28184500 |
| H | 0.79065600 | -2.04109000 | -2.17450600 |
| H | -0.21393500 | -2.21502500 | -0.72452500 |
| C | 3.15704500 | -2.21461300 | -1.09698900 |
| H | 3.15070100 | -1.66892400 | -2.04130300 |
| H | 3.19778400 | -3.27962800 | -1.34308800 |
| H | 4.06931700 | -1.97478600 | -0.55871300 |
| C | 1.93904300 | 0.12343100 | 2.49258400 |
| H | 0.91957200 | 0.47068000 | 2.60569400 |
| H | 2.57472500 | 0.75017400 | 3.12532600 |
| H | 1.99308000 | -0.89551000 | 2.87515600 |
| C | 1.44102500 | 2.91460500 | -1.60230000 |
| H | 2.06440800 | 3.09126600 | -2.47997800 |
| H | 1.52915000 | 3.80085000 | -0.97793400 |
| H | 0.41537900 | 2.85256300 | -1.95935300 |
| N | -1.63669000 | -0.35997100 | -0.03631900 |
| C | -0.78824000 | 0.75525000 | -0.73080400 |
| C | -1.38937000 | 2.01440000 | 0.01840800 |
| C | -2.58644100 | -1.22115500 | -0.84324100 |
| C | -1.95359800 | -0.00334200 | 1.37602500 |
| C | -1.44709500 | 1.44752700 | 1.45404400 |
| H | -2.08003200 | 2.06545900 | 2.09560000 |
| H | -0.44159700 | 1.49080000 | 1.87085800 |
| C | -4.06650200 | -0.75558400 | -1.04042500 |
| H | -4.61315800 | -0.58468800 | -0.12100500 |
| H | -4.59077500 | -1.54943600 | -1.57965600 |
| H | -4.13351000 | 0.13566800 | -1.66300800 |
| C | -1.21091700 | -0.95275500 | 2.33196300 |
| H | -1.72381900 | -1.91510300 | 2.39130100 |
| H | -1.15729200 | -0.54185700 | 3.34594000 |
| H | -0.20962500 | -1.12437200 | 1.95791400 |
| C | -0.75385700 | 3.41028000 | 0.16118300 |
| H | 0.25478300 | 3.40254700 | 0.55511000 |
| H | -1.36999800 | 3.95224700 | 0.88472400 |
| H | -0.77273800 | 3.98885400 | -0.76012700 |
| C | -2.11875200 | -1.40563600 | -2.31044000 |
| H | -2.33660100 | -0.51913300 | -2.91131800 |
| H | -2.69184400 | -2.22577100 | -2.74808000 |
| H | -1.07015300 | -1.64239700 | -2.42235400 |
| C | -2.67229300 | -2.61233800 | -0.16991900 |
| H | -1.69183600 | -3.05179900 | -0.00329400 |
| H | -3.25183700 | -3.29485400 | -0.79715000 |
| H | -3.17585700 | -2.55549600 | 0.79445600 |
| C | -3.42768300 | 0.01257000 | 1.84801000 |
| H | -4.03859000 | 0.74987300 | 1.33081200 |
| H | -3.41610600 | 0.28822100 | 2.90604100 |
| H | -3.91151200 | -0.96073100 | 1.78244800 |

| | | | |
|---|---|---|---|
| C | -2.78548300 | 2.31257900 | -0.55750400 |
| H | -2.69357500 | 2.68394200 | -1.58275100 |
| H | -3.27660300 | 3.09103900 | 0.03345400 |
| H | -3.43113600 | 1.44904700 | -0.56865700 |
| H | -1.17245300 | 0.37045900 | -1.66482700 |

Zero-point correction= 0.689106 (Hartree/Particle)
Thermal correction to Energy= 0.718798
Thermal correction to Enthalpy= 0.719742
Thermal correction to Gibbs Free Energy= 0.636394
Sum of electronic and zero-point Energies= -1052.560708
Sum of electronic and thermal Energies= -1052.531017
Sum of electronic and thermal Enthalpies= -1052.530073
Sum of electronic and thermal Free Energies= -1052.613421

**Table S36.** Cartesian coordinates and energy values of **3**$^{tBu\text{-}Me_2}$ for *max2-(R/S)*.

| | | | |
|---|---|---|---|
| N | 2.09285600 | 0.01611900 | 0.12262000 |
| C | 0.71549500 | -0.05939400 | 0.69720100 |
| H | 0.52533900 | 0.35527600 | 1.69395900 |
| C | 0.78573500 | -1.57104400 | 1.20251300 |
| C | 2.83063100 | 1.27120200 | -0.13348800 |
| C | 2.48342600 | -1.27178400 | -0.53621300 |
| C | 1.47405600 | -2.28266200 | 0.04822300 |
| H | 0.75737300 | -2.57653900 | -0.70859400 |
| H | 1.97023600 | -3.19571300 | 0.38379500 |
| C | 4.33332500 | 1.08179700 | -0.44451200 |
| H | 4.51727900 | 0.57951900 | -1.39231700 |
| H | 4.85782100 | 0.55764000 | 0.35222100 |
| H | 4.76703000 | 2.08229000 | -0.52444900 |
| C | 3.89875600 | -1.80090400 | -0.18136400 |
| H | 4.70166000 | -1.31278800 | -0.72449100 |
| H | 3.93854000 | -2.86023700 | -0.44702600 |
| H | 4.09861500 | -1.71865100 | 0.88707800 |
| C | 1.71748400 | -1.55634800 | 2.44254800 |
| H | 2.63630300 | -1.00529100 | 2.25855700 |
| H | 1.97112000 | -2.58038500 | 2.73203400 |
| H | 1.20700800 | -1.09180500 | 3.29179800 |
| C | 2.28577700 | 2.02358500 | -1.38016400 |
| H | 2.59896200 | 3.07187400 | -1.38916800 |
| H | 1.20685000 | 1.97765000 | -1.45585000 |
| H | 2.68391600 | 1.55891500 | -2.28371000 |
| C | 2.85452600 | 2.08435800 | 1.18272800 |
| H | 1.93471800 | 2.00296400 | 1.74482600 |
| H | 3.05936800 | 3.14189900 | 0.99991100 |
| H | 3.64748300 | 1.68963900 | 1.82166600 |
| C | 2.36878300 | -1.23560200 | -2.07487200 |
| H | 1.40117400 | -0.84322700 | -2.38925100 |
| H | 2.47816500 | -2.24543600 | -2.48267200 |
| H | 3.14289400 | -0.61430400 | -2.52799300 |
| C | -0.47427000 | -2.29901000 | 1.67181400 |
| H | -0.20968000 | -3.34025800 | 1.88862700 |
| H | -1.27982100 | -2.27564900 | 0.95636500 |
| H | -0.85152400 | -1.86739200 | 2.60008200 |
| N | -1.87320000 | -0.23790900 | -0.00853800 |
| C | -0.51688300 | 0.45266100 | -0.22787400 |
| C | -0.92405900 | 1.97562900 | -0.01330800 |
| C | -2.45055000 | -1.11755900 | -1.08312000 |
| C | -2.79557200 | 0.58083400 | 0.83683300 |
| C | -1.93747700 | 1.80450300 | 1.13330100 |
| H | -2.53607100 | 2.70621800 | 1.27855400 |
| H | -1.37471200 | 1.64673600 | 2.05871700 |
| C | -3.55912700 | -2.02005200 | -0.49374200 |
| H | -3.17778900 | -2.60980000 | 0.34035400 |
| H | -3.89797800 | -2.71403200 | -1.26676600 |
| H | -4.43175600 | -1.47480700 | -0.14727600 |
| C | -3.15687800 | -0.13049400 | 2.15583400 |
| H | -3.76313500 | -1.02177700 | 1.99253100 |
| H | -3.72402700 | 0.54617300 | 2.80294600 |
| H | -2.25379900 | -0.42651100 | 2.68620900 |
| C | 0.00341700 | 3.08454800 | 0.52124700 |

| | | | |
|---|---|---|---|
| H | 0.37490700 | 2.86532000 | 1.51669000 |
| H | -0.61806700 | 3.98031200 | 0.61739500 |
| H | 0.83436200 | 3.34962100 | -0.11830700 |
| C | -3.01229300 | -0.37626200 | -2.32664600 |
| H | -3.78780300 | 0.34477000 | -2.08881500 |
| H | -3.44571400 | -1.10632900 | -3.01572900 |
| H | -2.21212200 | 0.13569200 | -2.86507300 |
| C | -1.42370900 | -2.10848000 | -1.66401100 |
| H | -0.55378900 | -1.61838900 | -2.09670500 |
| H | -1.90552800 | -2.66446400 | -2.47085500 |
| H | -1.09255400 | -2.83213900 | -0.92605800 |
| C | -4.12071300 | 1.10369800 | 0.21833100 |
| H | -3.95456900 | 1.77419600 | -0.62129000 |
| H | -4.63187300 | 1.68142800 | 0.99256800 |
| H | -4.80799900 | 0.32236200 | -0.09602900 |
| C | -1.53933600 | 2.53828200 | -1.30555300 |
| H | -0.74860900 | 2.76402500 | -2.02697000 |
| H | -2.07001900 | 3.47261000 | -1.09975500 |
| H | -2.23096700 | 1.85534200 | -1.78132100 |
| H | -0.33208000 | 0.05696500 | -1.22320900 |

Zero-point correction= 0.688984 (Hartree/Particle)
Thermal correction to Energy= 0.718736
Thermal correction to Enthalpy= 0.719680
Thermal correction to Gibbs Free Energy= 0.636244
Sum of electronic and zero-point Energies= -1052.616805
Sum of electronic and thermal Energies= -1052.587052
Sum of electronic and thermal Enthalpies= -1052.586108
Sum of electronic and thermal Free Energies= -1052.669544

**Table S37.** Cartesian coordinates and energy values of radical-cation state of **3**$^{iPr\text{-}Me_2}$ for *anti-(R/R)*.

| | | | |
|---|---|---|---|
| N | 1.89829400 | 0.15922900 | 0.27881300 |
| C | 0.66190000 | -0.53293800 | 0.22489800 |
| H | 0.45667200 | -0.97816100 | 1.20286900 |
| C | 0.82023500 | -1.67499800 | -0.81740400 |
| C | 2.93741700 | -0.36927300 | -0.66386100 |
| C | 2.09393500 | -1.27058600 | -1.58203800 |
| H | 1.82232800 | -0.71442000 | -2.48076200 |
| H | 2.66305300 | -2.14209300 | -1.90780400 |
| C | 4.00437300 | -1.17301500 | 0.10958300 |
| H | 4.61507300 | -0.52464100 | 0.73769500 |
| H | 4.66933900 | -1.65004000 | -0.61317000 |
| H | 3.56986200 | -1.95050700 | 0.73495000 |
| C | 1.01611200 | -2.99341300 | -0.03924100 |
| H | 1.80165600 | -2.92298200 | 0.71343700 |
| H | 1.27964200 | -3.80129900 | -0.72518700 |
| H | 0.09159600 | -3.27972300 | 0.46952200 |
| C | 3.66138500 | 0.69427700 | -1.50657800 |
| H | 2.96398000 | 1.36157500 | -2.00740800 |
| H | 4.23247500 | 0.17195400 | -2.27757800 |
| H | 4.36639400 | 1.28605200 | -0.92813000 |
| C | -0.33799400 | -1.88102700 | -1.79089200 |
| H | -1.23543300 | -2.21582700 | -1.27423600 |
| H | -0.06475400 | -2.65388500 | -2.51351400 |
| H | -0.57220000 | -0.97607500 | -2.34947300 |
| N | -1.89816200 | -0.15962600 | 0.27852700 |
| C | -0.66185700 | 0.53276500 | 0.22506000 |
| H | -0.45665200 | 0.97748500 | 1.20329500 |
| C | -0.82032800 | 1.67559200 | -0.81634000 |
| C | -2.93743500 | 0.36981700 | -0.66340200 |
| C | -2.09400400 | 1.27155500 | -1.58120500 |
| H | -1.82246100 | 0.71586200 | -2.48021900 |
| H | -2.66313800 | 2.14323900 | -1.90646100 |
| C | -4.00385000 | 1.17334100 | 0.11098600 |
| H | -4.61447600 | 0.52476000 | 0.73895500 |
| H | -4.66897300 | 1.65105300 | -0.61117100 |
| H | -3.56878800 | 1.95026500 | 0.73667300 |
| C | -1.01648800 | 2.99347800 | -0.03734000 |
| H | -1.80232200 | 2.92255300 | 0.71498800 |
| H | -1.27979600 | 3.80178400 | -0.72288100 |

| | | | |
|---|---|---|---|
| H | -0.09217400 | 3.27951800 | 0.47192600 |
| C | -3.66195400 | -0.69305900 | -1.50650600 |
| H | -2.96501900 | -1.36071000 | -2.00758800 |
| H | -4.23277400 | -0.17022700 | -2.27736200 |
| H | -4.36726300 | -1.28458900 | -0.92818400 |
| C | 0.33789500 | 1.88253700 | -1.78964600 |
| H | 1.23505700 | 2.21807900 | -1.27290300 |
| H | 0.06416800 | 2.65517600 | -2.51231900 |
| H | 0.57286500 | 0.97775500 | -2.34816400 |
| C | -2.16592900 | -0.97352600 | 1.47746300 |
| C | -3.22506500 | -2.05732800 | 1.29281200 |
| C | -2.45017200 | -0.11882400 | 2.72858200 |
| H | -1.22369800 | -1.49781800 | 1.66789700 |
| H | -3.02194700 | -2.67962200 | 0.42132400 |
| H | -3.21241200 | -2.70061500 | 2.17456700 |
| H | -4.23108200 | -1.64713900 | 1.20697800 |
| H | -1.70251200 | 0.66443500 | 2.86686900 |
| H | -3.43255700 | 0.34891500 | 2.67760300 |
| H | -2.42616500 | -0.76011000 | 3.61184700 |
| C | 2.16609100 | 0.97212100 | 1.47841100 |
| C | 3.22463400 | 2.05657400 | 1.29436200 |
| C | 2.45106100 | 0.11639400 | 2.72866500 |
| H | 1.22364100 | 1.49576400 | 1.66960600 |
| H | 3.02083800 | 2.67957300 | 0.42353600 |
| H | 3.21204200 | 2.69906100 | 2.17670400 |
| H | 4.23081800 | 1.64695700 | 1.20774400 |
| H | 1.70371300 | -0.66725200 | 2.86647200 |
| H | 3.43358700 | -0.35096400 | 2.67696200 |
| H | 2.42709400 | 0.75688700 | 3.61250700 |

| | |
|---|---|
| Zero-point correction= | 0.632007 (Hartree/Particle) |
| Thermal correction to Energy= | 0.660438 |
| Thermal correction to Enthalpy= | 0.661382 |
| Thermal correction to Gibbs Free Energy= | 0.578066 |
| Sum of electronic and zero-point Energies= | -973.861794 |
| Sum of electronic and thermal Energies= | -973.833364 |
| Sum of electronic and thermal Enthalpies= | -973.832420 |
| Sum of electronic and thermal Free Energies= | -973.915736 |

**Table S38.** Cartesian coordinates and energy values of radical-cation state of **3**$^{iPr\text{-}Me_2}$ for *gauche-(R/R)*.

| | | | |
|---|---|---|---|
| N | -1.45096600 | -0.47777800 | 0.26802500 |
| C | -0.77915500 | 0.77520600 | 0.30035600 |
| H | -0.60264700 | 1.05817800 | 1.33626000 |
| C | -1.73127300 | 1.79240900 | -0.41320500 |
| C | -2.70627200 | -0.49784500 | -0.54256200 |
| C | -2.61870800 | 0.85788200 | -1.25735700 |
| H | -2.15158800 | 0.71222500 | -2.23530200 |
| H | -3.60691700 | 1.28380100 | -1.43487500 |
| C | -3.95427300 | -0.59992600 | 0.35677600 |
| H | -4.00909100 | -1.56212000 | 0.86479500 |
| H | -4.84315400 | -0.51037200 | -0.27095700 |
| H | -3.99057300 | 0.18807100 | 1.10573700 |
| C | -2.52824000 | 2.53816800 | 0.67493700 |
| H | -2.93991700 | 1.86366500 | 1.42565400 |
| H | -3.35666200 | 3.09174100 | 0.22757600 |
| H | -1.89033900 | 3.25631000 | 1.19413000 |
| C | -2.75861700 | -1.62583300 | -1.58697300 |
| H | -1.85316900 | -1.64643700 | -2.19587300 |
| H | -3.60062900 | -1.43255100 | -2.25541900 |
| H | -2.91175200 | -2.60757400 | -1.14506200 |
| C | -1.11421900 | 2.83895500 | -1.35213900 |
| H | -1.92705000 | 3.42052500 | -1.79361200 |
| H | -0.56337800 | 2.39261400 | -2.18217500 |
| H | -0.46047200 | 3.54313200 | -0.84161100 |
| N | 1.45095100 | -0.47782000 | -0.26800500 |
| C | 0.77917400 | 0.77518100 | -0.30034100 |
| H | 0.60266800 | 1.05814700 | -1.33624500 |
| C | 1.73132800 | 1.79236600 | 0.41320100 |
| C | 2.70628900 | -0.49789600 | 0.54253400 |
| C | 2.61874200 | 0.85782000 | 1.25735300 |

| | | | |
|---|---|---|---|
| H | 2.15161800 | 0.71215900 | 2.23529500 |
| H | 3.60695700 | 1.28372300 | 1.43487500 |
| C | 3.95425700 | -0.59994100 | -0.35685200 |
| H | 4.00906800 | -1.56211800 | -0.86490200 |
| H | 4.84316000 | -0.51039400 | 0.27085100 |
| H | 3.99052000 | 0.18808100 | -1.10579100 |
| C | 2.52831400 | 2.53807900 | -0.67495700 |
| H | 2.93998600 | 1.86354600 | -1.42564900 |
| H | 3.35674200 | 3.09165300 | -0.22760600 |
| H | 1.89042900 | 3.25621700 | -1.19417700 |
| C | 2.75868800 | -1.62589800 | 1.58692700 |
| H | 1.85327300 | -1.64651200 | 2.19587600 |
| H | 3.60073500 | -1.43262600 | 2.25533200 |
| H | 2.91180000 | -2.60763300 | 1.14499500 |
| C | 1.11431700 | 2.83894500 | 1.35212700 |
| H | 0.46058500 | 3.54313300 | 0.84159600 |
| H | 1.92717100 | 3.42049700 | 1.79358100 |
| H | 0.56347300 | 2.39263300 | 2.18217700 |
| C | 1.06665600 | -1.44518400 | -1.30074100 |
| C | 1.46243000 | -2.89283800 | -1.01991200 |
| C | 1.52690900 | -1.02485900 | -2.71133000 |
| H | -0.02980800 | -1.39750300 | -1.29107000 |
| H | 1.14099100 | -3.22688300 | -0.03583500 |
| H | 0.97848800 | -3.52890000 | -1.76357100 |
| H | 2.53636300 | -3.05517700 | -1.11023600 |
| H | 1.23982200 | -0.00064900 | -2.95261500 |
| H | 2.60911300 | -1.11177000 | -2.81096400 |
| H | 1.06516500 | -1.68211600 | -3.45080100 |
| C | -1.06673800 | -1.44513300 | 1.30079300 |
| C | -1.46259100 | -2.89277100 | 1.01999400 |
| C | -1.52699300 | -1.02474500 | 2.71136300 |
| H | 0.02972800 | -1.39751000 | 1.29113800 |
| H | -1.14116200 | -3.22685700 | 0.03592800 |
| H | -0.97869500 | -3.52884300 | 1.76367400 |
| H | -2.53653500 | -3.05504400 | 1.11031000 |
| H | -1.23985800 | -0.00054200 | 2.95262200 |
| H | -2.60920300 | -1.11159900 | 2.81098200 |
| H | -1.06529300 | -1.68200400 | 3.45086000 |

Zero-point correction= 0.631895 (Hartree/Particle)
Thermal correction to Energy= 0.660228
Thermal correction to Enthalpy= 0.661172
Thermal correction to Gibbs Free Energy= 0.578414
Sum of electronic and zero-point Energies= -973.873501
Sum of electronic and thermal Energies= -973.845168
Sum of electronic and thermal Enthalpies= -973.844224
Sum of electronic and thermal Free Energies= -973.926981

**Table S39.** Cartesian coordinates and energy values of radical-cation state of **3**$^{iPr\text{-}Me_2}$ for *anti-(S/S)*.

| | | | |
|---|---|---|---|
| N | -1.89877100 | 0.15969600 | 0.27855100 |
| C | -0.66322400 | -0.53328600 | 0.22472700 |
| C | -0.82222100 | -1.67564200 | -0.81694200 |
| C | -2.93836200 | -0.36846100 | -0.66398200 |
| C | -2.09516600 | -1.27003500 | -1.58216500 |
| H | -2.66476000 | -2.14096200 | -1.90863200 |
| H | -1.82257500 | -0.71359100 | -2.48040900 |
| C | -3.66222700 | 0.69525100 | -1.50651200 |
| H | -4.36678200 | 1.28726800 | -0.92776400 |
| H | -4.23386100 | 0.17305400 | -2.27720200 |
| H | -2.96502400 | 1.36241800 | -2.00783400 |
| C | 0.33627600 | -1.88358400 | -1.78967500 |
| H | 0.57166100 | -0.97935200 | -2.34889300 |
| H | 0.06274700 | -2.65683400 | -2.51177100 |
| H | 1.23311300 | -2.21873800 | -1.27219700 |
| C | -4.00543100 | -1.17173400 | 0.10975700 |
| H | -3.57102400 | -1.94861100 | 0.73592000 |
| H | -4.67012900 | -1.64943200 | -0.61279400 |
| H | -4.61641400 | -0.52294200 | 0.73716900 |
| C | -1.01987200 | -2.99349400 | -0.03819700 |
| H | -0.09573600 | -3.28082300 | 0.47066900 |

| | | | |
|---|---|---|---|
| H | -1.28441000 | -3.80128600 | -0.72387400 |
| H | -1.80532100 | -2.92183700 | 0.71443600 |
| N | 1.89877000 | -0.15972900 | 0.27855400 |
| C | 0.66322300 | 0.53325600 | 0.22479100 |
| C | 0.82222700 | 1.67572500 | -0.81675200 |
| C | 2.93837100 | 0.36853200 | -0.66391000 |
| C | 2.09518500 | 1.27021000 | -1.58200100 |
| H | 2.66478100 | 2.14117600 | -1.90836000 |
| H | 1.82261000 | 0.71386900 | -2.48031400 |
| C | 3.66224500 | -0.69508400 | -1.50655300 |
| H | 2.96504900 | -1.36219600 | -2.00795700 |
| H | 4.36679600 | -1.28716500 | -0.92786600 |
| H | 4.23388500 | -0.17280000 | -2.27718000 |
| C | -0.33626100 | 1.88376200 | -1.78947700 |
| H | -0.06273200 | 2.65709400 | -2.51148400 |
| H | -1.23310700 | 2.21884900 | -1.27197200 |
| H | -0.57163000 | 0.97958900 | -2.34879600 |
| C | 4.00543400 | 1.17171700 | 0.10993000 |
| H | 3.57102200 | 1.94852000 | 0.73618100 |
| H | 4.67013600 | 1.64950000 | -0.61256200 |
| H | 4.61641500 | 0.52285200 | 0.73726900 |
| C | 1.01985500 | 2.99349500 | -0.03786300 |
| H | 0.09570900 | 3.28076400 | 0.47101700 |
| H | 1.28440000 | 3.80136200 | -0.72345000 |
| H | 1.80529200 | 2.92176300 | 0.71477600 |
| H | 0.45700200 | 0.97742400 | 1.20299300 |
| H | -0.45701400 | -0.97755900 | 1.20288200 |
| C | 2.16610000 | -0.97318800 | 1.47798900 |
| C | 2.45135700 | -0.11805200 | 2.72856100 |
| C | 3.22429900 | -2.05797300 | 1.29374900 |
| H | 1.22344400 | -1.49653800 | 1.66884800 |
| H | 1.70464500 | 0.66620400 | 2.86633000 |
| H | 2.42657500 | -0.75874800 | 3.61223500 |
| H | 3.43430400 | 0.34847400 | 2.67733500 |
| H | 3.02054500 | -2.68064600 | 0.42267900 |
| H | 4.23062200 | -1.64862800 | 1.20746300 |
| H | 3.21134200 | -2.70072300 | 2.17589300 |
| C | -2.16611100 | 0.97303400 | 1.47806500 |
| C | -2.45138300 | 0.11777300 | 2.72854900 |
| C | -3.22430900 | 2.05783700 | 1.29392200 |
| H | -1.22345800 | 1.49636500 | 1.66898600 |
| H | -1.70467100 | -0.66649500 | 2.86625000 |
| H | -2.42661500 | 0.75838100 | 3.61228600 |
| H | -3.43432800 | -0.34875000 | 2.67726300 |
| H | -3.02054400 | 2.68059800 | 0.42291800 |
| H | -4.23063100 | 1.64850100 | 1.20758200 |
| H | -3.21136200 | 2.70049800 | 2.17613100 |

Zero-point correction= 0.631977 (Hartree/Particle)
Thermal correction to Energy= 0.660420
Thermal correction to Enthalpy= 0.661365
Thermal correction to Gibbs Free Energy= 0.578009
Sum of electronic and zero-point Energies= -973.861826
Sum of electronic and thermal Energies= -973.833383
Sum of electronic and thermal Enthalpies= -973.832438
Sum of electronic and thermal Free Energies= -973.915794

**Table S40.** Cartesian coordinates and energy values of radical-cation state of **3**$^{iPr\text{-}Me_2}$ for *gauche-(S/S)*.

| | | | |
|---|---|---|---|
| N | 1.45095100 | -0.47778900 | 0.26801200 |
| C | 0.77916400 | 0.77520700 | 0.30034900 |
| C | 1.73130500 | 1.79239600 | -0.41320600 |
| C | 2.70629500 | -0.49785700 | -0.54251200 |
| C | 2.61874100 | 0.85785300 | -1.25733900 |
| H | 3.60695300 | 1.28376600 | -1.43485400 |
| H | 2.15162900 | 0.71218100 | -2.23528500 |
| C | 2.75870300 | -1.62587500 | -1.58688900 |
| H | 2.91176800 | -2.60760800 | -1.14493400 |
| H | 3.60078000 | -1.43263700 | -2.25526500 |
| H | 1.85330900 | -1.64647300 | -2.19586900 |
| C | 1.11428200 | 2.83895000 | -1.35215200 |

| | | | |
|---|---|---|---|
| H | 0.56343800 | 2.39261400 | -2.18219000 |
| H | 1.92712900 | 3.42049900 | -1.79362200 |
| H | 0.46054600 | 3.54314300 | -0.84163500 |
| C | 3.95425200 | -0.59989500 | 0.35688900 |
| H | 3.99051600 | 0.18814000 | 1.10581200 |
| H | 4.84316400 | -0.51037100 | -0.27080600 |
| H | 4.00904700 | -1.56206400 | 0.86495800 |
| C | 2.52827400 | 2.53814000 | 0.67494400 |
| H | 1.89037400 | 3.25627800 | 1.19414600 |
| H | 3.35669600 | 3.09171700 | 0.22759000 |
| H | 2.93995000 | 1.86362700 | 1.42565200 |
| N | -1.45095000 | -0.47779100 | -0.26801100 |
| C | -0.77916400 | 0.77520600 | -0.30034800 |
| C | -1.73130700 | 1.79239400 | 0.41320600 |
| C | -2.70629600 | -0.49785900 | 0.54251100 |
| C | -2.61874200 | 0.85785100 | 1.25734000 |
| H | -3.60695400 | 1.28376300 | 1.43485600 |
| H | -2.15162800 | 0.71217800 | 2.23528500 |
| C | -2.75870700 | -1.62587800 | 1.58688600 |
| H | -1.85331400 | -1.64647700 | 2.19586900 |
| H | -2.91177100 | -2.60761000 | 1.14493000 |
| H | -3.60078500 | -1.43264000 | 2.25526100 |
| C | -1.11428600 | 2.83895000 | 1.35215100 |
| H | -1.92713400 | 3.42049900 | 1.79362100 |
| H | -0.46055100 | 3.54314400 | 0.84163400 |
| H | -0.56344100 | 2.39261600 | 2.18218900 |
| C | -3.95425100 | -0.59989400 | -0.35689200 |
| H | -3.99051300 | 0.18814300 | -1.10581400 |
| H | -4.84316400 | -0.51037000 | 0.27080200 |
| H | -4.00904600 | -1.56206200 | -0.86496400 |
| C | -2.52827700 | 2.53813600 | -0.67494500 |
| H | -1.89037800 | 3.25627300 | -1.19414900 |
| H | -3.35669900 | 3.09171300 | -0.22759100 |
| H | -2.93995300 | 1.86362000 | -1.42565100 |
| H | -0.60265700 | 1.05817600 | -1.33625200 |
| H | 0.60265700 | 1.05817800 | 1.33625300 |
| C | -1.06666000 | -1.44517400 | -1.30072600 |
| C | -1.52688300 | -1.02486000 | -2.71132900 |
| C | -1.46249500 | -2.89280500 | -1.01987100 |
| H | 0.02980500 | -1.39753000 | -1.29103400 |
| H | -1.23975400 | -0.00066600 | -2.95262800 |
| H | -1.06515600 | -1.68214900 | -3.45078200 |
| H | -2.60909000 | -1.11173100 | -2.81097400 |
| H | -1.14109700 | -3.22683200 | -0.03577400 |
| H | -2.53643400 | -3.05510300 | -1.11021500 |
| H | -0.97856100 | -3.52890900 | -1.76349900 |
| C | 1.06666300 | -1.44517200 | 1.30072800 |
| C | 1.52688600 | -1.02485700 | 2.71133000 |
| C | 1.46250000 | -2.89280300 | 1.01987400 |
| H | -0.02980200 | -1.39752900 | 1.29103600 |
| H | 1.23975500 | -0.00066200 | 2.95262900 |
| H | 1.06515900 | -1.68214500 | 3.45078400 |
| H | 2.60909200 | -1.11172600 | 2.81097500 |
| H | 1.14110200 | -3.22683100 | 0.03577700 |
| H | 2.53643900 | -3.05509900 | 1.11021800 |
| H | 0.97856700 | -3.52890700 | 1.76350300 |

Zero-point correction= 0.631895 (Hartree/Particle)
Thermal correction to Energy= 0.660228
Thermal correction to Enthalpy= 0.661172
Thermal correction to Gibbs Free Energy= 0.578415
Sum of electronic and zero-point Energies= -973.873500
Sum of electronic and thermal Energies= -973.845168
Sum of electronic and thermal Enthalpies= -973.844223
Sum of electronic and thermal Free Energies= -973.926980

**Table S41.** Cartesian coordinates and energy values of radical-cation state of **3**$^{iPr\text{-}Me_2}$ for *gauche1-(S/R-R/S)*.

| | | | |
|---|---|---|---|
| N | 1.49370500 | 0.59387500 | -0.03072100 |
| C | 0.76828500 | -0.44433100 | 0.60378500 |
| H | 0.40423100 | -0.09056700 | 1.57174700 |

| | | | |
|---|---|---|---|
| C | 1.76525800 | -1.61632500 | 0.85503800 |
| C | 2.93540700 | 0.27210200 | -0.27972300 |
| C | 2.95490600 | -1.25196300 | -0.05537200 |
| H | 2.85002500 | -1.75505400 | -1.01748800 |
| H | 3.90533700 | -1.57313400 | 0.37233400 |
| C | 3.82606500 | 1.02321200 | 0.73350800 |
| H | 3.83542100 | 2.09472100 | 0.53264900 |
| H | 4.85041300 | 0.66025400 | 0.62953100 |
| H | 3.51330300 | 0.86721000 | 1.76379400 |
| C | 2.15540900 | -1.59022700 | 2.34707300 |
| H | 2.50278000 | -0.60926800 | 2.67191900 |
| H | 2.95234800 | -2.31047900 | 2.54405000 |
| H | 1.29986200 | -1.86370000 | 2.97114300 |
| C | 3.44955800 | 0.60614200 | -1.68949900 |
| H | 2.83468200 | 0.16347400 | -2.46997500 |
| H | 4.45309400 | 0.18516000 | -1.78359600 |
| H | 3.52933900 | 1.67640900 | -1.86482500 |
| C | 1.25603100 | -3.02734600 | 0.53742700 |
| H | 0.43233300 | -3.32435100 | 1.19179100 |
| H | 2.06530400 | -3.74219900 | 0.70276600 |
| H | 0.93251400 | -3.13453400 | -0.49718900 |
| N | -1.73484000 | 0.05796800 | 0.34866400 |
| C | -0.70680000 | -0.84614700 | -0.06659100 |
| C | -0.89789500 | -1.04304300 | -1.59887600 |
| C | -2.56204300 | 0.61314100 | -0.76790500 |
| C | -1.72804500 | 0.19484800 | -1.98943500 |
| H | -2.35896600 | 0.00594600 | -2.85865200 |
| H | -1.05061300 | 1.01033600 | -2.25546900 |
| C | -2.71805100 | 2.14467900 | -0.74182000 |
| H | -3.38188000 | 2.48776400 | 0.04808000 |
| H | -3.15400900 | 2.45631000 | -1.69367800 |
| H | -1.75975900 | 2.65280400 | -0.63739600 |
| C | 0.36212400 | -1.09048600 | -2.45895600 |
| H | 0.93145300 | -0.17010900 | -2.36534600 |
| H | 0.07454500 | -1.20045400 | -3.50737100 |
| H | 1.00907700 | -1.93167500 | -2.21148600 |
| C | -3.97789800 | 0.00140900 | -0.79268900 |
| H | -3.96632600 | -1.08574100 | -0.80722700 |
| H | -4.48749300 | 0.34662200 | -1.69447700 |
| H | -4.56936400 | 0.33036300 | 0.06175400 |
| C | -1.67939400 | -2.35566500 | -1.81387000 |
| H | -1.04398200 | -3.22056800 | -1.61113200 |
| H | -2.01668500 | -2.42763900 | -2.85010900 |
| H | -2.55396800 | -2.43358900 | -1.16856200 |
| H | -0.83796800 | -1.79714300 | 0.45287000 |
| C | 0.89477600 | 1.92870000 | 0.04503800 |
| C | 1.31238600 | 2.88001200 | -1.07123300 |
| C | 1.03802700 | 2.58747000 | 1.43229700 |
| H | -0.17280000 | 1.72071300 | -0.06898100 |
| H | 1.21414200 | 2.41991300 | -2.05495300 |
| H | 0.66151600 | 3.75633800 | -1.04252200 |
| H | 2.33569800 | 3.23666900 | -0.95104400 |
| H | 0.78284900 | 1.89754900 | 2.23844100 |
| H | 2.04814300 | 2.95783400 | 1.60165000 |
| H | 0.35356300 | 3.43647700 | 1.49137800 |
| C | -2.14961000 | -0.01790900 | 1.75912000 |
| C | -3.01714200 | -1.25388600 | 2.06966400 |
| C | -2.78092700 | 1.26191400 | 2.30261100 |
| H | -1.21415600 | -0.16018100 | 2.31247700 |
| H | -2.58235000 | -2.16688700 | 1.65853300 |
| H | -3.08860000 | -1.37715600 | 3.15218100 |
| H | -4.02657600 | -1.14552900 | 1.67599600 |
| H | -2.16233800 | 2.13560900 | 2.09515200 |
| H | -3.78011500 | 1.43394500 | 1.90251900 |
| H | -2.87864500 | 1.16683100 | 3.38558200 |

Zero-point correction= 0.631888 (Hartree/Particle)
Thermal correction to Energy= 0.660291
Thermal correction to Enthalpy= 0.661235
Thermal correction to Gibbs Free Energy= 0.578040
Sum of electronic and zero-point Energies= -973.869069

Sum of electronic and thermal Energies= -973.840666
Sum of electronic and thermal Enthalpies= -973.839722
Sum of electronic and thermal Free Energies= -973.922917

**Table S42.** Cartesian coordinates and energy values of radical-cation state of **3**$^{iPr\text{-}Me_2}$ for *gauche2-(S/R-R/S)*.

| | | | |
|---|---|---|---|
| N | 1.73484400 | 0.05797000 | 0.34866500 |
| C | 0.70680400 | -0.84614500 | -0.06659300 |
| H | 0.83797400 | -1.79714300 | 0.45286400 |
| C | 0.89789900 | -1.04303100 | -1.59887900 |
| C | 2.56204200 | 0.61315400 | -0.76790300 |
| C | 1.72804000 | 0.19486700 | -1.98943100 |
| H | 1.05060300 | 1.01035400 | -2.25545600 |
| H | 2.35895900 | 0.00597400 | -2.85865300 |
| C | 3.97790000 | 0.00142900 | -0.79269600 |
| H | 4.56937100 | 0.33039100 | 0.06174100 |
| H | 4.48748600 | 0.34664000 | -1.69448900 |
| H | 3.96633300 | -1.08572100 | -0.80722700 |
| C | 1.67940700 | -2.35564700 | -1.81388100 |
| H | 2.55397800 | -2.43357100 | -1.16856900 |
| H | 2.01670500 | -2.42760800 | -2.85011900 |
| H | 1.04400000 | -3.22055600 | -1.61115500 |
| C | 2.71804800 | 2.14469300 | -0.74181100 |
| H | 1.75975400 | 2.65281500 | -0.63738800 |
| H | 3.15400700 | 2.45633000 | -1.69366500 |
| H | 3.38187300 | 2.48777500 | 0.04809300 |
| C | -0.36212000 | -1.09047900 | -2.45895800 |
| H | -1.00905800 | -1.93168300 | -2.21150500 |
| H | -0.07453800 | -1.20042200 | -3.50737500 |
| H | -0.93146300 | -0.17011200 | -2.36533100 |
| N | -1.49370800 | 0.59387200 | -0.03072000 |
| C | -0.76828500 | -0.44433300 | 0.60378300 |
| C | -1.76525500 | -1.61633100 | 0.85502800 |
| C | -2.93541000 | 0.27209700 | -0.27972100 |
| C | -2.95490400 | -1.25196900 | -0.05538000 |
| H | -3.90533400 | -1.57314600 | 0.37232300 |
| H | -2.85002000 | -1.75505200 | -1.01750000 |
| C | -3.44956300 | 0.60614600 | -1.68949500 |
| H | -3.52935200 | 1.67641400 | -1.86481000 |
| H | -4.45309500 | 0.18515600 | -1.78359800 |
| H | -2.83468100 | 0.16349200 | -2.46997400 |
| C | -1.25602600 | -3.02735000 | 0.53741100 |
| H | -0.93251600 | -3.13453400 | -0.49720800 |
| H | -2.06529600 | -3.74220600 | 0.70275400 |
| H | -0.43232200 | -3.32435400 | 1.19176800 |
| C | -3.82606900 | 1.02319600 | 0.73351600 |
| H | -3.51329900 | 0.86719400 | 1.76380000 |
| H | -4.85041400 | 0.66022800 | 0.62954400 |
| H | -3.83543600 | 2.09470500 | 0.53265800 |
| C | -2.15540700 | -1.59024000 | 2.34706200 |
| H | -1.29986000 | -1.86371300 | 2.97113100 |
| H | -2.95234400 | -2.31049600 | 2.54403400 |
| H | -2.50278300 | -0.60928400 | 2.67191100 |
| H | -0.40423200 | -0.09057300 | 1.57174800 |
| C | 2.14961900 | -0.01792300 | 1.75912000 |
| C | 2.78093300 | 1.26189600 | 2.30262500 |
| C | 3.01715600 | -1.25390000 | 2.06964700 |
| H | 1.21416800 | -0.16020400 | 2.31247700 |
| H | 2.16234200 | 2.13559100 | 2.09517700 |
| H | 2.87865400 | 1.16680000 | 3.38559500 |
| H | 3.78012000 | 1.43393300 | 1.90253300 |
| H | 2.58236900 | -2.16689700 | 1.65850000 |
| H | 4.02659100 | -1.14553300 | 1.67598300 |
| H | 3.08861200 | -1.37718700 | 3.15216200 |
| C | -0.89478800 | 1.92869900 | 0.04505000 |
| C | -1.03804600 | 2.58746200 | 1.43231100 |
| C | -1.31240400 | 2.88001400 | -1.07121700 |
| H | 0.17278900 | 1.72071700 | -0.06896900 |
| H | -0.78287300 | 1.89753700 | 2.23845300 |
| H | -0.35358000 | 3.43646800 | 1.49139900 |
| H | -2.04816200 | 2.95782800 | 1.60166000 |

| | | | |
|---|---|---|---|
| H | -1.21415900 | 2.41991600 | -2.05493800 |
| H | -2.33571800 | 3.23666500 | -0.95102500 |
| H | -0.66153900 | 3.75634300 | -1.04250600 |

Zero-point correction= 0.631888 (Hartree/Particle)
Thermal correction to Energy= 0.660291
Thermal correction to Enthalpy= 0.661235
Thermal correction to Gibbs Free Energy= 0.578040
Sum of electronic and zero-point Energies= -973.869069
Sum of electronic and thermal Energies= -973.840666
Sum of electronic and thermal Enthalpies= -973.839722
Sum of electronic and thermal Free Energies= -973.922917

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