Supporting Information

Total Synthesis of (±)-Spiroxin C

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Experimental Section

General: Reactions were carried out under a nitrogen atmosphere. Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were measured on a JASCO FT/IR-200 Fourier-transfer infrared spectrometer. ^{1}H NMR spectra were measured on JEOL JNM-EX270 (270 MHz), JEOL JNM-AL300 (300 MHz) and JEOL JNM-LA500 (500 MHz) spectrometers, and tetramethylsilane (0.00 ppm) was used as an internal standard. ^{13}C NMR spectra were measured on JEOL JNM-EX270 (67.8 MHz) and JEOL JNM-AL300 (75.45 MHz) spectrometers with $CDCl_3$ (77.0 ppm) as an internal standard (77.0 ppm). Mass spectra were taken on a JEOL JMS-600 or JMS-D300 mass spectrometer. Fuji Sylisia BW-127ZH (0.053-0.150 mm) was used for silica gel column chromatography.

Methoxymethyl ether 7b

To a stirred solution of **7a** (2.97 g, 16.9 mmol) in CH_2Cl_2 (80 mL) was added drpwise a solution of BCl_3 in hexane (1.0 M, 26.0 mL, 26.0 mmol) at –78 °C, and the whole was stirred for 30 min at the same temperature. After addition of 5% NaOH solution, the organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. Combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give a crude product (2.37 g), which was immediately employed for methoxymethylation without purification. To a stirred suspension of NaH (60% in oil, 981 mg, 20.4 mmol) in DMF (30 mL) was added a solution of the crude product in DMF (30 mL) under ice-cooling. Chloromethyl methyl ether (1.5 mL, 19.8 mmol) was added dropwise to the reaction mixture under ice-cooling, and the whole was stirred at the same temperature for 30 min. After addition of H_2O, the reaction mixture was extracted with AcOEt. The organic layer was washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 3/7) to afford **7b** (1.97 g 57%) as a colorless oil. IR ν_{max} (KBr): 2940, 1679, 1595, 1577, 1465, 1348, 1307 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.06 (2H, qn, *J* = 6 Hz), 2.62 (2H, t, *J* = 6 Hz), 2.91 (2H, t, *J* = 6 Hz), 6.88 (1H, d, *J* = 9 Hz), 7.03 (1H, d, *J* = 9 Hz), 7.34 (1H, t, *J* = 9 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 22.8, 30.7, 40.9, 56.3, 95.1, 114.8, 122.2, 123.3,

133.6, 146.8, 157.7, 197.2. Mass (EI) *m/z*: 206 (M^+, 25). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.00; H, 6.94.

Enol triflate 5b

To a stirred solution of **7b** (515 mg, 2.50 mmol) and **8** (1.28 g, 3.26 mmol) in THF (40 mL) was added dropwise a solution of NaHMDS in THF (1.0 M, 3.3 mL, 3.3 mmol) at –78 °C, and the whole was stirred at the same temperature for 30 min. After addition of H_2O, the reaction mixture was extracted with ether. Combined organic layers were washed with 10% NaOH solution, H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 1/19) to afford **5b** (801 mg, 95%) as a colorless oil. IR ν_{max} (KBr): 2953, 2901, 2835, 1646, 1599, 1576, 1469, 1418, 1324 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 2.35-2.42 (2H, m), 2.79 (2H, t, *J* = 8 Hz), 3.51 (3H, s), 5.23 (2H, s), 5.96 (1H, t, *J* = 5 Hz), 6.83 (1H, d, *J* = 8 Hz), 7.09 (1H, d, *J* = 8 Hz), 7.17 (1H, t, *J* = 8 Hz). ^{13}C-NMR (67.80 MHz, $CDCl_3$) δ_C: 22.1, 28.3, 56.4, 94.4, 113.8, 116.3, 117.7, 119.3, 121.1, 129.8, 139.0, 146.3, 152.7. Mass (EI) *m/z*: 338 (M^+, 100). HRMS Calcd for $C_{13}H_{13}F_3O_4S$: 338.0435. Found: 338.0445.

Triflate 11

To a stirred solution of **6** (1.48 g, 6.32 mmol) and diisopropylethylamine (1.70 mL, 9.78 mmol) in CH_2Cl_2 (40 mL) was added dropwise Tf_2O (1.60 mL, 9.53 mmol) under ice-cooling, and the whole was stirred at the same temperature for 30 min. After being diluted with CH_2Cl_2, the reaction mixture was washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was recrystallized from hexane to give **11** (1.86 g, 80%) as colorless crystals, mp 129 °C. IR ν_{max} (KBr): 2963, 2846, 1609, 1522, 1457, 1420, 1395, 1324 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 3.90, 3.94, 3.97 (each 3H, s), 6.79 (1H, d, *J* = 8 Hz), 6.91 (2H, s), 7.21 (1H, d, *J* = 8 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 55.6, 56.7, 57.8, 105.3, 108.0, 109.4, 116.8, 120.0, 120.2, 121.5, 139.2, 148.7, 151.1, 157.0. Mass (EI) *m/z*: 366 (M^+, 49). Anal. Calcd for $C_{14}H_{13}F_3O_6S$: C, 45.90; H, 3.58. Found: C, 45.91; H, 3.65.

Boronate 4c

A mixture of **11** (1.21 g, 3.31 mmol), diborane **10** (1.26 g, 4.96 mmol), KOAc (1.95 g, 19.8 mmol) and $Pd(PPh_3)_4$ (382 mg, 0.331 mmol) in DMF (40 mL) was stirred at 90 °C for 44 h. After cooling to room temperature, the reaction mixture was diluted with AcOEt, washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 3/7) to afford **4c** as a white powder, mp 121-124 °C. IR ν_{max} (KBr): 2976, 1592, 1521, 1466, 1331 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.43 (12H, s), 3.90 (3H, s), 3.96 (6H, s),

6.77 (2H, s), 6.89 (1H, d, J = 8 Hz), 7.43 (1H, d, J = 8 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 25.1, 56.1, 56.2, 57.3, 83.2, 105.3, 106.4, 106.7, 118.1, 131.0, 149.7, 151.4, 157.6. Mass (EI) *m/z*: 344 (M^+, 100). Anal. Calcd for $C_{19}H_{25}BO_5$: C, 66.30; H, 7.32;. Found: C, 66.25; H, 7.28.

Binaphthyl 3c

A mixture of **5b** (945 mg, 2.80 mmol), **4c** (960 mg, 2.79 mmol) and $Pd(PPh_3)_4$ (130 mg, 0.112 mmol) and $Bu_4NF{\cdot}H_2O$ (2.20 g, 8.43 mmol) in THF (60 mL) was refluxed for 2 h. After concentration under reduced pressure, the residue was dissolved in AcOEt. The solution was washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 1/9) to give **3c** (933 mg, 82%) as a white powder, mp 116-119 °C. IR ν_{max} (KBr): 2935, 2831, 1589, 1522, 1461, 1388 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 2.32-2.38 (2H, m), 2.81-2.93 (2H, m), 3.25, 3.90, 3.98 (each 3H, s), 4.05-4.15 (2H, AB), 5.93 (1H, t, J = 5 Hz), 6.60 (1H, d, J = 8 Hz), 6.74 (1H, d, J = 8 Hz), 6.77 (1H, d, J = 8 Hz), 6.87 (1H, d, J = 8 Hz), 6.90 (1H, d, J = 8 Hz), 7.00 (1H, t, J = 8 Hz), 7.21 (1H, d, J = 8 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 23.1, 29.5, 54.9, 55.2, 56.5, 57.6, 94.5, 106.2, 106.8, 107.3, 114.0, 118.7, 121.3, 125.2, 126.4, 127.2, 127.8, 134.2, 137.8, 141.6, 150.9, 151.4, 153.1, 155.2. Mass (EI) *m/z*: 406 (M^+, 100). Anal. Calcd for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. Found: C, 73.72; H, 6.50.

Phenol 13

To a stirred solution of **3c** (688 mg, 1.69 mmol) in MeOH (25 mL) and THF (25 mL) was added dropwise conc. HCl (6.0 mL) under ice-cooling, and the whole was stirred at room temperature 13 h. Precipitate formed was collected by filtration, washed with H_2O, and dried to give **13** (345 mg, 56%). The filtrate was neutralized with saturated $NaHCO_3$ solution, and concentrated under reduced pressure to give residue, which was extracted with AcOEt. The organic solution was washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by alumina column chromatography (AcOEt/hexane = 1/9) to give **13** (174 mg, 28%, total yield 84%) as a white solid, mp 180-185 °C. IR ν_{max} (KBr): 3464, 2933, 2833, 1584, 1522 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 2.29-2.37 (2H, m), 2.77-2.91 (2H, m), 3.36, 3.91, 4.00 (each 3H, s), 5.03 (1H, s), 5.75 (1H, t, J = 5 Hz), 6.54 (1H, d, J = 8 Hz), 6.74 (1H, d, J = 8 Hz), 6.80 (1H, d, J = 8 Hz), 6.84 (1H, d, J = 8 Hz), 6.90 (1H, d, J = 8 Hz), 6.99 (1H, t, J = 8 Hz), 7.38 (1H, d, J = 8 Hz). ^{13}C-NMR (67.8 MHz, $CDCl_3$) δ_C: 23.4, 29.6, 55.5, 56.4, 57.8, 96.1, 106.5, 107.8, 108.7, 115.3, 119.4, 119.5, 123.2, 126.0, 127.1, 128.9, 129.9, 137.5, 139.4, 150.8, 151.3, 152.2, 157.4. Mass (EI) *m/z*: 362 (M^+, 42). HRMS Calcd for $C_{23}H_{22}O_4$: 362.1517. Found: 362.1518.

Quinone monoacetal 14

To a stirred solution of PIFA (740 mg, 1.72 mmol) in MeCN (50 mL) and H_2O (25 mL) was added dropwise a solution of **13** (519 mg, 1.43 mmol) in THF (50 mL) under ice-cooling, and the whole was stirred under ice-cooling for 5 min. The reaction mixture was neutralized with saturated $NaHCO_3$ solution under ice-cooling, concentrated under reduced pressiure, and extracted with AcOEt. The organic solution was washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 2/3) to give **14** (457 mg, 92%) as a white solid, mp 156-158 °C. IR ν_{max} (KBr): 2936, 2833, 1676, 1649, 1567, 1455 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 2.33-2.39 (2H, m), 2.76-2.81 (2H, m), 3.14, 3.96 (each 3H, s), 6.04 (1H, dd, *J* = 3, 5 Hz), 6.45 (1H, d, *J* = 11 Hz), 6.79 (1H, d, *J* = 11 Hz), 6.83 (1H, d, *J* = 8 Hz), 6.89 (1H, d, *J* = 8 Hz), 7.03 (1H, d, *J* = 8 Hz), 7.08 (1H, t, *J* = 8 Hz), 7.53 (1H, d, *J* = 8 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 23.4, 29.3, 51.2, 56.1, 95.6, 113.1, 117.6, 118.8, 121.7, 122.5, 127.7 (2C), 132.1, 132.3, 136.3, 137.8, 138.0, 138.9, 140.5, 150.0, 159.7, 183.5. Mass (EI) *m/z*: 346 (M^+, 100). Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.16; H, 5.44.

Phenol 15

A solution of **14** (775 mg, 2.24 mmol) and LiCl (8.50 g, 97.8 mmol) in DMF (100 mL) was stirred and heated at 130 °C for 40 h. After cooling to room temperature, the reaction mixture was diluted with ether, washed with H_2O and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 1/4) to give **15** (493 mg, 66%) as an yellow syrup. IR ν_{max} (KBr): 2936, 1668, 1619, 1454, 1339 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 2.33-2.37 (2H, m), 2.75-2.81 (2H, m), 3.16 (3H, s), 6.08 (1H, dd, *J* = 3, 5 Hz), 6.52 (1H, d, *J* = 11 Hz), 6.82 (1H, d, *J* = 8 Hz), 6.90 (1H, d, *J* = 8 Hz), 6.96 (1H, d, *J* = 11 Hz), 7.00 (1H, d, *J* = 8 Hz), 7.08 (1H, t, *J* = 8 Hz), 7.51 (1H, d, *J* = 8 Hz), 12.40 (1H, s). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 23.4, 29.4, 51.4, 95.1, 112.4, 119.0, 119.2, 122.0, 122.6, 127.9, 128.4, 130.0, 131.5, 136.4, 137.4, 138.4 (2C), 145.1, 150.1, 161.9, 189.6. Mass (EI) *m/z*: 332 (M^+, 100). HRMS Calcd for $C_{21}H_{16}O_4$: 332.1048. Found: 332.1033.

Pivaloyl ester 16

To a stirred suspension of NaH (60% in oil, 85.0 mg, 1.95 mmol) in THF (12 mL) was added dropwise a solution of **15** (485 mg, 1.46 mmol) in THF (24 mL) under ice-cooling. Pivaloyl chloride (0.24 ml, 1.94 mmol) was added dropwise to the reaction mixture under ice-cooling, and the whole was stirred under ice-cooling for 1 h. The reaction mixture was diluted with ether, washed with 5% HCl, H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel

column chromatography to afford **16** (574 mg, 95%) as a white solid, mp 113-116 °C. IR ν_{max} (KBr): 2975, 2831, 1753, 1679, 1650, 1618, 1569, 1455 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.45 (9H, s), 2.34-2.40 (2H, m), 2.77-2.82 (2H, m), 3.15 (3H, s), 6.11 (1H, dd, *J* = 3, 6 Hz), 6.42 (1H, d, *J* = 12 Hz), 6.83 (1H, d, *J* = 9 Hz), 6.86 (1H, d, *J* = 12 Hz), 6.90 (1H, d, *J* = 9 Hz), 7.06 (1H, d, *J* = 9 Hz), 7.09 (1H, t, *J* = 9 Hz), 7.57 (1H, d, *J* = 9 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 23.5, 27.2, 29.3, 39.1, 51.4, 95.3, 118.9, 121.2, 121.9, 122.0, 125.2, 128.0, 129.1, 131.4, 135.7, 137.8, 138.1, 138.2, 138.4, 142.2, 150.0 (2C), 176.8, 182.6. Mass (EI) *m/z*: 416 (M^+, 89). HRMS Calcd for $C_{26}H_{24}O_5$: 416.1623. Found: 416.1625.

Quinone hemiacetal 17

To a stirred solution of **16** (579 mg, 1.40 mmol) in MeCN (60 mL) and THF (20 mL) was added dropwise 1.2 M H_2SO_4 (80 mL) under ice-cooling, and the whole was gradually warmed to room temperature under stirring for 24 h. Reddish precipitate formed was collected by filtration, washed with water, and dried to give **17** (210 mg, 38%). The filtrate was neutralized with saturated $NaHCO_3$ solution, concentrated under reduced pressure, and extracted with AcOEt. Combined organic layers were washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography to give **17** (180 mg, 32%, total 70%) as a reddish powder, mp 157-159 °C. IR ν_{max} (KBr): 3248, 2975, 2831, 1754, 1665, 1653, 1614, 1561, 1480 cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.46 (9H, s), 2.29-2.40 (2H, m), 2.81 (1H, m), 3.05 (1H, m), 4.46 (1H, s), 5.89 (1H, t, *J* = 5 Hz), 6.44 (1H, d, *J* = 8 Hz), 6.73 (2H, s), 6.86 (1H, d, *J* = 8 Hz), 7.00 (1H, d, *J* = 8 Hz), 7.26 (1H, d, *J* = 8 Hz), 7.60 (1H, d, *J* = 8 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 23.0, 27.2, 29.0, 39.2, 114.9, 120.4, 121.5, 123.8, 127.7, 128.1, 128.7, 131.0, 137.2, 137.3, 138.1, 139.2, 143.1, 149.1, 151.0, 176.8, 184.2, 185.2. Mass (EI) *m/z*: 402 (M^+, 80). HRMS Calcd for $C_{25}H_{22}O_5$: 402.1467. Found: 402.1474.

Bromoether 2

To a stirredsolution of **17** (153 mg, 0.381 mmol) in CH_2Cl_2 (10 mL) was added 2,4,4,6-tetrabromocyclohexadienone (**18**, 254 mg, 0.620 mmol) under ice-cooling. After being stirred for 15 min at the same temperature, the reaction mixture was concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 1/9) to give **2** (171 mg, 93%) as a white powder, mp 134-138 °C (decomp.). IR ν_{max} (KBr): 2974, 2256, 1757, 1678, 1598, 1454 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.42 (9H, s), 2.75-2.98 (2H, m), 3.02-3.15 (2H, m), 4.69 (1H, dd, *J* = 6, 12 Hz), 6.45 (1H, d, *J* = 11 Hz), 6.60 (1H, d, *J* = 9 Hz), 6.71 (1H, d, *J* = 9 Hz), 7.03 (1H, d, *J* = 9 Hz), 7.15 (1H, t, *J* = 9 Hz), 7.17 (1H, d, *J* = 11 Hz), 7.56 (1H, d, *J* = 9 Hz). ^{13}C-NMR

(75.45 MHz, $CDCl_3$) δ_C: 27.2, 28.9, 31.8, 29.1, 48.7, 88.2, 98.9, 114.3, 118.7, 120.5, 121.0, 124.0, 126.0, 130.1, 132.1, 135.9, 136.7, 141.1, 144.0, 148.5, 150.4, 176.4, 181.3. Mass (EI) *m/z*: 480 (M^+, 33). HRMS Calcd for $C_{25}H_{21}O_5Br$: 480.0572. Found: 480.0514.

Epoxide 19

To a stirred solution of **2** (37.2 mg, 0.0773 mmol) in CH_2Cl_2 (3.0 mL) containing a solution of TBHP in decane (5.0-6.0 M, 0.02 mL, ca 0.11 mmol) was added DBU (0.017 mL, 0.11 mmol) under ice-cooling, and the reaction mixture was stirred at room temperature for 18 h. After being diluted with CH_2Cl_2, the reaction mixture was washed with cold 5% HCl, H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 1/4) to afford **19** (21.0 mg, 66%) as a white powder, mp 56-61 °C. IR ν_{max} (KBr): 3330, 2954, 1671, 1593, 1477, 1454, 1354, 1318 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.77-2.89 (2H, m), 3.05-3.11 (2H, m), 3.77 (1H, d, *J* = 3 Hz), 4.20 (1H, d, *J* = 3 Hz), 4.70 (1H, dd, *J* = 6, 12 Hz), 6.61 (1H, d, *J* = 9 Hz), 6.72 (1H, d, *J* = 9 Hz), 6.92 (1H, d, *J* = 9 Hz), 7.13 (1H, t, *J* = 9 Hz), 7.53 (1H, d, *J* = 9 Hz), 9.34 (1H, s). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 28.8, 31.8, 48.6, 52.5, 53.1, 88.7, 102.3, 108.6, 113.9, 118.5, 120.9, 122.5, 129.3, 129.9, 132.1, 135.7, 139.1, 149.4, 159.1, 194.8. Mass (FAB) *m/z*: 413 ($M+H^+$). HRMS Calcd for $C_{20}H_{14}O_5Br$: 412.9974. Found: 413.0009.

Pivalate 20

To a strred suspension of NaH (60% in oil, 3.0 mg, 0.069 mmol) in THF (0.5 mL) was added dropwise a solution of **19** (20.0 mg, 0.0484 mmol) in THF (1.5 mL) under ice-cooling. Pivaloyl chloride (7 μL, 0.057 mmol) was added to the reaction mixture under ice-cooling, and the whole was stirred under ice-cooling for 1 h. The reaction mixture was diluted with ether, washed with H_2O, 5% HCl, H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography to give **20** (21.4 mg, 87%) as a white powder, mp 129-133 °C. IR ν_{max} (KBr): 2975, 1758, 1703, 1594, 1453, 1314 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.39 (9H, s), 2.78-2.93 (2H, m), 3.07-3.12 (2H, m), 3.75 (1H, d, *J* = 3 Hz), 4.15 (1H, d, *J* = 3 Hz), 4.71 (1H, dd, *J* = 6, 12 Hz), 6.61 (1H, d, *J* = 9 Hz), 6.72 (1H, d, *J* = 9 Hz), 7.08 (1H, d, *J* = 9 Hz), 7.15 (1H, t, *J* = 9 Hz), 7.59 (1H, d, *J* = 9 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 27.1, 28.8, 31.8, 39.2, 48.2, 51.9, 53.9, 88.1, 102.5, 114.2, 117.0, 121.0, 122.0, 124.9, 126.7, 130.1, 132.3, 140.7, 141.5, 148.6, 149.6, 176.4, 188.7. Mass (FAB) *m/z*: 497 ($M+H^+$). HRMS Calcd for $C_{25}H_{22}O_6Br$: 497.0616. Found: 497.0608.

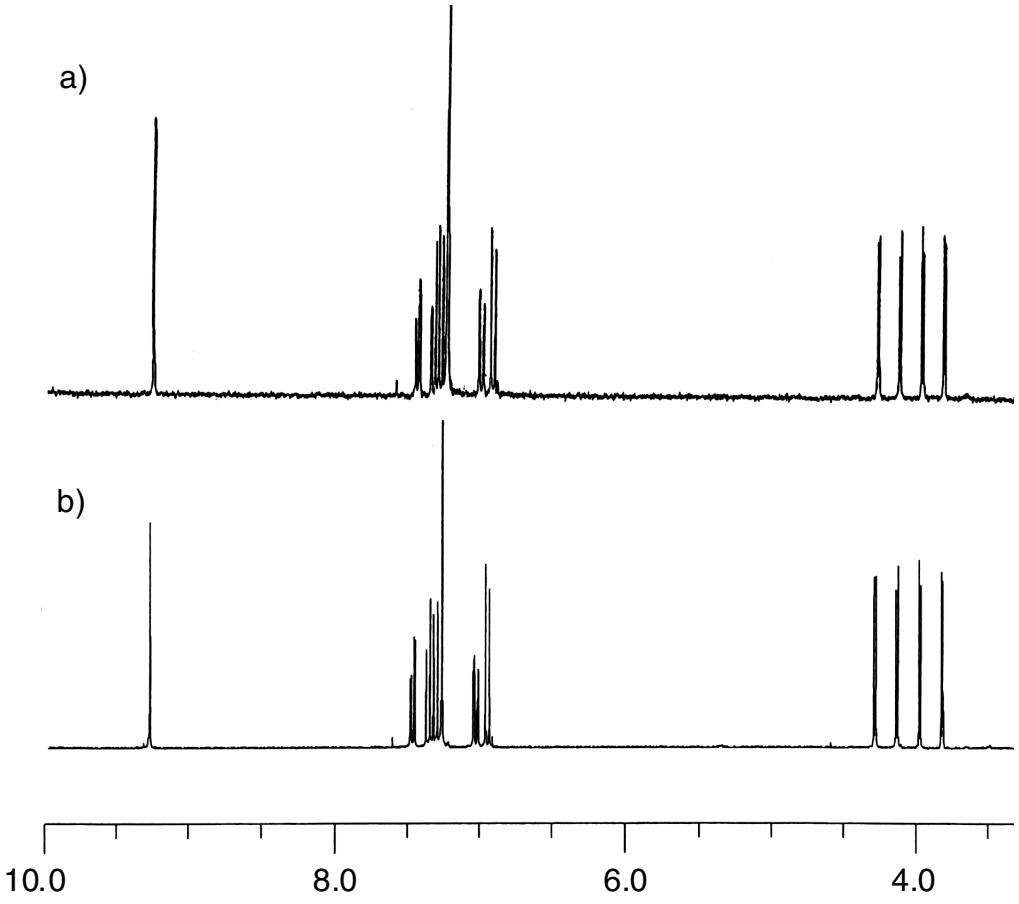
Enone 21

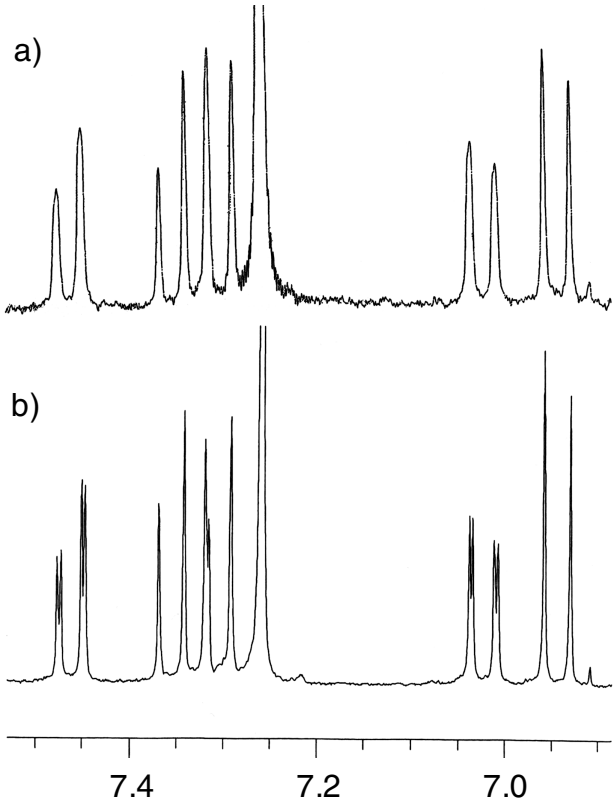
A solution of **20** (16.0 mg, 0.032 mmol) in C_6H_6 (1.0 mL) containing NBS (8.6 mg, 0.048 mmol) and AIBN (2.6 mg, 0.016 mmol) was stiired and refluxed. The same amounts of NBS and AIBN were added two times, after 2 h and 4 h, respectively, and the whole was kept refluxing for total of 6 h. The reaction mixture was diluted with AcOEt, washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant crude brimide was dissolved in DMSO (1.5 mL) containing $NaHCO_3$ (5.4 mg, 0.064 mmol), stirred at room temperature for 20 h , and diluted with AcOEt. The organic solution was washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 3/17) to afford **21** (3.7 mg, 27%) as a white powder, mp 170-172 °C (decomp.). IR ν_{max} (KBr): 2976, 1759, 1703, 1673, 1625, 1602, 1470, 1301 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.39 (9H, s), 3.80 (1H, d, *J* = 3 Hz), 4.23 (1H, d, *J* = 3 Hz), 6.76 (1H, d, *J* = 11 Hz), 6.99 (1H, d, *J* = 9 Hz), 7.06 (1H, d, *J* = 9 Hz), 7.22 (1H, t, *J* = 11 Hz), 7.26 (1H, d, *J* = 9 Hz), 7.39 (1H, t, *J* = 9 Hz), 7.64 (1H, d, *J* = 9 Hz). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 27.1, 39.2, 51.9, 54.0, 81.9, 104.1, 117.2, 119.3, 120.8, 125.0, 125.8, 127.5, 127.8, 130.4, 133.5, 139.6, 140.5, 140.6, 148.8, 149.3, 176.3, 183.2, 188.2. Mass (FAB) *m/z*: 480 ($M+H^+$). HRMS Calcd for $C_{25}H_{19}O_7$: 431.1063. Found: 431.1097.

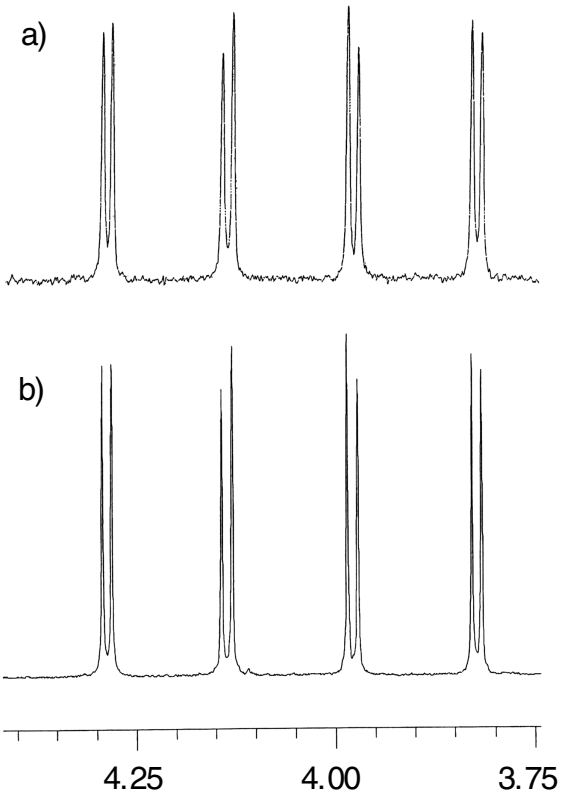
(±)-Spiroxin C (1c)

To a stirred solution of **21** (3.6 mg, 0.0084 mmol) in CH_2Cl_2 (0.5 mL) containing a solution of TBHP in decane (5.0-6.0 M, 0.003 mL, ca 0.017 mmol) was added DBU (0.003 mL, 0.020 mmol) under ice-cooling, and the whole was stirred at room temperature for 20 h. The reaction mixture was diluted with CH_2Cl_2, washed with 5% HCl, H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (AcOEt/hexane = 2/3) to give spiroxin C (**1c**, 1.8 mg, 59%) as a white powder, mp 162-165 °C (decomp.). IR ν_{max} (KBr): 3346, 3024, 2925, 1677, 1597, 1474, 1386, 1353, 1300 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.82 (1H, d, *J* = 3 Hz), 3.98 (1H, d, *J* = 3 Hz), 4.14 (1H, d, *J* = 3 Hz), 4.29 (1H, d, *J* = 3 Hz), 6.94 (1H, d, *J* = 9 Hz), 7.02 (1H, dd, *J* = 1.5, 9 Hz), 7.31 (1H, d, *J* = 9 Hz), 7.34 (1H, t, *J* = 9 Hz), 7.46 (1H, dd, *J* = 1.5, 9 Hz), 9.27 (1H, s). ^{13}C-NMR (75.45 MHz, $CDCl_3$) δ_C: 51.7, 52.4, 53.2, 53.5, 84.6, 103.6, 109.0, 119.5, 119.9, 122.5, 124.9, 125.7, 127.1, 130.5, 134.0, 139.2, 149.3, 159.7, 191.3, 194.3. Mass (FAB) *m/z*: 363 ($M+H^+$). HRMS Calcd for $C_{20}H_{11}O_7$: 363.0503. Found: 363.0504.

^{1}H-NMR (300 MHz) spectra for natural (a) and synthetic spiroxin C (b)




a)
b)
7.4
7.2
7.0


a)
b)
4.25
4.00
3.75