Supporting Information

Syntheses of 9-triptycylisothiocyanate, (10-amino-9-triptycyl)carboxylic acid and their derivatives

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EXPERIMENTAL**9-Triptycylamine 2**

To a solution of **1**^[1] (0.5 g, 1.7 mmol) in acetic acid (10 mL), a slurry of anhydrous SnCl₂ (1.9 g, 8.4 mmol) in conc. HCl (6.5 mL) was added via a dropping funnel in 10 min at 80 °C. After stirred for 5 h, the reaction mixture was cooled down to room temperature and filtered. The solids were washed with conc. HCl (3 mL × 3), suspended in 5% NaOH, filtered, and washed with water till the filtrate became neutral. Then the solids were collected and dried under reduced pressure to give **2** (0.37 g, 82%). A white solid, mp 218-219 °C (lit.^[2] 225 °C); ¹H-NMR (400 MHz, CDCl₃) δ 2.66 (s, 2 H), 5.50 (s, 1 H), 7.06-7.17 (m, 6 H), 7.44-7.50 (m, 3 H), 7.54-7.59 (m, 3 H); ¹³C-NMR (100 MHz, CDCl₃) δ 53.3, 64.3, 119.5, 123.4, 125.1, 125.4, 145.1, 146.8.

1-Benzyl-3-(9-triptycyl)-thiourea 4

To a solution of **3** (27.4 mg, 0.088 mmol) in THF (2 mL), benzylamine (9.5 mg, 0.089 mmol) was added. Then the mixture was stirred overnight at room temperature under nitrogen. After the reaction was complete (monitored by TLC), the mixture was concentrated in vacuo and **4** (33.2 mg, 90%) was isolated by preparative TLC (silica gel, eluted with EtOAc/PE (1/3, v/v)). A white solid, R_f = 0.51; mp 229-231 °C; ¹H-NMR (400 MHz, CDCl₃) δ 4.96 (d, *J* = 5.6 Hz, 2 H), 5.45 (s, 1 H), 5.96 (t, *J* = 5.2 Hz, 1 H), 6.93-7.14 (m, 6 H), 7.21-7.28 (m, 5 H), 7.35-7.43 (m, 4 H), 7.44-7.52 (m, 2 H), 7.73 (s, 1 H); ¹³C-NMR (100MHz, CDCl₃) δ 50.4, 53.5, 67.7, 117.7, 123.0, 124.2, 125.17, 125.22, 125.9, 126.7, 127.6, 128.1, 128.5, 137.0, 140.5, 142.6, 144.2, 145.0, 182.0; IR (KBr) 3424 (NH), 3379 (NH), 1538 (N-C=S), 1456 (C=C) cm⁻¹; HRMS-ESI

(positive) m/z: calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{NaS}^+$ ($\text{M}+\text{Na}$) $^+$, 441.1396; found, 441.1390.

Methyl (10-nitro-9-triptycyl)carboxylate **6**

Starting from methyl 10-nitroanthracene-9-carboxylate (**5**), **6** was prepared in 42% yield by the same method^[2] for the preparation of **1**. A white solid, mp 258-259 °C; ^1H -NMR (400 MHz, CDCl_3) δ 4.29 (s, 3 H), 7.15-7.23 (m, 6 H), 7.74-7.80 (m, 3 H), 7.82-7.89 (m, 3 H); ^{13}C -NMR (100 MHz, CDCl_3) δ 52.3, 61.2, 96.5, 121.8, 123.7, 126.2, 126.7, 140.5, 141.9, 169.6; IR (KBr) 1737 (C=O) cm^{-1} ; HRMS-ESI (positive) m/z: calcd for $\text{C}_{22}\text{H}_{15}\text{NNaO}_4^+$ ($\text{M}+\text{Na}$) $^+$, 380.0893; found, 380.0897.

Methyl (10-amino-9-triptycyl)carboxylate **7**

Following the same procedure for the reduction of **1**, **7** was prepared from **6** in 90% yield. A white solid, mp 263-264 °C; ^1H -NMR (400 MHz, CDCl_3) δ 2.64 (s, 2 H), 4.27 (s, 3 H), 7.08-7.19 (m, 6 H), 7.53-7.59 (m, 3 H), 7.77-7.82 (m, 3 H); ^{13}C -NMR (100 MHz, CDCl_3) δ 52.0, 60.8, 63.4, 119.3, 123.4, 125.3, 125.6, 143.0, 147.0, 170.6; IR (KBr) 1740 (C=O) cm^{-1} ; HRMS-ESI (positive) m/z: calcd for $\text{C}_{22}\text{H}_{18}\text{NO}_2^+$ ($\text{M}+\text{H}$) $^+$, 328.1332; found, 328.1330.

(10-Acetamido-9-triptycyl)carboxylic acid **9**

In a round flask (50 mL), **7** (0.75 g, 2.3 mmol) was dissolved in acetic anhydride (15 mL) at 80 °C (water bath) and the mixture was stirred for 5 h. After cooled down to room temperature, the mixture was poured into cooled water (100 mL), filtered, washed with water (5 mL $\times$ 3), and dried in vacuo to afford the acetyl protected product as a white powder (0.557 g, 1.5 mmol). Hydrolyzing this product according to the same procedure for preparing **8** gave **9** in 62% yield (two steps). A white solid, mp 363-364 °C; $^1\text{H-NMR}$ (600 MHz, $\text{DMSO-}d_6$) δ 2.51 (s, 3 H), 7.07-7.12 (m, 6 H), 7.43-7.48 (m, 3 H), 7.84-7.89 (m, 3 H), 8.86 (s, 1 H); $^{13}\text{C-NMR}$ (150 MHz, $\text{DMSO-}d_6$) δ 23.6, 60.1, 66.1, 122.0, 123.4, 124.7, 125.0, 142.2, 143.5, 170.5, 170.9; IR (KBr) 1710 (COOH), 1653 (CONH) cm^{-1} ; HRMS-ESI (negative) m/z : calcd for $\text{C}_{23}\text{H}_{16}\text{NO}_3^-$ (M-H) $^-$, 354.1136; found: 354.1133.

Benzyl 2-(10-acetamido-triptycene-9-carboxamido)acetate **10**

To a flask containing **9** (50.0 mg, 0.14 mmol) and HOBt (20.9 mg, 0.15 mmol), DMF (5 mL) was added. After stirred at room temperature for 15 min under nitrogen, the mixture was cooled to 0 °C with ice-water bath, and the solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) (29.7 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) and Et_3N (15.5 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) were sequentially added. The mixture was stirred at 0 °C for 10 min and at room temperature for 50 min, then glycine benzyl ester toluene-4-sulfonate (52.2 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) and Et_3N (16.8 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) were added at 0 °C. The reaction was allowed to stir at room temperature overnight. Then a solution of citric acid (10 w%, 10 mL) was added, and the resulting mixture was stirred at room temperature for 2 h. After diluted with water (15 mL), the reaction mixture was extracted with CH_2Cl_2 (5 mL $\times$ 3). The

combined organic phase was sequentially washed with citric acid (10 w%, 20 mL), saturated Na_2CO_3 (20 mL), and brine (20 mL), dried over anhydrous Na_2SO_4 , and evaporated. The product **10** (52.6 mg, 74%) was isolated from the residue by preparative TLC (silica gel, eluted with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (50/1, v/v)). A white solid, $R_f = 0.24$; mp 168-169 °C; ^1H -NMR (400 MHz, $\text{DMSO}-d_6$) δ 2.49 (s, 3 H), 4.32 (d, $J = 5.2$ Hz, 2 H), 5.31 (s, 2 H), 6.98-7.11 (m, 6 H), 7.35-7.54 (m, 6 H), 7.47-7.52 (m, 2 H), 8.12-8.19 (m, 3 H), 8.85 (s, 1 H), 8.91 (t, $J = 5.2$ Hz, 1 H); ^{13}C -NMR (100 MHz, $\text{DMSO}-d_6$) δ 24.1, 42.1, 59.1, 66.68, 66.71, 122.4, 124.7, 125.0, 125.3, 128.7, 129.0, 136.4, 143.6, 144.2, 169.5, 170.7, 170.8; IR (KBr) 1746 (COOBn), 1671 (CONH) cm^{-1} ; HRMS-ESI (positive) m/z : calcd for $\text{C}_{32}\text{H}_{27}\text{N}_2\text{O}_4^+$ ($\text{M}+\text{H}$) $^+$, 503.1965; found, 503.1955.

Methyl 10-isothiocyanate-triptycene-9-carboxylate **11**

Compound **11** was prepared in 62% yield according to the same method for the preparation of **3**. A white solid, $R_f = 0.39$ (EtOAc/PE (1/10, v/v)); mp 233-234 °C; ^1H -NMR (400 MHz, CDCl_3) δ 4.27 (s, 3 H), 7.12-7.24 (m, 6 H), 7.68-7.74 (m, 3 H), 7.75-7.82 (m, 3 H); ^{13}C -NMR (100MHz, CDCl_3) δ 52.2, 60.5, 72.0, 120.1, 123.7, 126.1, 126.4, 138.2, 141.2, 143.2, 169.7; IR (KBr) 2070 ($\text{N}=\text{C}=\text{S}$), 1735 ($\text{C}=\text{O}$) cm^{-1} ; HRMS-ESI (positive mode) m/z : calcd for ($\text{M}+\text{H}$) $^+$ $\text{C}_{23}\text{H}_{16}\text{NO}_2\text{S}^+$ 370.0896; found: 370.0897.

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¹H-NMR (400 MHz, CDCl₃)

^{13}C -NMR (100 MHz, D_2O)

^{13}C -NMR (151 MHz, DMSO- d_6)

¹H-NMR (400 MHz, CDCl₃)