Supporting Information for:

Acceleration of Thermal Back-Reaction and Finding of Non-Photochromic Isomer for Negative Photochromic Binaphthyl-Bridged Imidazole Dimer

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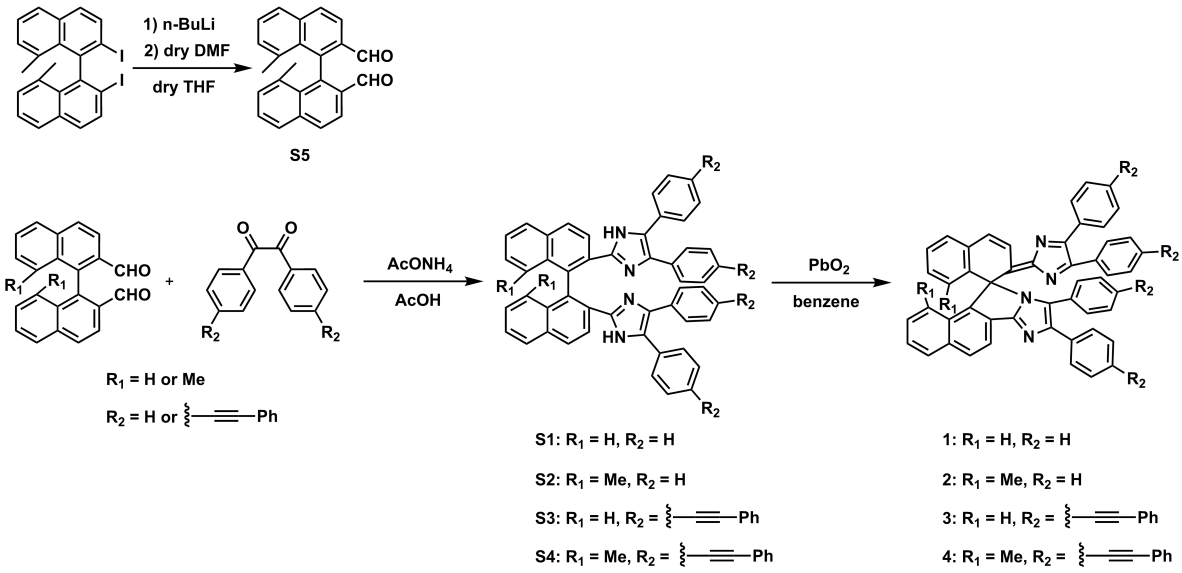
1. Syntheses

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Silica gel 60N, Kanto Chemical). ^{1}H NMR spectra were recorded at 400 MHz on a Bruker AVANCE III 400 NanoBay. $CDCl_3$, THF-d_8 and DMSO-d_6 were used as deuterated solvents. ESI-TOF-MS and APCI-TOF-MS spectra were recorded on a Bruker micrOTOF II-AGA1. All glassware was washed with distilled water and dried. Unless otherwise noted, all reagents and reaction solvents were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Co., Inc. and Kanto Chemical Co., Inc. and were used without further purification.

Scheme S1 Synthetic Scheme of **1**, **2**, **3**, and **4**.



2,2'-diiodo-8,8'-dimethyl-1,1'-binaphthalene was synthesized according to the literature.[S1]

[1,1'-binaphthalene]-2,2'-dicarbaldehyde was synthesized according to the literature.[S2]

1,2-bis(4-(phenylethynyl)phenyl)ethane-1,2-dione was synthesized according to the literature.[S3]

8,8'-Dimethyl-[1,1'-binaphthalene]-2,2'-dicarbaldehyde (S5)

A solution of 2,2'-diiodo-8,8'-dimethyl-1,1'-binaphthalene (80 mg, 0.15 mmol) in dry THF (4 mL) was cooled to −78 ºC. The solution was dropwise added n-BuLi (1.59 M, 0.288 mL, 0.456 mmol) at −78 ºC and stirred for 5 min. The mixture was added dropwise dry DMF (0.060 mL, 0.78 mmol) and the solution was stirred at 0 ºC for 3 h. The mixture was quenched with sat. NH_4Cl aq. at 0 ºC, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, and passed through a phase separator paper. The residue was separated by PTLC (hexane:CH_2Cl_2 = 1:2) to give the desired product as a white solid (30 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.29 (s, 2H), 8.08 (s, 4H), 7.88 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 1.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.4, 142.3, 137.5, 136.9, 134.7, 132.9, 132.1, 131.1, 129.2, 128.3, 121.6, 24.4. HRMS (APCI-TOF): calculated for $C_{24}H_{18}O_2$ $[M+H]^+$: 339.1380, found: 339.1366.

Compound S1

A solution of [1,1'-binaphthalene]-2,2'-dicarbaldehyde (32 mg, 0.10 mmol), benzil (50 mg, 0.24 mmol), ammonium acetate (240 mg, 3.1 mmol) in AcOH (5 mL) was stirred at 110 °C for 21 h. The mixture was neutralized with NH_3 aq. at 0 °C, and extracted with AcOEt. The organic layer was washed with water and brine, and passed through a phase separator paper. The residue was separated by silica gel column chromatography (hexane:AcOEt = 3:2) to give the desired product as a pale yellow solid (55 mg, 77%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 14.0 (s, 2H), 8.19 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.30–7.13 (m, 22H), 6.93(d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6, 133.6, 132.7, 132.0, 129.3, 128.4, 128.3, 128.2, 128.0, 127.4, 127.3, 127.0, 126.1. HRMS (ESI-TOF): calculated for $C_{50}H_{34}N_4$ $[M+H]^+$: 691.2856, found: 691.2869.

Compound 1

A solution of $K_3[Fe(CN)_6]$ (1300 mg, 4.0 mmol) and KOH (450 mg, 8.0 mmol) in water (20 mL) was degassed by N_2 bubbling and was added to a solution of **S1** (55 mg, 0.080 mmol) in benzene (40 mL) degassed by N_2 bubbling. The mixture was stirred for 8 h at room temperature in the dark, and extracted with AcOEt. The organic layer was washed with water and brine, and passed through a phase separator paper. After the removal of the solvents, the crude mixture was purified by recrystallization from AcOEt/hexane to give the desired product as a red crystal (30 mg, 55%). H NMR (400 MHz, THF-d_8) δ: 8.12 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 10.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.64-7.62 (m, 2H), 7.51–7.47 (m, 5H), 7.38–7.24 (m, 9H), 7.22–7.08 (m, 5H), 7.05 (d, J = 8.4 Hz, 1H), 7.02–6.95 (m, 4H), 6.56–6.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0, 164.9, 162.4, 153.6, 151.9, 142.0, 140.1, 137.2, 135.2, 133.9, 133.7, 133.6, 132.2, 131.5, 130.6, 130.4, 130.13, 130.11, 130.00, 129.96, 129.9, 129.24, 129.21, 128.7, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 127.3, 127.0, 126.7, 126.12, 126.10, 125.6, 122.5, 118.3, 66.4. HRMS (ESI-TOF): calculated for $C_{50}H_{32}N_4$ $[M+H]^+$: 689.2700, found: 689.2727.

Compound S2

A solution of 8,8'-dimethyl-[1,1'-binaphthalene]-2,2'-dicarbaldehyde (10 mg, 0.030 mmol), benzil (25 mg, 0.120 mmol), ammonium acetate (45 mg, 0.58 mmol) in AcOH (1 mL) was stirred at 110 °C for 27 h. The mixture was neutralized with NH_3 aq. at 0 °C, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, and passed through a phase separator paper. The residue was separated by PTLC (hexane:AcOEt = 3:1) to give the desired product as a pale yellow solid (13 mg, 61%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.9 (s, 2H), 8.06 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.30–7.20 (m, 8H), 7.12–7.08 (m, 14H), 1.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 137.3, 136.3, 135.4, 134.6, 134.5, 132.7, 132.2, 130.6, 130.2, 129.8, 128.5, 128.2, 128.1, 127.7, 127.5, 127.2, 126.9, 126.8, 24.6. HRMS (APCI-TOF): calculated for $C_{52}H_{38}N_4$ $[M+H]^+$: 719.3169, found: 719.3167.

Compound 2

A solution of **S2** (10 mg, 0.014 mmol), PbO_2 (50 mg) in benzene (0.5 mL) was stirred at r.t. for 2 h. The mixture was filtered with celite and the solvent was removed by evaporation. The red solid was further purified by recrystallization from CH_2Cl_2/hexane to give the desired product as a red crystal (5 mg, 50%). ^{1}H NMR (400 MHz, THF-d_8) δ: 8.17 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 9.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.55–7.53 (m, 2H), 7.49–7.47 (m, 2H), 7.39–7.36 (m, 3H), 7.33–7.18 (m, 7H), 7.13–7.07 (m, 3H), 7.02–6.91 (m, 6H), 6.60–6.54 (m, 3H), 2.25 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.7, 164.0, 161.9, 152.9, 147.6, 142.2, 142.1, 138.4, 135.7, 135.4, 135.1, 135.0, 134.5, 134.2, 133.7, 133.6, 132.4, 131.6, 130.2, 130.15, 130.05,

129.92, 129.89, 129.3, 128.68, 128.65, 128.56, 128.24, 128.17, 128.0, 127.8, 126.7, 126.5, 126.3, 126.0, 124.7, 118.0, 69.6, 22.1, 21.4. HRMS (ESI-TOF): calculated for $C_{52}H_{36}N_4$ $[M+H]^+$: 717.3013, found: 717.2998.

Compound S3

A solution of [1,1'-binaphthalene]-2,2'-dicarbaldehyde (15 mg, 0.048 mmol), 1,2-bis(4-(phenylethynyl)phenyl)ethane-1,2-dione (55 mg, 0.13 mmol), ammonium acetate (58 mg, 0.75 mmol) in AcOH (2 mL) and $CHCl_3$ (0.5 mL) was sealed and stirred at 110 ºC for 18 h. The mixture was neutralized with NH_3 aq. at 0 ºC, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, and passed through a phase separator paper. The residue was separated by PTLC twice (hexane:AcOEt = 3:1, and then hexane:CH_2Cl_2:AcOEt = 20:80:1) to give the desired product as a yellow solid (27 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (br, 2H), 8.72 (d, *J* = 8.0 Hz, 2H), 8.22 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.60–7.49 (m, 14H), 7.43–7.31 (m, 24H), 6.75 (d, *J* = 8.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.2, 134.2, 133.7, 132.7, 132.1, 131.9, 131.64, 131.60, 131.58, 129.7, 129.5, 129.2, 129.0, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6, 127.0, 126.6, 126.1, 123.3, 123.0, 122.6, 121.9, 90.7, 89.9, 89.6, 88.9. HRMS (ESI-TOF): calculated for $C_{82}H_{50}N_4$ $[M+H]^+$: 1091.4108, found: 1091.4108.

Compound 3

A solution of **S3** (13 mg, 0.012 mmol), PbO_2 (120 mg) in benzene (2 mL) was stirred at r.t. for 2 h. The mixture was filtered with celite and the solvent was removed by evaporation. The residue was purified by HPLC (reverse phase, RP-18, eluent: CH_3CN/MeOH = 1/2) to give the desired product as a red solid (4 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 9.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.58–7.51 (m, 12H), 7.49–7.42 (m, 7H), 7.39–7.28 (m, 17H), 7.24–7.20 (m, 3H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 9.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3, 164.0, 162.4, 154.3, 151.9, 141.9, 140.8, 137.1, 134.9, 134.7, 133.9, 132.9, 131.9, 131.8, 131.7, 131.6, 131.6, 131.5, 131.4, 130.3, 129.9, 129.7, 129.3, 129.1, 129.0, 128.6, 128.4, 128.3, 128.01, 127.98, 127.52, 127.47, 127.3, 127.0, 126.5, 126.2, 125.8, 125.5, 125.3, 123.5, 123.1, 123.03, 123.00, 122.9, 122.5, 120.9, 118.2, 130.3, 92.1, 91.7, 90.5, 89.9, 89.5, 89.3, 89.2, 89.0, 66.7. HRMS (ESI-TOF): calculated for $C_{82}H_{48}N_4$ $[M+H]^+$: 1089.3952, found: 1089.3960.

Compound S4

A solution of 8,8'-Dimethyl-[1,1'-binaphthalene]-2,2'-dicarbaldehyde (6.5 mg, 0.019 mmol), 1,2-bis(4-(phenylethynyl)phenyl)ethane-1,2-dione (23 mg, 0.056 mmol), ammonium acetate (20 mg, 0.26 mmol) in AcOH (0.5 mL) and $CHCl_3$ (0.2 mL) was sealed and stirred at 110 ºC for 18 h. The mixture was neutralized with NH_3 aq. at 0 ºC, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, and passed through a phase separator paper. The residue was separated by PTLC twice (hexane:AcOEt = 3:1, and then hexane:CH_2Cl_2:AcOEt = 20:80:1) to give the desired product as a yellow solid (8 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (d, *J* = 8.0 Hz, 2H), 8.17–8.14 (m, 4H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.56–7.48 (m, 14H), 7.43–7.31 (m, 22H), 6.66 (d, *J* = 8.0 Hz, 4H), 2.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.3, 137.2, 136.3, 135.6, 134.7, 134.3, 132.7, 132.4, 131.8, 131.63, 131.57, 130.8, 129.7, 129.6, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 127.4, 127.1, 126.6, 123.3, 123.1, 122.5, 121.8, 90.6, 89.8, 89.6, 89.0, 24.7. HRMS (ESI-TOF): calculated for $C_{84}H_{54}N_4$ $[M+H]^+$: 1119.4421, found: 1119.4434.

Compound 4

A solution of **S4** (8 mg, 0.0071 mmol), PbO_2 (100 mg) in benzene (2 mL) was stirred at r.t. for 2 h. The mixture was filtered with celite and the solvent was removed by evaporation. The residue was purified by HPLC (reverse phase, RP-18, eluent:

CH_3CN/MeOH = 1/2) to give the desired product as a red solid (5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 10.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.60–7.51 (m, 10H), 7.47–7.44 (m, 6H), 7.43–7.34 (m, 9H), 7.32–7.27 (m, 9H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 6.8 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.65–6.60 (m, 3H), 2.25 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.0, 163.1, 161.9, 153.4, 147.6, 142.9, 141.9, 138.5, 136.2, 135.8, 135.3, 135.1, 134.8, 134.4, 133.9, 133.6, 133.0, 132.6, 132.1, 131.71, 131.69, 131.5, 131.4, 131.3, 131.18, 130.2, 130.15, 130.0, 129.8, 129.4, 129.05, 128.98, 128.64, 128.57, 128.56, 128.5, 128.4, 128.41, 128.40, 128.2, 128.0, 126.8, 126.3, 126.2, 125.2, 125.1, 125.0, 123.5, 123.3, 123.04, 123.01, 122.9, 120.7, 117.9, 91.9, 91.6, 90.4, 89.9, 89.4, 89.3, 89.2, 89.0, 69.8, 22.1, 21.4. HRMS (ESI-TOF): calculated for $C_{84}H_{52}N_4$ $[M+H]^+$: 1117.4265, found: 1117.4265.

2. NMR Spectra

^{1}H NMR Spectra

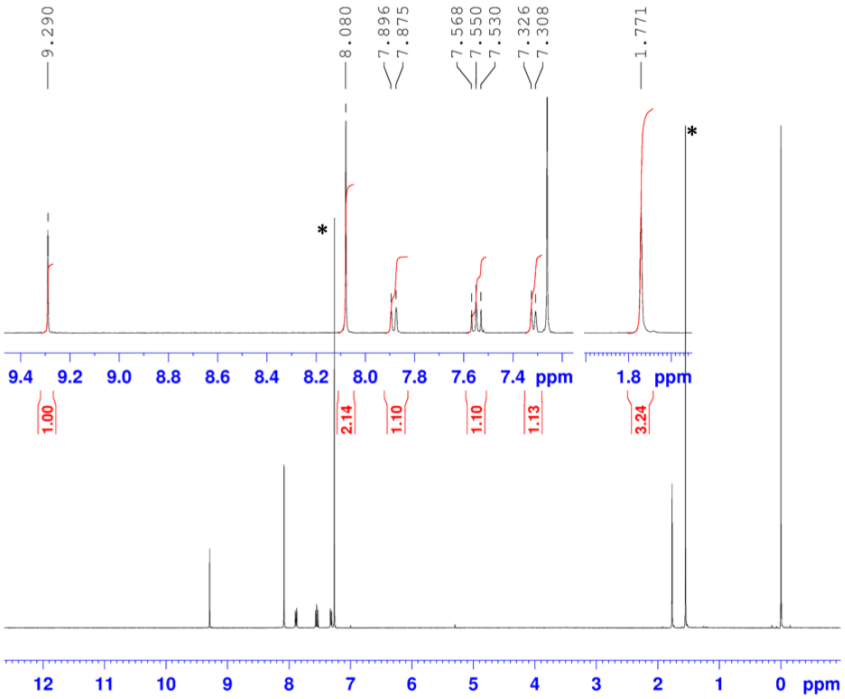


Fig. S1 ^{1}H NMR spectrum of **8,8'-Dimethyl-[1,1'-binaphthalene]-2,2'-dicarbaldehyde (S5)** in $CDCl_3$ (* solvent peaks).

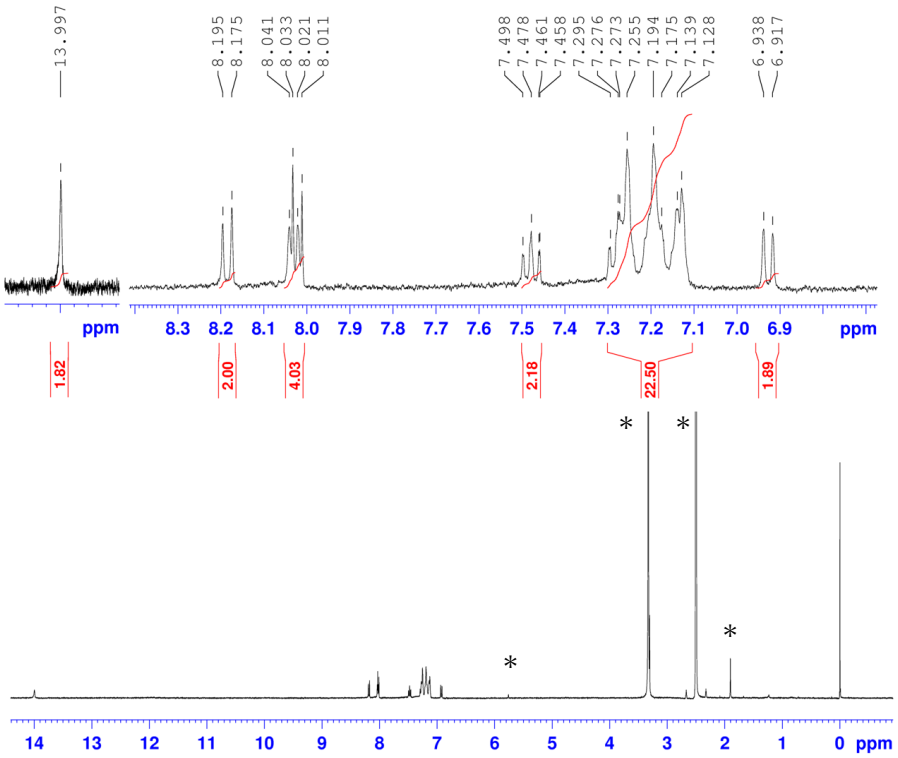


Fig. S2 ^{1}H NMR spectrum of **S1** in DMSO-d_6 (* solvent peaks).

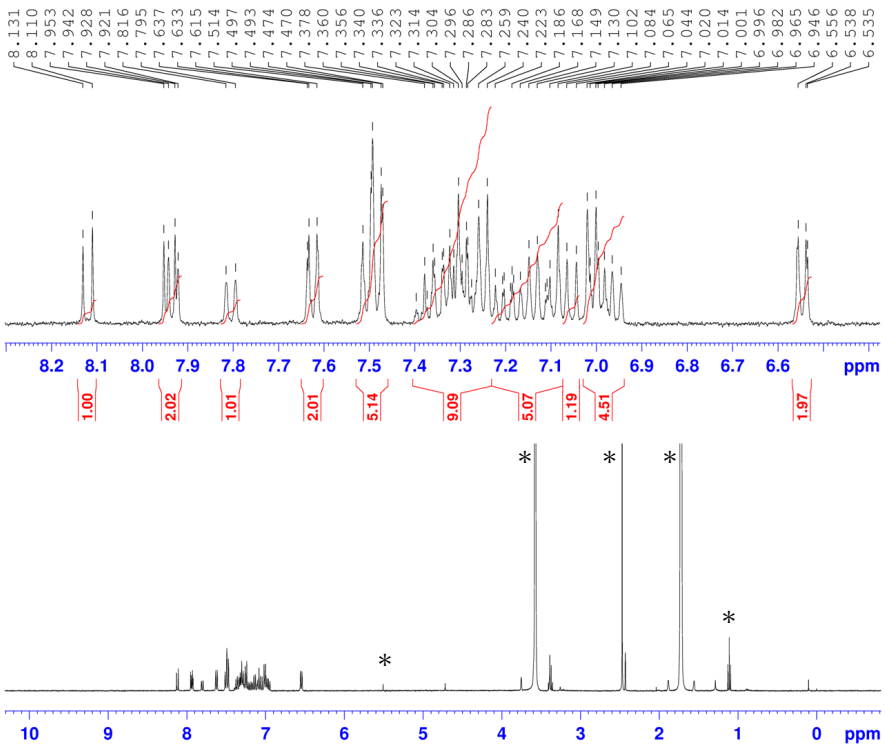


Fig. S3 ^{1}H NMR spectrum of **1** in THF-d_8 (* solvent peaks).

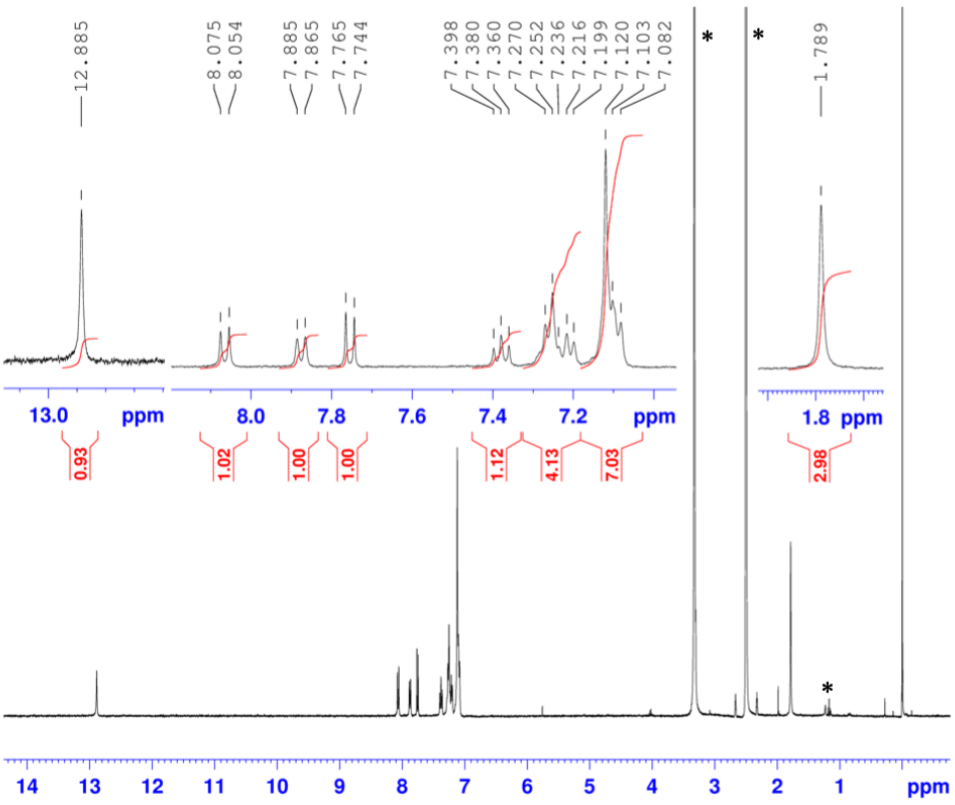


Fig. S4 ^{1}H NMR spectrum of **S2** in $CDCl_3$ (* solvent peaks).

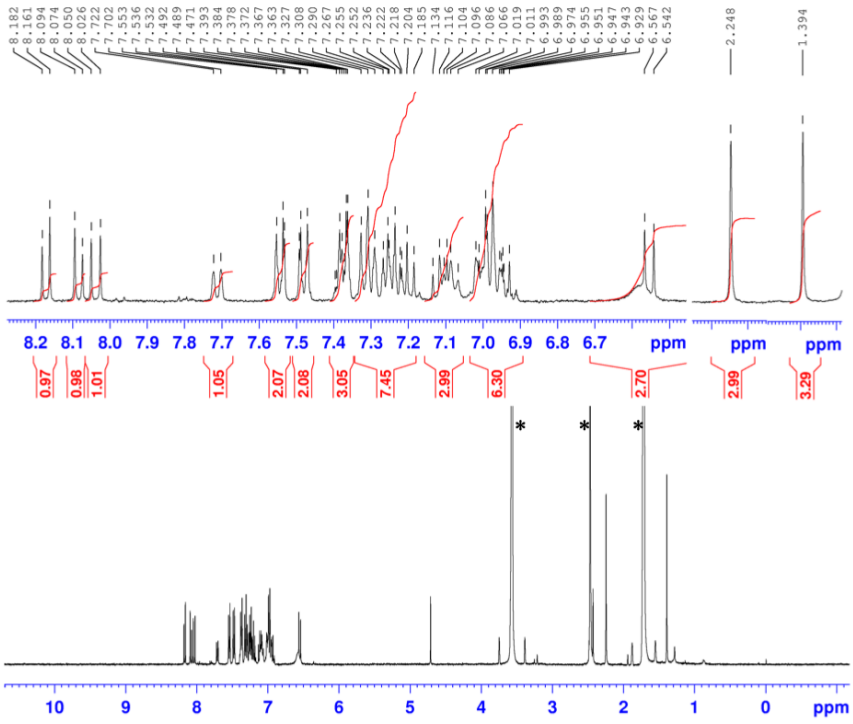


Fig. S5 ^{1}H NMR spectrum of **2** in THF-d_8 (* solvent peaks).

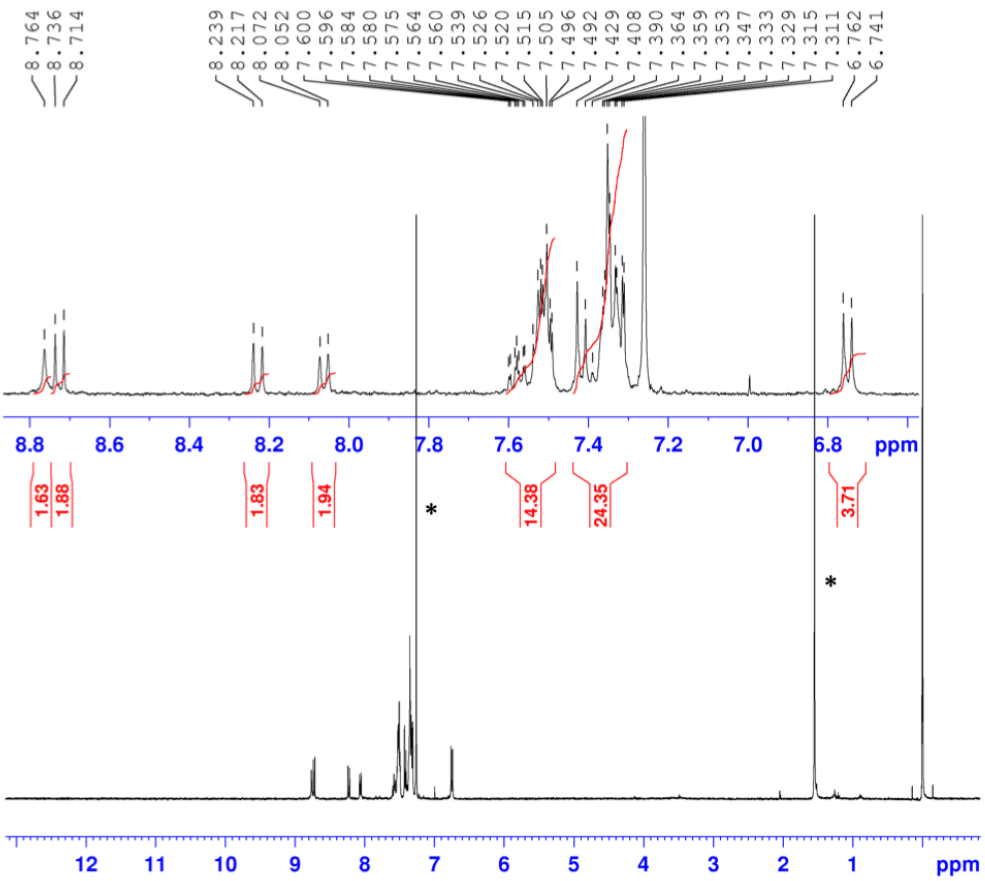


Fig. S6 ^{1}H NMR spectrum of **S3** in $CDCl_3$ (* solvent peaks).

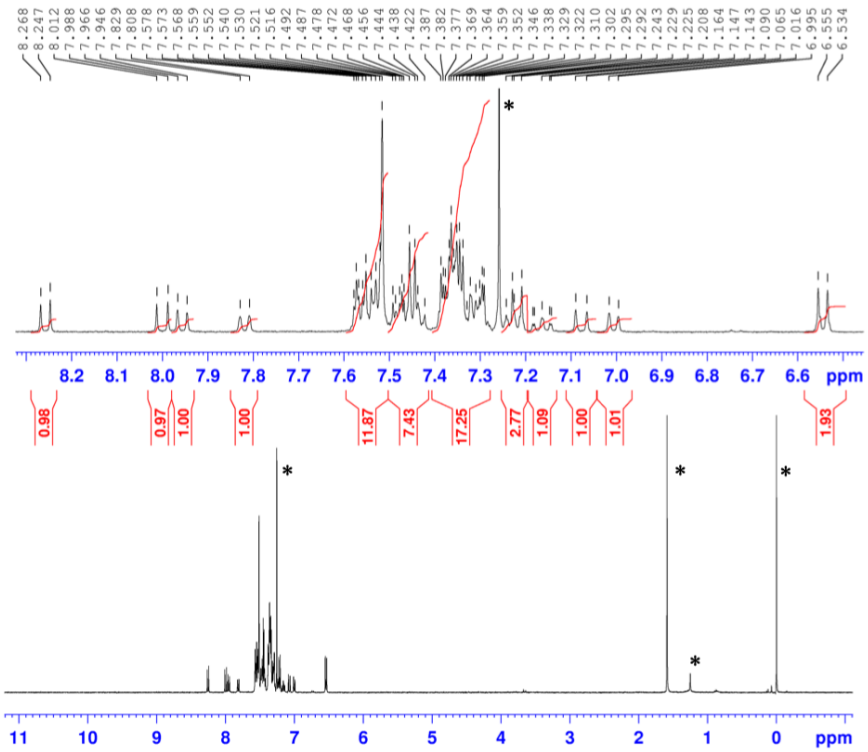


Fig. S7 ^{1}H NMR spectrum of **3** in $CDCl_3$ (* solvent peaks).

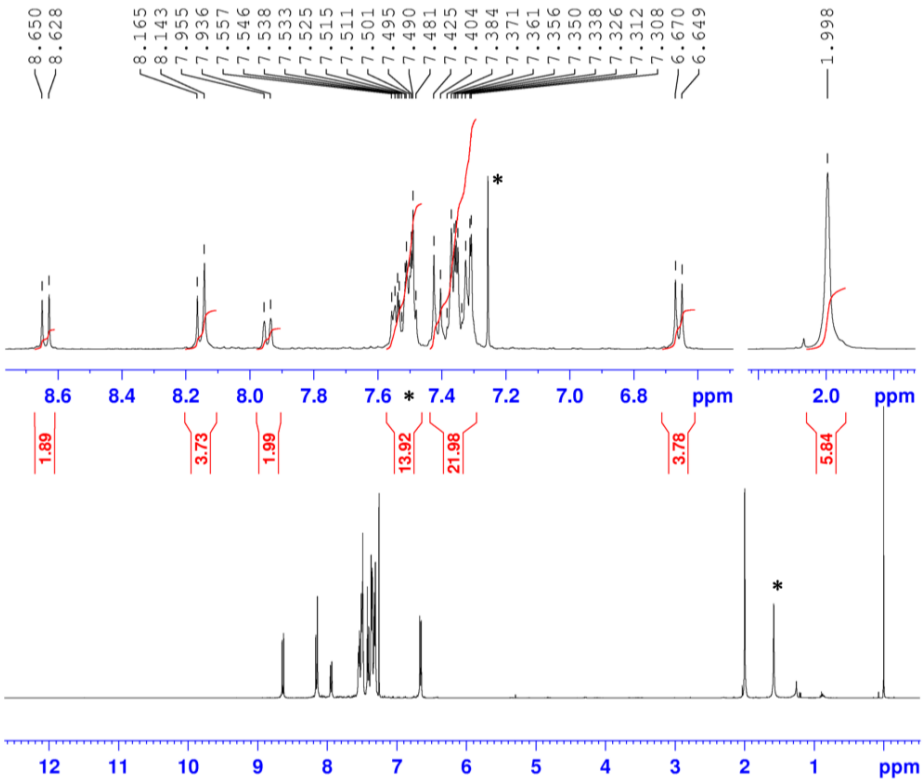


Fig. S8 ^{1}H NMR spectrum of **S4** in $CDCl_3$ (* solvent peaks).

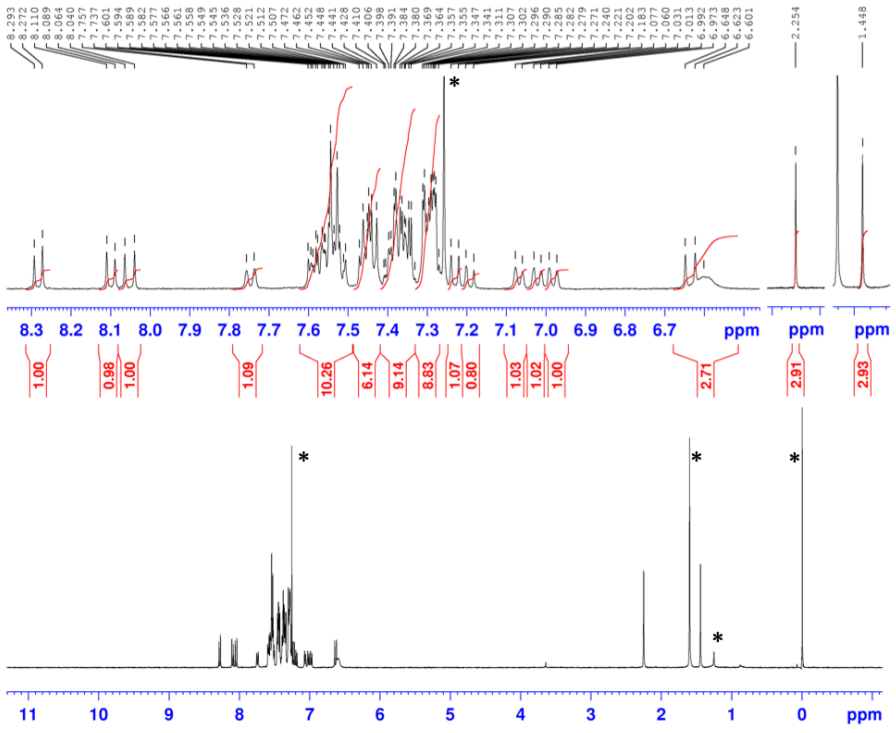


Fig. S9 ^{1}H NMR spectrum of **4** in $CDCl_3$ (* solvent peaks).

^{13}C NMR Spectra

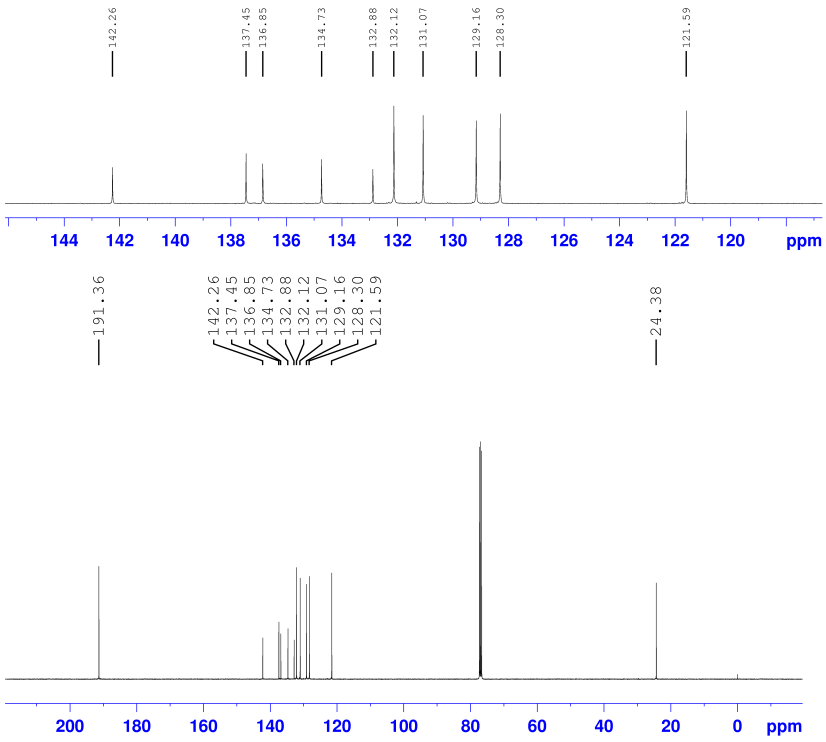


Fig. S10 ^{13}C NMR spectrum of **8,8'-Dimethyl-[1,1'-binaphthalene]-2,2'-dicarbaldehyde (S5)** in $CDCl_3$.

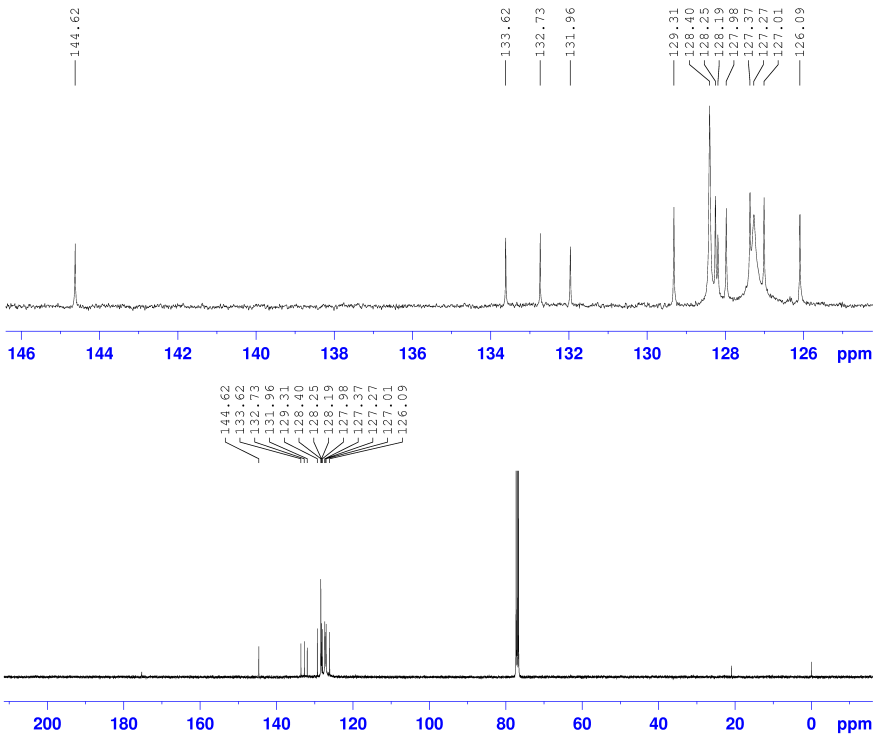


Fig. S11 ^{13}C NMR spectrum of **S1** in $CDCl_3$.

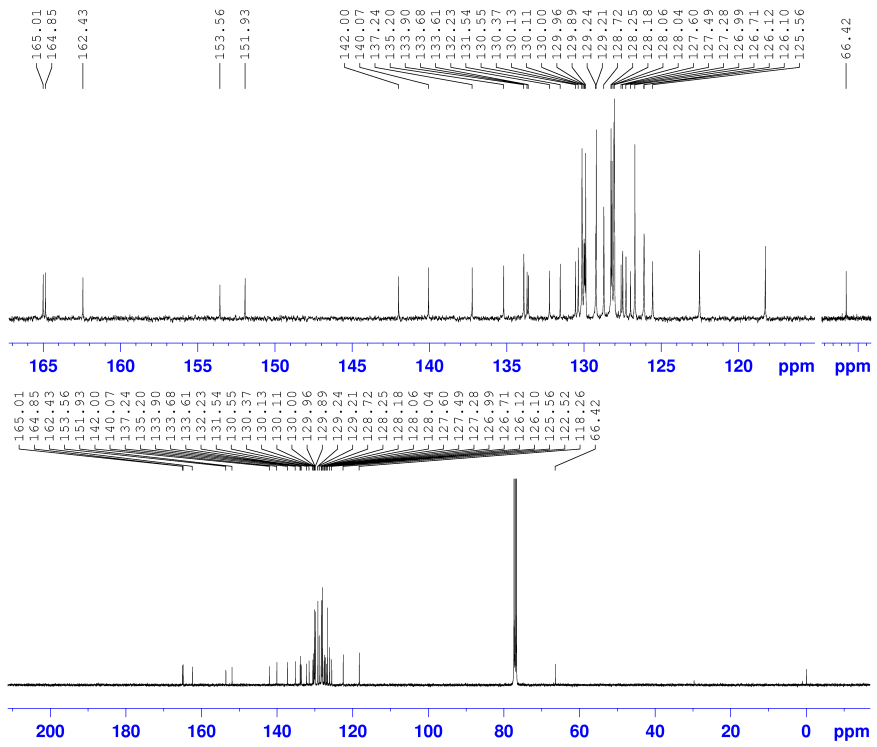


Fig. S12 ^{13}C NMR spectrum of **1** in $CDCl_3$.

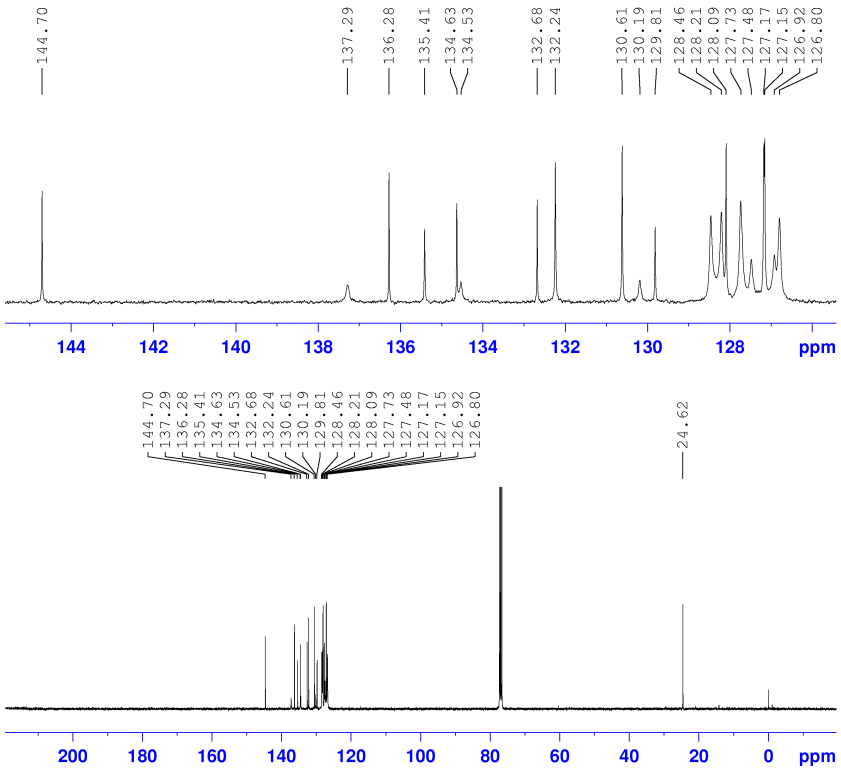


Fig. S13 ^{13}C NMR spectrum of **S2** in $CDCl_3$.

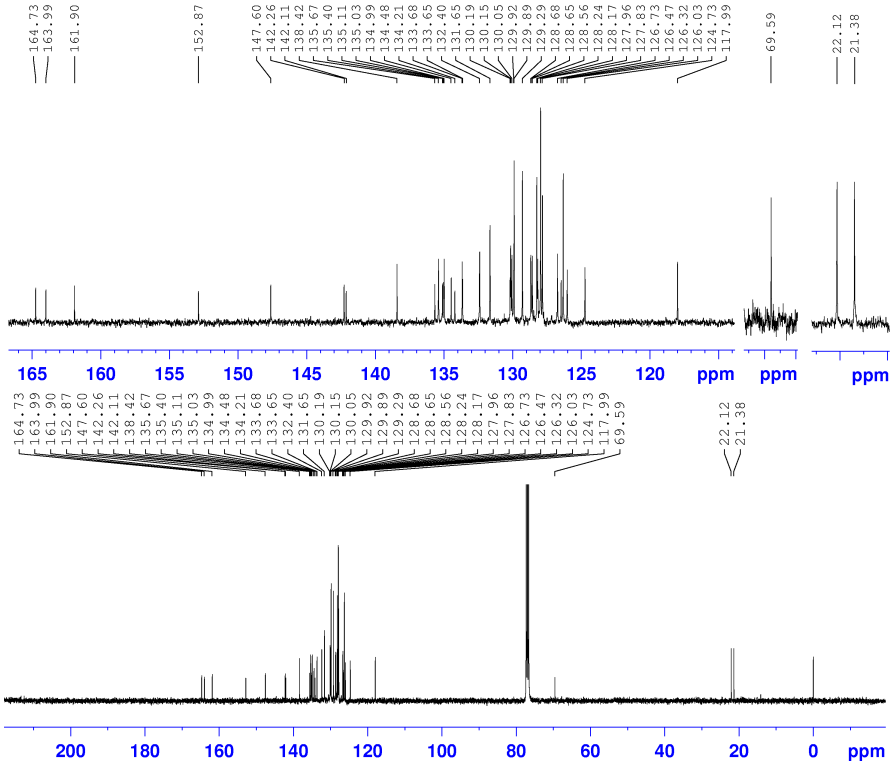


Fig. S14 ^{13}C NMR spectrum of **2** in $CDCl_3$.

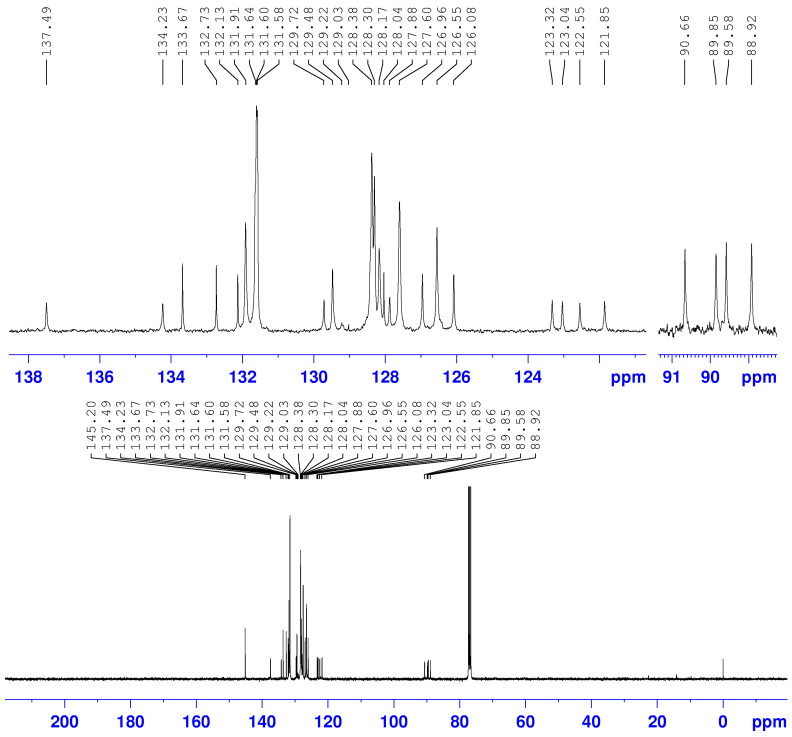


Fig. S15 ^{13}C NMR spectrum of **S3** in $CDCl_3$.

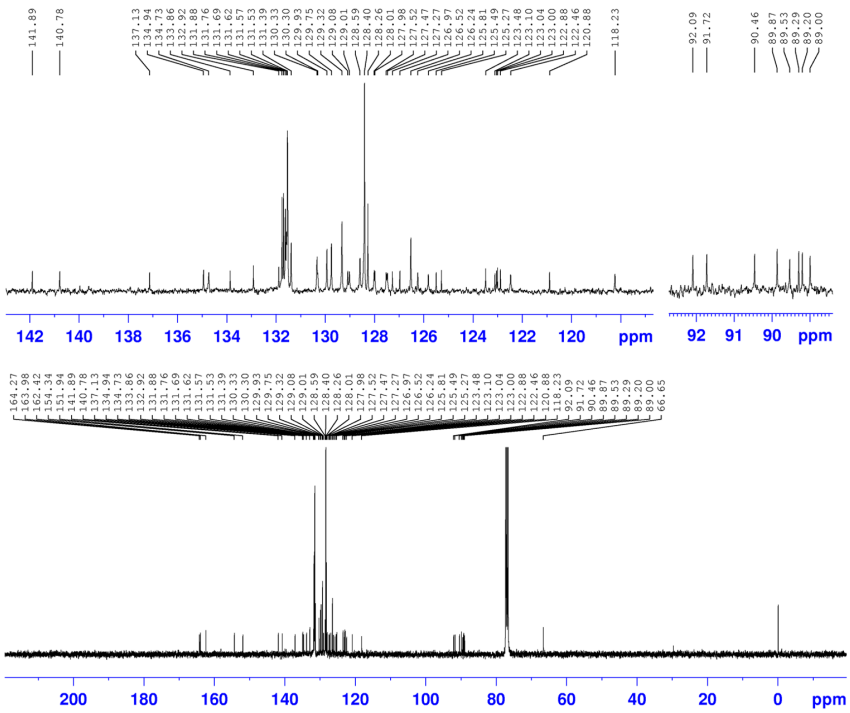


Fig. S16 ^{13}C NMR spectrum of **3** in $CDCl_3$.

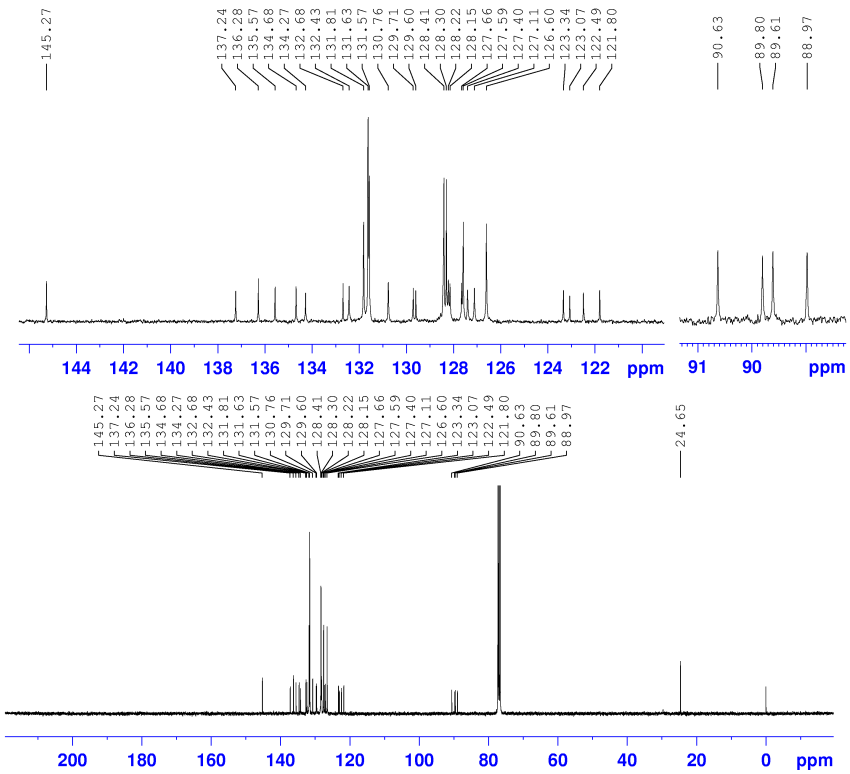


Fig. S17 ^{13}C NMR spectrum of **S4** in $CDCl_3$.

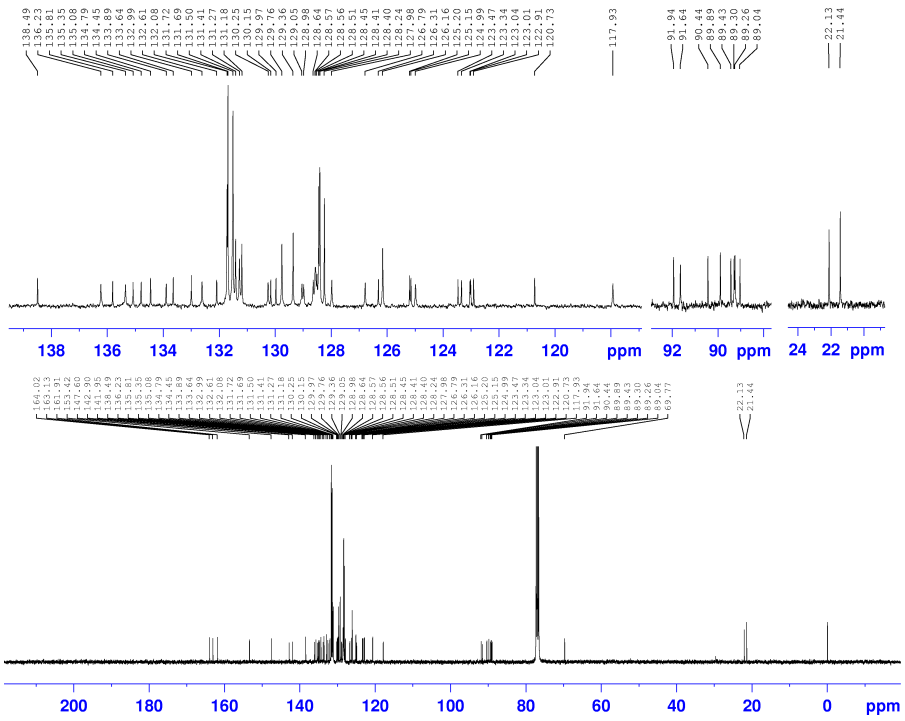


Fig. S18 ^{13}C NMR spectrum of **4** in $CDCl_3$.

3. HR-ESI-TOF MS Spectra

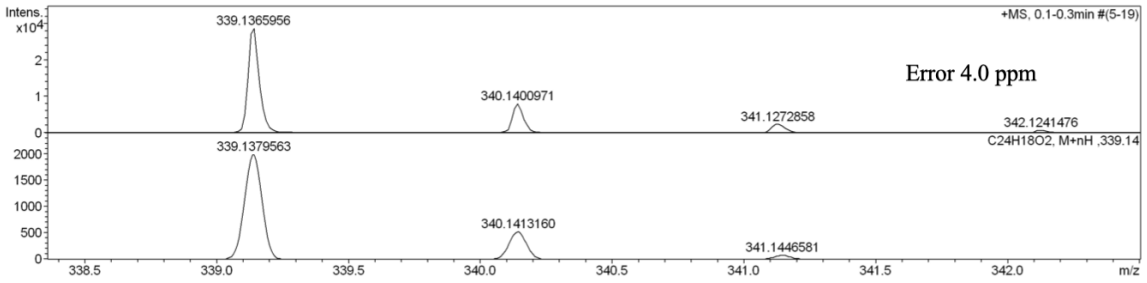


Fig. S19 HR-APCI-TOF MS spectra of **8,8'-dimethyl-[1,1'-binaphthalene]-2,2'-dicarbaldehyde (S5)**.

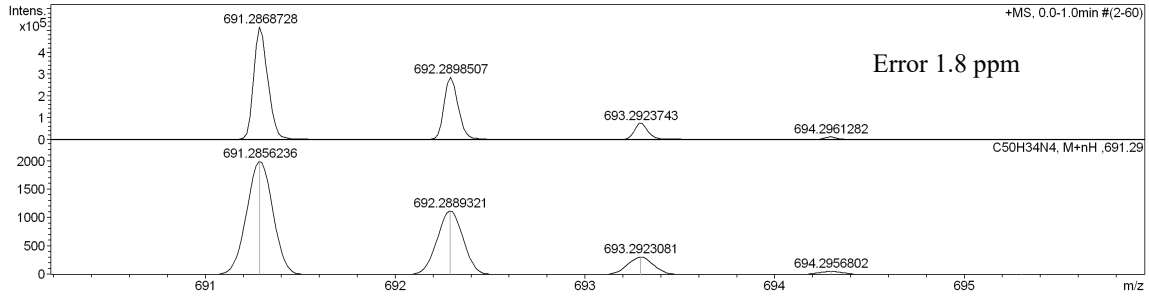


Fig. S20 HR-ESI-TOF MS spectra of **S1**.

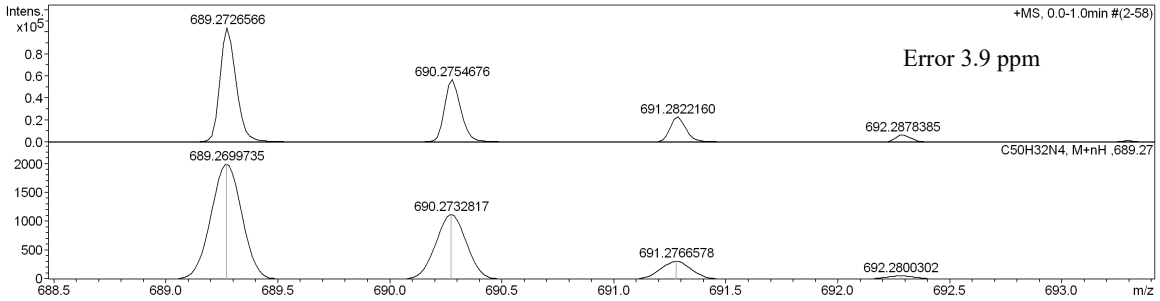


Fig. S21 HR-ESI-TOF MS spectra of **1**.

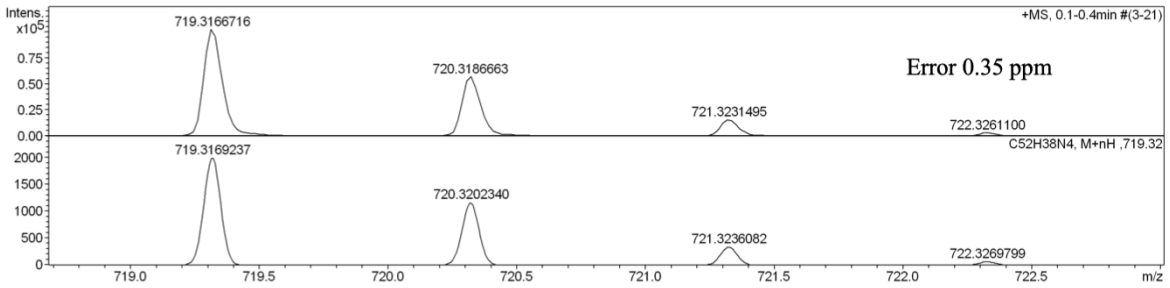


Fig. S22 HR-APCI-TOF MS spectra of **S2**.

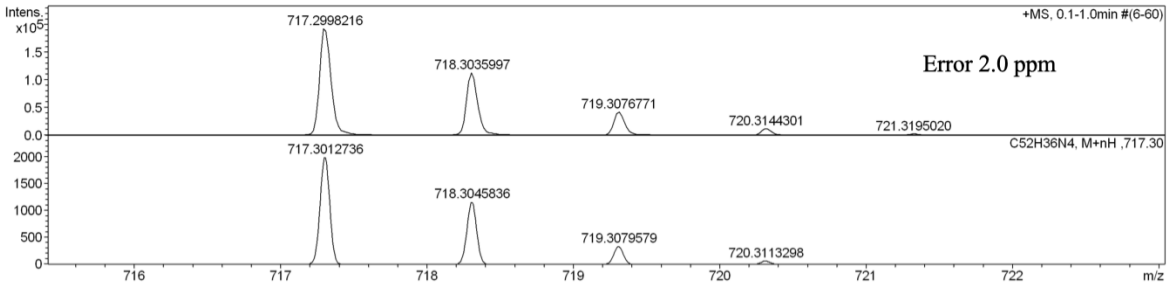


Fig. S23 HR-ESI-TOF MS spectra of **2**.

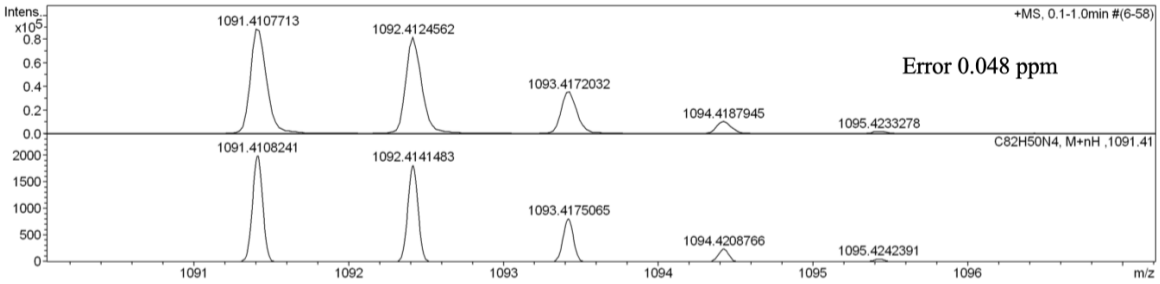


Fig. S24 HR-ESI-TOF MS spectra of **S3**.

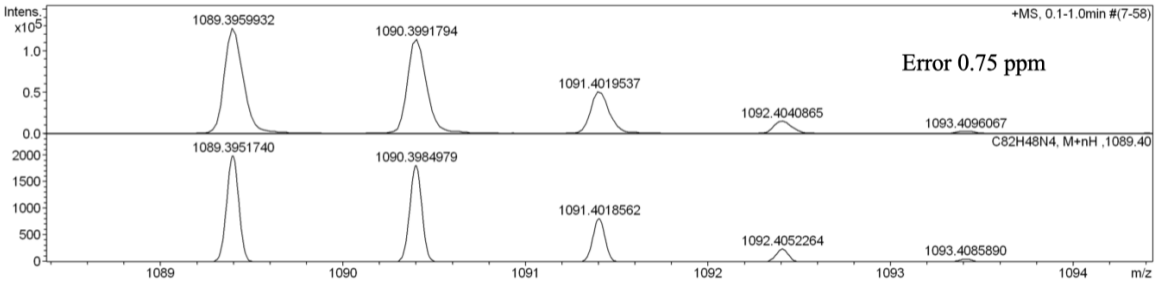


Fig. S25 HR-ESI-TOF MS spectra of **3**.

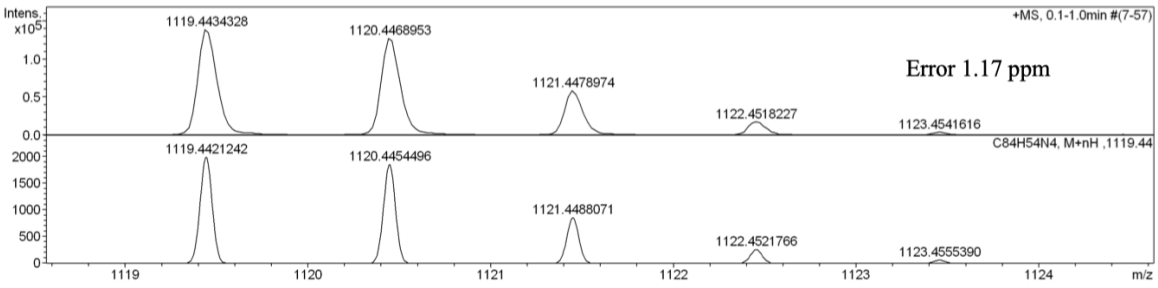


Fig. S26 HR-ESI-TOF MS spectra of **S4**.

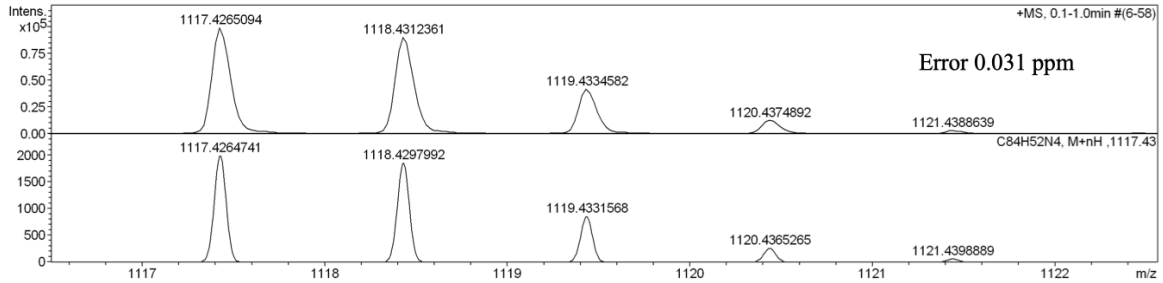


Fig. S27 HR-ESI-TOF MS spectra of **4**.

4. HPLC Chromatograms

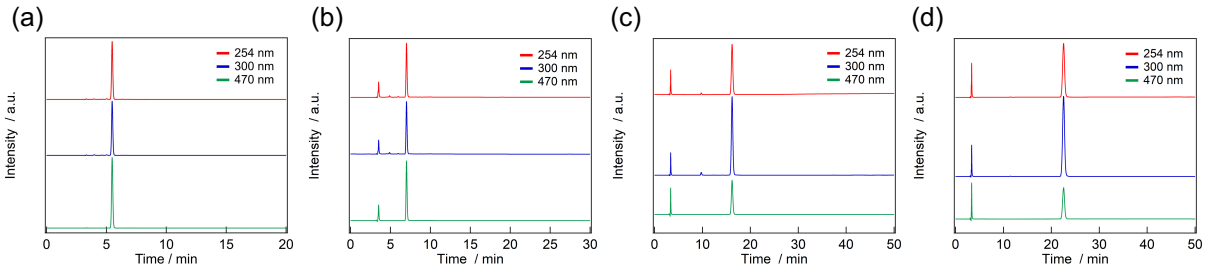


Fig. S28 HPLC chromatograms of (a) **1** (96% purity), (b) **2** (95% purity), (c) **3** (97% purity), and (d) **4** (98% purity). HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm×4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a PDA detector; the mobile phase was CH_3CN:MeOH = 1:1 with a flow rate of 1.0 mL/min (detection wavelength; 254, 300, and 470 nm).

5. X-ray Crystallographic Analyses

The diffraction data of the single crystal were collected on Rigaku XtaLAB mini II with Mo Kα radiation (λ = 0.71073 Å) at 100 K. The data integration and reduction were undertaken with Rigaku CrysAlis^{Pro}. The data refinement was carried out by Olex^2 software package with SHELXL program.[S4] All non-hydrogen atoms were anisotropically refined.

Table S1 Crystallographic Parameters of 5MR of **1**

Empirical formula	$C_{50}H_{32}N_4$	
Formula weight	688.79	
Temperature	106(8) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.5250(5) Å	α = 90°
	b = 14.4544(9) Å	β = 90°
	c = 26.1380(12) Å	γ = 90°
Volume	3598.6(3) Å^3	
Z	4	
Density (calculated)	1.271 g/cm^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	1440.0	
Theta range for data collection	4.202 to 61.118°	
Index ranges	-13<=h<=13, -17<=k<=20, -37<=l<=37	
Reflections collected	19914	
Independent reflections	8837 [R(int) = 0.0434]	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8837 / 0 / 487	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1102	
R indices (all data)	R1 = 0.0675, wR2 = 0.1176	
Largest diff. peak and hole	0.32 and -0.30 eÅ^{-3}	

Table S2 Crystallographic Parameters of 5MR of **2**

Empirical formula	$C_{52}H_{36}N_4$	
Formula weight	716.892	
Temperature	104(7) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 11.6158(3) Å	α = 90°
	b = 25.7155(8) Å	β = 94.105(3)°
	c = 12.4043(4) Å	γ = 90°
Volume	3695.73(19) $Å^3$	
Z	4	
Density (calculated)	1.288 g/cm^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	1504.8	
Theta range for data collection	4.56 to 52°	
Index ranges	-16<=h<=10, -35<=k<=36, -17<=l<=17	
Reflections collected	39620	
Independent reflections	7227 [R(int) = 0.0613]	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7227 / 189 / 523	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.0944	
R indices (all data)	R1 = 0.0960, wR2 = 0.1114	
Largest diff. peak and hole	0.48 and -0.43 $eÅ^{-3}$	

Table S3 Crystallographic Parameters of 8MR of **2**

Empirical formula	$C_{64}H_{48}N_4$
Formula weight	873.06
Temperature	105(8) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 13.5892(3) Å α = 90°
	b = 17.5461(4) Å β = 90°
	c = 19.4886(4) Å γ = 90°
Volume	4646.81(18) $Å^3$
Z	4
Density (calculated)	1.248 g/cm^3
Absorption coefficient	0.073 mm^{-1}
F(000)	1840.0
Theta range for data collection	4.33 to 61.336°
Index ranges	-19<=h<=17, -24<=k<=23, -26<=l<=27
Reflections collected	35777
Independent reflections	13363 [R(int) = 0.0391]
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10823 / 165 / 522
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1024
R indices (all data)	R1 = 0.0931, wR2 = 0.1144
Largest diff. peak and hole	0.24 and -0.21 $eÅ^{-3}$

6. Transient Absorption Spectroscopy

The visible light (470 nm) was irradiated to the benzene solution of **1**, **2**, **3**, and **4** in a quartz optical cuvette (optical length = 1 cm) using a LED light source (CL-H1-470-9-1, Asahi Spectra Co., Ltd.). The transient absorption spectra and the time variation of the transient absorbance were recorded on an Ocean FX multichannel detector (Ocean Optics, Inc). The power of the excitation light was measured using NOVA (OPHIR Optronics Solutions Ltd.) equipped with a power thermal sensor 30A-P17 (OPHIR Optronics Solutions Ltd.). CUV-QPOD (Ocean Optics, Inc) equipped with a TC 125 temperature controller (QUANTUM) was used as a cuvette holder. A deuterium and a halogen lamps DH-2000-BAL (Ocean Optics, Inc) were used as the probe beam, which were guided with a QP-600-1-SR optical fiber (Ocean Optics, Inc). Optical grade solvents were used for all measurements.

7. Laser Flash Photolysis Measurement

The laser flash photolysis experiments were performed by a TSP-2000 time-resolved spectrophotometer (Unisoku). A 10 Hz Qswitched Nd:YAG laser (Continuum Minilite II) with the third harmonic at 355 nm (pulse width = 5 ns) was employed as the excitation light source. The excitation pulse at 517 nm (pulse width, 5 ns) was provided by a Continuum Surelite II Q-Switched Nd:YAG coupled to a Continuum Panther EX OPO. A halogen lamp (OSRAM HLX 64623) was used as the probe beam arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a photomultiplier tube (Hamamatsu R2949) through a spectrometer (Unisoku MD200) for the time profile for the thermal isomerization. The excitation intensity was estimated by an energy detector (Gentec Electro-Optics QE12LP-S-MB) with an energy monitor (Genetic Electro-Optics MAESTRO). Optical grade solvents were used for all measurements.

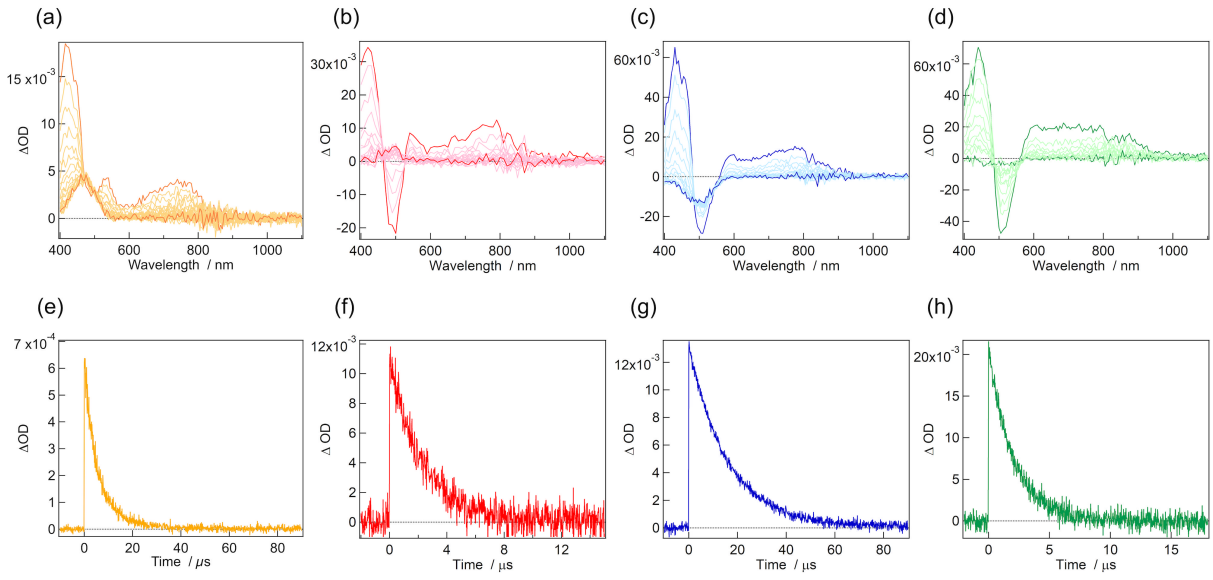


Fig. S29 Microsecond time-resolved absorption spectra of (a) **1**, (b) **2**, (c) **3**, and (d) **4** in benzene at 298 K upon 355-nm laser irradiation (4 mJ/pulse). (e-h) The time profiles of the transient absorbance at 750 nm.

8. Determination of Conversion Efficiency of 5MR

Using 1,2-bis(2-methylbenzo[*b*]thiophene-3-yl)-perfluorocyclopentene (DAE) as a standard, the photochemical reaction efficiencies of **1**–**4** from 5MR to the colorless isomers in response to visible light irradiation were estimated by nanosecond laser flash photolysis.[S2] The quantum yield of the photochemical ring-opening reaction of the closed-ring isomer of DAE has been previously reported.[S5] Because the open-ring isomer of DAE and the colorless isomers (6MR and 8MR) of **1**–**4** do not have any absorption bands in the visible light region, the ratio of the number of reacting molecules of DAE and 5MR can be calculated from the change in the absorbance (ΔOD) in the visible light region upon laser irradiation. The benzene solutions of the imidazole dimers and DAE were prepared and the absorbance at 517 nm, the excitation wavelength, was matched. The absorbance changes in the absorbance at 517 nm (ΔOD_{5MR} and ΔOD_{DAE}) associated with the photochromic reaction were plotted against the excitation laser energy (Fig. S30). ΔOD_{5MR} values were calculated as the average of the values in the time region where the thermal back reaction can be negligible. The reaction efficiencies of 5MR for **1**, **2**, **3**, and **4** were estimated to be 6.9×10^{-2}, 4.5×10^{-2}, 3.9×10^{-2}, and 1.7×10^{-2}, respectively, by the following equation,

$$\frac{\varphi_{5MR}}{\varphi_{DAE}} = \frac{\Delta OD_{5MR}}{\varepsilon_{5MR}} \times \frac{\varepsilon_{DAE}}{\Delta OD_{DAE}}$$

where φ_{DAE} is the quantum yield (0.35) of the ring-opening reaction of DAE, ε_{DAE} (0.91×10^4 M^{-1} cm^{-1}) is an absorption coefficient of the closed-ring isomer of DAE, and ε_{5MR} for **1**, **2**, **3**, and **4** (9.92×10^3, 1.62×10^4, 3.68×10^4, and 4.41×10^4 M^{-1} cm^{-1}, respectively) are absorption coefficients of 5MR.

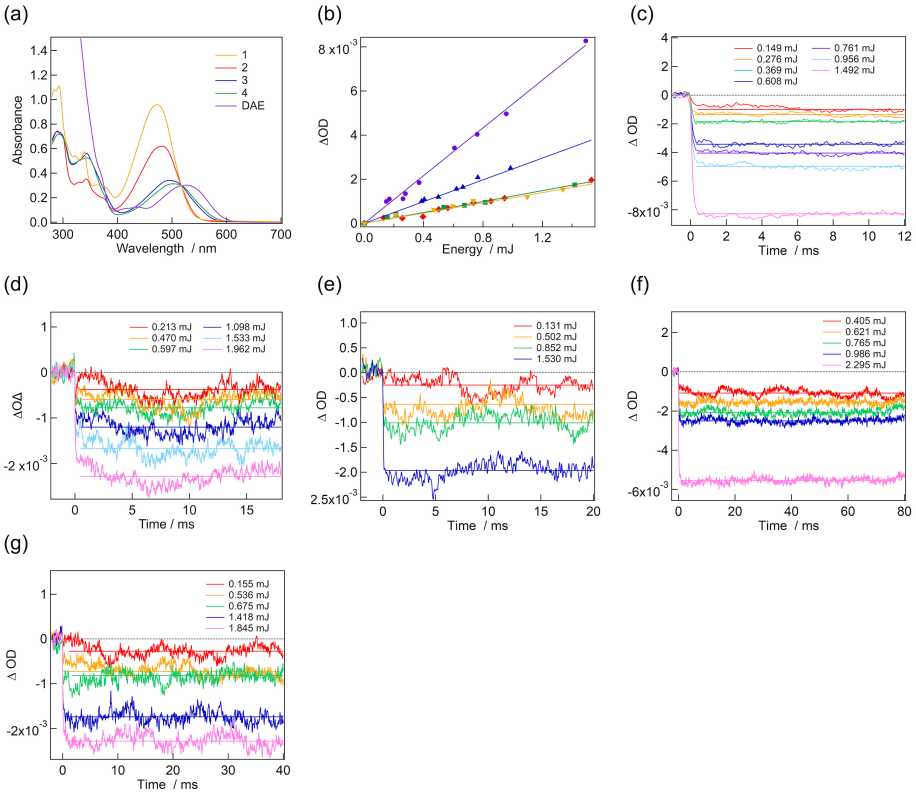


Fig. S30 (a) Absorption spectra of **1**–**4**, and DAE in benzene. (b) Laser power dependence of the absorbance changes. (c-g) Laser intensity dependence of the time profiles of transient absorbance at 517 nm of (c) DAE, (d) **1**, (e) **2**, (f) **3**, (g) **4**.

9. Measurement for Conversion Efficiency to 8MR of 2 and 4

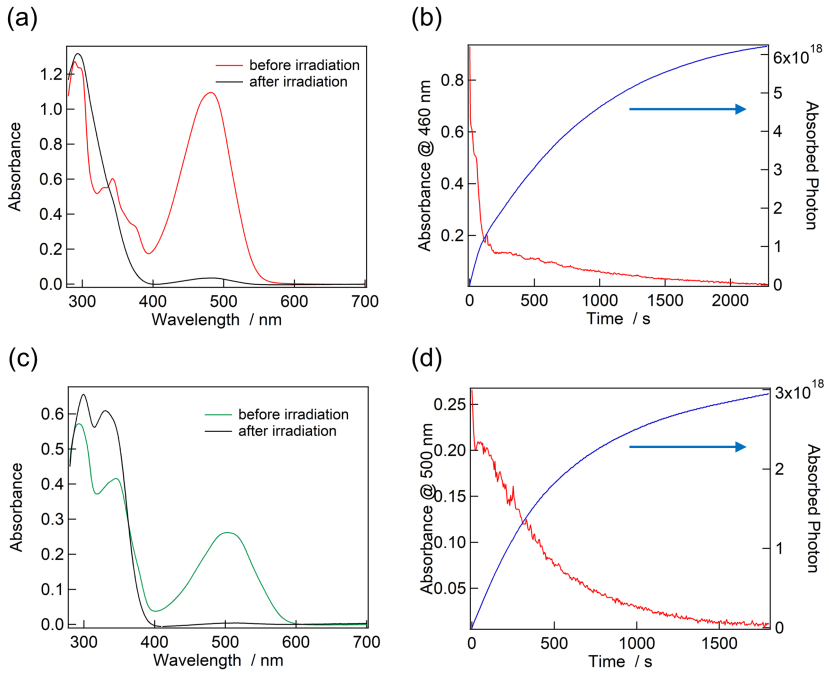


Fig. S31 Absorption spectra of (a) **2** and (c) **4** in benzene before 460 nm LED light irradiation (40.8 mW cm^{-2}) and after the light irradiation was stopped and the photogenerated 6MR completely returned to 5MR. Simultaneous measurements of the time profiles of the absorbance of (b) **2** and (d) **4** in benzene under the 460 nm LED light irradiation and the number of photons absorbed by the benzene solution. All measurements were performed using a photoreaction evaluation system Lightway PQY-01 (Shimadzu Co.).

10. Fatigue Resistance of 3

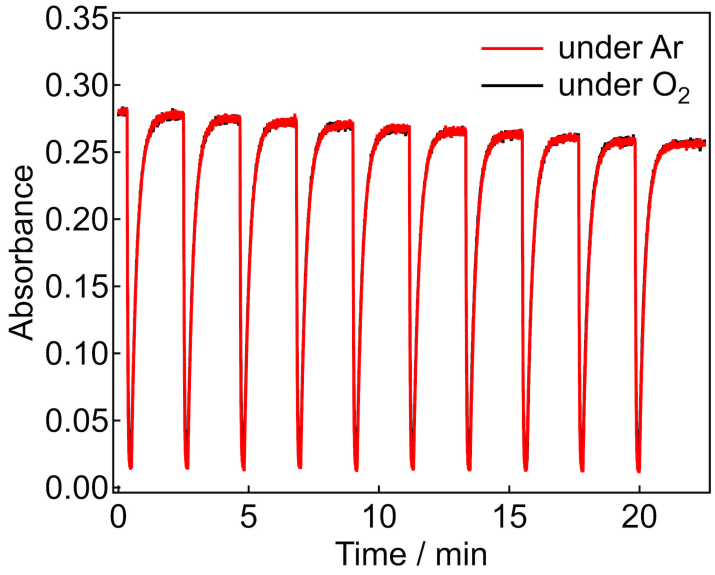


Fig. S32 Cycles of decoloration by light irradiation and the subsequent thermal coloration when the irradiation was ceased in the benzene solution of **3** (6.13×10^{-6} M) at 298 K. Absorbance was monitored at 500 nm. A 470 nm LED light source (Asahi Spectra Co., Ltd. CL-H1-470-9-1) was employed for the light irradiation.

11. DFT Calculations

All calculations were carried out using the Gaussian 16 program (Revision B.01).[S6] The molecular structures were fully optimized at the DFT CAM-B3LYP level of theory using the 6-31G(d) basis set. All optimized structures were confirmed to be stationary points by frequency analysis. No imaginary modes were found for the minima structures and only one imaginary mode was present for the transition states, proving the latter to be first order saddle points on the hyper-potential energy surface. Absorption spectra of biradicals were calculated at the TDDFT UMPW1PW91 level of theory using 6-31+G(d) basis set.

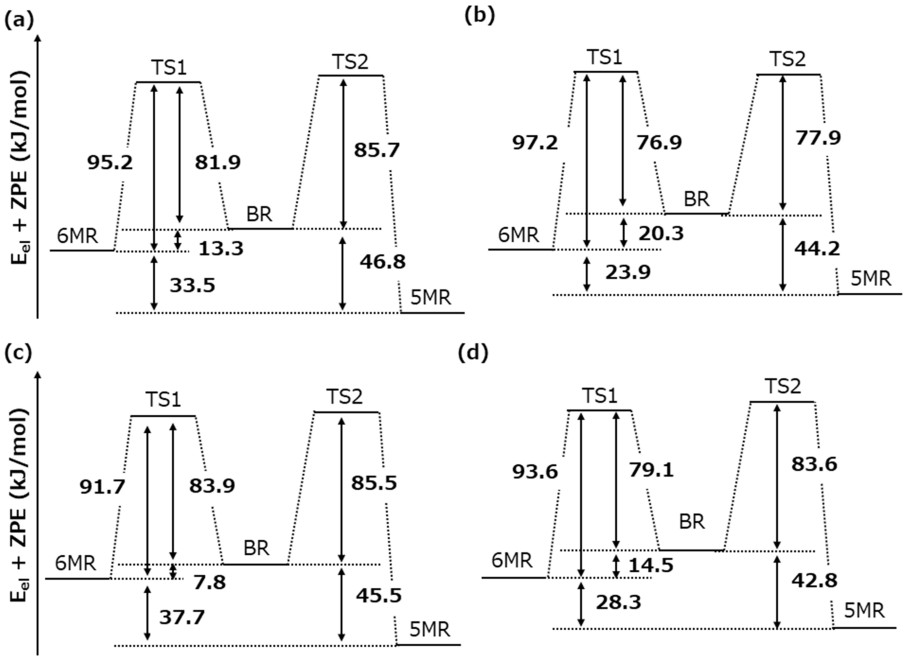


Fig. S33 Energy level diagrams of (a) **1**, (b) **2**, (c) **3**, and (d) **4**. Relative electronic energies in kJ/mol with unscaled zero-point correction.

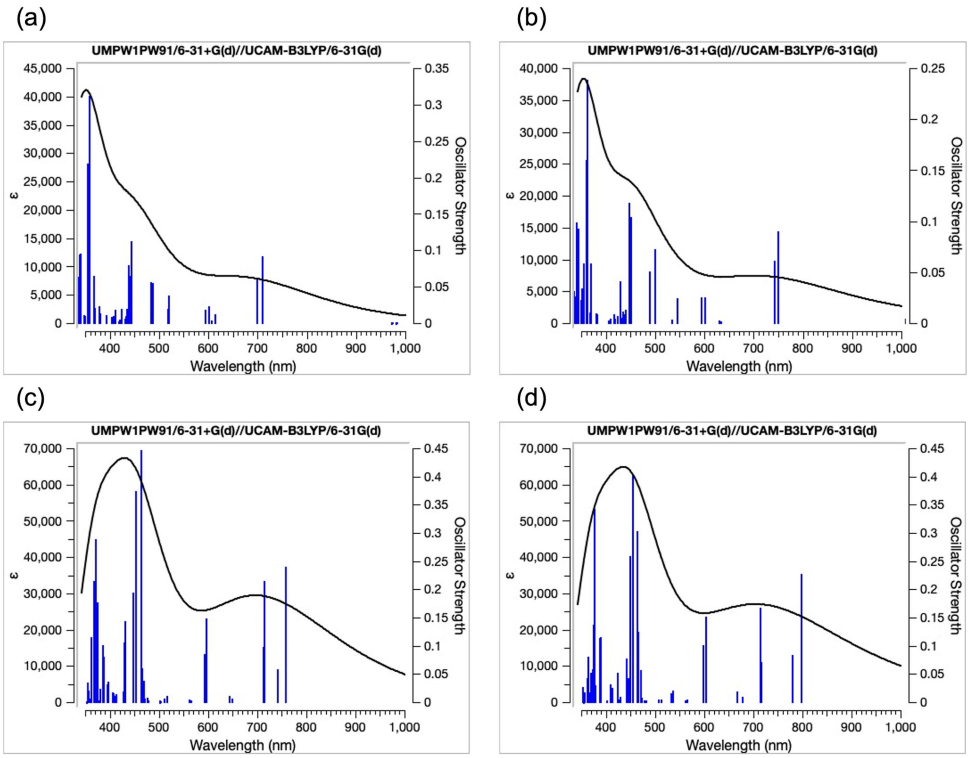


Fig. S34 Calculated absorption spectra of (a) **1-BR**, (b) **2-BR**, (c) **3-BR**, and (d) **4-BR**.

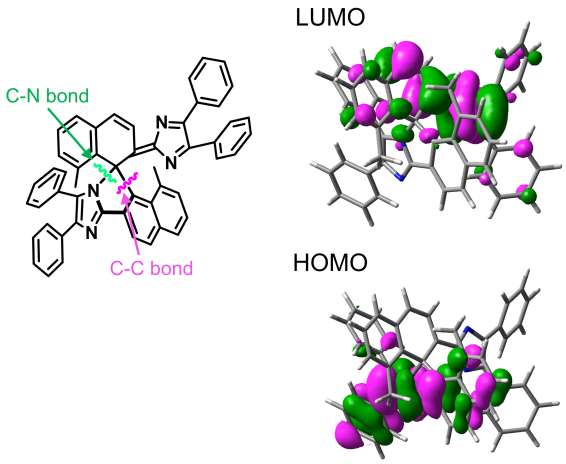


Fig. S35 HOMO and LUMO of 5MR of **2**.

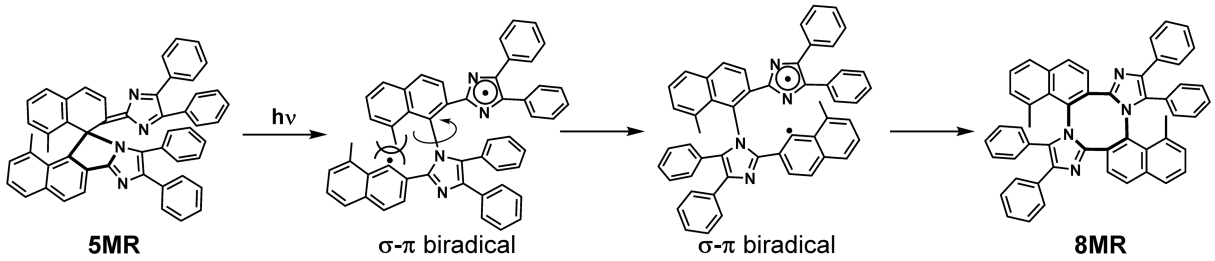


Fig. S36 Plausible reaction mechanism for the generation of 8MR of **2**.

Table S4. Standard Orientation of the Optimized Geometry for 5MR of **1**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-1.3757420	-1.1855110	-3.5882610	C	0.5042300	4.3883480	-2.4097480	H	3.0983210	-3.2176360	2.9881760
C	-1.6468970	-2.5128240	-3.7737000	C	0.9461300	5.6917040	-2.5864700	H	5.1906010	-3.6470150	4.2520390
C	-1.9960000	-3.3580870	-2.6861740	C	0.6597540	6.6655750	-1.6353100	H	7.0724900	-0.3734970	2.2128860
C	-2.0722310	-2.8285120	-1.3621950	C	-0.0822360	6.3222500	-0.5111040	H	4.9978100	0.0330510	0.9463470
C	-1.7878690	-1.4526020	-1.2026060	C	-0.5286700	5.0188000	-0.3332900	H	4.7897370	-2.0248060	-0.7535560
C	-1.4535830	-0.6645710	-2.2836330	C	3.9147640	-1.5829460	1.8706060	H	6.2613140	-1.5608940	-2.6727490
C	-1.8207550	-0.6086480	0.0949050	C	3.3140020	-0.5560920	-1.3098750	H	3.4998670	1.4107320	-4.0747910
C	-0.7939070	-1.0830000	1.1282490	C	3.9800230	-2.6098400	2.8179540	H	2.0102020	0.9263090	-2.1570600
C	-1.2361190	-1.5138600	2.4297040	C	5.1502400	-2.8412480	3.5256120	C	-2.2711780	-4.7331130	-2.8900300
C	-2.5263430	-1.4603550	2.8043020	C	6.2684260	-2.0418200	3.3072040	C	-4.8987160	-0.8863390	2.3733950
C	-3.5740600	-0.9662400	1.9284280	C	6.2080470	-1.0087620	2.3787950	C	-4.2648460	-0.0520980	-0.1910750
C	-3.2565530	-0.5445880	0.6314100	C	5.0402670	-0.7805930	1.6618170	C	-5.5752550	0.0292040	0.2613960
C	-1.2003530	0.6781110	-1.7949860	C	4.5113010	-1.2603820	-1.4698570	C	-5.8953260	-0.3912480	1.5497580
C	0.5419790	-1.0954330	0.8461270	C	5.3381250	-1.0018670	-2.5557170	C	-2.4166480	-3.7021610	-0.2981560
N	1.5019760	-1.4941150	1.7787540	C	4.9822580	-0.0365300	-3.4905910	C	-2.6746670	-5.0257260	-0.5344150
C	2.6418380	-1.3304250	1.1759250	C	3.7865210	0.6609660	-3.3439820	C	-2.6034090	-5.5503410	-1.8438160
C	2.3836450	-0.8369890	-0.2063480	C	2.9528570	0.4004040	-2.2668900	H	-2.2110420	-5.1283480	-3.9002950
N	1.0999000	-0.6960950	-0.3590200	H	-1.1026260	-0.5372620	-4.4134600	H	-5.1339510	-1.2143940	3.3820340
N	-0.7542410	1.8183220	-2.2465440	H	-1.5959830	-2.9480800	-4.7675790	H	-4.0211230	0.2769840	-1.1958970
C	-0.6829210	2.6340050	-1.1314710	H	-0.4661510	-1.8614380	3.1069230	H	-6.3471070	0.4189860	-0.3943180
C	-1.0892440	1.9495650	0.0063650	H	-2.8133750	-1.7781010	3.8026670	H	-6.9184190	-0.3318620	1.9069540
N	-1.4410930	0.7002660	-0.4586350	H	1.0050110	2.5579560	1.5593340	H	-2.4696480	-3.3161320	0.7127500
C	-1.1236260	2.3178490	1.4350890	H	0.9908040	3.1795440	3.9555040	H	-2.9354130	-5.6797740	0.2919000
C	-0.2317800	4.0287710	-1.2754580	H	-3.2806030	2.7729510	4.0236410	H	-2.8106790	-6.6018790	-2.0153550
C	-2.3280330	2.3825420	2.1411590	H	-3.2605360	2.1724640	1.6280400	H	5.6325020	0.1683350	-4.3356650
C	0.0567830	2.9576000	3.4487600	H	0.7136650	3.6269880	-3.1525180	H	7.1838060	-2.2220160	3.8624520
C	-1.1464720	3.0143080	4.1447040	H	1.5179660	5.9490380	-3.4733400	H	1.0061900	7.6854240	-1.7728050
C	-2.3372360	2.7255520	3.4882070	H	-0.3251680	7.0760390	0.2320780	H	-1.1553690	3.2844760	5.1962670
C	0.0685550	2.6090590	2.1050430	H	-1.1232930	4.7740030	0.5389750				

SCF Done: E(RCAM-B3LYP) = -2142.41471162 A.U.

Low frequencies --- -0.0003 -0.0002 0.0008 0.3711 1.5802 2.4193
Zero-point correction = 0.689400 (Hartree/Particle)
Thermal correction to Energy = 0.728970
Thermal correction to Enthalpy = 0.729915
Thermal correction to Gibbs Free Energy = 0.613562
Sum of electronic and zero-point Energies = -2141.725312
Sum of electronic and thermal Energies = -2141.685741
Sum of electronic and thermal Enthalpies = -2141.684797
Sum of electronic and thermal Free Energies = -2141.801150

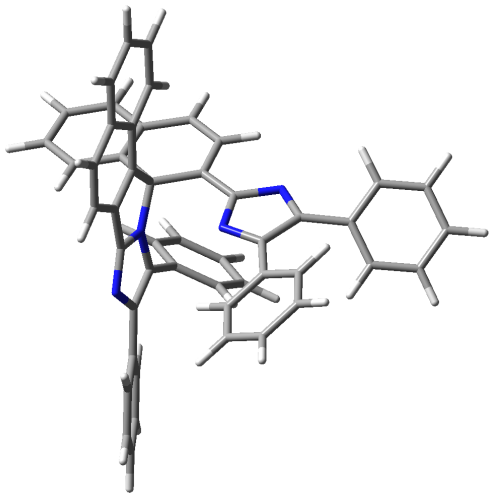


Table S5. Standard Orientation of the Optimized Geometry for 6MR of **1**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-1.4152240	-0.4905570	2.7739370	C	3.8143070	-0.8011700	1.9889090	H	2.4924740	0.5861870	-3.5072280
C	-2.5074060	-0.2117990	3.5462200	C	5.0017360	-1.0156560	2.6738570	H	4.7467270	0.8300060	-4.5154220
C	-3.6822480	0.3132850	2.9613420	C	5.2652360	-2.2584610	3.2417200	H	5.9929990	3.1488800	-1.1263950
C	-3.7502700	0.4692180	1.5473360	C	4.3372700	-3.2864580	3.1194950	H	3.7416010	2.9320630	-0.1470940
C	-2.6534400	0.0150080	0.7413180	C	3.1529260	-3.0783660	2.4234750	H	2.0100650	4.4729520	-1.7403050
C	-1.4805910	-0.3538550	1.3737430	C	2.9614370	1.7594340	-1.7771650	H	2.4007620	6.7948690	-1.0083770
C	-2.6643700	0.0217140	-0.7475530	C	1.1377370	3.8537500	0.1296280	H	0.7013180	5.8763240	2.8239900
C	-1.5002160	0.3890600	-1.3962930	C	3.2622730	1.1608310	-3.0040030	H	0.2879840	3.5444240	2.0698320
C	-1.4568790	0.5323610	-2.7960940	C	4.5267770	1.2927530	-3.5584160	C	-4.7699670	0.7388460	3.7674730
C	-2.5604180	0.2580650	-3.5534210	C	5.5118040	2.0119040	-2.8875490	C	-4.8264560	-0.6908040	-3.7437920
C	-3.7264930	-0.2685070	-2.9527380	C	5.2257820	2.5960200	-1.6593140	C	-4.8969430	-1.1076840	-0.9905150
C	-3.7739820	-0.4277370	-1.5382710	C	3.9561840	2.4754470	-1.1067440	C	-5.9279250	-1.5340200	-1.7831090
C	-0.2304870	-0.5499230	0.5244690	C	1.7297500	4.7750840	-0.7369610	C	-5.9082640	-1.3033420	-3.1766470
C	-0.2358740	0.5737940	-0.5675950	C	1.9478610	6.0839220	-0.3244290	C	-4.8794590	1.1507930	1.0146570
N	0.9743000	0.4636630	-1.3592150	C	1.5844480	6.4815800	0.9571710	C	-5.8980860	1.5804350	1.8212970
C	1.6230040	1.5548380	-1.1871250	C	0.9907000	5.5688330	1.8239520	C	-5.8589250	1.3519360	3.2147600
C	0.8316760	2.4721710	-0.2930080	C	0.7622380	4.2639750	1.4115710	H	-4.7053390	0.5869870	4.8414560
N	-0.2392530	1.8805660	0.0798960	H	-0.4830430	-0.8020900	3.2290190	H	-4.7772680	-0.5368080	-4.8182660
N	0.9828650	-0.4518960	1.3136650	H	-2.4649980	-0.3323920	4.6249590	H	-4.9243790	-1.3094340	0.0721490
C	1.6042860	-1.5616390	1.1638220	H	-0.5326940	0.8487060	-3.2641410	H	-6.7655760	-2.0612390	-1.3369860
C	0.8191650	-2.4570320	0.2429480	H	-2.5345360	0.3833830	-4.6320880	H	-6.7392900	-1.6329290	-3.7925220
N	-0.2492160	-1.8562690	-0.1231690	H	3.2761800	-3.4857610	-0.3797240	H	-4.9211350	1.3522820	-0.0475220
C	1.1518120	-3.8126710	-0.2381060	H	3.7570060	-5.7348610	-1.2660780	H	-6.7405290	2.1093580	1.3864320
C	2.8822660	-1.8328850	1.8522810	H	-0.4250120	-6.6882340	-1.1273250	H	-6.6804220	1.6841630	3.8419140
C	0.1145080	-4.7210380	-0.4662080	H	-0.9037360	-4.4126180	-0.2563890	H	1.7604820	7.5032430	1.2797440
C	2.7339940	-5.4555580	-1.0341090	H	3.5935830	0.1646240	1.5479300	H	6.5020320	2.1133810	-3.3209850
C	1.6987530	-6.3592860	-1.2434410	H	5.7236080	-0.2103010	2.7669320	H	6.1933240	-2.4249880	3.7799450
C	0.3877040	-5.9883660	-0.9597250	H	4.5343350	-4.2553180	3.5674770	H	1.9121600	-7.3506340	-1.6314530
C	2.4647010	-4.1887670	-0.5304330	H	2.4319830	-3.8835430	2.3325840				

SCF Done: E(RCAM-B3LYP) = -2142.40168391 A.U.

Low frequencies --- -1.1936 -0.0004 0.0002 0.0006 0.8587 0.9489
Zero-point correction = 0.689127 (Hartree/Particle)
Thermal correction to Energy = 0.728333
Thermal correction to Enthalpy = 0.729277
Thermal correction to Gibbs Free Energy = 0.614087
Sum of electronic and zero-point Energies = -2141.712557
Sum of electronic and thermal Energies = -2141.673351
Sum of electronic and thermal Enthalpies = -2141.672407
Sum of electronic and thermal Free Energies = -2141.787597

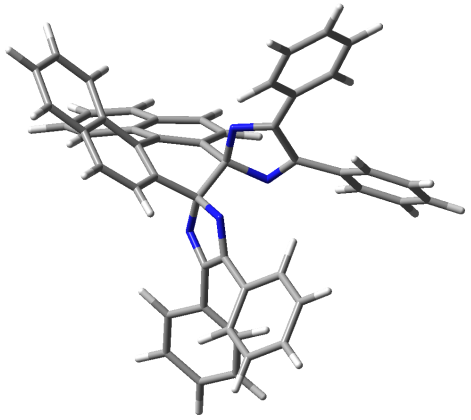


Table S6. Standard Orientation of the Optimized Geometry for BR of **1**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.4121670	1.7391710	2.8103930	C	-3.9208280	-2.1186730	3.4780640	H	4.1466730	-1.6258150	-3.5882920
C	0.5148570	2.6421260	3.2230460	C	-4.8652270	-2.8181480	4.2127720	H	5.4824650	-3.5255500	-4.4651790
C	1.2811060	3.3775750	2.2793770	C	-6.1154850	-3.0923860	3.6644030	H	5.2126460	-5.4559130	-0.6416310
C	1.0738430	3.1460230	0.8926420	C	-6.4153950	-2.6586580	2.3778310	H	3.9030780	-3.5584180	0.2265700
C	0.1119430	2.1765470	0.4681430	C	-5.4682050	-1.9664020	1.6348040	H	5.5528670	-1.6225530	0.5399760
C	-0.6391350	1.4884130	1.4222190	C	3.9643020	-2.4471530	-1.6184060	H	6.7234760	-1.9196700	2.6842970
C	-0.0888390	1.9897730	-1.0021200	C	3.7084440	-0.9579130	1.4374100	H	3.2282840	-0.5785320	4.7834910
C	0.6562780	1.0812630	-1.7547650	C	4.4015370	-2.4636650	-2.9493710	H	2.0590270	-0.2632740	2.6194130
C	0.4180000	0.9673410	-3.1578050	C	5.1414030	-3.5305140	-3.4345360	C	2.2357230	4.3349100	2.6904720
C	-0.5078200	1.7399040	-3.7826900	C	5.4430830	-4.6074700	-2.6049610	C	-2.2257680	3.5163730	-3.6885540
C	-1.2673520	2.6937430	-3.0532940	C	4.9960230	-4.6113870	-1.2883540	C	-1.8224450	3.7808590	-0.9434390
C	-1.0538320	2.8205980	-1.6532310	C	4.2632540	-3.5395530	-0.7956970	C	-2.7442260	4.5659340	-1.5851970
C	-1.6491450	0.5044410	1.0983140	C	5.0326010	-1.4137230	1.4672860	C	-2.9508180	4.4344320	-2.9739350
C	1.6656530	0.2092910	-1.1948820	C	5.6946150	-1.5734710	2.6772240	C	1.8453350	3.8955050	-0.0338580
N	2.3293990	-0.6973260	-1.9806930	C	5.0470650	-1.2833590	3.8730690	C	2.7639000	4.8187130	0.3924730
C	3.1446270	-1.3243030	-1.1565240	C	3.7354230	-0.8154590	3.8532910	C	2.9638880	5.0432260	1.7700380
C	2.9871310	-0.7249570	0.1868510	C	3.0732870	-0.6450320	2.6482010	H	2.3814750	4.4986700	3.7545510
N	2.0466320	0.2007950	0.1104470	H	-1.0131850	1.1849300	3.5202330	H	-2.3751980	3.4069090	-4.7591760
N	-2.3681280	-0.1179810	2.0864000	H	0.6746350	2.8235470	4.2821880	H	-1.6739370	3.8895450	0.1242650
C	-3.1978010	-0.9178080	1.4465630	H	1.0029300	0.2380400	-3.7036160	H	-3.3199960	5.2931590	-1.0214980
C	-2.9295680	-0.7906120	-0.0023460	H	-0.6759550	1.6428870	-4.8515960	H	-3.6834230	5.0609400	-3.4732970
N	-1.9814570	0.1166160	-0.1620530	H	-3.9465220	-3.3326380	-0.0987760	H	1.7022860	3.7291070	-1.0948600
C	-3.4806010	-1.5091410	-1.1505470	H	-4.7888200	-4.5039530	-2.0932210	H	3.3426310	5.3801010	-0.3342300
C	-4.2047330	-1.6950840	2.1730610	H	-3.9266160	-1.0504750	-4.4911930	H	3.6945860	5.7761360	2.0978780
C	-3.4615460	-0.8858120	-2.4066820	H	-3.0637400	0.1198380	-2.4814390	H	5.5652040	-1.4137040	4.8182710
C	-4.4283370	-3.4837970	-2.1811920	H	-2.9487270	-1.8860180	3.8976510	H	6.0199150	-5.4443170	-2.9866210
C	-4.4264420	-2.8478760	-3.4177890	H	-4.6281400	-3.1493540	5.2190870	H	-6.8558430	-3.6377220	4.2416200
C	-3.9387600	-1.5478990	-3.5263400	H	-7.3941290	-2.8542350	1.9509560	H	-4.7965180	-3.3663380	-4.2970240
C	-3.9606010	-2.8214610	-1.0542070	H	-5.7160190	-1.6167200	0.6391420				

SCF Done: E(UCAM-B3LYP) = -2142.39286414 A.U.
S**2 before annihilation 1.1135, after 0.9429

Low frequencies --- -1.1300 -0.2380 -0.0003 -0.0002 0.0005 1.0620
Zero-point correction = 0.685364 (Hartree/Particle)
Thermal correction to Energy = 0.725734
Thermal correction to Enthalpy = 0.726678
Thermal correction to Gibbs Free Energy = 0.606621
Sum of electronic and zero-point Energies = -2141.707500
Sum of electronic and thermal Energies = -2141.667130
Sum of electronic and thermal Enthalpies = -2141.666186
Sum of electronic and thermal Free Energies = -2141.786243

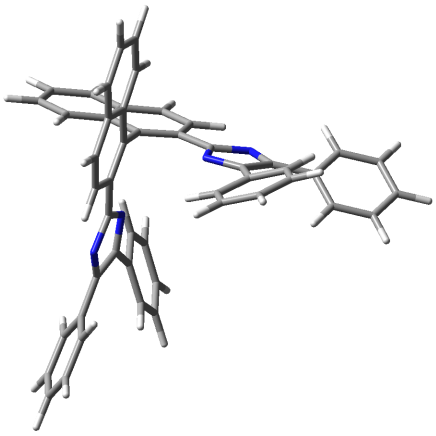


Table S7. Standard Orientation of the Optimized Geometry for TS1 of **1**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-1.6339160	1.1655650	2.6196740	C	3.5869400	0.4750140	2.0051010	H	2.6676050	-0.9604650	-2.9526510
C	-2.6980810	1.9478000	2.9651140	C	4.8691070	0.6300790	2.5066150	H	5.0672310	-1.2477630	-3.5138120
C	-3.8264760	2.0394070	2.1180170	C	5.5488190	-0.4626690	3.0381050	H	5.9958190	2.2908740	-1.2709400
C	-3.8625270	1.2676400	0.9216350	C	4.9345550	-1.7095460	3.0697970	H	3.6140670	2.5797100	-0.7322170
C	-2.7891230	0.3672130	0.6327850	C	3.6529910	-1.8709960	2.5604030	H	2.3095470	3.6211960	-2.7163470
C	-1.6697600	0.3717420	1.4490050	C	2.9721390	0.8387180	-1.8294230	H	2.7728510	6.0346770	-2.5028180
C	-2.7800650	-0.4775540	-0.5938410	C	1.0714340	3.5313930	-0.9558500	H	0.3384090	6.1915600	1.0282550
C	-1.6650070	-0.4485390	-1.4152320	C	3.4059120	-0.2485090	-2.6019700	H	-0.1382700	3.7632890	0.7963860
C	-1.6119660	-1.2384520	-2.5867070	C	4.7481070	-0.4066560	-2.9061360	C	-4.8996220	2.9164500	2.4184820
C	-2.6545520	-2.0496690	-2.9292540	C	5.6854060	0.5098020	-2.4347650	C	-4.8228690	-3.0848970	-2.3726830
C	-3.7748160	-2.1764730	-2.0764460	C	5.2693880	1.5809620	-1.6538420	C	-4.9086980	-1.6496220	0.0153780
C	-3.8277620	-1.4084280	-0.8781870	C	3.9233120	1.7477730	-1.3527020	C	-5.8925470	-2.5511380	-0.2869610
C	-0.4298810	-0.3481710	1.0792130	C	1.8877780	4.1798990	-1.8875050	C	-5.8625690	-3.2679840	-1.5042180
C	-0.4490050	0.3140340	-1.0524350	C	2.1449330	5.5396490	-1.7685600	C	-4.9540680	1.4754430	0.0328440
N	0.7767200	-0.1190590	-1.5062010	C	1.5940880	6.2650080	-0.7176350	C	-5.9628490	2.3477540	0.3387530
C	1.5460140	0.9399780	-1.5036350	C	0.7743780	5.6277580	0.2094000	C	-5.9486240	3.0667540	1.5548820
C	0.7218970	2.1089420	-1.0821290	C	0.5076410	4.2717840	0.0889330	H	-4.8602170	3.4813810	3.3457980
N	-0.4785800	1.6913260	-0.8099890	H	-0.7406480	1.1383920	3.2317770	H	-4.7710140	-3.6472130	-3.3009470
N	0.7765460	0.1329190	1.5425040	H	-2.6757780	2.5365100	3.8778610	H	-4.9424930	-1.1172790	0.9572350
C	1.5889620	-0.8930490	1.5257970	H	-0.7223310	-1.1872820	-3.2024690	H	-6.7015870	-2.7205940	0.4168120
C	0.8325420	-2.0766810	1.0253900	H	-2.6182480	-2.6381180	-3.8415830	H	-6.6553620	-3.9720500	-1.7373240
N	-0.3976320	-1.7186140	0.8069460	H	3.2170310	-2.8328020	-0.0546980	H	-4.9758390	0.9416970	-0.9084580
C	1.2974730	-3.4357950	0.7134080	H	3.9131220	-5.1241370	-0.6493340	H	-6.7794550	2.4925830	-0.3616950
C	2.9661220	-0.7812620	2.0122590	H	0.1487740	-6.6343030	0.7532120	H	-6.7609870	3.7471470	1.7908360
C	0.4320890	-4.5153910	0.9166040	H	-0.5505460	-4.3242820	1.3334640	H	1.7992330	7.3270440	-0.6237400
C	2.9394710	-4.9568800	-0.1992020	H	3.0390270	1.3197770	1.6049000	H	6.7372450	0.3849800	-2.6729020
C	2.0816120	-6.0276170	0.0266530	H	5.3411130	1.6074720	2.4863860	H	6.5528620	-0.3403700	3.4327440
C	0.8256400	-5.8028340	0.5829280	H	5.4524930	-2.5617500	3.4984310	H	2.3881660	-7.0354740	-0.2362330
C	2.5529600	-3.6672950	0.1430530	H	3.1772450	-2.8431180	2.6058030				

SCF Done: E(UCAM-B3LYP) = -2142.36195694 A.U.
S**2 before annihilation 0.4311, after 0.0757

Low frequencies --- -619.4875 -0.5220 -0.4702 0.0002 0.0006 0.0009
****** 1 imaginary frequencies (negative Signs) ******
Zero-point correction = 0.685672 (Hartree/Particle)
Thermal correction to Energy = 0.725033
Thermal correction to Enthalpy = 0.725978
Thermal correction to Gibbs Free Energy = 0.610965
Sum of electronic and zero-point Energies = -2141.676285
Sum of electronic and thermal Energies = -2141.636923
Sum of electronic and thermal Enthalpies = -2141.635979
Sum of electronic and thermal Free Energies = -2141.750991

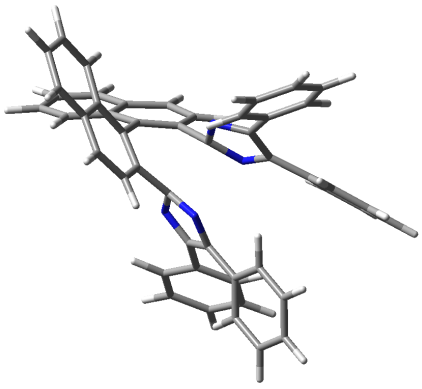


Table S8. Standard Orientation of the Optimized Geometry for TS2 of **1**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.5306500	2.1476820	2.9778610	C	-4.4184640	-1.9955580	3.1078120	H	4.7080700	-0.6728140	-3.1586800
C	0.3938110	3.1325690	3.1501150	C	-5.4754310	-2.7497620	3.5944030	H	6.5342230	-2.1094090	-4.0316360
C	1.1018270	3.6800470	2.0423230	C	-6.4561950	-3.2222980	2.7270720	H	6.0666440	-4.7213900	-0.6587850
C	0.8443640	3.1970290	0.7274380	C	-6.3752670	-2.9263450	1.3700280	H	4.2686220	-3.2796320	0.2118540
C	-0.1125390	2.1529380	0.5732530	C	-5.3196380	-2.1705780	0.8796410	H	5.4387160	-1.1084550	1.1029070
C	-0.7719630	1.6467780	1.6761470	C	4.3876390	-1.8614300	-1.4056070	H	6.3151200	-1.6086770	3.3491290
C	-0.5052420	1.6237890	-0.7723760	C	3.3793170	-1.0313940	1.7344340	H	2.3296840	-1.4830740	4.9371580
C	0.4837990	0.9418100	-1.5893000	C	5.0257870	-1.5542980	-2.6132560	H	1.4545610	-0.9595850	2.6748030
C	0.3332230	0.9169660	-3.0109890	C	6.0408920	-2.3640990	-3.0987560	C	2.0473960	4.7161360	2.2213020
C	-0.6852420	1.5617530	-3.6253050	C	6.4241040	-3.5023790	-2.3947120	C	-2.6832570	3.0131090	-3.5335400
C	-1.6579960	2.3096160	-2.8773250	C	5.7834490	-3.8266050	-1.2041770	C	-2.5096280	3.1363330	-0.7641520
C	-1.5697850	2.3605100	-1.4666440	C	4.7733440	-3.0118080	-0.7093410	C	-3.5126870	3.8131120	-1.4259040
C	-1.6449160	0.5482470	1.3734430	C	4.7528550	-1.2071900	1.9363300	C	-3.6032190	3.7523080	-2.8219260
C	1.5435950	0.2240980	-1.0202070	C	5.2465920	-1.4829750	3.2047210	C	1.5253880	3.8002660	-0.3605100
N	2.4863890	-0.4206930	-1.8022190	C	4.3783120	-1.5907920	4.2852850	C	2.4384950	4.8009420	-0.1519450
C	3.2843490	-1.0077700	-0.9485810	C	3.0112070	-1.4064520	4.0957010	C	2.7078740	5.2636700	1.1524390
C	2.8177900	-0.6847070	0.4254680	C	2.5149140	-1.1208280	2.8335300	H	2.2395880	5.0734820	3.2291640
N	1.7399750	0.0539280	0.3285890	H	-1.0831030	1.7244440	3.8095480	H	-2.7357170	2.9662460	-4.6176140
N	-2.5834250	-0.0173310	2.1223140	H	0.6036520	3.5246290	4.1411900	H	-2.4481780	3.1964690	0.3156720
C	-3.2118580	-0.8684410	1.2704790	H	1.0701170	0.3580510	-3.5736930	H	-4.2312490	4.3963010	-0.8594060
C	-2.5893530	-0.8149670	-0.0128260	H	-0.7803690	1.5321070	-4.7067890	H	-4.3907490	4.2893190	-3.3410170
N	-1.5721350	0.0549730	0.1029830	H	-2.7214380	-3.5125070	-0.0807350	H	1.3165920	3.4661770	-1.3706310
C	-2.7760050	-1.6750610	-1.1959820	H	-2.9934580	-4.9577380	-2.0619550	H	2.9525050	5.2467280	-0.9977830
C	-4.3203070	-1.7003630	1.7415000	H	-3.1296170	-1.4816580	-4.5729030	H	3.4304710	6.0591160	1.3050980
C	-2.8906350	-1.1186010	-2.4717890	H	-2.8752030	-0.0408390	-2.5830210	H	4.7660590	-1.8120430	5.2749800
C	-2.9693120	-3.8788230	-2.1814500	H	-3.6521580	-1.6148900	3.7733300	H	7.2170890	-4.1378940	-2.7767590
C	-3.0810310	-3.3138030	-3.4481970	H	-5.5349990	-2.9720530	4.6556360	H	-7.2828980	-3.8143760	3.1078750
C	-3.0407450	-1.9320420	-3.5887760	H	-7.1438390	-3.2794180	0.6891670	H	-3.1984640	-3.9490440	-4.3208560
C	-2.8173460	-3.0677320	-1.0656280	H	-5.2755680	-1.9293440	-0.1760480				

SCF Done: E(UCAM-B3LYP) = -2142.35893568 A.U.
S**2 before annihilation 0.5870, after 0.2201

Low frequencies ----1491.0814 -1.5587 -0.0006 0.0001 0.0005 0.6964
****** 1 imaginary frequencies (negative Signs) ******
Zero-point correction = 0.684087 (Hartree/Particle)
Thermal correction to Energy = 0.723940
Thermal correction to Enthalpy = 0.724884
Thermal correction to Gibbs Free Energy = 0.607262
Sum of electronic and zero-point Energies = -2141.674849
Sum of electronic and thermal Energies = -2141.634996
Sum of electronic and thermal Enthalpies = -2141.634052
Sum of electronic and thermal Free Energies = -2141.751674

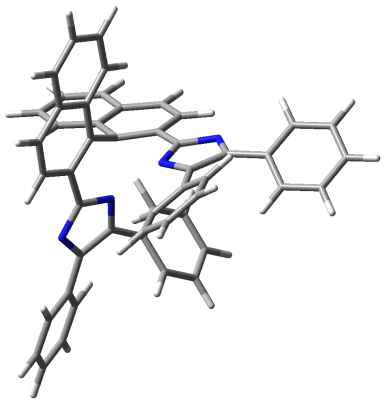


Table S9. Standard Orientation of the Optimized Geometry for 5MR of **2**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.6630340	-1.7602890	-3.2912630	C	-0.0743720	6.4294480	-2.6852890	H	5.1877710	-1.6861940	-0.1527680
C	-0.7759890	-3.1154460	-3.3487280	C	-0.8979440	6.1741430	-1.5951470	H	6.6771470	-1.7078910	-2.1162470
C	-1.1192900	-3.8735710	-2.2007920	C	-1.1644490	4.8678930	-1.2041730	H	3.7154950	0.4095980	-4.3889210
C	-1.3549500	-3.2500780	-0.9232260	C	4.1827400	-0.3919240	2.1834550	H	2.2118610	0.4141530	-2.4183590
C	-1.2849510	-1.8162200	-0.9092920	C	3.6070060	-0.6155460	-1.1509170	C	-1.2163310	-5.2788390	-2.3543610
C	-0.9359500	-1.1397670	-2.0668980	C	4.3157970	-0.9863630	3.4426530	C	-4.6076490	-0.6148300	2.5960990
C	-1.5861550	-0.7532140	0.2119920	C	5.4752440	-0.8136240	4.1838720	C	-4.1518360	-0.8340290	-0.1622940
C	-0.5201240	-0.7373930	1.3279170	C	6.5143890	-0.0342330	3.6838910	C	-5.4434930	-0.7960640	0.3750600
C	-0.9235850	-0.6076540	2.7016700	C	6.3851480	0.5728620	2.4399620	C	-5.6842190	-0.6933190	1.7356950
C	-2.2150060	-0.5518670	3.0544750	C	5.2284760	0.3945030	1.6914090	C	-1.6192880	-4.1335890	0.1841770
C	-3.3027250	-0.6490690	2.0995720	C	4.8672500	-1.2157800	-1.0756350	C	-1.7008760	-5.4897400	-0.0322300
C	-3.0511170	-0.7769280	0.7179680	C	5.7042140	-1.2311460	-2.1841350	C	-1.5169120	-6.0797570	-1.2948380
C	-0.9476090	0.2817580	-1.8167690	C	5.2957850	-0.6430970	-3.3759140	H	-1.0405030	-5.6988710	-3.3403150
C	0.8207440	-0.7199890	1.0521760	C	4.0400220	-0.0485340	-3.4597720	H	-4.7581400	-0.5201180	3.6673640
N	1.7793820	-0.6278320	2.0659010	C	3.1962490	-0.0391300	-2.3588320	H	-6.2837890	-0.8463700	-0.3103570
C	2.9197190	-0.5554840	1.4456870	H	-0.3952060	-1.1583950	-4.1524120	H	-6.7012870	-0.6680980	2.1135480
C	2.6686110	-0.6259340	-0.0184440	H	-0.5997650	-3.6480220	-4.2785200	H	-1.9010590	-6.1331700	0.8193840
N	1.3866320	-0.7232550	-0.2127070	H	-0.1305850	-0.5324910	3.4341910	H	-1.5946170	-7.1561460	-1.4094530
N	-0.6280710	1.3808920	-2.4446410	H	-2.4845990	-0.4289400	4.0992010	H	5.9535960	-0.6508770	-4.2397220
C	-0.8525590	2.3856060	-1.5209080	H	0.4223960	2.9146340	1.4314220	H	7.4214150	0.1021200	4.2647810
C	-1.3097720	1.8582940	-0.3211560	H	-0.0807170	3.9993340	3.5985420	H	0.1312750	7.4513440	-2.9894050
N	-1.3848790	0.4972530	-0.5563850	H	-4.2664750	3.2892710	2.9689120	H	-2.4299270	4.1872440	4.3745390
C	-1.6312400	2.4892230	0.9755750	H	-3.7563930	2.2156380	0.8024810	C	-4.0702270	-0.9150490	-1.6685410
C	-0.6031070	3.7887980	-1.8944410	H	0.6351300	3.2210030	-3.5443810	H	-3.4767150	-0.1045650	-2.0953840
C	-2.9512970	2.6028690	1.4186390	H	1.1175790	5.5482400	-4.2446190	H	-3.6346470	-1.8560610	-2.0103980
C	-0.8893550	3.6080110	2.9891020	H	-1.3454460	6.9974620	-1.0461210	H	-5.0752870	-0.8427340	-2.0904970
C	-2.2062100	3.7115240	3.4244250	H	-1.8239350	4.6891080	-0.3633580	C	-1.7624400	-3.6717890	1.6067370
C	-3.2359030	3.2079630	2.6370040	H	3.4946150	-1.5815990	3.8262840	H	-0.8732160	-3.1387710	1.9477750
C	-0.6037950	2.9998050	1.7735540	H	5.5691110	-1.2871980	5.1562650	H	-2.6230580	-3.0196690	1.7516420
C	0.2152860	4.0571250	-2.9971610	H	7.1864540	1.1925730	2.0497980	H	-1.8935900	-4.5339770	2.2650820
C	0.4774960	5.3625850	-3.3869810	H	5.1311620	0.8802760	0.7270720				

SCF Done: E(RCAM-B3LYP) = -2220.97558791 A.U.

Low frequencies --- -1.6973 -1.1643 -0.0004 0.0002 0.0004 1.1804

Zero-point correction	=	0.746280 (Hartree/Particle)
Thermal correction to Energy	=	0.788810
Thermal correction to Enthalpy	=	0.789754
Thermal correction to Gibbs Free Energy	=	0.667799
Sum of electronic and zero-point Energies	=	-2220.229308
Sum of electronic and thermal Energies	=	-2220.186778
Sum of electronic and thermal Enthalpies	=	-2220.185834
Sum of electronic and thermal Free Energies	=	-2220.307789

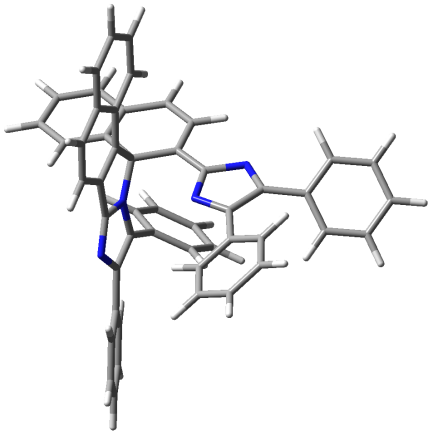


Table S10. Standard Orientation of the Optimized Geometry for 6MR of **2**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-1.2343750	-0.6745840	2.7396970	C	5.4694680	-2.3395840	3.1900890	H	2.1932900	4.5313170	-1.6068530
C	-2.3575710	-0.4919490	3.4942200	C	4.5480490	-3.3682720	3.0300630	H	2.5750320	6.8327350	-0.8084120
C	-3.5100530	0.1115490	2.9383580	C	3.3654450	-3.1441400	2.3360680	H	0.8955470	5.7930610	3.0017640
C	-3.5294550	0.4734630	1.5560450	C	3.1567700	1.8250290	-1.7284320	H	0.4911590	3.4823090	2.1810290
C	-2.4370860	0.0136910	0.7398780	C	1.3310950	3.8529860	0.2472060	C	-4.6220710	0.3946910	3.7698870
C	-1.2754560	-0.4132600	1.3588160	C	3.4540970	1.2654230	-2.9744180	C	-4.6684760	-0.3794230	-3.7509450
C	-2.4470060	0.0031540	-0.7476850	C	4.7153630	1.4197290	-3.5304140	C	-4.6118910	-1.3084210	-1.0873520
C	-1.2944660	0.4333010	-1.3807700	C	5.7005440	2.1223830	-2.8424870	C	-5.6643610	-1.5730710	-1.9337340
C	-1.2727030	0.6993530	-2.7605930	C	5.4180310	2.6674860	-1.5956440	C	-5.7294170	-1.0754610	-3.2498370
C	-2.4042670	0.5147690	-3.5017490	C	4.1516380	2.5245410	-1.0410570	C	-4.5985300	1.3239220	1.1055080
C	-3.5473320	-0.0940020	-2.9326100	C	1.9151530	4.8024430	-0.5940950	C	-5.6416110	1.5862190	1.9642300
C	-3.5490280	-0.4569710	-1.5503760	C	2.1282790	6.0996850	-0.1440330	C	-5.6904010	1.0881330	3.2808920
C	-0.0236020	-0.5724400	0.5053550	C	1.7678890	6.4576180	1.1500790	H	-4.5911690	0.0685890	4.8056420
C	-0.0315280	0.5898790	-0.5451200	C	1.1822680	5.5167180	1.9919180	H	-4.6506570	-0.0527170	-4.7867960
N	1.1765030	0.5089240	-1.3431050	C	0.9587580	4.2233840	1.5421610	H	-6.4577430	-2.2273290	-1.5825370
C	1.8218040	1.5967180	-1.1393170	H	-0.3145550	-1.0319800	3.1865400	H	-6.5906250	-1.3009950	-3.8711030
C	1.0301470	2.4829390	-0.2147840	H	-2.3608970	-0.7454410	4.5504150	H	-6.4397690	2.2397560	1.6227360
N	-0.0369850	1.8754990	0.1439680	H	-0.3613900	1.0657070	-3.2176950	H	-6.5447920	1.3119410	3.9121460
N	1.1854630	-0.4942600	1.3030730	H	-2.4222620	0.7714120	-4.5569830	H	1.9401270	7.4702140	1.5019240
C	1.8133810	-1.5953750	1.1199360	H	3.5004160	-3.4594250	-0.4796090	H	6.6882320	2.2413610	-3.2772440
C	1.0365760	-2.4647480	0.1676650	H	3.9971770	-5.6770050	-1.4338510	H	6.3962080	-2.5184170	3.7266610
N	-0.0328790	-1.8572710	-0.1845620	H	-0.1791590	-6.6596060	-1.3354840	H	2.1631850	-7.2918740	-1.8538840
C	1.3777750	-3.8032700	-0.3537030	H	-0.6739040	-4.4152480	-0.3958460	C	-4.5926160	-2.0470190	0.2321090
C	3.0899460	-1.8821510	1.8048120	H	3.7905880	0.1283600	1.5697990	H	-3.5768630	-2.2861940	0.5517240
C	0.3467890	-4.7105540	-0.6124630	H	5.9177300	-0.2742740	2.7851240	H	-5.0682330	-1.4855380	1.0394550
C	2.9719140	-5.4112640	-1.1959930	H	4.7488710	-4.3501860	3.4468730	H	-5.1384300	-2.9882390	0.1204370
C	1.9427910	-6.3143580	-1.4358980	H	2.6496200	-3.9500150	2.2157220	C	-4.5937540	2.0647770	-0.2127490
C	0.6288390	-5.9603500	-1.1441990	H	2.6840880	0.7031430	-3.4911360	H	-3.5816770	2.3072640	-0.5411210
C	2.6936310	-4.1623330	-0.6540860	H	4.9326830	0.9873800	-4.5021210	H	-5.0769080	1.5041070	-1.0161690
C	4.0153300	-0.8502000	1.9794790	H	6.1855040	3.2071060	-1.0496830	H	-5.1396310	3.0049440	-0.0935160
C	5.2010680	-1.0802890	2.6622830	H	3.9398080	2.9505630	-0.0668290				

SCF Done: E(RCAM-B3LYP) = -2220.96568421 A.U.

Low frequencies --- -1.2848 -0.0010 -0.0008 0.0004 0.3368 0.9555

Zero-point correction	=	0.745478 (Hartree/Particle)
Thermal correction to Energy	=	0.787723
Thermal correction to Enthalpy	=	0.788667
Thermal correction to Gibbs Free Energy	=	0.667499
Sum of electronic and zero-point Energies	=	-2220.220206
Sum of electronic and thermal Energies	=	-2220.177961
Sum of electronic and thermal Enthalpies	=	-2220.177017
Sum of electronic and thermal Free Energies	=	-2220.298185

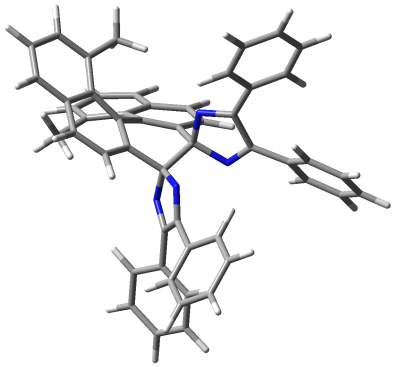


Table S11. Standard Orientation of the Optimized Geometry for 8MR of **2**.

	X	Y	Z		X	Y	Z		X	Y	Z
N	-0.9334570	0.5360940	2.2617270	H	6.0096360	1.7362170	3.2313370	H	3.6095750	1.6425300	3.8520430
N	1.4514780	-0.4832740	-0.3632270	C	-4.6862350	0.9661030	-0.2043050	C	-2.6341710	-3.1401680	-2.0109470
N	-1.4514350	-0.4832530	0.3632160	H	-4.9840520	0.7841320	0.8234050	C	-0.6301410	-0.4501550	1.4581130
N	0.9335020	0.5360120	-2.2617710	C	-2.8937790	3.6961430	4.3301470	C	-3.1442370	3.4401900	1.5760350
C	2.6342050	-3.1401040	2.0110370	H	-2.7880240	3.7925790	5.4067270	H	-3.2247040	3.3608390	0.4981540
C	0.6301870	-0.4502130	-1.4581270	C	-1.9733110	1.2134550	1.6654250	C	-3.9161320	1.4484880	-2.8288740
C	2.5238250	2.4213800	-2.3049410	C	4.6495600	-4.2401960	1.2728140	H	-3.6096990	1.6424010	-3.8520590
C	2.3963170	2.5700590	-3.6894970	H	5.4765370	-4.9229240	1.4398470	C	5.6436460	1.2661070	1.1643850
H	1.8939780	1.7905860	-4.2514520	C	3.5240870	4.6975600	-3.5991030	H	6.6915740	1.3105070	0.8842500
C	1.9733360	1.2134090	-1.6654750	H	3.9134300	5.5788160	-4.0998550	C	-2.5467090	-2.4150460	-0.7823290
C	-2.3962880	2.5701520	3.6894150	C	-3.5241000	4.6976290	3.5989810	C	-3.5053980	-2.7050730	0.2493940
H	-1.8939240	1.7907050	4.2513840	H	-3.9134520	5.5788910	4.0997140	C	-3.4074210	-2.1844290	1.6627020
C	1.6435630	-2.9780930	3.0107660	C	-2.9545020	1.1551210	-1.8699100	H	-3.5483470	-1.1048850	1.7407940
H	1.7443670	-3.5433840	3.9324560	H	-1.9038690	1.1332390	-2.1443220	H	-2.4340260	-2.4169650	2.1035910
C	3.3327630	0.9057540	0.5464650	C	0.4868510	-1.3883650	1.6375980	H	-4.1697310	-2.6646550	2.2808260
C	3.7072960	-4.0363750	2.2369780	C	4.5219160	-3.5883710	0.0309630	C	-0.5751790	-2.1536810	-2.8199610
H	3.7560980	-4.5573480	3.1884710	H	5.2414550	-3.8121630	-0.7510250	H	0.1949890	-2.0379850	-3.5743610
C	1.4773730	-1.4683800	0.6796270	C	3.1442170	3.4401700	-1.5761290	C	-1.6435170	-2.9782180	-3.0106740
C	0.5752270	-2.1535610	2.8200170	H	3.2246690	3.3608490	-0.4982450	H	-1.7443180	-3.5435560	-3.9323360
H	-0.1949350	-2.0378240	3.5744170	C	2.8937960	3.6960420	-4.3302520	C	-4.5219330	-3.5882710	-0.0308810
C	-2.5238150	2.4214320	2.3048660	H	2.7880570	3.7924460	-5.4068370	H	-5.2414980	-3.8119890	0.7511040
C	2.5467360	-2.4150490	0.7823790	C	-5.2610730	1.5038380	-2.4800090	C	3.4073850	-2.1846570	-1.6627030
C	-2.3146710	0.6009350	0.4765070	H	-6.0097500	1.7359900	-3.2313020	H	3.5483400	-1.1051250	-1.7409020
C	3.5053930	-2.7051730	-0.2493490	C	2.9544430	1.1551870	1.8698880	H	2.4339700	-2.4172080	-2.1035400
C	4.6862210	0.9662190	0.2043240	H	1.9038060	1.1332610	2.1442770	H	4.1696620	-2.6649640	-2.2808050
H	4.9840690	0.7842460	-0.8233770	C	3.6427940	4.5654710	-2.2202720	C	-1.4773330	-1.4683920	-0.6796070
C	-3.6428250	4.5655000	2.2201550	H	4.1183900	5.3483200	-1.6370550	C	-3.7072730	-4.0364350	-2.2368500
H	-4.1184450	5.3483230	1.6369230	C	-0.4868060	-1.3884270	-1.6375780	H	-3.7560700	-4.5574640	-3.1883120
C	2.3146870	0.6009340	-0.4765320	C	-5.6436940	1.2659310	-1.1643500	C	-4.6495590	-4.2401780	-1.2726900
C	-3.3327810	0.9056930	-0.5464740	H	-6.6916180	1.3102890	-0.8841930	H	-5.4765480	-4.9229000	-1.4396970
C	5.2609850	1.5040180	2.4800310	C	3.9160390	1.4486140	2.8288680				

SCF Done: E(RCAM-B3LYP) = -2221.03248782 A.U.

Low frequencies --- -2.0604 -1.8044 0.0002 0.0003 0.0006 0.8605

Zero-point correction	=	0.747754 (Hartree/Particle)
Thermal correction to Energy	=	0.789870
Thermal correction to Enthalpy	=	0.790814
Thermal correction to Gibbs Free Energy	=	0.670698
Sum of electronic and zero-point Energies	=	-2220.284734
Sum of electronic and thermal Energies	=	-2220.242618
Sum of electronic and thermal Enthalpies	=	-2220.241674
Sum of electronic and thermal Free Energies	=	-2220.361790

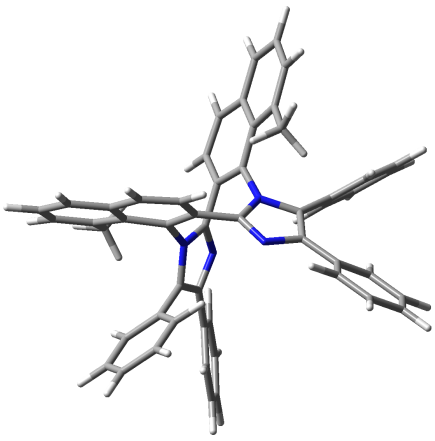


Table S12. Standard Orientation of the Optimized Geometry for BR of **2**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.0787870	1.0797730	2.9205720	C	-5.1466840	-4.1579370	3.8495180	H	5.6179890	-1.7340270	-0.4706610
C	1.0690960	1.8996120	3.3448440	C	-5.7771160	-3.4097150	2.8616070	H	7.2757880	-2.0166780	1.3275660
C	1.7088850	2.8022080	2.4549220	C	-5.0531680	-2.4948040	2.1083170	H	4.3966740	-0.6494500	4.2019070
C	1.3159950	2.8603550	1.0815270	C	3.5138110	-2.6427260	-2.1130050	H	2.7354820	-0.3500860	2.3846270
C	0.2493630	1.9901280	0.6542550	C	4.0503530	-1.0517210	0.8426770	C	2.7343170	3.6287070	2.9623080
C	-0.3592990	1.1138790	1.5650880	C	3.6037310	-2.7276830	-3.5085980	C	-2.7309080	3.4293500	-3.1495340
C	-0.2125610	1.9487410	-0.7706590	C	4.1770930	-3.8361150	-4.1115330	C	-1.9598410	3.8011440	-0.4600490
C	0.3748760	1.0055080	-1.6265760	C	4.6559160	-4.8866830	-3.3330120	C	-2.9665380	4.5374950	-1.0495300
C	-0.0859500	0.8775060	-2.9680840	C	4.5533590	-4.8220830	-1.9478810	C	-3.3642460	4.3665870	-2.3848770
C	-1.0787120	1.6694880	-3.4340380	C	3.9884100	-3.7087680	-1.3397280	C	2.0241970	3.7917830	0.2355120
C	-1.6936750	2.6420850	-2.6031310	C	5.3406550	-1.5137380	0.5536600	C	3.0167400	4.5729710	0.7894210
C	-1.2741340	2.8012690	-1.2451470	C	6.2767840	-1.6661370	1.5675240	C	3.3825710	4.5070850	2.1430150
C	-1.4487270	0.2097820	1.2467700	C	5.9395520	-1.3638990	2.8823940	H	2.9928370	3.5461970	4.0139020
C	1.4579100	0.1132230	-1.2595060	C	4.6628030	-0.8932020	3.1779440	H	-3.0089060	3.2697710	-4.1873390
N	1.8887500	-0.8465000	-2.1424740	C	3.7276260	-0.7294370	2.1682630	H	-3.4752770	5.2851680	-0.4489180
C	2.8604490	-1.4757910	-1.5149490	H	-0.4150280	0.3902920	3.5925310	H	-4.1631490	4.9764360	-2.7950740
C	3.0506090	-0.8272410	-0.2014490	H	1.3921500	1.8834780	4.3819860	H	3.5423150	5.2698870	0.1438860
N	2.1478540	0.1309230	-0.0854990	H	0.3822940	0.1286100	-3.5926050	H	4.1728330	5.1470360	2.5227940
N	-1.8977600	-0.6850400	2.1869910	H	-1.4281220	1.5710910	-4.4577190	H	6.6716150	-1.4886080	3.6744950
C	-2.8946510	-1.3196060	1.6055640	H	-4.0908800	-3.2591530	-0.3028390	H	5.1022120	-5.7560210	-3.8060840
C	-3.0316430	-0.7927390	0.2320830	H	-5.5171970	-3.8643550	-2.2167210	H	-5.7136700	-4.8762270	4.4337330
N	-2.1311850	0.1607140	0.0698690	H	-5.3326840	0.1816660	-3.6379480	H	-6.1567450	-2.1465100	-3.8872950
C	-3.9160900	-1.1854500	-0.8648870	H	-3.8819600	0.7815990	-1.7197440	C	-1.6723710	4.1361580	0.9854150
C	-3.6841550	-2.3134930	2.3373160	H	-2.0078130	-2.8979550	3.5357810	H	-1.8154450	3.2833860	1.6508590
C	-4.2594640	-0.2284680	-1.8302480	H	-3.2914370	-4.5551020	4.8658190	H	-0.6538050	4.4973180	1.1377620
C	-5.1752480	-2.8403000	-2.1036480	H	-6.8400100	-3.5334920	2.6789880	H	-2.3523950	4.9268300	1.3116480
C	-5.5282080	-1.8782190	-3.0435960	H	-5.5560770	-1.9034480	1.3518430	C	1.7792240	4.0014540	-1.2409290
C	-5.0657360	-0.5721030	-2.9036120	H	3.2140310	-1.9092700	-4.1031320	H	1.9417370	3.0932600	-1.8234390
C	-4.3768640	-2.4987290	-1.0202480	H	4.2489760	-3.8842570	-5.1937050	H	0.7665770	4.3468060	-1.4564430
C	-3.0635720	-3.0581470	3.3489650	H	4.9091380	-5.6451320	-1.3359780	H	2.4706970	4.7609030	-1.6140410
C	-3.7873850	-3.9774570	4.0919030	H	3.8966580	-3.6740540	-0.2602390				

SCF Done: E(UCAM-B3LYP) = -2220.95482360 A.U.
S**2 before annihilation 1.1164, after 0.9782

Low frequencies --- -1.2218 -0.9851 -0.0006 0.0002 0.0005 0.5366
Zero-point correction = 0.742335 (Hartree/Particle)
Thermal correction to Energy = 0.785619
Thermal correction to Enthalpy = 0.786563
Thermal correction to Gibbs Free Energy = 0.660491
Sum of electronic and zero-point Energies = -2220.212489
Sum of electronic and thermal Energies = -2220.169205
Sum of electronic and thermal Enthalpies = -2220.168261
Sum of electronic and thermal Free Energies = -2220.294332

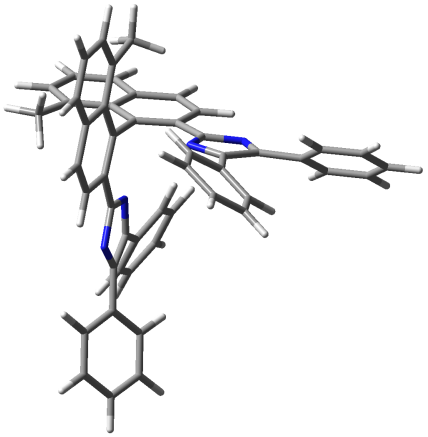


Table S13. Standard Orientation of the Optimized Geometry for TS1 of **2**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-1.4373540	1.0264550	2.6816860	C	5.7477220	-0.5788360	3.0245860	H	2.5073530	3.7110280	-2.6131300
C	-2.5204660	1.7571230	3.0710180	C	5.1272170	-1.8230310	3.0262930	H	2.9642790	6.1196990	-2.3398240
C	-3.6189730	1.9421970	2.2002730	C	3.8455200	-1.9660090	2.5117210	H	0.5234560	6.1842130	1.1898560
C	-3.6208880	1.3262170	0.9089140	C	3.1715780	0.9103830	-1.8025420	H	0.0533010	3.7613110	0.8978710
C	-2.5713710	0.3885330	0.6211290	C	1.2662570	3.5752650	-0.8576240	C	-4.6947120	2.7679500	2.6103560
C	-1.4641850	0.3268710	1.4563600	C	3.6068520	-0.1532720	-2.6063140	C	-4.6311790	-2.9192370	-2.5681880
C	-2.5635380	-0.4866840	-0.5853110	C	4.9493550	-0.3008610	-2.9144710	C	-4.6129640	-1.8743110	0.0545550
C	-1.4608140	-0.3981970	-1.4236310	C	5.8854180	0.6025160	-2.4162230	C	-5.6013500	-2.7204310	-0.3930960
C	-1.4201900	-1.0961750	-2.6484110	C	5.4678760	1.6499160	-1.6044460	C	-5.6467160	-3.2190270	-1.7095870
C	-2.4856170	-1.8528810	-3.0350620	C	4.1214960	1.8062240	-1.2990490	C	-4.6525890	1.7288160	-0.0146960
C	-3.5763330	-2.0654480	-2.1611700	C	2.0826900	4.2482920	-1.7717090	C	-5.6619560	2.5482690	0.4357650
C	-3.5913090	-1.4486940	-0.8700780	C	2.3362450	5.6053400	-1.6190800	C	-5.7189390	3.0423520	1.7534950
C	-0.2292680	-0.3905440	1.0638440	C	1.7817880	6.3034220	-0.5516990	H	-4.6721300	3.1876590	3.6119920
C	-0.2483480	0.3590490	-1.0373050	C	0.9620970	5.6417600	0.3581300	H	-4.5990650	-3.3398000	-3.5691740
N	0.9774660	-0.0592170	-1.5055670	C	0.6988680	4.2885530	0.2040020	H	-6.3621370	-3.0427990	0.3122650
C	1.7452420	1.0003820	-1.4741910	H	-0.5569730	0.9468550	3.3076500	H	-6.4581620	-3.8736000	-2.0121750
C	0.9201550	2.1557480	-1.0193650	H	-2.5374480	2.2459720	4.0408760	H	-6.4305800	2.8537480	-0.2685320
N	-0.2794350	1.7285010	-0.7564510	H	-0.5437420	-0.9966890	-3.2770250	H	-6.5467400	3.6750750	2.0582540
N	0.9780370	0.0732170	1.5438230	H	-2.4920010	-2.3444140	-4.0035810	H	1.9842160	7.3633190	-0.4314690
C	1.7875200	-0.9539680	1.4980660	H	3.4177390	-2.8550820	-0.1236530	H	6.9374850	0.4859210	-2.6574940
C	1.0287930	-2.1201030	0.9616990	H	4.1072690	-5.1306990	-0.7821710	H	6.7518920	-0.4708580	3.4230580
N	-0.2001540	-1.7518110	0.7512550	H	0.3257030	-6.6639090	0.5470780	H	2.5704030	-7.0461070	-0.4378120
C	1.4897610	-3.4712690	0.6122310	H	-0.3669520	-4.3690800	1.1915320	C	-4.6288140	-1.5397750	1.5288370
C	3.1647660	-0.8603090	1.9885310	H	3.2487440	1.2492510	1.6305710	H	-3.6254410	-1.5266340	1.9572280
C	0.6178880	-4.5523680	0.7764450	H	5.5510340	1.5046160	2.5211540	H	-5.0870200	-0.5707310	1.7381170
C	3.1312000	-4.9723330	-0.3340870	H	5.6403550	-2.6876550	3.4353980	H	-5.2087860	-2.2991930	2.0602050
C	2.2667250	-6.0451540	-0.1467580	H	3.3648490	-2.9365630	2.5336550	C	-4.6569690	1.4007010	-1.4902990
C	1.0077680	-5.8310620	0.4070100	H	2.8695150	-0.8557110	-2.9776830	H	-5.2573510	2.1459930	-2.0188670
C	2.7483010	-3.6917750	0.0441550	H	5.2696880	-1.1235700	-3.5462230	H	-3.6525390	1.4196110	-1.9159200
C	3.7917490	0.3926140	2.0116650	H	6.1933430	2.3492150	-1.2007250	H	-5.0865860	0.4198870	-1.7050790
C	5.0741030	0.5294150	2.5180960	H	3.8109760	2.6192260	-0.6544700				

SCF Done: E(UCAM-B3LYP) = -2220.92531362 A.U.
S**2 before annihilation 0.4445, after 0.0819

Low frequencies --- -622.0767 -0.3206 -0.0007 -0.0004 0.0003 1.6047
****** 1 imaginary frequencies (negative Signs) ******
Zero-point correction = 0.742139 (Hartree/Particle)
Thermal correction to Energy = 0.784569
Thermal correction to Enthalpy = 0.785513
Thermal correction to Gibbs Free Energy = 0.664179
Sum of electronic and zero-point Energies = -2220.183175
Sum of electronic and thermal Energies = -2220.140745
Sum of electronic and thermal Enthalpies = -2220.139801
Sum of electronic and thermal Free Energies = -2220.261135

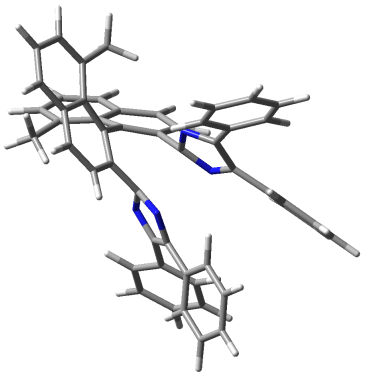


Table S14. Standard Orientation of the Optimized Geometry for TS2 of **2**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.2312540	2.8243920	2.0104750	C	-6.6011230	-1.4022200	4.0664040	H	5.7941130	-0.5821850	1.0301450
C	0.7308850	3.7487470	1.7623070	C	-5.9900690	-2.3488080	3.2519610	H	7.0152080	0.1860660	3.0253310
C	1.3575510	3.8407110	0.4878060	C	-4.9050830	-1.9989480	2.4587790	H	3.3105480	1.3629430	4.8447530
C	0.9909650	2.9615780	-0.5832450	C	4.4229360	-2.5270850	-0.4675360	H	2.0878310	0.6081060	2.8224800
C	-0.0072730	1.9682360	-0.2762040	C	3.8508020	-0.0681070	1.8079280	C	2.3339130	4.8440190	0.3004500
C	-0.5714750	1.9158620	0.9865660	C	4.8725230	-2.9538740	-1.7225710	C	-3.0423050	0.4259570	-4.0019810
C	-0.5179330	0.9209770	-1.2292440	C	5.8378990	-3.9437480	-1.8254300	C	-2.6071380	2.2717350	-1.9185330
C	0.4213670	-0.1282780	-1.6182420	C	6.3583260	-4.5345010	-0.6773210	C	-3.6884140	2.3704160	-2.7883650
C	0.1165290	-0.9667150	-2.7320420	C	5.9048370	-4.1306810	0.5733640	C	-3.9255210	1.4618650	-3.8161800
C	-1.0109690	-0.7799800	-3.4467160	C	4.9454360	-3.1320220	0.6803450	C	1.6090920	3.1883410	-1.8626030
C	-1.9298300	0.2843740	-3.1617900	C	5.2447330	-0.1732830	1.8701890	C	2.5501710	4.1892520	-1.9828120
C	-1.6895680	1.1887740	-2.0876110	C	5.9330940	0.2662120	2.9935050	C	2.9340040	5.0134250	-0.9140440
C	-1.5262860	0.8593670	1.1912120	C	5.2411700	0.8118540	4.0688640	H	2.5888560	5.4796640	1.1433180
C	1.5756540	-0.4423940	-0.8837760	C	3.8551150	0.9314220	4.0106540	H	-3.1852530	-0.2935730	-4.8022840
N	2.4253520	-1.4544020	-1.3069710	C	3.1648780	0.5034840	2.8874760	H	-4.3789110	3.1963330	-2.6506920
C	3.3634950	-1.5120810	-0.3988880	H	-0.7339120	2.7462490	2.9681550	H	-4.7893650	1.5809850	-4.4622650
C	3.0886020	-0.4700380	0.6211510	H	1.0385890	4.4498840	2.5326540	H	3.0078890	4.3492840	-2.9546310
N	1.9780970	0.1420720	0.2930120	H	0.8117230	-1.7627230	-2.9627160	H	3.6835520	5.7838510	-1.0643440
N	-2.5270600	0.8172050	2.0577150	H	-1.2462190	-1.4385130	-4.2772180	H	5.7807180	1.1492010	4.9485760
C	-3.2608650	-0.2617290	1.6588420	H	-1.0169340	-2.8207050	-0.2867900	H	7.1122540	-5.3114700	-0.7583070
C	-2.6551020	-0.8524240	0.5134380	H	-1.5778730	-4.7795120	-1.6907780	H	-7.4509150	-1.6782340	4.6833610
N	-1.5154090	-0.1731670	0.2954720	H	-5.6504140	-3.4436980	-1.9088950	H	-3.9006800	-5.0997110	-2.5058120
C	-3.0125610	-2.0321500	-0.2904230	H	-5.0807000	-1.4904710	-0.5079050	C	-2.5420440	3.3481530	-0.8603920
C	-4.4103380	-0.6895210	2.4658730	H	-4.6169390	1.2559050	3.3356040	H	-2.7594690	2.9551140	0.1355240
C	-4.3159840	-2.2176280	-0.7612630	H	-6.5717570	0.6439500	4.7326270	H	-1.5702520	3.8408440	-0.8122840
C	-2.3501490	-4.0611590	-1.4323450	H	-6.3548760	-3.3714650	3.2371830	H	-3.2917820	4.1113140	-1.0819550
C	-3.6520690	-4.2414360	-1.8888850	H	-4.4295700	-2.7530400	1.8439180	C	1.3040800	2.4155870	-3.1235110
C	-4.6333160	-3.3153530	-1.5508630	H	4.4494340	-2.4954660	-2.6093660	H	1.7746100	1.4295220	-3.1293770
C	-2.0320810	-2.9655310	-0.6412340	H	6.1848900	-4.2587030	-2.8046830	H	0.2349370	2.2702950	-3.2847030
C	-5.0195710	0.2500530	3.3091050	H	6.2952770	-4.5980750	1.4719180	H	1.6903490	2.9635840	-3.9866060
C	-6.1078730	-0.1008990	4.0928190	H	4.5870120	-2.8326880	1.6587020				

SCF Done: E(UCAM-B3LYP) = -2220.92420670 A.U.
S**2 before annihilation 0.5394, after 0.2018

Low frequencies ----1077.3289 -1.4287 -0.0005 0.0005 0.0008 1.4563
****** 1 imaginary frequencies (negative Signs) ******
Zero-point correction = 0.741398 (Hartree/Particle)
Thermal correction to Energy = 0.784016
Thermal correction to Enthalpy = 0.784960
Thermal correction to Gibbs Free Energy = 0.662053
Sum of electronic and zero-point Energies = -2220.182809
Sum of electronic and thermal Energies = -2220.140191
Sum of electronic and thermal Enthalpies = -2220.139247
Sum of electronic and thermal Free Energies = -2220.262154

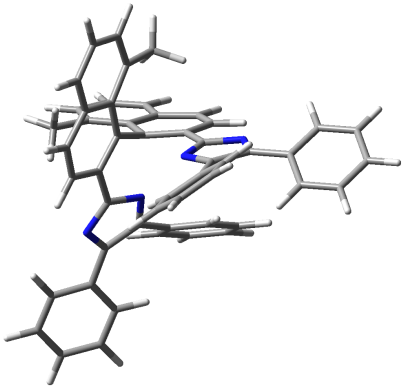


Table S15. Standard Orientation of the Optimized Geometry for 5MR of **3**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.2056480	-1.8695780	-5.3283550	C	-2.6076940	-1.1094860	-1.2950560	H	-9.7147010	-1.7779980	-0.7684060
C	-0.4491330	-1.1555470	-6.4687590	H	-0.6731640	-2.8306050	-5.1451170	C	-9.4903520	-5.6383570	-0.7738680
C	0.1604510	0.1073550	-6.6983200	H	-1.1236690	-1.5461480	-7.2251570	H	-7.3621990	-5.3586910	-0.9251570
C	1.0517550	0.6604480	-5.7294380	H	2.3092740	3.4789420	-1.9866880	C	-10.7319150	-5.0163600	-0.6876700
C	1.2846930	-0.1019550	-4.5615150	H	4.5963360	3.4164890	-2.8602380	H	-11.7781670	-3.1378030	-0.6186790
C	0.6746180	-1.3243930	-4.3758740	H	1.5657520	-0.3081990	1.0644410	H	-9.4234290	-6.7218190	-0.7755360
C	2.2129720	0.2295690	-3.3679100	H	2.9891000	0.9523900	2.6466820	H	-11.6361590	-5.6133240	-0.6219730
C	1.7764760	1.4932400	-2.6196150	H	6.3528020	0.4065960	0.0439640	C	-5.0200670	7.8018650	4.0956950
C	2.6831770	2.6057260	-2.5062750	H	4.9344000	-0.8656930	-1.5244570	C	-4.8692070	9.1816300	3.9053960
C	3.9390860	2.5607740	-2.9855990	H	-0.3379000	-4.3998900	-0.7232370	C	-5.8368000	7.3425990	5.1372240
C	4.4778730	1.3908860	-3.6559030	H	-0.5194580	-6.0288410	1.1346770	C	-5.5214950	10.0781320	4.7391040
C	3.6715490	0.2610280	-3.8413600	H	3.1625200	-4.5568870	2.7609830	H	-4.2369690	9.5383970	3.0994130
C	1.0919230	-1.8386410	-3.0845810	H	3.3407210	-2.9479460	0.9168860	C	-6.4859100	8.2450530	5.9669780
C	0.5414080	1.5838220	-2.0418570	H	-0.9966130	5.0705830	-1.0028780	H	-5.9542240	6.2745310	5.2856860
N	0.1279620	2.7101340	-1.3293110	H	-2.1639190	6.6865630	0.4729030	C	-6.3308310	9.6137630	5.7711430
C	-1.0638560	2.4157540	-0.8999060	H	-3.8912440	3.4237190	2.6544890	H	-5.3976230	11.1451770	4.5827870
C	-1.4252870	1.0574970	-1.3928980	H	-2.7475920	1.8228440	1.1744730	H	-7.1162880	7.8783460	6.7710230
N	-0.4181580	0.5840610	-2.0672450	H	-3.9943180	1.9885100	-1.1572880	H	-6.8399950	10.3176190	6.4220220
N	0.8070980	-2.8304010	-2.2859600	H	-6.0452180	0.6370740	-1.0163200	C	5.5914630	1.5003490	2.3611310
C	1.5483100	-2.5859070	-1.1437690	H	-3.7042010	-2.9499970	-1.2341770	C	6.2872130	2.1197190	3.1312740
C	2.2797880	-1.4118180	-1.2732160	H	-1.6417100	-1.5920720	-1.3999840	C	1.2061100	-6.3377240	3.1570360
N	1.9853200	-0.9692500	-2.5449320	C	-0.1031050	0.8399630	-7.8822950	C	1.1228150	-7.1326550	4.0641710
C	3.1477310	-0.6680490	-0.3420340	C	5.8046610	1.3704780	-4.1014200	C	7.1073830	2.8524450	4.0434650
C	1.4913400	-3.5360750	-0.0228020	C	4.2050000	-0.8623460	-4.4650520	C	6.5538340	3.4143930	5.2012860
C	4.5026960	-0.4588040	-0.6164700	C	5.5244620	-0.8754200	-4.8981390	C	8.4756290	3.0189150	3.7927670
C	3.4121850	0.5537970	1.7311370	C	6.3289700	0.2467120	-4.7170930	C	7.3527280	4.1253260	6.0848850
C	4.7686420	0.7686880	1.4519100	C	1.6370820	1.9273110	-5.9868940	H	5.4946140	3.2863380	5.3968100
C	5.3023480	0.2515120	0.2652060	C	1.3571650	2.6058750	-7.1424830	C	9.2684240	3.7310150	4.6809270
C	2.6165470	-0.1516580	0.8446600	C	0.4788650	2.0585990	-8.1036740	H	8.9058800	2.5836200	2.8971650
C	0.4173260	-4.4310930	0.0534800	H	-0.7823580	0.4126050	-8.6146380	C	8.7107030	4.2860010	5.8283680
C	0.3211630	-5.3445380	1.0877990	H	6.4222890	2.2513730	-3.9506570	H	6.9130840	4.5563450	6.9789320
C	1.3032260	-5.3989340	2.0860180	H	3.5827460	-1.7395260	-4.6091290	H	10.3276100	3.8532980	4.4768690
C	2.3865900	-4.5155440	2.0039380	H	5.9232750	-1.7622830	-5.3798070	H	9.3334170	4.8425840	6.5217470
C	2.4801830	-3.6043410	0.9651570	H	7.3599440	0.2417700	-5.0559120	C	1.0250490	-8.0716740	5.1362690
C	-1.8099380	3.3407360	-0.0344450	H	2.3082350	2.3631580	-5.2565680	C	2.0143600	-8.1257500	6.1270980
C	-2.6696900	0.2898560	-1.2547180	H	1.8128610	3.5746020	-7.3224670	C	-0.0616310	-8.9529070	5.2133210
C	-1.6441200	4.7195870	-0.2073450	H	0.2666560	2.6086550	-9.0149620	C	1.9162090	-9.0389600	7.1667900
C	-2.2904550	5.6195140	0.6200760	C	-6.2061080	-2.0305850	-1.0159580	H	2.8566620	-7.4446270	6.0697640
C	-3.1147950	5.1648020	1.6594580	C	-7.2137590	-2.6943070	-0.9428930	C	-0.1533400	-9.8635050	6.2558860
C	-3.2674030	3.7848020	1.8442560	C	-3.7834920	6.0906720	2.5149840	H	-0.8288650	-8.9130840	4.4475220
C	-2.6256080	2.8870240	1.0071780	C	-4.3500410	6.8753720	3.2391170	C	0.8336560	-9.9102120	7.2353460
C	-3.9212850	0.9072040	-1.1571830	C	-8.4040070	-3.4795990	-0.8566130	H	2.6893530	-9.0709150	7.9283030
C	-5.0786030	0.1500000	-1.0835970	C	-9.6581490	-2.8612500	-0.7694720	H	-1.0003280	-10.5409590	6.3043290
C	-5.0154040	-1.2489850	-1.1019010	C	-8.3326450	-4.8788060	-0.8579240	H	0.7593810	-10.6237970	8.0500420
C	-3.7611730	-1.8672010	-1.2120520	C	-10.8115850	-3.6273200	-0.6857920				

SCF Done: E(RCAM-B3LYP) = -3370.54341963 A.U.

Low frequencies --- -0.8933 -0.0028 -0.0020 -0.0013 0.1768 0.6122

Zero-point correction	=	1.058213 (Hartree/Particle)
Thermal correction to Energy	=	1.125163
Thermal correction to Enthalpy	=	1.126107
Thermal correction to Gibbs Free Energy	=	0.936201
Sum of electronic and zero-point Energies	=	-3369.485207
Sum of electronic and thermal Energies	=	-3369.418257
Sum of electronic and thermal Enthalpies	=	-3369.417313
Sum of electronic and thermal Free Energies	=	-3369.607218

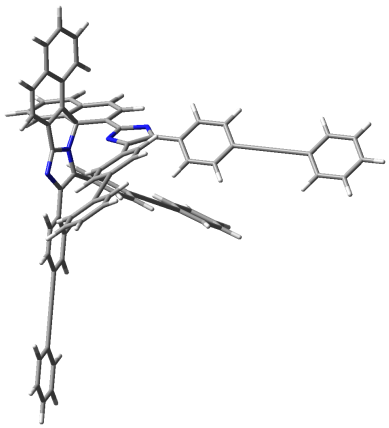


Table S16. Standard Orientation of the Optimized Geometry for 6MR of **3**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.1326330	-3.5680870	2.8798600	C	-4.5246590	-1.2188930	0.7785280	H	-10.8160100	1.4667510	-1.3230850
C	-0.5790470	-4.6200060	3.6289620	H	0.1603070	-2.6391640	3.3535670	C	-12.4805610	0.5854890	2.0541170
C	-1.0775570	-5.7846550	3.0019400	H	-0.6131510	-4.5497440	4.7124010	H	-10.5593990	-0.2032560	2.6171960
C	-1.0314980	-5.8893230	1.5823360	H	-0.5384900	-2.8102880	-3.3091810	C	-13.2245130	1.2065990	1.0558690
C	-0.4067740	-4.8427110	0.8251640	H	0.0111720	-4.8746380	-4.5458360	H	-13.2014520	2.0076500	-0.9406510
C	-0.0694600	-3.6708110	1.4766540	H	3.5381760	0.8726080	0.0882590	H	-12.9445770	0.3362070	3.0032760
C	-0.1993370	-4.9001850	-0.6480930	H	5.9085210	1.2109080	-0.4869600	H	-14.2704520	1.4431960	1.2242550
C	-0.4060870	-3.7403540	-1.3712980	H	6.6004410	-3.0080650	-0.1519400	C	-1.3416630	6.9721180	-5.0112190
C	-0.3432780	-3.7336700	-2.7776490	H	4.2057650	-3.3475020	0.4051850	C	-0.5493370	7.2017900	-6.1434830
C	-0.0222300	-4.8728260	-3.4601600	H	-0.3513490	1.4121570	1.4947830	C	-2.1118060	8.0214750	-4.4932620
C	0.3483800	-6.0442230	-2.7613700	H	-0.0423270	3.5521490	2.7120940	C	-0.5302590	8.4533810	-6.7413250
C	0.2989410	-6.0552160	-1.3380790	H	3.8072720	2.2189640	4.0511000	H	0.0475230	6.3899980	-6.5451460
C	0.3140270	-2.4594070	0.6351920	H	3.5085190	0.1057960	2.8195760	C	-2.0876480	9.2704040	-5.0964520
C	-0.6397830	-2.4428760	-0.6085780	H	-0.0569970	0.1981810	-3.5671290	H	-2.7255520	7.8446550	-3.6165320
N	-0.3514180	-1.2650730	-1.4037950	H	-0.0253180	2.4285150	-4.6511780	C	-1.2981010	9.4902800	-6.2207400
C	-1.4194920	-0.5573110	-1.4086400	H	-2.7753720	3.8862290	-1.7014810	H	0.0872320	8.6207130	-7.6182510
C	-2.4977710	-1.2738600	-0.6398960	H	-2.8308510	1.6617840	-0.6470880	H	-2.6881480	10.0766940	-4.6870530
N	-2.0241680	-2.3601750	-0.1581850	H	-4.2043790	-0.0246060	-2.3836340	H	-1.2811320	10.4686370	-6.6906470
N	0.1693210	-1.2184630	1.3723390	H	-6.5820660	0.4978010	-2.0060260	C	7.7940750	-0.6732600	-0.6744280
C	1.3209040	-0.6575960	1.3701530	H	-6.3296560	-1.1691770	1.9372200	C	8.9587430	-0.5050320	-0.9502910
C	2.2948980	-1.5137980	0.6057830	H	-3.9389370	-1.7165910	1.5432830	C	2.0854210	4.2588640	4.1676630
N	1.6963580	-2.5626700	0.1833780	C	-1.6737050	-6.8234280	3.7632690	C	2.2371670	5.2981300	4.7656990
C	3.7186090	-1.2634900	0.3114080	C	0.8205390	-7.1881290	-3.4560200	C	10.3354130	-0.3061110	-1.2767520
C	1.5580310	0.6231420	2.0633620	C	0.8308370	-7.1929840	-0.6703080	C	10.8264970	0.9815810	-1.5284600
C	4.5930850	-2.3510440	0.2245240	C	1.3109390	-8.2682440	-1.3675650	C	11.2123540	-1.3962290	-1.3495040
C	5.5383240	0.2133080	-0.2777750	C	1.2854560	-8.2807620	-2.7799160	C	12.1637480	1.1708290	-1.8451410
C	6.4189120	-0.8732310	-0.3475800	C	-1.6895490	-6.9988620	0.9830320	H	10.1484410	1.8264210	-1.4727000
C	5.9257830	-2.1609770	-0.0935190	C	-2.2860870	-7.9683760	1.7426370	C	12.5483720	-1.1993310	-1.6667270
C	4.2061480	0.0196800	0.0508280	C	-2.2592460	-7.8967840	3.1531840	H	10.8332510	-2.3937870	-1.1552040
C	0.5597120	1.6013560	2.0512520	H	-1.6751000	-6.7327230	4.8460340	C	13.0280570	0.0828060	-1.9152470
C	0.7314400	2.7926370	2.7334810	H	0.8262830	-7.1650830	-4.5422920	H	12.5335990	2.1729430	-2.0384600
C	1.9057730	3.0316300	3.4611200	H	0.8749930	-7.1973020	0.4107710	H	13.2190630	-2.0511860	-1.7205270
C	2.8999910	2.0454340	3.4830900	H	1.7221480	-9.1168120	-0.8295680	H	14.0739790	0.2338510	-2.1633660
C	2.7290260	0.8589920	2.7882720	H	1.6552980	-9.1460860	-3.3211230	C	2.4169250	6.5263960	5.4731350
C	-1.4616690	0.7696930	-2.0526300	H	-1.7375900	-7.0639370	-0.0958550	C	3.5920870	6.7621190	6.1983990
C	-3.9072800	-0.8897390	-0.4318840	H	-2.7920430	-8.7962600	1.2556680	C	1.4203720	7.5107360	5.4507090
C	-0.6638620	1.0073740	-3.1764950	H	-2.7229710	-8.6801490	3.7446180	C	3.7631370	7.9557670	6.8841340
C	-0.6398280	2.2540260	-3.7747980	C	-7.9910480	0.0210050	0.2135310	H	4.3643320	6.0006010	6.2164850
C	-1.4053300	3.3074480	-3.2540610	C	-9.1555020	0.2852500	0.4007080	C	1.5984440	8.7019660	6.1388570
C	-2.1897430	3.0741210	-2.1179990	C	-1.3832660	4.5948710	-3.8697960	H	0.5100560	7.3291970	4.8894980
C	-2.2197470	1.8202120	-1.5283270	C	-1.3640720	5.6842820	-4.3928800	C	2.7685300	8.9282590	6.8567910
C	-4.6614330	-0.2696240	-1.4311630	C	-10.5321440	0.5970230	0.6222240	H	4.6775800	8.1281750	7.4430620
C	-5.9997000	0.0237090	-1.2236600	C	-11.2883430	1.2222820	-0.3776950	H	0.8198680	9.4579980	6.1149210
C	-6.6153790	-0.2909420	-0.0057780	C	-11.1437710	0.2813410	1.8424310	H	2.9051010	9.8613420	7.3943840
C	-5.8579280	-0.9186380	0.9933980	C	-12.6246810	1.5233650	-0.1588710				

SCF Done: E(RCAM-B3LYP) = -3370.52872393 A.U.

Low frequencies --- -0.5844 -0.3988 -0.0019 -0.0014 0.0004 0.4254

Zero-point correction	=	1.057890 (Hartree/Particle)
Thermal correction to Energy	=	1.124482
Thermal correction to Enthalpy	=	1.125426
Thermal correction to Gibbs Free Energy	=	0.936541
Sum of electronic and zero-point Energies	=	-3369.470834
Sum of electronic and thermal Energies	=	-3369.404242
Sum of electronic and thermal Enthalpies	=	-3369.403297
Sum of electronic and thermal Free Energies	=	-3369.592183

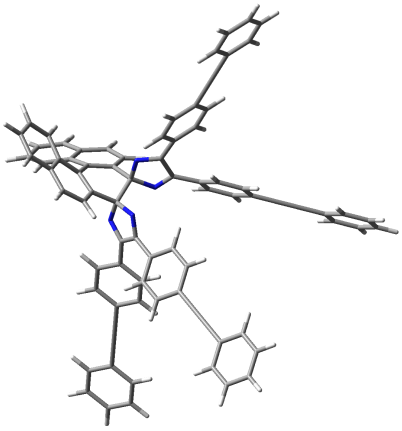


Table S17. Standard Orientation of the Optimized Geometry for BR of **3**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.0206440	-3.6069890	2.6321760	C	3.3931630	-2.2995720	0.4796050	H	9.4757060	-4.6942450	-2.4277690
C	1.0189920	-4.1696430	3.3615390	H	-0.5116350	-4.1716870	1.8771520	C	8.0954840	-8.2965130	-2.6964690
C	1.6940300	-3.4229570	4.3642080	H	1.3068620	-5.2040750	3.1964170	H	6.2948510	-7.5048000	-1.8242110
C	1.3189650	-2.0702860	4.5863450	H	0.6231500	3.1653020	3.2831440	C	9.3862580	-8.0144180	-3.1325690
C	0.2829760	-1.4795940	3.7971090	H	-1.1278900	3.6031830	4.9714620	H	10.8884420	-6.4934590	-3.3744350
C	-0.3743970	-2.2492910	2.8363590	H	-4.0164760	0.3137410	-1.2614310	H	7.7047360	-9.3065760	-2.7703710
C	-0.0912110	-0.0604910	4.0854040	H	-5.1157090	2.4618860	-1.7335860	H	10.0050730	-8.8038500	-3.5475080
C	0.5315260	1.0231680	3.4651220	H	-4.3706380	3.7381190	2.2930900	C	6.8565520	6.7798890	-4.1743630
C	0.1300280	2.3516340	3.7995820	H	-3.2476310	1.5784290	2.7632150	C	7.1441970	8.0876320	-3.7620460
C	-0.8349830	2.5862180	4.7261410	H	-2.5012910	-3.8080550	-1.1420640	C	7.2229620	6.3758670	-5.4648960
C	-1.4729950	1.5084100	5.3969340	H	-4.0572100	-4.8579650	-2.7643850	C	7.7834890	8.9677410	-4.6228030
C	-1.0959230	0.1756310	5.0752470	H	-7.1589130	-2.1795400	-1.4992810	H	6.8606880	8.4016700	-2.7632530
C	-1.4473170	-1.7536770	2.0010310	H	-5.6074500	-1.1286550	0.0957320	C	7.8619060	7.2615710	-6.3201450
C	1.5690890	0.8902610	2.4651950	H	3.6563870	4.0323410	1.4691360	H	7.0004220	5.3637560	-5.7853760
N	2.1072680	1.9936660	1.8561920	H	4.8092660	5.6142680	-0.0551760	C	8.1440370	8.5585030	-5.9027850
C	2.9905130	1.5115570	1.0038090	H	4.9789860	2.5648210	-3.0663460	H	8.0014780	9.9787650	-4.2931570
C	3.0097060	0.0398830	1.1494800	H	3.8518200	0.9930910	-1.5447900	H	8.1411830	6.9381720	-7.3180320
N	2.0964180	-0.2905180	2.0475930	H	5.5663190	0.2953510	0.1804180	H	8.6440730	9.2494660	-6.5742360
N	-2.0644840	-2.5708000	1.0898820	H	6.9663340	-1.4955750	-0.7556260	C	-5.4746090	4.4849680	-0.0248880
C	-2.9908680	-1.8155910	0.5322040	H	3.8034960	-4.3193830	-0.1060380	C	-6.0182630	5.5395080	-0.2579160
C	-2.8901470	-0.4619340	1.1183570	H	2.3998020	-2.5170660	0.8549430	C	-6.6121770	-4.1869630	-3.1768290
N	-1.9379190	-0.4868020	2.0363810	C	2.7217380	-3.9979390	5.1452290	C	-7.3743800	-4.7007700	-3.9621380
C	-3.5886720	0.7794500	0.8014400	C	-2.4700000	1.7330420	6.3739080	C	-6.6603530	6.7850700	-0.5342540
C	-3.9312070	-2.3758740	-0.4371940	C	-1.7452760	-0.8870160	5.7577860	C	-7.1786800	7.0491910	-1.8088710
C	-3.6773110	1.7745570	1.7876680	C	-2.7078520	-0.6400270	6.7012690	C	-6.7803220	7.7592510	0.4655560
C	-4.7233640	2.2599170	-0.7429490	C	-3.0768830	0.6843820	7.0150990	C	-7.8015890	8.2599980	-2.0736000
C	-4.8343290	3.2413200	0.2512680	C	2.0017560	-1.3433930	5.5967200	H	-7.0859290	6.2960030	-2.5839130
C	-4.2970980	2.9795970	1.5214200	C	2.9941580	-1.9262940	6.3404110	C	-7.4046080	8.9677150	0.1934750
C	-4.1113830	1.0488460	-0.4711560	C	3.3609510	-3.2688630	6.1142170	H	-6.3790790	7.5560450	1.4526230
C	-3.5191350	-3.4488870	-1.2405750	H	2.9963280	-5.0328300	4.9612840	C	-7.9166490	9.2219670	-1.0749930
C	-4.3890000	-4.0365300	-2.1387230	H	-2.7451530	2.7576650	6.6082720	H	-8.1993160	8.4543220	-3.0647670
C	-5.7118000	-3.5814980	-2.2513300	H	-1.4714790	-1.9088070	5.5235950	H	-7.4919480	9.7155450	0.9754590
C	-6.1330450	-2.5249500	-1.4330490	H	-3.1904520	-1.4684800	7.2100320	H	-8.4044910	10.1686380	-1.2850960
C	-5.2556580	-1.9313420	-0.5418770	H	-3.8406710	0.8697160	7.7639720	C	-8.2753990	-5.3075690	-4.8896870
C	3.7068610	2.3961100	0.0860860	H	1.7303600	-0.3101290	5.7772320	C	-9.5997030	-4.8610380	-4.9885890
C	3.8636250	-0.9784020	0.5465200	H	3.5027180	-1.3511300	7.1076730	C	-7.8466160	-6.3572370	-5.7126580
C	3.9663230	3.7168090	0.4796440	H	4.1493310	-3.7212390	6.7077540	C	-10.4718350	-5.4527720	-5.8904810
C	4.6023420	4.5982180	-0.3731470	C	6.2901110	-4.0636920	-1.0560470	H	-9.9328560	-4.0485850	-4.3517780
C	4.9851620	4.1927670	-1.6610050	C	6.9789450	-4.9433660	-1.5182700	C	-8.7244280	-6.9440400	-6.6122600
C	4.7051230	2.8808740	-2.0657440	C	5.6414800	5.1005500	-2.5436240	H	-6.8215820	-6.7038650	-5.6368610
C	4.0774340	1.9971530	-1.2047200	C	6.1985300	5.8706080	-3.2908570	C	-10.0379730	-6.4946250	-6.7041950
C	5.1642600	-0.7073810	0.0989360	C	7.7932010	-5.9820880	-2.0642990	H	-11.4958520	-5.0991250	-5.9588350
C	5.9583640	-1.7146520	-0.4207470	C	9.0940690	-5.7066000	-2.5058240	H	-8.3817950	-7.7566770	-7.2451690
C	5.4762880	-3.0273740	-0.5113480	C	7.3018400	-7.2902880	-2.1656180	H	-10.7226840	-6.9557980	-7.4090320
C	4.1803200	-3.3040070	-0.0482090	C	9.8819280	-6.7179850	-3.0354900				

SCF Done: E(UCAM-B3LYP) = -3370.52200492 A.U.
S**2 before annihilation 1.1235, after 1.0309

Low frequencies --- -0.0093 -0.0032 -0.0017 0.1174 0.6787 1.0116
Zero-point correction = 1.054124 (Hartree/Particle)
Thermal correction to Energy = 1.121831
Thermal correction to Enthalpy = 1.122776
Thermal correction to Gibbs Free Energy = 0.929710
Sum of electronic and zero-point Energies = -3369.467881
Sum of electronic and thermal Energies = -3369.400174
Sum of electronic and thermal Enthalpies = -3369.399229
Sum of electronic and thermal Free Energies = -3369.592295

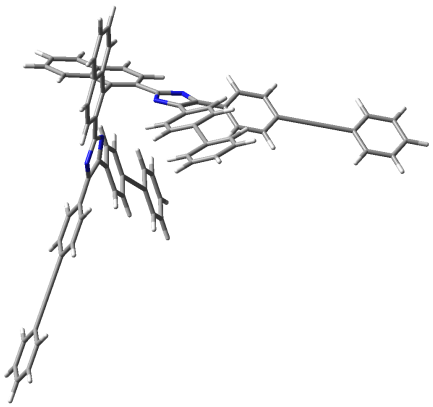


Table S18. Standard Orientation of the Optimized Geometry for TS1 of **3**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-2.0015820	-3.6323650	2.7246240	C	-4.5047270	-1.0576760	-0.0709460	H	-9.6953900	3.1222790	-2.6785830
C	-2.9884390	-4.5103010	3.0696610	H	-1.8312890	-2.7315610	3.3015620	C	-12.1179420	2.1300220	0.1673660
C	-3.2570080	-5.6409350	2.2642600	H	-3.6023550	-4.3315290	3.9478790	H	-10.5113970	0.8965000	0.8936240
C	-2.4528300	-5.8823550	1.1139460	H	0.7518550	-3.4797280	-2.9919650	C	-12.5320920	3.0235750	-0.8153970
C	-1.3503420	-5.0153800	0.8318720	H	1.8322710	-5.6487480	-3.4749710	H	-11.9786890	4.0765110	-2.6079890
C	-1.1775610	-3.8760640	1.6005580	H	2.9649030	0.2598860	0.0950280	H	-12.7954340	1.8487940	0.9675430
C	-0.4632800	-5.2293420	-0.3450550	H	5.3668870	0.4798860	-0.4116260	H	-13.5335070	3.4412960	-0.7838890
C	-0.2363380	-4.1718160	-1.2102540	H	6.0663950	-3.4452170	1.1685940	C	1.6592090	6.8802110	-3.5940360
C	0.6005890	-4.3304190	-2.3387900	H	3.6452140	-3.6693380	1.6619090	C	2.7935440	7.0336760	-4.4018560
C	1.2075580	-5.5255430	-2.5949690	H	-1.2511540	0.9067500	1.5607030	C	0.9805810	8.0214040	-3.1469290
C	1.0753200	-6.6050590	-1.6919500	H	-1.1564930	3.2588900	2.3428840	C	3.2358120	8.3007220	-4.7527050
C	0.2579460	-6.4494830	-0.5360160	H	2.9353800	2.6921870	3.4957400	H	3.3195570	6.1506500	-4.7485240
C	-0.2190330	-2.8129540	1.2194120	H	2.8430390	0.3675130	2.7047310	C	1.4289640	9.2852130	-3.5016430
C	-0.7599920	-2.8137320	-0.9369130	H	1.2040680	-0.1100750	-2.8778530	H	0.1030650	7.9035510	-2.5203600
N	-0.0709370	-1.7218340	-1.4140140	H	1.9970000	2.1518150	-3.5130160	C	2.5561200	9.4289970	-4.3045500
C	-0.9537510	-0.7587480	-1.5004840	H	-1.3798260	3.8802470	-1.5131020	H	4.1156680	8.4085440	-5.3792400
C	-2.2823200	-1.3146130	-1.1147660	H	-2.1744920	1.6372440	-0.9022700	H	0.8962790	10.1629190	-3.1492790
N	-2.1261910	-2.5593440	-0.7738710	H	-3.3640750	0.4873060	-2.8721230	H	2.9046350	10.4192910	-4.5805120
N	-0.4864090	-1.5170210	1.6048660	H	-5.6416310	1.4266110	-2.8058940	C	7.2739170	-1.3305210	0.0650440
C	0.6733500	-0.9092490	1.6135150	H	-6.4669510	-0.8101730	0.7591900	C	8.4523440	-1.2212630	-0.1811590
C	1.7166660	-1.8962120	1.2123340	H	-4.1762250	-1.7682060	0.6794870	C	0.9572210	4.4881320	3.4226660
N	1.1452980	-3.0490410	1.0271760	C	-4.3373360	-6.5110840	2.5590730	C	1.0021660	5.6307870	3.8149590
C	3.1492880	-1.7093890	0.9509960	C	1.7754710	-7.8214450	-1.8959770	C	9.8450790	-1.0924450	-0.4721120
C	0.7937990	0.4841840	2.0403230	C	0.2437600	-7.5104200	0.4123170	C	10.3439530	0.0813450	-1.0519300
C	4.0358010	-2.7565990	1.2262780	C	0.9499850	-8.6627740	0.1993030	C	10.7307350	-2.1383660	-0.1813670
C	4.9918340	-0.4222640	0.0591940	C	1.7135390	-8.8319850	-0.9774940	C	11.6969670	0.2027250	-1.3328770
C	5.8831930	-1.4609740	0.3572870	C	-2.8263590	-6.9568170	0.2591400	H	9.6593520	0.8919310	-1.2775690
C	5.3836230	-2.6333520	0.9429740	C	-3.8899830	-7.7643270	0.5569810	C	12.0825060	-2.0098460	-0.4650980
C	3.6440530	-0.5450210	0.3537660	C	-4.6475260	-7.5533790	1.7307590	H	10.3458050	-3.0478050	0.2673500
C	-0.3337960	1.3153820	1.9673550	H	-4.9258100	-6.3190050	3.4520210	C	12.5697240	-0.8407410	-1.0409250
C	-0.2815120	2.6218020	2.4118000	H	2.3788130	-7.9249830	-2.7936100	H	12.0726400	1.1167250	-1.7822070
C	0.9012370	3.1402120	2.9609530	H	-0.3271570	-7.3943540	1.3245520	H	12.7597110	-2.8266370	-0.2356710
C	2.0227300	2.3058700	3.0555810	H	0.9271100	-9.4529280	0.9433830	H	13.6280050	-0.7430080	-1.2618770
C	1.9692370	0.9991160	2.6021050	H	2.2601830	-9.7557670	-1.1397450	C	1.0559490	6.9804070	4.2795620
C	-0.5519900	0.5987900	-1.8727600	H	-2.2645990	-7.1265990	-0.6502480	C	-0.0843160	7.7931200	4.2326090
C	-3.6091510	-0.6867760	-1.0812150	H	-4.1576010	-8.5717290	-0.1174710	C	2.2494300	7.5086610	4.7889160
C	0.6384980	0.7705560	-2.5963180	H	-5.4819560	-8.2084110	1.9612960	C	-0.0285780	9.1030550	4.6854870
C	1.0820410	2.0314370	-2.9432010	C	-7.5217080	0.9313900	-0.9731410	H	-1.0090000	7.3848080	3.8390950
C	0.3560080	3.1719140	-2.5644980	C	-8.6364900	1.3975270	-0.9382850	C	2.2976080	8.8195750	5.2398200
C	-0.8211200	3.0047800	-1.8250800	C	0.8115590	4.4744220	-2.9238850	H	3.1328220	6.8803100	4.8255680
C	-1.2684790	1.7383030	-1.4866050	C	1.2005310	5.5770320	-3.2312070	C	1.1606580	9.6200010	5.1898070
C	-4.0349230	0.2113390	-2.0656900	C	-9.9542710	1.9476840	-0.8968350	H	-0.9180600	9.7239900	4.6452010
C	-5.3154520	0.7377370	-2.0344060	C	-10.3792750	2.8480180	-1.8825230	H	3.2274240	9.2189460	5.6325760
C	-6.2055500	0.3814820	-1.0126410	C	-10.8390900	1.5939050	0.1301880	H	1.2013000	10.6453830	5.5437190
C	-5.7810940	-0.5265660	-0.0316160	C	-11.6596370	3.3800430	-1.8388820				

SCF Done: E(UCAM-B3LYP) = -3370.49039252 A.U.
S**2 before annihilation 0.4056, after 0.0728

Low frequencies --- -634.4742 -0.4931 -0.0035 -0.0025 0.0005 0.1752
****** 1 imaginary frequencies (negative Signs) ******
Zero-point correction = 1.054487 (Hartree/Particle)
Thermal correction to Energy = 1.121214
Thermal correction to Enthalpy = 1.122158
Thermal correction to Gibbs Free Energy = 0.933836
Sum of electronic and zero-point Energies = -3369.435906
Sum of electronic and thermal Energies = -3369.369179
Sum of electronic and thermal Enthalpies = -3369.368234
Sum of electronic and thermal Free Energies = -3369.556557

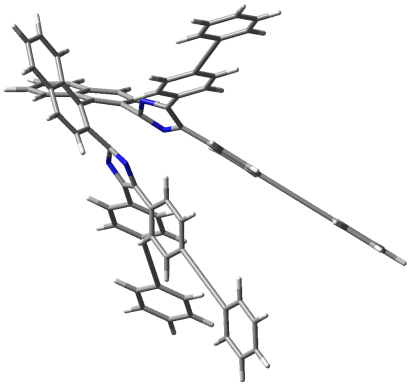


Table S19. Standard Orientation of the Optimized Geometry for TS2 of **3**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.7743250	-3.7928400	3.1399240	C	2.1610510	-2.8923870	-0.0664170	H	7.2031620	-7.1101800	-2.8924100
C	0.1665890	-4.2741960	3.9988010	H	-1.3800990	-4.4478590	2.5234730	C	4.5974500	-9.7831380	-3.9021940
C	0.9454090	-3.3962120	4.8052530	H	0.3356800	-5.3434230	4.0884260	H	3.1364140	-8.4601660	-3.0390120
C	0.7431740	-1.9889030	4.7205760	H	1.1363740	2.9145740	3.1845910	C	5.9446770	-9.9871690	-4.1835990
C	-0.2323650	-1.5072060	3.8009360	H	-0.6081350	3.7581720	4.7112220	H	7.9335680	-9.1800940	-4.0375850
C	-0.9616580	-2.3940180	3.0339110	H	-3.0375350	0.8185110	-1.3554650	H	3.8632280	-10.5312380	-4.1843140
C	-0.5637810	-0.0506500	3.6843910	H	-3.2387800	3.1352880	-2.1724520	H	6.2641270	-10.8949520	-4.6857790
C	0.4501330	0.8772130	3.2137330	H	-2.9732130	4.5786590	1.8553480	C	9.2878770	4.5213910	-3.0939300
C	0.3840730	2.2531790	3.5952490	H	-2.7904100	2.2565030	2.6717480	C	10.0059290	5.5577610	-2.4830750
C	-0.5770140	2.7091860	4.4317110	H	-4.0303050	-3.3867650	-0.5537130	C	9.6119270	4.1474650	-4.4046560
C	-1.5713060	1.8289410	4.9808510	H	-5.9924490	-3.7874050	-2.0196260	C	11.0238040	6.2027890	-3.1701230
C	-1.5652720	0.4586220	4.6301230	H	-7.4062130	0.1731440	-1.1789270	H	9.7555310	5.8483050	-1.4684450
C	-1.8465680	-1.7583280	2.0985120	H	-5.4615870	0.5637900	0.2757420	C	10.6310470	4.7971350	-5.0854630
C	1.4538310	0.4820730	2.3188380	H	4.6876800	2.6568480	1.9050070	H	9.0562740	3.3455150	-4.8786950
N	2.4233260	1.3660240	1.8799510	H	6.5173280	3.8116980	0.6918010	C	11.3394050	5.8253130	-4.4715530
C	3.1526430	0.6749410	1.0420340	H	5.8259400	1.2974730	-2.7130900	H	11.5737880	7.0046600	-2.6875830
C	2.6140550	-0.7099910	0.9874470	H	4.0249300	0.1402540	-1.4991980	H	10.8738280	4.4997370	-6.1008090
N	1.5632700	-0.7709830	1.7688210	H	5.1783480	-1.3664220	0.2615780	H	12.1363080	6.3319930	-5.0068230
N	-2.8321920	-2.2810830	1.3800420	H	5.9031540	-3.4268470	-0.8699380	C	-3.2388990	5.3608920	-0.6880900
C	-3.4386130	-1.2012320	0.8216600	H	1.8436810	-4.8079800	-0.9741770	C	-3.3383780	6.4967060	-1.0896400
C	-2.7531350	-0.0104020	1.2071000	H	1.1177720	-2.7393880	0.1851860	C	-7.9589570	-2.0543060	-2.5495390
N	-1.7244470	-0.4056550	1.9780130	C	1.9087810	-3.8991970	5.7100640	C	-8.9166510	-2.2448090	-3.2627750
C	-2.8985410	1.3709810	0.7195290	C	-2.5363140	2.3089150	5.8836240	C	-3.4561690	7.8383090	-1.5665560
C	-4.5909700	-1.3800260	-0.0589420	C	-2.5226120	-0.3881230	5.2177030	C	-3.5759270	8.0965760	-2.9384060
C	-2.8779720	2.4483910	1.6092950	C	-3.4657820	0.1037270	6.0954830	C	-3.4538630	8.9146790	-0.6697070
C	-3.1429130	2.9405540	-1.1097260	C	-3.4755930	1.4628790	6.4323820	C	-3.6903610	9.4003670	-3.3982760
C	-3.1225770	4.0190360	-0.2144740	C	1.4960710	-1.1442050	5.5756350	H	-3.5776360	7.2646470	-3.6344660
C	-2.9873650	3.7521620	1.1528790	C	2.4243990	-1.6642750	6.4395130	C	-3.5687530	10.2159060	-1.1366950
C	-3.0315210	1.6407540	-0.6481760	C	2.6385570	-3.0563090	6.5071440	H	-3.3611350	8.7168470	0.3928150
C	-4.7704760	-2.6102820	-0.7079160	H	2.0584920	-4.9739680	5.7627110	C	-3.6872720	10.4633560	-2.5006520
C	-5.8669450	-2.8330720	-1.5193690	H	-2.5263690	3.3632270	6.1450950	H	-3.7823830	9.5880490	-4.4635520
C	-6.8288100	-1.8299150	-1.7090430	H	-2.5227170	-1.4427030	4.9700850	H	-3.5657160	11.0418560	-0.4321650
C	-6.6595990	-0.6032800	-1.0514850	H	-4.2000010	-0.5685450	6.5270600	H	-3.7769260	11.4825580	-2.8633700
C	-5.5615560	-0.3844400	-0.2390780	H	-4.2161290	1.8468250	7.1267490	C	-10.0480240	-2.4692010	-4.1051300
C	4.2528160	1.3006410	0.3035230	H	1.3307510	-0.0730070	5.5470010	C	-11.0033910	-1.4619850	-4.2953690
C	3.0873150	-1.8952330	0.2717410	H	2.9936520	-1.0005770	7.0827700	C	-10.2186760	-3.6996890	-4.7533220
C	4.9559580	2.3563360	0.8986750	H	3.3741070	-3.4568310	7.1975420	C	-12.1009180	-1.6834540	-5.1143210
C	5.9707540	3.0029970	0.2190890	C	4.3452850	-5.4448630	-1.6712460	H	-10.8729920	-0.5087420	-3.7944130
C	6.3043920	2.6247250	-1.0901040	C	4.7016760	-6.4557870	-2.2303680	C	-11.3186870	-3.9139930	-5.5708410
C	5.5873620	1.5841650	-1.6948240	C	7.3511760	3.2903730	-1.7941270	H	-9.4802030	-4.4806620	-4.6071130
C	4.5788140	0.9310330	-1.0067150	C	8.2390340	3.8547430	-2.3895880	C	-12.2625090	-2.9083090	-5.7541930
C	4.4398640	-2.1064890	-0.0234430	C	5.1223290	-7.6503370	-2.8910400	H	-12.8345620	-0.8955860	-5.2541460
C	4.8523760	-3.2679510	-0.6538620	C	6.4769610	-7.8635720	-3.1781490	H	-11.4403060	-4.8714590	-6.0678280
C	3.9225250	-4.2527780	-1.0122990	C	4.1854690	-8.6243300	-3.2606280	H	-13.1223620	-3.0787950	-6.3944860
C	2.5686040	-4.0473700	-0.7056540	C	6.8814810	-9.0249000	-3.8199110				

SCF Done: E(UCAM-B3LYP) = -3370.48816144 A.U.
S**2 before annihilation 0.5800, after 0.2209

Low frequencies ----1619.7052 -0.6153 -0.0026 -0.0019 -0.0018 0.3520
****** 1 imaginary frequencies (negative Signs) ******
Zero-point correction = 1.052868 (Hartree/Particle)
Thermal correction to Energy = 1.120080
Thermal correction to Enthalpy = 1.121025
Thermal correction to Gibbs Free Energy = 0.930105
Sum of electronic and zero-point Energies = -3369.435294
Sum of electronic and thermal Energies = -3369.368081
Sum of electronic and thermal Enthalpies = -3369.367137
Sum of electronic and thermal Free Energies = -3369.558056

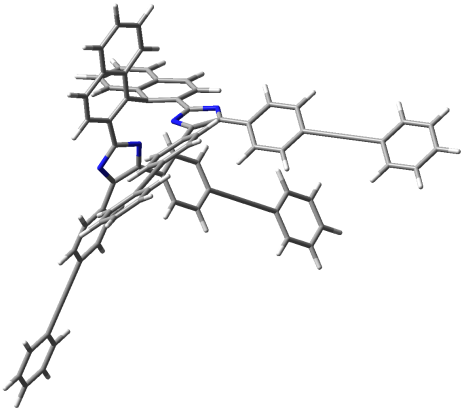


Table S20. Standard Orientation of the Optimized Geometry for 5MR of **4** .

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.8377190	2.3570950	-4.6030400	H	1.9782200	2.4572120	-6.4004950	H	12.0726530	5.7221300	-0.0832160
C	1.2575700	1.8963500	-5.8129920	H	-1.9052780	-3.2108680	-1.6911390	C	5.1514000	-7.5181280	4.5988340
C	0.7756390	0.6716810	-6.3405590	H	-4.1858440	-3.1543820	-2.5787610	C	4.9746570	-8.9005140	4.4556360
C	-0.1695370	-0.1443340	-5.6213610	H	-1.8908010	-0.2138410	1.0101330	C	5.9478040	-7.0376480	5.6465240
C	-0.6364170	0.3973630	-4.3764050	H	-3.5962460	-1.5666930	2.1846050	C	5.5817680	-9.7787810	5.3412650
C	-0.1161600	1.5965070	-3.9173830	H	-6.5653240	-0.2347870	-0.6089230	H	4.3581600	-9.2737280	3.6449170
C	-1.7325810	-0.0888720	-3.3566020	H	-4.8612360	1.1199150	-1.7747040	C	6.5516940	-7.9219350	6.5283540
C	-1.3003110	-1.3368470	-2.5579280	H	0.2144640	4.2579580	0.1350680	H	6.0851920	-5.9675270	5.7586130
C	-2.2436290	-2.3927340	-2.3134730	H	0.0689800	5.6747460	2.1618050	C	6.3711470	-9.2933890	6.3790670
C	-3.4901990	-2.3516850	-2.8045070	H	-3.7834180	4.0081780	3.0276200	H	5.4381350	-10.8480380	5.2211170
C	-3.9773990	-1.2716890	-3.6411280	H	-3.6383160	2.6112080	1.0173310	H	7.1665950	-7.5388130	7.3367220
C	-3.1573480	-0.1698960	-3.9611500	H	1.3306180	-4.8954830	-0.7081010	H	6.8449220	-9.9829900	7.0706560
C	-0.7425490	1.9453660	-2.6644980	H	2.4164610	-6.4789500	0.8620890	C	-6.1828410	-1.7810200	1.5378500
C	-0.0709390	-1.4270860	-1.9597320	H	4.1764460	-3.1746410	2.9531730	C	-7.0165450	-2.4459960	2.1066560
N	0.2871370	-2.5277560	-1.1773060	H	3.1122690	-1.6071400	1.3816950	C	-1.9549490	5.7487720	3.9120160
C	1.4686990	-2.2422100	-0.7139070	H	4.4345200	-1.8553700	-0.9434030	C	-2.0310780	6.4389980	4.9017280
C	1.8776150	-0.9155810	-1.2450440	H	6.4847590	-0.5090810	-0.7262010	C	-8.0004370	-3.2327840	2.7810470
N	0.9162070	-0.4563270	-1.9916590	H	4.1560000	3.0852500	-0.9523240	C	-7.6432540	-4.0283580	3.8774910
N	-0.6111330	2.8492670	-1.7320290	H	2.0941960	1.7324130	-1.1898790	C	-9.3350250	-3.2192180	2.3552480
C	-1.5391880	2.4930190	-0.7702400	C	1.2666380	0.2717100	-7.6081190	C	-8.6008180	-4.7911090	4.5299470
C	-2.2258370	1.3471850	-1.1494880	C	-5.2860910	-1.3617730	-4.1206090	H	-6.6104130	-4.0394280	4.2087180
N	-1.7046040	1.0358920	-2.3917710	C	-3.6999960	0.8636180	-4.7528340	C	-10.2872040	-3.9845000	3.0126130
C	-3.2561860	0.5410720	-0.4654740	C	-5.0155760	0.7356420	-5.2129650	H	-9.6133480	-2.6027230	1.5072050
C	-1.6822210	3.3143250	0.4416940	C	-5.8092480	-0.3598590	-4.9131300	C	-9.9240560	-4.7720470	4.1005400
C	-4.5812770	0.5281520	-0.9094580	C	-0.5225590	-1.4039160	-6.2258320	H	-8.3128860	-5.4036400	5.3786310
C	-3.8705900	-0.9777460	1.3162810	C	-0.0107170	-1.7328600	-7.4597090	H	-11.3186010	-3.9658910	2.6745180
C	-5.1970020	-0.9963330	0.8654610	C	0.8725590	-0.9033580	-8.1722850	H	-10.6712310	-5.3696650	4.6132690
C	-5.5395650	-0.2308370	-0.2564550	H	1.9689480	0.9270880	-8.1146500	C	-2.1217390	7.2541850	6.0713310
C	-2.9167700	-0.2196650	0.6574820	H	-5.8832110	-2.2286830	-3.8541230	C	-3.2496100	7.1864300	6.9000200
C	-0.6534210	4.2012590	0.7814250	H	-5.4223350	1.5337440	-5.8261140	C	-1.0842170	8.1338280	6.4077090
C	-0.7388070	4.9953820	1.9107050	H	-6.8249420	-0.4223050	-5.2902150	C	-3.3343450	7.9794830	8.0351110
C	-1.8639600	4.9334210	2.7437540	H	-0.2923770	-2.6879440	-7.8929810	H	-4.0541820	6.5061910	6.6418910
C	-2.9001940	4.0569990	2.3995830	H	1.2446240	-1.2116330	-9.1440040	C	-1.1756810	8.9239090	7.5443560
C	-2.8116530	3.2651720	1.2666410	C	6.6492500	2.1578810	-0.6841940	H	-0.2099600	8.1881800	5.7678630
C	2.1646850	-3.1485760	0.2107530	C	7.6554660	2.8184310	-0.5728490	C	-2.2993520	8.8501150	8.3614280
C	3.1188530	-0.1518670	-1.0601490	C	4.0006920	-5.8415670	2.9192520	H	-4.2135460	7.9176690	8.6690400
C	1.9667500	-4.5288500	0.0895740	C	4.5278860	-6.6104030	3.6887140	H	-0.3649860	9.6014650	7.7940990
C	2.5678210	-5.4103410	0.9692090	C	8.8442820	3.5996690	-0.4411770	H	-2.3682770	9.4695300	9.2502620
C	3.3783650	-4.9346450	2.0100890	C	10.0948160	2.9773090	-0.3332600	C	-2.9877740	2.1361300	-5.1471680
C	3.5632940	-3.5526370	2.1424870	C	8.7752060	4.9987960	-0.4181190	H	-2.6110890	2.6854770	-4.2824560
C	2.9665230	-2.6736250	1.2536570	C	11.2468930	3.7393450	-0.2054990	H	-2.1416070	1.9489920	-5.8112960
C	4.3652270	-0.7735190	-0.9328970	H	10.1496750	1.8941160	-0.3510160	H	-3.6836390	2.7926780	-5.6744410
C	5.5210970	-0.0196310	-0.8151740	C	9.9315220	5.7543170	-0.2899830	C	-1.3899830	-2.4362100	-5.5629870
C	5.4602040	1.3797210	-0.8153070	H	7.8075730	5.4818660	-0.5013240	H	-0.9785620	-2.7503810	-4.6021680
C	4.2105230	2.0020660	-0.9492840	C	11.1694900	5.1283350	-0.1834210	H	-2.4076710	-2.0849280	-5.3961170
C	3.0585530	1.2475730	-1.0772260	H	12.2106450	3.2466730	-0.1226210	H	-1.4532070	-3.3269660	-6.1926130
H	1.1960810	3.2863660	-4.1745600	H	9.8663230	6.8377590	-0.2730450				

SCF Done: E(RCAM-B3LYP) = -3449.10436518 A.U.

Low frequencies --- -0.3267 -0.0030 -0.0022 -0.0015 0.6483 0.8784

Zero-point correction	=	1.115130 (Hartree/Particle)
Thermal correction to Energy	=	1.185037
Thermal correction to Enthalpy	=	1.185981
Thermal correction to Gibbs Free Energy	=	0.990607
Sum of electronic and zero-point Energies	=	-3447.989235
Sum of electronic and thermal Energies	=	-3447.919329
Sum of electronic and thermal Enthalpies	=	-3447.918384
Sum of electronic and thermal Free Energies	=	-3448.113758

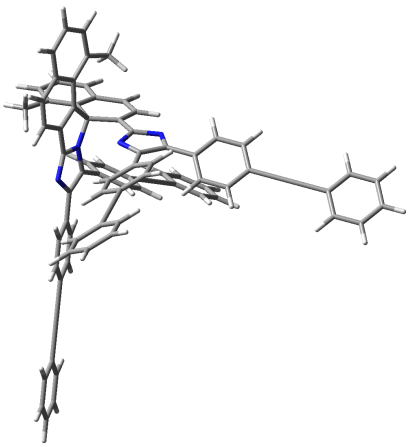


Table S21. Standard Orientation of the Optimized Geometry for 6MR of **4**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-0.0588850	-3.4167470	2.8666350	H	-0.3762510	-4.4862520	4.6853250	H	-14.2288860	1.8395430	1.2885450
C	-0.4470480	-4.4999800	3.6015620	H	-0.7052580	-2.6204470	-3.3170370	C	-1.2546610	7.1807330	-5.0202670
C	-1.0298780	-5.6262690	2.9745130	H	-0.3375520	-4.7379350	-4.5443360	C	-0.4657050	7.3970230	-6.1575120
C	-1.1542040	-5.6659530	1.5514040	H	3.5635500	1.0205070	0.0751280	C	-2.0067550	8.2419080	-4.4998760
C	-0.4858150	-4.6341050	0.8034810	H	5.9341350	1.3351540	-0.5123360	C	-0.4322480	8.6471260	-6.7578280
C	-0.0861590	-3.4848880	1.4625600	H	6.5807320	-2.8928180	-0.2018580	H	0.1171870	6.5760680	-6.5610620
C	-0.2257070	-4.6925500	-0.6601140	H	4.1859290	-3.2082140	0.3675330	C	-1.9682860	9.4892690	-5.1055660
C	-0.4595160	-3.5347080	-1.3804710	H	-0.3100850	1.5953420	1.5190720	H	-2.6178700	8.0754590	-3.6192840
C	-0.4872560	-3.5389700	-2.7855790	H	0.0324680	3.7231590	2.7488100	C	-1.1822070	9.6958160	-6.2347990
C	-0.2618260	-4.7035170	-3.4614210	H	3.8782120	2.3385090	4.0459350	H	0.1824840	8.8040390	-7.6386120
C	0.1587850	-5.8661100	-2.7739980	H	3.5461210	0.2376870	2.8021100	H	-2.5548460	10.3047890	-4.6942390
C	0.2826940	-5.8482280	-1.3503460	H	-0.0591950	0.3912980	-3.5710380	H	-1.1540100	10.6729780	-6.7066510
C	0.3038360	-2.2746420	0.6234110	H	-0.0015700	2.6192860	-4.6595210	C	7.7973870	-0.5690040	-0.7200900
C	-0.6632100	-2.2378090	-0.6092640	H	-2.7126440	4.1218840	-1.6962470	C	8.9621790	-0.4123650	-1.0021600
N	-0.3621530	-1.0642310	-1.4057020	H	-2.7939260	1.9003560	-0.6372980	C	2.1799960	4.3963280	4.1911460
C	-1.4195630	-0.3405350	-1.4039850	H	-4.2009710	0.2302510	-2.3655800	C	2.3480540	5.4296740	4.7950470
C	-2.5036390	-1.0407070	-0.6285470	H	-6.5694180	0.7858440	-1.9774020	C	10.3389580	-0.2270320	-1.3360840
N	-2.0430830	-2.1337150	-0.1487900	H	-6.3210870	-0.8789300	1.9670640	C	10.8430750	1.0565810	-1.5828010
N	0.1797550	-1.0380840	1.3714090	H	-3.9401500	-1.4596890	1.5626590	C	11.2029160	-1.3265660	-1.4213000
C	1.3380080	-0.4910430	1.3648710	C	-1.5286290	-6.6889420	3.7682700	C	12.1803670	1.2326300	-1.9068270
C	2.2961990	-1.3533570	0.5875670	C	0.4966370	-7.0293790	-3.5092970	H	10.1750570	1.9086970	-1.5174120
N	1.6816370	-2.3912510	0.1605720	C	0.9648470	-6.9509940	-0.7277870	C	12.5390580	-1.1428490	-1.7458150
C	3.7212100	-1.1185170	0.2867270	C	1.2918490	-8.0452850	-1.4957170	H	10.8136890	-2.3209760	-1.2309180
C	1.5953160	0.7817350	2.0655880	C	1.0199860	-8.1183740	-2.8757980	C	13.0317410	0.1353170	-1.9893120
C	4.5830560	-2.2151660	0.1894820	C	-1.9910580	-6.6892800	0.9842920	H	12.5603950	2.2316820	-2.0962080
C	5.5540390	0.3407310	-0.3058170	C	-2.4689140	-7.6837160	1.8070970	H	13.1996360	-2.0019080	-1.8093040
C	6.4220250	-0.7551890	-0.3860880	C	-2.2049200	-7.7231860	3.1901180	H	14.0777220	0.2760440	-2.2431780
C	5.9159610	-2.0385410	-0.1353660	H	-1.3805860	-6.6465700	4.8435870	C	2.5471480	6.6510430	5.5092160
C	4.2217230	0.1603810	0.0296160	H	0.3514460	-7.0225500	-4.5857900	C	3.7303860	6.8685950	6.2269850
C	0.6077010	1.7708330	2.0689320	H	1.8184240	-8.8696610	-1.0224940	C	1.5617060	7.6467230	5.5009270
C	0.7980900	2.9551970	2.7581740	H	1.2844810	-9.0121820	-3.4322230	C	3.9201990	8.0556280	6.9192380
C	1.9810050	3.1761730	3.4775660	H	-3.1112240	-8.4466730	1.3757310	H	4.4940360	6.0982790	6.2341390
C	2.9644290	2.1790190	3.4842660	H	-2.5930900	-8.5395100	3.7913190	C	1.7585350	8.8312460	6.1955140
C	2.7746940	0.9995230	2.7824980	C	-7.9743160	0.3311740	0.2494150	H	0.6451430	7.4792430	4.9455430
C	-1.4463080	0.9861030	-2.0494710	C	-9.1341710	0.6114210	0.4417960	C	2.9365400	9.0394820	6.9059230
C	-3.9065880	-0.6366760	-0.4141960	C	-1.3235230	4.8063850	-3.8741360	H	4.8407570	8.2139380	7.4722690
C	-0.6518120	1.2100960	-3.1784980	C	-1.2918560	5.8944610	-4.3993870	H	0.9884440	9.5961830	6.1825340
C	-0.6133080	2.4552390	-3.7791940	C	-10.5053730	0.9420960	0.6695640	H	3.0877930	9.9673500	7.4485870
C	-1.3604240	3.5205170	-3.2558600	C	-11.2580450	1.5756960	-0.3277580	C	1.4693140	-6.9405320	0.6977710
C	-2.1413590	3.3006150	-2.1147190	C	-11.1150790	0.6368330	1.8933750	H	1.7232390	-5.9339100	1.0344140
C	-2.1859700	2.0483330	-1.5225390	C	-12.5891080	1.8951100	-0.1028730	H	0.7469240	-7.3521520	1.4062690
C	-4.6568690	-0.0073770	-1.4106830	H	-10.7871720	1.8121360	-1.2759160	H	2.3742840	-7.5516690	0.7588470
C	-5.9899430	0.3046930	-1.1972010	C	-12.4465890	0.9593130	2.1111150	C	-2.4963300	-6.6779890	-0.4409350
C	-6.6041060	0.0001600	0.0240350	H	-10.5334180	0.1458300	2.6661440	H	-2.6062630	-5.6633450	-0.8273640
C	-5.8505770	-0.6364520	1.0205320	C	-13.1870770	1.5885910	1.1154100	H	-1.8444160	-7.2242260	-1.1264280
C	-4.5226150	-0.9554110	0.7997160	H	-13.1632050	2.3857360	-0.8826650	H	-3.4800120	-7.1548140	-0.4725550
H	0.2836380	-2.5095460	3.3494730	H	-12.9091800	0.7180040	3.0630250				

SCF Done: E(RCAM-B3LYP) = -3449.09271594 A.U.

Low frequencies --- -0.2489 -0.0022 -0.0017 -0.0007 0.2898 0.6253

Zero-point correction	=	1.114259 (Hartree/Particle)
Thermal correction to Energy	=	1.183882
Thermal correction to Enthalpy	=	1.184826
Thermal correction to Gibbs Free Energy	=	0.990049
Sum of electronic and zero-point Energies	=	-3447.978456
Sum of electronic and thermal Energies	=	-3447.908834
Sum of electronic and thermal Enthalpies	=	-3447.907890
Sum of electronic and thermal Free Energies	=	-3448.102667

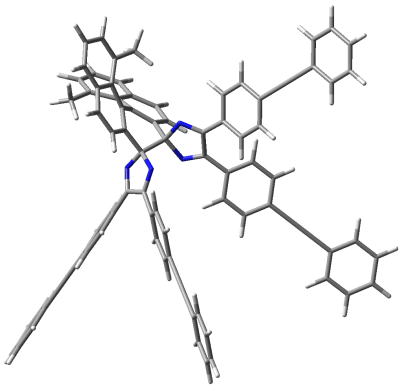


Table S22. Standard Orientation of the Optimized Geometry for BR of **4**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.8364440	-3.4085540	2.1483480	H	2.4645260	-4.6997630	2.5832360	H	12.9372550	-5.5444450	-2.2806640
C	1.9261200	-3.7954570	2.8527040	H	-0.3224920	3.0355810	2.8496940	C	4.7352330	7.7713480	-4.7775950
C	2.3934500	-3.0386780	3.9594480	H	-2.2118120	3.1023540	4.4404320	C	4.5037770	9.1288790	-4.5197180
C	1.7157560	-1.8426590	4.3525720	H	-4.1303430	-0.2032130	-1.2938880	C	5.3446840	7.4008100	-5.9835150
C	0.5477840	-1.4586640	3.6005160	H	-5.9647490	1.4321730	-1.3998140	C	4.8745320	10.0903600	-5.4483030
C	0.1168970	-2.2346170	2.5143790	H	-5.8989320	1.7938900	2.8741400	H	4.0316950	9.4169280	-3.5865740
C	-0.2127450	-0.2046230	3.9083720	H	-4.0384000	0.1617470	2.9780910	C	5.7126550	8.3679080	-6.9073640
C	0.1338720	0.9631490	3.2131700	H	-1.2096660	-3.4599180	-1.8850880	H	5.5240800	6.3500680	-6.1844240
C	-0.6111400	2.1598720	3.4153010	H	-2.2269330	-4.5797990	-3.8514780	C	5.4793090	9.7139100	-6.6434420
C	-1.6455750	2.1883920	4.2865940	H	-6.1284940	-3.5388560	-2.4061150	H	4.6904090	11.1393600	-5.2384100
C	-2.0235480	1.0308950	5.0158480	H	-5.1153330	-2.4143980	-0.4663320	H	6.1840230	8.0697420	-7.8386390
C	-1.3140650	-0.1983020	4.8387700	H	2.1797860	4.6336260	0.9890440	H	5.7682400	10.4685130	-7.3682930
C	-1.0514510	-1.9491320	1.7016930	H	2.8489990	6.3639290	-0.6577410	C	-7.1343590	2.6600250	0.6658440
C	1.2315510	1.0725670	2.2705580	H	4.3406090	3.2934750	-3.2543760	C	-8.0385730	3.4609280	0.6125790
N	1.4139400	2.2315020	1.5582540	H	3.6911180	1.5813790	-1.6108860	C	-4.8378640	-4.7740240	-4.3938670
C	2.4723880	2.0073860	0.8060410	H	5.3803410	1.7036810	0.3204090	C	-5.3367200	-5.3241010	-5.3479190
C	2.9774850	0.6560890	1.1216200	H	7.3825190	0.4436410	-0.3525370	C	-9.1067430	4.4070110	0.5482520
N	2.1637990	0.1149200	2.0125650	H	5.2902410	-3.2436830	0.2982010	C	-9.6385410	4.7942710	-0.6888000
N	-1.3126980	-2.7012110	0.5836960	H	3.2784040	-1.9730570	0.9930860	C	-9.6369600	4.9602880	1.7211940
C	-2.4406360	-2.2182320	0.1026140	C	3.5368580	-3.4966570	4.6486300	C	-10.6759370	5.7132600	-0.7474730
C	-2.8610780	-1.0966980	0.9669040	C	-3.1200110	1.1263160	5.9006870	H	-9.2286350	4.3670150	-1.5976560
N	-1.9821510	-0.9880370	1.9488470	C	-1.7712620	-1.3353320	5.6032640	C	-10.6744440	5.8786460	1.6547270
C	-3.9785370	-0.1635390	0.8575630	C	-2.8495130	-1.1801370	6.4496410	H	-9.2260710	4.6613180	2.6795270
C	-3.0842370	-2.8310790	-1.0587140	C	-3.5329420	0.0354720	6.6105020	C	-11.1967910	6.2577940	0.4221550
C	-4.4780580	0.4331300	2.0254170	C	2.2621470	-1.1177660	5.4754340	H	-11.0802470	6.0064230	-1.7112950
C	-5.5542690	1.1392380	-0.4397170	C	3.3817910	-1.6155640	6.1084030	H	-11.0777360	6.3010570	2.5697750
C	-6.0686070	1.7148000	0.7299340	C	4.0280120	-2.7972910	5.7129050	H	-12.0085750	6.9767680	0.3731600
C	-5.5110790	1.3479480	1.9646970	H	4.0131680	-4.4121710	4.3104170	C	-5.9266810	-5.9739700	-6.4748670
C	-4.5272720	0.2136340	-0.3757420	H	-3.6221700	2.0842880	6.0000150	C	-7.3191710	-6.0088250	-6.6255910
C	-2.2853140	-3.4702340	-2.0178100	H	-3.1847850	-2.0422160	7.0179110	C	-5.1205640	-6.5850550	-7.4442480
C	-2.8540410	-4.0986750	-3.1088090	H	-4.3751000	0.0979370	7.2925830	C	-7.8885030	-6.6408530	-7.7212990
C	-4.2479820	-4.1251240	-3.2692100	H	3.7840110	-1.0623160	6.9514440	H	-7.9443050	-5.5362250	-5.8756170
C	-5.0496340	-3.5069780	-2.3004680	H	4.9071980	-3.1400400	6.2493200	C	-5.6970470	-7.2151490	-8.5373300
C	-4.4760050	-2.8690510	-1.2139770	C	7.6317730	-2.2142880	-0.4805160	H	-4.0423620	-6.5587840	-7.3285550
C	2.9187500	2.9940190	-0.1764880	C	8.6157070	-2.8325690	-0.8144300	C	-7.0807770	-7.2452320	-8.6794900
C	4.1737240	-0.0498910	0.6717730	C	4.0327520	5.9376570	-3.0169060	H	-8.9685390	-6.6620640	-7.8282180
C	2.6689210	4.3529230	0.0635090	C	4.3548240	6.7783980	-3.8238110	H	-5.0631220	-7.6854680	-9.2825100
C	3.0364260	5.3145650	-0.8577390	C	9.7785150	-3.5622720	-1.2089510	H	-7.5290980	-7.7391130	-9.5358780
C	3.6528300	4.9471460	-2.0638190	C	10.9522140	-2.8871160	-1.5690550	C	-1.1646360	-2.7192240	5.5723380
C	3.8826430	3.5882680	-2.3165740	C	9.7609100	-4.9628860	-1.2411140	H	-1.1925630	-3.1683540	4.5783670
C	3.5223530	2.6281480	-1.3866870	C	12.0795510	-3.5991190	-1.9516140	H	-0.1241810	-2.7283710	5.9018900
C	5.3464660	0.6208120	0.2976830	H	10.9672420	-1.8027860	-1.5444090	H	-1.7267940	-3.3716040	6.2448940
C	6.4773140	-0.0848730	-0.0742820	C	10.8920640	-5.6681690	-1.6248470	C	1.7132110	0.1711990	6.0419660
C	6.4703580	-1.4862710	-0.0873240	H	8.8528270	-5.4867830	-0.9626750	H	1.7057740	0.9791350	5.3086830
C	5.3010330	-2.1591010	0.2994220	C	12.0535540	-4.9899140	-1.9808600	H	0.6940840	0.0669410	6.4185040
C	4.1766770	-1.4530150	0.6810060	H	12.9836230	-3.0658510	-2.2284760	H	2.3402320	0.4902920	6.8780580
H	0.4735080	-3.9800350	1.3042640	H	10.8673060	-6.7532080	-1.6462720				

SCF Done: E(UCAM-B3LYP) = -3449.08399979 A.U.
S**2 before annihilation 1.1248, after 1.0550

Low frequencies --- -0.8193 -0.4288 -0.0033 -0.0022 -0.0017 0.6428
Zero-point correction = 1.111075 (Hartree/Particle)
Thermal correction to Energy = 1.181717
Thermal correction to Enthalpy = 1.182661
Thermal correction to Gibbs Free Energy = 0.983137
Sum of electronic and zero-point Energies = -3447.972925
Sum of electronic and thermal Energies = -3447.902283
Sum of electronic and thermal Enthalpies = -3447.901338
Sum of electronic and thermal Free Energies = -3448.100863

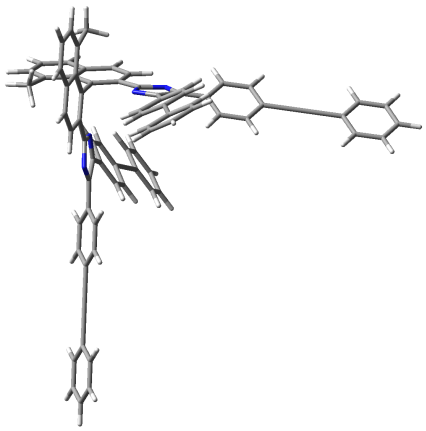


Table S23. Standard Orientation of the Optimized Geometry for TS1 of **4**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	-2.1506500	-3.3044410	2.7521500	H	-3.7019430	-3.9666430	4.0557690	H	-13.2140170	4.6459270	-0.7334540
C	-3.1665170	-4.1334470	3.1255430	H	0.4148930	-3.3187770	-3.0646280	C	2.1897380	6.9481660	-3.5802550
C	-3.5829420	-5.1912650	2.2848710	H	1.2294690	-5.5932870	-3.6128180	C	3.3240850	7.0190290	-4.3994470
C	-2.9096880	-5.4279940	1.0448370	H	3.0497300	0.2168710	0.0822230	C	1.6060580	8.1353230	-3.1190110
C	-1.7095980	-4.6806140	0.7900720	H	5.4586470	0.2465920	-0.4376080	C	3.8592920	8.2504800	-4.7475710
C	-1.4082140	-3.5832100	1.5848390	H	5.8453560	-3.7400030	1.0954600	H	3.7766450	6.1003810	-4.7570480
C	-0.7888200	-4.9733520	-0.3445350	H	3.4168560	-3.7721200	1.6018420	C	2.1470900	9.3630970	-3.4710510
C	-0.5231640	-3.9361940	-1.2276490	H	-1.0918180	1.1887460	1.5585190	H	0.7286330	8.0813500	-2.4836180
C	0.2346500	-4.1525900	-2.3972040	H	-0.8041210	3.5217180	2.3505810	C	3.2735660	9.4248260	-4.2853330
C	0.6984630	-5.4013180	-2.6850430	H	3.2298200	2.6178870	3.4924210	H	4.7382870	8.2942620	-5.3830010
C	0.5542410	-6.4576610	-1.7566970	H	2.9466730	0.3120660	2.6913980	H	1.6875540	10.2769200	-3.1076790
C	-0.1235760	-6.2346220	-0.5164150	H	1.2082350	0.0093270	-2.8894250	H	3.6947070	10.3870880	-4.5591820
C	-0.3659930	-2.6027200	1.2000900	H	2.1675450	2.2071630	-3.5202160	C	7.2148120	-1.7179730	0.0074520
C	-0.9446730	-2.5447150	-0.9440940	H	-1.0569530	4.1786940	-1.4939760	C	8.3968710	-1.7021170	-0.2449930
N	-0.1776630	-1.5069880	-1.4240990	H	-2.0167330	1.9999420	-0.8874790	C	1.4047610	4.5696010	3.4312910
C	-0.9851260	-0.4793470	-1.5024610	H	-3.2968760	0.9523200	-2.8565390	C	1.5437130	5.7029890	3.8283880
C	-2.3495460	-0.9336330	-1.1098200	H	-5.4979180	2.0584480	-2.7810290	C	9.7938590	-1.6837690	-0.5433480
N	-2.2860770	-2.1876530	-0.7716670	H	-6.4807270	-0.1266260	0.7763060	C	10.5925000	-2.8023160	-0.2715170
N	-0.5262380	-1.2917390	1.5958530	H	-4.2680380	-1.2521410	0.6872790	C	10.3839330	-0.5472270	-1.1116150
C	0.6782460	-0.7786670	1.5994080	C	-4.6900700	-5.9864530	2.6711020	C	11.9486810	-2.7810670	-0.5624030
C	1.6365480	-1.8430640	1.1847240	C	1.1161490	-7.7229890	-2.0575650	H	10.1368640	-3.6830330	0.1681730
N	0.9732480	-2.9454490	0.9963850	C	-0.0480360	-7.2782880	0.4760160	C	11.7407890	-0.5332350	-1.3998090
C	3.0779310	-1.7702950	0.9158880	C	0.5268120	-8.4799500	0.1314610	H	9.7667460	0.3194880	-1.3226250
C	0.9126040	0.5985530	2.0319730	C	1.0764440	-8.7311130	-1.1407950	C	12.5267860	-1.6482960	-1.1266660
C	3.8779740	-2.8891710	1.1739020	C	-3.5139700	-6.3668850	0.1322530	H	12.5580000	-3.6534320	-0.3477010
C	5.0141420	-0.6272910	0.0260090	C	-4.5998490	-7.0975440	0.5567730	H	12.1875520	0.3527620	-1.8400710
C	5.8197380	-1.7382630	0.3071370	C	-5.1731920	-6.9484160	1.8345920	H	13.5882900	-1.6345520	-1.3532710
C	5.2297010	-2.8727440	0.8832800	H	-5.1509620	-5.7978840	3.6364540	C	1.7085840	7.0416480	4.2985380
C	3.6625360	-0.6433700	0.3280080	H	1.5920580	-7.8608890	-3.0241570	C	0.6390610	7.9456470	4.2559810
C	-0.1435050	1.5191990	1.9651280	H	0.5872990	-9.2577290	0.8875160	C	2.9417640	7.4677580	4.8090130
C	0.0160400	2.8150460	2.4150650	H	1.5058890	-9.7032920	-1.3618560	C	0.8026910	9.2446490	4.7141980
C	1.2380680	3.2327880	2.9639290	H	-5.0546030	-7.7964260	-0.1395380	H	-0.3163050	7.6164870	3.8615970
C	2.2879010	2.3093100	3.0525440	H	-6.0219080	-7.5616180	2.1210990	C	3.0979440	8.7683620	5.2652670
C	2.1271100	1.0133390	2.5934720	C	-7.4062000	1.6962880	-0.9464150	H	3.7704550	6.7686770	4.8422870
C	-0.4833530	0.8453750	-1.8717090	C	-8.4831330	2.2439360	-0.9072090	C	2.0307170	9.6598610	5.2195690
C	-3.6253920	-0.2084480	-1.0702760	C	1.1654910	4.6106600	-2.9150380	H	-0.0326840	9.9368550	4.6772540
C	0.7127700	0.9292370	-2.6013900	C	1.6354340	5.6819000	-3.2201530	H	4.0576970	9.0881910	5.6588380
C	1.2491190	2.1542470	-2.9457380	C	-9.7562130	2.8904640	-0.8605530	H	2.1558160	10.6769360	5.5776530
C	0.6141360	3.3449730	-2.5582630	C	-10.6632960	2.5984380	0.1664630	C	-0.4662870	-7.1207980	1.9203430
C	-0.5682130	3.2646260	-1.8126520	C	-10.1144830	3.8248440	-1.8410510	H	-0.2370320	-6.1270030	2.3080160
C	-1.1088370	2.0343660	-1.4766970	C	-11.8985980	3.2281280	0.2086970	H	-1.5337990	-7.2936720	2.0731690
C	-3.9848910	0.7234140	-2.0498620	H	-10.3872630	1.8747880	0.9258860	H	0.0751530	-7.8496640	2.5294290
C	-5.2225300	1.3436430	-2.0133420	C	-11.3515810	4.4505350	-1.7923580	C	-3.1069980	-6.5399540	-1.3133060
C	-6.1347590	1.0500820	-0.9911300	H	-9.4132890	4.0513850	-2.6370640	H	-2.8286130	-5.5918220	-1.7758670
C	-5.7772940	0.1085660	-0.0149250	C	-12.2465560	4.1549290	-0.7689240	H	-2.2662890	-7.2258110	-1.4378090
C	-4.5441960	-0.5160180	-0.0595250	H	-12.5939060	2.9941720	1.0088060	H	-3.9515040	-6.9492140	-1.8741680
H	-1.8789880	-2.4425420	3.3492590	H	-11.6190640	5.1726730	-2.5574420				

SCF Done: E(UCAM-B3LYP) = -3449.05372111 A.U.
S**2 before annihilation 0.4197, after 0.0791

Low frequencies --- -637.2836 -1.1339 -0.4508 -0.0028 0.0008 0.0016
****** 1 imaginary frequencies (negative Signs) ******
Zero-point correction = 1.110917 (Hartree/Particle)
Thermal correction to Energy = 1.180725
Thermal correction to Enthalpy = 1.181669
Thermal correction to Gibbs Free Energy = 0.986846
Sum of electronic and zero-point Energies = -3447.942804
Sum of electronic and thermal Energies = -3447.872997
Sum of electronic and thermal Enthalpies = -3447.872052
Sum of electronic and thermal Free Energies = -3448.066875

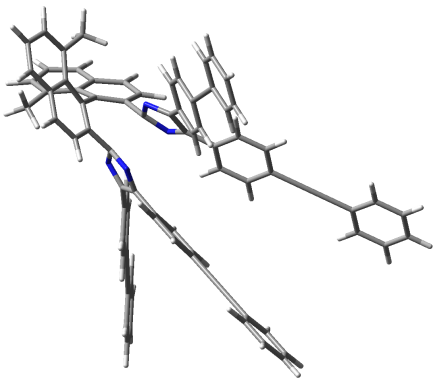
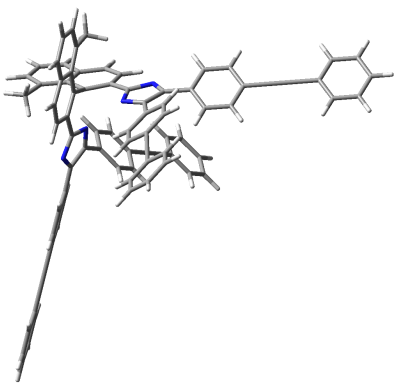


Table S24. Standard Orientation of the Optimized Geometry for TS2 of **4**.

	X	Y	Z		X	Y	Z		X	Y	Z
C	0.0999190	3.8290520	2.4903410	H	-1.2702650	5.2916590	3.2045480	H	-8.6204880	9.8313430	-4.3390710
C	-0.9186350	4.2663310	3.2725490	H	-0.6341880	-2.9594710	2.7287950	C	-8.4355520	-5.9099960	-3.3406730
C	-1.5533360	3.4040070	4.2084790	H	1.2399360	-3.5812690	4.2015770	C	-8.9171760	-7.0898270	-2.7585800
C	-1.1352170	2.0405000	4.3652930	H	2.9582860	-0.7220790	-1.4537940	C	-8.8619710	-5.5616220	-4.6289340
C	-0.0575740	1.6045210	3.5117190	H	3.6829140	-2.9984070	-2.0763400	C	-9.8046010	-7.8998860	-3.4517270
C	0.5066930	2.4840240	2.6024760	H	4.3258900	-3.9216580	2.0602540	H	-8.5873080	-7.3606580	-1.7613690
C	0.5226230	0.2129990	3.4891670	H	3.6101930	-1.6400930	2.6777270	C	-9.7495280	-6.3766960	-5.3160070
C	-0.3285660	-0.8400080	2.9401090	H	3.4238750	3.7548020	-0.9881270	H	-8.4893320	-4.6485880	-5.0807070
C	-0.0168720	-2.2071450	3.2010340	H	5.2833610	4.3904350	-2.5040580	C	-10.2231860	-7.5467020	-4.7307330
C	1.0104780	-2.5375920	4.0089970	H	7.3665590	0.8015940	-1.4226990	H	-10.1714960	-8.8120070	-2.9915690
C	1.8252670	-1.5462370	4.6527240	H	5.5254570	0.1805370	0.0841430	H	-10.0733280	-6.0976250	-6.3137980
C	1.6061010	-0.1576830	4.4222290	H	-4.1646420	-3.3461250	1.6405370	H	-10.9175430	-8.1826540	-5.2708480
C	1.5153680	1.9325000	1.7419110	H	-5.7608750	-4.7978060	0.4172450	C	4.4738820	-4.9352550	-0.4090050
C	-1.4077770	-0.5875370	2.0786630	H	-5.6733930	-2.0762880	-2.8960260	C	4.8310940	-6.0492450	-0.7131090
N	-2.1973010	-1.6301090	1.6169170	H	-4.1055950	-0.6276950	-1.6711600	C	7.5206250	2.9932210	-2.9456880
C	-3.0747580	-1.0685930	0.8279350	H	-5.4889310	0.5482100	0.1838780	C	8.4283760	3.2980260	-3.6840970
C	-2.8255180	0.3957490	0.8230810	H	-6.6475460	2.4589340	-0.8443350	C	5.2532670	-7.3653760	-1.0751820
N	-1.7870030	0.6369640	1.5841590	H	-2.9534800	4.6338990	-0.9851440	C	5.2564930	-7.7661320	-2.4176890
N	2.4010850	2.5799090	0.9915260	H	-1.7918680	2.7156920	0.0727160	C	5.6702050	-8.2737280	-0.0933970
C	3.2225060	1.5980720	0.5360860	C	-2.5975390	3.9407780	4.9942460	C	5.6672030	-9.0446140	-2.7659460
C	2.7794980	0.3364330	1.0223800	C	2.8256030	-1.9917040	5.5283420	H	4.9339580	-7.0643910	-3.1793530
N	1.6666000	0.5820170	1.7399160	C	2.4465410	0.7685510	5.1140480	C	6.0796880	-9.5506030	-0.4489400
C	3.2231410	-1.0229410	0.6583260	C	3.4205620	0.2719510	5.9740870	H	5.6687710	-7.9652770	0.9465870
C	4.3287700	1.9170810	-0.3650190	C	3.6231320	-1.0886110	6.1897910	C	6.0797270	-9.9403230	-1.7845160
C	3.6129730	-1.9405040	1.6366780	C	-1.7986650	1.2658410	5.3826950	H	5.6653330	-9.3437540	-3.8094990
C	3.6655430	-2.6987640	-1.0340360	C	-2.8071730	1.8503530	6.1193930	H	6.4008170	-10.2457120	0.3206480
C	4.0525320	-3.6188010	-0.0498970	C	-3.2256090	3.1768090	5.9343690	H	6.4006590	-10.9400690	-2.0599780
C	4.0211480	-3.2197370	1.2911880	H	-2.8831940	4.9760520	4.8330740	C	9.5009040	3.6574640	-4.5561520
C	3.2591720	-1.4230990	-0.6823370	H	2.9517410	-3.0602240	5.6750000	C	10.6146550	2.8188140	-4.6963750
C	4.2888330	3.1113040	-1.0990030	H	4.0529690	0.9842210	6.4939690	C	9.4548590	4.8538740	-5.2841020
C	5.3277260	3.4654330	-1.9390300	H	4.3983480	-1.4241960	6.8710900	C	11.6544840	3.1711140	-5.5443060
C	6.4491000	2.6340320	-2.0753900	H	-3.2965000	1.2524700	6.8825720	H	10.6521870	1.8921320	-4.1337970
C	6.4973700	1.4445940	-1.3352910	H	-4.0274410	3.5838440	6.5419930	C	10.4983600	5.1996840	-6.1301910
C	5.4567650	1.0948260	-0.4931710	C	-5.5522100	4.7773400	-1.5975920	H	8.5935800	5.5045270	-5.1768790
C	-4.0498000	-1.8743710	0.0867980	C	-6.1215430	5.7148070	-2.1061170	C	11.6004820	4.3610040	-6.2633690
C	-3.5475170	1.4876790	0.1679640	C	-6.7477330	-4.3648550	-2.0293520	H	12.5121670	2.5131920	-5.6446850
C	-4.5137850	-3.0690830	0.6524200	C	-7.5215080	-5.0732280	-2.6300390	H	10.4513720	6.1292450	-6.6890070
C	-5.3982770	-3.8802170	-0.0330300	C	-6.7941420	6.8225140	-2.7069980	H	12.4156370	4.6341460	-6.9261840
C	-5.8352080	-3.5295690	-1.3192290	C	-8.1736280	6.7706390	-2.9462640	C	2.4096080	2.2718440	4.9875010
C	-5.3552120	-2.3461390	-1.8950630	C	-6.0829090	7.9753240	-3.0649330	H	2.6841440	2.6046960	3.9836200
C	-4.4778450	-1.5303670	-1.2006900	C	-8.8232310	7.8483900	-3.5299120	H	1.4282600	2.6927620	5.2115470
C	-4.9232750	1.4319520	-0.0869570	H	-8.7252880	5.8786210	-2.6695130	H	3.1278100	2.7081510	5.6853810
C	-5.5801230	2.5079790	-0.6592330	C	-6.7393020	9.0491090	-3.6482940	C	-1.4852890	-0.1699890	5.7282370
C	-4.8785480	3.6722950	-0.9982200	H	-5.0147960	8.0164480	-2.8804590	H	-1.8679780	-0.8686910	4.9807770
C	-3.5022160	3.7334700	-0.7315320	C	-8.1095140	8.9895280	-3.8823980	H	-0.4170110	-0.3579440	5.8391740
C	-2.8513020	2.6624780	-0.1499830	H	-9.8923660	7.7977330	-3.7108360	H	-1.9581810	-0.4247770	6.6798950
H	0.6063250	4.4681750	1.7756170	H	-6.1786080	9.9374010	-3.9219430				

SCF Done: E(UCAM-B3LYP) = -3449.05119886 A.U.
S**2 before annihilation 0.5145, after 0.1782

Low frequencies ----1279.6855 -0.0029 -0.0020 -0.0012 0.6296 0.8536
****** 1 imaginary frequencies (negative Signs) ******
Zero-point correction = 1.110100 (Hartree/Particle)
Thermal correction to Energy = 1.180148
Thermal correction to Enthalpy = 1.181092
Thermal correction to Gibbs Free Energy = 0.984485
Sum of electronic and zero-point Energies = -3447.941099
Sum of electronic and thermal Energies = -3447.871051
Sum of electronic and thermal Enthalpies = -3447.870107
Sum of electronic and thermal Free Energies = -3448.066714



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