Supporting Information

for

# Reactivity Enhancement of a Diphosphene by Reversible *N*-Heterocyclic Carbene Coordination

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**Thermodynamic data of equilibrium between 1 and 3 from NMR spectroscopy:**

A 0.0805 M solution (0.4 mL of tol-d8) of **1** and **2** was taken in NMR tube and $^{31}P$, and $^{1}H$ spectra was measured 10 K interval starting at 253 K up to 293 K. The Integration of $^{31}P$ resonance of $P_2$ alone and adduct allowed the concentration of both the component to be measured. The equilibrium constants were calculated in usual way.

**Table S1** Concentrations for **1**, **2**, and **3** determined via $^{31}P$ NMR spectroscopy at a range of temperatures.

| **T / K** | **[1] / mM** | **[2] / mM** | **[3] / mM** | **K / M** | **$\Delta$G / kJ mol$^{-1}$** |
|---|---|---|---|---|---|
| 253 | 4.83 | 4.83 | 75.67 | 3243.62 | 17.01 |
| 263 | 7.24 | 7.24 | 73.25 | 1397.43 | 15.84 |
| 273 | 10.46 | 10.46 | 70.03 | 640.06 | 14.67 |
| 283 | 16.1 | 16.1 | 64.4 | 248.44 | 12.97 |
| 293 | 21.73 | 21.73 | 58.76 | 124.44 | 11.75 |

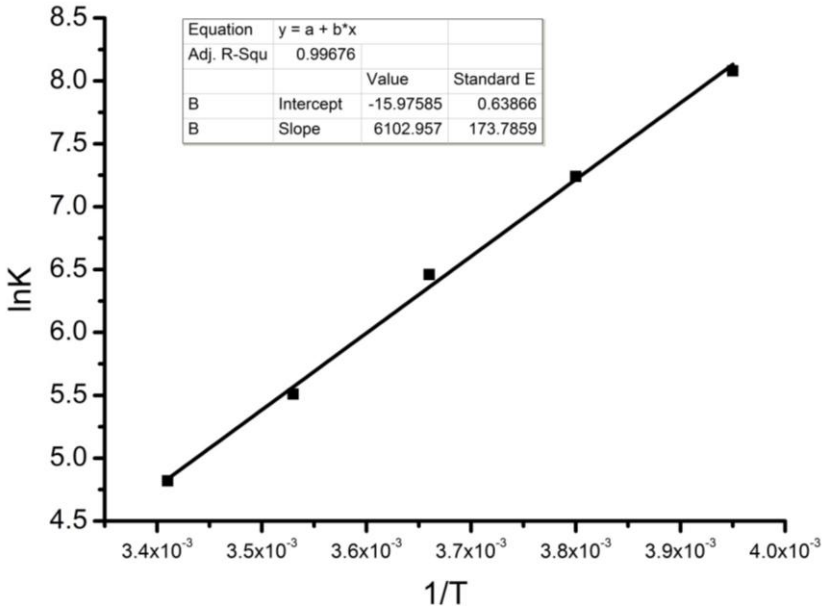



**Figure S1** Plot of 1/T vs lnK for the determination of the constant K for the equilibrium between **1+2** and **3**.

The linear regression of 1/T *vs* lnK allowed to determine the value of $\Delta H = -50.74 \pm 1.09$ kJmol$^{-1}$, $\Delta G_{298} = -11.15 \pm 1.07$ kJmol$^{-1}$, $\Delta S_{298} = -132.85 \pm 2.56$ Jmol$^{-1}$K$^{-1}$

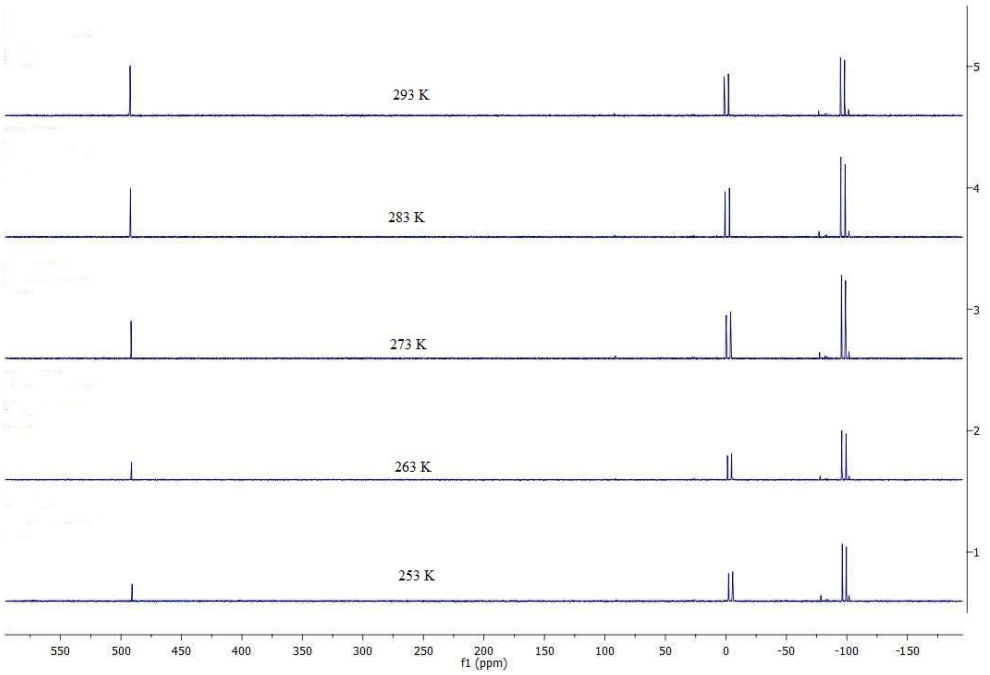



**Figure S2** VT-NMR spectra of 1:1 mixture of **1** and **2** in toluene-$d_8$.

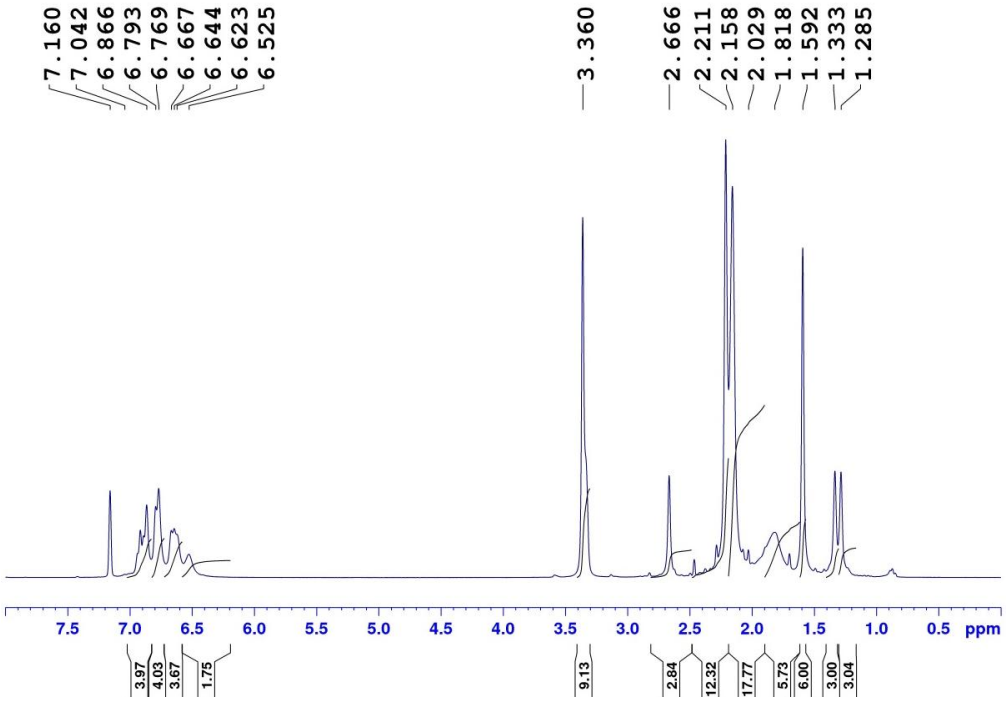



**Figure S3** $^1$H NMR spectrum of 1:2 mixture of **1** and **2** in benzene-$d_6$ at RT.

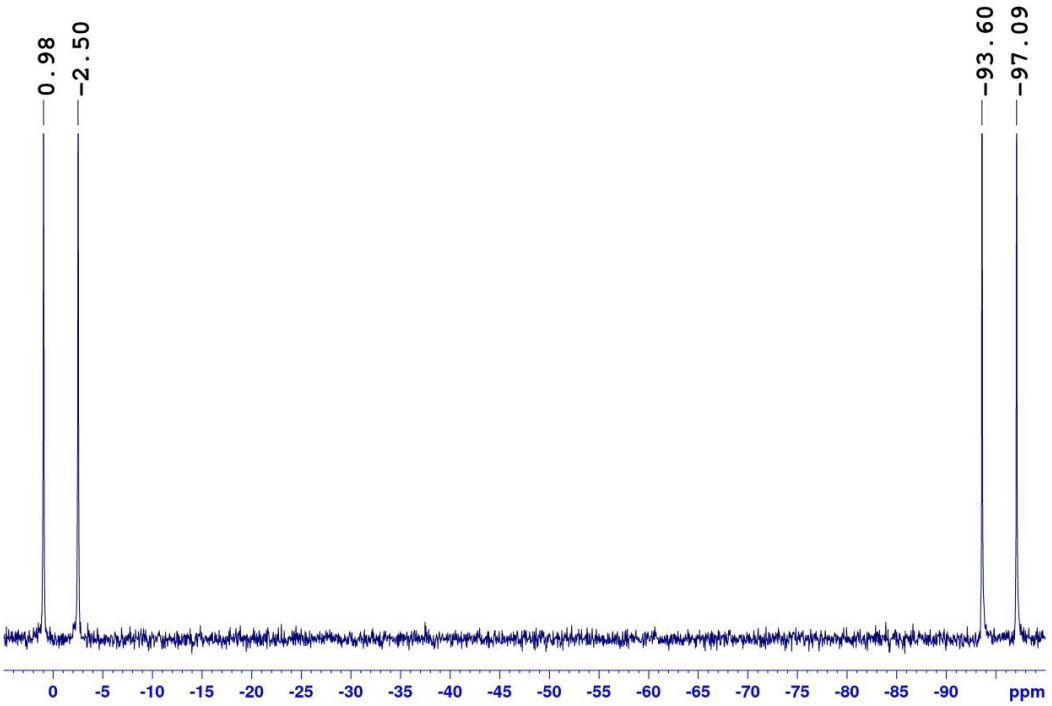



**Figure S4** $^{31}P\{^{1}H\}$ NMR spectrum of 1:2 mixture of **1** and **2** in benzene-$d_6$ at RT.

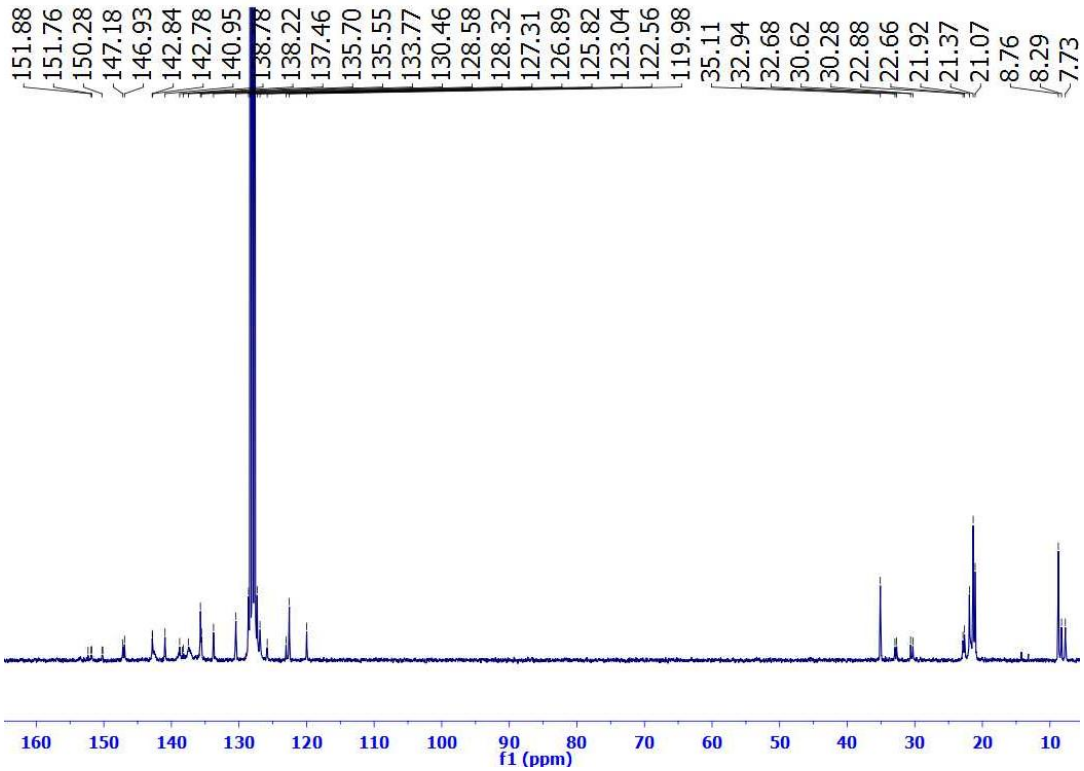



**Figure S5** $^{13}C\{^{1}H\}$NMR spectrum of 1:2 of **1** and **2** in benzene-$d_6$ at RT.

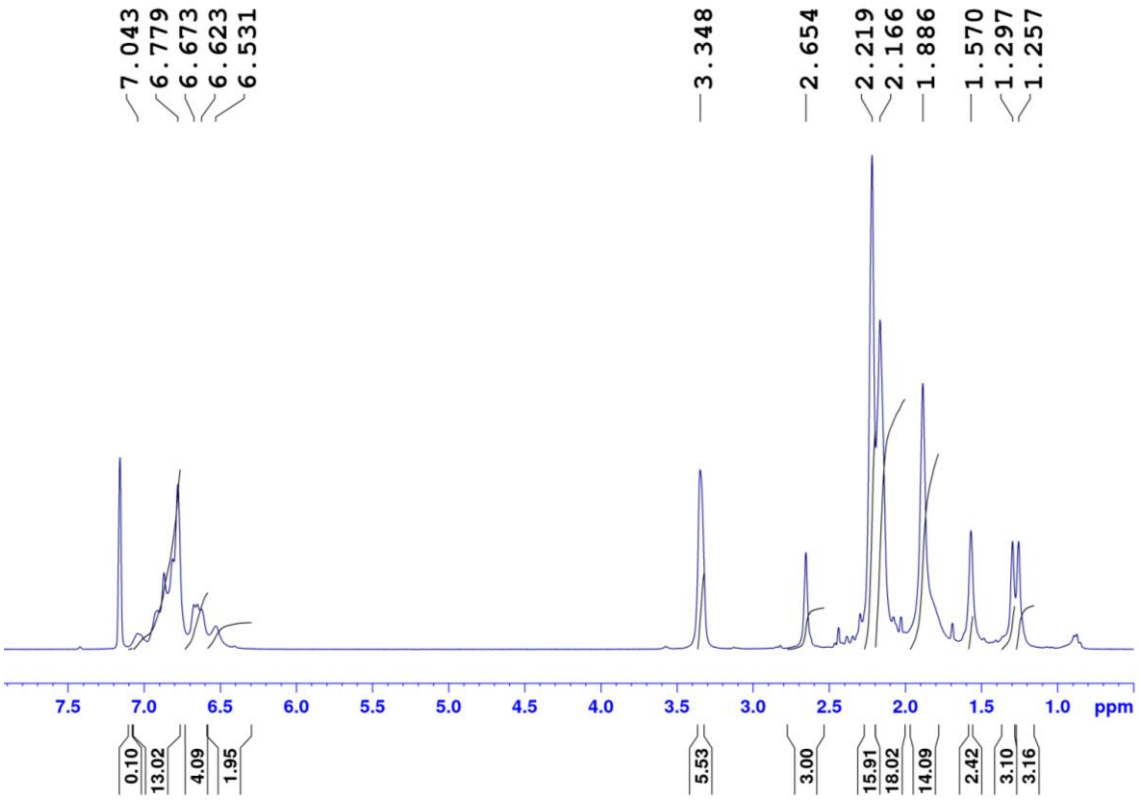



**Figure S6** $^{1}$H NMR spectrum of 1:1 of **1** and **2** in benzene-$d_6$ at RT.

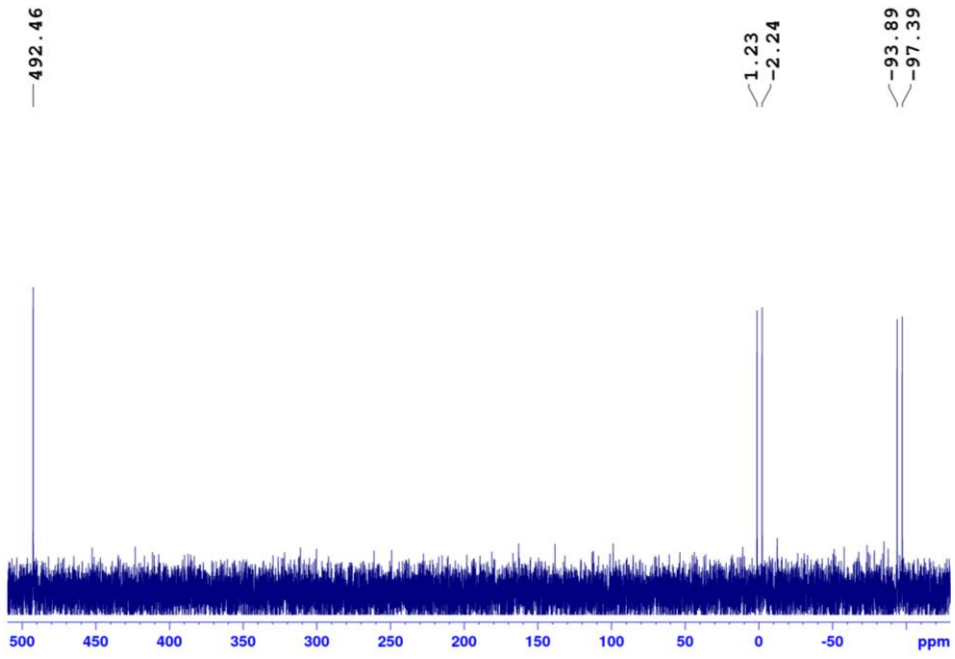



**Figure S7** $^{31}$P{$^{1}$H} NMR spectrum of 1:1 of **1** and **2** in benzene-$d_6$ at RT.

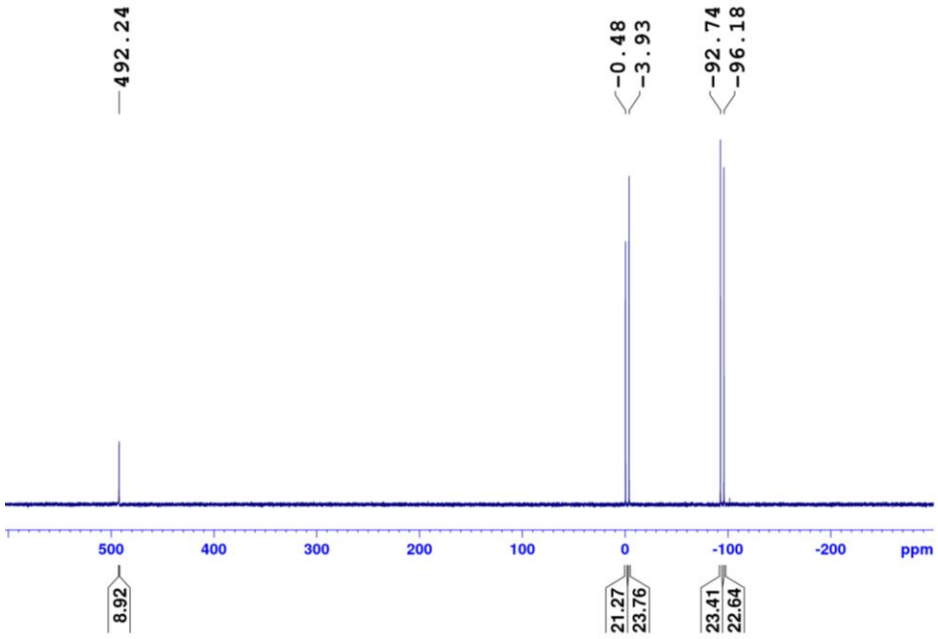



**Figure S8** $^{31}P\{^{1}H\}$ NMR spectrum of 1:1 of **1** and **2** in THF-$d_8$ at RT.

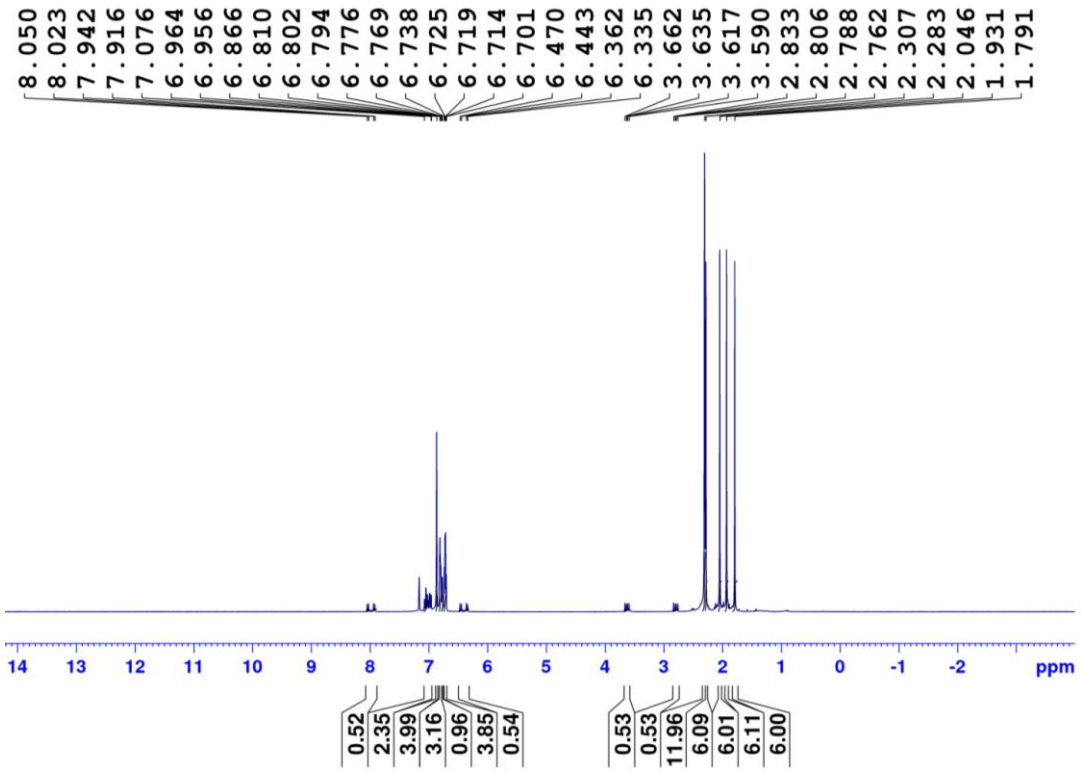



**Figure S9** $^{1}H$ NMR spectrum of **4** in benzene-$d_6$ at RT.

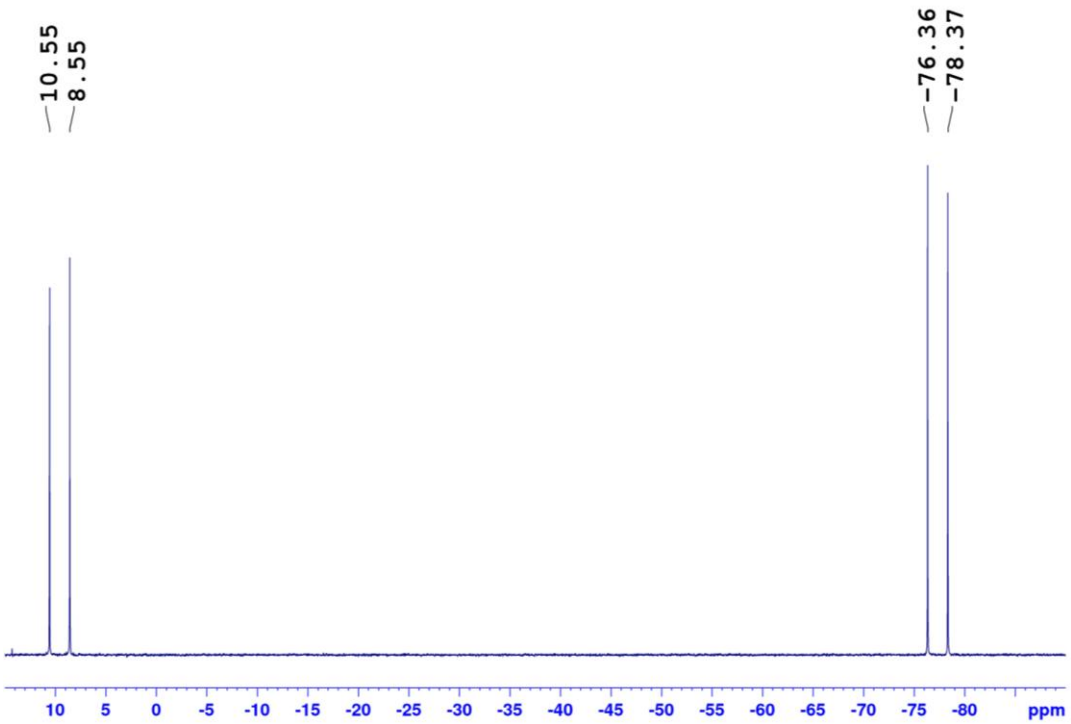



**Figure S10** $^{31}P\{^{1}H\}$ NMR spectrum of **4** in benzene-$d_6$ at RT.

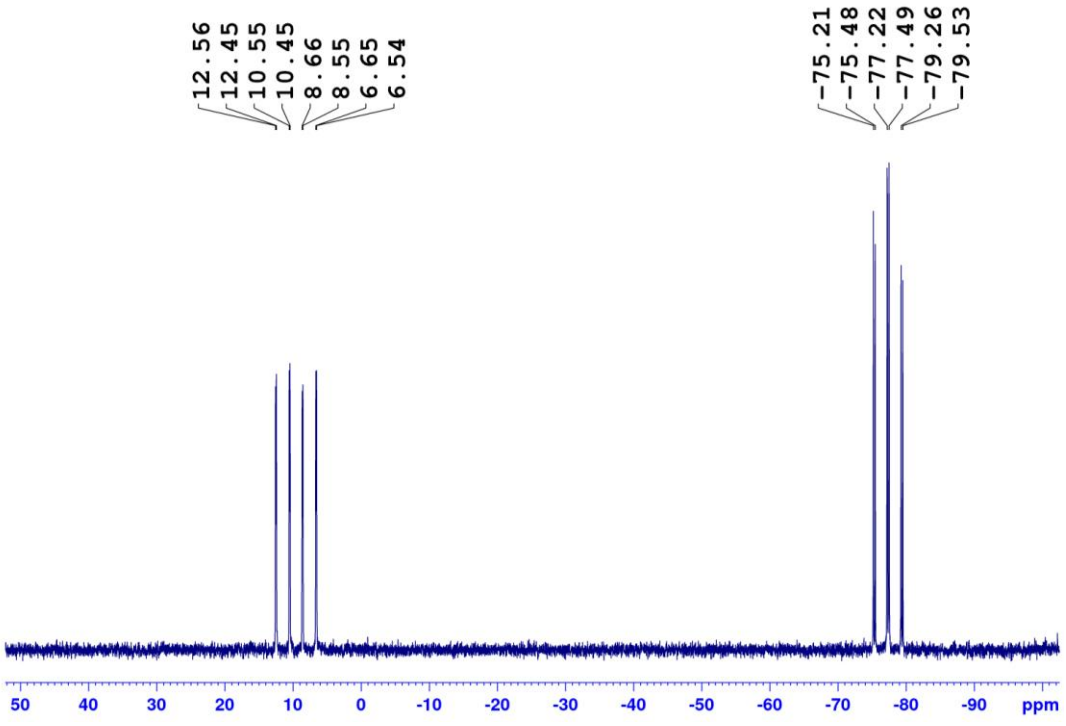



**Figure S11** $^{31}P$ NMR spectrum of **4** in benzene-$d_6$ at RT.

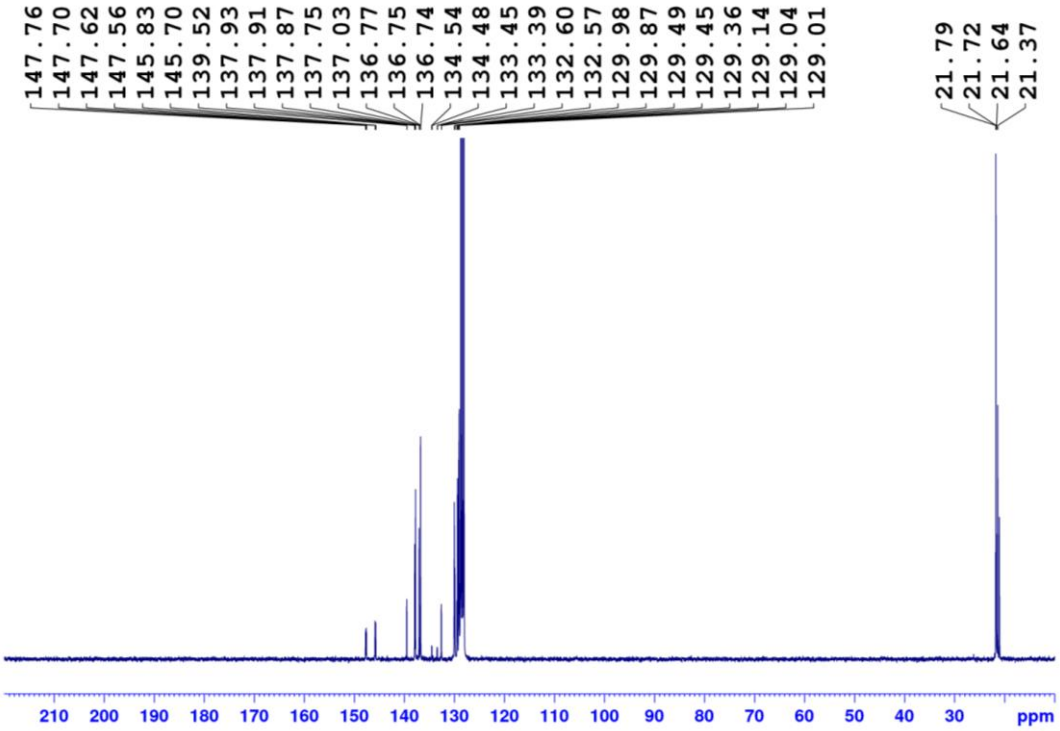



**Figure S12** $^{13}C\{H\}$ NMR spectrum of **4** in benzene-$d_6$ at RT.

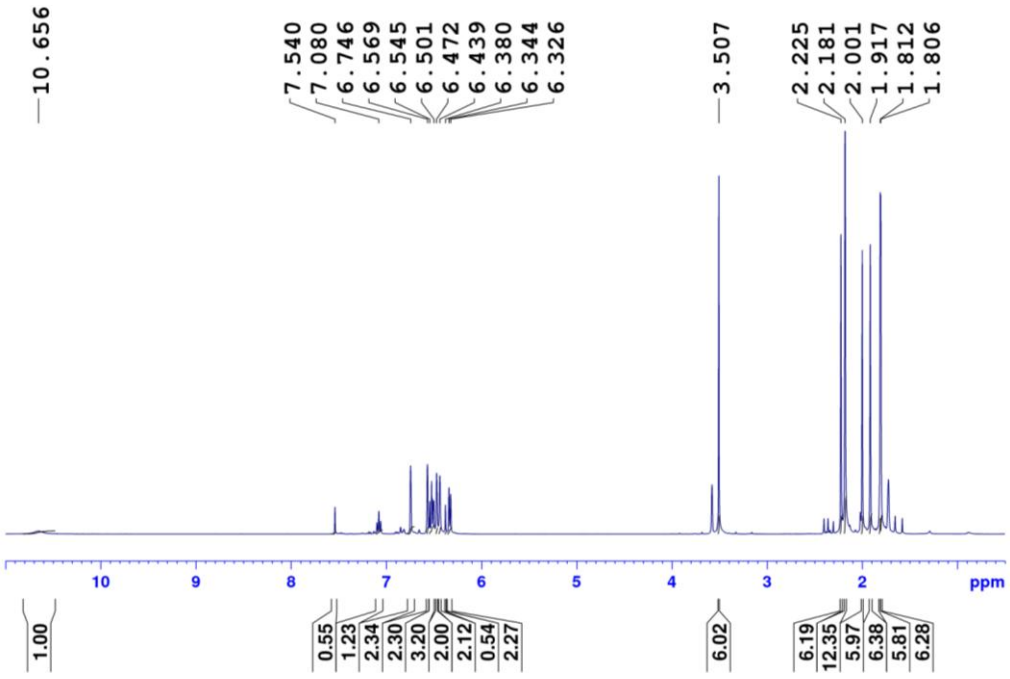



**Figure S13** $^{1}H$ NMR spectrum of **5** in THF-$d_8$ at RT.

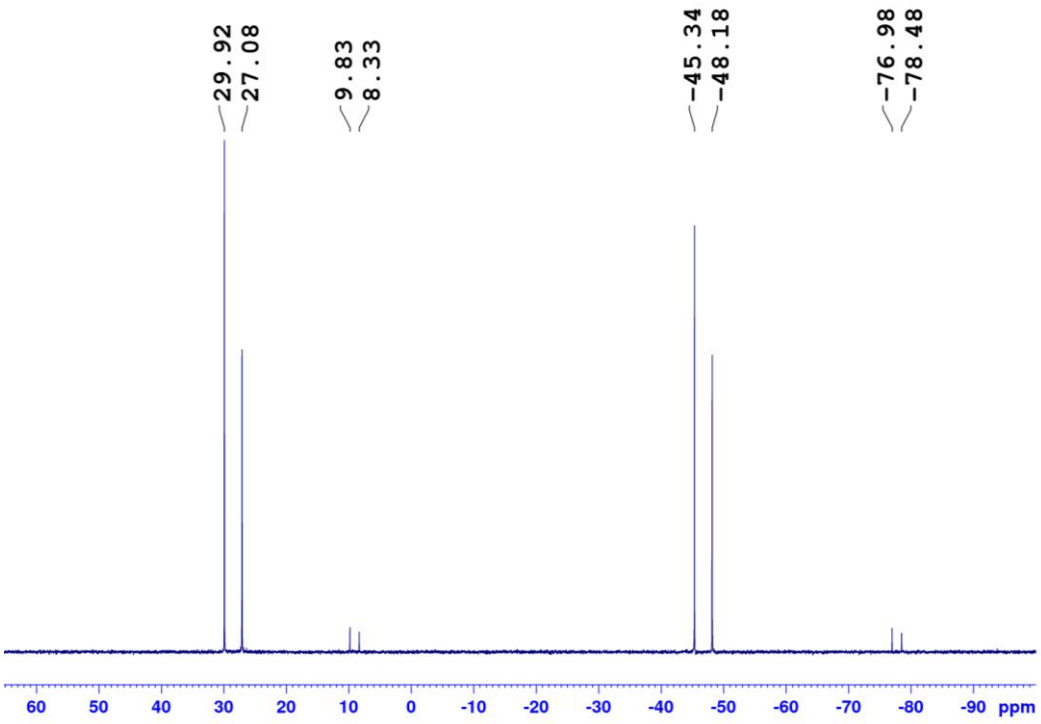



**Figure S14** $^{31}P\{^{1}H\}$ NMR spectrum of **5** (with 5% compound **4**)in THF-$d_8$ at RT.

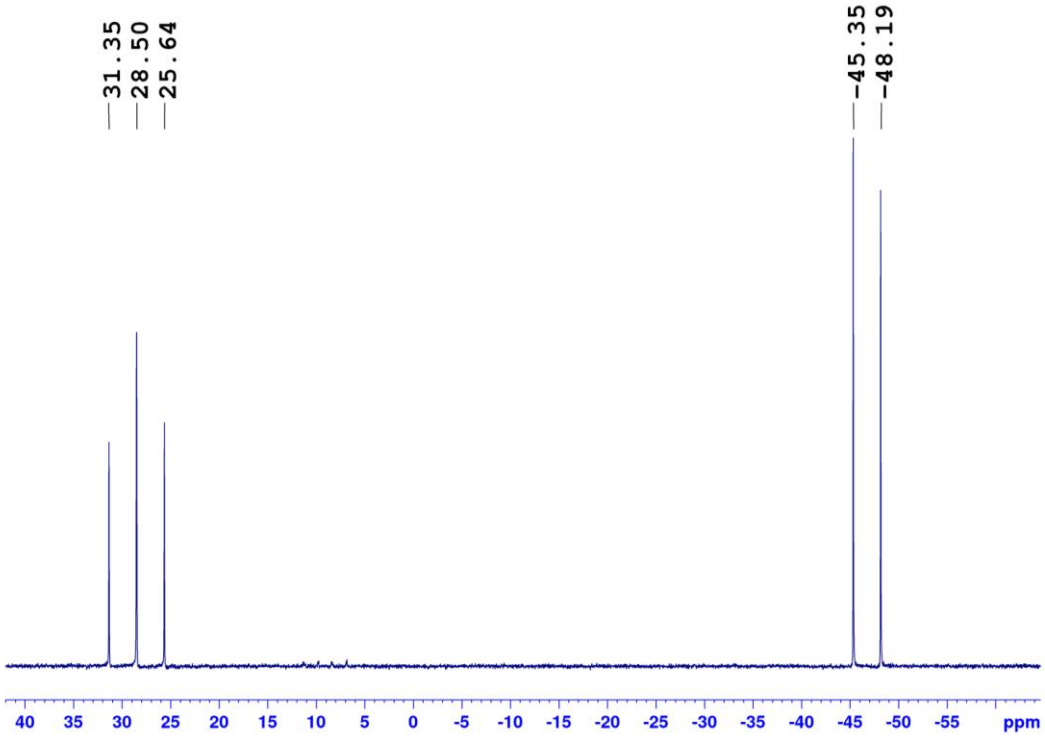



**Figure S15** $^{31}P$ NMR spectrum of **5** (with 5% compound **4**) in THF-$d_8$ at RT.

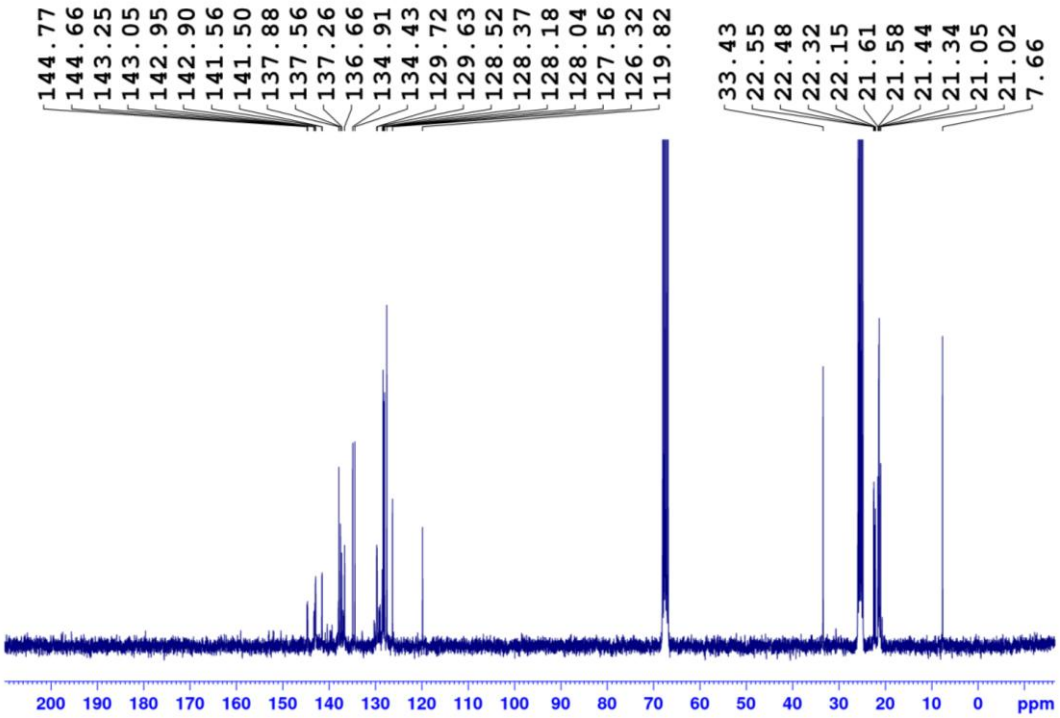



**Figure S16** $^{13}C\{^{1}H\}$ NMR spectrum of **5** in THF-$d_8$ at RT.

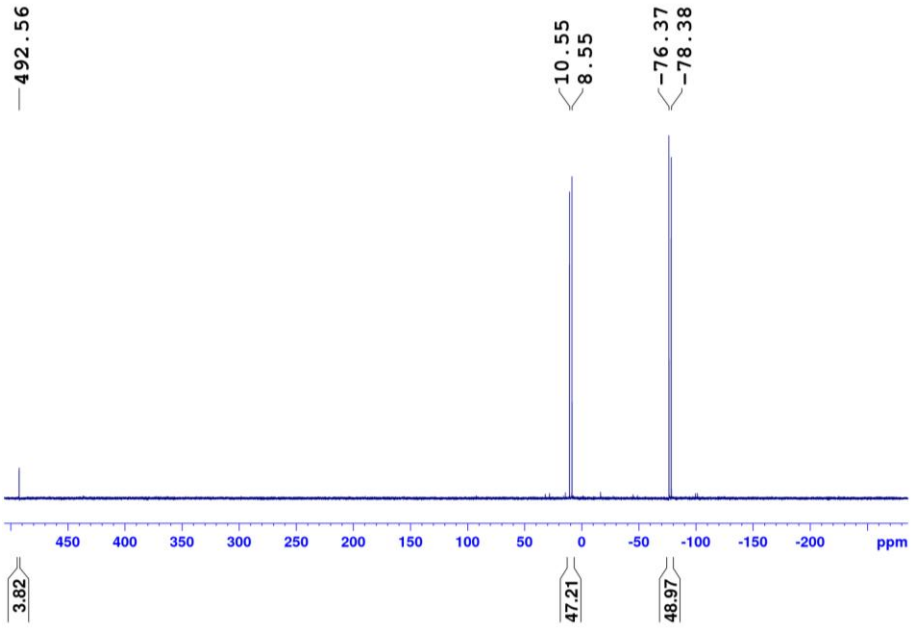



**Figure S17** $^{31}P\{^{1}H\}$ NMR spectrum from the crude reaction mixture of catalytic hydrolysis of **1** in THF in presence of one drop of benzene-$d_6$ at RT.

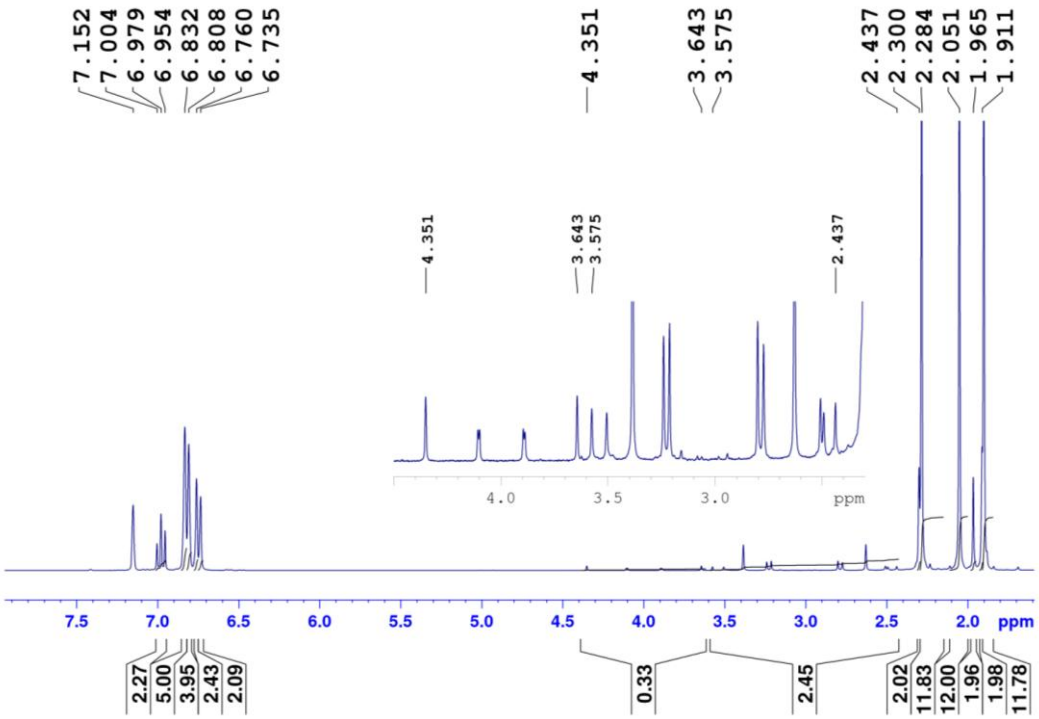



**Figure S18** $^{1}$H NMR spectrum of **6** in benzene-$d_6$ at RT.

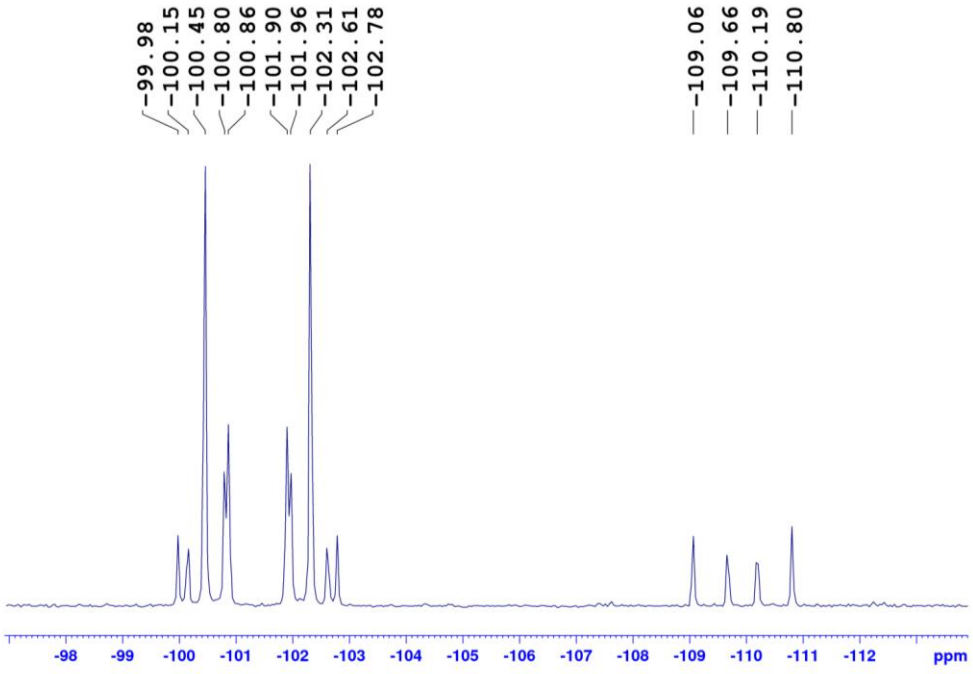



**Figure S19** $^{31}$P NMR spectrum of **6** in benzene-$d_6$ at RT.

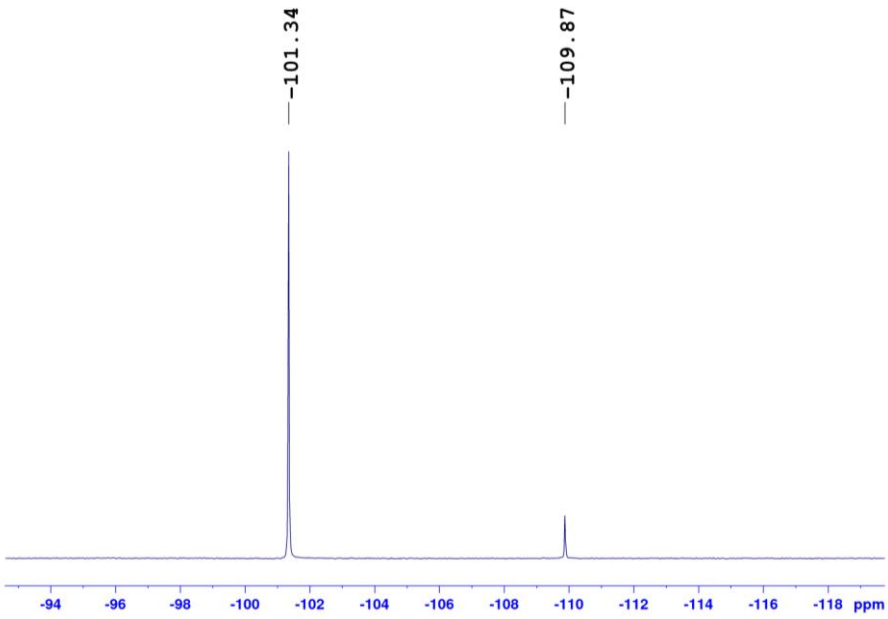



**Figure S20** $^{31}P\{H\}$ NMR spectrum of **6** in benzene-$d_6$ at RT. –50 °C.

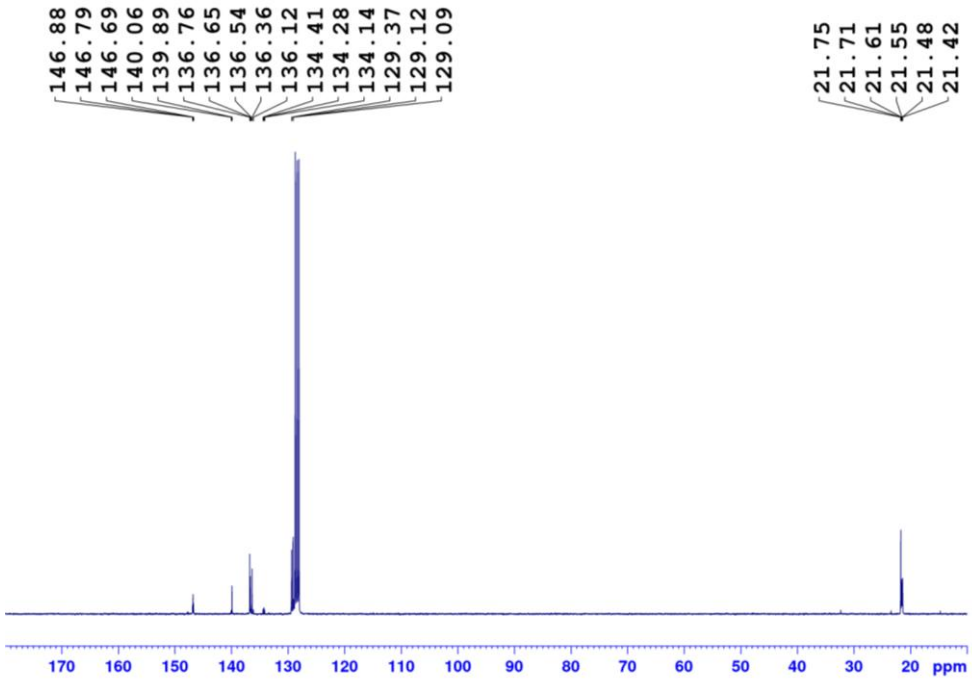



**Figure S21** $^{13}C\{H\}$ NMR spectrum of **6** in benzene-$d_6$ at RT.

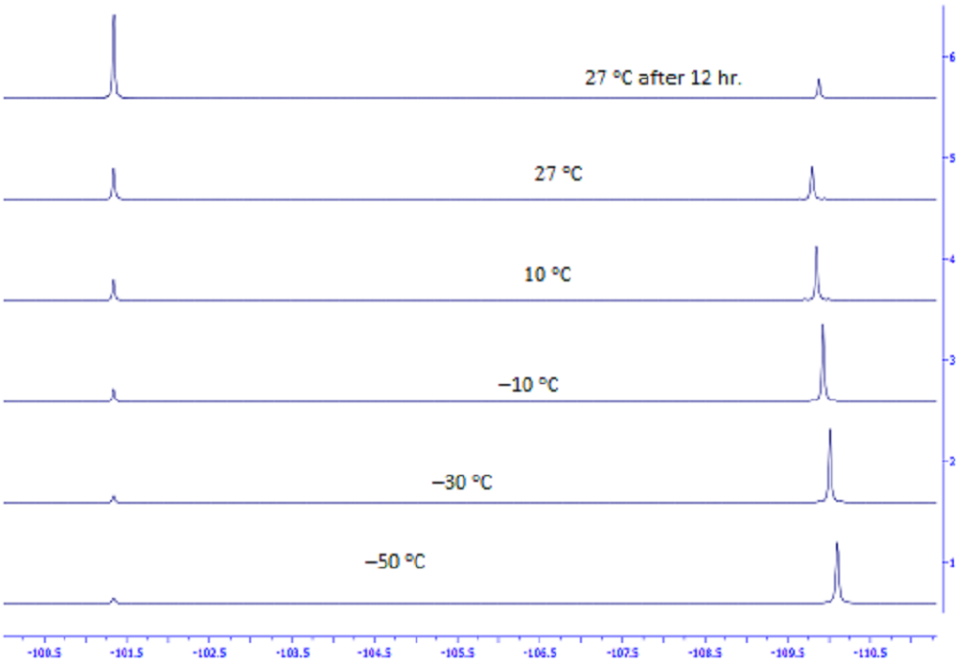



**Figure S22** VT-NMR spectra of **6** in toluene-$d_8$.

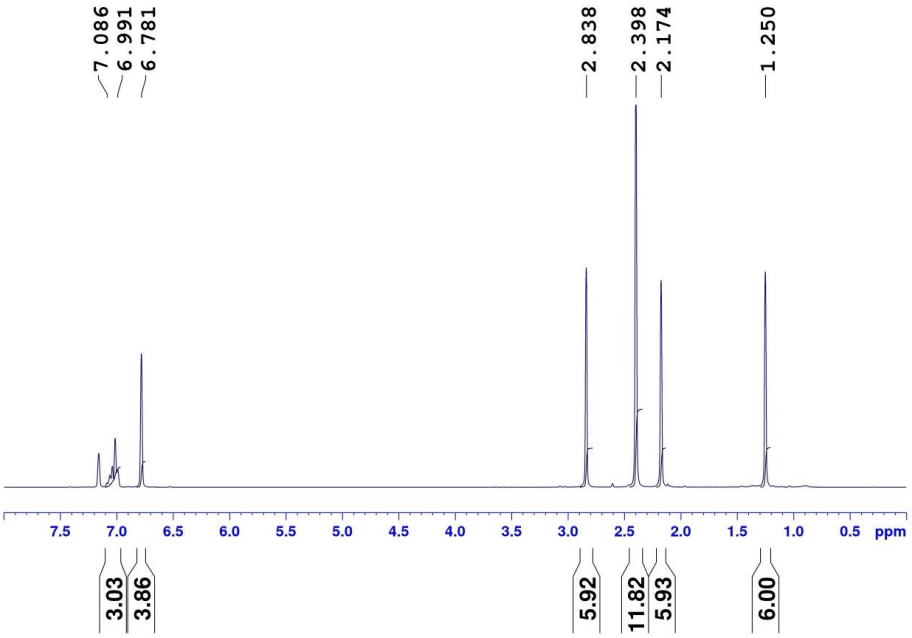



**Figure S23** $^1$H NMR spectrum of **7** in benzene-$d_6$ at RT.

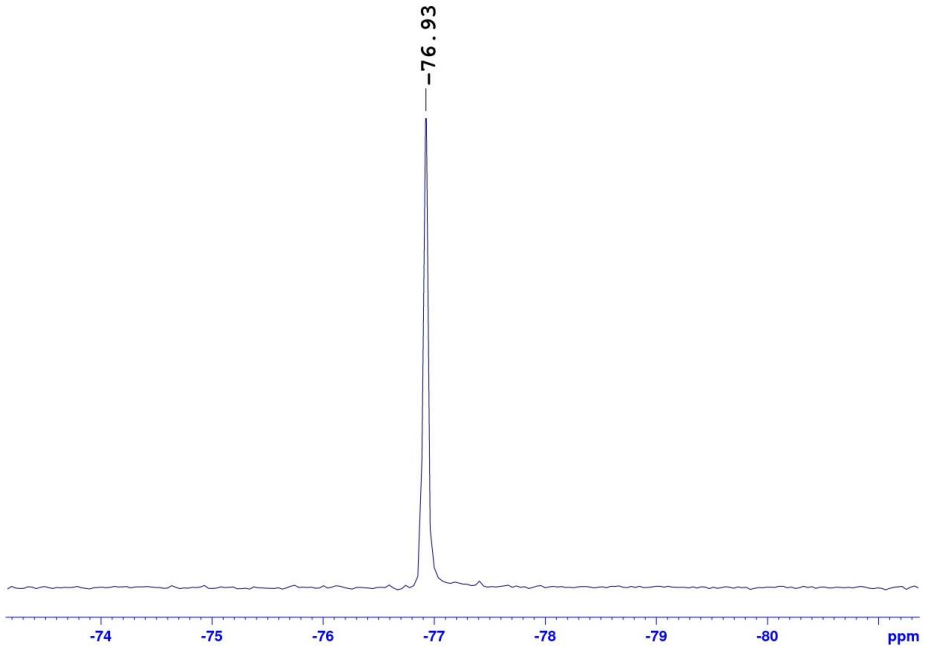



**Figure S24** $^{31}P\{^{1}H\}$ NMR spectrum of **7** in benzene-$d_6$ at RT.

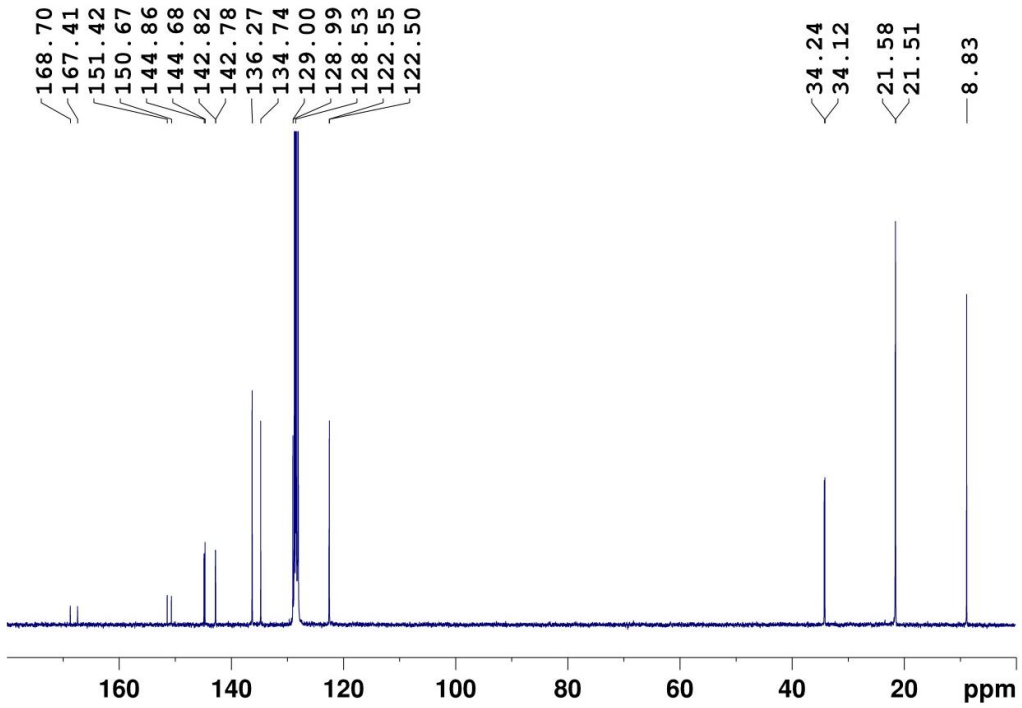



**Figure S25** $^{13}C\{^{1}H\}$ NMR spectrum of **7** in benzene-$d_6$ at RT.

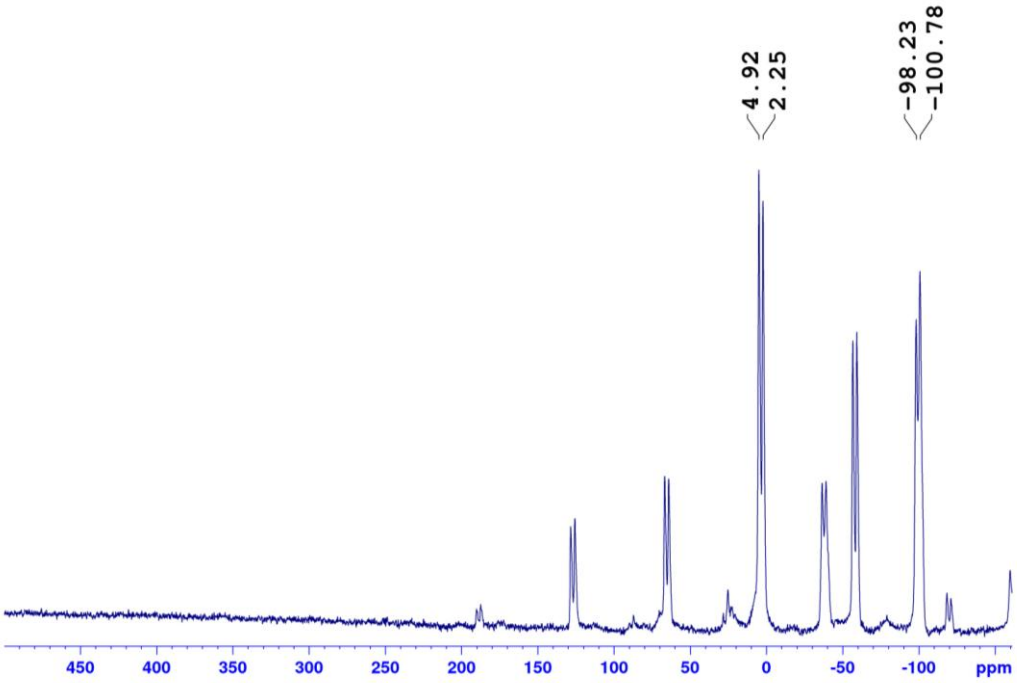



**Figure S26** CP-MAS $^{31}P\{^{1}H\}$ NMR spectrum of **3** at RT.

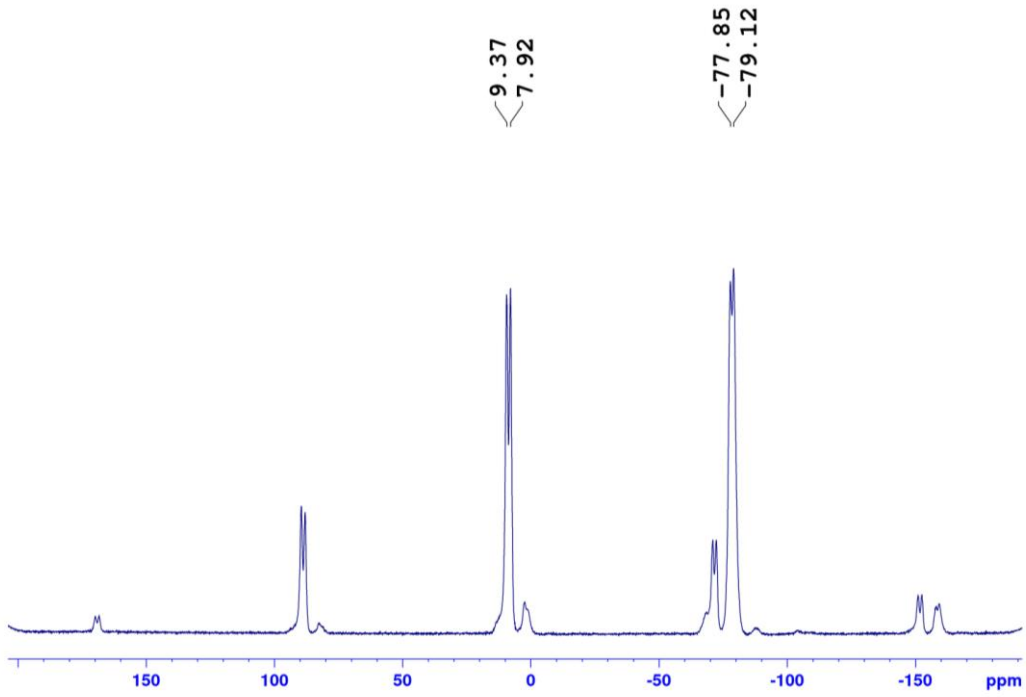



**Figure S27** CP-MAS $^{31}P\{^{1}H\}$ NMR spectrum of **4** at RT.

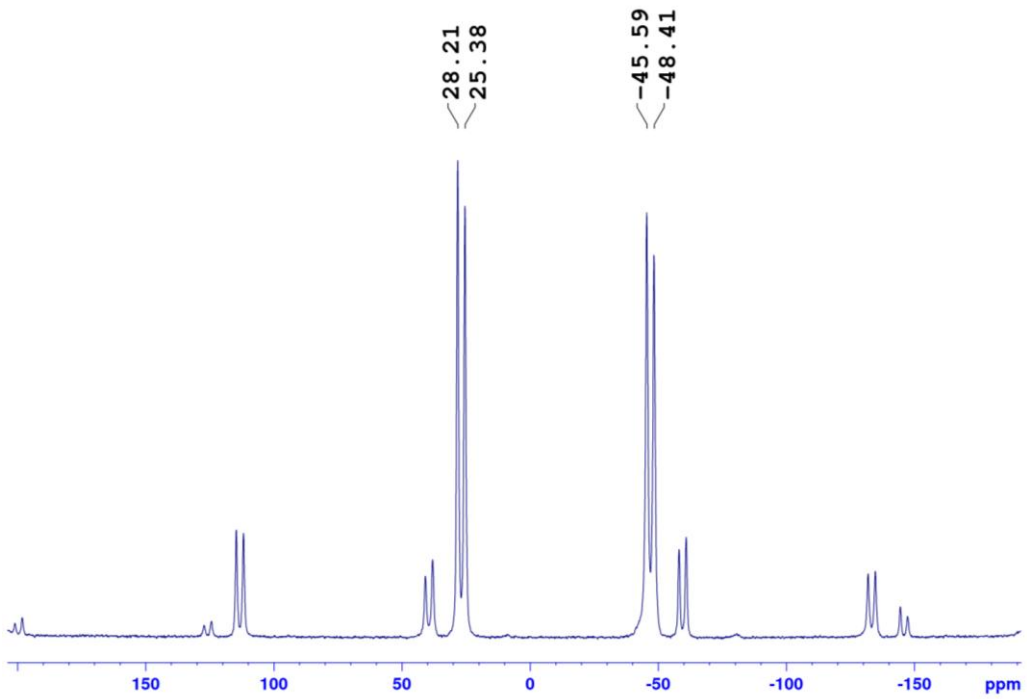



**Figure S28** CP-MAS $^{31}P\{^{1}H\}$ NMR spectrum of **5** at RT.

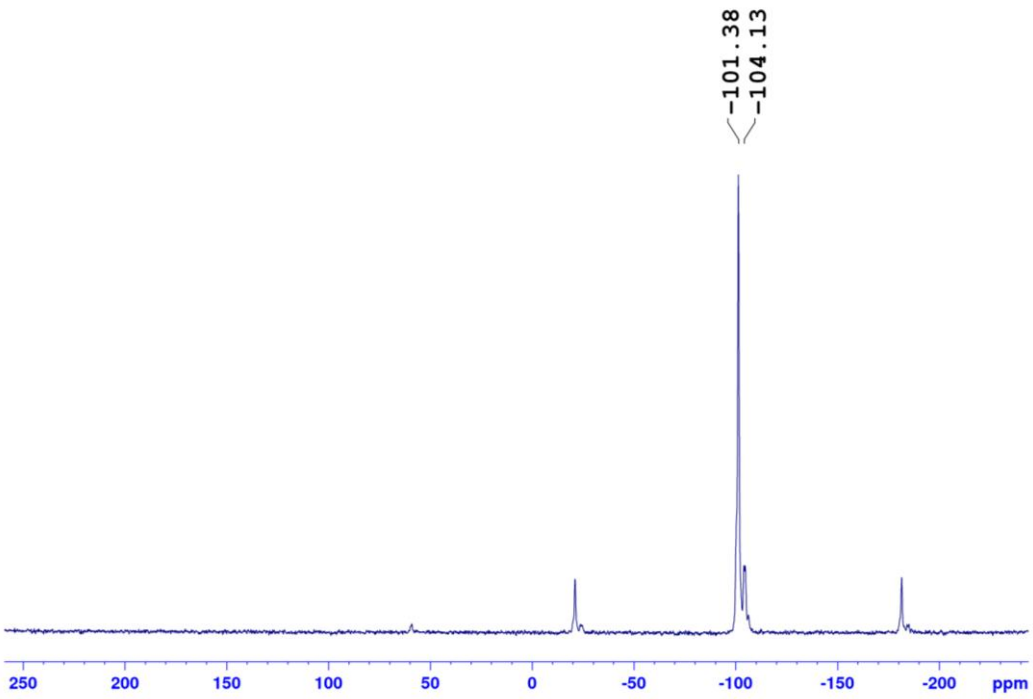



**Figure S29** CP-MAS $^{31}P\{^{1}H\}$ NMR spectrum of **6** at RT.

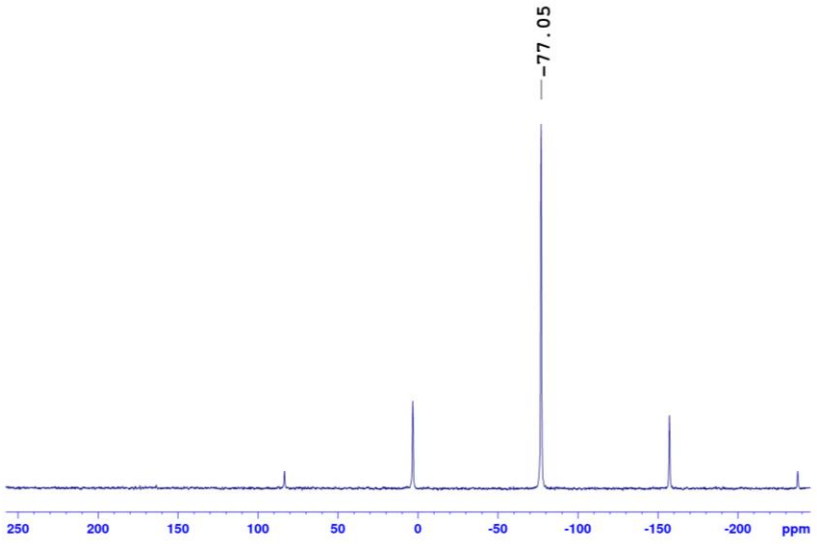



**Figure S30** CP-MAS $^{31}P\{^{1}H\}$ NMR spectrum of **7** at RT.

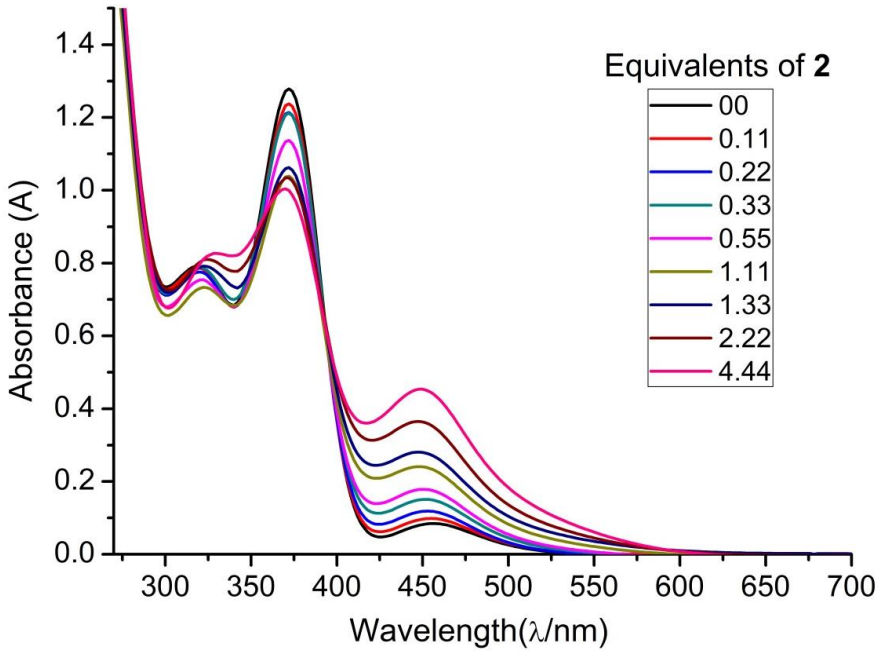



**Figure S31** UV/vis spectra of **1**(black line) in THF with increasing concentrations of **2**. There is clear isosbestic point at 392 nm. The absorbance at 448 nm is increasing while absorbance at 372 nm is decreasing when equilibrium shifted towards **3**.

**Table S2** Concentrations and absorbance for the UV/vis titration of **1** with **2**.

A series of solutions with the following concentrations of **1** and **2** were prepared. UV/vis spectra were recorded in THF at 298 K and the absorption maxima at 372 and448 nm were noted.

| **[1]/mM** | **[2]/mM** | **Equivalents of 2** | **Absorbance at $\lambda_{max}$ = 448 nm** | **Absorbance at $\lambda_{max}$ = 372 nm** |
|---|---|---|---|---|
| 1.0885 | 00 | 0 | 0.07986 | 1.27887 |
| 1.0885 | 0.1208 | 0.11 | 0.09496 | 1.23762 |
| 1.0885 | 0.2416 | 0.22 | 0.11675 | 1.21381 |
| 1.0885 | 0.3624 | 0.33 | 0.14963 | 1.21213 |
| 1.0885 | 0.6039 | 0.55 | 0.17802 | 1.13718 |
| 1.0885 | 1.2079 | 1.11 | 0.24104 | 1.03872 |
| 1.0885 | 1.4495 | 1.33 | 0.28081 | 1.06244 |
| 1.0885 | 1.9327 | 1.77 | 0.2989 | 1.06942 |
| 1.0885 | 2.4158 | 2.22 | 0.36518 | 1.03378 |
| 1.0885 | 2.8990 | 2.66 | 0.40283 | 1.05193 |
| 1.0885 | 3.3822 | 3.10 | 0.45361 | 1.04477 |
| 1.0885 | 3.8653 | 3.55 | 0.44189 | 1.o4033 |
| 1.0885 | 4.8317 | 4.44 | 0.45351 | 0.99947 |

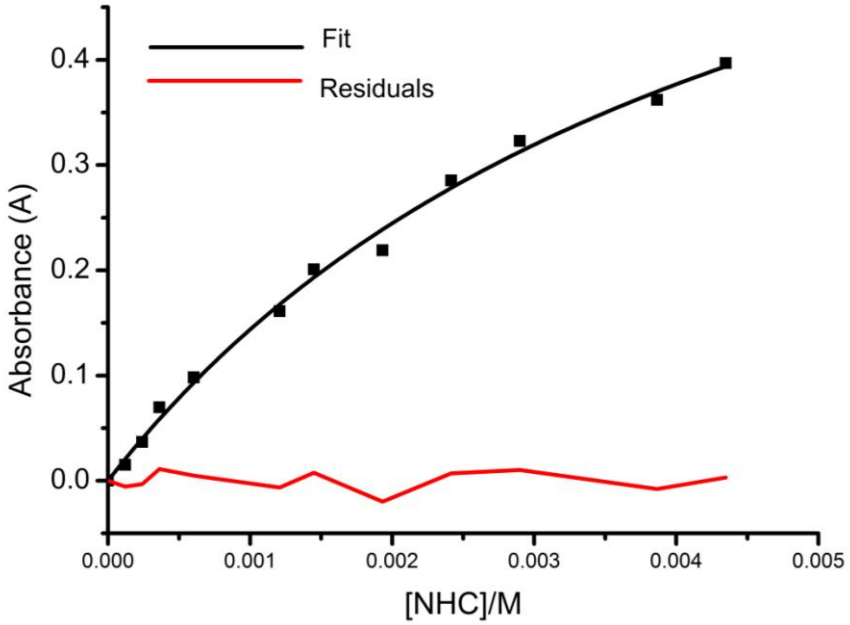



**Figure S32** Concentration of **2** vs absorbance at 448 nm with fixed concentration of **1**.

The resulting curve was fitted according to the equation describe by Aldrich-Wright.[S1] From the fitting process it is shown that the equilibrium constant *K* was 214.58 $M^{-1}$ at 298 K which corresponds to $\Delta G_{298} = -13.30$ $KJmol^{-1}$.

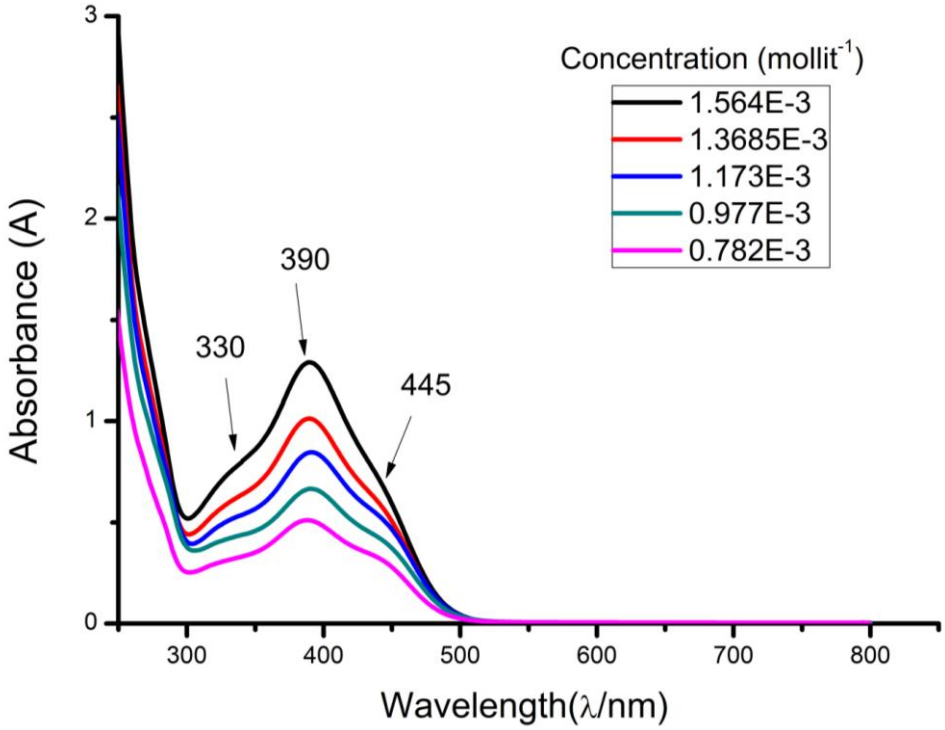



**Figure S33** UV/vis spectrum of compound **5.**

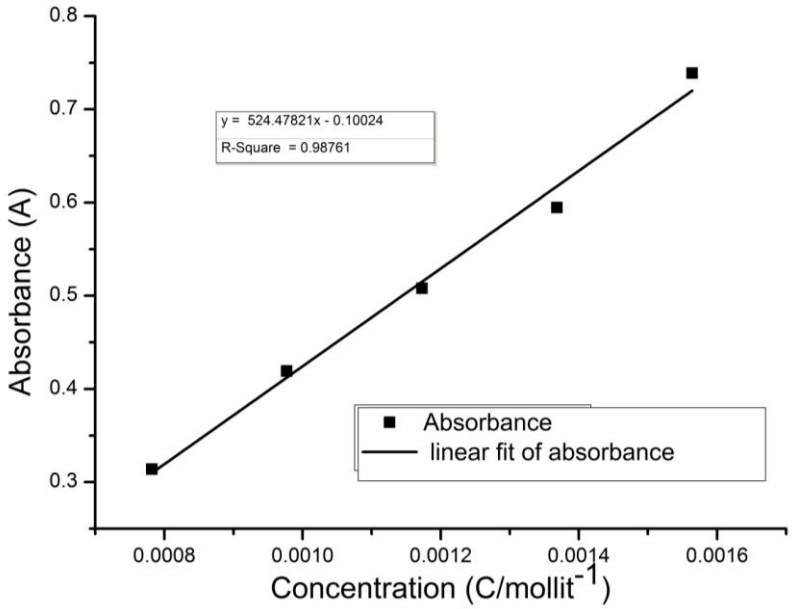



**Figure S34** Linear regression of **5** at 330 nm.

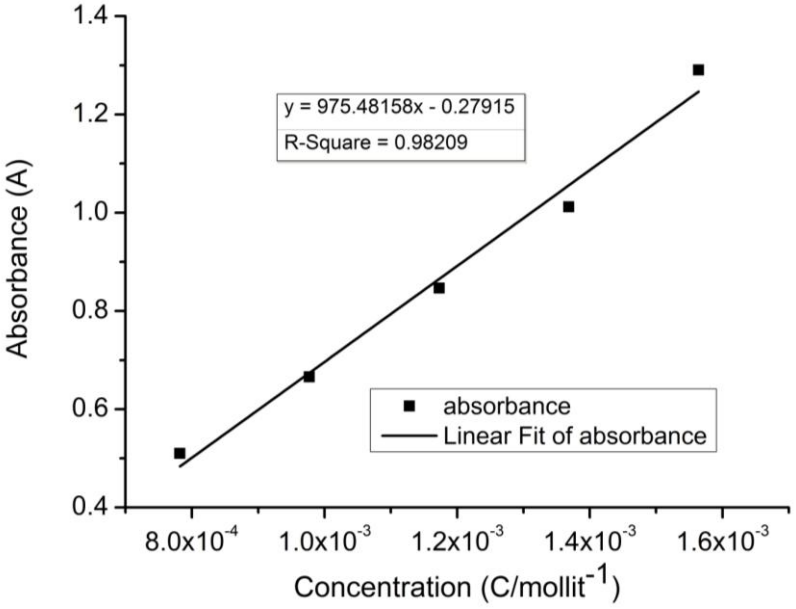



**Figure S35** Linear regression of **5** at 390 nm.

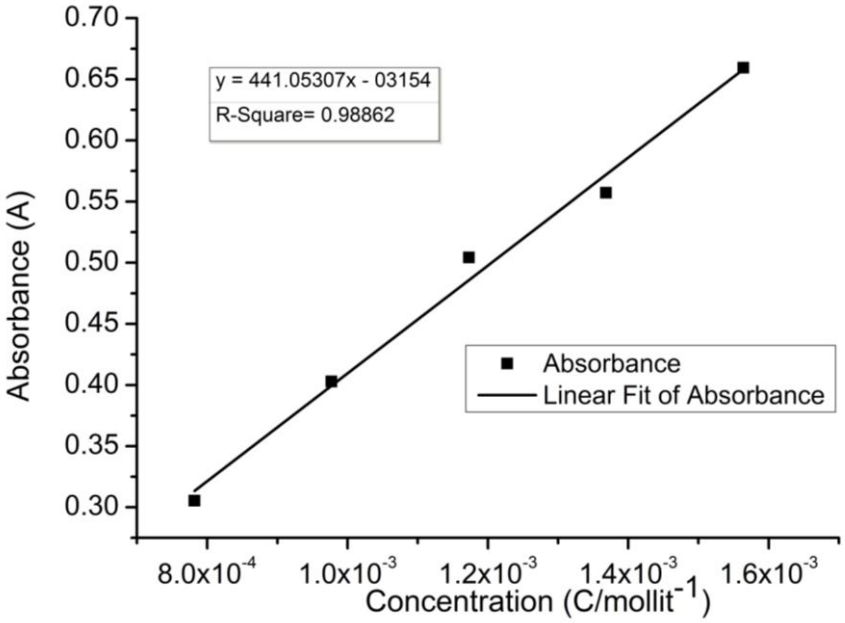



**Figure S36** Linear regression of **5** at 445 nm.

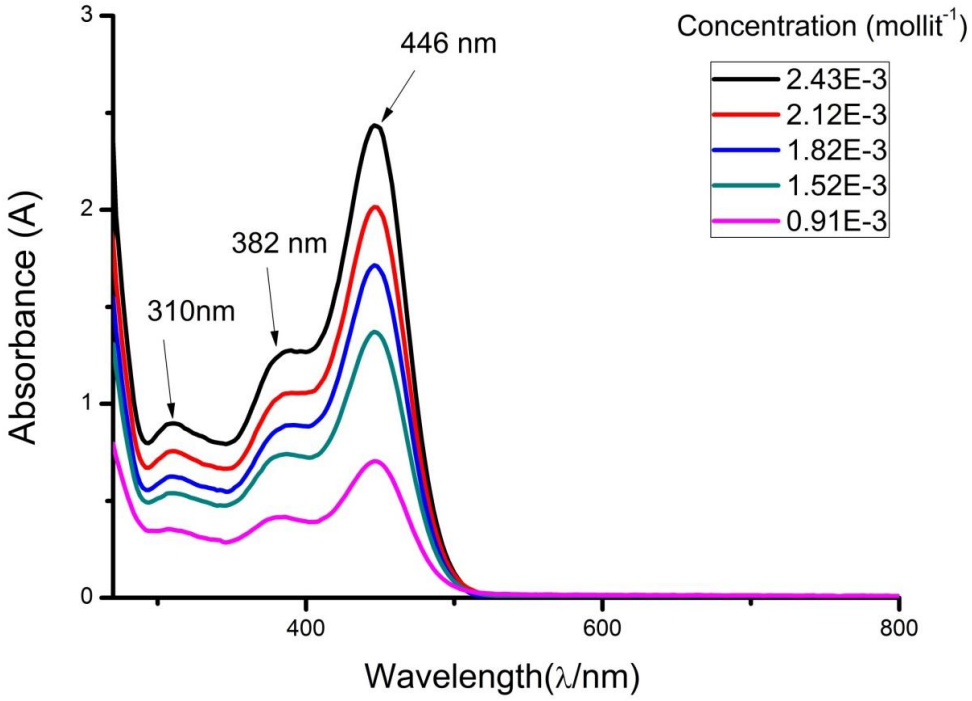



**Figure S37** UV/Vis spectrum of compound **7** in THF.

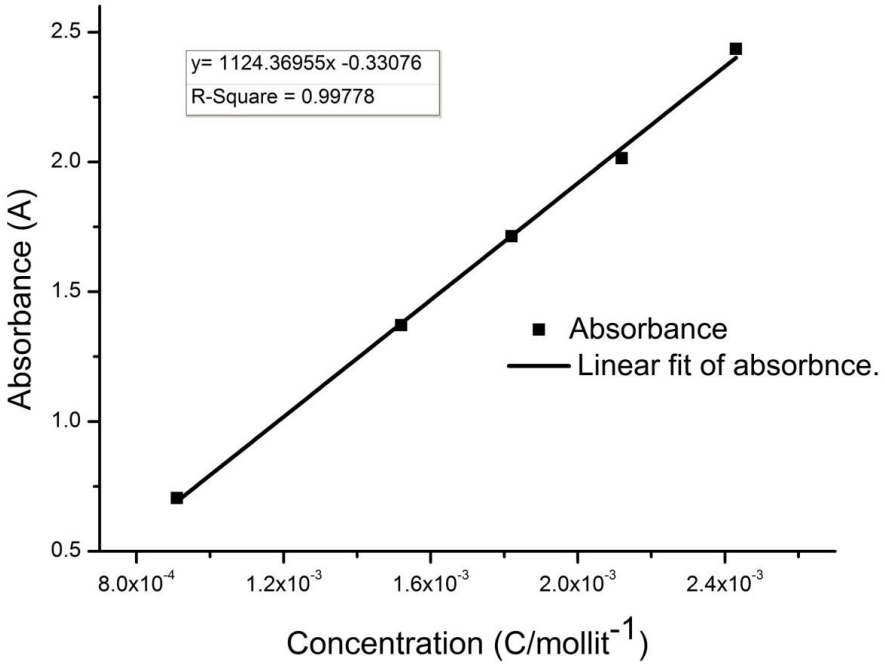



**Figure S38** Linear regression of compound **7** at 446 nm.

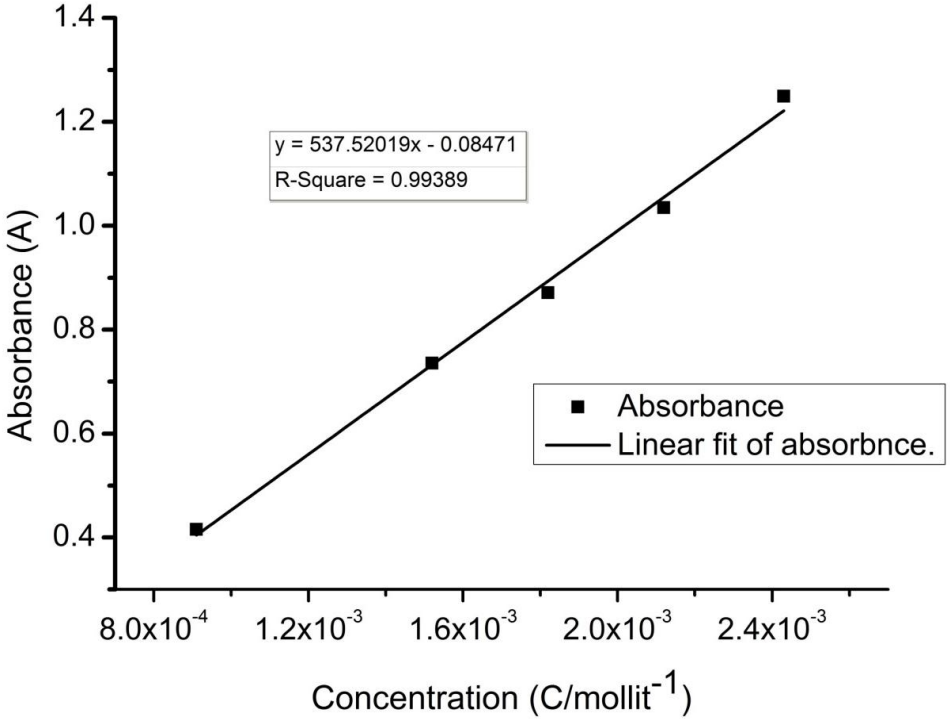



**Figure S39** Linear regression of compound **7** at 382 nm.

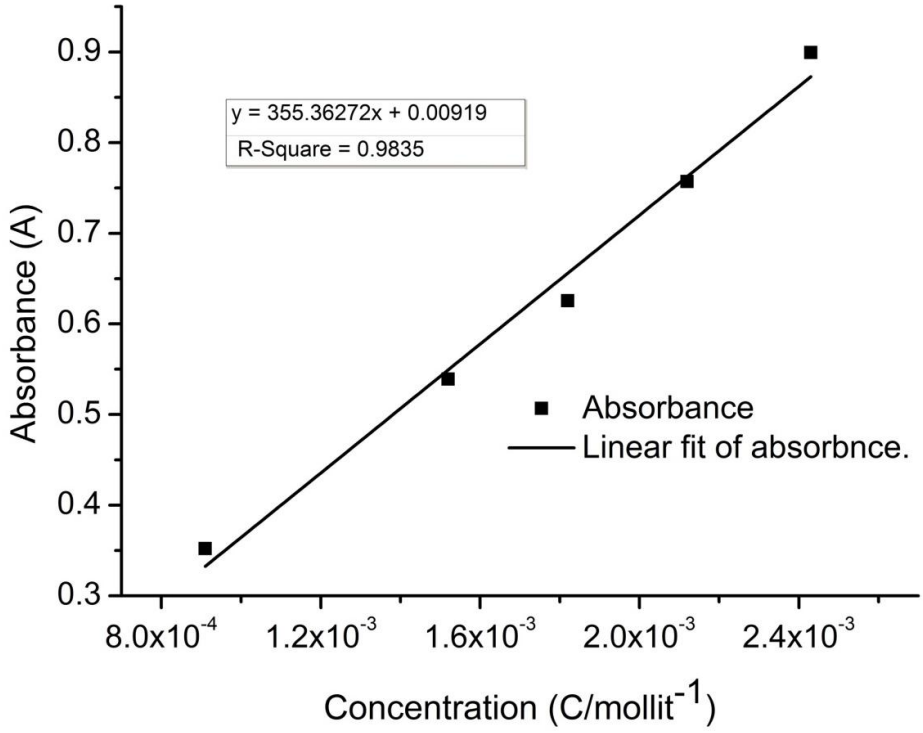



**Figure S40** Linear regression of compound **7** at 310 nm.

## NMR Simulation

Simulated NMR spectra of **6** for the AA'XX' spin system were calculated using SIMPSON 4.2.1[S2] using a 4-spin system (two $^{1}$H atoms and two $^{31}$P atoms) and acquisition parameters (spectral width and acquisition time) same as that used for the experiment. Simulated spectra were processed using Nmrglue[S3] and plotted using Matplotlib 2.0.2 in Python 3.6. The same chemical shift was used for the two $^{31}$P as well as the $^{1}$H atoms. The pairwise *J*-couplings between the atoms ($^{1}J_{(^{31}P,\ ^{31}P)}$, $^{3}J_{(^{1}H,\ ^{1}H)}$, $^{1}J_{(^{31}P,\ ^{1}H)}$, $^{2}J_{(^{31}P,\ ^{1}H)}$) were varied around the values calculated based on the known dependence of the splitting pattern on the values of these couplings. The values that fit both the multiplet pattern and the intensities are reported along with the simulated spectra in Figures S41 and S42.

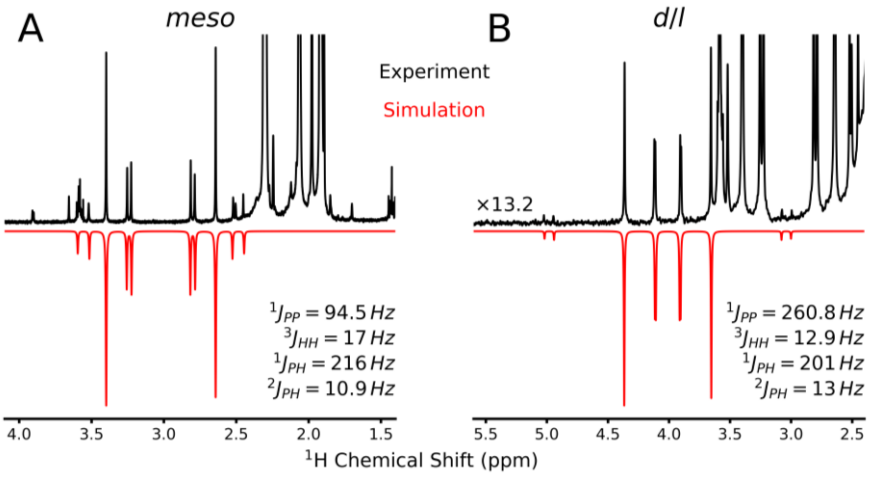



**Figure S41** Comparison between the experimental (black, upper curve) and simulated (red, lower curve) $^{1}$H NMR spectrum for the *meso* (A) and the *d*/*l* (B) compounds. The scalar couplings used for the simulations are shown at the lower right.

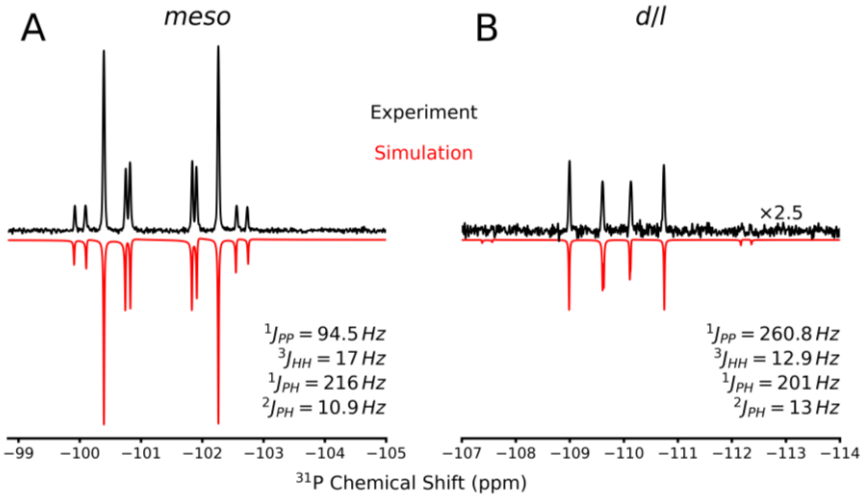



**Figure S42** Comparison between the experimental (black, upper curve) and simulated (red, lower, inverted curve) $^{31}$P NMR spectrum for the *meso* (A) and the *d*/*l* (B) compounds. The scalar couplings used for the simulations are shown at the lower right.

**Crystallographic Details**

Single crystal X-ray data of **3**, **5-7** were collected at 100 K and **4** collected at 151 K on a Bruker SMART APEX2 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography.[S4] Data integration and reduction were processed with SAINT software.[S5] An empirical absorption correction was applied to the collected reflections with SADABS.[S6] The structure was solved by direct methods using SHELXT[S7] and refined by full matrix least-squares method based on $F^2$ using SHELXL-2016[S7] via the Olex-2 software.[S8] All non-hydrogen-atoms were refined with anisotropic displacement parameters. Hydrogens were fixed in their ideal geometries, and their contributions included in the refinement. The program Diamond 3.2k version is used for the creating crystallographic figures.[S9]

**Table S3** Crystal data and structure refinement for compound **3** (CCDC: 1588456)

| | |
|---|---|
| Identification code | VC_AJ_180617 |
| Empirical formula | $C_{55}H_{62}N_2P_2$ |
| Formula weight | 813.00 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 10.9502(8) |
| b/Å | 20.9614(14) |
| c/Å | 20.7528(17) |
| α/° | 90 |
| β/° | 97.766(6) |
| γ/° | 90 |
| Volume/Å$^3$ | 4719.7(6) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.144 |
| μ/mm$^{-1}$ | 0.130 |
| F(000) | 1744.0 |
| Crystal size/mm$^3$ | 0.2 × 0.18 × 0.16 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.774 to 51.344 |
| Index ranges | -13 ≤ h ≤ 13, -25 ≤ k ≤ 25, -25 ≤ l ≤ 24 |
| Reflections collected | 58867 |
| Independent reflections | 8812 [$R_{int}$ = 0.2318, $R_{sigma}$ = 0.1292] |
| Data/restraints/parameters | 8812/0/548 |
| Goodness-of-fit on $F^2$ | 1.020 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1019, $wR_2$ = 0.2455 |
| Final R indexes [all data] | $R_1$ = 0.1815, $wR_2$ = 0.3108 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.56/-0.42 |

**Table S4** Crystal data and structure refinement for compound **4** (CCDC: 1588457)

| | |
|---|---|
| Identification code | sh3914 |
| Empirical formula | $C_{48}H_{52}OP_2$ |
| Formula weight | 706.83 |
| Temperature/K | 151.25 |
| Crystal system | orthorhombic |
| Space group | Pbca |
| a/Å | 16.9466(7) |
| b/Å | 20.6986(9) |
| c/Å | 23.0289(10) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 8077.9(6) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.162 |
| μ/mm$^{-1}$ | 0.142 |
| F(000) | 3024.0 |
| Crystal size/mm$^3$ | 0.442 × 0.27 × 0.154 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.538 to 55.948 |
| Index ranges | -22 ≤ h ≤ 21, -26 ≤ k ≤ 27, -30 ≤ l ≤ 27 |
| Reflections collected | 139724 |
| Independent reflections | 9733 [$R_{int}$ = 0.0620, $R_{sigma}$ = 0.0284] |
| Data/restraints/parameters | 9733/0/480 |
| Goodness-of-fit on F$^2$ | 1.025 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0616, $wR_2$ = 0.1624 |
| Final R indexes [all data] | $R_1$ = 0.0822, $wR_2$ = 0.1791 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.94/-0.55 |

**Table S5** Crystal data and structure refinement for compound **5** (CCDC: 1588458)

| | |
|---|---|
| Identification code | VC_AJ_SLNF |
| Empirical formula | $C_{55}H_{64}N_2OP_2$ |
| Formula weight | 831.02 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 16.2280(18) |
| b/Å | 16.3739(19) |
| c/Å | 17.6769(19) |
| α/° | 90 |
| β/° | 93.710(8) |
| γ/° | 90 |
| Volume/Å$^3$ | 4687.2(9) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.178 |
| μ/mm$^{-1}$ | 0.133 |
| F(000) | 1784.0 |
| Crystal size/mm$^3$ | 0.16 × 0.13 × 0.11 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.302 to 50.844 |
| Index ranges | $-19 \le h \le 19$, $-19 \le k \le 19$, $-21 \le l \le 21$ |
| Reflections collected | 50415 |
| Independent reflections | 8602 [$R_{int}$ = 0.1256, $R_{sigma}$ = 0.0828] |
| Data/restraints/parameters | 8602/0/561 |
| Goodness-of-fit on $F^2$ | 1.012 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0549, $wR_2$ = 0.1173 |
| Final R indexes [all data] | $R_1$ = 0.1117, $wR_2$ = 0.1454 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.35/-0.38 |

**Table S6** Crystal data and structure refinement for compound **6** (CCDC: 1588459)

| | |
|---|---|
| Identification code | DD_701 |
| Empirical formula | $C_{48}H_{52}P_2$ |
| Formula weight | 690.83 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 8.3846(12) |
| b/Å | 21.347(3) |
| c/Å | 11.6195(15) |
| α/° | 90 |
| β/° | 111.081(9) |
| γ/° | 90 |
| Volume/Å$^3$ | 1940.5(5) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.182 |
| μ/mm$^{-1}$ | 0.145 |
| F(000) | 740.0 |
| Crystal size/mm$^3$ | ? × ? × ? |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.816 to 52.21 |
| Index ranges | $-10 \le h \le 10$, $-26 \le k \le 26$, $-14 \le l \le 14$ |
| Reflections collected | 26426 |
| Independent reflections | 3854 [$R_{int}$ = 0.0631, $R_{sigma}$ = 0.0396] |
| Data/restraints/parameters | 3854/0/236 |
| Goodness-of-fit on F$^2$ | 1.042 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0421, $wR_2$ = 0.1039 |
| Final R indexes [all data] | $R_1$ = 0.0594, $wR_2$ = 0.1147 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.33/-0.28 |

**Table S7** Crystal data and structure refinement for compound **7** (CCDC: 1588460)

| | |
|---|---|
| Identification code | VC_AJ_689R |
| Empirical formula | $C_{31}H_{37}N_2P$ |
| Formula weight | 468.59 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 8.304(3) |
| b/Å | 23.286(8) |
| c/Å | 13.900(5) |
| α/° | 90 |
| β/° | 90.34(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 2687.8(17) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.158 |
| μ/mm$^{-1}$ | 0.123 |
| F(000) | 1008.0 |
| Crystal size/mm$^3$ | 0.19 × 0.16 × 0.14 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.412 to 59.208 |
| Index ranges | $-11 \le h \le 11$, $-31 \le k \le 32$, $-18 \le l \le 19$ |
| Reflections collected | 47573 |
| Independent reflections | 7476 [$R_{int}$ = 0.0829, $R_{sigma}$ = 0.0661] |
| Data/restraints/parameters | 7476/0/317 |
| Goodness-of-fit on F$^2$ | 1.022 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0556, $wR_2$ = 0.1330 |
| Final R indexes [all data] | $R_1$ = 0.1245, $wR_2$ = 0.1634 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.26/-0.31 |

**Computational Calculation**

*Computational Method:*

All theoretical calculations, in this paper are carried out using the Gaussian16 suite of program.[S10] The full geometry optimizations of **1-7** and were performed at B3LYP/6-311G(d,p) level of theory. Frequency analyses were performed to determine the ΔE, ΔH, and ΔG relative energies, as given in Table S8 in solution (CPCM method, Solvent = tetrahydrofuran) at B3LYP/6-311G(d,p) level of theory including D3 dispersion correction by Grimme.[S11,S12] Wiberg bond orders (WBI) as a criterion to estimate the bond orders of chemical structures were also calculated within the natural bond orbital (NBO) analysis for **1-7** (Table S8).[S13] The spin-spin couplings were calculated by the GIAO method (Solvent = benzene) for ***meso*-6** and ***d/l*-6** and selected parameters at B3LYP/6-311G(d,p) level of theory are given in Table S10. The GaussView 5.0 program was employed for visualization of the final geometries of the optimized structures.[S14]

**Table S8** Selected structural parameters of the compounds **1-7** at the B3LYP/6-311G(d,p) level of theory.

| | $P^1$-$P^2$ | $P^1$-$P^2$ (WBI) | $P^1$-$C^{NHC}$ | $P^1$-$C^{NHC}$ (WBI) | C-$P^1$-$P^2$-C (Dihedral) | Pyramidalization $P^1$-NHC | Charge $P^1$ | Charge $P^2$ | Hybridization $P^1$ | Hybridization $P^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 2.054 | 1.812 | - | - | 179.9 | - | 0.280 | 0.326 | *16.54% s; 82.85% p; 0.60% d* | *17.67% s; 81.76% p; 0.58% d* |
| **3** | 2.183 | 1.116 | 1.899 | 0.849 | 149.9 | 319.0 | 0.494 | -0.116 | *19.79% s; 79.88% p; 0.34% d* | *11.67% s; 87.77% p; 0.56% d* |
| | $P^1$-$P^2$ | $P^1$-$P^2$ (WBI) | $P^1$=O | $P^1$=O (WBI) | C-P1-$P^2$-C (Dihedral) | Pyramidalization $P^2$ | Charge $P^1$ | Charge $P^2$ | Hybridization $P^1$ | Hybridization $P^2$ |
| **4** | 2.251 | 0.870 | 1.510 | 1.252 | 170.0 | 291.7 | 1.410 | 0.258 | *22.86% s; 76.21% p; 0.93% d* | *10.64% s; 88.81% p; 0.54% d* |
| **5** | 2.159 | 1.092 | 1.539 | 0.969 | 174.3 | - | 1345 | -0.187 | *32.83% s; 66.43% p; 0.74% d* | *11.72% s; 87.72% p; 0.56% d* |
| ***meso*-6** | 2.298 | 0.954 | - | - | 179.9 | 290.9 | 0.296 | 0.296 | *10.40% s; 89.15% p; 0.45% d* | *10.40% s; 89.15% p; 0.45% d* |
| ***d/l*-6** | 2.289 | 0.950 | - | - | 176.6 | 294.3 | 0.297 | 0.297 | *11.45% s; 88.08% p; 0.46% d* | *11.45% s; 88.08% p; 0.46% d* |
| | $P^1$-$C^1$ | $P^1$-$C^1$ (WBI) | $P^1$-C8 | $P^1$-C8 (WBI) | C1-P1-C8 (Angle) | - | Charge $P^1$ | Charge $C^1$ | Hybridization $P^1$ | Hybridization $C^1$ |
| **7** | 1.792 | 1.188 | 1.861 | 0.976 | 102.3 | - | 0.154 | 0.152 | *16.70% s; 82.53% p; 0.78% d* | *41.44% S; 58.50% p; 0.06% d* |

**Table S9** Thermodynamic values of the reactions at the B3LYP-D3/6-311G(d,p) level of theory (CPCM method, Solvent = THF).

| | ΔE | ΔH | ΔG |
|---|---|---|---|
| **1 + 2 → 3** | **-22.7** | **-22.3** | **-6.7** |
| **1 + $H_2O$ → 4** | **-25.6** | **-25.3** | **-18.9** |
| **3 + $H_2O$ → 4 + 2** | **-2.9** | **-3.0** | **-12.1** |
| **3 + $H_2O$ → 5** | **-22.4** | **-25.1** | **-11.9** |
| **4 + 2 → 5** | **-19.4** | **-22.1** | **+0.15** |
| **1 + $NH_3BH_3$ → *dl*6 + $NH_2BH_2$** | **-21.2** | **-20.3** | **-22.9** |
| **3 + 2$NH_3BH3$ → *dl*6 + 10 + 2$NH_2BH_2$** | **-0.9** | **-1.7** | **-17.7** |
| ***meso*6 → *dl*6** | **+0.96** | **+0.34** | **+2.3** |

**Table S10** Selected *spin-spin* coupling values for the compounds ***meso*-6** (Left) and ***d/l*-6** (Right) at the B3LYP/6-311G(d,p) level of theory (CPCM, Solvent = Benzene).

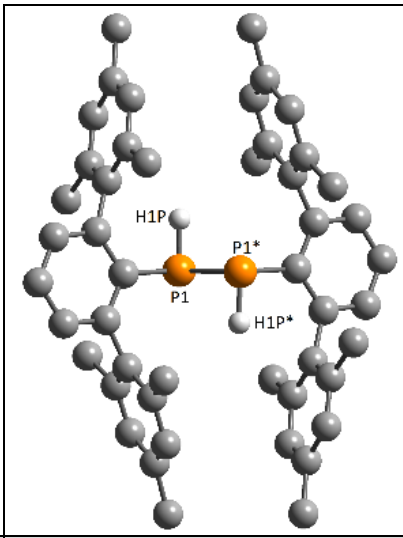
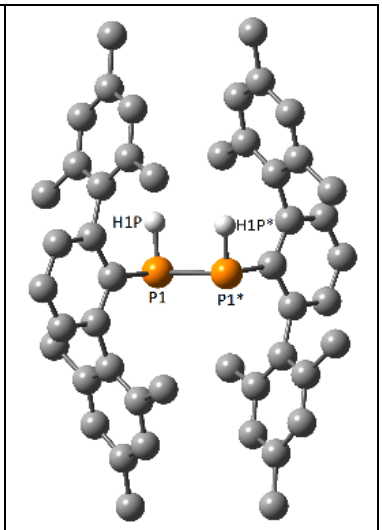
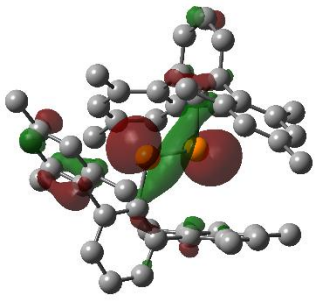
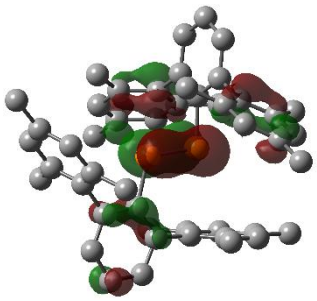
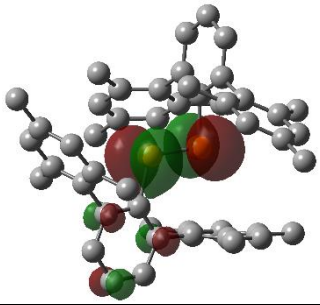
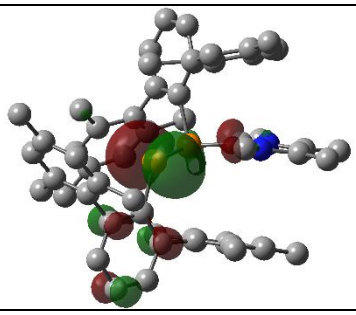
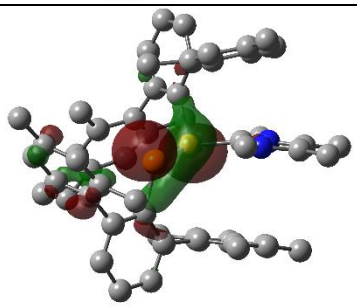
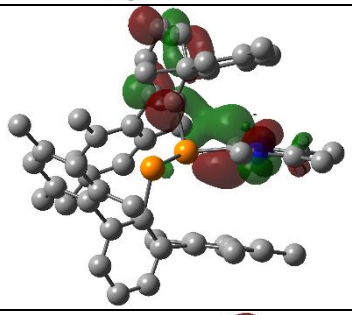
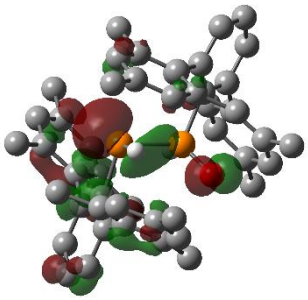
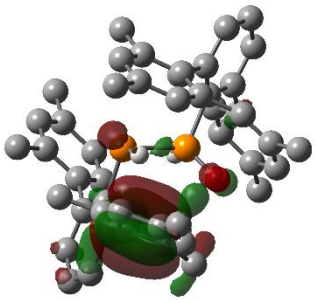
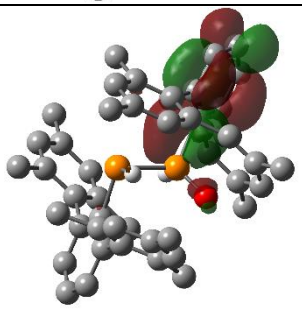
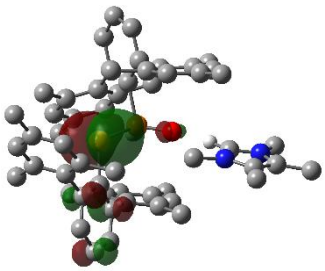
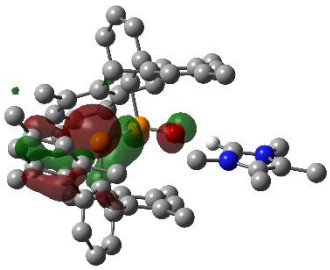
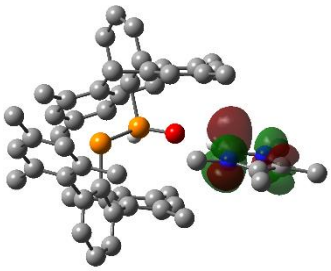
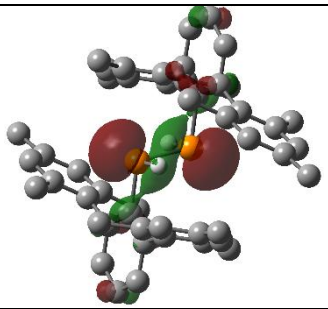
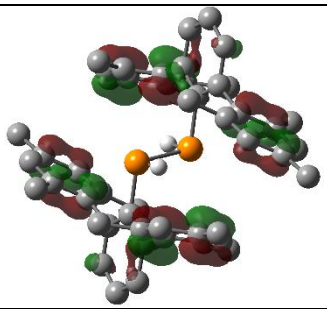
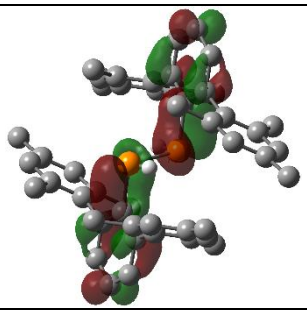
| |  |  |
|---|---|---|
| $^1J_{(P1\text{-}P1^*)}$ | 91.9 Hz | 315.0 Hz |
| $^3J_{(H1P\text{-}H1P^*)}$ | 12.2 Hz | 13.1 Hz |
| $^1J_{(P1\text{-}H1P)}$ | 155.0 Hz | 145.0 Hz |
| $^2J_{(P1^*\text{-}H1P^*)}$ | 155.0 Hz | 145.3 Hz |

**Table S11** Selected frontier molecular orbitals of the compounds **1-7** at the B3LYP/6-311G(d,p) level of theory.

| | HOMO | HOMO-1 | LUMO |
|---|---|---|---|
| **1** |  |  |  |
| **3** |  |  |  |
| **4** |  |  |  |
| **5** |  |  |  |
| ***meso*-6** |  |  |  |

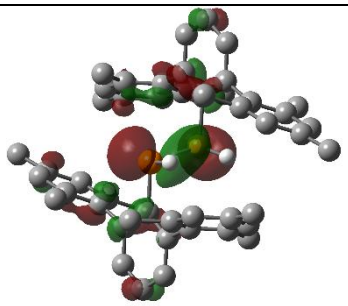
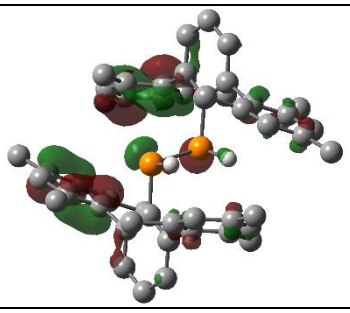
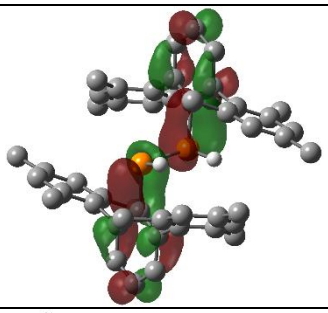
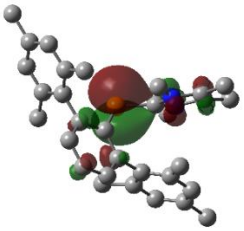
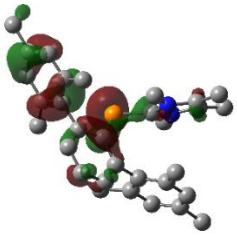
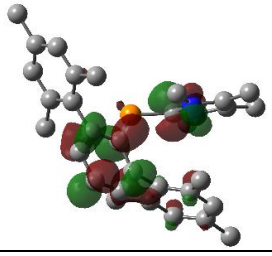
| | | | |
|---|---|---|---|
| ***d*/*l*-6** |  |  |  |
| **7** |  |  |  |

**Table S12** Cartesian coordinates and energy values of **1** in THF.

P,1.159223,0.114924,-0.123598
P,-0.875486,-0.090906,0.071202
C,-1.335805,-0.19189,1.864526
C,-2.745776,-0.255225,2.053124
C,-3.27719,-0.367631,3.340513
C,-2.4481,-0.418333,4.452792
C,-1.071171,-0.352986,4.278913
C,-0.497059,-0.237862,3.008708
C,1.000036,-0.171197,2.972793
C,1.75366,-1.360579,2.919227
C,3.145052,-1.283396,2.970956
C,3.813503,-0.06275,3.079984
C,3.047777,1.099389,3.147411
C,1.651758,1.069714,3.099422
C,0.875462,2.363998,3.162646
C,5.322401,-0.009518,3.115459
C,1.080573,-2.70746,2.79956
C,-3.7299,-0.202424,0.916559
C,-4.238755,1.038259,0.482954
C,-5.20053,1.061483,-0.526734
C,-5.679758,-0.108917,-1.118245
C,-5.170392,-1.324698,-0.667239
C,-4.206433,-1.394523,0.342023
C,-3.680293,-2.740379,0.782621
C,-6.724496,-0.050734,-2.20711
C,-3.746472,2.336582,1.078091
C,1.210257,0.180639,-1.992348
C,1.260893,1.436082,-2.635712
C,1.422537,1.489761,-4.02417
C,1.552592,0.326506,-4.774159
C,1.531158,-0.908339,-4.136115
C,1.369935,-1.001601,-2.749346
C,1.400332,-2.366795,-2.123377
C,0.258282,-3.194062,-2.168195
C,0.323799,-4.472793,-1.614142
C,1.490412,-4.966875,-1.026975
C,2.612944,-4.142852,-1.013755
C,2.592163,-2.853045,-1.552884
C,3.849252,-2.014965,-1.50938
C,1.524971,-6.348656,-0.418498
C,-1.028858,-2.72274,-2.80241
C,1.168557,2.728144,-1.875101
C,2.323775,3.285876,-1.289704
C,2.225837,4.508873,-0.62383
C,1.019375,5.201799,-0.524446
C,-0.106664,4.642835,-1.12729
C,-0.05516,3.422586,-1.805479
C,-1.307934,2.870552,-2.442641
C,0.938167,6.511965,0.22226
C,3.66231,2.588595,-1.365697
H,-4.354317,-0.413552,3.457774
H,-2.869829,-0.507096,5.447973
H,-0.413303,-0.388889,5.14056
H,3.721149,-2.203321,2.929705
H,3.546807,2.058891,3.245513
H,1.541817,3.203751,3.367622
H,0.106132,2.340326,3.938544
H,0.37055,2.565069,2.212787
H,5.746514,-0.190612,2.122182

H,5.73234,-0.770115,3.785713
H,5.678877,0.965616,3.453694
H,1.821638,-3.50776,2.768086
H,0.482539,-2.772562,1.88618
H,0.406897,-2.897801,3.639803
H,-5.588313,2.020958,-0.857411
H,-5.530774,-2.248114,-1.110774
H,-2.603781,-2.822348,0.603635
H,-3.837733,-2.907631,1.851691
H,-4.173711,-3.546817,0.237042
H,-6.37854,0.545436,-3.057086
H,-7.649985,0.408721,-1.845457
H,-6.969863,-1.048318,-2.576542
H,-2.698665,2.517613,0.818123
H,-3.806279,2.332216,2.169381
H,-4.333104,3.179384,0.707885
H,1.455142,2.458723,-4.510956
H,1.681728,0.382489,-5.849472
H,1.650895,-1.82034,-4.711109
H,-0.560207,-5.103133,-1.649803
H,3.538054,-4.51249,-0.581082
H,4.717813,-2.63553,-1.279921
H,3.779942,-1.241848,-0.737143
H,4.031806,-1.507207,-2.458899
H,2.550638,-6.690231,-0.263704
H,1.021426,-6.363672,0.554225
H,1.018048,-7.078091,-1.055995
H,-1.822129,-3.458628,-2.657385
H,-0.912604,-2.560655,-3.878042
H,-1.363251,-1.775498,-2.371187
H,3.121113,4.934495,-0.179496
H,-1.05324,5.172961,-1.077365
H,-1.565071,1.890452,-2.030301
H,-2.154169,3.53929,-2.274496
H,-1.189228,2.738789,-3.521559
H,1.797606,7.150707,0.001358
H,0.925259,6.348132,1.305265
H,0.03197,7.06346,-0.03741
H,3.701484,1.737399,-0.67808
H,4.469103,3.272087,-1.09405
H,3.862618,2.202551,-2.367442

Zero-point correction= 0.829936 (Hartree/Particle)
Thermal correction to Energy= 0.878296
Thermal correction to Enthalpy= 0.879240
Thermal correction to Gibbs Free Energy= 0.743189
Sum of electronic and zero-point Energies= -2541.790561
Sum of electronic and thermal Energies= -2541.742201
Sum of electronic and thermal Enthalpies= -2541.741257
Sum of electronic and thermal Free Energies= -2541.877308

**Table S13** Cartesian coordinates and energy values of **2** in THF.

N,1.060515,-0.708087,0.000098
N,-1.060524,-0.708066,0.000074
C,-0.000016,-1.567764,0.000189
C,0.680674,0.639596,-0.000023
C,-0.680662,0.639609,-0.000094
C,1.659023,1.76642,-0.000145
H,2.307357,1.745464,0.882682

H,1.138676,2.725506,-0.001679
H,2.309091,1.743575,-0.88163
C,-1.659006,1.766438,0.00018
H,-2.309197,1.743905,-0.881224
H,-1.138658,2.725524,-0.00109
H,-2.307214,1.745166,0.88309
C,-2.435357,-1.176807,-0.000203
H,-2.972771,-0.832791,0.88848
H,-2.97226,-0.833204,-0.889354
H,-2.401529,-2.264078,0.000055
C,2.435347,-1.176811,0.000013
H,2.972241,-0.833658,-0.889325
H,2.972762,-0.832342,0.888511
H,2.401548,-2.264086,0.000787

| | |
|---|---|
| Zero-point correction= | 0.181307 (Hartree/Particle) |
| Thermal correction to Energy= | 0.191583 |
| Thermal correction to Enthalpy= | 0.192527 |
| Thermal correction to Gibbs Free Energy= | 0.146438 |
| Sum of electronic and zero-point Energies= | -383.374856 |
| Sum of electronic and thermal Energies= | -383.364580 |
| Sum of electronic and thermal Enthalpies= | -383.363635 |
| Sum of electronic and thermal Free Energies= | -383.409725 |

**Table S14** Cartesian coordinates and energy values of **3** in THF.

P,-0.560779,-0.434131,0.401237
P,1.083137,0.653049,-0.539095
N,-2.600831,0.896943,-1.338136
N,-3.32616,-0.758958,-0.157091
C,1.432425,-1.620152,-2.469546
C,-1.818181,2.615552,1.63102
C,0.062578,-2.230455,-2.360919
C,-3.181031,2.846206,1.367407
C,-0.865909,3.595717,1.264068
C,0.554177,-1.817475,2.989181
C,-1.393752,1.483082,2.529849
C,3.225149,-0.028827,-2.091651
C,-0.28175,-0.580747,3.191258
C,-0.75973,0.26703,2.149141
C,-3.565661,4.003003,0.678778
H,-4.621186,4.166846,0.479248
C,1.90945,-0.485347,-1.758272
C,-1.295108,4.737949,0.585177
H,-0.556321,5.484947,0.309938
C,-0.960588,-1.789504,-3.219911
C,-0.145726,-3.3773,-1.568252
C,-2.638328,4.961633,0.275875
C,0.00295,-3.106019,3.097875
C,1.959233,-1.670875,2.898733
C,2.220607,-4.100335,2.880122
C,3.867958,1.160774,-1.431165
C,2.757691,-2.811779,2.830317
H,3.834287,-2.688833,2.759419
C,0.843848,-4.222378,3.02924
H,0.403806,-5.213066,3.108689
C,-2.239861,0.041737,-0.349335
C,2.248089,-2.258467,-3.416011
H,1.848394,-3.125596,-3.932882
C,3.688241,2.458163,-1.94907

C,3.995691,-0.681497,-3.053081
H,4.987107,-0.296061,-3.269348
C,-1.816452,2.018841,-1.85283
H,-2.171375,2.946651,-1.407389
H,-1.924299,2.058179,-2.936533
H,-0.766729,1.859703,-1.597483
C,2.612569,-0.310659,2.92831
H,2.403319,0.250686,2.011824
H,3.694644,-0.408917,3.025999
H,2.249013,0.286548,3.768543
C,3.523037,-1.806137,-3.719105
H,4.130883,-2.312231,-4.460627
C,-1.368773,-4.046649,-1.640697
H,-1.513788,-4.937152,-1.034638
C,-3.906686,0.648754,-1.748341
C,-1.606261,1.763241,3.889108
H,-2.092095,2.697233,4.150113
C,0.944546,-3.897889,-0.666458
H,1.833891,-4.174297,-1.239706
H,0.607548,-4.775491,-0.112239
H,1.252413,-3.139396,0.05659
C,-2.175482,-2.482866,-3.259115
H,-2.953694,-2.141101,-3.936504
C,4.344568,3.53202,-1.344979
H,4.192488,4.530857,-1.745215
C,0.583714,3.479092,1.666625
H,0.679306,3.406512,2.754378
H,1.146162,4.3527,1.332729
H,1.060294,2.594748,1.238048
C,-4.366045,-0.393844,-1.00093
C,-0.509534,-0.252576,4.532124
H,-0.132968,-0.92282,5.29696
C,-0.733723,-0.623463,-4.153103
H,-0.25821,0.214494,-3.640527
H,-1.675475,-0.285389,-4.593308
H,-0.065861,-0.906124,-4.973361
C,4.739906,0.963049,-0.344055
C,-4.259138,1.91786,1.880439
H,-3.924959,0.881885,1.917635
H,-5.154307,1.976158,1.257
H,-4.552059,2.190993,2.900164
C,-1.470839,-3.348723,3.339468
H,-2.042263,-2.423013,3.368177
H,-1.622514,-3.858404,4.296663
H,-1.894065,-3.995691,2.564629
C,-1.188136,0.902539,4.890072
H,-1.364733,1.140913,5.933134
C,5.374961,2.064078,0.234522
H,6.034969,1.90283,1.082493
C,3.112609,-5.313935,2.778937
H,3.441545,-5.474525,1.7466
H,2.594734,-6.218626,3.105341
H,4.01209,-5.199269,3.390168
C,2.797546,2.702193,-3.144315
H,3.144065,2.147734,-4.021251
H,2.773462,3.763787,-3.400536
H,1.774659,2.374258,-2.938592
C,-2.39539,-3.621687,-2.48653
C,-4.579818,1.452501,-2.80812
H,-4.574177,2.518892,-2.565354
H,-5.618058,1.138885,-2.917085

H,-4.092999,1.331409,-3.780618
C,-3.065864,6.215754,-0.449443
H,-4.147994,6.243801,-0.59428
H,-2.592857,6.289536,-1.433912
H,-2.780912,7.111845,0.110421
C,-3.378787,-1.872117,0.779645
H,-2.370887,-2.268811,0.885643
H,-4.033307,-2.646316,0.384112
H,-3.744909,-1.544997,1.755036
C,5.188404,3.358886,-0.24751
C,5.009082,-0.424198,0.188191
H,4.080141,-0.967514,0.37315
H,5.578049,-0.378707,1.119394
H,5.585393,-1.017508,-0.528755
C,-5.689448,-1.080612,-1.001445
H,-5.607906,-2.122301,-1.325936
H,-6.373353,-0.576574,-1.684319
H,-6.147759,-1.074727,-0.007952
C,-3.678798,-4.411502,-2.603574
H,-3.542956,-5.290292,-3.243545
H,-4.480233,-3.812897,-3.044257
H,-4.02011,-4.778,-1.630773
C,5.90704,4.533674,0.373542
H,6.827311,4.770428,-0.172741
H,6.186348,4.326984,1.409457
H,5.284916,5.432664,0.364857

Zero-point correction= 1.015711 (Hartree/Particle)
Thermal correction to Energy= 1.075962
Thermal correction to Enthalpy= 1.076906
Thermal correction to Gibbs Free Energy= 0.919413
Sum of electronic and zero-point Energies= -2925.201595
Sum of electronic and thermal Energies= -2925.141344
Sum of electronic and thermal Enthalpies= -2925.140400
Sum of electronic and thermal Free Energies= -2925.297893

**Table S15** Cartesian coordinates and energy values of **4** in THF.

P,0.506993,-0.642716,-0.572968
P,-0.823216,0.619807,0.733355
O,0.00098,-0.930133,-1.966539
C,-0.947781,2.186223,-0.270445
C,0.036168,3.184951,-0.068505
C,-0.087154,4.421043,-0.70993
H,0.677298,5.172457,-0.54573
C,-1.172607,4.696102,-1.530697
H,-1.261654,5.661388,-2.016888
C,-2.151369,3.728669,-1.710369
H,-3.01227,3.9376,-2.335775
C,-2.064888,2.473303,-1.094414
C,1.230819,3.002337,0.823672
C,1.109531,3.181769,2.219407
C,2.249976,3.09253,3.017113
H,2.149388,3.235507,4.089214
C,3.514168,2.847282,2.478044
C,3.61689,2.702256,1.096813
H,4.59155,2.52918,0.650566
C,2.501389,2.783533,0.257065
C,-0.219859,3.496101,2.86271
H,-0.738682,4.303067,2.339484

H,-0.082814,3.79576,3.903427
H,-0.881354,2.624384,2.849725
C,4.726664,2.735245,3.3708
H,4.795901,1.737344,3.817988
H,4.684109,3.455539,4.191807
H,5.649911,2.910885,2.814345
C,2.70745,2.685659,-1.238947
H,2.851581,3.679893,-1.676371
H,1.855368,2.238086,-1.751481
H,3.594105,2.091403,-1.467502
C,-3.222729,1.545335,-1.335174
C,-4.289437,1.512432,-0.414313
C,-5.41185,0.731415,-0.696252
H,-6.233228,0.721155,0.014376
C,-5.512007,-0.016616,-1.868883
C,-4.453879,0.044055,-2.77399
H,-4.517148,-0.516374,-3.702132
C,-3.312142,0.814605,-2.537527
C,-4.25096,2.316878,0.865092
H,-3.481694,1.948545,1.551735
H,-5.209893,2.26057,1.38362
H,-4.027986,3.370004,0.674982
C,-6.723183,-0.875571,-2.144411
H,-6.57961,-1.893776,-1.765219
H,-6.92061,-0.954331,-3.216148
H,-7.617568,-0.471986,-1.663673
C,-2.208201,0.838009,-3.566994
H,-1.91168,1.858782,-3.821351
H,-2.532079,0.341417,-4.484138
H,-1.322424,0.31682,-3.191829
C,1.055992,-2.171664,0.311286
C,2.364844,-2.640183,0.031953
C,2.78073,-3.861936,0.571397
H,3.784022,-4.21026,0.352569
C,1.931909,-4.626242,1.360625
H,2.267995,-5.575208,1.763999
C,0.646763,-4.171951,1.621154
H,-0.028848,-4.765534,2.226845
C,0.187208,-2.95565,1.102744
C,3.365247,-1.908999,-0.820187
C,4.351692,-1.116039,-0.201518
C,5.326657,-0.504265,-0.992903
H,6.08728,0.102376,-0.510222
C,5.358477,-0.664857,-2.377977
C,4.387799,-1.475802,-2.965299
H,4.406706,-1.632144,-4.039904
C,3.393948,-2.109468,-2.216008
C,4.380492,-0.927109,1.297677
H,5.207079,-0.276747,1.587914
H,4.499867,-1.880367,1.820282
H,3.455977,-0.474912,1.666673
C,6.406491,0.0214,-3.221231
H,7.242968,0.370964,-2.612177
H,5.987883,0.891294,-3.738867
H,6.80308,-0.64996,-3.98756
C,2.386384,-2.992679,-2.913165
H,2.285851,-3.959592,-2.413042
H,2.688581,-3.174668,-3.946269
H,1.400137,-2.519606,-2.919634
C,-1.227179,-2.581609,1.434945
C,-2.268844,-2.885869,0.537081

C,-3.585737,-2.606221,0.915344
H,-4.385869,-2.833243,0.218536
C,-3.899724,-2.054048,2.155116
C,-2.851998,-1.777789,3.035614
H,-3.073988,-1.352294,4.010121
C,-1.522703,-2.036725,2.703727
C,-1.997789,-3.513662,-0.810692
H,-1.476544,-2.820944,-1.477774
H,-2.933842,-3.805009,-1.290348
H,-1.372452,-4.405673,-0.715251
C,-5.329705,-1.774624,2.550392
H,-6.01909,-2.005422,1.736505
H,-5.46764,-0.723112,2.819052
H,-5.622953,-2.37215,3.419578
C,-0.433236,-1.735209,3.707142
H,-0.851131,-1.254134,4.593191
H,0.324809,-1.067861,3.289225
H,0.082058,-2.644725,4.029063
H,1.692796,0.121649,-0.535949
H,-2.004092,0.010619,0.254418

Zero-point correction= 0.854341 (Hartree/Particle)
Thermal correction to Energy= 0.907024
Thermal correction to Enthalpy= 0.907969
Thermal correction to Gibbs Free Energy= 0.760630
Sum of electronic and zero-point Energies= -2618.263464
Sum of electronic and thermal Energies= -2618.210780
Sum of electronic and thermal Enthalpies= -2618.209836
Sum of electronic and thermal Free Energies= -2618.357174

**Table S16** Cartesian coordinates and energy values of **5** in THF.

P,0.592069,-0.644898,0.455775
P,0.713319,1.433197,-0.118545
O,-0.662532,-1.484436,0.156207
C,3.414414,-2.136273,-2.357254
H,4.470966,-2.233592,-2.12798
C,2.867899,-0.857983,-2.462322
C,2.180938,-0.728265,2.824719
C,0.922817,0.652457,-2.986567
C,-2.18965,1.26629,2.765049
C,4.353174,-0.141915,1.674999
C,-0.171662,-0.205479,3.192908
C,2.64587,-3.288416,-2.537336
C,1.492186,-0.714777,-2.748008
C,0.884242,-0.507735,2.29689
C,3.396843,-1.11611,2.025077
C,1.295613,-3.12965,-2.834196
H,0.677684,-4.011003,-2.985732
C,-1.628803,-0.024221,2.847014
C,-0.38159,6.288683,0.249459
C,0.709495,-1.865467,-2.950894
C,2.401508,-0.619329,4.203163
H,3.402206,-0.794741,4.582839
C,-1.253986,4.373628,-0.982124
C,0.763586,1.001867,-4.334882
H,1.000635,0.258111,-5.089524
C,-3.576552,1.396646,2.627704
H,-3.998647,2.395844,2.567792
C,1.370884,-0.299977,5.074336

H,1.556262,-0.216799,6.139796
C,0.624995,1.593862,-1.961461
C,3.661814,-2.476906,1.776884
C,0.896821,5.953428,-0.195681
H,1.741015,6.568525,0.103879
C,0.04314,4.043645,-1.4153
C,0.133146,3.223756,-3.735999
H,-0.14507,4.23703,-4.008988
C,0.09649,-0.102509,4.565509
H,-0.724561,0.128993,5.235464
C,1.128726,4.850972,-1.020438
C,4.867241,-2.838549,1.170962
H,5.064915,-3.890514,0.985536
C,0.263427,2.911776,-2.382978
C,-3.853196,-0.974827,2.692962
H,-4.49653,-1.8513,2.696042
C,5.542164,-0.549203,1.065461
H,6.271958,0.207562,0.792016
C,-2.47419,-1.15228,2.826275
C,5.823248,-1.890844,0.809123
C,-1.445196,5.485452,-0.159484
H,-2.452263,5.728972,0.16838
C,-4.427512,0.293584,2.597058
C,-0.751596,-1.759569,-3.317473
H,-1.255572,-1.024287,-2.689783
H,-1.248701,-2.725929,-3.196985
H,-0.885388,-1.444066,-4.357189
C,0.358977,2.270773,-4.724392
H,0.252275,2.521751,-5.773948
C,-1.337482,2.509088,2.829468
H,-0.673269,2.497813,3.697259
H,-1.961355,3.40321,2.886833
H,-0.706342,2.587377,1.938842
C,4.122867,1.323532,1.957884
H,3.198689,1.673939,1.489026
H,4.950546,1.923888,1.5746
H,4.037003,1.515484,3.031675
C,-1.914417,-2.547055,2.969316
H,-1.234436,-2.764561,2.141829
H,-2.71795,-3.288561,2.978538
H,-1.346313,-2.657312,3.897312
C,3.755441,0.350649,-2.294531
H,4.788516,0.049338,-2.113246
H,3.423289,0.963159,-1.45177
H,3.729067,0.985421,-3.185097
C,3.271366,-4.658196,-2.422818
H,4.041358,-4.809511,-3.186673
H,2.525874,-5.448046,-2.542042
H,3.75198,-4.792739,-1.449009
C,2.668021,-3.551017,2.154655
H,2.39122,-3.490372,3.210719
H,3.082871,-4.543562,1.967104
H,1.742926,-3.458713,1.577264
C,-0.600802,7.468299,1.167051
H,-0.426319,7.192753,2.213289
H,-1.623859,7.845793,1.094493
H,0.080122,8.29034,0.930775
C,-2.435905,3.523328,-1.378805
H,-2.562838,3.485679,-2.464681
H,-3.358731,3.907377,-0.937417
H,-2.283475,2.497741,-1.031592

C,2.536163,4.5401,-1.471625
H,3.240295,5.276413,-1.078087
H,2.618284,4.536583,-2.562125
H,2.845177,3.550753,-1.123208
C,-5.927632,0.468842,2.528734
H,-6.356091,0.594114,3.52941
H,-6.414908,-0.400469,2.077982
H,-6.203618,1.354571,1.949839
C,7.138018,-2.302619,0.189511
H,7.943591,-2.29755,0.932201
H,7.433652,-1.619446,-0.611351
H,7.084311,-3.310458,-0.228547
H,1.722074,-1.413743,0.100125
N,-3.785874,-3.574996,-0.870436
N,-3.89948,-1.424467,-1.029114
C,-5.130521,-1.9168,-1.455266
C,-5.062052,-3.279998,-1.355716
C,-3.108416,-2.437392,-0.682245
H,-2.079082,-2.296094,-0.31778
C,-3.244307,-4.905283,-0.605736
H,-3.831965,-5.407911,0.163828
H,-2.219312,-4.793143,-0.258327
H,-3.250713,-5.504008,-1.517626
C,-6.063973,-4.339174,-1.666028
H,-5.703624,-5.025389,-2.438644
H,-6.986611,-3.8886,-2.030613
H,-6.313531,-4.933664,-0.781694
C,-6.231912,-1.020309,-1.907243
H,-6.5333,-0.329468,-1.114741
H,-7.106397,-1.604511,-2.192908
H,-5.931566,-0.422133,-2.772362
C,-3.485527,-0.018368,-0.9487
H,-3.519219,0.431382,-1.941099
H,-2.466926,0.006511,-0.56047
H,-4.141317,0.51803,-0.264697

Zero-point correction= 1.038753 (Hartree/Particle)
Thermal correction to Energy= 1.098433
Thermal correction to Enthalpy= 1.099377
Thermal correction to Gibbs Free Energy= 0.941391
Sum of electronic and zero-point Energies= -3001.669289
Sum of electronic and thermal Energies= -3001.609609
Sum of electronic and thermal Enthalpies= -3001.608665
Sum of electronic and thermal Free Energies= -3001.766651

**Table S17** Cartesian coordinates and energy values of ***d/l*-6** in THF.

P,0.055919,0.82572,0.788859
C,0.00169,2.364156,-0.265102
C,-3.437278,1.92558,-1.166865
C,1.231304,2.972926,-0.614486
C,-1.207294,2.992627,-0.661431
C,3.020213,2.905379,1.155126
C,2.583136,2.525967,-0.132858
C,3.482694,1.905883,-1.020442
C,-2.587352,2.566123,-0.248902
C,3.059524,1.477059,-2.406922
H,2.205222,0.796356,-2.367217
H,3.875772,0.958228,-2.912631
H,2.765383,2.329118,-3.026277

C,4.800733,1.68828,-0.609421
H,5.490202,1.216543,-1.301964
C,-5.289886,2.089969,0.413912
C,5.254189,2.063441,0.652197
C,-1.15734,4.149561,-1.44832
H,-2.090772,4.617762,-1.740621
C,1.234243,4.126834,-1.408781
H,2.187022,4.576912,-1.664311
C,-4.771603,1.695148,-0.815527
H,-5.42083,1.202031,-1.532292
C,4.342015,2.658869,1.524231
H,4.672329,2.961988,2.513916
C,-3.092325,2.969857,1.007334
C,0.051449,4.708306,-1.839465
H,0.069832,5.603998,-2.450577
C,-2.96002,1.520553,-2.543552
H,-3.00157,2.36392,-3.241426
H,-3.587466,0.724366,-2.948985
H,-1.926943,1.170537,-2.534297
C,2.099536,3.594794,2.133915
H,1.586276,4.445204,1.677964
H,2.658863,3.957651,2.998356
H,1.327969,2.909484,2.499271
C,-4.428541,2.720134,1.314874
H,-4.812774,3.045281,2.277728
C,6.691008,1.85395,1.066837
H,6.759469,1.28477,1.999179
H,7.196419,2.810239,1.237251
H,7.251569,1.314292,0.301204
C,-6.737345,1.85526,0.773208
H,-7.212137,2.775814,1.12533
H,-6.833299,1.116937,1.576347
H,-7.306598,1.490554,-0.08382
C,-2.226064,3.698266,2.008574
H,-1.420032,3.06373,2.389303
H,-2.819558,4.026947,2.863688
H,-1.751801,4.577234,1.564011
H,-1.332898,0.783128,1.063105
P,0.063992,-0.829925,-0.792155
C,0.010584,-2.364141,0.267964
C,3.492334,-1.894286,1.017565
C,-1.196739,-2.993228,0.666337
C,1.242329,-2.968008,0.622011
C,-3.07797,-2.977127,-1.007437
C,-2.577189,-2.571864,0.249477
C,-3.430187,-1.929913,1.164235
C,2.592254,-2.521221,0.135913
C,-2.957116,-1.522618,2.541591
H,-1.926083,-1.166641,2.534115
H,-3.589791,-0.730628,2.947051
H,-2.994269,-2.366874,3.238712
C,-4.762758,-1.698965,0.80747
H,-5.414294,-1.203442,1.520465
C,5.260856,-2.059704,-0.657264
C,-5.277059,-2.09529,-0.423391
C,1.246786,-4.115862,1.423828
H,2.199726,-4.563465,1.683255
C,-1.144983,-4.145944,1.460189
H,-2.077584,-4.614551,1.754181
C,4.809393,-1.676843,0.602686
H,5.499388,-1.199999,1.291102

C,-4.412971,-2.726712,-1.320481
H,-4.793009,-3.051055,-2.285252
C,3.027913,-2.910826,-1.14986
C,0.064605,-4.697901,1.856507
H,0.085298,-5.589932,2.473049
C,3.072542,-1.463284,2.404307
H,2.80946,-2.317739,3.03478
H,3.880067,-0.918158,2.895884
H,2.199715,-0.806562,2.368745
C,-2.207802,-3.705215,-2.005692
H,-1.727415,-4.578816,-1.557294
H,-2.799696,-4.041941,-2.858802
H,-1.406384,-3.067003,-2.390122
C,4.349077,-2.66621,-1.522172
H,4.680002,-2.980487,-2.508137
C,-6.727272,-1.875264,-0.781535
H,-6.827557,-1.305097,-1.710416
H,-7.24437,-2.828293,-0.932961
H,-7.254278,-1.331566,0.004324
C,6.69036,-1.828682,-1.085267
H,7.135355,-2.741051,-1.493115
H,6.752875,-1.064201,-1.867295
H,7.308017,-1.498299,-0.24787
C,2.107106,-3.609479,-2.121617
H,1.334209,-2.927732,-2.491104
H,2.665746,-3.977742,-2.984205
H,1.595267,-4.457077,-1.659000
H,-1.323371,-0.793622,-1.073869

Zero-point correction= 0.848425 (Hartree/Particle)
Thermal correction to Energy= 0.898898
Thermal correction to Enthalpy= 0.899842
Thermal correction to Gibbs Free Energy= 0.759007
Sum of electronic and zero-point Energies= -2542.992725
Sum of electronic and thermal Energies= -2542.942253
Sum of electronic and thermal Enthalpies= -2542.941308
Sum of electronic and thermal Free Energies= -2543.082143

**Table S18** Cartesian coordinates and energy values of ***meso*-6** in THF.

P,-0.168015,0.817696,0.78925
C,-0.363489,2.339537,-0.271387
C,-3.766512,1.598766,-1.08978
C,0.802659,3.054134,-0.641743
C,-1.628596,2.864051,-0.638733
C,2.621588,3.110147,1.100128
C,2.194499,2.715447,-0.188154
C,3.127123,2.18392,-1.097672
C,-2.96042,2.327518,-0.196212
C,2.73816,1.794358,-2.506889
H,1.712954,1.427704,-2.568094
H,3.403265,1.015785,-2.886495
H,2.809872,2.649974,-3.187581
C,4.463315,2.052075,-0.706384
H,5.174733,1.637414,-1.413738
C,-5.606423,1.652212,0.514558
C,4.905049,2.443727,0.553664
C,-1.692392,4.024943,-1.420234
H,-2.668485,4.412692,-1.690208
C,0.692744,4.204609,-1.431495

H,1.598319,4.733684,-1.706709
C,-5.074673,1.278026,-0.717354
H,-5.694234,0.726314,-1.416971
C,3.963313,2.959617,1.445746
H,4.28565,3.275392,2.433997
C,-3.475607,2.707618,1.060927
C,-0.5446,4.685245,-1.834512
H,-0.615526,5.580785,-2.441968
C,-3.246026,1.161789,-2.43942
H,-2.946867,2.014351,-3.055422
H,-4.008247,0.60159,-2.983563
H,-2.367762,0.518913,-2.333929
C,1.670031,3.724863,2.098991
H,1.086057,4.534516,1.654272
H,2.217579,4.128153,2.952951
H,0.959679,2.983263,2.476707
C,-4.78444,2.357554,1.394236
H,-5.17826,2.665185,2.358914
C,6.360449,2.348476,0.94383
H,6.482127,1.873438,1.921703
H,6.814596,3.342951,1.010839
H,6.932318,1.772128,0.214536
C,-7.024653,1.30269,0.897501
H,-7.534564,2.155518,1.354259
H,-7.050206,0.484726,1.625902
H,-7.606569,0.989301,0.028307
C,-2.650296,3.507956,2.042154
H,-1.789347,2.938616,2.405917
H,-3.249719,3.790963,2.909424
H,-2.256206,4.420733,1.587572
H,-1.553019,0.542093,0.900057
P,0.167118,-0.818718,-0.789685
C,0.364234,-2.340086,0.27127
C,3.769632,-1.600452,1.082561
C,-0.801318,-3.054167,0.644452
C,1.62995,-2.864687,0.636101
C,-2.624467,-3.110594,-1.093132
C,-2.194093,-2.715256,0.193921
C,-3.12426,-2.182761,1.105305
C,2.960864,-2.328542,0.190382
C,-2.73194,-1.792297,2.513347
H,-1.705886,-1.427705,2.572353
H,-3.394783,-1.011906,2.893187
H,-2.804282,-2.64695,3.195199
C,-4.461387,-2.050643,0.717153
H,-5.170918,-1.635045,1.425789
C,5.605058,-1.653136,-0.526923
C,-4.906373,-2.443133,-0.541441
C,1.695212,-4.025245,1.418042
H,2.671813,-4.413075,1.686052
C,-0.689959,-4.204286,1.434515
H,-1.595054,-4.733041,1.711912
C,5.076628,-1.279821,0.707048
H,5.698389,-0.72915,1.405593
C,-3.966981,-2.960067,-1.43547
H,-4.291859,-3.276637,-2.422642
C,3.472552,-2.70783,-1.068113
C,0.548157,-4.685059,1.835088
H,0.620142,-5.580344,2.442791
C,3.252438,-1.164032,2.433646
H,2.949379,-2.016363,3.047959

H,4.017818,-0.608782,2.978429
H,2.377241,-0.516602,2.33016
C,-1.675467,-3.726145,-2.093913
H,-1.089928,-4.53503,-1.649892
H,-2.225242,-4.130648,-2.945867
H,-0.96646,-2.984683,-2.474459
C,4.780855,-2.357744,-1.404641
H,5.172233,-2.665097,-2.370346
C,-6.362593,-2.34694,-0.928306
H,-6.487049,-1.860433,-1.900211
H,-6.814296,-3.341645,-1.006695
H,-6.934587,-1.780699,-0.191202
C,7.021349,-1.29991,-0.913396
H,7.507622,-2.125773,-1.439563
H,7.046646,-0.432208,-1.581954
H,7.625247,-1.057075,-0.036398
C,2.644622,-3.507013,-2.048075
H,1.787098,-2.93419,-2.41465
H,3.243723,-3.795378,-2.913808
H,2.245277,-4.416429,-1.591516
H,1.551944,-0.54255,-0.901492

Zero-point correction= 0.848463 (Hartree/Particle)
Thermal correction to Energy= 0.899919
Thermal correction to Enthalpy= 0.900864
Thermal correction to Gibbs Free Energy= 0.756899
Sum of electronic and zero-point Energies= -2542.994262
Sum of electronic and thermal Energies= -2542.942806
Sum of electronic and thermal Enthalpies= -2542.941862
Sum of electronic and thermal Free Energies= -2543.085826

**Table S19** Cartesian coordinates and energy values of **7** in THF.

P,-0.489714,0.343871,-1.094784
N,1.911516,1.78702,-1.326067
N,1.015209,2.067501,0.63477
C,-0.724696,-0.819176,0.339591
C,0.335636,-1.581016,0.912892
C,0.063661,-2.494009,1.939505
H,0.886607,-3.059738,2.364108
C,-1.232213,-2.722695,2.385151
H,-1.424144,-3.445261,3.170714
C,-2.280648,-2.035969,1.785906
H,-3.302118,-2.225914,2.098463
C,-2.05138,-1.094678,0.776966
C,-3.262295,-0.430638,0.181642
C,-3.766775,-0.86433,-1.063945
C,-4.914738,-0.26623,-1.582995
H,-5.293474,-0.608789,-2.541885
C,-5.589978,0.751871,-0.909106
C,-5.098995,1.143403,0.332972
H,-5.618728,1.919268,0.888654
C,-3.959247,0.561543,0.896123
C,-3.543269,0.99908,2.283695
H,-4.040719,0.394529,3.050599
H,-3.823227,2.040524,2.461346
H,-2.472028,0.892601,2.447068
C,-3.098438,-1.971289,-1.845542
H,-2.167745,-1.624443,-2.305026
H,-3.752057,-2.326139,-2.645287

H,-2.846095,-2.820723,-1.20654
C,-6.803636,1.413551,-1.517033
H,-7.417713,1.899224,-0.755036
H,-7.429921,0.68989,-2.045617
H,-6.511691,2.181019,-2.242555
C,1.757169,-1.553082,0.415681
C,2.084694,-2.231353,-0.784079
C,3.409415,-2.26108,-1.21573
H,3.644602,-2.786854,-2.137259
C,4.442183,-1.658615,-0.492102
C,4.111308,-1.036511,0.706265
H,4.897826,-0.584747,1.304914
C,2.79394,-0.989528,1.18129
C,1.034821,-2.95743,-1.588306
H,0.462498,-3.647168,-0.962431
H,1.494979,-3.530029,-2.396448
H,0.323459,-2.250879,-2.024869
C,5.871461,-1.729443,-0.97619
H,6.270914,-2.745058,-0.882652
H,6.520632,-1.06617,-0.400096
H,5.953255,-1.449648,-2.030791
C,2.556142,-0.375576,2.543108
H,1.532085,-0.030782,2.668733
H,3.233963,0.464807,2.714085
H,2.743504,-1.107861,3.336706
C,0.871366,1.369005,-0.537653
C,2.686924,2.734595,-0.657905
C,2.133179,2.904472,0.57276
C,2.177809,1.284798,-2.663714
H,1.64479,0.340077,-2.771891
H,3.248233,1.12315,-2.793566
H,1.817629,1.980622,-3.426626
C,3.897151,3.35212,-1.272244
H,4.67421,2.608726,-1.477947
H,4.32399,4.09859,-0.602278
H,3.659865,3.851979,-2.216645
C,2.554677,3.776759,1.707033
H,1.821235,4.561031,1.92275
H,3.498367,4.269567,1.472445
H,2.70099,3.199834,2.625414
C,-0.033685,2.142327,1.637552
H,-0.994203,2.201401,1.120205
H,0.114875,3.028148,2.252612
H,-0.045271,1.260252,2.27793

Zero-point correction= 0.598967 (Hartree/Particle)
Thermal correction to Energy= 0.633274
Thermal correction to Enthalpy= 0.634218
Thermal correction to Gibbs Free Energy= 0.533309
Sum of electronic and zero-point Energies= -1654.297079
Sum of electronic and thermal Energies= -1654.262772
Sum of electronic and thermal Enthalpies= -1654.261828
Sum of electronic and thermal Free Energies= -1654.362738

**Table S20** Cartesian coordinates and energy values of **$H_2O$** in THF.

O,0.,0.,0.1187102
H,0.,0.75704,-0.4748408
H,0.,-0.75704,-0.4748408

Zero-point correction= 0.021307 (Hartree/Particle)
Thermal correction to Energy= 0.024143
Thermal correction to Enthalpy= 0.025087
Thermal correction to Gibbs Free Energy= 0.003660
Sum of electronic and zero-point Energies= -76.432033
Sum of electronic and thermal Energies= -76.429198
Sum of electronic and thermal Enthalpies= -76.428254
Sum of electronic and thermal Free Energies= -76.449680

**Table S21** Cartesian coordinates and energy values of $\mathbf{NH_3{\cdot}BH_3}$ in THF.

N,-0.0000000556,0.,0.730063
H,0.769046,0.556361,1.09627
H,0.0972996763,-0.9441939208,1.09627
H,-0.866345843,0.3878329208,1.09627
B,-0.0000000556,0.,-0.933407
H,-0.120229,1.161239,-1.244073
H,1.0657768905,-0.4764981798,-1.244073
H,-0.9455480572,-0.6847408202,-1.244073

Zero-point correction= 0.069657 (Hartree/Particle)
Thermal correction to Energy= 0.073467
Thermal correction to Enthalpy= 0.074411
Thermal correction to Gibbs Free Energy= 0.047209
Sum of electronic and zero-point Energies= -83.196059
Sum of electronic and thermal Energies= -83.192250
Sum of electronic and thermal Enthalpies= -83.191305
Sum of electronic and thermal Free Energies= -83.218507

**Table S22** Cartesian coordinates and energy values of $\mathbf{NH_2BH_2}$ in THF.

N,-0.6106870625,-0.00003425,-0.00002875
H,-1.1630630625,0.84362875,-0.00009075
H,-1.1628910625,-0.84390425,0.00031025
B,0.7773449375,-0.00002625,-0.00005475
H,1.3575459375,-1.04221025,-0.00003475
H,1.3564929375,1.04285675,0.00029025

Zero-point correction= 0.047739 (Hartree/Particle)
Thermal correction to Energy= 0.050975
Thermal correction to Enthalpy= 0.051919
Thermal correction to Gibbs Free Energy= 0.025338
Sum of electronic and zero-point Energies= -82.027773
Sum of electronic and thermal Energies= -82.024537
Sum of electronic and thermal Enthalpies= -82.023593
Sum of electronic and thermal Free Energies= -82.050174

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