Supporting Information for

The Aromatic Claisen Rearrangement of a 1,2-Azaborine

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General Considerations

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk technique or a nitrogen-filled glovebox.

For air- and moisture-sensitive techniques, tetrahydrofuran, diethyl ether, and methylene chloride were purified by passing through a neutral alumina column under argon. All other solvents for air- and moisture-sensitive work were distilled after drying over calcium hydride. Allyl bromide was purchased from common commercial suppliers and distilled prior to use. All other chemicals and solvents were purchased and used as received. ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on Varian 500 or 600 MHz spectrometers or AVANCE NEO 500 MHz spectrometer. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constant (Hz). ^{1}H and ^{13}C spectra were internally referenced to residual solvent peaks (^{1}H CDCl$_3$: δ = 7.26 ppm, ^{13}C CDCl$_3$: δ = 77.16 ppm); ^{11}B spectra were externally referenced to a standard of BF$_3$•Et$_2$O (δ = 0.0 ppm). In ^{13}C NMR analysis, peaks for carbon atoms adjacent to a boron center were generally not observed owing to quadrupolar broadening.

All IR spectra were measured on a Bruker Alpha-P FT-IR equipped with a single crystal diamond ATR module, and values are reported in cm^{-1}.

High-resolution mass spectrometry (HRMS) data was generated in Boston College facilities using Direct Analysis in Real Time (DART) technique on a JEOL AccuTOF DART spectrometer.

Synthesis
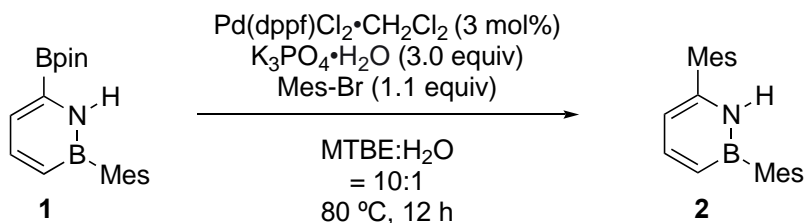
In a glovebox, an oven dried 150 mL pressure vessel was charged with a stir bar, compound **1**[1] (1.68 g, 5.20 mmol, 1.0 equiv.), 2-bromomesitylene (1.14 g, 5.72 mmol, 1.1 equiv.), Potassium phosphate tribasic monohydrate (3.59 g, 15.6 mmol, 3.0 equiv), Pd(dppf)Cl$_2$•CH$_2$Cl$_2$ (127.4 mg, 156 μmol, 3.0 mol%), methyl tert-butyl ether (20 mL), and H$_2$O (2.0 mL). The reaction mixture was allowed to stir in an oil bath at 80 ˚C for 12 hours. At the conclusion of the reaction, the reaction mixture was extracted three times with diethyl ether, and the combined organic layers were washed with brine, dried over MgSO$_4$, and passed through a glass frit filter. The crude mixture was concentrated *in vacuo* and purified by silica gel chromatography using gradient of 10% CH$_2$Cl$_2$ in hexane to obtain the product as white solid (1.45 g, 4.60 mmol, 88%).

^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.83 (dd, *J* = 11.1, 6.6 Hz, 1H), 7.66 (s br, 1H), 6.96 (s, 2H), 6.90 (s, 2H), 6.87 (dt, *J* = 11.1, 1.6 Hz, 1H), 6.28 (dt, *J* = 6.6, 1.6 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 2.25 (s, 6H), 2.17 (s, 6H). ^{13}C{^{1}H}NMR (CDCl$_3$, 151 MHz) δ 144.8, 144.3, 140.2, 138.2, 137.3, 136.4, 136.1, 128.4, 127.3, 111.1, 23.3, 21.3, 21.2, 20.0. Two carbon signals (for carbon atoms adjacent to boron) not observed. ^{11}B NMR (CDCl$_3$, 160 MHz) δ 35.8. IR ν 3353, 3015, 2916, 2856, 1609, 1540, 1446, 1376, 1341, 1267, 849, 771, 734, 705, 560, 542 cm^{-1}. HRMS (DART) [M+H]$^+$ calculated for C$_{22}$H$_{27}$BN 316.2237, found 316.2225.

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[1] A. W. Baggett, M. Vasiliu, B. Li, D. A. Dixon, S.-Y. Liu, *J. Am. Chem. Soc.* **2015**, *137*, 5536–5541.
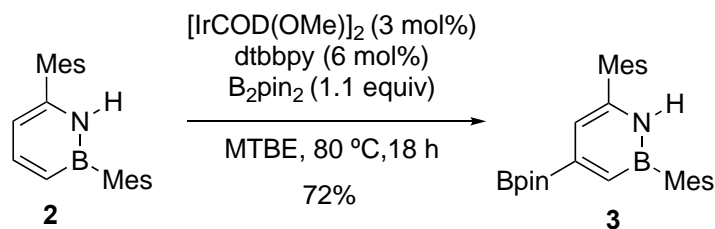
In a glovebox, a 15 mL pressure vessel was charged with a stir bar, compound **2** (350 mg, 1.11 mmol), B_2pin_2 (310 mg, 1.22 mmol, 1.1 equiv.), [Ir(COD)OMe]$_2$ (22.1 mg, 33.3 μmol, 3.0 mol%) , di-*tert*-butylbipyridine (17.9 mg, 66.6 μmol, 6.0 mol%) and methyl tert-butyl ether (6.0 mL). The mixture was allowed to stir at 80 °C in an oil bath until it was judged to be complete by ^{1}H NMR (approx.18 hours). At the conclusion of the reaction, the mixture was allowed to cool to room temperature, and concentrated *in vacuo*. The resulting crude residue was purified by column chromatography using a gradient of 10% ether in hexane to obtain the product as white solid (353 mg, 0.800 mmol, 72%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 (s, 1H), 7.45 (s, 1H), 6.89 (s, 2H), 6.83 (s, 2H), 6.58 (s, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 2.19 (s, 6H), 2.12 (s, 6H), 1.35 (s, 12H). ^{13}C{^{1}H}NMR (126 MHz, CDCl$_3$) δ 143.4, 140.1, 137.9, 137.0, 136.5, 136.2, 128.2, 127.2, 114.5, 84.0, 25.1, 23.4, 21.3, 21.2, 20.1. Three carbon signals (for carbon atoms adjacent to boron) not observed. ^{11}B NMR (160 MHz, CDCl$_3$) δ 35.0, 30.4. IR ν 3386, 3351, 2978, 2919, 2878, 1609, 1530, 1470, 1417, 1373, 1336, 1310, 1259, 1213, 1142, 864, 850, 772, 730, 694, 684 cm^{-1}. HRMS (DART) [M+H]$^+$ calcd. for C$_{28}$H$_{38}$B$_2$NO$_2$ 442.3089, found 442.3102.
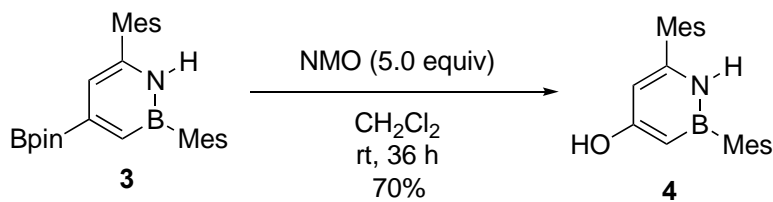
In a glovebox, a 20 mL vial was charged with compound **3** (362 mg, 820 mmol) N-methylmorpholine-N-oxide (481 mg, 4.10 mmol, 5.0 equiv.) and CH_2Cl_2 (4.0 mL) and allowed to stir at room temperature. Reaction conversion was monitored with ^{1}H NMR (approx. 36 hours). At the conclusion of the reaction, the mixture was concentrated *in vacuo*. The resulting crude residue was purified by column chromatography using a gradient of 20% ether in hexane to obtain the product as white solid. (191 mg, 0.577 mmol, 70%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.18 (br s, 1H), 6.91 (s, 2H), 6.85 (s, 2H), 5.88 (s, 1H), 5.69 (s, 1H), 5.09 (d, J = 4.6 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 2.22 (s, 6H), 2.16 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 166.8, 148.5, 140.2, 138.3, 137.2, 136.3, 135.5, 128.3, 127.2, 103.6, 23.2, 21.3, 21.2, 19.9. Two carbon signals (for carbon atoms adjacent to boron) not observed. ^{11}B NMR (160 MHz, CDCl$_3$) δ 37.3. IR ν 3495, 3369, 2915, 1618, 1555, 1459, 1172, 1136, 893, 852, 839, 743, 666, 562, 490 cm^{-1}. HRMS (DART) [M+H]$^+$ calcd. for C$_{22}$H$_{27}$BNO 332.2186, found 332.2179.
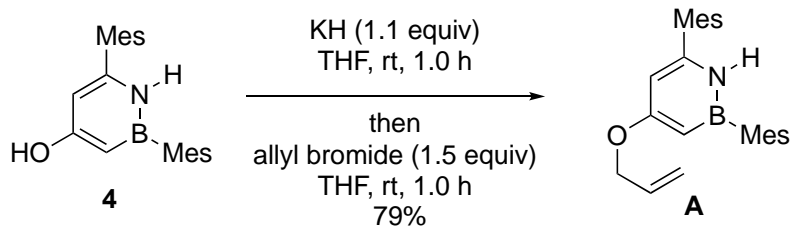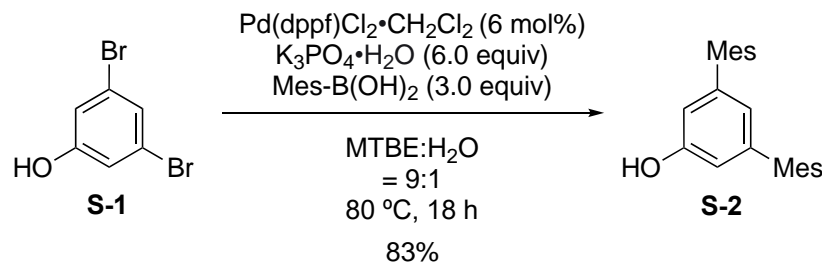
In a glovebox, compound **4** (359 mg, 1.08 mmol) was dissolved in tetrahydrofuran (8.0 mL). Potassium hydride (47.8 mg, 1.19 mmol, 1.1 equiv.) was added in small portions and the mixture was allowed to stir for an hour at room temperature. Allyl bromide (197 mg, 1.63 mmol, 1.5 equiv.) was added dropwise at room temperature and the mixture was allowed to stir for an additional hour. At the conclusion of the reaction, the crude mixture was concentrated *in vacuo* and purified by silica gel chromatography using gradient of 25% CH_2Cl_2 in hexane to obtain the product as a white solid (317 mg, 0.854 mmol, 79%).

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.13 (s, 1H), 6.92 (s, 2H), 6.87 (s, 2H), 6.15–6.07 (m, 1H), 5.94 (s, 1H), 5.80 (s, 1H), 5.44 (dd, J = 17.2, 1.6 Hz, 1H), 5.29 (dd, J = 10.6, 1.6 Hz, 1H), 4.55 (d, J = 5.5 Hz, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 2.24 (s, 6H), 2.18 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 169.1, 146.9, 139.8, 137.9, 136.9, 136.1, 135.5, 133.2, 128.1, 126.9, 117.5, 104.8, 67.6, 23.0, 21.00, 20.96, 19.7. Two signals for carbons adjacent to boron not observed. ^{11}B NMR (160 MHz, CDCl$_3$) δ 37.0. IR ν 3363, 2917, 2858, 1737, 1621, 1542, 1437, 1280, 1205, 1175, 1137, 1072, 996, 924, 850, 729 cm^{-1}. HRMS (DART) [M+H]$^+$ calcd. for C$_{25}$H$_{31}$BN 372.2499, found 372.2517.
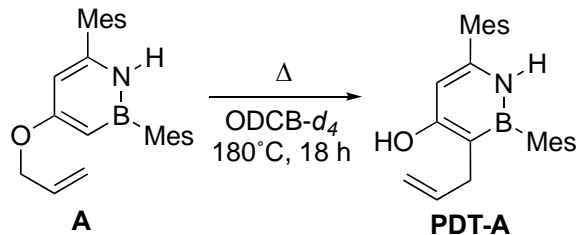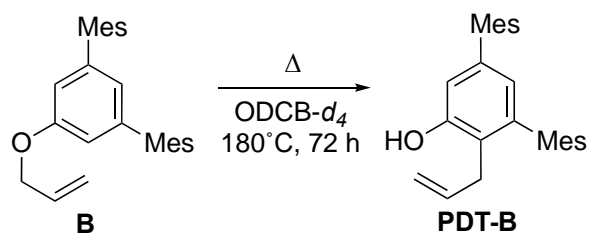
Claisen Rearrangement Product PDT-A: The product was obtained in full conversion after heating at 180 °C for 18 hours (87% NMR yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.13 (br s, 1H), 6.90 (s, 2H), 6.83 (s, 2H), 5.99– 5.92 (m, 1H), 5.90 (s, 1H), 5.80 (s, 1H), 5.20 (dd, J = 17.2, 1.7 Hz, 1H), 5.11 (dd, J = 10.0, 1.7 Hz, 1H), 3.10 (d, J = 2.9 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 2.16 (s, 6H), 2.15 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 165.1, 146.0, 139.9, 138.6, 137.9, 136.8, 136.1, 135.3, 128.1, 126.8, 115.2, 104.3, 32.1, 22.6, 21.0, 21.0, 19.7. Two signals for carbons adjacent to boron not observed. ^{11}B NMR (160 MHz, CDCl$_3$) δ 38.3. IR ν 3524, 3359, 2917, 2855, 1621, 1558, 1443, 1207, 1174, 1151, 1126, 1044, 910, 850, 830, 731, 562 cm^{-1}. HRMS (DART) [M+H]$^+$ calcd. for C$_{27}$H$_{31}$O 372.2493, found 372.2486.

Br / HO / Br **S-1** → Pd(dppf)Cl$_2$•CH$_2$Cl$_2$ (6 mol%), K$_3$PO$_4$•H$_2$O (6.0 equiv), Mes-B(OH)$_2$ (3.0 equiv), MTBE:H$_2$O = 9:1, 80 °C, 18 h, 83% → Mes / HO / Mes **S-2**

In a glovebox, an oven dried 50 mL pressure vessel was charged with a stir bar, 3,5-dibromophenol (**S-1**) (1.00 g, 3.97 mmol), mesitylboronic acid (1.95 g, 11.9 mmol, 3.0 equiv.), potassium phosphate tribasic monohydride (5.48 g, 23.82 mmol, 6.0 equiv.), Pd(dppf)Cl$_2$•CH$_2$Cl$_2$ (194 mg, 0.238 mmol, 6.0 mol%), methyl tert-butyl ether (13.5 mL), and H$_2$O (1.5 mL). The reaction mixture was allowed to stir at 80˚C in an oil bath for 18 hours. At the conclusion of the reaction, the reaction mixture was extracted three times with diethyl ether, and the combined organic layers were washed with brine, dried over MgSO$_4$, and passed through a glass frit filter. The crude mixture was concentrated *in vacuo* and purified by silica gel chromatography using a gradient of 20% ethyl acetate in hexane to obtain the product as white solid (1.09 g, 3.29 mmol, 83%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.95 (s, 4H), 6.61 (d, *J* = 1.4 Hz, 2H), 6.52 (t, *J* = 1.4 Hz, 1H), 4.88 (s, 1H), 2.35 (s, 6H), 2.09 (s, 12H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$) δ 155.6, 143.0, 138.7, 136.7, 135.9, 128.1, 123.2, 114.6, 21.1, 20.8. IR ν 3466, 2965, 2918, 2858, 1612, 1590, 1469, 1264, 1179, 1156, 1014, 901, 852, 793, 735, 719, 703, 570 cm^{-1}. HRMS (DART) [M+H]$^+$ calcd. for C$_{24}$H$_{27}$O 331.2062, found 331.2065.
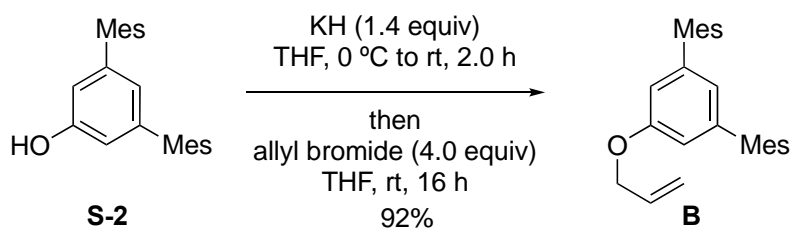
In a 100 mL round-bottom flask, compound **S-2** (1.09 g, 3.30 mmol) was dissolved in tetrahydrofuran (10.0 mL) and allowed to cool to 0 °C. Potassium hydride (185 mg, 4.61 mmol, 1.4 equiv.) was added dropwise, and the reaction mixture was allowed to stir for 3 hours in the absence of cooling. Allyl bromide (1.59 g, 13.2 mmol, 1.14 mL, 4.0 equiv.) was then added as a neat liquid in dropwise fashion, and the mixture was allowed to stir for an additional 16 hours at room temperature. At the conclusion of the reaction, the reaction mixture was extracted three times with diethyl ether, and the combined organic layers were washed with brine, dried over MgSO$_4$, and passed through a glass frit filter. The crude mixture was concentrated *in vacuo* and purified by silica gel chromatography using a gradient of 15% ethyl acetate in hexane to obtain the product as white solid (1.12 g, 3.02 mmol, 92%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.98 (s, 4H), 6.73 (d, $J = 1.4$ Hz, 2H), 6.57 (t, $J = 1.4$ Hz, 1H), 6.12 (m, 1H), 5.46 (dd, $J = 17.3, 1.4$ Hz, 1H), 5.33 (dd, $J = 10.7$, 1.4 Hz, 1H), 4.59 (d, $J = 5.3$ Hz, 2H), 2.37 (s, 6H), 2.12 (s, 12H). ^{13}C{^{1}H}NMR (151 MHz, CDCl$_3$) δ 158.8, 142.6, 139.0, 136.6, 135.9, 133.5, 128.1, 123.1, 117.7, 114.0, 68.8, 21.2, 20.8. IR ν 2919, 1612, 1586, 1486, 1451, 1378, 1265, 1227, 1192, 1016, 895, 734, 570 cm^{-1}. HRMS (DART) [M+H]$^+$ calculated for C$_{27}$H$_{31}$O 371.2375, found 371.2388.

Scheme showing B → PDT-B via Δ, ODCB-d_4, 180 °C, 72 h.

Claisen Rearrangement Product: The product was obtained with full conversion after heating at 180 °C in an oil bath for 72 hours. (94 % NMR yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.92 (s, 4H), 6.65 (d, J = 1.6 Hz, 1H), 6.46 (d, J = 1.6 Hz, 1H), 5.98 – 5.83 (m, 1H), 5.20 (s, 1H), 5.14 – 5.06 (m, 2H), 3.17 (d, J = 6.4 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 2.08 (s, 6H), 1.99 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 155.2, 142.0, 141.0, 138.7, 137.7, 136.5, 136.5, 136.4, 136.0, 135.9, 128.1, 123.4, 121.4, 116.5, 115.8, 77.2, 32.1, 21.19, 21.15, 20.8, 20.6. IR ν 3513, 2947, 2917, 1613, 1573, 1469, 1398, 1377, 1330, 1191, 1163, 1120, 917, 890, 849, 738, 569 , 411 cm^{-1}. HRMS (DART) [M+H]$^+$ calcd. for C$_{27}$H$_{31}$O 371.2369, found 371.2380.

A Sample Procedure for Kinetic Analysis

An aliquot was taken from a stock solution containing **A** or **B** (100 mM) and 1,3,5-trimethoxybenzene internal standard (100 mM) in 1,2-dichlorobenzene-d_4 (ODCB-d_4), diluted to 50 mM with ODCB-d_4, and loaded into a J–Young NMR tube. An NMR measurement was taken to establish the initial ratio of internal standard to analyte in the stock solution. The tube was then submerged in a temperature-controlled silicon oil bath pre-heated to the given temperature. At given timepoints, the J-Young tube was removed from the bath, and ^{1}HNMR integration measurements of the allylic protons were taken to establish the decay of **A** or **B** relative to the constant concentration of the internal standard. The raw data was processed in MestReNova with peak integrations normalized against 1,3,5-trimethoxybenzene as the internal standard at 5.940 ppm which was integrated from 5.955 to 5.925 ppm and normalized to 300 for each spectrum.

Kinetic Analysis for Compound A
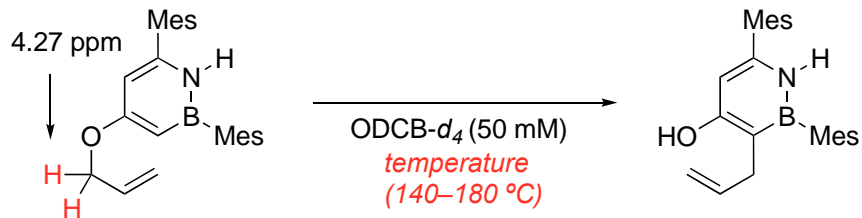
The decay of the ^{1}H NMR peak at 4.270 ppm was monitored throughout the course of the reaction which was integrated from 4.240 to 4.280 ppm and compared against 1,3,5-trimethoxybenzene as the internal standard at 5.940 pm (integrated from 5.955 to 5.925 ppm and normalized to 300).

Sample overlaid spectra of 50 mM [**A**] at 180 °C throughout the course of heating:
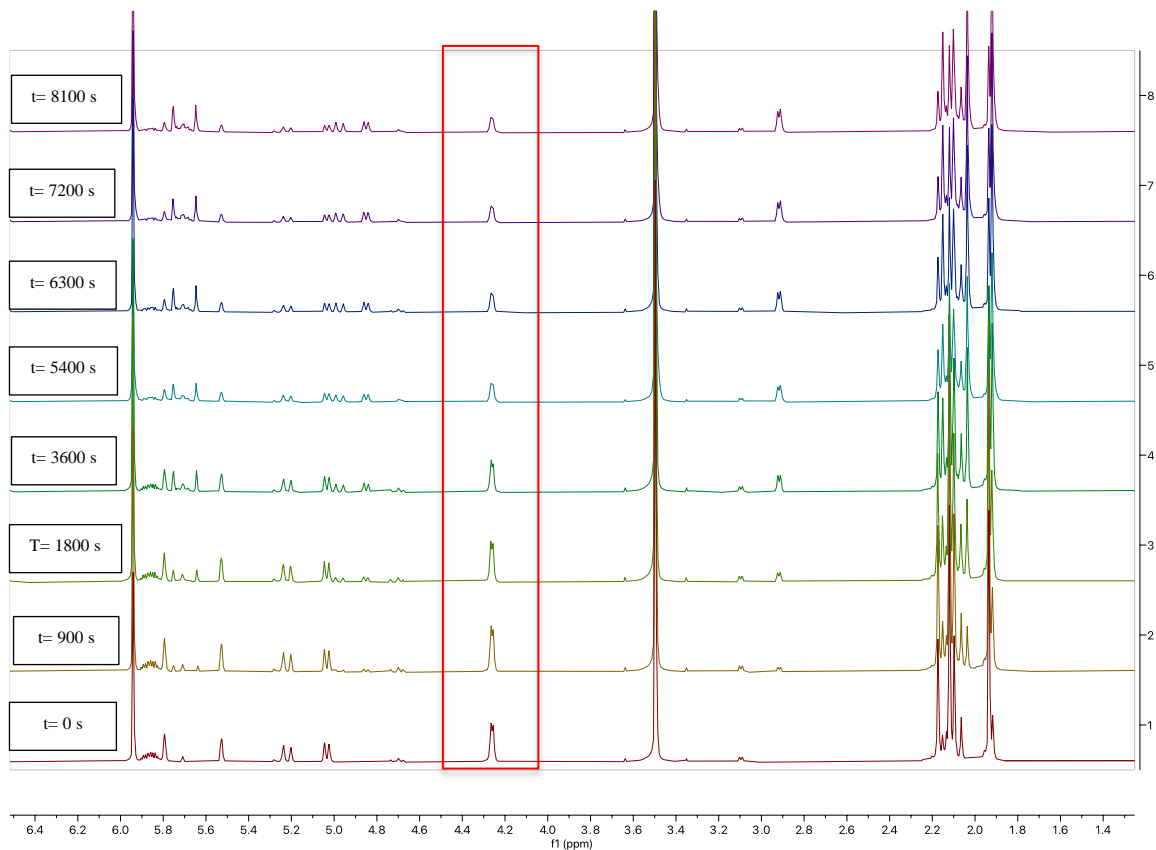
The data were fit to first-order decay according to the equation:

$$Conv_t = e^{-kt}$$

where "**Conv**" is the ratio of the allylic peak integration at time $= t$, to the integration at time $= 0$ s. The values of "**Conv**" begin at 1 for time $= 0$ s and decrease as the reaction progresses. Microsoft® Excel was used to plot the conversion vs the reaction time in order to determine the initial rate of the reaction and rate constant. The plot of ln (Conv$_t$) vs. time (s) gives a linear function consistent with first order dependence of the reaction on the concentration of the substrate:

Plot of ln (conversion) of **A** vs. time (s) at 180 ˚C:
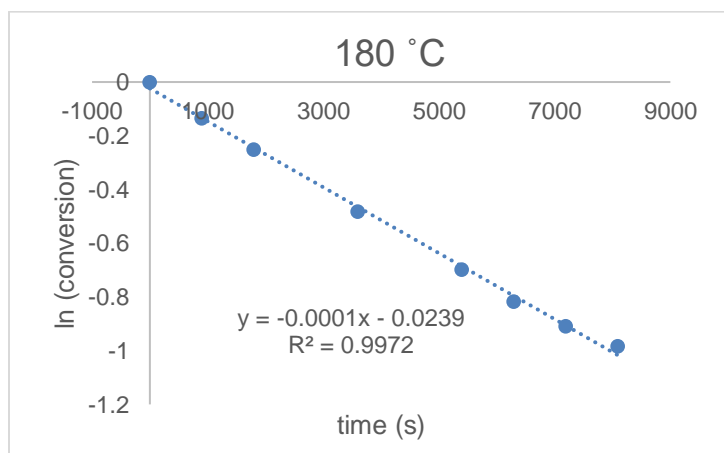
This experiment was repeated at five temperatures, 140, 150, 160, 170, and 180˚C with five independent runs per temperature.

Sample of reaction rates at different temperatures:
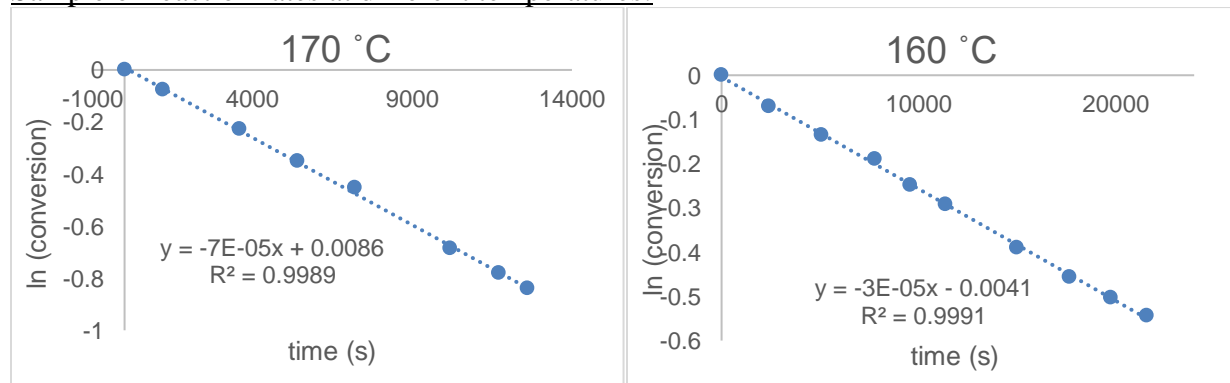
The first-order rate constant of the reaction can be extracted from the slope of equation of the line of best fit of the plot according to the equation:

$$ln(Conv_t) = -kt$$

Rate constants for the Claisen Rearrangement of Compound **A**:

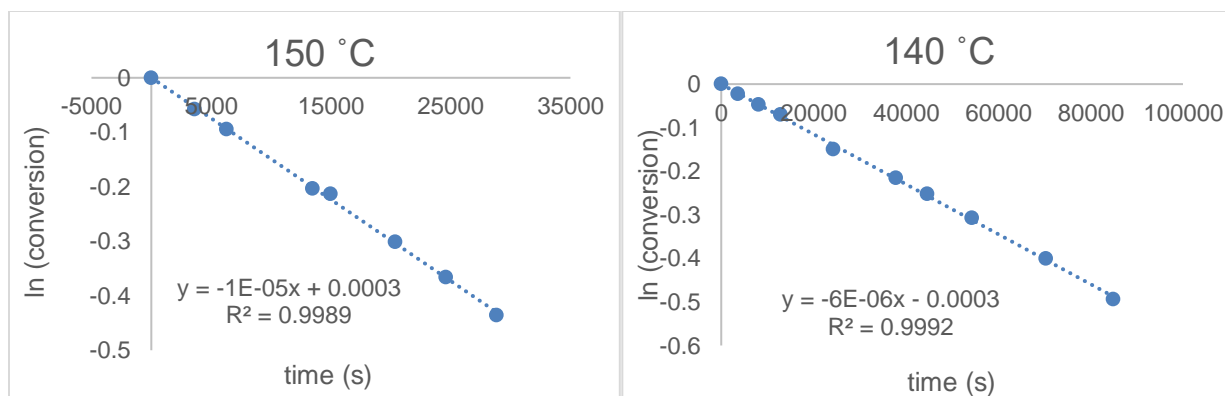| Temperature (°C)	$x\ 10^{-6}\ (s^{-1})$					
	1	2	3	4	5	average
140	5.2	6.0	5.8	5.9	5.7	5.7± 0.3
150	10	7	15	15	11	12±3
160	25	34	35	35	25	31±5
170	70	64	57	70	67	66±5
180	123	130	129	104	103	118±12

Eyring analysis:

The Eyring equation is: $k = \dfrac{\kappa k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}} = \dfrac{\kappa k_B T}{h} e^{-\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R}}$. Taking the natural logarithm and

rearranging yields: $\ln(\frac{k}{T}) = \dfrac{-\Delta H^{\ddagger}}{RT} + \dfrac{\Delta S^{\ddagger}}{R} + \ln(\frac{\kappa k_B}{h})$. With R as the gas constant (R = 8.31441 J·K⁻¹mol⁻¹), T as the reaction temperature (K), *h* as Planck's constant (h = 6.62617·10⁻³⁴ J·s), k_B as the Boltzmann constant (k_B = 1.380662·10⁻²³ J·K⁻¹), and the statistical factor κ set to 1.0. The average (*ln (k/T)*) for each temperature was plotted against inverse temperature (1/T (K⁻¹)) to give the Eyring plot.

				ln (k/T)		
Temperature	**1**	**2**	**3**	**4**	**5**	**average**
140	-18.19	-18.04	-18.08	-18.06	-18.09	**-18.09 $\pm$ 0.05**
150	-17.61	-17.90	-17.12	-17.16	-17.43	**-17.44 $\pm$ 0.29**
160	-16.67	-16.35	-16.32	-16.32	-16.66	**-16.46 $\pm$ 0.16**
170	-15.66	-15.75	-15.86	-15.67	-15.70	**-15.73 $\pm$ 0.07**
180	-15.12	-15.06	-15.07	-15.29	-15.29	**-15.17 $\pm$ 0.10**

BN Analog Eyring Plot

y = -14114x + 16.052
R² = 0.9952
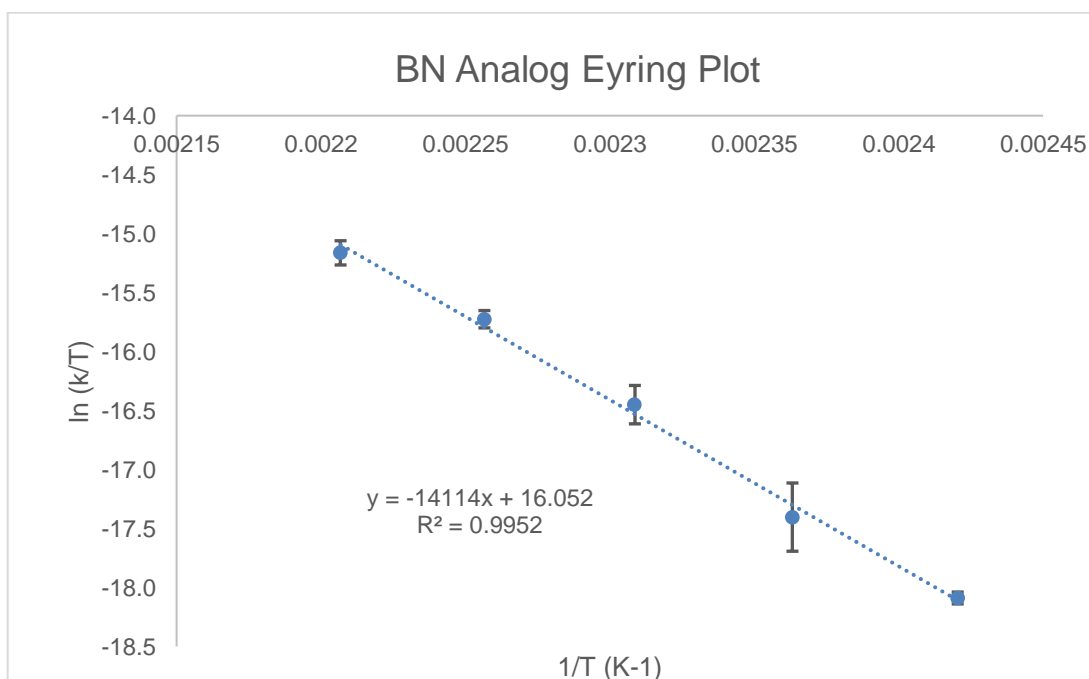
From the plot; $\Delta H^{\ddagger}$ was calculated from the slope, $\Delta S^{\ddagger}$ was calculated from the intercept, and $\Delta G^{\ddagger}$ was calculated from those values using the equation:

$$\Delta G^{\ddagger}_{298} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

The standard deviation of each activation parameter was calculated by first calculating the $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G_{298K}{}^{\ddagger}$ for each replicate, and then calculating the standard deviation from the average of the replicates.

	1	**2**	**3**	**4**	**5**	**Average**
$\Delta H^{\ddagger}$ (kcal/mol)	30.0	30.1	27.1	26.3	27.3	**28$\pm$ 2**
$\Delta S^{\ddagger}$ (e.u.)	-10.9	-10.6	-17.4	-19.3	-17.3	**-15 $\pm$ 4**
$\Delta G_{298K}{}^{\ddagger}$ (kcal/mol)	33.3	33.3	32.3	32.0	32.4	**32.7 $\pm$0.5**

Kinetic Analysis for Compound B
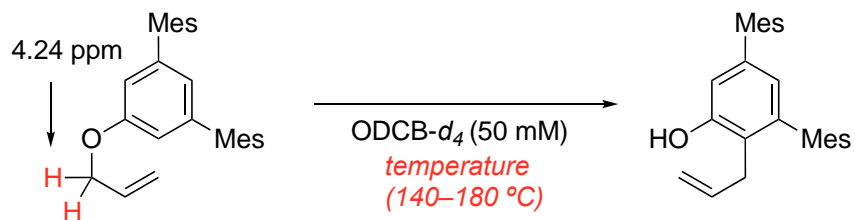
The decay of the ^{1}H NMR peak at 4.240 ppm was monitored and the throughout the course of the reaction which was integrated from 4.210 to 4.250 ppm and compared against 1,3,5-trimethoxybenzene as the internal standard at 5.940 pm (integrated from 5.955 to 5.925 ppm and normalized to 300).

Sample overlaid spectra of 50 mM [**B**] at 180 °C throughout the course of heating:
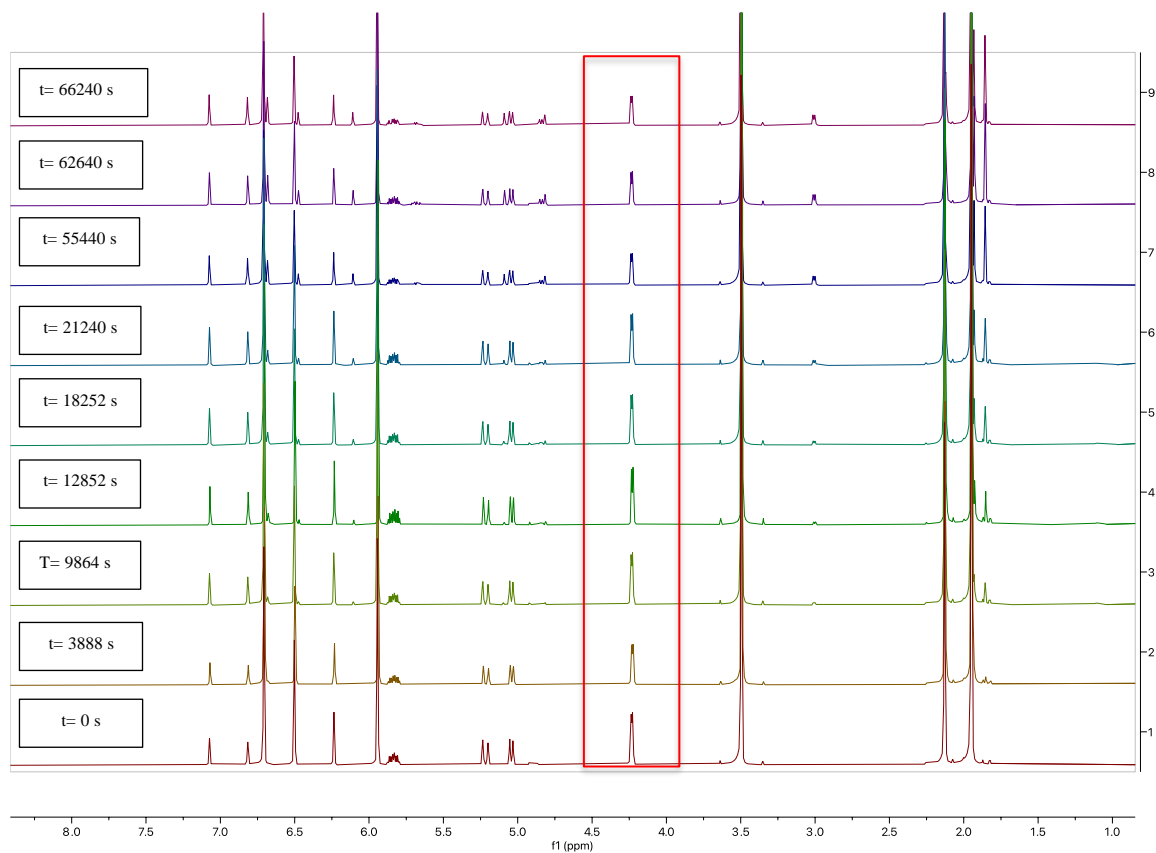
Plot of ln (conversion) of **B** vs. time (s) at 180 ˚C:
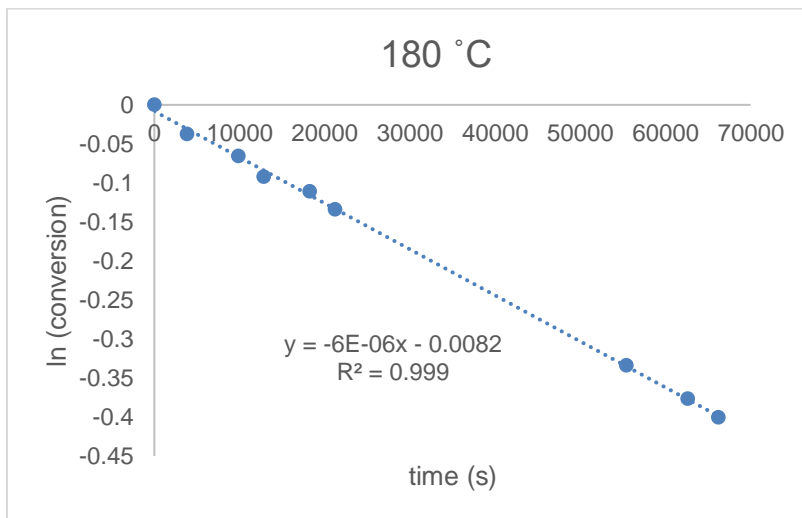
This experiment was repeated at five temperatures, 140, 150, 160, 170, and 180˚C with five

independent runs per temperature.

Summary of reaction rates determined from disappearance of SM over time at different

temperatures:

Rate constants for the Claisen Rearrangement of Compound B:

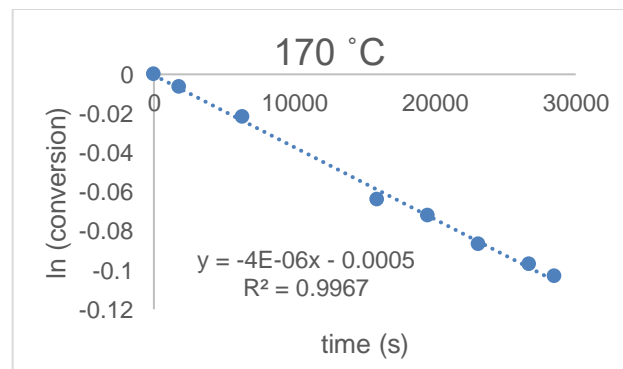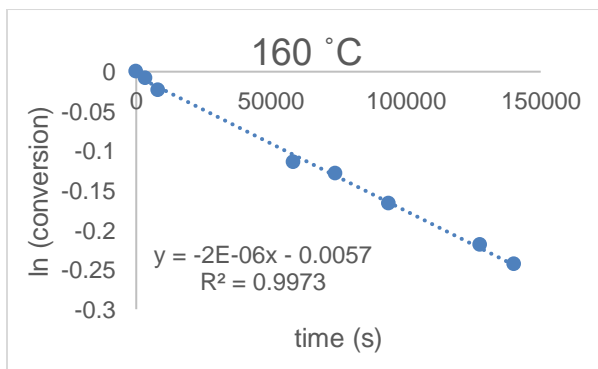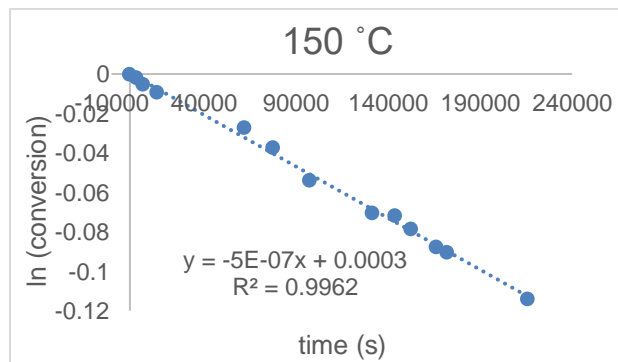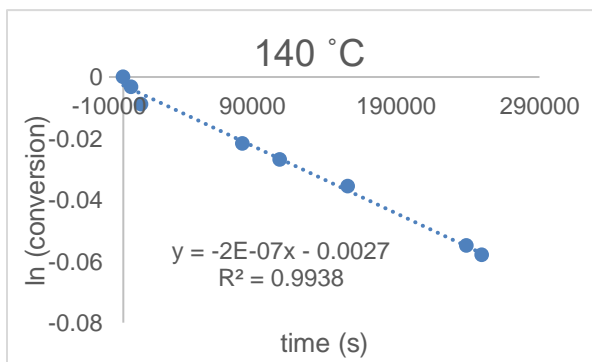| Temperature (˚C)	k (s^{-1} x 10^{-6})					
	1	2	3	4	5	average
140	0.22	0.33	0.34	0.31	0.29	**0.30 ±0.04**
150	0.55	0.52	0.43	0.54	0.51	**0.50 ±0.04**
160	2.19	1.84	1.70	1.24	1.23	**1.6 ±0.4**
170	4.24	4.54	3.68	2.67	2.81	**3.6 ±0.7**
180	6.58	7.15	7.50	5.90	5.25	**6.5 ±0.8**

Eyring Analysis:

Temperature(˚C)	$\ln (k/T)$					
	1	2	3	4	5	average
140	-21.37	-20.95	-20.93	-21.02	-21.07	**-21.07 ± 0.16**
150	-20.47	-20.51	-20.71	-20.47	-20.53	**-20.54 ±0.09**
160	-19.10	-19.28	-19.36	-19.67	-19.68	**-19.42 ±0.25**
170	-18.46	-18.40	-18.61	-18.93	-18.88	**-18.65 ±0.24**
180	-18.05	-17.97	-17.92	-18.16	-18.27	**-18.07 ±0.15**

Carbon Analog Eyring plot

$y = -15243x + 15.776$
$R^2 = 0.9855$

x-axis: 1/T (K^{-1}), y-axis: ln (k/T)
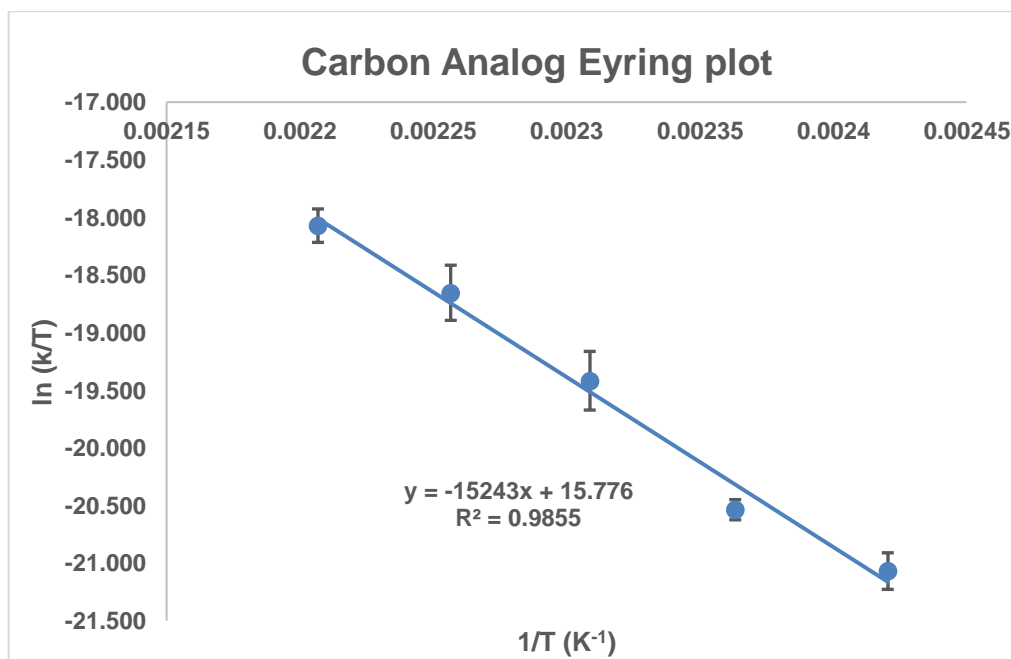
	1	2	3	4	5	Average
$\Delta H^{\ddagger}$ kcal/mol)	32.29	30.08	30.20	27.02	26.96	**29±2**
$\Delta S^{\ddagger}$ (e.u)	-11.31	-16.28	-16.16	-23.81	-24.02	**-18±5**
$\Delta G_{298K}^{\ddagger}$ (kcal/mol)	35.66	34.93	35.02	34.12	34.12	**34.8±0.6**

Butylated hydroxytoluene (BHT) Radical Trapping Experiments:

A 100mM stock solution of BHT, substrate **A** or **B**, and and 1,3,5-trimethoxybenzene internal standard (100 mM) in ODCB-d_4, was diluted to 50 mM and loaded into a J-Young tube. An NMR measurement was taken to establish the initial ratio of internal standard to analyte in the stock solution. The tube was then submerged in a temperature-controlled silicon oil bath pre-heated to the given temperature. At given timepoints, the J-Young tubes was removed from the bath, and ^{1}HNMR integration measurements were taken to establish the decay of **A** or **B** relative to the constant concentration of the internal standard. The raw data was processed the same as the previously mentioned kinetics experiments. No formation of the BHT adduct was observed, and the rate was not inhibited by the addition of the radical inhibitor.

Rate constant for **A**: $k_{170°C} = 75.9 \times 10^{-6}$ s^{-1}

Rate constant for **B**: $k_{170°C} = 3.82 \times 10^{-6}$ s^{-1}

Computational Details

All calculations were performed on the real systems with the Gaussian 16 package[2] and the PBE0[3] functional with D3 dispersion correction of Grimme with Becke–Johnson damping (DFT-*D3(BJ)*)[4]. All the atoms have been described with the 6-31G** basis set. All stationary points involved were fully optimized by taking into account solvent effect (o-DCB: o-dichlorobenzene) by means of the universal Solvation Model based on solute electron Density (SMD).[5] Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency for transition states (TS), corresponding to the expected process, and all frequencies are positive for *minima*. The connectivity of the transition states and their adjacent *minima* was confirmed by intrinsic reaction coordinate (IRC)[6] calculations. Standard thermodynamic corrections (T = 298 K, 1 atm) have been considered to express reaction paths in terms of standard Gibbs free energies. Molecular Orbitals (MOs) and geometrical structures were plotted, respectively, with the Chemcraft 1.8[7] and CYLview 1.0[8] programs. For the HOMO of **A**, the atomic orbital compositions (%) have been computed thanks to Multiwfn 3.6 package.[9]

[2] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
[3] C. Adamo, V. Barone, *J. Chem. Phys.,* **1999**, *110*, 6158–6169.
[4] (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104-154119. (b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* **2011**, *32*, 1456-1465.
[5] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B.* **2009**, *113*, 6378-6396.
[6] (a) K. Fukui, *Acc. Chem. Res.*, **1981**, *14*, 363-368. (b) H. P. Hratchian, H. B. Schlegel, in *Theory and Applications of Computational Chemistry: The First 40 Years*, Ed. C. E. Dykstra, G. Frenking, K. S. Kim, G. Scuseria, Elsevier, Amsterdam, **2005**, *195*.
[7] Chemcraft - graphical software for visualization of quantum chemistry computations. (https://www.chemcraftprog.com)
[8] CYLview 1.0, C. Y. Legault, University of Sherbrooke, 2009 (http://www.cylview.org)
[9] T. Lu, F. Chen, *J. Comput. Chem.*, **2012***, 33*, 580-592.

We computed the energy profiles for the unsubstituted compounds **A-H** and **B-H** (Mes groups replaced with H) to isolate the electronic effects from potential steric effects. As observed for **A**, the activation barrier ($\Delta G^{\ddagger}$: 31.6 kcal/mol) for **A-H** was computed to be lower in energy than that for the all-carbon compound **B-H** ($\Delta G^{\ddagger}$: 34.9 kcal/mol). Thus, the reaction with the BN analogue is still faster than with the CC analogue. These barriers were found to be slightly higher in energy than those calculated for **A** and **B**, respectively 0.4 (BN) and 0.9 (CC) kcal/mol. The formation of the corresponding dearomatized keto-intermediate was also determined to be more energetically favorable for the 1,2-azaborine derivative (ΔG: –2.0 kcal/mol for BN; ΔG: +9.2 kcal/mol for CC).
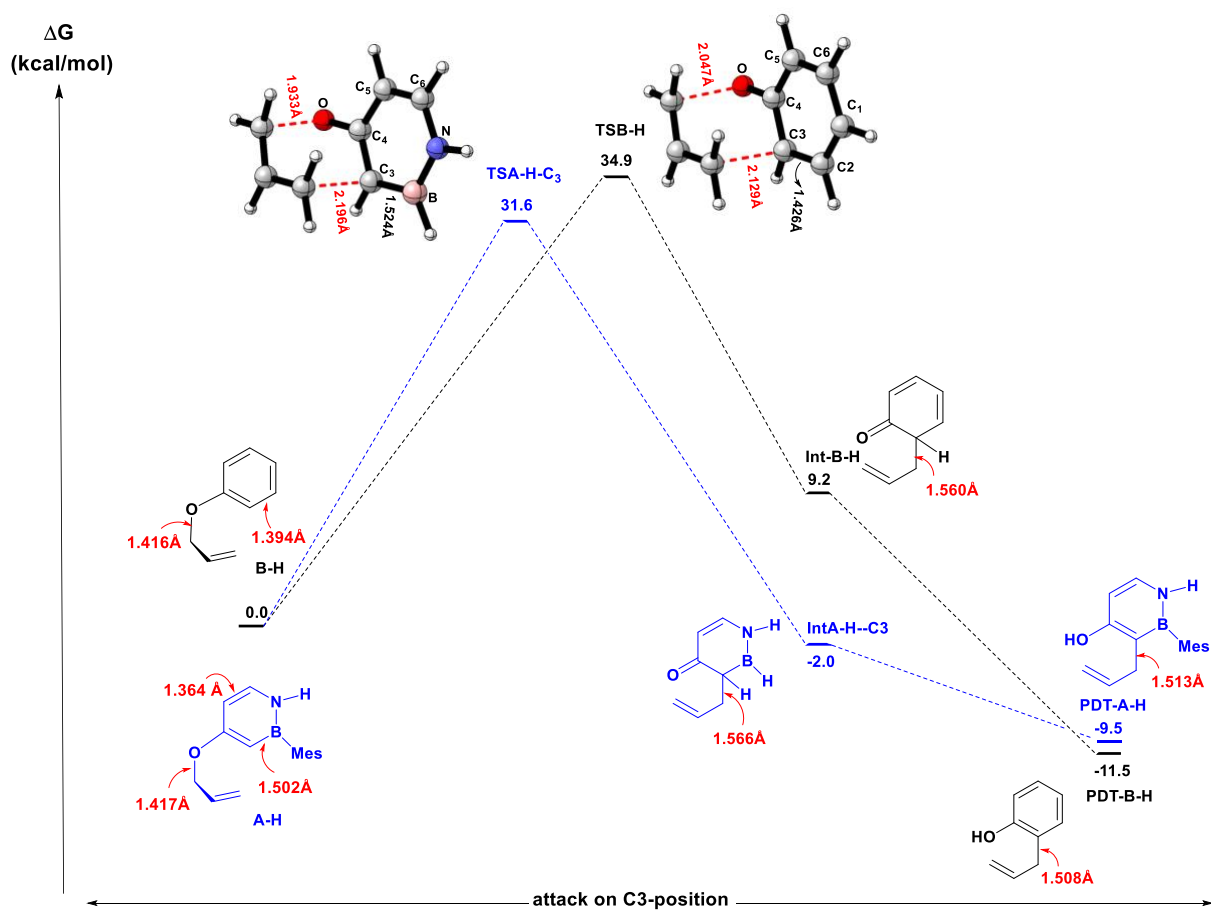

Figure S1. Calculated energy profiles for the aromatic Claisen rearrangement for the unsubstituted compounds **A-H** and **B-H** computed at SMD(o-DCB)-PBE0-D3(BJ)/6-31G** level of theory.

We analyzed the energy of the molecular orbitals involved in the process for reactants **A-H** and **B-H** to rationalize the experimental results. We noticed that the energetic position of the $\pi^*_{C=C}$ orbital of the O-allyl moiety is similar in all BN and CC compounds (at ~ +0.75 eV, Figure S2). In contrast, a significant difference (~ 1 eV) was observed for the relevant occupied molecular orbital centered on the π-system of the BN or CC ring (HOMO for **A** and **A-H**, HOMO-1 for **B-H** and HOMO-5 for **B**; Figure S2). It appears that the Mes groups exert an electron-donating effect that results in higher-energy π_{ring} orbital for **A** and **B** relative to the unsubstituted **A-H** and **B-H**, with a greater difference observed for the BN system (ΔE_{π}: 0.3 eV for BN and 0.1 eV for CC). Comparison of the activation barriers shows that the BN/CC isosterism effect on the rate is more striking in the unsubstituted system ($\Delta\Delta G^{\ddagger}$(BN/CC) : 3.3 kcal/mol) than the Mes-substituted system ($\Delta\Delta G^{\ddagger}$(BN/CC) : 2.8 kcal/mol). A good correlation was found between the energy of the occupied π orbital involved in the process and the activation barriers (Figure S3), suggesting dominant electronic effects.
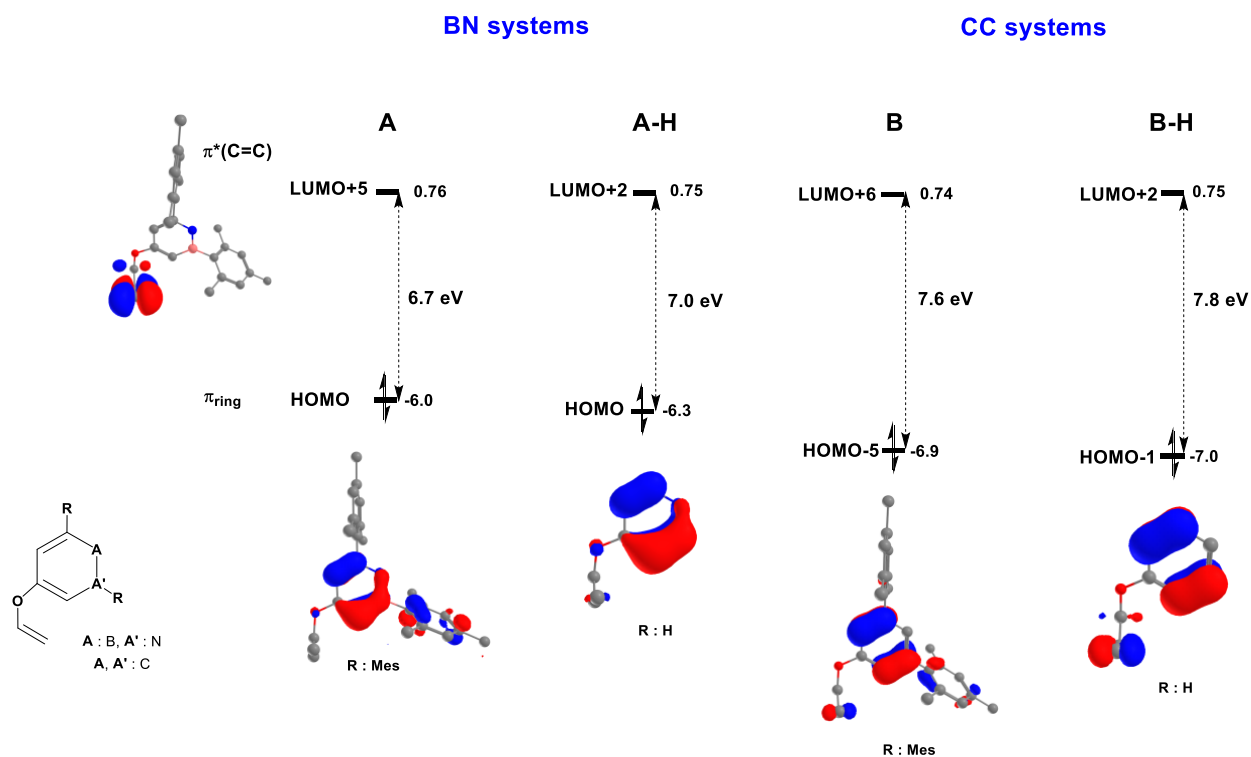
Figure S2. Orbital illustration and energy (in eV) of the occupied/vacant molecular orbitals involved in the Claisen rearrangement for compounds **A**, **A-H**, **B**, **B-H** computed at SMD(O-DCB)-PBE0-D3(BJ)/6-31G** level of theory.
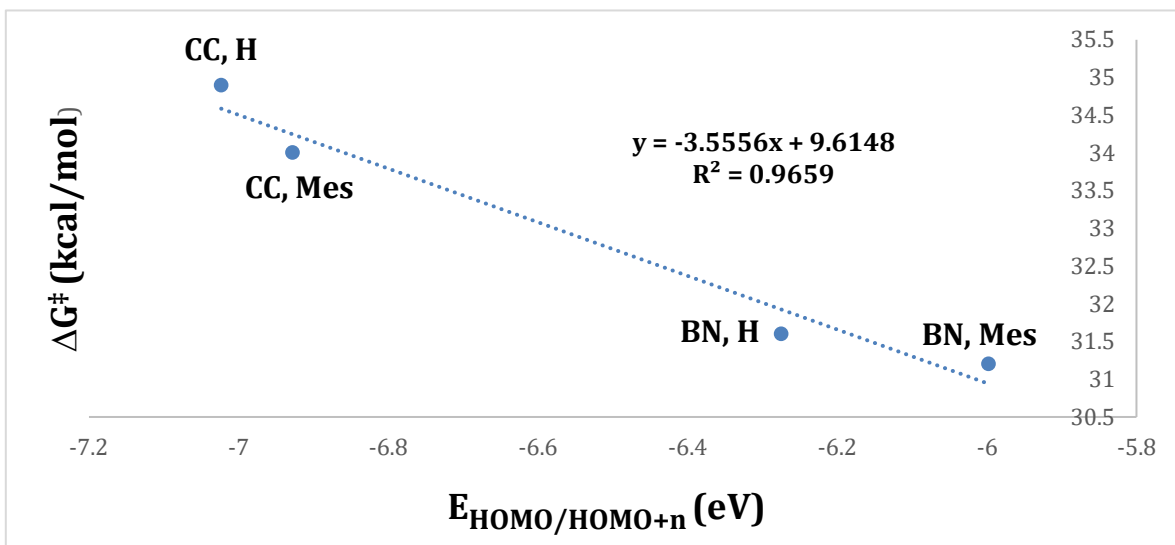
Figure S3. Correlation between activation barriers ($\Delta G^{\ddagger}$ in kcal/mol) and energy (in eV) of the occupied molecular orbital involved in the Claisen rearrangement (HOMO for BN compounds and HOMO-1/-5 for CC compounds) for compounds **A**, **A-H**, **B**, **B-H**.

NMR Spectra for New Compounds

11B NMR spectrum. Peak labeled 35.82.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	25.0
3	Pulse Sequence	s2pul
4	Number of Scans	512
5	Receiver Gain	30
6	Relaxation Delay	0.0100
7	Spectrometer Frequency	160.38
8	Nucleus	11B

1H NMR spectrum. Peaks labeled 7.67, 7.45, 7.45, 7.45, 7.26 cdcl3, 6.89, 6.83, 6.58, 6.58, 6.58, 2.30, 2.28, 2.19, 2.12, 1.35. Integrations: 0.85, 0.97, 2.00, 2.00, 1.01, 3.01, 2.93, 6.06, 6.20, 12.00.

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	25.0
3	Pulse Sequence	s2pul
4	Number of Scans	8
5	Receiver Gain	50
6	Relaxation Delay	10.0000
7	Spectrometer Frequency	499.88
8	Nucleus	1H

Mes

H

N

B

Mes

Bpin

Parameter	Value
1 Solvent	cdcl3
2 Temperature	25.0
3 Pulse Sequence	s2pul
4 Number of Scans	200
5 Receiver Gain	30
6 Relaxation Delay	1.0000
7 Spectrometer Frequency	125.71
8 Nucleus	13C

143.45
140.14
137.92
136.99
136.46
136.24
128.21
127.15
114.52
83.97
77.16 cdcl3
25.10
23.39
21.27
21.21
20.13

Mes

H

N

B

Mes

Bpin

Parameter	Value
1 Solvent	cdcl3
2 Temperature	25.0
3 Pulse Sequence	s2pul
4 Number of Scans	512
5 Receiver Gain	30
6 Relaxation Delay	0.0100
7 Spectrometer Frequency	160.38
8 Nucleus	11B

34.98
30.36

S-26

¹H NMR Spectrum

Structure label: Mes, N–H, HO, B, Mes

Peak labels: 7.26 cdcl3, 7.18, 6.91, 6.85, 5.88, 5.69, 5.09, 5.08, 2.31, 2.29, 2.22, 2.16

Parameter	Value
1 Solvent	cdcl3
2 Temperature	25.0
3 Pulse Sequence	s2pul
4 Number of Scans	8
5 Receiver Gain	40
6 Relaxation Delay	10.0000
7 Spectrometer Frequency	499.88
8 Nucleus	1H

Integration labels: 0.88, 2.02, 2.00, 0.99, 1.00, 1.01, 3.02, 3.01, 5.95, 5.91

f1 (ppm)

¹³C NMR Spectrum

Structure label: Mes, N–H, HO, B, Mes

Peak labels: 166.81, 148.47, 140.17, 138.30, 137.23, 136.26, 135.53, 128.34, 127.19, 103.58, 77.16 CDCl3, 23.19, 21.25, 21.21, 19.90

Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.1
3 Pulse Sequence	zgdepg
4 Number of Scans	512
5 Receiver Gain	16.0
6 Relaxation Delay	0.4561
7 Spectrometer Frequency	125.80
8 Nucleus	13C

f1 (ppm)

S-27

Mes

N—H

HO

B—Mes

	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.1
3	Pulse Sequence	zgbs
4	Number of Scans	500
5	Receiver Gain	12.7
6	Relaxation Delay	0.0000
7	Spectrometer Frequency	160.50
8	Nucleus	11B

—37.29

75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

Mes

N—H

O

B—Mes

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	25.0
3	Pulse Sequence	s2pul
4	Number of Scans	8
5	Receiver Gain	32
6	Relaxation Delay	10.0000
7	Spectrometer Frequency	599.68
8	Nucleus	1H

7.26 cdcl3
7.13
6.92
6.87
6.14
6.08
5.94
5.80
5.45
5.45
5.42
5.42
5.30
5.29
5.28
4.55
4.54
2.32
2.31
2.24
2.18

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

0.78
2.13
2.04
1.05
1.01
1.00
1.12
1.05
2.05
3.29
3.19
6.06
6.00

1H NMR spectrum

Parameter	Value
1 Solvent	cdcl3
2 Temperature	25.0
3 Pulse Sequence	s2pul
4 Number of Scans	8
5 Receiver Gain	40
6 Relaxation Delay	5.0000
7 Spectrometer Frequency	499.88
8 Nucleus	1H

13C NMR spectrum

Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.2
3 Pulse Sequence	zgdepg
4 Number of Scans	512
5 Receiver Gain	18.0
6 Relaxation Delay	0.4561
7 Spectrometer Frequency	125.80
8 Nucleus	13C
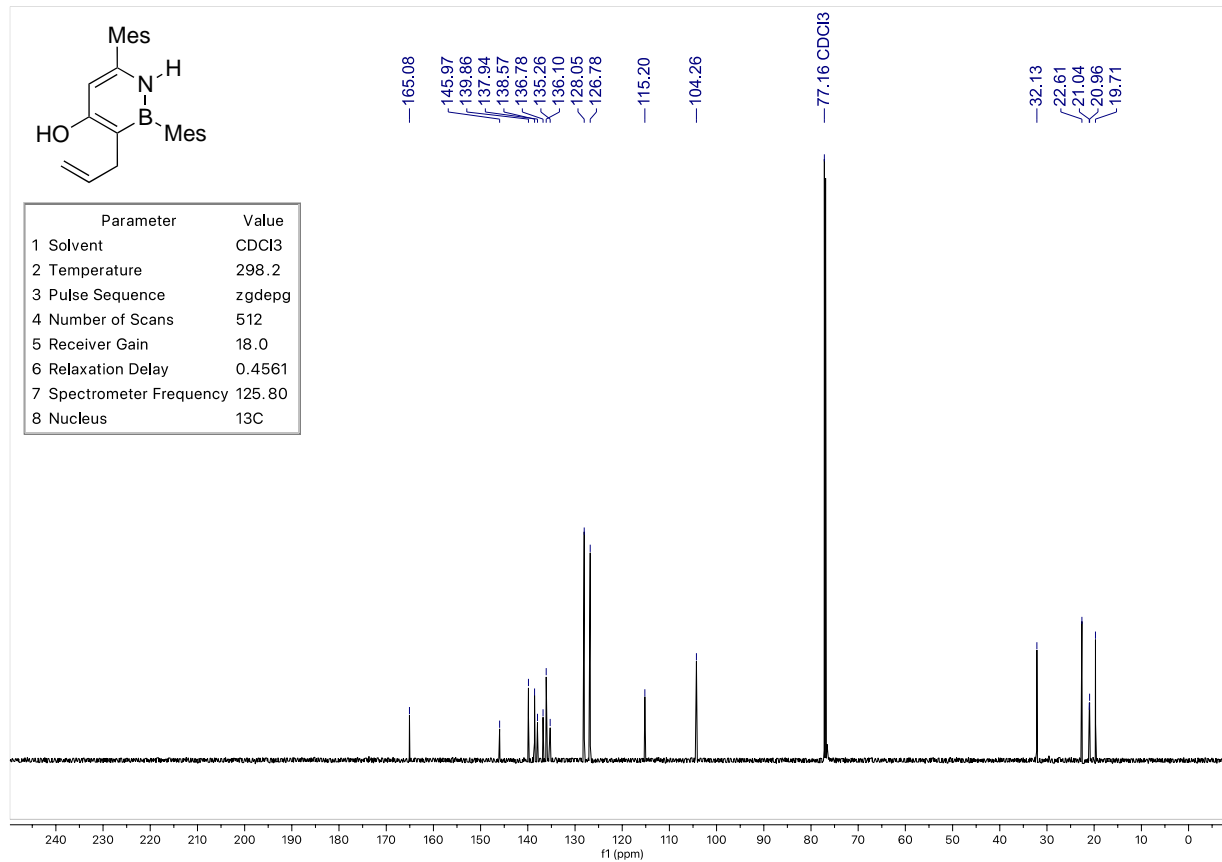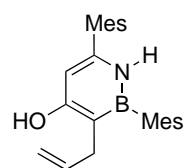
—38.28

Parameter	Value
1 Solvent	CDCl3
2 Temperature	298.1
3 Pulse Sequence	zgbs
4 Number of Scans	500
5 Receiver Gain	0.3
6 Relaxation Delay	0.0000
7 Spectrometer Frequency	160.50
8 Nucleus	11B

f1 (ppm)
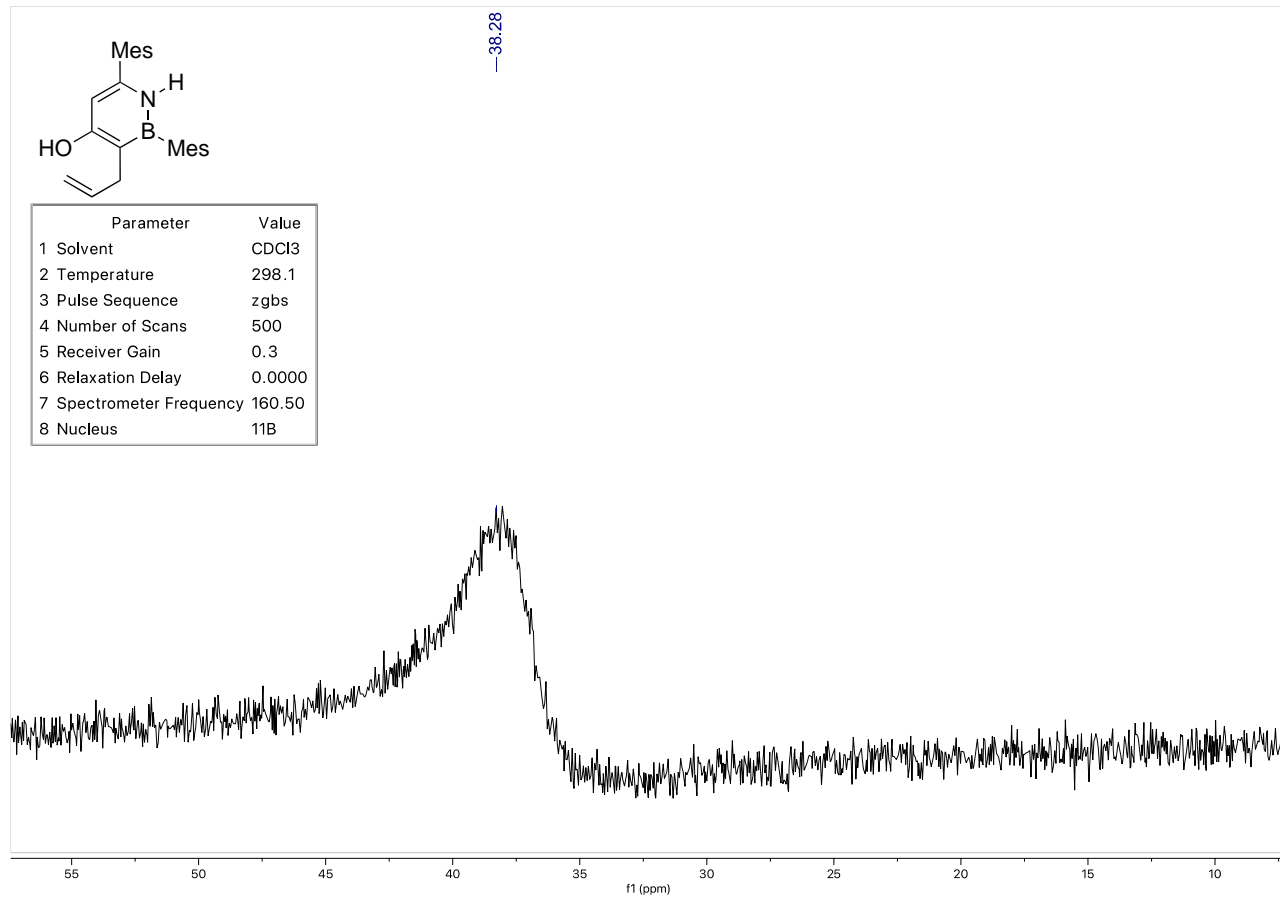
HSQC Spectrum of A-PDT to display regiochemistry:

	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298
3	Pulse Sequence	hsqcedetgpsisp2.3
4	Number of Scans	2
5	Receiver Gain	101.0
6	Relaxation Delay	1.0000
7	Spectrometer Frequency	(500.23, 125.79)
8	Nucleus	(1H, 13C)

Cross peak from H^a (5.90 ppm) and C^a (104.4 ppm)

¹H NMR spectrum

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	25.0
3	Pulse Sequence	s2pul
4	Number of Scans	8
5	Receiver Gain	26
6	Relaxation Delay	10.0000
7	Spectrometer Frequency	599.68
8	Nucleus	1H

¹³C NMR spectrum

	Parameter	Value
1	Solvent	cdcl3
2	Temperature	25.0
3	Pulse Sequence	s2pul
4	Number of Scans	100
5	Receiver Gain	30
6	Relaxation Delay	1.0000
7	Spectrometer Frequency	150.81
8	Nucleus	13C