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Supporting Information

The Dewar Isomer of 1,2-Dihydro-1,2-azaborinines: Isolation, Fragmentation, and Energy Storage

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1. Methods

General. Precursors **1, 3** and **5** were synthesized according to Liu et al.[1] All experiments were performed under anhydrous conditions using argon as protective gas or in a glove box. Dry solvents were collected from a commercially available solvent purification system. All NMR spectra (except for those that were used in the kinetic study) were recorded on Bruker Avance III HD 400 spectrometer. The NMR spectra were measured at room temperature in deuterated cyclohexane (*c*-C_6D_{12}) (Deutero GmbH) and deuterated dichloromethane (CD_2Cl_2) (Sigma Aldrich). The solvents were dried over molecular sieve (4 Å) and degassed by three freeze-pump-thaw cycles prior to photoreactions. The spectra were referenced to residual solvent signals (^{1}H, ^{13}C: $SiMe_4$)[2] and externally (^{11}B: $BF_3{\cdot}OEt_2$). Electron impact ionization mass spectrometry (EI-MS) was measured on an MSD 5977 (Agilent MSD), and high resolution mass spectrometry (EI-HRMS) was measured on a MAT95 (Finnigan MAT). UV-Vis spectra were measured on a Perkin Elmer Lambda 1050. Elemental analyses were performed on a HEKAtech Euro 3000 CHN analyzer. Irradiation was achieved with a low-pressure mercury lamp (UVP, 253.7 nm) and an Osram HBO-500-W/2 high pressure mercury lamp in an Oriel housing with quartz optics and a dichroic mirror (280 – 400 nm). Chromatography was done using silica gel (Machery-Nagel, 60 M, 0.04-0.063 mm).

Kinetic study. The kinetic constants were measured for T = 373, 370, 367, 364, 361 and 358 K using NMR spectroscopy (Bruker Avance III HDX 400). For each temperature three experiments were performed. A solution of **4** (15-20 mg) in 3.5-4 mL deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$) that was purchased from Deutero GmbH (dried over molecular sieve (4 Å) and degassed by three freeze-pump-thaw cycles) was placed in a J. Young quartz tube. The sample was allowed to reach the desired temperature. Every 3 min (373-361 K) or every 5 min (358 K) a ^{1}H NMR spectrum was recorded (16 scans; total t = 126 s) for at least 3 half-life periods. For determining the rate constants the integrals of the signals at 4.75 and 3.00 ppm were determined. The residual proton signal of the solvent was taken as a reference.

Table 1. Rate constants for the reaction **4** → **3** in $C_2D_2Cl_4$.

T [K]	k [s^{-1}]
373	0.0004662
370	0.0003543
367	0.0002527
364	0.0001865
361	0.0001388
358	0.0001023

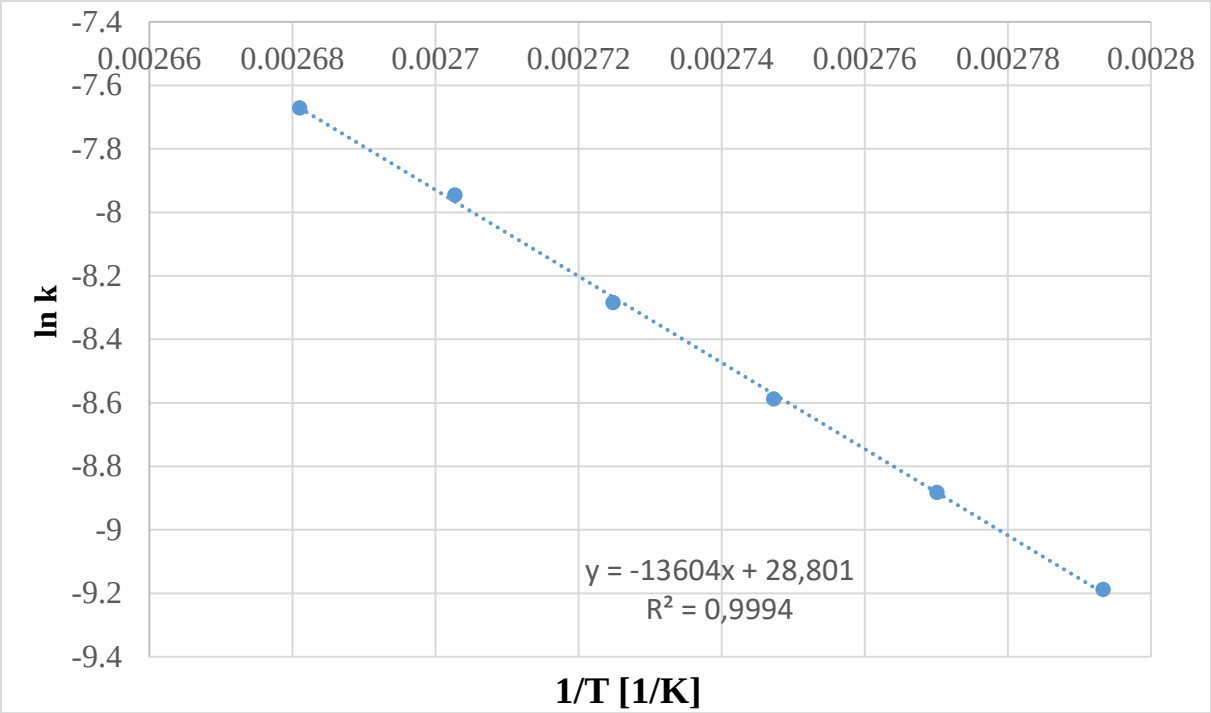


Figure S1. Arrhenius plot for the first order kinetic reaction **4** → **3**.

Quantum yield measurements. As light source for irradiation a VARIAN Cary Eclipse fluorescence spectrometer was used. Absorbance was measured using a PERKIN-ELMER Lambda 9 UV/VIS/NIR Spectrophotometer. As reference ferrioxalate actinometry[3] was taken. A solution of **3** in dry *n*-hexane was irradiated with 284 nm, and every 30 s the absorbance was measured until a 5% conversion to **4** was achieved. The absorbance at 284 nm was plotted vs. time. An example is shown in Figure S2.

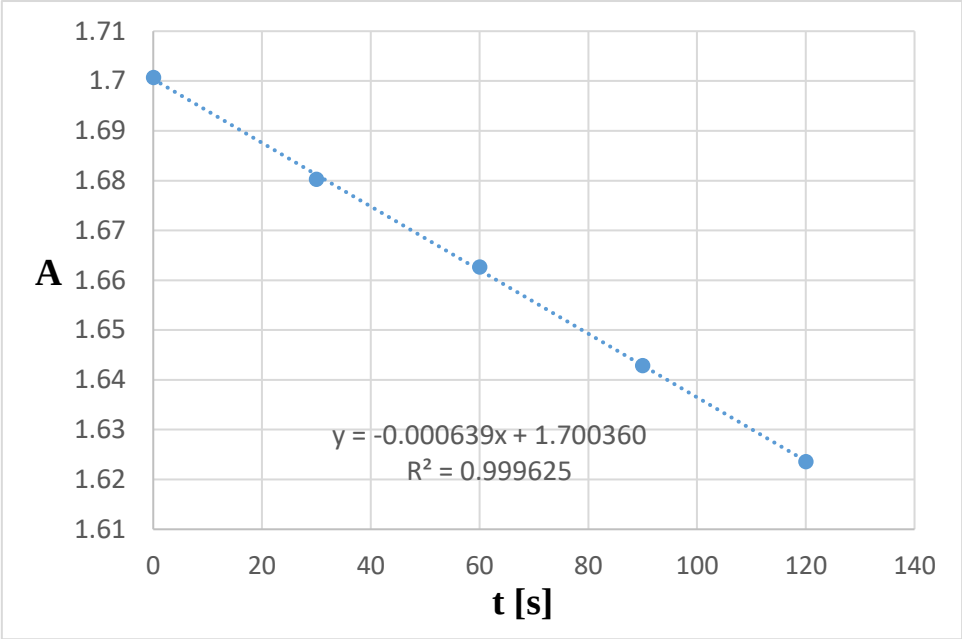


Figure S2. Example of a plot absorbance vs. time for the quantum yield determination of the photoreaction **3** → **4**.

Following equation[4] was used to calculate the quantum yield of the photoisomerization **3** → **4**:

$$\Phi = \frac{m \cdot V}{q_{n,p} \cdot \varepsilon(284\ nm) \cdot l}$$

Φ: quantum yield
m: slope of the fitting curve
V: volume of the irradiated sample
$q_{n,p}$: photon flux, amount basis
ε(284 nm): extinction coefficient of **3** at 284 nm
l: optical path length of the irradiation cell

Matrix experiments. Matrix experiments were performed by standard techniques[5] using a SHI CKW-21A displex closed-cycle helium cryostat (IR) and a CTI Cryogenics 8200 compressor (Brooks Automation) (UV). Compound **1** and **5** were sublimed from a glass flask at -80 °C and at room temperature respectively, and were condensed onto a cold CsI (IR) or sapphire (UV) window with a large excess of argon 6.0 (Westfalen AG), or neon 5.0 (Westfalen AG), which were dosed to 2.0 sccm by a mass flow controller (MKS mass flow PR400B). The deposition temperature was 30 K in the experiments with argon and 4 K in the experiments with neon.

FTIR spectra were measured between 4000 and 400 cm^{-1} on a Bruker V70 spectrometer using a resolution of 0.5 cm^{-1}. UV-Vis spectra were measured on a Perkin Elmer Lambda 1050.

Electronic Structure Computations. All geometries were optimized and harmonic vibrational frequencies, nuclear magnetic shielding tensors using the GIAO method[6] and nuclear spin-spin coupling constants[7] were computed with Becke's[8] hybrid functional in conjunction with the correlation functional of Lee, Yang, and Parr[9] as implemented[10] in Gaussian 09[11] and the 6-311+G**[12] basis set (B3LYP/6-311+G**). Chemical shifts were determined with reference to the experimental chemical shifts of tetramethylsilane (^{1}H, 0.0 ppm and ^{13}C, 0.0 ppm) and of **3** (^{11}B, 40.3 ppm) for mesityl **5** (^{11}B, 35.7 ppm) for chloro derivatives.

X-Ray Crystallography. Coumpound **8**: Crystals suitable for X-ray crystallography were grown by standard techniques from solutions using *n*-pentane at –20°C. Single crystals were selected, coated with Parabar 10312 (previously known as Paratone N, Hampton Research) and fixed on a microloop.

Data were collected on a Bruker APEX DUO instrument equipped with an IμS microfocus sealed tube and QUAZAR optics for MoK_{α} radiation (λ = 0.71073 Å). The data collection strategy was determined using COSMO[13] employing ω- and ϕ scans. Raw data were processed using APEX[14] and SAINT,[15] corrections for absorption effects were applied using SADABS.[16]

The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F^2 using SHELXTL [17] and Shelxle.[18]

2. Synthesis

Dewar isomer of 1,2-dihydro-1-tert-butyldimethylsilyl-2-mesityl-1,2-azaborinine **4**. A solution of **3** (20 mg, 0.064 mmol) in 0.5 mL dry *c*-C_6D_{12} was irradiated in J. Young quartz tube with 280-400 nm light for 4 hours at room temperature. The photoreaction was followed by ^{1}H and ^{11}B NMR. After the solvent was removed a colorless oil was obtained.

^{1}H NMR (400 MHz, *c*-C_6D_{12}): δ 6.63 (s, 2 H), 6.49 (t, $^3J_{HH}$ = 2.3 Hz, 1H), 6.32 (d, $^3J_{HH}$ = 2.3 Hz, 1H), 4.75 (t, $^3J_{HH}$ = 2.2 Hz, 1 H), 3.00 (d, $^3J_{HH}$ = 2.1 Hz, 1 H), 2.18 (s, 3 H), 2.16 (s, 6 H), 0.90 (s, 9 H), -0.07 (s, 3 H), -0.12 (s, 3 H). ^{13}C{^{1}H} NMR (400 MHz, *c*-C_6D_{12}): δ 143.9, 139.6, 138.2, 137.1, 127.4, 64.1, 44 (br.), 26.8, 22.6, 21.4, 18.8, -5.3, -5.6. ^{11}B{^{1}H} NMR (400 MHz, *c*-C_6D_{12}): δ 52.9. EI-HRMS found: 311.22127, calc. for $C_{19}H_{30}NSiB$ (M^+): 311.224058. EA found: C, 72.99; N, 4.45; H, 9.78; calc. for $C_{19}H_{30}NSiB$ C, 73.30; N, 4.50; H, 9.71.

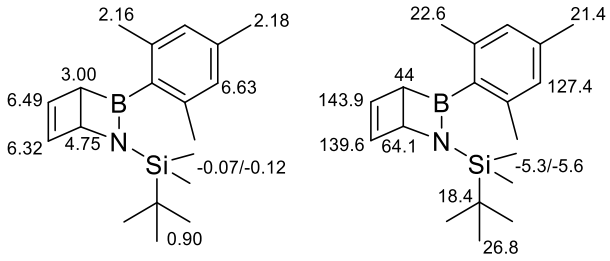


Figure S3. Assignments to **4** of ^{1}H (left) and ^{13}C signals (right) based on HSQC.

Dewar isomer of 1,2-dihydro-1-tert-butyldimethylsilyl-2-chloro-1,2-azaborinine **6**. A solution of **5** (25 mg, 0.11 mmol) in 0.5 mL dry *c*-C_6D_{12} was irradiated in J. Young quartz tube with 280-400 nm light for 16 hours at room temperature. The photoreaction was followed by ^{1}H and ^{11}B NMR.

^{1}H NMR (400 MHz, *c*-C_6D_{12}): δ 6.43 (t, $^3J_{HH}$ = 2.4 Hz, 1 H), 6.19 (d, $^3J_{HH}$ = 2.3 Hz, 1 H), 4.47 (t, $^3J_{HH}$ = 2.3 Hz, 1 H), 2.89 (s, 1 H), 0.93 (s, 9 H), 0.17 (s, 3 H), 0.13 (s, 3 H). ^{13}C{^{1}H} NMR (400 MHz, *c*-C_6D_{12}): δ 143.0, 140.0, 60.5, 43 (br.), 26.8, 18.8, -5.2, -5.7. ^{11}B{^{1}H} NMR (400 MHz, *c*-C_6D_{12}): δ 42.4.

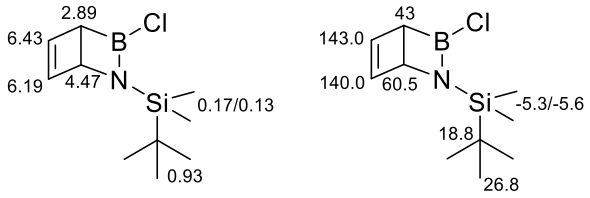


Figure S4. Assignments to **6** of ^{1}H (left) and ^{13}C signals (right) based on HSQC.

1,3-Di- tert-butyldimethylsilyl -2,4-dimesityl-1,3-diaza-2,4-diboretidine **8**. A solution of **4** (100 mg, 0.32 mmol) in 7 mL dry *c*-C_6D_{12} was irradiated in four NMR quartz tubes with 254 nm light for 17 hours at room temperature. The photoreaction was followed by ^{1}H and ^{11}B NMR. After removing the solvent the residues were combined and purified by column chromatography (silica, *n*-hexane, R_f = 0.47). Compound **8** was obtained as a colorless solid (30 mg, 0.058mmol, 36 %).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.81 (s, 2 H), 2.42 (s, 6 H), 2.28 (s, 3 H), 0.67 (s, 9 H), -0.30 (s, 6 H). $^{13}C\{^{1}H\}$6 NMR (400 MHz, *c*-C_6D_{12}): δ 138.2, 138.1, 127.3, 26.5, 23.0, 21.4, 18.3, -4.0. $^{11}B\{^{1}H\}$ NMR (400 MHz, *c*-C_6D_{12}): δ 46.8. EI-HRMS found: 517.37975, calc. for $C_{30}H_{51}N_2Si_2B_2$ ($M\text{-}1^{+}$): 517.377690. EA found: C, 69.21; N, 5.18; H, 10.13; calc. for $C_{30}H_{52}N_2Si_2B_2$ C, 69.49; N, 5.40; H, 10.11. UV/Vis (hexane, nm): 277, 265, 260.

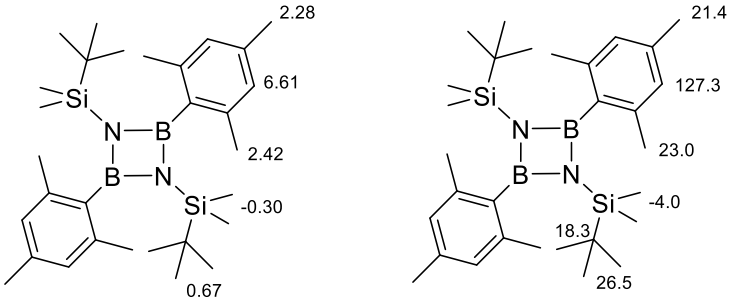
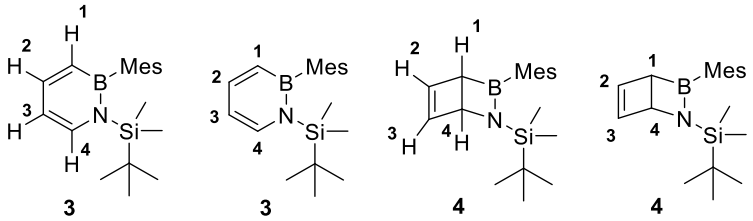


Figure S5. Assignments to **8** of ^{1}H (left) and ^{13}C signals (right) based on HSQC.

NMR signals of N-tert-butyldimethylsilyl-B-mesityl-iminoborane **9**. The compound is a transient intermediate that could not be isolated. Due to low concentration a ^{13}C NMR spectrum could not be recorded. In the ^{1}H spectrum (400 MHz, *c*-C_6D_{12}) of the mixture signals are detected at 6.76 (s), 0.97 (s), 0.10 (s) that decrease while signals at 2.42 (s), 2.26 (s) overlap with signals of the dimer **8**. Integration is precluded due to overlap with signals of precursor and products. $^{11}B\{^{1}H\}$ NMR (400 MHz, *c*-C_6D_{12}): δ 17.4.

3. NMR spectroscopic data and comparison with computational results

Table S2. Experimental (400 MHz, *c*-C_6D_{12}) and computed (B3LYP/6-311+G**) ^{1}H and ^{13}C NMR shifts of **3** and **4**. The computed spectra were referenced to $SiMe_4$ (B3LYP/6-311+G**). The computed ^{11}B downfield shift of **4** compared to **3** is 13.0 ppm (B3LYP/6-311+G**).

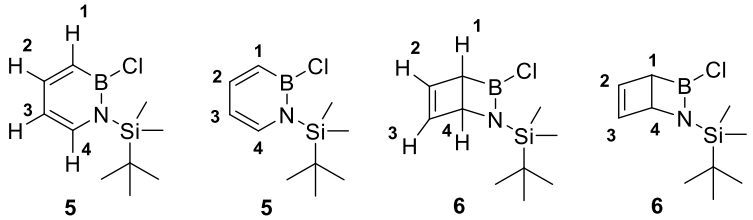


Assignment	3		4	
	δ_{exp} [ppm]	δ_{theor} [ppm]	δ_{exp} [ppm]	δ_{theor} [ppm]
B	40.3		52.9	53.3
H^1	6.56	6.85	3.00	3.16
H^2	7.45	7.90	6.49	7.05
H^3	6.27	6.59	6.32	6.84
H^4	7.37	7.62	4.75	4.84
C^1	133 (br.)	138.36	44 (br.)	47.52
C^2	143.0	149.97	143.9	154.13
C^3	112.2	116.97	139.6	148.12
C^4	138.2	147.24	64.1	67.45

Table S3. Computed total nuclear spin-spin coupling constants of **3** and **4** (B3LYP/6-311+G**).

	3	4
	J [Hz]	J [Hz]
H^1-H^4	0.73	2.54
H^2-H^4	0.95	1.64
H^3-H^4	8.09	0.03
H^1-H^2	12.16	1.14
H^1-H^3	1.24	0.72
H^2-H^3	7.32	2.65

Table S4. Experimental (400 MHz, *c*-C_6D_{12}) and computed (B3LYP/6-311+G**) ^{1}H- and ^{13}C-NMR shifts of **5** and **6**. The computed spectra were referenced to $SiMe_4$ (B3LYP/6-311+G**) for ^{1}H and ^{13}C. The computed ^{11}B downfield shift of **6** compared to **5** is 7.3 ppm (B3LYP/6-311+G**).



Assignment	5		6	
	δ_{exp} [ppm]	δ_{theor} [ppm]	δ_{exp} [ppm]	δ_{theor} [ppm]
B	35.7		42.4	43.0
H^1	6.59	6.96	2.89	2.98
H^2	7.39	7.73	6.43	6.93
H^3	6.17	6.45	6.19	6.60
H^4	7.14	7.46	4.47	4.52
C^1	130 (br.)	135.84	43 (br.)	47.31
C^2	145.0	151.18	143.0	153.00
C^3	111.9	117.07	140.0	148.21
C^4	138.1	146.38	60.5	64.15

Table S5. Computed (B3LYP/6-311+G**) total nuclear spin-spin couplings constants of **5** and **6**.

	5	**6**
	J [Hz]	J [Hz]
H^1-H^4	0.63	2.73
H^2-H^4	1.12	1.71
H^3-H^4	8.08	0.05
H^1-H^2	12.42	1.35
H^1-H^3	1.13	0.83
H^2-H^3	7.32	2.69

4. NMR Spectra

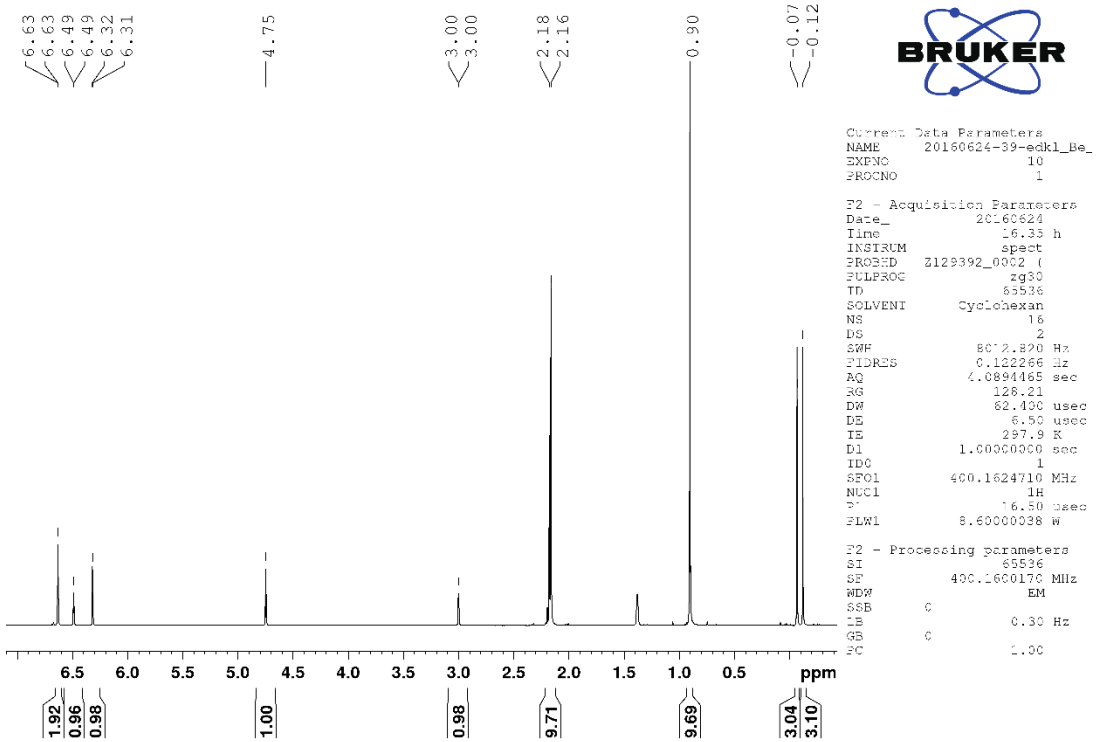


Figure S6. ^{1}H NMR (400 MHz, *c*-C_6D_{12}) spectrum of **4**.

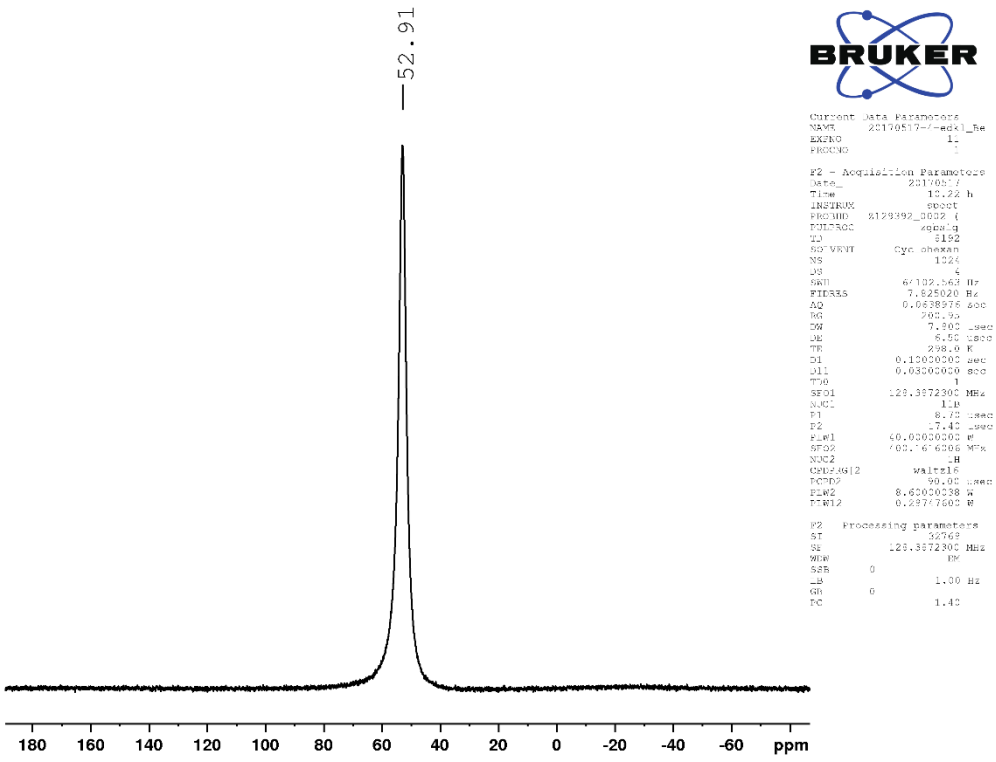


Figure S7. $^{11}B\{^{1}H\}$ NMR (400 MHz, *c*-C_6D_{12}) spectrum of **4**.

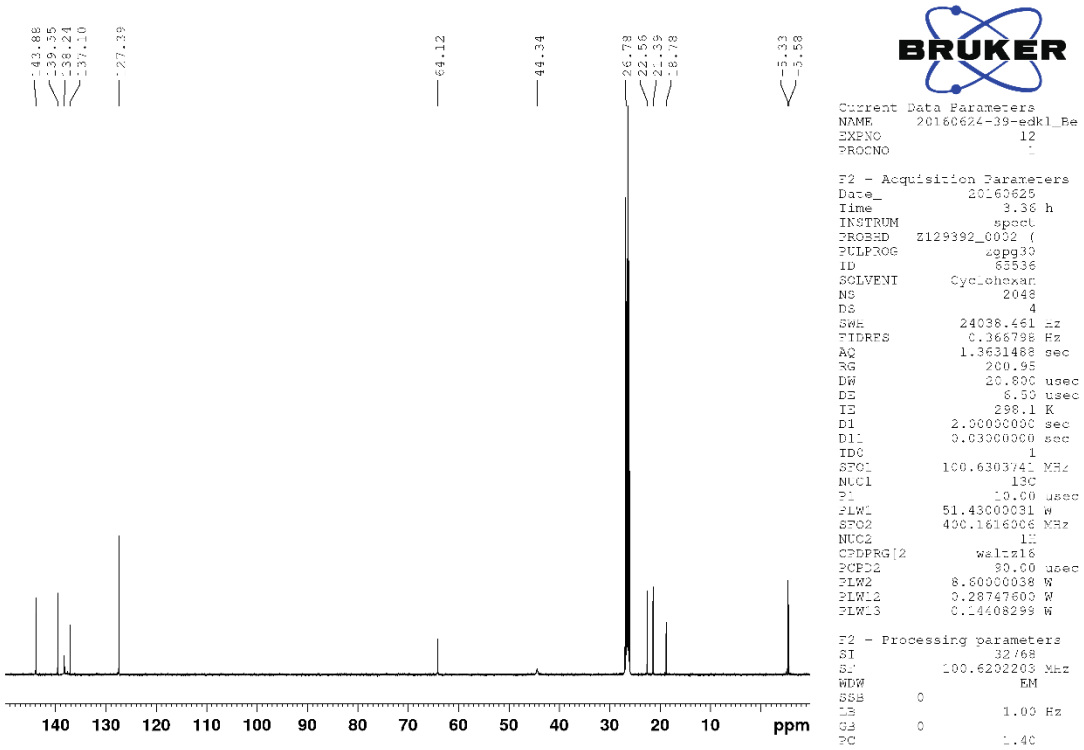


Figure S8. $^{13}C\{^{1}H\}$ NMR (400 MHz, *c*-C_6D_{12}) spectrum of **4**.

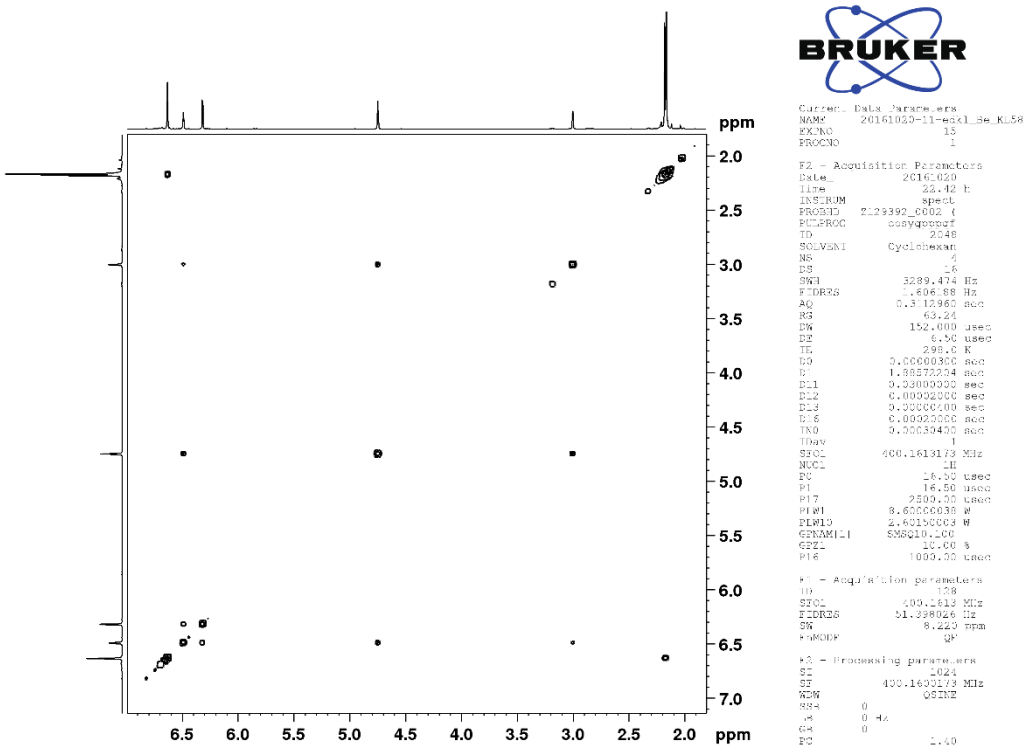


Figure S9. ^{1}H,^{1}H-COSY NMR (400 MHz, *c*-C_6D_{12}) spectrum of **4**.

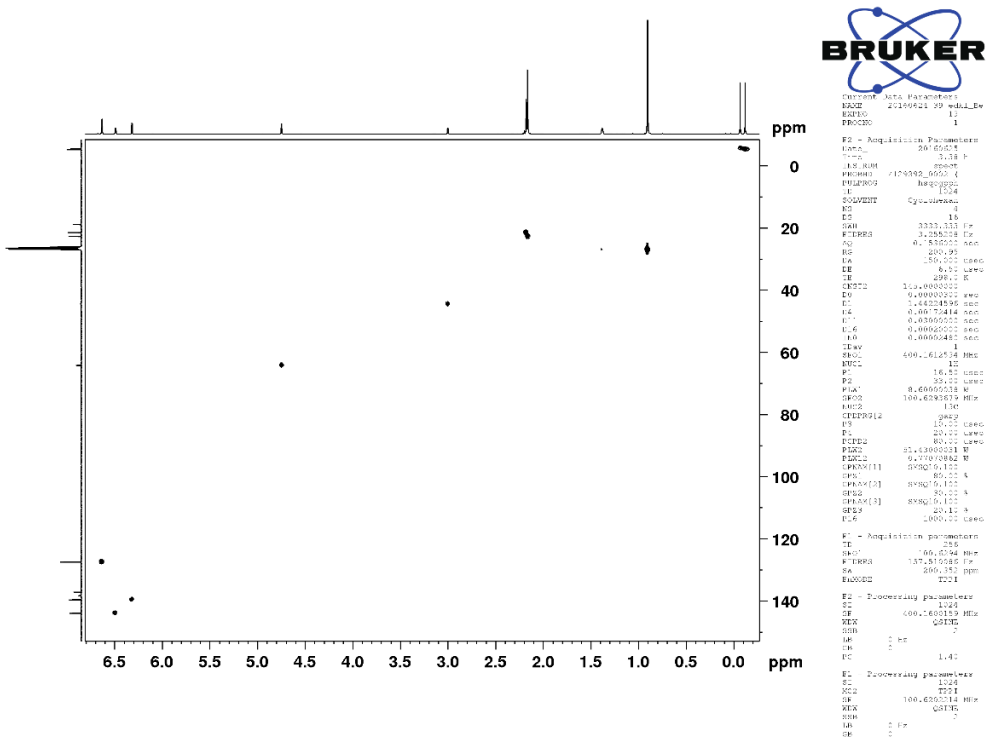


Figure S10. ^{1}H,^{13}C-HSQC NMR (400 MHz, *c*-C_6D_{12}) spectrum of **4**.

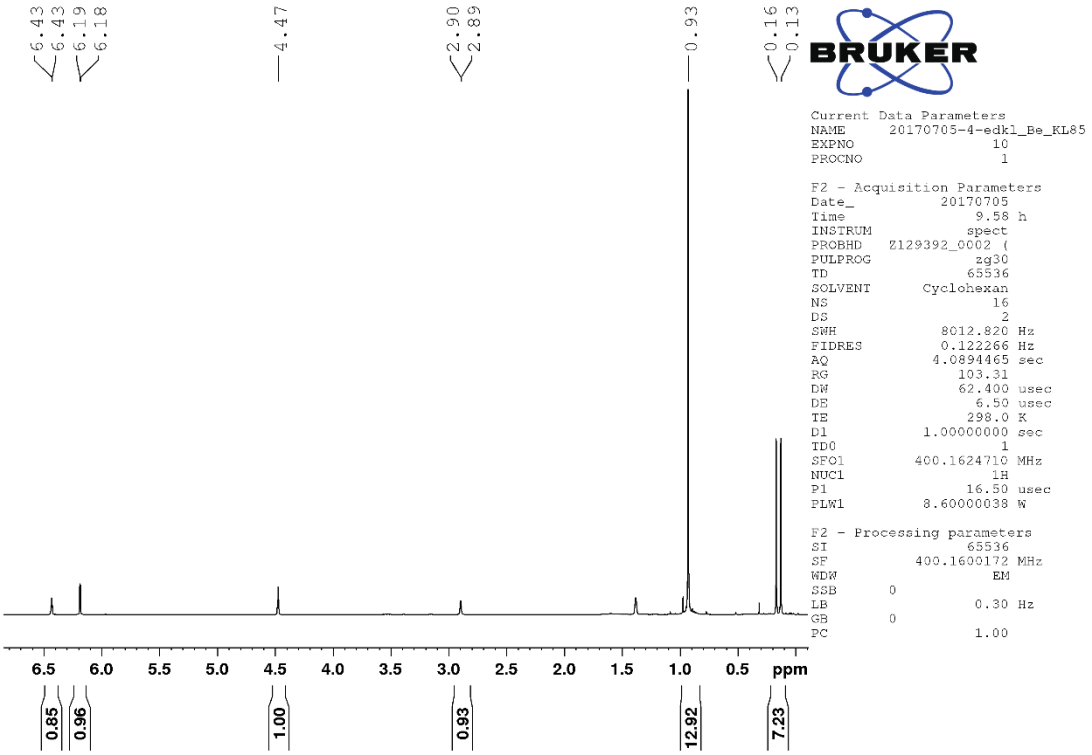


Figure S11. ^{1}H NMR (400 MHz, *c*-C_6D_{12}) spectrum of **6**.

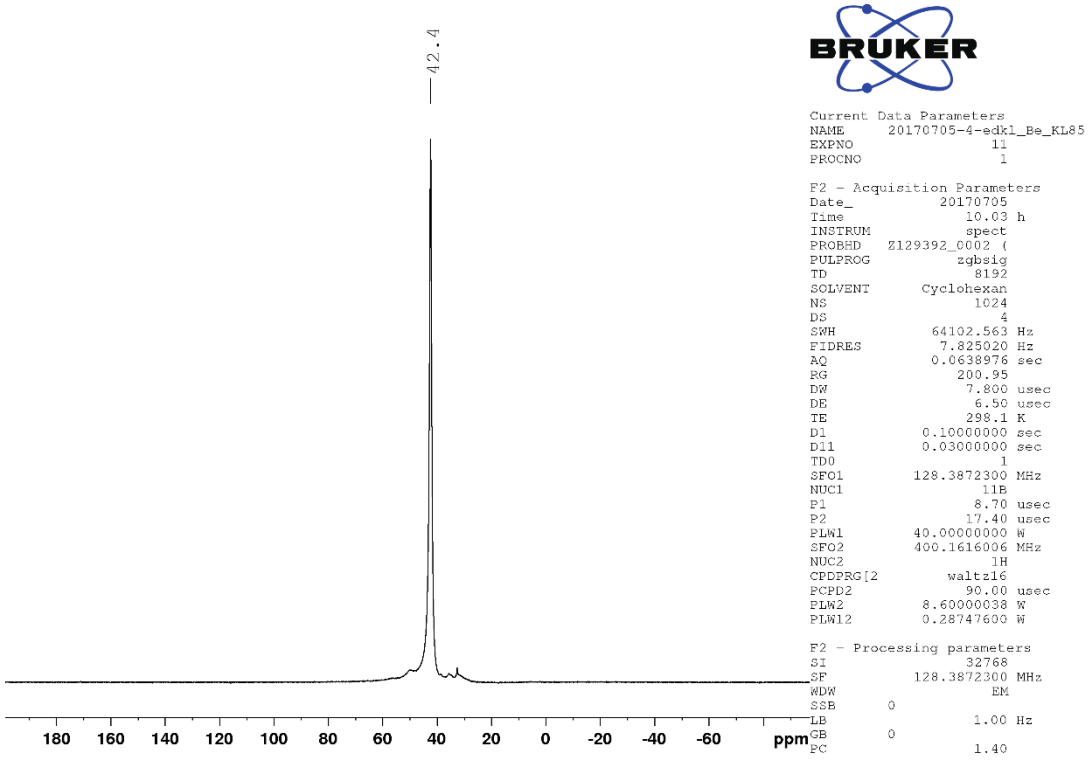


Figure S12. ^{11}B{^{1}H} NMR (400 MHz, *c*-C_6D_{12}) spectrum of **6**.

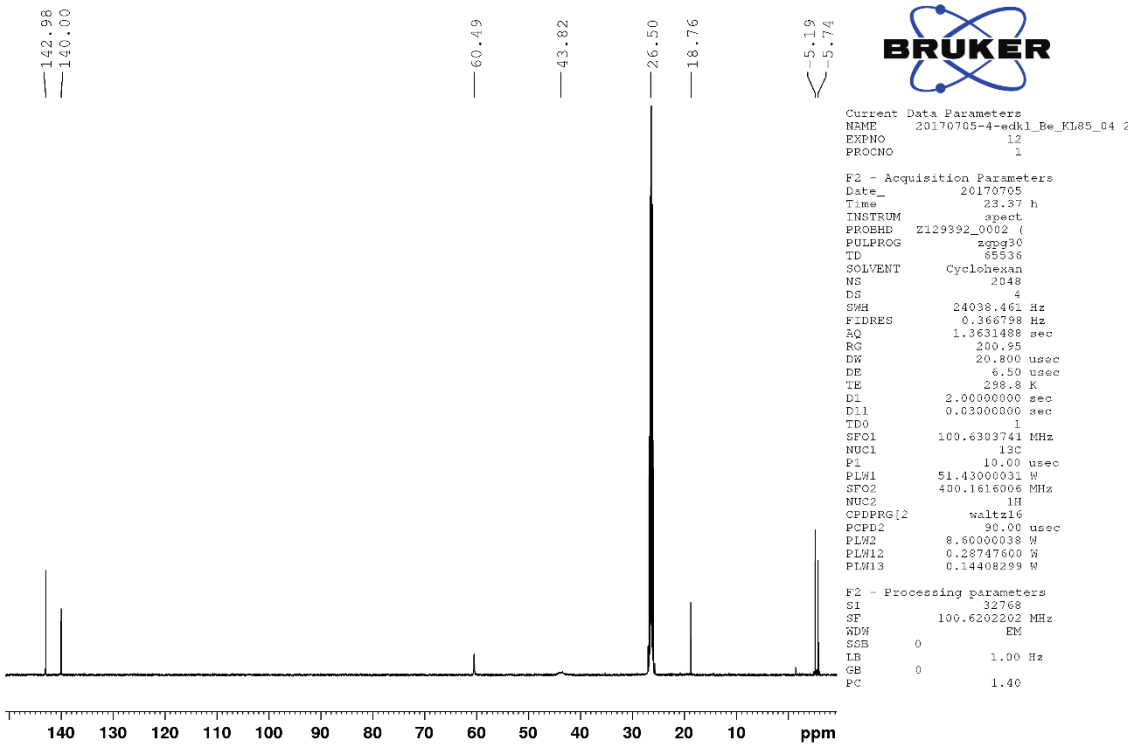


Figure S13. $^{13}C\{^{1}H\}$ NMR (400 MHz, *c*-C_6D_{12}) spectrum of **6**.

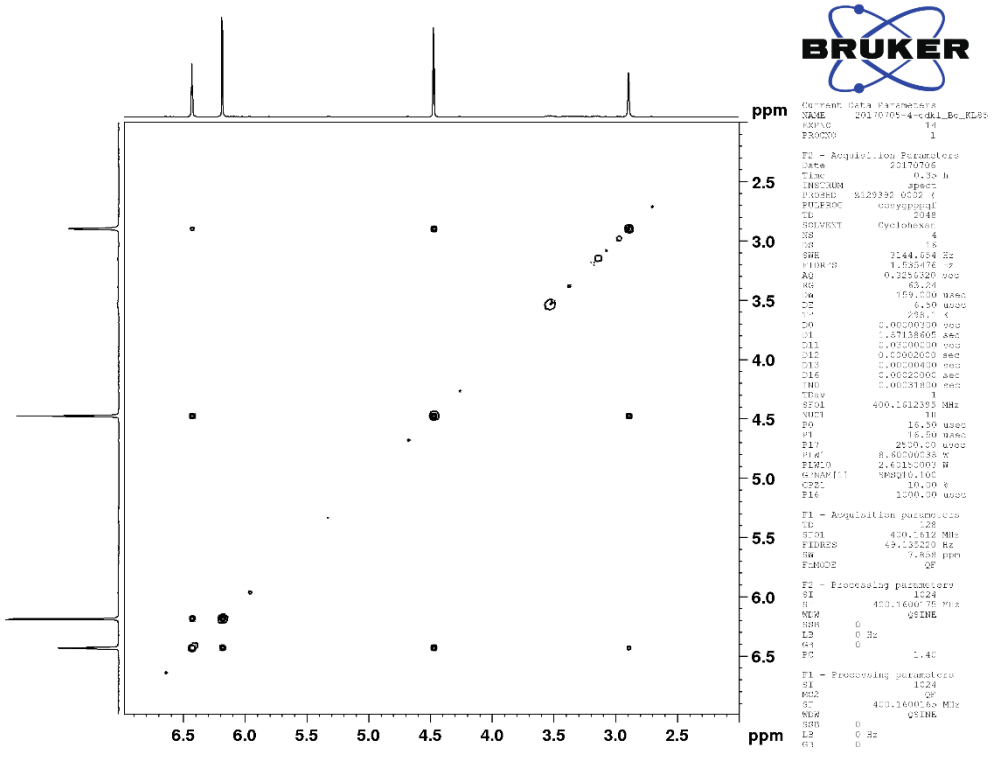


Figure S14. $^{1}H,^{1}H$-COSY NMR (400 MHz, *c*-C_6D_{12}) spectrum of **6**.

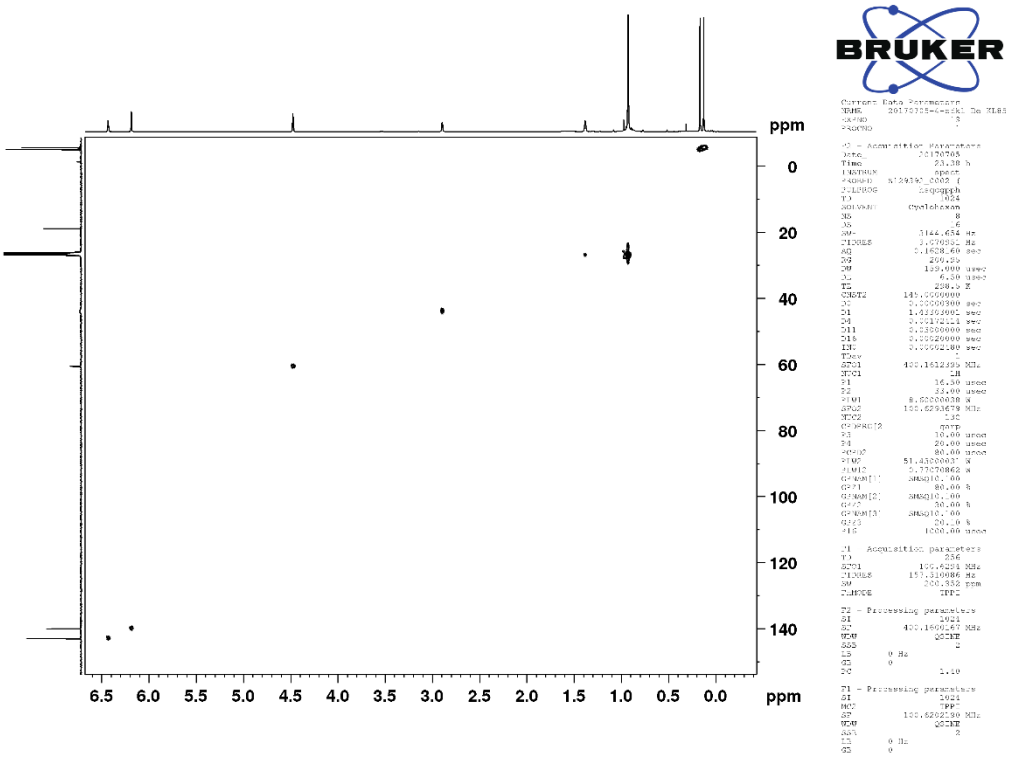


Figure S15. $^{1}H,^{13}C$-HSQC NMR (400 MHz, *c*-C_6D_{12}) spectrum of **6**.

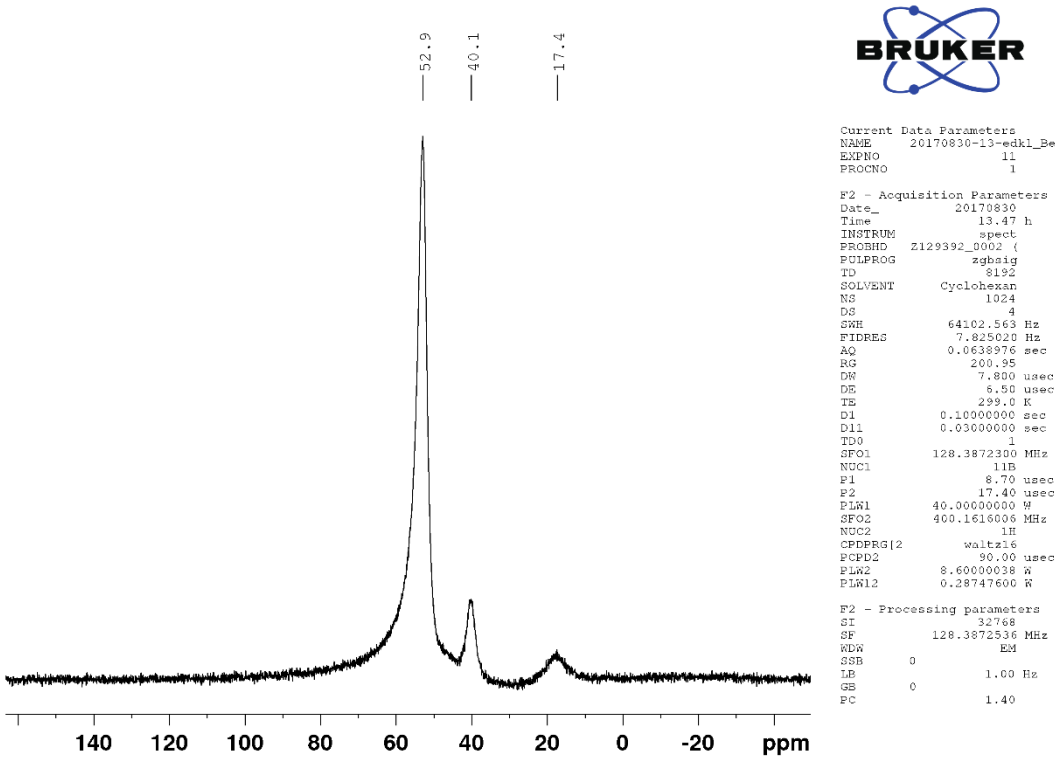


Figure S16. $^{11}B\{^{1}H\}$ NMR (400 MHz, *c*-C_6D_{12}) spectrum after photolysis of **4** with UV light (254 nm) indicating the formation of **9** by the signal at 17.4 ppm. The signal at 53 ppm belongs to **4** and the signal at 40 ppm belongs to **3**.

5. Results of Matrix Isolation Study

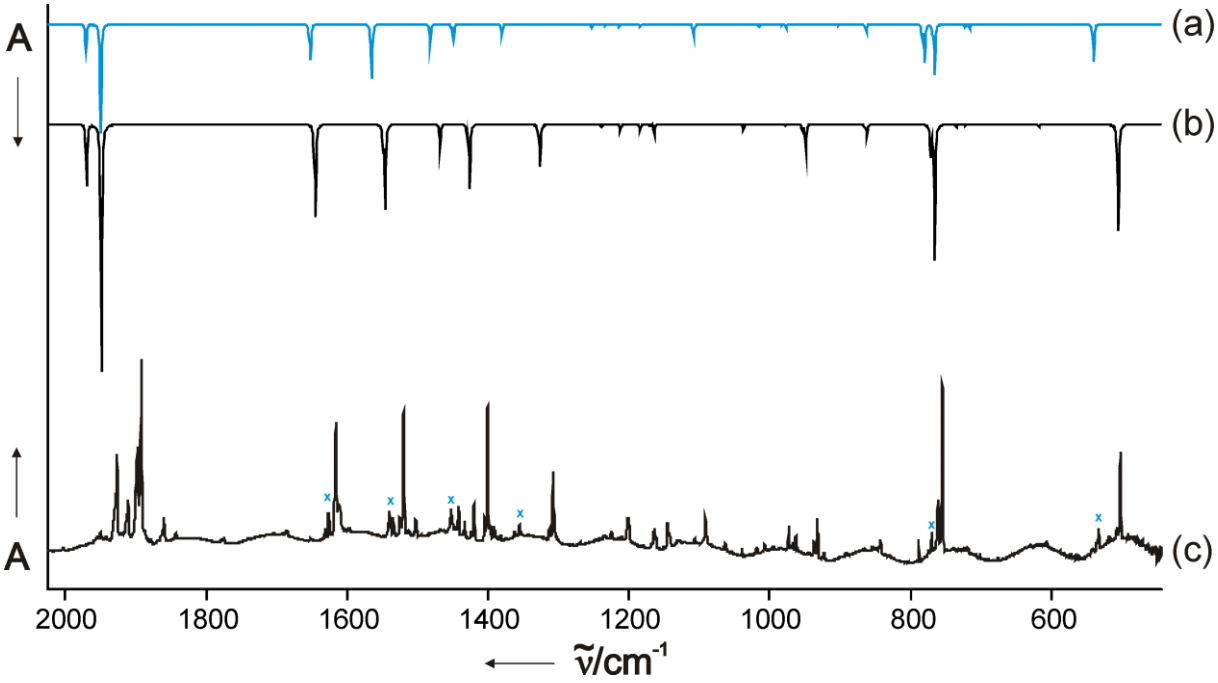


Figure S17. 1,2-Dideuterio-1,2-azaborinine. Computed (B3LYP/6-311+G**) IR spectra of 1-hydro-2-deuterio-1,2-azaborinine (trace a) and of 1,2-dideuterio-1,2-azaborinine (trace b) compared with the observed IR spectrum (Ne, 4 K, trace c) of 1,2-dideuterio-1,2-azaborinine. Signals that belong to 1-hydro-2-deuterio-1,2-azaborinine are marked (**x**).

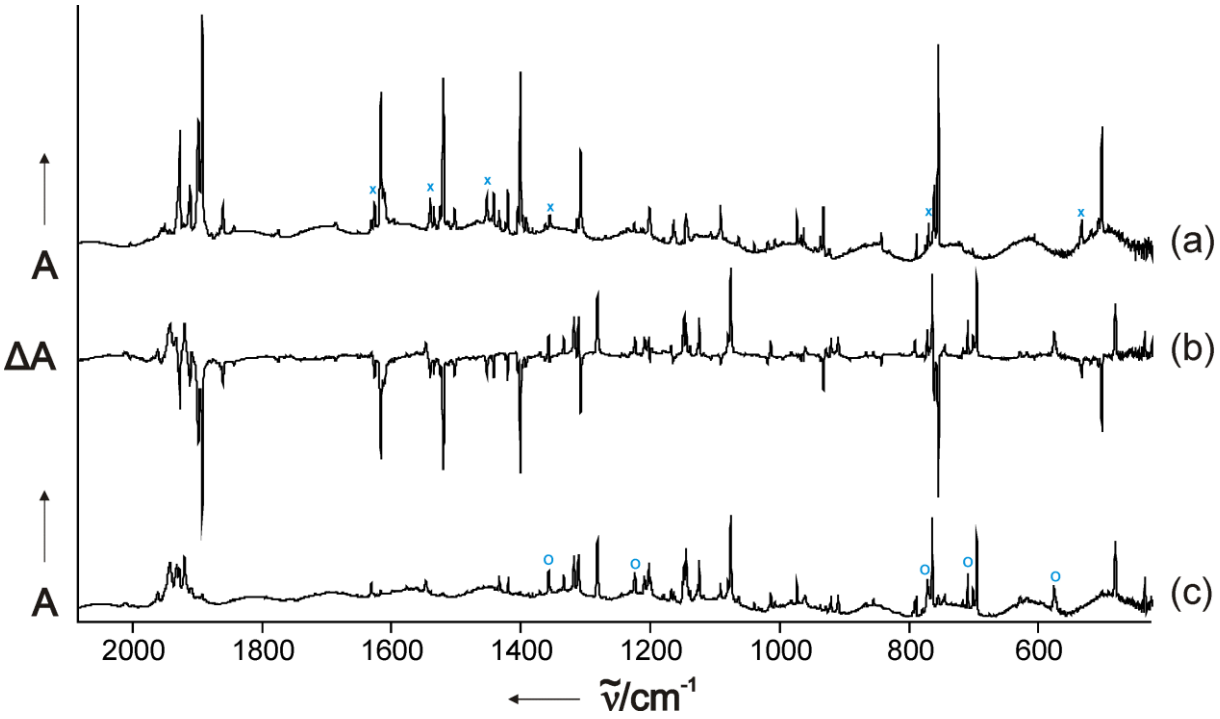


Figure S18. Observed IR spectra (Ne, 4 K) a) before and c) after irradiation (60 min, λ = 254 nm) of 1,2-dideuterio-1,2- azaborinine; b) difference spectrum: bands pointing downwards disappear and bands pointing upwards appear during irradiation. Signals that belong to 1-hydro-2-deuterio-1,2-azaborinine (**x**) and its Dewar valence isomer (**o**) are marked.

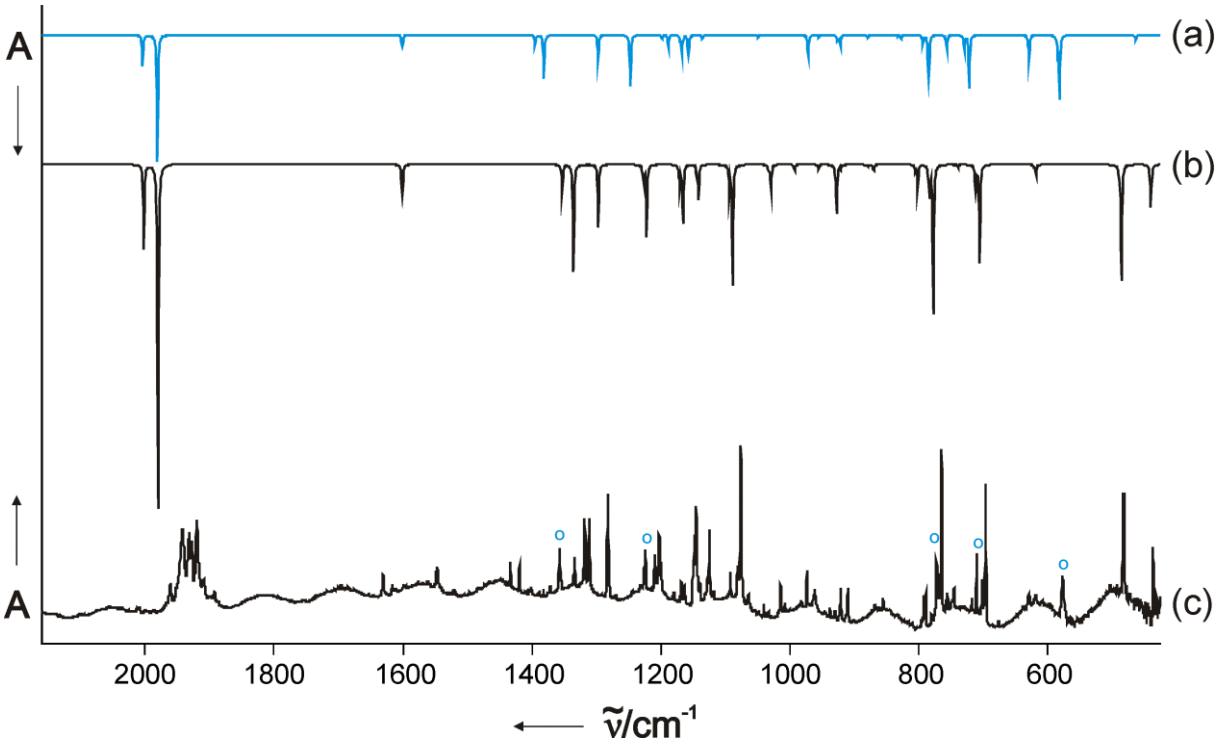


Figure S19. Dewar valence isomer of 1,2-Dideuterio-1,2-azaborinine. Computed (B3LYP/6-311+G**) IR spectra of the Dewar valence isomers of 1-hydro-2-deuterio-1,2-azaborinine (trace a) and of 1,2-dideuterio-1,2-azaborinine (trace b) compared with the observed IR spectrum after irradiation (60 min 254 nm, Ne, 4 K, trace c) of 1,2-dideuterio-1,2-azaborinine. Signals that belong to the Dewar valence isomer of 1-hydro-2-deuterio-1,2-azaborinine are marked (**o**).

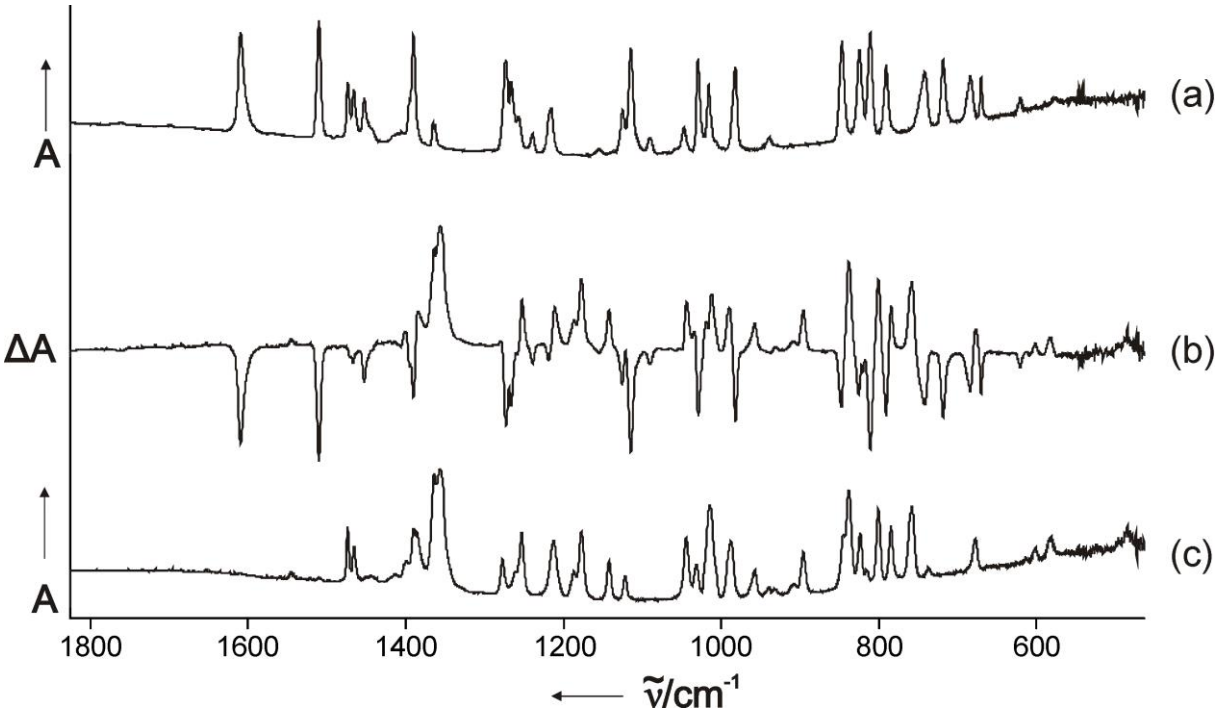


Figure S20. Observed IR spectra (Ar, 4 K) a) before and c) after irradiation (260 min, λ = 280-400 nm) of **5**; b) difference spectrum: bands pointing downwards disappear and bands pointing upwards appear during irradiation. The bands at 1473.8 and 1466.2 cm^{-1} are probably due to an unknown contamination.

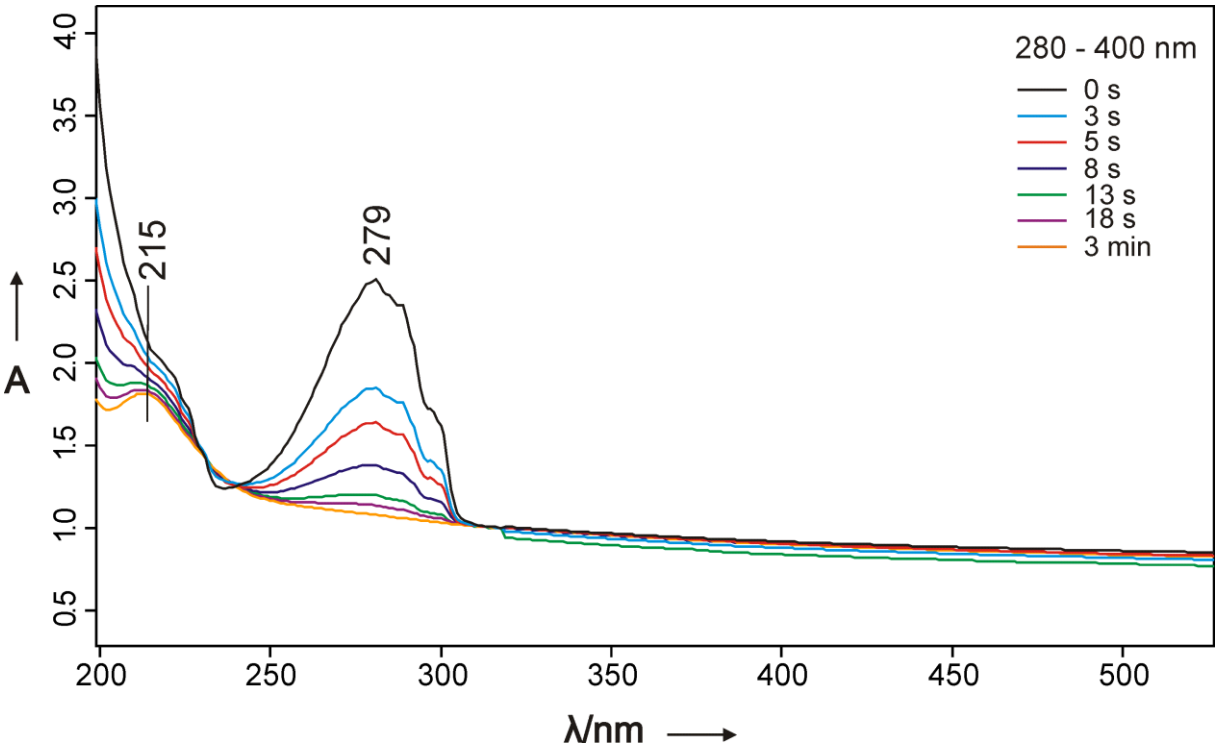


Figure S21. Observed UV/vis spectrum (Ar, 7 K) of **5** (black trace) and UV/vis spectra after irradiation with λ = 280-400 nm. After full conversion to **6** a band at 215 nm is observed.

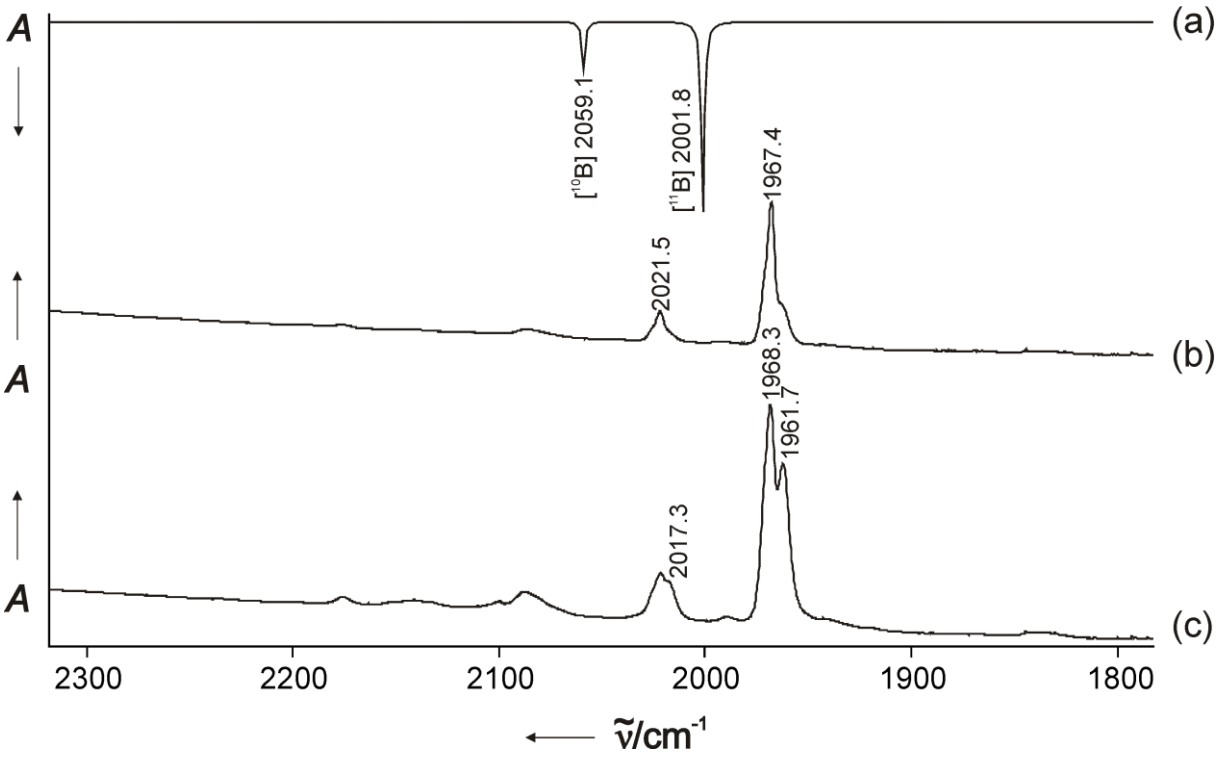


Figure S22. Computed (B3LYP/6-311+G**) IR spectrum (a) and observed (Ne, 4 K) and IR spectra of **7** after 3.5 hours (b) and 27 hours (c) of irradiation of **5** with 254 nm. The relative intensities of ^{11}B and ^{10}B are 4.5:1 in (b) and 4.4:1 in (c).

Table S6. Experimental and computed (B3LYP/6-311+G**) vibrational frequencies of 1,2-dihydro-1,2-azaborinine[19] (**1a**) and of 1,2-dideuterio-1,2-azaborinine (**1b**), computed intensities (in km mol^{-1}), and the corresponding isotopic shifts.

1a	**1b**		**1a**		**1b**			
ν_{exp} [cm^{-1}]	**ν_{exp} [cm^{-1}]**	**$\Delta\nu_{exp}$ [cm^{-1}]**	**ω_{theor} [cm^{-1}]**	**Intensity**	**ω_{theor} [cm^{-1}]**	**Intensity**	**$\Delta\omega_{theor}$ [cm^{-1}]**	**Assignment**
3046.3-3008.2	3046.3-2982.4		3201.5-3131.2		3201.5-3131.2			ν(CH)
3463.1	2564.1	899	3604.8	35.9	2640.9	25.4	963.9	ν(N-H,D)
2547.8-2527.0	1926.8-1892.4	621-634	2620.9	181.8	1949.5	136.7	671.4	ν(B-H,D)
1622.3	1616.1	6.2	1652.8	48.1	1645.5	48.9	7.3	ν(CC)
1543.4			1572.0	84.5	1549.7	45.8		ν(^{10}BN)
1540.1	1520.1	20.0	1569.0	84.0	1546.7	46.5	22.3	ν(^{11}BN)
1453.6, 1460.7			1486.8	32.2				δ(in-plane)
1430.3	1400.1	30.2	1459.5	21.3	1426.5	34.69	33.0	δ(in-plane)
	1307.7				1326.4	23.0		δ(in-plane) ν(BN)
903.4			924.4	49.3				δ(out-of-plane) ^{10}B
897.4			914.6	47.8				δ(out-of-plane) ^{11}B
816.7			830.5	21.2				δ(out-of-plane)
	754.8				766.1	74.7		δ(out-of-plane)
709.2			722.9	35.5				δ(out-of-plane)
574.2	502.2	72.0	584.4	67.5	505.6	52.6	78.8	δ(out-of-plane)

Table S7. Experimental and computed (B3LYP/6-311+G**) vibrational frequencies of Dewar valence isomer of 1,2-dihydro-1,2- azaborinine[19] (**2a**) and of 1,2-dideuterio-1,2-azaborinine (**2b**), computed intensities (in km mol^{-1}), and the corresponding isotopic shifts.

2a	**2b**		**2a**		**2b**			
ν_{exp} [cm^{-1}]	**ν_{exp} [cm^{-1}]**	**$\Delta\nu_{exp}$ [cm^{-1}]**	**ω_{theor} [cm^{-1}]**	**Intensity**	**ω_{theor} [cm^{-1}]**	**Intensity**	**$\Delta\omega_{theor}$ [cm^{-1}]**	**Assignment**
3117.8-2958.5	3117.8-2958.5		3199.3-3086.0		3199.3-3086.0			ν(CH)
3482.2	2585.0	897.2	3618.2	16.6	2655.7	15.3	962.5	ν(N-H,D)
2602.3-2566.5	1913.2-1948.0	618.5-689.1	2653.4[^{11}B] 2666.4[^{10}B]	177.8	1980.3[^{11}B] 2002.8[^{10}B]	129.0 137.3	673.1 663.6	ν(B-H,D)
	1546.7				1601.6	9.49		ν(CC)
1392.8	1333.7	59.1	1417.4	61.2	1353.7	43.4	63.7	ν(^{10}BN)
1374.5	1318.0; 1310.8	56.5; 63.7	1398.5	58.2	1335.3	40.5	63.2	ν(^{11}BN)
1283.6	1281.9	1.7	1298.0	23.0	1297.5	18.8	0.5	δ(in-plane)
1229.8	1075.6		1253.5	61.9	1088.4	45.0		ν(CN) δ(ring) [^{11}B]
1179.7	1202.3	-22.6	1201.5	16.6	1222.9	27.0	-21.4	δ(ring)
	1126.8		1179.3	18.0	1144.6	18.3	34.7	δ(ring) [^{10}B]
1161.0	1124.3	36.7	1175.2	20.7	1141.4	12.8	33.8	δ(ring) [^{11}B]
1143.7	1144.7	-1	1164.2	13.4	1165.5	19.9	-1.3	δ(out-of-plane)
	1080.3				1093.3	44.9		ν(CN) δ(ring) [^{10}B]
1039.3	1014.0	25.3	1055.2	1.2	1029.7	10.0	25.5	δ(out-of-plane)
	920.7; 909.6		924.3	13.6	927.7	16.4	-3.4	δ(ring)
	790.5				801.5	9.1		δ(out-of-plane)
753.0	769.4	-16.4	767.1	73.6	783.3	48.7	-16.2	δ(CH,^{10}BH)
747.6	764.2	-16.6	762.3	82.8	777.1	55.7	-14.8	δ(CH,^{11}BH)
	701.1		730.9	21.8	711.5	40.8	19.4	δ(CH,^{10}BH)
716.6	695.6	21.0	723.9	13.1	705.3	36.8	18.6	δ(CH,^{11}BH)
582.7	481.2	101.5	589.9	90.5	485.6	39.1	104.3	δ(NH,D)
468.3	435.7	32.6	472.2	4.5	439.4	12.9	32.8	δ(ND)

Table S8. Experimental vibrational frequencies of **5** in a neon and in an argon matrix.

Neon		Argon	
ν_{exp} [cm^{-1}]	rel. Intensity	ν_{exp} [cm^{-1}]	rel. Intensity
3090.7, 3081.2, 3054.8, 3046.8, 3042.3, 3004.7, 2971.0, 2948.7, 2939.6, 2907.4, 2888.9, 2871.0	2.91	3073.7, 3043.8, 3001.3, 2969.7, 2964.6, 2956.4, 2946.9, 2941.2, 2936.5, 2865.8	2.88
1614.1	1.00	1611.8	1.00
1512.7	0.67	1510.6	0.66
1476.7, 1469.4	0.62	1474.4, 1466.5, 1453.3	0.58
1398.9, 1393.5	0.64	1396.2, 1390.8	0.60
1369.2, 1365.8	0.09	1366.0, 1362.7	0.07
1280.1, 1275.4, 1269.6,1260.0	1.16	1274.5, 1267.0, 1258.1	1.09
1240.4	0.07	1238.3	0.08
1216.9	0.36	1214.6	0.31
1130.1, 1127.0, 1118.1, 1114.8	1.20	1125.4, 1114.6	1.04
1090.1	0.08	1088.2	0.06
1049.4	0.09	1047.2	0.12
1031.2	0.53	1029.7	0.45
1017.9	0.27	1015.4	0.23
982.9	0.56	980.8	0.56
848.8	0.61	846.5	0.65
826.2, 812.5	1.53	825.7, 823.7, 810.0	1.48
791.5	0.39	790.8	0.37
741.0	0.38	740.9, 739.0	0.41
720.5	0.36	719.0	0.39
688.2, 684.9	0.24	689.5, 686.5, 681.6	0.26
671.5	0.06	670.2	0.07
621.6	0.03	620.7	0.03
573.6	0.03	575.7	0.03
438.7	0.15	435.3	0.20
419.9	0.05	419.5	0.05

Table S9. Experimental vibrational frequencies of the Dewar isomer of **6** in a neon and in an argon matrix.

Neon		**Argon**
ν_{exp} [cm^{-1}]	**rel. Intensity**	**ν_{exp} [cm^{-1}]**
3119.2	0.02	3113.1
3062.5, 3051.3	0.06	3046.8, 3044.7
2964.4, 2938.5, 2914.8, 2906.9, 2893.2, 2869.3	1.22	2962.2, 2953.4, 2939.3, 2905.9, 2888.3, 2869.1
1477.2, 1469.2	0.16	1473.8, 1466.2
1393.2, 1389.2	0.23	1383.0
1366.8, 1364.8, 1358.0	1.00	1363.3, 1352.9
1280.2, 1255.7	0.33	1278.5, 1261.2, 1253.1
1213.5	0.22	1216.0
1190.1, 1180.0	0.24	1192.1, 1182.7
1144.0	0.08	1145.0
1124.2	0.03	1122.9
1046.2	0.19	1046.3
1036.2	0.04	1038.6
1018.9, 1007.6	0.46	1022.2, 1017.7
990.1	0.17	991.1
958.8	0.06	958.1
897.3	0.08	899.6, 896.1
846.6, 841.1	0.41	846.6, 838.7
824.4	0.12	822.9
802.1	0.16	801.0
786.0	0.13	784.1
758.8	0.22	
679.0	0.07	675.4
		600.8
584.3	0.06	582.5
		496.0

6. Results of Computational Chemistry Investigation

Table S10. Absolute energies (in a.u.) and relative energies including zero point vibrational energy corrections and relative Gibbs free energies (in kcal/mol) computed at the B3LYP/6-31G* level of theory and comparison with CCSD(T)/cc-pVQZ//CCSD(T)/TZ2P (ZPVE were obtained at CCSD(T)/DZP).

	E_{min} [a.u.]	ΔE_{ZPVE} [kcal/mol]	ΔG [kcal/mol]	ΔE_{ZPVE}[a] [kcal/mol]
1	-235.74590	-64.4	-64.4	-59.3
TS min→1	-235.60918	18.2	18.1	19.1
min	-235.61432	15.5	15.3	17.8
TS 2→min	-235.60874	18.8	18.8	22.2
2	-235.64030	0	0	0
3	-1111.54627	-51.9	-50.9	
TS 4→3	-1111.41677	26.1	26.7	
4	-1111.46071	0	0	
5	-1222.13191	-54.3	-53.5	
TS 6→5	-1221.99400	28.8	29.3	
6	-1222.04272	0	0	

[a] Data taken from Reference [20]

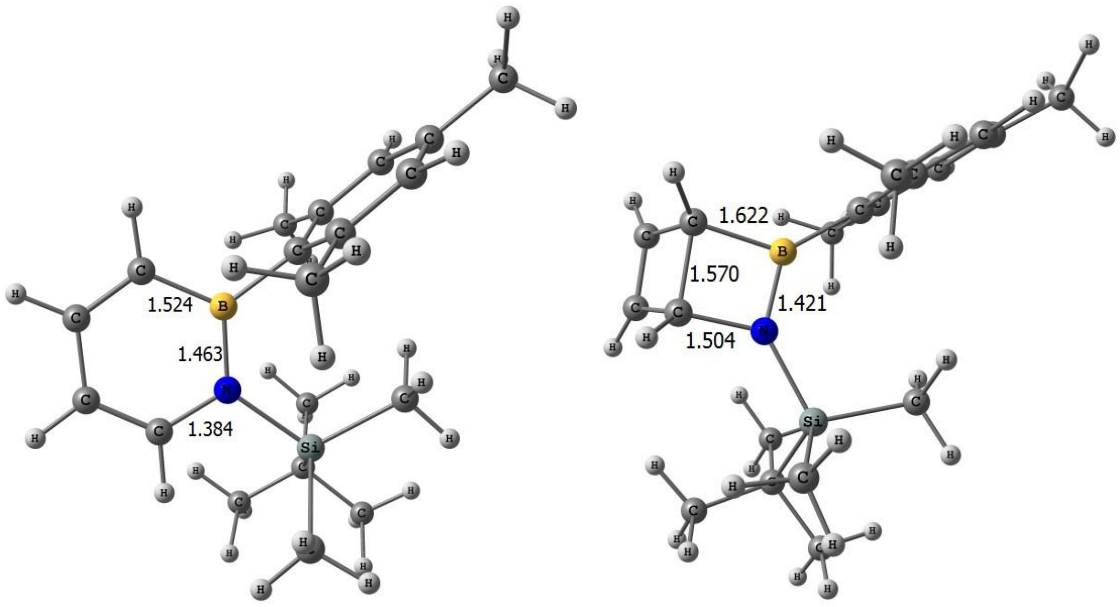


Figure S23. Geometry of **3** (left) and **4** (right) computed at the B3LYP/6-311+G** level of theory. Bond lengths are given in angstroms (Å).

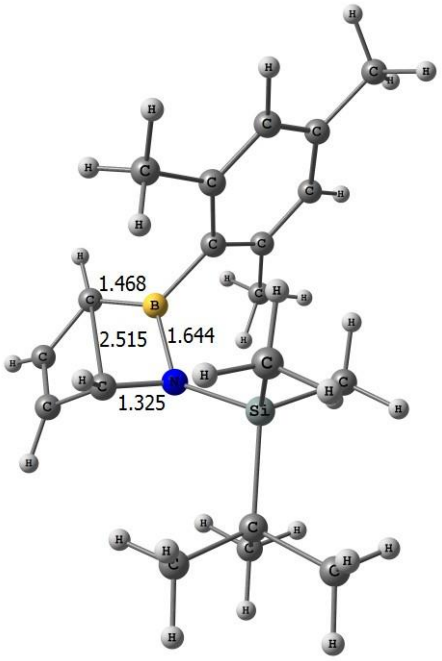


Figure S24. Geometry of **TS 4→3** computed at the B3LYP/6-311+G** level of theory. Bond lengths are given in angstroms (Å).

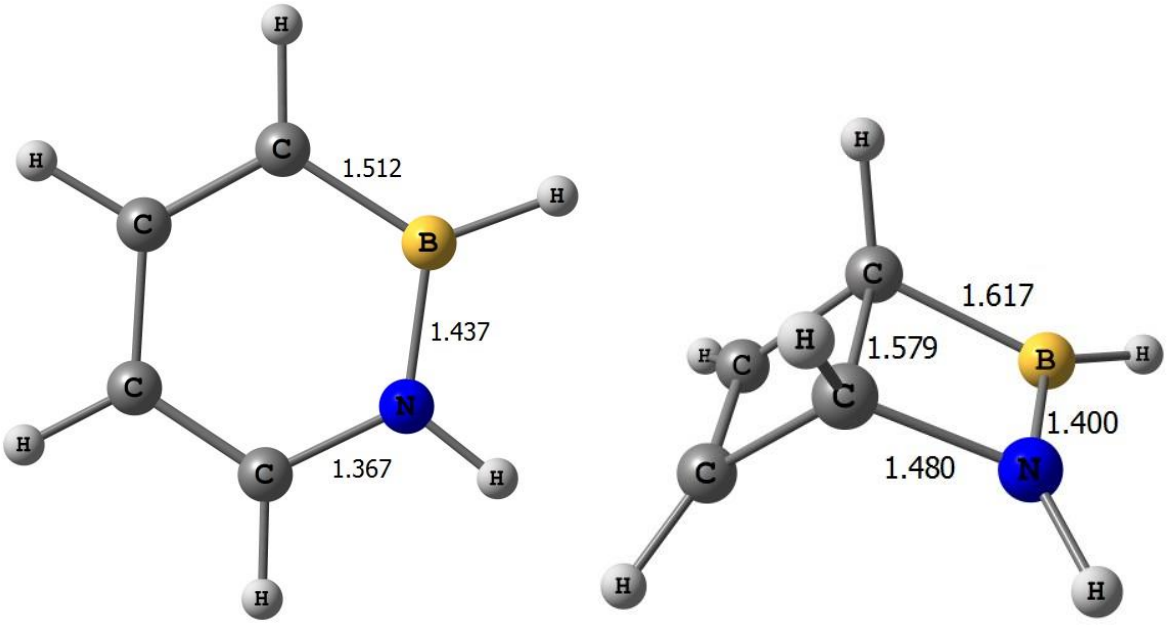


Figure S25. Geometry of **1** (left) and **2** (right) computed at the B3LYP/6-311+G** level of theory. Bond lengths are given in angstroms (Å).

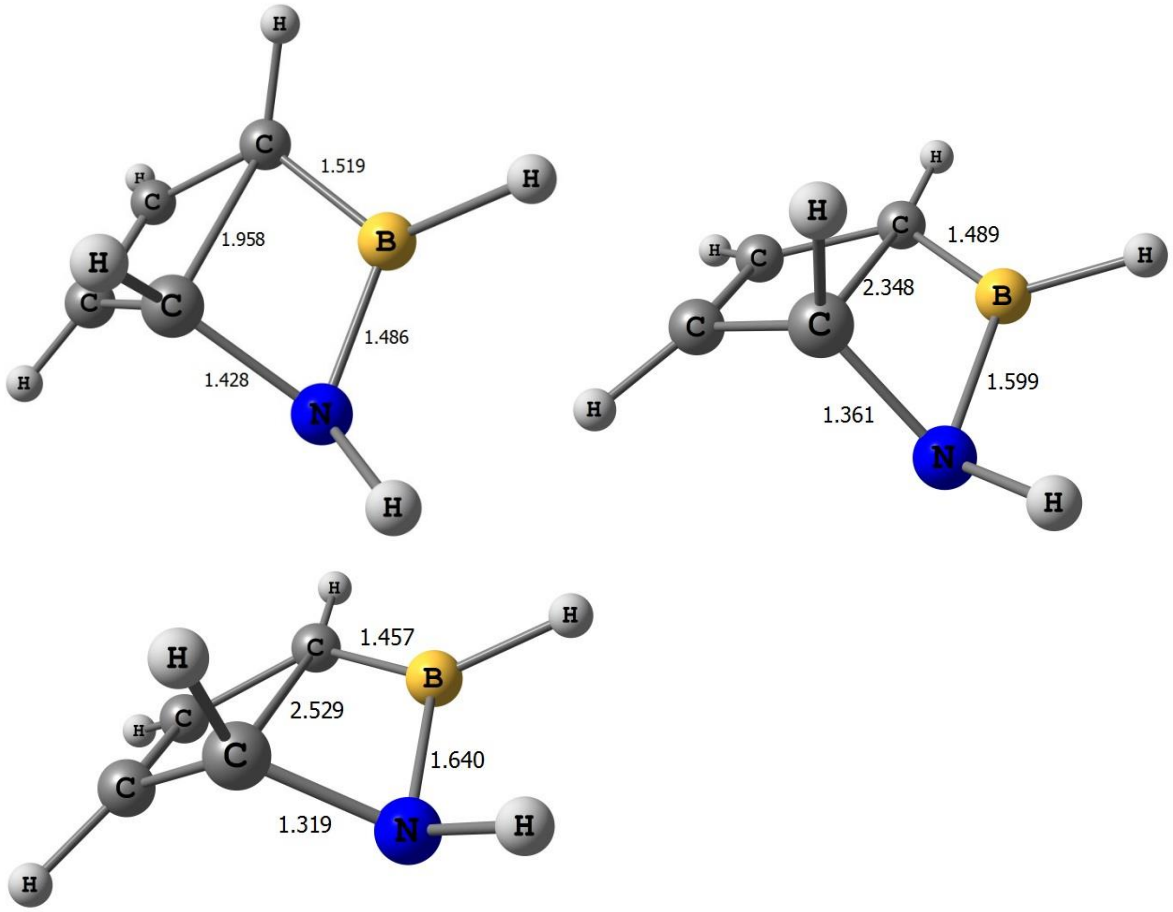


Figure S26. Geometry of **TS 2→min** (left top), **min** (right) and **TS min→1** (left bottom) (see Table S10) computed at the B3LYP/6-311+G** level of theory. Bond lengths are given in angstroms (Å).

7. Cartesian Coordinates of Optimized Structures

B3LYP/6-311+G**, in Ångstrom

Compound **1**

```
12
6       -0.050385000     -1.473777000      0.000000000
6       -1.208972000     -0.732899000      0.000000000
6       -1.189687000      0.689954000      0.000000000
6        0.000000000      1.361460000      0.000000000
7        1.185211000      0.680966000      0.000000000
5        1.278539000     -0.753307000      0.000000000
1       -0.135933000     -2.556229000      0.000000000
1        0.050781000      2.443956000      0.000000000
1       -2.113703000      1.253773000      0.000000000
1       -2.180796000     -1.221292000      0.000000000
1        2.019278000      1.251254000      0.000000000
1        2.365461000     -1.240119000      0.000000000
```

Compound **2**

```
12
6       -1.368989000      0.579606000     -0.281142000
6       -0.093743000      0.881754000      0.497288000
6       -1.225209000     -0.752825000     -0.260512000
1       -0.173056000      1.466623000      1.414299000
1       -1.764931000     -1.575576000     -0.713598000
5        1.292405000      0.796013000     -0.330326000
6        0.061803000     -0.688668000      0.553955000
1        0.119975000     -1.222720000      1.503362000
7        1.330107000     -0.597435000     -0.203333000
1       -2.100995000      1.238739000     -0.734348000
1        1.856652000     -1.366986000     -0.588767000
1        2.046406000      1.542702000     -0.863521000
```

Compound **3**

```
52
6       -2.106172000      1.908540000      0.206275000
6        0.333910000      2.848352000     -0.788093000
5        0.244228000      1.421294000     -0.261346000
7       -1.073117000      0.987159000      0.205027000
1       -3.056869000      1.574302000      0.603149000
1        1.267797000      3.247685000     -1.175066000
14      -1.593587000     -0.668425000      0.785559000
6       -0.145799000     -1.821420000      1.099933000
1       -0.549364000     -2.763968000      1.484305000
1        0.446473000     -2.040418000      0.211517000
1        0.533487000     -1.423691000      1.855017000
6       -2.785520000     -1.480103000     -0.500968000
6       -2.477593000     -0.402553000      2.435755000
1       -2.628728000     -1.365266000      2.932907000
1       -1.865739000      0.216321000      3.098703000
1       -3.455741000      0.075567000      2.346367000
6       -2.036270000     -1.755074000     -1.820496000
1       -1.680265000     -0.831172000     -2.283632000
1       -1.175864000     -2.414100000     -1.674657000
1       -2.705199000     -2.246536000     -2.538028000
6       -3.275103000     -2.825734000      0.085526000
1       -2.452974000     -3.517351000      0.288673000
1       -3.840070000     -2.689424000      1.012655000
1       -3.942771000     -3.319313000     -0.631207000
6       -4.026154000     -0.618436000     -0.817101000
1       -4.692540000     -1.168887000     -1.492945000
1       -4.606934000     -0.378029000      0.079058000
1       -3.762753000      0.317912000     -1.314477000
6       -0.763111000      3.666594000     -0.763271000
6       -1.997234000      3.191277000     -0.244364000
1       -0.714308000      4.691690000     -1.124146000
```

1	-2.866203000	3.836024000	-0.195798000
6	1.563752000	0.542724000	-0.175271000
6	2.318421000	0.537804000	1.023774000
6	2.095236000	-0.125219000	-1.295135000
6	3.523965000	-0.159022000	1.092981000
6	3.308174000	-0.819517000	-1.191419000
6	4.034027000	-0.859346000	-0.004651000
1	4.087873000	-0.146974000	2.022246000
1	3.698221000	-1.329852000	-2.068314000
6	1.845497000	1.304013000	2.241782000
1	1.653099000	2.354128000	2.002167000
1	0.911892000	0.899367000	2.646787000
1	2.591141000	1.271894000	3.039184000
6	5.335188000	-1.618616000	0.099884000
1	6.136601000	-0.983732000	0.489850000
1	5.241643000	-2.473607000	0.777859000
1	5.652197000	-1.999830000	-0.873254000
6	1.384363000	-0.124512000	-2.632625000
1	0.738231000	-1.001690000	-2.744343000
1	0.757575000	0.760533000	-2.760380000
1	2.103517000	-0.148725000	-3.455570000

Compound **4**

52			
6	-1.465166000	2.026037000	0.798990000
6	-0.054467000	2.693479000	0.625990000
5	0.400420000	1.161810000	0.347887000
7	-0.918272000	0.656030000	0.503652000
1	-2.016884000	2.105696000	1.737050000
1	0.402260000	3.264640000	1.436150000
14	-1.735609000	-0.917500000	0.580206000
6	-0.456512000	-2.246309000	0.205192000
1	-0.889495000	-3.240115000	0.353093000
1	-0.085728000	-2.190667000	-0.821150000
1	0.408319000	-2.157408000	0.866811000
6	-3.198519000	-1.008440000	-0.669145000
6	-2.383335000	-1.139296000	2.341684000
1	-2.956634000	-2.065612000	2.444929000
1	-1.551035000	-1.187014000	3.050312000
1	-3.032243000	-0.314936000	2.650422000
6	-2.723898000	-0.592611000	-2.076754000
1	-2.342268000	0.431356000	-2.092011000
1	-1.931636000	-1.249075000	-2.450101000
1	-3.555604000	-0.650471000	-2.790629000
6	-3.726985000	-2.458942000	-0.729326000
1	-2.970267000	-3.157808000	-1.096841000
1	-4.068301000	-2.815745000	0.247645000
1	-4.583981000	-2.518201000	-1.412218000
6	-4.358122000	-0.087437000	-0.231881000
1	-5.177406000	-0.142315000	-0.960199000
1	-4.768321000	-0.380338000	0.738967000
1	-4.056340000	0.961098000	-0.164003000
6	-0.706569000	3.454266000	-0.515591000
6	-1.906227000	2.866095000	-0.393228000
1	-0.308546000	4.186694000	-1.209887000
1	-2.821995000	2.907251000	-0.970511000
6	1.779392000	0.459224000	0.091804000
6	2.266799000	0.274332000	-1.218871000
6	2.584822000	0.049358000	1.176070000
6	3.512779000	-0.324230000	-1.421748000
6	3.824949000	-0.547553000	0.938318000
6	4.306946000	-0.749568000	-0.356087000
1	3.874416000	-0.455626000	-2.438067000
1	4.432821000	-0.855635000	1.784795000
6	2.124668000	0.260442000	2.602989000
1	2.863491000	-0.111893000	3.315631000
1	1.963480000	1.322032000	2.817863000
1	1.179147000	-0.252735000	2.805096000
6	5.636389000	-1.424330000	-0.595764000
1	6.090968000	-1.087913000	-1.530744000
1	6.339534000	-1.220732000	0.215697000
1	5.519793000	-2.511994000	-0.661570000
6	1.452944000	0.717085000	-2.416083000
1	0.548069000	0.112411000	-2.534108000
1	1.128842000	1.757590000	-2.320691000

```
1        2.030542000      0.631587000     -3.338972000
```

Compound **5**

```
33
6       -1.274684000     -1.696363000      0.176399000
6       -3.195540000      0.272819000     -0.407704000
5       -1.786798000      0.651398000     -0.026502000
7       -0.830400000     -0.388121000      0.278251000
1       -0.554177000     -2.471088000      0.400919000
1       -3.952717000      1.015717000     -0.635233000
14       0.933829000     -0.173949000      0.747866000
17      -1.319228000      2.398791000      0.027112000
6        1.177305000      1.315069000      1.869604000
1        2.116279000      1.184734000      2.417278000
1        1.220392000      2.261817000      1.332980000
1        0.372200000      1.388041000      2.605354000
6        2.005627000     -0.089379000     -0.843928000
6        1.404203000     -1.690024000      1.775650000
1        2.384088000     -1.512030000      2.228745000
1        0.693854000     -1.843734000      2.593493000
1        1.475696000     -2.622065000      1.211160000
6        1.624276000      1.119509000     -1.722224000
1        0.594008000      1.057834000     -2.080509000
1        1.732901000      2.068746000     -1.191420000
1        2.278148000      1.157352000     -2.602520000
6        3.486194000      0.048813000     -0.420590000
1        3.664986000      0.962963000      0.153387000
1        3.827640000     -0.800064000      0.179706000
1        4.125307000      0.094491000     -1.310759000
6        1.838456000     -1.379163000     -1.674910000
1        2.458371000     -1.324146000     -2.578261000
1        2.151131000     -2.271196000     -1.123658000
1        0.804512000     -1.525939000     -1.999885000
6       -3.518324000     -1.056230000     -0.470233000
6       -2.543898000     -2.049218000     -0.178192000
1       -4.520055000     -1.379202000     -0.742726000
1       -2.794189000     -3.101534000     -0.227564000
```

Compound **6**

```
33
6       -1.628560000     -1.324017000      0.725970000
6       -2.913361000     -0.539704000      0.259861000
5       -1.847043000      0.630941000      0.099061000
7       -0.734650000     -0.127161000      0.511085000
1       -1.567706000     -1.753532000      1.725863000
1       -3.773479000     -0.428393000      0.920619000
14       1.012870000      0.039130000      0.803757000
17      -1.946084000      2.340010000     -0.380886000
6        1.301192000      1.717310000      1.606333000
1        2.363532000      1.880732000      1.810397000
1        0.947773000      2.537189000      0.976949000
1        0.766019000      1.778181000      2.558444000
6        2.006186000     -0.120353000     -0.833715000
6        1.469288000     -1.338188000      2.009486000
1        2.526366000     -1.281475000      2.284414000
1        0.887969000     -1.249808000      2.932288000
1        1.289241000     -2.334768000      1.596652000
6        1.644013000      1.036118000     -1.788947000
1        0.579847000      1.043007000     -2.039899000
1        1.892561000      2.012821000     -1.364093000
1        2.202665000      0.936817000     -2.728237000
6        3.518835000     -0.061925000     -0.525671000
1        3.808885000      0.879947000     -0.049836000
1        3.838854000     -0.880935000      0.125658000
1        4.093929000     -0.143858000     -1.456434000
6        1.690319000     -1.459449000     -1.531448000
1        2.273519000     -1.547925000     -2.456674000
1        1.943625000     -2.321408000     -0.906043000
1        0.633711000     -1.534711000     -1.801606000
6       -2.969707000     -1.579823000     -0.851772000
6       -1.864038000     -2.235055000     -0.471060000
1       -3.656159000     -1.698509000     -1.682380000
```

```
1       -1.295140000     -3.055422000     -0.890746000
```

Compound **7**

```
25
6        0.877412000      1.814356000      1.538198000
14       0.564837000      0.769641000     -0.000074000
6        0.877300000      1.814271000     -1.538426000
7       -1.106624000      0.301995000      0.000004000
5       -2.321085000      0.002758000      0.000112000
17      -3.972937000     -0.410839000      0.000282000
6        1.641035000     -0.820941000     -0.000070000
6        1.334031000     -1.663228000     -1.255751000
6        3.137424000     -0.441847000     -0.000246000
6        1.334279000     -1.663048000      1.255794000
1        1.915302000      2.156768000      1.590759000
1        0.236684000      2.701084000      1.523687000
1        0.656364000      1.262024000      2.455210000
1        1.915137000      2.156844000     -1.590970000
1        0.656379000      1.261833000     -2.455405000
1        0.236429000      2.700898000     -1.524012000
1        3.414521000      0.139532000     -0.885038000
1        3.414694000      0.139689000      0.884390000
1        3.756714000     -1.347674000     -0.000224000
1        1.576617000     -1.126849000      2.178363000
1        0.280346000     -1.951448000      1.302707000
1        1.929943000     -2.584789000      1.248939000
1        1.929721000     -2.584953000     -1.248896000
1        0.280095000     -1.951658000     -1.302400000
1        1.576160000     -1.127151000     -2.178447000
```

Compound **8**

```
88
5        0.938321000      0.161832000     -0.009453000
7       -0.195531000      1.039284000      0.306022000
5       -0.967942000     -0.180563000      0.018679000
7        0.164509000     -1.058640000     -0.292504000
14       0.393266000     -2.729186000     -0.801655000
6       -1.301059000     -3.509435000     -1.087896000
1       -1.181886000     -4.521742000     -1.485104000
1       -1.895452000     -3.575784000     -0.173355000
1       -1.885305000     -2.939082000     -1.813208000
6        1.349283000     -3.772248000      0.511870000
6        1.345059000     -2.762266000     -2.433833000
1        1.521064000     -3.790681000     -2.764667000
1        0.775712000     -2.258395000     -3.220882000
1        2.315878000     -2.267033000     -2.354924000
6        0.735793000     -3.570856000      1.912201000
1        0.793728000     -2.529627000      2.238418000
1       -0.316266000     -3.871964000      1.944192000
1        1.270030000     -4.180825000      2.652299000
6        1.251432000     -5.270598000      0.145348000
1        0.221571000     -5.636853000      0.174704000
1        1.654489000     -5.480217000     -0.850704000
1        1.831152000     -5.868846000      0.859955000
6        2.841322000     -3.381594000      0.548628000
1        3.362409000     -3.955625000      1.326140000
1        3.340250000     -3.596258000     -0.400870000
1        2.991263000     -2.321725000      0.764229000
6       -2.515637000     -0.449085000      0.035233000
6       -3.171549000     -0.776788000      1.240478000
6       -3.277082000     -0.359332000     -1.148976000
6       -4.552863000     -0.984981000      1.246365000
6       -4.656789000     -0.572563000     -1.106575000
6       -5.315948000     -0.887670000      0.082265000
1       -5.045567000     -1.223007000      2.185426000
1       -5.232283000     -0.483068000     -2.024186000
6       -2.630284000     -0.062870000     -2.486043000
1       -3.294316000      0.525515000     -3.124069000
1       -1.694133000      0.489458000     -2.382983000
1       -2.401956000     -0.988961000     -3.025261000
6       -6.804964000     -1.136888000      0.104486000
1       -7.239060000     -0.872756000      1.071792000
```

1	-7.317924000	-0.558268000	-0.667513000
1	-7.028394000	-2.194182000	-0.076646000
6	-2.402578000	-0.949997000	2.532836000
1	-2.131848000	-1.999906000	2.687770000
1	-1.476613000	-0.371901000	2.541553000
1	-2.999078000	-0.637169000	3.393417000
6	2.484997000	0.438990000	-0.028260000
6	3.236962000	0.412691000	1.165512000
6	3.148566000	0.727933000	-1.240180000
6	4.611160000	0.660430000	1.128641000
6	4.524865000	0.966012000	-1.240550000
6	5.277389000	0.934186000	-0.065931000
1	5.175252000	0.639297000	2.057543000
1	5.020329000	1.188065000	-2.182135000
6	2.599923000	0.094767000	2.502439000
1	1.513102000	0.193371000	2.478216000
1	2.829288000	-0.929622000	2.814145000
1	2.977461000	0.759851000	3.284108000
6	2.394271000	0.840373000	-2.547957000
1	2.987539000	0.453114000	-3.380309000
1	1.451198000	0.291613000	-2.529422000
1	2.160341000	1.885850000	-2.774060000
6	6.769471000	1.163553000	-0.090848000
1	7.120372000	1.606470000	0.844377000
1	7.309066000	0.219884000	-0.228482000
1	7.057571000	1.826609000	-0.910142000
14	-0.459486000	2.701086000	0.830013000
6	-1.645742000	2.702881000	2.300685000
1	-2.586408000	2.195080000	2.074023000
1	-1.193419000	2.200546000	3.161068000
1	-1.884196000	3.725594000	2.609014000
6	1.190436000	3.424124000	1.391492000
1	1.633644000	2.819271000	2.186031000
1	1.922007000	3.487349000	0.582219000
1	1.043400000	4.431660000	1.791439000
6	-1.188428000	3.810961000	-0.572773000
6	-2.670314000	3.470394000	-0.831803000
6	-0.390449000	3.628824000	-1.878689000
1	0.668144000	3.875331000	-1.749468000
1	-0.449749000	2.603586000	-2.252585000
1	-0.785671000	4.289392000	-2.661367000
1	-2.818177000	2.422706000	-1.101851000
1	-3.059656000	4.082367000	-1.656043000
1	-3.291373000	3.673674000	0.045154000
6	-1.101447000	5.294652000	-0.148556000
1	-0.067682000	5.630256000	-0.029964000
1	-1.564912000	5.929941000	-0.914217000
1	-1.627372000	5.488583000	0.791751000

Compound **9**

44			
5	0.379061000	0.140384000	-0.321139000
7	-0.869430000	0.212920000	-0.459401000
14	-2.579852000	0.327350000	-0.668141000
6	-3.033870000	2.144643000	-0.903849000
1	-4.111957000	2.282601000	-1.030352000
1	-2.711833000	2.751974000	-0.053802000
1	-2.541661000	2.539856000	-1.797613000
6	-3.447697000	-0.400240000	0.887905000
6	-3.063382000	-0.634500000	-2.219127000
1	-4.134807000	-0.558096000	-2.427475000
1	-2.527475000	-0.236896000	-3.086263000
1	-2.810048000	-1.694550000	-2.132699000
6	-3.052166000	0.412446000	2.138258000
1	-1.970446000	0.405067000	2.299355000
1	-3.374331000	1.455918000	2.067020000
1	-3.524106000	-0.013608000	3.033107000
6	-4.980496000	-0.342628000	0.715694000
1	-5.341378000	0.682052000	0.582454000
1	-5.321075000	-0.932592000	-0.140821000
1	-5.477418000	-0.747677000	1.606608000
6	-3.019359000	-1.867916000	1.090970000
1	-3.496429000	-2.282389000	1.988537000
1	-3.309645000	-2.501076000	0.246805000
1	-1.937135000	-1.956687000	1.219638000

```
6        1.887731000      0.053601000     -0.146990000
6        2.545445000     -1.194213000     -0.246148000
6        2.640368000      1.222367000      0.112650000
6        3.928980000     -1.249902000     -0.081694000
6        4.022020000      1.122069000      0.270379000
6        4.684754000     -0.104647000      0.180686000
1        4.430932000     -2.209482000     -0.162041000
1        4.596795000      2.022388000      0.466088000
6        1.768684000     -2.458677000     -0.529925000
1        1.225095000     -2.388298000     -1.476805000
1        2.432204000     -3.323536000     -0.585990000
1        1.026903000     -2.653809000      0.250481000
6        6.176297000     -0.193936000      0.389222000
1        6.411822000     -0.342695000      1.448917000
1        6.606877000     -1.032855000     -0.162175000
1        6.679726000      0.720976000      0.068374000
6        1.965237000      2.570176000      0.214331000
1        2.689310000      3.357852000      0.430316000
1        1.452696000      2.829577000     -0.716995000
1        1.210736000      2.578878000      1.006633000
```

TS min→1

```
12
6       -0.836755000      1.158321000      0.120414000
5        0.610946000      1.224454000     -0.029277000
7        1.458061000     -0.117983000     -0.442412000
6        0.721161000     -0.814130000      0.401608000
6       -0.649185000     -1.191912000     -0.033265000
6       -1.471686000     -0.127040000     -0.108068000
1        1.122203000     -1.148349000      1.365263000
1       -1.442980000      2.028743000      0.346495000
1       -2.509933000     -0.218996000     -0.416016000
1       -0.828067000     -2.189193000     -0.419043000
1        1.391530000      2.083041000      0.227757000
1        2.424882000     -0.003079000     -0.145312000
```

min

```
12
6       -0.782331000      1.147465000      0.042457000
5        0.703153000      1.085165000     -0.043918000
7        1.466884000     -0.245618000     -0.495423000
6        0.638350000     -0.664845000      0.499060000
6       -0.674763000     -1.149944000      0.013335000
6       -1.506340000     -0.092329000     -0.123675000
1        0.923673000     -0.713323000      1.550681000
1       -1.311690000      2.063275000      0.298374000
1       -2.540601000     -0.145907000     -0.450940000
1       -0.793599000     -2.140976000     -0.409708000
1        1.449077000      1.936362000      0.322684000
1        2.439688000     -0.148011000     -0.210600000
```

TS 2→min

```
12
6       -0.384772000      1.151787000      0.122576000
5        1.071644000      0.876803000     -0.211082000
7        1.352462000     -0.563763000     -0.443740000
6        0.339331000     -0.613362000      0.560718000
6       -1.004711000     -0.970961000      0.010987000
6       -1.496470000      0.247240000     -0.233235000
1        0.592206000     -0.743105000      1.610826000
1       -0.583500000      2.031637000      0.736628000
1       -2.446904000      0.546013000     -0.661497000
1       -1.326791000     -1.963614000     -0.279597000
1        1.936363000      1.626219000      0.124203000
1        2.282904000     -0.823052000     -0.135253000
```

TS 4→3

```
52
6         0.405877000      3.025325000     -0.424572000
5         0.387288000      1.566194000     -0.263544000
7        -1.050289000      0.785011000     -0.107480000
6        -1.471999000      1.766045000      0.676730000
6        -1.888462000      3.063990000      0.067584000
6        -0.850208000      3.739491000     -0.458955000
1        -1.617394000      1.602321000      1.753730000
1         1.340367000      3.564181000     -0.549657000
1        -0.968858000      4.694909000     -0.963538000
1        -2.944627000      3.248805000     -0.100895000
14       -1.401927000     -0.961981000      0.209543000
6        -0.439753000     -2.050548000     -0.974424000
1         0.626358000     -2.051189000     -0.745645000
1        -0.802459000     -3.079727000     -0.890293000
1        -0.563561000     -1.737844000     -2.013392000
6        -1.005538000     -1.424622000      1.994381000
1        -1.350220000     -2.442059000      2.203024000
1         0.073508000     -1.403691000      2.163380000
1        -1.477773000     -0.766294000      2.728553000
6        -3.292971000     -1.130610000     -0.129583000
6        -3.607971000     -0.758389000     -1.593895000
1        -4.683965000     -0.858087000     -1.784181000
1        -3.321802000      0.271266000     -1.822874000
1        -3.091106000     -1.414169000     -2.300459000
6        -3.712513000     -2.599049000      0.114163000
1        -3.178382000     -3.296298000     -0.537422000
1        -3.548519000     -2.911344000      1.149767000
1        -4.782709000     -2.718616000     -0.093940000
6        -4.121363000     -0.229668000      0.807564000
1        -5.192110000     -0.385326000      0.625992000
1        -3.937900000     -0.447159000      1.864300000
1        -3.929296000      0.834311000      0.639583000
6         1.656573000      0.630873000     -0.118965000
6         2.306436000      0.418711000      1.120121000
6         2.227683000      0.069038000     -1.280632000
6         3.452800000     -0.376835000      1.178458000
6         3.381452000     -0.717110000     -1.185949000
6         4.002540000     -0.964964000      0.036420000
1         3.938439000     -0.531060000      2.138410000
1         3.804439000     -1.142632000     -2.092121000
6         1.819605000      1.085775000      2.387949000
1         0.776961000      0.844369000      2.611731000
1         2.422662000      0.781294000      3.246385000
1         1.874875000      2.174319000      2.299440000
6         5.226182000     -1.844592000      0.131381000
1         5.977137000     -1.412106000      0.798418000
1         4.971802000     -2.833587000      0.528304000
1         5.687864000     -1.991350000     -0.847565000
6         1.648998000      0.342864000     -2.652672000
1         1.888019000     -0.464103000     -3.350209000
1         0.565199000      0.468550000     -2.627471000
1         2.061408000      1.269641000     -3.065500000
```

TS 6→5

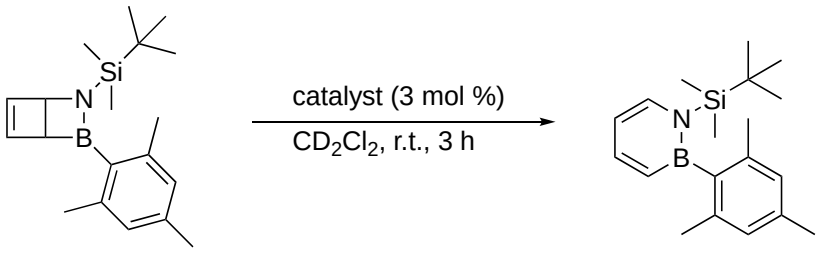
```
33
6        -3.191285000      0.237642000     -0.613940000
5        -1.841654000      0.633992000     -0.196464000
7        -0.729055000     -0.420609000      0.167283000
6        -1.639057000     -1.201426000      0.746228000
6        -2.577687000     -1.974607000     -0.124794000
6        -3.435163000     -1.176626000     -0.788348000
1        -1.620398000     -1.376274000      1.829768000
1        -3.969336000      0.966369000     -0.812197000
1        -4.174303000     -1.560605000     -1.486084000
1        -2.330794000     -3.007580000     -0.354676000
17       -1.369071000      2.340242000      0.163020000
14        0.993486000     -0.232998000      0.723669000
6         1.265691000      1.170531000      1.944984000
1         0.478767000      1.190459000      2.703780000
1         2.220459000      1.017892000      2.458898000
1         1.284007000      2.149234000      1.465535000
6         1.339702000     -1.864145000      1.609052000
1         2.398693000     -1.930455000      1.875036000
```

1	0.774544000	-1.939145000	2.543577000
1	1.098125000	-2.736811000	0.996722000
6	2.058320000	-0.059293000	-0.858561000
6	1.638564000	1.173691000	-1.685697000
1	2.290403000	1.265485000	-2.563269000
1	0.610634000	1.094274000	-2.046699000
1	1.720576000	2.104199000	-1.117721000
6	3.536589000	0.100593000	-0.435831000
1	3.698878000	1.003322000	0.160429000
1	3.900431000	-0.756075000	0.140372000
1	4.170289000	0.182093000	-1.327146000
6	1.915312000	-1.321739000	-1.734754000
1	2.516707000	-1.213204000	-2.645490000
1	2.264639000	-2.222485000	-1.220953000
1	0.878810000	-1.486259000	-2.041277000

8. Catalyzed Cycloreversion Reactions

General procedure for catalyst screening:

A 0.064 M CD_2Cl_2 stock solution of substrate (**4**) and internal standard (1,3,5-trimethoxybenzene) was prepared by dissolving 0.10 g **4** and 0.054 g 1,3,5-trimethoxybenzene in a 5.0 mL volumetric flask. Another stock solution consisting of 0.010 g of catalyst in 1.0 mL CD_2Cl_2 was prepared separately. A volume of catalyst solution corresponding to 3 mol % catalyst loading was added via microliter syringe to 0.50 mL (0.032 mmol **4**) of the substrate/internal standard solution. (For dimeric catalyst precursors, a volume corresponding to 1.5 mol % precursor was added.) After allowing the reaction mixture to stir at room temperature for 3 h, the conversion was determined by ^{1}H NMR (Table S11).



4 **3**

Table S11. Survey of catalysts for the cycloreversion reaction.

entry	catalyst	conversion (%)[a]
1	$(Cy_3P)_2(PhCH)RuCl_2$	15%
2	$[Ir(cod)Cl]_2$	12%
3	$Ni(CO)_2(PPh_3)_2$	0%
4	$Sc(OTf)_3$	0%
5	AgOTf	2%
6	IPrAuCl	0%
7	$Pt(PPh_3)_4$	5%
8	$Pd(PPh_3)_4$	0%
9	$RhCl(PPh_3)_3$	100%[b]
10	$[Rh(C_2H_4)_2Cl]_2$	100%[b]
11	$[Rh(cod)(PPh_3)_2]PF_6$	2%
12	$(nbd)_2RhBF_4$	0%
13	$[Rh(nbd)Cl]_2$	2%
14	$Rh(nbd)(PPh_3)Cl$ Polymer	1%
15	$[Rh(Cp^*)Cl_2]_2$	0%

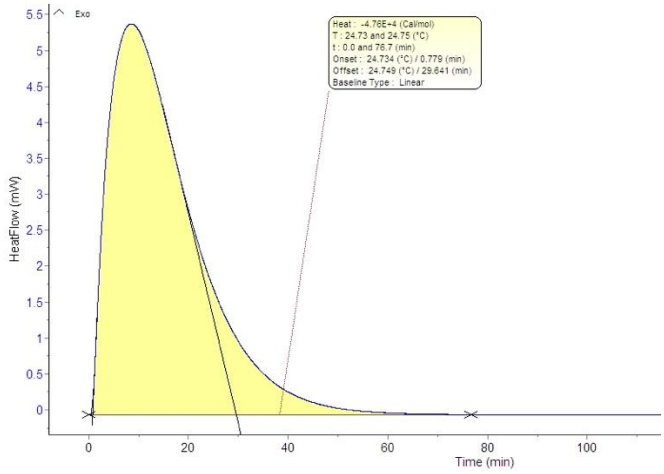
[a] determined by ^{1}H NMR integration based on 1,3,5-trimethoxybenzene as internal standard.
[b] Full conversion to **3** was observed within 1 h.

Calorimetric Experiment :

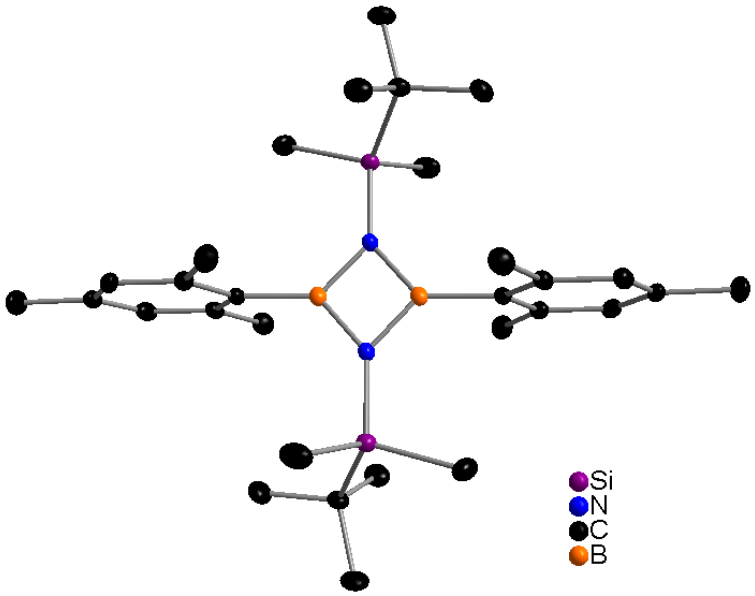
A 0.064 M CD_2Cl_2 stock solution of substrate (**4**) was prepared by dissolving 0.10 g **4** in a 5.0 mL volumetric flask. Another 0.011 M CD_2Cl_2 stock solution of Wilkinson's catalyst was also prepared by dissolving 0.020 g $RhCl(PPh_3)_3$ in a 2.0 mL volumetric flask. In a glovebox, 0.50 mL of substrate solution (0.032 mmol **4**) were added to the bottom of a Setaram-C80 calorimeter Hastelloy sample cell; the bottom half of the cell was sealed with a puncturable aluminum foil before 89 µL of catalyst solution (3 mol% catalyst) and an additional 0.30 mL CD_2Cl_2 solvent were added on top of the foil via microliter syringe. An empty reference cell was likewise prepared under N_2. Both cells were loaded into the Setaram-C80 calorimeter and were allowed to equilibrate at 25 °C until zero heat flow was achieved (which took approximately 3 hours). Data collection was initiated just prior to puncturing the aluminum foil and was continued until the observed heat flow had returned to zero, indicating completion of the reaction. (Complete conversion of starting material **4** to 1,2-azaborinine **3** was subsequently confirmed by ^{11}B NMR and ^{1}H NMR). The measured heat flow trace was integrated using the Setaram software SetSoft 2000 to determine the ΔH_{rxn} of the retro-isomerization (cycloreversion) reaction. The calorimetric measurements were repeated five times and the corresponding average value of ΔH_{rxn} with standard deviation is reported.

Trial	DH kcal/mol
1	-48.4
2	-48.8
3	-47.0
4	-47.6
5	-46.1

The average value of ΔH is –47.6 kcal/mol, with a standard deviation of ±0.968 kcal/mol. A representative heat-flow trace is shown below.



9. Summary of crystallographic data for compound 8



Empirical formula	C30 H52 B2 N2 Si2	
Formula weight	518.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.7079(8) Å	α= 90°.
	b = 15.5938(11) Å	β= 102.6590(10)°.
	c = 9.9606(7) Å	γ = 90°.
Volume	1622.8(2) $Å^3$	
Z	2	
Density (calculated)	1.061 Mg/m^3	
Absorption coefficient	0.129 mm^{-1}	
Crystal size	0.433 x 0.292 x 0.138 mm^3Reflections	
collected	36853	
Independent reflections	3569 [R(int) = 0.0294]	
Absorption correction	Numerical	
Max. and min. transmission	0.7457 and 0.7076	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3569 / 0 / 171	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0925	
R indices (all data)	R1 = 0.0370, wR2 = 0.0958	

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