**Experimental Part** 

## **General Experimental Methods**

Anhydrous dichloromethane was obtained by distillation from calcium hydride under nitrogen. Anhydrous THF and diethyl ether were obtained by distillation from sodium benzophenone ketyl under nitrogen. Other solvents were used as supplied by commercial sources. Petroleum ether refers to the fraction of light petroleum ether, boiling between 40-60 °C. Purification procedures were in accordance with the instructions in D. D. Perrin and W. L. F. Armarego, "Purification of Laboratory Chemicals", Fourth Edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free nitrogen. Flash chromatography was performed on silica gel (SDS, 60 Å C. C. 40-63 µm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on aluminum plates pre-coated with silica gel (Merck silica gel, 60 F<sub>254</sub>), which were visualized by the quenching of UV fluorescence when applicable ( $\lambda_{max} = 254$  nm and/or 366 nm) and/or by staining with anisaldehyde or vanillin in acidic ethanol followed by heating. When compounds could not be visualized with anisaldehyde or vanillin, a solution of phosphomolybdic acid in ethanol or a potassium permanganate aqueous solution were used. Infrared spectra were recorded as solutions in CDCl<sub>3</sub> using CaF<sub>2</sub> cells, on a Perkin-Elmer FT 1600 or FT 2000. Absorption maxima ( $v_{max}$ ) are reported in wavenumbers (cm<sup>-1</sup>) and only selected peaks are reported. Magnetic resonance spectra were recorded at ambient temperature on either a Bruker AMX 400, or a Bruker Avance DPX 400 instrument. Proton magnetic resonance spectra (<sup>1</sup>H NMR) were recorded at 400 MHz. The following abbreviations were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t =triplet, q = quartet and m = multiplet. Carbon magnetic resonance spectra (<sup>13</sup>C NMR) were recorded at 100 MHz. Chemical shifts ( $\delta_{\rm H}$ ,  $\delta_{\rm C}$ ) are quoted in parts per million (ppm) and are referenced to the residual solvent peak (CDCl<sub>3</sub>:  $\delta_{H}$  = 7.26 and  $\delta_{\rm C}$  = 77.0). High-resolution mass spectra were recorded by positive electron impact ionization (EI+) at 70 eV on a JEOL JMS-GCmate II mass

spectrometer. The quoted masses are accurate to  $\pm 5$  ppm. DLP corresponds to di-lauroyl peroxide (often sold under lauroyl peroxide or laurox).

# Molecules cited in the experimental part



## Molecules of chapter 3





# Molecules of chapter 4



4-11c



4-11d





# Molecules of chapter 5



186



5-7j











5-7p









5-10e





## Chapter 3

**General procedure A for radical addition:** A magnetically stirred solution of xanthate (1 equiv) and olefin (1.5 equiv to 3.0 equiv) were dissolved in ethyl acetate (1 ml/mmol of xanthate ) was refluxed for 15 min. DLP (5 mol%) was then added and additional DLP (5 mol%) was added every 60 min until total consumption of xanthate. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was either engaged in a new reaction or purified by flash chromatography on silica gel to yield the desired compounds.

General procedure B for reduction: The residue was dissolved in dioxane (10 mL/mmol) then triethylamine (3.3 equiv.) and a solution of  $H_3PO_2$  50% in water (3 equiv.) were added. The solution was refluxed for 15 min and AIBN (10%mol) was then added. After 1 hour, the solution was allowed to cool to room temperature, water and ethyl acetate were added. The organic layer was washed with water and brine, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield the desired compounds.

# 3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-3-ethoxythiocarbonylsulfanyl-propionic acid methyl ester (3-25)



Phthalimide (30 g, 0.21mol) and methyl acrylate (28.2 ml, 0.3 mol) with DBU (15.6 ml, 0.1 mmol) were stirred in acetonitrile (100 ml) at room temperature for 2 hours. The reaction mixture was then concentrated under reduced pressure and poured into petroleum ether to get a solid which was washed with water to yield pure product

**3-22** (45.4 g, 94%). **3-22** (2.1 g, 9.00 mmol), NBS (1.92 g, 10.08 mmol) in CCl<sub>4</sub> (150 ml) was heated at reflux under nitrogen for 5 h; the reaction was initiated by irradiation with a 300 W lamp. The reaction mixture was then cooled, filtered and washed with sodium thiosulfate. After extracting the solution with DCM, the organic layer was concentrated under reduced pressure to yield 2.3 g product **3-23** (83%) without further purification. **3-23** (2.3 g, 7.5 mmol) was dissolved in acetone (2 ml per mmol). Under a nitrogen atmosphere KSCSOEt (1.3 g, 8 mmol) was added portion wise over a period of five minutes. It was then left to stir for a further twenty minutes before the acetone was evaporated off under reduced pressure. The residue was then taken up in DCM/H<sub>2</sub>O and extracted. The DCM layers were dried over Na<sub>2</sub>SO<sub>4</sub> before being filtered and evaporated under reduced pressure to yield the crude xanthate. This was then purified by column chromatography using petroleum ether: ethyl acetate,  $25:1\sim10:1 \text{ v/v}$ , to obtain 2.1 g **3-25** as a pale yellow oil in 80% yield.

<sup>1</sup>**H NMR** (**400 MHz; CDCl**<sub>3</sub>):  $\delta_{\rm H}$  7.91-7.85 (m, 2H, CHPhth), 7.77-7.72 (m, 2H, CHPhth), 6.65 (dd,1H, J = 5.5 Hz, J =10.2 Hz, CHS), 4.67 (dq, 2H, J = 1.0 Hz, J = 7.1 Hz, -OCH<sub>2</sub>CH<sub>3</sub>), 3.66 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.49 (dd, 1H, J = 10.2 Hz, J = 16.5 Hz CHSC*H*H), 3.16 (dd, 1H, J = 5.5Hz, J = 16.5 Hz, CHSCH*H*), 1.44 (t, 3H, J = 7.1 Hz, -OCH<sub>2</sub>CH<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  209.7 (C=S), 169.4 (C=O), 166.5 (C=O), 134.4 (CPhth), 131.6 (CPhth), 123.7 (CPhth), 70.6 (OCH<sub>2</sub>CH<sub>3</sub>), 53.2 (CHS), 52.2 (CO<sub>2</sub>CH<sub>3</sub>), 37.2 (CH<sub>2</sub>), 13.7 (OCH<sub>2</sub>CH<sub>3</sub>);

**IR** (**CCl**<sub>4</sub>): v max 2963, 1780, 1726, 1555, 1377, 1226, 1051;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>15</sub>H<sub>15</sub>NO<sub>5</sub>S<sub>2</sub>: 353.0392 (353.0391).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-6-phenoxy-hexanoaic acid methyl ester (3-26-1)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and allyl phenyl ether (86 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 10:1 v/v) afforded 120 mg **3-26-1** (yield: 78%) as a pale yellow oil.

<sup>1</sup>**H NMR** (**400 MHz**; **CDCl**<sub>3</sub>):  $\delta_{\rm H}$  7.88-7.79 (2H, m, CHPhth), 7.76-7.68 (m, 2H, CHPhth), 7.27-7.18 (m, 2H, Ar), 6.90 (t, 1H, J=7.3Hz, Ar), 6.83 (d, 2H, J=7.9Hz, Ar), 4.76-4.66 (1H, m, NCH), 3.94 (t, 2H, J=6.1Hz), 3.60 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.21 (dd, 1H, J=9.5Hz, J=16.1Hz, CHHCO<sub>2</sub>Me), 2.82 (dd, 1H, J=5.3Hz, J=16.1Hz, CHHCO<sub>2</sub>Me), 2.31-2.18 (m, 1H), 1.98-1.90 (m, 1H), 1.78-1.69 (m, 2H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  170.9 (C=O), 168 (C=O), 158.5 (Cq-O), 133.8, (CPhth), 131.4 (CqPhth), 129.1 (Ar), 123 (CPhth), 120.3 (Ar), 114.1 (Ar), 66.5 (-CH<sub>2</sub>OPh), 51.5 (CO<sub>2</sub>CH<sub>3</sub>), 47.5 (NCH), 36.4 (CH<sub>2</sub>CO<sub>2</sub>), 28.6 (NCH*CH*<sub>2</sub>), 25.9 (CH<sub>2</sub>);

IR (CCl<sub>4</sub>): vmax 1777, 1746, 1721, 1245, 1201, 1174, 1006;

**HRMS (EI+):** *m/z* calculated (found) for C<sub>21</sub>H<sub>21</sub>NO<sub>5</sub>: 367.1420 (367.1421).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-6-(trimethylsilyl)-hexanoic acid methyl ester (3-26-2)



3-26-2

Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and allyl trimethylsilane (96 mg, 0.84 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 5:1 v/v) afforded 96 mg **3-26-2** (yield: 66%) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.87-7.78 (m, 2H, CHPhth), 7.75-7.66 (m, 2H, CHPhth), 4.71-4.64 (1H, m, NCH), 3.59 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.16 (dd, 1H, J=9.6Hz, J=16.0Hz, CH*H*CO<sub>2</sub>Me), 2.76 (dd, 1H, J=5.3Hz, J=16.0Hz, C*H*HCO<sub>2</sub>Me), 2.17-2.08 (m, 1H, CHCH*H*CH<sub>2</sub>), 1.73-1.68 (m, 1H, CHC*H*HCH<sub>2</sub>), 1.29-1.22 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>Si), 0.60-0.38 (m, 2H, CH<sub>2</sub>Si), -0.09 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  173.2 (OCO), 170 (NCO), 135.7 (CHPhth), 133.6 (CqPhth), 125 (CHPhth), 53.5 (CO<sub>2</sub>CH<sub>3</sub>), 49.4 (NCH), 38.5 (CH<sub>2</sub>CO<sub>2</sub>Me), 37.7 (CHCH<sub>2</sub>), 26.9, 25.2 (CH<sub>2</sub>SiMe<sub>3</sub>), 22.5, 17.8 (CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub>), 0.021 (SiMe<sub>3</sub>); **v**<sub>max</sub>(CCl<sub>4</sub>)/cm<sup>-1</sup>: 1776, 1745, 1716, 1249, 1204;

HRMS (EI+): *m/z* calculated (found) for C<sub>18</sub>H<sub>25</sub>NO<sub>4</sub>Si: 347.1553 (347.1546).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-6-cyano-hexanoic acid methyl ester (3-26-3)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and allyl cyanide (43 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 103 mg **3-26-3** (yield: 82%) as a pale yellow oil.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.89-7.81 (m, 2H, CHPhth), 7.77-7.69 (m, 2H, CHPhth), 4.71-4.63 (1H, m, NCH), 3.62 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.18 (dd, 1H, J=9.0Hz, J=16.3Hz, CH*H*CO<sub>2</sub>Me), 2.84 (dd, 1H, J=5.7Hz, J=16.3Hz, C*H*HCO<sub>2</sub>Me), 2.38 (t, 2H, J=7.2Hz, CH<sub>2</sub>CN), 2.30-2.20 (m, 1H, CH*H*CH<sub>2</sub>CN), 1.90-1.82 (m, 1H, C*H*HCH<sub>2</sub>CN), 1.68-1.58 (m, 2H, CHCH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  170.9 (OCO), 168.1 (NCO), 134.1 (CHPhth), 131.4 (CqPhth), 123.3 (CHPhth), 119 (CH<sub>2</sub>CN), 51.8 (CO<sub>2</sub>CH<sub>3</sub>), 46.7 (NCH), 36.5 (CH<sub>2</sub>CO<sub>2</sub>Me), 31.1(CHCH<sub>2</sub>), 22.2 (CH<sub>2</sub>CH<sub>2</sub>CN), 16.5 (CH<sub>2</sub>CN);

IR (CCl<sub>4</sub>): vmax 2248, 1776, 1745, 1716, 1211, 1172;

**HRMS (EI+)**: m/z calculated (found) for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>: 300.1110 (300.1100).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-8-cyano-octanoic acid methyl ester (3-26-4)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and hex-5-enenitrile (61 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 3:1 v/v) afforded 112 mg **3-26-4** (yield: 81%) as a pale yellow oil.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.87-7.78 (m, 2H, CHPhth), 7.75-7.68 (m, 2H, CHPhth), 4.71-4.62 (1H, m, NCH), 3.61 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.15 (dd, 1H, J=9.2Hz, J=16.1Hz, CH*H*CO<sub>2</sub>Me), 2.80 (dd, 1H, J=5.6Hz, J=16.1Hz, C*H*HCO<sub>2</sub>Me), 2.29 (t, 2H, J=7.1Hz, CH<sub>2</sub>CN), 2.05-1.97 (m, 1H, C*H*HCH<sub>2</sub>CN), 1.75-1.66 (m, 1H, CH*H*CH<sub>2</sub>CN), 1.64-1.57 (m, 2H, CHCH<sub>2</sub>), 1.51-1.43 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CN), 1.33-1.26 (m, 2H, CHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  171.1 (OCO), 168.1 (NCO), 133.8 (CHPhth), 131.5 (CqPhth), 123.14, 123.11 (CHPhth), 119.3 (CH<sub>2</sub>CN), 51.602 (CO<sub>2</sub>CH<sub>3</sub>), 47.6 (NCH), 36.6 (CH<sub>2</sub>CO<sub>2</sub>Me), 31.7 (CHCH<sub>2</sub>), 27.9 (CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.3 (CH<sub>2</sub>CH<sub>2</sub>CN), 25 (CH<sub>2</sub>CH<sub>2</sub>CN), 16.8 (CH<sub>2</sub>CN);

IR (CCl<sub>4</sub>): vmax 2249, 1776, 1744, 1712, 1206, 1178;

**HRMS (EI+)**: m/z calculated (found) for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: 328.1423 (328.1426).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-8,8,8-trifluoro-7-hydroxy-7-(trifluoromet hyl)-octanoic acid methyl ester (3-26-5)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and 1,1,1-Trifluoro-2-(trifluoromethyl)-pent-4-en-2-ol (133 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 10:1 v/v) afforded 106 mg **3-26-5** (yield: 57%) as a colorless oil.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.87-7.78 (m, 2H, CHPhth), 7.77-7.68 (m, 2H, CHPhth), 4.71-4.63 (1H, m, NCH), 3.71 (s, 1H, OH), 3.61 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.17 (dd, 1H, J=8.9Hz, J=16.4Hz, CH*H*CO<sub>2</sub>Me), 2.84 (dd, 1H, J=5.9Hz, J=16.4Hz, C*H*HCO<sub>2</sub>Me), 2.25-2.17 (m, 1H, CH<sub>2</sub>CH*H* (CF<sub>3</sub>)<sub>2</sub>), 2.09-2.02 (m, 1H, CH<sub>2</sub>C*H*H(CF<sub>3</sub>)<sub>2</sub>), 1.87-1.76 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>), 1.63-1.54 (m, 2H, CHCH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  171.3 (OCO), 168.6 (NCO), 134.2 (CHPhth), 131.5 (CqPhth), 123 (q, 1H, J=271.1Hz, *C*F<sub>3</sub>), 123.4 (CHPhth), 51.9 (CO<sub>2</sub>*C*H<sub>3</sub>), 47 (NCH), 36.6 (*C*H<sub>2</sub>CO<sub>2</sub>Me), 32.2 (CH*C*H<sub>2</sub>), 29.324 (*C*H<sub>2</sub>CH(OH)(CF<sub>3</sub>)<sub>2</sub>), 18.432 (CHCH<sub>2</sub>*C*H<sub>2</sub>);

IR (CCl<sub>4</sub>): vmax 3474, 1776, 1744, 1717, 1206, 1178;

**HRMS (EI+)**: m/z calculated (found) for C<sub>18</sub>H<sub>17</sub>F<sub>6</sub>NO<sub>5</sub>: 441.1011 (441.101).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-6-(2-oxocyclohexyl)-hexanoic acid methyl ester (3-26-6)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and 2-allylcyclohexanone (88 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 5:1 v/v) afforded 110 mg **3-26-6** (yield: 71%) as a colorless oil and a mixture of two diastereoisomers in a ratio 1:1.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>): *Mixture of diastereoisomer* :  $\delta_{\rm H}$  7.85-7.76 (m, 2H, CHPhth), 7.76-7.68 (m, 2H, CHPhth), 4.69-4.61 (1H, m, NCH), 3.60 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.21-3.13 (m, 1H, J=9.5Hz, J=16.1Hz, CH*H*CO<sub>2</sub>Me), 2.81-2.72(m, 1H, J=5.0Hz, J=16.0Hz, C*H*HCO<sub>2</sub>Me), 2.36-2.28 (m, 1H, C*H*COCH<sub>2</sub>), 2.26-2.17 (m, 2H, COC *H*<sub>2</sub>CH<sub>2</sub>), 2.09-1.95 (m, 3H, COCH<sub>2</sub>C*H*H, COCH<sub>2</sub>CH<sub>2</sub>C*H*H, CHC*H*H), 1.71-1.67 (m, 3H, COCH<sub>2</sub>CH*H*, COCH<sub>2</sub>CH*H*, CHC*H*H), 1.66-1.56 (m, 3H, COCH*C*H*H*, CHC*H*<sub>2</sub>CH<sub>2</sub>), 1.39-1.28 (m, 3H, COCH*C*H*H*, CHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Mixture of diastereoisomer* : δ<sub>C</sub> 212.9 (CHCO), 171.4, 171.3 (OCO), 168.3 (NCO), 133.9 (CHPhth), 131.8 (CqPhth), 123.2 (CHPhth), 51.7 (CO<sub>2</sub>CH<sub>3</sub>), 50.5 (NCH), 47.97, 47.92 (CHCO), 41.9 (COCH<sub>2</sub>), 36.7 (CH<sub>2</sub>CO<sub>2</sub>Me), 34, 33.8 (COCHCH<sub>2</sub>), 32.5 (NCHCH<sub>2</sub>), 28.9, 28.8 (COCH<sub>2</sub>CH<sub>2</sub>), 27.9 (COCHCH<sub>2</sub>), 24.9 (COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 23.9 (CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH);

**IR** (**CCl**<sub>4</sub>): vmax 1776, 1745, 1715, 1208, 1173;

HRMS (EI+): *m/z* calculated (found) for C<sub>21</sub>H<sub>25</sub>NO<sub>5</sub>: 371.1733 (371.1743).

acid



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and 2-Allyl-cyclopentanone (79 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 91 mg **3-26-7** (yield: 61%) as a colorless oil and a mixture of two diastereoisomers in a ratio 1:1.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): *Mixture of diastereoisomer* :  $\delta_H$  7.89-7.77 (m, 2H, CHPhth), 7.76-7.65 (m, 2H, CHPhth), 4.70-4.61 (1H, m, NCH), 3.60 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.17 (dd, 0.5 H, J=2.1Hz, J=9.5Hz, CH*H*CO<sub>2</sub>Me), 3.13 (dd, 0.5 H, J=2.1Hz, J=9.5Hz, CH*H*CO<sub>2</sub>Me), 2.79 (dd, 0.5 H, J=1.1Hz, J=5.3Hz, C*H*HCO<sub>2</sub>Me), 2.75 (dd, 0.5 H, J=1.0Hz, J=5.3Hz, C*H*HCO<sub>2</sub>Me), 2.30-2.21 (m, 1H, C*H*COCH<sub>2</sub>), 2.16-2.07 (m, 3H, COC*H*HCH<sub>2</sub>, COCH<sub>2</sub>C*H*H, COCH<sub>2</sub>C*H*CH), 2.01-1.92 (m, 2H, COCH*H*, COCH<sub>2</sub>CH*H*), 1.77-1.69 (m, 3H, COCH<sub>2</sub>CH<sub>2</sub>C*H*H, NCHCH<sub>2</sub>), 1.48-1.41 (m, 1H, COCHC*H*H), 1.34-1.21 (m, 3H, COCHCH*H*, NCHCH<sub>2</sub>C*H*<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Mixture of diastereoisomer* : δ<sub>C</sub> 171.4, 168.3 (NCO),
134 (CHPhth), 131.8 (CqPhth), 123.3 (CHPhth), 51.8 (CO<sub>2</sub>CH<sub>3</sub>), 48.9, 48.9 (NCH),
48, 47.9 (CHCO), 38.1 (CH<sub>2</sub>CO<sub>2</sub>Me), 36.8, 36.7 (COCH<sub>2</sub>), 32.4, 32.3, 29.6, 29.6,
29.2, 29.1, 24.5, 24.4, 20.7 (CH<sub>2</sub>);

**IR** (**CCl**<sub>4</sub>): vmax 1776, 1743, 1716, 1206, 1173;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>20</sub>H<sub>23</sub>NO<sub>5</sub>: 357.1576 (357.1575).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-6-(4-bromophenoxy)-hexanoic acid meth-yl ester (3-26-8)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and 1-(allyloxy)-4-bromobenzene (136 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 119 mg **3-26-8** (yield: 64%) as a yellow oil.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.88-7.78 (m, 2H, CHPhth), 7.75-7.66 (m, 2H, CHPhth), 7.34 (d, 2H, J=8.9Hz, Ar), 6.80 (d, 2H, J=8.9Hz, Ar), 4.75-4.68 (1H, m, NCH), 3.90 (dt, 2H, J=1.6Hz, J=6.4Hz, CH<sub>2</sub>OPhBr), 3.60 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.21 (dd, 1H, J=9.5Hz, J=16.1Hz, CHHCO<sub>2</sub>Me), 2.82 (dd, 1H, J=5.3Hz, J=16.1Hz, CHHCO<sub>2</sub>Me), 2.29-2.21 (m, 1H, NCHCH<sub>2</sub>CHH), 1.97-1.89 (m, 1H, NCHCH<sub>2</sub>CHH), 1.76-1.68 (m, 2H, NCHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 171.2 (C=O), 168.3, (C=O), 158.8 (Cq-O), 134.0, 133.9 (CPhth), 131.7 (CqPhth), 129.3 (Ar), 123.3, 123.2 (CPhth), 120.6 (Ar), 114.4 (Ar), 66.7 (*C*H<sub>2</sub>OPh), 51.8 (CO<sub>2</sub>*C*H<sub>3</sub>), 47.7 (NCH), 36.7 (*C*H<sub>2</sub>CO<sub>2</sub>), 28.9 (NCH*C*H<sub>2</sub>), 24.3 (*C*H<sub>2</sub>CH<sub>2</sub>OPh);

**IR** (**CCl**<sub>4</sub>): vmax 1776, 1745, 1716, 1241, 1173, 1047;

HRMS (EI+): *m/z* calculated (found) for C<sub>21</sub>H<sub>20</sub>BrNO<sub>5</sub>: 445.0525 (445.0534).

3,6-bis(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)hexanoic acid methyl ester (3-26-9)



3-26-9

Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and 2-allylisoindoline-1,3-dione (119 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 116 mg **3-26-9** (yield: 66%) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.84-7.75 (m, 4H, CHPhth), 7.75-7.64 (m, 4H, CHPhth), 4.73-4.64 (m, 1H, NCH), 3.67 (m, 2H, NCH<sub>2</sub>), 3.58 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.18 (dd, 1H, J=9.6Hz, J=16.1Hz, CH*H*CO<sub>2</sub>Me), 2.77 (dd, 1H, J=5.3Hz, J=16.1Hz, C*H*HCO<sub>2</sub>Me), 2.19-2.09 (m, 1H, NCH<sub>2</sub>C*H*H), 1.81-1.73 (m, 1H, NCH<sub>2</sub>CH*H*), 1.69-1.61 (m, 2H, NCHC*H*<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  171.1 (OCO), 168.2, 168.2(NCO), 133.9, 133.9 (CHPhth), 132, 131.7 (CqPhth), 123.3, 123.2 (CHPhth), 51.8 (CO<sub>2</sub>CH<sub>3</sub>), 47.5 (NCH), 37.3 (NCH<sub>2</sub>), 36.6 (CH<sub>2</sub>CO<sub>2</sub>Me), 29.6 (NCHCH<sub>2</sub>), 25.5 (NCH<sub>2</sub>CH<sub>2</sub>);

**IR** (**CCl**<sub>4</sub>): vmax 1776, 1745, 1718, 1206, 1173;

**HRMS (EI+)**: m/z calculated (found) for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>: 420.1321 (420.1322).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-6-acetoxy-hexanoic acid methyl ester (3-26-10)



3-26-10

Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and allyl acetate (64 mg 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate,  $10:1\sim4:1 \text{ v/v}$ ) afforded 99 mg **3-26-10** (yield: 71%) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.87-7.79 (m, 2H, CHPhth), 7.76-7.67 (m, 2H, CHPhth), 4.71-4.63 (1H, m, NCH), 4.04 (t, 2H, J=6.5Hz, CH<sub>2</sub>OAc), 3.60 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.18 (dd, 1H, J=9.4Hz, J=16.1Hz, CHHCO<sub>2</sub>Me), 2.80 (dd, 1H, J=5.4Hz, J=16.1Hz, CHHCO<sub>2</sub>Me), 2.01(s, 3H, OCOCH<sub>3</sub>), 1.87-1.76 (m, 2H, NCHCH<sub>2</sub>), 1.63-1.55 (m, 2H, NCHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  171.2 (OCO), 171 (OCO), 168.2 (NCO), 134 (CHPhth), 131.7 (CqPhth), 123.3 (CHPhth), 63.6 (CH<sub>2</sub>CH<sub>2</sub>OAc), 51.8 (CO<sub>2</sub>CH<sub>3</sub>), 47.7 (NCH), 36.7 (CH<sub>2</sub>CO<sub>2</sub>Me), 28.9 (NCHCH<sub>2</sub>), 25.5 (NCHCH<sub>2</sub>CH<sub>2</sub>);

**v**<sub>max</sub>(**CCl**<sub>4</sub>)/**cm**<sup>-1</sup>: 1777, 1744, 1717, 1237, 1173;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>17</sub>H<sub>19</sub>NO<sub>6</sub>: 333.1212 (333.1210).

3-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-6-phenyl-hexanoic acid methyl ester (3-26-11)



3-26-11

Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-25** (150 mg, 0.42 mmol) and allylbenzene (76 mg, 0.64 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate,  $10:1\sim5:1 \text{ v/v}$ ) afforded 112 mg **3-26-11** (yield: 76%) as a colorless oil.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  -7.85-7.79 (m, 2H, CHPhth), -7.75-7.66 (m, 2H, CHPhth), 7.23 (t, 2H, J=7.3Hz, Ar), 7.15 (t, 1H, Ar), 7.12 (d, 2H, J=6.9Hz, Ar), 4.74-4.66 (m, 1H, NCH), 3.6 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.17 (dd, 1H, J=9.5Hz, J=16.1Hz, CH*H*CO<sub>2</sub>Me), 2.77 (dd, 1H, J=5.3Hz, J=16.1Hz, C*H*HCO<sub>2</sub>Me), 2.66-2.58 (m, 2H, CH<sub>2</sub>Ph), 2.19-2.11 (m, 1H, CH*H*CH<sub>2</sub>Ph), 1.82-1.73 (m, 1H, C*H*HCH<sub>2</sub>Ph), 1.64-1.57 (m, 2H, NCHCH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 171.3 (OCO), 168.3 (NCO), 141.7 (CqAr), 133.9 (CHPhth), 131.7 (CqPhth), 128.3, 128.2, 125.8 (Ar), 123.2 (CHPhth), 51.7 (CO<sub>2</sub>CH<sub>3</sub>), 47.8 (NCH), 36.7 (CH<sub>2</sub>CO<sub>2</sub>Me), 35.2 (ArCH<sub>2</sub>), 31.8 (NCHCH<sub>2</sub>), 28.1 (ArCH<sub>2</sub>CH<sub>2</sub>); v<sub>max</sub>(CCl<sub>4</sub>)/cm<sup>-1</sup>: 1776, 1745, 1716, 1206, 1173;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>21</sub>H<sub>21</sub>NO<sub>4</sub>: 351.1471 (351.1471).

Dithiocarbonic acid [1-bis-(1,3-dioxo-1,3-dihydroisoindol-2-yl)-1-ethyl] ester *O*-ethyl ester (3-27)



To a solution of **SM-1** (4 g, 23 mmol) in CCl<sub>4</sub> (150 ml) NBS (4.8g, 27 mmol) was added and then the solution was heated at reflux under nitrogen for 2h; the reaction was initiated by irradiation with a 300 W lamp. The reaction mixture was then cooled, filtered and washed with sodium thiosulfate. After extracting the solution with DCM, the organic layer was concentrated under reduced pressure to obtain 4.9 g **SM-2** (yield: 85%) without further purification. **SM-2** (4.9 g, 20 mmol) was dissolved in acetone (2 ml per mmol). KSCSOEt (3.5 g, 22 mmol) was then added portion wise over a period of five minutes. It was then left to stir for further twenty minutes before the acetone was evaporated off under reduced pressure. The residue was then taken up in DCM/H<sub>2</sub>O and extracted. The DCM layers were dried over Na<sub>2</sub>SO<sub>4</sub> before being filtered and evaporated under reduced pressure to yield the crude xanthate. This was then purified by column chromatography using petroleum ether: ethyl acetate,  $10:1\sim4:1 \text{ v/v}$ , to obtain 4.8 g **3-27** (yield: 81%) as a pale yellow solid which was crystallized from ethyl acetate/ petroleum ether.

<sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>)**: δ<sub>H</sub> 7.85-7.76 (m, 2H, CHPhth), 7.77-7.69 (m, 2H, CHPhth), 6.34 (q, 1H, J=7.3Hz, CHS), 4.60 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 1.82 (d, 3H, J=7.3Hz), 1.37 (t, 3H, J=7.1Hz, OCH<sub>2</sub>CH<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  211.1 (C=S), 166.6 (C=O), 134.4 (CPhth), 131.7 (CPhth), 123.6 (CPhth), 70.3 (OCH<sub>2</sub>CH<sub>3</sub>), 53.4 (CHS), 20 (CHSCH<sub>3</sub>), 13.8 (OCH<sub>2</sub>CH<sub>3</sub>);

**IR** (**CCl**<sub>4</sub>): v max 2928, 1781, 1723, 1376, 1223, 1044;

HRMS (EI+): *m/z* calculated (found) for C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub>S<sub>2</sub>: 295.0337 (295.0346); MP:

103~104 °C.

### 2-(5-Phenoxypentan-2-yl)isoindoline-1,3-dione (3-27-1)



Following the general procedure A for radical addition, the reaction was carried out with a solution of 3-27 (100 mg, 0.34 mmol) and allyl phenyl ether (68 mg, 0.51 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 10:1 v/v) afforded 81 mg 3-27-1 (yield: 78%) as a colorless solid. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ<sub>H</sub> 7.89-7.78 (m, 2H, CHPhth), 7.74-7.63 (m, 2H, CHPhth), 7.24 (s, 2H, Ar), 6.91 (t, 1H, J=6.7Hz, Ar), 6.86 (d, 2H, J=7.8Hz, Ar), 4.50-4.41 (m, 1H, NCH), 3.95 (dt, 2H, J=1.6Hz, J=6.4Hz, CH<sub>2</sub>OPh), 2.31-2.20 (m, 1H,CHHCH<sub>2</sub>OPh), 1.99-1.92 (m, 1H, CHHCH<sub>2</sub>OPh), 1.82-1.74- (m, 2H, NCHCH<sub>2</sub>), 1.52 (d, 3H, J=6.9Hz, NCHCH<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>c</sub> 168.4 (C=O), 158.8 (Ar), 133.8 (CPhth), 131.8 (CqPhth), 129.3 (Ar), 123 (CPhth), 120.5 (Ar), 114.3 (Ar), 67 (CH<sub>3</sub>OPh), 47.1 (NCH), 30.1 (NCHCH<sub>2</sub>), 26.5 (NCHCH<sub>2</sub>CH<sub>2</sub>), 18.7 (NCHCH<sub>3</sub>);

IR (CCl<sub>4</sub>): vmax 2939, 1713, 1775, 1470, 1369, 1172, 1051;

HRMS (EI+): m/z calculated (found) for C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub>: 309.1365 (309.1372), MP: 97 °C.

#### 4-(1,3-Dioxoisoindolin-2-yl)pentyl acetate (3-27-2)



Following the general procedure A for radical addition, the reaction was carried out

with a solution of **3-27** (100 mg, 0.34 mmol) and allyl acetate (51 mg, 0.51 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 10:1 v/v) afforded 66 mg **3-27-2** (yield: 71%) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>)**: δ<sub>H</sub> 7.82-7.72 (m, 2H, CHPhth), 7.72-7.63 (m, 2H, CHPhth), 4.48-4.41 (m, 1H, NCH), 4.03 (t, 2H, J=6.5Hz, CH<sub>2</sub>OAc), 2.15-2.08 (m, 1H, CH*H*CH<sub>2</sub>OAc), 2.00 (s, 3H, OCOCH<sub>3</sub>), 1.84-1.76 (m, 1H, C*H*HCH<sub>2</sub>OAc), 1.63-1.54 (m, 2H, NCHCH<sub>2</sub>), 1.47 (d, 3H, J=6.9Hz, NCHCH<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>c</sub> 171 (CH<sub>3</sub>CO), 168.4 (C=O), 133.9 (CPhth), 131.9 (CqPhth), 123.1 (CPhth), 63.9 (CH<sub>2</sub>OAc), 47.1 (NCH), 30.2 (NCH*C*H<sub>2</sub>), 25.9 (NCHCH<sub>2</sub>*C*H<sub>2</sub>), 20.9 (*C*H<sub>3</sub>CO), 18.7 (NCH*C*H<sub>3</sub>);

**IR** (**CCl**<sub>4</sub>): vmax 2928, 1742, 1713, 1469, 1368, 1239, 1052;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>15</sub>H<sub>17</sub>NO<sub>4</sub>: 275.1158 (275.1151).

#### 2-(5-Phenylpentan-2-yl)isoindoline-1,3-dione (3-27-3)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-27** (100 mg, 0.34 mmol) and allylbenzene (60 mg, 0.51 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 10:1 v/v) afforded 75 mg **3-27-3** (yield: 76%) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>)**: δ<sub>H</sub> 7.86-7.77 (m, 2H, CHPhth), 7.74-7.66 (m, 2H, CHPhth), 7.29-7.21 (m, 2H, Ar), 7.16 (t, 1H, J=6.7Hz, Ar), 7.15 (d, 2H, J=7.8Hz, Ar), 4.43-4.37 (m, 1H, NCH), 2.69-2.56 (m, 2H, CH<sub>2</sub>Ph), 2.17-2.12 (m, 1H, CH*H*CH<sub>2</sub>Ph), 1.82-1.75 (m, 1H, C*H*HCH<sub>2</sub>Ph), 1.64-1.55 (m, 2H), 1.52 (d, 3H, J=6.9Hz, NCHCH<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>c</sub> 168.4 (C=O), 133.7 (CPhth), 131.9 (CqPhth), 141.961, 128.288, 128.207, 125.686 (Ar), 123 (CPhth), 47.1 (NCH), 35.4 (CH<sub>2</sub>Ph), 33.2 (NCH*C*H<sub>2</sub>), 28.6 (NCHCH<sub>2</sub>*C*H<sub>2</sub>), 18.649 (NCH*C*H<sub>3</sub>);
IR (CCl<sub>4</sub>): vmax 2937, 1713, 1775, 1468, 1378, 1141, 1037;
HRMS (EI+): *m/z* calculated (found) for C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub>: 293.1416 (293.1416).

5-(1,3-Dioxoisoindolin-2-yl)hexanenitrile (3-27-4)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-27** (100 mg, 0.34 mmol) and allyl cyanide (35 mg, 0.51 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 10:1 v/v) afforded 67 mg product **3-27-4** (yield: 82%) as a pale yellow oil.

<sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>)**: δ<sub>H</sub> 7.81-7.72 (m, 2H, CHPhth), 7.71-7.63 (m, 2H, CHPhth), 4.37-4.29 (m, 1H, NCH), 2.33 (t, 2H, J=7.2Hz, CH<sub>2</sub>CN), 2.25-2.17 (m, 1H, CH*H*CH<sub>2</sub>CN), 1.89-1.81 (m, 1H, C*H*HCH<sub>2</sub>CN), 1.62-1.54 (m, 2H, NCHCH<sub>2</sub>), 1.46 (d, 3H, J=7.2Hz, NCHCH<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>c</sub> 168.3 (C=O), 134 (CPhth), 131.7 (CqPhth), 123.1 (CPhth), 119.162 (CN), 46.3 (NCH), 32.5 (NCH*C*H<sub>2</sub>), 22.7 (NCHCH<sub>2</sub>*C*H<sub>2</sub>), 18.6 (NCH*C*H<sub>3</sub>), 16.688 (*C*H<sub>2</sub>CN);

**IR** (**CCl**<sub>4</sub>): vmax 2929, 1713, 1776, 1469, 1370, 1144, 1041;

**HRMS (EI+)**: m/z calculated (found) for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: 242.1055 (242.1057).

2-(5-(Trimethylsilyl)pentan-2-yl)isoindoline-1,3-dione (3-27-5)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-27** (100 mg, 0.34 mmol) and allyl trimethylsilane (78 mg, 0.68 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 10:1 v/v) afforded 64 mg **3-27-5** (yield: 66%) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>)**: δ<sub>H</sub> 7.86-7.77 (m, 2H, CHPhth), 7.74-7.66 (m, 2H, CHPhth), 4.42-4.33 (m, 1H, NCH), 2.11-2.03 (m, 1H, CH*H*CH<sub>2</sub>TMS), 1.81-1.72 (m, 1H, C*H*HCH<sub>2</sub>TMS), 1.67-1.59 (m, 2H NCHCH<sub>2</sub>) 1.45 (d, 3H, J=6.9Hz), 0.55-0.44 (m, 2H, CH<sub>2</sub>TMS), -0.08 (s, 9H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>c</sub> 168.5 (C=O), 133.7 (CPhth), 132 (CqPhth), 123 (CPhth), 46.9 (NCH), 37.3 (NCH*C*H<sub>2</sub>), 21.1 (NCHCH<sub>2</sub>*C*H<sub>2</sub>), 18.6 (NCH*C*H<sub>3</sub>), 16.1 (CH<sub>2</sub>TMS), -1.8 (TMS);

IR (CCl<sub>4</sub>): vmax 2927, 1712, 1774, 1378, 1248, 1108, 1025;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>16</sub>H<sub>23</sub>NO<sub>2</sub>Si: 289.1498 (289.1504).

4-Chloro-1-(1,3-dioxoisoindolin-2-yl)butyl-O-ethyl carbonodithioate (3-30)



To a solution of **SM-1** (4.25 g, 18 mmol) in  $CCl_4$  (150 ml), NBS (3.2g, 18 mmol) was added and then the solution was heated at reflux under nitrogen for 4h, meanwhile the reaction was initiated by irradiation with a 300 W lamp. The reaction mixture was

then cooled, filtered and washed with sodium thiosulfate. After extracting the solution with DCM, the organic layer was concentrated under reduced pressure to obtain 5 g **SM-3** (yield: 88%) without further purification. **SM-3** (5 g, 15.8 mmol), was dissolved in acetone (2 ml per mmol). KSCSOEt (2.4 g, 15 mmol) was added portion wise over a period of five minutes. It was then left to stir until the starting material was totally consumed by monitoring TLC. After concentrated the resulting solution the residue was then taken up in DCM/H<sub>2</sub>O and extracted 3 times. The DCM layers were dried over Na<sub>2</sub>SO<sub>4</sub> before being filtered and evaporated under reduced pressure to yield the crude xanthate. This was then purified by column chromatography using petroleum ether: ethyl acetate,  $10:1\sim4:1 \text{ v/v}$ , to obtain 4.8 g **3-30** (yield: 86%) as a pale yellow sticky liquid which was crystallized from ethyl acetate/ petroleum ether.

<sup>1</sup>**H NMR** (**400 MHz**; **CDCl**<sub>3</sub>):  $\delta_{\rm H}$  7.88-7.79 (m, 2H, CHPhth), 7.79-7.69 (m, 2H, CHPhth), 6.24 (dd, 1H, J=7.0Hz, J=9.1Hz, CHS), 4.60 (q, 2H, J=7.1Hz, OCH<sub>2</sub>CH<sub>3</sub>), 3.54 (t, 2H, J=6.5Hz, *CH*<sub>2</sub>Cl), 2.39-2.29 (m, 2H, CHS*CH*<sub>2</sub>), 1.92-1.81 (m, 2H, *CH*<sub>2</sub>CH<sub>2</sub>Cl), 1.38 (t, 3H, J=7.1Hz, OCH<sub>2</sub>CH<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 210.17 (C=S), 166.6 (C=O), 134.3 (CPhth), 131.3 (CPhth), 123.5 (CPhth), 70.4 (OCH<sub>2</sub>CH<sub>3</sub>), 56.8 (CHS), 43.5 (CH<sub>2</sub>Cl), 30.6 (CHSCH<sub>2</sub>), 29.3 (CH<sub>2</sub>CH<sub>2</sub>Cl), 13.6(OCH<sub>2</sub>CH<sub>3</sub>);

IR (CCl<sub>4</sub>): vmax 2934, 1767, 1731, 1386, 1232, 1076;

**HRMS (EI+)**: m/z calculated (found) for C<sub>15</sub>H<sub>16</sub>ClNO<sub>3</sub>S<sub>2</sub>: 357.0260 (357.0266); MP: 132~133 °C.

#### 8-Chloro-5-(1,3-dioxoisoindolin-2-yl)octanenitrile (3-32-1)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-30** (100 mg, 0.28 mmol) and allyl cyanide (40 mg, 0.33 mmol),

and needed 30 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 54 mg **3-32-1** (yield: 64%) as a pale yellow oil.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.88-7.79 (m, 2H, CHPhth), 7.79-7.70 (m, 2H, CHPhth), 4.27-4.18 (1H, m, NCH), 3.59-3.48 (m, 2H, *CH*<sub>2</sub>Cl), 2.36 (t, 2H, J=7.2Hz, CH<sub>2</sub>CN), 2.31-2.23 (m, 2H, NCHC*H*H, NCHCH*H*), 1.98-1.83 (m, 2H, NCHCH*H*, NCHC*H*H), 1.77-1.68 (m, 2H, *CH*<sub>2</sub>CH<sub>2</sub>Cl), 1.67-1.57 (m, 2H, NCHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  168.5 (NCO), 134.2 (CHPhth), 131.4 (CqPhth), 123.4 (CHPhth), 119.1 (*C*N), 50.2 (N*C*H), 44.1(*C*H<sub>2</sub>Cl), 31.3 (NCH*C*H<sub>2</sub>), 29.5 (NCH*C*H<sub>2</sub>), 29.4 (*C*H<sub>2</sub>CH<sub>2</sub>Cl), 22.5 (*C*H<sub>2</sub>CH<sub>2</sub>CN), 16.7 (*C*H<sub>2</sub>CN);

IR (CCl<sub>4</sub>): vmax 2938, 1771, 1733, 1389, 1236, 1078;

**HRMS (EI+)**: m/z calculated (found) for C<sub>16</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>2</sub>: 304.0979 (304.0985).

7-Chloro-4-(1,3-dioxoisoindolin-2-yl)heptyl acetate (3-32-2)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-30** (100 mg, 0.28 mmol) and allyl acetate (56 mg 0.56 mmol), and needed 30 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate,  $10:1\sim4:1 \text{ v/v}$ ) afforded 94 mg **3-32-2** (yield: 68%) as a colorless oil.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.86-7.77 (m, 2H, CHPhth), 7.77-7.66 (m, 2H, CHPhth), 4.28-4.19 (1H, m, NCH), 4.04 (t, 2H, J=6.5Hz, CH<sub>2</sub>OAc), 3.56-3.47 (m, 2H, CH<sub>2</sub>Cl), 2.26-2.17 (m, 2H, NCHCH<sub>2</sub>), 2.01 (s, 3H, OAc), 1.96-1.87 (m, 1H, NCHCHH), 1.85-1.78 (m, 1H, NCHCHH), 1.76-1.65 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>Cl), 1.28-1.19 (m, 2H, NCHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 171 (OCOCH<sub>3</sub>), 168.6 (NCO), 134 (CHPhth),

131.5 (CqPhth), 123.3 (CHPhth), 63.8 (CH<sub>2</sub>OAc) 50.9 (NCH), 44.2 (CH<sub>2</sub>Cl), 29.6 (NCHCH<sub>2</sub>), 29.5 (NCHCH<sub>2</sub>), 28.9 (CH<sub>2</sub>CH<sub>2</sub>Cl), 25.8 (CH<sub>2</sub>CH<sub>2</sub>OAc), 20.1 (OCH<sub>3</sub>);  $v_{max}$ (CCl<sub>4</sub>)/cm<sup>-1</sup>: 2989, 1712, 1766, 1389, 1268, 1046;

HRMS (EI+): *m/z* calculated (found) for C<sub>17</sub>H<sub>20</sub>ClNO<sub>4</sub>: 337.1081 (337.1087).

2-(1-Chloro-7-(trimethylsilyl)heptan-4-yl)isoindoline-1,3-dione (3-32-3)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-30** (100 mg, 0.28 mmol) and allyl trimethylsilane (96 mg, 0.84 mmol), and needed 30 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 5:1 v/v) afforded 96 mg **3-32-3** (yield: 61%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.88-7.79 (m, 2H, CHPhth), 7.78-7.67 (m, 2H, CHPhth), 4.28-4.19 (1H, m, NCH), 3.57-3.47 (m, 2H, *CH*<sub>2</sub>Cl), 2.22-2.11 (m, 2H, NCHC*H*<sub>2</sub>), 1.92-1.83 (m, 1H, NCHCH*H*), 1.77-1.69 (m, 3H, NCHC*H*H, *CH*<sub>2</sub>CH<sub>2</sub>Cl), 1.31-1.20 (m, 2H, NCHCH<sub>2</sub>C*H*<sub>2</sub>), 0.53-0.42 (m, 2H, *CH*<sub>2</sub>TMS), -0.09 (s, 9H, TMS); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  168.7 (NCO), 134 (CHPhth), 131.7 (CqPhth), 123.1 (CHPhth), 50.9 (NCH), 44.4 (*C*H<sub>2</sub>Cl), 36 (NCH*C*H<sub>2</sub>), 29.7 (NCH*C*H<sub>2</sub>), 29.6 (*C*H<sub>2</sub>CH<sub>2</sub>Cl), 20.9 (*C*H<sub>2</sub>CH<sub>2</sub>TMS), 16.093 (*C*H<sub>2</sub>TMS), -1.8 (TMS);

IR (CCl<sub>4</sub>): vmax 2934, 1756, 1346, 1287, 1023;

HRMS (EI+): *m/z* calculated (found) for C<sub>18</sub>H<sub>26</sub>ClNO<sub>2</sub>Si: 351.1421 (351.1416).

2,2'-(7-Chloroheptane-1,4-diyl)bis(isoindoline-1,3-dione) (3-32-4)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-30** (100 mg, 0.28 mmol) and 2-allylisoindoline-1,3-dione (104 mg, 0.56 mmol), and needed 35 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 116 mg **3-32-4** (yield: 64%) as a colorless oil.

<sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>)**: δ<sub>H</sub> 7.85-7.76 (m, 4H, CHPhth), 7.75-7.64 (m, 4H, CHPhth), 4.30-4.21 (1H, m, NCH), 3.71-3.62 (m, 2H, N*CH*<sub>2</sub>), 3.5 (t, 2H, J=6.3Hz, *CH*<sub>2</sub>Cl), 2.27-2.16 (m, 2H, NCH*CH*<sub>2</sub>), 1.92-1.84 (m, 1H, NCH*CHH*), 1.77-1.65 (m, 5H, NCH*CH*H, *CH*<sub>2</sub>CH<sub>2</sub>Cl, NCHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 168.5, 168.3 (NCO), 134, 133.9 (CHPhth), 132, 131.6 (CqPhth), 123.3, 123.2 (CHPhth), 50.8 (NCH), 44.2 (CH<sub>2</sub>Cl), 37.3 (NCH<sub>2</sub>), 29.6 (NCHCH<sub>2</sub>), 29.5 (NCHCH<sub>2</sub>), 29.5 (CH<sub>2</sub>CH<sub>2</sub>Cl), 25.7 (CH<sub>2</sub>NCH<sub>2</sub>);

IR (CCl<sub>4</sub>): vmax 2937, 1718, 1773, 1356, 1244, 1038;

**HRMS (EI+)**: m/z calculated (found) for C<sub>23</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>4</sub>: 424.1190 (424.1198).

#### 2-(1-Chloro-7-(4-methoxyphenyl)heptan-4-yl)isoindoline-1,3-dione (3-32-5)



Following the general procedure A for radical addition, the reaction was carried out

with a solution of 3-30 (100 mg, 0.28 mmol) and allyl phenyl ether (75 mg, 0.56 mmol), and needed 40 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 10:1 v/v) afforded 72 mg 3-32-5 (yield: 67%) as a pale yellow oil. <sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>):**  $\delta_{\rm H}$  7.87-7.76 (m, 2H, CHPhth), 7.75-7.68 (m, 2H, CHPhth), 7.03 (d, 2H, J=8.6Hz, Ar), 6.78 (d, 2H, J=8.6Hz, Ar), 4.31-4.22 (1H, m, NCH), 3.76 (s, 3H, ArOCH<sub>3</sub>), 3.55-3.46 (m, 2H, CH<sub>2</sub>Cl), 2.60-2.49 (m, 2H, CH<sub>2</sub>Ar), 2.22-2.13 (m, 2H, NCHCH<sub>2</sub>), 1.93-1.82 (m, 1H, NCHCHH), 1.78-1.63 (m, 3H, NCHCHH, CH<sub>2</sub>CH<sub>2</sub>Cl,), 1.59-1.50 (m, 2H, NCHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 168.7 (NCO), 157.8 (Ar), 134.03 (CHPhth), 134 (Ar), 131.7 (CqPhth), 129.3 (Ar), 123.3 (CHPhth), 113.8 (Ar), 55.3 (ArOCH<sub>3</sub>), 51.2 (NCH), 44.4 (CH<sub>2</sub>Cl), 34.5 (CH<sub>2</sub>Ar), 31.9 (NCHCH<sub>2</sub>), 29.7 (NCHCH<sub>2</sub>), 28.7 (CH<sub>2</sub>CH<sub>2</sub>Cl), 25.2 (CH<sub>2</sub>CH<sub>2</sub>Ar);

IR (CCl<sub>4</sub>): vmax 2946, 1778, 1723, 1343, 1223, 1067;

**HRMS (EI+):** m/z calculated (found) for C<sub>22</sub>H<sub>24</sub>ClNO<sub>3</sub>: 385.1445 (385.1442).

#### 2-(3-(4-Methoxyphenyl)propyl)-1-tosylpyrrolidine (3-33)



To a solution of 3-32-5 (72 mg, 0.18 mmol) in methanol (0.5 ml) was added 0.9 ml hydrazine in methanol (1M). The reaction was heated to reflux for 1h. Then the resulting solution was filtrated and the filtrate was concentrated under reduced pressure to get the residue. Without further purification, the residue was dissolved in 0.5 ml DCM and then 4-toluenesulfonyl chloride (35 mg, 0.18 mmol) and triethylamine (18 mg, 0.18 mmol) were added into the solution, which was stirred at room temperature for 8h. Finally, the solution was concentrated under reduced pressure to obtain the residue which was then purified by column chromatography using petroleum ether: ethyl acetate,  $10:1\sim4:1 \text{ v/v}$ , to afford 48 mg **3-33** (yield: 71%) as a pale yellow stick liquid.

<sup>1</sup>**H NMR** (**400 MHz**; **CDCl**<sub>3</sub>):  $\delta_{\rm H}$  7.70 (d, 2H, J=8.2Hz, Ts), 7.29 (d, 2H, J=8.2Hz, Ts), 7.10 (d, 2H, J=8.1Hz, Ar), 6.83 (d, 2H, J=8.6Hz, Ar), 3.79 (s, 3H, ArOC*H*<sub>3</sub>), 3.69-3.58 (m, 1H, NC*H*), 3.39-3.30 (m, 1H, NC*H*H), 3.24-3.16 (m, 1H, NCH*H*), 2.61-2.53 (m, 2H, ArC*H*<sub>2</sub>), 2.42 (s, 3H, ArC*H*<sub>3</sub>), 1.89-1.79 (m, 1H, NCH<sub>2</sub>C*H*H), 1.79-1.68 (m, 1H, NCH<sub>2</sub>CH*H*), 1.67-1.56 (m, 3H, NCHC*H*H, CHCH<sub>2</sub>C*H*<sub>2</sub>), 1.57-1.45 (m, 3H, NCHCH*H*, CHCH<sub>4</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  157.7 (Ar), 143.1 (Ts), 135 (Ts), 134.5 (Ar), 129.6 (Ar), 129.2 (Ts), 127.4 (Ts), 113.7 (Ar), 60.4 (OCH<sub>3</sub>), 55.2 (NCH<sub>2</sub>), 48.8 (NCH), 36.1 (CH<sub>2</sub>Ar), 34.9 (CHCH<sub>2</sub>), 30.7 (CHCH<sub>2</sub>), 28.3 (CH<sub>2</sub>CH<sub>2</sub>Ar), 24.1(NCH<sub>2</sub>CH<sub>2</sub>), 21.5 (ArCH<sub>3</sub>);

IR (CCl<sub>4</sub>): vmax 2986, 1778, 1722, 1333, 1287, 1054;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>21</sub>H<sub>27</sub>NO<sub>3</sub>S: 373.1712 (373.1717).

Dithiocarbonic acid [1,3-bis-(1,3-dioxo-1,3-dihydroisoindol-2-yl)] ester ethyl ester (3-34)



To a solution of **3-5** (3 g, 9.00 mmol) in CCl<sub>4</sub> (150 ml), NBS (1.92g, 10.08 mmol) was added, then the solution was heated at reflux under nitrogen for 3 h; the reaction was initiated by irradiation with a 300 W lamp. The reaction mixture was then cooled, filtered and washed with sodium thiosulfate. After extracting the solution with DCM, the organic layer was concentrated under reduced pressure to yield 3.2 g **3-6** (86%) without further purification. **3-6** (3.2 g, 7.7 mmol) was dissolved in acetone (2 ml per mmol). Under nitrogen protection KSCSOEt (1.36 g, 8.5 mmol) was added portion

wise over a period of five minutes. It was then left to stir for further twenty minutes before the acetone was evaporated off under reduced pressure. The residue was then taken up in DCM/H<sub>2</sub>O and extracted. The DCM layers were dried over Na<sub>2</sub>SO<sub>4</sub> before being filtered and evaporated under reduced pressure to yield the crude xanthate. This was then purified by column chromatography using petroleum ether: ethyl acetate,  $10:1\sim2:1 \text{ v/v}$  to obtain 2.9 g **3-34** (83%) as a white solid which was crystallized from ethyl acetate/ petroleum ether.

<sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>)**: δ<sub>H</sub> 7.88-7.79 (m, 2H, CHPhth), 7.85-7.76 (m, 2H, CHPhth), 7.78-7.69 (m, 2H, CHPhth), 7.75-7.64 (m, 2H, CHPhth), 6.31-6.22 (m, 1H,CHS) 4.61 (q, 2H, J=7.1Hz, COC*H*<sub>2</sub>CH<sub>3</sub>), 3.84-3.75 (m, 2H, NC*H*<sub>2</sub>), 2.77-2.68 (m, 2H, CHSC*H*<sub>2</sub>), 1.36 (t, 3H, J=7.1Hz, COCH<sub>2</sub>C*H*<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 210.2 (C=S), 168 (C=O), 166.6 (C=O), 134.3, 134 (CPhth), 131.8, 131.5 (CqPhth), 123.6, 123.2 (CPhth), 70.4 (OCH<sub>2</sub>CH<sub>3</sub>), 54.9 (CHS), 35 (CHSCH<sub>2</sub>), 31.4 (NCH<sub>2</sub>), 13.6 (OCH<sub>2</sub>CH<sub>3</sub>);

IR (CCl<sub>4</sub>): vmax 2983, 1777, 1724, 1542, 1394, 1228, 1112, 1049;

**HRMS (EI+)**: m/z calculated (found) for C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4</sub> [M-SCSOEt]: 333.0875 (333.0868); MP: 143~144 °C.

5,7-bis-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-heptanenitrile (3-35-1)



Following the general procedure A for radical addition, the reaction was carried out with a solution of Xanthate **3-34** (100 mg, 0.22 mmol) and allyl cyanide (23 mg, 0.33 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum

ether: ethyl acetate, 2:1 v/v) afforded 62 mg **3-35-1** (yield: 71%) as a pale yellow oil. <sup>1</sup>H NMR (**400 MHz; CDCl<sub>3</sub>**): δ<sub>H</sub> 7.85-7.76 (m, 2H, CHPhth), 7.82-7.73 (m, 2H, CHPhth), 7.77-7.68 (m, 2H, CHPhth), 7.74-7.65 (m, 2H, CHPhth), 4.27-4.18 (1H, m, NCH), 3.72-3.63 (m, 2H, NCH<sub>2</sub>), 2.62-2.53 (m, 1H, NCH<sub>2</sub>C*H*H), 2.39-2.28 (m, 3H, *CH*<sub>2</sub>CN, NCH<sub>2</sub>CH*H*), 2.28-2.19 (m, 1H, CH*H*CH<sub>2</sub>CN), 1.95-1.86 (m, 1H, *CH*HCH<sub>2</sub>CN), 1.66-1.57 (m, 2H, NCHCH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 168.5 (NCO), 168.2 (NCO), 134.2, 134 (CHPhth),
132, 131.7 (CqPhth), 123.4, 123.3 (CHPhth), 119.1 (CN), 48.3 (NCH), 35.2 (NCH<sub>2</sub>),
31.5 (NCH<sub>2</sub>CH<sub>2</sub>), 30.6 (NCHCH<sub>2</sub>), 22.5(CH<sub>2</sub>CH<sub>2</sub>CN), 16.8 (CH<sub>2</sub>CN);
IR (CCl<sub>4</sub>): vmax 2927, 1776, 1718, 1544, 1468, 1375, 1146, 1070;

**HRMS (EI+)**: m/z calculated (found) for C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>: 401.1376 (401.1380).

#### 2,2'-(6-Phenoxyhexane-1,3-diyl)-bis-(isoindoline-1,3-dione) (3-35-2)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-34** (100 mg, 0.22 mmol) and allyloxybenzene (44 mg, 0.33 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 68 mg **3-35-2** (yield: 66%) as a pale yellow oil. <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.87-7.78 (m, 2H, CHPhth), 7.81-7.72 (m, 2H,

CHPhth), 7.75-7.74 (m, 2H, CHPhth), 7.71-7.63 (m, 2H, CHPhth), 7.22 (dt, 2H, CHAr, J=7.5Hz, J=8.5Hz), 6.88 (t, 1H, CHAr, J=7.3Hz), 6.82 (d, 2H, CHAr, J=7.9Hz), 4.32-4.25 (1H, m, NCH), 3.91 (t, 2H, CH<sub>2</sub>OPh, J=1.3Hz, J=6.3Hz), 3.79-3.70 (m, 2H,

NCH<sub>2</sub>), 2.62-2.51 (m, 1H, NCH<sub>2</sub>C*H*H), 2.36-2.27 (m, 1H, NCH<sub>2</sub>C*H*H), 2.27-2.18 (m, 1H, CH*H*CH<sub>2</sub>OPh), 1.99-1.91 (m, 1H, C*H*HCH<sub>2</sub>OPh), 1.78-1.67 (m, 2H, NCHC*H*<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\rm C}$  168.5, 168.1 (NCO), 158.8 (CqPh), 133.9, 133.8 (CHPhth), 132, 131.8 (CqPhth), 129.3 (CHPh), 123.2, 123.1 (CHPhth), 120.5 (CHPh), 114.4 (CHPh), 67 (*C*H<sub>2</sub>OPh), 49.1(NCH), 35.3 (NCH<sub>2</sub>), 30.6 (NCH<sub>2</sub>CH<sub>2</sub>), 29.1 (NCH*C*H<sub>2</sub>), 26.2 (*C*H<sub>2</sub>CH<sub>2</sub>O),

IR (CCl<sub>4</sub>): vmax 2927, 1774, 1719, 1558, 1374, 1244, 1172, 1078;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub>: 468.1685 (468.1699).

#### 2,2'-(6-(2-Oxocyclohexyl)hexane-1,3-diyl)bis(isoindoline-1,3-dione) (3-35-3)



3-35-3

Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-34** (100 mg, 0.22 mmol) and 2-allylcyclohexanone (46 mg, 0.33 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 64 mg **3-35-3** (yield: 62%) as a colorless oil and a mixture of two diastereoisomers in a ratio 1:1.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>): *Mixture of diastereoisomer* :  $\delta_{\rm H}$  7.82-7.73 (m, 4H, CHPhth), 7.73-7.62 (m, 4H, CHPhth), 4.25-4.16 (1H, m, NCH), 3.70-3.61 (m, 2H, NCH<sub>2</sub>), 2.58-2.49 (m, 1H, NCH<sub>2</sub>CH*H*), 2.29-2.18 (m, 4H, NCH<sub>2</sub>C*H*H, COCH<sub>2</sub>, COCH ), 2.06-1.93 (m, 3H, COCH<sub>2</sub>C*H*H, COCH<sub>2</sub>CH<sub>2</sub>C*H*H, COCHCH<sub>2</sub>C*H*H, COCHCH<sub>2</sub>C*H*H, NCHCH<sub>2</sub>, 1.81-1.54 (m, 6H, COCH<sub>2</sub>CH*H*, COCH<sub>2</sub>CH*H*, COCHCH<sub>2</sub>CH*H*, NCHCH<sub>2</sub>,

#### COCH*C*H*H*), 1.26-1.13 (m, 3H, COCH*C*HH, CHCH<sub>2</sub>CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Mixture of diastereoisomer* :  $\delta_{\rm C}$  213, 212.9 (CO), 168.6, 168.1 (NCO), 133.9, 133.8 (CHPhth), 132, 131.8 (CqPhth), 123.179, 123.136 (CHPhth), 50.4, 50.3 (NCH), 49.3, 49.2 (COCH), 41.9 (COCH<sub>2</sub>), 35.3 (NCH<sub>2</sub>), 34, 33.8 (COCHCH<sub>2</sub>), 32.7, 32.6 (NCHCH<sub>2</sub>), 30.4 (NCHCH<sub>2</sub>CH<sub>2</sub>N), 29, 28.9 (COCH<sub>2</sub>CH<sub>2</sub>), 27.97, 27.92 (COCHCH<sub>2</sub>), 24.9, 24.8 (COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 24.1, 24 (COCHCH<sub>2</sub>CH<sub>2</sub>);

IR (CCl<sub>4</sub>): vmax 2924, 1774, 1717, 1558, 1374, 1251, 1005;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>: 472.1998 (472.1998).

2,2'-(6-Phenylhexane-1,3-diyl)bis(isoindoline-1,3-dione) (3-35-4)



3-35-4

Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-34** (100 mg, 0.22 mmol) and allylbenzene (39 mg, 0.33 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) afforded 67 mg **3-35-4** (yield: 68%) as a colorless oil.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.84-7.73 (m, 4H, CHPhth), 7.74-7.65 (m, 4H, CHPhth), 7.26-7.17 (m, 2H, CHAr), 7.15-7.08 (m, 3H, CHAr), 4.30-4.21 (1H, m, NCH), 3.75-3.59 (m, 2H, NCH<sub>2</sub>), 2.60-2.51 (m, 3H, NCH<sub>2</sub>C*H*H, CH<sub>2</sub>Ph), 2.31-2.22 (m, 1H, NCH<sub>2</sub>CH*H*), 2.16-2.07 (m, 1H, CH*H*CH<sub>2</sub>Ph), 1.83-1.72 (m, 1H, C*H*HCH<sub>2</sub>Ph), 1.59-1.51 (m, 2H, NCHC*H*<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 168.6, 168.1 (NCO), 141.8 (CqPh), 133.9, 133.8

(CHPhth), 132, 131.8 (CqPhth), 128.32, 128.25 (CHPh), 125.8 (CHPh), 123.2 (CHPhth), 49.1 (NCH), 35.4 (NCH<sub>2</sub>), 35.3 (CH<sub>2</sub>Ph), 32.1 (NCH*C*H<sub>2</sub>), 30.5 (NCH<sub>2</sub>*C*H<sub>2</sub>), 28.2 (*C*H<sub>2</sub>CH<sub>2</sub>Ph);

IR (CCl<sub>4</sub>): vmax 2928, 1774, 1717, 1558, 1468, 1374, 1172, 1072, 1005;

**HRMS (EI+)**: m/z calculated (found) for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>: 452.1736 (452.1745).

4,6-bis(1,3-Dioxoisoindolin-2-yl)hexyl acetate (3-35-5)



3-35-5

Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-34** (82 mg, 0.18 mmol) and allyl acetate (33 mg, 0.33 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1) afforded 55 mg product **3-35-5** (yield: 71%) as a colorless oil.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.85-7.76 (m, 4H, CHPhth), 7.75-7.66 (m, 4H, CHPhth), 4.29-4.21 (1H, m, NCH), 4.02 (t, 2H, CH<sub>2</sub>OAc, J=6.5Hz), 3.64-3.63 (m, 2H, NCH<sub>2</sub>), 2.61-2.52 (m, 1H, NCH<sub>2</sub>C*H*H), 2.33-2.25 (m, 1H, NCH<sub>2</sub>CH*H*), 2.17-2.08 (m, 1H, CH*H*CH<sub>2</sub>OAc), 2.0 (s, 3H, OCH<sub>3</sub>), 1.88-1.78 (m, 1H, C*H*HCH<sub>2</sub>OAc), 1.61-1.52 (m, 2H, NCHC*H*<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  171 (COCH<sub>3</sub>), 168.5 (NCO), 168.2(NCO), 134, 133.9 (CHPhth), 132, 131.7 (CqPhth), 123.229, 123.203 (CHPhth), 63.8 (CH<sub>2</sub>O), 49 (NCH), 35.2 (NCH<sub>2</sub>), 30.5 (NCH<sub>2</sub>CH<sub>2</sub>), 29.1 (NCHCH<sub>2</sub>), 25.6 (CH<sub>2</sub>CH<sub>2</sub>O), 20.9 (OCH<sub>3</sub>);

**IR** (**CCl**<sub>4</sub>): vmax 2927, 1773, 1712, 1558, 1468, 1365, 1235, 1172, 1038;

**HRMS (EI+):** m/z calculated (found) for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> [M-OAc]: 374.1345(374.1352).

Dithiocarbonic acid [1,3-bis-(1,3-dioxo-1,3-dihydroisoindol-2-yl)-3-ethoxythio -carbony lsulfanyl] ester *O*-ethyl ester (3-36)



**3-5** (3 g, 9.00 mmol), NBS (3.22 g, 18.08 mmol) in CCl<sub>4</sub> (150 ml) was heated at reflux under nitrogen for 3 h; the reaction was initiated by irradiation with a 300 W lamp. The reaction mixture was then cooled, filtered and washed with sodium thiosulfate. After extracting the solution with DCM, the organic layer was concentrated under reduced pressure to yield 3.7 g **3-7** (yield: 85%) without further purification. **3-7** (3.7 g, 7.7 mmol) was dissolved in acetone (2 ml per mmol). KSCSOEt (2.6 g, 16 mmol) was added portion wise over a period of five minutes. It was then left to stir for further half hour before the acetone was evaporated off under reduced pressure. The residue was then taken up in DCM/H<sub>2</sub>O and extracted. The DCM layers were dried over Na<sub>2</sub>SO<sub>4</sub> before being filtered and evaporated under reduced pressure to yield the crude xanthate. This was then purified by column chromatography using petroleum ether: ethyl acetate,  $10:1\sim2:1$  v/v, to obtain 2.6 g **3-36** (72%) and as a mixture of two diastereoisomers in a ratio 1.1:1. One diasereoisomer as a pale yellow solid was crystallized from ethyl acetate/ petroleum ether and another one as yellow oil remained in the solvent.

<sup>1</sup>**H NMR (400 MHz; CDCl<sub>3</sub>)**: *Diastereoisomer 1*: δ<sub>H</sub> 7.88-7.77 (m, 4H, CHPhth), 7.78-7.70 (m, 4H, CHPhth), 6.47 (dt, 2H, J=7.1Hz, J=8.7Hz, CHS), 4.70-4.59 (m, 4H,

J=7.1Hz, COC*H*<sub>2</sub>CH<sub>3</sub>), 3.45-3.34 (m, 1H, CHSC*H*HCHS), 3.21-3.10 (m, 1H, CHSCH*H*CHS), 1.42 (t, 6H, J=7.1Hz, 2COCH<sub>2</sub>C*H*<sub>3</sub>) *Diastereoisomer* 2: δ<sub>H</sub> 7.88-7.77 (m, 4H, CHPhth), 7.78-7.70 (m, 4H, CHPhth), 6.28-6.19 (m, 2H, CHS), 4.70-4.59 (m, 4H, J=7.1Hz, COC*H*<sub>2</sub>CH<sub>3</sub>), 3.30 (dd, 2H, J=8.3Hz, CHSC*H*<sub>2</sub>CHS), 1.31 (t, 6H, J=7.1Hz, 2COCH<sub>2</sub>C*H*<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{C}$  209.7 (C=S), 166.3 (C=O), 134.4 (CPhth), 131.4 (CqPhth), 123.5 (CPhth), 70.7 (OCH<sub>2</sub>), 54.7 (CHS), 36.2 (CH<sub>2</sub>), 13.6 (OCH<sub>2</sub>CH<sub>3</sub>);*Diastereoisomer* 2:  $\delta_{C}$  209.6 (C=S), 166.7 (C=O), 134.5 (CPhth), 131.6 (CqPhth), 123.7 (CPhth), 70.6 (OCH<sub>2</sub>), 54 (CHS), 36.1 (CH<sub>2</sub>), 13.5 (OCH<sub>2</sub>CH<sub>3</sub>);

IR (CCl<sub>4</sub>): vmax 2926, 1783, 1724, 1558, 1376, 1226, 1112, 1046;

**HRMS (EI+)**: m/z calculated (found) for C<sub>22</sub>H<sub>17</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub> [M-SCSOEt]: 453.0579 (453.0573).MP: *Diastereoisomer 1*: 172-173 °C

5,7-bis(1,3-Dioxoisoindolin-2-yl)undecanedinitrile (3-37-1)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and allyl cyanide (70 mg, 1.05 mmol), and needed 25 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 1:1 v/v) afforded 99 mg **3-37-1** (yield: 61%) as a colorless oil and two diastereoisomers in a ratio 2:1.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{\rm H}$  7.87-7.76 (m, 4H, CHPhth), 7.79-7.70 (m, 4H, CHPhth), 4.09-4.00 (m, 2H, 2NCH), 2.80-2.65 (m, 2H, CHCH<sub>2</sub>CH), 2.28 (t, 4H, J=7.2Hz, 2CH<sub>2</sub>CN), 2.18-2.07 (m, 2H, 2CHHCH<sub>2</sub>CN,), 1.89-1.78 (m, 2H, 2CHHCH<sub>2</sub>CN), 1.60-1.50 (m, 4H, 2NCHCH<sub>2</sub>); *Diastereoisomer* 2:  $\delta_{\rm H}$  7.67-7.54 (m, 8H, CHPhth), 4.29-4.17 (m, 2H, 2NCH), 2.99-2.88 (m, 1H, CHCHHCH ), 2.32 (t, 4H, J=7.2Hz, 2CH<sub>2</sub>CN), 2.32-2.20 (m, 1H, CHCHHCH ), 2.28-2.17 (m, 2H, 2CHHCH<sub>2</sub>CN,), 1.91-1.82 (m, 2H, 2CHHCH<sub>2</sub>CN), 1.62-1.50 (m, 4H, 2NCHCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{\rm C}$  168.5 (C=O), 134.2 (CPhth), 131.6 (CqPhth), 123.4 (CHPhth), 118.9 (CN), 47.5 (NCH), 33.5 (CHCH<sub>2</sub>CH), 31.9 (CHCH<sub>2</sub>CH<sub>2</sub>), 22.4 (*C*H<sub>2</sub>CH<sub>2</sub>CN), 16.7 (CH<sub>2</sub>CH<sub>2</sub>CN);*Diastereoisomer* 2:  $\delta_{\rm C}$  168.1 (C=O), 134.1 (CPhth), 131.2 (CqPhth), 123.1 (CHPhth), 119 (CN), 48.8 (NCH), 34.7 (CHCH<sub>2</sub>CH<sub>4</sub>), 31.3 (CHCH<sub>2</sub>CH<sub>2</sub>), 22.3 (*C*H<sub>2</sub>CH<sub>2</sub>CN), 16.6 (CH<sub>2</sub>CH<sub>2</sub>CN); **IR** (CCl<sub>4</sub>): vmax 2927, 1773, 1715, 1466, 1377, 1170, 1089;

**HRMS (EI+)**: *m/z* calculated (found) for C<sub>27</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>: 468.1798 (468.1816).

#### 2,2'-(1,9-Diphenoxynonane-4,6-diyl)bis(isoindoline-1,3-dione) (3-37-2)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and allyloxybenzene (140 mg, 1.05 mmol), and needed 25 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 112 mg **3-37-2** (yield: 53%) as a colorless oil

and two diastereoisomers in a ratio 2.4:1.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>): *Diastereoisomer 1*:  $\delta_{\rm H}$  7.87-7.74 (m, 4H, CHPhth), 7.78-7.65 (m, 4H, CHPhth), 7.28-7.13 (m, 4H, CHAr), 6.88 (t, 2H, J=7.3Hz, CHAr), 6.79 (d, 4H, J=7.8Hz, CHAr), 4.19-4.08 (m, 2H, 2NCH), 3.86 (t, 4H, J=6.3Hz, 2CH<sub>2</sub>OPh), 2.81-2.72 (m, 2H, J=7.4Hz, J=8.9Hz, CHC*H*<sub>2</sub>CH), 2.19-2.11 (m, 2H, 2C*H*HCH<sub>2</sub>OPh), 1.91 (m, 2H, 2C*H*HCH<sub>2</sub>OPh), 1.73-1.62 (m, 4H, 2NCHC*H*<sub>2</sub>); *Diastereoisomer 2*:  $\delta_{\rm H}$  7.66-7.53 (m, 8H, CHPhth), 7.18-7.07 (m, 4H, CHAr), 6.84 (t, 2H, J=7.3Hz, CHAr), 6.71 (d, 4H, J=7.8Hz, CHAr), 4.31-4.21 (m, 2H, 2NCH), 3.86 (t, 4H, J=6.3Hz, 2CH<sub>2</sub>OPh), 2.98-2.87 (m, 1H, CHC*H*HCH), 2.64-2.51 (m, 1H, CHCH*H*CH ), 2.22-2.11 (m, 2H, 2C*H*HCH<sub>2</sub>OPh), 1.96-1.87 (m, 2H, 2CH*H*CH<sub>2</sub>OPh), 1.76-1.61 (m, 4H, 2NCHC*H*<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Diastereoisomer 1*: δ<sub>C</sub> 168.7 (C=O), 158.8 (OCqPh), 133.9 (CPhth), 131.8 (CqPhth), 129.3 (CHPh), 123.2 (CHPhth), 120.5 (CHPh), 114.4 (CHPh), 67 (CH<sub>2</sub>OPh), 48.4 (NCH), 33.9 (CHCH<sub>2</sub>CH), 29.5 (CHCH<sub>2</sub>CH<sub>2</sub>), 26.3 (*C*H<sub>2</sub>CH<sub>2</sub>OPh);

*Diastereoisomer* 2: δ<sub>C</sub> 168.2 (C=O), 158.6 (OCqPh), 133.7 (CPhth), 131.4 (CqPhth), 129.2 (CHPh), 122.8 CHPhth), 120.4 (CHPh), 114.3 (CHPh), 66.8 (CH<sub>2</sub>OPh), 48.3 (NCH), 33.7 (CHCH<sub>2</sub>CH), 29.4 (CHCH<sub>2</sub>CH<sub>2</sub>), 26.2 (CH<sub>2</sub>CH<sub>2</sub>OPh);

**IR** (**CCl**<sub>4</sub>): vmax 2927, 1774, 1713, 1600, 1497, 1375, 1244, 1172, 1046;

**HRMS**: *m/z* calculated (found) for C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub> [M-OC<sub>6</sub>H<sub>5</sub>]: 509.2077 (509.2066).

#### 4,6-bis(1,3-dioxoisoindolin-2-yl)nonane-1,9-diyl diacetate (3-37-2)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and allyl acetate (105 mg, 1.05 mmol),

and needed 25 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 105 mg 3-37-2 (yield: 24%) as a colorless oil and as a mixture of two diastereoisomers in a ratio 1.9:1.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>): *Diastereoisomer 1*:  $\delta_{\rm H}$  7.79 (m, 4H, CHPhth), 7.72 (m, 4H, CHPhth), 4.24 (m, 2H, 2NCH), 3.98 (m, 4H, 2CH<sub>2</sub>OAc), 2.70 (m, 2H, J=7.3Hz, J=9.0Hz, CHCH<sub>2</sub>CH), 2.17 (m, 2H, 2CHHCH<sub>2</sub>OAc), 1.99 (s, 6H, 2OCH<sub>3</sub>), 1.77 (m, 2H, 2CHHCH<sub>2</sub>OAc), 1.50 (m, 4H, 2NCHCH<sub>2</sub>);

Diastereoisomer 2: δ<sub>H</sub> 7.61 (m, 8H, CHPhth), 4.24 (m, 2H, 2NCH), 3.98 (m, 4H, 2CH<sub>2</sub>OAc), 2.87 (m, 1H, CHCHHCH), 2.26 (m, 1H, CHCHHCH), 2.17 (m, 2H, 2CHHCH2OAc), 1.99 (s, 6H, 2OCH3), 1.77 (m, 2H, 2CHHCH2OAc), 1.50 (m, 4H,  $2NCHCH_2$ ;

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): Diastereoisomer 1: δ<sub>C</sub> 170.9 (CH<sub>3</sub>C=O), 168.6 (C=O), 134 (CPhth), 131.6 (CqPhth), 123.2 (CHPhth), 63.7(CH<sub>2</sub>OAc), 48.2 (NCH), 33.6 (CHCH<sub>2</sub>CH), 29.4 (CHCH<sub>2</sub>CH<sub>2</sub>), 25.5 (CH<sub>2</sub>CH<sub>2</sub>OAc), 20.8 (CH<sub>3</sub>C=O);

*Diastereoisomer* 2: δ<sub>C</sub> 170.8 (CH<sub>3</sub>C=O), 168.5 (C=O), 133.9 (CPhth), 131.6 (CqPhth), 123.1 (CHPhth), 63.7 (CH2OAc), 48.1 (NCH), 33.5 (CHCH2CH), 29.3 (CHCH2CH2), 25.5 (*C*H<sub>2</sub>CH<sub>2</sub>OAc), 20.7 (*C*H<sub>3</sub>C=O);

**IR (CCl4):** v max 2928, 1742, 1710, 1554, 1543, 1376, 1238, 1045;

**HRMS (EI+):** m/z calculated (found) for C<sub>29</sub>H<sub>30</sub>N<sub>2</sub>O<sub>8</sub>: 534.2002 (534.1995).

2,2'-(1,9-bis(Trimethylsilyl)nonane-4,6-diyl)bis(isoindoline-1,3-dione) (3-37-4)



Following the general procedure A for radical addition, the reaction was carried out

with a solution of **3-36** (200mg, 0.35 mmol) and allyl trimethylsilane (160 mg, 1.4 mmol), and needed 20 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 5:1 v/v) afforded 131 mg **3-37-4** (yield: 67%) as a colorless solid and two diastereoisomers in a ratio 1.9:1.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): Diastereoisomer 1:  $\delta_{\rm H}$  7.86-7.7- (m, 4H, CHPhth), (m, 4H, CHPhth), 4.13-4.01 (m, 2H, 2NCH), 2.69-2.59 (m, 2H, J=7.5Hz, 7.77-7.65 J=8.8Hz, CHCH<sub>2</sub>CH), 2.06-1.94 (m, 2H, 2NCHCHH), 1.76-1.60 (m, 2H, 2NCHCHH), 1.25-1.10 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>TMS), 0.48-0.31 (m, 4H, 2CH<sub>2</sub>TMS), -0.14 (s, 18H, 2TMS); *Diastereoisomer* 2: δ<sub>H</sub> 7.67-7.51 (m, 8H, CHPhth), 4.33-4.18 (m, 2H, 2NCH), 2.91-2.77 (m, 1H, CHCHHCH), 2.24-2.11 (m, 1H, CHCHHCH ), 2.08-1.93 2H, 2NCHCHH), 1.76-1.61 2H, 2NCHCHH), (m, (m, 1.25-1.10 (m, 4H,CH<sub>2</sub>CH<sub>2</sub>TMS), 0.57-0.41 (m, 4H, 2CH<sub>2</sub>TMS), -0.13 (s, 18H, 2TMS);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Diastereoisomer 1*:  $\delta_{C}$  168.7 (C=O), 133.8 (CPhth), 131.9 (CqPhth), 123.053 (CHPhth), 48.3 (NCH), 36.6 (CH*C*H<sub>2</sub>CH), 33.8 (CH*C*H<sub>2</sub>CH<sub>2</sub>), 20.716 (*C*H<sub>2</sub>CH<sub>2</sub>TMS), 16.1 (CH<sub>2</sub>*C*H<sub>2</sub>TMS), -1.8 (TMS); *Diastereoisomer 2*:  $\delta_{C}$  168.6 (C=O), 133.8 (CPhth), 131.7 (CqPhth), 122.8 (CHPhth), 48.2 (NCH), 36.5 (CH*C*H<sub>2</sub>CH), 33.7 (CH*C*H<sub>2</sub>CH<sub>2</sub>), 20.6 (*C*H<sub>2</sub>CH<sub>2</sub>TMS), 16 (CH<sub>2</sub>CH<sub>2</sub>TMS), -1.8 (TMS);

IR (CCl<sub>4</sub>): vmax 2954, 1773, 1712, 1468, 1375, 1249, 1173, 1053;

**HRMS (EI+)**: m/z calculated (found) for C<sub>31</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub>: 562.2683 (562.2688).MP: 122~125 °C

2,2'-(1,9-Diphenylnonane-4,6-diyl)bis(isoindoline-1,3-dione) (3-37-5)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and allylbenzene (124 mg, 1.05 mmol), and needed 30 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 116 mg **3-37-5** (yield: 58%) as a colorless oil and two diastereoisomers in a ratio 2.1:1.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{\rm H}$  7.85-7.74 (m, 4H, CHPhth), 7.75-7.68 (m, 4H, CHPhth), 7.25-7.16 (m, 4H, Ar), 7.17-7.08 (m, 2H, Ar), 7.12-7.01 (m, 4H, Ar), 4.14-4.03 (m, 2H, 2NCH), 2.72-2.63 (m, 2H CHCH<sub>2</sub>CH), 2.58-2.47 (m, 4H, 2CH<sub>2</sub>Ph), 2.06-1.97 (m, 2H, 2C*H*HCH<sub>2</sub>Ph), 1.77-1.66 (m, 2H, 2CH*H*CH<sub>2</sub>Ph), 1.53-1.42 (m, 4H, 2NCHCH<sub>2</sub>); *Diastereoisomer* 2:  $\delta_{\rm H}$  7.65-7.52 (m, 8H, CHPhth), 7.25-7.16 (m, 4H, Ar), 7.17-7.08 (m, 4H, Ar), 7.12-7.01 (m, 4H, Ar), 4.48-4.39 (m, 2H, 2NCH), 2.90-2.81 (m, 1H, CHCHHCH), 2.58-2.47 (m, 4H, 2CH<sub>2</sub>Ph), 1.81-1.72 (m, 2H, 2CH*H*CH<sub>2</sub>Ph), 1.57-1.42 (m, 4H, 2NCHCH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{C}$  168.7 (C=O), 133.9 (CPhth), 131.7 (CqPhth), 141.8, 128.3, 128.2, 125.7, 123.1 (Ar), 48.3 (NCH), 35.3 (CH<sub>2</sub>Ph), 33.7 (CH*C*H<sub>2</sub>CH), 32.4 (CH*C*H<sub>2</sub>CH<sub>2</sub>), 28.2 (CH<sub>2</sub>CH<sub>2</sub>Ph); *Diastereoisomer* 2:  $\delta_{C}$ 168.6 (C=O), 133.8 (CPhth), 131.7 (CqPhth), 128.3, 125.7, 122.9 (Ar), 48.3 (NCH), 35.3 (CH<sub>2</sub>Ph), 33.6 (CH*C*H<sub>2</sub>CH), 32.3 (CH*C*H<sub>2</sub>CH<sub>2</sub>), 28.1 (CH<sub>2</sub>CH<sub>2</sub>Ph);

IR (CCl<sub>4</sub>): vmax 2928, 1709, 1773, 1469, 1376, 1172, 1075;

**HRMS (EI+)**: *m/z* calculated (found) for: C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>: 570.2519 (570.2509).

2,2',2'',2'''-(Nonane-1,4,6,9-tetrayl)tetrakis(isoindoline-1,3-dione) (3-37-6)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and 2-allylisoindoline-1, 3-dione (196 mg, 1.05 mmol), and add 25 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 1:1 v/v) afforded 176 mg **3-37-6** (yield: 71%) as a colorless oil and two diastereoisomers in a ratio 2:1.

<sup>1</sup>**H NMR** (**400 MHz; CDCl**<sub>3</sub>): *Diastereoisomer 1*:  $\delta_{\rm H}$  7.87-7.76 (m, 8H, CHPhth), 7.79-7.68 (m, 8H, CHPhth), 4.14-4.03 (m, 2H, 2NCH), 3.69-3.58 (m, 4H, 2CH<sub>2</sub>NthPh), 2.77-2.65 (m, 2H, CHC*H*<sub>2</sub>CH), 2.11-2.02 (m, 2H, 2C*H*HCH<sub>2</sub>NthPh), 1.79-1.70 (m, 2H, 2CH*H*CH<sub>2</sub> NthPh), 1.61-1.52 (m, 4H, 2NCHC*H*<sub>2</sub>); *Diastereoisomer* 2:  $\delta_{\rm H}$  7.62-7.43 (m, 16H), 4.29-4.20 (m, 2H, 2NCH), 3.91-3.80 (m, 4H, 2CH<sub>2</sub>NthPh), 2.94-2.84 (m, 1H, CHC*H*HCH), 2.17-2.08 (m, 1H, CHC*HH*CH), 2.11-2.01 (m, 2H, 2C*H*HCH<sub>2</sub>NthPh), 1.78-1.69 (m, 2H, 2CH*H*CH<sub>2</sub> NthPh), 1.61-1.53 (m, 4H, 2NCHC*H*<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{C}$  168.6, 168.2 (C=O), 133.9, 133.8 (CPhth), 132, 131.7 (CqPhth), 123.2, 123.1 (CHPhth), 48.1 (NCH), 37.3 (CH<sub>2</sub>NthPh), 33.5 (CHCH<sub>2</sub>CH), 30.1 (CHCH<sub>2</sub>CH<sub>2</sub>), 25.6 (CH<sub>2</sub>CH<sub>2</sub>Phth); *Diastereoisomer* 2:  $\delta_{C}$  168.5, 168.4 (C=O), 133.8, 133.7 (CPhth), 131.9, 131.6 (CqPhth), 123.1, 122.8 (CHPhth), 48 (NCH), 37.2 (CH<sub>2</sub>NthPh), 33.4 (CHCH<sub>2</sub>CH), 30 (CHCH<sub>2</sub>CH<sub>2</sub>), 25.5 (CH<sub>2</sub>CH<sub>2</sub>Phth);

IR (CCl<sub>4</sub>): vmax 2927, 1775, 1719, 1469, 1395, 1375, 1264, 1050;

**HRMS (EI+)**: m/z calculated (found) for C<sub>41</sub>H<sub>32</sub>N<sub>4</sub>O<sub>8</sub> [M-C<sub>8</sub>H<sub>4</sub>NO<sub>2</sub>]: 562.1973 (562.1989).

2,2'-(1,1,1,13,13,13-Hexafluoro-2,12-dihydroxy-2,12-bis(trifluoromethyl)tridecan e-6,8-diyl)bis(isoindoline-1,3-dione) (3-37-7)





Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and 1,1,1-trifluoro-2-(trifluoromethyl)-pent-4-en-2-ol (218 mg, 1.05 mmol), and add 30 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 2:1 v/v) afforded 141 mg **3-37-7** (yield: 54%) as a colorless oil and two diastereoisomers in a ratio 2:1.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{\rm H}$  7.89-7.80 (m, 4H, CHPhth), 7.85-7.76 (m, 4H, CHPhth), 4.14-4.04 (m, 2H, 2NCH), 3.60 (s, 2H, CF<sub>3</sub>OH), 2.76 (dt, 2H, J=7.4Hz, J=8.9Hz, CHCH<sub>2</sub>CH), 2.08-1.97 (m, 2H, 2C*H*HCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH), 1.94-1.85 (m, 4H, 2C*H*<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH), 1.86-1.75 (m, 2H, 2C*H*HCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH), 1.58-1.46 (m, 4H, 2NCHC*H*<sub>2</sub>); *Diastereoisomer* 2:  $\delta_{\rm H}$  7.61-7.51 (m, 8H, CHPhth), 4.25-4.16 (m, 2H, 2NCH), 3.62 (s, 2H, CF<sub>3</sub>OH), 2.90-2.81 (m, 1H, CHC*H*HCH), 2.55-2.47 (m, 1H, CHCH*H*CH ), 2.06-1.97 (m, 2H, 2C*H*HCH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH), 1.95-1.84 (m, 4H, 2C*H*<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH), 1.87-1.76 (m, 2H, 2CH*H*CH<sub>2</sub>C(CF<sub>3</sub>)<sub>2</sub>OH), 1.57-1.46 (m, 4H, 2NCHC*H*<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Diastereoisomer 1*: δ<sub>C</sub> 169.1 (C=O), 134.3 (CPhth), 131.4 (CqPhth), 122.96 (q, CF<sub>3</sub>, J=286.8Hz), 123.4 (CHPhth), 76.3, 76.2, 76.2, 76, 75.9, 75.911, 75.7, 75.6 (C(CF<sub>3</sub>)<sub>2</sub>OH), 47.442 (NCH), 32.9 (CHCH<sub>2</sub>CH), 32.7

29.2  $(CH_2CH_2C(CF_3)_2OH),$ 18.4  $(CHCH_2CH_2),$  $(CH_2CH_2)$  $C(CF_3)_2OH);$ *Diastereoisomer* 2: δ<sub>C</sub> 168.9 (C=O), 134.2 (CPhth), 131.2 (CqPhth), 122.96 (q, CF<sub>3</sub>, J=286.8Hz), 123.3 (CHPhth), 76.3, 76.2, 76.2, 76, 75.9, 75.911, 75.7, 75.6 (NCH), 32.7  $(C(CF_3)_2OH),$ 47.5  $(CHCH_2CH),$ 29  $(CH_2CH_2C(CF_3)_2OH),$ 18.4(CH<sub>2</sub>CH<sub>2</sub> C(CF<sub>3</sub>)<sub>2</sub>OH);

IR (CCl<sub>4</sub>): vmax 2927, 1774, 1717, 1543, 1468, 1376, 1288, 1212;

**HRMS (EI+)**: m/z calculated (found) for C<sub>31</sub>H<sub>26</sub>F<sub>12</sub>N<sub>2</sub>O<sub>6</sub>: 750.1599 (750.1614).

2,2'-(1,7-Dicyclopentylheptane-3,5-diyl)bis(isoindoline-1,3-dione) (3-37-8)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and vinylcyclopentane (134 mg, 1.4 mmol), and needed 25 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 5:1 v/v) afforded 116 mg **3-37-8** (yield: 63%) as a colorless oil and two diastereoisomers in a ratio 1.9:1.

<sup>1</sup>**H NMR** (**400 MHz; CDCl**<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{\rm H}$  7.86-7.74 (m, 4H, CHPhth), 7.76-7.66 (m, 4H, CHPhth), 4.06-3.97 (m, 2H, 2NCH), 2.71-2.62 (m, 2H, J=7.6Hz, J=8.7Hz, CHCH<sub>2</sub>CH), 1.99-1.90 (m, 2H, CH<sub>2</sub>), 1.69-1.61 (m, 7H, 3.5CH<sub>2</sub>), 1.51-1.39 (m, 7H, 3.5CH<sub>2</sub>), 1.31-1.19 (m, 4H, 2CH<sub>2</sub>), 1.13-1.05 (m, 2H, CH<sub>2</sub>), 0.97-0.86 (m, 4H, 2CH<sub>2</sub>); *Diastereoisomer* 2:  $\delta_{\rm H}$  7.66-7.54 (m, 8H, CHPhth), 4.26-4.15 (m, 2H, 2NCH), 2.88-2.77 (m, 1H, CHCHHCH), 2.29-2.18 (m, 1H, CHCHHCH ), 2.05-1.94 (m, 2H, CH<sub>2</sub>), 1.68-1.58 (m, 7H, 3.5CH<sub>2</sub>), 1.49-1.39 (m, 7H, 3.5CH<sub>2</sub>), 1.31-1.19 (m, 4H, 2CH<sub>2</sub>), 1.13-1.05 (m, 2H, CH<sub>2</sub>), 1.31-1.19 (m, 4H, 2CH<sub>2</sub>), 1.68-1.58 (m, 7H, 3.5CH<sub>2</sub>), 1.49-1.39 (m, 7H, 3.5CH<sub>2</sub>), 1.31-1.19 (m, 4H, 2CH<sub>2</sub>), 1.13-1.05 (m, 2H, CH<sub>2</sub>), 0.96-0.85 (m, 4H, 2CH<sub>2</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Diastereoisomer 1*:  $\delta_{C}$  168.8 (C=O), 133.8 (CPhth), 131.8 (CqPhth), 123.1 (CHPhth), 48.9 (NCH), 39.8 (CH), 33.9, 32.7, 32.5, 32.2, 25.2, 25.1, 25.1 (CH<sub>2</sub>); *Diastereoisomer 2*:  $\delta_{C}$  168.3 (C=O), 133.7 (CPhth), 131.6 (CqPhth), 122.9 (CHPhth), 50.3 (NCH), 39.6 (CH), 33.7, 32.4, 32.3, 32.1, 25.1, 24.8, 24.6 (CH<sub>2</sub>);

IR (CCl<sub>4</sub>): vmax 2928, 1773, 1712, 1468, 1375, 1172, 1085;

HRMS (EI+): *m/z* calculated (found) for: C<sub>33</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>: 526.2832 (526.2841).

2,2'-(Nonadecane-9,11-diyl)bis(isoindoline-1,3-dione) (3-37-9)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and oct-1-ene (157 mg, 1.4 mmol), and needed 25 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 5:1 v/v) afforded 131 mg **3-37-9** (yield: 67%) as a colorless oil and two diastereoisomers in a ratio 1.7:1.

<sup>1</sup>**H NMR** (400 MHz; CDCl<sub>3</sub>): *Diastereoisomer* 1:  $\delta_{\rm H}$  7.86-7.74 (m, 4H, CHPhth), 7.77-7.66 (m, 4H, CHPhth), 4.08-3.97 (m, 2H, 2NCH), 2.72-2.61 (m, 2H, J=7.5Hz, J=8.9Hz, CHCH<sub>2</sub>CH), 1.99-1.86 (m, 2H, 2CHC*H*HCH<sub>2</sub>), 1.74-1.61 (m, 2H, 2CHCH*H*CH<sub>2</sub>), 1.28-1.03(m, 24H, 2(CH<sub>2</sub>)<sub>6</sub>), 0.81 (t, 6H, J=6.9Hz, 2CH<sub>2</sub>CH<sub>3</sub>); *Diastereoisomer* 2:  $\delta_{\rm H}$  7.67-7.52 (m, 8H, CHPhth), 4.28-4.15 (m, 2H, 2NCH), 2.90-2.75 (m, 1H, CHC*H*HCH), 2.30-2.17 (m, 1H, CHCH*H*CH ), 2.11-1.97 (m, 2H, 2CHC*H*HCH<sub>2</sub>), 1.77-1.64 (m, 2H, 2CHCH*H*CH<sub>2</sub>), 1.28-1.03 (m, 24H, 2(CH<sub>2</sub>)<sub>6</sub>), 0.82 (t, 6H, J=6.9Hz, 2CH<sub>2</sub>CH<sub>3</sub>);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): Diastereoisomer 1: δ<sub>C</sub> 168.8 (C=O), 133.8 (CPhth), 131.8 (CqPhth), 123.1 (CHPhth), 48.8 (NCH), 33.8 (CHCH<sub>2</sub>CH), 32.9 (CHCH<sub>2</sub>CH<sub>2</sub>), 31.7, 29.3, 29.2, 29.1, 26.4, 22.6 (CH<sub>2</sub>), 14 (CH<sub>3</sub>);Diastereoisomer 2: δ<sub>C</sub> 168.3 (C=O), 133.7 (CPhth), 131.6 (CqPhth), 122.9 CHPhth), 48.7 (NCH), 32.9 (CHCH<sub>2</sub>CH), 32.7 (CHCH<sub>2</sub>CH<sub>2</sub>), 31.6, 29.1, 29, 28.8, 26.3, 22.4 (CH<sub>2</sub>), 14 (CH<sub>3</sub>);
IR (CCl<sub>4</sub>): vmax 2928, 1772, 1709, 1468, 1376, 1172, 1082;

HRMS (EI+): *m/z* calculated (found) for: C<sub>35</sub>H<sub>46</sub>N<sub>2</sub>O<sub>4</sub>: 558.3458 (558.3449).

2,2'-(1,9-bis(4-Methoxyphenyl)nonane-4,6-diyl)bis(isoindoline-1,3-dione) (3-37-10)



Following the general procedure A for radical addition, the reaction was carried out with a solution of **3-36** (200mg, 0.35 mmol) and 4-Allylanisole (155 mg, 1.05 mmol), and needed 25 mol% of DLP to go to completion. The reduction was done following the general procedure B. Flash chromatography on silica gel (petroleum ether: ethyl acetate, 4:1 v/v) afforded 135 mg **3-37-10** (yield: 61%) as a colorless oil and two diastereoisomers in a ratio 2.5:1.

<sup>1</sup>**H NMR** (**400 MHz; CDCl<sub>3</sub>**): *Diastereoisomer 1*: δ<sub>H</sub> 7.86-7.73 (m, 4H, CHPhth), 7.76-7.66 (m, 4H, CHPhth), 6.96 (d, 4H, J=8.5Hz, Ar), 6.74 (d, 4H, J=8.6Hz, Ar), 4.10-4.01 (m, 2H, 2NCH), 3.74 (s, 6H, 2PhOCH<sub>3</sub>), 2.70-2.61 (m, 2H, CHC*H*<sub>2</sub>CH), 2.51-2.41 (m, 4H, 2PhCH<sub>2</sub>), 2.05-1.94 (m, 2H, 2C*H*HCH<sub>2</sub>PhOCH<sub>3</sub>), 1.71-1.62 (m, 2H, 2CH*H*CH<sub>2</sub>PhOCH<sub>3</sub>), 1.62-1.51 (m, 2H, NCHC*H*<sub>2</sub>), 1.54-1.43 (m, 2H, NCHC*H*<sub>2</sub>); *Diastereoisomer 2*: δ<sub>H</sub> 7.63-7.52 (m, 8H, CHPhth), 6.96 (d, 4H, J=8.6Hz, Ar), 6.73 (d, 4H, J=8.5Hz, Ar), 4.29-4.18 (m, 2H, 2NCH), 3.74 (s, 6H, 2PhOCH<sub>3</sub>), 2.91-2.82 (m, 1H, CHCHHCH), 2.52-2.41 (m, 4H, 2PhCH<sub>2</sub>), 2.30-2.21 (m, 1H, CHCHHCH ), 2.13-2.04 (m, 2H, 2CHHCH<sub>2</sub>PhOCH<sub>3</sub>), 1.77-1.66 (m, 2H, 2CHHCH<sub>2</sub>PhOCH<sub>3</sub>),1.62-1.51 (m, 2H, NCHCH<sub>2</sub>), 1.53-1.42 (m, 2H, NCHCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): Diastereoisomer 1: δ<sub>C</sub> 168.7 (C=O), 133.9 (CPhth), 157.6, 133.8, 131.8, 113.7 (Ar), 129.2 (CqPhth), 123.1 (CHPhth), 55.2 (OCH<sub>3</sub>), 48.4 (NCH), 34.4 (CH<sub>2</sub>Ph), 33.7 (CHCH<sub>2</sub>CH), 32.4 (CHCH<sub>2</sub>CH<sub>2</sub>), 28.4 (CH<sub>2</sub>CH<sub>2</sub>Ph); *Diastereoisomer* 2: δ<sub>C</sub> 168.6 (C=O), 133.7 (CPhth), 157.5, 133.4, 131.6, 113.6 (Ar), 129.2 (CqPhth), 122.9 (CHPhth), 55.1 (OCH<sub>3</sub>), 49.2 (NCH), 34.3 (CH<sub>2</sub>Ph), 33.6 (CHCH<sub>2</sub>CH), 32.1 (CHCH<sub>2</sub>CH<sub>2</sub>), 28.4 (CH<sub>2</sub>CH<sub>2</sub>Ph);

**IR** (**CCl**<sub>4</sub>): vmax 2929, 1774, 1717, 1513, 1375, 1247, 1176, 1042;

**HRMS (EI+)**: m/z calculated (found) for:  $C_{39}H_{38}N_2O_6$  [M- $C_8H_5NO_2$ ]: 483.241 (483.241).

#### 2,2'-(4-(2-Hydroxyethyl)cyclopentane-1,3-diyl)bis(isoindoline-1,3-dione) (3-40)



3-40

Triethylborane (1.0m solution in hexane, 0.14 mmol) was added every 30 minutes over two hours to a stirred solution of **3-36** (200mg, 0.35 mmol) and vinyl epoxide (49mg, 0.7 mmol) in DCM (0.5 ml) under nitrogen at room temperature. During the addition, the syringe needle was lowered into the solution. Furthermore, a small volume of air (about a quarter of the volume of the borane solution) was introduced by syringe following each addition of triethylborane. After stirring the reaction

mixture overnight, the mixture was diluted with DCM and then washed once with water and once with brine. The organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated. The residue was purified by chromatography on silica gel (petroleum ether: ethyl acetate: DCM, 10:4:1 v/v) to give 119 mg **3-40** (yield: 84%) as a colorless oil and four diastereoisomers in a ratio 5:4:1:1.

<sup>1</sup>**H** NMR (400 MHz; CDCl<sub>3</sub>): *Major Diastereoisomer 1*:  $\delta_{\rm H}$  7.89-7.79 (m, 4H, CHPhth), 7.75-7.66 (m, 4H, CHPhth), 5.19-5.11 (m, 1H, NCHCH), 4.86-4.77 (m, 1H, NCHCH<sub>2</sub>), 3.68-3.55 (m, 2H, CH<sub>2</sub>OH), 2.85-2.78 (m, 1H), 2.57-2.48 (m, 2H,), 2.33-2.24 (m, 1H, CHCH<sub>2</sub>CH<sub>2</sub>OH), 2.15-2.04 (m, 1H, NCHCHHNCH), 1.84-1.75 (m, 1H, NCHCHHCH), 1.72-1.63 (m, 1H, CHHCH<sub>2</sub>OH), 1.37-1.29 (m, 1H, CHHCH<sub>2</sub>OH); *Major Diastereoisomer 2*:  $\delta_{\rm H}$  7.89-7.79 (m, 4H, CHPhth), 7.75-7.66 (m, 4H, CHPhth), 4.91-4.80 (m, 1H, NCHCH), 4.62-4.51 (m, 1H, NCHCH<sub>2</sub>), 3.67-3.56 (m, 2H, CH<sub>2</sub>OH), 3.43-3.34 (m, 1H, NCHCHHNCH), 2.82 (dd, 1H, J=11.4Hz, NCHCHHCH), 2.51-2.40 (m, 1H, CHCH<sub>2</sub>CH<sub>2</sub>OH), 2.28-2.17 (m, 1H, NCHCHHNCH), 2.13-2.05 (m, 1H, NCHCHHCH), 1.74-1.65 (m, 1H, CHHCH<sub>2</sub>OH), 1.66-1.55 (m, 1H, CHHCH<sub>2</sub>OH), 1.38 (br, 1H, OH);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): *Major Diastereoisomer 1*  $\delta_{C}$  168.4, 168.2 (C=O), 134, 133.9 (CPhth), 131.98, 131.9 (CqPhth), 123.22, 123.16 (CPhth), 61.4 (CH<sub>2</sub>OH), 54.5 (NCH), 47.7 (NCH), 38.9 (CH), 35.7 (CH<sub>2</sub>), 35.2(CH<sub>2</sub>), 31.9 (CH);*Major Diastereoisomer 2*:  $\delta_{C}$  168.8, 168.3 (C=O), 134, 133.9 (CPhth), 131.9, 131.7 (CqPhth), 123.3 123.1 (CPhth), 61.6 (CH<sub>2</sub>OH), 50.2 (NCH), 49.7 (NCH), 37.4 (CHCH<sub>2</sub>CH<sub>2</sub>OH), 33.9 (NCHCH<sub>2</sub>CH), 33 (CH<sub>2</sub>CH<sub>2</sub>OH), 30.5 (CH),

IR (CCl<sub>4</sub>): vmax 2989, 1756, 1721, 1555, 1438, 1326, 1258;

**HRMS (EI+)**: *m/z* calculated (found) for: C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>: 404.1372 (404.1381).