

Supporting Information

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A General Approach to the Basiliolide/Transtaganolide Natural Products: Total Syntheses of Basiliolide B, *epi*-8-Basiliolide B, Transtaganolide C, and Transtaganolide D**

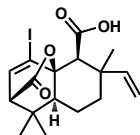
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I. Materials and Methods.

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Pd(*t*-Bu₃P)₂, *N,N'*-dicyclohexylcarbodiimide, 1,1-dimethoxy-2-chloro-acetaldehyde, *N,O*-bis(trimethylsilyl)acetamide, *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide, and imidazole were purchased from Sigma-Aldrich Chemical Company and used as received. Pd(PPh₃)₄¹ was prepared using known methods. Thin-layer chromatography (TLC), both preparatory and analytical, were performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, I₂, or KMnO₄ staining. ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. ¹H NMR, and ¹³C NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz) or on a Varian Unity Inova 500 (at 500 MHz). ¹H NMR spectra are reported relative to CDCl₃ (7.26 ppm). Data for ¹H NMR spectra are reported as follows: chemical shift, multiplicity, coupling constant (Hz), integration. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept. = septet, m = multiplet, comp. m = complex multiplet, app. = apparent, bs = broad singlet. ¹³C NMR spectra are reported relative to CDCl₃ (77.0 ppm). FTIR spectra were recorded on a Perkin Elmer SpectrumBX spectrometer and are reported in frequency of absorption (cm⁻¹). HRMS were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) or multimode-ESI/APCI. Crystallographic data were obtained from the Caltech X-ray Diffraction Facility.

II. Experimental Procedures



Iodoacid 6a. To a solution of **7a** (6.2 g, 15 mmol, 1.0 equiv) in toluene (75 mL) at 25 °C in a sealed tube was added *N,O*-bis(trimethylsilyl)acetamide (7.2 mL, 30 mmol 2.0 equiv). To the

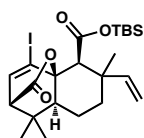
¹ M. R. Mason, J. G. Verkade *Organometallics* **1992**, *11*, 2212-2220.

reaction mixture was then added triethylamine (0.41 mL, 3.0 mmol, 0.20 equiv). The reaction mixture was heated to 110 °C and stirred for 20 minutes. The mixture was cooled to 25 °C and diluted with toluene (750 mL). The reaction mixture was then re-heated to 100 °C and stirred for 4 days. The mixture was cooled to 25 °C and extracted with saturated aqueous NaHCO₃ (7 x 100 mL). To the combined aqueous extracts was added 1 M aqueous HCl until pH = 3. The aqueous layer was then extracted with ethyl acetate (3 x 100 mL). The combined organics were dried over Na₂SO₄, and concentrated by rotary evaporation to yield 3.2 g (51%) of **6a** as a tan foam.

Major: ¹H NMR (500 MHz, CDCl₃) δ 6.93 (d, *J* = 6.5 Hz, 1H), 6.01 (dd, *J* = 10.5, 17.5 Hz, 1H), 5.05–5.02 (m, 2H), 3.00–2.94 (m, 2H), 1.68–1.42 (m, 5H), 1.29 (s, 3H), 1.08 (s, 3H), 1.00 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.7, 170.5, 148.0, 140.0, 111.5, 97.9, 84.7, 59.4, 56.5, 47.9, 39.8, 38.2, 36.8, 29.8, 24.5, 20.5, 18.4.

Minor: ¹H NMR (500 MHz, CDCl₃) δ 6.93 (d, *J* = 6.5 Hz, 1H), 6.35 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.09 (d, *J* = 11.0 Hz, 1H), 5.05–5.02 (m, 1H), 3.00–2.94 (m, 2H), 1.92–1.90 (m, 1H), 1.68–1.42 (m, 4H), 1.26 (s, 3H), 1.08 (s, 3H), 1.00 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.7, 170.4, 140.4, 140.3, 113.7, 97.4, 84.8, 61.0, 56.6, 48.0, 39.3, 38.7, 37.0, 29.8, 29.5, 24.5, 20.6.

FTIR (Neat Film NaCl) 3082, 2967, 2931, 1754, 1741, 1738, 1732, 1708, 1414, 1396, 1219, 1175, 964, 916, 874, 797, 736 cm⁻¹; HRMS (Multimode-ESI/APCI) *m/z* calc'd for C₁₇H₂₁O₄I [M+H]⁺: 417.0557, found 417.0553.



***tert*-Butyldimethylsilyl ester 6b.** To a solution of **6a** (46 mg, 0.11 mmol, 1.0 equiv) in dimethylformamide (0.30 mL) were added *tert*-butyldimethylsilylchloride (84 mg, 0.56 mmol, 5.0 equiv) and imidazole (76 mg, 1.1 mmol, 10 equiv). The reaction was warmed to 40 °C and then stirred for 12 hours. The reaction mixture was then diluted with saturated aqueous NaCl (1 mL) and extracted with diethyl ether/hexane (1:1) (3 x 2 mL). The combined organic extracts were washed with saturated aqueous KHSO₄ (1 mL) and then with saturated aqueous NaCl (3 x 1 mL). The combined organics were dried over Na₂SO₄, and concentrated by rotary evaporation. The crude oil was chromatographed (ethyl acetate in hexane 10⇒50% on SiO₂) to yield 39 mg (66%) of **6b** as a white powder.

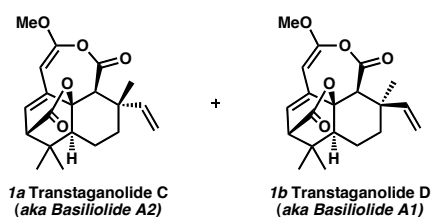
Procedure 2. To a solution of **6a** (180 mg, 0.43 mmol, 1.0 equiv) in acetonitrile (0.43 mL) was added *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide (1.0 g, 4.3 mmol, 10 equiv) at 25 °C and stirred for 15 minutes. The reaction mixture was diluted with saturated aqueous NaCl (1 mL) and extracted with diethyl ether/hexane (1:1) (3 x 2 mL). The combined organic extracts were washed with saturated aqueous KHSO₄ (1 mL) and then with saturated aqueous NaCl (3 x 1 mL). The combined organics were dried over Na₂SO₄, and concentrated by rotary evaporator. The crude oil was chromatographed (ethyl acetate in hexane 10⇒50% on SiO₂) to yield 150 mg (64%) of **6b** as a white powder.

Major: ¹H NMR (500 MHz, CDCl₃) δ 6.90 (d, *J* = 6.5 Hz, 1H), 6.03 (dd, *J* = 11.0, 17.5 Hz, 1H), 4.99 (d, *J* = 17.5 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 2.95 (s, 1H), 2.93 (d, *J* = 6.5 Hz, 1H), 1.66–1.39 (m, 4H), 1.32–1.29 (m, 1H), 1.26 (s, 3H), 1.07 (s, 3H), 0.99 (s, 3H), 0.91 (s, 9H), 0.29

(s, 3H), 0.27 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.6, 169.1, 149.2, 139.7, 110.5, 98.7, 84.6, 60.4, 56.7, 48.2, 40.1, 38.7, 36.9, 29.8, 25.5, 24.5, 20.7, 18.1, 17.5, -4.8, -4.8.

Minor: ^1H NMR (500 MHz, CDCl_3) δ 6.90 (d, J = 6.5 Hz, 1H), 6.40 (dd, J = 11.0, 17.5 Hz, 1H), 5.05 (dd, J = 1.0, 11.0 Hz, 1H), 5.03–4.98 (m, 1H), 2.91 (d, J = 6.5 Hz, 1H), 2.86 (s, 1H), 1.85 (dt, J = 3.5, 13.5 Hz, 1H), 1.66–1.39 (m, 3H), 1.36 (s, 3H), 1.34–1.29 (m, 1H), 1.05 (s, 3H), 0.98 (s, 3H), 0.90 (s, 9H), 0.30 (s, 3H), 0.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.6, 169.3, 141.3, 139.9, 112.9, 98.3, 84.7, 61.8, 56.8, 48.4, 39.6, 39.4, 37.2, 29.6, 25.6, 25.4, 24.4, 20.8, 17.5, -4.9, -4.9.

FTIR (Neat Film NaCl) 2959, 2929, 2857, 1760, 1716, 1708, 1471, 1284, 1250, 1173, 1022, 967, 840, 827, 789, 736 cm^{-1} ; HRMS (Multimode-ESI/APCI) m/z calc'd for $\text{C}_{23}\text{H}_{36}\text{O}_4\text{Si}$ $[\text{M}+\text{H}]^+$: 531.1422, found 531.1432.



Transtaganolides (1). In a nitrogen filled glovebox, to a solution of **6b** (16 mg, 0.030 mmol, 1.0 equiv) and $\text{Pd}(\text{PPh}_3)_4$ (35 mg, 0.030 mmol, 1 equiv) in dimethylformamide (0.30 mL, 0.10 M) was added tributyl(2-methoxyethynyl)stannane (**10**) (32 mg, 0.090 mmol, 3.0 equiv). The reaction was stirred at 31 $^\circ\text{C}$ for 16 h. The reaction mixture was then treated with water (30 μL) and stirred at room temperature for 1 hour. The mixture was diluted with ethyl acetate (1 mL) and washed with water (4 x 0.5 mL) and concentrated by rotary evaporation. The crude oil was purified by normal phase HPLC to yield 2.1 mg (21%) of transtaganolide C (**1a**) and 1.1 mg (10%) of transtaganolide D (**1b**) as white powders. Crystals were grown by slow evaporation from acetonitrile.

Procedure 2. In a nitrogen filled glovebox, to a solution of **6b** (16 mg, 0.030 mmol, 1.0 equiv) and $\text{Pd}(t\text{-Bu}_3\text{P})_2$ (15 mg, 0.030 mmol, 1.0 equiv) in dimethylformamide (0.30 mL, 0.10 M) was added tributyl(2-methoxyethynyl)stannane (**10**) (32 mg, 0.090 mmol, 3.0 equiv). The reaction was stirred at 31 $^\circ\text{C}$ for 10 hours. The reaction mixture was then treated with water (30 μL) and stirred at room temperature for 1 hour. The mixture was diluted with ethyl acetate (1 mL) and washed with water (4 x 0.5 mL) and concentrated by rotary evaporation. The crude oil was purified by normal phase HPLC to yield 2.0 mg (19%) of transtaganolide C (**1a**) and 1.0 mg (10%) of transtaganolide D (**1b**) as white powders.

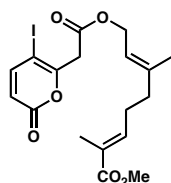
Transtaganolide C (**1a**).

^1H NMR (500 MHz, CDCl_3) δ 6.07 (dd, J = 1.5, 6.5 Hz, 1H), 5.80 (dd, J = 11.0, 17.5 Hz, 1H), 5.07 (d, J = 17.5 Hz, 1H), 5.03 (d, J = 11.0 Hz, 1H), 5.00 (d, J = 1.5 Hz, 1H), 3.71 (s, 3H), 3.23 (s, 1H), 3.06 (d, J = 6.5 Hz, 1H), 1.71–1.63 (m, 3H), 1.60 (s, 3H), 1.44 (m, 1H), 1.30 (m, 1H), 1.08 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.8, 162.3, 156.7, 146.5, 138.0, 123.6, 112.8, 87.3, 79.3, 56.3, 53.8, 50.6, 48.1, 38.4, 38.3, 33.3, 29.9, 24.8, 19.9, 19.2; FTIR (Neat Film NaCl) 2965, 2928, 2872, 1791, 1761, 1668, 1619, 1456, 1334, 1267, 1233, 1178, 1115, 970, 954, 828 cm^{-1} ; HRMS (Multimode-ESI/APCI) m/z calc'd for $\text{C}_{20}\text{H}_{24}\text{O}_5$ $[\text{M}+\text{H}]^+$:

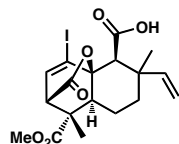
345.1697, found 345.1703; MP: 135-160 °C (at these temperatures decarboxylation is thought to occur, as the crystalline sample and the resulting liquid were vigorously bubbling throughout the measurement; thus it is unclear whether thermal decomposition precluded state change).

Transtaganolide D (1b).

^1H NMR (500 MHz, CDCl_3) δ 7.00 (dd, $J = 11.0, 17.5$ Hz, 1H), 6.09 (dd, $J = 1.0, 6.5$ Hz, 1H), 5.15 (dd, $J = 1.0, 11.0$ Hz, 1H), 5.05 (dd, $J = 1.0, 17.5$ Hz, 1H), 5.02 (d, $J = 1.0$ Hz, 1H), 3.73 (s, 3H), 3.13 (s, 1H), 3.06 (d, $J = 6.5$ Hz, 1H), 1.91 (dt, $J = 3.5, 13.5$ Hz, 1H), 1.64 (dq, $J = 3.0, 13.5$ Hz, 1H), 1.58 (m, 1H), 1.39 (dt, $J = 3.5, 13.5$ Hz, 1H), 1.33 (dd, $J = 4.5, 13.5$ Hz, 1H), 1.22 (s, 3H), 1.04 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.7, 162.6, 156.7, 142.9, 137.7, 123.9, 112.1, 87.3, 79.4, 56.3, 54.0, 53.3, 48.4, 40.5, 38.4, 33.3, 29.9, 28.5, 24.8, 20.5; FTIR (Neat Film NaCl) 2964, 2929, 2872, 1764, 1760, 1738, 1667, 1620, 1467, 1334, 1267, 1235, 1195, 1177, 1106, 1009, 954, 827 cm^{-1} ; HRMS (Multimode-ESI/APCI) m/z calc'd for $\text{C}_{20}\text{H}_{24}\text{O}_5$ $[\text{M}+\text{H}]^+$: 345.1697, found 345.1698; MP: 135-160 °C (at these temperatures decarboxylation is thought to occur, as the crystalline sample and the resulting liquid were vigorously bubbling throughout the measurement; thus it is unclear whether thermal decomposition precluded state change).



Ester 7b. To a solution of **12** (140 mg, 0.70 mmol, 1.0 equiv) and **13** (210 mg, 0.70 mmol, 1.0 equiv) in acetonitrile (7.0 mL) was added *N,N'*-dicyclohexylcarbodiimide (190 mg, 0.91 mmol, 1.3 equiv) at 0 °C. The reaction was warmed to 25 °C and stirred for seven additional hours. The reaction mixture was then filtered through a pad of Celite, and then concentrated by rotary evaporation. The crude reaction mixture was then chromatographed (ethyl acetate in hexane 0 \Rightarrow 30% on SiO_2) to give 300 mg (94%) of **7b** as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.45 (d, $J = 10.0$ Hz, 1H), 6.70 (tq, $J = 1.5, 7.5$ Hz, 1H), 6.06 (d, $J = 10.0$ Hz, 1H), 5.35 (tq, $J = 1.5, 7.0$ Hz, 1H), 4.67 (d, $J = 7.0$ Hz, 2H), 3.77 (s, 2H), 3.72 (s, 3H), 2.30 (q, $J = 7.5$ Hz, 2H), 2.16 (t, $J = 7.5$ Hz, 2H), 1.83 (q, $J = 1.5$ Hz, 3H), 1.72 (q, $J = 1.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.5, 166.6, 160.3, 157.9, 151.2, 142.0, 141.3, 128.0, 118.3, 116.1, 70.6, 62.5, 51.7, 42.6, 38.0, 26.8, 16.5, 12.4; FTIR (Neat Film NaCl) 2988, 2950, 1738, 1714, 1438, 1366, 1268, 1232, 1126, 1082, 1023, 955, 745 cm^{-1} ; HRMS (Multimode-ESI/APCI) m/z calc'd for $\text{C}_{18}\text{H}_{25}\text{NO}_6\text{I}$ $[\text{M}+\text{NH}_4]^+$: 478.0721, found 478.0725.



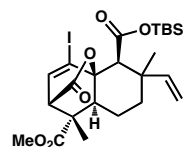
Iodoacid 6c. To a solution of **7b** (96 mg, 0.21 mmol, 1.0 equiv) in toluene (1.1 mL) in a sealed tube were successively added triethylamine (6.0 μL , 0.042 mmol, 0.20 equiv) and *N,O*-bis(trimethylsilyl)acetamide (100 μL , 0.42 mmol, 2.0 equiv). The reaction mixture was heated

to 110 °C and stirred for 20 minutes, then cooled to 25 °C. The reaction mixture was diluted with toluene (250 mL) and heated to 100 °C for 48 hours. The reaction was then cooled to 25 °C, the solvent removed by rotary evaporation, and the crude residue chromatographed (hexane/ethyl acetate/acetic acid, 1:1:0.01 on SiO₂) to give 64 mg (67%) of **6c** as a colorless foam.

Major: ¹H NMR (500 MHz, CDCl₃) δ 6.93 (d, *J* = 6.5 Hz, 1H), 6.02 (dd, *J* = 10.5, 17.5 Hz, 1H), 5.07–5.03 (m, 2H), 3.72 (s, 3H), 3.56–3.53 (m, 1H), 3.03 (s, 1H), 2.40–2.33 (m, 1H), 1.77–1.56 (m, 4H), 1.32 (s, 3H), 1.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 174.8, 169.2, 169.1, 147.9, 139.7, 111.6, 99.2, 84.2, 59.2, 53.0, 52.6, 47.8, 44.5, 40.0, 38.1, 20.8, 18.4.

Minor: ¹H NMR (500 MHz, CDCl₃) δ 6.93 (d, *J* = 6.5 Hz, 1H), 6.33 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.10 (d, *J* = 11.0 Hz, 1H), 5.07–5.03 (m, 1H), 3.72 (s, 3H), 3.56–3.53 (m, 1H), 2.97 (s, 1H), 2.40–2.33 (m, 1H), 1.98–1.95 (m, 1H), 1.77–1.56 (m, 3H), 1.38 (s, 3H), 1.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 174.8, 169.1, 169.0, 140.4, 140.0, 113.5, 98.8, 84.3, 60.6, 52.7, 48.0, 39.45, 38.5, 29.8, 20.8, 20.8, 20.8.

FTIR (Neat Film NaCl) 3080, 2951, 1756, 1739, 1734, 1700, 1559, 1506, 1457, 1211, 911, 756 cm⁻¹; HRMS (Multimode-ESI/APCI) *m/z* calc'd for C₁₈H₂₂O₆I [M+H]⁺: 461.0456, found 461.0460.



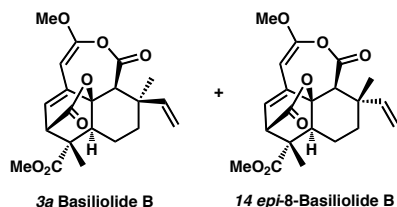
***tert*-Butyldimethylsilyl ester 6d.** To a solution of **6c** (89 mg, 0.11 mmol, 1.0 equiv) in dimethylformamide (0.52 mL) were added *tert*-butyldimethylsilylchloride (150 mg, 0.97 mmol, 5.0 equiv) and imidazole (130 mg, 1.9 mmol, 10 equiv). The reaction mixture was warmed to 40 °C and stirred for 3 hours. The crude mixture was then diluted with saturated aqueous NaCl (1 mL) and extracted with diethyl ether/hexane (1:1) (3 x 2 mL). The combined organic extracts were washed with saturated aqueous NaCl (3 x 1 mL), dried over Na₂SO₄, and concentrated by rotary evaporation to yield 76 mg (68%) of **6d** as a pale yellow powder.

Procedure 2. To a solution of **6c** (61 mg, 0.13 mmol, 1 equiv) in acetonitrile (0.13 mL, 1.0 M) was added *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide (320 mg, 1.3 mmol, 10 equiv) at 25 °C and stirred for 15 minutes. The reaction mixture was diluted with saturated aqueous NaCl (1 mL) and extracted with diethyl ether/hexane (1:1) (3 x 2 mL). The combined organic extracts were washed with saturated aqueous KHSO₄ (1 mL) and then with saturated aqueous NaCl (3 x 1 mL). The combined organics were dried over Na₂SO₄, and concentrated by rotary evaporator. The crude oil was chromatographed (ethyl acetate in hexane 10⇒50% on SiO₂) to yield 51 mg (66%) of **6d** as a white powder.

Major: ¹H NMR (500 MHz, CDCl₃) δ 6.92 (d, *J* = 6.5 Hz, 1H), 6.04 (dd, *J* = 10.5, 17.5 Hz, 1H), 5.01 (d, *J* = 10.5 Hz, 1H), 5.01 (d, *J* = 17.5 Hz, 1H), 3.72 (s, 3H), 3.53 (d, *J* = 6.5 Hz, 1H), 2.98 (s, 1H), 2.38–2.31 (m, 1H), 1.76–1.54 (m, 4H), 1.31 (s, 3H), 1.27 (s, 3H), 0.90 (s, 9H), 0.29 (s, 3H), 0.26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 174.9, 169.1, 168.9, 148.9, 139.4, 110.7, 99.9, 84.2, 60.4, 53.0, 52.7, 48.0, 44.7, 40.2, 38.5, 25.5, 20.9, 18.2, 17.5, –4.80, –4.80.

Minor: ¹H NMR (500 MHz, CDCl₃) δ 6.92 (d, *J* = 6.5 Hz, 1H), 6.37 (dd, *J* = 11.0, 17.5 Hz, 1H), 5.06 (d, *J* = 11.0 Hz, 1H), 5.03–4.99 (m, 1H), 3.72 (s, 3H), 3.51 (d, *J* = 6.5 Hz, 1H), 2.90 (s, 1H), 2.38–2.31 (m, 1H), 1.92–1.88 (m, 1H), 1.76–1.54 (m, 3H), 1.38 (s, 3H), 1.29 (s, 3H), 0.89 (s,

9H), 0.29 (s, 3H), 0.28 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 174.9, 169.1, 169.1, 141.0, 139.7, 113.0, 99.5, 84.3, 61.8, 52.9, 52.9, 48.3, 39.6, 39.0, 29.7, 25.3, 20.9, 20.8, 17.5, -4.90, -4.90. FTIR (Neat Film NaCl) 2951, 2928, 2856, 1767, 1733, 1717, 1447, 1274, 1251, 1215, 1191, 968, 843, 828, 792, 736 cm^{-1} ; HRMS (Multimode-ESI/APCI) m/z calc'd for $\text{C}_{24}\text{H}_{36}\text{O}_6\text{Si}$ $[\text{M}+\text{H}]^+$: 575.1320, found 575.1317.



Basiliolides (3a, 14). In a nitrogen filled glovebox, to a solution of **6d** (15 mg, 0.030 mmol, 1.0 equiv) and $\text{Pd}(\text{PPh}_3)_4$ (35 mg, 0.030 mmol, 1.0 equiv) in dimethylformamide (0.30 mL, 0.10 M) was added tributyl(2-methoxyethynyl)stannane (**10**) (53 mg, 0.050 mmol, 5.0 equiv). The reaction was stirred at 30 °C for 16 hours, then treated with water (30 μL) and stirred at 25 °C for an additional 1 hour. The mixture was then diluted with ethyl acetate (1 mL) and washed with water (4 x 0.5 mL) and concentrated by rotary evaporation. The crude oil was purified by normal phase HPLC to yield 0.6 mg (6%) of basiliolide B (**3a**) and 1.2 mg (12%) of *epi*-8-basiliolide B (**14**) as white powders.

Procedure 2. In a nitrogen filled glovebox, to a solution of **6b** (16 mg, 0.030 mmol, 1.0 equiv) and $\text{Pd}(t\text{-Bu}_3\text{P})_2$ (15 mg, 0.030 mmol, 1.0 equiv) in dimethylformamide (0.30 mL, 0.10 M) was added tributyl(2-methoxyethynyl)stannane (43 mg, 0.12 mmol, 4.0 equiv). The reaction was stirred at 30 °C for 10 hours, and then an addition aliquot (22 mg, 0.060 mmol, 2.0 equiv) of stannane **10** was added and stirred for an additional two hours. The reaction was treated with water (30 μL) and stirred at 25 °C for an additional 1 hour. The crude reaction mixture was diluted with ethyl acetate (1 mL) and washed with water (4 x 0.5 mL) and concentrated by rotary evaporation. . The crude oil was purified by normal phase HPLC to yield 0.6 mg (5%) of basiliolide B (**3a**) and 1.6 mg (14%) of *epi*-8-basiliolide B (**14**) as white powders.

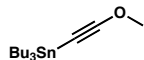
Basiliolide B (3a).

^1H NMR (500 MHz, CDCl_3) δ 7.00 (dd, J = 11.5, 18 Hz, 1H), 6.08 (d, J = 5.5 Hz, 1H), 5.17 (d, J = 11.5 Hz, 1H), 5.06 (d, J = 18 Hz, 1H), 4.96 (s, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.67 (d, J = 5.5 Hz, 1H), 3.17 (s, 1H), 2.29 (dd, J = 5.0, 12.5 Hz, 1H), 1.96 (dt, J = 3.0 Hz, 13.5 Hz, 1H), 1.74–1.65 (m, 2H), 1.54–1.48 (m, 1H), 1.30 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 175.2, 170.1, 162.3, 156.7, 142.7, 139.2, 123.4, 112.3, 87.0, 79.2, 56.4, 53.3, 52.9, 50.0, 44.8, 44.7, 40.2, 38.5, 28.6, 21.0, 20.8; FTIR (Neat Film NaCl) 2951, 2875, 1791, 1761, 1771, 1767, 1733, 1668, 1663, 1456, 1334, 1262, 1230, 1213, 1180, 1107, 1011, 960, 908, 833, 736 cm^{-1} ; HRMS (Multimode-ESI/APCI) m/z calc'd for $\text{C}_{21}\text{H}_{24}\text{O}_7$ $[\text{M}+\text{H}]^+$: 389.1595, found 389.1599.

epi-8-Basiliolide B (14).

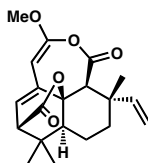
^1H NMR (500 MHz, CDCl_3) δ 6.06 (d, J = 6.0 Hz, 1H), 5.80 (dd, J = 10.5, 17.5 Hz, 1H), 5.09 (d, J = 10.5 Hz, 1H), 5.05 (d, J = 17.5 Hz, 1H), 4.94 (s, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.66 (d, J = 6.0 Hz, 1H), 3.26 (s, 1H), 2.25 (dd, J = 7.0, 12.0 Hz, 1H), 1.79–1.67 (m, 4H), 1.61 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 175.1, 170.1, 162.0, 146.2, 139.5, 123.2, 113.0, 87.0,

79.0, 56.3, 52.9, 50.5, 49.9, 44.7, 44.6, 38.5, 38.2, 21.0, 20.3, 19.3; FTIR (Neat Film NaCl) 2980, 2951, 2929, 1770, 1767, 1761, 1732, 1668, 1619, 1442, 1335, 1261, 1219, 1182, 1106, 971, 960, 918, 834, 732 cm^{-1} ; HRMS (Multimode-ESI/APCI) m/z calc'd for $\text{C}_{21}\text{H}_{24}\text{O}_7$ $[\text{M}+\text{H}]^+$: 389.1595, found 389.1604.



Tributyl(2-methoxyethynyl)stannane (10). To a solution of freshly distilled diethylamine (9.6 mL, 92 mmol, 3.9 equiv) in tetrahydrofuran (300 mL) at 0 °C was added *n*-butyllithium (2.5 M in hexanes, 32 mL, 80 mmol, 3.4 equiv). After stirring for 10 min, 1,1-dimethoxy-2-chloroacetaldehyde (4.0 mL, 26 mmol, 1.1 equiv) was added dropwise to the reaction mixture. The reaction was stirred for 2 hours at 0 °C. Tributyltin chloride (6.2 mL, 24 mmol, 1.0 equiv) was then added to the reaction mixture. The reaction was warmed to 23 °C over 1 hour and stirred for 8 hours. The volatiles were removed in *vacuo* and the reaction mixture was re-suspended in hexane (30 mL) and filtered through a glass frit under an argon atmosphere. The solution was then re-concentrated by rotary evaporation and distilled by Kugelrohr to yield 6.4 g (78%) of **10** as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 3.87 (s, 3H), 1.54 (m, 6H), 1.33 (sextet, $J = 7.5$ Hz, 6H), 0.94 (m, 6H), 0.90 (t, $J = 7.5$ Hz, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 114.7, 65.8, 31.5, 28.9, 27.0, 13.7, 11.2; FTIR (Neat Film NaCl) 2955, 2927, 2871, 2161, 1457, 1208, 1126, 910, 865 cm^{-1} ; Elemental analysis found: C, 52.40%; H, 8.54%. Calc'd for $\text{C}_{15}\text{H}_{30}\text{OSn}$: C, 52.20%; H, 8.76%.

III. Crystal Structure Analysis of:



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Contents

Table 1. Crystal data

Figures Minimum overlap, unit cell contents

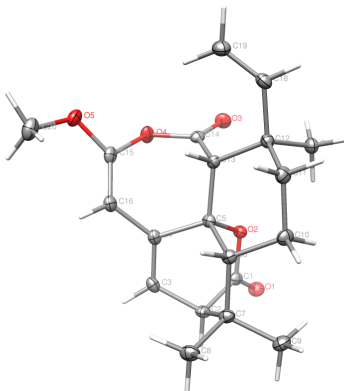
Table 2. Atomic Coordinates

Table 3. Full bond distances and angles

Table 4. Anisotropic displacement parameters

Table 5. Hydrogen atomic coordinates

Table 6. Observed and calculated structure factors (available upon request)



HMN02

Note: The crystallographic data have been deposited in the Cambridge Database (CCDC). The deposition number is 796908.

Table 1. Crystal data and structure refinement for HMN02 (CCDC 796908).

Empirical formula	C ₂₀ H ₂₄ O ₅
Formula weight	344.39
Crystallization Solvent	Acetonitrile
Crystal Habit	Plate
Crystal size	0.24 x 0.19 x 0.08 mm ³
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker KAPPA APEX II	
Wavelength	0.71073 Å MoK α	
Data Collection Temperature	100(2) K	
θ range for 9950 reflections used in lattice determination	2.46 to 31.12°	
Unit cell dimensions	a = 11.3376(4) Å	$\alpha = 90^\circ$
	b = 15.6613(5) Å	$\beta = 90^\circ$
	c = 19.2798(7) Å	$\gamma = 90^\circ$
Volume	3423.4(2) Å ³	
Z	8	
Crystal system	Orthorhombic	
Space group	P <i>bca</i>	
Density (calculated)	1.336 Mg/m ³	
F(000)	1472	
Data collection program	Bruker APEX2 v2009.7-0	
θ range for data collection	2.11 to 33.14°	
Completeness to $\theta = 33.14^\circ$	97.9 %	
Index ranges	$-17 \leq h \leq 17, -24 \leq k \leq 24, -28 \leq l \leq 28$	
Data collection scan type	ω scans; 8 settings	
Data reduction program	Bruker SAINT-Plus v7.66A	
Reflections collected	70734	
Independent reflections	6384 [$R_{\text{int}} = 0.0712$]	
Absorption coefficient	0.095 mm ⁻¹	
Absorption correction	None	
Max. and min. transmission	0.9924 and 0.9775	

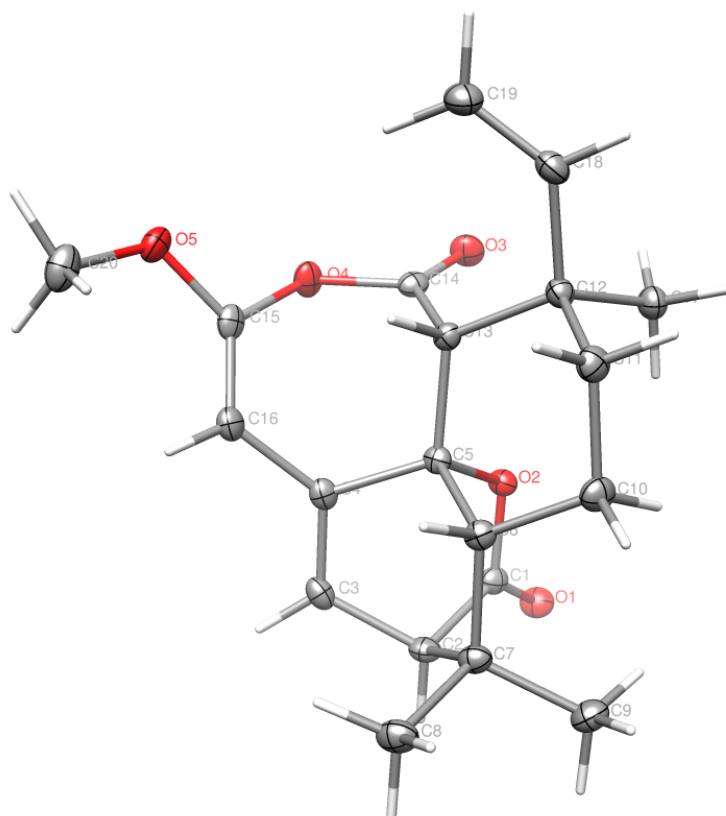
Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F ²
Data / restraints / parameters	6384 / 0 / 322
Treatment of hydrogen atoms	Unrestrained

Goodness-of-fit on F^2	1.673
Final R indices [$I > 2\sigma(I)$, 4393 reflections]	$R1 = 0.0432$, $wR2 = 0.0519$
R indices (all data)	$R1 = 0.0703$, $wR2 = 0.0533$
Type of weighting scheme used	

Sigma



Weighting scheme used	$w = 1/\sigma^2(F_o^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.368 and $-0.374 \text{ e.}\text{\AA}^{-3}$

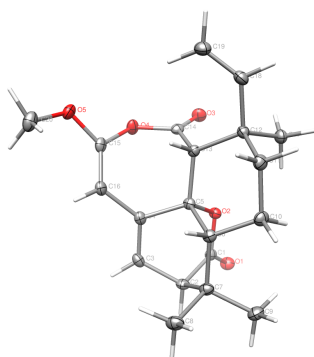
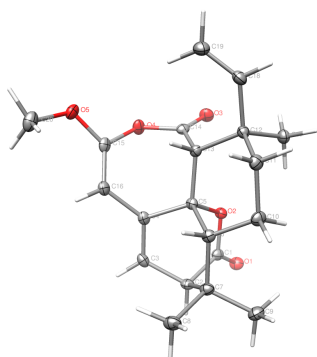
Special Refinement Details

Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K.

Refinement of F^2 against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2 , conventional R-factors (R) are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will

be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.



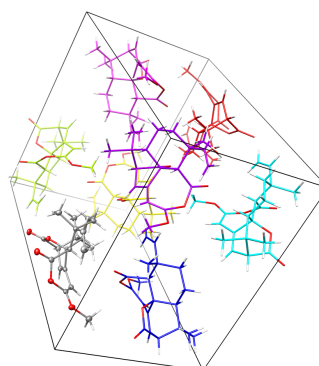
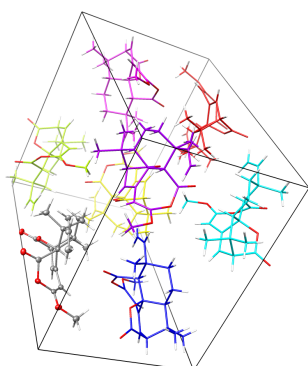
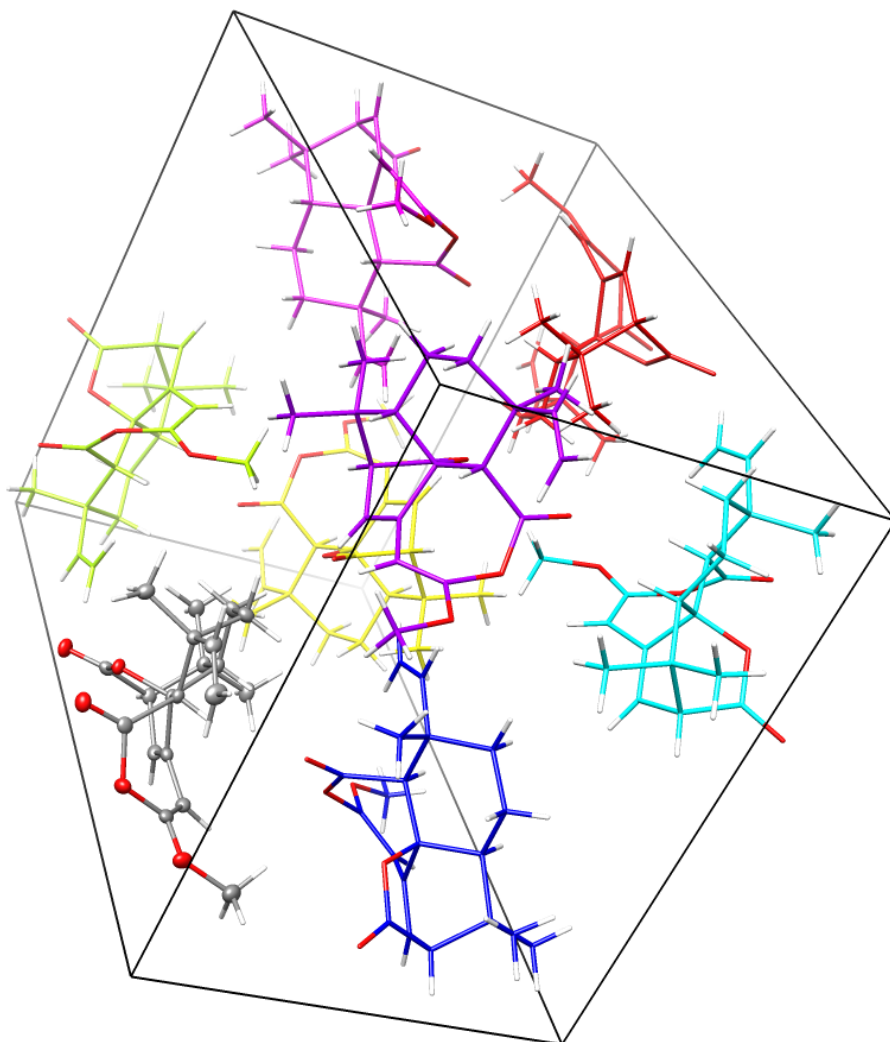


Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for HMN02 (CCDC 796908). $U(\text{eq})$ is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	-665(1)	1162(1)	5055(1)	19(1)
O(2)	-56(1)	1806(1)	6020(1)	13(1)
O(3)	-1466(1)	2178(1)	7396(1)	19(1)
O(4)	-223(1)	1263(1)	7857(1)	18(1)
O(5)	1084(1)	850(1)	8621(1)	20(1)
C(1)	126(1)	1285(1)	5465(1)	15(1)
C(2)	1354(1)	928(1)	5448(1)	15(1)
C(3)	1520(1)	472(1)	6129(1)	16(1)
C(4)	1335(1)	957(1)	6685(1)	14(1)
C(5)	973(1)	1863(1)	6489(1)	12(1)
C(6)	2001(1)	2267(1)	6072(1)	14(1)
C(7)	2226(1)	1707(1)	5410(1)	16(1)
C(8)	3497(1)	1372(1)	5414(1)	21(1)
C(9)	2014(1)	2184(1)	4728(1)	20(1)
C(10)	1808(1)	3218(1)	5947(1)	18(1)
C(11)	1571(1)	3682(1)	6629(1)	17(1)
C(12)	439(1)	3369(1)	6992(1)	14(1)
C(13)	598(1)	2402(1)	7117(1)	12(1)
C(14)	-453(1)	1977(1)	7450(1)	15(1)
C(15)	908(1)	942(1)	7932(1)	16(1)
C(16)	1599(1)	731(1)	7407(1)	16(1)
C(17)	-637(1)	3614(1)	6545(1)	18(1)
C(18)	328(1)	3843(1)	7675(1)	18(1)
C(19)	333(1)	3540(1)	8312(1)	23(1)
C(20)	2259(1)	605(1)	8824(1)	26(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for HMN02 (CCDC 796908).

O(1)-C(1)	1.2115(10)	C(6)-C(10)	1.5255(14)
O(2)-C(1)	1.3627(10)	C(6)-C(7)	1.5685(13)
O(2)-C(5)	1.4782(10)	C(6)-H(6)	0.968(9)
O(3)-C(14)	1.1951(11)	C(7)-C(8)	1.5328(13)
O(4)-C(15)	1.3858(11)	C(7)-C(9)	1.5313(14)
O(4)-C(14)	1.3896(11)	C(8)-H(8A)	1.013(10)
O(5)-C(15)	1.3499(10)	C(8)-H(8B)	0.995(10)
O(5)-C(20)	1.4414(13)	C(8)-H(8C)	0.985(10)
C(1)-C(2)	1.5005(13)	C(9)-H(9A)	0.979(11)
C(2)-C(3)	1.5072(14)	C(9)-H(9B)	1.006(10)
C(2)-C(7)	1.5710(13)	C(9)-H(9C)	0.994(10)
C(2)-H(2)	0.997(9)	C(10)-C(11)	1.5253(14)
C(3)-C(4)	1.3298(13)	C(10)-H(10A)	1.031(9)
C(3)-H(3)	0.955(10)	C(10)-H(10B)	0.987(10)
C(4)-C(16)	1.4684(13)	C(11)-C(12)	1.5422(13)
C(4)-C(5)	1.5244(13)	C(11)-H(11A)	0.999(10)
C(5)-C(13)	1.5361(13)	C(11)-H(11B)	0.973(9)
C(5)-C(6)	1.5512(13)	C(12)-C(18)	1.5159(13)

C(12)-C(17)	1.5431(13)	C(7)-C(8)-H(8B)	111.9(6)
C(12)-C(13)	1.5436(13)	H(8A)-C(8)-H(8B)	108.6(8)
C(13)-C(14)	1.5082(13)	C(7)-C(8)-H(8C)	109.3(6)
C(13)-H(13)	0.964(9)	H(8A)-C(8)-H(8C)	108.1(8)
C(15)-C(16)	1.3220(13)	H(8B)-C(8)-H(8C)	108.2(8)
C(16)-H(16)	0.924(9)	C(7)-C(9)-H(9A)	111.7(5)
C(17)-H(17A)	0.977(9)	C(7)-C(9)-H(9B)	113.1(5)
C(17)-H(17B)	0.979(9)	H(9A)-C(9)-H(9B)	108.7(8)
C(17)-H(17C)	1.025(10)	C(7)-C(9)-H(9C)	110.0(6)
C(18)-C(19)	1.3158(14)	H(9A)-C(9)-H(9C)	106.6(8)
C(18)-H(18)	0.954(10)	H(9B)-C(9)-H(9C)	106.5(7)
C(19)-H(19A)	1.017(11)	C(11)-C(10)-C(6)	110.82(8)
C(19)-H(19B)	0.975(10)	C(11)-C(10)-H(10A)	110.2(5)
C(20)-H(20A)	1.000(11)	C(6)-C(10)-H(10A)	110.6(5)
C(20)-H(20B)	1.041(9)	C(11)-C(10)-H(10B)	110.2(6)
C(20)-H(20C)	0.973(11)	C(6)-C(10)-H(10B)	109.4(6)
		H(10A)-C(10)-H(10B)	105.5(7)
C(1)-O(2)-C(5)	113.39(7)	C(10)-C(11)-C(12)	112.75(9)
C(15)-O(4)-C(14)	121.69(7)	C(10)-C(11)-H(11A)	110.8(5)
C(15)-O(5)-C(20)	115.58(8)	C(12)-C(11)-H(11A)	107.9(5)
O(1)-C(1)-O(2)	119.71(9)	C(10)-C(11)-H(11B)	111.0(5)
O(1)-C(1)-C(2)	127.90(9)	C(12)-C(11)-H(11B)	109.5(5)
O(2)-C(1)-C(2)	112.39(8)	H(11A)-C(11)-H(11B)	104.4(8)
C(1)-C(2)-C(3)	105.85(8)	C(18)-C(12)-C(17)	107.35(8)
C(1)-C(2)-C(7)	107.22(8)	C(18)-C(12)-C(11)	107.96(8)
C(3)-C(2)-C(7)	109.24(8)	C(17)-C(12)-C(11)	108.94(8)
C(1)-C(2)-H(2)	109.0(5)	C(18)-C(12)-C(13)	110.78(8)
C(3)-C(2)-H(2)	112.7(5)	C(17)-C(12)-C(13)	114.99(8)
C(7)-C(2)-H(2)	112.4(5)	C(11)-C(12)-C(13)	106.63(8)
C(4)-C(3)-C(2)	114.29(10)	C(14)-C(13)-C(5)	108.18(8)
C(4)-C(3)-H(3)	125.7(5)	C(14)-C(13)-C(12)	114.05(8)
C(2)-C(3)-H(3)	120.0(5)	C(5)-C(13)-C(12)	116.66(8)
C(3)-C(4)-C(16)	126.43(9)	C(14)-C(13)-H(13)	107.4(5)
C(3)-C(4)-C(5)	112.03(9)	C(5)-C(13)-H(13)	104.0(5)
C(16)-C(4)-C(5)	120.96(8)	C(12)-C(13)-H(13)	105.6(6)
O(2)-C(5)-C(4)	107.93(7)	O(3)-C(14)-O(4)	116.20(9)
O(2)-C(5)-C(13)	107.24(7)	O(3)-C(14)-C(13)	127.22(9)
C(4)-C(5)-C(13)	113.04(8)	O(4)-C(14)-C(13)	116.57(8)
O(2)-C(5)-C(6)	107.49(7)	C(16)-C(15)-O(5)	129.76(10)
C(4)-C(5)-C(6)	107.74(8)	C(16)-C(15)-O(4)	123.95(9)
C(13)-C(5)-C(6)	113.15(8)	O(5)-C(15)-O(4)	106.16(8)
C(10)-C(6)-C(5)	111.80(8)	C(15)-C(16)-C(4)	123.05(10)
C(10)-C(6)-C(7)	116.19(8)	C(15)-C(16)-H(16)	118.4(6)
C(5)-C(6)-C(7)	108.44(8)	C(4)-C(16)-H(16)	118.2(6)
C(10)-C(6)-H(6)	107.0(6)	C(12)-C(17)-H(17A)	112.3(5)
C(5)-C(6)-H(6)	104.9(5)	C(12)-C(17)-H(17B)	112.8(6)
C(7)-C(6)-H(6)	107.8(5)	H(17A)-C(17)-H(17B)	107.6(8)
C(8)-C(7)-C(9)	108.55(8)	C(12)-C(17)-H(17C)	107.9(6)
C(8)-C(7)-C(6)	109.91(8)	H(17A)-C(17)-H(17C)	109.8(8)
C(9)-C(7)-C(6)	113.58(9)	H(17B)-C(17)-H(17C)	106.2(7)
C(8)-C(7)-C(2)	109.02(9)	C(19)-C(18)-C(12)	129.26(11)
C(9)-C(7)-C(2)	108.60(8)	C(19)-C(18)-H(18)	118.9(5)
C(6)-C(7)-C(2)	107.10(8)	C(12)-C(18)-H(18)	111.9(5)
C(7)-C(8)-H(8A)	110.6(6)	C(18)-C(19)-H(19A)	122.3(5)

C(18)-C(19)-H(19B)	121.3(6)
H(19A)-C(19)-H(19B)	116.4(8)
O(5)-C(20)-H(20A)	111.9(6)
O(5)-C(20)-H(20B)	105.9(5)
H(20A)-C(20)-H(20B)	109.8(8)
O(5)-C(20)-H(20C)	111.0(6)
H(20A)-C(20)-H(20C)	109.4(9)
H(20B)-C(20)-H(20C)	108.8(8)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^4$) for HMN02 (CCDC 796908). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	155(4)	237(4)	178(4)	-35(3)	-36(3)	-13(3)
O(2)	109(3)	152(4)	138(3)	-23(3)	-18(3)	2(3)
O(3)	133(4)	227(4)	216(4)	-8(3)	18(3)	0(3)
O(4)	148(4)	191(4)	209(4)	62(3)	18(3)	-6(3)
O(5)	237(4)	214(4)	149(4)	33(3)	-27(3)	-10(3)
C(1)	162(5)	133(5)	149(5)	8(4)	22(4)	-20(4)
C(2)	142(5)	172(5)	139(5)	-43(4)	4(4)	6(4)
C(3)	129(5)	143(5)	219(6)	-2(5)	-9(4)	20(4)
C(4)	109(5)	135(5)	178(5)	11(4)	-4(4)	-12(4)
C(5)	89(4)	143(5)	126(5)	-13(4)	-27(4)	-6(4)
C(6)	105(5)	168(5)	137(5)	-6(4)	-7(4)	-13(4)
C(7)	121(5)	202(6)	142(5)	-15(4)	6(4)	4(4)
C(8)	137(5)	301(7)	198(6)	-29(6)	14(5)	19(5)
C(9)	186(6)	256(6)	149(6)	-1(5)	8(5)	-13(5)
C(10)	184(6)	171(6)	170(6)	17(4)	29(5)	-35(5)
C(11)	194(6)	138(5)	183(6)	7(5)	-3(5)	-25(5)
C(12)	144(5)	125(5)	145(5)	-5(4)	-11(4)	5(4)
C(13)	103(5)	144(5)	120(5)	1(4)	-11(4)	-5(4)
C(14)	169(5)	145(5)	124(5)	-32(4)	-7(4)	-17(4)
C(15)	163(5)	129(5)	185(6)	33(4)	-35(4)	-32(4)
C(16)	147(5)	137(5)	191(6)	16(4)	-19(5)	0(4)
C(17)	185(6)	176(6)	177(6)	11(5)	-17(5)	27(5)
C(18)	179(5)	147(6)	207(6)	-34(5)	-20(4)	26(4)
C(19)	283(7)	227(6)	185(6)	-55(5)	-29(5)	36(5)
C(20)	251(7)	275(7)	246(7)	60(6)	-81(5)	-46(6)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for HMN02 (CCDC 796908).

	x	y	z	U_{iso}
H(2)	1432(8)	540(6)	5040(4)	13(3)
H(3)	1765(8)	-111(6)	6135(4)	15(3)
H(6)	2683(8)	2213(6)	6371(4)	12(3)
H(8A)	3640(8)	988(7)	5000(5)	28(3)
H(8B)	3678(8)	1047(7)	5844(5)	27(3)
H(8C)	4047(9)	1858(7)	5384(5)	24(3)
H(9A)	2565(9)	2659(7)	4669(5)	22(3)
H(9B)	1186(9)	2407(6)	4683(4)	21(3)
H(9C)	2142(8)	1793(7)	4329(5)	26(3)
H(10A)	1119(8)	3314(6)	5607(4)	15(3)
H(10B)	2509(8)	3462(6)	5717(4)	21(3)
H(11A)	1493(8)	4310(7)	6551(4)	16(3)
H(11B)	2238(8)	3628(6)	6943(4)	13(3)
H(13)	1250(8)	2351(6)	7435(4)	11(3)
H(16)	2316(8)	476(6)	7503(4)	16(3)
H(17A)	-1382(8)	3537(6)	6793(4)	17(3)
H(17B)	-685(8)	3284(6)	6114(5)	21(3)
H(17C)	-544(9)	4240(7)	6401(4)	24(3)
H(18)	242(8)	4443(7)	7608(4)	21(3)
H(19A)	445(9)	2908(7)	8415(5)	31(3)
H(19B)	237(9)	3915(7)	8712(5)	30(3)
H(20A)	2450(8)	9(7)	8677(5)	24(3)
H(20B)	2279(8)	647(6)	9363(5)	28(3)
H(20C)	2843(9)	996(7)	8634(5)	35(3)

V. Spectra

