Electronic Supporting Information

Formal (2 + 2) ring expansion prevails over (4 + 2) cycloaddition of a kinetically stabilized benzoborirene with reactive cycloaddends

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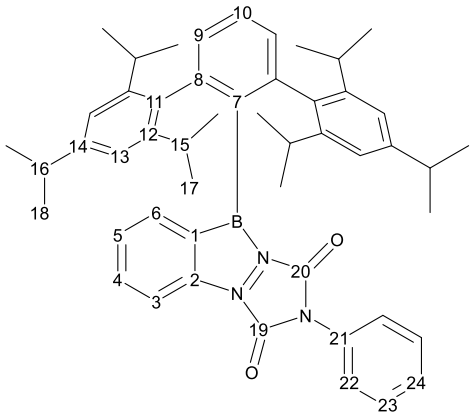
1. Experimental Methods

General procedures.

All experiments were performed under anhydrous conditions using argon as protective gas. The NMR spectra were recorded with either a *Bruker* Avance III HD 300 NanoBay NMR spectrometer (5 mm BBFO probe head) operating at 96.29 (^{11}B), a *Bruker* Avance III HD 400 NMR spectrometer (5 mm BBFO probe head) operating at 400.11 (^{1}H), 100.62 (^{13}C), 128.39 (^{11}B), a *Bruker* Avance III HDX NMR spectrometer (5 mm BBO probe head (^{1}H coil tunable for ^{19}F)) operating at 400.11 (^{1}H), 100.62 (^{13}C), 128.39 (^{11}B) and 161.97 MHz (^{31}P), a *Bruker* Avance III HDX 600 spectrometer (5 mm triple resonance probe head) operating at 600.13 (^{1}H), 150.90 MHz (^{13}C) and 242.94 (^{31}P) and a *Bruker* Avance III HDX 700 NMR (5 mm TXI probe head) operating at 700.29 (^{1}H) and 176.09 MHz (^{13}C). The chemical shifts are reported as δ in ppm relative to the following external standards: tetramethylsilane (^{1}H, ^{13}C), boron trifluoride etherate (^{11}B).[1] The chemical shifts were referenced using the chemical shift of the solvent ^{2}H resonance frequency as followed: Ξ = 32.08397 % for ^{11}B, Ξ = 25.145020 % for ^{13}C.[1] The multiplicity of the signals is abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, sept = septet and m = multiplet or br. = broad/unresolved. The proton and carbon signals were assigned via detailed analysis of ^{1}H, ^{13}C{^{1}H}-(UDEFT), ^{1}H-^{1}H-COSY, ^{1}H-^{1}H-NOESY, ^{1}H-^{13}C-HSQC and ^{1}H-^{13}C-HMBC NMR spectra. If not stated otherwise, NMR measurements were performed at 298 K. All commercially available compounds were purchased and used without further purification. Dry solvents were either purchased or taken from a *MBraun* solvent purification system MB-SPS-800. For HR-APCI-TOF-MS measurements a *Bruker* maXis 4G spectrometer (sample application: DIP) was used. Benzoborirene **1** was synthesized as described in the literature.[2] The size exclusion chromatography was performed on a LaboACE LC-7080 Plus device using a JAIGEL - 2.5 HR polymer-based GPC HPLC column (exclusion limit 2×10^4, theoretical plates> 28.000) from *Japan Analytical Industry Co*.

Synthesis.



Compound **2**. To 14.9 mg (0.026 mmol) **1**, dissolved in 6 mL benzene were added 4.6 mg (0.026 mmol) 4-phenyl-1,2,4-triazolin-3,5-dione, dissolved in 6 mL benzene and stirred overnight. The solvent was removed under reduced pressure and the remaining solid was purified by size exclusion chromatography (*n*-hexane/dichloromethane 60/40) to afford **2** as a colorless solid (13.1 mg, 0.018 mmol, 69%). Crystals suitable for X-ray crystallography were grown from a saturated pentane solution at -30 °C.

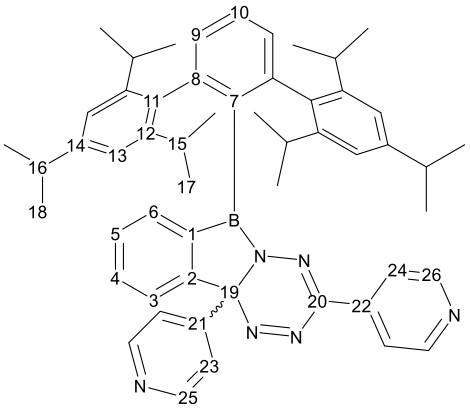
^{1}H (600.13 MHz, benzene-d$_6$): δ = 1.04 (d, 6*H*, **18**, $^{3}J_{HH}$ = 6.78 Hz), 1.05 (d, 6*H*, **18**, $^{3}J_{HH}$ = 6.71 Hz), 1.15 (d, 6*H*, **17.1**, $^{3}J_{HH}$ = 6.72 Hz), 1.20 (d, 6*H*, **17.2**, $^{3}J_{HH}$ = 6.86 Hz), 1.29 (d, 6*H*, **17.2**, $^{3}J_{HH}$ = 6.74 Hz), 1.30 (d, 6*H*, **17.1**, $^{3}J_{HH}$ = 6.87 Hz), 2.64 (sept, 2*H*, **16**, $^{3}J_{HH}$ = 6.91 Hz), 3.34 (sept, 2*H*, **15.1**, $^{3}J_{HH}$ = 6.78 Hz), 3.61 (sept, 2*H*, **15.2**, $^{3}J_{HH}$ = 6.71 Hz), 6.77 (dt, 1*H*, **4**, $^{3}J_{HH}$ = 7.51 Hz, $^{4}J_{HH}$ = 0.84 Hz), 6.88-6.91 (m, 1*H*, **5**), 6.95-6.97 (m, 1*H*, **24**), 7.02 (s, 2*H*, **13.1**), 7.07 (s, 2*H*, **13.2**), 7.11-7.14 (m, 2*H*, **23**), 7.33-7.36 (m, 1*H*, **10**), 7.36-7.37 (m, 1*H*, **3**), 7.39 (m, 2*H*, **9**), 7.61 (m, 2*H*, **22**), 7.67 (m, 1*H*, **6**) ppm;

^{13}C{^{1}H} (150.90 MHz, benzene-d$_6$): δ = 22.9 (**17.1**), 23.8 (**17.2**), 24.0 (**18**), 24.2 (**18**), 26.8 (**17.1**), 27.1 (**17.2**), 30.7 (**15.2**), 30.8 (**15.1**), 34.6 (**16**), 112.2 (**3**), 120.6 (**13.1**), 121.2 (**13.2**), 122.7 (**4**), 125.7 (**22**), 127.9 (**10**), 128.4 (**24**), 129.2 (**23**), 130.0 (**9**), 131.9 (**21**), 133.5 (**5**), 134.7 (**6**), 134.9 (**7**), 138.0 (**11**), 141.4 (**1**), 143.9 (**20**), 144.5 (**8**), 147.0 (**12.1**), 147.2 (**19**), 148.2 (**12.2**), 148.7 (**14**), ppm;

^{11}B (128.39 MHz, benzene-d$_6$): δ = 40.8 ppm;

HR-APCI-TOF-MS: APCI T_{Oven} = 350 °C, calc. for $C_{50}H_{59}BN_3O_2$ + H 744.47033 Da, found 744.47099 Da [M+H]•+.

Compound **3**. To 20.0 mg (0.035 mmol) **1**, dissolved in 8 mL benzene were added 8.3 mg (0.035 mmol) 3,5-di-(4-pyridinyl)-1,2,4,5-tetrazine dissolved in 8 mL benzene and stirred overnight. The solvent was removed under reduced pressure and the remaining solid was dissolved in pentane. Slow evaporation of the solvent yielded red crystals suitable for X-ray crystallography.

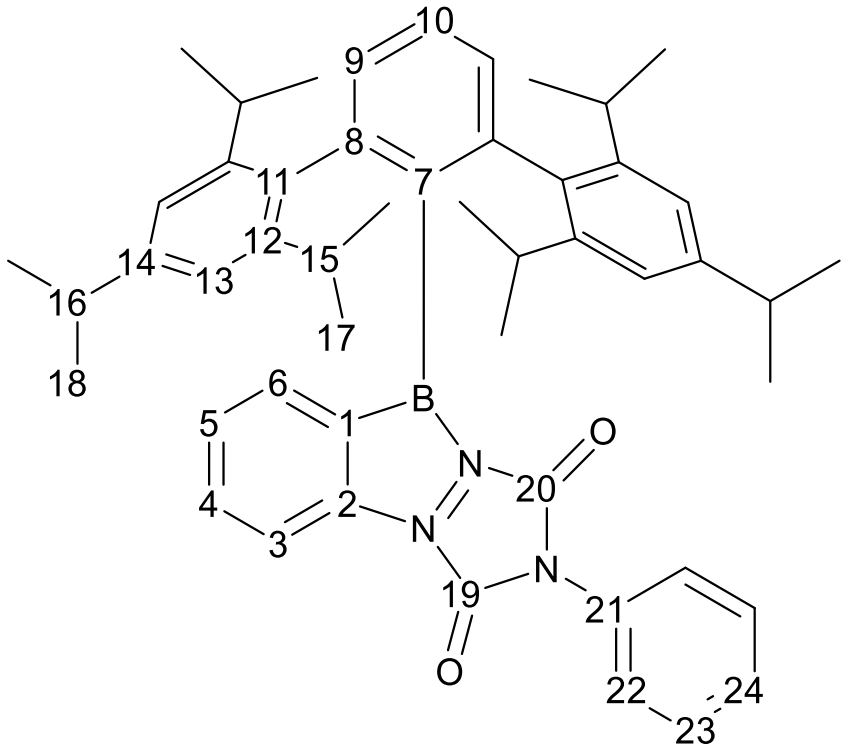


^{1}H (700.29 MHz, benzene-d$_6$): δ = 0.92 (d, 3*H*, **17.1**, $^{3}J_{HH}$ = 6.78 Hz), 0.98 (d, 3*H*, **17.2**, $^{3}J_{HH}$ = 6.82 Hz), 1.04 (d, 3*H*, **17.3**, $^{3}J_{HH}$ = 6.79 Hz), 1.07 (d, 3*H*, **17.2**), 1.08 (d, 3*H*, **18.1**), 1.09 (d, 3*H*, **17.4**), 1.13 (d, 6*H*, **17.1+18.2**), 1.15 (d, 3*H*, **17.4**, $^{3}J_{HH}$ = 6.80 Hz), 1,17 (d, 6*H*, **17.3+18.3**), 1.20 (d, 3*H*, **18.4**, $^{3}J_{HH}$ = 6.92 Hz), 2.69 (sept, 1*H*, **16**, $^{3}J_{HH}$ = 6.84 Hz), 2.70 (sept, 1*H*, **16**, $^{3}J_{HH}$ = 6.84 Hz), 2.93 (sept, 1*H*, **15.2**, $^{3}J_{HH}$ = 6.74 Hz), 3.02 (sept, 1*H*, **15.1**, $^{3}J_{HH}$ = 6.74 Hz), 3.37 (sept, 1*H*, **15.3**, $^{3}J_{HH}$ = 6.69 Hz), 3.72 (sept, 1*H*, **15.4**, $^{3}J_{HH}$ = 6.77 Hz), 6.37 (m, 1*H*, **23.1**), 6.85 (d, 1*H*, **24.1,** $^{4}J_{HH}$ = 1.40 Hz), 6.92-6.95 (m, 2*H*, **4**+**26.1**), 6.98 (dt, 1*H*, **5**, $^{3}J_{HH}$ = 7.40 Hz, $^{4}J_{HH}$ = 0.86 Hz), 7.02 (d, 1*H*, **24.2**, $^{4}J_{HH}$ = 1.62 Hz), 7.16 (s, 4*H*, **13**), 7.19 (d, 1*H*, **26.2**, $^{4}J_{HH}$ = 1.52 Hz), 7.25 (m, 1*H*, **3**), 7.34 (t, 1*H*, **10**, $^{3}J_{HH}$ = 7.59 Hz), 7.38 (dd, 1*H*, **9**, $^{3}J_{HH}$ = 7.55 Hz, $^{4}J_{HH}$ = 1.04 Hz), 7.41 (dd, 1*H*, **9**, $^{3}J_{HH}$ = 7.57 Hz, $^{4}J_{HH}$ = 0.93 Hz), 7.61 (d, 1*H*, **6**, $^{3}J_{HH}$ = 7.34 Hz), 7.68 (m, 1*H*, **23.2**), 8.29 (d, 1*H*, **25.1**, $^{3}J_{HH}$ = 5.73 Hz), 7.34 (d, 1*H*, **25.2**, $^{3}J_{HH}$ = 4.77 Hz) ppm (coupling constants not determinable due to signal overlap have been omitted);

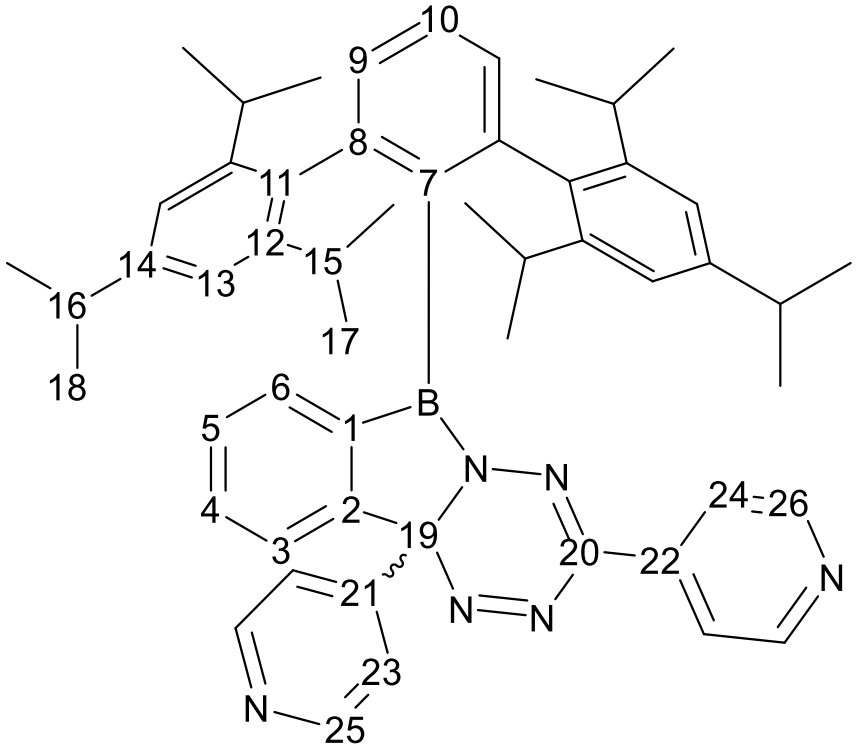
^{13}C{^{1}H} (176.09 MHz, benzene-d$_6$):δ = 21.8 (**17.1**), 22.4 (**17.2**), 23.1 (**17.3**), 23.4 (**17.4**), 23.9 (**18.1**), 24.0 (**18.3**), 24.5 (**18.2**), 24.5 (**18.4**), 26.6 (**17.4**), 27.1 (**17.3**), 27.1 (**17.2**), 27.4 (**17.1**), 30.7 (**15.4**), 31.0 (**15.3**), 31.0 (**15.2**), 31.3 (**15.1**), 34.5 (**16**), 34.7 (**16**), 84.1 (**19**), 120.3 (**26.1**), 120.6 (**24.1**), 120.7 (**23.2**), 121.1 (**24.2**), 121.4 (**26.2**), 121.9 (**23.1**), 123.5 (**3**), 127.8 (**10**), 128.3 (**5**), 128.6 (**13**), 129.9 (**9**), 130.1 (**9**), 133.6 (**4**), 134.6 (**6**), 136.9 (**11**), 137.5 (**1**), 138.2 (**11**), 143.2 (**8**), 144.6 (**8**), 145.0 (**20 o. 22**), 146.0 (**12.1**), 147.1 (**12.3**), 147.7 (**12.2**), 148.1 (**12.4**), 148.9 (**14**), 149.2 (**14**), 150.1 (**2**), 150.5 (**25.1**), 150.8 (**25.2**), 153.9 (**21**) ppm;

^{11}B (128.39 MHz, benzene-d$_6$): no signal could be obtained;

HR-APCI-TOF-MS: APCI T_{Oven} = 350 °C, calc. for $C_{54}H_{62}BN_6$ + H 805.51325 Da, found 805.51233 Da [M+H]•+.



2



3

Scheme S1. Atom numbering of compounds **2** and **3** used for NMR assignment.

2. NMR spectra

Solvent signals are denoted by an asterisk (*)

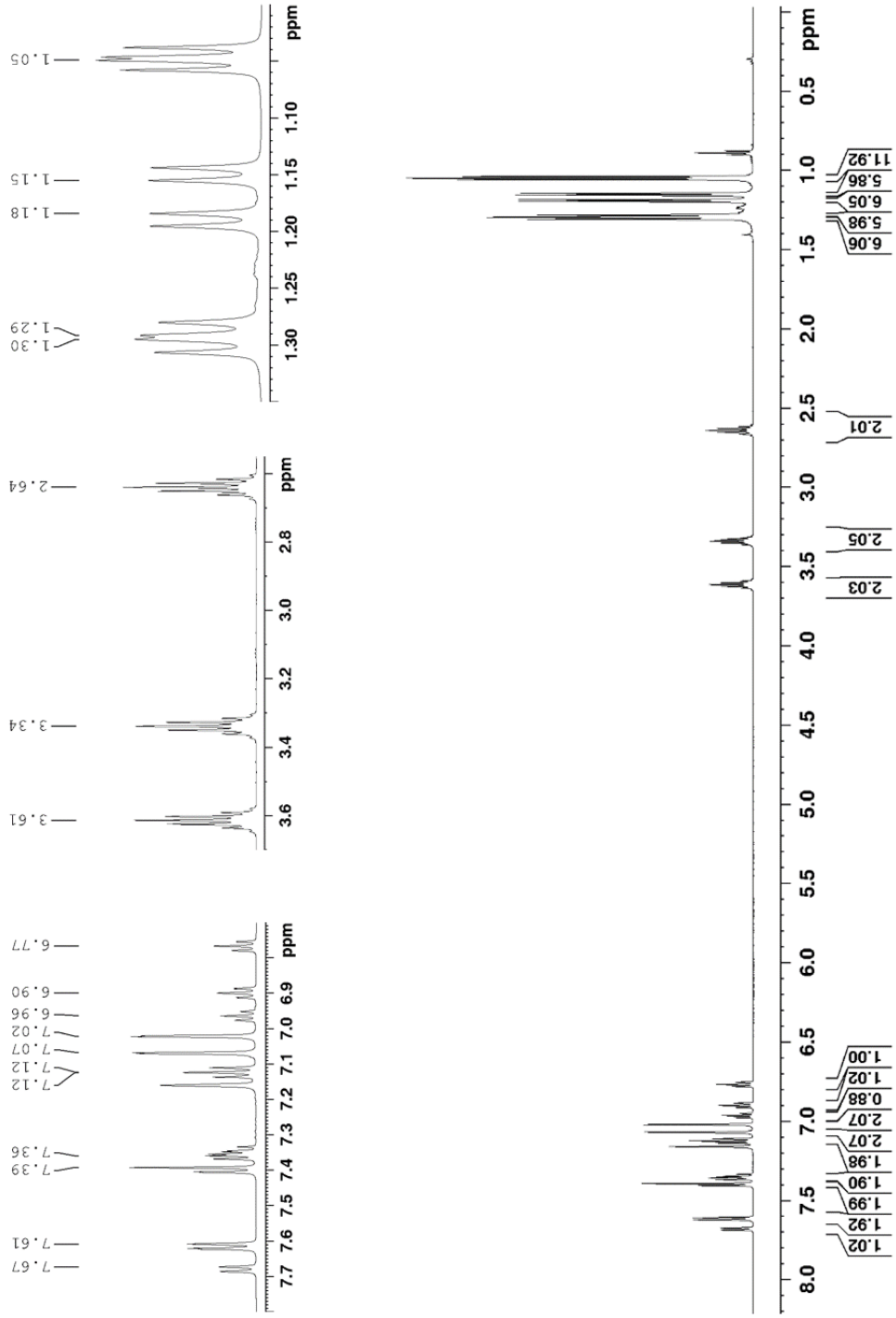


Figure S1. ^{1}H NMR spectrum of compound **2** in C_6D_6.

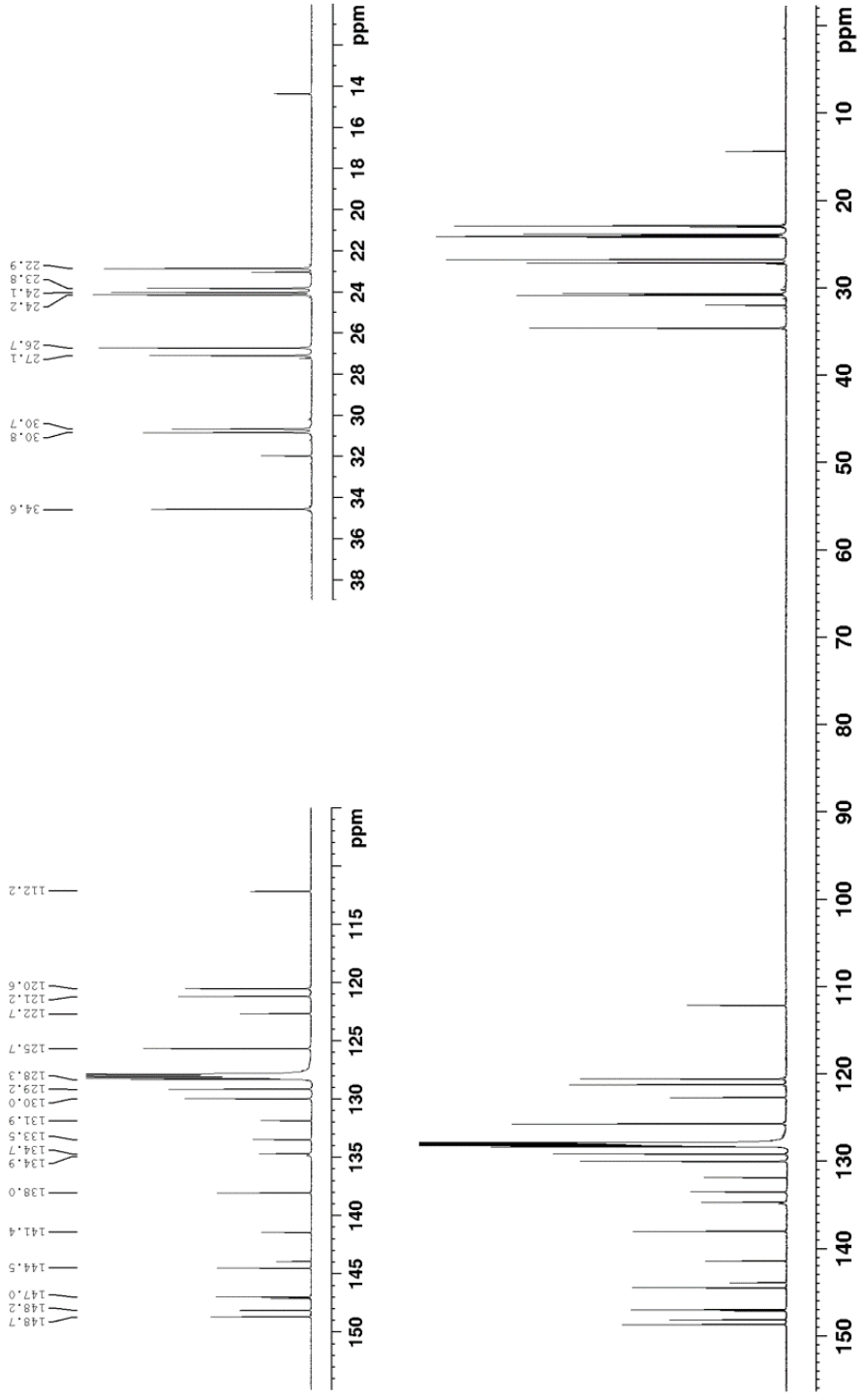


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** in C_6D_6.

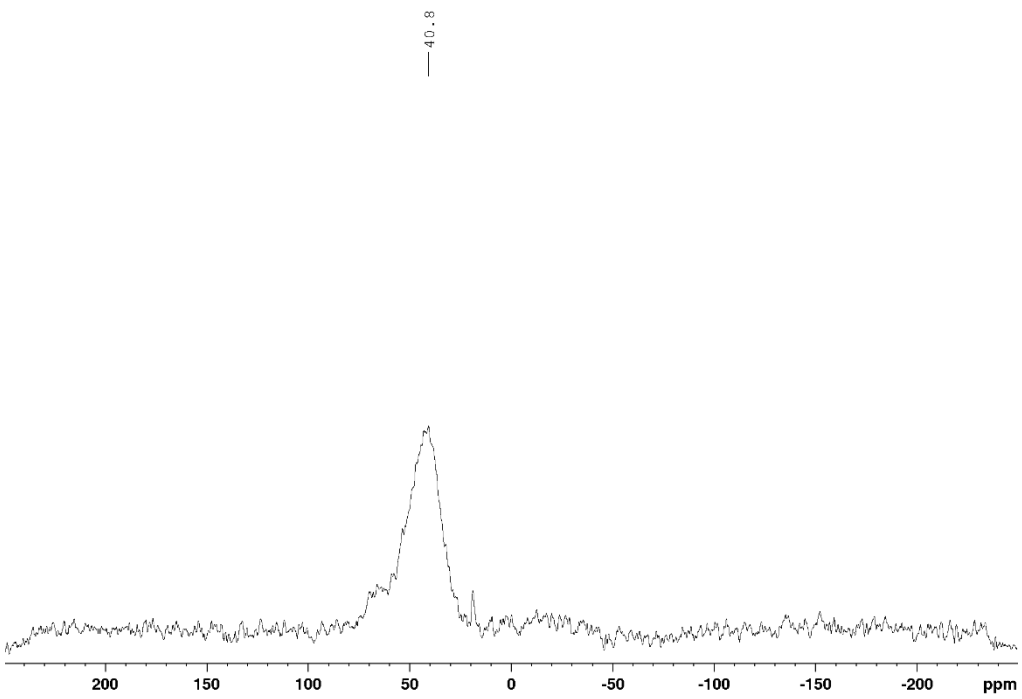


Figure S3. ^{11}B NMR spectrum of compound **2** in in C_6D_6.

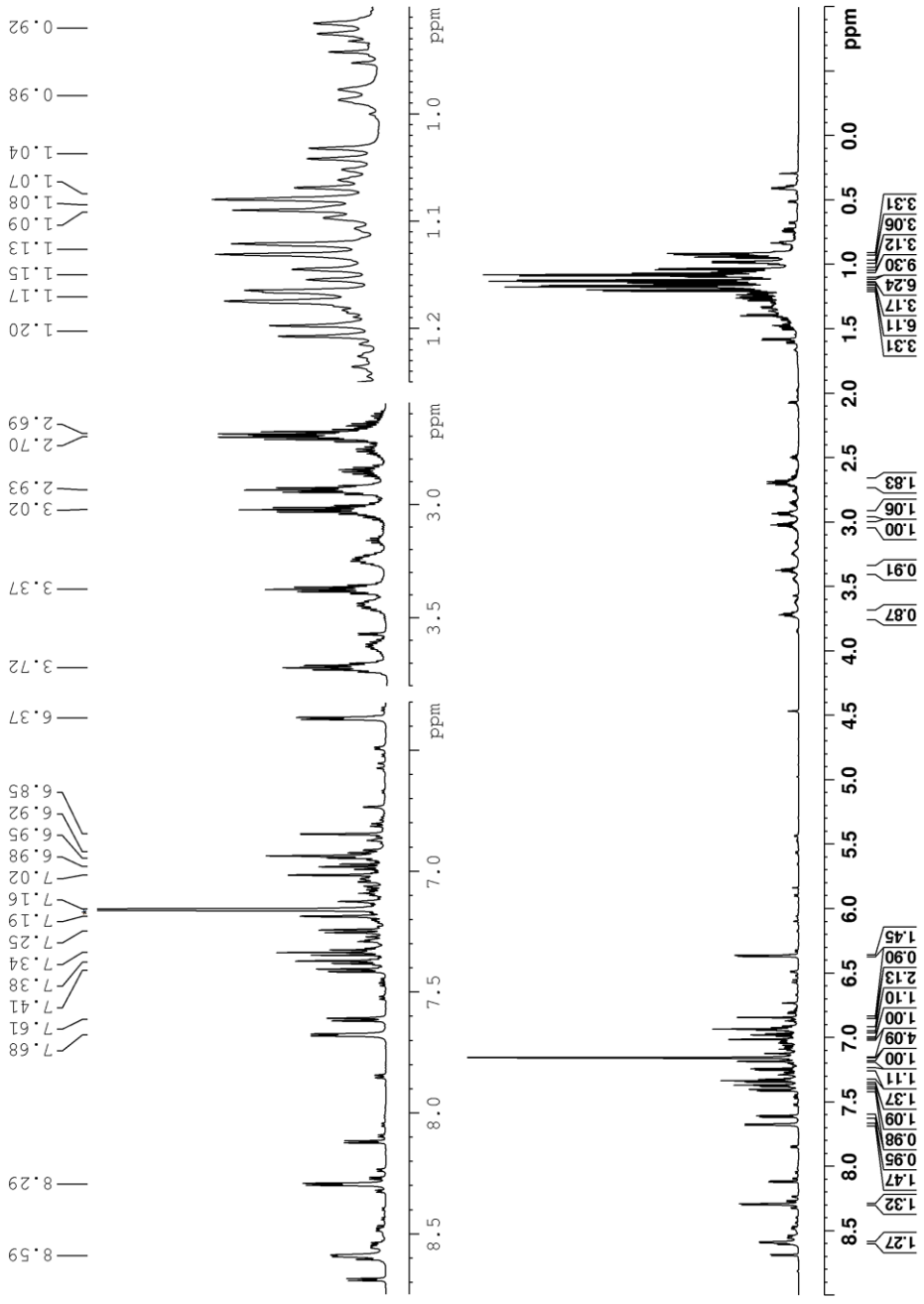


Figure S4. ^{1}H NMR spectrum of compound **3** in C_6D_6.

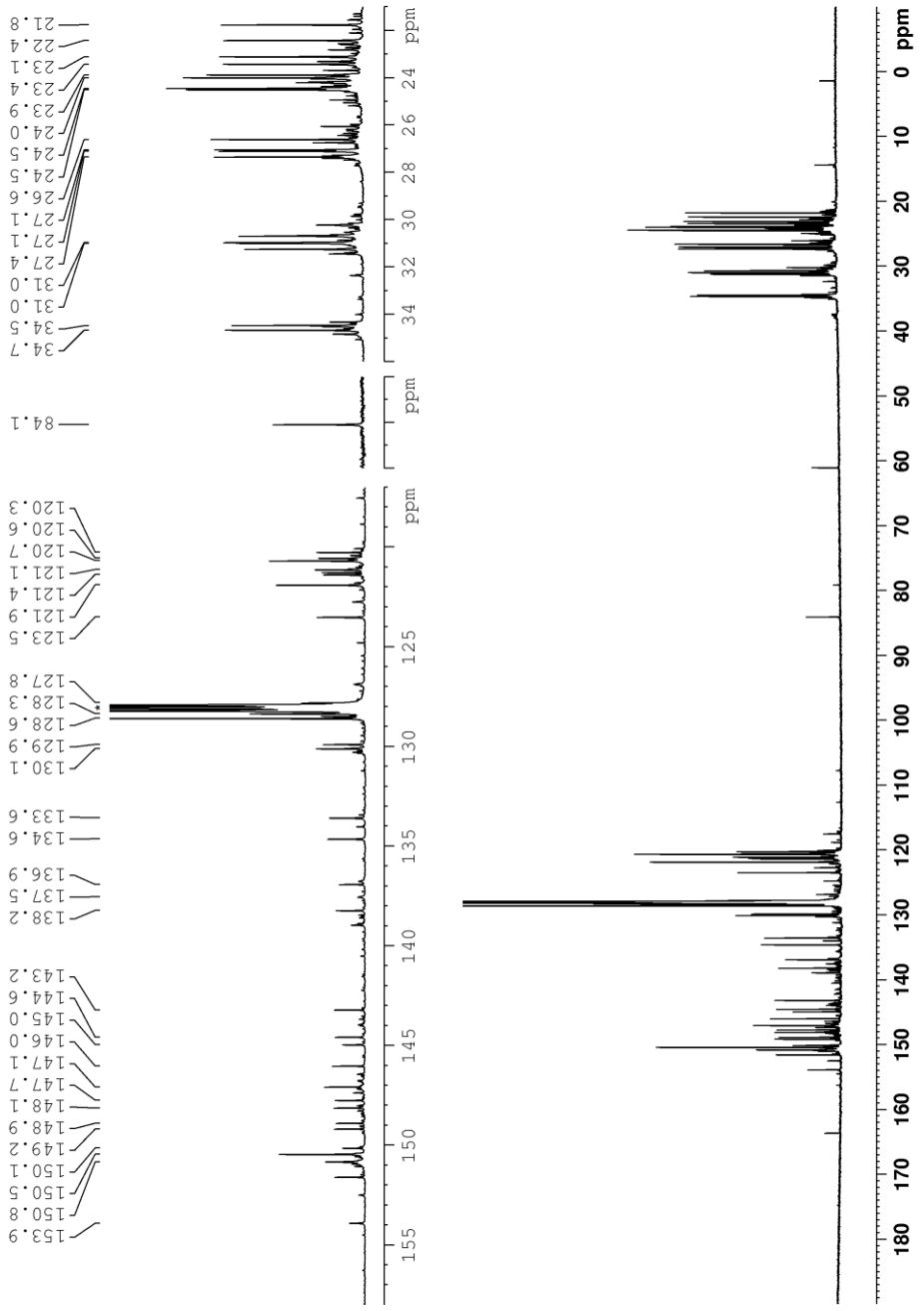


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** in C_6D_6.

3. Mass spectra

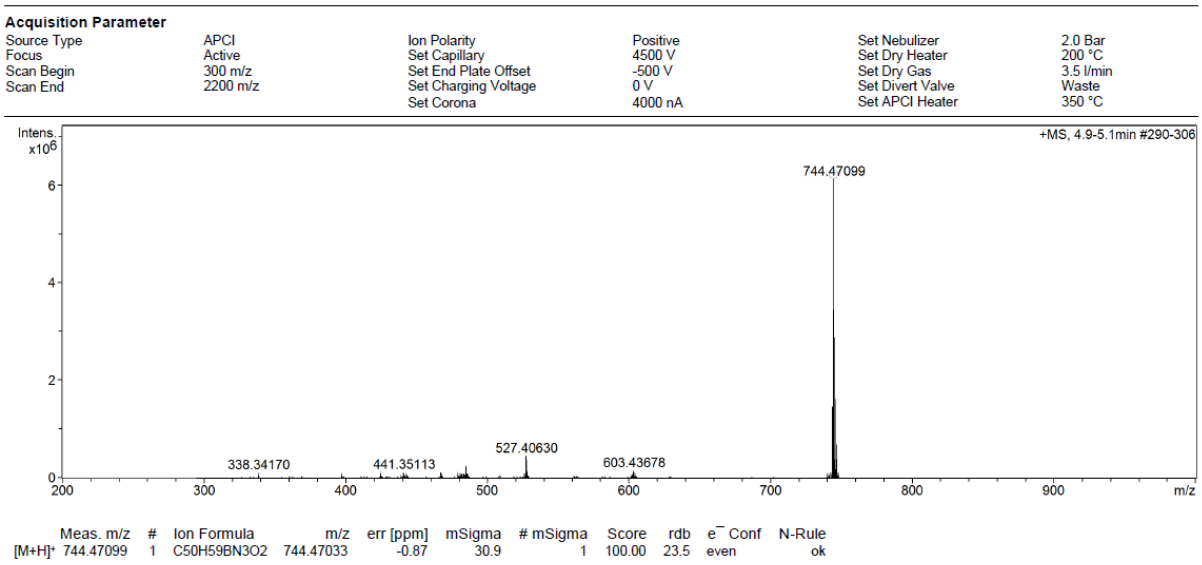


Figure S6. Mass spectrum of compound **2**.

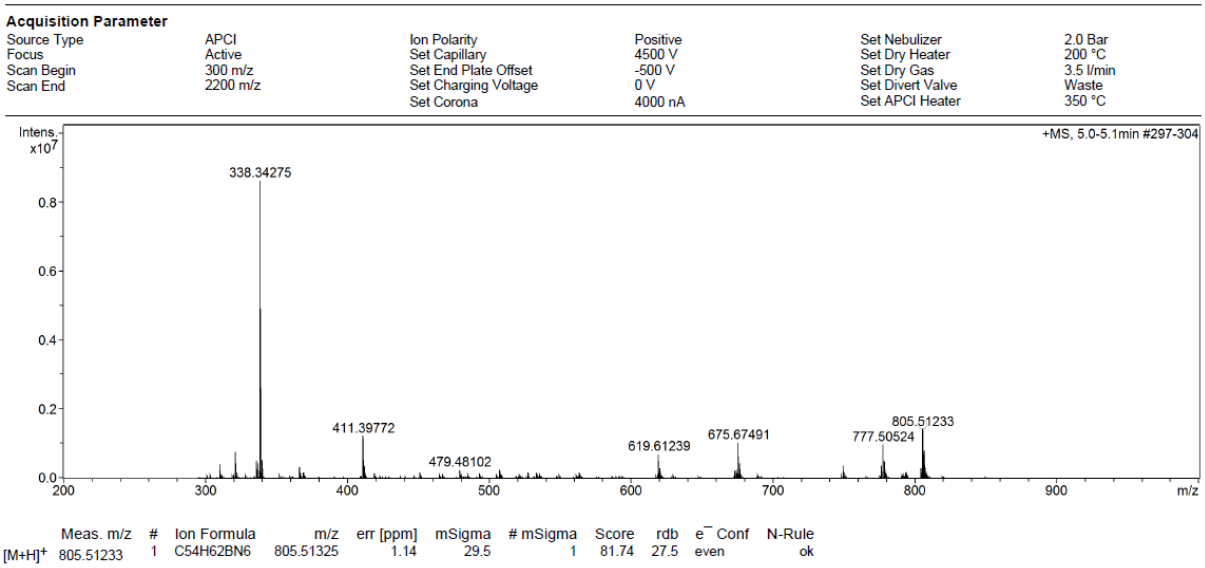


Figure S7. Mass spectrum of compound **3**.

4. X-ray crystallography

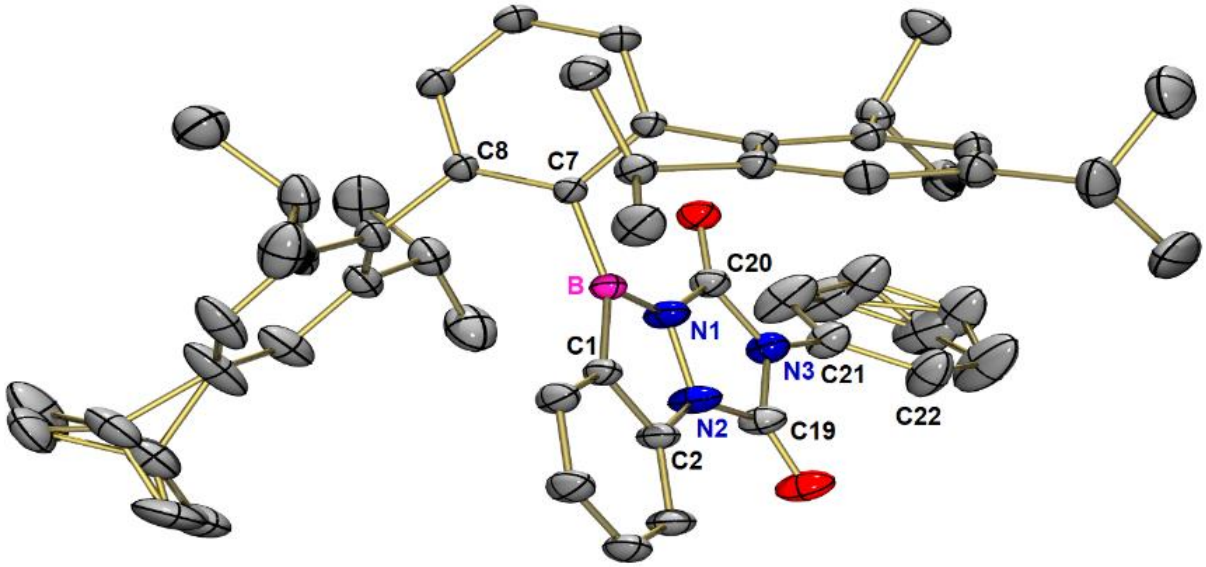


Figure S8. Molecular structure of **2** in the solid state. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: B–C1 155.4, B–C7 157.0, B–N1 144.8, N1–N2 139.4, N2–C2 138.8, C2–N2–N3 173.84, N1–B–C7–C8 91.74, C19–N3–C21–C22 -41.30. Angle sums [°]: B 360.00, N1 359.81, N2 359.09, C1 359.97, C2 360.00, C19 360.00, C20 360.00, N3 359.86.

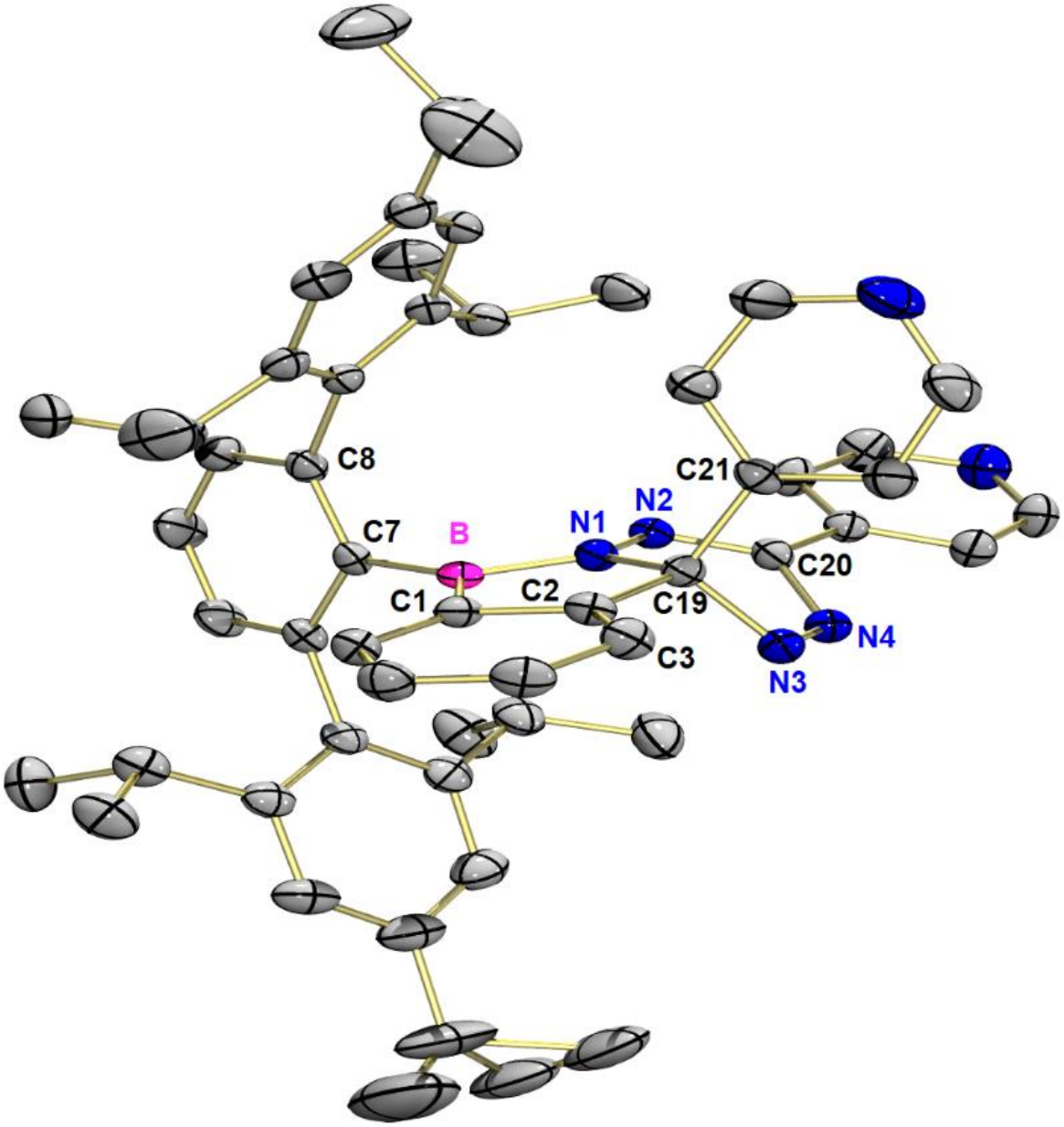


Figure S9. Molecular structure of the (R)-enantiomer of **3** in the solid state. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: B–C1 155.6, B–C7 157.3, B–N1 144.5, N1–C19 145.4, N3–C19 149.5, C19–C2 151.1, C19–C21 153.2, N1–N2 136.0, N2–C20 130.5, C20–N4 141.1, N2-N4 126.0, B–C19–C21 125.09, N1–B–C7–C8 -78.16, C3–C1–N2–N4 30.60.

Table S1. Crystallographic information for compounds **2** and **3**.

	2	**3**
Empirical formula	$C_{50}H_{58}BN_3O_2$	$C_{54}H_{61}BN_6$
Formula weight	743.861	804.89
Temperature [K]	149.99(10)	150.00(11)
Crystal system	triclinic	monoclinic
Space group	P -1	Cc
Unit cell dimensions	a = 12.3228(3) Å	a = 11.08430(10) Å
	b = 14.4609(3) Å	b = 33.8144(2) Å
	c = 14.8882(3) Å	c = 25.41950(10) Å
	α = 69.651(2)°	α = 90°
	β = 88.327(2)°	β = 93.8470(10)°
	γ = 69.674(2)°	γ = 90°
Volume [$Å^3$]	3219.9(1)	9505.99(11)
Z	2	8
Density (calculated) [Mg/m^3]	1.065	1.125
Crystal size [mm^3]	0.14×0.13×0.02	0.21×0.12×0.03
Crystal Color	colorless	red
Theta range for data collection	3.18° - 78.68°	2.613° - 68.250°
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 17, -18 ≤ l ≤ 18	-13 ≤ h ≤ 13, -40 ≤ k ≤ 40, -30 ≤ l ≤ 30
Reflections collected	75181	135487
Independent reflections	9378 [R(int) = 0.0180]	17102 [R(int) = 0.0229]
Goodness-of-fit on F2	1.0735	1.021
Final R Indices [I>2sigma(I)]	R1 = 0.0215, wR2 = 0.0524	R1 = 0.0329, wR2 = 0.0893
R Indices (all Data)	R1 = 0.0244, wR2 = 0.0538	R1 = 0.0334, wR2 = 0.0897
CCDC	2290575	2312526

Experimental Data

Crystals suitable for X-Ray crystallography were grown as described in the synthesis. 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 Rigaku XtaLAP Synergy-S single-crystal diffractometer, equipped with a HyPix-6000HE detector and monochromatic Cu-K_α radiation. Corrections for absorption effects were applied with CrysAlisPro 1.171.41.65a (Rigaku Oxford Diffraction, 2020). The structure was solved by direct methods (SHELXS),[3] and full-matrix least-squares structure refinements were performed with SHELXL-2014[4] implemented in Olex2 1.3-ac4.[5]

5. Computational Methods

The reactions of **1** with PTAD and 4,4'-bptz towards products **2** and **3**, respectively, were investigated using the r^{2}SCAN-3c methodology.[6] This "swiss army knife" composite method introduced by Grimme et al. combines the meta-generalized gradient approximation functional r^{2}SCAN[7] with a tailor-made triple-ζ basis (mTZVPP) set and corrections for dispersion interactions by the D4 method and for basis set superposition errors by the geometrical counter-poise correction scheme (gCP).[6] Geometries were optimized using r^{2}SCAN-3c and harmonic vibrational frequencies were computed to confirm the nature of stationary points as minimum or transition structures with 0 or 1 imaginary vibrational frequencies, respectively. The searches for transition structures at the r^{2}SCAN-3c level of theory were facilitated by preliminary semiempirical GFN-xTB[8] computations using either classical coordinate scans or the climbing-image nudged elastic band method combined with a saddle point search using an eigenvector following method starting from the location of the climbing image (NEB-TS) as implemented by Ásgeirsson et al. in ORCA.[9] All these computations were performed with ORCA 5.0.4.[10, 11]

For the investigation of the Diels-Alder reactivity of **1** towards PTAD and 4,4'-bptz a simplified model system was employed that has the bulky $Trip_2C_6H_3$ (Trip = 2,4,6-*iso*-$Pr_3C_6H_2$) substituent replaced by a phenyl ring giving **1'**. This simplification is motivated by the desire to investigate the inherent reactivity of **1'** in Diels-Alder reactions unbiased by steric effects. The geometries of stationary points were fully optimized using the M06-2X functional along with the 6-311+G** basis set.[12, 13] Harmonic vibrational frequencies were computed to confirm that the structures correspond to minima or transition states with zero or one imaginary vibrational frequencies, respectively. These computations were performed with Gaussian 16.[14]

Energies were refined by computed single point energies at the r^{2}SCAN-3c and M06-2X/6-311+G** geometries using the revDSD-PBEP86-D4[15] double hybrid functional along with the def2-QZVPP and appropriate fitting basis sets (def2-QZVPP/C and def2-JK) for the RI approximations.[16-18] The influence of benzene solvent was taken into account using the conductor-like polarizable continuum model (CPCM) as implemented in Orca.[19] The revDSD-PBEP86-D4 electronic energy, the Gibbs free energy correction obtained from harmonic vibrational frequencies computed at the r^{2}SCAN-3c or M06-2X/6-311+G** give the Gibbs energies at T = 298.15 K.[20] The correction of the standard state in solution compared to gas phase was considered by adding 1.89 kcal/mol for each species.[21] The r^{2}SCAN-3c and rev-DSD-PBEP86-D4 computations were performed with ORCA 5.0.4.[10, 11]

6. Diels-Alder Reactions of *B*-Phenylbenzoborirene 1'

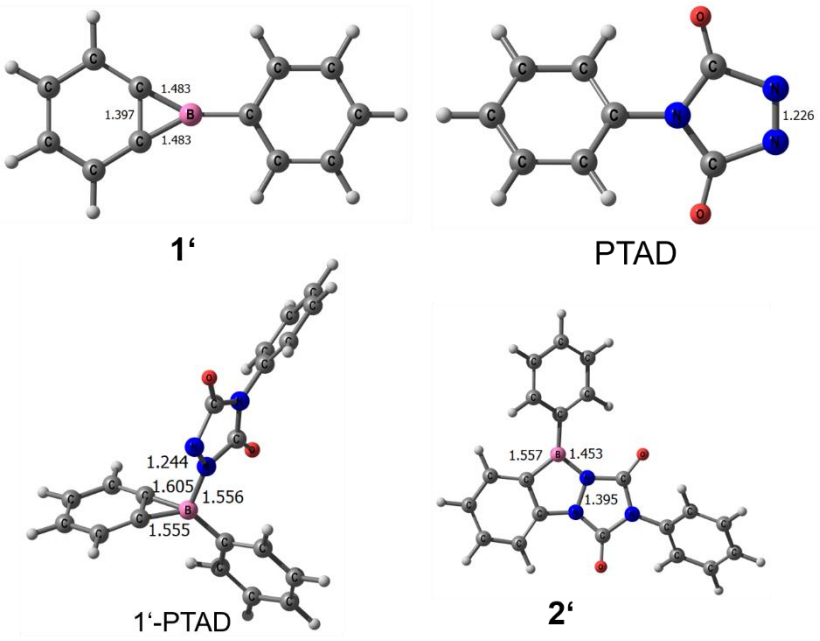


Figure S10. Structures of **1**', PTAD, the complex between **1**' and PTAD, and reaction product **2**' as computed at the M06-2X/6-311+G** level of theory. Important distances are given in Å.

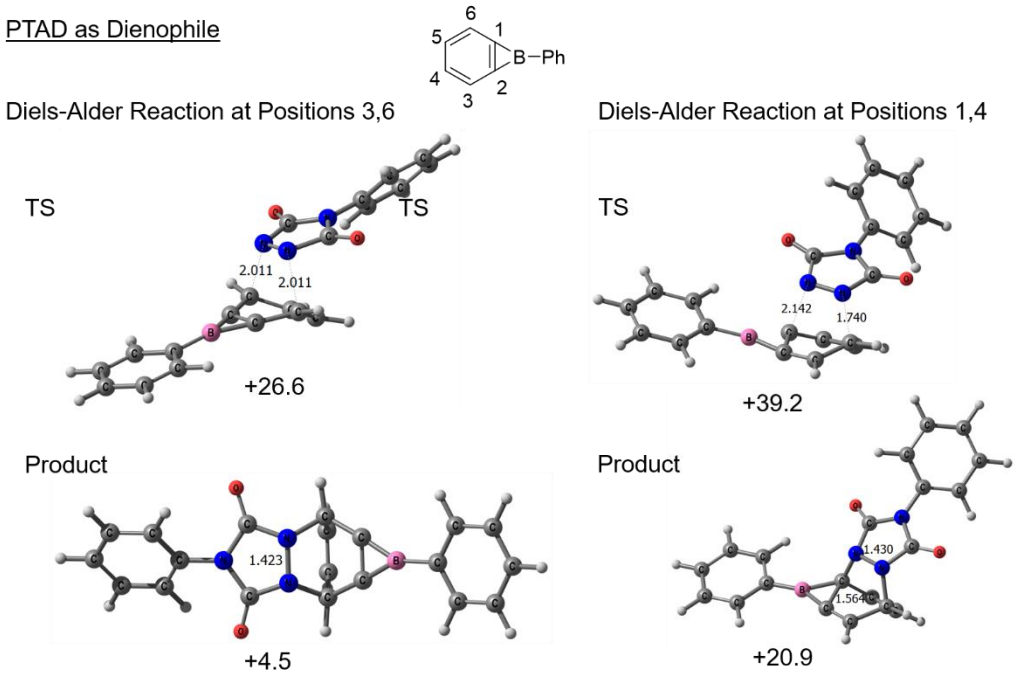


Figure S11. Structures of transition states (TS) and products of Diels-Alder reactions between **1**' and PTAD as computed at the M06-2X/6-311+G** level of theory. Important distances are given in Å, relative Gibbs free energies are given in kcal/mol and were computed at the revDSD-PBEP86-D4/def2-QZVPP(PCM:benzene)//M06-2X/6-311+G** level of theory.

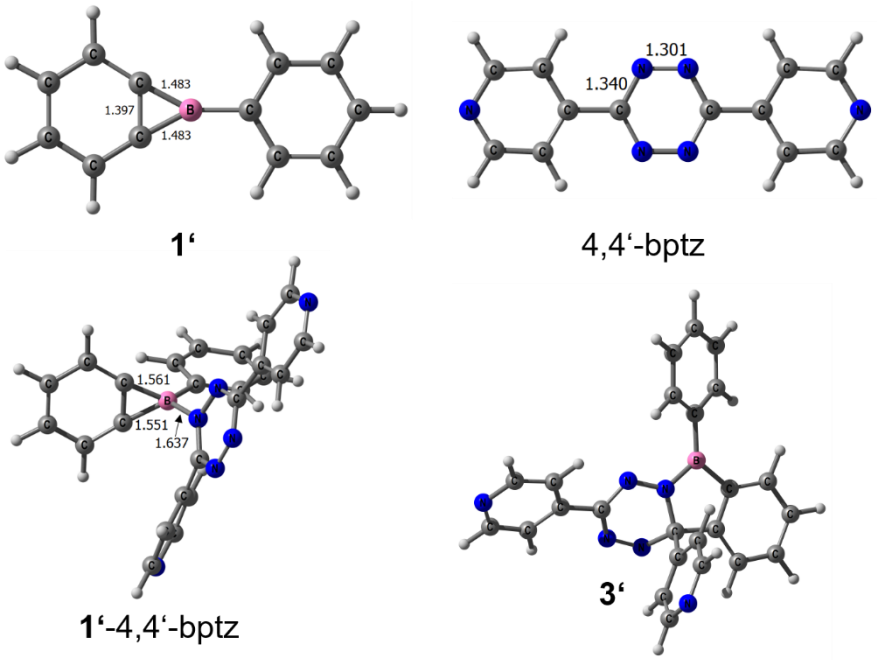
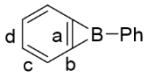
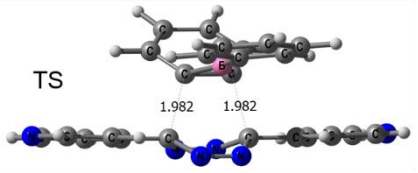


Figure S12. Structures of **1**', 4,4'-bptz, the complex between **1**' and 4,4'-bptz, and reaction product **3**' as computed at the M06-2X/6-311+G** level of theory. Important distances are given in Å.

Tetrazine as Diene



Diels-Alder Reaction at Bond a



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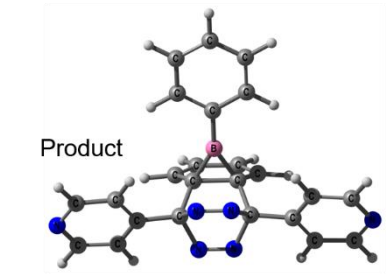
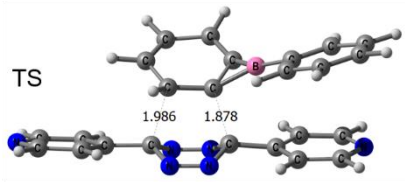
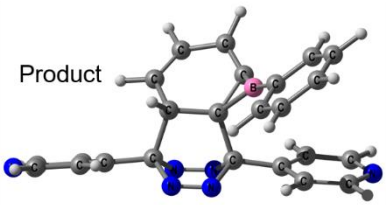


+22.1

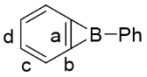
Diels-Alder Reaction at Bond b



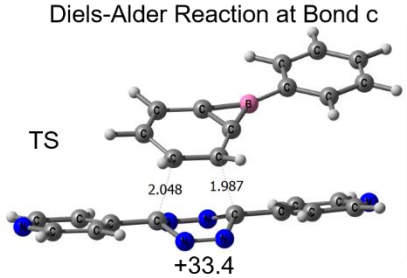
+44.6



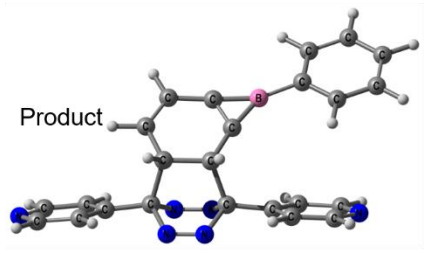
+34.6



Diels-Alder Reaction at Bond c

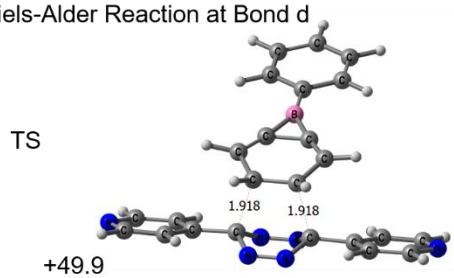


+33.4

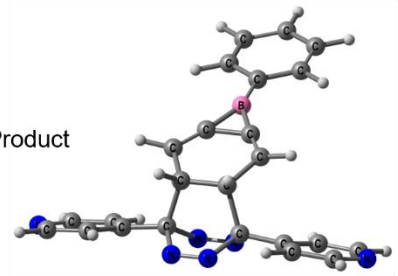


+17.7

Diels-Alder Reaction at Bond d



+49.9



+42.3

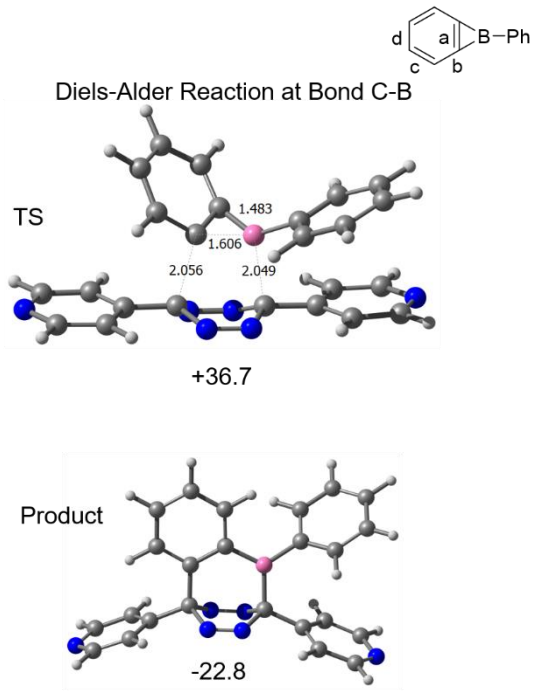


Figure S13. Structures of transition states (TS) and products of Diels-Alder reactions between **1**' and 4,4'-bptz as computed at the M06-2X/6-311+G** level of theory. Important distances are given in Å, and relative Gibbs free energies are given in kcal/mol and were computed at the revDSD-PBEP86-D4/def2-QZVPP(PCM:benzene)//M06-2X/6-311+G** level of theory.

7. Cartesian coordinates

a. Cartesian coordinates for reactions of 1 with PTAD and 4,4'-bptz to give products 2 and 3

1'
96
symmetry c1

6	7.714350000	18.841061000	4.078671000
6	8.159838000	17.622602000	4.638893000
6	9.080174000	17.630948000	5.685402000
1	9.415892000	16.686313000	6.105551000
6	9.562740000	18.836210000	6.185565000
1	10.280651000	18.834300000	7.001667000
6	7.644513000	16.323739000	4.111709000
6	6.478493000	15.763370000	4.655426000
6	5.997390000	14.564527000	4.126235000
1	5.093424000	14.122471000	4.541498000
6	6.635308000	13.916421000	3.073672000
6	7.787971000	14.495694000	2.545691000
1	8.298498000	14.007057000	1.718459000
6	8.305618000	15.688485000	3.046048000
6	5.718424000	16.439948000	5.782195000
1	6.249429000	17.364273000	6.037483000
6	4.301055000	16.830174000	5.341801000
1	4.329136000	17.446749000	4.437808000
1	3.795905000	17.396238000	6.132605000
1	3.695162000	15.942988000	5.125501000
6	5.684678000	15.564849000	7.041924000

1	5.138615000	14.632007000	6.862040000
1	5.185785000	16.092233000	7.862809000
1	6.697487000	15.302895000	7.365321000
6	6.086075000	12.619314000	2.515037000
1	5.196525000	12.362270000	3.107352000
6	5.645287000	12.779316000	1.054071000
1	4.904025000	13.578747000	0.952733000
1	5.202797000	11.850079000	0.677776000
1	6.498062000	13.028603000	0.412672000
6	7.093075000	11.470876000	2.659157000
1	7.988348000	11.656081000	2.055120000
1	6.653064000	10.525447000	2.322589000
1	7.409718000	11.354745000	3.700421000
6	9.555095000	16.282289000	2.419481000
1	9.787982000	17.211493000	2.952231000
6	10.760048000	15.345865000	2.578195000
1	10.933756000	15.105147000	3.632212000
1	11.666192000	15.813578000	2.176953000
1	10.603084000	14.403777000	2.040998000
6	9.326546000	16.643516000	0.945569000
1	9.144082000	15.747376000	0.341340000
1	10.206849000	17.150657000	0.534510000
1	8.461398000	17.304788000	0.832343000
6	5.931729000	19.537688000	1.863910000
6	5.229290000	20.279473000	0.907180000
1	5.296640000	21.362938000	0.833080000
6	4.434804000	19.544168000	0.045109000
1	3.860005000	20.053377000	-0.725042000
6	4.340371000	18.130125000	0.125897000
1	3.697765000	17.617524000	-0.586231000
6	5.036996000	17.398749000	1.071873000
1	4.960172000	16.314590000	1.121614000
6	5.838561000	18.144644000	1.943551000
5	6.719035000	18.842452000	2.908089000
6	8.206800000	20.057241000	4.603279000
6	9.127282000	20.044083000	5.649602000
1	9.497505000	20.987042000	6.043759000
6	7.725785000	21.358941000	4.051802000
6	6.572488000	21.953947000	4.585859000
6	6.118657000	23.154883000	4.037755000
1	5.223884000	23.622713000	4.444389000
6	6.772520000	23.772786000	2.977040000
6	7.912668000	23.159984000	2.459583000
1	8.435031000	23.624729000	1.626045000
6	8.402009000	21.962560000	2.977417000
6	5.795321000	21.312172000	5.722120000
1	6.315737000	20.390494000	6.006596000
6	4.380173000	20.921817000	5.274501000
1	4.413901000	20.273199000	4.393182000
1	3.856978000	20.389020000	6.076580000
1	3.788365000	21.807311000	5.016526000
6	5.754597000	22.218198000	6.959363000
1	5.215926000	23.149788000	6.752875000
1	5.244897000	21.713632000	7.787868000
1	6.765893000	22.481832000	7.286098000
6	6.248577000	25.069522000	2.393656000
1	5.379142000	25.367293000	2.996524000
6	5.771347000	24.877232000	0.947862000
1	5.000265000	24.101926000	0.890193000
1	5.353837000	25.808377000	0.548396000
1	6.601278000	24.575242000	0.298858000
6	7.287756000	26.194141000	2.482392000
1	8.163385000	25.971579000	1.862309000
1	6.863435000	27.141331000	2.131065000
1	7.632591000	26.329756000	3.512288000
6	9.636053000	21.329675000	2.359225000
1	9.838561000	20.395378000	2.895742000
6	10.867602000	22.230154000	2.521828000
1	11.043778000	22.467419000	3.576237000
1	11.761318000	21.735061000	2.125502000
1	10.741141000	23.175726000	1.982586000
6	9.404628000	20.970031000	0.885355000
1	9.249808000	21.868461000	0.276754000
1	10.272763000	20.437885000	0.480043000
1	8.522259000	20.332113000	0.771339000

PTAD
18

symmetry c1

N	0.442177000	-0.544092000	0.464622000
N	0.742586000	-0.659939000	1.655070000
C	-0.919651000	-1.150659000	0.219412000
C	-0.368352000	-1.366711000	2.396434000
N	-1.346719000	-1.633122000	1.448704000
O	-0.342932000	-1.615196000	3.564698000
O	-1.461186000	-1.175005000	-0.845227000
C	-2.588460000	-2.292465000	1.698098000
C	-2.608431000	-3.425120000	2.507145000
C	-3.754242000	-1.789544000	1.127135000
C	-4.957448000	-2.440930000	1.370244000
H	-3.718801000	-0.908256000	0.496460000
C	-3.822025000	-4.057248000	2.749364000
H	-1.690751000	-3.800466000	2.946132000
C	-4.995559000	-3.570819000	2.181447000
H	-5.869941000	-2.056822000	0.925055000
H	-3.845872000	-4.938639000	3.382582000
H	-5.939571000	-4.072185000	2.371202000

Complex between 1 and PTAD, **1-PTAD**

114

symmetry c1

C	1.993757000	-2.162573000	-2.283028000
C	1.588980000	-1.063989000	-1.550117000
C	0.836814000	-0.043313000	-1.991528000
C	0.460237000	0.046155000	-3.327624000
C	0.829589000	-1.040546000	-4.122761000
C	1.577084000	-2.115549000	-3.617686000
H	2.601961000	-2.975870000	-1.899446000
H	-0.111446000	0.874866000	-3.736514000
H	0.531641000	-1.059244000	-5.168276000
H	1.850182000	-2.929589000	-4.285159000
B	1.252341000	0.199001000	-0.492562000
N	0.369750000	-0.474949000	0.521332000
N	0.668523000	-0.603711000	1.762356000
C	-0.944943000	-1.134431000	0.201359000
C	-0.340980000	-1.384597000	2.378813000
N	-1.313156000	-1.689498000	1.401292000
O	-0.350087000	-1.725278000	3.534766000
O	-1.507813000	-1.131175000	-0.854025000
C	-2.558079000	-2.333942000	1.653557000
C	-2.595867000	-3.442541000	2.495325000
C	-3.721663000	-1.825509000	1.079826000
C	-4.936412000	-2.438088000	1.359982000
H	-3.672363000	-0.963572000	0.424487000
C	-3.821325000	-4.036330000	2.774149000
H	-1.681766000	-3.821786000	2.936608000
C	-4.991612000	-3.539204000	2.209467000
H	-5.845601000	-2.046046000	0.914333000
H	-3.856870000	-4.896613000	3.435452000
H	-5.944915000	-4.009948000	2.429498000
C	2.194426000	1.375656000	-0.003357000
C	1.646452000	2.471565000	0.710959000
C	3.556756000	1.438399000	-0.371457000
C	2.409615000	3.615559000	0.941476000
C	4.313904000	2.575447000	-0.078752000
C	3.739282000	3.673951000	0.544506000
H	1.959503000	4.454719000	1.464377000
H	5.368743000	2.584586000	-0.337244000
H	4.333095000	4.560665000	0.748254000
C	4.251561000	0.289994000	-1.024433000
C	4.542385000	-0.871398000	-0.279897000
C	4.668294000	0.383861000	-2.369450000
C	5.240384000	-1.911544000	-0.895257000
C	5.349371000	-0.686676000	-2.941802000
C	5.646176000	-1.843592000	-2.223148000
H	5.478508000	-2.805556000	-0.322129000
H	5.654091000	-0.616877000	-3.983016000
C	0.284462000	2.354631000	1.316468000
C	-0.871421000	2.369408000	0.511982000
C	0.175912000	2.088791000	2.696940000
C	-2.098670000	2.023400000	1.084956000
C	-1.079118000	1.774726000	3.229961000
C	-2.220811000	1.705841000	2.437702000
H	-2.993204000	2.012631000	0.466783000
H	-1.154442000	1.556008000	4.290820000
C	4.388019000	1.613037000	-3.218993000

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H        3.661314000      2.232714000     -2.680711000
C        3.774562000      1.257385000     -4.579880000
C        5.665627000      2.441437000     -3.424687000
H        6.102898000      2.758894000     -2.473872000
H        6.420674000      1.851535000     -3.957482000
H        5.452344000      3.336739000     -4.019792000
H        4.501748000      0.763441000     -5.234261000
H        3.443545000      2.168416000     -5.091128000
H        2.915356000      0.592846000     -4.462158000
C        4.169341000     -1.006483000      1.186004000
H        3.493868000     -0.185930000      1.444545000
C        5.415966000     -0.871058000      2.072282000
C        3.425170000     -2.313870000      1.480649000
H        2.568140000     -2.431002000      0.807686000
H        4.071918000     -3.190196000      1.358761000
H        3.055094000     -2.312912000      2.511662000
H        6.136306000     -1.670014000      1.861264000
H        5.141291000     -0.929531000      3.131678000
H        5.916673000      0.087351000      1.898727000
C        6.377034000     -2.999006000     -2.874895000
H        6.537622000     -3.761479000     -2.099535000
C        7.752181000     -2.576087000     -3.407160000
C        5.530115000     -3.630563000     -3.988496000
H        4.561616000     -3.965508000     -3.602957000
H        5.338611000     -2.907496000     -4.789300000
H        6.044887000     -4.492928000     -4.426898000
H        7.654085000     -1.842466000     -4.214999000
H        8.293837000     -3.440686000     -3.806742000
H        8.357610000     -2.123771000     -2.615414000
C       -3.583279000      1.386114000      3.021212000
H       -4.201568000      0.996638000      2.199230000
C       -4.246282000      2.674297000      3.535518000
C       -3.547664000      0.323856000      4.123251000
H       -3.013280000     -0.576451000      3.805426000
H       -3.060969000      0.701349000      5.029146000
H       -4.567495000      0.034226000      4.397774000
H       -3.651227000      3.106090000      4.348638000
H       -5.251518000      2.467947000      3.920105000
H       -4.324697000      3.424737000      2.742317000
C        1.370050000      2.177475000      3.634255000
H        2.278993000      2.139353000      3.024575000
C        1.459969000      1.040943000      4.658279000
C        1.340150000      3.531472000      4.364709000
H        1.297856000      4.371437000      3.665107000
H        0.456940000      3.594411000      5.011632000
H        2.230491000      3.648868000      4.992764000
H        0.632887000      1.065404000      5.376498000
H        2.387282000      1.145487000      5.232457000
H        1.459158000      0.061844000      4.176235000
C       -0.796849000      2.853734000     -0.925524000
H        0.161472000      2.521740000     -1.342139000
C       -0.792888000      4.392786000     -0.931742000
C       -1.909933000      2.322250000     -1.829547000
H       -1.967034000      1.229648000     -1.801092000
H       -2.888142000      2.733177000     -1.554342000
H       -1.719827000      2.629432000     -2.863584000
H       -1.724620000      4.779443000     -0.502439000
H       -0.703038000      4.770778000     -1.956490000
H        0.042502000      4.788001000     -0.346158000
```

TS1 for insertion of N into the B-C bond

```
114
symmetry c1
C        0.412652000     -2.735752000     -2.134176000
C        0.033048000     -1.595039000     -1.465951000
C       -0.335742000     -0.401280000     -1.982985000
C       -0.378041000     -0.255567000     -3.369532000
C       -0.114759000     -1.398106000     -4.119667000
C        0.278508000     -2.604614000     -3.521322000
H        0.746265000     -3.655867000     -1.667494000
H       -0.619150000      0.691404000     -3.844735000
H       -0.189941000     -1.357565000     -5.202856000
H        0.487528000     -3.466738000     -4.150309000
B       -0.047835000      0.095574000     -0.558033000
N       -0.765434000     -0.803517000      0.386392000
N       -0.398388000     -1.006060000      1.628563000
C       -2.151518000     -1.355198000      0.122698000
C       -1.375041000     -1.775848000      2.234385000
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N	-2.437936000	-1.994208000	1.289875000
O	-1.373109000	-2.185240000	3.372650000
O	-2.807484000	-1.189163000	-0.867862000
C	-3.683323000	-2.612411000	1.591667000
C	-3.703364000	-3.747678000	2.400222000
C	-4.867410000	-2.067933000	1.095846000
C	-6.077947000	-2.668492000	1.418421000
H	-4.836767000	-1.187365000	0.465794000
C	-4.924095000	-4.328943000	2.722020000
H	-2.776273000	-4.155205000	2.784398000
C	-6.112767000	-3.795265000	2.233940000
H	-7.000430000	-2.245033000	1.032268000
H	-4.941449000	-5.209174000	3.357548000
H	-7.062504000	-4.256597000	2.487226000
C	0.936626000	1.209172000	-0.067904000
C	0.402124000	2.268163000	0.700923000
C	2.298584000	1.240002000	-0.430453000
C	1.200883000	3.366827000	1.017289000
C	3.090946000	2.318963000	-0.034363000
C	2.541047000	3.392165000	0.655169000
H	0.770833000	4.190705000	1.579117000
H	4.152344000	2.303524000	-0.262113000
H	3.164447000	4.237476000	0.933190000
C	2.943115000	0.100321000	-1.152797000
C	3.256569000	-1.076302000	-0.444908000
C	3.280046000	0.211647000	-2.518460000
C	3.901221000	-2.115938000	-1.117067000
C	3.908725000	-0.860894000	-3.148418000
C	4.231177000	-2.031314000	-2.464546000
H	4.160473000	-3.021000000	-0.572224000
H	4.154408000	-0.778983000	-4.203716000
C	-0.991417000	2.151289000	1.227803000
C	-2.097578000	2.205431000	0.352370000
C	-1.188360000	1.876489000	2.597506000
C	-3.364636000	1.902092000	0.849642000
C	-2.479095000	1.595125000	3.048808000
C	-3.573183000	1.575210000	2.189910000
H	-4.220604000	1.919818000	0.179204000
H	-2.622975000	1.362471000	4.099287000
C	3.008169000	1.483461000	-3.307650000
H	2.210840000	2.032030000	-2.788987000
C	2.546025000	1.220901000	-4.747460000
C	4.257976000	2.378874000	-3.346205000
H	4.587381000	2.667561000	-2.346005000
H	5.084199000	1.846727000	-3.832044000
H	4.057735000	3.293186000	-3.916542000
H	3.373993000	0.879602000	-5.378865000
H	2.165523000	2.147195000	-5.191601000
H	1.758599000	0.465295000	-4.786368000
C	2.987367000	-1.208672000	1.044414000
H	2.234527000	-0.467202000	1.328143000
C	4.265964000	-0.891135000	1.835106000
C	2.431830000	-2.580319000	1.438569000
H	1.564305000	-2.845983000	0.824048000
H	3.180756000	-3.373961000	1.336608000
H	2.103533000	-2.562191000	2.482614000
H	5.061612000	-1.604096000	1.587998000
H	4.074816000	-0.948102000	2.912662000
H	4.629996000	0.115229000	1.602867000
C	4.897746000	-3.195065000	-3.169978000
H	5.180670000	-3.921896000	-2.395567000
C	6.174474000	-2.777735000	-3.908576000
C	3.914573000	-3.887943000	-4.123791000
H	3.028147000	-4.234432000	-3.582538000
H	3.579809000	-3.195125000	-4.904862000
H	4.383051000	-4.750681000	-4.610936000
H	5.950239000	-2.100655000	-4.740252000
H	6.680772000	-3.655258000	-4.325523000
H	6.868860000	-2.265088000	-3.235540000
C	-4.978159000	1.286593000	2.682922000
H	-5.526625000	0.838024000	1.841518000
C	-5.685768000	2.601790000	3.048044000
C	-5.032936000	0.303385000	3.854394000
H	-4.458696000	-0.605796000	3.650195000
H	-4.641437000	0.754109000	4.773235000
H	-6.070089000	0.012352000	4.051575000
H	-5.161054000	3.097787000	3.872938000
H	-6.718433000	2.413763000	3.363383000

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H       -5.702493000      3.292141000      2.198531000
C       -0.051082000      1.925199000      3.606100000
H        0.893262000      1.869987000      3.053803000
C       -0.050797000      0.773087000      4.615876000
C       -0.092293000      3.269230000      4.354615000
H       -0.088609000      4.121459000      3.668372000
H       -1.004556000      3.337902000      4.959130000
H        0.768233000      3.361846000      5.026945000
H       -0.919646000      0.808212000      5.282500000
H        0.841207000      0.846615000      5.248259000
H       -0.042932000     -0.199323000      4.121058000
C       -1.931072000      2.708531000     -1.074126000
H       -0.939758000      2.404937000     -1.432416000
C       -1.949006000      4.247087000     -1.063264000
C       -2.968180000      2.167755000     -2.060248000
H       -3.024512000      1.075632000     -2.028372000
H       -3.966341000      2.572817000     -1.859174000
H       -2.702556000      2.473076000     -3.078379000
H       -2.913300000      4.613405000     -0.692288000
H       -1.797077000      4.641290000     -2.074711000
H       -1.161789000      4.647010000     -0.416401000

Intermediate INT1
114
symmetry c1
C        1.074092000     -3.753225000      0.046921000
C        1.180681000     -2.380995000     -0.050104000
C        2.015339000     -1.666821000     -0.896534000
C        2.774265000     -2.380773000     -1.833611000
C        2.657287000     -3.763678000     -1.819813000
C        1.841791000     -4.438467000     -0.891196000
H        0.444483000     -4.250482000      0.776790000
H        3.437418000     -1.886710000     -2.535137000
H        3.229506000     -4.353064000     -2.530411000
H        1.806900000     -5.524063000     -0.913481000
B        1.698172000     -0.408286000     -0.072028000
N        0.531735000     -1.268078000      0.671848000
N        0.513345000     -1.426106000      2.089298000
C       -0.895546000     -1.141006000      0.148036000
C       -0.773969000     -1.539802000      2.442176000
N       -1.641876000     -1.402456000      1.227605000
O       -1.264773000     -1.723579000      3.539913000
O       -1.133163000     -0.928164000     -1.015305000
C       -3.052703000     -1.549095000      1.216470000
C       -3.651032000     -2.478807000      2.069931000
C       -3.832252000     -0.785074000      0.347366000
C       -5.212910000     -0.942111000      0.348482000
H       -3.358536000     -0.076906000     -0.319993000
C       -5.033667000     -2.616356000      2.063939000
H       -3.038022000     -3.062732000      2.744582000
C       -5.820737000     -1.849685000      1.209912000
H       -5.815542000     -0.344586000     -0.329479000
H       -5.496834000     -3.333236000      2.735522000
H       -6.900690000     -1.963377000      1.211553000
C        2.340358000      0.917471000      0.337599000
C        1.705737000      1.884258000      1.163857000
C        3.674145000      1.170073000     -0.092711000
C        2.424712000      3.002478000      1.588646000
C        4.363849000      2.286901000      0.369427000
C        3.746990000      3.194629000      1.220090000
H        1.918421000      3.744280000      2.197346000
H        5.383377000      2.450293000      0.031313000
H        4.286418000      4.071545000      1.567885000
C        4.401945000      0.322846000     -1.083775000
C        5.289791000     -0.675687000     -0.653312000
C        4.276371000      0.624933000     -2.452850000
C        6.057271000     -1.347136000     -1.606837000
C        5.056146000     -0.078619000     -3.370409000
C        5.960174000     -1.060811000     -2.965365000
H        6.753460000     -2.118634000     -1.284343000
H        4.957849000      0.151117000     -4.428849000
C        0.266990000      1.822463000      1.543994000
C       -0.726572000      2.059161000      0.561668000
C       -0.094837000      1.676377000      2.901042000
C       -2.058161000      2.105325000      0.967512000
C       -1.446851000      1.696036000      3.241316000
C       -2.441102000      1.906804000      2.293703000
H       -2.834005000      2.306672000      0.234299000
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H	-1.725154000	1.544738000	4.279849000
C	3.300677000	1.679733000	-2.948609000
H	2.892188000	2.199365000	-2.073884000
C	2.122649000	1.033554000	-3.691934000
C	3.988608000	2.737166000	-3.820542000
H	4.836048000	3.190161000	-3.295790000
H	4.361895000	2.308833000	-4.757205000
H	3.279844000	3.531178000	-4.079637000
H	2.467976000	0.500618000	-4.585630000
H	1.406302000	1.799118000	-4.010851000
H	1.592052000	0.315674000	-3.057248000
C	5.434917000	-1.025045000	0.816898000
H	4.661011000	-0.478517000	1.369082000
C	6.798915000	-0.567676000	1.352557000
C	5.215211000	-2.520107000	1.081180000
H	4.245599000	-2.852330000	0.697211000
H	5.993596000	-3.131223000	0.610901000
H	5.241297000	-2.718856000	2.157807000
H	7.614424000	-1.088078000	0.837419000
H	6.882996000	-0.781252000	2.423754000
H	6.940935000	0.507782000	1.204384000
C	6.795064000	-1.819096000	-3.977224000
H	7.459896000	-2.487110000	-3.412048000
C	7.673633000	-0.879596000	-4.811919000
C	5.911974000	-2.691659000	-4.879285000
H	5.300053000	-3.377755000	-4.284037000
H	5.235573000	-2.074295000	-5.481306000
H	6.524391000	-3.285888000	-5.566409000
H	7.063102000	-0.215260000	-5.433445000
H	8.324998000	-1.453383000	-5.480195000
H	8.301662000	-0.254615000	-4.169493000
C	-3.904023000	1.991017000	2.677036000
H	-4.485113000	1.788027000	1.766170000
C	-4.243645000	3.414503000	3.145641000
C	-4.314479000	0.957684000	3.729335000
H	-3.984840000	-0.047515000	3.452258000
H	-3.887549000	1.193612000	4.710527000
H	-5.404051000	0.947935000	3.840840000
H	-3.675668000	3.663012000	4.049891000
H	-5.310978000	3.502054000	3.379085000
H	-3.994344000	4.155272000	2.378632000
C	0.934320000	1.578846000	4.018863000
H	1.921237000	1.442359000	3.563879000
C	0.716302000	0.405596000	4.980902000
C	0.948482000	2.894311000	4.819716000
H	1.072576000	3.773803000	4.180368000
H	0.005197000	3.018062000	5.363859000
H	1.761077000	2.884076000	5.554908000
H	-0.249227000	0.471806000	5.492809000
H	1.498569000	0.422244000	5.748698000
H	0.751883000	-0.551706000	4.461730000
C	-0.362405000	2.387643000	-0.884316000
H	0.453032000	1.721208000	-1.192716000
C	0.157579000	3.832171000	-0.991142000
C	-1.500701000	2.189879000	-1.887960000
H	-1.931628000	1.188284000	-1.823487000
H	-2.294593000	2.933168000	-1.751248000
H	-1.112141000	2.320497000	-2.903549000
H	-0.625121000	4.536551000	-0.686009000
H	0.437126000	4.058849000	-2.026972000
H	1.031663000	4.001141000	-0.357510000

TS2 for ring enlargement from **INT1** to product **2**

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symmetry c1

C	-0.075710000	-2.962093000	-2.264460000
C	0.486904000	-1.925093000	-1.560437000
C	1.789842000	-1.454836000	-1.640440000
C	2.659284000	-2.116879000	-2.503971000
C	2.141617000	-3.173223000	-3.258664000
C	0.808366000	-3.581531000	-3.154452000
H	-1.112385000	-3.264367000	-2.163469000
H	3.699572000	-1.835723000	-2.609848000
H	2.795304000	-3.693541000	-3.953186000
H	0.451592000	-4.400560000	-3.772298000
B	1.466238000	-0.330161000	-0.578751000
N	0.020393000	-1.068523000	-0.459994000
N	0.624303000	-1.541640000	0.781644000

C	-1.434250000	-0.924348000	-0.281013000
C	-0.385416000	-1.593298000	1.689511000
N	-1.649871000	-1.292710000	1.006611000
O	-0.329332000	-1.903395000	2.860676000
O	-2.181088000	-0.678342000	-1.195760000
C	-2.941879000	-1.544117000	1.547235000
C	-3.121255000	-2.599299000	2.444211000
C	-4.028073000	-0.766887000	1.144981000
C	-5.291321000	-1.041770000	1.653950000
H	-3.882118000	0.043146000	0.442687000
C	-4.390568000	-2.853576000	2.949976000
H	-2.275054000	-3.199487000	2.752779000
C	-5.478933000	-2.078967000	2.561716000
H	-6.133749000	-0.433744000	1.337233000
H	-4.524806000	-3.670207000	3.653051000
H	-6.467542000	-2.284787000	2.960959000
C	2.003391000	1.080354000	-0.243623000
C	1.285909000	2.115456000	0.408910000
C	3.341703000	1.358098000	-0.644747000
C	1.856182000	3.380814000	0.551275000
C	3.887330000	2.629060000	-0.458793000
C	3.142755000	3.648977000	0.110089000
H	1.287926000	4.147204000	1.069017000
H	4.917952000	2.798858000	-0.757787000
H	3.575738000	4.635945000	0.247713000
C	4.283186000	0.342848000	-1.201454000
C	4.809691000	-0.663558000	-0.367460000
C	4.747875000	0.476631000	-2.526075000
C	5.800979000	-1.504210000	-0.875839000
C	5.740735000	-0.387306000	-2.986649000
C	6.282754000	-1.382259000	-2.175792000
H	6.214778000	-2.280317000	-0.236476000
H	6.084532000	-0.291760000	-4.013931000
C	-0.001005000	1.912536000	1.139293000
C	-1.247929000	2.240209000	0.566760000
C	0.093579000	1.569731000	2.504445000
C	-2.381577000	2.173564000	1.375483000
C	-1.077511000	1.481477000	3.257489000
C	-2.320949000	1.783523000	2.713265000
H	-3.350327000	2.436584000	0.957680000
H	-1.006542000	1.194239000	4.302255000
C	4.154524000	1.490507000	-3.491281000
H	3.389969000	2.062556000	-2.954701000
C	3.457502000	0.792788000	-4.668285000
C	5.210942000	2.482892000	-3.994211000
H	5.708611000	2.990700000	-3.161818000
H	5.983028000	1.976778000	-4.584461000
H	4.748308000	3.243236000	-4.633097000
H	4.171156000	0.218546000	-5.269958000
H	2.986129000	1.533066000	-5.324326000
H	2.683733000	0.104144000	-4.314872000
C	4.387291000	-0.814535000	1.084541000
H	3.446000000	-0.276657000	1.227604000
C	5.428389000	-0.158383000	2.003164000
C	4.127644000	-2.269765000	1.487204000
H	3.432149000	-2.751550000	0.793213000
H	5.051564000	-2.857836000	1.522718000
H	3.677289000	-2.300255000	2.484762000
H	6.399489000	-0.657953000	1.906360000
H	5.110533000	-0.225433000	3.049771000
H	5.564781000	0.899011000	1.750838000
C	7.321510000	-2.347725000	-2.708294000
H	7.668881000	-2.950492000	-1.857702000
C	8.537498000	-1.627664000	-3.302042000
C	6.691275000	-3.300967000	-3.734143000
H	5.841920000	-3.837698000	-3.298196000
H	6.327905000	-2.743705000	-4.605559000
H	7.422925000	-4.037464000	-4.084522000
H	8.263644000	-1.051405000	-4.192777000
H	9.303312000	-2.351849000	-3.600404000
H	8.979165000	-0.936548000	-2.577350000
C	-3.583143000	1.781439000	3.552290000
H	-4.425071000	1.630868000	2.861518000
C	-3.765347000	3.151163000	4.225154000
C	-3.627729000	0.657157000	4.589284000
H	-3.412033000	-0.314776000	4.136437000
H	-2.904519000	0.824947000	5.395383000
H	-4.621042000	0.609438000	5.048303000

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H       -2.938337000      3.347365000      4.917698000
H       -4.701724000      3.183815000      4.793933000
H       -3.780913000      3.957681000      3.484744000
C        1.441698000      1.461073000      3.208960000
H        2.225010000      1.404061000      2.445101000
C        1.606055000      0.238118000      4.114485000
C        1.683048000      2.747792000      4.017940000
H        1.589803000      3.642116000      3.394517000
H        0.953301000      2.830410000      4.831791000
H        2.686138000      2.738327000      4.459159000
H        0.861996000      0.219633000      4.918073000
H        2.595884000      0.268609000      4.584653000
H        1.506955000     -0.694596000      3.557661000
C       -1.355263000      2.745638000     -0.867369000
H       -0.576962000      2.238210000     -1.456003000
C       -1.088795000      4.260932000     -0.935216000
C       -2.709544000      2.469615000     -1.530976000
H       -3.011491000      1.425375000     -1.438759000
H       -3.495073000      3.106503000     -1.107963000
H       -2.645684000      2.708013000     -2.597804000
H       -1.794208000      4.793430000     -0.286662000
H       -1.229934000      4.621601000     -1.960386000
H       -0.075249000      4.518582000     -0.624562000

Product 2
114
symmetry c1
C       -0.691895000     -2.217156000     -1.854670000
C       -0.231379000     -1.199539000     -1.026849000
C        1.042098000     -0.594913000     -1.153741000
C        1.884409000     -1.080518000     -2.157430000
C        1.457520000     -2.104189000     -2.991682000
C        0.180729000     -2.659452000     -2.841468000
H       -1.678495000     -2.646173000     -1.721058000
H        2.882440000     -0.671356000     -2.264201000
H        2.119056000     -2.483348000     -3.764723000
H       -0.136591000     -3.458985000     -3.504988000
B        1.162659000      0.497292000     -0.059395000
N       -0.089978000      0.325591000      0.653879000
N       -0.911189000     -0.612897000      0.031795000
C       -0.634618000      0.627534000      1.894389000
C       -1.988130000     -0.941055000      0.829013000
N       -1.831449000     -0.114615000      1.965342000
O       -2.858411000     -1.748696000      0.592296000
O       -0.151518000      1.345145000      2.739134000
C       -2.757358000     -0.051288000      3.042385000
C       -4.124943000     -0.095581000      2.772410000
C       -2.293357000      0.060282000      4.352791000
C       -3.211602000      0.141763000      5.393099000
H       -1.229114000      0.098723000      4.550162000
C       -5.028370000     -0.028683000      3.825641000
H       -4.472901000     -0.193413000      1.751120000
C       -4.578067000      0.095308000      5.136484000
H       -2.850721000      0.235361000      6.412944000
H       -6.092902000     -0.068517000      3.615297000
H       -5.289434000      0.153541000      5.954719000
C        2.183627000      1.617879000      0.327998000
C        1.758823000      2.969428000      0.325460000
C        3.505596000      1.308461000      0.695983000
C        2.641160000      3.964034000      0.744219000
C        4.350288000      2.318333000      1.161209000
C        3.917482000      3.636998000      1.190999000
H        2.332659000      5.003678000      0.717837000
H        5.357828000      2.063840000      1.479615000
H        4.584998000      4.419811000      1.540438000
C        4.003012000     -0.085379000      0.513207000
C        3.499704000     -1.140441000      1.300065000
C        4.924724000     -0.357215000     -0.521974000
C        3.886476000     -2.447529000      1.004963000
C        5.281870000     -1.680711000     -0.774820000
C        4.758506000     -2.740423000     -0.038210000
H        3.494100000     -3.268252000      1.600428000
H        5.979883000     -1.891327000     -1.581768000
C        0.379257000      3.247719000     -0.176690000
C        0.053939000      2.863975000     -1.501145000
C       -0.636073000      3.735398000      0.676307000
C       -1.287377000      2.815424000     -1.879847000
C       -1.962038000      3.656533000      0.250533000
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C       -2.310915000      3.155087000     -1.000319000
H       -1.551034000      2.490234000     -2.881849000
H       -2.746448000      3.978175000      0.929184000
C        5.557982000      0.742885000     -1.364622000
H        5.059269000      1.687413000     -1.125382000
C        5.405724000      0.525420000     -2.875948000
C        7.042796000      0.894073000     -0.998234000
H        7.170649000      1.064770000      0.075346000
H        7.602490000     -0.012111000     -1.257433000
H        7.490878000      1.735778000     -1.538222000
H        5.868599000     -0.410851000     -3.205580000
H        5.892649000      1.342592000     -3.419512000
H        4.353887000      0.510407000     -3.178615000
C        2.627753000     -0.870527000      2.514953000
H        2.147625000      0.105395000      2.390894000
C        3.513058000     -0.767174000      3.766991000
C        1.522739000     -1.912539000      2.719071000
H        0.963838000     -2.096441000      1.794174000
H        1.924714000     -2.873013000      3.059355000
H        0.821783000     -1.568201000      3.487909000
H        4.041949000     -1.711003000      3.944299000
H        2.904713000     -0.538807000      4.649396000
H        4.260763000      0.024349000      3.650914000
C        5.103461000     -4.175386000     -0.377488000
H        4.630491000     -4.810250000      0.384723000
C        6.613961000     -4.435286000     -0.333342000
C        4.515465000     -4.564509000     -1.741339000
H        3.436074000     -4.382295000     -1.767711000
H        4.974480000     -3.974812000     -2.543643000
H        4.697422000     -5.623733000     -1.955532000
H        7.137400000     -3.859034000     -1.104331000
H        6.827360000     -5.495244000     -0.509963000
H        7.033220000     -4.154862000      0.638062000
C       -3.761809000      2.968493000     -1.390502000
H       -3.777534000      2.648095000     -2.441644000
C       -4.570938000      4.266365000     -1.282085000
C       -4.396846000      1.852600000     -0.548002000
H       -3.846234000      0.912406000     -0.664378000
H       -4.386910000      2.120442000      0.515082000
H       -5.437316000      1.679467000     -0.845840000
H       -4.634381000      4.609301000     -0.243514000
H       -5.593978000      4.112043000     -1.642434000
H       -4.113465000      5.066153000     -1.873093000
C       -0.325982000      4.400982000      2.006283000
H        0.615107000      3.984294000      2.382085000
C       -1.392749000      4.201570000      3.089789000
C       -0.141389000      5.913186000      1.772393000
H        0.589994000      6.127249000      0.988079000
H       -1.091956000      6.360879000      1.459076000
H        0.180838000      6.409812000      2.694959000
H       -2.306022000      4.766114000      2.869143000
H       -1.011717000      4.575483000      4.046297000
H       -1.650969000      3.148725000      3.221418000
C        1.145885000      2.640879000     -2.542802000
H        1.965318000      2.078960000     -2.080770000
C        1.717743000      4.007369000     -2.958583000
C        0.694433000      1.859979000     -3.777659000
H        0.216292000      0.912706000     -3.508797000
H       -0.002311000      2.440890000     -4.392851000
H        1.563336000      1.630440000     -4.403848000
H        0.932173000      4.629120000     -3.403414000
H        2.518316000      3.881094000     -3.696701000
H        2.126554000      4.540849000     -2.094995000
```

```
Tetrazine
26
symmetry c1
N        0.654080000      1.191699000     -0.000053000
C        1.285755000      0.000001000     -0.000005000
N        0.654080000     -1.191699000      0.000034000
N       -0.654080000     -1.191699000     -0.000023000
C       -1.285755000      0.000001000     -0.000007000
N       -0.654080000      1.191699000      0.000003000
N        5.561382000      0.000000000      0.000009000
C        2.756749000      0.000000000      0.000000000
N       -5.561382000      0.000000000      0.000009000
C       -2.756749000      0.000000000     -0.000001000
```

```
C       -3.475163000      1.199006000     -0.000606000
C       -4.863024000      1.140336000     -0.000573000
C        3.475163000      1.199006000      0.000648000
C        4.863023000      1.140336000      0.000623000
C        4.863023000     -1.140336000     -0.000610000
C        3.475163000     -1.199006000     -0.000643000
C       -4.863023000     -1.140336000      0.000586000
C       -3.475163000     -1.199006000      0.000609000
H       -2.959239000      2.152474000     -0.001095000
H       -5.445442000      2.060850000     -0.001042000
H        2.959239000      2.152474000      0.001164000
H        5.445441000      2.060850000      0.001128000
H        5.445441000     -2.060851000     -0.001111000
H        2.959239000     -2.152474000     -0.001163000
H       -5.445441000     -2.060851000      0.001061000
H       -2.959239000     -2.152474000      0.001094000
```

Complex **1-4,4'-bptz** bound by tetrazine nitrogen atom

```
122
symmetry c1
C        3.721009000      0.421267000      2.791581000
C        4.457502000      0.643538000      1.615915000
C        3.914306000      0.398711000      0.357064000
C        2.601847000     -0.068295000      0.340581000
C        1.925253000     -0.338991000      1.487515000
C        2.420314000     -0.082825000      2.758564000
B        1.193860000     -0.709387000      0.089906000
N        0.016318000      0.342875000      0.028451000
C        0.181129000      1.710805000      0.074621000
N       -1.211507000     -0.130899000      0.184951000
C       -2.157260000      0.724856000      0.578930000
N       -1.927573000      2.005777000      0.931509000
N       -0.756291000      2.497780000      0.598244000
C       -3.539325000      0.240223000      0.710076000
C       -4.603653000      1.136319000      0.588797000
C       -5.898177000      0.646791000      0.711124000
N       -6.187766000     -0.636442000      0.951891000
C       -5.159162000     -1.480436000      1.082115000
C       -3.828310000     -1.098580000      0.968771000
C        1.400614000      2.402413000     -0.365330000
C        1.970745000      2.180133000     -1.616398000
C        3.088541000      2.919229000     -1.973671000
N        3.668127000      3.825350000     -1.177948000
C        3.104345000      4.034992000      0.015692000
C        1.967359000      3.372522000      0.461348000
C        0.972879000     -2.169879000     -0.545259000
C        0.447528000     -2.399926000     -1.848264000
C        0.521507000     -3.659086000     -2.443523000
C        1.016662000     -4.751351000     -1.746544000
C        1.441576000     -4.572874000     -0.439703000
C        1.468774000     -3.305054000      0.149869000
H        4.186139000      0.630686000      3.751961000
H        5.472021000      1.025917000      1.695698000
H        4.492189000      0.598293000     -0.543707000
H        1.879257000     -0.288510000      3.678049000
H       -4.419857000      2.188734000      0.400118000
H       -6.747264000      1.321621000      0.611273000
H       -5.410602000     -2.520299000      1.287895000
H       -3.032997000     -1.824535000      1.082337000
H        1.546105000      1.447960000     -2.289421000
H        3.550110000      2.766993000     -2.949090000
H        3.586544000      4.774416000      0.653771000
H        1.547897000      3.579262000      1.439891000
H        0.136742000     -3.785421000     -3.452149000
H        1.039290000     -5.735947000     -2.205589000
H        1.784602000     -5.421987000      0.144534000
C       -0.290039000     -1.324429000     -2.586188000
C        0.366021000     -0.368870000     -3.389471000
C       -1.698941000     -1.248549000     -2.452030000
C       -0.352437000      0.746701000     -3.842679000
C       -2.359028000     -0.104303000     -2.909439000
C       -1.698391000      0.932713000     -3.560068000
H        0.167997000      1.494804000     -4.440217000
H       -3.435514000     -0.039089000     -2.755541000
C        2.026546000     -3.260767000      1.541661000
C        1.145691000     -3.118242000      2.638704000
C        3.402269000     -3.463791000      1.784950000
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C        1.641565000     -3.198057000      3.936765000
C        3.850618000     -3.487527000      3.109659000
C        2.996040000     -3.373456000      4.197496000
H        0.959007000     -3.106615000      4.778133000
H        4.918971000     -3.608192000      3.281797000
C        3.515922000     -3.393572000      5.620080000
H        2.639481000     -3.425826000      6.283056000
C        4.294440000     -2.108066000      5.933237000
C        4.367679000     -4.634275000      5.912120000
H        3.821304000     -5.551896000      5.672372000
H        5.291760000     -4.629842000      5.323656000
H        4.650480000     -4.665819000      6.970174000
H        5.168033000     -2.016847000      5.277712000
H        4.644925000     -2.106300000      6.971700000
H        3.667096000     -1.224028000      5.778393000
C       -2.426639000      2.191393000     -3.980776000
H       -1.689713000      2.847106000     -4.465253000
C       -2.989233000      2.934607000     -2.761894000
C       -3.533886000      1.892376000     -4.999595000
H       -3.134577000      1.362223000     -5.869939000
H       -4.318092000      1.268279000     -4.556486000
H       -4.001604000      2.821070000     -5.344486000
H       -3.736779000      2.320975000     -2.245130000
H       -3.475161000      3.868336000     -3.065886000
H       -2.197282000      3.179599000     -2.045809000
C        1.769178000     -0.519528000     -3.977972000
H        2.054045000      0.488579000     -4.315621000
C        1.672161000     -1.392142000     -5.242847000
C        2.898424000     -1.026390000     -3.081338000
H        2.929555000     -0.504181000     -2.123313000
H        2.799907000     -2.092552000     -2.873162000
H        3.856354000     -0.871586000     -3.591475000
H        1.414276000     -2.421506000     -4.973303000
H        2.635306000     -1.410574000     -5.765466000
H        0.907972000     -1.016252000     -5.930588000
C        4.511667000     -3.692226000      0.752955000
H        5.392602000     -3.210636000      1.201473000
C        4.364915000     -3.079589000     -0.639797000
C        4.845349000     -5.190691000      0.641768000
H        5.025374000     -5.635917000      1.625471000
H        4.024978000     -5.737927000      0.166278000
H        5.741586000     -5.333816000      0.026946000
H        3.680870000     -3.646683000     -1.274053000
H        5.345956000     -3.077088000     -1.129664000
H        4.009017000     -2.049931000     -0.589523000
C       -0.346481000     -2.917445000      2.434507000
H       -0.474776000     -2.468165000      1.445694000
C       -0.974668000     -1.952571000      3.445072000
C       -1.077190000     -4.266873000      2.443279000
H       -0.689249000     -4.929341000      1.662682000
H       -0.946469000     -4.766333000      3.410572000
H       -2.152469000     -4.131202000      2.272222000
H       -0.974222000     -2.357475000      4.462485000
H       -2.021606000     -1.760374000      3.185684000
H       -0.447143000     -0.992693000      3.459161000
C       -2.644928000     -2.360854000     -1.988177000
H       -3.521891000     -1.831034000     -1.592606000
C       -2.221900000     -3.363261000     -0.911391000
C       -3.126165000     -3.128202000     -3.235453000
H       -3.554243000     -2.453062000     -3.982968000
H       -2.290970000     -3.663237000     -3.700291000
H       -3.886912000     -3.865654000     -2.954744000
H       -1.619450000     -4.178078000     -1.315202000
H       -3.124974000     -3.808550000     -0.476005000
H       -1.642363000     -2.898573000     -0.115280000

Complex 1 with 4,4'-bptz through pyridine nitrogen atom
122
symmetry c1
C       -6.375306000      6.297896000      3.779861000
C       -6.992771000      5.055505000      3.586938000
C       -6.601722000      4.199132000      2.552971000
C       -5.564688000      4.638667000      1.737805000
C       -4.971703000      5.867485000      1.930102000
C       -5.340827000      6.733378000      2.947649000
B       -4.403167000      5.006412000      0.745313000
N        1.807308000      3.638371000      2.390022000
C        0.706199000      2.888820000      2.600821000
```

N	2.955223000	3.166502000	2.800735000
C	2.962725000	1.959975000	3.405893000
N	1.860243000	1.206679000	3.607493000
N	0.712823000	1.679550000	3.198792000
C	4.252219000	1.430111000	3.870675000
C	4.332707000	0.180052000	4.491677000
C	5.577185000	-0.272413000	4.910715000
N	6.712013000	0.418107000	4.756538000
C	6.622361000	1.612534000	4.161800000
C	5.431769000	2.161935000	3.703918000
C	-0.580227000	3.412356000	2.130859000
C	-0.652409000	4.631918000	1.445613000
C	-1.867984000	5.058738000	0.961251000
N	-3.001367000	4.360938000	1.167093000
C	-2.949699000	3.201355000	1.845479000
C	-1.761125000	2.692678000	2.325978000
C	-4.495649000	5.294153000	-0.831608000
C	-4.122116000	4.325685000	-1.800104000
C	-4.300044000	4.577743000	-3.163566000
C	-4.787528000	5.795527000	-3.612298000
C	-5.144536000	6.759990000	-2.682192000
C	-5.036102000	6.510937000	-1.311640000
H	-6.713301000	6.933204000	4.595455000
H	-7.797042000	4.756995000	4.255497000
H	-7.107706000	3.244028000	2.424256000
H	-4.886221000	7.711053000	3.098108000
H	3.443068000	-0.420941000	4.641755000
H	5.667054000	-1.242864000	5.396982000
H	7.555149000	2.162374000	4.044073000
H	5.415668000	3.135785000	3.227928000
H	0.236426000	5.229054000	1.282072000
H	-1.980149000	5.982522000	0.403923000
H	-3.901789000	2.702947000	1.987223000
H	-1.754802000	1.745888000	2.850876000
H	-4.062018000	3.794837000	-3.876731000
H	-4.901808000	5.984217000	-4.676211000
H	-5.535139000	7.720671000	-3.008026000
C	-3.557260000	2.988278000	-1.424376000
C	-2.197866000	2.688438000	-1.661917000
C	-4.400837000	1.995705000	-0.875902000
C	-1.702543000	1.437219000	-1.284536000
C	-3.857048000	0.764200000	-0.512390000
C	-2.508010000	0.466611000	-0.700823000
H	-0.655239000	1.203407000	-1.463205000
H	-4.507844000	0.006855000	-0.086038000
C	-5.567659000	7.582205000	-0.411547000
C	-6.942969000	7.607096000	-0.116551000
C	-4.729372000	8.602848000	0.067104000
C	-7.448366000	8.655113000	0.652307000
C	-5.275508000	9.630325000	0.833515000
C	-6.634240000	9.673803000	1.136991000
H	-8.508136000	8.676108000	0.895491000
H	-4.621993000	10.415678000	1.208012000
C	-1.261051000	3.653875000	-2.375842000
H	-1.690207000	4.660702000	-2.293908000
C	-5.902565000	2.215707000	-0.783415000
H	-6.072696000	3.271830000	-0.550477000
C	-3.241735000	8.609589000	-0.232878000
H	-3.011110000	7.672985000	-0.756198000
C	-7.879008000	6.523755000	-0.626639000
H	-7.263091000	5.650268000	-0.876723000
C	-7.209692000	10.776618000	2.002037000
H	-8.300012000	10.638927000	2.017123000
C	-1.930171000	-0.875147000	-0.296267000
H	-0.929914000	-0.943982000	-0.747136000
C	-1.761660000	-0.968434000	1.226749000
H	-1.348112000	-1.941524000	1.515060000
H	-1.086218000	-0.190511000	1.597240000
H	-2.729540000	-0.850608000	1.729097000
C	-2.760516000	-2.051595000	-0.823452000
H	-2.255439000	-3.000261000	-0.612077000
H	-3.745276000	-2.090169000	-0.345254000
H	-2.913622000	-1.973855000	-1.904374000
C	-6.583168000	1.386865000	0.307964000
H	-7.617299000	1.723641000	0.434354000
H	-6.620339000	0.321973000	0.050201000
H	-6.073249000	1.488195000	1.271786000
C	-6.554845000	1.917899000	-2.144009000

H	-6.152138000	2.565022000	-2.928187000
H	-6.378047000	0.874982000	-2.433153000
H	-7.637409000	2.081291000	-2.090765000
C	0.161961000	3.681980000	-1.799280000
H	0.165290000	3.764010000	-0.710755000
H	0.721705000	2.779426000	-2.067905000
H	0.713414000	4.534311000	-2.210650000
C	-1.157196000	3.299306000	-3.870634000
H	-0.492892000	4.003351000	-4.384814000
H	-0.741360000	2.291620000	-3.986761000
H	-2.126401000	3.318906000	-4.371501000
C	-2.402060000	8.659697000	1.050636000
H	-2.696096000	7.863121000	1.742685000
H	-1.334692000	8.551895000	0.819864000
H	-2.525484000	9.615282000	1.572034000
C	-2.871520000	9.761421000	-1.176592000
H	-3.092808000	10.730171000	-0.714269000
H	-1.802979000	9.738310000	-1.420715000
H	-3.440315000	9.698273000	-2.109866000
C	-8.595861000	6.980589000	-1.906601000
H	-7.884549000	7.224198000	-2.700715000
H	-9.263764000	6.193272000	-2.275124000
H	-9.198985000	7.874010000	-1.705484000
C	-8.906293000	6.077195000	0.419291000
H	-9.432020000	5.183869000	0.063264000
H	-8.424084000	5.837410000	1.370488000
H	-9.664739000	6.847668000	0.598831000
C	-6.921764000	12.170700000	1.432140000
H	-7.416393000	12.942774000	2.032230000
H	-5.847346000	12.386012000	1.436538000
H	-7.276135000	12.254686000	0.399880000
C	-6.704186000	10.659060000	3.446493000
H	-6.935428000	9.672010000	3.859757000
H	-5.617171000	10.795164000	3.489909000
H	-7.165122000	11.420973000	4.085594000

TS3 for reaction between **1-4,4'-bptz** to **INT2**

122

symmetry c1

C	-4.840981000	-1.137565000	-0.510456000
C	-4.037788000	-2.273784000	-0.460176000
C	-2.662991000	-2.178411000	-0.743771000
C	-2.214547000	-0.959577000	-1.162206000
C	-2.933359000	0.220511000	-1.213564000
C	-4.297977000	0.089861000	-0.855836000
B	-2.265355000	1.604583000	-1.309737000
N	-0.776662000	1.685314000	-1.434246000
C	0.117108000	0.810657000	-2.038314000
N	-0.214512000	2.835217000	-0.945415000
C	1.084235000	2.795448000	-0.701727000
N	1.895094000	1.735892000	-0.912380000
N	1.394905000	0.819513000	-1.759029000
C	1.662810000	3.999433000	-0.075405000
C	3.044218000	4.130959000	0.071625000
C	3.541611000	5.283959000	0.667093000
N	2.774148000	6.287679000	1.105769000
C	1.451524000	6.148734000	0.959352000
C	0.848009000	5.036534000	0.386871000
C	-0.374998000	-0.174393000	-2.987609000
C	0.082830000	-1.495157000	-2.919395000
C	-0.404177000	-2.408853000	-3.847678000
N	-1.288342000	-2.094302000	-4.798438000
C	-1.709206000	-0.823628000	-4.857196000
C	-1.287535000	0.171186000	-3.987528000
C	-2.955230000	3.005417000	-1.055266000
C	-2.960671000	3.973237000	-2.094017000
C	-3.355947000	5.283182000	-1.825499000
C	-3.728330000	5.670056000	-0.545922000
C	-3.805815000	4.714828000	0.456187000
C	-3.476192000	3.377951000	0.212430000
H	-5.893618000	-1.207590000	-0.251030000
H	-4.471909000	-3.246580000	-0.236659000
H	-2.031110000	-3.062603000	-0.707920000
H	-4.899317000	0.990393000	-0.793621000
H	3.707260000	3.347255000	-0.278070000
H	4.616232000	5.410168000	0.794335000
H	0.838088000	6.971779000	1.324643000
H	-0.232861000	4.971740000	0.306487000

H	0.797703000	-1.783194000	-2.156114000
H	-0.069296000	-3.445027000	-3.822719000
H	-2.416812000	-0.584496000	-5.650187000
H	-1.642135000	1.191164000	-4.099602000
H	-3.387200000	5.999403000	-2.641207000
H	-3.999089000	6.702199000	-0.341614000
H	-4.151817000	4.992049000	1.448034000
C	-3.799356000	2.383435000	1.291130000
C	-5.159955000	2.085375000	1.553700000
C	-2.800462000	1.745714000	2.048446000
C	-5.469218000	1.104970000	2.493291000
C	-3.161242000	0.765826000	2.974685000
C	-4.486061000	0.413735000	3.196276000
H	-6.514252000	0.868429000	2.677589000
H	-2.384427000	0.266499000	3.549016000
C	-2.612148000	3.641174000	-3.522954000
C	-1.353998000	4.049351000	-4.046367000
C	-3.540968000	3.029219000	-4.398726000
C	-1.011569000	3.729827000	-5.356883000
C	-3.142360000	2.754301000	-5.715637000
C	-1.885465000	3.061135000	-6.208858000
H	-0.036834000	4.029321000	-5.730752000
H	-3.865064000	2.289418000	-6.385227000
C	-1.351575000	2.179115000	1.963971000
H	-1.231911000	2.764715000	1.048198000
C	-6.316968000	2.813081000	0.878488000
H	-5.916007000	3.409380000	0.053793000
C	-4.845534000	-0.692051000	4.166296000
H	-3.911754000	-1.018225000	4.645340000
C	-4.997033000	2.627834000	-4.129196000
H	-5.528068000	2.955549000	-5.035621000
C	-0.375225000	4.906111000	-3.259019000
H	-0.623712000	4.819047000	-2.196950000
C	-1.490192000	2.716717000	-7.629020000
H	-2.338537000	2.184776000	-8.082453000
C	-1.227543000	3.980392000	-8.459297000
H	-1.006245000	3.718892000	-9.499859000
H	-2.094304000	4.648817000	-8.446643000
H	-0.368946000	4.534904000	-8.064397000
C	-0.274929000	1.780532000	-7.658368000
H	-0.454761000	0.876884000	-7.067296000
H	-0.044232000	1.480987000	-8.686514000
H	0.612033000	2.276081000	-7.247787000
C	-5.435137000	-1.897223000	3.420249000
H	-5.630776000	-2.725270000	4.110953000
H	-6.382817000	-1.628975000	2.938412000
H	-4.750427000	-2.245989000	2.640262000
C	-5.795522000	-0.208845000	5.268671000
H	-6.764304000	0.089201000	4.852533000
H	-5.979255000	-1.006779000	5.996619000
H	-5.377508000	0.653152000	5.798032000
C	-0.362389000	1.010118000	1.913595000
H	-0.320748000	0.474336000	2.868199000
H	-0.633622000	0.288840000	1.134800000
H	0.649422000	1.376683000	1.708107000
C	-1.022174000	3.117996000	3.135799000
H	-1.689276000	3.986844000	3.142818000
H	-1.137626000	2.597038000	4.093499000
H	0.010792000	3.477245000	3.060550000
C	-7.384487000	1.878072000	0.292049000
H	-6.966076000	1.172863000	-0.432347000
H	-7.892984000	1.299907000	1.070744000
H	-8.147592000	2.469966000	-0.225399000
C	-6.978695000	3.782271000	1.872091000
H	-7.764380000	4.364881000	1.377839000
H	-7.434506000	3.229454000	2.701480000
H	-6.251402000	4.477838000	2.300686000
C	-5.740302000	3.275522000	-2.962944000
H	-5.660586000	4.365705000	-2.979768000
H	-6.801402000	3.009601000	-3.031798000
H	-5.372070000	2.930230000	-1.996063000
C	-5.127742000	1.096702000	-4.076124000
H	-6.171740000	0.804630000	-3.913739000
H	-4.787486000	0.633772000	-5.007345000
H	-4.528291000	0.681697000	-3.263219000
C	1.086690000	4.478468000	-3.450756000
H	1.721114000	4.971871000	-2.707269000
H	1.217428000	3.395816000	-3.354423000

H	1.465111000	4.770059000	-4.436578000
C	-0.517594000	6.384501000	-3.660394000
H	-0.284454000	6.515563000	-4.723584000
H	-1.530326000	6.758235000	-3.491377000
H	0.176481000	7.002127000	-3.078833000

INT2

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symmetry c1

C	-4.574954000	-1.160844000	-0.275104000
C	-3.907796000	-2.361821000	-0.468526000
C	-2.698436000	-2.358899000	-1.152005000
C	-2.123149000	-1.180582000	-1.628408000
C	-2.729105000	0.083441000	-1.346228000
C	-3.988323000	0.014653000	-0.715042000
B	-2.185990000	1.573942000	-1.393407000
N	-0.743864000	1.799766000	-1.460838000
C	0.078352000	0.784982000	-1.920923000
N	-0.123294000	2.899329000	-0.919892000
C	1.105451000	2.672962000	-0.534705000
N	1.780177000	1.457569000	-0.587423000
N	1.245058000	0.526832000	-1.336982000
C	1.834072000	3.801067000	0.073797000
C	3.193572000	3.701175000	0.373589000
C	3.830611000	4.797187000	0.946127000
N	3.219192000	5.949413000	1.235460000
C	1.913244000	6.030306000	0.949306000
C	1.181156000	5.000380000	0.376963000
C	-0.457528000	-0.024247000	-2.945936000
C	-0.858945000	-1.393370000	-2.509289000
C	-1.149246000	-2.270585000	-3.698057000
N	-1.542825000	-1.806352000	-4.832766000
C	-1.606035000	-0.439690000	-4.996595000
C	-1.022005000	0.456530000	-4.126597000
C	-2.995251000	2.921281000	-1.125823000
C	-3.033185000	3.876603000	-2.176603000
C	-3.474096000	5.178972000	-1.935705000
C	-3.853121000	5.583084000	-0.665758000
C	-3.881486000	4.647815000	0.356328000
C	-3.507895000	3.317201000	0.142077000
H	-5.536121000	-1.128590000	0.229465000
H	-4.336787000	-3.300044000	-0.127744000
H	-2.201333000	-3.304474000	-1.353367000
H	-4.512737000	0.943542000	-0.543845000
H	3.735144000	2.785922000	0.163585000
H	4.892239000	4.743236000	1.185223000
H	1.425086000	6.972589000	1.195972000
H	0.121165000	5.118124000	0.174657000
H	-0.092990000	-1.858942000	-1.872223000
H	-0.983340000	-3.346484000	-3.618608000
H	-2.057744000	-0.092445000	-5.921785000
H	-0.950314000	1.506340000	-4.394548000
H	-3.525887000	5.873702000	-2.769009000
H	-4.160467000	6.608797000	-0.481880000
H	-4.228328000	4.931776000	1.346241000
C	-3.804307000	2.373217000	1.274491000
C	-5.159457000	2.045749000	1.533872000
C	-2.801446000	1.837572000	2.098729000
C	-5.455040000	1.131593000	2.541162000
C	-3.149004000	0.922107000	3.095115000
C	-4.463576000	0.536559000	3.317630000
H	-6.495259000	0.871672000	2.722667000
H	-2.368793000	0.503906000	3.726454000
C	-2.658994000	3.567121000	-3.602969000
C	-1.440898000	4.086849000	-4.119959000
C	-3.543652000	2.906290000	-4.487587000
C	-1.099129000	3.862368000	-5.450184000
C	-3.136624000	2.703687000	-5.814454000
C	-1.924480000	3.148725000	-6.315402000
H	-0.159629000	4.261485000	-5.822757000
H	-3.822551000	2.191177000	-6.488648000
C	-1.364799000	2.308716000	2.008982000
H	-1.253259000	2.864080000	1.072382000
C	-6.325287000	2.652893000	0.761537000
H	-5.921478000	3.248255000	-0.061982000
C	-4.806015000	-0.500761000	4.366103000
H	-3.868739000	-0.771124000	4.872145000
C	-4.965123000	2.400424000	-4.215404000

H	-5.506969000	2.642452000	-5.141651000
C	-0.486515000	4.929488000	-3.288097000
H	-0.761681000	4.814865000	-2.236365000
C	-1.531965000	2.905954000	-7.757448000
H	-2.307779000	2.266278000	-8.201884000
C	-1.495969000	4.220439000	-8.548756000
H	-1.268947000	4.031150000	-9.603718000
H	-2.456472000	4.741842000	-8.488558000
H	-0.724395000	4.891346000	-8.154203000
C	-0.192207000	2.166212000	-7.863097000
H	-0.208466000	1.229208000	-7.296561000
H	0.036931000	1.932623000	-8.908484000
H	0.628166000	2.778290000	-7.471850000
C	-5.368381000	-1.770384000	3.711477000
H	-5.552250000	-2.547141000	4.462228000
H	-6.318717000	-1.558945000	3.207174000
H	-4.672455000	-2.165224000	2.963892000
C	-5.771648000	0.046098000	5.424345000
H	-6.741804000	0.297539000	4.981321000
H	-5.948087000	-0.699268000	6.207711000
H	-5.371411000	0.951252000	5.891824000
C	-0.355598000	1.157100000	2.014086000
H	-0.375770000	0.609596000	2.962219000
H	-0.561867000	0.439194000	1.212140000
H	0.663479000	1.536143000	1.887475000
C	-1.066646000	3.295533000	3.149274000
H	-1.761079000	4.142087000	3.126518000
H	-1.165020000	2.804937000	4.124656000
H	-0.045653000	3.684787000	3.061095000
C	-7.261745000	1.602440000	0.147801000
H	-6.731236000	0.928807000	-0.532341000
H	-7.750585000	0.993654000	0.916180000
H	-8.050080000	2.099703000	-0.428198000
C	-7.123526000	3.606244000	1.664141000
H	-7.918004000	4.100454000	1.093714000
H	-7.589674000	3.060932000	2.492662000
H	-6.479226000	4.377771000	2.096418000
C	-5.767733000	3.049039000	-3.088864000
H	-5.737482000	4.140983000	-3.137040000
H	-6.813110000	2.731072000	-3.174532000
H	-5.408125000	2.745352000	-2.104891000
C	-4.991775000	0.870398000	-4.082540000
H	-6.023994000	0.517303000	-3.974821000
H	-4.553097000	0.380762000	-4.957554000
H	-4.428832000	0.545461000	-3.204984000
C	0.976941000	4.488650000	-3.444813000
H	1.595579000	4.963774000	-2.675875000
H	1.089557000	3.403560000	-3.352910000
H	1.385300000	4.783337000	-4.417742000
C	-0.608685000	6.417052000	-3.655581000
H	-0.353981000	6.576300000	-4.709870000
H	-1.622727000	6.792707000	-3.495578000
H	0.077743000	7.015796000	-3.045773000

TS4 from **INT2** to product **3**

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symmetry c1

C	-2.558149000	-2.909786000	1.718313000
C	-1.764471000	-4.054880000	1.799497000
C	-0.476470000	-4.061686000	1.270163000
C	0.004649000	-2.872061000	0.759723000
C	-0.727453000	-1.681711000	0.683354000
C	-2.052013000	-1.749711000	1.154977000
B	0.012903000	-0.395644000	0.238845000
N	1.442074000	-0.663332000	0.351952000
C	1.941986000	-1.974847000	0.515318000
N	2.272342000	0.352271000	0.726700000
C	3.316424000	0.030132000	1.434766000
N	3.568539000	-1.236474000	1.947705000
N	2.875845000	-2.206775000	1.437152000
C	4.236669000	1.108721000	1.827802000
C	5.430500000	0.823380000	2.492882000
C	6.269558000	1.878214000	2.835868000
N	6.002945000	3.160796000	2.573337000
C	4.851712000	3.421807000	1.940434000
C	3.944392000	2.448054000	1.549632000
C	1.480843000	-3.070374000	-0.349036000

C	2.074945000	-4.378302000	-0.204865000
C	1.805198000	-5.348987000	-1.133894000
N	1.078584000	-5.172795000	-2.261344000
C	0.646333000	-3.923642000	-2.475545000
C	0.827537000	-2.859943000	-1.614384000
C	-0.385761000	1.076868000	-0.145293000
C	0.069649000	1.608065000	-1.380723000
C	0.039772000	2.984853000	-1.600757000
C	-0.450955000	3.850648000	-0.633177000
C	-0.997609000	3.332464000	0.532660000
C	-1.003966000	1.956998000	0.775965000
H	-3.574005000	-2.922868000	2.101722000
H	-2.145412000	-4.955427000	2.273759000
H	0.128428000	-4.961578000	1.266738000
H	-2.671365000	-0.861870000	1.106000000
H	5.692457000	-0.199914000	2.737228000
H	7.207944000	1.678299000	3.352201000
H	4.643153000	4.471618000	1.736830000
H	3.022680000	2.720092000	1.044731000
H	2.713804000	-4.587448000	0.645482000
H	2.220121000	-6.346977000	-0.992332000
H	0.107548000	-3.748158000	-3.406914000
H	0.392092000	-1.897716000	-1.858442000
H	0.374548000	3.372295000	-2.558563000
H	-0.448332000	4.923167000	-0.806551000
H	-1.434533000	3.994946000	1.274532000
C	-1.742940000	1.472017000	1.985861000
C	-3.155139000	1.411857000	1.932242000
C	-1.077214000	1.111467000	3.168682000
C	-3.856529000	0.959246000	3.047440000
C	-1.824203000	0.662055000	4.259873000
C	-3.209377000	0.568915000	4.218219000
H	-4.940904000	0.903699000	2.996751000
H	-1.310533000	0.380154000	5.175988000
C	0.508982000	0.716368000	-2.506911000
C	1.880720000	0.578235000	-2.823559000
C	-0.450824000	0.051315000	-3.310640000
C	2.270726000	-0.299182000	-3.833696000
C	0.001547000	-0.815549000	-4.310219000
C	1.349321000	-1.034407000	-4.569969000
H	3.329312000	-0.409211000	-4.049014000
H	-0.737568000	-1.339181000	-4.915843000
C	0.423601000	1.266351000	3.314822000
H	0.843304000	1.428884000	2.315912000
C	-3.938818000	1.834514000	0.698267000
H	-3.238618000	1.889265000	-0.141766000
C	-3.988051000	0.040245000	5.405068000
H	-3.268705000	-0.112983000	6.221606000
C	-1.970403000	0.204553000	-3.229804000
H	-2.329262000	-0.220684000	-4.176762000
C	2.962784000	1.390488000	-2.133517000
H	2.547730000	1.786094000	-1.201731000
C	1.779117000	-1.976659000	-5.674988000
H	0.918906000	-2.623813000	-5.899442000
C	2.114165000	-1.183083000	-6.947371000
H	2.372495000	-1.859489000	-7.769777000
H	1.268790000	-0.562071000	-7.260563000
H	2.970119000	-0.521623000	-6.769851000
C	2.951276000	-2.876520000	-5.270925000
H	2.741396000	-3.415963000	-4.342134000
H	3.150557000	-3.612565000	-6.056984000
H	3.869140000	-2.295760000	-5.128276000
C	-4.621495000	-1.319334000	5.079084000
H	-5.139166000	-1.727377000	5.954468000
H	-5.354405000	-1.222787000	4.269357000
H	-3.859258000	-2.037969000	4.760516000
C	-5.045670000	1.037360000	5.892606000
H	-5.820714000	1.197012000	5.134683000
H	-5.538873000	0.662632000	6.796196000
H	-4.595328000	2.008196000	6.122265000
C	1.089626000	0.024866000	3.915048000
H	0.774734000	-0.141670000	4.950460000
H	0.844322000	-0.877784000	3.343774000
H	2.178200000	0.142131000	3.927154000
C	0.751792000	2.516144000	4.145550000
H	0.313091000	3.412907000	3.695413000
H	0.357264000	2.422463000	5.164017000
H	1.836935000	2.657738000	4.209128000

C	-5.043477000	0.841527000	0.310971000
H	-4.663935000	-0.181609000	0.228000000
H	-5.863336000	0.840995000	1.037155000
H	-5.468868000	1.121969000	-0.658812000
C	-4.545427000	3.231690000	0.896766000
H	-5.074894000	3.554242000	-0.006988000
H	-5.260911000	3.221494000	1.727291000
H	-3.776605000	3.974273000	1.126975000
C	-2.489641000	1.646935000	-3.197563000
H	-1.993554000	2.266823000	-3.951699000
H	-3.565075000	1.647590000	-3.409761000
H	-2.341955000	2.118662000	-2.223672000
C	-2.613340000	-0.629729000	-2.116836000
H	-3.700744000	-0.660039000	-2.251672000
H	-2.239270000	-1.659277000	-2.113506000
H	-2.410024000	-0.191993000	-1.137503000
C	4.206168000	0.557811000	-1.788465000
H	4.847583000	1.109466000	-1.093020000
H	3.942787000	-0.400918000	-1.330121000
H	4.805882000	0.343284000	-2.679633000
C	3.380617000	2.580649000	-3.012547000
H	3.803171000	2.226079000	-3.960025000
H	2.533701000	3.230842000	-3.248503000
H	4.143231000	3.180716000	-2.502697000

Product **3**

122

symmetry c1

C	-4.306072000	-1.713519000	-0.621583000
C	-3.208217000	-2.533415000	-0.886443000
C	-1.959355000	-1.977605000	-1.157763000
C	-1.841819000	-0.599343000	-1.146907000
C	-2.937463000	0.253764000	-0.917442000
C	-4.177855000	-0.329625000	-0.644960000
B	-2.432462000	1.726808000	-0.977986000
N	-0.984490000	1.557651000	-1.070389000
C	-0.557070000	0.167657000	-1.327147000
N	-0.071399000	2.465946000	-0.766204000
C	1.118908000	2.002024000	-0.462706000
N	1.290552000	0.674579000	-0.031872000
N	0.445395000	-0.207782000	-0.289870000
C	2.201822000	2.938560000	-0.154609000
C	3.498313000	2.479214000	0.089021000
C	4.497664000	3.406271000	0.359696000
N	4.297706000	4.726715000	0.413801000
C	3.049242000	5.155620000	0.187714000
C	1.981075000	4.319255000	-0.099456000
C	0.021790000	0.040068000	-2.732523000
C	1.348841000	-0.290532000	-2.995153000
C	1.766034000	-0.368412000	-4.322922000
N	0.965161000	-0.160633000	-5.369642000
C	-0.309675000	0.146205000	-5.102814000
C	-0.822569000	0.263652000	-3.819649000
C	-3.028237000	3.180147000	-0.979004000
C	-2.901492000	4.052742000	-2.087333000
C	-3.187685000	5.410465000	-1.921634000
C	-3.619557000	5.914793000	-0.703057000
C	-3.845320000	5.046073000	0.356428000
C	-3.577303000	3.684463000	0.222376000
H	-5.268571000	-2.161485000	-0.391384000
H	-3.324032000	-3.613430000	-0.866215000
H	-1.094846000	-2.608096000	-1.345334000
H	-5.035832000	0.294491000	-0.426276000
H	3.719526000	1.417051000	0.077044000
H	5.515826000	3.066204000	0.546777000
H	2.895219000	6.233032000	0.240751000
H	0.989881000	4.725986000	-0.273392000
H	2.056156000	-0.491600000	-2.198326000
H	2.802965000	-0.614860000	-4.549286000
H	-0.961791000	0.309697000	-5.958993000
H	-1.866344000	0.531860000	-3.678405000
H	-3.104579000	6.067767000	-2.782371000
H	-3.821636000	6.976555000	-0.593178000
H	-4.234059000	5.420079000	1.298842000
C	-3.922846000	2.729231000	1.321647000
C	-5.253790000	2.270904000	1.438521000
C	-2.934094000	2.251382000	2.200962000

C	-5.542155000	1.278845000	2.372966000
C	-3.270685000	1.251539000	3.115443000
C	-4.558874000	0.735067000	3.197698000
H	-6.560393000	0.906682000	2.448795000
H	-2.506912000	0.856742000	3.780052000
C	-2.575954000	3.598871000	-3.484935000
C	-1.303628000	3.853766000	-4.038703000
C	-3.590361000	3.059785000	-4.320414000
C	-1.048190000	3.538473000	-5.376028000
C	-3.263480000	2.728904000	-5.636521000
C	-2.007527000	2.961889000	-6.192517000
H	-0.062244000	3.745521000	-5.777265000
H	-4.041775000	2.303390000	-6.269213000
C	-1.552830000	2.879941000	2.228926000
H	-1.332561000	3.262151000	1.225188000
C	-6.381823000	2.878677000	0.617400000
H	-5.940696000	3.340774000	-0.273564000
C	-4.878269000	-0.401617000	4.145947000
H	-3.965787000	-0.608058000	4.722286000
C	-5.063750000	2.871265000	-3.953821000
H	-5.544496000	2.596575000	-4.902012000
C	-0.183465000	4.509436000	-3.250621000
H	-0.439681000	4.446667000	-2.188094000
C	-1.767536000	2.648629000	-7.658112000
H	-2.239245000	1.674005000	-7.858966000
C	-2.474719000	3.693672000	-8.538026000
H	-2.351563000	3.453819000	-9.600046000
H	-3.545372000	3.746041000	-8.318018000
H	-2.046525000	4.686597000	-8.358787000
C	-0.291199000	2.547130000	-8.044426000
H	0.259845000	1.849840000	-7.405256000
H	-0.200131000	2.202528000	-9.079499000
H	0.200880000	3.524888000	-7.985101000
C	-5.237024000	-1.673435000	3.364222000
H	-5.403541000	-2.514980000	4.046050000
H	-6.154047000	-1.524312000	2.782168000
H	-4.437618000	-1.942052000	2.665949000
C	-5.987586000	-0.034362000	5.138978000
H	-6.938390000	0.142305000	4.623784000
H	-6.146215000	-0.847329000	5.856063000
H	-5.734019000	0.873020000	5.696289000
C	-0.439895000	1.905458000	2.618685000
H	-0.478356000	1.653587000	3.684366000
H	-0.499990000	0.972263000	2.050375000
H	0.539181000	2.359273000	2.431721000
C	-1.557209000	4.089287000	3.179073000
H	-2.294688000	4.835991000	2.869316000
H	-1.801851000	3.772143000	4.199532000
H	-0.570153000	4.565541000	3.193372000
C	-7.437861000	1.872618000	0.144857000
H	-6.998367000	1.024703000	-0.388691000
H	-8.027951000	1.479168000	0.979485000
H	-8.135703000	2.368537000	-0.538501000
C	-7.070784000	3.989219000	1.428797000
H	-7.850388000	4.476567000	0.832263000
H	-7.538002000	3.566944000	2.326125000
H	-6.358150000	4.752075000	1.752127000
C	-5.773951000	4.146662000	-3.478546000
H	-5.543093000	4.998002000	-4.127480000
H	-6.858242000	3.986452000	-3.499678000
H	-5.496442000	4.414284000	-2.456326000
C	-5.332185000	1.716797000	-2.988184000
H	-6.408962000	1.516329000	-2.933258000
H	-4.828206000	0.797935000	-3.304327000
H	-4.988029000	1.967427000	-1.983087000
C	1.163457000	3.802179000	-3.464261000
H	1.906415000	4.181827000	-2.756399000
H	1.078530000	2.719815000	-3.328321000
H	1.556676000	3.982640000	-4.470229000
C	-0.044879000	5.994477000	-3.620894000
H	0.193013000	6.105244000	-4.685340000
H	-0.964963000	6.551383000	-3.422715000
H	0.765152000	6.455210000	-3.043234000

b. Cartesian coordinates for Diels-Alder reactions of 1’ with PTAD and 4,4’-bptz

Cartesian coordinates are given in Å and were computed at the M06-2X/6-311+G** level of theory.

1’
22
symmetry c1

B	-0.222827000	0.000000000	-0.000001000
C	-1.531459000	0.698430000	0.000015000
C	-2.726062000	1.440275000	-0.000022000
C	-2.726062000	-1.440275000	0.000021000
C	-3.893991000	0.711105000	-0.000023000
C	-3.893992000	-0.711105000	0.000027000
C	-1.531459000	-0.698430000	-0.000020000
H	-4.849704000	1.223934000	0.000081000
H	-4.849704000	-1.223933000	-0.000075000
H	-2.747148000	2.524257000	0.000122000
H	-2.747149000	-2.524257000	-0.000122000
C	1.314064000	0.000000000	0.000000000
C	2.031924000	1.203994000	-0.000037000
C	2.031924000	-1.203994000	0.000036000
C	3.421529000	1.207049000	0.000033000
H	1.488203000	2.142616000	0.000012000
C	3.421529000	-1.207049000	-0.000032000
H	1.488203000	-2.142617000	-0.000013000
C	4.115775000	0.000000000	0.000001000
H	3.964650000	2.144772000	-0.000084000
H	3.964650000	-2.144772000	0.000086000
H	5.199816000	0.000000000	0.000001000

PTAD
18
symmetry c1

N	2.977886000	-0.597881000	-0.135379000
N	2.977759000	0.598168000	0.135591000
C	1.569275000	-1.096095000	-0.245515000
C	1.569131000	1.096142000	0.245484000
N	0.760078000	-0.000003000	-0.000238000
O	1.281716000	2.217494000	0.492005000
O	1.282090000	-2.217536000	-0.491850000
C	-0.668484000	-0.000069000	-0.000201000
C	-1.349547000	1.075271000	-0.560676000
C	-1.349466000	-1.075371000	0.560466000
C	-2.738799000	1.070361000	-0.551297000
H	-0.801119000	1.904977000	-0.986814000
C	-2.738728000	-1.070447000	0.551408000
H	-0.800991000	-1.905067000	0.986551000
C	-3.434826000	-0.000042000	0.000115000
H	-3.276038000	1.906505000	-0.981311000
H	-3.275880000	-1.906566000	0.981579000
H	-4.517822000	-0.000004000	0.000244000

TS Diels Alder 1’ + PTAD at positions 3,6
40
symmetry c1

C	-0.241268000	1.003712000	1.615989000
C	0.601071000	1.492754000	0.568806000
C	1.838800000	0.781077000	0.434027000
C	-0.246938000	-0.346992000	1.865883000
C	1.834513000	-0.575182000	0.686238000
C	0.592142000	-1.183567000	1.065098000
N	-0.292128000	0.500945000	-0.935771000
N	-0.294445000	-0.789699000	-0.696462000
C	-1.645792000	-1.213059000	-0.389439000
C	-1.642315000	1.010602000	-0.801849000
N	-2.450431000	-0.084758000	-0.513948000
O	-1.977130000	-2.332912000	-0.139413000
O	-1.969731000	2.146605000	-0.970107000
B	3.102828000	0.043037000	0.260111000
H	-0.985118000	1.655502000	2.058482000

H	0.469567000	2.499704000	0.192601000
H	-0.997240000	-0.792735000	2.507857000
H	0.453269000	-2.257495000	1.074275000
C	-3.858224000	-0.047906000	-0.300794000
C	-4.428599000	1.039812000	0.355019000
C	-4.644671000	-1.104078000	-0.753090000
C	-5.803397000	1.065940000	0.554952000
C	-6.016342000	-1.068124000	-0.536365000
C	-6.599422000	0.014285000	0.114045000
H	-3.805466000	1.859655000	0.686148000
H	-4.183655000	-1.944085000	-1.254704000
H	-6.251165000	1.913796000	1.058751000
H	-6.630439000	-1.890010000	-0.883478000
H	-7.670210000	0.038905000	0.275084000
C	4.614872000	-0.008933000	0.003826000
C	5.318236000	-1.216270000	0.111475000
C	5.321572000	1.149724000	-0.345397000
C	6.687048000	-1.265528000	-0.121646000
C	6.690288000	1.104862000	-0.579926000
C	7.372351000	-0.103833000	-0.467479000
H	4.782092000	-2.120399000	0.378983000
H	4.787978000	2.089861000	-0.434083000
H	7.220437000	-2.204784000	-0.036024000
H	7.226115000	2.006883000	-0.850641000
H	8.440060000	-0.140730000	-0.650624000

Product Diels Alder 1’ + PTAD at positions 3,6

40

symmetry c1

C	-0.144210000	-1.192955000	1.967452000
C	-0.561945000	-1.469874000	0.525536000
C	-1.880220000	-0.786382000	0.309705000
C	-0.140640000	0.099794000	2.293717000
C	-1.876969000	0.536521000	0.643585000
C	-0.555722000	1.029747000	1.156301000
N	0.377484000	-0.663036000	-0.321471000
N	0.381012000	0.716672000	0.027536000
C	1.706706000	1.129400000	0.164534000
C	1.701489000	-1.096966000	-0.401680000
N	2.489884000	0.046491000	-0.247424000
O	2.077064000	2.207633000	0.540761000
O	2.062566000	-2.227292000	-0.587407000
B	-3.136973000	-0.038295000	0.146037000
H	0.189615000	-1.993326000	2.614512000
H	-0.470293000	-2.504633000	0.211042000
H	0.197719000	0.496201000	3.241890000
H	-0.458319000	2.089166000	1.371026000
C	3.909111000	0.090937000	-0.379567000
C	4.685536000	-0.980094000	0.053383000
C	4.497374000	1.218843000	-0.945911000
C	6.066361000	-0.917121000	-0.094207000
C	5.878888000	1.272152000	-1.074569000
C	6.666409000	0.205354000	-0.653468000
H	4.212653000	-1.852296000	0.482399000
H	3.878212000	2.046278000	-1.266204000
H	6.673365000	-1.751632000	0.235009000
H	6.338943000	2.150706000	-1.510014000
H	7.743337000	0.249361000	-0.760976000
C	-4.628282000	0.055129000	-0.210966000
C	-5.321542000	1.265640000	-0.080068000
C	-5.324809000	-1.069127000	-0.673208000
C	-6.670903000	1.351397000	-0.400834000
C	-6.674168000	-0.987870000	-0.995154000
C	-7.346778000	0.223453000	-0.858273000
H	-4.793390000	2.144068000	0.274907000
H	-4.799194000	-2.011852000	-0.780828000
H	-7.196311000	2.293258000	-0.296258000
H	-7.202124000	-1.864043000	-1.352449000
H	-8.399170000	0.288742000	-1.109415000

TS Diels Alder 1’ + PTAD at positions 1,4

40

symmetry c1

N	0.577404000	1.701243000	-1.094834000
C	0.085777000	3.031292000	-0.085959000
C	-1.365557000	3.109664000	-0.237233000
C	-1.993580000	2.003373000	0.213834000
C	-1.205140000	0.972585000	0.876804000

N	-0.185140000	0.630568000	-0.975015000
B	-2.621166000	0.661988000	0.473012000
C	-0.083416000	1.357892000	1.661825000
C	0.567360000	2.449174000	1.184366000
C	1.955602000	1.376222000	-0.771909000
C	0.652281000	-0.472622000	-0.614750000
N	1.966206000	0.015411000	-0.535641000
O	2.867921000	2.148806000	-0.800528000
O	0.293441000	-1.602671000	-0.470660000
C	3.113520000	-0.753588000	-0.188910000
C	4.083234000	-0.204407000	0.645462000
C	5.201314000	-0.960273000	0.975517000
C	5.344940000	-2.254423000	0.486918000
C	4.366190000	-2.793029000	-0.341722000
C	3.248241000	-2.045358000	-0.689958000
C	-3.731397000	-0.357962000	0.270795000
C	-3.492074000	-1.712522000	0.551036000
C	-4.491233000	-2.658660000	0.364890000
C	-5.744389000	-2.259593000	-0.093724000
C	-5.999949000	-0.919198000	-0.376974000
C	-4.996586000	0.023627000	-0.201972000
H	0.676693000	3.848417000	-0.482175000
H	-1.826219000	3.939299000	-0.759906000
H	0.261949000	0.788461000	2.516051000
H	1.499513000	2.814338000	1.597675000
H	3.967535000	0.805259000	1.016538000
H	5.960674000	-0.533782000	1.619475000
H	6.216750000	-2.840782000	0.750227000
H	4.472184000	-3.800295000	-0.725571000
H	2.480306000	-2.458164000	-1.329894000
H	-2.509614000	-2.013624000	0.898162000
H	-4.297921000	-3.703766000	0.574710000
H	-6.526022000	-2.997449000	-0.234880000
H	-6.976144000	-0.617778000	-0.737490000
H	-5.184876000	1.067136000	-0.430060000

Product Diels Alder 1’ + PTAD at positions 1,4

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symmetry c1

N	0.667455000	1.696289000	-0.746898000
C	0.081940000	2.899981000	-0.070138000
C	-1.340837000	2.979195000	-0.631788000
C	-2.039498000	1.886877000	-0.355036000
C	-1.208499000	0.832125000	0.447196000
N	-0.090844000	0.519264000	-0.455727000
B	-2.660621000	0.566535000	-0.029107000
C	-0.653637000	1.458989000	1.697130000
C	0.044983000	2.561242000	1.414711000
C	2.013280000	1.413362000	-0.534926000
C	0.799296000	-0.494190000	-0.101036000
N	2.081982000	0.036886000	-0.294671000
O	2.920035000	2.202010000	-0.579434000
O	0.511899000	-1.598206000	0.271612000
C	3.285965000	-0.712158000	-0.154990000
C	4.392581000	-0.149145000	0.474956000
C	5.558979000	-0.896607000	0.590640000
C	5.618054000	-2.195076000	0.097407000
C	4.502457000	-2.749052000	-0.522492000
C	3.334604000	-2.010165000	-0.657663000
C	-3.828106000	-0.397587000	-0.022112000
C	-3.647940000	-1.687401000	0.506421000
C	-4.697434000	-2.596060000	0.516733000
C	-5.937745000	-2.222509000	0.004361000
C	-6.134641000	-0.947333000	-0.524773000
C	-5.084299000	-0.041929000	-0.541524000
H	0.715598000	3.744886000	-0.322354000
H	-1.660593000	3.828321000	-1.226236000
H	-0.765515000	1.025699000	2.683032000
H	0.608707000	3.147633000	2.128984000
H	4.342144000	0.862669000	0.851723000
H	6.423730000	-0.458163000	1.073728000
H	6.528743000	-2.773344000	0.195470000
H	4.539465000	-3.760566000	-0.908198000
H	2.460933000	-2.435634000	-1.133150000
H	-2.672617000	-1.965326000	0.892835000
H	-4.554005000	-3.591335000	0.919468000
H	-6.758223000	-2.931097000	0.014148000
H	-7.103066000	-0.669771000	-0.923018000

```
H       -5.224836000      0.950506000     -0.955717000
```

4,4′-bptz

```
27
symmetry c1
N       -0.627453000     -1.184083000      0.010803000
C       -1.318796000     -0.007741000      0.100942000
N        0.644197000     -1.168307000      0.036663000
C        1.321687000      0.033839000      0.116892000
N        0.694254000      1.176468000      0.316154000
N       -0.620283000      1.097638000      0.324005000
C        2.781114000      0.007774000      0.021631000
C        3.518983000      1.189078000      0.125671000
C        4.901016000      1.100759000      0.021463000
N        5.551268000     -0.046411000     -0.172928000
C        4.837751000     -1.164636000     -0.270735000
C        3.449105000     -1.200487000     -0.180535000
C       -2.770400000     -0.002035000     -0.000989000
C       -3.472438000     -1.181582000      0.250400000
C       -4.861600000     -1.133706000      0.168071000
N       -5.539150000     -0.033540000     -0.146956000
C       -4.857613000      1.082127000     -0.403094000
C       -3.471898000      1.157736000     -0.345382000
H        3.039421000      2.146086000      0.283811000
H        5.513004000      1.992761000      0.097445000
H        5.396958000     -2.080350000     -0.428263000
H        2.914607000     -2.136963000     -0.264430000
H       -2.958405000     -2.097300000      0.511250000
H       -5.450340000     -2.022996000      0.364179000
H       -5.442798000      1.953434000     -0.675618000
H       -2.980221000      2.086262000     -0.615033000
H       -1.093517000      1.979942000      0.526461000
```

TS Diels-Alder 1′ + 4,4′-bptz at bond a

```
48
symmetry c1
C        0.725049000     -1.895250000      2.898349000
C       -0.724187000     -1.895537000      2.898359000
C       -1.440970000     -1.173589000      2.010085000
C       -0.726791000     -0.370183000      1.036593000
C        0.727058000     -0.369968000      1.036487000
C        1.441535000     -1.173089000      2.010012000
C        1.245940000     -0.953429000     -0.785019000
C        2.730296000     -0.932727000     -0.784317000
B       -0.000135000      0.945603000      0.879689000
C       -1.245591000     -0.953759000     -0.785102000
N       -0.630909000     -0.031763000     -1.635495000
N       -0.631862000     -2.203806000     -0.731100000
C       -2.729939000     -0.933358000     -0.784403000
N        0.631058000     -0.031608000     -1.635504000
N        0.632521000     -2.203650000     -0.731075000
C        3.416909000      0.234109000     -1.109779000
C        4.805616000      0.219687000     -1.057375000
N        5.524932000     -0.848186000     -0.710969000
C       -3.466533000     -2.057886000     -0.423372000
C       -4.854173000     -1.959731000     -0.406802000
N       -5.524593000     -0.849403000     -0.710961000
C        4.854768000     -1.958775000     -0.407204000
C        3.467147000     -2.057231000     -0.423749000
C       -4.805526000      0.218492000     -1.057812000
C       -3.416823000      0.233204000     -1.110284000
H        1.238743000     -2.479410000      3.653058000
H       -1.237638000     -2.479965000      3.653026000
H       -2.524910000     -1.183151000      2.013272000
H        2.525482000     -1.182253000      2.013176000
H        2.878122000      1.123194000     -1.412964000
H        5.369065000      1.112719000     -1.309211000
H       -2.968273000     -2.985320000     -0.171635000
H       -5.455927000     -2.821004000     -0.133946000
H        5.456723000     -2.820020000     -0.134704000
H        2.969104000     -2.984865000     -0.172326000
H       -5.369182000      1.111302000     -1.309971000
H       -2.878248000      1.122298000     -1.413819000
C       -0.000481000      2.446343000      0.646776000
C        1.207828000      3.151763000      0.533082000
C       -1.209112000      3.151259000      0.533358000
C        1.208785000      4.521712000      0.309068000
C       -1.210683000      4.521208000      0.309345000
```

C	-0.001103000	5.203153000	0.196488000
H	2.145320000	2.613312000	0.625334000
H	-2.146362000	2.612425000	0.625838000
H	2.144511000	5.060619000	0.222124000
H	-2.146650000	5.059731000	0.222619000
H	-0.001346000	6.272778000	0.020690000

Product Diels-Alder 1′ + 4,4′-bptz at bond a

48

symmetry c1

C	0.732888000	-0.522113000	3.208684000
C	-0.732693000	-0.522441000	3.208763000
C	-1.442611000	-0.451964000	2.075177000
C	-0.782001000	-0.219802000	0.769850000
C	0.781888000	-0.219806000	0.769703000
C	1.442677000	-0.451525000	2.075013000
C	1.233136000	-1.086053000	-0.442304000
C	2.724537000	-1.176093000	-0.586714000
B	-0.000068000	1.075887000	0.483655000
C	-1.233336000	-1.085902000	-0.442225000
N	-0.616126000	-0.490671000	-1.646800000
N	-0.614569000	-2.419263000	-0.226215000
C	-2.724756000	-1.175795000	-0.586635000
N	0.615962000	-0.490778000	-1.646839000
N	0.614225000	-2.419345000	-0.226236000
C	3.425163000	-0.161246000	-1.232012000
C	4.811331000	-0.246523000	-1.289740000
N	5.515744000	-1.245768000	-0.758341000
C	-3.445490000	-2.226083000	-0.029519000
C	-4.832741000	-2.210163000	-0.146053000
N	-5.515963000	-1.245221000	-0.758364000
C	4.832419000	-2.210568000	-0.145911000
C	3.445170000	-2.226358000	-0.029426000
C	-4.811445000	-0.245956000	-1.289594000
C	-3.425278000	-0.160800000	-1.231795000
H	1.245496000	-0.651728000	4.154175000
H	-1.245137000	-0.652428000	4.154291000
H	-2.522501000	-0.554426000	2.079915000
H	2.522618000	-0.553472000	2.079689000
H	2.901307000	0.666228000	-1.694556000
H	5.384017000	0.527300000	-1.791355000
H	-2.939917000	-3.039846000	0.473958000
H	-5.421744000	-3.018081000	0.276668000
H	5.421341000	-3.018466000	0.276958000
H	2.939519000	-3.040031000	0.474116000
H	-5.384047000	0.527994000	-1.791108000
H	-2.901353000	0.666716000	-1.694185000
C	0.000092000	2.568310000	0.233426000
C	1.209942000	3.273469000	0.114494000
C	-1.209547000	3.273861000	0.114665000
C	1.211419000	4.641103000	-0.120038000
C	-1.210611000	4.641491000	-0.119877000
C	0.000506000	5.320840000	-0.237247000
H	2.146611000	2.734126000	0.210832000
H	-2.146383000	2.734837000	0.211144000
H	2.146630000	5.179980000	-0.211355000
H	-2.145660000	5.180667000	-0.211089000
H	0.000666000	6.389225000	-0.420913000

TS Diels-Alder 1′ + 4,4′-bptz at bond b

48

symmetry c1

C	-2.139813000	-1.554493000	1.282820000
C	-1.399364000	-1.088341000	0.130471000
C	-0.042846000	-0.645622000	0.397240000
C	0.495904000	-0.813492000	1.742930000
C	-0.252824000	-1.245391000	2.791592000
C	-1.636030000	-1.522786000	2.551252000
C	-2.315248000	0.596985000	-0.383341000
N	-1.985006000	1.445726000	0.672247000
N	-0.765340000	1.730457000	0.785255000
C	0.094738000	1.141357000	-0.163187000
C	-3.754319000	0.257477000	-0.523018000
C	1.518167000	1.589054000	-0.059807000
N	-1.627170000	0.814000000	-1.579749000
N	-0.406209000	1.101928000	-1.473196000
C	2.054222000	1.962282000	1.169546000
C	3.408307000	2.273746000	1.234054000

N	4.230419000	2.233162000	0.186312000
C	3.699856000	1.891006000	-0.987656000
C	2.359657000	1.567403000	-1.167701000
C	-4.232703000	-0.345034000	-1.683297000
C	-5.577383000	-0.695758000	-1.741939000
N	-6.441983000	-0.491430000	-0.749118000
C	-5.971382000	0.089871000	0.354458000
C	-4.647284000	0.478460000	0.522967000
B	1.443273000	-1.050879000	0.628319000
H	-3.142044000	-1.935057000	1.118682000
H	-1.654538000	-1.542615000	-0.822809000
H	0.187530000	-1.523969000	3.743557000
H	-2.254725000	-1.871187000	3.370271000
H	1.431196000	2.001637000	2.053827000
H	3.853422000	2.565696000	2.180267000
H	4.382135000	1.865059000	-1.831556000
H	1.982395000	1.285097000	-2.141544000
H	-3.576376000	-0.520676000	-2.526333000
H	-5.978112000	-1.164602000	-2.635197000
H	-6.690984000	0.254528000	1.150351000
H	-4.315311000	0.948975000	1.439384000
C	2.785189000	-1.402181000	0.001847000
C	2.867957000	-1.769346000	-1.350860000
C	3.970118000	-1.255243000	0.736718000
C	4.099457000	-1.990814000	-1.949390000
C	5.205689000	-1.454047000	0.133227000
C	5.268006000	-1.824109000	-1.207037000
H	1.956216000	-1.862625000	-1.932225000
H	3.916055000	-0.957347000	1.778348000
H	4.156012000	-2.277276000	-2.992775000
H	6.117594000	-1.314441000	0.700802000
H	6.231760000	-1.979608000	-1.678206000

Product Diels-Alder 1′ + 4,4′-bptz at bond b

48

symmetry c1

C	1.972716000	0.048748000	2.107053000
C	1.352444000	0.455058000	0.788782000
C	-0.078399000	-0.040386000	0.657847000
C	-0.816181000	-0.344848000	1.926991000
C	-0.197143000	-0.405102000	3.115291000
C	1.266011000	-0.409251000	3.150126000
C	2.145525000	-0.214395000	-0.412852000
N	2.029518000	-1.664416000	-0.218830000
N	0.875514000	-2.091947000	-0.261343000
C	-0.149849000	-1.065445000	-0.524759000
C	3.579174000	0.229730000	-0.496128000
C	-1.502180000	-1.694445000	-0.716968000
N	1.406614000	0.170148000	-1.634053000
N	0.260590000	-0.273401000	-1.698254000
C	-1.874393000	-2.801629000	0.039985000
C	-3.159891000	-3.307281000	-0.112634000
N	-4.066872000	-2.791256000	-0.942484000
C	-3.697221000	-1.734703000	-1.663045000
C	-2.436412000	-1.149444000	-1.591212000
C	3.891962000	1.473813000	-1.036185000
C	5.222232000	1.876838000	-1.053142000
N	6.225951000	1.139118000	-0.579475000
C	5.914694000	-0.051267000	-0.070448000
C	4.617950000	-0.552773000	-0.002724000
B	-1.497103000	0.590689000	1.000728000
H	3.049585000	0.157659000	2.194022000
H	1.477072000	1.532899000	0.632487000
H	-0.741792000	-0.310040000	4.050101000
H	1.774786000	-0.657573000	4.074343000
H	-1.176814000	-3.259902000	0.729319000
H	-3.476649000	-4.170391000	0.464286000
H	-4.445846000	-1.327819000	-2.335626000
H	-2.191410000	-0.291174000	-2.202832000
H	3.119505000	2.108389000	-1.453101000
H	5.493600000	2.840976000	-1.471473000
H	6.744533000	-0.642048000	0.304771000
H	4.423220000	-1.532913000	0.412717000
C	-2.596552000	1.533860000	0.538525000
C	-2.401840000	2.328336000	-0.603270000
C	-3.827658000	1.604755000	1.208974000
C	-3.404228000	3.173851000	-1.058120000
C	-4.834057000	2.445103000	0.752556000

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C       -4.619746000      3.229017000     -0.379032000
H       -1.458238000      2.265030000     -1.136931000
H       -3.990325000      0.987718000      2.085735000
H       -3.246755000      3.783793000     -1.939491000
H       -5.784107000      2.490612000      1.271082000
H       -5.405807000      3.884773000     -0.735631000
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TS Diels-Alder 1′ + 4,4′-bptz at bond c

```
48
symmetry c1
C       -1.830449000     -1.838807000     -0.858719000
C       -1.663601000     -0.431146000     -1.227258000
C       -0.352602000      0.162393000     -1.230912000
C        0.717366000     -0.738466000     -0.865914000
C        0.503349000     -2.024260000     -0.448823000
C       -0.805495000     -2.619791000     -0.446210000
C       -2.639520000      0.555181000      0.278407000
N       -1.844431000      0.185393000      1.358673000
N       -0.670208000      0.639707000      1.363917000
C       -0.321100000      1.450129000      0.281554000
C       -4.020135000      0.009220000      0.255672000
C        1.065425000      1.990375000      0.297256000
N       -2.486915000      1.853747000     -0.187572000
N       -1.310488000      2.317441000     -0.176405000
B        1.902910000     -1.524988000     -0.475288000
C        1.463117000      2.938559000     -0.641389000
C        2.780046000      3.382861000     -0.615376000
N        3.690007000      2.955782000      0.260831000
C        3.292344000      2.055367000      1.158837000
C        2.002866000      1.537498000      1.219834000
C       -4.394140000     -1.032186000      1.101371000
C       -5.689856000     -1.527697000      1.004290000
N       -6.598813000     -1.069454000      0.144278000
C       -6.228292000     -0.071172000     -0.656762000
C       -4.961234000      0.501512000     -0.644689000
C        3.418141000     -1.628938000     -0.259432000
C        4.010268000     -2.763162000      0.312407000
C        5.382997000     -2.819081000      0.521723000
C        6.183691000     -1.738390000      0.159711000
C        5.614449000     -0.603844000     -0.413542000
C        4.241885000     -0.553529000     -0.621720000
H       -2.832564000     -2.246339000     -0.934378000
H       -2.389110000     -0.046584000     -1.936147000
H       -0.152760000      0.946749000     -1.953151000
H       -0.968934000     -3.658956000     -0.187571000
H        0.760624000      3.332168000     -1.365828000
H        3.119126000      4.120651000     -1.335723000
H        4.046358000      1.713785000      1.860860000
H        1.735539000      0.799351000      1.964382000
H       -3.693318000     -1.437566000      1.819641000
H       -6.011806000     -2.336193000      1.653022000
H       -6.983154000      0.293659000     -1.346052000
H       -4.716840000      1.322133000     -1.307577000
H        3.385559000     -3.603259000      0.596462000
H        5.830500000     -3.699798000      0.966977000
H        7.254086000     -1.780512000      0.325803000
H        6.236323000      0.239337000     -0.690392000
H        3.794650000      0.332238000     -1.061851000
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Product Diels-Alder 1′ + 4,4′-bptz at bond c

```
48
symmetry c1
C       -1.803746000     -1.913172000     -0.756955000
C       -1.722322000     -0.421003000     -1.012617000
C       -0.311795000      0.215702000     -1.013046000
C        0.757322000     -0.774077000     -0.736786000
C        0.562351000     -2.094264000     -0.503307000
C       -0.756918000     -2.712056000     -0.522048000
C       -2.562743000      0.371882000      0.068340000
N       -1.838542000      0.213069000      1.338545000
N       -0.707400000      0.697063000      1.347176000
C       -0.305413000      1.343820000      0.087010000
C       -3.990761000     -0.084715000      0.176710000
C        1.027174000      2.026766000      0.209363000
N       -2.495824000      1.786828000     -0.352208000
N       -1.366895000      2.275763000     -0.336700000
B        1.952753000     -1.579151000     -0.446417000
C        1.412407000      2.979031000     -0.729303000
```

C	2.684588000	3.531315000	-0.630391000
N	3.563012000	3.203719000	0.317480000
C	3.176700000	2.299100000	1.215559000
C	1.930509000	1.679635000	1.207146000
C	-4.396459000	-0.977959000	1.162747000
C	-5.722567000	-1.400333000	1.166775000
N	-6.631955000	-1.003151000	0.278603000
C	-6.230922000	-0.144694000	-0.657995000
C	-4.932238000	0.343072000	-0.754405000
C	3.470815000	-1.675083000	-0.232828000
C	4.090613000	-2.856113000	0.196179000
C	5.464236000	-2.904275000	0.402394000
C	6.238904000	-1.768381000	0.180063000
C	5.642086000	-0.586250000	-0.250557000
C	4.268397000	-0.543347000	-0.455586000
H	-2.806210000	-2.328282000	-0.791219000
H	-2.230749000	-0.218647000	-1.959513000
H	-0.111124000	0.729656000	-1.955706000
H	-0.893678000	-3.774686000	-0.364242000
H	0.735326000	3.295485000	-1.513521000
H	3.012185000	4.274974000	-1.350010000
H	3.904185000	2.040412000	1.978472000
H	1.675845000	0.942328000	1.956692000
H	-3.700317000	-1.329431000	1.912960000
H	-6.067945000	-2.094849000	1.926094000
H	-6.986099000	0.174417000	-1.369317000
H	-4.668286000	1.055484000	-1.526263000
H	3.487234000	-3.740512000	0.370842000
H	5.932654000	-3.822622000	0.736270000
H	7.309992000	-1.805102000	0.342798000
H	6.244052000	0.298362000	-0.422612000
H	3.801098000	0.378107000	-0.788700000

TS Diels-Alder 1′ + 4,4′-bptz at bond d

48

symmetry c1

N	-1.193060000	0.626199000	1.296110000
N	-1.193239000	-0.625941000	1.296127000
C	-1.951213000	-1.237020000	0.280102000
C	-0.989835000	-0.738075000	-1.302962000
C	-0.989645000	0.738307000	-1.302969000
C	-1.950864000	1.237472000	0.280064000
C	0.278846000	-1.447616000	-1.202895000
C	1.372414000	-0.725743000	-0.868552000
C	1.372609000	0.725357000	-0.868583000
C	0.279231000	1.447511000	-1.202938000
B	2.665009000	-0.000360000	-0.624173000
C	4.143188000	-0.000512000	-0.250282000
C	4.838191000	1.206788000	-0.078365000
C	6.186069000	1.208519000	0.254313000
C	6.857613000	-0.000749000	0.420033000
C	6.185837000	-1.209899000	0.254388000
C	4.837960000	-1.207934000	-0.078291000
C	-1.975931000	2.726805000	0.311616000
C	-1.976703000	-2.726342000	0.311638000
C	-2.928891000	3.433622000	-0.415633000
C	-2.880589000	4.823491000	-0.394792000
N	-1.971366000	5.523942000	0.281535000
C	-1.067324000	4.833829000	0.976421000
C	-1.020194000	3.444925000	1.024835000
C	-1.021186000	-3.444753000	1.024855000
C	-1.068719000	-4.833641000	0.976408000
N	-1.972948000	-5.523476000	0.281488000
C	-2.881955000	-4.822748000	-0.394840000
C	-2.929855000	-3.432864000	-0.415648000
N	-3.184970000	0.630390000	0.019977000
N	-3.185141000	-0.629595000	0.019998000
H	-1.720698000	-1.198793000	-1.961230000
H	-1.720399000	1.199190000	-1.961237000
H	0.291886000	-2.513824000	-1.402084000
H	0.292555000	2.513708000	-1.402166000
H	4.308693000	2.144332000	-0.208671000
H	6.715188000	2.144792000	0.385096000
H	7.910027000	-0.000843000	0.679884000
H	6.714779000	-2.146264000	0.385231000
H	4.308285000	-2.145387000	-0.208539000
H	-3.699986000	2.913844000	-0.970247000
H	-3.612656000	5.401017000	-0.950444000

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H       -0.337937000      5.420894000      1.525569000
H       -0.264360000      2.932054000      1.605354000
H       -0.265218000     -2.932108000      1.605401000
H       -0.339514000     -5.420932000      1.525557000
H       -3.614179000     -5.400050000     -0.950519000
H       -3.700785000     -2.912844000     -0.970267000
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Product Diels-Alder 1′ + 4,4′-bptz at bond d

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48
symmetry c1
N        1.240937000     -0.615166000      1.285794000
N        1.241110000      0.614952000      1.285794000
C        1.867476000      1.225464000      0.104046000
C        0.984781000      0.775955000     -1.142267000
C        0.984596000     -0.776116000     -1.142279000
C        1.867146000     -1.225854000      0.104053000
C       -0.362258000      1.464354000     -1.092532000
C       -1.453251000      0.741404000     -0.850007000
C       -1.453436000     -0.741076000     -0.850056000
C       -0.362580000     -1.464223000     -1.092599000
B       -2.751353000      0.000326000     -0.663823000
C       -4.223252000      0.000459000     -0.272723000
C       -4.916413000     -1.207487000     -0.095054000
C       -6.261291000     -1.209046000      0.248723000
C       -6.930961000      0.000685000      0.419879000
C       -6.261059000      1.210306000      0.248832000
C       -4.916182000      1.208523000     -0.094944000
C        1.977351000     -2.718634000      0.237990000
C        1.978074000      2.718217000      0.237970000
C        2.906834000     -3.424519000     -0.519113000
C        2.935803000     -4.810901000     -0.410849000
N        2.122135000     -5.509508000      0.379276000
C        1.239609000     -4.820837000      1.101484000
C        1.121998000     -3.434879000      1.068886000
C        1.122865000      3.434695000      1.068817000
C        1.240843000      4.820622000      1.101413000
N        2.123591000      5.509054000      0.379249000
C        2.937115000      4.810225000     -0.410828000
C        2.907783000      3.423850000     -0.519088000
N        3.185763000     -0.616304000     -0.116648000
N        3.185930000      0.615553000     -0.116657000
H        1.538176000      1.154906000     -2.005564000
H        1.537939000     -1.155180000     -2.005556000
H       -0.371560000      2.532059000     -1.290343000
H       -0.372089000     -2.531915000     -1.290461000
H       -4.387144000     -2.144463000     -0.230171000
H       -6.789780000     -2.145019000      0.383917000
H       -7.981287000      0.000774000      0.688157000
H       -6.789371000      2.146366000      0.384112000
H       -4.386736000      2.145412000     -0.229973000
H        3.606122000     -2.908061000     -1.164712000
H        3.652743000     -5.386447000     -0.987890000
H        0.587928000     -5.405539000      1.743122000
H        0.387410000     -2.925660000      1.678939000
H        0.388110000      2.925677000      1.678838000
H        0.589283000      5.405501000      1.743013000
H        3.654241000      5.385576000     -0.987833000
H        3.606969000      2.907203000     -1.164646000
```

TS Diels-Alder 1′ + 4,4′-bptz at bond C-B

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48
symmetry c1
C       -2.429760000      2.798967000     -0.709180000
C       -1.756761000      2.999560000     -1.930915000
C       -0.678258000      2.212018000     -2.295252000
C       -0.298262000      1.200047000     -1.420556000
C       -1.048720000      0.883495000     -0.240138000
C       -2.108687000      1.747336000      0.122032000
B        0.543008000      0.684061000     -0.313138000
N       -1.380278000     -1.612408000     -1.038432000
C       -1.749377000     -1.007350000      0.159916000
N       -0.137080000     -1.762208000     -1.205456000
C        0.687780000     -1.354757000     -0.172649000
N        0.212416000     -1.535858000      1.118413000
N       -1.028713000     -1.379921000      1.291657000
C        2.146387000     -1.551199000     -0.393286000
C        3.031344000     -1.651013000      0.676134000
C        4.389942000     -1.739089000      0.399491000
```

N	4.901250000	-1.737135000	-0.832280000
C	4.040079000	-1.656877000	-1.845516000
C	2.662319000	-1.560100000	-1.685498000
C	-3.217691000	-0.857890000	0.351347000
C	-4.052879000	-0.685615000	-0.749164000
C	-5.414783000	-0.533427000	-0.525531000
N	-5.973201000	-0.540282000	0.686418000
C	-5.163324000	-0.714653000	1.728539000
C	-3.784736000	-0.877632000	1.621292000
C	1.784434000	1.227590000	0.452487000
C	2.928900000	1.643722000	-0.236069000
C	4.063404000	2.057848000	0.452130000
C	4.061098000	2.078163000	1.844299000
C	2.921783000	1.690159000	2.544193000
C	1.794720000	1.261651000	1.851434000
H	-3.230863000	3.473259000	-0.430824000
H	-2.056901000	3.825860000	-2.565593000
H	-0.113494000	2.424057000	-3.195745000
H	-2.708223000	1.561385000	1.006183000
H	2.671425000	-1.636973000	1.696190000
H	5.104879000	-1.805872000	1.213329000
H	4.471827000	-1.663746000	-2.841606000
H	2.005717000	-1.485467000	-2.543165000
H	-3.645911000	-0.669019000	-1.752535000
H	-6.092501000	-0.396602000	-1.362054000
H	-5.636516000	-0.725172000	2.705357000
H	-3.169555000	-1.023694000	2.499287000
H	2.938182000	1.615459000	-1.321142000
H	4.950624000	2.356213000	-0.093822000
H	4.946228000	2.396130000	2.382917000
H	2.916999000	1.711300000	3.627825000
H	0.918566000	0.931540000	2.401614000

Product Diels-Alder 1’ + 4,4’-bptz at bond C-B

48

symmetry c1

C	-2.477032000	3.341560000	0.750442000
C	-1.177753000	3.812072000	0.894818000
C	-0.116751000	2.938909000	0.708447000
C	-0.317428000	1.584893000	0.386537000
C	-1.648227000	1.122797000	0.267538000
C	-2.712477000	2.006457000	0.440989000
B	0.917170000	0.667759000	0.208228000
N	-1.228222000	-0.809064000	-1.249874000
C	-1.931137000	-0.343193000	-0.013393000
N	-0.038448000	-1.064567000	-1.188947000
C	0.662080000	-0.919114000	0.133462000
N	-0.233002000	-1.382377000	1.210487000
N	-1.427432000	-1.142093000	1.148844000
C	1.898647000	-1.787122000	0.105698000
C	2.320839000	-2.499672000	1.223550000
C	3.513779000	-3.213492000	1.145620000
N	4.282424000	-3.264251000	0.060056000
C	3.859051000	-2.588507000	-1.008713000
C	2.688461000	-1.841544000	-1.039333000
C	-3.401554000	-0.664335000	-0.194732000
C	-4.001579000	-0.544216000	-1.444497000
C	-5.364594000	-0.797331000	-1.554938000
N	-6.139653000	-1.151348000	-0.530452000
C	-5.552506000	-1.266181000	0.659202000
C	-4.198324000	-1.035280000	0.883292000
C	2.339911000	1.252363000	-0.031509000
C	2.508216000	2.241191000	-1.015088000
C	3.764411000	2.760818000	-1.307505000
C	4.875852000	2.330664000	-0.590536000
C	4.729283000	1.369472000	0.405979000
C	3.479596000	0.822826000	0.667181000
H	-3.318425000	4.011365000	0.884148000
H	-0.994638000	4.848874000	1.149268000
H	0.897750000	3.301311000	0.825688000
H	-3.732988000	1.662315000	0.340832000
H	1.739230000	-2.500884000	2.135428000
H	3.865364000	-3.773259000	2.006980000
H	4.492185000	-2.640478000	-1.888800000
H	2.404017000	-1.305427000	-1.935906000
H	-3.421442000	-0.267236000	-2.314732000
H	-5.856223000	-0.711009000	-2.518815000
H	-6.195583000	-1.558243000	1.483508000

H	-3.777293000	-1.146924000	1.873132000
H	1.645025000	2.595973000	-1.569400000
H	3.873904000	3.505995000	-2.086532000
H	5.854748000	2.741919000	-0.807716000
H	5.592461000	1.033223000	0.967890000
H	3.391803000	0.055387000	1.428028000

8. References

1. R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, **73**, 1795-1818.
2. M. Sindlinger, M. Ströbele, C. Maichle-Mössmer and H. F. Bettinger, *Chem. Commun.*, 2022, **58**, 2818-2821.
3. G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, 1997.
4. G. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
6. S. Grimme, A. Hansen, S. Ehlert and J.-M. Mewes, *J. Chem. Phys.*, 2021, **154**, 064103.
7. J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew and J. Sun, *J. Phys. Chem. Lett.*, 2020, **11**, 8208-8215.
8. C. Bannwarth, S. Ehlert and S. Grimme, *J. Chem. Theory Comput.*, 2019, **15**, 1652-1671.
9. V. Ásgeirsson, B. O. Birgisson, R. Bjornsson, U. Becker, F. Neese, C. Riplinger and H. Jónsson, *J. Chem. Theory Comput.*, 2021, **17**, 4929-4945.
10. F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73-78.
11. F. Neese, *WIREs Comput. Mol. Sci.*, 2018, **8**, e1327.
12. Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
13. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.
14. 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, Williams, 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 16 Rev. C.01, Wallingford, CT, 2016.
15. G. Santra, N. Sylvetsky and J. M. L. Martin, *J. Phys. Chem. A*, 2019, **123**, 5129-5143.
16. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
17. C. Hättig, *Phys. Chem. Chem. Phys.*, 2005, **7**, 59.
18. F. Weigend, *J. Comput. Chem.*, 2008, **29**, 167-175.
19. V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001.
20. S. Grimme, *Chem. Eur. J.*, 2012, **18**, 9955-9964.
21. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.