# Replacing $C_6F_5$ groups with Cl and H atoms in frustrated Lewis pairs: $H_2$ additions and catalytic hydrogenations

Konstantin Chernichenko, Bianka Kótai, Martin Nieger, Sami Heikkinen, Imre Pápai,* and Timo Repo*

## *Table of contents*

Table of contents ..... 1
General experimental ..... 2
Analysis ..... 2
Crystal structure studies of 2c, 4c, 4e, 5c and 5e ..... 2
Preparations ..... 3
1-(2-iodophenyl)-2,2,6,6-tetramethylpiperidine ..... 4
1-[2-(Dichloroboryl)phenyl]-2,2,6,6-tetramethylpiperidine (1c) ..... 4
Dichloro(hydrido)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (4c) ..... 8
Trichloro[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (5c) ..... 13
1-{2-[Chloro(pentafluorophenyl)boryl]phenyl}-2,2,6,6-tetramethylpiperidine (1e) ..... 17
Chloro(hydrido)(pentafluorophenyl)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (4e) ..... 20
Dichloro(hydrido)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (5e) ..... 26
1-[2-(Chloroboryl)phenyl]-2,2,6,6-tetramethylpiperidine (1d) ..... 32
Chloro(dihydrido)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (4d) ..... 39
1-(2-Borylphenyl)-2,2,6,6-tetramethylpiperidine dimer (1b) ..... 44
2-(Dichloroboryl)-*N*,*N*-dimethylaniline (2c) ..... 46
Studies of reactivity ..... 49
Retrodismutation (reaction between 4c and 4b) ..... 49
Retrodismutation (reaction between 5c and 4b) ..... 49
Thermal decomposition of 4a ..... 51
Hydrogenation of alkynes catalyzed by 2c ..... 52
Selective 1D NOE measurements for $H_N$-$H_B$ distance determination ..... 52
Compound 4c ..... 53
Compound 4d ..... 54
Compound 4e ..... 55
Compound 4a ..... 57
Computational Details ..... 58
Isomeric forms of aminoboranes 1a-1f ..... 59
Gibbs free energy profiles for solvent = DCM ..... 62
Energy decomposition analysis ..... 63
H/Cl exchange in DCM ..... 65
H/Cl exchange between 1c and 4c ..... 65
Total energy data ..... 66
Cartesian coordinates of the optimized geometries ..... 67
References ..... 99

## *General experimental*

All the solvents were dried by conventional methods and stored over molecular sieves. Deutereited solvents were purchased from Eurisotop, stored over molecular sieves (3 Å) in a glovebox and used without additional purification. All operations were performed under an argon atmosphere by conventional Schlenk techniques or in a glovebox (Mbraun Unilab). Reagents were purchased from Sigma-Aldrich and dried by conventional methods if needed. Organometallics were purchased from Acros Organics or Sigma-Aldrich (*n*-butyllithium, boron trichloride solution), Strem (dimethyltin dichloride) and used as received. Hydrogen (5.0) was purchased from AGA and dried additionally by passing through a cylinder with molecular sieves. Hydrogenations (at 2.2 bar) were performed in thick-wall 25 ml Schlenk vessels or in J. Young valve NMR tubes purchased from Wilmad. High pressure NMR experiments (10 bar) were carried out in heavy wall Wilmad® quick pressure valve NMR tubes (5 mm o.d., 200 psi upper working pressure). Schlenk vessels were equiped with gas-tight teflon valves and Glindemann PTFE sealing rings.

## *Analysis*

NMR spectra were recorded at Varian Mercury 300 ($^{1}$H, $^{13}$C, $^{19}$F) or Varian Inova 500 ($^{1}$H, $^{13}$C, $^{11}$B) spectrometers.

If not otherwise stated:

- NMR spectra were recorded at 27 °C;
- $^{13}$C spectra were $^{1}$H decoupled;
- signals in $^{13}$C spectra are singlets;
- $^{11}$B spectra were not $^{1}$H decoupled;

Chemical shifts for the $^{1}$H and $^{13}$C spectra were referenced to the residual $^{1}$H/$^{13}$C resonances of the deuterated solvents:

- $C_6D_6$: δ = 7.16; δ = 128.00;
- $CD_2Cl_2$: δ = 5.32; δ = 53.84;

and are reported as parts per million relative to tetramethylsilane.

Chemical shifts for the $^{11}$B and $^{19}$F spectra were referenced to external standard ($BF_3{\cdot}Et_2O$, $CFCl_3$, respectively).

ESI-HRMS spectra were recorded at Bruker micrOTOF. A solution of sodium formate was used as a standard.

Elemental analysis was performed with vario Micro cube instrument in CHN mode.

## Crystal structure studies of 2c, 4c, 4e, 5c and 5e

The single-crystal X-ray diffraction studies of **4e**, **4c**, **5e** and **5c** were carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å). Direct Methods (SHELXS-97) were used for structure solution, and full-matrix least-squares refinement on $F^2$ (SHELXL-97, SHELXL-2013).[1] H atoms were localized by difference Fourier synthesis and refined using a riding model (H(N) and H(B) free). Semi-empirical absorptuion corrections were applied for all structures. The absolute structure was determined by refinement of Flack's x-parameter.[2]

**2c:** colorless crystals, $C_8H_{10}BCl_2N$, $M$ = 201.88, crystal size 0.50 x 0.08 x 0.04 mm, triclinic, space group P-1 (No.2): $a$ = 8.836(1) Å, $b$ = 8.394(1) Å, $c$ = 8.943(1) Å, $\alpha$ = 85.04(1)°, $\beta$ = 80.45(1)°, $\gamma$ = 69,04(1)°, $V$ = 472.50(11) Å$^3$, $Z$ = 2, $r$(calcd) = 1.419 Mg m$^{-3}$, $F$(000) = 208, $m$ = 0.627 mm$^{-1}$, 6082 reflections ($2q_{max}$ = 55°), 2157 unique [$R_{int}$ = 0.048],

111 parameters, R1 (for 1810 $I > 2s(I)$) = 0.045, wR2 (*all data*) = 0.114, GooF = 1.08, largest diff. peak and hole 0.473 and –0.335e Å$^{-3}$.

**4c:** colorless crystals, $C_{15}H_{24}BCl_2N$, $M$ = 300.06, crystal size 0.32 x 0.20 x 0.10 mm, orthorhombic, space group $Cmc2_1$ (No.36): $a$ = 11.1847(5) Å, $b$ = 11.3284(5) Å, $c$ = 12.5977(6) Å, $V$ = 1596.19(13) Å$^3$, $Z$ = 4, $\rho$(calcd) = 1.249 Mg m$^{-3}$, $F$(000) = 640, $\mu$ = 0.393 mm$^{-1}$, 16342 reflections ($2\theta_{max}$ = 55°), 1921 unique [$R_{int}$ = 0.028], 104 parameters, 1 restraint, R1 (for 1851 $I > 2\sigma(I)$) = 0.023, wR2 (*all data*) = 0.59, GooF = 1.09, largest diff. peak and hole 0.196 and –0.159 e Å$^{-3}$, x = 0.01(5).

**4e:** colorless crystals, $C_{21}H_{24}BClF_5N$, $M$ = 431.67, crystal size 0.50 x 0.20 x 0.15 mm, orthorhombic, space group $P2_12_12_1$ (No.19): $a$ = 10.8901(7) Å, $b$ = 12.3059(7) Å, $c$ = 15.2966(10) Å, $V$ = 2049.9(2) Å$^3$, $Z$ = 4, $\rho$(calcd) = 1.399 Mg m$^{-3}$, $F$(000) = 896, $\mu$ = 0.238 mm$^{-1}$, 47144 reflections ($2\theta_{max}$ = 55°), 4689 unique [$R_{int}$ = 0.032], 268 parameters, R1 (for 4364 $I > 2\sigma(I)$) = 0.032, wR2 (*all data*) = 0.086, GooF = 1.06, largest diff. peak and hole 0.435 and –0.185e Å$^{-3}$, x = -0.02(5).

**5c:** colorless crystals, $C_{15}H_{23}BCl_3N$, $M$ = 334.50, crystal size 0.30 x 0.12 x 0.08 mm, monoclinic, space group Cc (No.9): $a$ = 7.867(1) Å, $b$ = 15.592(2) Å, $c$ = 14.279(2) Å, $\beta$ = 104.89(2)°$V$ = 1692.7(4) Å$^3$, $Z$ = 4, $\rho$(calcd) = 1.313 Mg m$^{-3}$, $F$(000) = 704, $\mu$ = 0.531 mm$^{-1}$, 18128 reflections ($2\theta_{max}$ = 55°), 3894 unique [$R_{int}$ = 0.031], 184 parameters, 3 restraints, R1 (for 3675 $I > 2\sigma(I)$) = 0.034, wR2 (*all data*) = 0.086, GooF = 1.04, largest diff. peak and hole 0.779 and –0.477 e Å$^{-3}$, x = -0.03(5).

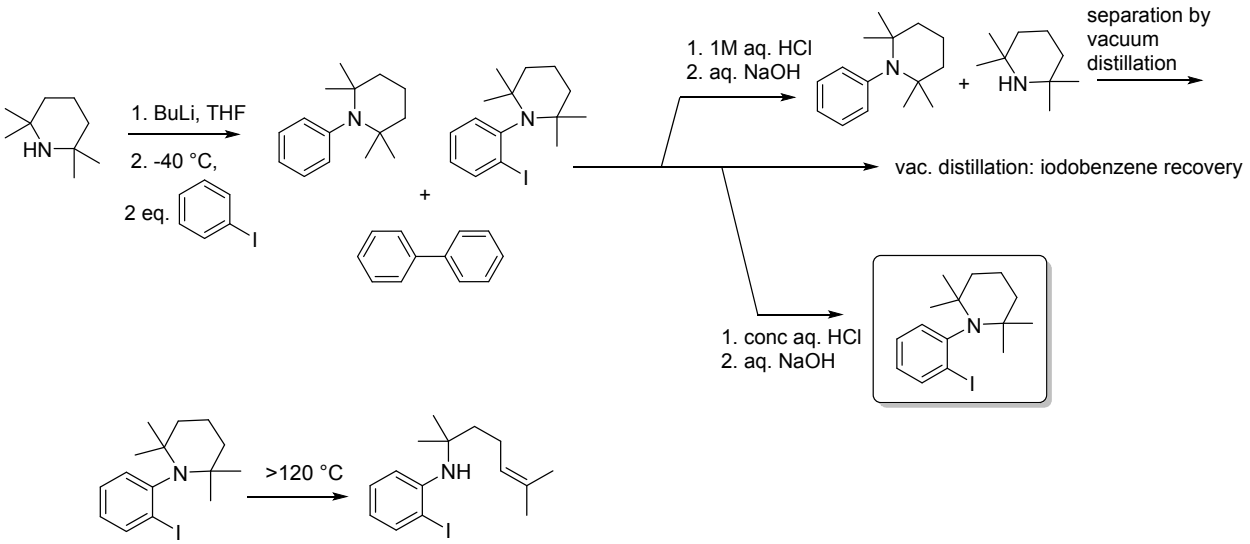
**5e:** colorless crystals, $C_{21}H_{23}BCl_2F_5N$, $M$ = 466.11, crystal size 0.21 x 0.18 x 0.15 mm, orthorhombic, space group Pbca (No.61): $a$ = 14.123(1) Å, $b$ = 15.558(1) Å, $c$ = 19.000(2) Å, $V$ = 4174.8(6) Å$^3$, $Z$ = 8, $\rho$(calcd) = 1.483 Mg m$^{-3}$, $F$(000) = 1920, $\mu$ = 0.363 mm$^{-1}$, 39511 reflections ($2\theta_{max}$ = 55°), 4789 unique [$R_{int}$ = 0.051], 274 parameters, 1 restraint, R1 (for 3875 $I > 2\sigma(I)$) = 0.041, wR2 (*all data*) = 0.087, GooF = 1.08, largest diff. peak and hole 0.406 and –0.274 e Å$^{-3}$.

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1511243 (**2c**), CCDC 912582 (**4e**), CCDC 912583 (**4c**), CCDC 912584 (**5e**) and CCDC 912585 (**5c**), respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

## *Preparations*

[2-(2,2,6,6-tetramethylpiperidin-1-yl)phenyl]lithium (**3**) was prepared as reported.[3]
Dichloro(pentafluorophenyl)borane was prepared by a modified procedure[4] starting from dimethyl[bis(pentafluorophenyl)]stannane and boron trichloride solution (1M solution in hexane) in a molar ratio 1:2.
Trimethylstannane was prepared as reported.[5]

## 1-(2-iodophenyl)-2,2,6,6-tetramethylpiperidine



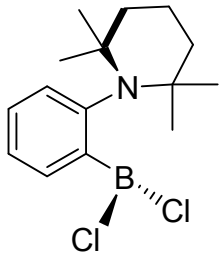

In a previous publication we reported on the preparation and isolation of the title compound.[3] Its separation from 1-phenyl-2,2,6,6-tetramethylpiperidine and biphenyl, the main by-products, was achieved by distillation in vacuum. This approach, however, requires relatively high vacuum during distillation due to a thermal instability of the title compound decomposing with opening a tetramethylpiperidine ring. In the modified protocol, we use acidic extraction that provides perfect separation of the components: First, unreacted 2,2,6,6-tetramethylpiperidine and 1-phenyl-2,2,6,6-tetramethylpiperidine are extracted with 1M aq. HCl, whereas much less basic 1-(2-iodophenyl)-2,2,6,6-tetramethylpiperidine with concentrated aq. HCl (12M). The low basicity of the title compound can be attributed to the extreme steric croudness around N atom that prevent its proper pyramidalization. During extractions, iodobenzene, biphenyl and other unpolar by-products remain in the organic phase. Giving the low yield of the reaction, the method enables easy recovery of the unreacted tetramethylpiperidine and iodobenzene.

TMP-Li was prepared as reported from 28.2 g of 2,2,6,6-tetramethylpiperidine in 300 ml of THF and 80 ml of 2.5 M butyllithium in hexane. To this solution kept at -50 - -40 °C, 80 g of iodobenzene in 100 ml of THF was added via syringe. The reaction was kept for 4 h at -40 °C and left over night immersed in the thermally isolated cooling bath in order to slowly warm up to room temperature. 50 ml of 1M aq. HCl was added to the reaction and the organic solvents were rotavapored. $CH_2Cl_2$ was added to the residue and the aqueous phase separated. The organic layer was extracted with two additional 50 ml portions of 1M aq. HCl. Then the organic layer was extracted with four 10 ml portions of conc. aq. HCl. The acidic extracts (conc. HCl) were combined, cautiously basified with aq. NaOH, and extracted with hexane. Hexane extracts were combined, dried over $Na_2SO_4$, and evaporated giving 29 g of pure title compound (42%).

The residual organic phase can be distilled recovering some iodobenzene.

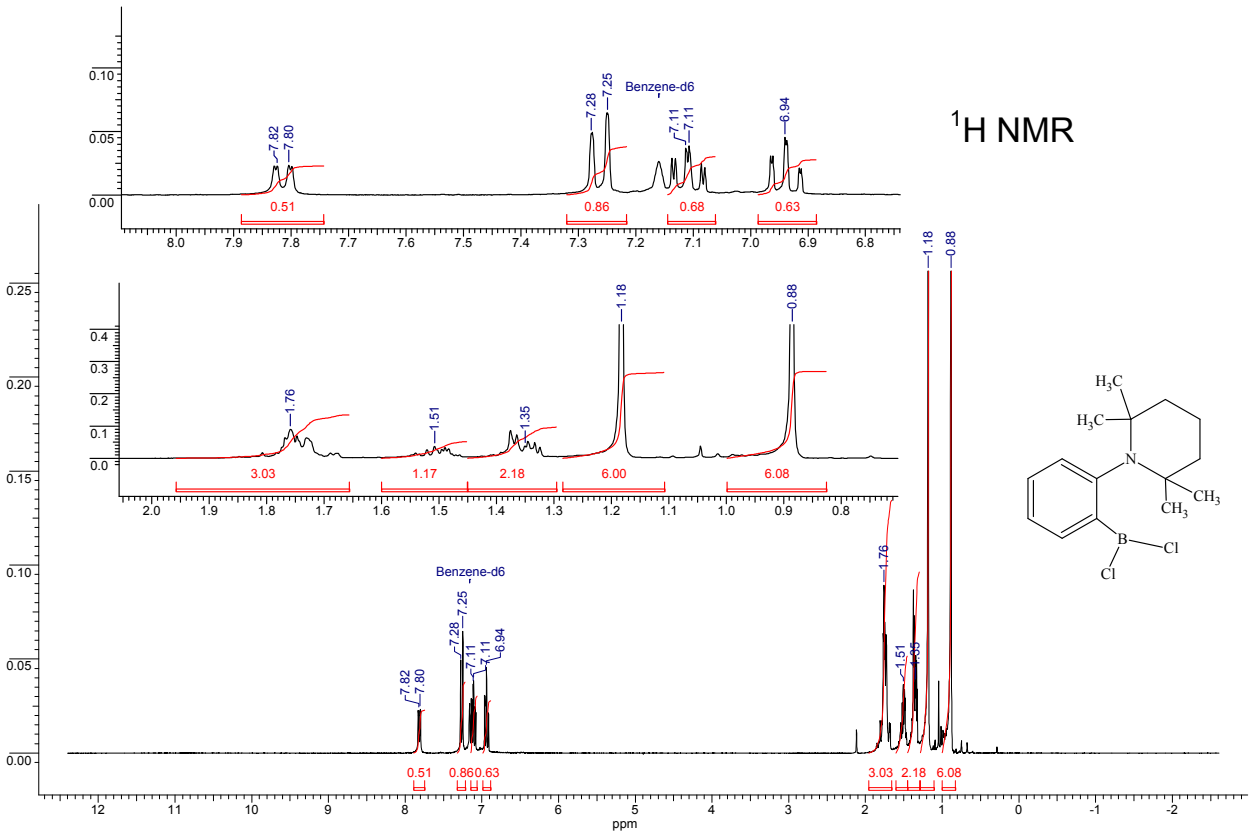
The 1M HCl extracts can be combined, basified with aq. NaOH, extracted with hexane, followed by evaporation and vacuum distillation of the hexane exctracts giving some tetramethylpiperidine and 1-phenyl-2,2,6,6-tetramethylpiperidine.

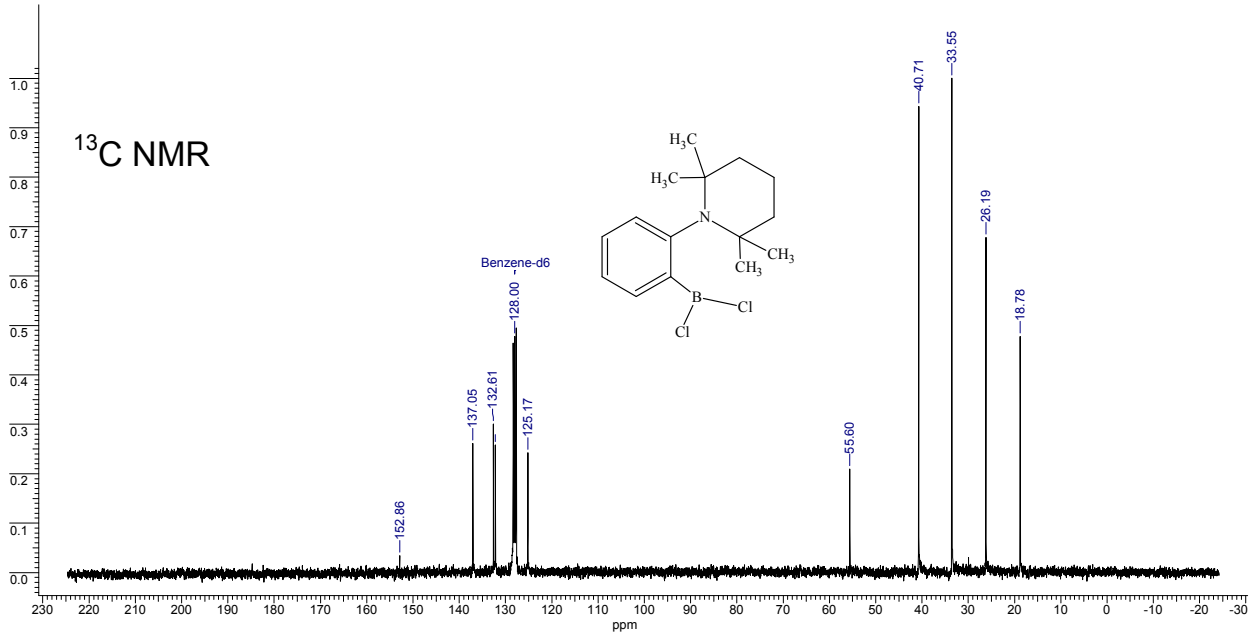
## 1-[2-(Dichloroboryl)phenyl]-2,2,6,6-tetramethylpiperidine (1c)

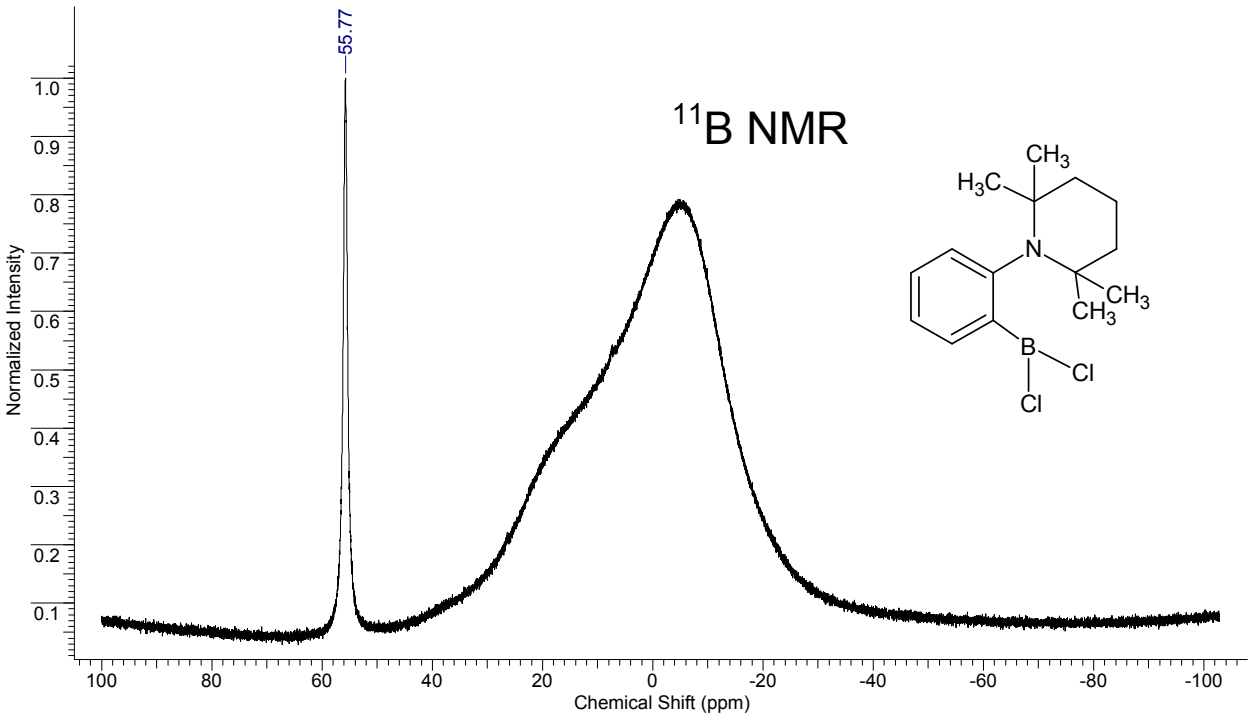


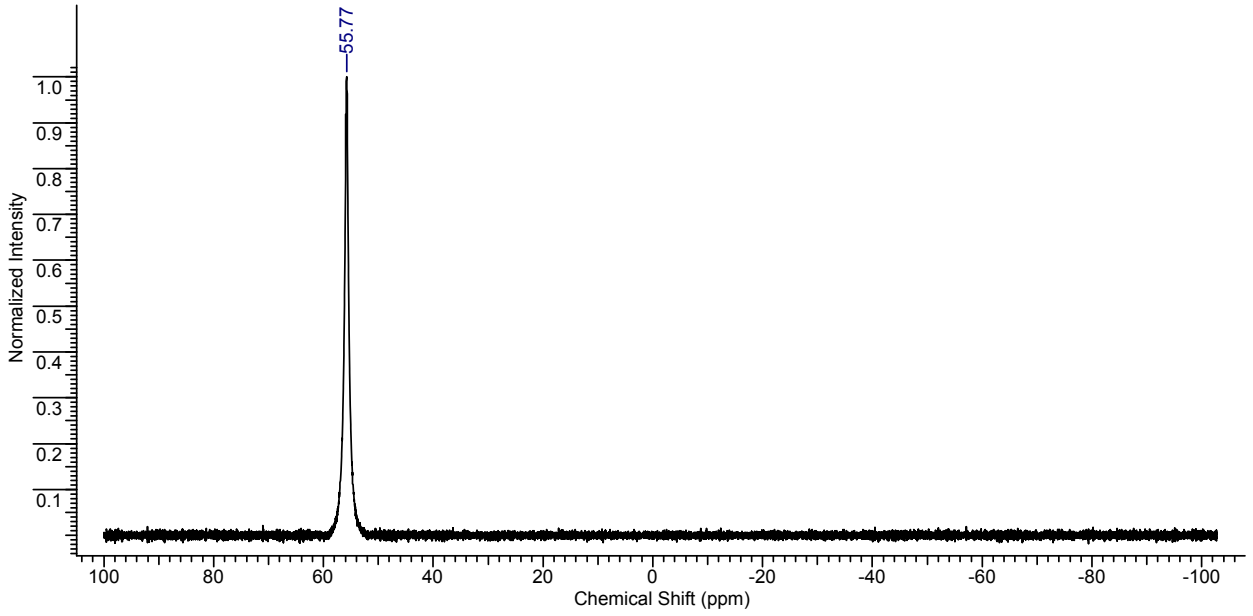

A solution of 450 mg of [2-(2,2,6,6-tetramethylpiperidin-1-yl)phenyl]lithium (2 mmol) in 6 ml of toluene was prepared in a 25 ml Schlenk tube and cooled to -90 °C. In another 25 ml Schlenk tube solution of $BCl_3$ (4 mmol, 4 ml of 1M solution in hexane) in 4 ml of toluene was prepared and cooled to -90 °C. The solution of lithium compound was transferred in one portion via canula to the Schlenk tube with a vigorously stirring solution of $BCl_3$. The empty Schlenk tube which was initially containing the lithium compound have been rinsed with additional 5 ml of toluene and the washing liquid was transferred to the reaction Schlenk tube as well. The immersed in a cooling bath reaction mixture was allowed to warm to room temperature naturally within 1 h and volatiles were stripped in vacuum. The residue was taken in 5 ml of hexane, filtered and washed additionally with 5 ml of hexane. Combined hexane extracts were evaporated to give 570 mg (95.6 %) of the target compound as a yellow oil, which slowly solidifies on standing into semi-solid crystalline material.

$^{1}$H (300 MHz, $C_6D_6$, $\delta$, ppm): 0.88 (s, 6H), 1.18 (s, 6H), 1.35 (m, 2H), 1.51 (m, 1H), 1.76 (m, 3H), 6.94 (td, J=7.4 Hz, J=1 Hz, 1H), 7.11 (td, J=7.7 Hz, J=1.9 Hz, 1H), 7.27 (d, J=8 Hz, 1H), 7.81 (dd, J=7.7 Hz, J=1.7 Hz, 1H).
$^{13}$C (125 MHz, $C_6D_6$, $\delta$, ppm, partial): 18.78, 26.19, 33.55, 40.71, 55.60, 125.17, 132.19, 132.61, 137.05, 152.86.
$^{11}$B (160 MHz, $C_6D_6$, $\delta$, ppm): 55.8 (s, $\nu_{1/2}$=140 Hz).
Elem. found: C, 60.55; H, 7.60; N, 4.67; calc. C, 60.44; H, 7.44; N, 4.70.

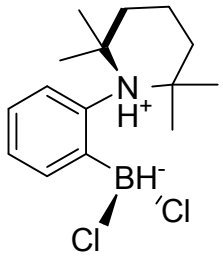

$^{1}$H NMR
Benzene-d6
7.82
7.80
7.28
7.25
7.11
7.11
6.94
1.76
1.51
1.35
1.18
0.88
0.51
0.86
0.68
0.63
3.03
1.17
2.18
6.00
6.08
ppm


$^{13}$C NMR
Benzene-d6
152.86
137.05
132.61
128.00
125.17
55.60
40.71
33.55
26.19
18.78
ppm


$^{11}$B NMR
55.77
Normalized Intensity
Chemical Shift (ppm)
CH3
H3C
N
CH3
CH3
B
Cl
Cl

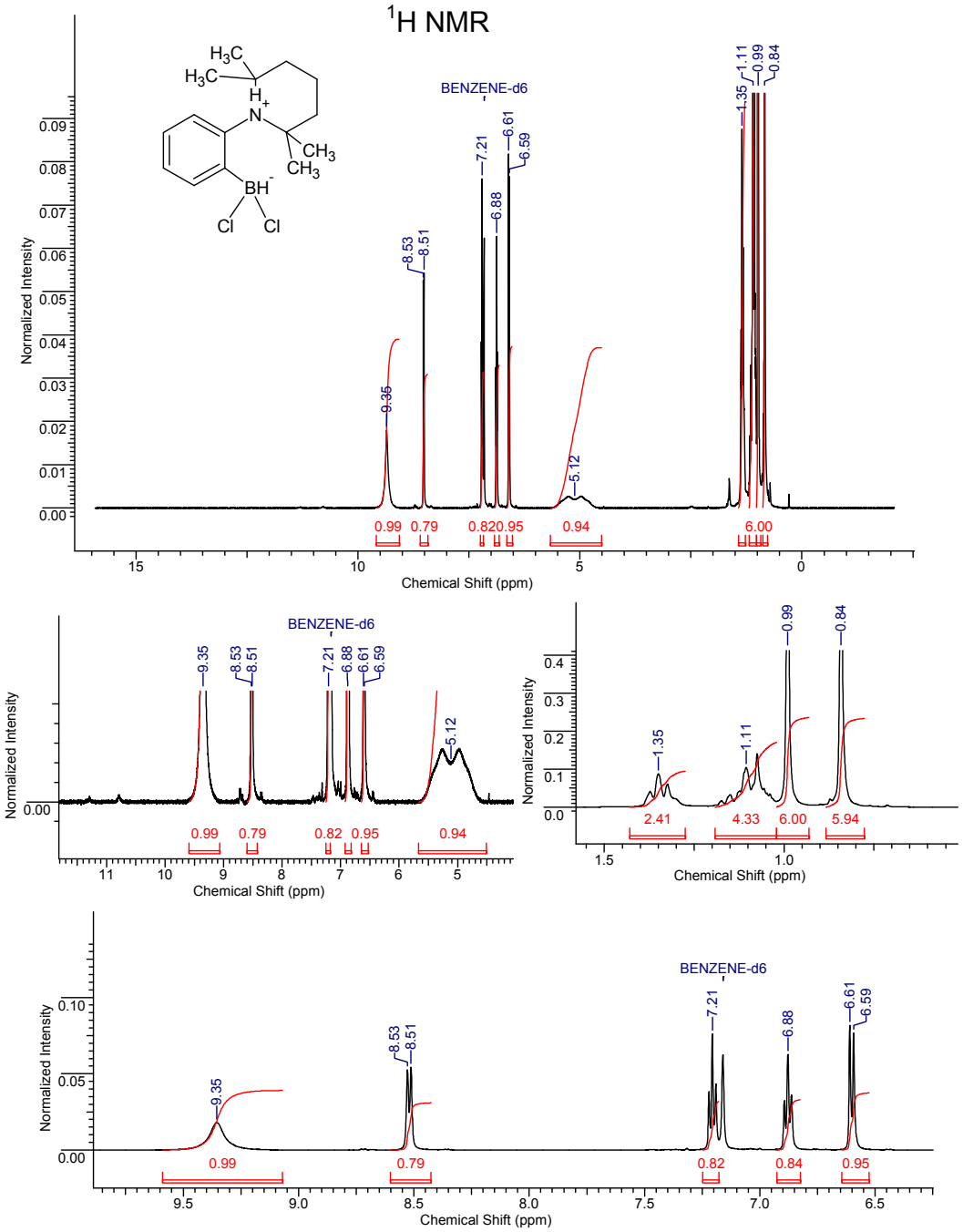

55.77
Normalized Intensity
Chemical Shift (ppm)

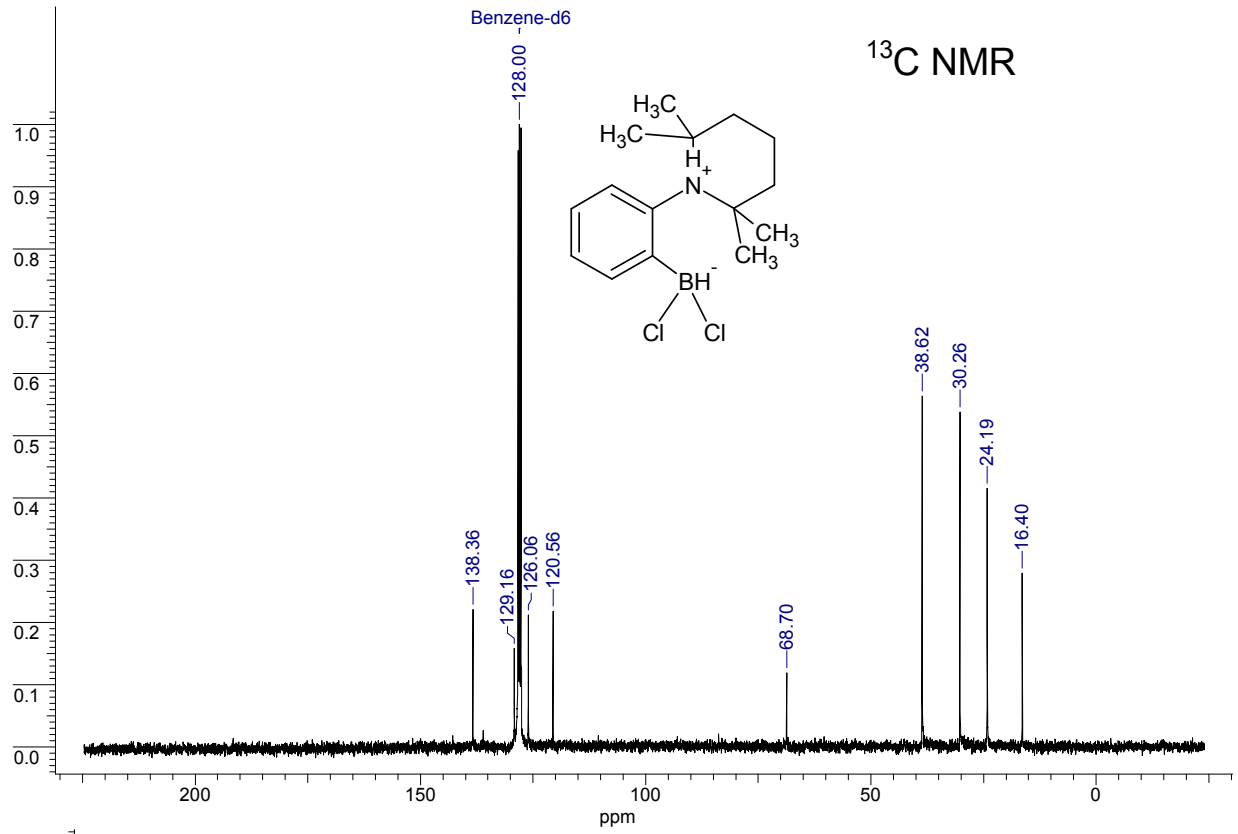
**Dichloro(hydrido)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (4c)**

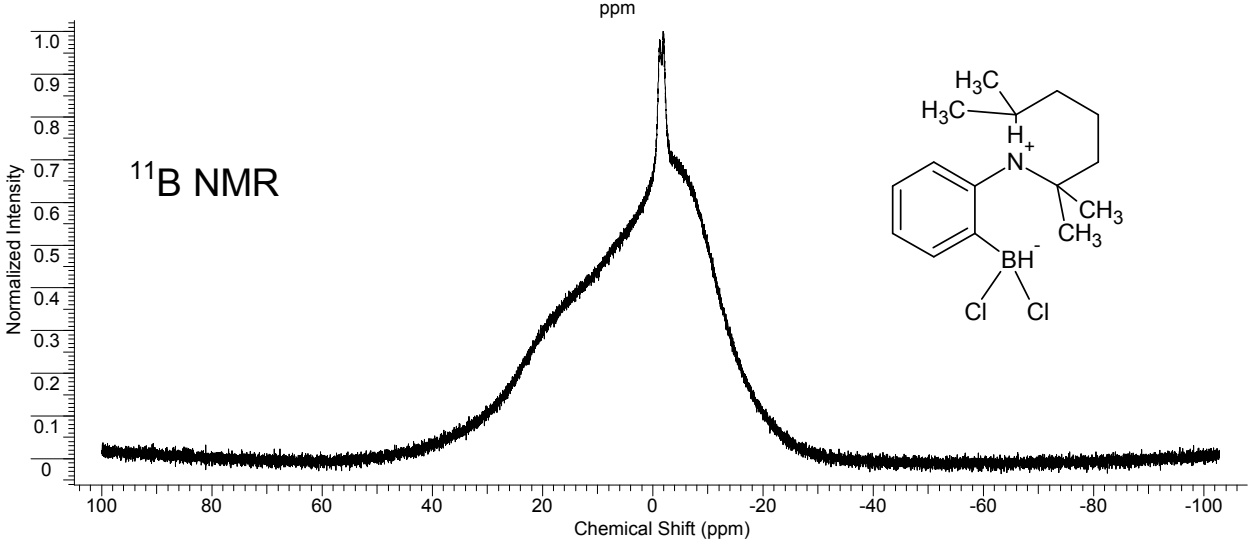


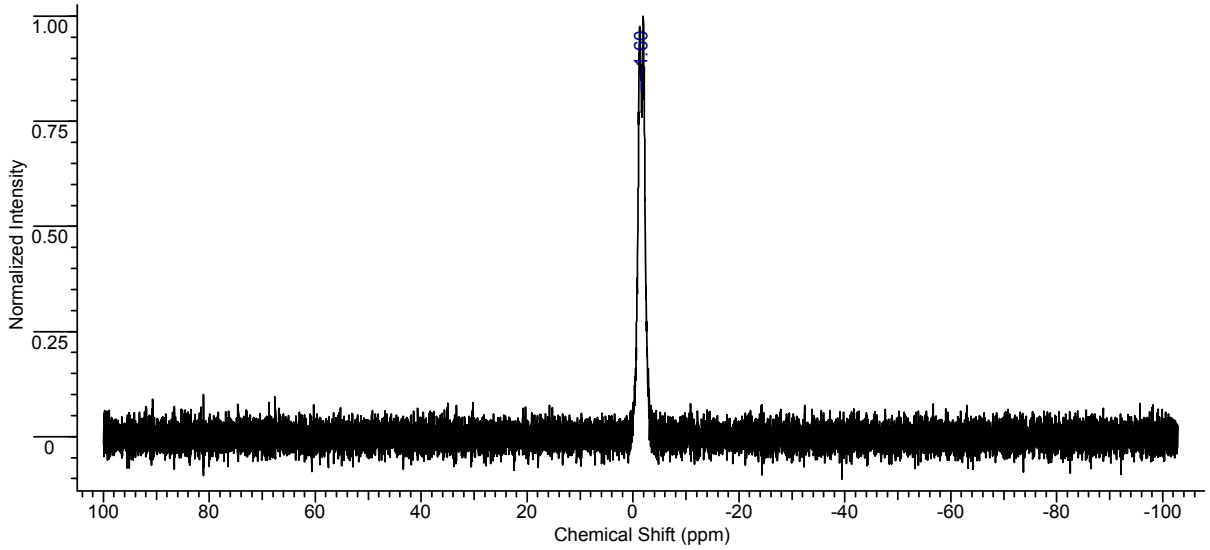

A 25 ml Schlenk tube containing a solution of 1-[2-(dichloroboryl)phenyl]-2,2,6,6-tetramethylpiperidine (300 mg, 1mmol) in 2 ml of toluene or $C_6D_6$ was filled with 2 bar of hydrogen by two freeze-pump-thaw cycles and stirred vigorously for 1 h at room temperature. Yellow colour disappeared in 3-10 min and the target compound precipitated as a white crystalline powder. The solvent was stripped in vacuum to yield 300 mg of a white powder (>99%).
Crystals suitable for X-ray diffraction were grown by slow evaporation of the $CDCl_3$-$C_6D_6$ solution.

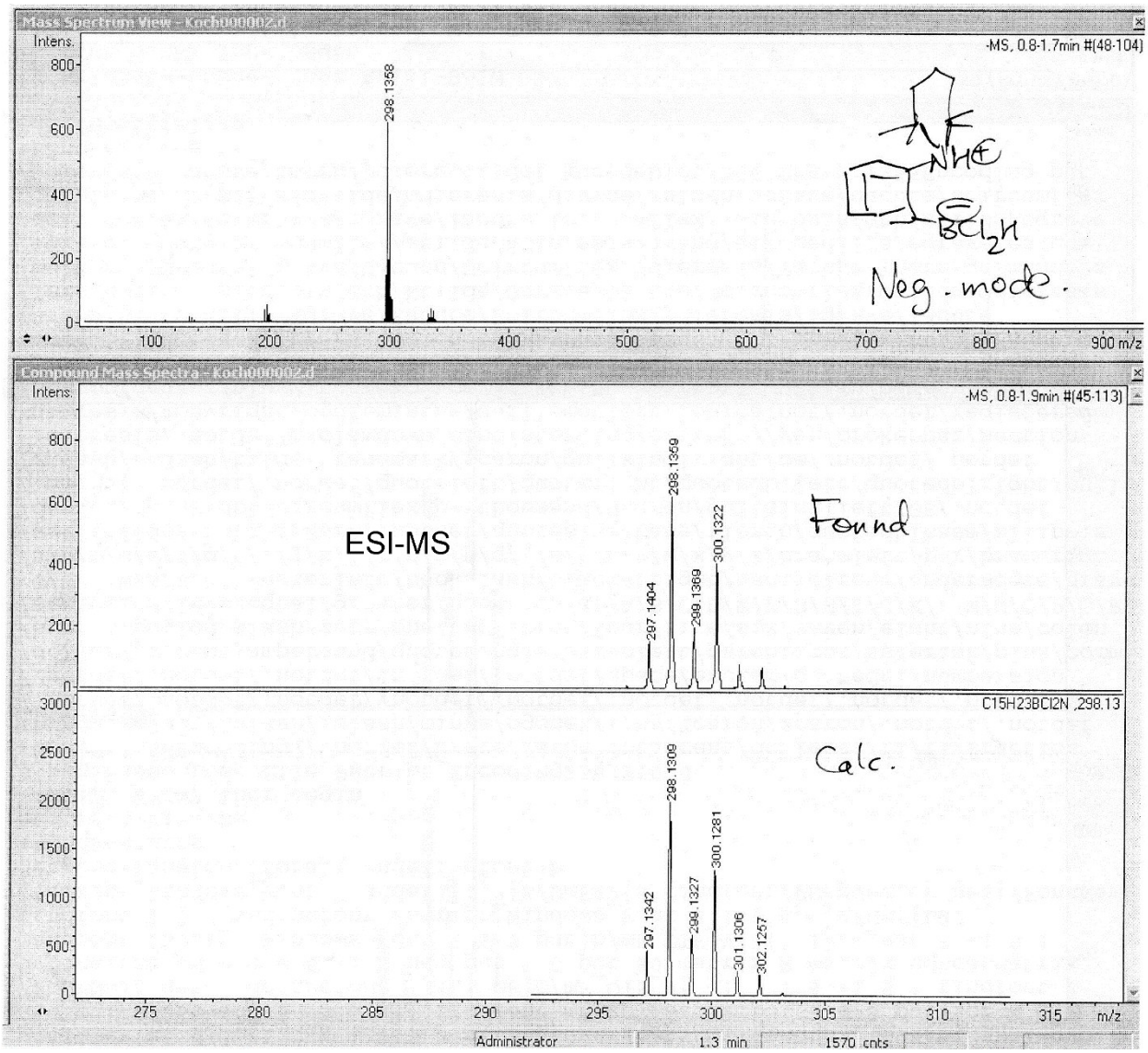
$^1$H (500 MHz, $C_6D_6$, δ, ppm): 0.84 (s, 6H), 0.99 (s, 6H), 1.11 (m, 4H), 1.35 (m, 2H), 5.12 (br. pseudo-d, J=144 Hz, 1H, B*H*), 6.60 (t, J=8.3 Hz, 1H), 6.88 (t, J=7.6 Hz, 1H), 7.21 (t, J=7.3 Hz, 1H), 8.52 (t, J=7.6 Hz, 1H), 9.35 (br. s, 1H, N*H*).
$^{13}$C (75 MHz, $C_6D_6$, 70 °C, δ, ppm, partial): 16.40, 24.19, 30.26, 38.62, 68.70, 120.56, 126.06, 129.16, 136.08, 138.36.
$^{11}$B (160 MHz, $C_6D_6$, δ, ppm): -1.6 (br. d, J = 100 Hz).
ESI-HRMS$^-$: $[M-H]^-$, calc.:298.1306, found: 298.1359.
Elem. found: C, 59.16; H, 8.11; N, 4.43; calc. C, 60.04; H, 8.06; N, 4.67.

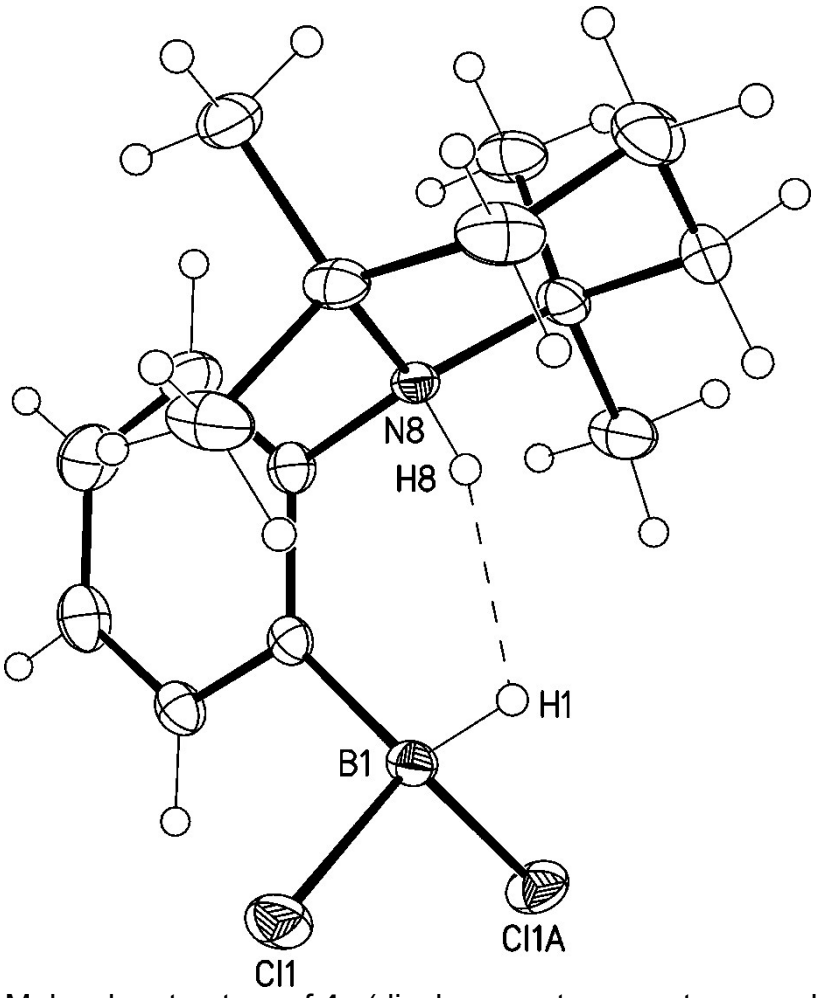

$^1$H NMR
BENZENE-d6
Normalized Intensity
Chemical Shift (ppm)
0.99 0.79 0.82 0.95 0.94 6.00
2.41 4.33 6.00 5.94


Benzene-d6
128.00
138.36
129.16
126.06
120.56
68.70
38.62
30.26
24.19
16.40
$^{13}$C NMR
ppm


$^{11}$B NMR
Normalized Intensity
Chemical Shift (ppm)

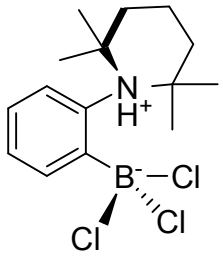

Normalized Intensity
Chemical Shift (ppm)


Mass Spectrum View - Koch000002.d
Intens.
-MS, 0.8-1.7min #(48-104)
298.1358
Neg. mode.
Compound Mass Spectra - Koch000002.d
-MS, 0.8-1.9min #(45-113)
ESI-MS
Found
298.1359
300.1322
297.1404
299.1369
C15H23BCl2N ,298.13
Calc.
298.1309
300.1281
297.1342
299.1327
301.1306
302.1257
m/z
Administrator
1.3 min
1570 cnts



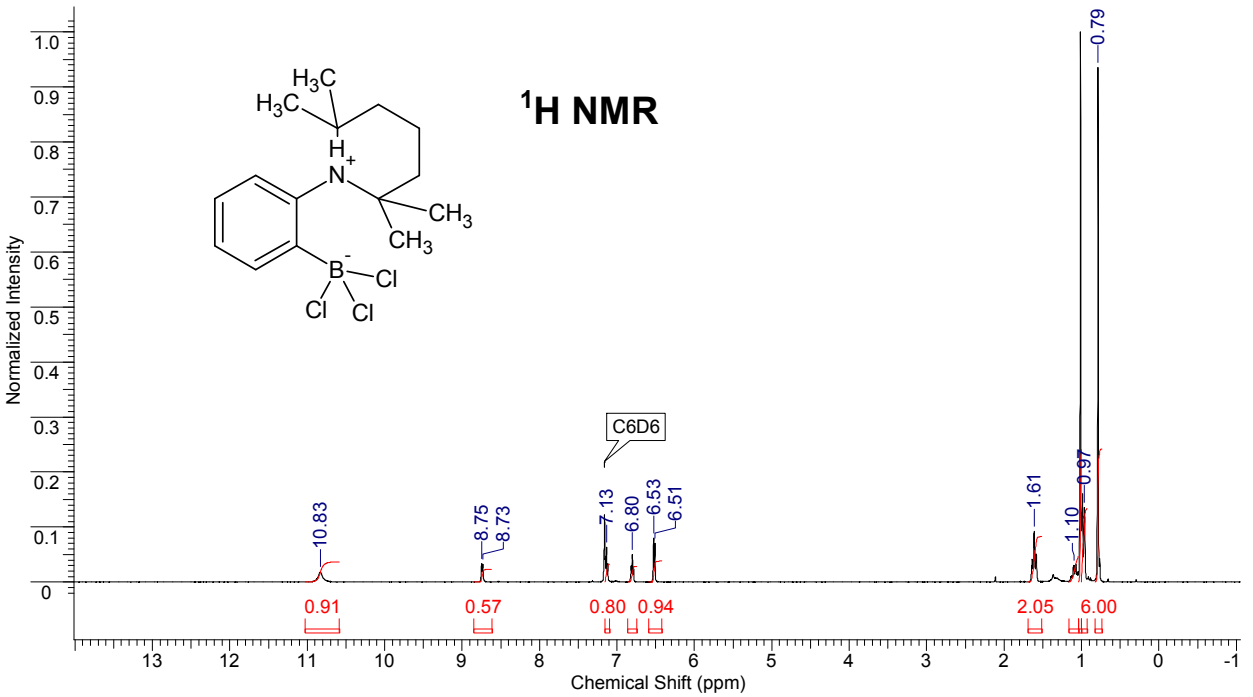
Molecular structure of **4c** (displacement parameters are drawn at 50% probability level).

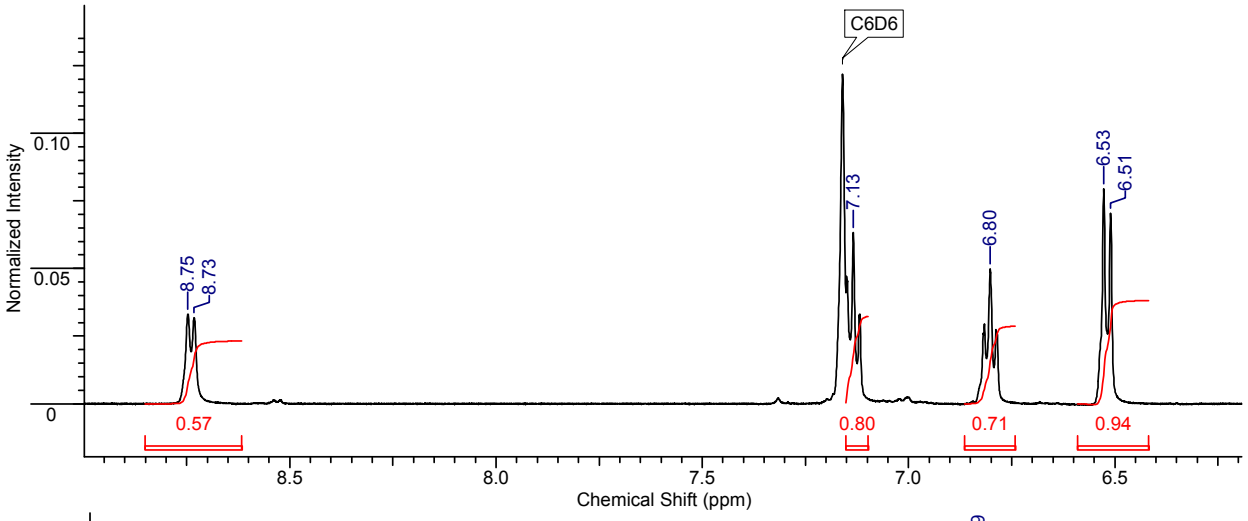
**Trichloro[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (5c)**

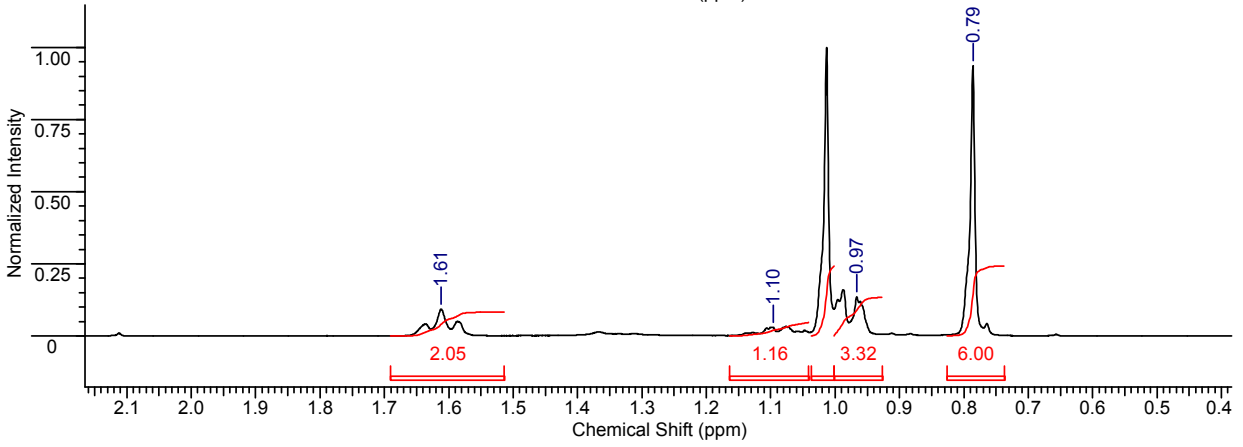


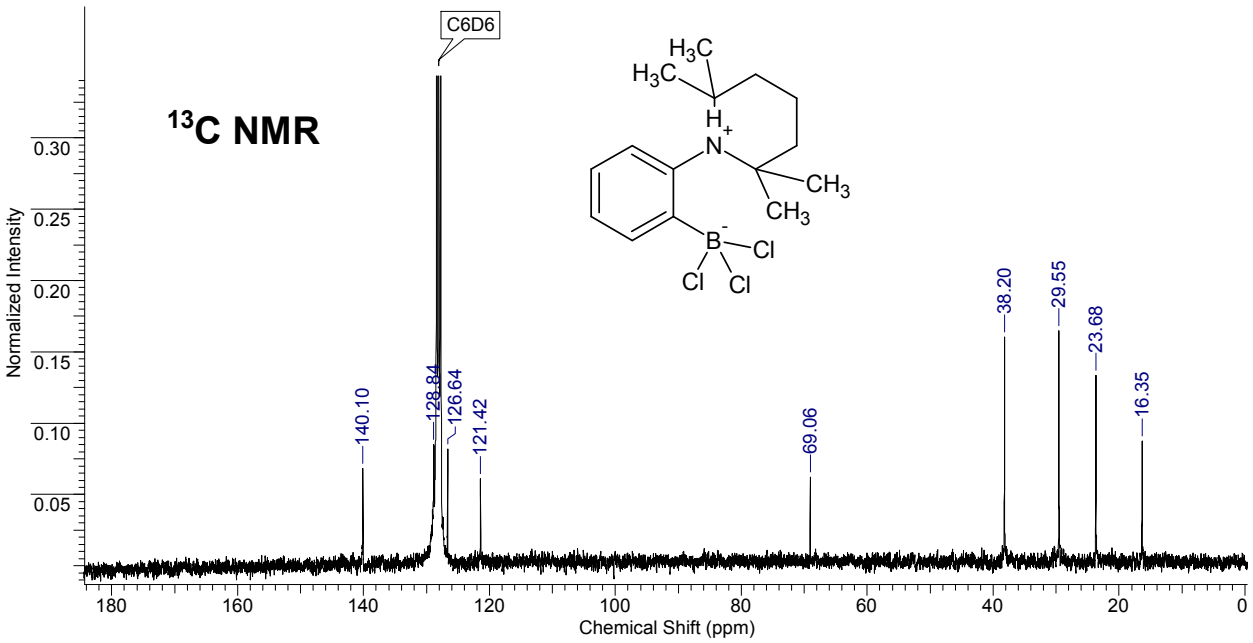
100 mg of dichloro(hydrido)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (0.33 mmol) and 2 ml of toluene were stirred in a 25 ml Schlenk tube for 24 h at 120 °C. Volatiles were stripped and the residue was recrystallized from a mixture of 2 ml of toluene and 0.5 ml of hexane. The precipitate was collected, 54 mg (48%). Crystals suitable for X-ray diffraction were collected from the crop.

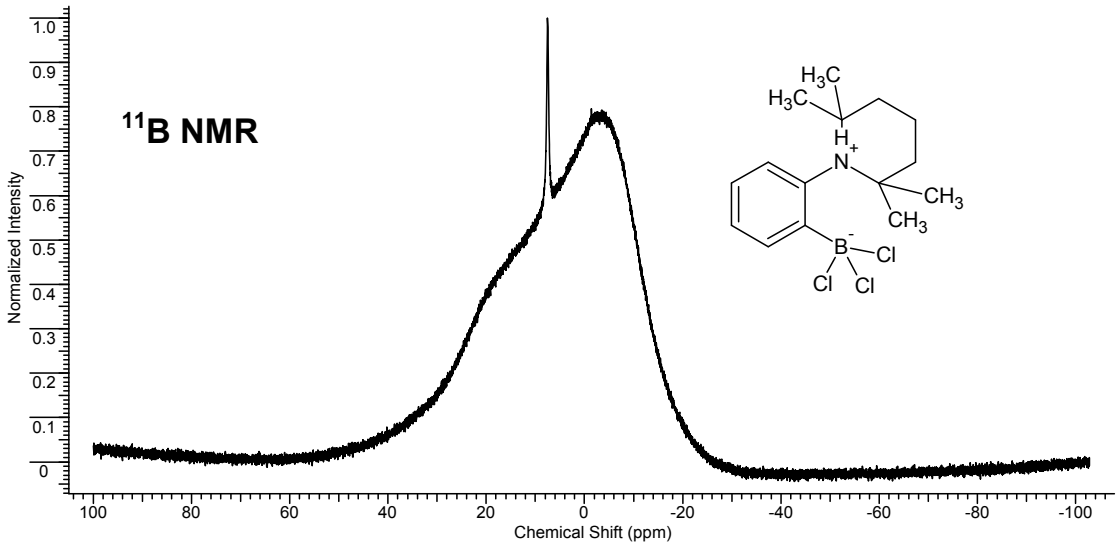
$^{1}$H (500 MHz, $C_6D_6$, δ, ppm): 0.79 (s, 6H), 0.98 (m, 3H), 1.01 (s, 6H), 1.09 (m, 1H), 1.61 (m, 2H), 6.52 (d, J=8.2 Hz, 1H), 6.80 (t, J=7.5 Hz, 1H), 7.13 (t, J=7.5 Hz, 1H), 8.74 (d, J=7.4 Hz, 1H), 10.83 (br. s, 1H, N***H***).
$^{13}$C (75 MHz, $C_6D_6$, partial, δ, ppm): 16.35, 23.68, 29.55, 38.20, 69.06, 121.42, 126.64, 128.84, 140.10.
$^{11}$B (160 MHz, $C_6D_6$, δ, ppm): 7.51 (s).
Elem.: found: C, 53.90; H, 7.44; N, 4.10; calc. C, 53.86; H, 6.93; N, 4.19.

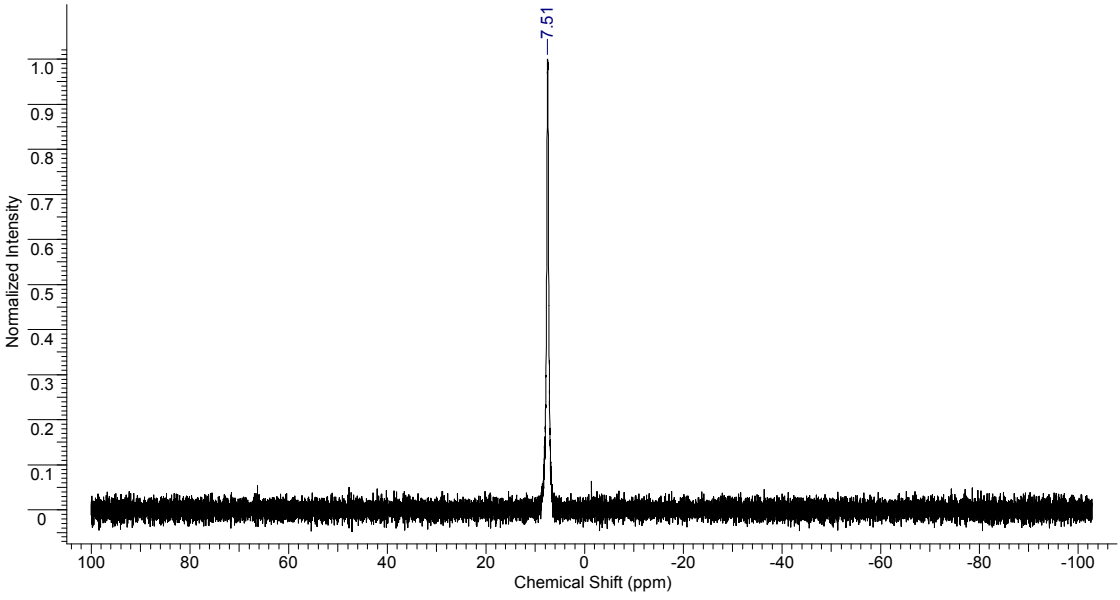

$^1$H NMR
Normalized Intensity
Chemical Shift (ppm)
C6D6
10.83
8.75
8.73
7.13
6.80
6.53
6.51
1.61
1.10
0.97
0.79
0.91
0.57
0.80
0.94
2.05
6.00

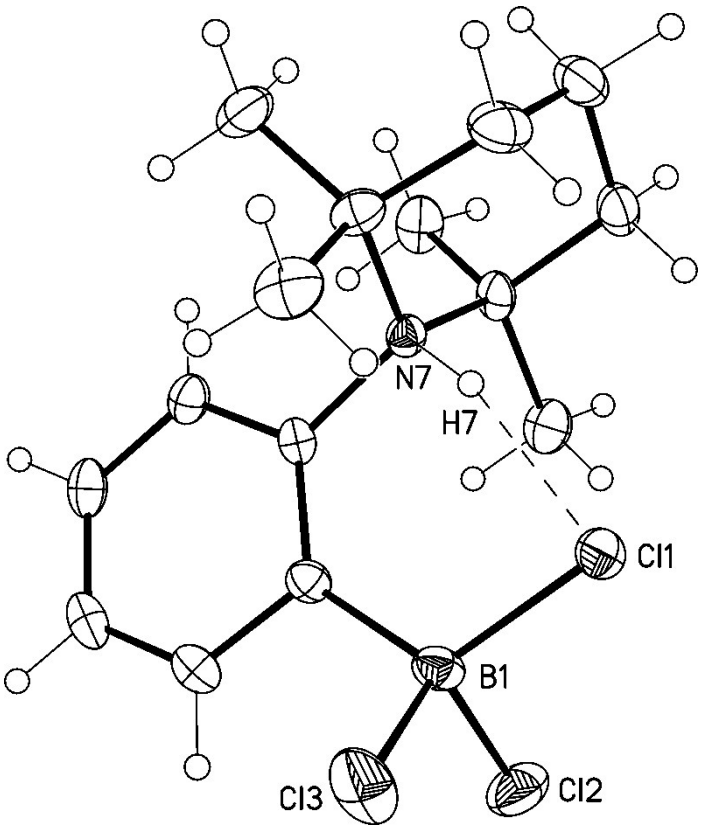

Normalized Intensity
Chemical Shift (ppm)
C6D6
8.75
8.73
7.13
6.80
6.53
6.51
0.57
0.80
0.71
0.94


Normalized Intensity
Chemical Shift (ppm)
1.61
1.10
0.97
0.79
2.05
1.16
3.32
6.00


$^{13}$C NMR
C6D6
Normalized Intensity
Chemical Shift (ppm)
140.10
128.84
126.64
121.42
69.06
38.20
29.55
23.68
16.35

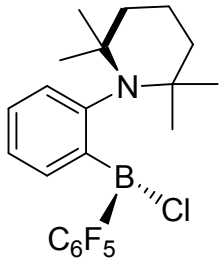

$^{11}$B NMR
Normalized Intensity
Chemical Shift (ppm)


7.51
Normalized Intensity
Chemical Shift (ppm)



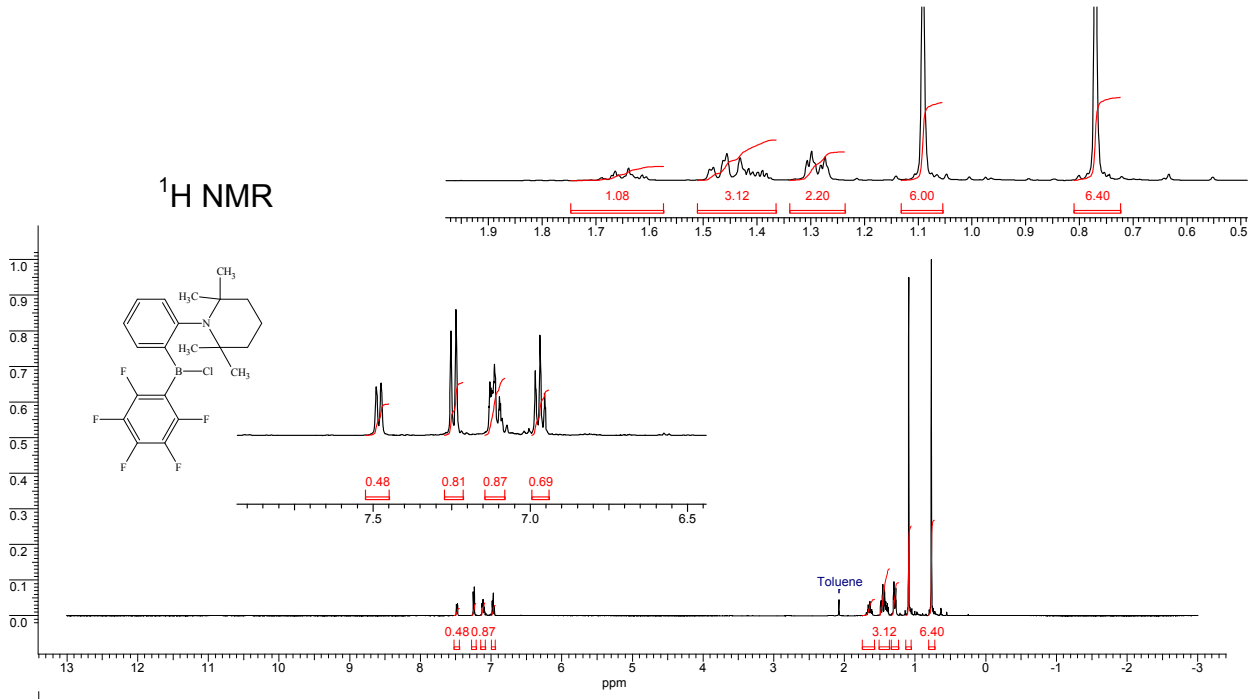
Molecular structure of **5c** (displacement parameters are drawn at 50% probability level).

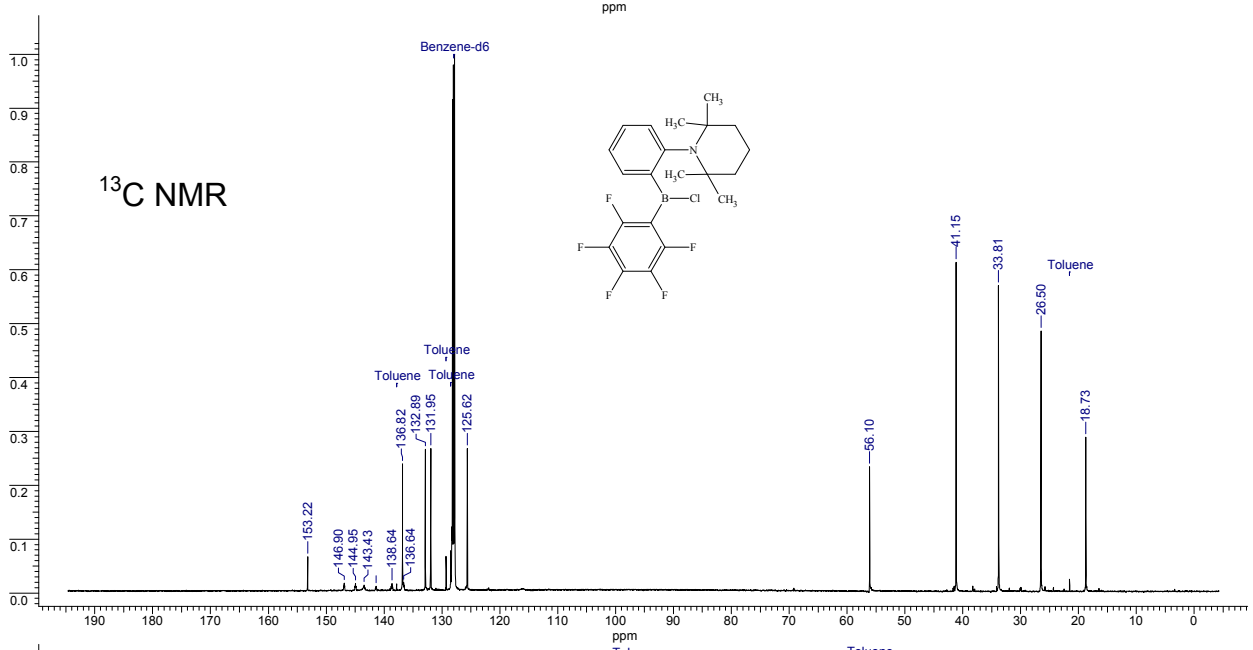
**1-{2-[Chloro(pentafluorophenyl)boryl]phenyl}-2,2,6,6-tetramethylpiperidine (1e)**

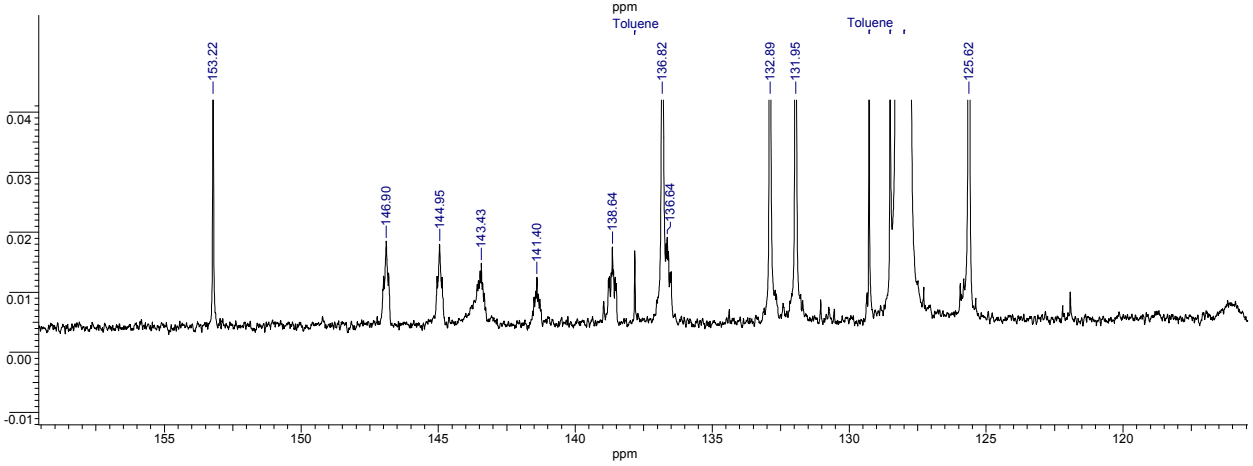


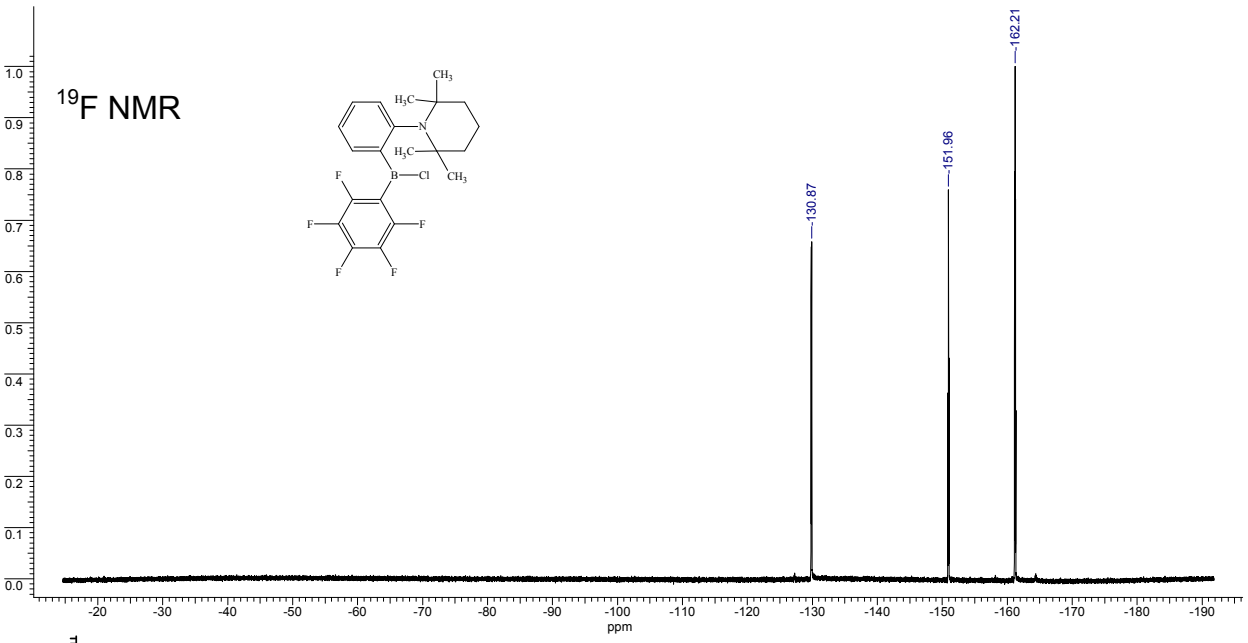

A solution of 450 mg of [2-(2,2,6,6-tetramethylpiperidin-1-yl)phenyl]lithium (2 mmol) in 5 ml of toluene was prepared in a 25 ml Schlenk tube and cooled to -90 °C. In another 25 ml Schlenk tube a solution of 500 mg of dichloro(pentafluorophenyl)borane (2 mmol) in 4 ml of toluene was prepared and cooled to -90 °C. The solution of dichloro(pentafluorophenyl)borane was transferred in one portion via canula to the Schlenk tube with the vigorously stirring solution of the lithium compound. The empty Schlenk tube which had initially contained dichloro(pentafluorophenyl)borane was rinsed with additional 5 ml of toluene and the washing liquid was transferred to the reaction Schlenk tube. The immersed in a cooling bath reaction mixture was allowed to warm to room temperature naturally and stirred over night. The precipitate was filtered, washed with 3 ml of toluene and discarded. The remaining solution was evaporated to dryness, redissolved in 5 ml of hexane and filtered again. The solid on filter was washed additionally with 5 ml of hexane. Combined hexane extracts were evaporated to give 823 mg (96 %) of the target compound as reddish oil.

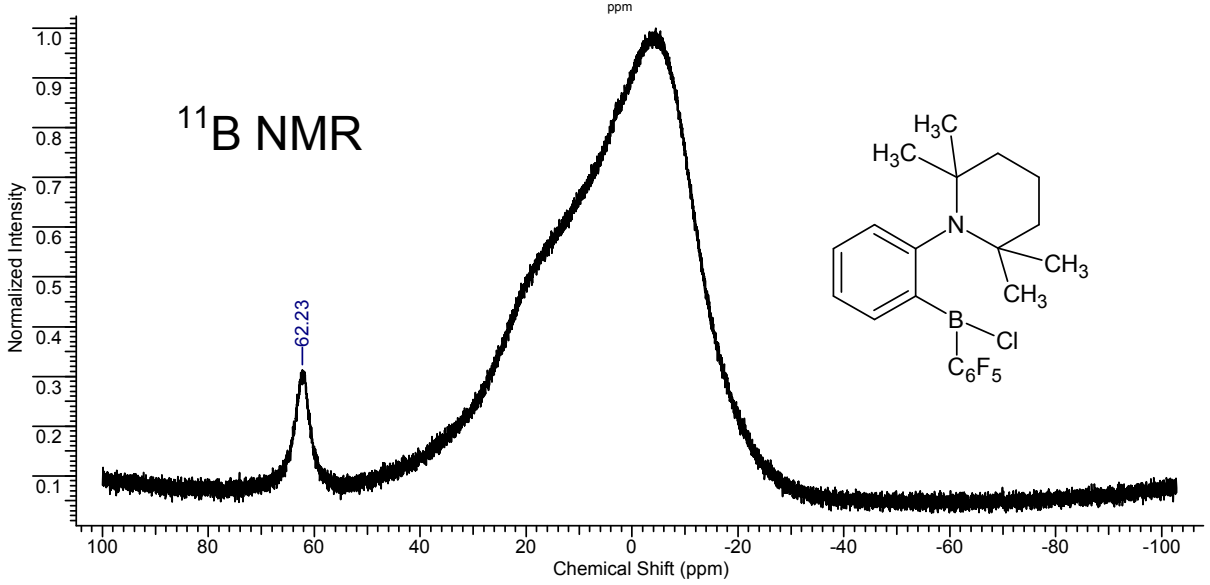
$^{1}$H NMR (500 MHz, $C_6D_6$, δ, ppm): 0.77(s, 6H), 1.09 (s, 6 H), 1.29 (m, 2 H), 1.44 (m, 3 H), 1.65 (m, 1 H), 6.97 (t, *J*=7.32 Hz, 1H), 7.12 (m, 1 H), 7.25 (d, *J*=8.30 Hz, 1 H), 7.48 (d, *J*=7.81 Hz, 1H).
$^{13}$C NMR (125 MHz, $C_6D_6$, δ, ppm, partial): 18.73, 26.50, 33.81, 41.15, 56.10, 125.62, 131.95, 132.89, 136.82, 137.64 (dm, J=250 Hz), 142.40 (dm, J=250 Hz), 145.95 (dm, J=240 Hz), 153.22.
$^{19}$F NMR (282 MHz, $C_6D_6$, δ, ppm): -162.2 (m), -151.96 (t, J= 21 Hz), -130.85 (m).
$^{11}$B NMR(160 MHz, $C_6D_6$, δ, ppm): 62.2 (br.s, $\nu_{1/2}$~480 Hz).
Elem. found: C, 59.31; H, 5.44; N, 3.22 ; calc. C, 58.70; H, 5.16; N, 3.26.

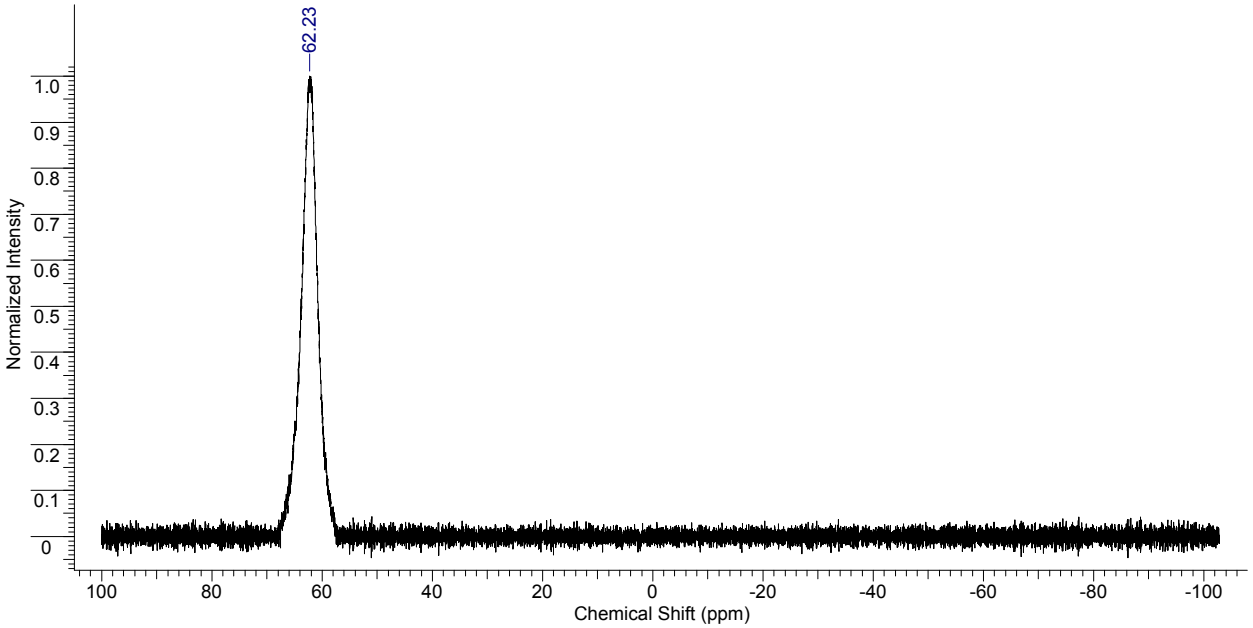

$^{1}$H NMR
1.08
3.12
2.20
6.00
6.40
0.48
0.81
0.87
0.69
Toluene
0.48
0.87
3.12
6.40
ppm


$^{13}$C NMR
Benzene-d6
Toluene
Toluene
Toluene
Toluene
153.22
146.90
144.95
143.43
138.64
136.64
136.82
132.89
131.95
125.62
56.10
41.15
33.81
26.50
18.73
ppm

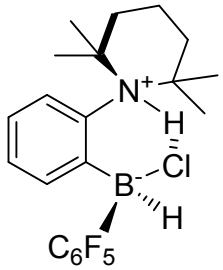

Toluene
Toluene
153.22
146.90
144.95
143.43
141.40
138.64
136.82
136.64
132.89
131.95
125.62
ppm


$^{19}$F NMR
-130.87
-151.96
-162.21
ppm


$^{11}$B NMR
62.23
Normalized Intensity
Chemical Shift (ppm)

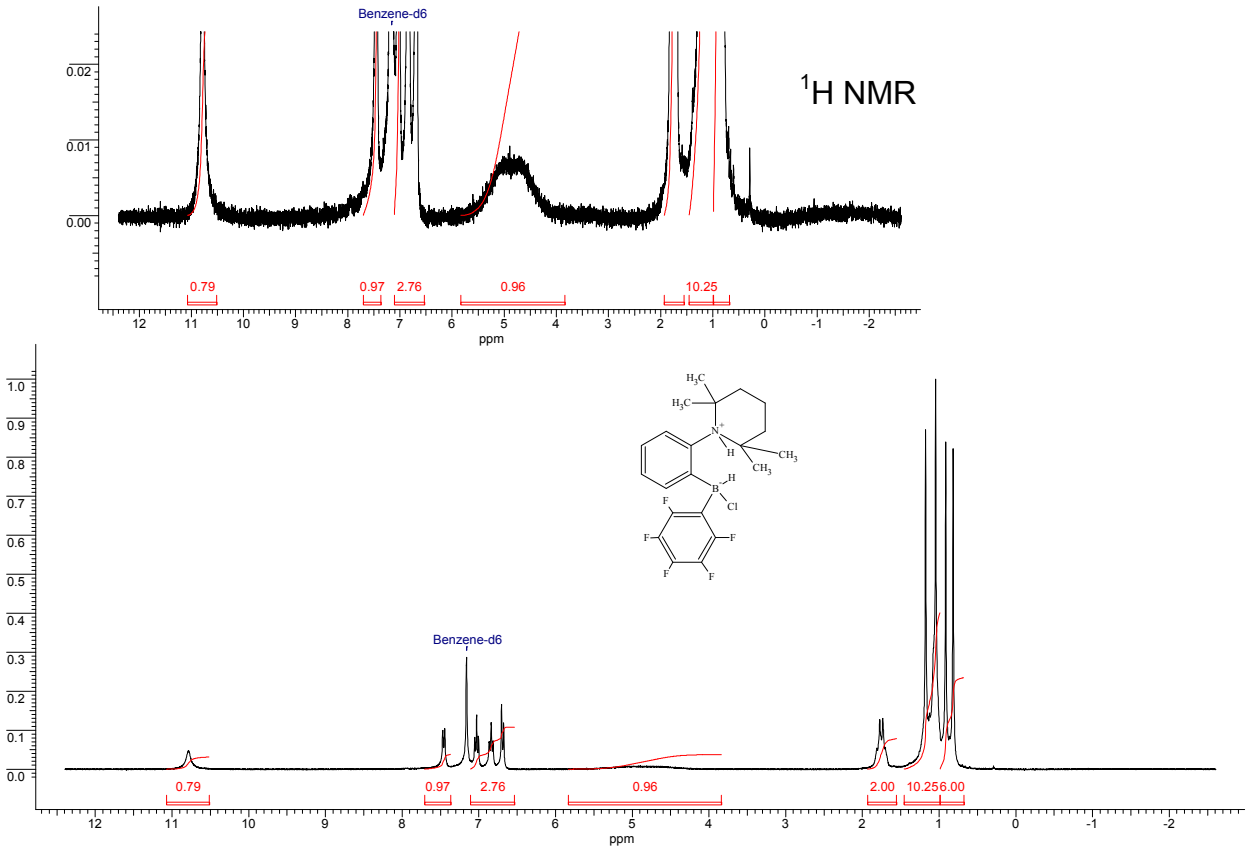

62.23
Normalized Intensity
Chemical Shift (ppm)

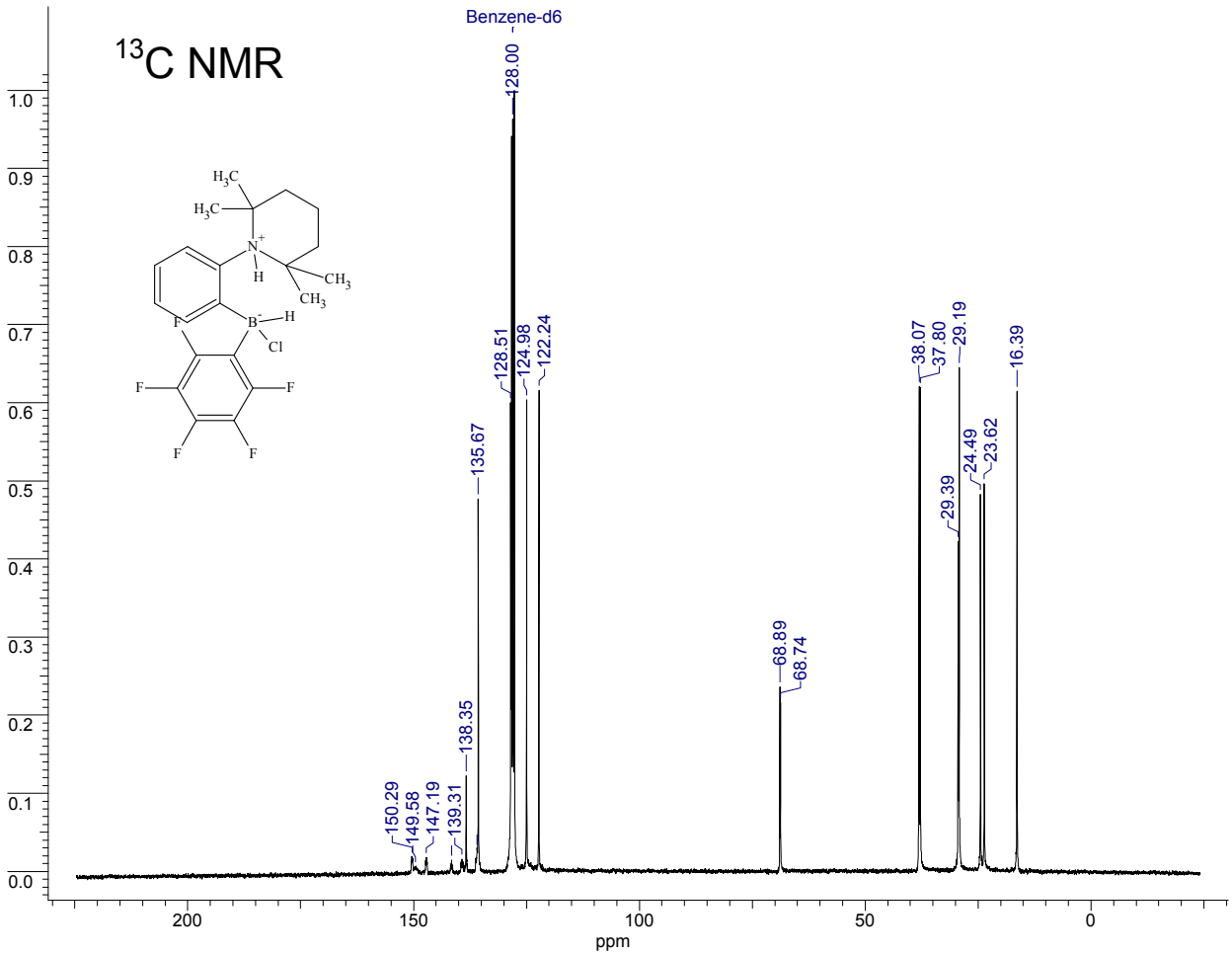
**Chloro(hydrido)(pentafluorophenyl)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (4e)**

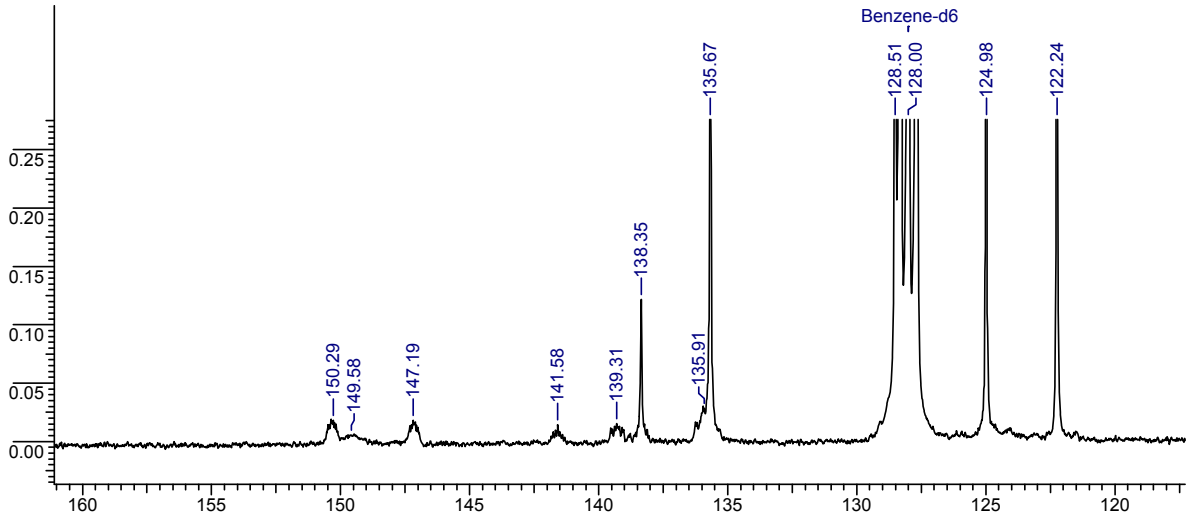


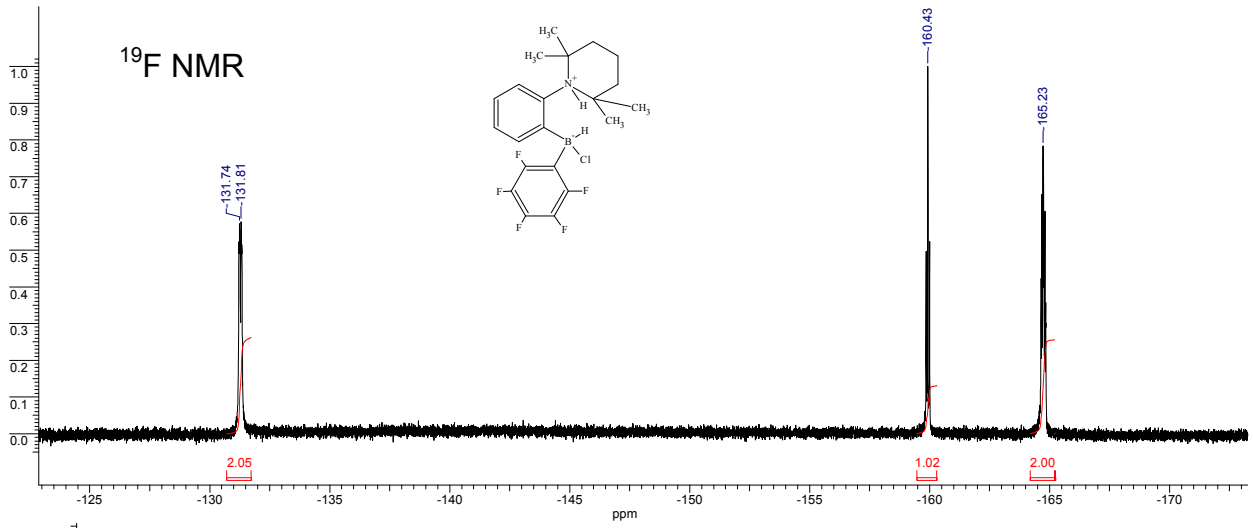
A 25 ml Schlenk tube containing a solution of 1-{2-[chloro(pentafluorophenyl)boryl]phenyl}-2,2,6,6-tetramethylpiperidine (300 mg, 0.7 mmol) in 5 ml of hexane was filled with 2 bar of hydrogen by two freeze-pump-thaw cycles and stirred vigorously at room temperature. The white precipitate was formed within minutes and the colour disappeared. The reaction was stirred additionally over night. The precipitate was filtered, washed with 5 ml of hexane, dried in vacuum to yield 300 mg of a white powder (>99%).
Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a $C_6D_6$ solution of the title compound, followed by slow evaporation of solvent.

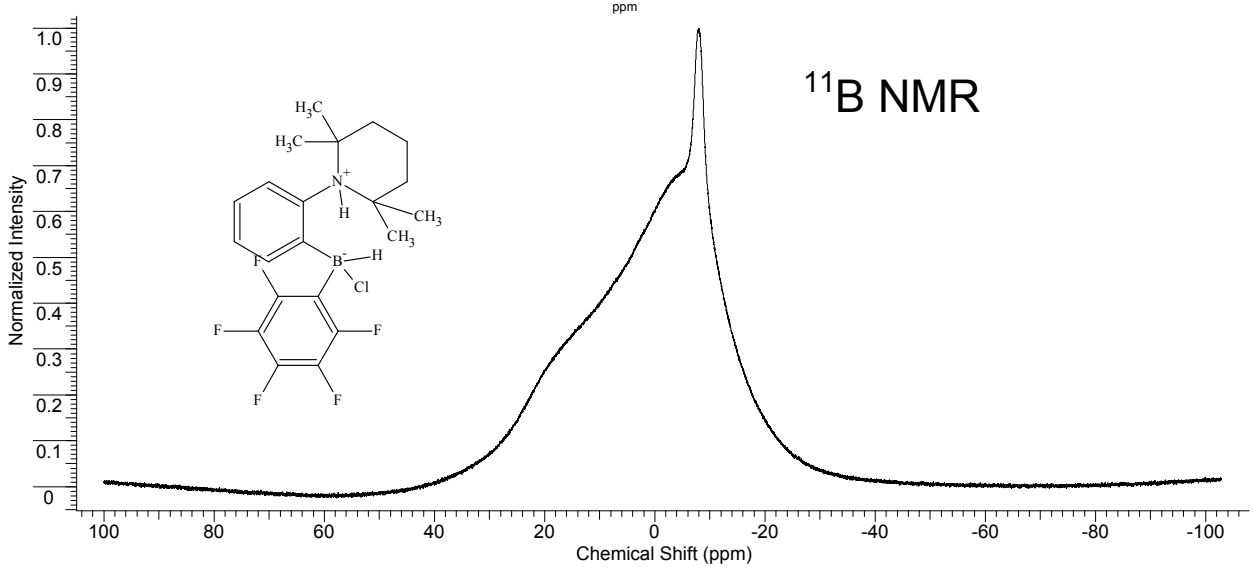
$^1$H NMR (300 MHz, $C_6D_6$, $\delta$, ppm): 0.82 (s, 3H),0.91 (s, 3H),0.95-1.30 (m, 4H), 1.05 (s, 3H),1.18 (s, 3H), 1.75 (pseudo-q, J=11 Hz, 2H), 4.84 (br. s, 1H, B***H***) 6.69 (d, J=8.2 Hz, 1H), 6.84 (t, J=7.7 Hz, 1H),7.03 (t, J=7.3 Hz, 1H), 7.45 (d, J=7.1 Hz, 1H), 10.78 (br. s, 1H, N***H***).
$^{13}$C NMR (75 MHz, $C_6D_6$, $\delta$, ppm, partial): 16.39, 23.62, 24.49, 29.19, 29.39, 37.80, 38.07, 68.74, 68.89, 122.24, 124.98, 128.51, 135.67, 137.61 (dm, J = 252 Hz), 138.35, 139.97 (dm, J = 245 Hz), 148.74 (dm, J = 240 Hz), 149.58 (br. m).
$^{19}$F NMR (282 MHz, $C_6D_6$, $\delta$, ppm): -131.7 (dm, J=23.6 Hz, 2F), -160.4 (t, J=20.6 Hz, 1F), 165.2 (m, 2F).
$^{11}$B NMR (53.7 MHz, $C_6D_6$, $\delta$ ppm): -8.0 (s, $\nu_{1/2}$~250 Hz)
ESI-HRMS$^-$: $[M-H]^-$, calc.:430.1538, found: 430.1597.
Elem. found: C, 58.17; H, 5.59; N, 3.25; calc. C, 58.43; H, 5.60; N, 3.24.

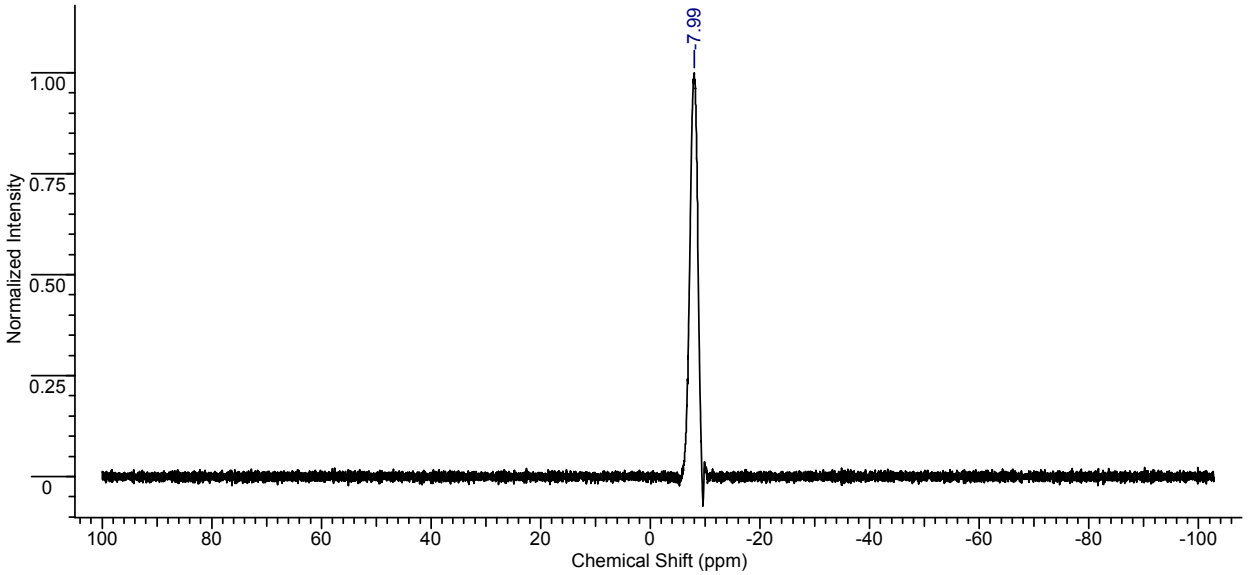

Benzene-d6
$^1$H NMR
0.79
0.97
2.76
0.96
10.25
ppm
Benzene-d6
0.79
0.97
2.76
0.96
2.00
10.25
6.00
ppm

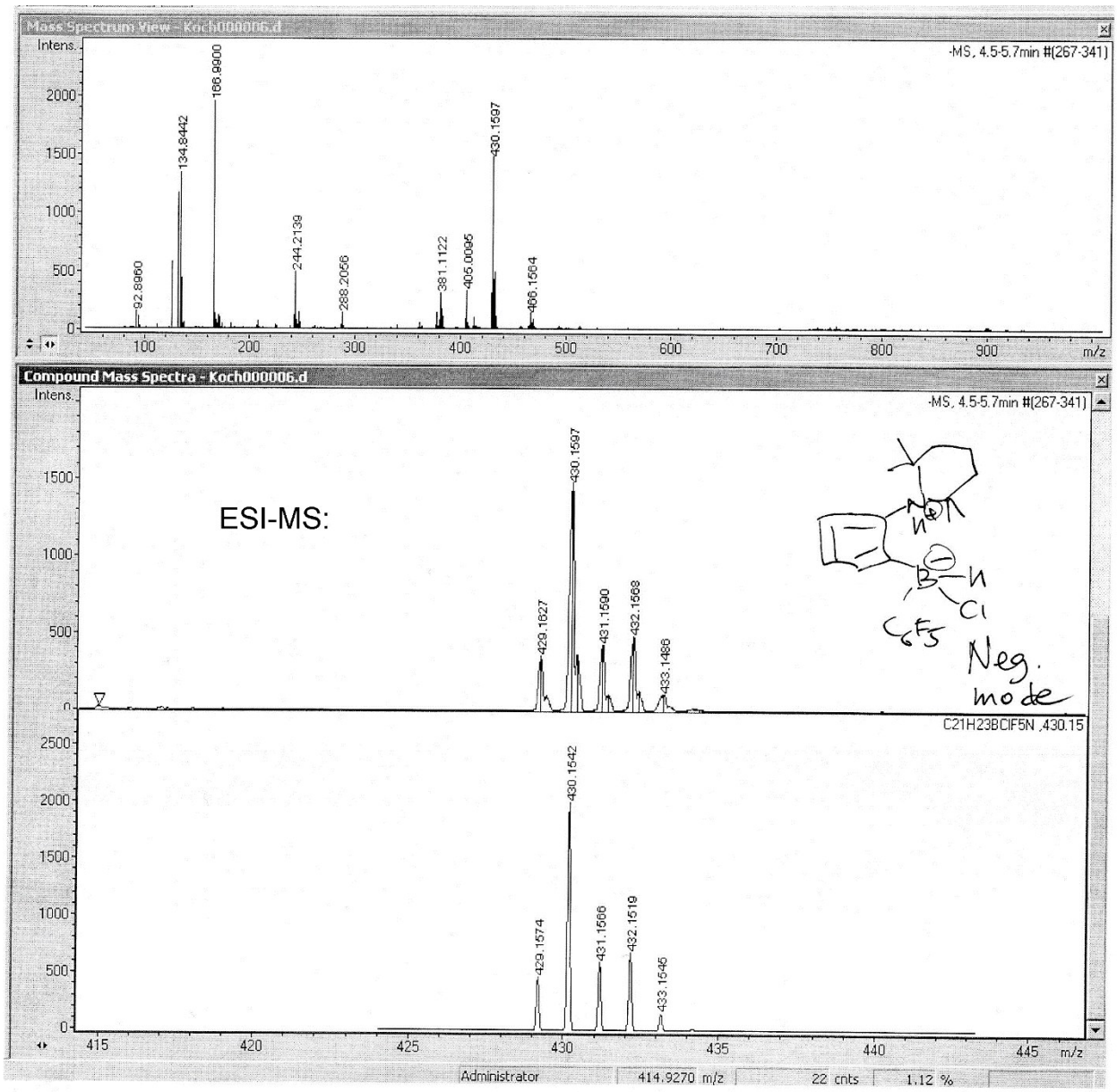

$^{13}$C NMR
Benzene-d6
128.00
128.51
124.98
122.24
135.67
138.35
150.29
149.58
147.19
139.31
68.89
68.74
38.07
37.80
29.19
29.39
24.49
23.62
16.39
ppm

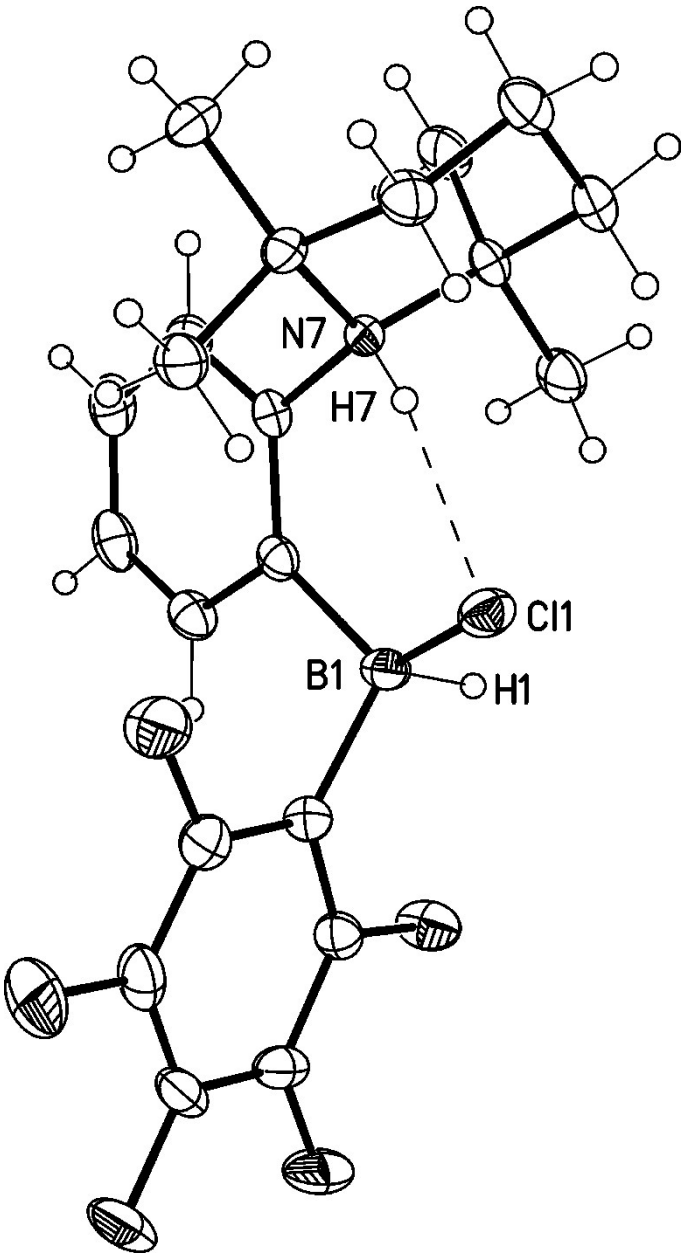

Benzene-d6
135.67
128.51
128.00
124.98
122.24
138.35
150.29
149.58
147.19
141.58
139.31
135.91


19F NMR
160.43
165.23
131.74
131.81
2.05
1.02
2.00
ppm


11B NMR
Normalized Intensity
Chemical Shift (ppm)

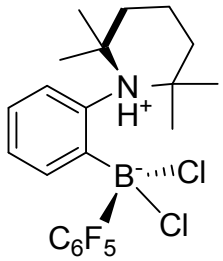

7.99
Normalized Intensity
Chemical Shift (ppm)


Mass Spectrum View - Koch000006.d
Intens.
-MS, 4.5-5.7min #(267-341)
166.9900
134.8442
430.1597
244.2139
288.2056
381.1122
406.0096
466.1564
92.8960
m/z
Compound Mass Spectra - Koch000006.d
ESI-MS:
430.1597
429.1627
431.1590
432.1568
433.1486
Neg. mode
C21H23BClF5N ,430.15
430.1542
429.1574
431.1566
432.1519
433.1545
Administrator
414.9270 m/z
22 cnts
1.12 %



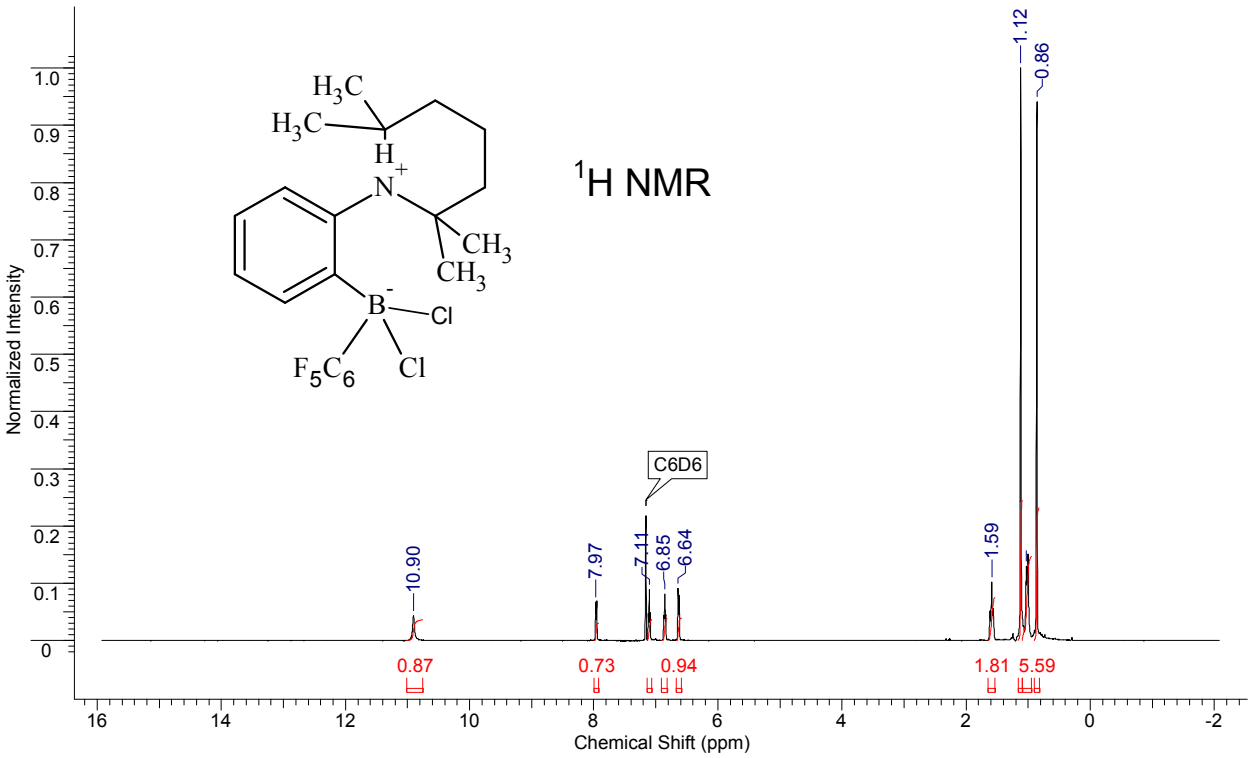

Molecular structure of **4e** (displacement parameters are drawn at 50% probability level).

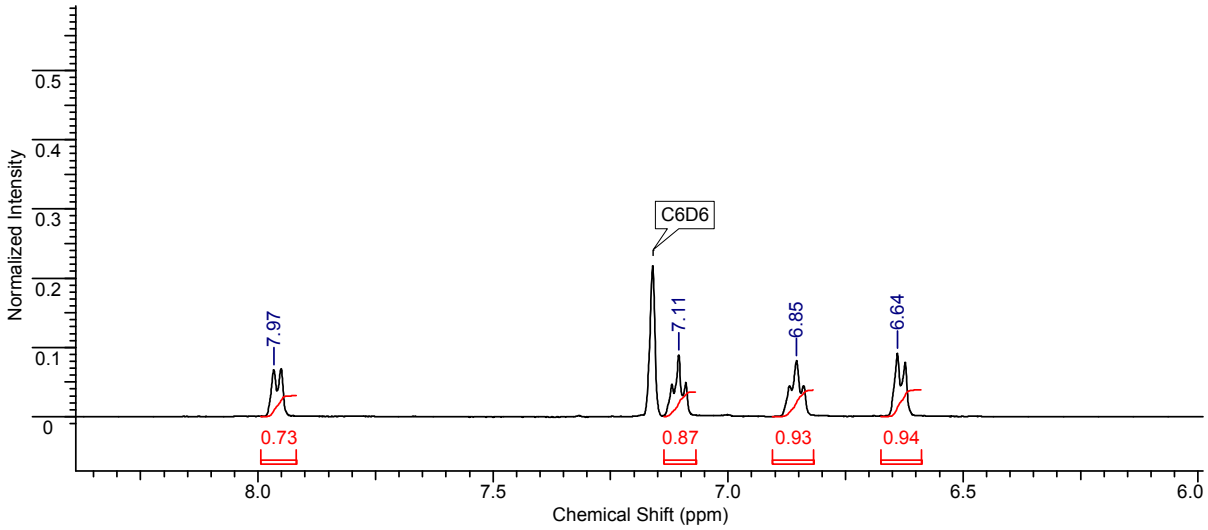
**Dichloro(hydrido)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (5e)**



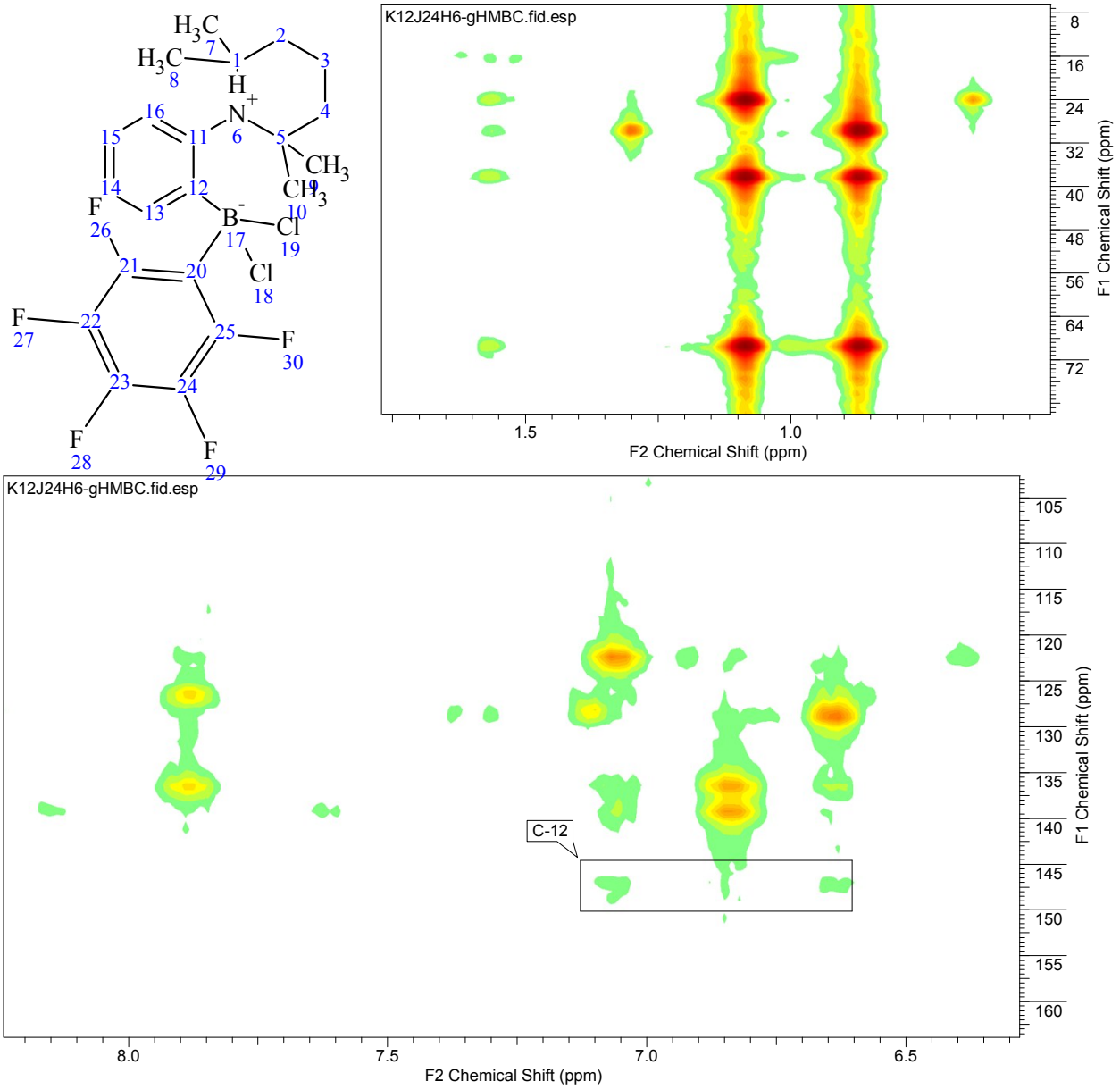

100 mg of chloro(hydrido)(pentafluorophenyl)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) and 2 ml of toluene were placed into a 25 ml Schlenk tube and heated for 24 h at 120 °C. $^{19}$F NMR showed full consumption of the starting material. Volatiles were stripped in vacuum, the residue was recrystallized from 7 ml of heptane, and precipitated crystalline material collected, 40 mg (37%). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a solution of the title compound in $C_6D_6$.

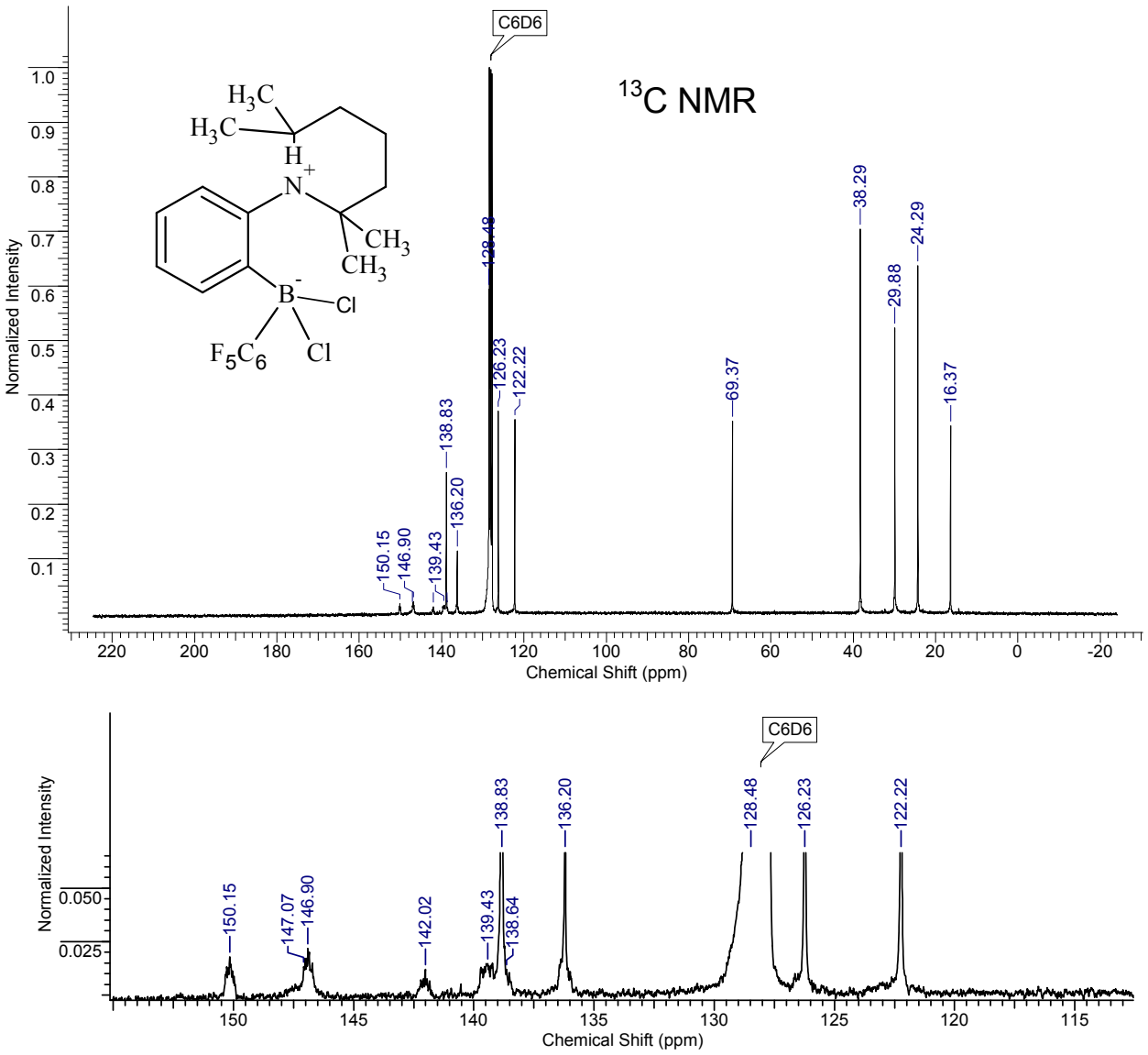
$^1$H (500 MHz, $C_6D_6$, δ, ppm): 0.86 (s, 6H), 1.00 (m, 4H), 1.12 (s, 6H), 1.59 (t, J=12 Hz, 2H), 6.63 (d, J=8.3 Hz, 1H), 6.85 (t, J=7.4 Hz, 1H), 7.11 (t, J=7.3 Hz, 1H), 7.96 (d, J=7.7 Hz, 1H), 10.90 (br. s, 1H, N***H***).
$^{13}$C (75 MHz, $C_6D_6$, δ, ppm, partial): 16.37, 24.29, 29.88, 38.29, 69.37, 122.22, 126.23, 128.48, 136.20, 138.83 (BC***C***N), 137.82 (dm, *J* = 245 Hz), 140.36 (dm, *J* = 250 Hz), 147.07 (br. m, B***C***CN), 148.53 (dm, *J* = 245 Hz).
$^{19}$F (282 MHz, $C_6D_6$, δ, ppm): -165.41 (m, 2F, *m*-F), -159.29 (t, *J* = 20.6 Hz, 1F, *p*-F), -128.20 (dd, *J* = 23.5, 8.5 Hz, 2F, *o*-F).
$^{11}$B (160 MHz, $C_6D_6$, δ, ppm): 3.05 (s).
Elem. found: C, 54.78; H, 5.30; N, 3.15; calc. C, 54.11; H, 4.97; N, 3.00;

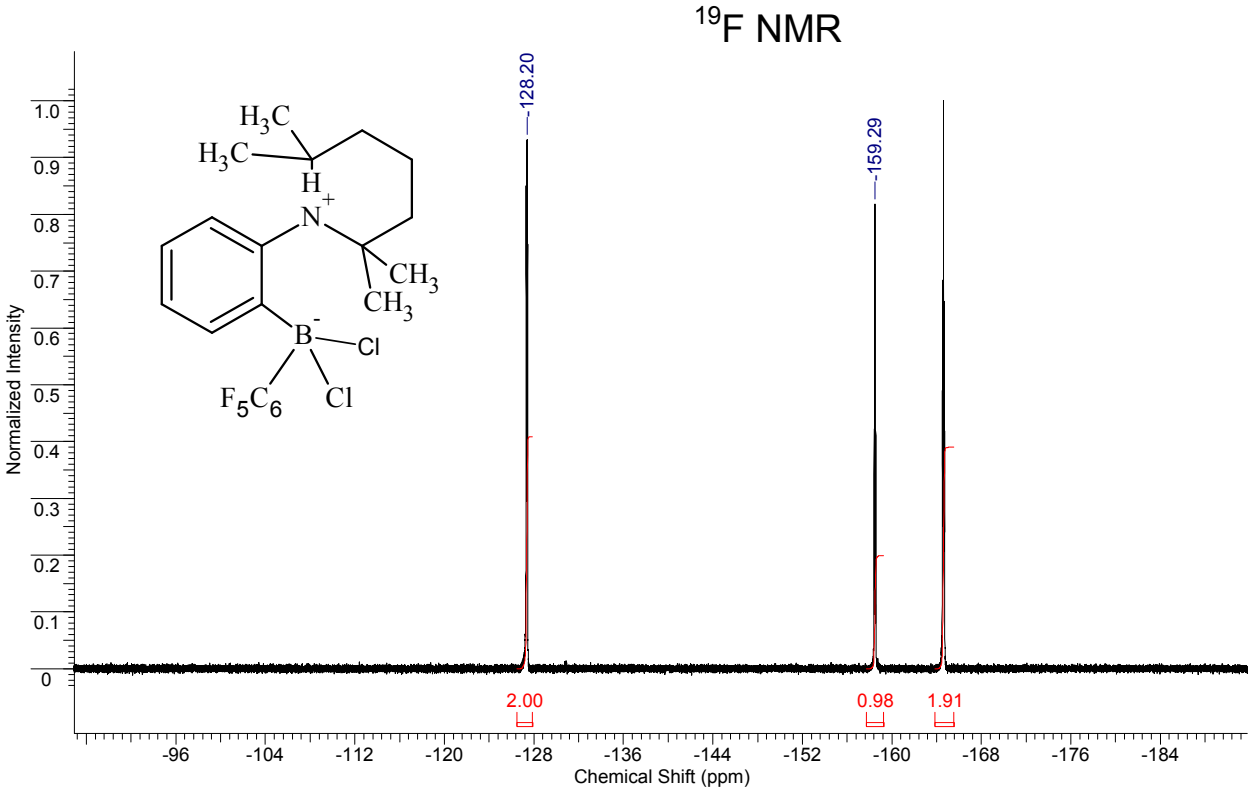

$^1$H NMR
Normalized Intensity
Chemical Shift (ppm)
C6D6
10.90
7.97
7.11
6.85
6.64
1.59
1.12
0.86
0.87
0.73
0.94
1.81
5.59

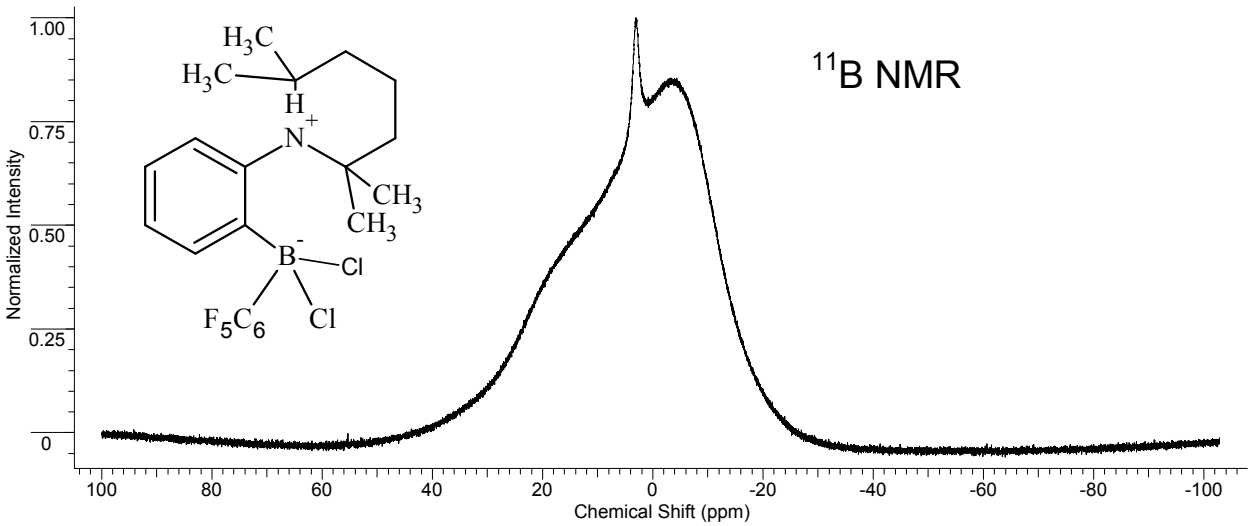

Normalized Intensity
Chemical Shift (ppm)
C6D6
7.97
7.11
6.85
6.64
0.73
0.87
0.93
0.94

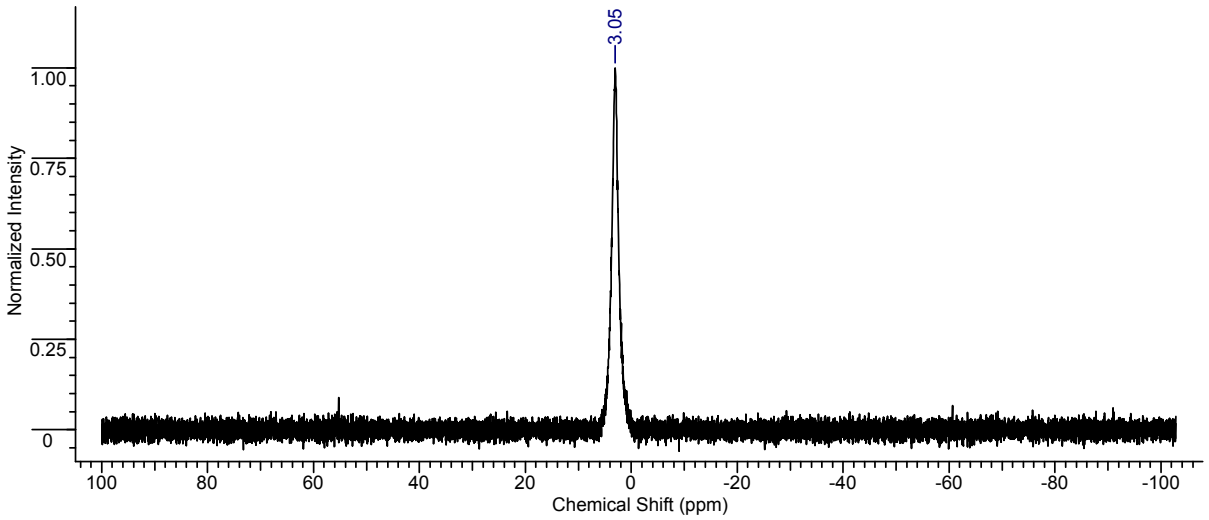
# gHMBC

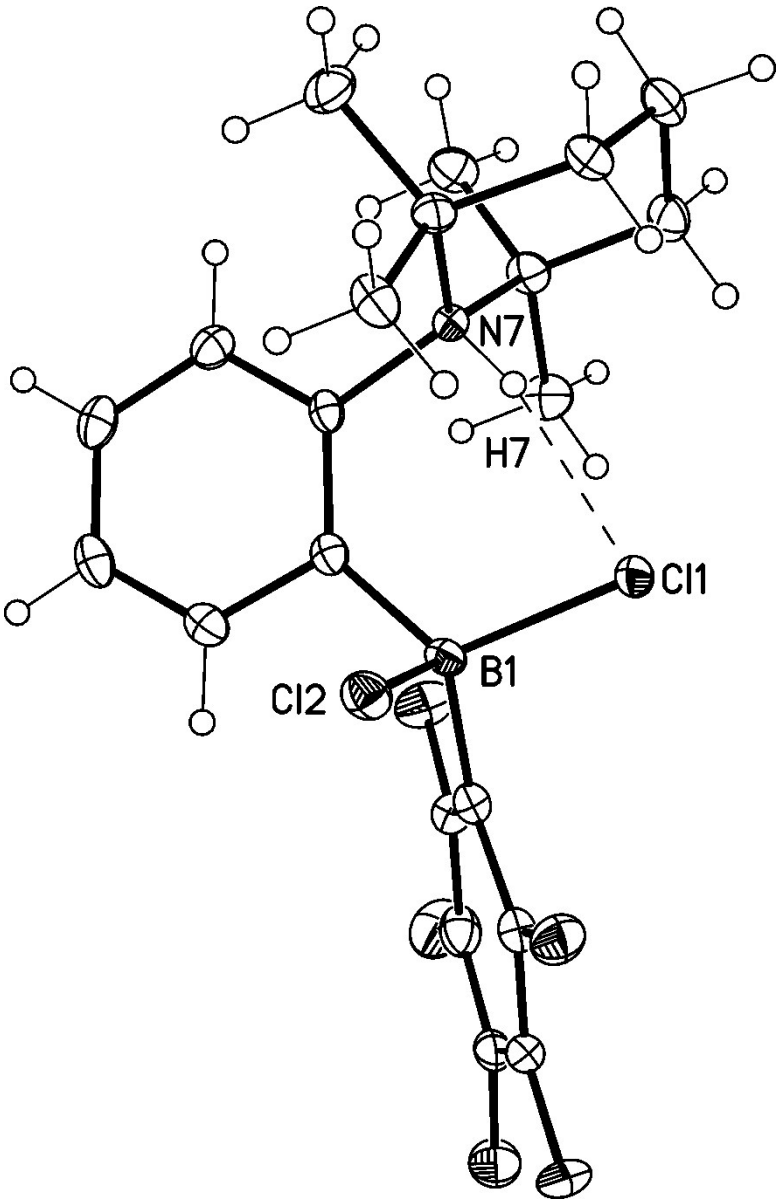

K12J24H6-gHMBC.fid.esp
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)
K12J24H6-gHMBC.fid.esp
C-12
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)


C6D6
$^{13}$C NMR
Normalized Intensity
Chemical Shift (ppm)
150.15
146.90
139.43
138.83
136.20
128.48
126.23
122.22
69.37
38.29
29.88
24.29
16.37
C6D6
Normalized Intensity
Chemical Shift (ppm)
150.15
147.07
146.90
142.02
139.43
138.64
138.83
136.20
128.48
126.23
122.22


19F NMR
128.20
159.29
2.00
0.98
1.91
Normalized Intensity
Chemical Shift (ppm)

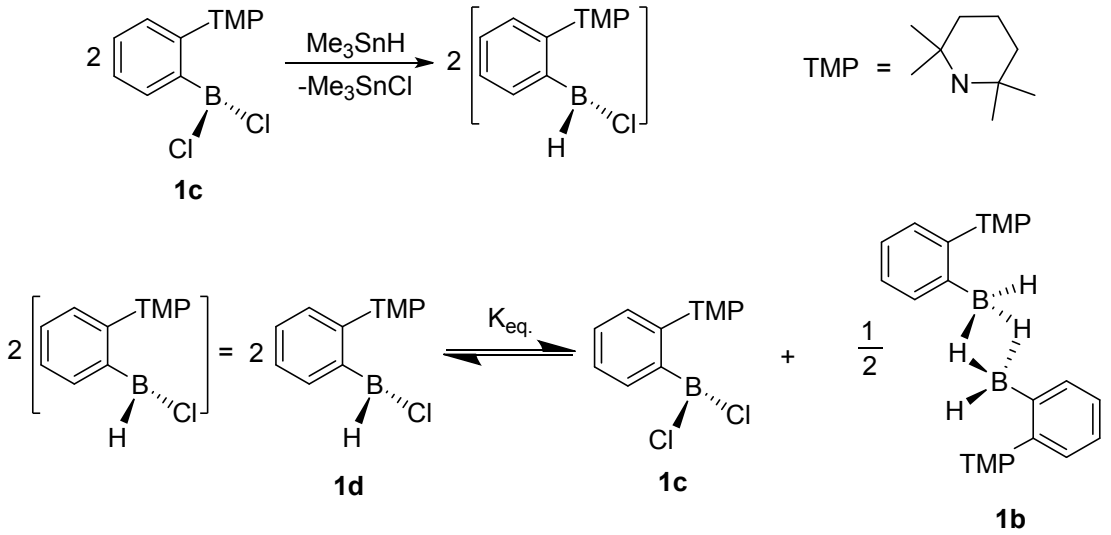

11B NMR
Normalized Intensity
Chemical Shift (ppm)


3.05
Normalized Intensity
Chemical Shift (ppm)




Molecular structure of **5e** (displacement parameters are drawn at 50% probability level).

## 1-[2-(Chloroboryl)phenyl]-2,2,6,6-tetramethylpiperidine (1d)



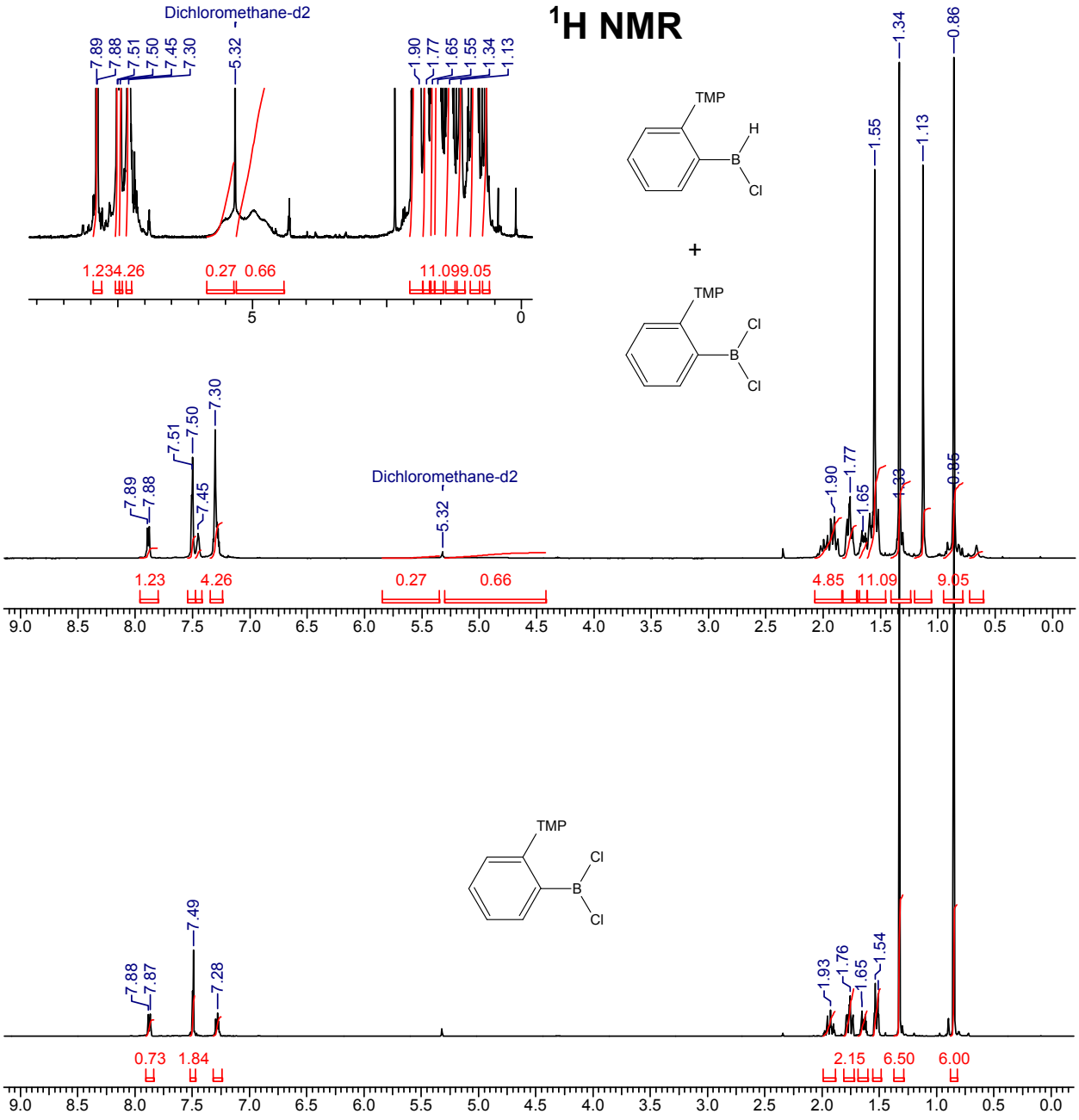

**Method A.** To a solution of 50 mg of 1-[2-(dichloroboryl)phenyl]-2,2,6,6-tetramethylpiperidine (0.167 mmol) in 1 ml of hexane and 1 ml of toluene in a 25 ml Schlenk tube 14 mg of trimethylstannane (85 mkmol, 0.5 eq.) were added. The mixture was stirred for 1 min and volatiles were stripped in vacuum. The residual greenish oil was redissolved in $CD_2Cl_2$ and analyzed by NMR. The analysis revealed two major components, the target compound (**1d**) and the starting material (**1a**) in a ratio app. 1:1.

**Method B.** To a solution of 100 mg of 1-[2-(dichloroboryl)phenyl]-2,2,6,6-tetramethylpiperidine (0.336 mmol) in 1 ml of hexane and 1 ml of toluene in a 25 ml Schlenk tube 56 mg of trimethylstannane (0.327 mmol) were added. The mixture was stirred for 1 min and volatiles were stripped in vacuum. The residual greenish oil was redissolved in the respective deuterated solvent and analyzed by NMR.

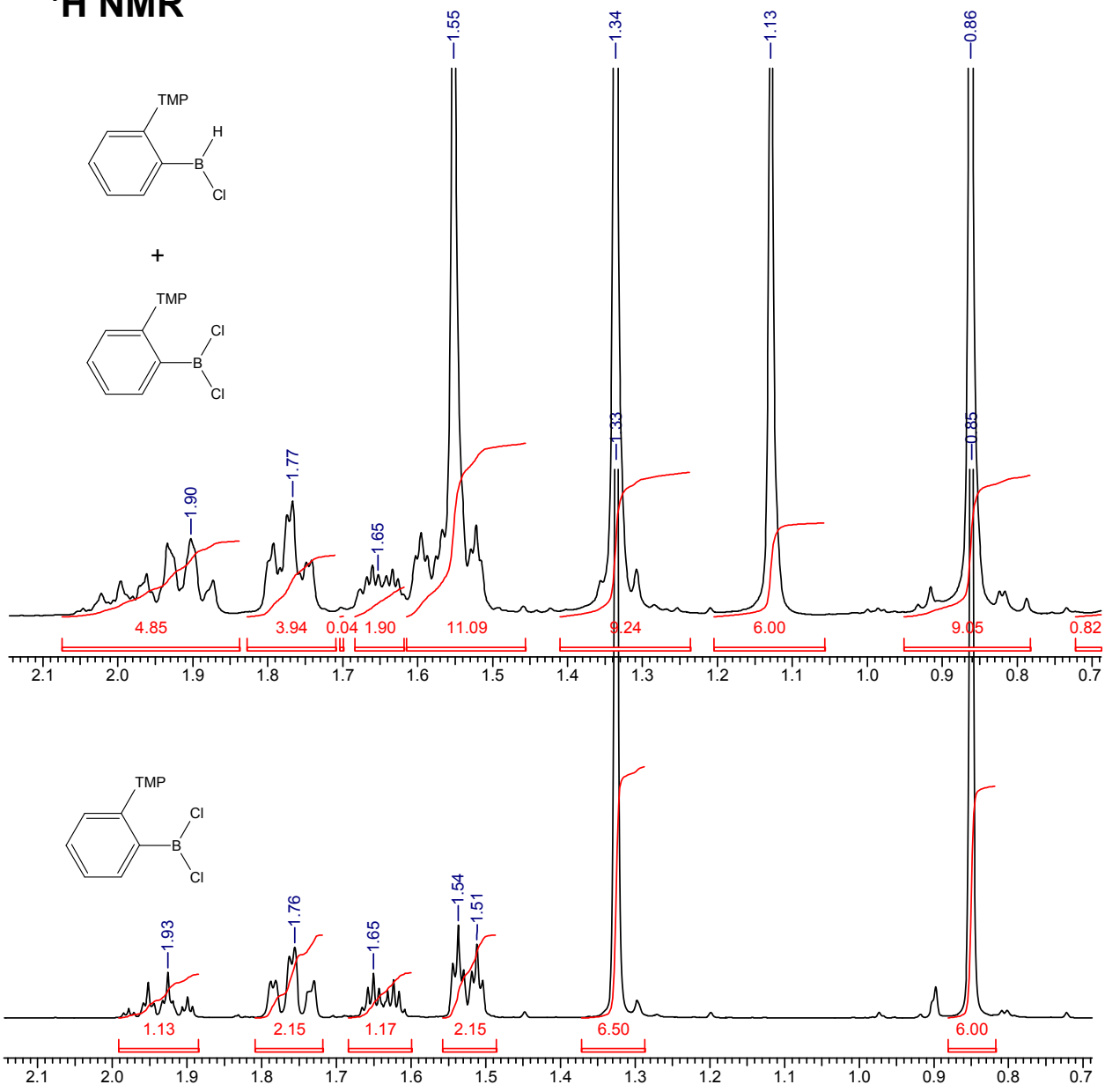
$^1$H (500 MHz, $CD_2Cl_2$, δ, ppm): 1.13 (s, 6H), 1.55 (s, 6H), 1.59 (dt, *J* = 14 Hz, *J* = 4 Hz, 2H), 1.79 (m, 1H), 1.90 (m, 2H), 2.01 (m, 1H), 5.14 (partially relaxed q, *J* = 120 Hz, 1H), 7.30 (m, 3H), 7.45 (m, 1H).
$^1$H/$^{13}$C gHSQC (500/125 MHz, $CD_2Cl_2$, δ, ppm, F2/F1): 7.47/129.77, 7.32/128.55, 7.32/122.36, 1.91/38.19, 1.59/38.19, 1.14/30.18, 1.56/27.58, 2.01/17.06, 1.80/17.00,
$^{13}$C (75 MHz, $CD_2Cl_2$, δ, ppm, partial): 17.27, 27.87, 30.47, 38.44, 62.18, 122.64, 128.40, 129.17, 130.02, 151.71.
$^{11}$B (160 MHz, $CD_2Cl_2$, δ, ppm): 18.7 (d, *J* = 111 Hz).
$^{11}$B (160 MHz, $C_6D_5CD_3$, δ, ppm): 30.2 (br. s).
Variable temperature $^{11}$B NMR shifts of **1d** in $CD_2Cl_2$ and toluene-$d_8$:

| T, °C | T, K | $^{11}$B, δ, ppm in $CD_2Cl_2$ |
|---|---|---|
| 50 | 323 | 23.2 |
| 27 | 300 | 18.7 |
| 0 | 273 | 14.5 |
| -12 | 261 | 13.0 |
| | | |
| | | |

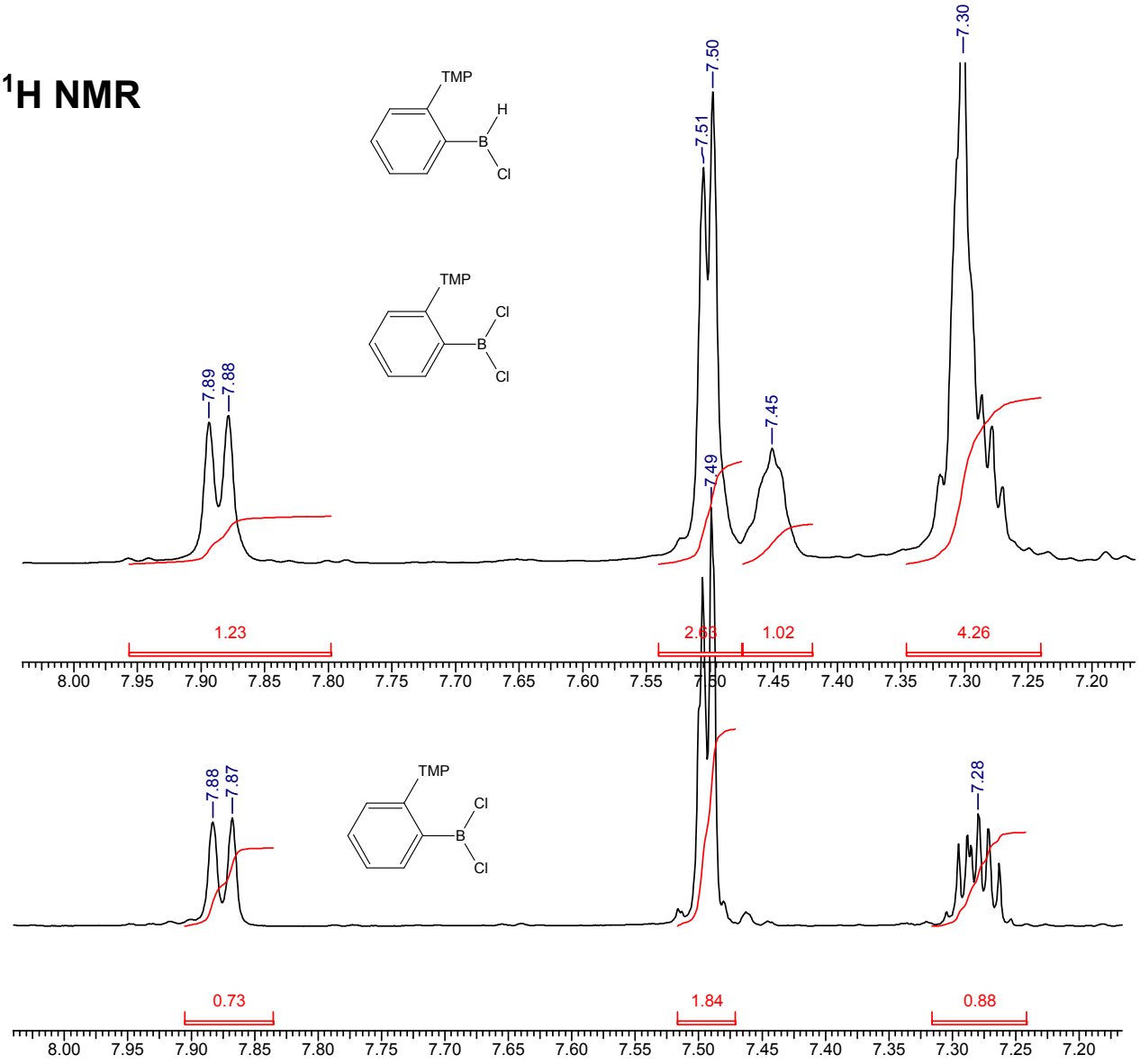
| T, °C | T, K | $^{11}$B, δ, ppm in toluene-$d_8$ |
|---|---|---|
| 90 | 363 | 41.6 |
| 75 | 348 | 39.4 |
| 50 | 323 | 35 |
| 27 | 300 | 30.2 |
| 8 | 281 | 25.8 |
| -12 | 261 | 20 |


$^1$H NMR
Dichloromethane-d2
TMP
H
B
Cl
+
TMP
Cl
B
Cl
Dichloromethane-d2
TMP
Cl
B
Cl

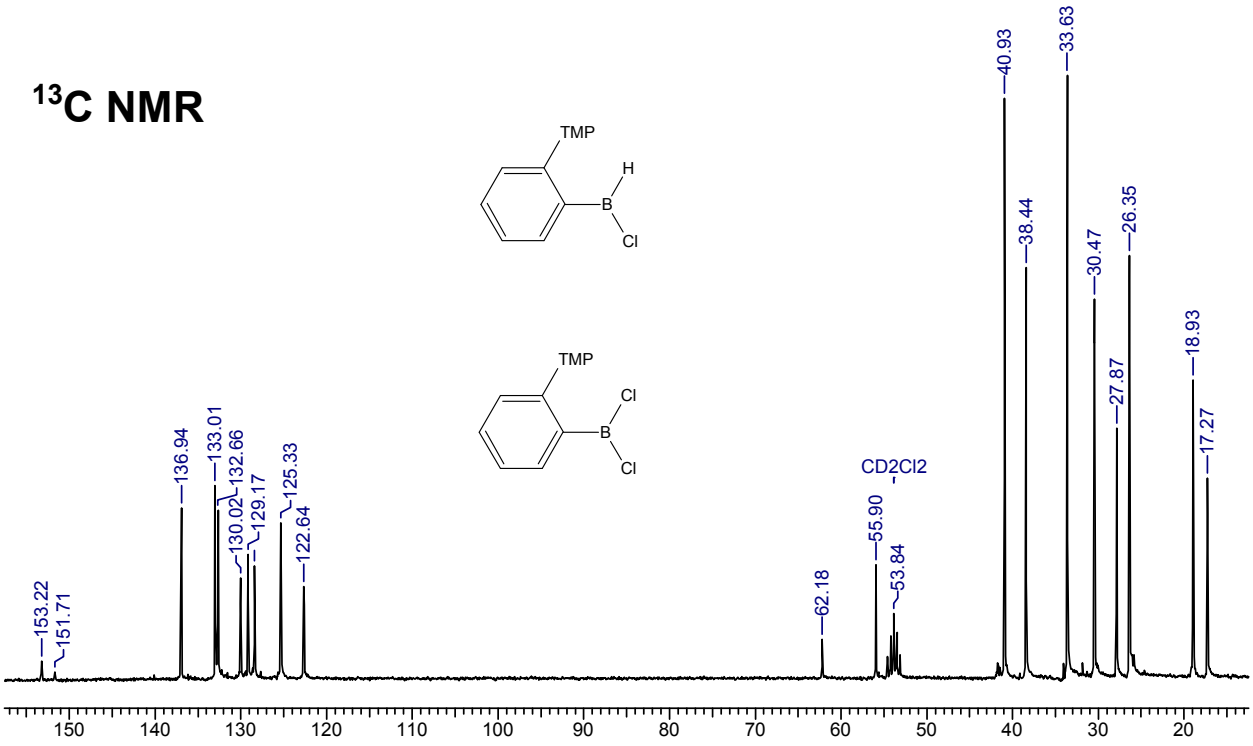
# $^1$H NMR


TMP
H
B
Cl
+
TMP
Cl
B
Cl
1.55
1.34
1.13
0.86
1.90
1.77
1.65
1.33
0.85
4.85
3.94
0.04
1.90
11.09
9.24
6.00
9.05
0.82
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
TMP
Cl
B
Cl
1.93
1.76
1.65
1.54
1.51
1.13
2.15
1.17
2.15
6.50
6.00
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7

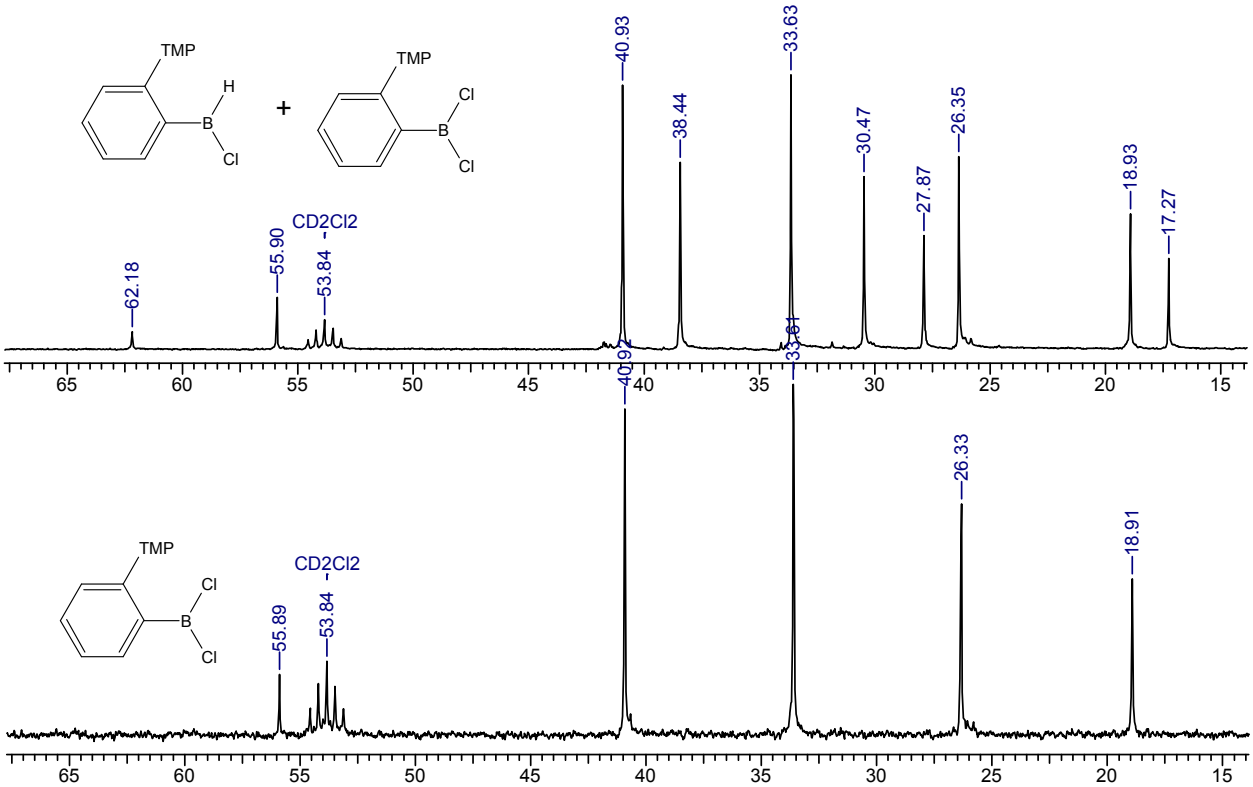
**$^1$H NMR**

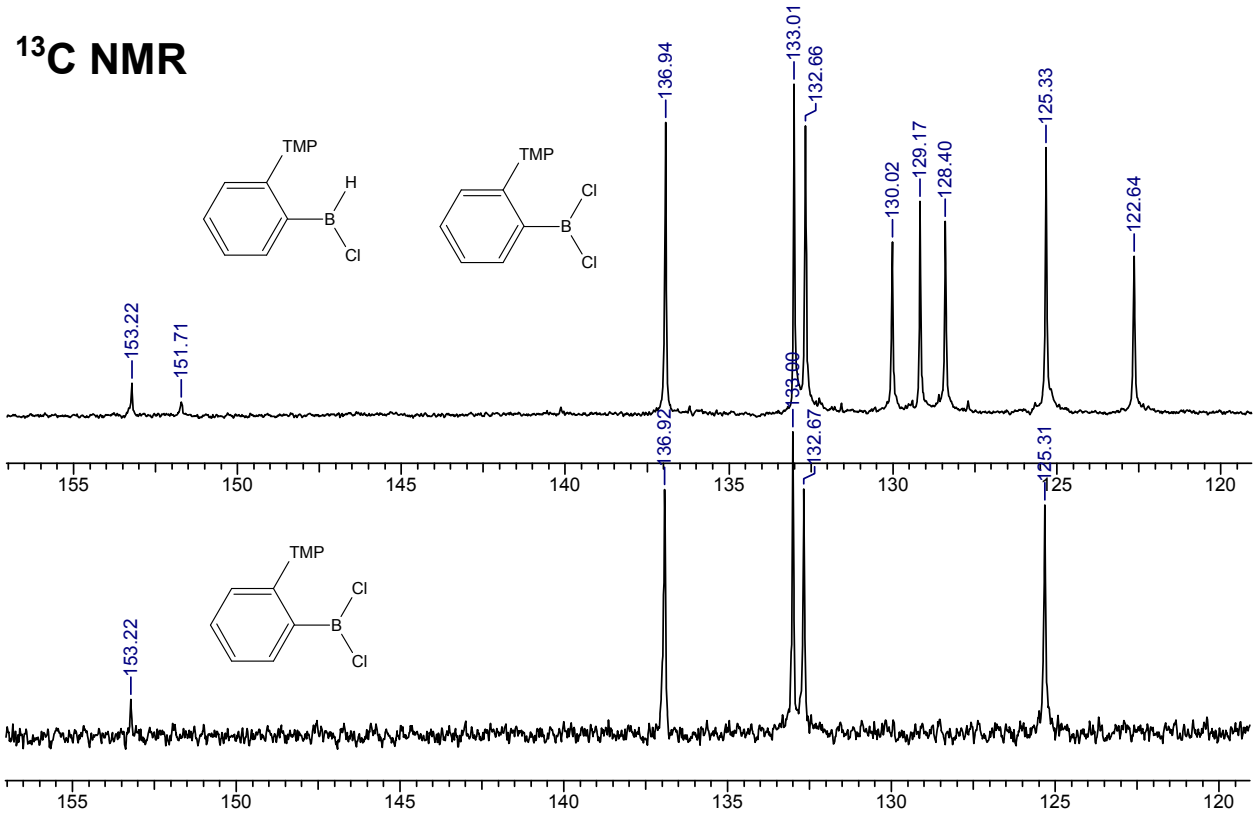

TMP
H
B
Cl
TMP
Cl
B
Cl
7.89
7.88
7.51
7.50
7.49
7.45
7.30
1.23
2.68
1.02
4.26
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.88
7.87
TMP
Cl
B
Cl
7.28
0.73
1.84
0.88

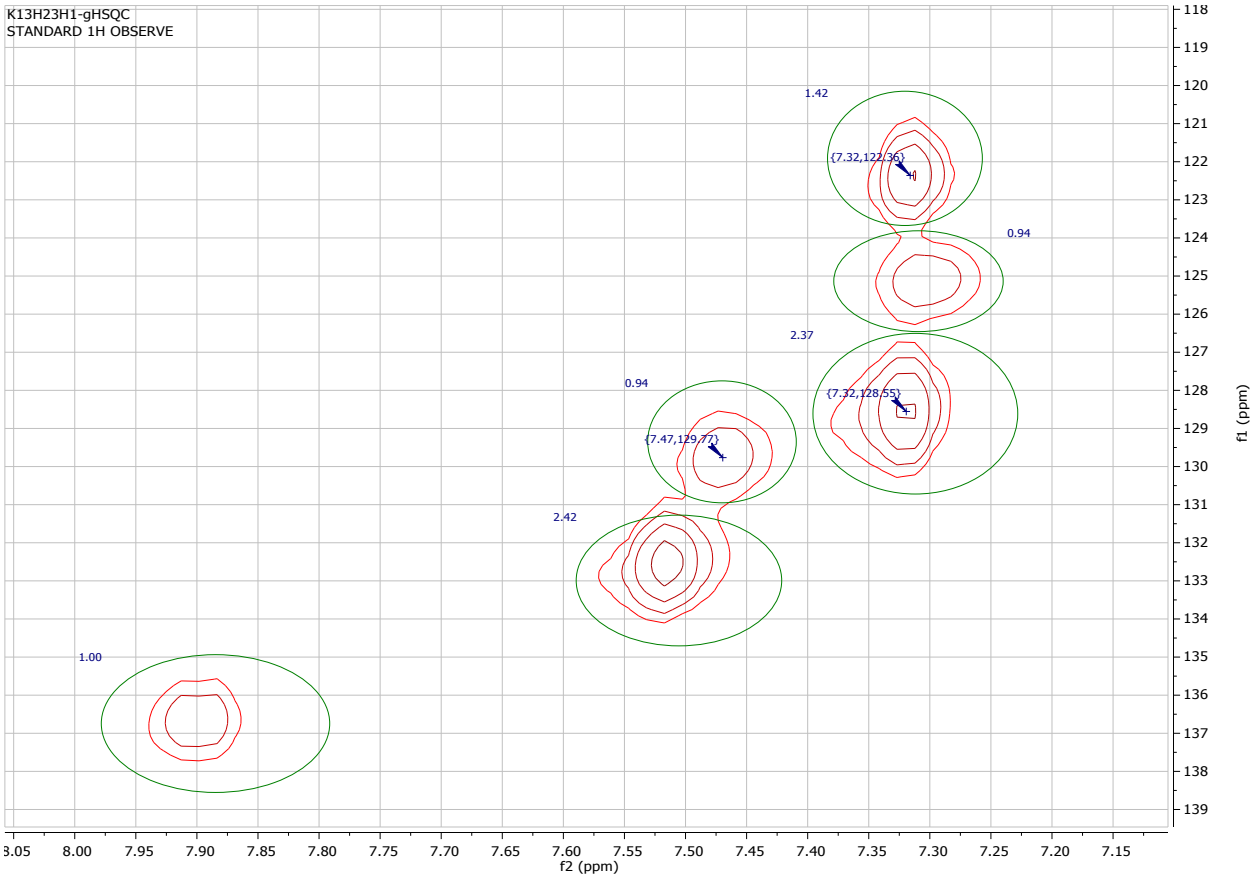
## $^{13}$C NMR

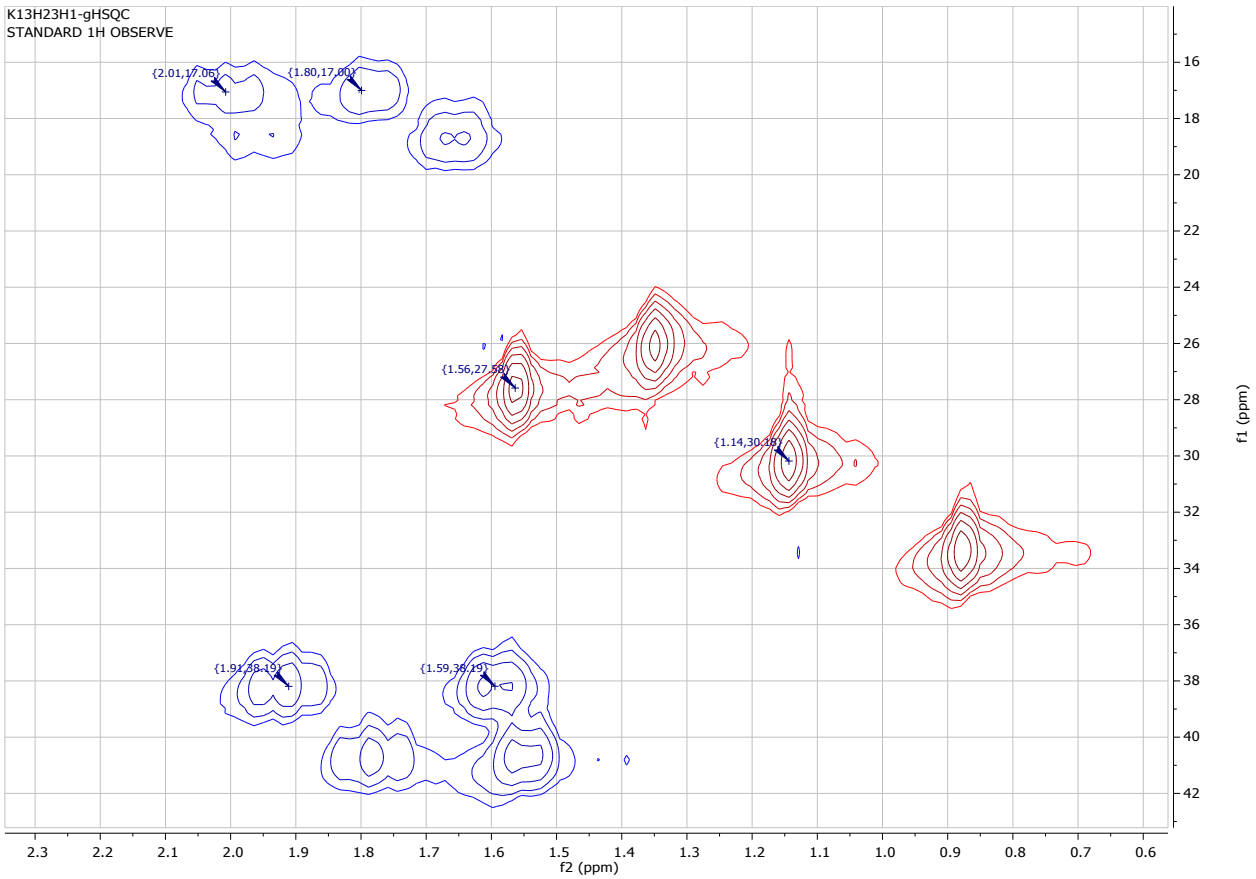


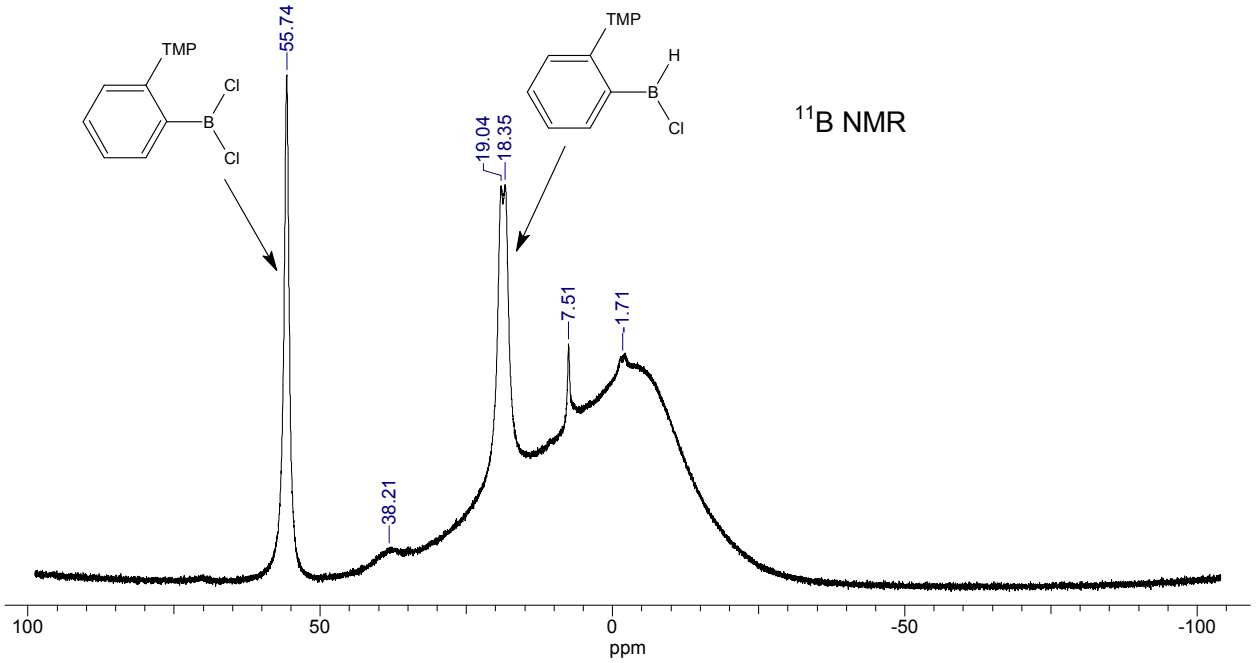

## $^{13}$C NMR



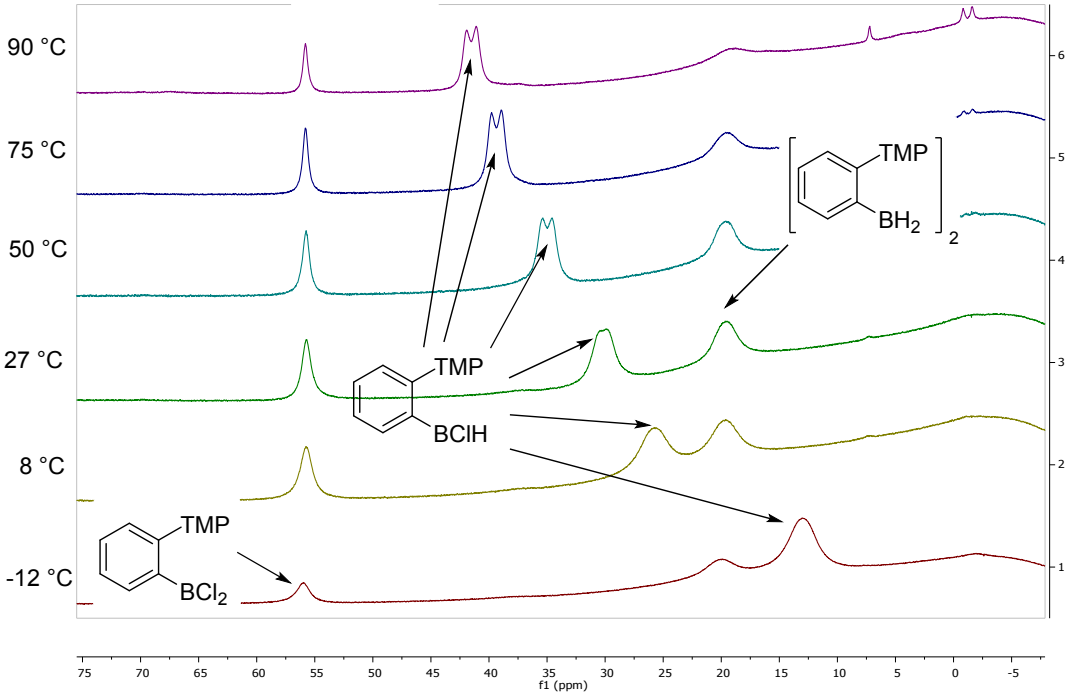

13C NMR
TMP
H
B
Cl
TMP
Cl
B
Cl
153.22
151.71
136.94
133.01
132.66
130.02
129.17
128.40
125.33
122.64
133.00
132.67
136.92
125.31
155
150
145
140
135
130
125
120
TMP
Cl
B
Cl
153.22


K13H23H1-gHSQC
STANDARD 1H OBSERVE
1.42
{7.32,122.36}
0.94
2.37
{7.32,128.55}
0.94
{7.47,129.72}
2.42
1.00
f2 (ppm)
f1 (ppm)

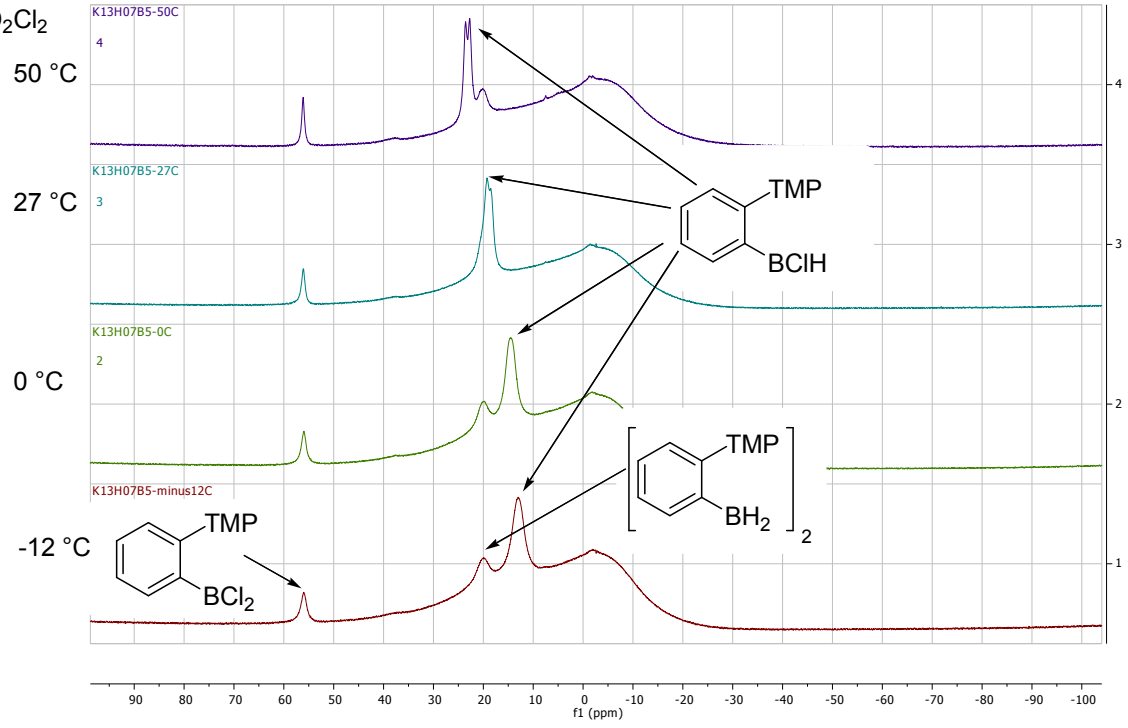

K13H23H1-gHSQC
STANDARD 1H OBSERVE
{2.01,17.06}
{1.80,17.00}
{1.56,27.58}
{1.14,30.18}
{1.91,38.19}
{1.59,38.19}
f2 (ppm)
f1 (ppm)


TMP
Cl
B
Cl
55.74
TMP
H
B
Cl
19.04
18.35
7.51
1.71
38.21
$^{11}$B NMR
ppm

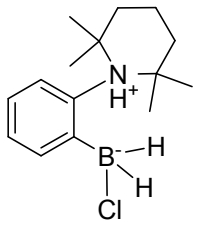
$^{11}$B VT NMR
in toluene-$d_8$




$^{11}$B VT NMR
in $CD_2Cl_2$

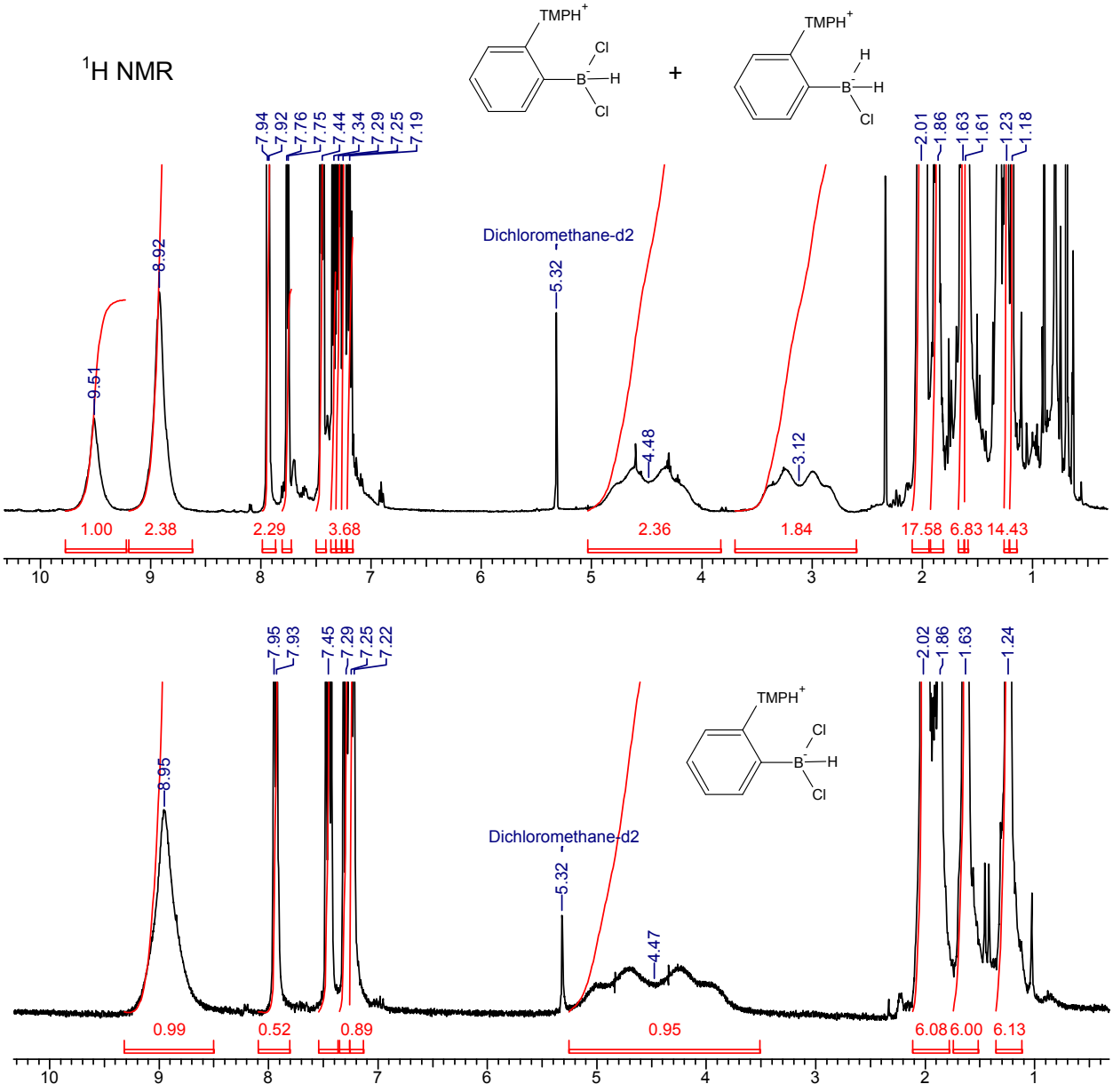


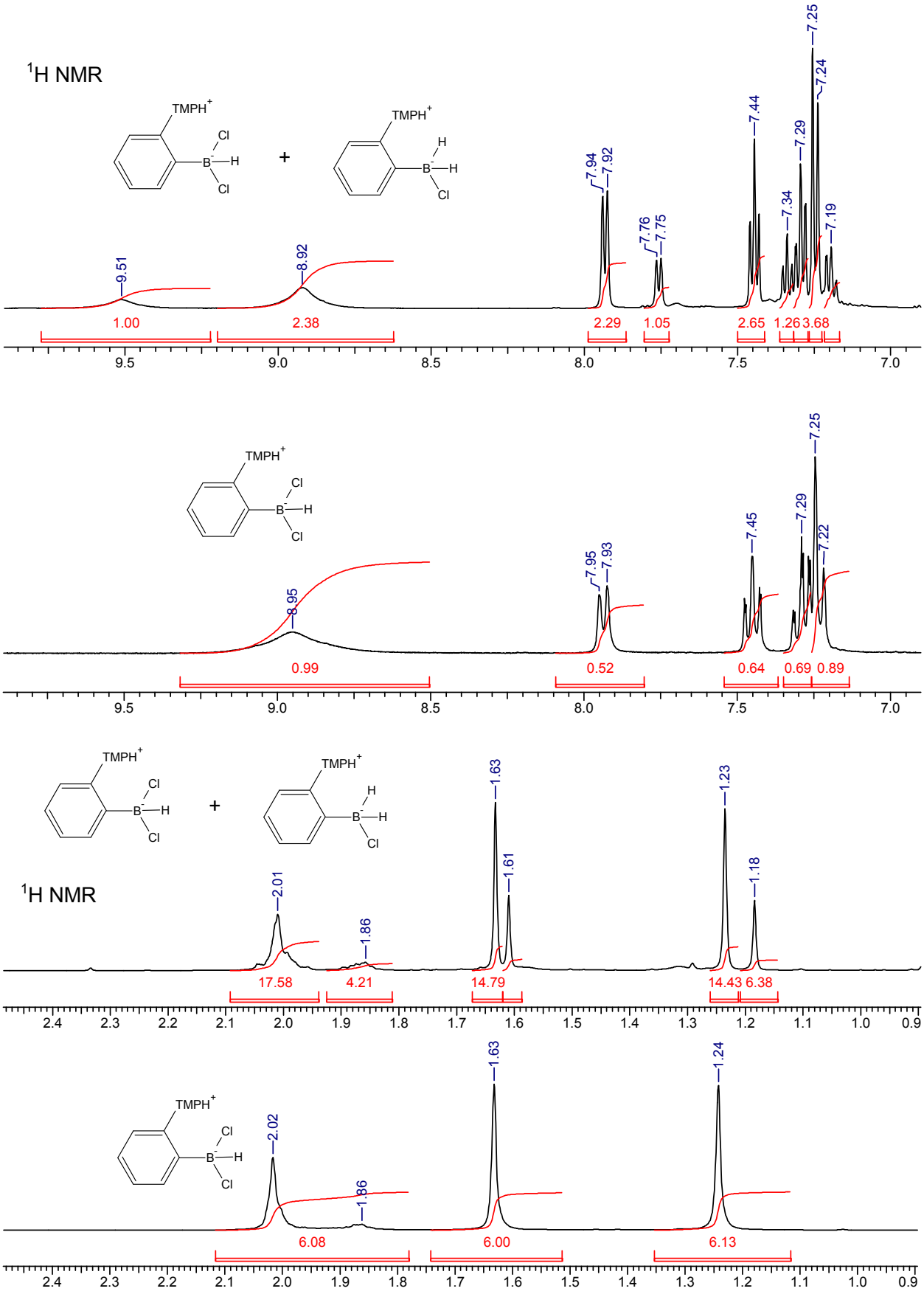

## Chloro(dihydrido)[2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) (4d)



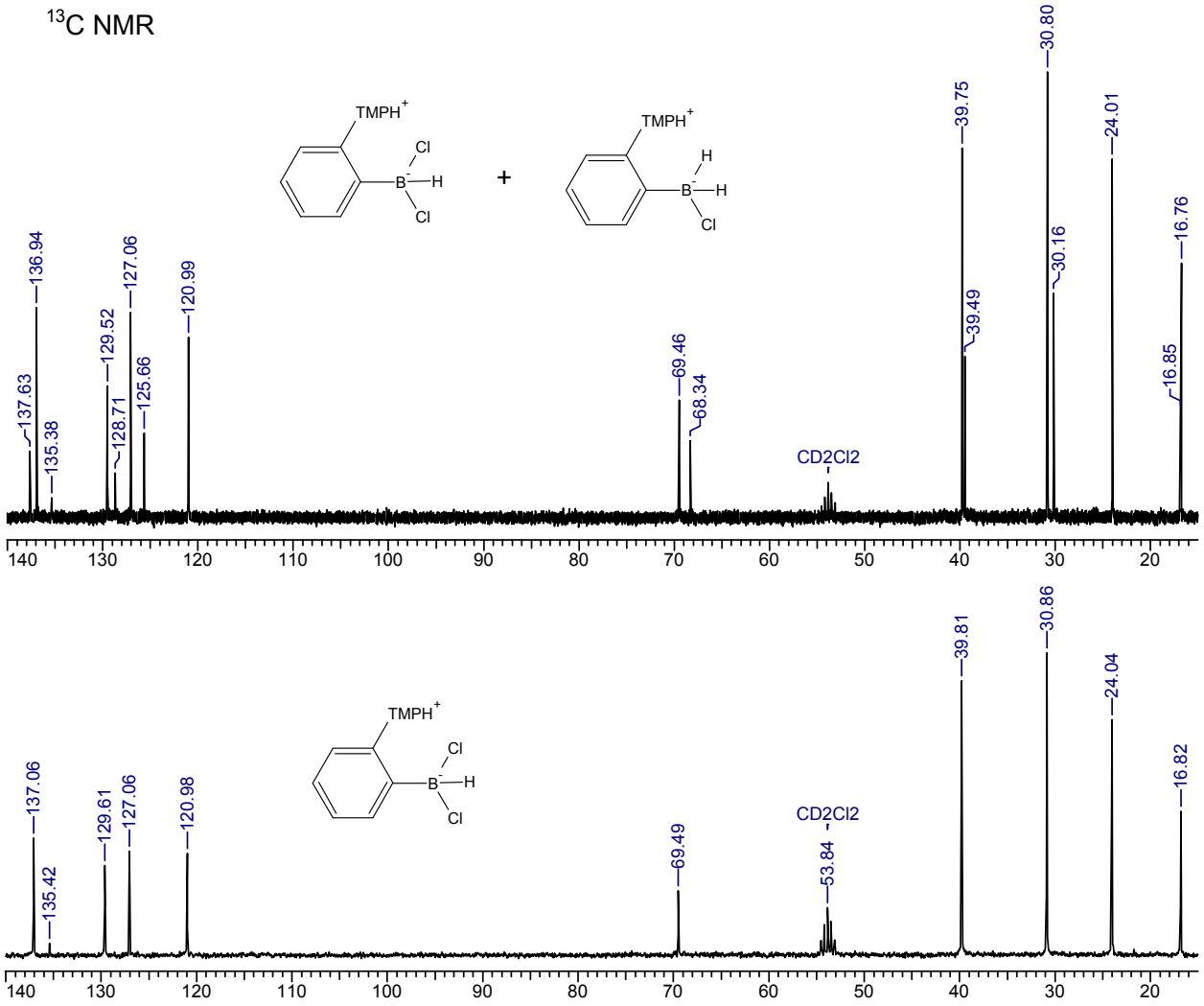
A 25 ml Schlenk tube containing a solution of app. 1:1 mixture of **1c** and **1d** in 1ml dichloromethane-$d_2$ (prepared from 50 mg of **1a** according to method A) was filled with 2.2 bar H2 by 5 pump-thaw cycles and stirred for 15 min at RT. Greenish color vanished within minutes. A colorless solution was transferred into an NMR tube and analyzed by NMR. Analysis revealed the presence of predominantly **4c** and **4d** in a ~1.4:1 ratio along with minor amounts of **1b** and some unidentified impurities.

$^{1}$H (500 MHz, $CD_2Cl_2$, δ, ppm): 1.18 (s, 6H), 1.61 (s, 6H), 1.80-2.01 (m, 6H), 3.12 (partially relaxed q, *J* = 85 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.24 (m, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 9.51 (br. s, 1H).
$^{13}$C (75 MHz, $CD_2Cl_2$, δ, ppm, partial): 16.85, 24.01, 30.16, 39.49, 68.34, 121.05, 125.66, 128.71, 137.63.
$^{11}$B (160 MHz, $CD_2Cl_2$, δ, ppm): -11.7 (t, *J* = 95 Hz).

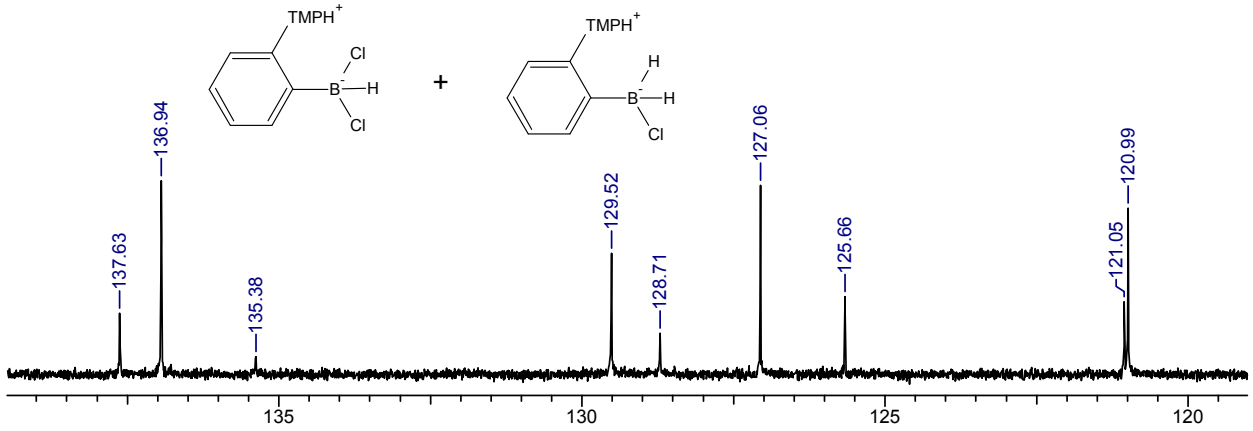


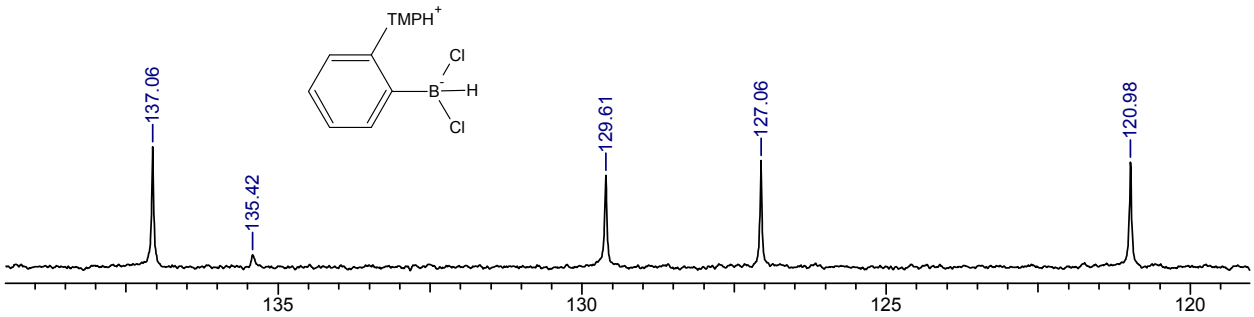

1H NMR
TMPH+
Cl
B
H
Cl
+
TMPH+
H
B
H
Cl
9.51
8.92
7.94
7.92
7.76
7.75
7.44
7.34
7.29
7.25
7.24
7.19
1.00
2.38
2.29
1.05
2.65
1.26
3.68
9.5
9.0
8.5
8.0
7.5
7.0
TMPH+
Cl
B
H
Cl
8.95
7.95
7.93
7.45
7.29
7.25
7.22
0.99
0.52
0.64
0.69
0.89
9.5
9.0
8.5
8.0
7.5
7.0
TMPH+
Cl
B
H
Cl
+
TMPH+
H
B
H
Cl
1H NMR
2.01
1.86
1.63
1.61
1.23
1.18
17.58
4.21
14.79
14.43
6.38
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
TMPH+
Cl
B
H
Cl
2.02
1.86
1.63
1.24
6.08
6.00
6.13
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9

$^{13}$C NMR

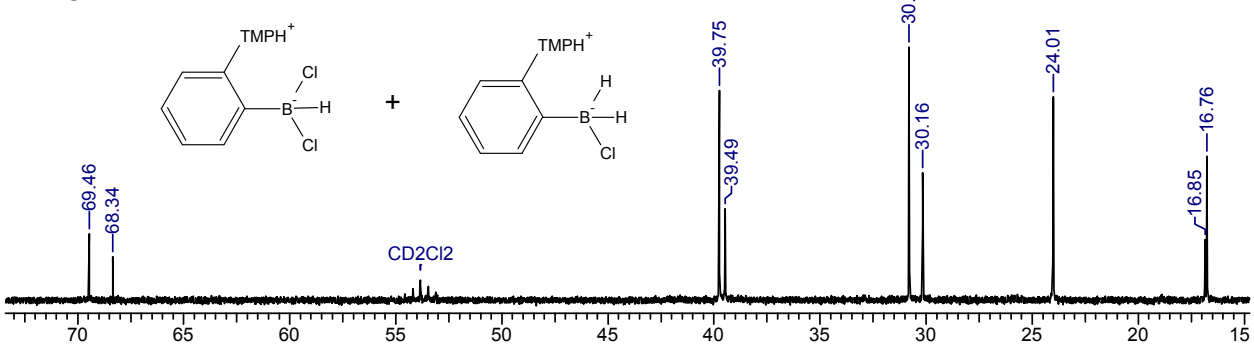

TMPH+
Cl
B
H
Cl
+
TMPH+
H
B
H
Cl
136.94
137.63
135.38
129.52
128.71
127.06
125.66
120.99
69.46
68.34
CD2Cl2
39.75
39.49
30.80
30.16
24.01
16.85
16.76
140
130
120
110
100
90
80
70
60
50
40
30
20
TMPH+
Cl
B
H
Cl
137.06
135.42
129.61
127.06
120.98
69.49
CD2Cl2
53.84
39.81
30.86
24.04
16.82
140
130
120
110
100
90
80
70
60
50
40
30
20

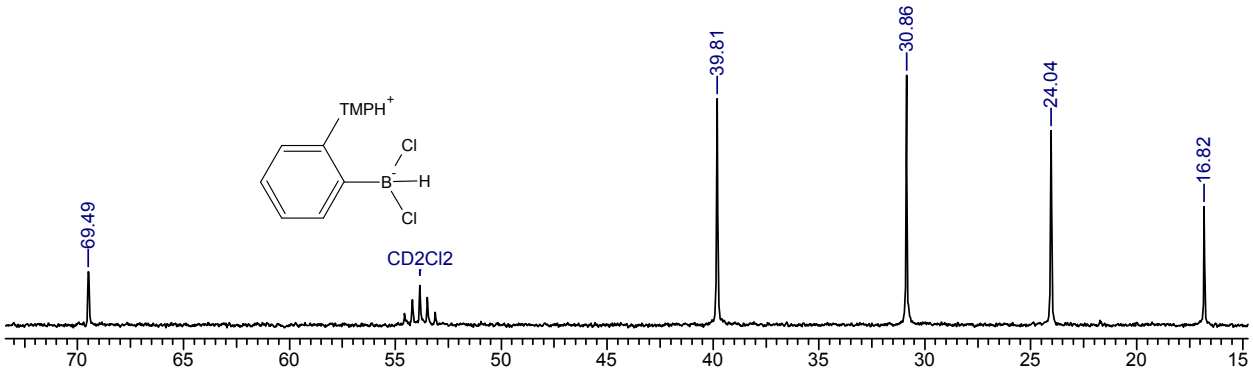
$^{13}$C NMR

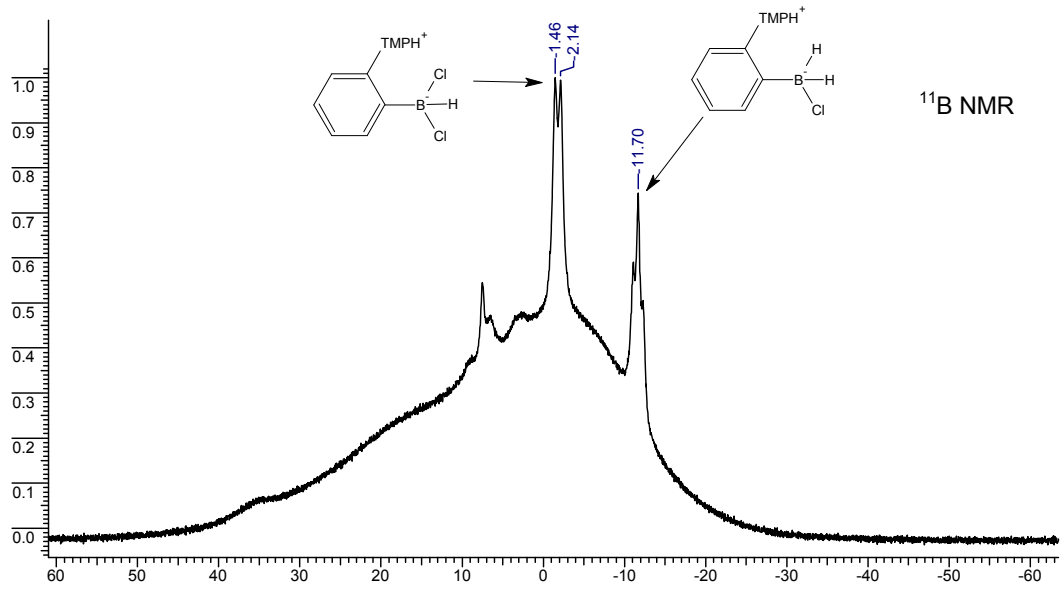


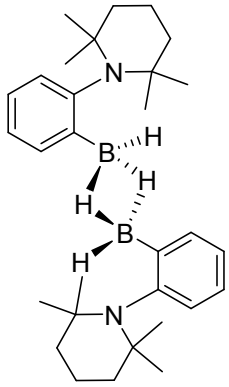

$^{13}$C NMR





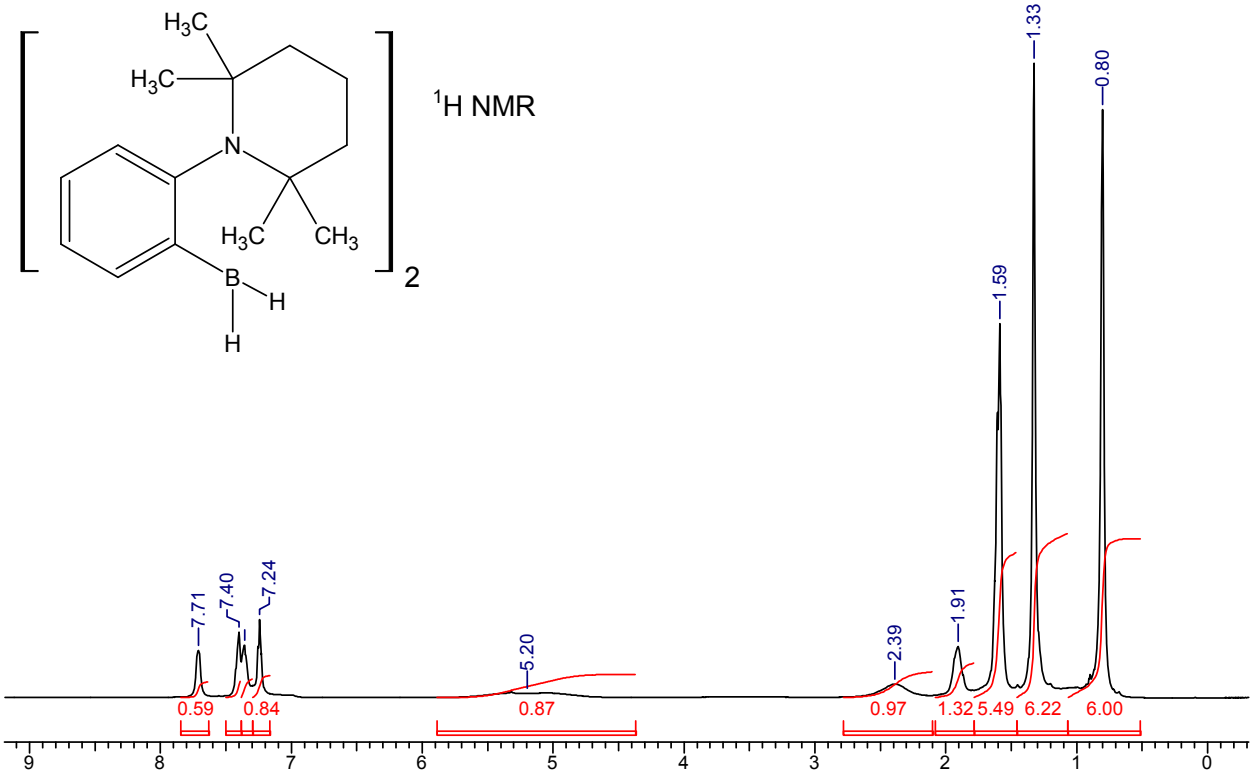

## 1-(2-Borylphenyl)-2,2,6,6-tetramethylpiperidine dimer (1b)

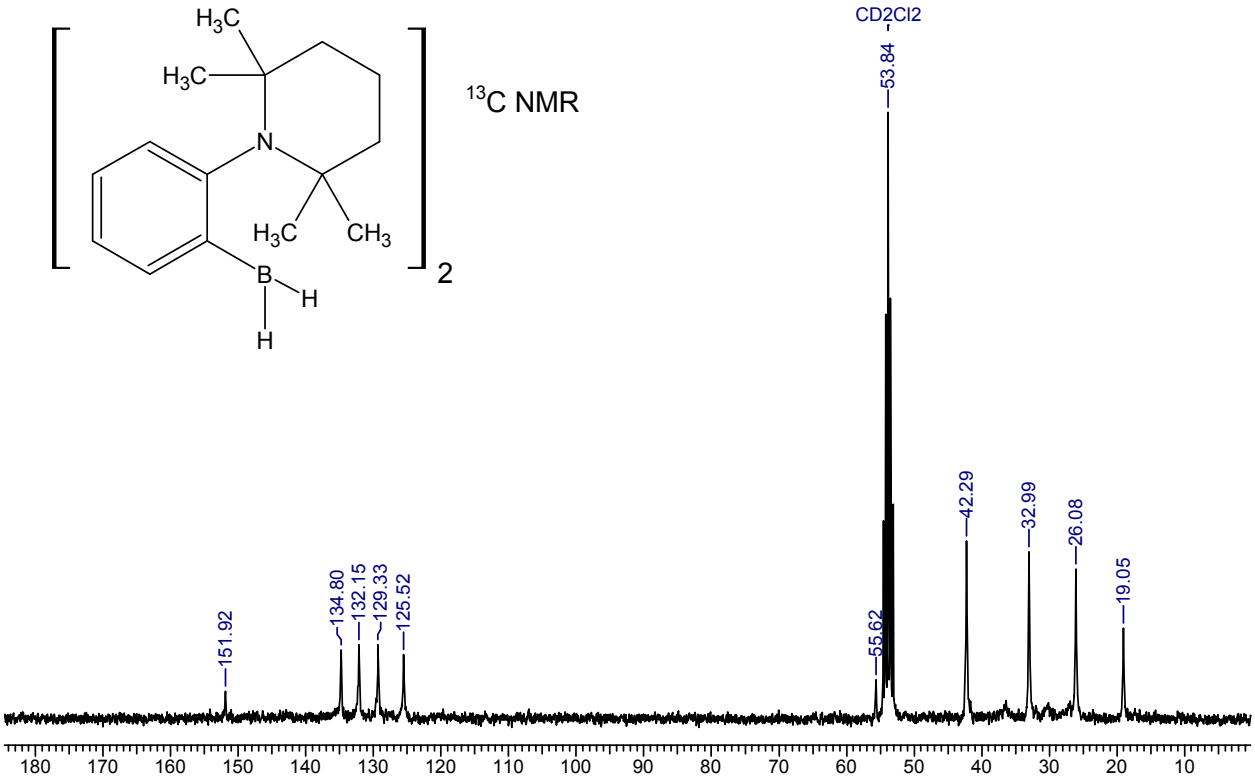


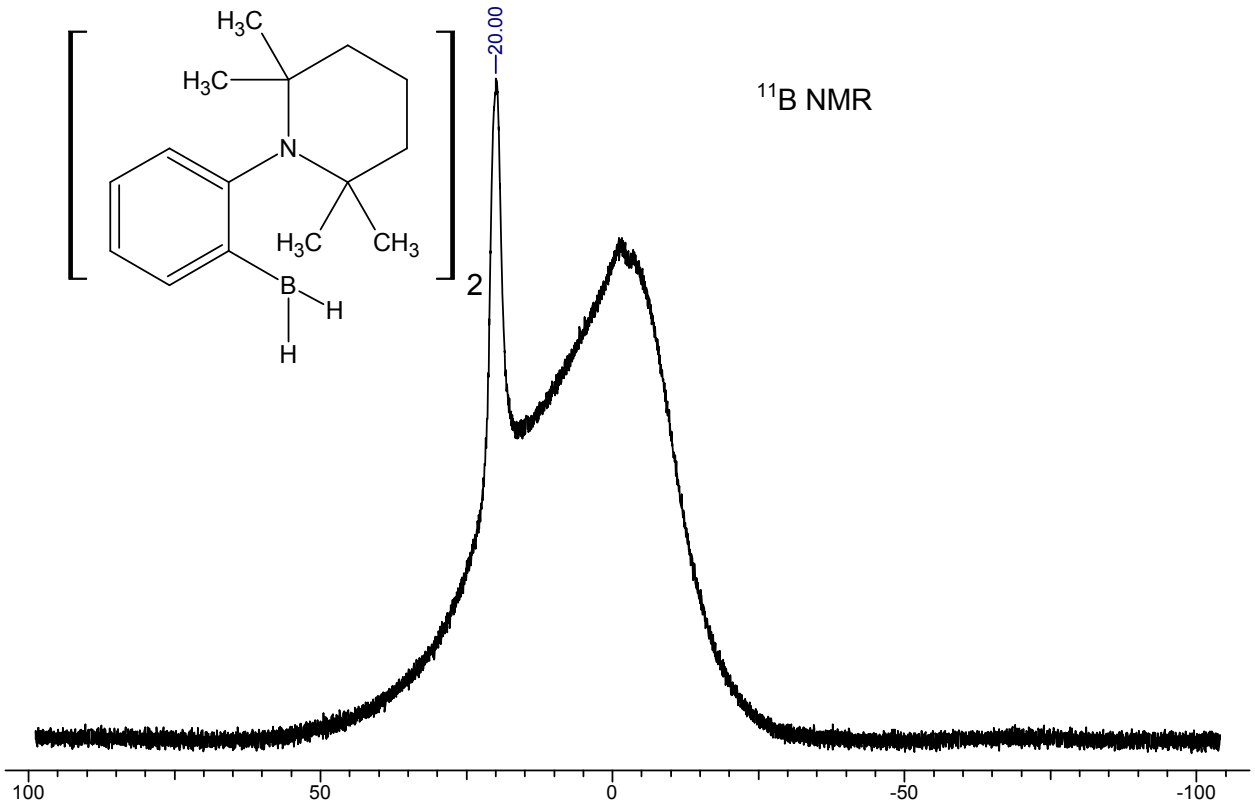

A solution of 980 mg (3.29 mmol) of dichloroborane **1c** in 7 ml of hexane was placed into a 25 ml Schlenk tube and 1100 mg of trimethylstannane (6.66 mmol) were added. A white precipitate formed instantly and the reaction became thick. The mixture was stirred for 20 min and evaporated in vacuum (1 mbar); the residue was then dried in vacuum for 1h at RT and then for 20 min at 50 °C. It was dissolved in 10 ml of hot hexane and filtered hot. The solution was evaporated in vacuum and dissolved in a hot mixture of 10 ml of hexane and 2 ml of toluene. It was filtered hot, heated to reflux and left cooling slowly for crystallization. 450 mg of the title compound were collected as white crystals. The crystallization Schlenk tubes were extracted with 5 ml of hot hexane and the extract was combined with the mother liquor left after crystallization. The combined solutions were evaporated and dissolved in 5 ml of hot hexane, filtered hot and left cooling slowly for crystallization. After cooling down to RT the solution was placed into a cooling bath (-10 °C) for 1 h. Crystals were filtered to give additional 153 mg of the title compound. Combined yield 603 mg (80.0 %).
A crystal suitable for X-ray analysis was collected from crop.

$^{1}$H (500 MHz, $CD_2Cl_2$, δ, ppm): 0.80 (br. s, 6H), 1.33 (br. s, 6H), 1.59 (m, 5H), 1.91 (br. s, 1H), 2.39 (br. s, 1H, B***H***), 5.20 (partially relaxed q, 1H, B***H***), 7.24 (br. s, 1H), 7.36 (br. s, 1H), 7.40 (br. s, 1H), 7.71(br. s, 1H).
$^{13}$C (75 MHz, $CD_2Cl_2$, δ, ppm, partial): 19.05, 26.08, 32.99, 42.29, 55.62, 125.52, 129.33, 132.15, 134.80, 151.92.

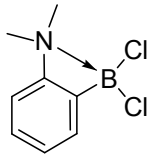
$^{11}$B (160 MHz, $CD_2Cl_2$, δ, ppm): 20.0 (br. s).
Elem. found: C, 78.73; H, 10.45; N, 6.23; calc. C, 78.61; H, 10.56; N, 6.11;






## 2-(Dichloroboryl)-*N*,*N*-dimethylaniline (2c)

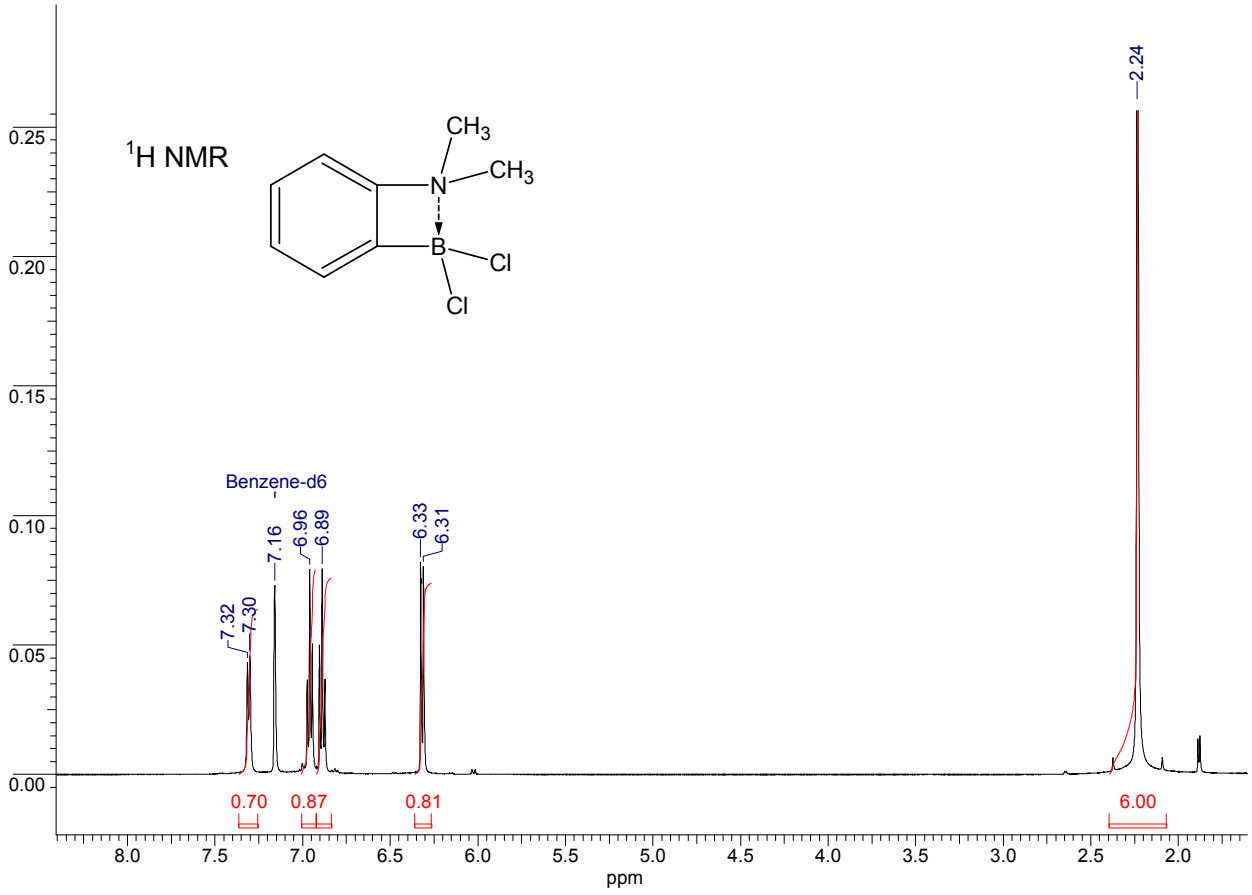


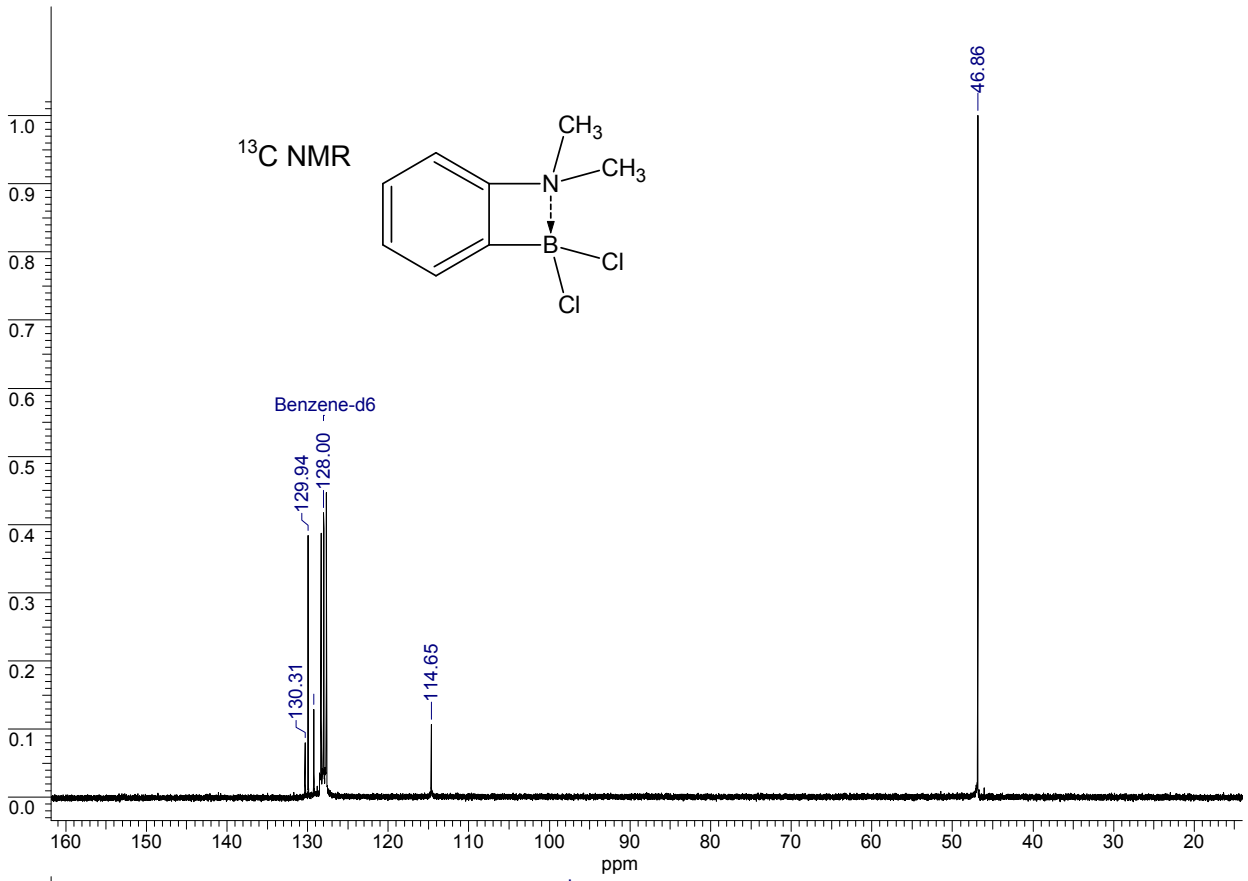

Into a 250 ml Schlenk tube, 20.4 g of *N*,*N*-dimethylaniline (168 mmol), 930 mg of *N,N,N′,N′*-tetramethylethylenediamine (5 mol%), 100 ml of of 1.6 M BuLi (160 mmol) in hexane or cyclohexane were placed and heated for 36 h at 70-75 °C. After cooling to room temperature, the solution was evaporated to half of the volume and the precipitate was filtered and washed with hexane (50 ml), giving after drying in vacuum 17.5 g (86 %) of crude 2-(dimethylamino)phenyllithium. The product can be recrystallized from 50 ml of toluene giving 7.85 g of analytically pure compound. Further mother liquor evaporation and recrystallization from toluene-hexane mixture (10 + 10 ml), can provide additional 7.0 g of the target compound (total yield 73%).

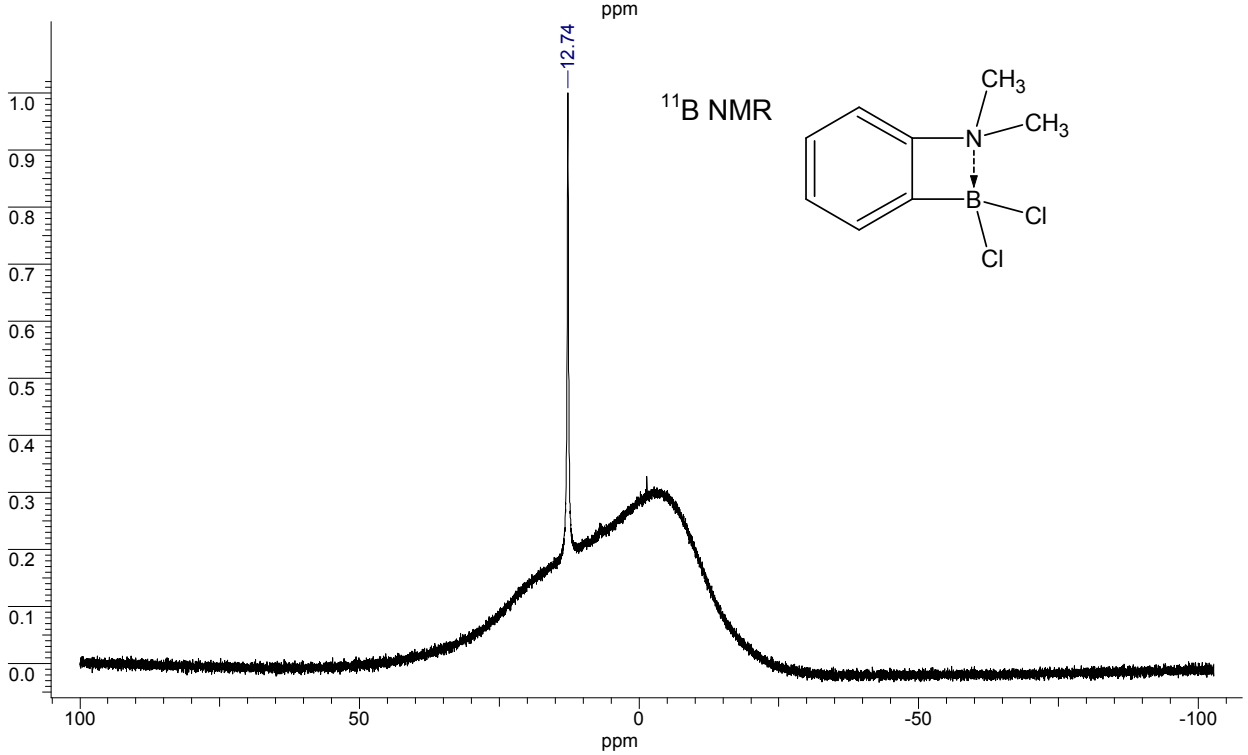
The slurry of 5 g of crude 2-(dimethylamino)phenyllithium (39.4 mmol) in 20 ml of toluene was cooled to -90 °C and was added via canula to a precooled to -90 °C solution of 80 ml of 1 M $BCl_3$ in 80 ml of hexane and 40 ml of toluene in a 250 ml Schlenk tube. The Schlenk tube containing originally organolithium was washed with additional 5 ml toluene that were transferred to the reaction mixture. The cooling bath was removed and the reaction was allowed to warm to room temperature naturally (3 h). The solvent was evaporated in vacuum reducing the volume to ~70 ml, then the slurry was filtered and the filter cake was washed with toluene (2 x 10 ml). The volatiles were evaporated to dryness and the solid white residue was heated at 80 °C (oil bath) in vacuum (1 mbar) for 1.5 h. The residue was recrystallized from benzene-hexane mixture (10 ml + 10 ml) and precipitate was washed with benzene (2 x 10 ml), hexane and dried, giving 2.68 g of the target compound. The mother liquor was evaporated to dryness and the semisolid residue

was washed on filter with toluene-hexane mixture (14 + 7 ml, respectively) and the residual white crystalline solid was dried (1.06 g, total 47%). Crystal suitable for XRD analysis was collected from the first crop.

$^{1}$H (500 MHz, $C_6D_6$, δ, ppm): 2.24 (s, 6 H), 6.32 (d, *J* = 7.97 Hz, 1 H), 6.89 (t, *J* = 7.80 Hz, 1 H), 6.96 (t, *J* = 7.40 Hz, 1 H), 7.31 (d, *J* = 7.14 Hz, 1 H).
$^{13}$C (75 MHz, $C_6D_6$, δ, ppm, no quaternary): 46.86, 114.65, 128.00, 129.24, 129.94, 130.31.
$^{1}$H/$^{13}$C gHSQC (500/125 MHz, $C_6D_6$, δ, ppm, F2/F1): 6.96/130.06, 6.89/129.90, 7.31/128.89, 6.31/114.59, 2.24/46.87.
$^{1}$H/$^{13}$C gHMBC (500/125 MHz, $C_6D_6$, δ, ppm, F2/F1): 2.23/152.67, 2.24/46.77, 6.32/152.63, 6.32/130.17, 6.32/143.11, 6.89/152.67, 6.89/129.05, 6.96/114.53, 7.31/129.67, 7.31/152.49.
$^{11}$B (160 MHz, $C_6D_6$, δ, ppm): 12.74 (s).
Elem. found: C, 47.47; H, 5.29; N, 6.93; calc. C, 47.59; H, 4.99; N, 6.94;

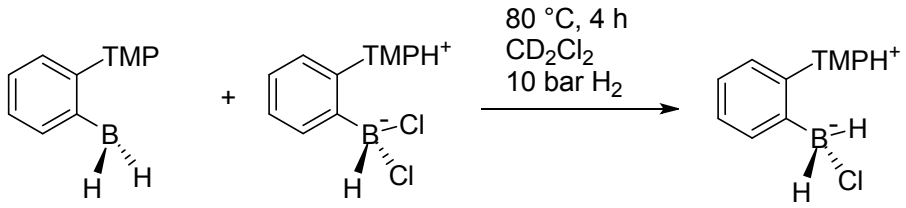



$^{13}$C NMR
CH3
CH3
N
B
Cl
Cl
Benzene-d6
46.86
129.94
128.00
130.31
114.65
ppm


$^{11}$B NMR
CH3
CH3
N
B
Cl
Cl
12.74
ppm

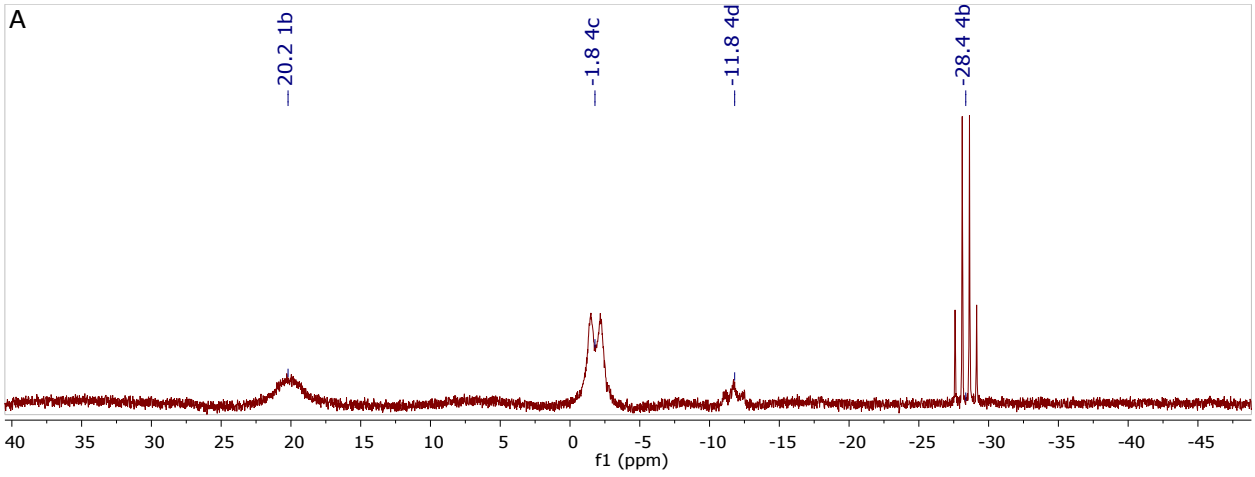
## *Studies of reactivity*

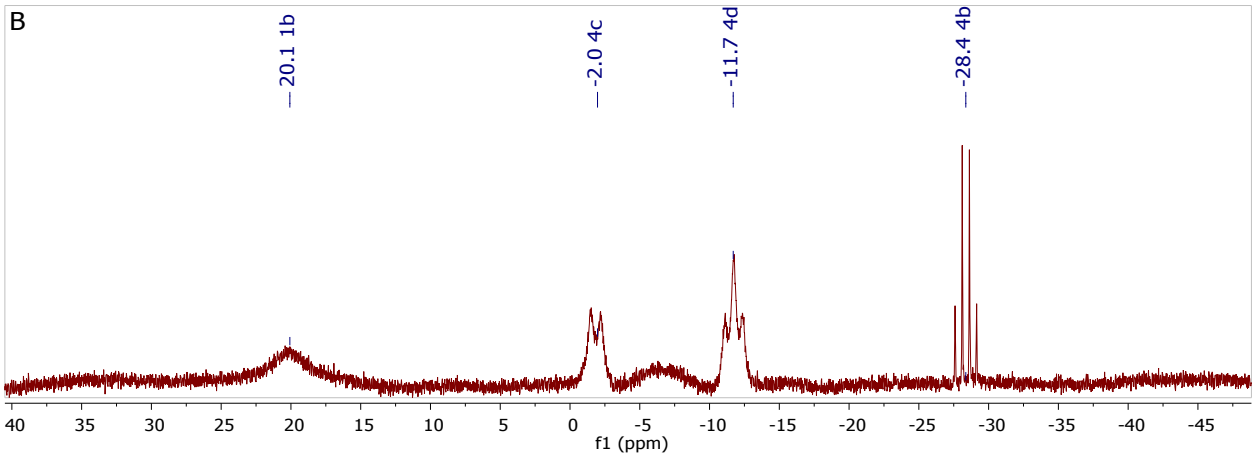
### Retrodismutation (reaction between 4c and 4b)



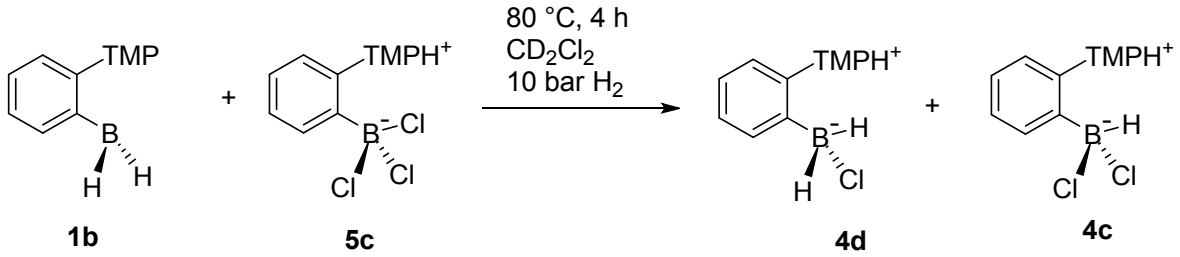

**1b** **4c** **4d**

A thick wall pressure NMR tube was charged with 15 mg of **4c** (0.05 mmol), 11 mg of **1b** (0.05 mmol as a monomer) and 0.2 ml of $CD_2Cl_2$. The NMR tube was charged with 10 bar of $H_2$ and monitored by $^{11}B$ NMR. After standing over night at room temperature minor amounts of **4d** were detected (see the $^{11}B$ spectrum A below). After heating for 4 h at 80 °C a mixture of **4d** and **4c** in a ~1.4 – 1.5 ratio was formed (see spectrum B), whereas no significant changes were observed on further heating.

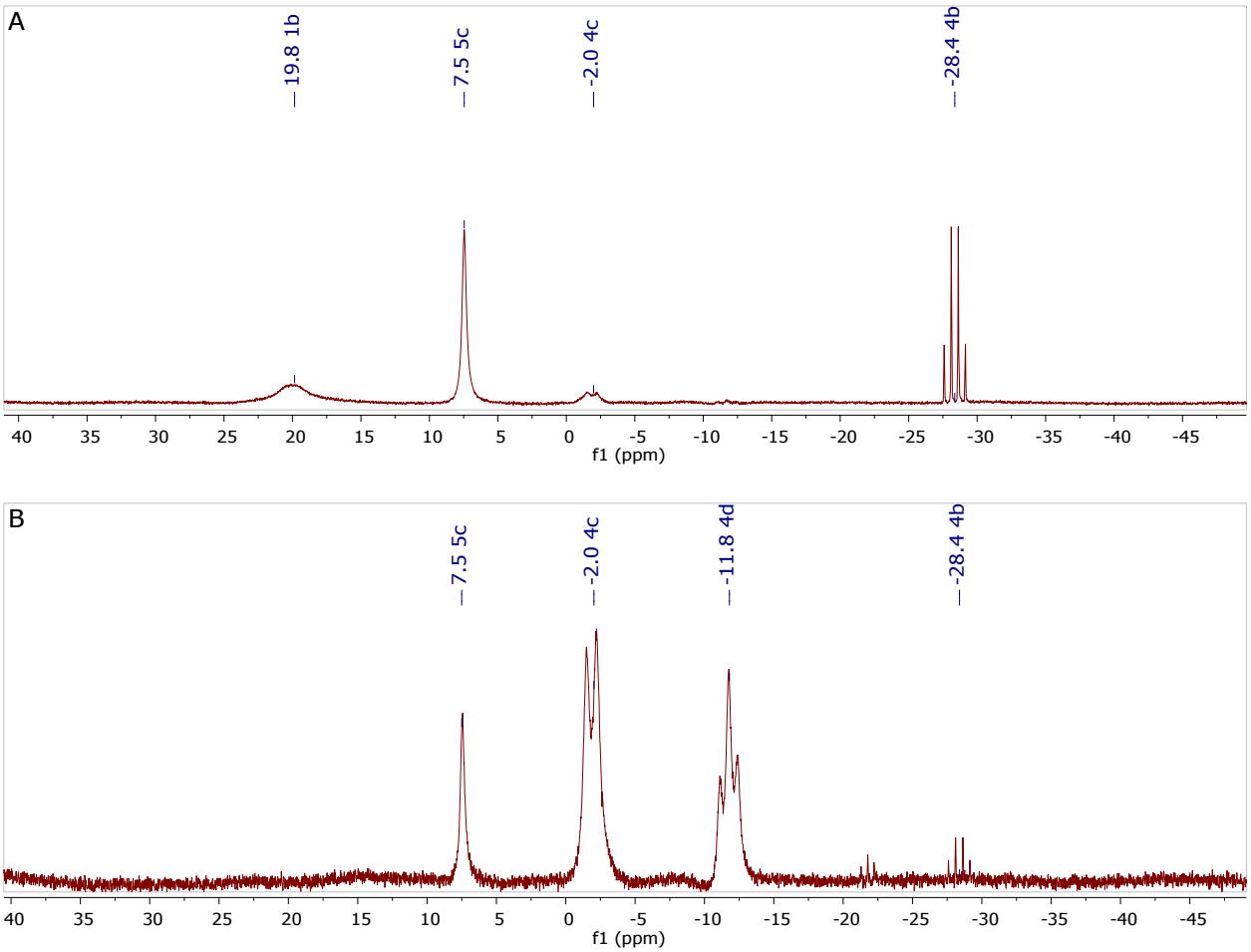


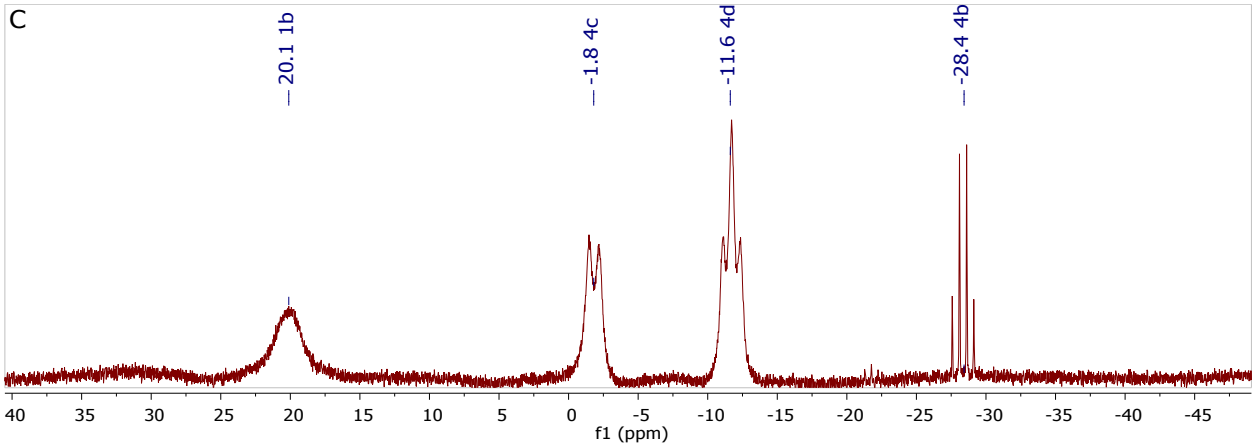




### Retrodismutation (reaction between 5c and 4b)

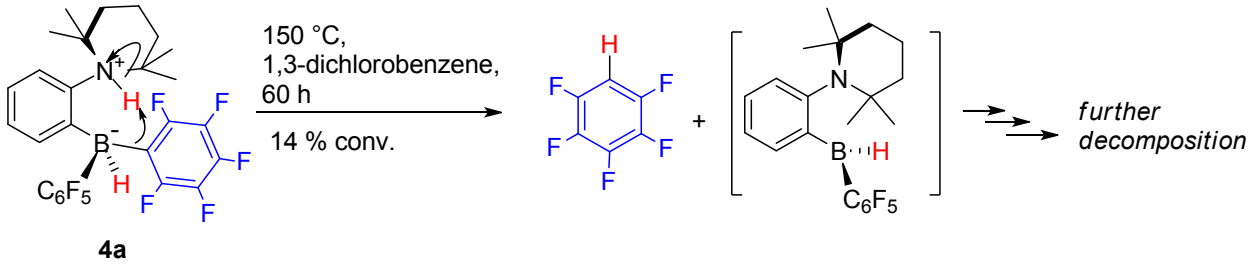



Similar to the previous experiment, the NMR tube was charged with 0.05 mmols of **1b** and **5c**, $CD_2Cl_2$ and $H_2$. **4c** was observed in minor amounts upon standing over night at room temperature ($^{11}B$ NMR spectrum A). After heating for 4 h at 80 °C **1b** and **4b** were completely consumed, producing a mixture of **5c**, **4c** and **4d** (spectrum B). Another 0.05 mmol of **1b** was added to the NMR tube and it was charged with $H_2$ again. Heating for 4 h at 80 °C resulted in complete consumption of **5c** and formation of the mixture of **1b**, **4b**, **4c** and **4d** much like in the previous experiment (spectrum C).



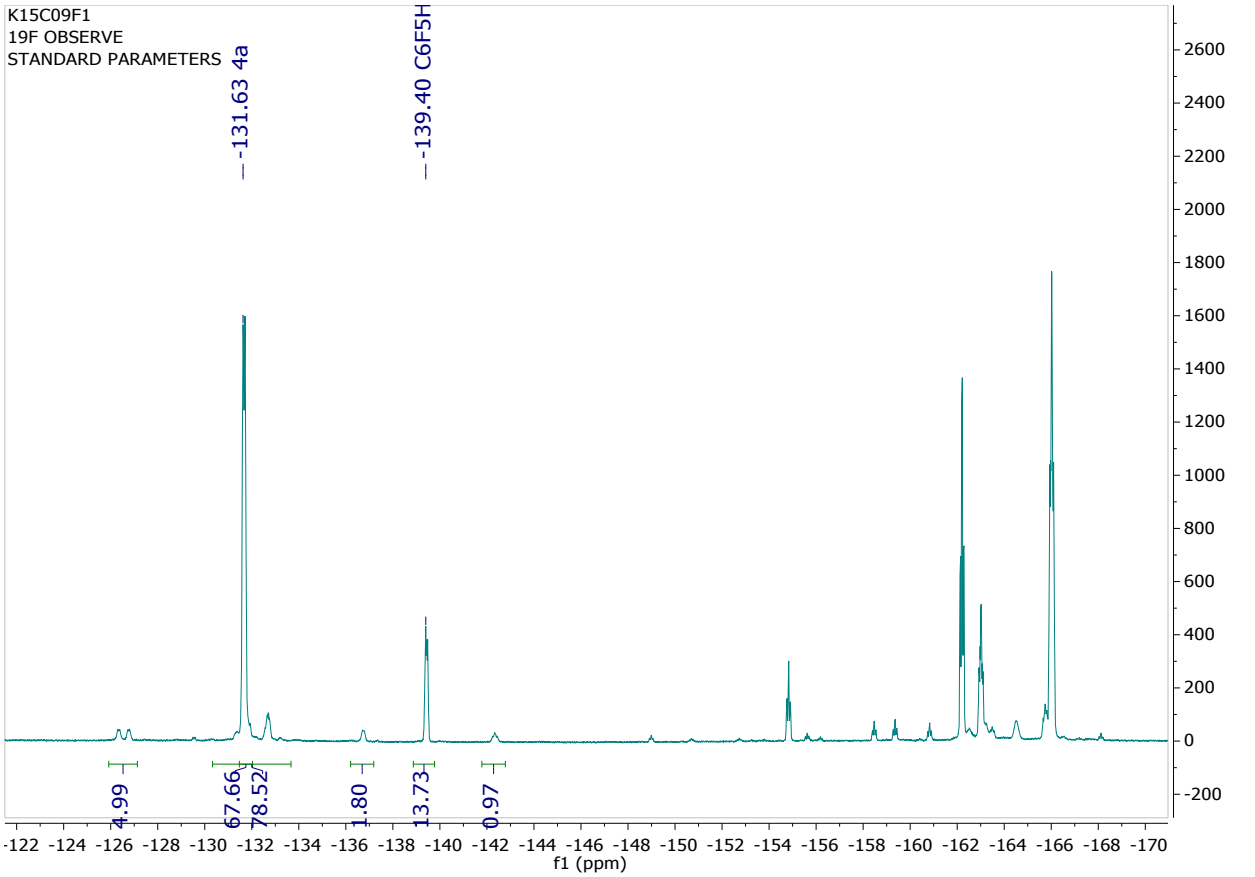



## Thermal decomposition of 4a




**4a**

**4a** (prepared as reported)[3] and 1,3-dichlorobenzene as a solvent were heated in the gas-tight NMR tube for 60 h at 150 °C. $^{19}F$ NMR analysis revealed formation of $C_6F_5H$ in ~14% yield along with novel unidentified $^{19}F$ resonanses.



## *Hydrogenation of alkynes catalyzed by 2c*

In a glovebox, 15.1 mg of aminoborane **2c** and 11.6 mg of 1,2,2,6,6-pentamethylpiperidine (0.075 mmol each) were dissolved in 1 ml of 1,2-dichloroethane. This solution was divided immediately on three equal parts and each was added into a 125 ml Schlenk tube containing 0.5 mmol of an internal alkyne. The Schlenk tube was charged with 2.2 bar of $H_2$ by three freeze-pump-thaw cycles and stirred at 100 °C on an oil bath.

The Schlenk tubes were cooled down to room temperature. The reaction mixtures were placed in the NMR tubes and analyzed by $^1$H NMR. The signal of 1,2-dichloroethane was suppressed (with the *presat* macro on Varian NMR instruments). Repetition delay between scans was set to at least 20 s for quantitative integration. The diphenylacetylene hydrogenation sample was evaporated and redissolved in benzene-$d_6$ providing good separation of the diphenylacetylene and *cis*-stilbene $^1$H NMR signals.

The benzylbutylacetylene hydrogenation sample was evaporated in vacuum, the residue was redissolved in hexane and passed through a column containing 2-3 ml of silica gel and eluted with additional volume of hexane. After evaporation of the solvent, the residue was weighted to determine the yield and analyzed by $^1$H and $^{13}$C NMR.

## *Selective 1D NOE measurements for $H_N$-$H_B$ distance determination*

Selective 1D NOE measurements were performed at 27 °C using Varian Unity Inova 500 spectrometer equipped with a 5 mm $^1$H-{X} pulsed field gradient inverse detection probe head utilizing the 1D DPFGSE-NOE pulse sequence (double pulsed field gradient spin-echo nuclear Overhauser effect)[6] using $CD_2Cl_2$ as solvent. Selective inversion of the resonance was accomplished using Gaussian 180° pulse with offset and pulse duration depending on the resonance frequency and required selectivity, respectively. The duration for hard rectangular 90° was 7.1 μs. In order to determine NOE-buildup for relevant protons, ten spectra with mixing times of 12, 20, 30, 40, 60, 100, 120, 150, 200 and 250 ms were measured for each selective excitation. The spectral width of 6000.6 Hz was covered by 12001 complex points resulting in acquisition time of 2 s. The number of transients was 64 and relaxation delay was 5 s. The FID was weighted by exponential function (line-broadening factors of 10 Hz and 2 Hz were applied for data focused in detecting $H_N$/$H_B$ and methyl signals, respectively) and was zero-filled up to 65536 complex points prior to Fourier transformation. NOE-signal intensities were obtained via integration from baseline corrected spectra (polynomial, cubic spline or segments). All 1D NOE-Spectra were processed using MestReNova 10.02 software (Mestrelab Research S.L. Santiago de Compostela, Spain).

NOE-signal intensities were scaled according to $n_An_B$, where $n_A$ and $n_B$ represent the number of chemically equivalent spins contributing to the observed NOE signal.[7, 8, 9] In addition, NOE-signal intensity was compensated for different degree of inversion by selective pulses and relaxation during DPFGSE-element. This was determined by comparing the intensities of selectively inverted signal recorded using the shortest mixing time of 12 ms.[10, 11] The inversion degree correction factors for each signal were calculated so, that their relative intensities would match the actual intensity ratio ratio observed in normal $^1$H-spectrum i.e. for instance CH vs $CH_3$ should give 1:3.

The distance $H_N$-$H_B$ in each molecule was determined by comparing cross relaxation rates (NOE-buildup rates) of $H_N$-$H_B$ system to reference system using Equation 1. Reference distances were obtained from X-ray diffraction coordinates by applying $r^{-3}$ averaging method for methyl protons[5, 12, 13] to calculate the reference distance.

$$r_{H-H} = r_{REF} \sqrt[6]{\frac{\sigma_{REF}}{\sigma_{H-H}}} \qquad \text{Eq. 1}$$

## Compound 4c

$H_N$-resonance at 8.97 ppm was selectively excited using 5950 µs selective Gaussian pulse and NOE-buildup at $H_B$-resonance (4.48 ppm) was monitored. Correspondingly, 1650 µs pulse was applied for $H_B$-resonance at 4.48 ppm and NOE-buildup at $H_N$-resonance (8.97 ppm) was monitored. These data were apodized using exponential function with 10 Hz line-broadening factor prior to Fourier transformation. For distance reference, equatorial methyl protons $Me_{7, 9}$ (1.25 ppm) were selectively inverted using 24500 µs pulse and NOE-buildup at axial $Me_{8, 10}$ (1.65 ppm) was monitored and subsequently $Me_{8, 10}$ (1.65 ppm) was excited by 25550 µs pulse and NOE-buildup at $Me_{7, 9}$ (1.25 ppm) was monitored. Reference datasets were apodized using exponential function (2 Hz line broadening factor). The correction factors for number of involved protons ($n_An_B$, see above) were 1 and 18 for $H_N/H_B$ and $Me_{7,9}/Me_{8, 10}$ (two 3x3 systems) data, respectively. Average interproton distance for $Me_7$-$Me_8$ and $Me_9$-$Me_{10}$ was 3.071 Å according to X-ray diffraction data and $r^{-3}$ averaging. Figures 1 and 2 show the NOE-buildup curves, as well as the fit of the linear function to the linear parts of the curves as well as corresponding function. Comparison of the averaged slopes between $H_N/H_B$-data and reference $Me_{7, 9}/Me_{8, 10}$-data resulted in 1.71 Å $H_N$-$H_B$-distance.

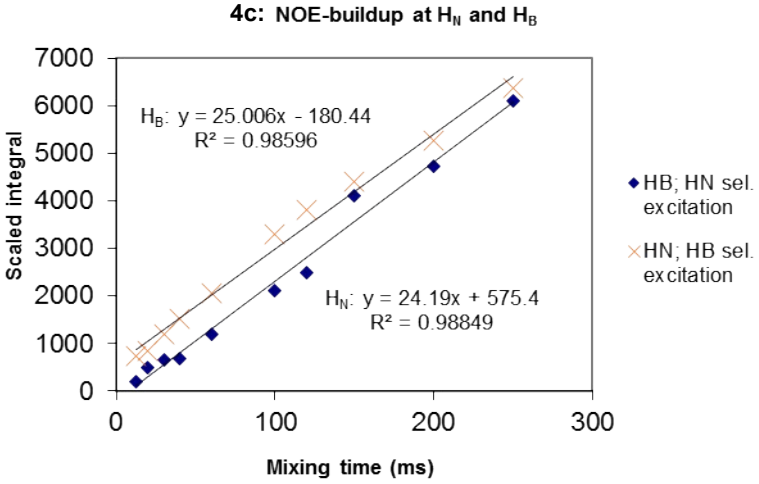



Figure 1. Compound **4c**, NOE-buildups at $H_B$ and $H_N$ (selective excitations at $H_N$ and $H_B$, respectively) to determine $H_N$-$H_B$-distance. Figure shows scaled integration results as a function of NOE-mixing time. Linear function is fitted to data in order to determine NOE-buildup rate (function, equation and $R^2$ are shown in the Figure).

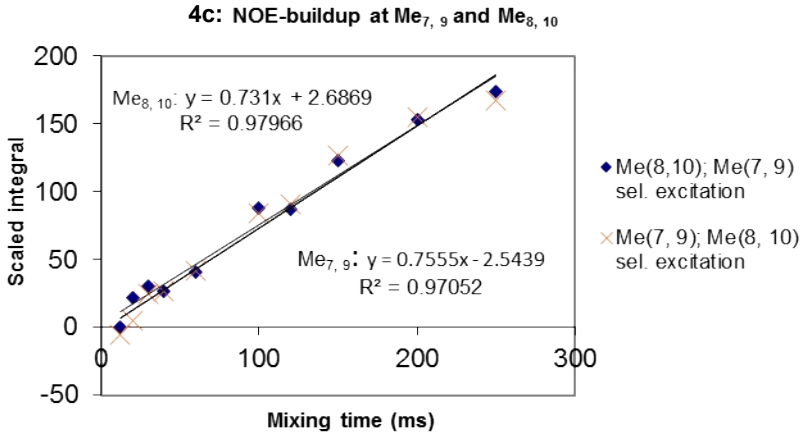



Figure 2. Compound **4c**, NOE-buildup at $Me_{8,10}$ and $Me_{7,9}$ (selective excitations at $Me_{7,9}$ and $Me_{8,10}$, respectively) to determine NOE-buildup corresponding to reference distance obtained from X-ray crystallographic data. Figure shows scaled integration results as a function of NOE-mixing time. Linear function is fitted to data in order to determine NOE-buildup rate (function, equation and $R^2$ are shown in the Figure).

## Compound 4d

$H_N$-resonance at 9.55 ppm was selectively excited using 5175 μs selective Gaussian pulse and NOE-buildup at $H_B$-resonance (3.11 ppm) was monitored. Correspondingly, 3450 μs pulse was applied for $H_B$-resonance at 3.11 ppm and NOE-buildup at $H_N$-resonance (9.55 ppm) was monitored. These data were apodized using exponential function with 10 Hz line-broadening factor prior to Fourier transformation. For distance reference, equatorial methyl protons $Me_{7,9}$ (1.20 ppm) were selectively inverted using 18400 μs pulse and NOE-buildup at axial $Me_{8,10}$ (1.61 ppm) was monitored and subsequently axial $Me_{8,10}$ (1.61ppm) was excited by 18100 μs pulse and NOE-buildup at equatorial $Me_{7,9}$ (1.20 ppm) was monitored. Reference datasets were apodized using exponential function (2 Hz line broadening factor). The correction factors for number of involved protons ($n_An_B$, see above) were as for $BHCl_2$-system. Average interproton distance for $Me_7$-$Me_8$ and $Me_9$-$Me_{10}$ was 3.113 Å according to X-ray diffraction data and $r^{-3}$ averaging. Figures 3 and 4 show the NOE-buildup curves, as well as the fit of the linear function to the linear parts of the curves as well as corresponding function. Comparison of the averaged slopes between $H_N/H_B$-data and reference $Me_{7,9}/Me_{8,10}$-data resulted in 1.87 Å $H_N$-$H_B$-distance.

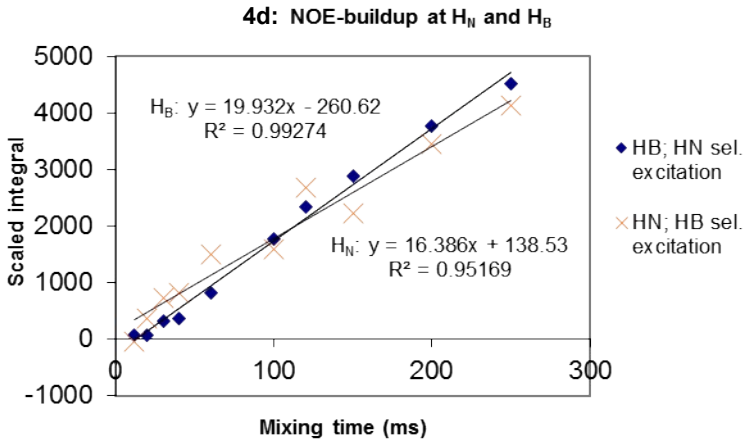



Figure 3. Compound **4d**, (NOE-buildups at $H_B$ and $H_N$ (selective excitations at $H_N$ and $H_B$, respectively) to determine $H_N$-$H_B$-distance. Figure shows scaled integration results as a function of NOE-mixing time. Linear function is fitted to data in order to determine NOE-buildup rate (function, equation and $R^2$ are shown in the Figure).

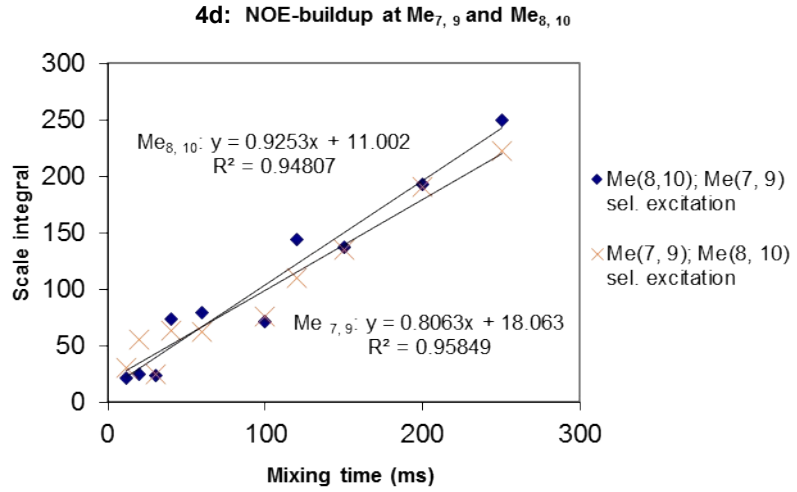



Figure 4. Compound **4d**, NOE-buildup at $Me_{8,10}$ and $Me_{7,9}$ (selective excitations at $Me_{7,9}$ and $Me_{8,10}$, respectively) to determine NOE-buildup corresponding to reference distance obtained from X-ray crystallographic data. Figure shows scaled integration results as a function of NOE-mixing time. Linear function is fitted to data in order to determine NOE-buildup rate (function, equation and $R^2$ are shown in the Figure).

## Compound 4e

$H_N$-resonance at 10.36 ppm was selectively excited using 6000 μs selective Gaussian pulse and NOE-buildup at $H_B$-resonance (4.19 ppm) was monitored. Correspondingly, 1850 μs pulse was applied for $H_B$-resonance at 4.19 ppm and

NOE-buildup at $H_N$-resonance (10.36 ppm) was monitored. These data were apodized using exponential function with 10 Hz line-broadening factor prior to Fourier transformation. In **4e**, all four methyls $Me_7$, $Me_8$, $Me_9$ and $Me_{10}$ have separate resonances. For distance reference, equatorial $Me_7$ (1.35 ppm) was selectively inverted using 29100 µs pulse and NOE-buildup at equatorial $Me_8$ (1.59 ppm) was monitored. In addition, another equatorial methyl, $Me_9$ (1.43 ppm) was excited by 29800 µs pulse and NOE-buildup at axial $Me_{10}$ (1.69 ppm) was monitored. Reference datasets were apodized using exponential function (2 Hz line broadening factor). The correction factors for number of involved protons ($n_An_B$, see above) were 1, 9 and 9 for $H_N/H_B$, $Me_7/Me_8$ and $Me_9/Me_{10}$ data, respectively. Average interproton distance for $Me_7$-$Me_8$ and $Me_9$-$Me_{10}$ was 3.058 Å according to X-ray diffraction data and $r^{-3}$ averaging. Figures 5 and 6 show the NOE-buildup curves, as well as the fit of the linear function to the linear parts of the curves as well as corresponding function. Comparison of the averaged slopes between $H_N/H_B$-data and reference datasets $Me_7/Me_8$ and $Me_7/Me_8$, resulted in 2.06 Å $H_N$-$H_B$-distance.

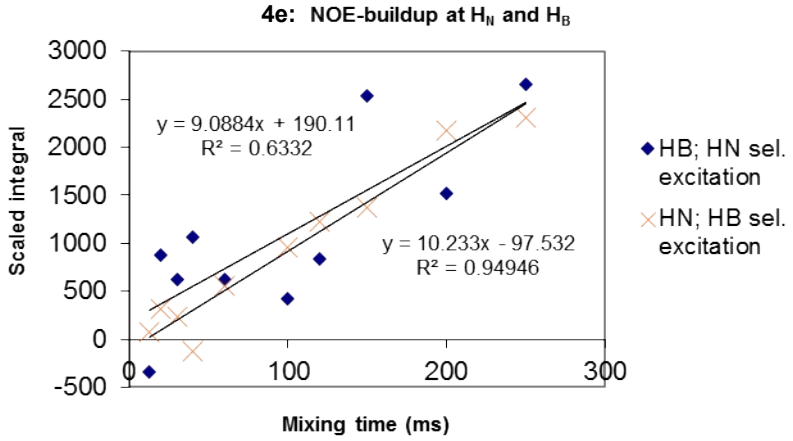



Figure 5. Compound **4e**, NOE-buildups at $H_B$ and $H_N$ (selective excitations at $H_N$ and $H_B$, respectively) to determine $H_N$-$H_B$-distance. Figure shows scaled integration results as a function of NOE-mixing time. Linear function is fitted to data in order to determine NOE-buildup rate (function, equation and $R^2$ are shown in the Figure).

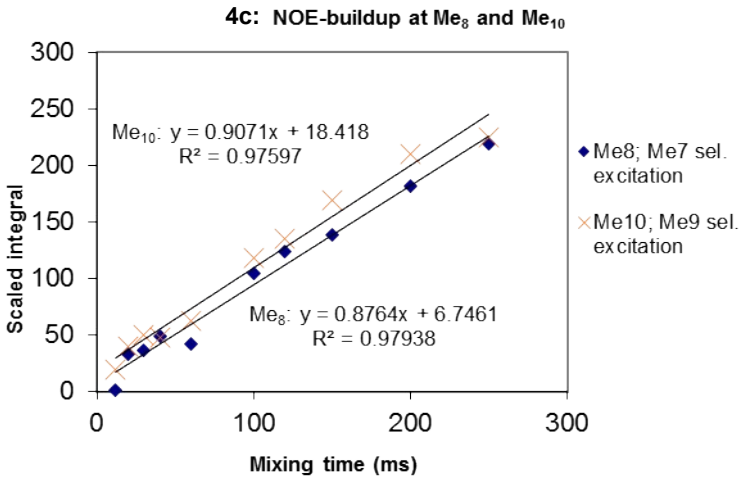



Figure 6. Compound **4e**, NOE-buildup at $Me_{8,}$ and $Me_{10}$ (selective excitations at $Me_7$ and $Me_{10}$ respectively) to determine NOE-buildup corresponding to reference distance obtained from X-ray crystallographic data. Figure shows scaled integration results as a function of NOE-mixing time. Linear function is fitted to data in order to determine NOE-buildup rate (function, equation and $R^2$ are shown in the Figure).

## Compound 4a

$H_N$-resonance at 9.22 ppm was selectively excited using 6000 µs selective Gaussian pulse and NOE-buildup at $H_B$-resonance (3.81 ppm) was monitored. Correspondingly, 2450 µs pulse was applied for $H_B$-resonance at 3.81 ppm and NOE-buildup at $H_N$-resonance (9.22 ppm) was monitored. These data were apodized using exponential function with 10 Hz line-broadening factor prior to Fourier transformation. In **4a**, two methyl resonances, equatorial $Me_{7, 9}$ and axial $Me_{8, 10}$, are close to each other (1.29 ppm and 1.38 ppm, respectively), and thus utilizing selective excitation for one of these, while monitoring NOE-buildup at another is not practical because close-by resonance will be affected by the selective pulse. Therefore, $H_N$-$Me_{8, 10}$ distance was chosen as distance reference, and corresponding NMR-data was obtained by selective inversion of $H_N$-resonance at 9.22 ppm and monitoring NOE-buildup at axial $Me_{8, 10}$-resonance (1.38 ppm). Reference datasets were apodized using exponential function (2 Hz line broadening factor). The correction factors for number of involved protons ($n_An_B$, see above) were 1 and 6 for $H_N/H_B$ and $H_N/Me_{8, 10}$ (two 1x3 systems) data, respectively. Average interproton distance for $H_N$-$Me_8$ and $H_N$-$Me_{10}$ was 2.603 Å according to X-ray diffraction data and $r^{-3}$ averaging. Figures 7 and 8 show the NOE-buildup curves, as well as the fit of the linear function to the linear parts of the curves as well as corresponding function. Comparison of the averaged slopes between $H_N/H_B$-data and reference datasets $H_{N,}/Me_8$ and $H_{N,}/Me_8$, resulted in 1.61 Å $H_N$-$H_B$-distance.

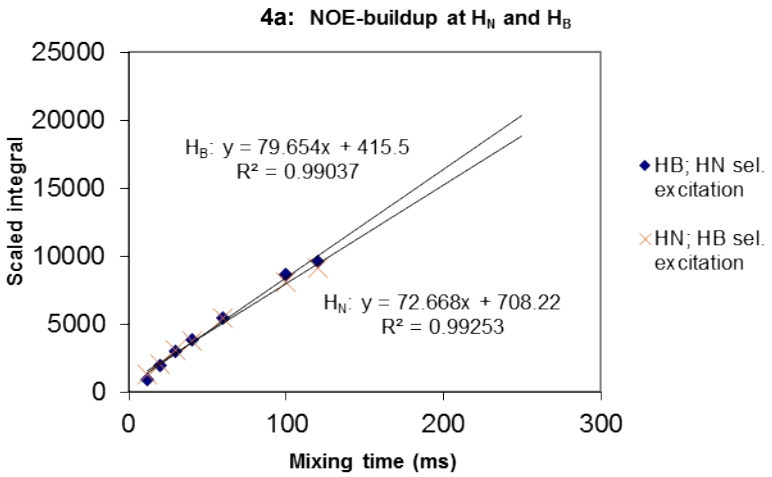



Figure 7. Compound **4a**, NOE-buildups at $H_B$ and $H_N$ (selective excitations at $H_N$ and $H_B$, respectively) to determine $H_N$-$H_B$-distance. Figure shows scaled integration results as a function of NOE-mixing time. Linear function is fitted to data in order to determine NOE-buildup rate (function, equation and $R^2$ are shown in the Figure).

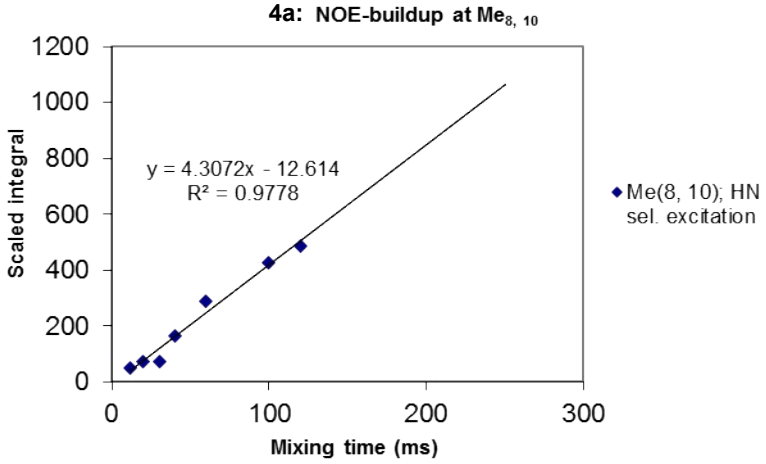



Figure 8. Compound **4a**, NOE-buildup at $Me_{8, 10,}$ (selective excitation at $H_N$-resonance) to determine NOE-buildup corresponding to reference distance obtained from X-ray crystallographic data. Figure shows scaled integration results as a function of NOE-mixing time. Linear function is fitted to data in order to determine NOE-buildup rate (function, equation and $R^2$ are shown in the Figure).

## *Computational Details*

The computational analysis presented in the paper was carried out by means of DFT calculations employing the dispersion-corrected, range-separated hybrid exchange-correlation functional ωB97X-D.[14]

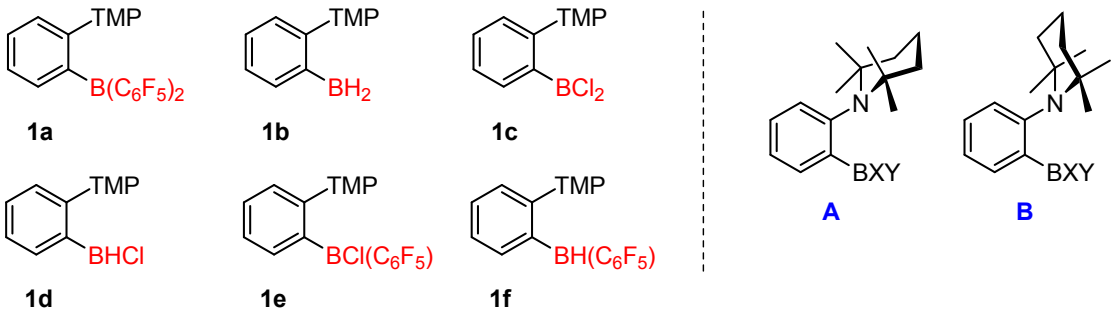
as implemented in *Gaussian 09*.[15] Geometry optimizations, vibrational analysis and calculations of solvent effects were carried out at the ωB97X-D/6311G(d,p-) level. The accuracy of electronic structure predictions was refined via additional single-point energy calculations with the larger 6-311++G(3df,3pd) basis set.[16] For numerical integrations, the ultra-fine integration grid was employed.

Transition states of the investigated elementary steps were identified from the structures of the intermediates via potential energy surface scan calculations followed by partial and subsequent full optimizations. The nature of the stationary points was characterized in terms of normal coordinate analysis. The computed harmonic frequencies were utilized to estimate the zero-point vibrational energies and also the thermal and entropic contributions to the gas-phase Gibbs free energies. The thermochemical data were obtained within the ideal gas – rigid rotor – harmonic oscillator approximation for $T$ = 298.15 K and $p$ = 1 atm. Concentration correction, corresponding to c = 1 mol/dm$^3$ in solvent phase (0.00302 a.u.), was added to Gibbs free energies. Solvent effects were computed at the ωB97X-D/6-311G(d,p) level using the integral equation formalism of the polarizable continuum model (IEFPCM).[17] The atomic radii and non-electrostatic terms in the IEFPCM calculations were taken from the SMD solvation model.[18] The solvents used in PCM calculations are toluene and dichloromethane (DCM), both used in our experiments.

The reported solution phase Gibbs free energies were obtained as a combination of ωB97X-D/6-311++G(3df,3pd) electronic energies and all additional terms computed at the ωB97X-D/6-311G(d,p) level (see Table C2 below).

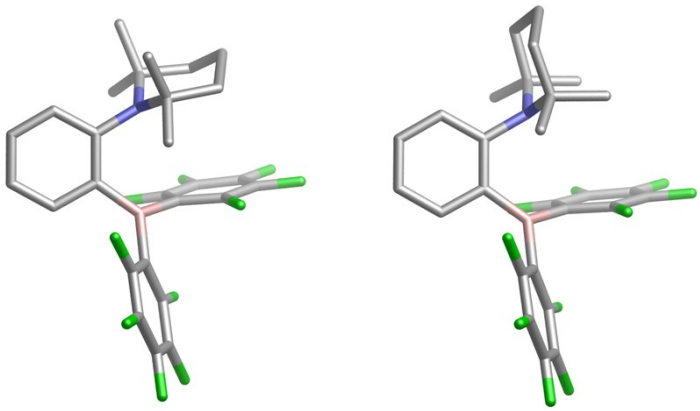
## Isomeric forms of aminoboranes 1a-1f

Various isomeric forms – open (unquenched), datively bound (covalent B-N bonds), and dimeric structures (with B-H-B bridges) – of *ortho*-phenylene-bridged aminoboranes TMP-$C_6H_4$-BXY (X, Y = H, Cl and $C_6F_5$) were examined computationally. The notation used in the main text for the entire series is shown in Scheme C1. For each possible isomer, we considered two structures differing in the conformation of the piperidine ring. In structure A, the phenyl group that connects the active sites of the FLP is in equatorial position of the ring, whereas in structure B, it is in axial position. In this section, we present the most stable structures identified computationally for the **1a-1f** series.




**Scheme C1**: Aminoboranes TMP-$C_6H_4$-BXY.

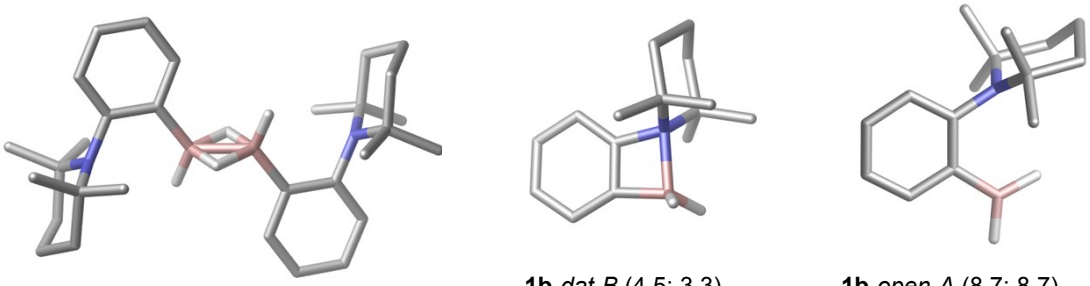
Aminoborane **1a** represents the bulkiest species in the series. Steric congestion in this molecule does not allow the formation of dative C-N bond, so only the open isomer could be located. Computations predict the A form to be more favored over the B conformer (see Figure C1).



**1a**-*open-A* (0.0) **1a**-*open-B* (2.4; 2.4)

**Figure C1**: Two conformers of aminoborane **1a** characterized computationally. Relative stabilities are given in parenthesis (in kcal/mol; with respect to the most stable form). The two numbers refer to two different solvents used in PCM calculations (toluene and DCM). Color code for atoms: C – gray, N – blue, B – pink, F – green. CH hydrogens are omitted for clarity.

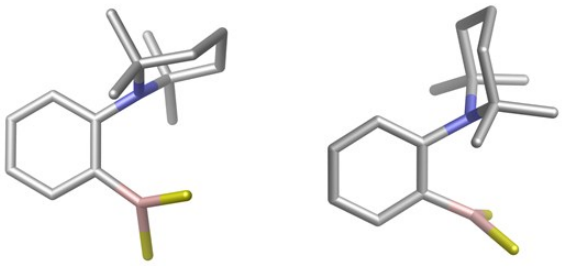
On the contrary, aminoborane **1b** has the smallets possible boryl site. The isomeric forms of this FLP have been described in our previous study.[19] Figure C2 display the most stable dimeric, datively bound and open structures. Among these isomers, the (**1b**)$_2$-*trans* dimeric structure is found the be the most stable form.



(**1b**)$_2$-*trans* (0.0) **1b**-*dat-B* (4.5; 3.3) **1b**-*open-A* (8.7; 8.7)

**Figure C2**: The most stable isomeric forms of aminoborane **1b** characterized computationally. Relative Gibbs free energies (in kcal/mol) are shown in parenthesis and they are computed with respect to half mol of (**1b**)$_2$-*trans*. For additional notes, see Figure C1.

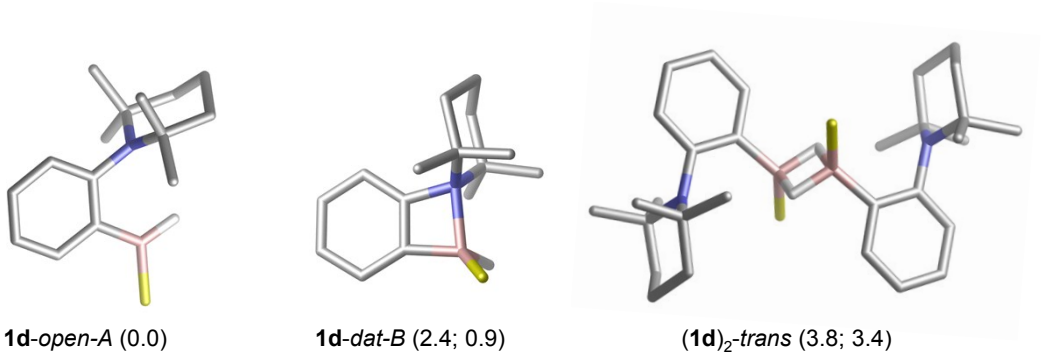
Despite the atomic chlorine substituent on the boryl unit in aminoborane **1c**, this FLP exhibits only open isomers similarly to **1a**, however, in this case the A and B forms are within 1 kcal/mol in free energy (Figure C3).



**1c**-*open-A* (0.0) **1c**-*open-B* (0.9; 0.6)

**Figure C3**: Two conformers of aminoborane **1c**. For relevant notes, see Figure C1. Color code used for Cl atoms: yellow.

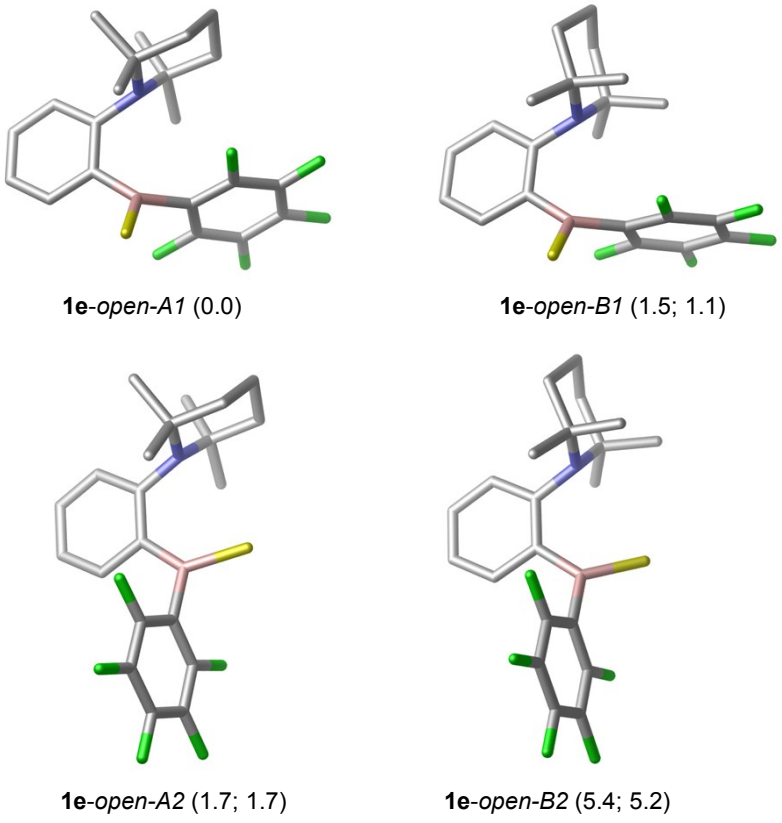
The three lowest lying structures of aminoborane **1d** are depicted in Figure C5. Although both C-N bond formation and dimerization are feasible, the open form **1d**-*open-A* is computed to be the most favored structure.



**1d**-*open-A* (0.0) **1d**-*dat-B* (2.4; 0.9) (**1d**)$_2$-*trans* (3.8; 3.4)

**Figure C4**: The most stable forms of aminoborane **1d**. For relevant notes, see Figure C1.

We located 4 different open conformers for aminoborane **1e** (two different positions of $Cl/C_6F_5$ groups in both A and B forms; see Figure C4). Among these conformers, **1e**-*open-A1* is found to be the most stable structure, but two other conformers (**1e**-*open-B1* and **1e**-*open-A2*) are fairly stable as well (they are within 2 kcal/mol relative to **1e**-*open-A1*).

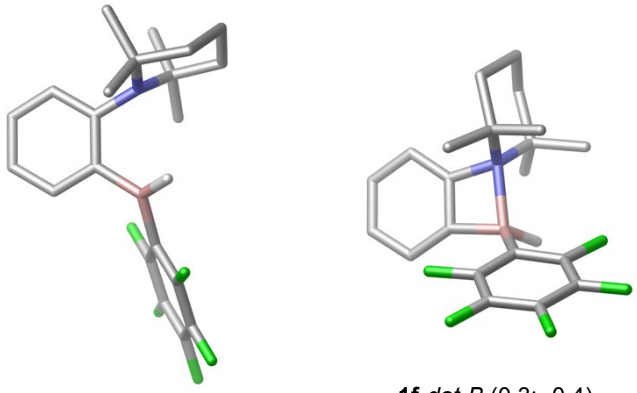


**1e**-*open-A1* (0.0) **1e**-*open-B1* (1.5; 1.1)

**1e**-*open-A2* (1.7; 1.7) **1e**-*open-B2* (5.4; 5.2)

**Figure C5**: The most stable forms of aminoborane **1e**. For relevant notes, see Figure C1.

Finally, the third FLP with mixed boryl substituents, aminoborane **1f**, is found to have their open and datively bound forms very close in free energy (see Figure C6).



**1f**-*open-A* (0.0)

**1f**-*dat-B* (0.3; -0.4)

**Figure C6**: Two conformers of aminoborane **1c** characterized computationally. For relevant notes, see Figure C1.

These results are in full agreement with our solution phase $^{11}B$ NMR observations, which indicate that all TMP-$C_6H_4$-$BX_2$ (X = H, Cl and $C_6F_5$) compounds exist only in their open forms, and also that the mixed TMP-$C_6H_4$-$BXY_2$ species exhibit equilibria between different isomeric forms.

## Gibbs free energy profiles for solvent = DCM

Calculations focusing on dihydrogen activation with aminoboranes **1a-1c** were carried out using two different solvents. The Gibbs free energy diagrams presented in the paper (Figure 2) include solvent effects obtained from PCM calculations with toluene. Results corresponding to DCM as a solvent are shown below in Figure C7.

The comparison of free energy data indicates that the computed barriers are not sensitive to the solvent (the difference is within 0.5 kcal/mol), however, the reaction free energies become significantly more favorable when using the more polarized DCM.[20] This effect has already been pointed out for the reaction with **1b** in our previous work,[19] and it was related to the zwitterionic nature of the adduct species. The stabilization effect of DCM (as compared to toluene) ranges between 2.7−6.2 kcal/mol depending on the X substituent in the TMP-$C_6H_4$-$BX_2$ aminoborane. The largest effect is found for X = Cl), and as a consequence, $H_2$ activation is predicted to be more exergonic as compared to the X = $C_6F_5$ case.

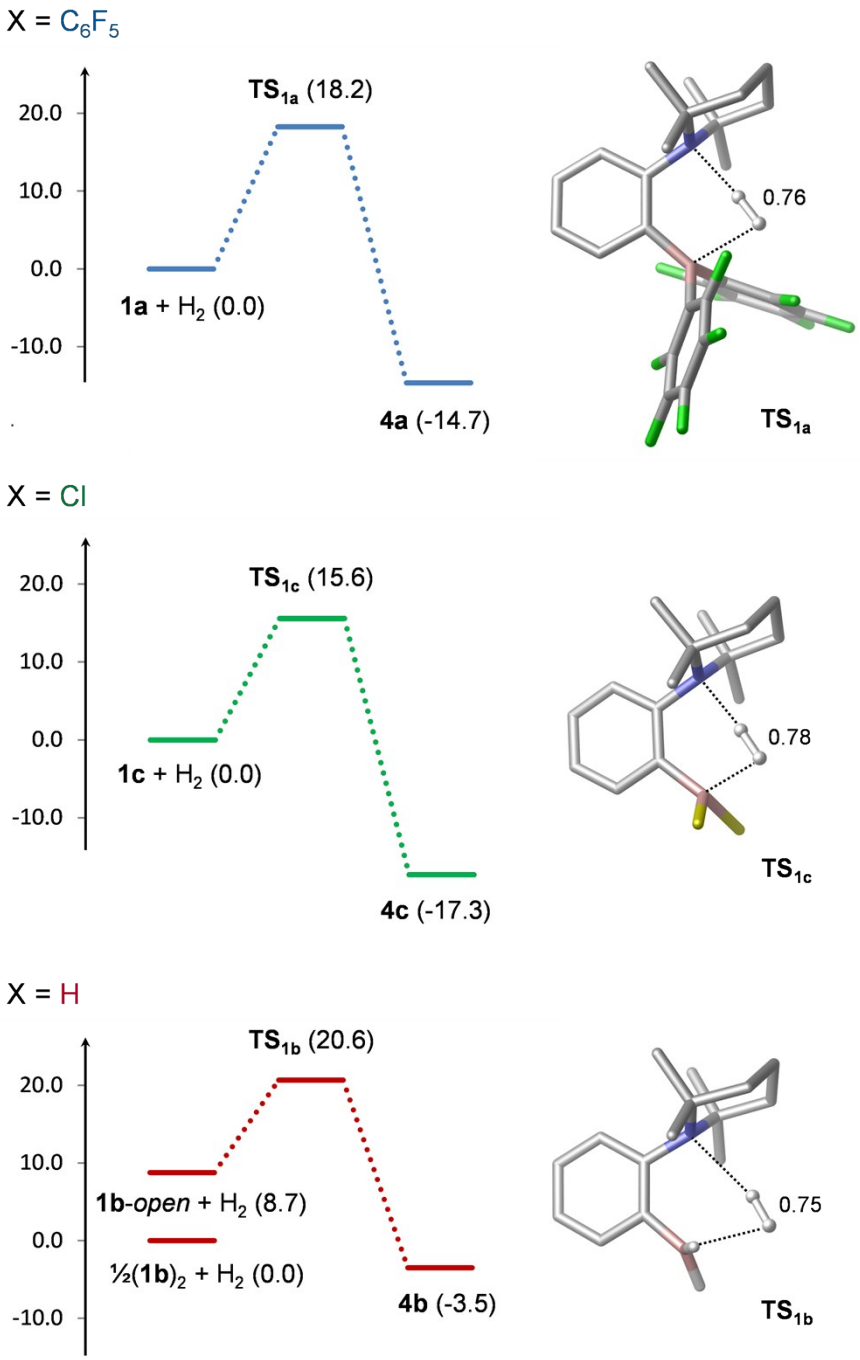



**Figure C7**: Computed Gibbs free energy profiles for dihydrogen activation by **1a**, **1b** and **1c**. Relative stabilities are given in parenthesis (in kcal/mol; with respect to separated reactants; solvent = DCM). H-H bond distances are in Å (the bond length of free $H_2$ is 0.74 Å). In TS structures, CH hydrogens are omitted for clarity.

## Energy decomposition analysis

The thermodynamics of hydrogen splitting with aminoboranes **1a**, **1c** and **1b** can be paralleled using the partitioning scheme introduced in our previous study.[21] In this procedure, the Gibbs free energy of hydrogen splitting is partitioned into five terms. Namely, $\Delta G_{HH}$ is the free energy of heterolytic dissociation of $H_2$ in toluene (constant for all FLPs); $\Delta G_{prep}$ is the amount of free energy required to the formation of the active form of the FLP; $\Delta G_{pa}$ and $\Delta G_{ha}$ are solution phase proton and hydride affinities; $\Delta G_{stab}$ is the free energy of the FLP-H$^+$ + FLP-H$^-$ → FLP + FLP-$H_2$ hypothetic reaction, which measures the intramolecular stabilizing effect. The overall reaction free energy $\Delta G$ is the sum of all these terms.

$$\Delta G = \Delta G_{HH} + \Delta G_{prep} + \Delta G_{pa} + \Delta G_{ha} + \Delta G_{stab} \quad (1)$$

The results of energy composition analysis carried out for the series of analogous reactions, namely for **1a-c** + $H_2$ → **4a-c**, are presented in Table C1. The computational methodology used in our present study is identical to that applied previously (geometry optimizations, the estimation of thermal, entropic and solvent effects we performed at M05-2X/6-31G(d) level; electronic energies obtained in single-point calculations at M05-2X/6-311++G(d,p) level). We note that this approach is not equivalent to that applied throughout our present work (here we used the ωB97X-D functional and a larger basis for single-point calculations; see Computational Details above), however, the two DFT methods give rather similar reaction free energies for the investigated reactions.[22]

**Table C1:** Partitioning of the overall Gibbs free energy of $H_2$ activation by compounds **1a**, **1c** and **1b**. [a]

| *Energy components* | **1a** | **1c** | **1b**-*open* |
|---|---|---|---|
| $\Delta G_{HH}$ | 128.8 | 128.8 | 128.8 |
| $\Delta G_{prep}$ | 0.0 | 0.0 | 5.0 |
| $\Delta G_{pa}$ | −42.9 | −47.5 | −50.3 |
| $\Delta G_{ha}$ | −55.1 | −52.3 | −33.5 |
| $\Delta G_{stab}$ | −44.2 | −38.8 | −48.5 |
| $\Delta G$ | −13.4 | −9.7 | 1.7 |

[a] Energy values in kcal/mol. For definition of free energy components and computational details, see ref. 9. The overall reaction free energy ΔG is the sum of all listed components.

As noted in the main text, aminoboranes **1a** and **1c** exists in their active open form in solution; however, the dimerization of **1b**-*open* causes reactant side stabilization ($\Delta G_{prep}$), which makes the splitting less favoured by 5 kcal/mol in this case. The energy decomposition analysis shows quite similar hydride affinities for **1c** and **1a**, but significantly lower $\Delta G_{ha}$ value for **1b**-*open*. The trend reflects the relative Lewis acidities of the parent $BX_3$ molecules (the computed hydride affinities are -72.5, -64.2 and -46.3 kcal/mol in the X = $C_6F_5$, Cl and H series). The proton affinities vary considerably in the series, which appears surprising at first sight, as the X boryl substituent is in distal position to the basic site. The N-H group of the protonated amine, however, interacts with the electron rich Cl and H substituents in **1c**$H^+$ and **1b**$H^+$ (protonated **1c** and **1b**), which provides stabilization for these protonated species (see Figure C8).[23] The last term ($\Delta G_{stab}$) is found to vary notably as well. The largest stabilization effect is obtained for **1b**, so it partially compensates the weak acidity of this compound bringing the overall thermodynamics close to neutral.These results highlight the importance of acid-base cooperativity in *ortho*-phenylene bridged FLPs.

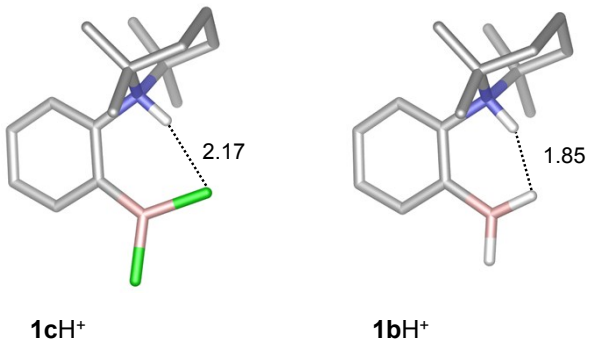



**Figure C8**: Stabilizing N-H···X interactions in protonated species **1c**$H^+$ and **1b**$H^+$. X···H bond distances are in Å.

## H/Cl exchange in DCM

The Gibbs free energy profile computed for the series of reactions shown in Scheme 5 of the paper corresponding to the more polar solvent DCM is shown in Figure C9. The obtained trends are similar to those found for toluene. The only notable difference is that the zwitterionic adduct species (**5c**, **4c**, **4d**, and **4b**) become more stable with respect to the neutral aminoboranes (**1c**, **1d** and **1b**).

The transition state identified for $H^-/Cl^-$ exchange between **1c** and **4c** is depicted in Figure C10.

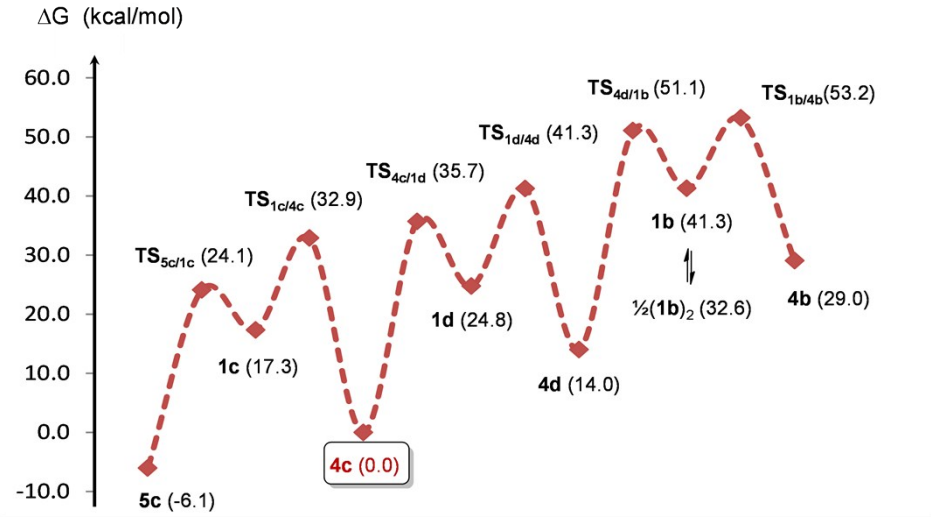
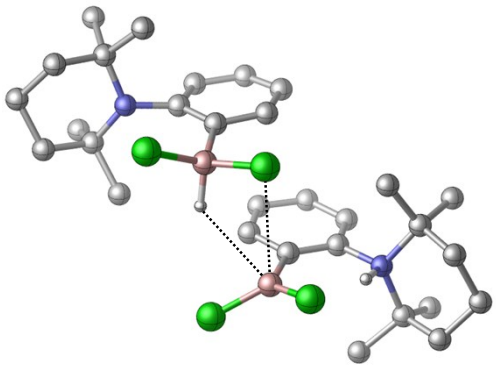



**Figure C9**: Computed Gibbs free energy profile for the series of reactions shown in Scheme 5 with solvent = DCM. The zero level of the diagram is arbitrarily chosen at 4c.

## H/Cl exchange between 1c and 4c

The transition state identified for $H^-/Cl^-$ exchange between **1c** and **4c** is depicted in Figure C10. We find that this transformation occurs in a single step via a concerted $H^-/Cl^-$ exchange. The exchange process is highly asynchronous: in $\mathbf{TS_{H/Cl}}$, the hydride transfer is almost completed, whereas the chloride transfer is only in the initial phase. The related activation barrier is fairly high ($\Delta G^{\ddagger}$ = 30.2 kcal/mol in toluene and 26.9 kcal/mol in DCM), but it is consistent with the experimental conditions (120 °C, 24 h).



$\mathbf{TS_{H/Cl}}$ (30.2; 26.9)

**Figure C10**: Geometry and Gibbs free energy of the transition state for the $H^-/Cl^-$ exchange between **1c** and **4c**. The two numbers in parenthesis refer to solvent = toluene and DCM, respectively.

## Total energy data

The energy data computed for the ωB97XD/6-311G(d,p) optimized geometries of the structures discussed in the manuscript and in the Supporting Information are listed in Table C2. Notation corresponds to that used in previous sections of the SI.

**Table C2:** Energy data (in atomic units) computed for ωB97XD/6-311G(d,p) optimized structures.[a]

| *structures* | $E_o$ | $G^o$ | $G_{sol}$ toluene | $G_{sol}$ DCM | $E_o'$ | $G$ toluene | $G$ DCM |
|---|---|---|---|---|---|---|---|
| *FLP isomers* | | | | | | | |
| **1a**-*open-A* | -2120.0069 | -2119.6222 | -2120.0199 | -2120.0259 | -2120.1882 | -2119.8135 | -2119.8196 |
| **1a**-*open-B* | -2120.0033 | -2119.6183 | -2120.0164 | -2120.0225 | -2120.1847 | -2119.8097 | -2119.8158 |
| (**1b**)$_2$-*trans* | -1331.2506 | -1330.5821 | -1331.2737 | -1331.2792 | -1331.3490 | -1330.7006 | -1330.7061 |
| **1b**-*dat-B* | -665.6100 | -665.2836 | -665.6235 | -665.6281 | -665.6591 | -665.3431 | -665.3477 |
| **1b**-*open-A* | -665.6012 | -665.2791 | -665.6125 | -665.6151 | -665.6503 | -665.3365 | -665.3391 |
| **1c**-*open-A* | -1584.9254 | -1584.6209 | -1584.9398 | -1584.9425 | -1584.9857 | -1584.6927 | -1584.6954 |
| **1c**-*open-B* | -1584.9230 | -1584.6193 | -1584.9377 | -1584.9409 | -1584.9832 | -1584.6912 | -1584.6943 |
| **1d**-*open-A* | -1125.2694 | -1124.9566 | -1125.2831 | -1125.2859 | -1125.3239 | -1125.0217 | -1125.0245 |
| **1d**-*dat-B* | -1125.2681 | -1124.9513 | -1125.2840 | -1125.2892 | -1125.3216 | -1125.0178 | -1125.0230 |
| (**1d**)$_2$-*trans* | -2250.5506 | -2249.8997 | -2250.5765 | -2250.5836 | -2250.6592 | -2250.0311 | -2250.0382 |
| **1e**-*open-A1* | -1852.4686 | -1852.1234 | -1852.4823 | -1852.4864 | -1852.5896 | -1852.2551 | -1852.2592 |
| **1e**-*open-B1* | -1852.4654 | -1852.1211 | -1852.4792 | -1852.4838 | -1852.5863 | -1852.2527 | -1852.2574 |
| **1e**-*open-A2* | -1852.4628 | -1852.1198 | -1852.4765 | -1852.4807 | -1852.5846 | -1852.2523 | -1852.2565 |
| **1e**-*open-B2* | -1852.4565 | -1852.1141 | -1852.4703 | -1852.4747 | -1852.5782 | -1852.2465 | -1852.2509 |
| **1f**-*open-A* | -1392.8048 | -1392.4524 | -1392.8178 | -1392.8221 | -1392.9213 | -1392.5789 | -1392.5832 |
| **1f**-*dat-B* | -1392.8107 | -1392.4533 | -1392.8243 | -1392.8296 | -1392.9253 | -1392.5785 | -1392.5838 |
| *$H_2$ activation* | | | | | | | |
| $H_2$ | -1.1761 | -1.1775 | -1.1757 | -1.1758 | -1.1766 | -1.1746 | -1.1747 |
| **$TS_{1a}$** | -2121.1682 | -2120.7682 | -2121.1811 | -2121.1865 | -2121.3500 | -2120.9598 | -2120.9652 |
| **4a** | -2121.2171 | -2120.8089 | -2121.2371 | -2121.2475 | -2121.3985 | -2121.0073 | -2121.0176 |
| **$TS_{1c}$** | -1586.0897 | -1585.7693 | -1586.1055 | -1586.1093 | -1586.1491 | -1585.8415 | -1585.8452 |
| **4c** | -1586.1313 | -1585.8029 | -1586.1584 | -1586.1711 | -1586.1893 | -1585.8850 | -1585.8976 |
| **$TS_{1b}$** | -666.7705 | -666.4347 | -666.7814 | -666.7840 | -666.8200 | -666.4922 | -666.4948 |
| **4b** | -666.8017 | -666.4559 | -666.8221 | -666.8327 | -666.8512 | -666.5227 | -666.5333 |
| *H/Cl exchange*[b] | | | | | | | |
| HCl | -460.8139 | -460.8250 | -460.8178 | -460.8196 | -460.8199 | -460.8319 | -460.8337 |
| **5c** + 3$H_2$ | -2049.3165 | -2049.0015 | -2049.3408 | -2049.3521 | -2049.3818 | -2049.0791 | -2049.0904 |
| **$TS_{5c/1c}$** + 3$H_2$ | -2049.2684 | -2048.9641 | -2049.2846 | -2049.2891 | -2049.3380 | -2049.0378 | -2049.0423 |
| **1c** + 3$H_2$ + HCl | -2049.2675 | -2048.9783 | -2049.2847 | -2049.2896 | -2049.3355 | -2049.0483 | -2049.0532 |
| **$TS_{1c/4c}$** + 2$H_2$ + HCl | -2049.2558 | -2048.9492 | -2049.2747 | -2049.2805 | -2049.3223 | -2049.0225 | -2049.0283 |
| **4c** + 2$H_2$ + HCl | -2049.2974 | -2048.9829 | -2049.3276 | -2049.3424 | -2049.3624 | -2049.0660 | -2049.0808 |
| **$TS_{4c/1d}$** + 2$H_2$ + HCl | -2049.2517 | -2048.9432 | -2049.2706 | -2049.2766 | -2049.3194 | -2049.0178 | -2049.0238 |
| **1d** + 2$H_2$ + 2HCl | -2049.2494 | -2048.9615 | -2049.2700 | -2049.2767 | -2049.3170 | -2049.0346 | -2049.0413 |
| **$TS_{1d/4d}$** + $H_2$ + 2HCl | -2049.2376 | -2048.9320 | -2049.2587 | -2049.2658 | -2049.3044 | -2049.0079 | -2049.0150 |
| **4d** + $H_2$ + 2HCl | -2049.2716 | -2048.9581 | -2049.3029 | -2049.3182 | -2049.3376 | -2049.0432 | -2049.0584 |
| **$TS_{4d/1b}$** + $H_2$ + 2HCl | -2049.2216 | -2048.9154 | -2049.2425 | -2049.2496 | -2049.2897 | -2048.9922 | -2048.9994 |
| **1b** + $H_2$ + 3HCl | -2049.2190 | -2048.9315 | -2049.2415 | -2049.2497 | -2049.2867 | -2049.0068 | -2049.0149 |
| (**1b**)$_2$ + $H_2$ + 3HCl | -2049.2431 | -2048.9434 | -2049.2659 | -2049.2742 | -2049.3110 | -2049.0206 | -2049.0289 |
| **$TS_{1b/4b}$** + 3HCl | -2049.2121 | -2048.9097 | -2049.2347 | -2049.2428 | -2049.2799 | -2048.9879 | -2048.9960 |
| **4b** + 3HCl | -2049.2434 | -2048.9308 | -2049.2754 | -2049.2915 | -2049.3111 | -2049.0184 | -2049.0345 |
| **$TS_{H/Cl}$** | -3171.0266 | -3170.3690 | -3171.0700 | -3171.0907 | -3171.1468 | -3170.5296 | -3170.5502 |

[a] Notation: $E_o$ and $E_o'$ refer to electronic energies computed at ωB97XD/6-311G(d,p) and ωB97XD/6-311++G(3df,3pd) level of DFT; $G^o$ and $G_{sol}$ denote gas-phase and solution-phase Gibbs free energies obtained from ωB97XD/6-311G(d,p) calculations. The last two columns are obtained as $G = E_o' + (G^o - E_o) + (G_{sol} - E_o) + 0.00302$ and the relative energies discussed in the manuscript and in the SI are obtained from these values. The value 0.00302 a.u. corresponds to concentration correction to the free energy when switching from p = 1 atm (ideal gas standard state) to c = 1mol/dm$^3$ (standard concentration in solution phase). [b] The stoichiometry is maintained by adding the appropriate number of $H_2$ and HCl molecules.

The total energy data related to the energy partitioning scheme are listed in Table C3. Energy data are computed for the M05-2X/6-31G(d) optimized geometries, single-point energies are from M05-2X/6-311++G(d,p) calculations.

**Table C3:** Energy data (in atomic units) computed for M05-2X/6-31G(d) optimized structures.[a]

| *structures* | $E_o$ | $G^o$ | $G_{sol}$ toluene | $E_o'$ | $G$ toluene |
|---|---|---|---|---|---|
| $H_2$ | -1.1637 | -1.1649 | -1.1607 | -1.1691 | -1.1642 |
| $H^-$ | -0.4482 | -0.4582 | -0.5434 | -0.5253 | -0.6275 |
| $H^+$ | 0.0000 | -0.0100 | -0.3245 | 0.0000 | -0.3315 |
| **1a** | -2119.8755 | -2119.4847 | -2119.8570 | -2120.4920 | -2120.0798 |
| **4a** | -2121.0713 | -2120.6556 | -2121.0581 | -2121.6972 | -2121.2654 |
| **1aH**$^-$ | -2120.5540 | -2120.1573 | -2120.5603 | -2121.1886 | -2120.7951 |
| **1aH**$^+$ | -2120.2651 | -2119.8592 | -2120.2786 | -2120.8750 | -2120.4796 |
| **1c** | -1584.8145 | -1584.5044 | -1584.8051 | -1585.0482 | -1584.7258 |
| **4c** | -1586.0063 | -1585.6715 | -1586.0040 | -1586.2456 | -1585.9055 |
| **1cH**$^-$ | -1585.4826 | -1585.1655 | -1585.5125 | -1585.7268 | -1585.4366 |
| **1cH**$^+$ | -1585.2040 | -1584.8798 | -1585.2279 | -1585.4362 | -1585.1329 |
| (**1b**)$_2$-*trans* | -1331.1478 | -1330.4660 | -1331.1239 | -1331.4832 | -1330.7746 |
| **1b**−*open−A* | -665.5541 | -665.2258 | -665.5432 | -665.7215 | -665.3792 |
| **4b** | -666.7343 | -666.3833 | -666.7297 | -666.9076 | -666.5489 |
| **1bH**$^-$ | -666.1879 | -665.8539 | -666.2172 | -666.3679 | -666.0601 |
| **1bH**$^+$ | -665.9494 | -665.6048 | -665.9729 | -666.1149 | -665.7908 |

[a] Notation: $E_o$ and $E_o'$ refer to electronic energies computed at M05-2X/6-31G(d) and M05-2X/6-311++G(d,p) level of DFT; $G^o$ and $G_{sol}$ denote gas-phase and solution-phase Gibbs free energies obtained from M05-2X/6-31G(d) calculations. The last column is obtained as $G = E_o' + (G^o - E_o) + (G_{sol} - E_o) + 0.00302$ and the relative energies discussed in the manuscript and in the SI are obtained from these values. The value 0.00302 a.u. corresponds to concentration correction to the free energy when switching from p = 1 atm (ideal gas standard state) to c = 1mol/dm$^3$ (standard concentration in solution phase).

## Cartesian coordinates of the optimized geometries

Cartesian coordinates optimized geometries are given below in standard XYZ format (units are in Å). First line indicates total number of atoms, second line shows the notation of the molecule (as defined above, see also Table S1). The structures are listed in the order as they appear in Tables C2 nd C3.

Geometries Optimized at ωB97XD/6-311G(d,p) level:

61
**1a**-*open-A*

| | | | |
|---|---|---|---|
| B | -0.6629650 | -0.2357070 | 0.4879430 |
| C | -0.0296490 | -1.5446750 | 1.0412210 |
| C | -0.8106920 | -2.2670490 | 1.9579710 |
| H | -1.7967160 | -1.8948260 | 2.2174470 |
| C | -0.3574040 | -3.4274700 | 2.5611740 |
| H | -0.9741930 | -3.9465390 | 3.2851730 |
| C | 0.8839930 | -3.9290980 | 2.1992420 |
| H | 1.2459300 | -4.8565660 | 2.6292440 |
| C | 1.6607880 | -3.2553560 | 1.2675850 |
| H | 2.6104450 | -3.6784900 | 0.9724360 |
| C | 1.2473440 | -2.0483090 | 0.6980960 |
| N | 2.0808650 | -1.3453390 | -0.2253810 |
| C | 3.4205300 | -0.8992260 | 0.2639370 |
| C | 3.8085660 | 0.3200110 | -0.5901930 |
| H | 3.0841380 | 1.1158210 | -0.3886630 |
| H | 4.7899390 | 0.6831350 | -0.2689450 |
| C | 3.8153780 | 0.0095460 | -2.0813580 |
| H | 4.6039140 | -0.7132190 | -2.3154800 |
| H | 4.0531900 | 0.9128010 | -2.6505190 |
| C | 2.4552280 | -0.5206910 | -2.5145610 |
| H | 2.4833370 | -0.8359420 | -3.5626260 |
| H | 1.7281940 | 0.2928540 | -2.4526190 |
| C | 1.9308010 | -1.6952290 | -1.6677990 |
| C | 2.6318060 | -3.0127780 | -2.0688390 |
| H | 2.2890410 | -3.3224910 | -3.0598380 |
| H | 2.3804070 | -3.8134200 | -1.3689000 |
| H | 3.7152510 | -2.9255210 | -2.1170210 |
| C | 0.4525450 | -1.8826960 | -2.0191160 |
| H | -0.1398900 | -1.0003990 | -1.7698110 |
| H | 0.0160130 | -2.7499020 | -1.5244560 |
| H | 0.3635950 | -2.0262260 | -3.0986730 |

| | | | |
|---|---|---|---|
| C | 4.5799380 | -1.9246240 | 0.2220010 |
| H | 4.8720450 | -2.2202140 | -0.7823000 |
| H | 4.3518090 | -2.8268570 | 0.7892010 |
| H | 5.4572130 | -1.4683350 | 0.6896510 |
| C | 3.3131960 | -0.4490740 | 1.7250500 |
| H | 2.4890380 | 0.2392890 | 1.8765770 |
| H | 4.2372010 | 0.0606230 | 2.0086140 |
| H | 3.1739790 | -1.2915880 | 2.4049810 |
| C | 0.1285340 | 1.1221610 | 0.3193140 |
| C | 0.7128520 | 1.7405200 | 1.4127740 |
| F | 0.5887520 | 1.1883460 | 2.6257220 |
| C | 1.4142150 | 2.9296680 | 1.3167300 |
| F | 1.9808320 | 3.4739320 | 2.3875050 |
| C | 1.5258920 | 3.5500490 | 0.0818640 |
| F | 2.2053880 | 4.6824630 | -0.0354880 |
| C | 0.9149230 | 2.9870420 | -1.0277990 |
| F | 1.0132030 | 3.5787440 | -2.2136260 |
| C | 0.2049740 | 1.8080740 | -0.8819360 |
| F | -0.4030940 | 1.3187260 | -1.9720430 |
| C | -2.2159580 | -0.1794400 | 0.1876500 |
| C | -2.9188510 | -1.2418420 | -0.3856790 |
| F | -2.3035590 | -2.3778980 | -0.7045910 |
| C | -4.2708590 | -1.1767930 | -0.6800780 |
| F | -4.8930250 | -2.2061690 | -1.2429680 |
| C | -4.9791990 | -0.0247160 | -0.3798280 |
| F | -6.2729280 | 0.0468510 | -0.6458630 |
| C | -4.3296090 | 1.0503040 | 0.2050570 |
| F | -5.0104280 | 2.1492780 | 0.5076770 |
| C | -2.9738310 | 0.9597570 | 0.4697200 |
| F | -2.4137880 | 2.0205620 | 1.0527060 |

61

**1a**-*open-B*

| | | | |
|---|---|---|---|
| B | -0.6745940 | -0.2290330 | 0.4832760 |
| C | 0.0861180 | -1.4504290 | 1.0574570 |
| C | -0.6274640 | -2.2650340 | 1.9551760 |
| H | -1.6618690 | -2.0232490 | 2.1767020 |
| C | -0.0476620 | -3.3513990 | 2.5833260 |
| H | -0.6159330 | -3.9474190 | 3.2874320 |
| C | 1.2668060 | -3.6782270 | 2.2772040 |
| H | 1.7354720 | -4.5428610 | 2.7342740 |
| C | 1.9809260 | -2.9123540 | 1.3693180 |
| H | 2.9936740 | -3.2010740 | 1.1246560 |
| C | 1.4251630 | -1.7829940 | 0.7595110 |
| N | 2.1617680 | -1.0031370 | -0.1935390 |
| C | 2.1721540 | -1.5741770 | -1.5860360 |
| C | 3.3634460 | -2.5360330 | -1.7700170 |
| H | 3.1994840 | -3.4234130 | -1.1476470 |
| H | 3.3784510 | -2.8843490 | -2.8080100 |
| C | 4.7010110 | -1.8957030 | -1.4113250 |
| H | 4.9406620 | -1.1038160 | -2.1281650 |
| H | 5.5039300 | -2.6330460 | -1.5003770 |
| C | 4.6752420 | -1.3339100 | 0.0070000 |
| H | 5.5875070 | -0.7602470 | 0.2027200 |
| H | 4.6830410 | -2.1631140 | 0.7220480 |
| C | 3.4603670 | -0.4233000 | 0.2964350 |
| C | 3.6875080 | 0.9584020 | -0.3578110 |
| H | 2.7366410 | 1.4719400 | -0.4875990 |
| H | 4.1776580 | 0.8997870 | -1.3281610 |
| H | 4.3269540 | 1.5696200 | 0.2834040 |
| C | 3.4089390 | -0.1706910 | 1.8103110 |
| H | 4.3419960 | 0.3124340 | 2.1092610 |
| H | 3.3102480 | -1.0840920 | 2.3951700 |
| H | 2.5872040 | 0.4904500 | 2.0809120 |
| C | 2.2279220 | -0.4647530 | -2.6525890 |
| H | 1.4771950 | 0.2972770 | -2.4533530 |
| H | 2.0092750 | -0.9030760 | -3.6298080 |
| H | 3.1954570 | 0.0226120 | -2.7334520 |
| C | 0.8775920 | -2.3449080 | -1.8623420 |
| H | 0.7109050 | -3.1690310 | -1.1683190 |

| | | | |
|---|---|---|---|
| H | 0.9299490 | -2.7592760 | -2.8716460 |
| H | 0.0082950 | -1.6851050 | -1.8223870 |
| C | -0.0207340 | 1.1872520 | 0.2574180 |
| C | 0.5489410 | 1.9013650 | 1.2981120 |
| F | 0.5491220 | 1.3852170 | 2.5327400 |
| C | 1.1055910 | 3.1565760 | 1.1241320 |
| F | 1.6603290 | 3.8025420 | 2.1438050 |
| C | 1.0834310 | 3.7378300 | -0.1345740 |
| F | 1.6225750 | 4.9344040 | -0.3238600 |
| C | 0.4943930 | 3.0656630 | -1.1954770 |
| F | 0.4730440 | 3.6179430 | -2.4035210 |
| C | -0.0663490 | 1.8202590 | -0.9733200 |
| F | -0.6433680 | 1.2000460 | -2.0130830 |
| C | -2.2278640 | -0.3286720 | 0.1985820 |
| C | -2.8163920 | -1.4385640 | -0.4083070 |
| F | -2.0791430 | -2.4857240 | -0.7741240 |
| C | -4.1708090 | -1.5096940 | -0.6897610 |
| F | -4.6858900 | -2.5787480 | -1.2859390 |
| C | -4.9944100 | -0.4510740 | -0.3420390 |
| F | -6.2916710 | -0.5094230 | -0.5956730 |
| C | -4.4574200 | 0.6669110 | 0.2764460 |
| F | -5.2489050 | 1.6750210 | 0.6232700 |
| C | -3.0966930 | 0.7129560 | 0.5269120 |
| F | -2.6398810 | 1.8047620 | 1.1428600 |

82

(**1b**)$_2$-*trans*

| | | | |
|---|---|---|---|
| B | 0.8206860 | 0.2284980 | 0.2661260 |
| H | -0.1731470 | 0.9168970 | -0.2873430 |
| H | 0.9234400 | 0.6049690 | 1.3892920 |
| C | 2.0564680 | 0.1432360 | -0.7092170 |
| C | 2.0744830 | -0.7753460 | -1.7655140 |
| H | 1.2270620 | -1.4393270 | -1.9037710 |
| C | 3.1452670 | -0.8665050 | -2.6425750 |
| H | 3.1313890 | -1.5925800 | -3.4476430 |
| C | 4.2301910 | -0.0173300 | -2.4802080 |
| H | 5.0731850 | -0.0680790 | -3.1607250 |
| C | 4.2366390 | 0.9015860 | -1.4395060 |
| H | 5.0849070 | 1.5627220 | -1.3212870 |
| C | 3.1689650 | 0.9919830 | -0.5421230 |
| N | 3.1857390 | 1.9246920 | 0.5437160 |
| C | 4.0802530 | 1.5845240 | 1.6806110 |
| C | 3.6218600 | 2.3831830 | 2.9122310 |
| H | 2.6481660 | 1.9911530 | 3.2282250 |
| H | 4.3263210 | 2.2006760 | 3.7298210 |
| C | 3.4814960 | 3.8727450 | 2.6374840 |
| H | 3.1355340 | 4.3903100 | 3.5370100 |
| H | 4.4513910 | 4.3135440 | 2.3821890 |
| C | 2.4839000 | 4.0720500 | 1.5071200 |
| H | 2.3554440 | 5.1350040 | 1.2793480 |
| H | 1.5095560 | 3.6908400 | 1.8348820 |
| C | 2.8705910 | 3.3358410 | 0.2126020 |
| C | 4.0023780 | 4.1012260 | -0.5085600 |
| H | 4.2699160 | 3.6080430 | -1.4451230 |
| H | 4.9025110 | 4.1950850 | 0.0980810 |
| H | 3.6651580 | 5.1122710 | -0.7557670 |
| C | 1.6443860 | 3.3793350 | -0.7096930 |
| H | 1.8324310 | 2.8940060 | -1.6695950 |
| H | 1.3760320 | 4.4210810 | -0.9038410 |
| H | 0.7872100 | 2.8968690 | -0.2352260 |
| C | 5.5864820 | 1.8320110 | 1.4380380 |
| H | 5.8222500 | 2.8781670 | 1.2456720 |
| H | 5.9522020 | 1.2377490 | 0.5991210 |
| H | 6.1518330 | 1.5254120 | 2.3232440 |
| C | 3.9224160 | 0.0941680 | 2.0158600 |
| H | 4.2977200 | -0.5455870 | 1.2142550 |
| H | 2.8763980 | -0.1574290 | 2.1965450 |
| H | 4.4923460 | -0.1313460 | 2.9212790 |
| B | -0.8206860 | -0.2284980 | -0.2661260 |
| H | 0.1731470 | -0.9168970 | 0.2873430 |

| | | | |
|---|---|---|---|
| H | -0.9234400 | -0.6049690 | -1.3892920 |
| C | -2.0564680 | -0.1432360 | 0.7092170 |
| C | -2.0744830 | 0.7753460 | 1.7655140 |
| H | -1.2270620 | 1.4393270 | 1.9037710 |
| C | -3.1452670 | 0.8665050 | 2.6425750 |
| H | -3.1313890 | 1.5925800 | 3.4476430 |
| C | -4.2301910 | 0.0173300 | 2.4802080 |
| H | -5.0731850 | 0.0680790 | 3.1607250 |
| C | -4.2366390 | -0.9015860 | 1.4395060 |
| H | -5.0849070 | -1.5627220 | 1.3212870 |
| C | -3.1689650 | -0.9919830 | 0.5421230 |
| N | -3.1857390 | -1.9246920 | -0.5437160 |
| C | -4.0802530 | -1.5845240 | -1.6806110 |
| C | -3.6218600 | -2.3831830 | -2.9122310 |
| H | -2.6481660 | -1.9911530 | -3.2282250 |
| H | -4.3263210 | -2.2006760 | -3.7298210 |
| C | -3.4814960 | -3.8727450 | -2.6374840 |
| H | -3.1355340 | -4.3903100 | -3.5370100 |
| H | -4.4513910 | -4.3135440 | -2.3821890 |
| C | -2.4839000 | -4.0720500 | -1.5071200 |
| H | -2.3554440 | -5.1350040 | -1.2793480 |
| H | -1.5095560 | -3.6908400 | -1.8348820 |
| C | -2.8705910 | -3.3358410 | -0.2126020 |
| C | -4.0023780 | -4.1012260 | 0.5085600 |
| H | -4.2699160 | -3.6080430 | 1.4451230 |
| H | -4.9025110 | -4.1950850 | -0.0980810 |
| H | -3.6651580 | -5.1122710 | 0.7557670 |
| C | -1.6443860 | -3.3793350 | 0.7096930 |
| H | -1.8324310 | -2.8940060 | 1.6695950 |
| H | -1.3760320 | -4.4210810 | 0.9038410 |
| H | -0.7872100 | -2.8968690 | 0.2352260 |
| C | -5.5864820 | -1.8320110 | -1.4380380 |
| H | -5.8222500 | -2.8781670 | -1.2456720 |
| H | -5.9522020 | -1.2377490 | -0.5991210 |
| H | -6.1518330 | -1.5254120 | -2.3232440 |
| C | -3.9224160 | -0.0941680 | -2.0158600 |
| H | -4.2977200 | 0.5455870 | -1.2142550 |
| H | -2.8763980 | 0.1574290 | -2.1965450 |
| H | -4.4923460 | 0.1313460 | -2.9212790 |

41

**1b**-*dat*-*B*

| | | | |
|---|---|---|---|
| C | -1.0631910 | 1.3006770 | -0.1344710 |
| N | -0.3040100 | 0.0001510 | -0.4514620 |
| C | -1.0625640 | -1.3007980 | -0.1349770 |
| C | -1.6422790 | -1.2481260 | 1.2887250 |
| C | -2.4658090 | -0.0006470 | 1.5774330 |
| C | -1.6427090 | 1.2472330 | 1.2892600 |
| C | 1.0702900 | 0.0001360 | 0.0922000 |
| C | 1.8288220 | 0.0005140 | -1.0605620 |
| C | 3.2126680 | 0.0006260 | -0.9477340 |
| C | 3.7749720 | 0.0003070 | 0.3280380 |
| C | 2.9766470 | -0.0001540 | 1.4722110 |
| C | 1.5858290 | -0.0002870 | 1.3767530 |
| B | 0.5371110 | 0.0005840 | -2.0055650 |
| C | -0.1018290 | -2.4979860 | -0.2066220 |
| C | -2.1767270 | -1.5484720 | -1.1633710 |
| C | -0.1033310 | 2.4985950 | -0.2059810 |
| C | -2.1777950 | 1.5479670 | -1.1625100 |
| H | 0.2794390 | -1.0029510 | -2.6180560 |
| H | 3.8540540 | 0.0009500 | -1.8229260 |
| H | 4.8540440 | 0.0003820 | 0.4407200 |
| H | 3.4436630 | -0.0004210 | 2.4506610 |
| H | 0.9718700 | -0.0006420 | 2.2687500 |
| H | -2.2467770 | -2.1489760 | 1.4321110 |
| H | -0.8192440 | -1.3141470 | 2.0080500 |
| H | -3.3841510 | -0.0006870 | 0.9823870 |
| H | -2.7834150 | -0.0009160 | 2.6237380 |
| H | -0.8196360 | 1.3132270 | 2.0085460 |
| H | -2.2475150 | 2.1478120 | 1.4330560 |

| | | | |
|---|---|---|---|
| H | 0.7042920 | 2.4289140 | 0.5220380 |
| H | -0.6788400 | 3.4002580 | 0.0165870 |
| H | 0.3319050 | 2.6068020 | -1.1987130 |
| H | -3.0757790 | 0.9632570 | -0.9779270 |
| H | -1.8284630 | 1.3432750 | -2.1741550 |
| H | -2.4660240 | 2.6001600 | -1.1112460 |
| H | 0.7057660 | -2.4277040 | 0.5213860 |
| H | 0.3334770 | -2.6057750 | -1.1993670 |
| H | -0.6766270 | -3.4001110 | 0.0159020 |
| H | -3.0746570 | -0.9634320 | -0.9796740 |
| H | -2.4652020 | -2.6005720 | -1.1115730 |
| H | -1.8267930 | -1.3444800 | -2.1749580 |
| H | 0.2791570 | 1.0042940 | -2.6176320 |

41

**1b**-*open-A*

| | | | |
|---|---|---|---|
| C | -1.0803060 | -1.2955990 | -0.0875870 |
| N | -0.3880020 | 0.0000980 | 0.1194860 |
| C | -1.0806610 | 1.2954590 | -0.0887460 |
| C | -2.4514340 | 1.2365410 | 0.6063610 |
| C | -3.2573620 | -0.0002740 | 0.2405450 |
| C | -2.4510340 | -1.2364550 | 0.6075800 |
| C | 1.0260680 | 0.0000630 | -0.0704390 |
| C | 1.8858030 | 0.0008470 | 1.0565450 |
| C | 3.2733380 | 0.0008240 | 0.8368280 |
| C | 3.8181040 | -0.0000890 | -0.4383230 |
| C | 2.9645130 | -0.0009880 | -1.5322320 |
| C | 1.5858430 | -0.0009050 | -1.3485050 |
| B | 1.3779350 | 0.0015040 | 2.5143620 |
| C | -1.2640850 | 1.7033410 | -1.5674230 |
| C | -0.2753140 | 2.4111370 | 0.5923000 |
| C | -1.2635910 | -1.7048030 | -1.5659040 |
| C | -0.2745060 | -2.4103570 | 0.5944270 |
| H | 0.2180900 | 0.0009320 | 2.7895700 |
| H | 3.9330940 | 0.0015190 | 1.6985210 |
| H | 4.8927760 | -0.0001400 | -0.5796350 |
| H | 3.3697200 | -0.0017070 | -2.5386860 |
| H | 0.9359010 | -0.0016430 | -2.2134830 |
| H | -2.2829710 | 1.2346000 | 1.6893260 |
| H | -3.0036510 | 2.1503080 | 0.3652650 |
| H | -4.2091550 | -0.0001430 | 0.7796230 |
| H | -3.5070340 | -0.0008620 | -0.8262210 |
| H | -3.0029900 | -2.1506280 | 0.3674540 |
| H | -2.2824250 | -1.2333620 | 1.6905210 |
| H | -0.2993120 | -1.7930290 | -2.0700980 |
| H | -1.8794400 | -1.0009780 | -2.1255890 |
| H | -1.7495600 | -2.6836350 | -1.6194850 |
| H | 0.6945320 | -2.5685220 | 0.1157930 |
| H | -0.8358780 | -3.3467000 | 0.5367790 |
| H | -0.1056450 | -2.1764480 | 1.6480550 |
| H | -1.8799900 | 0.9990180 | -2.1264500 |
| H | -0.2999020 | 1.7912410 | -2.0718080 |
| H | -1.7501630 | 2.6820790 | -1.6217760 |
| H | 0.6936330 | 2.5693250 | 0.1134860 |
| H | -0.1063400 | 2.1781940 | 1.6461190 |
| H | -0.8370760 | 3.3472020 | 0.5339210 |
| H | 2.1878650 | 0.0027230 | 3.3980200 |

41

**1c**-*open-A*

| | | | |
|---|---|---|---|
| C | 1.5907370 | 0.5328950 | -0.1835940 |
| C | 0.2893250 | 1.0487500 | 0.0063960 |
| C | 0.1354600 | 2.4274240 | 0.1736680 |
| C | 1.2144490 | 3.2966140 | 0.0980560 |
| C | 2.4909960 | 2.7982640 | -0.1151380 |
| C | 2.6708960 | 1.4293570 | -0.2234410 |
| N | -0.8329450 | 0.1690120 | 0.0501770 |
| C | -1.8206600 | 0.3043120 | -1.0590190 |
| C | -2.6243510 | -1.0053760 | -1.1298110 |
| C | -3.2445330 | -1.3893390 | 0.2057220 |

| | | | |
|---|---|---|---|
| C | -2.1426630 | -1.5340270 | 1.2447190 |
| C | -1.2719300 | -0.2751720 | 1.4017420 |
| C | -1.0670420 | 0.4668450 | -2.3869880 |
| C | -2.8044550 | 1.4944280 | -0.9637680 |
| C | -0.0525950 | -0.6782200 | 2.2426020 |
| C | -2.0286920 | 0.8012710 | 2.2098860 |
| H | -3.3938110 | -0.9018210 | -1.9011010 |
| H | -1.9488530 | -1.8053240 | -1.4497540 |
| H | -1.4896140 | -2.3609270 | 0.9439790 |
| H | -2.5604090 | -1.7907790 | 2.2234670 |
| H | -3.9805590 | -0.6413920 | 0.5204450 |
| H | -3.7885130 | -2.3332900 | 0.1092400 |
| H | 0.5217880 | -1.4713550 | 1.7578130 |
| H | 0.6119560 | 0.1637110 | 2.4464410 |
| H | -0.3986020 | -1.0717640 | 3.2015220 |
| H | -2.2064380 | 0.4405980 | 3.2270330 |
| H | -1.4390200 | 1.7176610 | 2.2857760 |
| H | -2.9977590 | 1.0512710 | 1.7804680 |
| H | -0.5360270 | 1.4199890 | -2.4394910 |
| H | -0.3479690 | -0.3379360 | -2.5353610 |
| H | -1.7861950 | 0.4409170 | -3.2098960 |
| H | -3.4903360 | 1.4550290 | -1.8150920 |
| H | -3.4088840 | 1.4862360 | -0.0587100 |
| H | -2.2838000 | 2.4510880 | -1.0207160 |
| H | -0.8501390 | 2.8242730 | 0.3722720 |
| H | 1.0560080 | 4.3625480 | 0.2197000 |
| H | 3.3423130 | 3.4661130 | -0.1732500 |
| H | 3.6761440 | 1.0437780 | -0.3497140 |
| B | 1.9343680 | -0.9814030 | -0.2935730 |
| Cl | 1.0462160 | -2.2023080 | -1.1998720 |
| Cl | 3.4154220 | -1.5737420 | 0.4854820 |

41

**1c**-*open-B*

| | | | |
|---|---|---|---|
| C | 1.5894380 | 0.7169280 | -0.0000330 |
| C | 0.2312300 | 1.0278920 | -0.0000670 |
| C | -0.1674180 | 2.3648920 | -0.0002190 |
| C | 0.7816790 | 3.3766840 | -0.0003270 |
| C | 2.1380640 | 3.0664860 | -0.0002910 |
| C | 2.5408930 | 1.7395120 | -0.0001480 |
| N | -0.6698720 | -0.0946330 | 0.0000520 |
| C | -1.4277280 | -0.2973170 | 1.2874860 |
| C | -2.8213650 | 0.3623900 | 1.2464450 |
| C | -3.6222560 | 0.0106120 | -0.0001570 |
| C | -2.8212040 | 0.3619950 | -1.2467650 |
| C | -1.4275670 | -0.2977340 | -1.2874120 |
| C | -0.6620230 | 0.3123460 | 2.4718780 |
| C | -1.5624070 | -1.8019050 | 1.5861180 |
| C | -0.6617030 | 0.3115200 | -2.4719120 |
| C | -1.5622220 | -1.8024200 | -1.5855600 |
| H | -3.3683180 | 0.0730190 | 2.1498300 |
| H | -2.6967000 | 1.4508090 | 1.2953400 |
| H | -2.6965280 | 1.4503970 | -1.2959900 |
| H | -3.3680400 | 0.0723370 | -2.1501300 |
| H | -3.8831090 | -1.0527180 | -0.0000050 |
| H | -4.5707040 | 0.5553660 | -0.0003050 |
| H | -0.5620810 | 1.3944070 | -2.3946370 |
| H | 0.3353160 | -0.1173530 | -2.5755790 |
| H | -1.2177080 | 0.0929700 | -3.3867120 |
| H | -0.6010860 | -2.3013050 | -1.4546160 |
| H | -2.2938130 | -2.3040420 | -0.9556210 |
| H | -1.8838480 | -1.9404980 | -2.6212150 |
| H | -0.5624010 | 1.3952080 | 2.3942450 |
| H | -1.2181460 | 0.0941040 | 3.3866790 |
| H | 0.3349850 | -0.1164830 | 2.5758220 |
| H | -1.8841670 | -1.9396410 | 2.6217780 |
| H | -2.2939120 | -2.3037440 | 0.9562530 |
| H | -0.6012500 | -2.3008250 | 1.4554660 |
| H | -1.2222700 | 2.6121700 | -0.0002490 |
| H | 0.4631780 | 4.4131060 | -0.0004420 |

| | | | |
|---|---|---|---|
| H | 2.8774860 | 3.8589120 | -0.0003780 |
| H | 3.5991640 | 1.4989830 | -0.0001280 |
| B | 1.9650960 | -0.7974120 | 0.0000990 |
| Cl | 2.3208390 | -1.6659370 | 1.4974530 |
| Cl | 2.3206380 | -1.6662370 | -1.4971290 |

41

**1d**-*open-A*

| | | | |
|---|---|---|---|
| C | 0.4908760 | 2.1737120 | 0.0008480 |
| C | 0.4911970 | 0.7775440 | 0.0001750 |
| C | 1.7304050 | 0.0928690 | -0.0002300 |
| C | 2.9143390 | 0.8454850 | -0.0000200 |
| C | 2.8987600 | 2.2303020 | 0.0005270 |
| C | 1.6788770 | 2.8934850 | 0.0009920 |
| N | -0.7261270 | 0.0336710 | -0.0000420 |
| C | -1.4449080 | -0.0552530 | 1.2962290 |
| C | -2.4127780 | -1.2491020 | 1.2369080 |
| C | -3.2976050 | -1.2436890 | -0.0002020 |
| C | -2.4133360 | -1.2476430 | -1.2377300 |
| C | -1.4454040 | -0.0537710 | -1.2961490 |
| C | -0.4333160 | -0.3452500 | 2.4142830 |
| C | -2.2152790 | 1.2207920 | 1.7006590 |
| C | -0.4342440 | -0.3427220 | -2.4148860 |
| C | -2.2156720 | 1.2228220 | -1.6990320 |
| B | 1.7700320 | -1.4528320 | -0.0007980 |
| Cl | 3.3146740 | -2.3252640 | -0.0007330 |
| H | -3.0167770 | -1.2517560 | -2.1508060 |
| H | -1.8183750 | -2.1681770 | -1.2381320 |
| H | -1.8178140 | -2.1696350 | 1.2360100 |
| H | -3.0158140 | -1.2542400 | 2.1502470 |
| H | -3.9619240 | -0.3725970 | 0.0004810 |
| H | -3.9456010 | -2.1248210 | -0.0005710 |
| H | 0.1506390 | -1.2411830 | 2.1907550 |
| H | 0.2568720 | 0.4867670 | 2.5706430 |
| H | -0.9718480 | -0.5162410 | 3.3500030 |
| H | -2.6777700 | 1.0750750 | 2.6813790 |
| H | -1.5416820 | 2.0758030 | 1.7835980 |
| H | -3.0085210 | 1.4763330 | 0.9985680 |
| H | 0.2559980 | 0.4893750 | -2.5705780 |
| H | 0.1496410 | -1.2389700 | -2.1925790 |
| H | -0.9731160 | -0.5125930 | -3.3506150 |
| H | -2.6787850 | 1.0779770 | -2.6795920 |
| H | -3.0084180 | 1.4781520 | -0.9963060 |
| H | -1.5418420 | 2.0776820 | -1.7817420 |
| H | -0.4522020 | 2.7036290 | 0.0012820 |
| H | 1.6486150 | 3.9778270 | 0.0015030 |
| H | 3.8274100 | 2.7889960 | 0.0006390 |
| H | 3.8664570 | 0.3261890 | -0.0003280 |
| H | 0.8066610 | -2.1431160 | -0.0013530 |

41

**1d**-*dat-B*

| | | | |
|---|---|---|---|
| C | -1.3083120 | -1.8250950 | -0.6214260 |
| C | -0.9557260 | -0.6029120 | -0.0711680 |
| C | -1.8632620 | 0.3148590 | 0.4114530 |
| C | -3.2217650 | 0.0422840 | 0.3320000 |
| C | -3.6157320 | -1.1693260 | -0.2293830 |
| C | -2.6739050 | -2.0898230 | -0.6928720 |
| N | 0.3381850 | 0.0664590 | 0.1664580 |
| C | 1.2118640 | -0.6827010 | 1.1942690 |
| C | 1.9522530 | -1.8556730 | 0.5264650 |
| C | 2.7150070 | -1.4837230 | -0.7350730 |
| C | 1.7804500 | -0.8022000 | -1.7230900 |
| C | 1.0537520 | 0.4299050 | -1.1542760 |
| C | 2.2039640 | 0.2844550 | 1.8538500 |
| C | 0.3394380 | -1.2834840 | 2.3093040 |
| C | 2.0619350 | 1.5751220 | -0.9483210 |
| C | 0.0233860 | 0.8757290 | -2.2040130 |
| B | -0.7529330 | 1.3119280 | 0.9422890 |
| Cl | -0.7130130 | 3.0499820 | 0.3152440 |

| | | | |
|---|---|---|---|
| H | 1.0385500 | -1.5230070 | -2.0813350 |
| H | 2.3331890 | -0.4690360 | -2.6067490 |
| H | 2.6299330 | -2.2799120 | 1.2733940 |
| H | 1.2269070 | -2.6420480 | 0.2929890 |
| H | 3.1419570 | -2.3827190 | -1.1877730 |
| H | 3.5622340 | -0.8353440 | -0.4932390 |
| H | 1.7063960 | 1.2019890 | 2.1688670 |
| H | 3.0408520 | 0.5493840 | 1.2129970 |
| H | 2.6162700 | -0.1982230 | 2.7427760 |
| H | 1.0011370 | -1.8300670 | 2.9853750 |
| H | -0.1772780 | -0.5201570 | 2.8877300 |
| H | -0.3987370 | -1.9870900 | 1.9250990 |
| H | 2.1919250 | 2.0948200 | -1.8995290 |
| H | 1.7128580 | 2.3056180 | -0.2230690 |
| H | 3.0452730 | 1.2211690 | -0.6434960 |
| H | 0.5697110 | 1.1114350 | -3.1203460 |
| H | -0.6949640 | 0.0902420 | -2.4379010 |
| H | -0.5210850 | 1.7662580 | -1.8967200 |
| H | -0.5891320 | -2.5448350 | -0.9902340 |
| H | -3.0108230 | -3.0268560 | -1.1216720 |
| H | -4.6701720 | -1.4104410 | -0.3081810 |
| H | -3.9624420 | 0.7476300 | 0.6922490 |
| H | -0.4940560 | 1.3221360 | 2.1066540 |

82

(**1d**)$_2$-*trans*

| | | | |
|---|---|---|---|
| C | 3.8626730 | -0.6105220 | -1.3844080 |
| N | 3.6011000 | 0.0021120 | -0.0510500 |
| C | 4.5652440 | -0.2611950 | 1.0642580 |
| C | 4.6779160 | -1.7868290 | 1.2136440 |
| C | 5.0543020 | -2.4785210 | -0.0908120 |
| C | 4.0416280 | -2.1245630 | -1.1707420 |
| C | 2.9791570 | 1.2943030 | -0.0285300 |
| C | 1.6231840 | 1.4044670 | 0.3325420 |
| C | 1.0519300 | 2.6782080 | 0.4254520 |
| C | 1.7807840 | 3.8282160 | 0.1642230 |
| C | 3.1055060 | 3.7134520 | -0.2281900 |
| C | 3.6915120 | 2.4587360 | -0.3256470 |
| B | 0.6802640 | 0.1642390 | 0.5727600 |
| B | -0.6802770 | -0.1642700 | -0.5729090 |
| C | -1.6232320 | -1.4044630 | -0.3326740 |
| C | -1.0520140 | -2.6782130 | -0.4256550 |
| C | -1.7808940 | -3.8282100 | -0.1644490 |
| C | -3.1056120 | -3.7134240 | 0.2279720 |
| C | -3.6915770 | -2.4586940 | 0.3255060 |
| C | -2.9791790 | -1.2942660 | 0.0284720 |
| N | -3.6010700 | -0.0020460 | 0.0511020 |
| C | -4.5653110 | 0.2613070 | -1.0641160 |
| C | -4.6780160 | 1.7869450 | -1.2134160 |
| C | -5.0543310 | 2.4785560 | 0.0911010 |
| C | -4.0415950 | 2.1245510 | 1.1709580 |
| C | -3.8625800 | 0.6105030 | 1.3845290 |
| C | -5.9822290 | -0.3431480 | -0.9124770 |
| C | -4.0100030 | -0.3122610 | -2.3746640 |
| C | -5.0656380 | 0.0276560 | 2.1606250 |
| C | -2.6457300 | 0.4250910 | 2.2985120 |
| C | 5.9821930 | 0.3432040 | 0.9126910 |
| C | 4.0098380 | 0.3124430 | 2.3747380 |
| C | 5.0658140 | -0.0277390 | -2.1604140 |
| C | 2.6458840 | -0.4250980 | -2.2984730 |
| H | -0.5838000 | 0.6083920 | 0.4902350 |
| Cl | -0.7258750 | 0.9020990 | -2.0208020 |
| H | -0.0046140 | -2.7756690 | -0.6978050 |
| H | -1.3130870 | -4.8020360 | -0.2501310 |
| H | -3.6876170 | -4.5990440 | 0.4577970 |
| H | -4.7261370 | -2.3821950 | 0.6307710 |
| H | -3.7078980 | 2.1648970 | -1.5543040 |
| H | -5.4111730 | 2.0129130 | -1.9944850 |
| H | -5.0765920 | 3.5627100 | -0.0531320 |
| H | -6.0644310 | 2.1917830 | 0.4030040 |

| | | | |
|---|---|---|---|
| H | -4.3127260 | 2.5861530 | 2.1260820 |
| H | -3.0679920 | 2.5345610 | 0.8767750 |
| H | -4.9353230 | -1.0428190 | 2.3329300 |
| H | -6.0197310 | 0.1806690 | 1.6628640 |
| H | -5.1296470 | 0.5081530 | 3.1409430 |
| H | -2.3786770 | -0.6243170 | 2.4325080 |
| H | -2.8699180 | 0.8423560 | 3.2829060 |
| H | -1.7760520 | 0.9620720 | 1.9196270 |
| H | -6.5788900 | 0.1201810 | -0.1298130 |
| H | -5.9441080 | -1.4173150 | -0.7276670 |
| H | -6.5224540 | -0.1986420 | -1.8523990 |
| H | -4.0113720 | -1.4047060 | -2.3708200 |
| H | -2.9972400 | 0.0308860 | -2.5678190 |
| H | -4.6458710 | 0.0193300 | -3.1996460 |
| H | 0.5837630 | -0.6083960 | -0.4903920 |
| Cl | 0.7260130 | -0.9023340 | 2.0204990 |
| H | 0.0045210 | 2.7756490 | 0.6975700 |
| H | 1.3129450 | 4.8020310 | 0.2498590 |
| H | 3.6874830 | 4.5990760 | -0.4580710 |
| H | 4.7260640 | 2.3822480 | -0.6309400 |
| H | 3.7077770 | -2.1647600 | 1.5544900 |
| H | 5.4110240 | -2.0127550 | 1.9947690 |
| H | 5.0765350 | -3.5626680 | 0.0534840 |
| H | 6.0644250 | -2.1917820 | -0.4026700 |
| H | 4.3127910 | -2.5862240 | -2.1258270 |
| H | 3.0680060 | -2.5345310 | -0.8765670 |
| H | 4.9355250 | 1.0427260 | -2.3328080 |
| H | 6.0198370 | -0.1807170 | -1.6625010 |
| H | 5.1299600 | -0.5083080 | -3.1406880 |
| H | 2.3789570 | 0.6243200 | -2.4326240 |
| H | 2.8700650 | -0.8425160 | -3.2828030 |
| H | 1.7761390 | -0.9619520 | -1.9195290 |
| H | 6.5788160 | -0.1200640 | 0.1299580 |
| H | 5.9441380 | 1.4173940 | 0.7280130 |
| H | 6.5224160 | 0.1985510 | 1.8525920 |
| H | 4.0112290 | 1.4048890 | 2.3708490 |
| H | 2.9970480 | -0.0306770 | 2.5678090 |
| H | 4.6456270 | -0.0191280 | 3.1997890 |

51

**1e**-*open-A1*

| | | | |
|---|---|---|---|
| C | 3.0097010 | 0.9506340 | -1.3108220 |
| C | 3.4181180 | 2.2562190 | -1.5463370 |
| C | 2.7601580 | 3.3141010 | -0.9359820 |
| C | 1.6974320 | 3.0473790 | -0.0888680 |
| C | 1.2417430 | 1.7387010 | 0.1242340 |
| C | 1.9131430 | 0.6650220 | -0.4925390 |
| N | 1.4994630 | -0.6817440 | -0.2114640 |
| C | 1.0515130 | -1.4901910 | -1.3895130 |
| C | 2.2867310 | -1.3499830 | 0.8797610 |
| B | -0.0174710 | 1.5593460 | 1.0135170 |
| C | -1.3399940 | 0.8322880 | 0.5673370 |
| Cl | -0.1129980 | 2.4238150 | 2.5594630 |
| C | -2.1008230 | 1.3869970 | -0.4499510 |
| C | -3.2554060 | 0.7883580 | -0.9256300 |
| C | -3.6609080 | -0.4198780 | -0.3790800 |
| C | -2.9278900 | -0.9967420 | 0.6476290 |
| C | -1.7983990 | -0.3505530 | 1.1197690 |
| F | -1.1283210 | -0.9241810 | 2.1231090 |
| F | -1.7057280 | 2.5310180 | -1.0171930 |
| F | -3.9601280 | 1.3436170 | -1.9047410 |
| F | -4.7523840 | -1.0204770 | -0.8320310 |
| F | -3.3100590 | -2.1603320 | 1.1630870 |
| C | 0.3595340 | -2.7552130 | -0.8554280 |
| C | 1.5975500 | -2.6688750 | 1.2723160 |
| C | 1.2423920 | -3.5535440 | 0.0883250 |
| C | 0.0024540 | -0.6956170 | -2.1750740 |
| C | 2.1414390 | -1.9023960 | -2.4093330 |
| C | 2.2830990 | -0.4595570 | 2.1282840 |
| C | 3.7657830 | -1.6273240 | 0.5346610 |

| | | | |
|---|---|---|---|
| H | 3.5670490 | 0.1401170 | -1.7567380 |
| H | 4.2684740 | 2.4422910 | -2.1930150 |
| H | 3.0808870 | 4.3351370 | -1.1056900 |
| H | 1.1952920 | 3.8717120 | 0.4058140 |
| H | -0.5446910 | -2.4536540 | -0.3152830 |
| H | 0.0369520 | -3.3607990 | -1.7074890 |
| H | 2.2525130 | -3.1962720 | 1.9725730 |
| H | 0.6772150 | -2.4291550 | 1.8111440 |
| H | 0.7145850 | -4.4457880 | 0.4362680 |
| H | 2.1422360 | -3.9060150 | -0.4276180 |
| H | 0.3769710 | 0.2790440 | -2.4957520 |
| H | -0.2799260 | -1.2570120 | -3.0693300 |
| H | -0.8931260 | -0.5450390 | -1.5772960 |
| H | 2.4624740 | -1.0516470 | -3.0118720 |
| H | 3.0210560 | -2.3506580 | -1.9522270 |
| H | 1.7192360 | -2.6376800 | -3.1000460 |
| H | 1.2629330 | -0.2424280 | 2.4492280 |
| H | 2.7758470 | -0.9919660 | 2.9457920 |
| H | 2.8151320 | 0.4810570 | 1.9739440 |
| H | 3.8894430 | -2.3809010 | -0.2422640 |
| H | 4.2801940 | -0.7171220 | 0.2217540 |
| H | 4.2766900 | -1.9983650 | 1.4272600 |

51

**1e**-*open-B1*

| | | | |
|---|---|---|---|
| C | 3.1146630 | 0.5768350 | -1.1710860 |
| C | 3.6646000 | 1.7835290 | -1.5726860 |
| C | 3.0399810 | 2.9801000 | -1.2405100 |
| C | 1.8674000 | 2.9489210 | -0.5070760 |
| C | 1.2719780 | 1.7350140 | -0.1304830 |
| C | 1.9137480 | 0.5286380 | -0.4567920 |
| N | 1.3570800 | -0.7003240 | 0.0297630 |
| C | 1.9801480 | -1.1887920 | 1.3126400 |
| C | 1.0381540 | -1.7380790 | -1.0107550 |
| B | -0.0719130 | 1.7723520 | 0.6448170 |
| C | -1.3680520 | 0.9621920 | 0.2771150 |
| Cl | -0.2450870 | 2.9553450 | 1.9584920 |
| C | -1.8397670 | 0.9570280 | -1.0289110 |
| C | -2.9622870 | 0.2449800 | -1.4167840 |
| C | -3.6639500 | -0.4800350 | -0.4669630 |
| C | -3.2405980 | -0.4794670 | 0.8538710 |
| C | -2.1189570 | 0.2513910 | 1.2060150 |
| F | -1.7437320 | 0.2141330 | 2.4862850 |
| F | -1.2060830 | 1.6624650 | -1.9703580 |
| F | -3.3677240 | 0.2517440 | -2.6814110 |
| F | -4.7386860 | -1.1702020 | -0.8185310 |
| F | -3.9113110 | -1.1767350 | 1.7634510 |
| C | 3.1425400 | -2.1593490 | 1.0219840 |
| C | 2.1797000 | -2.7589010 | -1.2105010 |
| C | 2.7480660 | -3.3032560 | 0.0947790 |
| C | 2.5390000 | -0.0173450 | 2.1334230 |
| C | 0.9340790 | -1.8688500 | 2.2140810 |
| C | 0.7513480 | -1.0796050 | -2.3683900 |
| C | -0.2561330 | -2.4801510 | -0.6213830 |
| H | 3.6335620 | -0.3443140 | -1.4015800 |
| H | 4.5956110 | 1.7907620 | -2.1287340 |
| H | 3.4720630 | 3.9274040 | -1.5407140 |
| H | 1.3907590 | 3.8829440 | -0.2300800 |
| H | 3.9671340 | -1.5937600 | 0.5715110 |
| H | 3.5173150 | -2.5526020 | 1.9726360 |
| H | 1.8059000 | -3.5773630 | -1.8347670 |
| H | 2.9871010 | -2.2867070 | -1.7807170 |
| H | 3.6188210 | -3.9310570 | -0.1147010 |
| H | 2.0179850 | -3.9546530 | 0.5858800 |
| H | 1.7517660 | 0.6743240 | 2.4424140 |
| H | 2.9934360 | -0.4234710 | 3.0399080 |
| H | 3.3030170 | 0.5497870 | 1.6004840 |
| H | 0.0354120 | -1.2576410 | 2.2822100 |
| H | 0.6467880 | -2.8632040 | 1.8807970 |
| H | 1.3456520 | -1.9795280 | 3.2207460 |

| | | | |
|---|---|---|---|
| H | 1.6260830 | -0.5989410 | -2.8043210 |
| H | 0.4192710 | -1.8536270 | -3.0639870 |
| H | -0.0371860 | -0.3320470 | -2.2968620 |
| H | -0.1170780 | -3.2067340 | 0.1757790 |
| H | -1.0133170 | -1.7662560 | -0.2995450 |
| H | -0.6397430 | -3.0251080 | -1.4876000 |

51

**1e**-*open-A2*

| | | | |
|---|---|---|---|
| C | -2.2740100 | 1.8753180 | 1.5529670 |
| C | -1.5021080 | 2.6560090 | 2.4035090 |
| C | -0.1423710 | 2.4160450 | 2.5198900 |
| C | 0.4260180 | 1.4058090 | 1.7622210 |
| C | -0.3323320 | 0.5834690 | 0.9079630 |
| C | -1.7262090 | 0.8254550 | 0.8138540 |
| N | -2.5488090 | 0.0253170 | -0.0301150 |
| C | -3.4968680 | -0.8942850 | 0.6585260 |
| C | -2.8726490 | 0.5961260 | -1.3658710 |
| B | 0.4874890 | -0.4884770 | 0.1435200 |
| C | 2.0551850 | -0.3050020 | -0.0219310 |
| Cl | -0.1134730 | -1.9811300 | -0.5860240 |
| C | 2.5762270 | 0.6766150 | -0.8510300 |
| C | 3.9388380 | 0.8470030 | -1.0350410 |
| C | 4.8200430 | 0.0164610 | -0.3596220 |
| C | 4.3351790 | -0.9699530 | 0.4864210 |
| C | 2.9660500 | -1.1179960 | 0.6364410 |
| F | 2.5251620 | -2.0628600 | 1.4708470 |
| F | 1.7490770 | 1.4919180 | -1.5125120 |
| F | 4.4061200 | 1.7909800 | -1.8445220 |
| F | 6.1274520 | 0.1680680 | -0.5188880 |
| F | 5.1830080 | -1.7548090 | 1.1417900 |
| C | -3.9079270 | -1.9866160 | -0.3435600 |
| C | -3.3357570 | -0.5485320 | -2.2832290 |
| C | -4.4160520 | -1.4222900 | -1.6625280 |
| C | -2.7742180 | -1.5779750 | 1.8285450 |
| C | -4.7683590 | -0.2400210 | 1.2474070 |
| C | -1.6067270 | 1.1984770 | -1.9904340 |
| C | -3.9337820 | 1.7185700 | -1.3474560 |
| H | -3.3298400 | 2.0859890 | 1.4570000 |
| H | -1.9674040 | 3.4569260 | 2.9677470 |
| H | 0.4720930 | 3.0178160 | 3.1788210 |
| H | 1.4946320 | 1.2416510 | 1.8415790 |
| H | -3.0343670 | -2.6154860 | -0.5423020 |
| H | -4.6655220 | -2.6221380 | 0.1255050 |
| H | -3.6789380 | -0.1178310 | -3.2292490 |
| H | -2.4663900 | -1.1755820 | -2.5084340 |
| H | -4.6707590 | -2.2385090 | -2.3446090 |
| H | -5.3381770 | -0.8505750 | -1.5101280 |
| H | -2.5179770 | -0.8686240 | 2.6190350 |
| H | -3.4335310 | -2.3345410 | 2.2618860 |
| H | -1.8611820 | -2.0717220 | 1.4963360 |
| H | -4.5211470 | 0.4836390 | 2.0256380 |
| H | -5.3833100 | 0.2570420 | 0.4989410 |
| H | -5.3837980 | -1.0140430 | 1.7151510 |
| H | -0.8070280 | 0.4598940 | -2.0627610 |
| H | -1.8374600 | 1.5363820 | -3.0038510 |
| H | -1.2348830 | 2.0578800 | -1.4289320 |
| H | -4.9144540 | 1.3722880 | -1.0239730 |
| H | -3.6258230 | 2.5389170 | -0.6956630 |
| H | -4.0478750 | 2.1292060 | -2.3548110 |

51

**1e**-*open-B2*

| | | | |
|---|---|---|---|
| C | 2.3440640 | -0.7376740 | 2.1277060 |
| C | 1.6381210 | -1.0590990 | 3.2768100 |
| C | 0.2640290 | -0.8710230 | 3.3230150 |
| C | -0.3775950 | -0.3629800 | 2.2078810 |
| C | 0.3194470 | 0.0036780 | 1.0400500 |
| C | 1.7168870 | -0.2009400 | 0.9998390 |
| N | 2.4515540 | 0.0868980 | -0.1936440 |

| | | | |
|---|---|---|---|
| C | 2.7817900 | -1.1169210 | -1.0248750 |
| C | 3.5019390 | 1.1501040 | -0.0718210 |
| B | -0.5602960 | 0.6275060 | -0.0713840 |
| C | -2.1084470 | 0.2877130 | -0.1424440 |
| Cl | -0.0316470 | 1.8078960 | -1.2689440 |
| C | -2.5502440 | -0.9912170 | -0.4484720 |
| C | -3.8943830 | -1.3153040 | -0.5355950 |
| C | -4.8420930 | -0.3331300 | -0.2931350 |
| C | -4.4399740 | 0.9543330 | 0.0295670 |
| C | -3.0869350 | 1.2445560 | 0.0938860 |
| F | -2.7331080 | 2.4865720 | 0.4298340 |
| F | -1.6625960 | -1.9621390 | -0.6856060 |
| F | -4.2808510 | -2.5479910 | -0.8446670 |
| F | -6.1328280 | -0.6255170 | -0.3648460 |
| F | -5.3507250 | 1.8890210 | 0.2765260 |
| C | 4.1742870 | -1.6735270 | -0.6609240 |
| C | 4.8906240 | 0.5609830 | 0.2569340 |
| C | 5.2682080 | -0.6087340 | -0.6497260 |
| C | 1.7466930 | -2.2285720 | -0.8032180 |
| C | 2.7109300 | -0.7788940 | -2.5268310 |
| C | 3.1052640 | 2.1522800 | 1.0223370 |
| C | 3.6021510 | 1.9707440 | -1.3748340 |
| H | 3.4098770 | -0.9180330 | 2.0989310 |
| H | 2.1628830 | -1.4719270 | 4.1315090 |
| H | -0.3005400 | -1.1277440 | 4.2113920 |
| H | -1.4533380 | -0.2306960 | 2.2437700 |
| H | 4.1150700 | -2.1438680 | 0.3277890 |
| H | 4.4312850 | -2.4708990 | -1.3664640 |
| H | 5.6375030 | 1.3578860 | 0.1750120 |
| H | 4.9102290 | 0.2328970 | 1.3017380 |
| H | 6.2104850 | -1.0498600 | -0.3120720 |
| H | 5.4521980 | -0.2507200 | -1.6679370 |
| H | 0.7466330 | -1.9067290 | -1.0991330 |
| H | 2.0209150 | -3.0837390 | -1.4252770 |
| H | 1.7017810 | -2.5702320 | 0.2316510 |
| H | 1.8084330 | -0.2025140 | -2.7365240 |
| H | 3.5669340 | -0.2142960 | -2.8891830 |
| H | 2.6733130 | -1.7060650 | -3.1049340 |
| H | 3.0851970 | 1.7102930 | 2.0185430 |
| H | 3.8342900 | 2.9656170 | 1.0353300 |
| H | 2.1213330 | 2.5812180 | 0.8160760 |
| H | 4.1385910 | 1.4568840 | -2.1694300 |
| H | 2.6100130 | 2.2286310 | -1.7417510 |
| H | 4.1479150 | 2.8960580 | -1.1726360 |

51

**1f**-*open-A*

| | | | |
|---|---|---|---|
| C | -2.5952240 | 2.1725340 | -0.6413480 |
| C | -2.0141840 | 3.3185340 | -1.1697200 |
| C | -0.6663460 | 3.3310630 | -1.5048230 |
| C | 0.0937930 | 2.1935560 | -1.2866070 |
| C | -0.4750030 | 1.0161880 | -0.7813270 |
| C | -1.8482500 | 1.0070910 | -0.4596480 |
| N | -2.4199730 | -0.1902450 | 0.0660330 |
| C | -2.4760510 | -0.2986460 | 1.5463740 |
| C | -3.4068780 | -0.8878640 | -0.7998840 |
| B | 0.3762960 | -0.2652120 | -0.6234020 |
| C | 1.9149590 | -0.2280870 | -0.2991470 |
| H | -0.0989770 | -1.3405720 | -0.8002440 |
| C | 2.7633770 | -1.1837140 | -0.8574330 |
| C | 4.1222160 | -1.2280810 | -0.5953480 |
| C | 4.6704170 | -0.3011520 | 0.2781010 |
| C | 3.8625390 | 0.6567380 | 0.8713940 |
| C | 2.5099380 | 0.6835220 | 0.5723480 |
| F | 1.7786910 | 1.6113580 | 1.1902840 |
| F | 2.2763350 | -2.0928240 | -1.7016720 |
| F | 4.9015060 | -2.1426730 | -1.1628610 |
| F | 5.9668150 | -0.3315880 | 0.5470560 |
| F | 4.3923430 | 1.5337190 | 1.7180350 |
| C | -2.6832250 | -1.7720510 | 1.9364320 |

| | | | |
|---|---|---|---|
| C | -3.8069450 | -2.4536900 | 1.1720800 |
| C | -3.5213860 | -2.3436900 | -0.3174920 |
| C | -3.5677980 | 0.5815710 | 2.1912260 |
| C | -1.1333430 | 0.1346100 | 2.1502370 |
| C | -2.8622500 | -0.9218920 | -2.2350290 |
| C | -4.8164110 | -0.2575080 | -0.8590380 |
| H | -3.6383570 | 2.1888410 | -0.3554200 |
| H | -2.6162380 | 4.2104200 | -1.3059780 |
| H | -0.2110450 | 4.2258470 | -1.9130860 |
| H | 1.1526010 | 2.2106770 | -1.5260060 |
| H | -1.7508850 | -2.3110820 | 1.7317530 |
| H | -2.8550870 | -1.8228040 | 3.0162130 |
| H | -3.8732270 | -3.5049950 | 1.4664030 |
| H | -4.7752150 | -2.0033370 | 1.4164080 |
| H | -2.5731130 | -2.8495360 | -0.5320980 |
| H | -4.2971950 | -2.8453270 | -0.9039520 |
| H | -3.4902010 | 0.5347290 | 3.2813530 |
| H | -3.4457450 | 1.6263380 | 1.8967230 |
| H | -4.5748230 | 0.2647130 | 1.9203030 |
| H | -0.9132030 | 1.1888570 | 1.9774730 |
| H | -1.1562170 | -0.0352500 | 3.2297760 |
| H | -0.3108640 | -0.4626990 | 1.7420960 |
| H | -3.5191790 | -1.5372000 | -2.8555740 |
| H | -1.8602490 | -1.3535670 | -2.2596540 |
| H | -2.8188350 | 0.0751240 | -2.6789070 |
| H | -5.4595550 | -0.8702850 | -1.4976870 |
| H | -5.2941640 | -0.1877310 | 0.1176020 |
| H | -4.7867710 | 0.7404950 | -1.2983800 |

51

**1f**-*dat-B*

| | | | |
|---|---|---|---|
| C | -3.1209290 | 1.7153980 | -0.2749860 |
| C | -3.1976820 | 3.0609500 | 0.0740260 |
| C | -2.1880930 | 3.6709400 | 0.8205870 |
| C | -1.0694180 | 2.9560330 | 1.2373220 |
| C | -0.9786700 | 1.6141520 | 0.8926640 |
| C | -1.9906660 | 1.0387370 | 0.1575360 |
| N | -1.5414280 | -0.3628270 | 0.0322590 |
| C | -1.2671020 | -0.7723030 | -1.4276980 |
| C | -2.4699210 | -1.3265540 | 0.8088620 |
| B | -0.1494500 | 0.2625850 | 1.0383630 |
| C | 1.3683720 | 0.1308470 | 0.5059680 |
| H | -0.2351010 | -0.2941580 | 2.0952890 |
| C | 2.0764410 | 1.1655100 | -0.0978330 |
| C | 3.4249260 | 1.0857040 | -0.4143760 |
| C | 4.1279270 | -0.0684800 | -0.1161840 |
| C | 3.4722410 | -1.1253920 | 0.4934010 |
| C | 2.1278970 | -0.9975270 | 0.7985400 |
| F | 1.5530320 | -2.0583040 | 1.3869940 |
| F | 1.4656960 | 2.3080600 | -0.4329800 |
| F | 4.0470600 | 2.1046990 | -1.0034060 |
| F | 5.4178380 | -0.1645390 | -0.4164450 |
| F | 4.1376260 | -2.2420070 | 0.7806380 |
| C | -2.5830370 | -1.1012250 | -2.1563140 |
| C | -3.7333290 | -1.6360340 | -0.0144830 |
| C | -3.4576760 | -2.1124410 | -1.4314610 |
| C | -0.6106100 | 0.3899440 | -2.1843510 |
| C | -0.3184510 | -1.9845270 | -1.4975570 |
| C | -2.9408760 | -0.6856630 | 2.1250070 |
| C | -1.7287120 | -2.6190090 | 1.1684310 |
| H | -3.9103770 | 1.2538560 | -0.8535350 |
| H | -4.0558650 | 3.6436940 | -0.2409960 |
| H | -2.2818820 | 4.7214200 | 1.0736330 |
| H | -0.2895660 | 3.4479310 | 1.8079680 |
| H | -3.1456480 | -0.1757920 | -2.3142740 |
| H | -2.3158370 | -1.4692270 | -3.1516710 |
| H | -4.3036860 | -2.3885470 | 0.5379200 |
| H | -4.3631200 | -0.7413480 | -0.0469040 |
| H | -4.4001200 | -2.2412220 | -1.9704580 |
| H | -2.9799800 | -3.0967700 | -1.4170020 |

| | | | |
|---|---|---|---|
| H | 0.3769040 | 0.6260450 | -1.7995830 |
| H | -0.4960440 | 0.0819410 | -3.2262510 |
| H | -1.2126220 | 1.2974710 | -2.1652260 |
| H | 0.3467160 | -2.0393830 | -0.6418530 |
| H | -0.8531380 | -2.9315010 | -1.5633430 |
| H | 0.2971030 | -1.9021710 | -2.3952120 |
| H | -3.5048330 | 0.2325170 | 1.9632570 |
| H | -3.6028600 | -1.4012460 | 2.6183250 |
| H | -2.1137170 | -0.4717670 | 2.7987190 |
| H | -1.5465270 | -3.2678020 | 0.3155300 |
| H | -0.7750420 | -2.4028690 | 1.6469350 |
| H | -2.3445810 | -3.1797550 | 1.8752680 |

2

$H_2$

| | | | |
|---|---|---|---|
| H | 0.0000000 | 0.0000000 | 0.3722040 |
| H | 0.0000000 | 0.0000000 | -0.3722040 |

63

**$TS_{1a}$**

| | | | |
|---|---|---|---|
| C | 2.7773030 | -1.1206300 | 2.3083120 |
| C | 2.0283860 | -0.8459080 | 1.1617220 |
| C | 0.6265930 | -0.7059240 | 1.2896180 |
| C | 0.0524170 | -0.9553640 | 2.5467460 |
| C | 0.8134140 | -1.2364570 | 3.6709830 |
| C | 2.1905180 | -1.2969480 | 3.5534320 |
| N | 2.6642220 | -0.8315990 | -0.1292970 |
| C | 3.5478400 | 0.3288230 | -0.4495060 |
| C | 3.8209760 | 0.3199560 | -1.9646020 |
| C | 4.3257920 | -1.0152280 | -2.4872840 |
| C | 3.3129360 | -2.0954500 | -2.1386690 |
| C | 3.0420300 | -2.1983280 | -0.6282050 |
| C | 2.7945990 | 1.6243940 | -0.1415560 |
| C | 4.8825110 | 0.4010420 | 0.3243300 |
| C | 1.8543660 | -3.1474320 | -0.4293170 |
| C | 4.2536470 | -2.8700580 | 0.0558550 |
| B | -0.4548330 | -0.1180900 | 0.3094660 |
| C | -1.8254820 | -0.9072790 | 0.0601320 |
| C | -0.5428530 | 1.4323940 | -0.0083050 |
| H | 3.6474920 | -3.0735990 | -2.4970250 |
| H | 2.3681210 | -1.8749400 | -2.6474140 |
| H | 2.8849750 | 0.5622400 | -2.4809420 |
| H | 4.5276440 | 1.1236470 | -2.1929450 |
| H | 5.3077130 | -1.2517270 | -2.0635590 |
| H | 4.4624500 | -0.9639940 | -3.5711840 |
| H | 1.8836660 | 1.6876290 | -0.7362590 |
| H | 2.5355070 | 1.7011750 | 0.9161940 |
| H | 3.4246440 | 2.4803400 | -0.3963420 |
| H | 5.4440340 | 1.2755170 | -0.0163090 |
| H | 4.7111380 | 0.5284240 | 1.3945480 |
| H | 5.5172510 | -0.4706320 | 0.1781300 |
| H | 1.6732930 | -3.3591510 | 0.6266340 |
| H | 0.9441340 | -2.7394040 | -0.8612760 |
| H | 2.0701700 | -4.0957310 | -0.9283010 |
| H | 4.3852460 | -3.8666530 | -0.3750410 |
| H | 5.1899530 | -2.3330910 | -0.0846710 |
| H | 4.0873090 | -3.0050720 | 1.1249290 |
| H | 3.8494750 | -1.2182350 | 2.2191330 |
| H | 2.8105050 | -1.5057740 | 4.4179230 |
| H | 0.3288710 | -1.4037500 | 4.6257000 |
| H | -1.0226480 | -0.8885210 | 2.6690060 |
| H | 0.9215090 | -0.4952240 | -1.4074000 |
| H | 0.2871240 | -0.4372400 | -1.8164650 |
| C | -2.0509430 | -1.9562340 | -0.8195690 |
| C | -3.2872910 | -2.5687200 | -0.9578630 |
| C | -4.3556690 | -2.1378350 | -0.1898000 |
| C | -4.1773790 | -1.0929320 | 0.7017600 |
| C | -2.9311610 | -0.4988940 | 0.7996650 |
| F | -1.0776730 | -2.4041880 | -1.6167320 |
| F | -3.4541780 | -3.5611880 | -1.8244390 |

| | | | |
|---|---|---|---|
| F | -5.5399190 | -2.7209990 | -0.3064380 |
| F | -5.1921220 | -0.6738990 | 1.4489660 |
| F | -2.8027170 | 0.5029840 | 1.6835630 |
| C | -1.0850970 | 1.8995110 | -1.2025200 |
| C | -1.1879660 | 3.2451670 | -1.5096440 |
| C | -0.7732080 | 4.1828920 | -0.5773600 |
| C | -0.2582250 | 3.7639550 | 0.6387680 |
| C | -0.1527860 | 2.4091540 | 0.9041280 |
| F | -1.5028280 | 1.0348340 | -2.1330390 |
| F | -1.6862190 | 3.6433380 | -2.6747090 |
| F | -0.8726040 | 5.4754100 | -0.8469110 |
| F | 0.1332290 | 4.6628820 | 1.5347800 |
| F | 0.3520800 | 2.0729860 | 2.0897570 |

63

**4a**

| | | | |
|---|---|---|---|
| C | 3.0211830 | -0.5694580 | 2.3563100 |
| C | 2.1758290 | -0.4389430 | 1.2581230 |
| C | 0.7814820 | -0.3574180 | 1.3602170 |
| C | 0.2792740 | -0.4827480 | 2.6637960 |
| C | 1.0947350 | -0.6345910 | 3.7723290 |
| C | 2.4758910 | -0.6620070 | 3.6248800 |
| N | 2.7367090 | -0.4393470 | -0.1104400 |
| C | 3.4665820 | 0.8517360 | -0.5524610 |
| C | 3.6192640 | 0.7627610 | -2.0788530 |
| C | 4.2511810 | -0.5317120 | -2.5728430 |
| C | 3.4243130 | -1.7215350 | -2.1013570 |
| C | 3.2993580 | -1.8119810 | -0.5741020 |
| C | 2.5497980 | 2.0290010 | -0.2207000 |
| C | 4.8063590 | 1.0748490 | 0.1451100 |
| C | 2.2586910 | -2.8721930 | -0.2099950 |
| C | 4.6287810 | -2.2103700 | 0.0648790 |
| B | -0.2089760 | -0.1219200 | 0.0737090 |
| C | -1.4700390 | -1.1656250 | 0.0480620 |
| C | -0.7788510 | 1.4047150 | -0.1058240 |
| H | 3.8545150 | -2.6617780 | -2.4550780 |
| H | 2.4167980 | -1.6575670 | -2.5301240 |
| H | 2.6241880 | 0.8633110 | -2.5290870 |
| H | 4.1970980 | 1.6315890 | -2.4041380 |
| H | 5.2868520 | -0.6163560 | -2.2290300 |
| H | 4.2900420 | -0.5228000 | -3.6645000 |
| H | 2.3787250 | 2.1281920 | 0.8518540 |
| H | 3.0250110 | 2.9436870 | -0.5812460 |
| H | 1.5828030 | 1.9359870 | -0.7150650 |
| H | 4.6858170 | 1.1578290 | 1.2247490 |
| H | 5.5546400 | 0.3175030 | -0.0733210 |
| H | 5.1989670 | 2.0307470 | -0.2083270 |
| H | 2.1918780 | -3.0201450 | 0.8682510 |
| H | 1.2719490 | -2.6206990 | -0.5939180 |
| H | 2.5638480 | -3.8154060 | -0.6686800 |
| H | 4.8646140 | -3.2126660 | -0.3000690 |
| H | 5.4644830 | -1.5682230 | -0.2003400 |
| H | 4.5564750 | -2.2762040 | 1.1489250 |
| H | 4.0939310 | -0.6042380 | 2.2344820 |
| H | 3.1250950 | -0.7611520 | 4.4867410 |
| H | 0.6523120 | -0.7180900 | 4.7584980 |
| H | -0.7900820 | -0.4293250 | 2.8155530 |
| H | 1.8502350 | -0.3841220 | -0.6553260 |
| H | 0.4004960 | -0.3333320 | -0.9743490 |
| C | -2.5862300 | -1.0182380 | 0.8620220 |
| C | -3.6809760 | -1.8674820 | 0.8345300 |
| C | -3.6950820 | -2.9243800 | -0.0594970 |
| C | -2.6177730 | -3.1043650 | -0.9091060 |
| C | -1.5473730 | -2.2257650 | -0.8446740 |
| F | -2.6534340 | 0.0015110 | 1.7377490 |
| F | -4.7158890 | -1.6764530 | 1.6510810 |
| F | -4.7326160 | -3.7555180 | -0.1029620 |
| F | -2.6239690 | -4.1106060 | -1.7834630 |
| F | -0.5559330 | -2.4529730 | -1.7289220 |
| C | -0.6959080 | 2.4540890 | 0.7985920 |

| | | | |
|---|---|---|---|
| C | -1.2017700 | 3.7219510 | 0.5480480 |
| C | -1.8316200 | 3.9816270 | -0.6558040 |
| C | -1.9378270 | 2.9691230 | -1.5945920 |
| C | -1.4148300 | 1.7198390 | -1.3031360 |
| F | -0.0788970 | 2.3000420 | 1.9808840 |
| F | -1.0821270 | 4.6925580 | 1.4545950 |
| F | -2.3227650 | 5.1913660 | -0.9121590 |
| F | -2.5332310 | 3.2080600 | -2.7628990 |
| F | -1.5344070 | 0.7856800 | -2.2589760 |

43

**$TS_{1c}$**

| | | | |
|---|---|---|---|
| C | 0.010859 | 0.027752 | 0.011063 |
| N | 0.013636 | 0.040453 | 1.509771 |
| C | -1.081134 | -0.643527 | 2.271308 |
| C | -2.428038 | -0.185205 | 1.686193 |
| C | -2.513005 | -0.341929 | 0.175495 |
| C | -1.387585 | 0.454433 | -0.467327 |
| C | 1.313003 | 0.001502 | 2.125977 |
| C | 1.847289 | 1.155838 | 2.726950 |
| C | 3.117229 | 1.075315 | 3.316566 |
| C | 3.851480 | -0.098961 | 3.322526 |
| C | 3.319907 | -1.233815 | 2.728658 |
| C | 2.066359 | -1.176483 | 2.140078 |
| B | 1.219597 | 2.596547 | 2.851583 |
| Cl | 1.859861 | 3.908121 | 1.809981 |
| C | -1.028536 | -0.180740 | 3.733315 |
| C | -1.021483 | -2.184835 | 2.287653 |
| C | 1.013318 | 1.074387 | -0.492946 |
| C | 0.396000 | -1.313439 | -0.646450 |
| Cl | 0.587635 | 3.125942 | 4.443911 |
| H | -3.227493 | -0.741801 | 2.184047 |
| H | -2.573657 | 0.871874 | 1.937715 |
| H | -1.527395 | 1.515052 | -0.227691 |
| H | -1.419813 | 0.369594 | -1.557534 |
| H | -2.453221 | -1.397857 | -0.109246 |
| H | -3.480176 | 0.020013 | -0.184281 |
| H | 0.793265 | 2.067379 | -0.099312 |
| H | 2.040281 | 0.820333 | -0.222895 |
| H | 0.955514 | 1.126712 | -1.583058 |
| H | 0.362938 | -1.196010 | -1.733206 |
| H | 1.414280 | -1.604957 | -0.386137 |
| H | -0.275084 | -2.130512 | -0.386645 |
| H | -0.111809 | -0.502653 | 4.231421 |
| H | -1.098484 | 0.904420 | 3.816626 |
| H | -1.874403 | -0.612602 | 4.274080 |
| H | -1.862975 | -2.564353 | 2.873980 |
| H | -1.088014 | -2.630377 | 1.296427 |
| H | -0.109314 | -2.541514 | 2.767617 |
| H | 1.660263 | -2.065915 | 1.679728 |
| H | 3.877174 | -2.163721 | 2.721699 |
| H | 4.830053 | -0.125169 | 3.787506 |
| H | 3.542108 | 1.958502 | 3.784153 |
| H | -0.350482 | 1.884930 | 1.881884 |
| H | -0.437866 | 2.637272 | 2.063136 |

43

**4c**

| | | | |
|---|---|---|---|
| C | 3.072820 | -0.524372 | -1.641507 |
| N | 2.446040 | -1.115866 | -0.352559 |
| C | 2.519250 | -2.644183 | -0.100442 |
| C | 2.012384 | -3.322219 | -1.381512 |
| C | 2.717019 | -2.855649 | -2.648171 |
| C | 2.526411 | -1.353905 | -2.812460 |
| C | 2.583471 | -0.273115 | 0.855939 |
| C | 1.417575 | 0.352394 | 1.297504 |
| C | 1.544375 | 1.150893 | 2.441286 |
| C | 2.752959 | 1.311364 | 3.096274 |
| C | 3.893544 | 0.669371 | 2.623211 |
| C | 3.812364 | -0.129516 | 1.495159 |

| | | | |
|---|---|---|---|
| B | -0.024605 | 0.200301 | 0.570682 |
| Cl | -0.615322 | 1.881849 | -0.025232 |
| C | 1.552970 | -2.955000 | 1.044959 |
| C | 3.909772 | -3.144049 | 0.283505 |
| C | 2.563088 | 0.913205 | -1.767534 |
| C | 4.599396 | -0.503254 | -1.636015 |
| Cl | -1.256412 | -0.573413 | 1.760155 |
| H | 2.118939 | -4.401448 | -1.246501 |
| H | 0.937854 | -3.124380 | -1.477084 |
| H | 1.456226 | -1.139392 | -2.920085 |
| H | 3.008958 | -0.993234 | -3.724257 |
| H | 3.780408 | -3.113857 | -2.621411 |
| H | 2.296247 | -3.374271 | -3.512666 |
| H | 1.473932 | 0.973835 | -1.724668 |
| H | 2.966500 | 1.558077 | -0.986050 |
| H | 2.885557 | 1.302901 | -2.735638 |
| H | 4.917636 | -0.034512 | -2.569892 |
| H | 4.990730 | 0.106029 | -0.822722 |
| H | 5.056783 | -1.489178 | -1.595996 |
| H | 1.897149 | -2.538333 | 1.992199 |
| H | 0.547295 | -2.574685 | 0.855893 |
| H | 1.489820 | -4.040444 | 1.149364 |
| H | 3.824854 | -4.216610 | 0.472034 |
| H | 4.659551 | -3.009936 | -0.492842 |
| H | 4.262808 | -2.684280 | 1.205338 |
| H | 4.698863 | -0.627131 | 1.129187 |
| H | 4.844028 | 0.789132 | 3.129676 |
| H | 2.811684 | 1.937872 | 3.979052 |
| H | 0.659136 | 1.653784 | 2.814910 |
| H | 1.431790 | -0.987818 | -0.540608 |
| H | -0.011286 | -0.523080 | -0.419515 |

43

**$TS_{1b}$**

| | | | |
|---|---|---|---|
| C | 1.802357 | -0.891511 | 2.998362 |
| C | 1.226963 | 0.178856 | 2.288997 |
| C | 1.782655 | 1.452801 | 2.422293 |
| C | 2.877017 | 1.686394 | 3.246759 |
| C | 3.419670 | 0.645302 | 3.982791 |
| C | 2.869552 | -0.624362 | 3.866847 |
| N | 0.041832 | -0.053180 | 1.507795 |
| C | 0.209090 | -0.016354 | 0.027469 |
| C | -1.042041 | -0.643369 | -0.611071 |
| C | -2.343757 | -0.036723 | -0.109459 |
| C | -2.414026 | -0.190845 | 1.402884 |
| C | -1.220462 | 0.450833 | 2.132370 |
| C | 1.406894 | -0.894662 | -0.354393 |
| C | 0.463632 | 1.377797 | -0.586938 |
| C | -1.267756 | -0.001029 | 3.600172 |
| C | -1.403706 | 1.985348 | 2.141887 |
| B | 1.515649 | -2.418900 | 2.838340 |
| H | 1.742402 | -2.982104 | 1.812242 |
| H | -0.600471 | -3.048652 | 2.353534 |
| H | -0.961094 | -0.551477 | -1.698605 |
| H | -1.043178 | -1.714832 | -0.379457 |
| H | -2.441841 | -1.258197 | 1.646878 |
| H | -3.335937 | 0.248270 | 1.796442 |
| H | -2.414158 | 1.018487 | -0.394810 |
| H | -3.195745 | -0.539072 | -0.576665 |
| H | -1.117824 | -1.076961 | 3.695790 |
| H | -0.510233 | 0.502717 | 4.203944 |
| H | -2.248154 | 0.244823 | 4.016896 |
| H | -2.339334 | 2.227700 | 2.654248 |
| H | -0.600211 | 2.478450 | 2.690150 |
| H | -1.458135 | 2.418597 | 1.144248 |
| H | 2.342345 | -0.504690 | 0.053151 |
| H | 1.273050 | -1.914144 | 0.007447 |
| H | 1.500399 | -0.925030 | -1.443254 |
| H | 0.580808 | 1.276716 | -1.669797 |
| H | -0.348468 | 2.081628 | -0.410886 |

| | | | |
|---|---|---|---|
| H | 1.387048 | 1.814075 | -0.202527 |
| H | 1.349184 | 2.281118 | 1.879148 |
| H | 3.286908 | 2.687138 | 3.326436 |
| H | 4.254883 | 0.819583 | 4.651600 |
| H | 3.287067 | -1.433969 | 4.459319 |
| H | -0.528238 | -2.380761 | 2.011697 |
| H | 1.325445 | -3.084699 | 3.815648 |

43

**4b**

| | | | |
|---|---|---|---|
| C | 3.820676 | -0.114146 | 1.519212 |
| C | 2.602203 | -0.272564 | 0.863566 |
| C | 1.410854 | 0.334442 | 1.270615 |
| C | 1.518303 | 1.139158 | 2.416130 |
| C | 2.713918 | 1.318090 | 3.091736 |
| C | 3.874722 | 0.690360 | 2.645273 |
| N | 2.467812 | -1.114597 | -0.342912 |
| C | 3.080555 | -0.527334 | -1.628883 |
| C | 2.503253 | -1.336647 | -2.799957 |
| C | 2.669515 | -2.843317 | -2.648131 |
| C | 1.988465 | -3.307561 | -1.366963 |
| C | 2.530248 | -2.634326 | -0.096963 |
| C | 2.592444 | 0.921571 | -1.736011 |
| C | 4.607758 | -0.529078 | -1.648571 |
| C | 1.584404 | -2.937969 | 1.070178 |
| C | 3.922866 | -3.151360 | 0.258028 |
| B | -0.016461 | 0.158441 | 0.515849 |
| H | -0.820946 | -0.351112 | 1.275787 |
| H | -0.405097 | 1.242337 | 0.117756 |
| H | 2.089485 | -4.388496 | -1.238645 |
| H | 0.914910 | -3.096515 | -1.437251 |
| H | 1.435669 | -1.102746 | -2.886888 |
| H | 2.979786 | -0.979946 | -3.716893 |
| H | 3.728553 | -3.120798 | -2.649321 |
| H | 2.219006 | -3.349091 | -3.505611 |
| H | 1.508463 | 0.994314 | -1.627705 |
| H | 3.052563 | 1.556534 | -0.977985 |
| H | 2.870404 | 1.301941 | -2.721876 |
| H | 4.921980 | -0.020994 | -2.563409 |
| H | 5.019819 | 0.032239 | -0.810994 |
| H | 5.048659 | -1.523530 | -1.661479 |
| H | 1.977778 | -2.558441 | 2.013951 |
| H | 0.594997 | -2.503132 | 0.915169 |
| H | 1.479731 | -4.022685 | 1.149594 |
| H | 3.826516 | -4.215541 | 0.486169 |
| H | 4.648370 | -3.056112 | -0.546996 |
| H | 4.315231 | -2.665222 | 1.150290 |
| H | 4.719452 | -0.603272 | 1.169311 |
| H | 4.813855 | 0.825755 | 3.168906 |
| H | 2.749064 | 1.949680 | 3.973141 |
| H | 0.622332 | 1.634637 | 2.775814 |
| H | 1.434786 | -0.965589 | -0.509020 |
| H | 0.045233 | -0.587213 | -0.488028 |

2

HCl

| | | | |
|---|---|---|---|
| H | 0.0000000 | 0.0000000 | -1.2112400 |
| Cl | 0.0000000 | 0.0000000 | 0.0712490 |

43

**5c**

| | | | |
|---|---|---|---|
| B | -1.633103 | 7.495271 | 7.248679 |
| Cl | -2.096580 | 7.579020 | 9.128215 |
| Cl | -3.185141 | 6.959285 | 6.371843 |
| Cl | -1.140193 | 9.226542 | 6.774984 |
| C | -0.419222 | 6.473641 | 6.836340 |
| C | -0.142808 | 6.469746 | 5.456362 |
| H | -0.732346 | 7.115340 | 4.816544 |
| C | 0.839702 | 5.685181 | 4.884121 |
| H | 1.006097 | 5.725488 | 3.813967 |

| | | | |
|---|---|---|---|
| C | 1.609421 | 4.848555 | 5.683234 |
| H | 2.384705 | 4.225509 | 5.253463 |
| C | 1.375001 | 4.817939 | 7.044281 |
| H | 1.970482 | 4.169495 | 7.668417 |
| C | 0.377663 | 5.618648 | 7.601687 |
| N | 0.160199 | 5.555187 | 9.062317 |
| H | -0.615208 | 6.228683 | 9.208303 |
| C | 1.277611 | 6.221027 | 9.916677 |
| C | 0.714544 | 6.344004 | 11.340808 |
| H | 1.510366 | 6.744950 | 11.973489 |
| H | -0.088658 | 7.088537 | 11.336067 |
| C | 0.177494 | 5.034336 | 11.904981 |
| H | 0.978293 | 4.294404 | 12.004280 |
| H | -0.209943 | 5.204768 | 12.912048 |
| C | -0.941352 | 4.508009 | 11.014450 |
| H | -1.763380 | 5.231675 | 11.005995 |
| H | -1.349233 | 3.574409 | 11.409901 |
| C | -0.507142 | 4.242291 | 9.564888 |
| C | -1.745867 | 4.008335 | 8.695162 |
| H | -2.413461 | 4.870796 | 8.683051 |
| H | -2.295983 | 3.162659 | 9.113757 |
| H | -1.478272 | 3.766183 | 7.665908 |
| C | 0.382400 | 3.003430 | 9.475453 |
| H | 1.291438 | 3.063130 | 10.069052 |
| H | 0.641418 | 2.762627 | 8.445778 |
| H | -0.202078 | 2.165489 | 9.862003 |
| C | 1.511153 | 7.619172 | 9.336835 |
| H | 1.959056 | 7.575982 | 8.343289 |
| H | 2.199612 | 8.147721 | 9.999916 |
| H | 0.591091 | 8.201595 | 9.274213 |
| C | 2.609458 | 5.472572 | 9.914811 |
| H | 3.053560 | 5.435398 | 8.921506 |
| H | 2.555749 | 4.465555 | 10.321436 |
| H | 3.293020 | 6.041518 | 10.549028 |

43

**$TS_{5c/1c}$**

| | | | |
|---|---|---|---|
| B | 0.271500 | -0.153940 | -0.090527 |
| Cl | -0.587237 | -0.354259 | 3.936233 |
| Cl | -0.696609 | -1.622705 | -0.214820 |
| Cl | -0.552603 | 1.252753 | 0.577346 |
| C | 1.680211 | -0.083674 | -0.750451 |
| C | 1.668962 | -0.143570 | -2.150992 |
| H | 0.724305 | -0.258201 | -2.673733 |
| C | 2.837919 | -0.053694 | -2.888740 |
| H | 2.804028 | -0.087172 | -3.971270 |
| C | 4.047553 | 0.061272 | -2.220964 |
| H | 4.977041 | 0.113666 | -2.776643 |
| C | 4.075506 | 0.090949 | -0.834149 |
| H | 5.031146 | 0.147662 | -0.335185 |
| C | 2.904229 | 0.034441 | -0.071395 |
| N | 2.933773 | 0.053722 | 1.371216 |
| H | 0.269656 | 0.020819 | 3.051412 |
| C | 3.436923 | 1.335441 | 1.971603 |
| C | 3.180163 | 1.286577 | 3.485629 |
| H | 3.567163 | 2.207109 | 3.931868 |
| H | 2.097889 | 1.287609 | 3.658862 |
| C | 3.784452 | 0.059693 | 4.147086 |
| H | 4.874575 | 0.061115 | 4.039952 |
| H | 3.577427 | 0.067792 | 5.220627 |
| C | 3.176166 | -1.180470 | 3.514153 |
| H | 2.108577 | -1.201981 | 3.750178 |
| H | 3.603428 | -2.089794 | 3.946729 |
| C | 3.347826 | -1.255571 | 1.986553 |
| C | 2.402303 | -2.352945 | 1.486374 |
| H | 1.365461 | -2.113250 | 1.728769 |
| H | 2.648168 | -3.295841 | 1.981340 |
| H | 2.481276 | -2.510588 | 0.408678 |
| C | 4.784553 | -1.721102 | 1.664936 |
| H | 5.550333 | -1.042176 | 2.038464 |

| | | | |
|---|---|---|---|
| H | 4.932978 | -1.857386 | 0.593072 |
| H | 4.953528 | -2.691908 | 2.138363 |
| C | 2.622995 | 2.501271 | 1.401808 |
| H | 2.717743 | 2.572831 | 0.315794 |
| H | 2.986809 | 3.438205 | 1.831681 |
| H | 1.567508 | 2.400882 | 1.648074 |
| C | 4.925858 | 1.682650 | 1.730600 |
| H | 5.107127 | 1.960809 | 0.691935 |
| H | 5.611890 | 0.881117 | 1.998270 |
| H | 5.185449 | 2.551845 | 2.341095 |

43

**$TS_{4c/1d}$**

| | | | |
|---|---|---|---|
| C | 0.044604 | 0.045031 | 0.067665 |
| N | 0.003437 | 0.060285 | 1.584165 |
| C | -0.664043 | -1.079392 | 2.318400 |
| C | -2.022147 | -1.376765 | 1.657425 |
| C | -1.928070 | -1.579284 | 0.153276 |
| C | -1.348115 | -0.322470 | -0.477396 |
| C | 1.275358 | 0.468823 | 2.160989 |
| C | 1.424244 | 1.747383 | 2.731181 |
| C | 2.695343 | 2.158888 | 3.160286 |
| C | 3.796416 | 1.320649 | 3.095480 |
| C | 3.638942 | 0.049653 | 2.567812 |
| C | 2.398742 | -0.359746 | 2.096437 |
| B | 0.256164 | 2.704869 | 3.083790 |
| Cl | -2.657477 | 2.233203 | 1.664713 |
| C | -0.928369 | -0.613128 | 3.755164 |
| C | 0.131720 | -2.399671 | 2.413747 |
| C | 0.392472 | 1.462352 | -0.408343 |
| C | 1.075011 | -0.906563 | -0.579468 |
| Cl | 0.383516 | 4.431665 | 2.745558 |
| H | -2.445206 | -2.259639 | 2.144652 |
| H | -2.713837 | -0.554364 | 1.859423 |
| H | -2.039953 | 0.506761 | -0.313686 |
| H | -1.260713 | -0.436990 | -1.561282 |
| H | -1.313884 | -2.454711 | -0.084110 |
| H | -2.921404 | -1.776875 | -0.258401 |
| H | -0.294839 | 2.207422 | -0.003092 |
| H | 1.408816 | 1.745539 | -0.126799 |
| H | 0.323692 | 1.502103 | -1.498494 |
| H | 0.945671 | -0.863580 | -1.663914 |
| H | 2.100054 | -0.602612 | -0.370065 |
| H | 0.950463 | -1.946918 | -0.279619 |
| H | 0.001361 | -0.376419 | 4.278054 |
| H | -1.570545 | 0.268613 | 3.775392 |
| H | -1.431127 | -1.410161 | 4.309074 |
| H | -0.505482 | -3.152572 | 2.884664 |
| H | 0.436030 | -2.792898 | 1.443988 |
| H | 1.016667 | -2.294045 | 3.041299 |
| H | 2.318139 | -1.340561 | 1.655913 |
| H | 4.484135 | -0.626231 | 2.501171 |
| H | 4.763927 | 1.658770 | 3.447463 |
| H | 2.816228 | 3.156422 | 3.568796 |
| H | -1.614863 | 1.427502 | 1.704186 |
| H | -0.698070 | 2.369663 | 3.698088 |

43

**$TS_{1d/4d}$**

| | | | |
|---|---|---|---|
| C | 0.015786 | -0.034275 | 0.038349 |
| N | 0.008030 | -0.044982 | 1.533861 |
| C | -1.158190 | 0.496237 | 2.293388 |
| C | -2.444511 | -0.100445 | 1.696418 |
| C | -2.533907 | 0.051249 | 0.185233 |
| C | -1.322915 | -0.613545 | -0.452090 |
| C | 1.290861 | 0.126240 | 2.158779 |
| C | 1.935157 | 1.366827 | 2.155599 |
| C | 3.182330 | 1.541824 | 2.736538 |
| C | 3.819319 | 0.462226 | 3.328840 |
| C | 3.195213 | -0.775613 | 3.332541 |

| | | | |
|---|---|---|---|
| C | 1.928420 | -0.971864 | 2.763898 |
| B | 1.380789 | -2.433866 | 2.968085 |
| Cl | 2.265197 | -3.784467 | 2.183977 |
| C | -1.058991 | 0.021115 | 3.750146 |
| C | -1.268277 | 2.034638 | 2.327661 |
| C | 1.135110 | -0.964004 | -0.453507 |
| C | 0.251618 | 1.340892 | -0.621158 |
| H | -0.246883 | -2.773029 | 2.015161 |
| H | -1.357846 | -0.527671 | -1.542179 |
| H | -1.345906 | -1.684001 | -0.217636 |
| H | -2.479324 | -1.167859 | 1.943473 |
| H | -3.302792 | 0.366834 | 2.188550 |
| H | -2.588455 | 1.108441 | -0.096006 |
| H | -3.452994 | -0.413132 | -0.183204 |
| H | -0.976700 | -1.065545 | 3.810949 |
| H | -0.200429 | 0.459230 | 4.263088 |
| H | -1.962100 | 0.322101 | 4.287312 |
| H | -2.131923 | 2.318575 | 2.935830 |
| H | -0.386824 | 2.483166 | 2.788285 |
| H | -1.404304 | 2.475725 | 1.340963 |
| H | 2.124770 | -0.577891 | -0.201942 |
| H | 1.044896 | -1.966474 | -0.031027 |
| H | 1.074693 | -1.050698 | -1.541486 |
| H | 0.228452 | 1.222751 | -1.708285 |
| H | -0.503506 | 2.079818 | -0.356141 |
| H | 1.232634 | 1.741228 | -0.362621 |
| H | 1.448099 | 2.212212 | 1.690068 |
| H | 3.653061 | 2.518378 | 2.721191 |
| H | 4.797425 | 0.578594 | 3.781214 |
| H | 3.709101 | -1.615795 | 3.789841 |
| H | -0.217947 | -2.024427 | 1.838130 |
| H | 0.733648 | -2.738718 | 3.919778 |

43

**4d**

| | | | |
|---|---|---|---|
| C | -0.633963 | -1.177101 | 2.320895 |
| N | 0.053981 | -0.015056 | 1.567493 |
| C | 0.039490 | 0.006034 | 0.022732 |
| C | -1.421287 | -0.196936 | -0.405844 |
| C | -2.082640 | -1.418613 | 0.218696 |
| C | -2.049165 | -1.297713 | 1.736576 |
| C | 1.293093 | 0.496804 | 2.190304 |
| C | 2.473720 | -0.241255 | 2.176943 |
| C | 3.601641 | 0.289217 | 2.781124 |
| C | 3.532604 | 1.541181 | 3.385904 |
| C | 2.344147 | 2.252169 | 3.380020 |
| C | 1.177955 | 1.756077 | 2.781294 |
| B | -0.182034 | 2.642652 | 2.788974 |
| Cl | -0.758165 | 2.903513 | 4.585687 |
| C | 0.497730 | 1.402401 | -0.411204 |
| C | 0.959326 | -1.029185 | -0.620444 |
| C | -0.734906 | -0.758238 | 3.789982 |
| C | 0.119034 | -2.503113 | 2.240200 |
| H | -1.131706 | 2.094770 | 2.212709 |
| H | -2.529397 | -2.157911 | 2.209744 |
| H | -2.623561 | -0.413480 | 2.037594 |
| H | -1.991077 | 0.697773 | -0.127631 |
| H | -1.440766 | -0.254143 | -1.497245 |
| H | -1.591019 | -2.339613 | -0.110460 |
| H | -3.119152 | -1.485768 | -0.120106 |
| H | -0.073526 | 2.191546 | 0.081750 |
| H | 1.555303 | 1.563567 | -0.199446 |
| H | 0.343748 | 1.490044 | -1.489142 |
| H | 0.920863 | -0.870425 | -1.700639 |
| H | 1.995139 | -0.893456 | -0.312354 |
| H | 0.663835 | -2.059136 | -0.433422 |
| H | 0.244510 | -0.720568 | 4.268295 |
| H | -1.205219 | 0.219597 | 3.913332 |
| H | -1.345195 | -1.498584 | 4.312333 |
| H | -0.436013 | -3.226442 | 2.841933 |

| | | | |
|---|---|---|---|
| H | 0.196640 | -2.909262 | 1.234087 |
| H | 1.115909 | -2.425600 | 2.671855 |
| H | 2.527110 | -1.213678 | 1.707991 |
| H | 4.528234 | -0.272802 | 2.779357 |
| H | 4.412730 | 1.960017 | 3.861209 |
| H | 2.297998 | 3.224020 | 3.859720 |
| H | -0.580831 | 0.786418 | 1.793504 |
| H | 0.005024 | 3.714753 | 2.263125 |

43

**$TS_{4d/1b}$**

| | | | |
|---|---|---|---|
| C | 0.081380 | -0.135887 | -0.070695 |
| C | 0.001339 | -0.044436 | 1.319810 |
| C | -1.276533 | 0.102444 | 1.908085 |
| C | -2.394927 | 0.225858 | 1.065383 |
| C | -2.299028 | 0.124645 | -0.314160 |
| C | -1.049369 | -0.068627 | -0.877743 |
| N | 1.199821 | -0.023665 | 2.136794 |
| C | 1.953687 | -1.326932 | 2.167286 |
| C | 3.136454 | -1.196941 | 3.142828 |
| C | 4.012698 | 0.013894 | 2.865373 |
| C | 3.160838 | 1.269256 | 2.969893 |
| C | 1.960938 | 1.275806 | 2.004748 |
| C | 1.009780 | -2.402958 | 2.716802 |
| C | 2.489786 | -1.847741 | 0.814387 |
| C | 1.022526 | 2.418384 | 2.417117 |
| C | 2.487379 | 1.619636 | 0.592951 |
| B | -1.638849 | -0.062827 | 3.399412 |
| H | -1.018443 | -0.758441 | 4.132768 |
| Cl | 0.942075 | 0.433386 | 5.715068 |
| H | 3.758305 | 2.162005 | 2.765028 |
| H | 2.806398 | 1.369408 | 3.998145 |
| H | 2.755874 | -1.129283 | 4.166164 |
| H | 3.718779 | -2.121288 | 3.091977 |
| H | 4.478452 | -0.061673 | 1.876713 |
| H | 4.829758 | 0.057986 | 3.590576 |
| H | 0.659838 | -2.147929 | 3.717949 |
| H | 0.138050 | -2.540589 | 2.072613 |
| H | 1.540076 | -3.357364 | 2.772709 |
| H | 3.097617 | -2.737151 | 1.000165 |
| H | 1.680294 | -2.149185 | 0.149209 |
| H | 3.119033 | -1.127078 | 0.292365 |
| H | 0.201955 | 2.544865 | 1.707843 |
| H | 0.595205 | 2.248333 | 3.407587 |
| H | 1.585980 | 3.354602 | 2.449540 |
| H | 3.054168 | 2.552400 | 0.653608 |
| H | 3.155467 | 0.860078 | 0.186819 |
| H | 1.676341 | 1.785666 | -0.115593 |
| H | 1.042478 | -0.244499 | -0.547978 |
| H | -0.938959 | -0.144746 | -1.954008 |
| H | -3.182113 | 0.205816 | -0.937082 |
| H | -3.367104 | 0.387563 | 1.519355 |
| H | 0.910900 | 0.193921 | 4.430117 |
| H | -2.656126 | 0.423286 | 3.799964 |

84

**$TS_{H/Cl}$**

| | | | |
|---|---|---|---|
| C | 4.2664790 | -0.2093870 | 1.4820540 |
| N | 4.0203330 | 0.3162040 | 0.1258530 |
| C | 5.1557430 | 0.5835440 | -0.7975980 |
| C | 6.0706530 | -0.6535410 | -0.8198720 |
| C | 6.4689050 | -1.1270370 | 0.5706130 |
| C | 5.2116940 | -1.4195080 | 1.3761960 |
| C | 2.8437890 | 1.0981420 | -0.1167100 |
| C | 1.7418920 | 0.5728370 | -0.8392990 |
| C | 0.7662580 | 1.5047010 | -1.2267960 |
| C | 0.7966510 | 2.8479250 | -0.8808520 |
| C | 1.8254990 | 3.3211460 | -0.0827710 |
| C | 2.8366560 | 2.4424690 | 0.2803820 |
| B | 1.4115730 | -1.0069730 | -1.0809780 |

| | | | |
|---|---|---|---|
| Cl | 0.0195030 | -1.2401270 | -2.4175830 |
| C | 4.6269410 | 0.7908660 | -2.2251760 |
| C | 5.9976840 | 1.8364150 | -0.4545410 |
| C | 2.9483500 | -0.7200790 | 2.0726470 |
| C | 4.8367230 | 0.8109670 | 2.4979020 |
| Cl | 2.7879270 | -2.1862900 | -1.5647480 |
| C | -0.5046850 | 0.1771470 | 1.6410270 |
| C | -1.6601310 | -0.2798540 | 0.9897070 |
| C | -2.6597340 | 0.6819140 | 0.7488970 |
| C | -2.5153820 | 1.9971800 | 1.1591360 |
| C | -1.3444010 | 2.4089770 | 1.7815580 |
| C | -0.3317870 | 1.4975500 | 2.0151370 |
| N | -3.9181930 | 0.2760200 | 0.0860420 |
| C | -4.1866770 | 0.9337690 | -1.3147820 |
| C | -5.3107590 | 0.0993870 | -1.9441550 |
| C | -6.5544070 | -0.0144970 | -1.0719020 |
| C | -6.2003680 | -0.6758770 | 0.2539750 |
| C | -5.1199790 | 0.0617750 | 1.0590570 |
| C | -2.9025780 | 0.7760110 | -2.1223630 |
| C | -4.5545660 | 2.4156810 | -1.2782140 |
| C | -4.6399620 | -0.8416890 | 2.1981460 |
| C | -5.6532430 | 1.3547670 | 1.6692640 |
| B | -1.6935300 | -1.8175310 | 0.6839360 |
| Cl | -0.8351680 | -2.9469670 | 1.7036910 |
| Cl | -2.7510390 | -2.5753890 | -0.5379770 |
| H | -5.5496840 | 0.5519530 | -2.9089970 |
| H | -4.9256770 | -0.9035830 | -2.1630570 |
| H | -5.8539270 | -1.6981360 | 0.0599850 |
| H | -7.0810680 | -0.7636320 | 0.8950220 |
| H | -7.0068850 | 0.9684650 | -0.9092880 |
| H | -7.3069160 | -0.6169460 | -1.5851540 |
| H | -4.2314680 | -1.7866230 | 1.8351060 |
| H | -3.8953690 | -0.3516620 | 2.8261980 |
| H | -5.5040270 | -1.0826910 | 2.8203340 |
| H | -6.4234170 | 1.0739520 | 2.3906950 |
| H | -4.8823710 | 1.8943800 | 2.2179220 |
| H | -6.1168580 | 2.0238910 | 0.9495590 |
| H | -2.1060960 | 1.4110580 | -1.7350110 |
| H | -2.5276320 | -0.2476240 | -2.1469220 |
| H | -3.1053890 | 1.0781340 | -3.1517670 |
| H | -4.7583130 | 2.7061430 | -2.3111950 |
| H | -5.4417590 | 2.6521590 | -0.6973000 |
| H | -3.7252120 | 3.0338420 | -0.9404370 |
| H | -3.3041790 | 2.7141000 | 0.9939830 |
| H | -1.2275380 | 3.4471520 | 2.0672160 |
| H | 0.6035010 | 1.8124920 | 2.4602070 |
| H | 0.2964060 | -0.5231780 | 1.8246820 |
| H | -3.7280450 | -0.6867890 | -0.2160710 |
| H | 0.9167890 | -1.4607240 | -0.0780250 |
| H | 5.4658840 | -1.7555620 | 2.3877710 |
| H | 4.6616480 | -2.2276200 | 0.8835890 |
| H | 5.5324840 | -1.4594660 | -1.3262220 |
| H | 6.9576930 | -0.4194700 | -1.4182310 |
| H | 7.0887780 | -0.3767340 | 1.0759200 |
| H | 7.0810320 | -2.0311820 | 0.4961070 |
| H | 3.9848420 | -0.0356240 | -2.5281630 |
| H | 4.0647650 | 1.7230350 | -2.3191520 |
| H | 5.4785300 | 0.8410900 | -2.9101590 |
| H | 6.7609820 | 1.9791960 | -1.2258310 |
| H | 5.3779310 | 2.7349180 | -0.4417850 |
| H | 6.5128900 | 1.7601660 | 0.5028010 |
| H | 2.2725530 | 0.1139390 | 2.2779300 |
| H | 2.4638840 | -1.4179950 | 1.3886790 |
| H | 3.1464560 | -1.2316180 | 3.0188460 |
| H | 4.9036110 | 0.3464100 | 3.4871370 |
| H | 5.8332450 | 1.1628250 | 2.2343500 |
| H | 4.1812180 | 1.6805070 | 2.5871660 |
| H | 3.6765950 | 2.8141050 | 0.8531330 |
| H | 1.8698920 | 4.3625180 | 0.2199890 |
| H | 0.0163910 | 3.5175050 | -1.2322060 |

| | | | |
|---|---|---|---|
| H | -0.0436990 | 1.1488150 | -1.8489340 |

Geometries Optimized at M05-2X/6-31G(d) level (for the energy partitioning scheme:

61

**1a**

| | | | |
|---|---|---|---|
| B | -0.6396600 | -0.0751170 | 0.5330000 |
| C | 0.0390780 | -1.2608100 | 1.2833650 |
| C | -0.6051460 | -1.7114160 | 2.4457770 |
| H | -1.5562200 | -1.2714450 | 2.7256640 |
| C | -0.0473900 | -2.6885360 | 3.2569530 |
| H | -0.5502800 | -3.0018130 | 4.1626080 |
| C | 1.1507510 | -3.2779830 | 2.8705400 |
| H | 1.5867310 | -4.0693960 | 3.4674970 |
| C | 1.7863870 | -2.8713260 | 1.7021990 |
| H | 2.6919970 | -3.3722100 | 1.3978290 |
| C | 1.2679370 | -1.8407960 | 0.9067000 |
| N | 1.9310860 | -1.3959970 | -0.2910590 |
| C | 3.3271770 | -0.8848980 | -0.1052420 |
| C | 3.7551110 | -0.2025760 | -1.4135290 |
| H | 3.0988130 | 0.6567870 | -1.5863120 |
| H | 4.7699460 | 0.1819170 | -1.2836600 |
| C | 3.6558190 | -1.1332230 | -2.6114660 |
| H | 4.2994850 | -2.0074840 | -2.4771450 |
| H | 3.9947680 | -0.6264930 | -3.5177800 |
| C | 2.1961510 | -1.5374520 | -2.7558430 |
| H | 2.0531750 | -2.2152420 | -3.6020350 |
| H | 1.6085150 | -0.6372490 | -2.9521860 |
| C | 1.6214530 | -2.2220680 | -1.5057090 |
| C | 2.1118730 | -3.6825110 | -1.4492440 |
| H | 3.1947190 | -3.7728780 | -1.5140440 |
| H | 1.6909380 | -4.2259200 | -2.2985400 |
| H | 1.7685480 | -4.1783200 | -0.5408050 |
| C | 0.1034410 | -2.2773330 | -1.6955370 |
| H | -0.3115490 | -1.2667590 | -1.7198120 |
| H | -0.3890440 | -2.8540510 | -0.9154690 |
| H | -0.1153480 | -2.7486850 | -2.6566610 |
| C | 4.4120200 | -1.9109660 | 0.3044610 |
| H | 4.3479470 | -2.1457320 | 1.3668360 |
| H | 5.3947180 | -1.4633630 | 0.1368580 |
| H | 4.3721780 | -2.8403290 | -0.2578320 |
| C | 3.3268000 | 0.1957520 | 0.9802300 |
| H | 2.7595440 | 1.0641590 | 0.6552560 |
| H | 4.3565370 | 0.5108590 | 1.1649950 |
| H | 2.9104760 | -0.1695640 | 1.9207280 |
| C | -2.1687530 | -0.0984620 | 0.1510440 |
| C | -2.9138580 | -1.2829860 | 0.0527670 |
| F | -2.3629010 | -2.4727840 | 0.2974300 |
| C | -4.2498350 | -1.3133410 | -0.3124470 |
| F | -4.9045170 | -2.4700110 | -0.3977610 |
| C | -4.9089480 | -0.1256600 | -0.5883920 |
| F | -6.1889430 | -0.1393670 | -0.9335570 |
| C | -4.2245430 | 1.0755130 | -0.4996070 |
| F | -4.8545360 | 2.2199830 | -0.7571100 |
| C | -2.8860550 | 1.0705450 | -0.1410340 |
| F | -2.3103430 | 2.2730300 | -0.0697620 |
| C | 0.1551070 | 1.2773010 | 0.3496380 |
| C | 0.4706350 | 2.0241030 | 1.4738910 |
| F | 0.0774190 | 1.5900420 | 2.6815400 |
| C | 1.1688240 | 3.2196210 | 1.4073790 |
| F | 1.4462590 | 3.9151060 | 2.5098370 |
| C | 1.5880620 | 3.6843920 | 0.1694620 |
| F | 2.2723840 | 4.8222890 | 0.0806750 |
| C | 1.2815200 | 2.9677370 | -0.9793010 |
| F | 1.6865220 | 3.4110790 | -2.1699320 |
| C | 0.5536470 | 1.7947560 | -0.8699880 |
| F | 0.2387130 | 1.1480230 | -2.0042470 |

63
**4a**

| | | | |
|---|---|---|---|
| C | 1.8771250 | -2.2347740 | 2.0705570 |
| C | 1.3599480 | -1.4785210 | 1.0191390 |
| C | 0.0578000 | -0.9706920 | 1.0025130 |
| C | -0.7004400 | -1.2369680 | 2.1539940 |
| C | -0.2104230 | -1.9698630 | 3.2250260 |
| C | 1.0843300 | -2.4807750 | 3.1819490 |
| N | 2.2064010 | -1.1898250 | -0.1720300 |
| C | 3.4431860 | -0.2832150 | 0.1202570 |
| C | 4.6450010 | -1.1388030 | 0.5310460 |
| C | 4.9411480 | -2.2908800 | -0.4267750 |
| C | 3.7133490 | -3.1793560 | -0.6067900 |
| C | 2.4618230 | -2.4358640 | -1.0762240 |
| C | 3.7877210 | 0.5442500 | -1.1294680 |
| C | 3.0872860 | 0.6931930 | 1.2434850 |
| C | 2.5903570 | -1.9617910 | -2.5297910 |
| C | 1.2496920 | -3.3650180 | -1.0001330 |
| B | -0.5865690 | -0.1466860 | -0.2673120 |
| C | -2.2021720 | -0.3634430 | -0.3360170 |
| C | -0.1118530 | 1.4156660 | -0.2058940 |
| H | 3.4897500 | -3.7023010 | 0.3257890 |
| H | 3.9113360 | -3.9540540 | -1.3521920 |
| H | 5.5002410 | -0.4594320 | 0.5799530 |
| H | 4.4996470 | -1.5189470 | 1.5437140 |
| H | 5.7656490 | -2.8868550 | -0.0315930 |
| H | 5.2771120 | -1.9086300 | -1.3927970 |
| H | 4.3280360 | 1.4323710 | -0.7997310 |
| H | 4.4354100 | 0.0164950 | -1.8243180 |
| H | 2.9042470 | 0.8810000 | -1.6681550 |
| H | 3.9615980 | 1.3240320 | 1.4126130 |
| H | 2.2522590 | 1.3342740 | 0.9608230 |
| H | 2.8422940 | 0.1883690 | 2.1749110 |
| H | 1.7850460 | -1.2713820 | -2.7912840 |
| H | 3.5426120 | -1.4918940 | -2.7552990 |
| H | 2.4963490 | -2.8370740 | -3.1734880 |
| H | 0.3372340 | -2.8637590 | -1.3168640 |
| H | 1.4426170 | -4.1988460 | -1.6780650 |
| H | 1.0956970 | -3.7658930 | -0.0005520 |
| H | 2.8801830 | -2.6311630 | 2.0385540 |
| H | 1.4773190 | -3.0643750 | 4.0041940 |
| H | -0.8362810 | -2.1494750 | 4.0899780 |
| H | -1.7120460 | -0.8538690 | 2.1964580 |
| H | 1.5732870 | -0.6149160 | -0.7441440 |
| H | -0.1438180 | -0.6165300 | -1.3066870 |
| C | -3.1861480 | 0.6169430 | -0.2915530 |
| C | -4.5468900 | 0.3430330 | -0.3771000 |
| C | -4.9766020 | -0.9644670 | -0.5126450 |
| C | -4.0359480 | -1.9812900 | -0.5633340 |
| C | -2.6922730 | -1.6589400 | -0.4756960 |
| F | -2.8719290 | 1.9183370 | -0.1725920 |
| F | -5.4419990 | 1.3342870 | -0.3289740 |
| F | -6.2786790 | -1.2449470 | -0.5953530 |
| F | -4.4319410 | -3.2516240 | -0.6966240 |
| F | -1.8294610 | -2.6938240 | -0.5335990 |
| C | -0.3202070 | 2.2122340 | 0.9164300 |
| C | 0.1645190 | 3.5033080 | 1.0429770 |
| C | 0.9046620 | 4.0556000 | 0.0052220 |
| C | 1.1286520 | 3.3108490 | -1.1386200 |
| C | 0.6043830 | 2.0267280 | -1.2224110 |
| F | -1.0330870 | 1.7294800 | 1.9450460 |
| F | -0.0639720 | 4.2219520 | 2.1449450 |
| F | 1.3940320 | 5.2917820 | 0.1131140 |
| F | 1.8536910 | 3.8181950 | -2.1414880 |
| F | 0.8893590 | 1.3554960 | -2.3646860 |

62
**1a**$H^-$

| | | | |
|---|---|---|---|
| C | 3.0714310 | -0.2799340 | 2.3473600 |
| C | 2.2876590 | -0.2343930 | 1.1826010 |

| | | | |
|---|---|---|---|
| C | 0.8760010 | -0.2185880 | 1.2718780 |
| C | 0.3414210 | -0.3082980 | 2.5687520 |
| C | 1.1172440 | -0.3804850 | 3.7187940 |
| C | 2.5025730 | -0.3547870 | 3.6116610 |
| N | 2.9519550 | -0.2458660 | -0.0919340 |
| C | 3.4923860 | 1.0292670 | -0.5960520 |
| C | 3.6230310 | 0.9367540 | -2.1253830 |
| C | 4.3544490 | -0.3156790 | -2.5920680 |
| C | 3.6218060 | -1.5375220 | -2.0504610 |
| C | 3.5327970 | -1.5358280 | -0.5162830 |
| C | 2.4894800 | 2.1499440 | -0.3060150 |
| C | 4.8391210 | 1.4642290 | 0.0246910 |
| C | 2.5830500 | -2.6701930 | -0.1145370 |
| C | 4.9161950 | -1.8911620 | 0.0779300 |
| B | -0.1391710 | -0.1029610 | -0.0106040 |
| C | -1.3368360 | -1.2483430 | 0.0481600 |
| C | -0.9088120 | 1.3544870 | -0.1620690 |
| H | 4.1084630 | -2.4630630 | -2.3752830 |
| H | 2.5983700 | -1.5402590 | -2.4389660 |
| H | 2.6100680 | 0.9184140 | -2.5394300 |
| H | 4.1182920 | 1.8424060 | -2.4910750 |
| H | 5.3946260 | -0.3070650 | -2.2504320 |
| H | 4.3845200 | -0.3464240 | -3.6852250 |
| H | 1.5196140 | 1.8978370 | -0.7310730 |
| H | 2.3624330 | 2.3179040 | 0.7635870 |
| H | 2.8485700 | 3.0759000 | -0.7648020 |
| H | 5.6597490 | 0.7910800 | -0.2194870 |
| H | 5.1049560 | 2.4596730 | -0.3434760 |
| H | 4.7494580 | 1.5242900 | 1.1102910 |
| H | 2.5541020 | -2.8035020 | 0.9677350 |
| H | 1.5772340 | -2.4633120 | -0.4705340 |
| H | 2.9351330 | -3.6015910 | -0.5679600 |
| H | 4.8670940 | -1.9273400 | 1.1662600 |
| H | 5.2089710 | -2.8857330 | -0.2723380 |
| H | 5.7023270 | -1.1955070 | -0.2109880 |
| H | 4.1488010 | -0.2640480 | 2.2479340 |
| H | 3.1320780 | -0.3951810 | 4.4935490 |
| H | 0.6412850 | -0.4446440 | 4.6910500 |
| H | -0.7340850 | -0.2970240 | 2.6826070 |
| H | 0.4583390 | -0.2712400 | -1.0485010 |
| C | -2.4750500 | -1.1492070 | 0.8417630 |
| C | -3.4964100 | -2.0885270 | 0.8710960 |
| C | -3.4180160 | -3.1988500 | 0.0500820 |
| C | -2.3208840 | -3.3401010 | -0.7806430 |
| C | -1.3264460 | -2.3711420 | -0.7738060 |
| F | -2.6562660 | -0.0845440 | 1.6544340 |
| F | -4.5614210 | -1.9277770 | 1.6725090 |
| F | -4.3905700 | -4.1224800 | 0.0578300 |
| F | -2.2416240 | -4.4044990 | -1.5951960 |
| F | -0.3219080 | -2.5855390 | -1.6443570 |
| C | -0.8291220 | 2.4631460 | 0.6734340 |
| C | -1.5059270 | 3.6555030 | 0.4421910 |
| C | -2.3174200 | 3.7811860 | -0.6696780 |
| C | -2.4312810 | 2.7096570 | -1.5387650 |
| C | -1.7346490 | 1.5416980 | -1.2690590 |
| F | -0.0575120 | 2.4579800 | 1.7751750 |
| F | -1.3815280 | 4.6895890 | 1.2901340 |
| F | -2.9783090 | 4.9246060 | -0.9072260 |
| F | -3.2086100 | 2.8175110 | -2.6287290 |
| F | -1.8916930 | 0.5504110 | -2.1668340 |

62

**1a**$H^+$

| | | | |
|---|---|---|---|
| C | -2.0107800 | -2.9213100 | 1.2716060 |
| C | -1.4175570 | -1.7759710 | 0.7556940 |
| C | -0.1215130 | -1.3845840 | 1.1299240 |
| C | 0.5270210 | -2.1812960 | 2.0900600 |
| C | -0.0743310 | -3.2953140 | 2.6561870 |
| C | -1.3420270 | -3.6747930 | 2.2302690 |
| N | -2.1353170 | -0.9836900 | -0.2713010 |

| | | | |
|---|---|---|---|
| C | -2.0684500 | -1.6319910 | -1.7063020 |
| C | -3.2417050 | -2.5939200 | -1.8755700 |
| C | -4.5985920 | -1.9511320 | -1.6018410 |
| C | -4.6629590 | -1.4022360 | -0.1786120 |
| C | -3.5385510 | -0.4279460 | 0.1859430 |
| C | -2.0839070 | -0.5197070 | -2.7591310 |
| C | -0.7377660 | -2.3667130 | -1.8548190 |
| C | -3.7504250 | 0.9309980 | -0.4989050 |
| C | -3.5198810 | -0.1954220 | 1.6979120 |
| B | 0.6953530 | -0.1697170 | 0.5662760 |
| C | 2.2122790 | -0.3214320 | 0.2539720 |
| C | 0.0240130 | 1.2395010 | 0.3253030 |
| H | -4.6833320 | -2.2278920 | 0.5351800 |
| H | -5.5966330 | -0.8546000 | -0.0266990 |
| H | -3.1961680 | -2.9624760 | -2.9029460 |
| H | -3.0952450 | -3.4650300 | -1.2316130 |
| H | -5.3853330 | -2.6950750 | -1.7310320 |
| H | -4.8022680 | -1.1643780 | -2.3305900 |
| H | -1.2945670 | 0.2118120 | -2.5774590 |
| H | -1.8678570 | -0.9846130 | -3.7218910 |
| H | -3.0328290 | -0.0058540 | -2.8578670 |
| H | -0.7193900 | -2.7969690 | -2.8571400 |
| H | 0.1095990 | -1.6815500 | -1.7774920 |
| H | -0.6062570 | -3.1723340 | -1.1359610 |
| H | -2.8406140 | 1.5368080 | -0.5014410 |
| H | -4.1199540 | 0.8491610 | -1.5163210 |
| H | -4.5003250 | 1.4790880 | 0.0712510 |
| H | -3.4489740 | -1.1185820 | 2.2670680 |
| H | -2.7107740 | 0.4637230 | 2.0085570 |
| H | -4.4639820 | 0.2842440 | 1.9591980 |
| H | -2.9910940 | -3.2322050 | 0.9470800 |
| H | -1.8154960 | -4.5583360 | 2.6369460 |
| H | 0.4492220 | -3.8756730 | 3.4035770 |
| H | 1.5296940 | -1.9108830 | 2.3962610 |
| H | -1.5754880 | -0.1303620 | -0.3612840 |
| C | 3.0963130 | 0.7612790 | 0.3634440 |
| C | 4.4481180 | 0.6630100 | 0.0851510 |
| C | 4.9636840 | -0.5533260 | -0.3443000 |
| C | 4.1280000 | -1.6544090 | -0.4842360 |
| C | 2.7847160 | -1.5255620 | -0.1795240 |
| F | 2.6567770 | 1.9495330 | 0.7848500 |
| F | 5.2482080 | 1.7110890 | 0.2245710 |
| F | 6.2484750 | -0.6628900 | -0.6227250 |
| F | 4.6189260 | -2.8108570 | -0.9116590 |
| F | 2.0257000 | -2.6116040 | -0.3625530 |
| C | 0.1311050 | 1.9164610 | -0.8879320 |
| C | -0.3888910 | 3.1836280 | -1.0900470 |
| C | -1.0066050 | 3.8339480 | -0.0262680 |
| C | -1.1168970 | 3.2056780 | 1.2089110 |
| C | -0.6007150 | 1.9285620 | 1.3615400 |
| F | 0.7229990 | 1.3065300 | -1.9259320 |
| F | -0.2944260 | 3.7801670 | -2.2702720 |
| F | -1.4975830 | 5.0487090 | -0.1939920 |
| F | -1.7036580 | 3.8274210 | 2.2222840 |
| F | -0.7002690 | 1.3541650 | 2.5667350 |

41

**1c**

| | | | |
|---|---|---|---|
| C | 1.5885920 | 0.5375440 | -0.1803810 |
| C | 0.2822110 | 1.0447400 | 0.0026230 |
| C | 0.1174110 | 2.4246790 | 0.1687390 |
| C | 1.1966580 | 3.2995760 | 0.1008910 |
| C | 2.4803770 | 2.8072290 | -0.1006360 |
| C | 2.6678660 | 1.4364530 | -0.2098530 |
| N | -0.8286520 | 0.1493470 | 0.0413540 |
| C | -1.8328060 | 0.3042670 | -1.0503340 |
| C | -2.6458660 | -0.9973300 | -1.1131840 |
| C | -3.2649070 | -1.3614560 | 0.2301390 |
| C | -2.1456690 | -1.5373220 | 1.2482080 |
| C | -1.2554530 | -0.2941740 | 1.3981070 |

| | | | |
|---|---|---|---|
| C | -1.0959870 | 0.4579910 | -2.3870030 |
| C | -2.8022990 | 1.5032280 | -0.9482960 |
| C | -0.0274670 | -0.7239210 | 2.2108920 |
| C | -1.9772330 | 0.7825760 | 2.2325100 |
| H | -3.4131120 | -0.8908110 | -1.8847440 |
| H | -1.9729700 | -1.8026700 | -1.4223610 |
| H | -1.5108560 | -2.3676070 | 0.9220670 |
| H | -2.5451370 | -1.7940190 | 2.2335450 |
| H | -3.9698290 | -0.5899580 | 0.5531060 |
| H | -3.8352290 | -2.2891890 | 0.1431650 |
| H | -0.3667120 | -1.1374570 | 3.1630220 |
| H | 0.5303820 | -1.5083850 | 1.6948080 |
| H | 0.6432260 | 0.1095220 | 2.4236590 |
| H | -2.1183140 | 0.4139910 | 3.2514820 |
| H | -1.3762630 | 1.6915210 | 2.2910340 |
| H | -2.9593640 | 1.0375600 | 1.8400520 |
| H | -1.8307300 | 0.4504090 | -3.1955120 |
| H | -0.5485310 | 1.4004080 | -2.4395930 |
| H | -0.3977380 | -0.3620320 | -2.5438330 |
| H | -3.5296490 | 1.4300630 | -1.7608720 |
| H | -3.3566910 | 1.5386940 | -0.0139230 |
| H | -2.2772680 | 2.4493470 | -1.0769200 |
| H | -0.8706840 | 2.8144300 | 0.3624050 |
| H | 1.0323200 | 4.3633200 | 0.2209960 |
| H | 3.3275370 | 3.4787900 | -0.1498590 |
| H | 3.6725620 | 1.0510970 | -0.3274350 |
| B | 1.9350800 | -0.9743820 | -0.2985700 |
| Cl | 3.4244610 | -1.5609790 | 0.4695160 |
| Cl | 1.0511660 | -2.1899060 | -1.2163070 |

43

**4c**

| | | | |
|---|---|---|---|
| C | -1.2292140 | -0.2949100 | 1.4277170 |
| N | -0.7536720 | 0.1336390 | 0.0146250 |
| C | -1.8090440 | 0.4372840 | -1.0817900 |
| C | -2.7551370 | -0.7702010 | -1.1131620 |
| C | -3.3553160 | -1.1032140 | 0.2489210 |
| C | -2.2299530 | -1.4391560 | 1.2218920 |
| C | 0.4229460 | 1.0316890 | -0.0002830 |
| C | 1.6535070 | 0.5010980 | -0.3988210 |
| C | 2.7184520 | 1.4204260 | -0.4334810 |
| C | 2.5796630 | 2.7539340 | -0.0833480 |
| C | 1.3385840 | 3.2344720 | 0.3265610 |
| C | 0.2559480 | 2.3697620 | 0.3658640 |
| B | 2.1432980 | -1.0053330 | -0.7849110 |
| Cl | 3.1699030 | -1.6780890 | 0.6423070 |
| C | -1.0591600 | 0.5256060 | -2.4132120 |
| C | -2.5861150 | 1.7387260 | -0.8913400 |
| C | -0.0011400 | -0.8339790 | 2.1616800 |
| C | -1.8301490 | 0.8322900 | 2.2633380 |
| Cl | 0.7096430 | -2.3102880 | -1.1297660 |
| H | -3.5349740 | -0.5537890 | -1.8467710 |
| H | -2.1978220 | -1.6376520 | -1.4808480 |
| H | -1.6828820 | -2.3103510 | 0.8471300 |
| H | -2.6237880 | -1.7059450 | 2.2052300 |
| H | -3.9630030 | -0.2744080 | 0.6219610 |
| H | -4.0220140 | -1.9619240 | 0.1533590 |
| H | 0.5057290 | -1.6143100 | 1.5940320 |
| H | -0.3414750 | -1.2638830 | 3.1060500 |
| H | 0.7201510 | -0.0468900 | 2.3803490 |
| H | -1.1062510 | 1.6239600 | 2.4454690 |
| H | -2.0827580 | 0.3978610 | 3.2325010 |
| H | -2.7409320 | 1.2591590 | 1.8521620 |
| H | -0.4421970 | -0.3560240 | -2.5861640 |
| H | -1.8038810 | 0.5874370 | -3.2093630 |
| H | -0.4298720 | 1.4140620 | -2.4595890 |
| H | -1.9398540 | 2.6088020 | -0.9819280 |
| H | -3.3088400 | 1.7882810 | -1.7083210 |
| H | -3.1432630 | 1.7972300 | 0.0391060 |
| H | -0.7071290 | 2.7379320 | 0.6836450 |

| | | | |
|---|---|---|---|
| H | 1.2109830 | 4.2707750 | 0.6110260 |
| H | 3.4342030 | 3.4172530 | -0.1253480 |
| H | 3.6903380 | 1.0509290 | -0.7377830 |
| H | -0.3592490 | -0.7610020 | -0.3400720 |
| H | 2.7924850 | -0.9968740 | -1.7900590 |

42

**1c**$H^-$

| | | | |
|---|---|---|---|
| C | 1.7113570 | -0.1207580 | -1.2870900 |
| N | 1.0302940 | 0.1017820 | 0.0000490 |
| C | 1.7114860 | -0.1208590 | 1.2871160 |
| C | 2.4292750 | -1.4789800 | 1.2361490 |
| C | 3.3049240 | -1.6410410 | -0.0001280 |
| C | 2.4291670 | -1.4788770 | -1.2363130 |
| C | -0.0863880 | 1.0036750 | 0.0000990 |
| C | -1.4021380 | 0.5028750 | 0.0000910 |
| C | -2.4446470 | 1.4420310 | 0.0000650 |
| C | -2.2218040 | 2.8123810 | 0.0000440 |
| C | -0.9152790 | 3.2945180 | 0.0000120 |
| C | 0.1391150 | 2.3904110 | 0.0000260 |
| B | -1.7821590 | -1.0664830 | 0.0000600 |
| Cl | -2.8608880 | -1.4428640 | -1.5614750 |
| C | 0.6639360 | -0.2089040 | 2.4041390 |
| C | 2.7137070 | 0.9826430 | 1.6960340 |
| C | 0.6636700 | -0.2087110 | -2.4039920 |
| C | 2.7134990 | 0.9828120 | -1.6960120 |
| Cl | -2.8612480 | -1.4428590 | 1.5613490 |
| H | 3.0148570 | -1.6005380 | 2.1534570 |
| H | 1.6599080 | -2.2572570 | 1.2234420 |
| H | 1.6598080 | -2.2571620 | -1.2236060 |
| H | 3.0146680 | -1.6003490 | -2.1536840 |
| H | 4.1151670 | -0.9046120 | -0.0001350 |
| H | 3.7783390 | -2.6275310 | -0.0001900 |
| H | 1.1608100 | -0.5150920 | -3.3295460 |
| H | -0.1090110 | -0.9358680 | -2.1556810 |
| H | 0.1792570 | 0.7534760 | -2.5762000 |
| H | 3.5584770 | 1.0644910 | -1.0127620 |
| H | 3.1093170 | 0.7662780 | -2.6931510 |
| H | 2.2093610 | 1.9489510 | -1.7410920 |
| H | -0.1089110 | -0.9358560 | 2.1557540 |
| H | 1.1611550 | -0.5156120 | 3.3295420 |
| H | 0.1797230 | 0.7533250 | 2.5766640 |
| H | 3.5585670 | 1.0644250 | 1.0126480 |
| H | 2.2095890 | 1.9487770 | 1.7413700 |
| H | 3.1097050 | 0.7659410 | 2.6930640 |
| H | 1.1585620 | 2.7551220 | -0.0000390 |
| H | -0.7182010 | 4.3609930 | -0.0000380 |
| H | -3.0592620 | 3.5015220 | 0.0000240 |
| H | -3.4607470 | 1.0640200 | 0.0000630 |
| H | -0.8653500 | -1.8395120 | 0.0001590 |

42

**1c**$H^+$

| | | | |
|---|---|---|---|
| C | 1.7254190 | 0.0787440 | -1.2924190 |
| N | 0.8402660 | 0.0483910 | 0.0067330 |
| C | 1.5324230 | -0.1210000 | 1.4059770 |
| C | 2.4576390 | -1.3362460 | 1.2708190 |
| C | 3.4176390 | -1.2533220 | 0.0889410 |
| C | 2.6184150 | -1.1643680 | -1.2066560 |
| C | -0.2895530 | 0.9960650 | -0.0032140 |
| C | -1.6241400 | 0.5281440 | -0.0702890 |
| C | -2.6250410 | 1.5182010 | -0.0921510 |
| C | -2.3410780 | 2.8769790 | -0.0500620 |
| C | -1.0224870 | 3.2940810 | 0.0383550 |
| C | 0.0019970 | 2.3503300 | 0.0648990 |
| B | -2.1489490 | -0.9498320 | -0.0975970 |
| Cl | -1.1307290 | -2.3869100 | -0.3800900 |
| C | 0.4222160 | -0.4358160 | 2.4087200 |
| C | 2.2855460 | 1.1115240 | 1.8944290 |
| C | 0.7701780 | -0.0535220 | -2.4784220 |

| | | | |
|---|---|---|---|
| C | 2.5518190 | 1.3474930 | -1.4827750 |
| Cl | -3.8351590 | -1.3131940 | 0.1553400 |
| H | 2.9997400 | -1.4341490 | 2.2132040 |
| H | 1.8421730 | -2.2379770 | 1.1683660 |
| H | 1.9917410 | -2.0588400 | -1.3047580 |
| H | 3.2771550 | -1.1491820 | -2.0767270 |
| H | 4.0943320 | -0.4019180 | 0.1909680 |
| H | 4.0426680 | -2.1464940 | 0.0687410 |
| H | 0.1412110 | -0.9410940 | -2.4045020 |
| H | 0.1389550 | 0.8275850 | -2.5939070 |
| H | 1.3755940 | -0.1536240 | -3.3805470 |
| H | 3.2294550 | 1.5715840 | -0.6650070 |
| H | 3.1634130 | 1.1810640 | -2.3713110 |
| H | 1.9277420 | 2.2141830 | -1.6895170 |
| H | -0.2365370 | 0.4168620 | 2.5730100 |
| H | -0.1707310 | -1.3007530 | 2.1062870 |
| H | 0.8953090 | -0.6837890 | 3.3599270 |
| H | 2.7072720 | 0.8471730 | 2.8657060 |
| H | 3.1122800 | 1.4119980 | 1.2580870 |
| H | 1.6215200 | 1.9577650 | 2.0588600 |
| H | 1.0237940 | 2.6845930 | 0.1386200 |
| H | -0.7781590 | 4.3467890 | 0.0873560 |
| H | -3.1470530 | 3.5973330 | -0.0763620 |
| H | -3.6596350 | 1.2126180 | -0.1439340 |
| H | 0.4047830 | -0.8732640 | -0.0978620 |

82

(**1b**)$_2$-*trans*

| | | | |
|---|---|---|---|
| B | 0.8180290 | 0.2454600 | 0.2783430 |
| H | -0.1860870 | 0.9123230 | -0.2920650 |
| H | 0.8926260 | 0.6300780 | 1.4021450 |
| C | 2.0664110 | 0.1668550 | -0.6828140 |
| C | 2.0949780 | -0.7575930 | -1.7359290 |
| H | 1.2536100 | -1.4270110 | -1.8718910 |
| C | 3.1715330 | -0.8473520 | -2.6099120 |
| H | 3.1648630 | -1.5761330 | -3.4106220 |
| C | 4.2531100 | 0.0094900 | -2.4454230 |
| H | 5.0982340 | -0.0384210 | -3.1211530 |
| C | 4.2518230 | 0.9322360 | -1.4043170 |
| H | 5.0946400 | 1.5973900 | -1.2820510 |
| C | 3.1779650 | 1.0190220 | -0.5095120 |
| N | 3.1906170 | 1.9482180 | 0.5820940 |
| C | 4.1128030 | 1.6111860 | 1.6991870 |
| C | 3.6915770 | 2.4285940 | 2.9291200 |
| H | 2.7121690 | 2.0645850 | 3.2575530 |
| H | 4.4038060 | 2.2348390 | 3.7358480 |
| C | 3.5834180 | 3.9188640 | 2.6354170 |
| H | 3.2808130 | 4.4599000 | 3.5351880 |
| H | 4.5530340 | 4.3264690 | 2.3352660 |
| C | 2.5491280 | 4.1154020 | 1.5356520 |
| H | 2.4208860 | 5.1746550 | 1.2958440 |
| H | 1.5858900 | 3.7403100 | 1.8983070 |
| C | 2.8918880 | 3.3618450 | 0.2414880 |
| C | 4.0036700 | 4.1090710 | -0.5226930 |
| H | 4.2239920 | 3.6101740 | -1.4670000 |
| H | 4.9265670 | 4.1969840 | 0.0475880 |
| H | 3.6620260 | 5.1205030 | -0.7573320 |
| C | 1.6403380 | 3.4067040 | -0.6430790 |
| H | 1.8027580 | 2.9229090 | -1.6072140 |
| H | 1.3693620 | 4.4492340 | -0.8250580 |
| H | 0.8027490 | 2.9213890 | -0.1392190 |
| C | 5.6170620 | 1.8262800 | 1.4301020 |
| H | 5.8679700 | 2.8578550 | 1.1909820 |
| H | 5.9632770 | 1.1864970 | 0.6185250 |
| H | 6.1794760 | 1.5480640 | 2.3252680 |
| C | 3.9376080 | 0.1291290 | 2.0546210 |
| H | 4.2953280 | -0.5225330 | 1.2562300 |
| H | 2.8896570 | -0.0990870 | 2.2483310 |
| H | 4.5150490 | -0.0891640 | 2.9561580 |
| B | -0.8180290 | -0.2454600 | -0.2783430 |

| | | | |
|---|---|---|---|
| H | 0.1860870 | -0.9123230 | 0.2920650 |
| H | -0.8926260 | -0.6300780 | -1.4021450 |
| C | -2.0664110 | -0.1668550 | 0.6828140 |
| C | -2.0949780 | 0.7575930 | 1.7359290 |
| H | -1.2536100 | 1.4270110 | 1.8718910 |
| C | -3.1715330 | 0.8473520 | 2.6099120 |
| H | -3.1648630 | 1.5761330 | 3.4106220 |
| C | -4.2531100 | -0.0094900 | 2.4454230 |
| H | -5.0982340 | 0.0384210 | 3.1211530 |
| C | -4.2518230 | -0.9322360 | 1.4043170 |
| H | -5.0946400 | -1.5973900 | 1.2820510 |
| C | -3.1779650 | -1.0190220 | 0.5095120 |
| N | -3.1906170 | -1.9482180 | -0.5820940 |
| C | -4.1128030 | -1.6111860 | -1.6991870 |
| C | -3.6915770 | -2.4285940 | -2.9291200 |
| H | -2.7121690 | -2.0645850 | -3.2575530 |
| H | -4.4038060 | -2.2348390 | -3.7358480 |
| C | -3.5834180 | -3.9188640 | -2.6354170 |
| H | -3.2808130 | -4.4599000 | -3.5351880 |
| H | -4.5530340 | -4.3264690 | -2.3352660 |
| C | -2.5491280 | -4.1154020 | -1.5356520 |
| H | -2.4208860 | -5.1746550 | -1.2958440 |
| H | -1.5858900 | -3.7403100 | -1.8983070 |
| C | -2.8918880 | -3.3618450 | -0.2414880 |
| C | -4.0036700 | -4.1090710 | 0.5226930 |
| H | -4.2239920 | -3.6101740 | 1.4670000 |
| H | -4.9265670 | -4.1969840 | -0.0475880 |
| H | -3.6620260 | -5.1205030 | 0.7573320 |
| C | -1.6403380 | -3.4067040 | 0.6430790 |
| H | -1.8027580 | -2.9229090 | 1.6072140 |
| H | -1.3693620 | -4.4492340 | 0.8250580 |
| H | -0.8027490 | -2.9213890 | 0.1392190 |
| C | -5.6170620 | -1.8262800 | -1.4301020 |
| H | -5.8679700 | -2.8578550 | -1.1909820 |
| H | -5.9632770 | -1.1864970 | -0.6185250 |
| H | -6.1794760 | -1.5480640 | -2.3252680 |
| C | -3.9376080 | -0.1291290 | -2.0546210 |
| H | -4.2953280 | 0.5225330 | -1.2562300 |
| H | -2.8896570 | 0.0990870 | -2.2483310 |
| H | -4.5150490 | 0.0891640 | -2.9561580 |

41

**1b**-*open-A*

| | | | |
|---|---|---|---|
| C | 1.0817990 | 1.2948110 | -0.0831070 |
| N | 0.3914520 | -0.0000440 | 0.1401220 |
| C | 1.0816720 | -1.2947110 | -0.0845240 |
| C | 2.4556890 | -1.2352900 | 0.5991160 |
| C | 3.2583510 | -0.0002160 | 0.2125750 |
| C | 2.4558050 | 1.2345070 | 0.6004780 |
| C | -1.0218480 | 0.0001170 | -0.0665830 |
| C | -1.8903850 | -0.0007750 | 1.0541320 |
| C | -3.2772440 | -0.0005890 | 0.8264310 |
| C | -3.8159680 | 0.0004260 | -0.4540240 |
| C | -2.9530120 | 0.0012520 | -1.5438470 |
| C | -1.5723600 | 0.0010860 | -1.3516100 |
| B | -1.3997580 | -0.0019970 | 2.5202460 |
| C | 1.2501700 | -1.7105010 | -1.5600200 |
| C | 0.2827930 | -2.4080690 | 0.6049110 |
| C | 1.2503790 | 1.7121770 | -1.5581480 |
| C | 0.2830480 | 2.4075390 | 0.6075000 |
| H | -0.2444330 | -0.0021730 | 2.8190090 |
| H | -3.9392680 | -0.0012870 | 1.6843920 |
| H | -4.8882590 | 0.0005460 | -0.6020670 |
| H | -3.3506890 | 0.0020300 | -2.5516560 |
| H | -0.9162310 | 0.0017360 | -2.2102250 |
| H | 2.2929660 | -1.2189630 | 1.6819300 |
| H | 3.0009820 | -2.1525610 | 0.3601610 |
| H | 4.2202390 | -0.0005470 | 0.7307280 |
| H | 3.4791440 | 0.0003640 | -0.8586850 |
| H | 3.0011870 | 2.1519880 | 0.3625340 |

| | | | |
|---|---|---|---|
| H | 2.2930730 | 1.2170050 | 1.6832720 |
| H | 0.2800820 | 1.8163120 | -2.0446890 |
| H | 1.8529960 | 1.0104120 | -2.1320710 |
| H | 1.7439030 | 2.6865730 | -1.6016470 |
| H | -0.6832980 | 2.5725360 | 0.1285130 |
| H | 0.8527260 | 3.3382130 | 0.5545700 |
| H | 0.1157970 | 2.1623120 | 1.6575480 |
| H | 1.8527970 | -1.0081470 | -2.1332110 |
| H | 0.2798450 | -1.8140580 | -2.0466300 |
| H | 1.7436400 | -2.6848760 | -1.6045950 |
| H | -0.6835820 | -2.5724340 | 0.1257640 |
| H | 0.1155840 | -2.1639300 | 1.6552220 |
| H | 0.8523550 | -3.3387570 | 0.5509900 |
| H | -2.2262770 | -0.0025830 | 3.3890810 |

42

**1b**$H^-$

| | | | |
|---|---|---|---|
| C | -1.0913730 | 1.2863570 | -0.1376620 |
| N | -0.3970060 | 0.0000140 | -0.0271450 |
| C | -1.0913400 | -1.2863060 | -0.1381110 |
| C | -2.3957380 | -1.2349020 | 0.6743300 |
| C | -3.2344830 | -0.0000880 | 0.3694740 |
| C | -2.3957640 | 1.2346350 | 0.6747690 |
| C | 1.0348150 | 0.0000450 | -0.1305640 |
| C | 1.8278700 | -0.0002150 | 1.0379110 |
| C | 3.2194440 | -0.0001670 | 0.8182890 |
| C | 3.8050790 | 0.0001150 | -0.4414580 |
| C | 2.9972410 | 0.0003660 | -1.5771990 |
| C | 1.6177790 | 0.0003260 | -1.4084660 |
| B | 1.3015820 | -0.0005820 | 2.5822020 |
| H | 1.7637950 | 0.9984480 | 3.1407200 |
| C | -0.2242710 | -2.3890180 | 0.4857700 |
| C | -1.3975280 | -1.7119160 | -1.5929290 |
| C | -0.2243340 | 2.3888810 | 0.4865940 |
| C | -1.3975890 | 1.7124620 | -1.5923290 |
| H | 1.7641270 | -0.9996740 | 3.1403650 |
| H | -2.9629640 | -2.1536240 | 0.4878610 |
| H | -2.1186390 | -1.2144500 | 1.7325370 |
| H | -2.1186580 | 1.2138110 | 1.7329670 |
| H | -2.9630100 | 2.1534120 | 0.4886310 |
| H | -3.5602290 | 0.0000950 | -0.6762240 |
| H | -4.1429280 | -0.0002060 | 0.9803440 |
| H | -0.8154590 | 3.3086210 | 0.5491370 |
| H | 0.0994330 | 2.0885760 | 1.4837510 |
| H | 0.6615630 | 2.5880000 | -0.1182070 |
| H | -2.1005210 | 1.0409280 | -2.0868190 |
| H | -1.8269210 | 2.7198660 | -1.6070090 |
| H | -0.4728930 | 1.7307310 | -2.1715710 |
| H | 0.0994980 | -2.0890360 | 1.4830240 |
| H | -0.8153710 | -3.3087930 | 0.5480110 |
| H | 0.6616270 | -2.5879110 | -0.1191050 |
| H | -2.1003820 | -1.0401630 | -2.0872330 |
| H | -0.4728070 | -1.7300720 | -2.1721360 |
| H | -1.8269410 | -2.7192800 | -1.6079530 |
| H | 0.9677370 | 0.0005170 | -2.2765610 |
| H | 3.4305960 | 0.0005870 | -2.5717530 |
| H | 4.8864680 | 0.0001370 | -0.5416100 |
| H | 3.8576460 | -0.0003650 | 1.6971590 |
| H | 0.0775100 | -0.0008010 | 2.6801590 |

62

**1b**$H^+$

| | | | |
|---|---|---|---|
| C | -2.0107800 | -2.9213100 | 1.2716060 |
| C | -1.4175570 | -1.7759710 | 0.7556940 |
| C | -0.1215130 | -1.3845840 | 1.1299240 |
| C | 0.5270210 | -2.1812960 | 2.0900600 |
| C | -0.0743310 | -3.2953140 | 2.6561870 |
| C | -1.3420270 | -3.6747930 | 2.2302690 |
| N | -2.1353170 | -0.9836900 | -0.2713010 |
| C | -2.0684500 | -1.6319910 | -1.7063020 |

| | | | |
|---|---|---|---|
| C | -3.2417050 | -2.5939200 | -1.8755700 |
| C | -4.5985920 | -1.9511320 | -1.6018410 |
| C | -4.6629590 | -1.4022360 | -0.1786120 |
| C | -3.5385510 | -0.4279460 | 0.1859430 |
| C | -2.0839070 | -0.5197070 | -2.7591310 |
| C | -0.7377660 | -2.3667130 | -1.8548190 |
| C | -3.7504250 | 0.9309980 | -0.4989050 |
| C | -3.5198810 | -0.1954220 | 1.6979120 |
| B | 0.6953530 | -0.1697170 | 0.5662760 |
| C | 2.2122790 | -0.3214320 | 0.2539720 |
| C | 0.0240130 | 1.2395010 | 0.3253030 |
| H | -4.6833320 | -2.2278920 | 0.5351800 |
| H | -5.5966330 | -0.8546000 | -0.0266990 |
| H | -3.1961680 | -2.9624760 | -2.9029460 |
| H | -3.0952450 | -3.4650300 | -1.2316130 |
| H | -5.3853330 | -2.6950750 | -1.7310320 |
| H | -4.8022680 | -1.1643780 | -2.3305900 |
| H | -1.2945670 | 0.2118120 | -2.5774590 |
| H | -1.8678570 | -0.9846130 | -3.7218910 |
| H | -3.0328290 | -0.0058540 | -2.8578670 |
| H | -0.7193900 | -2.7969690 | -2.8571400 |
| H | 0.1095990 | -1.6815500 | -1.7774920 |
| H | -0.6062570 | -3.1723340 | -1.1359610 |
| H | -2.8406140 | 1.5368080 | -0.5014410 |
| H | -4.1199540 | 0.8491610 | -1.5163210 |
| H | -4.5003250 | 1.4790880 | 0.0712510 |
| H | -3.4489740 | -1.1185820 | 2.2670680 |
| H | -2.7107740 | 0.4637230 | 2.0085570 |
| H | -4.4639820 | 0.2842440 | 1.9591980 |
| H | -2.9910940 | -3.2322050 | 0.9470800 |
| H | -1.8154960 | -4.5583360 | 2.6369460 |
| H | 0.4492220 | -3.8756730 | 3.4035770 |
| H | 1.5296940 | -1.9108830 | 2.3962610 |
| H | -1.5754880 | -0.1303620 | -0.3612840 |
| C | 3.0963130 | 0.7612790 | 0.3634440 |
| C | 4.4481180 | 0.6630100 | 0.0851510 |
| C | 4.9636840 | -0.5533260 | -0.3443000 |
| C | 4.1280000 | -1.6544090 | -0.4842360 |
| C | 2.7847160 | -1.5255620 | -0.1795240 |
| F | 2.6567770 | 1.9495330 | 0.7848500 |
| F | 5.2482080 | 1.7110890 | 0.2245710 |
| F | 6.2484750 | -0.6628900 | -0.6227250 |
| F | 4.6189260 | -2.8108570 | -0.9116590 |
| F | 2.0257000 | -2.6116040 | -0.3625530 |
| C | 0.1311050 | 1.9164610 | -0.8879320 |
| C | -0.3888910 | 3.1836280 | -1.0900470 |
| C | -1.0066050 | 3.8339480 | -0.0262680 |
| C | -1.1168970 | 3.2056780 | 1.2089110 |
| C | -0.6007150 | 1.9285620 | 1.3615400 |
| F | 0.7229990 | 1.3065300 | -1.9259320 |
| F | -0.2944260 | 3.7801670 | -2.2702720 |
| F | -1.4975830 | 5.0487090 | -0.1939920 |
| F | -1.7036580 | 3.8274210 | 2.2222840 |
| F | -0.7002690 | 1.3541650 | 2.5667350 |

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[23] Species **1a**$H^+$ with bulky $C_6F_5$ substituent lacks this stabilization interaction.