Metathesis chemistry of inorganic cumulenes driven by B–O bond formation

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Supporting information (58 pages)

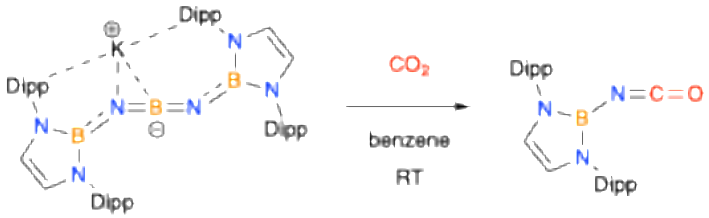
1. General considerations

All experiments were carried out under an atmosphere of dry argon or dinitrogen using standard Schlenk line or dry-box techniques. Solvents were degassed by sparging with argon and dried by passing through a column of appropriate drying agent using a commercially available Braun SPS and stored over potassium mirror under argon in a Teflon valve ampoule. NMR spectra were measured in d_6-benzene, with the solvent being dried over calcium hydride or molten potassium respectively, distilled, degassed by three freeze-pump-thaw-cycles and stored over 3 Å sieves. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured on a Bruker Avance III HD Nanobay 400 MHz or Bruker Avance III 500 MHz spectrometer, and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances; resonances are reported relative to tetramethylsilane (δ = 0 ppm). Assignments were confirmed using two-dimensional ^{1}H-^{1}H, ^{13}C-^{1}H, NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. The reported yields are the yields obtained after crystallisation and subsequent measurement of the material by single crystal-ray diffraction if not stated otherwise. Elemental analyses were carried out by London Metropolitan University or Elemental Microanalysis Ltd, Okehampton, Devon, UK.

2. Preparation of starting materials

K[(HCDippN)$_2$BNBNB(NDippCH)$_2$], **1**, [K$_2${(HCDippN)$_2$BN}$_2$B][{(C$_6$F$_5$)$_3$BCCH$_2$(DippN)$_2$BN}$_2$B], **3**, and (H$_2$CDippN)$_2$PPCO were prepared by literature procedures.[S1,S2]

3. Synthetic procedures, characterising data and representative spectra of new compounds



Scheme S1. Synthesis of $(HCDippN)_2BNCO$, **5**.

$(HCDippN)_2BNCO$, 5. A solution of **1** (100 mg 0.117 mmol) in benzene (5 mL) was degassed by three freeze-pump-thaw cycles, before CO_2 was admitted (at ca. 1 atm pressure), leading to a near colourless solution. After stirring for 12 h, volatiles were removed in vacuo and the resulting pale solid dissolved in 3 mL pentane. The solution was concentrated to ca. 1 mL and crystals of **5** were obtained upon standing at room temperature that were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

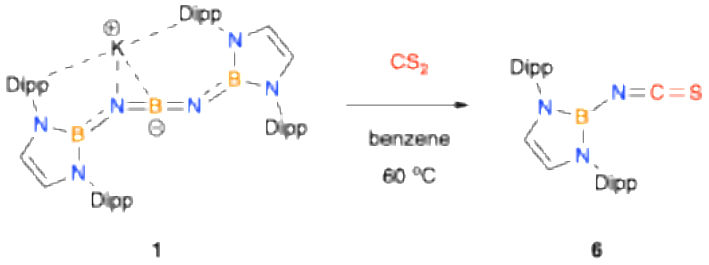
Yield: 89.6 mg (90.0 %)

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ_H 1.18 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, CH_3 of Dipp), 1.25 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, CH_3 of Dipp), 3.14 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.95 (s, 2H, CH of boryl), 7.12 (m, 4H, m-ArH of Dipp), 7.21, (m, 2H, p-ArH of Dipp).

$^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6, 298 K): δ_B 17.9 (boryl).

$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K): δ_C 24.1, 24.3 (CH_3 of Dipp), 28.8 (<u>C</u>H$(CH_3)_2$ of Dipp), 118.2 (CH of boryl), 123.9 (m-Ar of Dipp), 128.4 (p-Ar of Dipp), 136.8 (CN of Dipp), 146.5 (o-Ar of Dipp), not observed (N=C=O).

Elemental microanalysis: calc. for $C_{27}H_{36}BN_3O$ (%): C 75.52 H 8.45 N 9.79; meas. C 75.82 H 8.51 N 9.54.



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Scheme S2. Synthesis of $(HCDippN)_2BNCS$, **6**.

$(HCDippN)_2BNCS$, 6. 1 (100 mg 0.117 mmol) was dissolved in benzene (10 mL) and a drop of CS_2 (ca. 0.02 mL, excess) added. The solution was heated at 60 °C overnight with a colour change from orange to red. Volatiles were removed in vacuo and the residue extracted with pentane (10 mL). The resulting solution was concentrated to ca. 2 mL and colourless crystals of **6** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

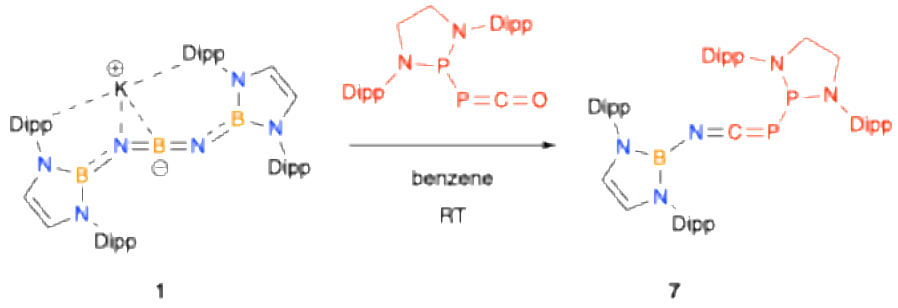
Yield: 51.3 mg (52.0 %)

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ_H 1.17 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, CH_3 of Dipp), 1.29 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, CH_3 of Dipp), 3.12 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.91 (s, 2H, CH of boryl), 7.13(m, 4H, m-ArH of Dipp), 7.20 (m, 2H, p-ArH of Dipp).

$^{11}B\{^{1}H\}$ NMR (160 MHz, C_6D_6, 298 K): δ_B 16.1 (boryl).

$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K): δ_C 24.0, 24.5 (CH_3 of Dipp), 28.9 (<u>C</u>H$(CH_3)_2$ of Dipp), 118.6 (CH of boryl), 123.9 (m-Ar of Dipp), 128.6 (p-Ar of Dipp), 136.4 (CN of Dipp), 146.3 (o-Ar of Dipp), not observed (N=C=S).

Elemental microanalysis: calc. for $C_{27}H_{36}BN_3S$ (%): C 72.80 H 8.15 N 9.43; meas. C 72.76 H 8.26 N 9.17.



Scheme S3. Synthesis of $(HCDippN)_2BNCPP(NDippCH_2)_2$, **7**.

$(HCDippN)_2BNCPP(NDippCH_2)_2$, 7. To a mixture of **1** (80 mg, 0.094 mmol) and $(CH_2DippN)_2PPCO$ (69.3 mg, 0.148 mmol) in a 25 mL Schlenk flask was added 5 mL benzene. The resulting solution was stirred for 12 h with a colour change to dark green. Volatiles were removed in vacuo and the residue extracted with pentane (3 mL). The resulting solution was concentrated to ca. 1 mL and colourless crystals of **7** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

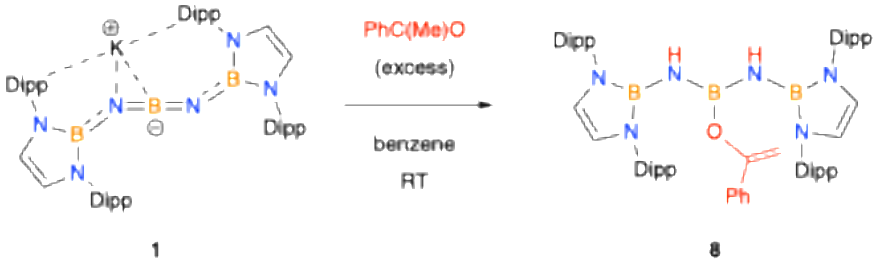
Yield: 88.6 mg (55.2 %)

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ_H 1.05 (d, $^3J_{H,H}$ = 7.0 Hz, 12H, CH_3 of boryl Dipp),1.13 (d, $^3J_{H,H}$ = 7.0 Hz, 12H, CH_3 of boryl Dipp), 1.19, 1.25, (d, $^3J_{H,H}$ = 6.6 Hz, 12H, CH_3 of phosphanyl Dipp),1.31 (d, $^3J_{H,H}$ = 6.6 Hz, 12H, CH_3 of phosphanyl Dipp), 3.03 (sept, $^3J_{H,H}$ = 7.0 Hz, 4H,C<u>H</u>$(CH_3)_2$ of boryl Dipp), 3.11, 3.58 (m, 4H, CH_2 of phosphanyl), 3.48, 3.76 (m, 4H,C<u>H</u>$(CH_3)_2$ of phosphanyl Dipp), 5.86 (s, 2H, CH of boryl), 7.04 (m, 4H, m-ArH of boryl Dipp), 7.10 (m, 6H, ArH of phosphanyl Dipp), 7.18 (m, 2H, p-ArH of boryl Dipp).

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ_B 16.0 (boryl).

^{31}P NMR (162 MHz, C_6D_6, 298 K): δ_P -183.3 (d, P<u>P</u>=C, $^1J_{P,P}$ = 298.0 Hz),165.6 (d, <u>P</u>P=C, $^1J_{P,P}$ = 298.0 Hz).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ_C 23.9, 24.4 (CH_3 of Dipp), 24.7, 25.2 (d, $^5J_{C,p}$ = 3.6 Hz, CH_3 of phosphanyl Dipp), 25.7,25.9 (CH_3 of phosphanyl Dipp), 28.8 (<u>C</u>H$(CH_3)_2$ of boryl Dipp), 28.9, 29.5 (d, $^4J_{C,P}$ = 7.3 Hz, <u>C</u>H$(CH_3)_2$ of phosphanyl Dipp), 54.9 (d, $^2J_{C,p}$ = 8.7 Hz, CH_2 of phosphanyl), 118.5 (CH of boryl), 123.6 (m-Ar of boryl Dipp), 123.9 (m-Ar of phosphanyl Dipp), 124.9 (p-Ar of phosphanyl Dipp), 127.5 (o-Ar of boryl Dipp), 136.8 (CN of boryl Dipp), 137.7, 137.8 (CN of phosphanyl Dipp), 146.2 (o-Ar of boryl Dipp), 148.7, 150.4 (o-Ar of phosphanyl Dipp), not observed (N=C=P)



Scheme S4. Synthesis of [{(HCDippN)$_2$BN}$_2$B]OC(CH$_2$)Ph, **8**.

[{(HCDippN)$_2$BN}$_2$B]OC(CH$_2$)Ph, 8. 1 (15 mg 0.018 mmol) was dissolved in benzene (4 mL) and a drop of acetophenone (0.01 mL, excess) added. The reaction mixture was stirred for 1 h with an accompanying colour change to light yellow. Volatiles were removed in vacuo and the residue extracted with pentane (3 mL). The resulting solution was concentrated to ca. 0.5 mL and yellow crystals of **8** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

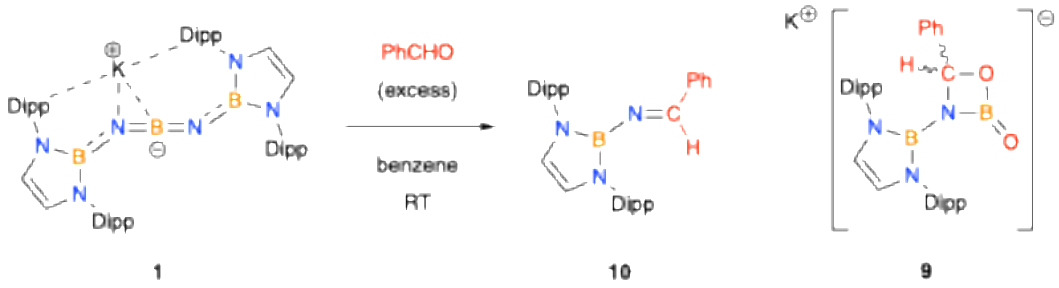
Yield: 7.8 mg (47.0 %)

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ_H 1.16 (d, $^3J_{H,H}$ = 6.6 Hz, 24H, CH_3 of Dipp), 1.18 (d, $^3J_{H,H}$ = 6.6 Hz, 24H, CH_3 of Dipp), 2.56 (br, 2H, NH), 3.12, 4.43 (s, each 1H, C=CH_2), 3.28 (sept, $^3J_{H,H}$ = 6.8 Hz, 8H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.97 (s, 2H, CH of boryl), 7.07 (m, 17H, ArH of Dipp).

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ_B 23.9 (boryl).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ_C 23.8, 25.5 (CH_3 of Dipp), 28.8 (<u>C</u>H$(CH_3)_2$ of Dipp), 97.7 (C=<u>C</u>H_2), 118.6 (CH of boryl), 124.2 (m-Ar of Dipp), 125.3, 128.8, 136.7 (Ph), 127.4 (p-Ar of Dipp), 139.6 (CN of Dipp), 146.3 (o-Ar of Dipp), 154.4 (<u>C</u>=CH_2).

Elemental microanalysis: calc. for $C_{60}H_{81}B_3N_6O$ (%): C 77.09 H 8.73 N 8.99; meas. C 76.89 H 8.51 N 9.12.



Scheme S5. Synthesis of (HCDippN)$_2$BN[κ^2-(C,B)-C(H)PhBO$_2$], **9** and (HCDippN)$_2$BNCHPh, **10**.

(HCDippN)$_2$BN[κ^2-(C,B)-C(H)PhBO$_2$], 9. **1**(100 mg 0.117 mmol) was dissolved in benzene (10 mL) and a drop of benzaldehyde (0.02 mL, excess) added. The resulting solution was stirred for 30 min, with an accompanying colour change to yellow. Volatiles were removed in vacuo, and the residue extracted with pentane (5 mL). The resulting solution was concentrated to ca. 0.5 mL and a mix of colourless crystals of **9** (unstable in solvent and briefly visible in NMR) and **10** were obtained which were suitable for X-ray crystallography.

(HCDippN)$_2$BNCHPh, 10. **1** (100 mg 0.117 mmol) was dissolved in benzene (10 mL) and a drop of benzaldehyde (0.02 mL, excess) added. The resulting solution was stirred for 12 h with a colour change to light yellow. Volatiles were removed in vacuo and the residue extracted with pentane (5 mL). The resulting solution was concentrated to ca. 2 mL and colourless crystals of **10** were obtained which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

Yield: 16.6 mg (14.4 %)

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ_H 1.27 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, CH_3 of Dipp), 1.29 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, CH_3 of Dipp), 3.43 (sept, $^3J_{H,H}$ = 6.9 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 6.19 (s, 2H, CH of boryl), 6.82 (m, m-ArH of Ph), 6.89 (m, p-ArH of Ph), 7.17 (m, m-ArH of Dipp), 7.22 (m, p-ArH of Dipp), 7.46 (m, o-ArH of Ph), 8.65 (s, PhC(H)=N).

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ_B 24.6 (boryl).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ_C 24.2, 24.4 (CH_3 of Dipp), 28.8 (<u>C</u>H$(CH_3)_2$ of Dipp), 119.0 (CH of boryl), 123.7 (m-Ar of Dipp), 128.6 (p-Ar of Dipp),128.6 (o-Ar of Ph), 128.7 (m-Ar of Ph), 131.2 (p-Ar of Ph), 138.8 (CN of Dipp), 146.6 (o-Ar of Dipp), 167.8 (C=N), overlap by solvent peak (Ph(<u>C</u>)-C=N).

Reactions of 3 with electrophiles

With MeI. **3** (15 mg, 0.011 mmol) was dissolved in C_6D_6 (0.4 mL) and a drop of MeI (0.01 mL, excess) added. The reaction mixture was heated at 60 °C overnight in a J-Young NMR tube with the formation of a white precipitate; monitoring by multinuclear NMR revealed essentially quantitative formation of **4** and $B(C_6F_5)_3$ (Figures S18 and S19).

With CO_2. A solution of **3** (15 mg, 0.011 mmol) in C_6D_6 (0.4 mL) was degassed by three freeze-pump-thaw cycles, before CO_2 was admitted (at ca. 1 atm pressure), leading to a near colourless solution; monitoring by multinuclear NMR revealed essentially quantitative formation of **5** (Figure S20).

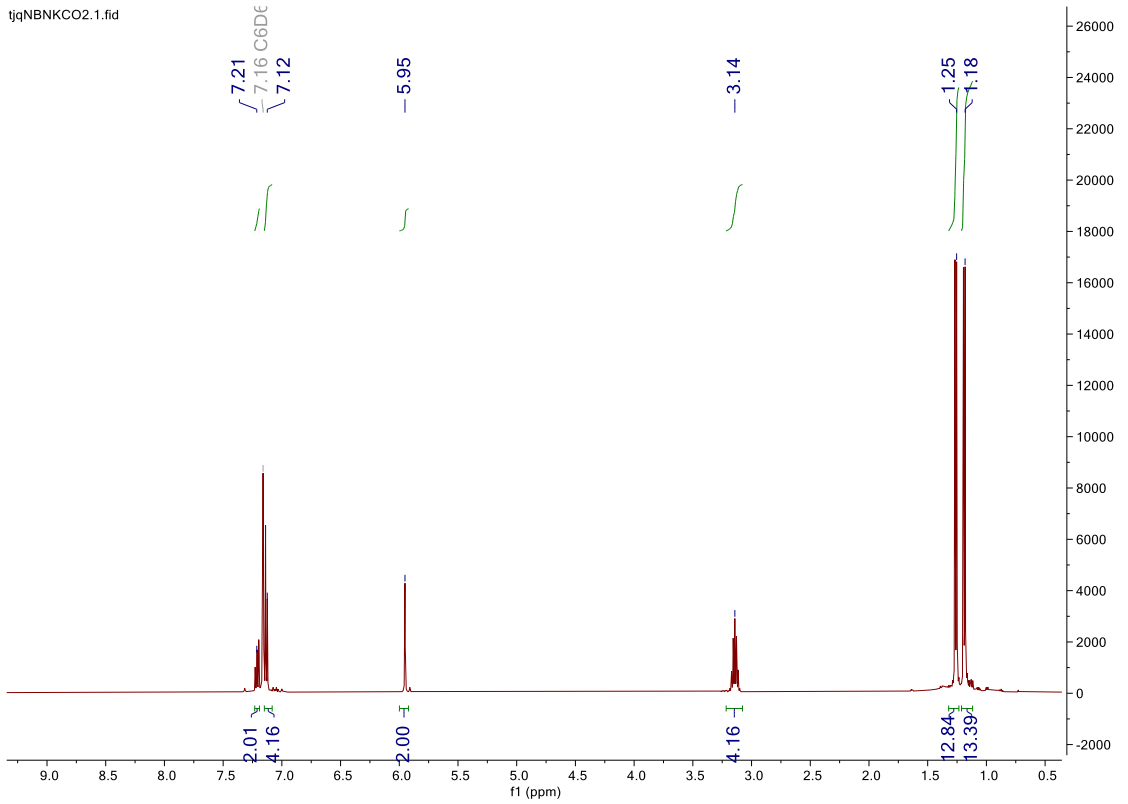


Figure S1: ^{1}H NMR spectrum of **5** (500 MHz, C_6D_6, 298 K).

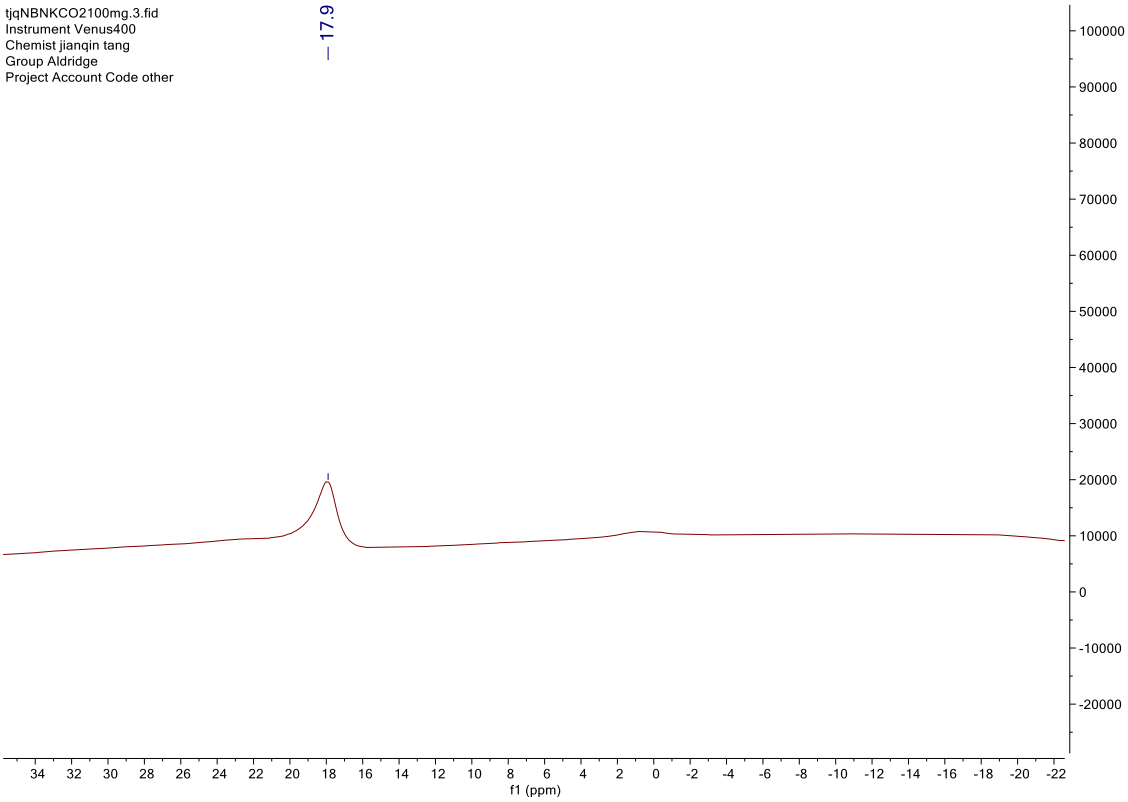


Figure S2: ^{11}B{^{1}H} NMR spectrum of **5** (128 MHz, C_6D_6, 298 K).

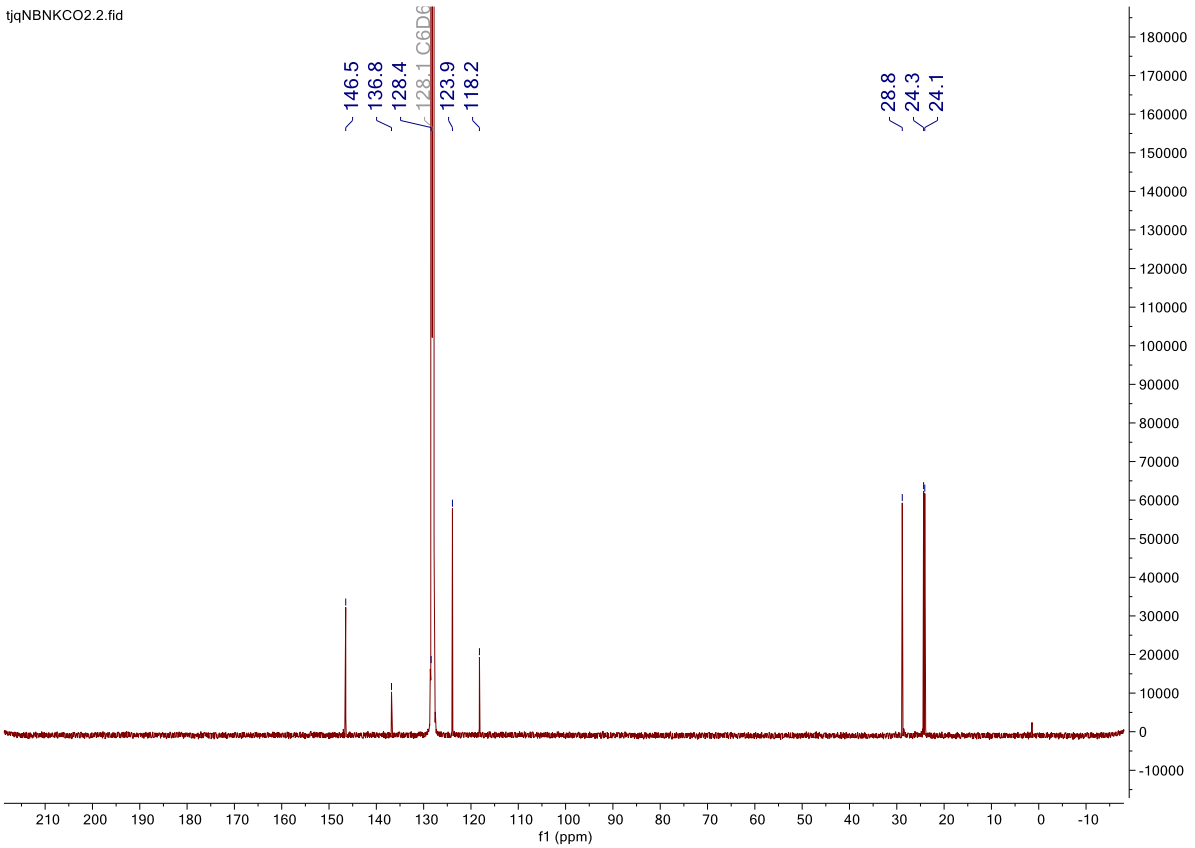


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of **5** (126 MHz, C_6D_6, 298 K).

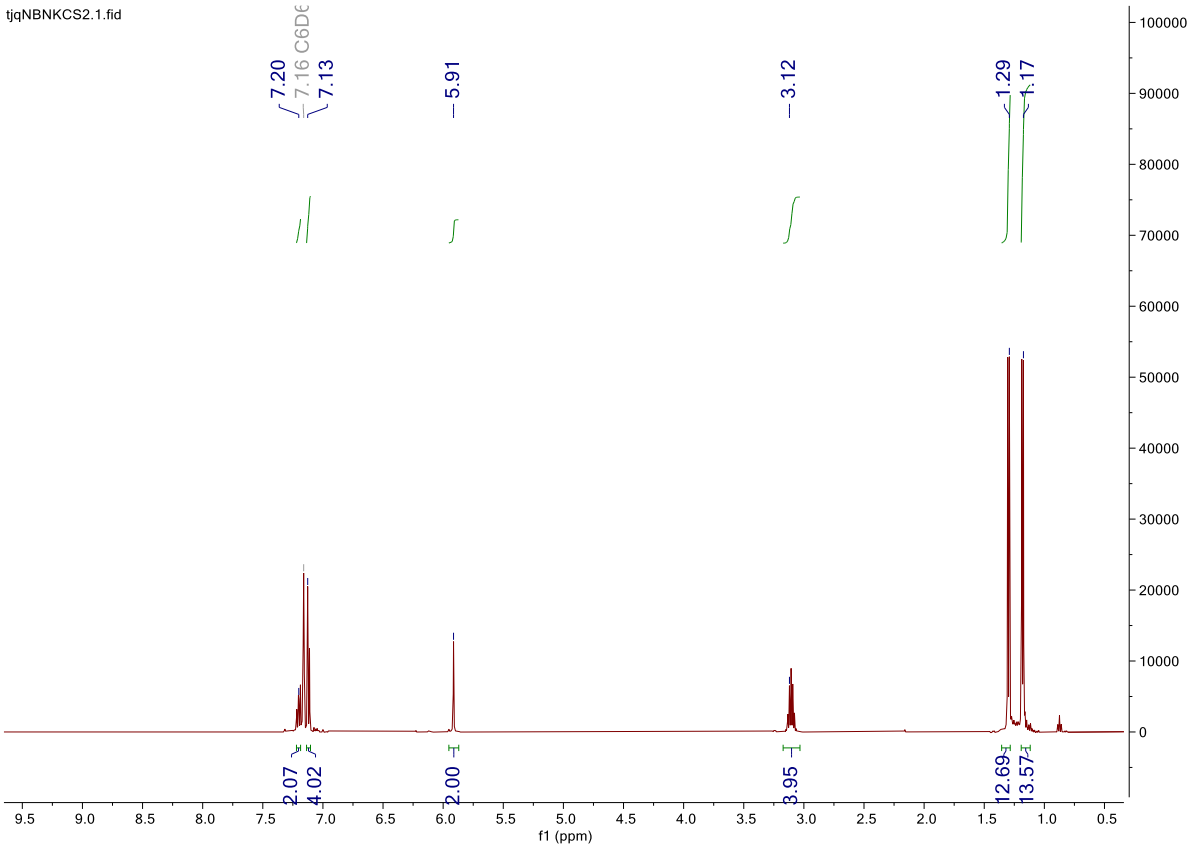


Figure S4: ^{1}H NMR spectrum of **6** (500 MHz, C_6D_6, 298 K).

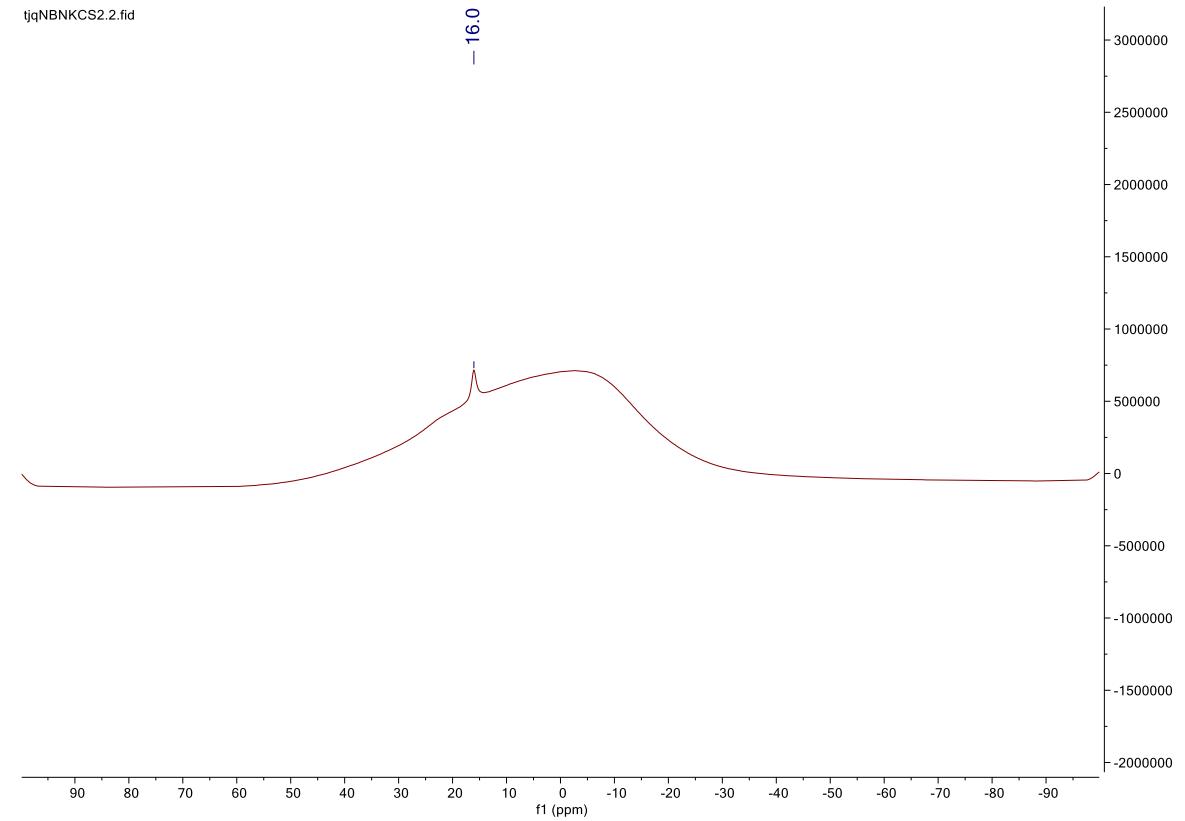


Figure S5: $^{11}B\{^{1}H\}$ NMR spectrum of **6** (160 MHz, C_6D_6, 298 K).

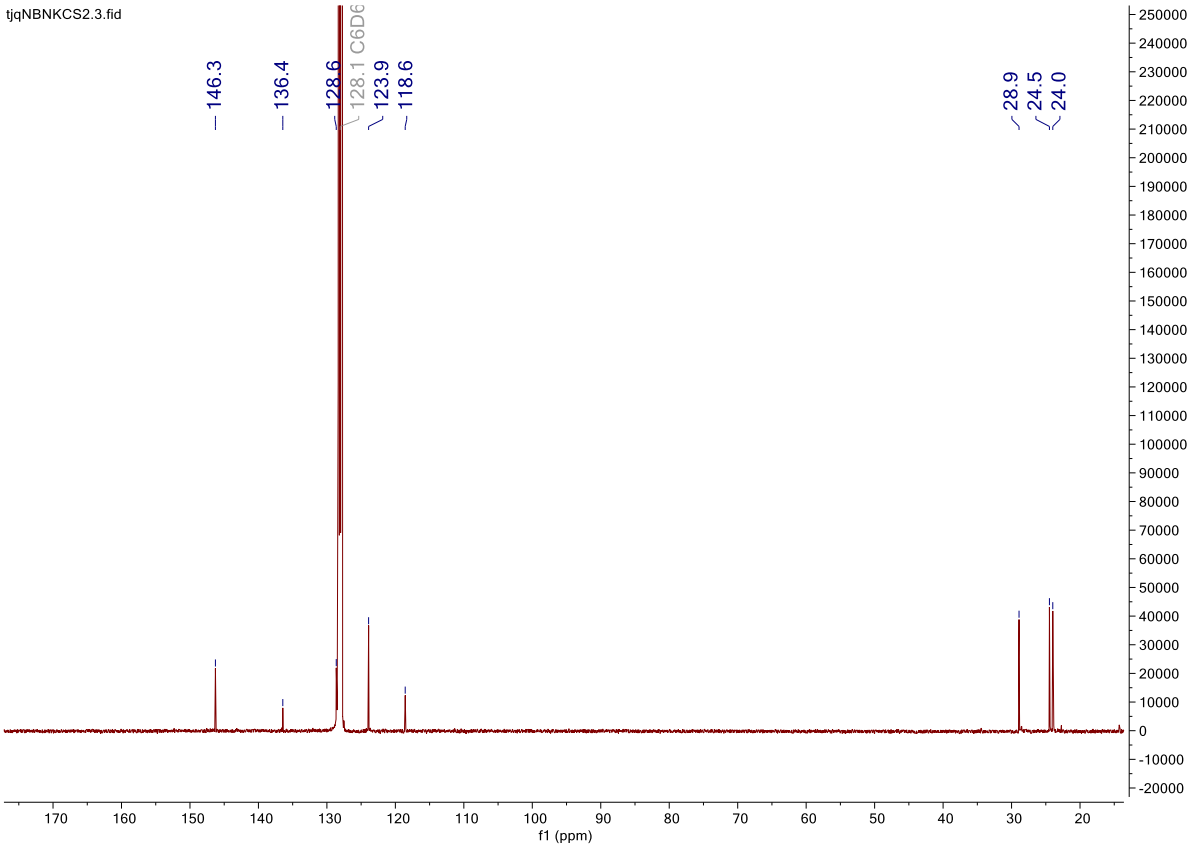


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, C_6D_6, 298 K).

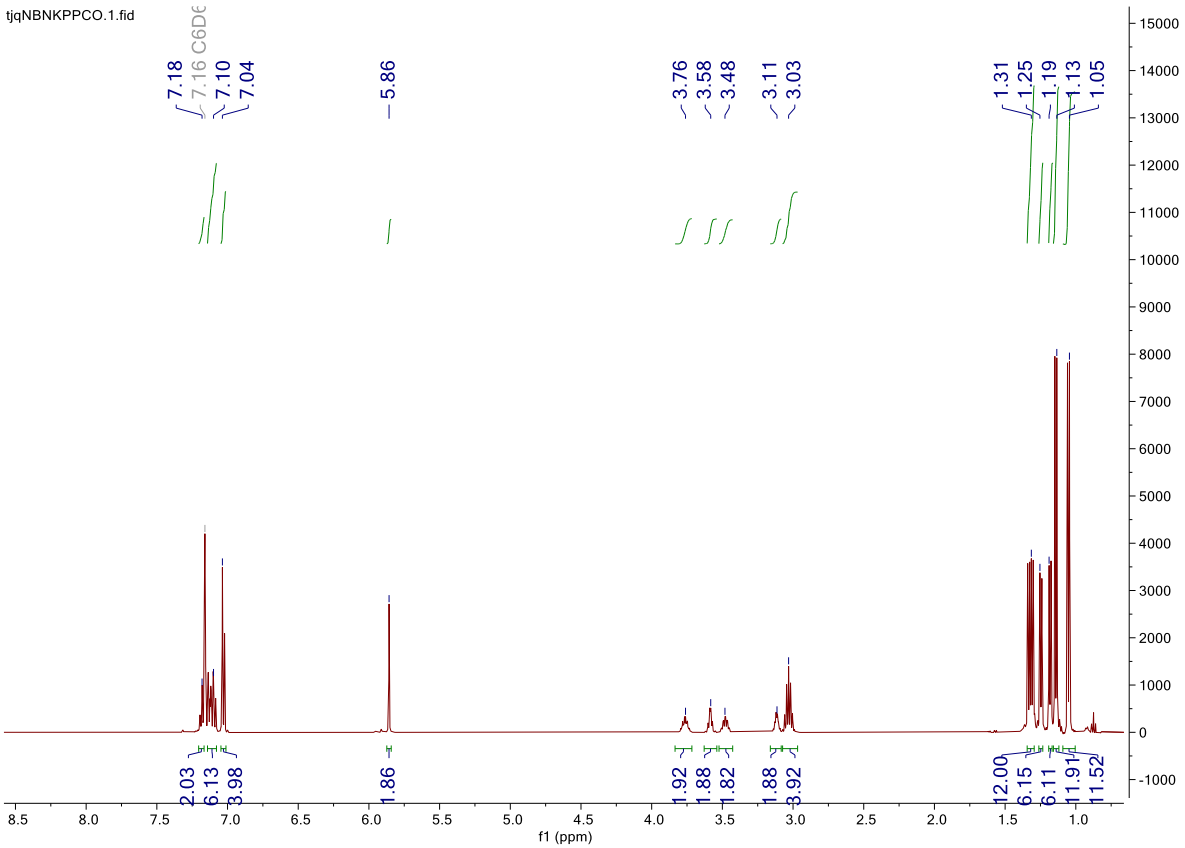


Figure S7: ^{1}H NMR spectrum of **7** (500 MHz, C_6D_6, 298 K).

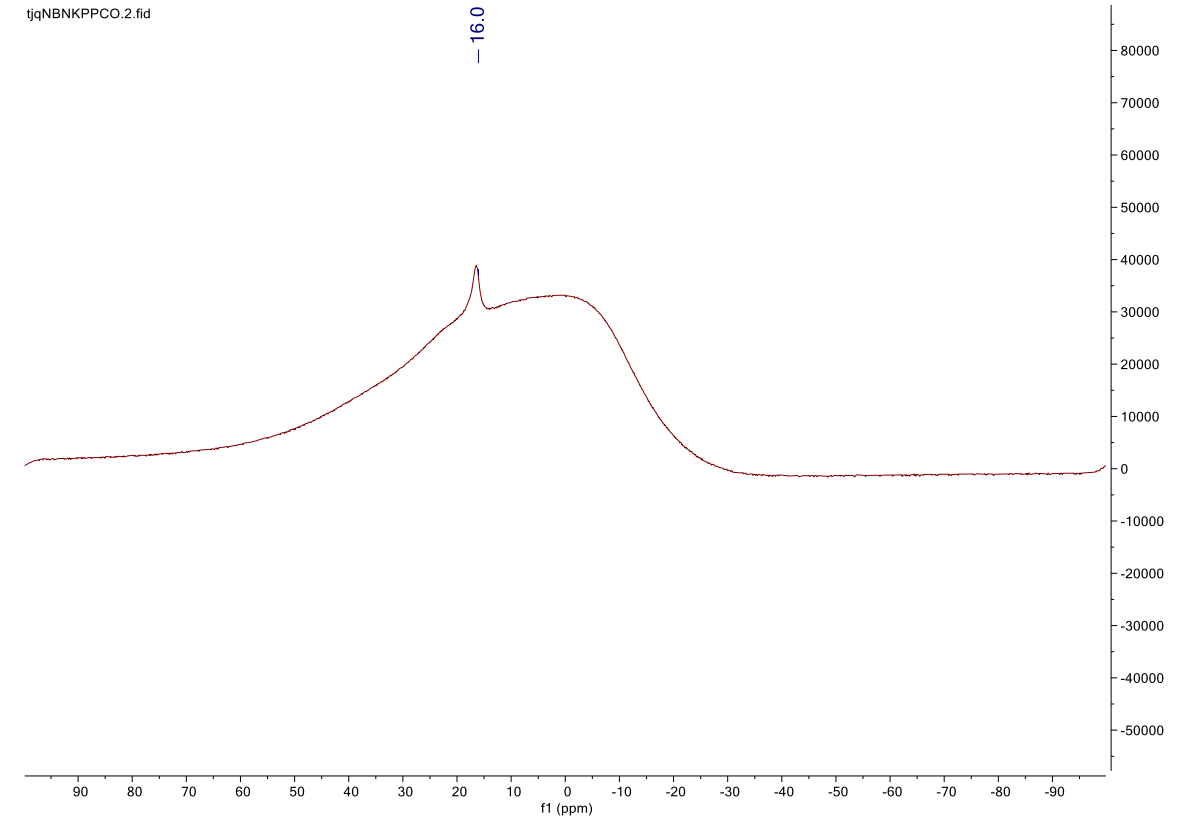


Figure S8: ^{11}B{^{1}H} NMR spectrum of **7** (160 MHz, C_6D_6, 298 K).

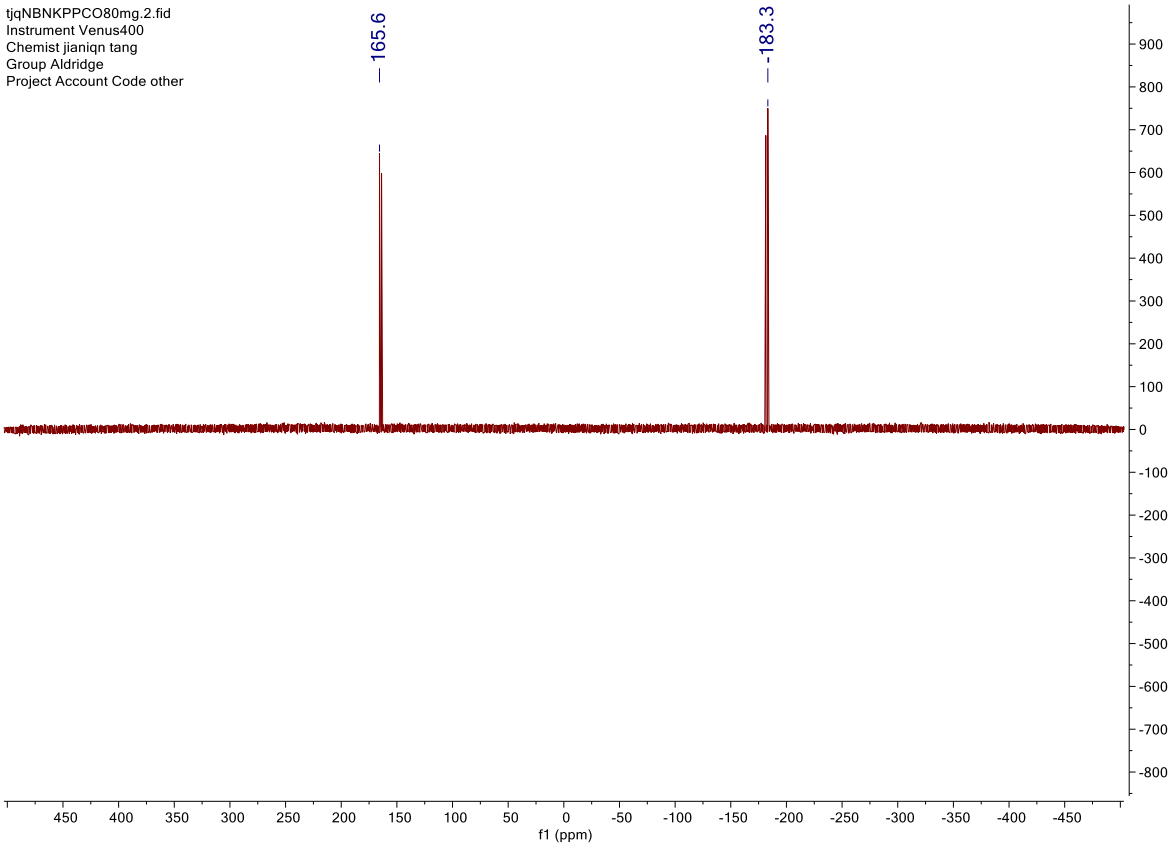


Figure S9: ^{31}P NMR spectrum of **7** (162 MHz, C_6D_6, 298 K).

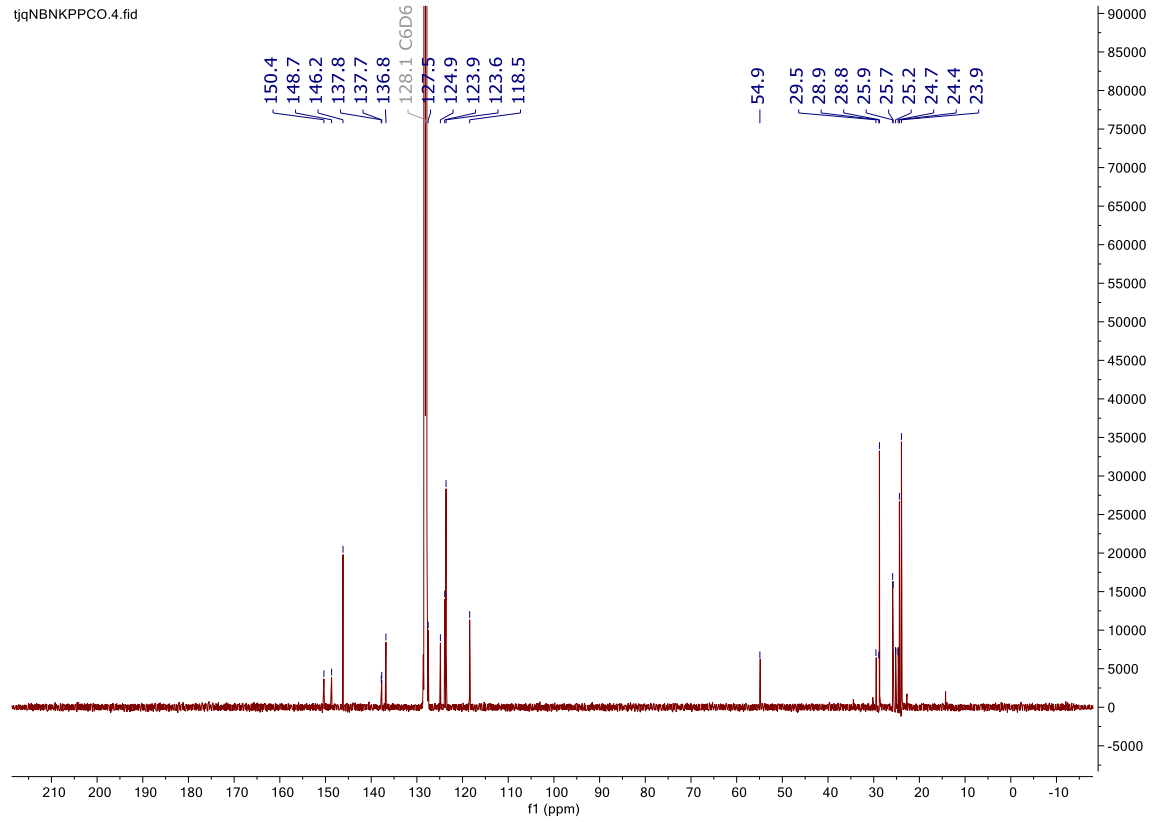


Figure S10: $^{13}C\{^1H\}$ NMR spectrum of **7** (126 MHz, C_6D_6, 298 K).

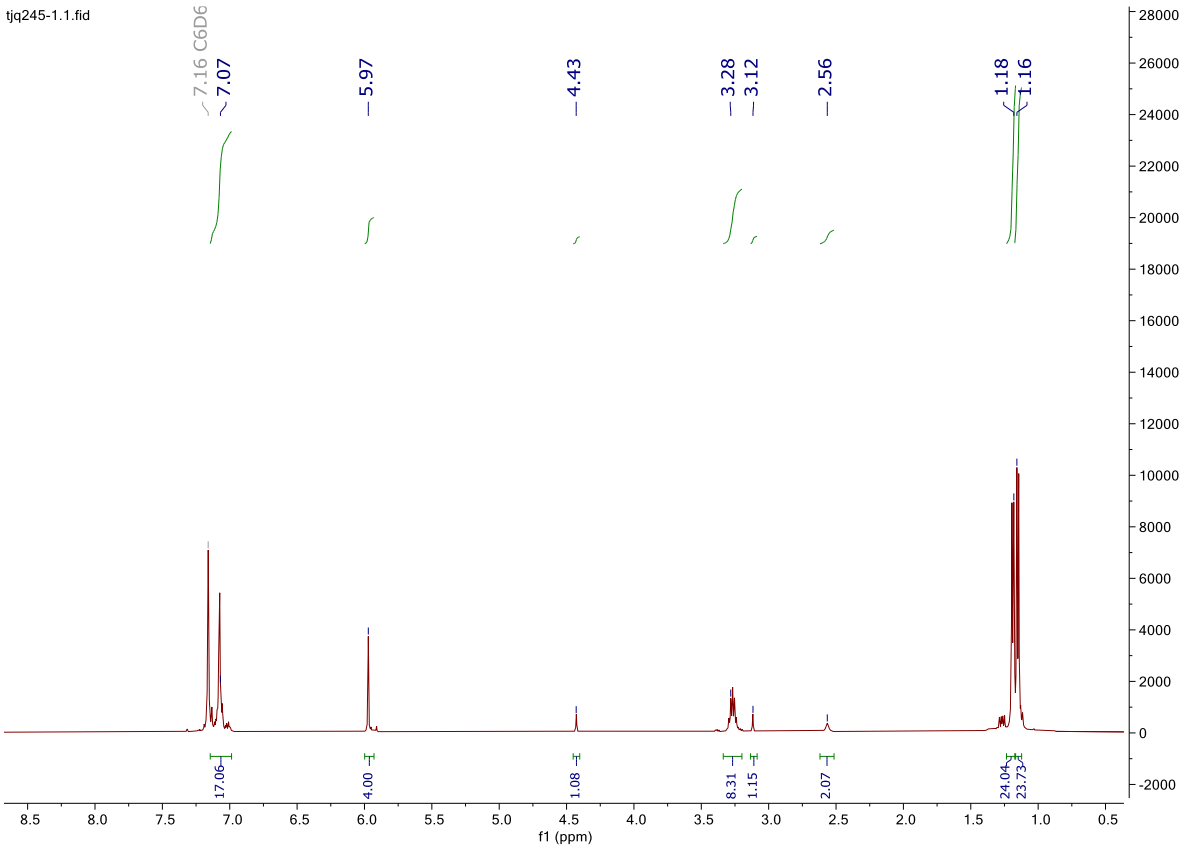


Figure S11: ^{1}H NMR spectrum of **8** (500 MHz, C_6D_6, 298 K).

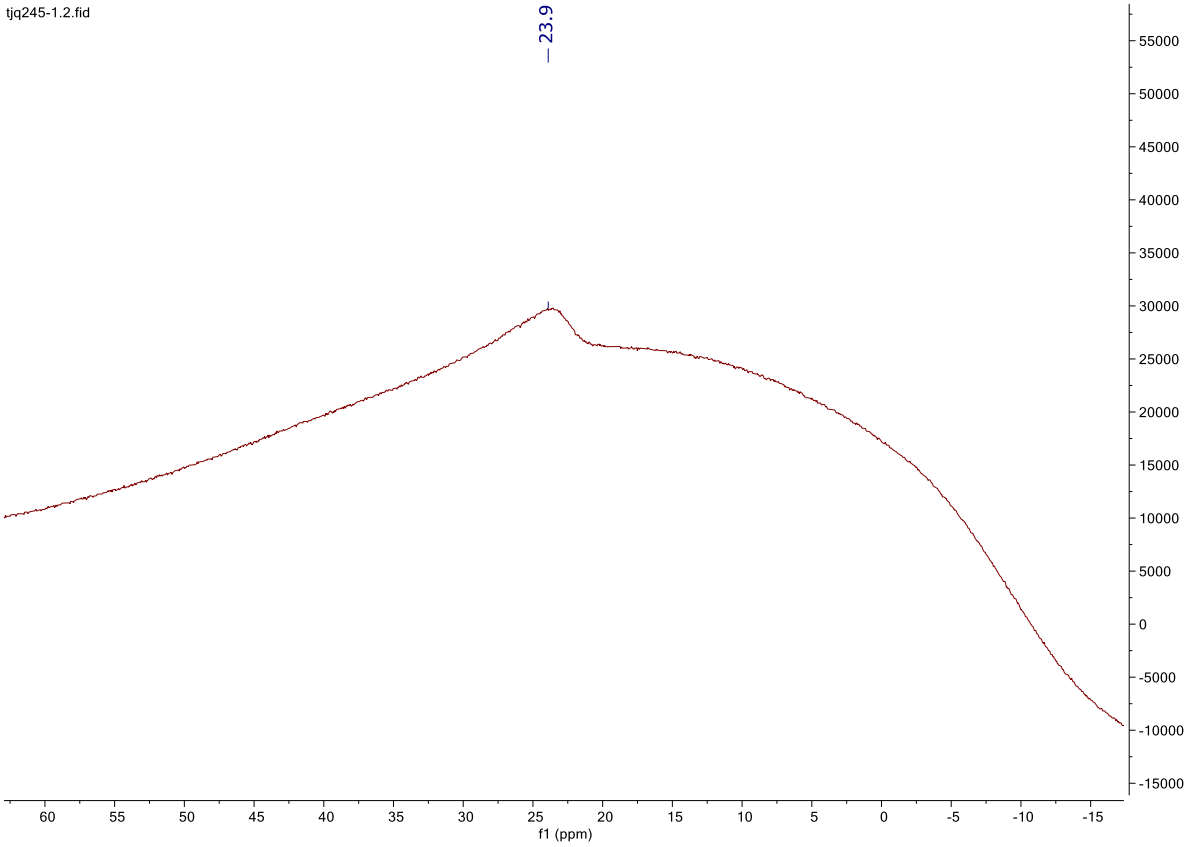


Figure S12: ^{11}B{^{1}H} NMR spectrum of **8** (160 MHz, C_6D_6, 298 K).

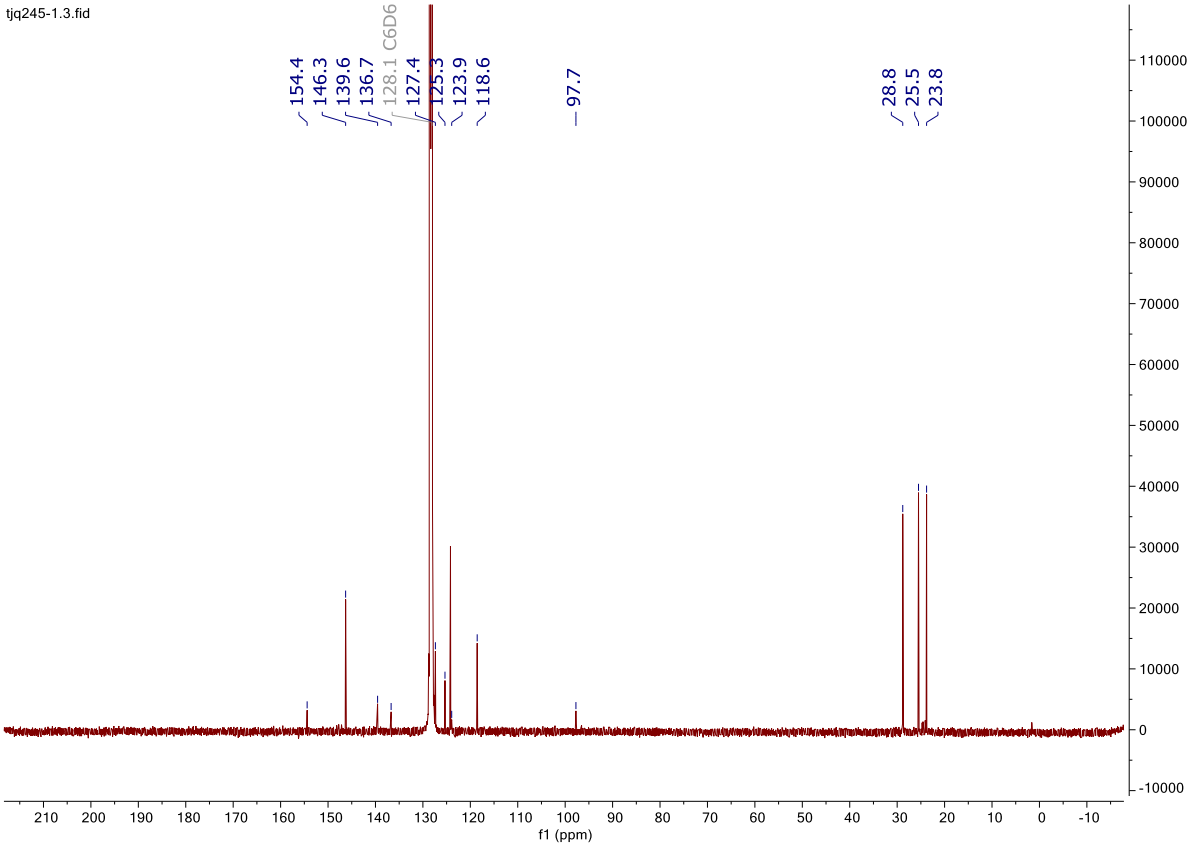


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **8** (126 MHz, C_6D_6, 298 K).

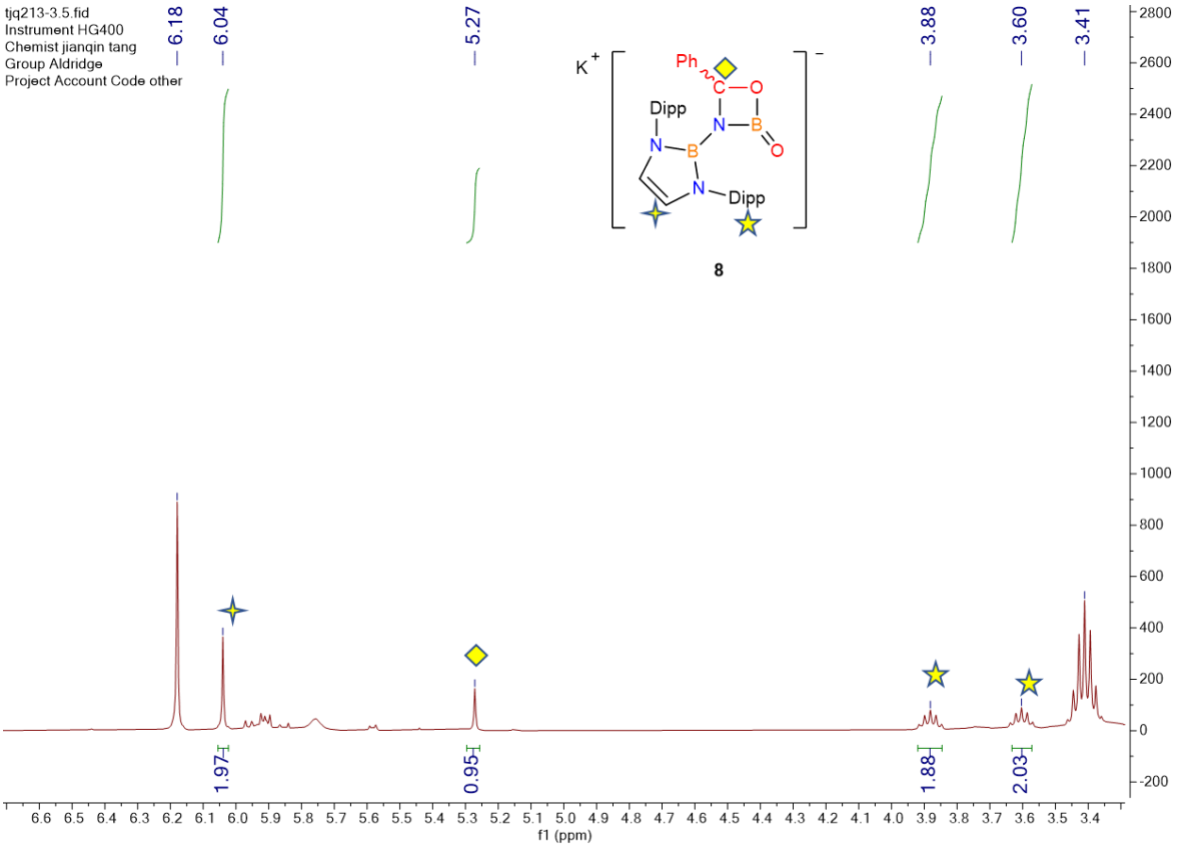


Figure S14: ^{1}H NMR spectrum(part) of **9** (400 MHz, C_6D_6, 298 K).

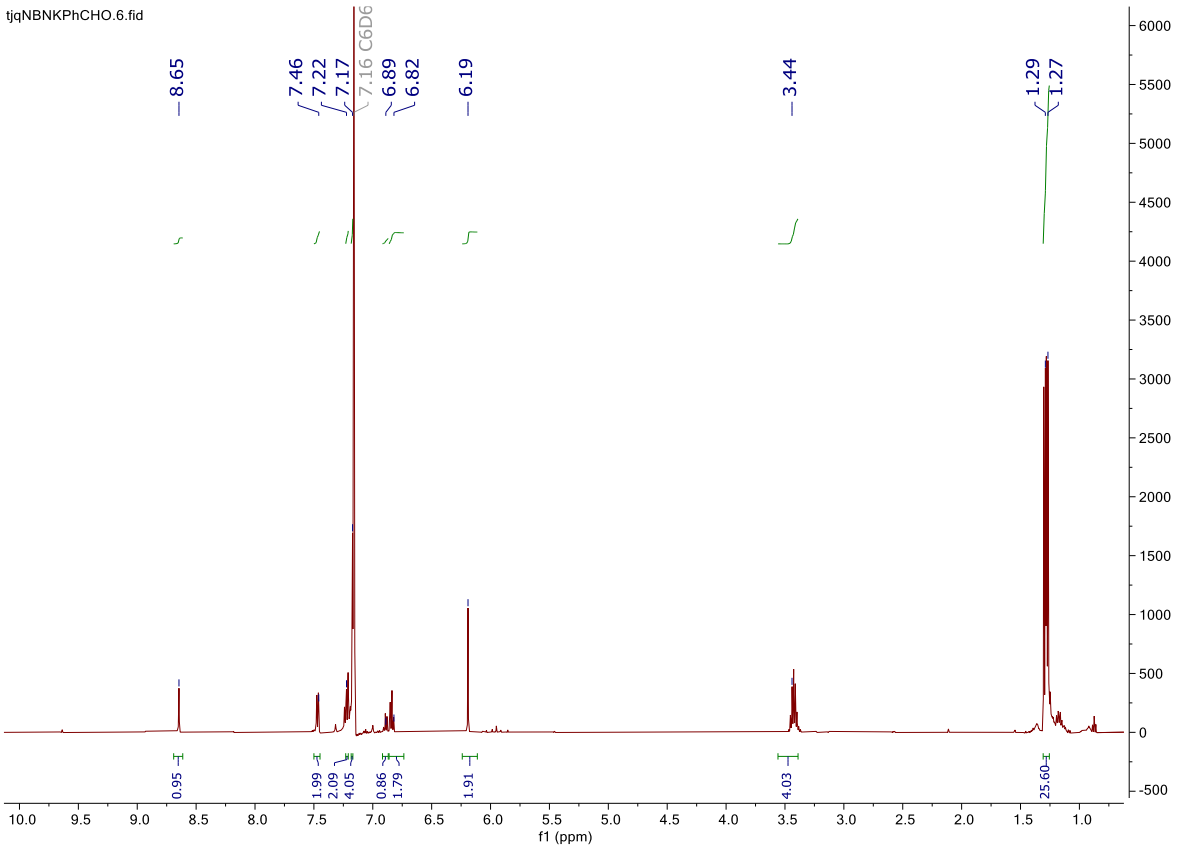


Figure S15: ^{1}H NMR spectrum of **10** (500 MHz, C_6D_6, 298 K).

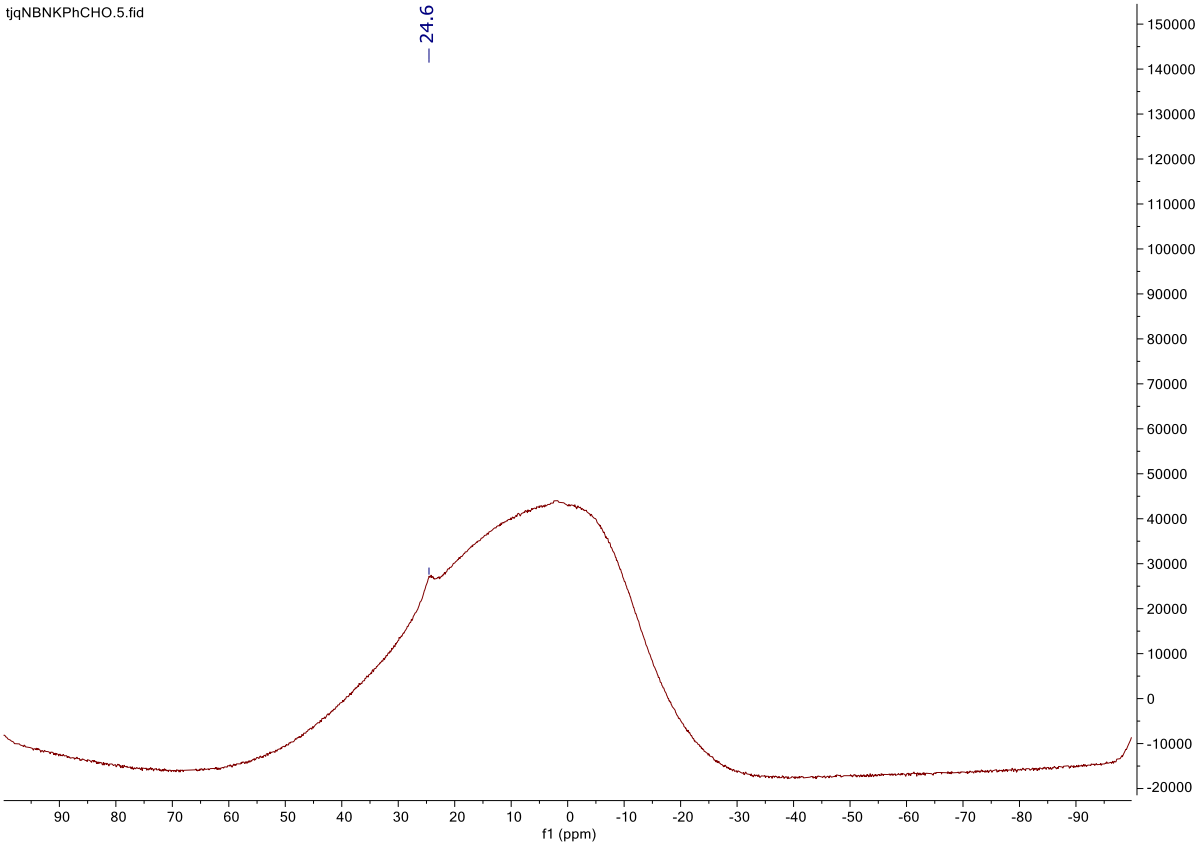


Figure S16: ^{11}B{^{1}H} NMR spectrum of **10** (160 MHz, C_6D_6, 298 K).

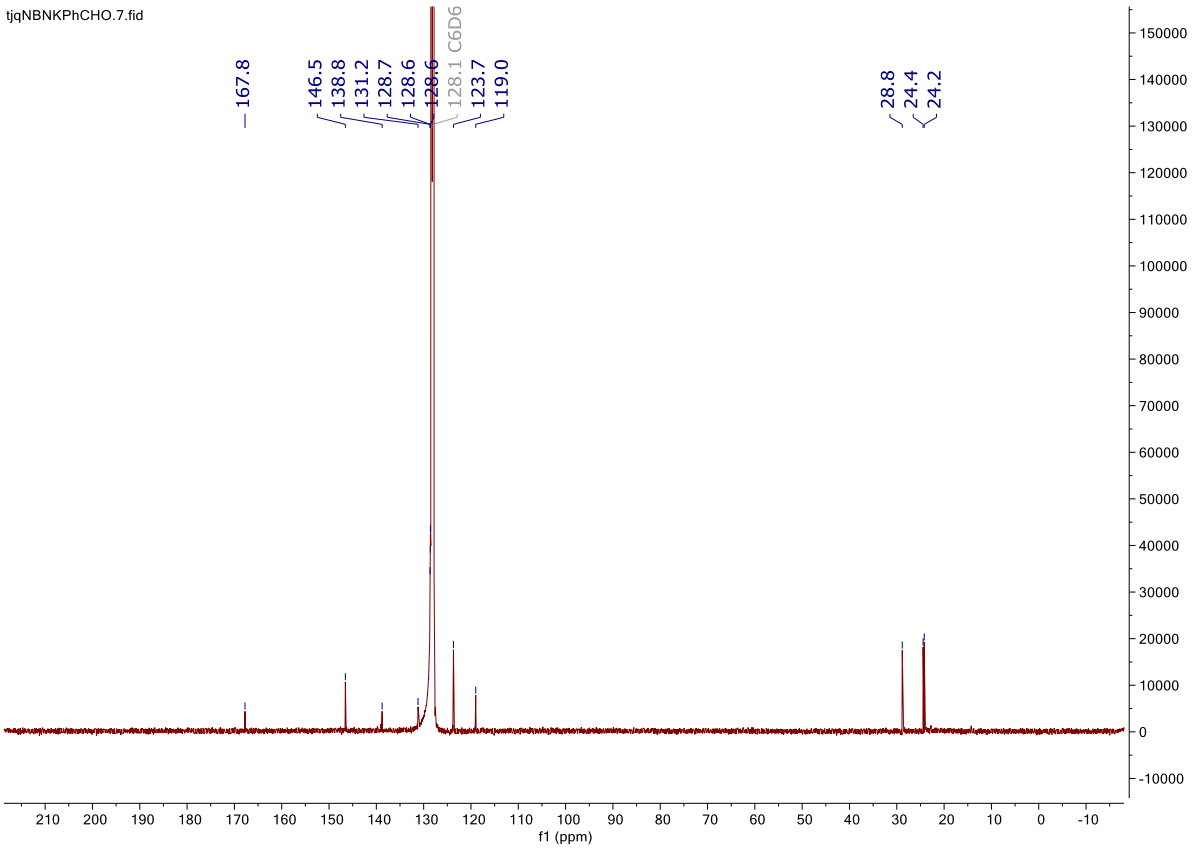


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of **10** (126 MHz, C_6D_6, 298 K).

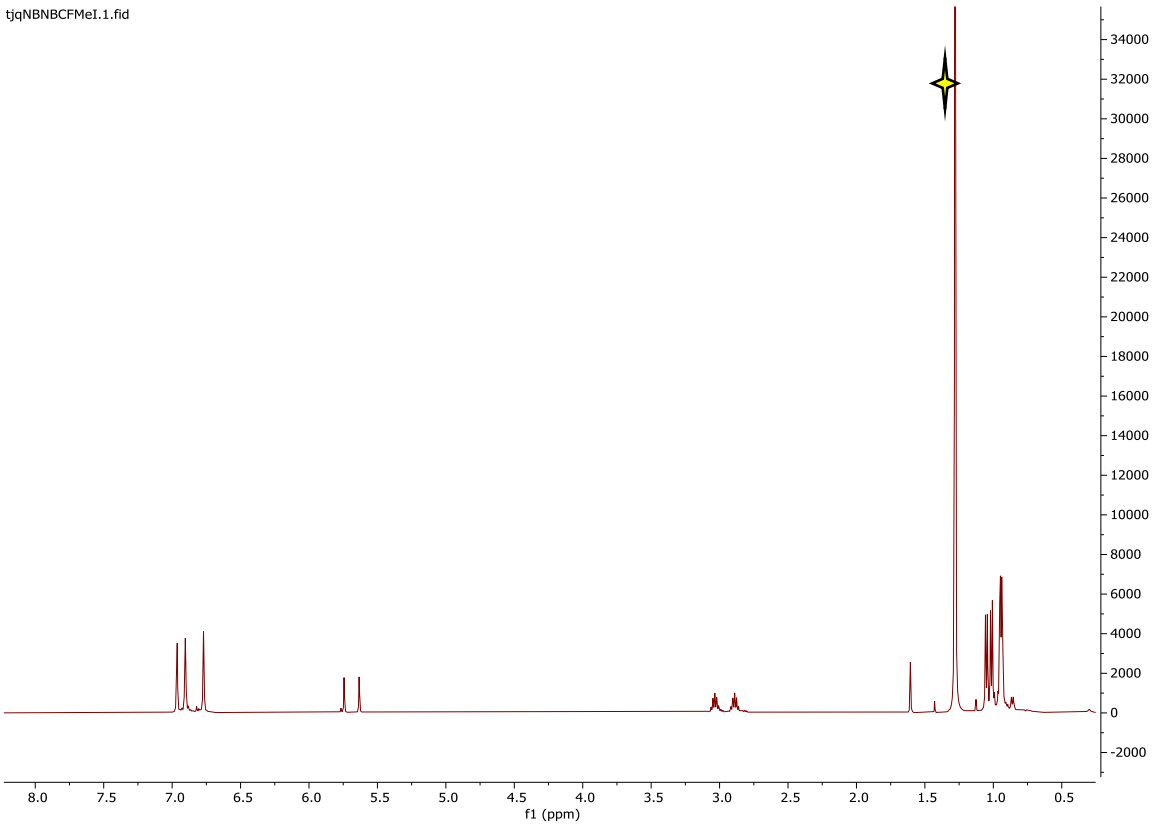


Figure S18. ^{1}H NMR monitoring of the reaction of **3** with MeI, showing the formation of **4** (500 MHz, C_6D_6, 298 K) (yellow star: excess MeI).

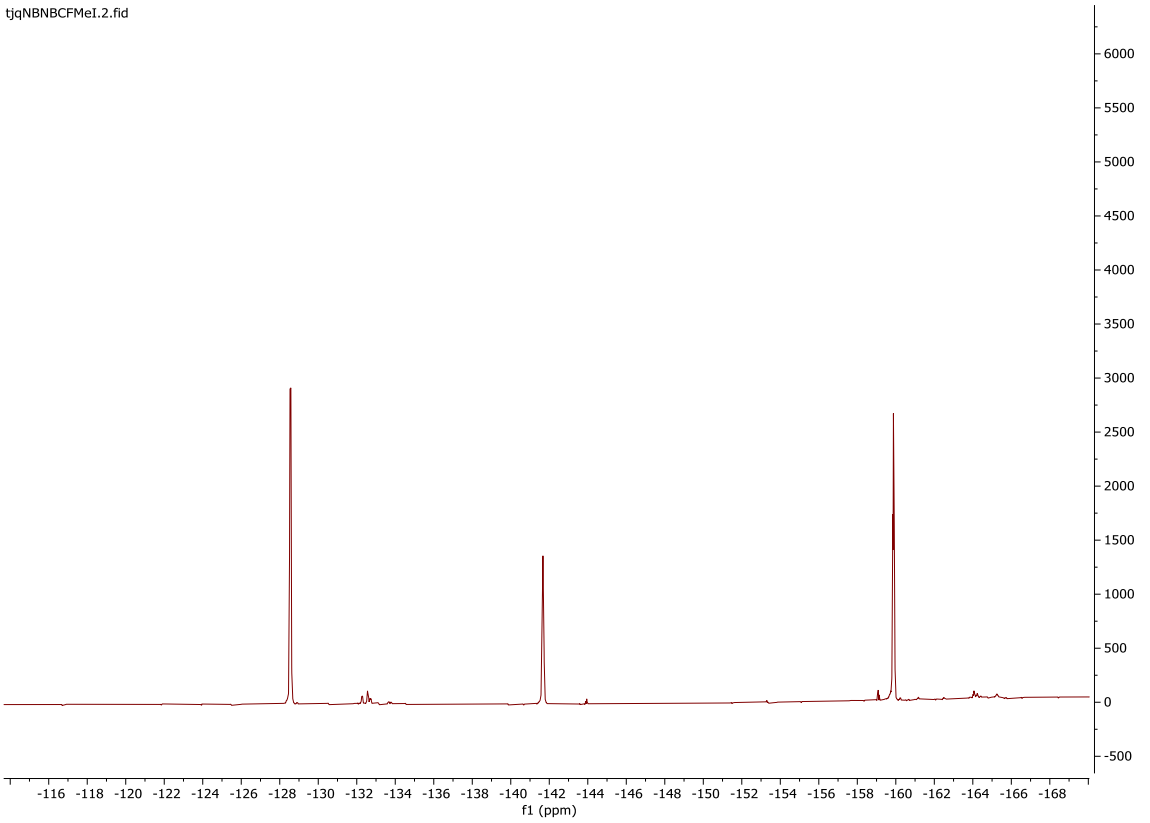


Figure S19. ^{19}F NMR monitoring of the reaction of **3** with MeI, showing the formation of $B(C_6F_5)_3$ (470 MHz, C_6D_6, 298 K).

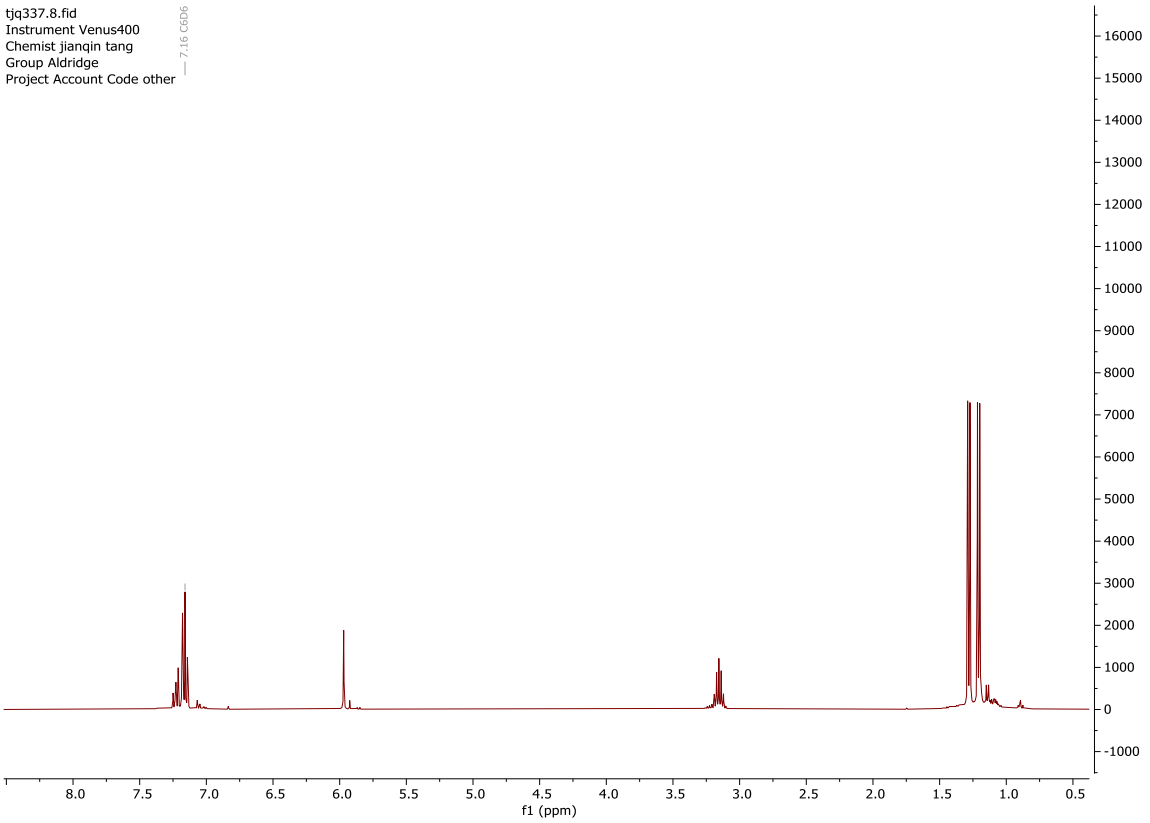


Figure S20. ^{1}H NMR monitoring of the reaction of **3** with CO_2, showing the formation of **5** (400 MHz, C_6D_6, 298 K).

4. Details of X-ray crystallography

Single-crystal X-ray diffraction data for all compounds were collected on an Oxford Diffraction/Agilent SuperNova diffractometer equipped with a 135 mm Atlas CCD area detector or a Rigaku XtaLAB Synergy-DW VHF equipped with a PhotonJet-R dual wavelength rotating anode and HyPix-Arc 150° detector. Crystals were selected under Paratone-N oil, mounted on MiTeGen Micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[S3] Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[S4] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite.[S4] Structures were solved ab initio from the integrated intensities using SHELXT[S5] and refined on F^2 using SHELXL[S6] with the graphical interface OLEX2.[S7] Selected crystallographic data are summarised in Tables S1-S3, and full details are given in the supplementary deposited CIF files (2377740-45). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Selected crystallographic data and refinement parameters for compounds **5** and **6**.

compound	**5**	**6**
Empirical formula	$C_{27}H_{36}BN_3O$	$C_{27}H_{36}BN_3S$
Fw /g mol^{-1}	429.4	445.46
T/K	100.00(10)	100.00(10)
Cell setting	monoclinic	monoclinic
Space group	$P2_1/c$	I2/a
a/Å	12.67284(7)	16.90996(6)
b/Å	9.17962(5)	9.55705(3)
c/Å	22.43254(13)	33.35081(10)
α/°	90	90
β/°	96.7556(5)	94.9584(3)
γ/°	90	90
V/Å^3	2591.50(3)	5369.63(3)
Z	4	8
ρ_{calc}g/cm^3	1.101	1.102
μ/mm^{-1}	0.512	1.189
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Reflections collected	56620	109063
Independent reflections	5317 [R_{int} = 0.0229]	5534 [R_{int} = 0.0239]
parameters	297	311
GooF	1.026	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.1008	R_1 = 0.0353, wR_2 = 0.0895
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.1021	R_1 = 0.0359, wR_2 = 0.0900
CCDC ref	2377740	2377741

Table S2. Selected crystallographic data and refinement parameters for compounds **7** and **8**.

compound	**7**	**8**
Empirical formula	$C_{53}H_{74}BN_5P_2$	$C_{60}H_{81}B_3N_6O$
Fw /g mol^{-1}	853.92	934.73
T/K	100.00(10)	100.00(10)
Cell setting	monoclinic	monoclinic
Space group	$P2_1/c$	C2/c
a/Å	12.89680(10)	22.24980(10)
b/Å	19.8442(2)	13.50310(10)
c/Å	40.8371(5)	37.4373(2)
α/°	90	90
β/°	96.9990(10)	99.0810(10)
γ/°	90	90
V/Å^3	10373.42(18)	11106.73(12)
Z	8	8
ρ_{calc}g/cm^3	1.094	1.118
μ/mm^{-1}	1.04	0.498
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Reflections collected	167460	67625
Independent reflections	21356 [R_{int} = 0.0625]	11344 [R_{int} = 0.0205]
parameters	1691	698
GooF	1.084	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0581, wR_2 = 0.1446	R_1 = 0.0406, wR_2 = 0.1037
Final R indexes [all data]	R_1 = 0.0767, wR_2 = 0.1516	R_1 = 0.0460, wR_2 = 0.1074
CCDC ref	2377742	2377745

Table S3. Selected crystallographic data and refinement parameters for compounds **9** and **10**.

compound	**9**	**10**
Empirical formula	$C_{45}H_{52.4}B_2KN_3O_2$	$C_{33}H_{42}BN_3$
Fw /g mol^{-1}	728.01	491.5
T/K	100.00(10)	100.00(10)
Cell setting	tetragonal	monoclinic
Space group	I-4	$P2_1/n$
a/Å	22.7178(7)	9.70980(10)
b/Å	22.7178(7)	16.9985(2)
c/Å	15.9414(8)	17.7195(2)
α/°	90	90
β/°	90	93.8430(10)
γ/°	90	90
V/Å^3	8227.3(7)	2918.06(6)
Z	8	4
ρ_{calc}g/cm^3	1.175	1.119
μ/mm^{-1}	1.428	0.487
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
Reflections collected	30711	24546
Independent reflections	8001 [R_{int} = 0.0416]	24546
parameters	527	345
GooF	1.016	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1556	R_1 = 0.0501, wR_2 = 0.1745
Final R indexes [all data]	R_1 = 0.0595, wR_2 = 0.1600	R_1 = 0.0541, wR_2 = 0.1774
CCDC ref	2377743	2377744

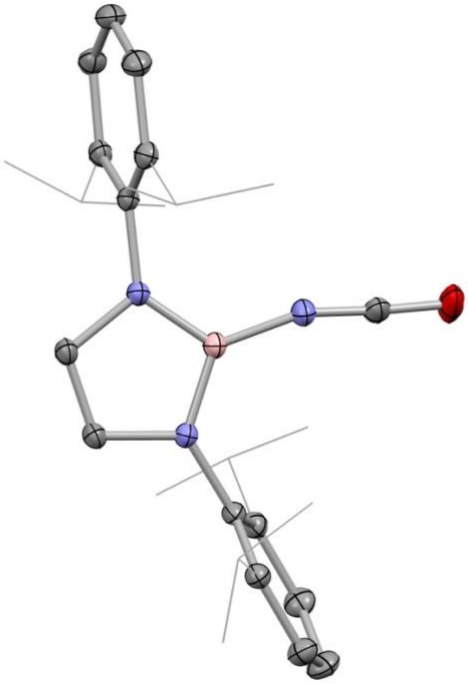


Figure S16. Molecular structure of **5** in the solid state as determined by X-ray crystallography. All Hs omitted and ^{i}Pr groups shown in wireframe format for clarity; thermal ellipsoids shown at the 35% probability level.

5. Details of quantum chemical calculations

Geometry optimizations were carried out using the Gaussian 16 package with the M06-2X functional.[S8,S9] The def2-SVP basis set was used for all atoms.[S10,S11] Frequency calculations at same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states), and provide the thermal corrections of Gibbs free energy. Single-point energy calculations were performed at the M06-2X/def2-TZVP level of theory for the modelling of compounds in solution (benzene).[S12,S13] The gas-phase geometry was used for all the solution phase calculations. The SMD method was used with the corresponding solvent, while Bondi radii were chosen as the atomic radii to define the molecular cavity.[S14,S15] The corrections of Gibbs free energy from frequency calculations were added to the single-point energies to obtain the Gibbs free energy in solution. All energies reported in the paper correspond to the reference state of 1 mol/L, 298 K.

Table S6. Calculated energies of intermediates and transition states.

Species	Thermal Corrections of Gibbs Free Energies (Hartree)	Solvation Energies (Hartree)
1 (anionic component)	1.061871	-2428.25269
PhCHO	0.080626	-345.564694
(boryl)N=C(H)Ph	0.615977	-1471.941512
IN3	0.632052	-1647.489932
IN2	0.522271	-1301.886084
BO2	-0.008553	-175.532068
IN1	1.173277	-2773.848201
TS1	1.169813	-2773.797297
TS2	1.169729	-2773.805785
TS3	0.629418	-1647.439945
TS4	0.626958	-1647.444168

Coordinates for optimised geometries

PhCHO

C	3.43481100	1.01852900	0.00937100
C	4.82327200	1.02236600	-0.14245000
C	5.51885600	2.22997400	-0.15353600
C	4.82160500	3.42964200	-0.01229200
C	3.43166300	3.42750800	0.14005300
C	2.73709000	2.22344900	0.15091800
H	5.35663000	0.07452100	-0.25152700
H	6.60307600	2.23792600	-0.27216800
H	5.36456300	4.37618600	-0.02104400
H	2.89460200	4.37063000	0.25021700
H	1.65259700	2.18442400	0.26754100
C	2.69222400	-0.26919900	0.02065100
O	1.50054700	-0.36040800	0.14595600
H	3.33093100	-1.17893200	-0.09929800

1 (anionic component only)

N	3.76389000	0.76964700	0.20547100
N	-3.61635700	-0.76975400	0.51321800
N	2.42913000	2.44059900	-0.62093100
N	1.35455300	0.10758500	-0.38722900
N	-1.25591700	-0.19916600	-0.29940400
N	-2.37801300	-2.52448100	-0.28650300
C	4.15619600	-0.31657700	1.02686800
C	4.47803400	1.97194400	0.17631700
H	5.50816000	2.03144500	0.52131400
C	0.25363600	3.50211800	-0.29852100
C	-4.03469200	0.47671900	1.03434200
C	3.69485900	2.95378600	-0.33094900
H	3.94446800	3.99734100	-0.51460200
C	-4.34455000	1.52965900	0.14699200

C	-4.36051400	-1.94877000	0.60495300
H	-5.37058400	-1.95795900	1.00993500
C	-1.61950900	-3.77209200	-2.24228200
C	4.85660700	-1.40413800	0.46731000
C	-1.40075400	-3.32964600	-0.92011800
C	-4.24034700	1.30923100	-1.35409400
H	-3.29004400	0.77817600	-1.51771300
C	-0.19938600	-3.62641700	-0.24255400
C	-3.63274300	-2.98304100	0.11825400
H	-3.91413500	-4.03090300	0.03165200
C	-4.07099100	0.66672800	2.43157600
C	0.02287600	-3.14034100	1.18127000
H	-0.37771100	-2.11734400	1.23654900
C	-2.82221500	-3.26074400	-3.01971000
H	-3.67294500	-3.19304500	-2.32618700
C	1.38159300	3.62635800	-2.47841800
C	1.35560100	3.20987000	-1.13103500
C	0.24309600	3.05053200	1.15386500
H	0.66068400	2.03376300	1.17387200
C	-0.65010900	-4.57497300	-2.84990800
H	-0.80471500	-4.93503700	-3.86823600
B	0.04750900	-0.04373200	-0.38128600
C	-4.82109000	2.94357000	2.06498000
H	-5.13201300	3.90991200	2.46712000
C	-3.53493800	-0.41902100	3.35119300
H	-3.79189200	-1.39211300	2.90924700
C	-4.73585100	2.75877400	0.68743400
H	-4.97288400	3.58995800	0.02230500
C	3.81135400	-0.30033400	2.39303900
C	-0.80355100	4.24459500	-0.83473100
H	-1.67405700	4.46357800	-0.21439800
C	-4.48523900	1.90601000	2.92924800

H	-4.52391400	2.07133000	4.00719200
B	-2.29611400	-1.07401100	-0.05462100
C	5.22476000	-2.46357200	1.30100700
H	5.76458800	-3.31608200	0.88510200
C	0.52898200	-4.89452500	-2.18313500
H	1.28536600	-5.50936700	-2.67508300
C	2.49133300	3.13395700	-3.39347900
H	3.42696400	3.12895900	-2.81527400
C	0.31841100	4.39259300	-2.96460800
H	0.32411800	4.73323400	-4.00111400
C	-1.15608300	2.96651600	1.75811100
H	-1.62772500	3.95782000	1.85744500
H	-1.09618900	2.53517300	2.76878700
H	-1.81026800	2.31782500	1.15499200
C	-0.76617000	4.70185600	-2.14892300
H	-1.59880800	5.28626000	-2.54629400
C	-2.52424300	-1.83992200	-3.52058800
H	-1.70069500	-1.86549900	-4.25176900
H	-2.21388200	-1.18254900	-2.69479900
H	-3.40919200	-1.40366200	-4.00983100
C	1.49448300	-3.06599100	1.58034800
H	1.58419700	-2.61710400	2.58035600
H	2.06426900	-2.43284100	0.88141100
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H	1.69606000	-4.64031700	-0.39751700
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H	-5.39332500	-0.55283500	-1.36600400
H	-5.29263100	0.26196900	-2.94597100
H	-6.35760200	0.91832000	-1.67582000
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H	2.91178100	1.62512200	2.22958000

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H	-1.84815500	-3.98772800	1.93353800
H	-0.63513400	-3.64593200	3.19528200
C	4.90489200	-2.45092900	2.65694200
H	5.19636600	-3.28837300	3.29405500
C	-4.17518600	2.60646700	-2.15646900
H	-5.12538300	3.16364100	-2.11269200
H	-3.97559600	2.37725700	-3.21348200
H	-3.36621400	3.25850500	-1.79765100
C	5.10895200	-1.44184200	-1.02871600
H	5.23238800	-0.39899700	-1.35725600
C	1.15356500	3.95003500	1.99969400
H	2.18207700	3.96305900	1.61024300
H	1.18670100	3.59061100	3.04108800
H	0.77145200	4.98386800	2.00763900
C	-3.24014400	-4.16489600	-4.17811900
H	-4.18113700	-3.80163400	-4.61730600
H	-3.39104000	-5.20416300	-3.84949100
H	-2.48720500	-4.16736200	-4.98145200
C	2.71083100	4.01090500	-4.62482500
H	1.85729600	3.95424700	-5.31806400
H	3.59930200	3.66906600	-5.17624600
H	2.85869400	5.06673000	-4.35232300
C	-2.00223000	-0.32776600	3.39652700
H	-1.57361500	-0.27141600	2.38357300
H	-1.57049700	-1.19751400	3.91628900
H	-1.69671800	0.58167700	3.93876200
C	3.87149700	-2.00735500	-1.73916700

H	3.99908900	-1.97291300	-2.83272600
H	2.96319400	-1.44660100	-1.46958500
H	3.71727700	-3.05860600	-1.44517000
C	6.36643800	-2.21819600	-1.41746800
H	6.25001000	-3.29686000	-1.22881200
H	7.25018500	-1.86838700	-0.86282800
H	6.56400000	-2.09909600	-2.49318600
C	3.57649600	1.41409500	4.24685500
H	2.97190900	2.26431200	4.59770200
H	4.60028400	1.77227200	4.06357400
H	3.61396300	0.67606000	5.06359500
C	-4.12206700	-0.38094300	4.76101100
H	-3.79527100	0.51451100	5.31205200
H	-3.77976300	-1.25556100	5.33375000
H	-5.22233400	-0.38833500	4.74402600
C	1.53320700	0.32641000	3.21950000
H	1.51408800	-0.46195500	3.99080800
H	1.10644300	-0.08243300	2.29052300
H	0.89037800	1.15338800	3.56193900
C	2.19855800	1.68362800	-3.80473800
H	2.03131000	1.04450000	-2.92563000
H	3.03319400	1.26760900	-4.39058900
H	1.28792500	1.64619500	-4.42339800

TS1

N	0.69781500	1.96236200	7.85609900
N	1.96108300	3.12576500	6.34144500
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N	4.33317500	5.40005900	12.59312400
N	2.01081500	3.97511600	8.77182500
N	4.12117000	4.93832100	10.06357700
C	0.31027500	1.30296200	9.05104400

C	-1.02617400	1.39551700	9.48796400
C	4.18246500	4.09525300	13.14712100
C	3.07245000	3.82814500	5.81233400
C	3.44885300	8.17931700	10.34871600
C	0.55292000	1.39159600	6.58567700
H	-0.09683200	0.53517200	6.41694600
C	4.27334600	8.79225500	9.38717700
C	1.29944300	2.08218700	5.69212100
H	1.39170800	1.92612800	4.61993000
C	-1.39610600	0.72998000	10.65997100
H	-2.42678300	0.78454200	11.01415600
C	4.14759600	7.63729600	12.62095700
H	4.10480800	8.68473700	12.91043600
C	5.28945800	3.42980500	13.70613800
C	4.25856200	3.13031400	5.48991500
C	1.28095200	0.59603500	9.79364100
C	3.00193900	5.23043800	5.68738700
C	-1.99690300	2.28090600	8.72389200
H	-1.75941900	2.17641200	7.65471200
C	-0.45715400	0.00402200	11.38934700
H	-0.75813400	-0.50942200	12.30516500
C	4.35661400	6.54591500	13.39226100
H	4.52473900	6.48759700	14.46569400
C	1.56489700	9.48810700	9.58828600
H	0.50368300	9.74215800	9.64435400
C	2.90262900	3.49140800	13.13052400
C	2.07770700	8.50357000	10.43723500
C	0.86641600	-0.05233900	10.96361900
H	1.60107700	-0.59965300	11.55661200
C	3.71781300	9.77139000	8.55693000
H	4.34900900	10.24842000	7.80374700
C	1.73099400	5.99164700	6.02545400

H	1.09666000	5.32681600	6.62331400
C	5.27392600	5.23888300	4.82937700
H	6.13577900	5.79093200	4.44917400
C	5.33747600	3.85700300	4.97772700
H	6.25812400	3.32970200	4.71626900
C	2.37949700	10.13162300	8.66235400
H	1.96346900	10.89692100	8.00423800
C	1.67277900	4.25075900	12.65423800
H	1.97328400	4.89841600	11.81826500
C	4.11399100	5.91609700	5.19025300
H	4.06936800	7.00243200	5.08721400
C	4.38461000	1.62380000	5.67135500
H	3.53894600	1.29437500	6.29101600
C	5.10747200	2.14392300	14.22720000
H	5.96270500	1.61560700	14.65554800
C	5.70191900	8.34277800	9.17278700
H	5.97749700	7.70248500	10.02019700
C	2.77211100	2.19965200	13.64744500
H	1.79997300	1.70590500	13.61272700
C	6.66627100	4.06916700	13.76243100
H	6.59659800	5.04405300	13.26183400
C	3.86382900	1.52678700	14.19044600
H	3.74198800	0.51460600	14.58054600
C	1.13937800	7.76153600	11.37456500
H	1.74906200	7.12595900	12.02999300
C	2.72889600	0.52420200	9.33455300
H	2.98594900	1.46820000	8.83317800
C	-3.46298800	1.89981300	8.91916200
H	-3.79731200	2.09786600	9.94942600
H	-3.63896400	0.83550400	8.70287200
H	-4.10002500	2.49808800	8.25091400
C	6.69984500	9.50005900	9.11632900

H	6.53166100	10.14067800	8.23611900
H	7.72275500	9.10043400	9.04175600
H	6.63754300	10.13222000	10.01476800
C	2.91347100	-0.61906800	8.32902600
H	3.95414100	-0.63875600	7.97179500
H	2.25328700	-0.49818700	7.45694200
H	2.68944100	-1.59075700	8.80017800
C	1.15099000	5.14739700	13.78597900
H	0.85243800	4.52973100	14.64811000
H	0.26842800	5.71380500	13.44898700
H	1.91226800	5.86633400	14.12147900
C	0.55805800	3.35449800	12.12535900
H	0.92716200	2.67792100	11.34300000
H	-0.22939100	3.97672700	11.67669100
H	0.09123200	2.75507700	12.92315100
C	1.99833600	7.23591300	6.87011300
H	2.58450000	7.99296000	6.32457300
H	2.54838800	6.98140500	7.79017800
H	1.04952700	7.70981100	7.16563900
C	0.97060900	6.33919000	4.74080700
H	0.02877400	6.86080100	4.97233700
H	0.73196400	5.43008400	4.16915400
H	1.57651400	6.99586700	4.09572900
B	3.05778100	4.44728200	9.35460000
C	3.73077200	0.41322500	10.48171700
H	3.68977900	-0.56683000	10.98774200
H	3.55975300	1.20410400	11.22752800
H	4.74053500	0.57075800	10.07971500
C	0.34689600	8.71076300	12.27577400
H	1.01971600	9.35973600	12.85573700
H	-0.27172000	8.13755600	12.98302800
H	-0.32835200	9.35524200	11.69150900

B	4.12734100	5.80353600	11.20466500
C	5.76878600	7.48831300	7.90318200
H	5.09804100	6.61893300	7.97692100
H	6.78976500	7.11426000	7.74008400
H	5.46757900	8.08263300	7.02367300
B	1.59210500	3.10809200	7.75583900
C	0.21212100	6.84171900	10.57104800
H	-0.42293900	7.42575100	9.88502500
H	-0.45037300	6.27649400	11.24597400
H	0.78293200	6.11659200	9.96907900
C	7.09296000	4.32494500	15.21212200
H	7.18021900	3.37834600	15.76845700
H	6.36178900	4.95569900	15.73880400
H	8.07164400	4.82763400	15.24524400
C	7.71518200	3.23374600	13.02263200
H	8.68012900	3.76290000	12.99846000
H	7.40933400	3.03950500	11.98512100
H	7.87253500	2.26444500	13.52158300
C	4.29847700	0.90700500	4.31834600
H	4.31691900	-0.18524100	4.45735900
H	3.38100300	1.16943700	3.77240000
H	5.15549600	1.18386100	3.68269700
C	5.65901200	1.22001800	6.41739800
H	5.65989600	1.66470000	7.42422800
H	5.70235800	0.12261100	6.50687700
H	6.56667400	1.53349000	5.87577100
C	-1.76209800	3.74995500	9.10212900
H	-0.70167900	4.02405500	8.99498700
H	-2.36659200	4.41851600	8.46938200
H	-2.05180900	3.91706700	10.15223700
O	4.93287300	2.87014900	9.01980600
C	5.34086700	3.74868200	9.84684200

C	6.59010200	4.53997300	9.43508200
C	7.13821200	4.29829200	8.17343300
C	7.24854400	5.42000800	10.29840700
C	8.32845300	4.91242100	7.78595500
H	6.60000100	3.61179000	7.51883500
C	8.43670000	6.04361100	9.91379300
H	6.82341700	5.62017400	11.28688400
C	8.98501700	5.78536400	8.65589500
H	8.74561500	4.71178700	6.79620000
H	8.93839600	6.73018900	10.59975700
H	9.91917700	6.26506600	8.35586400
H	5.45309400	3.44771400	10.92135500

IN1

N	0.59398700	2.04417900	7.84671200
N	2.06410300	3.05240300	6.39990800
N	3.79144700	7.29941000	11.36469900
N	4.32341100	5.47021000	12.62823400
N	2.02964000	3.96186000	8.83652200
N	4.11983100	5.03271600	10.10034700
C	0.17969500	1.34788500	9.00718100
C	-1.12750300	1.53640700	9.50222700
C	4.28565100	4.14017600	13.13273900
C	3.18720200	3.70527200	5.85229400
C	3.28378300	8.23818200	10.42223300
C	0.52238900	1.42892000	6.59077200
H	-0.17657000	0.61795100	6.39326100
C	4.14635000	8.86852300	9.50896300
C	1.37862100	2.03341500	5.73728200
H	1.53026000	1.84111600	4.67649500
C	-1.52785800	0.82174600	10.63336900
H	-2.53543500	0.95416500	11.03122400

C	3.95181500	7.67921700	12.70110100
H	3.82734200	8.71527400	13.00728800
C	5.44776300	3.54868500	13.66123000
C	4.32152800	2.95980300	5.45349000
C	1.07977700	0.47250700	9.64712300
C	3.18015500	5.11258200	5.73009200
C	-2.02911600	2.55005000	8.81910300
H	-1.82839900	2.47195200	7.73998500
C	-0.65364600	-0.06397400	11.26275900
H	-0.98147400	-0.61898500	12.14432300
C	4.27110300	6.59870100	13.44975900
H	4.45793700	6.53698500	14.51979600
C	1.42768800	9.55593000	9.62058700
H	0.36588900	9.80965600	9.63849900
C	3.06402400	3.42610700	13.07035500
C	1.90796700	8.55144100	10.46376600
C	0.63669300	-0.23270000	10.77311400
H	1.32182100	-0.91855200	11.27788200
C	3.62141400	9.86654100	8.67976200
H	4.28002700	10.36336400	7.96317000
C	1.96117700	5.93949100	6.10327600
H	1.23398600	5.26574100	6.57059500
C	5.40444300	5.02068400	4.75001900
H	6.26705900	5.53454600	4.32095800
C	5.40210100	3.63473000	4.87622700
H	6.27725400	3.06184200	4.55624700
C	2.27966700	10.22204500	8.74305100
H	1.88881500	11.00418900	8.08931900
C	1.77829700	4.09710600	12.60553500
H	2.01503500	4.72843900	11.73706800
C	4.30391000	5.74813400	5.19246900
H	4.30596000	6.83768700	5.10487400

C	4.43009100	1.45788200	5.68527500
H	3.50751600	1.12167200	6.17578900
C	5.38095300	2.22754800	14.11907000
H	6.27738900	1.75664400	14.52973200
C	5.59357800	8.44472300	9.35587000
H	5.80902700	7.71121400	10.14441400
C	3.05246000	2.10177600	13.51589100
H	2.13166400	1.52182300	13.44221300
C	6.76272500	4.30447000	13.74245300
H	6.61983800	5.26450400	13.22636600
C	4.19839600	1.50428200	14.03691400
H	4.16597500	0.46693400	14.37528100
C	0.95210100	7.74391400	11.32519400
H	1.54061700	7.25348700	12.11274700
C	2.50488500	0.29018000	9.14920200
H	2.69623500	1.05692600	8.38513400
C	-3.51844000	2.30008300	9.04631400
H	-3.80019900	2.47361700	10.09679100
H	-3.80485200	1.27079200	8.78257700
H	-4.11420600	2.99228100	8.43280000
C	6.56968700	9.61093800	9.52276100
H	6.43782900	10.36406800	8.72966600
H	7.60584200	9.24376500	9.46301100
H	6.43365400	10.11212400	10.49269600
C	2.68071700	-1.07923800	8.48495800
H	3.70578000	-1.18888100	8.09807900
H	1.98059700	-1.19843000	7.64467900
H	2.49798400	-1.89485800	9.20402600
C	1.22033100	4.98920700	13.72391400
H	0.96215600	4.37521100	14.60194100
H	0.30426400	5.49603300	13.38122500
H	1.93916800	5.75854200	14.03841300

C	0.71000300	3.11991900	12.13147400
H	1.09871300	2.44983100	11.35363100
H	-0.12113900	3.68113900	11.68206100
H	0.29878300	2.51705200	12.95762600
C	2.29555800	7.02265800	7.12638400
H	3.01045700	7.75906400	6.72450300
H	2.72767800	6.57195500	8.03252400
H	1.38695300	7.57088900	7.42055100
C	1.31784200	6.53488100	4.84572800
H	0.40652300	7.09494500	5.10689400
H	1.04589800	5.74575600	4.12888300
H	2.00758400	7.22923200	4.33915200
B	3.32080500	4.11585400	9.21857200
C	3.52895900	0.51486700	10.26351300
H	3.44648600	-0.24701100	11.05651900
H	3.39729700	1.50841600	10.71668700
H	4.54847400	0.47495000	9.85213400
C	-0.10850800	8.60091100	12.01722300
H	0.34689700	9.42147600	12.59181400
H	-0.69792200	7.98071400	12.70938500
H	-0.81399000	9.03942400	11.29450700
B	4.04618200	5.87540900	11.25320900
C	5.78653500	7.74088900	8.00958600
H	5.11827600	6.87142600	7.92628600
H	6.82210400	7.38560700	7.90311900
H	5.56646700	8.42772500	7.17444100
B	1.60904300	3.12154100	7.81447100
C	0.30781800	6.63944800	10.47722800
H	-0.31661800	7.08047500	9.68195500
H	-0.34159600	6.00517300	11.10235500
H	1.05001600	5.98322800	9.99104500
C	7.13062400	4.61258200	15.19800800

H	7.27325300	3.68146700	15.76897300
H	6.33909700	5.19134300	15.69560200
H	8.06648200	5.18986400	15.25020300
C	7.89801400	3.55167200	13.04198900
H	8.80826100	4.17017000	13.00892000
H	7.62787900	3.29203300	12.00846500
H	8.14514800	2.61999800	13.57446300
C	4.55964400	0.69060300	4.36630700
H	4.59483800	-0.39423800	4.55120200
H	3.71077700	0.89870200	3.69812000
H	5.48218200	0.97098400	3.83295800
C	5.58299600	1.12813500	6.63946800
H	5.42880200	1.63590400	7.60261500
H	5.63589800	0.04106800	6.81197000
H	6.55383600	1.44772300	6.22579500
C	-1.64077700	3.97019300	9.25130800
H	-0.55792900	4.14233100	9.14275100
H	-2.18198900	4.72130800	8.65425500
H	-1.90831100	4.12341400	10.31000900
O	4.48721000	3.28048400	8.97249900
C	5.20440000	4.06823400	9.88832500
C	6.48559000	4.64340600	9.32026200
C	6.83975200	4.40601200	7.99187800
C	7.33190100	5.41316800	10.12564000
C	8.03829500	4.90741900	7.48243200
H	6.15627200	3.83046800	7.36718200
C	8.52694800	5.92025100	9.61712600
H	7.04683900	5.61476100	11.16255000
C	8.88893900	5.65860300	8.29329500
H	8.30044000	4.71312200	6.43992400
H	9.17952600	6.51912200	10.25602100
H	9.82767100	6.04891500	7.89515100

H	5.45136900	3.48991300	10.80522200

TS2

N	0.45559600	1.81853700	7.55503600
N	1.68129700	3.22460500	6.22390100
N	3.46708900	7.32044500	11.31034800
N	4.03782900	5.67246400	12.81358600
N	2.28433700	3.16303200	8.72341100
N	4.38458100	5.15085400	10.27386600
C	-0.02730300	1.02878400	8.62992800
C	-1.28629900	1.32421300	9.19004600
C	4.39390500	4.47014000	13.46820200
C	2.82131300	3.87180500	5.67195400
C	3.10499500	8.11574500	10.19767900
C	0.02301100	1.70243100	6.22966200
H	-0.79224300	1.03760100	5.95146500
C	4.09445700	8.54486500	9.28452400
C	0.76002200	2.52249500	5.44165200
H	0.69533200	2.67431300	4.36636300
C	-1.75229800	0.53796400	10.24801700
H	-2.72655800	0.74831600	10.69157700
C	3.28178900	7.77915600	12.61830200
H	2.93508700	8.79045200	12.82074300
C	5.60464700	4.40631400	14.19308600
C	3.98695800	3.11739500	5.43853000
C	0.78088100	-0.00369700	9.15358900
C	2.77581400	5.25154300	5.38710900
C	-2.04346300	2.55544400	8.72351300
H	-1.87990900	2.65986900	7.64094200
C	-0.97575200	-0.49691500	10.75944700
H	-1.34624500	-1.09700900	11.59275800
C	3.62543700	6.81654200	13.50212500

H	3.59593700	6.85011600	14.58968200
C	1.42237900	9.35884500	8.98127900
H	0.38708700	9.67233400	8.84227700
C	3.55675100	3.33848500	13.34362500
C	1.75186100	8.49532500	10.03062000
C	0.28277400	-0.75391000	10.22383000
H	0.89154000	-1.55043200	10.65256800
C	3.70994700	9.37982400	8.22959200
H	4.45900900	9.71765300	7.51231400
C	1.53666600	6.05063400	5.74161700
H	0.66763000	5.40979200	5.52257900
C	5.06400900	5.11847800	4.58872100
H	5.94224000	5.60881100	4.16285300
C	5.10131800	3.76287400	4.89158900
H	6.01829600	3.19360600	4.71979600
C	2.39120700	9.80146900	8.08635600
H	2.11451100	10.46501800	7.26442000
C	2.23506400	3.43244700	12.59518500
H	2.40949700	4.05715700	11.70677700
C	3.91052100	5.85794500	4.84245200
H	3.89647000	6.92493900	4.61648400
C	4.06710100	1.63739800	5.77439700
H	3.08707100	1.32726300	6.16479400
C	5.95240500	3.20052200	14.80900800
H	6.88116000	3.12822900	15.37657500
C	5.54580200	8.13865400	9.48280700
H	5.52984900	7.07025100	9.74626800
C	3.95789000	2.14733500	13.95614200
H	3.33467200	1.25783400	13.85818400
C	6.54938400	5.60095300	14.20217800
H	5.94132900	6.50947800	14.32435500
C	5.13898000	2.07707800	14.68832400

H	5.43180000	1.13842500	15.16297200
C	0.67474600	7.89363000	10.92472400
H	1.02974600	7.93542600	11.96366900
C	2.15051600	-0.29435900	8.55727500
H	2.62145500	0.67871400	8.35669900
C	-3.55015800	2.48322700	8.96401500
H	-3.78994700	2.51469400	10.03801700
H	-3.98660600	1.56494300	8.54336000
H	-4.04614300	3.34663300	8.49680700
C	6.17351600	8.91503500	10.64728300
H	6.18122800	9.99644500	10.43194700
H	7.21356100	8.58985700	10.80636000
H	5.61801700	8.75090200	11.58194200
C	2.02293300	-1.04414100	7.22556500
H	3.01934300	-1.21214100	6.78647700
H	1.42317200	-0.47815700	6.49871200
H	1.54621500	-2.02535800	7.38204500
C	1.18910600	4.14815400	13.45929700
H	1.02622900	3.59573700	14.39902300
H	0.22866600	4.20511600	12.92442700
H	1.50815800	5.17177500	13.70600800
C	1.70169200	2.08704700	12.10470100
H	2.47132100	1.54044300	11.53954000
H	0.84559900	2.24358100	11.42980800
H	1.35845300	1.45116300	12.93739900
C	1.53080000	6.35283900	7.24433500
H	2.39324800	6.98351900	7.51362000
H	1.59746100	5.43727300	7.84808800
H	0.61613500	6.90138300	7.51770500
C	1.39270700	7.34525600	4.94341400
H	0.41395900	7.80307600	5.14979000
H	1.47482500	7.17489100	3.85903300

H	2.15796900	8.07927500	5.24036700
B	3.32192000	3.20677000	9.47207800
C	3.08297900	-1.04673100	9.50455500
H	2.74941600	-2.08358600	9.67146900
H	3.15867200	-0.54241300	10.47851500
H	4.09224500	-1.08963600	9.07037100
C	-0.65794400	8.63842300	10.87211200
H	-0.53825000	9.71142200	11.08521100
H	-1.35018700	8.21492300	11.61464900
H	-1.13696800	8.53699600	9.88566600
B	3.99730300	5.93577100	11.35437400
C	6.39780200	8.28331500	8.22329500
H	5.93161600	7.78000100	7.36213600
H	7.38244700	7.82120400	8.38823600
H	6.56517600	9.34010200	7.95607800
B	1.53510600	2.79517800	7.60886400
C	0.46367300	6.41294700	10.58063000
H	0.00403200	6.31739600	9.58697100
H	-0.20732900	5.93943200	11.31363300
H	1.41178600	5.85394000	10.56004700
C	7.56293500	5.56732600	15.34530900
H	8.30035200	4.76139500	15.20655800
H	7.07437900	5.41804100	16.31977900
H	8.12001500	6.51507700	15.37997500
C	7.27376500	5.72300100	12.85368800
H	7.96322500	6.58136200	12.86447200
H	6.56597700	5.86735300	12.02439500
H	7.85991200	4.81282500	12.64809900
C	4.34119700	0.79883100	4.52222500
H	4.34317600	-0.27384000	4.77025400
H	3.57277200	0.97355200	3.75467700
H	5.32212400	1.04374800	4.08513300

C	5.10957400	1.36969600	6.86517800
H	4.88079000	1.92116000	7.78868000
H	5.14048400	0.29487900	7.10745400
H	6.11895900	1.67565500	6.54387100
C	-1.44193100	3.79354100	9.40220100
H	-0.35556100	3.85570000	9.23767600
H	-1.90636500	4.71665900	9.02205500
H	-1.61221200	3.74582100	10.49020000
O	4.37285100	2.82790000	10.18747400
C	5.20368800	4.03570500	10.42860400
C	6.34711600	3.94634300	9.42007100
C	6.31452300	4.68571300	8.23599800
C	7.42112000	3.08321400	9.65795500
C	7.35514700	4.57532000	7.31248600
H	5.45854400	5.34516900	8.06814300
C	8.45741200	2.96586000	8.73315000
H	7.43478700	2.49774400	10.58166100
C	8.42837900	3.71785100	7.55712100
H	7.32271200	5.16377100	6.39359400
H	9.29303400	2.29101500	8.93087600
H	9.24311900	3.63682900	6.83435900
H	5.63218600	3.84893800	11.43191200

IN2

O	12.03478100	10.01509200	10.30164100
N	12.48609000	7.55076300	10.91495300
N	10.35774800	6.35934600	11.80642400
N	12.36467900	5.30031000	12.14887400
C	8.05718400	9.24609100	11.46522600
H	7.89633700	10.23305400	11.90076300
C	9.30886900	7.18675400	11.34447800
C	7.21160600	8.79657500	10.45677400

H	6.38671000	9.42509600	10.11480100
C	13.72196200	4.93835500	12.29210800
C	8.49621000	6.74765600	10.27620800
C	9.11343700	8.45475100	11.92791900
C	7.43583500	7.55765000	9.86185800
H	6.78939200	7.22995300	9.04601800
C	15.65200100	4.57733700	13.70377600
H	16.13366800	4.61154200	14.68233100
B	11.80720300	6.53262100	11.54333600
B	12.22455200	8.82349300	10.58357300
C	14.32946000	5.00859300	13.56465900
C	10.14439400	5.16160300	12.48861500
H	9.14593000	4.83735100	12.77722300
C	16.37390600	4.12881700	12.60149700
H	17.40809200	3.79960700	12.72236900
C	8.87344700	5.48599600	9.51650900
H	9.24289800	4.74731400	10.24294100
C	11.32898600	4.54243400	12.70314600
H	11.52116600	3.59742100	13.20793800
C	14.45810400	4.52873200	11.16050800
C	10.00696300	8.91793700	13.06635800
C	10.18853400	10.43357100	13.11262400
H	9.25321700	10.95688600	13.37103800
H	10.56650400	10.79097300	12.14331200
H	10.92938200	10.69074900	13.88512300
C	15.78578500	4.12685400	11.33970500
H	16.37304300	3.80519400	10.47864700
C	12.79904400	3.36802000	9.66329100
H	12.32596600	3.37803800	8.66905200
H	12.00528500	3.43488400	10.42055400
H	13.31765400	2.40250600	9.78428000
C	13.79511200	4.52715000	9.79214200

H	13.24237900	5.47754500	9.72358400
C	14.79258900	4.49560000	8.63612800
H	15.32406700	3.53135700	8.57888300
H	15.53955000	5.29725600	8.72782400
H	14.26011600	4.63444700	7.68378600
C	13.62344600	7.19747600	14.50906800
H	14.65612200	7.56274800	14.62931500
H	12.98806900	7.70606800	15.25124300
H	13.28646000	7.47849000	13.49975000
C	13.58314800	5.67469700	14.70961500
C	14.10581400	5.29697900	16.09411900
H	14.13780400	4.20588100	16.23499400
H	13.45480200	5.72560600	16.87047800
H	15.11911300	5.69279200	16.26572300
C	10.03180200	5.81225100	8.56225900
H	10.38568800	4.90243000	8.05232400
H	10.87513500	6.27127700	9.10035400
H	9.69469900	6.53003400	7.79743000
C	7.71100700	4.84921700	8.75688400
H	6.84490400	4.67108400	9.41209600
H	8.02468500	3.88500500	8.32975200
H	7.37980900	5.48278800	7.91929300
C	9.49087700	8.35761300	14.39645800
H	10.15264700	8.65348900	15.22567200
H	9.44689400	7.25845100	14.36645100
H	8.47887300	8.73897200	14.61069500
H	12.52958200	5.36461700	14.65428700
H	11.00063300	8.48606600	12.88647700

7

N	3.16497200	6.04311000	5.63085300
N	3.40439400	6.16717000	3.36415700

N	4.28436600	8.18723000	4.77463000
C	2.93538600	6.38827800	6.99478700
C	2.61125100	4.90528100	5.04497400
H	2.14680200	4.12663500	5.64513900
C	2.75571300	4.97619200	3.69868700
H	2.44025800	4.26881700	2.93519600
C	3.62855500	6.57899300	2.02031800
C	5.13295900	8.68630500	3.97210600
H	5.52961800	8.12932200	3.09830900
C	1.81649700	7.18249900	7.30551000
C	2.88295900	7.66530700	1.50565500
C	5.04427400	5.11661800	7.60393200
H	4.77390600	4.51506200	6.72269100
C	3.81723500	5.92539400	7.98931600
C	4.60360600	5.92332000	1.24779400
C	1.81470200	8.34980800	2.34809600
H	2.20950900	8.45123600	3.36983000
C	5.66744400	10.05665700	4.11467700
C	6.50840500	10.57677000	3.12521700
H	6.76370700	9.95861900	2.26073200
C	5.45169400	4.79328100	1.80883000
H	5.18979700	4.66899900	2.86858500
C	3.13678800	8.06912700	0.19322900
H	2.58403700	8.90829400	-0.22892600
C	1.60515700	7.52579900	8.64526000
H	0.74954900	8.15000900	8.91125000
C	4.80565100	6.35117800	-0.07003900
H	5.55270600	5.84792900	-0.68802800
C	0.87338200	7.69042500	6.22594800
H	1.09808600	7.14313500	5.29802100
C	5.33265700	10.84349900	5.22528500
H	4.68086500	10.41170400	5.98689000

C	3.56141500	6.28315700	9.31529400
H	4.22678100	5.93672200	10.10700900
C	5.83467900	12.13470600	5.33799700
H	5.57712100	12.74615600	6.20415900
C	4.08274500	7.41436000	-0.59413500
H	4.25738400	7.74227000	-1.62003000
C	6.67138100	12.65153200	4.34395000
H	7.06311400	13.66595200	4.43542300
C	7.00792200	11.87315000	3.23730600
H	7.66044400	12.27686900	2.46189100
C	2.46674100	7.08056000	9.64153200
H	2.28420300	7.35386200	10.68209900
C	0.54915100	7.48589700	2.42627000
H	0.10734500	7.36285000	1.42524400
H	-0.20077000	7.96391600	3.07585100
H	0.76436600	6.48768400	2.83304000
C	1.11705700	9.17992200	5.95538700
H	0.88893700	9.77883500	6.85142200
H	0.46939400	9.53411800	5.13763700
H	2.16595300	9.35871000	5.67711900
C	-0.59448900	7.42199100	6.56614200
H	-0.76767400	6.35638400	6.77382700
H	-1.23882600	7.71808000	5.72488100
H	-0.91851900	7.99760600	7.44643700
C	5.51161200	4.15916300	8.69911200
H	5.92455100	4.70271600	9.56232600
H	6.31073300	3.50951200	8.31417100
H	4.69115400	3.52099700	9.05779600
C	6.94435000	5.13203700	1.74154300
H	7.28557800	5.23712900	0.70045200
H	7.54002000	4.33439400	2.20931000
H	7.16256300	6.07378600	2.26565400

C	6.17954400	6.06166300	7.18941700
H	5.86241800	6.73662100	6.38216500
H	7.05665800	5.49159100	6.84771500
H	6.48452800	6.68345000	8.04531300
C	1.47257600	9.75913300	1.86900500
H	2.37379100	10.38099100	1.76619200
H	0.80491900	10.24495700	2.59482100
H	0.94791500	9.74556000	0.90134600
B	3.69186100	6.87857300	4.58692100
C	5.15674100	3.47137600	1.09315600
H	4.09271300	3.20503600	1.16801900
H	5.74819800	2.65343700	1.53027200
H	5.41053500	3.53778600	0.02383000

TS3

O	11.34381400	9.49350400	9.61756700
O	14.29141900	9.30411400	10.64231400
N	12.58194000	7.60594700	10.92222700
N	10.49384100	6.08345800	11.00272600
C	14.11699000	8.29250300	11.37457800
N	12.38879100	5.21301200	11.95619800
C	13.96088200	8.57016000	12.87288700
C	7.93867200	8.64907700	10.19342900
H	7.49638500	9.54583500	10.62892200
C	9.50443000	6.82355200	10.29922200
C	13.05680900	9.55018300	13.30234900
H	12.42428500	10.03590800	12.55323800
C	7.50579500	8.20830600	8.94848600
H	6.71815800	8.75010400	8.42115200
C	13.63017800	4.97906500	12.59761100
C	9.11695700	6.39760300	9.01161100
C	8.94255600	7.97048000	10.88914800

C	8.09884800	7.09605100	8.35794100
H	7.77617400	6.78166500	7.36450300
C	14.93521700	4.61293500	14.58830400
H	15.02103400	4.52471200	15.67045200
C	12.98940000	9.91073500	14.64459300
H	12.27555900	10.67134900	14.96999100
B	11.89792600	6.41063100	11.26451900
B	12.00620600	8.64812900	10.19985800
C	13.68550700	4.85711900	14.00621900
C	10.22400300	4.80695800	11.50080900
H	9.24014000	4.35529400	11.39324000
C	16.08744800	4.50337900	13.81613000
H	17.05071700	4.32668900	14.29861700
C	14.80896700	7.97915200	13.80675700
H	15.51971400	7.21809300	13.47168800
C	9.88417400	5.28374900	8.31543100
H	10.12579100	4.51436800	9.06373100
C	11.33806200	4.29546900	12.06630500
H	11.48443700	3.32116100	12.52567500
C	14.78822100	4.85489300	11.79980100
C	13.84535300	9.31273900	15.57850900
H	13.79775200	9.60201300	16.63059500
C	9.41130500	8.44960200	12.25256900
C	9.35102700	9.96877100	12.40154200
H	8.31470800	10.34102100	12.44600900
H	9.87106900	10.44458200	11.55689200
H	9.84689300	10.26718100	13.33786500
C	16.01337700	4.62644600	12.43276200
H	16.92248200	4.54210700	11.83688100
C	14.75740100	8.34875900	15.15504500
H	15.43163900	7.87575200	15.87363800
C	14.08149900	3.60924300	9.74129700

H	13.97753800	3.66050200	8.64651300
H	13.08768800	3.41781000	10.17041300
H	14.73619100	2.75680900	9.98480700
C	14.68020600	4.91421200	10.28230000
H	13.98893200	5.73270300	10.03449800
C	16.00416800	5.22479900	9.58806300
H	16.72551800	4.39818800	9.69193200
H	16.45948600	6.14215100	9.98880200
H	15.83007200	5.37737900	8.51329200
C	11.71809100	6.34636400	14.72290700
H	12.39771200	7.17936300	14.94940700
H	10.87158100	6.38925400	15.42562300
H	11.31525900	6.49650900	13.71397200
C	12.43298600	4.99522200	14.87541600
C	12.70548500	4.74183600	16.35860900
H	13.17090100	3.76166500	16.53822900
H	11.75863700	4.77518200	16.91632300
H	13.36349200	5.52079300	16.77508300
C	11.21202500	5.84083500	7.78285300
H	11.80581900	5.04436100	7.30762400
H	11.81117100	6.28968200	8.58800300
H	11.01999000	6.62830900	7.03802200
C	9.10064400	4.60487700	7.19304500
H	8.11337200	4.26037100	7.53565000
H	9.65956400	3.73436700	6.81897100
H	8.94806400	5.28398600	6.34009100
C	8.63609200	7.73556300	13.36473200
H	9.00190200	8.05112900	14.35414400
H	8.75462300	6.64391200	13.28826800
H	7.56162600	7.97232400	13.29786700
H	14.77451100	7.39277700	11.24588500
H	10.46992100	8.17107700	12.35374400

H	11.72304100	4.22033200	14.54487300

IN3

O	11.28738700	9.51740000	9.80386600
O	13.64116200	9.45523000	10.69655200
N	12.57552700	7.69287300	11.14509000
N	10.56510500	6.11827300	11.05743200
C	13.85841700	8.29631200	11.46176400
N	12.42844300	5.28111600	12.11208400
C	14.06119500	8.64213600	12.92874300
C	7.97432000	8.58017100	10.06367100
H	7.47487500	9.46550200	10.45852200
C	9.60335600	6.82592600	10.28226900
C	13.21440400	9.58776200	13.52183700
H	12.42990500	10.04221800	12.91095100
C	7.62520800	8.10261600	8.80565800
H	6.84117200	8.60022600	8.23101200
C	13.69453200	5.05728400	12.69909600
C	9.31752100	6.37744000	8.97788900
C	8.97021800	7.95885500	10.82000600
C	8.30513400	7.01832300	8.25908300
H	8.05946900	6.68365900	7.25004600
C	15.07612900	4.70089300	14.64446600
H	15.19383300	4.60476200	15.72393700
C	13.39066000	9.95403100	14.85207000
H	12.72760300	10.69469300	15.30404800
B	11.93472100	6.47400900	11.41753100
B	12.28361900	9.00481800	10.37983800
C	13.80764600	4.93123000	14.10250600
C	10.30590900	4.82894900	11.52524400
H	9.33949300	4.35683200	11.36050100
C	16.20206000	4.60995800	13.83091000

H	17.18404400	4.43852600	14.27627000
C	15.08143000	8.07400800	13.68818000
H	15.73971800	7.33120700	13.23014200
C	10.21009900	5.33237900	8.32712700
H	10.47179700	4.57872000	9.08499200
C	11.39472700	4.33345700	12.15370100
H	11.53612600	3.35673900	12.61042100
C	14.82763900	4.96018600	11.86060500
C	14.41993500	9.38322000	15.60949600
H	14.55967300	9.67474200	16.65261700
C	9.36812200	8.48252700	12.18790000
C	9.20368000	9.99549000	12.30897900
H	8.14452000	10.30180900	12.30909000
H	9.73306100	10.47396500	11.47151300
H	9.64084200	10.34188000	13.25895800
C	16.07692900	4.74247100	12.45142700
H	16.96640900	4.67076600	11.82467600
C	15.26200100	8.44012700	15.02558600
H	16.06430800	7.98134600	15.60791700
C	14.04855000	3.73159600	9.81543000
H	13.92561400	3.78647200	8.72301400
H	13.06070800	3.54790400	10.26080800
H	14.70134200	2.87402800	10.04579400
C	14.66886600	5.03012000	10.34805800
H	13.96731300	5.84824000	10.12769400
C	15.97020200	5.33742200	9.60999800
H	16.68304100	4.49957300	9.67391600
H	16.45978300	6.23852700	10.00822100
H	15.75852300	5.51024200	8.54508000
C	12.06437400	6.53718700	14.99149900
H	12.82640300	7.22040700	15.39435400
H	11.16080100	6.61372800	15.61588100

H	11.80762000	6.88010000	13.98008000
C	12.58173300	5.09246400	14.99469000
C	12.81490100	4.63073700	16.43236200
H	13.20573100	3.60319100	16.47972900
H	11.86778800	4.66414100	16.99009300
H	13.52435700	5.29366200	16.95206300
C	11.51181200	6.01561800	7.88253600
H	12.22091100	5.28061700	7.46864100
H	11.98762200	6.54609200	8.72030100
H	11.29439700	6.76940000	7.11031400
C	9.55777300	4.60000800	7.15596100
H	8.58728400	4.16445000	7.43799900
H	10.21308200	3.78749900	6.80773200
H	9.39312100	5.27395200	6.30112600
C	8.62466700	7.72810600	13.29515400
H	8.94506900	8.08109800	14.28828400
H	8.82223900	6.64667600	13.23622900
H	7.53685000	7.88468700	13.20788100
H	14.73731400	7.71370700	11.11176200
H	10.44190900	8.28122200	12.30031300
H	11.78334300	4.46310900	14.57378000

TS4

O	11.23153600	10.52323500	10.53472800
O	13.60183800	9.68715400	10.48560600
N	12.75685500	7.27301600	11.17952900
N	10.61701900	5.85407300	11.11491000
C	13.77659500	8.02004900	11.41062800
N	12.44250200	4.95297200	12.19413700
C	14.00202400	8.56567500	12.79825400
C	8.26998800	8.58593900	10.23223500
H	7.86248000	9.50072500	10.66137600

C	9.70456400	6.65669700	10.38404100
C	13.07955400	9.41736300	13.41907900
H	12.20664100	9.76659300	12.86004800
C	7.91000000	8.21761000	8.94049900
H	7.20844900	8.83385500	8.37459600
C	13.68595400	4.76894700	12.83675700
C	9.38853200	6.30133800	9.05581600
C	9.15873400	7.81065400	10.98277200
C	8.46668400	7.08372700	8.35562800
H	8.19971800	6.82278800	7.33029600
C	15.00643300	4.58046500	14.85262300
H	15.08070000	4.55073400	15.94022800
C	13.28556300	9.83031200	14.73229500
H	12.56814400	10.50586400	15.20276300
B	12.00254600	6.16798500	11.47600600
B	12.39571700	10.10938600	10.47488700
C	13.75449500	4.72836900	14.24765800
C	10.31324900	4.57091300	11.57713800
H	9.33318000	4.12758300	11.41169600
C	16.16721500	4.49638800	14.09014300
H	17.13708900	4.39220100	14.58073200
C	15.11400200	8.12271600	13.51598700
H	15.82074600	7.43734500	13.03933400
C	10.14585200	5.16978500	8.37818600
H	10.29754800	4.36973500	9.11772000
C	11.37838300	4.04426800	12.22546800
H	11.47275600	3.06581000	12.69202100
C	14.85916200	4.68269500	12.05125500
C	14.40215400	9.38687600	15.44800000
H	14.55674300	9.71054700	16.47937400
C	9.52136900	8.17629800	12.41402700
C	9.19016600	9.62136500	12.77944600

H	8.10053000	9.78817000	12.82156100
H	9.64844400	10.31036500	12.05606400
H	9.59088700	9.84228400	13.78161800
C	16.09080600	4.55244600	12.70177400
H	17.00773000	4.49054000	12.11467900
C	15.31143800	8.52463900	14.83933700
H	16.17879300	8.15770900	15.39227700
C	14.17516600	3.36421700	10.02549900
H	14.08767400	3.37957500	8.92812300
H	13.17514700	3.18576500	10.44442500
H	14.82838100	2.52196500	10.30640100
C	14.76386300	4.68710500	10.53246600
H	14.06700600	5.49292200	10.25820200
C	16.09207700	4.97509700	9.83546600
H	16.81155800	4.15094900	9.96898400
H	16.55465000	5.90022400	10.21002100
H	15.92447900	5.09458600	8.75529600
C	12.10533200	6.42906100	15.05072900
H	12.92006000	7.05226000	15.45106200
H	11.20138500	6.59987500	15.65574000
H	11.90138500	6.76887900	14.02531000
C	12.50140200	4.94766400	15.08296900
C	12.63745600	4.46748300	16.52726400
H	12.98868800	3.42598700	16.58352100
H	11.66307800	4.53067400	17.03340000
H	13.33978400	5.09742500	17.09498900
C	11.53365100	5.67610000	7.95884000
H	12.14174400	4.85512000	7.54651800
H	12.06800100	6.12539700	8.80906500
H	11.43007900	6.45372400	7.18563500
C	9.41120600	4.56191900	7.18456700
H	8.38934100	4.25195900	7.45033200

H	9.95565400	3.67907800	6.81736900
H	9.34403300	5.27361500	6.34718000
C	8.86248100	7.21089500	13.40807000
H	9.12805300	7.48972300	14.43968800
H	9.17823200	6.17078400	13.24505900
H	7.76511400	7.26130700	13.31388400
H	14.71903000	7.87051000	10.85124400
H	10.61463100	8.06456800	12.49086600
H	11.68139400	4.37871400	14.62116500

BO_2^-

B	-2.05658400	1.17410800	-0.41303100
O	-1.14070900	0.31678300	-0.47463400
O	-2.97205700	2.03194900	-0.35258700

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