Electronic Supplementary Information for

Functionalization of pentacene-5,7,12,14-tetraone with geminal enediyne and 1,3-dithiole groups

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1. Procedures for Preparation of P1-P3

Synthesis of P1

Compound **2** (100 mg, 0.153 mmol) and **6** (134 mg, 0.306 mmol) were mixed with *i*-Pr2NH (1 mL) in a mixed solvent of DMF (1.5 mL) and toluene (2.5 mL). The mixture was stirred at room temperature for 5 min, and to this mixture was added $Pd(PPh_3)_4$ (35 mg, 0.031 mmol) and CuI (3.0 mg, 0.016 mmol). The mixture was heated at 65 ℃ under N_2 for 24 h. The reaction mixture was then cooled to room temperature and the resulting precipitate was collected by vacuum filtration and washed with MeOH several times to afford **P1** (150 mg, 0.125 mmol, 82 %) as a shiny black solid.

Synthesis of P2

Compound **3** (100 mg, 0.139 mmol) and K_2CO_3 (85.1 mg, 0.616 mmol) were stirred in THF/MeOH (1:1, 10 mL) under N_2 for 1 h. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated under vacuum, giving desilylated **3**. The desilylated intermediate was added to a solution of diiodobenzene **7** (179 mg, 0.278 mmol) and *i*-Pr_2NH (1.0 mL) in DMF (1.5 mL) and toluene (2.5 mL). The mixture was stirred at room temperature for 5 min and to the mixture were added $Pd(PPh_3)_4$ (32 mg, 0.028 mmol) and CuI (2.7 mg, 0.0014 mmol). The mixture was heated at 65 ℃ under N_2 for 24 h. The reaction mixture was then cooled to room temperature and the resulting precipitate was collected by vacuum filtration and washed with MeOH several times to afford **P2** (110 mg, 0.0903 mmol, 65%) as shiny black solid.

Ru-catalyzed reaction of compound 3

Compound **3** (150 mg, 0.209 mmol) and K_2CO_3 (127 mg, 0.917 mmol) were stirred in THF/MeOH (1:1, 10 mL) under N_2 for 1 h. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2, washed with water, dried over MgSO4, concentrated under vacuum, giving desilylated **3**. The desilylated intermediate was diluted in 1,2-dichloroethane (5 mL). This solution was drawn into a syringe to be used in the next step.

$RuCl_2(PPh_3)(\eta 6$-*p*-cymene) (24 mg, 0.042 mmol) and NH_4PF_6 (14 mg, 0.084 mmol) were dissolved in 1,2-dichloroethane (15 mL). The mixture was heated to 75 ℃ under N_2, and to this reaction mixture the solution of desilylated **3** was slowly added *via* a syringe over a period of 6

h. After addition, the reaction mixture was heated for another 12 h. The reaction mixture was then cooled to room temperature. The resulting precipitate was collected by vacuum filtration and washed with MeOH and CH_2Cl_2 to afford black solid product (85 mg, 0.20 mmol, 94%).

2. Characterizations of P1-P3

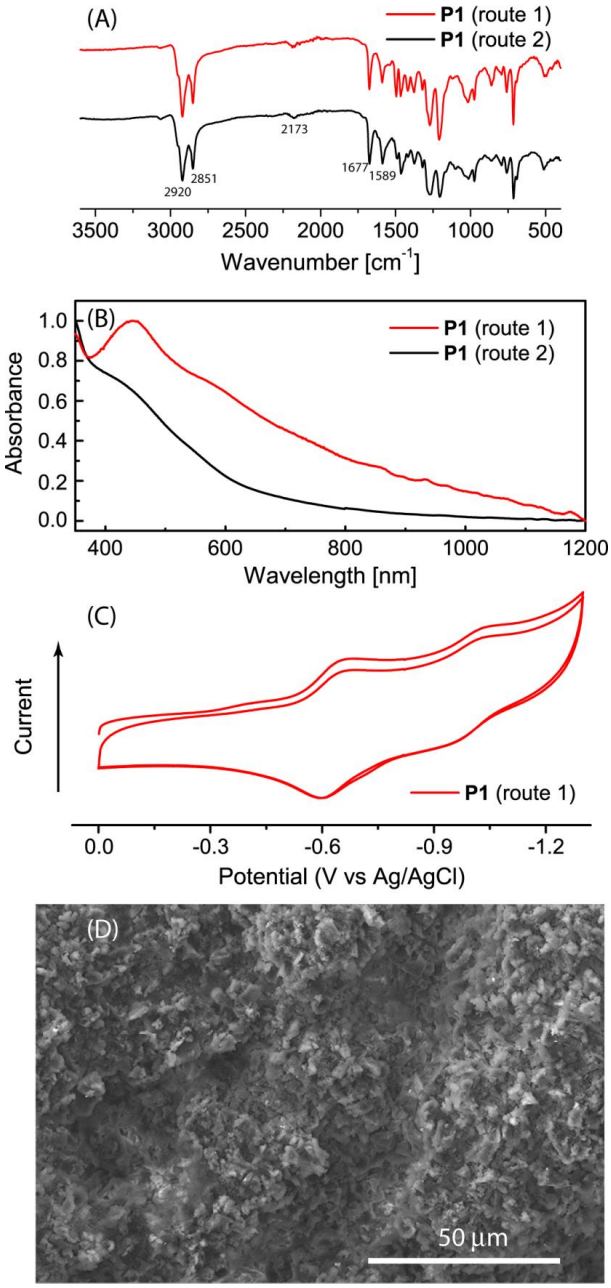

Fig. S-1 (A) IR spectra of **P1** and **P2**. (B) UV-Vis absorption spectra of **P1** measured in DMF. (C) CV scans of **P1**. Experimental conditions: solvent: DMF; electrolyte: Bu_4NPF_6 (0.1 M); working electrode: glassy carbon; reference electrode: Ag/AgCl; counter electrode: Pt wire; scan rate: 100 mV/s. (D) SEM image of **P1**.

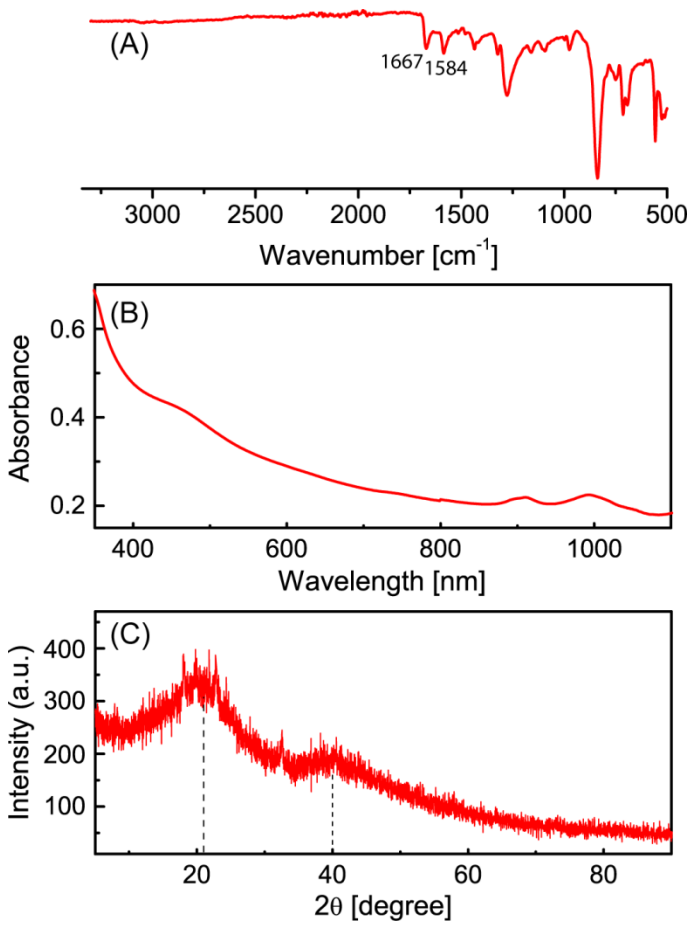

Fig. S-2 (A) IR spectrum of **P3** resulting from Ru-catalyzed cyclization reactions. (B) UV-Vis-NIR spectrum of **P3** suspended in DMF. (C) Powder XRD patterns of **P3**.

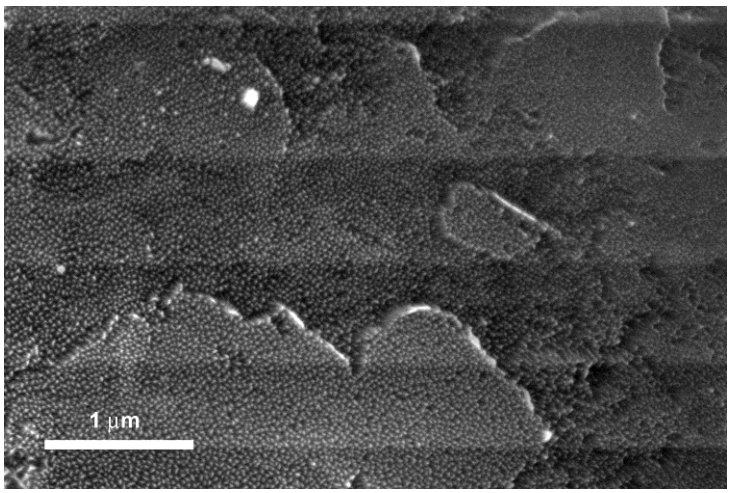

Fig. S-3 SEM image of **P3** prepared from Ru-catalyzed reactions of desilyated **3**.

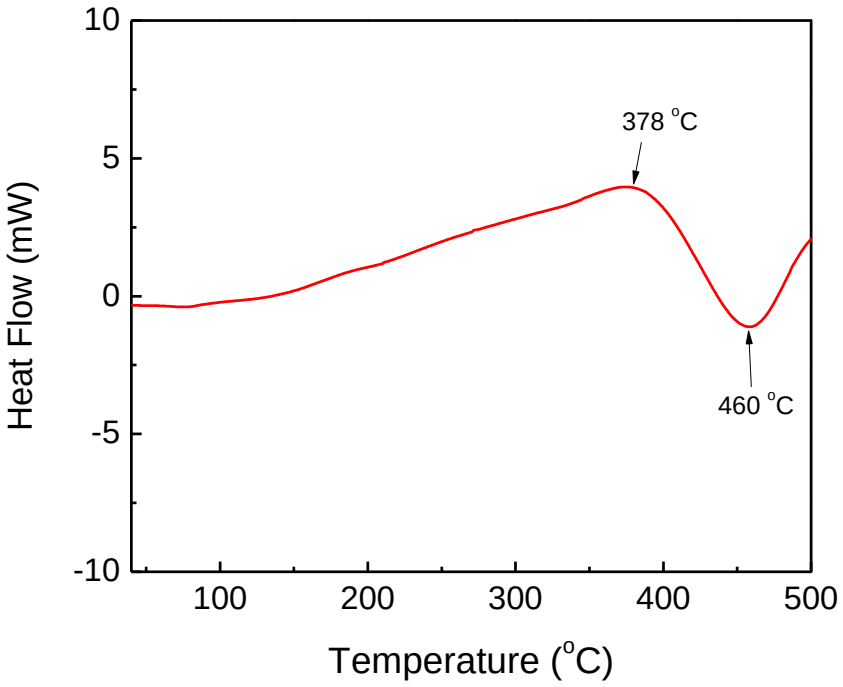

Fig. S-4 DSC trace of **P1** (scan rate: 10 ℃/min, under nitrogen).

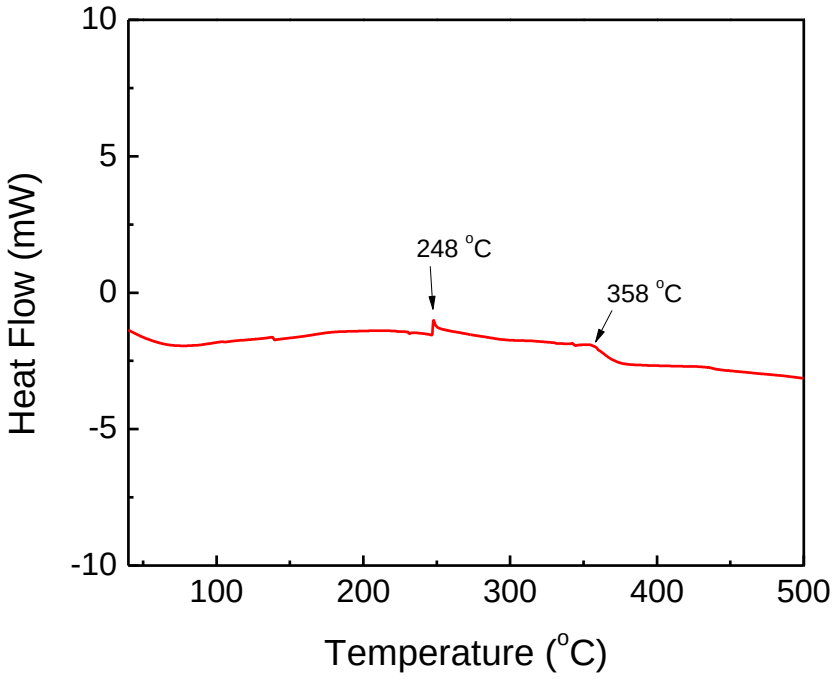

Fig. S-5 DSC trace of **P3** (scan rate: 10 ℃/min, under nitrogen).

3. NMR Spectra for New Compounds

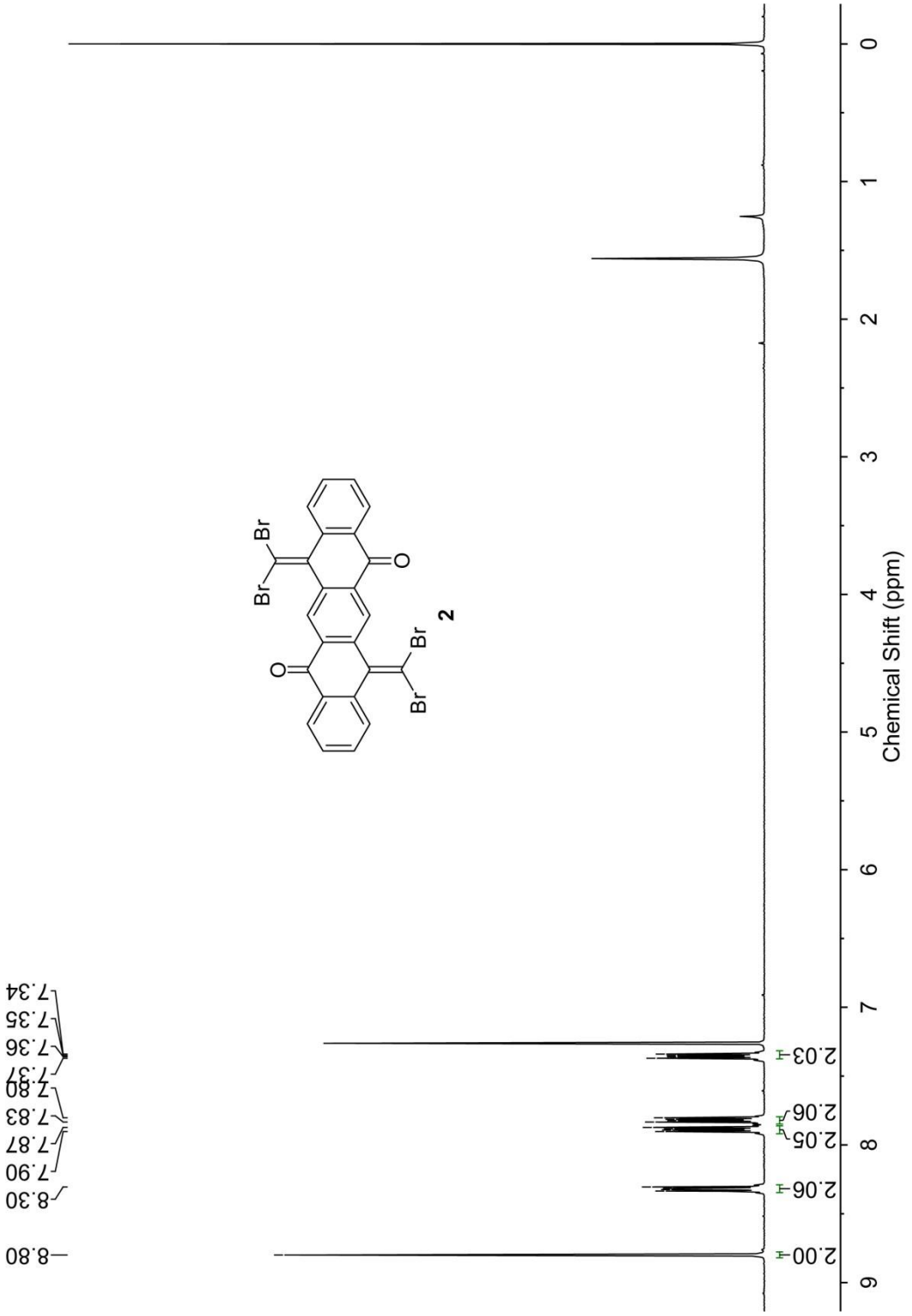

Fig. S-6 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **2**.

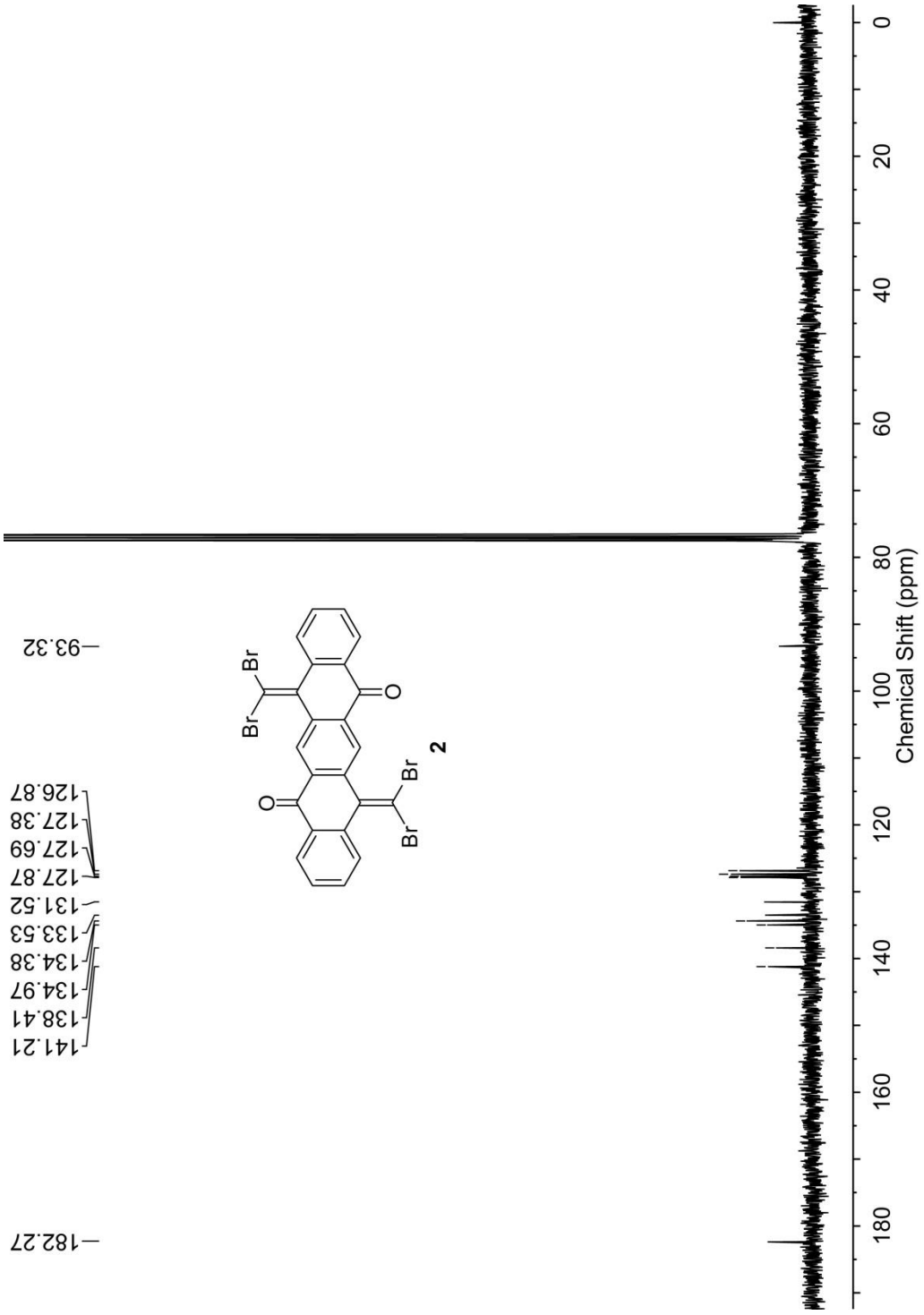

Fig. S-7 ^{13}C NMR (75 MHz, $CDCl_3$) of compound **2**.

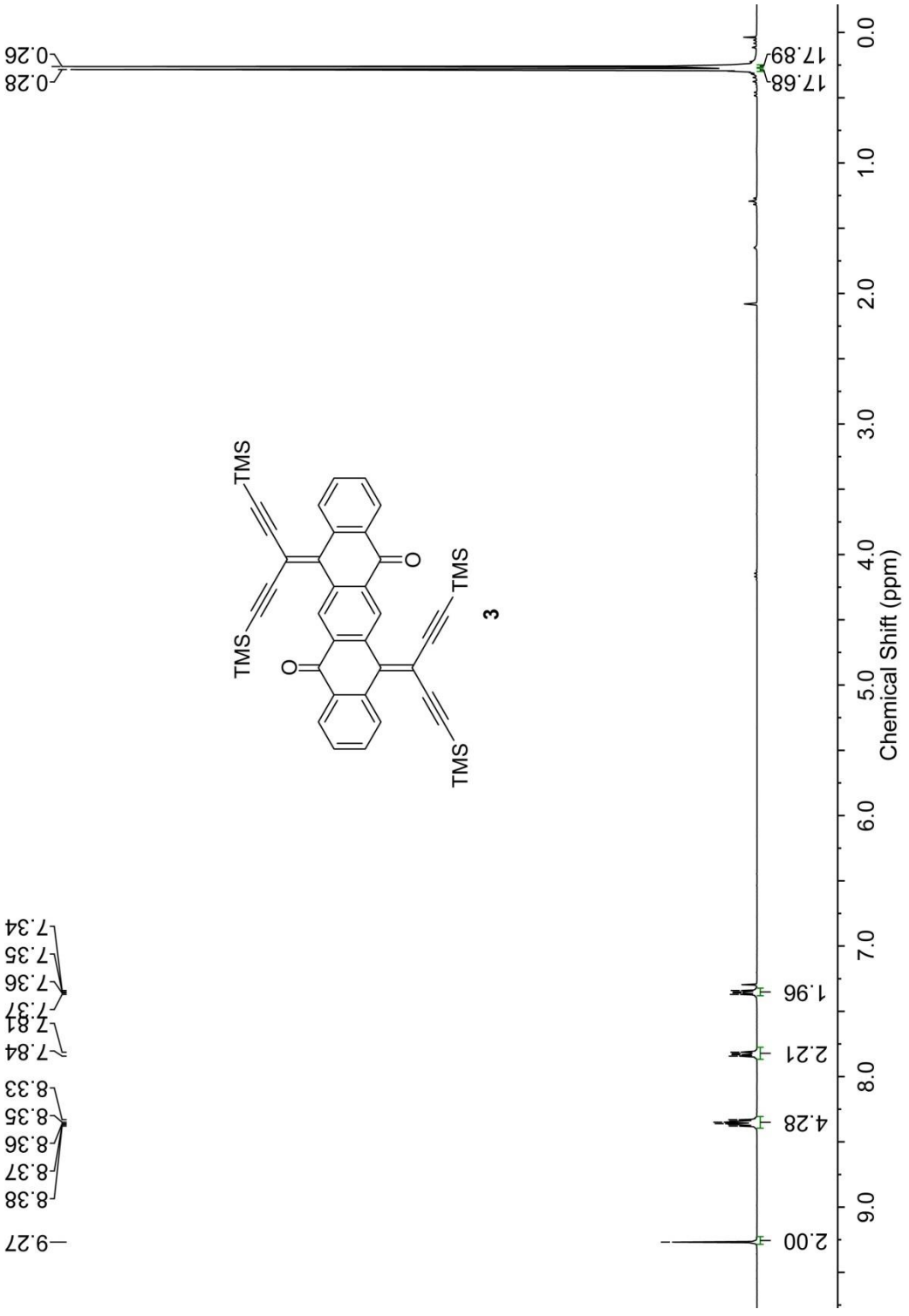

Fig. S-8 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **3**.

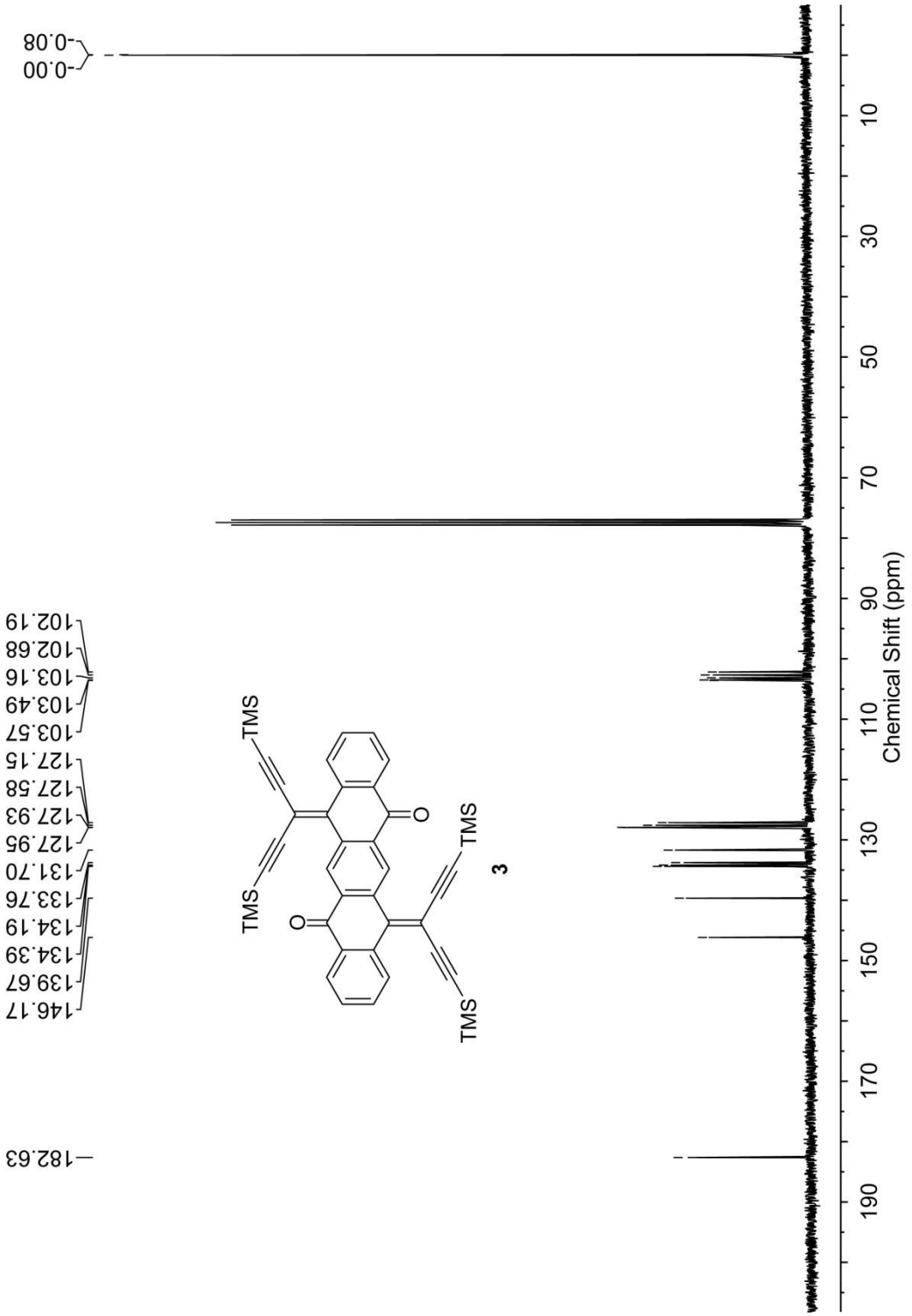

Fig. S-9 ^{13}C NMR (75 MHz, $CDCl_3$) of compound **3**.

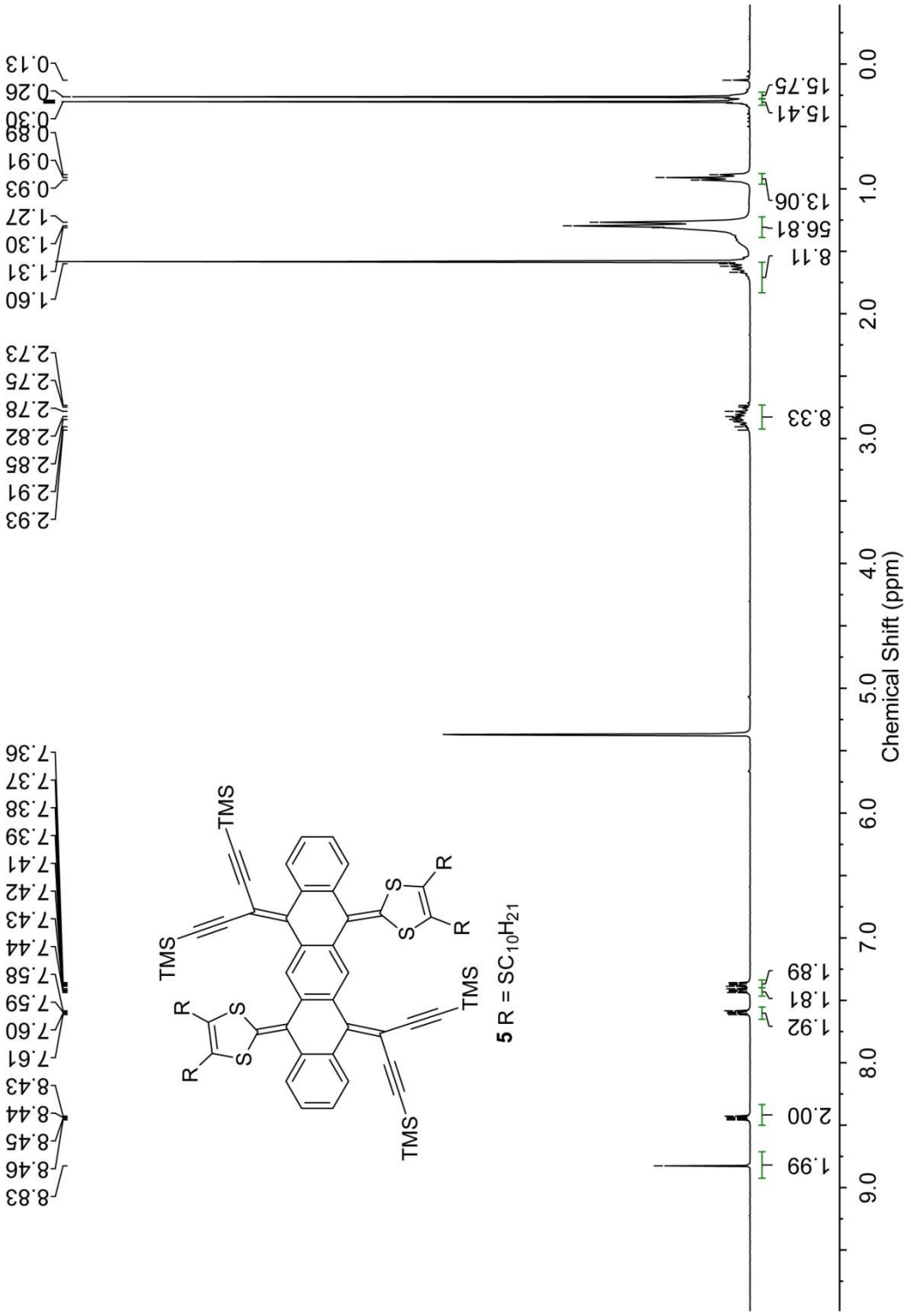

Fig. S-10 ^{1}H NMR (300 MHz, CD_2Cl_2) of compound **5**.

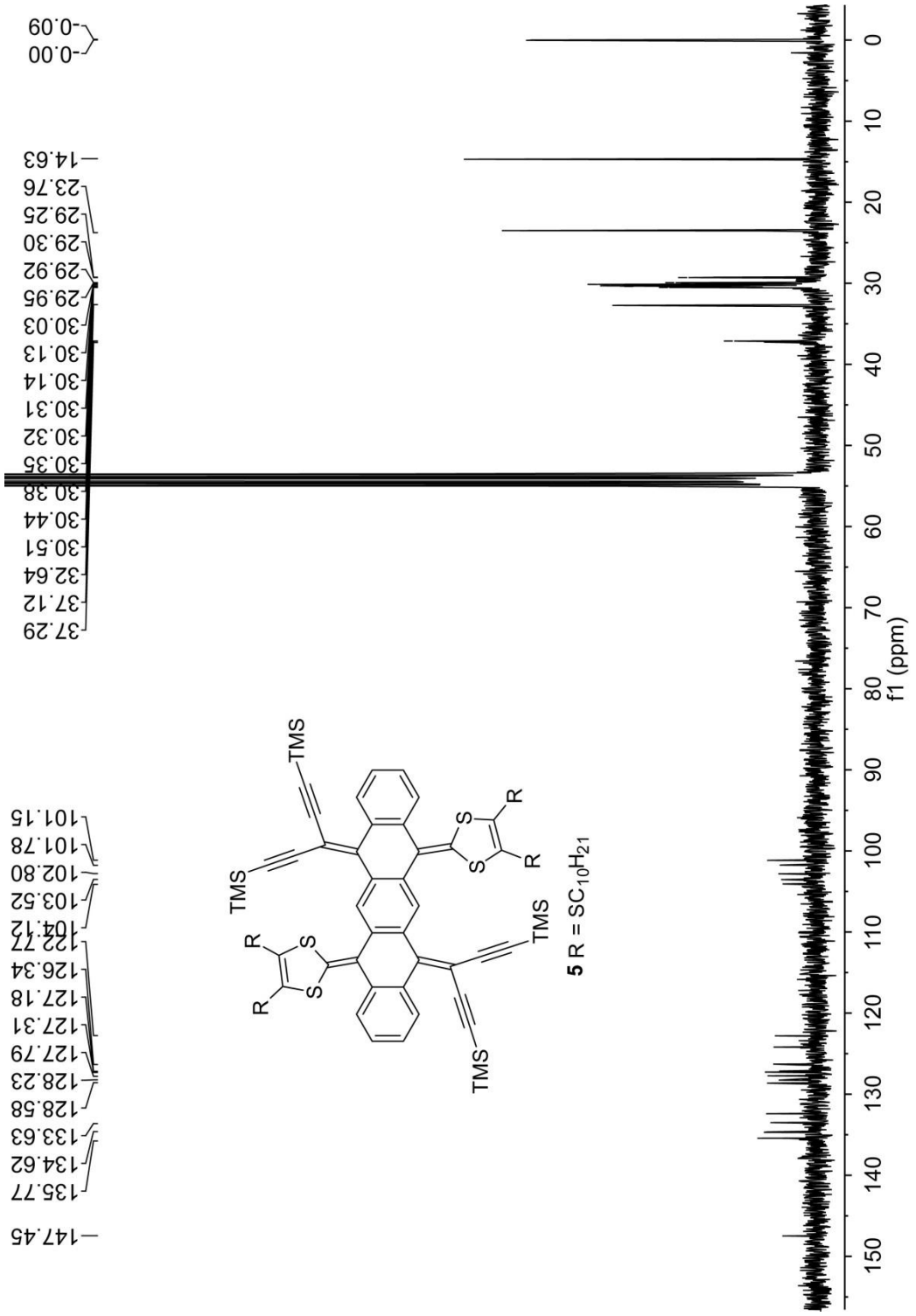

Fig. S-11 ^{13}C NMR (75 MHz, CD_2Cl_2) of compound **5**.

4. DFT Calculation Results

Cartesian coordinates and optimized **3** (*cis* conformer): *E*(RB3LYP) = -1378.00275315 a.u.; Dipole Moment = 0.8167 Debye; Basis Set = 6-31G(d)

C	-2.53675900	1.41345600	0.10820600
C	-3.67625000	0.71601600	-0.52813000
C	-5.85285600	-0.71056400	-1.63342200
C	-3.65914600	-0.69736100	-0.60742200
C	-4.78426900	1.39171900	-1.06857700
C	-5.85285600	0.68773400	-1.61728000
C	-4.75255700	-1.39615100	-1.13364100
H	-4.80190200	2.47338800	-1.07824700
H	-6.68969200	1.23682400	-2.04046200
H	-4.69972800	-2.47987200	-1.15301600
H	-6.69485800	-1.25486200	-2.05153100
C	-1.23248100	0.72357600	0.02462500
C	1.23248100	-0.72357600	0.02462500
C	-0.00230600	1.39069800	-0.01297500
C	-1.20436500	-0.69086200	-0.04039500
C	0.00230600	-1.39069800	-0.01297500
C	1.20436500	0.69086200	-0.04039500
H	0.05341800	2.46991600	-0.05448500
H	-0.05341800	-2.46991600	-0.05448500
C	-2.69920900	2.56538600	0.85625100
C	-2.46169300	-1.47307500	-0.19629300
C	2.46169300	1.47307500	-0.19629300
C	2.53675900	-1.41345600	0.10820600
C	3.65914600	0.69736100	-0.60742200
C	5.85285600	-0.68773400	-1.61728000

C	4.75255700	1.39615100	-1.13364100
C	3.67625000	-0.71601600	-0.52813000
C	4.78426900	-1.39171900	-1.06857700
C	5.85285600	0.71056400	-1.63342200
H	4.69972800	2.47987200	-1.15301600
H	4.80190200	-2.47338800	-1.07824700
H	6.69485800	1.25486200	-2.05153100
H	6.68969200	-1.23682400	-2.04046200
C	2.69920900	-2.56538600	0.85625100
O	2.48147000	2.69535500	-0.08318300
O	-2.48147000	-2.69535500	-0.08318300
C	-1.64160500	3.20924700	1.57282300
C	-3.95851100	3.20152700	1.09901600
H	-5.86371700	4.32686900	1.63648600
C	-4.96238400	3.81143500	1.39273500
H	-0.06702700	4.33625700	2.77000200
C	-0.82519300	3.82162400	2.22393200
C	1.64160500	-3.20924700	1.57282300
C	3.95851100	-3.20152700	1.09901600
H	5.86371700	-4.32686900	1.63648600
C	4.96238400	-3.81143500	1.39273500
H	0.06702700	-4.33625700	2.77000200
C	0.82519300	-3.82162400	2.22393200

Cartesian coordinates and optimized **3** (*trans* conformer): *E*(RB3LYP) = -1378.00177508 a.u.; Dipole Moment = 0.0005 Debye; Basis Set = 6-31G(d)

C	-3.19444500	-2.11221700	-0.16312500
C	-2.79119200	-0.81230800	0.08320700
C	-3.76179700	0.29759200	0.21460900

C	-3.41783000	1.57257700	-0.29490900
C	-2.05131300	1.84829100	-0.80608700
C	-1.00795800	0.85738400	-0.42120200
C	0.32731700	1.25165700	-0.51000200
C	1.36581600	0.42013000	-0.07423100
C	1.00795600	-0.85738100	0.42118900
C	2.05131000	-1.84828900	0.80607100
O	1.77488200	-2.87874800	1.41287000
C	3.41782900	-1.57257300	0.29489900
C	3.76179500	-0.29758700	-0.21461900
C	2.79118900	0.81231300	-0.08321800
C	3.19444600	2.11221900	0.16311400
C	4.55938300	2.51886800	0.30980500
C	5.66771200	2.97666700	0.47711000
H	6.65623000	3.35015500	0.62140700
C	2.30032100	3.20119500	0.41222500
C	1.64152200	4.18842000	0.65106100
H	1.02165200	5.03523900	0.84188600
C	5.01939500	-0.14984700	-0.82497300
C	5.91719500	-1.21283300	-0.87734600
C	5.59146500	-2.45014400	-0.31287400
C	4.34012100	-2.62577000	0.26491900
H	4.03647700	-3.57818000	0.68728700
H	6.30109900	-3.27199700	-0.34510400
H	6.87698800	-1.07417700	-1.36769100
H	5.28950900	0.79470500	-1.27830600
C	-0.32731900	-1.25165400	0.50999000
C	-1.36581800	-0.42012600	0.07422000
H	-0.52429700	-2.22626000	0.93421500
H	0.52429400	2.22626200	-0.93422900

O	-1.77488300	2.87875200	-1.41288000
C	-4.34012100	2.62577600	-0.26492500
C	-5.59146100	2.45015400	0.31287500
C	-5.91719100	1.21284400	0.87734900
C	-5.01939300	0.14985600	0.82497300
H	-5.28950500	-0.79469500	1.27831000
H	-6.87698100	1.07419000	1.36770200
H	-6.30109400	3.27200800	0.34511000
H	-4.03647600	3.57818600	-0.68729400
C	-2.30031400	-3.20118900	-0.41222900
C	-1.64151500	-4.18842700	-0.65101100
H	-1.02180500	-5.03547600	-0.84133900
C	-4.55938000	-2.51887200	-0.30981800
C	-5.66770200	-2.97668900	-0.47711900
H	-6.65620700	-3.35020500	-0.62143600

Cartesian coordinates and optimized **5** (*cis* conformer): *E*(RB3LYP) = -3051.28175927 a.u.; Dipole Moment = 0.7461 Debye; Basis Set = 6-31G(d)

C	2.51787400	1.39822100	0.23656100
C	3.42173200	0.74482300	1.20594900
C	5.02761500	-0.60096400	3.07200900
C	3.42173200	-0.67398100	1.24473200
C	4.22462700	1.45908200	2.10637400
C	5.02764100	0.79359700	3.02956600
C	4.22580100	-1.32502200	2.19153600
H	4.20437700	2.54213900	2.09247700
H	5.63639500	1.36421100	3.72538600
H	4.19131800	-2.40662200	2.27297100
H	5.63221200	-1.12765200	3.80536000

C	1.22039900	0.70387400	0.09437800
C	-1.22039900	-0.70387400	0.09437800
C	0.00028700	1.39140700	0.08463500
C	1.22532600	-0.71515200	0.11738100
C	-0.00028700	-1.39140700	0.08463500
C	-1.22532600	0.71515200	0.11738100
H	0.01699700	2.47352000	0.14994900
H	-0.01699700	-2.47352000	0.14994900
C	2.87104500	2.50365300	-0.50322500
C	2.53025600	-1.39126400	0.30473300
C	-2.53025600	1.39126400	0.30473300
C	-2.51787400	-1.39822100	0.23656100
C	-3.42173200	0.67398100	1.24473200
C	-5.02764100	-0.79359700	3.02956600
C	-4.22580100	1.32502200	2.19153600
C	-3.42173200	-0.74482300	1.20594900
C	-4.22462700	-1.45908200	2.10637400
C	-5.02761500	0.60096400	3.07200900
H	-4.19131800	2.40662200	2.27297100
H	-4.20437700	-2.54213900	2.09247700
H	-5.63221200	1.12765200	3.80536000
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C	1.46718600	3.56034700	-2.47058900
C	-2.05308100	-3.04843500	-1.54309700

C	-4.14197500	-3.15519100	-0.39467700
H	-6.12360300	-4.27528400	-0.35516400
C	-5.18948500	-3.76197400	-0.38114400
H	-0.94039100	-3.98273100	-3.29489600
C	-1.46718600	-3.56034700	-2.47058900
C	2.91360100	-2.51168100	-0.37383800
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S	1.89652200	-3.32252700	-1.59737200
S	4.52997100	-3.26823900	-0.22535200
C	4.33294400	-4.38409300	-1.56892000
H	5.18153500	-5.00958100	-1.82095700
C	3.14703800	-4.40872200	-2.18535600
H	2.88920000	-5.05873900	-3.01358900
S	-1.89652200	3.32252700	-1.59737200
S	-4.52997100	3.26823900	-0.22535200
C	-3.14703800	4.40872200	-2.18535600
H	-2.88920000	5.05873900	-3.01358900
C	-4.33294400	4.38409300	-1.56892000
H	-5.18153500	5.00958100	-1.82095700

Cartesian coordinates and optimized **5** (*trans* conformer): *E*(RB3LYP) = -3051.28501525 a.u.; Dipole Moment = 0.0024 Debye; Basis Set = 6-31G(d)

C	-5.19609600	3.34144400	1.35045000
S	-5.20234300	1.96745800	0.25380300
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C	-2.82584000	0.58104000	-0.22457700
C	-1.37721600	0.31489500	-0.10198700
C	-0.96776300	-1.00963300	0.20143300
C	0.39881600	-1.29453000	0.29758400

C	1.37721400	-0.31486100	0.10198500
C	2.82583600	-0.58101000	0.22457100
C	3.56857800	0.53216500	0.85484600
C	4.61723500	0.33735500	1.76544800
C	5.26610700	1.41922300	2.35720000
C	4.86362700	2.72106400	2.05790200
C	3.81518300	2.93484500	1.16651100
C	3.16129400	1.85824100	0.54985500
C	2.01604000	2.03686400	-0.36832000
C	0.96776200	1.00966600	-0.20143800
C	-0.39881700	1.29456300	-0.29758800
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C	1.96350800	3.02868700	-1.32455100
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C	0.05785700	3.34127200	-3.12505400
H	-0.69775200	3.47482900	-3.86531000
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H	3.48608300	3.94554700	0.95782600
H	5.35099500	3.56917600	2.53067500
H	6.06738800	1.24200500	3.06944500
H	4.89838900	-0.67097500	2.05169000
C	3.43319800	-1.69372000	-0.28548600
S	2.56915300	-2.98237600	-1.17738300
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C	-4.61721900	-0.33732600	-1.76547800
C	-5.26608300	-1.41919300	-2.35724100
C	-4.86360400	-2.72103500	-2.05794300
C	-3.81516700	-2.93481600	-1.16654400
H	-3.48606800	-3.94551800	-0.95785700
H	-5.35096700	-3.56914700	-2.53072200
H	-6.06735800	-1.24197500	-3.06949300
H	-4.89837400	0.67100400	-2.05172100
C	-1.96351500	-3.02865900	1.32453500
C	-3.01459200	-3.97735100	1.53899300
C	-3.85271800	-4.80907000	1.80696200
H	-4.60991900	-5.52691100	2.02619300
C	-0.89986000	-3.16088800	2.27391000
C	-0.05782800	-3.34121300	3.12501100
H	0.69869600	-3.47468800	3.86434700
S	-2.56919400	2.98236000	1.17746600
C	-4.01054600	3.79785500	1.76609100
H	-3.86367500	4.64468100	2.42652500
H	-6.15774600	3.76089900	1.62265900

Cartesian coordinates and optimized **8**: *E*(RB3LYP) = -1378.40070265 a.u.; Dipole Moment = 1.4170 Debye; Basis Set = 6-31G(d)

C	2.19838600	-1.92608100	-0.25914700
C	3.57819200	-1.40525500	-0.11546100
C	3.81578200	-0.01914100	0.02386300

C	2.72289800	0.90258700	0.04427300
C	3.00535400	2.27899000	0.15732800
C	1.92251500	3.20466700	0.18624800
C	0.62857000	2.79115500	0.09443100
C	0.28660800	1.39889800	-0.01858300
C	-1.06490100	0.95490300	-0.09301900
C	-1.35586600	-0.43313800	-0.02567800
C	-0.28660800	-1.39888000	-0.01862000
C	1.06490100	-0.95488700	-0.09306400
C	1.35587000	0.43314900	-0.02569700
C	-0.62856000	-2.79114800	0.09435400
C	-1.92249700	-3.20466200	0.18623800
C	-3.00534000	-2.27898300	0.15738800
C	-2.72289500	-0.90258300	0.04431600
C	-3.81578500	0.01913800	0.02388500
C	-3.57820800	1.40524800	-0.11547300
C	-2.19838700	1.92610100	-0.25907100
O	-2.03468100	3.11908900	-0.52506700
C	-4.64311200	2.30150900	-0.14576700
C	-5.96371200	1.84535700	-0.03144400
C	-6.21655900	0.49018100	0.10040000
C	-5.16048000	-0.44796100	0.12616700
C	-5.40023800	-1.85038800	0.24483100
C	-4.35703500	-2.73107400	0.25655800
H	-4.53696800	-3.79940800	0.34443100
H	-6.42559500	-2.20332000	0.32136800
H	-7.23878900	0.12837500	0.18301400
H	-6.78571800	2.55508700	-0.05005000
H	-4.42091300	3.35690500	-0.26204100
H	-2.14516700	-4.26392000	0.28919400
H	0.17080000	-3.51373800	0.10486700

H	-0.17078500	3.51375100	0.10503600
H	2.14518800	4.26392200	0.28922500
C	4.35705400	2.73107100	0.25645800
C	5.40024900	1.85037500	0.24475900
C	5.16048000	0.44794600	0.12615500
C	6.21654700	-0.49021100	0.10047000
C	5.96368700	-1.84539200	-0.03131000
C	4.64308900	-2.30153100	-0.14567200
H	4.42088100	-3.35693000	-0.26192100
H	6.78568300	-2.55513500	-0.04983900
H	7.23877900	-0.12841500	0.18309700
H	6.42561000	2.20330200	0.32127500
H	4.53699700	3.79940700	0.34428600
O	2.03468100	-3.11904500	-0.52526500

Table S-1 TD-DFT calculated electronic transitions, oscillator strength (*f*), and MO composition for compounds **3** and **5** (*trans* and *cis* conformers)

Entry	$\lambda_{max(}$exp)	$\lambda_{max(}$calcd)	*f*	MO composition
	436	457	0.345	H→L(93.4%), H→L+2(2.8%)
		407	0.004	H-7→L(5.9%), H-6→L(5.3%), H-3→L+1(9.4%), H-2→L(68.7%), H-2→L+2(3.2%)
		368	0.071	H-7→L(10.1%), H-4→L(13.7%), H-2→L(3.0%), H-1→L+1(10.6%), H→L+2(58.0%)
3				
trans		363	0.052	H-4→L(73.7%), H→L+3(16.7%)
	358	350	0.150	H-7→L(22.8%), H-6→L(33.5%), H-5→L+1(2.4%), H-4→L(2.8%), H-2→L(14.3%), H-1→L+1(5.2%), H→L+2(14.1%)
		339	0.217	H-7→L(3.1%), H-6→L(27.2%), H-1→L+1(56.8%), H→L+2(6.0%)

	436	459	0.287	H→L(93.9%), H→L+2(2.5%)
		376	0.103	H-6→L(3.4%), H-1→L(11.6%), H-1→L+2(5.2%), H→L+1(76.5%)
		369	0.066	H-7→L(4.7%), H-5→L(3.7%), H-4→L(23.7%), H-
3				1→L+1(9.7%), H→L+2(54.8%)
cis		364	0.034	H-5→L(2.7%), H-4→L(67.2%), H→L+2(20.4%)
	358	350	0.130	H-6→L+1(2.4%), H-5→L(64.8%), H-2→L(11.8%), H-1→L+1(2.3%), H→L+2(12.9%)
		341	0.158	H-7→L(15.0%), H-5→L(5.3%), H-4→L(3.0%), H-1→L+1(63.5%), H→L+2(6.4%)
	516	519	0.153	H→L(95.8%), H-2→L(2.5%)
5	407	402	0.093	H-2→L(53.6%), H-1→L+1(40.1%), H→L+2(3.6%)
trans		380	0.473	H-2→L(39.3%), H-1→L+1(56.0%)
		368	0.342	H-2→L(2.8%), H→L+2(88.9%), H→L+4(2.9%)
	337	349	0.038	H-1→L+3(16.1%), H-1→L+5(11.2%), H→L+2(4.1%), H→L+4(62.4%)
	516	541	0.157	H→L(96.3%)
5	407	406	0.003	H-2→L(16.8%), H-1→L+1(68.9%), H→L+2(12.4%)
cis		387	0.340	H-1→L+1(12.5%), H→L+2(83.4%)
		378	0.449	H-2→L(79.1%), H-1→L+1(16.5%)
		361	0.004	H-3→L(16.8%), H-2→L+1(20.6%), H-1→L+2(58.2%)
	337	337	0.013	H-4→L(2.4%), H-1→L+5(16.4%), H→L+4(74.0%)
		336	0.002	H-2→L+1(8.5%), H-1→L+2(6.6%), H-1→L+4(10.6%), H→L+3(51.9%), H→L+5(17.7%)