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Supplemental Material.

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The general synthesis of cholesterol squaraines was carried out according to Scheme 1.

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N-methyl-N-(carboxypropyl)aniline N-methyl-N-(carboxypropyl) aniline was prepared as previously¹ by alkylation of N-methylaniline with ethyl-4-bromobutyrate in the presence of sodium acetate and iodine, followed by hydrolysis of the ester product in 5% KOH.

1-Chloro-2-(p-dibutylanilino)cyclobutene-3,4-dione was prepared by Friedel-Crafts acylation of N,N dibutylaniline with 1,2 dichlorocyclobutene-3,4- dione in methylene chloride with AlCl₃ as a catalyst. The procedure described by Chen¹ et. al. was followed, except that the product was isolated by flash chromatography using chloroform as eluent.

1-(p-Dibutylanilino)-2-hydroxycyclobutene-3,4-dione was prepared following the procedure of Chen¹ by hydrolysis of the above chlorodione with a 18 % HCl solution. The product was isolated by gradient column chromatography changing the eluent from chloroform to chloroform: methanol (1:1) and finally to methanol.

(S)-N-methyl-N-(cholesteryl-4-butanoate)aniline The (S) ester was prepared according to a literature procedure²: 0.5 g N-methyl-N-(carboxypropyl) aniline (2.59 mmol) in 15 ml CH₂Cl₂ was placed in a round bottom flask and the resulting solution stirred. 0.158 g (1.295 mmol) dimethylaminopyridine and 1 g (2.59 mmol) cholesterol were added. After the mixture was cooled to 0 °C, 0.587 g (2.85 mmol) dicyclohexylcarbodiimide was added. The mixture was stirred for five minutes at 0 °C and then overnight at 20 °C. The

mixture was filtered. The solvent in the filtrate was evaporated. The ester product was isolated by column chromatography using methylene chloride as eluent. Yield: 0.5 g, 15 %. 1 H(NMR) δ (ppm): 7.26 (m, 2H), 6.72 (m, 3H), 5.41 (m, 1H), 4.64 (broad m, 1H), 3.40 (t, 2H), 2.96 (s, 3H), 2.35- 0.68 (m, 43H).

(S)-para-(N-methyl-N-(cholesteryl-4-butanoate)amino) phenyl (N,N-di-butyl-amino)phenylsquaraine (1). The squaraine was prepared according to a literature procedure³. 0.45 g cholesteryl ester dissolved in 10 ml isopropanol and 0.12g (0.4 mmol) squaric acid derivative. The mixture was refluxed for five hours in the presence of 0.52 g (2.25 mmol, 0.6 ml) tributyl orthoformate under an inert atmosphere (N_2). The mixture was cooled and filtered. The dark blue precipitate was washed with an excess of cold isopropanol and dried in a vacuum desiccator overnight. The product was purified by column chromatography, using (CHCl₃: acetone= 60: 1). Yield: 15%. ¹H NMR (CDCl₃) δ (ppm): 8.40 (dd, 4H), 6.78 (dd, 4H), 5.45 (m,1H), 4.65 (m, 1H), 3.58 (t, 2H), 3.46 (t, 2H), 3.17 (s, 3H), 2.38- 0.7 (m, 59H). UV- VIS: λ_{max} (CHCl₃): 634 nm. Melting point: (decomp., 180°C).

References

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- 3. Law, K. Y.; Bailey, F. C. Can. J. Chem. 1993, 71, 494.