

Supporting Information

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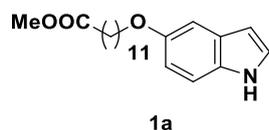
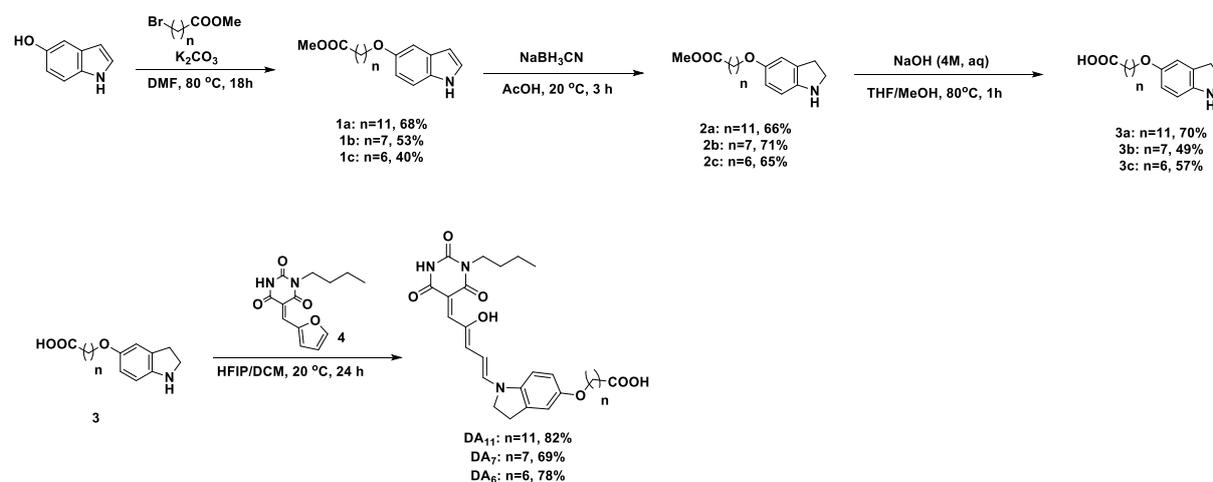
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Supporting Information

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1. Synthesis



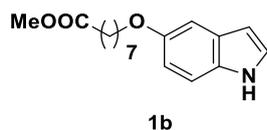
Compound **1a**

A mixture of 5-hydroxyindole (509 mg, 3.8 mmol, 1.0 equiv.), methyl 12-bromododecanoate (1.35 g, 4.56 mmol, 1.2 equiv.) and potassium carbonate (1.06 g, 7.6 mmol, 2.0 equiv.) in DMF (5 mL) was heated at 80 °C for 18 h. The reaction mixture was diluted with ethyl acetate (20 mL) after cool down to room temperature, washed with brine (1 x 20 mL), water (2 x 20 mL) and brine (1 x 20 mL) sequentially. The organic layer was dried over Na₂SO₄ and the filtrate was concentrated under reduced pressure. The crude was purified by flash column chromatography on SiO₂ (*n*-hexane/ethyl acetate = 5/1, *R_f* = 0.5) to afford compound **1a** (897 mg, 2.60 mmol, 68% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 8.14 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 7.14 (t, *J* = 2.9 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.45 (t, *J* = 2.7 Hz, 1H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.79 (p, *J* = 6.8 Hz, 2H), 1.62 (q, *J* = 7.2 Hz, 2H), 1.50 – 1.42 (m, 2H), 1.35 (td, *J* = 10.7, 8.2, 3.6 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 12H).

¹³C NMR (151 MHz, CDCl₃) δ 174.49, 153.63, 130.99, 128.32, 124.84, 112.94, 111.66, 103.48, 103.46, 102.29, 68.86, 51.51, 34.17, 29.60, 29.55, 29.52, 29.47, 29.28, 29.18, 26.17, 25.00.

HR-MS (ESI⁺) calculated for C₂₁H₃₂NO₃ [M+H]⁺ *m/z* 346.2382, found 346.2383.



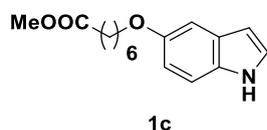
Compound **1b**

A mixture of 5-hydroxyindole (1.08 g, 8.1 mmol, 1.0 equiv.), methyl 7-bromoheptanoate (2.32 g, 9.7 mmol, 1.2 equiv.) and potassium carbonate (2.25 g, 16.2 mmol, 2.0 equiv.) in DMF (7 mL) was heated at 80 °C for 18 h. The reaction mixture was diluted with ethyl acetate (20 mL) after cool down to room temperature, washed with brine (1 x 20 mL), water (2 x 20 mL) and brine (1 x 20 mL) sequentially. The organic layer was dried over Na₂SO₄ and the filtrate was concentrated under reduced pressure. The crude was purified by flash column chromatography on SiO₂ (*n*-hexane/ethyl acetate = 5/1, *R_f* = 0.3) to afford compound **1c** (1.30 g, 4.5 mmol, 55% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 8.67 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 2.7 Hz, 1H), 7.14 (d, *J* = 3.0 Hz, 1H), 6.99 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.55 (d, *J* = 3.4 Hz, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.75 (d, *J* = 2.6 Hz, 3H), 2.40 (t, *J* = 7.6 Hz, 2H), 1.87 (q, *J* = 7.2 Hz, 2H), 1.72 (p, *J* = 7.3 Hz, 2H), 1.54 (q, *J* = 7.5 Hz, 2H), 1.47 – 1.38 (m, 5H).

¹³C NMR (151 MHz, CDCl₃) δ 174.64, 153.53, 131.30, 128.46, 125.26, 112.73, 111.99, 103.48, 101.97, 68.81, 51.56, 34.13, 29.56, 29.18, 26.10, 25.01.

HR-MS (ESI⁺) calculated for C₁₈H₂₆NO₃ [M+H]⁺ *m/z* 290.1756, found 290.1755.



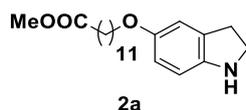
Compound **1c**

A mixture of 5-hydroxyindole (554 mg, 4.2 mmol, 1.0 equiv.), methyl 7-bromoheptanoate (1.11 g, 5.0 mmol, 1.2 equiv.) and potassium carbonate (1.22 g, 8.8 mmol, 2.0 equiv.) in DMF (5 mL) was heated at 80 °C for 18 h. The reaction mixture was diluted with ethyl acetate (20 mL) after cool down to room temperature, washed with brine (1 x 20 mL), water (2 x 20 mL) and brine (1 x 20 mL) sequentially. The organic layer was dried over Na₂SO₄ and the filtrate was concentrated under reduced pressure. The crude was purified by flash column chromatography on SiO₂ (*n*-hexane/ethyl acetate = 5/1, *R_f* = 0.5) to afford compound **1d** (458 mg, 1.66 mmol, 40.0% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 8.07 (s, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.17 (t, *J* = 2.8 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.47 (ddd, *J* = 3.1, 2.0, 0.9 Hz, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.67 (s, 3H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.67 (p, *J* = 7.6 Hz, 2H), 1.51 (dtd, *J* = 9.4, 7.4, 5.5 Hz, 2H), 1.44 – 1.36 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 174.29, 153.58, 130.94, 128.28, 124.77, 112.92, 111.61, 103.45, 102.35, 68.61, 51.50, 34.04, 29.30, 28.94, 25.83, 24.90.

HR-MS (ESI⁺) calculated for C₁₆H₂₂NO₃ [M+H]⁺ *m/z* 276.1600, found 276.1595.



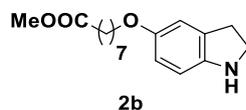
Compound **2a**

To a solution of Compound **1a** (217 mg, 0.63 mmol, 1.0 equiv.) in acetic acid (4 mL), sodium cyanoborohydride (119 mg, 1.89 mmol, 3.0 equiv.) was added in one portion. The reaction mixture was stirred at 20 °C for 3 h. The reaction was quenched by adding H₂O (5 mL) in an ice bath. The pH of reaction mixture was adjusted to ~7 by adding 4 M NaOH solution. The reaction mixture was extracted with ethyl acetate (3 x 15 mL) and the combined organic layer was washed with brine (1 x 15 mL). The organic layer was dried over Na₂SO₄ and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on SiO₂ (*n*-hexane/ethyl acetate = 2/1, *R_f* = 0.10) to afford compound **2a** (145 mg, 0.42 mmol, 66.1% yield) as an off-white solid.

¹H NMR (600 MHz, CDCl₃) δ 6.76 (s, 1H), 6.59 (d, *J* = 2.1 Hz, 2H), 3.87 (t, *J* = 6.6 Hz, 2H), 3.67 (s, 3H), 3.53 (t, *J* = 8.3 Hz, 2H), 3.00 (t, *J* = 8.3 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.73 (p, *J* = 6.8 Hz, 2H), 1.62 (p, *J* = 7.4 Hz, 2H), 1.42 (p, *J* = 7.4, 7.0 Hz, 2H), 1.35 – 1.26 (m, 12H).

¹³C NMR (151 MHz, CDCl₃) δ 174.39, 153.13, 145.09, 131.13, 113.13, 112.39, 110.23, 68.99, 51.46, 47.80, 34.14, 30.49, 29.56, 29.52, 29.48, 29.44, 29.42, 29.26, 29.16, 26.09, 24.97.

HR-MS (ESI⁺) calculated for C₂₁H₃₄NO₃ [M+H]⁺ *m/z* 348.2539, found 348.2539.



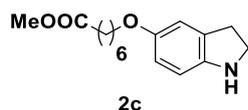
Compound **2b**

To a solution of Compound **1b** (1.7 g, 5.9 mmol, 1.0 equiv.) in acetic acid (6 mL), sodium cyanoborohydride (1.1 g, 17.6 mmol, 3.0 equiv.) was added in one portion. The reaction mixture was stirred at 20 °C for 3 h. The reaction was quenched by adding H₂O (5 mL) in an ice bath. The pH of reaction mixture was adjusted to ~7 by adding 4 M NaOH solution. The reaction mixture was extracted with ethyl acetate (3 x 15 mL) and the combined organic layer was washed with brine (1 x 15 mL). The organic layer was dried over Na₂SO₄ and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on SiO₂ (*n*-hexane/ethyl acetate = 2/1, *R_f* = 0.15) to afford compound **2c** (1.2 g, 4.0 mmol, 71% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 6.75 (s, 1H), 6.58 (d, *J* = 2.7 Hz, 2H), 3.87 (t, *J* = 6.2 Hz, 2H), 3.67 (d, *J* = 2.0 Hz, 3H), 3.51 (t, *J* = 8.0 Hz, 2H), 2.99 (t, *J* = 8.3 Hz, 2H), 2.31 (t, *J* = 7.3 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.64 (p, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.7 Hz, 2H), 1.40 – 1.28 (m, 5H).

¹³C NMR (151 MHz, CDCl₃) δ 174.57, 174.27, 153.18, 144.87, 131.25, 113.10, 112.30, 110.44, 68.82, 51.46, 47.70, 34.05, 30.46, 29.71, 29.39, 29.12, 29.07, 29.04, 28.99, 25.92, 25.84, 24.88.

HR-MS (ESI⁺) calculated for C₁₈H₂₈NO₃ [M+H]⁺ *m/z* 292.1913, found 292.1912.



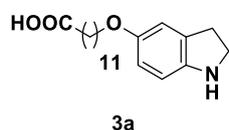
Compound **2c**

To a solution of Compound **1c** (164 mg, 0.59 mmol, 1.0 equiv.) in acetic acid (6 mL), sodium cyanoborohydride (112 mg, 1.78 mmol, 3.0 equiv.) was added in one portion. The reaction mixture was stirred at 20 °C for 3 h. The reaction was quenched by adding H₂O (5 mL) in an ice bath. The pH of reaction mixture was adjusted to ~7 by adding 4 M NaOH solution. The reaction mixture was extracted with ethyl acetate (3 x 15 mL) and the combined organic layer was washed with brine (1 x 15 mL). The organic layer was dried over Na₂SO₄ and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on SiO₂ (*n*-hexane/ethyl acetate = 2/1, *R_f* = 0.15) to afford compound **2d** (107 mg, 0.38 mmol, 65.0% yield) as a white solid.

¹H NMR (600 MHz, CDCl₃) δ 6.73 (d, *J* = 1.8 Hz, 1H), 6.59 – 6.51 (m, 2H), 3.85 (t, *J* = 6.5 Hz, 2H), 3.65 (s, 3H), 3.49 (q, *J* = 9.8, 8.3 Hz, 3H), 2.97 (t, *J* = 8.3 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.72 (dt, *J* = 14.5, 6.6 Hz, 2H), 1.64 (p, *J* = 7.5 Hz, 2H), 1.50 – 1.41 (m, 2H), 1.41 – 1.33 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 174.14, 152.84, 145.36, 130.99, 113.01, 112.29, 110.01, 68.68, 51.42, 47.75, 33.95, 30.43, 29.26, 28.88, 25.75, 24.85.

HR-MS (ESI+) calculated for C₁₆H₂₄NO₃ [M+H]⁺ *m/z* 278.1756, found 278.1755.



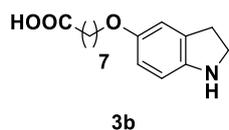
Compound **3a**

To a solution of Compound **2a** (443 mg, 1.27 mmol) in methanol (2 mL) and tetrahydrofuran (2 mL), an aqueous NaOH solution (4 M, 1 mL) was added and the reaction mixture was then heated at 80 °C for 1 h. After cooling to room temperature, volatile solvents were removed under reduced pressure. The pH of reaction mixture was adjusted to ~7 by adding 1 M HCl solution that off-white precipitate formed. The filtered precipitate was washed with H₂O (10 mL) to afford compound **3a** as an off-white solid (297 mg, 0.89 mmol, 70.0% yield).

¹H NMR (400 MHz, 9:1 CDCl₃ with 0.03% v/v TMS:CD₃OD) δ 6.77 (s, 1H), 6.69 – 6.58 (m, 2H), 3.89 (t, *J* = 6.6 Hz, 2H), 3.51 (t, *J* = 8.2 Hz, 2H), 3.02 (t, *J* = 8.3 Hz, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.74 (q, *J* = 7.0 Hz, 2H), 1.61 (t, *J* = 7.3 Hz, 2H), 1.43 (t, *J* = 7.5 Hz, 2H), 1.36 – 1.26 (m, 12H).

¹³C NMR (151 MHz, 9:1 CDCl₃ with 0.03% v/v TMS:CD₃OD) δ 176.95, 153.62, 144.09, 131.69, 113.24, 112.21, 111.28, 68.99, 49.47, 49.33, 49.19, 49.05, 48.90, 48.76, 48.62, 47.42, 34.16, 30.40, 29.45, 29.42, 29.36, 29.31, 29.29, 29.21, 29.08, 25.94, 24.89.

HR-MS (ESI+) calculated for C₂₀H₃₂NO₃ [M+H]⁺ *m/z* 334.2382, found 348.2384.



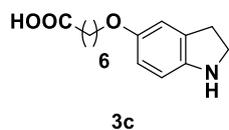
Compound 3b

To a solution of Compound **2b** (107 mg, 0.35 mmol, 1.0 equiv.) in methanol (2 mL) and tetrahydrofuran (2 mL), an aqueous NaOH solution (4 M, 1 mL) was added and the reaction mixture was then heated at 80 °C for 1 h. After cooling to room temperature, volatile solvents were removed under reduced pressure. The pH of reaction mixture was adjusted to ~7 by adding 1 M HCl solution that off-white precipitate formed. The filtered precipitate was washed with H₂O (10 mL) to afford compound **3c** as an off-white solid (49.5 mg, 0.17 mmol, 49.0% yield).

¹H NMR (600 MHz, DMSO) δ 6.68 (d, *J* = 2.5 Hz, 1H), 6.49 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 3.81 (t, *J* = 6.5 Hz, 2H), 3.35 (t, *J* = 8.4 Hz, 5H), 2.85 (d, *J* = 16.7 Hz, 2H), 2.20 (t, *J* = 7.4 Hz, 2H), 1.63 (p, *J* = 6.7 Hz, 2H), 1.50 (p, *J* = 7.3 Hz, 2H), 1.37 (td, *J* = 8.8, 8.1, 4.3 Hz, 2H), 1.34 – 1.26 (m, 4H).

¹³C NMR (151 MHz, DMSO) δ 175.00, 151.81, 146.84, 130.77, 113.22, 112.48, 109.34, 68.53, 47.39, 34.14, 30.34, 29.34, 28.99, 28.98, 25.92, 24.93.

HR-MS (ESI+) calculated for C₁₇H₂₆NO₃ [M+H]⁺ *m/z* 278.1756, found 278.1755.



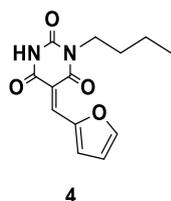
Compound 3c

To a solution of Compound **2c** (100 mg, 0.36 mmol, 1.0 equiv.) in methanol (2 mL) and tetrahydrofuran (2 mL), an aqueous NaOH solution (4 M, 1 mL) was added and the reaction mixture was then heated at 80 °C for 1 h. After cooling to room temperature, volatile solvents were removed under reduced pressure. The pH of reaction mixture was adjusted to ~7 by adding 1 M HCl solution that off-white precipitate formed. The filtered precipitate was washed with H₂O (10 mL) to afford compound **3d** as an off-white solid (54.1 mg, 0.20 mmol, 57.0% yield).

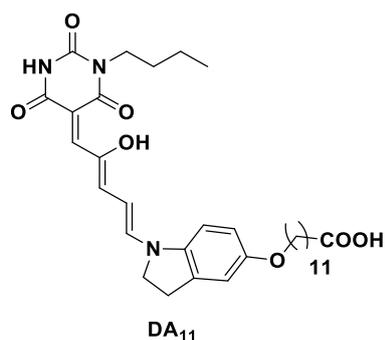
¹H NMR (600 MHz, DMSO) δ 6.68 (d, *J* = 2.2 Hz, 1H), 6.48 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 3.80 (t, *J* = 6.5 Hz, 2H), 2.84 (t, *J* = 8.4 Hz, 2H), 2.20 (t, *J* = 7.4 Hz, 2H), 1.63 (p, *J* = 6.6 Hz, 2H), 1.50 (p, *J* = 7.4 Hz, 2H), 1.37 (dt, *J* = 14.8, 7.1 Hz, 2H), 1.31 (q, *J* = 8.5, 8.0 Hz, 2H).

¹³C NMR (151 MHz, DMSO) δ 174.54, 151.36, 146.40, 130.33, 112.77, 112.03, 108.89, 68.03, 46.95, 33.63, 29.90, 28.82, 28.36, 25.35, 24.49.

HR-MS (ESI+) calculated for C₁₅H₂₂NO₃ [M+H]⁺ *m/z* 264.1600, found 264.1593.



The Compound 4 was synthesized as previously reported[1, 2].

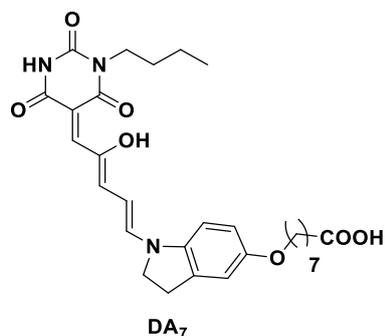


DA₁₁

Compound **3** (26.34 mg, 0.079 mmol, 1.0 equiv.) and Compound **4** (20.71 mg, 0.079 mmol, 1.0 equiv.) were suspended in dichloromethane (0.8 mL). After adding hexafluoro-2-propanol (0.2 mL), the reaction mixture was stirred at 20 °C for 24 h under air. Undissolved solid was filtered off and washed with THF solution (3 mL). The filtrate was concentrated under reduced pressure. The residue was dissolved in THF (1 mL). After introducing *n*-hexane (10 mL), the recrystallized **DA₁₁** (38.7 mg, 0.065 mmol, 82.2% yield) was obtained as a black solid.

¹H NMR (600 MHz, DMSO) δ 12.72 (s, 1H), 12.00 (s, 1H), 10.93 (s, 1H), 8.55 (d, *J* = 11.7 Hz, 1H), 7.46 (dd, *J* = 9.0, 6.5 Hz, 1H), 7.09 (d, *J* = 12.7 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 2H), 6.94 (dd, *J* = 8.9, 2.5 Hz, 2H), 6.82 (d, *J* = 3.6 Hz, 1H), 6.14 (t, *J* = 11.9 Hz, 2H), 4.25 (t, *J* = 7.6 Hz, 3H), 3.97 (t, *J* = 6.5 Hz, 3H), 3.81 (s, 1H), 3.73 (dt, *J* = 15.0, 7.6 Hz, 3H), 3.25 (t, *J* = 7.7 Hz, 4H), 2.19 (td, *J* = 7.4, 3.8 Hz, 4H), 1.70 (p, *J* = 6.7 Hz, 3H), 1.63 (s, 1H), 1.53 – 1.42 (m, 8H), 1.39 (q, *J* = 7.4 Hz, 4H), 1.28 (dtt, *J* = 29.3, 14.4, 7.7 Hz, 14H), 0.92 – 0.85 (m, 6H).

HR-MS (ESI⁻) calculated for C₃₀H₃₈N₃O₇ [M-H]⁻ *m/z* 594.3179, found 594.3178.

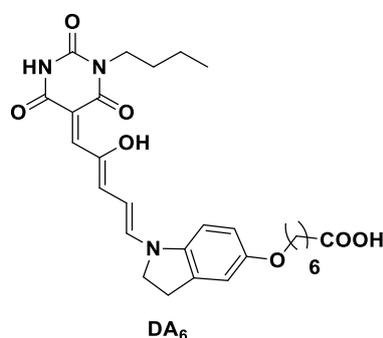


DA₇

Compound **3b** (25.0 mg, 0.09 mmol, 1.0 equiv.) and Compound **4** (22.5 mg, 0.09 mmol, 1.0 equiv.) were suspended in dichloromethane (0.8 mL). After adding hexafluoro-2-propanol (0.2 mL), the reaction mixture was stirred at 20 °C for 24 h under air. Undissolved solid was filtered off and washed with THF solution (3 mL). The filtrate was concentrated under reduced pressure. The residue was dissolved in THF (1 mL). After introducing *n*-hexane (10 mL), the recrystallized **DA₇** (65.6 mg, 0.12 mmol, 69.0% yield) was obtained as a green solid.

¹H NMR (600 MHz, (CD₃)₂SO) δ (ppm) 8.51 (dd, J = 23.2, 11.4 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 12.6 Hz, 1H), 7.01 – 6.90 (m, 2H), 6.82 (s, 1H), 6.14 (t, J = 11.9 Hz, 1H), 4.24 (t, J = 7.3 Hz, 2H), 3.97 (t, J = 6.4 Hz, 2H), 3.72 (dd, J = 14.6, 7.3 Hz, 2H), 2.19 (t, J = 7.3 Hz, 4H), 1.74 – 1.66 (m, 3H), 1.52 – 1.43 (m, 6H), 1.32 (dt, J = 20.0, 11.7 Hz, 17H).

HR-MS (ESI⁻) calculated for C₃₀H₃₈N₃O₇ [M-H]⁻ m/z 538.2553, found 538.2552.



DA₆

Compound **3c** (35 mg, 0.13 mmol, 1.0 equiv.) and Compound **4** (34.9 mg, 0.13 mmol, 1.0 equiv.) were suspended in dichloromethane (0.8 mL). After adding hexafluoro-2-propanol (0.2 mL), the reaction mixture was stirred at 20 °C for 24 h under air. Undissolved solid was filtered off and washed with THF solution (3 mL). The filtrate was concentrated under reduced pressure. The residue was dissolved in THF (1 mL). After introducing *n*-hexane (10 mL), the recrystallized **DA₆** (54.7 mg, 0.10 mmol, 78.0% yield) was obtained as a green solid.

¹H NMR (400 MHz, (CD₃)₂SO) δ (ppm) 8.51 (t, J = 13.0 Hz, 1H), 7.46 (d, J = 8.9 Hz, 1H), 7.09 (d, J = 12.7 Hz, 1H), 7.01 – 6.89 (m, 2H), 6.82 (s, 1H), 6.14 (t, J = 12.2 Hz, 1H), 4.24 (t, J = 7.1 Hz, 2H), 3.97 (t, J = 6.4 Hz, 3H), 2.50 (d, J = 1.4 Hz, 6H), 2.21 (t, J = 7.3 Hz, 3H), 1.80 – 1.60 (m, 3H), 1.58 – 1.19 (m, 15H).

HR-MS (ESI⁻) calculated for C₂₈H₃₄N₃O₇ [M-H]⁻ m/z 524.2397, found 524.2392.

2. Supporting Figures

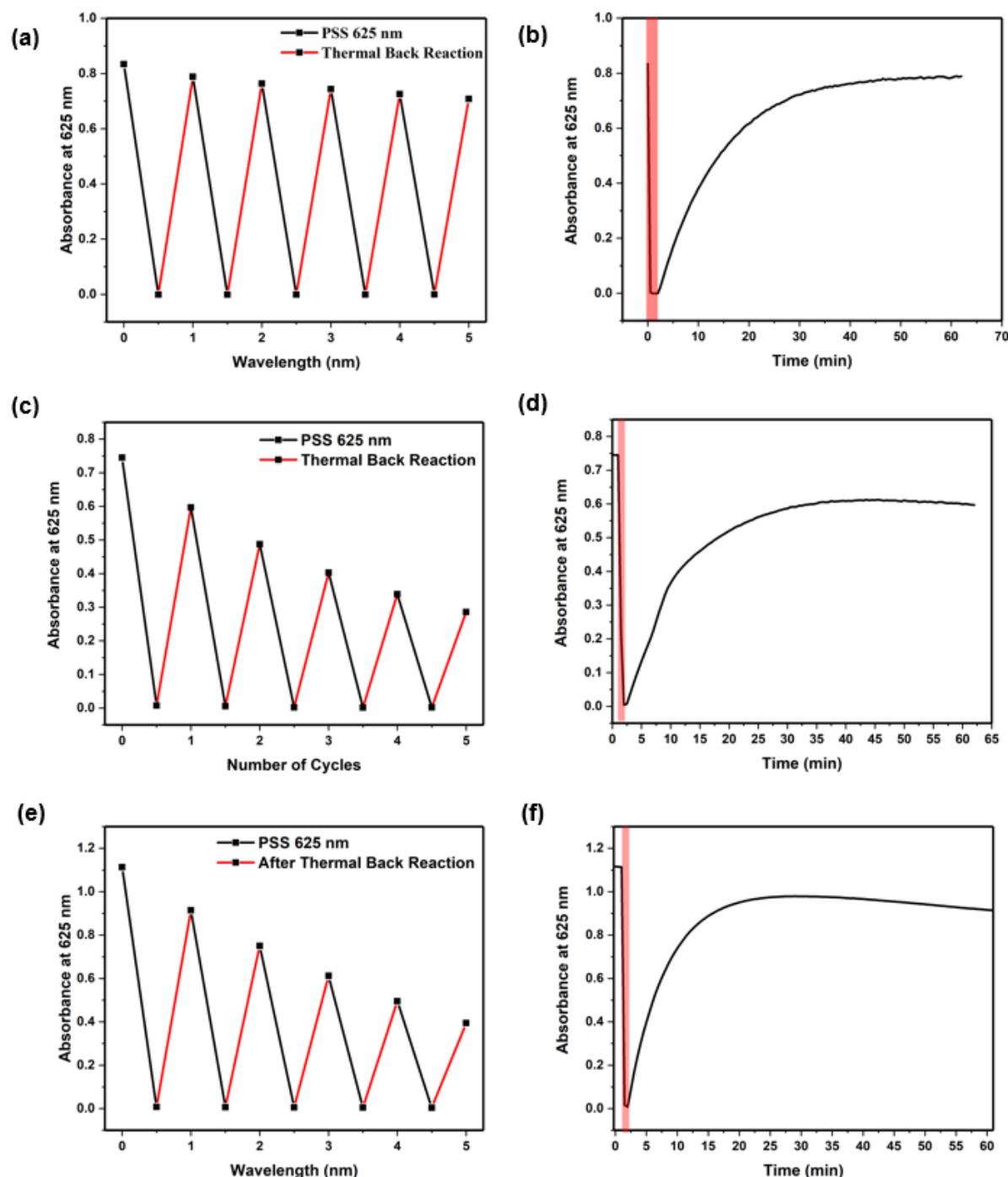


Figure S1. Multiple photoswitching cycles of (a) DA₁₁, (c) DA₇, (e) DA₆, alternative irradiation at 625 nm (black) over 1 min and thermal back reaction at 20 °C over 60 min (blue). Time-course of the photoisomerization process of (b) DA₁₁, (d) DA₇, (f) DA₆, in MilliQ water, monitored at λ_{\max} 625 nm (red area: white-light irradiation period). Irradiation of UV-vis sample was carried out at 20 °C using a Thorlabs model M625F2 high-power LED (625 nm, 1.0 A) positioned at a distance of 1 cm from the sample.

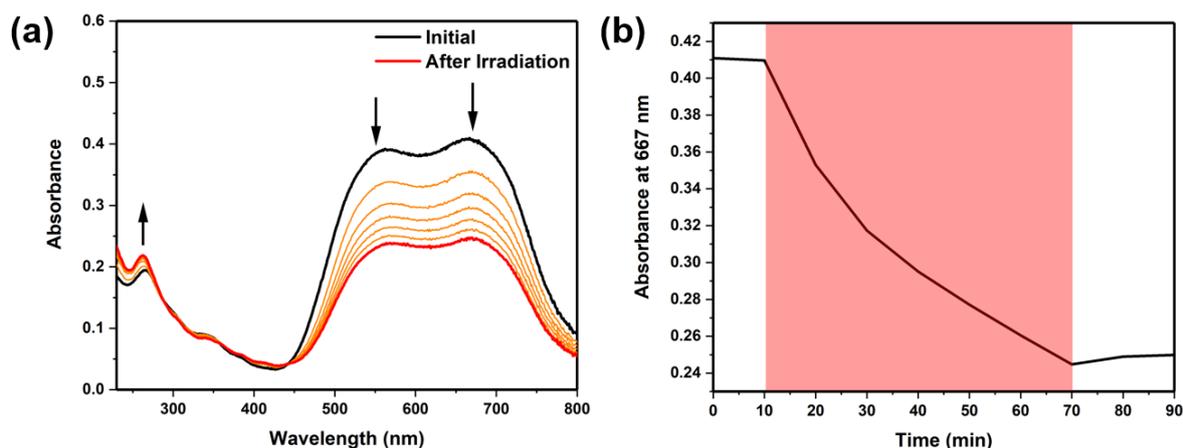


Figure S2. a) UV-vis absorption spectra of an aqueous solution of **DA₁₁** (43 μM) at initial (black-line) and white-light irradiation over 60 min (orange-line) and white-light irradiation over 60 min (red-line) at 20 °C. (b) Time-course of the photoisomerization process of **DA₁₁** in MilliQ water, monitored at λ_{max} 667 nm (red area: white-light irradiation period). Irradiation of UV-vis samples was carried out at 20 °C using a light guide equipped BBZM-I xenon light source (380–800 nm, 300 W) positioned at a distance of 1 cm from the sample.

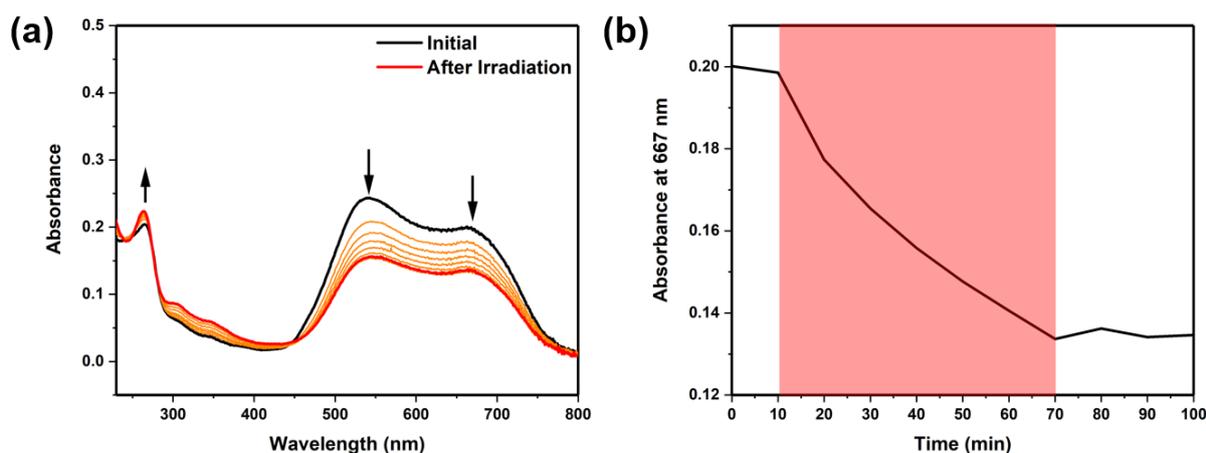


Figure S3. a) UV-vis absorption spectra of an aqueous solution of **DA₇** (43 μM) at initial (black-line) and white-light irradiation over 60 min (orange-line) and white-light irradiation over 60 min (red-line) at 20 °C. (b) Time-course of the photoisomerization process of **DA₇** in MilliQ water, monitored at λ_{max} 667 nm (red area: white-light irradiation period). Irradiation of UV-vis samples was carried out at 20 °C using a light guide equipped BBZM-I xenon light source (380–800 nm, 300 W) positioned at a distance of 1 cm from the sample.

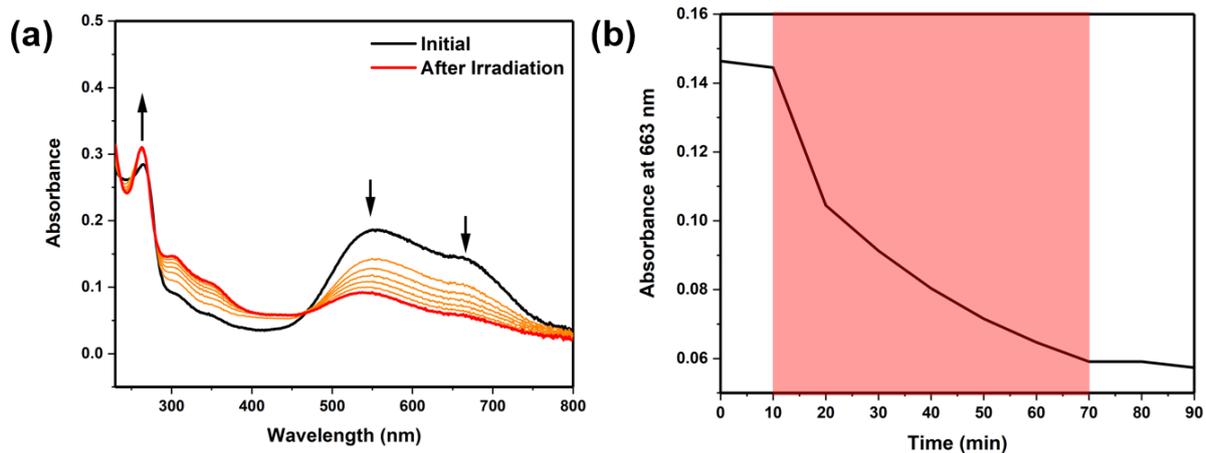


Figure S4. a) UV-vis absorption spectra of an aqueous solution of **DA₆** (43 μM) at initial (black-line) and white-light irradiation over 60 min (orange-line) and white-light irradiation over 60 min (red-line) at 20 °C. (b) Time-course of the photoisomerization process of **DA₆** in MilliQ water, monitored at λ_{max} 663 nm (red area: white-light irradiation period). Irradiation of UV-vis samples was carried out at 20 °C using a light guide equipped BBZM-I xenon light source (380–800 nm, 300 W) positioned at a distance of 1 cm from the sample.

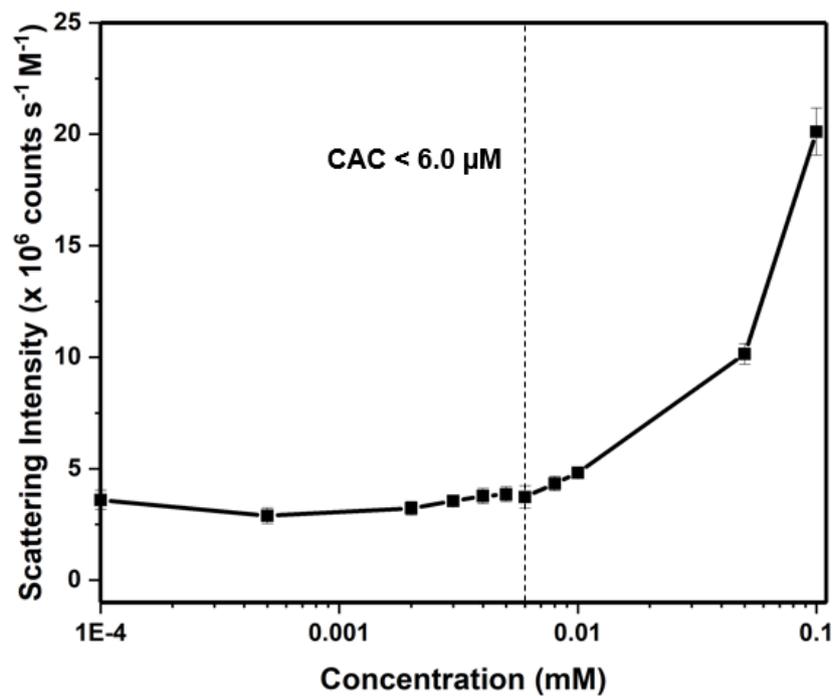


Figure S5. Dynamic light scattering assay for determination of critical aggregation concentration of DA₁₁ (concentration: 1.0 x 10⁻⁴ to 0.1 mM).

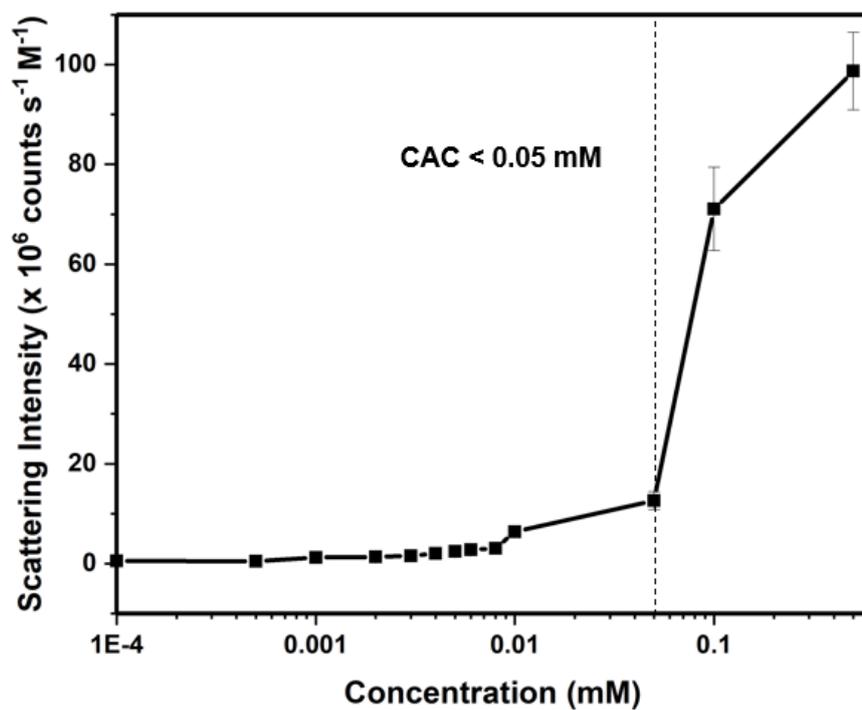


Figure S6. Dynamic light scattering assay for determination of critical aggregation concentration of DA₇ (concentration: 1.0 x 10⁻⁴ to 0.5 mM).

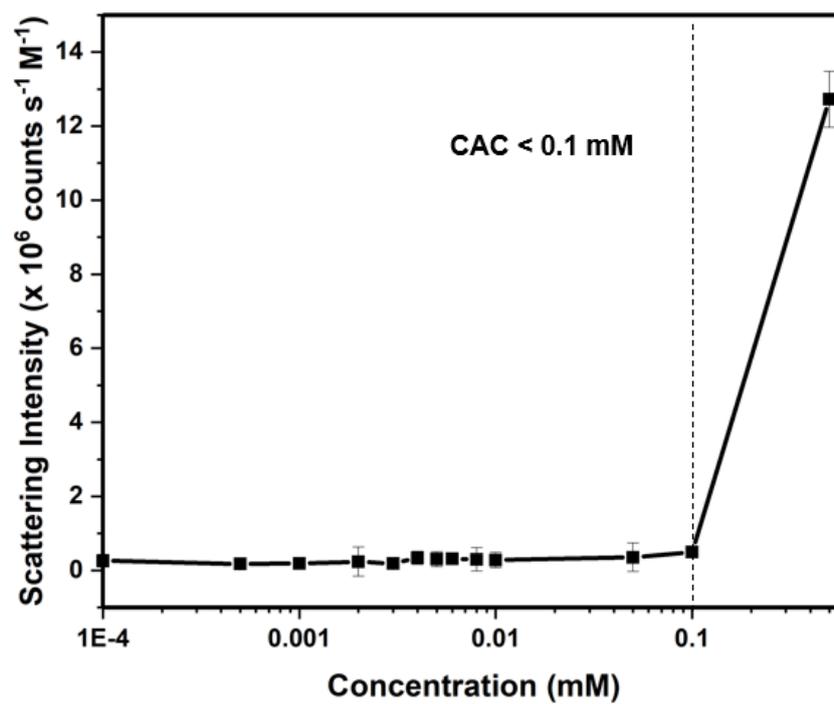


Figure S7. Dynamic light scattering assay for determination of critical aggregation concentration of **DA₆** (concentration: 1.0×10^{-4} to 0.5 mM).

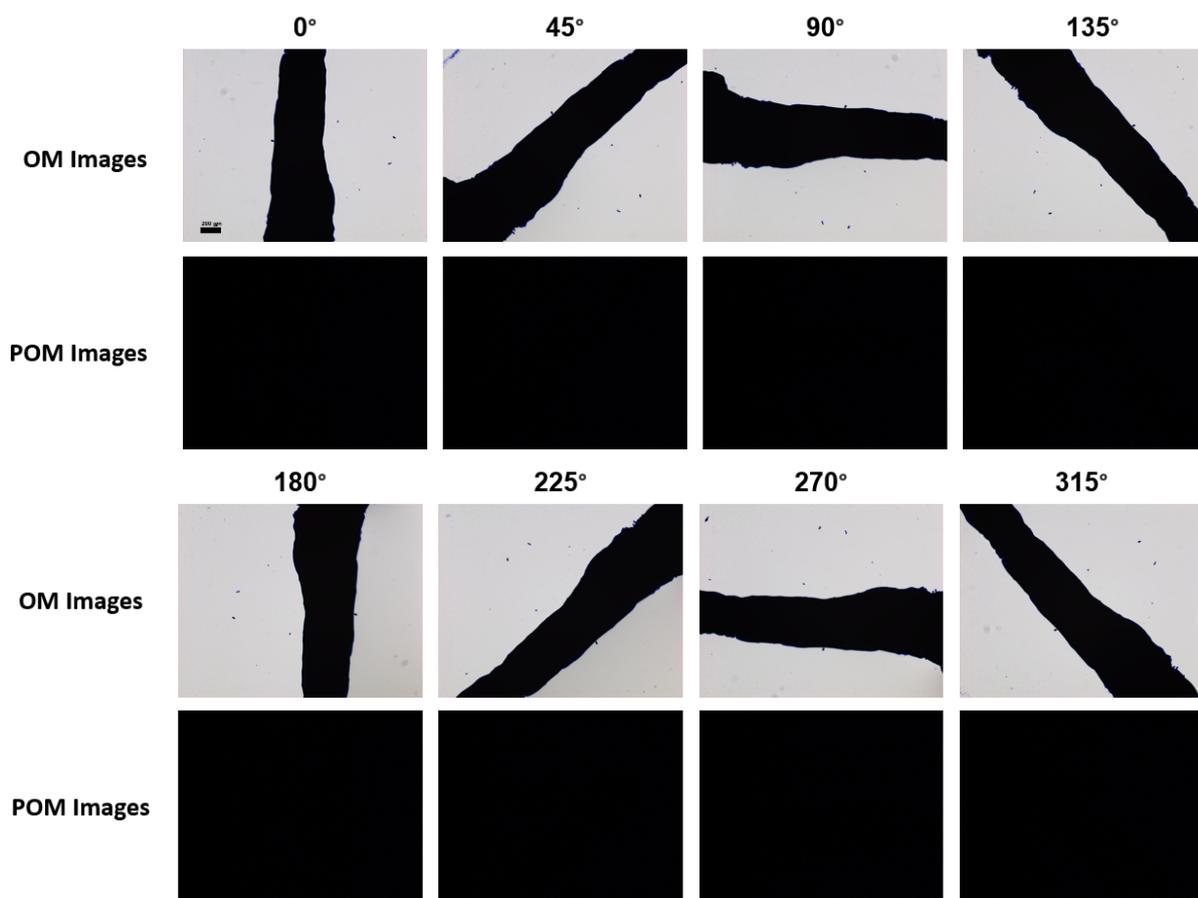


Figure S8. Optical microscopic images of a macroscopic soft scaffold composed of DA_{11} prepared from a solution of CaCl_2 (150 mM) under crossed polarizers. The POM and OM images of the soft scaffold were tilted at 0° , 45° , 90° , 135° , 180° , 225° , 270° and 315° relative to the transmission axis of the analyzer. Scale bar $200 \mu\text{m}$ for all panels.

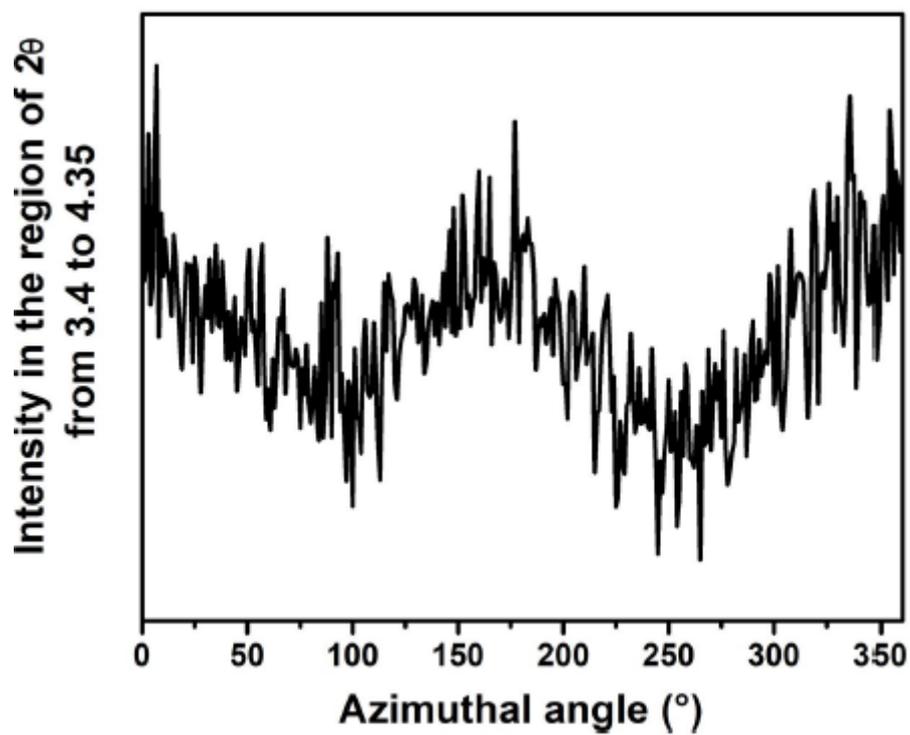


Figure S9. Full-width half maximum of $d = 2.24$ nm of the **DA₁₁** soft scaffold prepared from CaCl_2 solution (150 mM) at various azimuthal angle.

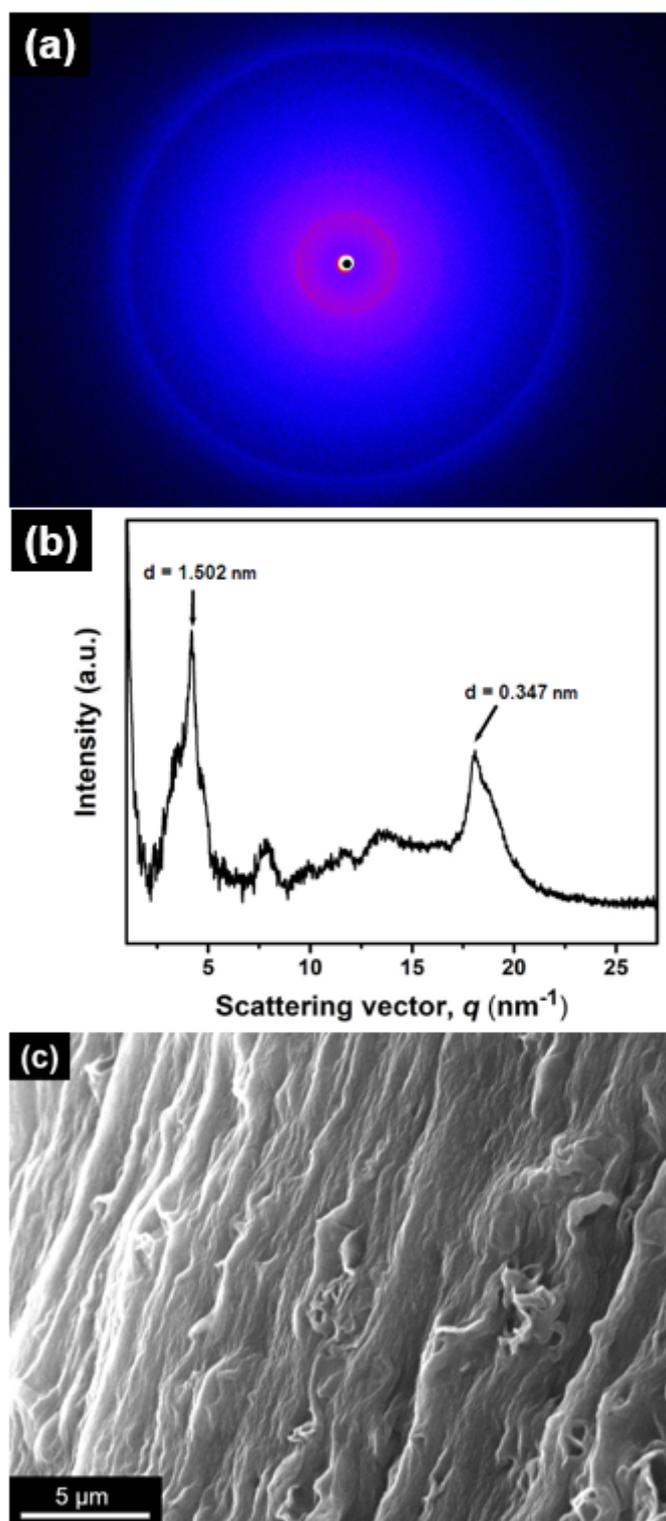


Figure S10. (a) 2D-WAXD image of **DA₇** macroscopic soft scaffold with 20 min X-ray exposure time. (b) 1D-WAXD pattern of **DA₇** macroscopic soft scaffold of 2D WAXD image in (a). (c) SEM image of a macroscopic scaffold composed of **DA₇** prepared from a solution of CaCl_2 (150 mM).

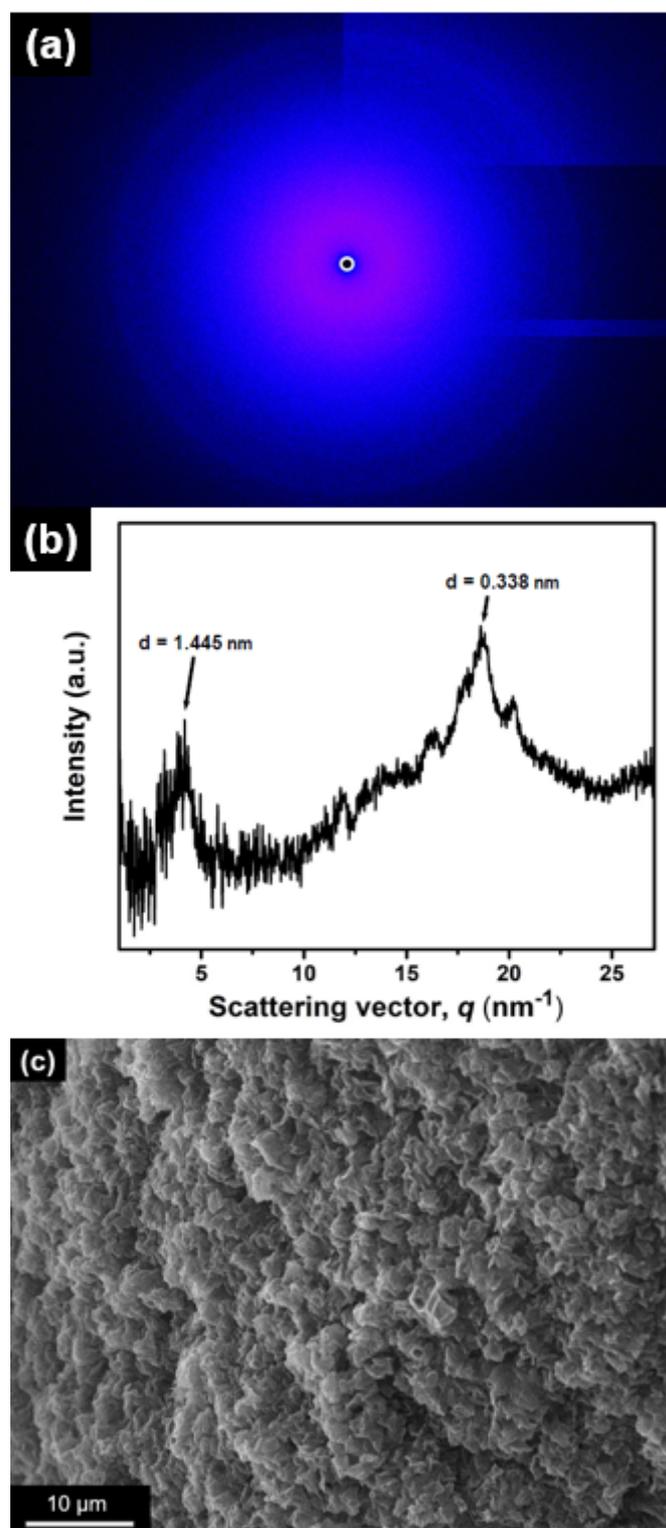


Figure S11. (a) 2D-WAXD image of **DA₆** macroscopic soft scaffold with 20 min X-ray exposure time. (b) 1D-WAXD pattern of **DA₆** macroscopic soft scaffold of 2D WAXD image in (a). (c) SEM image of a macroscopic scaffold composed of **DA₆** prepared from a solution of CaCl_2 (150 mM).

3. Analytical Data

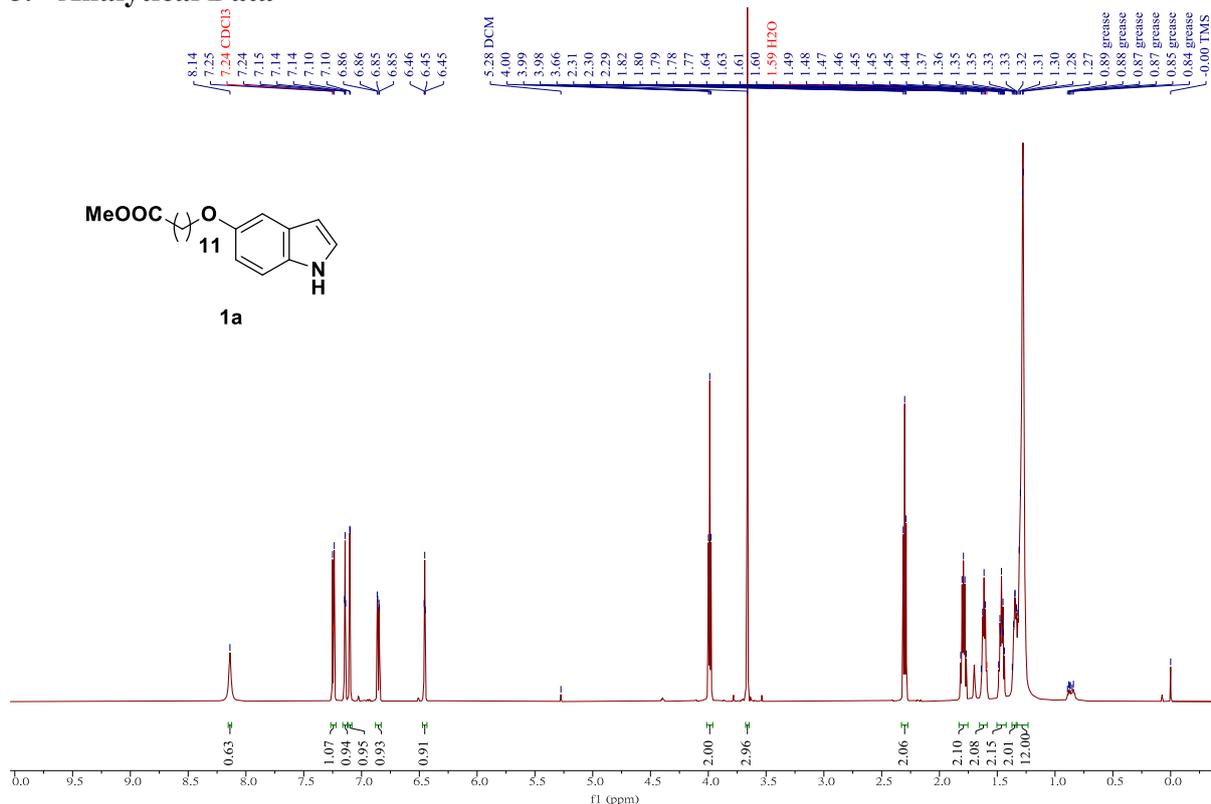


Figure S12. ¹H NMR spectrum (600 MHz, 25 °C) of compound **1a** in CDCl₃ with 0.03% v/v TMS.

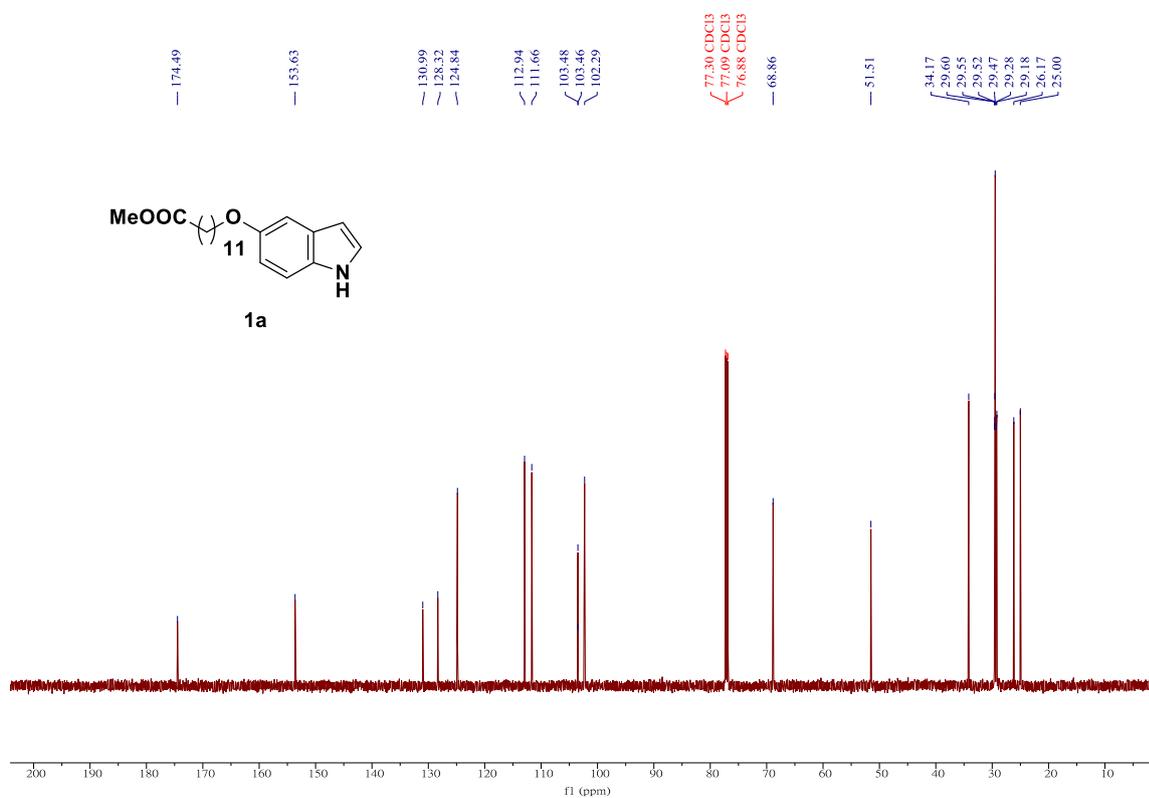


Figure S13. ¹³C NMR spectrum (151 MHz, 25 °C) of compound **1a** in CDCl₃ with 0.03% v/v TMS.

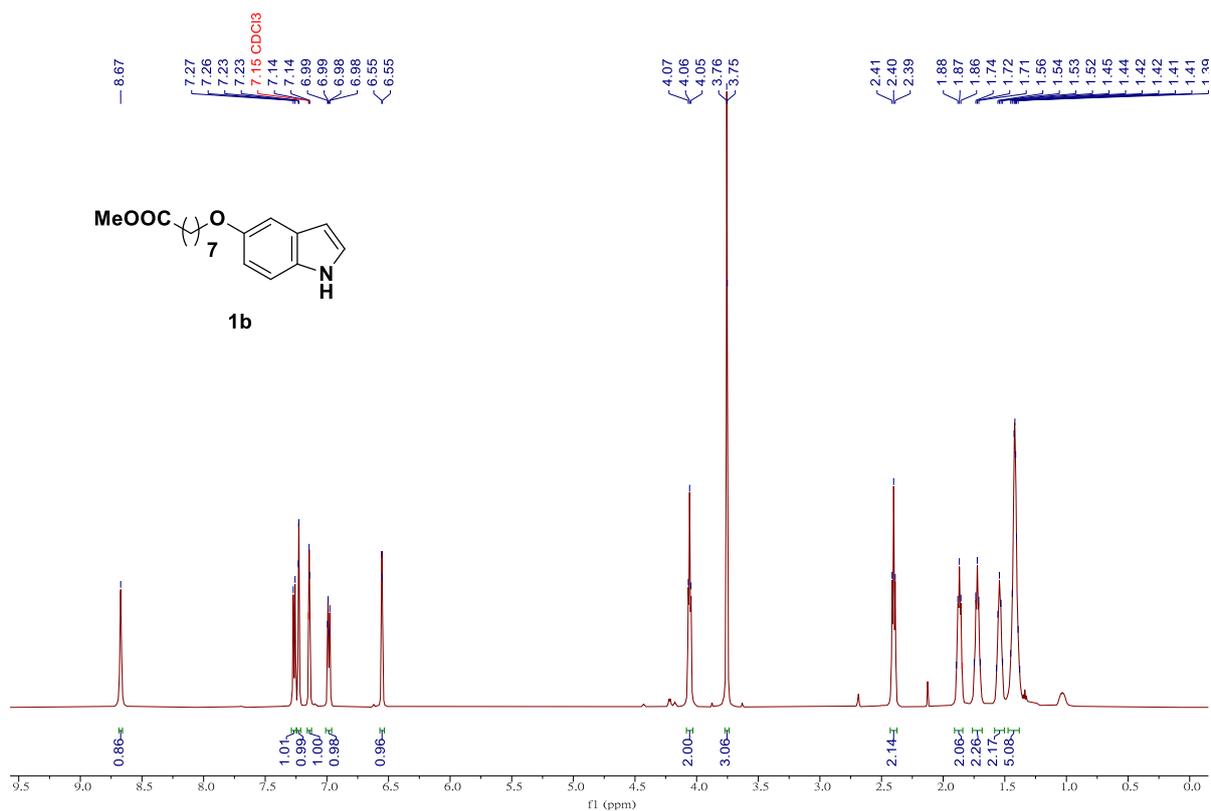


Figure S14. ¹H NMR spectrum (600 MHz, 25 °C) of compound **1b** in CDCl₃ with 0.03% v/v TMS.

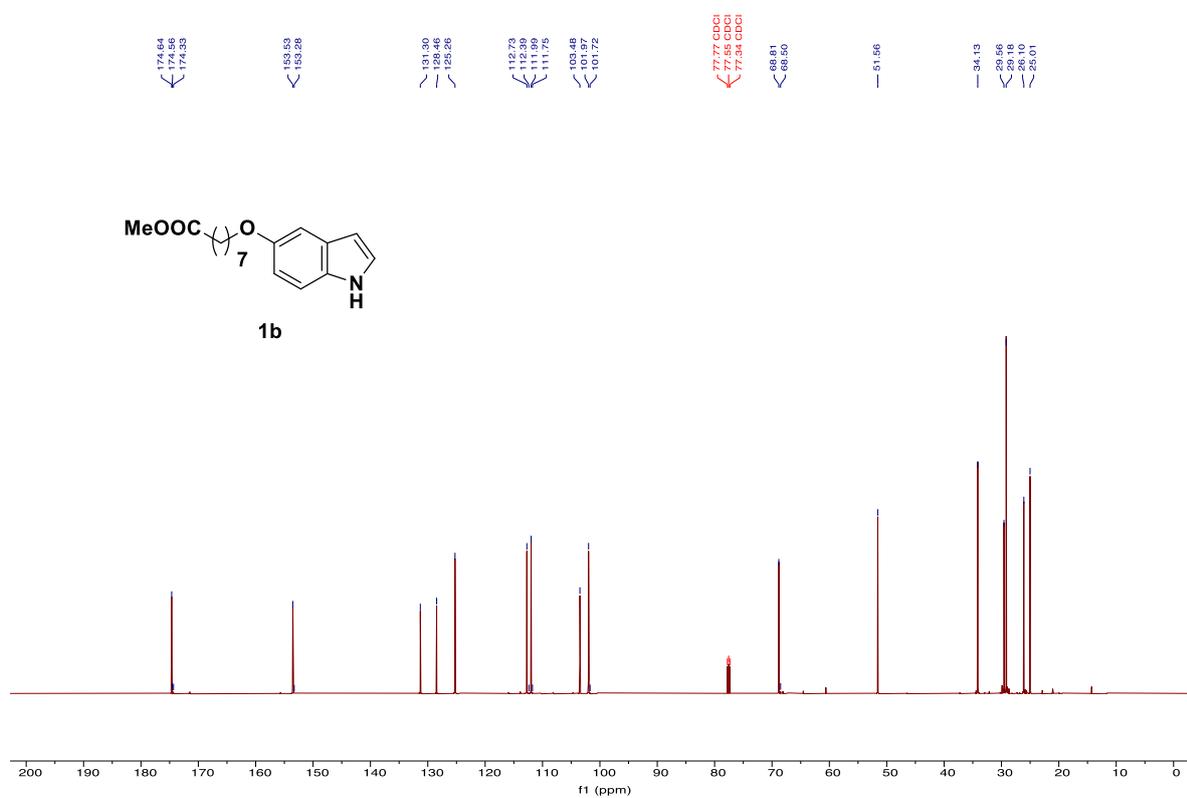


Figure S15. ¹³C NMR spectrum (151 MHz, 25 °C) of compound **1b** in CDCl₃ with 0.03% v/v TMS.

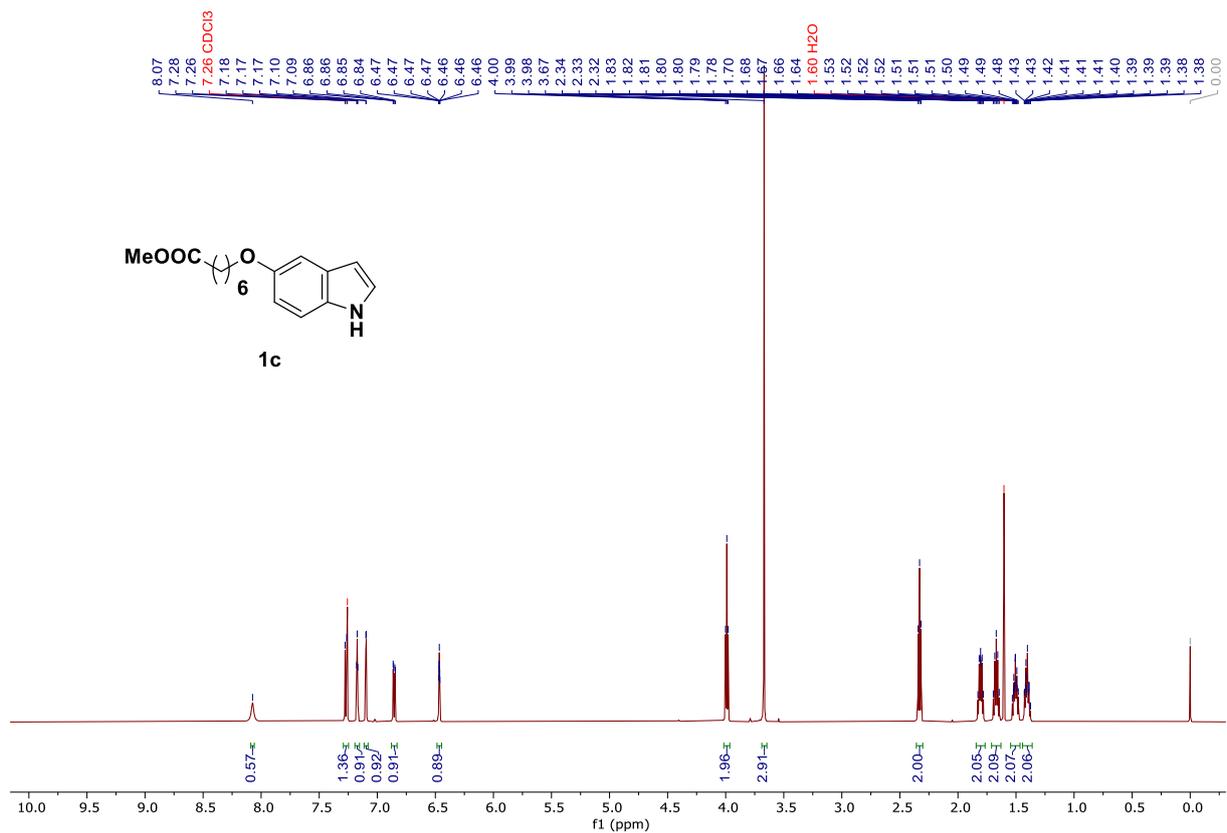


Figure S16. ¹H NMR spectrum (600 MHz, 25 °C) of compound **1c** in CDCl₃ with 0.03% v/v TMS.

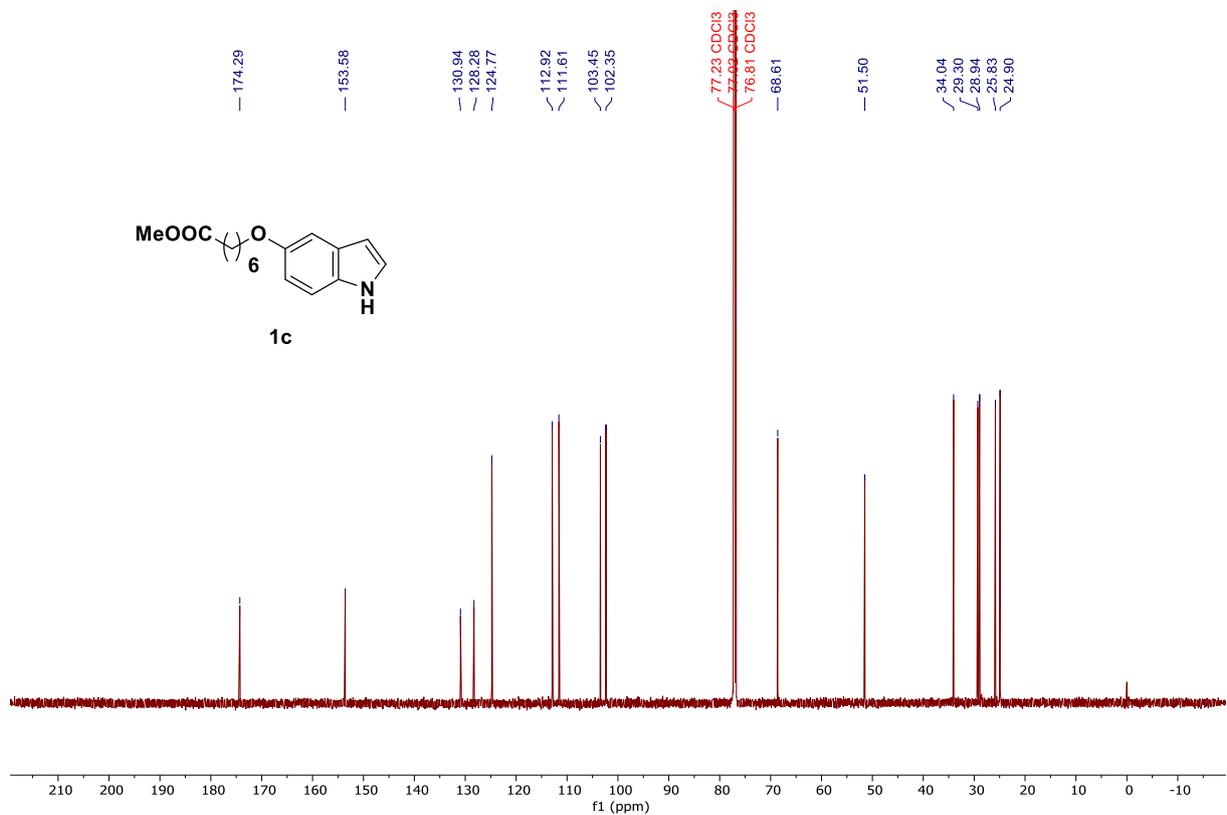


Figure S17. ¹³C NMR spectrum (151 MHz, 25 °C) of compound **2a** in CDCl₃ with 0.03% v/v TMS.

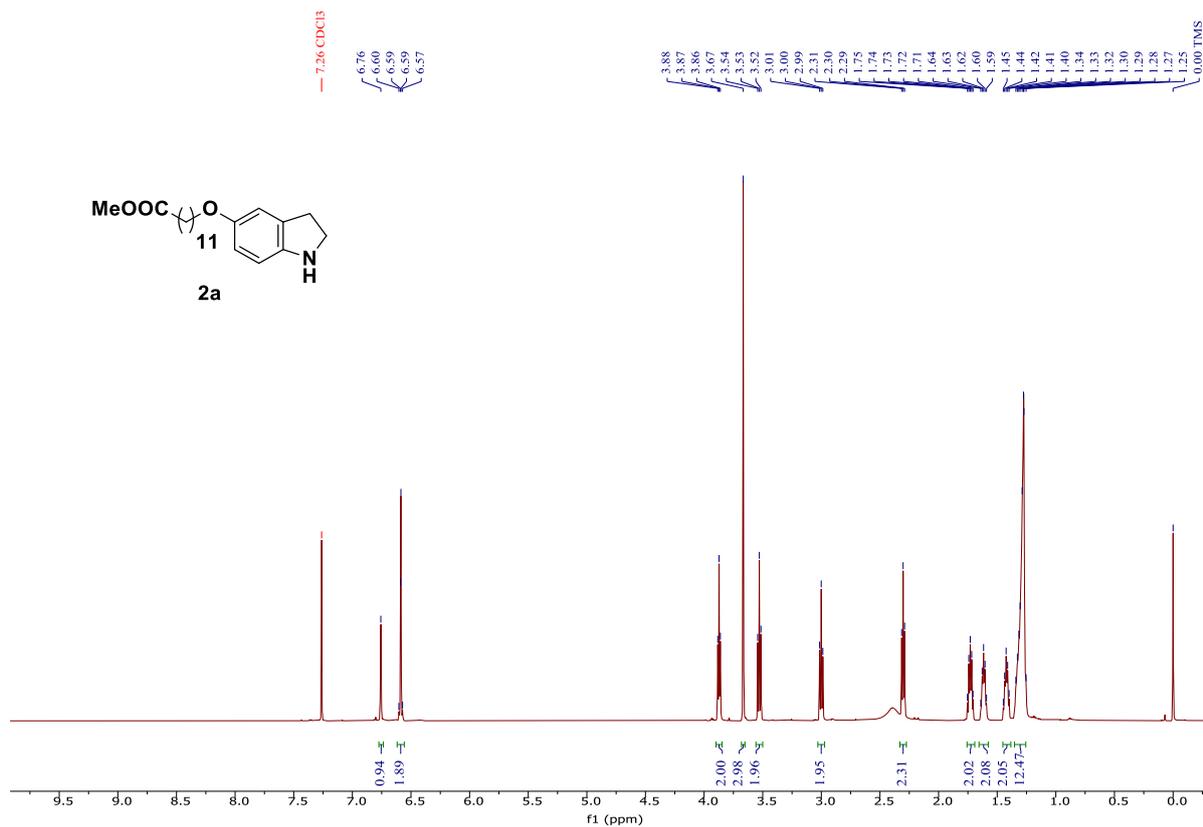


Figure S18. ¹H NMR spectrum (600 MHz, 25 °C) of compound **2a** in CDCl₃ with 0.03% v/v TMS.

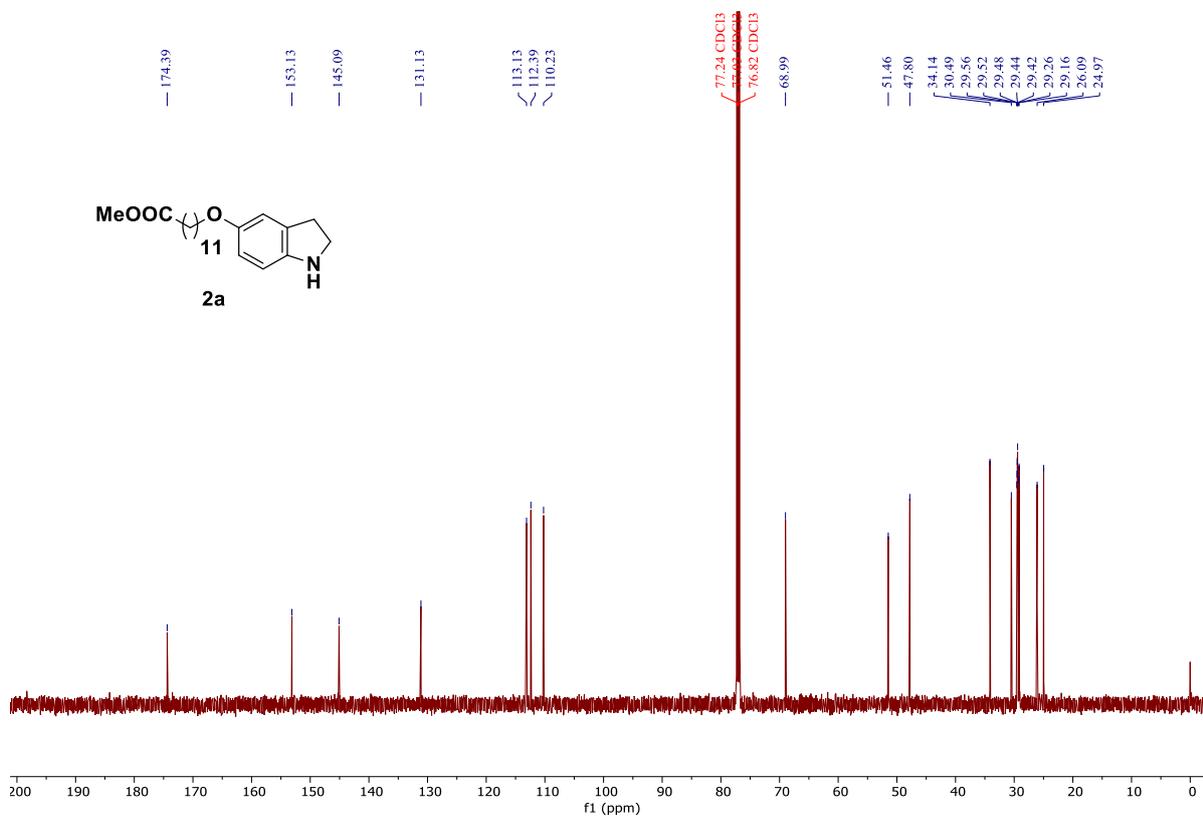
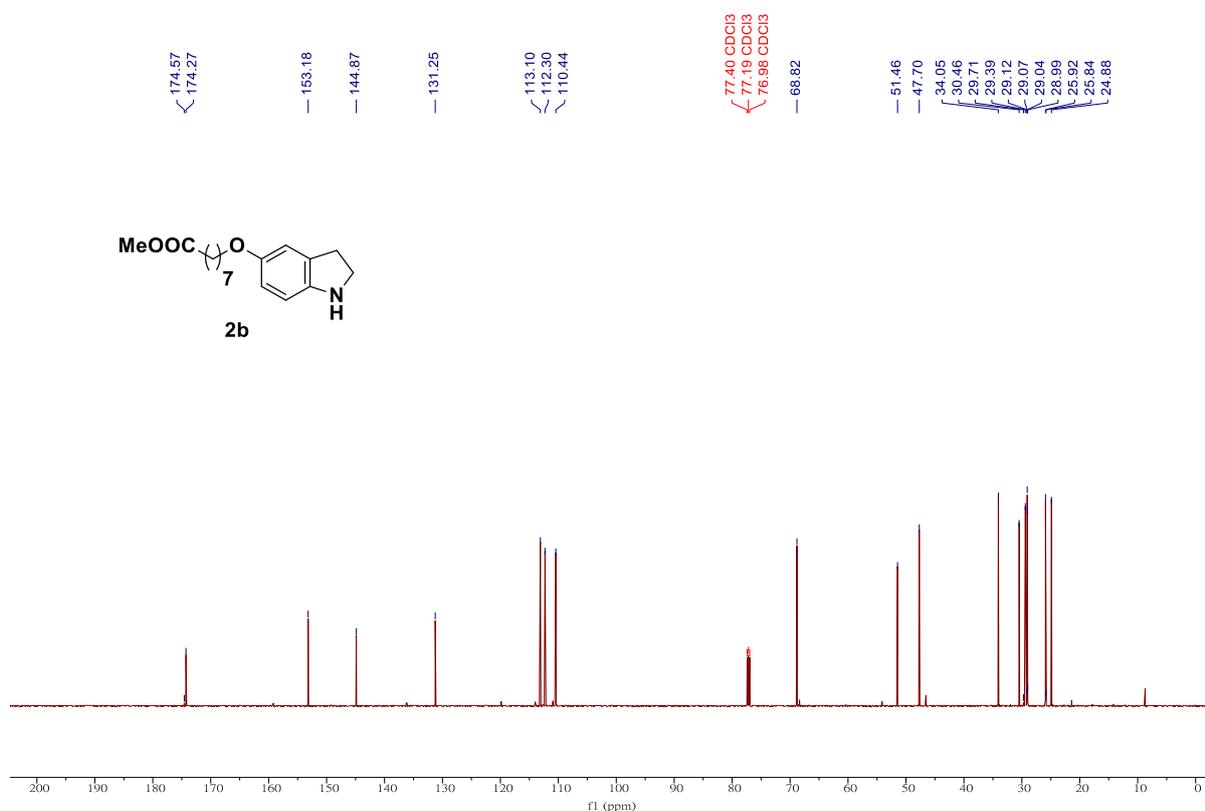
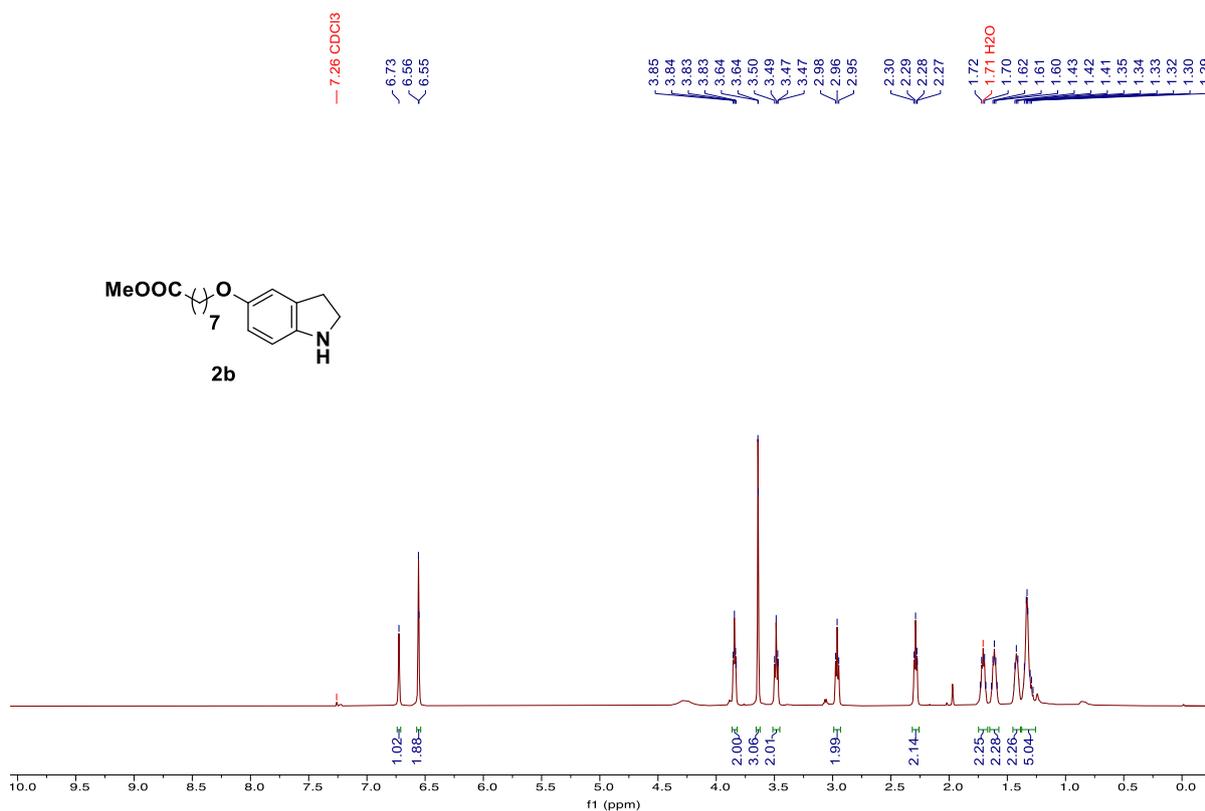


Figure S19. ¹³C NMR spectrum (151 MHz, 25 °C) of compound **2a** in CDCl₃ with 0.03% v/v TMS.



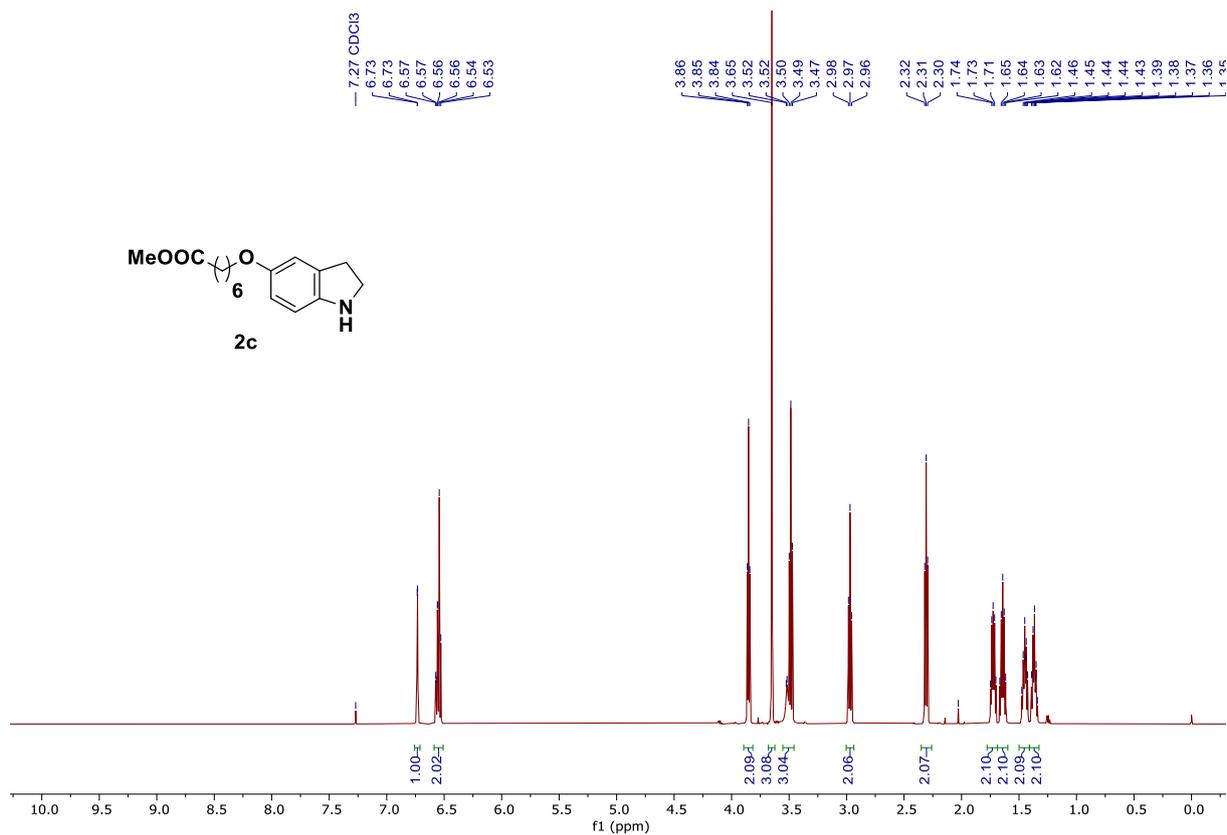


Figure S22. ^1H NMR spectrum (600 MHz, 25 °C) of compound **2c** in CDCl_3 with 0.03% v/v TMS.

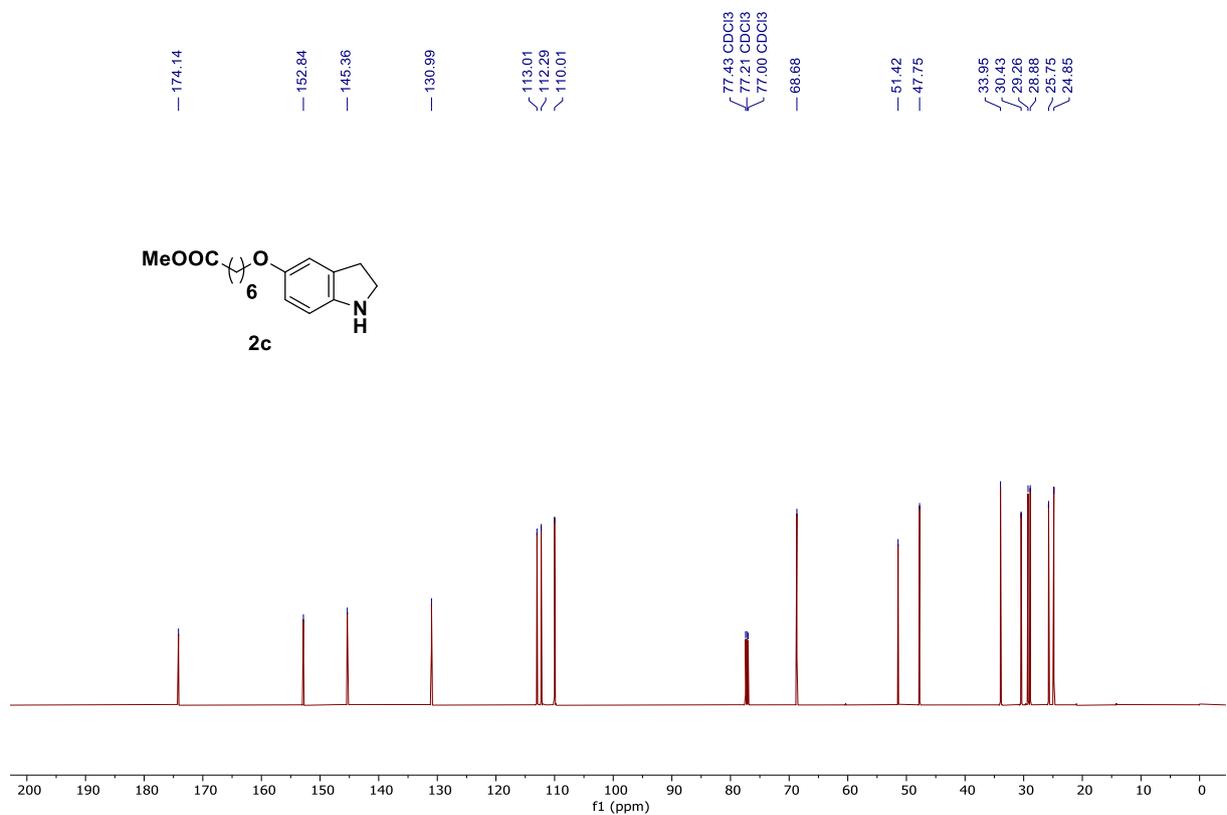


Figure S23. ^{13}C NMR spectrum (151 MHz, 25 °C) of compound **2c** in CDCl_3 with 0.03% v/v TMS.

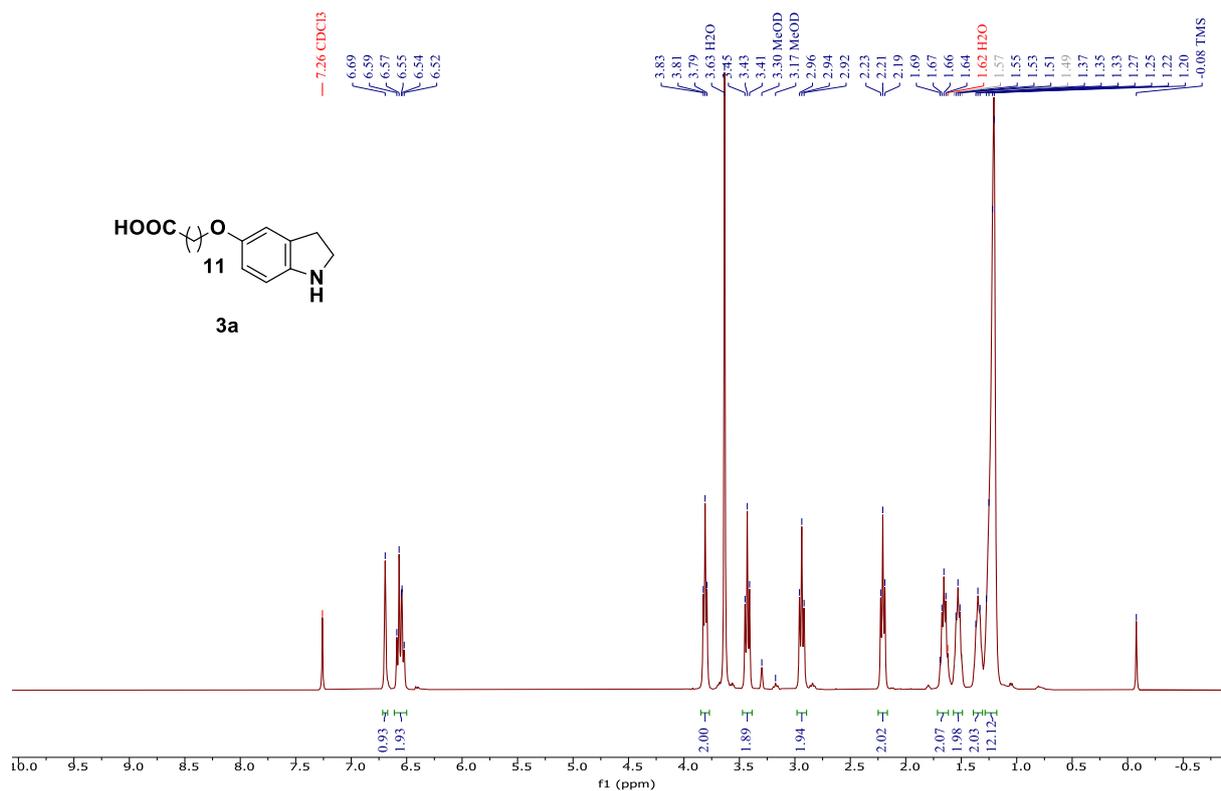


Figure S24. ¹H NMR spectrum (600 MHz, 25 °C) of compound **3a** in 9:1 CDCl₃ with 0.03% v/v TMS:CD₃OD.

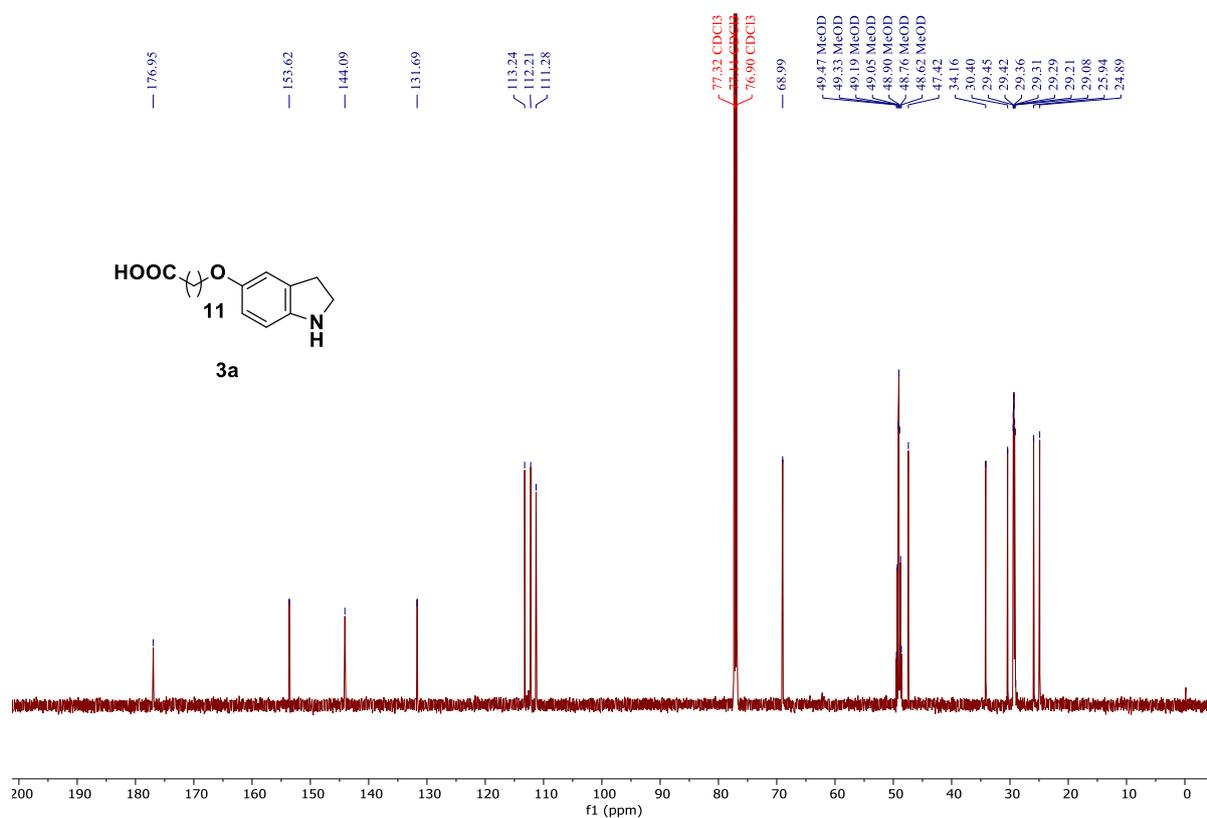


Figure S25. ¹³C NMR spectrum (151 MHz, 25 °C) of compound **3a** in 9:1 CDCl₃ with 0.03% v/v TMS:CD₃OD.

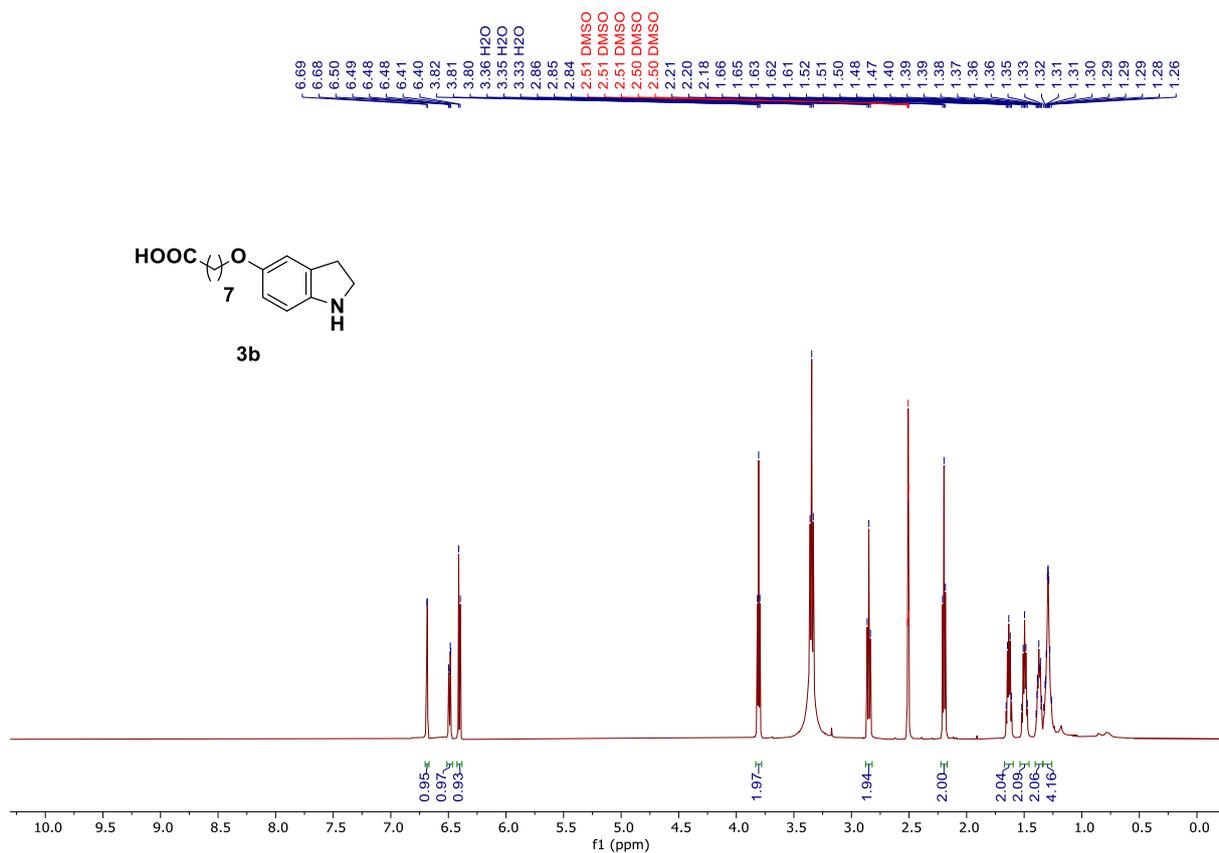


Figure S26. ¹H NMR spectrum (600 MHz, 25 °C) of compound **3b** in DMSO-d₆.

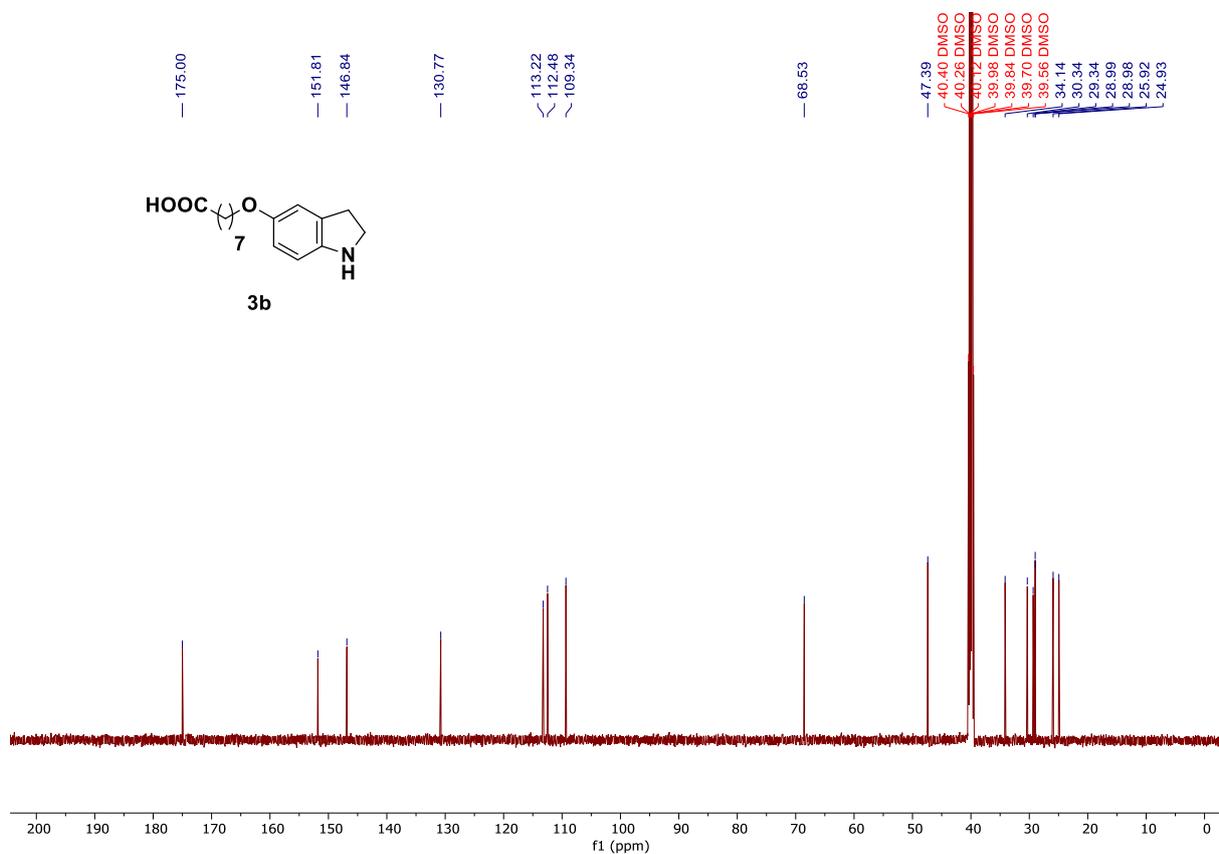


Figure S27. ¹³C NMR spectrum (151 MHz, 25 °C) of compound **3b** in DMSO-d₆.

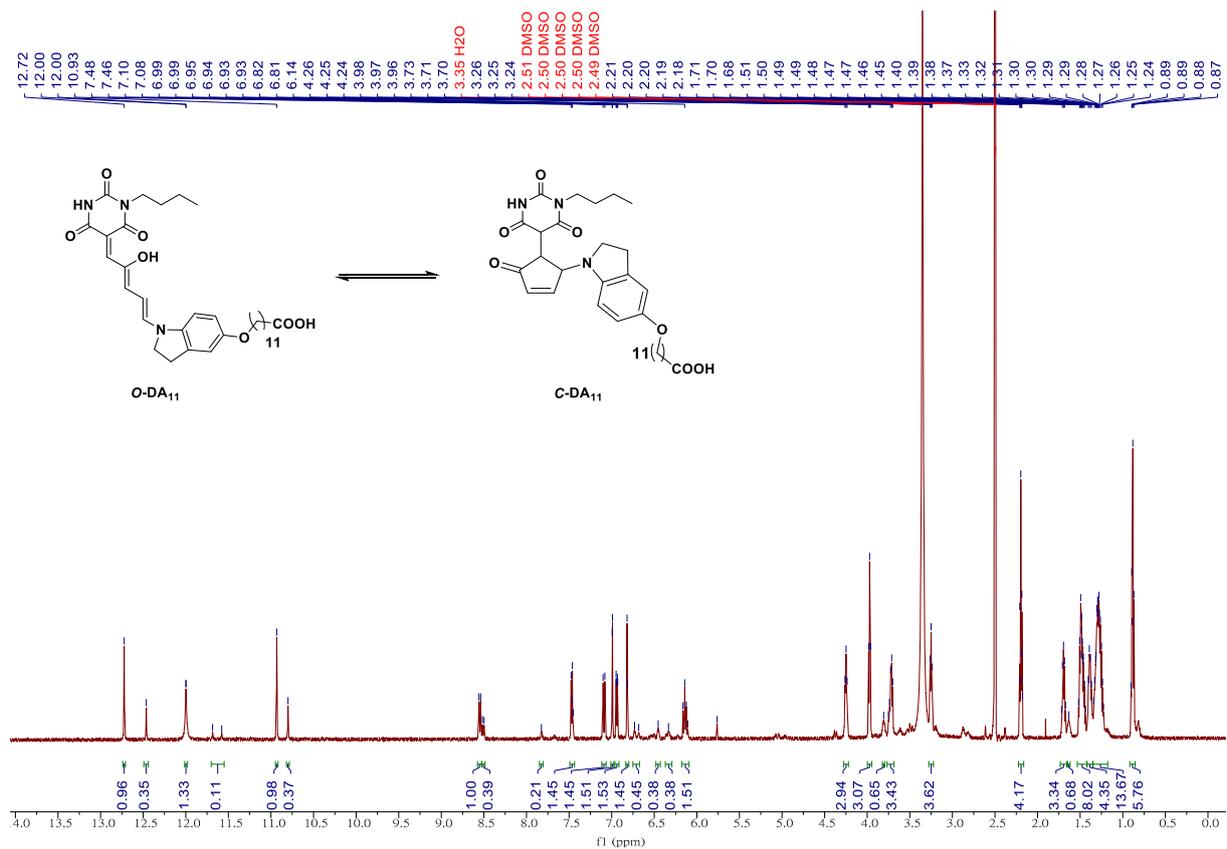


Figure S30. ¹H NMR spectrum (600 MHz, 25 °C) of DA₁₁ in DMSO-d₆.

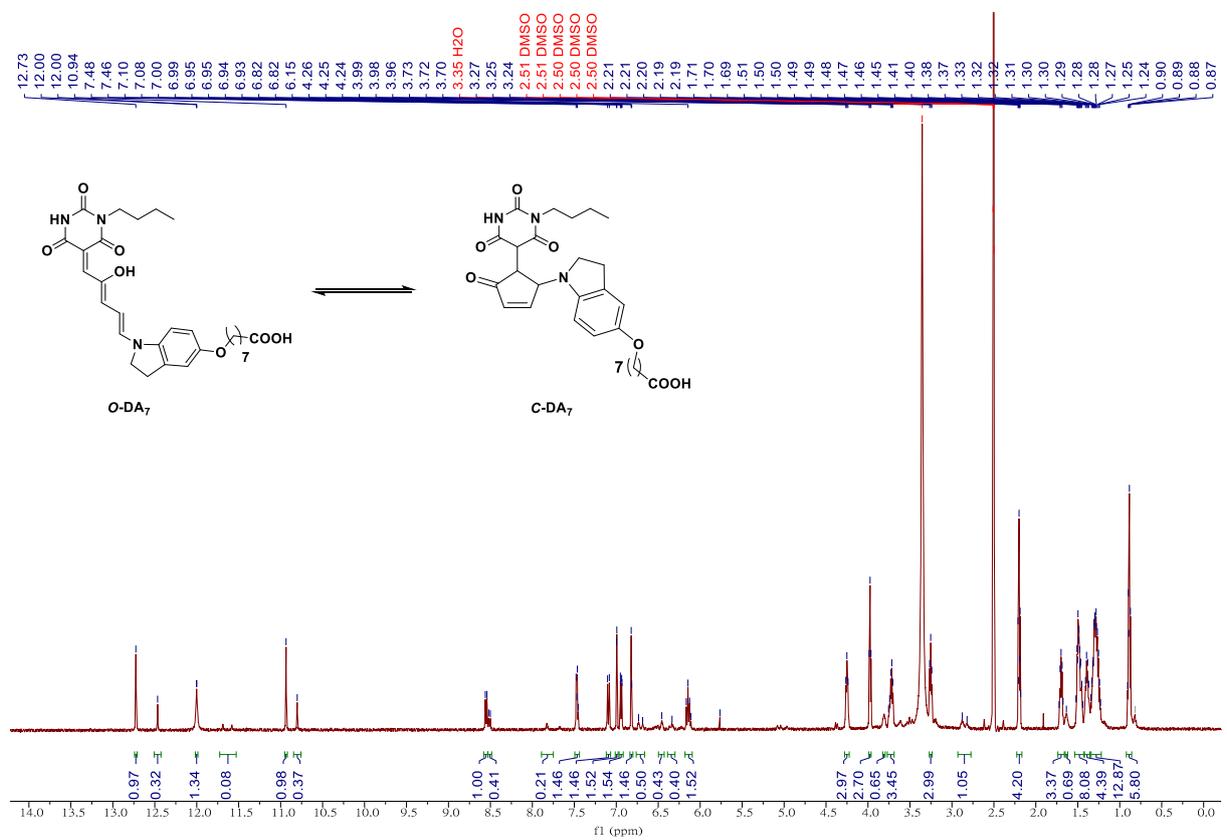


Figure S31. ¹H NMR spectrum (600 MHz, 25 °C) of DA₇ in DMSO-d₆.

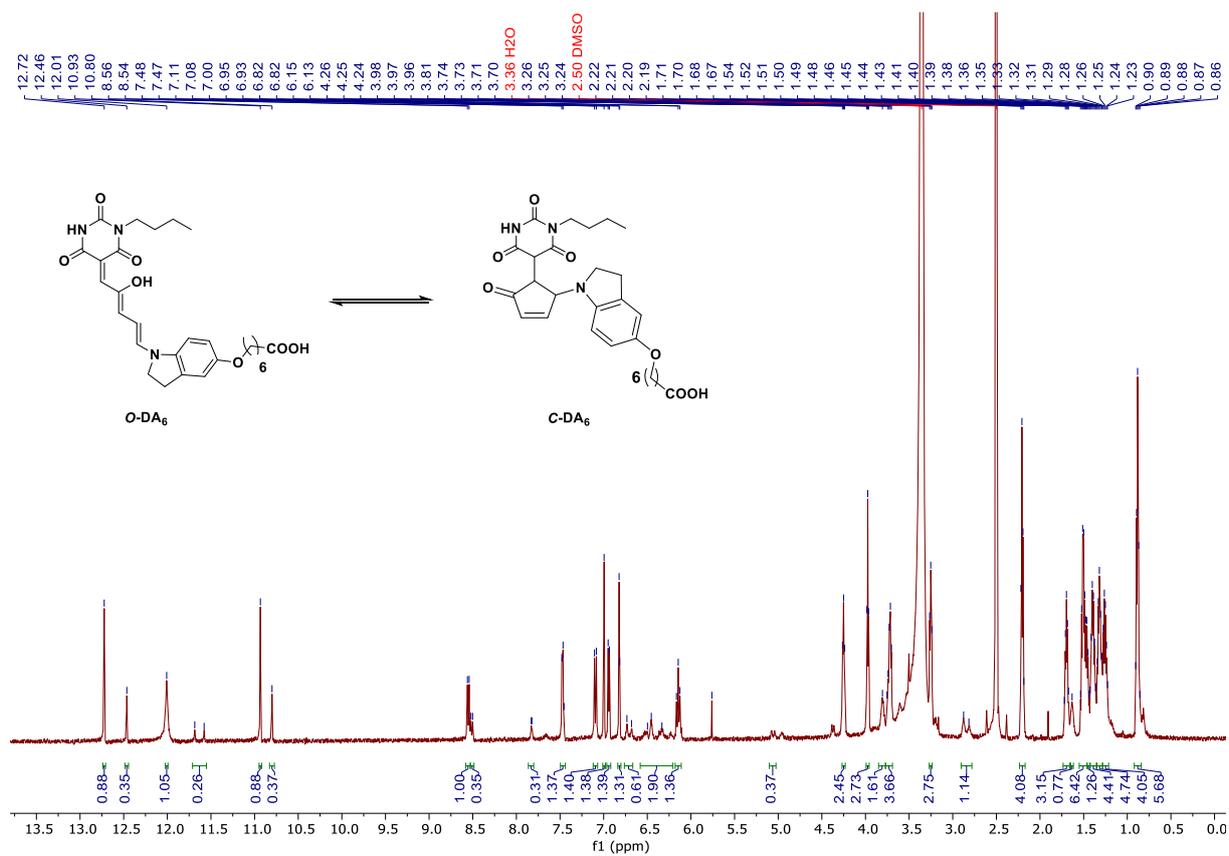


Figure S32. ¹H NMR spectrum (600 MHz, 25 °C) of DA₆ in DMSO-d₆

4. References

1. Cheung, L.-H.; Kajitani, T.; Leung, F. K.-C. *J. Colloid Interface Sci.* **2022**, *628*, 984-993.
2. Leung, F. K.-C.; Cui, J.-F.; Hui, T.-W.; Zhou, Z.-Y.; Wong, M.-K. *RSC Adv.* **2014**, *4* (51), 26748-26756.