

### Supporting Information for the manuscript:

**Title: “First Synthesis of Non-Symmetrical "Phthalimidoyl Active Ester" Bi-dentate Cross-Linking Reagents having Acid Chloride, 2-Benzothiazole, or 1-Benzotriazol Group”**

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#### **Experimental Section**

All the melting points were measured using micro melting point apparatus. The IR spectra were obtained on a HORIBA FT-710 spectrometer. The <sup>1</sup>H-NMR spectra were obtained on a JMN-A400 spectrometer (400 MHz) in CDCl<sub>3</sub> using TMS as an internal standard. <sup>13</sup>C-NMR spectra were obtained on a JMN-A400 spectrometer (100 MHz) in CDCl<sub>3</sub> using TMS as internal standard. Mass spectra were obtained on a JEOL-JMS-D300 mass spectrometer. The elemental analyses were performed by using a Yanaco CHN-corder MT-5. All the reactions were monitored by thin layer chromatography (TLC) using Merck, Kieselgel 60 F<sub>254</sub>. Column chromatography and Preparative thin layer chromatography (PLC) was performed on a Merck, Kieselgel 60 PF<sub>254</sub>. All the reagents were of highest quality and further purified by distillation or recrystallization. All the solvents were further purified by general method.

#### **1. General procedure for the synthesis of 3-(phthalimidoyloxycarbonyl)butyric acid chloride (1):**

Method (A): Glutaryl dichloride (1457.4 mg, 8.62 mmol) was added to a solution of *N*-hydroxyphthalimide (469.81 mg, 2.87 mmol) and pyridine (749.07 μl, 2.87 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7 ml) at rt under N<sub>2</sub> and stirred for 3 h. Hexane was added to the reaction mixture, than the precipitate was removed by glass funnel. The solution was concentrated by evaporation and purification by GTO and finally repeated re-crystallization from Hexane/AcOEt to yield acid chloride **1** as a white solid (373 mg, 44%); Method (B): *N*-hydroxyphthalimide (1000.0 mg, 6.13 mmol) and 4-DMAP (1123.9 mg, 9.19 mmol), were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (8 ml) and this solution was added to a solution of glutaric anhydride (1049.1 mg, 9.19 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 ml). The reaction mixture was stirred for 3 h under N<sub>2</sub> at 0 °C. Then, the reaction mixture was neutralized by 1N HCl solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with 1N HCl (4×) and then, H<sub>2</sub>O, and dried over anhydrous MgSO<sub>4</sub>, and concentrated under vacuum, to give **2** (87%) as a colorless solid. Thionyl chloride

(316.1  $\mu\text{l}$ , 4.33 mmol) was added to a solution of compound **2** (1000 mg, 3.60 mmol) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (13 ml) under  $\text{N}_2$ . The mixture was refluxed with stirring for 4 h. Then, the solvent was removed under vacuum. The residue was purified by repeated re-crystallization from Hexane-AcOEt to yield acid chloride **1** (979 mg, 92%); mp 88.5-90  $^\circ\text{C}$  (colorless solid from Hexane/AcOEt);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  2.13-2.21 (m, 2H), 2.80 (t,  $J = 7.9$  Hz, 2H), 3.13 (t,  $J = 7.2$  Hz, 2H), 7.79-7.83 (m, 2H), 7.88-7.92 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.9, 29.2, 45.2, 123.9, 124.0, 128.7, 134.7, 134.8, 161.7, 168.5, 173.1.  $\nu_{\text{max}}/\text{cm}^{-1}$  1805, 1791, 1741 (CO). Elemental analysis (%) calc. for  $\text{C}_{13}\text{H}_{10}\text{ClNO}_5$ : C, 52.81; H, 3.41; N, 4.74. Found: C, 53.02; H, 3.56; N, 4.78.

## 2. General procedure for the synthesis of *N*-oxyphthalimidyl carbonyl butyric acid (**2**):

*N*-hydroxyphthalimide (1000.0 mg, 6.13 mmol) and 4-DMAP (898.6 mg, 7.36 mmol), were dissolved in  $\text{CH}_2\text{Cl}_2$  (8 ml) and this solution was added to a solution of glutaric anhydride (768.70 mg, 6.74 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 ml). The reaction mixture was stirred about 4 hours under  $\text{N}_2$  at 0  $^\circ\text{C}$  temperature. Then the reaction mixture was neutralized by 1N HCl solution and extract with  $\text{CH}_2\text{Cl}_2$  and  $\text{H}_2\text{O}$ , washed with 1N HCl (4 $\times$ ), dried over anhydrous  $\text{MgSO}_4$ , and concentrated under vacuum, to give **2** (1477 mg, 87%) as a colorless solid; mp 119-120  $^\circ\text{C}$  (from  $\text{CH}_2\text{Cl}_2$ /Hexane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  2.09-2.16 (m, 2H), 2.58 (t,  $J = 7.2$  Hz, 2H), 2.80 (t,  $J = 7.2$  Hz, 2H), 7.77-7.82 (m, 2H), 7.87-7.91 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.6, 29.9, 32.3, 124.0, 124.0, 128.9, 134.8, 161.9, 168.9, 177.8.  $\nu_{\text{max}}/\text{cm}^{-1}$  3131(OH), 1787, 1741, 1704 (CO)  $\text{cm}^{-1}$ ; Elemental analysis (%) calc. for  $\text{C}_{13}\text{H}_{11}\text{NO}_6$ : C, 56.32; H, 4.00; N, 5.05. Found: C, 55.89; H, 4.02; N, 4.96.

## 3. General procedure for the synthesis of

### 4-(2-benzothiazolyloxycarbonyl)butyric-*N*-hydroxyphthalimide ester (**4**):

2-hydroxybenzothiazole (25 mg, 0.17 mmol) and DABCO (37.9 mg, 0.33 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (1 ml). This solution was added dropwisely to a solution of **1** (50 mg, 0.17 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 ml) at 0  $^\circ\text{C}$  under  $\text{N}_2$  and stirred for 1h. Then, the reaction mixture was neutralized by dil. AcOH solution and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with water, dried over anhydrous  $\text{MgSO}_4$ , and condensed under vacuum. The residue was purified with silica gel column chromatography (Hexane/AcOEt = 1:1) to yield **4** (31.9 mg, 46%); mp 150.3-150.6  $^\circ\text{C}$  (colorless solid from  $\text{CH}_2\text{Cl}_2$ /Hexane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  2.23-2.30 (m, 2H), 2.86 (t,  $J = 7.4$  Hz, 2H), 3.32 (t,  $J = 7.0$  Hz, 2H), 7.25-7.28 (m, 1H), 7.32-7.39 (m, 2H), 7.78-7.81 (m,

2H), 7.80-7.90 (m, 2H), 8.33 (d,  $J = 8.4$ , 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.3, 29.9, 37.5, 117.8, 121.8, 121.9, 123.9, 125.5, 127.0, 128.8, 134.7, 161.8, 169.0, 172.9.  $\nu_{\text{max}}/\text{cm}^{-1}$  1787, 1739, 1714 (CO); Elemental analysis (%) calc. for  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_6\text{S}$ : C, 58.53; H, 3.44; N, 6.83; Found: C, 57.94; H, 3.52; N, 6.81.

#### 4. General procedure for the synthesis of

##### 4-(1-Benzotriazoleoxa)butyric-*N*-hydroxyphthalimide ester (5):

Compound **2** (1000mg, 3.82 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (8 ml) and this solution was added to a solution of benzotriazole (456.4 mg, 3.82 mmol) and  $N,N'$ -diisopropylcarbodiimide (948.1 mg, 4.59 mmol) in  $\text{CH}_2\text{Cl}_2$  (17 ml). The solution was stirred for 1 h under  $\text{N}_2$  at 0 °C. After condensation and filtration of precipitate, purification was made by silica gel column chromatography (Hexane/AcOEt = 1:1) to yield **5** (1215 mg, 84%); mp 155.8-156.7 °C (colorless solid from  $\text{CH}_2\text{Cl}_2$ /Hexane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  2.37-2.44 (m, 2H), 2.95 (t,  $J = 7.2$  Hz, 2H), 3.65 (t,  $J = 7.2$  Hz, 2H), 7.50-7.54 (m, 1H), 7.65-7.69 (m, 2H), 7.78-7.82 (m, 2H), 7.87-7.90 (m, 2H), 8.12-8.15 (m, 1H), 8.29-8.31(m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.2, 30.0, 34.1, 114.4, 120.2, 124.0, 126.2, 128.9, 130.5, 134.8, 146.2, 161.8, 168.9, 171.3.  $\nu_{\text{max}}/\text{cm}^{-1}$  1812, 1785, 1752 (CO); Elemental analysis (%) calc. for  $\text{C}_{19}\text{H}_{14}\text{N}_4\text{O}_5$ : C, 60.32; H, 3.73; N, 14.81. Found: C, 60.46; H, 3.73; N, 14.85.

##### 5. Preparation of *N*-(3-phenylpropionyloxy)phthalimide (6):

DCC (1786.8 mg, 8.66 mmol) was added to a solution of hydrocinnamic acid (500.0 mg, 6.66 mmol) and *N*-hydroxyphthalimide (1412.2 mg, 8.66 mmol) in  $\text{CH}_2\text{Cl}_2$  at 0 °C and stirred for 3 h. The precipitate was filtered and washed with  $\text{CH}_2\text{Cl}_2$ . Purification by preparative TLC yielded **6** (902.2 mg, 92%) as colorless solid; mp 84-85 °C (colorless solid from  $\text{CH}_2\text{Cl}_2$ /Hexane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.96-3.00 (m, 2H), 3.10 (t,  $J = 7.2$  Hz, 2H), 7.23-7.27 (m, 3H), 7.31-7.35 (m, 2H), 7.77-7.81 (m, 2H), 7.86-7.91 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.55, 32.71, 123.99, 126.72, 128.31, 128.73, 128.92, 134.77, 139.18, 161.90, 168.89;  $\nu_{\text{max}}/\text{cm}^{-1}$  1746, 1738 (CO)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{17}\text{H}_{13}\text{NO}_4$ : C, 69.15; H, 4.44; N, 4.74; Found C, 69.14; H, 4.52; N, 4.69

##### 6. Preparation of *N*-(3-phenylpropionyloxy)benzotriazole (7):

DCC (892.9 mg, 4.33 mmol) was added to a solution of hydrocinnamic acid (500.0 mg, 3.329 mmol) and 1-hydroxybenzotriazole (584.8 mg, 4.33 mmol) in  $\text{CH}_2\text{Cl}_2$  at 0 °C and stirred for 3 h. The precipitate was filtered and washed with  $\text{CH}_2\text{Cl}_2$ . Purification by preparative TLC yielded **7** (862.42 mg, 96%) as colorless solid; mp 92-93 °C (colorless solid from AcOEt/Hexane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.17 (t,  $J = 7.6$  Hz, 2H), 3.48 (t,  $J = 7.6$  Hz, 2H), 7.20-7.33 (m, 5H), 7.54-7.58 (m, 1H), 7.75-7.79 (m, 1H), 8.00 (d,  $J = 8.4$  Hz,

1H), 8.40 (d,  $J = 8.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.90, 36.51, 115.52, 116.06, 126.58, 126.77, 128.37, 128.63, 132.51, 133.04, 139.46, 169.11;  $\nu_{\text{max}}/\text{cm}^{-1}$  1736 (CO)  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$ : C, 67.40; H, 4.90; N, 15.72. Found: C, 67.68; H, 5.01; N, 15.80.

### 7.3 Preparation of 3-phenylpropionyloxybenzothiazole (8):

DCC (44.36 mg, 0.21 mmol) was added to a solution of hydrocinnamic acid (25.0 mg, 0.16 mmol) and 2-hydroxybenzothiazole (32 mg, 0.21 mmol) in  $\text{CH}_2\text{Cl}_2$  at rt and stirred for 3 h. The precipitate was filtered and washed with  $\text{CH}_2\text{Cl}_2$ . Purification by preparative TLC yielded **8** (29 mg, 64%) as colorless solid; mp 83-84 °C (colorless solid from  $\text{CH}_2\text{Cl}_2$ /Hexane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.09 (t,  $J = 7.4$  Hz, 2H), 3.45 (t,  $J = 7.6$  Hz, 2H), 7.18-7.37 (m, 7H), 8.25-8.27 (dd,  $J = 8.2$  Hz, 8.3 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.40, 40.63, 76.68, 77.00, 77.32, 117.77, 121.89, 125.45, 126.30, 126.98, 128.51, 128.53, 134.69, 140.25, 170.99, 173.33;  $\nu_{\text{max}}/\text{cm}^{-1}$  1681 (CO), 1456 (C=N)  $\text{cm}^{-1}$ .  
Anal. Calcd for  $\text{C}_{16}\text{H}_{13}\text{NO}_2\text{S}$ : C, 67.82; H, 4.62; N, 4.94. Found C, 67.89; H, 4.75; N, 4.98

### 8. General procedure for the preparation of *N*-(3-Phenylpropionyl)benzotriazole (9):

A mixture of hydrocinnamic acid (26.5 mg, 0.18 mmol) and 1-(methanesulfonyl)benzotriazole (35 mg, 0.18 mmol) and  $\text{Et}_3\text{N}$  (25 mg, 0.24 mmol) were refluxed in THF (1 ml) overnight. The solvent was evaporated and the residue was dissolved in  $\text{CHCl}_3$ . The organic layer was washed with water, dried over anhydrous  $\text{MgSO}_4$ , and evaporated to give a crude product *N*-(3-phenylpropionyl)benzotriazole **9** (37.8 mg). Yield 85%; mp 58-59 °C (colorless solid from AcOEt/Hexane);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.23 (t,  $J = 7.6$  Hz, 2H), 3.76 (t,  $J = 3.0$  Hz, 2H) 7.19-7.32 (m, 5H), 7.47-7.51 (m, 1H), 7.62-7.66 (m, 1H) 8.10 (dd,  $J = 8.3$  Hz, 8.3 Hz, 1H) 8.28 (dd,  $J = 8.0$  Hz, 8.3 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.12, 37.05, 114.35, 120.11, 126.10, 126.48, 128.42, 128.60, 130.36, 131.00, 139.76, 146.10, 171.58;  $\nu_{\text{max}}/\text{cm}^{-1}$  1755 (CO)  $\text{cm}^{-1}$ .

Benzotriazole (179.8 mg, 1.509 mmol) was added to a solution of hydrocinnamic acid (200.0 mg, 1.509 mmol) and DCC (374.8 mg, 1.810 mmol) in  $\text{CH}_2\text{Cl}_2$  at rt and stirred for over night. The precipitate was filtered and washed with  $\text{CH}_2\text{Cl}_2$ . Purification by preparative TLC yielded **9** (215.3 mg, 57%).

### 9. Preparation of 3-Phenylpropionic acid benzyl ester (10):

*Typical procedure:* 4-DMAP (21.5 mg, 0.17 mmol) was added to a solution of benzyl alcohol (20.2 mg, 0.17 mmol) and 3-phenylpropionyloxybenzothiazole (50.0 mg, 0.176 mmol) **8** in CH<sub>2</sub>Cl<sub>2</sub> at rt and stirred for 1 h. The mixture was then neutralized by dil. AcOH solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, successively washed with water and brine, and dried over anhydrous MgSO<sub>4</sub>. Removal of solvent in vacuo gave a colorless oil crude product, which was purified by preparative TLC yielded **10** as colorless liquid (37.6 mg). Yield 89%; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.68 (t, *J* = 7.8 Hz, 2H), 2.96 (t, *J* = 8.0 Hz, 2H) 5.10 (s, 2H), 7.17-7.34 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 30.91, 35.86, 66.24, 126.23, 128.18, 128.27, 128.47, 128.51, 135.89, 140.37, 172.69;  $\nu_{\max}/\text{cm}^{-1}$  1734 (CO) cm<sup>-1</sup>.

DCC (82.5 mg, 0.399 mmol) was added to a solution of hydrocinnamic acid (30.0 mg, 0.199 mmol) and benzyl alcohol (43.1 mg, 0.399 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) at rt and stirred for 19 h. The precipitate was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. Purification by preparation TLC (AcOEt/Hexane; 1:5) yielded **10** as colorless liquid (25.6 mg, 53%).

DCC (82.5 mg, 0.399 mmol) was added to a solution of hydrocinnamic acid (30.0 mg, 0.199 mmol) benzyl alcohol (43.1 mg, 0.399 mmol) and 4-DMAP (48.7 mg, 0.399 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) at rt and stirred for 1 h. The precipitate was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. Purification by preparative TLC (AcOEt/Hexane; 1:10) yielded **10** as colorless liquid (39.7 mg, 83%).

DCC (82.5 mg, 0.399 mmol) was added to a solution of hydrocinnamic acid (30.0 mg, 0.199 mmol) 1-hydroxybenzotriazole (54.0 mg, 0.399 mmol) benzyl alcohol (43.1 mg, 0.399 mmol) and 4-DMAP (48.7 mg, 0.399 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) at 0 °C and stirred for 1 h. The precipitate was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub>. Purification by preparative TLC (AcOEt/Hexane; 1:10) yielded **10** as colorless liquid (47.6 mg, 99%).

#### **10. Preparation of *N*-Benzyl-3-phenylpropanamide (11):**

*Typical procedure:* Benzylamine (33.9 mg, 0.32 mmol) was added to a solution of *N*-(3-phenylpropionyloxy)benzotriazole (50.0 mg, 0.19 mmol) **6** in CH<sub>2</sub>Cl<sub>2</sub> at rt and stirred for 5 min. The mixture was then neutralized by dil. AcOH solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, successively washed with water and brine, and dried over anhydrous MgSO<sub>4</sub>. Removal of solvent in vacuo gave a solid product, which was purified by preparative TLC yielded **11** (43.1 mg). Yield 96%; mp 76-77 °C (colorless solid from AcOEt-Hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.51 (t, *J* = 7.6 Hz, 2H), 2.99 (t, *J* = 6.8 Hz, 2H) 4.39 (d, *J* = 6.0 Hz, 2H), 7.13-7.31 (m, 10H); <sup>13</sup>C NMR

(CDCl<sub>3</sub>)  $\delta$  31.69, 38.50, 43.55, 126.23, 127.44, 127.72, 128.37, 128.53, 128.63, 138.10, 140.73, 171.80;  $\nu_{\max}/\text{cm}^{-1}$  1639 (CO)  $\text{cm}^{-1}$ . Anal. Calcd for C<sub>16</sub>H<sub>17</sub>NO: C, 80.30; H, 7.16; N, 5.85; Found C, 80.34; H, 7.16; N, 5.90

### 11. Preparation of 3-Phenylthiopropionic S-benzyl ester (12):

*Typical procedure:* 4-DMAP (22.8 mg, 0.19 mmol) was added to a solution of benzyl mercaptane (23.2 mg, 0.19 mmol) and *N*-(3-phenylpropionyloxy)benzotriazole (50.0 mg, 0.19 mmol) **6** in CH<sub>2</sub>Cl<sub>2</sub> at rt. and stirred for 3 min. The mixture was then neutralized by diluted acetic acid and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated successively washed with water and brine, and dried over anhydrous MgSO<sub>4</sub>. Removal of solvent in vacuo gave a colorless oil crude product, which was purified by preparative TLC yielded **12** as colorless liquid (34.4 mg). Yield 72%; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.87 (m, 2H), 2.99 (t, *J* = 7.6 Hz, 2H) 4.12 (s, 2H), 7.15-7.31 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  31.38, 33.14, 45.20, 126.33, 127.21, 128.28, 128.51, 128.58, 128.78, 137.52, 139.92, 197.82;  $\nu_{\max}/\text{cm}^{-1}$  1686 (CO)  $\text{cm}^{-1}$ .

### 12. 3-cholesteroyl-4-(phthalimidoyloxycarbonyl)butyrate (13):

*Typical procedure:* To a stirred solution of DMAP (4.4 mg, 0.04 mmol) and cholesterol (14.1 mg, 0.04 mmol) solution was dropwise added to a solution of **5** (15 mg, 0.04 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) at rt under N<sub>2</sub> and stirred for overnight. Then the reaction mixture was neutralized by NaHCO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried over anhydrous MgSO<sub>4</sub>, and concentrated under vacuum, to give crude product which was purified by flash chromatography yielded **13** (16 mg, 68%); colorless solid; mp 83-85 °C (from CH<sub>2</sub>Cl<sub>2</sub>/Hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.67 (s, 3H), 0.86 (dd, *J* = 1.6 Hz, 6.4 Hz, 6H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.94-1.04 (m, 5H), 1.05-1.17 (m, 6H), 1.23-1.37 (m, 5H), 1.42-1.58 (m, 7H), 1.78-1.88 (m, 3H), 1.93-2.03 (m, 2H) 2.06-2.13 (m, 2H), 2.33 (d, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 4.60-4.68 (m, 1H), 5.38 (d, *J* = 4 Hz, 1H), 7.77-7.81 (m, 2H), 7.86-7.91 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  11.8, 18.7, 19.3, 19.9, 21.0, 22.5, 22.8, 23.8, 24.3, 27.8, 27.9, 28.2, 30.07, 31.8, 31.9, 33.1, 35.8, 36.2, 36.6, 36.9, 38.1, 39.5, 39.7, 42.3, 49.9, 56.1, 56.7, 74.2, 122.7, 123.9, 128.8, 134.8, 139.6, 161.8, 169.1, 171.9.  $\nu_{\max}/\text{cm}^{-1}$  1814, 1789, 1741 (CO). Elemental analysis (%) calc. for C<sub>40</sub>H<sub>55</sub>NO<sub>6</sub>: C, 74.38; H, 8.58; N, 2.17. Found: C, 74.79; H, 8.71; N, 2.18.

### 13. General procedure for the synthesis of 3-cholesteroyl-4-(benzylaminocarbonyl)butyrate (14):

DABCO (4.15 mg, 0.04 mmol) and benzylamine (4.05  $\mu$ l, 0.04 mmol) solution was dropwise added to a solution of compound **13** (20 mg, 0.04 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.5 ml) at rt under  $\text{N}_2$  and stirred for 2 h. Then the reaction mixture was neutralized by diluted acetic acid solution and extracted with  $\text{CH}_2\text{Cl}_2$ , and dried over anhydrous  $\text{MgSO}_4$ , and concentrated under vacuum, to give **14** (32 mg, 91%) as colorless solid; mp 115-117  $^\circ\text{C}$  (from  $\text{CH}_2\text{Cl}_2/\text{Hexane}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.67 (s, 3H), 0.86 (dd,  $J = 1.6$  Hz, 7.2 Hz, 6H), 0.91 (d,  $J = 6.4$  Hz, 3H), 0.94-1.04 (m, 5H), 1.08-1.21 (m, 6H), 1.24-1.39 (m, 6H), 1.42-1.61 (m, 7H), 1.78-1.87 (m, 3H), 1.94-2.02 (m, 4H), 2.25-2.29 (m, 4H), 2.35 (t,  $J = 7.0$  Hz, 2H), 4.43 (d,  $J = 5.6$  Hz, 1H), 4.55-4.63 (m, 1H), 5.36 (d,  $J = 4.4$  Hz, 2H), 5.86 (s, 1H), 7.26-7.37 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  11.82, 18.7, 19.3, 20.9, 22.5, 22.8, 23.8, 24.2, 27.8, 27.9, 28.2, 31.8, 31.9, 33.6, 35.5, 35.8, 36.1, 36.6, 36.9, 38.1, 39.5, 39.7, 42.3, 43.6, 49.9, 56.1, 56.6, 74.0, 122.7, 127.5, 127.8, 128.7, 138.2, 139.5, 171.9, 172.6;  $\nu_{\text{max}}/\text{cm}^{-1}$  1729, 1639 (CO); Elemental analysis (%) calc. for  $\text{C}_{39}\text{H}_{59}\text{NO}_3$ : C, 79.41; H, 10.08; N, 2.37. Found: C, 78.93; H, 9.87; N, 2.35.











































































































