Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Insertion of carbon monoxide into an unsymmetrical diborene to form an oxaborirane

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Contents

1. Synthesis of compounds 2b, 3a and 3b and their spectral data.

General considerations:
All reactions were performed under a dry argon atmosphere with standard Schlenk and glove box techniques; solvents were dried over Na metal, K metal or CaH_2 and degassed prior to use. The ^{1}H, ^{11}B, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AVIII 400MHz BBFO or JEOL ECA400 spectrometer at 298 K unless otherwise stated. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sep = septet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System. Compound **1a** and **1b** were prepared according to the literature procedures.[S1]

Synthesis of compound 2b. 1 atm of CO gas was aerated to a toluene (5 ml) solution of **1b** (100 mg, 0.10 mmol) at room temperature. The mixture was stirred at room temperature for 30 min. After removal of all volatiles under vacuum, the residual solid was extracted with pentane. Slow evaporation of the solvent in the glove box at −5 °C yielded compound **2b** as yellow crystals (79 mg, 77%).
Mp: 191–192 °C (dec).
^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 7.36 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.32 (s, 2H, Ar*H*), 7.25 – 7.20 (m, 4H, Ar*H*), 7.10 (dd, *J* = 7.3, 1.8 Hz, 1H, Ar*H*), 5.45 (broad, 2H, C*H*$(CH_3)_2$), 4.72 (d, *J* = 22.0 Hz, 1H, CH_2), 4.10 (d, *J* = 22.0 Hz, 1H, CH_2), 3.40 (sep, *J* = 6.9 Hz, 1H, C*H*$(CH_3)_2$), 3.33 – 3.24 (m, 3H, C*H*$(CH_3)_2$), 3.07 (s, 3H, OCH_3), 1.56 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.51 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.40 (s, 6H, C(CH_3)), 1.33 (s, 9H, C(CH_3)$_3$), 1.28 (d, *J* = 6.3 Hz, 6H, CH(CH_3)$_2$), 1.11 (d, *J* = 6.7 Hz, 6H, CH(CH_3)$_2$), 0.99 (broad, 12H, CH(CH_3)$_2$), 0.84 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.38 (s, 9H, Si(CH_3)$_3$), 0.33 (s, 9H, Si(CH_3)$_3$).
^{13}C NMR (101 MHz, C_6D_6, 298 K) δ 149.1 (*C*-Ar), 146.0 (*C*-Ar), 145.5 (*C*-Ar), 145.1 (*C*-Ar), 139.1 (*C*-Ar), 137.5 (*C*-Ar), 133.1 (*C*H-Ar), 128.5 (*C*H-Ar), 125.6 (*C*H-Ar), 124.8 (*C*CH_3), 124.5 (*C*H-Ar), 124.2 (d, *J* = 3.2 Hz, *C*H-Ar), 114.1 (*C*-Ar), 53.4 (O*C*H_3), 51.9 (*C*H$(CH_3)_2$), 43.1 (*C*H_2), 34.6 (*C*$(CH_3)_3$), 31.7 (C(*C*H_3)$_3$), 28.8 (*C*H$(CH_3)_2$), 28.5 (*C*H$(CH_3)_2$), 28.26 (*C*H$(CH_3)_2$), 25.5 (CH(*C*H_3)$_2$), 25.3 (CH(*C*H_3)$_2$), 24.8 (CH(*C*H_3)$_2$), 24.7 (CH(*C*H_3)$_2$), 24.2 (CH(*C*H_3)$_2$), 22.5 (CH(*C*H_3)$_2$), 21.6 (CH(*C*H_3)$_2$), 9.5 (C*C*H_3), 0.7 (Si(*C*H_3)$_3$), 0.6 (Si(*C*H_3)$_3$).
^{11}B NMR (128 MHz, C_6D_6, 298 K) δ 40.5 (br), 26.3 (br), 2.8, −14.7.
HRMS (ESI) m/z: Calcd for $C_{56}H_{90}B_4N_4O_2Si_2Br$: 1029.6158 $[(M+H)]^+$; Found: 1029.6183.

Synthesis of compound 3a. 1-Adamantyl isocyanide (16.1 mg, 0.10 mmol) was added to a toluene (5 ml) solution of **1a** (90 mg, 0.10 mmol) at room temperature. The mixture was stirred at room temperature for 30 min. After removal of all volatiles under vacuum, the residue was extracted with *n*-pentane. Slow evaporation of the solvent in glove box at −5 °C yielded compound **3a** as yellow crystals (71 mg, 67%).
Mp: 216–218 °C (dec).
^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 7.43 – 7.38 (m, 4H, Ar*H*), 7.22 – 7.20 (m, 3H, Ar*H*),

7.11 – 7.05 (m, 2H, Ar*H*), 3.68 (broad, 1H, C*H*(CH_3)$_2$), 3.52 – 3.32 (m, 5H, C*H*(CH_3)$_2$, CH_2), 3.06 (s, 3H, OCH_3), 2.01 (d, *J* = 11.5 Hz, 3H, Ad*H*), 1.87 (d, *J* = 11.1 Hz, 3H, Ad*H*), 1.77 (s, 3H, Ad*H*), 1.72 (d, *J* = 6.8 Hz, 3H, Ad*H*), 1.55 (d, *J* = 6.8 Hz, 3H, Ad*H*), 1.35 (s, 9H, C(CH_3)$_3$), 1.34 – 1.27 (m, 12H, CH(CH_3)$_2$), 1.24 – 1.15 (m, 12H, CH(CH_3)$_2$), 0.86 (d, *J* = 10.5 Hz, 9H, P(CH_3)$_3$), 0.29 (s, 9H, Si(CH_3)$_3$), 0.08 (s, 9H, Si(CH_3)$_3$).
^{13}C NMR (101 MHz, C_6D_6, 298 K) δ 148.9 (*C*-Ar), 145.6 (d, *J* = 25.2 Hz, *C*-Ar), 145.1 (d, *J* = 21.2 Hz, *C*-Ar), 140.4 (*C*-Ar), 137.3 (*C*-Ar), 132.7 (d, *J* = 5.5 Hz, *C*H-Ar), 127.9 (*C*H-Ar) 125.8 (d, *J* = 27.9 Hz, *C*H-Ar), 125.0 (*C*H-Ar), 124.6 (*C*H-Ar), 124.1 (*C*H-Ar), 114.0 (*C*-Ar). 58.2 (*C*-Ad), 53.0 (O*C*H_3), 43.1 (*C*H_2-Ad), 38.7 (*C*H_2), 36.0 (*C*H_2-Ad), 34.5 (*C*(CH_3)$_3$), 31.7 (*C*H-Ad), 28.6 (d, *J* = 5.9 Hz, *C*H(CH_3)$_2$), 27.9 (d, *J* = 14.6 Hz, *C*H(CH_3)$_2$), 25.7 (CH(*C*H_3)$_2$), 25.2 (CH(*C*H_3)$_2$), 24.8 (CH(*C*H_3)$_2$), 24.7 (CH(*C*H_3)$_2$), 23.9 (CH(*C*H_3)$_2$), 23.6 (CH(*C*H_3)$_2$), 9.77 (d, *J* = 37.6 Hz, P(*C*H_3)$_3$), 1.14 (Si(*C*H_3)$_3$), 0.37 (Si(*C*H_3)$_3$).
^{11}B NMR (128 MHz, C_6D_6, 298 K) δ 38.6 (br), 24.3 (br), −0.4, −20.5.
^{31}P NMR (162 MHz, C_6D_6, 298 K) δ −18.3 (br).
HRMS (ESI) m/z: Calcd for $C_{58}H_{94}B_4N_3OSi_2PBr$: 1058.6229 $[(M+H)]^+$; Found: 1058.6278.

Synthesis of compound 3b. 1-Adamantyl isocyanide (16.1 mg, 0.10 mmol) was added to a toluene (5 ml) solution of **1b** (100 mg, 0.10 mmol) at room temperature. The mixture was stirred at room temperature for 30 min. After removal of all volatiles under vacuum, the residue was extracted with the mixed solvent of diethyl ether and *n*-pentane. Slow evaporation of the solvent in glove box at −5 °C yielded compound **3b** as yellow crystals (84 mg, 72%).
Mp: 218–220 °C (dec).
^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 7.38 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.36 (s, 2H, Ar*H*), 7.25 (dd, *J* = 7.3, 1.7 Hz, 1H, Ar*H*), 7.16 (m, 2H, Ar*H*), 7.12 – 7.04 (m, 2H, Ar*H*), 5.62 (broad, 2H, C*H*(CH_3)$_2$), 3.60 – 3.50 (m, 4H, C*H*(CH_3)$_2$, CH_2), 3.45 (sep, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 3.24 (d, *J* = 18.6 Hz, 1H, CH_2), 3.09 (s, 3H, OCH_3), 2.28 (d, *J* = 11.6 Hz, 3H, Ad*H*), 2.04 (d, *J* = 11.5 Hz, 3H, Ad*H*), 1.88 (s, 3H, Ad*H*), 1.67 (d, *J* = 6.8 Hz, 3H, Ad*H*), 1.59 – 1.57 (m, 9H, Ad*H*, C(CH_3)), 1.41 (s, 9H, C(CH_3)$_3$), 1.40 – 1.33 (m, 12H, CH(CH_3)$_2$), 1.24 (broad, 6H, CH(CH_3)$_2$), 1.19 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.14 (d, *J* = 6.9 Hz, 6H, CH(CH_3)$_2$), 0.98 (broad, 6H, CH(CH_3)$_2$), 0.34 (s, 9H, Si(CH_3)$_3$), 0.08 (s, 9H, Si(CH_3)$_3$).
^{13}C NMR (101 MHz, C_6D_6, 298 K) δ 147.6 (*C*-Ar), 146.2 (*C*-Ar), 145.9 (*C*-Ar), 145.0 (*C*-Ar), 140.7 (*C*-Ar), 137.6 (*C*-Ar), 132.7 (*C*H-Ar), 127.5 (*C*H-Ar), 125.8 (*C*H-Ar), 125.3 (*C*CH_3), 124.8 (*C*H-Ar), 124.6 (*C*H-Ar), 123.7 (*C*H-Ar), 113.6 (*C*-Ar), 59.2 (*C*-Ad), 52.9 (O*C*H_3), 42.6 (*C*H_2-Ad), 38.2 (*C*H_2), 36.2 (*C*H_2-Ad), 34.5 (*C*(CH_3)$_3$), 31.8 (*C*H-Ad), 30.1 (*C*H(CH_3)$_2$), 28.4 (d, *J* = 3.4 Hz, *C*H(CH_3)$_2$), 27.7 (*C*H(CH_3)$_2$), 26.1 (CH(*C*H_3)$_2$), 25.8 (CH(*C*H_3)$_2$), 25.6 (CH(*C*H_3)$_2$), 25.0 (CH(*C*H_3)$_2$), 24.5 (CH(*C*H_3)$_2$), 23.7 (CH(*C*H_3)$_2$), 22.6 (CH(*C*H_3)$_2$), 10.1 (C*C*H_3), 1.4 (Si(*C*H_3)$_3$), 0.8 (Si(*C*H_3)$_3$).
^{11}B NMR (128 MHz, C_6D_6, 298 K) δ 38.0 (br), 25.2 (br), 0.0, −20.2.
HRMS (ESI) m/z: Calcd for $C_{66}H_{105}B_4N_5OSi_2Br$: 1162.7413 $[(M+H)]^+$; Found: 1162.7460.

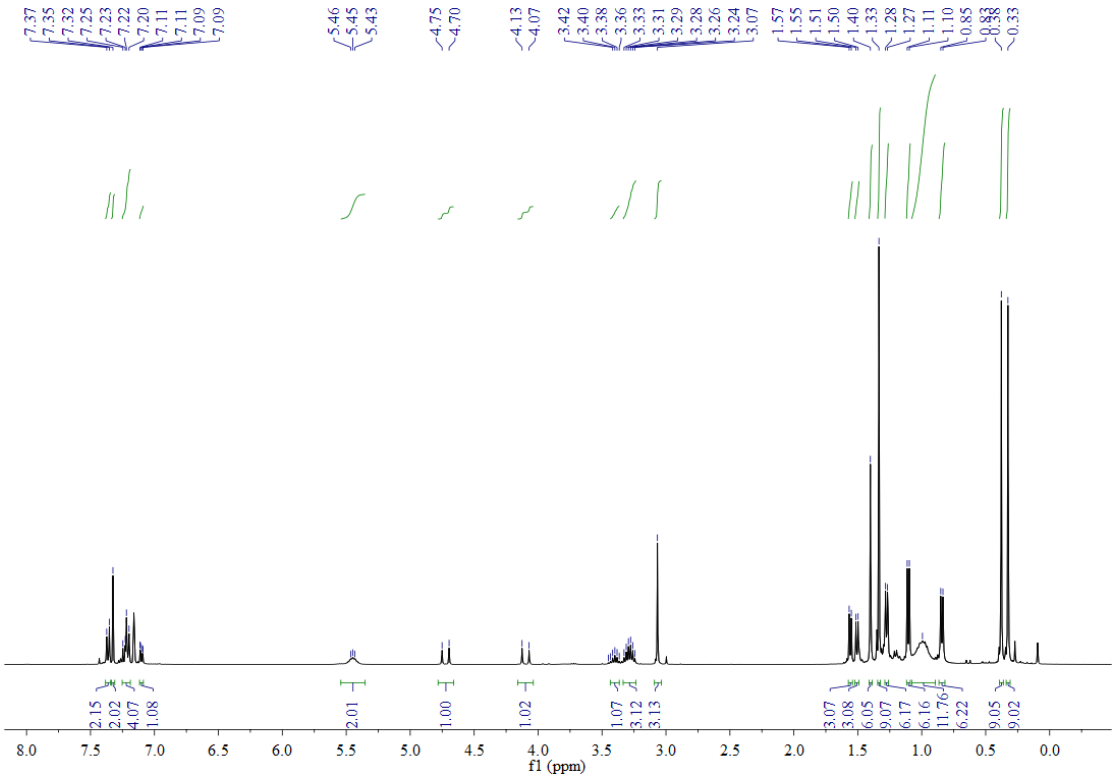

Figure S1. ^{1}H NMR spectrum of **2b** in C_6D_6 at 298 K.

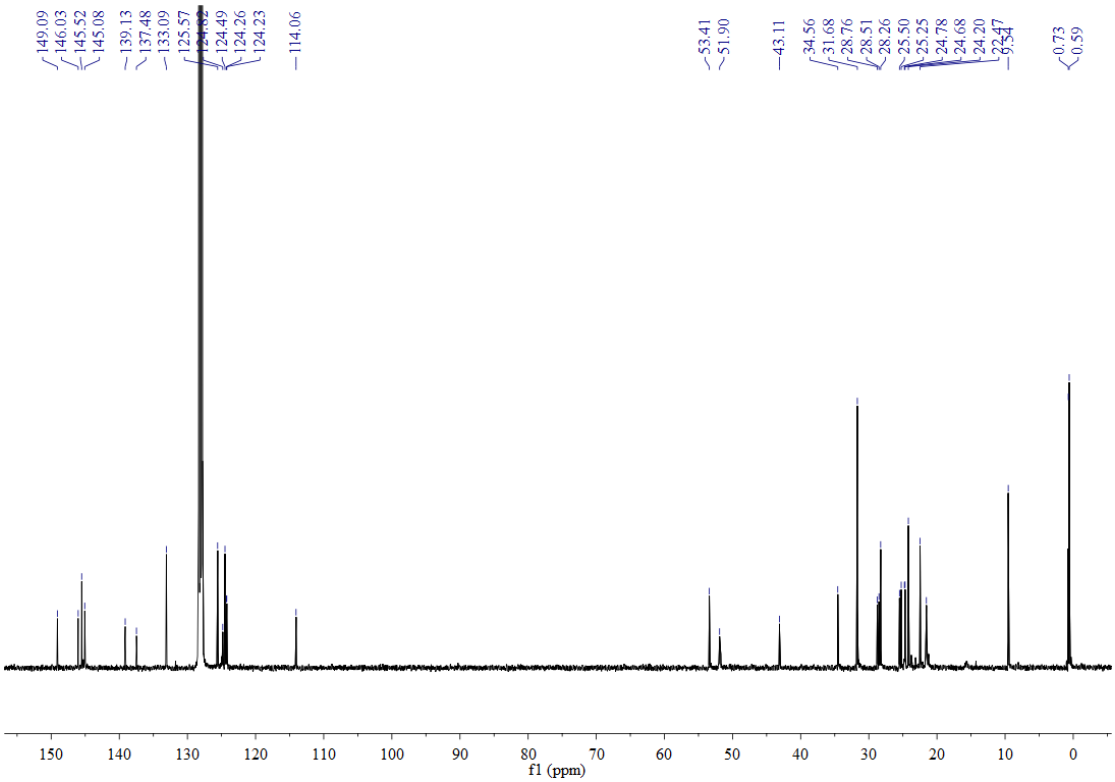

Figure S2. ^{13}C NMR spectrum of **2b** in C_6D_6 at 298 K.

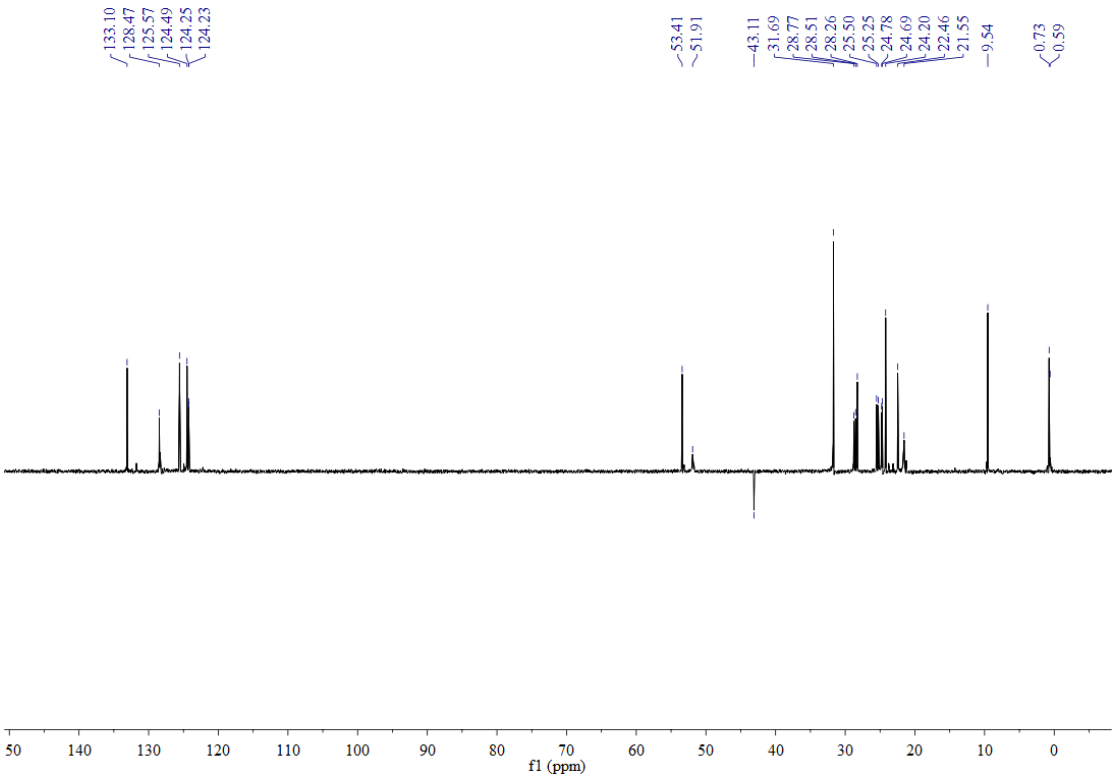

Figure S3. ^{13}C (DEPT 135) NMR spectrum of **2b** in C_6D_6 at 298 K.

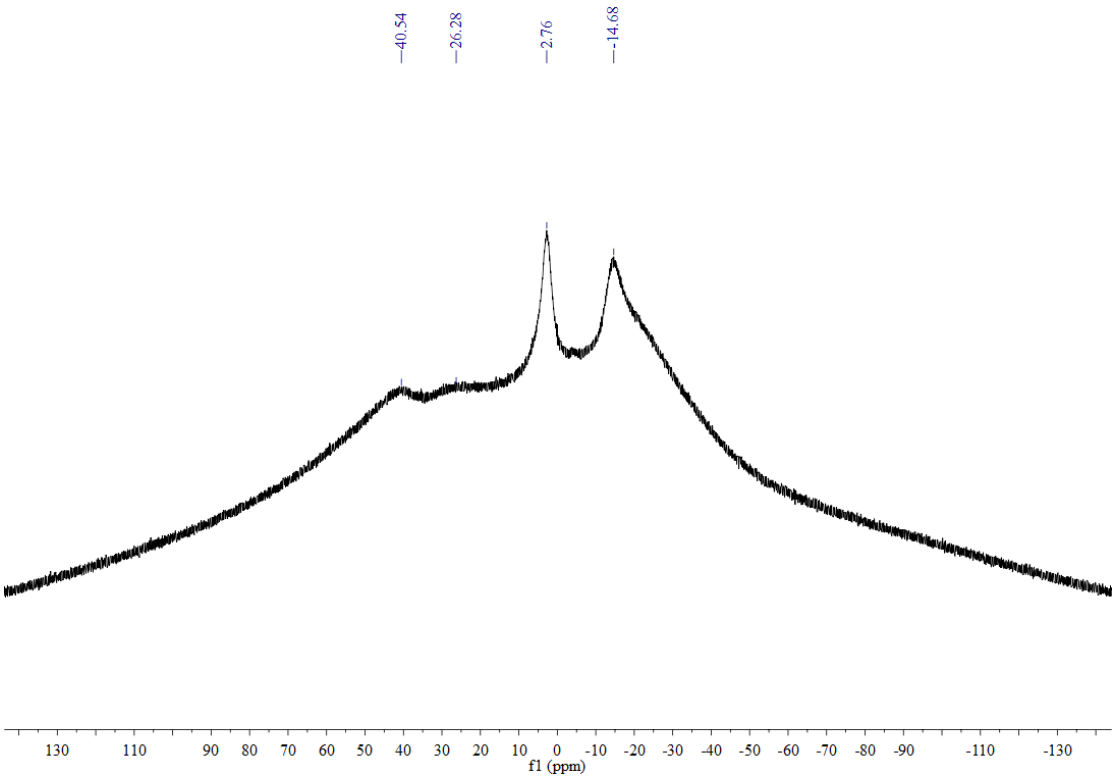

Figure S4. ^{11}B NMR spectrum of **2b** in C_6D_6 at 298 K.

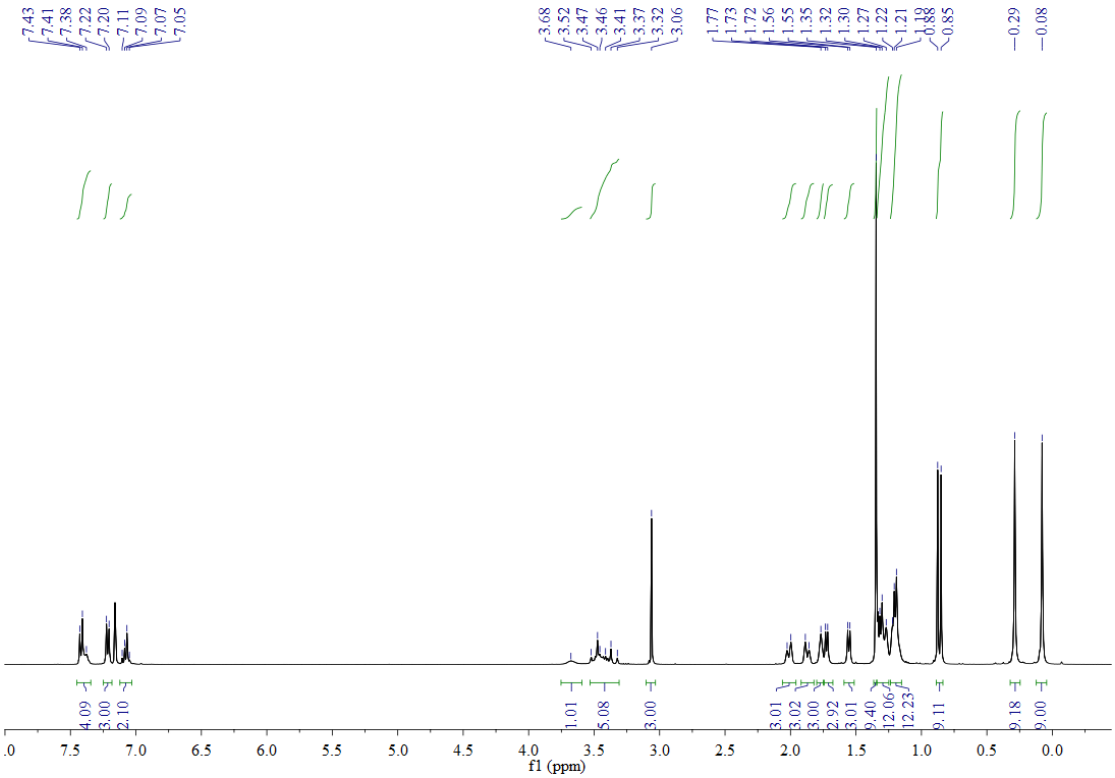

Figure S5. ^{1}H NMR spectrum of **3a** in C_6D_6 at 298 K.

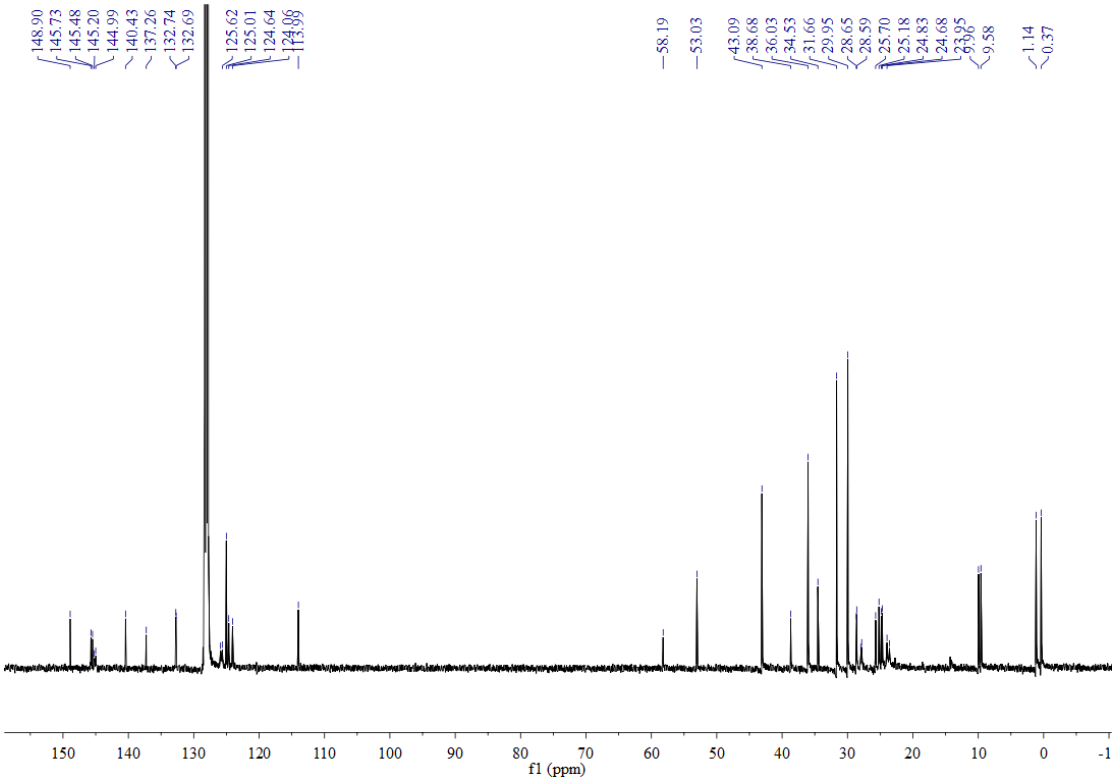

Figure S6. ^{13}C NMR spectrum of **3a** in C_6D_6 at 298 K.

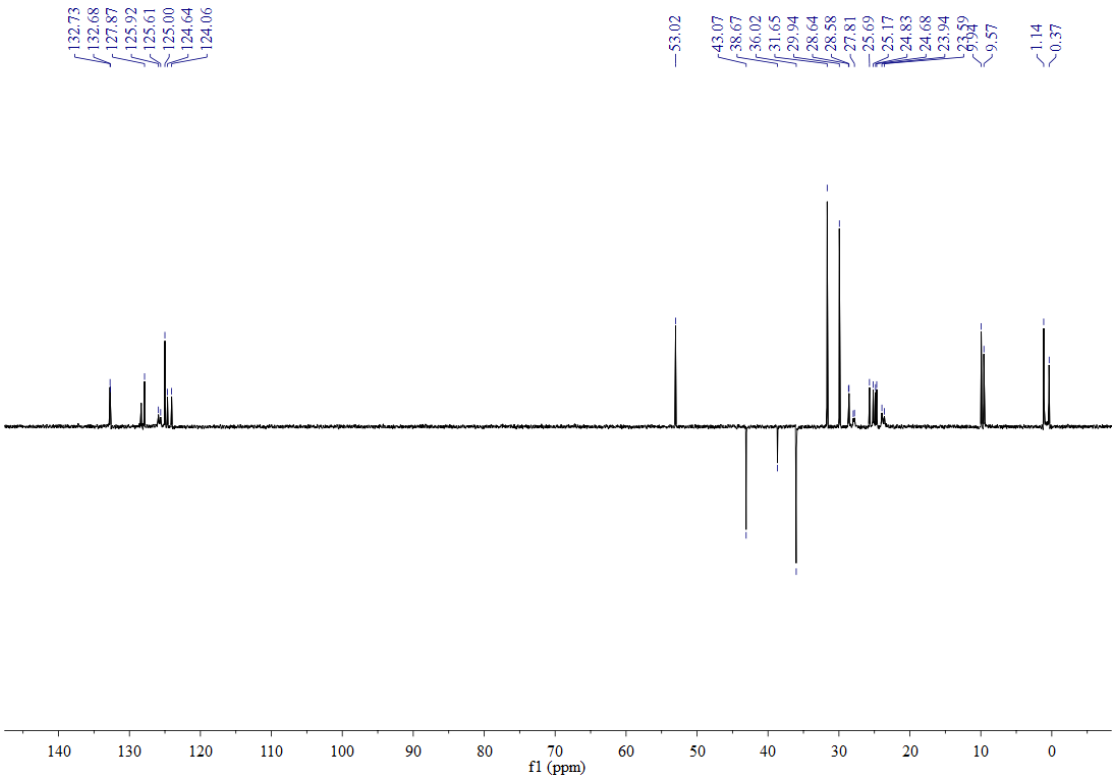

Figure S7. ^{13}C (DEPT 135) NMR spectrum of **3a** in C_6D_6 at 298 K.

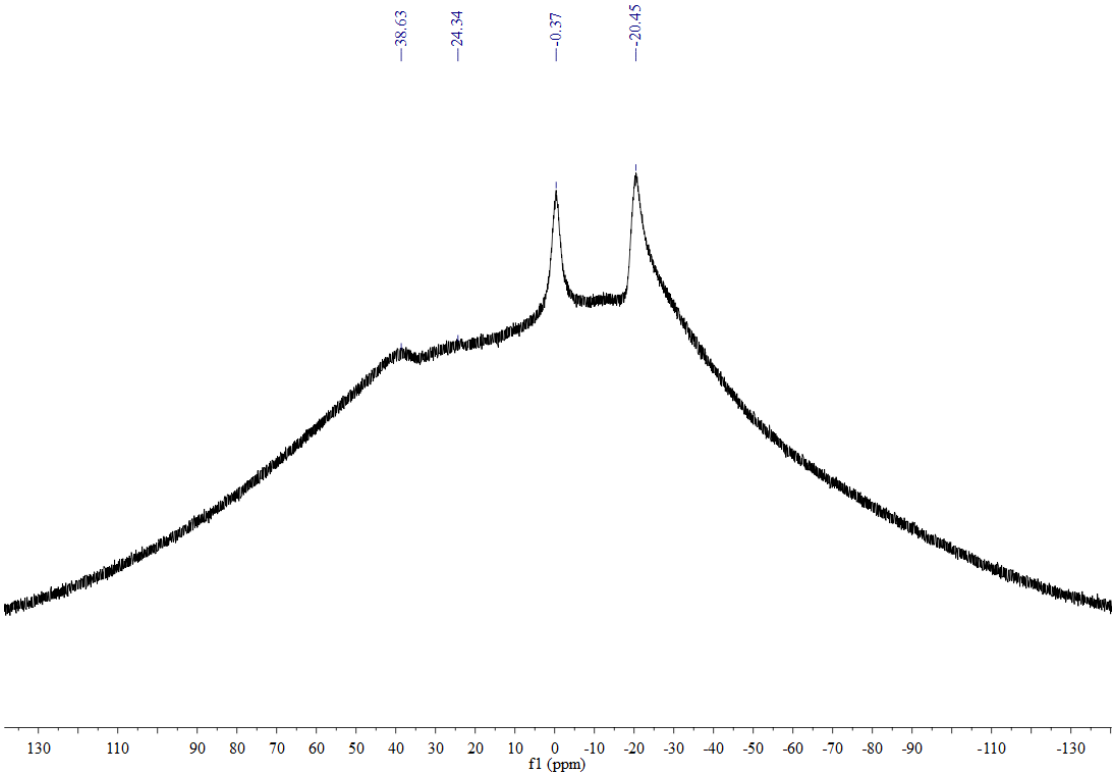

Figure S8. ^{11}B NMR spectrum of **3a** in C_6D_6 at 298 K.

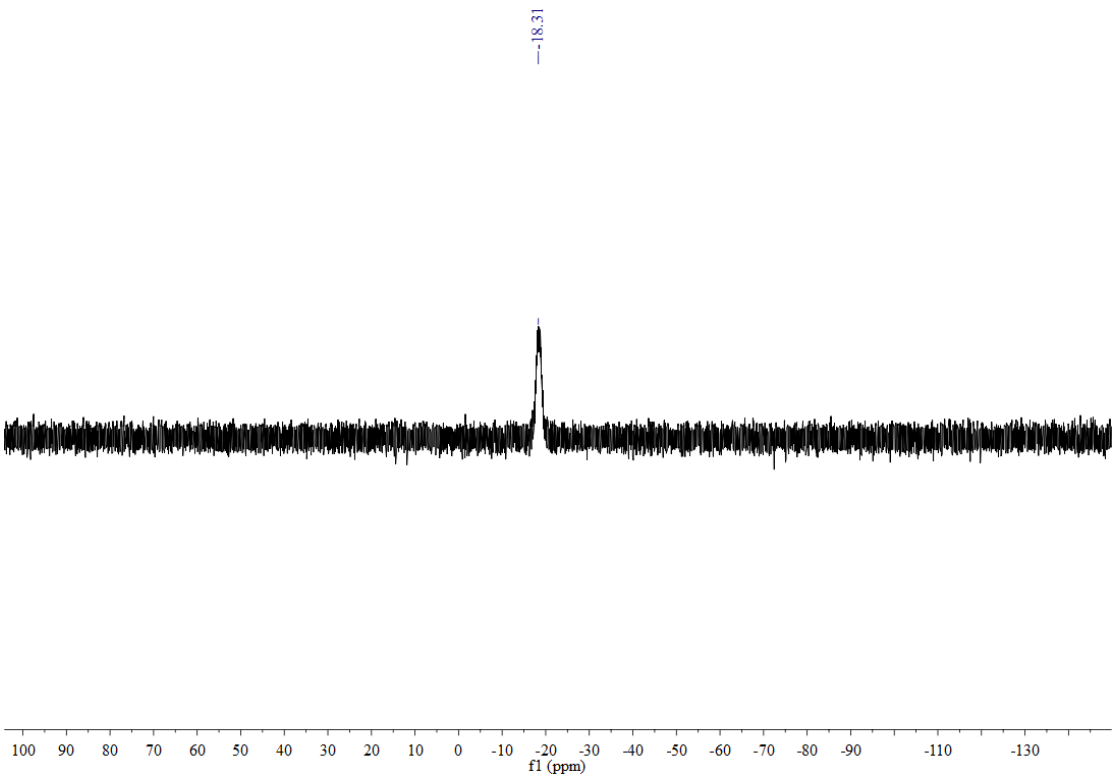

Figure S9. ^{31}P NMR spectrum of **3a** in C_6D_6 at 298 K.

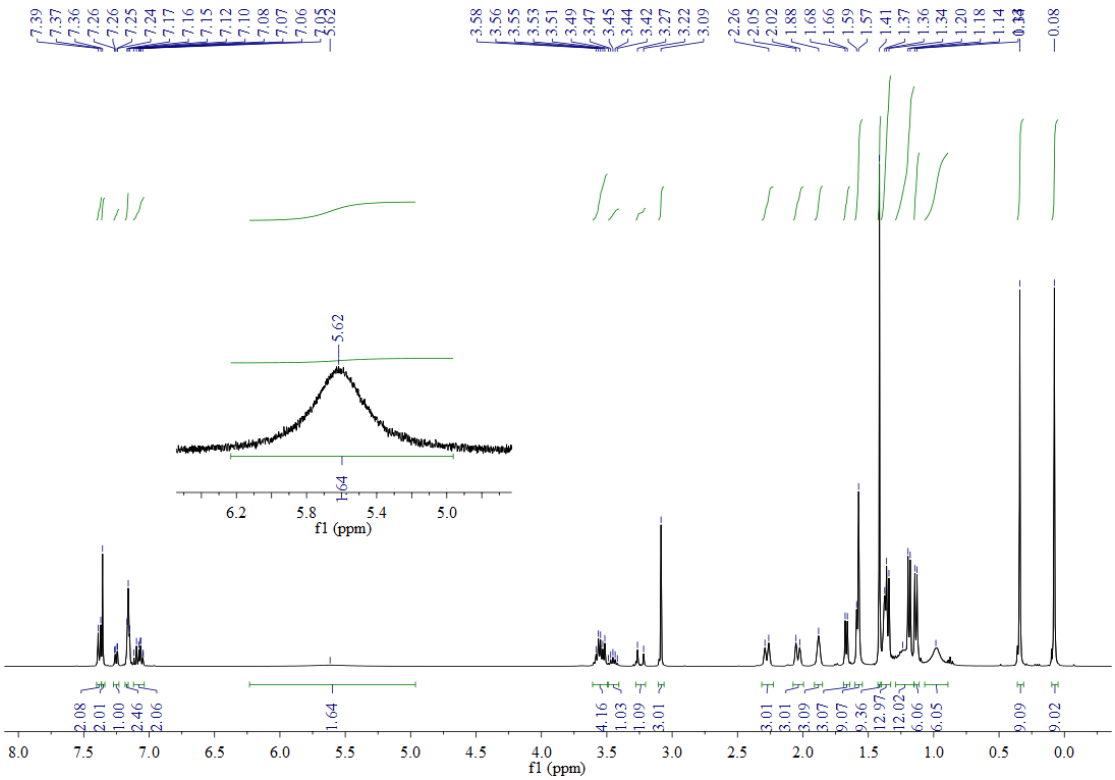

Figure S10. ^{1}H NMR spectrum of **3b** in C_6D_6 at 298 K.

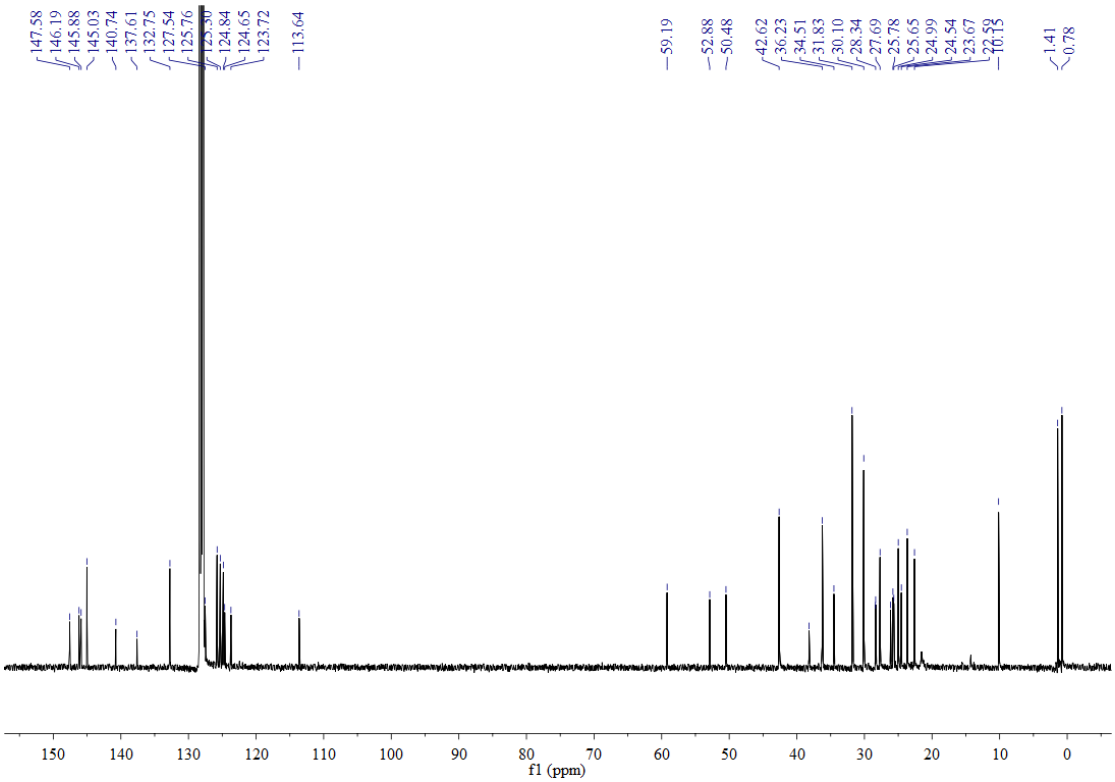

Figure S11. ^{13}C NMR spectrum of **3b** in C_6D_6 at 298 K.

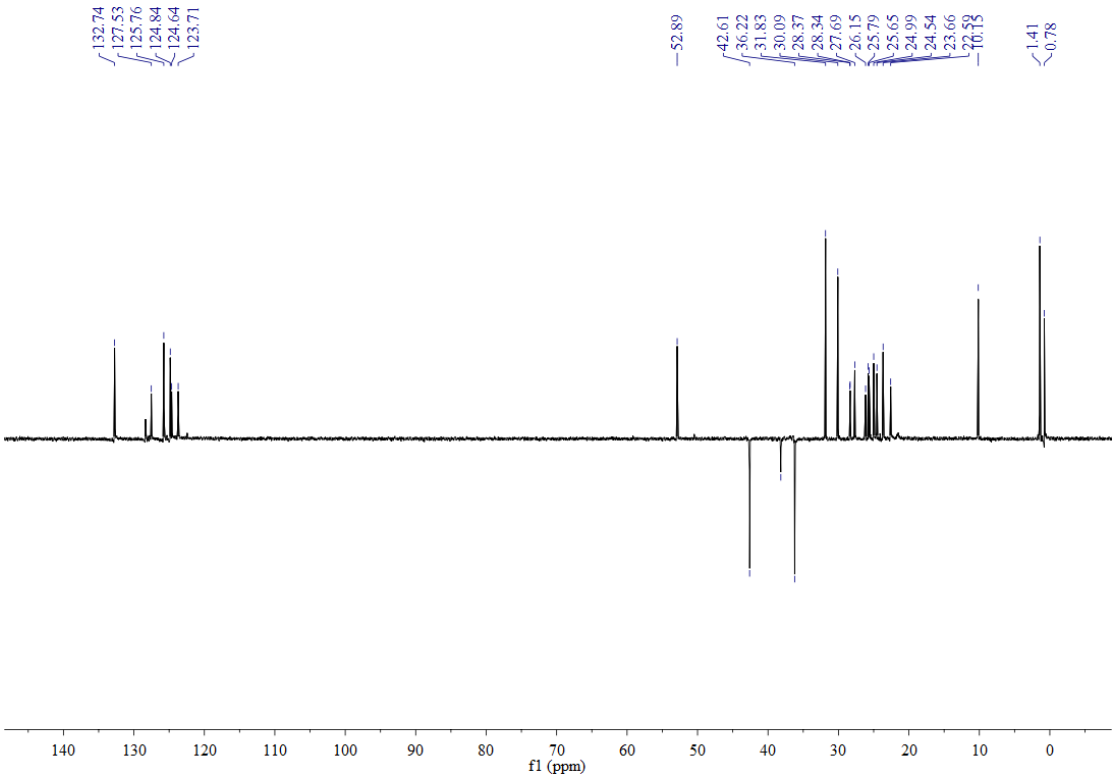

Figure S12. ^{13}C (DEPT 135) NMR spectrum of **3b** in C_6D_6 at 298 K.

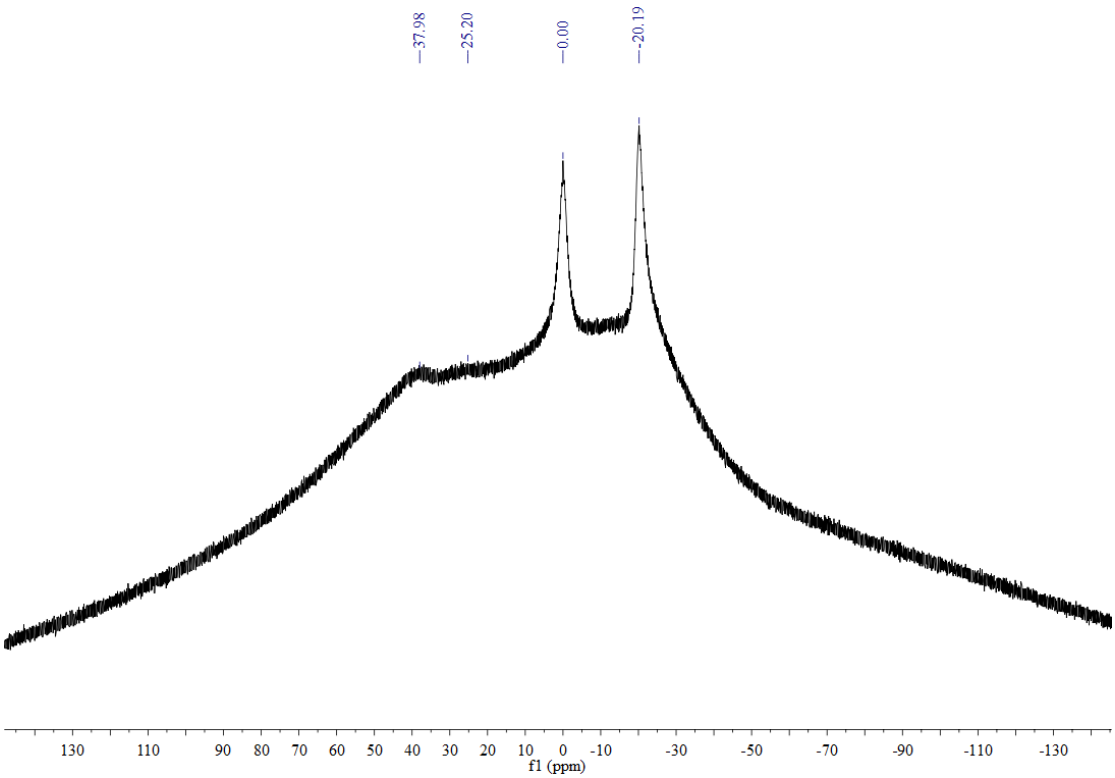

Figure S13. ^{11}B NMR spectrum of **3b** in C_6D_6 at 298 K.

2. Crystal structural parameters and selected bond parameters for 2b, 3a and 3b.

X-ray data collection and structural refinement. Intensity data for compounds **2b, 3a** and **3b** was collected using a Bruker APEX II diffractometer, or a Bruker X8 CCD Diffractometer. The structure was solved by direct phase determination (SHELX-2014) and refined for all data by full-matrix least squares methods on *F2*.[S2] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 2269514-2269516 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic Data.

	2b	**3a**	**3b**
formula	$C_{56}H_{89}B_4BrN_4O_2Si_2$	$C_{58}H_{93}B_4BrN_3OPSi_2$	$2(C_{66}H_{104}B_4BrN_5OSi_2)$, $2(C_7H_8)$
fw	1029.64	1058.65	2510.00
T (K)	100	100	100
space group	P 1 21/n 1	-P 2ybc	P 1 21 1
a (Å)	16.7671(7)	16.8585(4)	18.5522(11)
b (Å)	22.9883(8)	22.2787(4)	18.6558(11)
c (Å)	16.9632(8)	17.7793(5)	21.0049(13)
α (deg.)	90	90	90
β (deg.)	113.7304(16)	112.927(1)	91.3956(17)
γ (deg.)	90	90	90
V (Å^3)	5985.6(4)	6150.1(3)	7267.8(8)
Z, D (g/cm^3)	4, 1.143	4, 1.143	2, 1.147
F(000)	2208.0	2272.0	2704.0
GOF	1.032	1.020	0.965
R_1	0.0640	0.0536	0.0742
wR_2 (all data)	0.1286	0.1323	0.1384

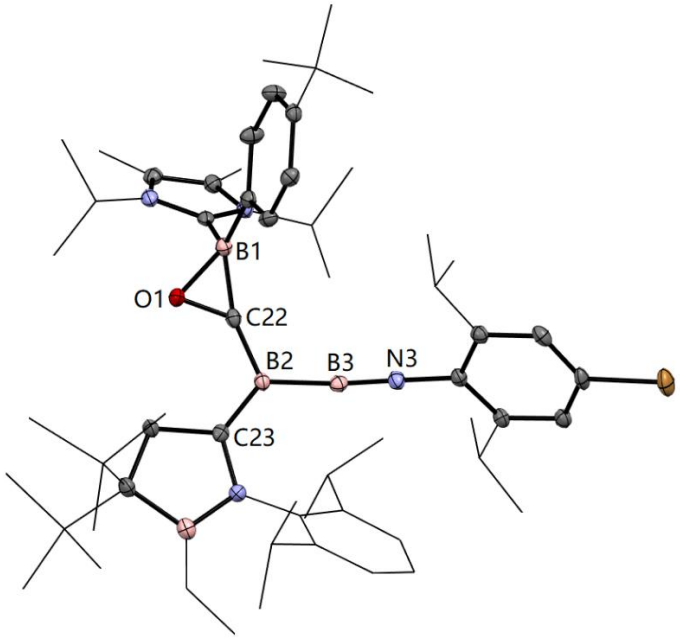

Figure S14. Solid-state structure of **2b**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): C23–B2: 1.497(3), B2–C22: 1.500(3), C22–B1: 1.551(3), C22–O1: 1.338(3), B1–O1: 1.549(3), B2–B3: 1.656(4), B3–N3: 1.256(3); C23–B2–B3: 127.4(2), C23–B2–C22: 116.6(2), C22–B2–B3: 115.25(19), B2–C22–O1: 131.5(2), B2–C22–B1: 163.3(2), O1–C22–B1: 64.32(15), C22–O1–B1: 64.53(15), O1–B1–C22: 51.15(12).

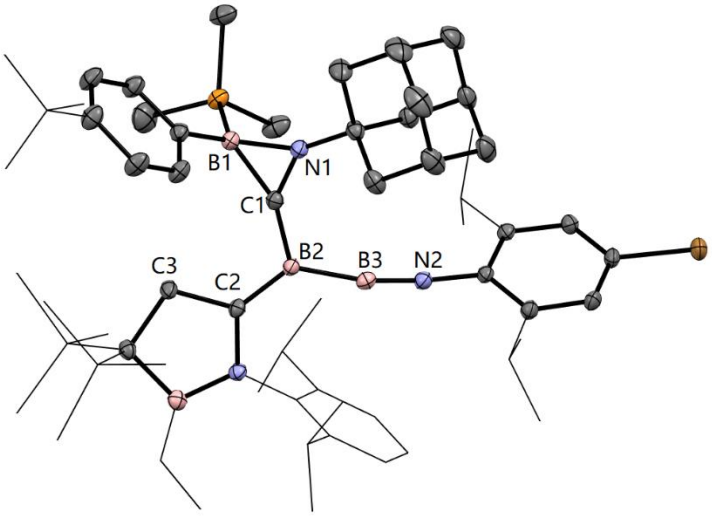

Figure S15. Solid-state structure of **3a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): C2–B2: 1.476(2), B2–C1: 1.524(2), C1–B1: 1.603(3), C1–N1: 1.307(2), B1–N1: 1.514(2), B2–B3: 1.660(3), B3–N2: 1.256(2); C2–B2–B3: 129.19(15), C2–B2–C1: 114.62(15), C1–B2–B3: 115.86(14), B2–C1–B1: 156.08(15), B2–C1–N1: 142.17(16), B1–C1–N1: 61.73(11), C1–B1–N1: 49.47(10), B1–N1–C1: 68.79(12).

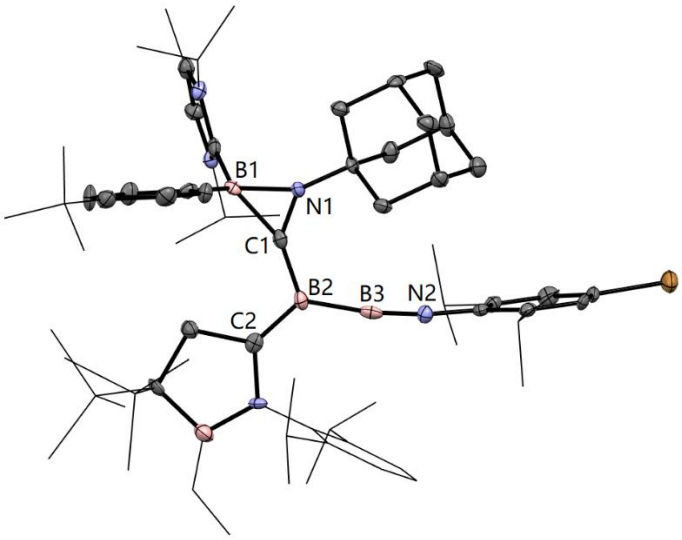

Figure S16. Solid-state structure of **3b**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): C2–B2: 1.480(9), B2–C1: 1.536(10), C1–B1: 1.623(10), C1–N1: 1.308(8), B1–N1: 1.533(8), B2–B3: 1.664(11), B3–N2: 1.264(9); C2–B2–B3: 127.1(6), C2–B2–C1: 113.3(6), C1–B2–B3: 119.6(6), B2–C1–B1: 156.4(6), B2–C1–N1: 141.4(6), B1–C1–N1: 62.0(4), C1–B1–N1: 48.9(3), B1–N1–C1: 69.1(4).

3. Theoretical calculations.

Computational Details. All density functional theory calculations were performed with the Gaussian 16 suite of programs.[S3] The geometry optimization, frequency calculations, Natural bond order (NBO) analysis, GIAO for ^{11}B NMR on compound **2b** and **3a** were done at B3LYP-D3(BJ)/6-311G(d,p) level. NBO analyses were performed with NBO 6.0 program.[S4]

Table S2. Experimental and calculated ^{11}B NMR chemical shifts of **2b**.

2b (^{11}B ppm)	*B*-OMe	*B*N	cAAC-*B*	IPr-*B*
Exp.	40.5	26.3	2.8	-14.7
Cal.	37.7	22.5	-1.9	-16.4

Table S3. Cartesian coordinates of optimized **2b**.

B	-0.21694200	2.84928400	-0.50747400
B	-0.92020600	-0.05190600	-0.46717100
B	0.51019700	-0.83966400	-0.58681300
B	-3.85372200	-2.11079100	0.80631600
Br	7.27716900	-3.52022800	0.15646000
C	-0.04129700	3.56030500	-1.92901100
C	-2.14127600	4.87894700	-1.87647000
H	-2.03015800	4.54472800	-0.84895000
C	-2.25456900	6.40279300	-1.86325300
H	-2.51342200	6.81815600	-2.83730600
H	-1.32302200	6.85818700	-1.52071000
H	-3.04418600	6.68661200	-1.16448100
C	-3.36119100	4.16831500	-2.46067600
H	-4.25029300	4.44664500	-1.89054300
H	-3.23302900	3.08876100	-2.38194000
H	-3.53431100	4.43480600	-3.50572600
C	-1.10491900	5.64819600	-4.77267000
H	-0.67459700	5.52217300	-5.76604400
H	-0.99105900	6.69931800	-4.49546500
H	-2.17177100	5.43540300	-4.84840000
C	-0.42046100	4.73618200	-3.81097000
C	0.76560900	4.07501600	-3.96558100
C	1.69789900	4.10087400	-5.12937100
H	2.03415200	3.10161300	-5.40631000
H	2.58347900	4.70889400	-4.92782300
H	1.19407000	4.53120000	-5.99469500
C	3.45171300	3.13733700	-2.53552200
H	3.74629600	3.35603000	-3.56231400
H	4.21111700	2.48203800	-2.10681500
H	3.44588700	4.06439000	-1.95948200
C	2.09616700	2.44000800	-2.45258000
H	1.91314300	2.18544900	-1.41030200
C	2.01168200	1.14766500	-3.25805700
H	1.02624300	0.69497900	-3.14320100
H	2.74634900	0.44181600	-2.86907800
H	2.21657800	1.30126200	-4.31962200
C	0.64632300	3.38924000	0.69907600
C	1.51938800	4.47537100	0.58743500
H	1.59163100	5.01069500	-0.35569000
C	2.31536900	4.90133400	1.65256200
H	2.97680500	5.74438200	1.50168200
C	2.26597300	4.26105700	2.89124100
C	1.38170400	3.17687200	3.01467900
H	1.31011300	2.64747300	3.95814600
C	0.60133800	2.75041400	1.95090000
H	-0.04827000	1.89143500	2.08221400
C	3.12296900	4.68957000	4.08831300
C	4.04112300	5.87509400	3.75345100
H	4.63151400	6.14162900	4.63377900
H	3.46904600	6.75808100	3.45719900
H	4.73761300	5.62996700	2.94749300
C	4.00823900	3.50739000	4.53512700
H	3.40850800	2.65026200	4.84634900
H	4.63646600	3.80137800	5.38126800
H	4.65891600	3.18040200	3.72049800
C	2.19967900	5.10639900	5.25248300
H	1.54875500	4.28607000	5.56142300
H	1.56412800	5.94598500	4.95933000
H	2.79346900	5.41080200	6.11972900
C	-0.82457300	1.43554800	-0.50725500

C	-2.23633800	-0.62558100	-0.05901700
C	-3.50694200	0.17418900	0.12347300
H	-3.86274100	0.44227000	-0.88021800
H	-3.29210800	1.13340500	0.59245900
C	-4.54073900	-0.71033400	0.88627900
C	-4.00223800	-4.60561500	1.03732700
H	-3.86928000	-4.85463000	-0.01594000
H	-4.76996100	-5.24945200	1.46664900
H	-3.05800900	-4.77285600	1.55508500
C	-2.94706800	0.35243800	3.31652400
H	-2.27294500	-0.50409900	3.33949400
H	-3.02364500	0.74080900	4.33698400
H	-2.48260300	1.12602700	2.70069700
C	-5.74295600	1.42345100	2.82819200
H	-5.68215900	1.82879500	3.84290400
H	-6.79466600	1.21411300	2.61850300
H	-5.40906100	2.20376700	2.13883900
C	-5.36532000	-1.45326500	3.82637000
H	-4.77594100	-2.37045100	3.77169600
H	-6.39433500	-1.71005100	3.56887400
H	-5.35437700	-1.10244500	4.86306200
C	-6.77183000	0.94048900	-0.54224300
H	-5.99831700	1.48144800	-1.09463900
H	-7.04794500	1.54633400	0.32222300
H	-7.64897000	0.86446100	-1.19263900
C	-7.53349800	-1.64781100	0.94955200
H	-7.84968800	-1.05485500	1.81123300
H	-7.17348000	-2.61262600	1.31381000
H	-8.41569500	-1.82310700	0.32641700
C	-5.92220700	-1.75990100	-1.64769600
H	-6.83670700	-1.76998100	-2.24841000
H	-5.64972000	-2.79728500	-1.43953600
H	-5.13063300	-1.32149300	-2.26203300
C	-1.57871800	-3.00719000	0.01924200
C	-0.71508400	-3.39235900	1.05732500
C	0.06518600	-4.53483400	0.87383700
H	0.73623200	-4.85550800	1.66030000
C	0.00322600	-5.25912400	-0.30960800
H	0.61055400	-6.14768900	-0.43324700
C	-0.80124300	-4.81814100	-1.35217700
H	-0.80361400	-5.36015500	-2.29042300
C	-1.59641800	-3.67913500	-1.21374100
C	-2.40798600	-3.16921400	-2.39260000
H	-3.04112000	-2.35866400	-2.03438000
C	-3.32588100	-4.24164200	-2.99547200
H	-2.75299100	-5.07172300	-3.41723500
H	-3.93084400	-3.81300900	-3.79869100
H	-4.00853800	-4.65209400	-2.24767100
C	-1.46943700	-2.58028600	-3.46023900
H	-0.84114300	-1.79839900	-3.03128100
H	-2.04851500	-2.14929600	-4.28243100
H	-0.81526300	-3.35243700	-3.87490000
C	-0.62853900	-2.59069300	2.34498300
H	-0.97171300	-1.58217200	2.11152100
C	0.81253800	-2.46545500	2.85593400
H	1.18590500	-3.41014900	3.26091800
H	0.85843200	-1.72546800	3.65904200
H	1.48217500	-2.14920600	2.05733000
C	-1.54426100	-3.17213400	3.43486800
H	-1.25544300	-4.20063100	3.67101600
H	-2.59078400	-3.17690400	3.12617000
H	-1.47088600	-2.58320900	4.35327800
C	2.92774500	-1.82044800	-0.43785600

C	3.78431600	-1.25009200	0.53929100
C	5.06989300	-1.76547700	0.69934200
H	5.73731700	-1.34048900	1.43655900
C	5.49588700	-2.82649700	-0.08371100
C	4.66476900	-3.40680100	-1.03128700
H	5.02306500	-4.24189400	-1.61640300
C	3.37418400	-2.91744100	-1.21847000
C	2.44194500	-3.52052300	-2.25253500
H	1.43755900	-3.45651400	-1.83152000
C	2.72942200	-4.99267300	-2.56003300
H	3.66894900	-5.12156700	-3.10571400
H	1.93253900	-5.40344900	-3.18598300
H	2.78457200	-5.58834400	-1.64617600
C	2.44748400	-2.68778500	-3.54541400
H	2.14243300	-1.66232400	-3.34147700
H	1.75218500	-3.10835000	-4.27822100
H	3.44664200	-2.67276300	-3.99168500
C	3.32966600	-0.05881400	1.36391000
H	2.23900700	-0.04600500	1.33728800
C	3.76114800	-0.12666700	2.83331100
H	3.46785800	-1.07353400	3.29134500
H	3.29213300	0.68665700	3.39109500
H	4.84349400	-0.01685200	2.94778600
C	3.81277800	1.24675500	0.71319700
H	3.39470700	2.11900900	1.21918100
H	3.50601000	1.27665600	-0.33188400
H	4.90517200	1.31112800	0.74348900
N	0.98096700	3.36160500	-2.78551700
N	-0.89333900	4.41516000	-2.53477400
N	1.67383700	-1.32577900	-0.61959100
N	-2.52018600	-1.94406400	0.24186700
O	-1.68521500	2.41909800	-0.24862200
O	-4.46026300	-3.26301800	1.19352100
Si	-4.66492400	-0.12185200	2.69201100
Si	-6.18780300	-0.78739100	-0.04761600

Table S4. Cartesian coordinates of optimized **3a**.

Br	-8.47988248	-0.00495143	-0.87410732
P	1.88357428	2.49050492	3.25819955
Si	4.49068651	-2.34160464	2.10956424
Si	5.21275036	-1.33121976	-0.83466869
O	3.36181026	-4.06981759	-0.66742031
N	-2.56285758	-0.95859080	0.06287098
N	1.55029358	-2.38401211	-0.16041092
N	-0.13504754	2.23421709	1.27432810
C	-3.90143263	-0.84631009	-0.15040746
C	-6.61510530	-0.38140958	-0.57945573
C	-4.79123701	-0.74299699	0.95253061
C	-6.14201211	-0.49821201	0.71976177
H	-6.82899192	-0.40273223	1.54932617
C	1.45201296	-1.10614323	0.39505636
C	2.86636595	-0.58539940	0.55484851
H	2.97833777	-0.01815684	1.47693119
H	3.03360210	0.15248794	-0.23656963
C	-5.77204111	-0.54120709	-1.66682007
H	-6.16943137	-0.46754745	-2.67053434
C	2.35741668	2.83604198	0.26724251
C	-1.54209066	-4.43161955	0.00875489
H	-2.13759301	-4.96338855	0.74065295
C	3.85668188	-1.78373996	0.41218415

C	0.42811639	1.05956188	1.12786013
C	-0.38192053	-3.76932115	0.41368982
C	-4.41357942	-0.78539350	-1.46957981
C	0.07993773	-3.81790375	1.85998805
H	0.79098866	-3.00653819	1.99499132
C	-4.28741947	-0.99101254	2.36267187
H	-3.21662345	-0.78029393	2.36112760
C	-1.36696504	2.90727607	0.86122387
C	0.36239883	-3.08177913	-0.55770520
C	3.08008834	-2.26835159	3.37586409
H	2.50571375	-3.19639163	3.36622172
H	2.37693899	-1.45382988	3.18675444
H	3.48465768	-2.14706656	4.38563075
C	-2.57107074	2.32129848	1.62196558
H	-2.40222622	2.42522247	2.70002833
H	-2.65365095	1.25756613	1.40093078
C	-1.95022223	-4.40399676	-1.31712550
H	-2.86075307	-4.91110842	-1.61465273
C	0.80977354	-2.31257263	-2.94327709
H	1.84743969	-2.36094038	-2.61052569
C	3.50464905	3.60183994	0.49374625
H	3.74017115	3.94980915	1.49545115
C	2.13606422	2.44289545	-1.06660653
H	1.27208419	1.83033521	-1.29708452
C	0.80670637	-5.14092783	2.15431851
H	0.14643607	-5.99613784	1.98353227
H	1.13964494	-5.17610138	3.19588121
H	1.68642421	-5.26235095	1.51811176
C	-1.59522420	2.73904522	-0.65449549
H	-1.66452874	1.67376606	-0.88537814
H	-0.73265734	3.14219558	-1.19245351
C	-1.19287537	-3.72771794	-2.26721204
H	-1.51983914	-3.72456779	-3.29823480
C	4.38866034	3.94626448	-0.53192612
H	5.26431612	4.53184840	-0.28504288
C	-0.02504477	-3.05484844	-1.90982407
C	3.00635917	2.78559775	-2.08903234
H	2.78533419	2.44523978	-3.09429284
C	0.65713791	1.62875687	4.29510841
H	0.94270959	1.66403892	5.34750761
H	0.58299664	0.59352020	3.95964923
H	-0.31674874	2.09880262	4.15868261
C	2.60600903	-5.08297666	-1.32703835
H	1.72220495	-5.36946095	-0.75666511
H	3.26274101	-5.94633273	-1.43657385
H	2.28992493	-4.74754141	-2.31665286
C	-1.23289008	4.40050376	1.19187325
H	-0.35865488	4.80797894	0.67416942
H	-1.06051474	4.51561159	2.26891606
C	-1.05651053	-3.57476525	2.85822379
H	-1.57242972	-2.64159271	2.63115841
H	-0.65248731	-3.50874135	3.87256518
H	-1.79354688	-4.38182519	2.85115055
C	-3.85497556	3.06134474	1.20649056
H	-4.70531161	2.63773974	1.74751223
C	4.16392457	3.54170584	-1.84746937
C	-4.07958251	2.88940054	-0.30527636
H	-5.00128475	3.39913386	-0.60477866
H	-4.20601034	1.83196428	-0.54578106
C	-4.46885072	-2.48168305	2.70248910
H	-5.53155175	-2.74122238	2.71858367
H	-4.04257196	-2.71575003	3.68247886
H	-3.97796796	-3.10848804	1.95631472

C	-4.93818464	-0.10476997	3.43021966
H	-4.83779081	0.95422398	3.18465164
H	-4.46062079	-0.27645408	4.39901447
H	-6.00256289	-0.32379225	3.55241949
C	-3.49584963	-0.95608695	-2.66570145
H	-2.53758438	-1.29648552	-2.27403318
B	-1.33316423	-0.80695162	0.30854600
C	1.93866083	4.20264379	3.90749410
H	0.98291214	4.68582148	3.69911407
H	2.72333397	4.76553630	3.40123952
H	2.12357331	4.21164289	4.98358899
C	-2.51366321	5.14451296	0.77717659
H	-2.40725283	6.20762194	1.01564602
C	3.49869185	1.75517899	3.69417572
H	3.76375715	1.97742479	4.72943058
H	4.26917846	2.14178487	3.02719399
H	3.44186897	0.67484481	3.56579880
C	5.10540837	3.88809767	-3.00619207
C	0.43482722	-0.82214805	-3.01074521
H	-0.58753992	-0.70023088	-3.37492591
H	1.10547749	-0.29473390	-3.69577150
H	0.49889171	-0.35474649	-2.02838027
C	-2.88052667	3.47621695	-1.06877894
H	-3.03364096	3.35357724	-2.14510366
C	0.75130107	-2.94274402	-4.33990211
H	0.97235397	-4.01303852	-4.31286983
H	1.48222471	-2.46026761	-4.99374331
H	-0.23155294	-2.81482379	-4.80159379
C	5.14823125	-4.10603258	2.09266321
H	5.42831541	-4.41272831	3.10544442
H	6.02715466	-4.20819962	1.45369516
H	4.39136945	-4.79989605	1.72151014
C	-4.01147702	-2.02699242	-3.63719445
H	-4.95424146	-1.73103673	-4.10587487
H	-4.17603604	-2.97529662	-3.12133435
H	-3.28541282	-2.19303111	-4.43871708
B	2.91159739	-2.87496752	-0.19566975
C	-3.26772327	0.37901760	-3.39073214
H	-2.59790021	0.24791665	-4.24595753
H	-2.82141875	1.11496763	-2.72165159
H	-4.21080636	0.79036151	-3.76266265
C	5.97647589	0.34480618	-0.41836659
H	5.22752243	1.14038914	-0.41690071
H	6.72539684	0.60316763	-1.17356022
H	6.47484904	0.34544890	0.55205349
B	0.20091787	-0.35524679	0.66373893
C	-3.71413372	4.55641988	1.54133610
H	-3.57468772	4.69036451	2.62047139
H	-4.62992050	5.09030180	1.26662062
C	-2.73559176	4.97187270	-0.73649900
H	-1.89328488	5.40111406	-1.29023796
H	-3.63582556	5.51380823	-1.04508425
B	1.37173229	2.30996595	1.38383908
C	5.86599823	-1.20840473	2.74746442
H	6.09890808	-1.46006823	3.78696401
H	5.58268440	-0.15402076	2.71308335
H	6.78484038	-1.32226331	2.16747659
C	4.35156888	4.77603016	-4.01875891
H	3.47127019	4.26770114	-4.41772355
H	5.00291665	5.03409522	-4.85922422
H	4.01736399	5.70294956	-3.54564726
C	4.43086743	-1.17021486	-2.54790041
H	4.08353165	-2.13810442	-2.91818744

H	5.16093152	-0.78129548	-3.26382151
H	3.58229155	-0.48122506	-2.53798513
C	6.56005012	-2.64596492	-0.91668300
H	7.16622525	-2.67394147	-0.00757176
H	7.23361613	-2.45080286	-1.75666186
H	6.11335409	-3.63297486	-1.05783532
C	5.56452643	2.59118964	-3.70575321
H	6.10217760	1.94632630	-3.00789676
H	6.23094257	2.82777916	-4.54041332
H	4.72113465	2.02261311	-4.10147123
C	6.35623158	4.64403159	-2.53299122
H	6.10029865	5.59954780	-2.06813570
H	7.00304673	4.85508845	-3.38828834
H	6.93296180	4.05496668	-1.81522066

Table S5. Cartesian coordinates of optimized **1b'** and **CO**.

B	0.02081900	-1.42045900	-0.11011900
B	0.41731900	0.15486800	0.09895700
B	-0.93158100	1.09147800	0.08134900
B	3.69584100	2.07895100	0.23779800
C	0.82579200	-2.60213700	-0.75016800
C	0.56696700	-3.95285000	-0.43369000
H	-0.21481700	-4.18826500	0.28662300
C	1.29252400	-4.99641200	-1.00725600
H	1.07788800	-6.02560600	-0.73020300
C	2.29450200	-4.71825900	-1.93917100
C	2.55862800	-3.39123500	-2.29178400
H	3.33252900	-3.16540000	-3.02039100
C	1.83116000	-2.35626200	-1.70920200
H	2.02723400	-1.32749900	-1.99662800
C	1.80955500	0.63951900	0.26667200
C	3.01805400	-0.19656000	0.64054500
H	2.96291000	-1.19407800	0.20837400
H	2.99274100	-0.34425100	1.73238700
C	4.29288900	0.62019700	0.26114700
C	4.01552500	4.53856800	0.17273400
H	4.89883400	5.17729700	0.25355600
H	3.34766000	4.73554500	1.01694500
H	3.48188900	4.77396800	-0.75320800
C	1.31859100	3.02417600	0.00807000
C	1.04150700	3.42003500	-1.30183100
C	0.13566400	4.45408900	-1.53768500
H	-0.07428400	4.76530600	-2.55720700
C	-0.50314700	5.08282000	-0.46750000
H	-1.21392300	5.88309400	-0.65157700
C	-0.23560900	4.67469900	0.84030400
H	-0.74084200	5.15345100	1.67388400
C	0.67389200	3.64611800	1.07892800
C	-3.36656700	2.04701600	-0.09876400
C	-4.46573700	1.44134600	0.55086000
C	-5.75991100	1.91904800	0.36446000
H	-6.58715000	1.43442300	0.87849600
C	-6.00196100	3.01384900	-0.46910100
C	-4.92256100	3.62687900	-1.11112900
H	-5.09447200	4.48146700	-1.76138100
C	-3.62468000	3.15781500	-0.93220700
N	2.25431700	1.97418800	0.24872900
N	-2.11297300	1.55672000	0.05188900
O	4.47339500	3.19159600	0.17455600
Si	4.85482100	0.22028900	-1.49318000
Si	5.69010600	0.41360400	1.49258200

H	-4.27250300	0.59080300	1.19535400
H	-2.78343400	3.63013700	-1.42776000
H	-7.01259900	3.38467700	-0.61310000
H	2.86127300	-5.52747900	-2.39148000
H	5.20168600	-1.22068600	-1.63062700
H	3.76293200	0.51663100	-2.46446600
H	6.04168400	1.02907400	-1.87961600
H	6.90768300	1.17157200	1.10091600
H	5.24934700	0.88312900	2.83822500
H	6.06744400	-1.02307700	1.62963100
H	0.88645300	3.30722000	2.08802400
H	1.53594900	2.90723900	-2.12114200
N	-2.51436900	-1.86698300	-0.65842200
N	-2.05405600	-1.83802100	1.45839200
C	-1.50109400	-1.75647900	0.22802500
C	-3.72973700	-2.00690200	0.01422300
C	-3.43863300	-1.99925000	1.35183500
C	-2.26969500	-1.76982700	-2.11684100
C	-1.23491300	-1.65669900	2.67840000
H	-0.25031000	-1.39949200	2.27506300
H	-1.21396300	-1.49587900	-2.17909800
C	-5.06957800	-2.05262400	-0.64116200
H	-5.39898000	-1.04693600	-0.92672200
H	-5.07722900	-2.68409700	-1.53289800
H	-5.80923600	-2.45564000	0.05564600
C	-4.38060200	-2.09386700	2.50606100
H	-4.56045600	-1.11764800	2.97093800
H	-5.34601500	-2.47429000	2.16322300
H	-4.01660000	-2.77088300	3.28322700
C	-2.44114600	-3.13144900	-2.79009600
H	-3.47491400	-3.48873100	-2.74157200
H	-2.16345200	-3.05230800	-3.84615800
H	-1.78893500	-3.87257600	-2.31867900
C	-3.07118100	-0.63669800	-2.75818500
H	-2.68824900	-0.46708700	-3.76982800
H	-4.13531000	-0.87050600	-2.84339100
H	-2.95487500	0.28539000	-2.18422600
C	-1.10923900	-2.95475200	3.47521400
H	-0.39373100	-2.81023900	4.29124600
H	-2.05962900	-3.26819600	3.91843100
H	-0.73904600	-3.76423000	2.83820300
C	-1.71127900	-0.45450500	3.49367300
H	-1.83311700	0.41418100	2.84025100
H	-2.65221800	-0.64674400	4.01707500
H	-0.95517300	-0.21603400	4.24881400
C	4.27063800	-3.60140000	0.56899600
O	3.47238600	-3.64844500	1.37980700

Table S6. Cartesian coordinates of optimized **TS1**.

B	-0.05890300	-1.56476900	0.35741000
B	0.54781600	-0.01278300	0.33386000
B	-0.64011600	1.09571200	0.10129300
B	4.05285300	1.45145800	0.08504700
C	0.62517600	-2.86576700	-0.27400400
C	0.21883100	-4.16973900	0.06665700
H	-0.54963900	-4.30114300	0.82614300
C	0.78182000	-5.29675400	-0.53295400
H	0.45109000	-6.29040000	-0.24067700
C	1.76961400	-5.14785700	-1.50831800
C	2.18588900	-3.86585700	-1.87338900
H	2.95427400	-3.73566800	-2.63094900

C	1.61973200	-2.74724700	-1.26354900
H	1.93110500	-1.75142700	-1.56425400
C	1.99949000	0.29414200	0.39884100
C	3.09931200	-0.61909600	0.89552500
H	2.93534300	-1.65429700	0.59099100
H	3.04230000	-0.64109400	1.99767300
C	4.46782900	-0.02476600	0.43899700
C	4.69845100	3.75435400	-0.60371500
H	5.66077400	4.21839800	-0.83506900
H	4.21690800	4.30871500	0.20790200
H	4.05250100	3.80042900	-1.48558900
C	1.82211700	2.63627000	-0.32403200
C	1.37872500	2.70864000	-1.64720300
C	0.62887000	3.80442800	-2.06972300
H	0.28109700	3.85746300	-3.09722800
C	0.32268400	4.83025500	-1.17384200
H	-0.26450600	5.68217500	-1.50358000
C	0.76171600	4.75329200	0.14881400
H	0.52216300	5.54815400	0.84977800
C	1.50299000	3.65232700	0.57737900
C	-2.86760300	2.44914800	-0.20200000
C	-4.06096100	1.81968500	-0.62304000
C	-5.25144200	2.53452800	-0.71914400
H	-6.15473200	2.02573700	-1.04863100
C	-5.29334300	3.89413600	-0.40113400
C	-4.11965800	4.52869400	0.01473700
H	-4.13658200	5.58659200	0.26606300
C	-2.92399300	3.82401300	0.11474200
N	2.61236300	1.52778200	0.09988000
N	-1.71633800	1.74347300	-0.08206800
O	4.96600600	2.41087500	-0.22254700
Si	5.06319200	-0.82901800	-1.15640600
Si	5.78385200	-0.09167600	1.77375100
H	-4.02449400	0.76401700	-0.86770800
H	-2.01074200	4.31125300	0.43668300
H	-6.22348600	4.44983700	-0.47676600
H	2.20922500	-6.02246700	-1.98020400
H	5.22970100	-2.29948600	-0.98703900
H	4.06780700	-0.61465600	-2.24635100
H	6.36103600	-0.25880200	-1.60546600
H	7.08608600	0.45115300	1.30446800
H	5.33876300	0.69733000	2.95828100
H	6.00735300	-1.49334200	2.23150000
H	1.84134000	3.56850800	1.60557300
H	1.62130900	1.89687200	-2.32557000
N	-2.41394300	-1.96351900	-0.74043100
N	-2.56276400	-1.28629500	1.31542700
C	-1.67219800	-1.63196900	0.34934500
C	-3.77536200	-1.85488600	-0.45144300
C	-3.86901000	-1.43479500	0.84508000
C	-1.81969100	-2.09248900	-2.09531500
C	-2.16364600	-0.77146100	2.64847500
H	-1.10271400	-0.55729700	2.52938700
H	-0.74992700	-2.12108000	-1.91367900
C	-4.88157600	-2.18032300	-1.40048500
H	-4.80124200	-1.62965100	-2.34137200
H	-4.91244900	-3.24850600	-1.64127700
H	-5.84014100	-1.91363000	-0.95050200
C	-5.10532800	-1.11827200	1.62039600
H	-5.29075700	-0.03870800	1.64384100
H	-5.96784200	-1.59335300	1.14722800
H	-5.05798600	-1.48057800	2.64979500
C	-2.18916100	-3.40851100	-2.77589300

H	-3.23506100	-3.44911300	-3.09078800
H	-1.56880200	-3.52480000	-3.67023400
H	-1.97977800	-4.25155600	-2.11099100
C	-2.09951600	-0.83478500	-2.92284000
H	-1.51282700	-0.87972700	-3.84649200
H	-3.15214900	-0.73631600	-3.20348000
H	-1.80325800	0.05719900	-2.36335500
C	-2.35068800	-1.84133800	3.72554400
H	-1.92013900	-1.48907500	4.66865700
H	-3.40896200	-2.05914000	3.90275900
H	-1.84571000	-2.76887200	3.44330600
C	-2.83425700	0.55957800	2.99799600
H	-2.79794100	1.24691700	2.15212300
H	-3.86878700	0.44051700	3.32699700
H	-2.27748400	1.00975000	3.82642100
C	0.50702300	-2.15030800	2.33807300
O	1.43010200	-2.05449000	3.01875800

Table S7. Cartesian coordinates of optimized **Int1**.

B	0.12625600	1.88029800	0.44888400
B	-0.59003300	0.07231400	0.93532700
B	0.66640900	-0.95932300	0.77620900
B	-4.03819500	-1.41124400	0.33158900
C	-0.70823000	2.85314700	-0.49170200
C	-0.35068500	4.21409300	-0.52522300
H	0.44348100	4.57023100	0.12820800
C	-0.98505900	5.11858900	-1.37784600
H	-0.68376800	6.16324400	-1.38001600
C	-2.00845400	4.68422600	-2.22243500
C	-2.38488300	3.34076400	-2.20493000
H	-3.18143600	2.98660000	-2.85397800
C	-1.73880600	2.44476600	-1.35298800
H	-2.02697700	1.39739200	-1.36048900
C	-2.03327400	-0.23105300	0.79872000
C	-3.17711900	0.69149700	1.18313000
H	-3.01507000	1.70531800	0.80453000
H	-3.15148200	0.79248400	2.27802400
C	-4.51132000	0.03954300	0.70256200
C	-4.56710800	-3.74293900	-0.35283200
H	-5.50921800	-4.28279700	-0.47576600
H	-3.97936100	-4.21577100	0.43955900
H	-3.99711600	-3.79210100	-1.28554500
C	-1.74365400	-2.52157700	-0.00266200
C	-1.39603700	-2.64726900	-1.34893700
C	-0.58550300	-3.70476700	-1.75998300
H	-0.32097700	-3.80610000	-2.80876800
C	-0.11403400	-4.62836600	-0.82488200
H	0.52078900	-5.44973500	-1.14385200
C	-0.45094300	-4.49065700	0.52244200
H	-0.07371000	-5.19963500	1.25308000
C	-1.26489300	-3.43729400	0.93560100
C	2.96351600	-2.16175900	0.41038900
C	3.16763800	-3.05666800	-0.66287000
C	4.43359300	-3.57370300	-0.92925300
H	4.56407800	-4.25588200	-1.76600000
C	5.52893000	-3.22960100	-0.13397300
C	5.33370500	-2.36775900	0.94917100
H	6.17157400	-2.10288400	1.58994800
C	4.07410500	-1.84501000	1.22282300
N	-2.59259300	-1.44884000	0.40633100
N	1.75275400	-1.59657100	0.63907700

O	-4.89854200	-2.39897300	-0.02239100
Si	-5.18837100	0.82754900	-0.87062300
Si	-5.82052700	0.00556700	2.05130700
H	2.31481300	-3.33387500	-1.27183100
H	3.91906600	-1.17849900	2.06408500
H	6.51375700	-3.63549700	-0.34553700
H	-2.50820800	5.38616800	-2.88440300
H	-5.32420300	2.30050300	-0.71384800
H	-4.27331900	0.57399200	-2.02069300
H	-6.51771000	0.26105200	-1.22098800
H	-7.07585300	-0.64198700	1.58945100
H	-5.29904200	-0.74512400	3.22848800
H	-6.14792400	1.38668500	2.50568200
H	-1.52795200	-3.30702400	1.98046100
H	-1.76614400	-1.91363100	-2.05876200
N	2.11167900	1.12771300	-1.09202600
N	2.72843300	1.81200200	0.87469000
C	1.64128900	1.62486700	0.08133400
C	3.49041200	0.96796100	-1.02876300
C	3.88178800	1.39240300	0.21308700
C	1.20372700	0.81573700	-2.22046100
C	2.62771100	2.35994500	2.24852400
H	1.60694700	2.73394200	2.30677200
H	0.21807100	0.82639200	-1.75878300
C	4.33678400	0.37318600	-2.10457200
H	4.22954700	-0.71669800	-2.13171100
H	4.08955200	0.77245900	-3.09194700
H	5.38796400	0.59855500	-1.91265200
C	5.25932800	1.39582800	0.78895000
H	5.26860600	1.04029100	1.82148500
H	5.89256500	0.71583400	0.21593700
H	5.71933000	2.39064200	0.77025600
C	1.26323900	1.92418700	-3.27157300
H	2.24524200	1.97049600	-3.75540000
H	0.51241000	1.73390800	-4.04513100
H	1.04406400	2.89461300	-2.81858600
C	1.40613100	-0.58880000	-2.78729500
H	0.54964400	-0.82014000	-3.42933800
H	2.30768000	-0.68095600	-3.39670100
H	1.43683600	-1.32262600	-1.98141300
C	3.56633500	3.54820000	2.46496900
H	3.28602100	4.04853900	3.39726500
H	4.61435100	3.25212500	2.55227200
H	3.47346000	4.27268800	1.64938300
C	2.77427300	1.25680600	3.29827900
H	2.10184700	0.42465000	3.07603500
H	3.79816300	0.87354600	3.35296300
H	2.51010500	1.65802000	4.28158900
C	-0.34030600	1.49260900	1.83446200
O	-0.67810700	1.77020200	2.96401200

Table S8. Cartesian coordinates of optimized **TS2**.

B	-0.70653000	-2.18603100	0.25515300
B	0.94825700	-0.00144700	0.74805800
B	-0.19389800	1.07142000	0.25101300
B	4.51877100	1.01310500	0.14532800
C	-0.38455100	-3.43932800	-0.59481600
C	-1.36404900	-4.39744600	-0.92291700
H	-2.37642900	-4.27049600	-0.54539400
C	-1.05973900	-5.51179100	-1.70237000
H	-1.82927800	-6.24304100	-1.93499500

C	0.24040400	-5.68692700	-2.18069300
C	1.23190600	-4.75100200	-1.86987100
H	2.24457100	-4.88688500	-2.23924500
C	0.92256000	-3.64611600	-1.08390700
H	1.69367100	-2.92009400	-0.84591800
C	2.40198000	0.22020500	0.84727700
C	3.42724700	-0.75475100	1.38207300
H	3.06269100	-1.78614200	1.34175100
H	3.58067400	-0.54748700	2.45374500
C	4.75600200	-0.47945100	0.60049100
C	5.37709700	3.17827600	-0.68583800
H	6.38577400	3.59168600	-0.76960300
H	4.82042100	3.73284100	0.07627100
H	4.85941000	3.29376100	-1.64364400
C	2.39632000	2.43497200	-0.17856100
C	2.15048000	2.54511000	-1.54974600
C	1.40686700	3.61858900	-2.03964400
H	1.21774500	3.70150200	-3.10652400
C	0.89627300	4.57552300	-1.16155300
H	0.30319300	5.40225700	-1.54107200
C	1.13841400	4.46149400	0.20852900
H	0.73470600	5.19974300	0.89520100
C	1.88527800	3.39293700	0.70051100
C	-2.25948100	2.63481300	-0.14327300
C	-2.51329100	3.29845600	-1.36331700
C	-3.64638400	4.09420600	-1.52058800
H	-3.82027700	4.59124900	-2.47190600
C	-4.55382700	4.26138200	-0.47168200
C	-4.30162800	3.62912400	0.74974400
H	-4.98793100	3.76443200	1.58270300
C	-3.17417000	2.83136800	0.91540000
N	3.12269700	1.31830000	0.32448300
N	-1.19025900	1.81849500	0.00802400
O	5.51277900	1.80618600	-0.34008100
Si	4.79679100	-1.52238100	-0.96694700
Si	6.30560500	-0.69540200	1.63018800
H	-1.80021700	3.17731100	-2.17171300
H	-2.97008100	2.34133800	1.86191200
H	-5.43525000	4.88286300	-0.59913300
H	0.48200900	-6.55190200	-2.79264200
H	4.73100400	-2.97720300	-0.64412100
H	3.62048400	-1.20947000	-1.82793000
H	6.02711400	-1.27947400	-1.76787800
H	7.54169400	-0.45077700	0.83998400
H	6.28529800	0.25124300	2.78254900
H	6.39031100	-2.07507700	2.19178700
H	2.06758400	3.27709500	1.76416300
H	2.53157100	1.77528700	-2.21417200
N	-2.89758100	-1.10770800	-0.64680500
N	-2.80992400	-1.24780200	1.52300300
C	-2.16846100	-1.60368900	0.38647600
C	-3.99457600	-0.40307500	-0.15408500
C	-3.94647000	-0.50320200	1.21186000
C	-2.49890100	-1.28282700	-2.06849900
C	-2.27381800	-1.58590100	2.86740300
H	-1.44087400	-2.26122200	2.66426900
H	-1.54742100	-1.81077900	-2.01141500
C	-4.96085300	0.37350800	-0.98546900
H	-4.51357300	1.30906100	-1.33591300
H	-5.31522600	-0.19025600	-1.85156700
H	-5.83334200	0.63526000	-0.38414800
C	-4.90462300	0.05719100	2.20993800
H	-4.39044500	0.51711000	3.05644000

H	-5.50444700	0.83698400	1.73722400
H	-5.58510800	-0.70610700	2.60443600
C	-3.48152800	-2.19069400	-2.80963100
H	-4.46175000	-1.72421200	-2.94139300
H	-3.08057800	-2.41007200	-3.80422800
H	-3.61168400	-3.13866000	-2.28110400
C	-2.23902600	0.05020300	-2.76868500
H	-1.77432300	-0.15484000	-3.73883300
H	-3.15574200	0.61529600	-2.95000200
H	-1.55974400	0.66345600	-2.17379100
C	-3.29867100	-2.34617800	3.71017900
H	-2.79538800	-2.74782800	4.59503400
H	-4.11587200	-1.70800300	4.05577000
H	-3.72189100	-3.18592700	3.14955000
C	-1.69485200	-0.34871000	3.55557200
H	-0.97157200	0.14635600	2.90286500
H	-2.46976400	0.37042900	3.83864700
H	-1.17579700	-0.66133600	4.46694600
C	0.42192700	-1.41886800	1.02422200
O	0.76470600	-2.29730500	1.87705400

Table S9. Cartesian coordinates of optimized **2b'**.

B	2.00331900	-0.72985000	0.83374100
B	-0.92344200	-0.16635400	0.66662400
B	-1.00363900	1.47207600	0.55603200
B	-4.14678000	-2.06688900	-0.00932900
C	2.87749000	-0.45566000	2.12361700
C	4.13509200	0.16876700	2.06278400
H	4.53366700	0.47724400	1.09725600
C	4.89564200	0.40596300	3.20985900
H	5.86343200	0.89519700	3.12897500
C	4.41278900	0.01168700	4.45742100
C	3.16727800	-0.61628600	4.54396800
H	2.78366200	-0.92801100	5.51245600
C	2.41432600	-0.84236300	3.39360400
H	1.44742500	-1.33253600	3.47162300
C	-2.02541000	-1.15503700	0.51916100
C	-1.87175800	-2.66209500	0.58941700
H	-1.71778200	-2.94526500	1.64202300
H	-0.95087700	-2.97899100	0.08918100
C	-3.17655600	-3.30310200	0.01670500
C	-6.43838500	-1.12727500	-0.21211300
H	-7.42403600	-1.59934600	-0.21064600
H	-6.35035300	-0.47467900	-1.08592800
H	-6.32554900	-0.51791600	0.68925200
C	-3.80796600	0.47762400	0.16082400
C	-4.03439600	1.23016600	1.31480100
C	-4.46270100	2.55156600	1.20626400
H	-4.62788200	3.13995500	2.10370900
C	-4.66787200	3.12100800	-0.05152800
H	-4.99426200	4.15337000	-0.13333700
C	-4.43915100	2.36644200	-1.20310800
H	-4.59217400	2.80789800	-2.18394900
C	-4.00118200	1.04648300	-1.09883100
C	-0.68674400	4.05329300	0.25365900
C	-1.44925200	4.77873900	-0.68689100
C	-1.21848000	6.13625400	-0.89190600
H	-1.81730500	6.67427200	-1.62308100
C	-0.22925800	6.80976000	-0.17126800
C	0.52915200	6.10291500	0.76569600
H	1.29928400	6.61428700	1.33806800

C	0.30740300	4.74535300	0.98008500
N	-3.36602700	-0.87734100	0.26209000
N	-0.88054600	2.72419600	0.43698100
O	-5.47551900	-2.17477900	-0.25947500
Si	-3.85209600	-4.70000500	1.07297000
Si	-2.90733600	-3.84829700	-1.76471500
H	-2.21753600	4.24930700	-1.23987700
H	0.88877200	4.19162100	1.71128900
H	-0.05351700	7.86903900	-0.33495100
H	4.99978100	0.19106500	5.35431000
H	-2.82668100	-5.76729100	1.25436200
H	-4.20452600	-4.18426600	2.42638300
H	-5.06072500	-5.31883100	0.46813300
H	-4.14503000	-4.40507900	-2.37204600
H	-2.46572800	-2.68435300	-2.58573000
H	-1.83724300	-4.88353900	-1.84441700
H	-3.79665600	0.45116900	-1.98371900
H	-3.85626000	0.77555000	2.28394400
N	2.80928100	0.39865100	-1.42544800
N	3.56539200	-1.60666700	-1.09035200
C	2.77533500	-0.64298600	-0.56684200
C	3.63171700	0.09337400	-2.51183300
C	4.10745200	-1.17498400	-2.30221100
C	2.06777800	1.66208800	-1.15875000
C	3.80804100	-2.88184100	-0.37106400
H	3.11974200	-2.83779900	0.47201700
H	1.47095100	1.42978700	-0.27818800
C	3.87947500	0.99446300	-3.67670700
H	3.02084400	1.03015800	-4.35607700
H	4.09856300	2.01842400	-3.36537900
H	4.73728200	0.63247100	-4.24875800
C	4.98797100	-1.99508100	-3.18665200
H	4.42788000	-2.77966600	-3.70773100
H	5.44251700	-1.35732900	-3.94846400
H	5.79901600	-2.47656800	-2.63426400
C	3.01842100	2.80146000	-0.79111500
H	3.65313000	3.10970300	-1.62823100
H	2.42226300	3.66547700	-0.48261300
H	3.65938600	2.51158700	0.04712400
C	1.09535500	2.00074800	-2.28624700
H	0.45745200	2.82302600	-1.95439800
H	1.60244900	2.31237600	-3.20348400
H	0.45115000	1.14316400	-2.50250400
C	5.23138500	-2.93653700	0.18656500
H	5.33978000	-3.83361400	0.80468900
H	5.98908200	-2.98158100	-0.60179500
H	5.42466600	-2.06414200	0.81681200
C	3.41745100	-4.09428200	-1.21631900
H	2.40654800	-3.97230400	-1.61676100
H	4.10900200	-4.27322700	-2.04397200
H	3.42453800	-4.98515200	-0.58056800
C	0.46940600	-0.69992400	0.79165500
O	0.99562200	-1.91889900	0.89063300

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