Supporting Information for

"Minimal Complementary Hydrogen Bonded Double helices"

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General Methods. Chemicals were purchased from Aldrich and used as received. All non-deuterated solvents were dried using an Innovative Technology solvent purification system SPS-400-5. Chromatography was performed on Merck 240-400 mesh silica gel-60. CDCl$_3$ and acetone-d$_6$ were purchased from Cambridge Isotope Laboratories and dried over 3Å (acetone) or 4Å (chloroform) molecular sieves before use. $^1$H and $^{13}$C NMR spectra were collected on a Varian Mercury 400 MHz spectrometer. Spectra are reported with residual solvent peak as reference from TMS. EI and CI (CH$_4$) mass spectra were obtained on a Finnigan MAT 8200 mass spectrometer and ESI mass spectra were obtained using Micromass LCT instrumentation. $^1$H NMR titration experiments were performed on a Varian Inova 600 MHz spectrometer. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.
**H NMR Titration Data.**

![Graph showing chemical shift of N-H in indole vs concentration of 8 (M)]

Figure S1 $^1$H NMR titration of 14b with 8 following indole N-H$^a$ ($K_a=3616 \pm 73$ M$^{-1}$).

![Graph showing chemical shift of N-H in indole vs concentration of 8 (M)]

Figure S2 $^1$H NMR titration of 14b with 8 following indole N-H$^c$ ($K_a=3705 \pm 97$ M$^{-1}$).
Figure S3 $^1$H NMR titration of 14b with 8 following thiazine dioxide N-H$^b$ ($K_a$=3810 ±108 M$^{-1}$)

**Experimental Procedures, Synthesis and Characterization.**

**1:** Concentrated sulfuric acid (1mL) was added to a mixture of 1,4-dibromo-2,3-butanedione (82.6 mmol, 20.0 g) and trimethylorthoformate (182 mmol, 19.5 g) in a 100mL flask under a nitrogen atmosphere. The reaction solution was stirred for 16 hours. Water (100 mL) and CH$_2$Cl$_2$ (100 mL) were added, separated and the organic layer was further washed with 10% HCl and saturated NaCl solutions. The solvent was dried with MgSO$_4$, evaporated under reduced pressure and the crude product dissolved in hexane and filtered to remove some insoluble precipitates. The filtrate was cooled to -78°C and
the resulting white solid collected to give pure product (21.5 g, 89% yield). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 4.44(s, 2 H), 3.50(s, 2 H), 3.30(s, 6 H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) ppm 216.2, 102.4, 50.3, 35.8, 29.6; El HRMS (m/z) calculated for C\(_6\)H\(_{10}\)Br\(_2\)O\(_3\) [M\(^+\)] 289.9447; found 288.9483.

2: 2-Mercapto-propriophenone\(^1\) (8.30 g, 50.0 mmol) and 1,4-Dibromo-3,3-dimethoxy-butan-2-one (1) (14.5 g, 50.0 mmol) were dissolved in CH\(_3\)CN (200mL) and the solution purged with N\(_2\) for 5 min. K\(_2\)CO\(_3\) (13.8 g, 100 mmol) was quickly added and the reaction mixture was stirred for 2 days before the slurry was filtered through celite, and washed with CH\(_2\)Cl\(_2\) (3 \( \times \) 40 mL). The filtrate was concentrated under reduced pressure to give pure product, pale yellow oil (18 g, 96%). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 8.02 (d, 2H, \( J = 7.2 \) Hz), 7.57 (t, 1H, \( J = 7.5 \) Hz), 7.47 (t, 2H, \( J = 7.8 \) Hz), 4.52 (q, 1H, \( J = 6.8 \) Hz), 3.73 (m, 2H), 3.47 (s, 2H), 3.27 (s, 3H), 3.23 (s, 3H), 1.55 (d, 3H, \( J = 7.0 \) Hz); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) ppm 202.6, 196.2, 135.1, 132.9, 128.4, 128.3, 101.7, 50.0, 49.8, 41.2, 37.6, 29.4, 16.4; CI HRMS (m/z) calculated for C\(_{15}\)H\(_{19}\)BrO\(_4\)S [(M+H\(^+\)] 375.0266; found 375.0272.

3: A CH\(_2\)Cl\(_2\) (5 mL) solution of m-CPBA (77 %, 0.28 g, 1.3 mmol) was dropwise added into a CH\(_2\)Cl\(_2\) (5 mL) solution of 2 (0.23 g, 0.6 mmol) at -78\(^\circ\)C. The mixture was stirred vigorously and slowly warmed to room temperature over 5h. The reaction solution was quenched with aqueous NaHCO\(_3\) and extracted with CH\(_2\)Cl\(_2\) (3 \( \times \) 8 mL). The combined organic layers were washed with H\(_2\)O and dried over anhydrous MgSO\(_4\). The crude product was concentrated under reduced pressure to give the pure waxy product (0.23g, 95%). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 8.03 (d, 2H, \( J = 8.2 \) Hz), 7.64 (t, 1H, \( J = 7.7 \) Hz).

\(^1\) G. M. Coppola, R. E. Damon, H. Yu, Synlett 1995, 1143.
Hz), 7.52 (t, 2H, J = 7.7 Hz), 5.47 (q, 1H, J = 7.2 Hz), 4.66 (m, 2H), 3.44 (m, 2H), 3.32 (s, 3H), 3.26 (s, 3H), 1.75 (d, 3H, J = 7.2 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 199.1, 193.5, 135.3, 134.4, 129.0, 109.8, 101.6, 64.2, 59.2, 50.4, 40.2, 28.9, 12.3; CI HRMS (m/z) calculated for C$_{15}$H$_{19}$BrO$_6$S [(M+H)$^+$] 407.0164; found 407.0157.

4: Sulfone 3 (0.95 g, 2.5 mmol) and ammonium acetate (1.13 g, 15 mmol) in glacial acetic acid (40 mL) were refluxed for 36h under an N$_2$ atmosphere. When cooled down, the reaction mixture was diluted with H$_2$O, extracted with CH$_2$Cl$_2$, washed with sat. NaHCO$_3$ solution, and dried over MgSO$_4$. The crude product was concentrated under reduced pressure and purified with flash chromatography (hexanes / ethyl acetate: 1/1) to give a yellow solid (0.60 g, 62%). $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.57 (s, 1H), 7.51 (m, 3H), 7.41 (m, 2H), 5.99 (s, 1H), 3.55 (s, 2H), 3.31 (s, 6H), 2.10 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 141.5, 138.3, 129.8, 128.9, 128.2, 110.5, 107.2, 98.7, 97.6, 49.7, 33.1, 8.4; EI HRMS (m/z) calculated for C$_{15}$H$_{18}$BrNO$_4$S [M$^+$] 387.0140; found 387.0147.

5: Thiazine dioxide 4 (0.60 g, 1.5 mmol) was dissolved in formic acid (60 mL) and the solution was refluxed for 18h. When cooled down, the reaction mixture was diluted with H$_2$O, extracted with CH$_2$Cl$_2$, washed with aqueous NaHCO$_3$, and dried over MgSO$_4$. The organic layer was concentrated under reduced pressure to give pure product, a brown solid with quantitative yield (0.52 g). $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.80 (s, 1H), 7.52 (m, 3H), 7.38 (m, 2H), 6.64 (s, 1H), 4.32 (s, 2H), 2.11 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 186.4, 139.3, 133.5, 132.9, 130.5, 129.3, 128.3, 111.4, 105.1, 27.2, 8.8; EI HRMS (m/z) calculated for C$_{13}$H$_{12}$BrNO$_3$S [M$^+$] 340.9721; found 340.9717.
6: A solution of deprotected thiazine dioxide 5 (1.26g, 3.8mmol) in CH$_2$Cl$_2$ (20mL) and a solution of NaSH (0.2g, 3.8mmol) in H$_2$O (10mL) were separately purged with N$_2$ for 5 min before they were quickly mixed. The reaction mixture was stirred vigorously under N$_2$ atmosphere for 16h at room temperature, and monitored by $^1$H NMR. Upon completion of the reaction, the aqueous layer was acidified to approximately pH 3 with aqueous 1M HCl solution, separated and extracted further with CH$_2$Cl$_2$ (2×15mL). The organic layers were combined, washed with H$_2$O, brine, and dried over MgSO$_4$. The crude product was concentrated under reduced pressure and purified with flash chromatography (3%CH$_3$OH in CH$_2$Cl$_2$) to give a white solid (0.90 g, 87%). $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.96 (s, 2H), 7.46 (m, 6H), 7.35 (m, 4H), 6.77 (s, 2H), 3.93 (s, 4H), 2.02 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 188.9, 139.5, 134.9, 132.9, 130.3, 129.1, 128.4, 110.9, 104.2, 35.8, 8.7; EI HRMS (m/z) calculated for C$_{26}$H$_{24}$N$_2$O$_6$S$_3$ [M$^+$] 556.0796; found 556.0781.

7: Urea hydrogen peroxide (UHP) (5.0 mmol, 0.51 g) was introduced to a solution of trifluoroacetic anhydride (TFAA) (4.0 mmol, 0.83 g) in acetonitrile (10 mL) and the resulting solution was stirred for 3 minutes. Thioether 6 (1.3 mmol, 0.73 g) dissolved in acetonitrile (10 mL) was slowly added and the reaction was stirred for 2 hours. The solution was diluted with water (100mL) and the resulting precipitate was collected by filtration. The solid crude sulfone and ammonium acetate (0.20 g) in glacial acetic acid (20 mL) were refluxed for 40 hours. The reaction solution was cooled down and diluted with water (20 mL) and the resulting precipitate was collected and purified using preparative TLC (10% CH$_3$OH in CH$_2$Cl$_2$) to give a white solid (0.40 g, 74% yield). M.P. 331.5-333 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ ppm 11.33(s, 1H), 10.52(s, 2H), 7.54(m, 2H).
10H), 6.59(s, 2H), 6.53(s, 2H), 1.89(s, 6H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ ppm 158.5, 152.3, 148.2, 142.9, 136.9, 131.7, 129.4, 128.8, 124.2, 123.0, 19.6; ESI HRMS (m/z) calculated for C$_{26}$H$_{23}$S$_3$O$_6$N$_3$Na [(M+Na)$^+$] 592.0647; found 592.0633.

8: 2,6-Diiodo-3,5-dimethylpyridine$^2$ (1.0 g, 2.8 mmol), 2-tributylstannylpyridine (1.4 g, 5.6 mmol) and Pd(PPh$_3$)$_4$ (0.2 g, 0.17 mmol) were dissolved in dry toluene and refluxed for 24 h. The reaction solution was cooled down, filtered through Celite and washed with CH$_2$Cl$_2$ (3 × 20 mL). The filtrate was wash with water and the organics was dried over anhydrous MgSO$_4$. The crude product was concentrated under reduced pressure and purified with flash chromatography to give a white solid (0.42 g, 57% yield). M.P. 170.5-171.5 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.67(d, $J$=4.7 Hz, 2H), 7.92(d, $J$=8.0 Hz, 2H), 7.79(dd, $J$=7.2, 8.0 Hz, 2H), 7.53 (s, 1H), 7.28 (m, 2H), 2.56 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 158.7, 152.7, 148.0, 142.5, 136.4, 131.7, 124.2, 122.3, 19.5; El HRMS (m/z) calculated for C$_{17}$H$_{15}$N$_3$ [M$^+$] 261.1266; found 261.1258.

9a: Methyl 2-ethylacetoacetate (20.0 mmol, 2.88 g) and 1.08 g NaOH were dissolved and stirred for 10 hours in a water/ethanol solution. A diazonium salt was prepared from aniline (20.0 mmol, 1.86 g), concentrated HCl (10 mL) and aqueous solution of sodium nitrate (20.0 mmol, 1.38 g) in an ice bath according to standard procedures. The diazonium salt was added to the pre-prepared sodium carboxylate solution at 0°C. The resulting solution was modified to pH 7-8 with sodium acetate and stirred at room temperature for 2 hours. The precipitate was collected, dried and refluxed overnight in formic acid (20 mL). The reaction solution was cooled down and diluted with water (100 mL). The precipitate was crude product and purified with the flash chromatography...

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(CH$_2$Cl$_2$) to give light yellow solid (16.6 g, 49% yield). $^1$H and $^{13}$C NMR data were in agreement with those reported in the literature.$^3$

9b: Prepared as described for 9a, starting from ethyl (2-ethyl)propionylacetate$^4$ and aniline (46% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 9.25(s, 1H), 7.69(m, 1H), 7.40-7.33(m, 2H), 7.12 (m, 1H), 2.98(q, $J$=7.2Hz, 2H), 2.64(s, 3H), 1.30(t, $J$=7.2Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 194.0, 136.1, 132.5, 129.1, 126.3, 121.2, 120.1, 118.0, 112.0, 34.4, 11.3, 8.2; EI HRMS (m/z) calculated for C$_{12}$H$_{13}$NO [M$^+$] 187.0997; found 187.0994.

10a: Trimethylphenylammonium tribromide (3.76 g, 100 mmol) was added to a THF (50mL) solution of 9a (1.73 g, 10 mmol). The reaction mixture was refluxed over an hour and filtered through celite. The filtrate was concentrated under reduced pressure and further purified with the flash chromatography (1.45 g, 74% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 9.03(s, 1H), 7.71(m, 1H), 7.38(m, 2H), 7.16 (m, 1H), 5.17(q, $J$=6.6Hz, 1H), 2.72(s, 3H), 1.95(d, $J$=6.6Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 186.7, 137.0, 129.8, 129.0, 127.3, 121.6, 120.6, 112.1, 43.7, 20.2, 11.2; EI HRMS (m/z) calculated for C$_{12}$H$_{12}$NOBr [M$^+$] 265.0098; found 265.0094.

10b: Prepared as described in the case of 10a, by reacting 9b with trimethylphenylammonium tribromide (82% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) δ ppm 11.59(s, 1H), 7.72(m, 1H), 7.43(m, 1H), 7.31(m, 1H), 7.08(m, 1H), 4.77(s, 2H), 2.59(s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ ppm 184.2, 136.8, 129.5, 127.8, 126.1,

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120.1, 119.7, 119.5, 112.5, 34.9, 10.5; EI HRMS (m/z) calculated for C$_{11}$H$_{10}$BrON [M$^+$] 250.9946, found 250.9906.

11: Bromoacylskatole 10b (6.60 g, 24.9 mmol) and potassium thioacetate (3.13 g, 27.4 mmol) were dissolved in dry DMF (200 mL) under a nitrogen atmosphere. The reaction solution was stirred for 12 hours and diluted with water (600 mL). The precipitate was collected, dried (MgSO$_4$) and dissolved in methanol (200 mL). Cysteamine hydrochloride (2.84 g, 25.0 mmol) and NaHCO$_3$ (2.1 g, 25 mmol) were added into the reaction solution. The reaction mixture was degassed for 5 minutes and stirred overnight. The reaction solution was quenched with 10% aqueous HCl, diluted with water (100 mL) and extracted with CH$_2$Cl$_2$ (3×200 mL). The organic layer was dried over anhydrous MgSO$_4$ and concentrated under reduced pressure. The crude product was purified using flash column chromatography to give a light yellow oil (2.8 g, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 9.09 (s, 1H), 7.70 (m, 1H), 7.38(m, 2H), 7.16(m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ ppm 187.7, 136.7, 130.9, 128.9, 127.1, 121.5, 120.5, 119.4, 112.1, 32.9, 11.4; EI HRMS calcd. for C$_{11}$H$_{11}$NOS [M$^+$] 219.0561, found : 219.0565.

12a: To a solution of 10a (1.00 g, 3.97 mmol) in aceton (15 mL), sodium sulfide nonahydrate (0.48 g, 2.0 mmol) in water (10 mL) was added dropwise at 0°C under a nitrogen atmosphere. The reaction mixture was stirred for about 16 h. and the crude product was washed with water (3x50 mL) to get rid of impurities and aqueous wastes, yielding pure yellowish brown solid (1.2 g, 81% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) δ ppm 11.52 (s, 2H), 7.68 (d, J=8.2Hz, 2H), 7.40 (d, J=8.2Hz, 2H), 7.28 (dt, J=7.0Hz, J=1.2Hz, 2H), 7.05 (dt, J=7.0Hz, J=1.2Hz, 2H), 4.06 (s, 4H) 2.56 (s, 6H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ ppm 187.4, 136.5, 130.7, 127.9, 125.8, 120.8, 119.6, 118.8,
112.5, 40.0, 10.6; ESI HRMS (m/z) calcd. for C$_{22}$H$_{20}$N$_2$O$_2$S [M$^+$] 376.1245, found : 376.1229.

**12b:** Compounds **11** (0.38g, 1.9mmol) and **10b** (0.5g, 1.8mmol) was dissolved in 20mL dry acetonitrile under a N$_2$ atmosphere. Triethylamine (0.3mL) was added. The reaction mixture was stirred for 6 hours at room temperature. The reaction solution was quenched by 10% aqueous HCl, diluted with water (100mL). The precipitate is pure product without any further purification (0.6 g, 86% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) δ ppm 11.54(s, 1H), 11.52(s, 1H), 7.71(m, 2H), 7.42(m, 2H), 7.28(m, 2H), 7.07 (m, 2H), 4.59(q, $J$=6.8Hz, 1H), 4.10(d, $J$=15.5Hz, 1H), 4.02(d, $J$=15.5Hz, 1H), 2.58(s, 3H), 2.54(s, 3H), 1.53(d, $J$=6.8Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ ppm 189.5, 187.8, 136.6, 130.1, 127.9, 125.7, 120.8, 119.6, 118.7, 112.4, 42.9, 37.5, 16.6, 10.5; ESI HRMS (m/z) calculated for C$_{22}$H$_{20}$SN$_3$O$_2$ 390.1402, found 390.1413.

**13a:** To a solution of **12a** (0.36g, 0.96mmol) in acetonitrile (10mL), UHP (0.36g, 3.83mmol) dissolved in acetonitrile solution (5mL) of TFAA (0.6g, 2.86mmol), was added drop wise at room temperature and stirred for 2 h. and the crude product was washed with water (3x25ml), filtered and air dried yielding pure yellowish brown solid which was further purified with flash column chromatography (1:1 Hexanes:EtOAc). Light yellow 0.35 g (yield 90%). $^1$H NMR (400 MHz, DMSO-$d_6$) δ ppm 11.75(s, 2H), 7.75(d, $J$=8.2Hz, 2H), 7.46(d, $J$=8.2Hz, 2H), 7.35(dt, $J$=8.2Hz, $J$=1.2Hz, 2H), 7.11(dt, $J$=7.42Hz, $J$=0.8Hz, 2H), 5.18 (s, 4H), 2.63 (s, 6H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ ppm 181.5, 137.0, 131.3, 127.8, 126.7, 121.2, 121.1, 120.0, 112.6, 61.8, 54.9, 10.6; EI HRMS calcd. for C$_{22}$H$_{20}$N$_2$O$_4$S [M$^+$] 408.1144, found : 408.1152.
13b: Prepared as described in the case of 13a, starting from 12b, giving a 76% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 9.34(s, 1H), 9.08 (s, 1H), 7.58 (m, 2H), 7.43 (m, 4H), 7.16 (m, 2H), 5.29 (q, J=7.0Hz, 1H), 4.79 (q, J=14.5Hz, 2H), 2.72 (s, 6H), 2.69 (s, 6H), 1.86 (d, J=7.0Hz, 3H); EI HRMS calcd. for C$_{23}$H$_{22}$N$_2$O$_4$S [M]$^+$: 408.1300, found : 408.1347.

14a: To a solution of 13a (1.12g, 2.74mmol) in acetic acid (20mL), ammonium acetate (2.53g, 33mmol) was added in two portions at an interval of 5 h and the reaction mixture was refluxed for 26 h. The crude product was washed with water (3x25 ml), filtered and air dried giving yellowish brown solid (0.91 g, 85 % yield). M.P. 280-282 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ ppm 11.29 (s, 2H), 10.63 (s, 1H), 7.62 (d, J=7.8Hz, 2H), 7.44 (d, J=8.2Hz, 2H), 7.23 (t, J=7.8Hz, 2H), 7.09 (t, 7.8Hz, 2H), 6.32 (s, 2H), 2.47 (s, 6H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ ppm 136.6, 135.8, 128.2, 126.6, 123.3, 119.4, 119.2, 112.0, 111.5, 102.9, 9.5; EI HRMS calcd. for C$_{22}$H$_{19}$N$_3$O$_2$S [M]$^+$ 389.1198, found : 389.1192.

14b: This compound was prepared as described in the case of 14a, starting from 13b, giving a 64% yield. M.P. 250-251.5 °C; $^1$H NMR (400 MHz, DMSO-$d_6$) δ ppm 11.32(s, 2H), 11.23(s, 1H), 10.52(s, 1H), 7.61(m, 2H), 7.43(m, 2H), 7.22 (m, 2H), 7.08 (m, 2H), 6.19(s, 1H), 2.45(s, 3H), 2.29(s, 3H), 1.98(s, 3H); $^{13}$C NMR (100MHz, DMSO-$d_6$) δ ppm 137.1, 136.1, 135.9, 133.0, 128.3, 127.7, 126.5, 123.3, 122.8, 119.4, 119.2, 119.0, 112.0, 111.5, 111.4, 99.1, 9.5, 9.3, 8.7; EI HRMS calcd. for C$_{22}$H$_{19}$N$_3$O$_2$S [M]$^+$ 389.1198, found : 389.1192.
Chemical Shift (ppm)

CHLOROFORM-d

N

H

O

SH
Supplementary Material (ESI) for Chemical Communications
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14b

Chemical Shift (ppm)

DMSO-d6

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Chemical Shift (ppm)
HPLC Analysis of 7, 8, 14a and 14b to verify bulk purity

HPLC analysis was carried out using a high performance liquid chromatograph equipped with an automatic injector, diode array detector (wavelength range 190-600 nm), degasser, and inline filter on a Microsorb-CN column (particle size 5μm; 4.6 id × 200 mm). Mobile phases: Method A (compound 7): 25% H₂O/75% MeCN – 100% MeCN over 10 min, linear gradient, flow rate 1 mL/min. Method B (compounds 8, 14a, and 14b): 70% H₂O/30% MeCN – 100% MeCN over 25 min, linear gradient, flow rate 1 mL/min.

HPLC chromatogram (Method A, t_R 3.7 min) and UV spectrum of 7:
HPLC chromatogram (Method B, $t_R$ 4.2 min) and UV spectrum of 8:
HPLC chromatogram (Method B, $t_R$ 19.3 min) and UV spectrum of 14a:
HPLC chromatogram (Method B, $t_R$ 20.0 min) and UV spectrum of 14b: