Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Application of nonmetallic frustrated cations in the activation of small molecules

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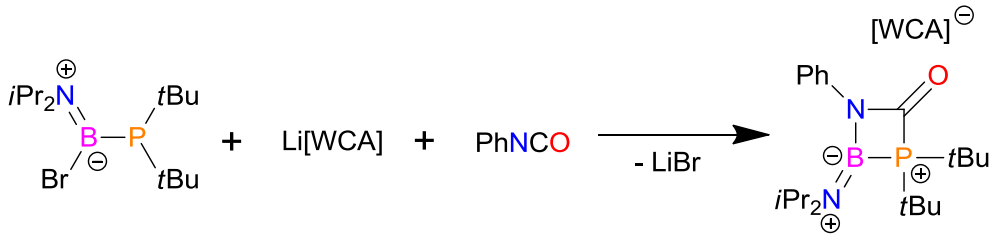
Experimental section

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 was 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 3.5 software. Elemental analyses of all compounds 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). (iPr$_2$N)B(Br)PtBu$_2$[1] and Li[Al(OC(CF$_3$)$_3$)$_4$][2] were prepared according to literature procedures.

Preparation of 3



1 **3**

Scheme S1. Synthesis of **3**

A solution of phenyl isocyanate in CH_2Cl_2 (0.25 M, 1 mL) was added dropwise to a stirred suspension of **1** (0.084 g, 0.250 mmol) and Li[Al(OC(CF$_3$)$_3$)$_4$] (0.244 g, 0.250 mmol) in CH_2Cl_2 (4 mL) at -70 °C. The mixture was allowed to warm to room temperature and stirred overnight. Filtration to separate the white precipitate of LiBr, followed by the evaporation of the solvent under reduced pressure, afforded a light yellow oily residue. Slow cooling of the resulting oil layered with 2 mL of pentane to +4 °C gave suitable light yellow crystals for X-ray diffraction. Yield: 56.0% (0.200 g, 0.140 mmol). **Elemental analysis** calc. for $C_{37}H_{37}AlBF_{36}N_2O_5P$ (1342.41 g/mol): C, 33.10; H, 2.78; N, 2.09. Found: C, 33.50; H, 2.61; N 2.00.

NMR data of 3

^{11}B NMR (CD_2Cl_2): δ 28.7 (bd, $^1J_{BP}$ = 119.3 Hz).

^{31}P{^{1}H} NMR (CD_2Cl_2): δ 66.8 (bm).

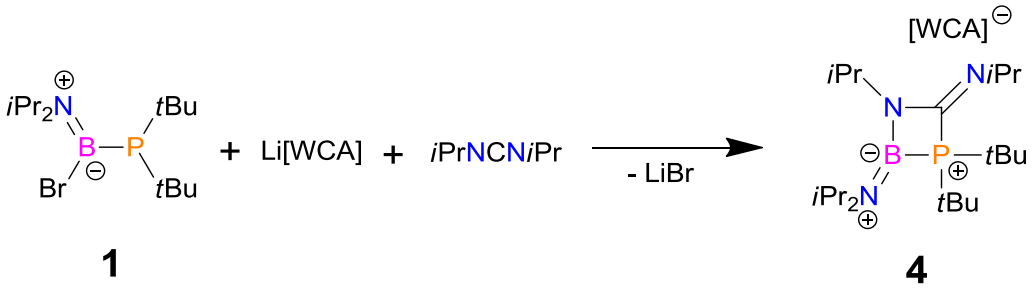
^{1}H NMR (CD_2Cl_2): δ 7.49 (1 H, m, *p*-C***H*** of Ph); 7.47 (2 H, m, *o*-C***H*** of Ph); 7.07 (2 H, m, *o*-C***H*** of Ph); 3.50 (1 H, sept, $^3J_{HH}$ = 6.7 Hz, C***H***$(CH_3)_2$); 3.39 (1 H, dsept, $^3J_{HH}$ = 7.0 Hz, $^4J_{PH}$ = 1.5 Hz, C***H***$(CH_3)_2$); 1.62 (18 H, d, $^3J_{PH}$ = 17.5 Hz, C(C***H***$_3)_3$); 1.34 (6 H, d, $^3J_{HH}$ = 6.7 Hz, CH(C***H***$_3)_2$); 0.92 (6 H, d, $^3J_{HH}$ = 7.0 Hz, CH(C***H***$_3)_2$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 165.0 (d, $^1J_{CP}$ = 66.2 Hz, N***C***O); 135.6 (d, $^3J_{CP}$ = 20.1 Hz, *ipso*-***C*** of Ph); 130.4 (s, *p*-***C***H of PPh); 130.2 (s, *o*-***C***H of PPh); 126.9 (s, *m*-***C***H of PPh); 121.2 (q, $^1J_{CF}$ = 292.6 Hz, OC(***C***$F_3)_3$); 59.9 (d, $^3J_{CP}$ = 6.3 Hz, ***C***H$(CH_3)_2$); 47.2 (d, $^3J_{CP}$ = 6.3 Hz, ***C***H$(CH_3)_2$); 37.3 (d, $^1J_{CP}$ = 11.9 Hz, ***C***$(CH_3)_3$); 28.4 (d, $^2J_{CP}$ = 1.9 Hz, C(***C***$H_3)_3$); 23.6 (s, CH(***C***$H_3)_2$); 22.5 (s, CH(***C***$H_3)_2$).

^{27}Al NMR (CD_2Cl_2): δ 34.2 (s, [***Al***$(OC(CF_3)_3)_4]^-$).

^{19}F{^{1}H} (CD_2Cl_2): δ -75.7 (s, OC(C***F***$_3)_3$).

Preparation of 4



Scheme S2. Synthesis of **4**

A solution of *N,N'*-diisopropylcarbodiimide in CH_2Cl_2 (0.25 M, 1 mL) was added dropwise to a stirred suspension of **1** (0.084 g, 0.250 mmol) and Li[$Al(OC(CF_3)_3)_4$] (0.244 g, 0.250 mmol) in CH_2Cl_2 (4 mL) at -70 °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 and left at -20 °C to afford colourless crystals. Yield: 61% (0.207 g, 0.153 mmol). **Elemental analysis** calc. for $C_{37}H_{46}AlBF_{36}N_3O_4P$ (1349.49 g/mol): C, 32.93; H, 3.44; N, 3.11. Found: C, 33.20; H, 3.23; N, 3.01.

NMR data of 4

^{11}B NMR (CD_2Cl_2): δ 27.4 (bd, $^1J_{BP}$ = 106.4 Hz).

^{31}P{^{1}H} NMR (CD_2Cl_2): δ 69.2 (bm).

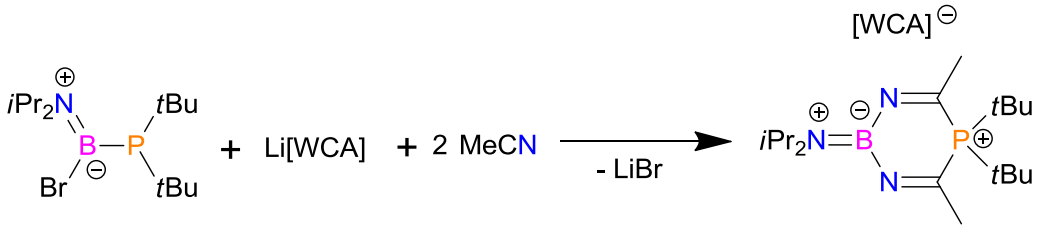
^{1}H NMR (CD_2Cl_2): δ 4.05 (1 H, dsept, $^3J_{HH}$ = 6.7 Hz, $^4J_{PH}$ = 1.4 Hz, N(P)CNC***H***$(CH_3)_2$); 3.46 (2 H, m, C***H***$(CH_3)_2$); 3.16 (1 H, dsept, $^3J_{HH}$ = 6.0 Hz, $^4J_{PH}$ = 2.8 Hz, N(B)CNC***H***$(CH_3)_2$); 1.47 (18 H, d, $^3J_{PH}$ = 17.0 Hz, C(C***H***$_3)_3$, overlapped with N(P)CNCH(C***H***$_3)_2$); 1.44 (dd, 6 H, $^3J_{HH}$ = 6.7 Hz, $^5J_{PH}$ = 1.2 Hz, N(P)CNCH(C***H***$_3)_2$, overlapped with C(C***H***$_3)_3$); 1.26 (12 H, d, $^3J_{HH}$ = 6.9 Hz, CH(C***H***$_3)_2$); 1.20 (6 H, d, $^3J_{HH}$ = 6.0 Hz, N(B)CNCH(C***H***$_3)_2$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 137.8 (d, $^1J_{CP}$ = 21.4 Hz, N***C***N); 121.2 (q, $^1J_{CF}$ = 293.1 Hz, OC(***C***F$_3)_3$); 57.6 (d, $^3J_{CP}$ = 10.9 Hz, N(B)CN***C***H$(CH_3)_2$); 53.3 (d, $^3J_{CP}$ = 16.9 Hz, N(P)CN***C***H$(CH_3)_2$); 36.1 (d, $^1J_{CP}$ = 10.9 Hz, ***C***$(CH_3)_3$); 29.1 (d, $^2J_{CP}$ = 2.7 Hz, C(***C***H$_3)_3$); 24.1 (s, N(B)CNCH(***C***H$_3)_2$); 22.6 (very bs, CH(***C***H$_3)_2$); 18.6 (s, N(P)CNCH(***C***H$_3)_2$). The ***C***H$(CH_3)_2$ atoms were not detected at the ^{13}C{^{1}H} spectrum.

^{27}Al NMR (CD_2Cl_2): δ 34.2 (s, [***Al***$(OC(CF_3)_3)_4]^-$).

^{19}F{^{1}H} (CD_2Cl_2): δ -75.7 (s, OC(C***F***$_3)_3$).

Preparation of 5



1 **5**

Scheme S3. Synthesis of **5**

A solution of acetonitrile in CH_2Cl_2 (0.25 M, 2 mL) was added dropwise to a stirred suspension of **1** (0.084 g, 0.250 mmol) and Li[Al(OC(CF$_3)_3)_4$] (0.244 g, 0.250 mmol) in CH_2Cl_2 (4 mL) at -70 °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 and layered with 2 mL of pentane. Storage at +4 °C gave suitable yellow crystals for X-ray diffraction. Cooling to -20 °C of the mother liquor gave an additional crop. Yield: 50% (0.165 g, 0.126 mmol). **Elemental analysis** calc. for $C_{34}H_{38}AlBF_{36}N_3O_4P$ (1305.39 g/mol): C, 31.28; H, 2.93; N, 3.22. Found: C, 31.04; H, 2.84; N, 2.95.

NMR data of 5

^{11}B NMR (CD_2Cl_2): δ 22.6 (s).

^{31}P{^{1}H} NMR (CD_2Cl_2): δ -32.7 (s).

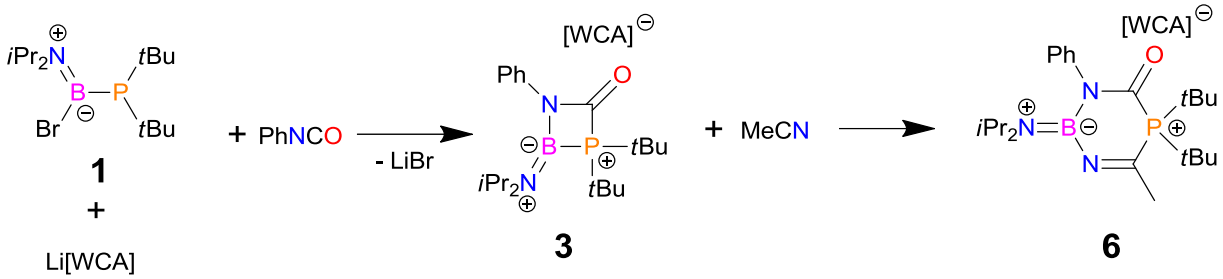
^{1}H NMR (CD_2Cl_2): δ 4.18 (2 H, bs, C***H***$(CH_3)_2$); 2.67 (6 H, d, $^3J_{PH}$ = 6.2 Hz, NCC***H***$_3$); 1.50 (18 H, d, $^3J_{PH}$ = 16.1 Hz, C(C***H***$_3)_3$); 1.24 (12 H, d, $^3J_{HH}$ = 6.8 Hz, CH(C***H***$_3)_2$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.9 (s, N***C***CH_3); 121.2 (q, $^1J_{CF}$ = 292.3 Hz, OC(***C***$F_3)_3$); 47.3 (s, ***C***$H(CH_3)_2$); 38.3 (d, $^1J_{CP}$ = 14.5 Hz, ***C***$(CH_3)_3$); 35.3 (d, $^2J_{CP}$ = 32.7 Hz, NC***C***H_3); 29.0 (s, C(***C***$H_3)_3$); 23.2 (s, CH(***C***$H_3)_2$).

^{27}Al NMR (CD_2Cl_2): δ 34.2 (s, [***Al***$(OC(CF_3)_3)_4]^-$).

^{19}F{^{1}H} (CD_2Cl_2): δ -75.7 (s, OC(C***F***$_3)_3$).

Preparation of 6



Scheme S4. Synthesis of **6**

A solution of phenyl isocyanate in CH_2Cl_2 (0.25 M, 1 mL) was added dropwise to a stirred suspension of **1** (0.084 g, 0.250 mmol) and Li[Al(OC$(CF_3)_3)_4$] (0.244 g, 0.250 mmol) in CH_2Cl_2 (4 mL) at -70 °C. The mixture was allowed to warm to room temperature and stirred overnight. After checking of the reaction progress by ^{11}B, ^{31}P{^{1}H} and ^{31}P NMR (100% conversion of **1** into **3**), to the stirred resulting mixture, a solution of acetonitrile in CH_2Cl_2 (0.25 M, 1 mL) was added dropwise at -70 °C. Again, 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 and layered with 2 mL of pentane. Storage at +4 °C gave suitable crystals for X-ray diffraction. Drying of crystals under high vacuum resulted in the removal of non-coordinated solvent molecule. Yield: 41% (0.142 g, 0.103 mmol). **Elemental analysis** calc. for $C_{39}H_{40}AlBF_{36}N_3O_5P$ (1383.46 g/mol): C, 33.85; H, 2.91; N, 3.04. Found: C, 34.05; H, 2.82; N, 2.95.

NMR data of 6

^{11}B NMR (CD_2Cl_2): δ 26.6 (s).

^{31}P{^{1}H} NMR (CD_2Cl_2): δ 10.9 (s).

^{1}H NMR (CD_2Cl_2): δ 7.42 (2 H, m, *o*-C***H*** of Ph); 7.34 (1 H, m, *p*-C***H*** of Ph); 7.16 (2 H, m, *m*-C***H*** of Ph); 3.40 (1 H, sept, $^3J_{HH}$ = 6.6 Hz, C***H***$(CH_3)_2$); 3.25 (1 H, sept, $^3J_{HH}$ = 6.9 Hz, C***H***$(CH_3)_2$); 2.75 (3 H, d, $^3J_{PH}$ = 5.9 Hz, NCC***H***$_3$); 1.58 (18 H, d, $^3J_{PH}$ = 16.7 Hz, C(C***H***$_3)_3$); 1.33 (6 H, d, $^3J_{HH}$ = 6.9 Hz, CH(C***H***$_3)_2$); 0.56 (6 H, d, $^3J_{HH}$ = 6.6 Hz, CH(C***H***$_3)_2$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 163.0 (d, $^1J_{CP}$ = 77.3 Hz, N***C***O); 159.1 (d, $^2J_{CP}$ = 10.9 Hz, N***C***CH_3); 136.9 (d, $^3J_{CP}$ = 3.1 Hz, *ipso*-***C*** of Ph); 129.5 (s, *o*-***C***H of PPh); 128.7 (s, *p*-***C***H of PPh); 127.1 (s, *m*-***C***H of PPh); 121.3 (q, $^1J_{CF}$ = 293.0 Hz, OC(***C***$F_3)_3$); 50.1 (s, ***C***H$(CH_3)_2$); 46.2 (s, ***C***H$(CH_3)_2$); 39.2 (d, $^1J_{CP}$ = 14.5 Hz, ***C***$(CH_3)_3$); 33.8 (d, $^2J_{CP}$ = 34.6 Hz, NC***C***H_3); 28.1 (s, C(***C***$H_3)_3$); 25.2 (s, CH(***C***$H_3)_2$); 19.7 (s, CH(***C***$H_3)_2$).

^{27}Al NMR (CD_2Cl_2): δ 34.2 (s, [***Al***$(OC(CF_3)_3)_4]^-$).

^{19}F{^{1}H} (CD_2Cl_2): δ -75.7 (s, OC(C***F***$_3)_3$).

NMR spectra of isolated compounds

Abbreviations

s	deuterated solvent (residual signal)
g	grease
★	impurity
●	*i*Pr_2NBBr_2
●	*t*Bu_2PH

NMR spectra of 3

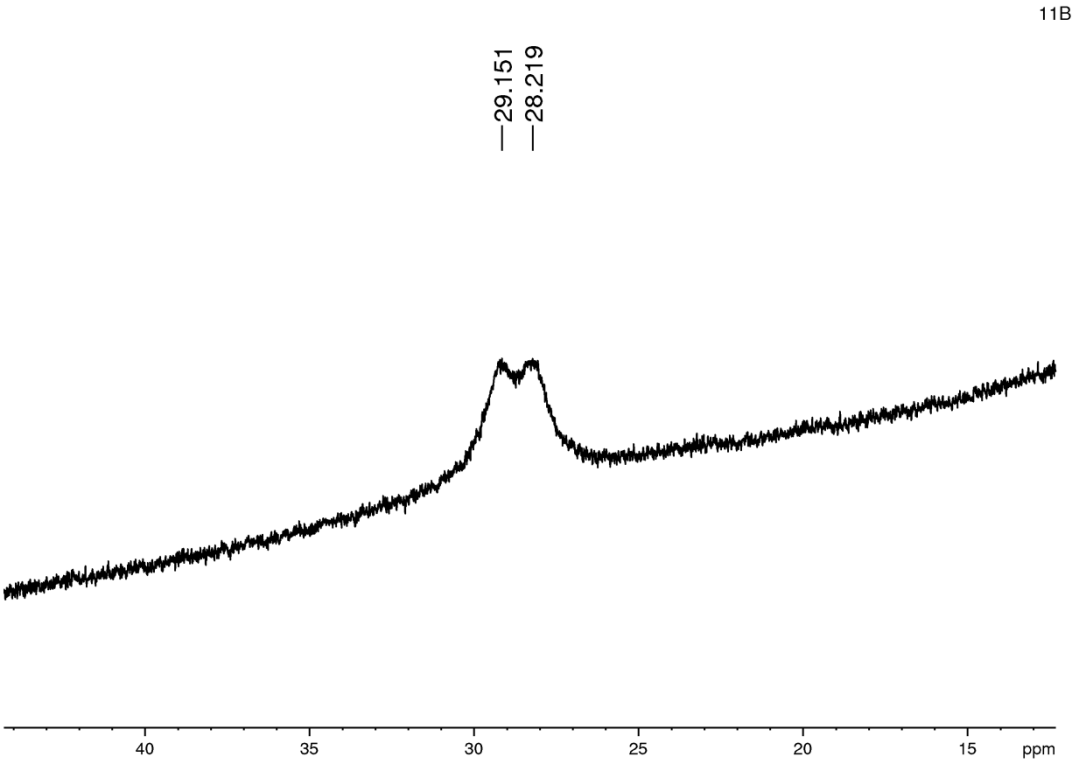


Figure S1. ^{11}B spectrum (CD_2Cl_2) of **3**

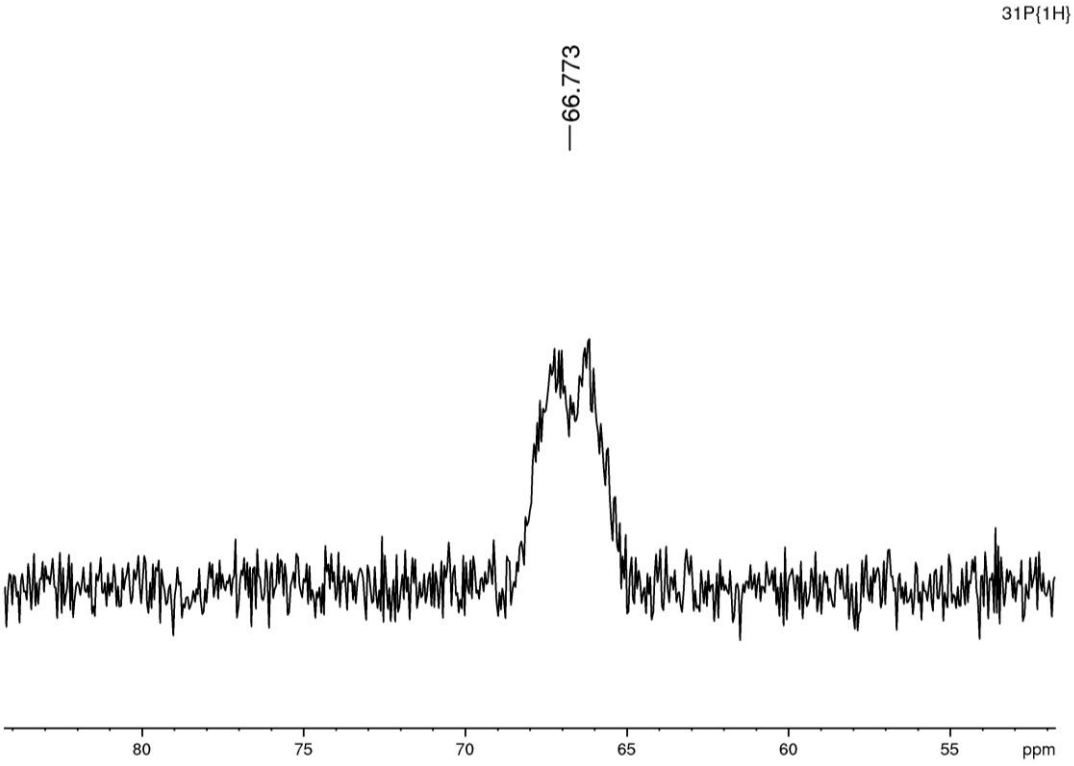


Figure S2. $^{31}P\{^1H\}$ spectrum (CD_2Cl_2) of **3**

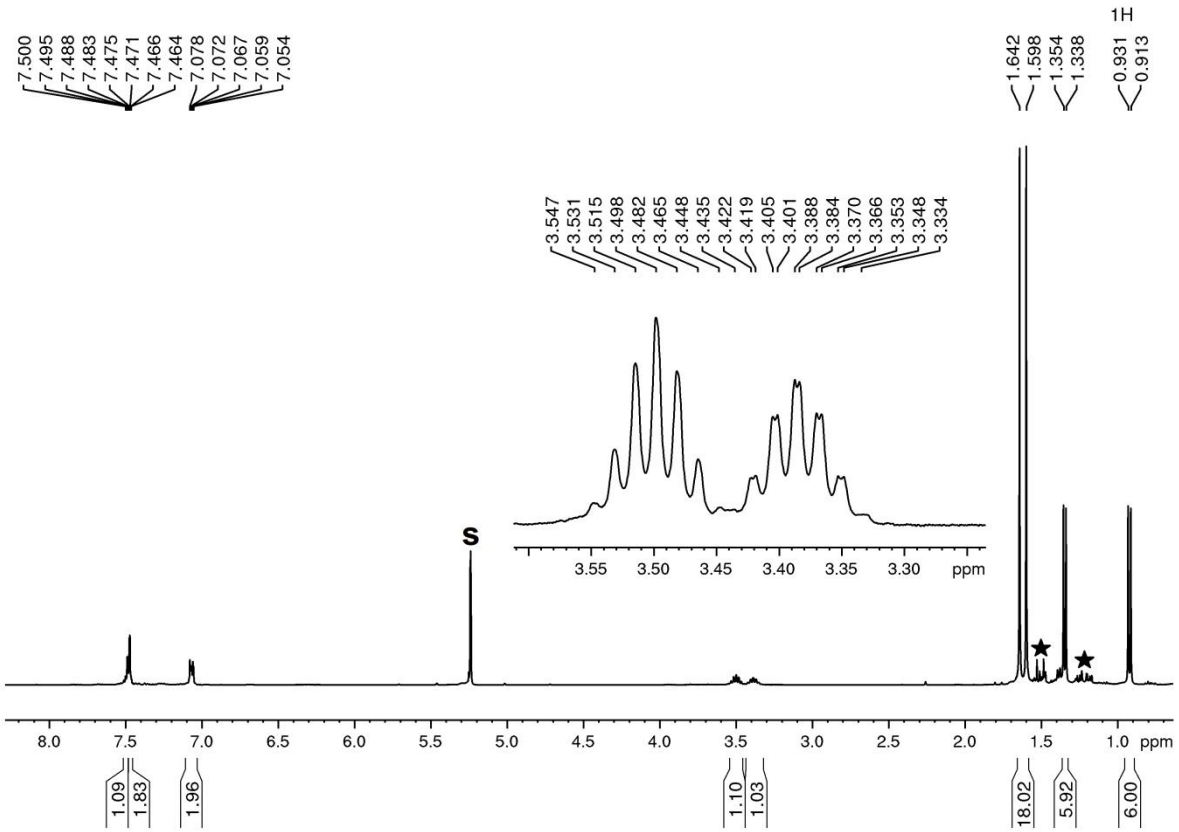


Figure S3. ^{1}H spectrum (CD_2Cl_2) of **3**

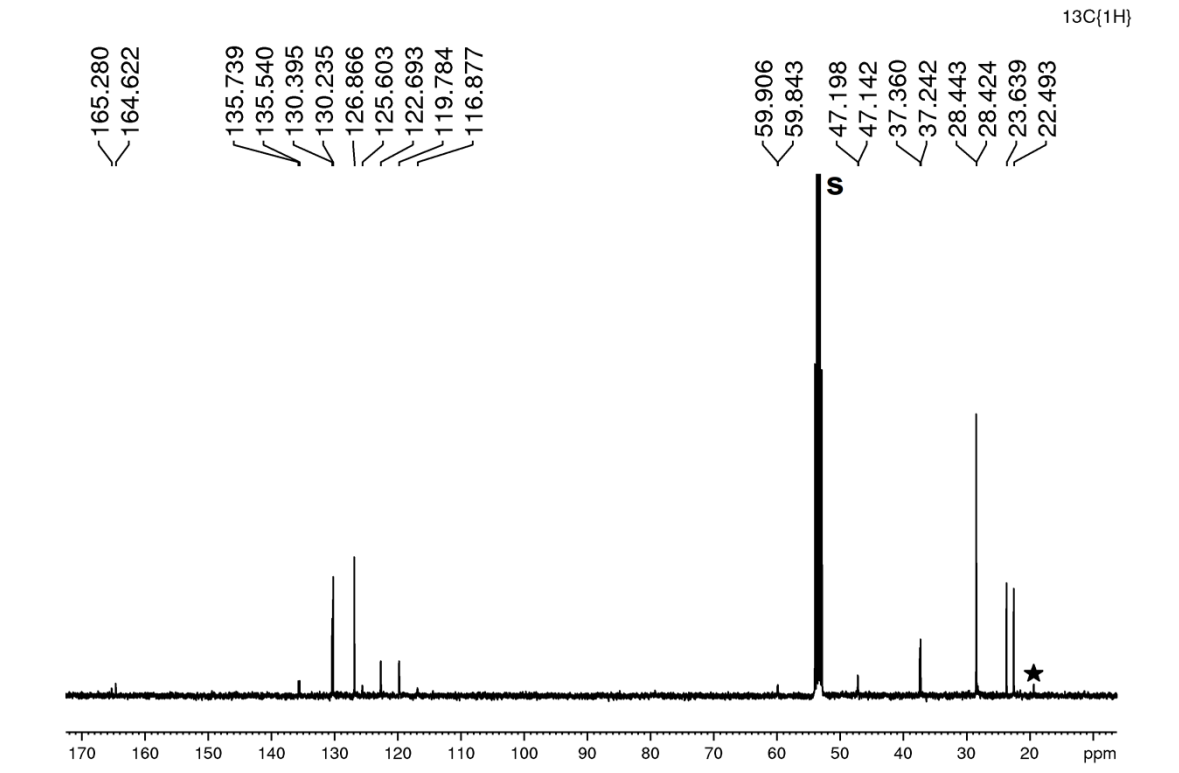


Figure S4. $^{13}C\{^{1}H\}$ spectrum (CD_2Cl_2) of **3**

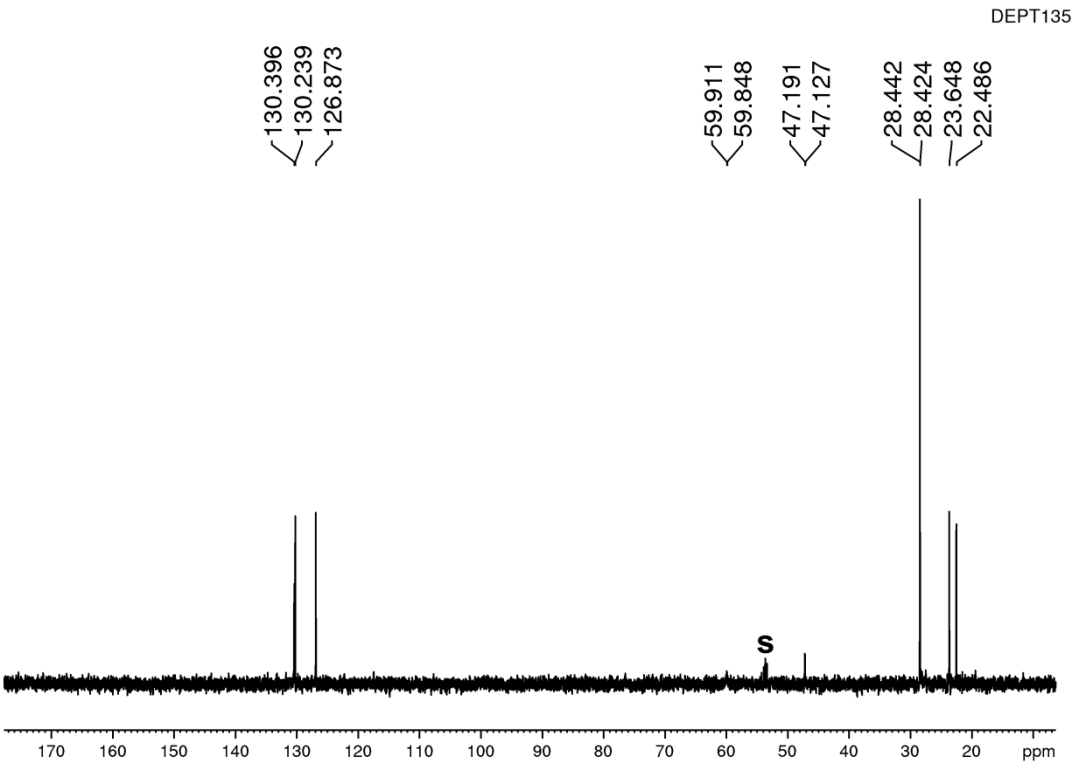


Figure S5. ^{135}DEPT spectrum (CD_2Cl_2) of **3**

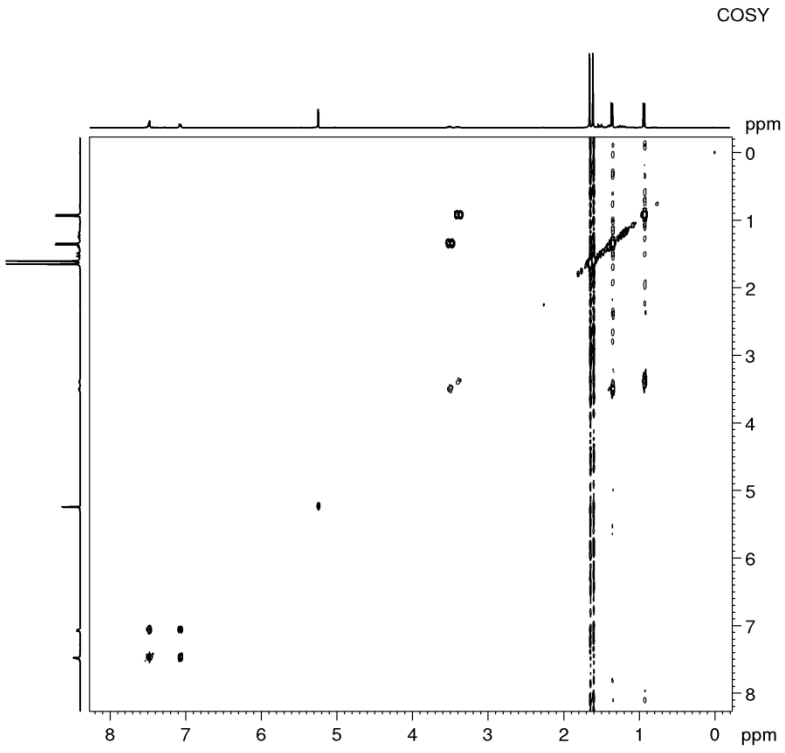


Figure S6. COSY spectrum (CD_2Cl_2) of **3**

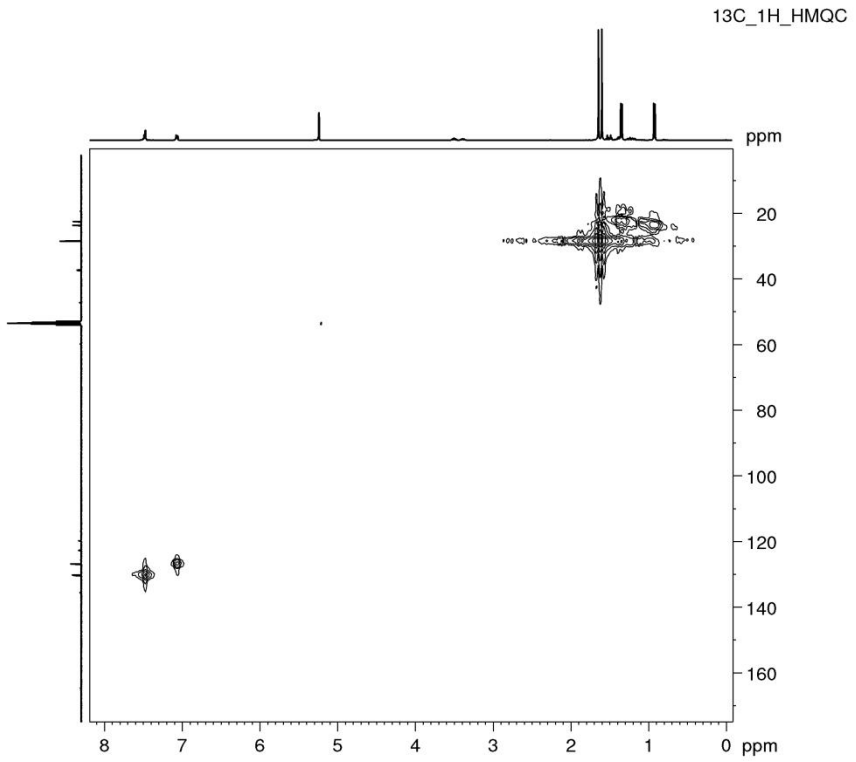


Figure S7. ^{13}C ^{1}H HMQC spectrum (CD_2Cl_2) of **3**

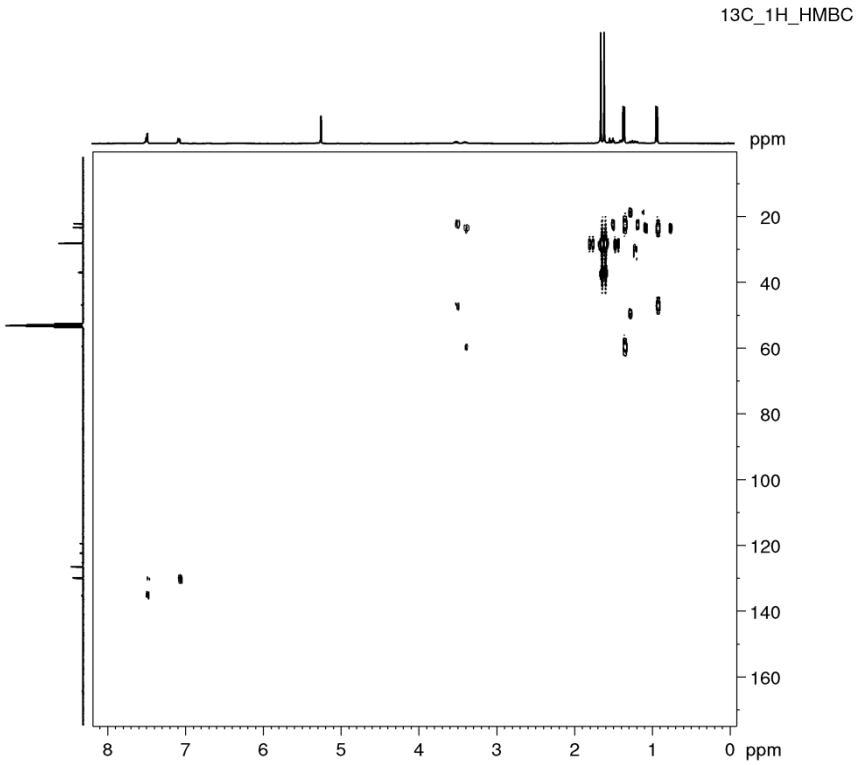


Figure S8. ^{13}C ^{1}H HMBC spectrum (CD_2Cl_2) of **3**

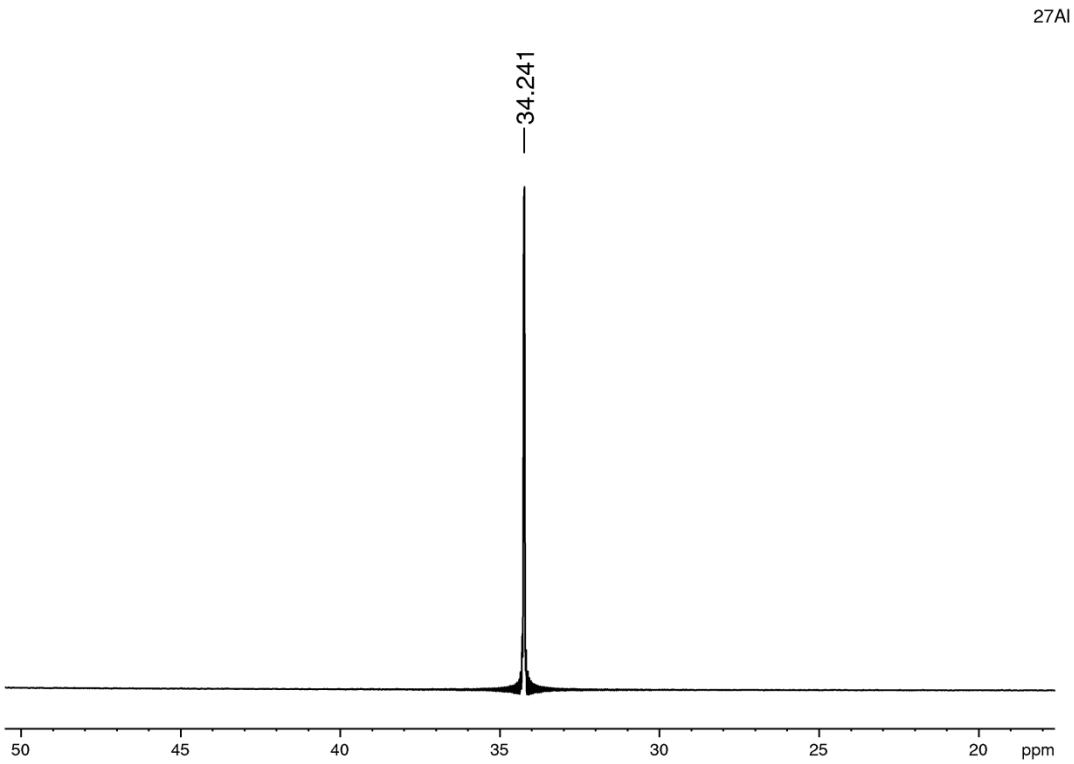


Figure S9. ^{27}Al spectrum (CD_2Cl_2) of **3**

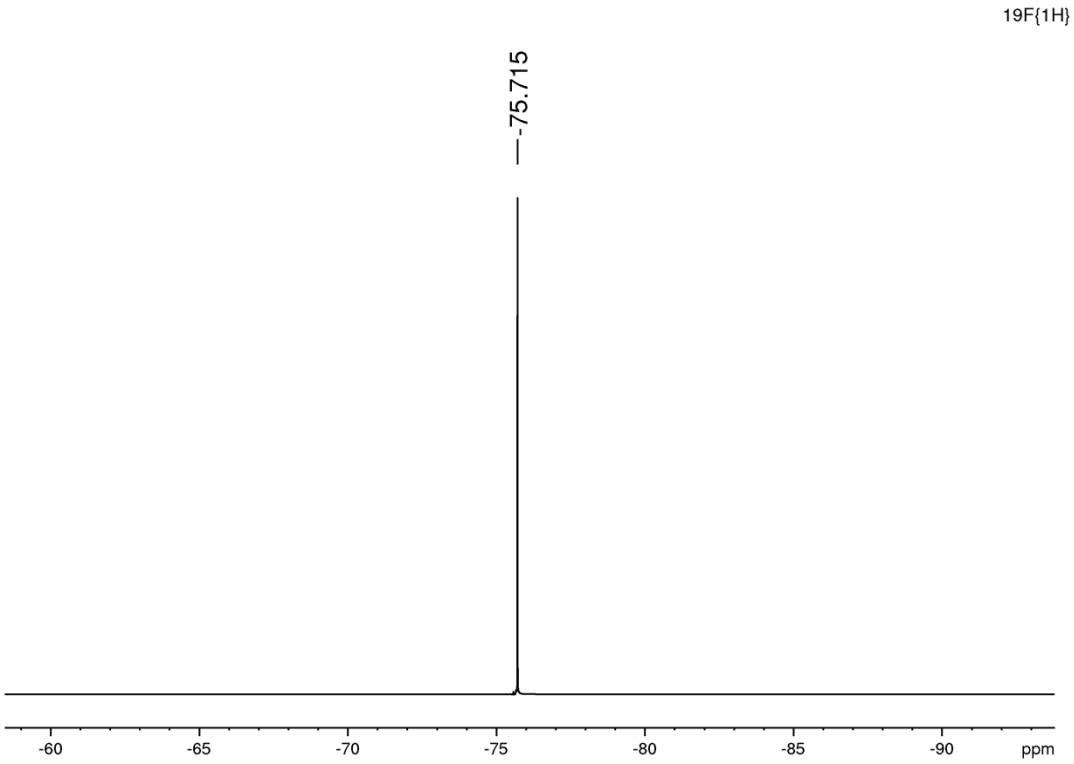


Figure S10. $^{19}F\{^{1}H\}$ spectrum (CD_2Cl_2) of **3**

NMR spectra of 4

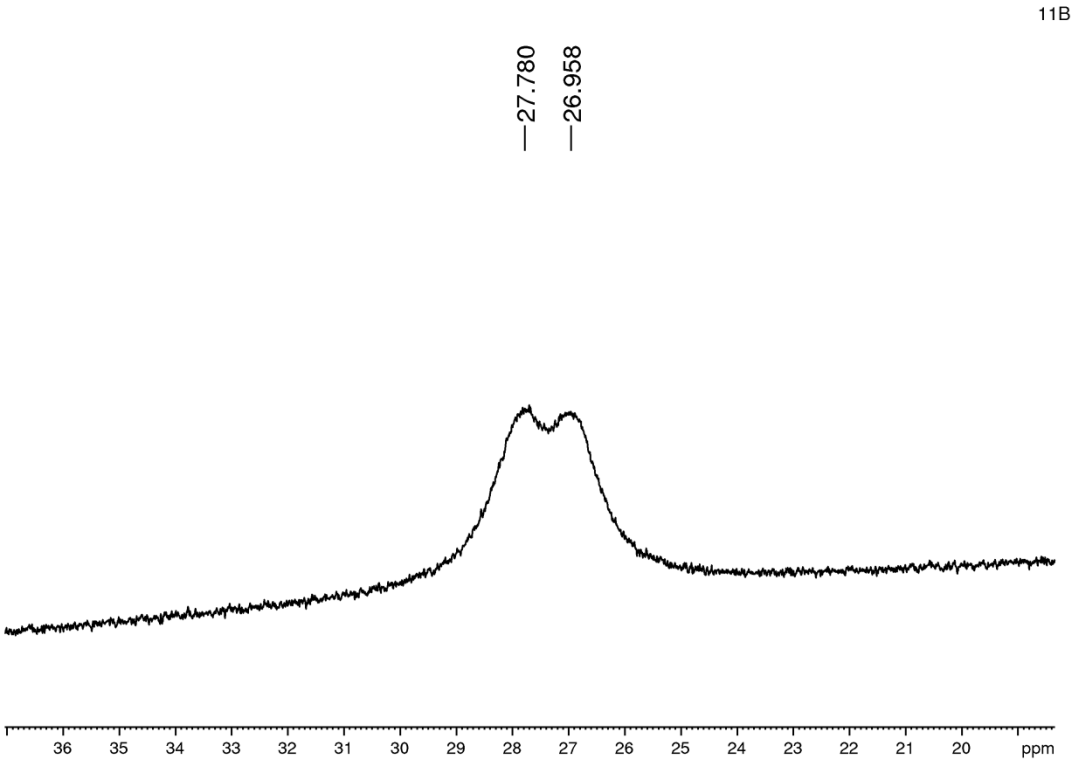


Figure S11. ^{11}B spectrum (CD_2Cl_2) of **4**

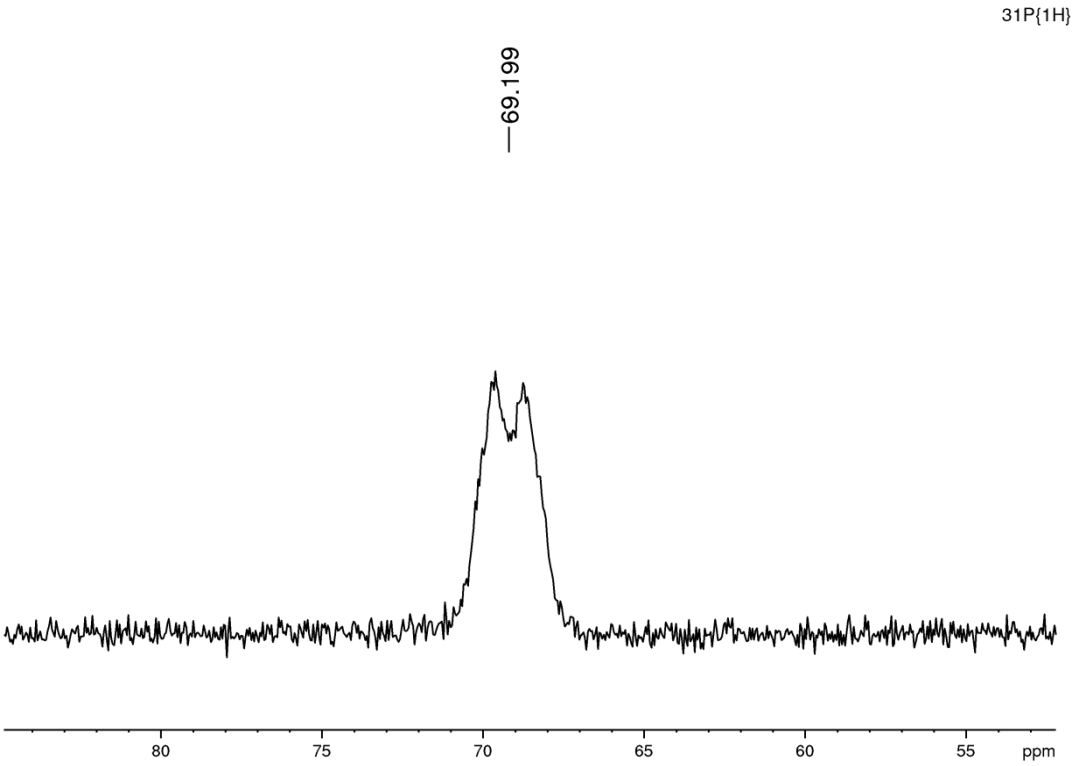


Figure S12. $^{31}P\{^1H\}$ spectrum (CD_2Cl_2) of **4**

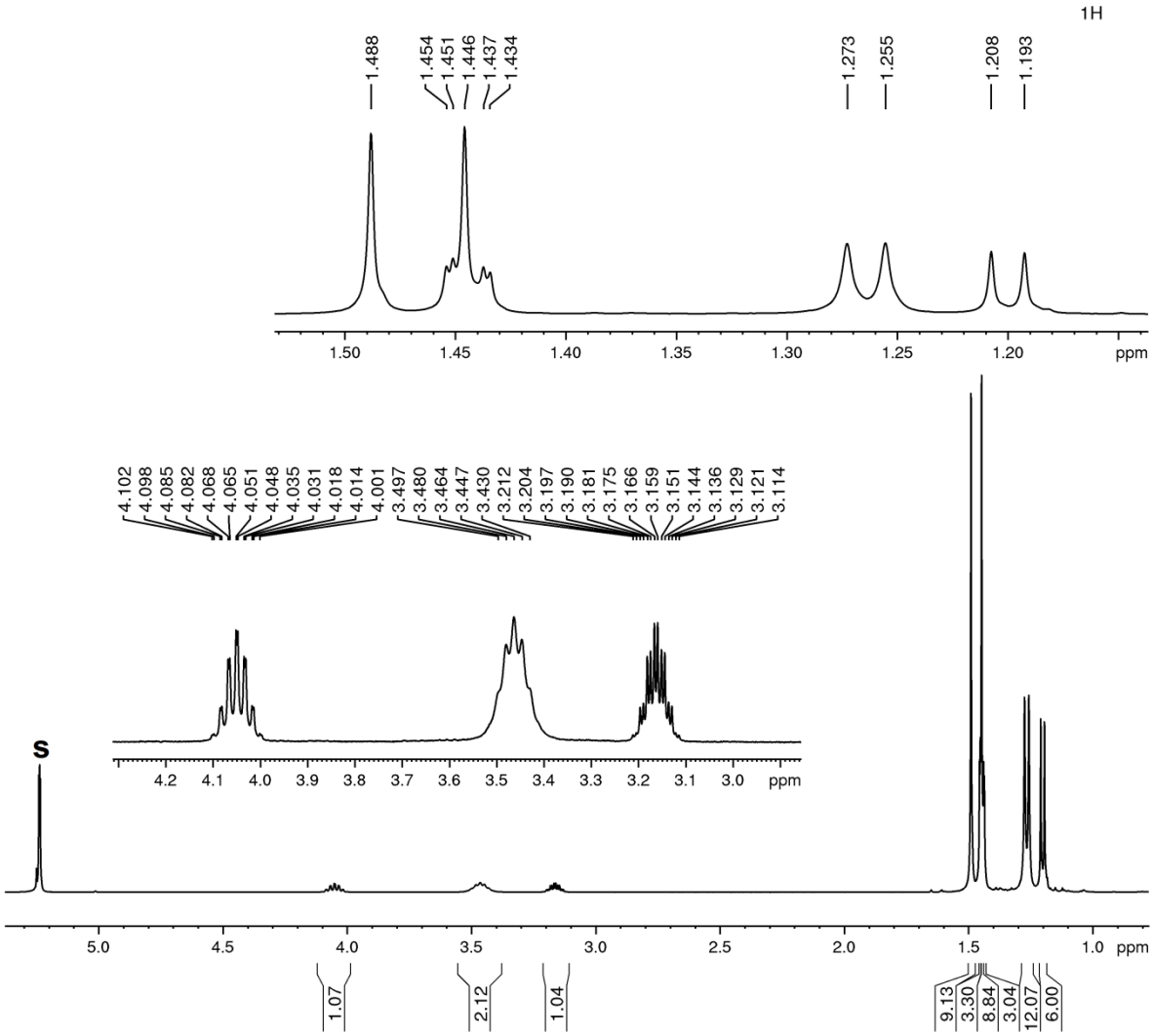


Figure S13. ^{1}H spectrum (CD_2Cl_2) of **4**

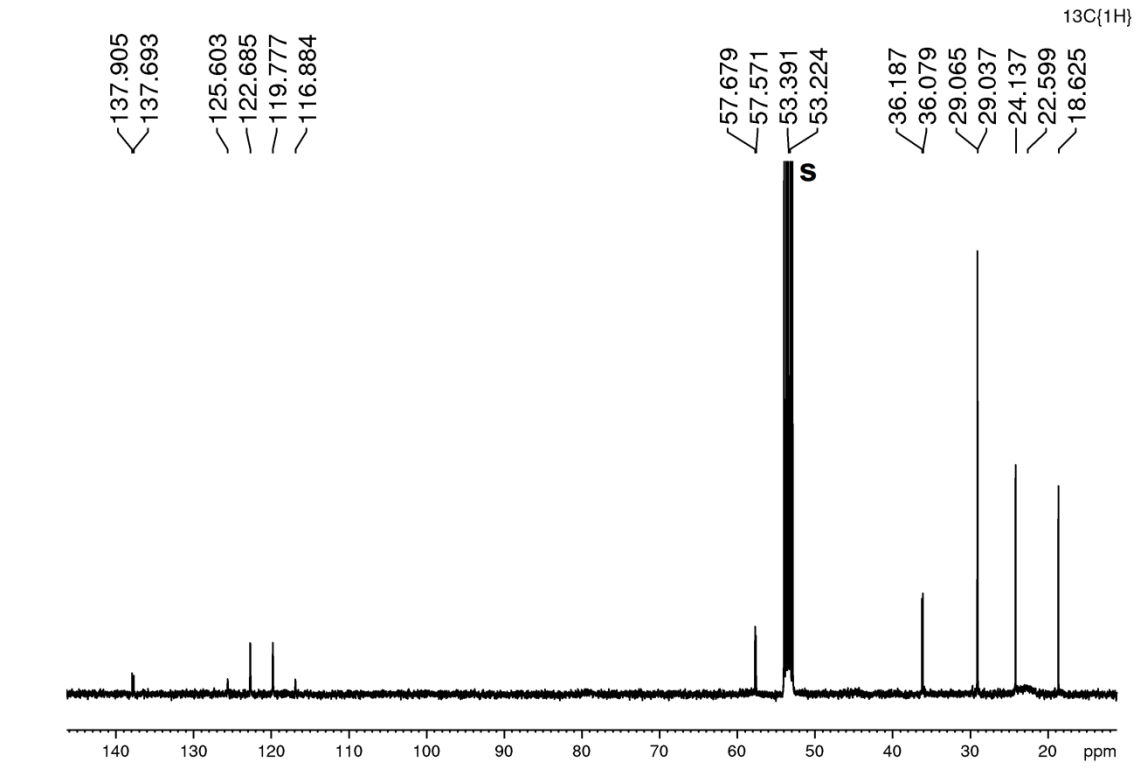


Figure S14. $^{13}C\{^{1}H\}$ spectrum (CD_2Cl_2) of **4**

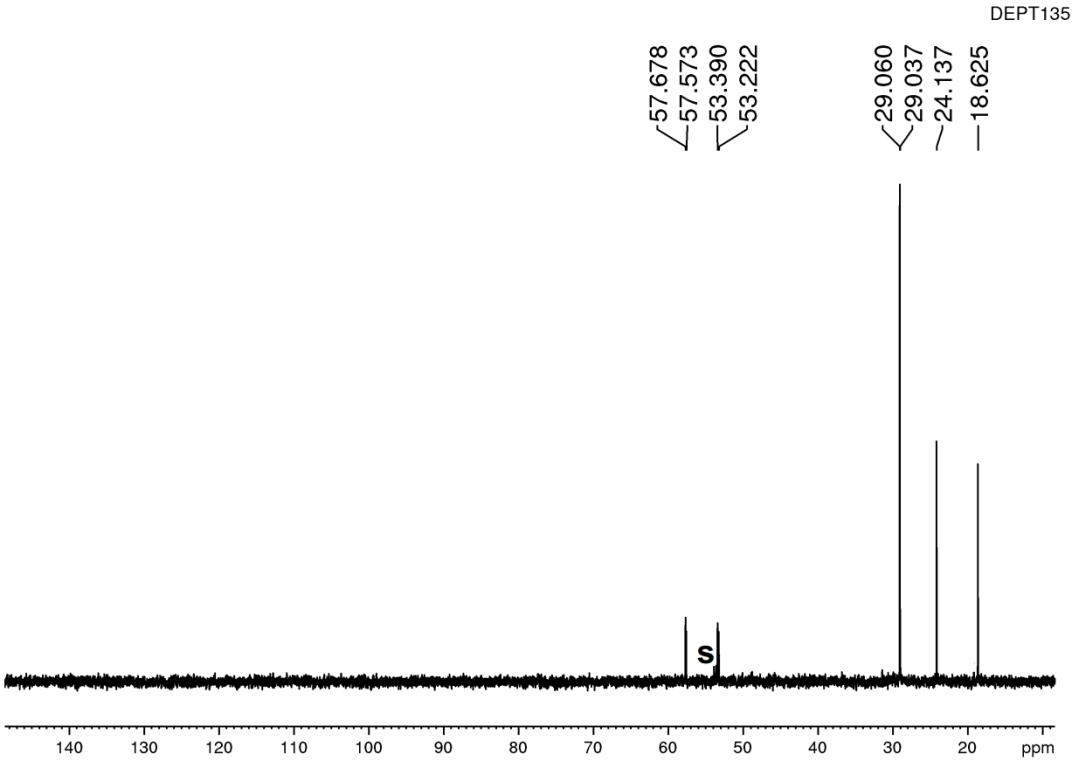


Figure S15. ^{135}DEPT spectrum (CD_2Cl_2) of **4**

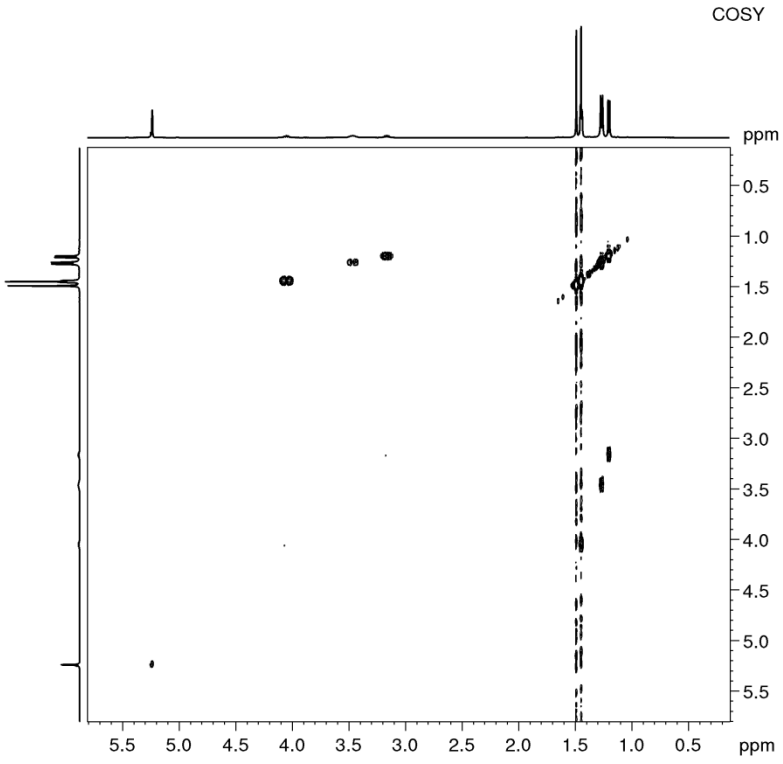


Figure S16. COSY spectrum (CD_2Cl_2) of **4**

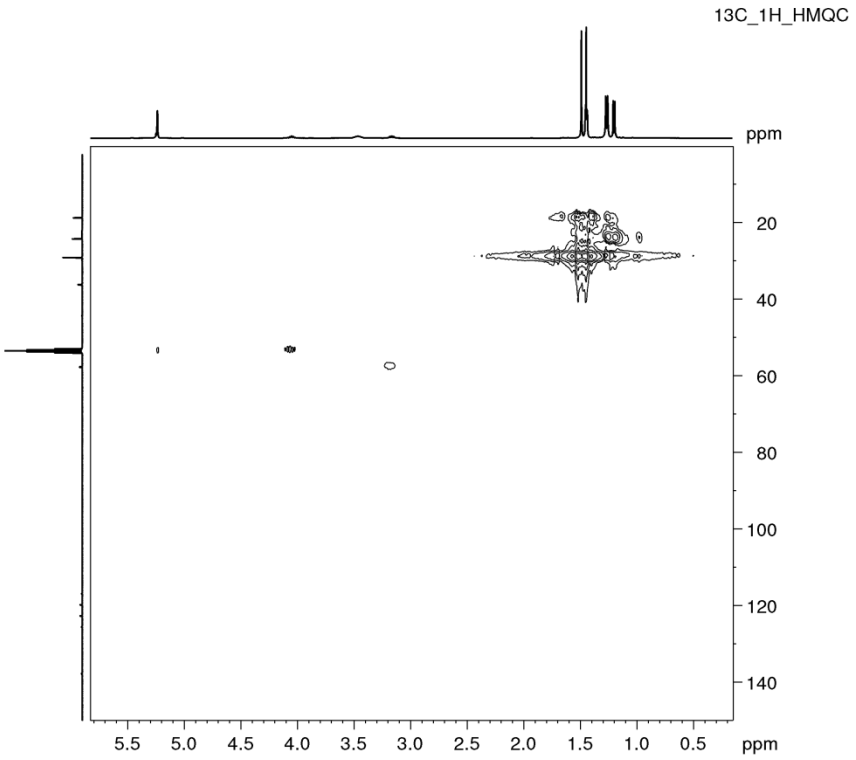


Figure S17. ^{13}C ^{1}H HMQC spectrum (CD_2Cl_2) of **4**

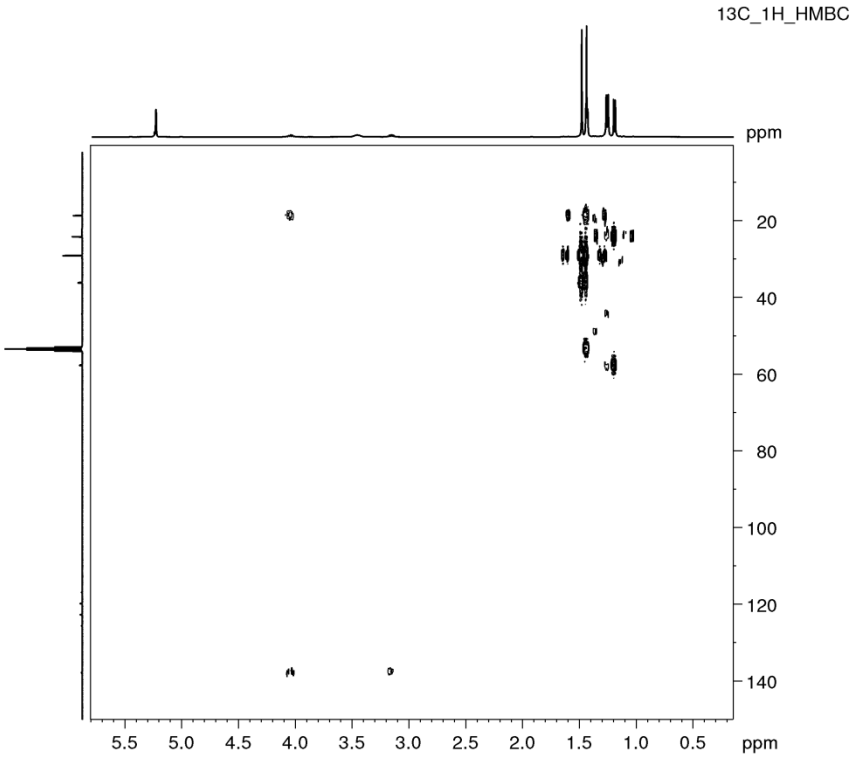


Figure S18. ^{13}C ^{1}H HMBC spectrum (CD_2Cl_2) of **4**

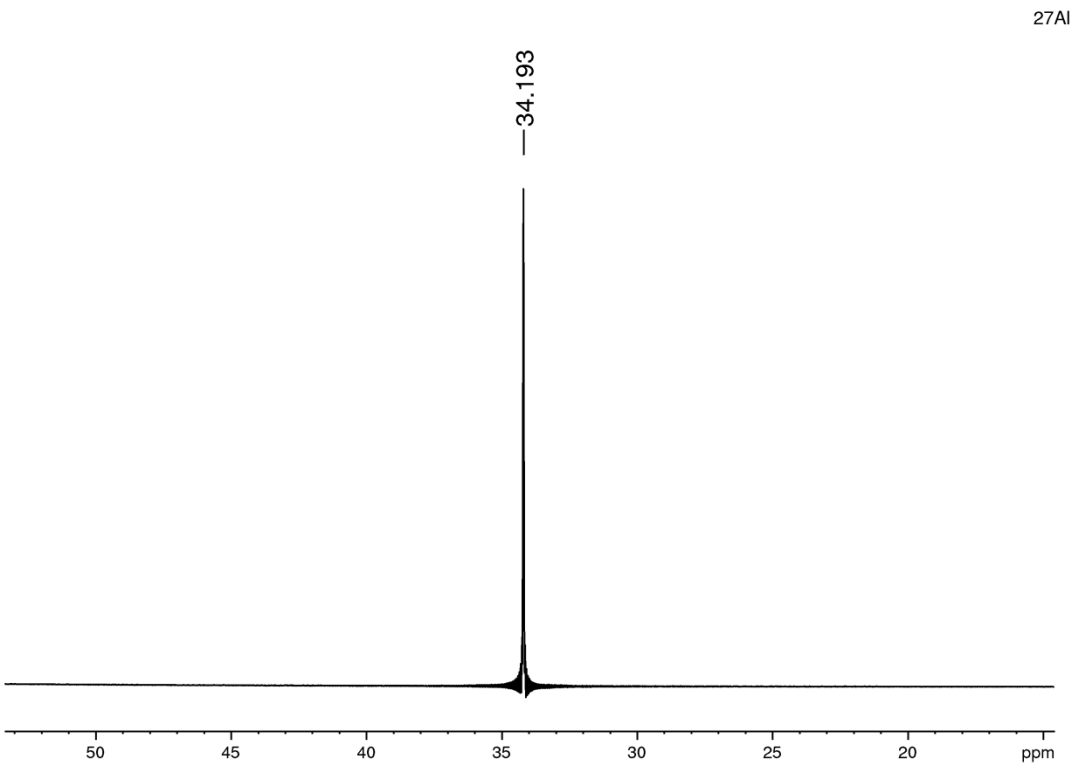


Figure S19. ^{27}Al spectrum (CD_2Cl_2) of **4**

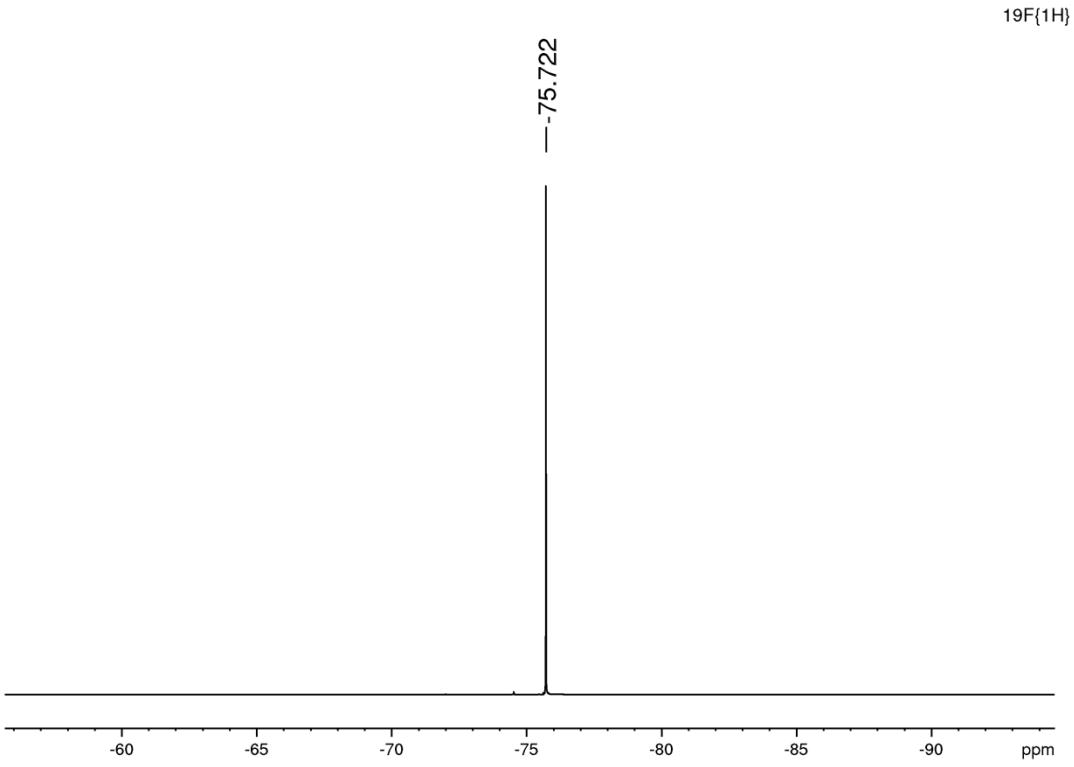


Figure S20. $^{19}F\{^{1}H\}$ spectrum (CD_2Cl_2) of **4**

NMR spectra of 5

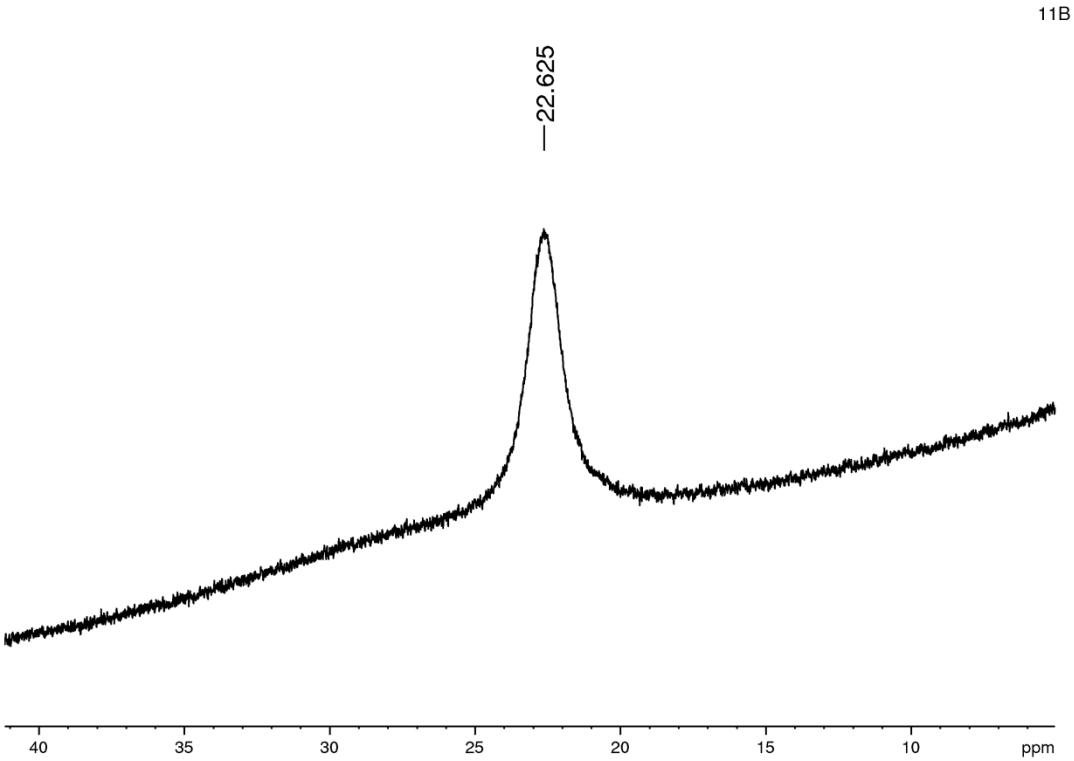


Figure S21. ^{11}B spectrum (CD_2Cl_2) of **5**

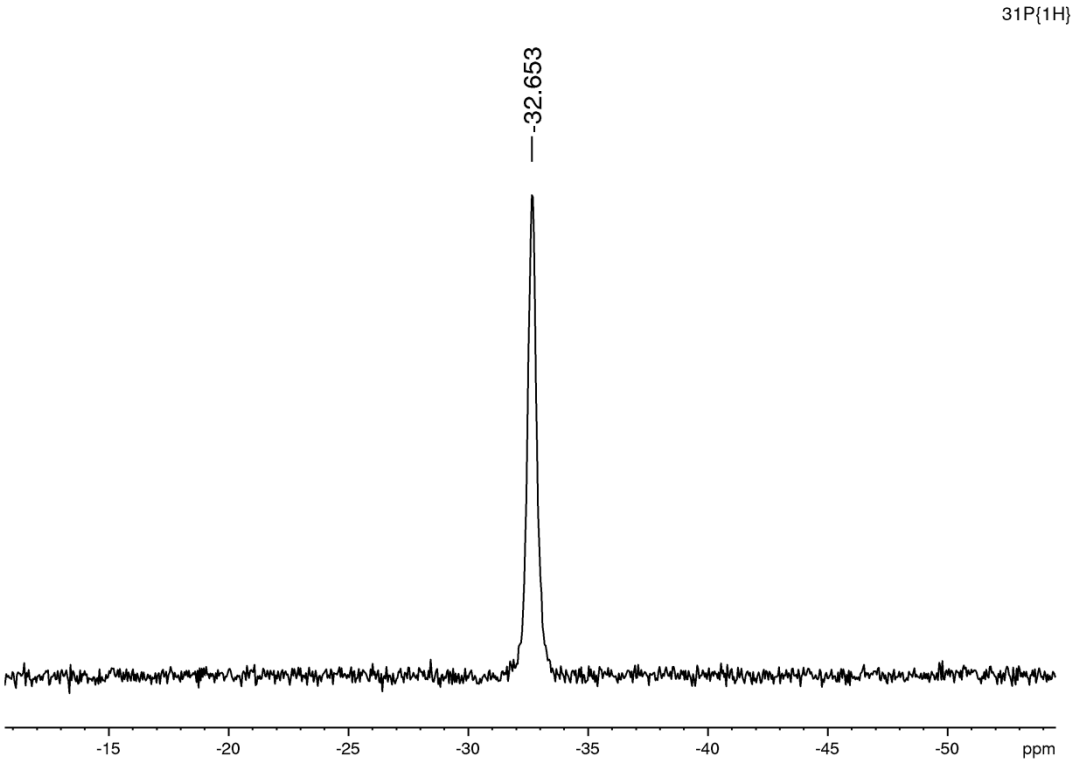


Figure S22. $^{31}P\{^1H\}$ spectrum (CD_2Cl_2) of **5**

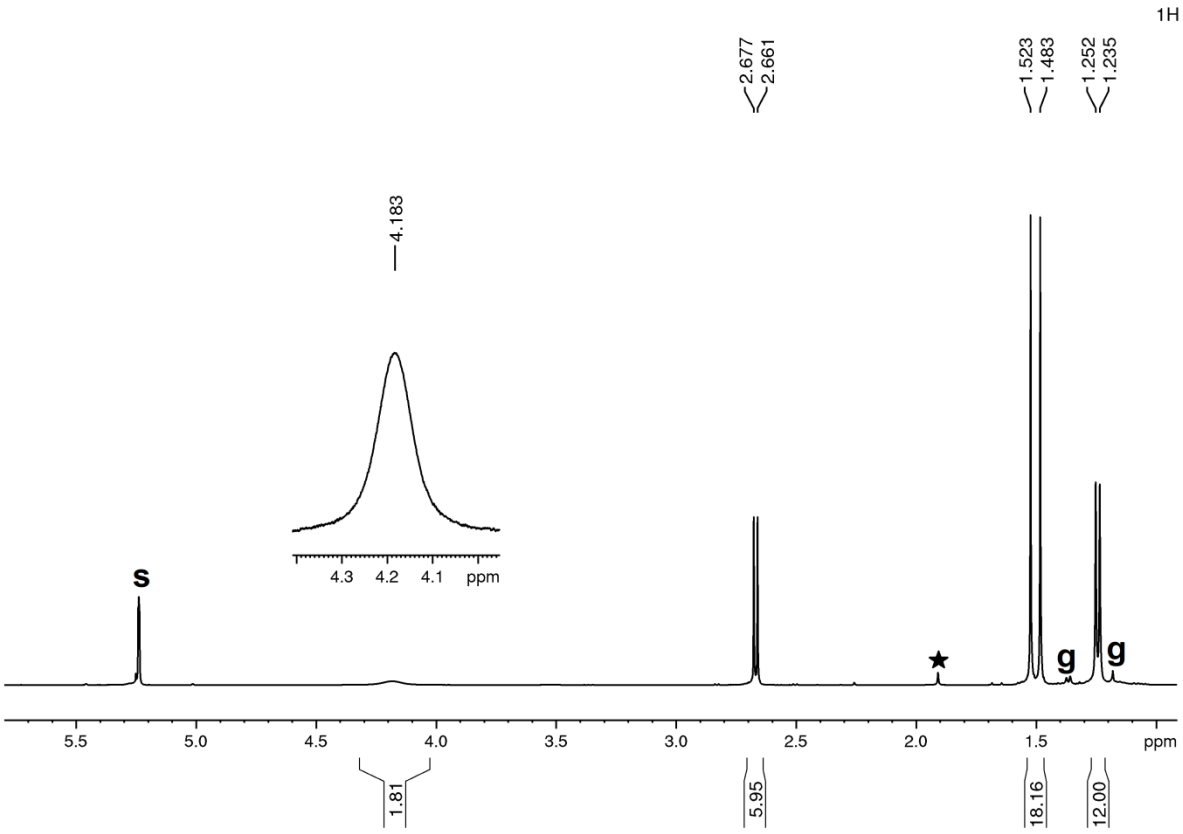


Figure S23. ^{1}H spectrum (CD_2Cl_2) of **5**

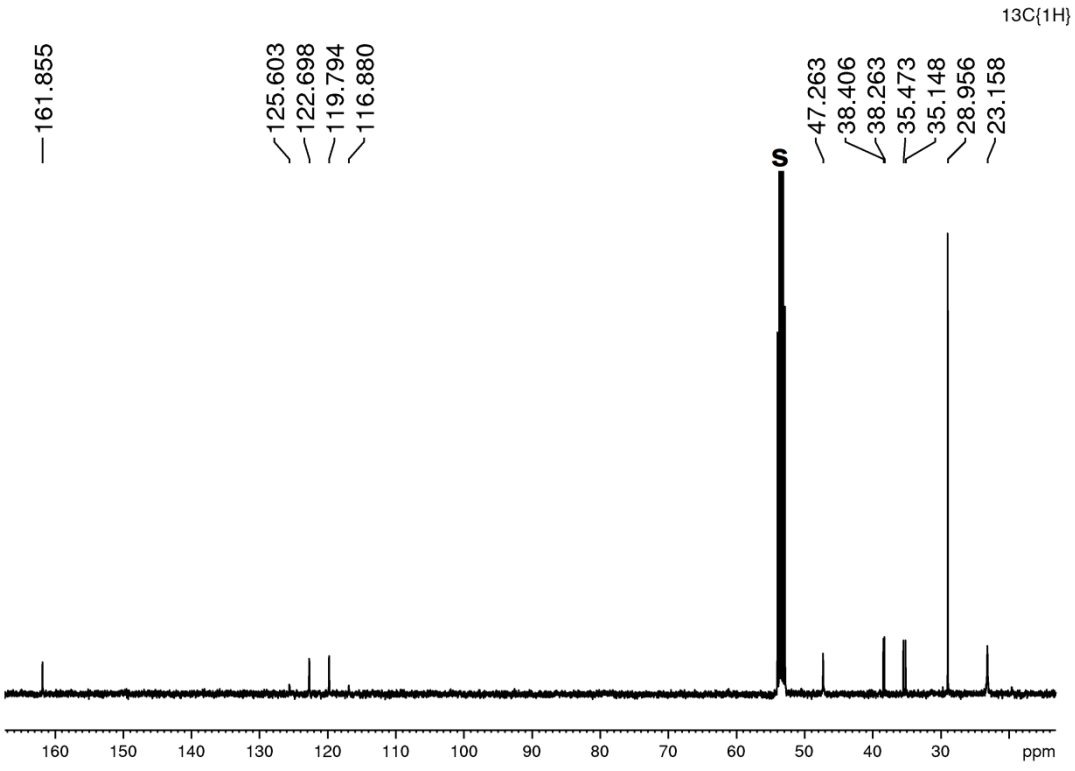


Figure S24. $^{13}C\{^{1}H\}$ spectrum (CD_2Cl_2) of **5**

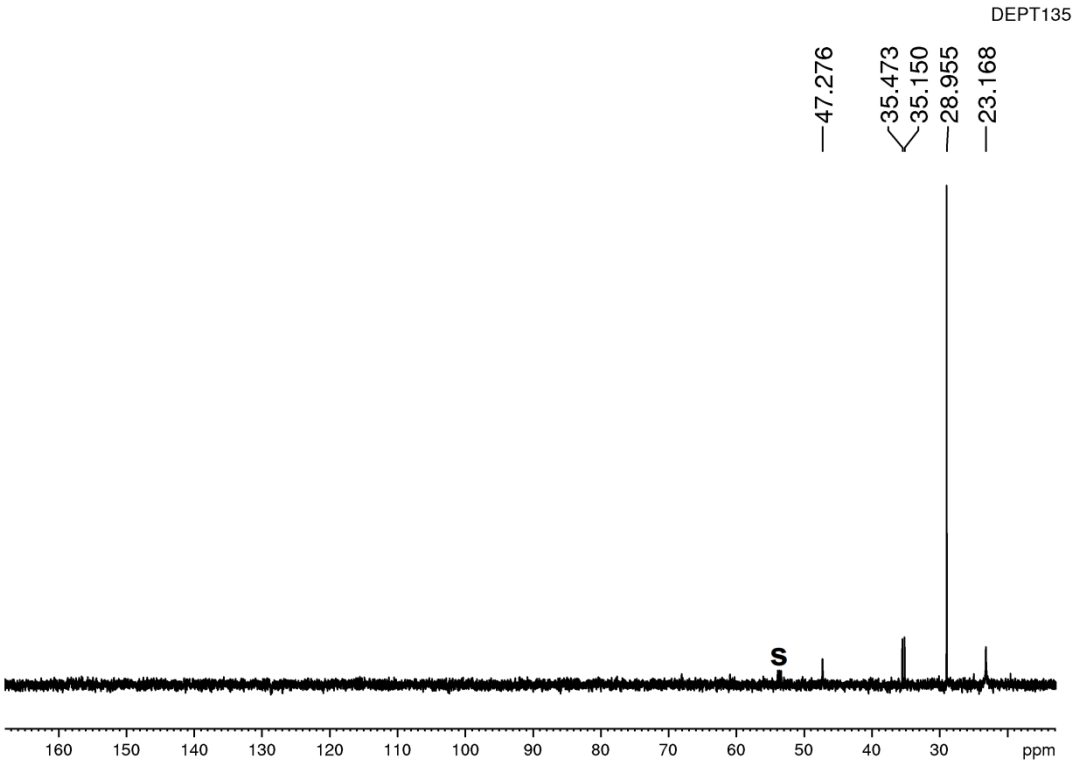


Figure S25. ^{135}DEPT spectrum (CD_2Cl_2) of **5**

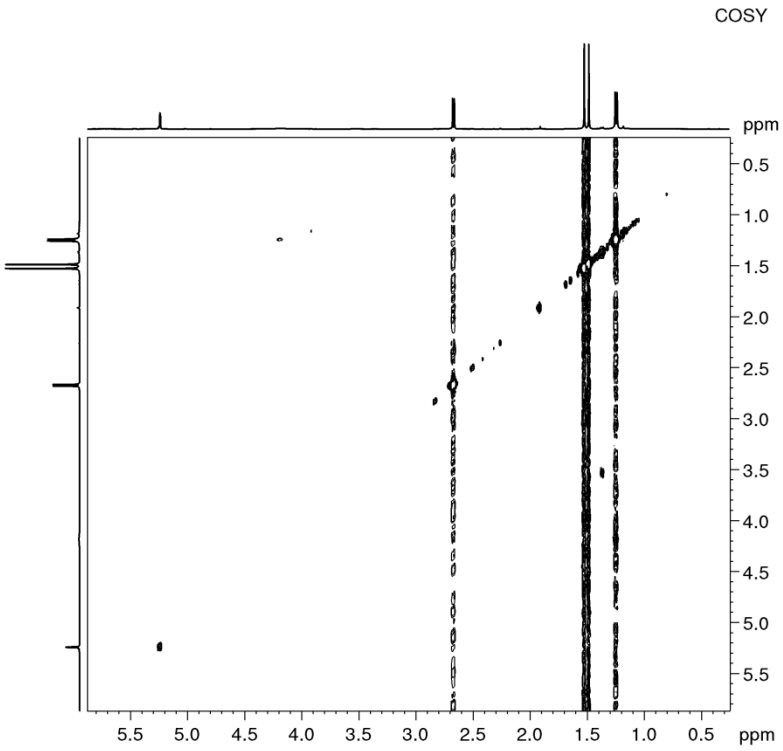


Figure S26. COSY spectrum (CD_2Cl_2) of **5**

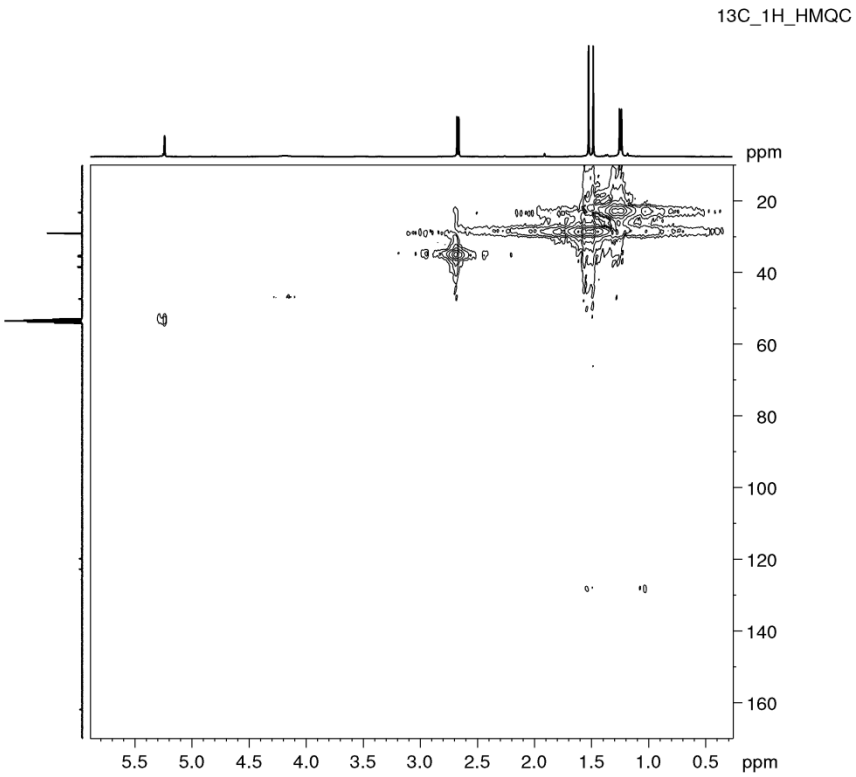


Figure S27. ^{13}C ^{1}H HMQC spectrum (CD_2Cl_2) of **5**

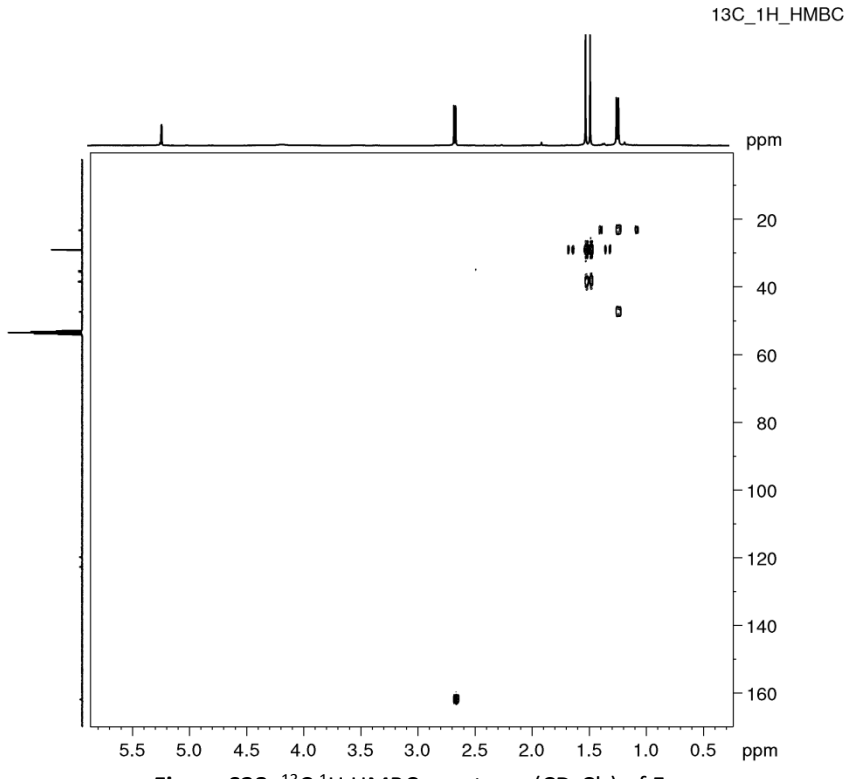


Figure S28. ^{13}C ^{1}H HMBC spectrum (CD_2Cl_2) of **5**

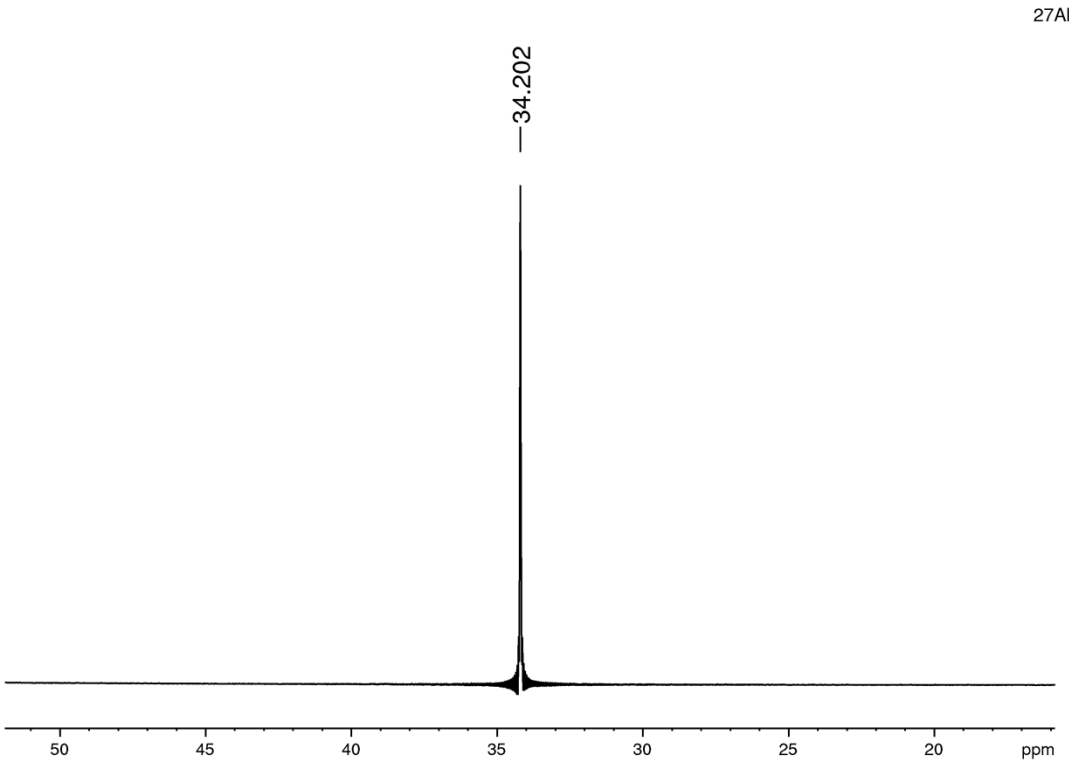


Figure S29. ^{27}Al spectrum (CD_2Cl_2) of **5**

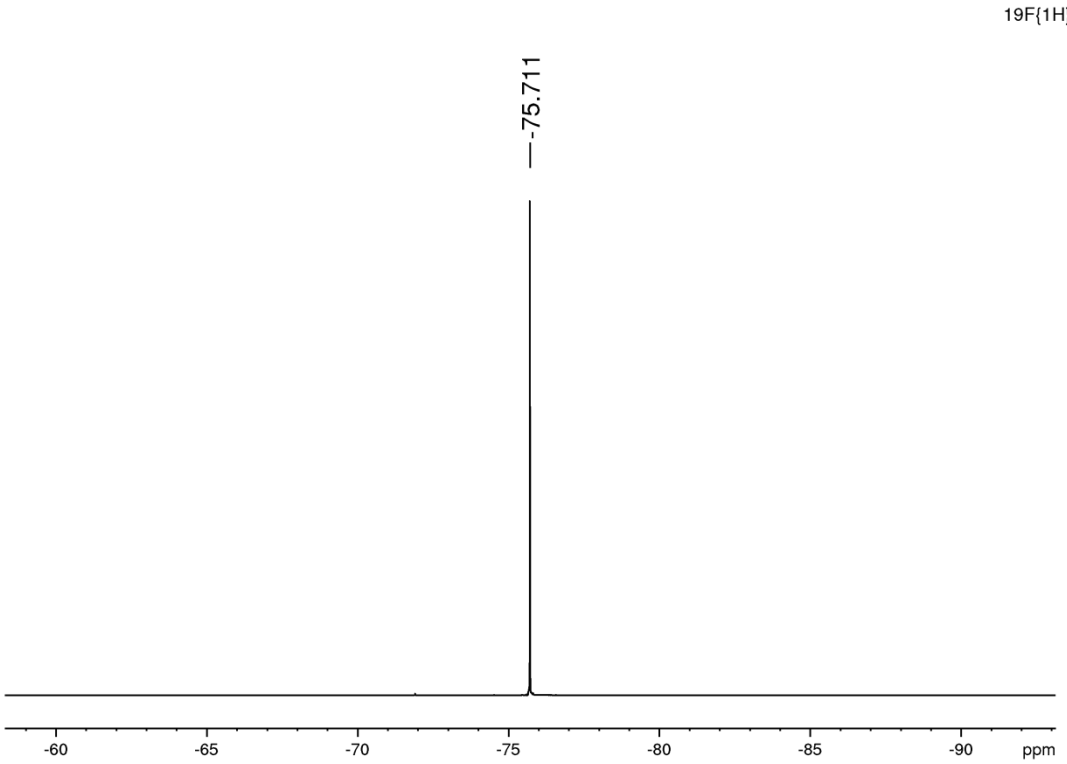


Figure S30. $^{19}F\{^{1}H\}$ spectrum (CD_2Cl_2) of **5**

NMR spectra of 6

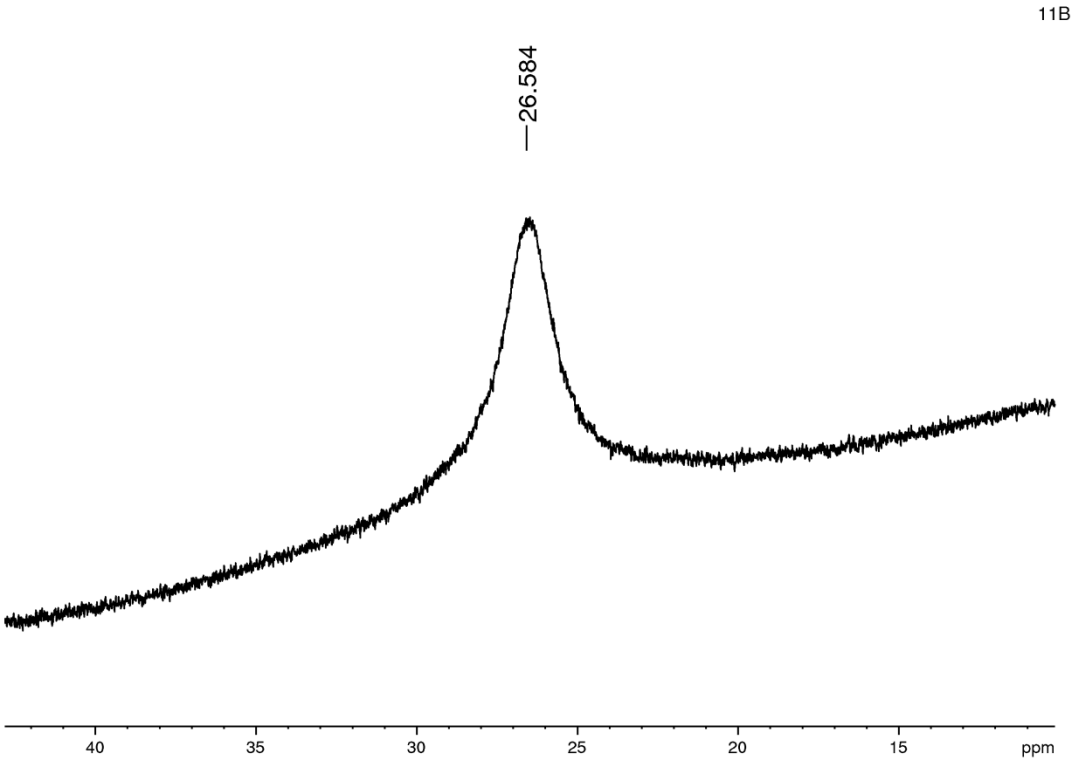


Figure S31. ^{11}B spectrum (CD_2Cl_2) of **6**

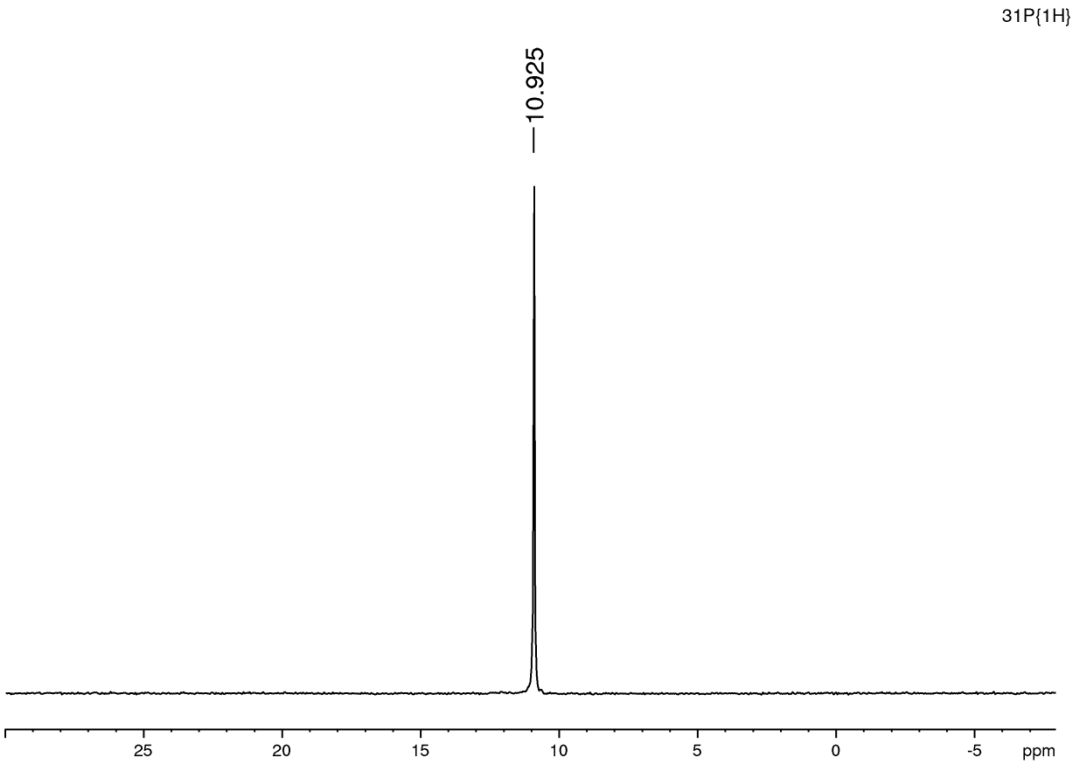


Figure S32. $^{31}P\{^{1}H\}$ spectrum (CD_2Cl_2) of **6**

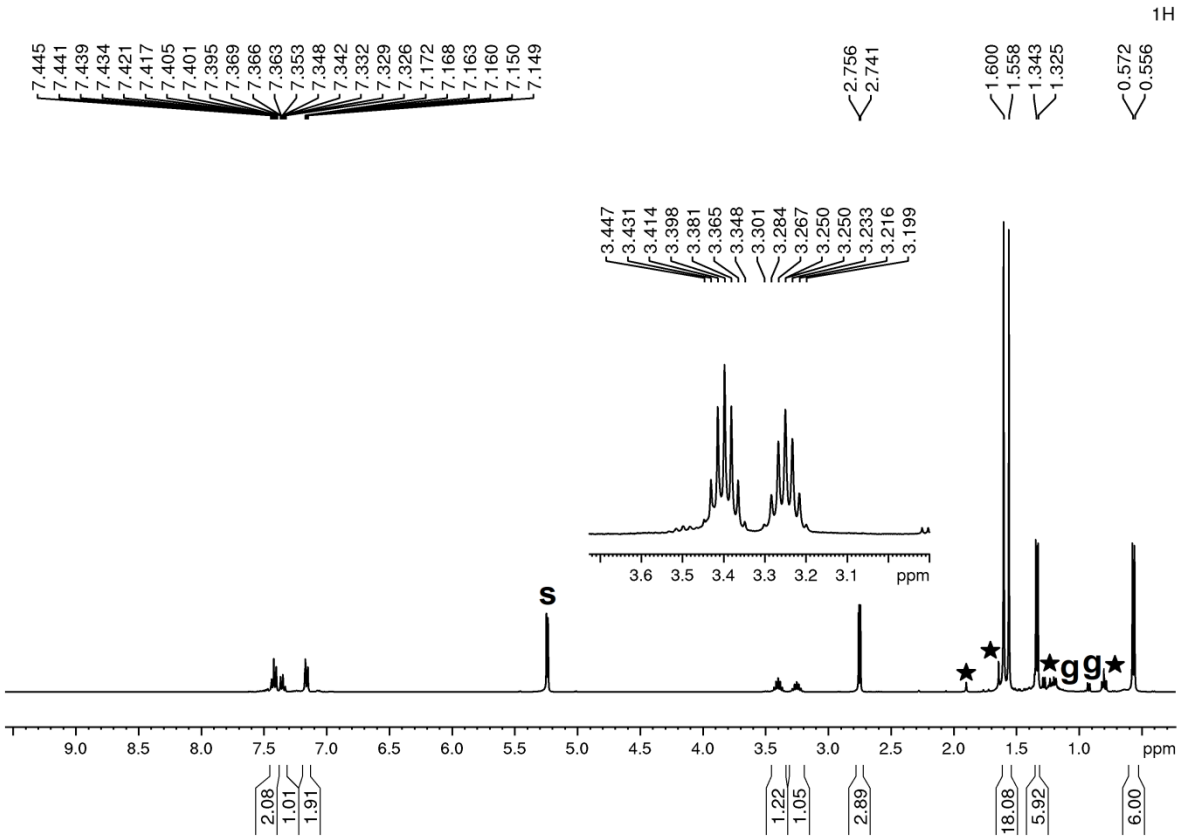


Figure S33. ^{1}H spectrum (CD_2Cl_2) of **6**

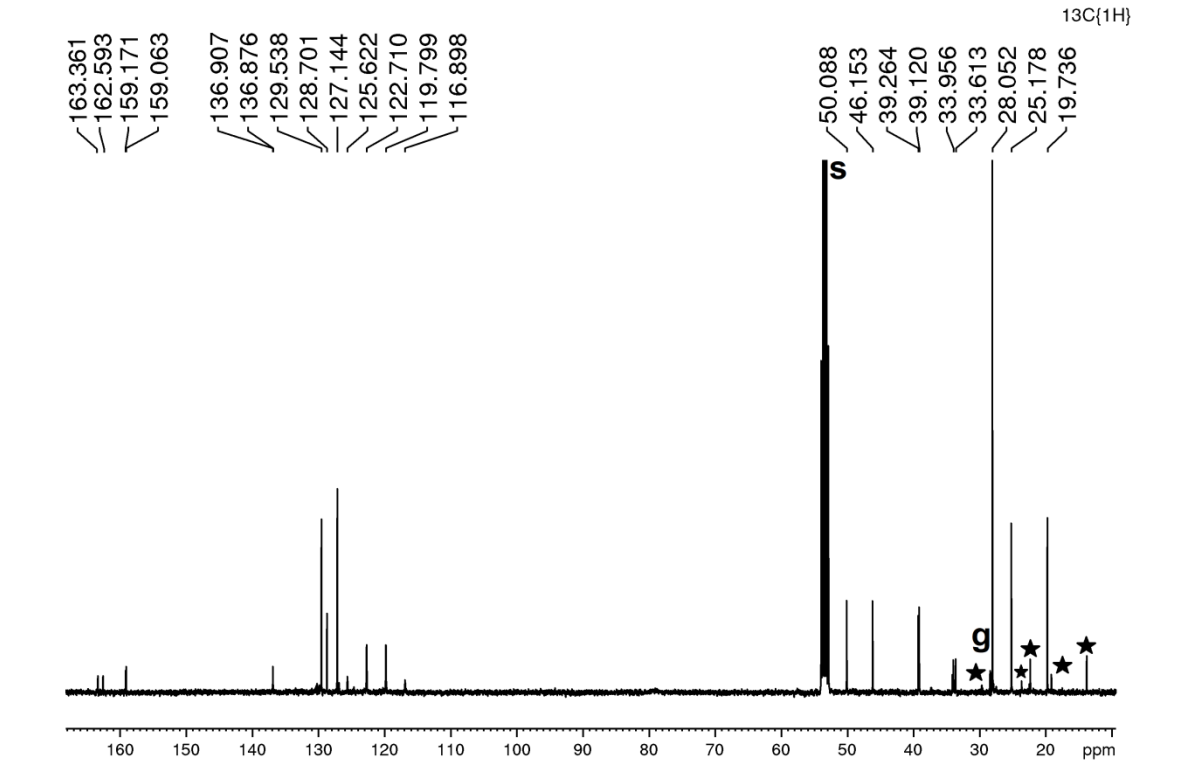


Figure S34. $^{13}C\{^{1}H\}$ spectrum (CD_2Cl_2) of **6**

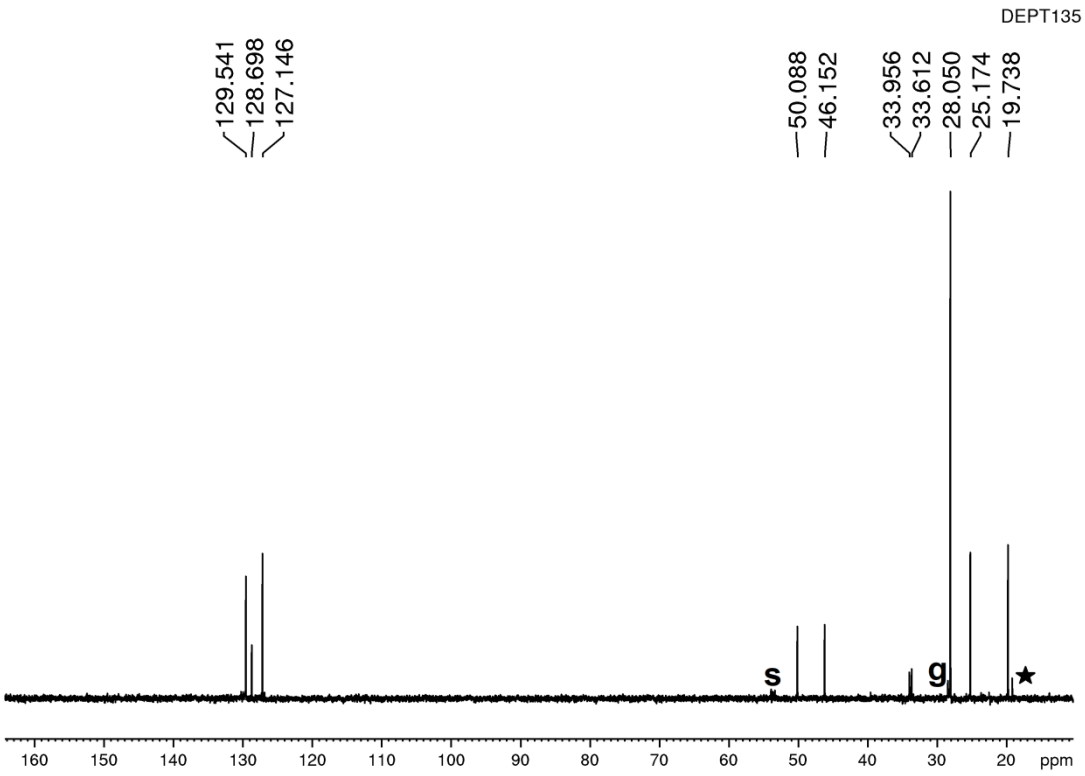


Figure S35. ^{135}DEPT spectrum (CD_2Cl_2) of **6**

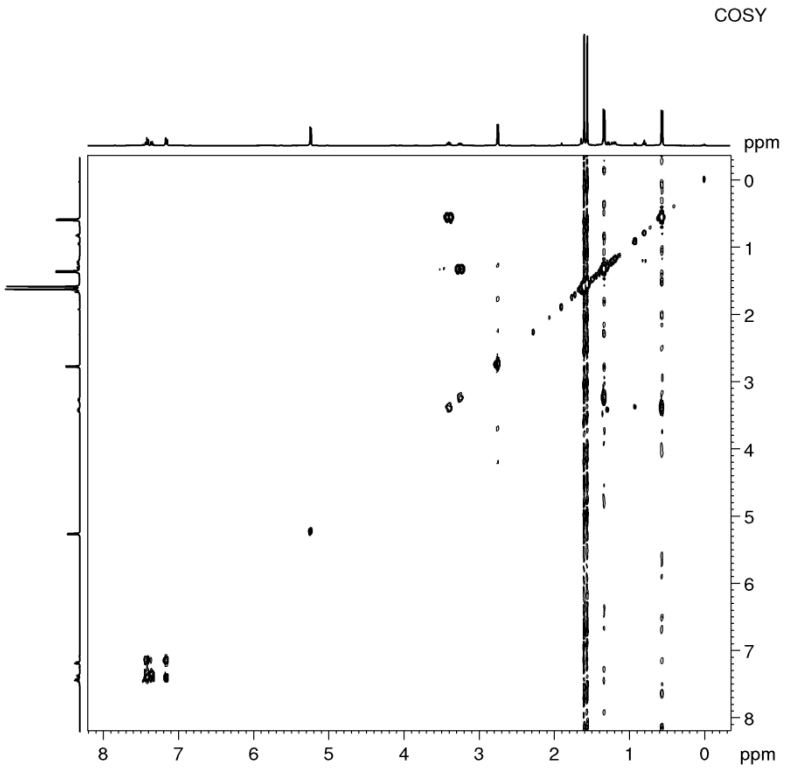


Figure S36. COSY spectrum (CD_2Cl_2) of **6**

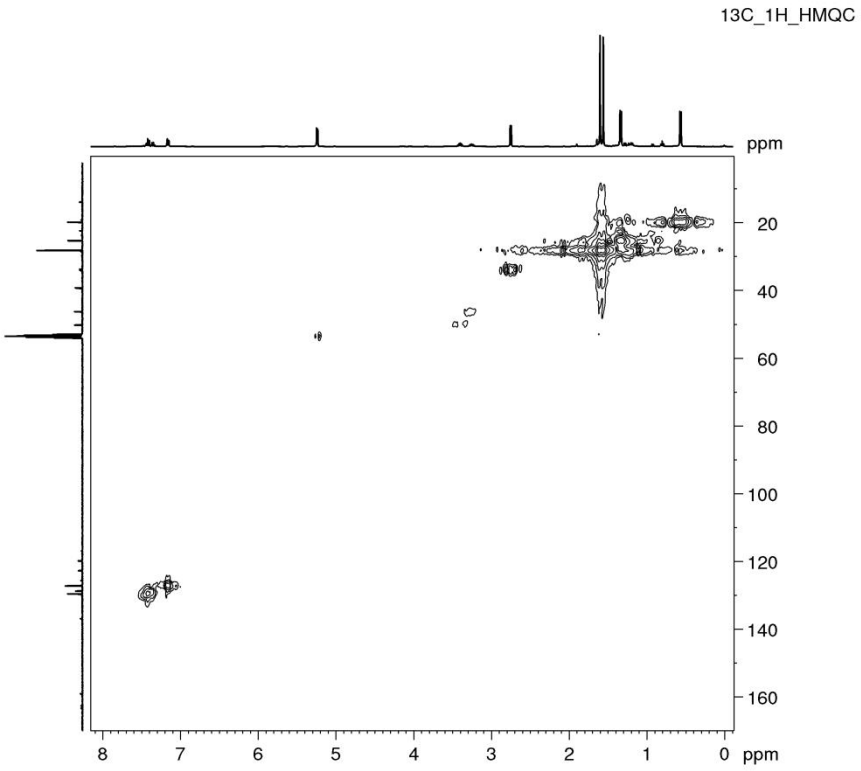


Figure S37. ^{13}C ^{1}H HMQC spectrum (CD_2Cl_2) of **6**

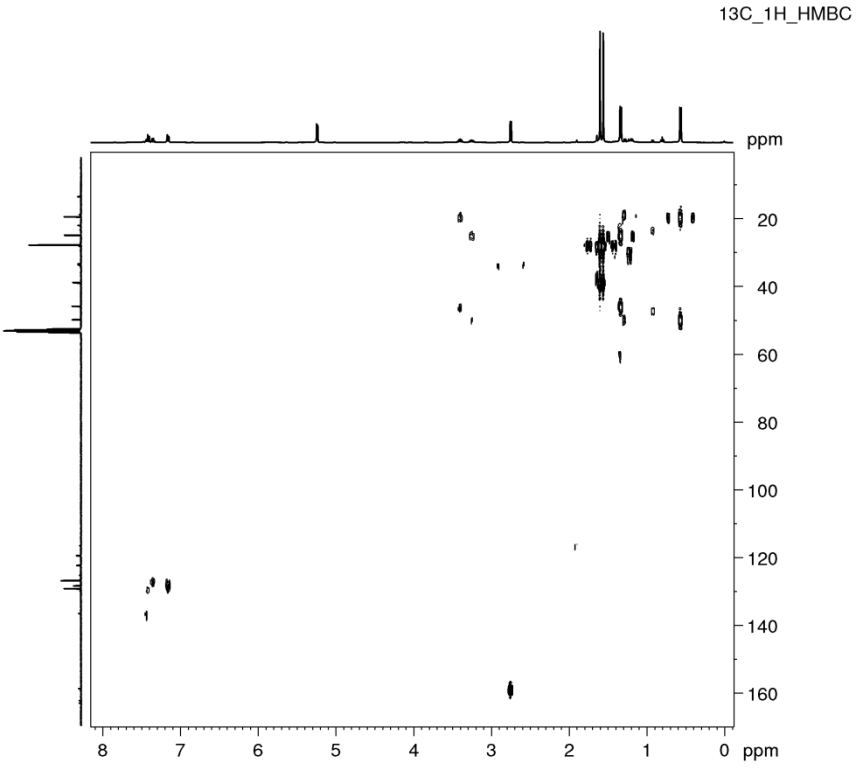


Figure S38. ^{13}C ^{1}H HMBC spectrum (CD_2Cl_2) of **6**

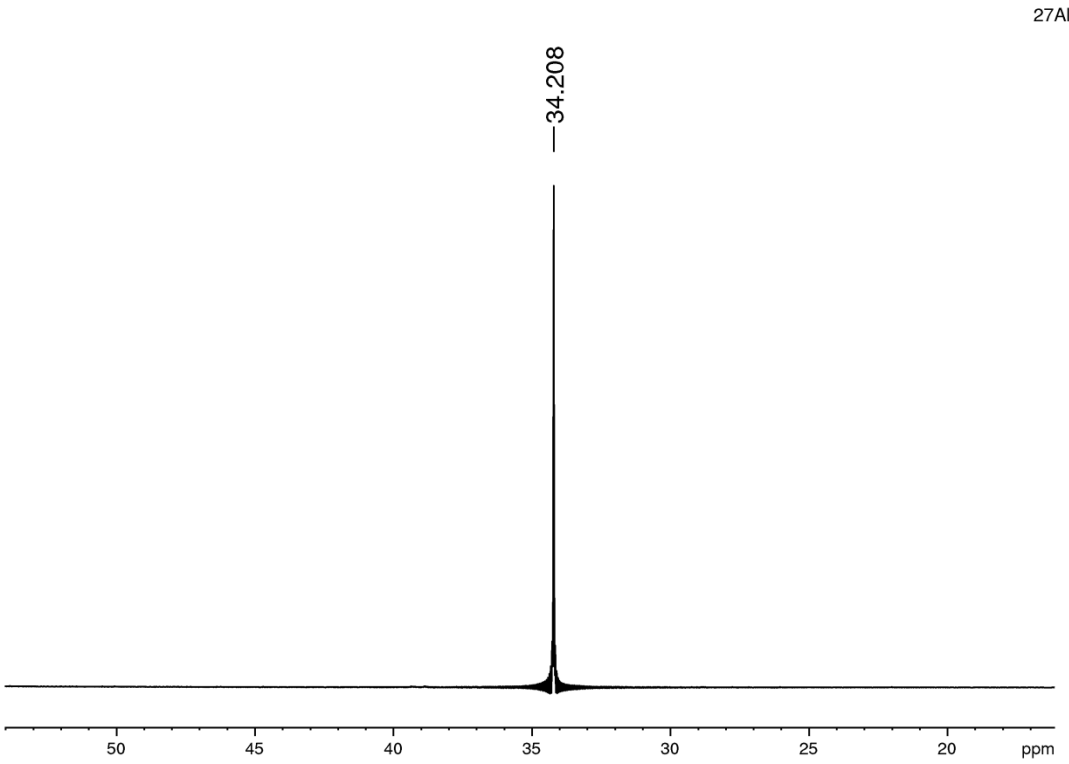


Figure S39. ^{27}Al spectrum (CD_2Cl_2) of **6**

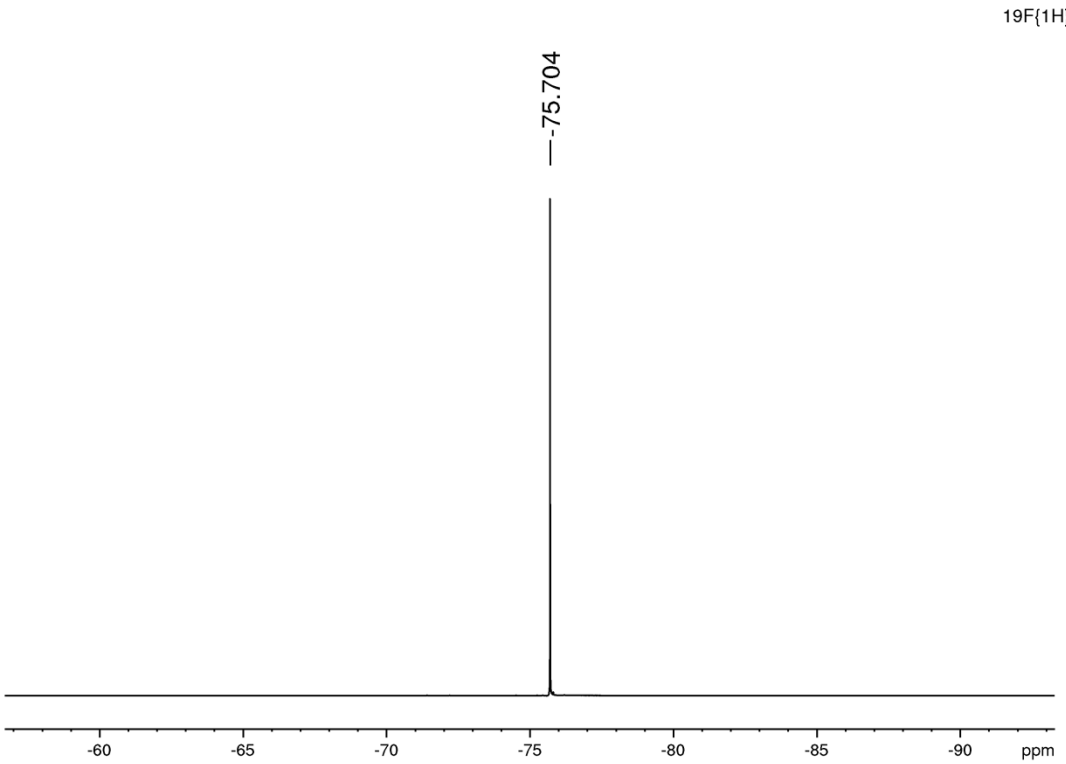
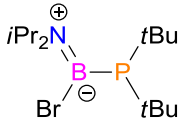
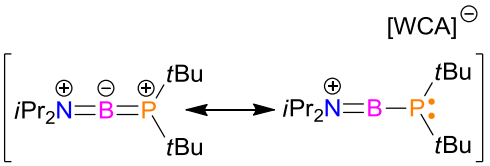
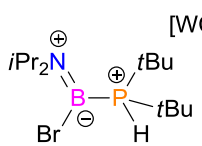
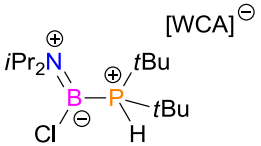


Figure S40. $^{19}F\{^{1}H\}$ spectrum (CD_2Cl_2) of **6**

Reaction of 1 with $Li[Al(OC(CF_3)_3)_4]$ – monitoring of reaction progress by ^{11}B and $^{31}P\{^1H\}$ NMR

Progress of the reaction between **1** (0.084 g, 0.25 mmol) and $Li[Al(OC(CF_3)_3)_4]$ (0.244 g, 0.250 mmol) mixed at -50 °C in CD_2Cl_2 was monitored by ^{11}B and $^{31}P\{^1H\}$ NMR. Spectra were recorded at -25 °C, 0 °C, 25 °C, and at 25 °C after 30 and 60 minutes.

Table S1. ^{11}B and $^{31}P\{^1H\}$ NMR shifts for **1**, and probable assignments of ^{11}B and $^{31}P\{^1H\}$ NMR signals for **2** and **7**

	1	**2**	**7**	
			7-Br	**7-Cl**
				
^{11}B NMR (CD_2Cl_2)	δ 38.2 (s)	δ 67.5 (bs)	δ 27.3 (d, $^1J_{BP}$ = 154.5 Hz)	δ 29.9 (d, $^1J_{BP}$ = 162.2 Hz)
$^{31}P\{^1H\}$ NMR (CD_2Cl_2)	δ -10.9 (s)	δ 51.5 (bs)	δ 12.2 (m)	δ 12.2 (m)

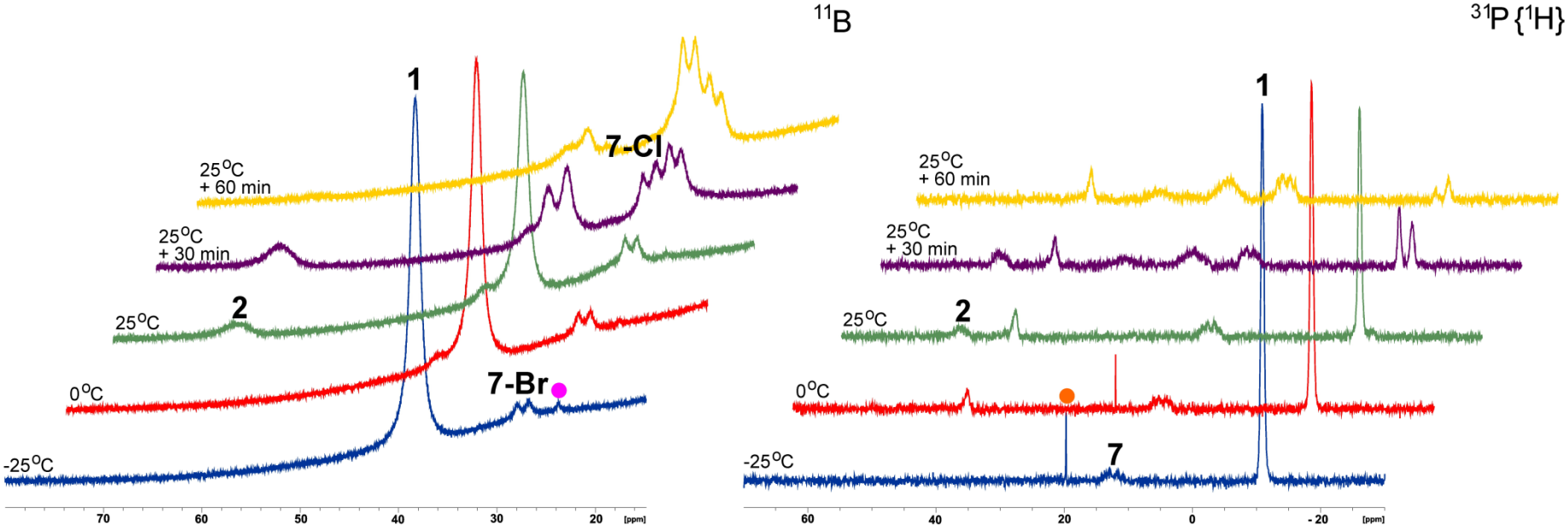


Figure S41. Monitoring of reaction progress by ^{11}B and $^{31}P\{^1H\}$ NMR. Reaction of **1** with $Li[Al(OC(CF_3)_3)_4]$

X-ray structure analysis

Generally all structures exhibit high degree of disorder which is located mainly in the aluminate anion. The $[Al(OC(CF_3)_3)_4]^-$ anion has many modes of deformation which makes it difficult to model. We found useful a model in which trifluoromethyl tetrahedral groups are arranged with horizontal C-F bond going in clockwise or anticlockwise direction in both parts. Sometimes also tilting on O-atom of the whole alkoxy group must have been taken into account. Without any disorder model at the flexible anions, R_1 indices rise well above 20%.

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*α 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 not performed because data absorption coefficient < 0.5 mm^{-1}, for all data. The structures were solved using intrinsic phasing implemented in SHELXT and refined anisotropically using the program packages Olex2[3] and SHELX-2015.[4,5] 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 **3** contains two cations and two anions in the asymmetric unit (Z' = 2). Both symmetry independent cations are fully ordered. Anions turned out to be substantially disordered. Disorder of the anion with Al1 was modelled with CF_3 groups running clockwise and anticlockwise at pivot atom O2 in both parts (with site occupation factors of 0.849(5)/0.151(5)). Anion containing Al2 atom was modelled as disordered in all alkoxy branches at O7, O8, O9 and O10. Only O8 atom was left in one position and related CF_3 groups running in opposite directions with s.o.f. of 0.656(4)/0.344(4). The other groups were modelled as disordered over two positions with the following occupation factors: 0.781(8)/0.219(8) at O7, 0.778(9)/ 0.222(9) at O9 and 0.716(5)/ 0.284(5) at O10. Several restraints were necessary to make refinement stable.

Structure **4** contained one cation and one anion in the asymmetric unit. The cation position was well defined and the anion was again disordered, but less than in other structures. We applied disorder model of CF_3 running in opposite directions for alkyloxy groups hanging at O1 and O3. Terminal CF_3 groups bound to C22-O1 were refined as disordered over two positions with occupation

factors of 0.702(5)/0.298(5). Groups attached at C30-O3 were refined to s.o.f. of 0. 695(6)/0.305(6). Several restraints were applied to bond lengths in these parts to get stable refinement.

Structure **5** contains one positive and one negative ion in the asymmetric unit. The anion is again strongly disordered. Two perfuoro *t*-butoxy groups OC_4F_9 containing O2 and O3 were refined as disordered over two positions, with occupation factors of 0.702(7)/0.298(7) and 0.775(5)/0.225(5), respectively. Terminal CF_3 groups bound to C31-O4 were refined as disordered over two positions with occupation factors of 0.692(7))/0.308(7). Several restraints were applied to C-F and F-F distances in order to get stable refinement. The cation is placed in the well-defined position with relatively small displacement ellipsoids for all atoms.

Asymmetric unit of structure **6** contains one cation, one anion and a solvent molecule of dichloromethane (perhaps not fully occupied). The solvent was strongly disordered and was cut out using the solvent mask (squeeze) procedure.[3] Program finds four voids of volume ca. 152Å^3, containing 40.6 electron charge, each. Exceptionally, one finds some disorder also in the cation in structure **6**. One *tert*-butyl group C16-C19 was refined as disordered over two positions with s.o.f. of 0.68(3)/0.32(3). Disorder of the anion was more demanding. We found best results with a model where two perfuoro *t*-butoxy groups OC_4F_9 containing O3 and O5 were disordered over three positions with occupation factors of 0.666(3) / 0.127(3) / 0.207(3) and 0.418(3) / 0.290(3) / 0.292(3), respectively. Naturally, many restraints were applied to C-F, C-C and F-F distances in order to get stable, meaningful refinement.

Crystallographic data for all structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. **CCDC 2240178 – 2240181**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S2. Crystal data and structure refinement for **3**, **4**, **5**, and **6**

	3	**4**	**5**	**6**
CCDC deposition No	2240178	2240179	2240180	2240181
Chemical formula	$C_{16}AlF_{36}O_4^-$ $\cdot C_{21}H_{37}BN_2OP^+$	$C_{16}AlF_{36}O_4^-$ $\cdot C_{21}H_{46}BN_3P^+$	$C_{16}AlF_{36}O_4^-$ $\cdot C_{18}H_{38}BN_3P^+$	$C_{16}AlF_{36}O_4^-$ $\cdot C_{23}H_{40}BN_3OP^+$
M_r [g·mol^{-1}]	1342.44	1349.53	1305.43	1383.50
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
Temperature [K]	120	120	120	120
a [Å] b [Å] c [Å]	17.0561(3) 40.9364(7) 17.3489(3)	10.5987(11) 16.314(3) 32.120(3)	18.6108(4) 14.3902(4) 20.5231(4)	14.2923(11) 27.525(3) 14.8101(11)
α [°] β [°] γ [°]	90 118.929(1) 90	90 98.263(1) 90	90 113.982(1) 90	90 94.220(6) 90
V [Å^3]	10601.8(3)	5496.1(13)	5021.9(2)	5810.3(8)
Z	8	4	4	4
Radiation type λ [Å]	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}]	1.682	1.631	1.727	1.582
μ [mm^{-1}]	0.24	0.23	0.25	0.22
Crystal size [mm]	0.24 × 0.15 × 0.13	0.37 × 0.11 × 0.09	0.37 × 0.31 × 0.27	0.43 × 0.14 × 0.07
F(000)	5360	2712	2608	2768
R_{int}	0.028	0.046	0.032	0.043
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	54894 21431 16051	45571 10771 8023	49002 9860 8240	50956 10678 8106
$R[F^2 > 2\sigma(F^2)]$	0.072	0.083	0.098	0.098
$wR(F^2)$	0.179	0.203	0.269	0.264
S	1.06	1.10	1.02	1.02
No. of reflections	21431	10771	9860	10678
No. of parameters	1788	875	915	1009
No. of restraints	88	75	114	358
$\Delta>_{max}$ [e·Å^{-3}] $\Delta>_{min}$ [e·Å^{-3}]	0.68 -0.58	0.89 -0.66	1.08 -0.69	1.20 -0.90

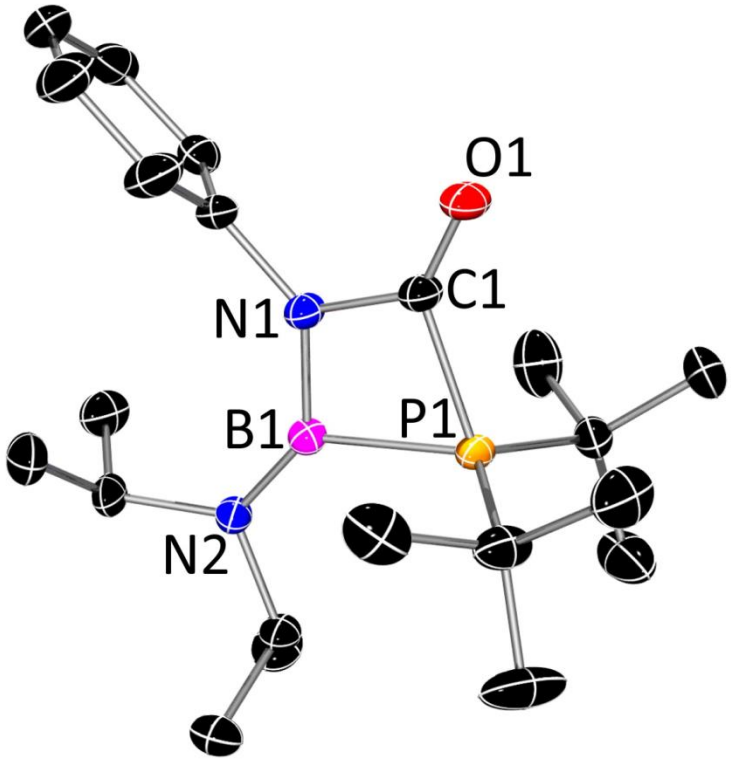


Figure S42. Molecular structure of **3**$^{+}$. The counterion and hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 40% probability level. Important bond distances [Å]: B1 – P1 1.964(4); B1 – N1 1.472(4); B1 – N2 1.371(4); P1 – C1 1.872(3); C1 – O1 1.194(4); C1 – N1 1.398 (4). Important angles [°]: N1 – B1 – N2 139.1(3); N2 – B1 – P1 132.2(3); P1 – B1 – N1 88.6(2); C1 – P1 – B1 72.40(15); B1 – P1 – C14 116.32(18); C14 – P1 – C18 120.7(2); C18 – P1 – C1 109.91(17); C1 – P1 – C14 109.91(17); C18 – P1 – B1 117.70(18); B1 – N1 – C1 104.3(3); C1 – N1 – C2 119.4(3); C2 – N1 – B1 136.3(3); B1 – N2 – C8 126.9(3); C8 – N2 – C11 114.3(3); C11 – N2 – B1 118.8(3); O1 – C1 – P1 135.4(3); P1 – C1 – N1 94.7(2); N1 – C1 – O1 129.9(3).

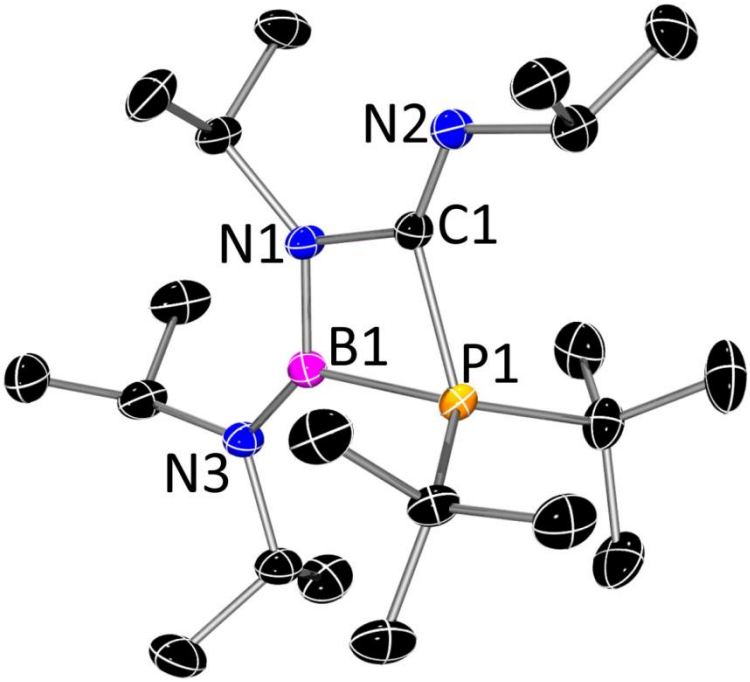


Figure S43. Molecular structure of **4**$^{+}$. The counterion and hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 40% probability level. Important bond distances [Å]: B1 – P1 1.963(5); B1 – N1 1.450(6); B1 – N3 1.382(6); P1 – C1 1.871(4); C1 – N1 1.411(5); C1 – N2 1.249(5). Important angles [°]: N1 – B1 – N3 138.7(4); N3 – B1 – P1 132.6(3); P1 – B1 – N1 88.7(3); C1 – P1 – B1 72.57(19); B1 – P1 – C14 115.1(2); C14 – P1 – C18 118.3(2); C18 – P1 – C1 113.9(2); C1 – P1 – C14 111.81(19); C18 – P1 – B1 116.6(2); B1 – N1 – C1 105.0(3); C1 – N1 – C2 120.1(3); C2 – N1 – B1 134.8(3); C1 – N2 – C5 121.0(4); B1 – N3 – C8 126.4(4); C8 – N3 – C11 113.5(3); C11 – N3 – B1 120.0(4); N1 – C1 – P1 93.6(3); P1 – C1 – N2 139.7(3); N2 – C1 – N1 126.7(4).

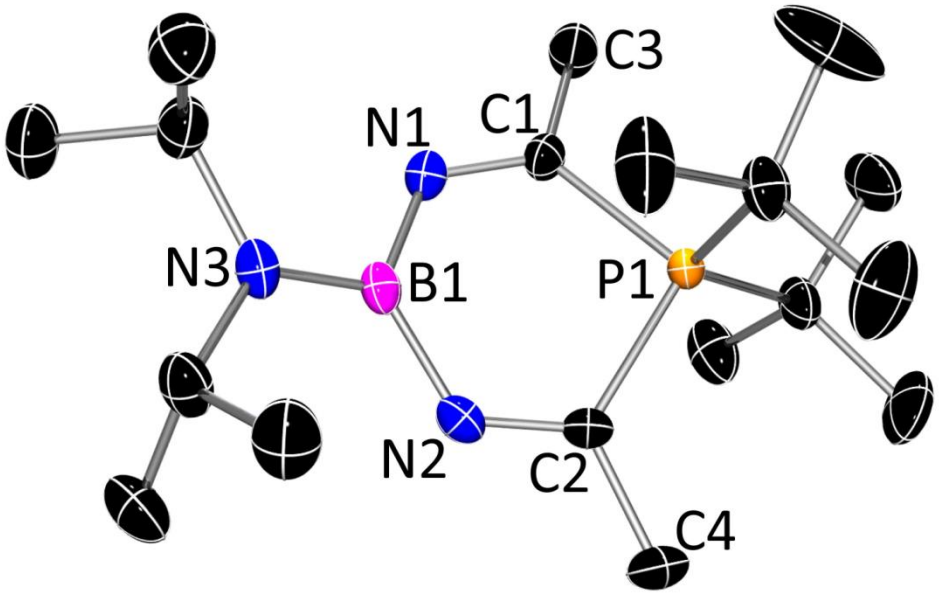


Figure S44. Molecular structure of $\mathbf{5}^{+}$. The counterion and hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 40% probability level. Important bond distances [Å]: B1 – N1 1.483(6); B1 – N2 1.466(6); B1 – N3 1.387(6); P1 – C1 1.873(4); P1 – C2 1.879(4); C1 – C3 1.509(6); C1 – N1 1.261(5); C2 – C4 1.502(6); C2 – N2 1.259(5). Important angles [°]: N1 – B1 – N2 120.1(3); N2 – B1 – N3 121.8(4); N3 – B1 – N1 118.1(4); C1 – P1 – C2 100.57(18); C2 – P1 – C11 111.2(2); C11– P1 – C1 111.6(2); C11– P1 – C15 117.3(2); C15 – P1 – C1 107.06(19); C2 – P1 – C15 107.7(2); B1 – N1 – C1 125.2(3); B1 – N2 – C2 124.6(3); B1 – N3 – C5 121.2(4); C5 – N3 – C8 114.8(3); C8 – N3 – B1 123.9(4); N1 – C1 – P1 118.7(3); P1 – C1 – C3 120.0(3); C3 – C1 – N1 121.3(4); N2 – C2 – P1 119.5(3); P1 – C2 – C4 120.4(3); C4 – C2 – N2 120.1(4).

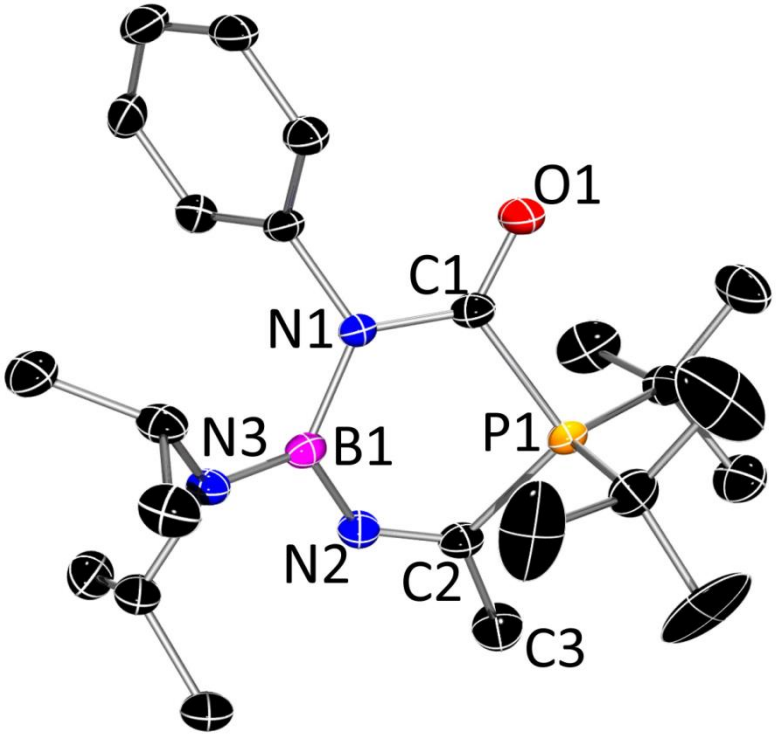


Figure S45. Molecular structure of $\mathbf{6}^{+}$. The counterion and hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 40% probability level. Important bond distances [Å]: B1 – N1 1.494(6); B1 – N2 1.460(6); B1 – N3 1.375(7); P1 – C1 1.873(4); P1 – C2 1.870(5); C1 – O1 1.215(6); C1 – N1 1.356(6); C2 – C3 1.505(6); C2 – N2 1.258(6). Important angles [°]: N1 – B1 – N2 117.0(4); N2 – B1 – N3 119.6(4); N3 – B1 – N1 123.4(4); C1 – P1 – C2 102.2(2); C2 – P1 – C16 110.4(2); C16 – P1 – C1 105.8(2); C16 – P1 – C20 117.8(2); C20 – P1 – C1 105.9(2); C2 – P1 – C20 113.1(2); B1 – N1 – C1 122.6(4); C1 – N1 – C4 115.4(3); C4 – N1 – B1 121.6(4); B1 – N2 – C2 129.5(4); B1 – N3 – C10 123.4(4); C10 – N3 – C13 114.0(4); C13 – N3 – B1 122.5(4); O1 – C1 – P1 115.6(4); P1 – C1 – N1 118.0(3); N1 – C1 – O1 126.3(4); N2 – C2 – P1 116.3(3); P1 – C2 – C3 121.1(4); C3 – C2 – N2 122.6(4).

DFT calculations

General methods

The stationary point structures (energy minima and first-order saddle points) of all systems investigated in this work were calculated using density functional theory (DFT) method, especially ωB97xD[6] hybrid functional with the 6-311++G(d,p)[7] Pople's basis set of triple-zeta quality. The corresponding harmonic frequencies were computed at the same level of theory to characterize the nature of stationary points. The Gibbs free energies of resulted structures were estimated using ωB97xD/6-311++G(d,p) electronic energies, 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).[8] Natural Bond Orbital and Natural Resonance Theory computations were performed with the NBO 7.0 module.[9] All calculations were completed with Gaussian16 (Rev.C.01) software,[10] excluding NBO and NRT analyzes for which Gaussian 09 (Rev.D.01) program package was used.[11]

Structures

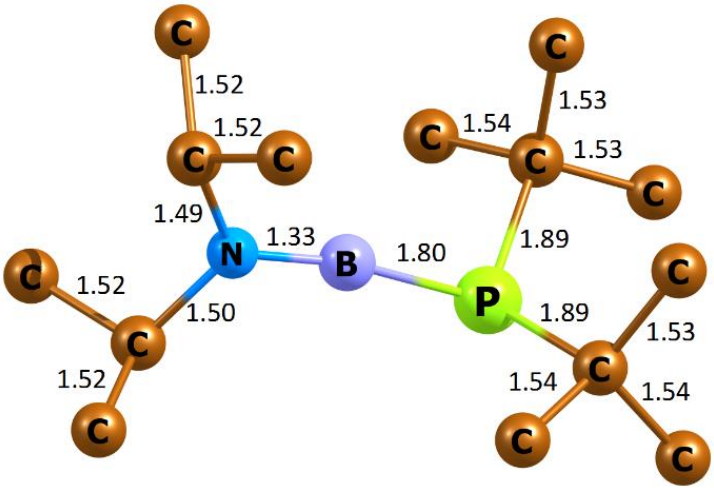


Figure S46. The ωB97xD/6-311++G(d,p) equilibrium geometry of the $\mathbf{2}^{+}$ system. The hydrogen atoms are omitted for clarity. The bond lengths are given in Å.

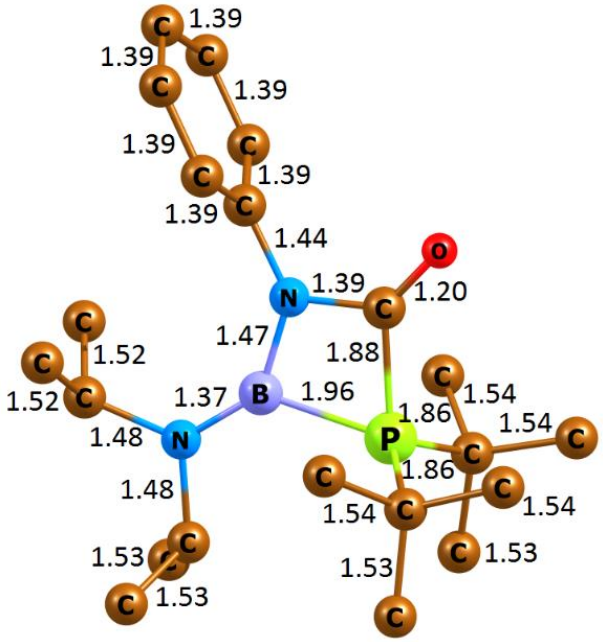


Figure S47. The ωB97xD/6-311++G(d,p) equilibrium geometry of the **3**$^{+}$ system. The hydrogen atoms are omitted for clarity. The bond lengths are given in Å.

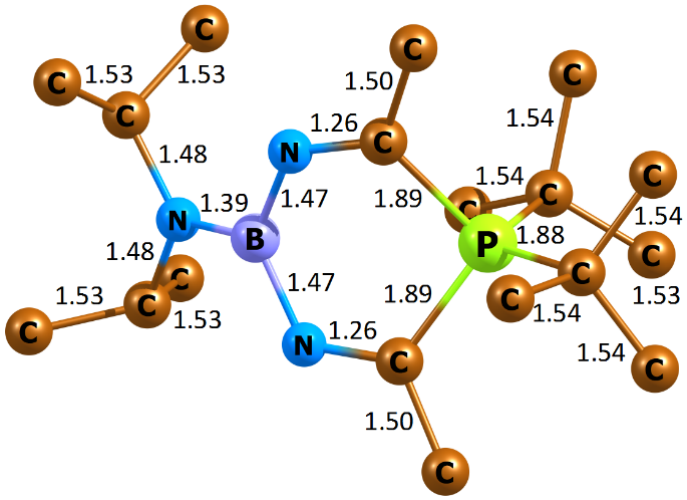


Figure S48. The ωB97xD/6-311++G(d,p) equilibrium geometry of the **5**$^{+}$ system. The hydrogen atoms are omitted for clarity. The bond lengths are given in Å.

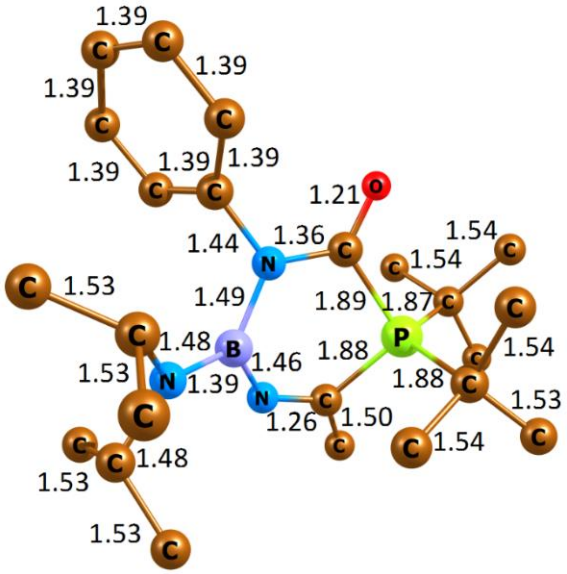


Figure S49. The ωB97xD/6-311++G(d,p) equilibrium geometry of the **6**$^{+}$ system. The hydrogen atoms are omitted for clarity. The bond lengths are given in Å.

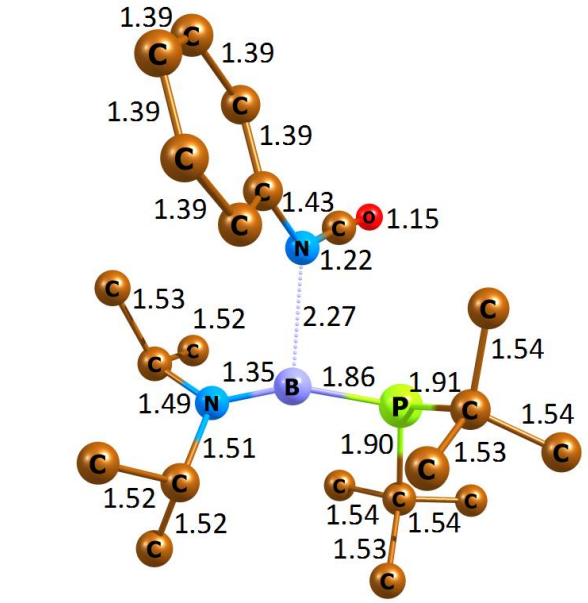


Figure S50. The ωB97xD/6-311++G(d,p) transition state structure (TS) found for the reaction of $\mathbf{2}^{+}$ with PhNCO. The hydrogen atoms are omitted for clarity. Selected interatomic distances are given in Å.

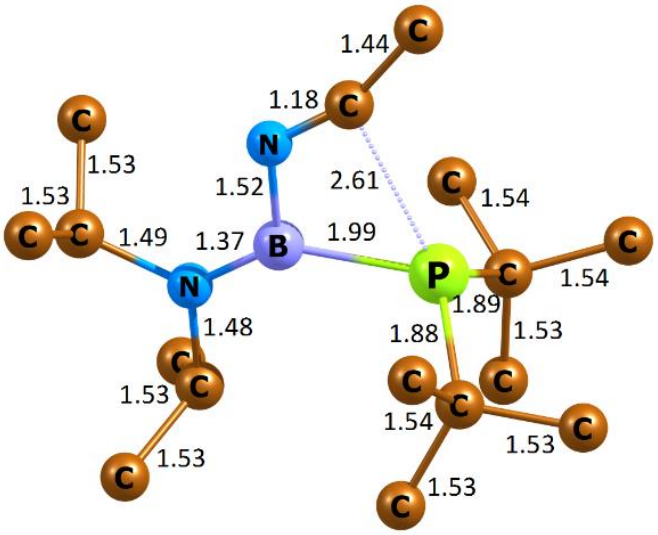


Figure S51. The ωB97xD/6-311++G(d,p) transition state structure (TS1) found for the reaction of $\mathbf{2}^{+}$ with 2 equiv of MeCN. The hydrogen atoms are omitted for clarity. Selected interatomic distances are given in Å.

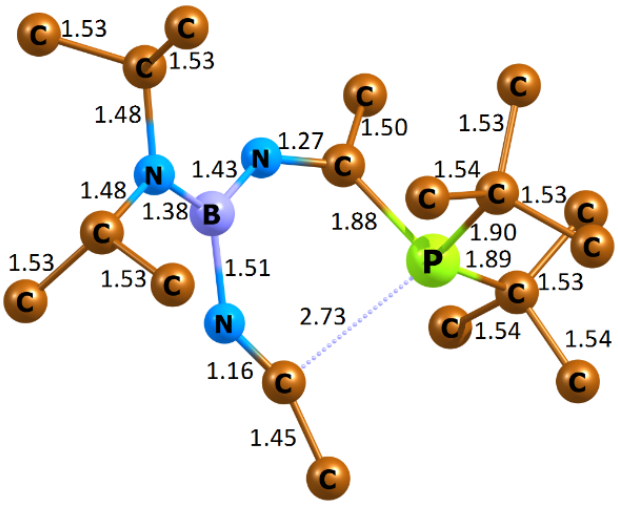


Figure S52. The ωB97xD/6-311++G(d,p) transition state structure (TS2) found for the reaction of $\mathbf{2}^{+}$ with 2 equiv of MeCN. The hydrogen atoms are omitted for clarity. Selected interatomic distances are given in Å.

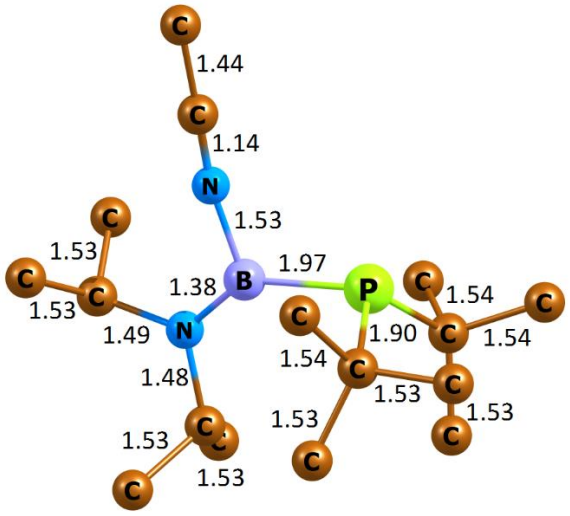


Figure S53. The ωB97xD/6-311++G(d,p) intermediate product (IP1) found for the reaction of $\mathbf{2}^{+}$ with 2 equiv of MeCN. The hydrogen atoms are omitted for clarity. Selected interatomic distances are given in Å.

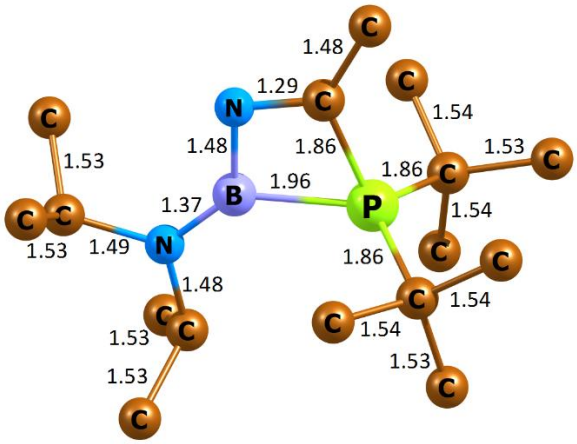


Figure S54. The ωB97xD/6-311++G(d,p) intermediate product (IP2) found for the reaction of $\mathbf{2}^{+}$ with 2 equiv of MeCN. The hydrogen atoms are omitted for clarity. Selected interatomic distances are given in Å.

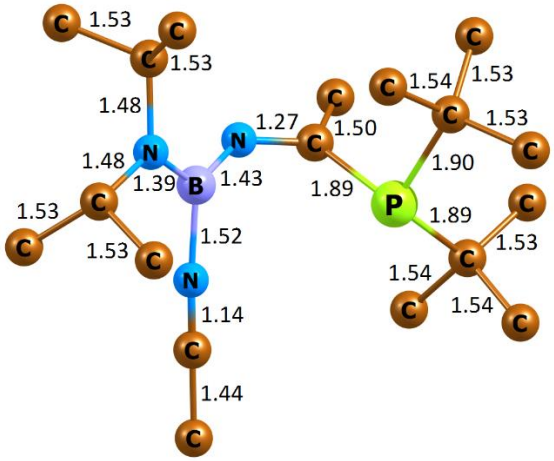


Figure S55. The ωB97xD/6-311++G(d,p) intermediate product (IP3) found for the reaction of $\mathbf{2}^{+}$ with 2 equiv of MeCN. The hydrogen atoms are omitted for clarity. Selected interatomic distances are given in Å.

Cartesian coordinates

The Cartesian coordinates of all systems investigated in this contribution.

2^{+}

P	1.177055000	-0.045296000	-0.643774000
N	-1.873979000	-0.060724000	-0.059105000
C	-2.658498000	-0.305970000	-1.315600000
H	-1.915879000	-0.340142000	-2.117400000
B	-0.549649000	-0.041777000	-0.148416000
C	-2.605663000	0.125245000	1.229697000
H	-3.631540000	-0.188691000	1.034474000
C	2.006802000	-1.587810000	0.057486000
C	-2.605250000	1.595924000	1.631472000
H	-1.591877000	1.933452000	1.866408000
H	-3.222382000	1.730448000	2.522077000
H	-3.004794000	2.226652000	0.836346000
C	1.797033000	1.984832000	1.281110000
H	0.758271000	2.010937000	1.617875000
H	2.229287000	2.977580000	1.443022000
H	2.342142000	1.279227000	1.907237000
C	-2.017471000	-0.777988000	2.306203000
H	-2.032615000	-1.823088000	1.990656000
H	-2.603739000	-0.684584000	3.222079000
H	-0.986563000	-0.493023000	2.542081000
C	1.896591000	1.643592000	-0.210062000
C	-3.347709000	-1.662948000	-1.241299000
H	-2.624059000	-2.456025000	-1.042826000
H	-3.831833000	-1.866837000	-2.198308000
H	-4.118738000	-1.687533000	-0.467456000
C	-3.613312000	0.846301000	-1.594633000
H	-4.389550000	0.925236000	-0.829723000
H	-4.107305000	0.668500000	-2.551865000
H	-3.076925000	1.795172000	-1.655237000
C	3.362640000	1.658588000	-0.663212000
H	3.978880000	0.975834000	-0.074026000
H	3.762004000	2.666885000	-0.520235000
H	3.466012000	1.400371000	-1.719932000
C	1.085502000	2.658118000	-1.029944000
H	1.160756000	2.467906000	-2.102839000
H	1.477669000	3.660045000	-0.832072000
H	0.027204000	2.660484000	-0.749723000
C	2.565182000	-1.387436000	1.468446000
H	3.372797000	-0.653164000	1.488923000
H	2.981958000	-2.339125000	1.813497000
H	1.792571000	-1.079715000	2.175550000
C	3.137499000	-1.972013000	-0.909957000
H	2.754414000	-2.172444000	-1.913259000
H	3.622379000	-2.881008000	-0.541693000
H	3.900292000	-1.193748000	-0.980376000
C	0.940878000	-2.692555000	0.063246000
H	0.170058000	-2.510274000	0.816971000
H	1.424505000	-3.642708000	0.307543000
H	0.461529000	-2.808506000	-0.913070000

3^{+}

P	1.463920000	-0.700708000	-0.004197000
O	-0.311136000	-2.926435000	-0.134413000
N	-0.965616000	-0.677530000	-0.039750000
N	-0.184375000	1.871163000	0.033182000
C	-0.089481000	-1.751801000	-0.079459000
C	-2.381538000	-0.912494000	-0.023608000
C	-3.032959000	-1.044133000	1.195997000
H	-2.472085000	-0.945081000	2.118337000
C	-4.399610000	-1.293064000	1.213805000
H	-4.915271000	-1.389718000	2.161762000
C	-5.100200000	-1.420715000	0.018968000
H	-6.166300000	-1.614378000	0.035349000
C	-4.433827000	-1.308707000	-1.196819000
H	-4.976590000	-1.418151000	-2.128088000
C	-3.067111000	-1.059373000	-1.222158000
H	-2.534165000	-0.974024000	-2.162189000
C	-1.440446000	2.660555000	-0.030505000
H	-1.129028000	3.705354000	-0.030509000
C	-2.187463000	2.421598000	-1.338106000
H	-1.525307000	2.578693000	-2.192508000
H	-3.023664000	3.120332000	-1.415808000
H	-2.594387000	1.411165000	-1.391458000
C	-2.306476000	2.456020000	1.207639000
H	-2.715936000	1.446225000	1.251106000
H	-3.146183000	3.154808000	1.185605000
H	-1.729416000	2.639783000	2.116572000
C	1.059054000	2.679709000	0.101441000
H	1.880658000	1.962165000	0.147594000
C	1.263176000	3.513855000	-1.160673000
H	1.240858000	2.883277000	-2.052763000
H	2.235406000	4.009813000	-1.115310000
H	0.501540000	4.289537000	-1.270382000
C	1.123541000	3.512372000	1.378877000
H	0.356269000	4.290019000	1.402586000
H	2.095664000	4.006408000	1.441800000
H	0.999362000	2.880083000	2.261225000
C	2.378528000	-0.840353000	-1.621484000
C	1.336047000	-0.513798000	-2.706746000
H	0.509036000	-1.228220000	-2.716335000
H	1.831359000	-0.572725000	-3.679117000
H	0.927958000	0.495486000	-2.602403000
C	2.896204000	-2.273130000	-1.813836000
H	3.706337000	-2.514600000	-1.125851000
H	3.290465000	-2.356230000	-2.830380000
H	2.103508000	-3.015943000	-1.699604000
C	3.531012000	0.170430000	-1.689076000
H	3.198575000	1.198587000	-1.527429000
H	3.964063000	0.120326000	-2.691845000
H	4.326184000	-0.058278000	-0.979172000
C	2.308120000	-0.993201000	1.630244000
C	2.961192000	-2.382477000	1.650503000
H	2.266858000	-3.169972000	1.348531000
H	3.278526000	-2.591190000	2.675822000
H	3.848437000	-2.429182000	1.018601000
C	1.192847000	-0.927317000	2.689476000
H	0.657855000	0.026252000	2.676116000
H	1.657491000	-1.030303000	3.673363000
H	0.471256000	-1.740223000	2.578940000
C	3.347348000	0.102316000	1.903753000
H	4.149050000	0.113449000	1.164813000
H	3.801007000	-0.101549000	2.877622000
H	2.898687000	1.096664000	1.954684000
B	-0.087123000	0.502051000	0.011112000

5^{+}

P	1.568326000	0.049771000	-0.063024000
N	-0.673155000	1.257589000	-1.044740000
N	-0.691977000	-1.279250000	-0.816633000
N	-2.719621000	0.068496000	-0.319535000
C	0.550802000	1.447328000	-0.826711000
C	0.532785000	-1.445380000	-0.580573000
C	1.435950000	0.170053000	1.810961000
C	0.033810000	0.691361000	2.161042000
H	-0.135918000	1.709056000	1.804745000
H	-0.053268000	0.699260000	3.250687000
H	-0.759650000	0.045632000	1.779344000
C	2.492851000	1.131004000	2.369427000
H	3.504301000	0.735855000	2.268326000
H	2.296867000	1.254764000	3.437872000
H	2.446751000	2.121238000	1.911075000
C	1.614236000	-1.226987000	2.425511000
H	0.794342000	-1.895503000	2.154480000
H	1.601743000	-1.117316000	3.513004000
H	2.561654000	-1.695336000	2.155177000
C	3.296994000	-0.038661000	-0.790264000
C	4.096446000	1.265296000	-0.611158000
H	3.688054000	2.094760000	-1.182095000
H	5.101329000	1.074519000	-0.997062000
H	4.201247000	1.568993000	0.428265000
C	4.096658000	-1.174372000	-0.129453000
H	4.323844000	-0.953524000	0.914835000
H	5.049689000	-1.257838000	-0.658274000
H	3.609470000	-2.145530000	-0.185658000
C	3.117542000	-0.295260000	-2.297796000
H	2.633548000	-1.246650000	-2.518017000
H	4.109127000	-0.316391000	-2.756874000
H	2.547247000	0.499291000	-2.785142000
C	-3.402905000	1.368825000	-0.165574000
H	-2.681837000	2.119734000	-0.487432000
C	-3.747618000	1.655484000	1.296125000
H	-4.484289000	0.950577000	1.691999000
H	-4.170662000	2.659143000	1.384293000
H	-2.853098000	1.604693000	1.921781000
C	-4.620356000	1.478122000	-1.083168000
H	-4.336417000	1.288709000	-2.120991000
H	-5.036380000	2.486580000	-1.018936000
H	-5.413667000	0.777258000	-0.808998000
C	-3.521284000	-1.122424000	0.044729000
H	-4.499872000	-0.742637000	0.342532000
C	-3.750816000	-2.045857000	-1.150648000
H	-4.186427000	-1.488803000	-1.983572000
H	-4.444106000	-2.843914000	-0.871499000
H	-2.814699000	-2.497513000	-1.481694000
C	-2.954309000	-1.858811000	1.258071000
H	-1.994070000	-2.324275000	1.026749000
H	-3.647357000	-2.644985000	1.568899000
H	-2.821243000	-1.173270000	2.099087000
B	-1.391226000	0.011535000	-0.726330000
C	1.210506000	2.760540000	-1.125798000
H	1.827165000	3.103830000	-0.292281000
H	0.429481000	3.492944000	-1.326584000
H	1.848935000	2.681284000	-2.009425000
C	1.161269000	-2.807906000	-0.655028000
H	1.921305000	-2.865220000	-1.435927000
H	0.372218000	-3.525107000	-0.878315000
H	1.633783000	-3.080517000	0.290821000

6^{+}

P	2.059250000	0.087554000	-0.024819000
O	0.839193000	2.401997000	0.516968000
N	-0.636276000	0.755321000	-0.084556000
N	0.162941000	-1.291172000	-1.334400000
N	-1.948600000	-1.409415000	-0.060919000
C	0.592232000	1.267785000	0.174702000
C	-1.735307000	1.690983000	-0.132052000
C	-2.396712000	1.859872000	-1.341655000
H	-2.067193000	1.312313000	-2.217836000
C	-3.482426000	2.724868000	-1.416044000
H	-4.002017000	2.853154000	-2.358211000
C	-3.896810000	3.419344000	-0.285938000
H	-4.744761000	4.091796000	-0.342599000
C	-3.220378000	3.252581000	0.919016000
H	-3.539015000	3.795051000	1.801318000
C	-2.135709000	2.389731000	1.000104000
H	-1.608663000	2.253268000	1.936941000
C	2.343887000	-1.861555000	-2.207608000
H	2.748329000	-1.188487000	-2.968269000
H	1.786232000	-2.654784000	-2.704606000
H	3.184035000	-2.292520000	-1.658323000
C	1.408243000	-1.128490000	-1.296686000
C	-2.793604000	-0.993888000	1.078862000
H	-2.324867000	-0.107234000	1.501817000
C	-2.805117000	-2.044181000	2.192377000
H	-3.311685000	-2.965050000	1.893238000
H	-3.339032000	-1.641338000	3.056173000
H	-1.790540000	-2.297315000	2.508155000
C	-4.206954000	-0.612200000	0.641881000
H	-4.180858000	0.175284000	-0.113192000
H	-4.771036000	-0.245144000	1.502679000
H	-4.748559000	-1.469230000	0.231900000
C	-2.332594000	-2.695949000	-0.693876000
H	-3.279169000	-2.977350000	-0.230220000
C	-2.615603000	-2.531124000	-2.185806000
H	-3.347911000	-1.736074000	-2.347335000
H	-3.025134000	-3.461660000	-2.587462000
H	-1.705575000	-2.290085000	-2.737340000
C	-1.342656000	-3.822956000	-0.401020000
H	-0.396187000	-3.656760000	-0.918475000
H	-1.758239000	-4.775168000	-0.741453000
H	-1.147176000	-3.900599000	0.670901000
C	2.290875000	-0.764710000	1.631757000
H	2.740001000	1.118776000	2.685843000
C	3.697787000	-1.369861000	1.725540000
H	3.911306000	-2.065544000	0.910770000
H	3.753547000	-1.934476000	2.659769000
H	4.475417000	-0.606430000	1.759376000
C	3.471570000	1.136483000	-0.662233000
C	2.923696000	1.909218000	-1.876580000
H	2.496146000	1.247284000	-2.635268000
H	3.760072000	2.438171000	-2.340368000
H	2.176110000	2.647711000	-1.588506000
C	4.663446000	0.272165000	-1.110597000
H	5.052371000	-0.369818000	-0.322213000
H	5.463476000	0.961859000	-1.392066000
H	4.442825000	-0.336239000	-1.984759000
C	3.949512000	2.112219000	0.426544000
H	3.138859000	2.720929000	0.822734000
H	4.684302000	2.778476000	-0.033675000
H	4.450973000	1.592579000	1.245097000
B	-0.845810000	-0.670446000	-0.479540000
C	1.244751000	-1.882252000	1.752718000
H	0.222282000	-1.504315000	1.697402000
H	1.365235000	-2.342477000	2.736761000
H	1.371442000	-2.661728000	0.999271000
C	2.068719000	0.262651000	2.753163000
H	2.260149000	-0.239264000	3.705176000
H	1.039714000	0.627851000	2.770809000

TS

P	1.691520000	-0.877272000	0.458408000
O	-0.742730000	-1.448133000	3.209664000
N	-1.347870000	-0.656935000	1.055306000
N	-0.029524000	1.683841000	-0.118441000
C	-1.087058000	-1.092218000	2.169685000
C	-2.581197000	-0.795091000	0.346806000
C	-3.779598000	-1.001617000	1.023037000
H	-3.796133000	-1.074140000	2.104912000
C	-4.959734000	-1.099040000	0.298460000
H	-5.893219000	-1.260344000	0.824209000
C	-4.947615000	-0.983780000	-1.087846000
H	-5.872636000	-1.056118000	-1.646902000
C	-3.744920000	-0.776127000	-1.752171000
H	-3.724038000	-0.687361000	-2.831714000
C	-2.558541000	-0.681861000	-1.036431000
H	-1.622086000	-0.522562000	-1.554063000
C	-0.800882000	2.613951000	0.758598000
H	-0.588723000	3.603114000	0.352829000
C	-2.313789000	2.411516000	0.713018000
H	-2.676321000	2.231365000	-0.298783000
H	-2.791762000	3.317856000	1.091422000
H	-2.627776000	1.583457000	1.347599000
C	-0.266413000	2.574004000	2.185203000
H	-0.402502000	1.587280000	2.637739000
H	-0.817430000	3.291776000	2.795836000
H	0.792559000	2.832394000	2.223781000
C	0.406681000	2.206990000	-1.460611000
H	0.951291000	1.382432000	-1.930606000
C	-0.803178000	2.523612000	-2.333101000
H	-1.477827000	1.669508000	-2.410458000
H	-0.457370000	2.781615000	-3.335952000
H	-1.362377000	3.377311000	-1.943001000
C	1.353387000	3.396868000	-1.345148000
H	0.852011000	4.288126000	-0.962637000
H	1.728885000	3.636228000	-2.342315000
H	2.210416000	3.178632000	-0.707837000
C	1.496615000	-2.162829000	-0.934407000
C	0.294031000	-3.049598000	-0.580582000
H	0.411473000	-3.515043000	0.400952000
H	0.219486000	-3.846962000	-1.326540000
H	-0.648623000	-2.503371000	-0.596784000
C	2.752298000	-3.046052000	-0.949315000
H	3.635734000	-2.507742000	-1.294864000
H	2.580340000	-3.871024000	-1.647198000
H	2.961548000	-3.477822000	0.032340000
C	1.292043000	-1.538311000	-2.319108000
H	0.354637000	-0.979572000	-2.376904000
H	1.242695000	-2.334766000	-3.068858000
H	2.107432000	-0.869614000	-2.598276000
C	3.358882000	0.026881000	0.452853000
C	4.391000000	-0.911997000	1.103603000
H	4.060588000	-1.245847000	2.090378000
H	5.328426000	-0.361369000	1.230283000
H	4.606091000	-1.790665000	0.496533000
C	3.191668000	1.239117000	1.381273000
H	2.522940000	1.992852000	0.966087000
H	4.169117000	1.708746000	1.525087000
H	2.812531000	0.947368000	2.364585000
C	3.856722000	0.478993000	-0.921833000
H	4.057339000	-0.364318000	-1.584728000
H	4.797224000	1.025691000	-0.797801000
H	3.149926000	1.145817000	-1.418964000
B	0.422904000	0.448481000	0.161445000

TS1

P	1.282802000	0.368834000	-0.076321000
N	-0.792739000	2.088936000	-0.099744000
N	-1.816856000	-0.207989000	0.063777000
C	0.185629000	2.729623000	-0.259904000
C	1.786330000	-0.738565000	-1.517243000
C	0.830578000	-0.372513000	-2.665080000
H	-0.200588000	-0.662056000	-2.450033000
H	1.141250000	-0.895370000	-3.574868000
H	0.847589000	0.700815000	-2.879491000
C	1.747317000	-2.249178000	-1.269225000
H	2.443540000	-2.553363000	-0.485544000
H	2.045518000	-2.764742000	-2.188383000
H	0.749857000	-2.606591000	-1.007598000
C	3.211513000	-0.327998000	-1.929408000
H	3.275570000	0.743703000	-2.134832000
H	3.485232000	-0.864905000	-2.843419000
H	3.951493000	-0.575080000	-1.166779000
C	1.907342000	-0.226548000	1.598399000
C	1.256069000	-1.513693000	2.115466000
H	0.190046000	-1.371711000	2.300081000
H	1.718168000	-1.784736000	3.070798000
H	1.384820000	-2.357337000	1.436624000
C	3.430610000	-0.400026000	1.534927000
H	3.717035000	-1.271381000	0.942281000
H	3.813124000	-0.552835000	2.549135000
H	3.925885000	0.481931000	1.119400000
C	1.571469000	0.916309000	2.572410000
H	2.066475000	1.848382000	2.288538000
H	1.912373000	0.645861000	3.576671000
H	0.493221000	1.098161000	2.632844000
C	-1.710035000	-1.677257000	0.194532000
H	-0.643267000	-1.884850000	0.265544000
C	-2.249737000	-2.403116000	-1.035481000
H	-3.326391000	-2.259633000	-1.156005000
H	-2.069376000	-3.475154000	-0.928377000
H	-1.753840000	-2.064267000	-1.946899000
C	-2.362955000	-2.173086000	1.483909000
H	-2.006834000	-1.609536000	2.348854000
H	-2.113023000	-3.225784000	1.632372000
H	-3.452295000	-2.094014000	1.449166000
C	-3.203172000	0.331773000	-0.016550000
H	-3.859463000	-0.536524000	0.045095000
C	-3.535760000	1.229437000	1.172096000
H	-3.333071000	0.713988000	2.113346000
H	-4.596615000	1.489338000	1.144975000
H	-2.960433000	2.157054000	1.149463000
C	-3.467300000	0.996484000	-1.365292000
H	-2.894831000	1.919460000	-1.479133000
H	-4.527774000	1.245890000	-1.447443000
H	-3.208378000	0.321241000	-2.184005000
B	-0.696651000	0.576067000	0.007265000
C	1.031914000	3.876674000	-0.482588000
H	0.395642000	4.764203000	-0.547479000
H	1.582021000	3.736074000	-1.414008000
H	1.736841000	3.974375000	0.343562000

TS2

P	-1.692638000	0.138989000	0.018646000
N	0.568785000	-0.611920000	-1.330661000
N	0.969119000	1.692579000	-0.468465000
N	2.766815000	-0.035963000	-0.297211000
C	-0.688601000	-0.794328000	-1.268132000
C	0.016126000	2.267505000	-0.128378000
C	-1.483117000	-0.997970000	1.524999000
C	-0.086661000	-0.702788000	2.094966000
H	0.707663000	-0.963966000	1.393174000
H	0.066312000	-1.309214000	2.993420000
H	0.026278000	0.348233000	2.375013000
C	-1.580279000	-2.490997000	1.189600000
H	-2.530757000	-2.751815000	0.720672000
H	-1.497063000	-3.069581000	2.115545000
H	-0.767486000	-2.809256000	0.532001000
C	-2.524002000	-0.636778000	2.592323000
H	-2.529590000	0.433112000	2.816731000
H	-2.272123000	-1.168713000	3.514990000
H	-3.531612000	-0.942313000	2.306237000
C	-3.478606000	0.282929000	-0.572484000
C	-4.277299000	-1.020833000	-0.674356000
H	-3.836285000	-1.735308000	-1.368900000
H	-5.285719000	-0.790627000	-1.034002000
H	-4.382399000	-1.506514000	0.297667000
C	-4.204247000	1.239614000	0.394950000
H	-4.370031000	0.801831000	1.378023000
H	-5.185121000	1.479661000	-0.027102000
H	-3.661854000	2.179495000	0.524906000
C	-3.421733000	0.996316000	-1.936627000
H	-2.888346000	1.948792000	-1.869471000
H	-4.443492000	1.214562000	-2.261363000
H	-2.950817000	0.404204000	-2.720862000
C	3.243222000	-1.424387000	-0.487171000
H	2.409600000	-1.958228000	-0.944709000
C	3.560582000	-2.107832000	0.842357000
H	4.407719000	-1.642115000	1.353518000
H	3.820192000	-3.153221000	0.660206000
H	2.699010000	-2.082868000	1.513442000
C	4.417684000	-1.476216000	-1.463002000
H	4.148958000	-1.005789000	-2.411591000
H	4.685123000	-2.517436000	-1.658300000
H	5.306531000	-0.976465000	-1.067944000
C	3.718732000	0.897102000	0.346564000
H	4.639530000	0.328916000	0.484251000
C	4.068346000	2.081813000	-0.552259000
H	4.409210000	1.731995000	-1.529166000
H	4.872330000	2.663614000	-0.094655000
H	3.214992000	2.746821000	-0.700574000
C	3.255471000	1.322999000	1.739544000
H	2.379566000	1.973903000	1.696456000
H	4.054433000	1.874941000	2.240731000
H	3.007067000	0.450134000	2.347093000
B	1.480452000	0.286619000	-0.690807000
C	-1.306998000	-1.787576000	-2.214353000
H	-1.737565000	-2.618498000	-1.649295000
H	-0.535298000	-2.169685000	-2.882624000
H	-2.111900000	-1.351942000	-2.805714000
C	-0.806369000	3.378634000	0.301363000
H	-1.651437000	3.497589000	-0.376118000
H	-0.188411000	4.279822000	0.301153000
H	-1.176439000	3.171885000	1.306446000

IP1

P	1.276454000	0.758147000	-0.340879000
N	-1.367905000	1.644381000	-0.418294000
N	-1.444740000	-0.748510000	0.135925000
C	-1.716958000	2.713462000	-0.631096000
C	2.106575000	-0.569860000	-1.414374000
C	1.142744000	-0.819578000	-2.584756000
H	0.214941000	-1.295727000	-2.263146000
H	1.620800000	-1.477633000	-3.317628000
H	0.885042000	0.113897000	-3.094778000
C	2.512595000	-1.898522000	-0.770449000
H	3.203076000	-1.753932000	0.062805000
H	3.031196000	-2.509034000	-1.517999000
H	1.661838000	-2.481581000	-0.419013000
C	3.374869000	0.092902000	-1.987904000
H	3.140522000	1.033937000	-2.491345000
H	3.832255000	-0.581437000	-2.720038000
H	4.119353000	0.296506000	-1.216032000
C	1.946764000	0.815738000	1.431429000
C	1.671636000	-0.403506000	2.315408000
H	0.602375000	-0.527919000	2.492783000
H	2.148362000	-0.256908000	3.291195000
H	2.065487000	-1.329427000	1.893903000
C	3.459316000	1.068375000	1.364873000
H	4.002685000	0.189774000	1.009836000
H	3.829491000	1.298400000	2.369576000
H	3.702631000	1.912142000	0.713495000
C	1.267628000	2.040203000	2.069364000
H	1.477059000	2.955623000	1.510307000
H	1.640755000	2.171518000	3.090517000
H	0.181336000	1.915087000	2.135322000
C	-0.857655000	-2.033818000	0.581526000
H	0.210292000	-1.848078000	0.654555000
C	-1.082958000	-3.162224000	-0.422879000
H	-2.138337000	-3.431933000	-0.509970000
H	-0.545141000	-4.051040000	-0.084629000
H	-0.712641000	-2.901335000	-1.414856000
C	-1.353181000	-2.422329000	1.975225000
H	-1.252429000	-1.595437000	2.680540000
H	-0.755974000	-3.259565000	2.342691000
H	-2.398406000	-2.741389000	1.968479000
C	-2.932659000	-0.766457000	0.028843000
H	-3.219924000	-1.792788000	0.253113000
C	-3.614156000	0.104467000	1.082518000
H	-3.232831000	-0.127387000	2.078725000
H	-4.687430000	-0.098887000	1.072470000
H	-3.480026000	1.171247000	0.901415000
C	-3.408183000	-0.496697000	-1.396767000
H	-3.235627000	0.533458000	-1.711534000
H	-4.482161000	-0.686042000	-1.459395000
H	-2.901269000	-1.161237000	-2.099592000
B	-0.637354000	0.335819000	-0.133296000
C	-2.172738000	4.048602000	-0.898935000
H	-2.767099000	4.040292000	-1.814404000
H	-1.307226000	4.701921000	-1.020768000
H	-2.786334000	4.387968000	-0.062508000

IP2

P	-1.107257000	-0.131644000	-0.022978000
N	0.443780000	-2.027279000	-0.266994000
N	1.984891000	0.069841000	0.013577000
C	-0.841657000	-1.958756000	-0.256204000
C	-1.829121000	0.701108000	-1.525362000
C	-1.292395000	-0.069403000	-2.743150000
H	-0.198910000	-0.092796000	-2.767593000
H	-1.630913000	0.443586000	-3.647040000
H	-1.665392000	-1.095142000	-2.784884000
C	-1.318436000	2.149863000	-1.585234000
H	-1.621856000	2.744119000	-0.723002000
H	-1.741288000	2.621502000	-2.476549000
H	-0.231169000	2.191783000	-1.676507000
C	-3.361128000	0.667352000	-1.506722000
H	-3.753137000	-0.346550000	-1.396306000
H	-3.725518000	1.062091000	-2.459109000
H	-3.773072000	1.293663000	-0.713567000
C	-1.841189000	0.262601000	1.643612000
C	-1.901363000	1.783643000	1.837176000
H	-0.928428000	2.260389000	1.690582000
H	-2.215190000	1.985551000	2.864861000
H	-2.629956000	2.252823000	1.173613000
C	-3.239837000	-0.354624000	1.788686000
H	-3.961073000	0.071452000	1.091849000
H	-3.597068000	-0.149906000	2.801802000
H	-3.228584000	-1.438407000	1.657946000
C	-0.890710000	-0.359888000	2.680858000
H	-0.806987000	-1.444210000	2.571496000
H	-1.291767000	-0.159428000	3.677690000
H	0.112450000	0.070848000	2.631163000
C	2.023624000	1.536387000	0.185400000
H	0.979548000	1.857998000	0.223195000
C	2.670249000	2.216830000	-1.018464000
H	3.731820000	1.970670000	-1.103509000
H	2.587806000	3.301130000	-0.916878000
H	2.173823000	1.915161000	-1.944405000
C	2.670030000	1.934403000	1.509708000
H	2.160571000	1.456522000	2.349702000
H	2.602362000	3.017026000	1.637376000
H	3.727705000	1.661634000	1.547131000
C	3.288803000	-0.638676000	-0.059116000
H	4.058250000	0.128389000	0.041788000
C	3.446784000	-1.612639000	1.105481000
H	3.311072000	-1.098459000	2.059790000
H	4.447821000	-2.050106000	1.088826000
H	2.717645000	-2.423355000	1.037037000
C	3.474704000	-1.308724000	-1.417781000
H	2.743440000	-2.107571000	-1.561137000
H	4.474838000	-1.743983000	-1.481771000
H	3.363336000	-0.581276000	-2.225128000
B	0.798624000	-0.599136000	-0.082881000
C	-1.797791000	-3.083882000	-0.389149000
H	-2.294738000	-3.259191000	0.569770000
H	-1.268392000	-3.989365000	-0.686245000
H	-2.577399000	-2.847769000	-1.117425000

IP3

P	1.598533000	0.000330000	0.285241000
N	-0.458050000	0.073264000	-1.490241000
N	-1.238792000	-1.860107000	-0.189804000
N	-2.574526000	0.250922000	-0.122136000
C	0.804270000	0.201779000	-1.416528000
C	-0.981599000	-2.953118000	0.021752000
C	1.864160000	1.817312000	0.775800000
C	0.468915000	2.322794000	1.172201000
H	-0.210523000	2.320231000	0.317405000
H	0.542217000	3.355548000	1.529179000
H	0.025812000	1.716367000	1.966732000
C	2.424733000	2.752631000	-0.301796000
H	3.375595000	2.408415000	-0.710218000
H	2.593883000	3.740040000	0.141431000
H	1.718954000	2.887078000	-1.124696000
C	2.771988000	1.859435000	2.012687000
H	2.447702000	1.156048000	2.784941000
H	2.737625000	2.866064000	2.442061000
H	3.813167000	1.647013000	1.762075000
C	3.245748000	-0.890193000	0.003086000
C	4.359008000	-0.131842000	-0.725278000
H	4.067177000	0.191228000	-1.724992000
H	5.228491000	-0.789689000	-0.833331000
H	4.684602000	0.744421000	-0.161352000
C	3.759596000	-1.320050000	1.391247000
H	4.098470000	-0.476596000	1.992810000
H	4.612503000	-1.994239000	1.259495000
H	2.991753000	-1.856162000	1.955934000
C	2.894762000	-2.181377000	-0.759087000
H	2.140044000	-2.763661000	-0.221764000
H	3.791327000	-2.803863000	-0.842074000
H	2.528664000	-1.999804000	-1.770819000
C	-2.820732000	1.631001000	-0.599216000
H	-1.910075000	1.931945000	-1.120057000
C	-3.052195000	2.615957000	0.547142000
H	-4.027837000	2.476898000	1.019664000
H	-3.023236000	3.635199000	0.155129000
H	-2.281883000	2.521821000	1.313814000
C	-3.963451000	1.659204000	-1.613235000
H	-3.752873000	0.989594000	-2.450193000
H	-4.088289000	2.672458000	-2.002551000
H	-4.911852000	1.359438000	-1.157968000
C	-3.634119000	-0.338348000	0.727582000
H	-4.384914000	0.444197000	0.839366000
C	-4.348601000	-1.516507000	0.064649000
H	-4.674893000	-1.249287000	-0.942546000
H	-5.230731000	-1.782320000	0.652149000
H	-3.720547000	-2.406389000	-0.002295000
C	-3.125068000	-0.655814000	2.132703000
H	-2.382580000	-1.457159000	2.130720000
H	-3.957258000	-0.974653000	2.765002000
H	-2.669077000	0.229144000	2.581557000
B	-1.428757000	-0.395549000	-0.556821000
C	1.569136000	0.500560000	-2.677668000
H	2.290698000	1.304208000	-2.536865000
H	0.871444000	0.763251000	-3.473304000
H	2.132045000	-0.382999000	-2.989536000
C	-0.672347000	-4.325316000	0.313302000
H	-0.157415000	-4.763720000	-0.543134000
H	-1.600501000	-4.865052000	0.509333000
H	-0.027575000	-4.359412000	1.193590000

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