

Supporting Information

Synthesis and Properties of Benzophenone–Spiropyran and Naphthalene–Spiropyran Conjugates

Massimiliano Tomasulo,[†] Sireesha L. Kaanumal,[†] Salvatore Sortino^{*,‡} and Francisco M. Raymo^{*,†}

Center for Supramolecular Science, Department of Chemistry, University of Miami, 1301 Memorial Drive, Florida, 33146-0431 and Dipartimento di Scienze Chimiche, Università di Catania, viale Andrea Doria 8, Catania, I-95125, Italy

E-Mail: ssortino@unict.it; fraymo@miami.edu

• General Methods and Experimental Procedures for the Synthesis of 20–22	S2
• High-Performance Liquid Chromatograms of SP2	S4
• High-Performance Liquid Chromatograms of SP3	S5
• High-Performance Liquid Chromatograms of SP5	S6
• High-Performance Liquid Chromatograms of SP7	S7

General Methods and Experimental Procedures for the Synthesis of 20–22

General Methods. Chemicals were purchased from commercial sources and used as received. CH_2Cl_2 , MeCN, PhH and PhMe were distilled over CaH_2 . THF was distilled over Na and Ph_2CO . All reactions were monitored by thin-layer chromatography, using aluminum sheets coated with silica (60, F_{254}). High performance liquid chromatography (HPLC) was performed with BDS analytical (column dimensions = 4.6×250 mm, flow rate = 1.0 mL min^{-1} , injection volume = $20 \mu\text{L}$, sample concentration = 0.1 – 2.0 mM) and semi-preparative (column dimensions = 21.4×250 mm, flow rate = 10 mL min^{-1} , injection volume = 10 mL , sample concentration = 0.1 mM) columns. The retention time (RT) and the peak asymmetry (PA) were determined at a wavelength of 330 nm. The average purity parameter (APP) was calculated for the peak heart in the wavelength range 230 – 700 nm. Melting points (mp) are uncorrected. Fast atom bombardment mass spectra (FABMS) were recorded in a 3-nitrobenzyl alcohol matrix. All absorption and emission spectra were recorded in degassed solutions, using quartz cells with a path length of 1.0 cm. The samples were irradiated at 254 nm (0.4 mW cm^{-2}) for 10 min in degassed solutions. Time-resolved absorption spectra were recorded at a right-angle geometry after excitation with the fourth harmonic of a Nd-YAG laser [pulse width = 6 ns (FWHM), wavelength = 266 nm]. The monitoring beam was supplied by a ceramic xenon lamp and delivered through quartz fiber-optical cables. The laser pulse was probed by a fiber that synchronized the spectrometer with a digitizer, operating in the pre-trigger mode. The signals from a compact photomultiplier were initially captured by the digitizer and then transferred to a personal computer that controlled the experiment with commercial software. The energy of the laser pulse was measured at each laser shot with a pyroelectric energy monitor.

3,5-Bis-(naphth-2'-ylmethoxy)-benzyl Alcohol (I). A suspension of 2-bromomethylnaphthalene (6.0 g, 27 mmol), 3,5-dihydroxybenzyl alcohol (1.9 g, 14 mmol) and K_2CO_3 (9.4 g, 68 mmol) in degassed MeCN (50 mL) was stirred at 45°C under N_2 for 2 d. After cooling the mixture down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (3×25 mL). The organic phase was dried over MgSO_4 and the solvent was distilled off under reduced pressure. The residue was crystallized from hexane/PhMe (2 : 1 , v/v) to afford **I** (5.1 g, 90%) as a pale yellow solid. FABMS: $m/z = 421[\text{M} + \text{H}]^+$; $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta = 4.66$ (2H , s), 5.23 (4H , s), 6.66 (1H , t, 2 Hz), 6.69 (2H , d, 2 Hz), 7.48 – 7.54 (6H , m), 7.84 – 7.91 (8H , m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 65.6$, 70.5 , 101.7 , 106.1 , 125.6 , 126.4 , 126.6 , 126.7 , 128.1 , 128.3 , 128.7 , 133.4 , 133.6 , 134.6 , 143.9 , 160.5 .

3,5-Bis-(naphth-2'-ylmethoxy)-benzyl Bromide (4). A solution of **I** (2.16 g, 5 mmol) and PPh_3 (1.62 g, 6.16 mmol) in MeCN (30 mL) was stirred at ambient temperature and under N_2 for 20 min. Then, CBr_4 (1.87 g, 6 mmol) was added and the mixture was maintained at ambient temperature and under N_2 for 60 h. The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO_2 : hexane \rightarrow hexane/ CH_2Cl_2 (1 : 1 , v/v)] to afford **4** (1.94 g, 78%) as white solid. FABMS: $m/z = 483[\text{M} + \text{H}]^+$; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 4.44$ (2H , s), 5.21 (4H , s), 6.69 (1H , t, 2 Hz), 6.75 (2H , d, 2 Hz), 7.53 – 7.57 (6H , m), 7.89 – 7.92 (8H , m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 33.8$, 70.6 , 102.6 , 108.6 , 125.6 , 126.2 , 126.4 , 126.7 , 127.8 , 128.0 , 128.7 , 133.4 , 133.5 , 134.3 , 140.1 , 160.4 .

3,5-Bis-(naphth-2'-ylmethoxy)-toluene (20). A solution of **4** (83 mg, 0.2 mmol) and NaBH_4 (5 mg, 0.1 mmol) in MeCN (20 mL) was stirred at ambient temperature

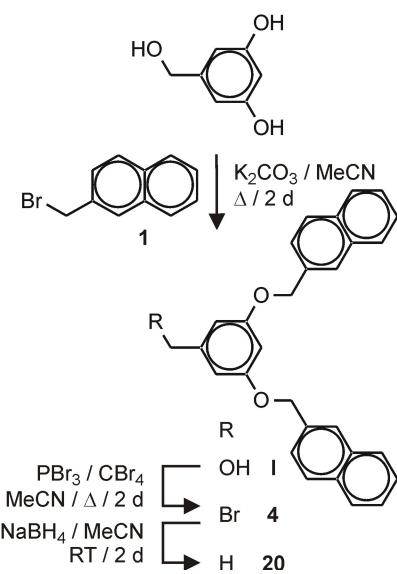


Figure S1. Synthesis of the bromide **4** and of the model compound **20**.

and under Ar for 2 d. The solvent was distilled off under reduced pressure and the residue was dissolved in CH_2Cl_2 (25 mL). The resulting solution was washed with H_2O (2×10 mL) and the organic phase was dried over MgSO_4 . The solvent was distilled off under reduced pressure and the residue was purified by column chromatography [SiO_2 , hexane/ CH_2Cl_2 (1:1, v/v)] to afford **20** (37 mg, 54 %) as a white solid. FABMS: $m/z = 405[\text{M} + \text{H}]^+$; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 2.36$ (3H, s), 5.22 (4H, s), 6.54 (2H, d, 2 Hz), 6.59 (1H, t, 2 Hz), 7.51–7.57 (6H, m), 7.86–7.91 (8H, m); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): $\delta = 22.3, 70.7, 99.8, 108.9, 125.7, 126.5, 126.6, 126.7, 128.2, 128.4, 128.8, 133.5, 133.8, 135.0, 140.8, 160.4$.

4-Acetoxybenzophenone (21). A solution of 4-hydroxybenzophenone (242 mg, 1.2 mmol), MeCOCl (128 μL , 1.8 mmol) and Et_3N (336 μL , 2.4 mmol) in CH_2Cl_2 (20 mL) was heated under reflux for 12 h. After cooling down to ambient temperature, the mixture was washed with H_2O (10 mL). The organic phase was dried over MgSO_4 and the solvent was distilled off under reduced pressure to give **21** (245 mg, 81%) as a white solid. FABMS: $m/z = 241[\text{M} + \text{H}]^+$; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 2.34$ (3H, s), 7.20–7.24 (2H, m), 7.47–7.50 (2H, m), 7.58–7.61 (1H, m), 7.79–7.81 (2H, m), 7.84–7.87 (2H, m); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): $\delta = 21.3, 121.6, 128.5, 130.1, 131.3, 132.5, 135.2, 137.5, 154.0, 169.1, 195.6$.

4-Methoxybenzophenone (22). A solution of 4-hydroxybenzophenone (404 mg, 2 mmol) in MeCN (20 mL) and aqueous KOH (2 M, 1.0 mL) was stirred at ambient temperature for 15 min. The solvent was distilled off under reduced pressure and the residue was washed with MeCN (2 mL) to afford a yellow solid (410 mg). The solid was dissolved in MeCN (25 mL) and, after the addition of MeI (120 μL , 1.9 mmol), the solution was heated under reflux and Ar for 3 h. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was suspended in CH_2Cl_2 (20 mL) and filtered. The solvent was distilled off under reduced pressure to yield **22** (298 mg, 69%) as a white solid. FABMS: $m/z = 213[\text{M} + \text{H}]^+$; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 3.88$ (3H, s), 6.95–6.99 (2H, m), 7.45–7.49 (2H, m), 7.55–7.59 (1H, m), 7.75–7.78 (2H, m), 7.82–7.85 (2H, m); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): $\delta = 55.6, 114.1, 128.6, 129.9, 130.3, 132.0, 132.7, 138.4, 163.4, 195.7$.

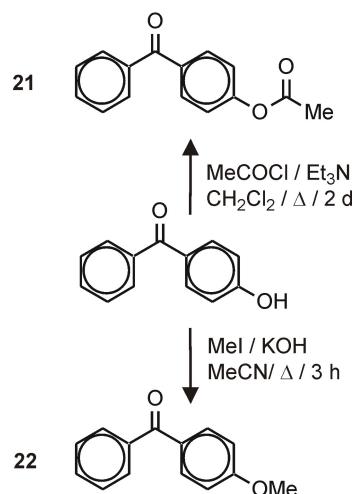
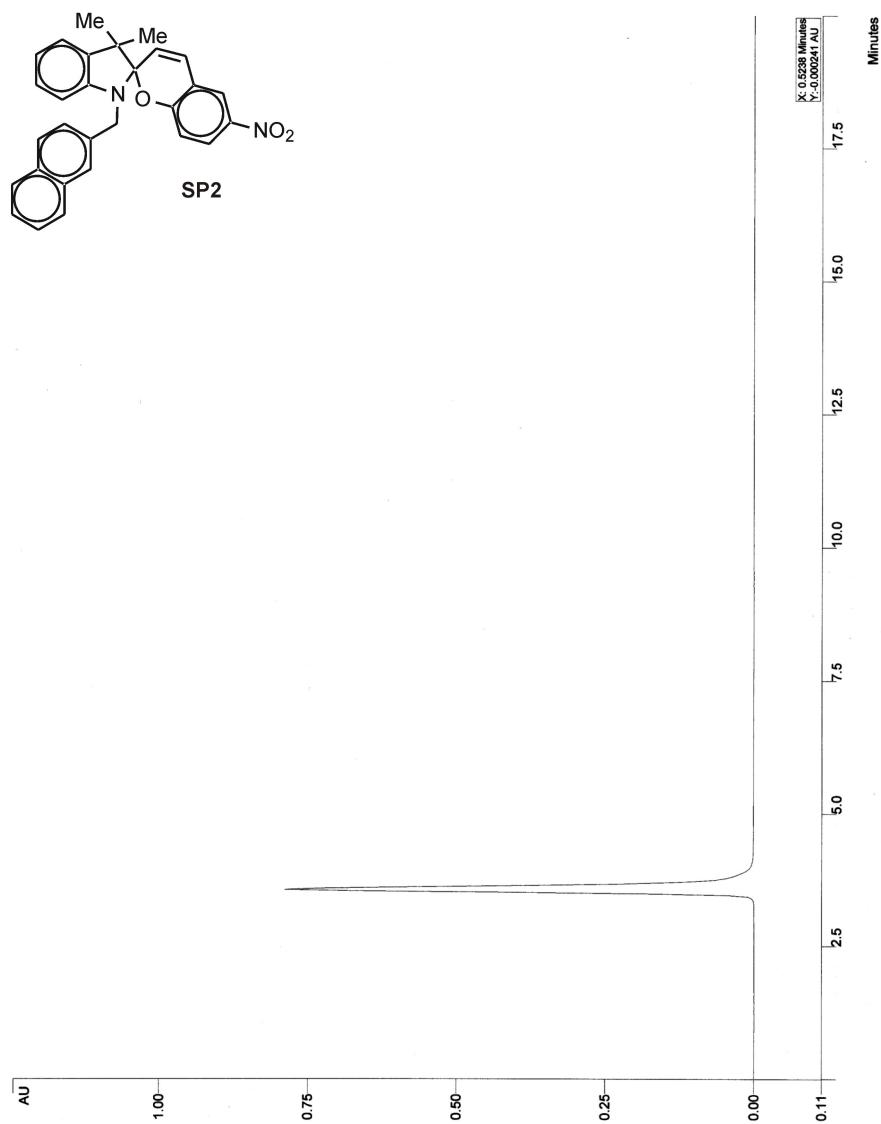
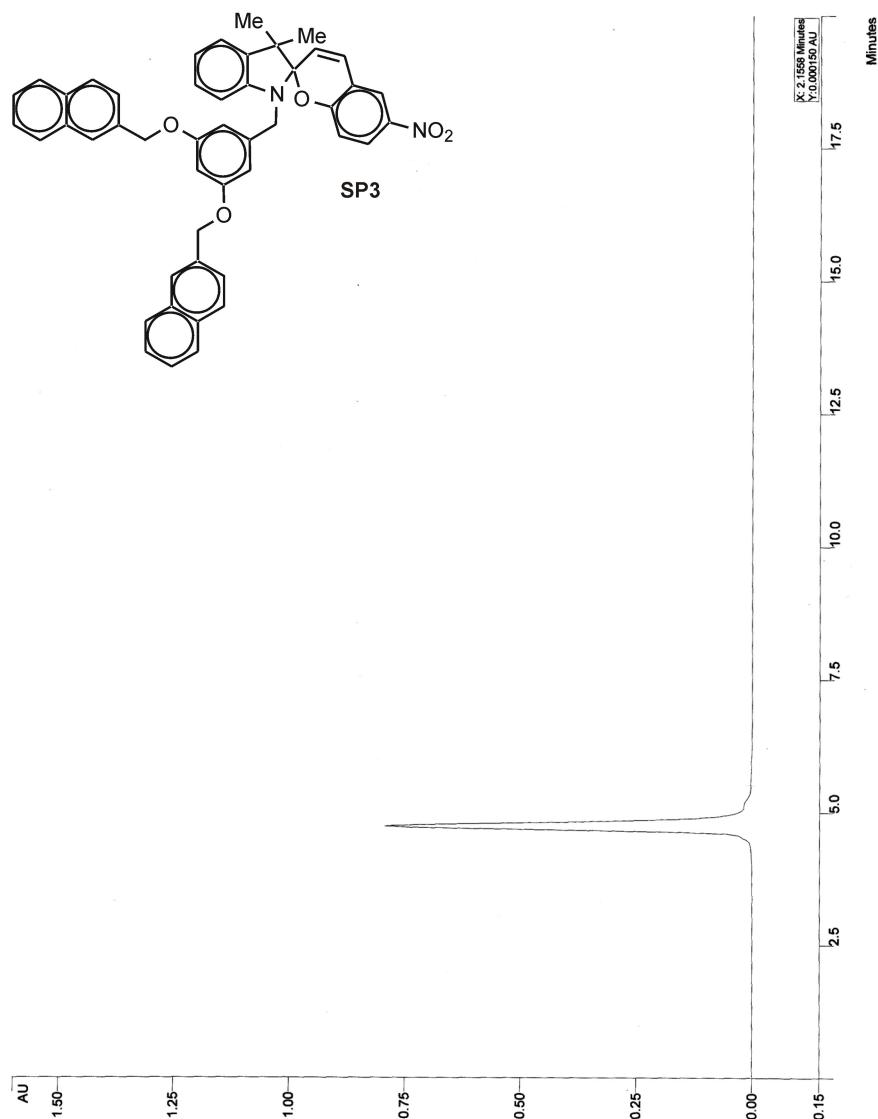
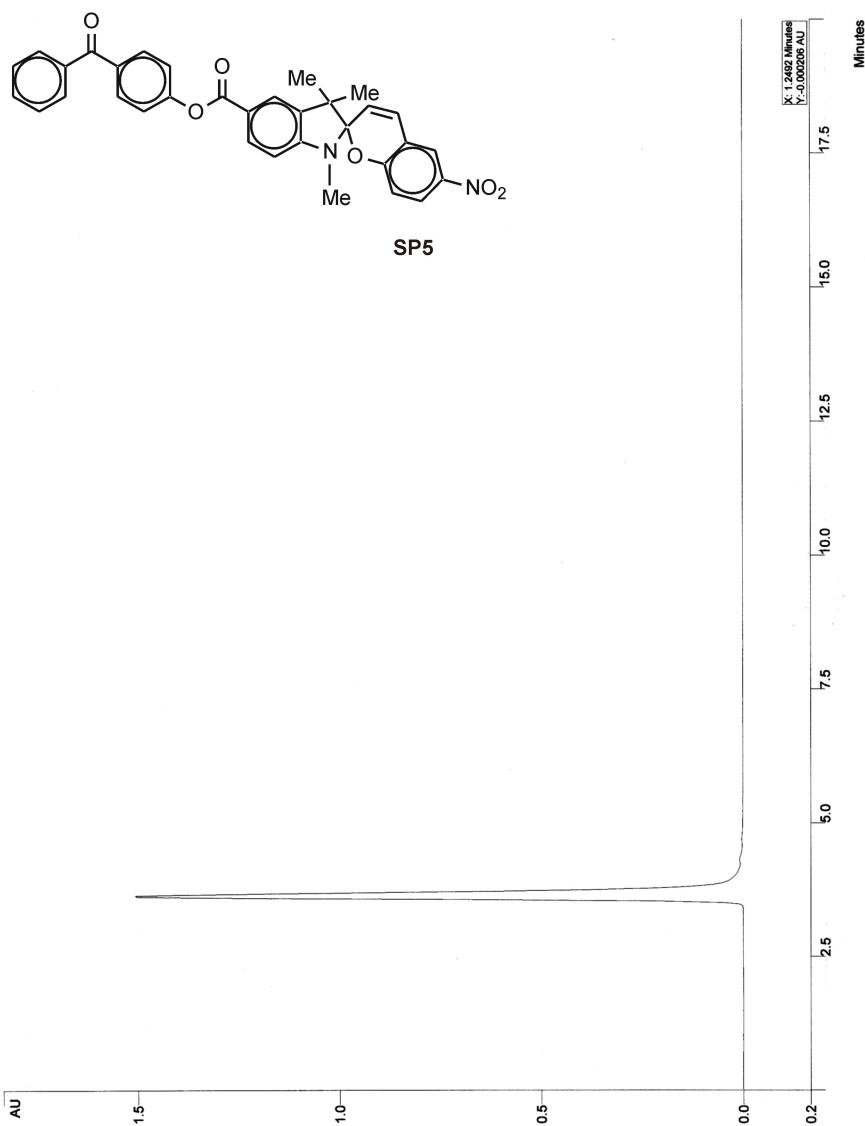


Figure S2. Synthesis of the model compounds **21** and **22**.

High-Performance Liquid Chromatograms of SP2

High-Performance Liquid Chromatograms of SP3

High-Performance Liquid Chromatograms of SP5

High-Performance Liquid Chromatograms of SP7