SUPPORTING INFORMATION FOR:

Naphthalene Based Calixarenes: Unusual Regiochemistry of a Friedel-Crafts Alkylation

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Experimental Section

General. All reagents employed were commercially available. Anhydrous CH_2Cl_2 was obtained by distillation from CaH_2. Anhydrous diethyl ether was obtained by distillation from sodium benzophenone. All other solvents were purchased commercially and used without further purification. ^1H NMR spectra were obtained on either a Bruker AMX-360 spectrometer at 360 MHz or a Bruker DRX-400 at 400 MHz and were referenced to tetramethylsilane (TMS). ^{13}C NMR spectra were obtained on either a Bruker AMX-360 at 90 MHz or a Bruker DRX-400 at 100 MHz and were referenced to $CDCl_3$ (77.0 ppm).

1,8-Diallyl-2,7-dimethoxynaphthalene (11). 2,7-Bisallyloxynaphthalene (**9**)[1] (8.00 g, 33.3 mmol) in *N,N*-diethylaniline (125 mL) was refluxed for 1 h under Ar. After cooling to room temperature, the solvent was removed in vacuo to yield 1,8-diallyl-2,7-dihydroxynaphthalene (**10**), which was methylated, without purification, by heating to 60 ^oC for 16 h with potassium carbonate (18.43 g, 133 mmol) and methyl iodide (8.30 mL, 133 mmol) in THF (135 mL). After cooling to room temperature, sodium hydride (1.33 g, 33.3 mmol) was added and the resulting mixture was stirred for two hours. The reaction was quenched with saturated ammonium chloride. The mixture was extracted with CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$. Solvents were then removed in vacuo, and the residue was purified by chromatography (40:60 Hexanes/ CH_2Cl_2). Recrystallization from hexanes gave compound **11**

(4.80 g, 54% from compound **9**) as white crystals (mp 189.4-194.0 ^{o}C); ^{1}H NMR ($CDCl_3$): ∂ 7.70 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.20 (ddt, *J* = 17.3 Hz, 10.8 Hz, 4.9 Hz, 2H), 5.06 (dd, J = 9.8 Hz, 1.6 Hz, 2 H), 4.82 (dd, J =17.3 Hz, 1.8 Hz, 2 H), 4.11 (s, 6H, OCH_3), 3.89 (m, 4H, $ArCH_2$). ^{13}C NMR ($CDCl_3$): ∂ 157.2, 139.6, 135.5, 130.0, 126.8, 120.9, 115.0, 111.5, 57.2, 31.5. IR (neat, cm^{-1}): 3076 (w), 2998 (m), 2936 (m), 2835 (m), 1614 (s), 1516 (s), 1461 (m), 1255 (s), 1132 (s), 1049 (s). HRMS for M^{+} calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1450.

2,7-Dimethoxy-1,8-dipropylnaphthalene (12). Five percent palladium on carbon (1.70 g) in ethyl acetate (120 mL) was purged with H_2 for 40 min. A solution of compound **11** (4.10 g, 16.0 mmol) in ethyl acetate (40 mL) was added via syringe and the mixture was stirred for 3.5 h under an atmosphere of H_2. (The reaction was followed by TLC using SiO_2 plates pre-treated with $AgNO_3$.) The mixture was then filtered through celite, washing with ethyl acetate. Solvents were removed in vacuo to yield compound **12**, which was recrystallized from hexanes to give colorless crystals (4.10 g, 94%) (mp 68.0-69.6 ^{o}C). ^{1}H NMR ($CDCl_3$): ∂ 7.61 (d, *J* = 9.1 Hz, 2H), 7.17 (d, *J* = 9.1 Hz, 2H), 3.91 (s, 6H, OCH_3), 3.06 (m, 4H, $ArCH_2$), 1.66 (m, 4H), 1.06 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): ∂ 156.2, 133.4, 128.8, 126.5, 124.7, 111.0, 56.7, 29.0, 24.6, 14.4. IR (neat, cm^{-1}): 2954 (s), 2870 (m), 2835 (w), 1614 (s). 1517 (s), 1464 (m), 1251, (s), 1131 (s), 1047 (m). HRMS for M+H^{+} calcd for $C_{18}H_{25}O_2$ 273.1855, found 273.1851.

3-Formyl-2,7-dimethoxy-1,8-dipropylnaphthalene (13). A mixture of compound **12** (2.00 g, 7.35 mmol) and TMEDA (2.77 mL, 18.4 mmol) in diethyl ether (75 mL) was cooled to 0 ^{o}C under Ar. A solution of n-BuLi (1.6 M in hexanes) (9.19 mL, 14.7 mmol) was added dropwise over 12 min. The solution was allowed to warm to room temperature and was then brought to reflux for 13 h. The solution was cooled to 0 ^{o}C, and DMF (2.28 mL, 29.4 mmol) was added. The resulting mixture was stirred at 0 ^{o}C for 2 h and was quenched by slowly adding 10 mL of 4N HCl. After extraction with CH_2Cl_2 the combined organic layers were washed consecutively with 5% HCl and saturated $NaHCO_3$, and were dried over $MgSO_4$. Solvents were removed in vacuo, and the resulting crude product was purified by chromatography (50:50 Hexanes/CH_2Cl_2) to yield compound **13** (1.26 g, 57%) as a colorless oil. ^{1}H NMR ($CDCl_3$): ∂ 10.35 (s, 1H, ArCHO), 8.18 (s, 1H), 7.77 (d, J = 9.1 Hz, 1H), 7.22 (d, J = 9.1 Hz, 1H), 3.94 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 3.09 (m, 4H, ArCH2), 1.61 (m, 4H), 1.06 (t, J = 7.3 Hz, 3H), 1.04 (t, J = 7.5, 3H). ^{13}C NMR ($CDCl_3$): ∂ 190.3, 158.2, 156.9, 136.5, 132.5, 131.5, 130.9, 127.0, 125.5, 125.2, 112.2, 63.7, 56.2, 28.7, 28.2, 25.3, 24.3, 14.1. HRMS for $M+H^+$ calcd for $C_{19}H_{25}O_3$ 301.1804, found 301.1791.

3-Hydroxymethyl-2,7-dimethoxy-1,8-dipropylnaphthalene (14). A mixture of compound **13** (0.918 g, 3.06 mmol) and sodium borohydride (0.289 g, 7.65 mmol) in absolute ethanol (30 mL) was stirred at room temperature for 16 h under Ar. The reaction was quenched with 13 mL of 10% HCl and extracted with CH_2Cl_2. The combined organic layers were washed consecutively with brine and 5% HCl and were dried over $MgSO_4$. Solvents were removed in vacuo, and the crude product was purified by chromatography, eluting with CH_2Cl_2, to give carbinol **14** (0.850 g, 92%) as an oil. ^{1}H NMR ($CDCl_3$): ∂ 7.57 (s, 1H), 7.57 (d, J = 8.9 Hz, 1H), 7.14 (d, J = 9.0 Hz, 1H), 4.79 (s, 2H), 3.79 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.09 (m, 4H), 2.72 (s, 1H, OH), 1.55 (m, 4H), 1.01 (t, J = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): ∂ 155.8, 155.5, 132.7, 130.4, 128.7, 128.1, 127.8, 125.3, 112.1, 61.8, 61.7, 56.6, 29.0, 28.2, 25.4, 24.6, 14.2. IR (neat, cm^{-1}): 3600-

3150 (m), 2955 (s), 2870 (m), 2836 (m), 1606 (m), 1501 (s), 1465 (m), 1367 (m), 1249 (s), 1143 (s), 1025 (s). HRMS for M^+ calcd for $C_{19}H_{26}O_3$ 302.1882, found 302.1869.

Naphthyl calix[3]arene (15). A solution of compound **14** (0.321 g, 1.06 mmol) in dichloromethane (6.5 mL) was cooled to 0 °C under Ar. Trifluoromethane sulfonic acid (0.0095 mL, 0.106 mmol) was added. The mixture was warmed to room temperature for 5 h. Solvent was removed in vacuo and the crude product was purified by chromatography (50:50 Hexanes/CH_2Cl_2) to give cyclic trimer **15** (0.069 g, 23%) as an oil. ^1H NMR ($CDCl_3$): ∂ 7.70 (s, 1H), 7.27 (s, 1H), 4.25 (s, 2H), 3.88 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 3.07 (m, 4H), 1.48 (m, 4H), 0.90 (m, 6H). ^{13}C NMR ($CDCl_3$): ∂ 156.0, 155.3, 136.5, 133.0, 130.6, 130.4, 127.0, 126.1, 123.9, 114.7, 61.2, 56.9, 36.0, 29.6, 28.2, 25.2, 24.4, 14.1. IR (neat, cm^{-1}): 2954 (s), 1595 (s). HRMS for $M+H^+$ calcd for $C_{57}H_{73}O_6$ 853.5407, found 853.5404.

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(1) Prajer-Janczewska, L.; Wróblewski, J. *Pol. J. Chem.* **1980**, *54*, 1431-1437.

NOESY Spectrum for Naphthyl Calix[3]arene **15**: