Supporting Information

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SI Methods

General Synthetic Scheme. Formation of the Grignard reagent of 9-bromonon-1-ene (1) was followed by treatment with (*R*)-propylene oxide in the presence of CuBr to afford a high yield of the alcohol **18**. Glycosylation of **18** with dibenzoyl ascarylose (2) proceeded in 73% yield to generate **19**. Treatment of **19** with the Grubbs second-generation ruthenium catalyst in the presence of an excess of methyl acrylate afforded a nearly quantitative yield of **20,** which was then hydrolyzed to give the target compound **6**.

General Synthetic Methods. All reactions were performed under a nitrogen atmosphere. Chemicals and solvents were purchased from commercial suppliers and used as received. Methylene chloride and THF were dried by passing through an activated alumina column before use. All flash chromatography was performed with 230–400 mesh silica gel purchased from EMD Chemicals as the stationary phase. NMR spectra were recorded on a Bruker Avance 300 NMR (300 MHz for ^{1}H, 75 MHz for ^{13}C). Deuterated chloroform and deuterated methanol for NMR were purchased from Cambridge Isotope Laboratories. Optical rotation data were obtained on a Rudolph Research Analytical Autopol IV automatic polarimeter. HRMS of synthetic intermediates was performed at the University of Illinois at Urbana–Champaign Mass Spectrometry Facility.

Synthesis of Intermediate 18. To a suspension of 91 mg (3.7 mmol) magnesium turnings in 1.5 mL THF was added 1 mL of a solution of 766 mg (3.73 mmol) 9-bromonon-1-ene (1) in 3.0 mL of THF dropwise over the course of 9 min. The resulting mixture was then warmed to reflux over the course of 12 min. The rest of the THF solution of 9-bromonon-1-ene was then added dropwise over the course of 5 min. The resulting mixture was allowed to reflux for an additional 30 min and then allowed to cool to 23 °C. In a separate flask, a suspension of 0.18 mL (2.6 mmol) (*R*)-propylene oxide and 37 mg (0.26 mmol) CuBr in 3.0 mL of THF was cooled to −78 °C. To the cooled solution of propylene oxide and CuBr was added the previously prepared Grignard solution dropwise over the course of 5 min. The dry ice-acetone bath was promptly removed and the solution was allowed to warm to 23 °C. 2.5 mL of saturated ammonium chloride solution was then added ≈45 min after the dry ice-acetone bath had been removed. Five milliliters of H_2O and 10 mL of diethyl ether were then added and the resulting layers were separated. The aqueous layer was extracted with an additional 10 mL of diethyl ether and the combined extracts were dried over anh. $MgSO_4$. Filtration and evaporation of volatiles afforded 592 mg of an oil. Silica gel chromatography (50% hexanes in dichloromethane–100% dichloromethane) afforded 431.9 mg (90%) of a colorless oil of low viscosity. $[\alpha]_D^{20} = -7.1$ *c* 2.6 (methanol); HRMS calculated for $C_{12}H_{24}O$ 184.1827, found 184.1828; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.81 (m, 1H); 4.98 (d, 1H, J = 17.1 Hz); 4.92 (d, 1H, J = 9.9 Hz); 3.79 (m, 1H); 2.03 (m, 2H); 1.22–1.50 (m, 14H); 1.18 (d, 3H, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.2; 114.1; 68.2; 39.4; 33.8; 29.6; 29.5; 29.4; 29.1; 28.9; 25.7; 23.5.

Synthesis of Intermediate 19. A suspension of 99.0 mg (0.278 mmol) of dibenzoyl ascarylose (2), 82.0 mg (0.444 mmol) of alcohol (**18**) and 30 mg of crushed 3-Å molecular sieves in 3 mL of dichloromethane was cooled to 0 °C. To this suspension was added 0.15 mL (1.2 mmol) of BF_3OEt_2 at once. The resulting mixture was stirred at 0 °C for 2 h and then 3 mL of sat. $NaHCO_3$ solution was added. An additional 10 mL of dichloromethane was added and the resulting layers were separated. The aqueous layer was extracted with an additional 2 × 10 mL dichloromethane and the combined extracts were dried over anh. $MgSO_4$. Filtration and evaporation of volatiles afforded 166.8 mg of an oil. Silica gel chromatography (30% hexanes in dichloromethane) afforded 106.6 mg (73%) of a colorless oil. $[\alpha]_D^{20} = -4.0$ *c* 0.15 (methanol); HR-ESIMS (*m/z*): $[M+Na]^+$ calculated for $C_{32}H_{42}O_6Na$ 545.2879, found 545.2877; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, 2H, J = 7.2 Hz); 8.04 (d, 2H, J = 7.2 Hz); 7.59 (m, 2H); 7.46 (m, 4H); 5.81 (m, 1H); 5.19 (td, 1H, J = 10.8 Hz, J = 4.5 Hz); 5.15 (m, 1H); 4.98 (d, 1H, J = 17.1 Hz); 4.95 (s, 1H); 4.92 (d, 1H, J = 9.9 Hz); 4.13 (dq, 1H, J = 9.9 Hz, J = 6.3 Hz); 3.85 (m, 1H); 2.42 (dt, 1H, J = 13.2 Hz, J = 3.9 Hz); 2.22 (t, 1H, J = 12.6 Hz); 2.04 (m, 2H); 1.64 (m, 1H); 1.24–1.54 (m, 13H); 1.28 (d, 3H, J = 6.3 Hz); 1.19 (d, 3H, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8; 165.7; 139.1; 133.2; 133.1; 130.1; 130.0; 129.9; 129.6; 128.4; 114.1; 93.9; 72.7; 71.3; 70.8; 67.0; 37.2; 33.8; 29.8; 29.62; 29.60; 29.5; 29.2; 29.0; 25.8; 19.2; 17.9.

Synthesis of Intermediate 20. A solution of 49.9 mg (0.096 mmol) of **19**, 8.0 mg (9.4 μmol) of the Grubbs second-generation ruthenium catalyst, and 43 μL (0.48 mmol) of methyl acrylate in 3 mL of dichloromethane was warmed from 23 °C to reflux over a period of 3 min. Reflux was maintained for 105 min and then the reaction mixture was allowed to cool to 23 °C. Evaporation of volatiles afforded 71.5 mg of an oil. Silica gel chromatography (30% hexanes in dichloromethane–100% dichloromethane) afforded 55.0 mg (99%) of a colorless oil. $[\alpha]_D^{20} = -3.4$ *c* 0.38 (methanol); HR-ESIMS (*m/z*): $[M+Na]^+$ calculated for $C_{34}H_{44}O_8Na$ 603.2934, found 603.2924; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, 2H, J = 7.2 Hz); 8.04 (d, 2H, J = 7.2 Hz); 7.58 (m, 2H); 7.47 (m, 4H); 6.96 (dt, 1H, J = 15.9 Hz, J = 6.9 Hz); 5.81 (d, 1H, J = 15.6 Hz); 5.18 (m, 1H); 5.15 (m, 1H); 4.95 (s, 1H); 4.12 (m, 1H); 3.84 (m, 1H); 3. 71 (s, 3H); 2.41 (d, 1H, J = 13.2 Hz); 2.20 (m, 2H); 1.64 (m, 1H); 1.25–1.55 (m, 13H); 1.28 (d, 3H, J = 6.3 Hz); 1.19 (d, 3H, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.1; 165.8; 165.7; 149.6; 133.2; 133.1; 130.1; 130.0; 129.9; 129.6; 128.4; 120.9; 93.9; 72.7; 71.3; 70.8; 67.0; 51.3; 37.2; 32.2; 29.8; 29.6; 29.5; 29.4; 29.2; 28.0; 25.7; 19.2; 17.9.

Synthesis of Compound 6. A mixture of 50.2 mg (86.4 μmol) of **20** in 4 mL of 2 M LiOH and 2.5 mL of THF was stirred vigorously and warmed from 23 °C to reflux over a period of 2 min. The mixture was refluxed for 6 h and 40 min and then allowed to cool to 23 °C. Then, 2 N HCl was added until pH ≈ 2. The resulting mixture was extracted with 6 × 10 mL of EtOAc. The combined extracts were dried over anhydrous $MgSO_4$. Filtration and evaporation of volatiles afforded 42.0 mg of a residue. Silica gel chromatography (5–50% *i*PrOH in dichloromethane) afforded 17.5 mg (57%) of an oil. $[\alpha]_D^{20} = -56.1$ *c* 0.33 (methanol); HR-ESIMS (*m/z*): $[M+Na]^+$ calculated for $C_{19}H_{34}O_6Na$ 381.2253, found 381.2243; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (dt, 1H, J = 15.6 Hz, J = 6.9 Hz); 5.82 (d, 1H, J = 15.3 Hz); 4.70 (s, 1H); 3.81 (m, 1H); 3.78 (m, 1H); 3.68 (m, 1H); 3.60 (td, 1H, J = 10.5 Hz, J = 4.5 Hz); 2.22 (m, 2H); 2.07 (dt, 1H, J = 12.9 Hz, J = 3.6 Hz); 1.84 (t, 1H, J = 12.2 Hz); 1.20–1.60 (m, 14H); 1.27 (d, 3H, J = 6.3 Hz); 1.12 (d, 3H, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7; 152.2; 120.5; 96.2; 71.8; 69.9; 69.4; 68.2; 37.2; 35.2; 32.2; 29.5; 29.4; 29.3; 29.0; 27.8; 25.6; 19.0; 17.6.

1. Gaubert, P Linstead, RP, Rydon, HN (1937) Olefinic acids. XVI. Synthesis of Δ10-undecenoic acid. *J Chem Soc* 1971–1674.

2. Jeong PY, *et al.* (2005) Chemical structure and biological activity of the *Caenorhabditis elegans* dauer-inducing pheromone. *Nature* 433:541–545.

A

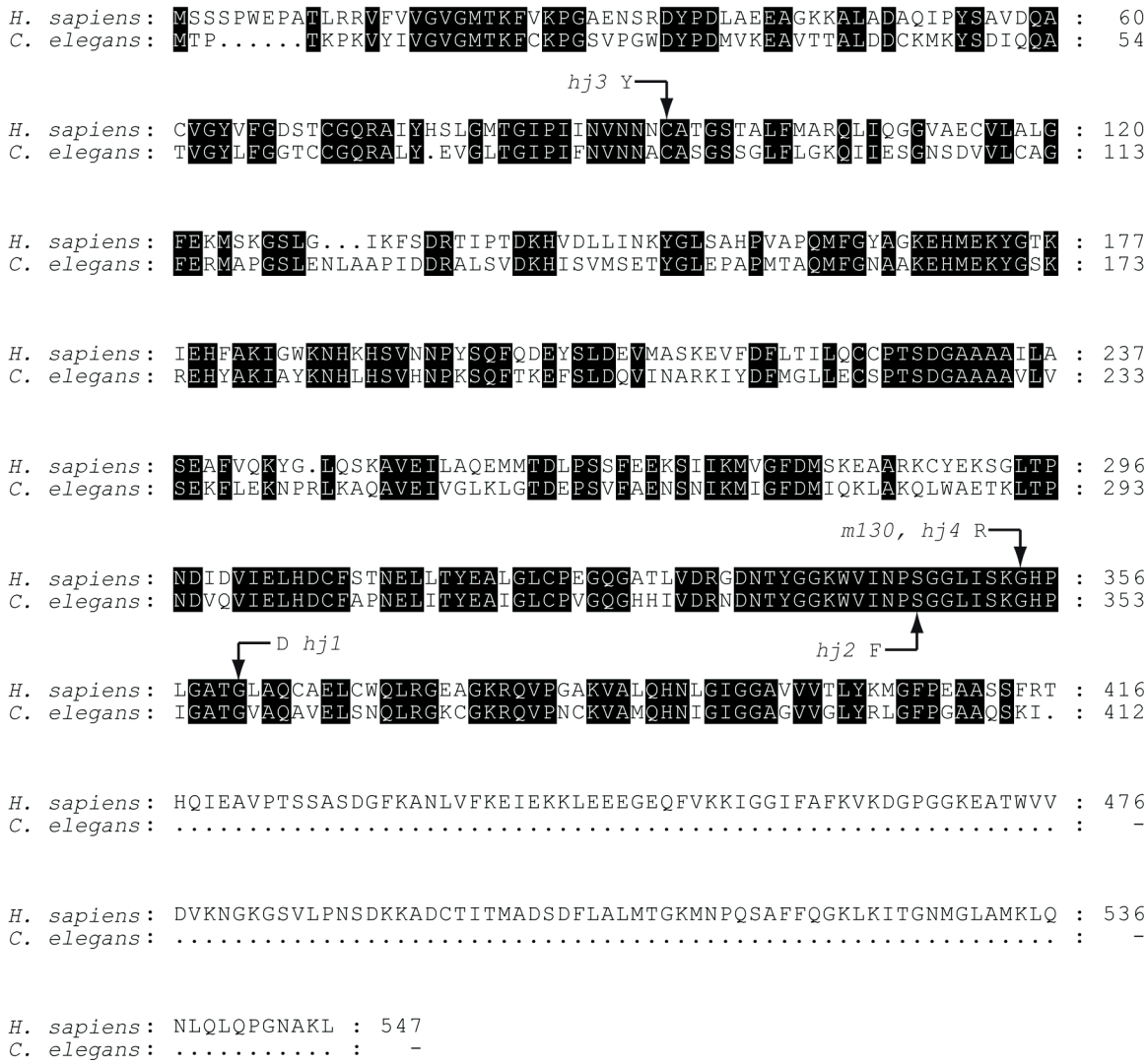


Fig. S1. Protein sequence comparisons. (*A*) Protein sequence comparison of *C. elegans* DAF-22 and human SCPx (NP_002970.2). Mutations associated with alleles hj1, hj2, hj3, and hj4, as well as the original *daf-22* allele *m130*, are indicated with arrows. (*B*) Protein sequence comparison of *C. elegans* DHS-28 and human D-bifunctional protein (P51659). Mutations associated with alleles hj5, hj6, hj7, and hj8 are indicated with arrows.

B

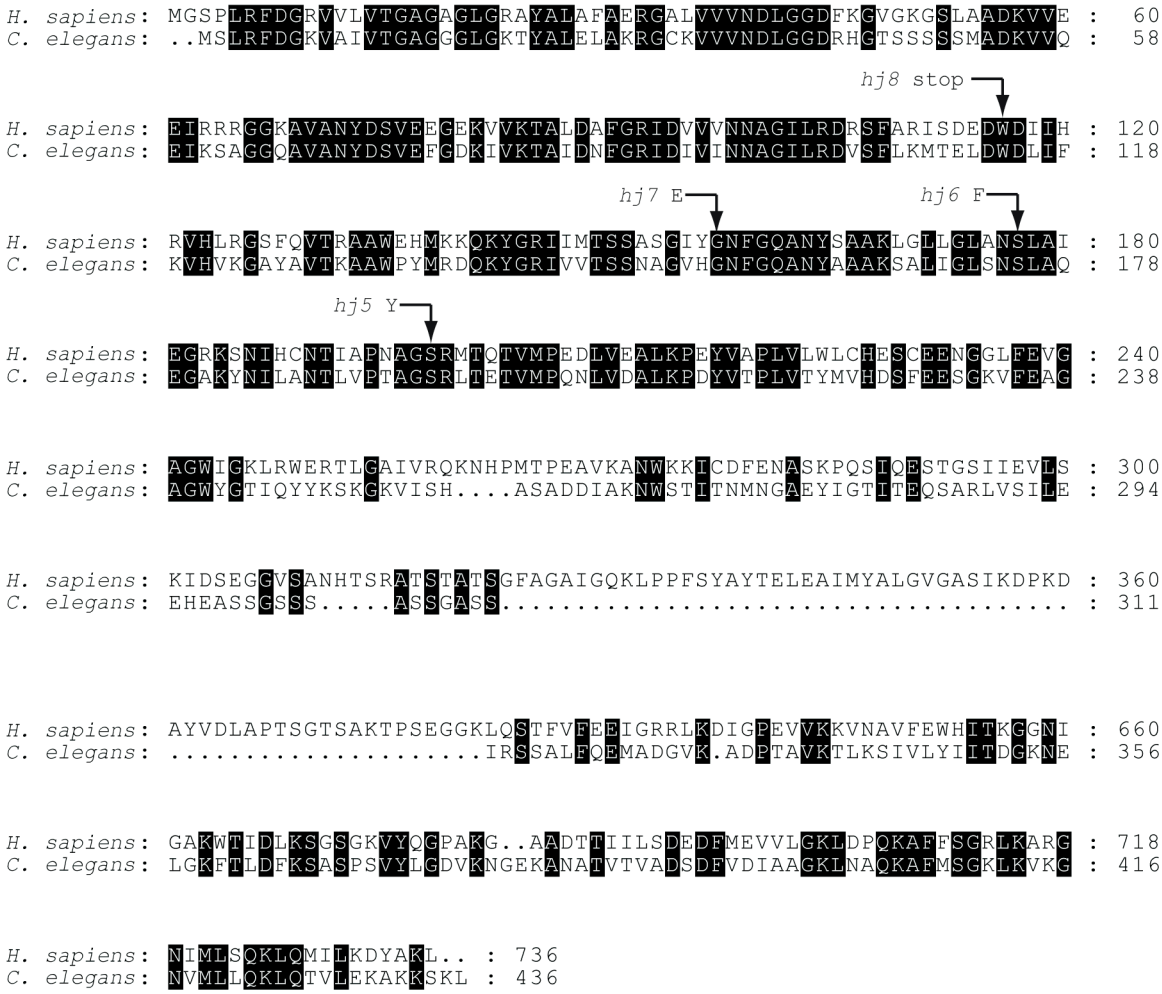


Fig. S1. Continued

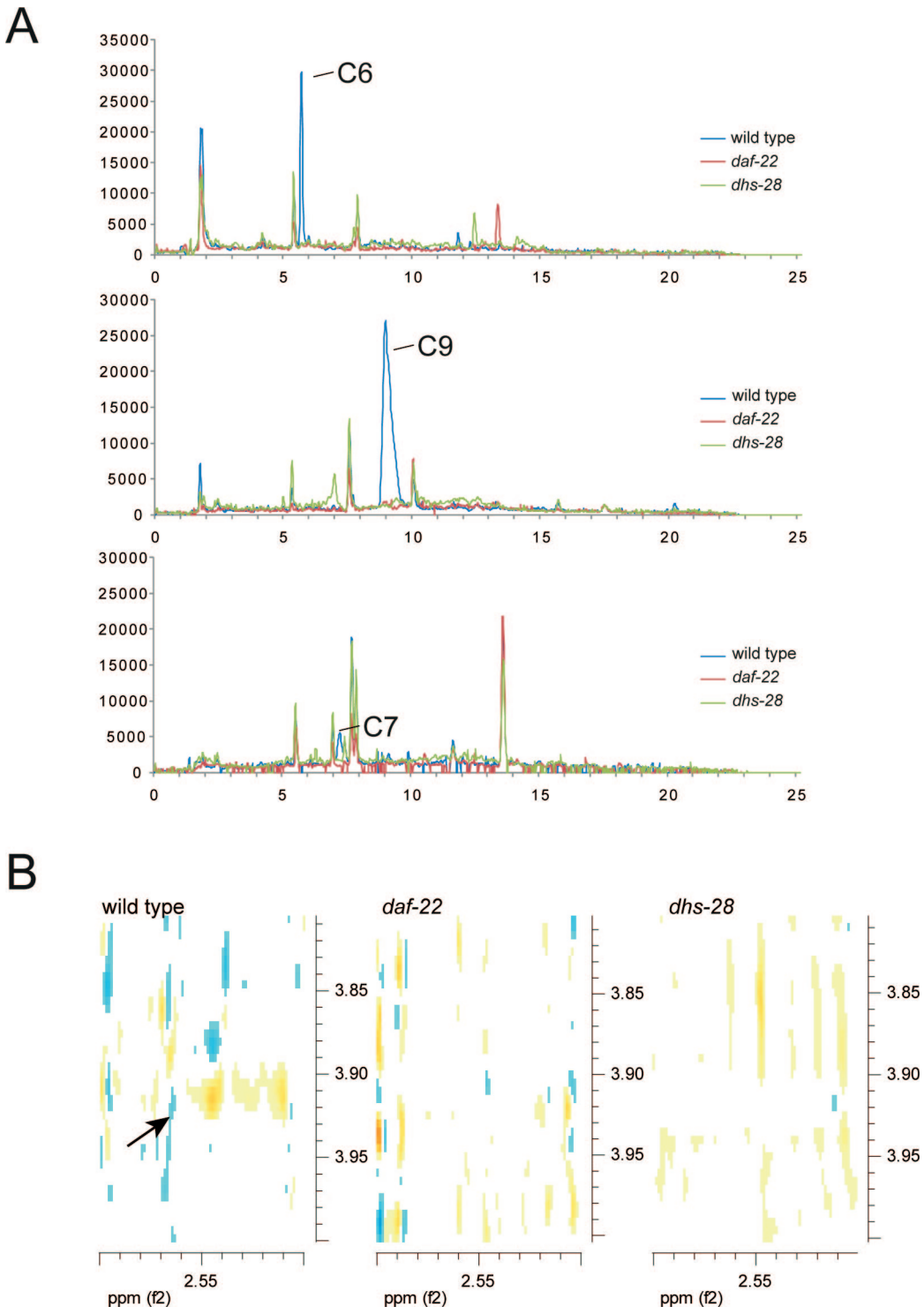


Fig. S2. Analysis of ascarosides C6, C9, C7, and C3 in conditioned medium extracts from wild-type, *daf-22*, or *dhs-28* short-term cultures. (*A*) LCMS traces of conditioned medium extracts from wild-type, *daf-22*, or *dhs-28* short-term cultures. Total positive ion traces have been selected for the mass of ascaroside C6 $[M+Na]^+$ (*Top*), ascaroside C9 $[M+Na]^+$ (*Middle*), or ascaroside C7 $[M+Na]^+$ (*Bottom*). The peaks consistent with the mass and retention time of ascarosides C6, C9, and C7 have been indicated. Ascarosides C7 and C3 were present at relatively low concentrations in the control (wild-type) short-term cultures under the cultivation conditions that were used. Ascaroside C3 could not be detected by LCMS and was monitored by using dqf-COSY instead. (*B*) dqf-COSY spectra of conditioned medium extracts from wild-type, *daf-22*, or *dhs-28* short-term cultures. Cross-peak indicated with arrow in the expanded region is used to monitor the presence of ascaroside C3. This cross-peak is the one between H2 and H3b of ascaroside C3.

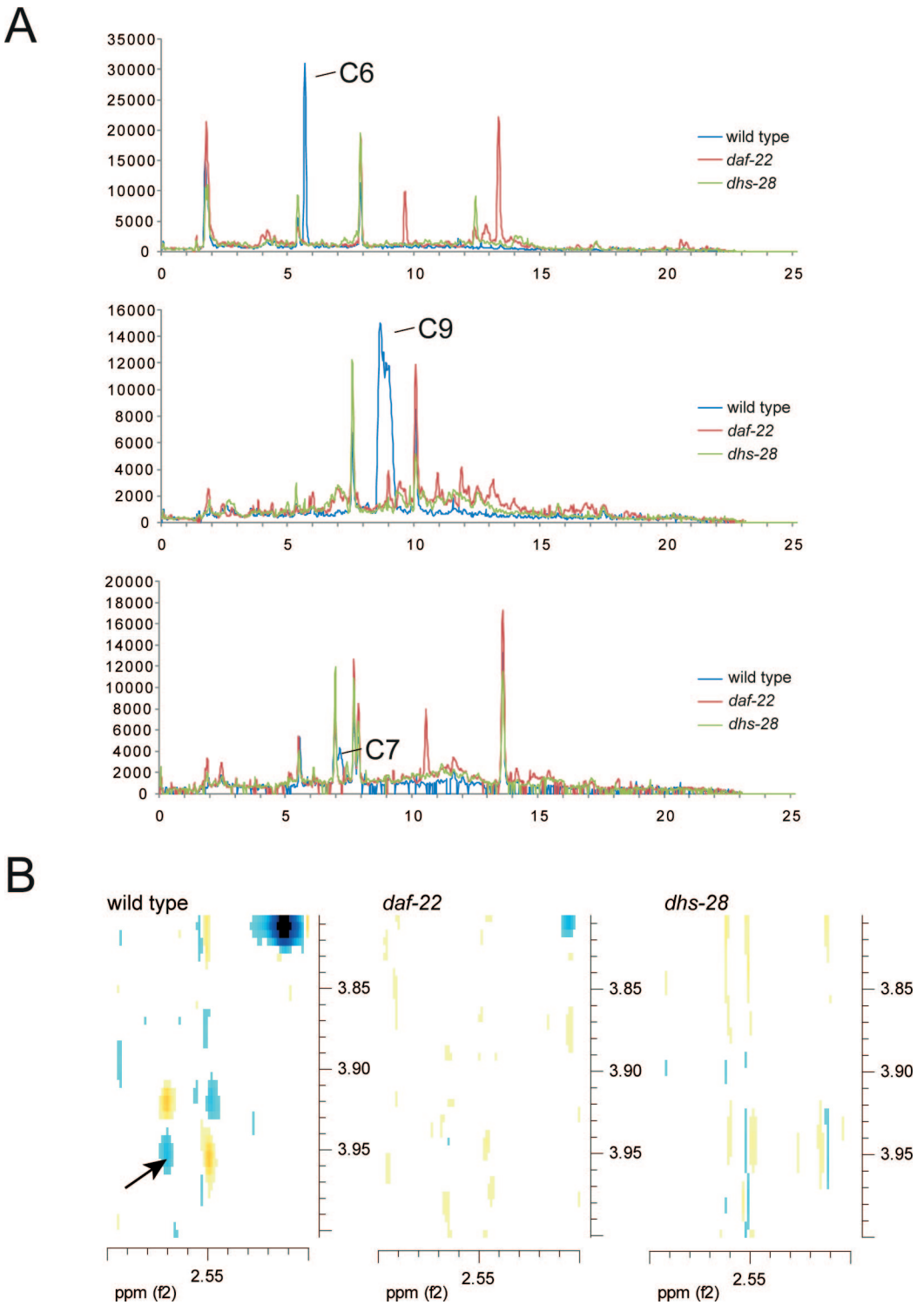


Fig. S3. Analysis of ascarosides C6, C9, C7, and C3 in conditioned medium extracts from wild-type, *daf-22*, or *dhs-28* long-term cultures. (*A*) LCMS traces of conditioned medium extracts from wild type, *daf-22*, or *dhs-28* long-term cultures. Total positive ion traces have been selected for the mass of ascaroside C6 $[M+Na]^+$ (*Top*), ascaroside C9 $[M+Na]^+$ (*Middle*), or ascaroside C7 $[M+Na]^+$ (*Bottom*). The peaks consistent with the mass and retention time of ascarosides C6, C9, and C7 have been indicated. Ascarosides C7 and C3 were present at relatively low concentrations in the control (wild-type) short-term cultures under the cultivation conditions that were used. Ascaroside C3 could not be detected by LCMS and was monitored by using dqf-COSY instead. (*B*) dqf-COSY spectra of conditioned medium extracts from wild-type, *daf-22*, or *dhs-28* long-term cultures. Cross-peak indicated with arrow in the expanded region is used to monitor the presence of ascaroside C3. This cross-peak is the one between H2 and H3b of ascaroside C3.

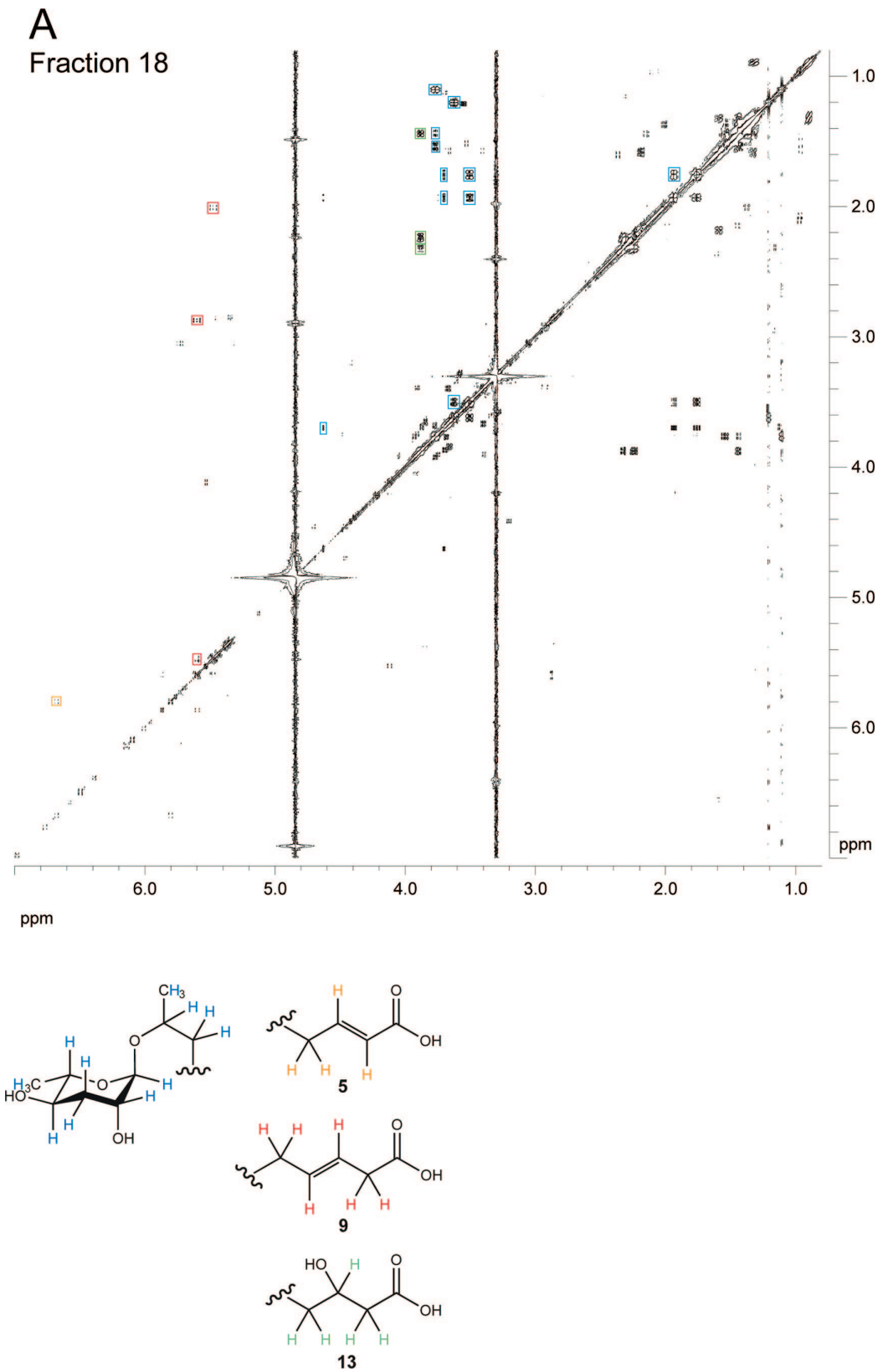


Fig. S4. dqf-COSY spectra of active fractions following HPLC fractionation of conditioned medium extracts from long-term *dhs-28* cultures. Each figure part (*A*–*F*) represents a different fraction. The long-chain ascarosides present in each fraction are indicated below each spectrum. Important correlations have been boxed in the spectrum and the responsible protons have been highlighted in the molecular structures. The structural assignment of long-chain ascaroside **17** is tentative.

B

Fraction 19

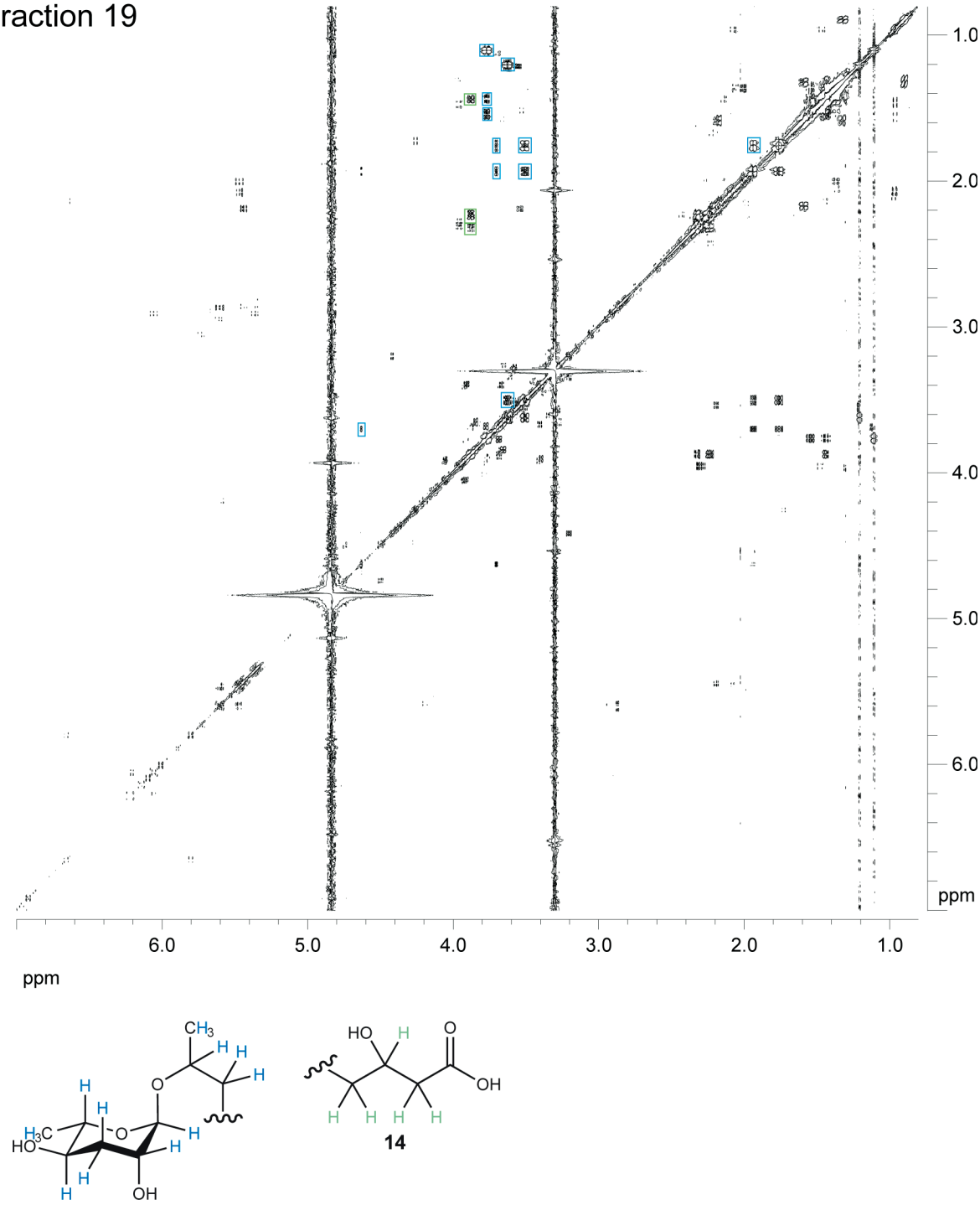
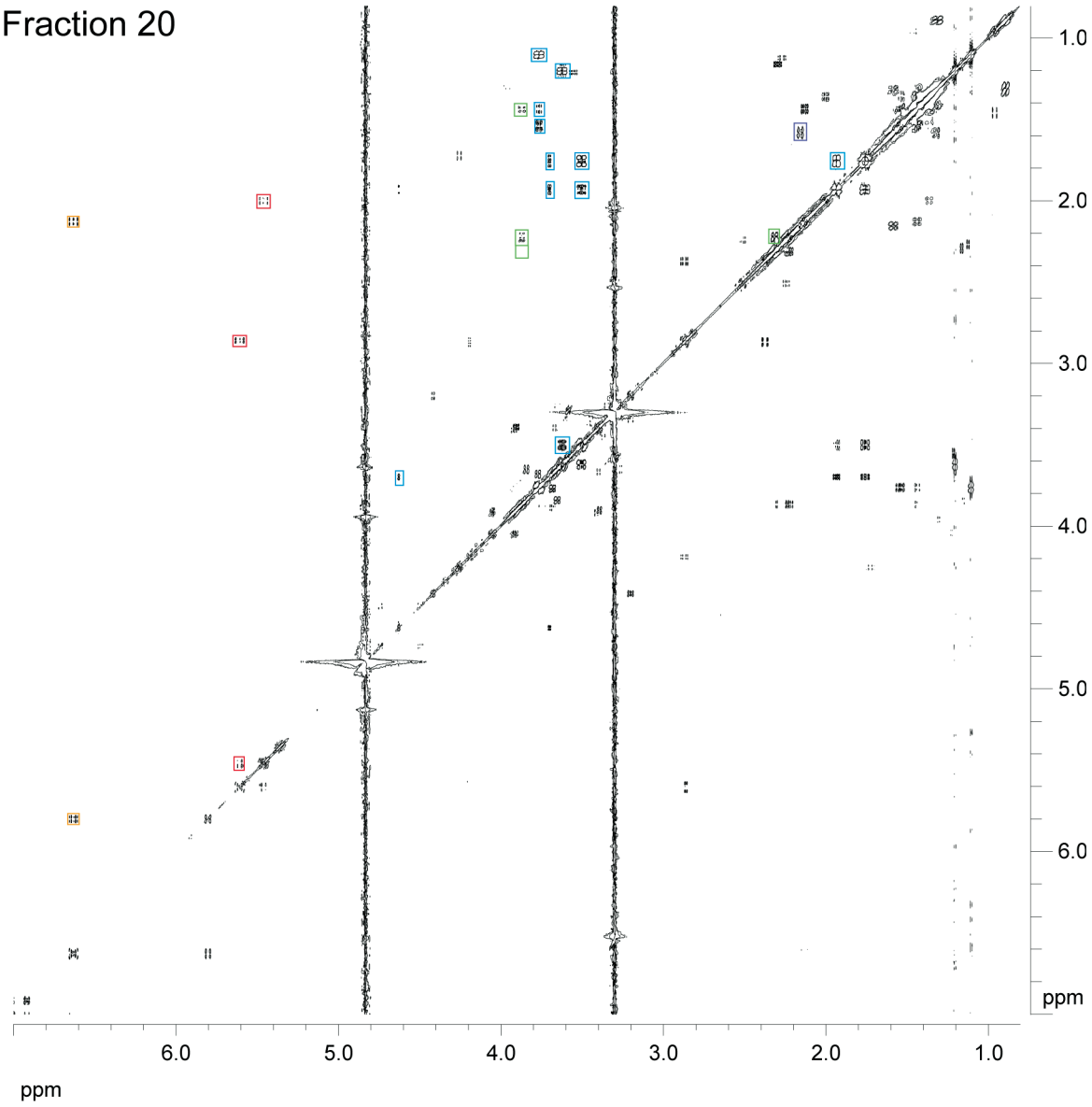
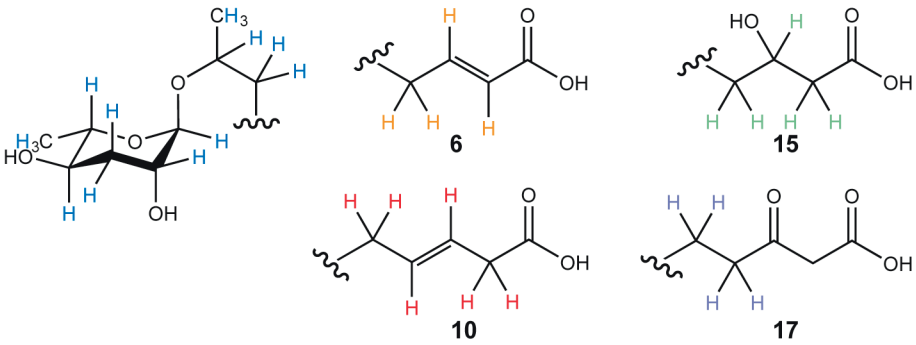


Fig. S4. Continued

C

Fraction 20





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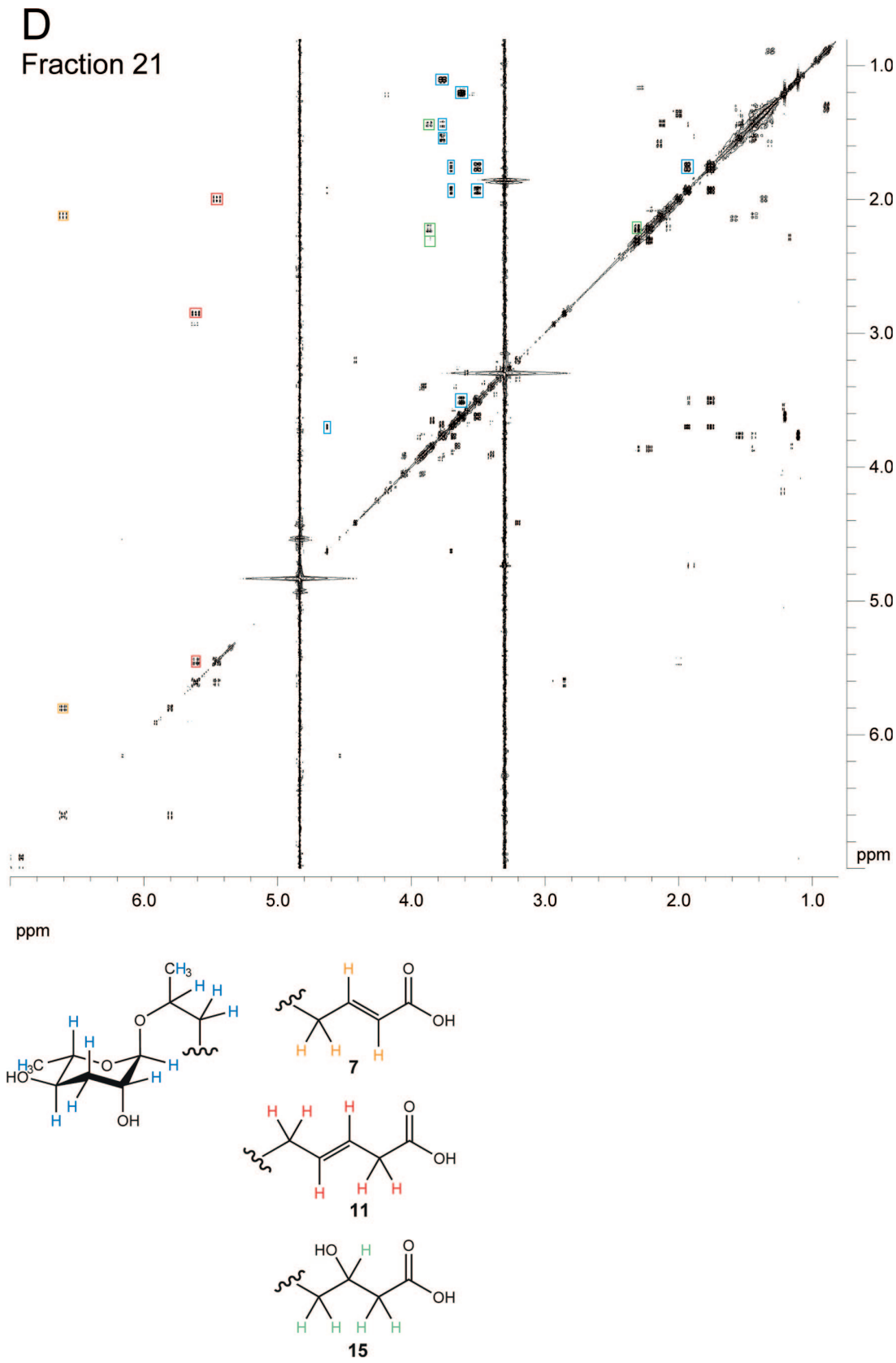

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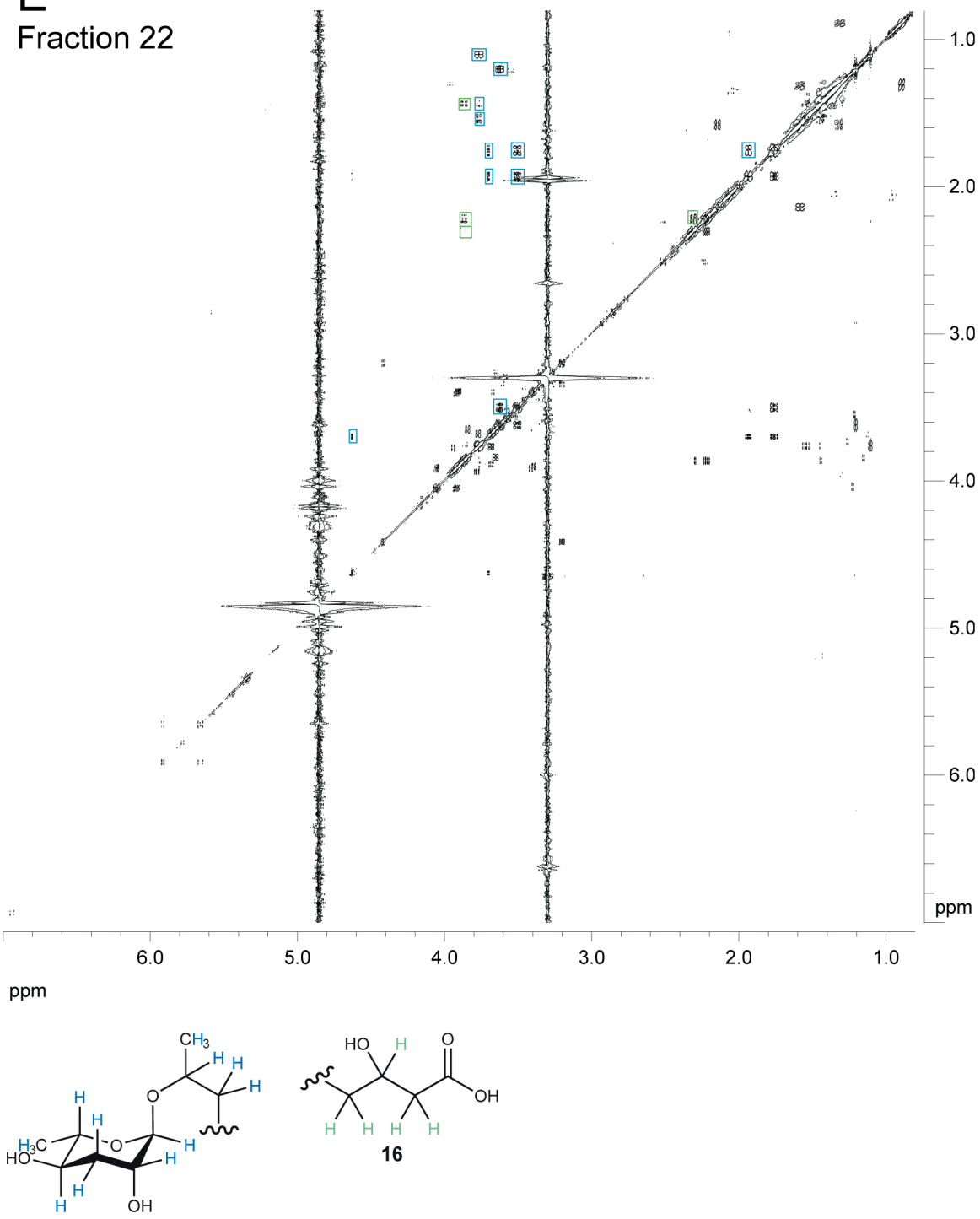

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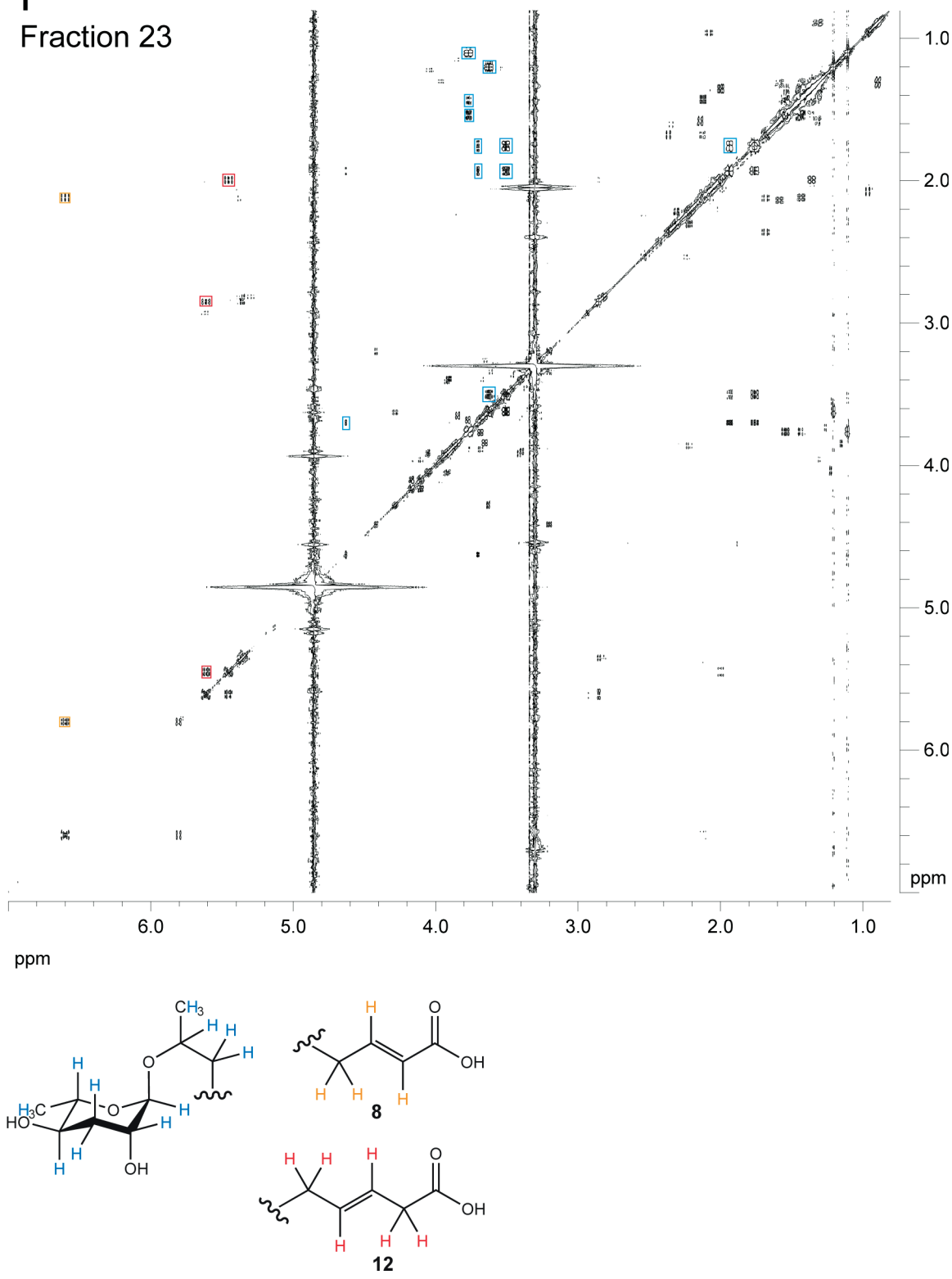

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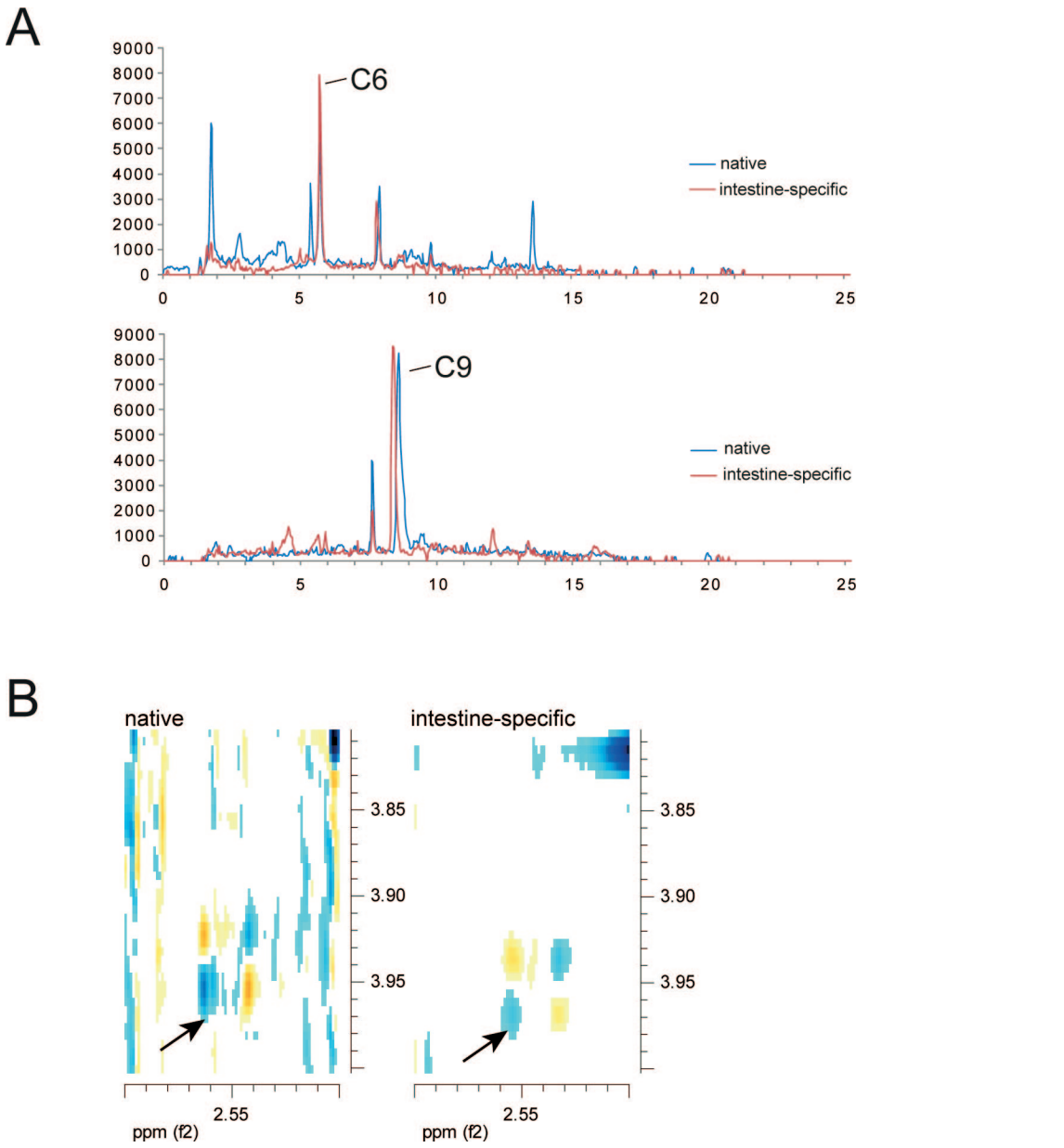

Fig. S5. Analysis of ascarosides C6, C9, and C3 in conditioned medium extracts from transgenic worms expressing *daf-22* under its native promotor or an intestine-specific promoter. (*A*) LCMS traces of conditioned medium extracts from transgenic worms expressing *daf-22* under its native promotor or an intestine-specific promoter. Total positive ion traces have been selected for the mass of ascaroside C6 [M+Na]+ (*Upper*) or ascaroside C9 [M+Na]+ (*Lower*). The peaks consistent with the mass and retention time of ascarosides C6 and C9 have been indicated. The slight shift in the C9 peak can be eliminated by including acid in the running buffer. Ascaroside C7 could not be detected by either LCMS or dqf-COSY. Ascaroside C3 could not be detected by LCMS and was monitored by using dqf-COSY instead. (*B*) dqf-COSY spectra of conditioned medium extracts from transgenic worms expressing *daf-22* under its native promotor or an intestine-specific promoter. Cross-peak indicated with arrow in the expanded region is used to monitor the presence of ascaroside C3. This cross-peak is the one between H2 and H3b of ascaroside C3.

Table S1. ^{1}H data derived from dqf-COSY spectra of natural *5–8* and synthetic *6* in methanol-d_4

No.	**5** δ_H mult. (J (Hz))	**6**, natural δ_H mult. (J (Hz))	**6**, synthetic δ_H mult. (J (Hz))	**7** δ_H mult. (J (Hz))	**8** δ_H mult. (J (Hz))
2	5.81, d ($J_{2,3}$=15.7)	5.81, d ($J_{2,3}$=15.7)	5.81, d ($J_{2,3}$=15.4)	5.81, d ($J_{2,3}$=15.7)	5.81, d ($J_{2,3}$=15.7)
3	6.69, dt ($J_{3,4}$=7.4)	6.64, dt ($J_{3,4}$=7.2)	6.61, dt ($J_{3,4}$=7.0)	6.61, dt ($J_{3,4}$=7.2)	6.61, dt ($J_{3,4}$=6.8)
4	2.16, m	2.14, m	2.14, m	2.13, m	2.13, m
5	n.d.	n.d.	n.d.	n.d.	n.d.
6	n.d.	n.d.	n.d.	n.d.	n.d.
7	n.d.	n.d.	n.d.	n.d.	n.d.
8	n.d.	n.d.	n.d.	n.d.	n.d.
9	n.d.	n.d.	n.d.	n.d.	n.d.
10	1.45, m; 1.56, m	n.d.	n.d.	n.d.	n.d.
11	3.78, m ($J_{11,12}$=5.9)	1.45, m; 1.55, m	1.49, m; 1.56, m	n.d.	n.d.
12	1.11, d	3.77, m ($J_{12,13}$=5.9)	3.78, m ($J_{12,13}$=6.0)	1.45, m; 1.56, m	n.d.
13		1.11, d	1.12, d	3.78, m ($J_{13,14}$=5.9)	1.45, m; 1.56, m
14				1.11, d	3.78, m ($J_{14,15}$=6.1)
15					1.11, d
1′	4.64, br. s	4.64, br. s	4.64, br. s	4.64, br. s	4.64, br. s
2′	3.71, dt ($J_{1',2'}$=4.7, $J_{2',3'ax}$=3.5)	3.71, dt ($J_{1',2'}$=5.2, $J_{2',3'ax}$=3.9)	3.71, dt ($J_{1',2'}$=4.8, $J_{2',3'ax}$=3.2)	3.71, dt ($J_{1',2'}$=5.2, $J_{2',3'ax}$=3.3)	3.71, dt ($J_{1',2'}$=4.8, $J_{2',3'ax}$=3.4)
3′ ax	1.77, ddd ($J_{3'ax,4'}$=11.7, $J_{3'ax,3'eq}$=12.9)	1.77, ddd ($J_{3'ax,4'}$=12.4, $J_{3'ax,3'eq}$=13.1)	1.77, ddd ($J_{3'ax,4'}$=11.7, $J_{3'ax,3'eq}$=13.2)	1.77, ddd ($J_{3'ax,4'}$=11.7, $J_{3'ax,3'eq}$=13.7)	1.77, ddd ($J_{3'ax,4'}$=11.6, $J_{3'ax,3'eq}$=12.9)
3′ eq	1.94, dt ($J_{2',3'eq}$=3.5)	1.94, dt ($J_{2',3'eq}$=3.3)	1.95, dt ($J_{2',3'eq}$=3.2)	1.94, dt ($J_{2',3'eq}$=3.3)	1.94, dt ($J_{2',3'eq}$=2.7)
4′	3.51, ddd ($J_{3'eq,4'}$=4.7)	3.51, ddd ($J_{3'eq,4'}$=5.2)	3.51, ddd ($J_{3'eq,4'}$=5.3)	3.51, ddd ($J_{3'eq,4'}$=5.2)	3.51, ddd ($J_{3'eq,4'}$=4.8)
5′	3.63, dq ($J_{4',5'}$=9.4)	3.63, dq ($J_{4',5'}$=9.8)	3.64, dq ($J_{4',5'}$=9.5)	3.63, dq ($J_{4',5'}$=9.8)	3.63, dq ($J_{4',5'}$=9.5)
6′	1.20, d ($J_{5',6'}$=5.9)	1.20, d ($J_{5',6'}$=6.5)	1.21, d ($J_{5',6'}$=6.4)	1.20, d ($J_{5',6'}$=6.5)	1.21, d ($J_{5',6'}$=6.1)

Table S2. ^{1}H data derived from dqf-COSY spectra of natural 9–12 in methanol-d_4

No.	**9** δ_H mult. (J (Hz))	**10** δ_H mult. (J (Hz))	**11** δ_H mult. (J (Hz))	**12** δ_H mult. (J (Hz))
2	2.89, d ($J_{2,3}$=6.5)	2.87, d ($J_{2,3}$=6.9)	2.86, d ($J_{2,3}$=6.8)	2.86, d ($J_{2,3}$=6.8)
3	5.61, dt ($J_{3,4}$=15.2)	5.61, dt ($J_{3,4}$=15.1)	5.62, dt ($J_{3,4}$=15.0)	5.62, dt ($J_{3,4}$=15.0)
4	5.49, dt ($J_{4,5}$=7.0)	5.47, dt ($J_{4,5}$=6.5)	5.46, dt ($J_{4,5}$=6.5)	5.46, dt ($J_{4,5}$=6.8)
5	2.02, m	2.01, m	2.01, m	2.01, m
6	1.39, m	1.37, m	1.37, m	1.36, m
7	n.d.	n.d.	n.d.	n.d.
8	n.d.	n.d.	n.d.	n.d.
9	n.d.	n.d.	n.d.	n.d.
10	1.45, m; 1.56, m	n.d.	n.d.	n.d.
11	3.78, m ($J_{11,12}$=5.9)	1.45, m; 1.55, m	n.d.	n.d.
12	1.11, d	3.77, m ($J_{12,13}$=5.9)	1.45, m; 1.56, m	n.d.
13		1.11, d	3.78, m ($J_{13,14}$=5.9)	1.45, m; 1.56, m
14			1.11, d	3.78, m ($J_{14,15}$=6.1)
15				1.11, d
1′	4.64, br. s	4.64, br. s	4.64, br. s	4.64, br. s
2′	3.71, dt ($J_{1',2'}$=4.7, $J_{2',3'ax}$=3.5)	3.71, dt ($J_{1',2'}$=5.2, $J_{2',3'ax}$=3.9)	3.71, dt ($J_{1',2'}$=5.2, $J_{2',3'ax}$=3.3)	3.71, dt ($J_{1',2'}$=4.8, $J_{2',3'ax}$=3.4)
3′ ax	1.77, ddd ($J_{3'ax,4'}$ =11.7, $J_{3'ax,3'eq}$ =12.9)	1.77, ddd ($J_{3'ax,4'}$=12.4, $J_{3'ax,3'eq}$=13.1)	1.77, ddd ($J_{3'ax,4'}$=11.7, $J_{3'ax,3'eq}$=13.7)	1.77, ddd ($J_{3'ax,4'}$=11.6, $J_{3'ax,3'eq}$=12.9)
3′ eq	1.94, dt ($J_{2',3'eq}$ =3.5)	1.94, dt ($J_{2',3'eq}$=3.3)	1.94, dt ($J_{2',3'eq}$=3.3)	1.94, dt ($J_{2',3'eq}$=2.7)
4′	3.51, ddd ($J_{3'eq,4'}$=4.7)	3.51, ddd ($J_{3'eq,4'}$=5.2)	3.51, ddd ($J_{3'eq,4'}$=5.2)	3.51, ddd ($J_{3'eq,4'}$=4.8)
5′	3.63, dq ($J_{4',5'}$=9.4)	3.63, dq ($J_{4',5'}$=9.8)	3.63, dq ($J_{4',5'=9.8}$)	3.63, dq ($J_{4',5'}$=*9.5*)
6′	1.20, d ($J_{5',6'}$=5.9)	1.20, d ($J_{5',6'}$=6.5)	1.20, d ($J_{5',6'}$=6.5)	1.21, d ($J_{5',6'}$=6.1)

Table S3. ^{1}H data derived from dqf-COSY spectra of natural *13–16* in methanol-d_4

No.	**13**δ_H mult. (J (Hz))	**14**δ_H mult. (J (Hz))	**15**δ_H mult. (J (Hz))	**16**δ_H mult. (J (Hz))
2a	2.25, dd ($J_{2a,2b}$=15.3) ($J_{2a,3}$=8.2)	2.24, dd ($J_{2a,2b}$=15.1) ($J_{2a,3}$=8.2)	2.23, dd ($J_{2a,2b}$=15.1) ($J_{2a,3}$=7.9)	2.23, dd ($J_{2a,2b}$=15.1) ($J_{2a,3}$=8.2)
2b	2.34, dd ($J_{2b,3}$=4.7)	2.33, dd ($J_{2b,3}$=4.7)	2.32, dd ($J_{2b,3}$=4.6)	2.32, dd ($J_{2b,3}$=4.8)
3	3.89, ddd ($J_{3,4}$=7.6)	3.88, ddd ($J_{3,4}$=7.9)	3.88, ddd ($J_{3,4}$=7.9)	3.88, ddd ($J_{3,4}$=8.2)
4	1.46, m	1.44, m	1.45, m	1.44, m
5	n.d.	n.d.	n.d.	n.d.
6	n.d.	n.d.	n.d.	n.d.
7	n.d.	n.d.	n.d.	n.d.
8	n.d.	n.d.	n.d.	n.d.
9	n.d.	n.d.	n.d.	n.d.
10	n.d.	n.d.	n.d.	n.d.
11	n.d.	n.d.	n.d.	n.d.
12	1.45, m; 1.56, m	n.d.	n.d.	n.d.
13	3.78, m ($J_{13,14}$=5.9)	1.45, m; 1.56, m	n.d.	n.d.
14	1.11, d	3.78, m ($J_{14,15}$=5.9)	1.45, m; 1.55, m	n.d.
15		1.11, d	3.77, m ($J_{15,16}$=5.9)	1.45, m; 1.55, m
16			1.11, d	3.77, m ($J_{16,17}$=6.2)
17				1.11, d
1′	4.64, br. s	4.64, br. s	4.64, br. s	4.64, br. s
2′	3.71, dt ($J_{1',2'}$=4.7, $J_{2',3'ax}$=3.5)	3.71, dt ($J_{1',2'}$=5.2, $J_{2',3'ax}$=3.9)	3.71, dt ($J_{1',2'}$=5.2, $J_{2',3'ax}$=3.9)	3.71, dt ($J_{1',2'}$=4.8, $J_{2',3'ax}$=4.1)
3′ ax	1.77, ddd ($J_{3'ax,4'}$ =11.7, $J_{3'ax,3'eq}$ =12.9)	1.77, ddd ($J_{3'ax,4'}$=11.8, $J_{3'ax,3'eq}$=13.1)	1.77, ddd ($J_{3'ax,4'}$=12.4, $J_{3'ax,3'eq}$=13.1)	1.77, ddd ($J_{3'ax,4'}$=11.6, $J_{3'ax,3'eq}$=13.0)
3′ eq	1.94, dt ($J_{2',3'eq}$ =3.5)	1.95, dt ($J_{2',3'eq}$=2.6)	1.94, dt ($J_{2',3'eq}$=3.3)	1.94, dt ($J_{2',3'eq}$=2.7)
4′	3.51, ddd ($J_{3'eq,4'}$=4.7)	3.51, ddd ($J_{3'eq,4'}$=4.7)	3.51, ddd ($J_{3'eq,4'}$=5.2)	3.51, ddd ($J_{3'eq,4'}$=4.8)
5′	3.63, dq ($J_{4',5'}$=9.4)	3.63, dq ($J_{4',5'}$=9.8)	3.63, dq ($J_{4',5'}$=9.8)	3.63, dq ($J_{4',5'}$=8.9)
6′	1.20, d ($J_{5',6'}$=5.9)	1.21, d ($J_{5',6'}$=5.9)	1.20, d ($J_{5',6'}$=6.5)	1.21, d ($J_{5',6'}$=6.2)

Table S4. ^{1}H data derived from the dqf-COSY spectrum of natural *17* in methanol-d_4

No.	**17** δ_H mult. (J (Hz))
4	2.16, t ($J_{4,5}$=7.5)
5	1.59, m
6	n.d.
7	n.d.
8	n.d.
9	n.d.
10	n.d.
11	n.d.
12	n.d.
13	n.d.
14	1.45, m; 1.55, m
15	3.77, m ($J_{15,16}$=5.9)
16	1.11, d
1′	4.64, br. s
2′	3.71, dt ($J_{1',2'}$=5.2, $J_{2',3'ax}$=3.9)
3′ ax	1.77, ddd ($J_{3'ax,4'}$=12.4, $J_{3'ax,3'eq}$=13.1)
3′ eq	1.94, dt ($J_{2',3'eq}$=3.3)
4′	3.51, ddd ($J_{3'eq,4'}$=5.2)
5′	3.63, dq ($J_{4',5'}$=9.8)
6′	1.20, d ($J_{5',6'}$=6.5)