

Supporting Information

Modulation of intramolecular heterodimer-induced fluorescence quenching of tricarboyanine dye for the development of fluorescent sensor

Tomoya Hirano,^{*a} Jun Akiyama,^b Shuichi Mori^b and Hiroyuki Kagechika^{*a,b}

^a*Institutes of Biomaterials and Bioengineering, Tokyo Medical and Dental University, 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan. Fax: +81-3-5280-8127; Tel: +81-3-5280-8128; E-mail: hiraomc@tmd.ac.jp, kage.omc@tmd.ac.jp; Tel: +81-5280-8127; Fax: +81-3-5280-8127*

^b*Graduate School of Biomedical Sciences, Tokyo Medical and Dental University, 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan.*

Materials and Reagents

All reagents were purchased from Sigma-Aldrich Chemical Co., Tokyo Kasei Kogyo Co, Wako Pure Chemical Industries, and Kanto Kagaku Co., Inc. Silica gel for column chromatography was purchased from Kanto Kagaku Co., Inc.. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance 500 spectrometer. Mass spectral data was obtained on Bruker Daltonics microTOF-2focus in the positive and negative ion detection modes. Melting points were taken on a Yanagimoto micro melting point apparatus and are uncorrected. Elemental analyses were carried out by Yanaco MT-6 CHN CORDER spectrometer.

Preparation of 1a: Compound **1a** was prepared from **8** (19 mg, 18 μ mol) and **9a** (5.4 mg, 25 μ mol) according to the procedure described for **1e** in 72% (13 mg, 13 μ mol) as a green powder. ¹H NMR (500 MHz, CDCl₃) δ 8.19 (1 H, br s), 8.02 (1 H, br s), 7.99 (2 H, d, J = 7.8 Hz), 7.92 (2 H, d, J = 14.2 Hz), 7.38-7.29 (9 H, m), 7.18 (2 H, dd, J = 7.6, 7.4 Hz), 7.02 (2 H, d, J = 7.9 Hz), 6.90 (2 H, d, J = 8.6 Hz), 5.92 (2 H, d, J = 14.2 Hz), 3.92 (4 H, t, J = 7.3 Hz), 3.69 (2 H, t, J = 5.6 Hz), 3.64-3.55 (8 H, m), 3.37 (2 H, m), 2.90 (2 H, t, J = 7.7 Hz), 2.65 (4 H, t, J = 6.0 Hz), 2.57 (2 H, t, J = 7.7 Hz), 2.02 (2 H, quintet, J = 6.0 Hz), 1.83 (4 H, sextet, J = 7.4 Hz), 1.31 (12 H, s), 1.02 (6 H, t, J = 7.4 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 173.1, 172.4, 167.6, 165.2, 158.1, 142.6, 142.1, 141.0, 136.4, 134.6, 130.9, 130.6, 128.5, 128.2, 127.6, 125.2, 122.5, 121.8, 114.3, 110.3, 99.3, 70.3, 70.2, 69.9, 69.8, 49.2, 45.8, 39.8, 39.1, 38.2, 31.1, 27.9, 24.3, 21.1, 20.7, 11.6; HRMS (ESI⁺) Calcd for C₅₈H₇₁N₄O₅ (M-I): 903.5419; Found: 903.5397.

Preparation of 1b: Compound **1b** was prepared from **8** (31 mg, 30 μ mol) and **9b** (11 mg, 42 μ mol) according to the procedure described for **1e** in 59% (19 mg, 18 μ mol) as a green powder. ^1H NMR (500 MHz, CDCl_3) δ 8.61 (1 H, s), 8.35 (1 H, br s), 8.25 (1 H, br s), 8.09 (1 H, dd, J = 8.6, 1.7 Hz), 7.97 (1 H, dd, J = 7.5, 1.5 Hz), 7.91 (2 H, d, J = 14.2 Hz), 7.82 (1 H, d, J = 8.6 Hz), 7.78 (1 H, dd, J = 7.1, 1.5 Hz), 7.46 (1 H, ddd, J = 7.1, 6.9, 1.5 Hz), 7.43 (1 H, ddd, J = 7.5, 6.9, 1.5 Hz), 7.31-7.27 (6 H, m), 7.16 (2 H, dd, J = 7.5, 7.5 Hz), 7.00 (2 H, d, J = 7.9 Hz), 6.89 (2 H, d, J = 8.7 Hz), 6.39 (2 H, d, J = 14.2 Hz), 3.90 (4 H, t, J = 7.4 Hz), 3.74-3.55 (10 H, m), 3.39 (2 H, m), 2.90 (2 H, t, J = 8.0 Hz), 2.62 (4 H, t, J = 6.0 Hz), 2.55 (2 H, t, J = 8.0 Hz), 2.01 (2 H, quintet, J = 6.0 Hz), 1.82 (4 H, sextet, J = 7.4 Hz), 1.29 (12 H, s), 1.00 (6 H, t, J = 7.4 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 173.1, 172.3, 167.6, 165.1, 158.1, 142.5, 142.0, 141.0, 136.2, 134.6, 132.7, 131.7, 130.5, 129.4, 128.5, 128.2, 127.9, 127.5, 127.0, 126.1, 125.2, 124.4, 122.4, 121.8, 114.2, 110.3, 99.3, 70.2, 70.2, 69.9, 69.8, 49.1, 45.7, 39.9, 39.1, 38.2, 31.0, 27.8, 24.2, 21.1, 20.7, 11.5; HRMS (ESI^+) Calcd for $\text{C}_{62}\text{H}_{73}\text{N}_4\text{O}_5$ (M-I^-): 953.5575; Found: 953.5579.

Preparation of 1c: Compound **1c** was prepared from **8** (18 mg, 18 μ mol) and **9c** (7.7 mg, 26 μ mol) according to the procedure described for **1e** in 72% (14 mg, 13 μ mol) as a green powder. ^1H NMR (500 MHz, CDCl_3) δ 8.27 (1 H, br s), 8.21 (1 H, br s), 8.11 (2 H, d, J = 8.4 Hz), 7.92 (2 H, d, J = 14.2 Hz), 7.61 (2 H, d, J = 8.4 Hz), 7.59 (2 H, d, J = 7.8 Hz), 7.41 (2 H, dd, J = 7.8, 7.4 Hz), 7.34-7.29 (7 H, m), 7.18 (2 H, dd, J = 7.6, 7.4 Hz), 7.01 (2 H, d, J = 7.9 Hz), 6.90 (2 H, d, J = 8.6 Hz), 5.91 (2 H, d, J = 14.2 Hz), 3.91 (4 H, t, J = 7.4 Hz), 3.72 (2 H, t, J = 5.4 Hz), 3.67-3.57 (8 H, m), 3.39 (2 H, q, J = 5.6 Hz), 2.92 (2 H, t, J = 7.6 Hz), 2.63 (4 H, t, J = 6.1 Hz), 2.59 (2 H, t, J = 7.6 Hz), 2.00 (2 H, quintet, J = 6.1 Hz), 1.83 (4 H, sextet, J = 7.4 Hz), 1.30 (12 H, s), 1.02 (6 H, t, J = 7.4 Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 173.1, 172.4, 167.3, 165.2, 158.1, 143.4, 142.6, 142.0, 141.0, 140.5, 136.3, 133.4, 130.5, 128.7, 128.5, 128.2, 127.5, 127.2, 126.9, 125.2, 122.5, 121.8, 114.3, 110.2, 99.3, 70.3, 70.2, 69.9, 69.8, 49.2, 45.8, 39.8, 39.2, 38.2, 31.1, 27.8, 24.2, 21.1, 20.7, 11.6; HRMS (ESI^+) Calcd for $\text{C}_{64}\text{H}_{75}\text{N}_4\text{O}_5$ (M-I^-): 979.5732; Found: 979.5711.

Preparation of 1d: Compound **1d** was prepared from **8** (17 mg, 16 μ mol) and **9d** (8.7 mg, 28 μ mol) according to the procedure described for **1e** in 48% (8.8 mg, 7.8 μ mol) as a green powder. ^1H NMR (500 MHz, CDCl_3) δ 8.31 (2 H, br s), 8.05 (2 H, d, J = 8.8 Hz), 7.93 (2 H, d, J = 14.2 Hz), 7.33-7.30 (8 H, m), 7.18 (2 H, dd, J = 7.5, 7.3 Hz), 7.10 (1 H, t, J = 7.4 Hz), 7.02-6.98 (4 H, m), 6.98 (2 H, d, J = 8.8 Hz), 6.90 (2 H, d, J = 8.6 Hz), 5.91 (2 H, d, J = 14.2 Hz), 3.91 (4 H, t, J = 7.4 Hz), 3.71-3.54 (10 H, m), 3.37 (2 H, q, J = 5.5 Hz), 2.90 (2 H, t, J = 7.8 Hz), 2.64 (4 H, t, J = 6.1 Hz), 2.57 (2 H, t, J = 7.8 Hz), 2.01 (2 H, quintet, J = 6.1 Hz), 1.84 (4 H, sextet, J = 7.4 Hz), 1.31 (12 H, s), 1.02 (6 H, t, J = 7.4 Hz); ^{13}C NMR

(125 MHz, CDCl₃) δ 173.1, 172.4, 167.0, 165.3, 159.7, 158.1, 156.4, 142.7, 142.0, 141.0, 130.6, 129.8, 129.7, 128.5, 125.2, 123.7, 122.5, 121.8, 119.5, 117.7, 114.2, 110.2, 99.3, 70.2, 69.9, 69.7, 69.2, 49.2, 45.8, 39.8, 39.2, 38.7, 38.2, 31.1, 27.9, 24.2, 20.7, 11.6; HRMS (ESI⁺) Calcd for C₆₄H₇₅N₄O₆ (M-I): 995.5681; Found: 995.5653.

Preparation of 11a: Compound **11a** was prepared from **10a** (0.49 g, 2.0 mmol) and 3-(*p*-hydroxyphenyl)propionic acid (**3**, 0.26 g, 2.2 mmol) according to the procedure described for **5** in 66% (0.52 g, 1.3 mmol) as a white powder. ¹H NMR (500 Hz, CDCl₃) δ 7.07 (1 H, s), 7.04 (2 H, d, *J* = 8.3 Hz), 6.79 (2 H, d, *J* = 8.3 Hz), 5.24 (1 H, br s), 4.62 (1 H, br s), 3.17-3.10 (4 H, m), 2.88 (2 H, t, *J* = 6.9 Hz), 2.44 (2 H, t, *J* = 6.9 Hz), 1.50-1.06 (12 H, m), 1.46 (9 H, s); HRMS (ESI⁺) Calcd for C₂₂H₃₆N₂NaO₄ (M+Na⁺): 415.2567; Found: 415.2568.

Preparation of 12a: Compound **12a** was prepared from **11a** (0.13 g, 0.33 mmol) and **6** (0.20 g, 0.30 mmol) according to the procedure described for **7** in 43% (0.13 g, 0.13 mmol) as a green solid. ¹H NMR (500 MHz, CDCl₃) δ 7.94 (2 H, d, *J* = 14.2 Hz), 7.87 (1 H, br s), 7.36-7.30 (6 H, m), 7.18 (2 H, dd, *J* = 7.5, 7.2 Hz), 7.03 (2 H, d, *J* = 7.9 Hz), 6.91 (2 H, d, *J* = 8.7 Hz), 5.95 (2 H, d, *J* = 14.2 Hz), 4.54 (1 H, br s), 3.95 (4 H, t, *J* = 7.4 Hz), 3.13 (2 H, m), 3.07 (2 H, m), 2.92 (2 H, t, *J* = 8.0 Hz), 2.67 (4 H, t, *J* = 6.0 Hz), 2.59 (2 H, t, *J* = 8.0 Hz), 2.04 (2 H, quintet, *J* = 6.0 Hz), 1.85 (4H, sextet, *J* = 7.4 Hz), 1.50-1.43 (4 H, m), 1.43 (9 H, s), 1.32 (12 H, s), 1.24 (8 H, m), 1.02 (6 H, t, *J* = 7.4 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 172.8, 172.3, 165.2, 158.1, 156.0, 142.6, 142.1, 141.1, 136.5, 130.6, 128.5, 125.2, 122.5, 122.0, 114.1, 110.2, 99.4, 49.2, 45.8, 39.5, 38.3, 31.2, 29.9, 29.4, 29.2, 29.2, 28.4, 27.9, 27.0, 26.8, 24.3, 21.1, 20.7, 11.6; HRMS (ESI⁺) Calcd for C₅₈H₇₉N₄O₄ (M-I): 895.6095; Found: 895.6089.

Preparation of 13a: Compound **13a** was prepared from **12a** (12 mg, 12 μ mol) according to the procedure described for **8** in quant. (13 mg, 12 μ mol) as a green solid. ¹H NMR (500 MHz, CD₃CD) δ 7.98 (2 H, d, *J* = 14.2 Hz), 7.37 (2 H, d, *J* = 7.4 Hz), 7.36 (2 H, dd, *J* = 7.8, 7.5 Hz), 7.24 (2 H, d, *J* = 7.8 Hz), 7.24 (2 H, d, *J* = 8.7 Hz), 7.20 (2 H, dd, *J* = 7.5, 7.4 Hz), 7.02 (2 H, d, *J* = 8.7 Hz), 6.14 (2 H, d, *J* = 14.2 Hz), 4.06 (4 H, t, *J* = 7.4 Hz), 3.08 (2 H, t, *J* = 7.2 Hz), 2.89 (2 H, t, *J* = 7.6 Hz), 2.83 (2 H, t, *J* = 7.9 Hz), 2.72 (4 H, t, *J* = 6.0 Hz), 2.39 (2 H, t, *J* = 7.9 Hz), 2.03 (2 H, quintet, *J* = 6.0 Hz), 1.83 (4 H, sextet, *J* = 7.4 Hz), 1.64-1.29 (12 H, m), 1.33 (12 H, s), 1.01 (6 H, t, *J* = 7.4 Hz).

Preparation of 2a: Compound **2a** was prepared from **13a** (14 mg, 14 μ mol) and **9e** (9.6 mg, 26 μ mol) according to the procedure described for **1e** in 77% (12 mg, 11 μ mol) as a green powder. ¹H NMR (500

MHz, CDCl₃) δ 8.01 (2 H, d, J = 8.5 Hz), 7.94 (1 H, br s), 7.91 (2 H, d, J = 14.2 Hz), 7.86 (2 H, d, J = 9.1 Hz), 7.82 (2 H, d, J = 8.5 Hz), 7.32-7.27 (6 H, m), 7.25 (1 H, br s), 7.17 (2 H, dd, J = 7.5, 7.4 Hz), 7.01 (2 H, d, J = 7.9 Hz), 6.89 (2 H, d, J = 8.6 Hz), 6.73 (2 H, d, J = 9.1 Hz), 5.91 (2 H, d, J = 14.2 Hz), 3.92 (4 H, t, J = 7.4 Hz), 3.41 (2 H, q, J = 6.8 Hz), 3.14 (2 H, q, J = 6.8 Hz), 2.91 (2 H, t, J = 7.6 Hz), 2.63 (4 H, t, J = 5.9 Hz), 2.58 (2 H, t, J = 7.6 Hz), 2.00 (2 H, quintet, J = 5.9 Hz), 1.81 (4 H, sextet, J = 7.4 Hz), 1.62-1.27 (12 H, m), 1.29 (12 H, s), 1.00 (6 H, t, J = 7.4 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 172.8, 172.3, 166.9, 165.1, 158.1, 154.7, 152.7, 143.7, 142.5, 142.1, 141.0, 136.3, 130.6, 128.5, 128.1, 125.3, 125.2, 122.4, 122.1, 121.9, 114.2, 111.5, 110.3, 99.4, 49.1, 45.8, 40.3, 40.1, 39.3, 38.2, 31.1, 29.1, 29.0, 28.7, 28.6, 27.9, 27.9, 26.5, 24.2, 21.0, 20.7, 11.6; HRMS (ESI⁺) Calcd for C₆₈H₈₄N₇O₃ (M-I): 1046.6630; Found: 1046.6626.

Preparation of 11b: Compound **11b** was prepared from **10b** (0.28 g, 0.82 mmol) and 3-(*p*-hydroxyphenyl)propionic acid (**3**, 0.21 g, 1.2 mmol) according to the procedure described for **5** in 57% (0.23 g, 0.47 mmol) as colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.03 (2 H, d, J = 8.4 Hz), 6.78 (2 H, d, J = 8.4 Hz), 6.59 (1 H, br s), 5.90 (1 H, br s), 5.21 (1 H, br s), 3.68-3.33 (18 H, m), 3.27 (2 H, m), 2.89 (2 H, t, J = 7.1 Hz), 2.43 (2 H, t, J = 7.1 Hz), 1.44 (9 H, s); HRMS (ESI⁺) Calcd for C₂₄H₄₀N₂NaO₈ (M+Na⁺): 507.2677; Found: 507.2668.

Preparation of 13b: Compound **12b** was prepared from **11b** (0.12 g, 0.25 mmol) and **6** (0.18 mg, 0.27 mmol) according to the procedure described for **7**, and used in the next step without further purification. Compound **13b** was prepared from crude **12b** in trifluoroacetic acid (3.5 ml) according to the procedure described for **8** in 18% (2 step, 51 mg, 45 μ mol) as green powder. ¹H NMR (500 MHz, CDCl₃) δ 8.30 (2 H, br s), 8.13 (1 H, br s), 7.93 (2 H, d, J = 14.2 Hz), 7.31 (2 H, dd, J = 7.9, 7.4 Hz), 7.29 (2 H, d, J = 7.4 Hz), 7.23 (2 H, d, J = 8.6 Hz), 7.18 (2 H, dd, J = 7.4, 7.4 Hz), 7.02 (2 H, d, J = 7.9 Hz), 6.92 (2 H, d, J = 8.6 Hz), 5.92 (2 H, d, J = 14.2 Hz), 3.91 (4 H, t, J = 7.4 Hz), 3.80-3.35 (16 H, m), 3.34 (2 H, m), 3.17 (2 H, m), 2.86 (2 H, t, J = 8.0 Hz), 2.64 (4 H, t, J = 5.8 Hz), 2.46 (2 H, t, J = 8.0 Hz), 2.02 (2 H, quintet, J = 5.8 Hz), 1.83 (4 H, sextet, J = 7.4 Hz), 1.31 (12H, s), 1.01 (6H, t, J = 7.4 Hz).

Preparation of 2b: Compound **2b** was prepared from **13b** (24 mg, 21 μ mol) and **9e** (13 mg, 36 μ mol) according to the procedure described for **1e** in 73% (20 mg, 15 μ mol) as a green powder. ¹H NMR (500 MHz, CDCl₃) δ 8.00 (2 H, d, J = 8.6 Hz), 7.90 (2 H, d, J = 14.2 Hz), 7.87 (2 H, d, J = 9.2 Hz), 7.83 (2 H, d, J = 8.6 Hz), 7.60 (2 H, br s), 7.31 (2 H, dd, J = 7.9, 7.4 Hz), 7.28-7.25 (4 H, m), 7.17 (2 H, dd, J = 7.4, 7.4 Hz), 7.03 (2 H, d, J = 7.9 Hz), 6.92 (2 H, d, J = 8.6 Hz), 6.75 (2 H, d, J = 9.2 Hz), 5.99 (2 H, d, J =

14.2 Hz), 3.98 (4 H, t, $J = 7.4$ Hz), 3.96-3.51 (18 H, m), 3.37 (2 H, m), 3.10 (6 H, s), 2.89 (2 H, t, $J = 8.0$ Hz), 2.67 (4 H, t, $J = 5.8$ Hz), 2.51 (2 H, t, $J = 8.0$ Hz), 2.02 (2 H, quintet, $J = 5.8$ Hz), 1.84 (4 H, sextet, $J = 7.4$ Hz), 1.31 (12 H, s), 1.02 (6 H, t, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 172.6, 172.1, 167.0, 164.8, 158.2, 154.8, 152.7, 143.6, 142.3, 142.1, 141.0, 135.9, 134.7, 130.3, 128.5, 128.2, 125.3, 125.1, 122.3, 122.1, 114.3, 111.4, 110.4, 99.6, 70.4, 70.4, 70.4, 70.4, 70.2, 70.1, 69.8, 69.7, 49.0, 45.8, 40.3, 39.8, 39.0, 38.1, 30.8, 27.8, 24.3, 21.1, 20.7, 11.6; HRMS (ESI^+) Calcd for $\text{C}_{70}\text{H}_{88}\text{N}_7\text{O}_7$ (M-I): 1138.6740; Found: 1138.6716.

Preparation of 12c: Compound **12c** was prepared from **11c** (0.11 g, 0.46 mmol) and **6** (0.20 g 0.30 mmol) according to the procedure described for **7** in 40% (0.10 g, 0.12 mmol) as a green powder. ^1H NMR (500 MHz, CDCl_3) δ 7.84 (2 H, d, $J = 14.2$ Hz), 7.28 (2 H, dd, $J = 7.9, 7.5$ Hz), 7.20 (2 H, d, $J = 7.1$ Hz), 7.15 (2 H, d, $J = 8.4$ Hz), 7.12 (2 H, dd, $J = 7.5, 7.1$ Hz), 7.05 (2 H, d, $J = 7.9$ Hz), 6.93 (2 H, d, $J = 8.4$ Hz), 5.99 (2 H, d, $J = 14.2$ Hz), 4.72 (1 H, br s), 3.99 (4 H, t, $J = 7.4$ Hz), 3.21 (2 H, m), 2.68 (2 H, t, $J = 7.3$ Hz), 2.65 (4 H, t, $J = 6.0$ Hz), 1.99 (2 H, quintet, $J = 6.0$ Hz), 1.62 (4 H, sextet, $J = 7.4$ Hz), 1.29 (9 H, s), 1.27 (12 H, s), 0.96 (6 H, t, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 176.5, 171.9, 164.1, 158.3, 155.7, 142.1, 141.9, 140.8, 133.1, 130.4, 128.5, 124.9, 122.0, 114.5, 99.8, 48.8, 45.8, 41.9, 35.1, 28.2, 27.7, 24.2, 21.0, 20.6, 11.4; HRMS (ESI^+) Calcd for $\text{C}_{49}\text{H}_{62}\text{N}_3\text{O}_3$ (M-I): 740.4786; Found: 740.4774.

Preparation of 13c: Compound **13c** was prepared from **12c** (43 mg, 49 μmol) according to the procedure described for **8** in 96% (36 mg, 47 μmol) as a green solid. ^1H NMR (500 MHz, CD_3CD) δ 7.97 (2 H, d, $J = 14.2$ Hz), 7.37 (2 H, dd, $J = 7.9, 7.5$ Hz), 7.36 (2 H, d, $J = 7.3$ Hz), 7.30 (2 H, t, $J = 8.7$ Hz), 7.25 (2 H, d, $J = 7.9$ Hz), 7.20 (2 H, dd, $J = 7.5, 7.3$ Hz), 7.10 (2 H, d, $J = 8.7$ Hz), 6.15 (2 H, d, $J = 14.2$ Hz), 4.07 (4 H, t, $J = 7.4$ Hz), 3.00 (2 H, t, $J = 7.3$ Hz), 2.85 (2 H, t, $J = 7.3$ Hz), 2.73 (4 H, t, $J = 6.0$ Hz), 2.03 (2 H, quintet, $J = 6.0$ Hz), 1.83 (4 H, sextet, 7.4 Hz), 1.34 (12 H, s), 1.01 (6 H, t, $J = 7.4$ Hz).

Preparation of 2c: Compound **2c** was prepared from **13c** (36 mg, 47 μmol) and **9e** (21 mg, 57 μmol) according to the procedure described for **1e** in 66% (25 mg, 28 μmol) as a green powder. ^1H NMR (500 MHz, CDCl_3) δ 8.39 (1 H, br s), 8.10 (2 H, d, $J = 8.6$ Hz), 7.86 (2 H, d, $J = 14.2$ Hz), 7.82 (2 H, d, $J = 9.2$ Hz), 7.69 (2 H, d, $J = 8.6$ Hz), 7.35 (2 H, d, $J = 8.6$ Hz), 7.25 (2 H, dd, $J = 7.9, 7.4$ Hz), 7.16 (2 H, d, $J = 7.4$ Hz), 7.09 (2 H, dd, $J = 7.4, 7.4$ Hz), 6.97 (2 H, d, $J = 7.9$ Hz), 6.90 (2 H, d, $J = 8.6$ Hz), 6.72 (2 H, d, $J = 9.2$ Hz), 5.90 (2 H, d, $J = 14.2$ Hz), 3.89 (4 H, t, $J = 7.4$ Hz), 3.67 (2 H, m), 3.06 (6 H, s), 3.02 (2

H, t, $J = 7.3$ Hz), 2.62 (4 H, t, $J = 6.0$ Hz), 1.99 (2 H, quintet, $J = 6.0$ Hz), 1.78 (4 H, sextet, $J = 7.4$ Hz), 1.22 (12 H, s), 0.97 (6 H, t, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 172.1, 166.8, 164.7, 158.2, 154.4, 152.6, 143.6, 142.3, 142.0, 140.9, 134.8, 134.2, 130.9, 128.5, 128.4, 125.1, 125.1, 122.3, 121.9, 121.9, 114.2, 111.4, 110.3, 99.5, 49.0, 45.8, 41.2, 40.2, 34.3, 27.8, 24.2, 21.1, 20.7, 11.5; HRMS (ESI^+) Calcd for $\text{C}_{59}\text{H}_{67}\text{N}_6\text{O}_2$ (M-I): 891.5320; Found: 891.5294.