Supplementary Information

Activation of small molecules by ambiphilic NHC-stabilized phosphinoborenium cation: formation of boreniums with B-O-C, B-O-B, and B-O-P structural motifs

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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. Solvent 1,2-difluorobenzene was dried over CaH_2 and distilled under argon. Pentane and petroleum ether were dried with sodium-potassium alloy and distilled under argon. 1D (^{1}H, ^{11}B, $^{31}P\{^{1}H\}$, ^{31}P, ^{13}C, ^{27}Al, $^{19}F\{^{1}H\}$, ^{19}F) and 2D NMR spectra were recorded on a Bruker AV400 MHz spectrometer (external standard TMS for ^{1}H 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, $^{31}P\{^{1}H\}$ and ^{31}P NMR spectra of reaction mixtures. Data were processed using Bruker's Topspin 3.6.4 software.

Elemental analyses of all compounds were performed using Elementar Vario MACRO CHN (Elementar Analysesysteme GmbH, Germany) micro elemental analyzer. Analyses were performed in Instrumental Analysis Laboratory, Faculty of Chemistry, Nicolaus Copernicus University in Toruń. (iPr$_2$N)B(Br)PtBu$_2$[1], IMe$_4$[2], Li[Al(OC(CF$_3$)$_3$)$_4$][3] were prepared according to literature procedures.

IR spectra were recorded in the range 4000–400 cm^{-1} with a Nicolet iS50 FT–IR spectrometer equipped with a Specac Quest single-reflection diamond attenuated total reflectance (ATR) accessory. Samples were prepared by suspending the compounds in Cargille Immersion Oil (LOT number: 101491). Immersion oil was evacuated under high vaccum, afterwards samples were prepared in glovebox.

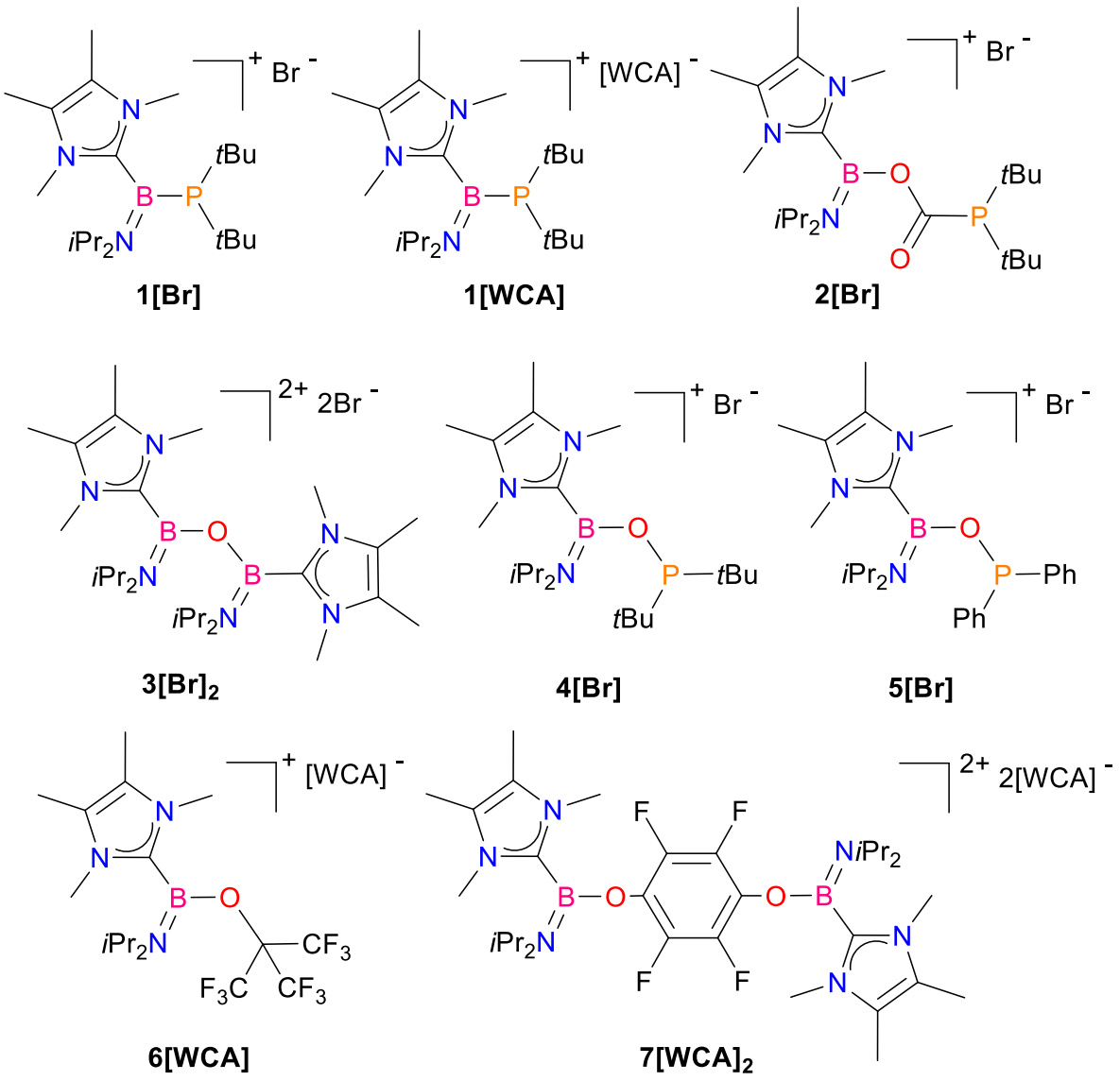
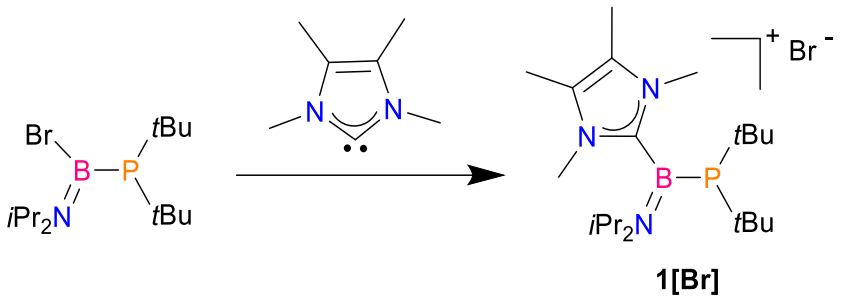


Chart 1. Comparison of the structures of the obtained borenium cations.

Table S 1. Abbreviations

Symbol	Reference	Symbol	Reference
s	solvent		**1[Br]**
g	grease		**2[Br]**
	impurity		**3[Br]$_2$**
	imidazolium salt		**4[Br]**
	*t*Bu$_2$PH		**5[Br]**
	*t*Bu$_2$PPPh$_2$		**6[WCA]**
	*t*Bu$_2$P(O)H		
	*i*Pr$_2$NH		

Synthesis of 1[Br]



1[Br]

Scheme S 1. Synthesis of **1[Br]**

The Schlenk flask was charged with (bromo)phosphinoborane (iPr$_2$N)B(Br)PtBu$_2$ (0.720 g, 2.140 mmol, 1.0 eq) and NHC (0.300 g, 2.416 mmol, 1.1 eq). The petroleum ether (15 ml) was added dropwise at -40 °C. The mixture was stirred at -40 °C for 15 minutes, afterwards the reaction mixture was allowed to warm up to room temperature and stirred overnight. The suspension was filtered and resulting white precipitate was washed three times with 15 ml of petroleum ether. All the volatiles was removed under reduced pressure, crude product **[1Br]** was obtained as a white powder. Yield: 87% (0.860 g, 1.868 mmol).

Elemental analysis calc. for $C_{21}H_{44}N_3PBBr$ (460.28 g/mol): C, 54.80; H, 9.64; N, 9.13. Found: C, 54.13; H, 9.59; N, 9.02.

NMR data of 1[Br]

^{11}B NMR (CD_2Cl_2): δ 40.9 (s).

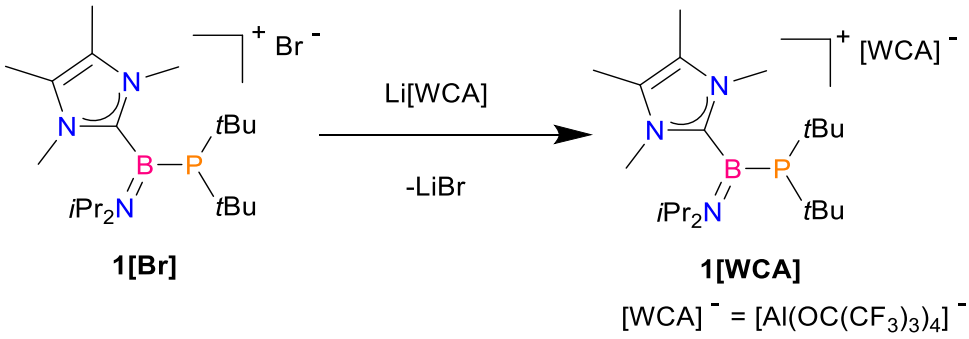
^{31}P{^{1}H} NMR (CD_2Cl_2): δ 5.2 (s).

^{1}H NMR (CD_2Cl_2): δ 5.12 (1H, m, C**H**(CH$_3$)$_2$); 3.70 (6H, s, N-C**H**$_3$ of IMe$_4$); 3.58 (1H, sept, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$); 2.34 (6H, s, C**H**$_3$ of IMe$_4$); 1.44 (6H, d, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$); 1.22 (6H, d, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$ overlapped with signal of C(C**H**$_3$)$_3$); 1.21 (18H, d, $^3J_{PH}$ = 12.3 Hz, C(C**H**$_3$)$_3$ overlapped with signal of CH(C**H**$_3$)$_2$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 129.3 (s, **C**=**C** of IMe$_4$); 54.3 (d, $^3J_{CP}$ = 27.0 Hz, **C**H(CH$_3$)$_2$ overlapped with solvent); 53.9 (s, **C**H(CH$_3$)$_2$, overlapped with solvent); 36.5 (d, $^4J_{CP}$ = 2.7 Hz N-**C**H$_3$ of IMe$_4$); 33.4 (d, $^1J_{CP}$ = 20.0 Hz, **C**(CH$_3$)$_3$) overlapped with C(**C**H$_3$)$_3$); 33.4 (d, $^2J_{CP}$ = 12.7 Hz, C(**C**H$_3$)$_3$) overlapped with **C**(CH$_3$)$_3$); 25.8 (s, **C**H(CH$_3$)$_2$); 23.7 (s, **C**H(CH$_3$)$_2$); 9.6 (s, C=C-**C**H$_3$ of IMe$_4$). The carbene carbon atom was not detected at the ^{13}C{^{1}H} spectrum; however, a chemical shift of

the carbene carbon atom was identified at 151.4 ppm based on the ^{13}C ^{1}H HMBC spectrum (a coupling of N-C**H**$_3$ of IMe$_4$ protons with carbene carbon atom).

Synthesis of 1[WCA]



Scheme S 2. Reaction of **1[Br]** with Li[WCA].

The Schlenk flask was charged with **1[Br]** (0.092 g, 0.200 mmol) and Li[WCA] (0.195 g, 0.200 mmol, 1.0 eq). The CH_2Cl_2 (2 ml) was added dropwise at room temperature and the suspension was stirred overnight. The solution was filtered through a syringe filter and solvent was removed under reduced pressure. Crude product **1[WCA]** was obtained as yellowish powder. Yield: 80% (0.216 g, 0.160 mmol).

Single crystals suitable for an X-ray diffraction analysis were obtained from CH_2Cl_2 solution (1 ml) of **1[WCA]** layered with petroleum ether (2 ml) stored in +4 °C.

Elemental analysis calc. for $C_{37}H_{44}N_3PBO_4F_{36}Al{\cdot}CH_2Cl_2$ (1432.40 g/mol): C, 31.86; H, 3.24; N, 2.93. Found: C, 31.70; H, 3.22; N, 2.90.

NMR data of 1[WCA]

^{11}B NMR (CD_2Cl_2): δ 40.6 (s).

^{31}P{^{1}H} NMR (CD_2Cl_2): δ 6.8 (s).

^{1}H NMR (CD_2Cl_2): δ 5.10 (1H, m, C**H**$(CH_3)_2$); 3.64 (6H, s, N-C**H**$_3$ of IMe$_4$); 3.52 (1H, sept, $^{3}J_{HH}$ = 6.9 Hz, C**H**$(CH_3)_2$); 2.26 (6H, s, C**H**$_3$ of IMe$_4$); 1.44 (6H, d, $^{3}J_{HH}$ = 6.9 Hz, CH(C**H**$_3)_2$); 1.22 (18H, d, $^{3}J_{PH}$ = 12.3 Hz, C(C**H**$_3)_3$); 1.18 (6H, d, $^{3}J_{HH}$ = 6.9 Hz, CH(C**H**$_3)_2$).

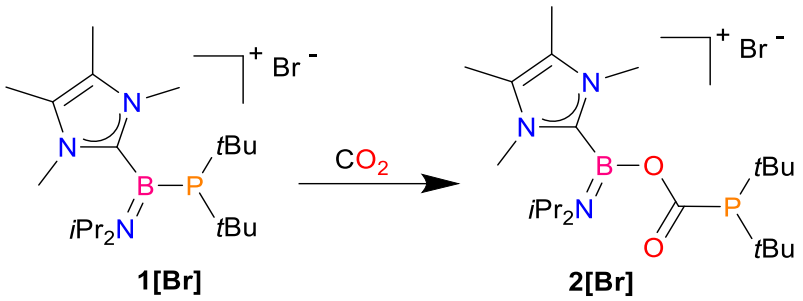
^{13}C{^{1}H} NMR (CD_2Cl_2): δ 128.3 (s, **C**=**C** of IMe$_4$); 121.3 (q, $^{1}J_{CF}$ = 297.1 Hz, OC(**C**F$_3$),); 53.5 (d, $^{3}J_{CP}$ = 27.0 Hz, **C**H$(CH_3)_2$ overlapped with solvent); 53.1 (s, **C**H$(CH_3)_2$, overlapped with solvent); 35.3 (d, $^{4}J_{CP}$ = 2.7 Hz N-**C**H$_3$ of IMe$_4$); 32.7 (d, $^{1}J_{CP}$ = 20.0 Hz, **C**$(CH_3)_3$) overlapped with C(**C**H$_3)_3$); 32.5

(d, $^{2}J_{CP}$ = 12.7 Hz, C(**C**H_3)$_3$) overlapped with **C**(CH_3)$_3$); 24.4 (s, CH(**C**H_3)$_2$); 22.7 (s, CH(**C**H_3)$_2$); 8.2 (s, C=C-**C**H_3 of IMe_4). The carbene carbon atom was not detected at the $^{13}C\{^{1}H\}$ spectrum; however, a chemical shift of the carbene carbon atom was identified at 151.2 ppm based on the ^{13}C ^{1}H HMBC spectrum (a coupling of N-C**H**$_3$ of IMe_4 protons with carbene carbon atom).

^{27}Al NMR (CD_2Cl_2): δ 34.6 (s, [***Al***(OC(CF_3)$_3$)$_4$]$^-$).

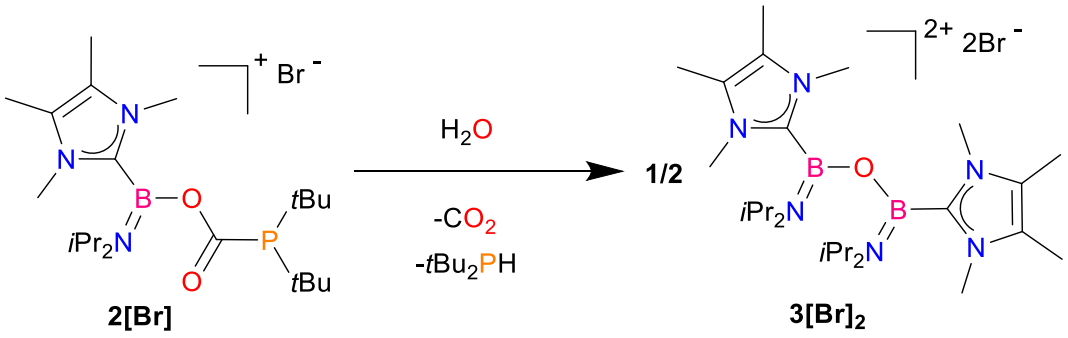
^{19}F NMR (CD_2Cl_2): δ -75.7 (s, OC(C***F***$_3$)$_3$).

Synthesis of 2[Br]



Scheme S 3. Synthesis of **2[Br]**, reaction of **1[Br]** with CO_2

1[Br] (0.230 g, 0.500 mmol) was dissolved in CH_2Cl_2 (5 ml). A solution was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr, and backfilled with CO_2 (1 atm). The reaction mixture was allowed to warm up to room temperature and stirred for 3 hours. ^{11}B and $^{31}P\{^1H\}$ of the yellowish reaction mixture revealed a quantitative conversion of **1[Br]** into **2[Br]**. The solvent was removed under reduced pressure and the residue was dried under vacuum giving **2[Br]** as a beige powder. The product is very sensitive to hydrolysis therefore imidazolium salt $[IMe_4H][Br]$ and $\mathbf{3[Br]_2}$ traces are observed in product (based on ^1H NMR spectroscopy). Yield: 90% (0.228 g, 0.452 mmol).



Scheme S 4. Hydrolysis of **2[Br]** (formation of $\mathbf{3[Br]_2}$)

A small quantity (0.040 g, 0.049 mmol) of needle-like crystals of $\mathbf{3[Br]_2}$, suitable for an X-ray diffraction, were obtained after numerous attempts at crystallizing **2[Br]**.

NMR tube was charged with **2[Br]** (0.020 g, 0.043 mmol) and non-anhydrous CD_2Cl_2 (0.5 ml) was added. The transformation of **2[Br]** into $\mathbf{3[Br]_2}$ was monitored by ^1H, ^{11}B, $^{31}P\{^1H\}$, NMR spectroscopy.

NMR data of 2[Br]

^{11}B NMR (CD_2Cl_2): δ 25.3 (s).

^{31}P{^{1}H} NMR (CD_2Cl_2): δ 51.6 (s).

^{1}H NMR (CD_2Cl_2): δ 3.74 (6H, s, N-C**H**$_3$ of IMe_4); 3.49 (1H, sept, $^{3}J_{HH}$ = 7.0 Hz, C**H**$(CH_3)_2$); 3.25 (1H, sept, $^{3}J_{HH}$ = 6.9 Hz, C**H**$(CH_3)_2$); 2.31 (6H, s, C**H**$_3$ of IMe_4); 1.42 (6H, d, $^{3}J_{HH}$ = 7.0 Hz, CH(C**H**$_3)_2$); 1.24 (18H, d, $^{3}J_{PH}$ = 12.3 Hz, C(C**H**$_3)_3$); 1.19 (6H, d, $^{3}J_{HH}$ = 6.9 Hz, CH(C**H**$_3)_2$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 180.5 (d, $^{1}J_{CP}$ = 41.7 Hz, P-**C**(=O)-O-B); 128.5 (s, **C**=**C** of IMe_4); 53.9 (s, **C**H$(CH_3)_2$ overlapped with solvent); 53.4 (s, **C**H$(CH_3)_2$, overlapped with solvent); 34.6 (s, N-**C**H$_3$ of IMe_4); 33.2 (d, $^{1}J_{CP}$ = 21.2 Hz, **C**$(CH_3)_3$); 29.7 (d, $^{2}J_{CP}$ = 12.7 Hz, C(**C**H$_3)_3$); 23.4 (s, CH(**C**H$_3)_2$); 21.8 (s, CH(**C**H$_3)_2$); 8.9 (s, C=C-**C**H$_3$ of IMe_4). The carbene carbon atom was not detected at the ^{13}C{^{1}H} spectrum; however, a chemical shift of the carbene carbon atom was identified at 148.0 ppm based on the ^{13}C ^{1}H HMBC spectrum (a coupling of N-C**H**$_3$ of IMe_4 protons with carbene carbon atom).

IR data of 2[Br]

Wavelength: 1675 cm^{-1} B-O-(**C=O**)-P bond stretching.

NMR data of 3[Br]$_2$

^{11}B NMR (CD_2Cl_2): δ 22.3 (broad signal, 601 Hz, overlapped with **2[Br]**).

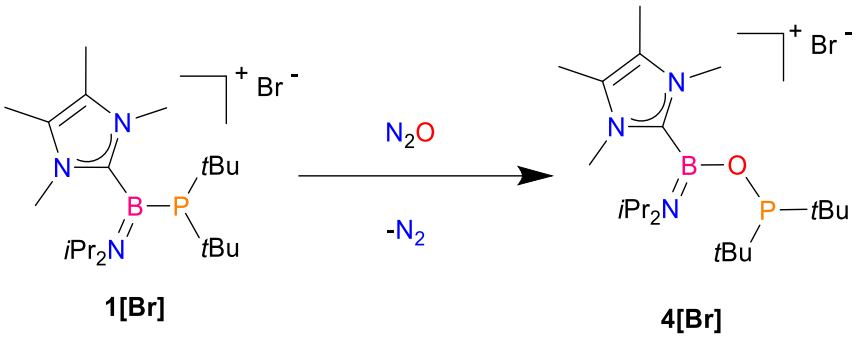
^{1}H NMR (CD_2Cl_2): δ 3.70 (12H, s, N-C**H**$_3$ of IMe_4); 3.62 (2H, m, C**H**$(CH_3)_2$); 2.82 (2H, m, C**H**$(CH_3)_2$); 2.39 (12H, s, C**H**$_3$ of IMe_4); 1.57 (12H, d, $^{3}J_{HH}$ = 7.0 Hz, CH(C**H**$_3)_2$); 1.16 (12H, d, $^{3}J_{HH}$ = 6.7 Hz, CH(C**H**$_3)_2$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 129.1 (s, **C**=**C** of IMe_4); 53.8 (s, **C**H$(CH_3)_2$ overlapped with solvent and **2[Br]**); 53.4 (s, **C**H$(CH_3)_2$, overlapped with solvent and **2[Br]**); 35.9 (s, N-**C**H$_3$ of IMe_4); 23.4 (s, CH(**C**H$_3)_2$); 21.8 (s, CH(**C**H$_3)_2$); 9.3 (s, C=C-**C**H$_3$ of IMe_4).The carbene carbon atom was not detected at the ^{13}C{^{1}H} spectrum; however, a chemical shift of the carbene carbon atom was identified at 149.0 ppm based on the ^{13}C ^{1}H HMBC spectrum (a coupling of N-C**H**$_3$ of IMe_4 protons with carbene carbon atom).

Synthesis of 4[Br]

Method A

Reaction of 1[Br] with N_2O



1[Br] **4[Br]**

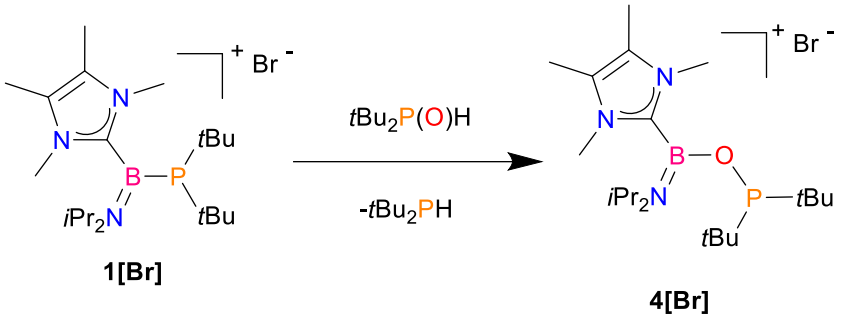
Scheme S 5. Synthesis of **4[Br]**, reaction of **1[Br]** with N_2O

1[Br] (0.092 g, 0.200 mmol) was dissolved in 1,2-difluorobenzene (2 ml). A solution was slowly frozen in a liquid nitrogen bath, evacuated to 0.01 Torr, and backfilled with N_2O (1 atm). The reaction mixture was allowed to warm to room temperature and stirred at 50 °C for a week. Progress of the reaction was monitored by ^{11}B and $^{31}P\{^1H\}$ NMR spectroscopy. The solvent and all volatiles were removed under reduced pressure. Crude product was re-dissolved in CH_2Cl_2 (1 ml) and layered with pentane (2 ml). Storing the solution in room temperature afforded **4[Br]** as colourless crystals. Yield: 65% (0.062 g, 0.130 mmol).

Due to the product's high sensitivity to hydrolysis, the isolated product was contaminated with imidazolium salt. Single crystals suitable for an X-ray diffraction analysis were obtained by keeping the solution at -22 °C.

Method B

Reaction of 1[Br] with tBu$_2$P(O)H



1[Br] **4[Br]**

Scheme S 6. Synthesis of **4[Br]**, reaction of **1[Br]** with tBu$_2$P(O)H

A solution of tBu$_2$P(=O)H (0.032 g, 0.200 mmol, 1.0 eq) in CH_2Cl_2 (1 ml) was added dropwise to the stirred solution of **1[Br]** (0.092 g, 0.200 mmol, 1.0 eq) in CH_2Cl_2 (1 ml) at -40 °C. Afterwards, the reaction mixture was kept at -40 °C for 5 minutes. The mixture was allowed to warm up to room temperature and stirred over a week. Solvent and all volatiles were removed under reduced pressure and the residue was dried under vacuum resulting **4[Br]** as beige powder. The product is very sensitive to hydrolysis, therefore is contaminated with imidazolium salt [IMe$_4$H][Br]. Yield: 96% (0.091 g, 0.191 mmol).

NMR data of 4[Br]

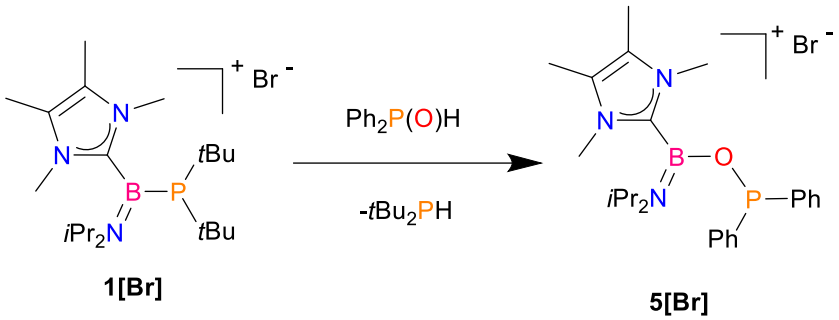
^{11}B NMR (CD_2Cl_2): δ 25.5 (s).

^{31}P{^{1}H} NMR (CD_2Cl_2): δ 163.7 (s).

^{1}H NMR (CD_2Cl_2): δ 3.70 (6H, s, N-C**H**$_3$ of IMe$_4$); 3.44 (1H, sept, $^3J_{HH}$ = 7.0 Hz, C**H**(CH$_3$)$_2$); 2.93 (1H, sept, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$); 2.33 (6H, s, C**H**$_3$ of IMe$_4$); 1.45 (6H, d, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$); 1.11 (6H, d, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$ overlapped with signal of C(C**H**$_3$)$_3$); 1.11 (18H, d, $^3J_{PH}$ = 12.3 Hz, C(C**H**$_3$)$_3$ overlapped with signal of CH(C**H**$_3$)$_2$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 128.1 (s, **C**=**C** of IMe$_4$); 53.5 (d, $^4J_{CP}$ = 27.0 Hz, **C**H(CH$_3$)$_2$ overlapped with solvent); 53.1 (s, **C**H(CH$_3$)$_2$, overlapped with solvent); 35.2 d, $^4J_{CP}$ = 2.7 Hz N-**C**H$_3$ of IMe$_4$); 35.0 (s, **C**(CH$_3$)$_3$); 27.3 (d, $^2J_{CP}$ = 15.7 Hz, C(**C**H$_3$)$_3$); 23.4 (s, CH(**C**H$_3$)$_2$); 22.0 (s, CH(**C**H$_3$)$_2$); 8.7 (s, C=C-**C**H$_3$ of IMe$_4$). The carbene carbon atom was not detected at the ^{13}C{^{1}H} spectrum; however, a chemical shift of the carbene carbon atom was identified at 147.7 ppm based on the ^{13}C ^{1}H HMBC spectrum (a coupling of N-C**H**$_3$ of IMe$_4$ protons with carbene carbon atom).

Synthesis of 5[Br]



Scheme S 7. Synthesis of **5[Br]**, reaction of **1[Br]** with $Ph_2P(O)H$

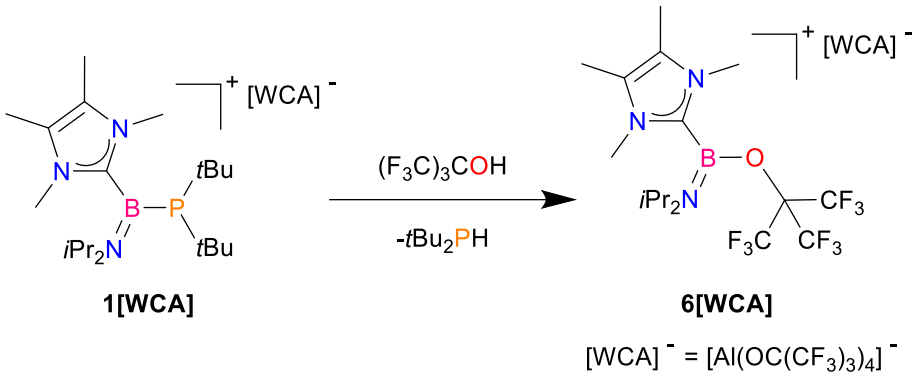
A solution of $Ph_2P(=O)H$ (0.041 g, 0.200 mmol, 1.0 eq) in CH_2Cl_2 (1 ml) was added dropwise to the stirred solution of **1[Br]** (0.092 g, 0.200 mmol, 1.0 eq) in CH_2Cl_2 (1 ml) at -40 °C. Afterwards, the reaction mixture was kept at -40 °C for 5 minutes. The mixture was allowed to warm up to room temperature and stirred in the dark over a week. Progress of the reaction was monitored by ^{11}B and $^{31}P\{^1H\}$ spectroscopy.

NMR data for reaction mixture of 5[Br]

^{11}B NMR (CD_2Cl_2): δ 25.4 (s).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 112.3 (s).

Synthesis of 6[WCA]



1[WCA] **6[WCA]**

$[WCA]^- = [Al(OC(CF_3)_3)_4]^-$

Scheme S 8. Synthesis of **6[WCA]**, reaction of **1[WCA]** with $(F_3C)_3COH$.

A dichloromethane solution of $(F_3C)_3COH$ (c = 0.4 M, 0.5 ml, 1.33 eq) was added dropwise to the stirred solution of **1[WCA]** (0.202 g, 0.150 mmol, 1.0 eq) in CH_2Cl_2 (2 ml) at -30 °C. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The solvent and all volatiles were removed under reduced pressure. The resulting solid residue was re-dissolved in CH_2Cl_2 (2 ml). Keeping the solution at +4 °C afforded the first crop **6[WCA]** as colourless crystals (0.094 g, 0.065 mmol) suitable for an X-ray diffraction analysis. Keeping the mother liquor at -22 °C afforded a second crop (0.025 g, 0.017 mmol) of **6[WCA]**. Yield: 55% (0.119 g, 0.082 mmol).

Elemental analysis calc. for $C_{33}H_{26}AlN_3BO_5F_{45}$ (1437.30 g/mol): C, 27.58; H, 1.82; N, 2.92. Found: C, 27.53; H, 2.01; N, 3.58.

NMR data of 6[WCA]

^{11}B NMR (CD_2Cl_2): δ 23.7 (s).

^{1}H NMR (CD_2Cl_2): δ 3.62 (6H, s, N-C**H**$_3$ of IMe$_4$); 3.55 (1H, m, C**H**$(CH_3)_2$); 2.81 (1H, sept, $^3J_{HH}$ = 7.0 Hz, C**H**$(CH_3)_2$); 2.23 (6H, s, C**H**$_3$ of IMe$_4$); 1.40 (6H, d, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3)_2$); 1.15 (6H, d, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3)_2$).

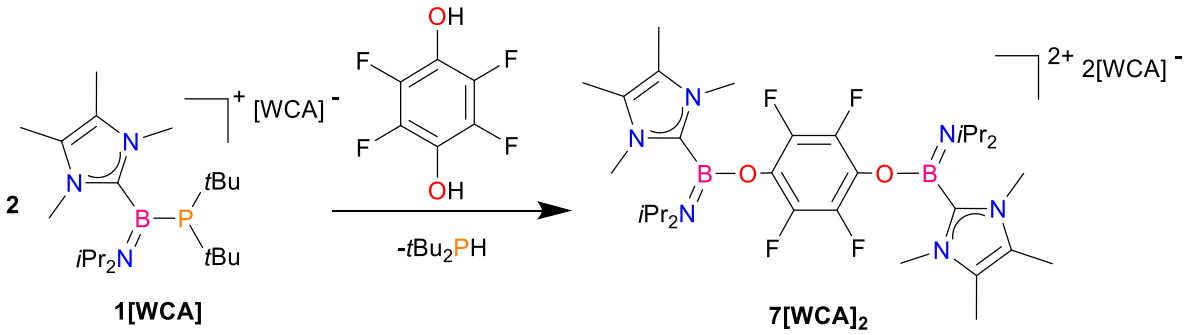
^{13}C{^{1}H} NMR (CD_2Cl_2): δ 129.2 (s, **C**=**C** of IMe$_4$); 121.0 (q, $^1J_{CF}$ = 297.1 Hz, OC(**C**F$_3$) of [***Al***$(OC(CF_3)_3)_4]^-$); 119.4 (q, $^1J_{CF}$ = 297.1 Hz, B-OC(**C**F$_3$)); 53.6 (s, **C**H$(CH_3)_2$ overlapped with solvent); 53.1 (s, **C**H$(CH_3)_2$, overlapped with solvent); 34.3 (s, N-**C**H$_3$ of IMe$_4$); 21.9 (s, CH(**C**H$_3)_2$); 21.3 (s, CH(**C**H$_3)_2$); 8.2 (s, C=C-**C**H$_3$ of IMe$_4$). The carbene carbon atom was not detected at the ^{13}C{^{1}H} spectrum; however, a chemical shift of the carbene carbon atom was identified at

151.2 ppm based on the ^{13}C ^{1}H HMBC spectrum (a coupling of N-C**H**$_3$ of lMe$_4$ protons with carbene carbon atom).

^{27}Al NMR (CD_2Cl_2): δ 34.6 (s, [***Al***$(OC(CF_3)_3)_4]^-$).

^{19}F NMR (CD_2Cl_2): δ -72.02 (s, 9F, B-OC(C**F**$_3$)); -75.8(s, 36F, [*Al*$(OC(C\mathbf{F}_3)_3)_4]^-$).

Synthesis of 7[WCA]$_2$



Scheme S 9. Synthesis of **7[WCA]$_2$**.

A suspension of 2,3,5,6-tetrafluorobenzene-1,4-diole (0.055 g, 0.302 mmol, 1.0 eq) in CH_2Cl_2 (6.5 ml) was added dropwise to the stirred solution of **1[WCA]** (0.812 g, 0.603 mmol, 2.0 eq) in CH_2Cl_2 (1.5 ml) at -40 °C. The reaction mixture was kept at -40 °C for 10 minutes, afterwards the suspension was allowed to warm up to room temperature and stirred for 45 minutes. ^{11}B and $^{31}P\{^1H\}$ of the colourless reaction mixture revealed a quantitative conversion of **1[WCA]** into **7[WCA]$_2$**. The solvent and all volatiles were removed under reduced pressure. Product **7[WCA]$_2$** was obtained as a white powder. Yield: 92.7% (0.724 g, 0.280 mmol).

Colourless crystals of **7[WCA]$_2$** suitable for an X-ray diffraction analysis were obtained by storing the CH_2Cl_2 solution at +4 °C. Subsequently keeping mother liquor at -22 °C afforded a second crop of **7[WCA]$_2$**. Yield: 25% (0.195 g, 0.075 mmol).

Elemental analysis calc. for $C_{64}H_{52}B_2F_{76}N_6O_{10}Al_2$ (2584.59 g/mol): C, 29.74; H, 2.03; N, 3.25. Found: C, 29.71; H, 2.17; N, 3.20.

NMR data for 7[WCA]$_2$

^{11}B NMR (CD_2Cl_2): δ 25.2 (s).

^1H NMR (CD_2Cl_2): δ 3.63 (12H, s, N-C**H**$_3$ of IMe$_4$); 3.55 (2H, sept, $^3J_{HH}$ = 6.9 Hz, C**H**(CH$_3$)$_2$); 2.92 (2H, sept, $^3J_{HH}$ = 7.0 Hz, C**H**(CH$_3$)$_2$); 2.22 (12H, s, C**H**$_3$ of IMe$_4$); 1.47 (12H, d, $^3J_{HH}$ = 6.9 Hz, CH(C**H**$_3$)$_2$); 1.21 (12H, d, $^3J_{HH}$ = 7.0 Hz, CH(C**H**$_3$)$_2$).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.5 (dm, $^1J_{CF}$ = 253.0 Hz, **C**-F of fluorinated linker); 129.6 (s, **C**=**C** of IMe$_4$); 128.0 (m, *ipso*-**C** of fluorinated linker); 121.0 (q, $^1J_{CF}$ = 297.1 Hz, OC(**C**F$_3$) of [Al(OC(CF$_3$)$_3$)$_4$]$^-$); 53.7 (s, **C**H(CH$_3$)$_2$ overlapped with solvent); 53.1 (s, **C**H(CH$_3$)$_2$, overlapped with solvent); 33.7 (s, N-**C**H$_3$ of IMe$_4$); 22.7 (s, CH(**C**H$_3$)$_2$); 21.3 (s, CH(**C**H$_3$)$_2$); 8.2 (s, C=C-**C**H$_3$ of IMe$_4$).

The carbene carbon atom was not detected at the $^{13}C\{^{1}H\}$ spectrum; however, a chemical shift of the carbene carbon atom was identified at 142.5 ppm based on the ^{13}C ^{1}H HMBC spectrum (a coupling of N-C**H**$_3$ of IMe$_4$ protons with carbene carbon atom).

^{27}Al NMR (CD_2Cl_2): δ 34.6 (s, [**Al**$(OC(CF_3)_3)_4]^-$).

^{19}F NMR (CD_2Cl_2): δ -75.8(s, 72F, [*Al*$(OC(C\mathbf{F}_3)_3)_4]^-$); -157.2 (s, 4F).

NMR spectra

NMR spectra for 1[Br]

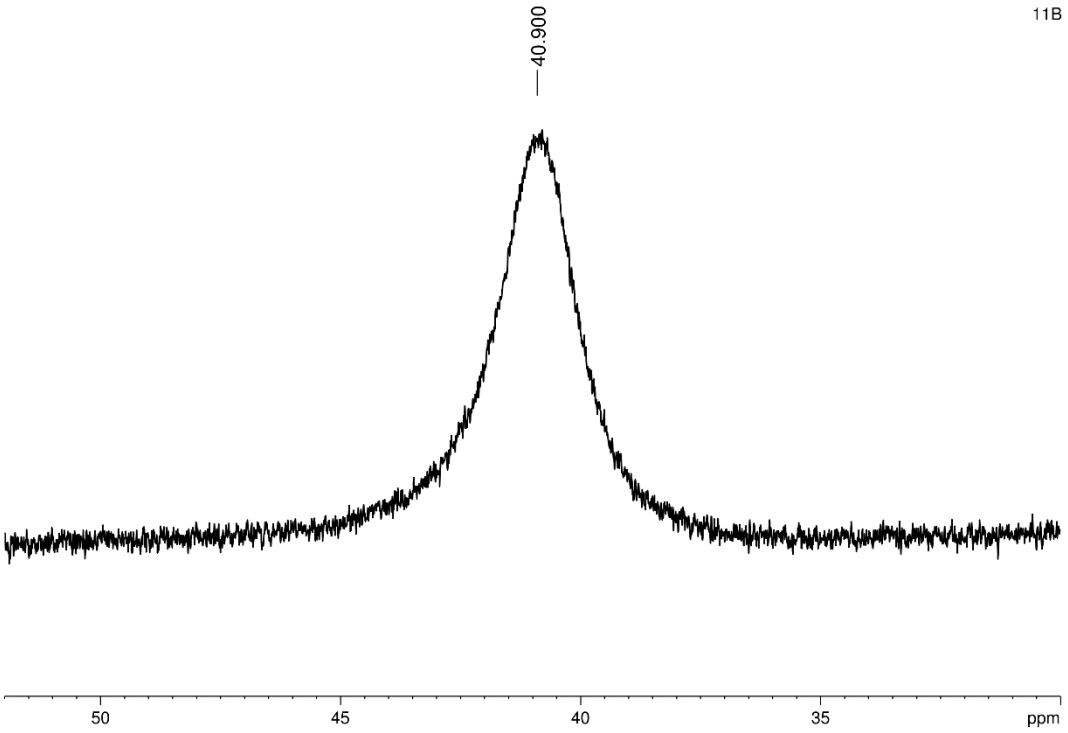


Figure S 1. ^{11}B spectrum of **1[Br]** (CD_2Cl_2)

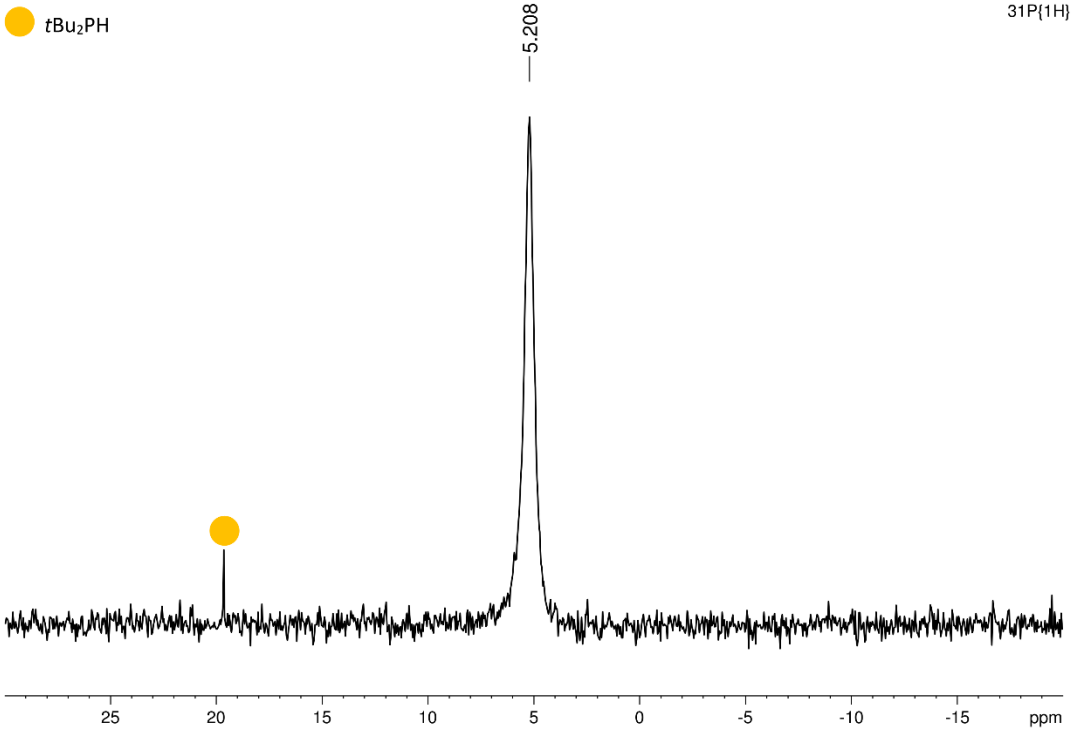


Figure S 2. $^{31}P\{^{1}H\}$ spectrum of **1[Br]** (CD_2Cl_2)

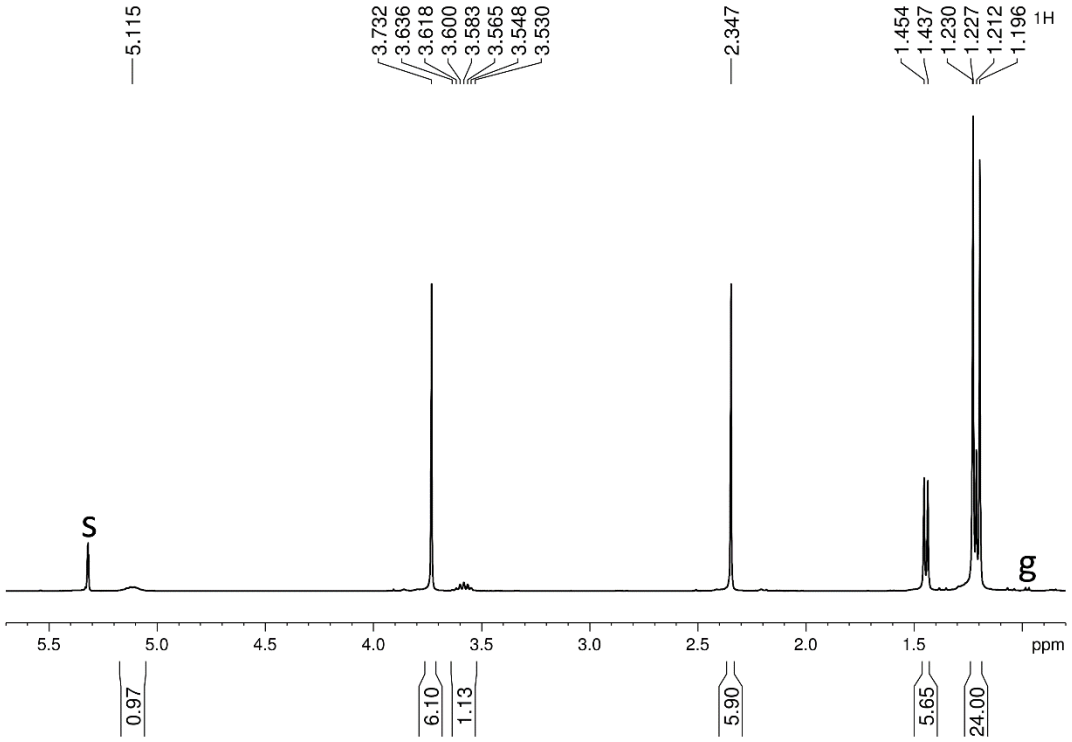


Figure S 3. ^{1}H spectrum of **1[Br]** (CD_2Cl_2)

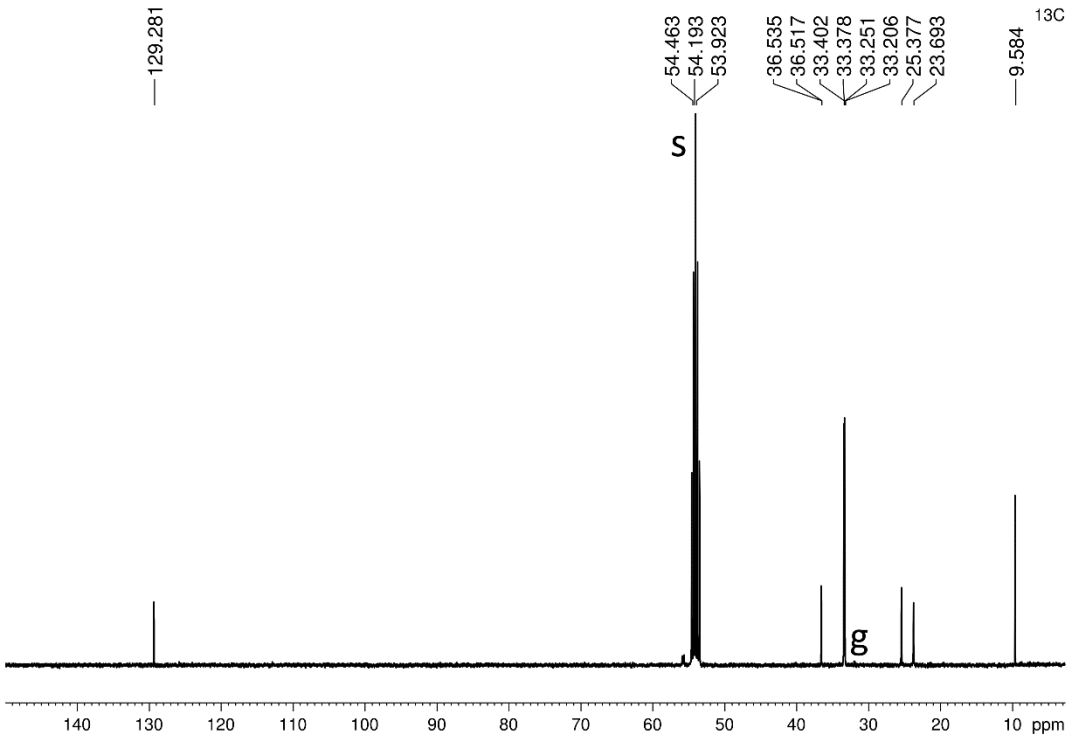


Figure S 4. $^{13}C\{^{1}H\}$ spectrum of **1[Br]** (CD_2Cl_2)

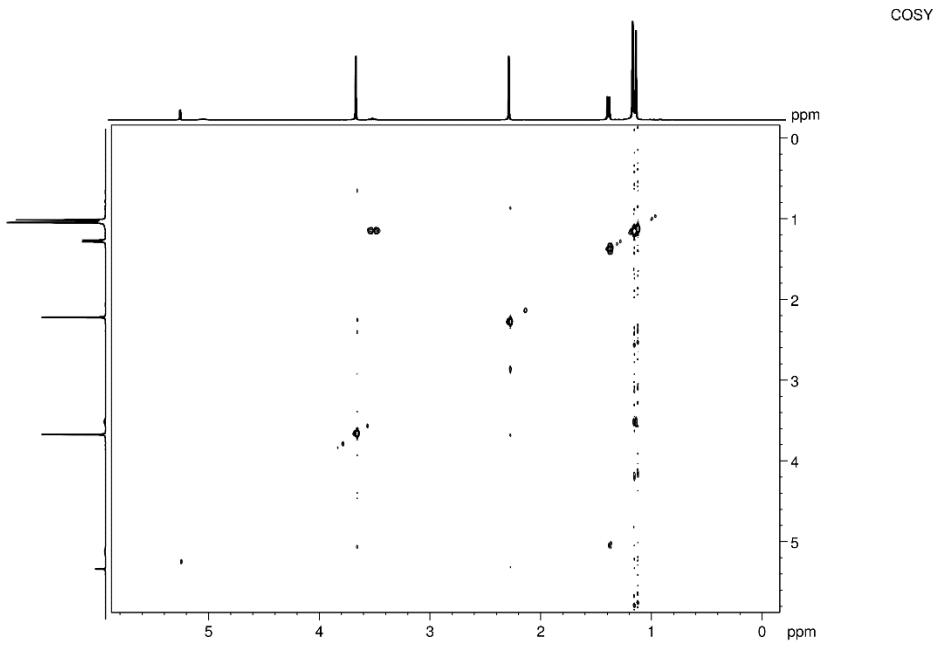


Figure S 5. COSY spectrum of **1[Br]** (CD_2Cl_2)

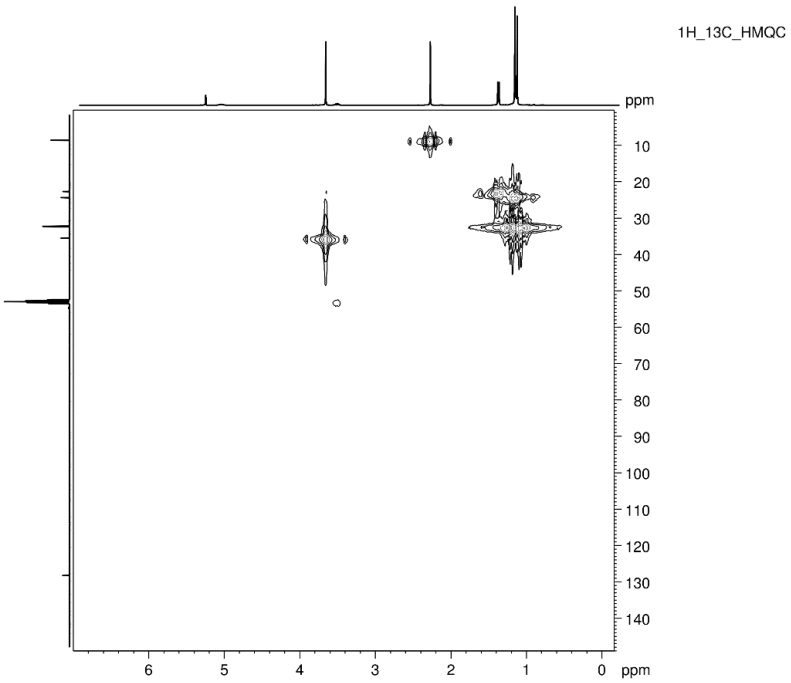


Figure S 6. ^{13}C ^{1}H HMQC spectrum of **1[Br]** (CD_2Cl_2)

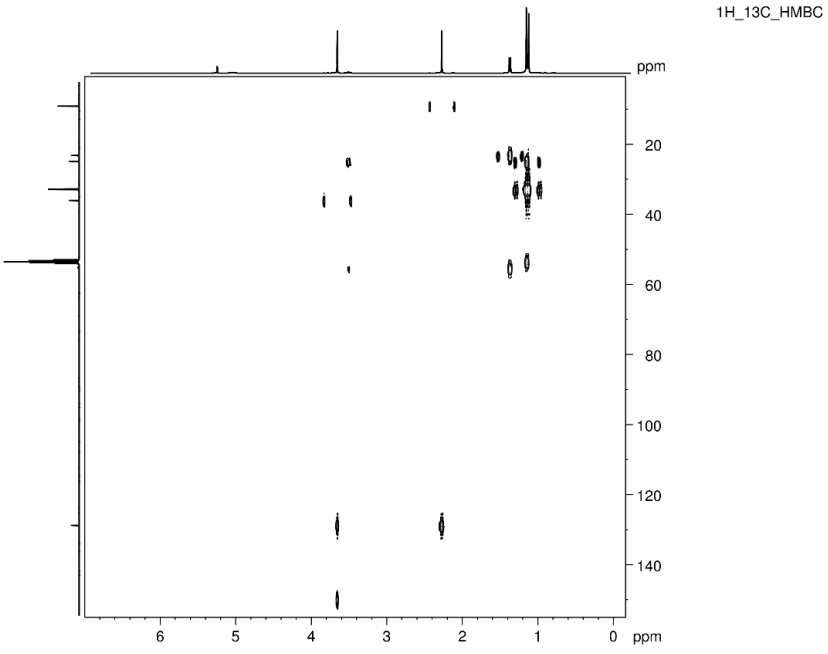


Figure S 7. ^{13}C ^{1}H HMBC spectrum of **1[Br]** (CD_2Cl_2)

NMR spectra for 1[WCA]

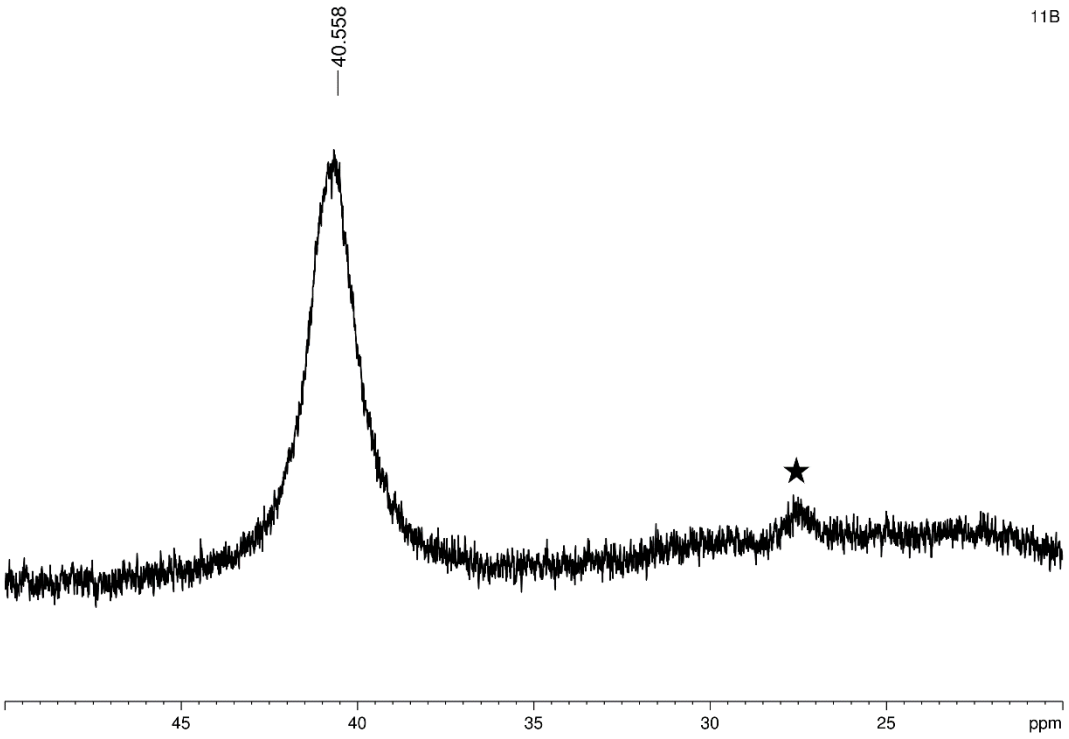


Figure S 8. ^{11}B spectrum of **1[WCA]** (CD_2Cl_2)

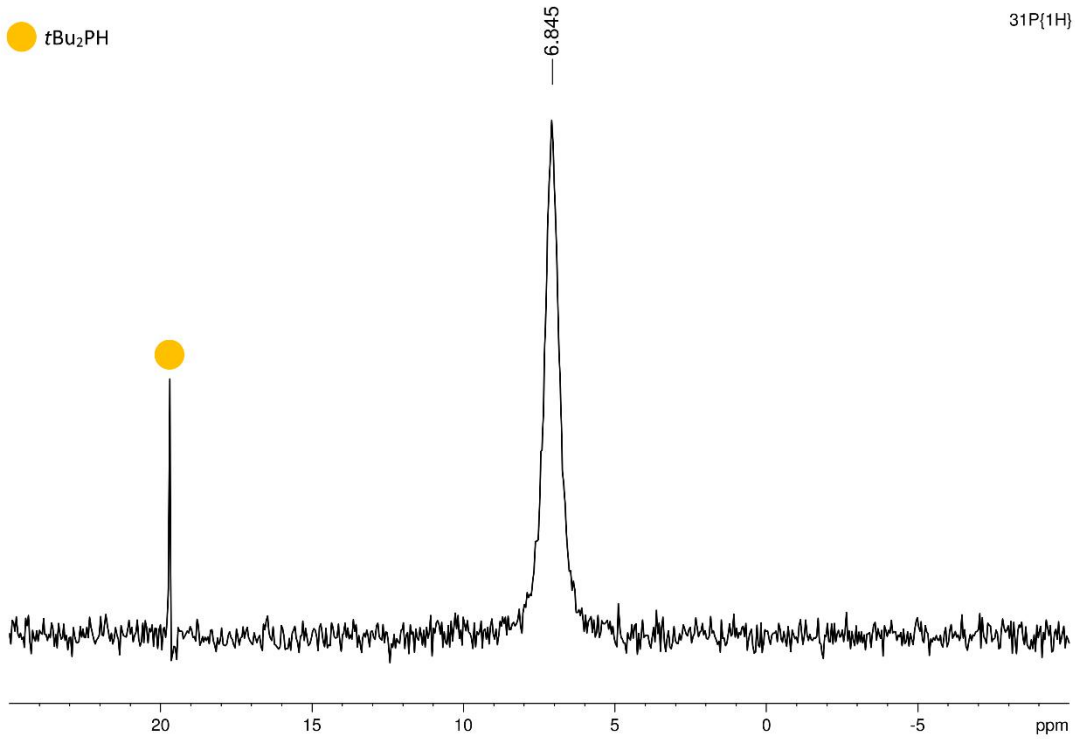


Figure S 9. $^{31}P\{^1H\}$ spectrum of **1[WCA]** (CD_2Cl_2)

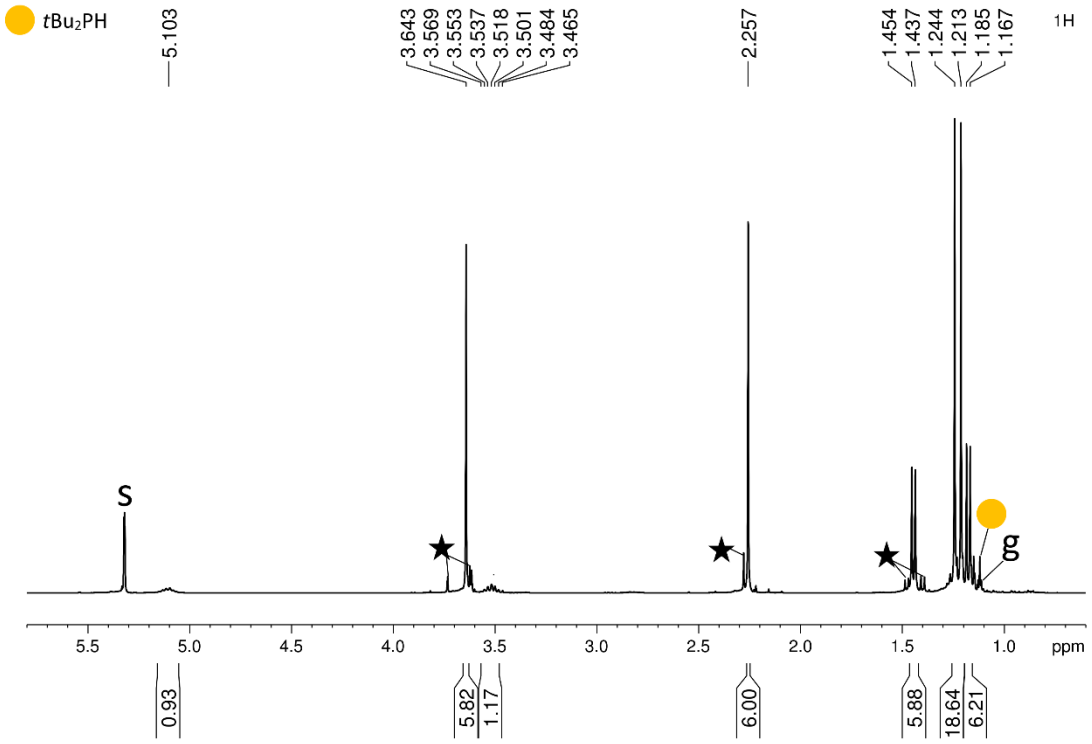


Figure S 10. ^{1}H spectrum of **1[WCA]** (CD_2Cl_2)

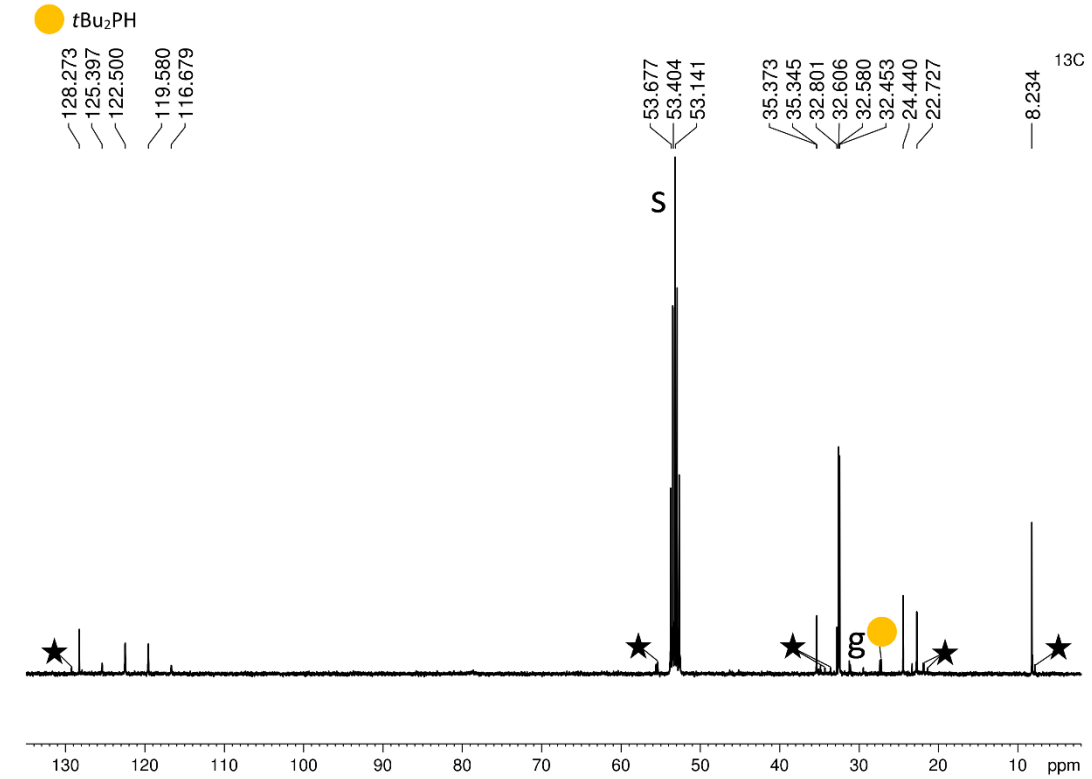


Figure S 11. $^{13}C\{^{1}H\}$ spectrum of **1[WCA]** (CD_2Cl_2)

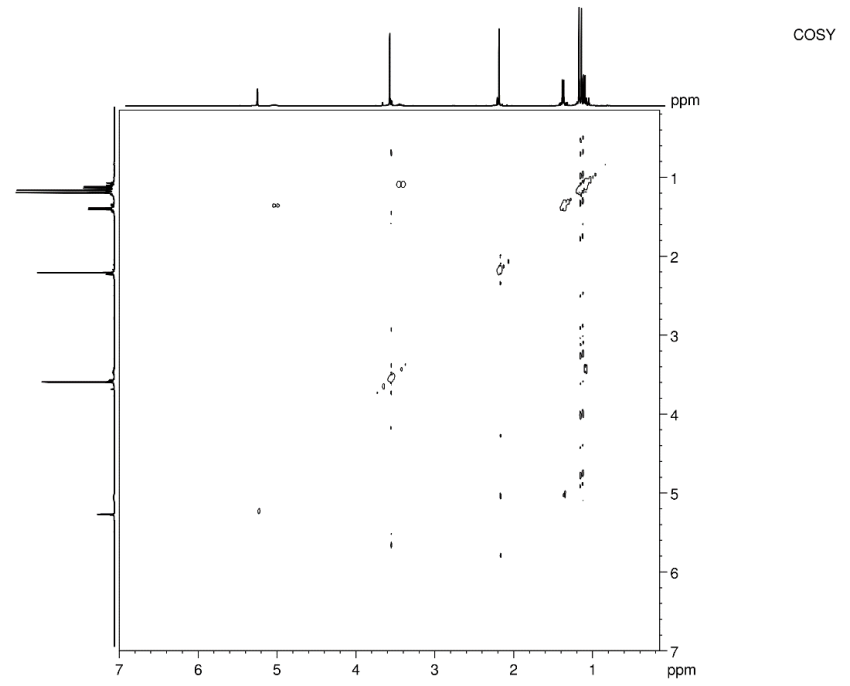


Figure S 12. COSY spectrum of **1[WCA]** (CD_2Cl_2)

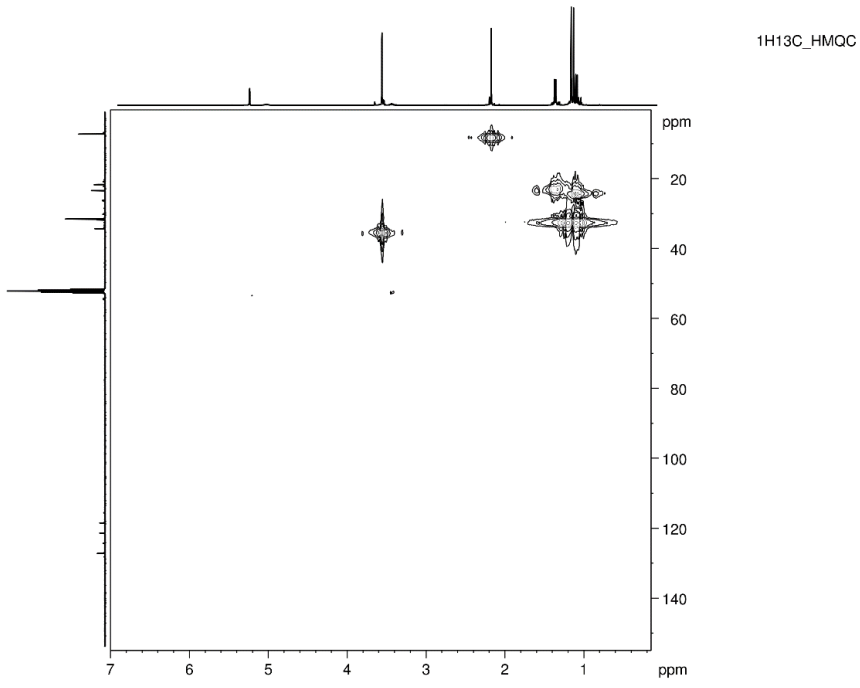


Figure S 13. ^{13}C ^{1}H HMQC spectrum of **1[WCA]** (CD_2Cl_2)

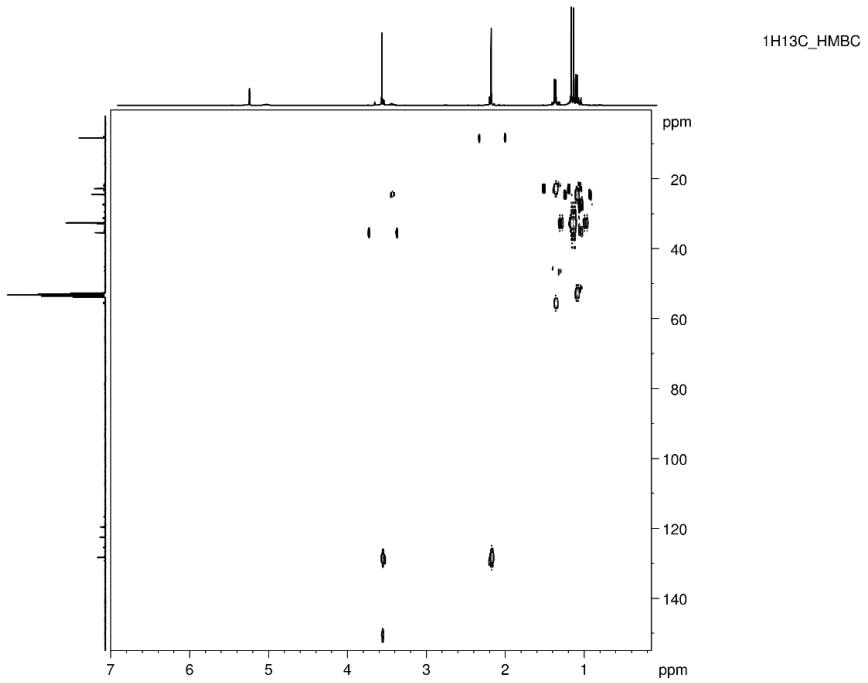


Figure S 14. ^{13}C ^{1}H HMBC spectrum of **1[WCA]** (CD_2Cl_2)

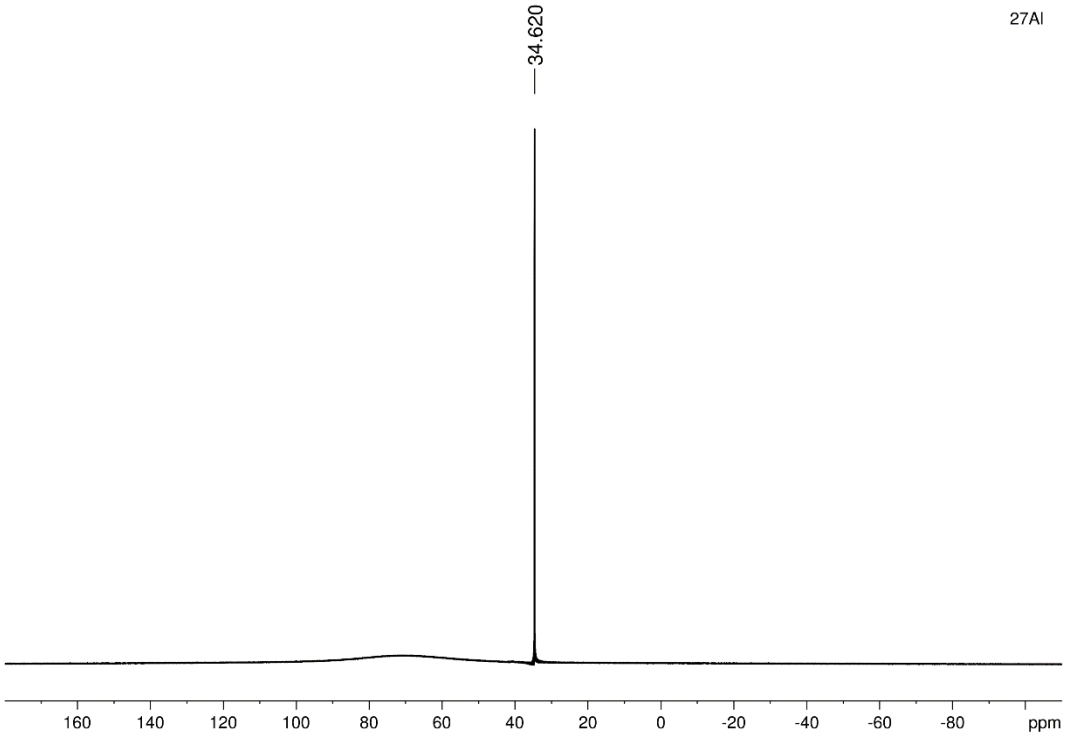


Figure S 15. ^{27}Al spectrum of **1[WCA]** (CD_2Cl_2)

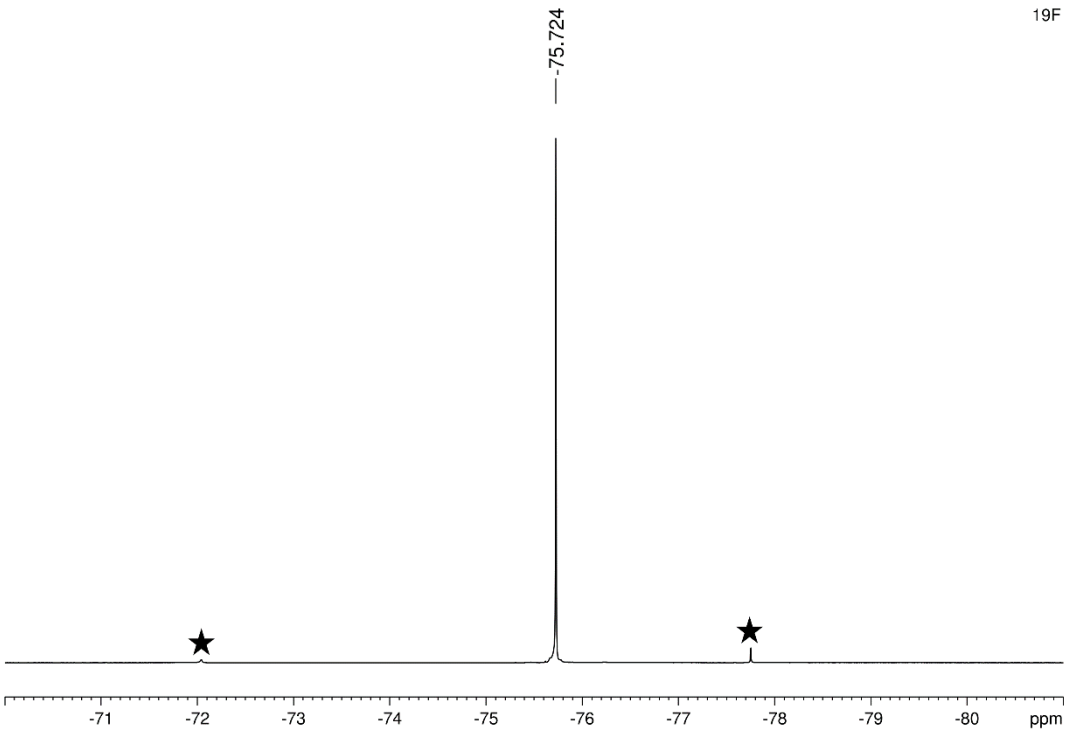


Figure S 16. ^{19}F spectrum of **1[WCA]** (CD_2Cl_2)

NMR spectra for 2[Br]

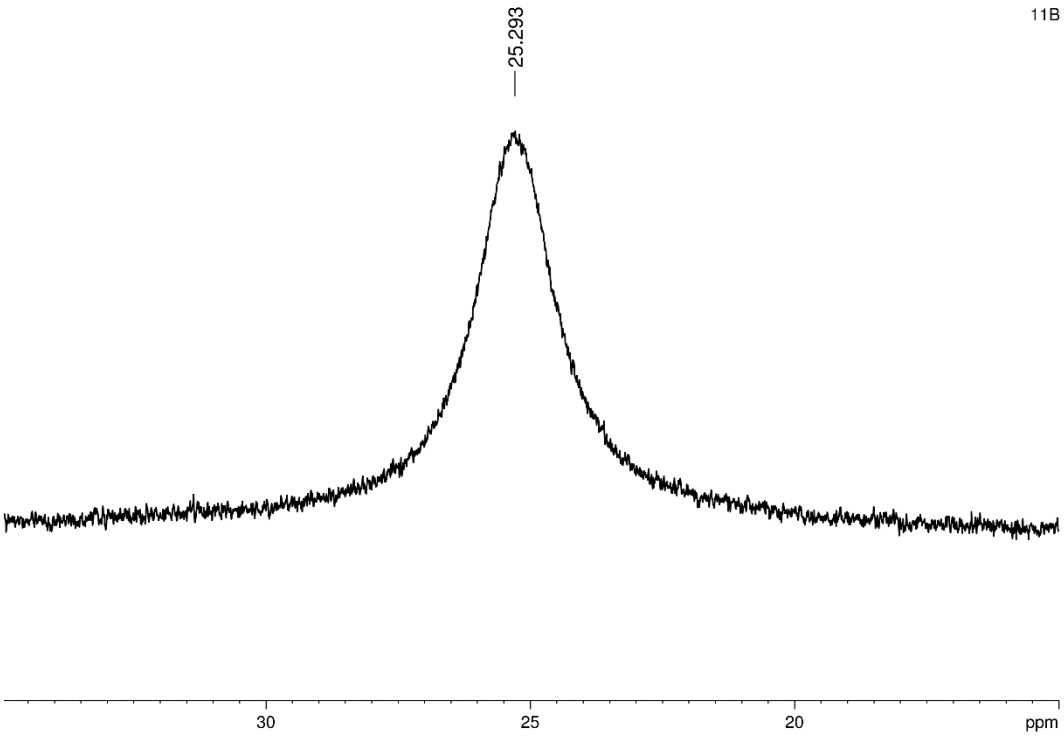


Figure S 17. ^{11}B spectrum of reaction mixture for **2[Br]** (CD_2Cl_2)

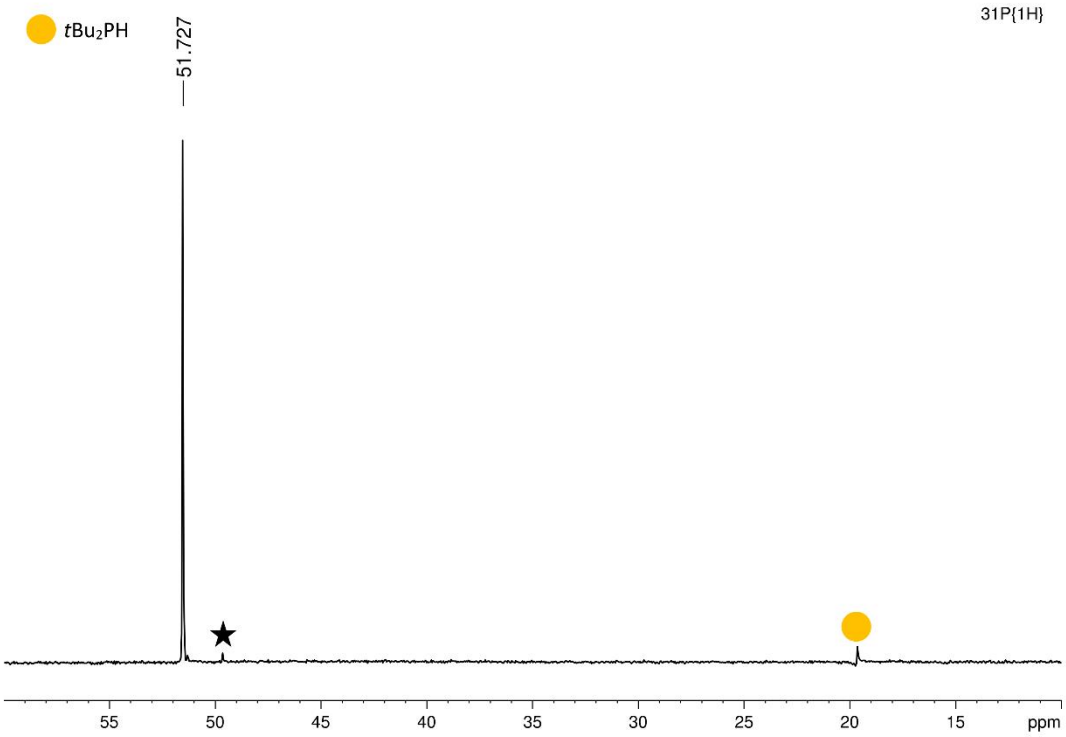


Figure S 18. $^{31}P\{^1H\}$ spectrum of reaction mixture for **2[Br]** (CD_2Cl_2)

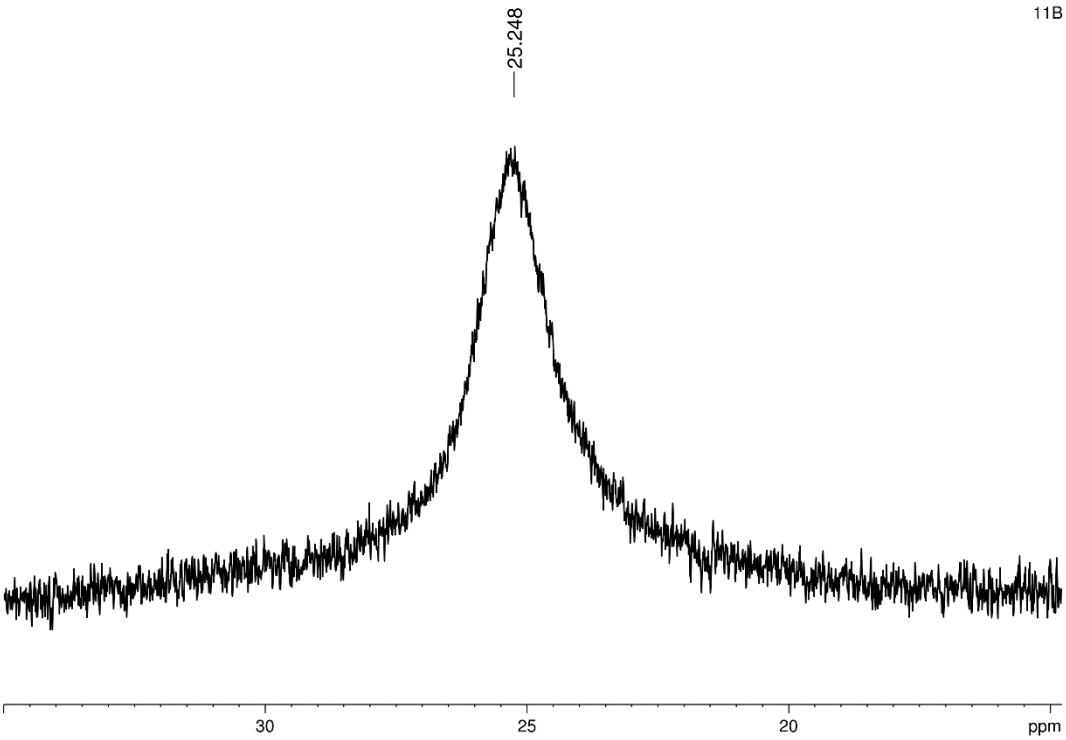


Figure S 19. ^{11}B spectrum of **2[Br]** (CD_2Cl_2)

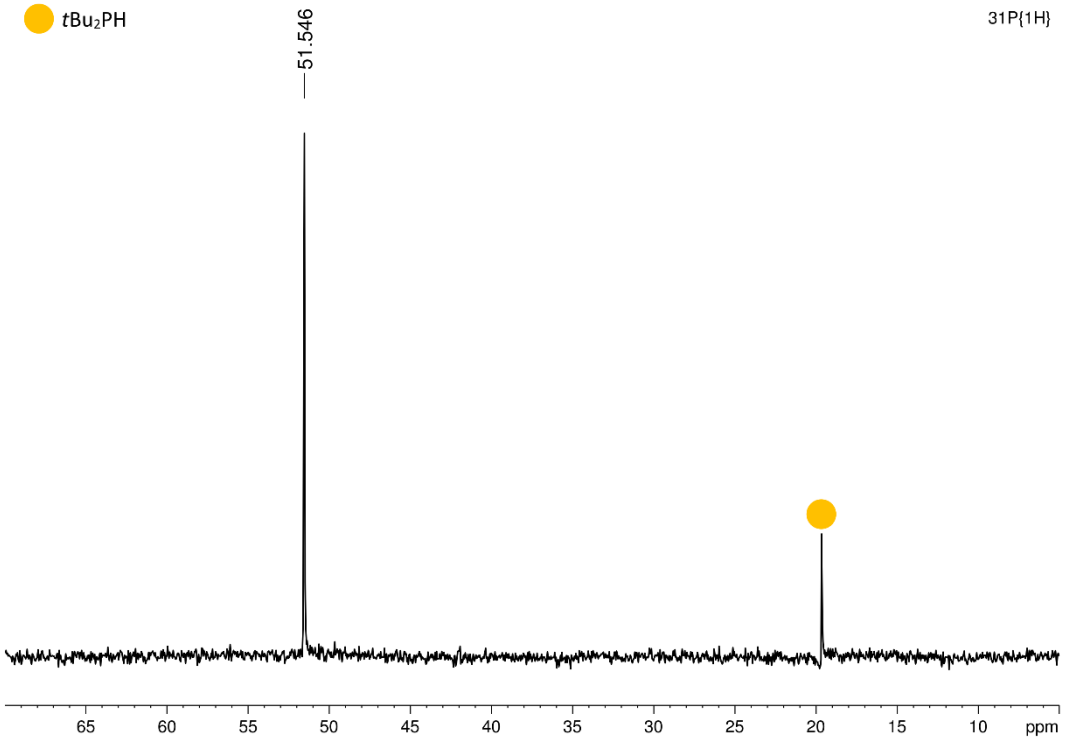


Figure S 20. $^{31}P\{^1H\}$ spectrum of **2[Br]** (CD_2Cl_2)

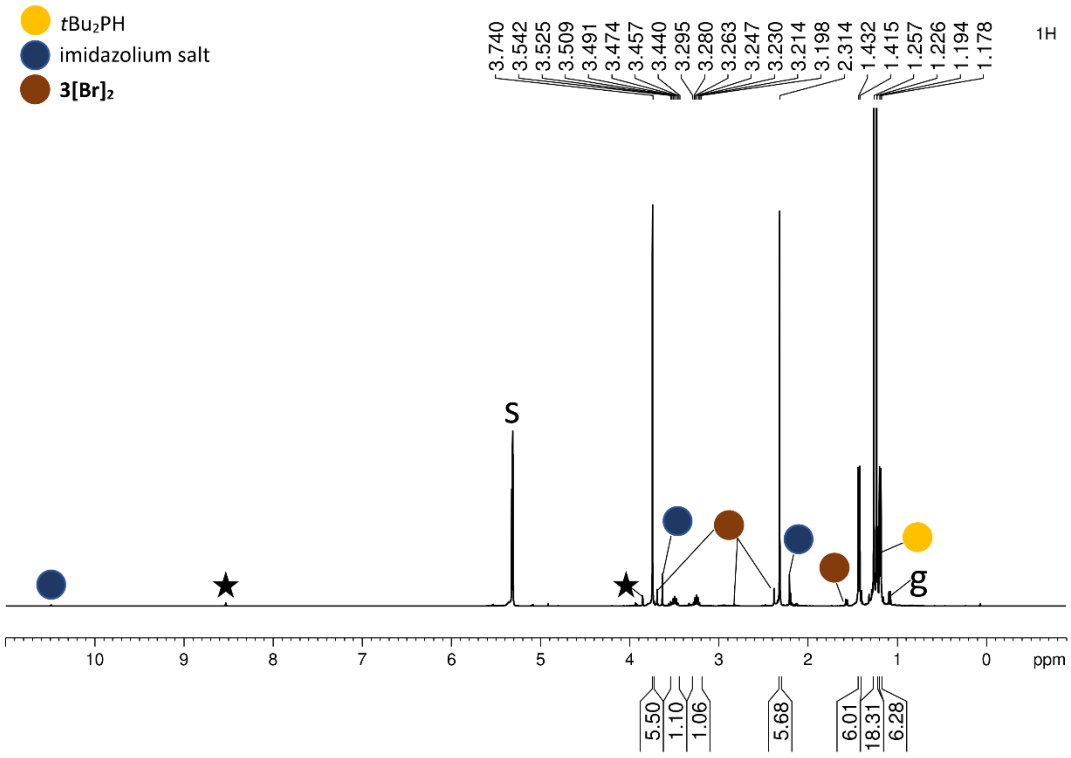


Figure S 21. ^{1}H spectrum of **2[Br]** (CD_2Cl_2)

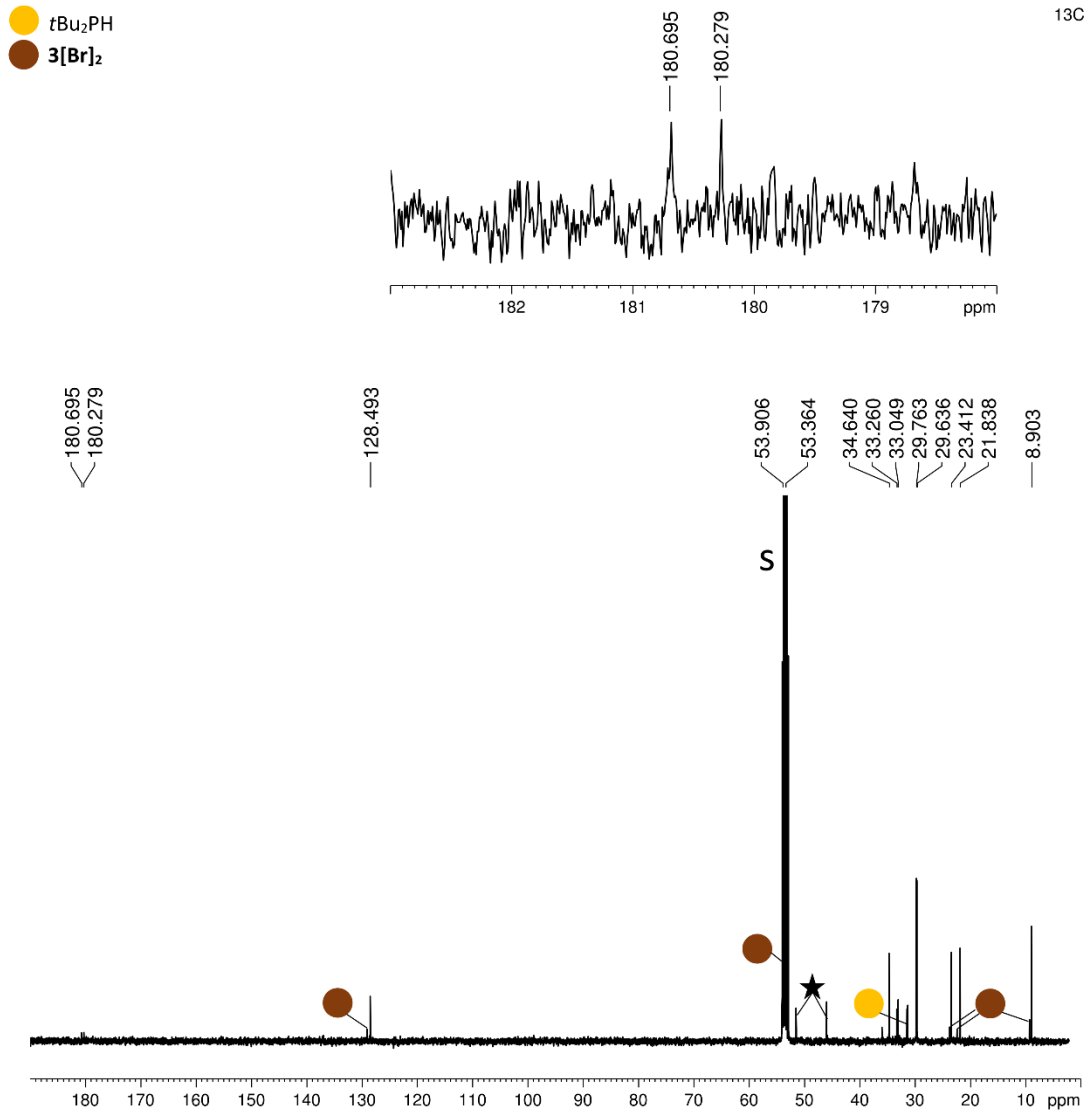


Figure S 22. $^{13}C\{^{1}H\}$ spectrum of **2[Br]** (CD_2Cl_2)

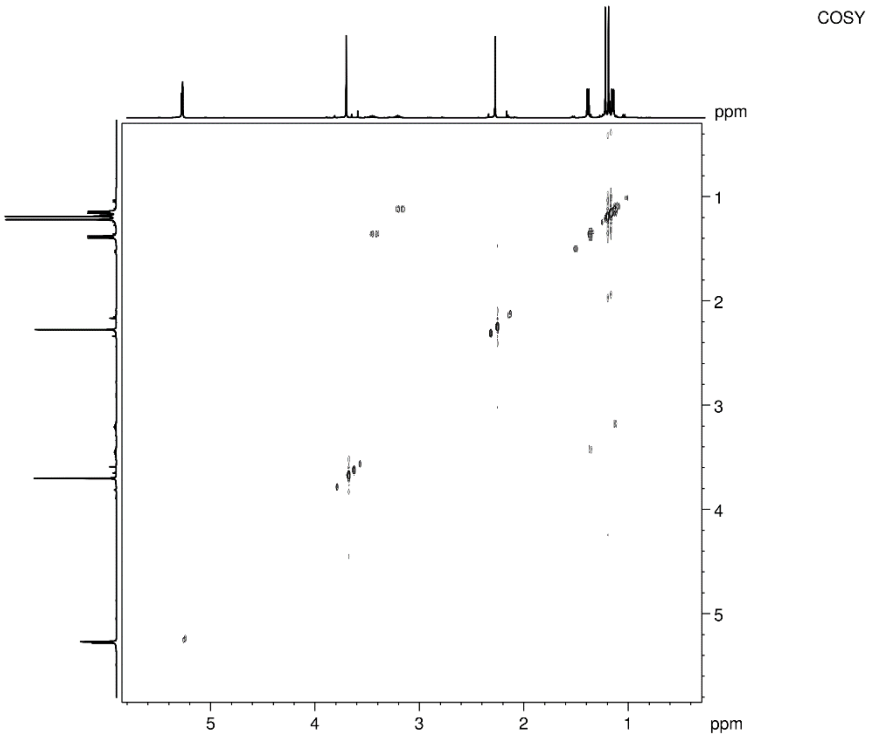


Figure S 23. COSY spectrum of **2[Br]** (CD_2Cl_2)

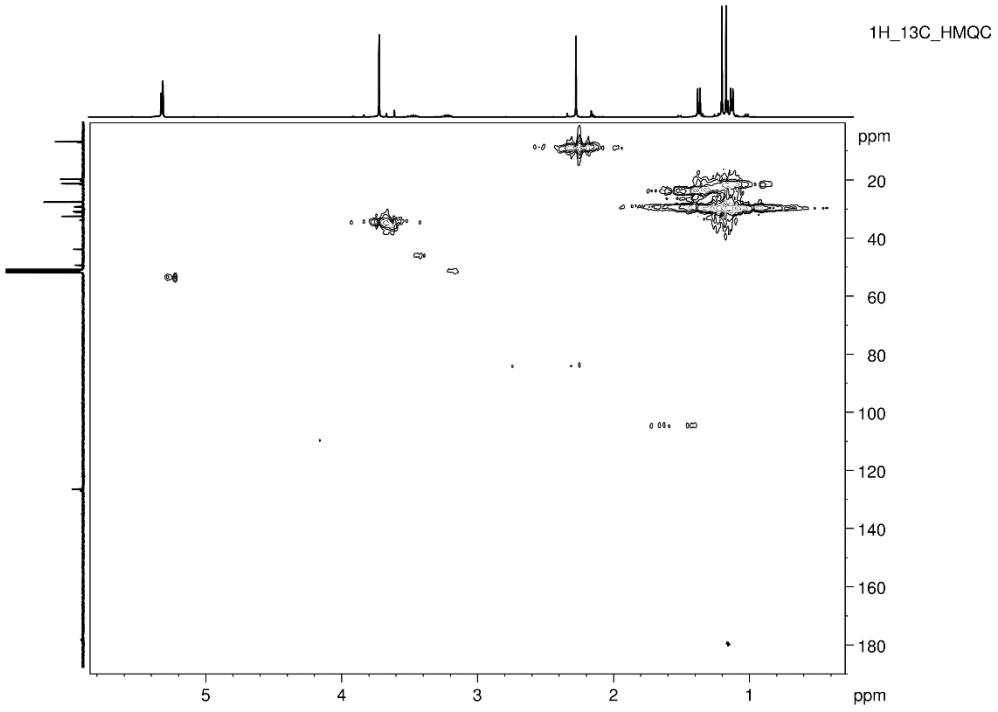


Figure S 24. ^{13}C ^{1}H HMQC spectrum of **2[Br]** (CD_2Cl_2)

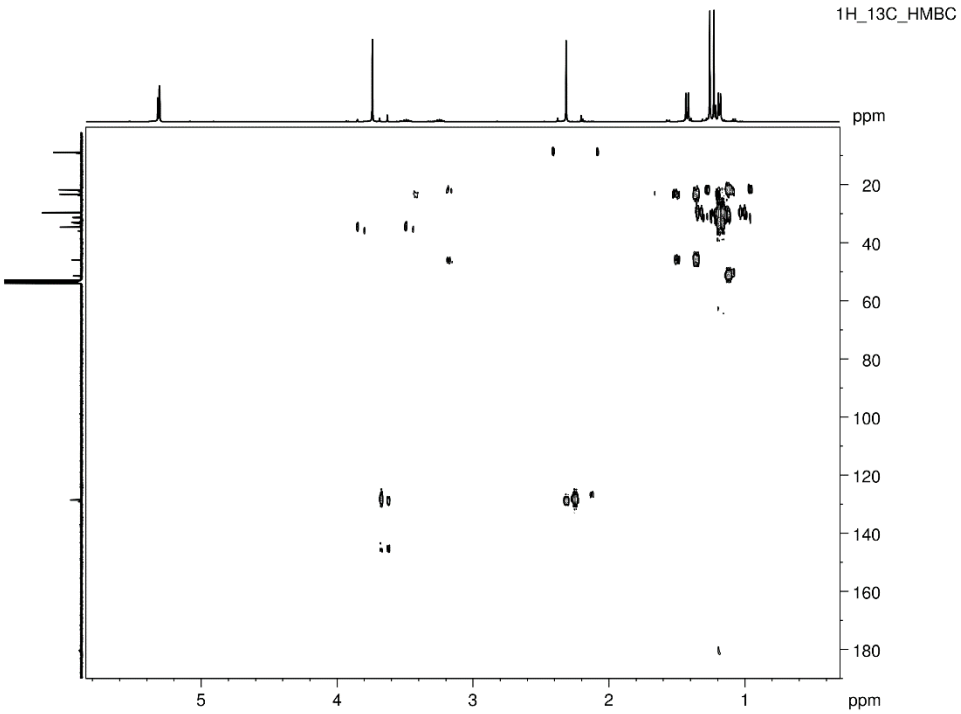


Figure S 25. ^{13}C ^{1}H HMBC spectrum of **2[Br]** (CD_2Cl_2)

NMR spectra of hydrolysis of 2[Br] (formation of $3[Br]_2$)

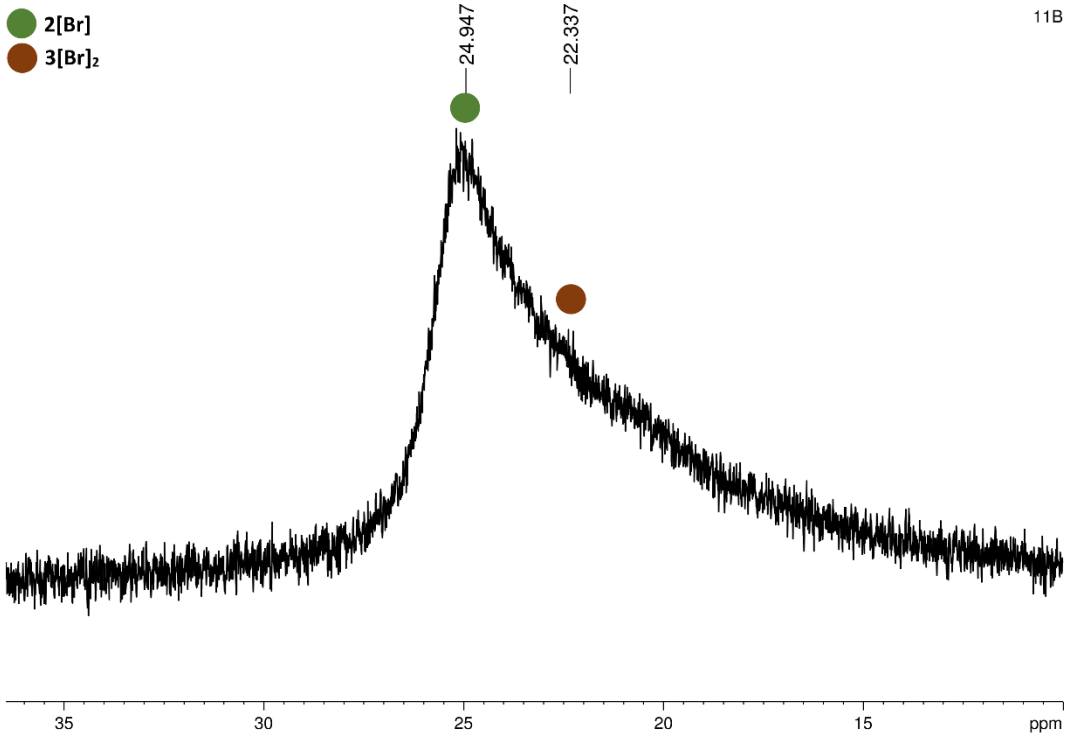


Figure S 26. ^{11}B spectrum after overnight hydrolysis of **2[Br]** (formation of **3[Br]₂**) (CD_2Cl_2)

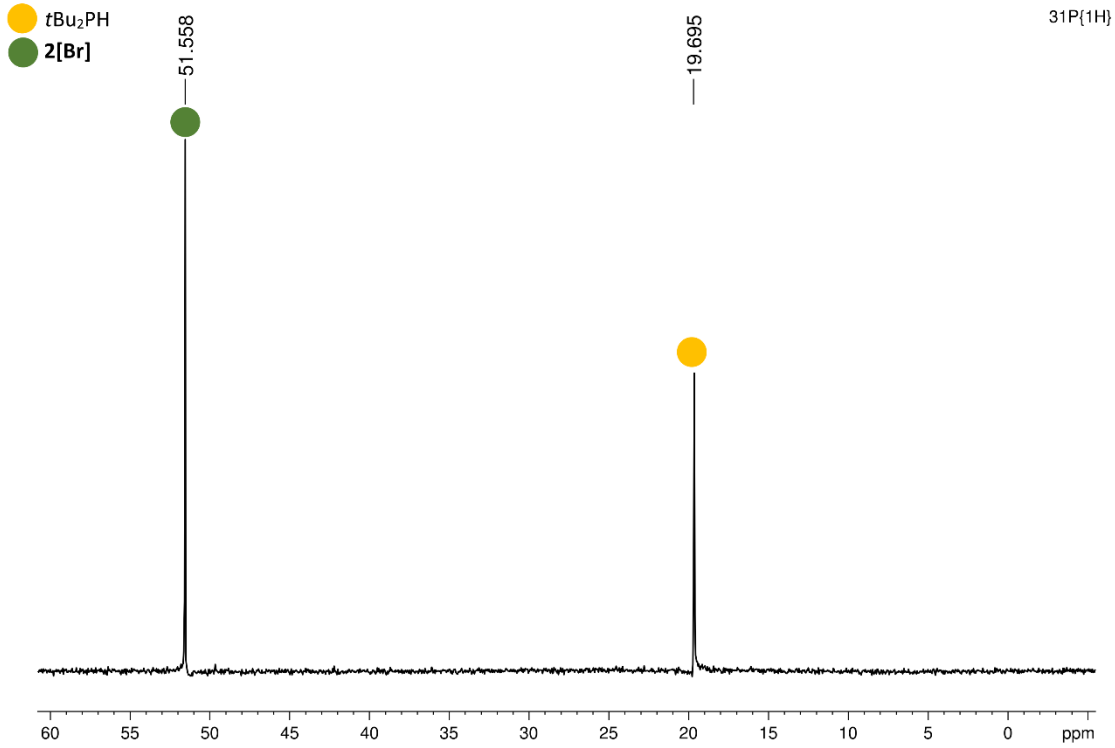


Figure S 27. $^{31}P\{^1H\}$ spectrum after overnight hydrolysis of **2[Br]** (formation of **3[Br]₂**) (CD_2Cl_2)

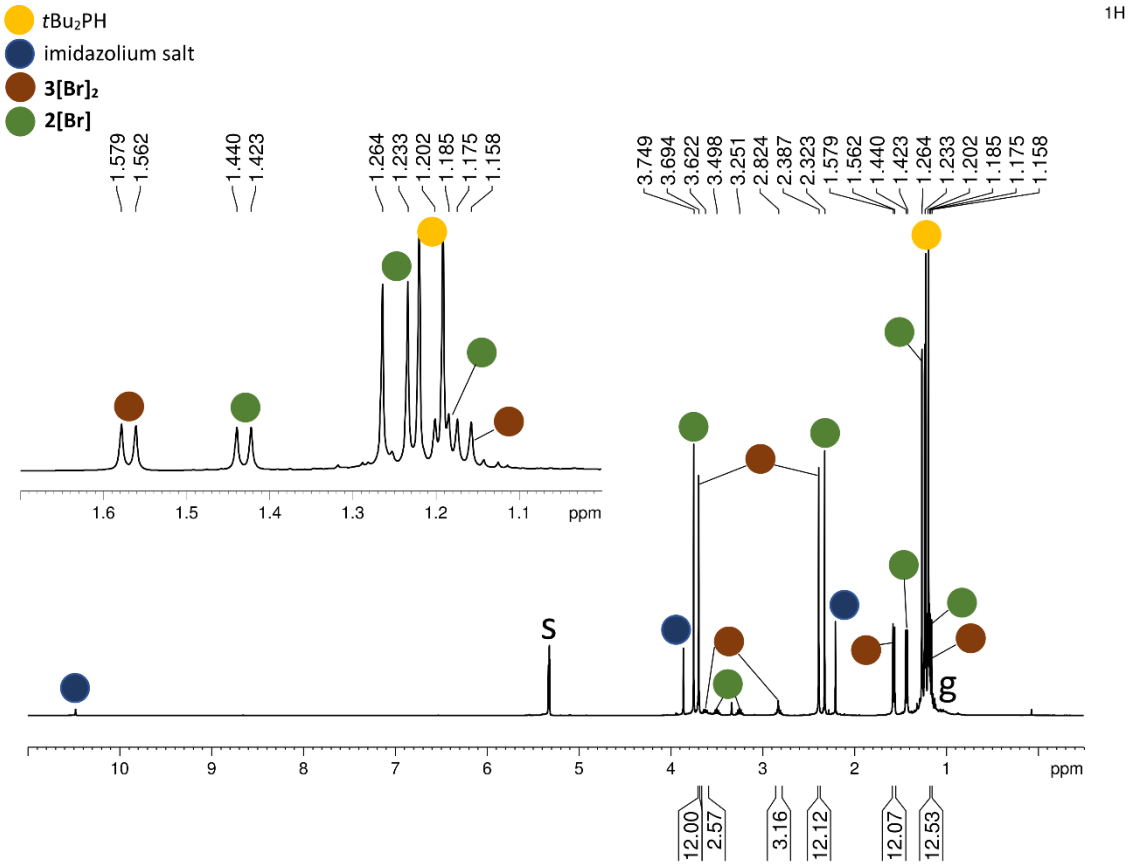


Figure S 28. ^{1}H spectrum after overnight hydrolysis of **2[Br]** (formation of **3[Br]$_2$**) (CD_2Cl_2)

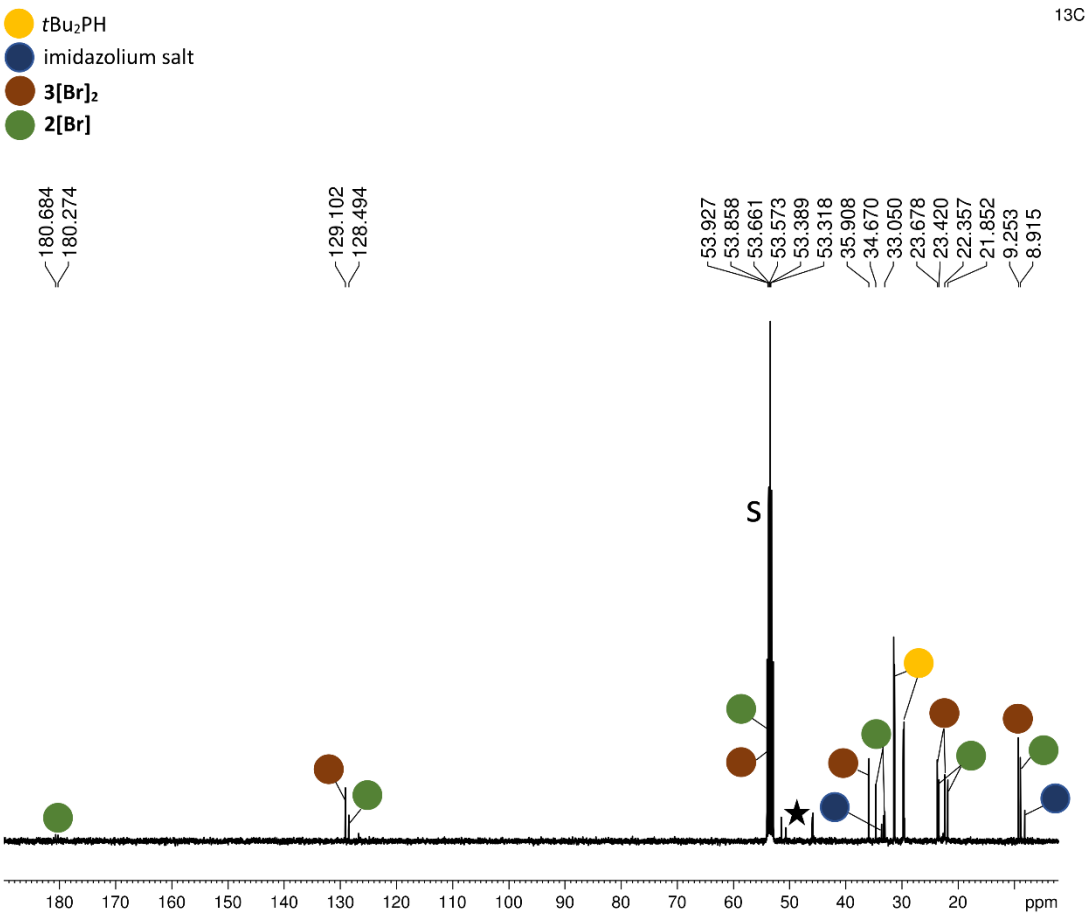


Figure S 29. $^{13}C\{^{1}H\}$ spectrum after overnight hydrolysis of **2[Br]** (formation of **3[Br]₂**) (CD_2Cl_2)

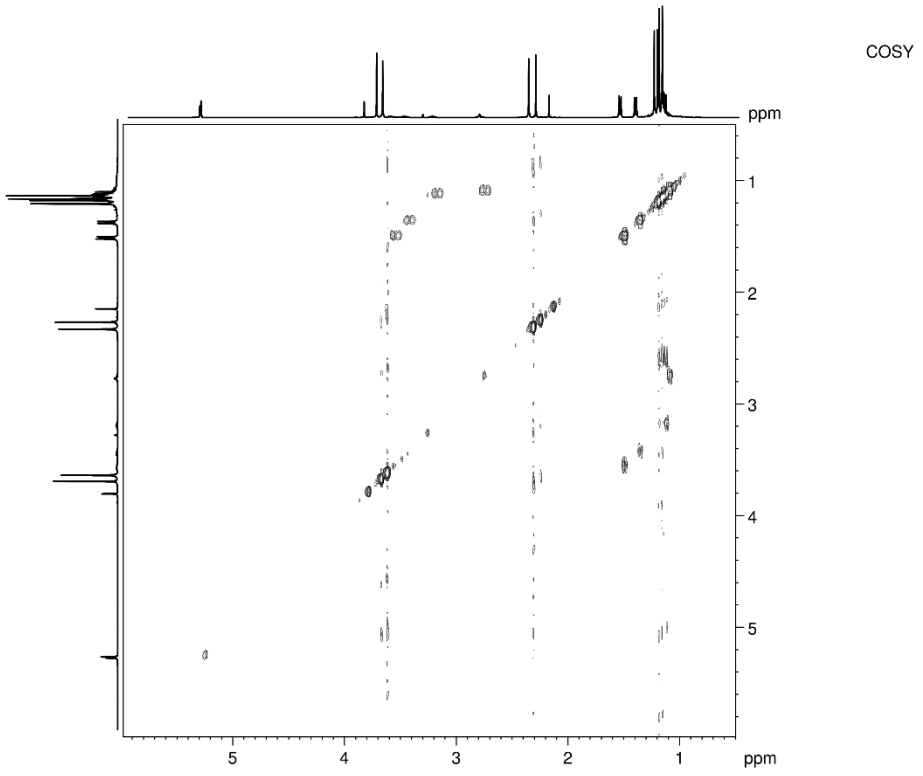


Figure S 30. COSY spectrum after overnight hydrolysis of **2[Br]** (formation of **3[Br]$_2$**) (CD_2Cl_2)

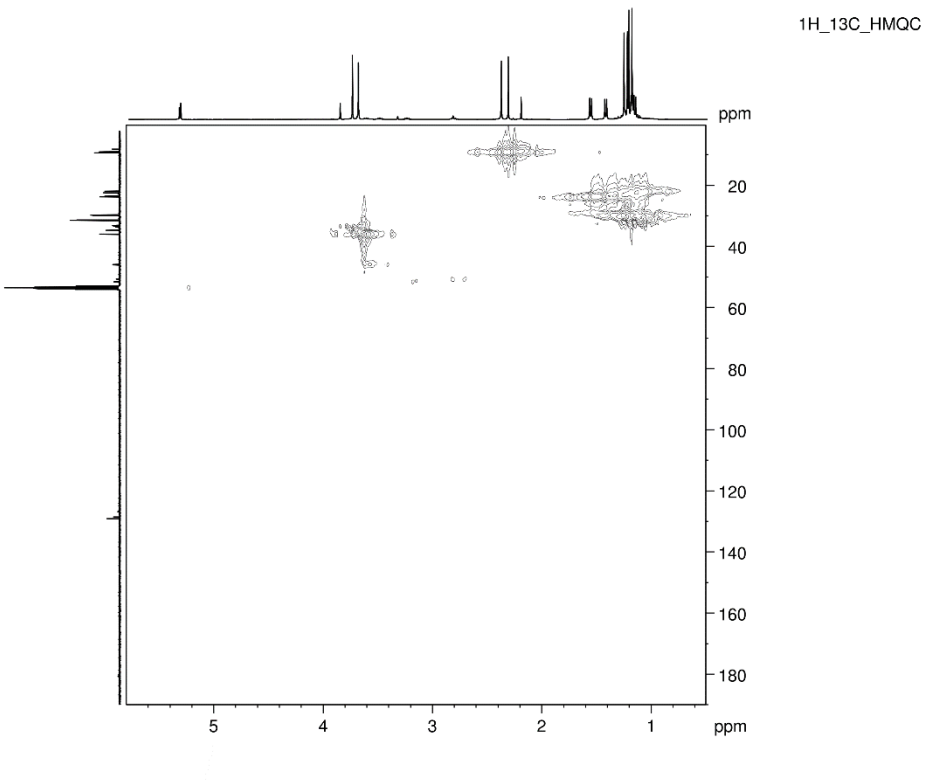


Figure S 31. ^{13}C ^{1}H HMQC spectrum after overnight hydrolysis of **2[Br]** (formation of **3[Br]$_2$**) (CD_2Cl_2)

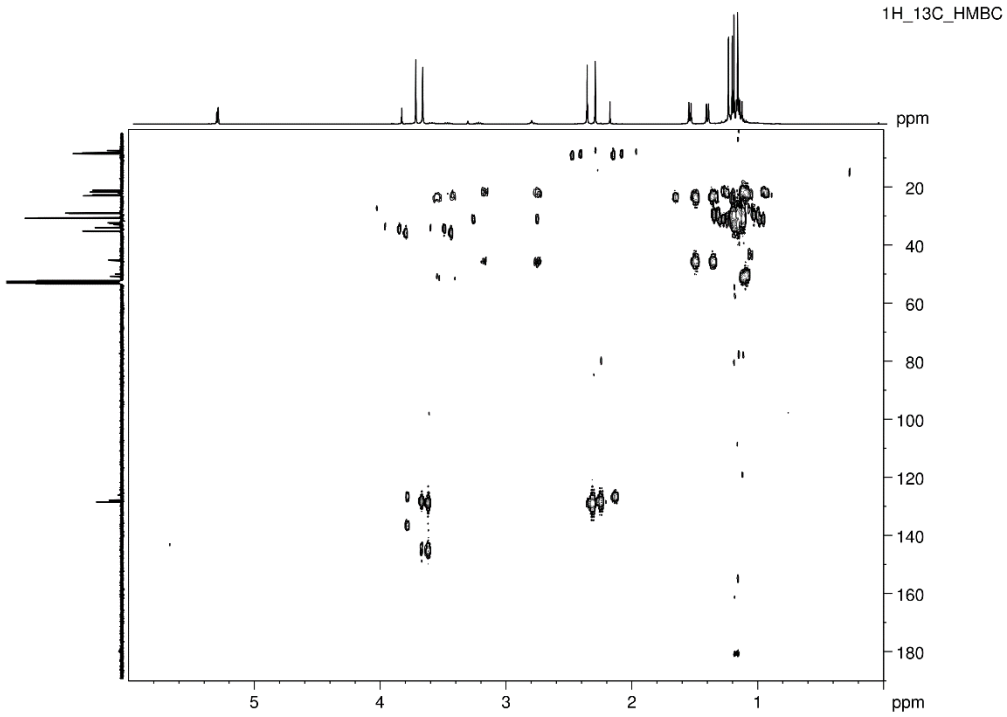


Figure S 32. ^{13}C ^{1}H HMBC after overnight hydrolysis of **2[Br]** (formation of **3[Br]$_2$**) (CD_2Cl_2)

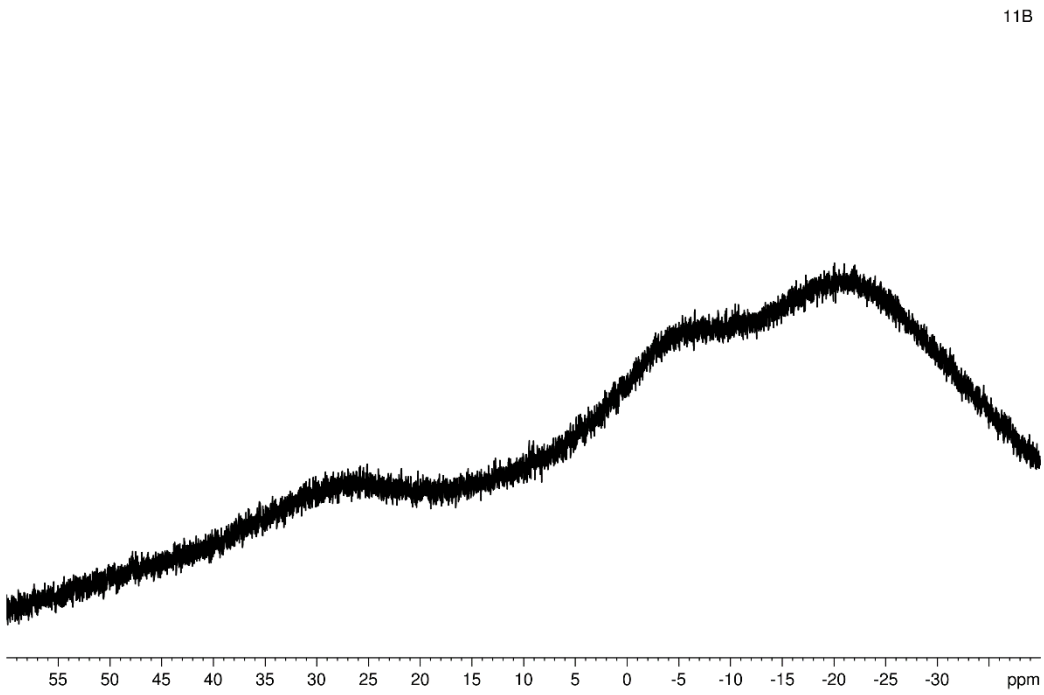


Figure S 33. ^{11}B spectrum after 7 days hydrolysis of **2[Br]** (CD_2Cl_2)

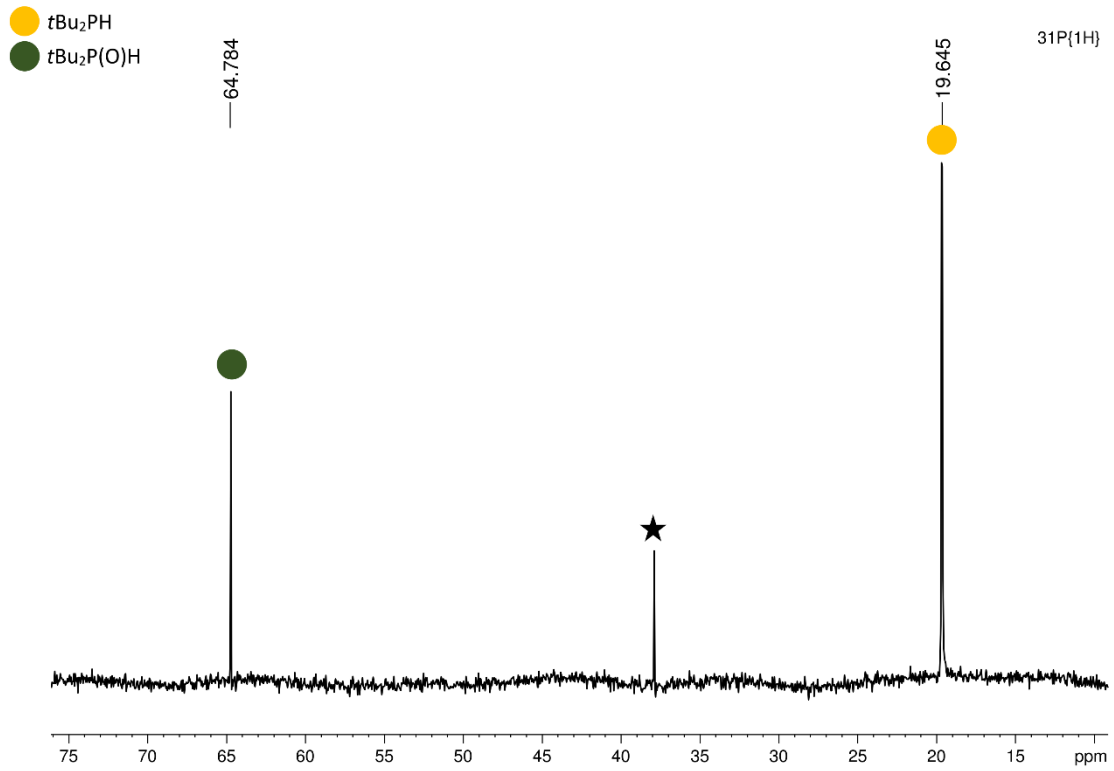


Figure S 34. $^{31}P\{^{1}H\}$ spectrum after 7 days hydrolysis of **2[Br]** (CD_2Cl_2)

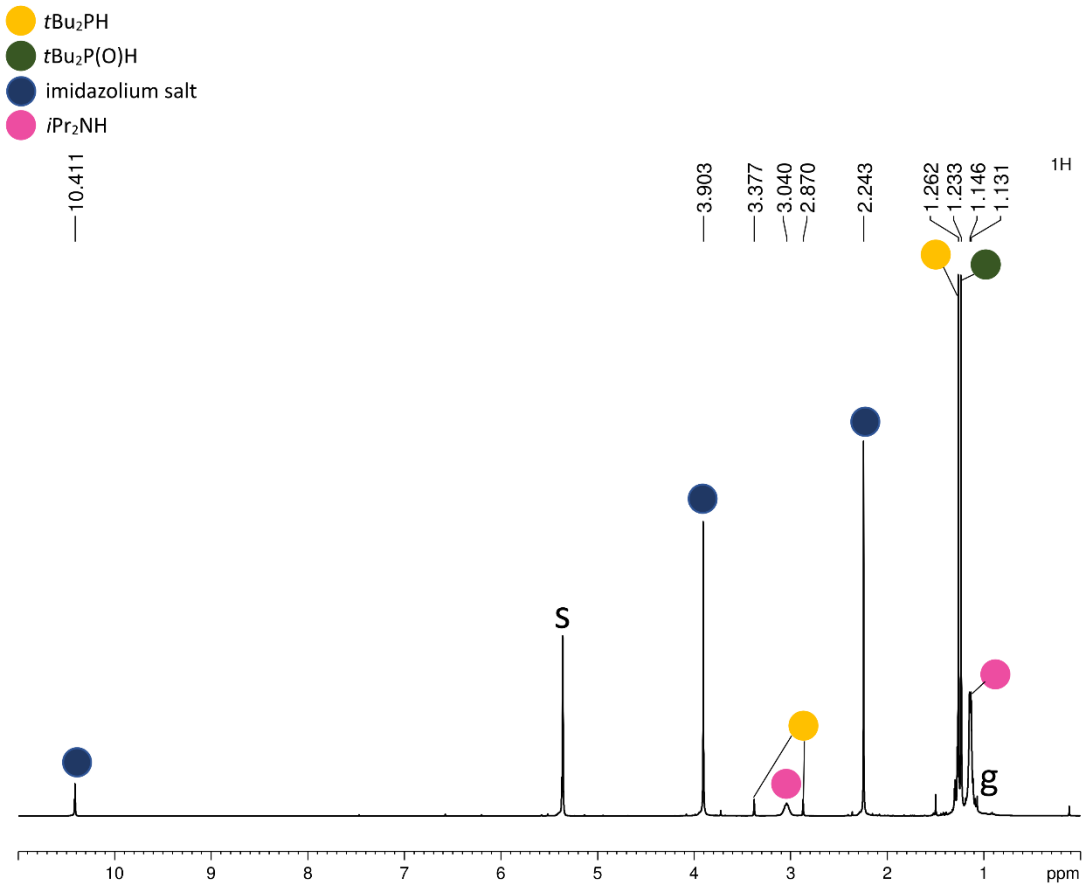


Figure S 35. ^{1}H spectrum after 7 days hydrolysis of **2[Br]** (CD_2Cl_2)

NMR spectra for reaction mixture 1[Br] + N_2O

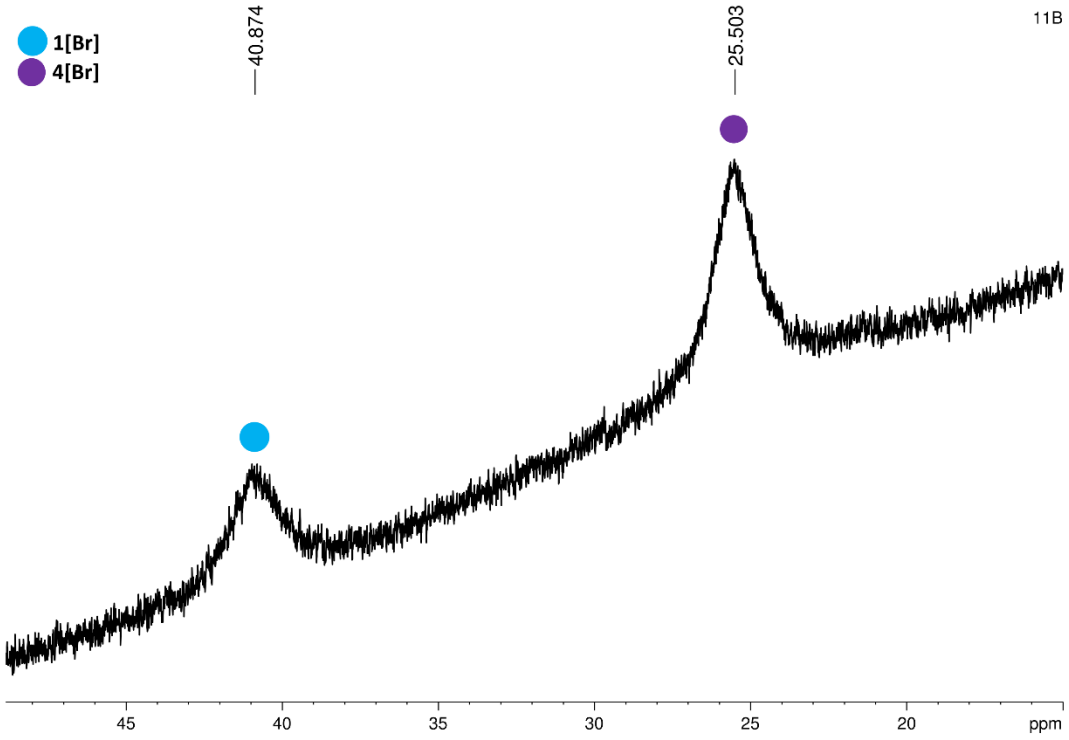


Figure S 36. ^{11}B spectrum of reaction mixture **1[Br] + N_2O** after 7 days at 50 °C (CD_2Cl_2)

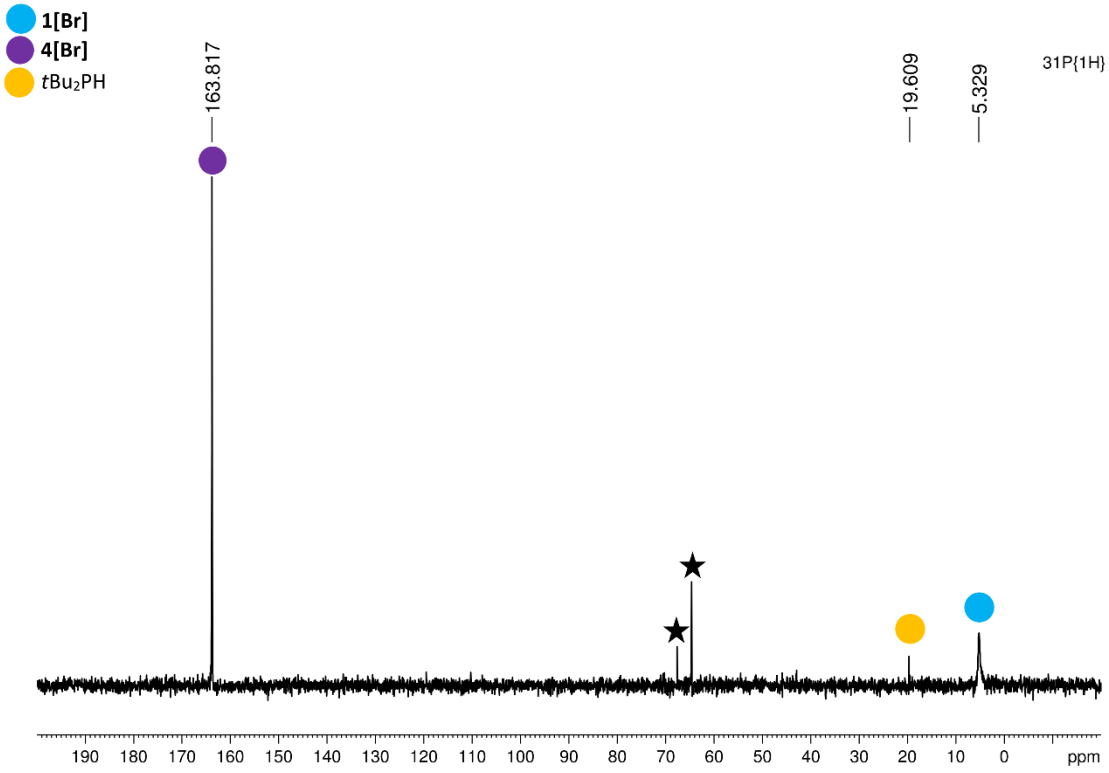


Figure S 37. $^{31}P\{^1H\}$ spectrum of reaction mixture **1[Br] + N_2O** after 7 days at 50 °C (CD_2Cl_2)

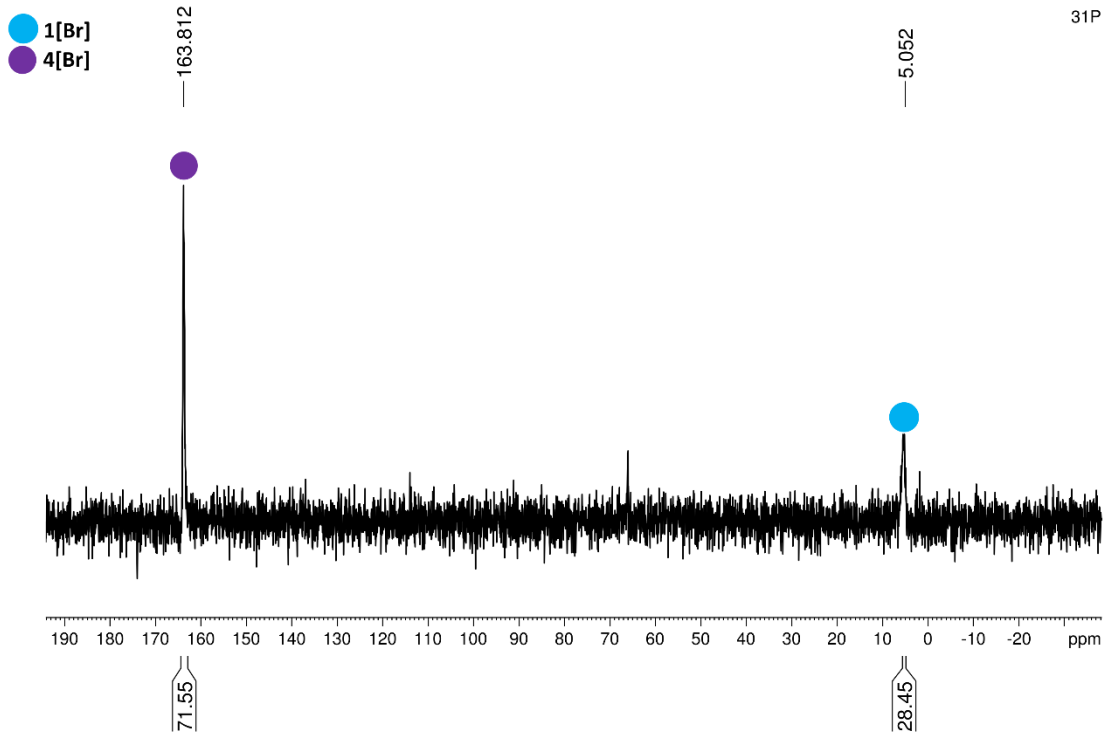


Figure S 38. ^{31}P spectrum of reaction mixture **1[Br] + N_2O** after 7 days at 50 °C (CD_2Cl_2)

NMR spectra for 4[Br]

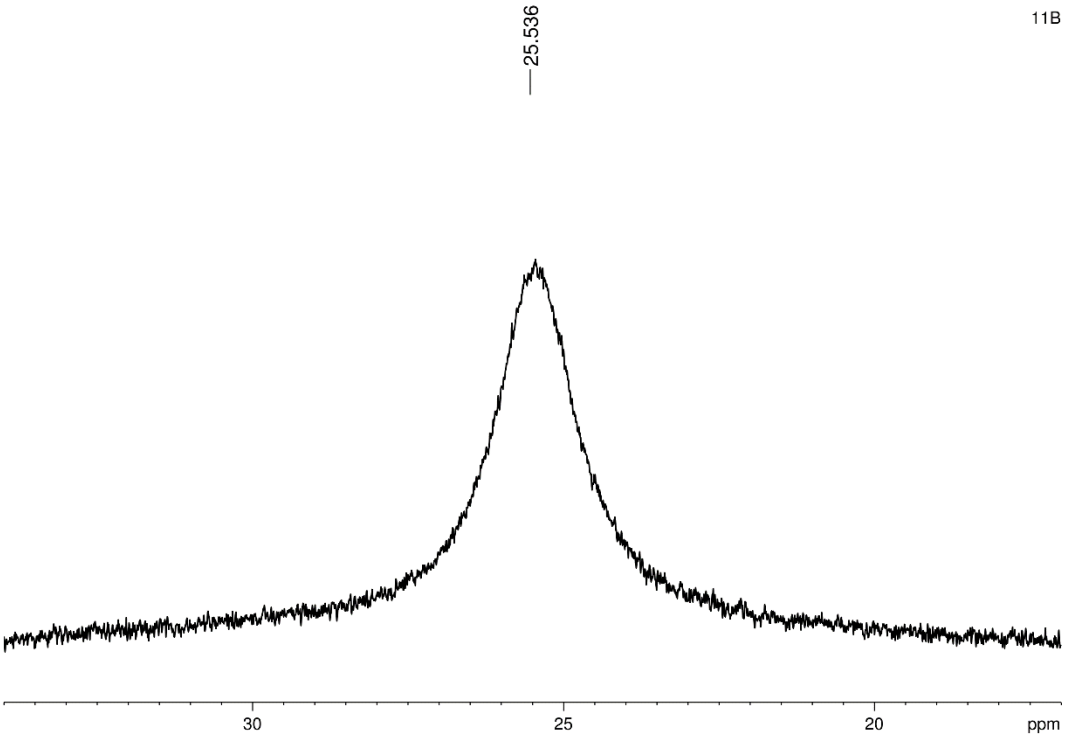


Figure S 39. ^{11}B spectrum of reaction mixture for **4[Br]** (CD_2Cl_2)

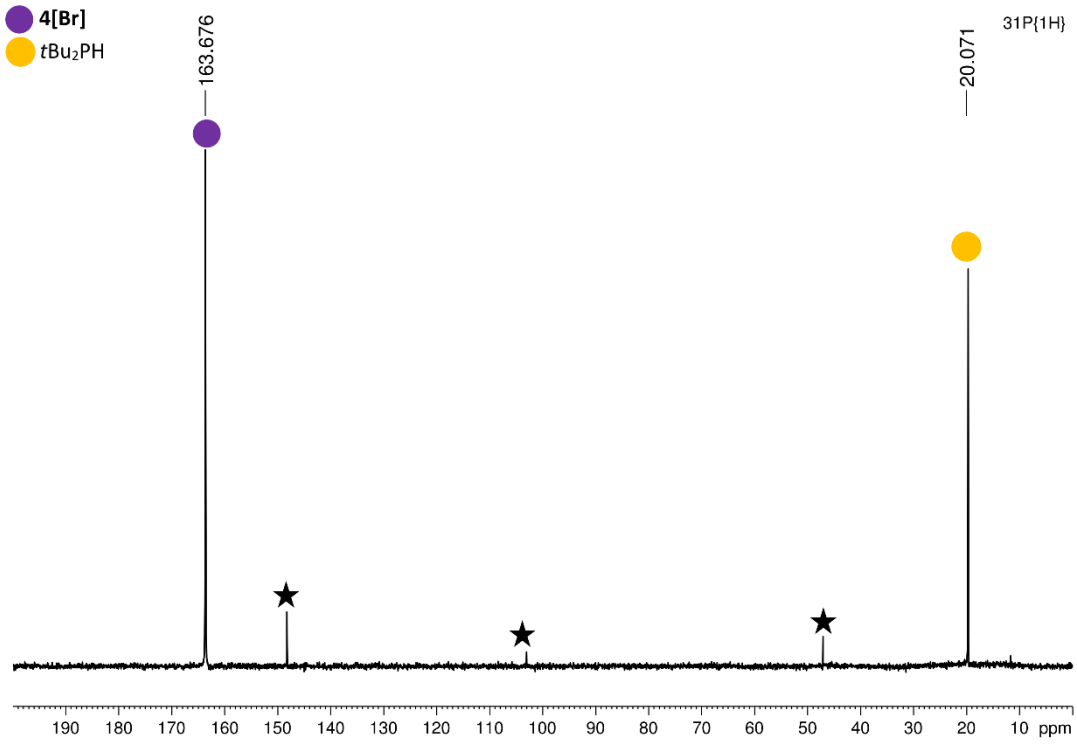


Figure S 40. $^{31}P\{^1H\}$ spectrum of reaction mixture for **4[Br]** (CD_2Cl_2)

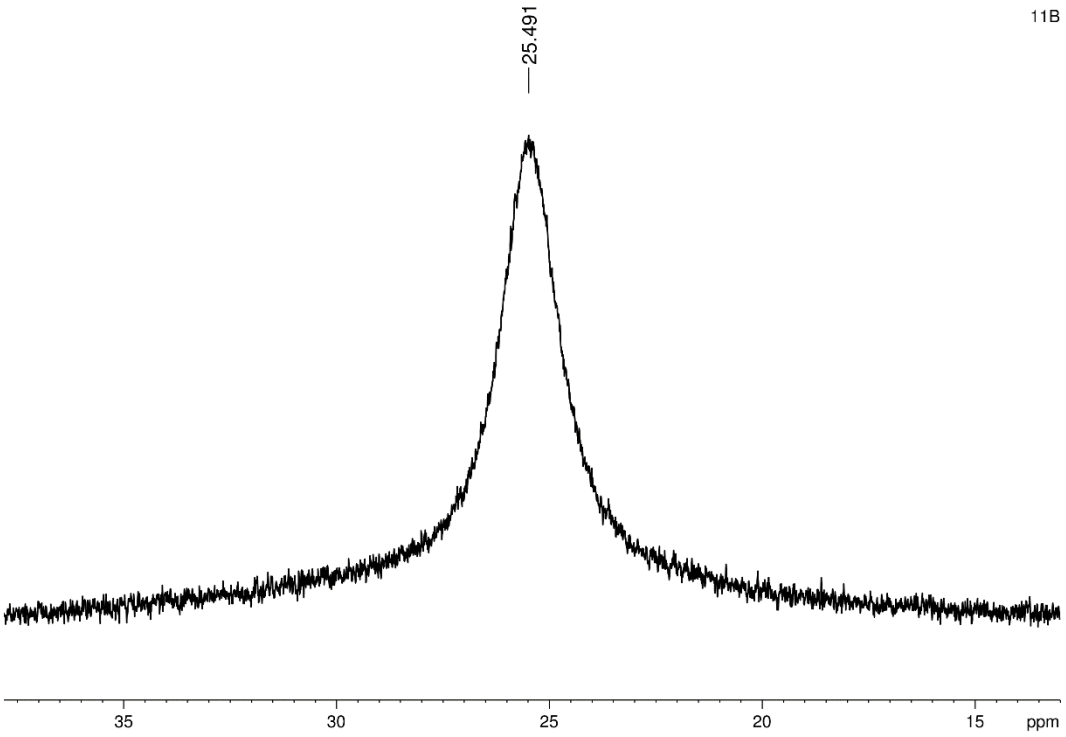


Figure S 41. ^{11}B spectrum of **4[Br]** (CD_2Cl_2)

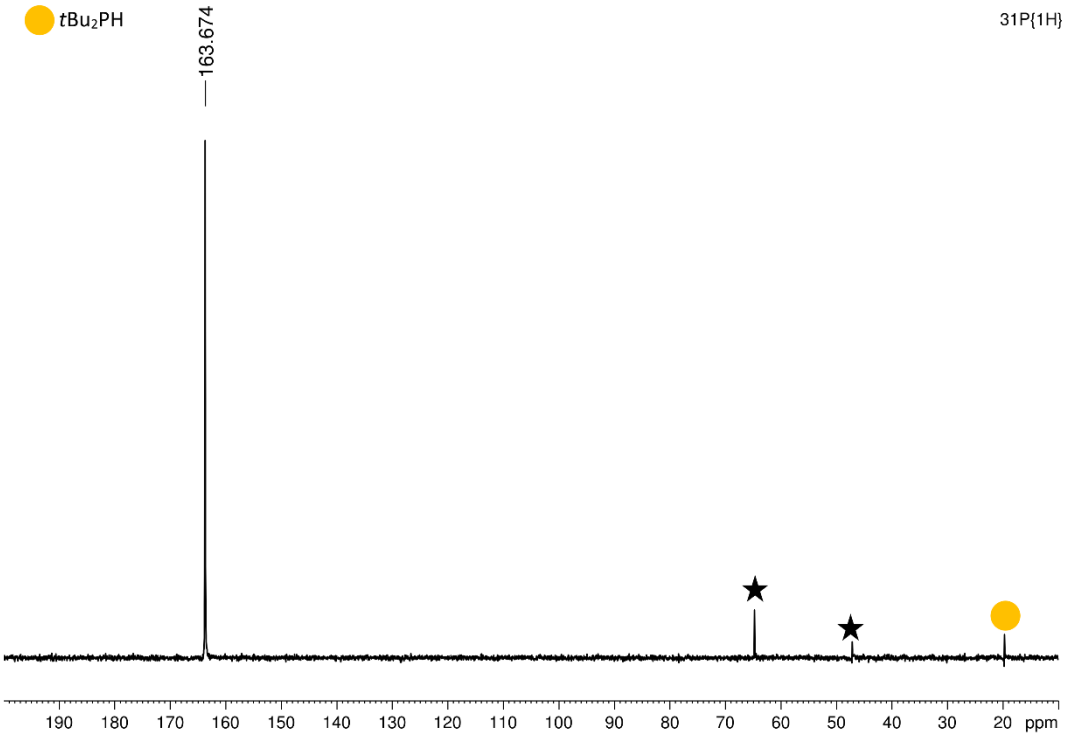


Figure S 42. $^{31}P\{^1H\}$ spectrum of **4[Br]** (CD_2Cl_2)

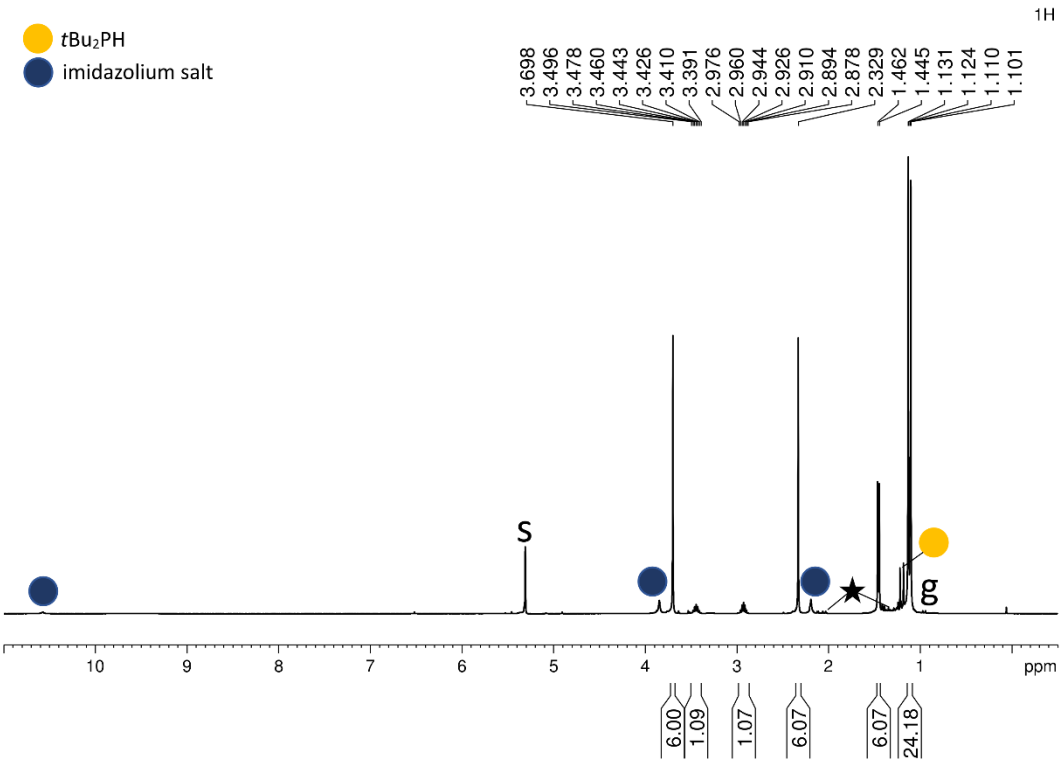


Figure S 43. ^{1}H spectrum of **4[Br]** (CD_2Cl_2)

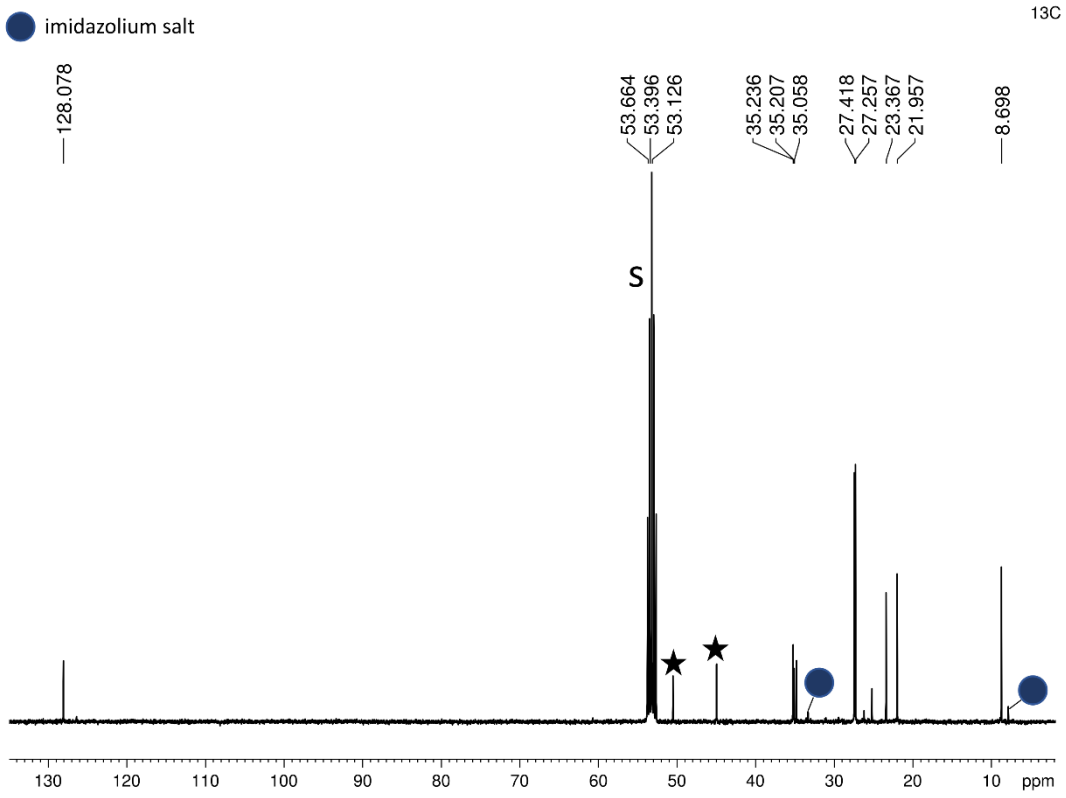


Figure S 44. $^{13}C\{^{1}H\}$ spectrum of **4[Br]** (CD_2Cl_2)

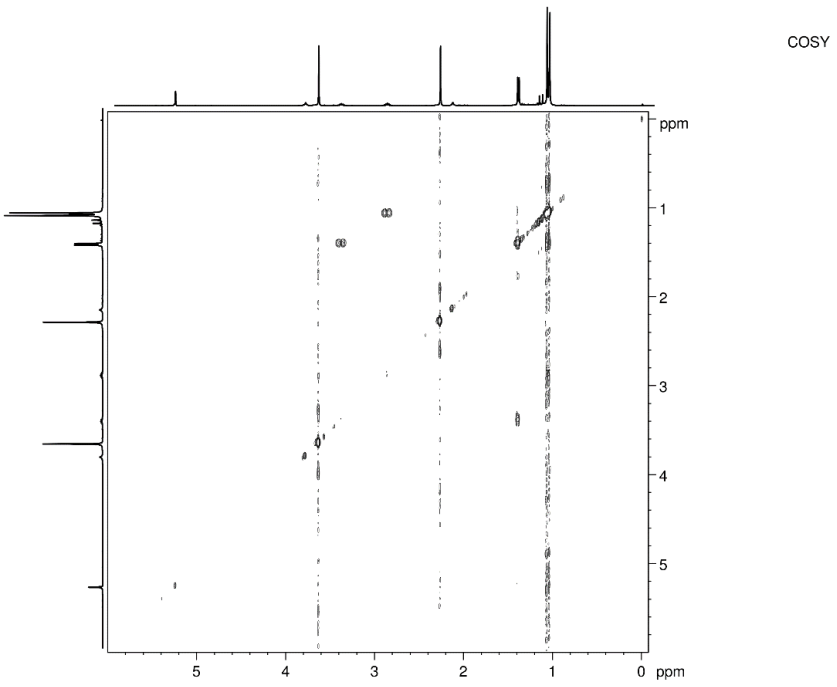


Figure S 45. COSY spectrum of **4[Br]** (CD_2Cl_2)

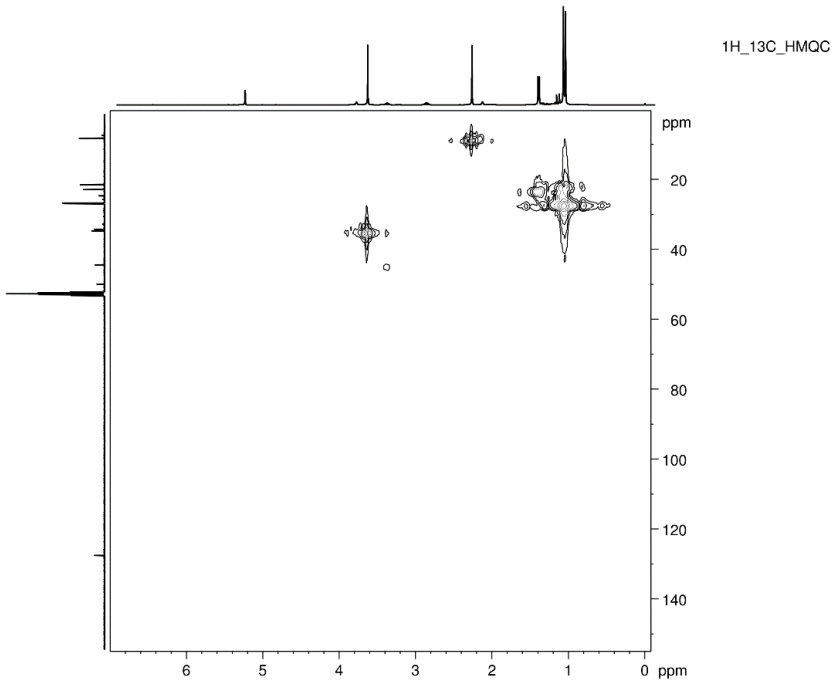


Figure S 46. ^{13}C ^{1}H HMQC spectrum of **4[Br]** (CD_2Cl_2)

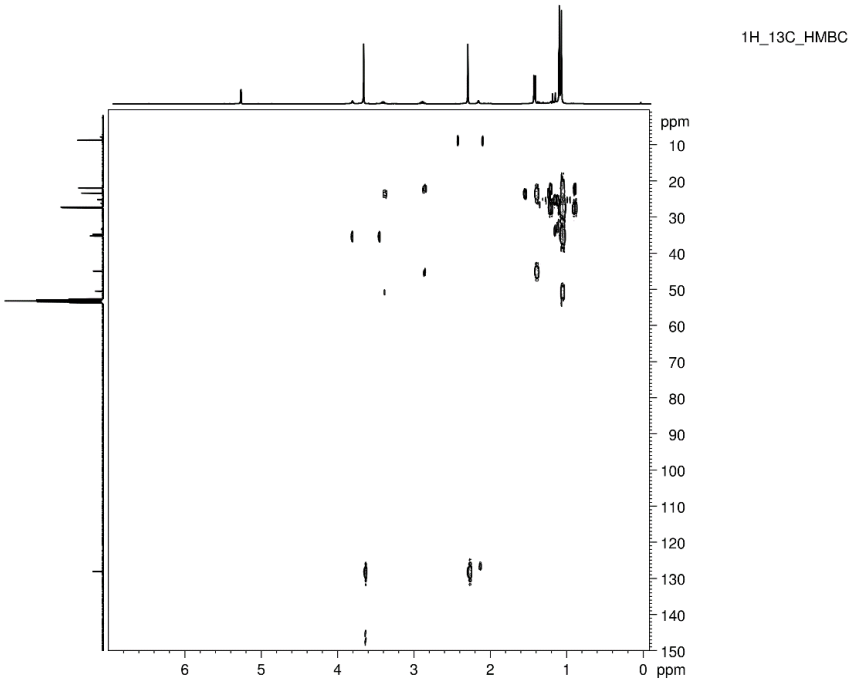


Figure S 47. ^{13}C ^{1}H HMBC spectrum of **4[Br]** (CD_2Cl_2)

NMR spectra for reaction mixture 5[Br]

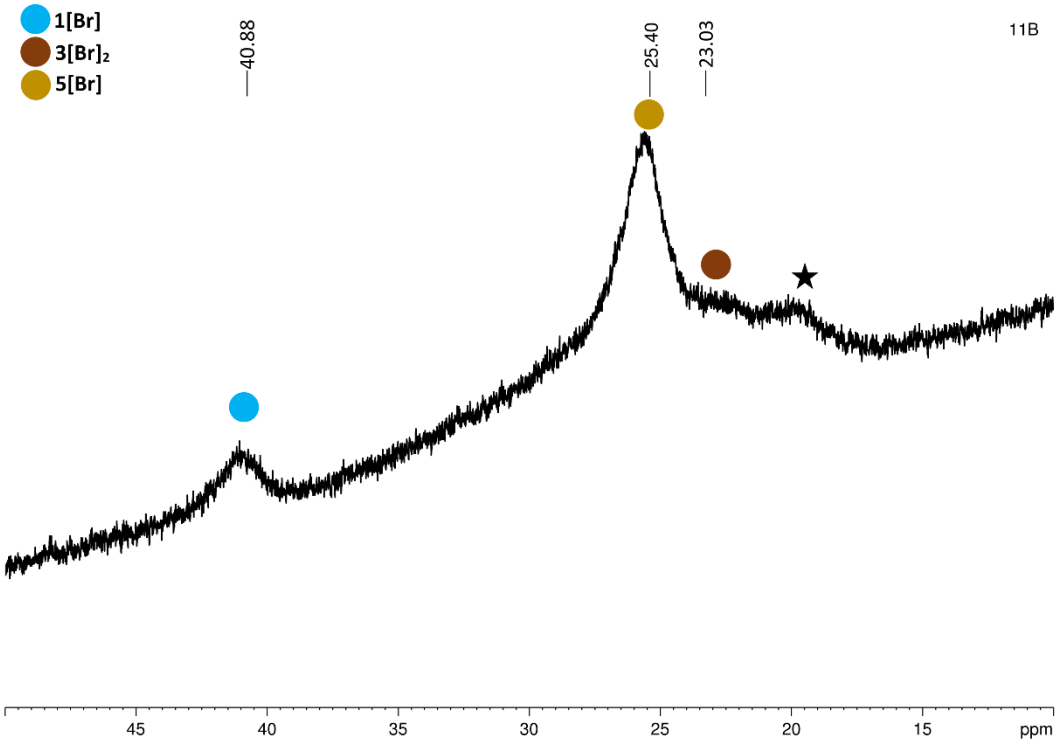


Figure S 48. ^{11}B spectrum of the reaction mixture for synthesis of **5[Br]**

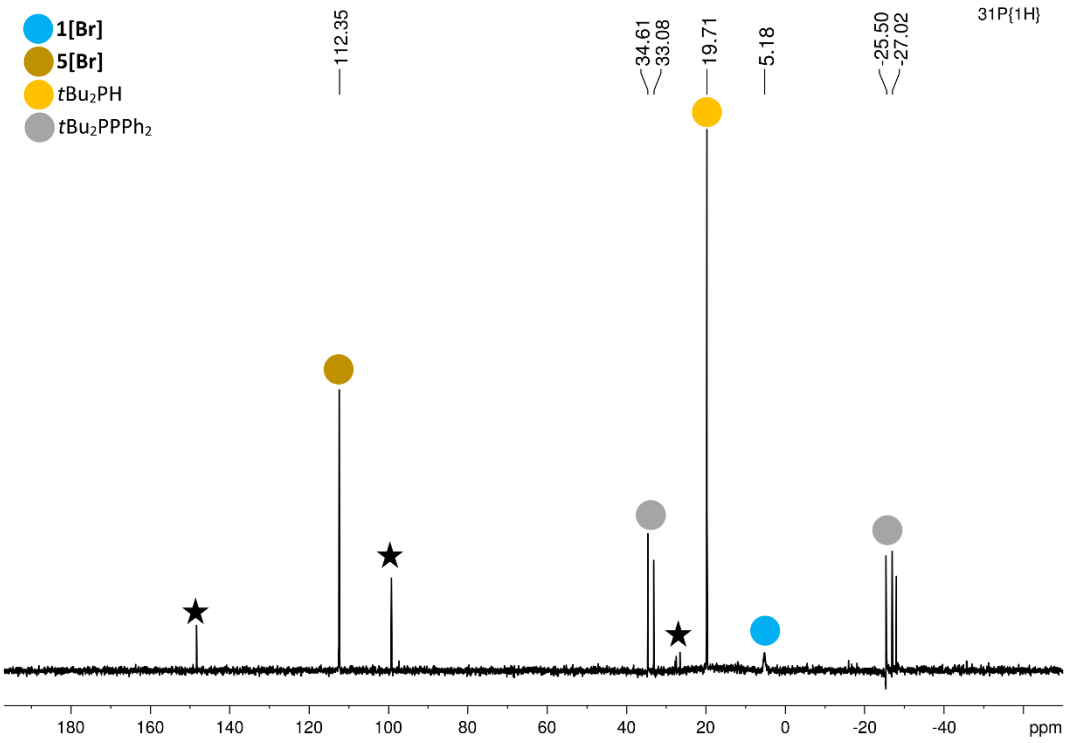


Figure S 49. $^{31}P\{^{1}H\}$ spectrum of the reaction mixture for synthesis of **5[Br]**

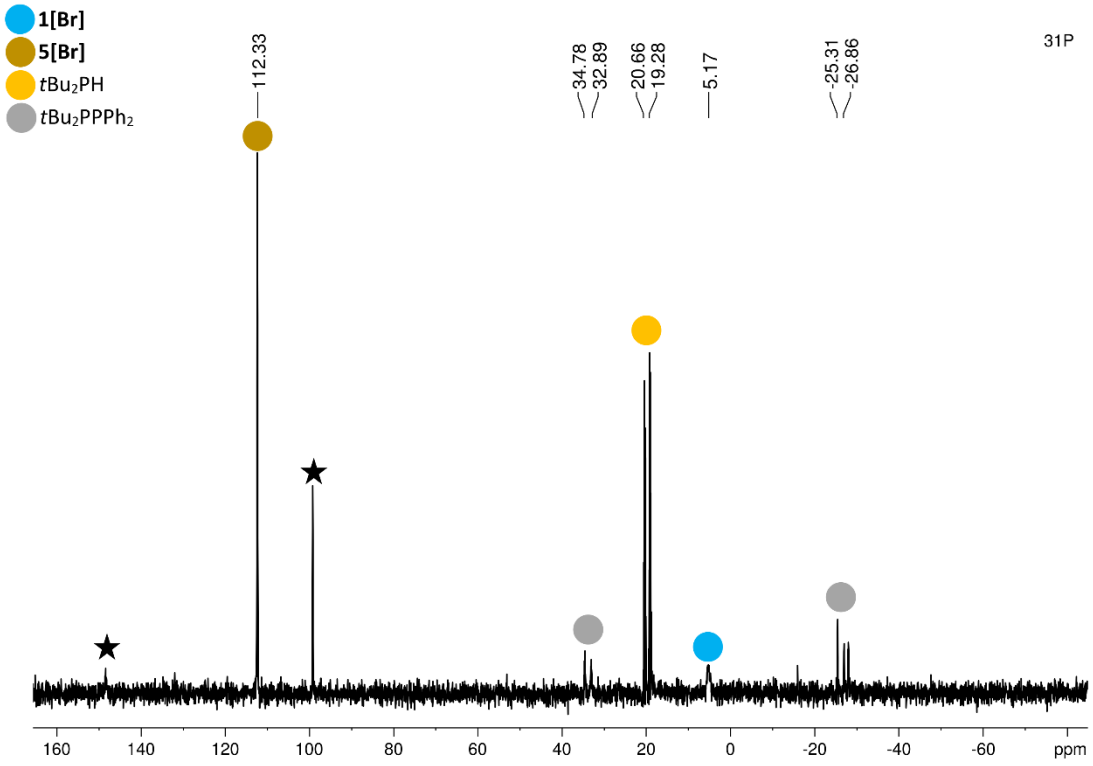


Figure S 50. ^{31}P spectrum of the reaction mixture for synthesis of **5[Br]**

NMR spectra for 6[WCA]

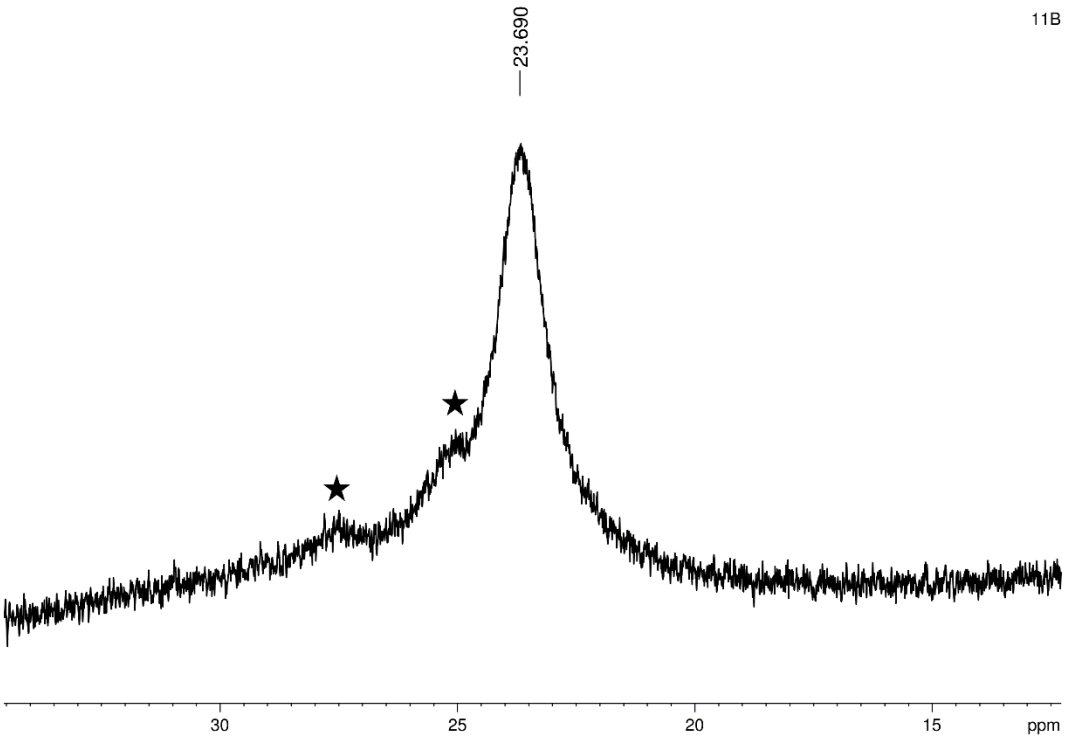


Figure S 51. ^{11}B spectrum of reaction mixture for **6[WCA]** (CD_2Cl_2)

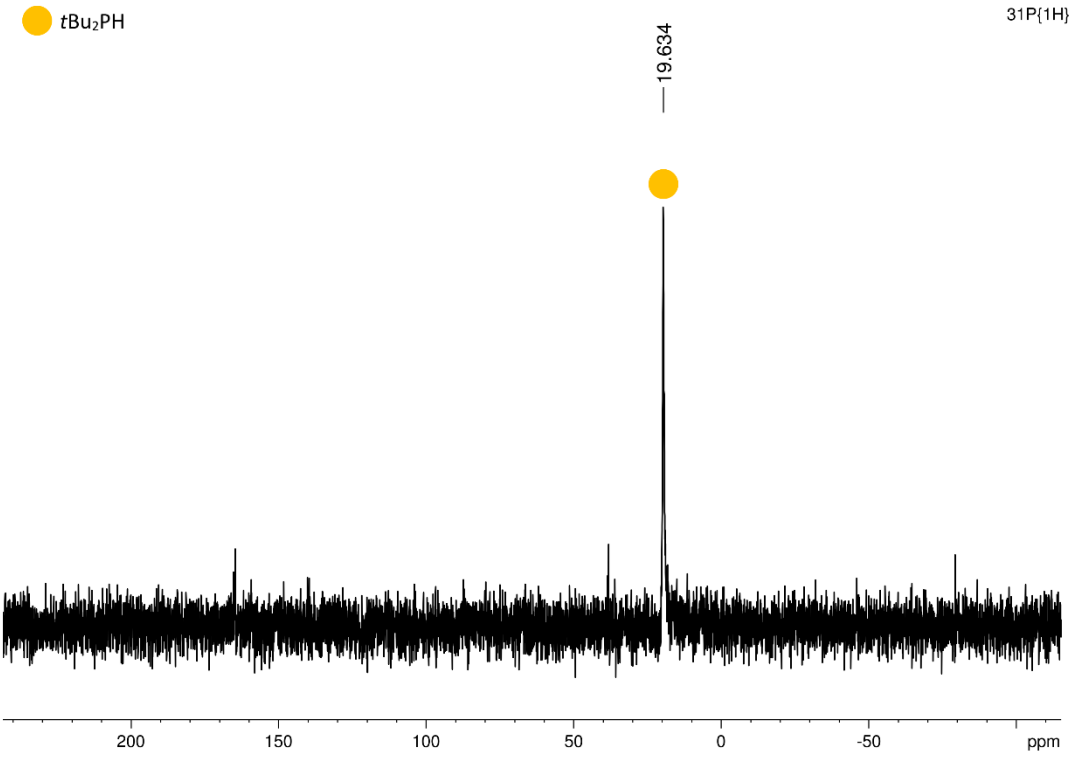


Figure S 52. $^{31}P\{^1H\}$ spectrum of reaction mixture for **6[WCA]** (CD_2Cl_2)

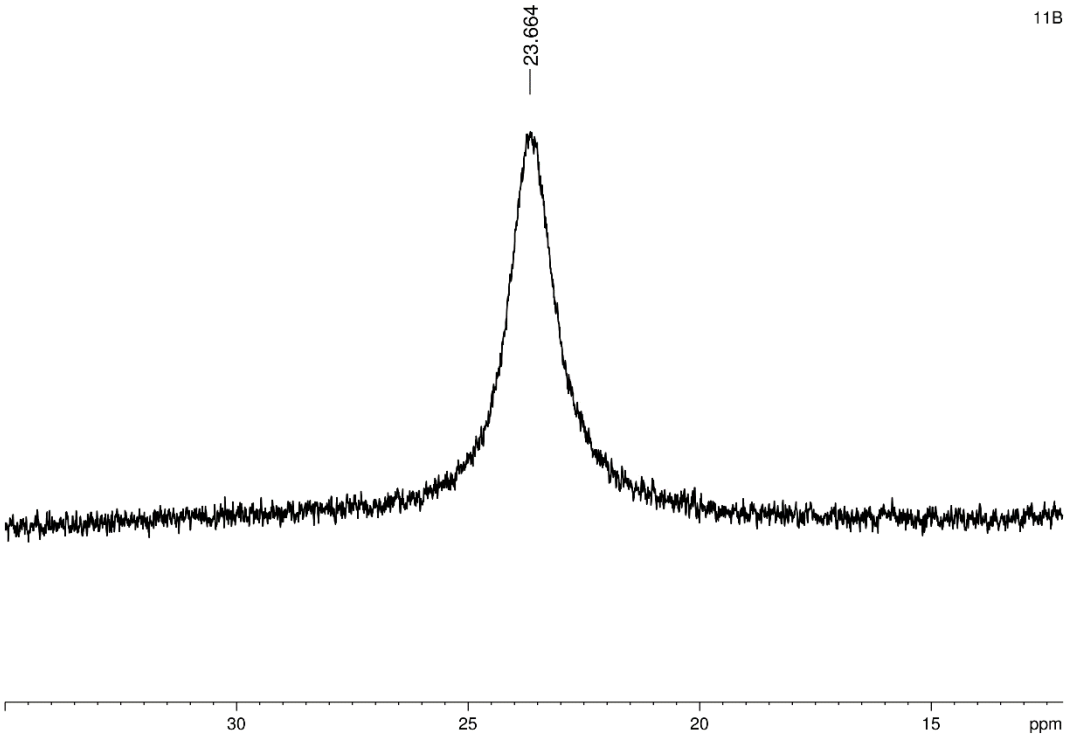


Figure S 53. ^{11}B spectrum of **6[WCA]** (CD_2Cl_2)

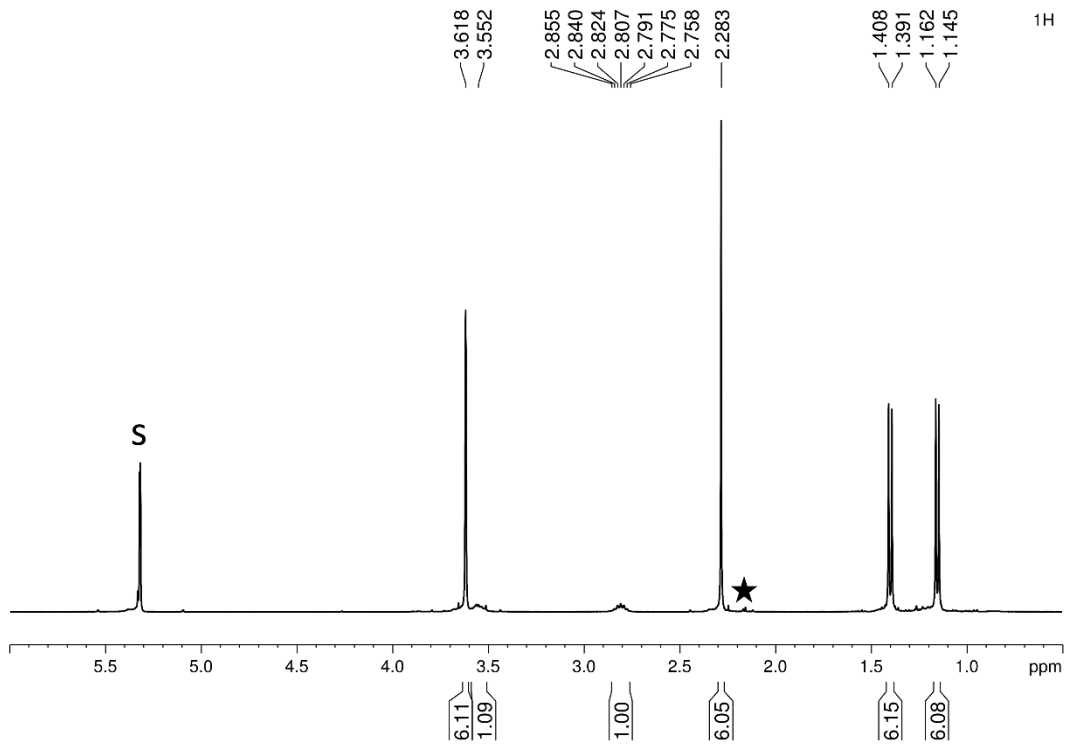


Figure S 54. ^{1}H spectrum of **6[WCA]** (CD_2Cl_2)

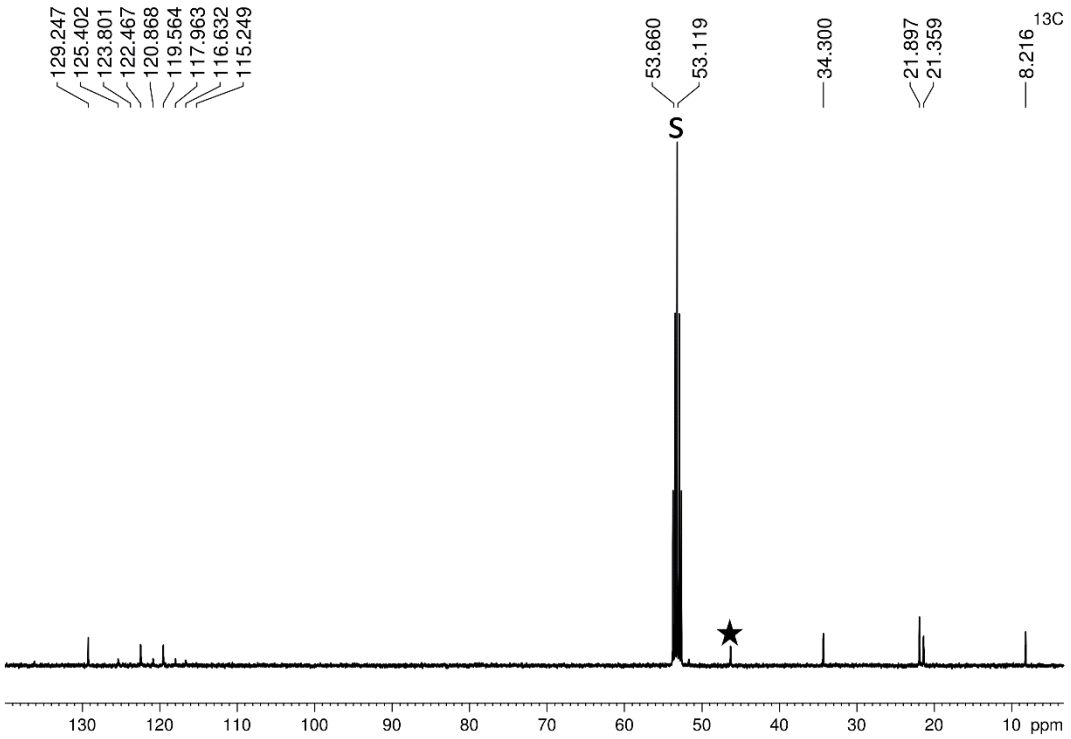


Figure S 55. $^{13}C\{^{1}H\}$ spectrum of **6[WCA]** (CD_2Cl_2)

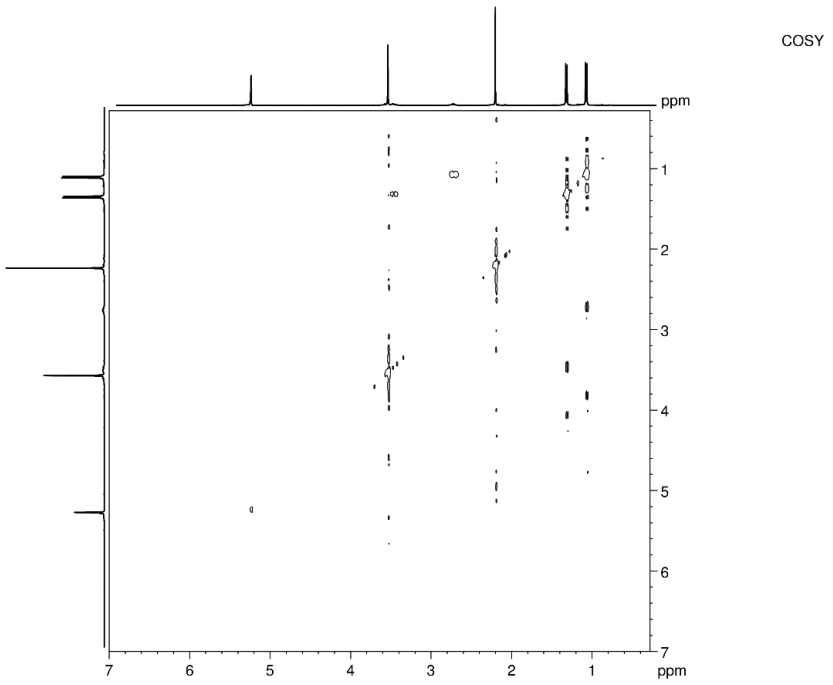


Figure S 56. COSY spectrum of **6[WCA]** (CD_2Cl_2)

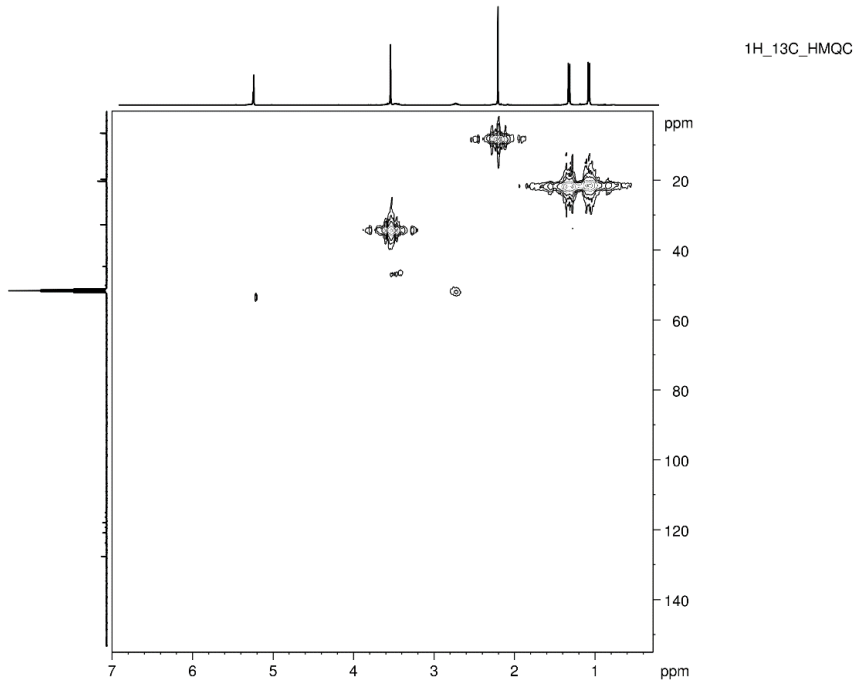


Figure S 57. ^{13}C ^{1}H HMQC spectrum of **6[WCA]** (CD_2Cl_2)

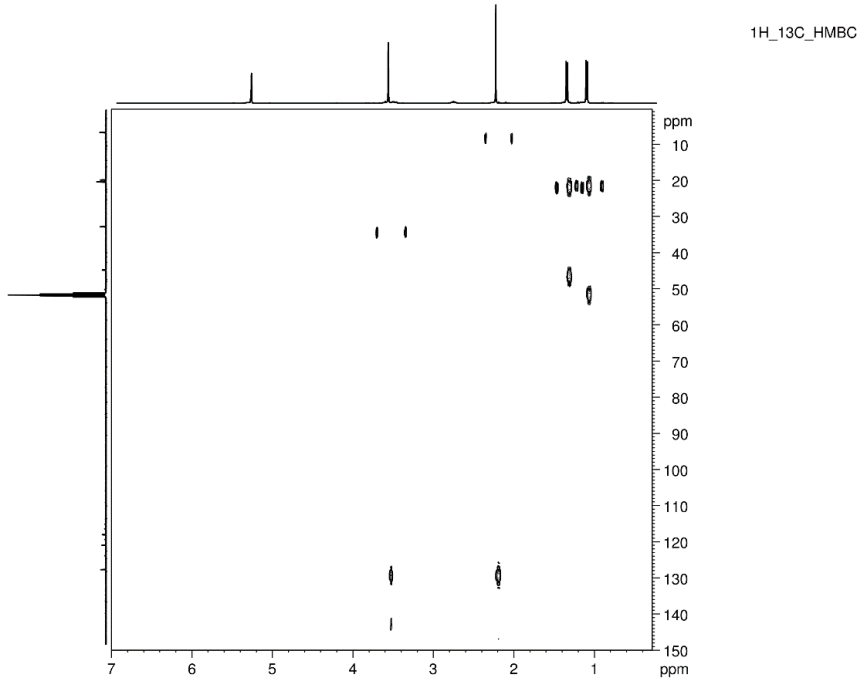


Figure S 58. ^{13}C ^{1}H HMBC spectrum of **6[WCA]** (CD_2Cl_2)

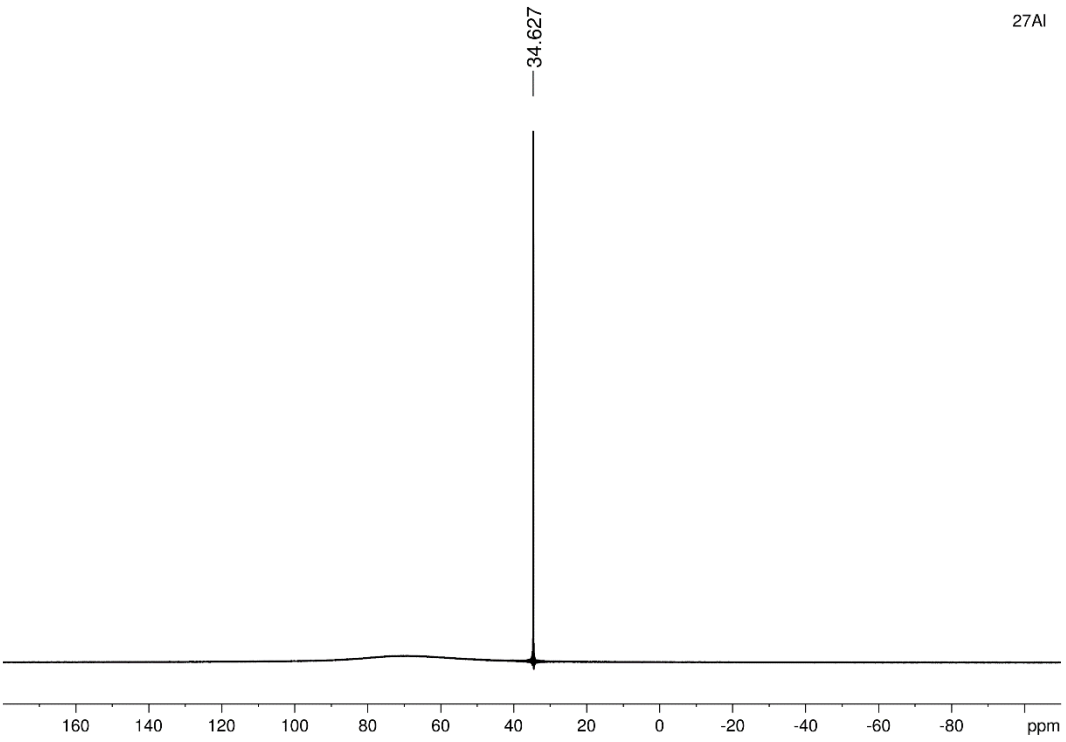


Figure S 59. ^{27}Al spectrum of **6[WCA]** (CD_2Cl_2)

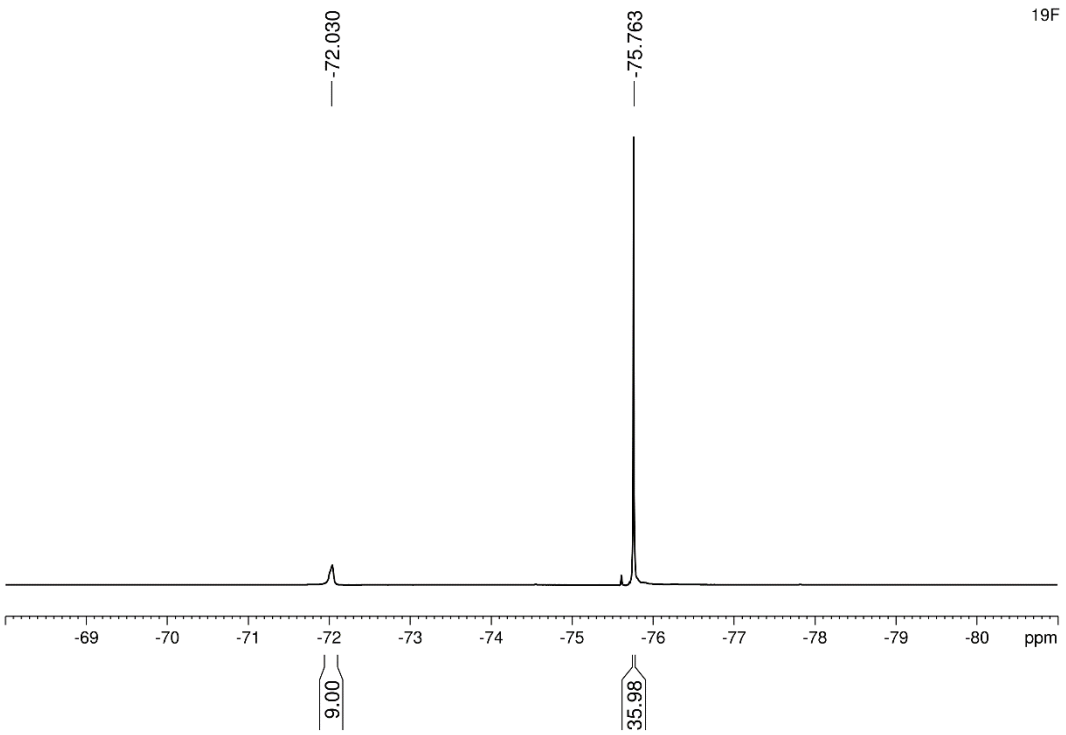


Figure S 60. ^{19}F spectrum of **6[WCA]** (CD_2Cl_2)

NMR spectra for 7[WCA]$_2$

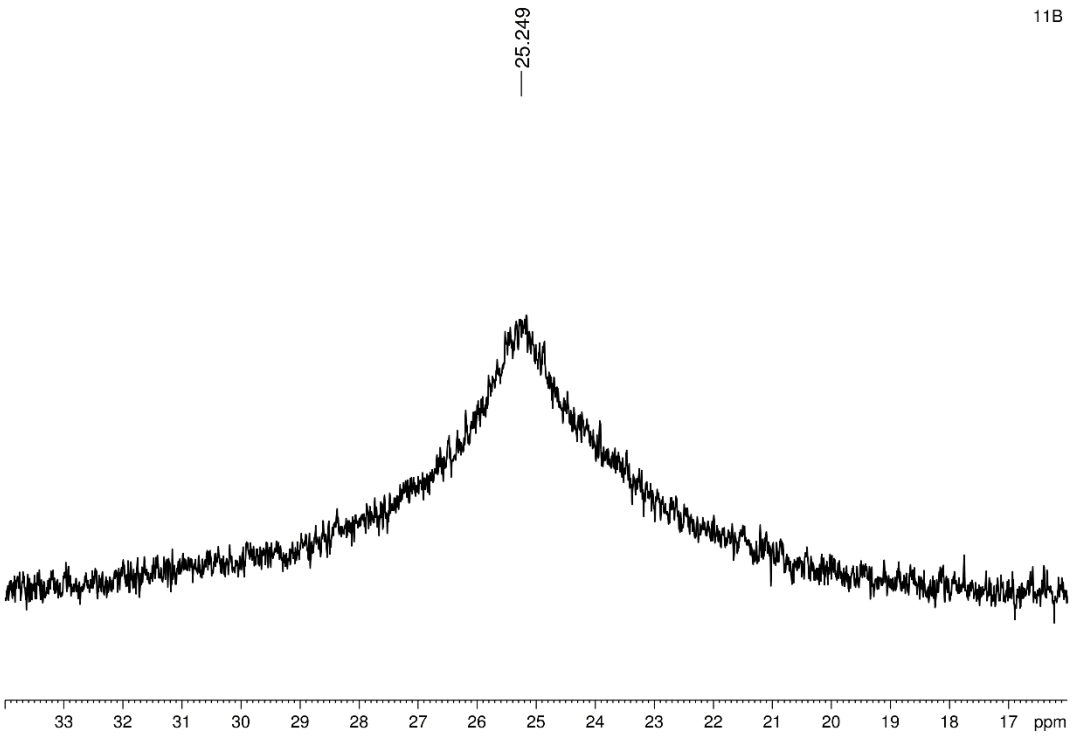


Figure S 61. ^{11}B spectrum of reaction mixture for **7[WCA]$_2$** (CD_2Cl_2)

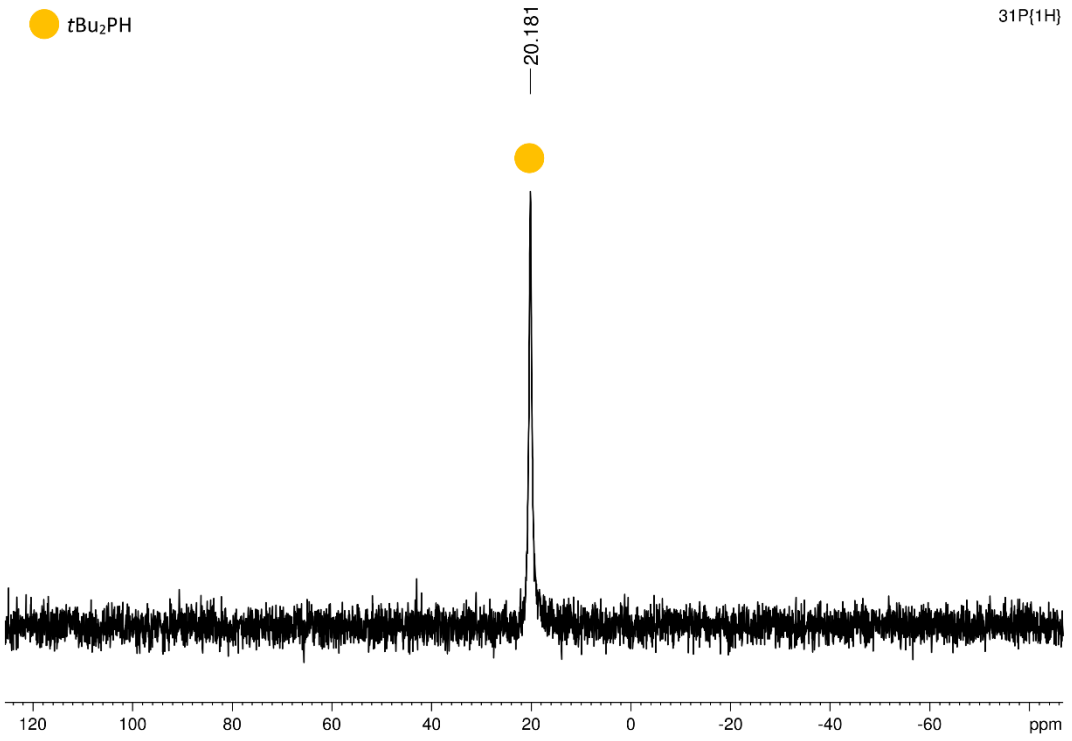


Figure S 62. $^{31}P\{^1H\}$ spectrum of reaction mixture for **7[WCA]$_2$** (CD_2Cl_2)

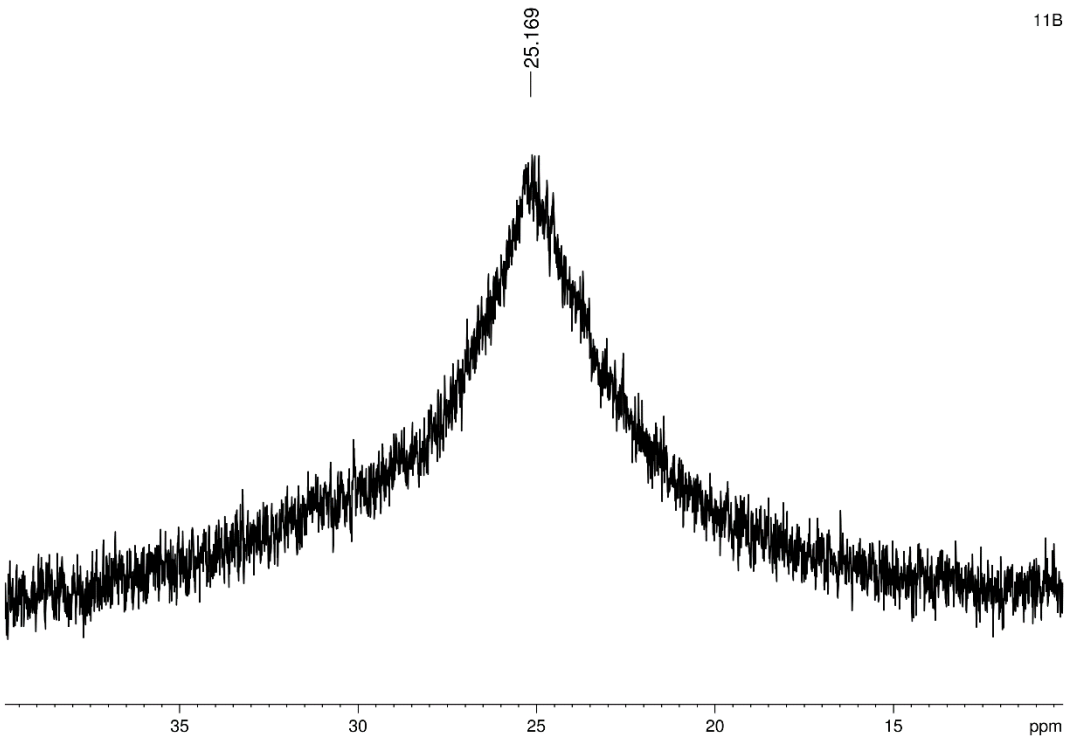


Figure S 63. ^{11}B spectrum of **7[WCA]₂** (CD_2Cl_2)

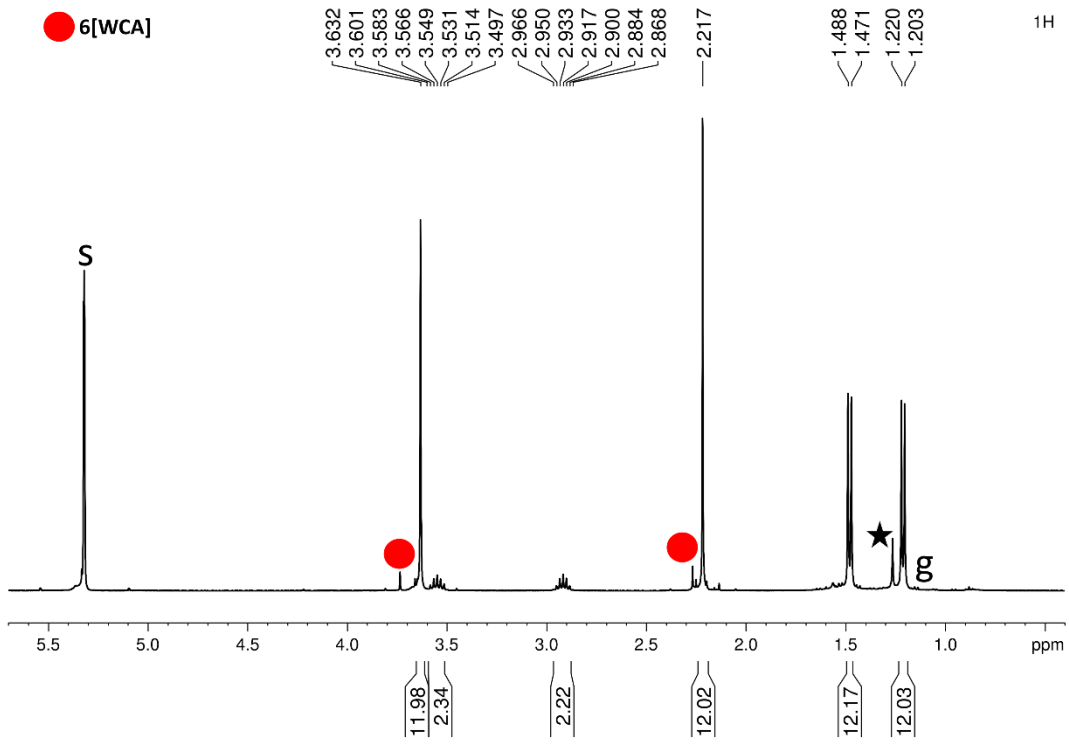


Figure S 64. ^{1}H spectrum of **7[WCA]₂** (CD_2Cl_2)

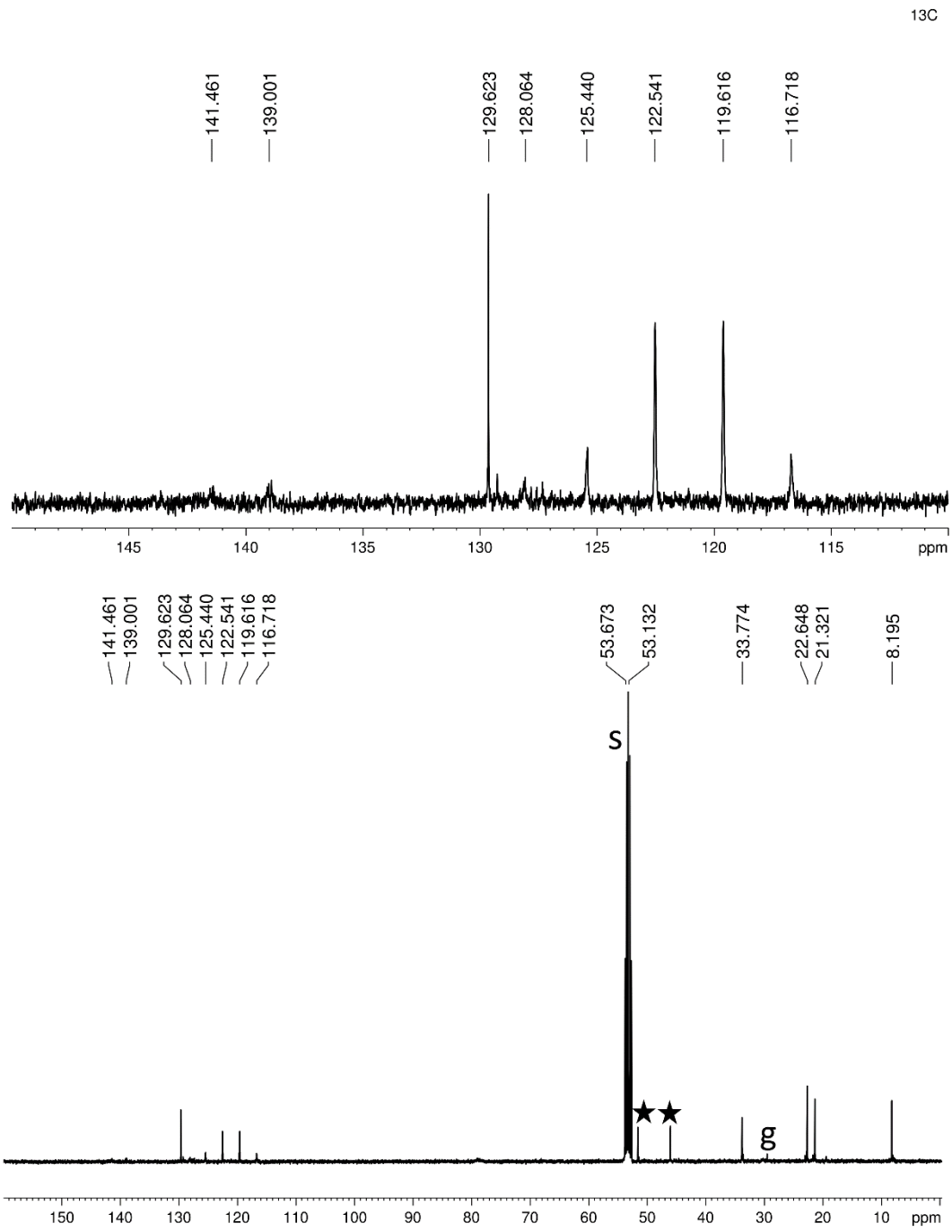


Figure S 65. $^{13}C\{^{1}H\}$ spectrum of **7[WCA]₂** (CD_2Cl_2)

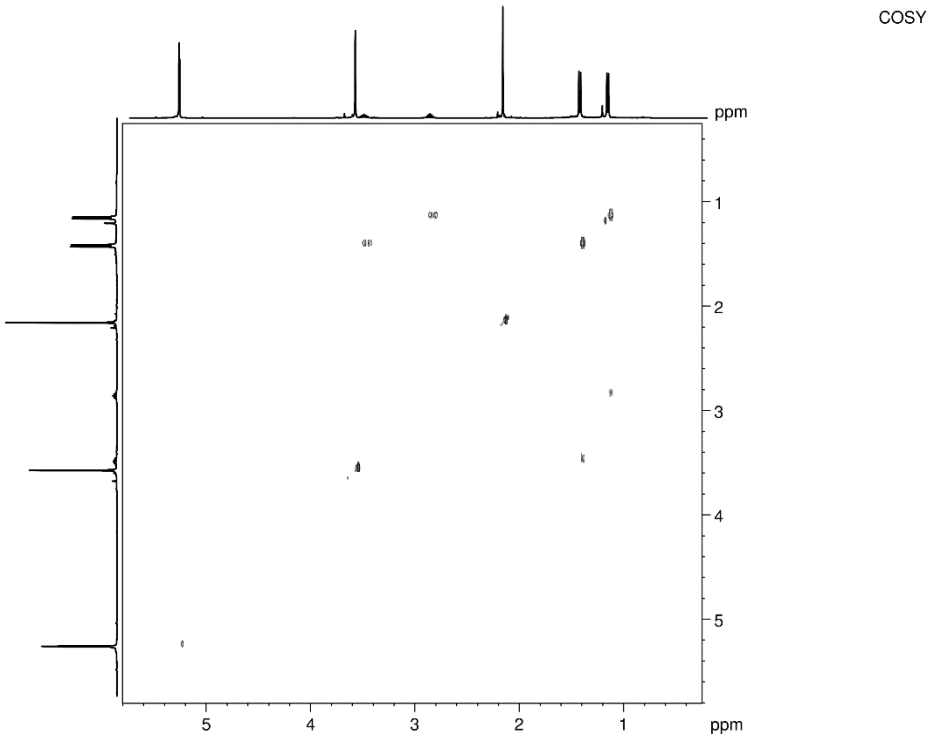


Figure S 66. COSY spectrum of **7[WCA]$_2$** (CD_2Cl_2)

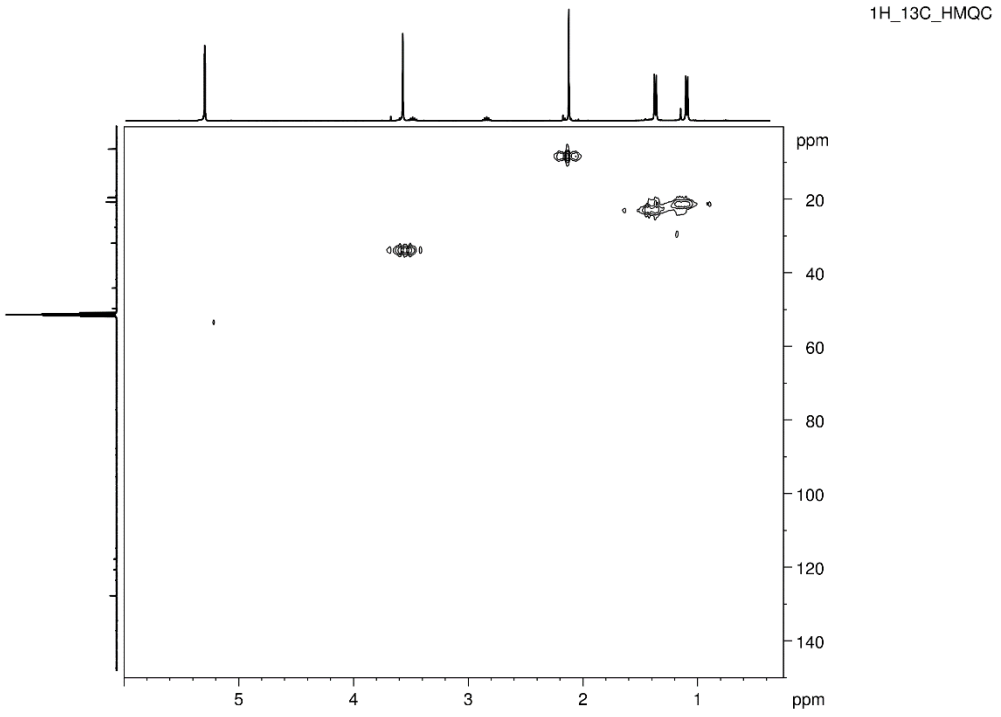


Figure S 67. ^{13}C ^{1}H HMQC spectrum of **7[WCA]$_2$** (CD_2Cl_2)

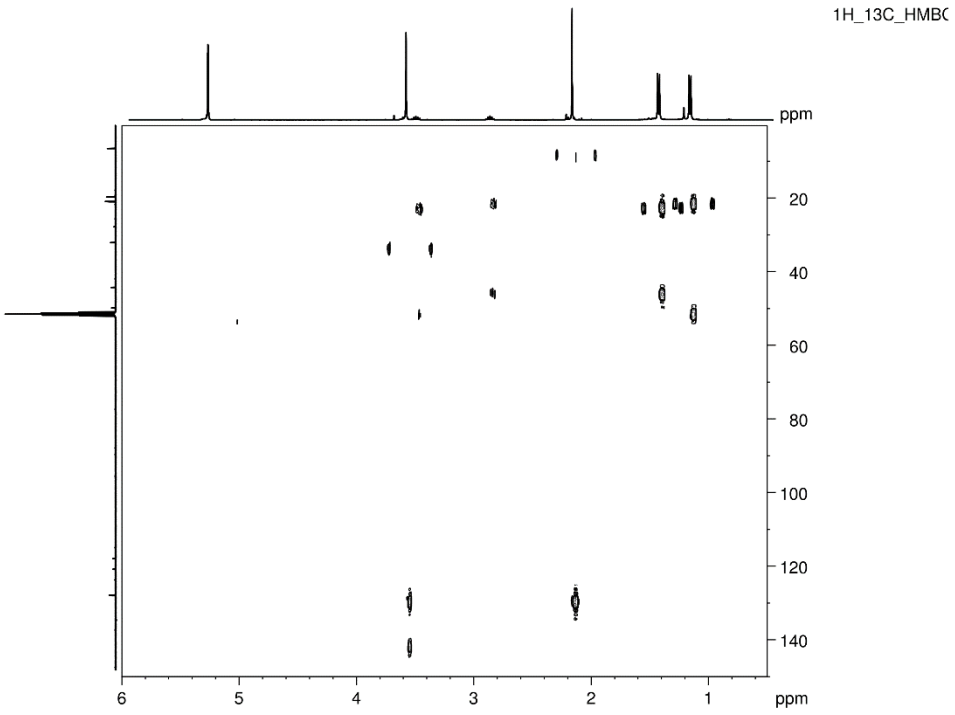


Figure S 68. ^{13}C ^{1}H HMBC spectrum of **7[WCA]$_2$** (CD_2Cl_2)

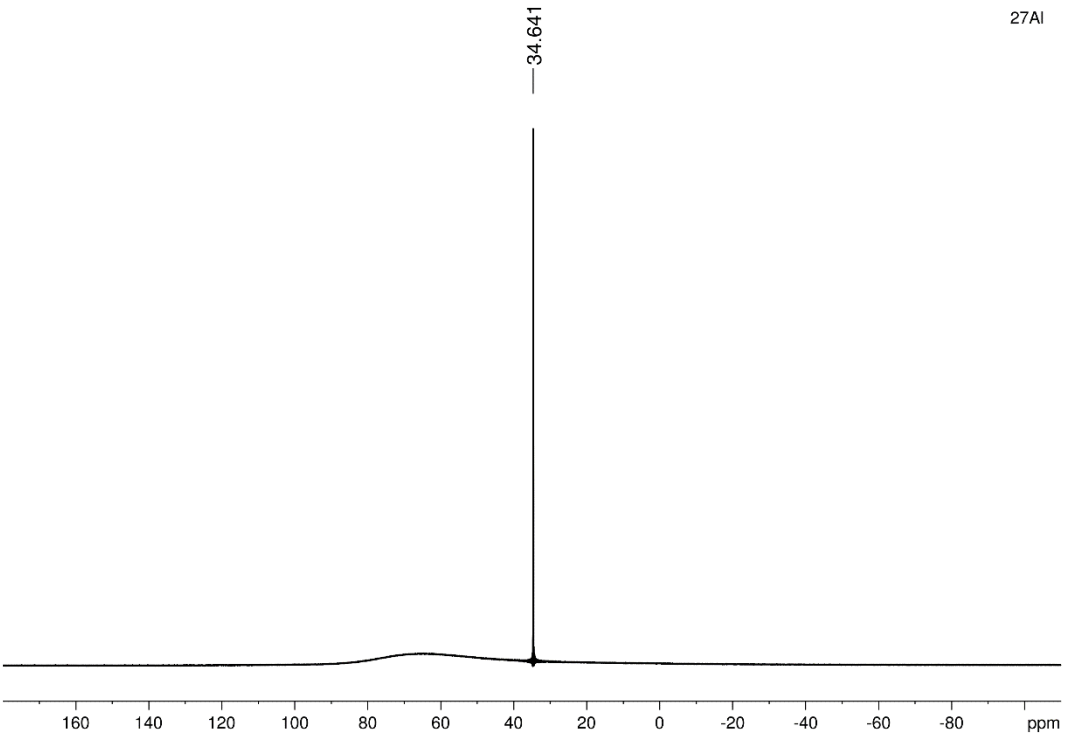


Figure S 69. ^{27}Al spectrum of **7[WCA]$_2$** (CD_2Cl_2)

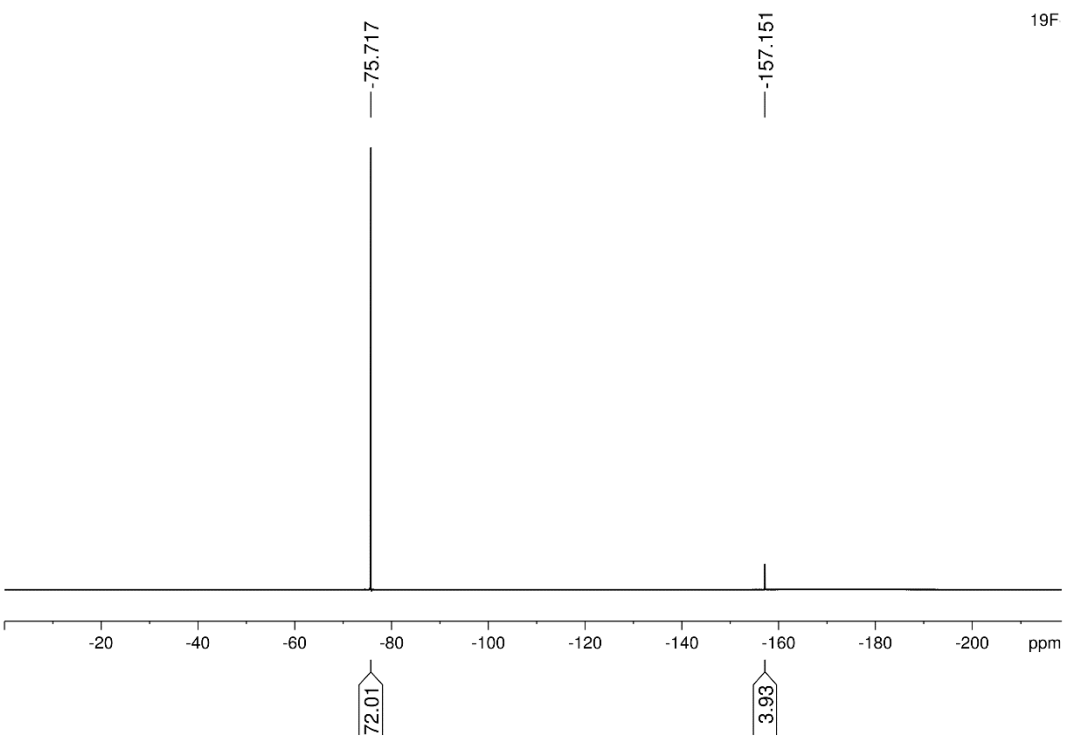


Figure S 70. ^{19}F spectrum of **7[WCA]$_2$** (CD_2Cl_2)

IR spectra

IR spectra for 2[Br]

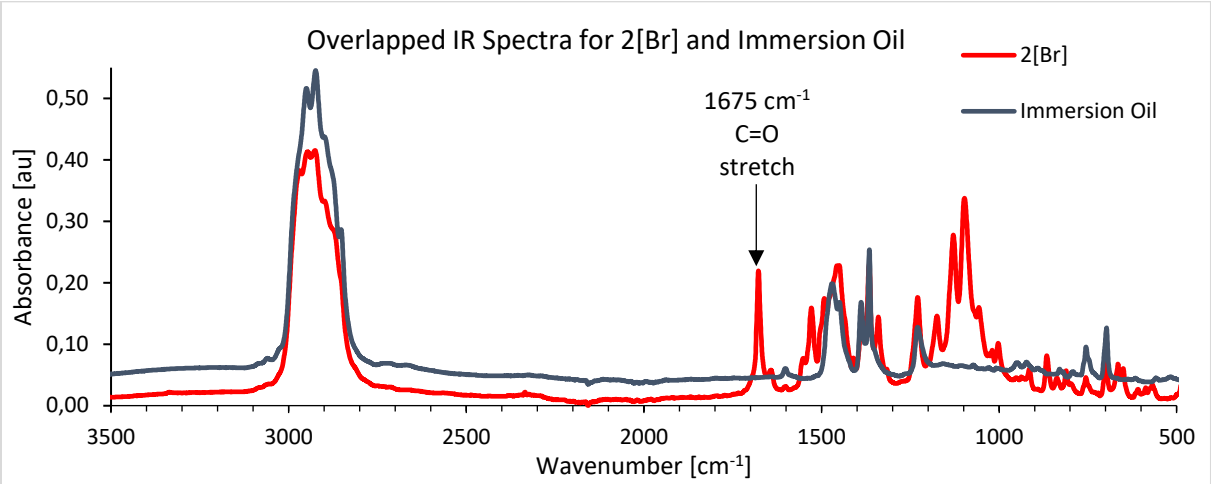


Figure S 71. Overlapped IR spectrum of 2[Br] suspended in Immersion Oil with Immersion Oil

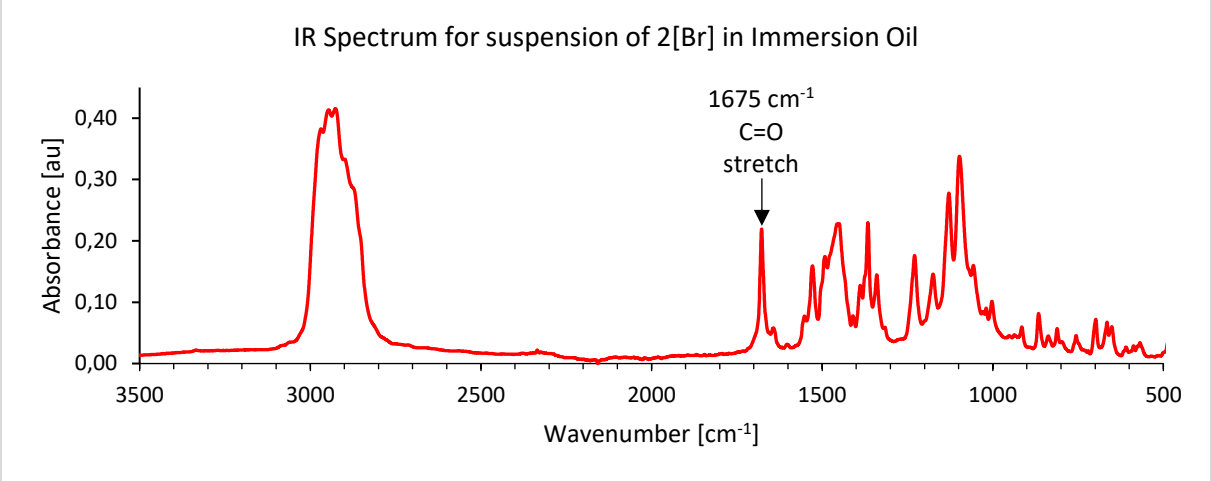


Figure S 72. IR spectrum of 2[Br] suspended in Immersion Oil

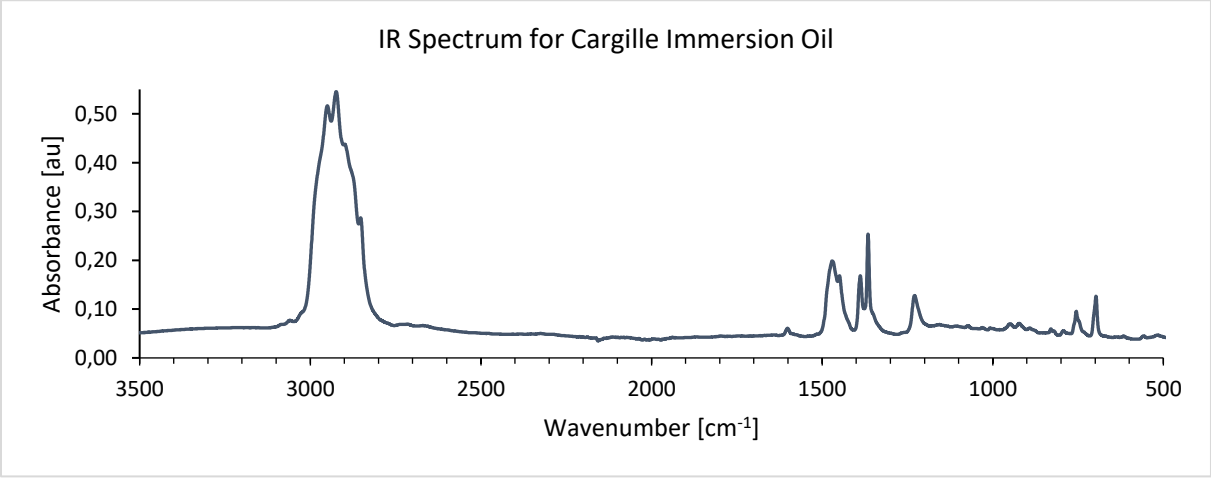


Figure S 73. IR spectrum of Immersion Oil

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 MoKα radiation of a microfocus X-ray source (GeniX 3D Mo High Flux, Xenocs, Sassenage, France, 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. In the case of **1[WCA]** CuKα radiation of a microfocus X-ray source (GeniX 3D Cu High Flux, Xenocs, Sassenage, France, 50 kV, 0.6 mA, and λ = 1.54186 Å). Data collection and data reduction were controlled by using the X-Area 1.75 program (STOE, 2015). Numerical absorption correction was performed for all structures with high absorption coefficients, μ > 0.5 mm^{-1} (i.e. accept **4[Br]**). The structures were solved using intrinsic phasing implemented in SHELXT and refined anisotropically using the program packages Olex2[4] and SHELX-2015[5,6]. 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[WCA]** ($C_{21}H_{43}BN_3P^+ \cdot C_{16}AlF_{36}O_4^-$ + [solvent]) contains one phosphinoborenium cation and one aluminate anion in the asymmetric unit (Z = 4, space group $P2_1/n$). The anion was modeled as disordered in three branches mainly by rotation of relevant CF_3 groups at atom C22 (occupation factors 0.817/0.183), at atom C26 (occupation factors 0.739/0.261) and at atom C34 (0.875/0.125). Several restraints were necessary to make the refinement stable. Additionally, the SQUEEZE procedure was performed to remove residual electron density from disordered solvent molecules of petroleum ether, perhaps with non-integer occupation, modeled as C_6H_{14}, at (0 0 ½) and (½ ½ 0). The voids had the volume of 245.2 $Å^3$ and contained ca 55.1 e charge on average. Numerical absorption correction was performed due to high absorption coefficient for Cu radiation μ, in spite of absence of heavy atoms in the structure.

Asymmetric unit of structure **3[Br]$_2$** ($C_{26}H_{52}B_2N_6O^{2+}\cdot 2(CH_2Cl_2)\cdot 2Br^-$) contains one diborenium cation of double positive charge, two bromides and two (solvating) molecules of dichloromethane. (Z=2, space group $P\bar{1}$). The structure was solved and refined without any special treatment.

Structure **4[Br]** ($C_{21}H_{44}BN_3OP^+$, $C_6H_4F_2$, Br^-) contains one borenium cation, one bromide anion and one molecule of 1,2-difluorobenzene (solvent) in the asymmetric unit (Z=4, space group $P2_12_12_1$). The structure was solved and refined without any problems but a high residual electron density peak remained. There are two B-level warnings generated by checkCIF procedure. However, in our opinion, the alerts are due to formation of solid solution including another cation with B-P*t*Bu$_2$ group instead of B-O-P*t*Bu$_2$. Direction of Q1-B1 is similar to the direction of the B-O bond.

Structure **6[WCA]** ($C_{17}H_{26}BF_9N_3O^+ \cdot C_{16}AlF_{36}O_4^-$) contains one cation and one anion in the asymmetric unit (Z=2, space group $P\bar{1}$). Perfluoroalkoxy group with O4 atom was refined as disordered over two positions with occupation factors of 0.796/0.204. Several restraints were necessary to make refinement stable. The parts differ mainly in the rotation of CF_3 groups. Nevertheless, the present study is not focused on the conformation of this anion. The cation is placed in the well defined position with relatively small displacement ellipsoids for all atoms. No absorption correction was performed due to the low absorption coefficient μ.

Structure **7[WCA]$_2$** ($C_{16}AlF_{36}O_4^- \cdot 0.5(C_{32}H_{52}B_2F_4N_6O_2^{2+}) \cdot CH_2Cl_2$) contains half of the dication, one WCA anion and one CH_2Cl_2 solvent molecule in the asymmetric unit (Z=4, space group $P2_1/n$). All four alkoxy branches of $C_{16}AlF_{36}O_4^-$ were refined as disordered over two positions with occupation factors of 0.893/0.107; 0.573/0.427; 0.548/0.452 and 0.739/0.261 for groups containing O2, O3, O4 and O5, respectively.

Deposition numbers 2367523 (for **1[WCA]**), 2367524 (for **3[Br]$_2$**), 2367525 (for **4[Br]**), and 2367526 (for **6[WCA]**) and 2379821 (for **7[WCA]$_2$**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe www.ccdc.cam.ac.uk/structures.

Table S 2. Crystal data and structure refinement for **1[WCA], 3[Br]$_2$, 4[Br]**, **6[WCA]**, **7[WCA]$_2$**

	1[WCA]	**3[Br]$_2$**	**4[Br]**	**6[WCA]**
CCDC deposition No	2367523	2367524	2367525	2367526
Chemical formula	$C_{21}H_{43}BN_3P^{+\cdot}$ $\cdot C_{16}AlF_{36}O_4^-$ $\cdot 0.5[C_6H_{14}]$	$(C_{26}H_{52}B_2N_6O)^{2+}$ $\cdot 2(Br^-)\cdot 2(CH_2Cl_2)$	$C_{21}H_{44}BN_3OP^+\cdot Br^-$ $\cdot C_6H_4F_2$	$C_{17}H_{26}BF_9N_3O^+$ $\cdot C_{16}AlF_{36}O_4^-$
M_r [g·mol^{-1}]	1389.59	816.02	590.37	1437.36
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P\overline{1}$	$P2_12_12_1$	$P\overline{1}$
Temperature [K]	120	120	120	120
a [Å] *b* [Å] *c* [Å]	20.8857(5) 10.4808(3) 26.6399(6)	9.4236(5) 12.6085(7) 16.8285 (11)	10.6429(2) 16.5905(6) 18.1520(4)	10.7476(19) 15.641(3) 15.787(4)
α [°] *β* [°] *γ* [°]	90 104.993(2) 90	89.856(5) 82.239(5) 86.530(5)	90 90 90	75.259(17) 81.060(17) 84.851(15)
V [Å^3]	5632.9(3)	1977.3(2)	3205.12(13)	2531.6(9)
Z	4	2	4	2
Radiation type λ [Å]	Cu *K*α 1.5406	Mo *K*α 0.71073	Mo *K*α 0.71073	Mo *K*α 0.71073
Calculated density [g·cm^{-3}]	1.206	1.302	1.828	1.713
μ [mm^{-1}]	2.07	2.35	1.37	0.25
Crystal size [mm]	0.41 × 0.19 × 0.14	0.32 × 0.03 × 0.02	0.41 × 0.25 × 0.15	0.2 × 0.12 × 0.03
F(000)	2700	844	1248	1416
R_{int}	0.021	0.060	0.036	0.049
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	 22952 8669 7684	 17723 7377 5163	 40069 8655 7952	 35942 13620 8449
$R[F^2 > 2\sigma(F^2)]$	0.097	0.080	0.044	0.056
$wR(F^2)$	0.249	0.165	0.110	0.110
S	1.07	1.19	1.15	1.04
No. of reflections	8669	7377	8655	13620
No. of parameters	918	404	339	852
No. of restraints	291	0	0	7
$\Delta>_{max}$ [e·Å^{-3}] $\Delta>_{min}$ [e·Å^{-3}]	1.12 -1.08	1.11 -1.16	1.22 -0.29	0.42 -0.39

	7[WCA]$_2$
CCDC deposition No	2379821
Chemical formula	$C_{16}AlF_{36}O_4^-$ ·0.5($C_{32}H_{52}B_2F_4N_6O_2^{2+}$)·$CH_2Cl_2$
M_r [g·mol^{-1}]	1377.27
Crystal system	monoclinic
Space group	$P2_1/n$
Temperature [K]	120
a [Å] *b* [Å] *c* [Å]	17.9189 (9) 16.7776 (8) 18.8717 (10)
α [°] *β* [°] *γ* [°]	90 115.592 (4) 90
V [Å^3]	5116.9 (5)
Z	4
Radiation type λ [Å]	Mo *K*α 0.71073
Calculated density [g·cm^{-3}]	1.788
μ [mm^{-1}]	0.33
Crystal size [mm]	0.12 × 0.09 × 0.08
F(000)	2724
R_{int}	0.070
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33476, 9528, 5449
$R[F^2 > 2\sigma(F^2)]$	0.095
$wR(F^2)$	0.197
S	1.13
No. of reflections	9528
No. of parameters	1042
No. of restraints	649
Δ>$_{max}$ [e·Å^{-3}] Δ>$_{min}$ [e·Å^{-3}]	0.56 -0.45

Structure of 1[WCA]

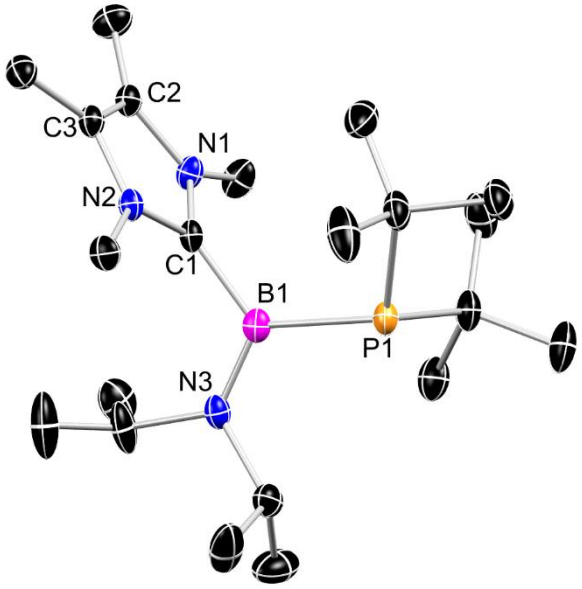


Figure S 74. Molecular structure of **1[WCA]**. The thermal ellipsoids are shown at a 30% probability level. The anion [WCA] and hydrogen atoms are omitted for clarity. Important bond distances [Å]: P1 – B1 1.994(5); N3 – B1 1.393(6); B1 – C1 1.604(7). Important angles [°]: N3 – B1 – P1 119.7(3); P1 – B1 – C1 122.3(3); C1 – B1 – N3 117.8(3).

Structure of $3[Br]_2$

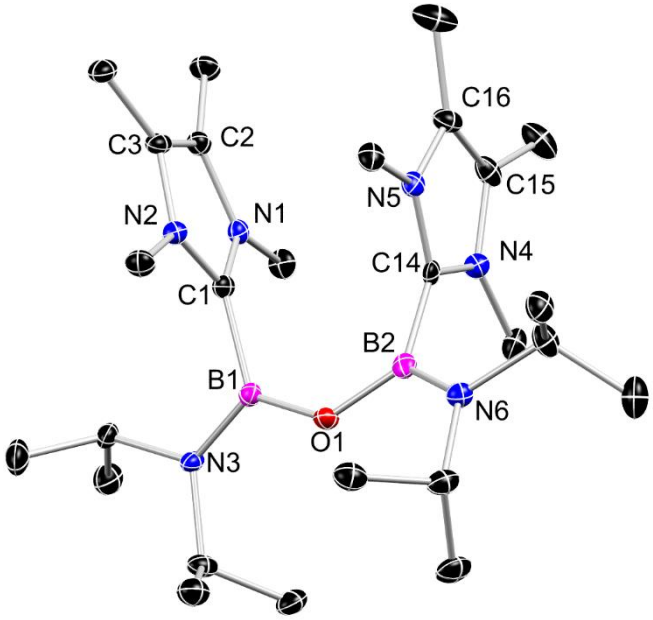


Figure S 75. Molecular structure of **$3[Br]_2$**. The thermal ellipsoids are shown at a 30% probability level. The two bromide anions, two solvent (CH_2Cl_2) molecules, and hydrogen atoms are omitted for clarity. Important bond distances [Å]: O1 – B1 1.394(9); O1 – B2 1.409(9); N3 – B1 1.373(9); N6 – B2 1.380(1); C1 – B1 1.590(1); C14 – B2 1.580(1). Important angles [°]:C1 – B1 – N3 118.3(6); N3 – B1 – O1 122.0(6); O1 – B2 – N6 121.9(6);N6 – B2 – C14 119.0(6); C14 – B2 – O1 119.(6); B2 – O1 – B1 131.4(6); O1 – B1 –C1 119.5(6).

Structure of 4[Br]

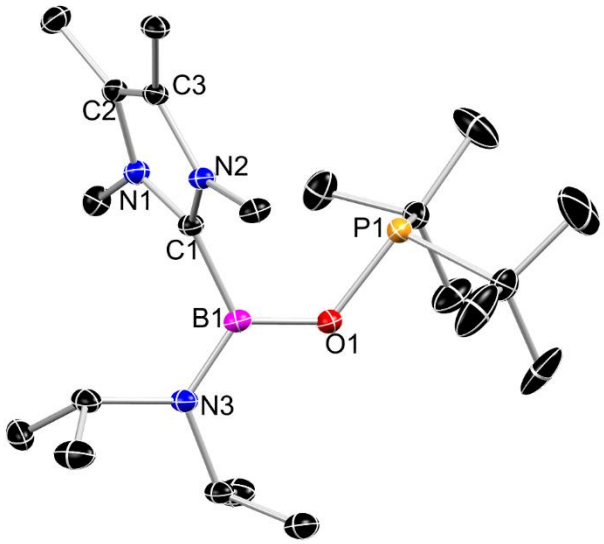


Figure S 76. Molecular structure of **4[Br]**. The thermal ellipsoids are shown at a 30% probability level. The bromide anion and hydrogen atoms are omitted for clarity. Important bond distances [Å]: O1 – B1 1.376(4); N3 – B1 1.393(4); C1 – B1 1.602(5); P1 – O1 1.668(3). Important angles [°]: P1 – O1 – B1 126.1(2); O1 – B1 – C1 118.8(3); C1 – B1 – N3 119.5(3); N3 – B1 – O1 121.7(3).

Structure of 6[WCA]

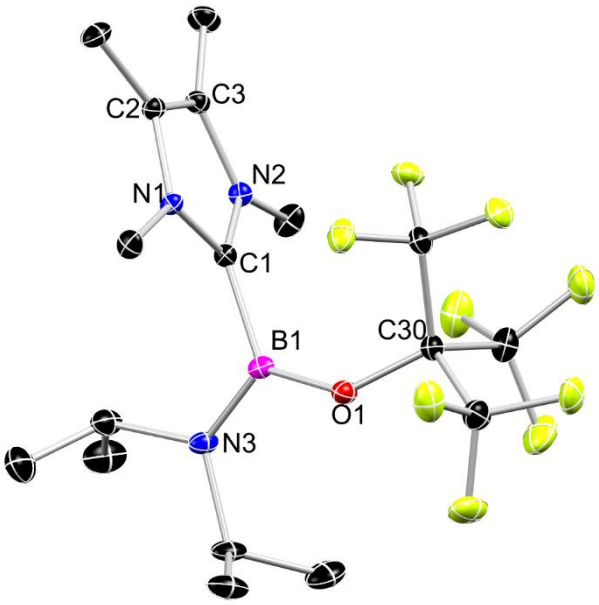


Figure S 77. Molecular structure of **6[WCA]**. The thermal ellipsoids are shown at a 30% probability level. The anion [WCA] and hydrogen atoms are omitted for clarity. Important bond distances [Å]: C1 – B1 1.595(4); O1 – C30 1.387(3); O1 – B1 1.395 (3); N3 – B1 1.386(4). Important angles [°]: O1 – B1 – C1 122.2(2); C1 – B1 – N3 118.9(2); N3 – B1 – O1 118.8(2); B1 – O1 – C30 137.2(2).

Structure of 7[WCA]$_2$

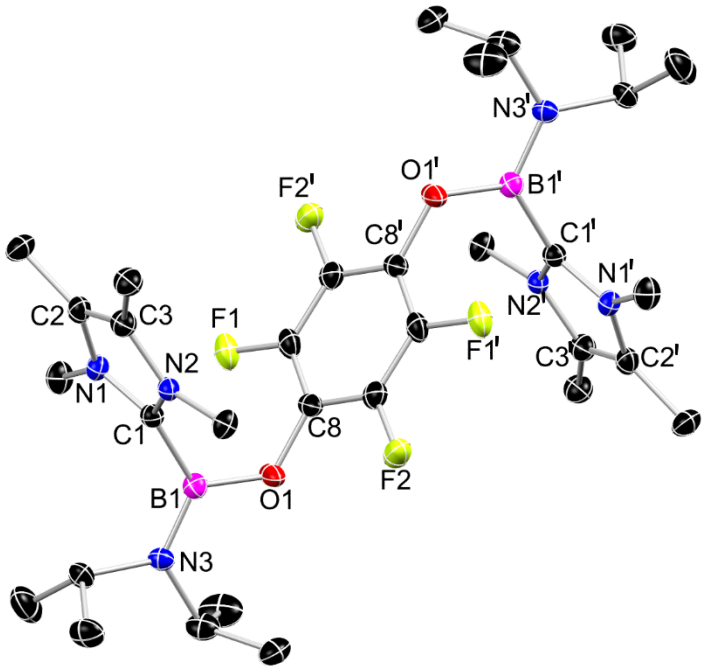


Figure S 78. Molecular structure of **7[WCA]$_2$**. The thermal ellipsoids are shown at a 30% probability level. The two anions [WCA], hydrogen atoms, and solvent molecule (CH_2Cl_2) are omitted for clarity. Important bond distances [Å]: C1 – B1 1.575(8); B1 – O1 1.390(1); O1 – C8 1.367(8); N3 – B1 1.388(9). Important angles [°]: C1 – B1 – O1 117.8(6); B1 – O1 – C8 124.5(5); C1 – B1 – N3 123.0(6); N3 – B1 – O1 119.1(6).

DFT calculations

General methods

The equilibrium structures and corresponding harmonic vibrational frequencies of all systems investigated in this work were calculated using density functional theory (DFT) with the ωB97xD[7] hybrid functional, and the 6-311++G(d,p)[8] basis set. Gibbs free energies (ΔG^{298}) related to the considered synthesis paths for the studied molecules were established accordingly, using ωB97xD/6-311++G(d,p) electronic energies with zero-point energy corrections, thermal corrections, and entropy contributions (at T=298.15 K). The effects of surrounding solvent molecules (dichloromethane) were obtained using the polarizable continuum model (the integral equation formalism variant: IEFPCM)[9]. The Natural Bond Orbital analysis was performed with the Gaussian NBO 7 module[10] All calculations were performed with Gaussian16 (Rev.C.01) software[11].

The Gibbs free energy profile corresponding to the activation of secondary phosphine oxide by $\mathbf{1}^{+}$ is presented in Figure S79, while the Cartesian coordinates of the equilibrium structures of all stationary points of the studied reaction are gathered in Table S3. In each case, the relevance of the transition state was confirmed by the analysis of the imaginary mode and IRC calculations. According to our calculations, the formation of the B-O bond in the adduct of *t*Bu_2P(O)H with $\mathbf{1}^{+}$ (labeled **IP** -*intermediate product*) proceeds via the transition state (labeled **TS1**) and requires surmounting a kinetic barrier of 24.7 kcal/mol. In the next reaction step, the proton transfer (from *t*Bu_2P(H)-O-B to the phosphorus of the phosphido group) requires overcoming a kinetic barrier of 29.0 kcal/mol. This leads to the final products and results in the departure of *t*Bu_2PH. The corresponding transition state (labeled **TS2** with the imaginary vibration of *i*1022 cm^{-1}) primarily indicates proton migration but is also associated with the P-B bond breakage in the substrate $\mathbf{1}^{+}$. Since the calculated kinetic barriers (at ωB97xD/6-311++G(d,p) level of theory) are substantial and seem to be overestimated, we decided to recalculate the electronic energies of all stationary points found for this reaction pathway at the MP2/6-311++G** level of theory. Our calculations indicate that both barriers have been reduced by 6 and 7.2 kcal/mol, which is more consistent with the fact that the reaction occurs within a reasonable time.

Table S 3. Cartesian coordinates (in Å) of all studied molecules determined at the ωB97xD/ 6-311++G(d,p) theory level in dichloromethane solution (using PCM model).

1^{+}			
15	1.632423000	-0.799865000	-0.632045000
7	-2.206567000	0.052365000	-0.825045000
7	-1.773965000	-0.327322000	1.241995000
7	0.597635000	1.922797000	-0.177784000
6	-1.238862000	0.135430000	0.104059000
6	-3.088788000	-0.713640000	1.040003000
6	-3.363145000	-0.473957000	-0.270172000
6	-1.088443000	-0.436509000	2.518801000
1	-0.090063000	-0.016134000	2.425317000
1	-1.633263000	0.121992000	3.280141000
6	-4.600249000	-0.685402000	-1.066760000
1	-4.966674000	0.253775000	-1.488646000
1	-5.384396000	-1.099754000	-0.434833000
1	-4.425480000	-1.382796000	-1.889869000
6	-2.124195000	0.518849000	-2.202927000
1	-2.811916000	1.351899000	-2.347440000
1	-2.388136000	-0.289478000	-2.883435000
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6	1.680900000	3.051277000	-2.087979000
1	1.039843000	3.935507000	-2.026720000
1	1.225228000	2.337786000	-2.779170000
1	2.642329000	3.366280000	-2.500877000
6	2.650862000	3.346553000	0.228919000
1	2.271649000	4.370814000	0.199161000
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1	2.615079000	2.997192000	1.261519000
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6	-0.566180000	2.954485000	1.782637000
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1	0.349596000	2.772179000	2.348723000
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1	4.022276000	-2.574991000	-0.059852000
1	4.756138000	-1.715828000	1.295321000
1	4.532740000	-0.895056000	-0.259456000
6	2.951022000	0.219597000	1.657277000
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1	2.027788000	0.691579000	2.002127000
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6	1.845486000	-3.509645000	-1.297505000
1	2.678665000	-3.158378000	-1.912031000

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6	0.184224000	-2.163836000	-2.525018000
1	-0.567020000	-1.376235000	-2.515110000
1	-0.302637000	-3.074405000	-2.890997000
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5	0.279763000	0.563795000	-0.155566000
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1	3.484939000	0.931700000	1.027465000
1	2.026532000	-3.112564000	1.519697000
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7	-1.310745000	2.111917000	0.072838000
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6	-3.033794000	-2.229494000	-0.532271000
6	-1.333128000	-0.874988000	2.346592000
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6	-2.493284000	-0.676944000	-2.431308000
1	-3.532561000	-0.604275000	-2.750876000
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1	-2.018432000	0.295962000	-2.536522000
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1	0.515981000	4.646322000	1.464394000
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6	-3.254451000	1.856433000	1.653968000
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6	-3.649286000	2.218190000	-0.819644000
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1	5.513659000	1.824392000	0.328522000
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1	1.938727000	3.919739000	-3.134916000
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6	2.459419000	3.904308000	-0.217225000
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1	2.467827000	4.633693000	-1.025490000
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1	1.766070000	2.291656000	2.033498000
6	1.927668000	-3.243639000	0.900403000
1	2.908543000	-3.627392000	1.183287000
6	1.369555000	-4.191052000	-0.159711000
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1	3.586367000	-0.470448000	-0.162397000
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1	4.309742000	-3.396317000	-0.619496000
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5	1.130676000	-1.044635000	-0.035638000
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1	-3.134775000	-3.535024000	1.017461000
4^+			
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6	-3.176510000	-0.194601000	1.172756000
6	-3.784500000	1.115545000	0.655922000
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1	-0.231928000	-1.924252000	-1.971335000
1	-1.203111000	-1.644226000	-3.420852000
6	-4.262934000	-1.272010000	1.293033000
1	-3.851402000	-2.240626000	1.595151000
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1	-3.805311000	-2.733863000	-1.028540000
1	-3.100265000	-2.955744000	-2.629373000
1	-2.173322000	-3.398831000	-1.189490000
6	-3.259216000	-0.261952000	-2.232318000
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6	-2.576914000	0.060683000	2.568976000
1	-2.150821000	-0.849400000	3.000133000
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7	1.622134000	-1.203481000	1.279868000
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7	1.013151000	2.040000000	-0.108009000
6	2.487645000	-2.257571000	1.043514000
6	0.997444000	-0.921527000	2.563605000
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6	2.878299000	-3.217769000	2.109072000
1	2.000296000	-3.699492000	2.545958000
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1	3.426713000	-2.718284000	2.911824000
6	2.467771000	2.270694000	-0.016286000
1	2.936024000	1.286193000	0.037802000
6	0.177420000	3.257381000	-0.214608000

1	0.869803000	4.093665000	-0.325778000
6	2.843647000	3.008076000	1.268798000
1	2.468752000	2.468813000	2.142363000
1	3.930677000	3.085508000	1.348328000
1	2.436568000	4.022742000	1.288274000
6	2.339426000	-0.599140000	-2.154126000
1	3.382399000	-0.330562000	-2.323036000
1	2.039245000	-1.370886000	-2.862112000
1	1.716202000	0.280885000	-2.295885000
6	3.024555000	2.964947000	-1.260279000
1	2.686208000	4.000979000	-1.340786000
1	4.115969000	2.980092000	-1.212624000
1	2.728181000	2.439316000	-2.170583000
6	3.746602000	-3.021746000	-1.093753000
1	4.579145000	-2.436017000	-1.491860000
1	4.160347000	-3.827885000	-0.489623000
1	3.212415000	-3.468845000	-1.935827000
6	-0.618894000	3.507083000	1.065631000
1	0.049782000	3.584460000	1.925871000
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1	-1.325506000	2.697953000	1.250011000
5	0.456368000	0.764254000	-0.005305000
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1	-1.455448000	2.457845000	-1.407049000
1	-1.204814000	4.203925000	-1.575499000
1	-0.088565000	3.070652000	-2.356079000
1	-3.015986000	1.833502000	0.367009000
6	-0.986706000	-1.267706000	-2.416336000
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1	-2.918209000	0.771147000	-2.132203000
1	-1.798557000	0.828454000	2.537660000
1	-3.363219000	0.416033000	3.242415000
1	-4.988776000	-0.969132000	2.054550000
6^{+}			
6	2.033414000	-0.315698000	2.403289000
1	2.998576000	-0.013893000	2.808428000
1	1.362394000	0.539439000	2.415459000
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6	2.236165000	2.593170000	0.041919000
6	2.723248000	3.328691000	-1.205580000
1	2.232129000	4.296782000	-1.331954000
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6	2.489342000	3.387673000	1.322479000
1	2.148670000	2.835217000	2.200967000
1	3.560432000	3.573602000	1.428436000
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6	-1.158356000	3.352638000	0.923897000
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1	-1.715415000	4.291541000	0.878844000
1	-1.874948000	2.535984000	0.859688000
7	2.212165000	-0.762207000	1.028052000
7	0.815971000	2.186955000	-0.076334000
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7	2.096573000	-0.884498000	-1.114875000
6	3.058088000	-1.796200000	-0.721061000

6	3.129196000	-1.720831000	0.638175000
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1	1.506694000	-1.474369000	-3.036842000
1	0.963415000	0.140365000	-2.541766000
6	3.801563000	-2.636190000	-1.696083000
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1	4.514737000	-3.272182000	-1.174006000
1	3.122098000	-3.280701000	-2.259239000
6	3.970123000	-2.457733000	1.617473000
1	4.607406000	-1.775690000	2.185765000
1	3.351618000	-3.014808000	2.325301000
1	4.614063000	-3.166094000	1.098645000
1	1.613103000	-1.119063000	3.006876000
1	2.545216000	2.732342000	-2.103204000
1	0.449012000	4.218308000	-0.141713000
6	-0.147442000	3.308983000	-0.218028000
6	-0.800294000	3.322412000	-1.598977000
1	-1.411870000	4.221826000	-1.704619000
1	-1.443768000	2.455284000	-1.746241000
1	-0.040029000	3.332143000	-2.383271000
8	-0.896671000	0.521085000	-0.322108000
6	-1.746186000	-0.506520000	-0.002304000
6	-3.065187000	-0.199182000	-0.801745000
9	-2.891484000	-0.467806000	-2.095651000
9	-3.383663000	1.084763000	-0.693314000
9	-4.088888000	-0.923104000	-0.353474000
6	-1.214162000	-1.924778000	-0.422430000
9	-0.639611000	-1.862417000	-1.620371000
9	-2.193747000	-2.820174000	-0.478845000
9	-0.300337000	-2.368756000	0.446524000
9	-2.845314000	0.512992000	1.867151000
6	-2.048468000	-0.498655000	1.537797000
9	-0.904514000	-0.345497000	2.210488000
5	0.452330000	0.853224000	-0.100383000
9	-2.619532000	-1.629238000	1.939779000
7^{2+}			
9	-1.858287000	0.672056000	1.853193000
9	0.760708000	1.018074000	2.392554000
8	-2.674268000	-0.354190000	-0.576689000
7	-2.934414000	-2.248524000	2.408712000
7	-1.936290000	-3.281700000	0.810466000
7	-4.808675000	-1.457505000	-0.350264000
6	-2.802697000	-2.297358000	1.077731000
6	-2.140753000	-3.214658000	3.000267000
6	-1.505882000	-3.869078000	1.986061000
6	-3.820730000	-1.347439000	3.135285000
1	-4.257465000	-0.638058000	2.435436000
1	-3.253643000	-0.803670000	3.888969000
1	-4.614972000	-1.922028000	3.611696000
6	-2.082072000	-3.399494000	4.474020000
1	-1.708291000	-2.500160000	4.969602000
1	-1.415645000	-4.224519000	4.721573000
1	-3.069706000	-3.627668000	4.882337000
6	-0.534483000	-4.993887000	1.998625000

1	-0.937760000	-5.870822000	1.485857000
1	-0.305379000	-5.278313000	3.024239000
1	0.399961000	-4.712307000	1.507078000
6	-1.520660000	-3.697090000	-0.522865000
1	-2.082100000	-3.135154000	-1.267175000
1	-1.729505000	-4.757765000	-0.655240000
1	-0.454075000	-3.514361000	-0.653376000
6	-1.368808000	-0.194631000	-0.276781000
6	-0.948678000	0.332952000	0.939355000
6	0.395064000	0.514724000	1.215892000
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1	-6.483181000	-0.921201000	-1.440678000
6	-4.814487000	-0.684871000	-2.725374000
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1	-4.784658000	-1.729523000	-3.044565000
6	-5.523903000	0.872257000	-0.835777000
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1	-5.038632000	-3.068978000	0.929966000
6	-6.021181000	-3.552685000	-0.887732000
1	-6.648478000	-3.106189000	-1.663946000
1	-6.578655000	-4.381882000	-0.446384000
1	-5.119691000	-3.951454000	-1.359731000
6	-6.874127000	-1.997823000	0.935112000
1	-6.579419000	-1.268223000	1.692957000
1	-7.394031000	-2.819363000	1.432634000
1	-7.586823000	-1.519295000	0.258988000
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9	1.858287000	-0.672056000	-1.853193000
9	-0.760708000	-1.018074000	-2.392554000
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7	2.934414000	2.248524000	-2.408712000
7	1.936290000	3.281700000	-0.810466000
7	4.808675000	1.457505000	0.350264000
6	2.802697000	2.297358000	-1.077731000
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1	3.253643000	0.803670000	-3.888969000
1	4.614972000	1.922028000	-3.611696000
6	2.082072000	3.399494000	-4.474020000
1	1.708291000	2.500160000	-4.969602000
1	1.415645000	4.224519000	-4.721573000
1	3.069706000	3.627668000	-4.882337000
6	0.534483000	4.993887000	-1.998625000
1	0.937760000	5.870822000	-1.485857000
1	0.305379000	5.278313000	-3.024239000
1	-0.399961000	4.712307000	-1.507078000
6	1.520660000	3.697090000	0.522865000
1	2.082100000	3.135154000	1.267175000
1	1.729505000	4.757765000	0.655240000

1	0.454075000	3.514361000	0.653376000
6	1.368808000	0.194631000	0.276781000
6	0.948678000	-0.332952000	-0.939355000
6	-0.395064000	-0.514724000	-1.215892000
6	5.456135000	0.566322000	1.343644000
1	6.483181000	0.921201000	1.440678000
6	4.814487000	0.684871000	2.725374000
1	3.798169000	0.289093000	2.731866000
1	5.406866000	0.122521000	3.451042000
1	4.784658000	1.729523000	3.044565000
6	5.523903000	-0.872257000	0.835777000
1	6.018458000	-0.908780000	-0.137844000
1	6.097257000	-1.485089000	1.535538000
1	4.526797000	-1.305989000	0.738721000
6	5.652362000	2.541809000	-0.196311000
1	5.038632000	3.068978000	-0.929966000
6	6.021181000	3.552685000	0.887732000
1	6.648478000	3.106189000	1.663946000
1	6.578655000	4.381882000	0.446384000
1	5.119691000	3.951454000	1.359731000
6	6.874127000	1.997823000	-0.935112000
1	6.579419000	1.268223000	-1.692957000
1	7.394031000	2.819363000	-1.432634000
1	7.586823000	1.519295000	-0.258988000
5	3.482383000	1.333006000	-0.010547000
TS1 (*i*42 cm^{-1})			
15	0.148329000	1.574139000	-0.913440000
7	1.549411000	-2.359156000	-0.233364000
7	2.883222000	-0.700290000	-0.035199000
7	0.579372000	0.311988000	1.983614000
6	1.577009000	-1.039991000	0.041709000
6	3.666669000	-1.792886000	-0.368639000
6	2.822751000	-2.844702000	-0.492781000
6	3.470946000	0.616435000	0.139458000
1	4.186839000	0.593741000	0.959945000
1	3.988307000	0.906782000	-0.774712000
6	3.078927000	-4.271755000	-0.823676000
1	2.518087000	-4.581175000	-1.709141000
1	2.796961000	-4.931002000	0.001537000
1	4.138444000	-4.422268000	-1.026740000
6	0.415588000	-3.259040000	-0.120369000
1	0.628510000	-4.017237000	0.635353000
1	0.236371000	-3.748384000	-1.077826000
1	-0.451294000	-2.681976000	0.169404000
6	1.085356000	1.576414000	2.532625000
1	1.261515000	2.201458000	1.671393000
6	0.100448000	2.315061000	3.448092000
1	-0.250758000	1.666745000	4.257228000
1	-0.769787000	2.680550000	2.905966000
1	0.593044000	3.177634000	3.906105000
6	2.431259000	1.467453000	3.272295000
1	3.151014000	0.849362000	2.739861000
1	2.316397000	1.053270000	4.277954000
1	2.859726000	2.467673000	3.383056000
6	0.577989000	-0.765187000	2.999538000

6	1.737987000	-1.775689000	2.942380000
1	1.556977000	-2.581194000	2.229969000
1	1.848257000	-2.242782000	3.925277000
1	2.686437000	-1.299934000	2.690514000
6	-0.751607000	-1.501722000	3.141023000
1	-1.549765000	-0.791767000	3.359369000
1	-0.689497000	-2.208543000	3.974052000
1	-1.017869000	-2.055025000	2.240403000
6	0.801469000	3.409816000	-0.890514000
6	-0.287921000	4.208409000	-1.643248000
1	-0.471692000	3.856710000	-2.654225000
1	0.023606000	5.257537000	-1.709445000
1	-1.234149000	4.169888000	-1.097483000
6	0.848781000	4.054196000	0.503558000
1	0.848727000	5.141228000	0.370808000
1	1.760276000	3.812088000	1.052041000
6	2.162294000	3.666642000	-1.550023000
1	2.968536000	3.121469000	-1.055320000
1	2.396517000	4.734883000	-1.472262000
6	0.671212000	0.838891000	-2.625381000
6	0.152802000	1.743253000	-3.759132000
1	-0.904893000	1.986085000	-3.630039000
1	0.257889000	1.204137000	-4.707321000
1	0.716218000	2.671112000	-3.857500000
6	2.160922000	0.563404000	-2.892381000
1	2.289142000	0.321593000	-3.953979000
1	2.521905000	-0.297203000	-2.331450000
6	-0.072484000	-0.492278000	-2.802850000
1	0.158446000	-1.213619000	-2.022900000
1	0.213825000	-0.937736000	-3.762035000
1	-1.152323000	-0.337145000	-2.830165000
5	0.454174000	0.069411000	0.529224000
6	5.139234000	-1.692580000	-0.548434000
1	5.626363000	-1.317756000	0.355244000
1	5.554972000	-2.674188000	-0.771994000
1	5.394666000	-1.021477000	-1.372986000
1	2.691745000	1.338479000	0.351037000
1	0.702776000	-0.244306000	3.950289000
1	-0.021144000	3.803437000	1.113768000
1	2.174895000	3.413431000	-2.609488000
1	2.800150000	1.416553000	-2.675206000
8	-1.103218000	-0.728151000	0.224012000
15	-2.524986000	-0.342017000	-0.273027000
6	-3.436498000	-1.717090000	-1.173300000
6	-3.569114000	0.499942000	1.005021000
6	-4.079449000	-1.048649000	-2.404522000
1	-4.724501000	-0.208613000	-2.139500000
1	-3.327891000	-0.690354000	-3.111979000
1	-4.696264000	-1.790677000	-2.918921000
6	-4.532220000	-2.375446000	-0.322482000
1	-4.138622000	-2.791781000	0.606538000
1	-5.349507000	-1.693734000	-0.088428000
1	-4.955334000	-3.200655000	-0.902308000
6	-2.490132000	-2.828330000	-1.640281000
1	-3.043041000	-3.468225000	-2.334130000

1	-1.609540000	-2.456898000	-2.160661000
1	-2.174676000	-3.450683000	-0.803355000
6	-2.646233000	1.568000000	1.603373000
1	-2.254029000	2.246696000	0.840524000
1	-3.211336000	2.154648000	2.333607000
1	-1.799297000	1.101724000	2.102756000
6	-4.750885000	1.188579000	0.303291000
1	-5.284456000	1.787707000	1.046636000
1	-4.419848000	1.864874000	-0.489694000
1	-5.466476000	0.479399000	-0.116588000
6	-4.075054000	-0.419536000	2.129921000
1	-4.998164000	-0.929518000	1.861076000
1	-3.342394000	-1.171654000	2.421407000
1	-4.283521000	0.195181000	3.009981000
1	-2.415067000	0.660270000	-1.247519000
Intermediate product (IP)			
15	0.073472000	1.612827000	-0.817832000
7	1.714313000	-2.256550000	-0.404259000
7	2.914628000	-0.524205000	-0.047969000
7	0.465939000	0.118298000	2.006666000
6	1.633353000	-0.962310000	-0.036700000
6	3.785654000	-1.534438000	-0.426519000
6	3.026241000	-2.632216000	-0.651787000
6	3.404793000	0.824308000	0.184580000
1	4.104767000	0.830410000	1.017923000
1	3.914181000	1.181213000	-0.710066000
6	3.397058000	-4.010781000	-1.069191000
1	2.857765000	-4.311605000	-1.970766000
1	3.177051000	-4.740208000	-0.284975000
1	4.464159000	-4.060715000	-1.282575000
6	0.633508000	-3.223395000	-0.448191000
1	0.912290000	-4.105996000	0.128185000
1	0.440407000	-3.519746000	-1.479742000
1	-0.250953000	-2.770576000	-0.021129000
6	1.110382000	1.265278000	2.656109000
1	1.315183000	1.968613000	1.861859000
6	0.210418000	1.977896000	3.674211000
1	-0.097511000	1.297307000	4.474295000
1	-0.689337000	2.382477000	3.212424000
1	0.752776000	2.807549000	4.137783000
6	2.459143000	0.963966000	3.338030000
1	3.088093000	0.307092000	2.739832000
1	2.326798000	0.491454000	4.315446000
1	3.000774000	1.900001000	3.501933000
6	0.399948000	-1.043633000	2.921809000
6	1.459619000	-2.147565000	2.744675000
1	1.163151000	-2.885052000	1.998929000
1	1.570041000	-2.685315000	3.690870000
1	2.438006000	-1.750371000	2.471244000
6	-0.982093000	-1.678920000	3.047351000
1	-1.714081000	-0.923226000	3.332871000
1	-0.963284000	-2.443748000	3.829983000
1	-1.304258000	-2.151919000	2.118292000
6	0.600935000	3.467342000	-0.610646000
6	-0.536525000	4.273262000	-1.278147000

1	-0.687998000	4.024165000	-2.325496000
1	-0.297707000	5.342081000	-1.221650000
1	-1.481754000	4.109526000	-0.753890000
6	0.609807000	3.933374000	0.852127000
1	0.525560000	5.025294000	0.863903000
1	1.540920000	3.689581000	1.365252000
6	1.938950000	3.887237000	-1.232676000
1	2.783975000	3.347522000	-0.801554000
1	2.099941000	4.953765000	-1.036089000
6	0.650965000	1.053789000	-2.574294000
6	0.079888000	2.021656000	-3.627237000
1	-0.991849000	2.183411000	-3.486521000
1	0.225254000	1.583137000	-4.621038000
1	0.580678000	2.990001000	-3.630263000
6	2.156446000	0.900401000	-2.846462000
1	2.306476000	0.735029000	-3.919916000
1	2.575837000	0.034665000	-2.335154000
6	-0.001875000	-0.305244000	-2.872439000
1	0.273225000	-1.073874000	-2.153713000
1	0.321268000	-0.647722000	-3.861599000
1	-1.089961000	-0.224787000	-2.901945000
5	0.384420000	-0.012282000	0.514291000
6	5.252154000	-1.319221000	-0.546050000
1	5.684838000	-0.987428000	0.401153000
1	5.742544000	-2.248470000	-0.832763000
1	5.484254000	-0.567061000	-1.304777000
1	2.570832000	1.479625000	0.399448000
1	0.592702000	-0.623484000	3.909963000
1	-0.230459000	3.535954000	1.423916000
1	1.962434000	3.754773000	-2.314128000
1	2.729855000	1.783457000	-2.571405000
8	-1.029108000	-0.801745000	0.145867000
15	-2.466373000	-0.399918000	-0.330092000
6	-3.344072000	-1.788052000	-1.237013000
6	-3.532578000	0.443161000	0.938307000
6	-4.013513000	-1.128337000	-2.459403000
1	-4.686814000	-0.313697000	-2.188029000
1	-3.275846000	-0.740419000	-3.165900000
1	-4.605375000	-1.887792000	-2.977476000
6	-4.410401000	-2.492055000	-0.387508000
1	-4.001312000	-2.889431000	0.543189000
1	-5.254264000	-1.842503000	-0.156593000
1	-4.798592000	-3.334437000	-0.966871000
6	-2.357805000	-2.850808000	-1.729640000
1	-2.891857000	-3.505479000	-2.424107000
1	-1.505558000	-2.428292000	-2.259323000
1	-2.000264000	-3.467846000	-0.906052000
6	-2.632976000	1.498593000	1.595894000
1	-2.228574000	2.198409000	0.860904000
1	-3.228897000	2.060092000	2.321334000
1	-1.794809000	1.029029000	2.108867000
6	-4.669682000	1.156162000	0.184721000
1	-5.225408000	1.758244000	0.909176000
1	-4.294521000	1.832418000	-0.588373000
1	-5.377633000	0.458650000	-0.267061000

6	-4.127928000	-0.475576000	2.020902000
1	-5.066925000	-0.924557000	1.702528000
1	-3.455763000	-1.274879000	2.325036000
1	-4.338869000	0.130783000	2.905810000
1	-2.354379000	0.600603000	-1.300882000
TS2 (*i*1022 cm^{-1})			
15	-0.026257000	1.456708000	-0.972178000
7	1.939709000	-2.100950000	-0.273039000
7	2.896634000	-0.221044000	0.067777000
7	0.543138000	0.261111000	2.036009000
6	1.690139000	-0.826870000	0.083340000
6	3.895164000	-1.104959000	-0.299095000
6	3.289836000	-2.298945000	-0.516978000
6	3.186857000	1.160158000	0.401363000
1	3.747580000	1.206506000	1.335319000
1	3.777523000	1.607367000	-0.398086000
6	3.839511000	-3.618483000	-0.926018000
1	3.383081000	-3.968776000	-1.855187000
1	3.667360000	-4.377151000	-0.158013000
1	4.914031000	-3.540845000	-1.086494000
6	0.975824000	-3.182081000	-0.354168000
1	1.279962000	-3.995510000	0.305435000
1	0.917391000	-3.550696000	-1.379318000
1	0.013493000	-2.794205000	-0.047015000
6	0.168102000	1.498116000	2.719653000
1	-0.240920000	2.140866000	1.952411000
6	-0.914710000	1.355435000	3.804453000
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1	-0.510336000	0.968570000	4.743901000
1	-1.720436000	0.697078000	3.487872000
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1	2.134852000	2.457572000	2.587933000
1	1.832435000	1.641090000	4.123498000
1	1.043028000	3.180849000	3.776622000
6	0.994037000	-0.780552000	2.988433000
6	2.493116000	-1.121439000	2.980554000
1	2.781873000	-1.787741000	2.164964000
1	2.742193000	-1.637296000	3.912872000
1	3.101865000	-0.216974000	2.929195000
6	0.162005000	-2.064302000	2.971220000
1	-0.899000000	-1.844697000	3.092531000
1	0.475672000	-2.715035000	3.793145000
1	0.284009000	-2.622750000	2.044076000
6	0.142340000	3.374723000	-0.912636000
6	-1.051134000	3.975752000	-1.681303000
1	-1.070025000	3.700912000	-2.732911000
1	-0.991606000	5.068676000	-1.626557000
1	-1.999343000	3.670093000	-1.233315000
6	0.058077000	3.937877000	0.509688000
1	0.090654000	5.030047000	0.440273000
1	0.898214000	3.631096000	1.132072000
6	1.457971000	3.891933000	-1.513632000
1	2.329266000	3.513721000	-0.975210000
1	1.471334000	4.984178000	-1.431457000
6	0.647576000	0.859101000	-2.666423000

6	0.018746000	1.685136000	-3.803562000
1	-1.069137000	1.732096000	-3.713033000
1	0.252255000	1.191995000	-4.753305000
1	0.408779000	2.700095000	-3.867530000
6	2.173810000	0.852648000	-2.847499000
1	2.399945000	0.679648000	-3.905611000
1	2.643338000	0.044815000	-2.288572000
6	0.138014000	-0.572859000	-2.876944000
1	0.429664000	-1.246911000	-2.075494000
1	0.555705000	-0.967775000	-3.808836000
1	-0.949274000	-0.591130000	-2.974331000
5	0.327107000	-0.044271000	0.590360000
6	5.319960000	-0.695230000	-0.409959000
1	5.456800000	0.061489000	-1.187639000
1	5.687852000	-0.281654000	0.532453000
1	5.937484000	-1.555338000	-0.665624000
1	2.256328000	1.702280000	0.514408000
1	0.823150000	-0.348521000	3.974831000
1	-0.879946000	3.680677000	1.005052000
1	1.573240000	3.649124000	-2.568282000
1	2.645006000	1.791898000	-2.561981000
8	-0.963034000	-0.908074000	0.319830000
15	-2.359342000	-0.556038000	-0.404355000
6	-3.110550000	-2.130743000	-1.131120000
6	-3.534745000	0.198210000	0.843338000
6	-3.999475000	-1.659071000	-2.298511000
1	-4.773973000	-0.955901000	-1.992782000
1	-3.403938000	-1.188706000	-3.085711000
1	-4.499075000	-2.531348000	-2.730668000
6	-3.932175000	-2.949114000	-0.123267000
1	-3.335577000	-3.227961000	0.748306000
1	-4.831381000	-2.438013000	0.215767000
1	-4.251728000	-3.873418000	-0.615640000
6	-2.046289000	-3.079220000	-1.696551000
1	-2.554399000	-3.806209000	-2.337227000
1	-1.289104000	-2.583187000	-2.299071000
1	-1.559289000	-3.639260000	-0.900427000
6	-2.990806000	1.613783000	1.096999000
1	-3.044552000	2.226025000	0.193904000
1	-3.592684000	2.097739000	1.871688000
1	-1.961879000	1.597868000	1.441226000
6	-4.945224000	0.373695000	0.258426000
1	-5.534327000	0.959453000	0.970898000
1	-4.928430000	0.929077000	-0.683657000
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1	-1.689420000	0.696935000	-1.160103000

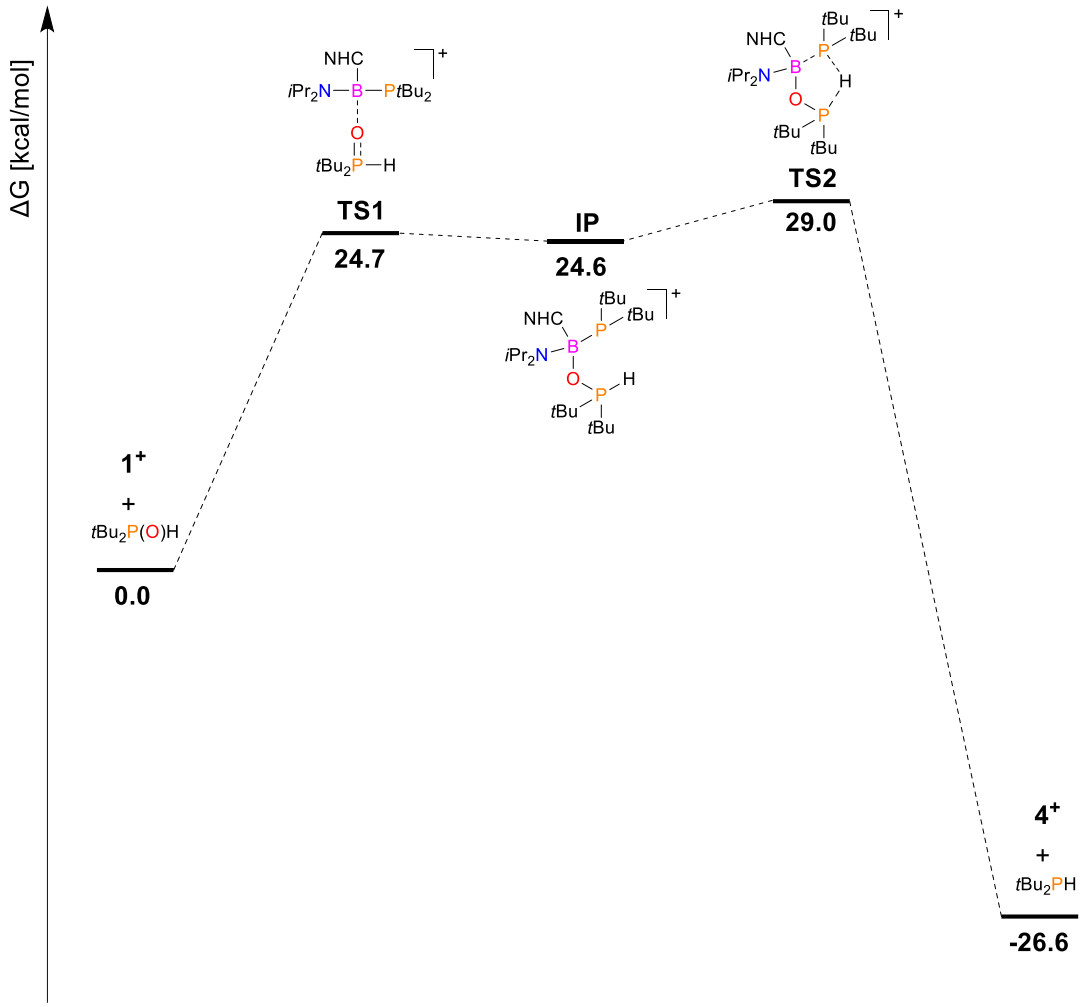

Figure S 79. Gibbs free energy profile for the reaction of **1**$^{+}$ with *t*Bu$_2$P(O)H.

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