

Supporting Information

Asymmetric Phthalocyanine Synthesis by ROMP-Capture-Release

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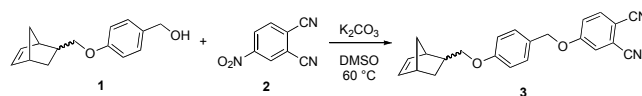
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General Procedures: All reactions were run under a nitrogen or argon atmosphere unless otherwise noted. All chemicals were purchased from Aldrich, Acros Organics, and Alfa Aesar used without further purification unless otherwise noted. Compounds **1**,¹ **4**,² **7**,³ and **12**⁴ were prepared according to literature procedures. DMSO was dried over freshly activated 4 Å molecular sieves. CH₂Cl₂ was distilled from CaH₂. THF was distilled from sodium and benzophenone. Melting points were uncorrected. ¹H NMR spectra were recorded at Bruker DRX-500 MHz spectrometer with ¹³C operating frequencies of 125 MHz. ¹H NMR spectra were obtained in CDCl₃ or CD₂Cl₂-DMSO-*d*₆ (95:5) were calibrated using residual CHCl₃ (δ 7.27 ppm) or residual CH₂Cl₂ (δ 5.32 ppm) as an internal reference respectively, with chemical shifts reported in ppm from TMS. ¹³C NMR spectra were obtained in CDCl₃ or CD₂Cl₂-DMSO-*d*₆ (95:5) were calibrated using residual CHCl₃ (δ 77.0 ppm) or CH₂Cl₂ (δ 53.8 ppm) as an internal reference respectively. Gel permeation chromatography was carried out in CH₂Cl₂ on a series of two Jordi FlashGel DVB 500 Å (10 mm x 500 mm) operating at 3 mL/min. IR spectra were recorded on a Nicolet IR100 FT-IR spectrometer. Mass spectra were obtained from Mass Spectrometry Facility, Department of Chemistry, University of Arizona. Elemental Analysis data were obtained from NuMega Resonance Labs, Inc, San Diego, CA. Flash column chromatography⁵ and TLC were performed using silica gel 60 and Silica Gel 60 F₂₅₄ plates respectively from EMD.

Experimental Procedures:

4-(4-((1R, 4R)-Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)benzyloxy)phthalonitrile (**3**).



A mixture of anhydrous K₂CO₃ (1.92 g, 13.92 mmol), norbornenyl tagged benzyl alcohol **1** (0.80 g, 3.48 mmol) and 4-nitrophthalonitrile **2** (0.50 g, 2.90 mmol) in anhydrous DMSO (8 ml) was stirred at 60 °C for 16 h under Ar. The reaction mixture was cooled to room temperature and poured into water (30 mL). The solution was extracted with CH₂Cl₂ (3×50 mL), and the combined organic layers were dried over MgSO₄ and filtered. The filtrate was concentrated in vacuo and purified by silica gel column chromatography (SiO₂, 1:6 hexanes-CH₂Cl₂) to give phthalonitrile **3** as a colorless solid (300 mg, 58% yield): mp = 122-123 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, *J* = 8.5 Hz, 1H), 7.33-7.29 (m, 3H), 7.24 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.90 (d, *J* =

¹ Fuchter, M. J.; Hoffman, B.; Barrett, A. *J. Org. Chem.* **2005**, *70*, 5086-5091.

² Wöhrle, D.; Eskes, M.; Shigehara, K.; Yamada, A. *Synthesis* **1993**, 194-196.

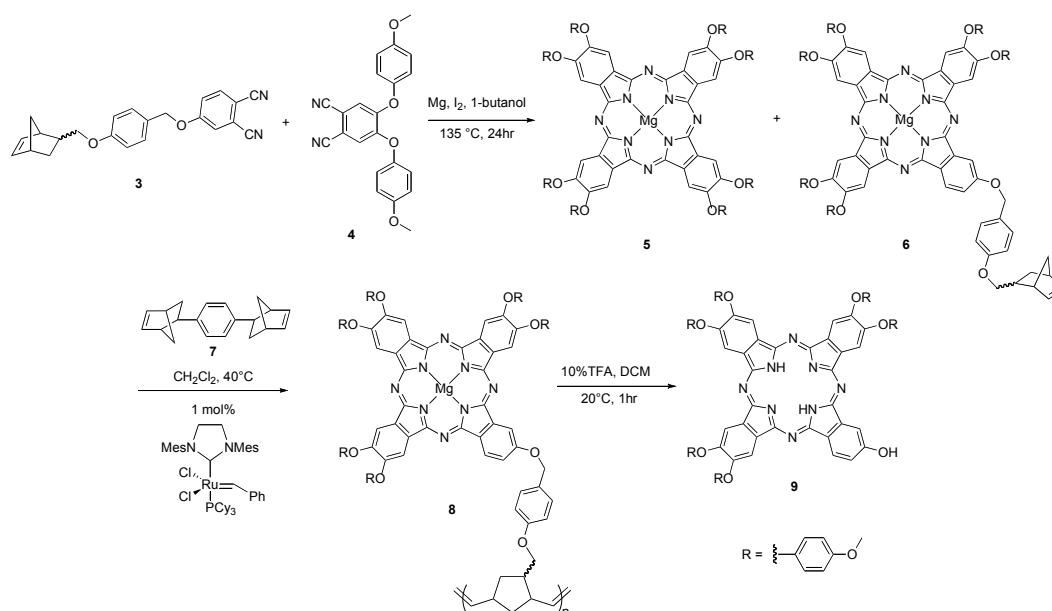
³ Barrett, A.G.M.; Hopkins, B.T.; Love, A.C.; Tedeschi, L. *Org. Lett.*, **2004**, *6*, 835-837.

⁴ Haas, M.; Liu, S. X.; Neels, A.; Decurtins, S. *Eur. J. Org. Chem.* **2006**, *24*, 5467-5478.

⁵ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.

8.5 Hz, 2H), 6.17 (m, 1H), 5.94 (m, 1H), 5.07 (s, 2H), 3.72 (dd, $J = 9.0, 6.0$ Hz, 1H), 3.55 (t, $J = 9.0$ Hz, 1H), 3.03 (br s, 1H), 2.85 (br s, 1H), 2.56 (m, 1H), 1.92 (m, 1H), 1.48 (d, $J = 7.0$ Hz, 1H), 1.36 (m, 1H), 0.62 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 161.7, 159.6, 137.6, 136.8, 136.3, 135.1, 132.2, 129.3, 129.3, 126.2, 126.1, 119.9, 119.7, 117.3, 115.6, 115.2, 114.8, 107.2, 72.3, 71.5, 70.9, 49.4, 45.0, 43.8, 43.6, 42.2, 41.5, 38.5, 38.3, 29.6, 29.0; IR (film) 3091, 2954, 2226, 1596, 1502, 1242 cm^{-1} ; MS (MALDI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: m/z 379.1422, found 379.1522. Analysis calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2$: C, 77.51 %; H, 5.66 %; N, 7.86 %; Found: C, 77.79 %; H, 6.01 %; N, 7.92 %.

2,3,9,10,16,17-Hexa(4-methoxyphenoxy)-23-hydroxyphthalocyanine (9).



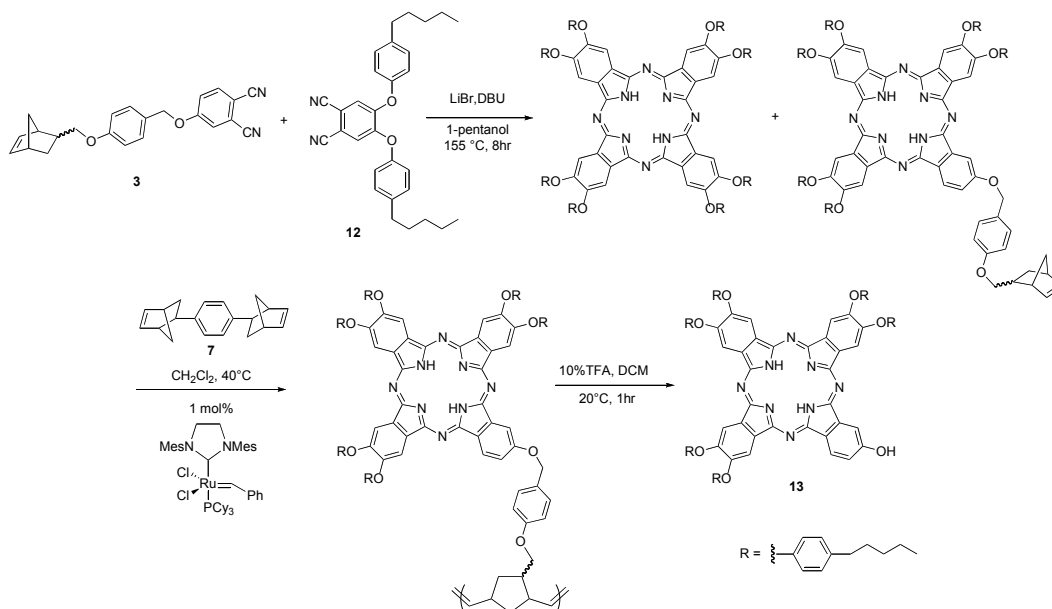
A mixture of Mg (24 mg, 0.99 mmol) and I_2 (ca. 1 crystal) in 1-butanol (5 mL) was heated to reflux for 24 h under N_2 . The mixture was allowed to cool and norbornenyl-tagged phthalonitrile **3** (30 mg, 0.084 mmol) and phthalonitrile **4** (188 mg, 0.505 mmol) were added as solids. The mixture was heated at reflux for 24 h, and then allowed to cool to RT whence the product precipitated. The mixture was poured into 20 mL MeOH and centrifuged for 10 min. The green solid layer was filtered, washed with MeOH, and purified by flash chromatography (SiO_2 , 95:5 CH_2Cl_2 -MeOH). The collected green elution was concentrated in vacuo to give a mixture of **5** and **6** as a green residue (140 mg) that was taken on without further manipulation.

To a solution of the mixture of **5** and **6** (140 mg) in degassed CH_2Cl_2 (3 mL) under N_2 was added cross-linker **7** (11 mg, 0.042 mmol) and Grubb's catalyst (2 mg, 2.4 μmol). The resulting mixture was heated to 40 $^\circ\text{C}$ for 12 h. A combination of CH_2Cl_2 (2 mL), MeCN (1 mL), and ethyl vinyl ether (1 mL) was added, and the resulting mixture was maintained at 40 $^\circ\text{C}$ for an additional 1 h. The polymer was filtered, washed with CH_2Cl_2 (3 \times 10 mL), and further extracted with CH_2Cl_2 (Soxhlet) for 24 h to give crosslinked ROM polymer **8** (60 mg) as a blue solid.

A mixture of ROM polymer **8** (60 mg) and a degassed solution of 10% trifluoroacetic acid in CH_2Cl_2 (5 mL) was stirred at room temperature under Ar for 1 h, and then filtered by fritted

syringe. The filtrate was concentrated in vacuo to remove trifluoroacetic acid and CH₂Cl₂, dried in vacuo to give Pc **9** (20 mg, 19% based on **3**). MS (MALDI) calcd for C₇₄H₅₅N₈O₁₃ [M+H]⁺: *m/z* 1263.3889, found 1263.6238; UV-Vis: λ_{max} 701 nm (ε = 1.26×10⁵ M⁻¹cm⁻¹).

2,3,9,10,16,17-Hexa(4-pentylphenoxy)-23-hydroxyphthalocyanine (**13**).



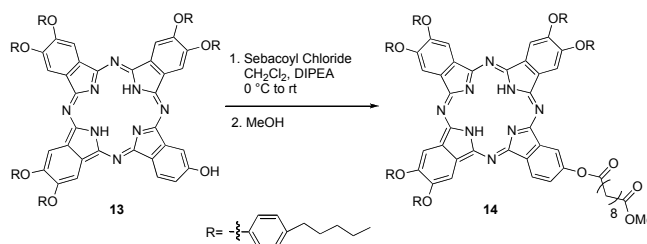
A mixture of phthalonitrile **3** (320 mg, 0.9 mmol), phthalonitrile **12** (1.65 g, 3.6 mmol), DBU (683 mg, 4.5 mmol) and LiBr (10 mg, 0.11 mmol) in 60 mL 1-pentanol was maintained at reflux under Ar for 8 h. The reaction mixture was allowed to cool to RT, poured in MeOH, and the resulting precipitate was filtered, washed with MeOH, air dried and then chromatographed (SiO₂, 95:5 CH₂Cl₂-MeOH). The green elution was collected and concentrated in vacuo. The resultant green residue and cross-linker **7** (50mg, 0.2 mmol) were dissolved in degassed CH₂Cl₂ (20 mL) under N₂.

To this solution was added Grubb's catalyst (8 mg, 9.6 μmol), and the mixture was maintained at 40 °C for 12 h. A combination of CH₂Cl₂ (3 mL), MeCN (1.5 mL), and ethyl vinyl ether (1.5 mL) was added, and the resulting mixture was heated to 40 °C for another 1 h. The polymer was filtered off and washed with CH₂Cl₂ (3×100 mL) and further extracted with CH₂Cl₂ (Soxhlet) for 48 h.

The crosslinked Pc polymer was rinsed out of the thimble with CH₂Cl₂ and the mixture was concentrated to 20 mL. 2 mL trifluoroacetic acid was added to the suspension of polymer Pc, and the mixture was stirred at RT under Ar for 1 h. The reaction mixture was then washed with water (20 mL), aqueous NaHCO₃ (20 mL), and the organic layer was dried over MgSO₄, filtered, evaporated. The crude product was purified by flash column chromatography (SiO₂, 95:5 CH₂Cl₂-MeOH) to give **13** as a green solid (0.16 g, 12% based on **3**): R_f = 0.2 (100% CH₂Cl₂); ¹H NMR (500 MHz, 95:5 CD₂Cl₂-DMSO-*d*₆) δ 9.69 (br s, 1H), 8.54 (br s, 1H), 8.49 (br s, 1H), 8.36 (br s, 1H), 8.34 (br s, 1H), 8.27 (br s, 1H), 8.21 (br s, 1H), 8.11 (br s, 1H), 7.50 (br s, 1H), 7.30-7.23 (m, 24H), 2.69-2.64 (m, 12H), 1.68 (m, 12H), 1.40 (m, 24H), 0.95 (m, 18H); ¹³C NMR

(125 MHz, 95:5 CD₂Cl₂-DMSO-*d*₆) δ 160.7, 156.0, 156.0, 155.6, 155.50, 155.46, 155.1, 151.0, 150.8, 150.6, 150.5, 149.6, 149.5, 138.7, 138.5, 138.4, 138.0, 138.0, 137.0, 132.9, 132.7, 132.4, 132.2, 130.8, 130.5, 130.0, 130.0, 129.9, 129.8, 126.6, 124.1, 119.3, 119.2, 118.9, 118.7, 118.6, 118.1, 114.1, 114.0, 113.4, 113.3, 112.6, 108.0, 35.57, 35.56, 35.50, 35.48, 31.95, 31.93, 31.89, 31.72, 31.65, 22.90, 22.86, 14.24, 14.19; IR (film) 3523, 3291, 2942, 1606, 1453, 1281-1019 cm⁻¹; UV-Vis (100% DCM) λ_{\max} 700.5 nm ($\epsilon = 1.46 \times 10^5$ M⁻¹cm⁻¹); MS (MALDI) calcd for C₉₈H₁₀₃N₈O₇ [M+H]⁺: *m/z* 1503.7950, found 1503.792; Analysis calcd for C₉₈H₁₀₂N₈O₇: C 78.27, H 6.84, N 7.45%; Found: C 78.58, H 7.21, N 7.48%.

1-[2,3,9,10,16,17-Hexa(4-pentylphenoxy)-phthalocyanine-23-yl]-10-methyl-decanedioate (14).



A solution of asymmetric Pc **13** (70 mg, 46 μ mol) and diisopropylethyl amine (75 mg, 0.58 mmol) in 10 mL CH₂Cl₂ was stirred at room temperature under Ar for 10 min. The resulting mixture was added dropwise to a solution of sebacyl chloride (300 mg, 1.25 mmol) in 10 mL CH₂Cl₂ at 0 °C. After finishing addition, the mixture was allowed to warm up to room temperature and stirred under Ar for 3 h. Solvent was evaporated and the residue was precipitated into 20 mL MeOH. The precipitate was filtered and washed thoroughly with MeOH. The crude product was purified by column chromatography (silica gel, 100% CH₂Cl₂) to give 35 mg (44% yield) of green solid. *R_f* = 0.3 (100% DCM); ¹H NMR (500 MHz, 95:5 CD₂Cl₂-DMSO-*d*₆) δ 8.356 (d, *J* = 8.0 Hz, 1H), 8.240 (br s, 1H), 8.187 (br s, 4H), 8.142 (br s, 1H), 8.044 (br s, 1H), 7.574 (d, *J* = 8.0 Hz, 1H), 7.367-7.202 (m, 24H), 3.665 (s, 3H), 2.828 (t, *J* = 7.5 Hz, 2H), 2.723-2.625 (m, 12H), 2.367 (t, *J* = 7.5 Hz, 3H), 1.968 (m, *J* = 7.5 Hz, 2H), 1.744-1.594 (m, 16H), 1.552-1.403 (m, 30H), 1.002-0.950 (m, 18H); ¹³C NMR (125 MHz, 95:5 CD₂Cl₂/DMSO-*d*₆) δ 174.2, 172.5, 155.94, 155.88, 155.7, 155.6, 155.3, 154.9, 152.5, 151.7, 151.4, 150.8, 150.6, 150.2, 149.9, 139.2, 138.8, 138.5, 138.4, 138.32, 138.26, 130.2, 130.1, 129.9, 123.6, 123.4, 119.6, 119.1, 118.6, 118.5, 118.3, 118.2, 115.4, 114.1, 114.0, 113.9, 112.9, 111.9, 51.5, 35.70, 35.67, 35.6, 34.9, 34.4, 32.1, 32.0, 31.77, 31.75, 29.8, 29.7, 29.6, 25.41, 25.38, 23.00, 22.96, 14.31, 14.26; IR (film) 3291, 2931, 1749, 1605, 1452, 1274-1016 cm⁻¹; UV-Vis (100% DCM) λ_{\max} 698.5 nm ($\epsilon = 1.55 \times 10^5$ M⁻¹cm⁻¹); MS (MALDI) calcd for C₁₀₉H₁₂₁N₈O₁₀ [M+H]⁺: *m/z* 1701.9206, found 1702.221; Elemental analysis calcd for C₁₀₉H₁₂₀N₈O₁₀: C 76.91, H 7.11, N 6.58%; found: C 77.02, H 7.52, N 6.65%.

The ^1H and ^{13}C NMR spectra for compounds **3**, **13**, and **14**.

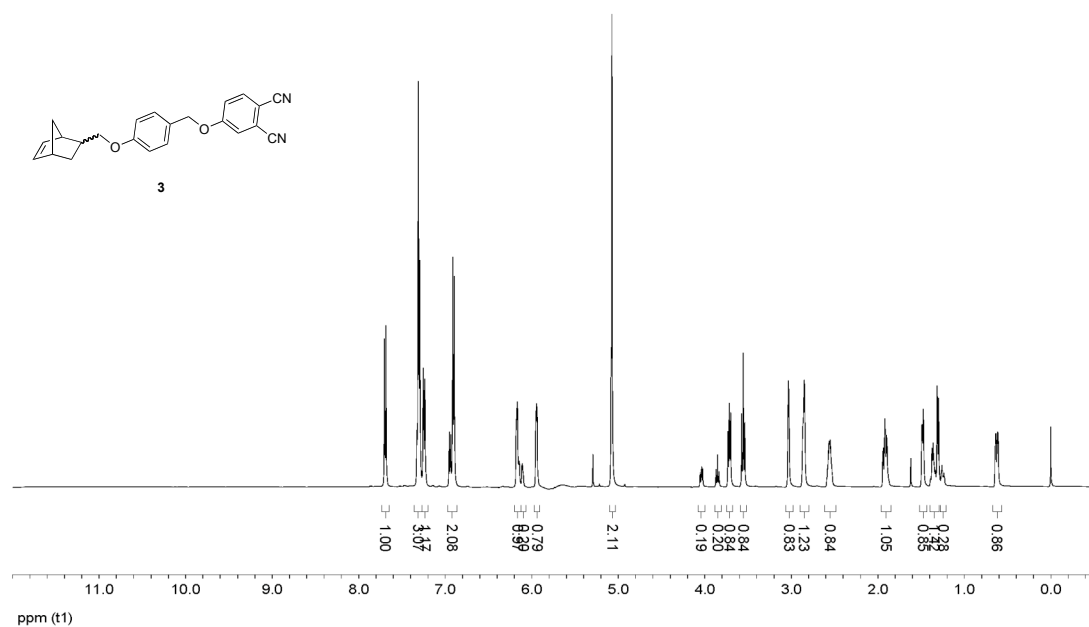


Figure S1. ^1H NMR (CDCl₃, 500 MHz) spectrum of phthalonitrile **3**.

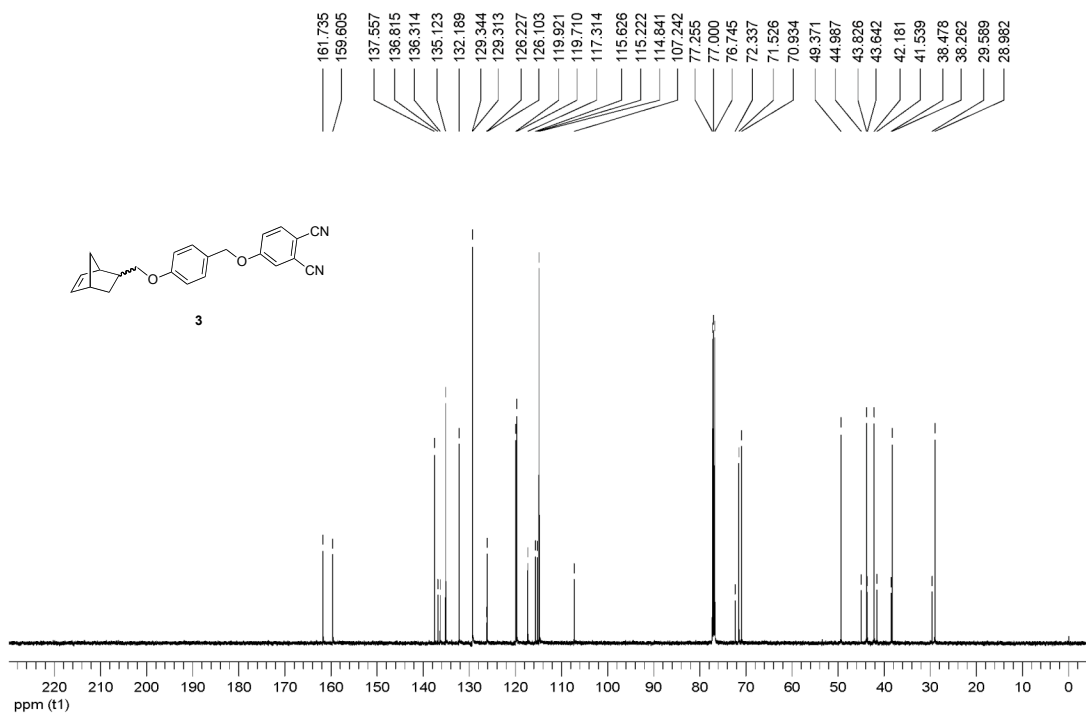


Figure S2. ^{13}C NMR (CDCl₃, 125 MHz) spectrum of phthalonitrile **3**.

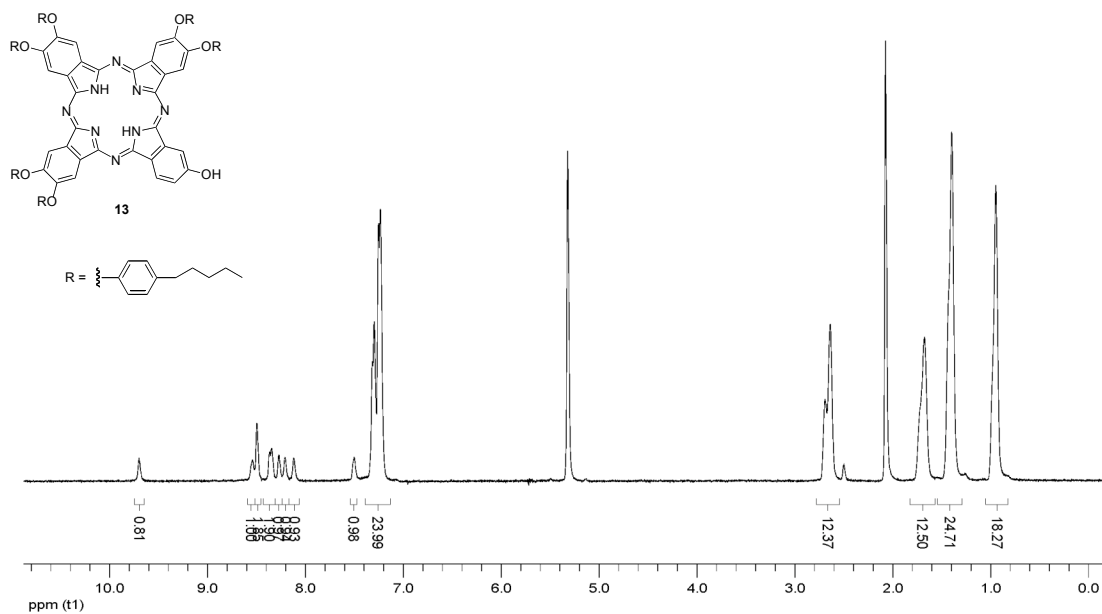


Figure S3. $^1\text{H NMR}$ (500MHz, 95:5 $\text{CD}_2\text{Cl}_2/\text{DMSO}-d_6$) spectrum of Pc 13.

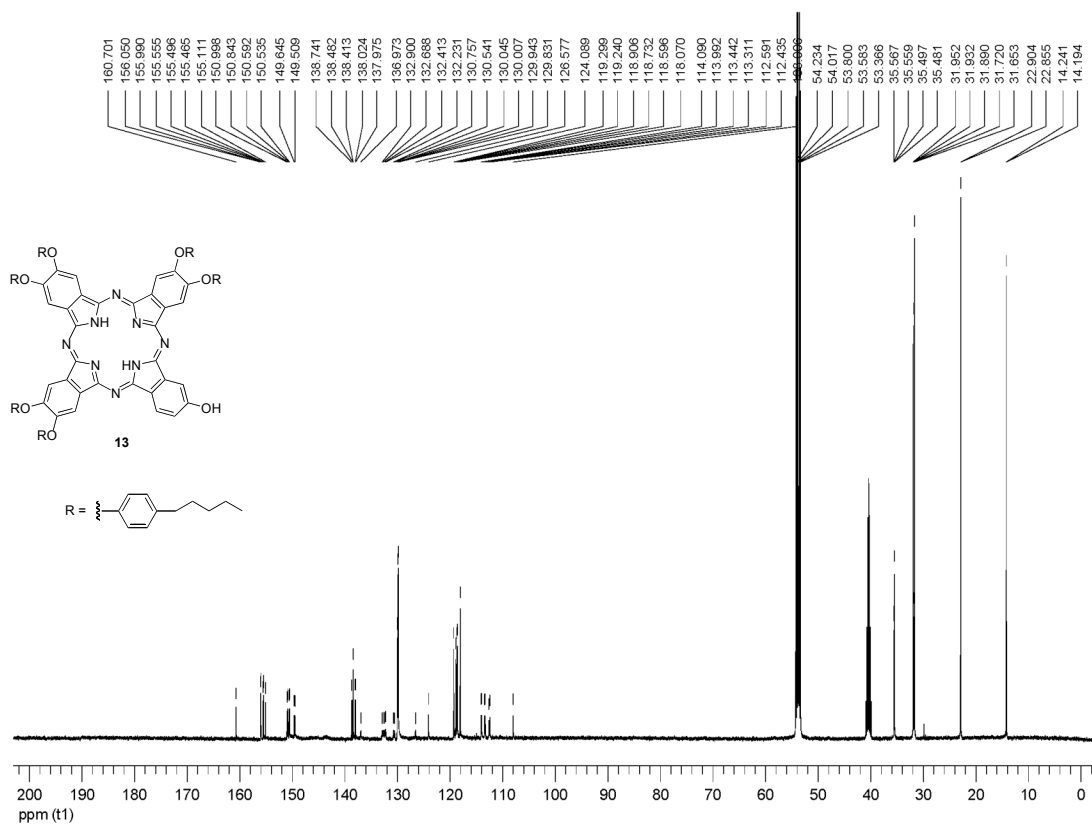


Figure S4. $^{13}\text{C NMR}$ (125 MHz, 95:5 $\text{CD}_2\text{Cl}_2/\text{DMSO}-d_6$) spectrum of Pc 13.

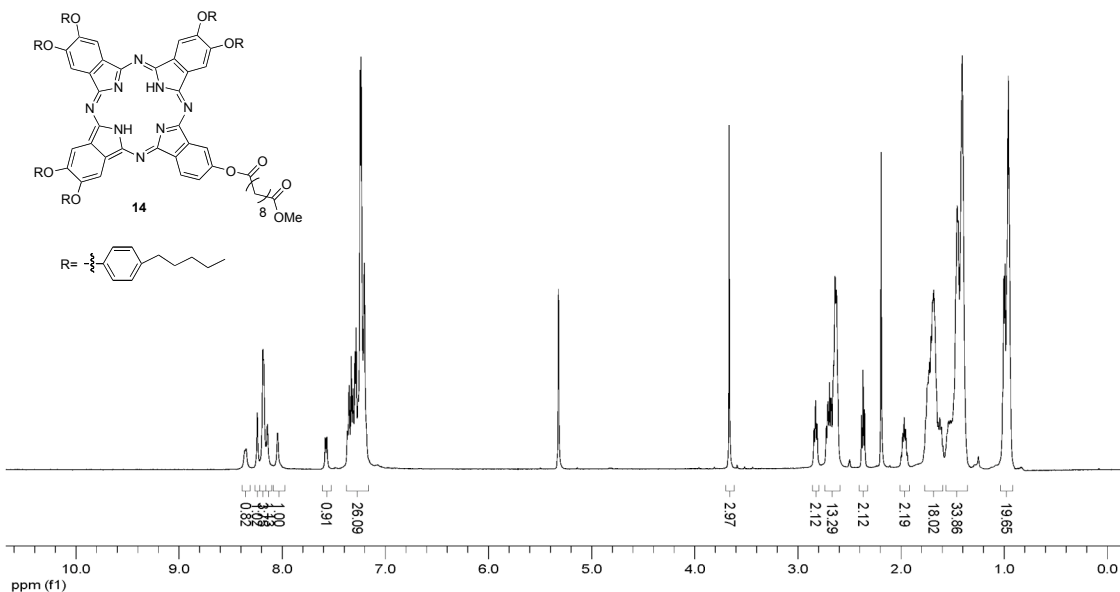


Figure S5. ^1H NMR (500 MHz, 95:5 $\text{CD}_2\text{Cl}_2/\text{DMSO}-d_6$) spectrum of Pc 14.

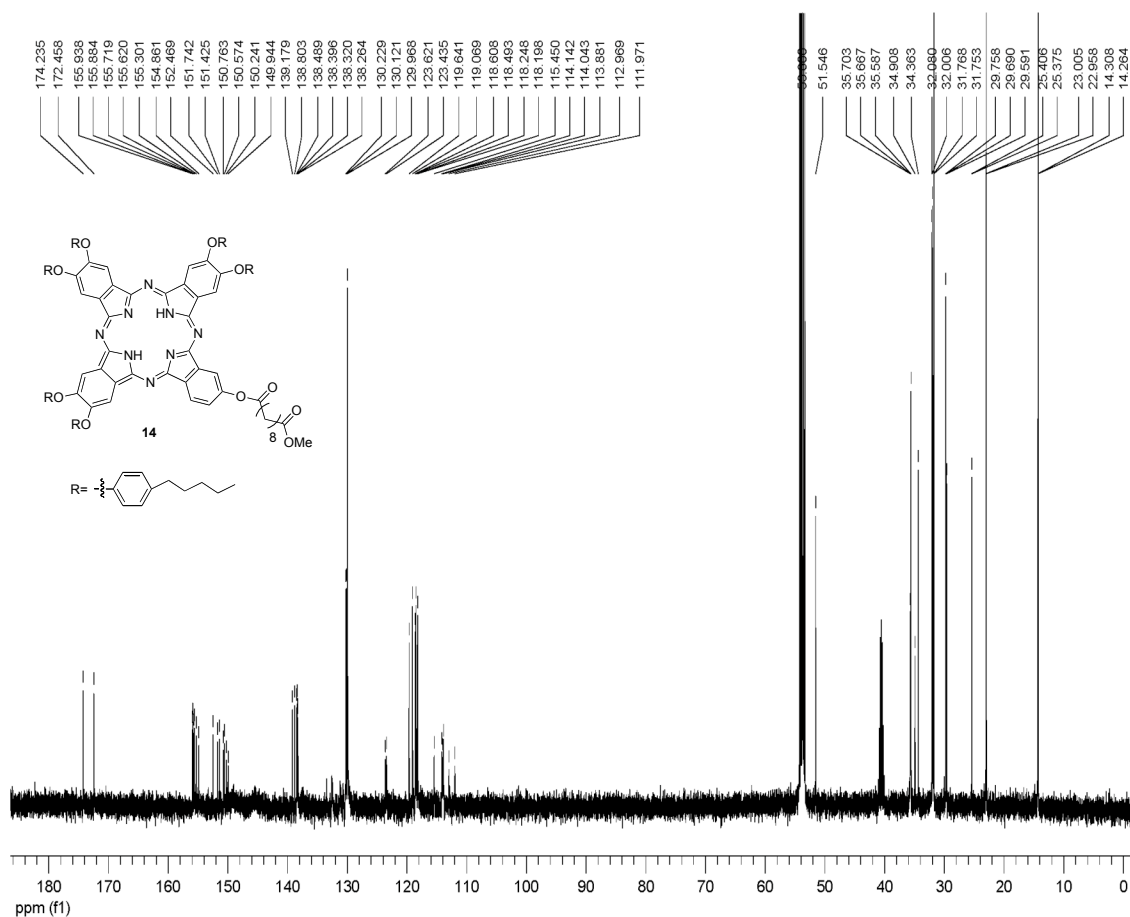


Figure S6. ^{13}C NMR (125 MHz, 95:5 $\text{CD}_2\text{Cl}_2/\text{DMSO}-d_6$) spectrum of Pc 14.

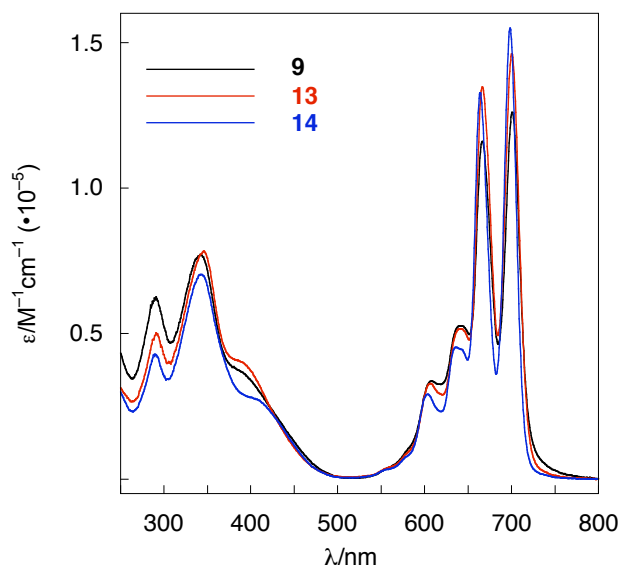


Figure S7. UV-Vis spectrum of asymmetric Pcs **9**, **13**, and **14** in CH_2Cl_2 .