Supplementary Materials: Olefin Hydroborations with Diamidocarbene–BH$_3$ Adducts at Room Temperature

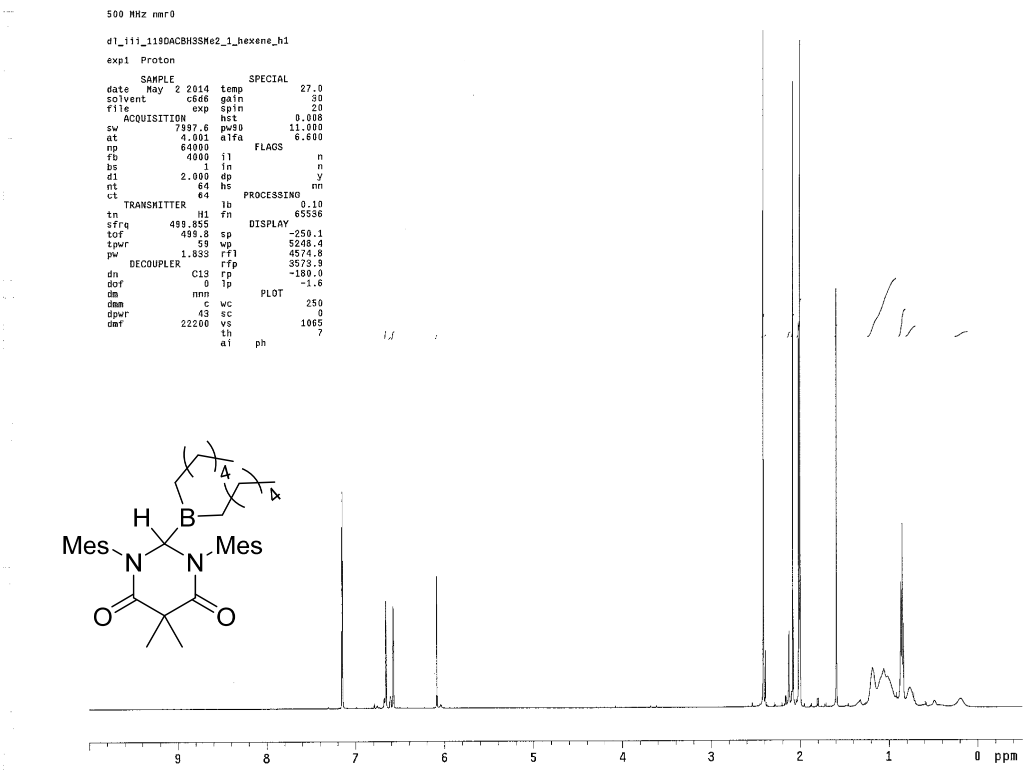
Dominika N. Lastovickova and Christopher W. Bielawski

Colorless single crystals were grown via the slow evaporation of a benzene solution of **10**. This compound crystallized in the primitive triclinic space group *P*-1 with two molecules of **10** in the asymmetric unit. Crystallographic measurements were carried out on a Rigaku AFC-12 (Rigaku, Tokyo, Japan via Rigaku Americas Corporation, The Woodlands, TX, USA) with a Saturn 724+ CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 120 K using a Rigaku X-Stream stream low-temperature device (Rigaku, Tokyo, Japan via Rigaku Americas Corporation). A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using CrystalClear 1.4.0 (Rigaku, Tokyo, Japan via Rigaku Americas Corporation, 2008) [1]. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinements on F2 using the SHELXL-2014/6 package (Shelx, Göttingen, Germany) allowed location of the remaining non-hydrogen atoms [2]. Key details of the crystal and structure refinement data are summarized in Table S1. Cambridge Crystallographic Data Center (CCDC 1498521) contains the crystallographic data for the crystal structure reported herein.

Table S1. Summary of crystal data, data collection, and structure refinement details for **10**.

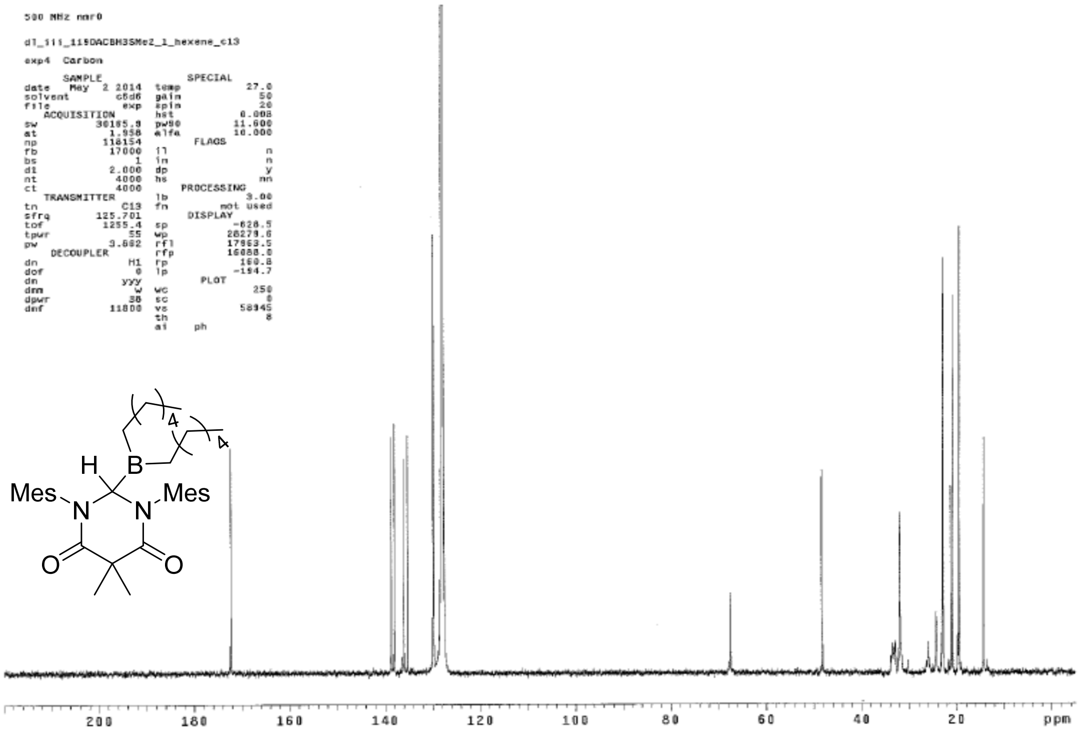
Parameter	DAC–BH$_3$ *cis*-3-hexene (10)
formula	$C_{30}H_{43}N_2O_2B$
M_r	474.5
crystal size (mm^3)	0.20 × 0.20 × 0.20
crystal system	triclinic
space group	*P*-1
a (Å)	9.4460 (13)
b (Å)	12.5512 (21)
c (Å)	12.8280 (17)
α (°)	97.463 (6)
β (°)	110.784 (9)
γ (°)	96.693 (5)
V (Å^3)	1387.99 (60)
Z	2
ϱ_{calc} (g cm^{-3})	1.14
μ (mm^{-1})	0.070
F (000)	516.0
T (K)	120 (2)
scan mode	ω
	−10 ⟶ +11
hkl range	−14 ⟶ +14
	−15 ⟶ +15
measd. reflns.	16265
unique reflns. [R_{int}]	4766 [0.090]
refinement reflns	4766
refined parameters	326
GOF on F^2	1.264
R1 [a] (all data)	0.135 (0.191)
wR2 [b] (all data)	0.348 (0.388)
ϱ_{fin} (max/min)	0.976
(e Å^{-3})	−0.512

[a] $R1 = \left(\sum \left\| Fo \right| - \left| Fc \right\|\right) / \sum \left| Fo \right|$; [b] $wR2 = \left\{ \left[\sum w\left(Fo^2 - Fc^2\right)^2 \right] / \sum w\left(Fo^2\right)^2 \right\}^{1/2}$.



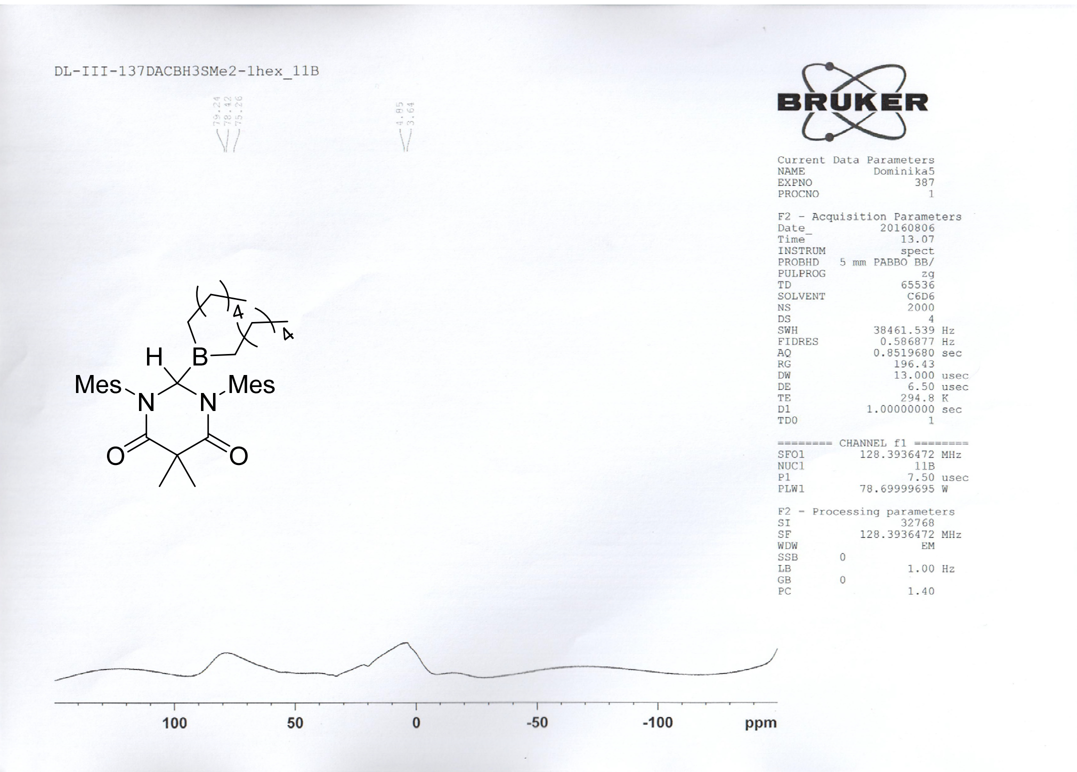
```
500 MHz nmr0

dl_iii_119DACBH3SMe2_1_hexene_h1

exp1  Proton

      SAMPLE              SPECIAL
date   May  2 2014  temp            27.0
solvent        c6d6  gain              30
file            exp  spin              20
   ACQUISITION       hst            0.008
sw           7997.6  pw90          11.000
at            4.001  alfa           6.600
np            64000         FLAGS
fb             4000  il                 n
bs                1  in                 n
d1            2.000  dp                 y
nt               64  hs                nn
ct               64       PROCESSING
   TRANSMITTER       lb              0.10
tn               H1  fn             65536
sfrq        499.855         DISPLAY
tof           499.8  sp            -250.1
tpwr             59  wp            5248.4
pw            1.833  rfl           4574.8
    DECOUPLER        rfp           3573.9
dn              C13  rp            -180.0
dof               0  lp              -1.6
dm              nnn           PLOT
dmm               c  wc               250
dpwr             43  sc                 0
dmf           22200  vs              1065
                     th                 7
                     ai     ph
```

Figure S1. ^{1}H NMR spectrum of **3**.



```
500 MHz nmr0

dl_iii_119DACBH3SMe2_1_hexene_c13

exp4  Carbon

      SAMPLE              SPECIAL
date   May  2 2014  temp            27.0
solvent        c6d6  gain              50
file            exp  spin              20
   ACQUISITION       hst            0.008
sw          30165.9  pw90          11.600
at            1.958  alfa          10.000
np           118154         FLAGS
fb            17000  il                 n
bs                1  in                 n
d1            2.000  dp                 y
nt             4000  hs                nn
ct             4000       PROCESSING
   TRANSMITTER       lb              3.00
tn              C13  fn          not used
sfrq        125.701         DISPLAY
tof          1255.4  sp            -628.5
tpwr             55  wp           28279.6
pw            3.882  rfl          17963.5
    DECOUPLER        rfp          16088.8
dn               H1  rp             160.8
dof               0  lp            -194.7
dm              yyy           PLOT
dmm               w  wc               250
dpwr             38  sc                 0
dmf           11800  vs             58945
                     th                 8
                     ai     ph
```

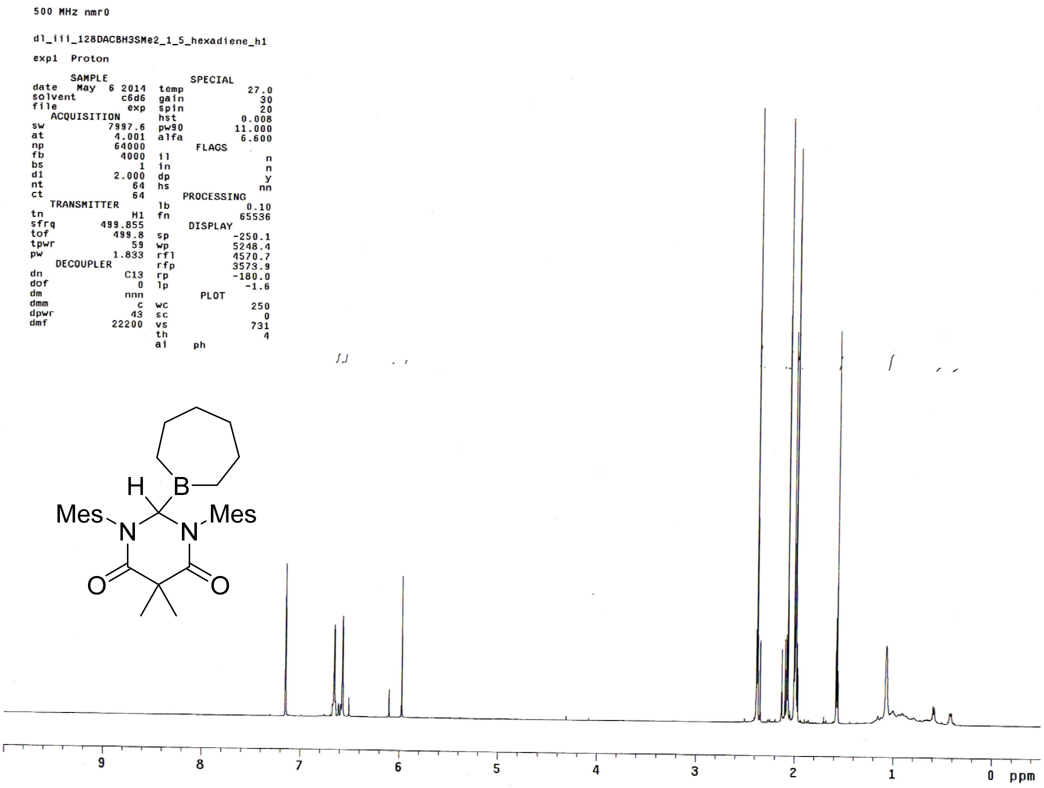
Figure S2. ^{13}C NMR spectrum of **3**.



```
DL-III-137DACBH3SMe2-1hex_11B
```

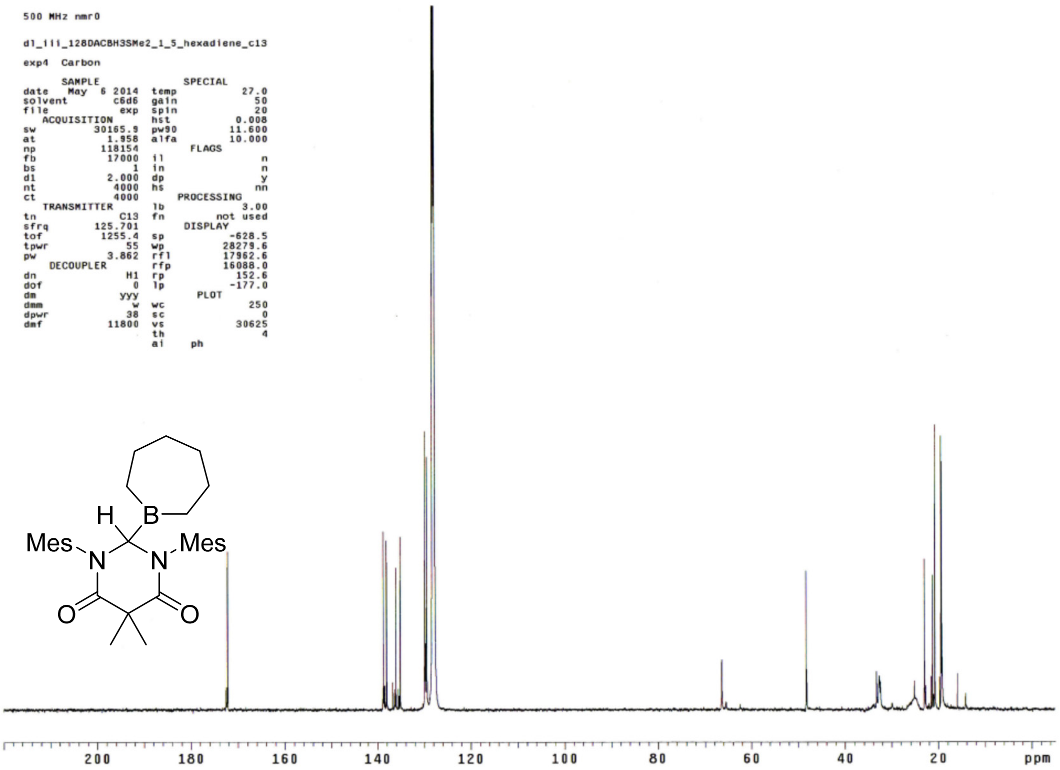
```
Current Data Parameters
NAME            Dominika5
EXPNO                 387
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160806
Time                13.07
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG                zg
TD                  65536
SOLVENT              C6D6
NS                   2000
DS                      4
SWH             38461.539 Hz
FIDRES           0.586877 Hz
AQ              0.8519680 sec
RG                 196.43
DW                 13.000 usec
DE                   6.50 usec
TE                  294.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          128.3936472 MHz
NUC1                  11B
P1                   7.50 usec
PLW1          78.69999695 W

F2 - Processing parameters
SI                  32768
SF            128.3936472 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

Figure S3. ^{11}B NMR spectrum of **3**.



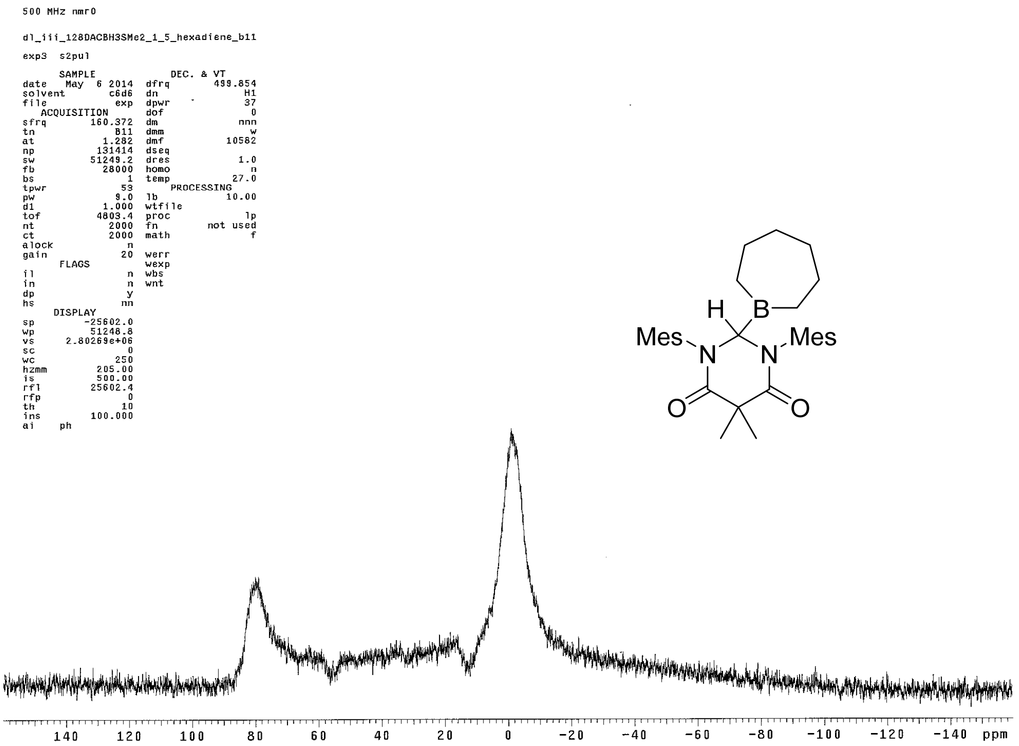
```
500 MHz nmr0

dl_iii_128DACBH3SMe2_1_5_hexadiene_h1

exp1  Proton

      SAMPLE                  SPECIAL
date    May  6 2014   temp            27.0
solvent        c6d6   gain              30
file            exp   spin              20
    ACQUISITION       hst            0.008
sw           7997.6   pw90          11.000
at            4.001   alfa           6.600
np            64000          FLAGS
fb             4000   il                 n
bs                1   in                 n
d1            2.000   dp                 y
nt               64   hs                nn
ct               64        PROCESSING
    TRANSMITTER       lb              0.10
tn               H1   fn             65536
sfrq        499.855          DISPLAY
tof           499.8   sp            -250.1
tpwr             59   wp            5248.4
pw            1.833   rfl           4570.7
     DECOUPLER        rfp           3573.9
dn              C13   rp            -180.0
dof               0   lp              -1.6
dm              nnn           PLOT
dmm               c   wc               250
dpwr             43   sc                 0
dmf           22200   vs               731
                      th                 4
                      ai     ph
```

Figure S4. ^{1}H NMR spectrum of **4**.



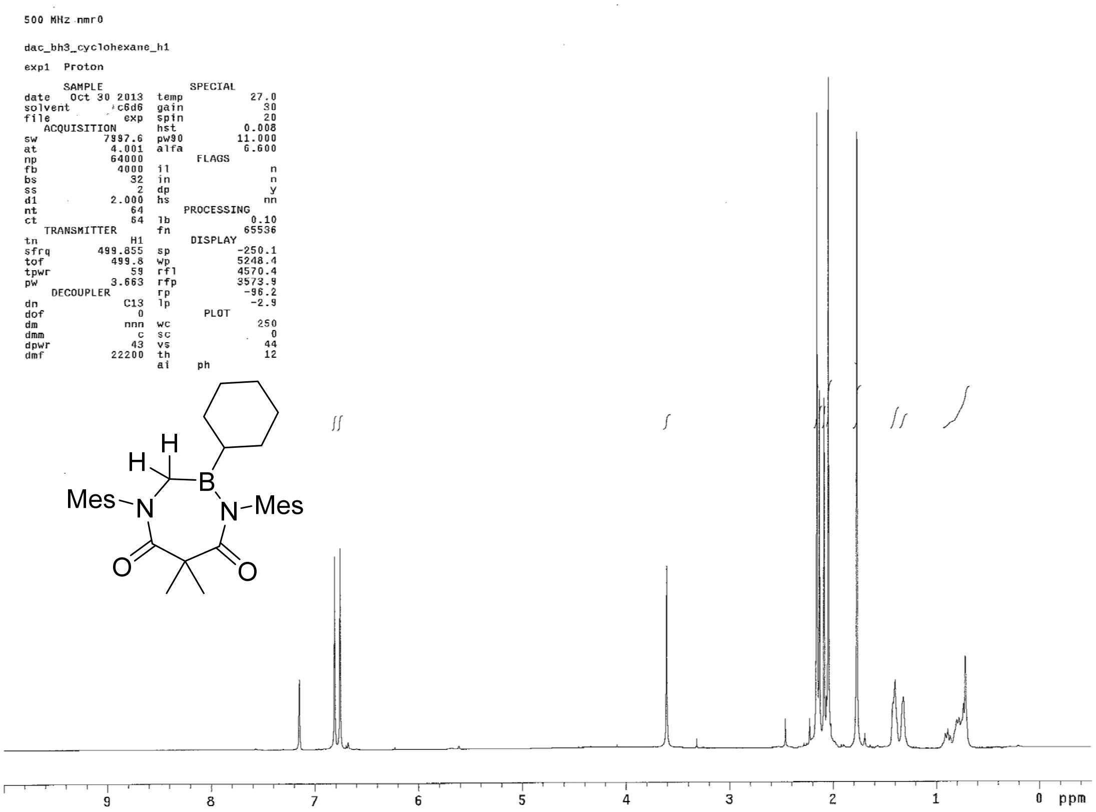
```
500 MHz nmr0

dl_iii_128DACBH3SMe2_1_5_hexadiene_c13

exp4  Carbon

      SAMPLE               SPECIAL
date   May  6 2014  temp           27.0
solvent        c6d6  gain             50
file            exp  spin             20
   ACQUISITION       hst           0.008
sw          30165.9  pw90         11.600
at            1.958  alfa         10.000
np           118154         FLAGS
fb            17000  il                n
bs                1  in                n
d1            2.000  dp                y
nt             4000  hs               nn
ct             4000       PROCESSING
   TRANSMITTER       lb             3.00
tn              C13  fn         not used
sfrq        125.701         DISPLAY
tof          1255.4  sp           -628.5
tpwr             55  wp          28279.6
pw            3.862  rfl         17962.6
    DECOUPLER        rfp         16088.0
dn               H1  rp            152.6
dof               0  lp           -177.0
dm              yyy          PLOT
dmm               w  wc              250
dpwr             38  sc                0
dmf           11800  vs            30625
                     th                4
                     ai    ph
```

Figure S5. ^{13}C NMR spectrum of **4**.



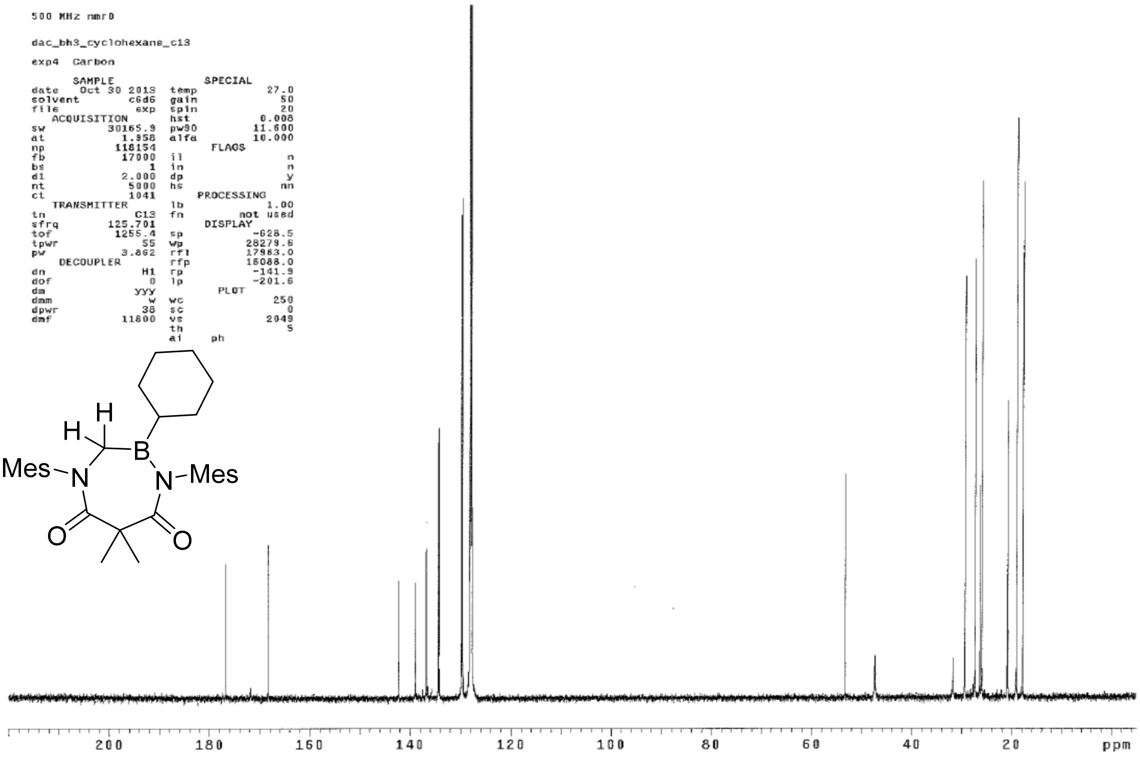
```
500 MHz nmr0

dl_iii_128DACBH3SMe2_1_5_hexadiene_b11

exp3  s2pul

      SAMPLE              DEC. & VT
date   May  6 2014  dfrq        499.854
solvent        c6d6  dn               H1
file            exp  dpwr             37
   ACQUISITION       dof               0
sfrq        160.372  dm              nnn
tn              B11  dmm               w
at            1.282  dmf           10582
np           131414  dseq
sw          51249.2  dres            1.0
fb            28000  homo              n
bs                1  temp           27.0
tpwr             53      PROCESSING
pw              9.0  lb            10.00
d1            1.000  wtfile
tof          4803.4  proc             lp
nt             2000  fn         not used
ct             2000  math              f
alock             n
gain             20  werr
      FLAGS          wexp
il                n  wbs
in                n  wnt
dp                y
hs               nn
     DISPLAY
sp         -25602.0
wp          51248.8
vs      2.80269e+06
sc                0
wc              250
hzmm         205.00
is           500.00
rfl         25602.4
rfp               0
th               10
ins         100.000
ai    ph
```

Figure S6. ^{11}B NMR spectrum of **4**.



```
500 MHz nmr0

dac_bh3_cyclohexane_h1

exp1  Proton

      SAMPLE                  SPECIAL
date   Oct 30 2013  temp             27.0
solvent        c6d6  gain               30
file            exp  spin               20
   ACQUISITION      hst             0.008
sw           7997.6  pw90          11.000
at            4.001  alfa           6.600
np            64000         FLAGS
fb             4000  il                 n
bs               32  in                 n
ss                2  dp                 y
d1            2.000  hs                nn
nt               64       PROCESSING
ct               64  lb              0.10
   TRANSMITTER       fn             65536
tn               H1        DISPLAY
sfrq        499.855  sp            -250.1
tof           499.8  wp            5248.4
tpwr             59  rfl           4570.4
pw            3.663  rfp           3573.9
    DECOUPLER        rp             -96.2
dn              C13  lp              -2.9
dof               0          PLOT
dm              nnn  wc               250
dmm               c  sc                 0
dpwr             43  vs                44
dmf           22200  th                12
                     ai     ph
```

Figure S7. ^{1}H NMR spectrum of **6**.



```
500 MHz nmr0

dac_bh3_cyclohexane_c13

exp4  Carbon

      SAMPLE                  SPECIAL
date   Oct 30 2013  temp             27.0
solvent        c6d6  gain               50
file            exp  spin               20
   ACQUISITION      hst             0.008
sw          30165.9  pw90          11.600
at            1.958  alfa          10.000
np           118154         FLAGS
fb            17000  il                 n
bs                1  in                 n
d1            2.000  dp                 y
nt             5000  hs                nn
ct             1041       PROCESSING
   TRANSMITTER       lb              1.00
tn              C13  fn          not used
sfrq        125.701        DISPLAY
tof          1255.4  sp            -628.5
tpwr             55  wp           28279.6
pw            3.862  rfl          17963.0
    DECOUPLER        rfp          18088.0
dn               H1  rp            -141.9
dof               0  lp            -201.6
dm              yyy          PLOT
dmm               w  wc               250
dpwr             38  sc                 0
dmf           11800  vs              2049
                     th                 5
                     ai     ph
```

Figure S8. ^{13}C NMR spectrum of **6**.

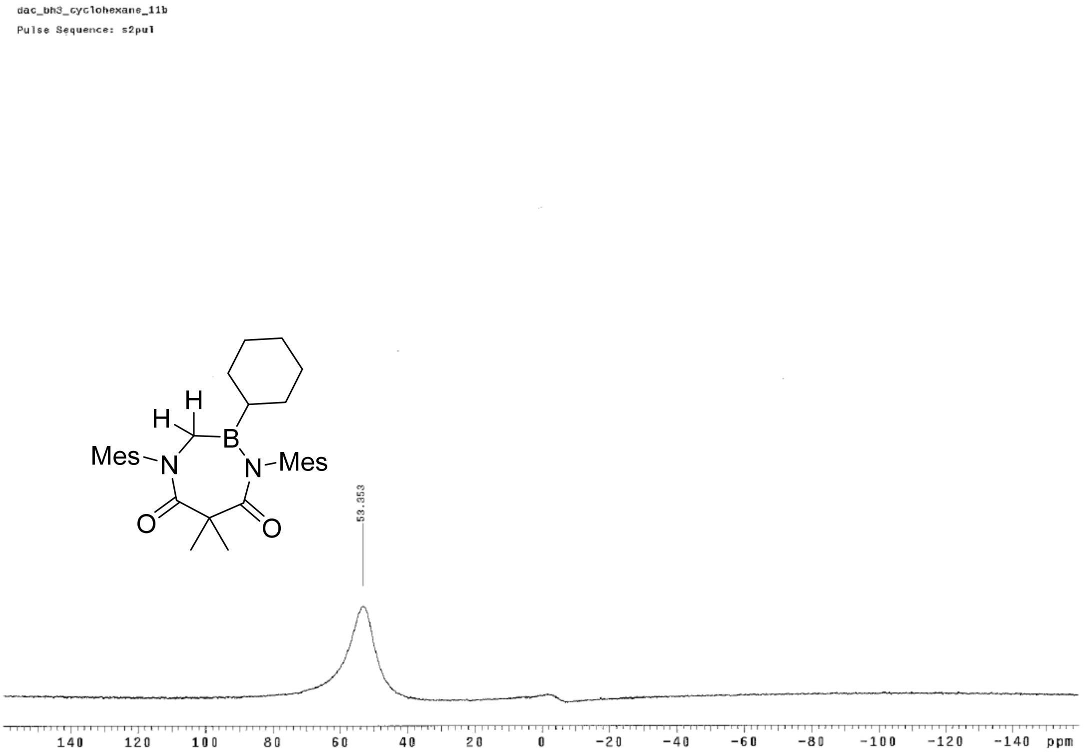


Figure S9. ^{11}B NMR spectrum of **6**.

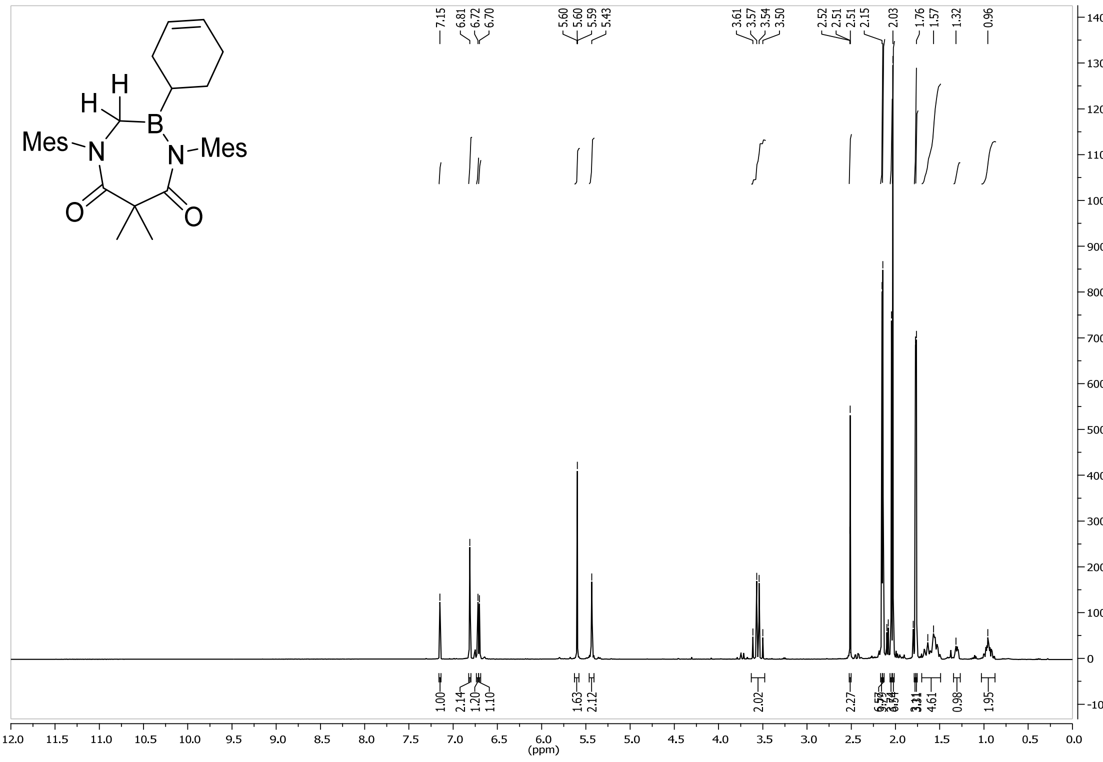


Figure S10. ^{1}H NMR spectrum of **7**.

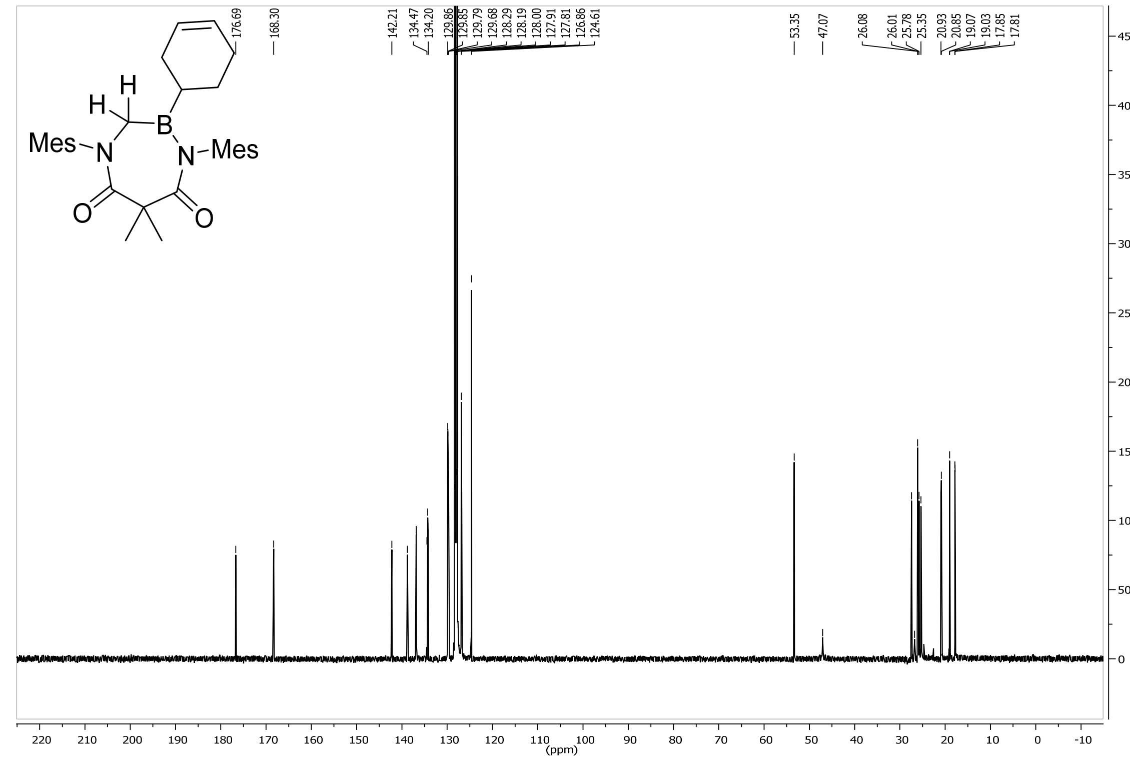


Figure S11. ^{13}C NMR spectrum of **7**.

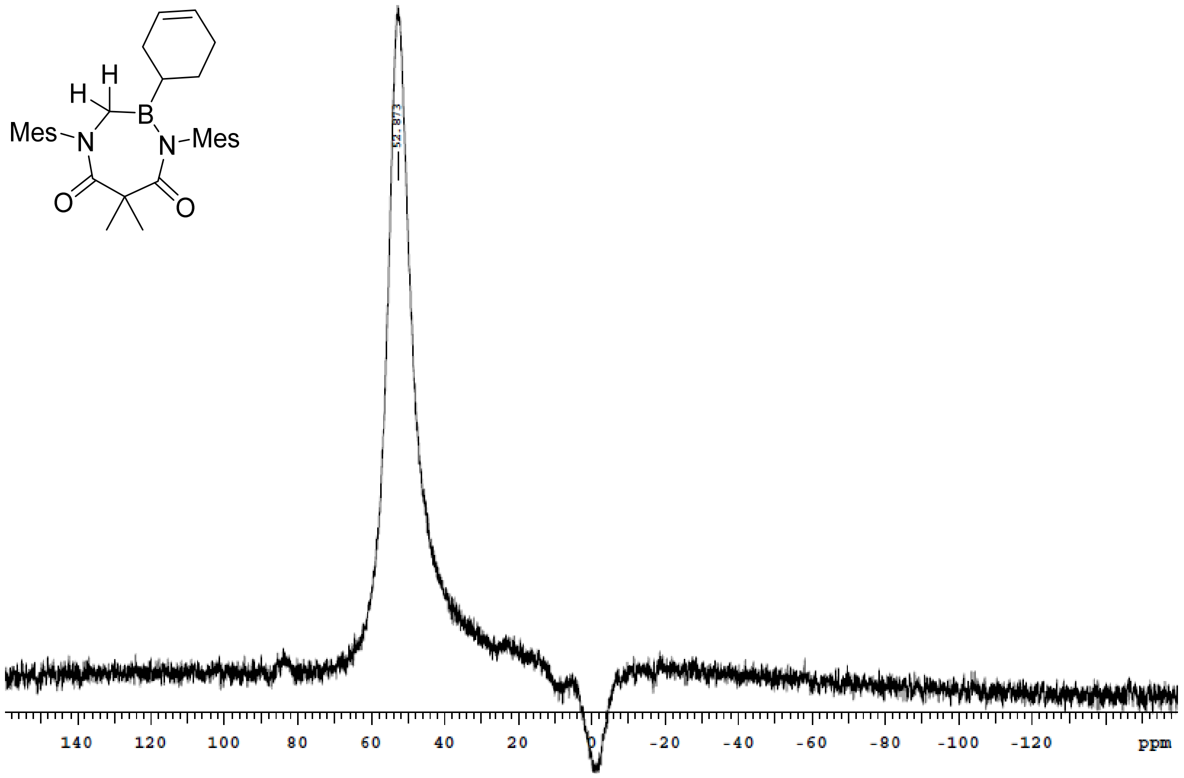
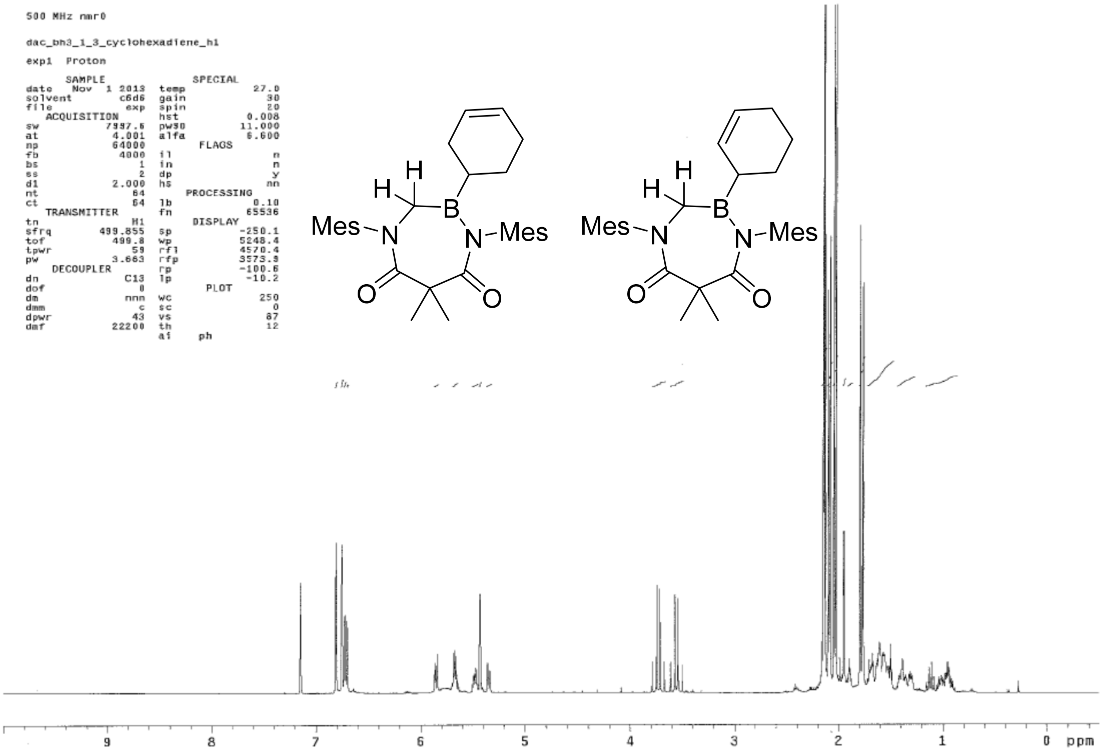
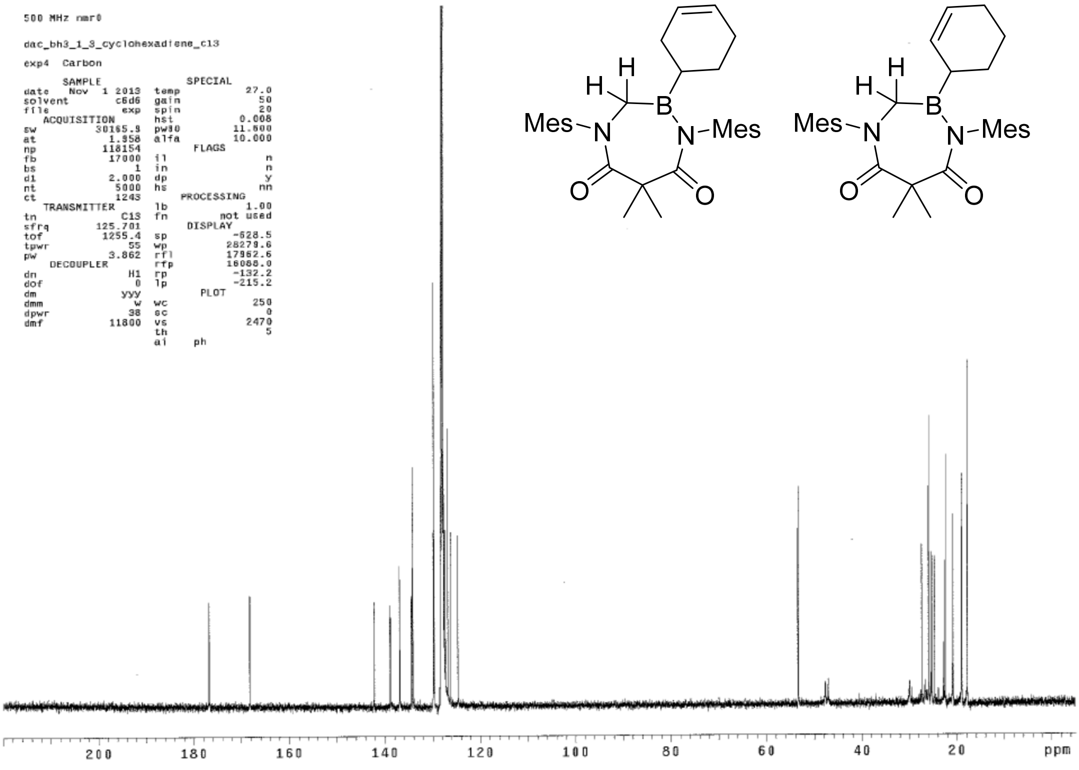


Figure S12. ^{11}B NMR spectrum of **7**.



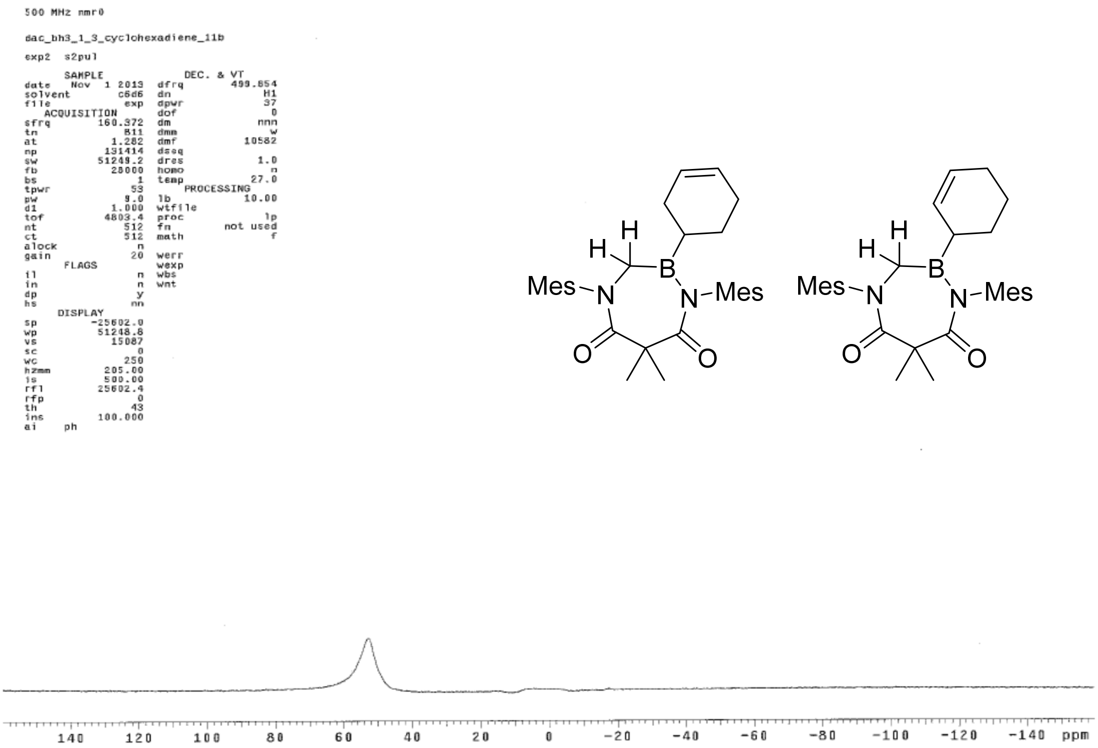
```
500 MHz nmr0

dac_bh3_1_3_cyclohexadiene_h1

exp1  Proton

       SAMPLE               SPECIAL
date    Nov  1 2013  temp            27.0
solvent         c6d6  gain              30
file             exp  spin              20
    ACQUISITION       hst            0.008
sw            7997.6  pw90          11.000
at             4.001  alfa           6.600
np             64000         FLAGS
fb              4000  il                 n
bs                 1  in                 n
ss                 2  dp                 y
d1             2.000  hs                nn
nt                64        PROCESSING
ct                64  lb              0.10
    TRANSMITTER       fn             65536
tn                H1         DISPLAY
sfrq         499.855  sp            -250.1
tof            499.8  wp            5248.4
tpwr              59  rfl           4570.4
pw             3.663  rfp           3573.9
     DECOUPLER        rp            -100.6
dn               C13  lp             -10.2
dof                0          PLOT
dm               nnn  wc               250
dmm                c  sc                 0
dpwr              43  vs                87
dmf            22200  th                12
                      ai     ph
```

Figure S13. ^{1}H NMR spectrum of **7** and **8**.



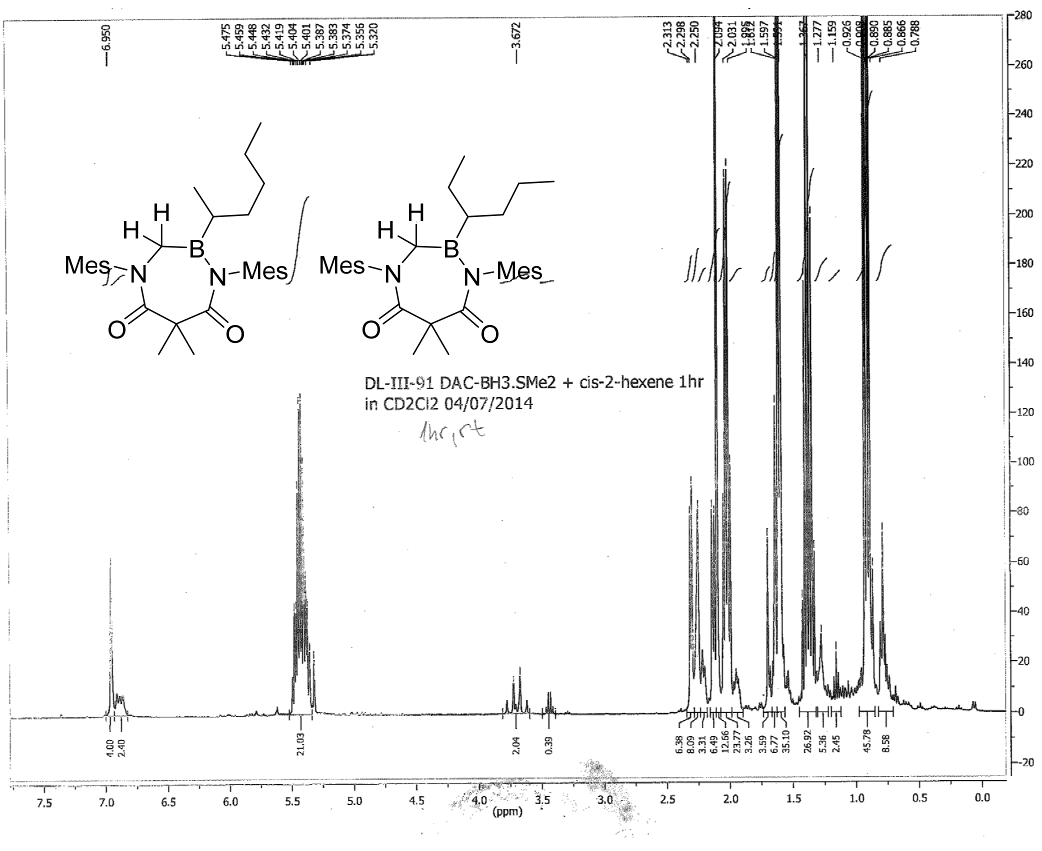
```
500 MHz nmr0

dac_bh3_1_3_cyclohexadiene_c13

exp4  Carbon

       SAMPLE               SPECIAL
date    Nov  1 2013  temp            27.0
solvent         c6d6  gain              50
file             exp  spin              20
    ACQUISITION       hst            0.008
sw           30165.9  pw90          11.600
at             1.958  alfa          10.000
np            118154         FLAGS
fb             17000  il                 n
bs                 1  in                 n
d1             2.000  dp                 y
nt              5000  hs                nn
ct              1243        PROCESSING
    TRANSMITTER       lb              1.00
tn               C13  fn          not used
sfrq         125.701         DISPLAY
tof           1255.4  sp            -628.5
tpwr              55  wp           28279.6
pw             3.862  rfl          17962.6
     DECOUPLER        rfp          16088.0
dn                H1  rp            -132.2
dof                0  lp            -215.2
dm               yyy          PLOT
dmm                w  wc               250
dpwr              38  sc                 0
dmf            11800  vs              2470
                      th                 5
                      ai     ph
```

Figure S14. ^{13}C NMR spectrum of **7** and **8**.



```
500 MHz nmr0

dac_bh3_1_3_cyclohexadiene_11b

exp2  s2pul

       SAMPLE                DEC. & VT
date    Nov  1 2013     dfrq       499.854
solvent        c6d6     dn              H1
file            exp     dpwr            37
   ACQUISITION          dof              0
sfrq        160.372     dm             nnn
tn              B11     dmm              w
at            1.282     dmf          10582
np           131414     dseq
sw          51249.2     dres           1.0
fb            28000     homo             n
bs                1     temp          27.0
tpwr             53         PROCESSING
pw              9.0     lb           10.00
d1            1.000     wtfile
tof          4803.4     proc            lp
nt              512     fn        not used
ct              512     math             f
alock             n
gain             20     werr
       FLAGS            wexp
il                n     wbs
in                n     wnt
dp                y
hs               nn
      DISPLAY
sp         -25602.0
wp          51248.8
vs            15087
sc                0
wc              250
hzmm         205.00
is           500.00
rfl         25602.4
rfp               0
th               43
ins         100.000
ai     ph
```

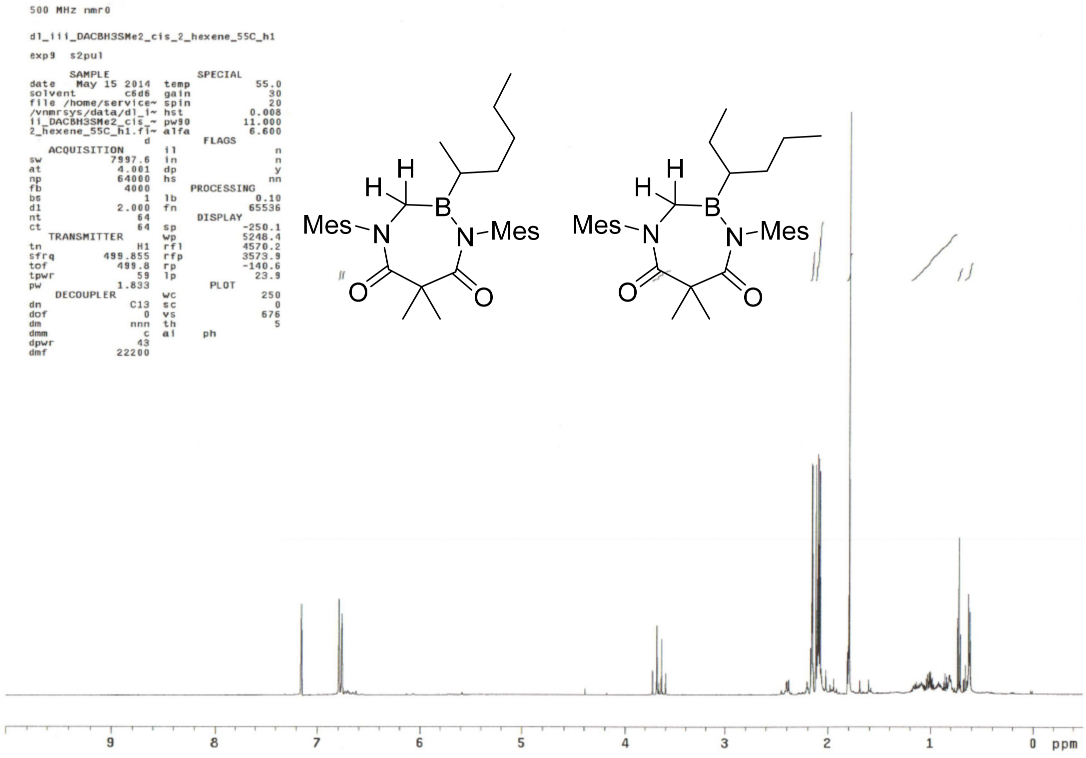
Figure S15. ^{11}B NMR spectrum of **7** and **8**.



DL-III-91 DAC-BH3.SMe2 + cis-2-hexene 1hr in CD2Cl2 04/07/2014

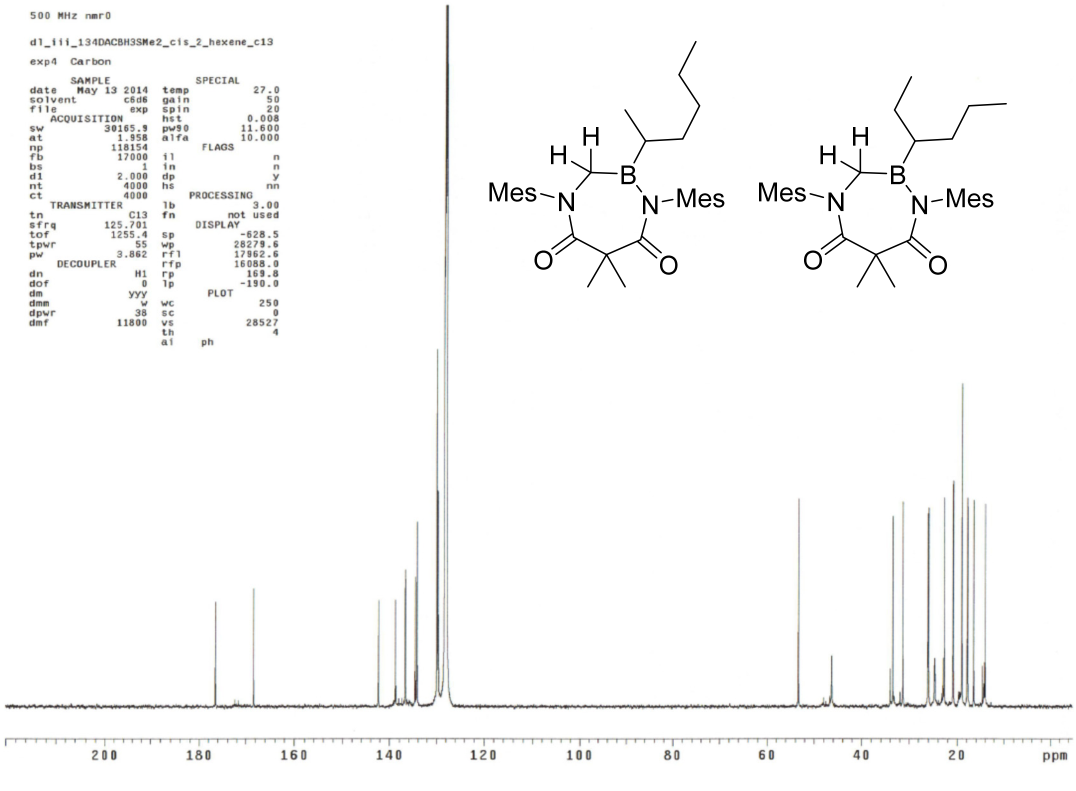
1hr, rt

Figure S16. ^{1}H NMR spectrum of **9** and **10** obtained from *cis*-2-hexene.



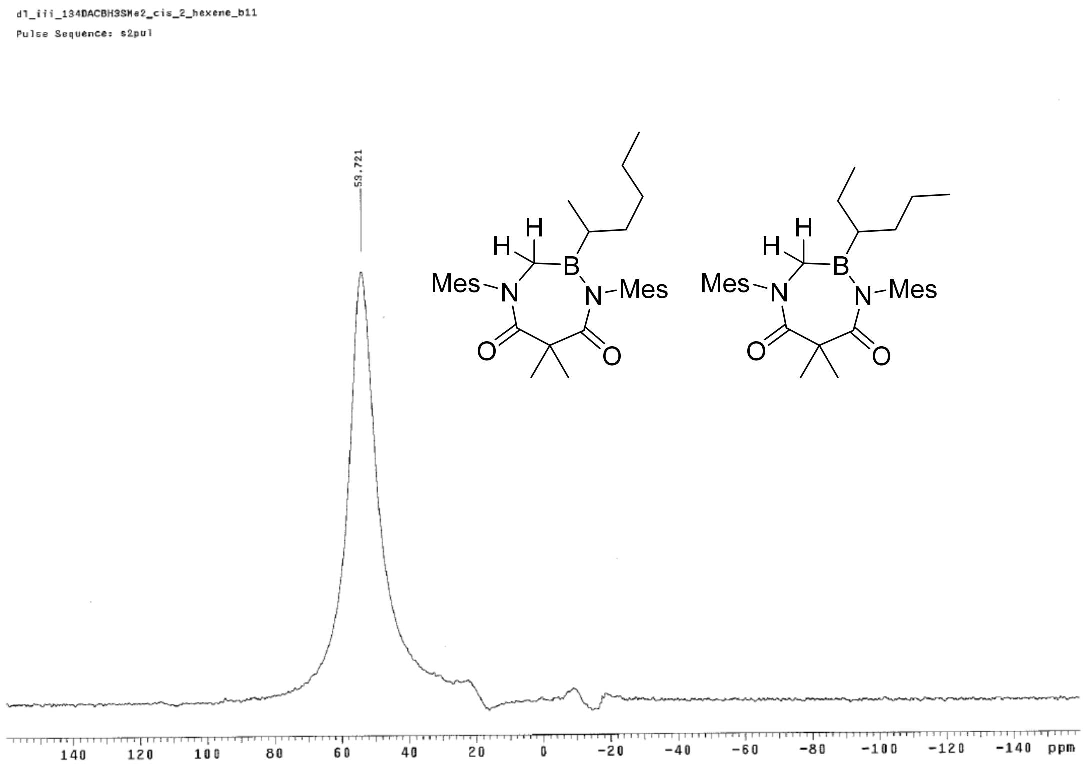
```
500 MHz nmr0

dl_iii_DACBH3SMe2_cis_2_hexene_55C_h1

exp9  s2pul

      SAMPLE               SPECIAL
date   May 15 2014  temp           55.0
solvent        c6d6  gain             30
file /home/service~ spin             20
/vnmrsys/data/dl_i~ hst           0.008
ii_DACBH3SMe2_cis_~ pw90         11.000
2_hexene_55C_h1.fi~ alfa          6.600
                  d         FLAGS
    ACQUISITION     il                n
sw           7997.6  in                n
at            4.001  dp                y
np            64000  hs               nn
fb             4000       PROCESSING
bs                1  lb            0.10
d1            2.000  fn           65536
nt               64         DISPLAY
ct               64  sp          -250.1
    TRANSMITTER      wp          5248.4
tn               H1  rfl         4570.2
sfrq        499.855  rfp         3573.9
tof           499.8  rp          -140.6
tpwr             59  lp            23.9
pw            1.833          PLOT
     DECOUPLER       wc             250
dn              C13  sc               0
dof               0  vs             676
dm              nnn  th               5
dmm               c  ai      ph
dpwr             43
dmf           22200
```

Figure S17. Variable Temperature (VT) ^{1}H NMR spectrum of **9** and **10** obtained from *cis*-2-hexene at 55 °C.



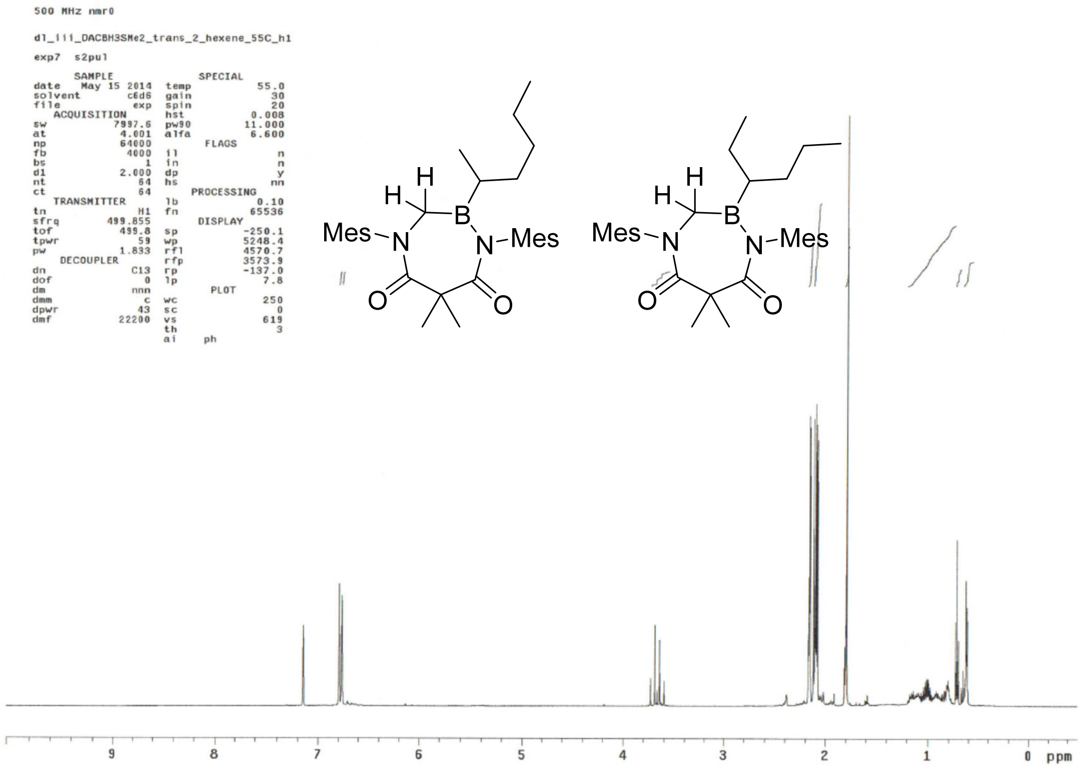
```
500 MHz nmr0

dl_iii_134DACBH3SMe2_cis_2_hexene_c13

exp4  Carbon

      SAMPLE               SPECIAL
date   May 13 2014  temp           27.0
solvent        c6d6  gain             50
file            exp  spin             20
    ACQUISITION     hst           0.008
sw          30165.9  pw90         11.600
at            1.958  alfa         10.000
np           118154         FLAGS
fb            17000  il                n
bs                1  in                n
d1            2.000  dp                y
nt             4000  hs               nn
ct             4000       PROCESSING
    TRANSMITTER      lb            3.00
tn              C13  fn        not used
sfrq        125.701         DISPLAY
tof          1255.4  sp          -628.5
tpwr             55  wp         28279.6
pw            3.862  rfl        17962.6
     DECOUPLER       rfp        16088.0
dn               H1  rp           169.8
dof               0  lp          -190.0
dm              yyy          PLOT
dmm               w  wc             250
dpwr             38  sc               0
dmf           11800  vs           28527
                     th               4
                     ai      ph
```

Figure S18. ^{13}C NMR spectrum of **9** and **10** obtained from *cis*-2-hexene.



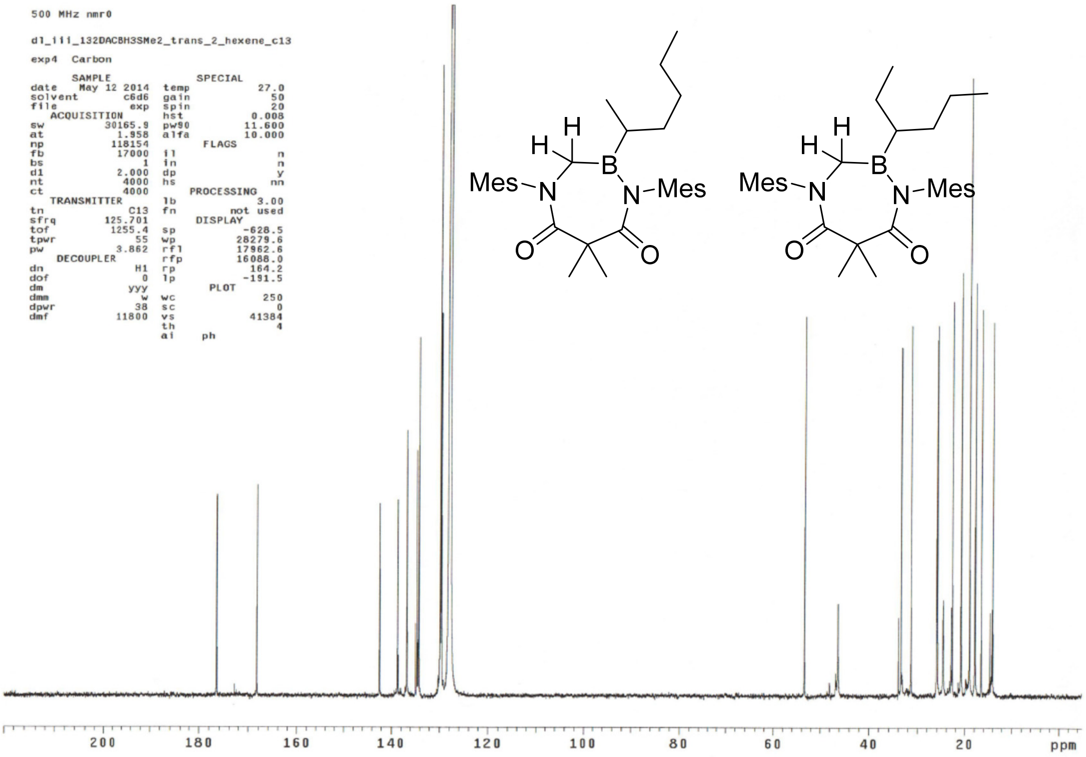
```
d1_iii_134DACBH3SMe2_cis_2_hexene_b11
Pulse Sequence: s2pul
```

Figure S19. ^{11}B NMR spectrum of **9** and **10** obtained from *cis*-2-hexene.



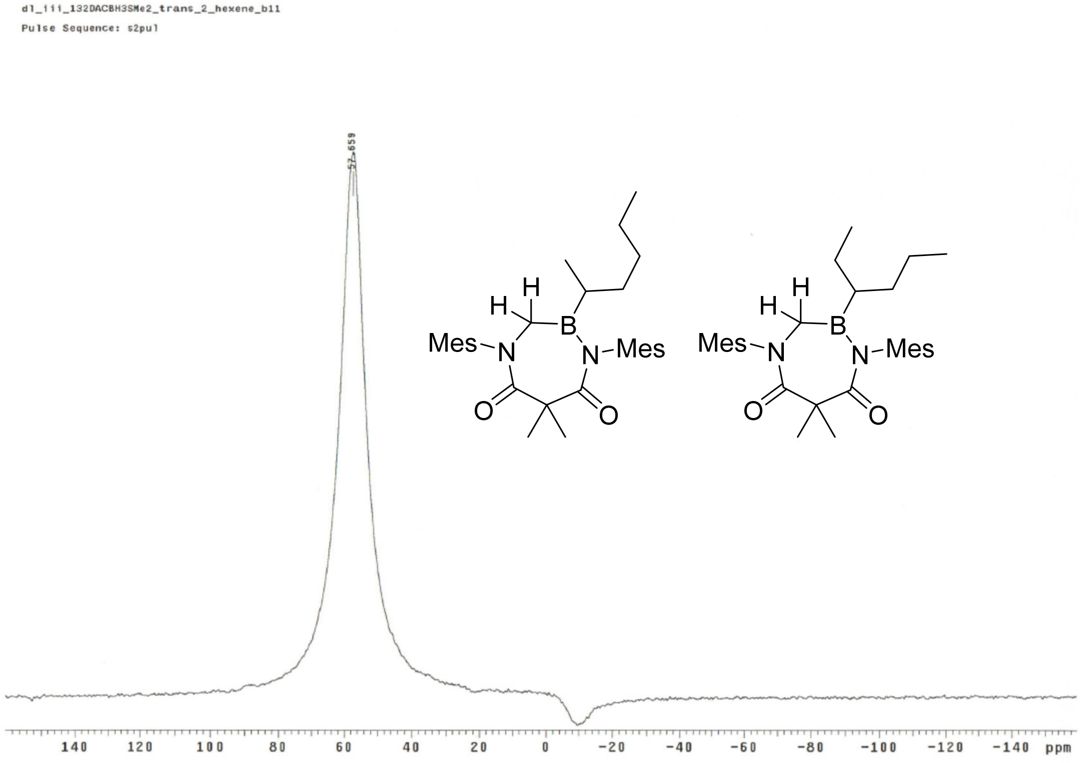
```
500 MHz nmr0

d1_iii_DACBH3SMe2_trans_2_hexene_55C_h1

exp7  s2pul
        SAMPLE              SPECIAL
date    May 15 2014   temp          55.0
solvent        c6d6   gain            30
file            exp   spin            20
    ACQUISITION       hst          0.008
sw           7997.6   pw90        11.000
at            4.001   alfa         6.600
np            64000          FLAGS
fb             4000   il               n
bs                1   in               n
d1            2.000   dp               y
nt               64   hs              nn
ct               64        PROCESSING
    TRANSMITTER       lb            0.10
tn               H1   fn           65536
sfrq        499.855          DISPLAY
tof           499.8   sp          -250.1
tpwr             59   wp          5248.4
pw            1.833   rfl         4570.7
     DECOUPLER        rfp         3573.9
dn              C13   rp          -137.0
dof               0   lp             7.8
dm              nnn            PLOT
dmm               c   wc             250
dpwr             43   sc               0
dmf           22200   vs             619
                      th               3
                      ai     ph
```

Figure S20. VT ^{1}H NMR spectrum of **9** and **10** obtained from *trans*-2-hexene at 55 °C.



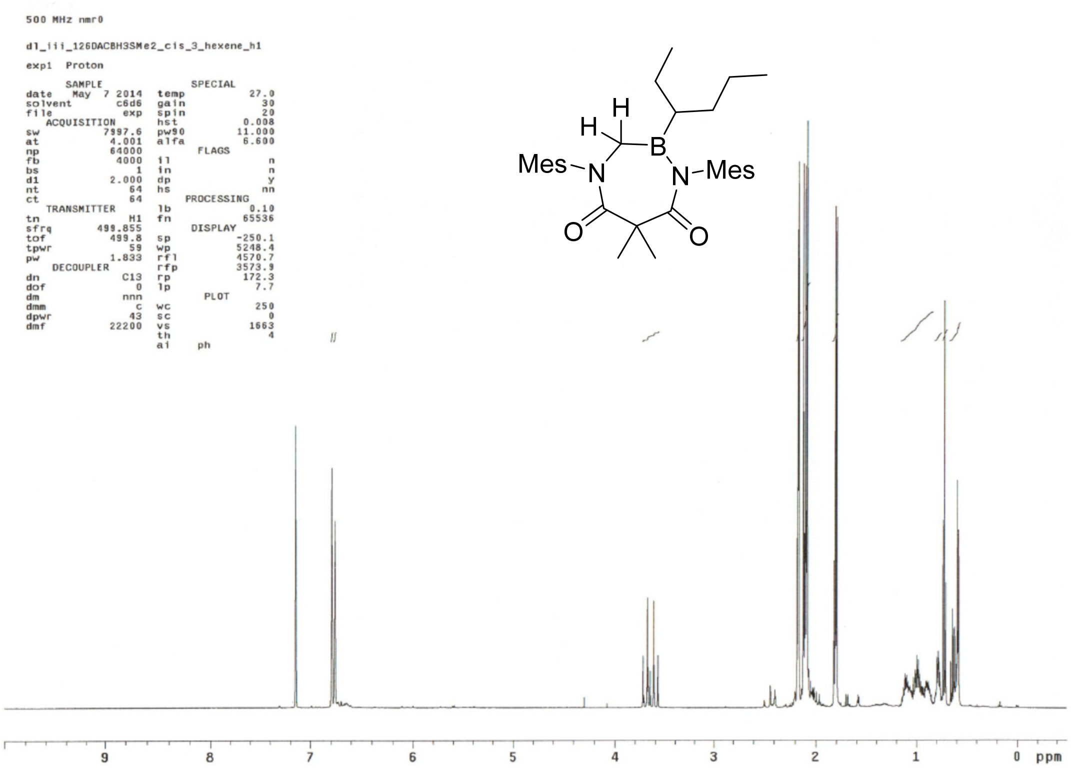
```
500 MHz nmr0

d1_iii_132DACBH3SMe2_trans_2_hexene_c13

exp4  Carbon

      SAMPLE                SPECIAL
date    May 12 2014   temp            27.0
solvent        c6d6   gain              50
file            exp   spin              20
   ACQUISITION        hst            0.008
sw          30165.9   pw90          11.600
at            1.958   alfa          10.000
np           118154          FLAGS
fb            17000   il                 n
bs                1   in                 n
d1            2.000   dp                 y
nt             4000   hs                nn
ct             4000       PROCESSING
   TRANSMITTER        lb              3.00
tn              C13   fn          not used
sfrq        125.701         DISPLAY
tof          1255.4   sp            -628.5
tpwr             55   wp           28279.6
pw            3.862   rfl          17962.6
    DECOUPLER         rfp          16088.0
dn               H1   rp             164.2
dof               0   lp            -191.5
dm              yyy           PLOT
dmm               w   wc               250
dpwr             38   sc                 0
dmf           11800   vs             41384
                      th                 4
                      ai     ph
```

Figure S21. ^{13}C NMR spectrum of **9** and **10** obtained from *trans*-2-hexene.



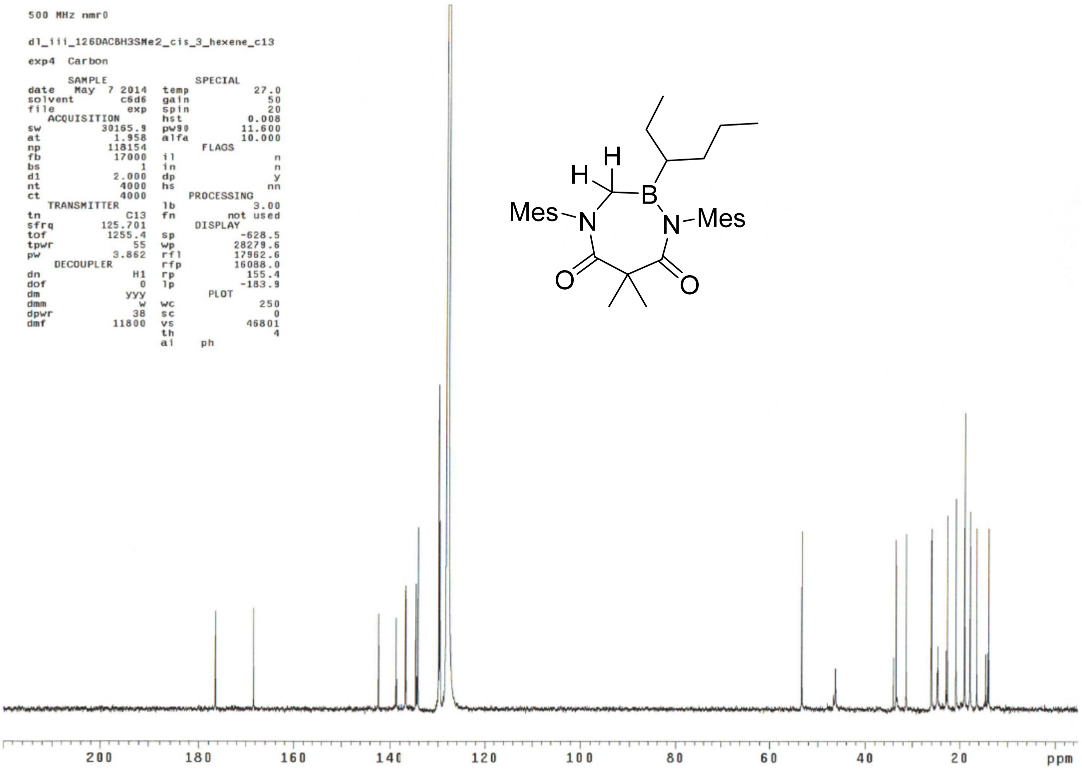
```
d1_iii_132DACBH3SMe2_trans_2_hexene_b11
Pulse Sequence: s2pul
```

Figure S22. ^{11}B NMR spectrum of **9** and **10** obtained from *trans*-2-hexene.



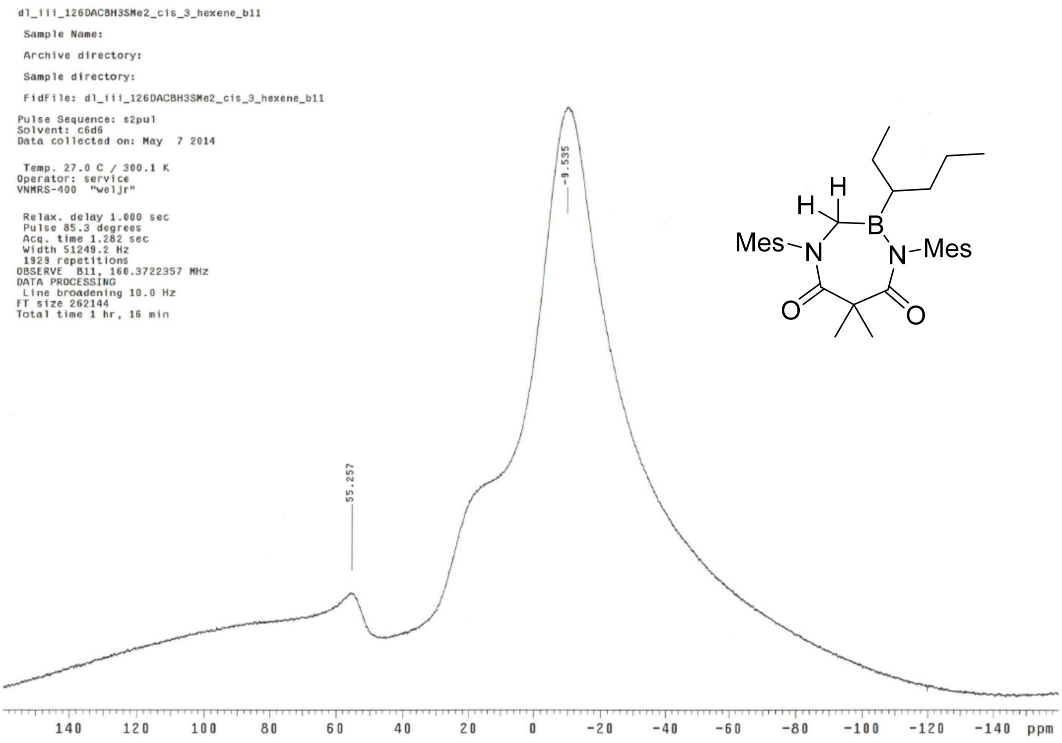
```
500 MHz nmr0

dl_iii_126DACBH3SMe2_cis_3_hexene_h1

exp1  Proton

       SAMPLE              SPECIAL
date   May  7 2014   temp            27.0
solvent        c6d6   gain              30
file            exp   spin              20
    ACQUISITION       hst            0.008
sw           7997.6   pw90          11.000
at            4.001   alfa           6.600
np            64000          FLAGS
fb             4000   il                 n
bs                1   in                 n
d1            2.000   dp                 y
nt               64   hs                nn
ct               64        PROCESSING
    TRANSMITTER       lb              0.10
tn               H1   fn             65536
sfrq        499.855          DISPLAY
tof           499.8   sp            -250.1
tpwr             59   wp            5248.4
pw            1.833   rfl           4570.7
     DECOUPLER        rfp           3573.9
dn              C13   rp             172.3
dof               0   lp               7.7
dm              nnn           PLOT
dmm               c   wc               250
dpwr             43   sc                 0
dmf           22200   vs              1663
                      th                 4
                      ai     ph
```

Figure S23. ^{1}H NMR spectrum of **10** obtained from *cis*-3-hexene.



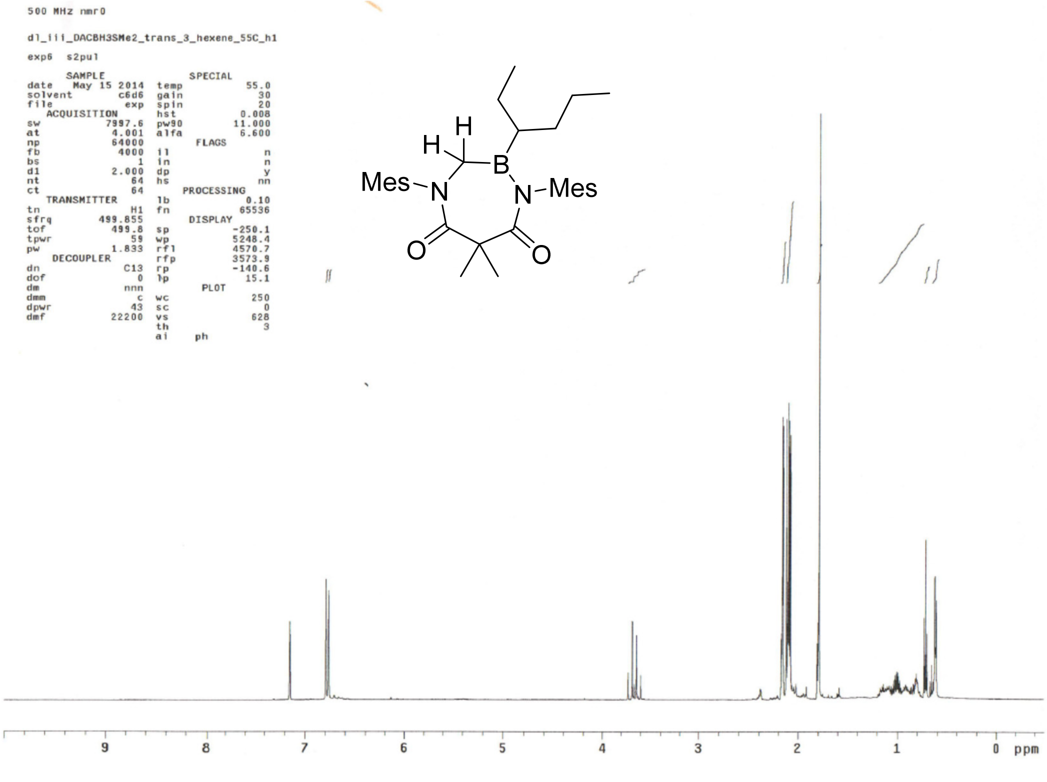
```
500 MHz nmr0

dl_iii_126DACBH3SMe2_cis_3_hexene_c13

exp4  Carbon

       SAMPLE              SPECIAL
date   May  7 2014   temp            27.0
solvent        c6d6   gain              50
file            exp   spin              20
    ACQUISITION       hst            0.008
sw          30165.9   pw90          11.600
at            1.958   alfa          10.000
np           118154          FLAGS
fb            17000   il                 n
bs                1   in                 n
d1            2.000   dp                 y
nt             4000   hs                nn
ct             4000        PROCESSING
    TRANSMITTER       lb              3.00
tn              C13   fn          not used
sfrq        125.701          DISPLAY
tof          1255.4   sp            -628.5
tpwr             55   wp           28279.6
pw            3.862   rfl          17962.6
     DECOUPLER        rfp          16088.0
dn               H1   rp             155.4
dof               0   lp            -183.9
dm              yyy           PLOT
dmm               w   wc               250
dpwr             38   sc                 0
dmf           11800   vs             46801
                      th                 4
                      ai     ph
```

Figure S24. ^{13}C NMR spectrum of **10** obtained from *cis*-3-hexene.



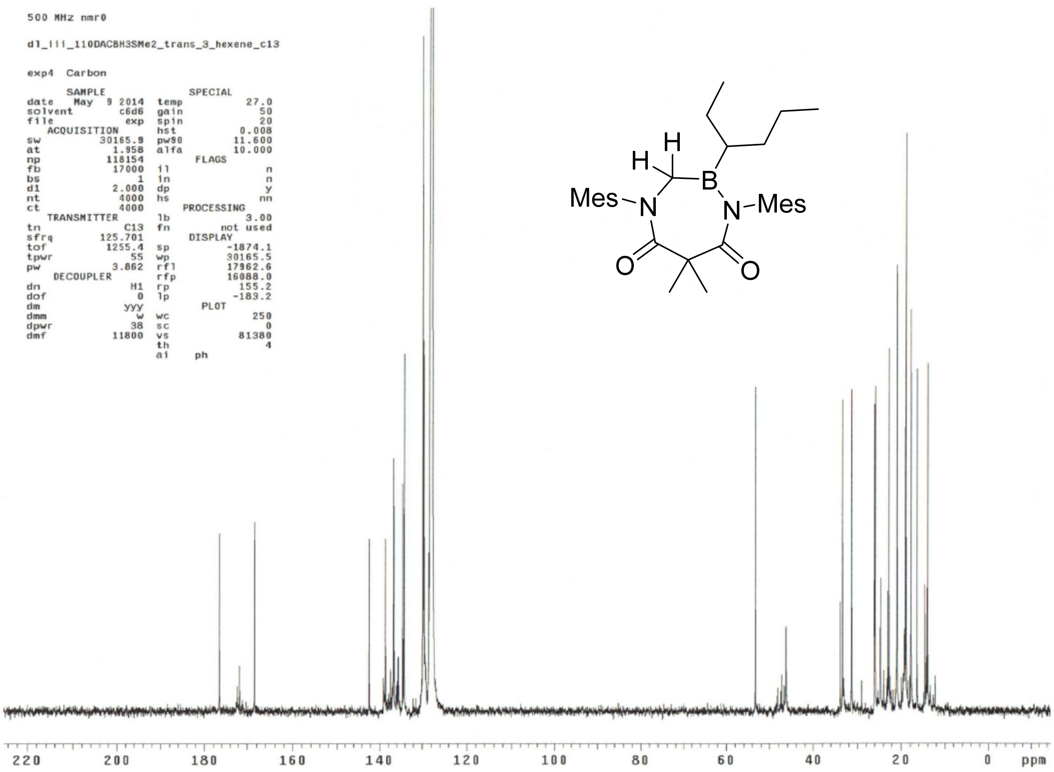
```
dl_iii_126DACBH3SMe2_cis_3_hexene_b11

 Sample Name:

 Archive directory:

 Sample directory:

 FidFile: dl_iii_126DACBH3SMe2_cis_3_hexene_b11

Pulse Sequence: s2pul
Solvent: c6d6
Data collected on: May  7 2014

 Temp. 27.0 C / 300.1 K
Operator: service
VNMRS-400  "weljr"

 Relax. delay 1.000 sec
 Pulse 85.3 degrees
 Acq. time 1.282 sec
 Width 51249.2 Hz
 1929 repetitions
OBSERVE  B11, 160.3722357 MHz
DATA PROCESSING
 Line broadening 10.0 Hz
FT size 262144
Total time 1 hr, 16 min
```

Figure S25. ^{11}B NMR spectrum of **10** obtained from *cis*-3-hexene.



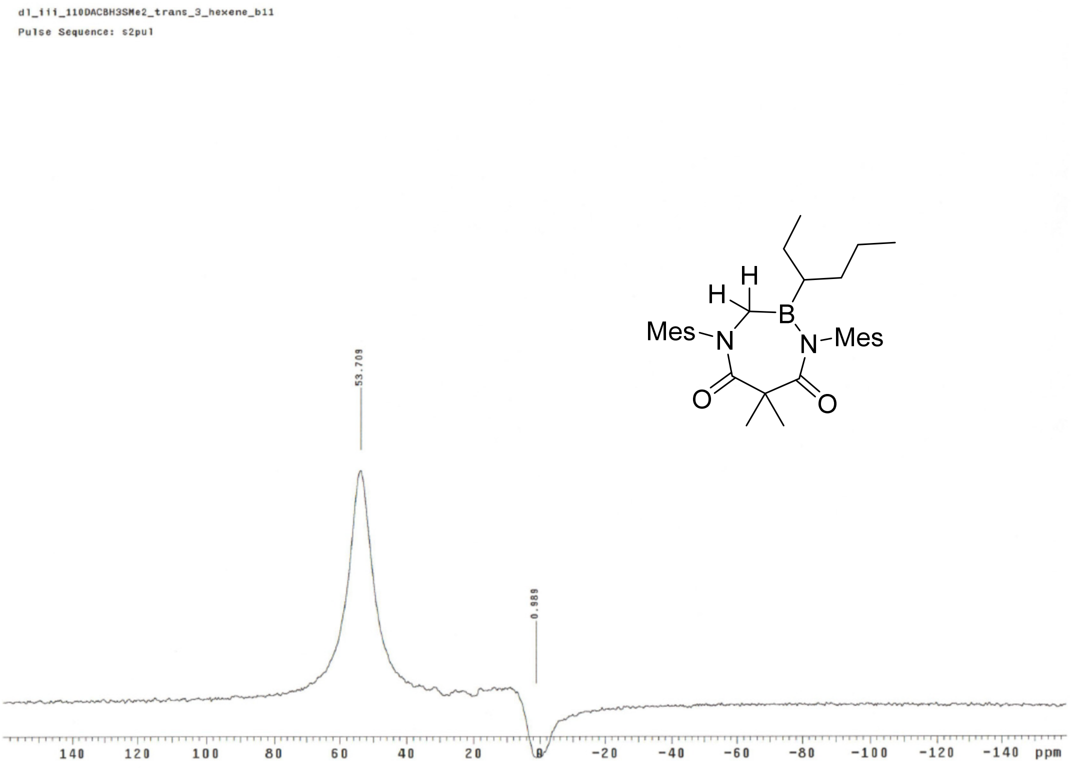
```
500 MHz nmr0

dl_iii_DACBH3SMe2_trans_3_hexene_55C_h1

exp6  s2pul

      SAMPLE                 SPECIAL
date   May 15 2014  temp             55.0
solvent       c6d6  gain               30
file           exp  spin               20
   ACQUISITION      hst             0.008
sw          7997.6  pw90           11.000
at           4.001  alfa            6.600
np           64000         FLAGS
fb            4000  il                  n
bs               1  in                  n
d1           2.000  dp                  y
nt              64  hs                 nn
ct              64       PROCESSING
   TRANSMITTER      lb               0.10
tn              H1  fn              65536
sfrq       499.855         DISPLAY
tof          499.8  sp             -250.1
tpwr            59  wp             5248.4
pw           1.833  rfl            4570.7
    DECOUPLER       rfp            3573.9
dn             C13  rp             -140.6
dof              0  lp               15.1
dm             nnn           PLOT
dmm              c  wc                250
dpwr            43  sc                  0
dmf          22200  vs                628
                    th                  3
                    ai     ph
```

Figure S26. VT ^{1}H NMR spectrum **10** obtained from *trans*-3-hexene at 55 °C.



```
500 MHz nmr0

dl_iii_110DACBH3SMe2_trans_3_hexene_c13

exp4  Carbon

     SAMPLE                    SPECIAL
date    May  9 2014   temp              27.0
solvent        c6d6   gain                50
file            exp   spin                20
   ACQUISITION        hst              0.008
sw          30165.9   pw90            11.600
at            1.958   alfa            10.000
np           118154          FLAGS
fb            17000   il                   n
bs                1   in                   n
d1            2.000   dp                   y
nt             4000   hs                  nn
ct             4000         PROCESSING
   TRANSMITTER        lb                3.00
tn              C13   fn            not used
sfrq        125.701          DISPLAY
tof          1255.4   sp             -1874.1
tpwr             55   wp             30165.5
pw            3.862   rfl            17962.6
    DECOUPLER         rfp            16088.0
dn               H1   rp               155.2
dof               0   lp              -183.2
dm              yyy            PLOT
dmm               w   wc                 250
dpwr             38   sc                   0
dmf           11800   vs               81380
                      th                   4
                      ai     ph
```

Figure S27. ^{13}C NMR spectrum of **10** obtained from *trans*-3-hexene.



```
dl_iii_110DACBH3SMe2_trans_3_hexene_b11
Pulse Sequence: s2pul
```

Figure S28. ^{11}B NMR spectrum of **10** obtained from *trans*-3-hexene.

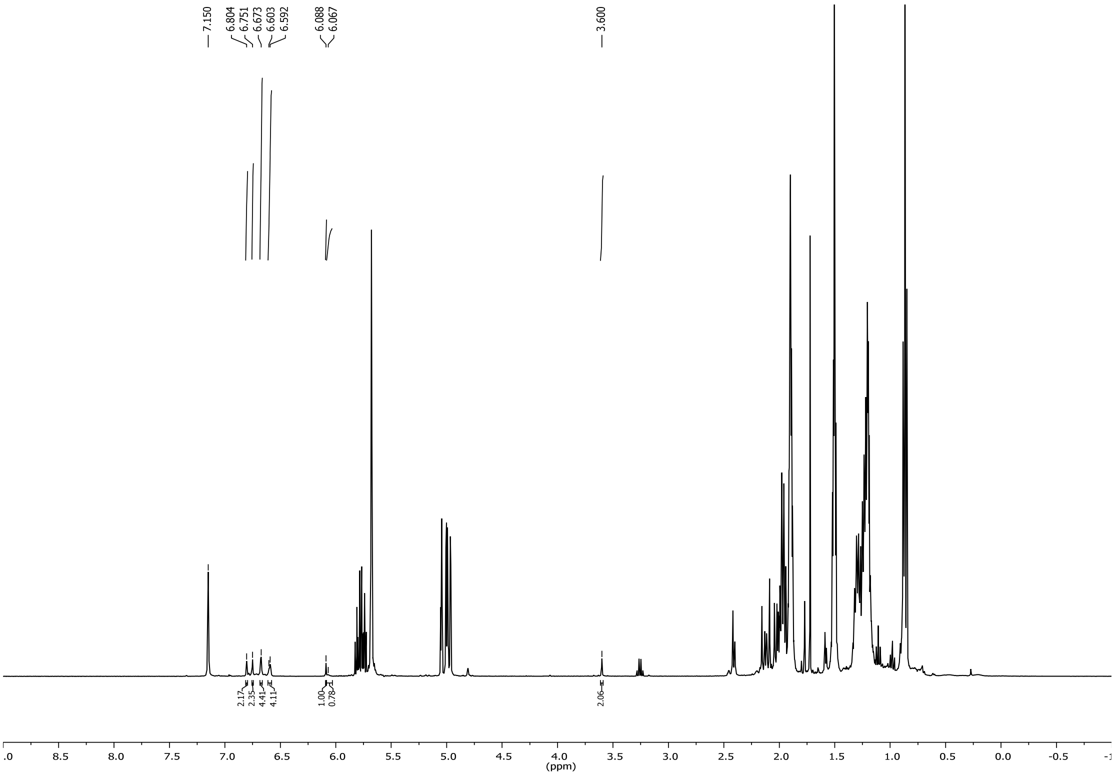


Figure S29. Crude ^{1}H NMR spectrum of **6**, **11** and **12** obtained from reaction shown in Scheme 8.

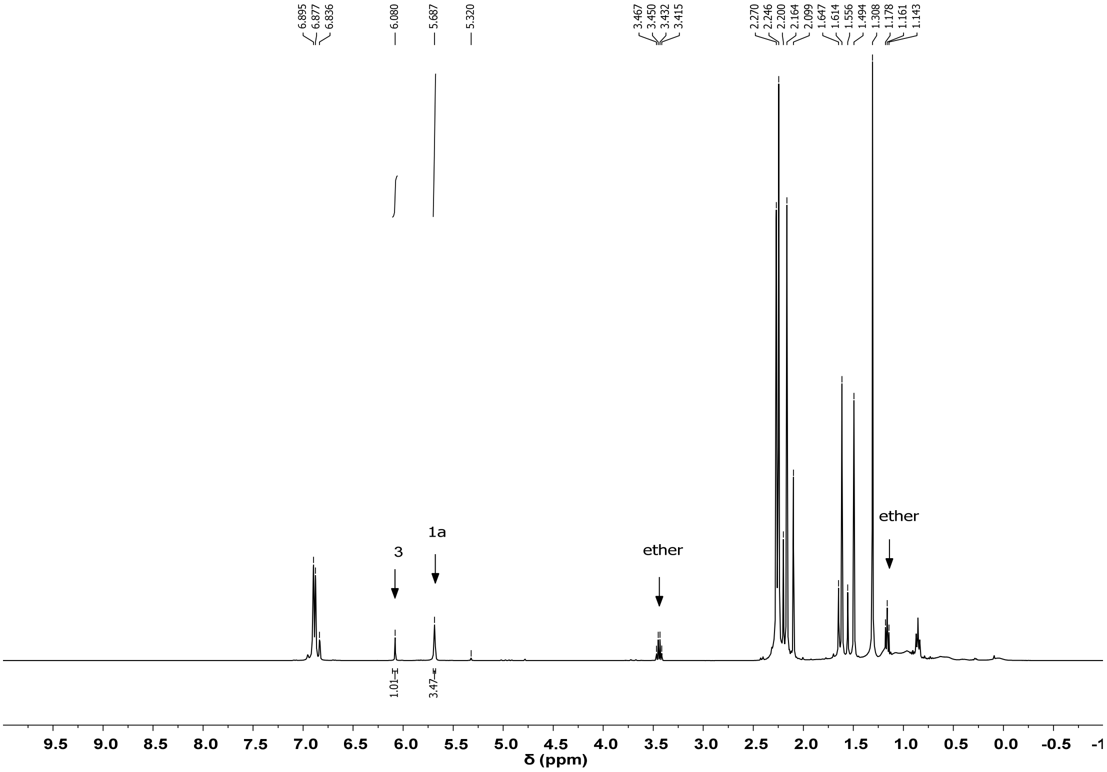


Figure S30. Crude ^{1}H NMR spectrum recorded after combining **1a** and 0.5 equiv of 1-hexene in CD_2Cl_2.

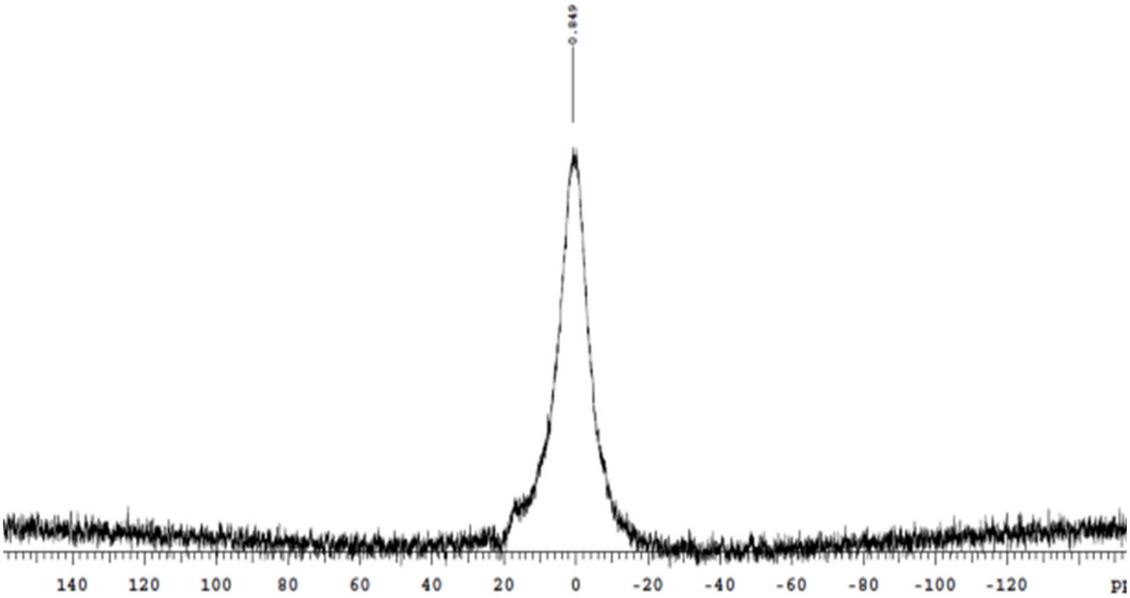


Figure S31. ^{11}B NMR spectrum of C_6D_6 as a reference.

References

1. Otwinowski, Z; Minor, W. *Methods in Enzymology: Macromolecular Crystallography, Part A;* Carter, C.W., Jr., Sweet, R.M., Eds.; Academic Press: San Diego, CA, USA, 1997; Volume 276, pp. 307–326.
2. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *A64*, 112–122.