Supplementary Information

Phosphinoborinium cation: a synthon for cationic B-P bond systems

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Experimental section

Experimental details

All manipulations were performed under a dry argon atmosphere employing flame-dried Schlenk-type glassware on a vacuum line or in a glovebox. Solvents, dichloromethane and dichloromethane-d_2 were dried over P_2O_5 and distilled under argon. Pentane and petroleum ether were dried with sodium-potassium alloy and distilled under argon. Toluene was dried with K/benzophenone and also distilled under argon. C_6D_6, was purified with metallic sodium. 1D (^1H, ^{11}B, $^{31}P\{^1H\}$, ^{31}P, ^{13}C, ^{27}Al, $^{19}F\{^1H\}$, ^{19}F) and 2D NMR spectra were recorded on a Bruker AV400 MHz spectrometer (external standard TMS for ^1H and ^{13}C; $BF_3 \cdot Et_2O$ for ^{11}B, 85% H_3PO_4 for ^{31}P; $[Al(H_2O)_6]^{3+}$ for ^{27}Al, $CFCl_3$ for ^{19}F) at ambient temperature. Reaction progress was monitored by ^{11}B, $^{31}P\{^1H\}$ and ^{31}P NMR spectra of reaction mixtures. Data were processed using Bruker's Topspin 3.5 software. Elemental analysis of **1** was performed using Elementar Vario El Cube CHNS micro elemental analyzer, while elemental analyses of **A**[WCA]$_2$, **B**[WCA], and **D**[WCA] were performed using Thermo Scientific Flash 2000 organic elemental analyzer. The principle of quantitative CHNS analysis is based on complete combustion of sample within high-temperature reactor, followed by an accurate and precise determination of produced elemental gases by TCD detector (thermal conductivity detector). tBuPhPLi[1], (Cy$_2$N)BBr$_2$[2], and Li[Al(OC(CF$_3$)$_3$)$_4$][3] were prepared according to literature procedures.

Preparation of 1
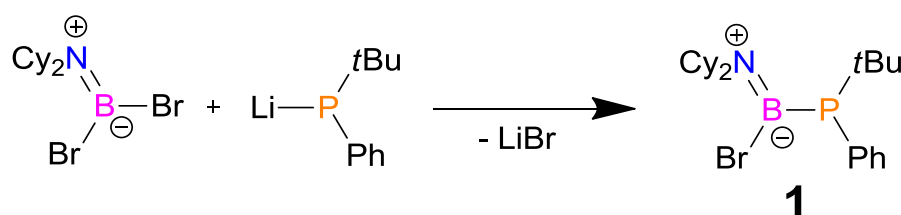
Scheme S1. Synthesis of **1**

A solution of (Cy$_2$N)BBr$_2$ (0.702 g, 2 mmol) in toluene (6 mL) was added dropwise to a stirred suspension of tBuPhPLi (0.344 g, 2 mmol) in toluene (5 mL) at -30 °C. The mixture was allowed to warm to room temperature and stirred overnight. Afterwards, the solvent was removed under reduced pressure and obtained crude product was extracted with 20 mL of petroleum ether. Filtration to separate the white precipitate of LiCl, followed by the evaporation of the solvent under reduced pressure, afforded a light yellow oily residue. Slow cooling of the resulting oil layered with 3 mL of petroleum ether to -20 °C gave suitable crystals for X-ray diffraction. Yield: 50.8% (0.443 g,

1.016 mmol). **Elemental analysis** calc. for $C_{22}H_{36}BBrNP$ (436.22 g/mol): C, 60.57; H, 8.318; N, 3.21. Found: C, 60.80; H, 8.405; N, 3.25.

NMR data of 1

^{11}B NMR (C$_6$D$_6$): δ 39.0 (s).

^{31}P{^{1}H} NMR (C$_6$D$_6$): δ D1: -20.3 (s).

^{1}H NMR (C$_6$D$_6$): δ 7.71 (2 H, br s, *o*-C*H* of Ph); 7.14 – 7.05 (3 H, m, overlapped signals of *m*-C*H* and *p*-C*H* of Ph); 4.07 (1 H, br s, C*H* of Cy); 2.88 (1 H, br s, C*H*$_2$ of Cy, overlapped with δ 2.81 C*H* of Cy); 2.81 (1 H, br s, C*H* of Cy, overlapped with δ 2.88 C*H*$_2$ of Cy); 1.75 – 1.62 (3 H, m, overlapped signals of C*H*$_2$ of Cy); 1.60 – 1.46 (4 H, m, overlapped signals of C*H*$_2$ of Cy); 1.41 (9 H, d, $^3J_{PH}$ = 13. 3 Hz, C(C*H*$_3$)$_3$); 1.37 – 1.29 (2 H, m, overlapped signals of C*H*$_2$ of Cy); 1.28 – 0.91 (7 H, m, overlapped signals of C*H*$_2$ of Cy); 0.69 (2 H, br s, C*H*$_2$ of Cy); 0.52 (1 H, br s, C*H*$_2$ of Cy).

^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 138.4 (d, $^2J_{CP}$ = 17.0 Hz, *o*-*C*H of Ph); 136.9 (d, $^1J_{CP}$ = 10.4 Hz, *ipso*-*C*P of Ph); 128.4 (s, *p*-*C*H of Ph); 127.8 (d, $^3J_{CP}$ = 6.3 Hz, *m*-*C*H of Ph, overlapped with solvent); 63.3 (d, $^3J_{CP}$ = 28.3 Hz, *C*H of Cy); 58.8 (s, *C*H of Cy); 32.7 (br s, *C*H$_2$ of Cy); 31.6 (br s, *C*H$_2$ of Cy); 30.4 (d, $^1J_{CP}$ = 10.8 Hz, *C*(CH$_3$)$_3$); 30.1 (br s, *C*H$_2$ of Cy); 29.3 (d, $^2J_{CP}$ = 13.4 Hz, C(*C*H$_3$)$_3$); 26.8 (br s, *C*H$_2$ of Cy); 26.0 (br s, *C*H$_2$ of Cy); 25.6 (br s, *C*H$_2$ of Cy); 25.4 (s, *C*H$_2$ of Cy); 25.3 (s, *C*H$_2$ of Cy).

Preparation of A[WCA]$_2$, B[WCA] and C[WCA]
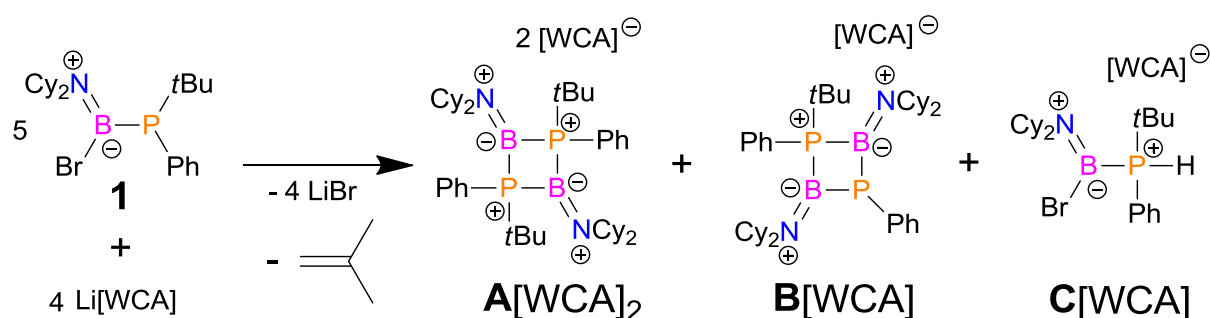
Scheme S2. Synthesis of **A**[WCA]$_2$, **B**[WCA] and **C**[WCA]

A solution of **1** (0.109 g, 0.250 mmol) in CH$_2$Cl$_2$ (2 mL) was added dropwise to a stirred suspension of Li[Al(OC(CF$_3$)$_3$)$_4$] (0.244 g, 0.250 mmol) in CH$_2$Cl$_2$ (3 mL) at -30 °C. The mixture was allowed to warm to room temperature and stirred overnight. After filtration of the precipitated LiBr, the resulting solution was concentrated to the half of volume. Cooling to +4 °C yielded colourless crystals of **A**[WCA]$_2$. Drying of crystals under high vacuum resulted in the removal of non-coordinated solvent

molecules. Yield: 32.0 % (0.042 g, 0.016 mmol). **Elemental analysis** calc. for $C_{76}H_{72}Al_2B_2F_{72}N_2O_8P_2$ (2646.81 g/mol): C, 34.49; H, 2.742; N, 1.06. Found: C, 35.02; H, 3.030; N, 1.81. The isolated product contains conformational isomers **trans** and **cis** in a molar ratio of 1 : 0.19 which are visible at $^{31}P\{^1H\}$ and ^1H spectra. The molar ratio was determined by integration of well-separated C**H** signals of Cy groups at ^1H spectrum.

After separation of obtained **A**[WCA]$_2$ crystals, the mother liquor was layered with pentane (3 mL) and stored at +4 °C that gave colourless crystals of **B**[WCA]. Drying of crystals under high vacuum resulted in the removal of non-coordinated solvent molecules. Yield: 61.0% (0.050 g, 0.031 mmol). **Elemental analysis** calc. for $C_{56}H_{63}AlB_2F_{36}N_2O_4P_2$ (1622.60 g/mol): C, 41.45; H, 3.914; N, 1.73. Found: C, 41.80; H, 3.370; N, 2.28.

Colourless crystals of **C**[WCA] were obtained by cooling the mother liquor to -20°C of as a mixture with additional crop of **B**[WCA] in a very low yield because of its tendency to decompose. Thus, complete NMR characterization and elemental analysis for **C**[WCA] were not performed.

NMR data of A[WCA]$_2$

^{11}B NMR (CD$_2$Cl$_2$): δ 36.0 (br s).

$^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 11.7 (br s, **trans** isomer); 14.1 (br s, **cis** isomer).

^1H NMR (CD$_2$Cl$_2$): trans: δ 7.86 (2 H, m, *p*-C**H** of Ph); 7.74 (4 H, m, *m*-C**H** of Ph, overlapped with *m*-C**H** of Ph of *cis*); 7.357 (4 H, m, *p*-C**H** of Ph); 3.76 (4 H, m, C**H** of Cy); 2.08 – 1.94 (10 H, m, C**H**$_2$ of Cy, overlapped with *cis*); 1.93 – 1.84 (6 H, m, C**H**$_2$ of Cy, overlapped with *cis*); 1.68 – 1.62 (4 H, m, C**H**$_2$ of Cy, overlapped with *cis*); 1.57 (18 H, *pseudo*-t, N = 9.4 Hz, C(C**H**$_3$)$_3$)*; 1.54 – 1.48 (4 H, m, C**H**$_2$ of Cy, overlapped with *cis*); 1.45 – 1.39 (4 H, m, C**H**$_2$ of Cy, overlapped with *cis*); 1.34 – 1.28 (2 H, m, C**H**$_2$ of Cy, overlapped with *cis*); 1.16 (2 H, s, C**H**$_2$ of Cy, overlapped with *cis*); 1.07 – 0.93 (8 H, m, C**H**$_2$ of Cy, overlapped with *cis*); 0.53 (4 H, m, C**H**$_2$ of Cy, overlapped with *cis*).

cis: δ 7.82 (2 H, m, *p*-C**H** of Ph); 7.57 (4 H, m, *m*-C**H** of Ph, overlapped with *trans*); 7.35 (4 H, m, *p*-C**H** of Ph); 3.65 (4 H, m, C**H** of Cy); 2.08 – 1.94 (10 H, m, C**H**$_2$ of Cy, overlapped with *trans*); 1.93 – 1.84 (6 H, m, C**H**$_2$ of Cy, overlapped with *trans*); 1.71 (18 H, *pseudo*-t, N = 9.8 Hz, C(C**H**$_3$)$_3$)*; 1.68 – 1.62 (4 H, m, C**H**$_2$ of Cy, overlapped with *trans*); 1.54 – 1.48 (4 H, m, C**H**$_2$ of Cy, overlapped with *trans*); 1.45 – 1.39 (4 H, m, C**H**$_2$ of Cy, overlapped with *trans*); 1.34 – 1.28 (2 H, m, C**H**$_2$ of Cy, overlapped with *trans*); 1.16 (2 H, s, C**H**$_2$ of Cy, overlapped with *trans*); 1.07 – 0.93 (8 H, m, C**H**$_2$ of Cy, overlapped with *trans*); 0.53 (4 H, m, C**H**$_2$ of Cy, overlapped with *trans*).

¹³C{¹H} NMR (CD₂Cl₂): δ 136.5 (s, *p-C*H of Ph); 132.7 (*pseudo*-t, N = 5.0 Hz, *o-C*H of Ph)*; 132.3 (*pseudo*-t, N = 5.7 Hz, *m-C*H of Ph)*; 121.2 (q, $^1J_{CF}$ = 293.1 Hz, OC(*C*F₃)); 115.1 (s, *ipso-C*P of Ph); 71.8 (*pseudo*-t, N = 7.1 Hz, *C*H of Cy)*; 41.1 (*pseudo*-t, N = 12.2 Hz, *C*(CH₃)₃)*; 38.2 (s, *C*H₂ of Cy); 33.4 (s, *C*H₂ of Cy); 29.9 (s, C(*C*H₃)₃); 26.4 (s, *C*H₂ of Cy); 26.0 (s, *C*H₂ of Cy); 24.2 (s, *C*H₂ of Cy).

²⁷Al NMR (CD₂Cl₂): δ 34.3 (s, [*Al*(OC(CF₃)₃)₄]⁻).

¹⁹F{¹H} (CD₂Cl₂): δ -75.7 (s, OC(C*F*₃)₃).

*Virtual coupling of P atoms with H or C atoms, respectively.

NMR data of B[WCA]

¹¹B NMR (CD₂Cl₂): δ 35.1 (br s).

³¹P{¹H} NMR (CD₂Cl₂): δ 6.5 (d, $^1J_{PP}$ = 391.0 Hz, P(*t*Bu)Ph); -17.3 (d, $^1J_{PP}$ = 391.0 Hz, PPh).

¹H NMR (CD₂Cl₂): δ 7.73 – 7.62 (4 H, m, overlapped signals of *m*-C*H* of Ph); 7.61 – 7.49 (4 H, m, overlapped signals of *o*-C*H* of Ph); 7.48 – 7.41 (2 H, m, overlapped signals of *p*-C*H* of Ph); 2.93 (2 H, m, C*H* of Cy); 2.78 (2 H, m, C*H* of Cy); 1.69 (2 H, m, C*H*₂ of Cy); 1.62 (9 H, d, $^3J_{PH}$ = 16.7 Hz, C(C*H*₃)₃); 1.58 – 1.46 (8 H, m, overlapped signals of C*H*₂ of Cy); 1.45 – 1.35 (6 H, m, overlapped signals of C*H*₂ of Cy); 1.35 – 0.84 (20 H, m, overlapped signals of C*H*₂ of Cy); 0.47 (2 H, m, C*H*₂ of Cy); -0.41 (2 H, m, C*H*₂ of Cy).

¹³C{¹H} NMR (CD₂Cl₂): δ 138.0 (d, $^3J_{CP}$ = 9.1 Hz, *m-C*H of Ph); 132.5 (dd, $^3J_{CP}$ = 35.9 Hz, $^5J_{CP}$ = 3.0 Hz, *m-C*H of Ph); 131.9 (dd, $^3J_{CP}$ = 9.1 Hz, $^5J_{CP}$ = 1.8 Hz, *m-C*H of Ph); 130.2 (s, *o-C*H of Ph); 130.1 (s, *o-C*H of Ph); 129.9 (s, *p-C*H of Ph); 129.7 (s, *p-C*H of Ph); 121.2 (q, $^1J_{CF}$ = 292.7 Hz, OC(*C*F₃)); 67.1 (m, *C*H of Cy); 55.5 (dd, $^3J_{CP}$ = 7.2 Hz, $^3J_{CP}$ = 2.0 Hz, *C*H of Cy); 34.1 (s, *C*H₂ of Cy); 33.3 (s, *C*H₂ of Cy, overlapped with *C*(CH₃)₃); 33.3 (dd, $^1J_{CP}$ = 22.7 Hz, $^3J_{CP}$ = 12.8 Hz, *C*(CH₃)₃, overlapped with *C*H₂ of Cy); 32.4 (s, *C*H₂ of Cy); 31.2 (s, *C*H₂ of Cy); 29.6 (d, $^2J_{CP}$ = 2.8 Hz, C(*C*H₃)₂); 25.4 (d, $^4J_{CP}$ = 6.6 Hz, *C*H₂ of Cy); 25.3 (d, $^4J_{CP}$ = 5.7 Hz, *C*H₂ of Cy); 24.7 (s, *C*H₂ of Cy); 23.7 (s, *C*H₂ of Cy). The aromatic *ipso*-C atoms directly bound with phosphorus atom were not detected at the ¹³C{¹H} spectrum.

²⁷Al NMR (CD₂Cl₂): δ 34.2 (s, [*Al*(OC(CF₃)₃)₄]⁻).

¹⁹F{¹H} (CD₂Cl₂): δ -75.7 (s, OC(C*F*₃)₃).

NMR data of C[WCA]

¹¹B NMR (CD₂Cl₂): δ 27.3 (br s).

$^{31}P\{^1H\}$ **NMR (CD$_2$Cl$_2$):** δ -3.1 (br s, for ^{31}P $^1J_{PH}$ = 346.9 Hz).

Preparation of D[WCA]
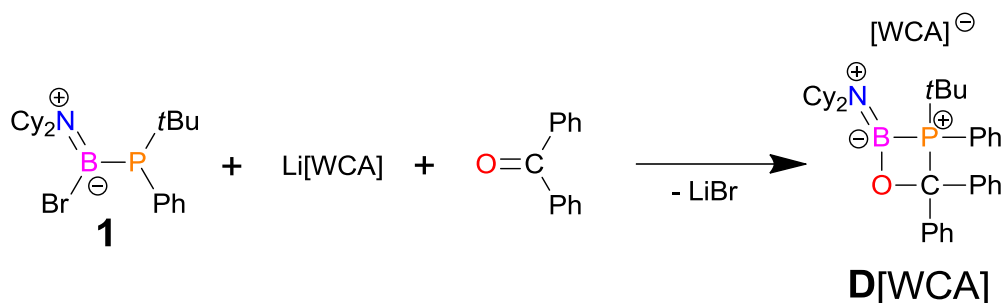
Scheme S3. Synthesis of **D**[WCA]

Method A: A solution of **1** (0.109 g, 0.250 mmol) in CH$_2$Cl$_2$ (2 mL) was added dropwise to a stirred suspension of Li[Al(OC(CF$_3$)$_3$)$_4$] (0.244 g, 0.250 mmol) and benzophenone (0.045 g, 0.250 mmol) in CH$_2$Cl$_2$ (3 mL) at -50 °C. The mixure was allowed to warm to room temperature and stirred overnight. After filtration of the precipitated LiBr, the resulting solution was concentrated to the half of volume and left at -20 °C to afford colourless crystals of **D**[WCA]. Yield: 40% (0,152 g, 0.101 mmol).

Method B: A solution of **1** (0.109 g, 0.250 mmol) in CH$_2$Cl$_2$ (2 mL) was added dropwise to a stirred suspension of Li[Al(OC(CF$_3$)$_3$)$_4$] (0.244 g, 0.250 mmol) in CH$_2$Cl$_2$ (3 mL) at -30 °C. The mixture was allowed to warm to room temperature and stirred for 3.5 h. ^{11}B and $^{31}P\{^1H\}$ NMR of the yellow reaction mixture revealed the complete conversion of **1** into **A**[WCA]$_2$. Therefore, after this time, the mixture was cooled to -50 °C and a solution of benzophenone (0.045 g, 0.250 mmol) in CH$_2$Cl$_2$ (1 mL) was added dropwise. The resulting mixture was again allowed to warm to room temperature and stirred overnight. Precipitated LiBr was separated by filtration and the resulting solution was concentrated to the half of volume. Cooling to -20 °C yielded colourless crystals of **D**[WCA]. Yield: 33% (0.123 g, 0.082 mmol).

Elemental analysis calc. for C$_{51}$H$_{46}$AlBF$_{36}$NO$_5$P (1505.62 g/mol): C, 40.68; H, 3.080; N, 0.93. Found: C, 41.08; H, 3.160; N, 1.17.

NMR data of D[WCA]

^{11}B **NMR (CD$_2$Cl$_2$):** δ 29.3 (s).

$^{31}P\{^1H\}$ **NMR (CD$_2$Cl$_2$):** δ 68.4 (s).

¹H NMR (CD₂Cl₂): δ 7.62 (2 H, m, *m-C**H** of Ph); 7.58 (1 H, m, *p-C**H** of PPh); 7.53 (2 H, m, *o-C**H** of Ph); 7.47 (1 H, m, *p-C**H** of Ph); 7.42 (2 H, m, *m-C**H** of PPh); 7.31 (2 H, m, *o-C**H** of PPh); 7.16 – 7.04 (5 H, m, overlapped signals of *o-C**H**, *m-C**H**, and *p-C**H** of Ph); 3.07 (2 H, m, C**H** of Cy); 2.05 (2 H, m, C**H₂** of Cy); 1.95 – 1.79 (6 H, m, overlapped signals of C**H₂** of Cy); 1.79 – 1.57 (6 H, m, overlapped signals of C**H₂** of Cy); 1.36 (2 H, m, C**H₂** of Cy); 1.26 (9 H, d, $^3J_{PH}$ = 17.9 Hz, PC(C**H₃**)₃); 1.22 – 1.08 (4 H, m, overlapped signals of C**H₂** of Cy).

¹³C{¹H} NMR (CD₂Cl₂): δ 137.0 (d, $^2J_{CP}$ = 1.84 Hz, *ipso-**C*** of Ph); 135.1 (s, *p-**C***H of PPh); 135.1 (s, *p-**C***H of Ph); 133.8 (d , $^2J_{CP}$ = 8.2 Hz, *o-**C***H of PPh); 130.5 (d, $^3J_{CP}$ = 11.7 Hz, *m-**C***H of PPh); 130.2 (d, $^4J_{CP}$ = 2.7 Hz, *m-**C***H of Ph); 129.3 (d, $^3J_{CP}$ = 1.8 Hz, *o-**C***H of Ph, overlapped with *p-**C***H of Ph); 129.3 (d, $^5J_{CP}$ = 2.8 Hz, *p-**C***H of Ph, overlapped with *o-**C***H of Ph); 128.7 (d, $^4J_{CP}$ = 1.8 Hz, *m-**C***H of Ph); 126.6 (d, $^3J_{CP}$ = 3.5 Hz, *o-**C***H of Ph, overlapped with other *o-**C***H of Ph and *m-**C***H of Ph); 126.5 (bs, *o-**C***H of Ph, overlapped with other *o-**C***H of Ph and *m-**C***H of Ph); 126.5 (d, $^4J_{CP}$ = 2.9 Hz, *m-**C***H of Ph, overlapped with other two signals of *o-**C***H of Ph);); 121.2 (q, $^1J_{CF}$ = 291.4 Hz, OC(**C**F₃)); 116.6 (d, $^1J_{CP}$ = 44.5 Hz, *ipso-**C***P of PPh); 95.7 (d, $^1J_{CP}$ = 29.1 Hz, **C**-O); 61.4 ($^3J_{CP}$ = 4.5 Hz, **C**H of Cy); 56.0 ($^3J_{CP}$ = 5.5 Hz, **C**H of Cy); 38.0 (d, $^1J_{CP}$ = 10.9 Hz, **C**(CH₃)₃); 34.4 (s, **C**H₂ of Cy); 34.0 (s, **C**H₂ of Cy); 32.5 (s, **C**H₂ of Cy); 32.3 (s, **C**H₂ of Cy); 27.5 (d, $^2J_{CP}$ = 1.8 Hz, C(**C**H₃)₂); 26.3 (d, $^4J_{CP}$ = 9.9 Hz, **C**H₂ of Cy); 25.7 (s, **C**H₂ of Cy); 25.5 (s, **C**H₂ of Cy); 25.1 (s, **C**H₂ of Cy); 24.7 (s, **C**H₂ of Cy); 24.0 (s, **C**H₂ of Cy). One of two aromatic *ipso*-C atoms directly bound with C-O was not detected at the ¹³C{¹H} spectrum.

²⁷Al NMR (CD₂Cl₂): δ 34.2 (s, [**Al**(OC(CF₃)₃)₄]⁻).

¹⁹F{¹H} (CD₂Cl₂): δ -75.7 (s, OC(C**F₃**)₃).

Trapping of isobutene
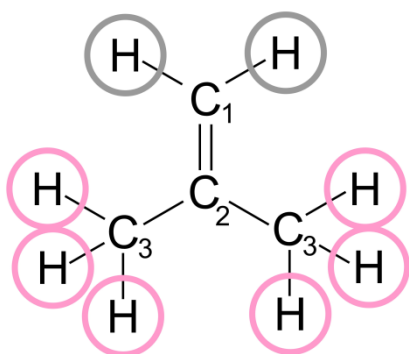
A solution of **1** (0.109 g, 0.250 mmol) in CD₂Cl₂ (2 mL) was added dropwise to a stirred suspension of Li[Al(OC(CF₃)₃)₄] (0.244 g, 0.250 mmol) in CD₂Cl₂ (3 mL) at -30 °C. The mixture was allowed to warm to room temperature and stirred overnight. Afterwards, the reaction vessel was connected with a vacuum line via a Schlenk tube placed in liquid nitrogen. Isobutene[4] was collected together with deuterated solvent CD₂Cl₂. Note, isobutene exhibits good solubility in hydrocarbons.

NMR:

^{1}H NMR (CD$_2$Cl$_2$): δ 4.65 (2 H, sept, $^4J_{HH}$ = 1.16 Hz, =C*H*$_2$); 1.72 (6 H, t, $^4J_{HH}$ = 1.16 Hz, C*H*$_3$).

^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 110.1 (s, ***C***$_1$); 23.8 (s, ***C***$_3$). Carbon ***C***$_2$ was not detected in the ^{13}C{^{1}H}.

NMR spectra of isolated compounds

Abbreviations

s	deuterated solvent (residual signal)
g	grease
★	impurity
🟣	Cy$_2$NBBr$_2$
🟠	*t*BuPhPH

NMR spectra of 1
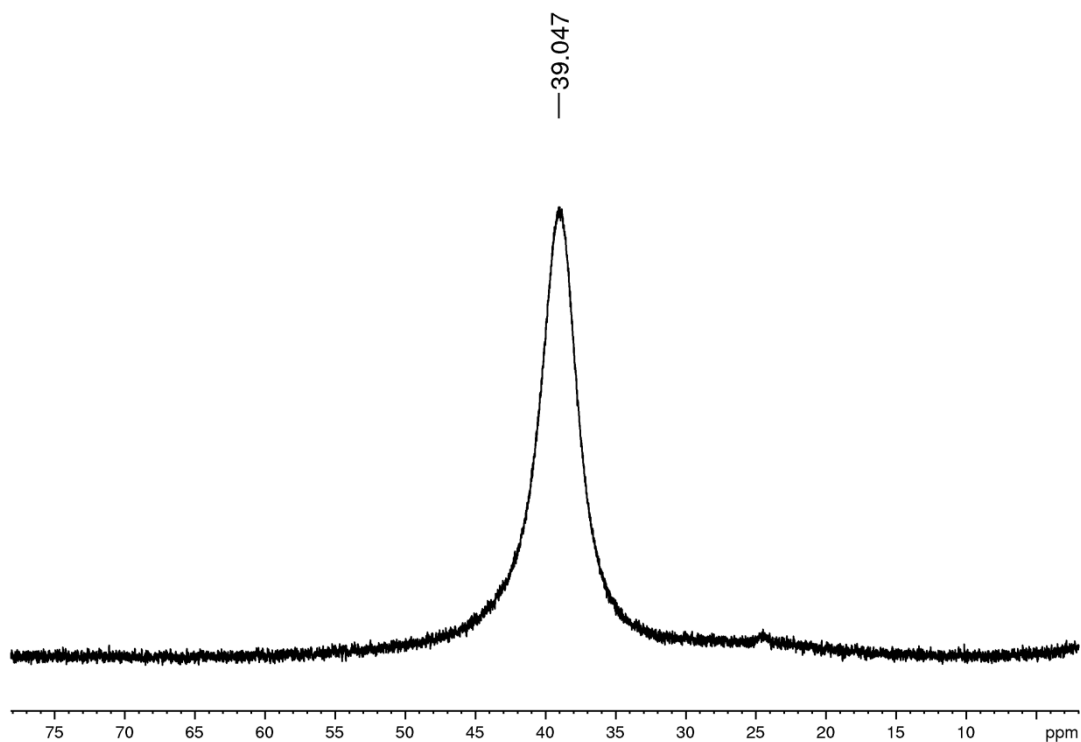
Figure S1. ^{11}B spectrum (C$_6$D$_6$) of **1**
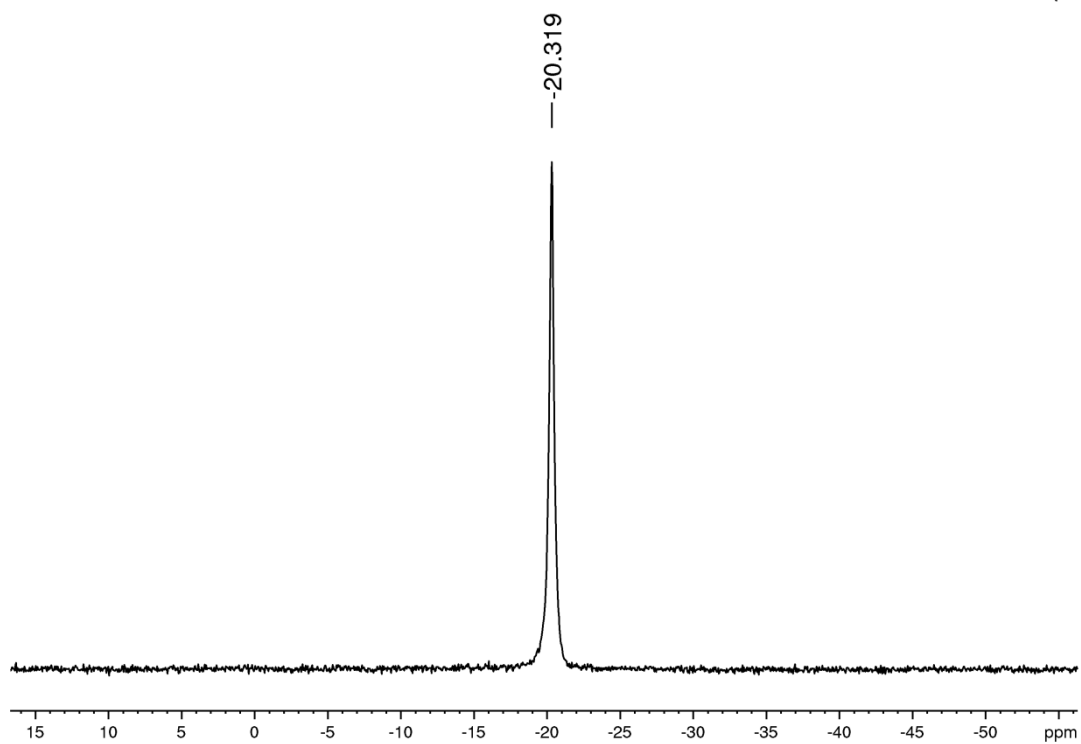
Figure S2. $^{31}P\{^1H\}$ spectrum (C$_6$D$_6$) of **1**
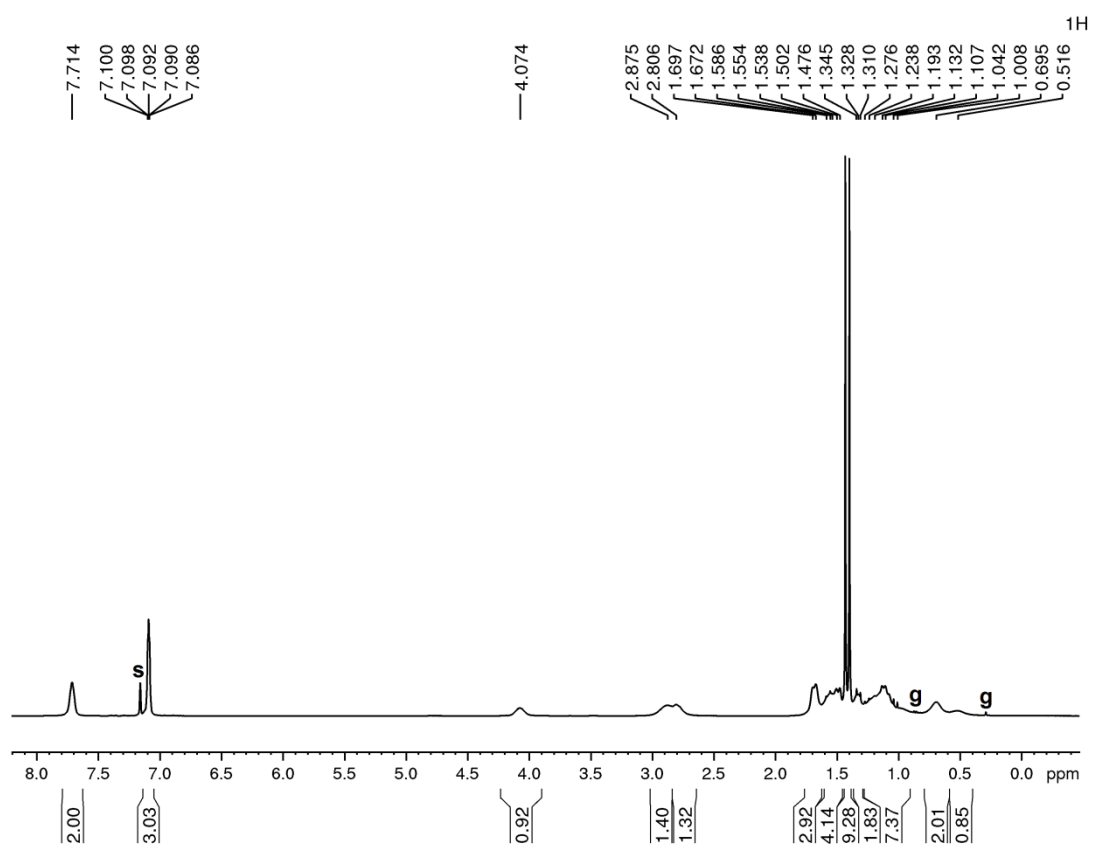
Figure S3. ^1H spectrum (C$_6$D$_6$) of **1**

13C{1H}

138.488
138.318
136.977
136.875
128.380
127.801
127.739

63.459
63.178
58.779

32.689
31.558
30.478
30.371
30.052
29.401
29.267
26.836
26.031
25.623
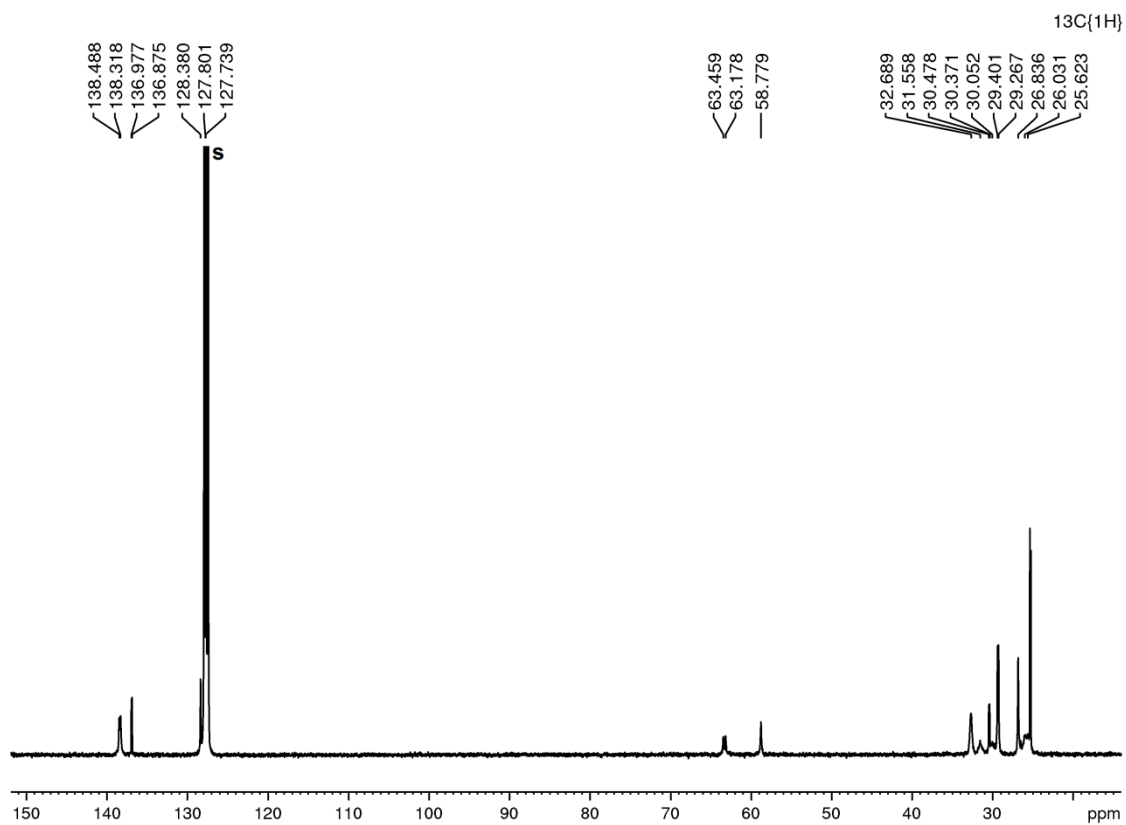
Figure S4. $^{13}C\{^1H\}$ spectrum (C_6D_6) of **1**

DEPT135

138.494
138.333
128.384
127.803
127.728

63.446
63.163
58.768

32.671
31.625
30.079
29.400
29.266
26.836
26.029
25.585
25.375
25.263
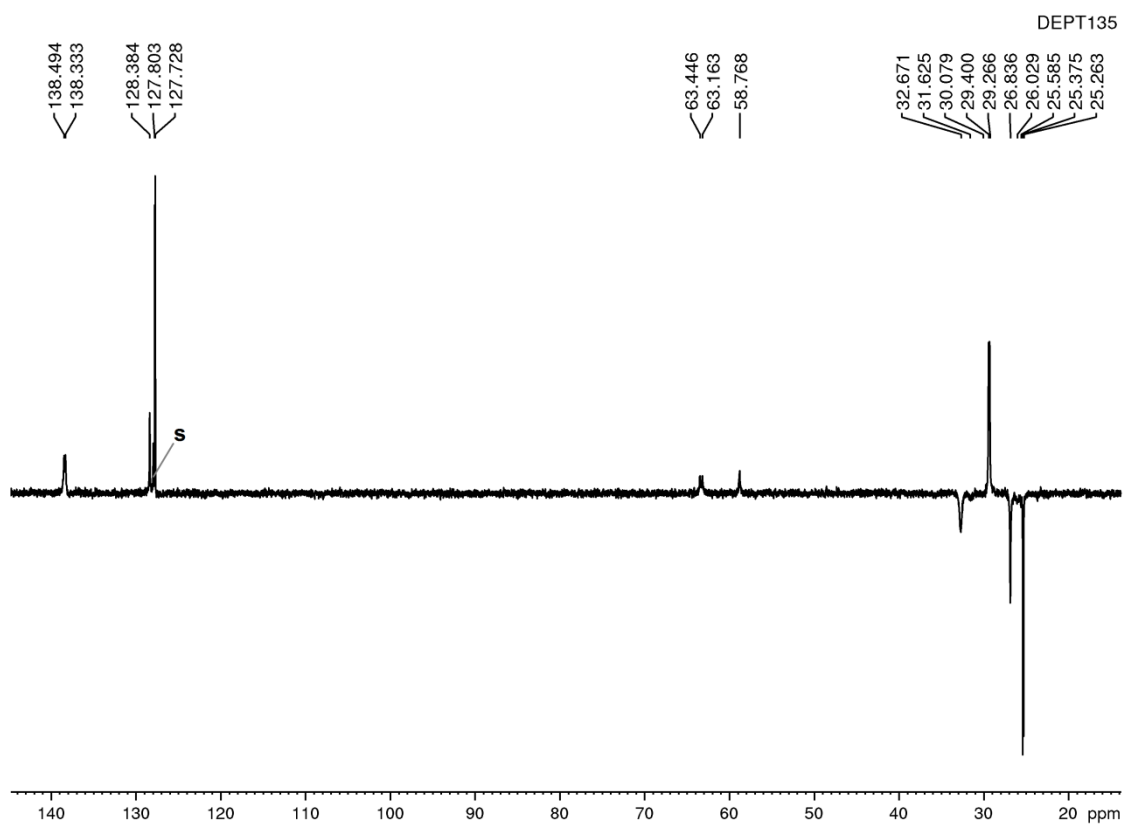
Figure S5. ^{135}DEPT spectrum (C_6D_6) of **1**

NMR spectra of A[WCA]$_2$
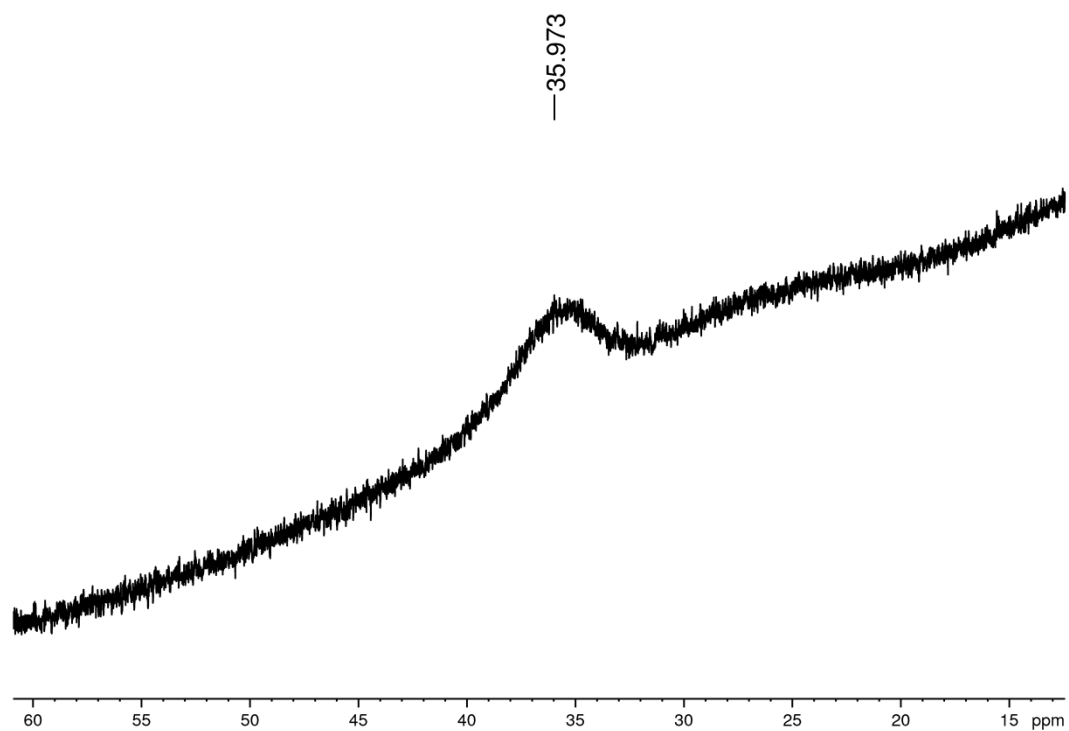
Figure S6. ^{11}B spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$
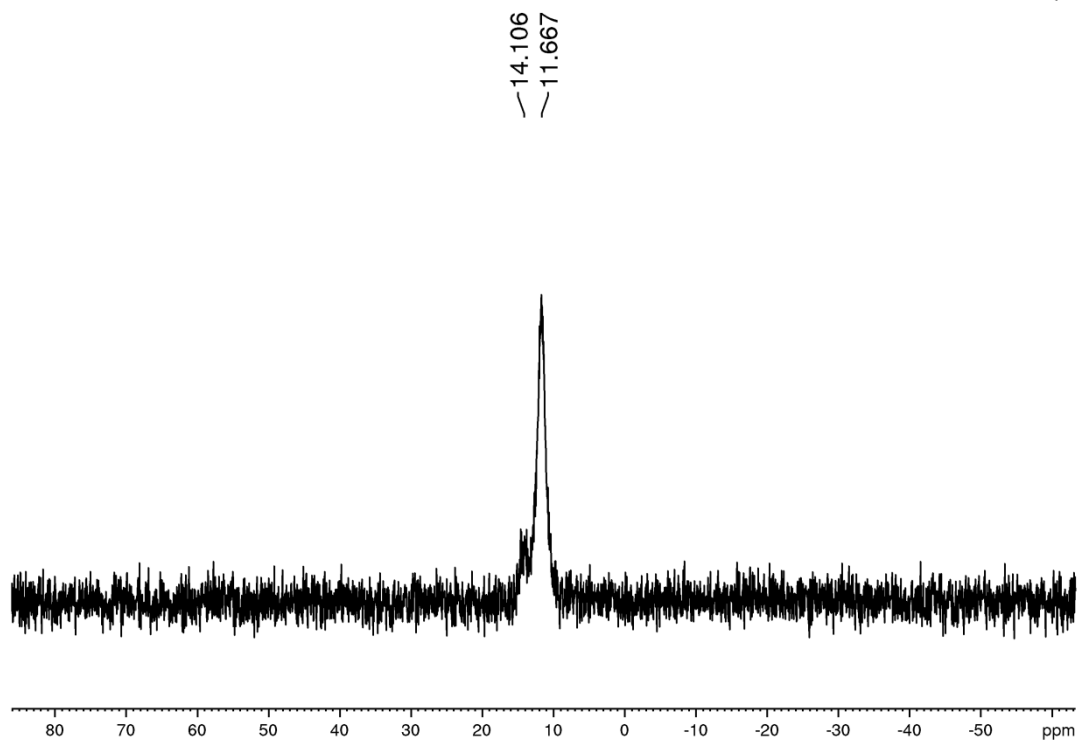
Figure S7. ^{31}P{^{1}H} spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$
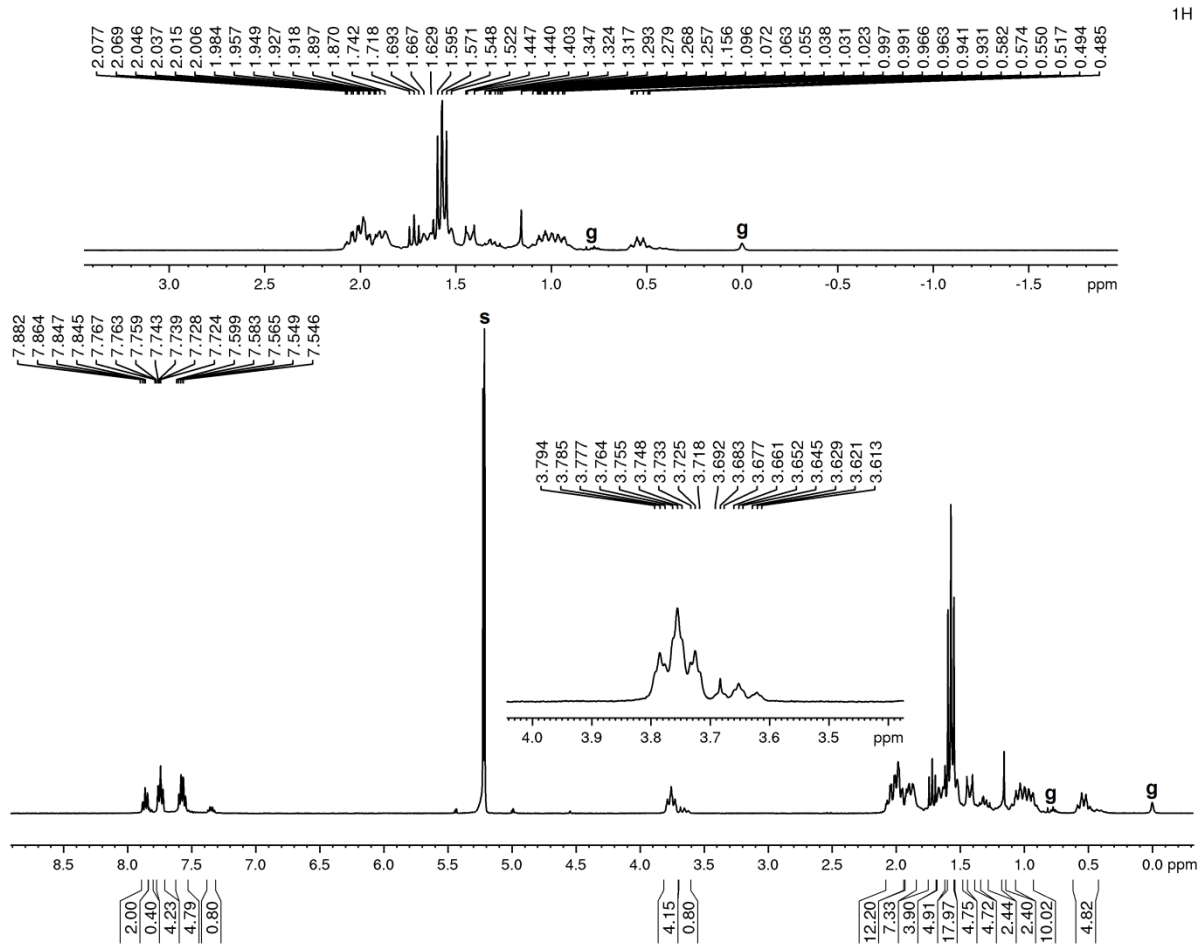
Figure S8. ^{1}H spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$

136.456
132.724
132.720
132.674
132.671
132.624
132.621
132.378
132.322
132.264
125.623
122.685
119.773
116.859
115.094

71.855
71.785
71.715

41.245
41.124
41.002
38.176
33.441
29.868
26.423
26.048
24.156

S

140 130 120 110 100 90 80 70 60 50 40 30 ppm
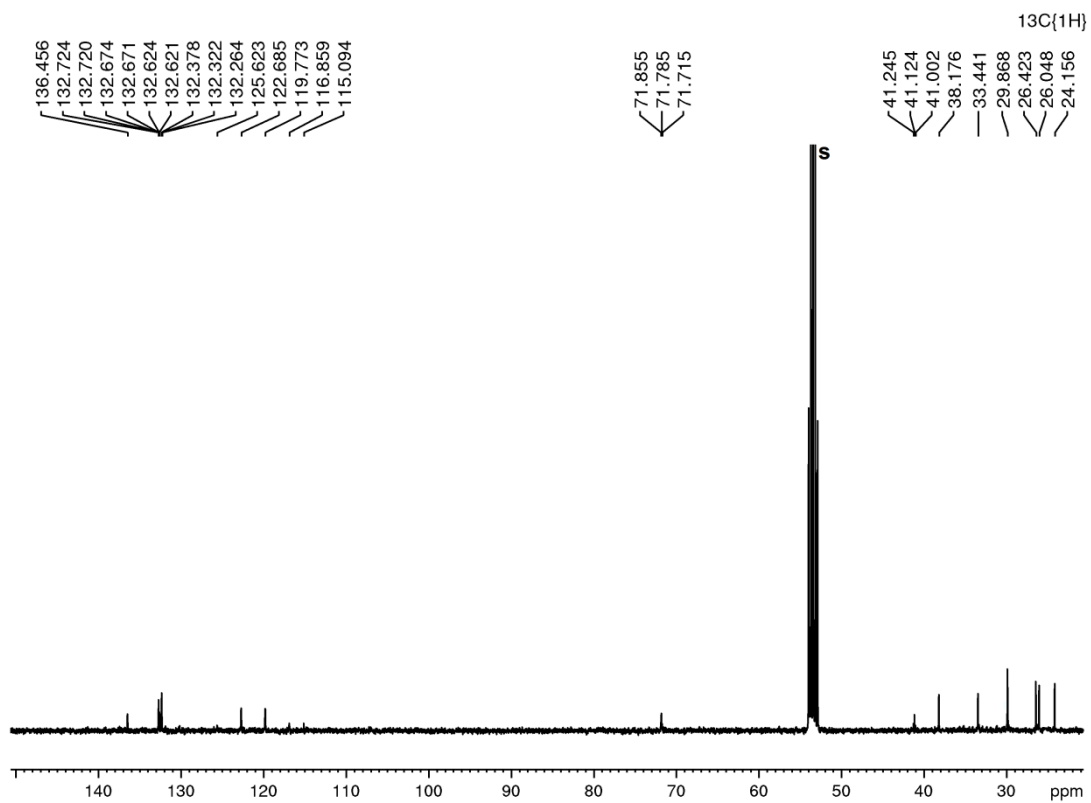
Figure S9. $^{13}C\{^1H\}$ spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$

136.462
132.722
132.673
132.623
132.378
132.322
132.267

71.868
71.784
71.731

38.174
33.439
29.857
26.414
26.046
24.146

S

140 130 120 110 100 90 80 70 60 50 40 30 ppm
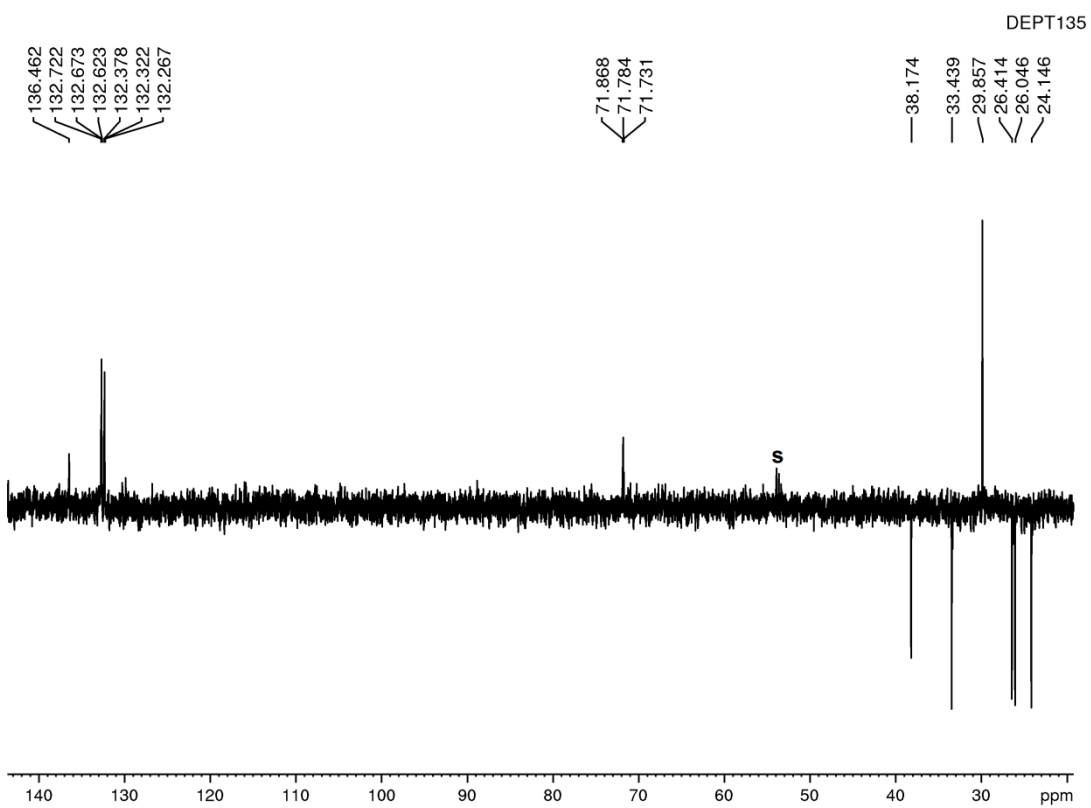
Figure S10. ^{135}DEPT spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$
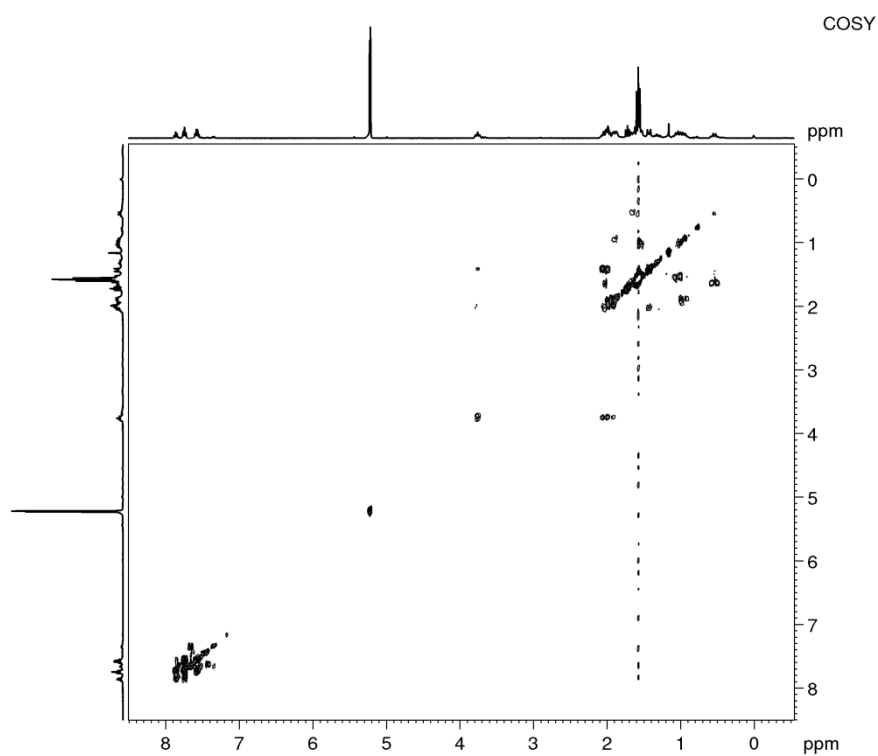
Figure S11. COSY spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$
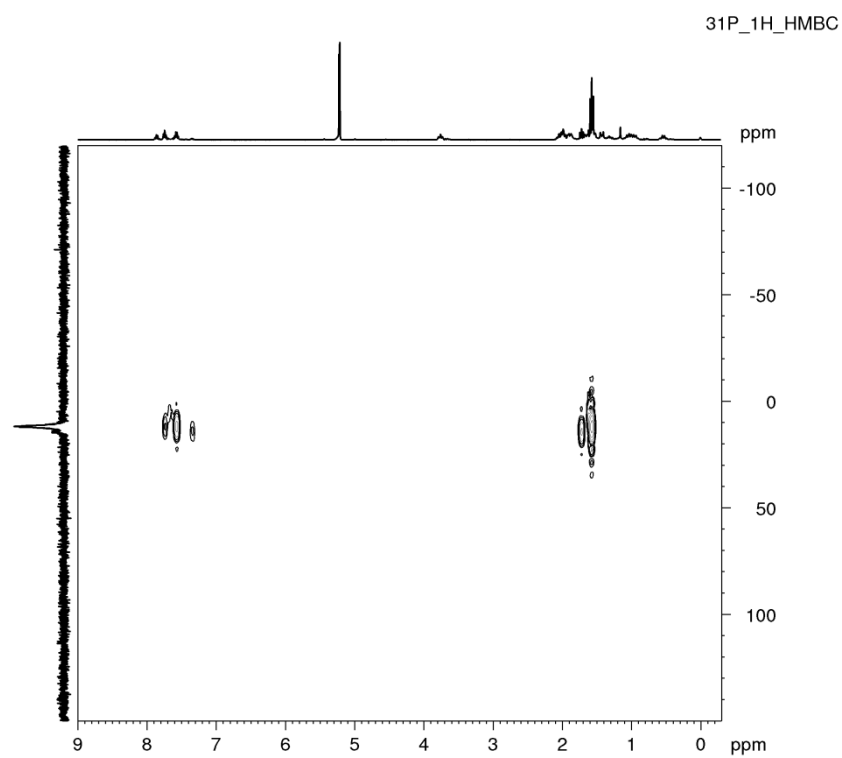
Figure S12. ^{31}P ^{1}H HMBC spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$
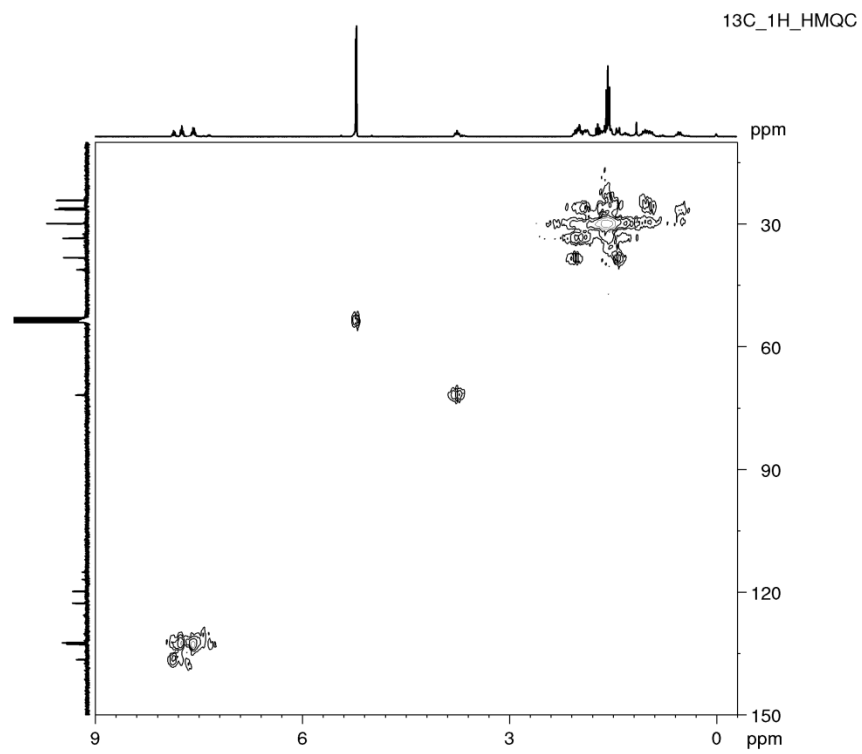
Figure S13. ^{13}C ^{1}H HMQC spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$
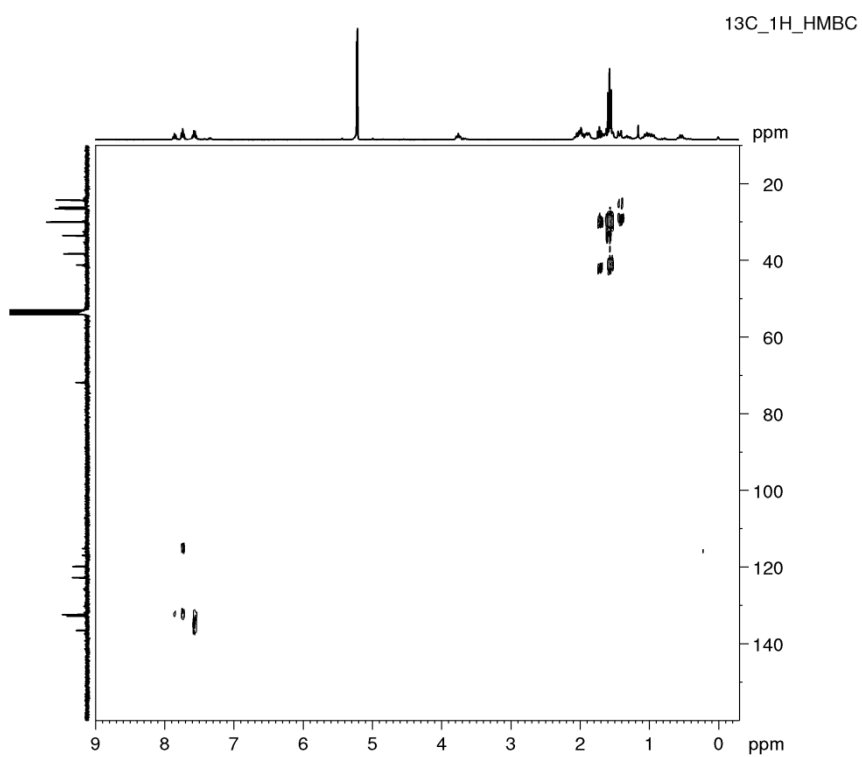
Figure S14. ^{13}C ^{1}H HMBC spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$

34.269
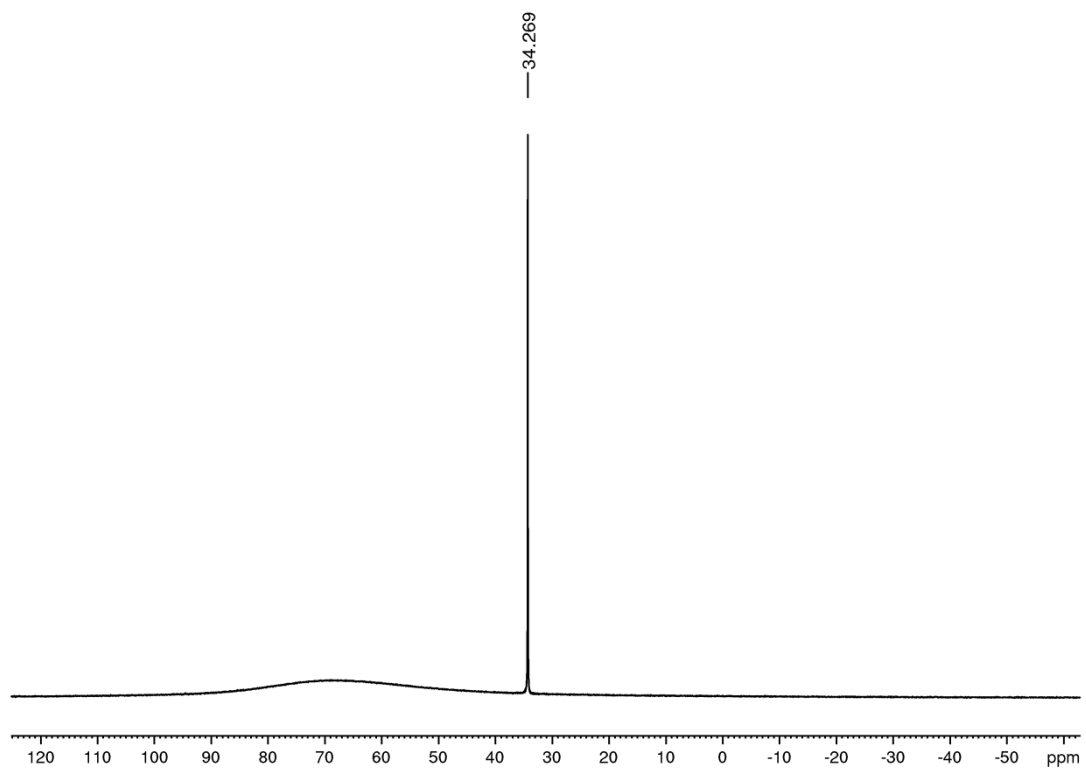
Figure S15. ^{27}Al spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$

-75.676
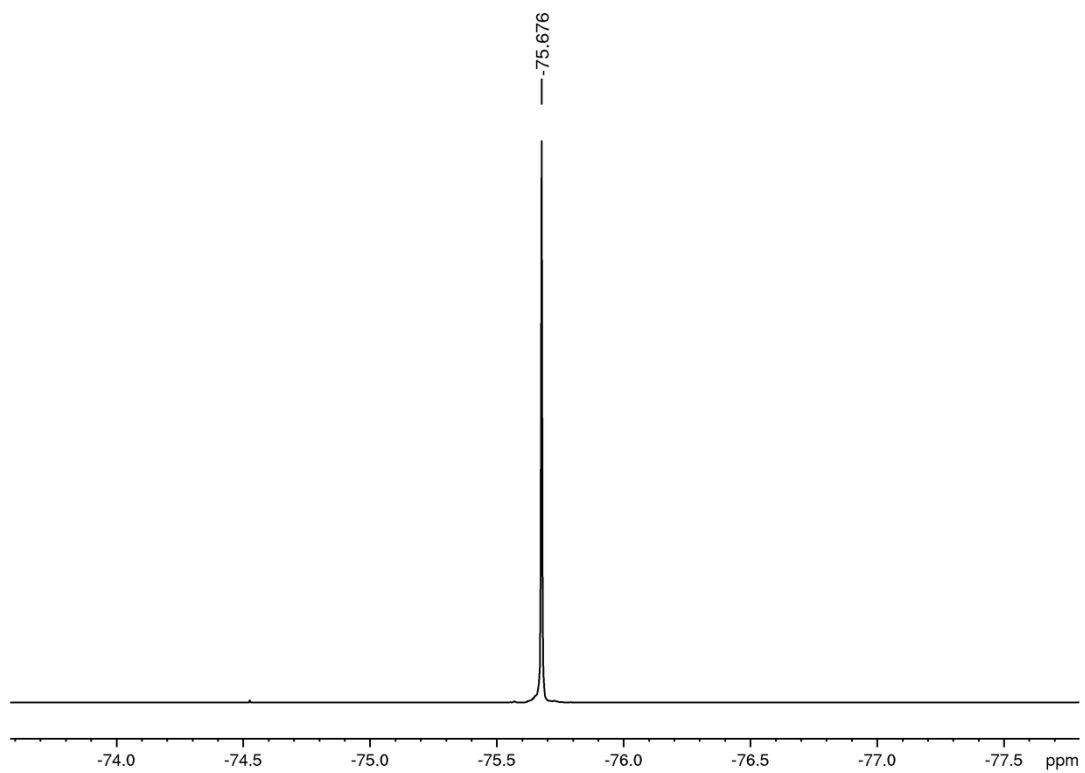
Figure S16. ^{19}F{^{1}H] spectrum (CD$_2$Cl$_2$) of **A**[WCA]$_2$

NMR spectra of B[WCA]

11B

—35.105

55 50 45 40 35 30 25 20 15 ppm
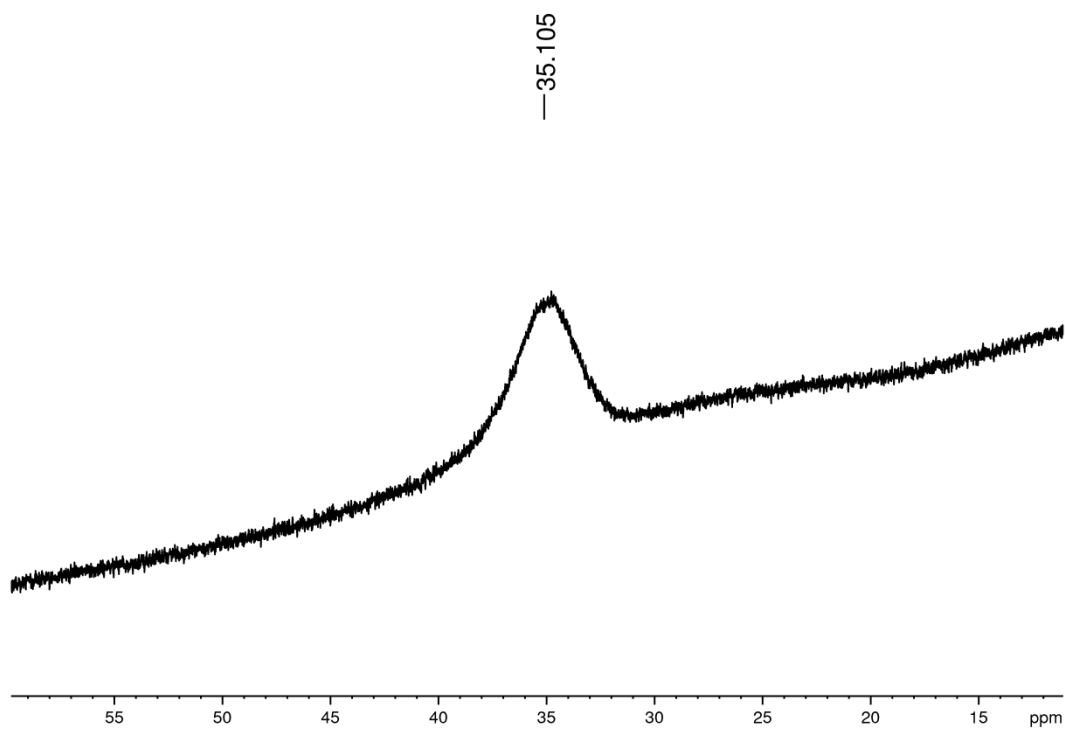
Figure S17. [11]B spectrum (CD$_2$Cl$_2$) of **B**[WCA]

31P{1H}

—7.742
—5.327

—-16.123
—-18.546

45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 ppm
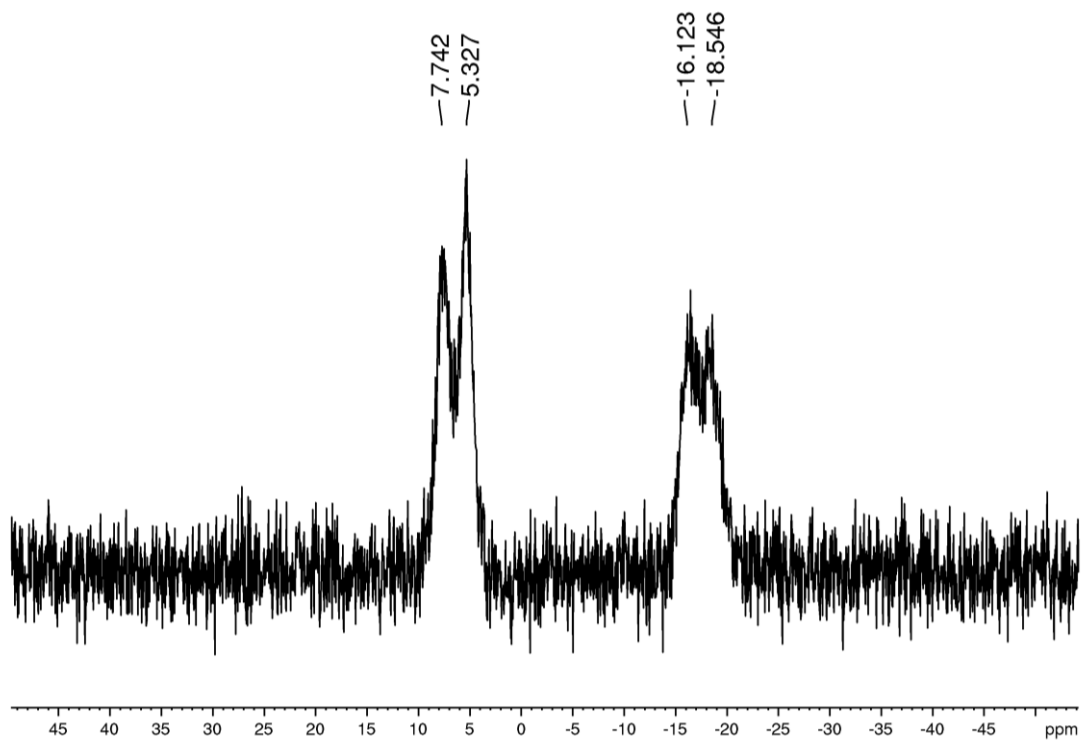
Figure S18. [31]P{[1]H} spectrum (CD$_2$Cl$_2$) of **B**[WCA]
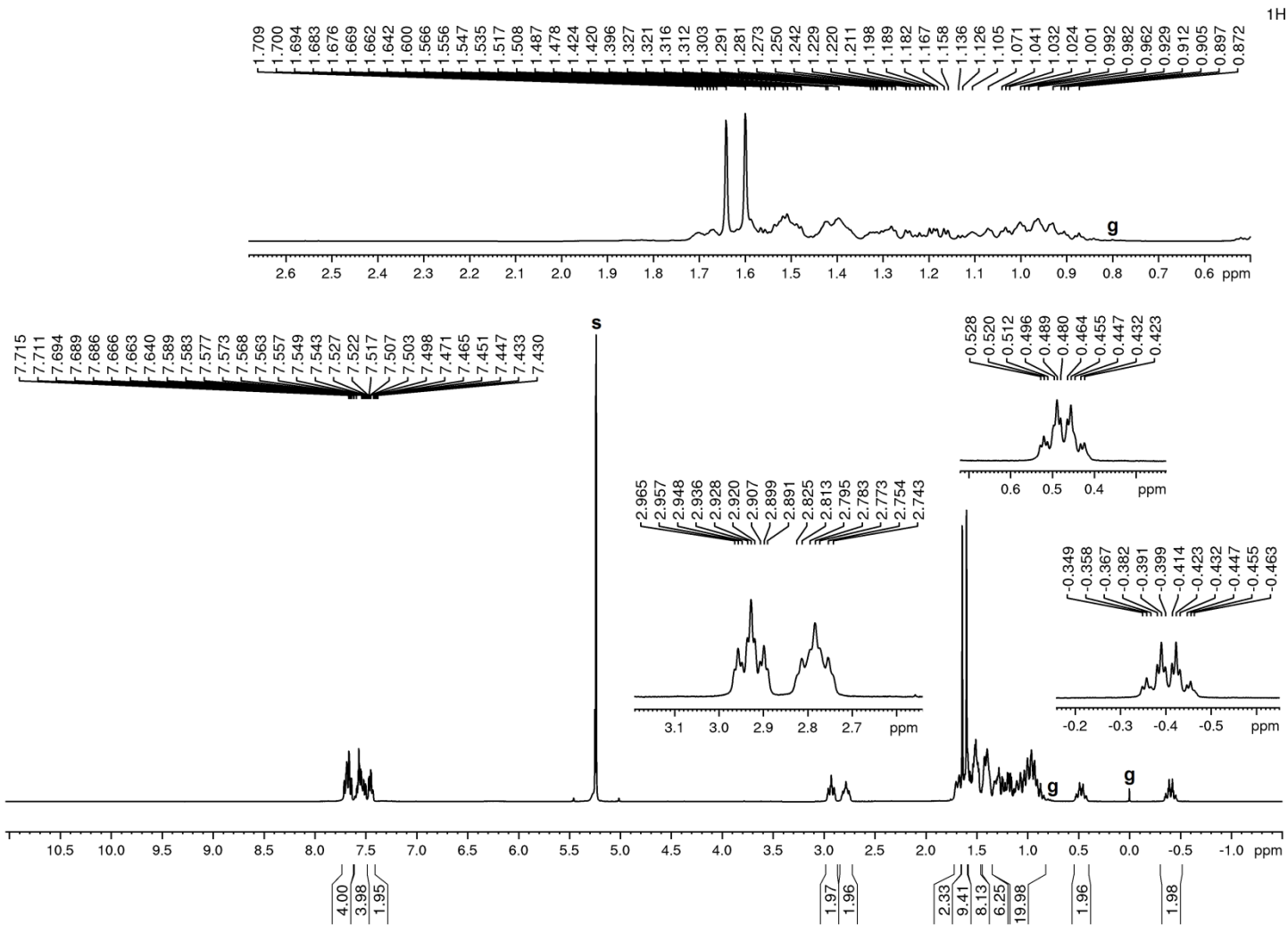
Figure S19. ^{1}H spectrum (CD$_2$Cl$_2$) of **B**[WCA]

138.078
137.988
132.666
132.637
132.309
132.279
131.933
131.916
131.842
131.824
130.244
130.142
129.830
129.720
125.653
122.698
119.789
116.946

67.210
67.125
67.037
55.535
55.514
55.462
55.441
34.119
33.519
33.392
33.337
33.293
33.166
32.415
31.225
29.658
29.631
25.475
25.408
25.301
25.247

S
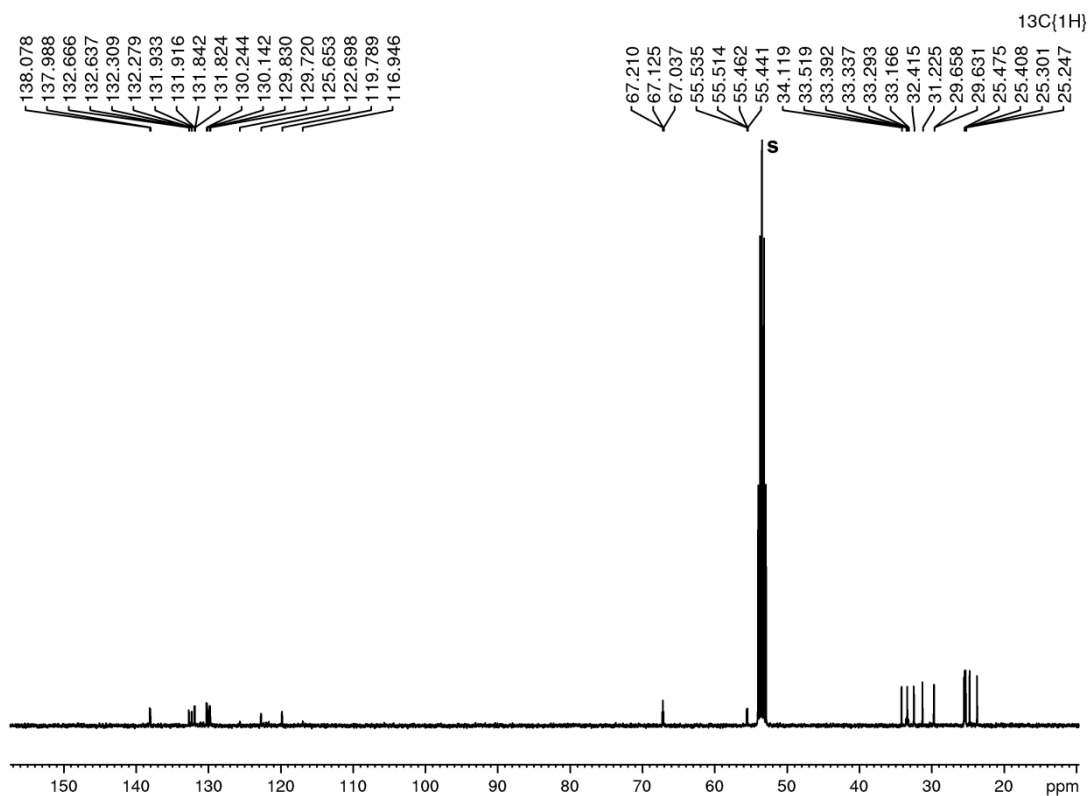
Figure S20. $^{13}C\{^{1}H\}$ spectrum (CD$_2$Cl$_2$) of **B**[WCA]

138.079
137.987
132.665
132.637
132.315
132.277
131.929
131.912
131.839
131.821
131.820
130.242
130.140
129.828
129.718

67.207
67.122
67.035
55.530
55.512
55.458
55.440
34.115
33.334
32.411
31.221
29.655
29.629
25.471
25.405
25.298
25.243
24.701
23.673

S
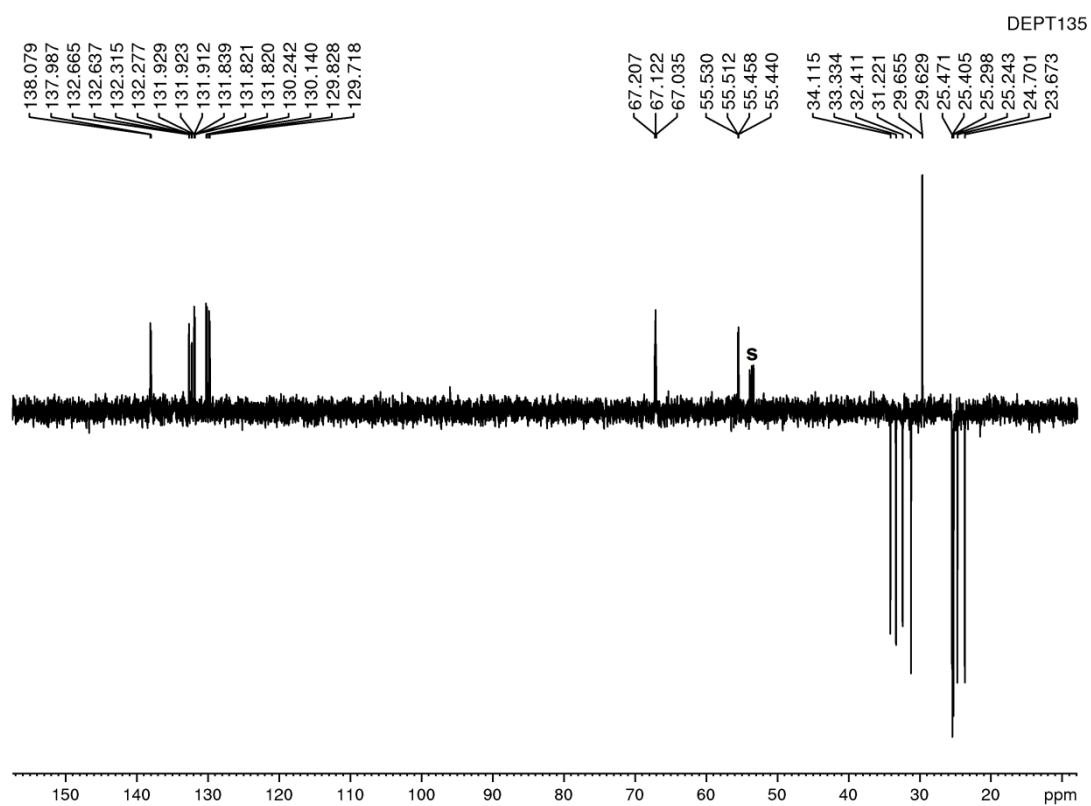
Figure S21. DEPT135 spectrum (CD$_2$Cl$_2$) of **B**[WCA]
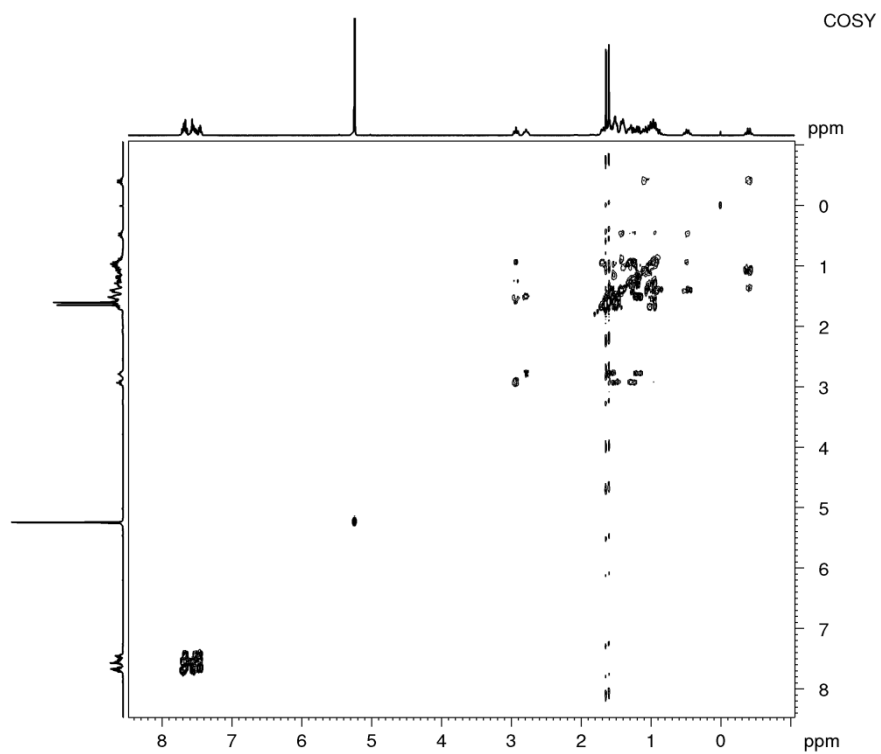
Figure S22. COSY spectrum (CD$_2$Cl$_2$) of **B**[WCA]
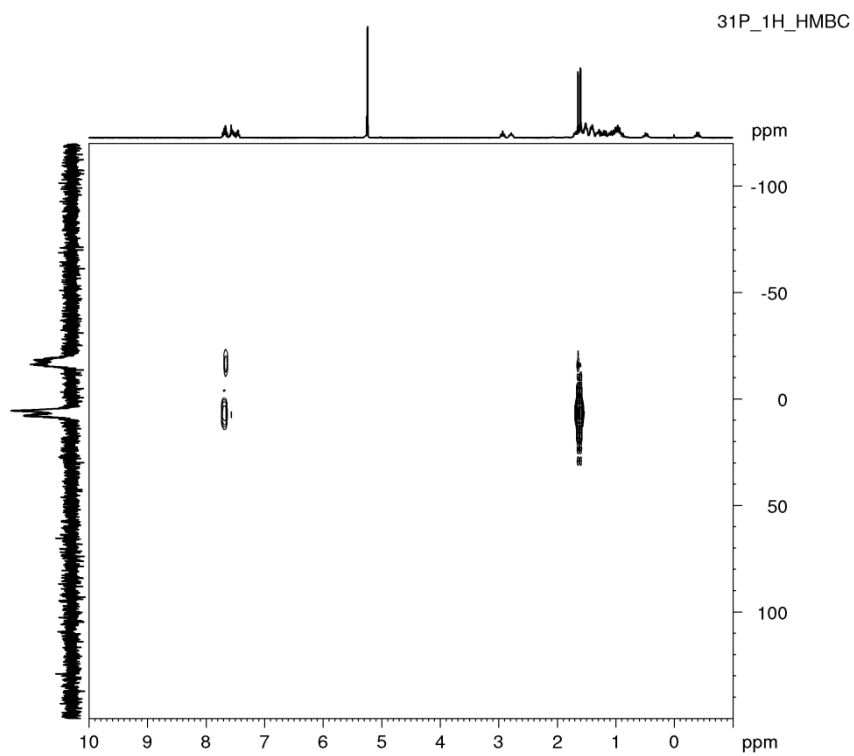
Figure S23. ^{31}P ^{1}H HMBC spectrum (CD$_2$Cl$_2$) of **B**[WCA]
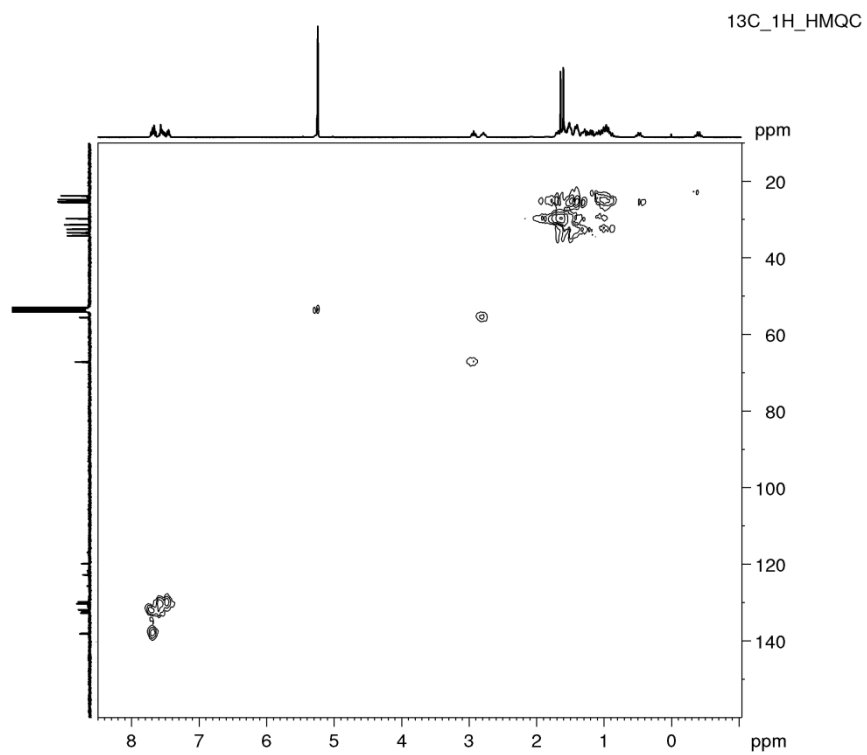
Figure S24. ^{13}C ^{1}H HMQC spectrum (CD$_2$Cl$_2$) of **B**[WCA]
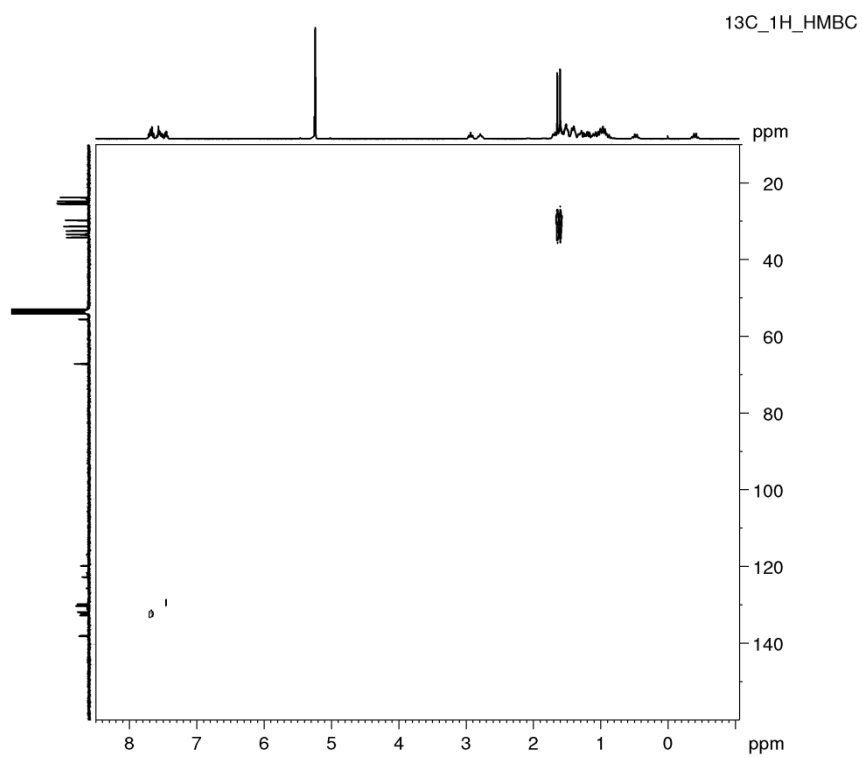
Figure S25. ^{13}C ^{1}H HMBC spectrum (CD$_2$Cl$_2$) of **B**[WCA]

—34.204

120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 ppm
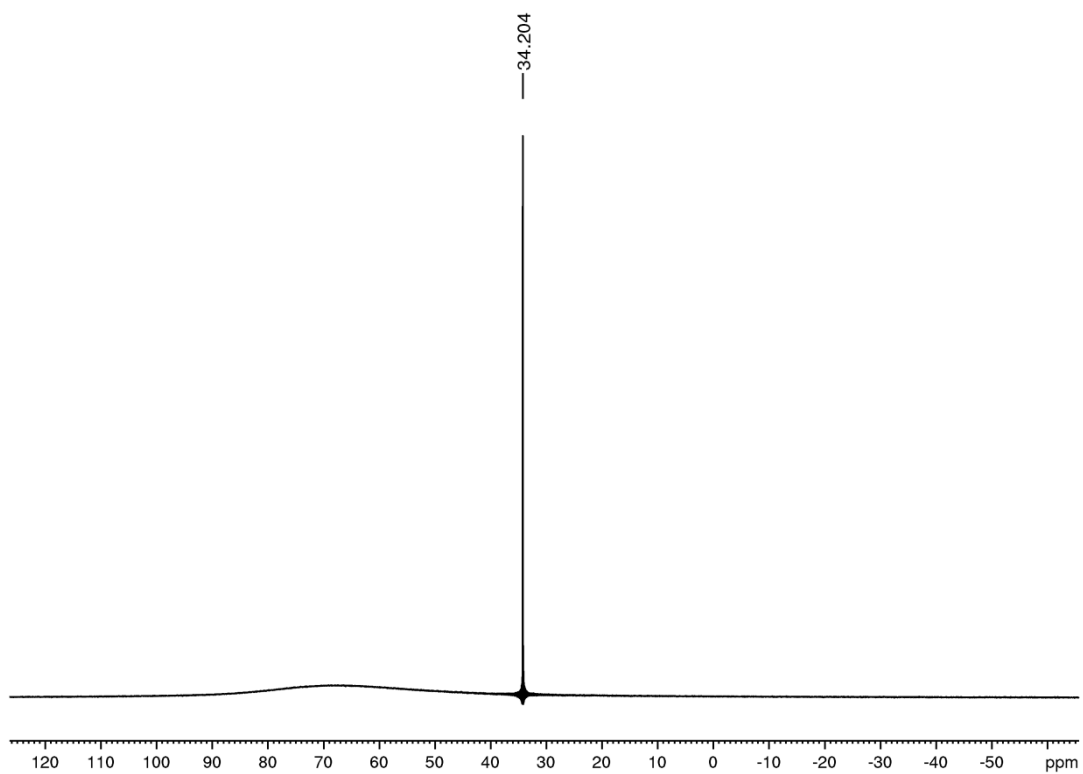
Figure S26. ^{27}Al spectrum (CD$_2$Cl$_2$) of **B**[WCA]

—-75.735

-74.0 -74.5 -75.0 -75.5 -76.0 -76.5 -77.0 -77.5 ppm
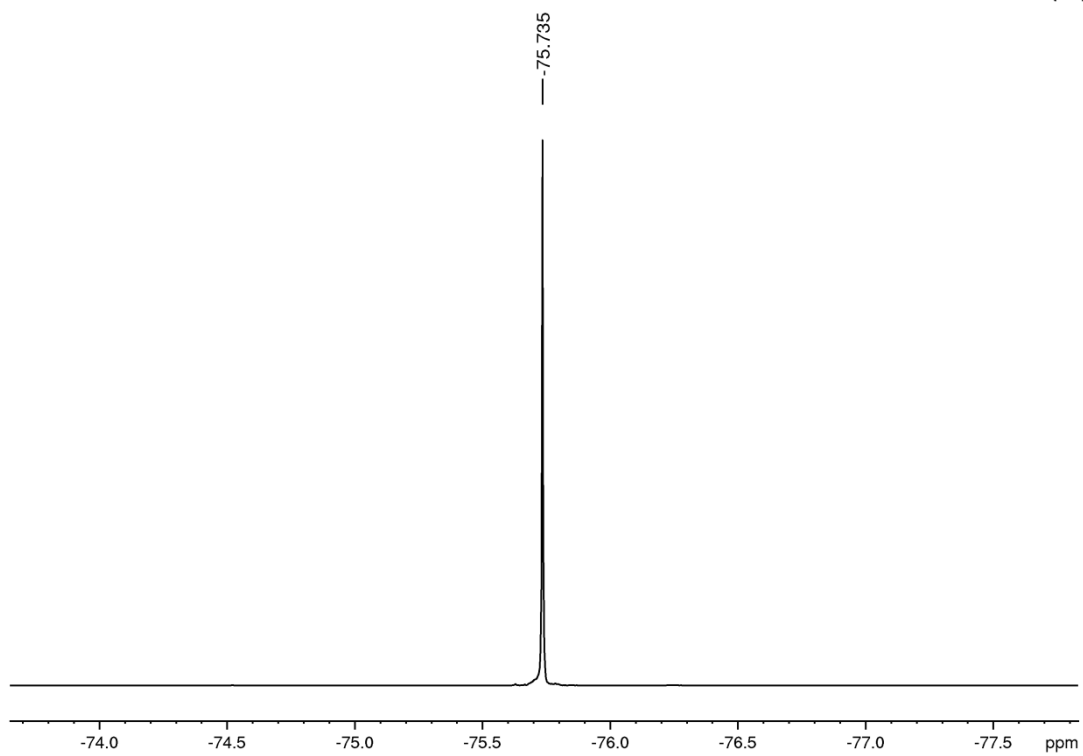
Figure S27. ^{19}F{^{1}H} spectrum (CD$_2$Cl$_2$) of **B**[WCA]

NMR spectra of D[WCA]

—29.304
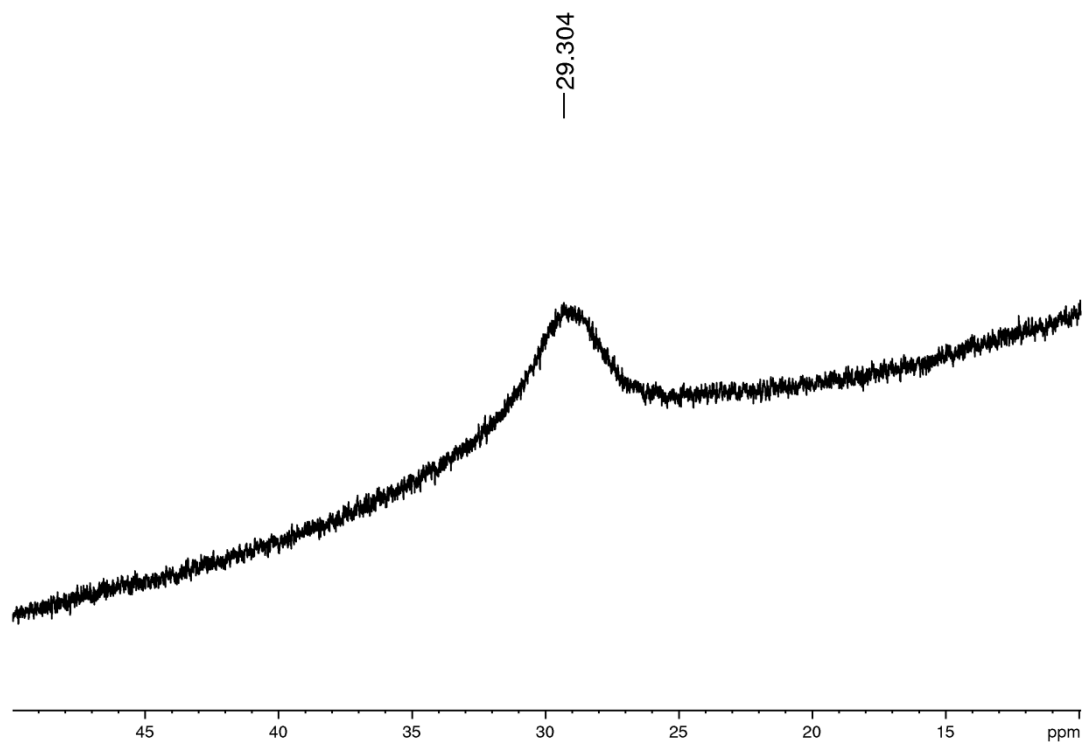
Figure S28. ^{11}B spectrum (CD$_2$Cl$_2$) of **D**[WCA]

—68.397
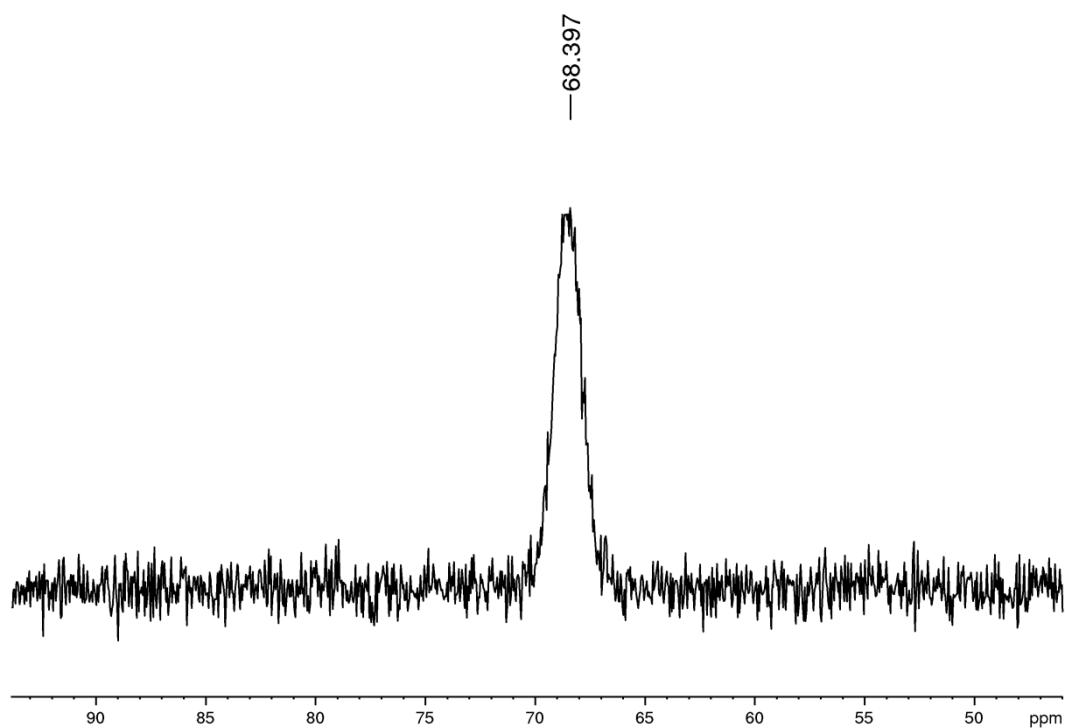
Figure S29. ^{31}P{^{1}H} spectrum (CD$_2$Cl$_2$) of **D**[WCA]
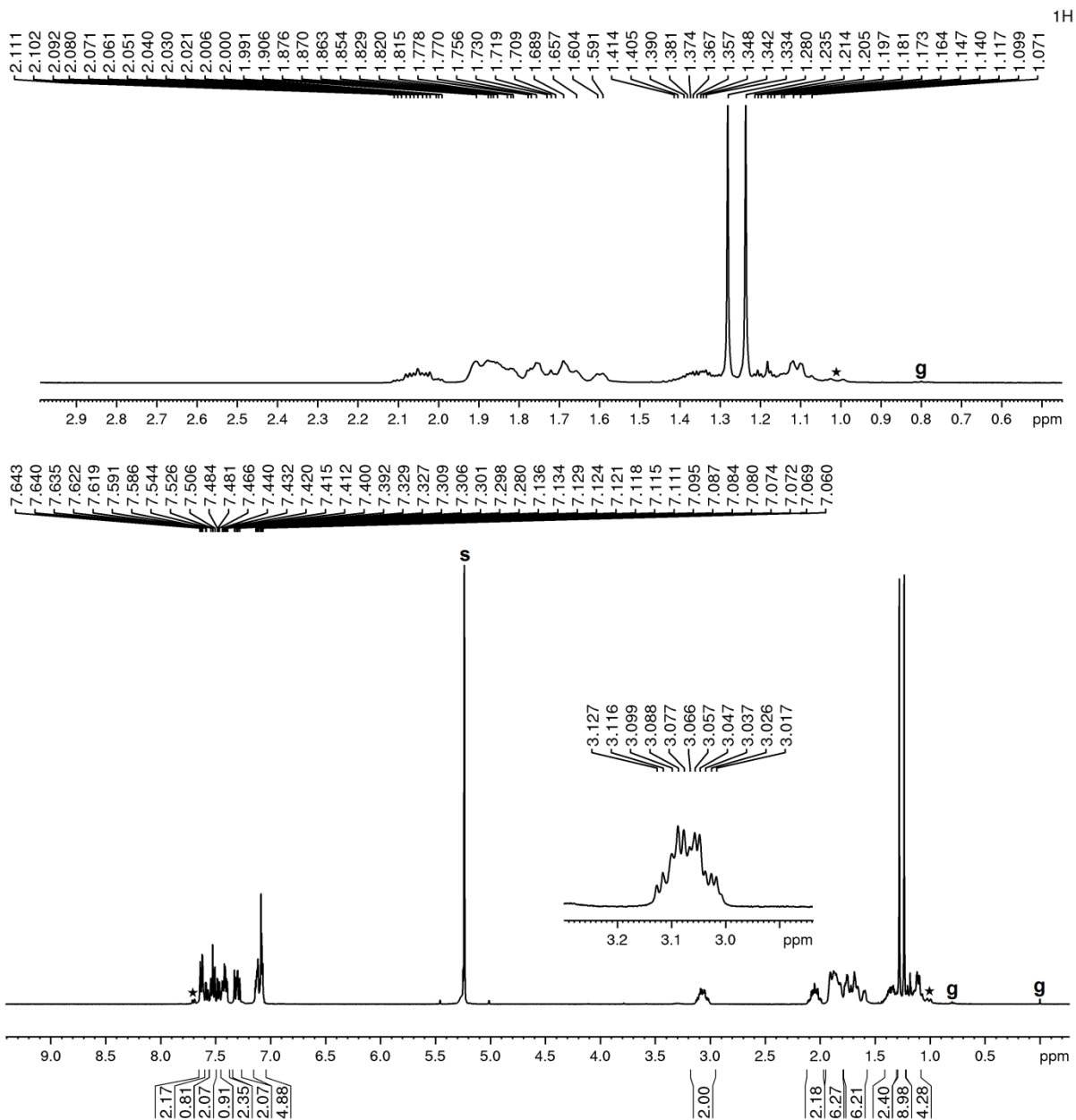
Figure S30. ^{1}H spectrum (CD$_2$Cl$_2$) of **D**[WCA]
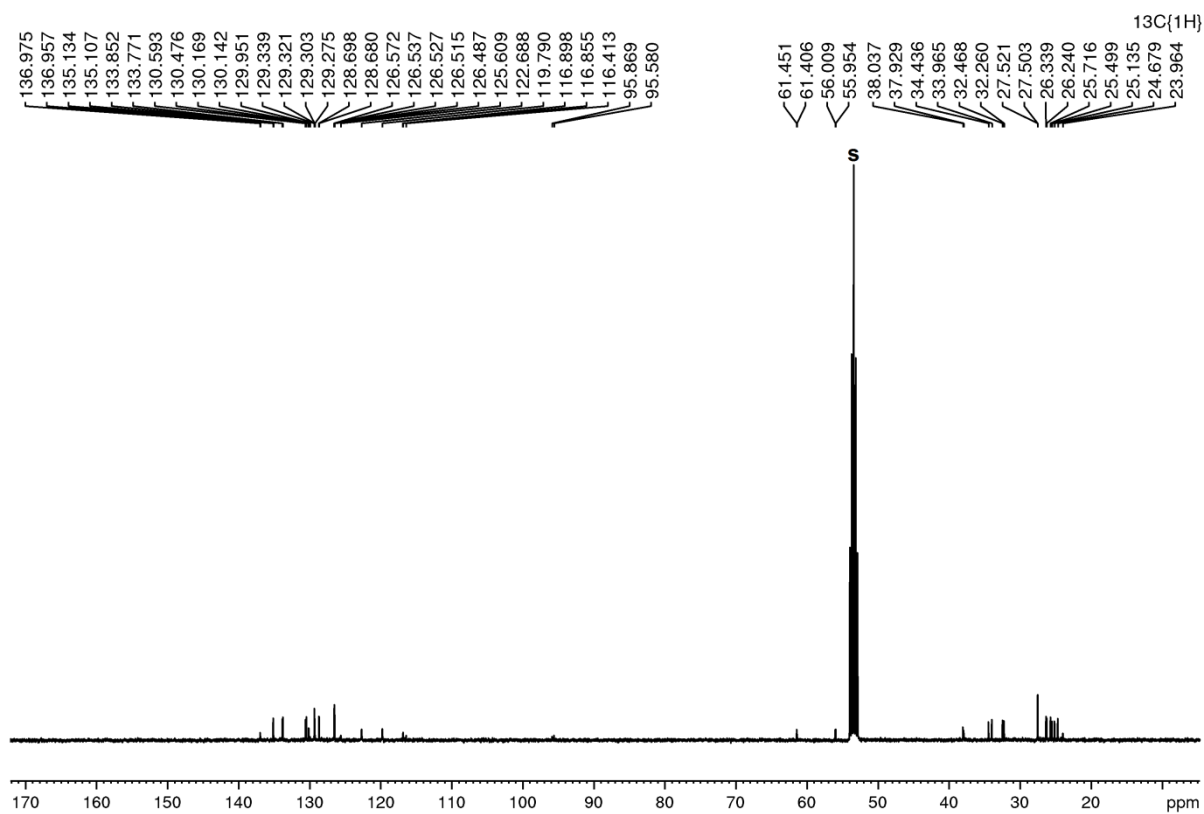
Figure S31. $^{13}C\{^1H\}$ spectrum (CD$_2$Cl$_2$) of **D**[WCA]
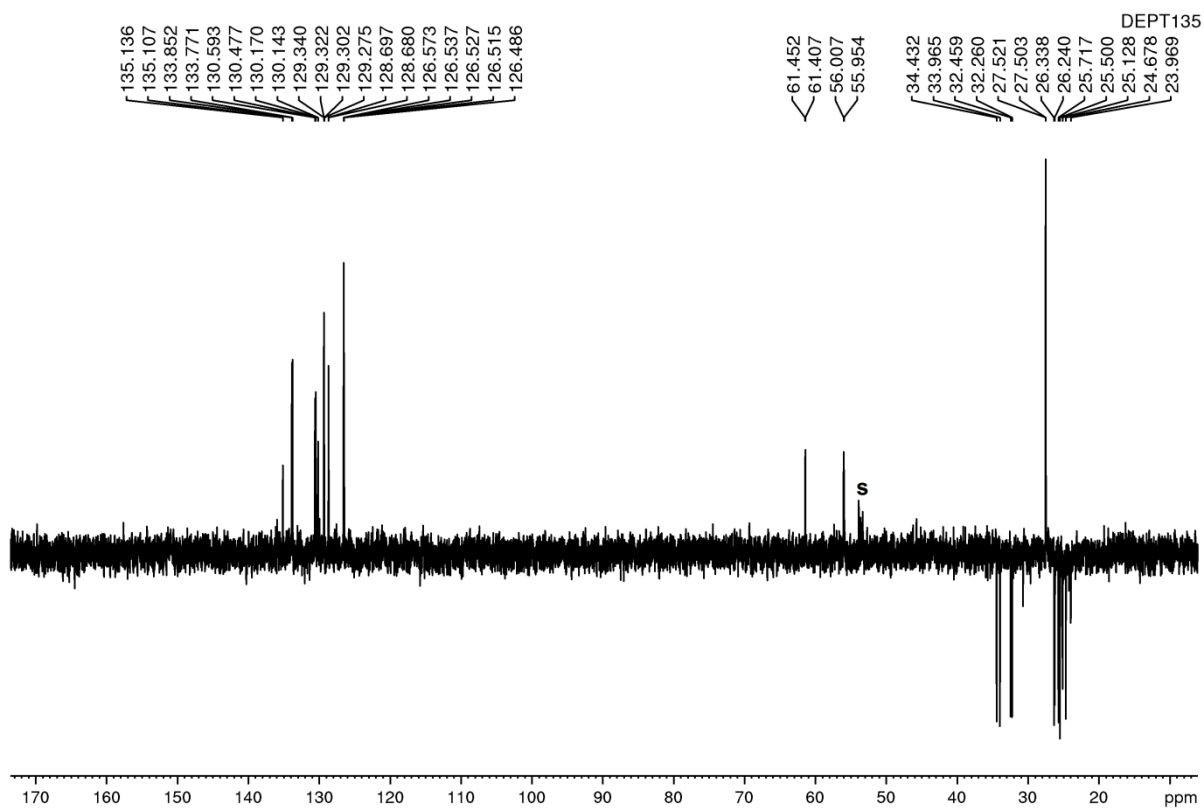
Figure S32. DEPT135 spectrum (CD$_2$Cl$_2$) of **D**[WCA]
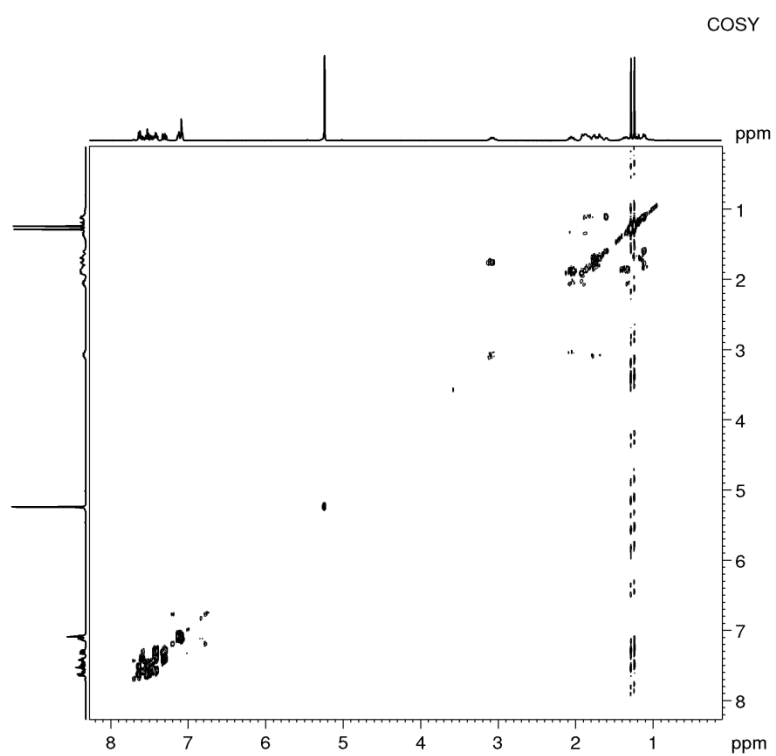
Figure S33. COSY spectrum (CD$_2$Cl$_2$) of **D**[WCA]
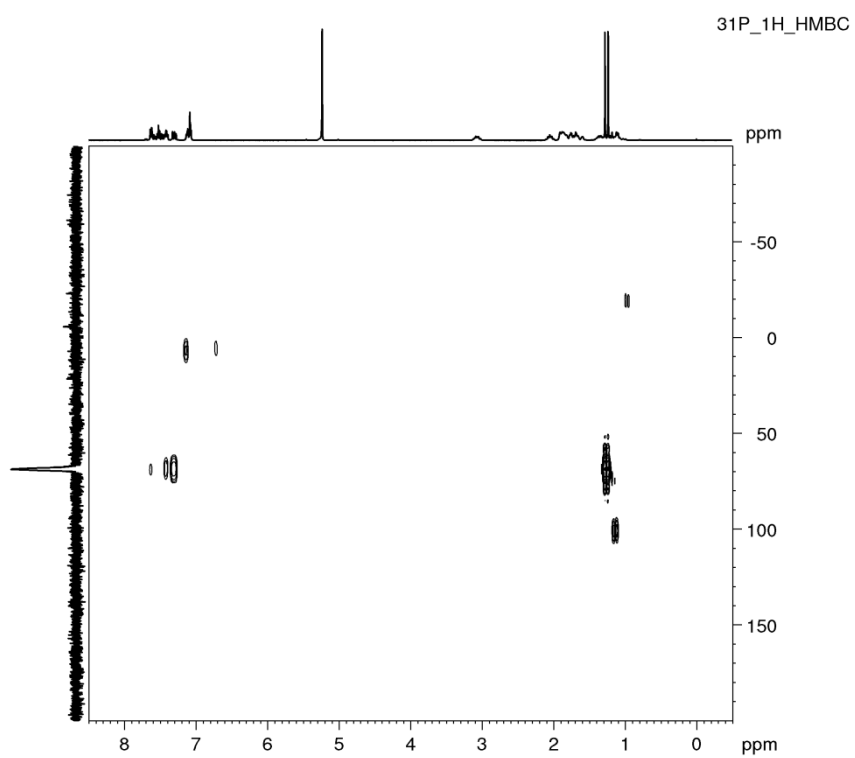
Figure S34. ^{31}P ^{1}H HMBC spectrum (CD$_2$Cl$_2$) of **D**[WCA]
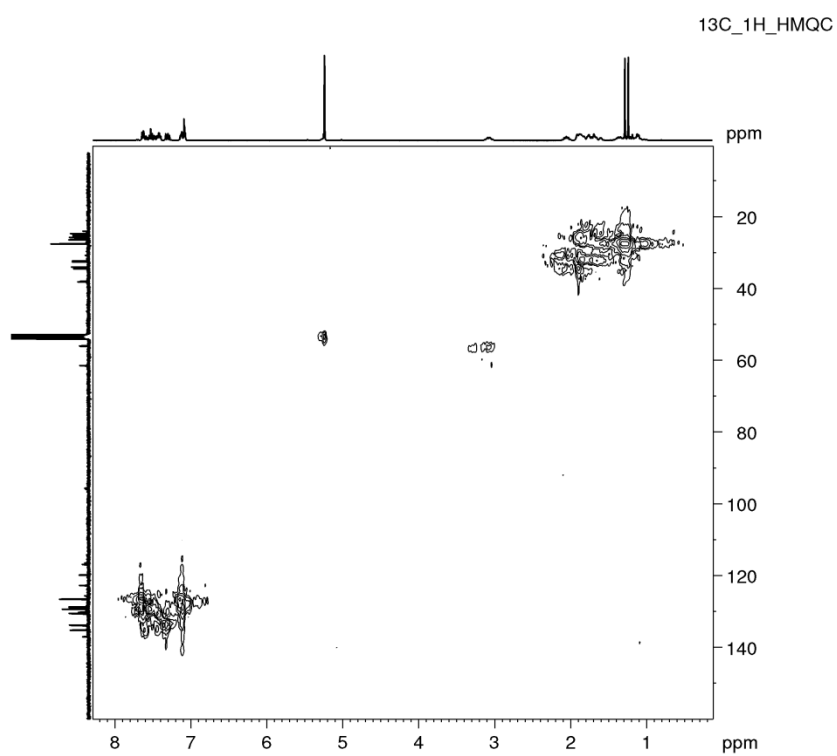
Figure S35. ^{13}C ^{1}H HMQC spectrum (CD$_2$Cl$_2$) of **D**[WCA]
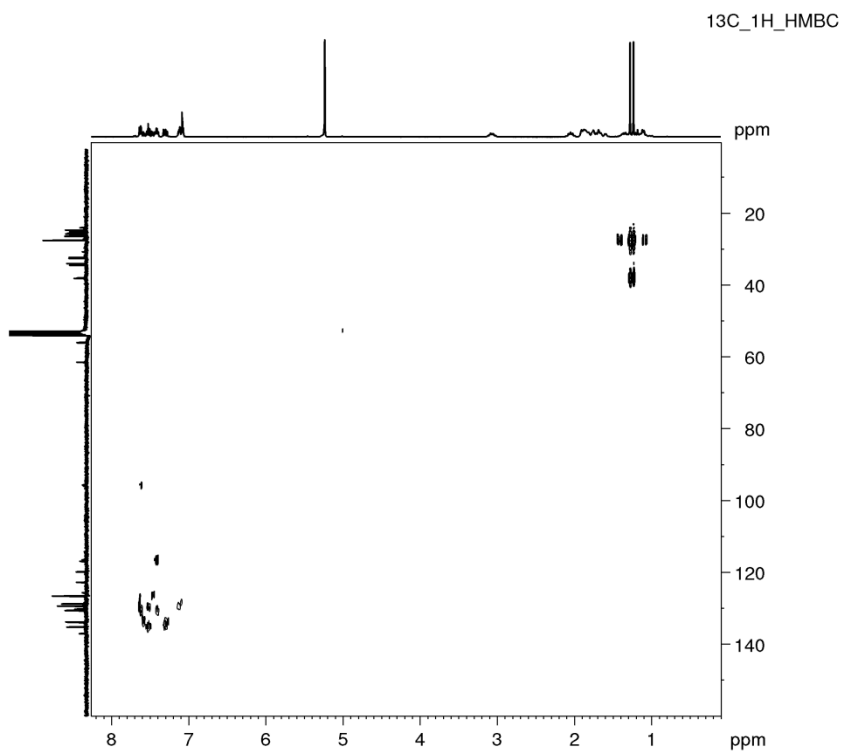
Figure S36. ^{13}C ^{1}H HMBC spectrum (CD$_2$Cl$_2$) of **D**[WCA]
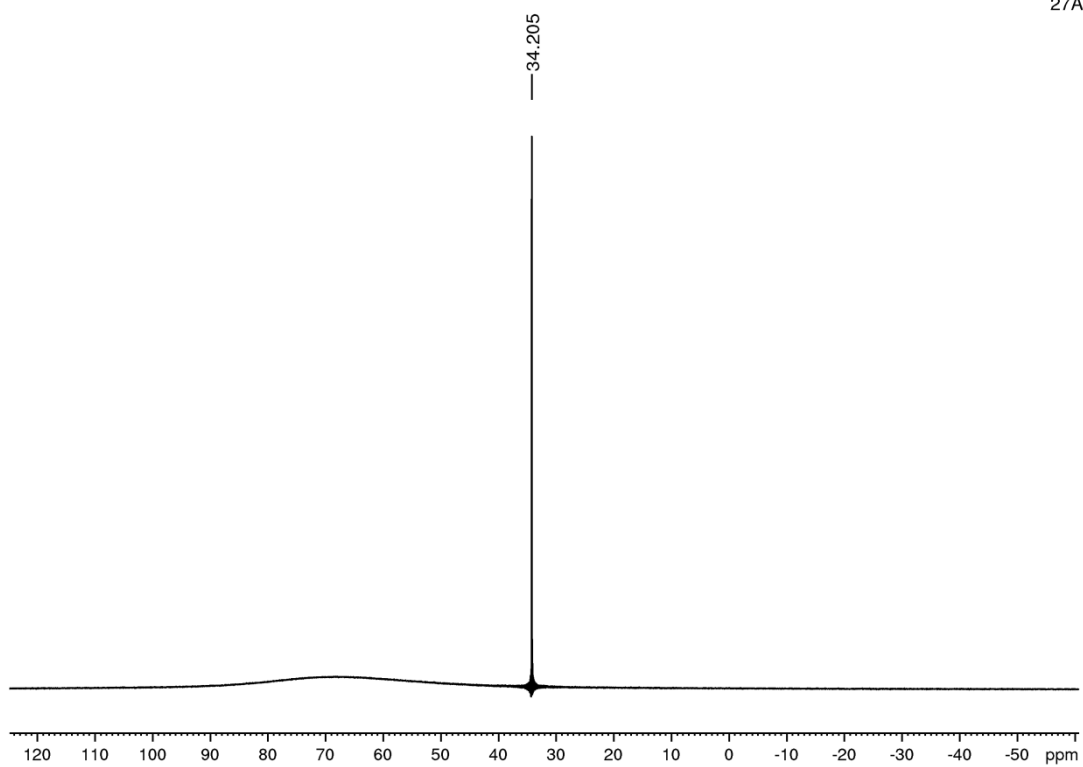
Figure 37. ^{27}Al spectrum (CD$_2$Cl$_2$) of **D**[WCA]
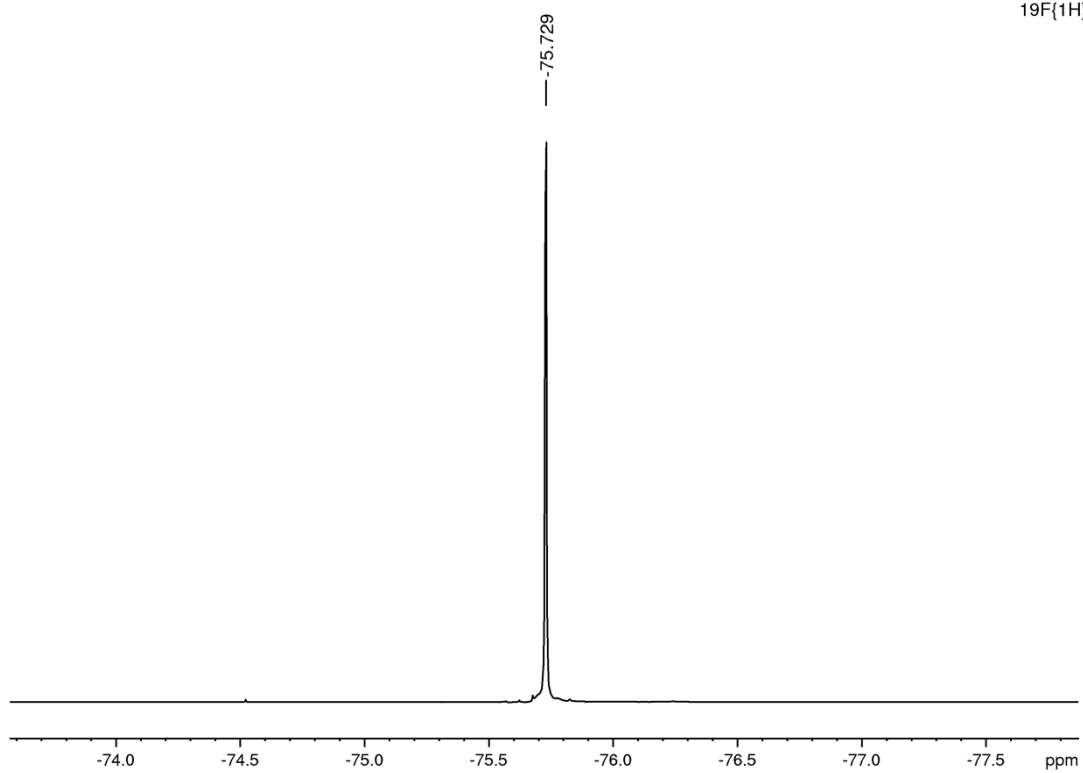
Figure S38. ^{19}F{^{1}H} spectrum (CD$_2$Cl$_2$) of **D**[WCA]

NMR of B[WCA] and C[WCA] crystals mixture
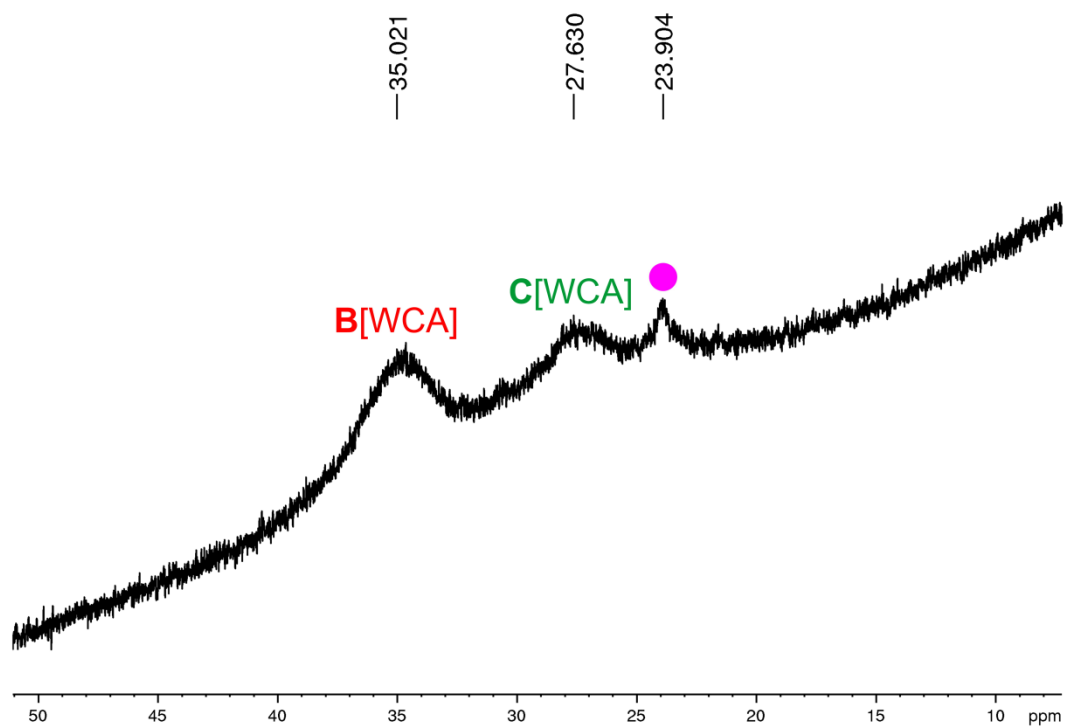
Figure S39. ^{11}B spectrum (CD$_2$Cl$_2$) of **B**[WCA] and **C**[WCA] crystals mixture
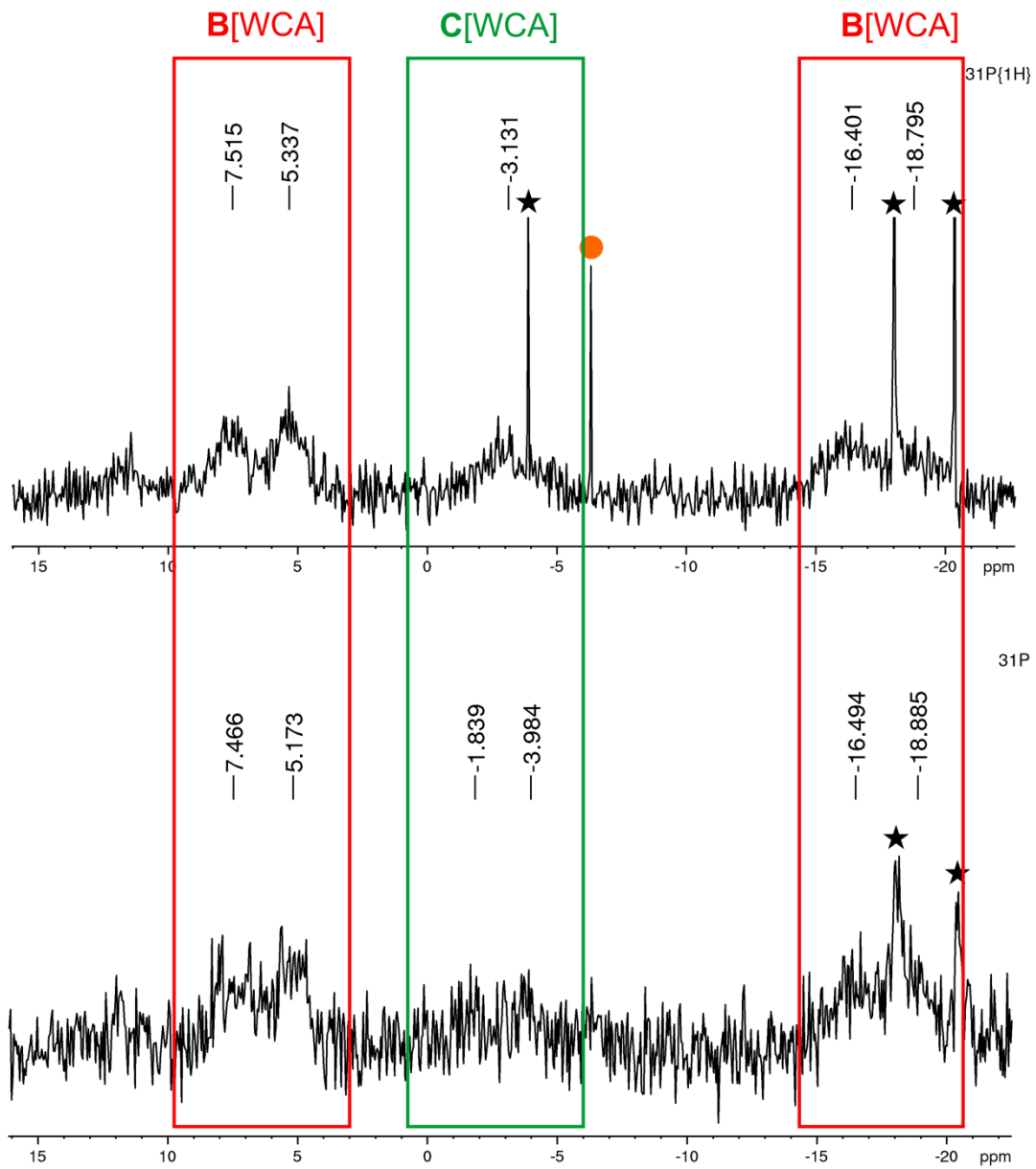
Figure S40. $^{31}P\{^1H\}$ and ^{31}P spectra (CD$_2$Cl$_2$) of of **B**[WCA] and **C**[WCA] crystals mixture

NMR spectra of isobutene

4.661
4.657
4.654
4.652
4.649
4.646
4.643

1.725
1.722
1.719

s

g

g

1.66

6.00

6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
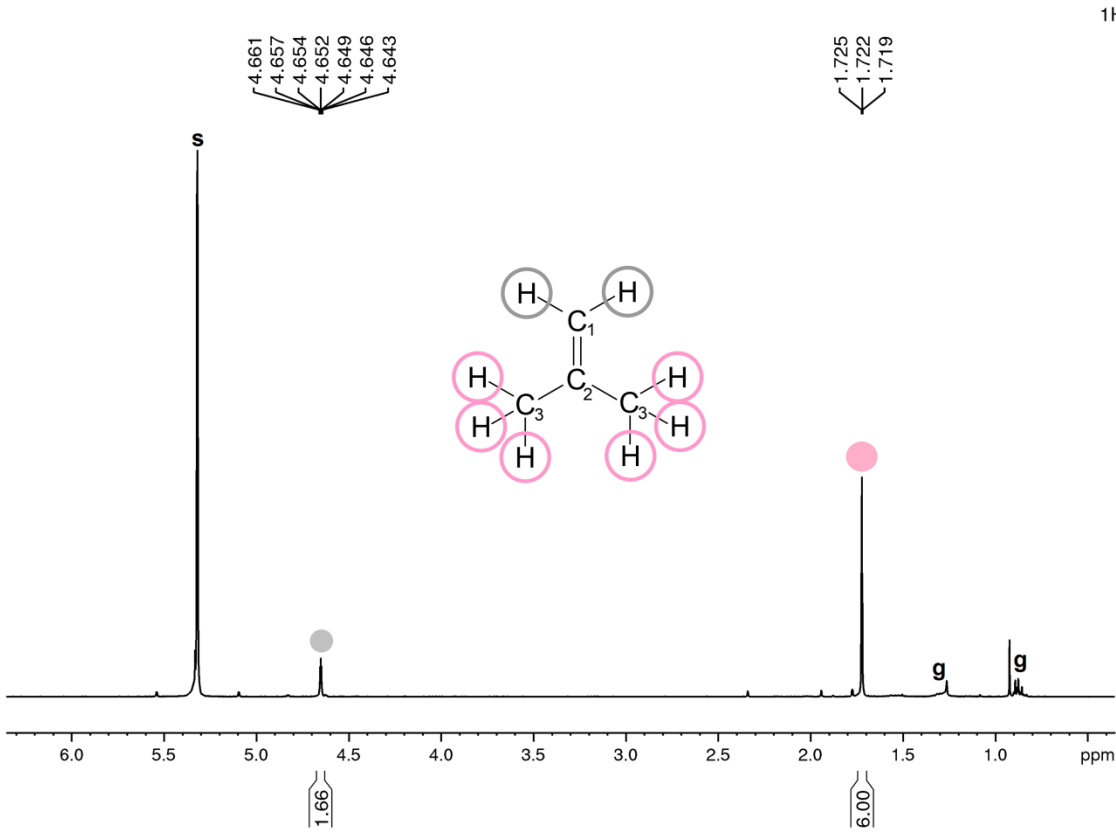
Figure S41. ^{1}H spectrum (CD$_2$Cl$_2$) of isobutene

13C{1H}

110.117

23.764

s

C$_1$

C$_3$

150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
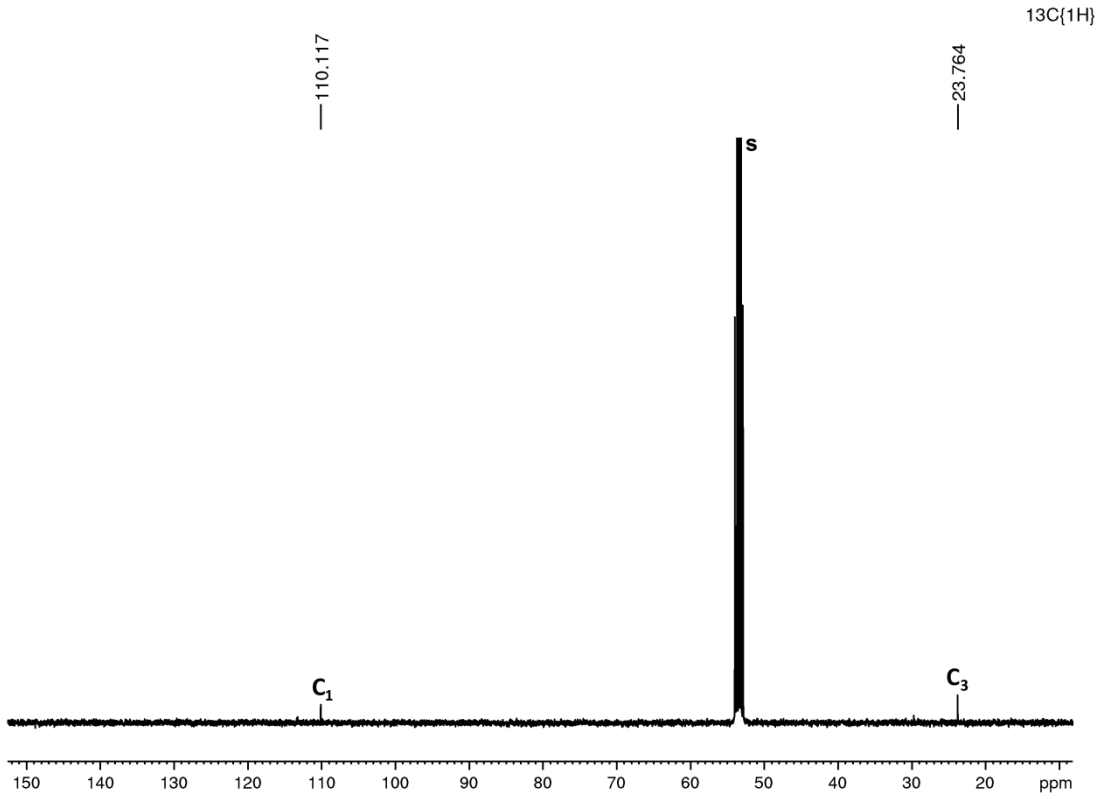
Figure S42. ^{13}C{^{1}H} spectrum (CD$_2$Cl$_2$) of isobutene
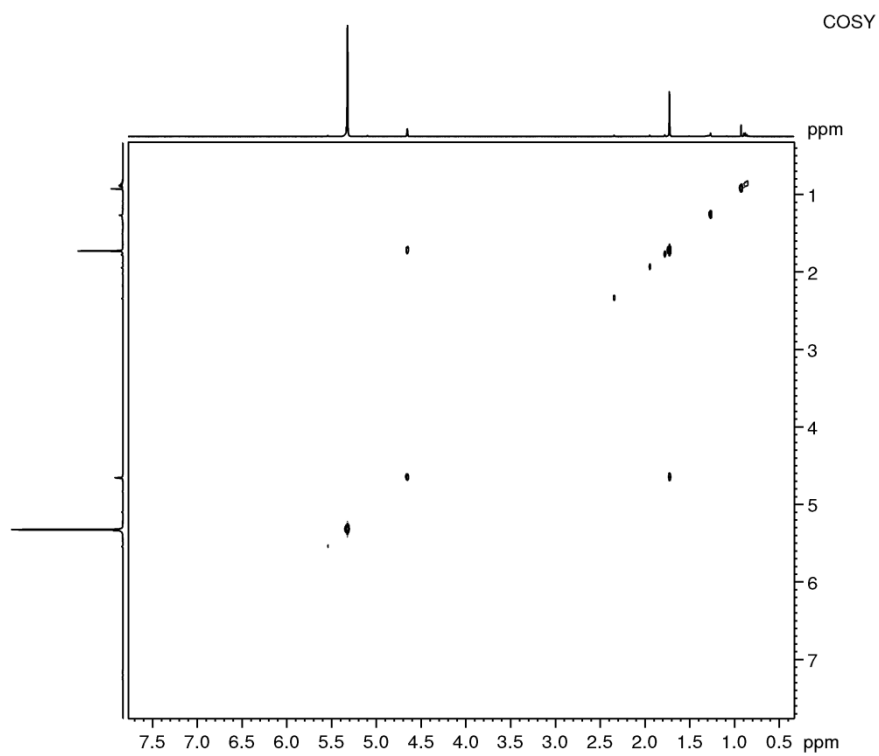
Figure S43. COSY spectrum (CD$_2$Cl$_2$) of isobutene
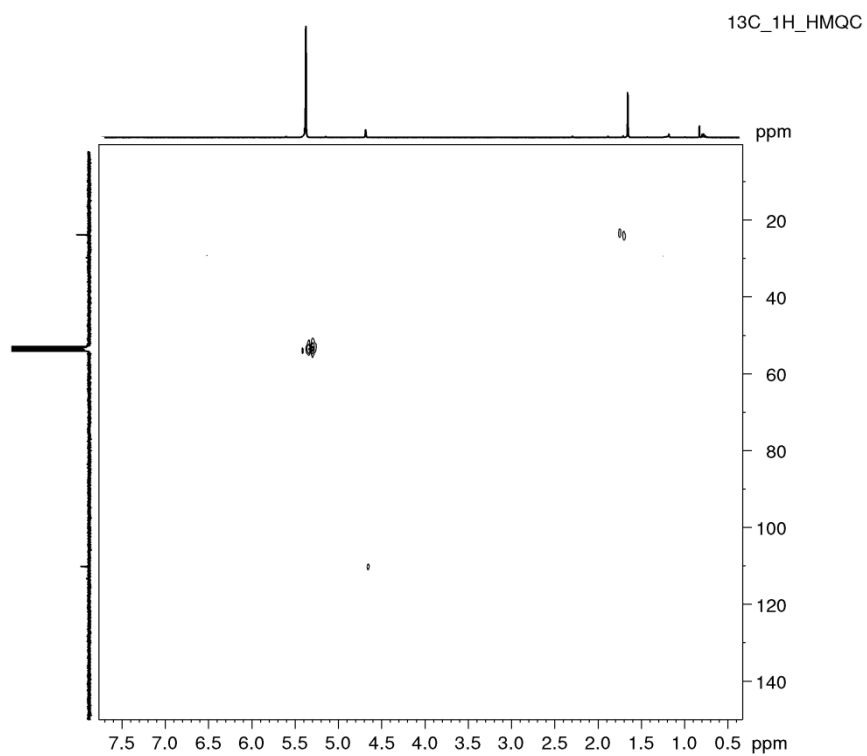
Figure S44. ^{13}C ^{1}H HMBC spectrum (CD$_2$Cl$_2$) of isobutene

NMR of reaction mixtures

NMR spectra were recorded after an overnight stirring of the resulting reaction mixtures.
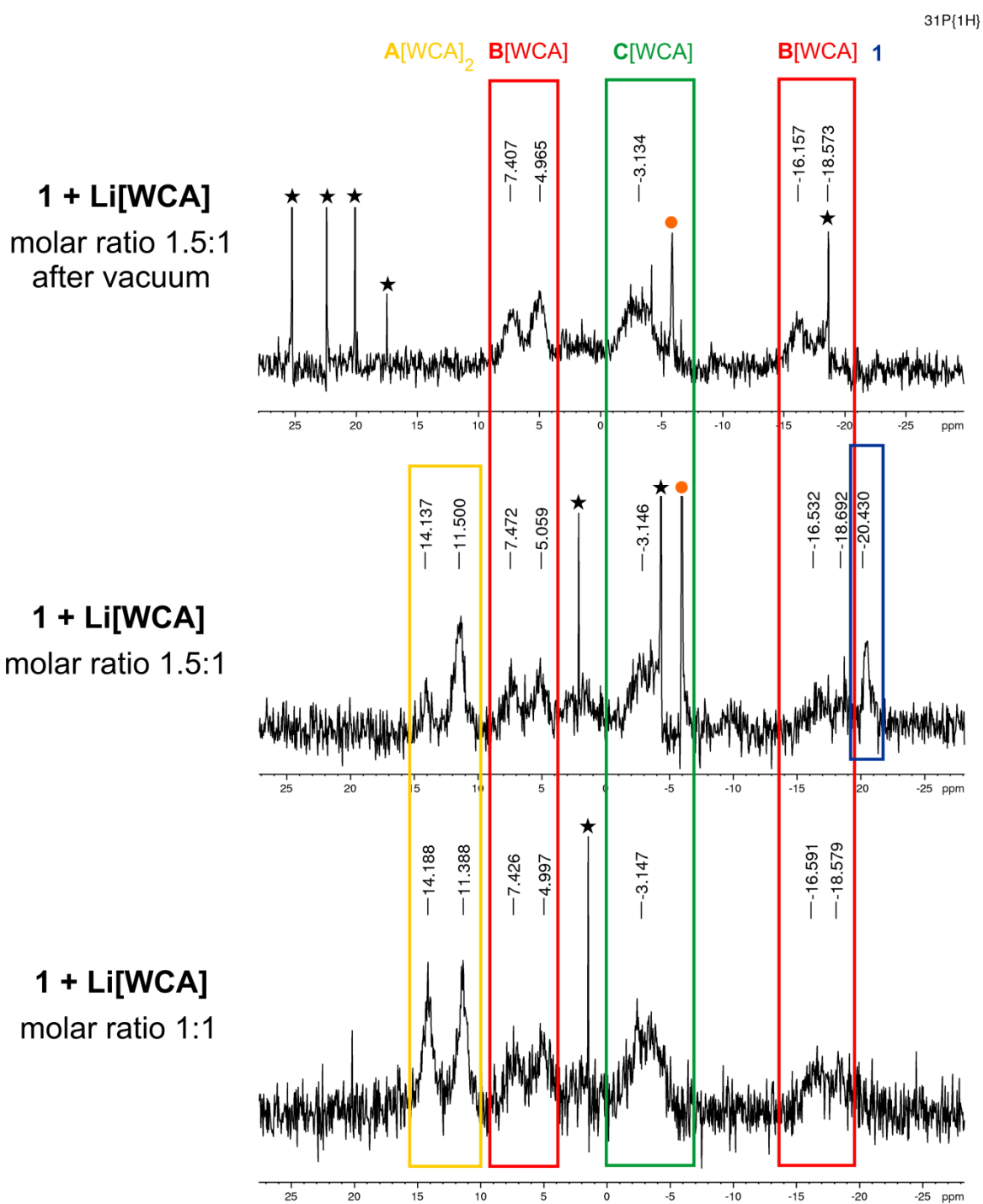
Figure S45. $^{31}P\{^1H\}$ NMR spectra (C_6D_6) of **1** + **Li[WCA]** reaction mixtures

X-ray structure analysis

X-ray structure analysis details

Diffraction intensity data for all crystals were collected on an IPDS 2T dual beam diffractometer (STOE & Cie GmbH, Darmstadt, Germany) at 120.0(2) K with Mo $K\alpha$ radiation of a microfocus X-ray source (GeniX 3D Mo High Flux, Xenocs, Sassenage, 50 kV, 1.0 mA, and λ = 0.71069 Å). Investigated crystals were thermostated under a nitrogen stream at 120 K using the CryoStream-800 device (Oxford CryoSystem, UK) during the entire experiment. Data collection and data reduction were controlled by using the X-Area 1.75 program (STOE, 2015). Absorption correction was performed only for data with absorption coefficient > 0.5 mm^{-1}, i.e **1** and **C**[WCA]. The structures were solved using intrinsic phasing implemented in SHELXT and refined anisotropically using the program packages Olex2[5] and SHELX-2015[6,7]. Positions of hydrogen atoms were calculated geometrically taking into account isotropic temperature factors. All H-atoms were refined as riding on their parent atoms with the usual restraints.

Structure **1** was refined without any special treatment. Absorption correction, by the integration method, was applied. Structure **A**[WCA]$_2$ contained disordered anion. One perfuoro-*t*-butyl group C_4F_9 bound to O1 was refined as disordered over two positions with occupation factors of 0.839(9)/0.161(9). Several restraints were applied to C-F bond lengths in this part to get stable refinement. The cation, as well as the molecules of CH_2Cl_2, occupied well defined positions and have relatively small displacement ellipsoids for all atoms. Structure **B**[WCA], contained disordered anion and disordered $CHCl_3$ molecules (solvent). Three perfuoro-*t*-butoxy groups OC_4F_9 containing O1, O3 and O4 were refined as disordered over two positions, with occupation factors of 0.614(3)/0.386(3), 0.741(4)/0.259(4) and 0.592(2)/0.408(2), respectively. Several restraints were applied to C-F and F-F distances in order to get stable refinement. Solvent $CHCl_3$ molecules were refined as disordered over two positions with occupation factors equal to 0.596(5)/0.404(5). The cation is placed in the well-defined position with relatively small displacement ellipsoids for all atoms. Structure **C** required absorption correction, by the integration method, but was refined as fully ordered with no special treatment. Structure **D**[WCA] was refined with no special treatment.

Crystallographic data for all structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. **CCDC 2163474-2163477** and **2184829**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

Table S1. Crystal data and structure refinement for **1**, **A**[WCA]$_2$, **B**[WCA], **C**[WCA], and **D**[WCA].

	1	**A**[WCA]$_2$	**B**[WCA]	**C**[WCA]	**D**[WCA]
CCDC deposition No	2163474	2163475	2163476	2163477	2184829
Chemical formula	C$_{22}$H$_{36}$BBrNP	C$_{16}$AlF$_{36}$O$_4$· ·0.5(C$_{44}$H$_{72}$B$_2$N$_2$P$_2$)· ·2(CH$_2$Cl$_2$)	C$_{16}$AlF$_{36}$O$_4$· ·C$_{40}$H$_{63}$B$_2$N$_2$P$_2$· ·CHCl$_3$	C$_{22}$H$_{37}$BBrNP· ·AlC$_{16}$F$_{36}$O$_4$	C$_{16}$AlF$_{36}$O$_4$· ·C$_{35}$H$_{46}$BNOP
M$_r$ [g·mol^{-1}]	436.21	1493.29	1741.99	1404.35	1505.65
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Temperature [K]	120	120	120	120	120
a [Å]	9.933(4)	14.6428(8)	12.7391(3)	12.081(3)	12.7439 (9)
b [Å]	10.340(3)	15.3495(10)	15.3673(4)	14.550(3)	15.5369 (12)
c [Å]	11.952(3)	25.7474(14)	20.1094(5)	15.910(5)	16.9795 (12)
α [°]	78.12(2)	90	89.963(2)	76.92(2)	108.554 (5)
β [°]	89.80(3)	105.268(4)	74.734(2)	79.54(2)	92.179 (6)
γ [°]	71.83(2)	90	73.552(2)	76.776(18)	107.303 (6)
V [Å^3]	1139.0(6)	5582.7(6)	3630.76(16)	2626.8(12)	3010.1 (4)
Z	2	4	2	2	2
Radiation type λ [Å]	Mo $K\alpha$ 0.71073	Mo $K\alpha$ 0.71073	Mo $K\alpha$ 0.71073	Mo $K\alpha$ 0.71073	Mo $K\alpha$ 0.71073
Calculated density [g·cm^{-1}]	1.272	1.777	1.593	1.776	1.661
μ [mm^{-1}]	1.88	0.42	0.32	1.00	0.22
Crystal size [mm]	0.41 × 0.24 × 0.21	0.42 × 0.23 × 0.16	0.22 × 0.16 × 0.11	0.41 × 0.19 × 0.12	0.24 × 0.16 × 0.13
F(000)	460	2976	1760	1392	1512
R_{int}	0.038	0.034	0.027	0.057	0.049
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13150 6101 5007	34189 10939 8075	56689 19572 14862	38603 14165 9727	23915 11775 7045
$R[F^2 > 2\sigma(F^2)]$	0.034	0.087	0.041	0.079	0.069
$wR(F^2)$	0.091	0.272	0.112	0.242	0.206
S	1.06	1.02	1.07	1.05	1.03
No. of reflections	6101	10939	19572	14165	11775
No. of parameters	238	846	1365	756	869
No. of restraints	0	21	20	0	0
Δ$>_{max}$ [e·Å^{-3}]	0.46	1.68	0.54	1.46	0.70
Δ$>_{min}$ [e·Å^{-3}]	-0.46	-1.56	-0.49	-1.33	-0.36

X-ray structure of 1
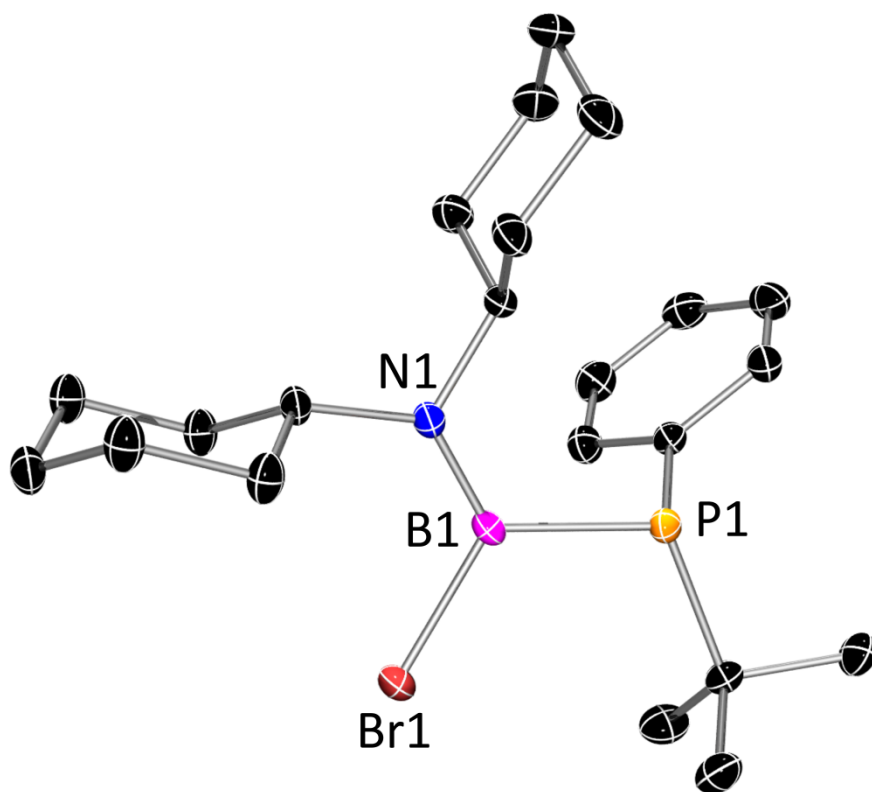
Figure S46. Molecular structure of **1**. The thermal ellipsoids are shown at the 50% probability level. Important bond distances [Å]: B1–Br1 1.966(2); B1–P1 1.954(2); B1–N1 1.393(2). Important angles [°]: P1–B1–N1 119.7(1), N1–B1–Br1 120.1(1), Br1–B1–P1 119.9(1); B1–P1–C1 112.92(8), C1–P1–C5 102.52(8), C5–P1–B1 101.87(8); B1–N1–C11 127.9(1), C11–N1–C17 113.0(1), C17–N1–B1 119.0(1).

X-ray structure of A[WCA]$_2$
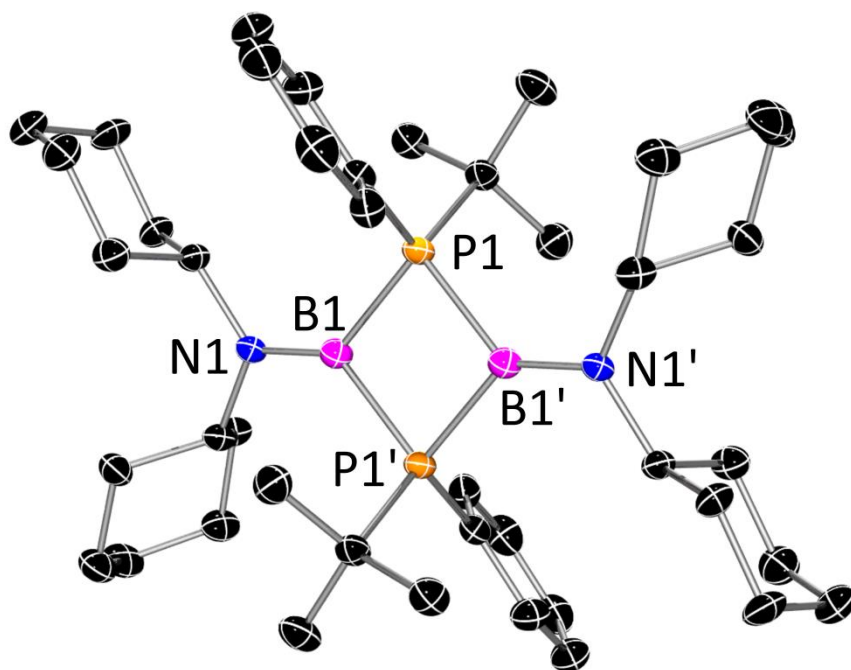
Figure S47. Molecular structure of phosphaborinium cation **A^{2+}**. Counterions are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. Important bond distances [Å]: B1–P1 1.979(4); B1' – P1 1.981(5); B1–N1 1.377(6). Important angles [°]: P1–B1–N1 133.03(3), N1–B1 – P1' 132.7(3), P1'–B1–P1 94.1(2); B1–P1–C1 111.5(2), C1–P1–C5 113.4(2), C5–P1–B1' 116.7(2), B1'–P1–B1 85.9(2), B1–P1–C5 115.0(2), C1–P1–B1' 111.5(2); B1–N1–C11 119.1(3), C11–N1–C17 122.4(3), C17–N1–B1 118.5(3).

X-ray structure of B[WCA]
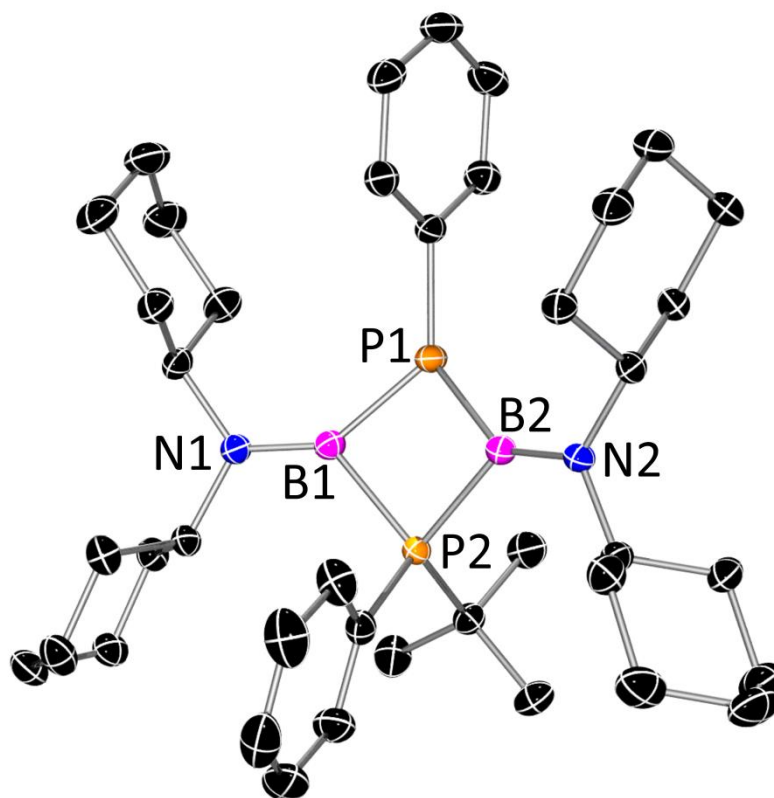
Figure S48. Molecular structure of borinium-phosphaborene adduct **B⁺**. The counterion is omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. Important bond distances [Å]: B1–P1 1.881(2); B2 – P1 1.882(2); B1 – P2 1.970(2); B2 – P2 1.963(2); B1–N1 1.376(2); B2 – N2 1.380(2). Important angles [°]: P1–B1–N1 142.3(1), N1–B1–P2 128.9(1), P2–B1–P1 88.76(7); P1–B2–N2 141.2(1), N2–B2–P2 129.8(1), P2–B2–P1 88.96(7); B1–P1–C1 130.76(7), C1–P1–B2 127.61(7), B2–P1–B1 91.01(7); B1–P2 –C19 109.98(7), C19–P2–C25 113.57(6), C25–P2–B2 116.07(7), B2–P2–B1 86.06(7); B1–P2– C25 117.44(7), C19–P2–B2 110.74(7); B1–N1–C7 123.0(1), C7–N1–C13 115.8(1), C13–N1–B1 121.1(1); B2–N2–C29 121.8(1), C29–N2–C35 115.7(1), C35–N2–B2 122.5(1).

X-ray structure of C[WCA]
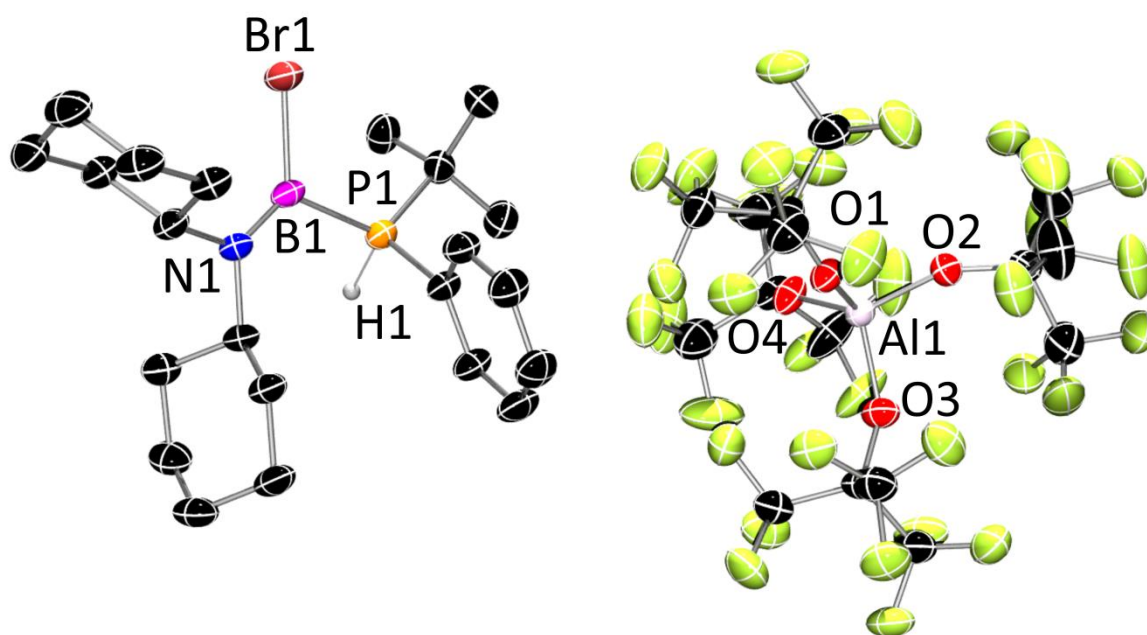
Figure S49. Molecular structure of **C**[WCA]. The thermal ellipsoids are shown at the 50% probability level. Important bond distances [Å]: B1–Br1 1.926(2); B1–P1 1.967(5); P1–H1 1.45(4); B1–N1 1.370(6). Important angles [°]: P1–B1–N1 120.3(3), N1–B1–Br1 125.6(3), Br1–B1–P1 113.7(2); B1–P1–C1 120.5(2), C5–P1–B1 104.0(2), C1–P1–C5 112.1(2); B1–N1–C11 121.2(3), C11–N1–C17 113.1(3), C17–N1–B1 125.6(3).

X-ray structure of D[WCA]
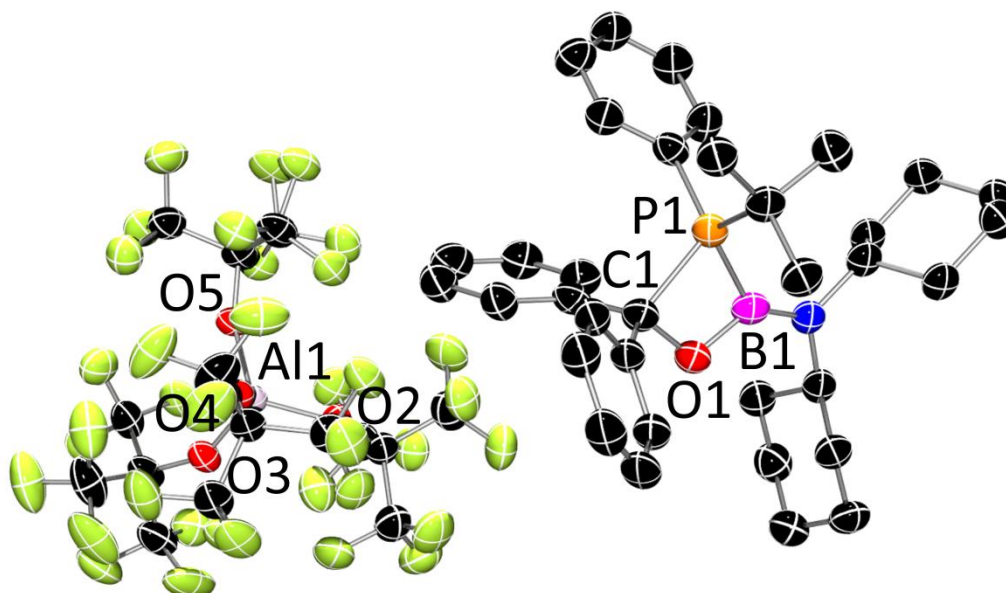
Figure S50. Molecular structure of of **D**[WCA]. The thermal ellipsoids are shown at the 50% probability level. Important bond distances [Å]: B1–P1 1.958(6); B1–O1 1.387(5); B1–N1 1.359(6); P1–C1 1.941(5); C1–O1 1.465(7). Important angles [°]: P1–B1–N1 138.1(4), N1–B1–O1 129.4(4), O1–B1–P1 92.4(3); B1–P1–C1 71.2(2), C1–P1–C26 121.2(2), C26–P1–C30 111.0(2), C30–P1–C1 112.3(2), C30–P1–B1 118.2(2), B1–P1–C26 117.9(2); B1–N1–C14 121.8(4), C14–N1–C20 116.8(3), C20–N1–B1 121.4(4), P1–C1–C2 112.5(3), C2–C1–C8 116.5(4), C8–C1–O1 110.3(4), O1–C1–P1 90.7(3), P1–C1–C8 114.9(3), C2–C1–O1 108.8(4); B1–O1–C1 105.4(3).

DFT calculations

General methods

All calculations presented in the paper were performed using the Gaussian 09[8] program package. Molecular geometries of all compounds were optimized using density functional theory at the M06-2X functional by Truhlar *et al*[9] with 6-31+G(d,p) basis set, including the presence of a solvent (CH_2Cl_2) using the CPCM polarizable conductor calculation model.[10] The M06-2X exchange-correlation functional has been chosen as it has good overall performance for the description of main-group element compounds. Molecular geometries were energy-optimized, and the most stable (the lowest energy) conformer was identified during the potential energy surface scanning. The nature of the final solvent-phase geometries as local minima (no imaginary frequencies) on the potential energy surface was then validated by harmonic frequency calculations at the same level of theory. Values of calculated energies, enthalpies and Gibbs free-energies derived from thermochemical calculations were corrected for the zero-point energy (ZPE). NBO analysis was performed for optimized gas-phase structures derived from X-ray analysis at M06-2X//6-31+G(d,p) level of theory by applying the NBO 3.1[11] module built-in Gaussian 09 and 'BNDIDX' keyword to calculate Wiberg bond orders.

Table S2. Selected computational parameters obtained for considered systems (in atomic units A.U.): ε_0 - electronic energy; $\varepsilon_{0 + ...}$ - sum of electronic and: E_{zpe} - zero-point energies, E_{therm} - thermal energies, H – thermal enthalpies, G - thermal free energies calculated at M06-2X//6-31+G(d,p) level of theory including presence of a solvent (CH_2Cl_2, CPCM model).

Compound	E_{electr} [A.U.]	$\varepsilon_0 + E_{ZPE}$ [A.U.]	$\varepsilon_0 + E_{therm}$ [A.U.]	$\varepsilon_0 + H$ [A.U.]	$\varepsilon_0 + G$ [A.U.]
1	-3852.492468	-3851.939890	-3851.912571	-3851.911627	-3851.997295
2$^+$	-1280.429892	-1279.879315	-1279.853054	-1279.852110	-1279.937176
3$^+$	-2560.507288	-2559.412462	-2559.361585	-2559.360641	-2559.495498
***cis*-A^{2+}**	-2560.938590	-2559.828025	-2559.776988	-2559.776044	-2559.909119
***trans*-A^{2+}**	-2560.949111	-2559.839522	-2559.788289	-2559.787344	-2559.920685
B$^+$	-2403.370054	-2402.387285	-2402.341282	-2402.340338	-2402.465693
C$^+$	-3852.924383	-3852.360441	-3852.332851	-3852.331907	-3852.418774
(Cy$_2$N)BBr$_2$	-5693.661190	-5693.324023	-5693.307554	-5693.306610	-5693.370003
[WCA]$^-$	-4746.532389	-4746.300476	-4746.246958	-4746.246014	-4746.394477
(CH$_3$)$_2$CH=CH$_2$	-157.149305	-157.040920	-157.035594	-157.034650	-157.068258
LiBr	-2579.450738	-2579.450075	-2579.447283	-2579.446339	-2579.472435
Li[WCA]	-4753.980769	-4753.745292	-4753.691127	-4753.690183	-4753.835507
Br$^-$	-2571.961538	-2571.961538	-2571.960122	-2571.959178	-2571.977714
***t*BuPhPH**	-731.252281	-731.028368	-731.016543	-731.015599	-731.066302

Table S3. Selected computational parameters obtained for considered systems (in atomic units A.U.): ε_0 - electronic energy; $\varepsilon_{0\,+\,...}$ - sum of electronic and: E_{zpe} - zero-point energies, E_{therm} - thermal energies, H – thermal enthalpies, G - thermal free energies calculated at M06-2X//6-31+G(d,p) level of theory in a vacuum.

Compound	E_{electr} [A.U.]	$\varepsilon_0 + E_{ZPE}$ [A.U.]	$\varepsilon_0 + E_{therm}$ [A.U.]	$\varepsilon_0 + H$ [A.U.]	$\varepsilon_0 + G$ [A.U.]
1	-3852.488267	-3851.934795	-3851.907553	-3851.906609	-3851.992101
2$^+$	-1280.380208	-1279.829021	-1279.802807	-1279.801863	-1279.886909
3$^+$	-2560.464175	-2559.368163	-2559.317322	-2559.316378	-2559.450589
***cis*-A^{2+}**	-2560.781962	-2559.670758	-2559.619828	-2559.618884	-2559.751379
***trans*-A^{2+}**	-2560.793126	-2559.683391	-2559.632102	-2559.631158	-2559.764660
B$^+$	-2403.327258	-2402.343220	-2402.297287	-2402.296342	-2402.421334
C$^+$	-3852.873059	-3852.308993	-3852.281228	-3852.280284	-3852.368260
(Cy$_2$N)BBr$_2$	-5693.658023	-5693.320288	-5693.303868	-5693.302924	-5693.366210
[WCA]$^-$	-4746.489241	-4746.257328	-4746.203810	-4746.202866	-4746.351329
(CH$_3$)$_2$CH=CH$_2$	-157.147838	-157.039218	-157.033894	-157.032950	-157.066557
LiBr	-2579.387606	-2579.386339	-2579.383793	-2579.382849	-2579.408317
Li[WCA]	-4753.966153	-4753.730676	-4753.676511	-4753.675567	-4753.820891
Br$^-$	-2571.868836	-2571.868836	-2571.86742	-2571.866476	-2571.885012
***t*BuPhPH**	-731.248491	-731.024243	-731.012455	-731.011511	-731.062106

Solvent-phase calculations

Table S4. Values of ΔH^o_{298K}, ΔG^o_{298K}, [kcal mol^{-1}] and K$_{298K}$ calculated at M06-2X//6-31+G(d,p) level of theory, including the presence of a solvent (CH$_2$Cl$_2$, CPCM model). [(A] Theoretical molar ration of *cis*-A^{2+}/*trans*-A^{2+}.

Reaction step	ΔH^o_{298K}	ΔG^o_{298K}	K$_{298K}$
2$^+$ + 2$^+$ = A^{2+}	-53.23	-29.67	2.11E+21
A^{2+} + 1 = 3$^+$ + C$^+$	4.11	2.37	1.97E-02
3$^+$ = B$^+$ + (CH$_3$)$_2$C=CH$_2$	-9.19	-24.62	4.98E+17
C$^+$ + Br$^-$ = *t*BuPhPH + (Cy$_2$N)BBr$_2$	-19.93	-25.50	2.11E+18
cis-A^{2+} = *trans*-A^{2+} [(A]	-7.24	-7.41	2.10E+05
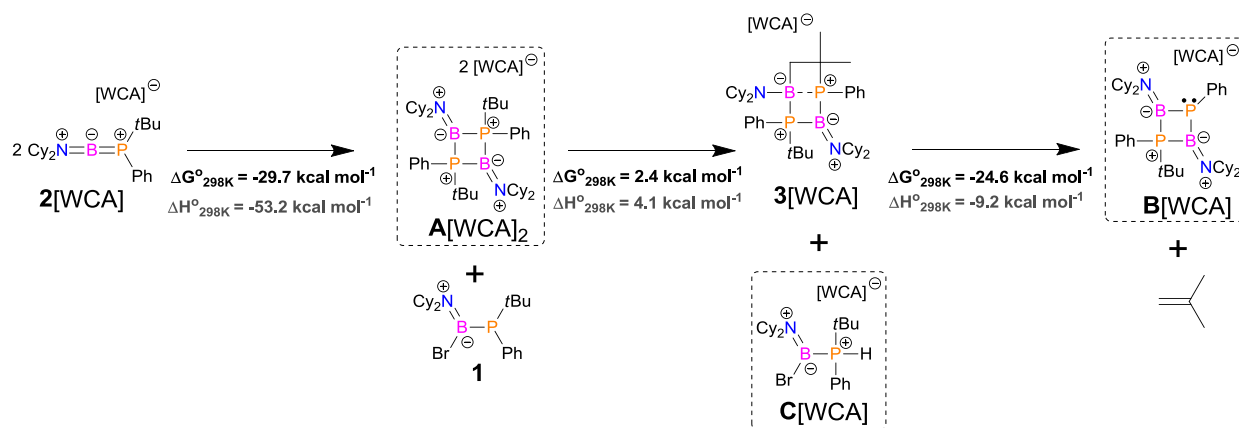
Scheme S4. Thermodynamics of considered transformations calculated at M06-2X//6-31+G(d,p) level of theory, including the presence of a solvent (CH$_2$Cl$_2$, CPCM model).
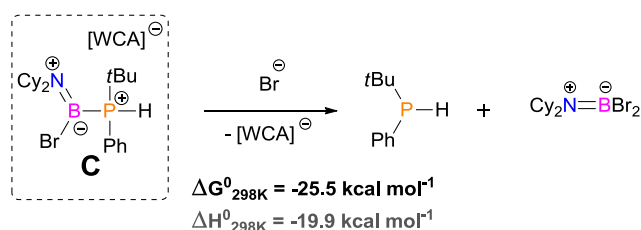
Scheme S5. Thermodynamics of decomposition of **C** calculated at M06-2X//6-31+G(d,p) level of theory, including the presence of a solvent (CH$_2$Cl$_2$, CPCM model).

Gas-phase calculations

Table S5. Values of ΔH^{o}_{298K}, ΔG^{o}_{298K}, [kcal mol^{-1}] and K_{298K} calculated at M06-2X//6-31+G(d,p) level of theory in a vacuum. [A] Theoretical molar ration of *cis*-**A^{2+}**/*trans*-**A^{2+}**.

Reaction step	ΔH^{o}_{298K}	ΔG^{o}_{298K}	K_{298K}
$2^{+} + 2^{+} = A^{2+}$	-17.57	5.86	9.38E-02
$A^{2+} + 1 = 3^{+} + C^{+}$	-37.71	-39.76	9.32E+06
$3^{+} = B^{+} + (CH_3)_2C{=}CH_2$	-8.27	-23.89	1.54E+04
$C^{+} + Br^{-} = tBuPhPH + (Cy_2N)BBr_2$	-107.37	-112.09	3.63E+80
cis-A^{2+} = *trans*-$A^{2+(A}$	-7.86	-8.50	1.29E+06
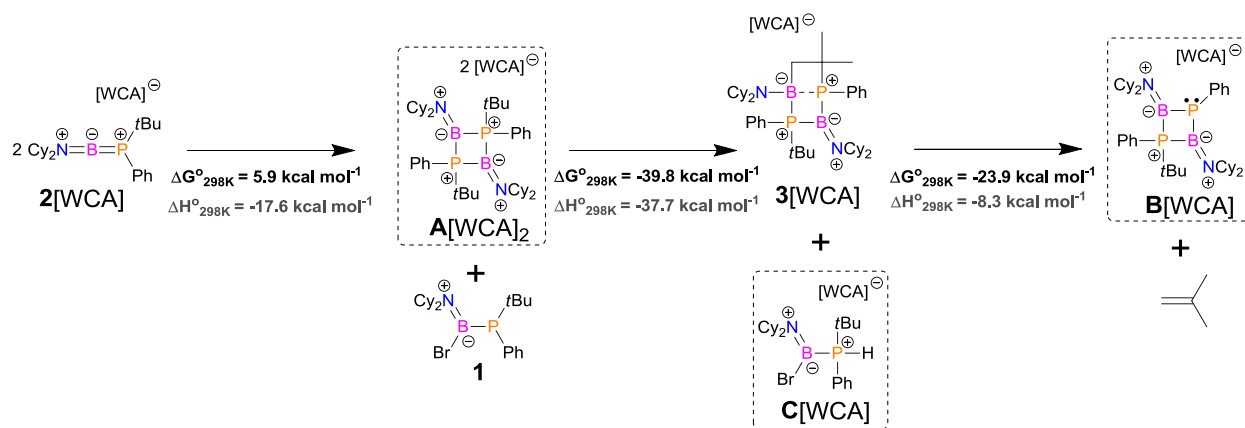
Scheme S6. Thermodynamics of considered transformations calculated at M06-2X//6-31+G(d,p) level of theory in a vacuum.
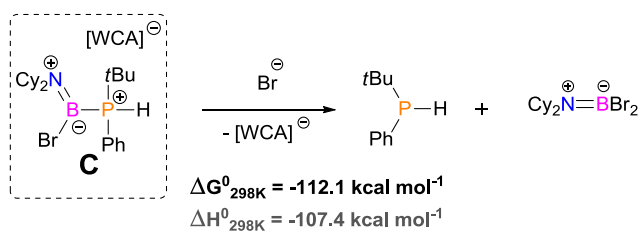
Scheme S7. Thermodynamics of decomposition of **C** calculated at M06-2X//6-31+G(d,p) level of theory in a vacuum.

Frontier molecular orbitals of selected compounds

HOMO
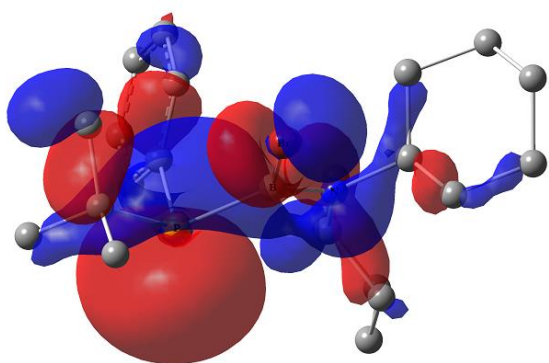
LUMO
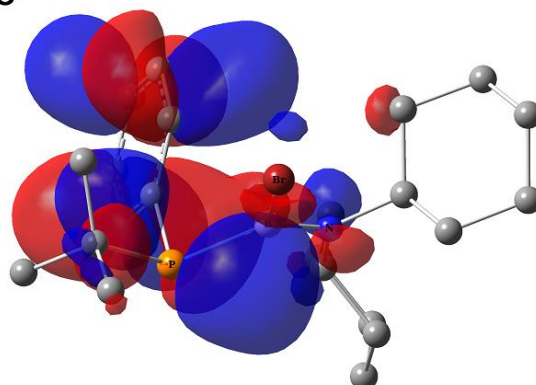
Figure S51. HOMO-LUMO Kohn–Sham orbitals of **1** calculated for gas-phase structures at M06-2X//6-31+G(d,p) level of theory. Isovalue = 0.0004 e⁻/au³
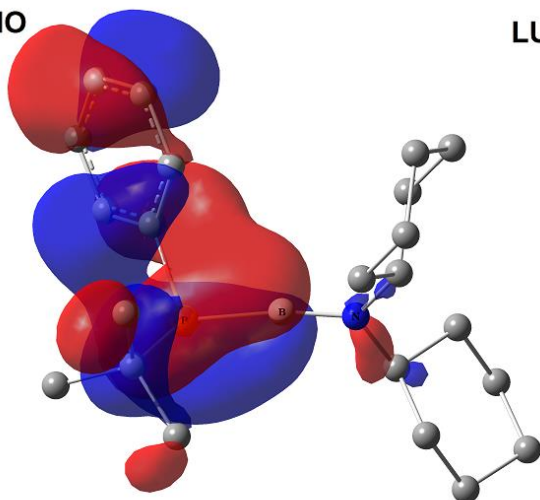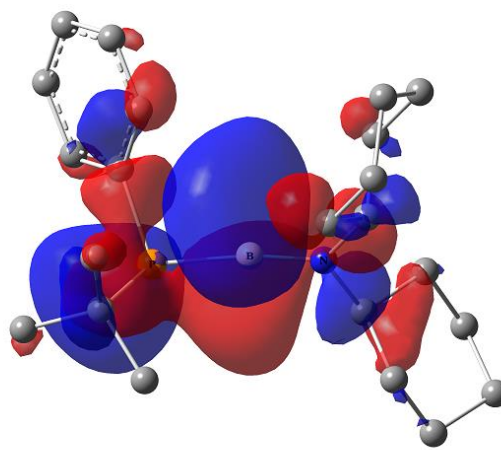
HOMO

LUMO

Figure S52. HOMO-LUMO Kohn–Sham orbitals of **2⁺** calculated for gas-phase structures at M06-2X//6-31+G(d,p) level of theory. Isovalue = 0.0004 e⁻/au³
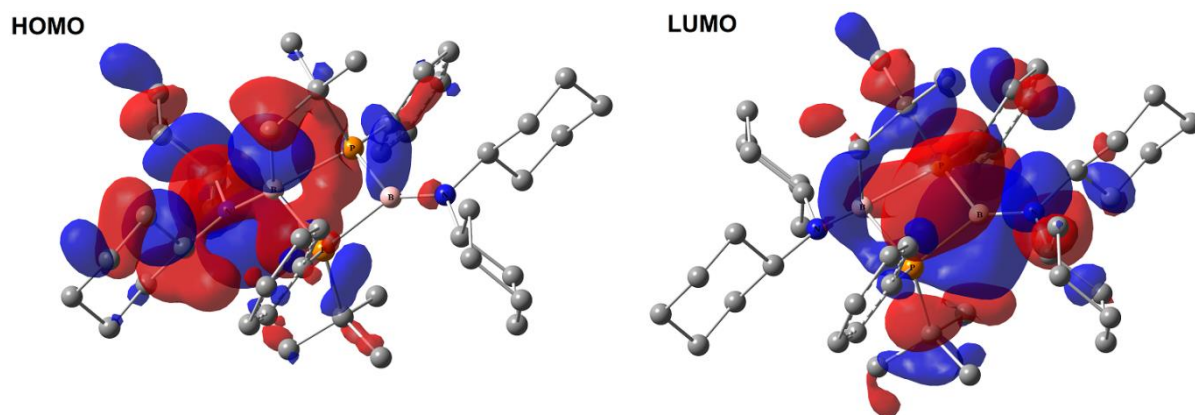
HOMO

LUMO

Figure S53. HOMO-LUMO Kohn–Sham orbitals of **3⁺** calculated for gas-phase structures at M06-2X//6-31+G(d,p) level of theory. Isovalue = 0.0004 e⁻/au³
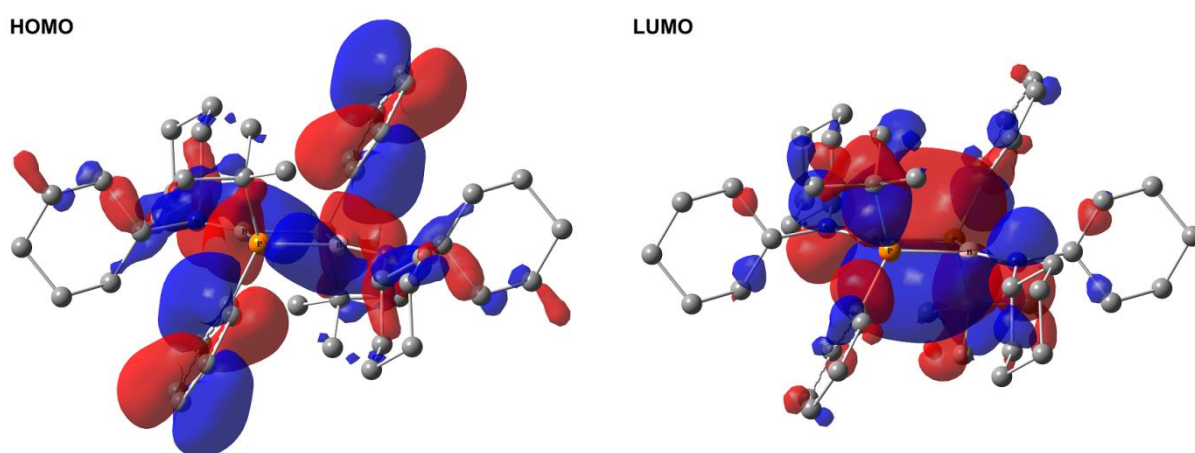
HOMO

LUMO

Figure S54. HOMO-LUMO Kohn–Sham orbitals of ***trans*-A²⁺** calculated for gas-phase structures at M06-2X//6-31+G(d,p) level of theory. Isovalue = 0.0004 e⁻/au³
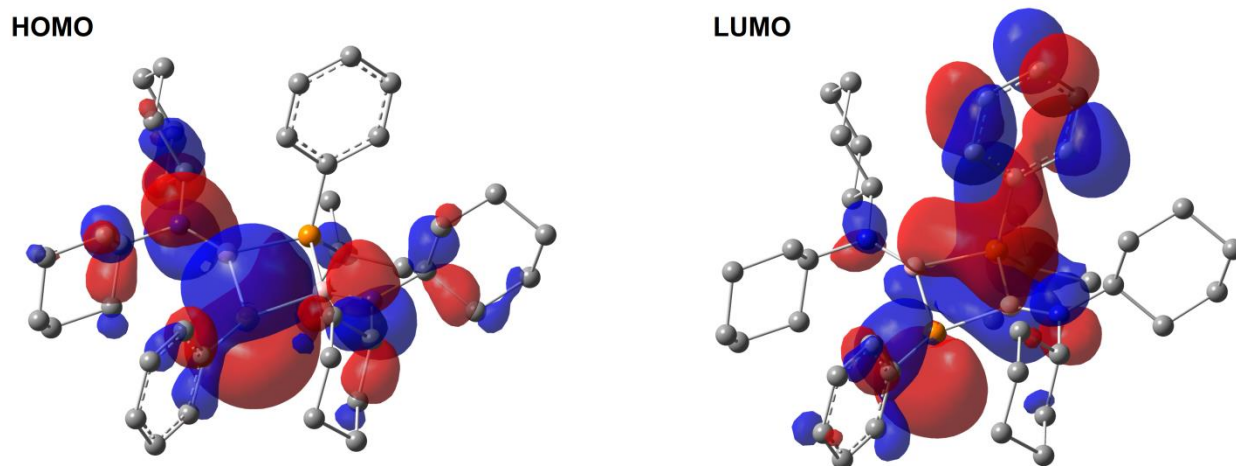
HOMO

LUMO

Figure S55. HOMO-LUMO Kohn–Sham orbitals of **B⁺** calculated for gas-phase structures at M06-2X//6-31+G(d,p) level of theory. Isovalue = 0.02 e⁻/au³

Optimized structures and Cartesian coordinates

Hydrogen atoms were omitted for clarity. Presented structures were optimized at M06-2X//6-31+G(d,p) level of theory, including the presence of a solvent (CH_2Cl_2, CPCM model).
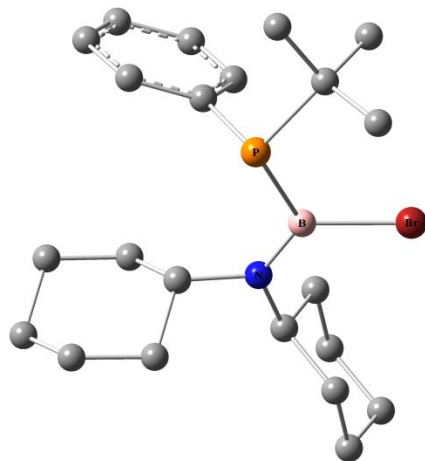
Figure S56. Optimized structure of **1**

0 1

Br	0.34526700	-2.72974000	0.00366500
C	-3.07727500	-1.71588000	-0.78792800
P	-1.82202600	-0.30770200	-0.96833600
N	1.00693200	0.09601800	-0.37807100
B	-0.02265300	-0.84220400	-0.42681100
C	-4.43445500	-1.07425800	-1.12251000
H	-4.69745100	-0.29316100	-0.40063400
H	-5.21657800	-1.84250400	-1.08691900
H	-4.43444100	-0.63221600	-2.12423500
C	-3.18193400	-2.36726600	0.59417900
H	-2.23844100	-2.81333700	0.91480400
H	-3.93789600	-3.16225900	0.55648600
H	-3.50130700	-1.64223800	1.34885500
C	-2.75494600	-2.76472800	-1.86175800
H	-2.70285500	-2.30908900	-2.85684900
H	-3.55099500	-3.51936800	-1.87917000
H	-1.80971200	-3.27443900	-1.66326800
C	-2.18455400	0.77278000	0.49203500
C	-2.80603800	2.00977700	0.28289400

H	-3.08987900	2.30001300	-0.72617400
C	-3.04742100	2.88184700	1.34676000
H	-3.52156300	3.84095100	1.16167800
C	-2.67254100	2.52361300	2.64037800
H	-2.85481700	3.20139500	3.46856400
C	-2.05788100	1.29013100	2.86680100
H	-1.76028900	1.00566600	3.87155200
C	-1.81292400	0.42662400	1.80136000
H	-1.31575300	-0.52256800	1.99054600
C	2.38948100	-0.12544700	0.11180800
H	2.87571400	0.85417600	0.05167900
C	3.23367000	-1.04328100	-0.78051800
H	3.16905500	-0.69217200	-1.81700900
H	2.84405700	-2.06440700	-0.75626000
C	4.68728400	-1.03931500	-0.29645400
H	5.28650100	-1.71858100	-0.91168000
H	5.11182300	-0.03348200	-0.42687800
C	4.77863300	-1.43445400	1.18062300
H	5.82173700	-1.41084800	1.51422400
H	4.42950900	-2.47005600	1.29799000
C	3.92361800	-0.51441200	2.05748300
H	4.32517000	0.50766100	2.00468000
H	3.98071100	-0.82387600	3.10627500
C	2.46304300	-0.50888500	1.59445100
H	2.02487800	-1.49836300	1.75604100
H	1.87340200	0.21065200	2.17573600
C	0.76198100	1.48923000	-0.82023200
H	-0.26736200	1.53423700	-1.18760500
C	1.64423300	1.87869900	-2.01330800
H	2.70636000	1.85839100	-1.73492600
H	1.50294800	1.14311800	-2.81384900
C	1.28499000	3.28614800	-2.50115900
H	1.93474300	3.56604400	-3.33679000
H	0.25516900	3.28285400	-2.88470400
C	1.39404400	4.30890000	-1.36772000

H	2.43946700	4.36678900	-1.03319400
H	1.11817300	5.30548700	-1.72852100
C	0.50846700	3.90784800	-0.18565900
H	-0.54448200	3.91864600	-0.50143800
H	0.60176500	4.63265300	0.63004100
C	0.86001900	2.50590200	0.32355900
H	1.87714800	2.52030400	0.73855300
H	0.17931300	2.20782600	1.12918800
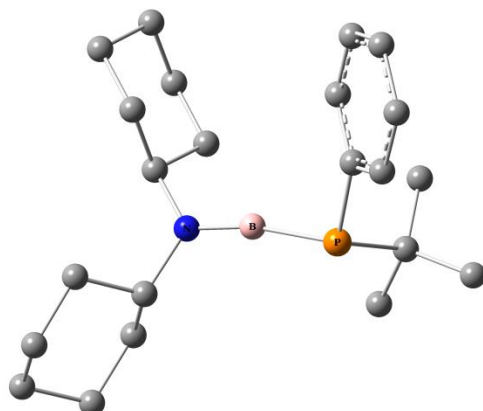
Figure S57. Optimized structure of **2⁺**

1 1

C	-2.09285500	-1.79809100	1.69029700
P	-1.52237600	-1.45604200	-0.07911300
N	1.27161200	-0.03004000	-0.04444500
B	0.03064900	-0.49663500	0.02898200
C	-3.24250200	-2.80747400	1.56454200
H	-4.07909400	-2.39263400	0.99234500
H	-3.61036000	-3.05026400	2.56716600
H	-2.91496800	-3.73414000	1.08456800
C	-2.57790700	-0.53986600	2.41007900
H	-1.77287000	0.19079900	2.53655600
H	-2.93571200	-0.82214300	3.40683800
H	-3.40654100	-0.06218700	1.87988600
C	-0.90528200	-2.42468400	2.42797300
H	-0.51275800	-3.30068500	1.90208100
H	-1.23806800	-2.74776600	3.42021700

H	-0.09082200	-1.70539500	2.57088400
C	-2.69642400	-0.31961700	-0.89981300
C	-3.56606400	-0.87160000	-1.84990500
H	-3.50656400	-1.92891800	-2.09162300
C	-4.50636100	-0.06574200	-2.49047200
H	-5.17821600	-0.50150200	-3.22239700
C	-4.57585100	1.29493400	-2.19608900
H	-5.30374700	1.92231700	-2.70013600
C	-3.71096400	1.85236500	-1.25320700
H	-3.76360400	2.91086000	-1.02067700
C	-2.77904800	1.04920900	-0.60162700
H	-2.12665600	1.48980900	0.14786800
C	1.64632300	1.33700800	0.41635500
H	2.73544300	1.33755500	0.52934200
C	1.00959400	1.63196800	1.77510400
H	1.31804400	0.87071800	2.50014700
H	-0.08600200	1.56715500	1.67486400
C	1.38130500	3.03765700	2.25164900
H	0.89598900	3.23767800	3.21137600
H	2.46460600	3.08061100	2.42644400
C	0.98894800	4.09284100	1.21479900
H	1.29064200	5.08730000	1.55749400
H	-0.10474900	4.10720600	1.10974900
C	1.62104400	3.78748400	-0.14491900
H	2.71397500	3.86167600	-0.06563400
H	1.30648800	4.52343900	-0.89079700
C	1.24532900	2.38369900	-0.62733800
H	0.15809800	2.32241100	-0.78119900
H	1.71894600	2.15967100	-1.58760000
C	2.33352500	-0.94494000	-0.58477500
H	1.80455500	-1.83228300	-0.95680200
C	3.27140900	-1.38342000	0.54144000
H	3.77031900	-0.50627700	0.97281100
H	2.68713900	-1.85621000	1.33811400
C	4.32966400	-2.34746200	-0.00633500

H	5.01434300	-2.62896500	0.79910000
H	3.83789700	-3.26909000	-0.34485900
C	5.09566900	-1.72227100	-1.17426700
H	5.65634700	-0.84886300	-0.81449000
H	5.82868600	-2.43329800	-1.56767600
C	4.13800300	-1.28522100	-2.28481800
H	3.63675200	-2.16819000	-2.70300100
H	4.68673600	-0.81250900	-3.10464900
C	3.08160000	-0.30813200	-1.75510800
H	3.57986400	0.61127700	-1.42125300
H	2.37204700	-0.03694600	-2.54355200
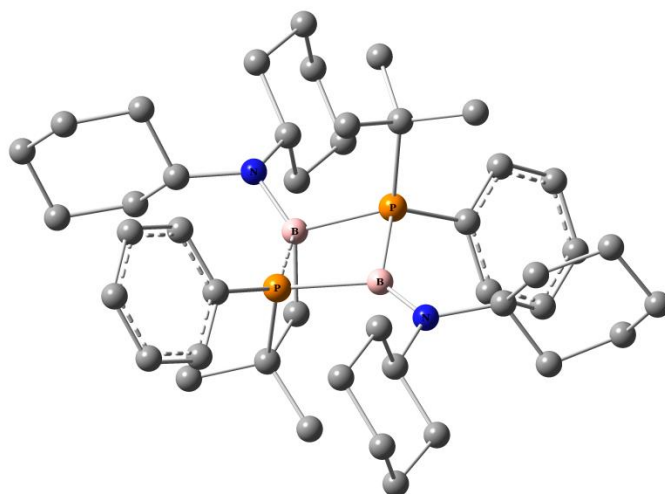
Figure S58. Optimized structure of **3⁺**

1 1

P	-0.13425582	-1.25608052	-0.46257681
N	2.68612276	-0.10967648	0.04724916
C	-0.19983854	-1.29066648	-2.34989627
C	-1.57606376	-1.71368900	-2.88243281
H	-1.85873062	-2.73182666	-2.60632599
H	-1.53643398	-1.67279855	-3.97670167
H	-2.35017193	-1.02237495	-2.54207865
C	0.04971752	0.14996483	-2.82832451
H	-0.72875817	0.82439953	-2.45851144
H	0.00854182	0.16250029	-3.92277788
H	1.03504787	0.52946140	-2.53388820

C	0.89703392	-2.21149670	-2.89533045
H	1.89375682	-1.84233152	-2.63946966
H	0.82282183	-2.22907543	-3.98832311
H	0.80115596	-3.23942159	-2.53397696
C	0.03085215	-2.92125236	0.26070334
C	-0.59143452	-4.05200879	-0.28384806
H	-1.15815318	-3.98580213	-1.20596611
C	-0.48863810	-5.28545925	0.35659458
H	-0.96953531	-6.15477584	-0.07970557
C	0.22325603	-5.40212312	1.55031011
H	0.30162947	-6.36480786	2.04466590
C	0.83157220	-4.27822969	2.10767259
H	1.38737472	-4.35735668	3.03651077
C	0.73497577	-3.04607629	1.46576879
H	1.21527684	-2.17737244	1.90783577
C	3.48079063	1.12295774	0.31909256
H	2.79918607	1.77521717	0.87993170
C	3.84506586	1.86752243	-0.97418364
H	4.50483840	1.24651788	-1.58898552
H	2.92924699	2.04555690	-1.55275317
C	4.54480238	3.19607088	-0.66500625
H	4.84433244	3.67422908	-1.60310756
H	3.83437603	3.87486528	-0.17699462
C	5.75272861	2.99783956	0.25218799
H	6.51426980	2.39961248	-0.26691035
H	6.20981457	3.96435457	0.48725953
C	5.33950170	2.27683855	1.53600750
H	4.62197158	2.89766151	2.09126605
H	6.20352015	2.12652219	2.19053156
C	4.70239116	0.92073074	1.21680764
H	5.45048939	0.30175503	0.70901345
H	4.40795284	0.40682734	2.13805829
C	3.33935688	-1.41289436	-0.25529095
H	2.50798868	-2.06536762	-0.54763076
C	4.00059622	-2.11680449	0.94091190

H	4.93917326	-1.62958239	1.21571532
H	3.34780285	-2.07896589	1.81835836
C	4.30767924	-3.56505039	0.54268462
H	3.36953041	-4.08401349	0.29724658
H	4.75370537	-4.09450374	1.39058095
C	5.24817093	-3.59937204	-0.66554613
H	6.21202300	-3.15631310	-0.38009890
H	5.44770748	-4.63348026	-0.96400240
C	4.66506204	-2.81672344	-1.84540496
H	3.76134924	-3.32897178	-2.20475780
H	5.37248769	-2.79820134	-2.68015723
C	4.30115733	-1.37967865	-1.44849466
H	5.21562432	-0.83395995	-1.18494605
H	3.84042983	-0.85331647	-2.29240901
B	1.31591487	-0.00285281	-0.00277577
P	0.07973015	1.47120845	0.40158845
N	-2.78436898	0.07781503	-0.15060344
C	-0.19473003	1.33139480	2.24077191
C	1.04372590	1.13197451	3.10994746
H	1.66543095	2.03382893	3.14695288
H	0.73017288	0.90162979	4.13445197
H	1.66504668	0.30225040	2.75479784
C	-1.08725594	0.06092129	2.06527056
H	-0.58483092	-0.83285226	2.45510655
H	-2.00972701	0.17174760	2.64766524
C	-1.02386088	2.51261755	2.74678041
H	-1.92202545	2.67249577	2.14163511
H	-1.34609335	2.29450489	3.77168184
H	-0.44708862	3.44246022	2.75684575
C	0.39610068	3.16137128	-0.19630324
C	1.22306484	4.04502070	0.50945513
H	1.74196754	3.71944832	1.40784576
C	1.38011195	5.35719777	0.06834789
H	2.02311293	6.03544540	0.62014052
C	0.71577549	5.79507315	-1.07768258

H	0.84188655	6.81706037	-1.41985455
C	-0.12078506	4.92419713	-1.77520915
H	-0.65253846	5.26536663	-2.65734516
C	-0.28948853	3.61402798	-1.33133697
H	-0.96778805	2.95091522	-1.86129028
C	-3.50506312	-1.20646894	-0.16787057
H	-2.78980270	-1.93041959	-0.59550874
C	-3.85786397	-1.78810898	1.21745760
H	-4.60383624	-1.15416926	1.71289072
H	-2.96279867	-1.79095899	1.85075791
C	-4.39747513	-3.21631662	1.08797615
H	-4.65567921	-3.61063239	2.07663324
H	-3.60222342	-3.86215572	0.68658820
C	-5.60665811	-3.27170748	0.15334384
H	-6.43078143	-2.69340834	0.59417501
H	-5.96090216	-4.30258568	0.04629449
C	-5.25870879	-2.68304331	-1.21512812
H	-4.49040960	-3.30884627	-1.69269148
H	-6.13374634	-2.69772029	-1.87338173
C	-4.73044011	-1.25046576	-1.08719904
H	-5.52714547	-0.61433780	-0.68057585
H	-4.47213427	-0.85302121	-2.07438234
C	-3.47804115	1.36898614	-0.02709403
H	-2.67722219	2.09114924	0.19666451
C	-4.08644601	1.87872452	-1.34466228
H	-4.95733154	1.27837060	-1.62775938
H	-3.34223364	1.76722404	-2.14347750
C	-4.52490644	3.33911500	-1.19873239
H	-3.64510397	3.96478581	-0.98678897
H	-4.95278903	3.70037131	-2.13996861
C	-5.53630336	3.48837196	-0.05897616
H	-6.44441716	2.92255883	-0.31027257
H	-5.83424441	4.53628822	0.05380031
C	-4.96235231	2.95754509	1.25701373
H	-4.11039822	3.58708791	1.55268415

H	-5.70493760	3.03641107	2.05813286
C	-4.49028304	1.50447581	1.12192052
H	-5.35893694	0.85975324	0.93386678
H	-4.03568346	1.16440466	2.06039705
B	-1.45230404	-0.00261859	0.44729172
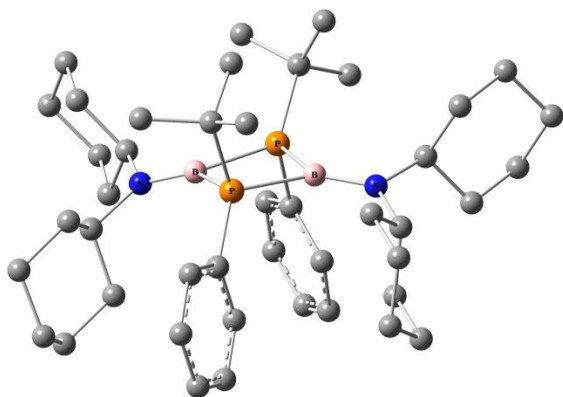
Figure S59. Optimized structure of *cis*-**A**$^{2+}$

2 1

P	-0.09707468	1.26692555	0.92793999
P	0.05531142	-1.57638335	0.38163192
N	2.68332277	-0.00734540	0.26505937
N	-2.70735424	-0.30656684	0.16632955
C	3.45944654	1.19352888	-0.16709386
H	4.51176180	0.89806960	-0.13428948
C	3.32498032	2.39703748	0.76002280
H	3.66080644	2.12038452	1.76383180
H	2.27845597	2.70988933	0.82542376
C	4.13992774	3.58075608	0.23025984
H	4.00888518	4.43474806	0.90198955
H	5.20764083	3.32391699	0.24361385
C	3.72039612	3.94058823	-1.19522743
H	4.30221413	4.79298963	-1.55919212
H	2.66330442	4.24735851	-1.19515965
C	3.89833699	2.73856557	-2.12380134
H	4.96332585	2.47507142	-2.17889613
H	3.57769212	2.98240427	-3.14155475
C	3.10164789	1.53444408	-1.61865074

H	2.03270517	1.76578622	-1.66206509
H	3.26576849	0.66103061	-2.25707264
C	3.48861788	-1.25881839	0.30101490
H	2.76897532	-2.07210184	0.42052972
C	4.38936413	-1.26435831	1.54307941
H	3.77484815	-1.08889066	2.43434045
H	5.10904513	-0.43769934	1.47854459
C	5.14523625	-2.59280585	1.65499116
H	5.81712131	-2.55616840	2.51758934
H	4.42919409	-3.40379072	1.84699175
C	5.92493508	-2.90306496	0.37563181
H	6.42207695	-3.87380102	0.46405677
H	6.71219568	-2.14984777	0.23759317
C	5.00136360	-2.89020997	-0.84417209
H	5.56644522	-3.09038985	-1.75917015
H	4.26110135	-3.69828304	-0.74842633
C	4.28344168	-1.54211003	-0.97834613
H	3.61325272	-1.54651348	-1.84304446
H	5.03674927	-0.76437176	-1.14961750
C	0.24620777	-1.91726655	-1.40956528
C	1.25002787	-2.79404546	-1.84631382
H	1.87553539	-3.32809466	-1.13721739
C	1.45195830	-3.00626815	-3.20567934
H	2.22713287	-3.69388089	-3.52775123
C	0.66663959	-2.33603506	-4.14528113
H	0.83010945	-2.50025510	-5.20496923
C	-0.32818006	-1.46035283	-3.71933507
H	-0.94760813	-0.93828920	-4.44093723
C	-0.54123885	-1.25175923	-2.35693634
H	-1.33007293	-0.57391504	-2.04885030
C	-0.01206610	-3.22093768	1.36101587
C	-0.57887099	-4.32627585	0.45544814
H	-1.58548714	-4.10775488	0.09145169
H	-0.63944657	-5.23610782	1.06106686
H	0.05672676	-4.53893115	-0.40407540

C	-0.92251079	-3.05326075	2.58762060
H	-0.45214131	-2.45763103	3.37011742
H	-1.10198177	-4.05024946	3.00121228
H	-1.89655765	-2.62058472	2.34448204
C	1.38840397	-3.62277547	1.84284716
H	2.04258270	-3.92848409	1.02215096
H	1.27463415	-4.48957423	2.50188051
H	1.87529653	-2.82955827	2.41957719
C	-3.33184087	-1.65933570	0.10085510
H	-2.51164754	-2.37150833	0.23083241
C	-4.30419502	-1.85661888	1.27180463
H	-5.15943595	-1.17786234	1.16552118
H	-3.80829621	-1.59842613	2.21445940
C	-4.81243499	-3.30154420	1.29015205
H	-3.96974639	-3.98368221	1.47472704
H	-5.51193544	-3.43138799	2.12101010
C	-5.47824452	-3.66200647	-0.03958717
H	-6.37425410	-3.04126205	-0.17321388
H	-5.80988209	-4.70463529	-0.02632543
C	-4.52393441	-3.42897864	-1.21218025
H	-5.02099887	-3.64666137	-2.16192211
H	-3.67535509	-4.12246906	-1.13589366
C	-4.00042473	-1.98685658	-1.23866736
H	-3.28500148	-1.86502919	-2.05832565
H	-4.84046020	-1.30612984	-1.42345068
C	-3.65156459	0.80376425	-0.16196741
H	-4.65388922	0.36783766	-0.12181387
C	-3.62413246	1.94235827	0.85096901
H	-2.62194403	2.38390892	0.89204877
H	-3.86431684	1.54385871	1.84154097
C	-4.60963769	3.04644487	0.45857885
H	-5.63368615	2.65187054	0.49632800
H	-4.55182512	3.85634036	1.19215641
C	-4.31375716	3.56407487	-0.94948660
H	-5.01868176	4.35604977	-1.21976657

H	-3.30616191	4.00717486	-0.96894285
C	-4.38343449	2.42120759	-1.96319657
H	-4.15105700	2.77978354	-2.97070067
H	-5.40608941	2.02185059	-1.99387927
C	-3.40982071	1.29992767	-1.59248811
H	-3.49476118	0.46867766	-2.29974203
H	-2.38723531	1.68401901	-1.65800663
B	1.34831841	-0.04852033	0.56755225
B	-1.37898615	-0.18823721	0.48402841
C	-0.16025976	2.80488264	-0.04318932
C	-0.21245225	2.68857267	-1.43887658
C	-0.14107055	4.07571122	0.54403237
C	-0.26281736	3.82633893	-2.23787509
H	-0.20721599	1.71048677	-1.91479989
C	-0.19179977	5.21235926	-0.26142574
H	-0.08026887	4.20207786	1.61758883
C	-0.25713086	5.09069735	-1.64823791
H	-0.30435777	3.72148345	-3.31670303
H	-0.17762936	6.19256891	0.20238468
H	-0.29725240	5.97901296	-2.26955304
C	-0.11010663	1.52793774	2.81279039
C	-1.34575035	2.30612662	3.28279013
C	-0.16871792	0.12945029	3.44029343
C	1.18438542	2.20717567	3.27408493
H	-1.48603865	3.27026007	2.79207311
H	-2.25364513	1.71564114	3.15941031
H	-1.21739535	2.49414295	4.35358600
H	0.69644598	-0.48783641	3.17122701
H	-0.15334934	0.24184209	4.52924532
H	-1.09687190	-0.38818263	3.18280646
H	1.11747218	2.32532304	4.36020225
H	2.05537329	1.58352467	3.06171435
H	1.34468483	3.19697298	2.84268078
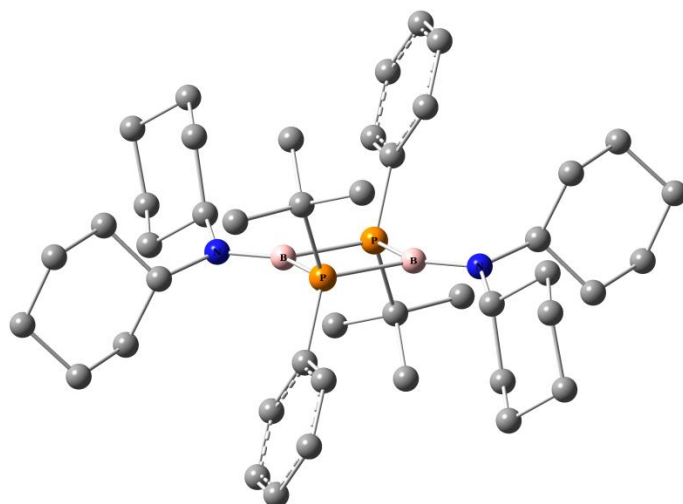
Figure S60. Optimized structure of *trans*-A²⁺

2 1

P	0.00314314	-1.32858174	0.57817139
N	-2.70648188	-0.04334961	-0.11463315
C	-0.11893943	-1.45783797	2.46165387
C	1.27578615	-1.64855123	3.07255044
H	1.73637446	-2.59937701	2.79334023
H	1.16535798	-1.65148853	4.16168042
H	1.95282446	-0.82864487	2.81035947
C	-0.71495078	-0.13406885	2.96527022
H	-0.11812145	0.73654925	2.67027002
H	-0.72918202	-0.15873918	4.05929717
H	-1.74272934	0.01006490	2.62083929
C	-1.04205715	-2.62166013	2.83378977
H	-2.05420648	-2.47790782	2.44613213
H	-1.11038326	-2.66104020	3.92592129
H	-0.66529834	-3.58520204	2.48251715
C	0.05653757	-2.93905936	-0.25272973
C	0.86626697	-3.98117183	0.21635883
H	1.48105976	-3.86161295	1.10306183
C	0.88202818	-5.19941599	-0.45703755
H	1.50726781	-6.00522954	-0.08747860
C	0.10125005	-5.38192071	-1.59870851
H	0.11824594	-6.33374742	-2.11876325

C	-0.70329842	-4.34541573	-2.06940203
H	-1.31688975	-4.48236157	-2.95337795
C	-0.72886010	-3.12662541	-1.39698519
H	-1.36653823	-2.32849440	-1.76639576
C	-3.42064743	1.25869687	-0.29290514
H	-2.70724453	1.89934923	-0.82529807
C	-3.67977920	1.93239820	1.06415436
H	-4.35218965	1.31530743	1.66870375
H	-2.72952887	2.01443241	1.60796260
C	-4.29939387	3.32119876	0.87284700
H	-4.52382249	3.75148720	1.85358523
H	-3.56576383	3.98451950	0.39722367
C	-5.55431677	3.26401693	0.00161127
H	-6.32980492	2.67604513	0.51105006
H	-5.95779863	4.27087133	-0.14285786
C	-5.23813076	2.61926952	-1.34821353
H	-4.50631176	3.23743284	-1.88712343
H	-6.13369382	2.56936840	-1.97425727
C	-4.67776257	1.20507541	-1.16096253
H	-5.44714844	0.59146185	-0.68058045
H	-4.44457816	0.75393090	-2.13099985
C	-3.43901092	-1.32114349	0.12698712
H	-2.65048313	-2.03905711	0.38968638
C	-4.10885749	-1.89426188	-1.13266976
H	-4.99000895	-1.30931715	-1.40489677
H	-3.41933614	-1.85048399	-1.98280022
C	-4.55286894	-3.33224446	-0.84606821
H	-3.67441869	-3.95061417	-0.61183076
H	-5.01430911	-3.75736574	-1.74230561
C	-5.53317247	-3.36069179	0.32953930
H	-6.44139167	-2.80923628	0.05166432
H	-5.83721806	-4.38913209	0.54680223
C	-4.91667603	-2.72494341	1.57771860
H	-4.07740230	-3.34750377	1.91700819
H	-5.64208112	-2.70132882	2.39608056

C	-4.41490777	-1.29909953	1.30737777
H	-5.27064893	-0.65133699	1.08503275
H	-3.92323860	-0.89687667	2.20071801
B	-1.33948830	-0.04028729	-0.09067461
P	-0.00314449	1.32858308	-0.57817003
N	2.70648082	0.04335008	0.11463242
C	0.11893596	1.45784157	-2.46165243
C	-1.27579009	1.64856072	-3.07254608
H	-1.73637442	2.59938773	-2.79333343
H	-1.16536407	1.65149926	-4.16167627
H	-1.95283086	0.82865643	-2.81035494
C	0.71494177	0.13407108	-2.96527177
H	0.11810981	-0.73654532	-2.67027186
H	0.72917127	0.15874299	-4.05929870
H	1.74272038	-0.01006688	-2.62084279
C	1.04205697	2.62166117	-2.83378816
H	2.05420655	2.47790470	-2.44613281
H	1.11038105	2.66104283	-3.92591975
H	0.66530221	3.58520381	-2.48251319
C	-0.05653905	2.93905980	0.25273280
C	-0.86627009	3.98117192	-0.21635372
H	-1.48106399	3.86161321	-1.10305600
C	-0.88203152	5.19941547	0.45704376
H	-1.50727242	6.00522875	0.08748641
C	-0.10125192	5.38191991	1.59871378
H	-0.11824797	6.33374614	2.11876939
C	0.70329823	4.34541529	2.06940522
H	1.31689071	4.48236094	2.95338036
C	0.72886009	3.12662556	1.39698728
H	1.36653951	2.32849483	1.76639623
C	3.42064651	-1.25869661	0.29290225
H	2.70724449	-1.89934944	0.82529573
C	3.67977634	-1.93239691	-1.06415815
H	4.35218584	-1.31530566	-1.66870809
H	2.72952522	-2.01443083	-1.60796507

C	4.29939148	-3.32119753	-0.87285272
H	4.52381864	-3.75148527	-1.85359159
H	3.56576226	-3.98451868	-0.39722871
C	5.55431573	-3.26401617	-0.00161889
H	6.32980304	-2.67604397	-0.51105852
H	5.95779790	-4.27087062	0.14284896
C	5.23813179	-2.61926964	1.34820682
H	4.50631378	-3.23743343	1.88711752
H	6.13369585	-2.56936877	1.97424915
C	4.67776307	-1.20507550	1.16095759
H	5.44714803	-0.59146158	0.68057450
H	4.44458026	-0.75393146	2.13099554
C	3.43901022	1.32114432	-0.12698489
H	2.65048281	2.03905886	-0.38968270
C	4.10885658	1.89425926	1.13267367
H	4.99000741	1.30931314	1.40489978
H	3.41933474	1.85047990	1.98280365
C	4.55286935	3.33224218	0.84607587
H	3.67441976	3.95061315	0.61183928
H	5.01430925	3.75736095	1.74231459
C	5.53317373	3.36069149	-0.32953087
H	6.44139223	2.80923447	-0.05165660
H	5.83722040	4.38913205	-0.54679109
C	4.91667754	2.72494671	-1.57771209
H	4.07740469	3.34750873	-1.91700073
H	5.64208317	2.70133345	-2.39607361
C	4.41490774	1.29910262	-1.30737509
H	5.27064822	0.65133880	-1.08503114
H	3.92323883	0.89688243	-2.20071666
B	1.33948718	0.04028811	0.09067471
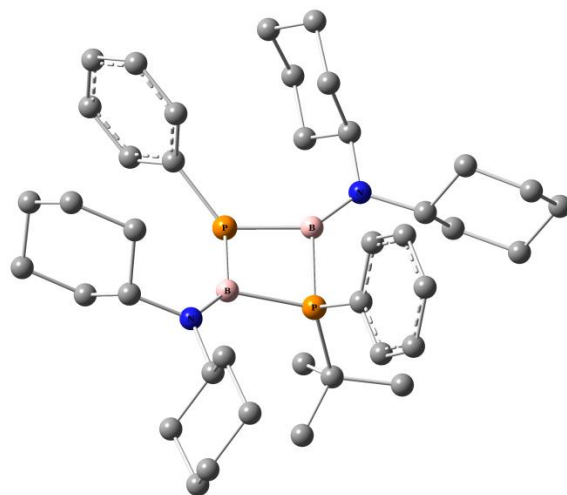
Figure S61. Optimized structure of **B⁺**

1 1

P	-0.13053500	1.34371000	0.76479000
P	0.12011500	-1.36826000	0.67319800
N	2.68755300	0.19071100	0.25614400
N	-2.67983500	-0.28685500	0.17330100
C	-0.28531900	3.07829400	0.21877100
C	-0.34165300	3.43452500	-1.13681600
H	-0.29016800	2.66699000	-1.90425300
C	-0.46315400	4.77113000	-1.50732700
H	-0.50651700	5.03551900	-2.55904800
C	-0.52716100	5.76535400	-0.52871100
H	-0.62113100	6.80677300	-0.81931100
C	-0.46976700	5.42031700	0.82057900
H	-0.51911800	6.18959200	1.58426800
C	-0.35015800	4.08130400	1.19442200
H	-0.30775700	3.81579800	2.24718000
C	3.41580500	1.44370800	-0.05435400
H	4.47160800	1.17792500	-0.17768800
C	3.32861900	2.43859700	1.10738100
H	3.75167500	1.97492300	2.00608000
H	2.27517000	2.65772000	1.32401700
C	4.04128200	3.75020600	0.77224900
H	3.93464000	4.45024400	1.60726200
H	5.11696400	3.56288000	0.64793200

C	3.48167900	4.35644100	-0.51658300
H	3.98883300	5.29939200	-0.74609000
H	2.41521100	4.58869300	-0.37319500
C	3.63353900	3.37553000	-1.68166600
H	4.70217800	3.19644000	-1.86506700
H	3.22103800	3.80268200	-2.60202500
C	2.93733300	2.04673100	-1.37873900
H	1.85771900	2.21348900	-1.31649200
H	3.10378600	1.32217000	-2.18418400
C	3.48120300	-1.05362700	0.21389500
H	2.79816500	-1.86389700	0.49429900
C	4.61740100	-1.05740500	1.24234100
H	4.20815000	-0.85096300	2.23810900
H	5.33449500	-0.25763900	1.01784500
C	5.35164700	-2.40157300	1.21851600
H	6.17087400	-2.38851100	1.94411700
H	4.66161700	-3.19851500	1.53116800
C	5.87778200	-2.71293800	-0.18469300
H	6.38675400	-3.68221700	-0.19229600
H	6.62342400	-1.95656400	-0.46606300
C	4.73935800	-2.70649100	-1.20745200
H	5.12160100	-2.90732700	-2.21337200
H	4.03711700	-3.51745100	-0.96741100
C	3.98475400	-1.37272500	-1.19731500
H	3.12700700	-1.40752800	-1.88159500
H	4.65267300	-0.57313200	-1.54597600
C	0.29693300	-2.41421700	-0.81126100
C	1.05195800	-3.59252300	-0.82605900
H	1.51653400	-3.97079800	0.07858000
C	1.21862000	-4.30017100	-2.01514900
H	1.80418100	-5.21371600	-2.01502400
C	0.64184700	-3.83465000	-3.19600100
H	0.77512100	-4.38765700	-4.11993500
C	-0.10691400	-2.65807100	-3.18786500
H	-0.55925600	-2.28997300	-4.10288900

C	-0.28001100	-1.94916700	-2.00154000
H	-0.86224100	-1.03019800	-2.00779800
C	0.11309800	-2.32415800	2.28968500
C	-0.79274100	-3.55588000	2.17423500
H	-1.83377300	-3.27148400	1.99874100
H	-0.75549300	-4.10041500	3.12377900
H	-0.47937200	-4.23969100	1.38099800
C	-0.44920400	-1.36540800	3.35164700
H	0.17789400	-0.47694700	3.47189200
H	-0.47742700	-1.89518600	4.30934100
H	-1.46700400	-1.03938000	3.11287800
C	1.53687800	-2.72752200	2.69784300
H	1.99064000	-3.45163300	2.01652800
H	1.48888900	-3.19613300	3.68650200
H	2.19368900	-1.85511500	2.77301900
C	-3.23763300	-1.64862100	0.03089100
H	-2.38532300	-2.33882500	0.08135600
C	-4.18986900	-2.00144800	1.17910800
H	-5.05088500	-1.32004500	1.16932100
H	-3.67675300	-1.85113100	2.13703800
C	-4.68873300	-3.44469500	1.04702800
H	-3.84216100	-4.13595300	1.16407900
H	-5.39240600	-3.66702500	1.85524300
C	-5.33931800	-3.68503900	-0.31724200
H	-6.24202500	-3.06464500	-0.40255800
H	-5.65873900	-4.72854700	-0.40409300
C	-4.37623200	-3.32816600	-1.45173700
H	-4.85375600	-3.48126700	-2.42454600
H	-3.50484400	-3.99768800	-1.41471100
C	-3.89968400	-1.87714100	-1.33319300
H	-3.18766000	-1.63920800	-2.13117600
H	-4.76086000	-1.20684600	-1.45324200
C	-3.64208000	0.82935200	0.00693000
H	-4.64043200	0.38208600	-0.05656600
C	-3.64851800	1.75541500	1.22715200

H	-2.64428700	2.16355300	1.39227900
H	-3.90720200	1.16949000	2.11715700
C	-4.61565100	2.92450500	1.02900000
H	-5.64433700	2.54493800	0.95594300
H	-4.58025800	3.58226000	1.90346100
C	-4.27096500	3.69924500	-0.24514400
H	-4.95550900	4.54391600	-0.37500300
H	-3.25605900	4.11575400	-0.15175100
C	-4.32863300	2.77746500	-1.46536400
H	-4.06817100	3.32624000	-2.37671100
H	-5.35800400	2.41519800	-1.59505400
C	-3.38488400	1.58376500	-1.30076400
H	-3.48079200	0.88903200	-2.14294000
H	-2.35004000	1.94043500	-1.29557400
B	1.32861300	0.17630600	0.50247200
B	-1.33947600	-0.06852600	0.43294600
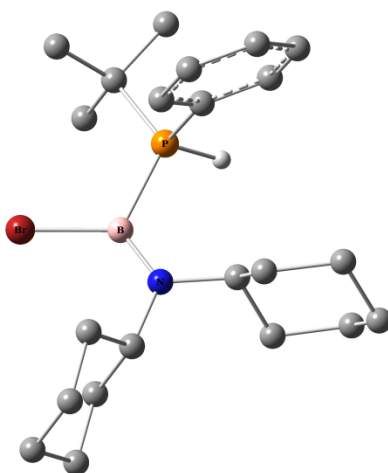
Figure S62. Optimized structure of **C⁺**

1 1

Br	0.52427500	-2.67373100	0.23945400
C	-2.90757300	-1.91770500	-0.96994600
P	-1.73319600	-0.50151500	-0.73198100
N	1.07300600	0.16462500	-0.34832700
B	0.15990200	-0.86383900	-0.32262800
C	-4.23453500	-1.28860800	-1.42612300
H	-4.65179500	-0.62048500	-0.66659900

H	-4.95257500	-2.09816800	-1.59061800
H	-4.12787200	-0.73740000	-2.36534500
C	-3.12700100	-2.68215200	0.34145900
H	-2.21199600	-3.14983100	0.70945000
H	-3.85839900	-3.47343500	0.14861900
H	-3.53618900	-2.03286800	1.12133400
C	-2.34428800	-2.82421500	-2.07346600
H	-2.18578300	-2.27543100	-3.00731100
H	-3.07701100	-3.61316900	-2.27150000
H	-1.40784800	-3.30017800	-1.77593000
C	-2.31382000	0.61975000	0.56002300
C	-3.05122300	1.76421400	0.23702100
H	-3.29732600	1.99085700	-0.79697400
C	-3.46054700	2.62554100	1.25288900
H	-4.02492300	3.51795300	1.00463600
C	-3.14198700	2.34188800	2.58077200
H	-3.46161300	3.01617800	3.36836100
C	-2.41014300	1.19771700	2.90150400
H	-2.15976900	0.98002700	3.93408300
C	-1.98618500	0.33694900	1.89319200
H	-1.39936900	-0.54254600	2.14956900
C	2.49807400	0.04092400	0.07223200
H	2.92290400	1.04012700	-0.06327700
C	3.31590800	-0.88460400	-0.83361300
H	3.17651000	-0.58113000	-1.87748300
H	2.96562500	-1.91694300	-0.74187100
C	4.79463400	-0.81043000	-0.43940000
H	5.37618500	-1.49908500	-1.06013200
H	5.17394500	0.20060700	-0.64350200
C	4.98947400	-1.13155200	1.04536200
H	6.04848200	-1.05083700	1.31149800
H	4.69245300	-2.17311100	1.23120200
C	4.15234000	-0.20457900	1.93181700
H	4.50574300	0.82896600	1.81115600
H	4.28171500	-0.46355200	2.98726500

C	2.66728000	-0.27883400	1.56127500
H	2.28781700	-1.28038500	1.78413100
H	2.08109700	0.43468700	2.15219500
C	0.69899900	1.53503000	-0.77659200
H	-0.35174600	1.51435500	-1.07743500
C	1.47582000	1.98871400	-2.01719200
H	2.54957500	2.04776700	-1.80042900
H	1.34213500	1.24844300	-2.81404300
C	0.97966300	3.36811900	-2.46447000
H	1.55668100	3.70078300	-3.33258300
H	-0.06723200	3.28825400	-2.78879300
C	1.07825800	4.38827400	-1.32760900
H	2.13367600	4.52428100	-1.05430200
H	0.70596300	5.36205400	-1.66124900
C	0.29676000	3.91623700	-0.09921400
H	-0.77146400	3.85107600	-0.35091000
H	0.38619300	4.63882900	0.71772400
C	0.78472800	2.54306600	0.37464000
H	1.81921800	2.62986300	0.73091000
H	0.17632800	2.18343300	1.21346200
H	-1.82937000	0.21766600	-1.93241100
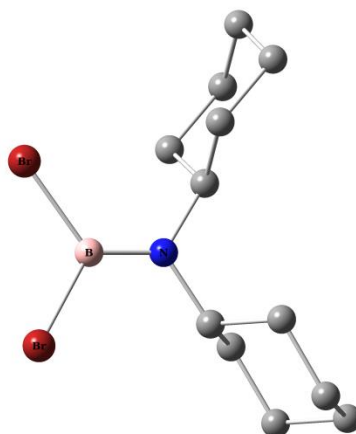
Figure S63. Optimized structure of **(Cy₂N)BBr₂**

0 1

Br	-2.38323800	-1.39890900	0.00001200
N	0.17993700	0.05392900	-0.00000900
B	-0.45482800	-1.17346600	-0.00000500

C	-0.51804400	1.36564300	-0.00000500
H	0.28308500	2.11176500	-0.00001200
C	-1.32114200	1.64094400	1.27563900
H	-0.68189300	1.45644100	2.14686700
H	-2.17516700	0.96096100	1.34541000
C	-1.82090900	3.08928700	1.26514600
H	-2.42293400	3.28088900	2.15925100
H	-0.95958200	3.77094100	1.30857400
C	-2.63238300	3.38455300	0.00000900
H	-2.96443900	4.42826800	0.00001100
H	-3.53781100	2.76161900	0.00001600
C	-1.82092800	3.08928500	-1.26513900
H	-0.95960100	3.77093900	-1.30858000
H	-2.42296600	3.28088700	-2.15923600
C	-1.32116200	1.64094200	-1.27563700
H	-2.17518900	0.96095900	-1.34539400
H	-0.68192600	1.45643800	-2.14687500
C	1.65847000	0.16773100	-0.00000800
H	2.05333300	-0.84944000	-0.00001200
C	2.18410000	0.83919300	1.27328500
H	1.81048800	1.86883500	1.35222900
H	1.81214900	0.28972200	2.14576600
C	3.71627100	0.86708700	1.26130700
H	4.08378500	1.37471300	2.15889800
H	4.09769600	-0.16253100	1.29890800
C	4.24654700	1.55340200	0.00000500
H	3.92733500	2.60506100	0.00001000
H	5.34159400	1.55183400	0.00000700
C	3.71627600	0.86710000	-1.26130800
H	4.09770100	-0.16251700	-1.29891800
H	4.08379300	1.37473600	-2.15889200
C	2.18410400	0.83920500	-1.27329300
H	1.81049300	1.86884800	-1.35222800
H	1.81215700	0.28974200	-2.14578100
Br	0.53053200	-2.85439200	-0.00001000
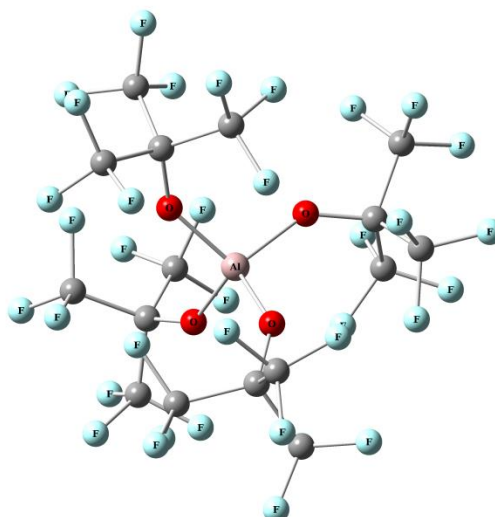
Figure S64. Optimized structure of **[WCA]**⁻

-1 1

Al	0.00733700	0.01307700	-0.01943700
F	1.23334300	-3.36520000	-0.10518800
F	1.12404700	-4.47053000	1.75293200
F	2.83135800	-3.20986200	1.33636800
F	-1.43864000	-1.35402000	2.19983000
F	-1.19989500	-3.17398200	1.06527900
F	-0.88140000	-3.19050400	3.20209400
F	2.60250400	-1.14538300	3.05772100
F	0.64811100	-1.00429400	3.95986500
F	1.69677200	-2.90074900	3.93163700
F	-3.05653800	1.39641600	2.41494000
F	-2.34823300	3.26558400	3.23342800
F	-1.25076700	1.43209800	3.59462900
F	-3.10301900	3.27526400	0.48271400
F	-1.52290500	4.65326200	1.01553200
F	-1.31772700	3.38131000	-0.72350200
F	0.92863700	3.39967800	0.78676800
F	0.29709600	3.62041300	2.84157500
F	1.05210100	1.71868900	2.13470600
F	-3.33933200	0.82430500	-1.05308300
F	-4.45727800	-0.91369100	-1.68428200
F	-3.37933100	-0.94077000	0.19073900

F	-2.95492800	-3.20891100	-1.27709100
F	-3.10254900	-2.56595100	-3.33945400
F	-1.19181000	-3.14971200	-2.51748800
F	-2.88747400	0.14888800	-3.69348200
F	-0.96377400	-0.82213000	-3.88591400
F	-1.15738700	0.94560700	-2.66265300
F	3.77720200	2.16761900	-2.93975600
F	1.77287800	2.87752500	-2.55775000
F	3.27156300	3.01666600	-1.01317900
F	3.42175900	-0.98091000	-0.33673400
F	3.31728800	0.90462300	0.71219000
F	4.72319700	0.64650500	-0.91018100
F	3.52007600	-0.55984100	-3.07548800
F	1.70772800	0.42968800	-3.72161200
F	1.59685000	-1.21246400	-2.32497200
O	-1.10450500	1.15628100	0.70280800
O	-0.99248400	-1.08077800	-0.95452100
O	0.92691800	-1.00402700	1.06944400
C	0.78570400	-2.09314000	1.85022100
C	1.50393200	-3.30797300	1.19491600
C	-0.71083500	-2.46536300	2.08591500
C	1.44869100	-1.78572800	3.22455100
C	-1.11651600	2.31473500	1.39048800
C	-1.96184100	2.10349300	2.68076500
C	-1.77392600	3.42729300	0.52416400
C	0.31577200	2.77803300	1.79738400
C	-2.05745900	-1.05908900	-1.78059900
C	-3.33219500	-0.51200000	-1.06574600
C	-2.33013600	-2.52108700	-2.24045100
C	-1.76859300	-0.18075200	-3.03135300
O	1.19152000	0.97689800	-0.88006600
C	2.39353500	0.84970500	-1.47724100
C	2.81022800	2.25167300	-2.00998700
C	3.48404700	0.34638300	-0.48146600
C	2.31081800	-0.14186700	-2.67303800
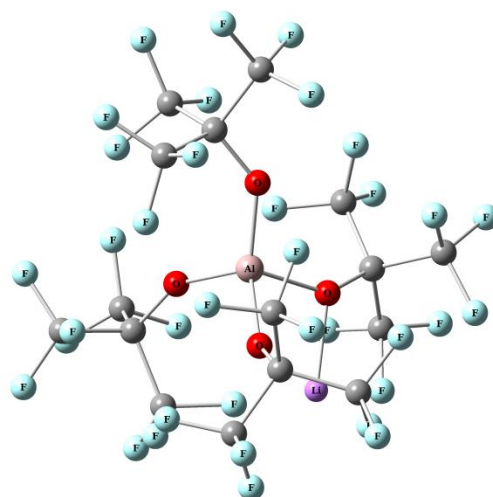
Figure S65. Optimized structure of **Li[WCA]**

0 1

Al	-0.12444100	0.02926600	-0.07795800
F	0.25972700	-1.06925500	-3.56264700
F	0.84602100	-3.13070600	-3.87707600
F	2.34026700	-1.62487000	-3.41937300
F	-0.74105400	-2.89548600	-0.09450300
F	-1.36955600	-2.65289900	-2.14659800
F	-0.19704700	-4.38108400	-1.58005200
F	3.18735700	-2.23961600	-0.92168500
F	1.87737200	-3.63979900	0.06838700
F	2.55041200	-4.04015300	-1.94867900
F	-1.29306200	-2.42803500	2.99267000
F	0.18952000	-2.26909300	4.55824400
F	0.75236400	-2.99252200	2.59329100
F	-1.52684100	0.02643100	4.12570100
F	0.46538500	0.43480400	4.87647800
F	-0.32433600	1.56804700	3.21008000
F	2.18608600	0.78773500	2.68935300
F	2.46933400	-1.09281600	3.71008500
F	2.32415700	-1.04040300	1.55247200
F	-3.15071200	-0.34077300	1.59195700
F	-4.90698500	-0.42231000	0.32531500
F	-3.24356700	-1.75694100	-0.03216800

F	-3.99226700	-0.62746100	-2.38007200
F	-4.84096300	1.27650200	-1.78728500
F	-2.97209100	1.20784100	-2.87606600
F	-4.02221200	2.10685700	0.81830900
F	-2.83684500	2.90746900	-0.79638900
F	-1.85766400	2.00183800	0.90272900
F	2.71121300	4.43383700	0.08049600
F	1.70620900	3.26328500	1.59559100
F	3.56771100	2.55861400	0.75769500
F	1.94162300	1.66591400	-2.86050100
F	3.40056700	0.99936100	-1.41759600
F	3.43146500	3.04633500	-2.11563400
F	0.95408400	4.18181400	-2.03903400
F	-0.15439000	3.90255600	-0.20113100
F	-0.37542700	2.48651700	-1.81821300
O	-0.28323700	-0.49840100	1.55741400
O	-1.63131900	0.14702200	-0.90067900
O	0.94904500	-1.07689800	-1.00123600
C	0.92660600	-2.28284000	-1.64274000
C	1.08578200	-2.02947800	-3.16584300
C	-0.38031200	-3.07578300	-1.36525100
C	2.14150800	-3.09790800	-1.11434400
C	0.28901200	-0.67563500	2.76384600
C	-0.02925900	-2.12168100	3.24847500
C	-0.28798400	0.36146300	3.77152500
C	1.83589900	-0.49371100	2.71415500
C	-2.90763500	0.52111000	-0.60791000
C	-3.57538900	-0.52258600	0.33688600
C	-3.69778300	0.59895600	-1.94189800
C	-2.92582100	1.91440500	0.08882500
O	1.20430700	1.24025100	-0.05379100
C	1.64806800	2.40484800	-0.61249100
C	2.41785800	3.19652900	0.48049600
C	2.61373900	2.06166300	-1.78799800
C	0.49037300	3.27256100	-1.17866500

Li   2.54556800 -0.32383200 -0.29667200
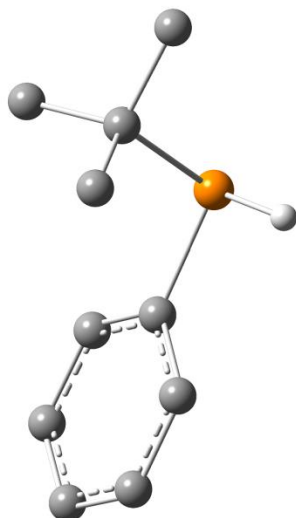
Figure S66. Optimized structure of *t*BuPhPH

0 1

C	1.97953700	0.02250300	0.29308800
P	0.89963400	-0.01588300	-1.25772400
C	1.59105100	-1.04632800	1.31567800
H	0.57105600	-0.89763200	1.68352600
H	2.27068300	-0.99847300	2.17608200
H	1.65789400	-2.05237800	0.88723600
C	1.86869500	1.41349500	0.92659300
H	2.14110400	2.20188300	0.21659500
H	2.54705400	1.48101600	1.78563900
H	0.85289000	1.60893400	1.28665500
C	3.41684700	-0.21420600	-0.18854200
H	3.52572600	-1.19912800	-0.65596300
H	4.10337500	-0.17040900	0.66547200
H	3.72820000	0.54663600	-0.91200200
C	-0.80387800	-0.03889800	-0.56453100
C	-1.48168300	-1.22328100	-0.24167300
H	-0.99206300	-2.18239500	-0.38898500
C	-2.77755300	-1.18525600	0.27183500
H	-3.28913300	-2.11203400	0.51313400
C	-3.41281700	0.03950000	0.48075100
H	-4.42034200	0.06876800	0.88369900

C	-2.75101300	1.22528400	0.16262300
H	-3.24170700	2.18158300	0.31521800
C	-1.46110300	1.18380500	-0.36657900
H	-0.96185300	2.11267100	-0.63349200
H	1.00411100	-1.41051000	-1.49242800

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