Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

for

Organocatalytic Asymmetric Synthesis of Cornolactones A and B, and Formal Synthesis of Brasoside and Littoralisone

Hui Hou,[†,‡] Qi Gu,[†] Xuan Wang,[†] Dequn Sun,[‡] and Bing-Feng Sun[*,†]

[†]CAS Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, 345 Lingling Road, Shanghai 200032, China.

[‡]Marine College, Shandong University at Weihai, 180 Wenhua West Road, Weihai 264209, China.

bfsun@sioc.ac.cn

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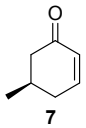
General Procedures

All non-aqueous reactions were run under a positive pressure of argon. Anhydrous solvents were obtained using standard drying techniques. Commercial grade reagents were used without further purification unless stated otherwise. Flash chromatography was performed on 300-400 mesh silica gel with the indicated solvent systems. ^{1}H NMR were recorded on a Bruker 400 (400 MHz) spectrometer and chemical shifts are reported in ppm down field from TMS, using TMS (0.00 ppm) or residual $CDCl_3$ (7.26 ppm) as an internal standard. Data are reported as: (s = singlet, br = broad, d= doublet, t = triplet, q = quartet, m = multiplet; *J* = coupling constant in Hz, integration.). ^{13}C NMR spectra were recorded on a Bruker 400 (100 MHz) spectrometer, using proton decoupling unless otherwise noted. Chemical shifts are reported in ppm down field from TMS, using the central resonance of $CDCl_3$ (77.00 ppm) as the internal standard. HRMS were recorded by using either FTMS-7 or IonSpec 4.7 spectrometers. IR spectra were recorded on Nicolet iN 10 MX.

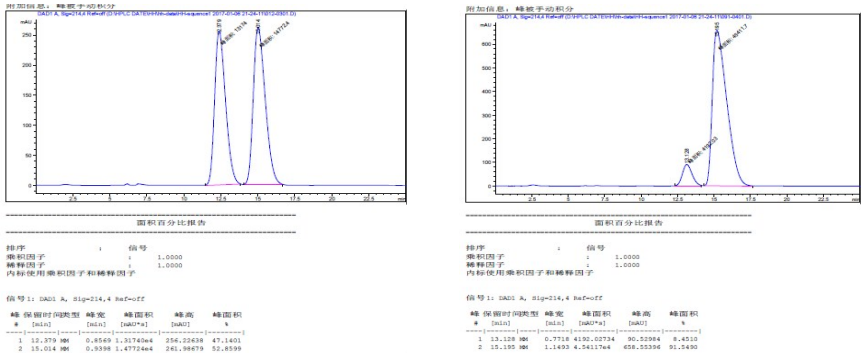
Experimental procedures and data of compounds

(R)-5-methylcyclohex-2-en-1-one (7)

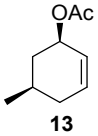


To a solution of *tert*-butyl-3-oxobutanoate (**10**) (30.0 g, 190 mmol, 1.0 equiv) was added catalyst **12** (6.2 g, 19 mmol, 0.1 equiv) before cooling down to −78℃. Then aldehyde **11** (23.5 mL, 285 mmol, 1.5 equiv) was added slowly at -78 ℃ and the mixture was stirred at −78 ℃ for 24 h. Toluene (350 mL) and TsOH (7.2 g, 38 mmol, 0.2 equiv) was added to the mixture and stirred at 80 ℃ for 36 h before being quenched with saturated aqueous $NaHCO_3$ solution. The reaction mixture was transferred to a separatory funnel and extracted with CH_2Cl_2. The organic phases were combined and dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (PE/EA = 15/1) and then distilled under reduced pressure to afford **7** (10.8 g, 98.8 mmol, 52% yield, ee = 83%) as a colorless oil.

(Chromatogram: AS-H; *n*-Hexane/*i*-PrOH = 98/2; 0.5 mL/min; 214 nm).



(1R, 5R)-5-methylcyclohex-2-en-1-yl acetate (13)

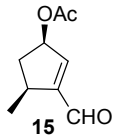


To a solution of **7** (12.4 g, 113 mmol, 1.0 equiv) in dry DCM (300 mL) was added Dibal-H (1.0 M in hexane, 169 mL, 169 mmol, 1.5 equiv) at −78 ℃ under argon. The mixture was stirred at −78 ℃ for 2 h before being quenched with methanol. The solvent was removed under reduced pressure, followed by slow addition of water to the residue. The mixture was transferred to a separatory funnel and extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford the crude alcohol product as a colorless oil.

To a stirred solution of the above crude alcohol product (12.7 g, 113 mmol, 1.0 equiv, assuming quantitative yield in the preceding step), Et_3N (31.3 mL, 226 mmol, 2.0 equiv), DMAP (1.38 g, 11.3 mmol, 0. 1 equiv) in DCM was added acetic anhydride (16.0 mL, 169.5 mmol, 1.5 equiv) at 0 ℃. The mixture was stirred for 1.5 h at this temperature before being quenched with addition of water. The mixture was extracted with EtOAc and the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4. Then solvent was evaporated under vacuum and the residue was purified by flash chromatography (PE/EA = 100/1) to give compound **13** (15.0 g, 97 mmol) as a colorless oil in 86% yield for two steps.

$\boldsymbol{R_f}$ = 0.60 (PE/EA = 10/1); $[\alpha]_D^{25}$ = –14.6º (*c* = 1.50, $CHCl_3$); **IR** (film): 3034, 2953, 2927, 1732, 1653, 1240, 1023, 990, 740 cm^{-1}; **^{1}H NMR** (400 MHz,$CDCl_3$): δ 5.84 (m, 1H), 5.55 (m, 1H), 5.38 (m, 1H), 2.07 (m, 4H), 1.84 (m, 1H), 1.67 (m, 1H), 1.25 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 170.8, 130.6, 126.7, 70.7, 36.7, 33.4, 27.8, 21.8, 21.3; **LRMS** (ESI): 177$(M+Na)^+$; **HRMS** (DART): Calcd for $C_9H_{18}O_2N$: 172.1332, Found: 172.1332.

(1R, 4S)-3-formyl-4-methylcyclopent-2-en-1-yl acetate (15)



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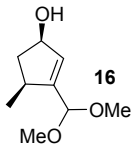
Compound **13** (6.2 g, 40.6 mmol, 1.0 equiv) was dissolved in DCM (200 mL) and MeOH (200 mL) before cooling down to −78℃. The mixture was subjected to ozone until the solution turned blue. The mixture was then flushed with O_2 gas for 10 min, followed by addition of PPh_3 (10.6 g, 40.6 mmol, 1.0 equiv). The resulting solution was stirred for 4 hours at rt., after which the solvent was evaporated under vacuum to give **14** as a crude product.

To the solution of crude **14** (7.6 g, 40.6 mmol, assuming quantitative yield in the preceding step, 1.0 equiv) in DCM (800 mL) was added Bn_2NH (3.9 mL, 20.3 mmol, 0.5 equiv), CF_3COOH (1.5 mL, 20.3 mmol, 0.5 equiv). The mixture was stirred at the room temperature for 4 h before being concentrated by removal of organic solvent. The residue was purified by flash chromatography (PE/EA = 15/1-10/1) to give compound **15** (5.9 g, 35.1 mmol, 87% for two steps).

$\boldsymbol{R_f}$ = 0.50 (PE/EA = 5/1); $[\alpha]_D^{25}$ = +153.1 (*c* = 1.50, $CHCl_3$); **IR** (film): 2920, 2361, 1734, 1716, 1684 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 6.70 (t, *J* = 3.6 Hz, 1H), 5.70 (m, 1H), 2.98 (m, 1H), 2.65 (m, 1H), 2.07 (s, 3H), 1.56 (m, 1H), 1.23 (d,

J = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 189.9, 170.5, 153.5, 146.1, 77.5, 38.6, 35.9, 21.0, 20.2; **LRMS** (ESI): 167$(M-H)^+$; **HRMS**(DART): Calcd for $C_{13}H_{14}O_2NF_2S$: 286.0707, Found: 286.0708.

(1R, 4S)-3-(dimethoxymethyl)-4-methylcyclopent-2-en-1-ol (16)

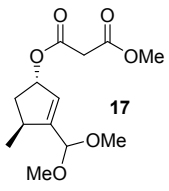


To a solution of compound **15** (5.7 g, 33.8 mmol, 1.0 equiv) in MeOH (70 mL) was added $HC(OMe)_3$ (36.9 mL, 337.5 mmol, 10 equiv), PPTS (1.7 g, 6.8 mmol, 0.2 equiv). After addition, the solution was stirred at room temperature for 6 h before the solvent was evaporated under vacuum. The organic residue was dissolved in saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The organic layers were combined and dried over sodium sulfate. Removal of solvent under reduced pressure gave crude acetal (5.6 g).

To a solution of crude acetal (2.7 g, 12.6 mmol, assuming 100% purity, 1.0 equiv) in MeOH was added K_2CO_3 (2.0 g, 14.7 mmol, 1.2 equiv). The mixture was stirred at room temperature for 2 h before quenched with H_2O. The mixture was transferred to a separatory funnel and extracted with EtOAc. The organic layers were combined and dried over sodium sulfate. The dried solution was filtered and concentrated under reduced pressure. The organic residue was purified by flash chromatography (PE/EA = 5/1) to give **16** (2.2 g, 12.8 mmol, 78% over two steps).

R_f = 0.40 (PE/EA = 2/1); $[\alpha]_D^{25}$ = −80.5° (c = 1.50, $CHCl_3$); **IR** (film): 3385, 2960, 2933, 2874, 1685, 1456, 1158, 1053, 713 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.89 (s, 1H), 4.94 (s, 1H), 4.79 (m, 1H), 3.39 (s, 3H), 3.22 (s, 3H), 2.61 (m, 2H), 1.48 (m, 1H), 1.33 (m, 1H), 1.17 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 147.9, 131.6, 100.0, 75.7, 54.1, 51.2, 43.0, 38.1, 20.5; **LRMS** (ESI): 195 $(M+Na)^+$; **HRMS** (DART): Calcd for $C_9H_2O_3N$: 190.1438, Found: 190.1436.

(1S, 4S)-3-(dimethoxymethyl)-4-methylcyclopent-2-en-1-yl methyl malonate (17)

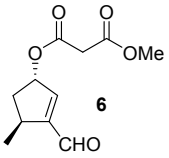


To a solution of **16** (100 mg, 0.58 mmol, 1.0 equiv) in toluene (3 mL) was added Ph_3P (228 mg, 0.87 mmol, 1.5 equiv), monomethyl malonate (103 μL, 0.87 mmol, 1.5 equiv) under argon before cooling down to −78 ℃. Then to the mixture was added slowly DEAD (137 μL, 0.87 mmol, 1.5 equiv) over 10 min and the mixture was stirred at −78 ℃ for 6 h.

Then the reaction mixture was quenched with water and was extracted with EtOAc. The solvent was evaporated under vacuum and the residue was purified by flash chromatography (PE/EA = 15/1) to give **17** in 64% yield as a yellowish oil.

$\boldsymbol{R_f}$ = 0.25 (PE/EA = 5/1); $[\alpha]_D^{25}$ = −45.8° (*c* = 1.0, $CHCl_3$); **IR** (film): 2957, 2831, 1752, 1733, 1437, 1332, 1273, 1194, 1154, 1096 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.88 (s, 1H), 5.75 (m, 1H), 4.90 (s, 1H), 3.73 (s, 3H), 3.35 (d, *J* = 8.8 Hz, 5H), 3.24 (s, 3H), 2.92 (m, 1H), 2.16 (m, 1H), 1.90 (m, 1H), 1.10 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 167.0, 166.3, 152.0, 126.7, 99.7, 80.0, 53.9, 52.4, 51.4, 41.5, 39.6, 38.0, 19.5; **LRMS** (ESI): 295 $(M+Na)^+$; **HRMS** (DART): Calcd for $C_{13}H_{24}O_6N$: 290.1598, Found: 290.1596.

(1S, 4S)-3-formyl-4-methylcyclopent-2-en-1-yl methyl malonate (6)

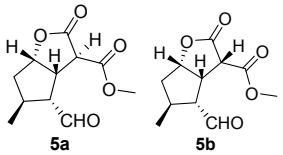


To the solution of **17** (600 mg, 2.2 mmol, 1.0 equiv) in THF (50 mL) was added HCl (1.0 M in H_2O, 4.4 mL, 4.4 mmol, 2.0 equiv) and the mixture was stirred for 2 h at room temperature before being quenched by adding saturated aq. $NaHCO_3$. The mixture was transferred to a separatory funnel and extracted with EtOAc. The combined organics were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (PE/EA = 15/1-10/1) to give **6** (472 mg, 2.1 mmol, 95%) as a yellowish oil.

$\boldsymbol{R_f}$ = 0.30 (PE/EA = 4/1); $[\alpha]_D^{25}$ = −19.1° (*c* = 1.0, $CHCl_3$); **IR** (film): 2959, 2873, 1735, 1685, 1438, 1154 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 6.70 (s, 1H), 5.96 (m, 1H), 3.75 (s, 3H), 3.39 (s, 2H), 3.19 (s, 1H), 2.21 (m, 1H), 2.07 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 189.7, 166.7, 166.1, 154.1, 145.3, 79.2, 52.6, 41.2, 39.2, 35.8, 19.6; **LRMS** (ESI): 249 $(M+Na)^+$; HRMS(DART): Calcd for $C_{11}H_{18}O_5N$: 244.1179, Found: 244.1178.

Methyl (3R, 3aS, 4R, 5S, 6aS)-4-formyl-5-methyl-2-oxohexahydro-2H-cyclopenta[b]furan-3-carboxylate (5a)

Methyl (3S, 3aS, 4R, 5S, 6aS)-4-formyl-5-methyl-2-oxohexahydro-2H-cyclopenta[b]furan-3-carboxylate (5b)



To the solution of TBAF (1.0 M in THF, 440 μL, 0.44 mmol,

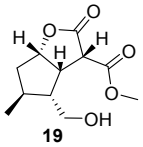
0.5 equiv) in THF (40 mL) was added dropwise the solution of compound **6** (200 mg, 0.88 mmol, 1.0 equiv) in THF (10 mL) at 0 ℃. The mixture was stirred at 0 ℃for 10 min before warming up to room temperature and then it was stirred for 5 h at this temperature. The reaction was quenched with saturated aq. NH_4Cl (5 mL) at 0 ℃ and the mixture was extracted with CH_2Cl_2. The combined organic solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (PE/EA = 4/1-2/1) to give the mixture of **5a** and **5b** in 78% yield as a yellowish oil. Minor amount of pure **5a** was obtained for analytic purpose.

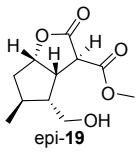
5a: R_f = 0.30 (PE/EA = 1/1); $[\alpha]_D^{25}$ = −14.6° (*c* = 1.50, $CHCl_3$); **IR** (film): 3648, 2959, 2873, 2848, 1735, 1685, 1438, 1270, 1021 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 5.11 (t, *J* = 14.0 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, J_1 = 13.2 Hz, J_2 = 7.6 Hz, 1H), 3.54 (d, *J* = 6.0 Hz, 1H), 2.63 (m, 1H), 2.37 (m, 1H), 2.27 (dd, J_1 = 14.4 Hz, J_2 = 6.4 Hz, 1H), 1.59 (m, 1H), 1.189 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 200.9, 171.3, 167.8, 83.0, 60.7, 53.4, 48.5, 43.6, 41.0, 32.9, 17.5); **LRMS** (ESI): 249 $(M+Na)^+$; **HRMS** (DART): Calcd for $C_{11}H_{17}O_5N$: 227.0914, Found: 227.0912.

5b: R_f = 0.30 (PE/EA = 1/1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 5.17 (t, *J* = 12.0 Hz , 1H), 3.80 (s, 3H), 3.73 (m, 1H), 3.35 (d, *J* = 3.2 Hz,1H), 2.90 (m, 1H), 2.66 (m, 1H), 2.17 (dd, J_1 = 14.4 Hz, J_2 = 8.0 Hz, 1H), 1.14 (m, 1H), 1.09 (d, *J* = 7.2 Hz , 3H).

Methyl (3S, 3aS, 4R, 5S, 6aS)-4-(hydroxymethyl)-5-methyl-2-oxohexahydro-2H-cyclopenta[b]furan-3-carboxylate (19)

Methyl (3R, 3aS, 4R, 5S, 6aS)-4-(hydroxymethyl)-5-methyl-2-oxohexahydro-2H-cyclopenta[b]furan-3-carboxylate (*epi*-19)





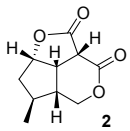
To a mixture of **5a/5b** (130 mg, 0.57 mmol, 1.0 equiv) in THF (10 mL) was added $NaBH_4$ (7 mg, 0.17 mmol, 0.3 equiv) at 0 ℃ and the mixture was stirred at 0 ℃ for 10 min before being quenched with H_2O (10 mL). The mixture was transferred to a separatory funnel and extracted with CH_2Cl_2. The organic layers were combined and dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated under reduced

pressure, the residue was purified by flash chromatography (PE/EA = 2/1) to give the mixture of **19** and *epi*-**19** (113 mg, 0.50 mmol) in 87% yield as an oil. Minor amount of pure *epi*-**19** was obtained for analytic purpose.

epi-**19**: $\boldsymbol{R_f}$ = 0.30 (PE/EA = 1/1); $[\alpha]_D^{25} = -6.7^o$ (*c* = 1.50, $CHCl_3$); **IR**(film): 3355, 2956, 2920, 2872, 1768, 1733, 1685, 1436, 1364, 1261, 1162 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.08 (t, *J* = 12.8 Hz, 1H), 3.89 (m, 1H), 3.81 (s, 3H), 3.62 (m, 1H), 3.44 (m, 1H), 2.20 (m, 1H), 1.91-1.78 (m, 3H), 1.49 (m, 1H), 1.03 (d, *J* = 5.6 Hz , 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 172.4, 169.1, 83.7, 60.9, 53.3, 50.4, 47.7, 45.6, 41.3, 32.6, 17.3; **LRMS** (ESI): 229 $(M+H)^+$; **HRMS** (DART): Calcd for $C_{11}H_{17}O_5N$: 229.1071, Found: 229.1069.

19: $\boldsymbol{R_f}$ = 0.30 (PE/EA = 1/1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.14 (m, 1H), 3.79 (m, 4H), 3.59 (m, 1H), 3.51 (d, *J* = 4 Hz, 1H), 3.19 (m, 1H), 2.38 (m, 1H), 2.04 (m, 2H), 1.85 (m, 1H), 1.50 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H).

(1S, 2aS, 2a1S, 4aS, 7aR)-1-methylhexahydro-4H-3,6-dioxacyclopenta[cd]indene-4,5(1H)-dione (2)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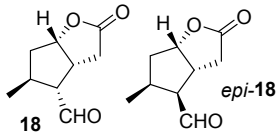
To the solution of **19**/*epi*-**19** (50 mg, 0.22 mmol) in toluene (10 mL) was added Amberlyst-15 (60 mg) and the mixture was heated to reflux for 1 h. The solution concentrated under reduced pressure and the residual was purified by flash chromatography (PE/EA=1/1) to give Cornolactone B (**2**) (37 mg, 0.19 mmol, 87%) as a colorless oil.

$\boldsymbol{R_f}$ = 0.20 (PE/EA = 1/1); $[\alpha]_D^{25} = -5.3^o$ (*c* = 1.0, MeOH); **IR**(film): 2961, 2923, 2853, 1778, 1654, 1458, 1260, 1095, 1029, 799 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.06 (t, *J* = 11.2 Hz, 1H), 4.47 (dd, J_1 = 12.4 Hz, J_2 = 5.6 Hz, 1H), 4.06 (dd, J_1 = 12.4 Hz, J_2 = 8.8 Hz, 1H), 3.79 (d, *J* = 9.6 Hz, 1H), 3.37 (dt, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 1H), 2.39 (dd, J_1 = 14.4 Hz, J_2 = 6.4 Hz,1H), 2.18-2,04 (m, 2H), 1.71 (ddd, J_1 = 14.8 Hz, J_2 = 8 Hz, J_3 = 4.8 Hz), 1.14 (d, *J* = 6.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 169.9, 164.4, 84.8, 68.5, 45.4, 42.8, 42.0, 40.9, 34.0, 19.1; **LRMS** (ESI): 219 $(M+Na)^+$; **HRMS**(DART): Calcd for $C_{10}H_{13}O_4$: 197.0808, Found: 197.0807.

(3aR, 4R, 5S, 6aS)-5-methyl-2-oxohexahydro-2H-cyclopenta[b]furan-4-carbaldehyde (18)

(3aR, 4S, 5S, 6aS)-5-methyl-2-oxohexahydro-2H-cyclopenta[b]furan-4-carbaldehyde (*epi*-18)



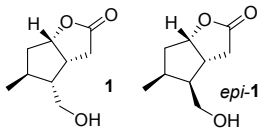
To the mixture of **5a/5b** (230 mg, 1.0 mmol, 1.0 equiv) in DMSO (15 mL) was added the solution of NaCl (290 mg, 5.0 mmol, 5.0 equiv) in H_2O (10 mL). The mixture was refluxed for 3 h before being quenched with H_2O. The mixture was diluted with EtOAc and washed with water for three times, the organic layer was dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated under reduced pressure. The residual was purified by flash chromatography (PE/EA = 3/1-1/1) to give **18** (48 mg, 2.29 mmol, 29%) and *epi*-**18** (73 mg, 0.43 mmol, 43%) as a colorless oil.

18: $\boldsymbol{R_f}$ = 0.33 (PE/EA = 2/1); $[\alpha]_D^{25}$ = +31.1° (*c* = 1.0, $CHCl_3$); **IR(**film): 3841, 2962, 2874, 1770, 1196, 655 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.82 (d, *J* = 1.2 Hz, 1H), 5.05 (t, *J* = 13.2 Hz,1H), 3.37 (m, 1H), 2.69 (dd, J_1 = 22.8 Hz, J_2 = 10.8 Hz, 1H), 2.53-2.39 (m, 3H), 2.27 (dd, J_1 = 14.4 Hz, J_2 = 6.0 Hz, 1H), 1.52 (m, 1H), 1.13 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 201.5, 176.4, 84.1, 61.3, 41.3, 39.2, 32.1, 30.5, 17.4; **LRMS** (ESI): 191 $(M+Na)^+$; **HRMS**(DART): Calcd for $C_9H_{13}O_3$: 169.0859, Found: 169.0859.

epi-**18**: $\boldsymbol{R_f}$ = 0.30 (PE/EA = 2/1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 5.05 (t, *J* = 13.2 Hz, 1H), 3.41 (m, 1H), 2.89 (dd, J_1 = 22.8 Hz, J_2 = 10.8 Hz, 1H), 2.81 (dd, *J* = 8.0 Hz, 1H), 2.71 (m, 1H), 2.30 (dd, J_1 = 22.8 Hz, J_2 = 10.8 Hz, 1H), 2.16 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 1.56 (m, 1H), 1.18 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): 202.7, 176.8, 85.0, 61.8, 39.9, 37.1, 35.2, 35.1, 15.1.

(3aR, 4R, 5S, 6aS)-4-(hydroxymethyl)-5-methylhexahydro-2H-cyclopenta-[b]furan-2-one (1)

(3aR, 4S, 5S, 6aS)-4-(hydroxymethyl)-5-methylhexahydro-2H-cyclopenta-[b]furan-2-one (*epi*-1)



To a solution of **18** (64 mg, 0.38 mmol, 1.0 equiv) in THF (10 mL) was added $NaBH_4$ (14 mg, 0.38 mmol, 1.0 equiv) at 0 ℃. The mixture was stirred at 0 ℃ for 10 min before being quenched with water. The mixture was transferred to a separatory funnel and

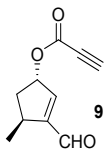
extracted with EtOAc. The organic layers were combined and dried over anhydrous sodium sulfate. The dried solution was filtered and concentrated under reduced pressure. The residual was purified by flash chromatography (PE/EA = 1/1-1/2) to give Cornolactone A (**1**) (57 mg, 0.34 mmol, 89%) as a colorless oil.

By employing the same procedure, e*pi*-**18** was converted to *epi*-**1** in 83% yield as a colorless oil.

1: R_f = 0.33 (PE/EA = 1/1); $[\alpha]_D^{25}$ = +14.7° (*c* = 1.0, CH_2Cl_2); **IR** (film): 3420, 2957, 1755, 1363, 1195, 1019, 657 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.99 (t, *J* = 6.0 Hz, 1H), 3.86 (dd, J_1 = 10.4 Hz, J_2 = 3.6 Hz, 1H), 3.59 (dd, J_1 = 10.8, J_2 = 8.8 Hz, 1H), 3.17-3.09 (m, 1H), 2.66-2.62 (m, 2H), 2.20 (dd, J_1 = 14.0 Hz, J_2 = 5.0 Hz, 1H), 1.85-1.75 (m, 2H), 1.47-1.40 (m, 1H), 1.02 (d, *J* = 5.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 178.2, 84.6, 61.4, 50.8, 41.8, 40.3, 32.9, 29.6, 17.6; **LRMS** (ESI): 193 $(M+Na)^+$, 171 $(M+H)^+$; **HRMS** (DART): Calcd for $C_9H_{15}O_3$: 171.1016, Found: 171.1015.

epi-**1**: R_f = 0.33 (PE/EA = 1/1); $[\alpha]_D^{25}$ = -17.7° (*c* = 0.6, $CHCl_3$); **IR**(film): 3536, 2925, 1758, 1233, 1075, 1019, 975.759 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.02 (td, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 3.80-3.73 (m, 1H), 3.53 (t, *J* = 16.0 Hz, 1H), 2.89-2.86 (m, 1H), 2.45-2.34 (m, 2H), 2.10-2.04 (m, 1H), 1.96-1.90 (m, 1H), 1.81-1.73 (m, 1H), 0.98 (d, *J* = 8.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 177.7, 85.7, 62.4, 51.8, 41.0, 40.5, 35.8, 33.5, 14.6; **LRMS** (ESI): 193 $(M+Na)^+$, 171 $(M+H)^+$; **HRMS** (DART): Calcd for $C_9H_{15}O_3$: 171.1016, Found: 171.1015.

(1S, 4S)-3-formyl-4-methylcyclopent-2-en-1-yl propiolate (9)

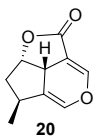


To the solution of **16** (400 mg, 2.3 mmol, 1.0 equiv) in THF (25 mL) was added Ph_3P (914 mg, 3.5 mmol, 1.5 equiv), propiolic acid (215 μL, 3.5 mmol, 1.5 equiv) under argon before cooling down to −78 ℃. Then to the mixture above was added slowly DEAD (551 μL, 3.5 mmol, 1.5 equiv) and the mixture was stirred at −78 ℃ before being quenched with saturated aq. $NaHCO_3$. The mixture was transferred to a separatory funnel and extracted with EtOAc. The organic layers were combined and dried over sodium sulfate and concentrated under reduced pressure.

The residue obtained was taken up in THF and was added a solution of aq. HCl (1.0 M, 3.5 mL, 3.5 mmol, 1.5 equiv). The mixture was stirred for 3 h at room temperature before being quenched with saturated aq. $NaHCO_3$. The mixture was extracted with EtOAc and the combined organic solutions were dried over anhydrous Na_2SO_4. The dried solution was filtered and concentrated under reduced pressure. The residual was purified by flash chromatography (PE/EA = 15/1) to give **9** (344 mg, 1.9 mmol, 84% over two steps) as a clear yellowish oil.

***R**f* = 0.40 (PE/EA = 5/1); $[\alpha]_D^{25} = -108.0^{o}$ (*c* = 0.75, $CHCl_3$); **IR** (film): 3257, 2965, 2115, 1715, 1686, 1230, 1162, 943, 756 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 6.70 (t, *J* = 4 Hz, 1H), 5.99-5.95 (m, 1H), 3.27-3.18 (m, 1H), 2.92 (s, 1H), 2.31-2.24(m, 1H), 2.11-2.05 (m, 1H), 1.17 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 189.6, 154.5, 152.2, 144.4, 80.1, 75.3, 74.3, 39.2, 35.9, 19.5; **LRMS** (ESI): 177$(M-H)^+$.

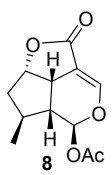
(1S, 2aS, 2a^{1}S)-1-methyl-1,2,2a,2a^1-tetrahydro-4H-3,6-dioxacyclopenta-[cd]-inden-4-one (20)


20

The solution of **9** (50 mg, 0.28 mmol) in chlorobenzene (14 mL) was refluxed for 8 h before concentrated under reduced pressure. The residual was purified by flash chromatography (PE/EA = 15/1) to give recovered **9** (15 mg) and pure **20** (29 mg, 0.16 mmol) in 58% yield (83% brsm) as a white foamy.

***R**f* = 0.33 (PE/EA = 5/1); $[\alpha]_D^{25} = -42.9^{o}$ (*c* = 0.75, $CHCl_3$); **IR** (film): 3469, 2980, 2873, 1740, 1677, 1618, 1346, 1131, 1010, 769 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 5.29 (q, *J* = 7.6 Hz, 1H), 3.42 (m, 1H), 3.07 (m, 1H), 2.29 (dd, J_1 = 13.6 Hz, J_2 = 7.2 Hz, 1H), 1.60 (m, 1H), 1.14 (d, *J* = 8.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 168.7, 151.1, 136.8, 123.6, 106.5, 80.7, 76.6, 41.8, 38.0, 37.6, 19.5; **LRMS** (ESI): 179 $(M+H)^+$, 201 $(M+Na)^+$; **HRMS** (DART): Calcd for $C_{10}H_{11}O_3$: 179.0703, Found: 179.0702.

(1S, 2aS, 2a1S, 7S, 7aR)-1-methyl-4-oxo-1,2,2a,2a1,7,7a-hexahydro-4H-3,6-dioxacyclopenta[cd]inden-7-yl acetate (8)

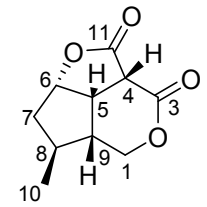

8

To the solution of compound **20** (50 mg, 0.28 mmol, 1.0 equiv) in dry toluene (10 mL) was added CH_3COOH (320 μL, 5.62 mmol, 20 equiv),

CBr_4 (740 mg, 2.24 mmol, 8.0 equiv) and PPTS (280 mg, 1.12 mmol, 4.0 equiv) at room temperature. The mixture was refluxed for 5 h before being concentrated under reduced pressure to give the crude product which was purified by flash chromatography (PE/EA = 5/1) to give **8** (39 mg, 0.17 mmol, 62%) as a yellowish oil.

***R**_f* = 0.50 (PE/EA = 2/1); $[\alpha]_D^{25} = -34.6^o$ (*c* = 1.0, $CHCl_3$); **IR** (film) : 3481, 2924, 2852, 1755, 1660, 1609, 1449, 1366, 1216, 1170, 754, 739 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 2.4 Hz, 1H), 6.35 (s, 1H), 5.07 (t, *J* = 7.6 Hz,1H), 3.43 (m, 1H), 2.16 (m, 1H), 2.13 (s, 3H), 1.99 (m, 2H), 1.68 (m, 1H), 1.07 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 170.1, 169.1, 148.2, 103.5, 88.8, 81.0, 45.0, 42.0, 38.1, 31.7, 20.9, 17.6; **LRMS** (ESI): 239 $(M+H)^+$, 261 $(M+Na)^+$; **HRMS** (DART): Calcd for $C_{12}H_{15}O_5$: 239.0914, Found: 239.0913.

Comparison of the literature data with this work



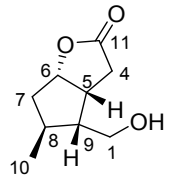
Cornolactone B (**2**)

$[\alpha]_D^{25} = -5.30^o$ (c = 1.0, MeOH)

lit.[1] $[\alpha]_D^{18} = -7.5^o$ (c = 0.02, MeOH)

Position	**lit.**[1]		**this work**	
	^{13}C	**^{1}H**	**^{13}C**	**^{1}H**
1	68.8	4.47 (dd, J = 12.2, 4.8 Hz, 1H) 4.05 (dd, J = 12.2, 8.0 Hz, 1H)	68.5	4.47 (dd, J = 12.4, 5.6 Hz, 1H) 4.06 (dd, J =12.4, 8.8 Hz, 1H)
3	164.7		164.4	
4	45.7	3.8 (d, J = 9.6 Hz, 1H)	45.4	3.79 (d, J = 9.6 Hz, 1H)
5	42.3	3.35 (dt, J = 9.5, 6.4 Hz, 1H)	42.0	3.37 (dt, J =12.0, 8.0 Hz, 1H)
6	85.1	5.04 (t, J = 5.5 Hz, 1H)	84.8	5.06 (t, J =11.2 Hz, 1H)
7	41.2	2.36 (dd, J = 14.8, 6.8 Hz, 1H) 1.68 (ddd, J = 14.8, 9.4, 5.6 Hz, 1H)	40.9	2.39 (dd, J =14.4, 9.6 Hz, 1H) 1.71 (ddd, J =14.8, 8.0, 4.8 Hz, 1H)
8	34.2	2.04 (m, 1H)	34.0	2.18-2.04 (m, 2H)
9	43.1	2.10 (m, 1H)	42.8	
10	19.4	1.12 (d, J = 6.7 Hz, 3H)	19.1	1.14 (d, J = 6.4 Hz, 3H)
11	170.2		169.9	

[1] He,Y.Q.; Peng,J.N.; Hamann, M.T.; West, L.M. *J. Nat. Prod.* **2014**, *77*, 2138−2143.



Cornolactone A (**1**)

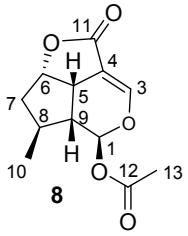
$[\alpha]_D^{25}$ = +4.6° (*c* = 1.0°, CH_3OH); $[\alpha]_D^{25}$ = +14.7° (*c* = 1.0, CH_2Cl_2)

lit.[1] $[\alpha]_D^{18}$ = +3.3° (*c* = 0.2, CH_3OH); lit.[2] $[\alpha]_D^{25}$ = +14.73° (*c* = 0.9°, CH_2Cl_2)

Position	**lit.**[1]		**lit.**[2]		**this work**	
	^{13}C	**^{1}H**	**^{13}C**	**^{1}H**	**^{13}C**	**^{1}H**
1	61.4	3.87 (dd, *J* = 11.0, 4.0 Hz, 1H) 3.58 (dd, *J* = 11.0, 9.0 Hz, 1H)	60.8	3.88 (dd, *J* = 4, 10.6 Hz, 1H) 3.62 (dd, *J* = 8.8, 10.6 Hz, 1H)	61.6	3.86 (dd, *J* = 10.4, 3.6 Hz, 1H) 3.59 (dd, *J* = 10.8, 8.8 Hz, 1H)
4	29.7	2.66 (dd, *J* = 18.8, 4.7 Hz, 1H) 2.59 (dd, *J* = 18.8, 9.8 Hz, 1H)	29.5	2.64-2.69 (m, 1H)	29.6	2.66-2.62 (m, 1H)
5	40.2	3.14 (m, 1H)	40.0	3.10-3.22 (m, 1H)	40.3	3.17-3.09 (m, 1H)
6	84.9	5.00 (t, *J* = 6.0 Hz, 1H)	84.9	5.02 (t, *J* = 6 Hz, 1H)	84.6	4.99 (t, *J* = 6.0 Hz, 1H)
7	41.9	2.20 (dd, *J* = 14.0, 5.0 Hz, 1H) 1.44 (ddd, *J* = 14.0, 11.8, 5.5 Hz, 1H)	41.4	2.23 (dd, *J* = 5, 14 Hz, 1H) 1.40-1.52, ddd, *J* = 5.5, 11.9,17.4 Hz, 1H)	41.9	2.20 (dd, *J* = 14.0, 5.0 Hz, 1H) 1.47-1.40 (m, 1H)
8	32.8	1.82 (m, 1H)	32.5	1.90-1.72 (m, 1H)	32.9	1.85-1.75 (m, 1H)
9	50.6	1.79 (m, 1H)	50.4	1.90-1.72 (m, 1H)	50.8	1.85-1.75 (m, 1H)
10	17.6	1.02 (d, *J* = 5.6 Hz, 3H)	17.3	1.05 (d, *J* = 6.5 Hz, 3H)	17.6	1.02 (d, *J* = 5.6 Hz, 3H)
11	178.3		178.5		177.8	

[1] He, Y. Q.; Peng, J. N.; Hamann, M. T.; West, L. M. *J. Nat. Prod*. **2014**, *77*, 2138−2143.

[2] Piccinini, P.; Vidari, G.; Zononi, G. *J. Am. Chem. Soc*. **2004**, *126*, 5088−5089.



8

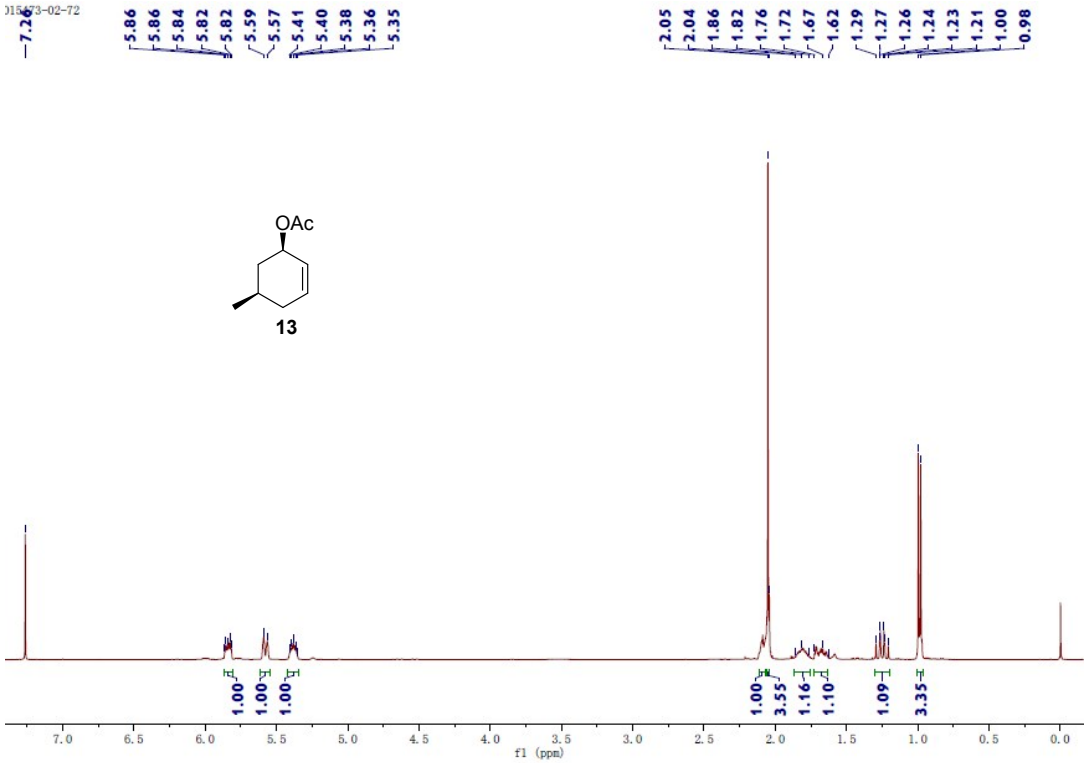
$[\alpha]_D^{25} = -34.64^o$ (c = 1.0, $CHCl_3$)

lit.[4] $[\alpha]_D^{25} = -229.2^o$ (c = 1.0, $CHCl_3$)

Position	**lit.**[4]		**this work**	
	^{13}C	**^{1}H**	**^{13}C**	**^{1}H**
1	88.8	6.35 (s, 1H)	88.8	6.35 (s, 1H)
3	103.6	7.31 (d, J = 2.7 Hz, 1H)	103.5	7.31 (d, J = 2.4 Hz, 1H)
4	148.3		148.3	
5	42.0	3.42 (m, 1H)	42.0	3.43 (m, 1H)
6	81.1	5.06 (t, J = 4.6 Hz, 1H)	81.0	5.07 (t, J = 8.0 Hz, 1H)
7	31.8	1.98 (m, 1H) 1.24 (m, 1H)	31.7	1.99 (m, 2H)
8	20.9	1.66 (m, 1H)	20.9	1.68 (m, 1H)
9	38.1	2.20-2.10 (m, 1H)	38.1	2.16 (m, 1H)
10	17.6	1.07 (d, J = 6.3 Hz, 3H)	17.6	1.07 (d, J = 6.0 Hz, 3H)
11	170.1		170.1	
12	169.2		169.1	
13	45.0	2.20-2.10 (m, 3H)	45.0	2.13 (s, 3H)

[4] Mangion, I. K.; MacMillan, D. W. C. *J. Am. Chem. Soc*. **2005**, *127,* 3696.

NMR Spectra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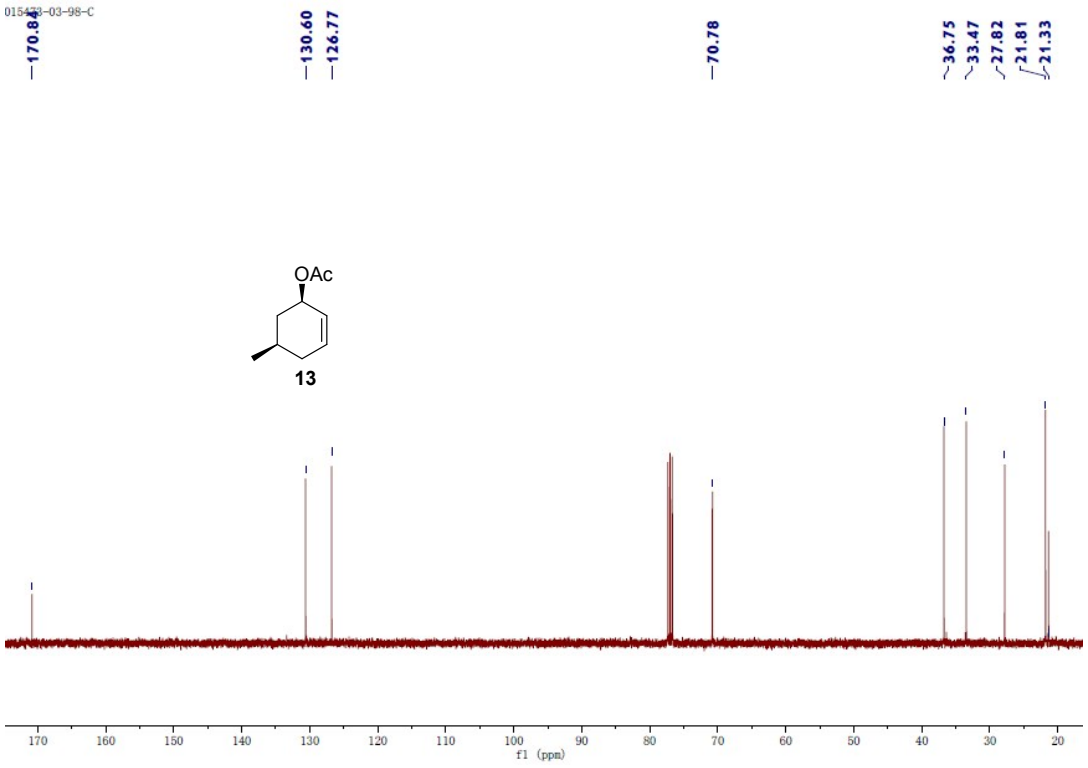
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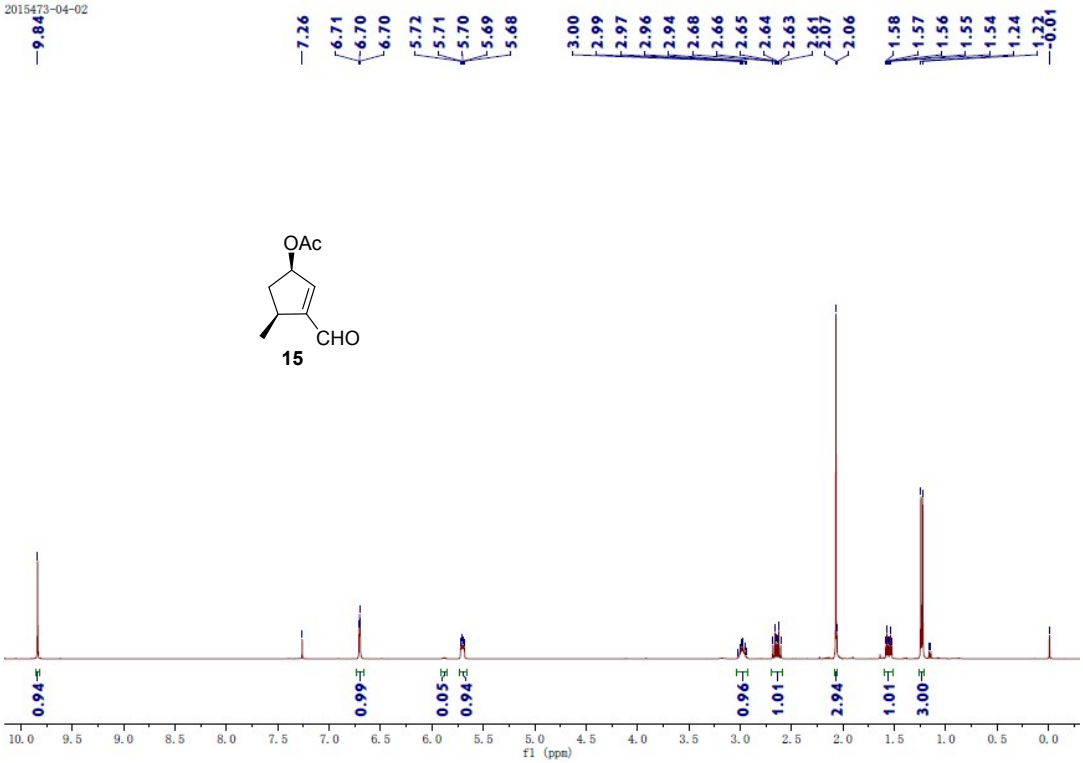
2015473-04-02
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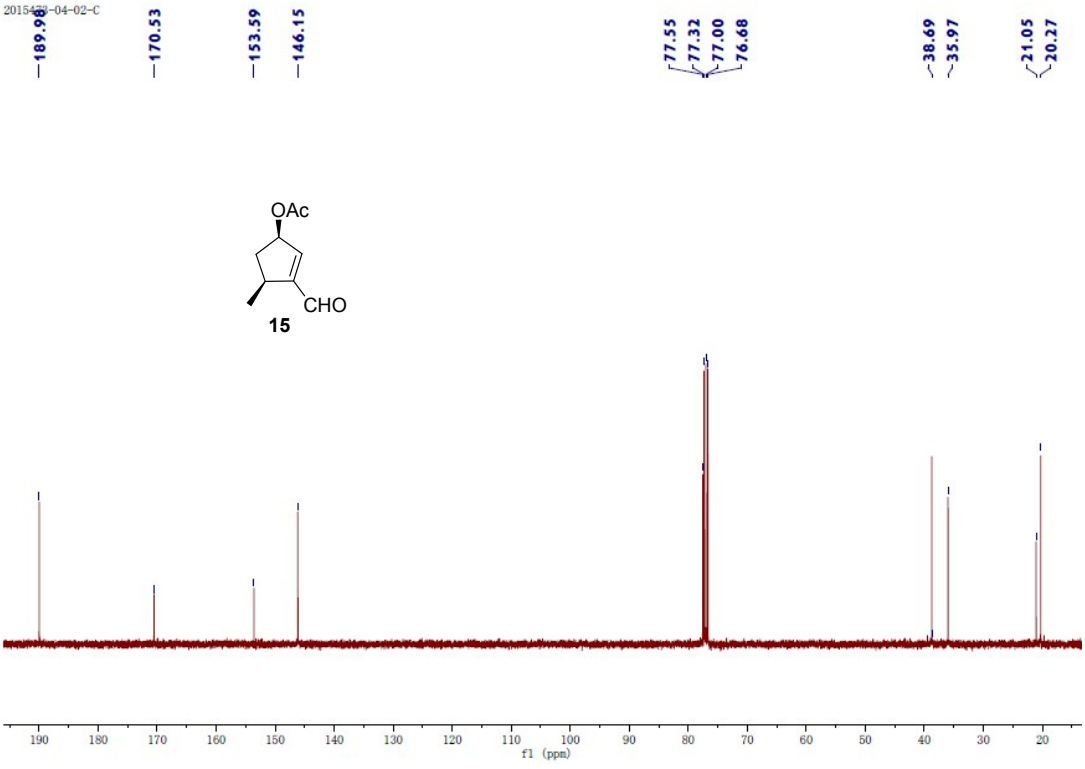
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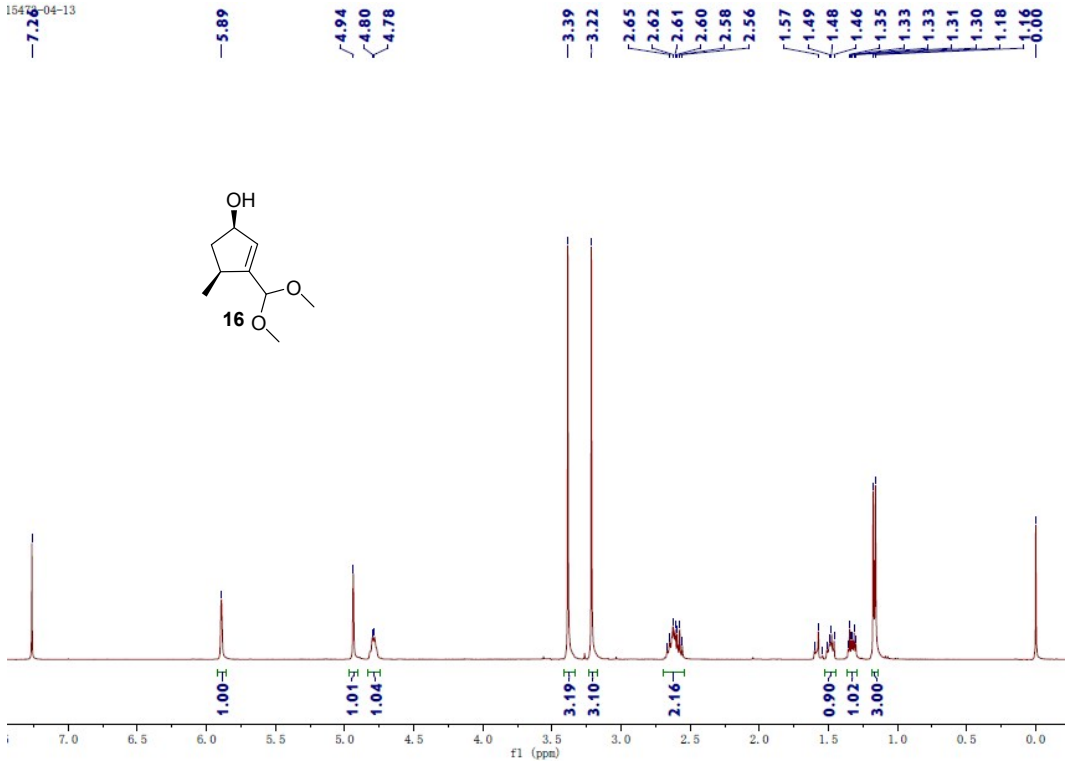
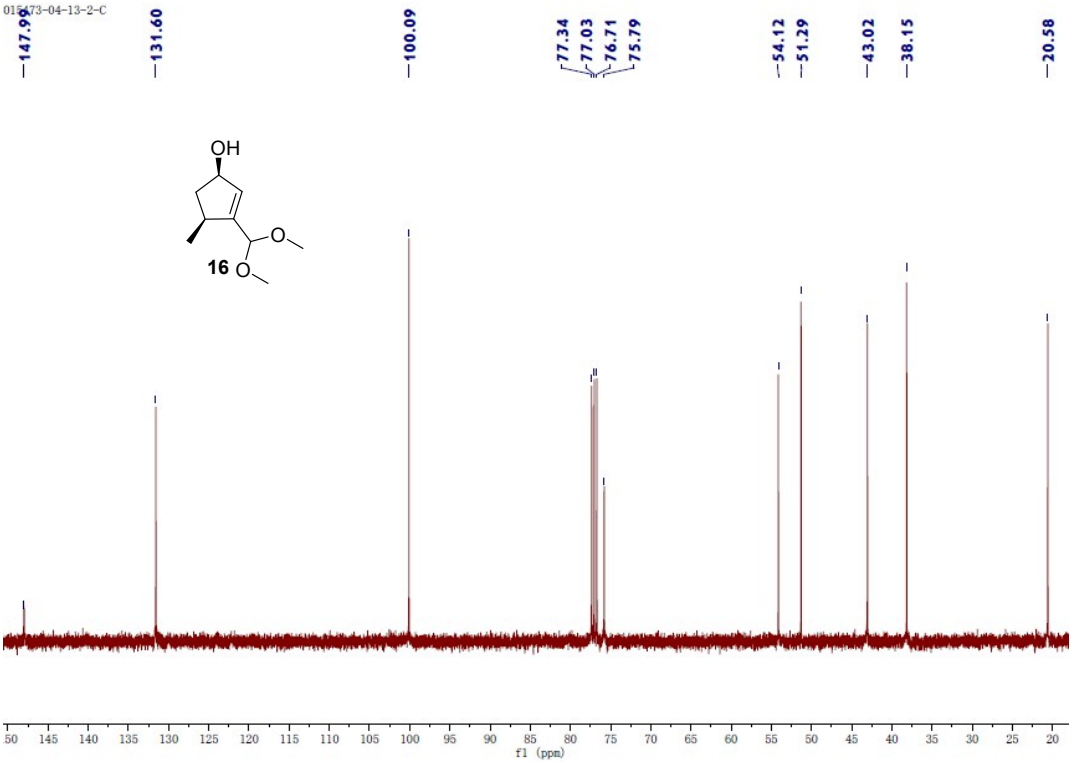
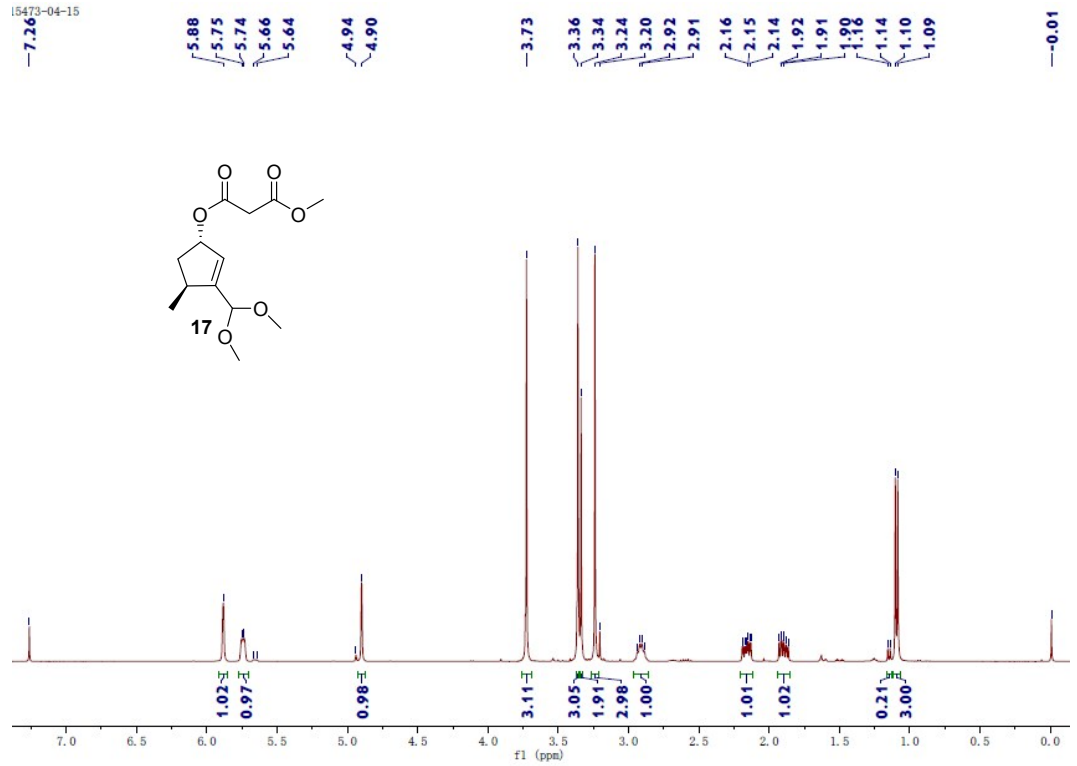
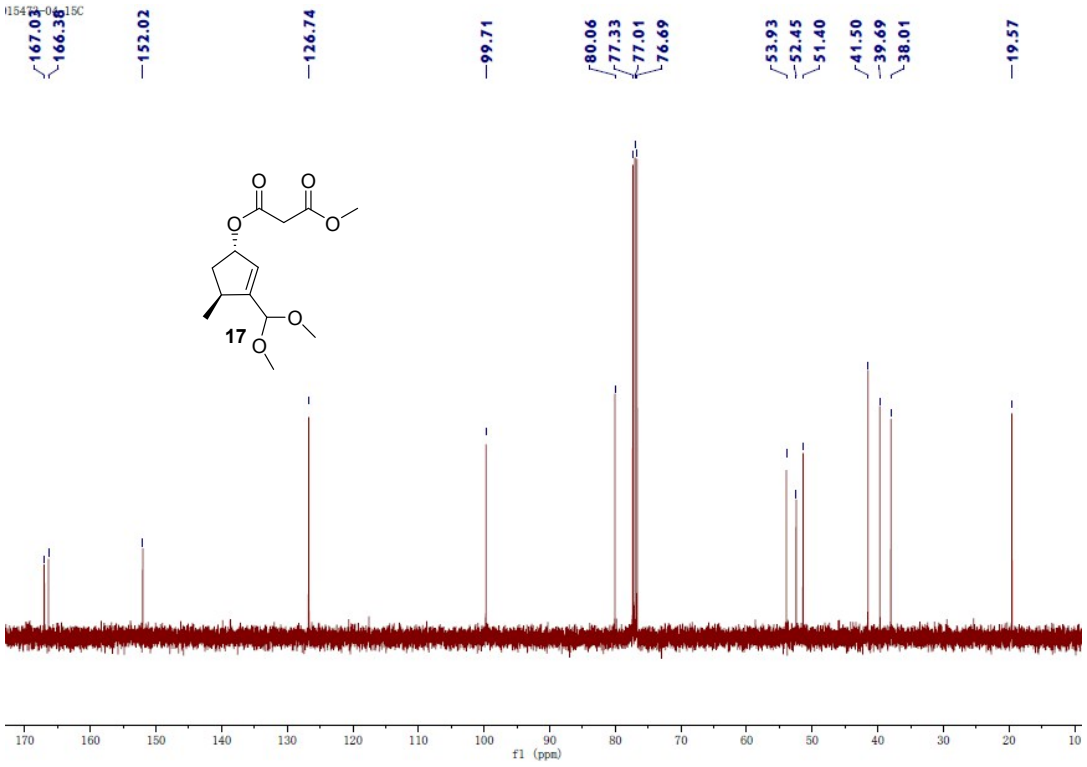
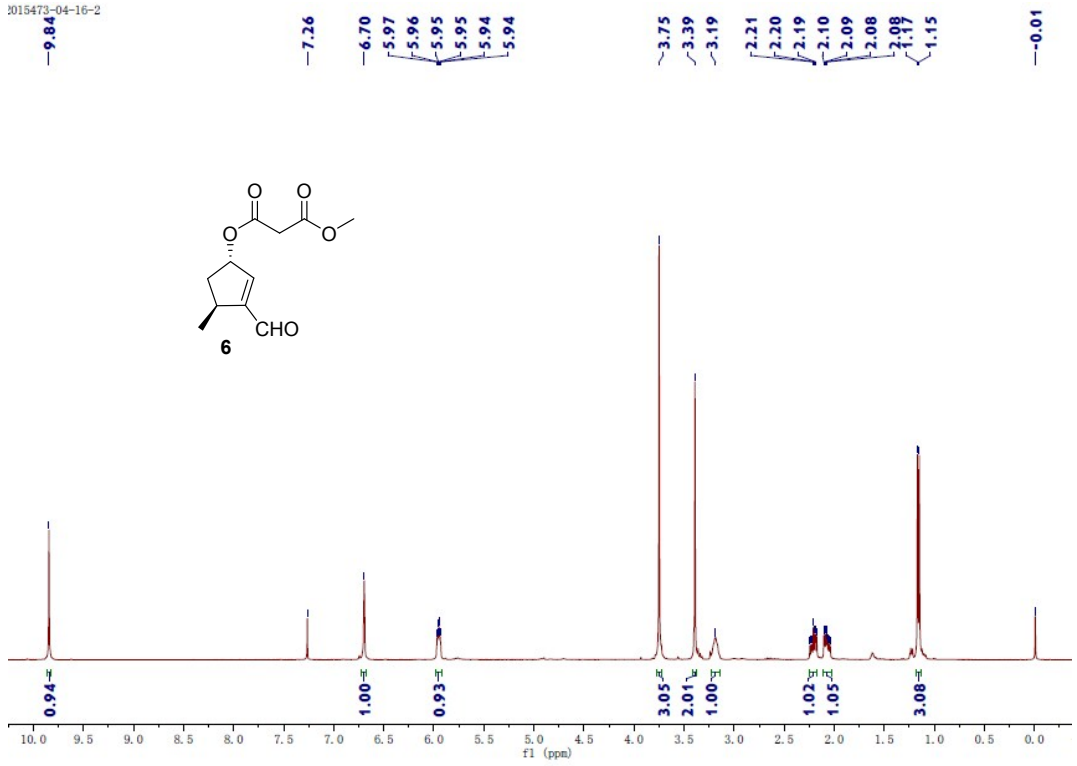
15
f1 (ppm)

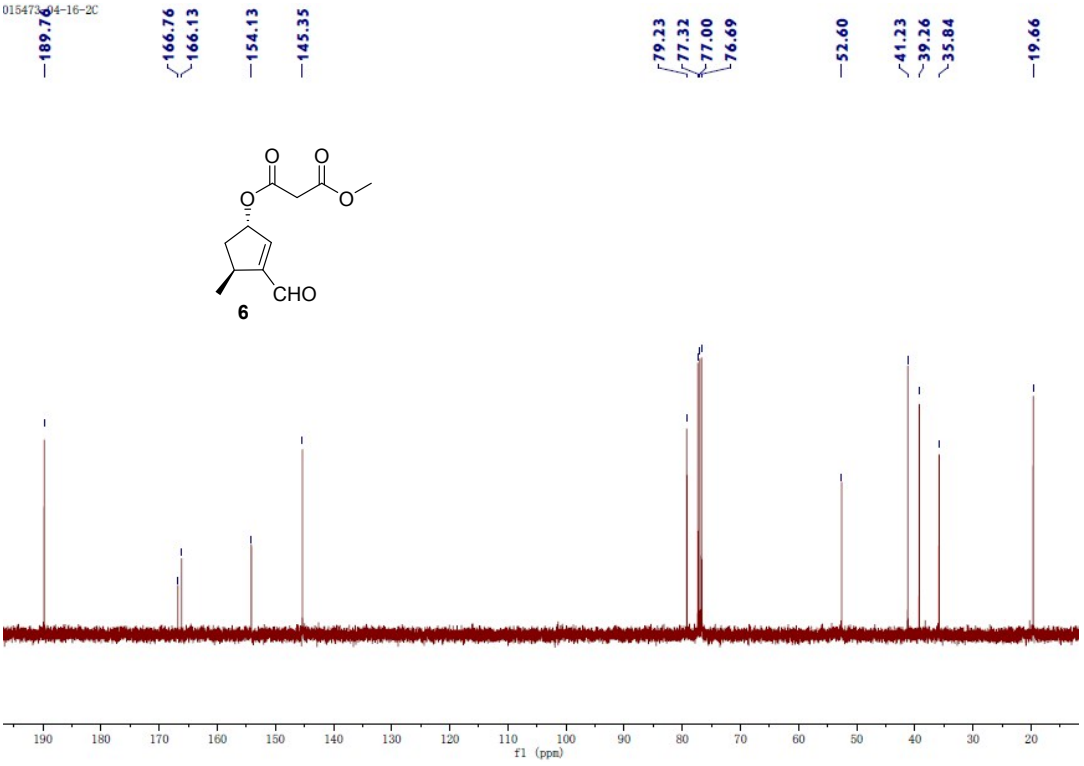

15473-04-13
7.26
5.89
4.94
4.80
4.78
3.39
3.22
2.65
2.62
2.61
2.60
2.58
2.56
1.57
1.49
1.48
1.46
1.35
1.33
1.33
1.31
1.30
1.18
1.16
0.00
OH
O
O
16
1.00
1.01
1.04
3.19
3.10
2.16
0.90
1.02
3.00
f1 (ppm)


015473-04-13-2-C
147.99
131.60
100.09
77.34
77.03
76.71
75.79
54.12
51.29
43.02
38.15
20.58
OH
O
O
16
f1 (ppm)

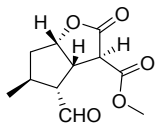

15473-04-15
7.26
5.88
5.75
5.74
5.66
5.64
4.94
4.90
3.73
3.36
3.34
3.24
3.20
2.92
2.91
2.16
2.15
2.14
1.92
1.91
1.90
1.18
1.14
1.10
1.09
0.01
17
1.02
0.97
0.98
3.11
3.05
1.91
2.98
1.00
1.01
1.02
0.21
3.00
f1 (ppm)


167.03
166.38
152.02
126.74
99.71
80.06
77.33
77.01
76.69
53.93
52.45
51.40
41.50
39.69
38.01
19.57
17
f1 (ppm)

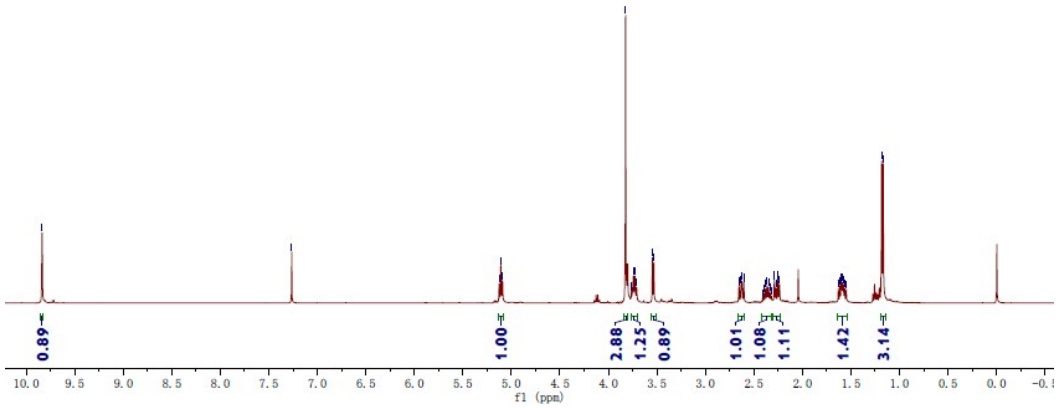

2015473-04-16-2
9.84
7.26
6.70
5.97
5.96
5.95
5.95
5.94
5.94
3.75
3.39
3.19
2.21
2.20
2.19
2.10
2.09
2.08
2.08
1.17
1.15
0.01
O
O
O
O
CHO
6
0.94
1.00
0.93
3.05
2.01
1.00
1.02
1.05
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


015473-04-16-2C
189.76
166.76
166.13
154.13
145.35
79.23
77.32
77.00
76.69
52.60
41.23
39.26
35.84
19.66
O
O
O
O
CHO
6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

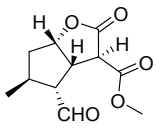

9.80
7.26
5.13
5.11
5.09
3.82
3.74
3.73
3.71
3.55
3.53
2.62
2.60
2.29
1.61
1.60
1.59
1.58
1.58
1.56
1.55
1.18
1.17


H
O
O
H
H
O
O
CHO

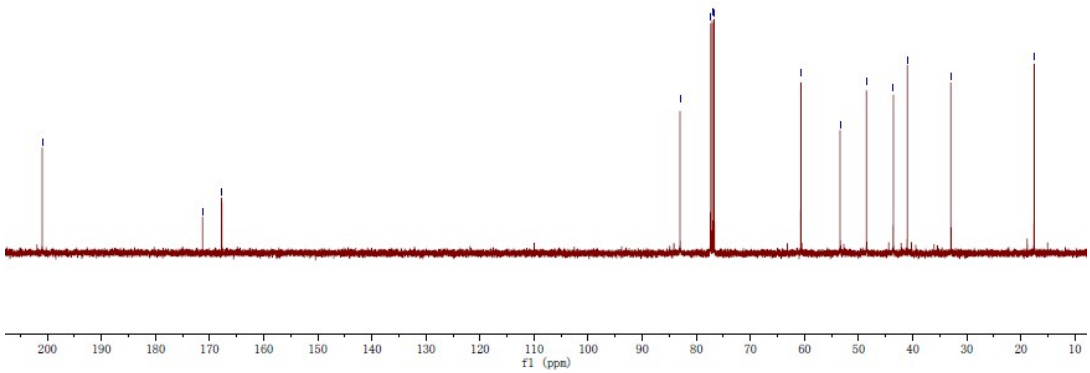
5a

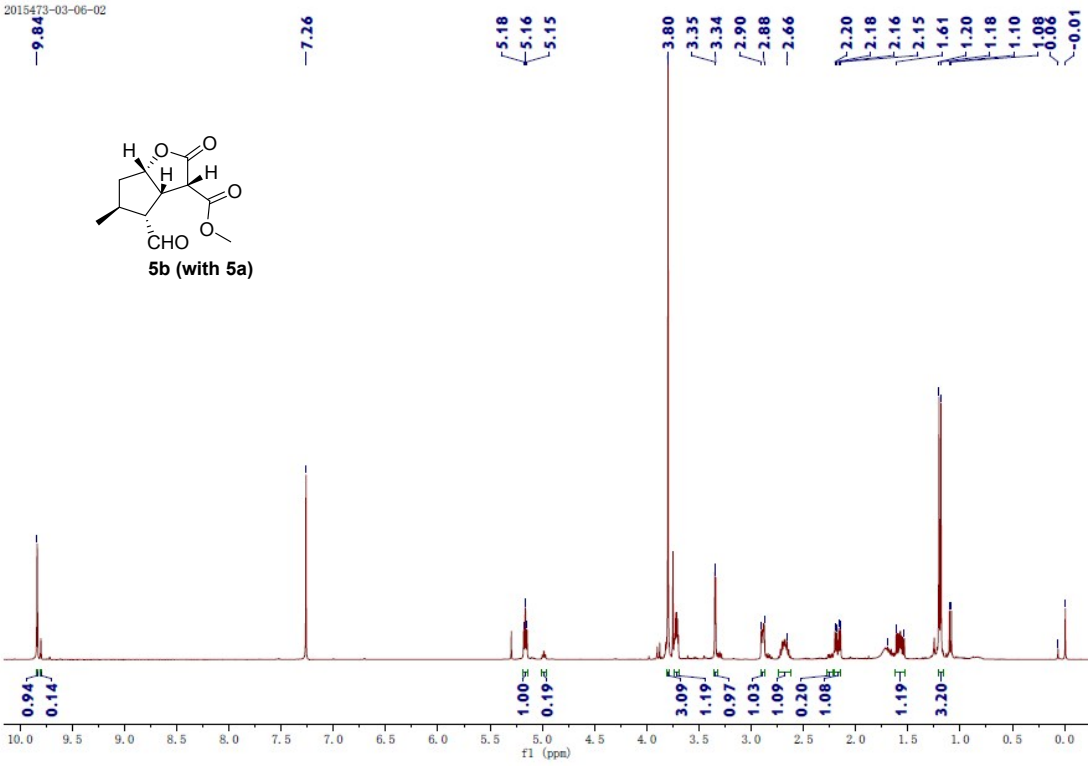

0.89
1.00
2.88
1.25
0.89
1.01
1.08
1.11
1.42
3.14
f1 (ppm)


200.81
171.29
167.76
83.02
77.35
77.03
76.71
60.67
53.43
48.54
43.58
40.99
32.93
17.54

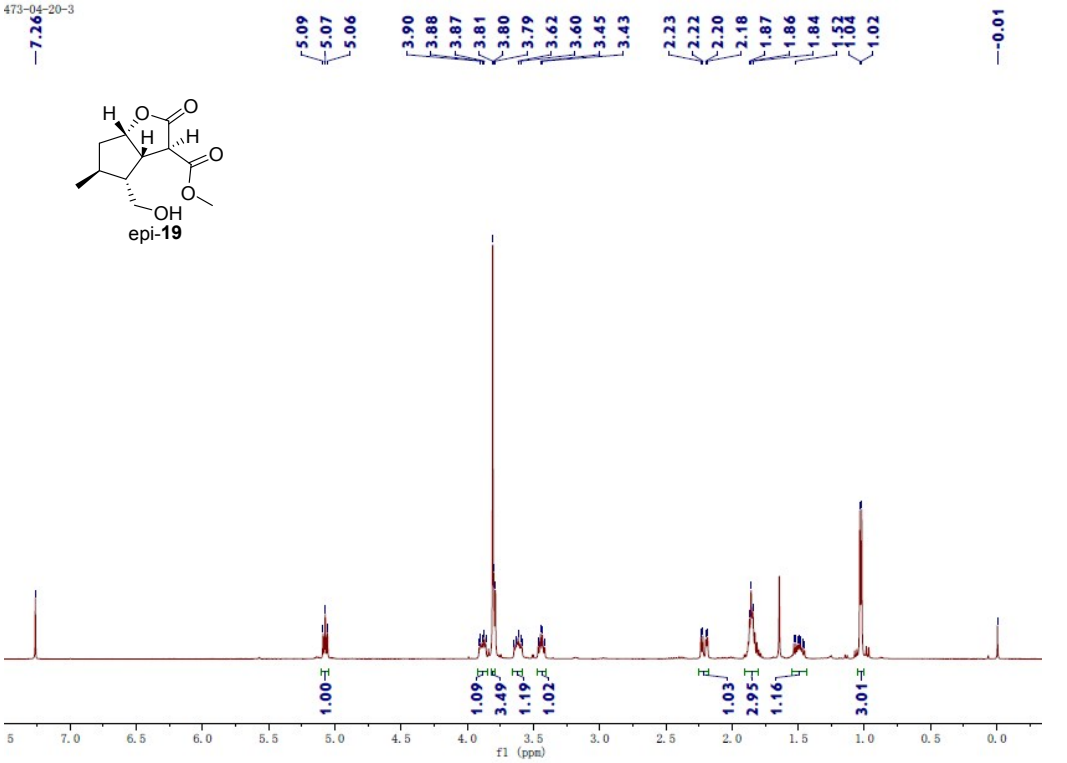

H
O
O
H
H
O
O
CHO

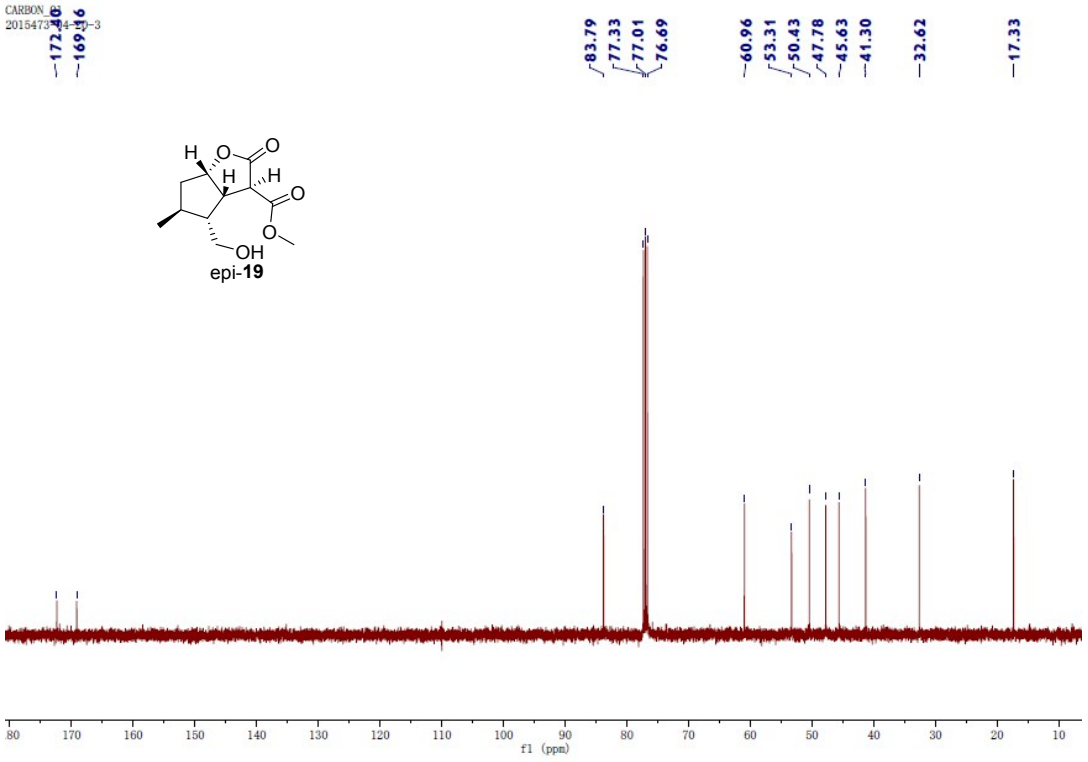
5a

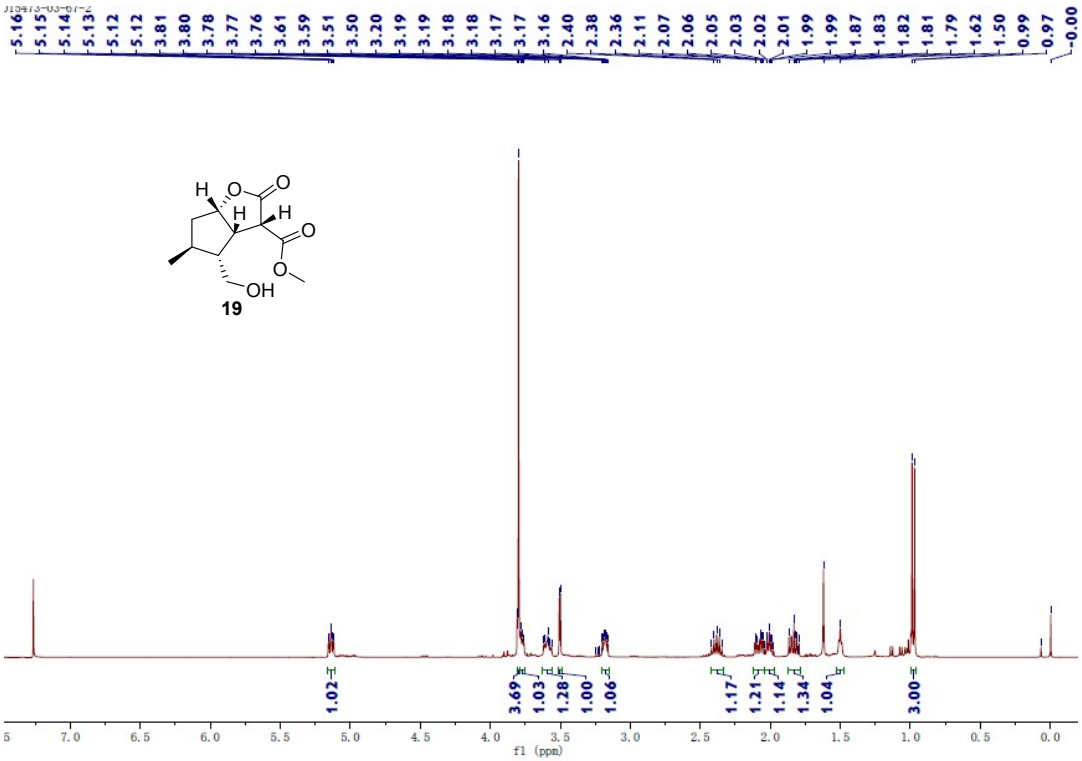

f1 (ppm)

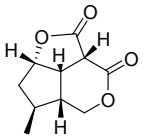

2015473-03-06-02
9.84
7.26
5.18
5.16
5.15
3.80
3.35
3.34
2.90
2.88
2.66
2.20
2.18
2.16
2.15
1.61
1.20
1.18
1.10
1.08
0.08
-0.01
H
O
O
H
H
O
O
CHO
0.94
0.14
1.00
0.19
3.09
1.19
0.97
1.03
1.09
0.20
1.08
1.19
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5b (with 5a)

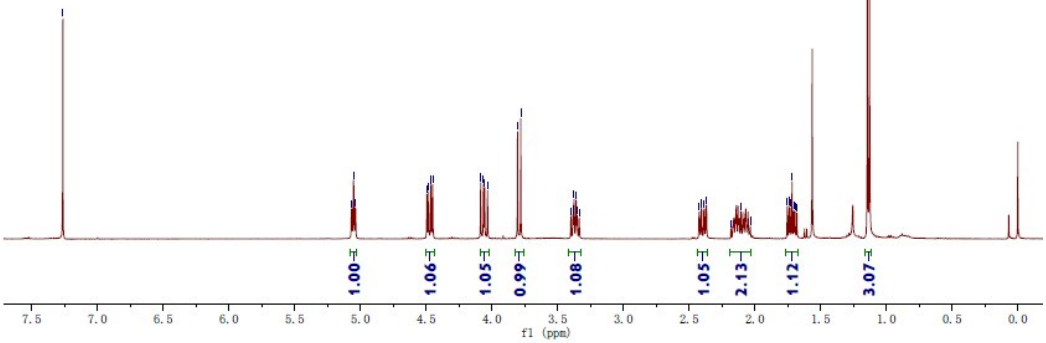

473-04-20-3
7.26
5.09
5.07
5.06
3.90
3.88
3.87
3.81
3.80
3.79
3.62
3.60
3.45
3.43
2.23
2.22
2.20
2.18
1.87
1.86
1.84
1.52
1.04
1.02
0.01
H
O
O
H
H
O
O
OH
epi-19
1.00
1.09
3.49
1.19
1.02
1.03
2.95
1.16
3.01
f1 (ppm)

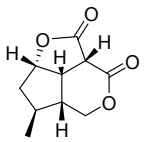

CARBON
172.46
169.16
83.79
77.33
77.01
76.69
60.96
53.31
50.43
47.78
45.63
41.30
32.62
17.33
H
O
O
H
H
O
O
OH
epi-19
f1 (ppm)


5.16 5.15 5.14 5.13 5.12 5.12 3.81 3.80 3.78 3.77 3.76 3.61 3.59 3.51 3.50 3.20 3.19 3.19 3.18 3.18 3.17 3.17 3.16 2.40 2.38 2.36 2.11 2.07 2.06 2.05 2.03 2.02 2.01 1.99 1.99 1.87 1.83 1.82 1.81 1.79 1.62 1.50 0.99 0.97 0.00
H
O
O
H
H
O
O
OH
19
1.02
3.69
1.03
1.28
1.00
1.06
1.17
1.21
1.14
1.34
1.04
3.00
f1 (ppm)

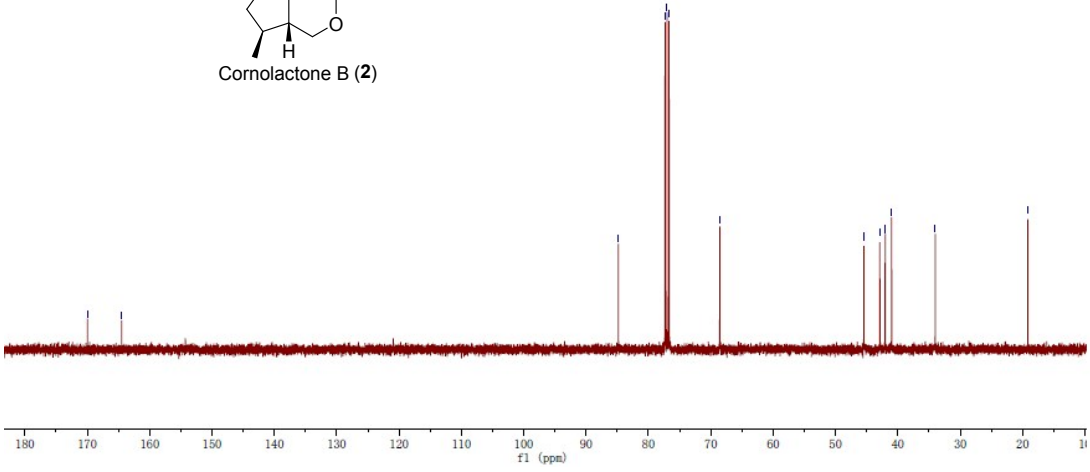


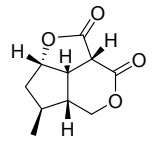
Cornolactone B (**2**)



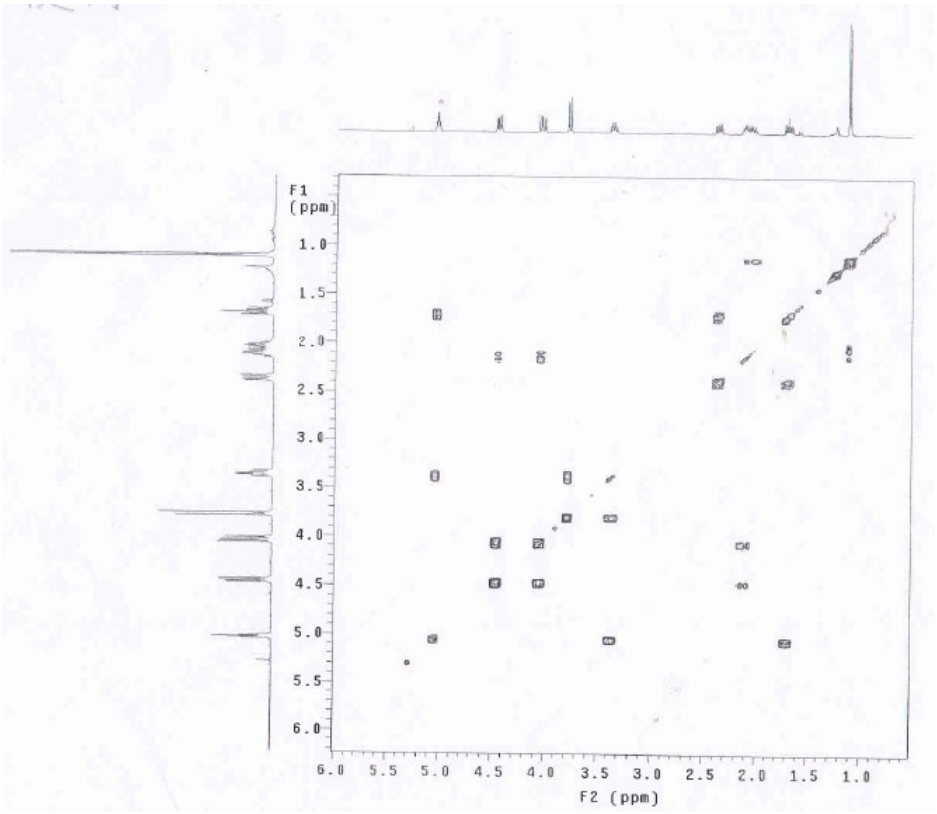


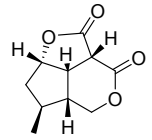
Cornolactone B (**2**)



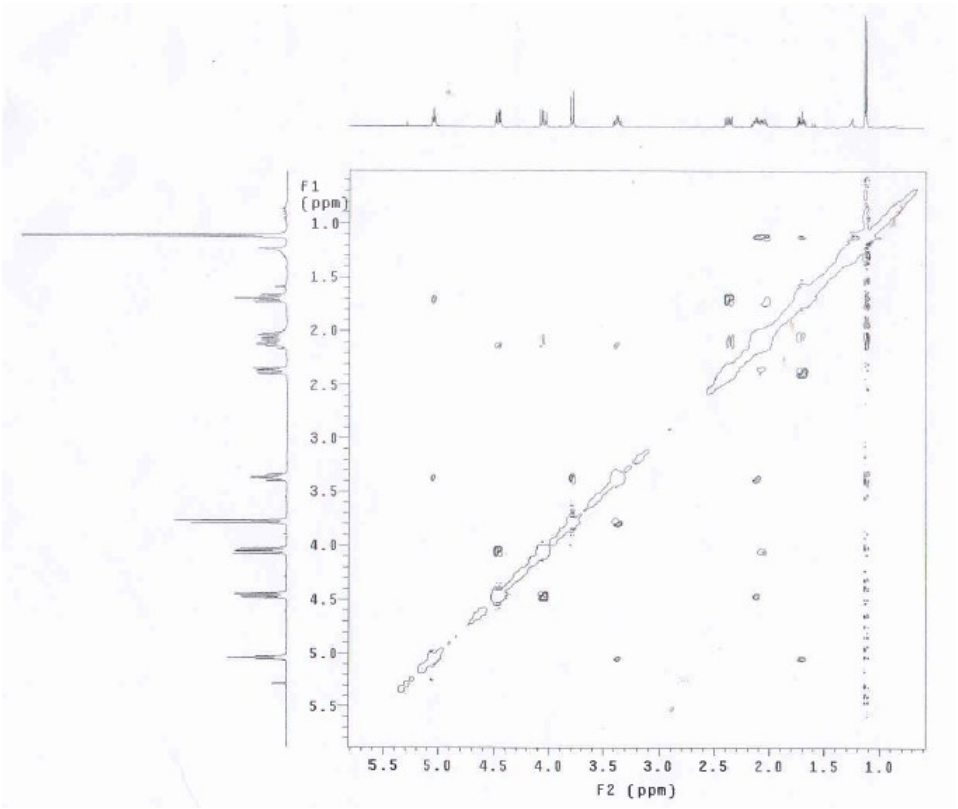


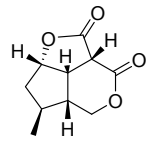
Cornolactone B (**2**)
(COSY)



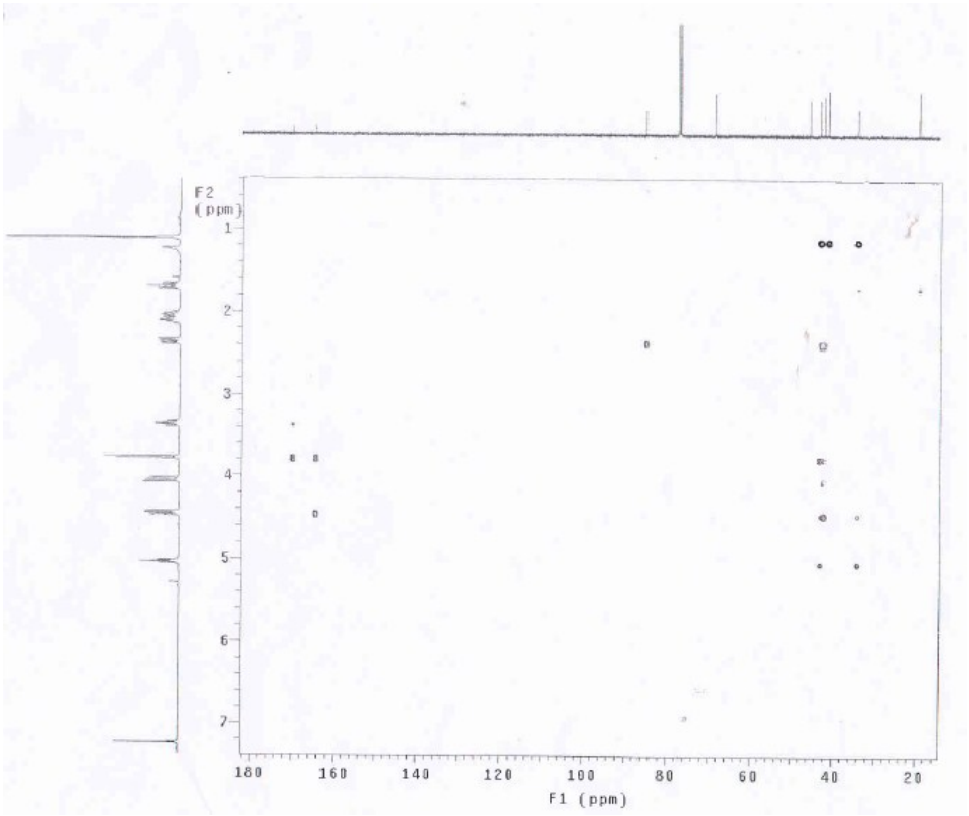


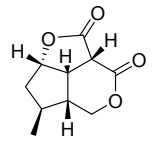
Cornolactone B (**2**)
(NOESY)



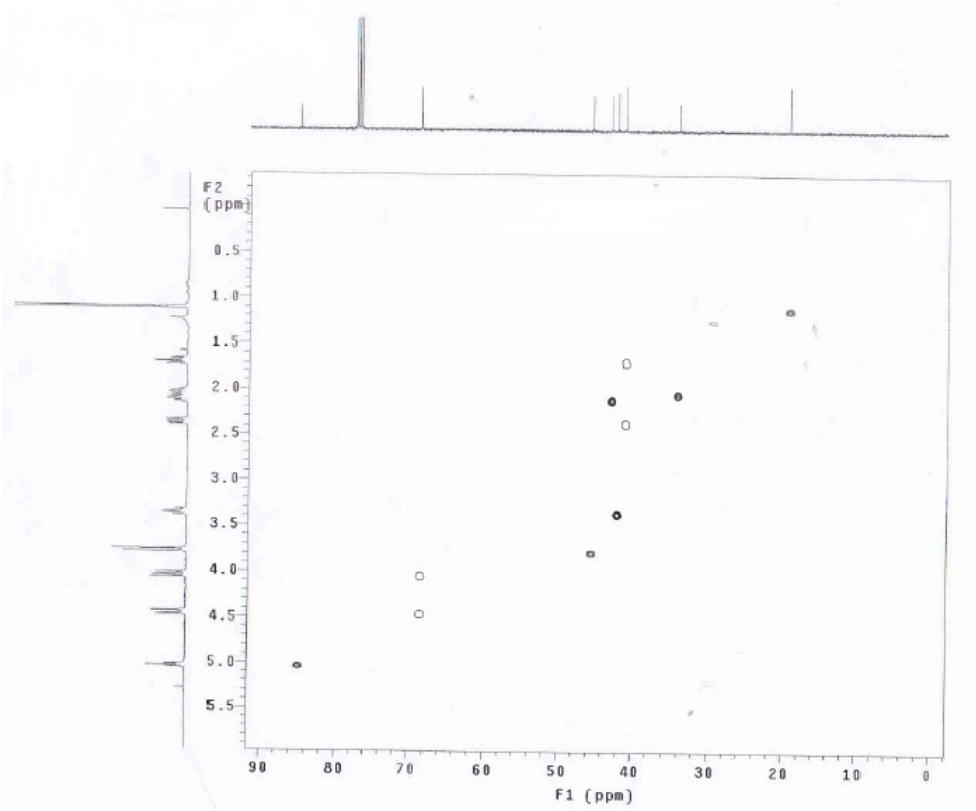


Cornolactone B (**2**)
(HMBC)

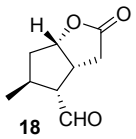




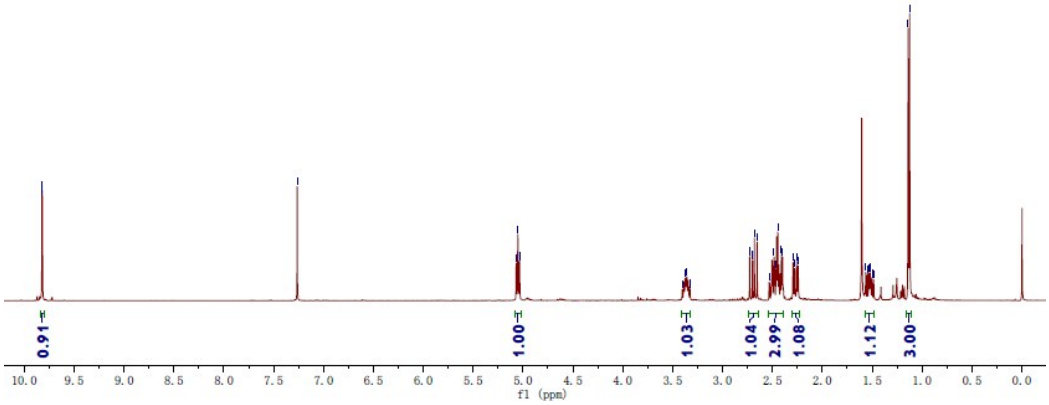
Cornolactone B (**2**)
(HSQC)



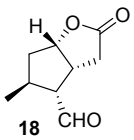

9.82
9.81
7.26
5.07
5.05
5.03
3.40
3.37
3.36
3.33
2.68
2.65
2.45
2.41
1.55
1.54
1.52
1.50
1.48
1.14
1.12


H
O
O
CHO

18

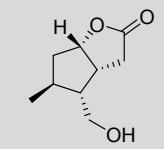

0.91
1.00
1.03
1.04
2.99
1.08
1.12
3.00
f1 (ppm)


201.50
176.42
84.05
77.32
77.00
76.69
61.38
41.37
39.21
32.12
30.50
17.44

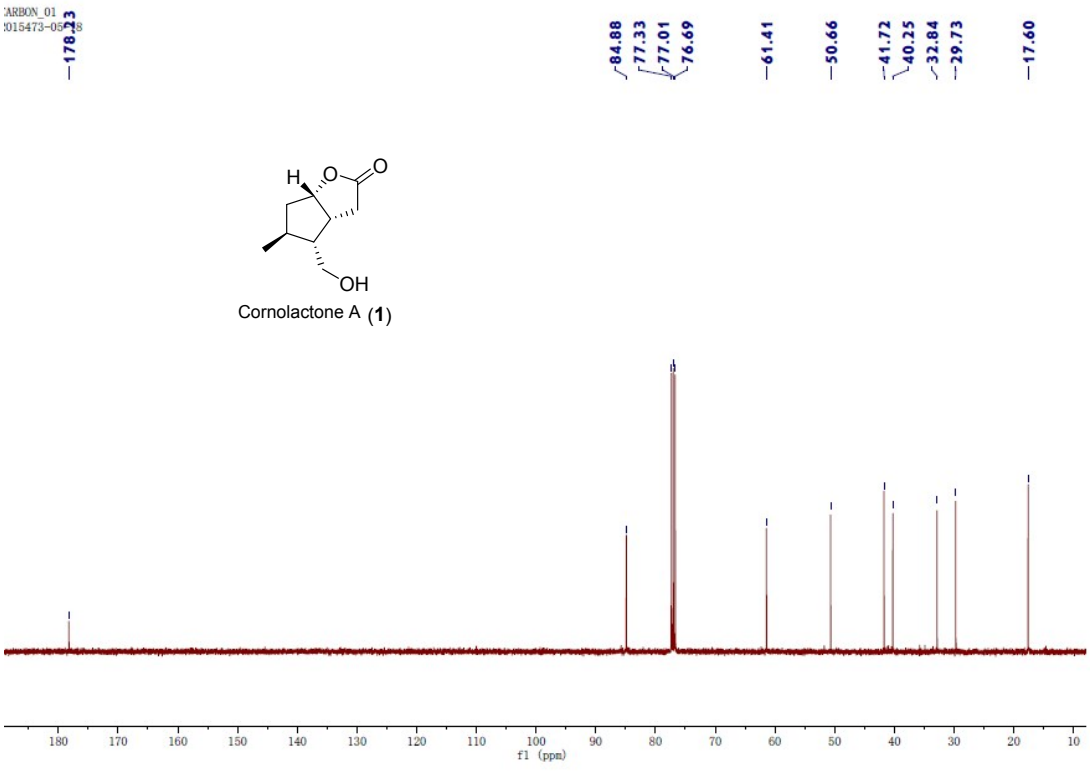

H
O
O
CHO

18

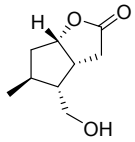
f1 (ppm)



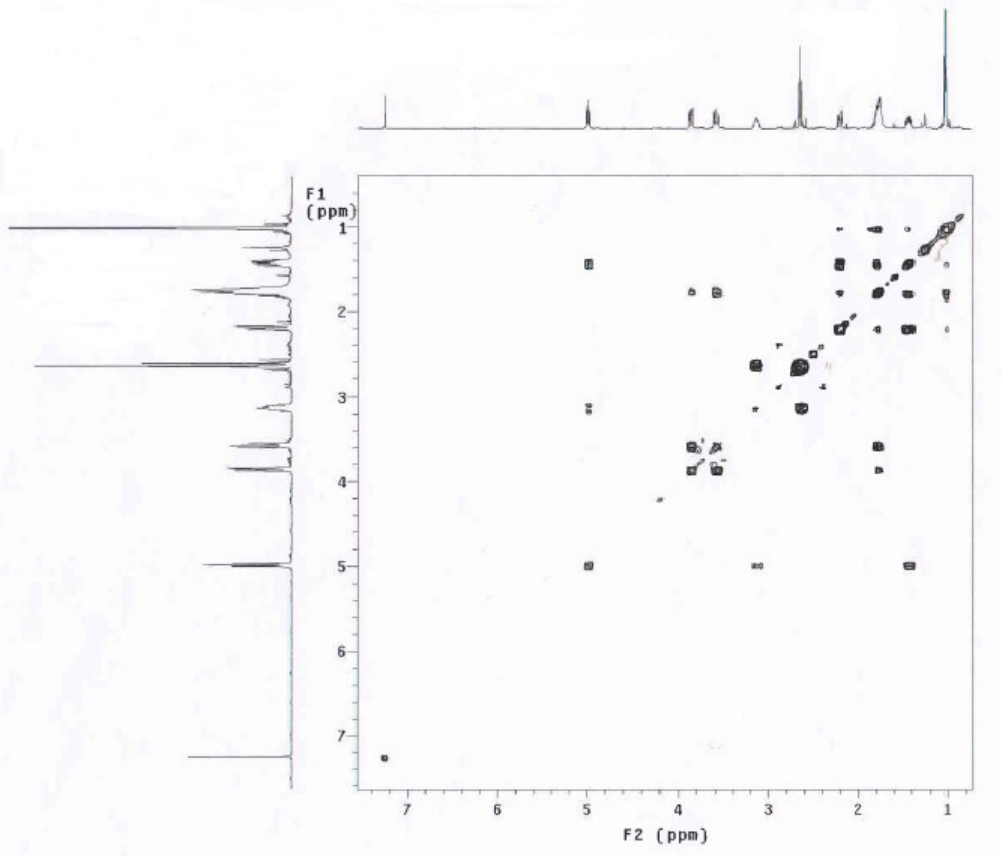
Cornolactone A (**1**)

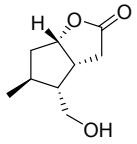


Cornolactone A (**1**)

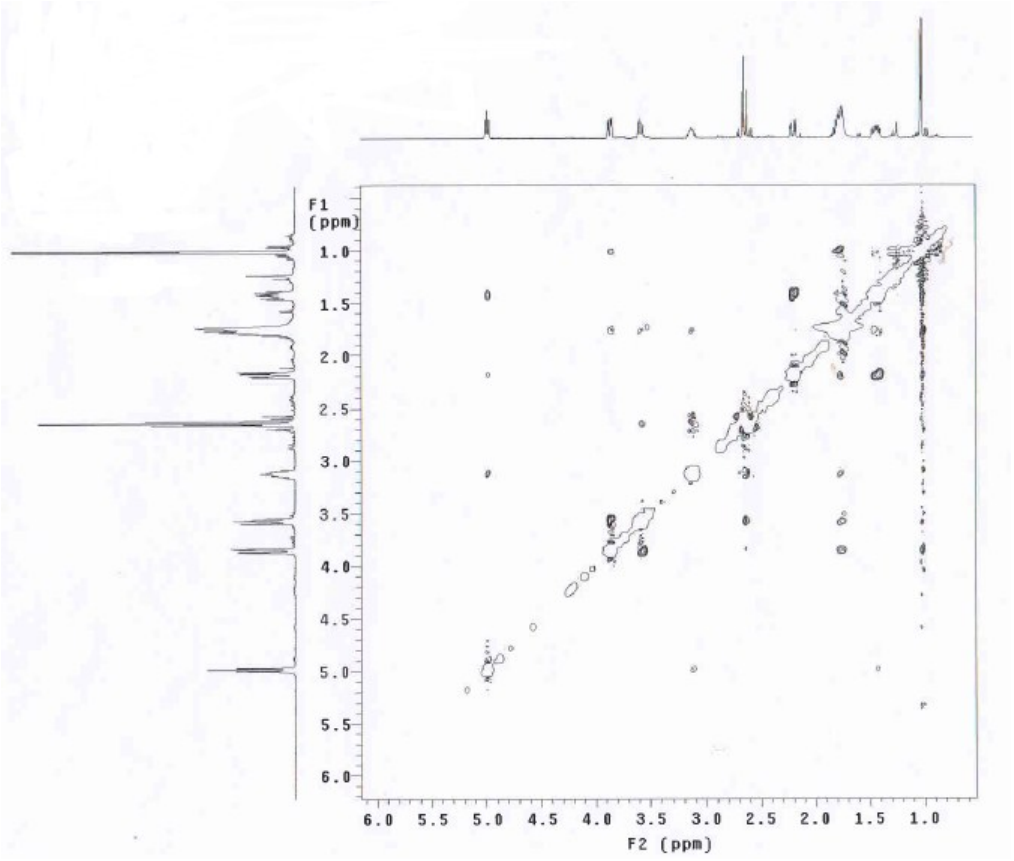


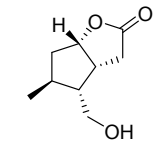
Cornolactone A (**1**)
(COSY)



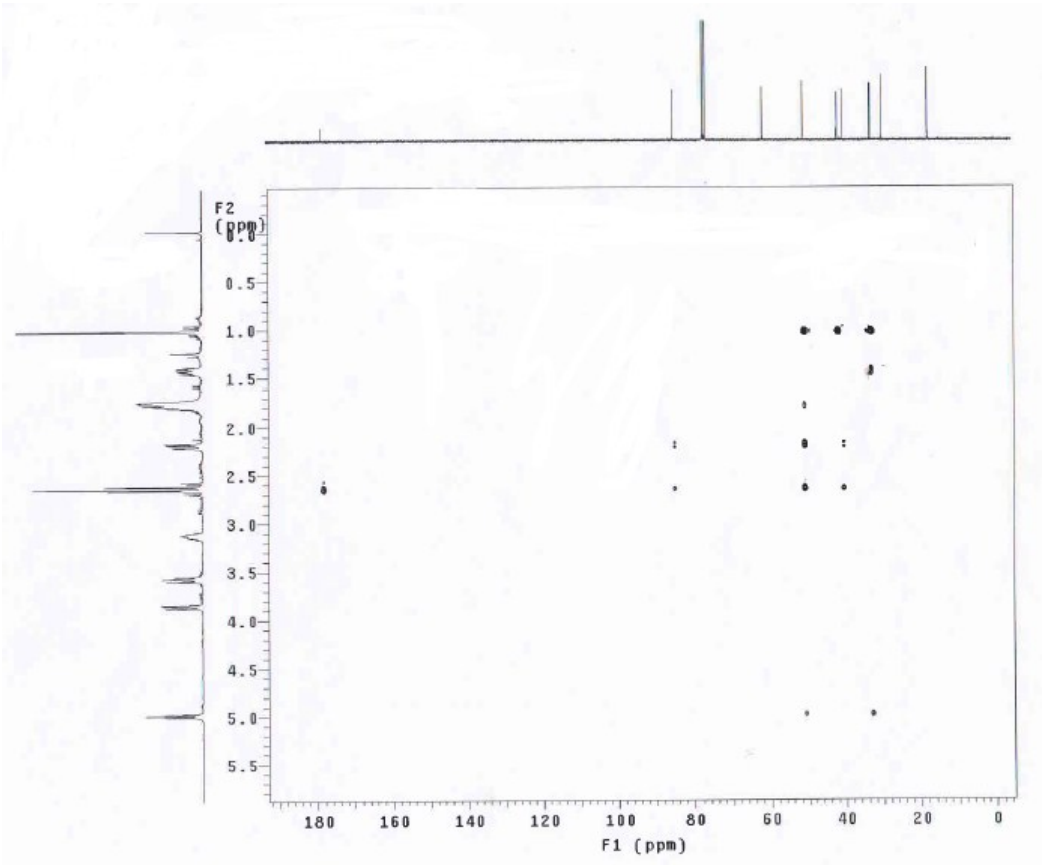


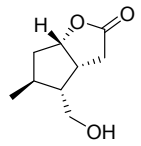
Cornolactone A (**1**)
(NOESY)



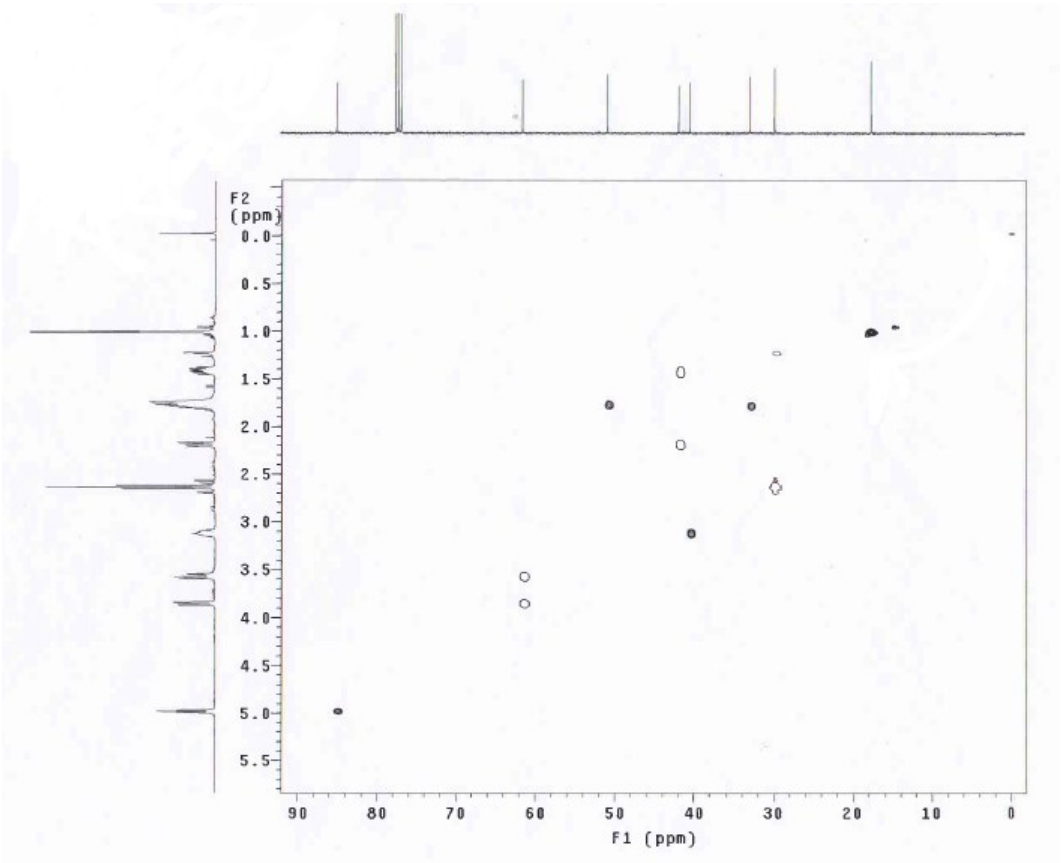


Cornolactone A (**1**)
(HMBC)

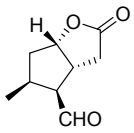




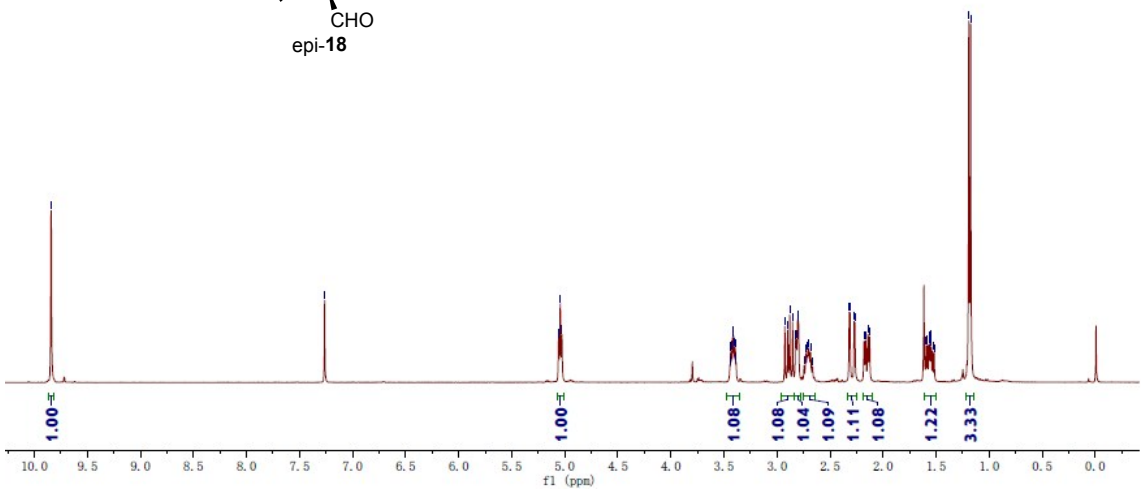
Cornolactone A (**1**)
(HSQC)

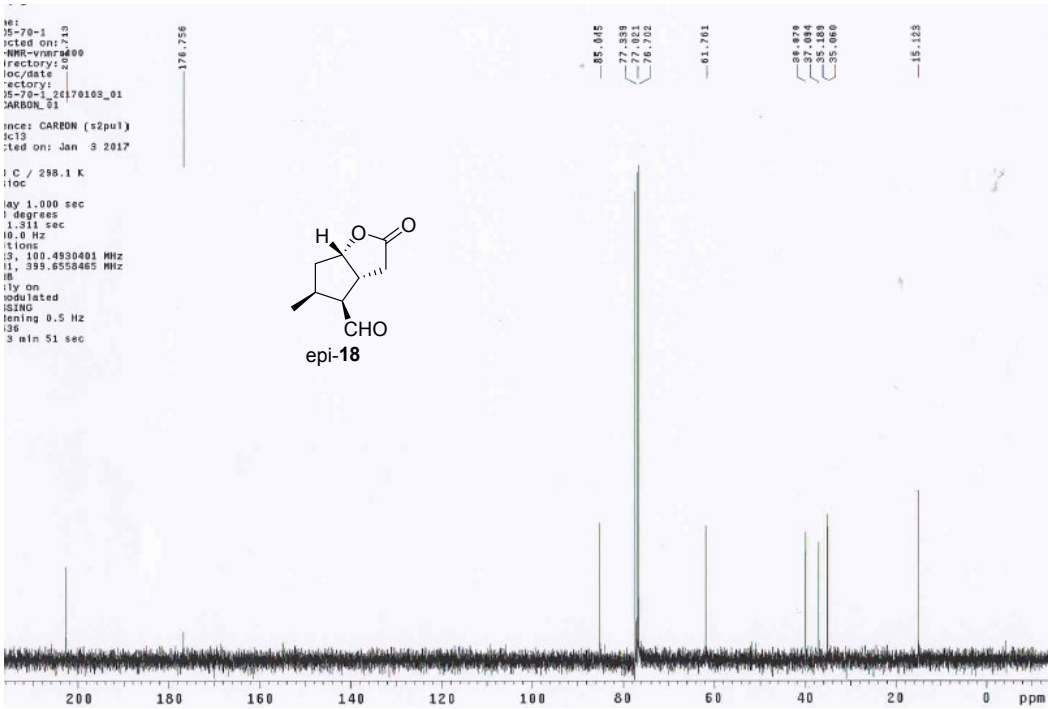



9.84
7.26
5.06
5.04
5.03
2.93
2.90
2.88
2.85
2.80
2.80
2.32
2.31
2.27
2.27
2.14
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.19


H
O
O
CHO

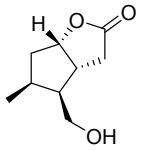
epi-**18**


1.00
1.00
1.08
1.08
1.04
1.09
1.11
1.08
1.22
3.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

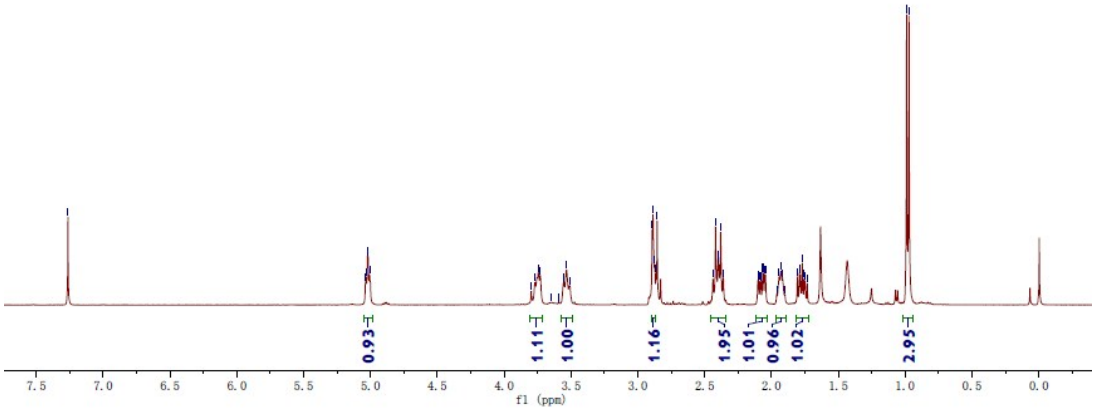

176.756
85.045
77.339
77.021
76.702
61.761
30.978
30.094
35.189
35.060
15.123
H
O
O
CHO
200 180 160 140 120 100 80 60 40 20 0 ppm

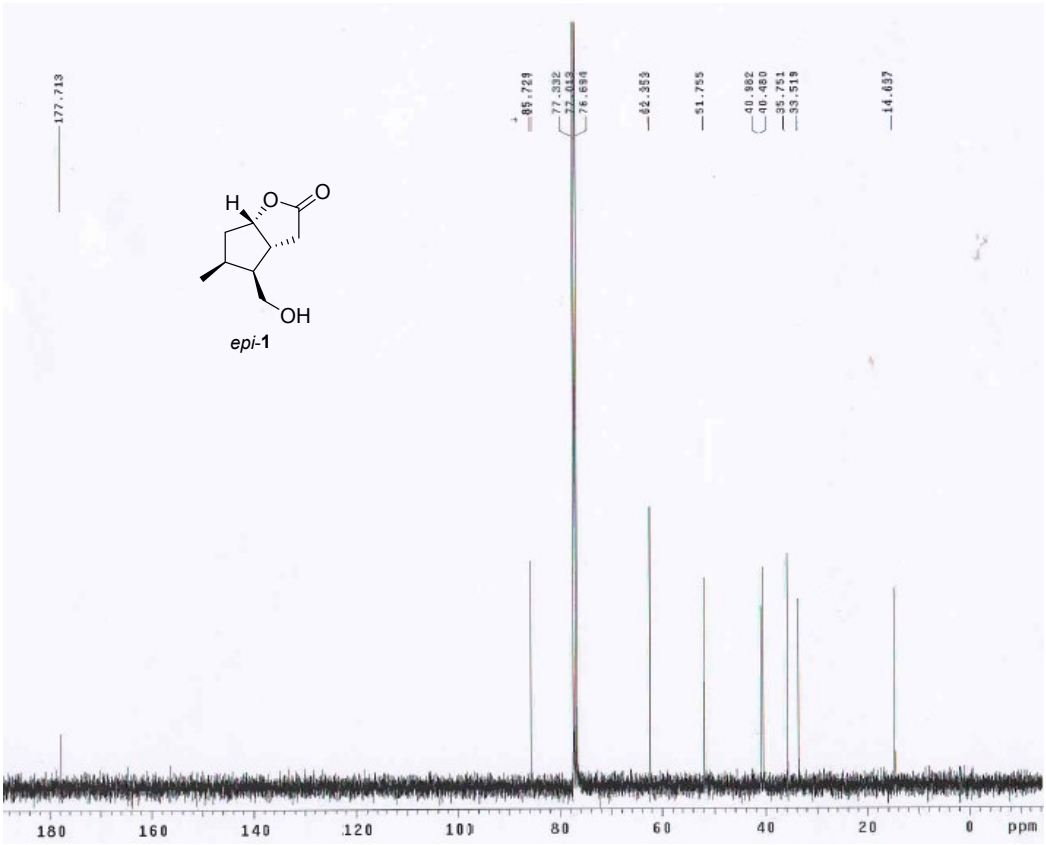
epi-**18**


7.26
5.04
5.03
5.02
5.02
5.02
5.01
3.80
3.77
3.74
3.73
3.55
3.53
3.51
2.89
2.89
2.87
2.86
2.86
2.44
2.42
2.40
2.39
2.38
2.36
2.10
2.10
2.08
2.08
2.07
2.06
2.05
2.04
1.96
1.94
1.93
1.92
1.81
1.79
1.78
1.77
1.75
1.75
1.73
0.99
0.97


H
O
O
OH

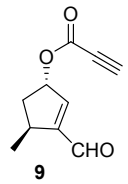
epi-**1**


0.93
1.11
1.00
1.16
1.95
1.01
0.96
1.02
2.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

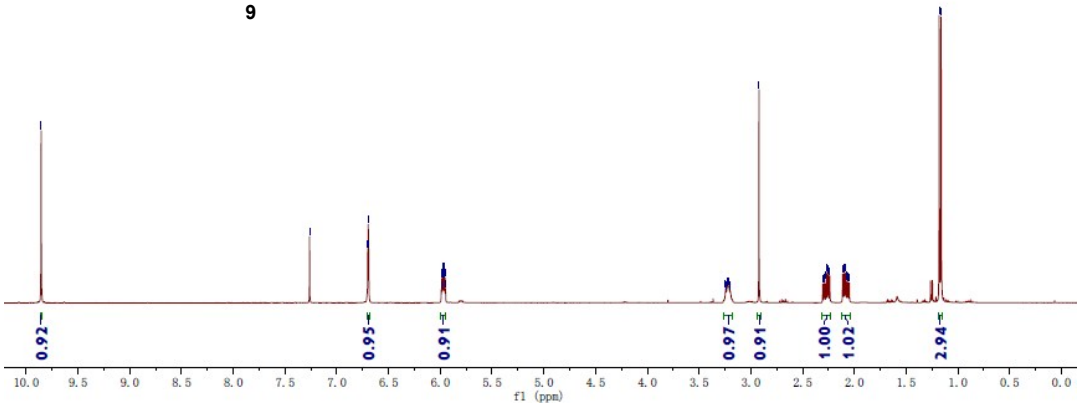

177.713
85.729
77.332
77.013
76.694
62.353
51.755
40.982
40.480
35.751
33.519
14.637
H
O
O
OH
180
160
140
120
100
80
60
40
20
0
ppm

epi-**1**

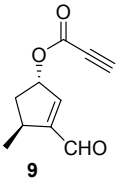

9.86
7.26
6.70
6.70
6.69
5.99
5.98
5.97
5.97
5.96
5.95
5.95
3.24
3.23
3.22
3.22
3.21
3.21
3.20
2.92
2.27
2.26
2.10
2.09
2.08
1.18
1.16


O
O
CHO

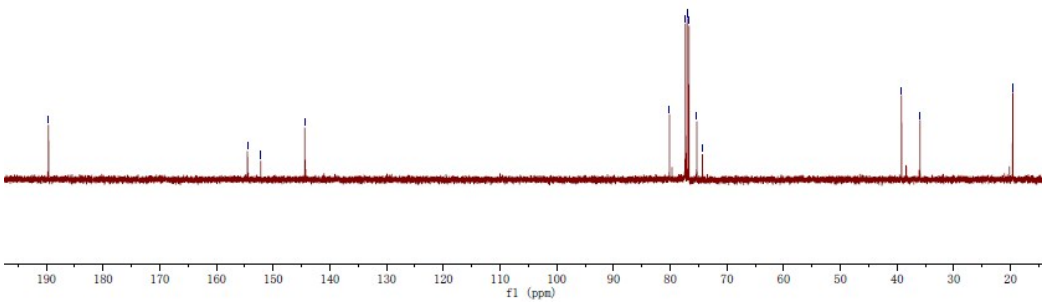
9


0.92
0.95
0.91
0.97
0.91
1.00
1.02
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

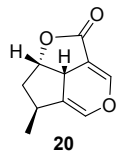

I-68
189.62
154.53
152.20
144.41
80.12
77.32
77.00
76.68
75.30
74.31
39.20
35.93
19.59


O
O
CHO

9

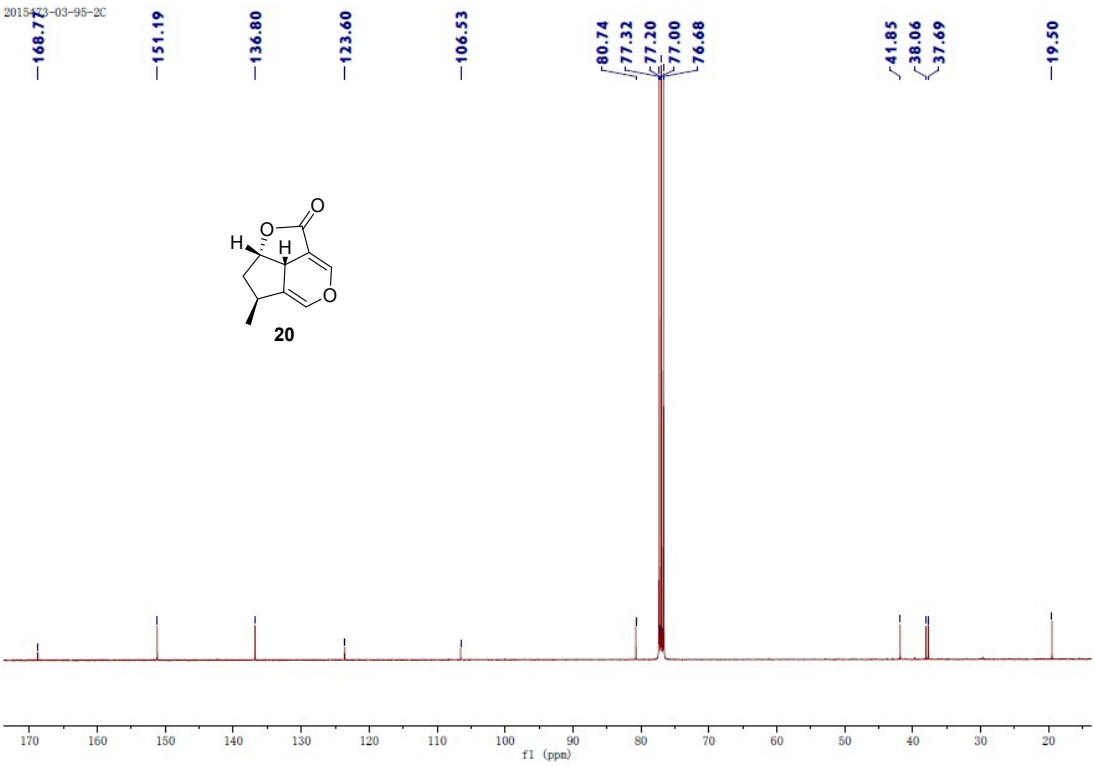

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


7.59
7.58
7.26
6.71
6.70
5.32
5.30
5.28
5.26
3.43
3.41
3.10
3.08
3.07
3.05
3.03
2.31
2.30
2.28
2.26
1.62
1.61
1.15
1.13


O
O
H
H
O

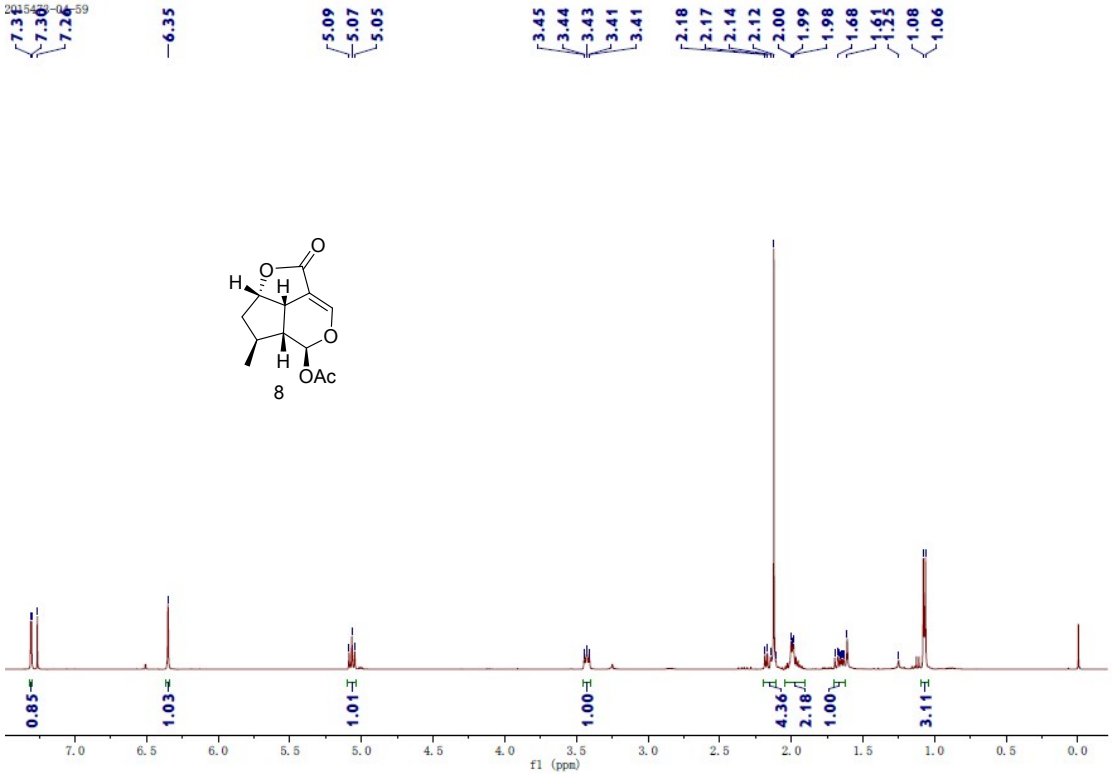
20

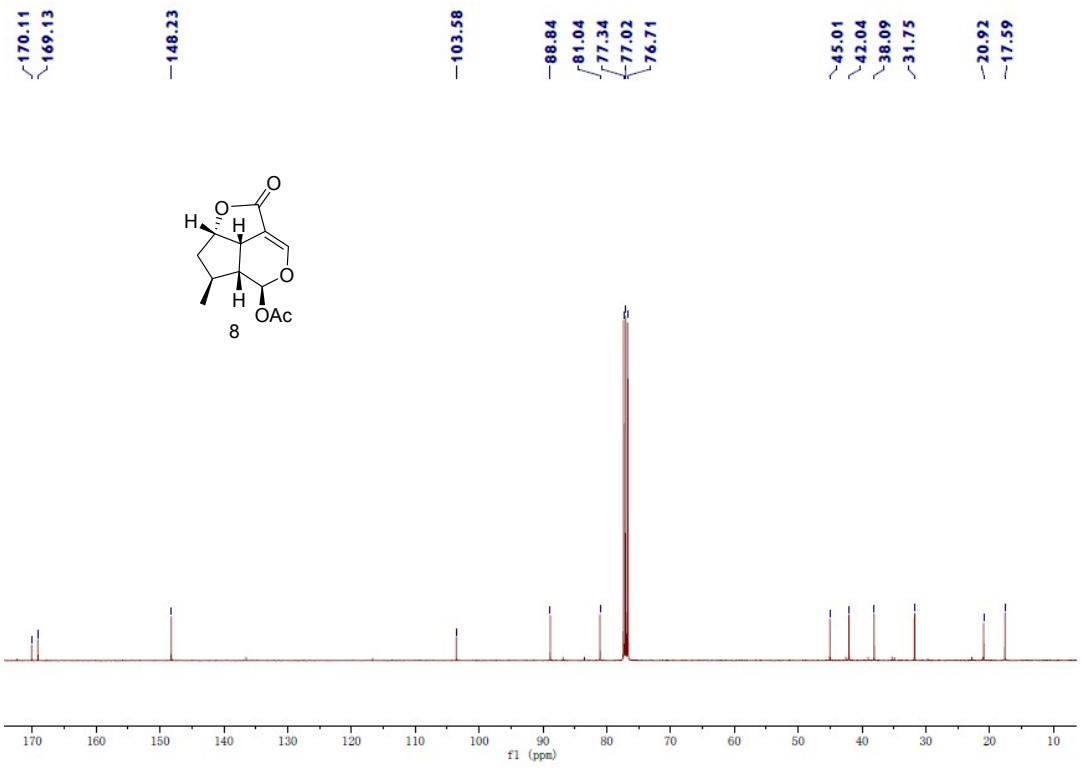
0.84
0.83
0.95
0.93
0.98
1.00
1.16
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

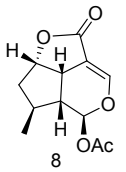

168.77
151.19
136.80
123.60
106.53
80.74
77.32
77.20
77.00
76.68
41.85
38.06
37.69
19.50
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

O
O
H
H
O

20

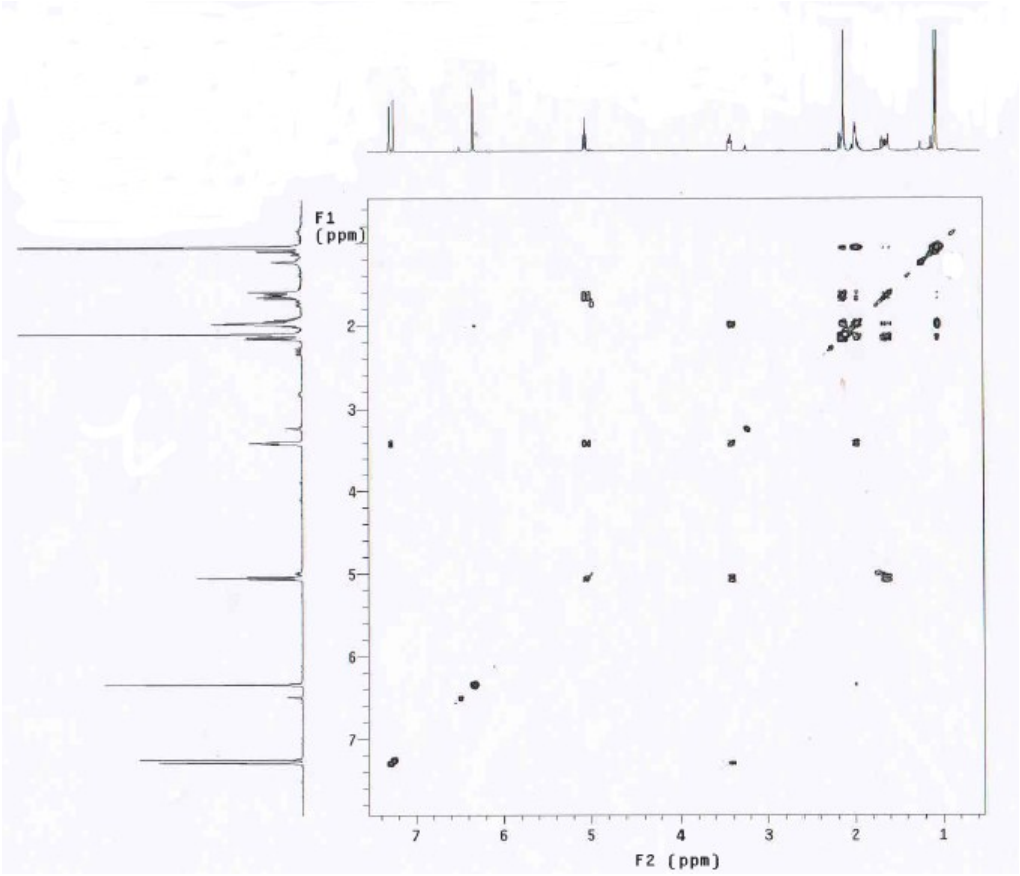

7.31
7.30
7.26
6.35
5.09
5.07
5.05
3.45
3.44
3.43
3.41
3.41
2.18
2.17
2.14
2.12
2.00
1.99
1.98
1.68
1.61
1.25
1.08
1.06
O
O
H
H
O
H
OAc
8
0.85
1.03
1.01
1.00
4.36
2.18
1.00
3.11
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

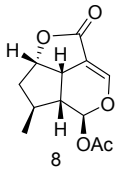

170.11
169.13
148.23
103.58
88.84
81.04
77.34
77.02
76.71
45.01
42.04
38.09
31.75
20.92
17.59
O
O
H
H
O
H
OAc
8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



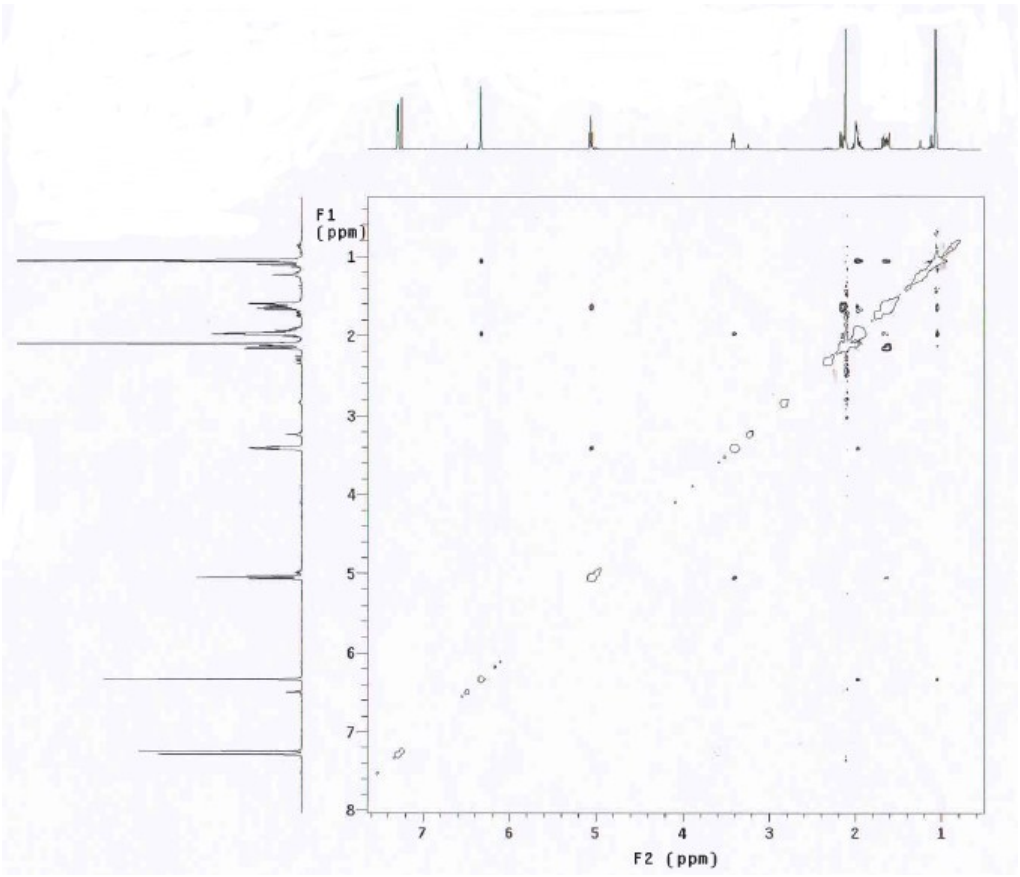
8

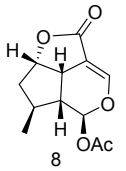
(COSY)



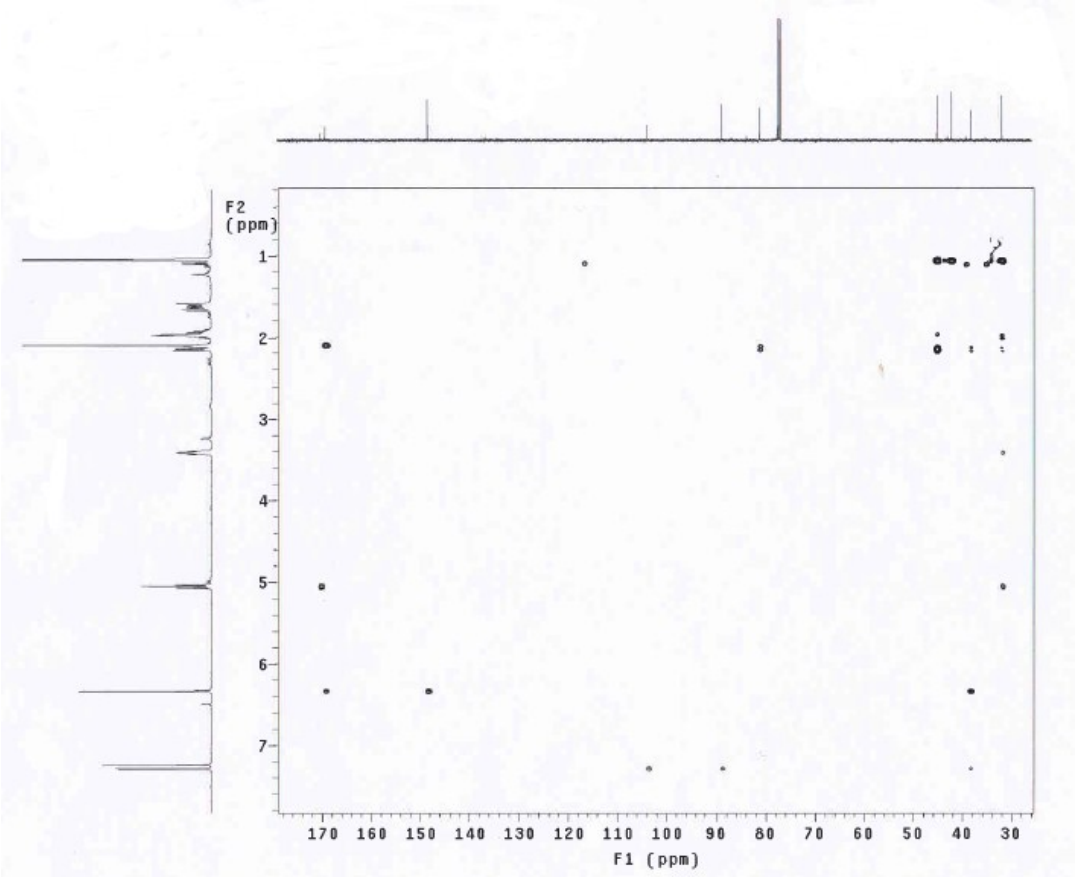


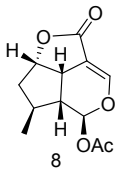
8
(NOESY)



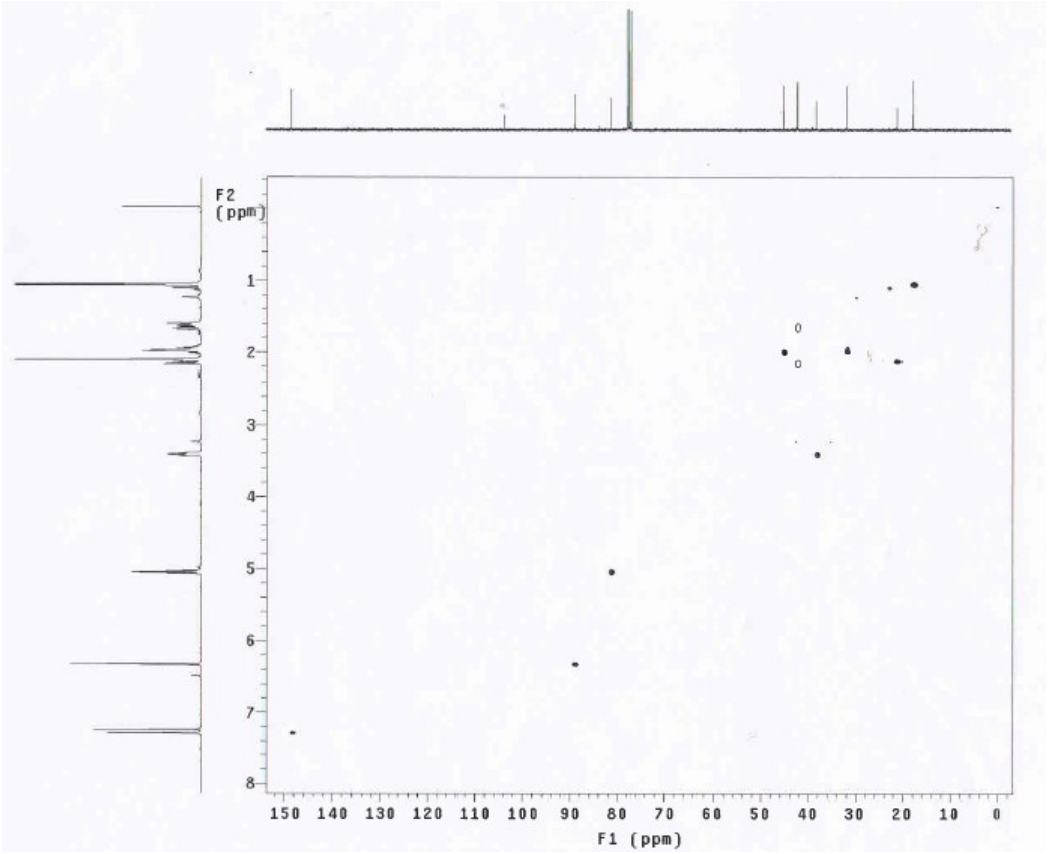

O
O
H
H
O
H
OAc

8
(HMBC)


F2
(ppm)
1
2
3
4
5
6
7
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
F1 (ppm)


O
O
H
H
O
H
OAc

8
(HSQC)


F2
(ppm)
1
2
3
4
5
6
7
8
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
F1 (ppm)