Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information 1

A Facile and Versatile Preparation of Bilindiones and Biladienones from Tetraarylporphyrins

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Coupled Oxidation of *meso*-Tetraphenylporphyrin

A solution of [FeCl (TPP)] (100 mg) in pyridine (6 mL) was added to oxygen-saturated chloroform (50 mL) immediately followed by the addition of solid *L*- (+)-ascorbic acid (500 mg). After stirring at room temperature for 30 min, the solution was filtered. The brown filtrate was washed with water, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting brown residue was dissolved in pyridine (2.5 mL) and was cooled in an ice bath. Then a solution of $NaBF_4$ (1.22M aq., 25 mL) was added. After stirring for 1h, the dark green precipitate was collected by filtration and washed with water. This product was dissolved in acetone (50 mL) and then 1M HCl (10 mL) was added and the resulting solution was stirred for 1h at room temperature in the dark. The mixture was poured into ice water (150 mL) and extracted with CH_2Cl_2 (100 mL × 3). The combined organic extracts were washed with water (100 mL × 3) and dried over Na_2SO_4. Evaporation of the solvent and separation by column chromatography (SiO_2, CH_2Cl_2/acetone = 19/1) afforded a purple solid of **1** (64.7 mg, 70 %) and a red solid of **2** (13.9 mg, 15 %).

Biladienone (1). ^{1}H NMR ($CDCl_3$) δ 6.11 (m, 3H), 6.14 (d, 1H, J = 5 Hz), 6.28 (s, 1H), 6.44 (d, 1H, J = 4 Hz), 6.72 (d, 1H, J = 5 Hz), 6.78 (dd, 1H, J = 6.5, J = 2.5 Hz), 6.83 (d, 1H, J = 5.5 Hz), 7.29-7.47 (m, 18H), 7.81 (d, 2H, J = 9 Hz), 9.87 (br s, 1H), 10.75 (br s, 1H), 12.46 (br s, 1H); UV-vis ($CHCl_3$) λ_{max} 348, 562 nm; MS (FAB) *m/z*, 664 ($[M]^+$), 647 ($[M\text{-}OH]^+$)

Biladienone (2). ^{1}H NMR (CD_2Cl_2) δ 6.07 (dd, 1H J = 3.5, J = 2.8 Hz), 6.24 (dd, 1H J = 5.7, J = 1.8 Hz), 6.32 (d, 1H J = 4.3 Hz), 6.40 (d, 1H J = 4 Hz), 6.50 (d, 1H J = 4.3 Hz), 6.68 (d, 1H, J = 4.3 Hz), 6.80 (dd, 1H J = 4.0, J = 2.8 Hz), 7.20 (s, 1H) 7.34-7.57 (m, 18H), 7.74 (dd, 1H, J = 5.7, J = 1.8 Hz), 9.78 (s, 1H), 10.86 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 76 (sp^3), 111-145 (sp^2), 171, 185 (carbonyl); UV-vis ($CHCl_3$) λ_{max} 315, 358, 532 nm; MS (FAB) *m/z*, 665 ($[M+H]^+$), 647 ($[M\text{-}OH]^+$). HRMS (FAB) ($[M]^+$) *m/z*, Calcd for $C_{44}H_{33}N_4O_3$ 665.2553, found 665.2547.

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Coupled Oxidation of TPP at High Temperature.

The reaction was carried out under the condition of refluxing in chloroform for 1.5 hr. Except for the reaction temperature and reaction time, the procedure was the same as the reaction at room temperature.

Bilindione (3). Yield 23 %. ^{1}H NMR (CD_2Cl_2) δ(ppm) 6.21 (d, 2H, J = 5.5 Hz) 6.51 (d, 2H J = 4.4 Hz) 6.75 (d, 2H, J = 4.4 Hz) 7.00 (d, 2H, J = 5.5 Hz) 7.38 (m, 10H) 7.53 (m, 5H) 8.14 (br s, 2H) 12.0 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 114-139(sp^2), 167 (carbonyl); UV-vis ($CHCl_3$) λ_{max} 334, 400, 616 nm; HRMS (FAB) ($[M]^+$) *m/z*, calcd for $C_{37}H_{26}N_4O_2$ 558.2056, found 558.2053.

Bilindione (4). Yield 23 %. ^{1}H NMR (CD_2Cl_2) δ 6.09 (dd, 1H, J = 5.8 Hz, J = 1.5 Hz), 6.25 (dd, 1H, J = 5.8 Hz, J = 1.5 Hz), 6.30 (d, J = 4.3 Hz), 6.43 (d, 1H, J = 4.3 Hz) 6.61 (d, 1H, J = 4.3 Hz), 6.74 (d, 1H, J = 4.3 Hz), 7.00 (dd, 1H, J = 5.5 Hz, J = 1.2 Hz), 7.1 (br s, 1H), 7.3-7.5 (m, 15H), 7.58 (dd, 1H, J = 8.3, J = 1.6 Hz), 9.11 (s, 1H), 12.35 (br s, 1H); UV-vis ($CHCl_3$) λ_{max} 332, 400, 612 nm; MS (FAB) *m/z*, ($[M]^+$) 558. HRMS (FAB) ($[M]^+$) *m/z*, Calcd for $C_{37}H_{26}N_4O_2$ 558.2055, found 558.2070.

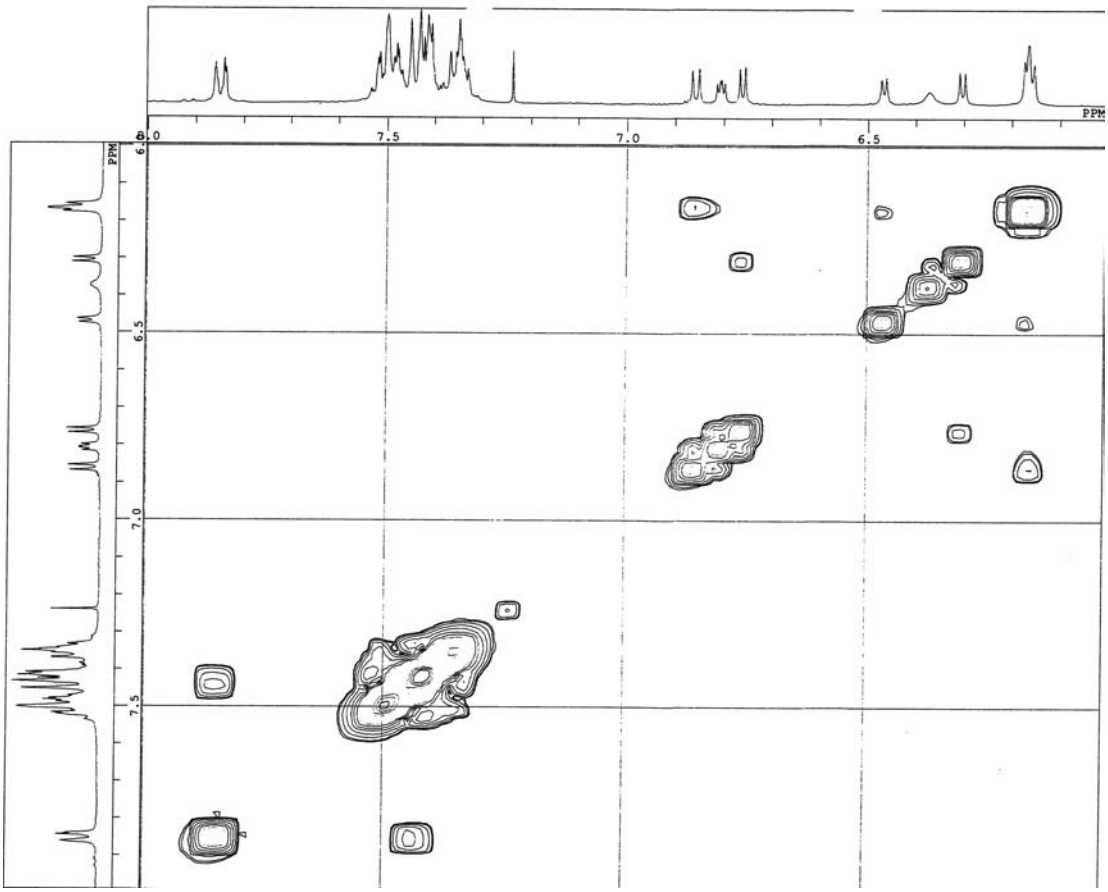

Figure S1. ^{1}H-^{1}H COSY of **1** ($CDCl_3$)

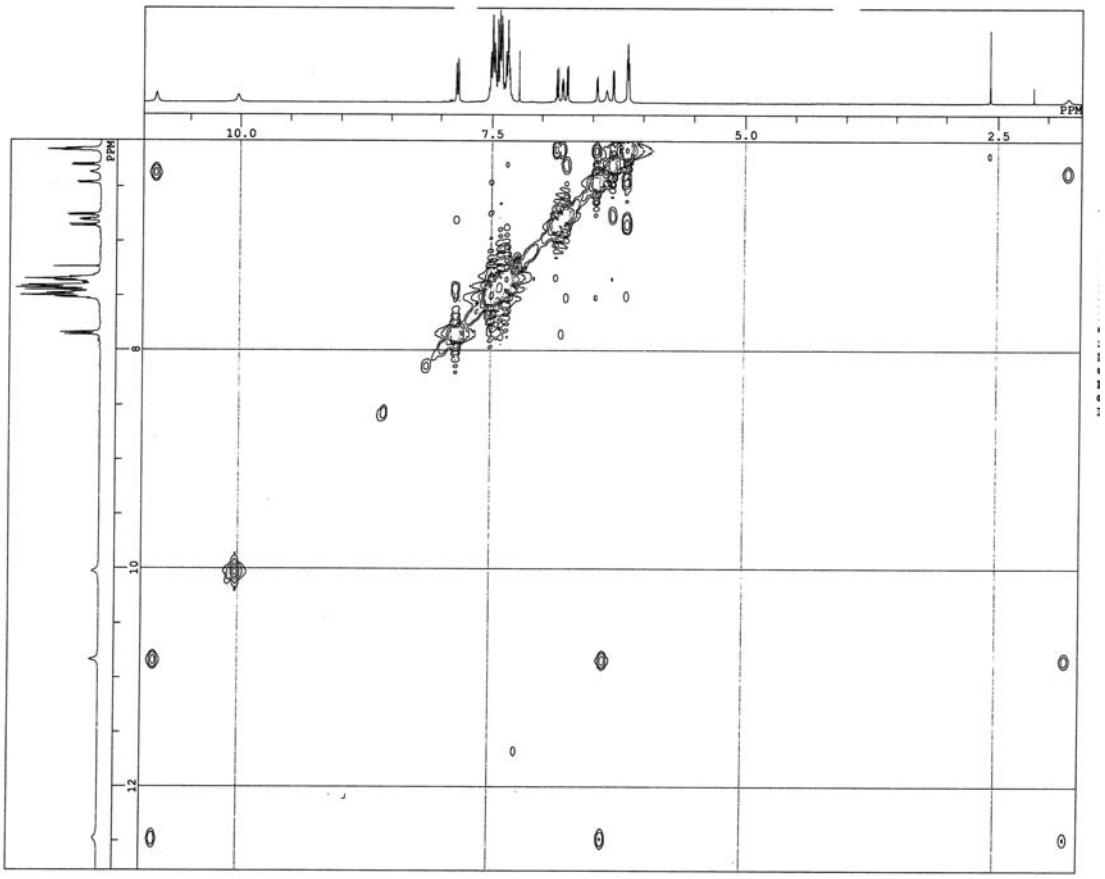

Figure S2. NOESY of **1** ($CDCl_3$)

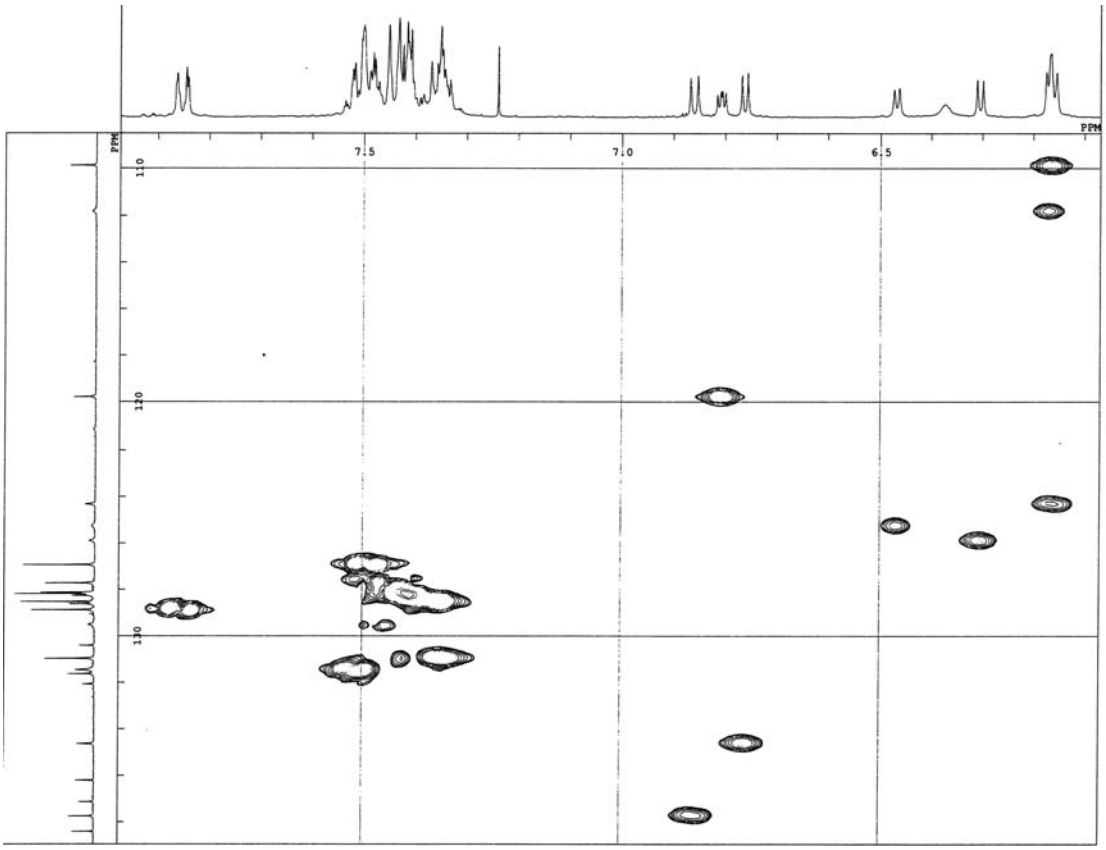

Figure S3. HMQC of **1** ($CDCl_3$)

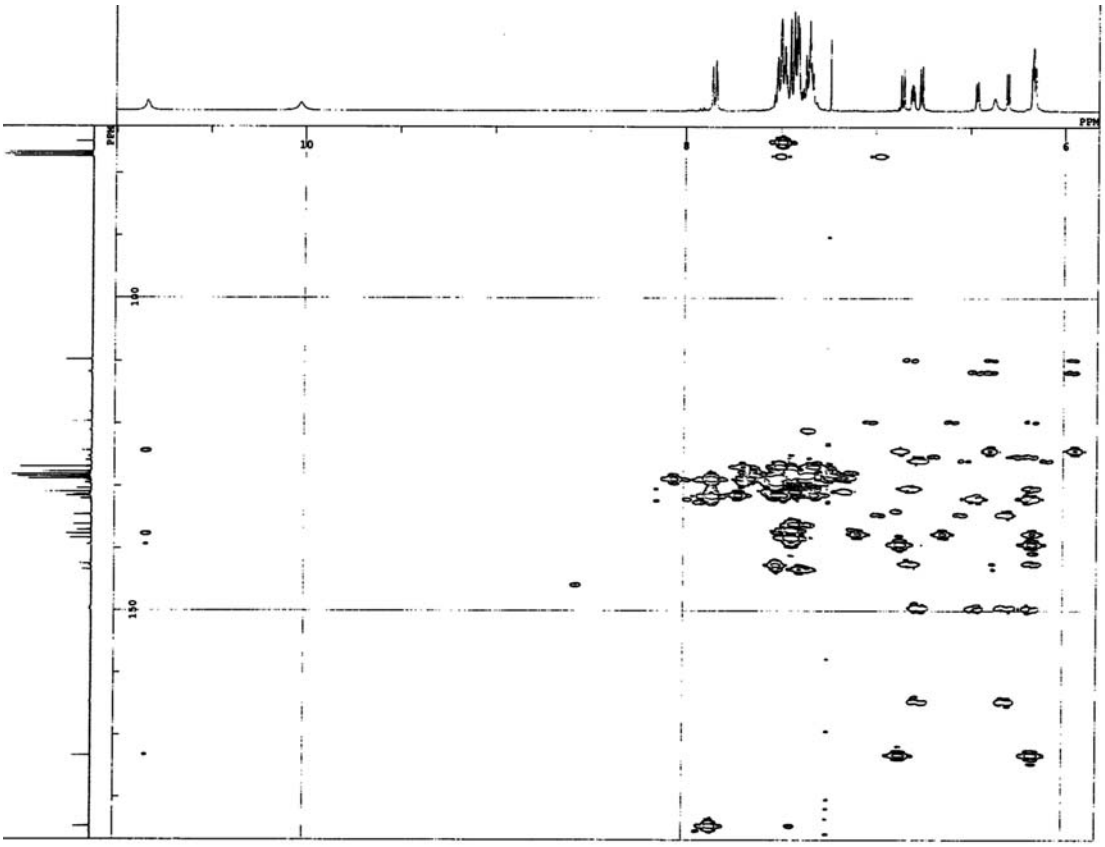

Figure S4. HMBC of **1** ($CDCl_3$)