Supplementary Material (ESI) for Chemical Communications

Assembly of a Planar, Tricyclic B_4N_8 Framework With *s*-Indacene Structure

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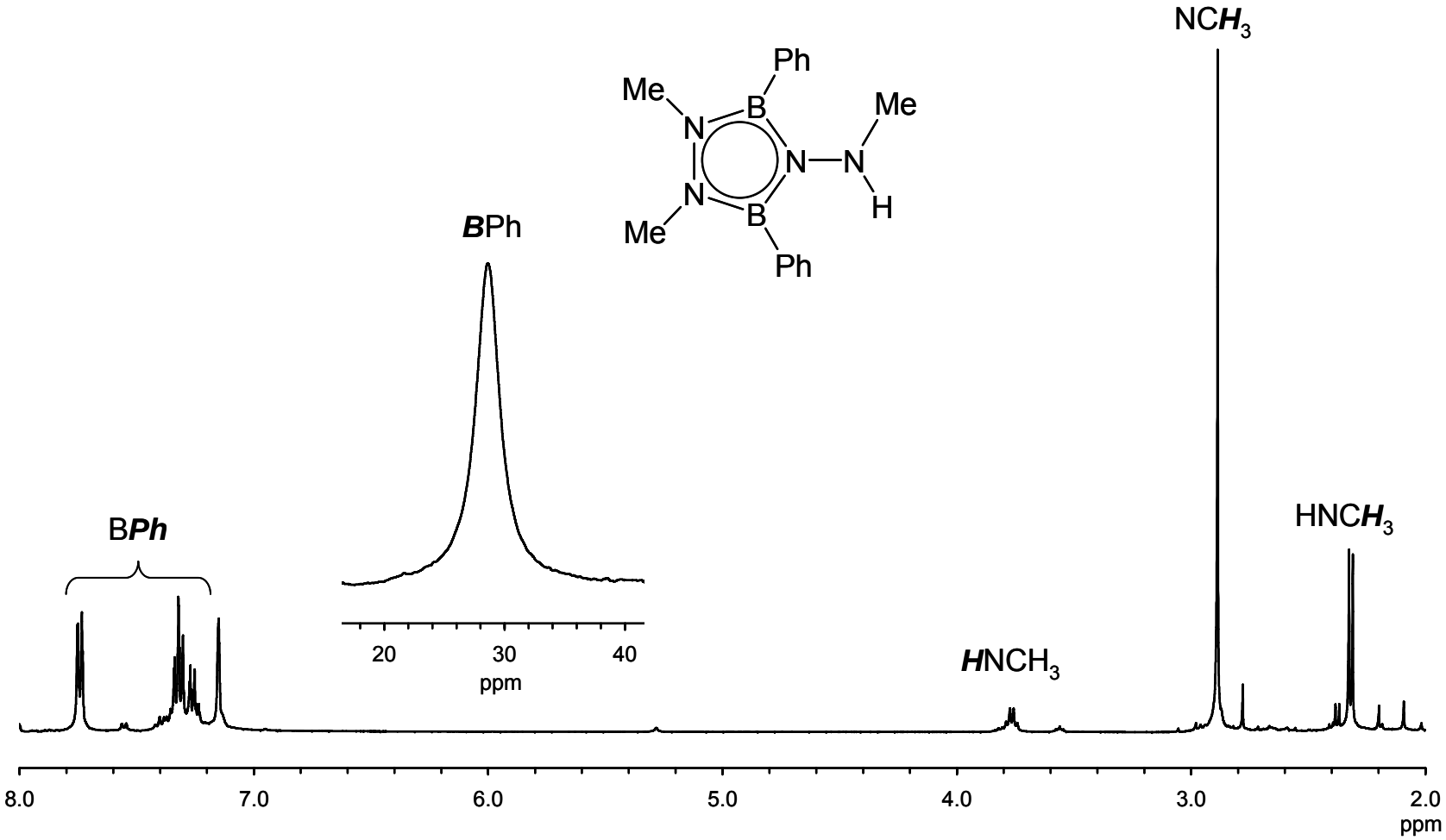
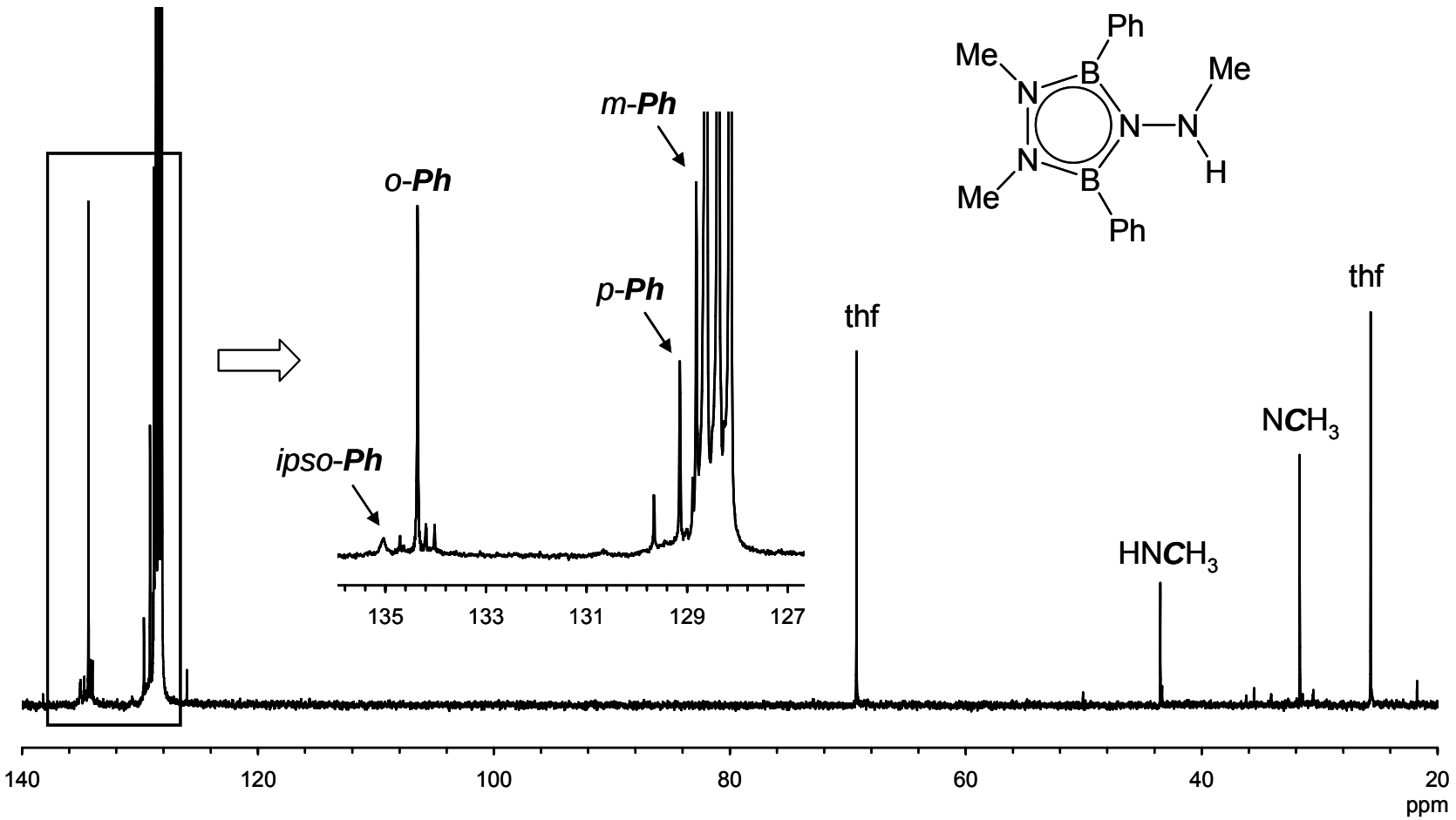
– Supplementary Information –

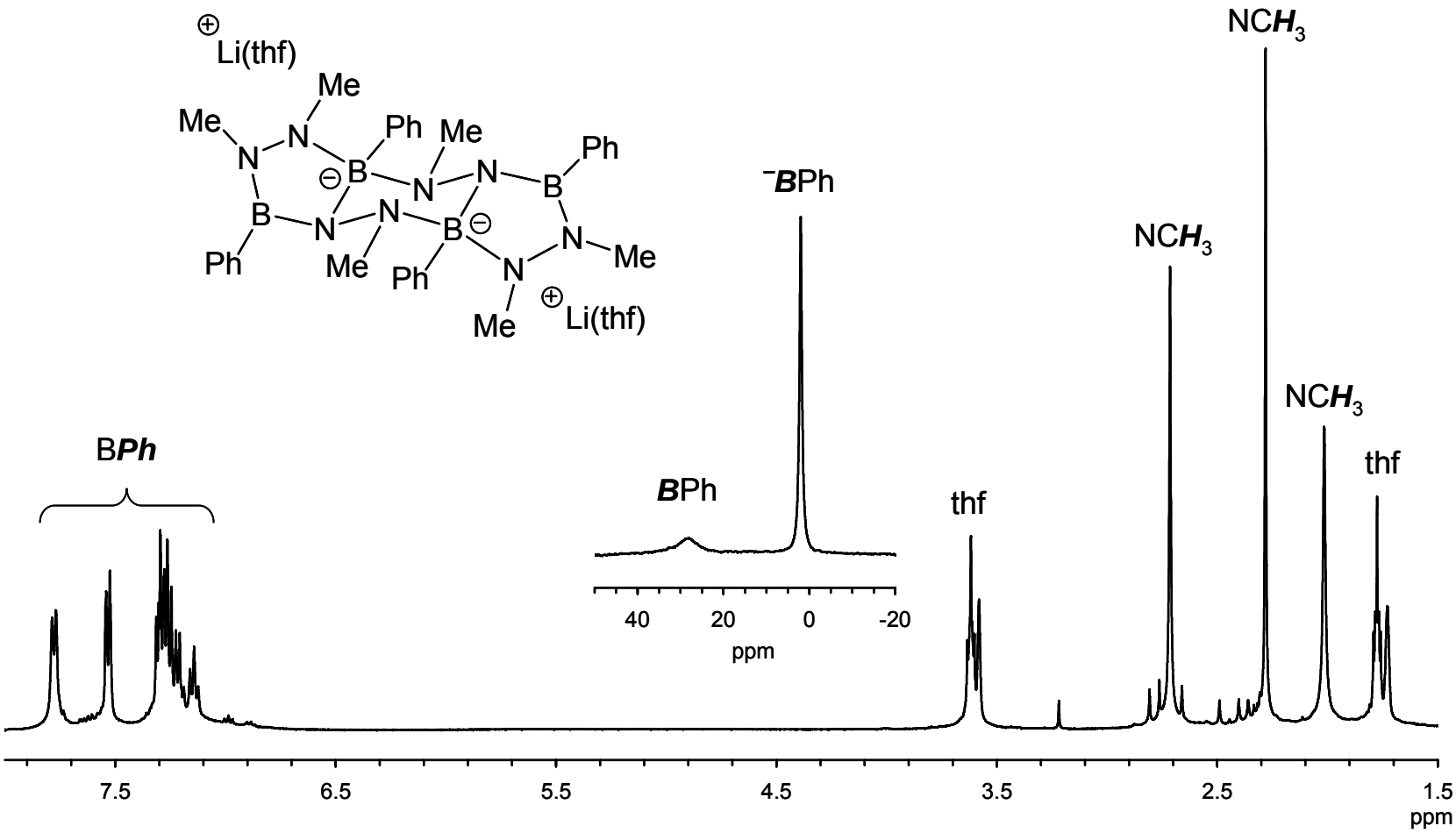
^{1}H and ^{11}B NMR Spectra of 1,2-dimethyl-3,5-diphenyl-4-methylamino-1,2,4-triaza-3,5-diborolidine (**2**) in C_6D_6



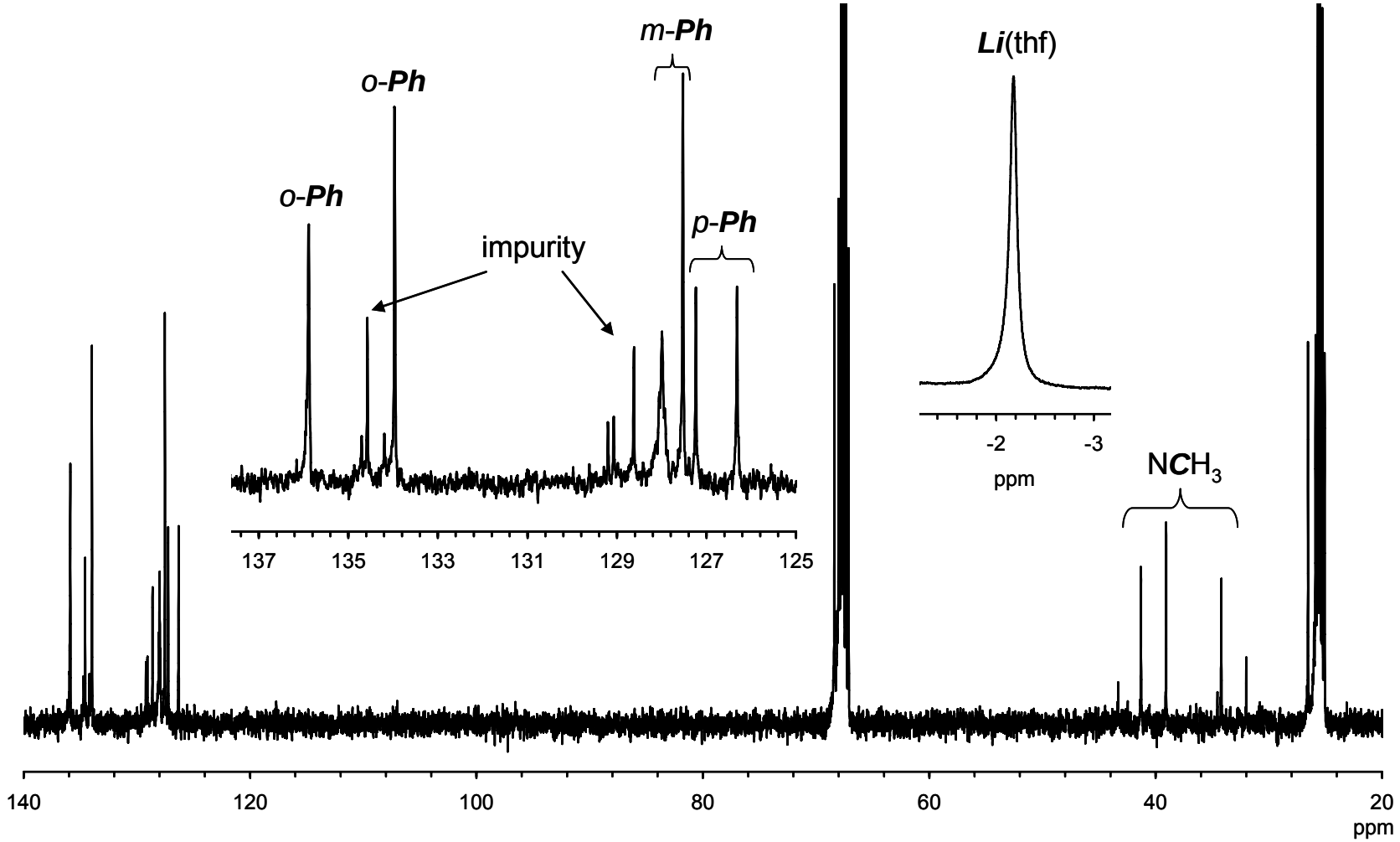
^{13}C NMR Spectrum of 1,2-dimethyl-3,5-diphenyl-4-methylamino-1,2,4-triaza-3,5-diborolidine (**2**) in C_6D_6



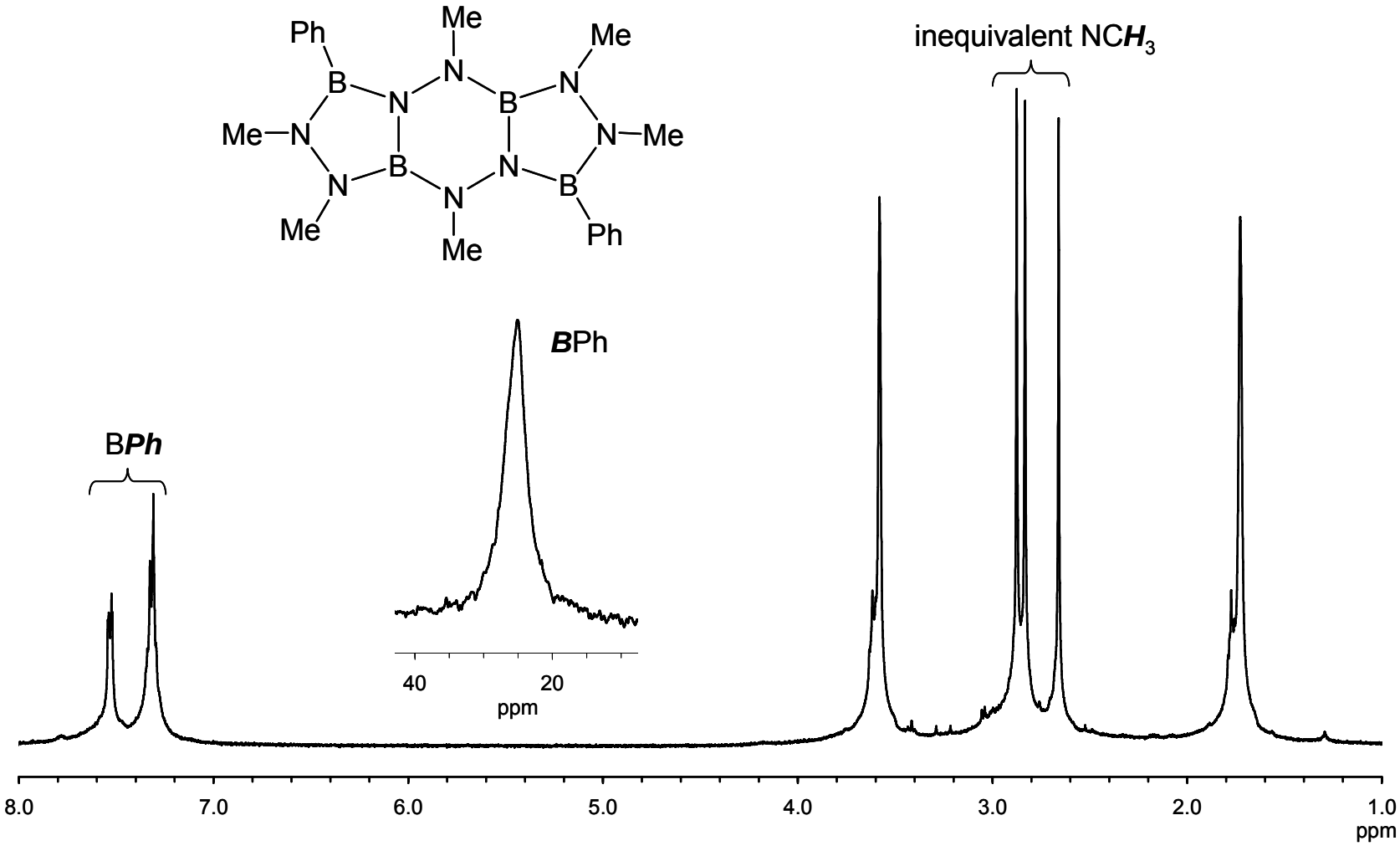
^{1}H and ^{11}B NMR Spectra of the dilithium salt (**3**) in THF-d_8



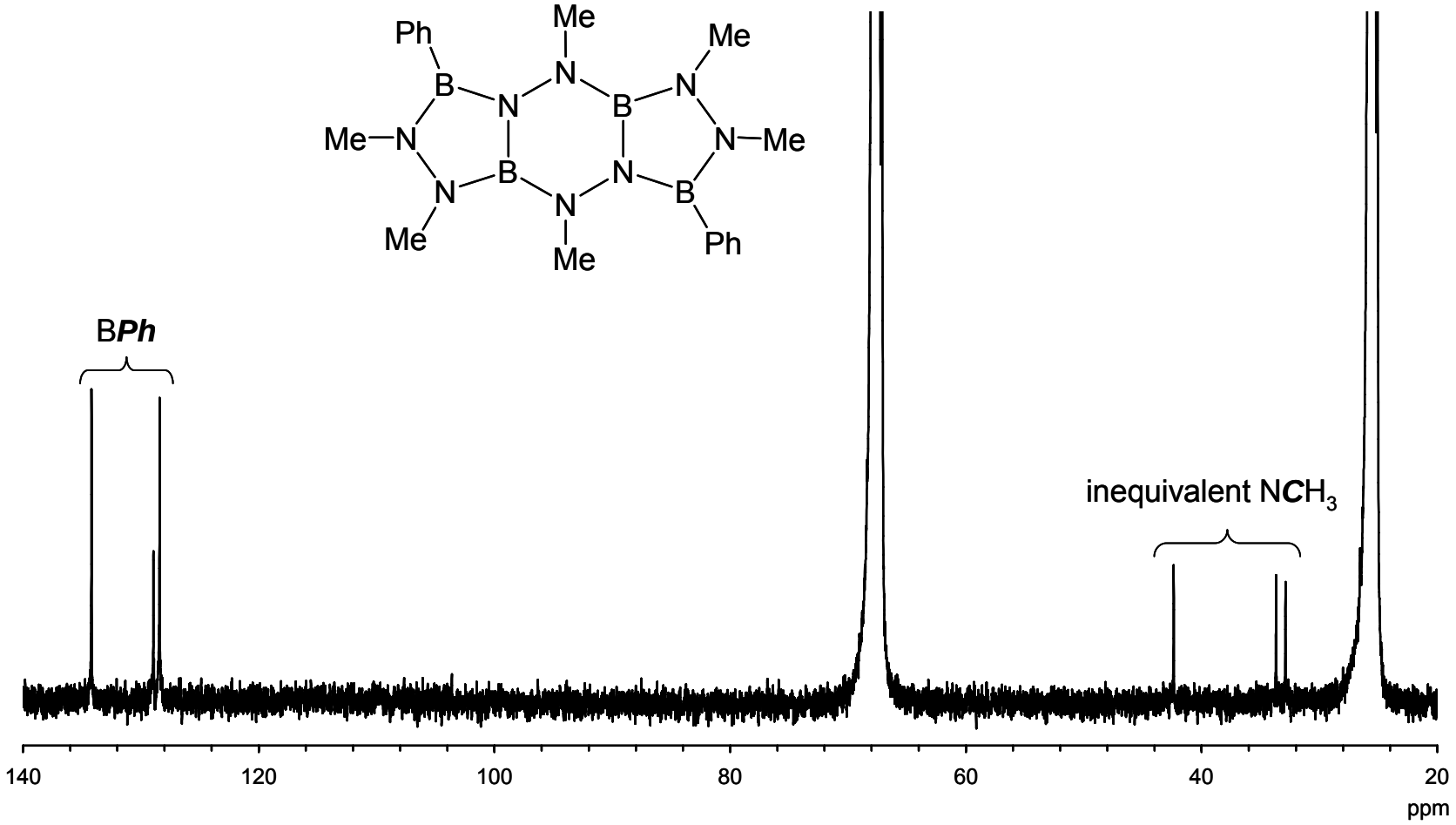
^{13}C and ^{7}Li NMR Spectra of the dilithium salt (**3**) in THF-d_8



^{1}H and ^{11}B NMR Spectra of the tricyclic tetrahydrazidotetraborane (**4**) in THF-d_8



^{13}C NMR Spectrum of the tricyclic tetrahydrazidotetraborane (**4**) in THF-d_8



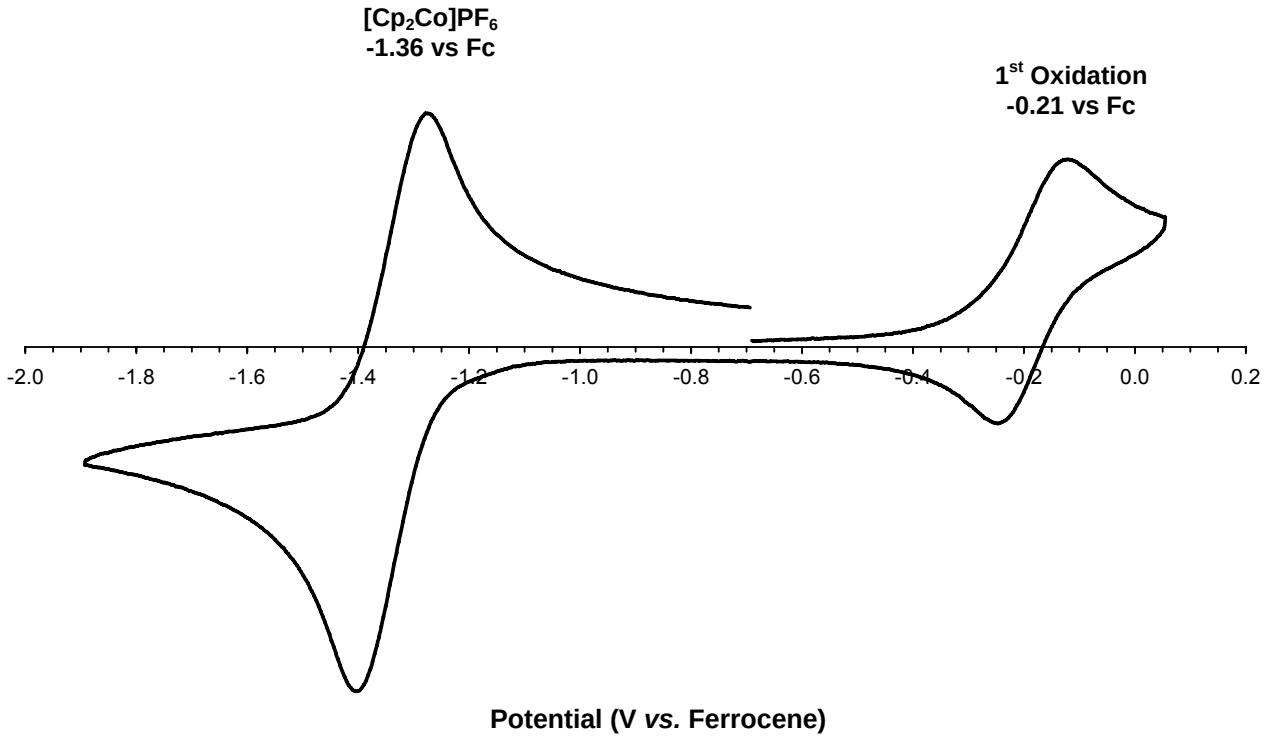


Fig. S1 Cyclovoltammogram of **4** in the presence of the internal standard $[Cp_2Co]PF_6$ ($[Cp_2Co]^{0/+1}$ with E^0 = –1.36 V *vs.* ferrocene and -0.82 V *vs.* the SCE) at 200 ms scan rate. The measurements were performed in THF at an analyte concentration of 1 mM, and using 0.1 M $[n\text{Bu}_4\text{N}]PF_6$ as a supporting electrolyte.

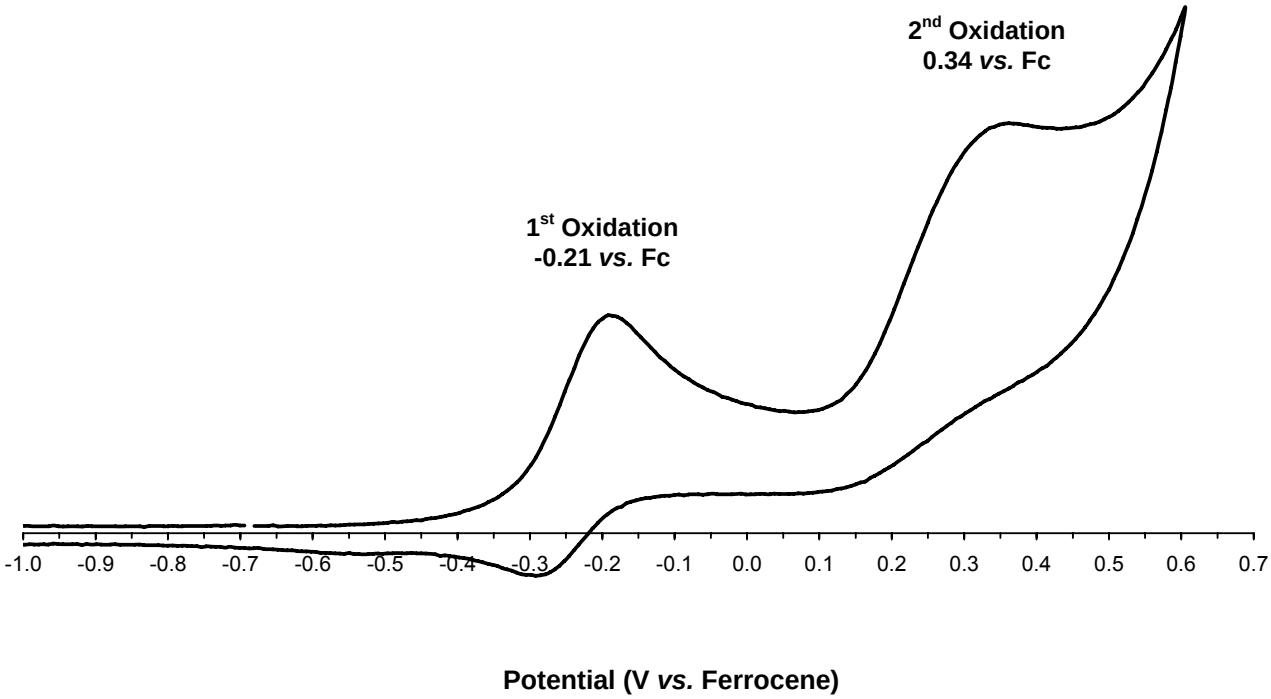


Fig. S2 Cyclovoltammogram of **4** in the absence of the internal standard at 50 ms scan rate. The measurements were performed in THF at an analyte concentration of 1 mM, and using 0.1 M [*n*Bu_4N]PF_6 as a supporting electrolyte.

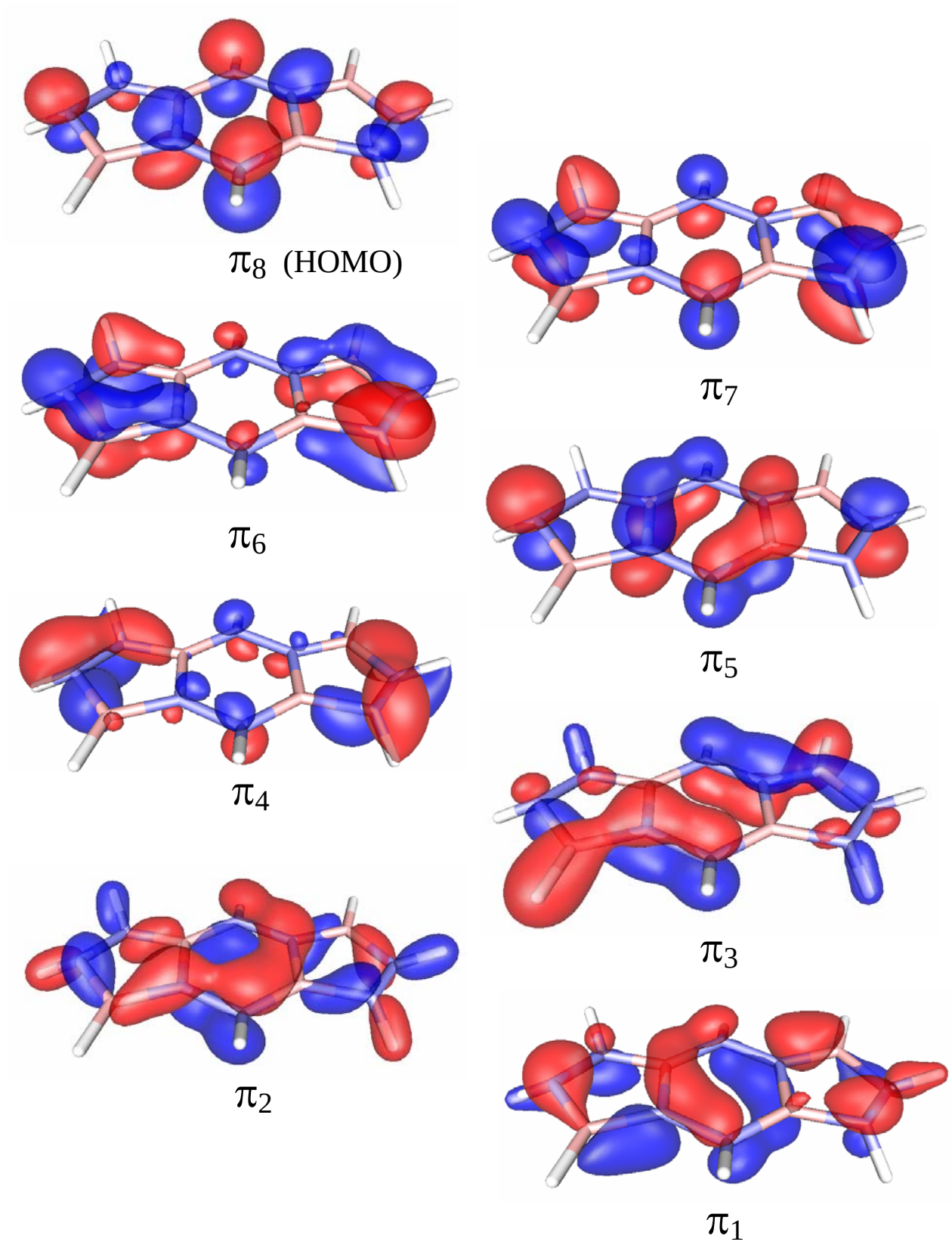
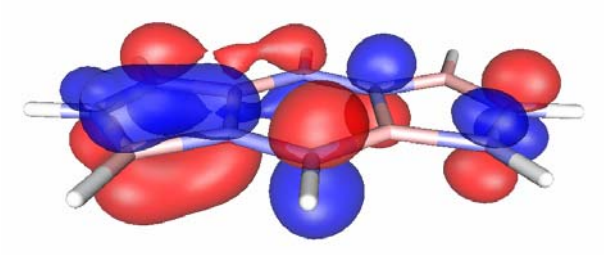
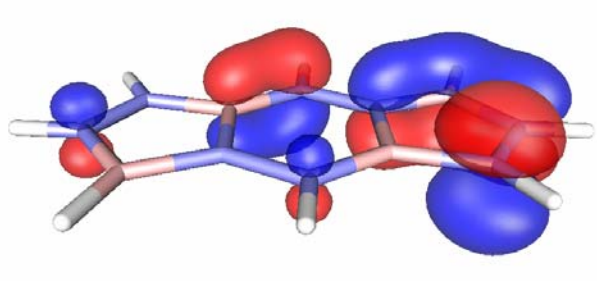


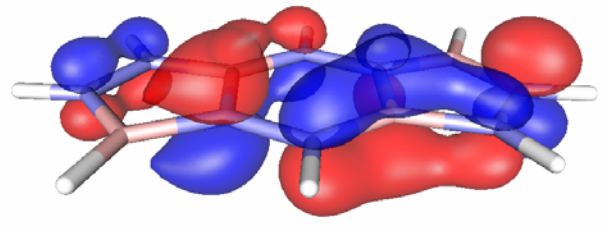
Fig. S3 Occupied π-like Kohn-Sham orbitals of **4**. For simplicity, orbitals are shown for a structure in which Me and Ph substituents attached to nitrogen and boron atoms have been replaced with hydrogen atoms.



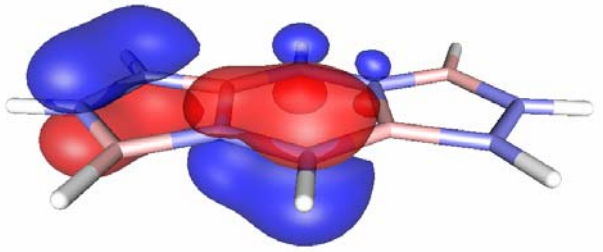
π_7 (HOMO)



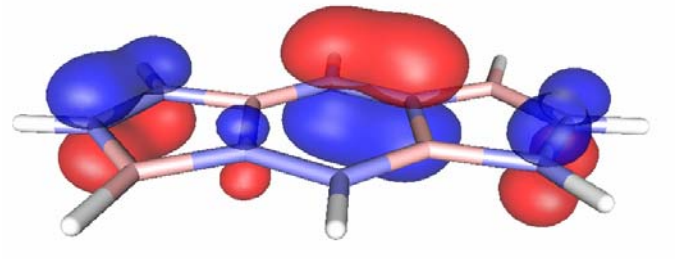
π_6



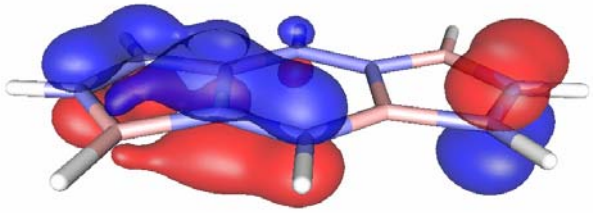
π_5



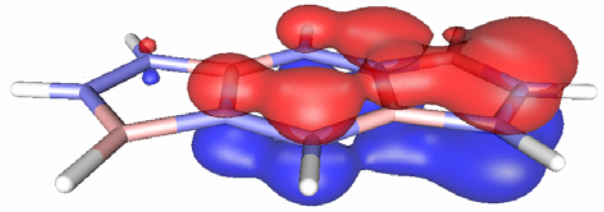
π_4



π_3



π_2



π_1

Fig. S4 Occupied π-symmetric Kohn-Sham α-orbitals of open-shell singlet $[\mathbf{4}]^{2+}$. For simplicity, orbitals are shown for a structure in which Me and Ph substituents attached to nitrogen and boron atoms have been replaced with hydrogen atoms.

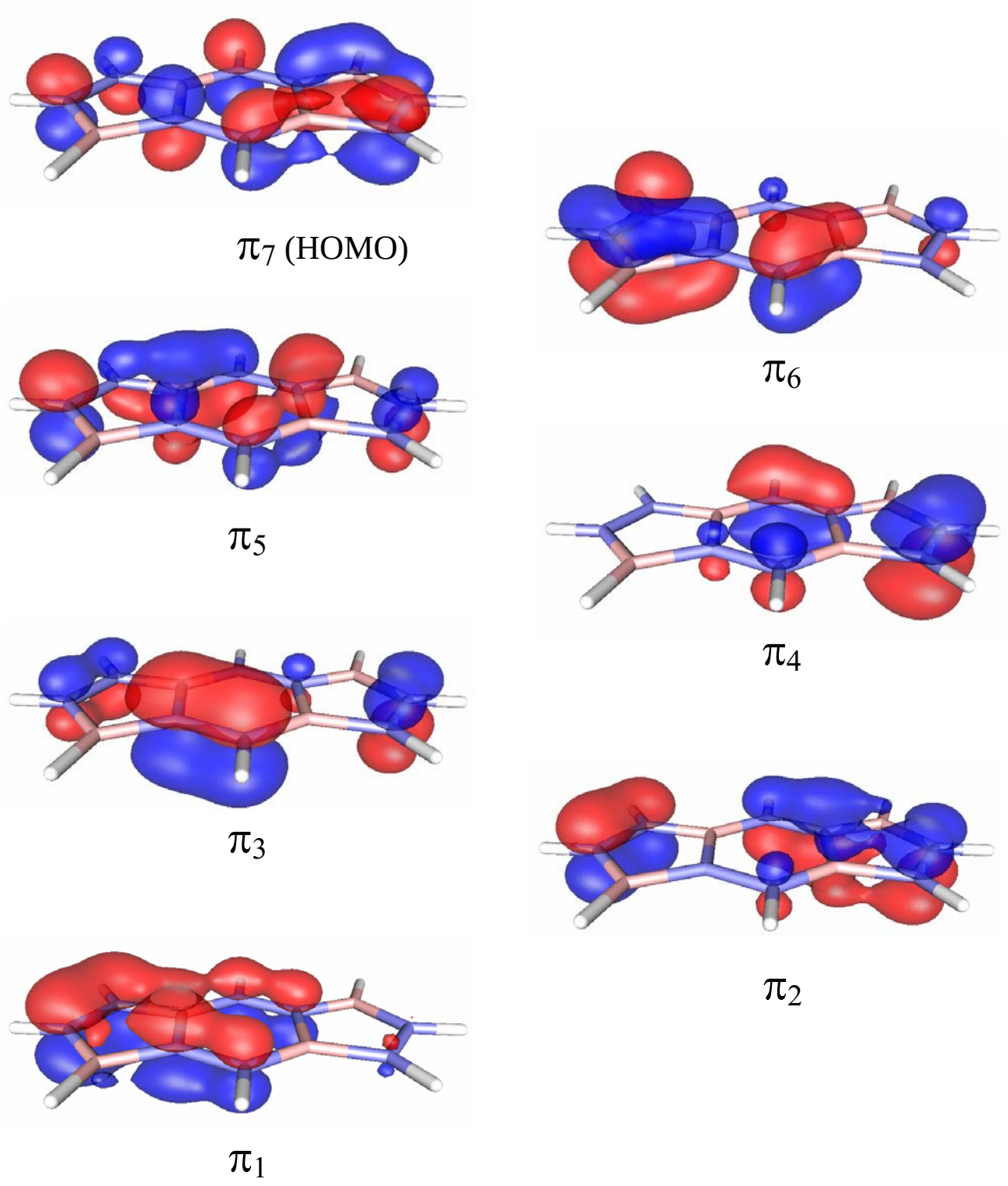
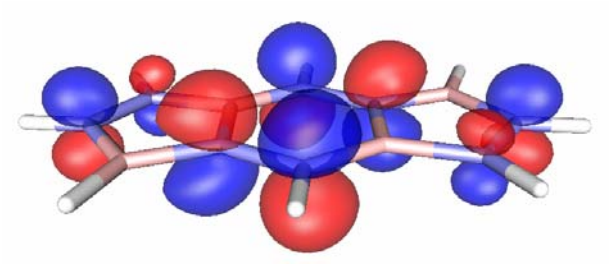
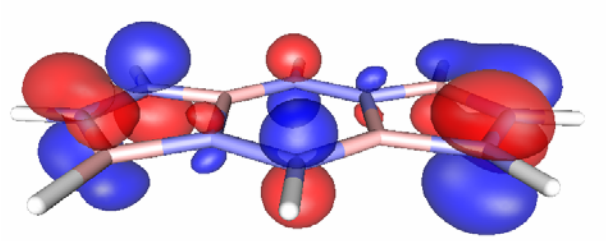


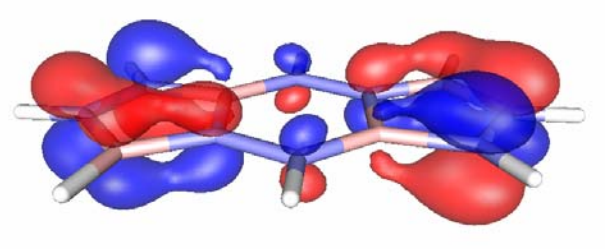
Fig. S5 Occupied π-symmetric Kohn-Sham β-orbitals of open-shell singlet $[\mathbf{4}]^{2+}$. For simplicity, orbitals are shown for a structure in which Me and Ph substituents attached to nitrogen and boron atoms have been replaced with hydrogen atoms.



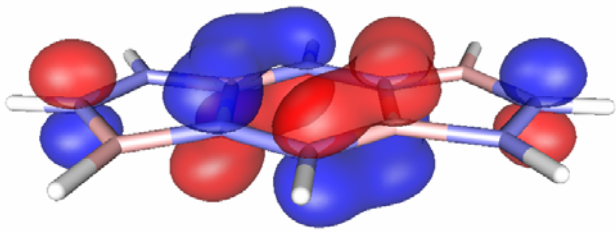
π_8 (SOMO)



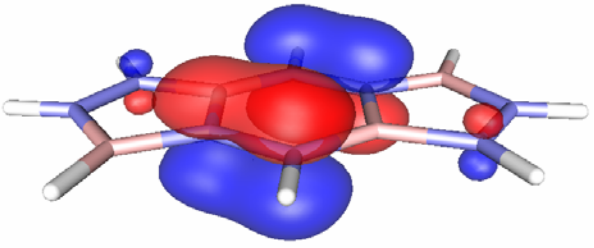
π_7 (SOMO)



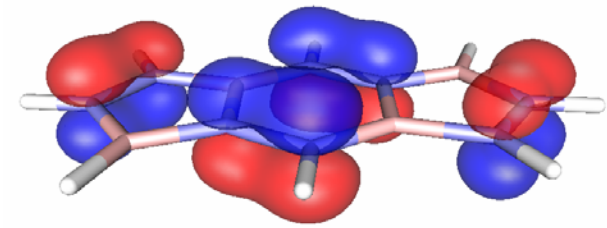
π_6



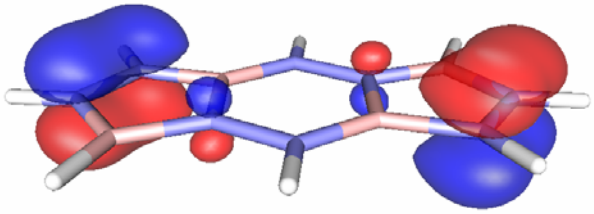
π_5



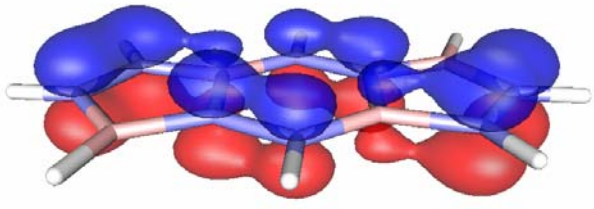
π_4



π_3



π_2



π_1

Fig. S6 Occupied π-symmetric Kohn-Sham α-orbitals of triplet $[\mathbf{4}]^{2+}$. For simplicity, orbitals are shown for a structure in which Me and Ph substituents attached to nitrogen and boron atoms have been replaced with hydrogen atoms.

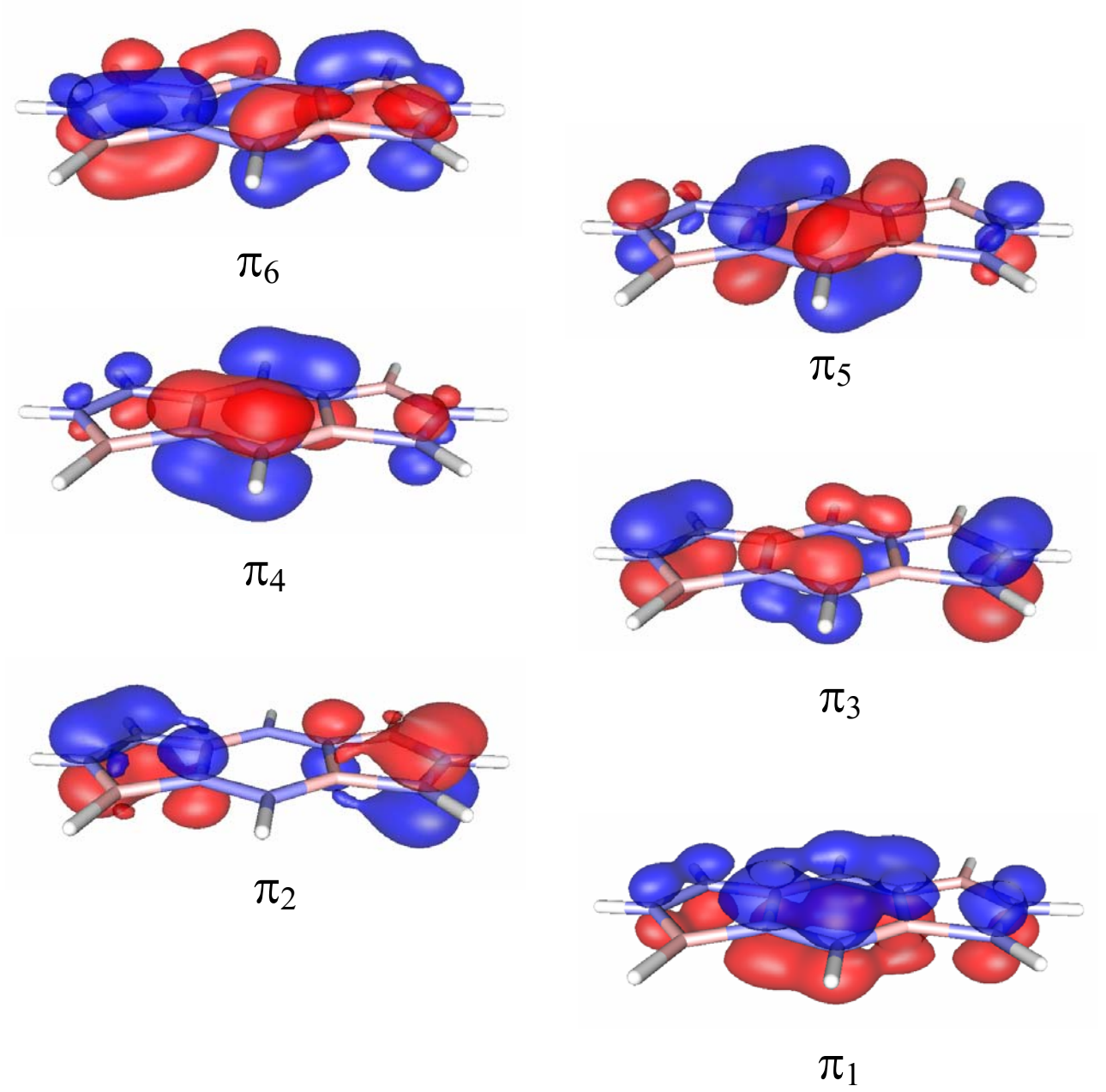


Fig. S7 Occupied π-symmetric Kohn-Sham β-orbitals of triplet $[\mathbf{4}]^{2+}$. For simplicity, orbitals are shown for a structure in which Me and Ph substituents attached to nitrogen and boron atoms have been replaced with hydrogen atoms.

Optimized coordinates of **4** and [**4**]$^{2+}$ in mol2 format:

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  46 H     7.5238    1.8285    0.2220 H     1 RES1    0.0000
  47 H     5.6863    2.4325    1.7690 H     1 RES1    0.0000
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  50 C    -6.3662   -0.3320    0.7968 C.2   1 RES1    0.0000
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  53 C    -4.3102   -1.0161   -0.9287 C.2   1 RES1    0.0000
  54 H    -4.9972    1.0891    1.6266 H     1 RES1    0.0000
  55 H    -7.1663   -0.0649    1.4792 H     1 RES1    0.0000
  56 H    -7.5238   -1.8285   -0.2220 H     1 RES1    0.0000
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34	H	-1.6008	4.3990	0.9191	H	1	RES1	0.0000
35	H	0.0707	3.9829	0.5752	H	1	RES1	0.0000
36	H	-4.5810	2.5485	-0.0177	H	1	RES1	0.0000
37	H	-3.6985	3.6194	1.0865	H	1	RES1	0.0000
38	H	-3.5127	3.8074	-0.6781	H	1	RES1	0.0000
39	C	-4.5012	-0.7608	-1.1105	C.2	1	RES1	0.0000
40	C	-5.7579	-1.3394	-1.2025	C.2	1	RES1	0.0000
41	C	-6.6516	-1.2296	-0.1452	C.2	1	RES1	0.0000
42	C	-6.2924	-0.5307	1.0000	C.2	1	RES1	0.0000
43	C	-5.0423	0.0634	1.0867	C.2	1	RES1	0.0000
44	H	-3.8204	-0.8451	-1.9530	H	1	RES1	0.0000
45	H	-6.0438	-1.8725	-2.1019	H	1	RES1	0.0000
46	H	-7.6326	-1.6852	-0.2156	H	1	RES1	0.0000
47	H	-6.9898	-0.4456	1.8254	H	1	RES1	0.0000
48	H	-4.7809	0.6056	1.9911	H	1	RES1	0.0000
49	C	4.5012	0.7608	1.1105	C.2	1	RES1	0.0000
50	C	5.7579	1.3394	1.2025	C.2	1	RES1	0.0000
51	C	6.6516	1.2296	0.1452	C.2	1	RES1	0.0000
52	C	6.2924	0.5307	-1.0000	C.2	1	RES1	0.0000
53	C	5.0423	-0.0634	-1.0867	C.2	1	RES1	0.0000
54	H	3.8204	0.8451	1.9530	H	1	RES1	0.0000
55	H	6.0438	1.8725	2.1019	H	1	RES1	0.0000
56	H	7.6326	1.6852	0.2156	H	1	RES1	0.0000
57	H	6.9898	0.4456	-1.8254	H	1	RES1	0.0000

```
  58 H     4.7809    -0.6056    -1.9911 H     1 RES1    0.0000
@<TRIPOS>BOND
    1     1     2     1
    2     1    36     1
    3     1    37     1
    4     1    38     1
    5     2     3     1
    6     2     5     1
    7     3     4     1
    8     3     9     1
    9     4    33     1
   10     4    34     1
   11     4    35     1
   12     5     6     1
   13     5    19     1
   14     6     7     1
   15     6     9     1
   16     7     8     1
   17     7    13     1
   18     8    27     1
   19     8    28     1
   20     8    29     1
   21     9    10     1
   22    10    11     1
   23    10    12     1
   24    11    30     1
   25    11    31     1
   26    11    32     1
   27    12    13     1
   28    12    17     1
   29    13    14     1
   30    14    15     1
   31    14    18     1
   32    15    16     1
   33    15    17     1
   34    16    21     1
   35    16    22     1
   36    16    23     1
   37    17    20     1
   38    18    24     1
   39    18    25     1
   40    18    26     1
   41    19    39     1
   42    19    43     1
   43    20    49     1
   44    20    53     1
   45    39    40     1
   46    39    44     1
   47    40    41     1
   48    40    45     1
```

```
   49    41    42    1
   50    41    46    1
   51    42    43    1
   52    42    47    1
   53    43    48    1
   54    49    50    1
   55    49    54    1
   56    50    51    1
   57    50    55    1
   58    51    52    1
   59    51    56    1
   60    52    53    1
   61    52    57    1
   62    53    58    1
@<TRIPOS>SUBSTRUCTURE
     1 RES1       1


@<TRIPOS>MOLECULE
Triplet [4]2+
   58    62     1
 SMALL
 NO_CHARGES
 ****
 ****
@<TRIPOS>ATOM
    1  C    -3.6448    3.1011    0.1787  C.3   1 RES1    0.0000
    2  N    -2.5848    2.1173    0.1690  N.pl3 1 RES1    0.0000
    3  N    -1.2975    2.4914    0.1390  N.pl3 1 RES1    0.0000
    4  C    -0.9377    3.8911    0.2485  C.3   1 RES1    0.0000
    5  B    -2.7382    0.6373    0.1261  B     1 RES1    0.0000
    6  N    -1.3884    0.1585    0.1233  N.pl3 1 RES1    0.0000
    7  N    -0.9051   -1.1465    0.1452  N.3   1 RES1    0.0000
    8  C    -1.8426   -2.1747    0.5639  C.3   1 RES1    0.0000
    9  B    -0.4753    1.2821    0.0457  B     1 RES1    0.0000
   10  N     0.9051    1.1465   -0.1452  N.3   1 RES1    0.0000
   11  C     1.8426    2.1747   -0.5639  C.3   1 RES1    0.0000
   12  N     1.3884   -0.1585   -0.1233  N.pl3 1 RES1    0.0000
   13  B     0.4753   -1.2821   -0.0457  B     1 RES1    0.0000
   14  N     1.2975   -2.4914   -0.1390  N.pl3 1 RES1    0.0000
   15  N     2.5848   -2.1173   -0.1690  N.pl3 1 RES1    0.0000
   16  C     3.6448   -3.1011   -0.1787  C.3   1 RES1    0.0000
   17  B     2.7382   -0.6373   -0.1261  B     1 RES1    0.0000
   18  C     0.9377   -3.8911   -0.2485  C.3   1 RES1    0.0000
   19  C    -4.1142   -0.0495    0.0379  C.2   1 RES1    0.0000
   20  C     4.1142    0.0495   -0.0379  C.2   1 RES1    0.0000
   21  H     4.5806   -2.5687   -0.0274  H     1 RES1    0.0000
   22  H     3.5095   -3.8266    0.6261  H     1 RES1    0.0000
   23  H     3.6884   -3.6257   -1.1377  H     1 RES1    0.0000
   24  H     1.0426   -4.4047    0.7119  H     1 RES1    0.0000
```

```
  25 H    -0.0922   -3.9634   -0.5866 H    1 RES1   0.0000
  26 H     1.5682   -4.3851   -0.9872 H    1 RES1   0.0000
  27 H    -1.2886   -3.0526    0.8841 H    1 RES1   0.0000
  28 H    -2.4177   -1.8120    1.4171 H    1 RES1   0.0000
  29 H    -2.5374   -2.4421   -0.2332 H    1 RES1   0.0000
  30 H     1.2886    3.0526   -0.8841 H    1 RES1   0.0000
  31 H     2.5374    2.4421    0.2332 H    1 RES1   0.0000
  32 H     2.4177    1.8120   -1.4171 H    1 RES1   0.0000
  33 H    -1.0426    4.4047   -0.7119 H    1 RES1   0.0000
  34 H    -1.5682    4.3851    0.9872 H    1 RES1   0.0000
  35 H     0.0922    3.9634    0.5866 H    1 RES1   0.0000
  36 H    -4.5806    2.5687    0.0274 H    1 RES1   0.0000
  37 H    -3.6884    3.6257    1.1377 H    1 RES1   0.0000
  38 H    -3.5095    3.8266   -0.6261 H    1 RES1   0.0000
  39 C    -4.4603   -0.8059   -1.0912 C.2  1 RES1   0.0000
  40 C    -5.7150   -1.3849   -1.1998 C.2  1 RES1   0.0000
  41 C    -6.6405   -1.2333   -0.1752 C.2  1 RES1   0.0000
  42 C    -6.3155   -0.4904    0.9527 C.2  1 RES1   0.0000
  43 C    -5.0690    0.1079    1.0530 C.2  1 RES1   0.0000
  44 H    -3.7540   -0.9236   -1.9081 H    1 RES1   0.0000
  45 H    -5.9749   -1.9517   -2.0864 H    1 RES1   0.0000
  46 H    -7.6197   -1.6908   -0.2579 H    1 RES1   0.0000
  47 H    -7.0372   -0.3739    1.7528 H    1 RES1   0.0000
  48 H    -4.8346    0.6841    1.9436 H    1 RES1   0.0000
  49 C     4.4603    0.8059    1.0912 C.2  1 RES1   0.0000
  50 C     5.7150    1.3849    1.1998 C.2  1 RES1   0.0000
  51 C     6.6405    1.2333    0.1752 C.2  1 RES1   0.0000
  52 C     6.3155    0.4904   -0.9527 C.2  1 RES1   0.0000
  53 C     5.0690   -0.1079   -1.0530 C.2  1 RES1   0.0000
  54 H     3.7540    0.9236    1.9081 H    1 RES1   0.0000
  55 H     5.9749    1.9517    2.0864 H    1 RES1   0.0000
  56 H     7.6197    1.6908    0.2579 H    1 RES1   0.0000
  57 H     7.0372    0.3739   -1.7528 H    1 RES1   0.0000
  58 H     4.8346   -0.6841   -1.9436 H    1 RES1   0.0000
@<TRIPOS>BOND
   1    1    2    1
   2    1   36    1
   3    1   37    1
   4    1   38    1
   5    2    3    1
   6    2    5    1
   7    3    4    1
   8    3    9    1
   9    4   33    1
  10    4   34    1
  11    4   35    1
  12    5    6    1
  13    5   19    1
  14    6    7    1
  15    6    9    1
```

```
  16     7     8     1
  17     7    13     1
  18     8    27     1
  19     8    28     1
  20     8    29     1
  21     9    10     1
  22    10    11     1
  23    10    12     1
  24    11    30     1
  25    11    31     1
  26    11    32     1
  27    12    13     1
  28    12    17     1
  29    13    14     1
  30    14    15     1
  31    14    18     1
  32    15    16     1
  33    15    17     1
  34    16    21     1
  35    16    22     1
  36    16    23     1
  37    17    20     1
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  41    19    39     1
  42    19    43     1
  43    20    49     1
  44    20    53     1
  45    39    40     1
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  48    40    45     1
  49    41    42     1
  50    41    46     1
  51    42    43     1
  52    42    47     1
  53    43    48     1
  54    49    50     1
  55    49    54     1
  56    50    51     1
  57    50    55     1
  58    51    52     1
  59    51    56     1
  60    52    53     1
  61    52    57     1
  62    53    58     1
@<TRIPOS>SUBSTRUCTURE
    1 RES1       1
```