Supporting Information

From Closed-Shell Edge-Extended Kekulenes to Open-Shell Carbonylated Cycloarene Diradicaloid

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1. Experimental Section

1.1 General

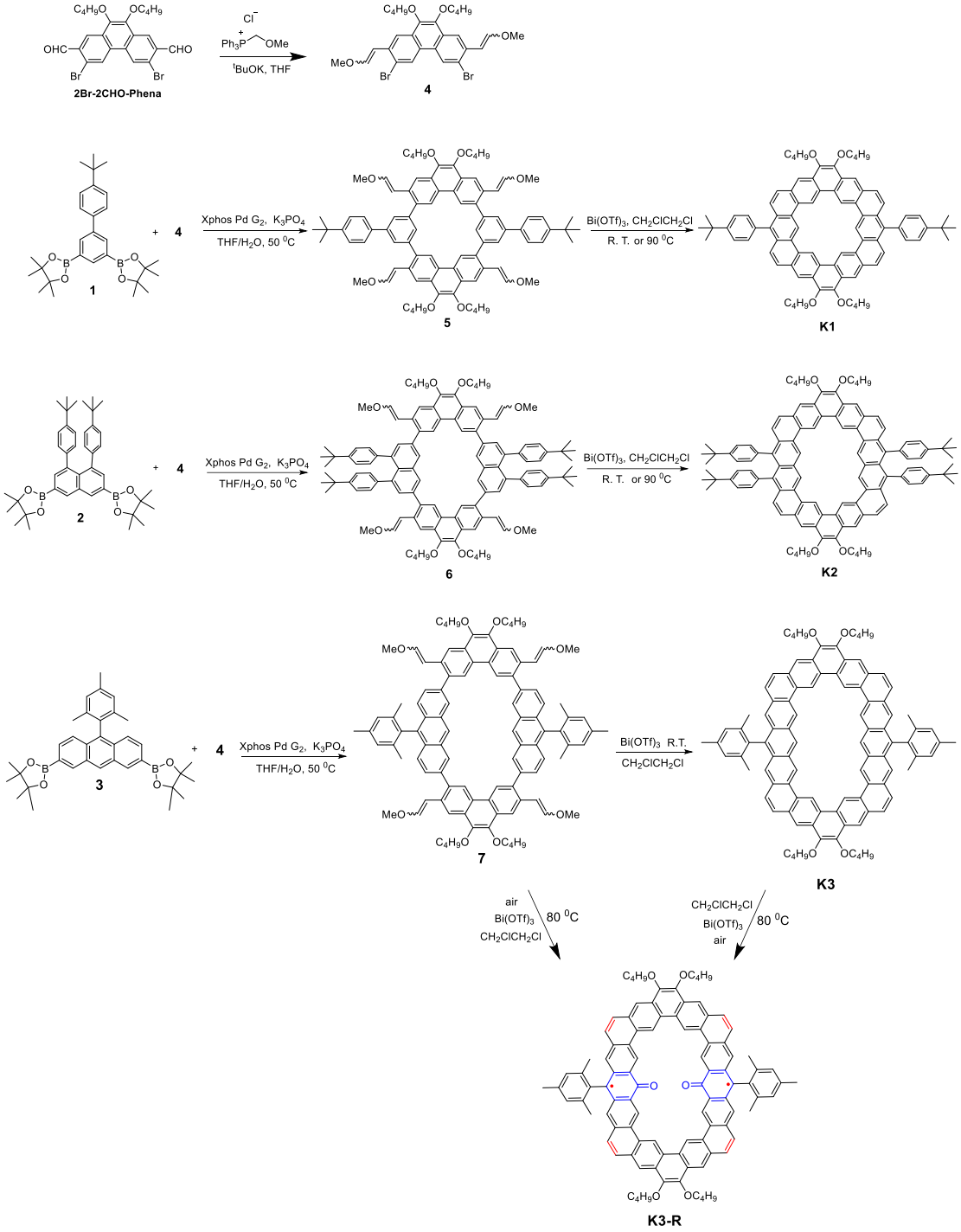
All chemicals and reagents were purchased from commercial sources and used as received unless otherwise specified. Compounds **1**, **2**, **3** and **2Br-2CHO-Phena** were synthesized according to the previous literature[1]. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 NMR Spectrometer. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); m (multiplet). HRMS were measured on a Thermo Scientific Q exactive combined quadrupole Orbitrap mass spectrometer with APCI/ESI ion source. Ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra were acquired from PerkinElmer Lambda 750 spectrophotometer. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out on a CorrTest Instrument Model CS350H with electrochemical system utilizing the three-electrode configuration consisting of a platinum wire (working electrode), platinum wire (counter electrode) and Ag/AgCl electrode (reference electrode) in dichloromethane with n-tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. Potentials were calibrated with the ferrocene/ferrocenium couple.

Continuous wave X-band ESR spectra were obtained with a JEOL (FA200) spectrometer using a variable temperature liquid nitrogen cryostat. The VT ESR data of K3-R in the frozen solutions were fitted by Bleaney-Bowers equation (1),

$$IT = \frac{C}{k_B[3+\exp(-2J/k_BT)]} \quad (1)$$

where C is a constant and -2J is correlated to the excitation energy from the ground state to the first excited state.

1.2 Synthetic procedures and characterization data



Compound **4**:

To a solution of (methoxymethyl)triphenylphosphonium chloride (5.22 g, 15.2 mmol) in dry THF (100 mL) was added ^{t}BuOK (1.71 g, 15.2 mmol) at ice bath (0 ^{0}C) under nitrogen atmosphere. After stirring for 30 mins, a solution of **2Br-2CHO-Phena** (2.00

g, 3.74 mmol) in dry THF (30 mL) was added and the mixture was stirred at room temperature for 24 h. The reaction was quenched with water and extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over Na2SO4. After removal of the solvent under vacuum, the residue was purified by silica gel chromatography (DCM: PE = 1:3) to afford compound **4** (1.30 g, 59%) as white solid. Two isomers did not need to be separated and purified, and were directly used for the next step. HRMS analysis (APCI, *m/z*): calculated for ($C_{28}H_{32}Br_2O_4$): 591.0733, found 591.0740 (error: 0.0007).

Compound **5**:

Compound **1** (320 mg, 0.690 mmol), **4** (408 mg, 0.690 mmol), K_3PO_4 aqueous solution (0.5 mol/L, 150 mL), THF (150 mL) were degassed for three times before and after the addition of catalyst Xphos Pd G2 (30 mg, 0.038 mmol). The mixture was stirred and heated at 50 ^{0}C for 24 h. After cooling to room temperature, the organic solvent was removed under reduced pressure, then H_2O and DCM were added. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness, the residue was purified by flash column chromatography (pure DCM) to afford the pale-yellow solid, which was further purified by GPC, using AR grade chloroform as eluent to give **5** (55 mg, 14.7%) as white solid. The ^{13}C NMR spectrum of **5** is omitted due to the multiple *Z*/*E* vinyl isomers. HRMS analysis (ESI, *m/z*): calculated for ($[C_{88}H_{96}O_8]$ + Na)$^+$: 1303.6997, found 1303.7010 (error: 0.0013).

Compound **K1**:

A mixture of **5** (55 mg, 0.043 mmol) and $Bi(OTf)_3$ (15 mg, 0.022 mmol) in 1,2-dichloroethane (40 mL) was stirred for 24 h under N_2 atmosphere. The organic solvent was removed under the reduced pressure. The residue was first purified by a short column (Silica gel, DCM) to remove the catalyst, and then further purified by GPC using chloroform as eluent to give pure compound **K1** as yellow solid (31 mg, 63%). ^{1}H NMR (400 MHz, 298K, $CDCl_3$): δ ppm 10.46 (s, 2H), 10.40 (s, 4H), 8.77 (s, 4H), 7.96 (d, *J* = 9.2 Hz, 4H), 7.80 (d, *J* = 9.4 Hz, 4H), 7.71 (d, *J* = 8.0 Hz, 4H), 7.55 (d, *J* =

7.9 Hz, 4H), 4.46 (t, *J* = 6.6 Hz, 8H), 2.15 – 2.03 (m, 8H), 1.85 – 1.71 (m, 8H), 1.57 (d, *J* = 8.1 Hz, 18H), 1.16 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (400 MHz, $CDCl_3/CS_2$ 10:1): δ ppm 150.1, 143.6, 138.1, 135.6, 131.3, 130.6, 129.1, 129.0 128.1, 127.7, 127.0, 126.9, 126.0, 125.3, 120.9, 116.4, 115.2, 73.4, 34.7, 33.1, 31.7, 20.0, 14.5. HRMS analysis (APCI, m/z): calculated for ($C_{84}H_{80}O_4$): 1153.6129, found 1153.6121 (error: 0.0008).

Compound **6**:

Compound **2** (300 mg, 0.460 mmol), **4** (274 mg, 0.460 mmol), K_3PO_4 aqueous solution (0.5 mol/L, 150 mL), THF (150 mL) were degassed for three times before and after the addition of catalyst Xphos Pd G2 (30 mg, 0.038 mmol). The mixture was stirred and heated at 50 ^{0}C for 24 h. After cooling to room temperature, the organic solvent was removed under reduced pressure, then H_2O and DCM were added. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness, the residue was purified by flash column chromatography (pure DCM) to afford the pale-yellow solid, which was further purified by GPC, using AR grade chloroform as eluent to give **6** (26 mg, 6.8%) as white solid. The ^{13}C NMR spectrum of **6** is omitted due to the multiple *Z*/*E* vinyl isomers. HRMS analysis (APCI, *m/z*): calculated for ($[C_{116}H_{124}O_8]$ + H)$^+$: 1646.9403, found 1646.9360 (error: 0.0043).

Compound **K2**:

A mixture of **6** (26 mg, 0.016 mmol) and $Bi(OTf)_3$ (15 mg, 0.022 mmol) in 1,2-dichloroethane (40 mL) was stirred for 24 h under N_2 atmosphere. The organic solvent was removed under the reduced pressure. The residue was first purified by a short column (Silica gel, DCM) to remove the catalyst, and then further purified by GPC using chloroform as eluent to give pure compound **K2** as yellow solid (15 mg, 62%). ^{1}H NMR (400 MHz, 298K, $CDCl_3$): ppm 10.39 (s, 4H), 9.93 (s, 4H), 8.62 (s, 4H), 7.61 (d, *J* = 9.8 Hz, 4H), 7.14 (d, *J* = 8.2 Hz, 12H), 6.91 (d, *J* = 7.8 Hz, 8H), 4.44 (t, *J* = 6.7 Hz, 8H), 2.10 – 1.98 (m, 12H), 1.74 (d, *J* = 7.6 Hz, 12H), 1.62 (s, 18H), 1.43 (d, *J* = 7.4 Hz, 36H), 1.27 (s, 8H), 1.11 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (400 MHz, $CDCl_3/CS_2$ 10:1): δ ppm 148.1, 143.4, 139.1, 138.3, 131.6, 131.4, 130.6129.4, 129.0, 128.3, 127.8, 127.5,

127.1, 127.0, 125.8, 123.8, 123.2, 121.2, 116.9, 110.0, 73.4, 34.4, 33.0, 31.7, 19.9, 14.3. HRMS analysis (APCI, m/z): calculated for ($C_{112}H_{108}O_4$): 1517.8320, found 1517.8324 (error: 0.0004).

Compound **7**:

Compound **3** (330 mg, 0.600 mmol), **4** (355 mg, 0.600 mmol), K_3PO_4 aqueous solution (0.5 mol/L, 150 mL), THF (150 mL) were degassed for three times before and after the addition of catalyst Xphos Pd G2 (30 mg, 0.038 mmol). The mixture was stirred and heated at 50 ^{0}C for 24 h. After cooling to room temperature, the organic solvent was removed under reduced pressure, then H_2O and DCM were added. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness, the residue was purified by flash column chromatography (pure DCM) to afford the pale-yellow solid, which was further purified by GPC, using AR grade chloroform as eluent to give **7** (28 mg, 6.4%) as pale-yellow solid. The ^{13}C NMR spectrum of **7** is omitted due to the multiple *Z*/*E* vinyl isomers. HRMS analysis (APCI, *m/z*): calculated for ($C_{102}H_{100}O_8$): 1453.7491, found 1453.7493 (error: 0.0002).

Compound **K3**:

A mixture of **7** (28 mg, 0.019 mmol) and $Bi(OTf)_3$ (15 mg, 0.022 mmol) in 1,2-dichloroethane (40 mL) was stirred for 24 h under N_2 atmosphere. The organic solvent was removed under the reduced pressure. The residue was first purified by a short column (Silica gel, DCM) to remove the catalyst, and then further purified by GPC using chloroform as eluent to give pure compound **K3** as red solid (16 mg, 64%). ^{1}H NMR (400 MHz, 298K, $CDCl_3/CS_2$ 3:1): ppm δ 10.52 (s, 4H), 9.96 (s, 4H), 9.50 (s, 4H), 8.59 (d, *J* = 18.1 Hz, 4H), 8.18 (s, 4H), 7.89 – 7.54 (m, 8H), 7.30 (s, 4H), 4.67 – 4.31 (m, 8H), 2.78 – 2.48 (m, 6H), 2.14 – 2.01 (m, 12H), 1.96 (s, 12H), 1.79 (td, *J* = 14.8, 7.4 Hz, 12H), 1.18 (t, *J* = 7.4 Hz, 18H). ^{13}C NMR (400 MHz, $CDCl_3/CS_2$ 3:1): δ ppm 144.0, 142.3, 138.0, 131.5, 131.3, 130.6, 129.8, 129.4, 128.9, 128.8, 128.7, 128.3, 128.0, 127.8, 127.7, 124.8, 123.0, 121.6, 117.2, 116.7, 110.0, 73.4, 33.1, 21.6, 20.5, 20.0, 14.4. HRMS analysis (APCI, m/z): calculated for ($C_{98}H_{84}O_4$): 1325.6442, found

1325.6441 (error: 0.0001).

Compound **K3-R**:

Method 1: A mixture of **K3** (20 mg, 0.015 mmol) and $Bi(OTf)_3$ (10 mg, 0.015 mmol) in dry1,2-dichloroethane (40 mL) was stirred and heated at 80 ^{0}C for 24 h under N_2 atmosphere. The organic solvent was removed under the reduced pressure. The residue was first purified by a short column (Silica gel, DCM) to remove the catalyst, and then further purified by GPC using chloroform as eluent to give pure compound **K3-R** as black solid (12 mg, 59%).

Method 2: A mixture of **7** (32 mg, 0.022 mmol) and $Bi(OTf)_3$ (15 mg, 0.022 mmol) in dry1,2-dichloroethane (40 mL) was stirred and heated at 80 ^{0}C for 24 h under N_2 atmosphere. The organic solvent was removed under the reduced pressure. The residue was first purified by a short column (Silica gel, DCM) to remove the catalyst, and then further purified by GPC using chloroform as eluent to give pure compound **K3-R** as black solid (9 mg, 30%). HRMS analysis (APCI, m/z): calculated for ($C_{98}H_{83}O_6^{2\cdot}$): 1355.6184, found 1355.6176 (error: 0.0008).

2. Additional spectra

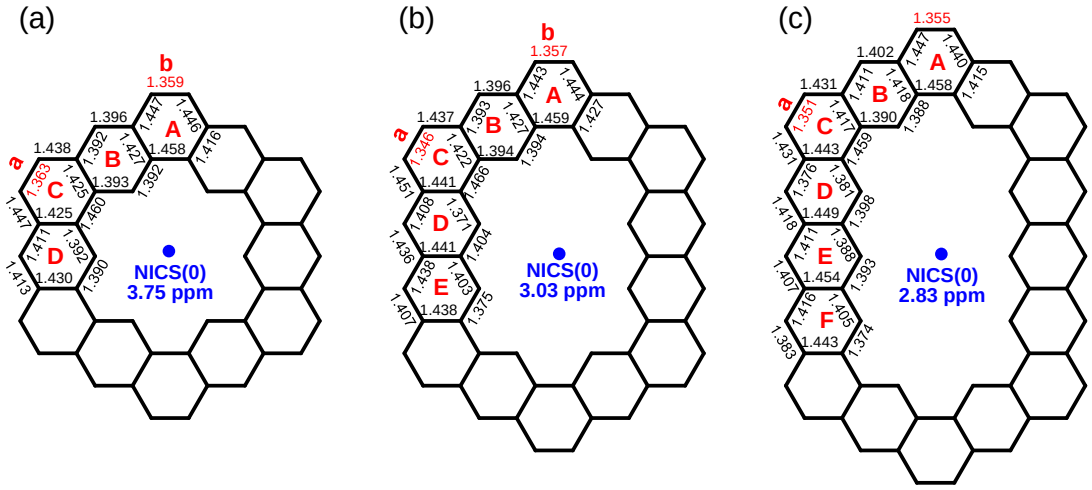


Figure S1. The selected bond lengths (in Å) of the backbone for (a)**K1**, (b)**K2** and (c)**K3**. The red numbers in individual rings are the calculated HOMA values. The blue numbers are the NICS(0) values of the dummy atoms in the center of cavities. Hydrogen atoms and alkoxy substituents are omitted for clarity.

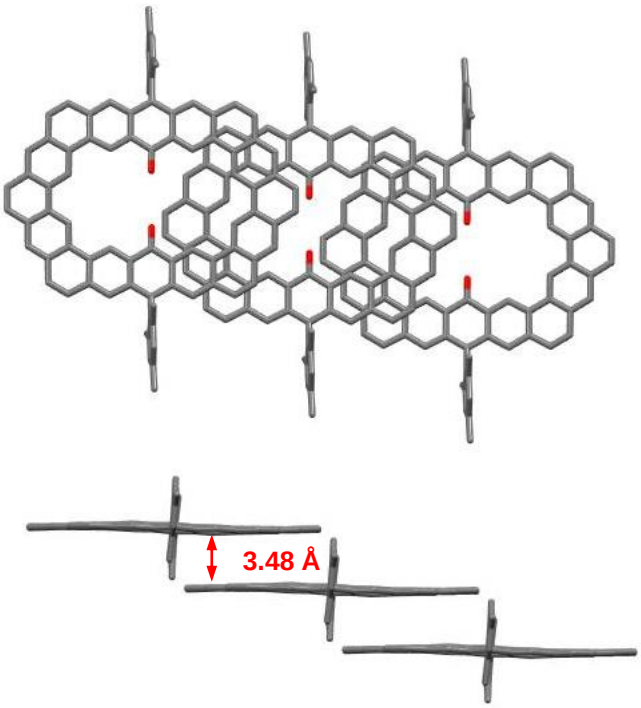


Figure S2. The crystal packing of **K3-R**. (a) Top view. (b) Side view.

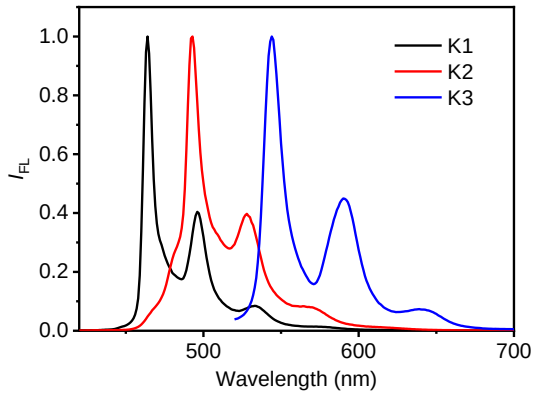


Figure S3 The normalized fluorescence spectra of **K1-K3** measured in chloroform.

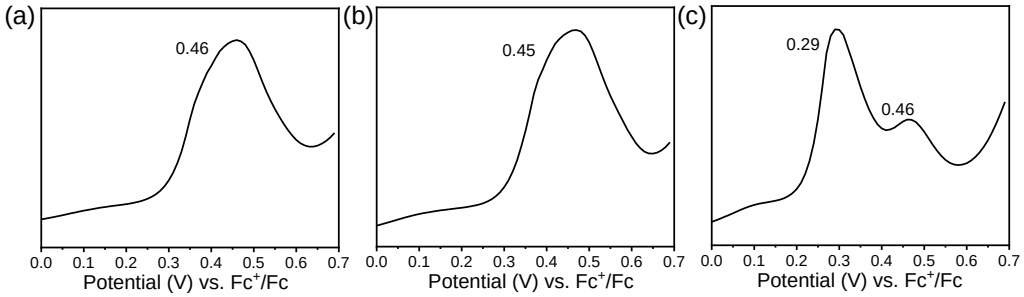


Figure S4. Differential pulse voltammograms (DPV) of (a)**K1**, (b)**K2** and (c)**K3** in chloroform solutions.

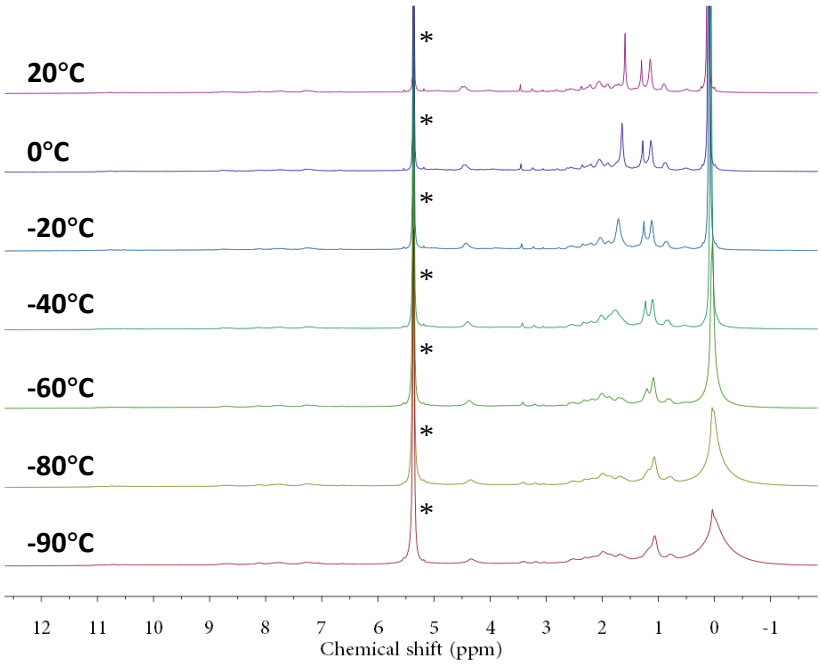


Figure S5. VT ^{1}H NMR spectra of **K3-R** in CD_2Cl_2 (500 MHz); the peaks labelled * indicate residual solvent (10 mg/mL).

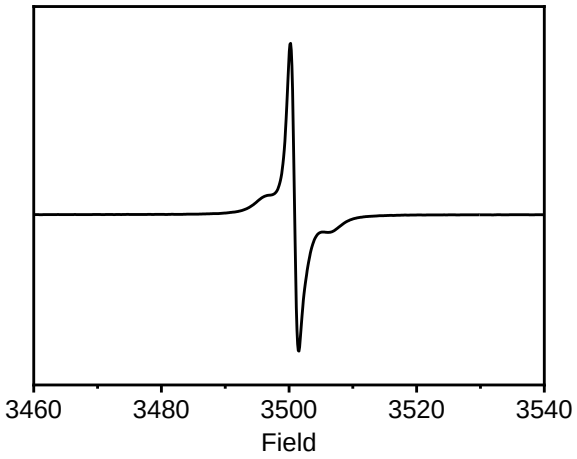


Figure S6. ESR spectrum of **K3-R** measured in DCM solution at room temperature.

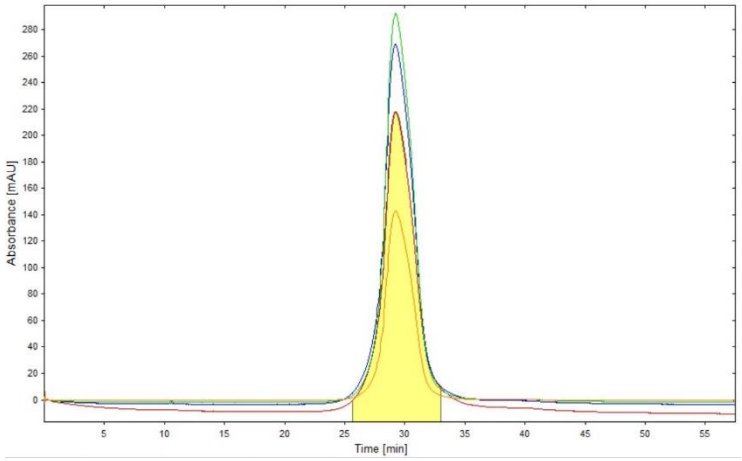


Figure S7. HPLC curves of **K3-R** in the first cycle (CHCl3 as eluant at a rate of 1 ml/min).

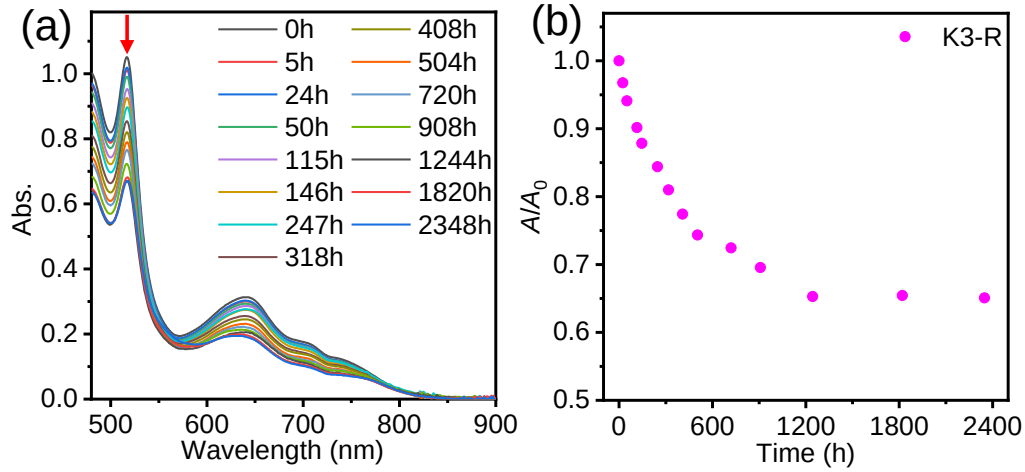


Figure S8. (a) Change of the absorption spectrum of **K3-R** in $CHCl_3$ with time under ambient air and light conditions. (b) The plots of the absorbance of **K3-R** at 506 nm with time.

3. Theoretical calculations

Density functional theory (DFT) calculations were performed with the Gaussian09 program suite[2] with Becke's threeparameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-31G(d,p) basis set for all atoms.[3] Time-dependent DFT (TD-DFT) calculations were performed under the same level of theory and basis set as solvation of chloroform. The radical character of the electronic ground state and transition energies to higher states of K3-R were calculated using the unrestricted UCAM-B3LYP/6-31G(d,p) method based on the geometry optimized at the UB3LYP/6-31G(d,p) level of theory.[4] The diradical character (y_0) was calculated according to Yamaguchi's scheme: $y_0 = 1 - (2T/(1 + T^2))$, and $T = (n_{HOMO} - n_{LUMO})/2$ (n_{HOMO} is the occupation number of the HOMO, n_{LUMO} is the occupation number of the LUMO).[5] NICS values were calculated by using the standard GIAO procedure (NMR pop=NCSall)[6] with the assistance of Multiwfn.[7] ACID plot was calculated by using the method developed by Herges.[8] The iso-chemical shielding surface (ICSS)[7, 9] calculations were carried out to analyze two-dimensional nucleus induced chemical shifts (2D-NICS) depending on various planes.

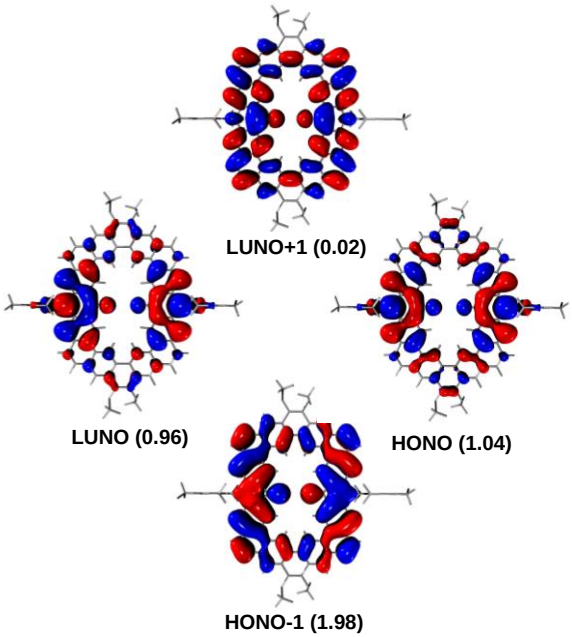


Figure S9. Calculated (UB3LYP/6-31G(d,p)) frontier natural orbital profiles of **K3-R** at the open-shell singlet ground state with isovalue of 0.01. The numbers in the parentheses are the calculated occupation numbers.

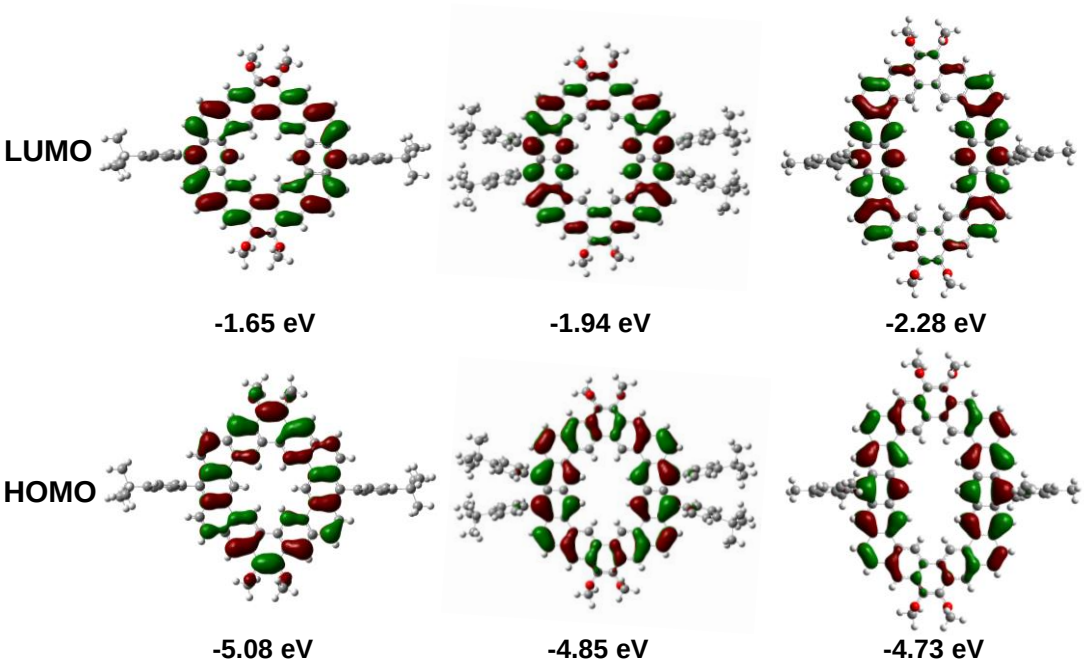


Figure S10. Calculated frontier molecular orbital profiles of the closed-shell expanded kekulene: (a) **K1**, (b) **K2** and (c) **K3**.

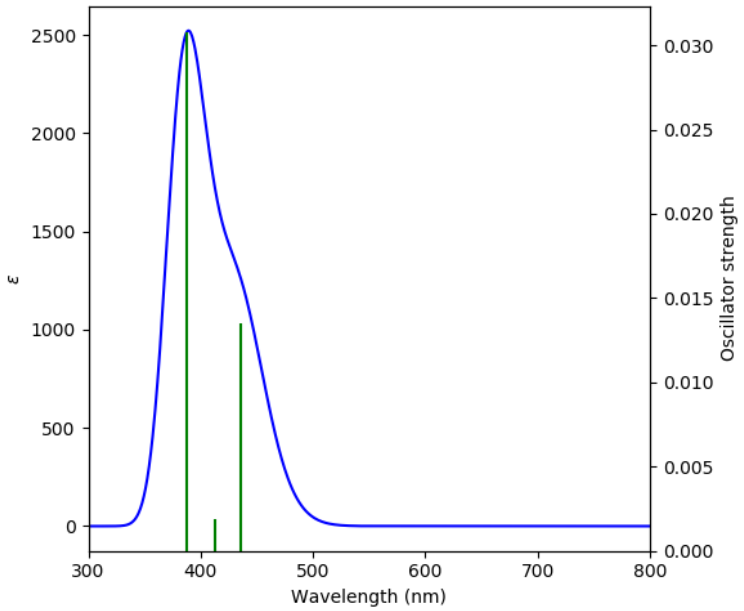


Figure S11. TD DFT simulated spectrum of **K1**.

Table S1. Selected TD-DFT (RB3LYP/6-31G(d,p) calculated energies, oscillator strength and compositions of major electronic transitions of **K1**.

Wavelength (nm)	Osc. Strength	Major contribs
435.23	0.0135	H-2->L+2 (11%), H-1->L+1 (28%), HOMO->LUMO (53%)
420.11	0	H-3->LUMO (12%), H-2->L+1 (24%), H-1->L+2 (31%), HOMO->L+3 (31%)

414.61	0	H-2->LUMO (19%), H-1->L+3 (19%), HOMO->L+2 (50%)
412.99	0.0019	H-1->LUMO (46%), HOMO->L+1 (48%)
410.91	0	H-2->L+1 (11%), H-1->L+2 (31%), HOMO->L+3 (44%)
397.65	0	H-2->LUMO (62%), HOMO->L+2 (34%)
392.88	0	H-3->LUMO (13%), H-2->L+1 (56%), H-1->L+2 (29%)
387.22	0.0308	H-3->L+3 (20%), H-2->L+2 (62%), HOMO->LUMO (10%)
385.44	0	H-3->LUMO (64%), HOMO->L+3 (22%)
383.84	0	H-3->L+1 (30%), H-1->L+3 (63%)

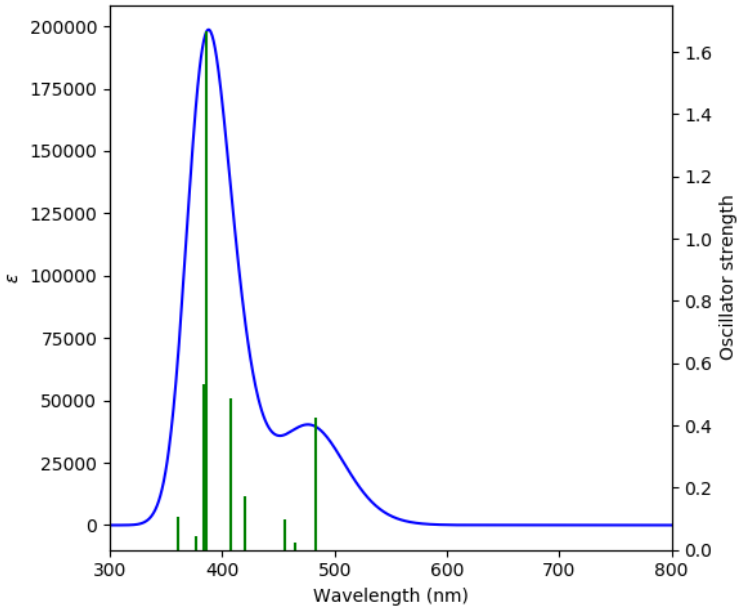


Figure S12. TD DFT simulated spectrum of **K2**.

Table S2. Selected TD-DFT (RB3LYP/6-31G(d,p) calculated energies, oscillator strength and compositions of major electronic transitions of **K2**.

Wavelength (nm)	Osc. Strength	Major contribs
483.73	0.4254	HOMO->LUMO (90%)
479.11	0	H-1->LUMO (55%), HOMO->L+1 (41%)
472.75	0	H-1->LUMO (42%), HOMO->L+1 (56%)
464.48	0.0247	H-3->L+1 (10%), H-2->LUMO (50%), H-1->L+3 (15%), HOMO->L+2 (24%)
455.36	0.0974	H-1->L+1 (90%)
455.09	0	H-3->LUMO (23%), H-2->L+1 (61%)
446.61	0	H-2->L+1 (13%), H-1->L+2 (29%), HOMO->L+3 (53%)
422.95	0	H-3->LUMO (64%), H-2->L+1 (21%), H-1->L+2 (11%)
420.19	0.1727	H-3->L+1 (36%), H-2->LUMO (29%), H-1->L+3 (33%)
416.00	0	H-1->L+2 (52%), HOMO->L+3 (34%)
407.90	0.4874	H-2->LUMO (14%), H-1->L+3 (22%), HOMO->L+2 (60%)

398.04	0	H-4->LUMO (18%), H-3->L+2 (13%), H-2->L+3 (57%)
386.15	1.6682	H-3->L+1 (49%), H-1->L+3 (29%), HOMO->L+2 (13%)
383.08	0.5318	H-4->L+1 (26%), H-2->L+2 (55%)
377.26	0.0435	H-4->L+1 (56%), H-2->L+2 (32%)
374.43	0	H-4->LUMO (71%), H-2->L+3 (25%)
370.09	0	H-6->L+1 (35%), H-5->LUMO (63%)
370.01	0.0009	H-6->LUMO (62%), H-5->L+1 (36%)
361.99	0	H-3->L+2 (66%), H-2->L+3 (14%)
360.63	0.1085	H-7->LUMO (15%), H-4->L+1 (13%), HOMO->L+4 (62%)

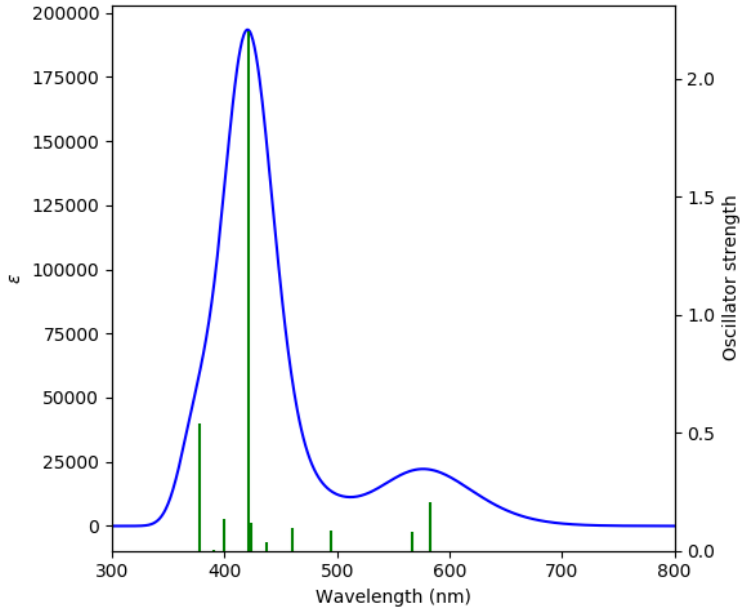


Figure S13. TD DFT simulated spectrum of **K3**.

Table S3. Selected TD-DFT (RB3LYP/6-31G(d,p) calculated energies, oscillator strength and compositions of major electronic transitions of **K3**.

Wavelength (nm)	Osc. Strength	Major contribs
582.69	0.2053	H-1->L+1 (24%), HOMO->LUMO (75%)
580.86	0	H-1->LUMO (41%), HOMO->L+1 (59%)
578.34	0	H-1->LUMO (59%), HOMO->L+1 (41%)
566.86	0.0811	H-1->L+1 (76%), HOMO->LUMO (24%)
494.37	0.0849	H-3->L+1 (12%), H-2->LUMO (54%), H-1->L+2 (14%), HOMO->L+3 (17%)
493.80	0	H-3->LUMO (19%), H-2->L+1 (76%)
471.62	0	H-1->L+3 (33%), HOMO->L+2 (58%)
461.41	0	H-3->LUMO (77%), H-2->L+1 (17%)
459.78	0.0968	H-3->L+1 (51%), H-2->LUMO (31%), H-1->L+2 (17%)
444.01	0	H-1->L+3 (61%), HOMO->L+2 (37%)

437.03	0.0391	H-1->L+2 (47%), HOMO->L+3 (42%)
426.40	0	H-4->LUMO (70%)
424.02	0.1174	H-4->L+1 (88%)
421.41	2.2037	H-3->L+1 (27%), H-2->LUMO (12%), H-1->L+2 (20%), HOMO->L+3 (38%)
401.91	0	H-5->L+1 (21%), H-4->LUMO (22%), H-1->L+4 (42%)
399.43	0.1342	H-5->LUMO (21%), HOMO->L+4 (66%)
390.26	0.0015	H-5->LUMO (47%), H-2->L+3 (12%), H-1->L+5 (18%), HOMO->L+4 (18%)
382.50	0	H-2->L+2 (34%), H-1->L+4 (38%), HOMO->L+5 (13%)
377.94	0.5403	H-5->LUMO (26%), H-1->L+5 (67%)
377.05	0	H-5->L+1 (70%), H-2->L+2 (17%), H-1->L+4 (10%)

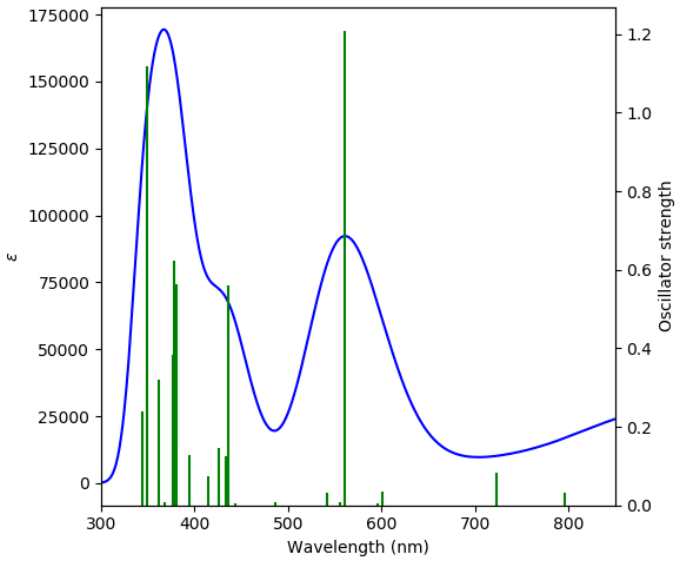


Figure S14. TD DFT simulated spectrum of **K3-R**.

Table S4. Selected TD-DFT (RB3LYP/6-31G(d,p) calculated energies, oscillator strength and compositions of major electronic transitions of **K3-R**.

Wavelength (nm)	Osc. Strength	Major contribs
2285.42	0.2712	HOMO->LUMO (141%)
921.82	0.3627	H-1->LUMO (96%)
864.48	0	H-2->LUMO (99%)
796.30	0.0334	H-3->LUMO (90%), HOMO->L+1 (10%)
735.24	0	H-4->LUMO (95%)
723.11	0.0843	H-3->LUMO (10%), HOMO->L+1 (89%)
668.85	0	HOMO->L+2 (92%)
600.49	0.0343	H-5->LUMO (64%), HOMO->L+3 (32%)
596.42	0.0042	H-7->LUMO (95%)

596.34	0	H-6->LUMO (83%), HOMO->L+4 (16%)
596.22	0	H-6->LUMO (16%), HOMO->L+4 (83%)
560.79	1.2091	H-5->LUMO (31%), HOMO->L+3 (59%)
557.53	0	H-11->LUMO (14%), H-9->LUMO (84%)
555.34	0.0091	H-10->LUMO (99%)
552.39	0	H-11->LUMO (85%), H-9->LUMO (12%)
543.89	0	H-8->LUMO (93%)
541.56	0.0323	H-12->LUMO (94%)
534.53	0	H-13->LUMO (95%)
485.93	0.0073	HOMO->L+6 (96%)
476.13	0	HOMO->L+5 (94%)
443.32	0	H-16->LUMO (40%), HOMO->L+7 (56%)
443.20	0.0053	H-14->LUMO (92%)
436.03	0.5592	H-1->L+1 (81%)
433.63	0.1242	H-15->LUMO (83%)
433.09	0	H-16->LUMO (55%), HOMO->L+7 (33%)
426.27	0.1465	HOMO->L+8 (86%)
422.35	0	H-2->L+1 (46%), H-1->L+2 (43%)
414.55	0.0732	H-17->LUMO (94%)
406.00	0	H-2->L+1 (40%), H-1->L+2 (53%)
403.20	0	H-4->L+1 (42%), H-2->L+3 (12%), H-1->L+4 (37%)
394.50	0.1275	H-3->L+1 (75%), H-1->L+3 (19%)
382.08	0	H-18->LUMO (99%)
380.93	0.5626	H-2->L+2 (91%)
377.87	0.6227	H-19->LUMO (24%), H-3->L+1 (13%), H-1->L+3 (50%)
376.66	0	H-4->L+1 (47%), H-3->L+2 (15%), H-1->L+4 (24%)
376.19	0.3821	H-19->LUMO (75%), H-1->L+3 (16%)
373.47	0	H-20->LUMO (49%), H-3->L+2 (24%), H-1->L+4 (18%)
368.52	0.0079	H-4->L+2 (88%)
364.12	0	H-20->LUMO (37%), H-3->L+2 (54%)
361.64	0.3207	H-4->L+4 (30%), H-3->L+3 (40%), H-1->L+6 (14%)
355.58	0	H-2->L+3 (74%), H-1->L+4 (14%)
355.35	0	HOMO->L+9 (93%)
353.89	0.0001	H-21->LUMO (97%)
351.35	0	H-4->L+3 (44%), H-3->L+4 (36%), H-1->L+5 (10%)
349.36	1.1177	H-2->L+4 (90%)
344.33	0.2398	H-4->L+4 (40%), H-3->L+3 (42%)
341.74	0.0001	H-13->L+2 (27%), H-12->L+1 (34%), H-7->L+1 (19%)
341.41	0	H-13->L+1 (30%), H-12->L+2 (30%), H-6->L+1 (20%)
341.09	0	H-4->L+3 (27%), H-3->L+4 (46%)
337.93	0	HOMO->L+11 (99%)

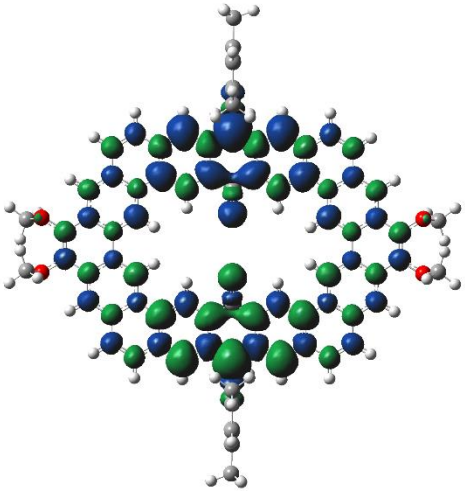


Figure S15. Calculated (UB3LYP/6-31G(d,p)) spin density distribution map of **K3-R** at the open-shell singlet state.

Coordinates of theoretically optimized structures.

K1

Atomic Type	Coordinates (Angstroms) X	Y	Z	Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.69841	-2.51681	0.015848	H	9.864566	-0.48084	-2.11013
H	-6.782	-2.53342	0.037508	C	10.08555	0.006729	-0.01611
O	-1.40072	-7.35809	-0.01756	C	9.356712	0.276417	1.149607
C	-5.00753	-3.68995	-0.00123	H	9.872086	0.49164	2.07856
H	-5.5455	-4.63437	0.006411	C	7.959974	0.274871	1.154792
O	1.406445	-7.35655	0.066631	H	7.427942	0.486208	2.078099
C	-3.56746	-3.72778	-0.01787	C	5.69841	2.516805	-0.01585
C	-2.84147	-4.92936	-0.02269	H	6.782004	2.533418	-0.03751
H	-3.37181	-5.8757	-0.01405	O	1.400711	7.358093	0.017567
C	-1.43911	-4.94676	-0.01973	C	5.007533	3.689951	0.001228
C	-0.68271	-6.181	-0.01413	H	5.545501	4.634369	-0.00642
C	1.443382	-4.94553	0.033222	O	-1.40644	7.356554	-0.06661
C	0.687715	-6.18021	0.044252	C	3.567455	3.727778	0.017868
C	2.845695	-4.92714	0.048413	C	2.841468	4.929359	0.022688
H	3.376622	-5.87312	0.059921	H	3.371805	5.875698	0.014048
C	3.570964	-3.72519	0.036357	C	1.439108	4.946763	0.019729
C	5.01108	-3.68579	0.049774	C	0.682708	6.180996	0.014135
H	5.549923	-4.62928	0.079148	C	-1.44338	4.945533	-0.03322
C	5.701089	-2.51221	0.026231	C	-0.68771	6.180213	-0.04425
H	6.784886	-2.52759	0.038162	C	-2.84569	4.927144	-0.04841
C	5.033298	-1.23028	-0.00341	H	-3.37662	5.87312	-0.05992
C	5.734608	0.002186	-0.00592	C	-3.57096	3.725186	-0.03635
C	5.031923	1.233976	-0.00346	C	-5.01108	3.685791	-0.04977
C	3.601313	1.22623	0.008858	H	-5.54992	4.629281	-0.07914
C	2.940236	0.000692	0.021384	C	-5.70109	2.512208	-0.02623
H	1.862958	-0.00046	0.070005	H	-6.78489	2.527586	-0.03816
C	3.602743	-1.22394	0.001961	C	-5.0333	1.230285	0.003411
C	2.863273	-2.48526	0.000751	C	-5.73461	-0.00219	0.005917
C	1.468944	-2.5234	-0.03557	C	-5.03192	-1.23398	0.003459
H	0.930906	-1.59119	-0.10902	C	-3.60131	-1.22623	-0.00886
C	0.731588	-3.70689	-0.00636	C	-2.94024	-0.00069	-0.02138
C	-0.72793	-3.70725	-0.00541	H	-1.86296	0.000463	-0.07
C	-1.46578	-2.52382	0.009722	C	-3.60274	1.223941	-0.00196
H	-0.92714	-1.59046	0.059505	C	-2.86327	2.485266	-0.00074
C	-2.86053	-2.48689	-0.00836	C	-1.46894	2.523401	0.035579
C	7.231844	0.002708	-0.00892	H	-0.93091	1.591187	0.109016
C	7.954436	-0.2696	-1.18046	C	-0.73159	3.706889	0.006365
H	7.416617	-0.48222	-2.10007	C	0.72793	3.707253	0.005415
C	9.346676	-0.26662	-1.17982	C	1.465782	2.523823	-0.00972

Atomic Type	Coordinates (Angstroms) X	Y	Z	Atomic Type	Coordinates (Angstroms) X	Y	Z
H	0.927135	1.590462	-0.0595	H	1.626606	-7.53114	2.13863
C	2.860527	2.48689	0.008358	C	-11.6244	-0.0009	0.061669
C	-7.23185	-0.00271	0.008914	C	11.62442	0.000886	-0.06169
C	-7.95444	0.269589	1.180456	C	-12.1136	-1.05755	1.080512
H	-7.41663	0.4822	2.100069	H	-11.7399	-0.85557	2.088569
C	-9.34668	0.266605	1.179814	H	-13.2085	-1.06378	1.126606
H	-9.86457	0.480815	2.11012	H	-11.7798	-2.06056	0.795441
C	-10.0856	-0.00673	0.016093	C	-12.2511	-0.32805	-1.30683
C	-9.35671	-0.27641	-1.14962	H	-13.3427	-0.31273	-1.22561
H	-9.87208	-0.49162	-2.07858	H	-11.9677	0.403178	-2.07081
C	-7.95997	-0.27486	-1.1548	H	-11.9612	-1.32269	-1.66111
H	-7.42793	-0.48618	-2.07811	C	-12.1214	1.397774	0.498051
C	-1.27856	-8.13453	-1.21799	H	-11.7996	2.166829	-0.21169
H	-1.91981	-9.00759	-1.08129	H	-13.216	1.415305	0.545317
H	-1.62517	-7.56195	-2.08637	H	-11.7411	1.674834	1.485668
H	-0.24484	-8.45348	-1.3787	C	12.12135	-1.39778	-0.4981
C	1.278554	8.134525	1.217999	H	11.74114	-1.67481	-1.48573
H	1.625158	7.56194	2.086375	H	13.21596	-1.41532	-0.54536
H	1.919803	9.007585	1.081307	H	11.7996	-2.16685	0.211619
H	0.24483	8.453477	1.378705	C	12.11363	1.05756	-1.08051
C	-1.28203	8.116086	-1.27765	H	11.77985	2.060568	-0.79541
H	-1.924	8.990631	-1.15457	H	13.2085	1.063777	-1.12662
H	-0.24813	8.433189	-1.44068	H	11.73986	0.855616	-2.08857
H	-1.62654	7.531185	-2.13862	C	12.25111	0.328014	1.306815
C	1.282054	-8.11606	1.277693	H	11.96126	1.322654	1.661108
H	0.248161	-8.43314	1.440754	H	11.96766	-0.40322	2.070787
H	1.924007	-8.99061	1.154609	H	13.34273	0.312667	1.225597

K2

Atomic Type	Coordinates (Angstroms) X	Y	Z	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1.40428	8.535522	0.382553	C	-2.87973	3.684426	0.223932
O	1.40605	8.533765	0.424846	C	-7.32709	1.4737	-0.22564
C	-3.76731	0.000087	0.010947	C	0.730327	4.878679	0.299623
C	-3.65217	2.438116	0.148818	C	-7.32609	-1.4747	0.256194
C	-3.04215	-1.2031	-0.06213	C	1.484274	3.699518	0.246939
H	-1.96144	-1.11852	-0.0592	H	0.95664	2.756938	0.220902
C	2.879603	3.683834	0.211279	C	-9.5652	-2.035	-0.51554
C	-5.85507	-1.28671	0.020207	H	-10.2291	-2.20119	-1.35622
C	-3.04222	1.203575	0.080095	C	3.567408	4.934023	0.240475
H	-1.9615	1.119846	0.068396	C	-1.43137	6.124961	0.316057
C	-3.65191	-2.43781	-0.12954	C	-5.21224	-0.00013	0.013572

Atomic	Coordinates (Angstroms)			Atomic	Coordinates (Angstroms)		
Type	X	Y	Z	Type	X	Y	Z
C	-5.72386	3.781635	0.107226	H	-13.3546	3.094909	-0.10308
H	-6.80353	3.835891	0.063532	H	-11.9315	3.593479	0.81632
C	-5.09475	-2.47488	-0.07348	C	-12.3387	-2.80185	-0.13561
C	-3.56687	4.935249	0.233422	H	-13.3541	-3.09529	0.14958
C	-5.00649	4.93141	0.178804	H	-11.9335	-3.59385	-0.77377
H	-5.52037	5.889094	0.191501	H	-12.4165	-1.88865	-0.73484
C	-1.48477	3.699486	0.272294	C	-12.1538	-1.49394	1.987965
H	-0.95849	2.755785	0.281393	H	-12.1806	-0.54047	1.450702
C	-0.73003	4.87888	0.305168	H	-11.62	-1.33103	2.928743
C	-9.56398	2.034654	0.552019	H	-13.1837	-1.7762	2.233876
H	-10.2255	2.201512	1.39444	C	-12.1596	1.493265	-1.94452
C	-10.0388	-2.17651	0.795646	H	-11.6283	1.330015	-2.88664
C	-10.0412	2.175448	-0.75791	H	-13.1901	1.775871	-2.18783
C	-8.23453	1.695205	0.813865	H	-12.1854	0.539882	-1.40706
H	-7.89735	1.614944	1.842893	C	-11.4713	3.918514	-1.88064
C	-9.12576	1.938329	-1.79685	H	-11.0093	4.719638	-1.29453
H	-9.44442	2.035274	-2.83077	H	-12.4931	4.225788	-2.13053
C	-5.85542	1.286317	0.006689	H	-10.913	3.826371	-2.81688
C	-8.2365	-1.69544	-0.78088	C	-11.4663	-3.91939	1.922027
H	-7.90226	-1.61433	-1.81081	H	-12.4876	-4.22643	2.174502
C	-5.09509	2.474863	0.094892	H	-10.9056	-3.82749	2.856843
C	0.685129	7.359054	0.389139	H	-11.006	-4.72059	1.33471
C	-7.80073	1.599988	-1.54005	O	1.404328	-8.53552	-0.38247
H	-7.11365	1.451358	-2.36844	O	-1.40608	-8.53378	-0.42439
C	-2.83263	6.123662	0.287326	C	3.767308	-9.7E-05	-0.01097
H	-3.35256	7.075288	0.307826	C	3.652171	-2.43812	-0.14892
C	1.432533	6.123706	0.337474	C	3.04215	1.203088	0.062174
C	2.833811	6.122061	0.309706	H	1.961444	1.118494	0.059367
H	3.353709	7.073824	0.323668	C	-2.8796	-3.68385	-0.2112
C	-9.1204	-1.94019	1.832131	C	5.85507	1.286709	-0.02021
H	-9.43612	-2.03779	2.866874	C	3.042225	-1.20358	-0.08015
C	5.723667	3.78144	0.093916	H	1.961501	-1.11985	-0.06847
H	6.803146	3.835991	0.045826	C	3.651916	2.437792	0.129593
C	-11.4871	2.590311	-1.08653	C	2.879742	-3.68443	-0.22404
C	-0.68353	7.360593	0.350707	C	7.327097	-1.47369	0.225532
C	-7.79603	-1.60187	1.571843	C	-0.73033	-4.87869	-0.29958
H	-7.10663	-1.4539	2.398419	C	7.326078	1.474682	-0.25623
C	-11.4838	-2.59112	1.128092	C	-1.48427	-3.69953	-0.24704
C	5.006859	4.930466	0.181334	H	-0.95665	-2.75693	-0.22139
H	5.520936	5.887912	0.201577	C	9.565241	2.034938	0.515409
C	-12.3385	2.801396	0.17943	H	10.22914	2.201099	1.356064
H	-12.4147	1.888331	0.779048	C	-3.5674	-4.93405	-0.24017

Atomic Type	Coordinates (Angstroms) X	Y	Z	Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.43138	-6.12496	-0.31613	H	-5.52092	-5.88794	-0.20108
C	5.212232	0.000119	-0.01363	C	12.33848	-2.8014	-0.1794
C	5.723868	-3.78164	-0.10747	H	12.41475	-1.88838	-0.77909
H	6.803548	-3.83589	-0.06383	H	13.35465	-3.09489	0.103143
C	5.094749	2.474869	0.073545	H	11.9315	-3.59353	-0.81623
C	3.566883	-4.93525	-0.23362	C	12.33865	2.801982	0.135373
C	5.006504	-4.93141	-0.17908	H	13.35408	3.095445	-0.14986
H	5.520388	-5.88909	-0.19187	H	11.93347	3.594033	0.773457
C	1.48477	-3.6995	-0.2723	H	12.4165	1.88885	0.734693
H	0.958485	-2.7558	-0.28123	C	12.15378	1.493815	-1.98805
C	0.730037	-4.87889	-0.30519	H	12.18056	0.540396	-1.4507
C	9.564016	-2.03461	-0.55207	H	11.62001	1.330834	-2.92883
H	10.22551	-2.20146	-1.39447	H	13.18373	1.776038	-2.23396
C	10.03876	2.176472	-0.79579	C	12.15963	-1.4931	1.944453
C	10.0412	-2.17537	0.757878	H	11.62833	-1.32979	2.886569
C	8.234565	-1.69518	-0.81395	H	13.19009	-1.77569	2.187774
H	7.89741	-1.61492	-1.84298	H	12.18542	-0.53976	1.406921
C	9.125738	-1.93826	1.796792	C	11.47128	-3.91835	1.880751
H	9.444372	-2.03519	2.830716	H	11.00934	-4.71953	1.294702
C	5.855421	-1.28632	-0.00681	H	12.49311	-4.22559	2.130697
C	8.236546	1.695382	0.780801	H	10.91293	-3.82613	2.816972
H	7.90236	1.61423	1.810742	C	11.46625	3.919255	-1.9224
C	5.095104	-2.47487	-0.09505	H	12.4875	4.226256	-2.17495
C	-0.68512	-7.35907	-0.38887	H	10.90549	3.827234	-2.85718
C	7.800709	-1.59995	1.539959	H	11.00598	4.72053	-1.33517
H	7.1136	-1.45132	2.368329	C	-1.30406	-9.26482	-1.65481
C	2.832637	-6.12367	-0.28749	H	-1.941	-10.1441	-1.5392
H	3.352566	-7.07529	-0.30802	H	-1.66719	-8.66151	-2.49519
C	-1.43253	-6.12373	-0.33721	H	-0.27271	-9.57489	-1.84546
C	-2.8338	-6.12209	-0.30933	C	1.297465	-9.33923	0.801518
H	-3.3537	-7.07385	-0.32316	H	0.266322	-9.66411	0.96674
C	9.120319	1.940202	-1.83224	H	1.939034	-10.2074	0.637863
H	9.435997	2.037837	-2.867	H	1.65269	-8.78541	1.678536
C	-5.72366	-3.78146	-0.09371	C	-1.29731	9.339261	-0.80135
H	-6.80314	-3.83601	-0.04561	H	-1.65217	8.785411	-1.67851
C	11.48708	-2.59021	1.08654	H	-1.93912	10.20729	-0.63787
C	0.683539	-7.36061	-0.35062	H	-0.26619	9.664375	-0.96632
C	7.795958	1.601897	-1.5719	C	1.30391	9.264649	1.655344
H	7.106525	1.453961	-2.39845	H	1.940851	10.14391	1.539908
C	11.48382	2.591089	-1.1283	H	0.272545	9.574697	1.845938
C	-5.00685	-4.93049	-0.18098	H	1.666944	8.661218	2.495677

K3

Atomic Type	Coordinates (Angstroms) X	Y	Z	Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-9.79412	1.377236	0.01967	H	2.536553	6.877258	-0.02666
O	-9.78608	-1.43254	-0.01873	C	4.969412	5.731888	-0.01644
C	-7.35735	-2.86366	-0.00548	H	4.984043	6.818573	-0.01893
H	-8.30445	-3.39255	-0.00239	C	6.134209	5.034418	-0.00711
C	-7.37558	-1.45813	-0.00737	H	7.0851	5.560626	-0.0025
C	-6.13844	-0.74585	0.005159	C	-0.02096	7.36843	-0.03173
C	-4.95174	-1.48708	0.018911	C	-0.02079	8.078287	1.188214
H	-4.01377	-0.95253	0.038132	C	-0.02155	9.476862	1.162588
C	-4.91913	-2.87863	0.014714	H	-0.01785	10.01857	2.106074
C	-8.61193	-0.71028	-0.01791	C	-0.02504	10.19435	-0.03652
C	-8.61581	0.661747	0.018294	C	-0.02139	9.472779	-1.23318
C	-7.38372	1.416591	0.00739	H	-0.01756	10.01127	-2.1785
C	-6.14256	0.711305	-0.00548	C	-0.02058	8.074125	-1.25408
C	-4.96007	1.459221	-0.01943	C	-0.01521	7.341028	-2.57638
H	-4.01909	0.929958	-0.03904	H	-0.01676	8.045072	-3.41262
C	-4.9353	2.850927	-0.01499	H	-0.89153	6.692125	-2.67879
C	-6.17997	3.552467	-0.00413	H	0.866595	6.699156	-2.67606
C	-7.37339	2.822196	0.005504	C	-0.0156	7.349716	2.51303
H	-8.32346	3.345736	0.002546	H	-0.01677	8.056636	3.346857
C	-6.16248	4.999822	-0.00735	H	0.865931	6.707799	2.614847
H	-7.11632	5.520677	-0.00271	H	-0.89219	6.701553	2.61778
C	-5.00163	5.703831	-0.01671	C	-0.05926	11.70462	-0.0391
H	-5.02241	6.79042	-0.01919	H	-1.09099	12.07829	-0.04305
C	-3.70992	5.052533	-0.02206	H	0.436799	12.11505	-0.92379
C	-3.67602	3.603166	-0.02059	H	0.431171	12.11792	0.847382
C	-2.44413	2.986098	-0.02111	C	-6.15982	-3.58719	0.003999
H	-2.3646	1.904845	-0.0161	O	9.794149	-1.37722	-0.01911
C	-1.22635	3.705796	-0.02446	O	9.786118	1.432496	0.0192
C	-1.2441	5.15418	-0.02735	C	7.357356	2.863669	0.005712
C	-2.52483	5.778258	-0.02608	H	8.304464	3.392556	0.002635
H	-2.57521	6.862886	-0.02685	C	7.375593	1.458145	0.007635
C	-0.0165	5.868511	-0.02915	C	6.138452	0.745858	-0.00501
C	1.215065	5.161058	-0.02729	C	4.951753	1.487085	-0.01886
C	1.20542	3.7126	-0.02439	H	4.013781	0.952536	-0.03826
C	-0.00855	3.027	-0.0234	C	4.91914	2.878631	-0.0146
H	-0.00551	1.939624	-0.02112	C	8.611932	0.710285	0.018267
C	2.427241	2.999759	-0.02096	C	8.615827	-0.66175	-0.01792
H	2.353838	1.918077	-0.01602	C	7.383732	-1.41658	-0.00715
C	3.655632	3.623762	-0.02032	C	6.142569	-0.7113	0.005623
C	3.68141	5.073305	-0.0218	C	4.960079	-1.45921	0.01949
C	2.492255	5.792358	-0.02591	H	4.019107	-0.92994	0.038977

Atomic Type	Coordinates (Angstroms) X	Y	Z	Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.935304	-2.85092	0.015092	H	0.017856	-10.0184	-2.10678
C	6.179977	-3.55246	0.004247	C	0.025036	-10.1944	0.035826
C	7.373401	-2.82219	-0.00529	C	0.021386	-9.47291	1.232529
H	8.323474	-3.34573	-0.00229	H	0.017562	-10.0115	2.177796
C	6.162493	-4.99982	0.007336	C	0.020579	-8.07423	1.253563
H	7.11633	-5.52067	0.0027	C	0.015237	-7.34128	2.575948
C	5.001635	-5.70382	0.01654	H	0.016822	-8.04542	3.412113
H	5.022415	-6.79041	0.018894	H	0.891542	-6.69238	2.678419
C	3.70993	-5.05253	0.02194	H	-0.86658	-6.69944	2.675727
C	3.676027	-3.60316	0.020698	C	0.015557	-7.34947	-2.51346
C	2.444139	-2.9861	0.021481	H	0.01704	-8.05629	-3.34737
H	2.364597	-1.90484	0.016798	H	-0.86617	-6.70781	-2.6153
C	1.226356	-3.7058	0.024708	H	0.891957	-6.70101	-2.61803
C	1.244106	-5.15418	0.027245	C	0.059261	-11.7046	0.038136
C	2.52484	-5.77826	0.025866	H	1.090989	-12.0783	0.036057
H	2.57522	-6.86288	0.026491	H	-0.43173	-12.1151	0.925626
C	0.016515	-5.86851	0.028892	H	-0.43624	-12.1179	-0.84555
C	-1.21506	-5.16106	0.027181	C	6.159827	3.587193	-0.00386
C	-1.20541	-3.7126	0.024639	C	10.56354	-1.26983	-1.22582
C	0.008563	-3.027	0.023848	H	11.43947	-1.90608	-1.08463
H	0.00552	-1.93963	0.021867	H	9.987141	-1.63096	-2.08568
C	-2.42723	-2.99976	0.021335	H	10.87787	-0.2375	-1.40332
H	-2.35382	-1.91808	0.016744	C	10.55653	1.32944	1.225643
C	-3.65562	-3.62376	0.020423	H	10.87711	0.298978	1.402805
C	-3.6814	-5.0733	0.021685	H	11.42856	1.970992	1.08431
C	-2.49225	-5.79236	0.025688	H	9.978256	1.686906	2.085775
H	-2.53655	-6.87726	0.026292	C	-10.5568	-1.32926	-1.22495
C	-4.9694	-5.73188	0.016285	H	-9.9787	-1.68638	-2.08533
H	-4.98404	-6.81857	0.018634	H	-11.4287	-1.97099	-1.08357
C	-6.1342	-5.03441	0.007123	H	-10.8776	-0.2988	-1.40175
H	-7.08509	-5.56062	0.002523	C	-10.5635	1.26959	1.226364
C	0.020969	-7.36843	0.031305	H	-11.4395	1.905832	1.085277
C	0.020798	-8.07819	-1.18873	H	-10.8778	0.237211	1.403692
C	0.02156	-9.47674	-1.16324	H	-9.98713	1.630611	2.086288

K3-R

Atomic Type	Coordinates (Angstroms) X	Y	Z	Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-8.58911	-0.66367	-0.01732	O	-0.00305	-1.6901	0.250279
H	2.526001	-6.83675	0.019304	C	7.344626	-2.84085	-0.00744
C	7.350145	-1.44645	-0.00619	H	8.294856	-3.36277	-0.01517

Atomic	Coordinates (Angstroms)			Atomic	Coordinates (Angstroms)		
Type	X	Y	Z	Type	X	Y	Z
C	6.152158	-3.56774	0.010303	H	-0.00326	-10.0041	2.102232
C	6.130088	-5.00908	-0.00214	C	-0.01373	-10.1287	-0.03885
H	7.080435	-5.53409	-0.02369	C	-0.01307	-9.38538	-1.21529
C	4.969288	-5.70232	0.007527	H	-0.0101	-9.90265	-2.17135
H	4.978971	-6.78794	-0.00729	C	-0.01412	-7.9927	-1.20433
C	3.691333	-5.03402	0.039973	C	-0.01199	-7.22528	-2.50127
C	2.486863	-5.75251	0.045005	H	-0.88949	-6.5771	-2.58185
C	1.235749	-5.11396	0.077454	H	-0.01327	-7.90396	-3.35649
C	-0.01052	-5.82887	0.064705	H	0.868192	-6.58069	-2.58151
C	-1.2542	-5.10948	0.077739	C	-0.00438	-7.34526	2.558312
C	-2.50762	-5.74349	0.04561	H	-0.00454	-8.06328	3.380769
H	-2.55064	-6.82758	0.02005	H	-0.88093	-6.70063	2.671321
C	-3.70949	-5.02066	0.040661	H	0.876781	-6.70613	2.666789
C	-4.98986	-5.68433	0.008349	C	-0.0449	-11.634	-0.07421
H	-5.00349	-6.76991	-0.00637	H	-1.07483	-12.0068	-0.06293
C	-6.14815	-4.9869	-0.00135	H	0.465858	-12.0642	0.790764
H	-7.10039	-5.50847	-0.02285	H	0.431724	-12.0218	-0.97774
C	-6.16502	-3.54549	0.010977	O	-9.75947	-1.38021	-0.02451
C	-7.35485	-2.81429	-0.00683	O	-9.75437	1.41553	0.02476
H	-8.30696	-3.33277	-0.01456	C	8.58911	0.663669	0.01739
C	-7.35534	-1.41989	-0.00566	H	-2.526	6.836754	-0.01934
C	-6.11913	-0.71943	0.01035	C	-7.35015	1.446454	0.006235
C	-4.94377	-1.45797	0.038823	O	0.003046	1.6901	-0.2503
H	-4.00046	-0.93491	0.060338	C	-7.34463	2.840851	0.007475
C	-4.92716	-2.85068	0.04118	H	-8.29486	3.362767	0.015212
C	-3.68358	-3.6016	0.066982	C	-6.15216	3.567738	-0.01028
C	-2.43542	-2.97323	0.116371	C	-6.13009	5.009081	0.002157
H	-2.33139	-1.89644	0.151872	H	-7.08044	5.534086	0.023726
C	-1.25901	-3.68433	0.122304	C	-4.96929	5.702324	-0.00753
C	-0.00526	-2.91347	0.173337	H	-4.97897	6.787944	0.007289
C	1.245694	-3.68884	0.122064	C	-3.69133	5.034022	-0.03999
C	2.424671	-2.98199	0.115949	C	-2.48686	5.75251	-0.04504
H	2.324546	-1.90483	0.151504	C	-1.23575	5.113956	-0.07751
C	3.670537	-3.61488	0.066383	C	0.01052	5.828868	-0.06476
C	4.916824	-2.86845	0.040541	C	1.254195	5.109484	-0.07779
C	4.938463	-1.47581	0.038203	C	2.50762	5.743489	-0.04564
H	3.99705	-0.94936	0.059696	H	2.550638	6.827577	-0.02007
C	6.11649	-0.74152	0.00977	C	3.709486	5.020664	-0.04067
C	-8.58665	0.69471	0.017778	C	4.989858	5.684325	-0.00833
C	-0.01333	-7.31972	0.02783	H	5.003487	6.769906	0.006395
C	-0.01036	-8.0507	1.226674	C	6.14815	4.9869	0.001388
C	-0.00926	-9.44208	1.171757	H	7.100389	5.508471	0.022898

Atomic	Coordinates (Angstroms)			Atomic	Coordinates (Angstroms)		
Type	X	Y	Z	Type	X	Y	Z
C	6.165016	3.545485	-0.01095	C	0.011943	7.225257	2.501223
C	7.354847	2.814293	0.006884	H	0.88945	6.577093	2.581827
H	8.306956	3.332773	0.014635	H	0.013189	7.903929	3.356444
C	7.355335	1.419886	0.005703	H	-0.86823	6.580655	2.581439
C	6.119129	0.719428	-0.01033	C	0.004425	7.345279	-2.55836
C	4.943765	1.457971	-0.03882	H	0.004597	8.063302	-3.38081
H	4.000458	0.934912	-0.06034	H	0.880987	6.700661	-2.67136
C	4.927154	2.850681	-0.04117	H	-0.87673	6.706146	-2.66685
C	3.683577	3.601604	-0.06699	C	0.0449	11.63403	0.074164
C	2.435418	2.973229	-0.11641	H	1.074787	12.00687	0.060861
H	2.331383	1.896437	-0.15192	H	-0.46755	12.06415	-0.78982
C	1.259004	3.684332	-0.12236	H	-0.42999	12.02172	0.978619
C	0.005253	2.91347	-0.17343	O	9.759458	1.380228	0.024625
C	-1.2457	3.688844	-0.12212	O	9.754357	-1.41555	-0.0247
C	-2.42467	2.981989	-0.11599	C	-10.5224	1.291971	1.220186
H	-2.32455	1.904832	-0.15155	H	-9.94291	1.626145	2.087409
C	-3.67054	3.614875	-0.0664	H	-11.391	1.93964	1.095578
C	-4.91683	2.868453	-0.04054	H	-10.8469	0.259969	1.374175
C	-4.93847	1.475813	-0.03821	C	-10.5266	-1.25402	-1.22023
H	-3.99705	0.94936	-0.05973	H	-11.3977	-1.89839	-1.0958
C	-6.11649	0.741524	-0.00975	H	-10.8472	-0.22083	-1.37454
C	8.586652	-0.69471	-0.01772	H	-9.94809	-1.59054	-2.08719
C	0.013332	7.319724	-0.02787	C	10.52239	-1.29195	-1.2201
C	0.010386	8.050717	-1.22672	H	11.39103	-1.93959	-1.09546
C	0.009295	9.442089	-1.17179	H	9.942986	-1.62613	-2.08735
H	0.003305	10.00408	-2.10226	H	10.84693	-0.25994	-1.37407
C	0.01374	10.12875	0.03884	C	10.52658	1.253987	1.220327
C	0.013048	9.385373	1.215261	H	10.84716	0.220785	1.374624
H	0.010068	9.902634	2.17132	H	11.39771	1.898315	1.095882
C	0.014093	7.992679	1.204292	H	9.948123	1.590532	2.087296

4. X-ray crystallographic data

Table S5. X-ray crystal data and structure refinement details for **K1**, **K2**, **K3** and **K3-R** (CCDC 2223047-2223050).

	K1	**K2**	**K3**	**K3-R**
formula	$C_{84}H_{80}O_4$	$C_{119}H_{116}O_4$	$C_{98}H_{84}O_4$	$C_{100}H_{84}Cl_6O_6$
formula wt.	1153.48	1610.11	1325.65	1594.37
T (K)	173(2)	173	173(2)	173(2)
wavelength (Å)	1.54178	1.54178	1.54178	1.54178
crystal size	0.160 × 0.150 × 0.120	0.300 × 0.100 × 0.060	0.160 × 0.150 × 0.120	0.160 × 0.150 × 0.140
crystal syst.	Triclinic	Triclinic	Triclinic	Triclinic
space group	P-1	P-1	P-1	P-1
a (Å)	8.553(2)	8.6954(2)	9.5464(8)	10.2129(3)
b (Å)	11.731(3)	15.6090(3)	11.1446(7)	14.2075(4)
c (Å)	15.988(6)	17.0505(4)	19.3904(8)	16.4062(4)
α (deg.)	94.57(2)	103.955(1)	87.388(4)	64.469(2)
β (deg.)	104.856(10)	92.887(1)	88.255(6)	74.622(2)
γ (deg.)	96.380(13)	99.039(1)	79.150(7)	69.798(2)
V (Å^3)	1531.1(8)	2208.59(8)	2023.5(2)	1996.82(10)
Z/$D_{calcd.}$ (mg/m^3)	1/1.251	1/1.211	1/1.088	1/1.326
μ (mm^{-1})	0.576	0.543	0.498	2.419
F (000)	616.0	862.0	704	834
max / min transmission	0.683/0.753	0.660/0.753	0.555/0.753	0.595/0.753

5. ^{1}H, ^{13}C NMR spectroscopy and high-resolution mass spectra of the target compounds

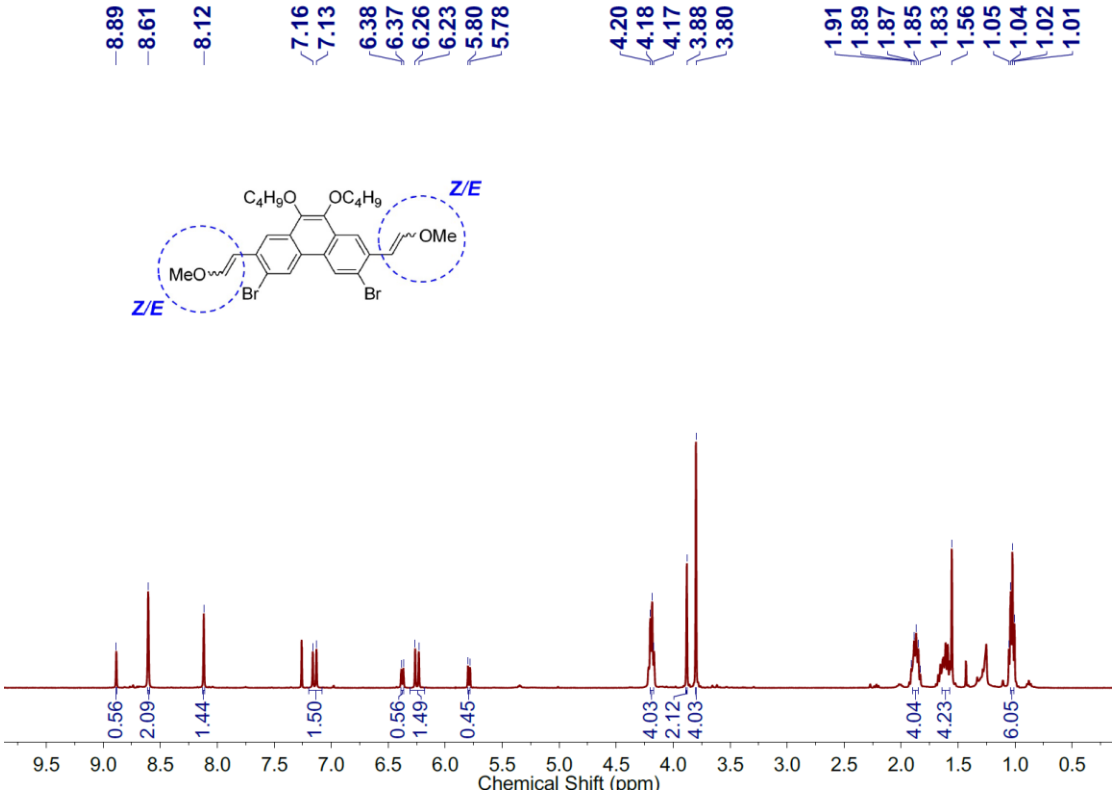


Figure S16. ^{1}H NMR spectrum of **4** in $CDCl_3$ (400 MHz, 298 K).

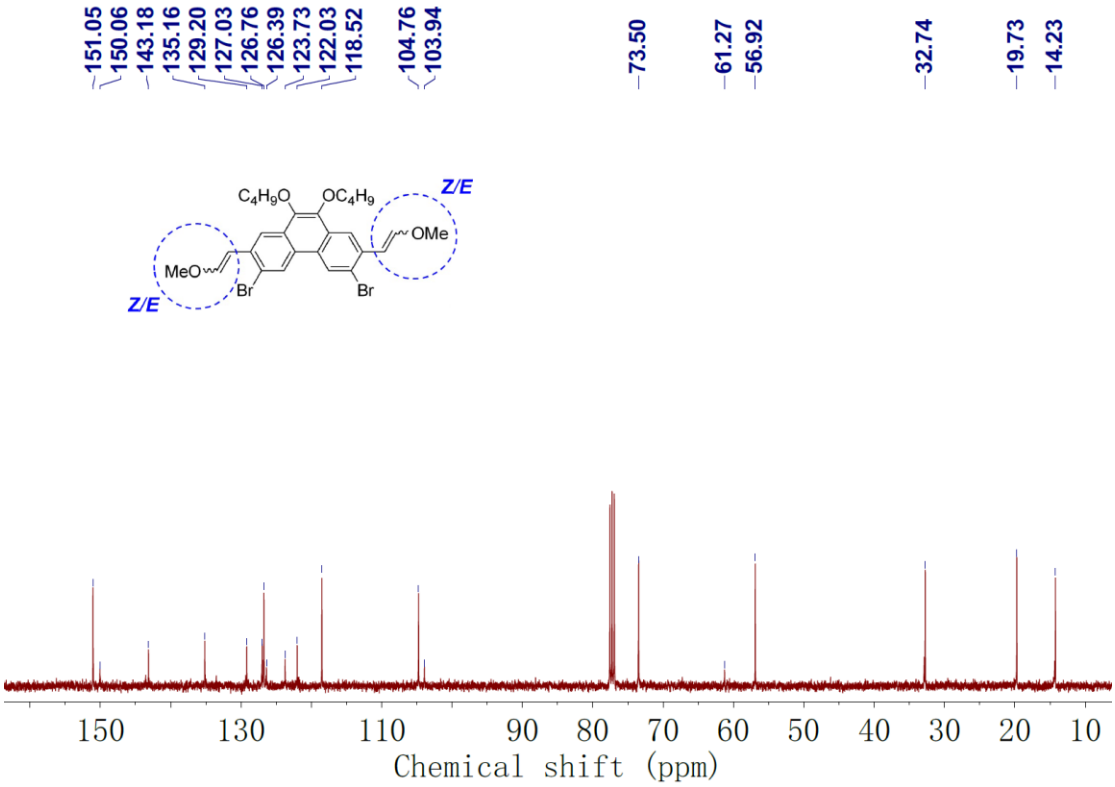


Figure S17. ^{13}C NMR spectrum of **4** in $CDCl_3$ (400 MHz, 298 K).

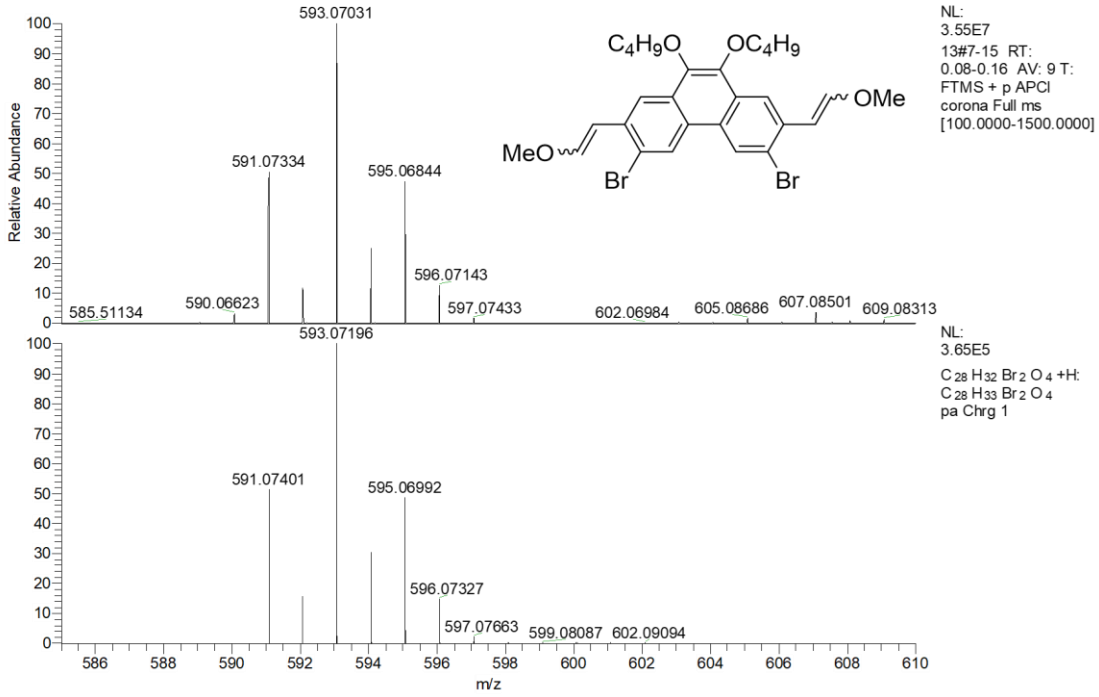


Figure S18. HRMS spectrum of **4** (APCI).

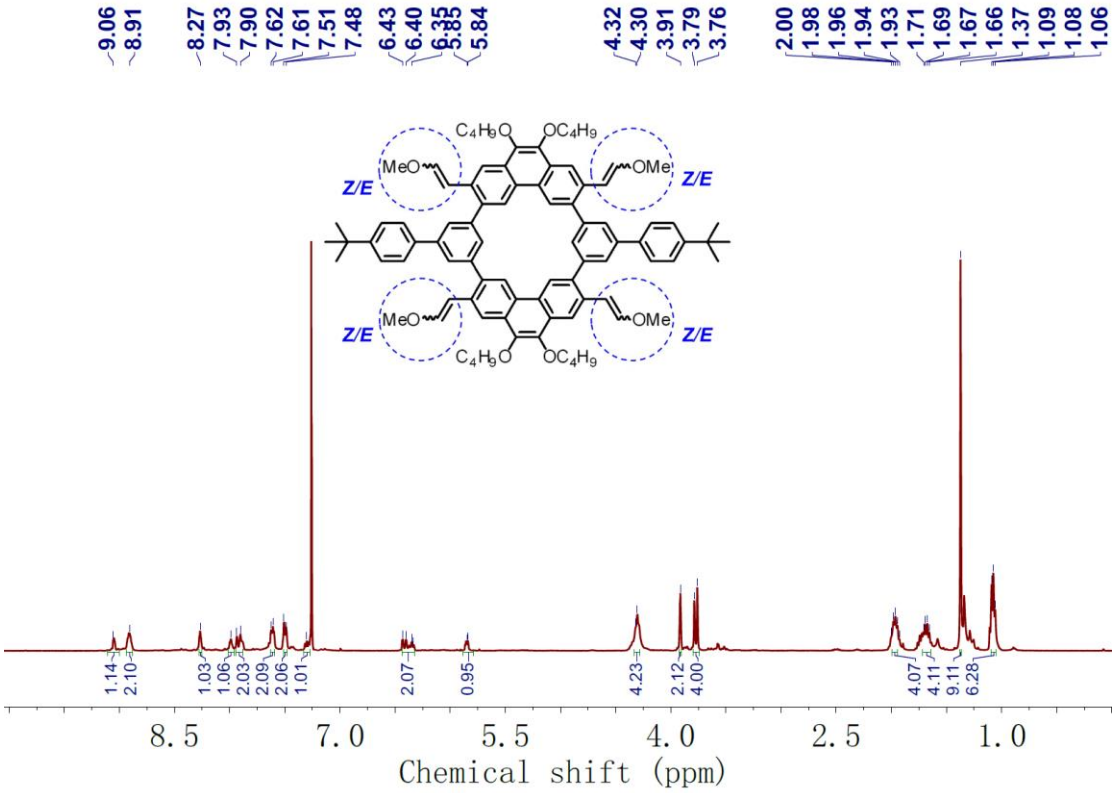


Figure S19. ^{1}H NMR spectrum of **5** in $CDCl_3$ (400 MHz, 298 K).

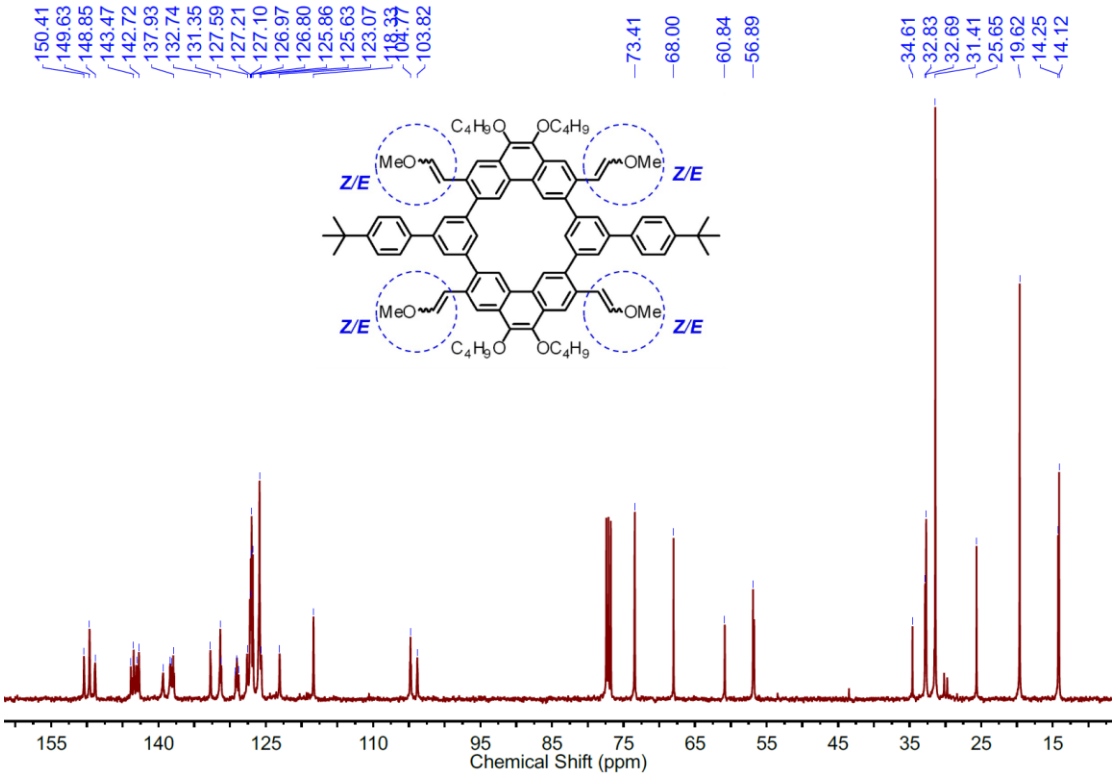


Figure S20. ^{13}C NMR spectrum of **5** in $CDCl_3$ (400 MHz, 298 K).

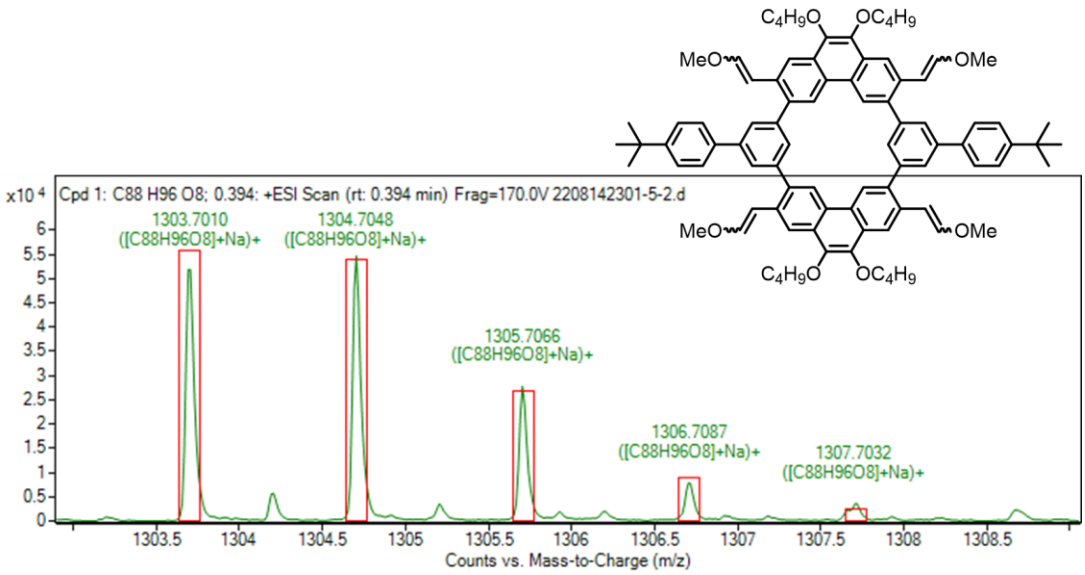


Figure S21. HRMS spectrum of **5** (ESI).

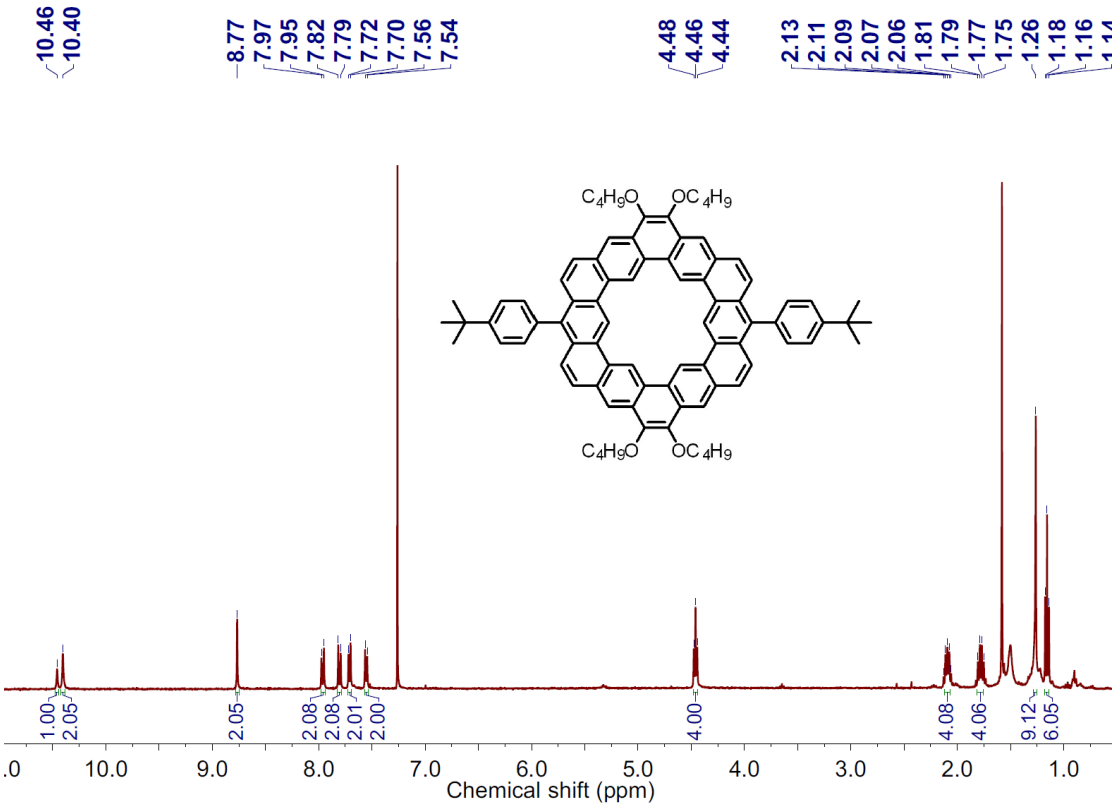


Figure S22. ^{1}H NMR spectrum of **K1** in $CDCl_3/CS_2$ 10:1 (400 MHz, 298 K).

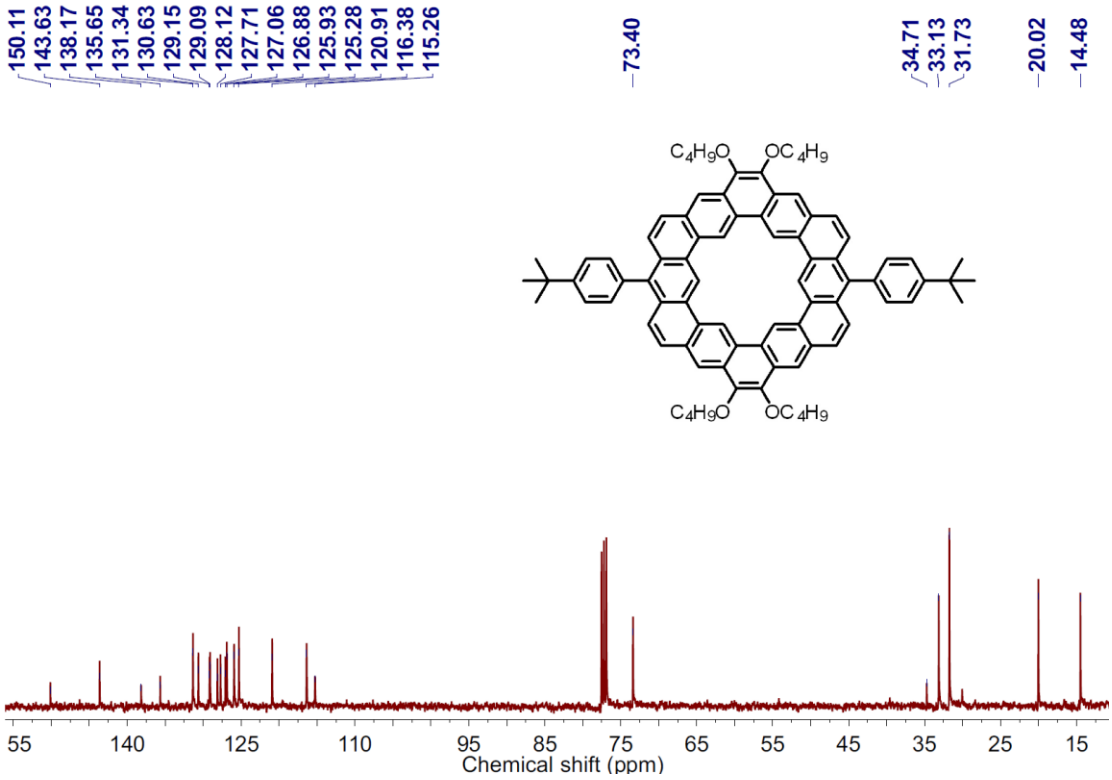


Figure S23. ^{13}C NMR spectrum of **K1** in $CDCl_3/CS_2$ 10:1 (400 MHz, 298 K).

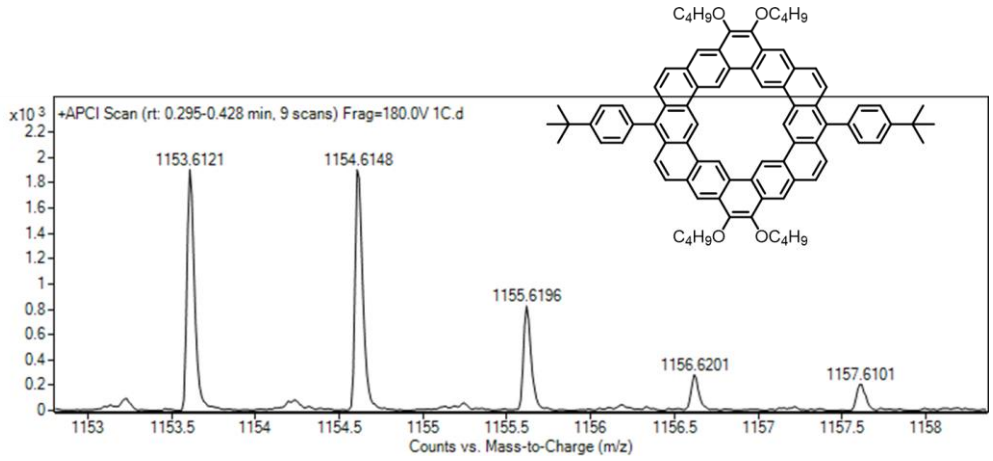


Figure S24. HRMS spectrum of **K1** (APCI).

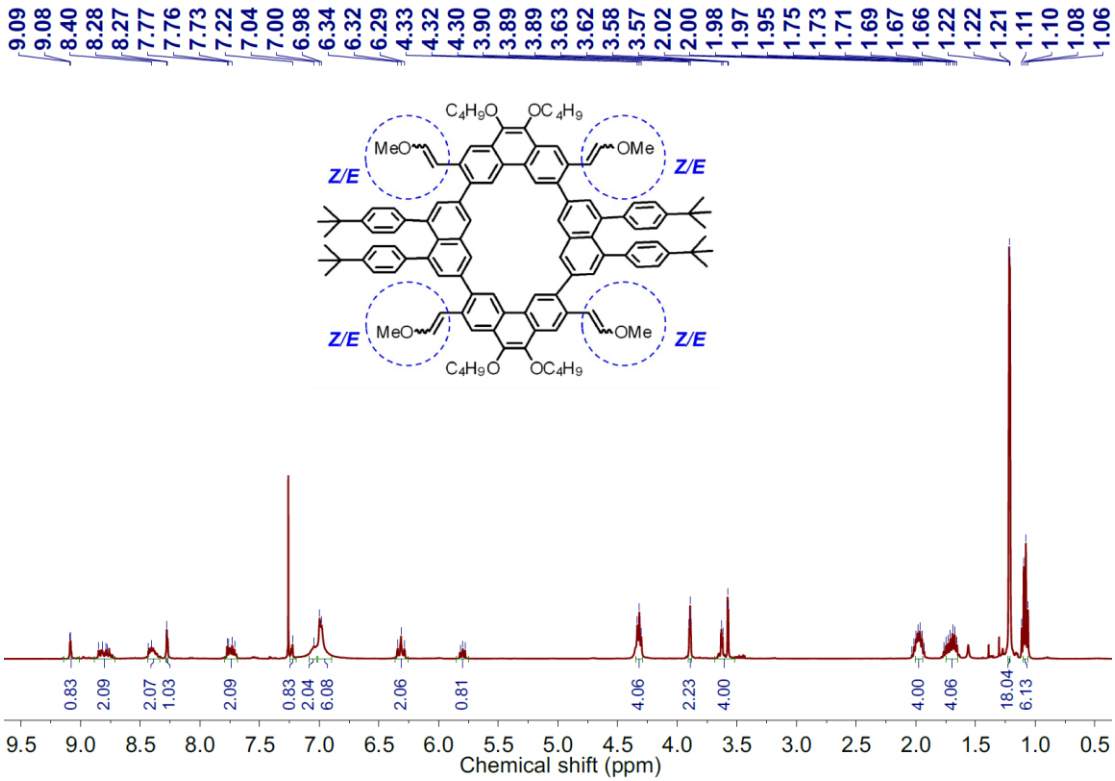


Figure S25. ^{1}H NMR spectrum of **6** in $CDCl_3$ (400 MHz, 298 K).

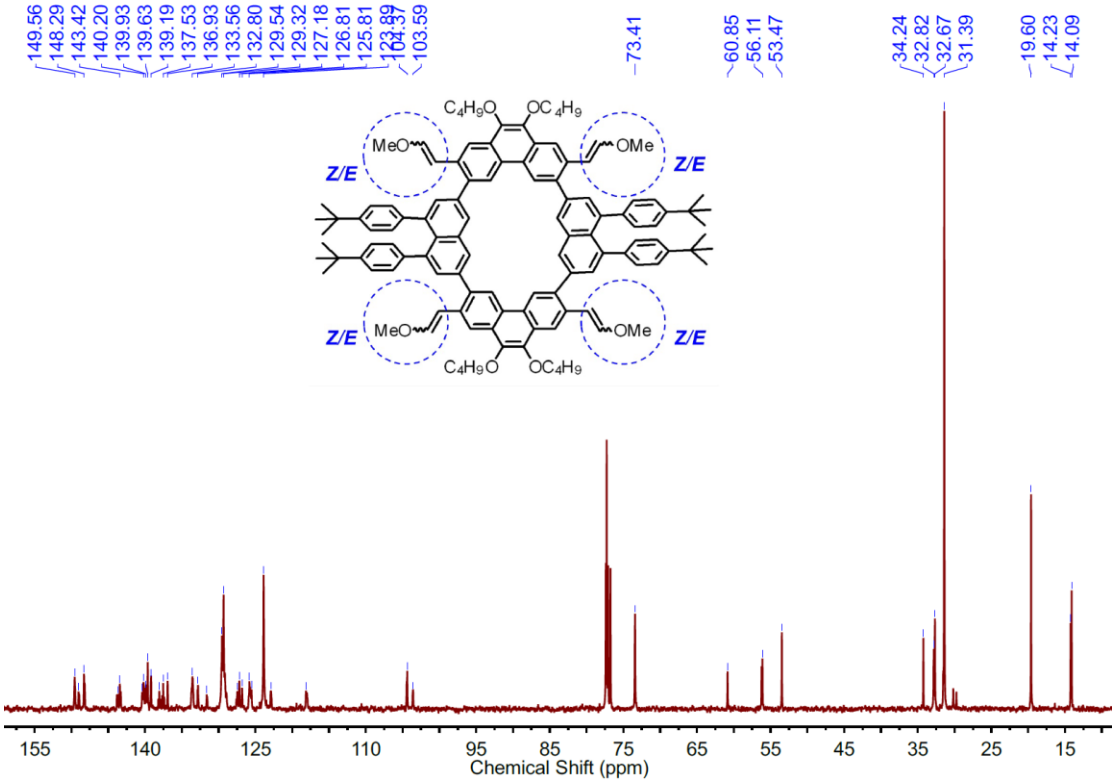


Figure S26. ^{13}C NMR spectrum of **6** in $CDCl_3$ (400 MHz, 298 K).

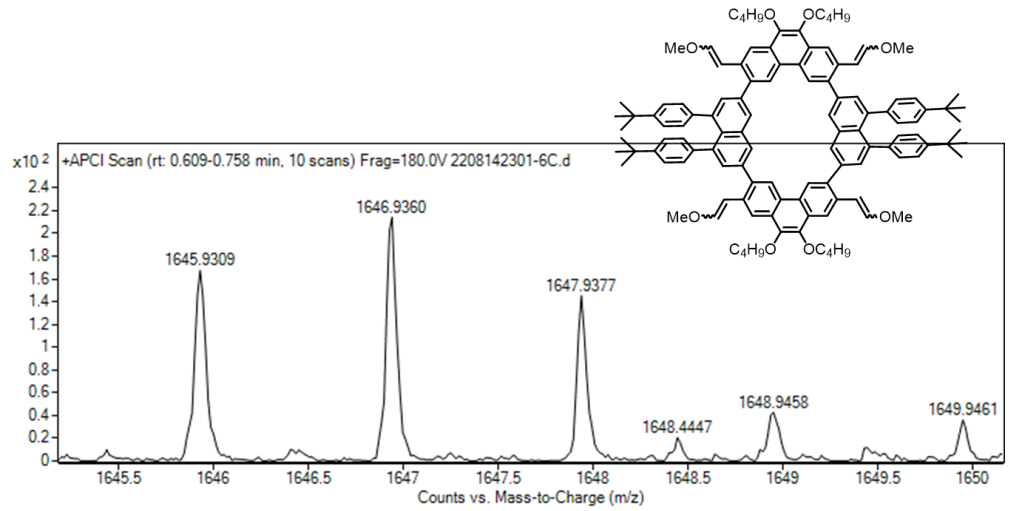


Figure S27. HRMS spectrum of **6** (APCI).

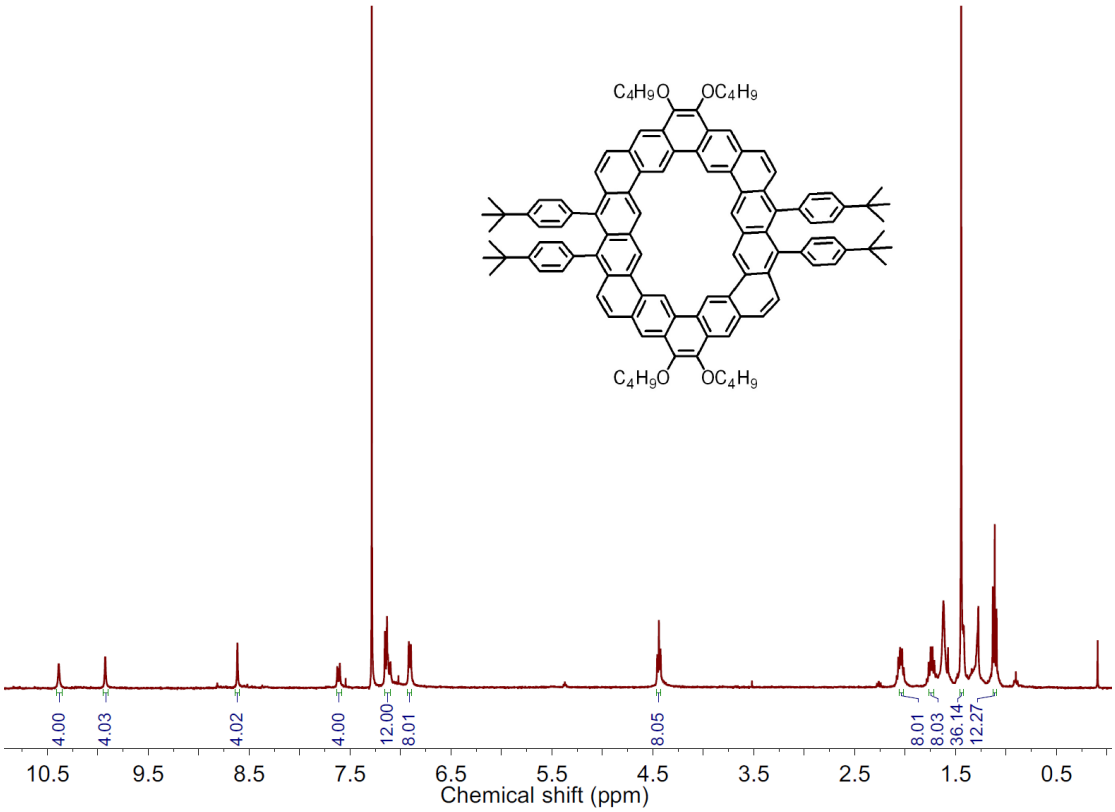


Figure S28. ^{1}H NMR spectrum of **K2** in $CDCl_3/CS_2$ 10:1 (400 MHz, 298 K).

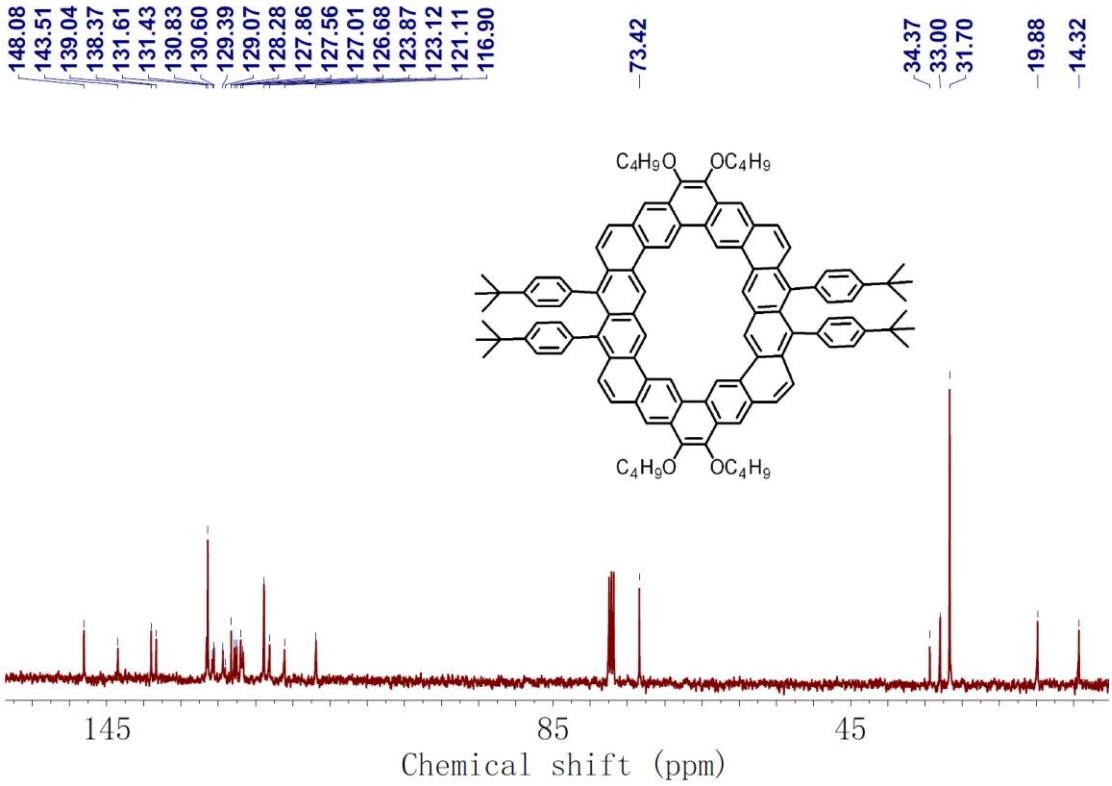


Figure S29. ^{13}C NMR spectrum of **K2** in $CDCl_3/CS_2$ 10:1 (400 MHz, 298 K).

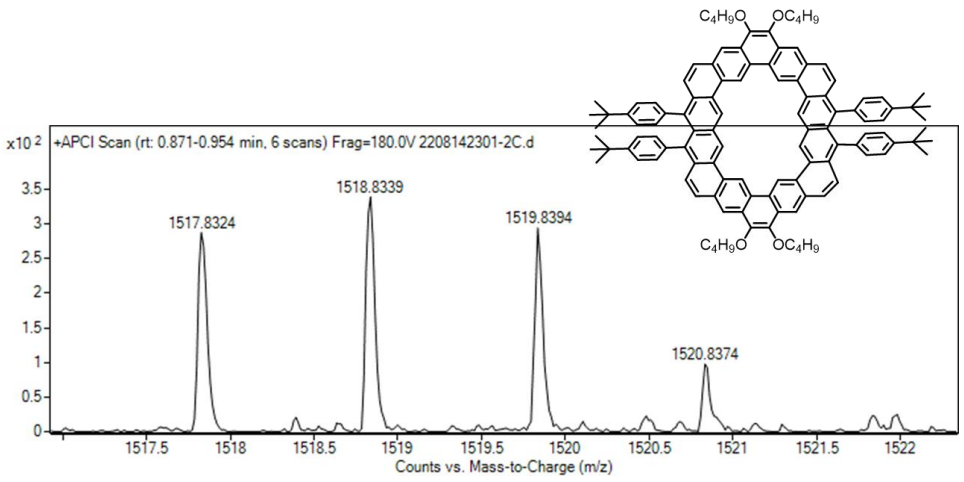


Figure S30. HRMS spectrum of **K2** (APCI).

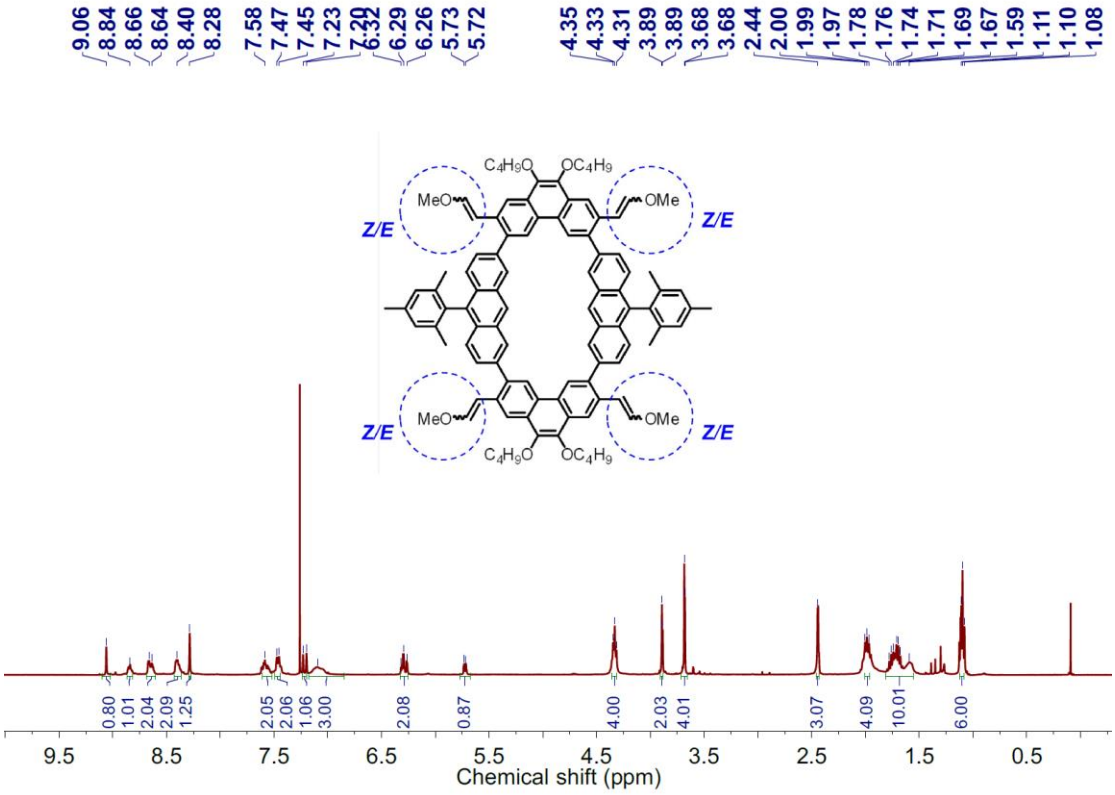


Figure S31. ^{1}H NMR spectrum of **7** in $CDCl_3$ (400 MHz, 298 K).

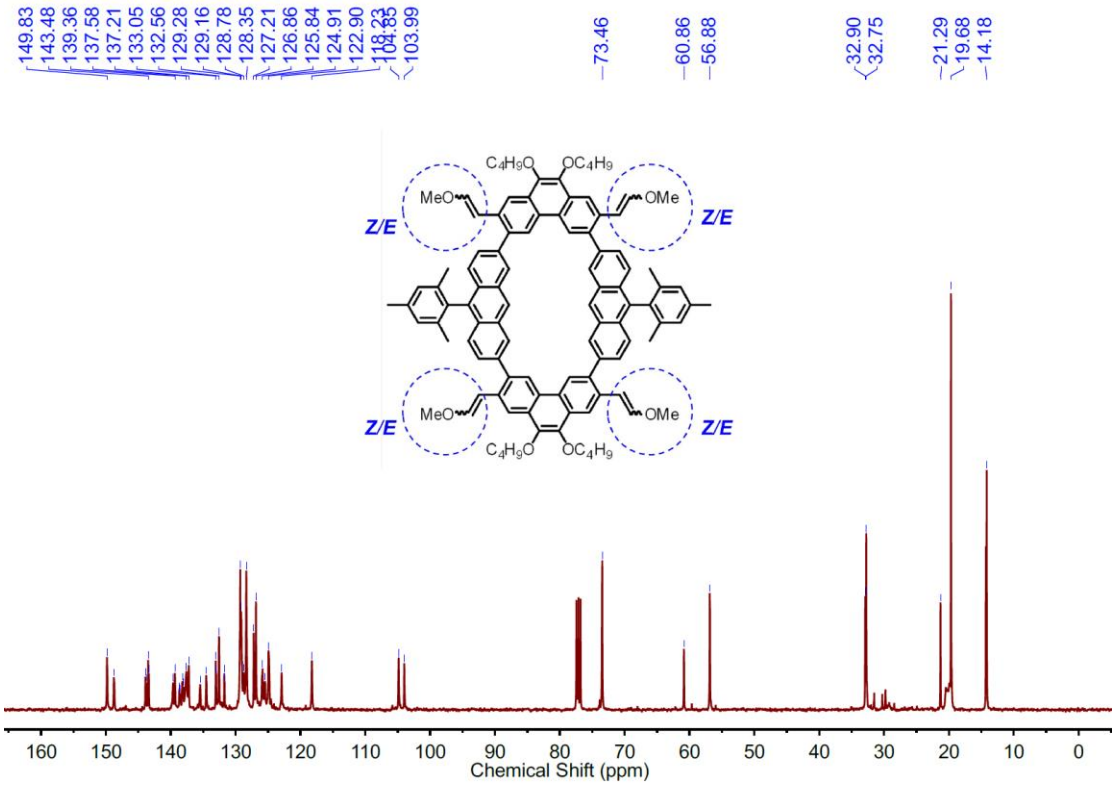


Figure S32. ^{13}C NMR spectrum of **7** in $CDCl_3$ (400 MHz, 298 K).

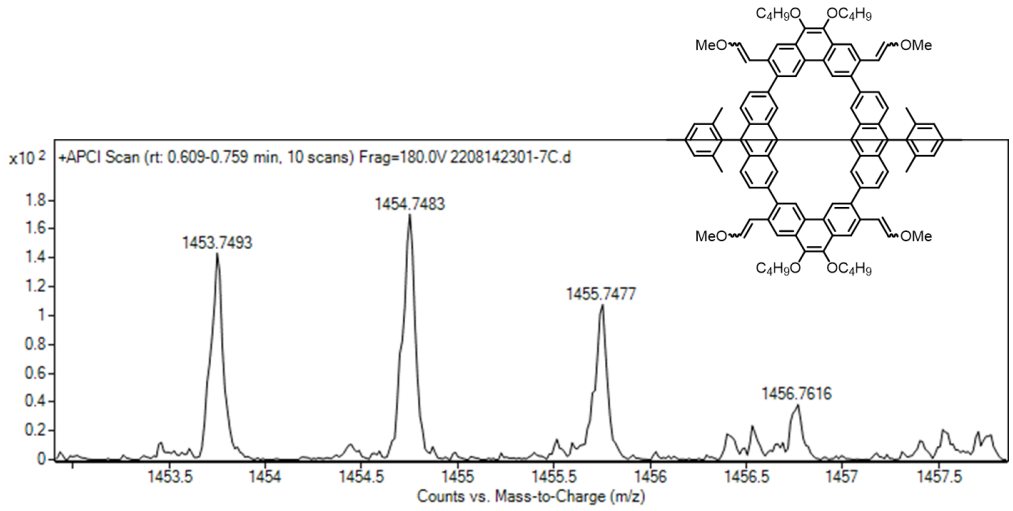


Figure S33. HRMS spectrum of **7** (APCI).

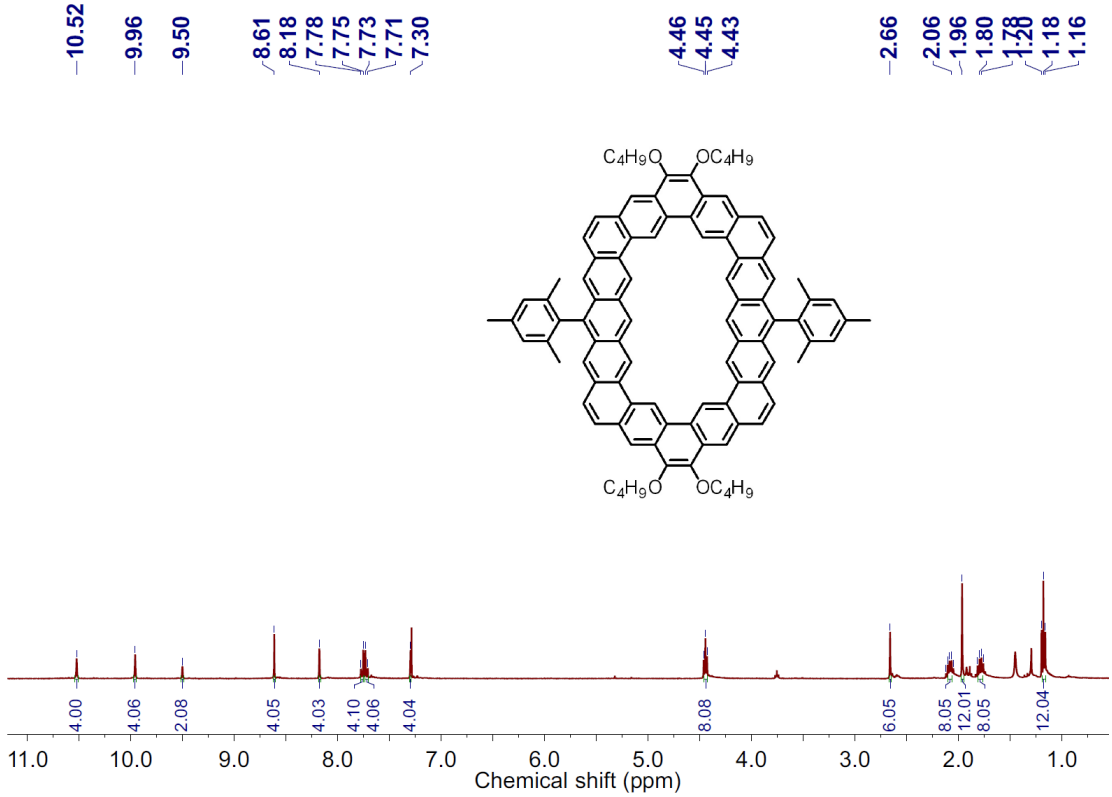


Figure S34. ^{1}H NMR spectrum of **K3** in $CDCl_3/CS_2$ 3:1 (400 MHz, 298 K).

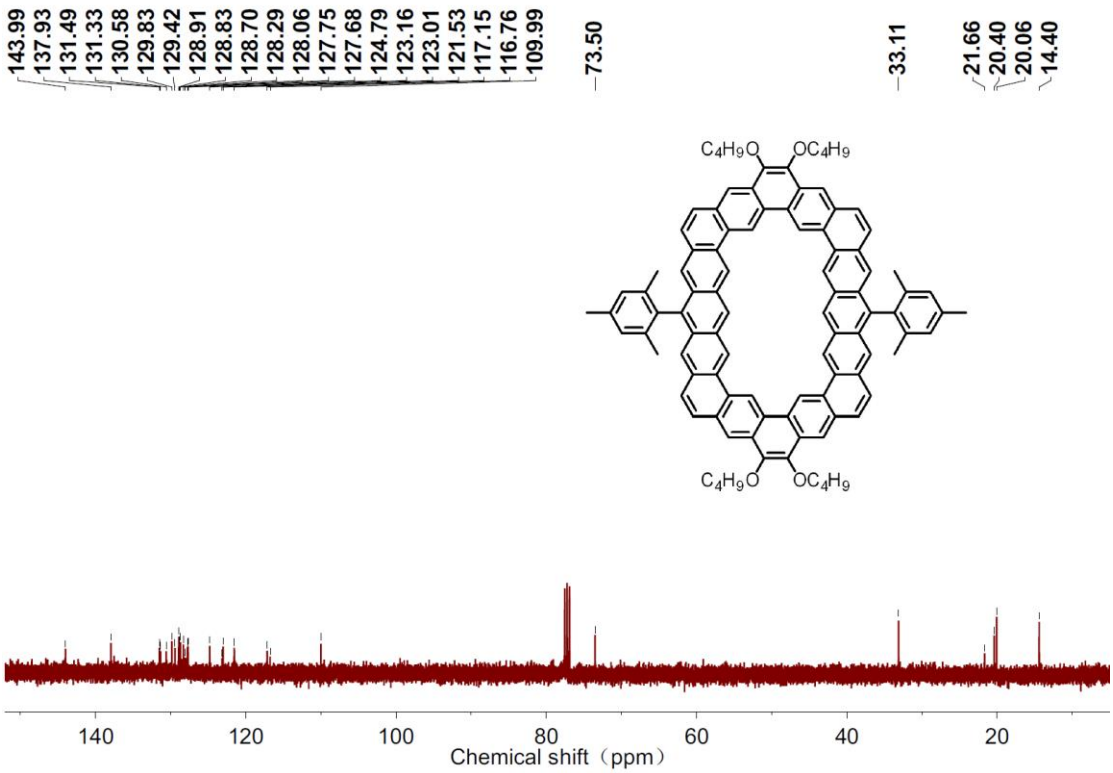


Figure S35. ^{13}C NMR spectrum of **K3** in $CDCl_3/CS_2$ 3:1 (400 MHz, 298 K).

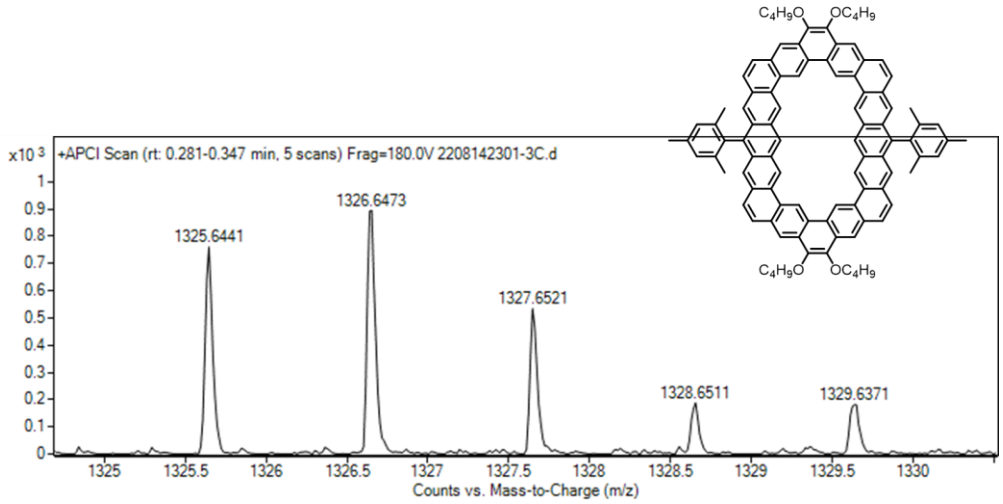


Figure S36. HRMS spectrum of **K3** (APCI).

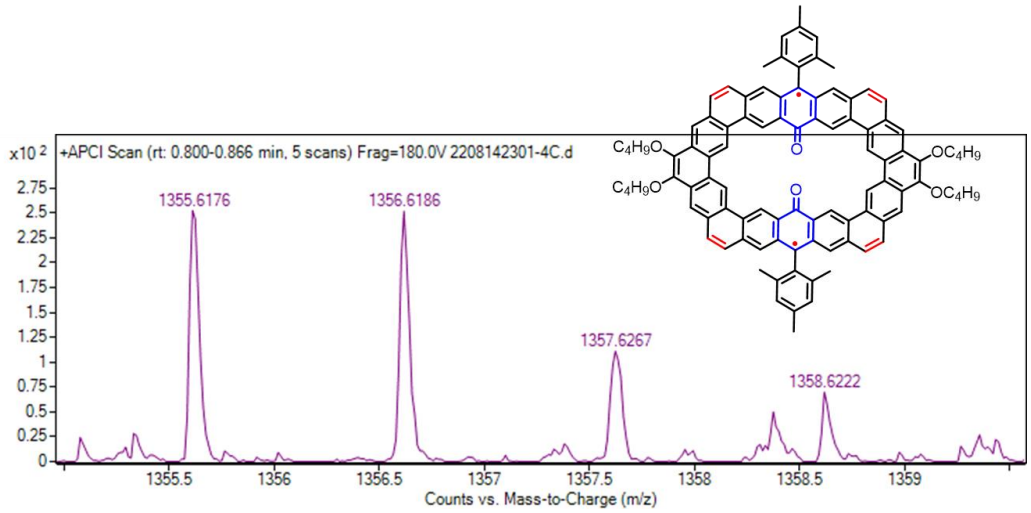


Figure S37. HRMS spectrum of **K3-R** (APCI).

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