

Topologically-controlled regiospecific *bis*-functionalization of C₇₀ using a Diels-Alder reaction

Venkata S. Pavan K. Neti,^a Maira R. Cerón,^a A. Duarte-Ruiz,^{b*} Marilyn M. Olmstead,^{c*} Alan Balch^{c*} and Luis Echegoyen^{*a}

^a Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States
E-mail: echegoyen@utep.edu, Tel/Fax: +1 (915) 747-7573/(915) 747-8807

^b Departamento de Química, Universidad Nacional de Colombia, Bogota, Colombia, E-mail:
aduarter@unal.edu.co, Tel + 571-3 16 5000, Fax +571- 3 16 5220

^c Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, CA, 95616, United States. E-mail: mmolmstead@ucdavis.edu; albalch@ucdavis.edu; Fax +1 (530) 752 2820; Tel +1 (530) 752 0941

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Section A:

Synthesis of 1 and 2:

A homogeneous mixture of C_{70} (0.1g, 0.11mmol) and anthracene (43 mg, 0.22mmol) were degassed and flame sealed in an ampule. The ampule was further heated at 240 °C for 2 hours and cooled down naturally. The ampule was broken and the solid was dissolved in CS_2 and then purified by silica gel column chromatography. First fraction was un-reacted C_{70} , second and third fractions were **1** and **2**, as identified by spectroscopy.

Section B. 1H and ^{13}C NMR spectra of 1 and 2:

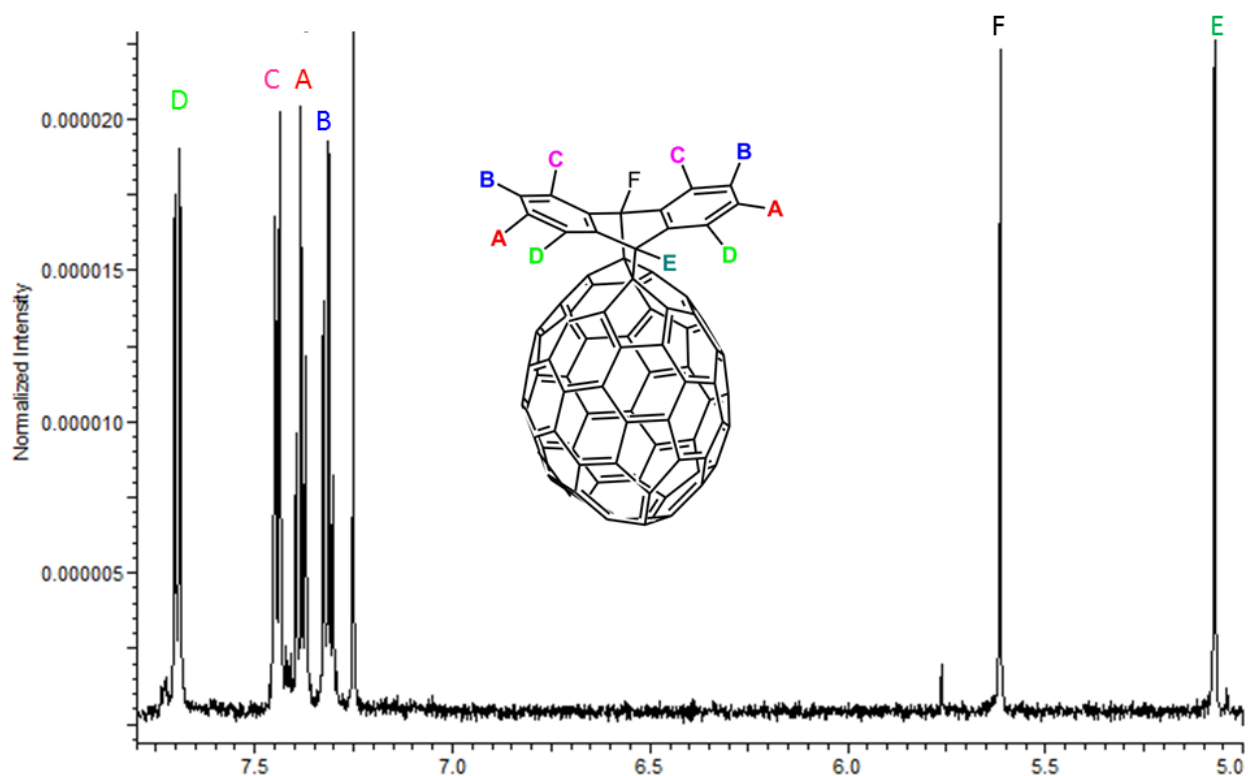


Figure S1. 1H -NMR spectrum of **1** (600 MHz, 298K, $CS_2/CDCl_3$ (7:3)). H_e (s, 5.07), H_f (s, 5.62), H_d (d, 7.69-7.7, $J = 6$ Hz), H_c (d, 7.44-7.45, $J = 6$ Hz), H_a (t, 7.37-7.40, $J = 18$ Hz) and H_b (t, $J = 18$ Hz, 7.3-7.33ppm).

^{13}C NMR spectrum of 1:

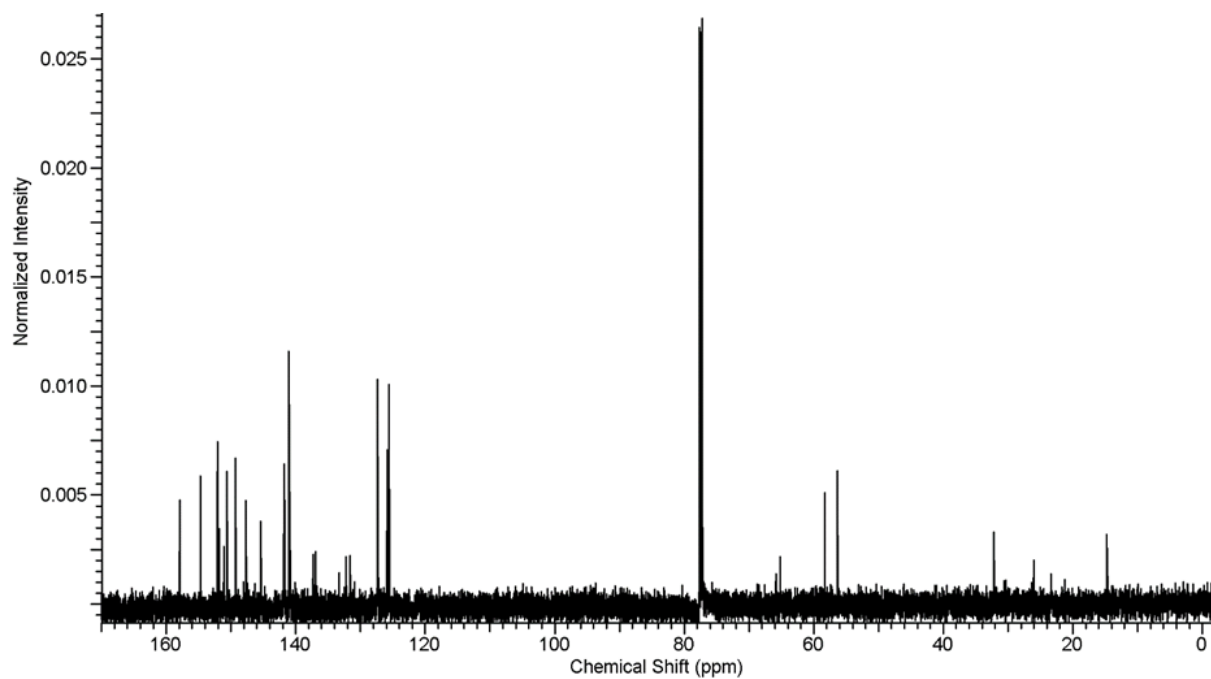


Figure S2: ^{13}C -NMR spectrum of **1** (600 MHz, 298K, $\text{CS}_2/\text{CDCl}_3$ (7:3)). $\delta = 159.54, 155.93, 152.82, 152.47, 152.32, 152.09, 151.89, 151.63, 151.36, 151.12, 150.92, 150.48, 149.85, 148.62, 146.72, 142.96, 142.64, 141.13, 140.98, 138.68, 138.05, 137.77, 137.48, 136.95, 127.82, 127.41, 126.93, 126.54, 68.89, 65.26, 64.93, 57.87, \text{ and } 56.22\text{ppm}$.

¹H-NMR spectrum of 2:

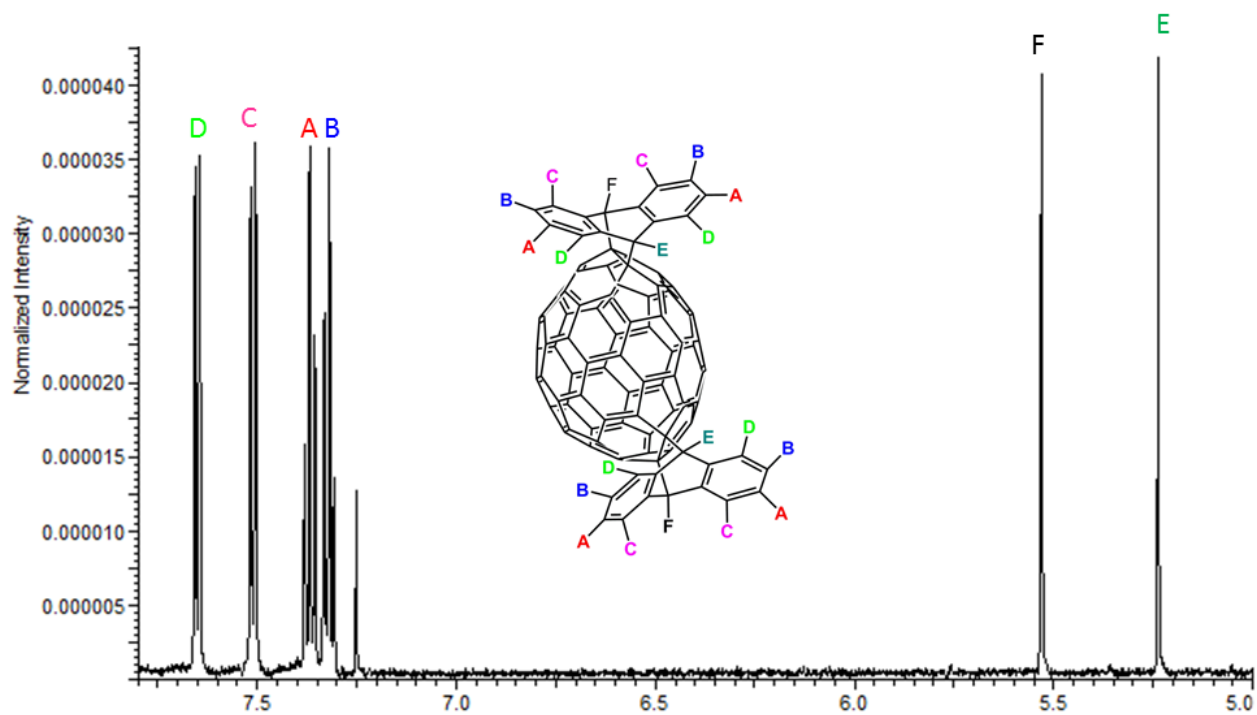


Figure S3. ¹H-NMR spectrum of **2** (600 MHz, 298K, CS₂/CDCl₃ (7:3)). H_e (s, 5.24), H_f (s, 5.53), H_d (d, 7.65-7.68, *J* = 18Hz), H_c (d, 7.51-7.52, *J* = 6Hz), H_a (t, 7.36-7.38, *J* = 12Hz) and H_b (t, *J* = 12Hz, 7.31-7.33ppm).

¹³C NMR spectrum of 2:

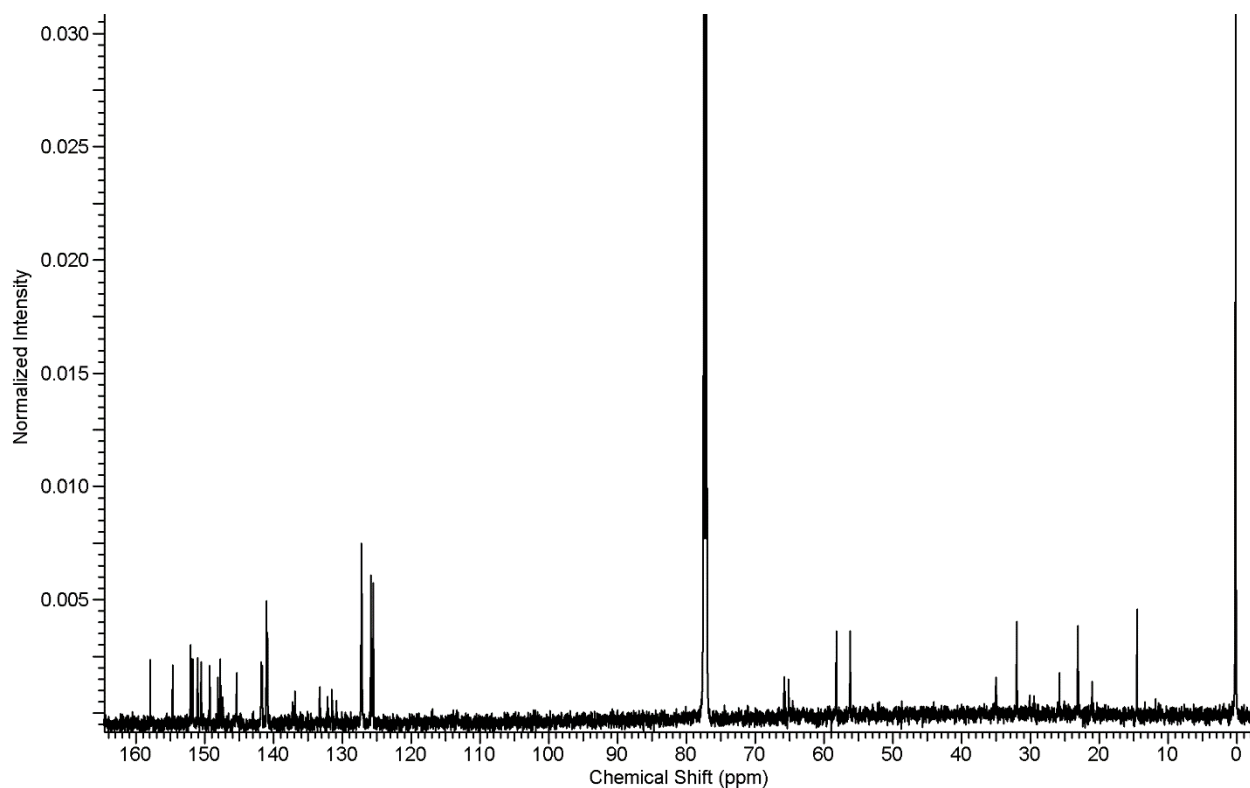


Figure S4: ¹³C-NMR spectrum of **2** (600 MHz, 298K, CS₂/CDCl₃). δ = 159.94, 159.23, 157.55, 156.88, 156.21, 155.72, 154.91, 153.7, 152.93, 151.36, 150.32, 149.45, 148.34, 147.62, 146.66, 145.86, 145.67, 144.80, 144.48, 143.31, 142.15, 141.18, 140.54, 139.50, 138.81, 137.33, 136.25, 135.77, 134.17, 133.21, 132.54, 131.29, 130.67, 130.12, 129.37, 128.92, 127.81, 127.25, 126.95, 125.66, 68.89, 67.34, 57.99, 57.88, and 55.11 ppm.

Section C. UV-Vis spectral profiles

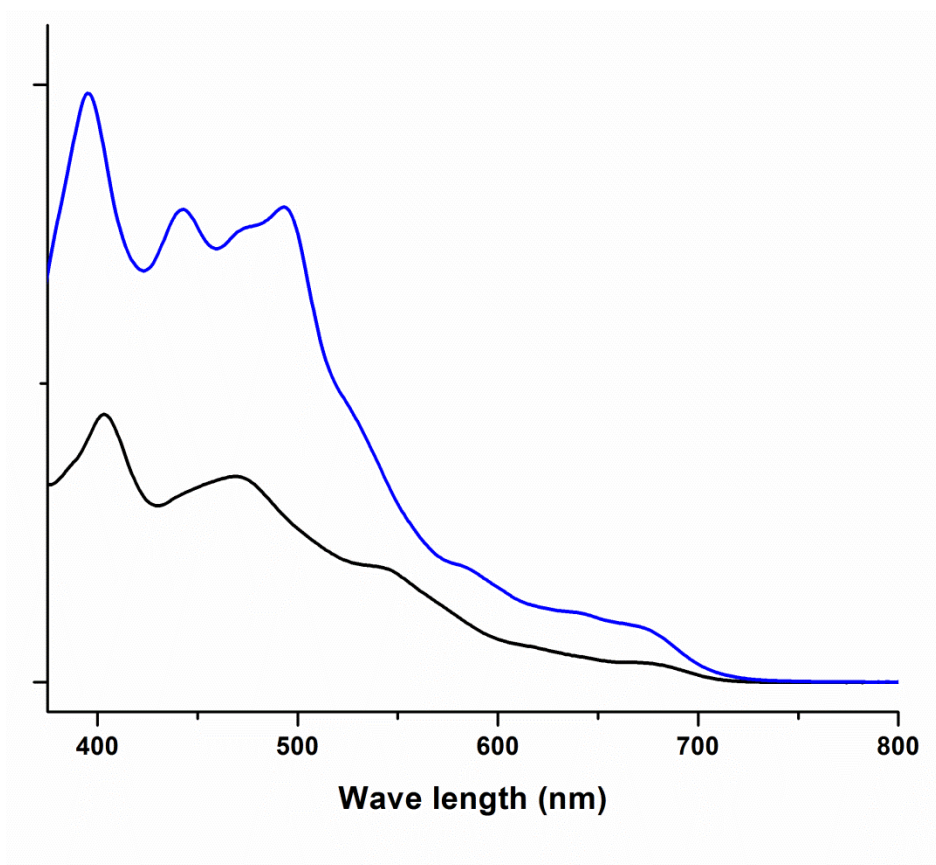


Figure S5. UV-Vis spectra of **1** (black) and **2** (blue) in CS₂.

Section D. FT-IR spectral profiles

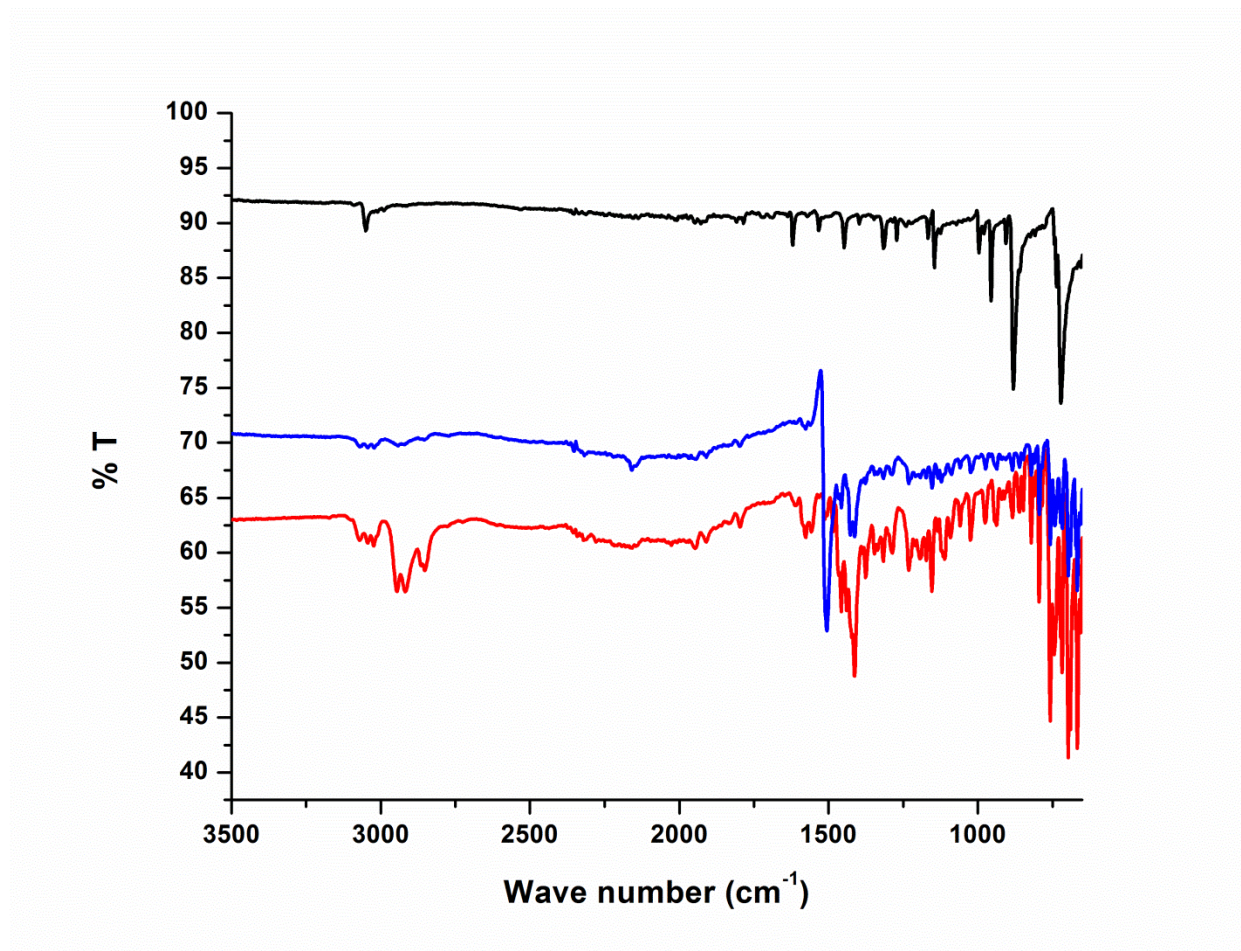


Figure S6. FT-IR spectra of spectra of C₇₀ (black), 1 (blue) and 2 (red).

Section E. HPLC profile of crude and isolated compounds

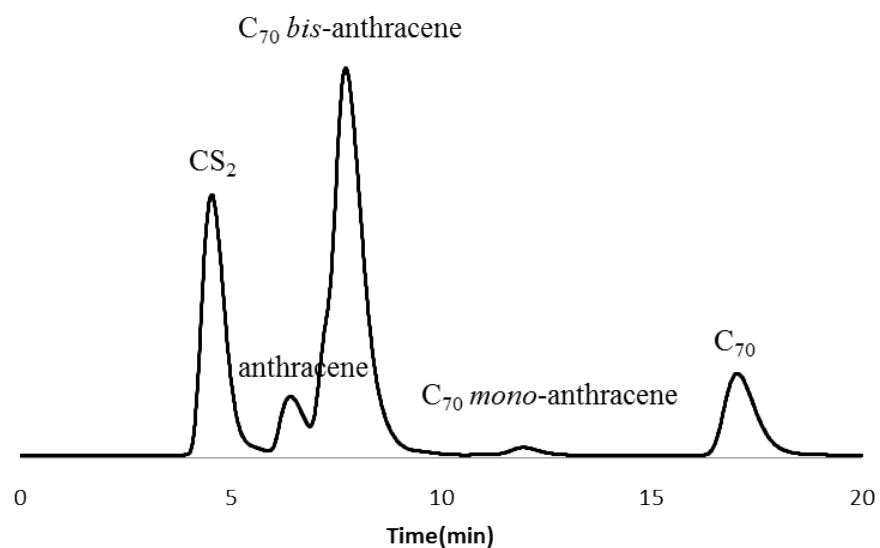


Figure S7. HPLC chromatogram of crude of the reaction between C₇₀ (10mg, 0.012mmol) and anthracene (4mg, 0.02mmol). Conditions: 5-PBB column ($\varphi = 4.6\text{ID} \times 250\text{mm}$); toluene; flow rate: 1.2mL/min; wavelength: 320nm; room temperature.

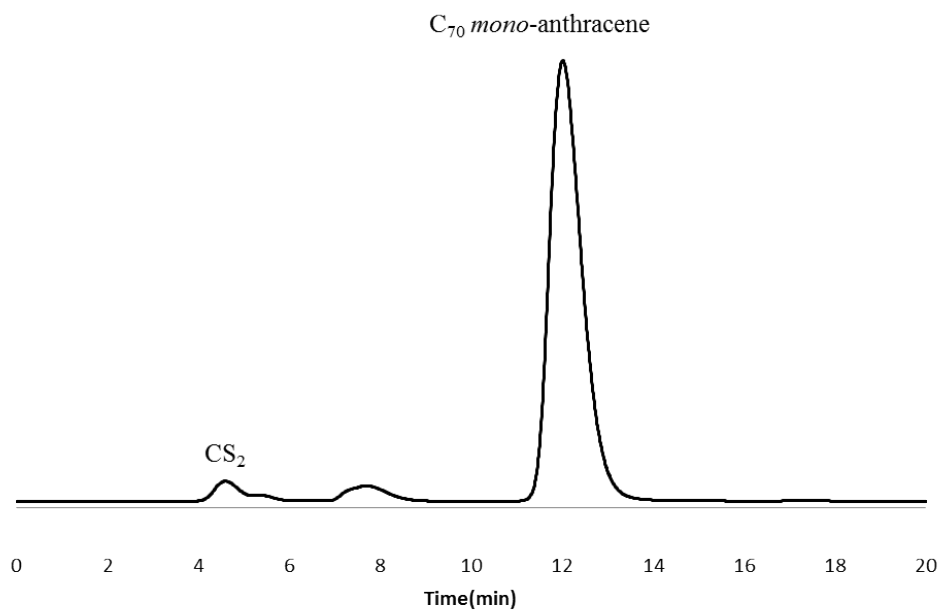


Figure S8. HPLC chromatogram of C₇₀ mono-anthracene. Conditions: 5-PBB column ($\varphi = 4.6\text{ID} \times 250\text{mm}$); toluene; flow rate: 1.2mL/min; wavelength: 320nm; room temperature.

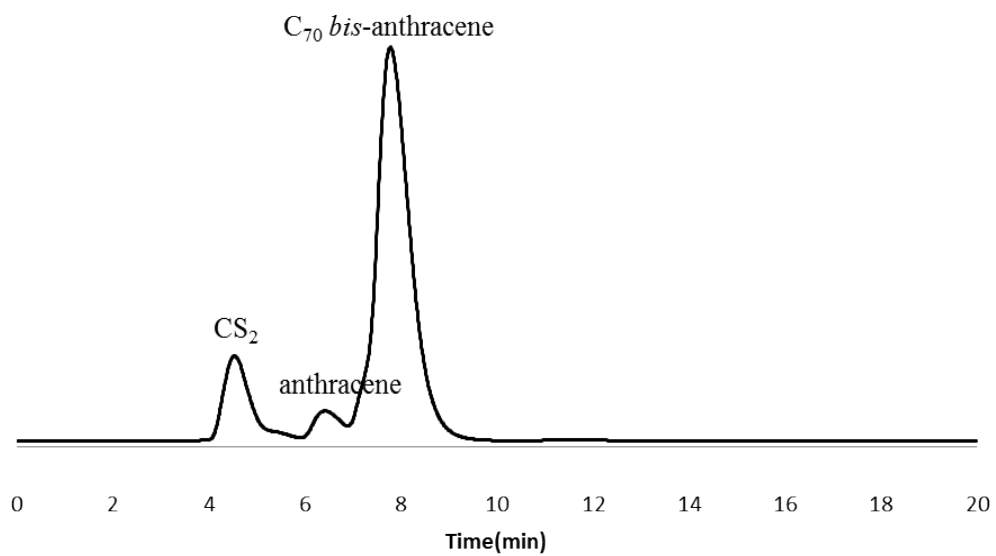


Figure S9. HPLC chromatogram of C₇₀ bis-anthracene. Conditions: 5-PBB column ($\varphi = 4.6\text{ID} \times 250\text{mm}$); toluene; flow rate: 1.2mL/min; wavelength: 320nm; room temperature.