Total Syntheses of Xiamycins A, C, F, H and Oridamycin A and Preliminary Evaluation of their Anti-Fungal Properties

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1. Experimental Procedures and Spectroscopic Data

Unless otherwise stated, all reactions were performed in oven-dried glassware under a nitrogen atmosphere. Reagents were used as received from their commercial supplier. Dry solvents (THF, PhMe, PhH, MeCN, Et_2O, MeOH, NEt_3) were obtained from a JC Meyer Phoenix SDS Solvent System, methylene chloride (DCM) and diisopropylamine (DIPA) were freshly distilled from calcium hydride prior to use. Thin layer chromatography was performed on Merck KGaA TLC Silica gel 60 F_{254} plates visualized by UV light (254 nm/366 nm) and stained with *p*-anisaldehyde, $KMnO_4$, or ceric ammonium molybdate (CAM). Products were purified by flash column chromatography on silica gel (0.040 – 0.063 mm) or by a Yamazen Smart Flash EPCLC W-Prep 2XY (dual channel) automated flash chromatography system on prefilled, premium, universal columns using ACS grade solvents.

NMR spectra were recorded on Bruker AVB-400 (supported by NSF Grant CHE-0130862), DRX-500 (supported by NIH grant RR 02424A-01, NSF Grant CHE 82-08992 and CHE 9633007), AV-500 (supported by NIH Grant 1S10RR016634-01), AV-600 (supported by NIH Grant SRR023679A) or AV-700 MHz instruments. Chemical shifts for ^{1}H NMR are reported as δ (parts per million) relative to the residual signals of $CDCl_3$ at 7.26 ppm, methanol-d_4 at 3.31 ppm or benzene C_6D_6 at 7.16. Chemical shifts for ^{13}C NMR are reported as δ (parts per million) relative to the signal of $CDCl_3$ at 77.16 ppm, methanol-d_4 at 49.00 ppm or benzene C_6D_6 at 128.06. The following abbreviations are used to describe splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, m = multiplet. Coupling constants *J* are given in Hertz. Irradiation of reaction mixtures was performed using a Luzchem photobox (UVB/310 nm: LZC lamps; UVA/350 nm: Hitachi FL8BL-B lamps), a Kessil A160WE blue LED lamp, or a Sunlite tungsten halogen lamp (600W).

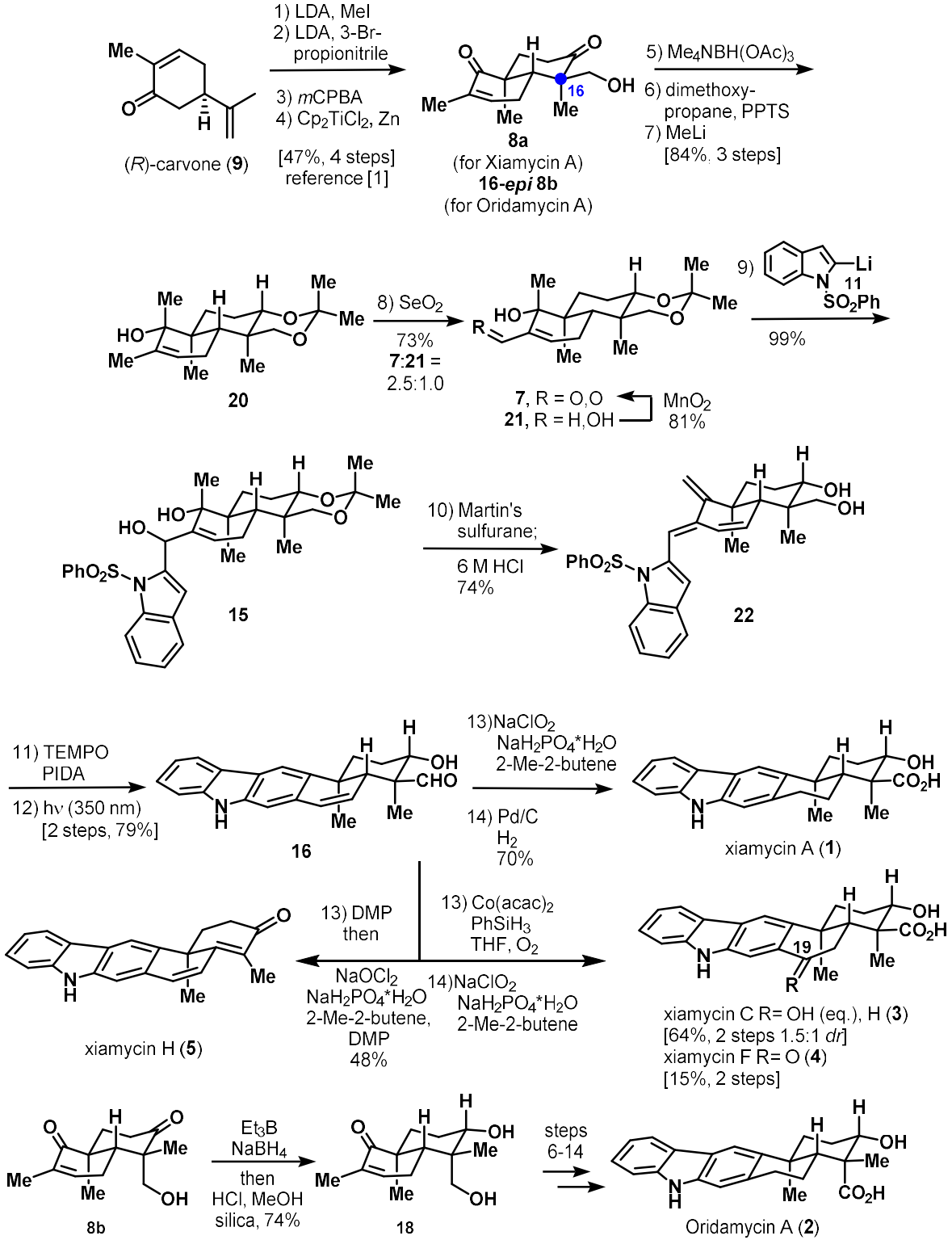
Mass spectra were recorded at the QB3/Chemistry Mass Spectrometry Facility at the University of California, Berkeley, on a Finnigan/Thermo LTQ-FT instrument (ESI), and the data acquired and processed using the XcaliburTM software.

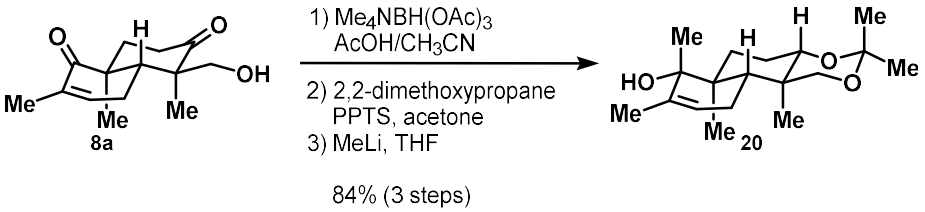
IR spectroscopic data were recorded on a Bruker ALPHA FT-IR spectrometer and reported in [cm^{-1}]. Samples are loaded onto the diamond surface either neat or as a solution in organic solvent and the data acquired after the solvent had evaporated.

X-Ray data were collected on a Bruker APEX-II CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) or a MicroStar-H X8 APEX-II diffractometer with Cu-Kα radiation (λ = 1.54178 Å). CYLview was used for graphic rendering.

UV-Vis experiments were performed on a Agilent Cary 60 Spectrophotometer using a dual beam mode between 800 and 200 nm.

Graphical Overview





(4a*S*,5*R*,6*S*,8a*S*)-6-Hydroxy-5-(hydroxymethyl)-2,5,8a-trimethyl-4a,5,6,7,8,8a-hexahydro naphthalen-1(4*H*)-one (10): To a solution of $Me_4NHB(OAc)_3$ (10.2 g of >90% pure Acros material, 34.9 mmol, 5.50 equiv) in 22.5 mL of MeCN (0.280 M) was added 22.5 mL of glacial AcOH (0.280 M) under N_2, and the resulting colorless solution was stirred 30 min at room temperature, after which time it was added via cannula to a stirring solution of ketone **8a** (1.50 g, 6.35 mmol, 1.00 equiv) dissolved in 22.5 mL MeCN at room temperature. The clear solution was stirred for 3 h at room temperature and then quenched by addition of sat. aq. Rochelle's salt solution. The resulting milky biphasic mixture was diluted with EtOAc and vigorously stirred for 1 h. A solution of sat. aq. $NaHCO_3$ was carefully added while stirring. After the gas evolution ceased, the aq. layer was extracted four times with EtOAc, washed three times with sat. aq. $NaHCO_3$, followed by sat. aq. NaCl solution and dried over $MgSO_4$. This material was used in the next reaction without further purification. An analytical sample was prepared by flash column chromatography (PE:EtOAc = 1:1) to afford diol **10** as a white solid. Suitable crystals for X-ray analysis were obtained after crystallization from a Hexane/EtOAc (1:1) solution.

(4a*S*,6a*S*,10a*S*,10b*R*)-3,3,6a,8,10b-Pentamethyl-1,4a,5,6,6a,10,10a,10b-octahydro-7*H*-naphtho[2,1-d][1,3]dioxin-7-one (23): To a solution of crude diol in acetone (80.0 mL, 80.0 mM) was added PPTS (399 mg, 1.58 mmol, 0.250 equiv), followed by 2,2-dimethoxypropane (7.90 mL, 63.5 mmol, 10.0 equiv) at room temperature. After stirring for 14 h, the reaction mixture was quenched by the addition of sat. aq. $NaHCO_3$. The aq. layer was extracted three times with EtOAc, washed with sat. aq. NaCl solution and dried over $MgSO_4$. After removal of the solvent *in vacuo*, this material was used in the next reaction without further purification. An analytical sample was prepared by flash column chromatography (PE:EtOAc = 3:1) to afford acetonide **23** as a white solid.

(4a*S*,6a*S*,7*S*,10a*S*,10b*R*)-3,3,6a,7,8,10b-Hexamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-*H*-naphtho[2,1-d][1,3]dioxin-7-ol (20): MeLi (8.70 mL of a 1.60 M Et_2O solution, 14.0 mmol,

2.20 equiv) was added dropwise to a solution of the crude acetonide in THF (63.0 mL, 0.100 M) at –78 °C. After being stirred for 1.5 h at –78 °C, the reaction mixture was quenched by the addition of sat. aq. NH_4Cl. The aq. layer was extracted three times with EtOAc, washed with sat. aq. NaCl solution and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was purified by gradient flash chromatography (Yamazen, eluting with 13-34% EtOAc in hexanes) to afford 1.56 g (84%, over 3 steps) of alcohol **20** as a white solid.

(4a*S*,5*R*,6*S*,8a*S*)-6-Hydroxy-5-(hydroxymethyl)-2,5,8a-trimethyl-4a,5,6,7,8,8a-hexahydronaphthalen-1(4*H*)-one (10):

$[\alpha]_D^{22}$ –21.4 (c = 1.00, MeOH); lit.[1] **$[\alpha]_D^{27}$** -20.3 (c = 1.00, MeOH)

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.64 (d, *J* = 4.8 Hz, 1H), 3.68-3.58 (m, 2H), 3.39 (d, *J* = 10.6 Hz, 1H), 3.04 (br s, 2H), 2.39-2.29 (m, 1H), 2.18 (d, *J* = 19.1 Hz, 1H), 1.91 (d, *J* = 14.3 Hz, 1H), 1.79 (dd, *J* = 11.5, 4.2 Hz, 1H), 1.75 (d, *J* = 4.0 Hz, 1H), 1.72 (s, 3H), 1.70-1.60 (m, 1H), 1.47 (td, *J* = 14.0, 4.0 Hz, 1H), 1.06 (s, 3H), 0.99 (s, 3H) ppm.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 205.4, 143.4, 133.2, 75.4, 69.6, 44.4, 42.9, 42.5, 31.4, 26.6, 24.1, 17.9, 16.4, 11.9 ppm.

IR (neat): ν = 3410, 2933, 1657, 1356, 1039, 998, 733, 544 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M+H]^+$ calcd. for $C_{14}H_{23}O_3$, 239.1640; found 239.1640.

R_f = 0.23 (Hexane:EtOAc = 1:3), UV-active, blue spot (CAM).

(4a*S*,6a*S*,10a*S*,10b*R*)-3,3,6a,8,10b-pentamethyl-1,4a,5,6,6a,10,10a,10b-octahydro-7*H*-naphtho[2,1-d][1,3]dioxin-7-one (23):

$[\alpha]_D^{22}$ –39.3 (c = 1.00, MeOH)

^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.60 (d, *J* = 5.5 Hz, 1H), 3.52-3.47 (m, 3H), 2.34 (ddt, *J* = 18.8, 11.7, 2.3 Hz, 1H), 2.02-1.90 (m, 2H), 1.73 (s, 3H), 1.67-1.55 (m, 4H), 1.41 (s, 6H), 1.19 (s, 3H), 1.07 (s, 3H) ppm.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 204.7, 142.3, 133.6, 99.3, 76.7, 71.9, 45.0, 44.5, 37.2, 31.9, 29.9, 23.6, 23.5, 19.2, 18.5 16.5, 12.9 ppm.

IR (neat): ν = 2989, 2943, 2864, 1672, 1444, 1392, 1205, 1042, 846 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M+H]^+$ calcd. for $C_{17}H_{27}O_3$, 279.1960; found 279.1954.

R_f = 0.51 (Hexane:EtOAc = 2:1), UV-active, blue spot (CAM).

M.p. = 79 °C

(4a*S*,6a*S*,7*S*,10a*S*,10b*R*)-3,3,6a,7,8,10b-hexamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-*H*-naphtho[2,1-d][1,3]dioxin-7-ol (20):

[α]D^{22} –27.9 (c = 1.00, MeOH)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.29 (s, 1H), 3.52-3.47 (m, 1H), 3.46 (s, 2H), 2.02-1.90 (m, 1H), 1.70 (s, 3H), 1.69-1.60 (m, 4H), 1.56-1.49 (m, 2H), 1.45 (s, 3H), 1.42 (s, 3H), 1.29 (s, 3H), 1.22 (s, 1H), 1.17 (s, 3H), 1.07 (s, 3H) ppm.

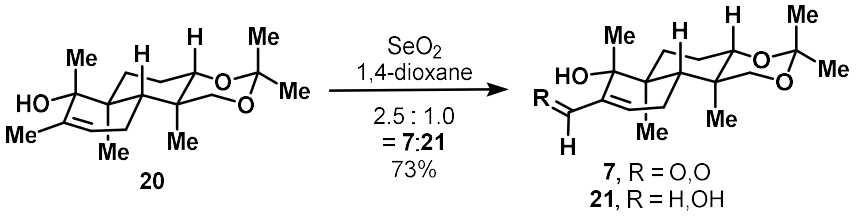
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 138.7, 121.1, 99.2, 77.9, 77.5, 72.7, 40.8, 40.4, 37.1, 30.5, 30.0, 23.8, 23.7, 23.1, 19.4, 18.0, 15.7, 12.4 ppm.

IR (neat): ν = 3499, 2987, 2943, 2897, 1452, 1378, 1284, 1206, 1102, 860 cm^{-1}.

HRMS (EI, *m*/*z*): $[M]^+$ calcd. for $C_{18}H_{30}O_3$, 294.2195; found 294.2192.

R$_f$ = 0.48 (Hexane:EtOAc = 2:1), non UV-active, blue spot (CAM).

M.p. = 182 °C



(4a*S*,6a*S*,7*R*,10a*S*,10b*R*)-7-Hydroxy-3,3,6a,7,10b-pentamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1*H*-naphtho[2,1-d][1,3]dioxine-8-carbaldehyde (15); **(4a*S*,6a*S*,7*R*,10a*S*, 10b*R*)-8-(hydroxymethyl)-3,3,6a,7,10b-pentamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1*H*-naphtho[2,1-d][1,3]dioxin-7-ol (7)**: A mixture of alcohol **20** (1.69 g, 5.76 mmol, 1.00 equiv) and selenium dioxide (1.60 g, 14.4 mmol, 2.50 equiv) was dissolved in 1,4-dioxane (58.0 mL, 0.100 M) and then placed in an oil bath at 90 °C. After stirring for 2h, the resulting brown mixture was cooled to room temperature and quenched by the addition of distilled water. The aq. phase was extracted three times with EtOAc and the combined organic layers were washed with sat. aq. NaCl solution. The solution was dried over $MgSO_4$ and concentrated *in vacuo*. The crude products were purified by gradient flash chromatography (Yamazen, eluting with 13-34% EtOAc in hexanes) to afford 0.910 g of aldehyde **7** as a yellow solid and 0.370 g (73% combined yield, **7**:**21** = 2.5:1.0) of alcohol **21** as a yellow foam.

(4a*S*,6a*S*,7*R*,10a*S*,10b*R*)-7-Hydroxy-3,3,6a,7,10b-pentamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1*H*-naphtho[2,1-d][1,3]dioxine-8-carbaldehyde (24):

$[\alpha]_D^{22}$ –60.1 (c = 1.00, MeOH)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.35 (s, 1H), 6.67 (br s, 1H), 4.20 (s, 1H), 3.55-3.47 (m, 3H), 2.42-2.32 (m, 1H), 2.15-2.07 (m, 1H), 1.77-1.64 (m, 3H), 1.57-1.50 (m, 2H), 1.46 (s, 3H), 1.43 (s, 6H), 1.21 (s, 3H), 1.05 (s, 3H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 196.3, 151.6, 145.0, 99.3, 77.3, 75.9, 72.5, 40.2, 39.7, 37.0, 30.0, 29.4, 25.4, 25.1, 23.6, 19.3, 15.7, 12.4 ppm.

IR (neat): ν = 3498, 2987, 2942, 1688, 1638, 1378, 1221, 1208, 862 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{18}H_{27}O_4$, 307.1915; found 307.1915.

R_f = 0.57 (Hexane:EtOAc = 1:1), UV-active, blue spot (CAM).

M.p. = 195 °C

(4a*S*,6a*S*,7*R*,10a*S*,10b*R*)-8-(Hydroxymethyl)-3,3,6a,7,10b-pentamethyl-4a,5,6,6a,7,10,-10a,10b-octahydro-1*H*-naphtho[2,1-d][1,3]dioxin-7-ol (21):

$[\alpha]_D^{22}$ –8.0 (c = 0.80, MeOH)

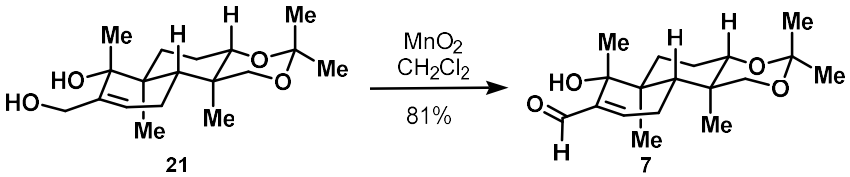
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.57 (br s, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 3.92 (d, *J* = 11.6 Hz, 1H), 3.54-3.41 (m, 3H), 2.23 (br s, 2H), 2.09-1.99 (m, 1H), 1.76 (dt, *J* = 18.4, 4.5 Hz, 1H), 1.70-1.58 (m, 3H), 1.58-1.50 (m, 2H), 1.45 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.17 (s, 3H), 1.04 (s, 3H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 141.1, 125.6, 99.2, 78.9, 72.6, 65.2, 40.6, 40.3, 37.1, 30.0, 29.8, 24.9, 23.8, 22.9, 19.3, 15.8, 12.3 ppm.

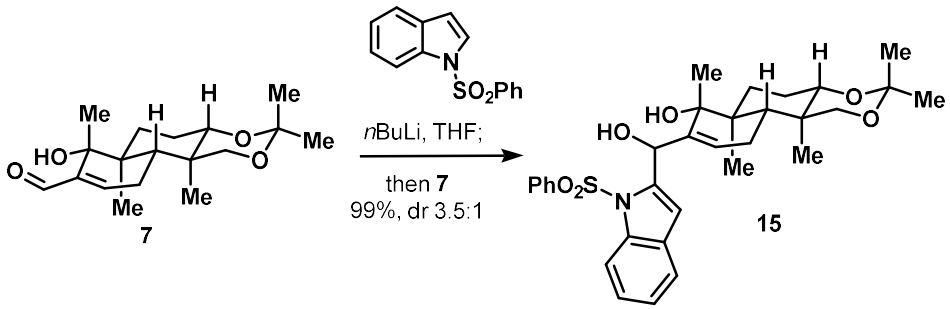
IR (neat): ν = 3407, 2988, 2943, 2898, 2876, 1378, 1258, 1205, 1100, 1075, 859, 737 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{18}H_{29}O_4$, 309.2070; found 309.2071.

R_f = 0.19 (Hexane:EtOAc = 1:1), UV-active, blue spot (CAM).



A mixture of alcohol **21** (600 mg, 1.95 mmol, 1.00 equiv) and manganese dioxide (2.03 g, 23.3 mmol, 12.0 equiv) in DCM (32.0 mL, 60.0 mM) was stirred for 16 h at room temperature. After filtering through celite (EtOAc eluent), the solution was concentrated *in vacuo* and the crude material was purified by gradient flash chromatography (Yamazen, eluting with 24-45% EtOAc in hexanes) to afford 489 mg (81%) of aldehyde **7** as a yellow solid.



(4a*S*,6a*S*,7*R*,10a*S*,10b*R*)-8-(Hydroxy(1-(phenylsulfonyl)-1*H*-indol-2-yl)methyl)-3,3,6a,7, 10b-pentamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1*H*-naphtho[2,1-d][1,3]dioxin-7-ol (15): Trace water was removed from 1-(phenylsulfonyl)-1*H*-indole (3.65 g, 14.2 mmol, 3.50 equiv) via azeotropic distillation with benzene. Then, it was dissolved in THF (700 mL) and cooled to –78°C. A solution of *n*BuLi (8.75 ml of a 1.60 M solution in pentane, 14.0 mmol, 3.45 equiv) was added dropwise. The yellow solution was stirred at 0 °C for 1 h. During this time, trace water was removed from aldehyde **7** (1.25 g, 4.04 mmol, 1.00 equiv) via azeotropic distillation with benzene. Then it was dissolved in THF (20.0 mL) and added via cannula transfer into the solution containing the 2-lithio-indole over the course of 5 minutes at –78°C.

After stirring the resulting solution at –78°C for 1 h, the solution was warmed to 0 °C and stirred additional 1 h before being quenched with sat. aq. NH_4Cl. The aq. layer was extracted three times with EtOAc and the combined organic layers were washed with sat. aq. NaCl, dried over $MgSO_4$, filtered, and concentrated. The residue was purified via gradient flash chromatography (Yamazen, eluting with 46-67% EtOAc in hexanes) to yield a mixture of diastereomers of alcohol **15** as a yellow foam (2.27 g, 99% combined yield, dr = 3.5:1) which was used in the next reaction. Analytical samples were prepared via gradient flash chromatography (Yamazen, eluting with 39-59% EtOAc in hexanes).

Major isomer:

$[\alpha]_D^{22}$ –42.0 (c = 1.00, MeOH)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.51-7.47 (m, 2H), 7.40-7.34 (m, 2H), 7.30-7.27 (m, 1H), 7.25-7.20 (m, 1H), 6.91 (s, 1H), 6.16 (s, 1H), 5.05 (br s, 1H), 4.09 (br s, 1H), 3.55-3.49 (m, 1H), 3.48-3.43 (m, 1H), 3.42-3.37 (m, 1H), 2.43 (br s, 1H), 1.94-1.84 (m, 1H), 1.75-1.66 (m, 2H), 1.65-1.62 (m, 2H), 1.61 (s, 3H), 1.59-1.53 (m, 2H), 1.46 (s, 3H), 1.42 (s, 3H), 1.13 (s, 3H), 1.07 (s, 3H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 142.3, 141.9, 138.6, 137.5, 133.8, 129.6, 129.3 (2x), 126.4 (2x), 125.3, 124.7, 124.0, 121.1, 115.0, 112.7, 99.2, 79.8, 77.9, 72.5, 68.1, 40.7, 40.3, 37.0, 30.0, 29.9, 24,7, 23.8, 22.9, 19.4, 15.9, 12.2 ppm.

IR (neat): ν = 3418, 2989, 2944, 1447, 1372, 1173, 1091, 726 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{32}H_{38}NO_6S$, 564.2425; found 564.2414.

R_f = 0.36 (Hexane:EtOAc = 1:1), UV-active, blue spot (CAM).

Minor isomer:

$[\alpha]_D^{22}$ +58.0 (c = 1.00, MeOH)

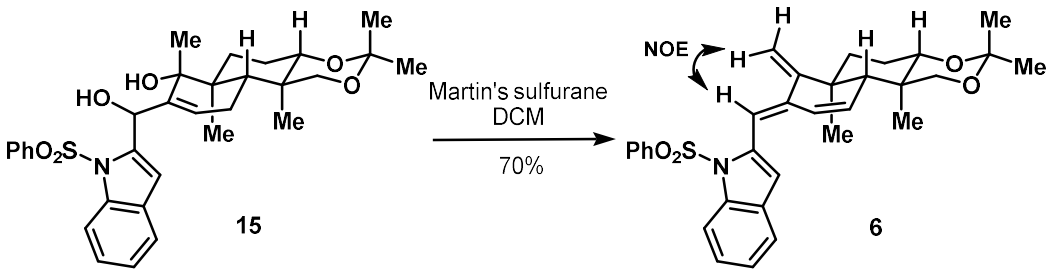
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.55-7.49 (m, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.43-7.39 (m, 2H), 7.34-7.27 (m, 1H), 7.25-7.20 (m, 1H), 6.76 (s, 1H), 6.05 (d, *J* = 3.7 Hz, 1H), 5.85 (br s, 1H), 3.54-3.34 (m, 3H), 3.11 (d, *J*= 4.9 Hz, 1H), 2.19-2.09 (m, 1H), 1.85 (dt, *J* = 18.5, 4.8 Hz, 1H), 1.76 (s, 1H), 1.70-1.76 (m, 1H), 1.66-1.60 (m, 1H), 1.55-1.49 (m, 1H), 1.47 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 144.1, 143.0, 138.3, 137.5, 134.1, 129.4 (2x), 129.0, 126.7 (2x), 125.8, 125.1, 124.1, 121,3, 114.9, 111.4, 99.2, 77.9, 72.6, 66.0, 40.7, 40.6, 37.1, 30.2, 30.0, 24.7, 23.8, 23.1, 19.4, 16.0, 12.5 ppm.

IR (neat): ν = 3422, 2989. 2943, 1448, 1172, 1091, 738, 726, 590 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{32}H_{38}NO_6S$, 564.2425; found 564.2414.

R_f = 0.33 (Hexane:EtOAc = 1:1), UV-active, blue spot (CAM).



1-(Phenylsulfonyl)-2-((*E*)-((4a*S*,6a*S*,10a*R*,10b*R*)-3,3,6a,10*b*-tetramethyl-7-methylene-5,6,6a,7,10a,10b-hexahydro-1*H*-naphtho[2,1-d][1,3]dioxin-8(4a*H*)-ylidene)methyl)-1*H*-indole (6): Martin's sulfurane (5.00 g, 7.44 mmol, 2.40 equiv) was added as a solid to a solution of alcohol **15** (1.76 g, 3.10 mmol, 1.00 equiv) in DCM (74.4 mL, 40.0 mM) at room temperature. After being stirred for 20 min, the reaction mixture was quenched by the addition of sat. aq. $NaHCO_3$. The aq. layer was extracted three times with DCM, washed with sat. aq. NaCl solution and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was purified by gradient flash chromatography (Yamazen, eluting with 5-26% EtOAc in hexanes) to afford 1.15 g (70%) of compound **6** as a yellow solid. The double bond geometry was confirmed by a 2D-NOESY experiment.

$[\alpha]_D^{22}$ –151.2 (c = 1.00, MeOH)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.50-7.44 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.36-7.24 (m, 2H), 7.24-7.20 (m, 1H), 7.08 (s, 1H), 6.54 (s, 1H), 6.51 (d, *J* = 10.1 Hz, 1H), 5.59 (d, *J* = 10.1 Hz, 1H), 5.29 (s, 1H), 4.84 (s, 1H), 3.61 (d, *J* = 10.4 Hz, 2H), 3.49 (d, *J* = 10.7 Hz, 1H), 2.11 (s, 1H), 1.92-1.80 (m, 3H), 1.73-1.65 (m, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 1.15 (s, 3H), 1.12 (s, 3H) ppm.

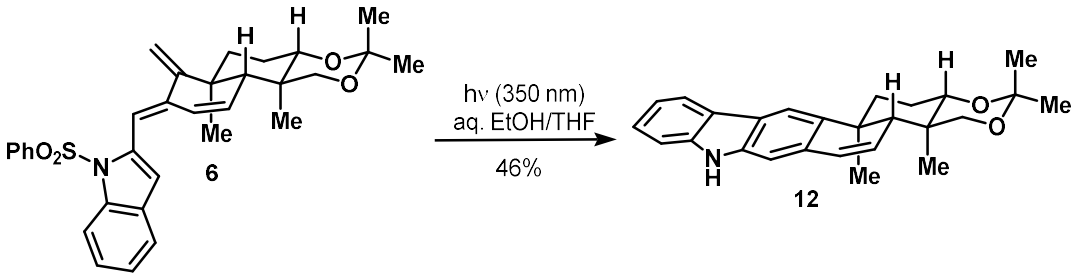
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 156.9, 138.6, 138.4, 137.2, 137.0, 133.8, 130.11, 130.0, 129.1 (2x), 126.7 (2x), 125.9, 125.1, 124.2, 120.8, 115.4, 115.3, 113.6, 105.3, 99.5, 71.8, 49.0, 40.5, 36.9, 34.5, 29.9, 24.2, 21.0, 19.4, 12.8 ppm.

IR (neat): ν = 2990, 2940, 2864, 1370, 1174, 1146, 1091, 725 cm^{-1}.

HRMS (ESI, *m/z*): $[M+H]^+$ calcd. for $C_{32}H_{36}O_4NS$, 530.2360; found 530.2359.

R_f = 0.48 (Hexane:EtOAc = 3:1), UV-active, green spot (*p*-anisaldehyde).

M.p. = 131 °C



(4a*R*,4b*R*,13b*S*,15a*S*)-2,2,4a,13b-Tetramethyl-4,4a,4b,8,13b,14,15,15a-octahydro-[1,3]-dioxino[5',4':5,6]naphtho[2,1-b]carbazole (12): A pyrex glass tube (11 cm tall, 1 cm diameter), equipped with a screw cap, was charged with a solution of acetonide **6** (57.0 mg, 0.108 mmol, 1.00 equiv) in 5% aq. ethanol (10.7 mL) and THF (1.20 mL). The vessel was degassed by bubbling a stream of nitrogen through the solution for 45 min. The pale yellow solution was then irradiated for 1 h with UV-A light (350 nm) in a Luzchem photobox at room temperature. After reducing the EtOH *in vacuo*, the residue was dissolved in EtOAc and water. The aq. layer was extracted three times with EtOAc and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Gradient flash chromatography (Yamazen, eluting with 5-26% EtOAc in hexanes) provided 19.0 mg (46%) of carbazole **12** as a yellow oil.

The stability of the product against irradiation with UV-A (350 nm) light was confirmed by irradiating 5 mg of **33** in 5% aq. EtOH (1.60 mL, 8.00 mM) for 2 h at room temperature. After the work-up described above, the material was fully recovered indicating no change by TLC and NMR analysis.

$[\alpha]_D^{22}$ –105.2 (c = 1.00, MeOH)

^{1}H-NMR (700 MHz, C_6D_6): δ = 8.09 (d, *J* = 8.2 Hz, 1H), 7.82 (s, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.85 (s, 1H), 6.69 (dd, *J* = 9.3, 2.7 Hz, 1H), 6.63 (br s, 1H), 5.70-5.65 (m, 1H), 3.68 (d, *J* = 10.6 Hz, 1H), 3.46 (dd, *J* = 11.7, 2.9 Hz, 1H),

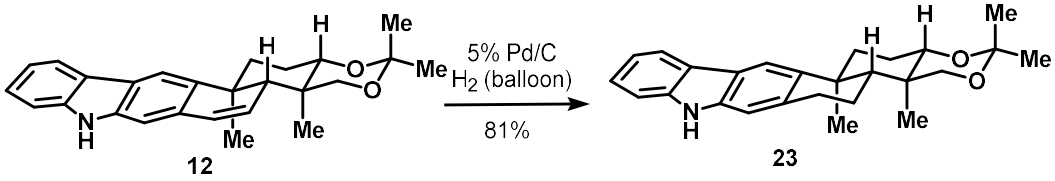
3.28 (d, *J* = 10.6 Hz, 1H), 2.08 (d, *J* = 12.8 Hz, 1H), 1.93-1.84 (m, 1H), 1.75-1.67 (m, 2H), 1.61 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.18 (s, 3H) ppm.

^{13}C-NMR (176 MHz, C_6D_6): δ = 140.7, 140.5, 138.4, 131.8, 130.0, 127.4, 125.8, 124.3, 123.2, 120.3, 119.8, 113.8, 111.0, 109.0, 99.3, 77.2, 71.9, 47.4, 38.3, 36.4, 35.1, 30.4, 24.8, 22.8, 19.5, 13.8 ppm.

IR (neat): ν = 3412, 2937, 2859, 1736, 1449, 1333, 1257, 1194, 811 cm^{-1}.

HRMS (ESI, *m*/*z*): [M–H]$^-$ calcd. for $C_{26}H_{28}O_2N$, 386.2117; found 386.2120.

R_f = 0.46 (Hexane:EtOAc = 3:1), UV-active, pink spot (*p*-anisaldehyde).



(4a*R*,4b*R*,13b*S*,15a*S*)-2,2,4a,13b-Tetramethyl-4,4a,4b,5,6,8,13b,14,15,15a-decahydro-[1,3]dioxino[5',4':5,6]naphtho[2,1-b]carbazole (23): Hydrogen from a balloon was bubbled through a mixture of carbazole **12** (19.0 mg, 0.0490 mmol, 1.00 equiv) and 5% Pd/C (11.5 mg, 0.110 mmol, 2.20 equiv) in MeOH (1.60 mL, 30.0 mM) for 1 min. The mixture was then vigorously stirred under an atmosphere of hydrogen (balloon) for 4 h at room temperature. After filtering the mixture through celite (EtOAc/MeOH eluent), the solution was concentrated *in vacuo* and the crude material was purified by gradient flash chromatography (Yamazen, eluting with 5-26% EtOAc in hexanes) to afford 15.0 mg (81%) of carbazole **23** as a colorless oil.

$[\alpha]_D^{22}$ +47.7 (c = 0.60, MeOH)

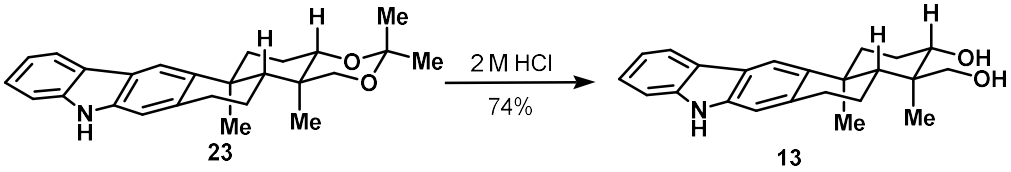
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.6 Hz, 1H), 7.93 (s, 1H), 7.84 (br s, 1H), 7.36 (d, *J* = 3.7 Hz, 2H), 7.19 (dt, *J* = 7.7, 3.9 Hz, 1H), 7.08 (s, 1H), 3.70-3.61 (m, 2H), 3.53 (d, *J* = 10.7 Hz, 1H), 3.19-3.11 (m, 1H), 3.09-2.99 (m, 1H), 2.63 (d, *J* = 12.5 Hz, 1H), 1.97-1.79 (m, 4H), 1.76-1.70 (m, 1H), 1.67-1.60 (m, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 1.33 (s, 3H), 1.22 (s, 3H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 141.9, 140.1, 138.2, 133.5, 125.5, 123.7, 122.0, 120.0, 119.3, 115.4, 110.6, 110.0, 99.2, 77.5, 72.7, 46.1, 38.2, 37.9, 37.2, 30.4, 30.0, 26.6, 24.7, 19.4, 18.3, 12.4 ppm.

IR (neat): ν = 2989, 2940, 1465, 1379, 1242, 1108, 853, 728 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{26}H_{30}NO_2$, 388.2282; found 388.2276.

R_f = 0.44 (Hexane:EtOAc = 3:1), UV-active, purple spot (*p*-anisaldehyde).



(3S,4R,4aR,13bS)-4-(hydroxymethyl)-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazol-3-ol (34):

To a solution of carbazole **23** (15.0 mg, 0.0380 mmol, 1.00 equiv) in THF (400 µL) was added 2.00 M aq. HCl (400 µL) and the mixture was vigorously stirred for 1 h at room temperature. The solution was quenched by the addition of sat. aq. $NaHCO_3$ at 0 °C. The mixture was warmed to room temperature and additional sat. aq. $NaHCO_3$ was added until the gas evolution ceased. Solid NaCl was added and the aq. layer was extracted five times with EtOAc and dried over $MgSO_4$. After removal of the solvent *in vacuo*, gradient flash chromatography (Yamazen, eluting with 50-70% EtOAc in hexanes) afforded 10.0 mg (74%) of diol **13** as a pale yellow oil.

$[\alpha]_D^{22}$ +58.4 (c = 0.50, MeOH)

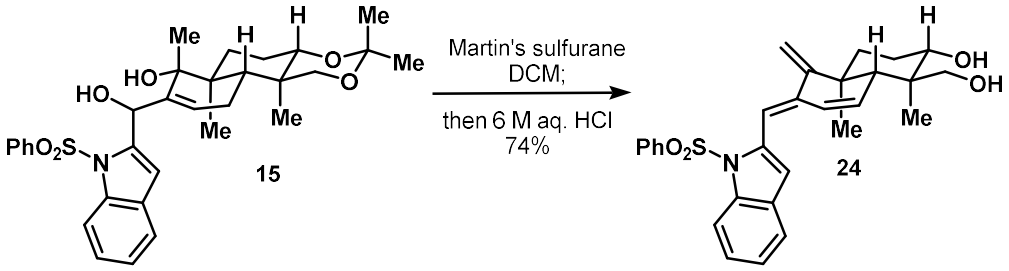
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 7.5 Hz, 1H), 7.94 (s, 1H), 7.84 (br s, 1H), 7.36 (d, *J* = 3.5 Hz, 2H), 7.19 (dt, *J* = 7.6, 3.9 Hz, 1H), 7.07 (s, 1H), 3.84 (d, *J* = 10.6 Hz, 1H), 3.80-3.75 (m, 1H), 3.52 (d, *J* = 10.6 Hz, 1H), 3.17-3.10 (m, 1H), 3.08-3.02 (m, 1H), 2.58-2.53 (m, 1H), 1.93-1.86 (m, 3H), 1.81-1.76 (m, 1H), 1.75-1.69 (m, 1H), 1.55 (d, *J* = 10.2 Hz, 1H), 1.33 (s, 3H), 1.07 (s, 3H) ppm.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 141.4, 140.0, 138.1, 133.5, 125.4, 123.6, 121.9, 119.9, 119.2, 115.6, 110.4, 109.7, 76.9, 72.3, 44.9, 42.2, 37.7, 37.4, 31.0, 27.8, 25.8, 19.3, 11.2 ppm.

IR (neat): ν = 3413, 2938, 2872, 1466, 1441, 1264, 1066, 1015, 732 cm^{-1}.

HRMS (ESI, *m*/*z*): [M–H]⁻ calcd. for $C_{23}H_{26}NO_2$, 348.1969; found 348.1963.

R_f = 0.25 (Hexane:EtOAc = 1:2), UV-active, blue spot (CAM).



(1*R*,2*S*,4a*S*,8a*R*,E)-1-(Hydroxymethyl)-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1*H*-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalen-2-ol (24): Martin's sulfurane (5.00 g, 7.44 mmol, 2.40 equiv) was added as a solid to a solution of alcohol **15** (1.76 g, 3.10 mmol, 1.00 equiv) in DCM (37.2 mL, 80.0 mM) at room temperature. After being stirred for 25 min, an aq. solution of 6 M HCl (37.2 mL) was added at 0 °C. The resulting brown solution was stirred at room temperature for 1.5 h before being quenched by the addition of sat. aq. $NaHCO_3$ at 0 °C. The mixture was warmed to room temperature and additional sat. aq. $NaHCO_3$ was added unter stirring until the gas evolution ceased. The mixture was transferred into a sep. funnel and solid NaCl was added. The aq. layer was then extracted four times with EtOAc and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the crude material was purified by gradient flash chromatography (Yamazen, eluting with 50-70% EtOAc in hexanes) affording 1.1 g (74%) of diol **24** as a yellow solid in 95% purity.

(1*R*,2*S*,4a*S*,8a*R*,E)-1-(Hydroxymethyl)-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1*H*-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalen-2-ol (24):

$[\alpha]_D^{22}$ –178.3 (c = 1.00, MeOH)

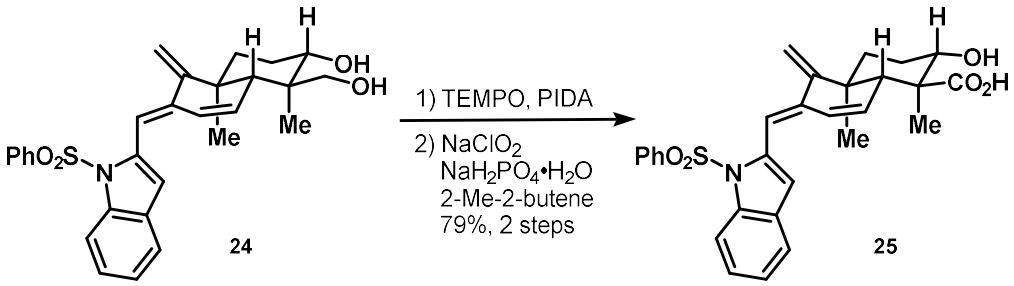
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.51-7.41 (m, 2H), 7.41-7.33 (m, 3H), 7.08 (s, 1H), 6.55 (s, 1H), 6.52 (d, *J* = 10.4 Hz, 1H), 5.72 (d, *J* = 10.1 Hz, 1H), 5.30 (s, 1H), 4.85 (s, 1H), 3.75 (d, *J* = 10.4 Hz, 2H), 3.47 (d, *J* = 10.6 Hz, 1H), 2.47 (br s, 2H), 2.18 (s, 1H), 1.93-1.74 (m, 4H), 1.11 (s, 3H), 1.00 (s, 3H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 156.7, 138.6, 138.5, 137.2, 137.1, 133.7, 131.1, 130.1, 129.1, 126.7, 125.9, 125.1, 124.2, 120.7, 115.3, 115.1, 113.6, 105.8, 76.7, 71.1, 47.6, 42.0, 40.2, 33.9, 27.5, 20.1, 11.6 ppm.

IR (neat): ν = 3382, 2935, 1447, 1370, 1174, 1090, 725 cm^{-1}.

R_f = 0.22 (Hexane:EtOAc = 1:2), UV-active, blue spot (CAM).

M.p. = 181 °C



(1*S*,2*S*,4a*S*,8a*R*,*E*)-2-Hydroxy-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1*H*-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalene-1-carbaldehyde (26): To a solution of diol **24** (706 mg, 1.45 mmol, 1.00 equiv) in DCM (11.9 mL) and H_2O (11.9 mL) was added TEMPO (294 mg, 1.88 mmol, 1.30 equiv), followed by PIDA (604 mg, 0.570 mmol, 1.30 equiv) as solids in one portion. The resulting orange-brown mixture was vigorously stirred for 4 h at room temperature before being quenched by the addition of sat. aq. $NaHCO_3$ and sat. aq. NaS_2O_3 (ca. 4:1). The mixture was transferred into a sep. funnel and solid NaCl was added. The aq. layer was then extracted four times with EtOAc, washed with sat. aq. NaCl, dried over $MgSO_4$, and filtered. After removal of the solvent *in vacuo*, this material was used in the next reaction without further purification. Alternatively the sample was purified by by gradient flash chromatography (Yamazen, eluting with 30-50% EtOAc in hexanes) affording 564 mg (80%) of aldehyde **25** as an orange foam

(1*S*,2*S*,4a*S*,8a*R*,*E*)-2-Hydroxy-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1*H*-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalene-1-carboxylic acid (25): To a solution of the crude aldehyde in acetone (13.9 mL), H_2O (6.90 mL), and 2-Me-2-butene (1.32 mL, 17.3 mmol, 12.0 equiv) was added a mixture of $NaClO_2$ (861mg, 9.50 mmol, 6.00 equiv, ~90% techn.) and NaH_2PO_4•H_2O (1.99 g, 14.4 mmol, 10.0 equiv) at 0 °C. The mixture was

warmed to room temperature and stirred for 2 h before being quenched by the addition of sat. aq. NaCl and sat. aq. NH_4Cl (ca. 1:1). The mixture was transferred into a sep. funnel and solid NaCl was added. The aq. layer was then extracted six times with EtOAc and dried over $MgSO_4$. After concentrating the solution *in vacuo*, the crude material was purified by gradient flash chromatography (Yamazen, eluting with 0-10% MeOH in DCM) to afford 569 mg (78%) of acid **25** as a yellow oil.

(1*S*,2*S*,4a*S*,8a*R*,*E*)-2-Hydroxy-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1*H*-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalene-1-carbaldehyde (26):

$[\alpha]_D^{22}$ –186.5 (c = 1.00, MeOH)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.50 (s, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.55-7.45 (m, 2H), 7.36 (q, *J* = 7.8 Hz, 3H), 7.29 (d, *J* = 9.3 Hz, 1H), 6.59 (s, 1H), 6.55 (dd, *J* = 10.0, 2.7 Hz, 1H), 5.46-5.36 (m, 2H), 4.93 (s, 1H), 3.96 (d, *J* = 9.6 Hz, 1H), 2.64 (s, 1H), 2.08-2.00 (m, 1H), 1.99-1.83 (m, 3H), 1.76 (br s, 1H), 1.22 (s, 3H), 1.16 (s, 3H) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 205.9, 155.9, 138.4, 138.1, 137.3, 136.7, 133.8, 130.1, 129.1 (3x), 126.7 (2x), 126.4, 125.2, 124.2, 120.8, 116.1, 115.3, 113.8, 106.1, 72.0, 54.7, 45.7, 39.1, 33.8, 27.1, 20.0, 9.8 ppm.

IR (neat): ν = 2932, 1722, 1447, 1368, 1173, 1119, 724 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{29}H_{28}NSO_4$, 486.1745; found 486.1743.

R_f = 0.21 (Hexane:EtOAc = 2:1), UV-active, blue spot (CAM).

(1*S*,2*S*,4a*S*,8a*R*,*E*)-2-Hydroxy-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1*H*-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalene-1-carboxylic acid (25):

$[\alpha]_D^{22}$ –173.6 (c = 0.50, MeOH)

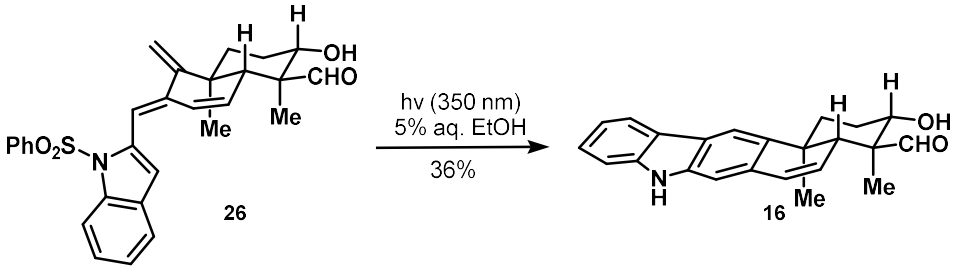
^{1}H-NMR (700 MHz, CD_3OD): δ = 8.19 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.39-7.34 (m, 2H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.01 (s, 1H), 6.62 (s, 1H), 6.51 (d, *J* = 9.7 Hz, 1H), 5.63 (d, *J* = 9.7 Hz, 1H), 5.29 (s, 1H), 4.90 (s, 1H), 4.12-4.07 (m, 1H), 2.74 (s, 1H), 1.92-1.82 (m, 4H), 1.20 (s, 3H), 1.12 (s, 3H) ppm.

^{13}C-NMR (176 MHz, CD_3OD): δ = 180.2, 158.7, 139.9, 139.4, 138.5, 138.1, 135.1, 133.3, 131.7, 130.2 (2x), 127.6 (2x), 126.4, 126.1, 125.3, 122.0, 116.2, 116.1, 114.8, 105.6, 75.7, 53.6, 50.9, 40.8, 35.2, 28.1, 20.7, 12.4 ppm.

IR (neat): ν = 3357, 2927, 1697, 1447, 1359, 1173, 1088, 970, 748, 685 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{29}H_{28}NO_5S$, 502.1694; found 502.1681.

R_f = 0.38 (7% MeOH in DCM), UV-active, blue spot (CAM).



(3*S*,4*S*,4a*R*,13b*S*)-3-Hydroxy-4,13b-dimethyl-2,3,4,4a,8,13b-hexahydro-1*H*-naphtho[2,1-b]carbazole-4-carbaldehyde (16): A pyrex glass tube (11 cm tall, 1 cm diameter), equipped with a screw cap, was charged with a solution of aldehyde **26** (90.0 mg, 0.184 mmol, 1.00 equiv) in 5% aq. ethanol (9.00 mL, 20.0 mM). The vessel was degassed by bubbling a stream of nitrogen through the solution for 45 min. The mixture was then irradiated for 4 h with UV-A light (350 nm) in a Luzchem photobox at room temperature. After reducing the EtOH *in vacuo*, the residue was dissolved in EtOAc and sat. aq. NaCl. The aq. layer was extracted four times with EtOAc and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo* the crude material was purified by gradient flash chromatography (Yamazen, eluting with 13-42% EtOAc in Hexanes) provided 23 mg (36%) of carbazole **16** as a white foam.

$[\alpha]_D^{22}$ –24.2 (c = 0.90, MeOH)

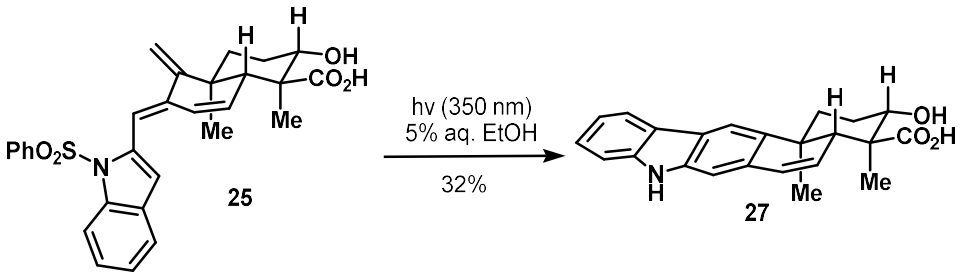
^{1}H-NMR (700 MHz, CD_3OD): δ = 9.48 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.99 (br s, 1H), 7.85 (s, 1H), 7.43-7.36 (m, 2H), 7.22 (t, *J* = 6.4 Hz, 1H), 7.13 (s, 1H), 6.71 (dd, *J* = 9.5, 2.9 Hz, 1H), 5.66 (dd, *J* = 9.5, 2.0 Hz, 1H), 3.98 (dd, *J* = 10.8, 4.2 Hz, 1H), 2.76 (s, 1H), 2.49 (d, *J* = 12.4 Hz, 1H), 2.12-2.07 (m, 1H), 2.07-1.95 (m, 2H), 1.62 (br s, 1H), 1.34 (s, 3H), 1.19 (s, 3H) ppm.

^{13}C-NMR (176 MHz, CD_3OD): δ = 206.3, 140.2, 139.1, 138.1, 131.2, 130.7, 127.1, 125.9, 123.7, 123.0, 120.1, 119.7, 113.8, 110.8, 109.1, 71.8, 54.5, 44.5, 37.2, 34.5, 27.3, 22.0, 10.3 ppm.

IR (neat): ν = 3294, 2937, 2825, 1717, 1242, 1023, 716 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{23}H_{22}NO_2$, 344.1656; found 344.1653.

R_f = 0.25 (Hexane:EtOAc = 2:1), UV-active, blue spot (CAM).



(3*S*,4*S*,4a*R*,13b*S*)-3-Hydroxy-4,13b-dimethyl-2,3,4,4a,8,13b-hexahydro-1*H*-naphtho-[2,1-b]carbazole-4-carboxylic acid (27): A pyrex glass tube (11 cm tall, 1 cm diameter), equipped with a screw cap, was charged with a solution of acid **25** (43mg, 0.085 mmol, 1.0 equiv) in 5% aq. ethanol (9.50 mL). The vessel was degassed by bubbling a stream of nitrogen through the solution for 45 min. The mixture was then irradiated for 1.5 h with UV-A light (350 nm,) in a Luzchem photobox at room temperature. After reducing the EtOH *in vacuo*, the residue was dissolved in EtOAc, water, and sat. aq. NaCl. The aq. layer was extracted six times with EtOAc and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude material was purified by gradient flash chromatography (Yamazen, eluting with 0-10% MeOH in DCM) to afford 10 mg (32%) of acid **27** as a pale yellow solid.

The stability of the product against irradiation with UV-A (350 nm) light was confirmed by irradiating 5.0 mg of **27** in 5% aq. EtOH (1.7 mL, 0.0080 M) for 2 h at room temperature. After the work-up described above, the material was fully recovered indicating no change by TLC and NMR analysis.

$[\alpha]_D^{22}$ –6.9 (c = 1.00, MeOH)

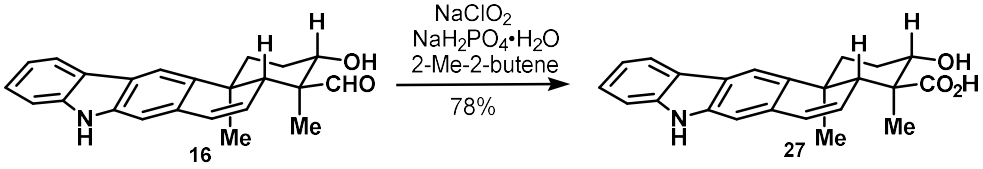
^{1}H-NMR (700 MHz, CD_3OD): δ = 8.00 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.14-7.10 (m, 2H), 6.70 (dd, *J* = 9.7, 2.7 Hz, 1H), 5.80 (d, *J* = 9.7 Hz, 1H), 4.18 (dd, *J* = 11.7, 4.2 Hz, 1H), 2.83 (br s, 1H), 2.49 (d, *J* = 12.4 Hz, 1H), 2.04-1.98 (m, 3H), 1.35 (s, 3H), 1.15 (s, 3H) ppm.

^{13}C-NMR (176 MHz, CD_3OD): δ = 180.6, 142.0, 140.2, 139.9, 132.3, 131.0, 128.9, 126.2, 124.7, 123.8, 120.7, 119.6, 114.1, 111.6, 109.8, 75.7, 53.5, 49.6, 38.7, 35.9, 28.5, 22.3, 12.9 ppm.

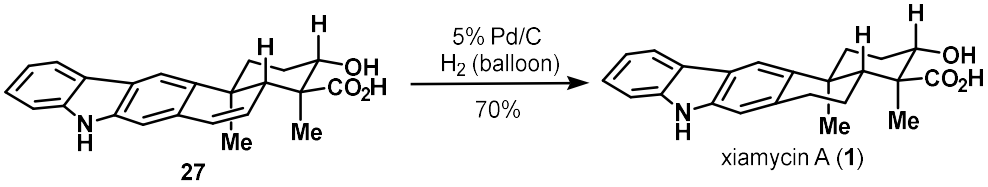
IR (neat): ν = 2926, 1699, 1447, 1371, 1243, 1144, 1075, 734, 588 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{23}H_{22}NO_3$, 360.1605; found 360.1598.

R_f = 0.35 (7% MeOH in DCM), UV-active, blue spot (CAM).



(3*S*,4*S*,4a*R*,13b*S*)-3-Hydroxy-4,13b-dimethyl-2,3,4,4a,8,13b-hexahydro-1*H*-naphtho-[2,1-b]carbazole-4-carboxylic acid (27): To a solution of the aldehyde **16** (90.7 mg, 0.263 mmol, 1.00 equiv) in acetone (3.50 mL), H_2O (1.75 mL), and 2-Me-2-butene (335 μL, 3.16 mmol, 12.0 equiv) was added a mixture of $NaClO_2$ (143 mg, 1.58 mmol, 6.00 equiv, ~90% techn.) and NaH_2PO_4•H_2O (363 mg, 2.63 mmol, 10.0 equiv) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h before being quenched by the addition of sat. aq. NaCl and sat. aq. NH_4Cl (ca. 1:1). The mixture was transferred into a sep. funnel and solid NaCl was added. The aq. layer was then extracted six times with EtOAc and dried over $MgSO_4$. After concentrating the solution *in vacuo*, the crude material was purified by gradient flash chromatography (Yamazen, eluting with 0-10% MeOH in DCM) to afford 74 mg (78%) of acid **27** as a yellow foam.



Xiamycin A (10): Hydrogen from a balloon was bubbled through a mixture of carbazole **27** (10 mg, 0.027 mmol, 1.0 equiv) and 5% Pd/C (9.0 mg, 0.080 mmol, 3.0 equiv) in MeOH (900 μL) for 1 min. The mixture was then vigorously stirred under an atmosphere of hydrogen (balloon) for 3.5 h at room temperature. After filtering the mixture through celite (EtOAc/MeOH eluent), the solution was concentrated *in vacuo* and the crude material was purified by preparative thin layer chromatography (10% MeOH in DCM) to afford 7 mg (70%) of xiamycin A **(10)** as a pale yellow solid. The hydrogenation reaction can also be performed using crude carbazole **27** to give xiamycin A in the same overall yield (22%, 2 steps, 1 purification).

[α]D22 +123.5 (c = 0.40, MeOH); lit.[2] **[α]D23** +137.6 (c = 0.40, MeOH)

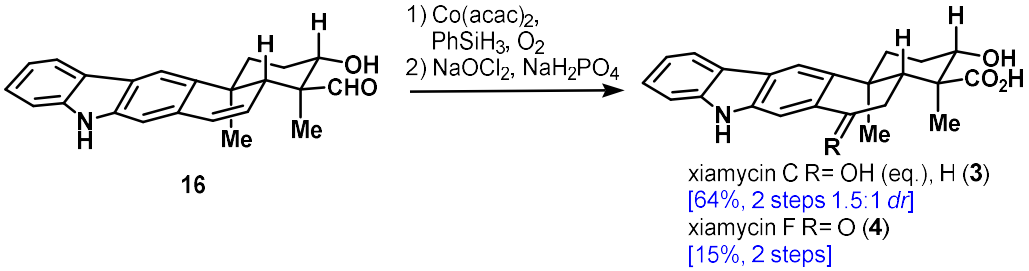
1H-NMR (700 MHz, CD_3OD): δ = 7.97 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 4.10 (dd, *J* = 10.5, 7.5 Hz, 1H), 3.15-3.08 (m, 1H), 3.08-2.99 (m, 1H), 2.64 (d, *J* = 12.8 Hz, 1H), 2.14 (d, *J* = 11.8 Hz, 1H), 2.08-1.98 (m, 1H), 1.93-1.88 (m, 2H), 1.78-1.72 (m, 1H), 1.58-1.53 (m, 1H), 1.30 (s, 3H), 1.25 (s, 3H) ppm.

13C-NMR (176 MHz, CD_3OD): δ = 181.3, 142.0, 141.8, 140.1, 134.0, 126.0, 124.6, 123.1, 120.6, 119.3, 116.4, 111.4, 110.8, 76.3, 54.9, 47.9, 39.0, 32.1, 28.7, 26.3, 22.6, 11.4 ppm.

IR (neat): ν = 3409, 2932, 1694, 1465, 1242, 1066 cm^{-1}.

HRMS (ESI, *m/z*): $[M–H]^-$ calcd. for $C_{23}H_{24}NO_3$, 362.1762; found 362.1754.

Rf = 0.25 (7% MeOH in DCM), UV-active, blue spot (CAM).



Xiamycin C and F (10): Oxygen from a balloon was bubbled through a mixture of carbazole **45** (15 mg, 0.043 mmol, 1.0 equiv), $Co(acac)_2$ (3.3 mg, 0.013 mmol, 0.30 equiv), and $PhSiH_3$ (8.0 ul, 0.067 mmol, 1.5 equiv) in THF (900 µL) for 1 min. The mixture was then stirred under an atmosphere of oxygen (balloon) for 12 h at room temperature. This mixture was then filtered through a silica plug with EtOAc and concentrated *in vacuo*. The crude mixture of diastereomeric alcohols and ketone was then directly subjected Pinnick oxidation conditions as the crude mixture decomposed upon all attempts at characterization and separation. The hydration reaction can also be performed with HFIP as the solvent which led to increased relative yield of the alcohols, and a shorter reaction time of 1 hour.

To a solution of the crude aldehydes in acetone (0.8 mL), H_2O (0.4 mL), and 2-Me-2-butene (115 µL, 1.1 mmol, 25 equiv) was added a mixture of $NaClO_2$ (27 mg, 0.3 mmol, 7.0 equiv, ~90% techn.) and $NaH_2PO_4•H_2O$ (60 mg, 0.44 mmol, 10 equiv) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h before being quenched by the addition of sat.

aq. NaCl and sat. aq. NH_4Cl (ca. 1:1). The mixture was transferred into a sep. funnel and solid NaCl was added. The aq. layer was then extracted six times with EtOAc and dried over $MgSO_4$. After concentrating the solution in vacuo, the crude material was purified by preporatory thin layer chromatography (95:5:1 DCM:MeOH:AcOH) to afford 10.4 mg (64% 1.5:1 *dr*) xiamycin C as an amorphous yellow solid, and 2.4 mg (16%) xiamycin F as an amorphous yellow solid. Notably, the choice of solvent in the Mukaiyama hydration had a dramatic effect on the product distribution. Using HFIP led to the exclusive formation of the alcohols (i.e., 3 and its C19 epimer) in 90% yield

Xiamycin C (3):

$[\alpha]_D^{22}$ +120.6 (c = 0.10, MeOH); lit.[x] **$[\alpha]_D^{20}$** +123.6(c = 0.1, MeOH)

^{1}H-NMR (600 MHz, CD_3OD) δ8.00 (d, J = 7.7 Hz, 1H),7.94 (s, 1H), 7.58 (s, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.31 (dd, J = 7.9, 8.0 Hz, 1H), 7.10 (d, J = 7.9, 8.0 Hz 1H), 4.89 (m, 1H), 4.09 (dd, J = 8.0, 6.6 Hz, 1H), 2.63 (ddd, J = 13.2, 3.4, 3.2, Hz, 1H), 2.19 (d, J = 12.6 Hz, 1H) ,2.09 – 1.95 (m, 2H), 1.93 – 1.82 (m, 3H), 1.75 – 1.65 (m, 1H), 1.38 (s, 3H),1.26 (s, 3H).

^{13}C-NMR (151MHz, CD_3OD): δ = 180.4, 142.3, 142.1, 140.1, 137.9, 126.3, 124.5, 124.0, 120.8, 119.3, 116.3, 111.5, 110.1, 76.8, 72.3, 55.1, 46.0, 39.2, 39.0, 33.3, 28.4, 26.9, 12.7.

IR (neat): ν = 3670, 2932, 1684, 1352, 1242, 1066 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{23}H_{24}NO_4$, 378.1711; found 378.1708.

R_f = 0.18 (10% MeOH in DCM), UV-active, blue spot (CAM).

C19epi-Xiamycin C:

$[\alpha]_D^{22}$ +117.2 (c = 0.40, MeOH);

^{1}H-NMR (700 MHz, CD_3OD): δ = 7.97 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 4.10 (dd, *J* = 10.5, 7.5 Hz, 1H), 3.15-3.08 (m, 1H), 3.08-2.99 (m, 1H), 2.64 (d, *J* = 12.8 Hz, 1H), 2.14 (d, *J* = 11.8 Hz, 1H), 2.08-1.98 (m, 1H), 1.93-1.88 (m, 2H), 1.78-1.72 (m, 1H), 1.58-1.53 (m, 1H), 1.30 (s, 3H), 1.25 (s, 3H) ppm.

^{13}C-NMR (176 MHz, CD_3OD): δ = 181.3, 142.0, 141.8, 140.1, 134.0, 126.0, 124.6, 123.1, 120.6, 119.3, 116.4, 111.4, 110.8, 76.3, 54.9, 47.9, 39.0, 32.1, 28.7, 26.3, 22.6, 11.4 ppm.

IR (neat): ν = 3409, 2932, 1694, 1465, 1242, 1066 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{23}H_{24}NO_4$, 378.1711; found 378.1708.

R_f = 0.14 (10% MeOH in DCM), UV-active, blue spot (CAM).

Xiamycin F (4):

[α]D22 +130.1 (c = 0.40, MeOH)

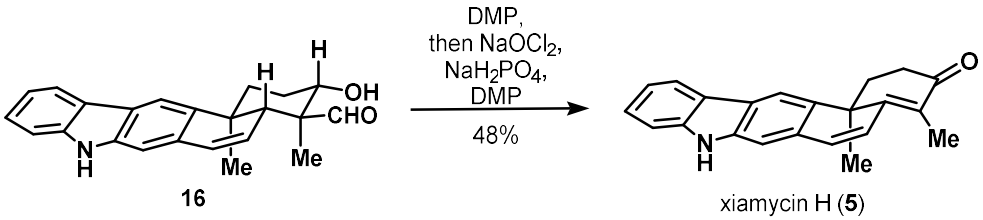
1H-NMR (700 MHz, CD_3OD): δ = 7.97 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 4.10 (dd, *J* = 10.5, 7.5 Hz, 1H), 3.15-3.08 (m, 1H), 3.08-2.99 (m, 1H), 2.64 (d, *J* = 12.8 Hz, 1H), 2.14 (d, *J* = 11.8 Hz, 1H), 2.08-1.98 (m, 1H), 1.93-1.88 (m, 2H), 1.78-1.72 (m, 1H), 1.58-1.53 (m, 1H), 1.30 (s, 3H), 1.25 (s, 3H) ppm.

13C-NMR (226 MHz, CD_3OD): δ = 201.1, 180.1, 147.7, 144.0, 139.6, 130.1, 129.4, 128.8, 123.8, 122.3, 120.4, 116.2, 112.3, 110.7, 76.0, 54.3, 46.9, 38.8, 38.7, 38.3, 28.4, 24.9, 11.1

IR (neat): ν = 3411, 2945, 1694, 1646, 1470, 1240, 1070 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{23}H_{22}NO_4$, 376.1554; found 376.1552.

Rf = 0.34 (10% MeOH in DCM), UV-active, blue spot (CAM).



Xiamycin H (5): Dess-Martin periodinane (14 mg, 0.032 mmol, 1.1 equiv) (DMP) was added to a solution of carbazole **16** (10 mg, 0.029 mmol, 1.0 equiv) in DCM (900 µL). The mixture was then vigorously stirred at room temperature for 30 minutes. To this mixture mixture was added acetone (900 µL), water (450 µL) and 2-Me-2-butene (85 µL, 0.8 mmol, 25 equiv), followed by $NaOCl_2$ (18 mg, 0.3 mmol, 7.0 equiv, ~90% techn.), $NaH_2PO_4•H_2O$ (40 mg, 0.29 mmol, 10 equiv), and DMP (25 mg, 0.058 mmol, 2 equiv). This yellow heterogenous mixture was stirred vigorously at room temperature for 3 hours. The reaction mixture was diluted with sat. aq. NaCl and extracted 3 times with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by preparative thin layer chromatography (30% EtOAc in Hexanes) to afford 4.3 mg (48%) of xiamycin H (**5**) as a bright yellow amorphous solid.

Comparison of the spectral data for xiamycin H to the natural sample[5] showed strong agreement in the ^{1}H-NMR, but poor resolution made comparison of the ^{13}CNMR difficult (presumably due to its sparing solubility in CD_3OD).

[α]D^{22} +41.5 (c = 0.40, $CHCl_3$);

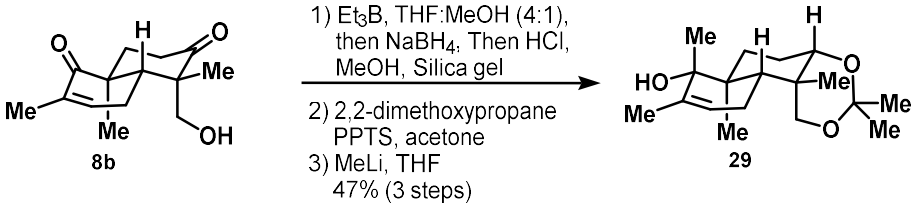
^{1}H-NMR (600 MHz, CD_3OD) δ = 8.16 (s, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 9.8 Hz, 1H), 6.76 (d, *J* = 9.8 Hz, 1H), 3.00 – 2.95 (m, 1H), 2.89 – 2.82 (m, 1H), 2.71 – 2.64 (m, 1H), 2.38 – 2.32, 1.92 (s, 3H), 1.49 (s, 3H).

^{13}C NMR (151 MHz, MeOD) δ = 200.5, 160.2, 156.3, 142.5, 140.1, 137.8, 136.6, 130.1, 129.4, 127.0, 125.0, 124.3, 123.4, 121.1, 120.0, 116.5, 111.8, 40.6, 35.1, 34.9, 31.3, 10.6.

IR (neat): ν = 2932, 1644, 1602, 1558, 1465, 1242, 1066 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{22}H_{18}NO$, 312.1394; found 312.1392.

R_f = 0.4 (33% EtOAc in Hexanes), UV-active, visibly yellow spot.



(4a*S*,5*S*,6*S*,8a*S*)-6-hydroxy-5-(hydroxymethyl)-2,5,8a-trimethyl-4a,5,6,7,8,8a-hexahydronaphthalen-1(4H)-one (18): Et_3B (7.81 mL of a 1.00M THF solution, 1.10 equiv) was added to a mixture of THF (56.8 mL) and MeOH (14.2 mL) under a N_2 atmosphere and the resulting colorless solution was stirred for 1 hour at room temperature. The solution was cooled to –78 °C after which 1.70 g of ketone **8b** (7.10 mmol, 1.00 equiv) in THF (10.0 mL) was added dropwise and stirred at –78 °C for 30 minutes. $NaBH_4$ (402 mg, 10.6 mmol, 1.50 equiv) was added as a solid and the resulting solution was stirred at –78 °C for 3 hours. The solution was diluted with EtOAc and quenched by the addition of sat. aq. NH_4Cl. The aq. layer was extracted three time with EtOAc and the combined organic layers were washed with sat. aq. NaCl, and dried over $MgSO_4$. After the removal of solvent *in vacuo* the resulting boronate ester was loaded onto a silica gel column that was further acidifed with conc. HCl, and eluted with methanol. After removal of solvent *in vacuo* this material was used in the next reaction without further purification. An analytical sample was prepared by flash column chromatography (PE:EtOAc = 1:1) to afford diol **18** as a white solid. Suitable crystals for X-ray analysis were obtained after crystallization from a Hexane/EtOAc (1:1) solution.

(4a*S*,6a*S*,10a*S*,10b*S*)-3,3,6a,8,10b-pentamethyl-1,4a,5,6,6a,10,10a,10b-octahydro-7H-naphtho[2,1-d][1,3]dioxin-7-one (28): To a solution of crude diol in acetone (98.0 mL, 80.0 mM) was added PPTS (490 mg, 1.95 mmol, 0.250 equiv), followed by 2,2-dimethoxypropane (9.80 mL, 78.1 mmol, 10.0 equiv) at room temperature. After stirring for 14 h, the reaction mixture was quenched by the addition of sat. aq. $NaHCO_3$. The aq. layer was extracted three times with EtOAc, washed with sat. aq. NaCl solution and dried over $MgSO_4$. After removal of the solvent *in vacuo*, this material was used in the next reaction without further purification. An analytical sample was prepared by flash column chromatography (PE:EtOAc = 3:1) to afford acetonide **28** as a white solid.

(4a*S*,6a*S*,7*S*,10a*S*,10b*S*)-3,3,6a,7,8,10b-hexamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1H-naphtho[2,1-d][1,3]dioxin-7-ol (29): MeLi (10.7 mL of a 1.60 M Et_2O solution, 17.2 mmol, 2.20 equiv) was added dropwise to a solution of the crude acetonide in THF (78.0 mL, 0.100 M) at –78 °C. After being stirred for 1.5 h at –78 °C, the reaction mixture was quenched by the addition of sat. aq. NH_4Cl. The aq. layer was extracted three times with EtOAc, washed with sat. aq. NaCl solution and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was purified by gradient flash chromatography (Yamazen, eluting with 13-34% EtOAc in hexanes) to afford 1.09 g (47%, over 3 steps) of alcohol **29** as a white solid.

(4a*S*,5*S*,6*S*,8a*S*)-6-hydroxy-5-(hydroxymethyl)-2,5,8a-trimethyl-4a,5,6,7,8,8a-hexahydronaphthalen-1(4H)-one (18):

$[\alpha]_D^{22}$ –28.2 (c = 1.00, MeOH)

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 6.67 (dt, *J* = 6.1, 1.9 Hz, 1H), 4.26 (d, *J* = 11.0 Hz, 1H), 3.72 (s, 2H), 3.48 (d, *J* = 11.0 Hz, 1H), 3.45-3.36 (m, 1H), 2.43-2.30 (m, 1H), 2.19 (ddt, *J* = 19.0, 11.7, 2.5 Hz, 1H), 1.91 (d, *J* = 14.1 Hz, 1H), 1.86-1.76 (m, 2H), 1.70 (dt, *J* = 2.8, 1.4 Hz, 3H), 1.64 (dd, *J* = 11.7, 4.2 Hz, 1H), 1.51-1.40 (m, 1H), 1.21 (s, 3H), 0.95 (s, 3H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$) δ = 205.2, 143.8, 133.0, 80.0, 64.4, 48.8, 44.4, 42.5, 31.5, 27.3, 23.9, 21.9, 18.1, 16.3 ppm.

IR (neat): ν = 3417, 2944, 1660, 1353, 1032, 991, 739, 547 cm^{-1}.

HRMS (EI, *m*/*z*): $[M]^+$ calcd. for $C_{14}H_{22}O_3$, 238.1569; found 238.1572.

R_f = 0.22 (Hexane:EtOAc = 1:3), UV-active, blue spot (CAM).

M.p. = 136 °C

(4a*S*,6a*S*,10a*S*,10b*S*)-3,3,6a,8,10b-pentamethyl-1,4a,5,6,6a,10,10a,10b-octahydro-7H-naphtho[2,1-d][1,3]dioxin-7-one (28):

[α]D22 –42.7 (c = 1.00, MeOH)

^{1}H-NMR (700 MHz, $CDCl_3$) δ = 6.64 (d, *J* = 5.9 Hz, 1H), 4.06 (d, *J* = 11.4 Hz, 1H), 3.47 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.28 (d, *J* = 11.5 Hz, 1H), 2.30 (dt, *J* = 18.9, 5.1 Hz, 1H), 2.16 (ddt, *J* = 18.8, 11.8, 2.5 Hz, 1H), 1.96 (dtd, *J* = 13.2, 8.1, 4.6 Hz, 1H), 1.88 (ddd, *J* = 13.5, 7.9, 5.2 Hz, 1H), 1.78 (ddd, *J* = 13.9, 8.4, 4.6 Hz, 1H), 1.74 (d, *J* = 2.7 Hz, 3H), 1.69 (dt, *J* = 12.0, 5.4 Hz, 2H), 1.42 (s, 3H), 1.36 (s, 3H), 1.18 (s, 6H) ppm.

^{13}C-NMR (176 MHz, $CDCl_3$) δ = 204.7, 142.6, 133.4, 99.2, 75.7, 64.2, 45.9, 44.0, 37.7, 27.8, 26.9, 25.2, 25.1, 24.2, 23.3, 19.8, 16.5 ppm.

IR (neat): ν = 2988, 2949, 2876, 1670, 1445, 1432, 1247, 1153, 1077, 864 cm^{-1}.

HRMS (EI, *m*/*z*): $[M+H]^+$ calcd. for $C_{17}H_{27}O_3$, 279.1960; found 279.1959.

R_f = 0.49 (Hexane:EtOAc = 2:1), UV-active, blue spot (CAM).

(4a*S*,6a*S*,7*S*,10a*S*,10b*S*)-3,3,6a,7,8,10b-hexamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1H-naphtho[2,1-d][1,3]dioxin-7-ol (29):

[α]D22 –33.2 (c = 1.00, MeOH)

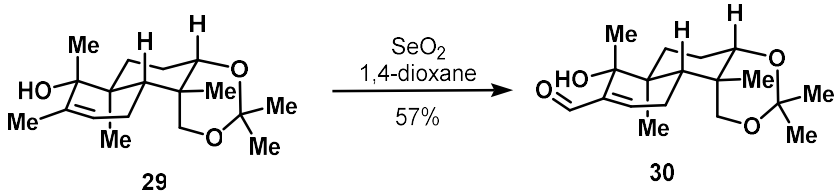
^{1}H-NMR (600 MHz, $CDCL_3$) δ = 5.33 (ddt, *J* = 3.8, 2.5, 1.4 Hz, 1H), 4.08 (d, *J* = 11.4 Hz, 1H), 3.51 (dd, *J* = 7.9, 3.1 Hz, 1H), 3.23 (d, *J* = 11.4 Hz, 1H), 1.98 (dd, *J* = 17.4, 1.6 Hz, 1H), 1.94-1.88 (m, 1H), 1.82-1.73 (m, 1H), 1.72-1.50 (m, 8H), 1.42 (s, 3H), 1.37 (s, 3H), 1.28 (s, 3H), 1.17 (s, 3H), 1.11 (s, 3H) ppm.

^{13}C-NMR (151 MHz, CDCl3) δ 138.68, 121.41, 98.99, 78.09, 76.02, 64.14, 42.44, 39.35, 37.37, 27.37, 26.59, 26.09, 25.19, 25.11, 23.09, 22.88, 17.97, 17.83 ppm.

IR (neat): ν = 3511, 2986, 2961, 2952, 2897, 1454, 1378, 1250, 1098 cm^{-1}.

HRMS (EI, *m*/*z*): $[M]^+$ calcd. for $C_{18}H_{30}O_3$, 294.2195; found 294.2199.

R_f = 0.46 (Hexane:EtOAc = 2:1), non UV-active, blue spot (CAM).



29 30

(4a*S*,6a*S*,7*R*,10a*S*,10b*S*)-7-hydroxy-3,3,6a,7,10b-pentamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1H-naphtho[2,1-d][1,3]dioxine-8-carbaldehyde (29): A mixture of alcohol **29** (1.00 g, 3.40 mmol, 1.00 equiv) and selenium dioxide (940 mg, 8.50 mmol, 2.50 equiv) was dissolved in 1,4-dioxane (34.0 mL, 0.100 M) and then placed in an oil bath at 90 °C. After stirring for 2 h, the resulting brown mixture was cooled to room temperature and quenched by the addition of distilled water. The aq. phase was extracted three times with EtOAc and the combined organic layers were washed with sat. aq. NaCl solution. The solution was dried over $MgSO_4$ and concentrated *in vacuo*. The crude products were purified by gradient flash chromatography (Yamazen, eluting with 13-34% EtOAc in hexanes) to afford 600 mg of aldehyde **30** (57%) as an orange solid, in this case no allylic alcohol was isolated.

(4a*S*,6a*S*,7*R*,10a*S*,10b*R*)-7-Hydroxy-3,3,6a,7,10b-pentamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1*H*-naphtho[2,1-d][1,3]dioxine-8-carbaldehyde (30):

$[\alpha]_D^{22}$ –119.1 (c = 1.00, MeOH)

^{1}H-NMR (500 MHz, $CDCl_3$) δ = 9.39 (s, 1H), 6.73 (dd, *J* = 4.7, 2.5 Hz, 1H), 4.14 (d, *J* = 11.3 Hz, 1H), 3.57 (dd, *J* = 7.8, 2.8 Hz, 1H), 3.28 (d, *J* = 11.3 Hz, 1H), 2.45 (dt, *J* = 20.4, 5.0 Hz, 1H), 2.26-2.16 (m, 1H), 1.94 (dd, *J* = 13.7, 5.6 Hz, 1H), 1.86 -1.77 (m, 1H), 1.69 (ddt, *J* = 17.3, 12.1, 7.1 Hz, 3H), 1.45 (d, *J* = 4.9 Hz, 6H), 1.41 (s, 3H), 1.23 (s, 3H), 1.16 (s, 3H) ppm.

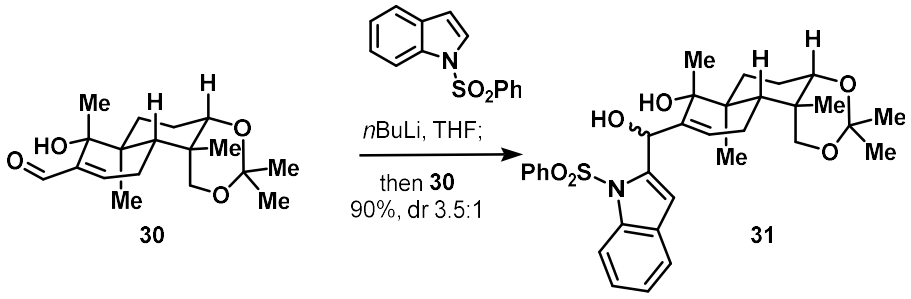
^{13}C-NMR (176 MHz, $CDCl_3$) δ 196.24, 151.67, 144.98, 99.27, 76.08, 75.61, 64.00, 41.22, 39.01, 37.32, 26.45, 26.33, 26.08, 25.17, 24.92, 24.87, 18.18 ppm.

IR (neat): ν = 3515, 2988, 2944, 2899, 1739, 1670, 1638, 1457, 1286, 1221, 1208, 1157, 863 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{18}H_{27}O_4$, 307.1915; found 307.1916.

R_f = 0.54 (Hexane:EtOAc = 1:1), UV-active, blue spot (CAM).

M.p. = 184°C



(4a*S*,6a*S*,7*R*,10a*S*,10b*S*)-8-(hydroxy(1-(phenylsulfonyl)-1H-indol-2-yl)methyl)-3,3,6a,7,10b-pentamethyl-4a,5,6,6a,7,10,10a,10b-octahydro-1H-naphtho[2,1-d][1,3]dioxin-7-ol (31): Trace water was removed from 1-(phenylsulfonyl)-1*H*-indole (1.17 g, 4.55 mmol, 3.50 equiv) via azeotropic distillation with benzene. Then, it was dissolved in THF (30.0 mL) and cooled to –78°C. A solution of *n*BuLi (2.80 ml of a 1.60 M solution in pentane, 4.49 mmol, 3.45 equiv) was added dropwise. The yellow solution was stirred at 0 °C for 1 h. During this time, trace water was removed from aldehyde **30** (400 mg, 1.30 mmol, 1.00 equiv) via azeotropic distillation with benzene. Then it was dissolved in THF (8.00 mL) and added via cannula transfer into the solution containing the 2-lithio-indole over the course of 5 minutes at –78°C. After stirring the resulting solution at –78°C for 1 h, the solution was warmed to 0 °C and stirred additional 1 h before being quenched with sat. aq. NH_4Cl. The aq. layer was extracted three times with EtOAc and the combined organic layers were washed with sat. aq. NaCl, dried over $MgSO_4$, filtered, and concentrated. The residue was purified via gradient flash chromatography (Yamazen, eluting with 46-67% EtOAc in hexanes) to yield a mixture of diastereomers of alcohol **31** as a yellow foam (661 mg, 90% combined yield, *dr* = 3.5:1) which was used in the next reaction. Analytical samples were prepared via gradient flash chromatography (Yamazen, eluting with 39-59% EtOAc in hexanes).

Major isomer:

$[\alpha]_D^{22}$ –25.4 (c = 1.00, MeOH)

^{1}H-NMR (700 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.4 Hz, 1H), 7.80-7.75 (m, 2H), 7.56-7.50 (m, 2H), 7.45-7.39 (m, 2H), 7.34-7.30 (m, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.19 (s, 1H), 5.15 (dd, *J* = 4.8, 2.5 Hz, 1H), 4.07 (d, *J* = 11.5 Hz, 2H), 3.56 (dd, *J* = 7.7, 3.1 Hz, 1H), 3.20 (d, *J* = 11.4 Hz, 1H), 2.33 (s, 1H), 2.02-1.91 (m, 2H), 1.79-1.62 (m, 6H), 1.59 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 1.28 (s, 1H), 1.21 (s, 3H), 1.17 (s, 3H) ppm.

^{13}C-NMR (176 MHz, CDCl3) δ = 142.2, 142.0, 138.6, 137.5, 133.7, 129.5, 129.2, 126.3, 125.6, 124.6, 123.9, 121.0, 114.9, 112.4, 99.2, 79.9, 75.7, 67.9, 64.1, 60.4, 41.8, 39.7, 37.5, 27.1, 26.4, 26.0, 25.3, 25.0, 24.6, 22.8, 18.2, 14.2 ppm.

IR (neat): ν = 3460, 2986, 2933, 1447, 1372, 1173, 1091, 1020, 726, 592 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{32}H_{38}NO_6S$, 564.2425; found 564.2422.

R_f = 0.35 (Hexane:EtOAc = 1:1), UV-active, blue spot (CAM).

Minor isomer:

$[\alpha]_D^{22}$ +31.1 (c = 0.4, MeOH)

^{1}H NMR (500 MHz, Chloroform-d) δ 8.08 (d, J = 8.3 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.56 – 7.51 (m, 1H), 7.49 – 7.41 (m, 3H), 7.30 (dd, J = 7.3, 1.4 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 6.78 (s,

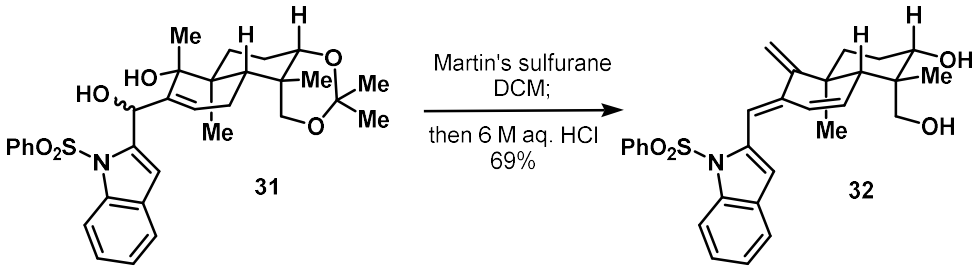
1H), 6.05 (d, J = 5.4 Hz, 1H), 5.82 (dd, J = 4.9, 2.4 Hz, 1H), 4.08 (d, J = 11.3 Hz, 1H), 3.54 (dd, J = 7.3, 3.1 Hz, 1H), 3.22 (d, J = 11.2 Hz, 1H), 2.96 (d, J = 5.6 Hz, 1H), 2.14 (dt, J = 18.2, 4.9 Hz, 1H), 1.93 (d, J = 18.0 Hz, 3H), 1.74 (dd, J = 11.7, 5.0 Hz, 2H), 1.68 – 1.59 (m, 2H), 1.44 (d, J = 16.4 Hz, 9H), 1.17 (d, J = 7.4 Hz, 6H) ppm.

^{13}C-NMR (151 MHz, $CDCl_3$): δ = 144.2, 143.5, 138.4, 137.6, 134.1, 129.5, 129.1, 126.7, 126.2, 125.1, 124.1, 121.2, 114.9, 111.3, 99.4, 78.2, 75.5, 66.2, 64.5, 42.1, 39.8, 37.7, 27.0, 26.3, 26.2, 25.3, 25.1, 24.4, 23.2, 18.7 ppm.

IR (neat): ν = 3460, 2986, 2933, 1447, 1372, 1173, 1091, 1020, 726, 592 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M+Na]^+$ calcd. for $NaC_{32}H_{37}NO_6S$, 588.2390; found 588.2396.

R_f = 0.33 (Hexane:EtOAc = 1:1), UV-active, blue spot (CAM).



(1*S*,2*S*,4a*S*,8a*R*,*E*)-1-(hydroxymethyl)-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1H-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalen-2-ol (32): Martin's sulfurane (1.43 g, 2.12 mmol, 2.40 equiv) was added as a solid to a solution of alcohol **31** (500 mg, 0.885 mmol, 1.00 equiv) in DCM (8.90 mL, 0.100 M) at room temperature. After being stirred for 25 min, an aq. solution of 6 M HCl (8.90 mL) was added at 0 °C. The resulting brown solution was stirred at room temperature for 1.5 h before being quenched by the addition of sat. aq. $NaHCO_3$ at 0 °C. The mixture was warmed to room temperature and additional sat. aq. $NaHCO_3$ was added unter stirring until the gas evolution ceased. The mixture was transferred into a sep. funnel and solid NaCl was added. The aq. layer was then extracted four times with EtOAc and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the crude material was purified by gradient flash chromatography (Yamazen, eluting with 50-70% EtOAc in hexanes) affording 299 mg (69%) of diol **32** as an orange foam.

(1*S*,2*S*,4a*S*,8a*R*,*E*)-1-(hydroxymethyl)-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1H-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalen-2-ol (32):

[α]D^{22} –148.0 (c = 1.00, MeOH)

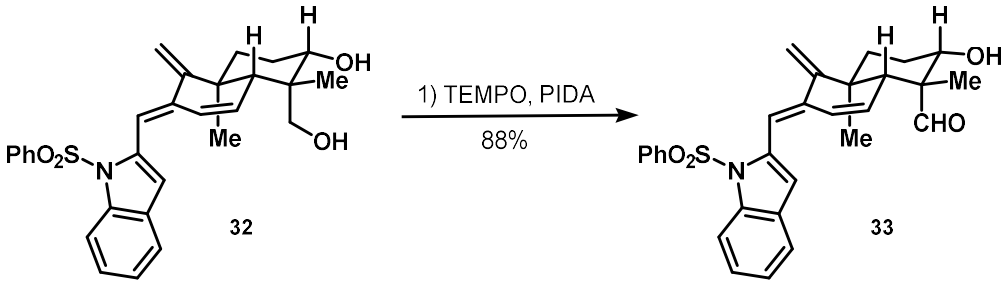
^{1}H-NMR (700 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 8.4 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.37-7.31 (m, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 6.58 (s, 1H), 6.55 (dd, *J* = 10.1, 3.3 Hz, 1H), 5.90 (dd, *J* = 10.1, 2.1 Hz, 1H), 5.32 (s, 1H), 4.86 (s, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 3.62 (dd, *J* = 11.5, 4.8 Hz, 1H), 3.41 (d, *J* = 11.6 Hz, 1H), 2.26 (s, 1H), 2.07-2.01 (m, 1H), 1.99 (dq, *J* = 9.1, 4.1 Hz, 1H), 1.88 (dt, *J* = 13.1, 3.5 Hz, 1H), 1.81 (td, *J* = 13.3, 3.8 Hz, 1H), 1.34 (s, 3H), 1.06 (s, 3H) ppm.

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 156.7, 138.6, 138.5, 137.2, 137.1, 133.7, 131.1, 130.1, 129.1, 126.7, 125.9, 125.1, 124.2, 120.7, 115.3, 115.1, 113.6, 105.8, 76.7, 71.1, 47.6, 42.0, 40.2, 33.9, 27.5, 20.1, 11.6 ppm.

IR (neat): ν = 3386, 2960, 2919, 1449, 1371, 1174, 1120, 1090, 725, 570 cm^{-1}.

HRMS (ESI, *m*/*z*): [M–H]$^-$ calcd. for $C_{29}H_{28}NSO_4$, 488.1901; found 488.1897.

R_f = 0.21 (Hexane:EtOAc = 1:2), UV-active, blue spot (CAM).



(1*R*,2*S*,4a*S*,8a*R*,*E*)-2-hydroxy-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1H-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalene-1-carbaldehyde (33): To a solution of diol **32** (210 mg, 0.440 mmol, 1.00 equiv) in DCM (3.60 mL) and H_2O (3.60 mL) was added TEMPO (89.0 mg, 0.570 mmol, 1.30 equiv), followed by PIDA (183 mg, 0.570 mmol, 1.30 equiv) as solids in one portion. The resulting orange-brown mixture was vigorously stirred for 4 h at room temperature before being quenched by the addition of sat. aq. $NaHCO_3$ and sat. aq. NaS_2O_3 (ca. 4:1). The mixture was transferred into a sep. funnel and solid NaCl was added. The aq. layer was then extracted four times with EtOAc, washed with sat. aq. NaCl, dried over $MgSO_4$, and filtered. After removal of the solvent *in vacuo*, the crude material was

purified by gradient flash chromatography (Yamazen, eluting with 30-50% EtOAc in hexanes) affording aldehyde **33** (185 mg, 88%) as a pale orange foam.

(1*R*,2*S*,4a*S*,8a*R*,*E*)-2-hydroxy-1,4a-dimethyl-5-methylene-6-((1-(phenylsulfonyl)-1H-indol-2-yl)methylene)-1,2,3,4,4a,5,6,8a-octahydronaphthalene-1-carbaldehyde (33):

$[\alpha]_D^{22}$ –125.6 (c = 1.00, MeOH)

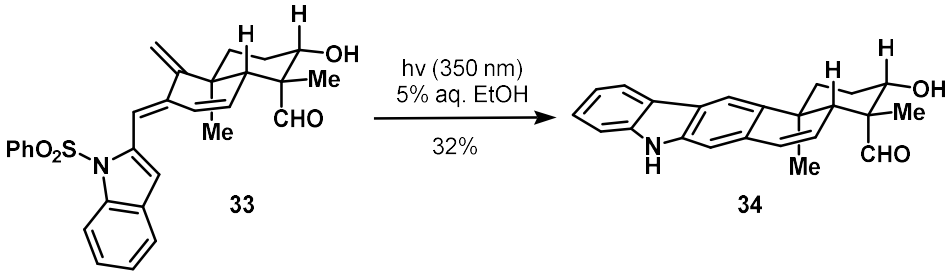
^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.77 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.32 (dt, *J* = 14.9, 7.8 Hz, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.64-6.58 (m, 1H), 6.57 (s, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 5.39 (s, 1H), 4.92 (s, 1H), 3.35 (s, 1H), 3.22 (d, *J* = 10.3 Hz, 1H), 2.32 (s, 1H), 2.12 (dt, *J* = 13.9, 4.2 Hz, 1H), 2.05-1.96 (m, 1H), 1.92-1.86 (m, 1H), 1.80 (td, *J* = 13.4, 3.7 Hz, 1H), 1.39 (s, 3H), 1.32-1.21 (m, 1H), 0.98 (s, 3H).

^{13}C-NMR (151 MHz, CDCl3) δ = 207.5, 154.8, 138.4, 137.7, 137.1, 136.5, 133.6, 129.9, 128.9, 128.2, 126.5, 126.1, 125.1, 124.0, 120.6, 116.0, 115.1, 113.5, 106.9, 53.4, 52.2, 39.9, 34.0, 28.6, 19.1, 18.9 ppm.

IR (neat): ν = 3536, 2976, 2932, 2919, 1734, 1448, 1371, 1173, 1119, 1074, 724, 507 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{29}H_{28}NSO_4$, 486.1745; found 486.1741.

R_f = 0.18 (Hexane:EtOAc = 2:1), UV-active, blue spot (CAM).



(3*S*,4*R*,4a*R*,13b*S*)-3-hydroxy-4,13b-dimethyl-2,3,4,4a,8,13b-hexahydro-1H-naphtho[2,1-b]carbazole-4-carboxylic acid (34): A pyrex glass tube (11 cm tall, 1 cm diameter), equipped with a screw cap, was charged with a solution of aldehyde **33** (90.0 mg, 0.184 mmol, 1.00 equiv) in 5% aq. ethanol (9.00 mL, 20.0 mM). The vessel was degassed by bubbling a stream of nitrogen through the solution for 45 min. The mixture was then irradiated for 4 h with UV-A light (350 nm) in a Luzchem photobox at room temperature. After reducing the EtOH *in vacuo*, the residue was dissolved in EtOAc and sat. aq. NaCl. The aq. layer was extracted four times with EtOAc and the combined organic layers were dried over $MgSO_4$, filtered and

concentrated *in vacuo* the crude material was purified by gradient flash chromatography (Yamazen, eluting with 13-42% EtOAc in Hexanes) provided 20 mg (36%) of carbazole **34** as a white foam.

[α]D22 –181.1 (c = 1.00, MeOH)

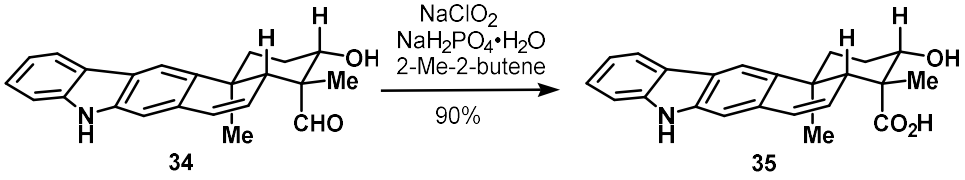
1H-NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H), 8.06–8.02 (m, 2H), 7.88 (s, 1H), 7.39 (m 2H), 7.26 – 7.22 (m, 1H), 7.12 (s, 1H), 6.78 (dd, *J* = 9.7, 3.2 Hz, 1H), 6.28 (dd, *J* = 9.7, 2.7 Hz, 1H), 3.41 (s, 2H), 2.49 (dt, *J* = 12.7, 3.3 Hz, 1H), 2.37 (t, *J* = 3.0 Hz, 1H), 2.19 (dd, *J* = 13.0, 4.0 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.94 (td, *J* = 13.5, 13.1, 3.6 Hz, 1H), 1.43 (s, 3H), 1.02 (s, 3H).

13C-NMR (101 MHz, CD_3OD): δ = 208.0, 140.0, 138.0, 138.0, 130.8, 130.3, 125.7, 125.1, 123.4, 122.9, 120.0, 119.5, 114.1, 110.6, 108.9, 52.0, 51.1, 37.8, 34.7, 28.8, 20.8, 19.0.

IR (neat): ν = 3294, 2937, 2825, 1717, 1242, 1023, 716 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{23}H_{22}NO_2$, 344.1656; found 344.1654.

R_f = 0.20 (Hexane:EtOAc = 2:1), UV-active, blue spot (CAM).



(3*S*,4*R*,4a*R*,13b*S*)-3-hydroxy-4,13b-dimethyl-2,3,4,4a,8,13b-hexahydro-1H-naphtho[2,1-b]carbazole-4-carboxylic acid (34): To a solution of the aldehyde **34** (20 mg, 0.058 mmol, 1.0 equiv) in acetone (900 µL), H_2O (450 µL), and 2-Me-2-butene (152 µL, 3.16 mmol, 25.0 equiv) was added a mixture of $NaClO_2$ (36.5 mg, 0.406 mmol, 7.00 equiv, ~90% techn.) and NaH_2PO_4•H_2O (80.0 mg, 0.578 mmol, 10.0 equiv) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h before being quenched by the addition of sat. aq. NaCl and sat. aq. NH_4Cl (ca. 1:1). The mixture was transferred into a sep. funnel and solid NaCl was added. The aq. layer was then extracted six times with EtOAc and dried over $MgSO_4$. After concentrating the solution *in vacuo*, the crude material was purified by gradient flash chromatography (Yamazen, eluting with 0-10% MeOH in DCM) to afford 18.8 mg (90%) of acid **35** as a yellow foam.

[α]D22 –123.1 (c = 1.00, MeOH)

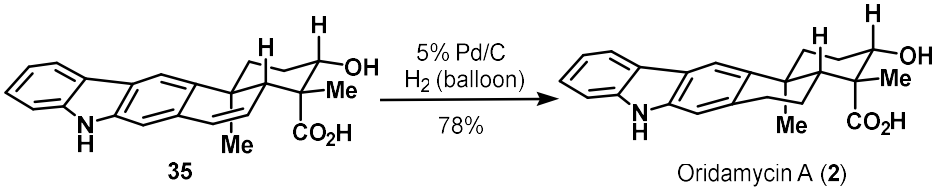
^{1}H-NMR (400 MHz, CD_3OD): δ = δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.80 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.33 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.14 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.09 (s, 1H), 6.60 (d, *J* = 9.9 Hz, 1H), 6.46 (d, *J* = 9.9 Hz, 1H), 3.26 (dd, *J* = 12.1, 4.3 Hz, 1H), 2.38 (dt, *J* = 13.0, 3.6 Hz, 1H), 2.28 – 2.17 (m, 2H), 1.92 (dt, *J* = 12.8, 3.8 Hz, 1H), 1.80 – 1.70 (m, 1H), 1.49 (s, 3H), 1.24-1.28 (m, 1H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, CD_3OD): δ = 180.5, 141.9, 140.0, 139.1, 132.2, 129.8, 128.2, 126.2, 124.7, 123.6, 120.6, 119.6, 114.9, 111.6, 109.4, 78.9, 52.7, 39.3, 36.3, 29.8, 24.1, 21.2.

IR (neat): ν = 3403, 2982, 2970, 1736, 1478, 1372, 1244, 1042 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{23}H_{22}NO_3$, 360.1605; found 360.1601.

R_f = 0.25 (7% MeOH in DCM), UV-active, blue spot (CAM).



Oridamycin A (2): Hydrogen from a balloon was bubbled through a mixture of crude carbazole **35** and 5% Pd/C (32.7 mg, 0.308 mmol, 2.00 equiv) in MeOH (0.900 mL) for 1 min. The mixture was then vigorously stirred under an atmosphere of hydrogen (balloon) for 3.5 h at room temperature. After filtering the mixture through celite (EtOAc/MeOH eluent), the solution was concentrated *in vacuo* and the crude material was purified by preparative thin layer chromatography (10% MeOH in DCM) to afford 10.7 mg (20%, 3 steps) of oridamycin A (**2**) as a pale yellow solid.

$[\alpha]_D^{22}$ +100.3 (c = 0.4, MeOH) lit[6]: **$[\alpha]_D^{30}$** +93.3 (c = 0.2, MeOH)

^{1}H-NMR (700 MHz, CD_3OD) δ = 7.96 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 3.26 (d, *J* = 11.5 Hz, 1H), 3.10 (dd, *J* = 16.2, 4.6 Hz, 1H), 2.98 (ddd, *J* = 16.2, 4.6 Hz, 1H), 2.60 (dd, *J* = 13.2, 2.0 Hz, 1H), 2.34 (d, *J* = 13.2 Hz, 1H), 2.25 (dd, *J* = 13.9, 6.0 Hz, 1H), 2.20-2.15 (m, 1H), 1.98-1.92 (m, 1H), 1.65-1.60 (m, 1H), 1.54 (m, 1H), 1.51 (s, 3H), 1.29 (s, 3H) ppm.

^{13}C NMR (176 MHz, CD_3OD): δ = 181.0, 142.0, 140.3, 140.1, 134.5, 126.1, 124.6, 123.2, 120.6, 119.3, 117.5, 111.4, 110.7, 79.0, 54.0, 49.9, 39.9, 39.6, 34.0, 30.2, 24.8, 24.5, 22.5.

IR (neat): ν = 3412, 2980, 1695, 1465, 1259, 1089 cm^{-1}.

HRMS (ESI, *m*/*z*): $[M–H]^-$ calcd. for $C_{23}H_{24}NO_3$, 362.1762; found 362.1756.

R_f = 0.25 (7% MeOH in DCM), UV-active, blue spot (CAM).

M.p. = 183 °C lit.[6] **M.p.** = 180 °C.

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic Xiamycin A (1)

Sarpong (700 MHz, CD_3OD)	**Natural[3] (500 MHz, CD_3OD)**	**Ang Li[2] (400 MHz, CD_3OD)**
7.97 (d, *J* = 8.0 Hz, 1H)	7.96 (d, *J* = 8.0 Hz, 1H)	7.97 (d, *J* = 8.0 Hz, 1H)
7.94 (s, 1H)	7.91 (s, 1H)	7.93 (s, 1H)
7.35 (d, *J* = 8.0 Hz, 1H)	7.35 (d, *J* = 8.0 Hz, 1H)	7.35 (d, *J* = 8.0 Hz, 1H)
7.29 (t, *J* = 7.9 Hz, 1H)	7.28 (dt, *J* = 7.0, 1.0 Hz, 1H)	7.29 (t, *J* = 7.2 Hz, 1H)
7.09 (t, *J* = 7.5 Hz, 1H)	7.08 (dt, *J* = 7.0, 1.0 Hz, 1H)	7.09 (d, *J* = 7.2 Hz, 1H)
7.07 (s, 1H)	7.07 (s, 1H)	7.06 (s, 1H)
4.10 (dd, *J* = 10.5, 7.5 Hz, 1H)	4.09 (dd, *J* = 10.5, 7.5 Hz, 1H)	4.10 (dd, *J* = 10.4, 7.3 Hz, 1H)
3.15-3.08 (m, 1H) 3.08-2.99 (m, 1H)	3.09 (m, 2H)	3.15-3.01 (m, 1H) 3.11-2.96 (m, 1H)
2.64 (d, *J* = 12.8 Hz, 1H)	2.58 (dt, *J* = 13.1, 1.5 Hz, 1H)	2.62 (dd, *J* = 13.2, 3.0, 1H)
2.14 (d, *J* = 11.8 Hz, 1H)	2.18 (dd, *J* = 12.6, 2.3 Hz, 1H)	2.16 (dd, *J* = 12.4, 1.8 Hz, 1H)
2.08-1.98 (m, 1H)	2.00 (qd, *J* = 12.6, 7.3 Hz, 1H)	2.08-1.95 (m, 1H)
1.93-1.88 (m, 2H)	1.90 (m, 1H) 1.86 (qd, *J* = 13.1, 2.9 Hz, 1H)	1.93-1.89 (m, 1H) 1.89-1.85 (m, 1H)
1.78-1.72 (m, 1H)	1.76 (dt, *J* = 12.3, 6.7 Hz, 1H)	1.78-1.70 (m, 1H)
1.58-1.53 (m, 1H)	1.56 (m, 1H)	1.54 (dd, *J* = 13.0, 7.2 Hz, 1H)
1.30 (s, 3H)	1.28 (s, 3H)	1.29 (s, 3H)
1.25 (s, 3H)	1.23 (s, 3H)	1.24 (s, 3H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic Xiamycin A (1)

Sarpong (176 MHz, CD_3OD)	**Natural[3] (151 MHz, CD_3OD)**	**Ang Li[2] (101 MHz, CD_3OD)**
181.3	181.3	181.2
142.0	142.0	142.0
141.8	141.8	141.8
140.1	140.1	140.1
134.0	134.0	134.0
126.0	126.0	126.0
124.6	124.7	124.7
123.1	123.1	123.1
120.6	120.5	120.6
119.3	119.3	119.3
116.4	116.3	116.3
111.4	111.5	111.4
110.8	110.8	110.8
76.3	76.3	76.3
54.9	54.9	54.9
47.9	47.9	47.9
39.0	39.0	39.0
38.3	38.3	38.3
32.1	32.0	32.0
28.7	28.6	28.6
26.3	26.3	26.3
22.6	22.6	22.6
11.4	11.4	11.4

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic Xiamycin C (3)

Sarpong (600 MHz, CD_3OD)	**Natural[4] (500 MHz, CD_3OD)**
8.00 (d, *J* = 7.7 Hz, 1H)	8.00 (d, *J* = 8.0 Hz, 1H)
7.94 (s, 1H)	7.94 (s, 1H)
7.58 (s, 1H)	7.58 (s, 1H)
7.37 (d, *J* = 8.0 Hz, 1H)	7.38 (d, *J* = 8.0 Hz, 1H)
7.31 (dd, *J* = 7.9, 8.0 Hz, 1H)	7.31 (dd, *J* = 8.0, 8.0 Hz, 1H)
7.10 (d, *J* = 7.9, 8.0 Hz 1H)	7.10 (dd, *J* = 8.0, 8.0 Hz, 1H)
4.89 (m, 1H)	4.91 (dd, *J* = 10.0, 7.5 Hz, 1H)
4.09 (dd, *J* = 8.0, 6.6 Hz, 1H)	4.08 (dd, *J* = 8.0, 6.5 Hz, 1H)
2.63 (ddd, *J* = 13.2, 3.4, 3.2, Hz, 1H)	2.62 (ddd, *J* = 13.0, 3.5, 3.5 Hz, 1H)
2.19 (d, *J* = 12.6 Hz, 1H)	2.20 (dd, *J* = 12.0, 2.0 Hz, 1H)
2.09 – 1.95 (m, 2H)	1.97 (m, 2H)
1.93 – 1.82 (m, 3H)	1.93 (m, 1H)
	1.89 (m, 2H)
1.75 – 1.65 (m, 1H)	1.70 (m, 1H)
1.38 (s, 3H)	1.38 (s, 3H)
1.26 (s, 3H)	1.26 (s, 3H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic Xiamycin C (3)

Sarpong (176 MHz, CD_3OD)	**Natural[4] (125 MHz, CD_3OD)**
180.4	182.0
142.3	142.4
142.1	141.7
140.1	140.2
137.9	137.6
126.3	126.4
124.5	124.4
124.0	124.1
120.8	120.8
119.3	119.4
116.3	116.3

111.5	111.6
110.1	110.1
76.8	76.3
72.3	72.2
55.1	54.8
46.0	46.1
39.2	39.2
39.0	39.0
33.3	33.2
28.4	28.5
26.9	26.8
12.7	11.9

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic Xiamycin F (4)

Sarpong (700 MHz, CD_3OD)	**Natural[5] (500 MHz, CD_3OD)**
8.16–8.13 (d, *J* = 7.6 Hz, 1H)	8.16 (d, *J* = 8.0 Hz, 1H)
8.12 (s, 1H)	8.12 (s, 1H)
8.05 (s, 1H)	8.06 (s, 1H)
7.47–7.42 (m, 2H)	7.47 (m, 1H) 7.47 (m, 1H)
7.19 (td, *J* = 6.8, 2.0 Hz, 1H)	7.20 (m, 1H)
4.13–4.06 (m, 1H)	4.13 (m, 1H)
2.91 (t, *J* = 15.9 Hz, 1H)	2.96 (m, 1H)
2.72–2.64 (m, 2H)	2.73 (m, 2H) 2.67 (m, 1H)
2.57 (d, *J* = 11.8 Hz, 1H)	2.43 (d, *J* = 17.5 Hz, 1H)
1.98–1.90 (m, 3H)	1.96 (m, 2H) 1.94 (m, 1H)
1.35 (s, 3H)	1.39 (s, 3H)
1.30 (s, 3H)	1.33 (s, 3H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic Xiamycin F (4)

Sarpong (176 MHz, CD_3OD)	Natural[5] (150 MHz, CD_3OD)
201.1	201.3
180.1	180.0
147.7	147.5
144.0	143.9
139.6	139.6
130.1	130.2
129.4	129.5
128.8	128.6
123.8	123.8
122.3	122.2
120.4	120.3
116.2	116.1
112.3	112.2
110.7	110.7
76.0	76.8
54.3	54.3
46.9	46.8
38.8	38.7
38.7	38.2
38.3	38.2
28.4	28.3
24.9	24.8
11.2	11.2

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic Xiamycin H (5)

Sarpong (700 MHz, CD_3OD)	**Natural[5] (500 MHz, CD_3OD)**
8.16 (s)	8.16 (s)
8.06 (d, *J* = 7.9 Hz, 1H)	8.07 (d, *J* = 8.0 Hz, 1H)
7.42 (d, *J* = 8.1 Hz, 1H)	7.43 (d, *J* = 7.8 Hz, 1H)
7.36 (t, *J* = 7.5 Hz, 1H)	7.36 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H)
7.35 (s, 1H)	7.35 (s, 1H)
7.15 (t, *J* = 7.5 Hz, 1H)	7.15 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H)
7.05 (d, *J* = 9.8 Hz, 1H)	7.05 (d, *J* = 9.6 Hz, 1H)
6.76 (d, *J* = 9.8 Hz, 1H)	6.76 (d, *J* = 9.6 Hz, 1H)
2.98 (m, 1H)	2.98 (m, 1H)
2.85 (m, 1H)	2.85 (m, 1H)
2.66 (m, 1H)	2.67 (m, 1H)
2.35 (m, 1H)	2.35 (m, 1H)
1.92 (s, 3H)	1.92 (s, 3H)
1.49 (s, 3H)	1.49 (s, 3H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic Xiamycin H (5)

Sarpong (176 MHz, CD_3OD)	**Natural[5] (151 MHz, CD_3OD)**
200.5	200.7
160.2	160.2
156.3	142.6
140.1	139.5
137.8	138.0
136.6	136.7
130.1	130.3
129.4	129.4
127.0	127.2
125.1	125.8
124.3	124.4
123.4	123.6
121.1	121.2

120.2	120.2
116.5	116.7
111.8	112.0
111.8	112.0
40.6	40.7
35.1	35.2
34.9	35.0
31.3	31.4
10.6	10.7

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic Oridamycin A (2)

Sarpong (700 MHz, CD_3OD)	**Natural[7] (600 MHz, CD_3OD)**	**Ang Li[2] (400 MHz, CD_3OD)**
7.96 (d, *J* = 8.0 Hz, 1H)	7.93 (d, *J* = 8.0 Hz, 1H)	7.96 (d, *J* = 8.0 Hz, 1H)
7.96 (s, 1H)	7.93 (s, 1H)	7.95 (s, 1H)
7.34 (d, *J* = 8.0 Hz, 1H)	7.32 (d, *J* = 8.0 Hz, 1H)	7.34 (d, *J* = 8.0 Hz, 1H)
7.28 (t, *J* = 7.6 Hz, 1H)	7.25 (dt, *J* = 8.1, 1.4 Hz, 1H)	7.28 (t, *J* = 7.6 Hz, 1H)
7.08 (d, *J* = 7.6 Hz, 1H)	7.05 (dt, *J* = 8.1, 1.4 Hz, 1H)	7.08 (d, *J* = 7.6 Hz, 1H)
7.07 (s, 1H)	7.03 (s, 1H)	7.05 (s, 1H)
3.26 (d, *J* = 11.5 Hz, 1H)	3.22 (dd, *J* = 12.2, 4.6 Hz, 1H)	3.24 (dd, *J* = 12.1, 4.3 Hz, 1H)
3.10 (dd, *J* = 16.2, 4.6 Hz, 1H)	3.06 (ddd, *J* = 16.3, 5.4, 2.3, 1H)	3.08 (dd, *J* = 16.5. 4.0, 1H)
2.98 (dd, *J* = 16.5, 4.6 Hz, 1H)	2.94 (ddd, *J* = 16.3, 5.4, 2.3, 1H)	3.01-2.89 (m, 1H)
2.60 (dd, *J* = 13.2, 2.0 Hz, 1H)	2.57 (dt, *J* = 13.6, 3.6 Hz, 1H)	2.59 (dd, *J* = 13.2, 2.0, 1H)
2.38-2.31 (m, 1H)	2.30 (dq, *J* = 12.6, 2.3 Hz, 1H)	2.38-2.26 (m, 1H)
2.25 (dd, *J* = 13.9, 6.0 Hz, 1H)	2.23 (m, 1H)	2.25-2.19 (m, 1H)
2.20-2.15 (m, 1H)	2.09 (dt, *J* = 12.7, 5.4, 1H)	2.19-2.06 (m, 1H)
1.98-1.92 (m, 1H)	1.90 (qd, *J* = 13.6, 3.6 Hz, 1H)	1.97-1.89 (m, 1H)
1.65-1.60 (m, 1H)	1.58 (dt, *J* = 13.6, 4.1 Hz, 1H)	1.59 (ddd, *J* = 13.6, 13.6, 3.5 1H)
1.57-1.45 (m, 4H)	1.56 (m, 1H) 1.48 (s, 3H)	1.54 (dd, *J* = 13.0, 7.2 Hz, 1H) 1.49 (s, 3H)
1.29 (s, 3H)	1.26 (s, 3H)	1.27 (s, 3H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic Oridamycin A (2)

Sarpong (176 MHz, CD_3OD)	**Natural[7] (151 MHz, CD_3OD)**	**Ang Li[2] (101 MHz, CD_3OD)**
181.0	181.0	181.0
142.0	142.0	142.1
140.3	140.3	140.4
140.1	140.1	140.1
134.5	134.5	134.5
126.0	126.1	126.1
124.6	124.6	124.6
123.2	123.2	123.3
120.6	120.6	120.6
119.3	119.3	119.4
117.5	117.5	117.5
111.4	111.4	111.4
110.7	110.7	110.7
79.0	79.1	79.1
54.0	54.1	54.1
49.8	49.8	49.8
39.9	40.0	40.0
39.6	39.6	39.6
34.0	34.0	34.0
30.2	30.3	30.3
24.8	24.8	24.8
24.5	24.6	24.6
22.5	22.5	22.5

Chemical Shifts of ^{1}H-NMR for Omura/Nagamitsu and Sarpong's *trans*-diol

Sarpong (600 MHz, $CDCl_3$)	**Omura/Nagamitsu[1] (400 MHz, $CDCl_3$)**
6.64 (d, *J* = 4.8 Hz, 1H)	6.82–6.79 (m, 1H)
3.68-3.58 (m, 2H)	3.62–3.58 (m, 1H)
3.39 (d, *J* = 10.6 Hz, 1H)	3.53 (d, *J*=11.2 Hz, 1H)
3.04 (br s, 2H)	3.27 (d, *J*=11.2 Hz, 1H)
2.39-2.29 (m, 1H)	2.43–2.27 (m, 2H)
2.18 (d, *J* = 19.1 Hz, 1H)	2.01 (dd, *J*=10.9, 4.8 Hz, 1H)
1.91 (d, *J* = 14.3 Hz, 1H)	1.86 (dt, *J*=13.9, 3.4 Hz, 1H)
1.79 (dd, *J* = 11.5, 4.2 Hz, 1H), 1.75 (d, *J* = 4.0 Hz, 1H)	1.76–1.68 (m, 2H)
1.72 (s, 3H)	1.72–1.70 (m, 3H)
1.70-1.60 (m, 1H)	
1.47 (td, *J* = 13.9, 3.3 Hz, 1H)	1.47–1.39 (m, 1H)
1.06 (s, 3H)	1.07 (s, 3H)
0.99 (s, 3H)	0.85 (s, 3H)

Chemical Shifts of ^{13}C-NMR for for Nagamitsu and Sarpong *trans*-diol

Sarpong (156 MHz, $CDCl_3$)	**Omura/Nagamitsu [1] (101 MHz, $CDCl_3$)**
205.4	207.7
143.4	146.3
133.2	133.7
75.4	72.5
69.6	65.5
44.4	45.5
42.9	44.0
42.5	42.6
31.4	32.7
26.6	27.2

24.1	24.9
17.9	18.2
16.4	16.4
11.9	12.9

2. Fungitoxicity assessment

The technical materials were evaluated for antifungal activity against three plant pathogens *Ustilago maydis*, *Zymoseptoria tritici* and *Magnaporthe oryzae* in 96-well microtitre plate-based growth inhibition assays. Test materials were prepared as 1 mg/ml stock solutions in DMSO and a five-fold dilution series was prepared. 2 µl of the diluted compounds were added to two replicate wells to deliver a final test concentration of 10 ppm once inoculated. Wells then received 200 µl of cells in minimal growth media containing 20 g glucose, 3 g K_2HPO_4 , 3 g KH_2PO_4 and 6.7 g yeast nitrogen base without amino acids (BD Difco, BD291920) per liter. *Z. tritici* spores were collected from a 3-day old yeast malt agar plate that is maintained at 18°C under black light for 12 hours and dark for 12 hours. *M. oryzae* spores were collected from 12 to18-day old potato dextrose agar plates supplemented with 16 g per liter rice flour and maintained at 22°C under 12 hours white fluorescent light and 12 hours dark. *U. maydis* spores were taken from a 24-hour shake flask culture in potato dextrose broth maintained at 24°C and 120 rpm. Final cell densities were 1 X 10^5 cells ml^{-1} (*Z. tritici*), 4 X 10^4 cells ml^{-1} (*M. oryzae*) and 5 X 10^4 cells ml^{-1} (*U. maydis*). Test plates were incubated in the dark for 48 hr (*U. maydis*) or 72 hr (*M. oryzae* and *Z. tritici*) at 22ºC (M. oryzae and Z. tritici) or 24ºC (*U. maydis*), and initial and final cell density readings determined using a NepheloStar nephelometer (BMG LABTECH Gmb, D-77799 Ortenberg, Germany). Percentage growth inhibition was calculated by reference to control wells containing only growth media, amended with 2 ul DMSO, and inoculum.

Summary of bioactivity

Compound	Wheat leaf blotch % Growth Inhibition (10 ppm)	Rice blast % Growth Inhibition (10 ppm)	Corn smut % Growth Inhibition (10 ppm)
Xiamycin H (**5**)	100	50	40
25	40	0	30
19Epi-Xiamycin C (**3**)	20	10	10
8a	20	0	30
20	10	10	0
21	10	0	30
7	10	10	50
15 major	5	35	15
8b	5	5	0
Xiamycin F (**4**)	0	10	10
Xiamycin C (**3**)	0	10	10
Min triene diol	0	30	0
16	0	30	0
Xiamycin A (**1**)	0	15	5
27	0	5	5
13	0	30	20
23	0	50	0

3. References

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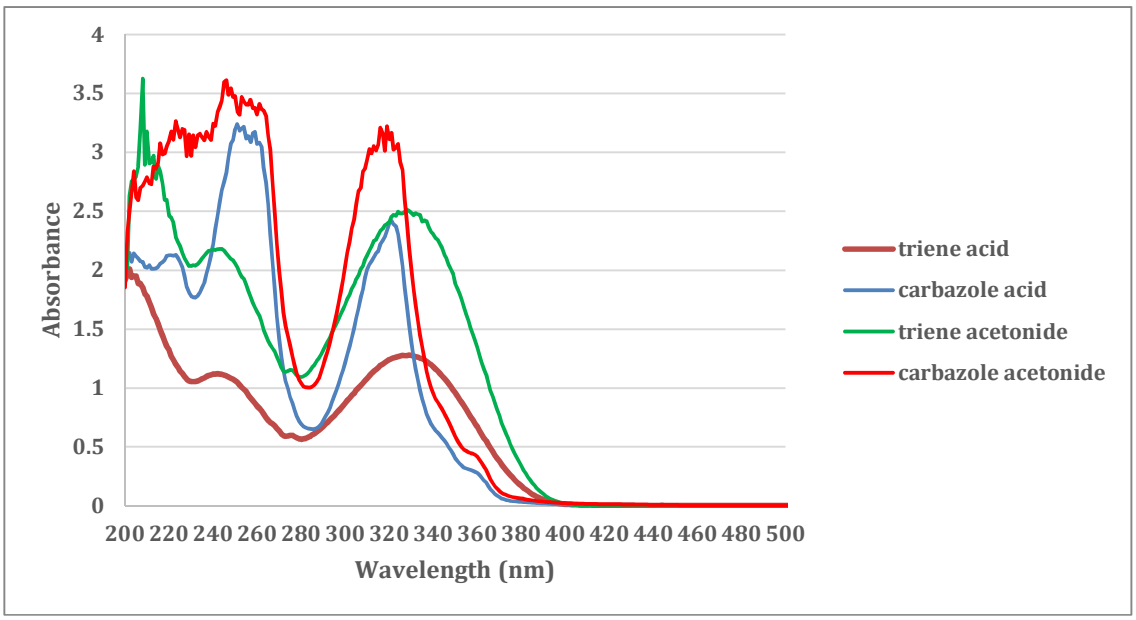
4. UV Absorption



5. Crystallographic Data

Table 1. Crystal data and structure refinement for mp001 (CCDC 1831586)

Identification code	mp001	
Empirical formula	C14 H22 O3	
Formula weight	238.31	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.2602(5) Å	α= 90°.
	b = 8.3489(6) Å	β= 90°.
	c = 20.4643(15) Å	γ = 90°.
Volume	1240.44(15) $Å^3$	
Z	4	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.705 mm^{-1}	
F(000)	520	

Crystal size	0.100 x 0.040 x 0.040 mm^3
Theta range for data collection	4.321 to 68.329°.
Index ranges	-8<=h<=8, -10<=k<=9, -24<=l<=24
Reflections collected	18197
Independent reflections	2259 [R(int) = 0.0248]
Completeness to theta = 67.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.753 and 0.708
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2259 / 0 / 165
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0722
R indices (all data)	R1 = 0.0263, wR2 = 0.0724
Absolute structure parameter	0.06(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.217 and -0.160 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for mp001. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5288(2)	5140(2)	5101(1)	15(1)
C(2)	7066(2)	5306(2)	5448(1)	18(1)
C(3)	7040(2)	5137(2)	6180(1)	24(1)
C(4)	8604(2)	5575(2)	5108(1)	16(1)
C(5)	8691(2)	5723(2)	4381(1)	16(1)
C(6)	6795(2)	5938(2)	4064(1)	13(1)
C(7)	5368(2)	4775(2)	4368(1)	14(1)
C(8)	5893(2)	2982(2)	4326(1)	18(1)
C(9)	3470(2)	5050(2)	4062(1)	16(1)
C(10)	3543(2)	4956(2)	3315(1)	17(1)
C(11)	4886(2)	6175(2)	3040(1)	16(1)
C(12)	6867(2)	5959(2)	3302(1)	14(1)
C(13)	7785(2)	4479(2)	2993(1)	18(1)
C(14)	8024(2)	7410(2)	3077(1)	17(1)

O(1)	3819(2)	5228(2)	5395(1)	20(1)
O(2)	4922(2)	6145(2)	2340(1)	20(1)
O(3)	7397(2)	8923(1)	3316(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for mp001.

C(1)-O(1)	1.227(2)
C(1)-C(2)	1.481(2)
C(1)-C(7)	1.530(2)
C(2)-C(4)	1.335(2)
C(2)-C(3)	1.504(2)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-C(5)	1.494(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.532(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.550(2)
C(6)-C(12)	1.5598(19)
C(6)-H(6)	1.0000
C(7)-C(9)	1.531(2)
C(7)-C(8)	1.547(2)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.531(2)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.518(2)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-O(2)	1.4324(18)
C(11)-C(12)	1.546(2)
C(11)-H(11)	1.0000
C(12)-C(13)	1.540(2)
C(12)-C(14)	1.545(2)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-O(3)	1.429(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
O(2)-H(2)	0.88(3)
O(3)-H(3)	0.84(2)
O(1)-C(1)-C(2)	121.06(13)
O(1)-C(1)-C(7)	121.75(14)
C(2)-C(1)-C(7)	117.12(13)
C(4)-C(2)-C(1)	119.58(14)

C(4)-C(2)-C(3)	123.13(15)
C(1)-C(2)-C(3)	117.28(14)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-C(5)	124.71(15)
C(2)-C(4)-H(4)	117.6
C(5)-C(4)-H(4)	117.6
C(4)-C(5)-C(6)	113.13(13)
C(4)-C(5)-H(5A)	109.0
C(6)-C(5)-H(5A)	109.0
C(4)-C(5)-H(5B)	109.0
C(6)-C(5)-H(5B)	109.0
H(5A)-C(5)-H(5B)	107.8
C(5)-C(6)-C(7)	110.92(12)
C(5)-C(6)-C(12)	113.20(12)
C(7)-C(6)-C(12)	115.52(12)
C(5)-C(6)-H(6)	105.4
C(7)-C(6)-H(6)	105.4
C(12)-C(6)-H(6)	105.4
C(1)-C(7)-C(9)	109.64(12)
C(1)-C(7)-C(8)	104.86(13)
C(9)-C(7)-C(8)	110.12(13)
C(1)-C(7)-C(6)	107.11(12)
C(9)-C(7)-C(6)	110.08(12)
C(8)-C(7)-C(6)	114.79(13)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-C(10)	111.66(12)
C(7)-C(9)-H(9A)	109.3
C(10)-C(9)-H(9A)	109.3
C(7)-C(9)-H(9B)	109.3
C(10)-C(9)-H(9B)	109.3
H(9A)-C(9)-H(9B)	107.9
C(11)-C(10)-C(9)	111.04(12)
C(11)-C(10)-H(10A)	109.4
C(9)-C(10)-H(10A)	109.4
C(11)-C(10)-H(10B)	109.4
C(9)-C(10)-H(10B)	109.4
H(10A)-C(10)-H(10B)	108.0
O(2)-C(11)-C(10)	111.80(13)
O(2)-C(11)-C(12)	109.17(12)
C(10)-C(11)-C(12)	112.95(12)
O(2)-C(11)-H(11)	107.6

C(10)-C(11)-H(11)	107.6
C(12)-C(11)-H(11)	107.6
C(13)-C(12)-C(14)	105.72(12)
C(13)-C(12)-C(11)	110.71(12)
C(14)-C(12)-C(11)	108.07(12)
C(13)-C(12)-C(6)	114.63(12)
C(14)-C(12)-C(6)	108.99(12)
C(11)-C(12)-C(6)	108.51(11)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(3)-C(14)-C(12)	114.69(13)
O(3)-C(14)-H(14A)	108.6
C(12)-C(14)-H(14A)	108.6
O(3)-C(14)-H(14B)	108.6
C(12)-C(14)-H(14B)	108.6
H(14A)-C(14)-H(14B)	107.6
C(11)-O(2)-H(2)	109.6(14)
C(14)-O(3)-H(3)	109.0(17)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for mp001. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	20(1)	9(1)	16(1)	1(1)	0(1)	0(1)
C(2)	23(1)	13(1)	16(1)	-2(1)	-4(1)	2(1)
C(3)	28(1)	28(1)	16(1)	0(1)	-4(1)	4(1)
C(4)	19(1)	12(1)	18(1)	-1(1)	-6(1)	1(1)
C(5)	15(1)	16(1)	18(1)	1(1)	-1(1)	1(1)
C(6)	14(1)	12(1)	13(1)	-1(1)	0(1)	1(1)
C(7)	14(1)	13(1)	14(1)	0(1)	0(1)	0(1)
C(8)	21(1)	13(1)	19(1)	-1(1)	-1(1)	-2(1)
C(9)	14(1)	20(1)	16(1)	-1(1)	0(1)	-1(1)
C(10)	14(1)	21(1)	17(1)	-2(1)	-3(1)	-1(1)
C(11)	17(1)	18(1)	13(1)	-2(1)	-2(1)	1(1)
C(12)	15(1)	14(1)	12(1)	0(1)	0(1)	-1(1)
C(13)	18(1)	20(1)	17(1)	-3(1)	1(1)	2(1)
C(14)	20(1)	17(1)	14(1)	2(1)	-1(1)	-2(1)
O(1)	21(1)	22(1)	16(1)	-2(1)	4(1)	-3(1)
O(2)	23(1)	22(1)	13(1)	1(1)	-4(1)	-5(1)

O(3)	27(1)	16(1)	18(1)	1(1)	-7(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for mp001.

	x	y	z	U(eq)
H(3A)	8305	5050	6343	36
H(3B)	6350	4171	6300	36
H(3C)	6446	6078	6374	36
H(4)	9723	5678	5344	19
H(5A)	9280	4751	4199	19
H(5B)	9475	6652	4266	19
H(6)	6380	7035	4194	16
H(8A)	5098	2361	4619	26
H(8B)	7182	2844	4457	26
H(8C)	5732	2605	3876	26
H(9A)	3004	6116	4194	20
H(9B)	2600	4233	4229	20
H(10A)	3927	3866	3182	21
H(10B)	2300	5158	3135	21
H(11)	4452	7261	3176	19
H(13A)	8082	4707	2535	27
H(13B)	6939	3566	3015	27
H(13C)	8918	4224	3231	27
H(14A)	9313	7249	3220	20
H(14B)	8022	7442	2593	20
H(2)	4200(30)	5370(30)	2196(11)	33(6)
H(3)	7900(30)	9110(30)	3677(12)	34(6)

Table 1 Crystal data and structure refinement for IB001 (CCDC 1831587)

Identification code	IB001
Empirical formula	$C_{14}H_{24}O_4$
Formula weight	256.33
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.21010(10)

b/Å	11.2298(3)
c/Å	16.4264(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1330.01(5)
Z	4
ρ_{calc}g/cm^3	1.280
μ/mm^{-1}	0.749
F(000)	560.0
Crystal size/mm^3	0.05 × 0.05 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.54 to 157.698
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -20 ≤ l ≤ 12
Reflections collected	14075
Independent reflections	2801 [R_{int} = 0.0452, R_{sigma} = 0.0303]
Data/restraints/parameters	2801/0/182
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0353, wR_2 = 0.0923
Final R indexes [all data]	R_1 = 0.0386, wR_2 = 0.0961
Largest diff. peak/hole / e Å^{-3}	0.20/-0.18
Flack parameter	-0.11(10)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for IB001. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	4401(2)	6426.1(13)	5729.1(9)	22.0(3)
O1	5088(2)	912.8(14)	6645.0(9)	24.1(3)
O3	1109(2)	6680.5(13)	6529.7(9)	23.6(3)
O4	7943(2)	7212.0(16)	5574.0(11)	28.8(4)
C4	3698(3)	2854.7(18)	6658.0(12)	17.7(4)
C5	2253(3)	3393.7(19)	6065.1(12)	17.6(4)

C14	1511(3)	5454.0(18)	6698.2(12)	20.0(4)
C7	329(3)	1559.2(19)	6301.8(13)	23.0(4)
C6	322(3)	2889.5(19)	6243.5(13)	22.2(4)
C3	3673(3)	1496.9(19)	6553.2(12)	20.8(4)
C11	4313(3)	5145.0(18)	5775.2(12)	19.2(4)
C12	2290(3)	4776.7(18)	5950.4(12)	17.6(4)
C10	5683(3)	4679.7(19)	6402.4(13)	20.7(4)
C8	3292(3)	3048.8(18)	7570.9(12)	22.0(4)
C13	1114(3)	5069(2)	5193.7(12)	22.1(4)
C9	5629(3)	3321.0(19)	6442.2(13)	20.5(4)
C2	1862(3)	902(2)	6411.6(12)	23.4(4)
C1	1844(4)	-435(2)	6422.8(15)	28.5(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for IB001. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	19.4(8)	20.2(7)	26.4(8)	4.6(6)	-1.7(6)	-2.4(6)
O1	23.0(7)	23.1(7)	26.3(7)	1.3(6)	1.9(6)	4.3(6)
O3	22.0(7)	19.3(7)	29.6(8)	0.5(6)	2.1(6)	2.8(6)
O4	22.0(8)	33.9(9)	30.4(8)	11.3(7)	-0.4(7)	0.9(7)
C4	14.8(9)	19.0(9)	19.3(9)	0.5(7)	1.3(8)	-0.3(7)
C5	15.3(9)	18.2(9)	19.2(9)	-2.3(8)	-1.0(7)	-0.2(7)
C14	19.2(9)	19.4(10)	21.4(9)	0.3(8)	0.7(8)	1.0(7)
C7	20.8(10)	23.6(10)	24.7(10)	-1.7(8)	0.8(8)	-6.3(8)
C6	17.2(10)	22.5(10)	26.8(10)	-0.4(8)	-0.7(8)	-1.5(8)
C3	21.4(10)	21.4(10)	19.7(9)	0.5(8)	1.9(8)	2.7(8)
C11	20.2(10)	18.1(9)	19.3(9)	1.9(8)	0.0(8)	-0.7(7)
C12	16.4(9)	19.6(10)	16.9(9)	-0.1(7)	-1.8(7)	0.2(8)
C10	16.0(9)	22.3(10)	23.7(10)	2.5(8)	-0.6(7)	-0.8(7)
C8	24.3(10)	22.2(10)	19.5(9)	1.1(8)	0.0(8)	-0.4(8)
C13	18.7(9)	25.2(10)	22.4(10)	2.8(8)	-3.7(8)	-0.8(8)
C9	17.5(9)	20.9(10)	23.1(10)	1.2(8)	0.3(8)	2.9(8)
C2	29.2(11)	20.9(10)	20(1)	-1.0(8)	1.8(8)	-4.2(9)
C1	36.5(12)	19.4(10)	29.7(11)	-0.1(9)	0.7(10)	-3.8(9)

Table 4 Bond Lengths for IB001.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C11	1.442(2)	C14	C12	1.550(3)
O1	C3	1.222(2)	C7	C6	1.497(3)
O3	C14	1.434(2)	C7	C2	1.341(3)
C4	C5	1.550(3)	C3	C2	1.485(3)
C4	C3	1.535(3)	C11	C12	1.543(3)

C4	C8	1.543(3)	C11	C10	1.520(3)
C4	C9	1.529(3)	C12	C13	1.540(3)
C5	C6	1.532(3)	C10	C9	1.528(3)
C5	C12	1.565(3)	C2	C1	1.502(3)

Table 5 Bond Angles for IB001.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	C4	C5	108.04(16)	O2	C11	C12	108.59(16)
C3	C4	C8	104.31(16)	O2	C11	C10	110.48(16)
C8	C4	C5	115.33(16)	C10	C11	C12	113.32(16)
C9	C4	C5	109.43(16)	C14	C12	C5	112.68(16)
C9	C4	C3	108.97(16)	C11	C12	C5	107.72(16)
C9	C4	C8	110.48(17)	C11	C12	C14	111.02(16)
C4	C5	C12	116.88(16)	C13	C12	C5	107.43(16)
C6	C5	C4	110.30(16)	C13	C12	C14	109.61(16)
C6	C5	C12	113.90(16)	C13	C12	C11	108.22(16)
O3	C14	C12	113.05(16)	C11	C10	C9	110.84(16)
C2	C7	C6	124.08(19)	C10	C9	C4	112.04(16)
C7	C6	C5	112.21(17)	C7	C2	C3	119.92(19)
O1	C3	C4	120.65(18)	C7	C2	C1	123.0(2)
O1	C3	C2	120.79(19)	C3	C2	C1	117.1(2)
C2	C3	C4	118.33(17)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for IB001.

Atom	*x*	*y*	*z*	U(eq)
H5	2590.14	3063.95	5519.3	21
H14A	362	5054.92	6883.89	24
H14B	2424.66	5410.92	7147.05	24
H7	-824.52	1155.06	6258.24	28
H6A	-139.39	3227.14	6762.13	27
H6B	-540.35	3136.55	5805.74	27
H11	4669.65	4815.74	5231.66	23
H10A	5375.54	5012.91	6943.82	25
H10B	6950.36	4944.02	6257.08	25
H8A	3463.11	3891.5	7706.5	33
H8B	4143.69	2563.95	7896.86	33
H8C	2010.59	2814.25	7688.92	33
H13A	1500.83	4560.2	4739.71	33
H13B	1291.47	5906.6	5045.42	33
H13C	-198.36	4926.25	5314.39	33
H9A	6528.44	3041.79	6855.58	25
H9B	6008.65	2991.02	5908.75	25
H1A	567.49	-720.16	6360.58	43
H1B	2349.47	-719.42	6941.4	43
H1C	2604.35	-738.12	5973.69	43

H3	2110(50)	6990(30)	6336(18) 33(8)
H4A	8850(50)	7070(30)	5870(20) 42(9)
H2	5600(60)	6610(30)	5690(20) 59(11)
H4B	8370(50)	7720(40)	5190(20) 56(10)

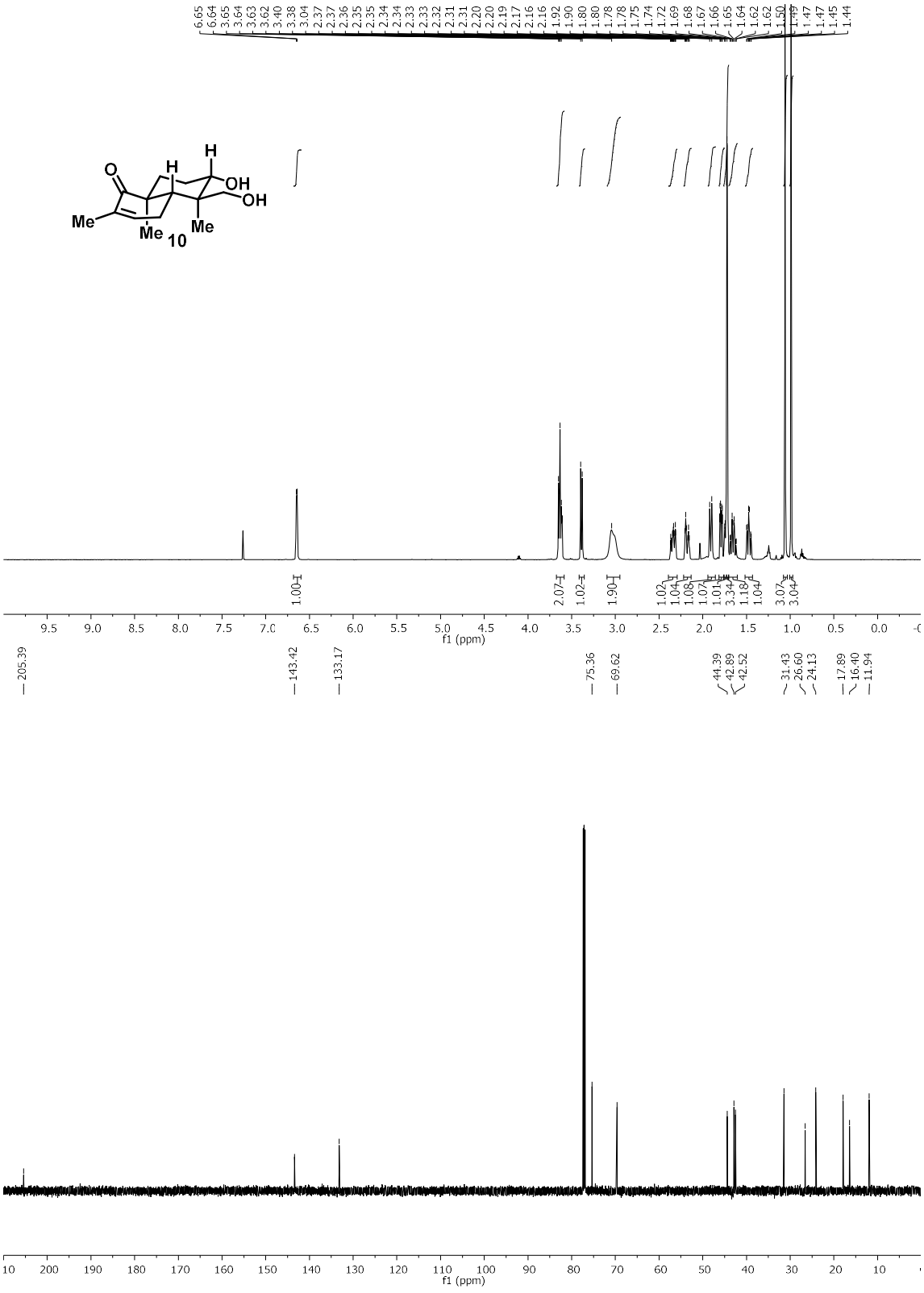
Crystal structure determination of [IB001]

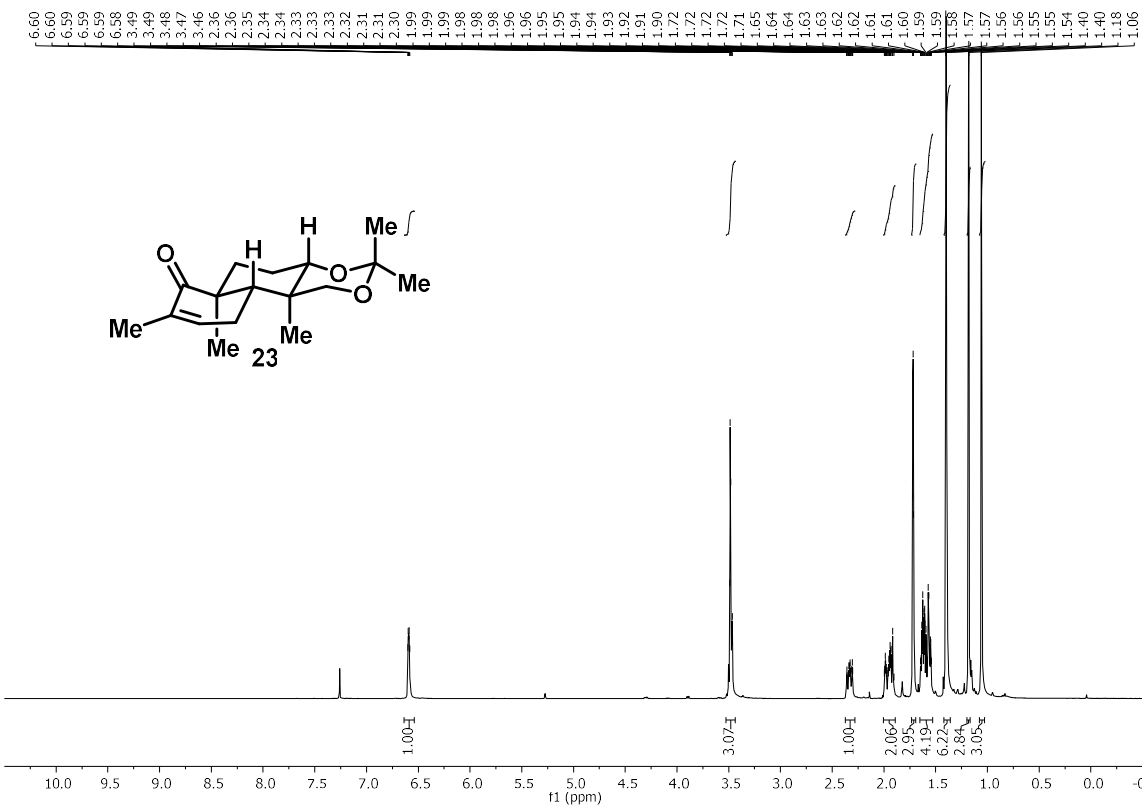
Crystal Data for $C_{14}H_{24}O_4$ (M =256.33 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.21010(10) Å, b = 11.2298(3) Å, c = 16.4264(3) Å, V = 1330.01(5) Å^3, Z = 4, T = 100(2) K, μ(CuKα) = 0.749 mm^{-1}, *Dcalc* = 1.280 g/cm^3, 14075 reflections measured (9.54° ≤ 2Θ ≤ 157.698°), 2801 unique (R_{int} = 0.0452, R_{sigma} = 0.0303) which were used in all calculations. The final R_1 was 0.0353 (I > 2σ(I)) and wR_2 was 0.0961 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Copies of ^{1}H- and ^{13}C-NMR Spectra

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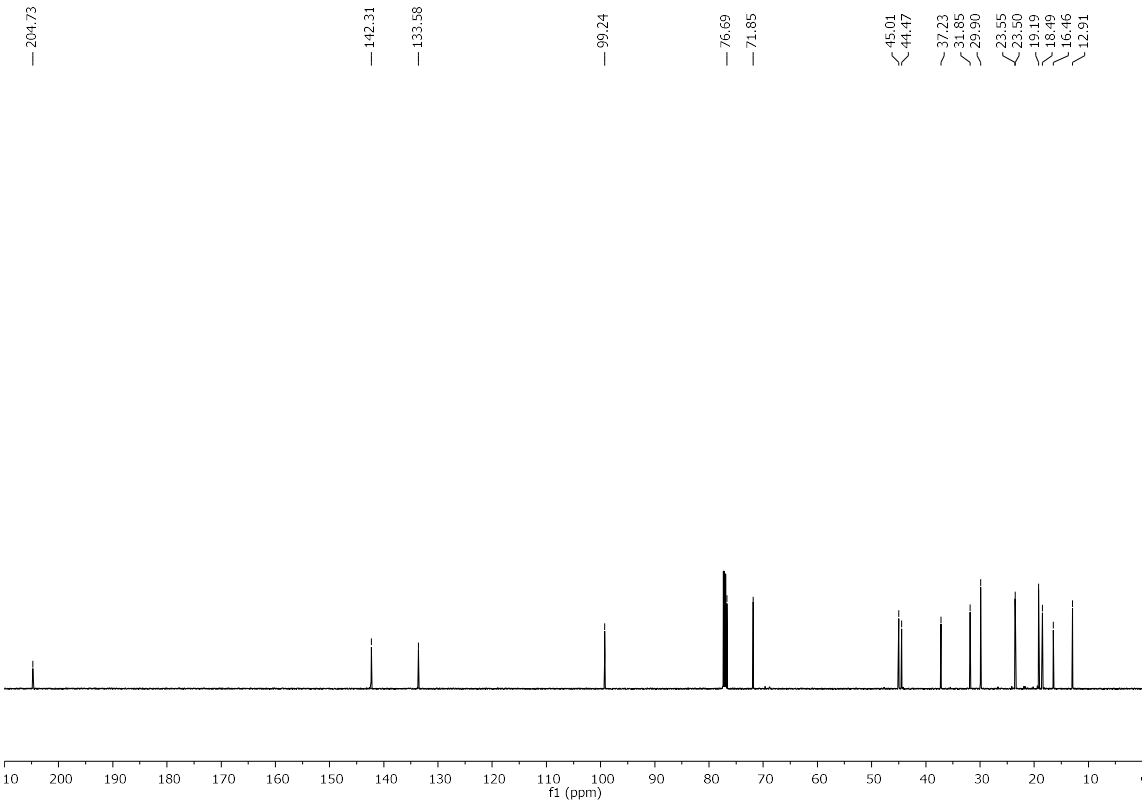
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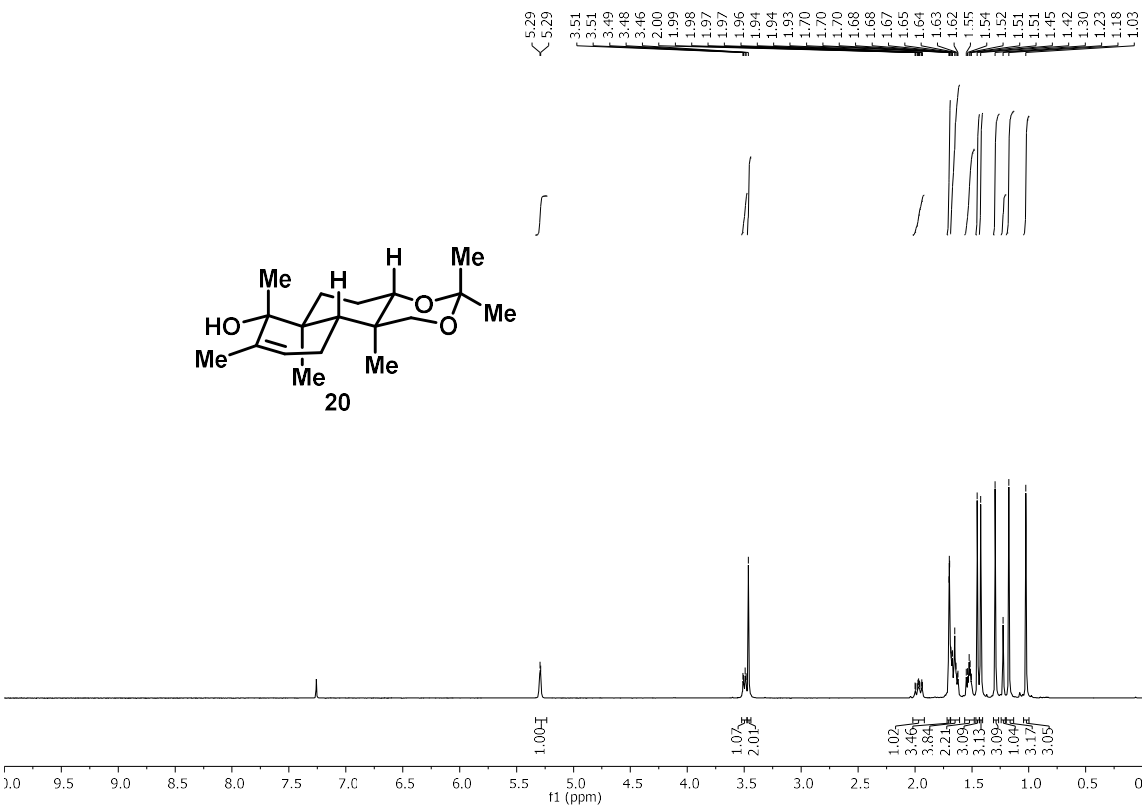
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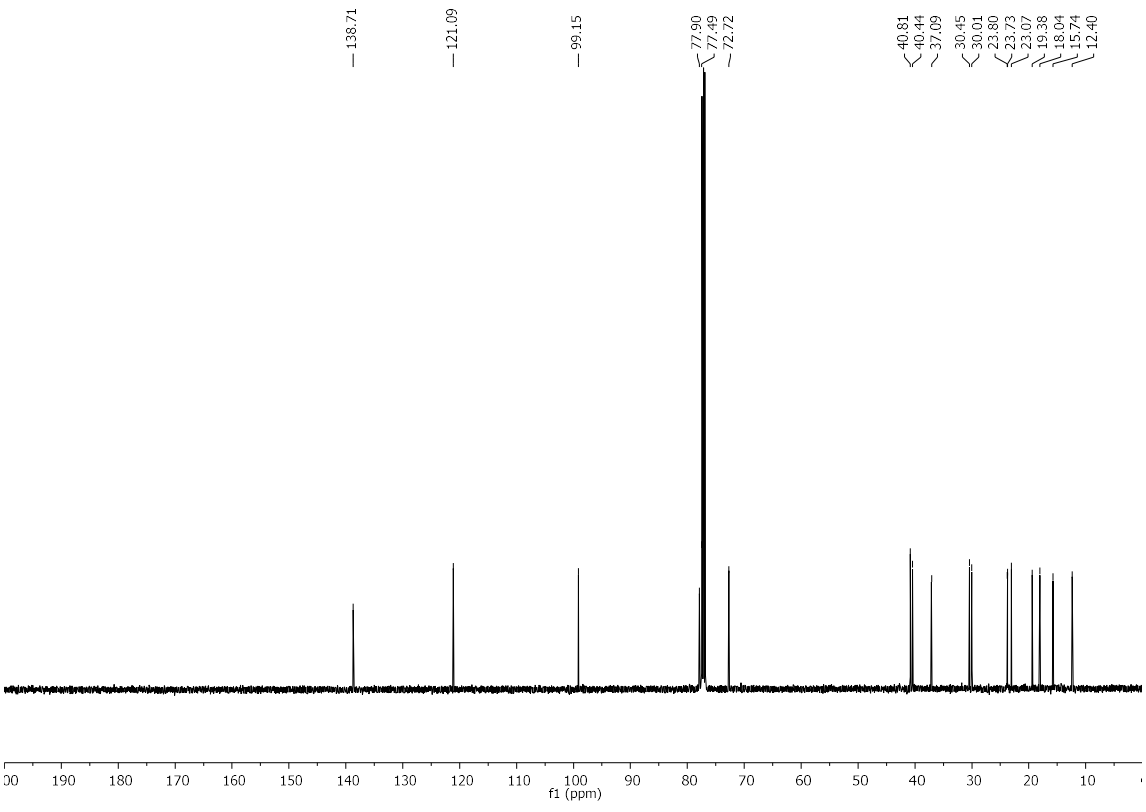
f1 (ppm)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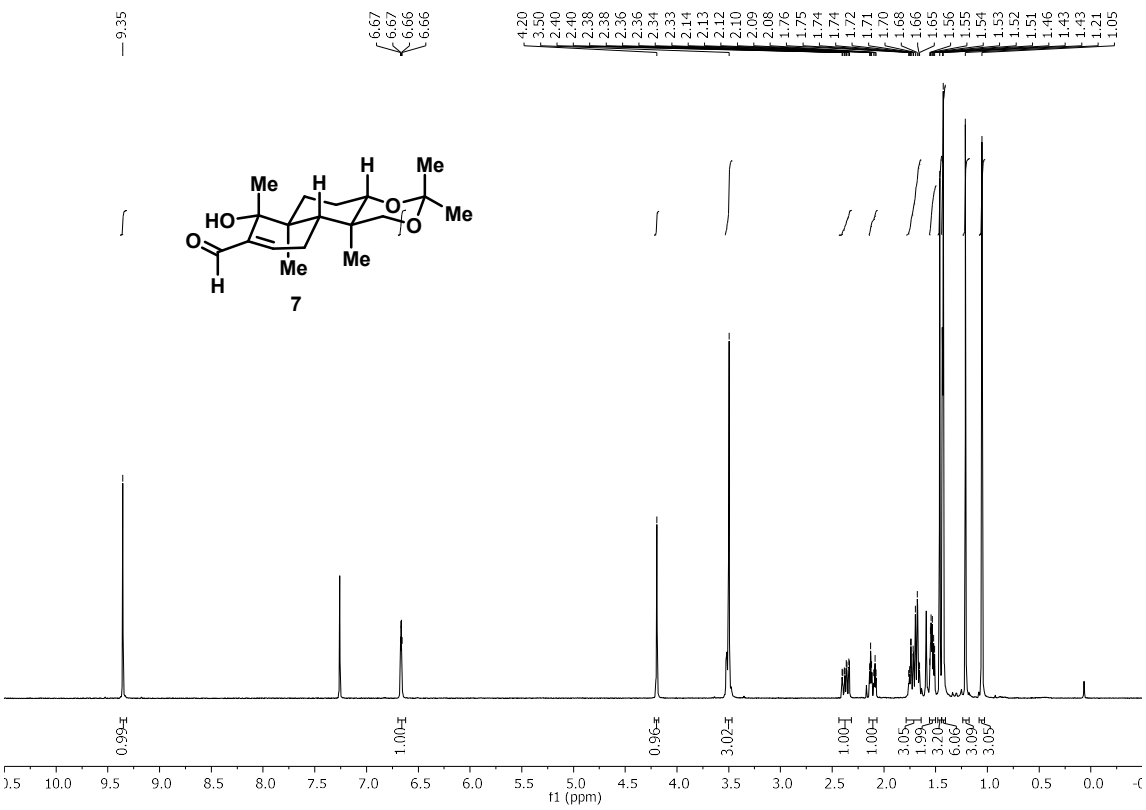
23.73
23.07
19.38
18.04
15.74
12.40
f1 (ppm)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6.67
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2.36
2.34
2.33
2.14
2.13
2.12
2.10
2.09
2.08
1.76
1.75
1.74
1.74
1.72
1.71
1.70
1.68
1.66
1.65
1.56
1.55
1.54
1.53
1.52
1.51
1.46
1.43
1.43
1.21
1.05
Me
H
H
Me
HO
O
O
Me
Me
Me
O
H
7
0.99
1.00
0.96
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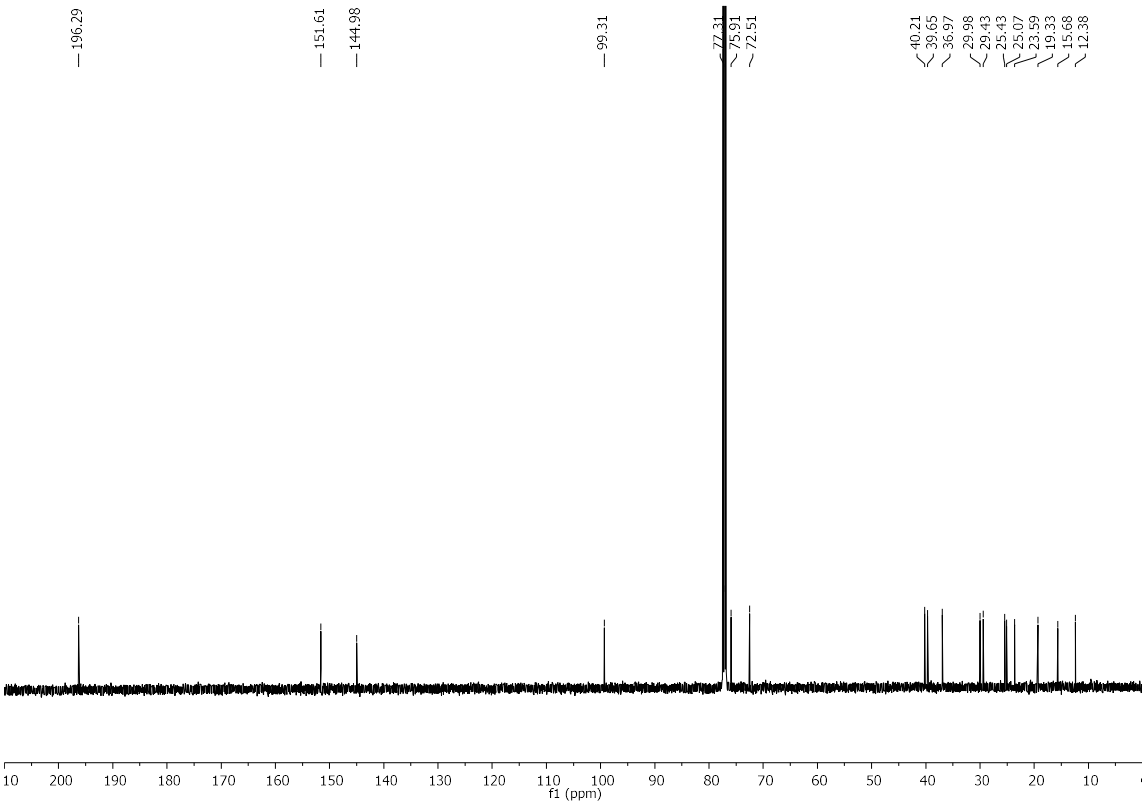
1.00
1.00
3.05
1.99
3.20
6.06
3.09
3.05
f1 (ppm)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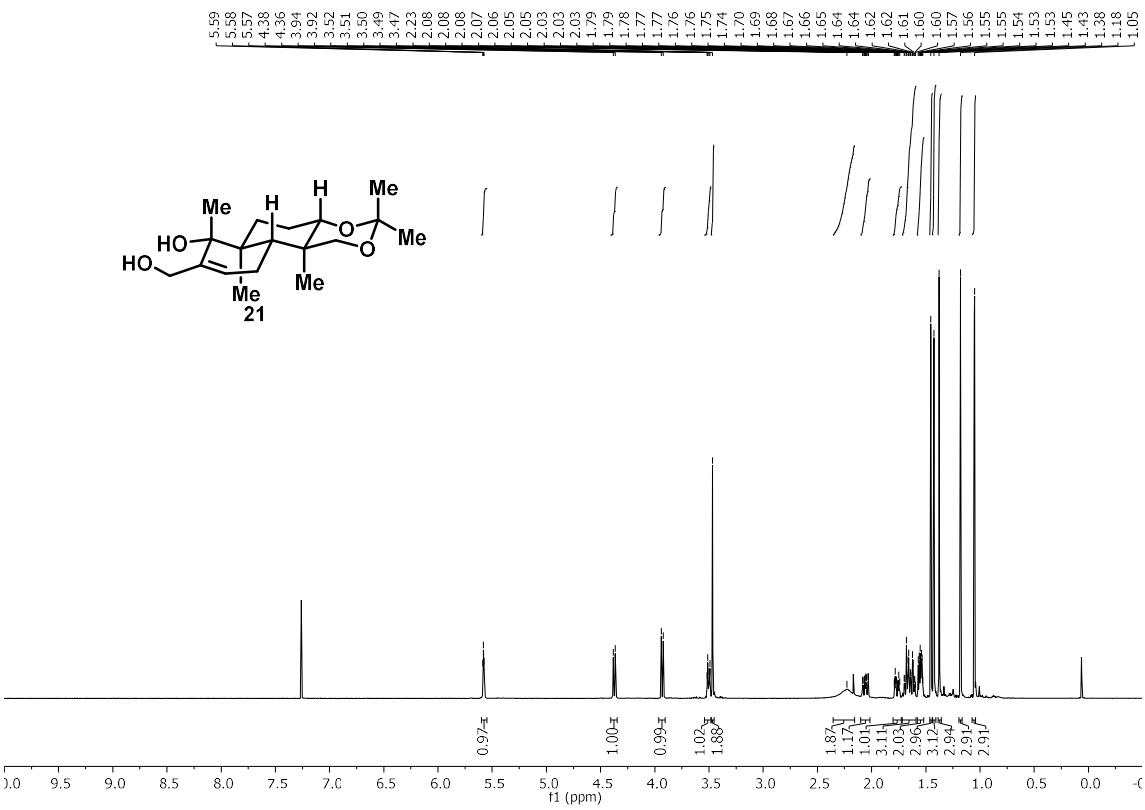
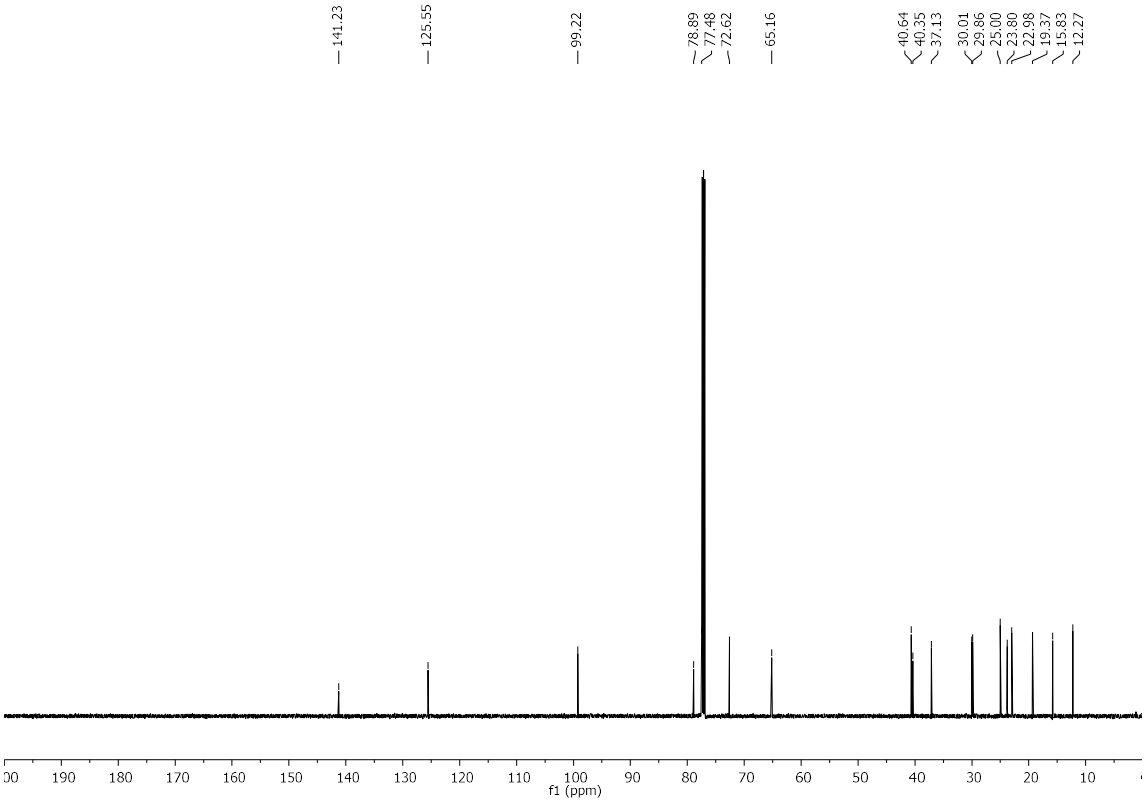
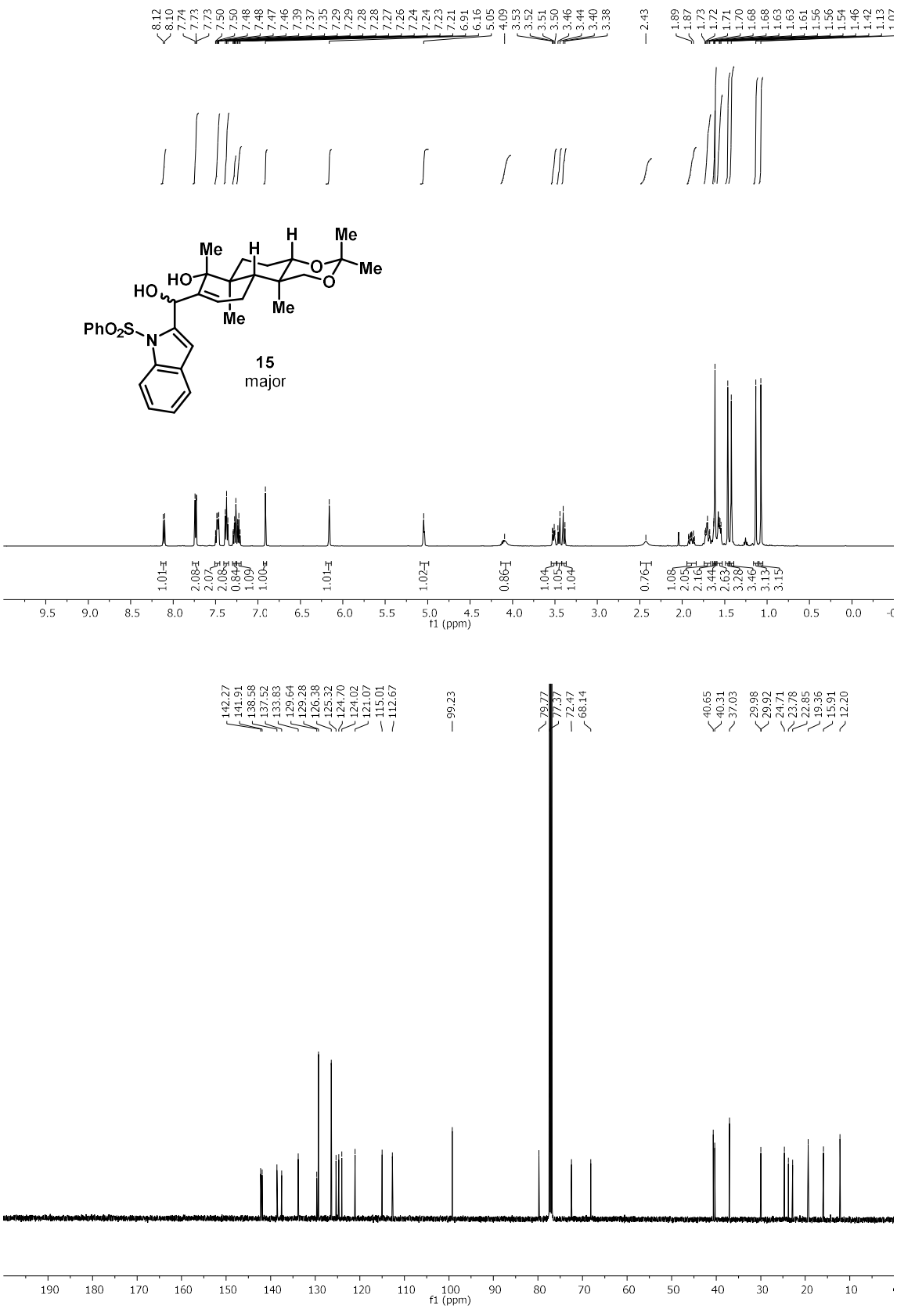
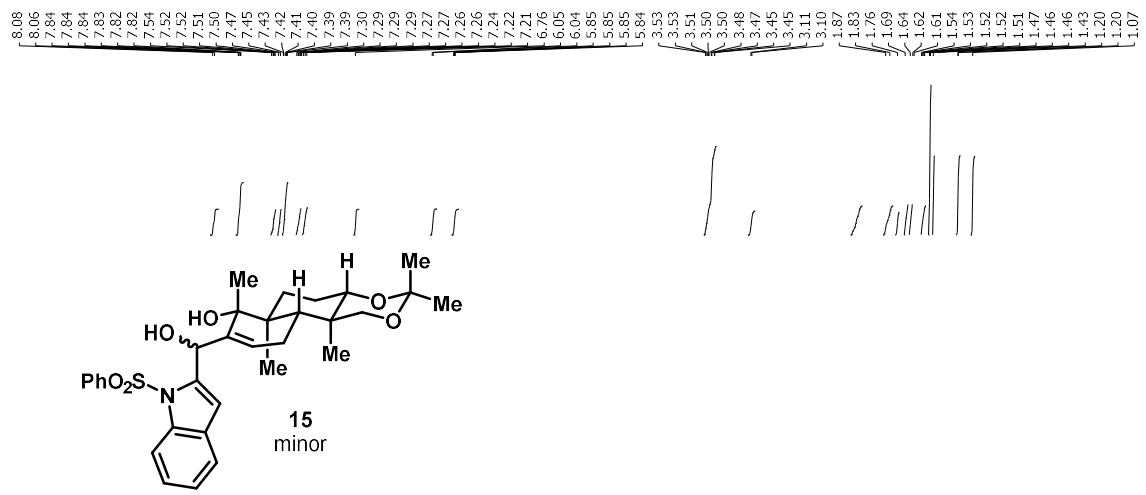
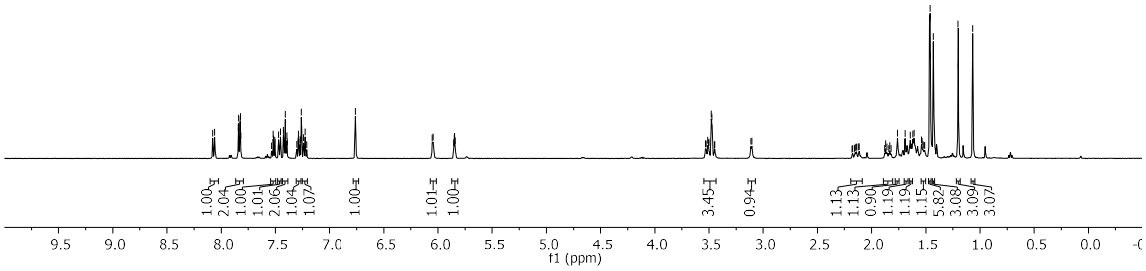
144.98
99.31
77.31
75.91
72.51
40.21
39.65
36.97
29.98
29.43
25.43
25.07
23.59
19.33
15.68
12.38
f1 (ppm)


5.59 5.58 5.57 4.38 4.36 3.94 3.92 3.52 3.51 3.50 3.49 3.47 2.23 2.08 2.08 2.08 2.07 2.06 2.05 2.05 2.03 2.03 2.03 1.79 1.79 1.78 1.77 1.77 1.76 1.76 1.75 1.74 1.70 1.69 1.68 1.67 1.66 1.65 1.64 1.64 1.62 1.62 1.61 1.60 1.60 1.57 1.56 1.55 1.55 1.54 1.53 1.53 1.45 1.43 1.38 1.18 1.05
Me
H
H
Me
HO
O
Me
HO
O
Me
Me
21
0.97 1.00 0.99 1.02 1.88 1.87 1.17 1.01 3.11 2.03 2.96 3.12 2.94 2.91 2.91
f1 (ppm)


141.23 125.55 99.22 78.89 77.48 72.62 65.16 40.64 40.35 37.13 30.01 29.86 25.00 23.80 22.98 19.37 15.83 12.27
f1 (ppm)


15
major
f1 (ppm)
f1 (ppm)


Me
H
Me
HO
HO
O
O
Me
Me
Me
PhO2S
N
15
minor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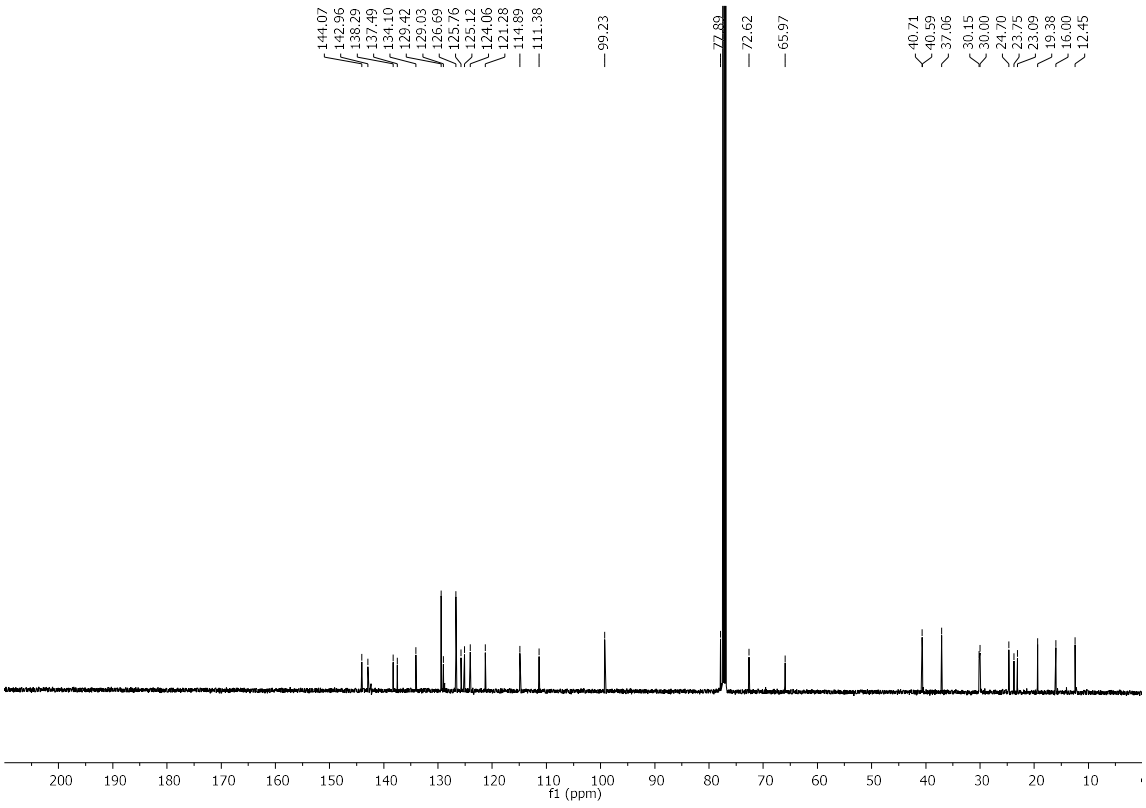
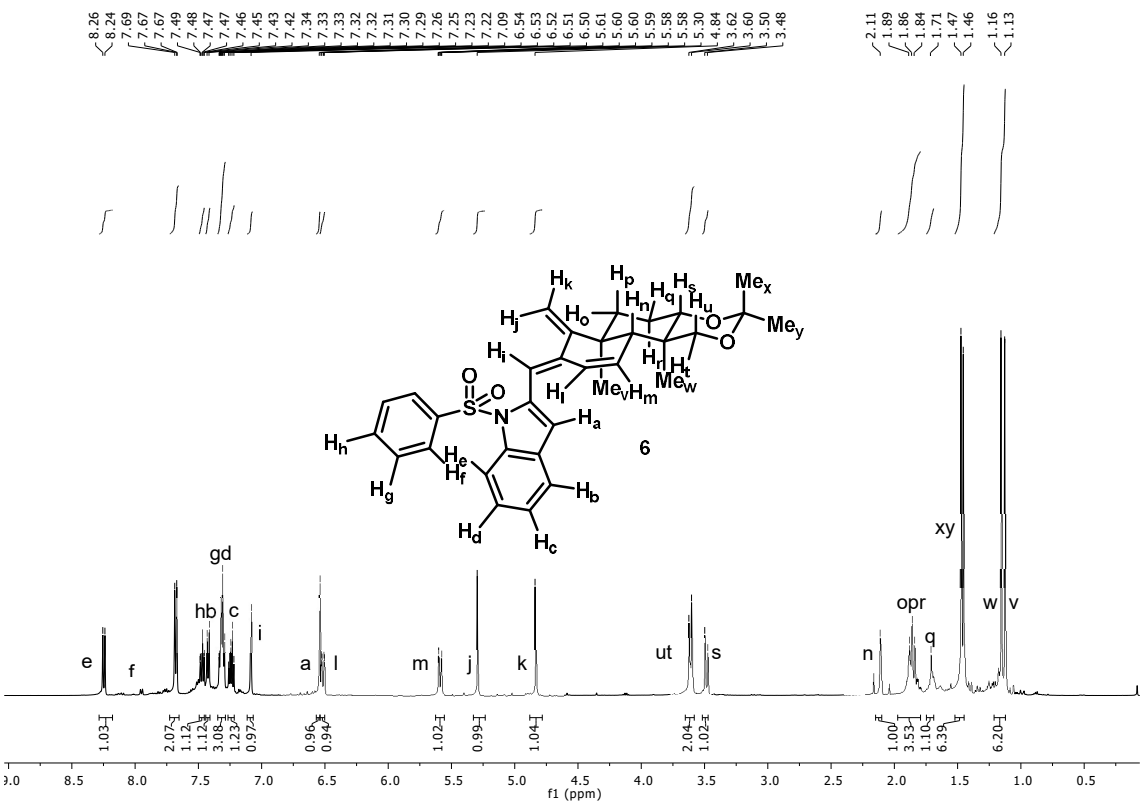

f1 (ppm)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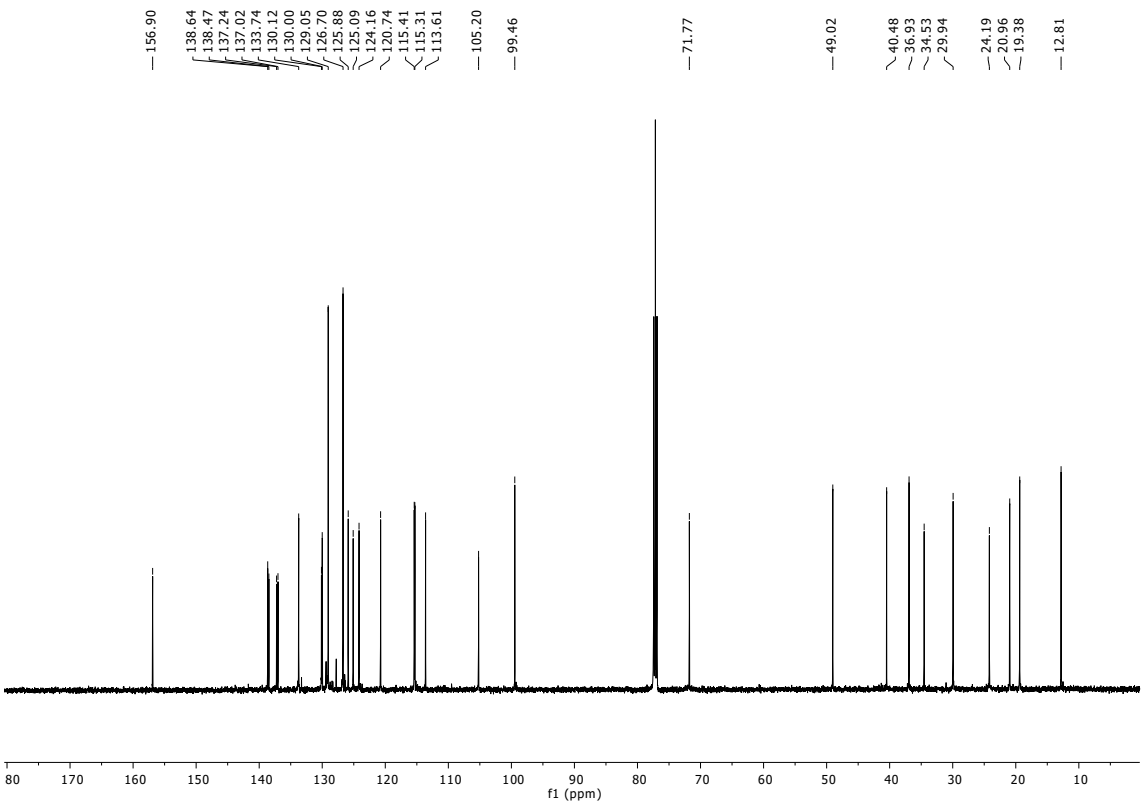
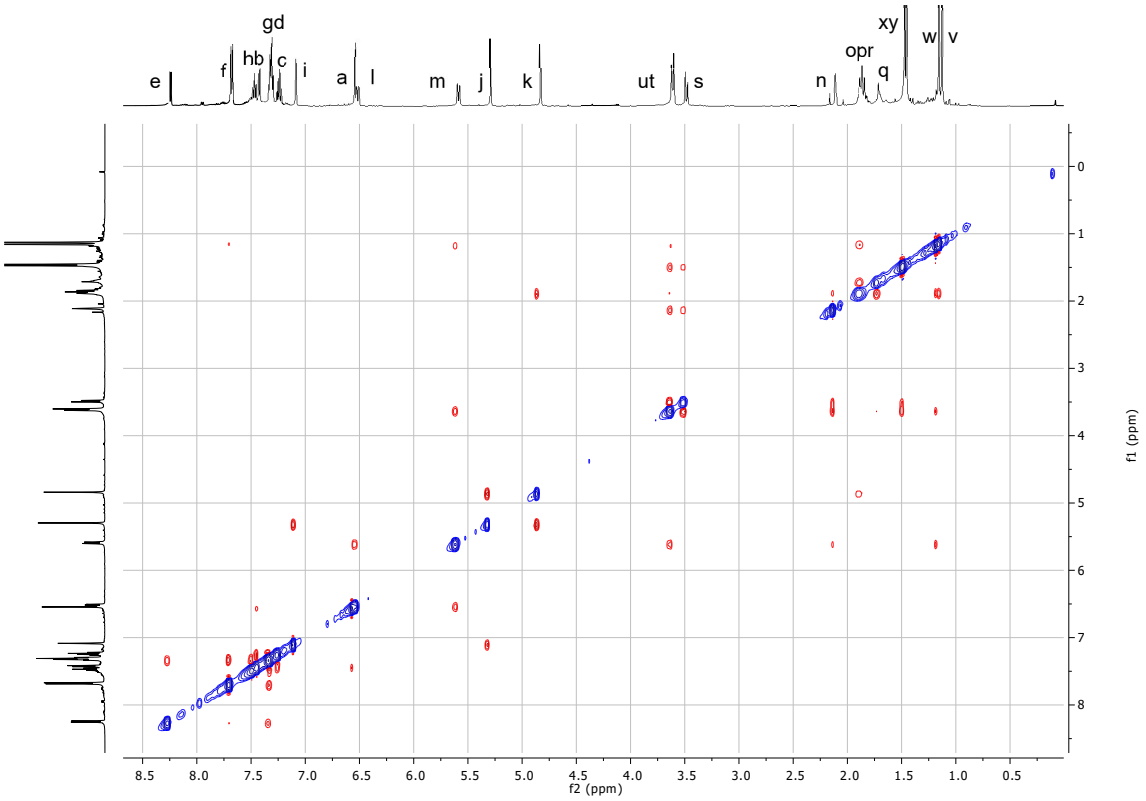
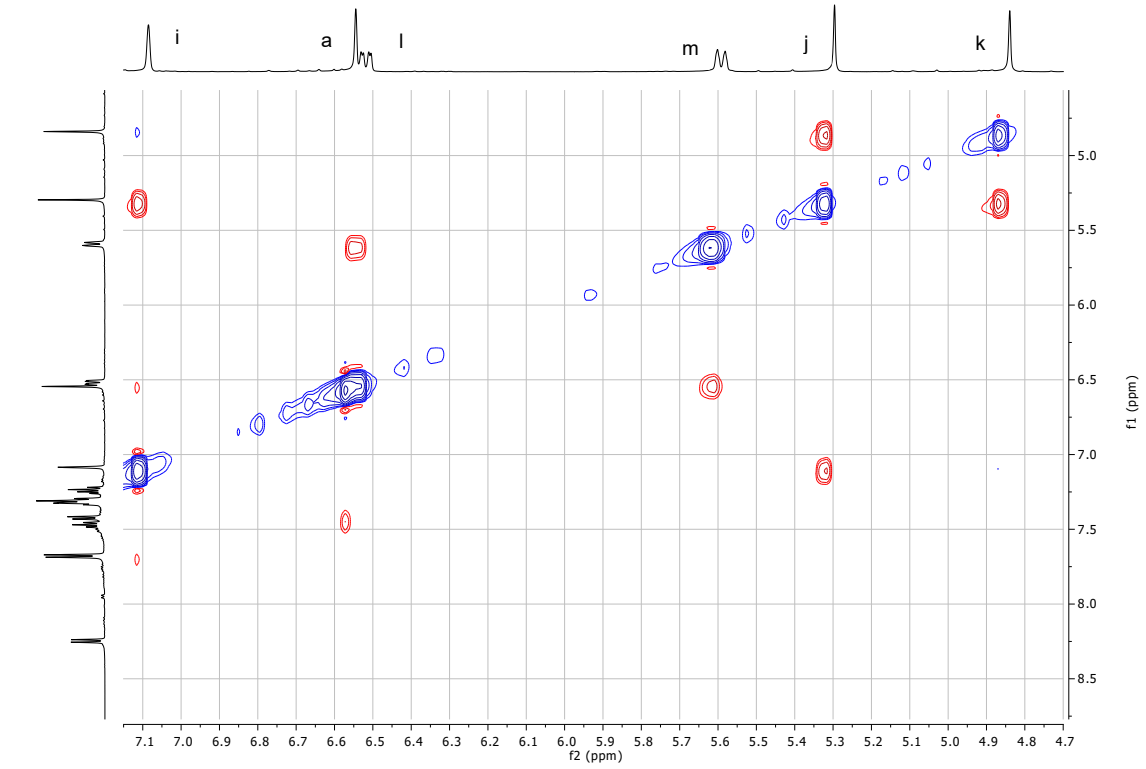
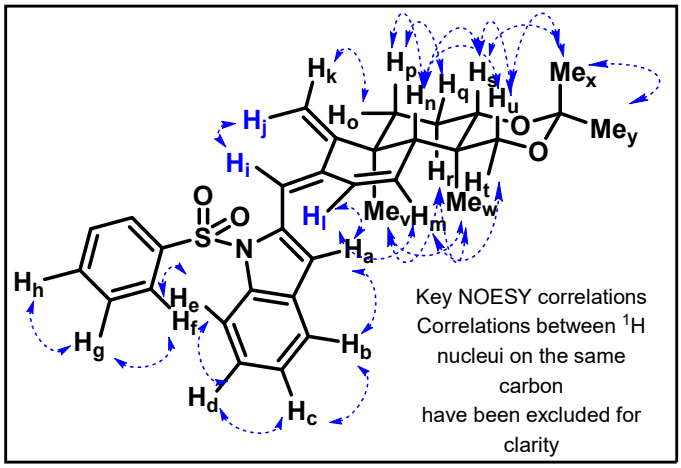
2.11 1.89 1.86 1.84 1.71 1.47 1.46 1.16 1.13
6
gd
hb
c
i
e
f
a
l
m
j
k
ut
s
n
opr
q
xy
w
v
1.03 2.07 1.12 1.12 3.08 1.23 0.97 0.96 0.94 1.02 0.99 1.04 2.04 1.02 1.00 3.53 1.10 6.39 6.20
f1 (ppm)


156.90 138.64 138.47 137.24 137.02 133.74 130.12 130.00 129.05 126.70 125.88 125.09 124.16 120.74 115.41 115.31 113.61 105.20 99.46 71.77 49.02 40.48 36.93 34.53 29.94 24.19 20.96 19.38 12.81
f1 (ppm)

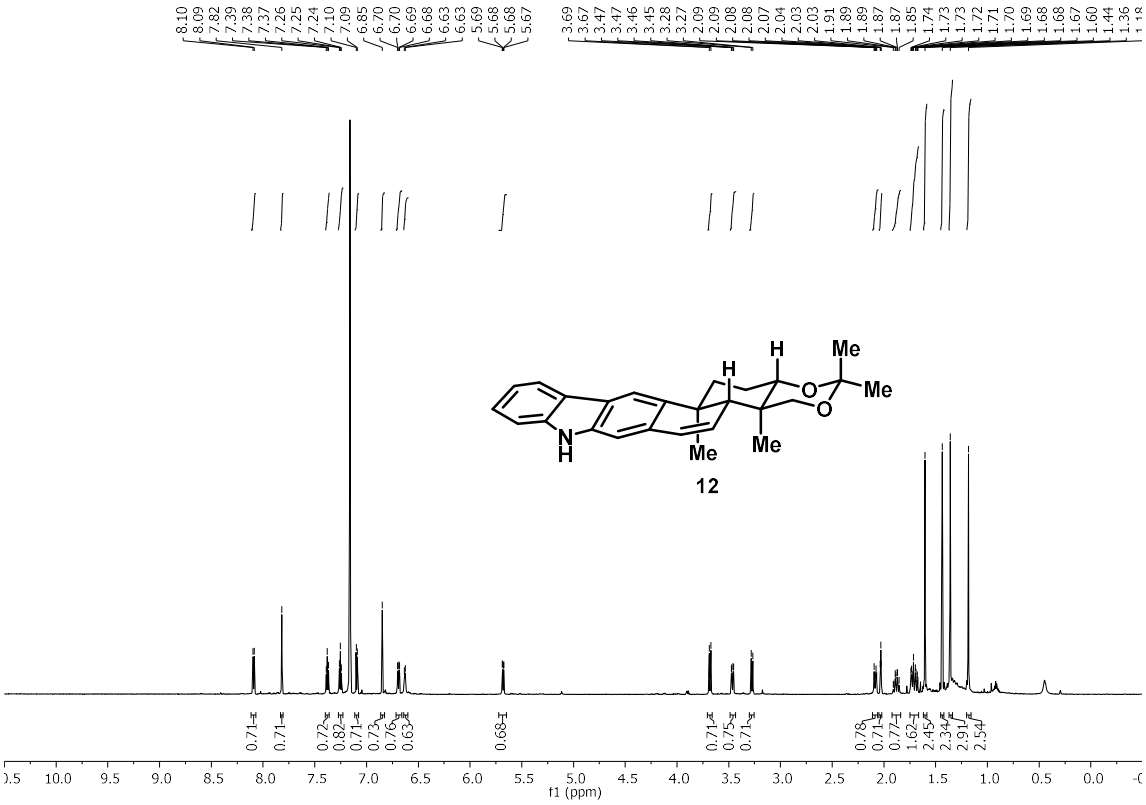

gd
e
f
hb
c
i
a
l
m
j
k
ut
s
n
opr
q
xy
w
v
f1 (ppm)
f2 (ppm)

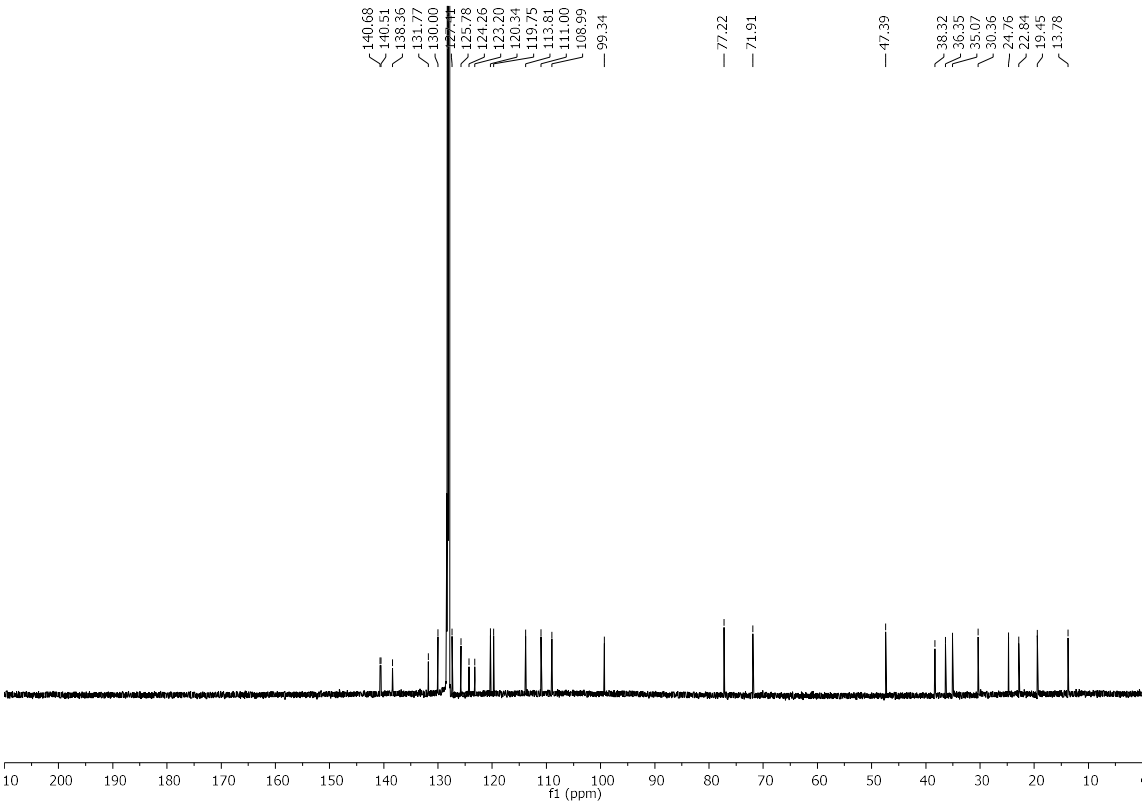

i
a
l
m
j
k
f1 (ppm)
f2 (ppm)

NOESY correlations for compound 6



^{1}H signal	NOESY correlation
a	b, l
b	a, c
c	b, d
d	c, e
e	d
f	g
g	f, h
h	g
i	j
j	i, k
k	j, o
l	a, m
m	l, w, t
n	p, s, u
o	k, p, q, r
p	n, o, q, s
q	o, p, r
r	o, q, v, w
s	p, n, x
t	m, u, w
u	n, s, t, x
v	r, w
w	m, r, t, v
x	s, u, y
y	x


8.10
8.09
7.82
7.39
7.38
7.37
7.26
7.25
7.24
7.10
7.09
6.85
6.70
6.70
6.69
6.68
6.63
6.63
5.69
5.68
5.68
5.67
3.69
3.67
3.47
3.47
3.46
3.45
3.28
3.27
2.09
2.09
2.08
2.08
2.07
2.04
2.03
2.03
1.91
1.89
1.89
1.87
1.87
1.85
1.74
1.73
1.73
1.72
1.71
1.70
1.69
1.68
1.68
1.67
1.60
1.44
1.36
H
H
Me
O
Me
O
N
H
Me
Me
12
0.71
0.71
0.72
0.82
0.71
0.73
0.76
0.63
0.68
0.71
0.75
0.71
0.78
0.71
0.77
1.62
2.45
2.34
2.91
2.54
f1 (ppm)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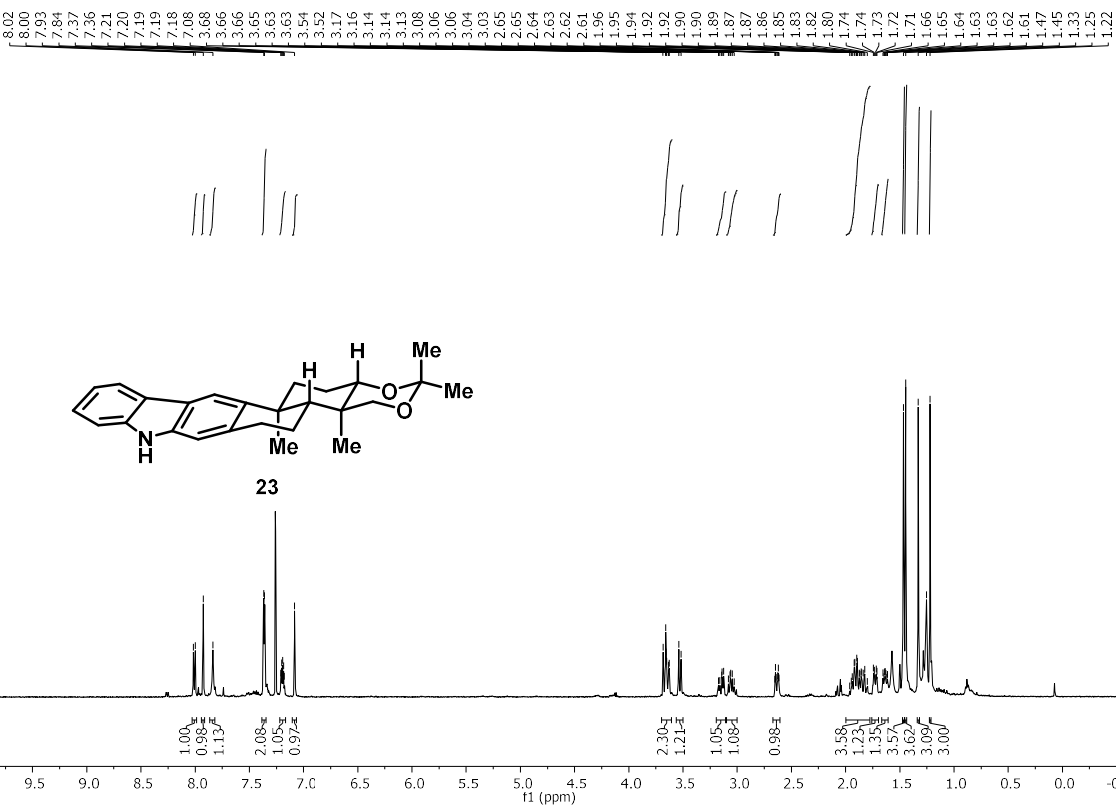
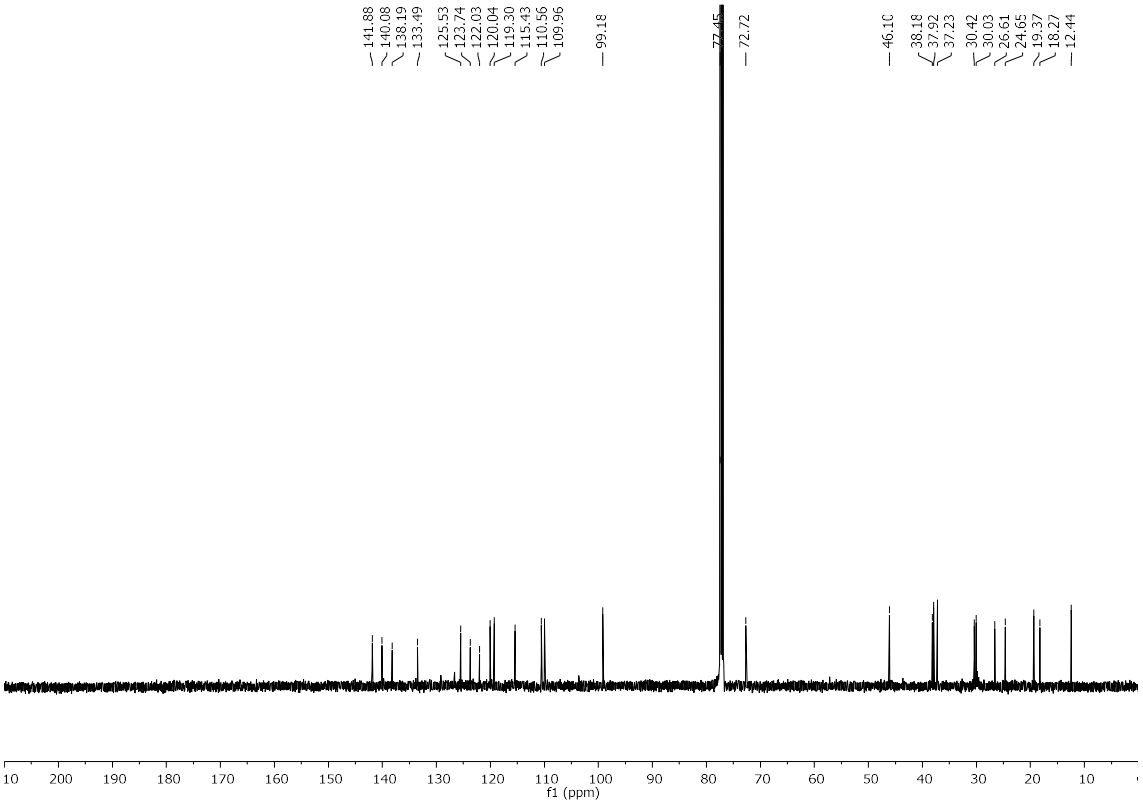
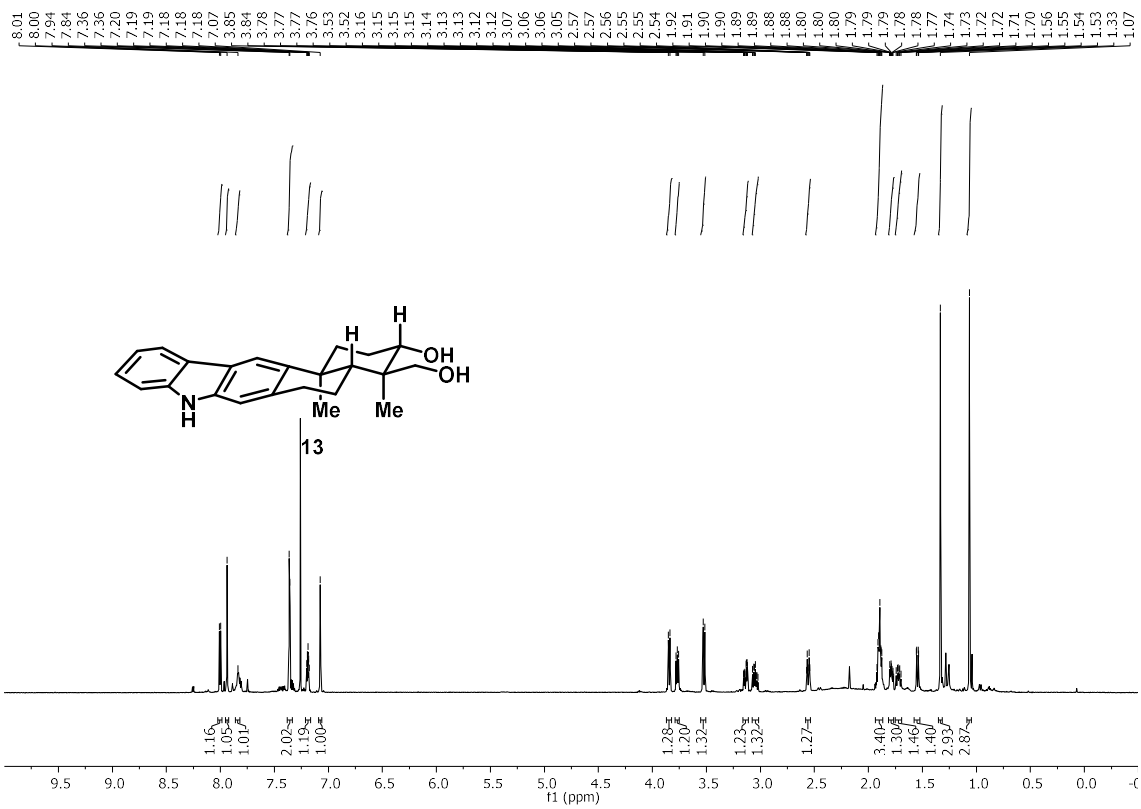
140.51
138.36
131.77
130.00
125.78
124.26
123.20
120.34
119.75
113.81
111.00
108.99
99.34
77.22
71.91
47.39
38.32
36.35
35.07
30.36
24.76
22.84
19.45
13.78
f1 (ppm)


8.02 8.00 7.93 7.84 7.37 7.36 7.21 7.20 7.19 7.19 7.18 7.08 3.68 3.66 3.66 3.65 3.63 3.63 3.54 3.52 3.17 3.16 3.14 3.14 3.13 3.08 3.06 3.06 3.04 3.03 2.65 2.64 2.63 2.62 2.61 1.96 1.95 1.94 1.92 1.92 1.90 1.90 1.89 1.87 1.87 1.86 1.85 1.83 1.82 1.80 1.74 1.74 1.73 1.72 1.71 1.66 1.65 1.64 1.63 1.63 1.62 1.61 1.47 1.45 1.33 1.25 1.22
H
H
Me
O
Me
O
N
H
Me
Me
23
1.00 0.98 1.13 2.08 1.05 0.97 2.30 1.21 1.05 1.08 0.98 3.58 1.23 1.35 3.57 3.62 3.09 3.00
f1 (ppm)


141.88 140.08 138.19 133.49 125.53 123.74 122.03 120.04 119.30 115.43 110.56 109.96 99.18 77.45 72.72 46.10 38.18 37.92 37.23 30.42 30.03 26.61 24.65 19.37 18.27 12.44
f1 (ppm)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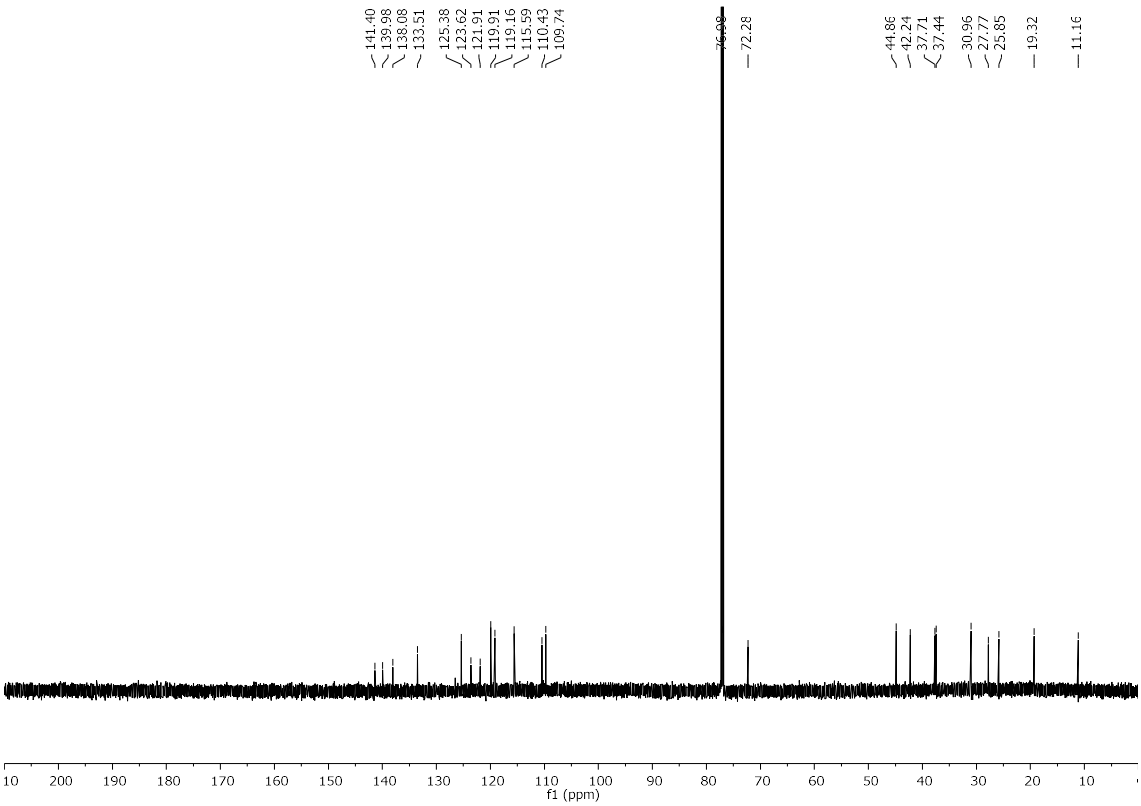
H
H
OH
OH
N
H
Me
Me
13
1.16
1.05
1.01
2.02
1.19
1.00
1.28
1.20
1.32
1.23
1.32
1.27
3.40
1.30
1.46
1.40
2.93
2.87
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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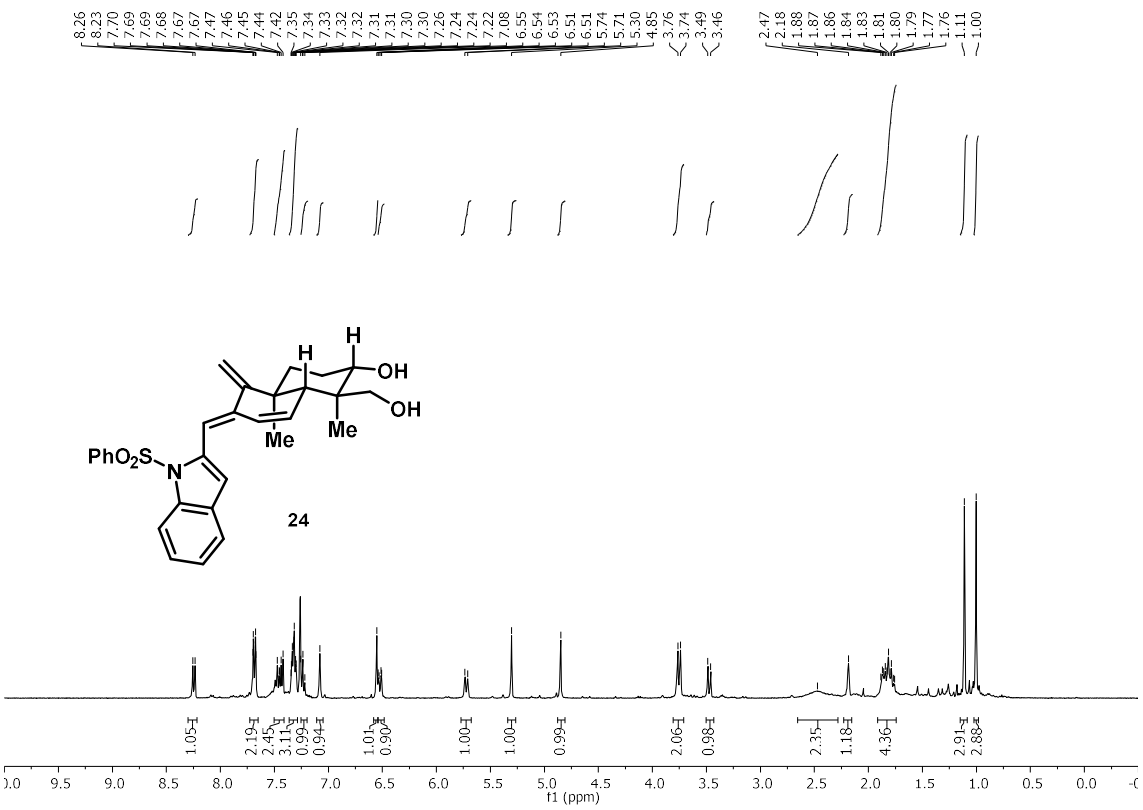
123.62
121.91
119.91
119.16
115.59
110.43
109.74
76.99
72.28
44.86
42.24
37.71
37.44
30.96
27.77
25.85
19.32
11.16
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.67
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7.44
7.42
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.31
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6.54
6.53
6.51
6.51
5.74
5.71
5.30
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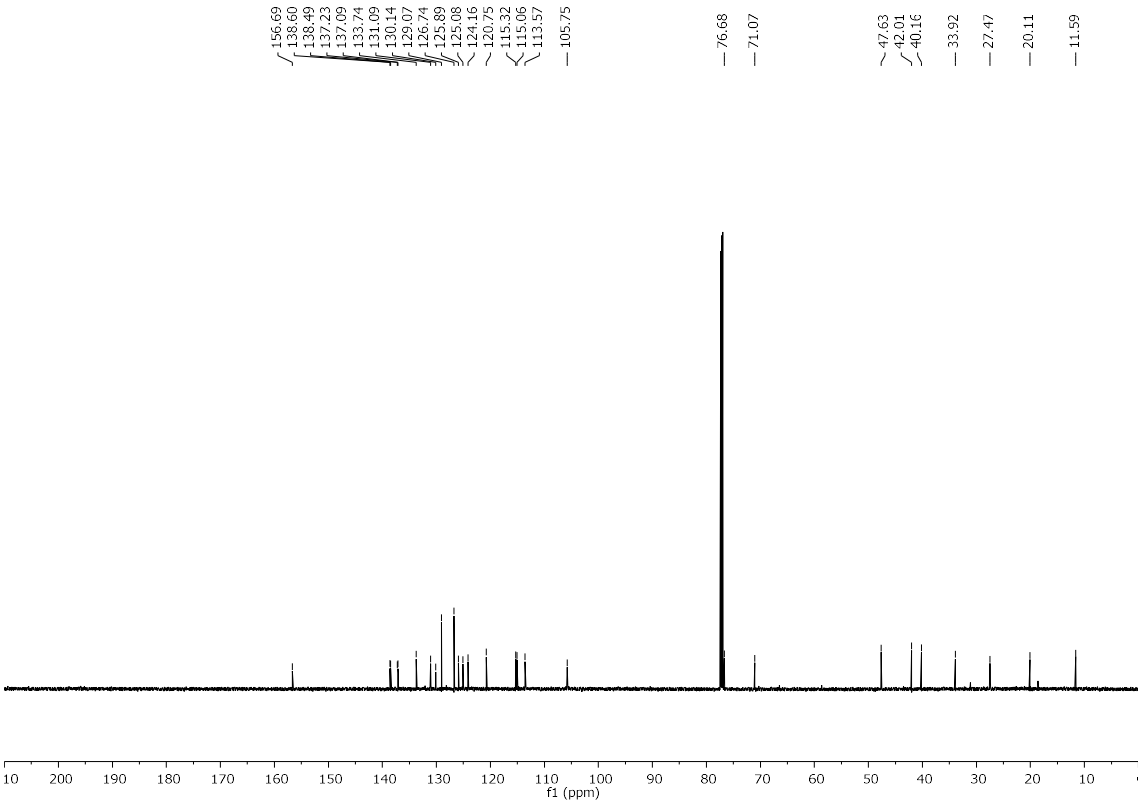
3.76
3.74
3.49
3.46
2.47
2.18
1.88
1.87
1.86
1.84
1.83
1.81
1.80
1.79
1.77
1.76
1.11
1.00
H
H
OH
OH
Me
Me
PhO2S
N
24
1.05
2.19
2.45
3.11
0.99
0.94
1.01
0.90
1.00
1.00
0.99
2.06
0.98
2.35
1.18
4.36
2.91
2.88
f1 (ppm)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129.07
126.74
125.89
125.08
124.16
120.75
115.32
115.06
113.57
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71.07
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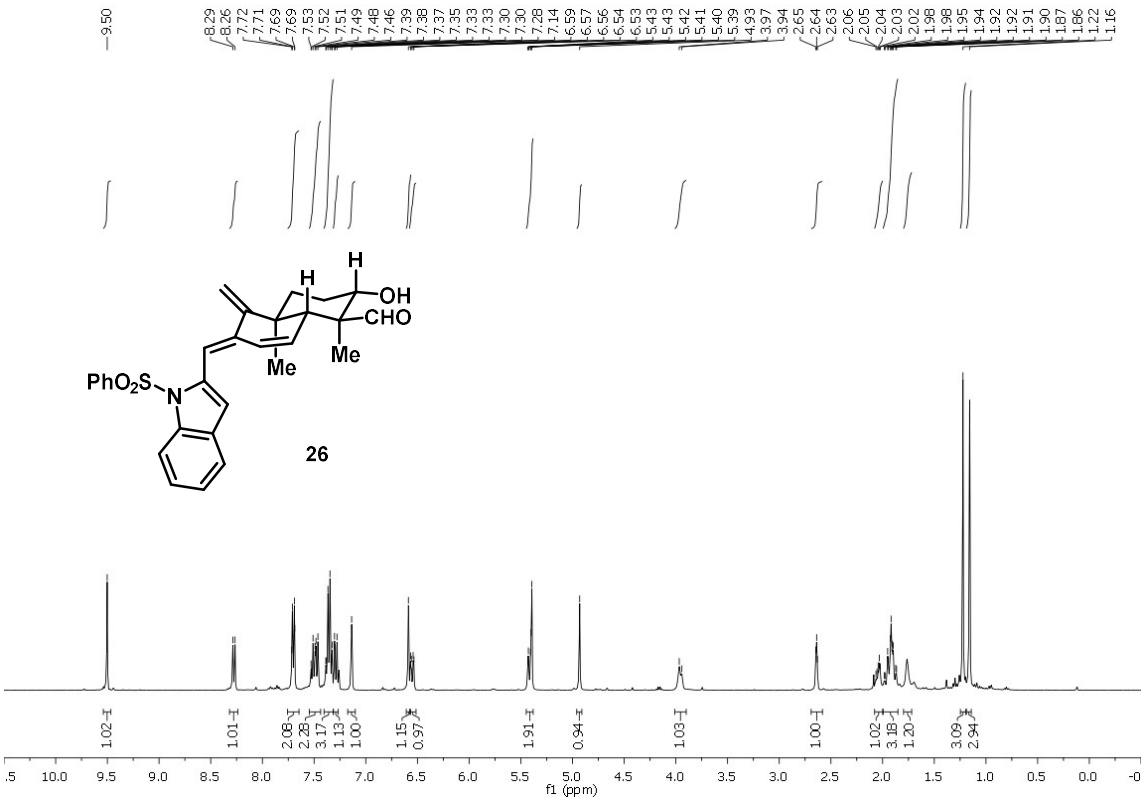
42.01
40.16
33.92
27.47
20.11
11.59
f1 (ppm)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7.39
7.38
7.37
7.35
7.33
7.33
7.30
7.30
7.28
7.14
6.59
6.57
6.56
6.54
6.53
5.43
5.43
5.42
5.41
5.40
5.39
4.93
3.97
3.94
2.65
2.64
2.63
2.06
2.05
2.04
2.03
2.02
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1.98
1.95
1.94
1.92
1.92
1.91
1.90
1.87
1.86
1.22
1.16
H
H
OH
CHO
Me
Me
PhO2S
N
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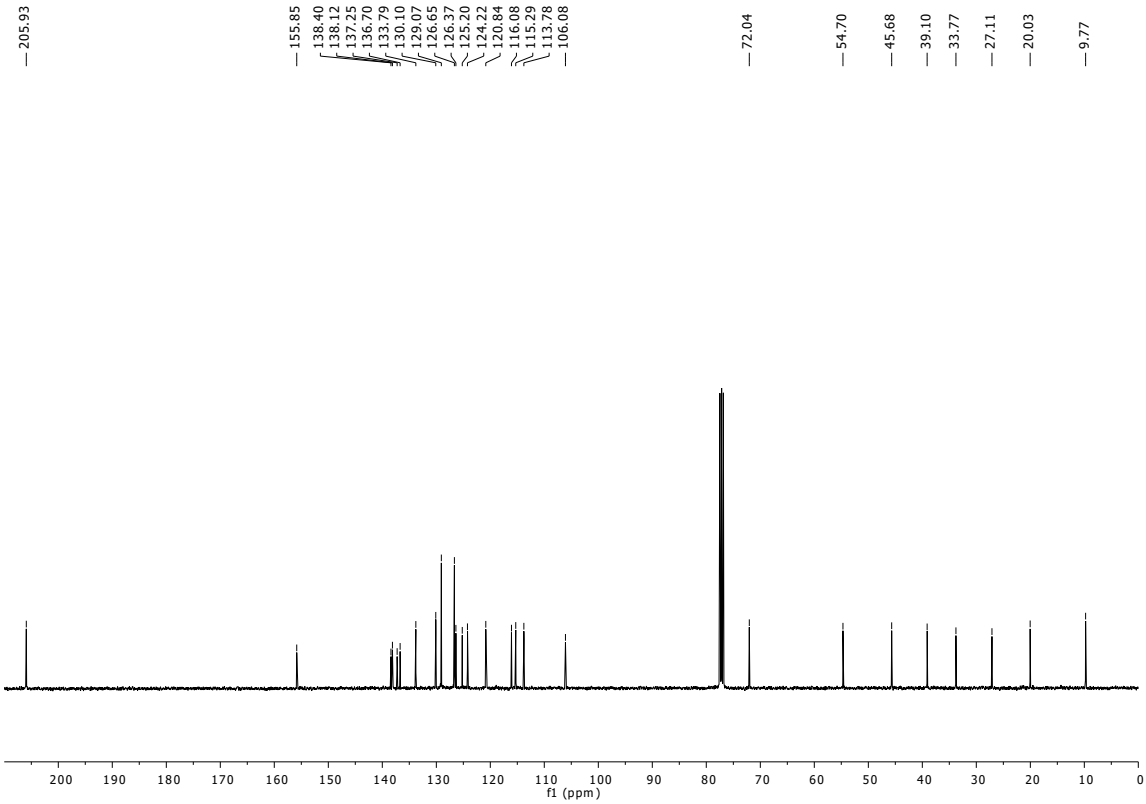
1.02
1.01
2.08
2.28
3.17
1.13
1.00
1.15
0.97
1.91
0.94
1.03
1.00
1.02
3.18
1.20
3.09
2.94
f1 (ppm)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136.70
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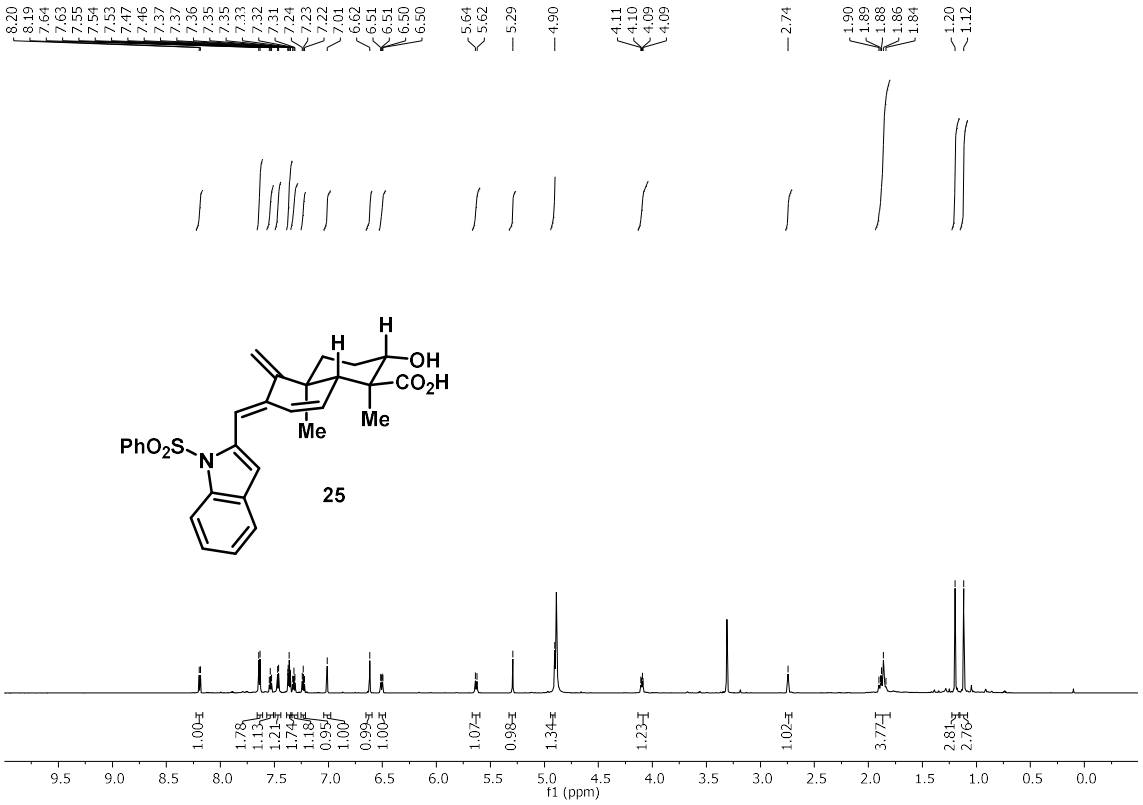
126.65
126.37
125.20
124.22
120.84
116.08
115.29
113.78
106.08
72.04
54.70
45.68
39.10
33.77
27.11
20.03
9.77
f1 (ppm)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7.35
7.35
7.33
7.32
7.31
7.24
7.23
7.22
7.01
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6.51
6.51
6.50
6.50
5.64
5.62
5.29
4.90
4.11
4.10
4.09
4.09
2.74
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1.89
1.88
1.86
1.84
1.20
1.12
H
H
OH
CO2H
Me
Me
PhO2S
N
25
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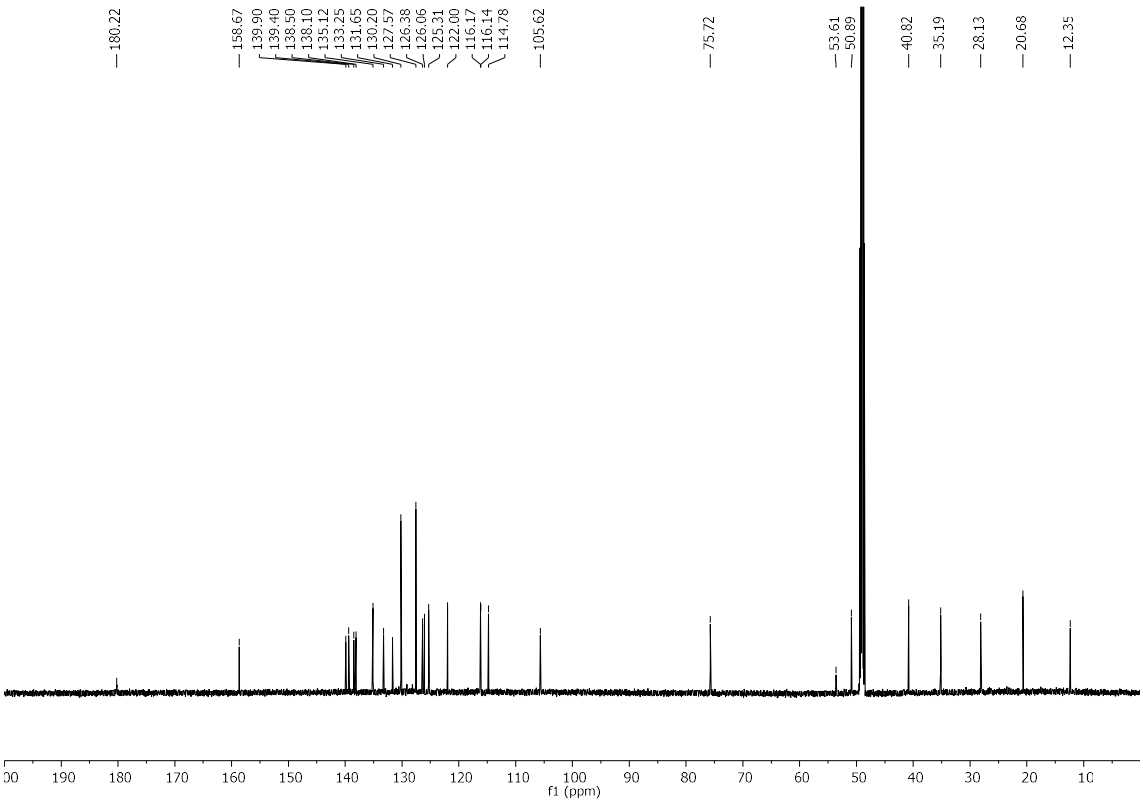
1.78
1.13
1.21
1.74
1.18
0.95
1.00
0.99
1.00
1.07
0.98
1.34
1.23
1.02
3.77
2.81
2.76
f1 (ppm)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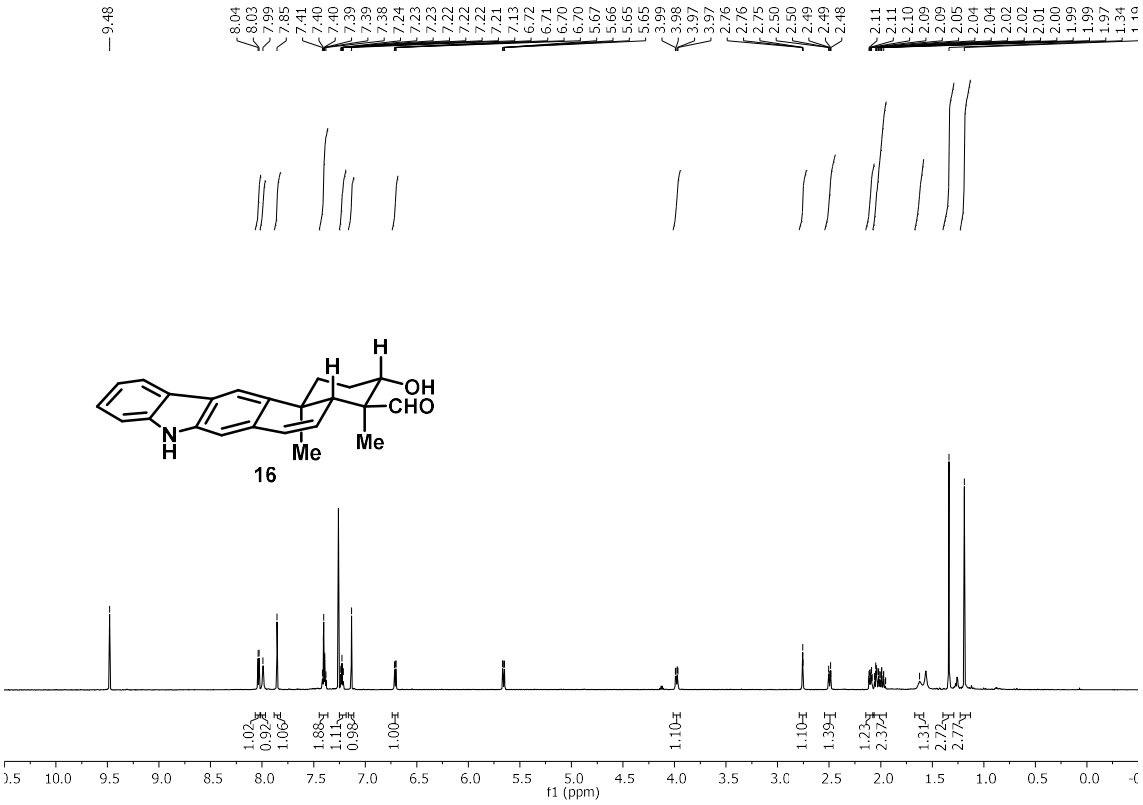
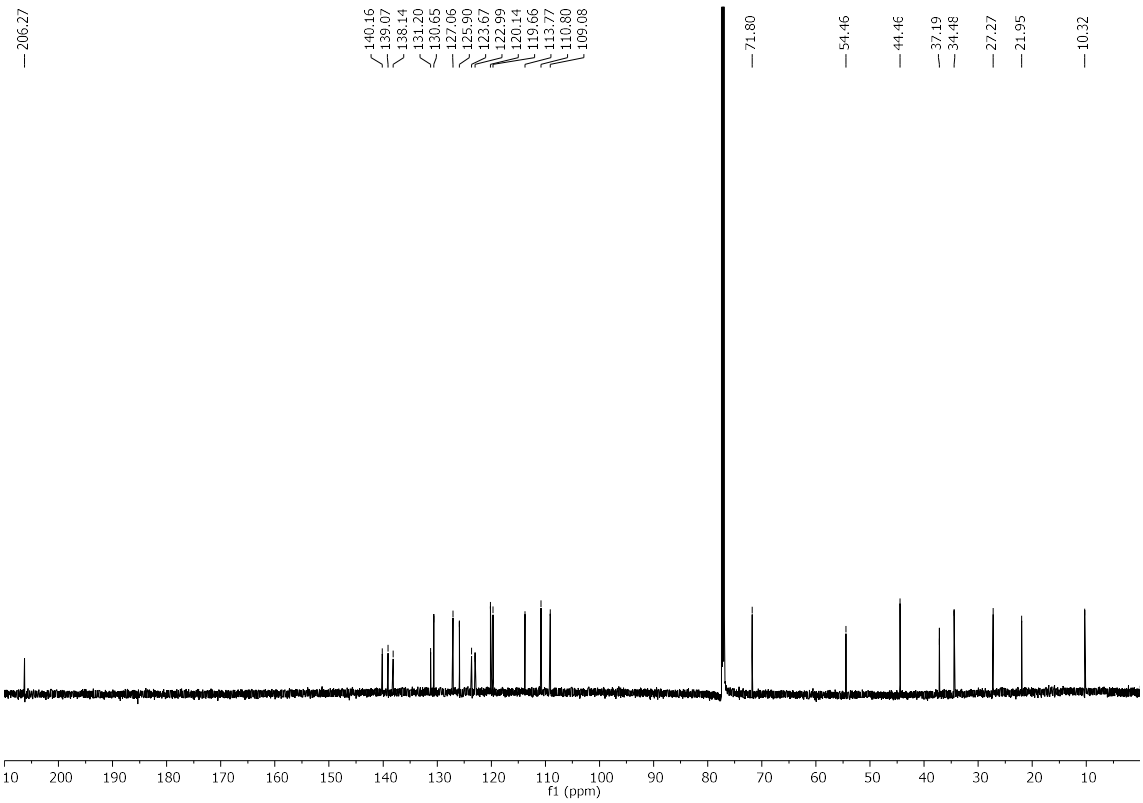
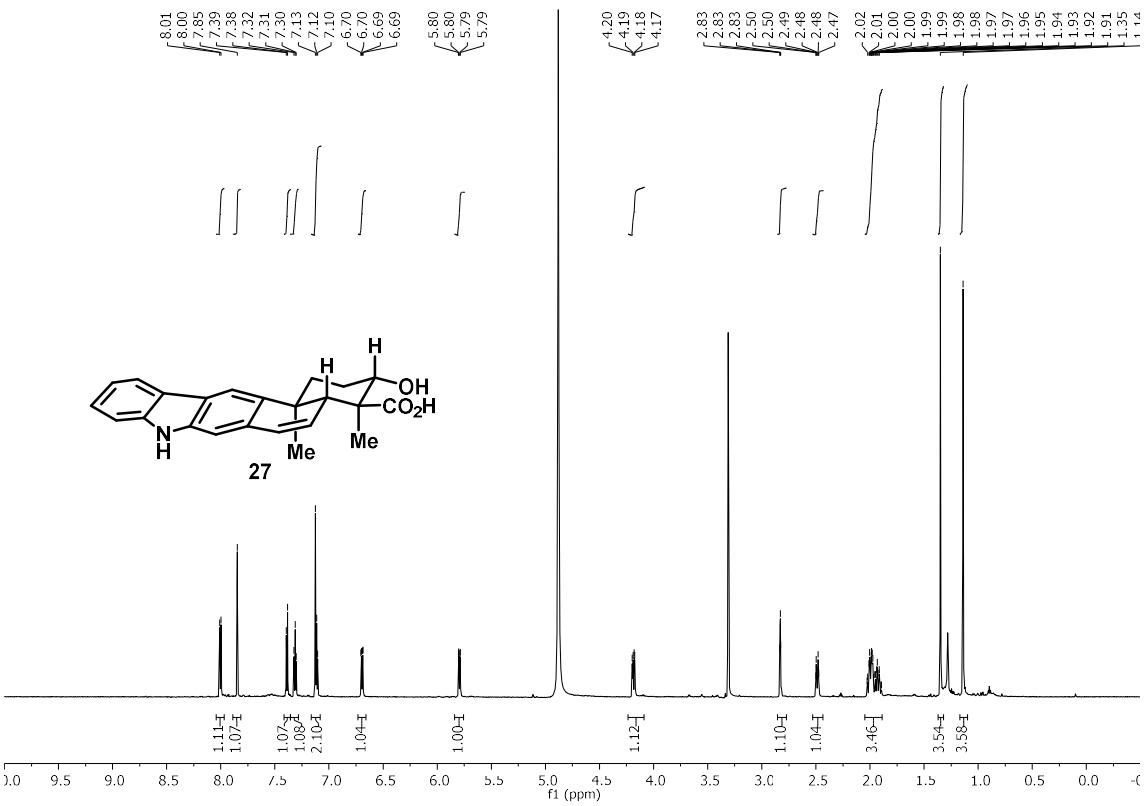
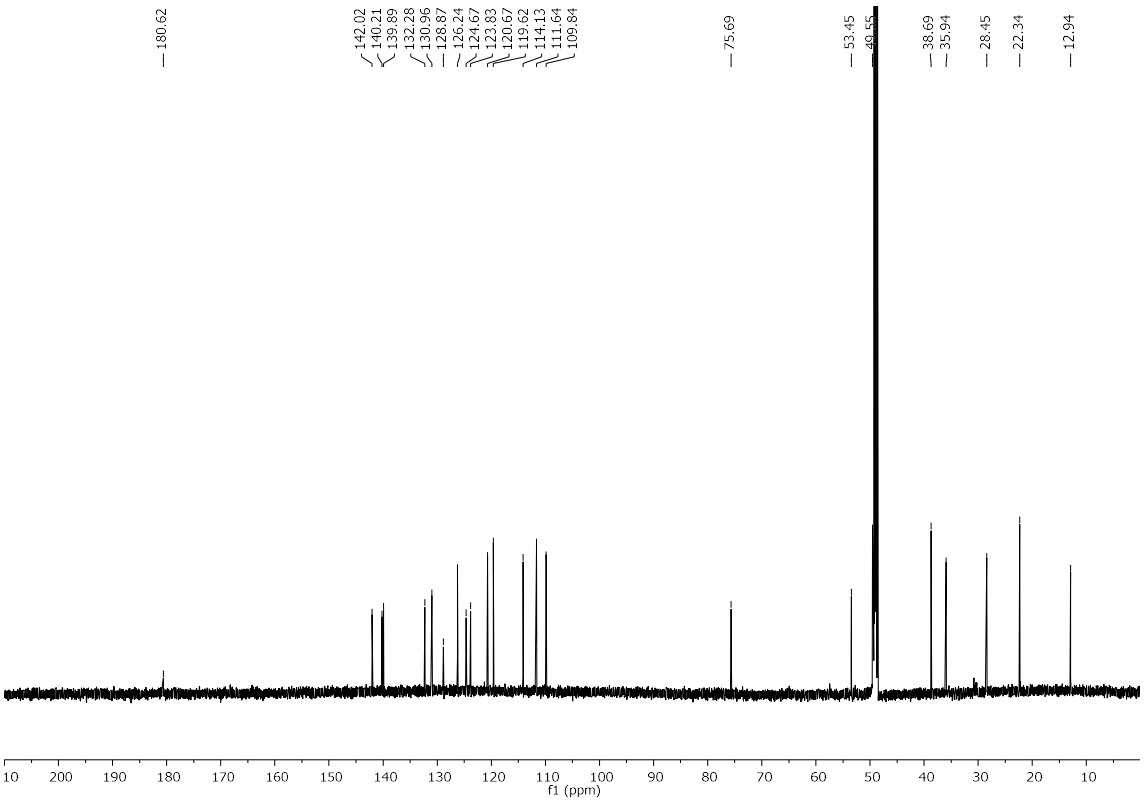
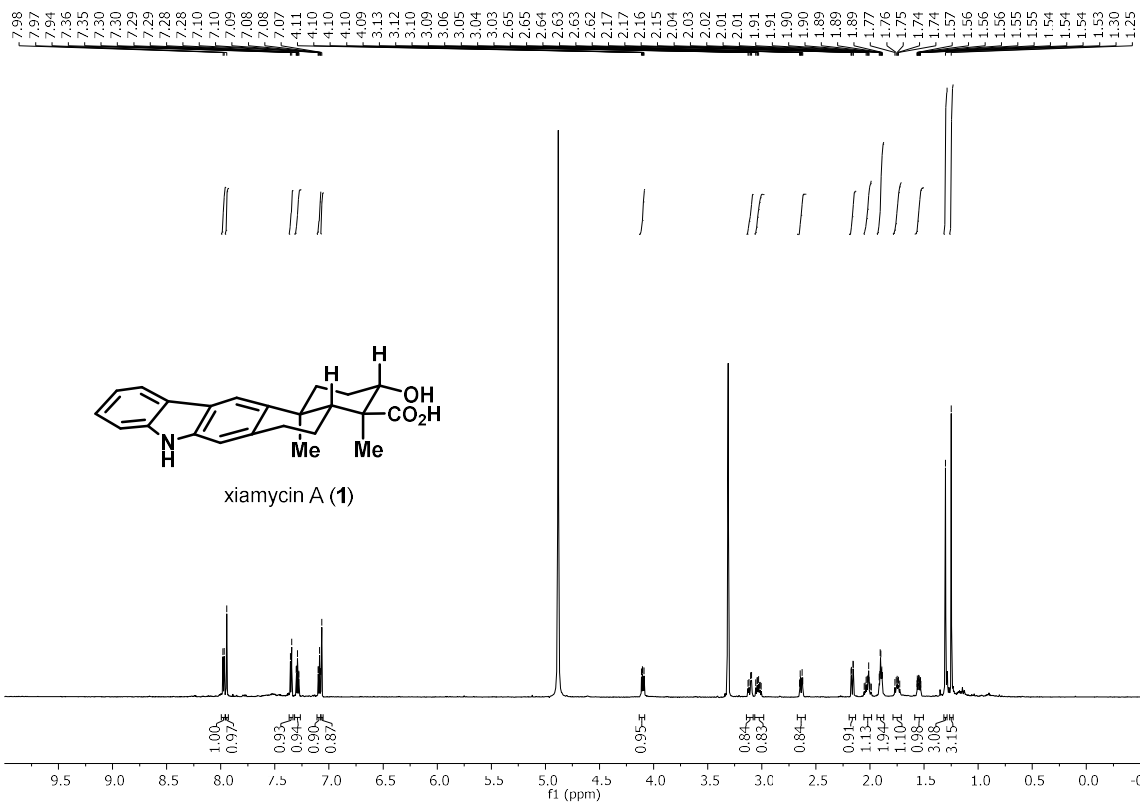
126.06
125.31
122.00
116.17
116.14
114.78
105.62
75.72
53.61
50.89
40.82
35.19
28.13
20.68
12.35
f1 (ppm)

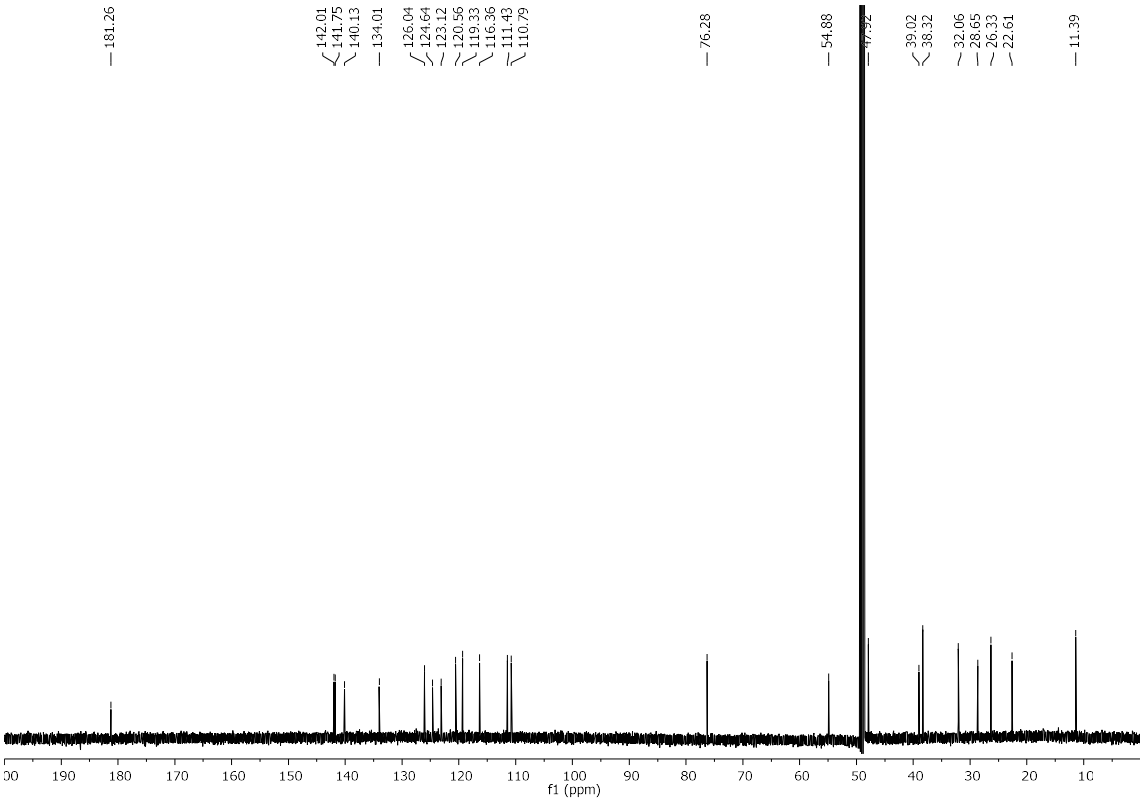

9.48
8.04
8.03
7.99
7.85
7.41
7.40
7.40
7.39
7.39
7.38
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.13
6.72
6.71
6.70
6.70
5.67
5.66
5.65
5.65
3.99
3.98
3.97
3.97
2.76
2.76
2.75
2.50
2.50
2.49
2.49
2.48
2.11
2.11
2.10
2.09
2.09
2.05
2.04
2.04
2.02
2.02
2.01
2.00
1.99
1.99
1.97
1.34
H
H
OH
CHO
N
H
Me
Me
16
1.02
0.92
1.06
1.88
1.11
0.98
1.00
1.10
1.10
1.39
1.23
2.37
1.31
2.72
2.77
f1 (ppm)

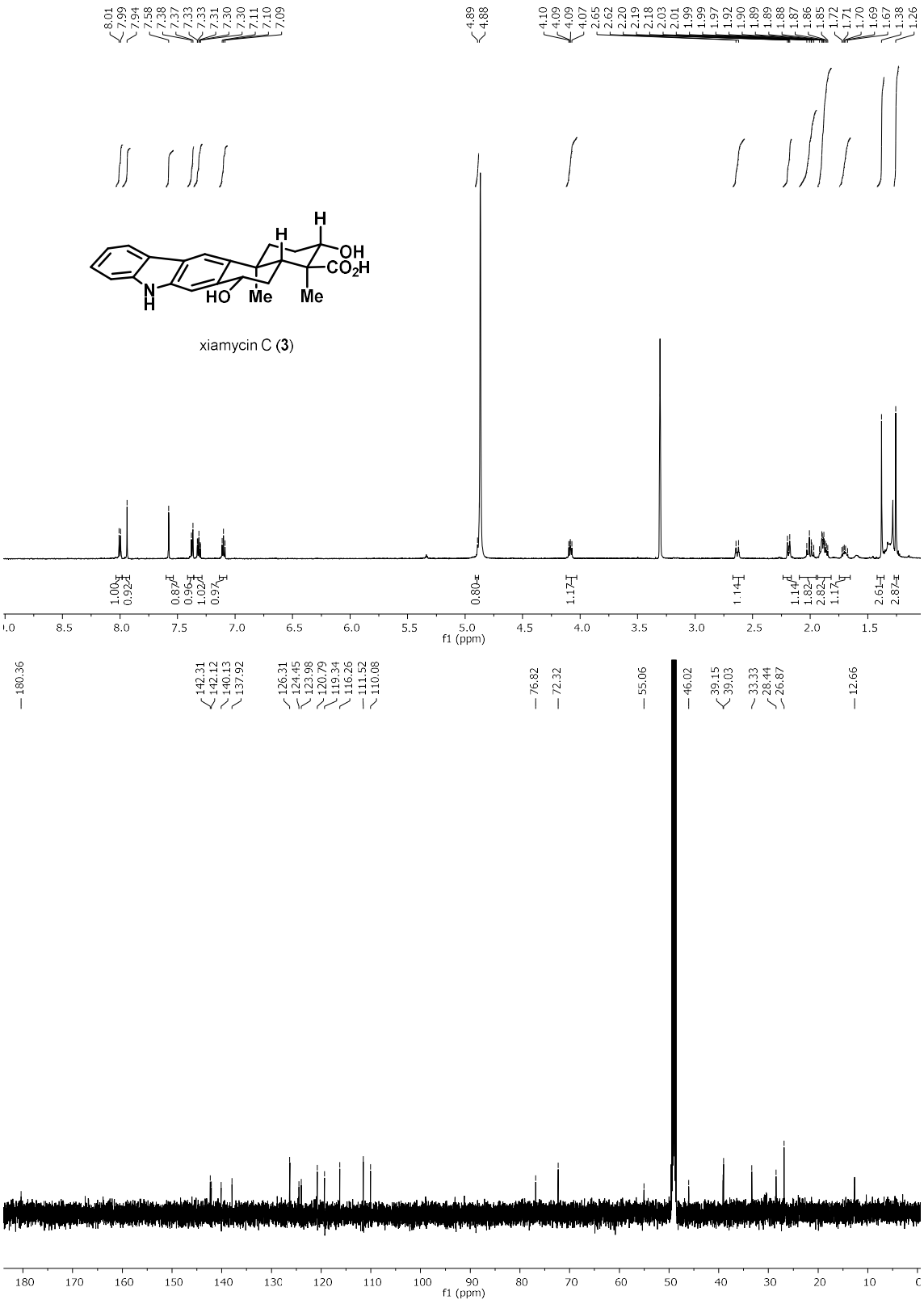

206.27
140.16
139.07
138.14
131.20
130.65
127.06
125.90
123.67
122.99
120.14
119.66
113.77
110.80
109.08
71.80
54.46
44.46
37.19
34.48
27.27
21.95
10.32
f1 (ppm)

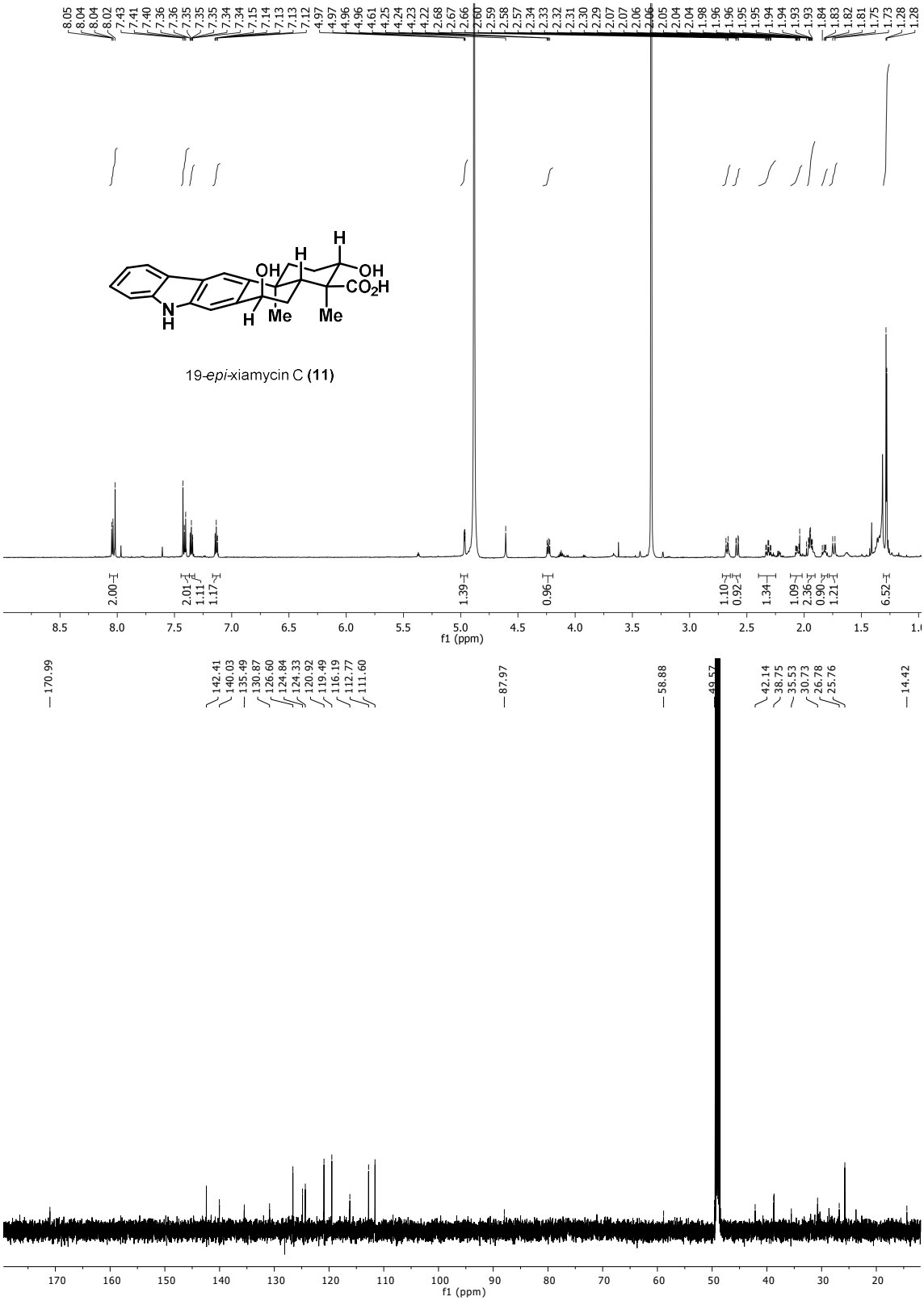

8.01
8.00
7.85
7.39
7.38
7.32
7.31
7.30
7.13
7.12
7.10
6.70
6.70
6.69
6.69
5.80
5.80
5.79
5.79
4.20
4.19
4.18
4.17
2.83
2.83
2.83
2.50
2.50
2.49
2.48
2.48
2.47
2.02
2.01
2.00
2.00
1.99
1.99
1.98
1.98
1.97
1.97
1.96
1.95
1.94
1.93
1.92
1.91
1.35
H
H
OH
CO2H
N
H
Me
Me
27
1.11
1.07
1.07
1.08
2.10
1.04
1.00
1.12
1.10
1.04
3.46
3.54
3.58
f1 (ppm)

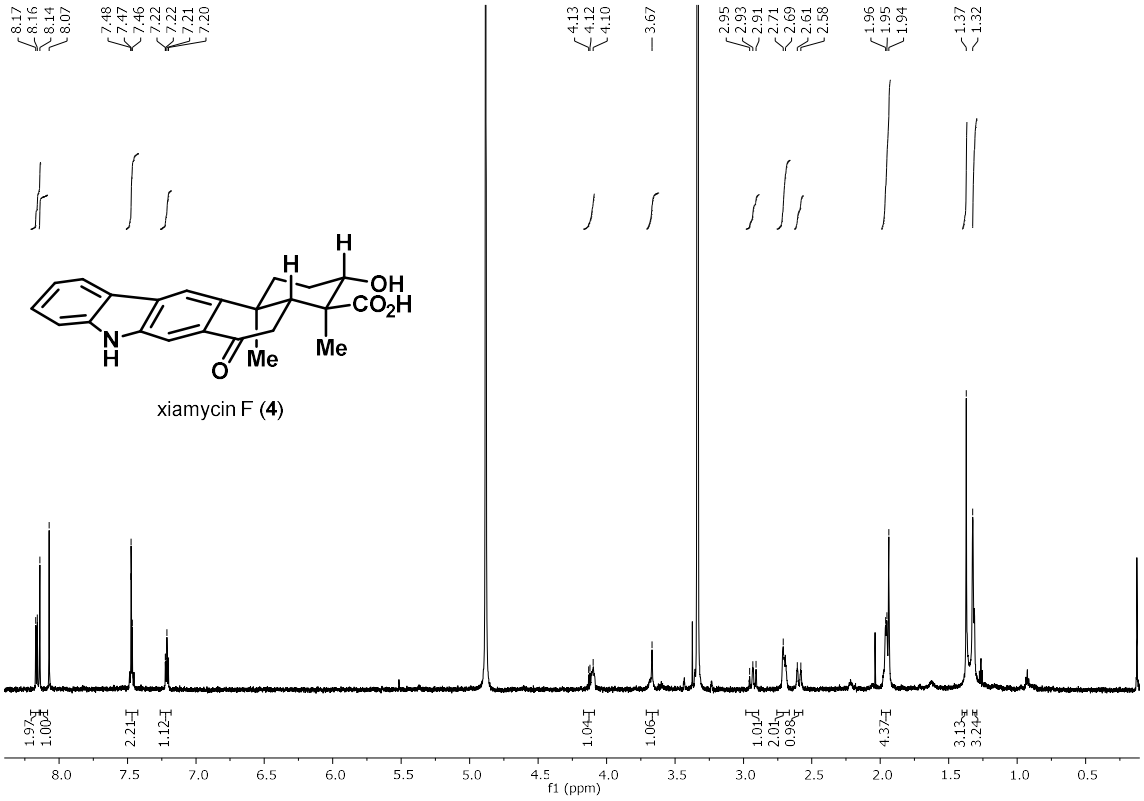

180.62
142.02
140.21
139.89
132.28
130.96
128.87
126.24
124.67
123.83
120.67
119.62
114.13
111.64
109.84
75.69
53.45
49.55
38.69
35.94
28.45
22.34
12.94
f1 (ppm)


7.98 7.97 7.94 7.36 7.35 7.30 7.30 7.29 7.29 7.28 7.28 7.10 7.10 7.09 7.08 7.08 7.07 4.11 4.10 4.10 4.09 3.13 3.12 3.10 3.09 3.06 3.05 3.04 3.03 2.65 2.64 2.63 2.63 2.62 2.17 2.17 2.16 2.15 2.04 2.03 2.02 2.01 2.01 1.91 1.91 1.90 1.90 1.89 1.89 1.89 1.77 1.76 1.75 1.74 1.74 1.57 1.56 1.56 1.56 1.55 1.55 1.54 1.54 1.54 1.53 1.30 1.25
H
H
OH
CO2H
N
H
Me
Me
xiamycin A (1)
1.00
0.97
0.93
0.94
0.90
0.87
0.95
0.84
0.83
0.84
0.91
1.13
1.94
1.10
0.98
3.08
3.15
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)

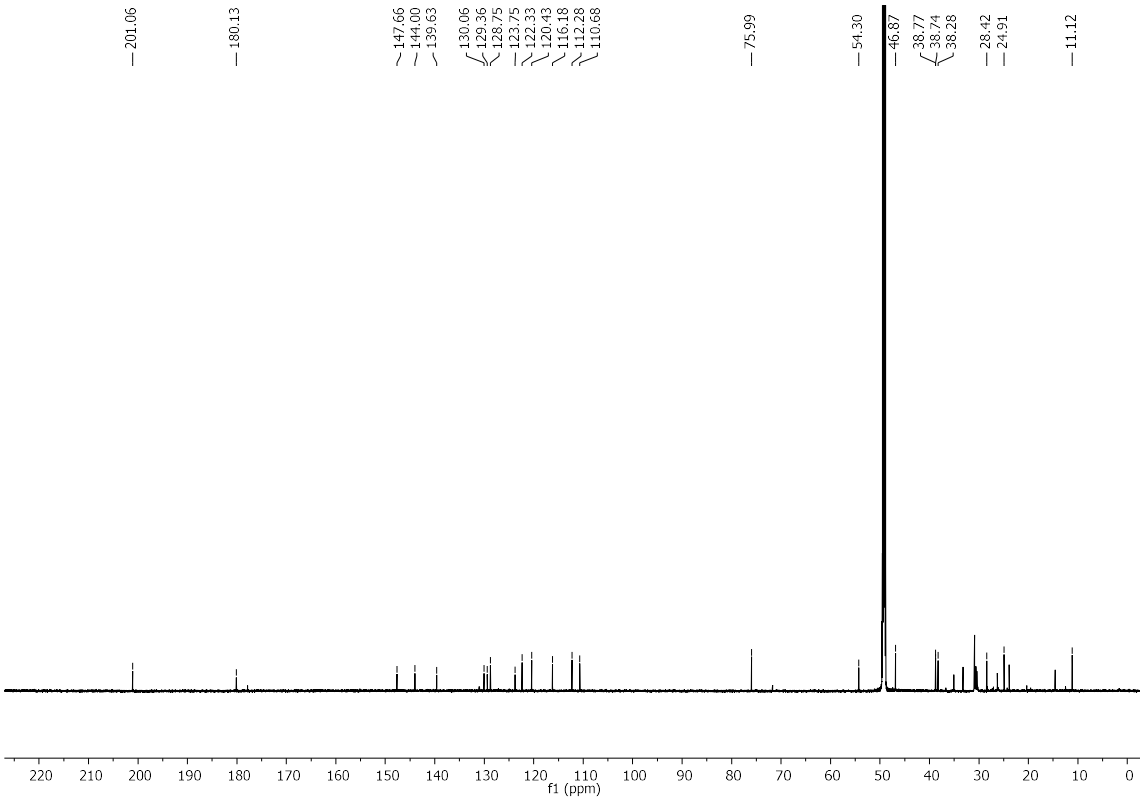

181.26
142.01
141.75
140.13
134.01
126.04
124.64
123.12
120.56
119.33
116.36
111.43
110.79
76.28
54.88
47.92
39.02
38.32
32.06
28.65
26.33
22.61
11.39
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

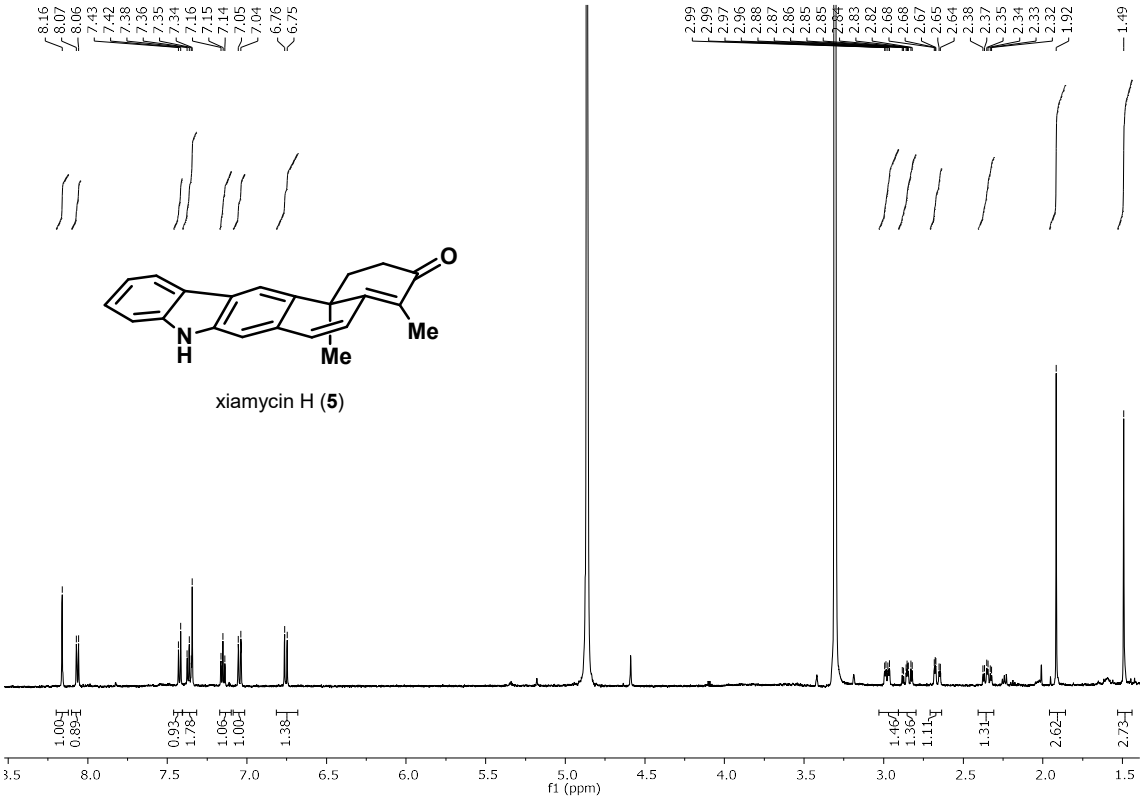

8.01
7.99
7.94
7.58
7.38
7.37
7.33
7.33
7.31
7.30
7.30
7.11
7.10
7.09
4.89
4.88
4.10
4.09
4.09
4.07
2.65
2.62
2.20
2.19
2.18
2.03
2.01
1.99
1.99
1.97
1.92
1.90
1.89
1.89
1.88
1.87
1.86
1.85
1.72
1.71
1.70
1.69
1.67
1.38
1.26
H
H
OH
CO2H
N
H
HO
Me
Me
xiamycin C (3)
1.00
0.92
0.87
0.96
1.02
0.97
0.80
1.17
1.14
1.14
1.82
2.82
1.17
2.61
2.87
f1 (ppm)
180.36
142.31
142.12
140.13
137.92
126.31
124.45
123.98
120.79
119.34
116.26
111.52
110.08
76.82
72.32
55.06
46.02
39.15
39.03
33.33
28.44
26.87
12.66
f1 (ppm)


8.05 8.04 8.04 8.02 7.43 7.41 7.40 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.15 7.14 7.13 7.13 7.12 4.97 4.97 4.96 4.96 4.61 4.25 4.24 4.23 4.22 2.68 2.67 2.66 2.60 2.59 2.58 2.57 2.34 2.33 2.32 2.31 2.30 2.29 2.07 2.07 2.06 2.06 2.05 2.04 2.04 1.98 1.96 1.96 1.95 1.95 1.94 1.94 1.93 1.93 1.84 1.83 1.82 1.81 1.75 1.73 1.28 1.28
OH
H
H
OH
CO2H
N
H
H
Me
Me
19-epi-xiamycin C (11)
2.00 2.01 1.11 1.17 1.39 0.96 1.10 0.92 1.34 1.09 2.36 0.90 1.21 6.52
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
f1 (ppm)
170.99 142.41 140.03 135.49 130.87 126.60 124.84 124.33 120.92 119.49 116.19 112.77 111.60 87.97 58.88 49.57 42.14 38.75 35.53 30.73 26.78 25.76 14.42
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

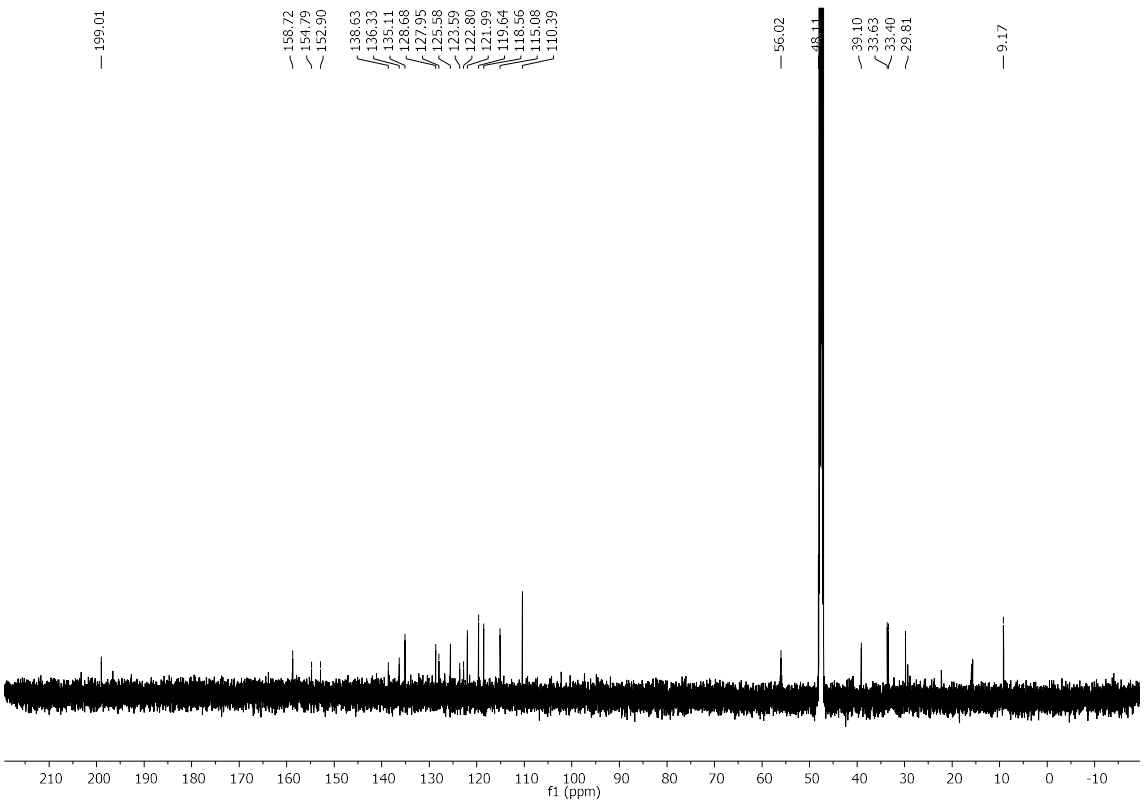

8.17
8.16
8.14
8.07
7.48
7.47
7.46
7.22
7.22
7.21
7.20
4.13
4.12
4.10
3.67
2.95
2.93
2.91
2.71
2.69
2.61
2.58
1.96
1.95
1.94
1.37
1.32
H
H
OH
CO2H
N
H
O
Me
Me
1.97
1.00
2.21
1.12
1.04
1.06
1.01
2.01
0.98
4.37
3.13
3.24
f1 (ppm)

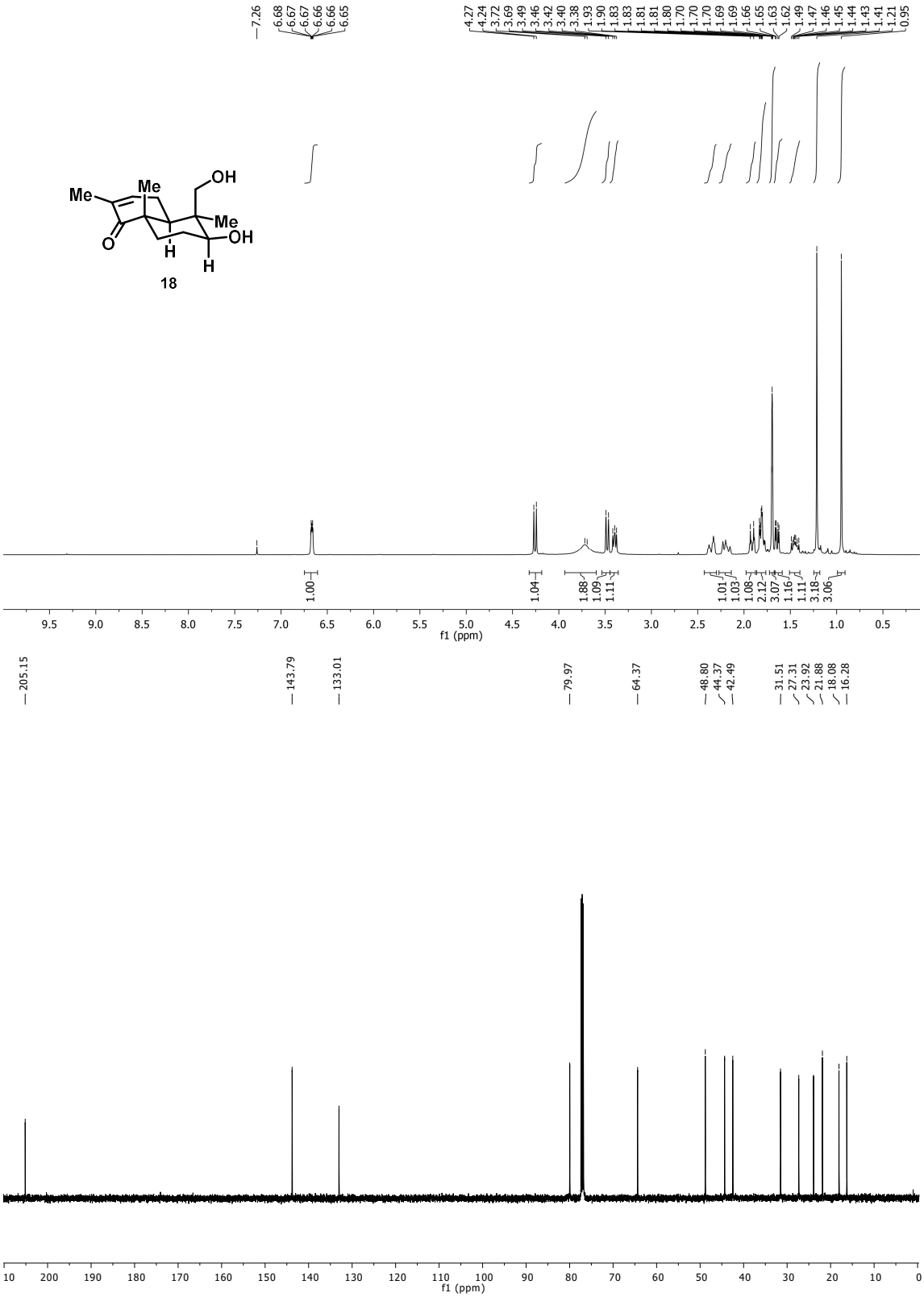
xiamycin F (**4**)

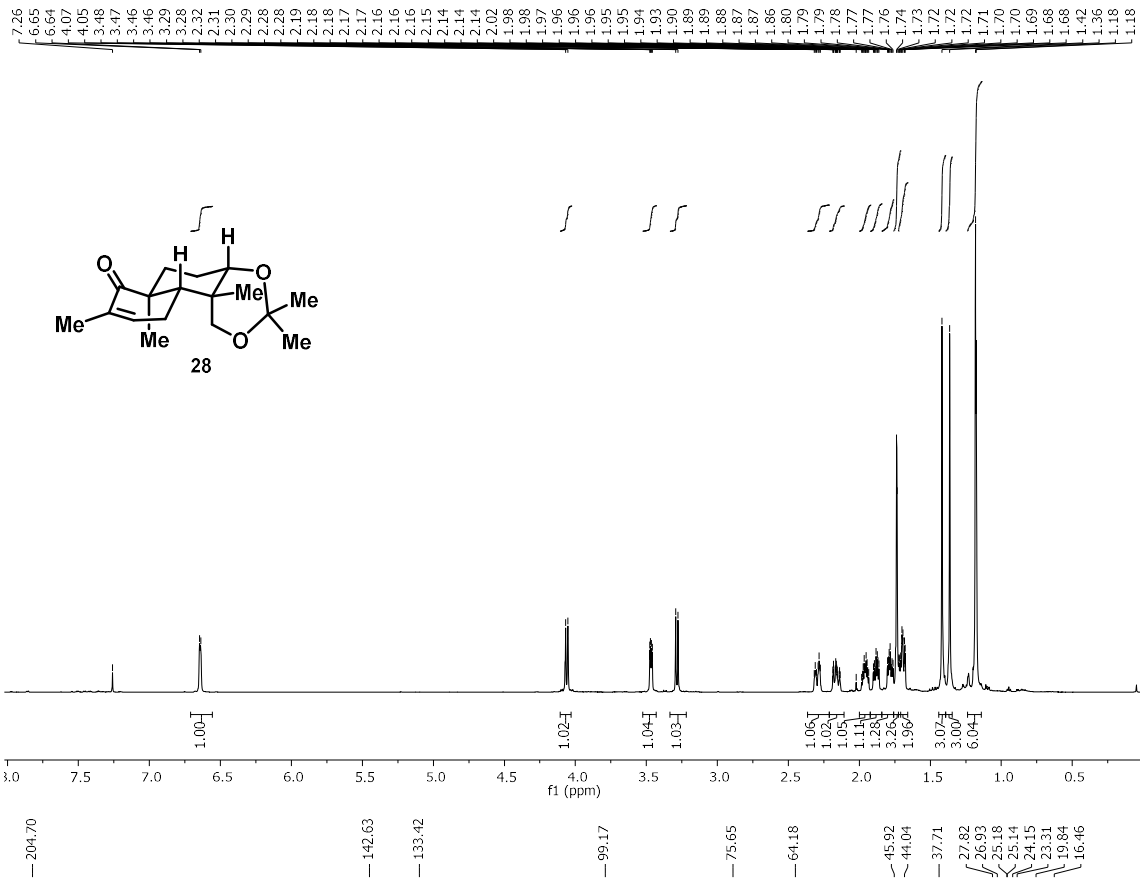

201.06
180.13
147.66
144.00
139.63
130.06
129.36
128.75
123.75
122.33
120.43
116.18
112.28
110.68
75.99
54.30
46.87
38.77
38.74
38.28
28.42
24.91
11.12
f1 (ppm)

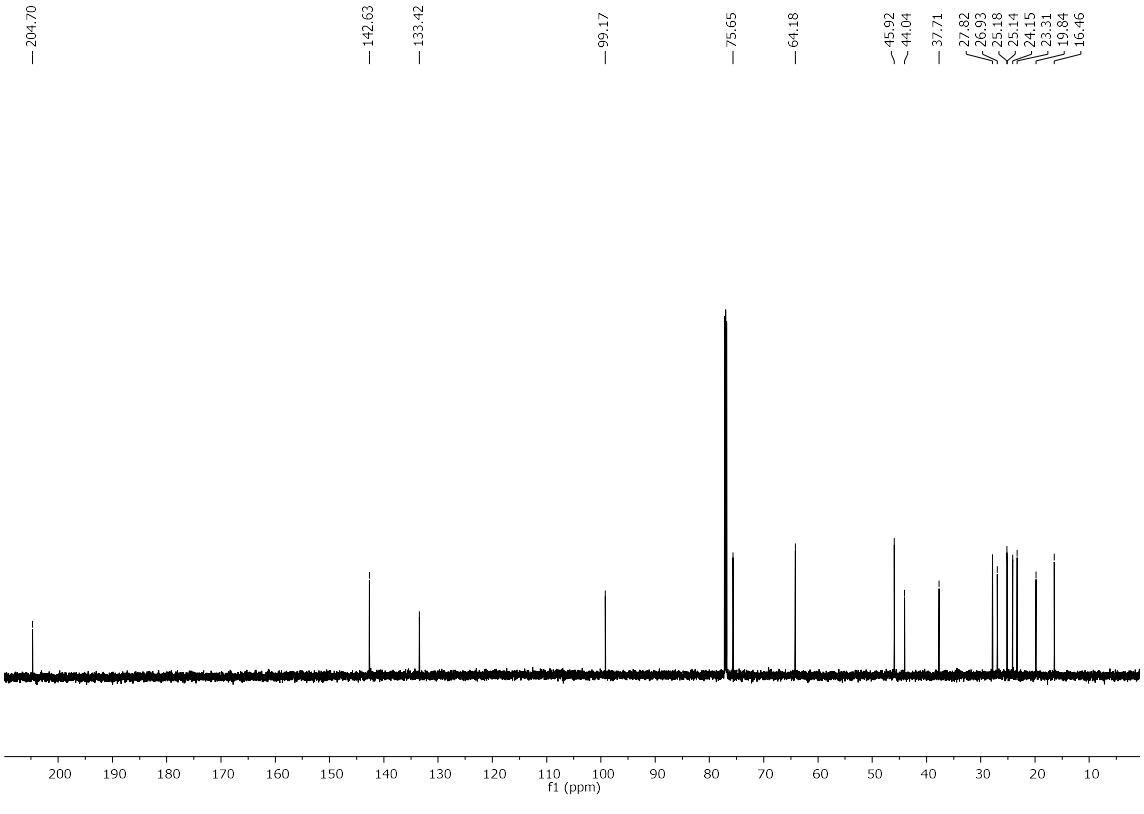

8.16
8.07
8.06
7.43
7.42
7.38
7.36
7.35
7.34
7.16
7.15
7.14
7.05
7.04
6.76
6.75
2.99
2.99
2.97
2.96
2.88
2.87
2.86
2.85
2.85
2.84
2.83
2.82
2.68
2.68
2.67
2.65
2.64
2.38
2.37
2.35
2.34
2.33
2.32
1.92
1.49
O
Me
N
H
Me
1.00
0.89
0.93
1.78
1.06
1.00
1.38
1.46
1.36
1.14
1.31
2.62
2.73
f1 (ppm)

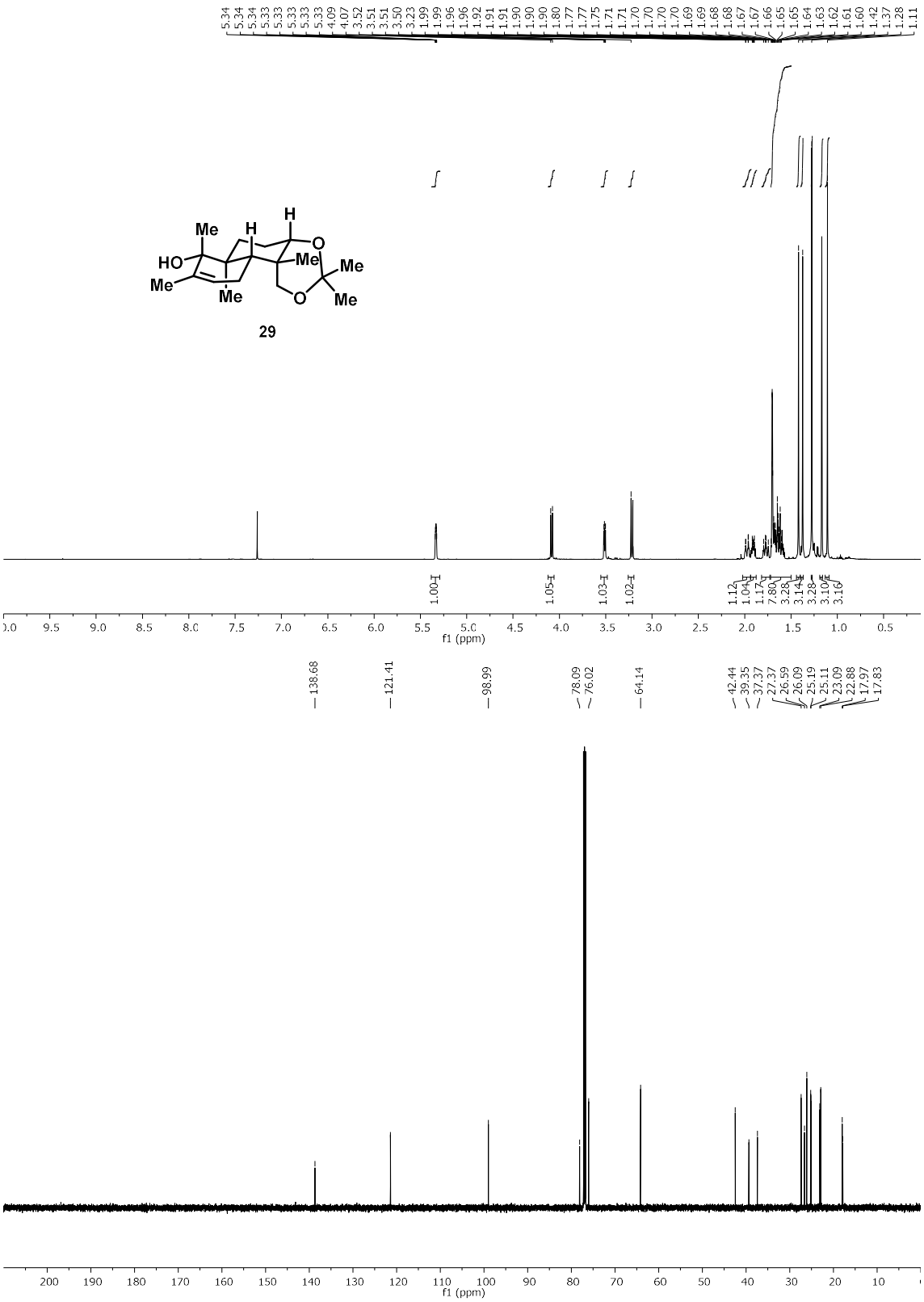
xiamycin H (**5**)

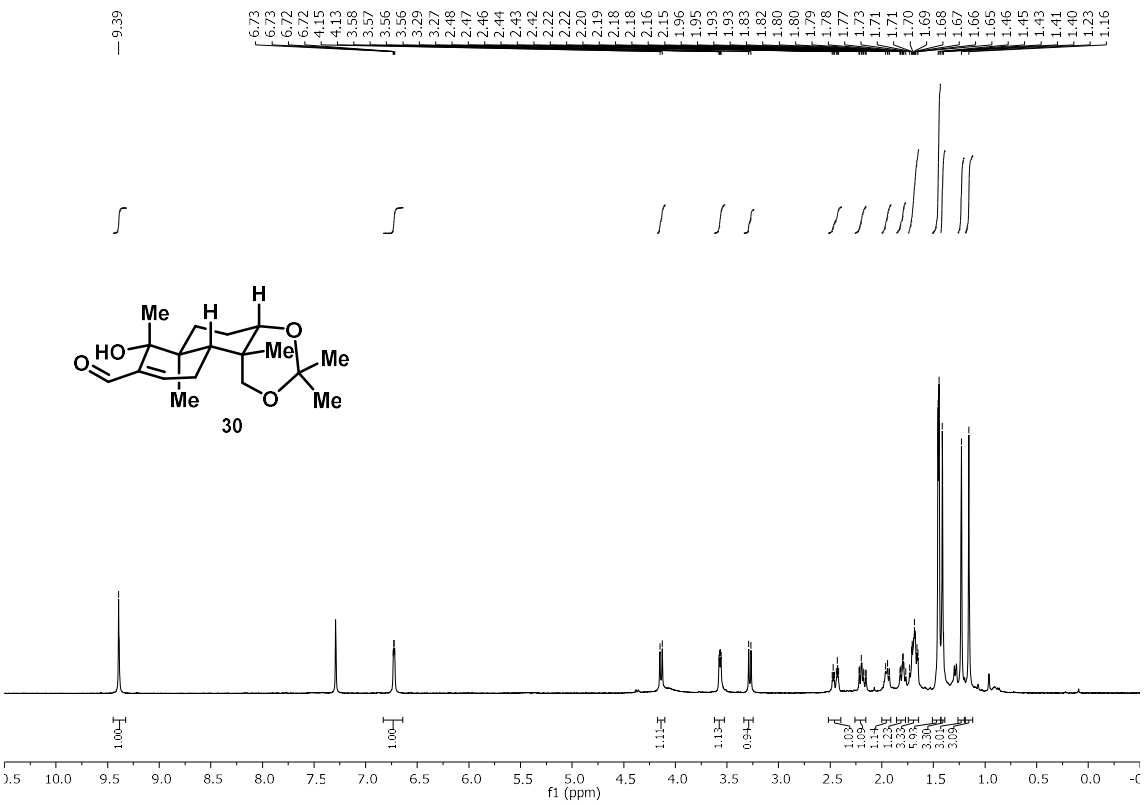

199.01
158.72
154.79
152.90
138.63
136.33
135.11
128.68
127.95
125.58
123.59
122.80
121.99
119.64
118.56
115.08
110.39
56.02
48.11
39.10
33.63
33.40
29.81
9.17
f1 (ppm)


7.26
6.68
6.67
6.67
6.66
6.66
6.65
4.27
4.24
3.72
3.69
3.49
3.46
3.42
3.40
3.38
1.93
1.90
1.83
1.83
1.81
1.81
1.80
1.70
1.70
1.70
1.69
1.69
1.66
1.65
1.63
1.62
1.49
1.47
1.46
1.45
1.44
1.43
1.41
1.21
0.95
Me
Me
OH
Me
OH
O
H
H
18
1.00
1.04
1.88
1.09
1.11
1.01
1.03
1.08
2.12
3.07
1.16
1.11
3.18
3.06
f1 (ppm)
205.15
143.79
133.01
79.97
64.37
48.80
44.37
42.49
31.51
27.31
23.92
21.88
18.08
16.28
f1 (ppm)


7.26 6.65 6.64 4.07 4.05 3.48 3.47 3.46 3.46 3.29 3.28 2.32 2.31 2.30 2.29 2.28 2.28 2.19 2.18 2.18 2.17 2.17 2.16 2.16 2.16 2.15 2.14 2.14 2.14 2.02 1.98 1.98 1.97 1.96 1.96 1.96 1.95 1.95 1.94 1.93 1.90 1.89 1.89 1.88 1.87 1.87 1.86 1.80 1.79 1.79 1.78 1.77 1.77 1.76 1.74 1.73 1.72 1.72 1.72 1.71 1.70 1.70 1.69 1.68 1.68 1.42 1.36 1.18 1.18
O
H
H
O
Me
Me
Me
Me
O
Me
28
1.00 1.02 1.04 1.03 1.06 1.02 1.05 1.11 1.28 3.26 1.96 3.07 3.00 6.04
f1 (ppm)


204.70 142.63 133.42 99.17 75.65 64.18 45.92 44.04 37.71 27.82 26.93 25.18 25.14 24.15 23.31 19.84 16.46
f1 (ppm)


5.34 5.34 5.34 5.33 5.33 5.33 5.33 5.33 4.09 4.07 3.52 3.51 3.51 3.50 3.23 1.99 1.99 1.96 1.96 1.92 1.91 1.91 1.91 1.90 1.90 1.90 1.80 1.77 1.77 1.75 1.71 1.71 1.70 1.70 1.70 1.70 1.69 1.69 1.68 1.68 1.67 1.67 1.66 1.65 1.65 1.64 1.63 1.62 1.61 1.60 1.42 1.37 1.28 1.11
Me
H
H
O
HO
Me
Me
Me
Me
Me
O
Me
29
1.00 1.05 1.03 1.02 1.12 1.04 1.17 7.80 3.28 3.14 3.28 3.10 3.16
f1 (ppm)
138.68 121.41 98.99 78.09 76.02 64.14 42.44 39.35 37.37 27.37 26.59 26.09 25.19 25.11 23.09 22.88 17.97 17.83
f1 (ppm)


9.39
6.73
6.73
6.72
6.72
4.15
4.13
3.58
3.57
3.56
3.56
3.29
3.27
2.48
2.47
2.46
2.44
2.43
2.42
2.22
2.22
2.20
2.19
2.18
2.18
2.16
2.15
1.96
1.95
1.93
1.93
1.83
1.82
1.80
1.80
1.79
1.78
1.77
1.73
1.71
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.46
1.45
1.43
1.41
1.40
1.23
1.16
Me
H
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Me
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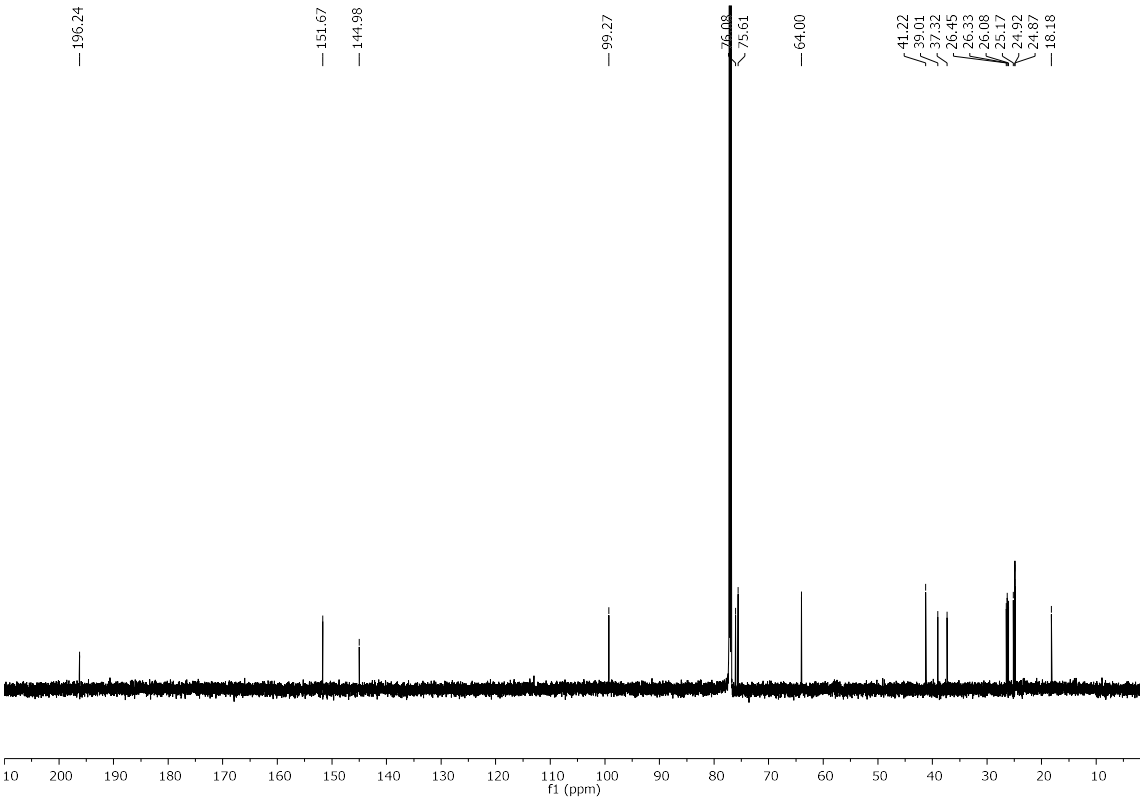
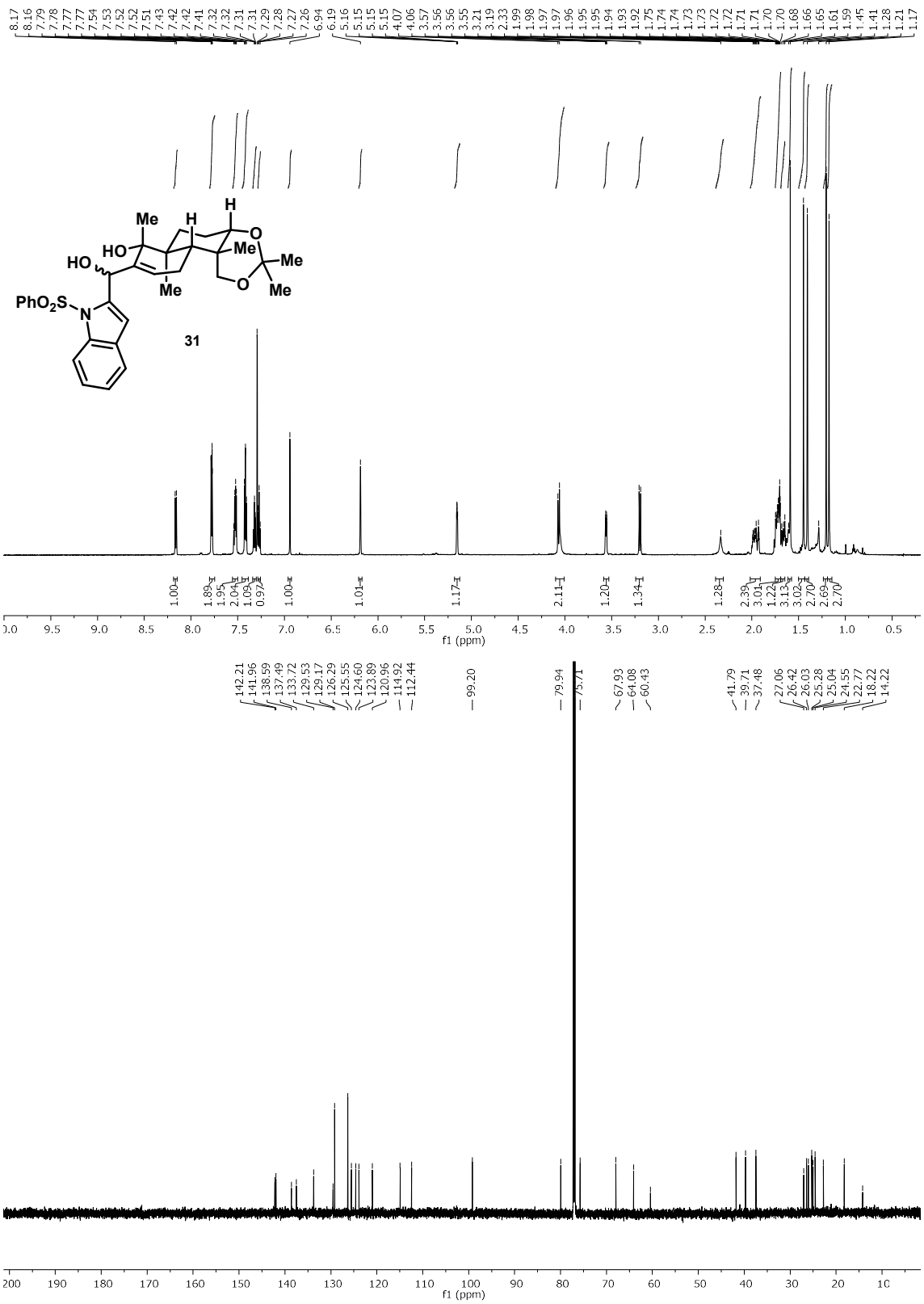
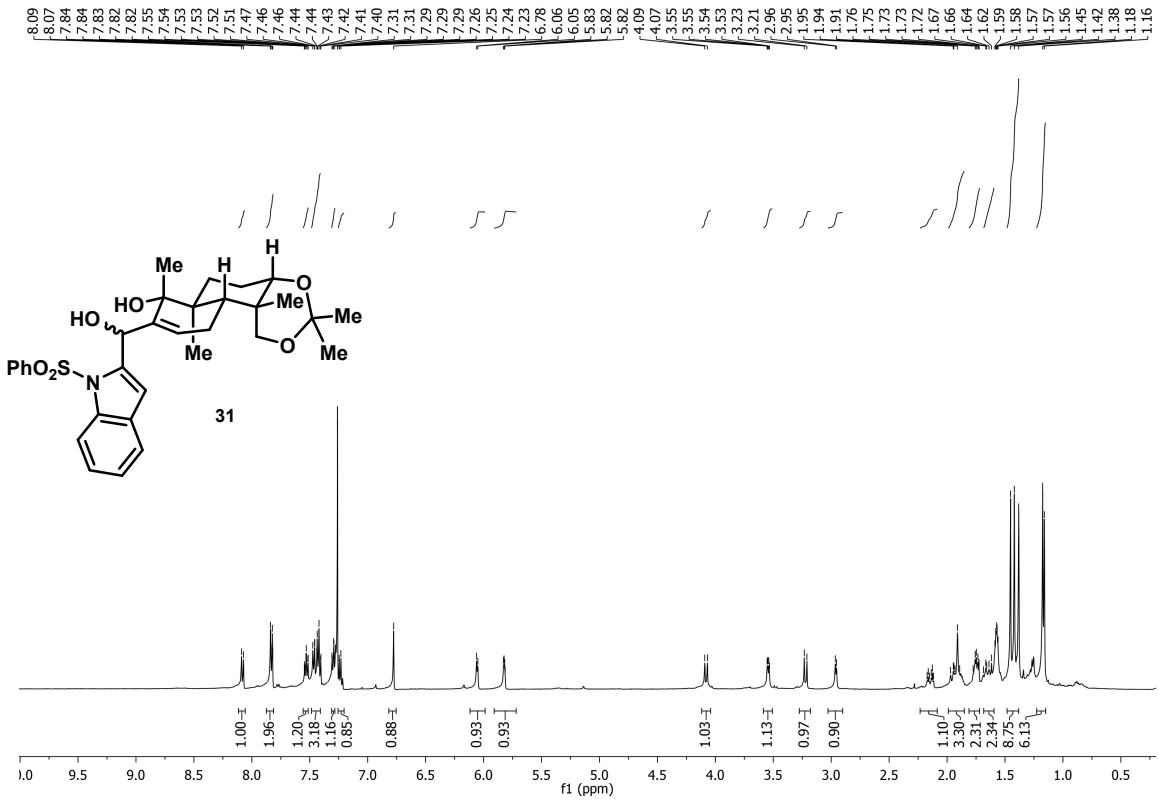
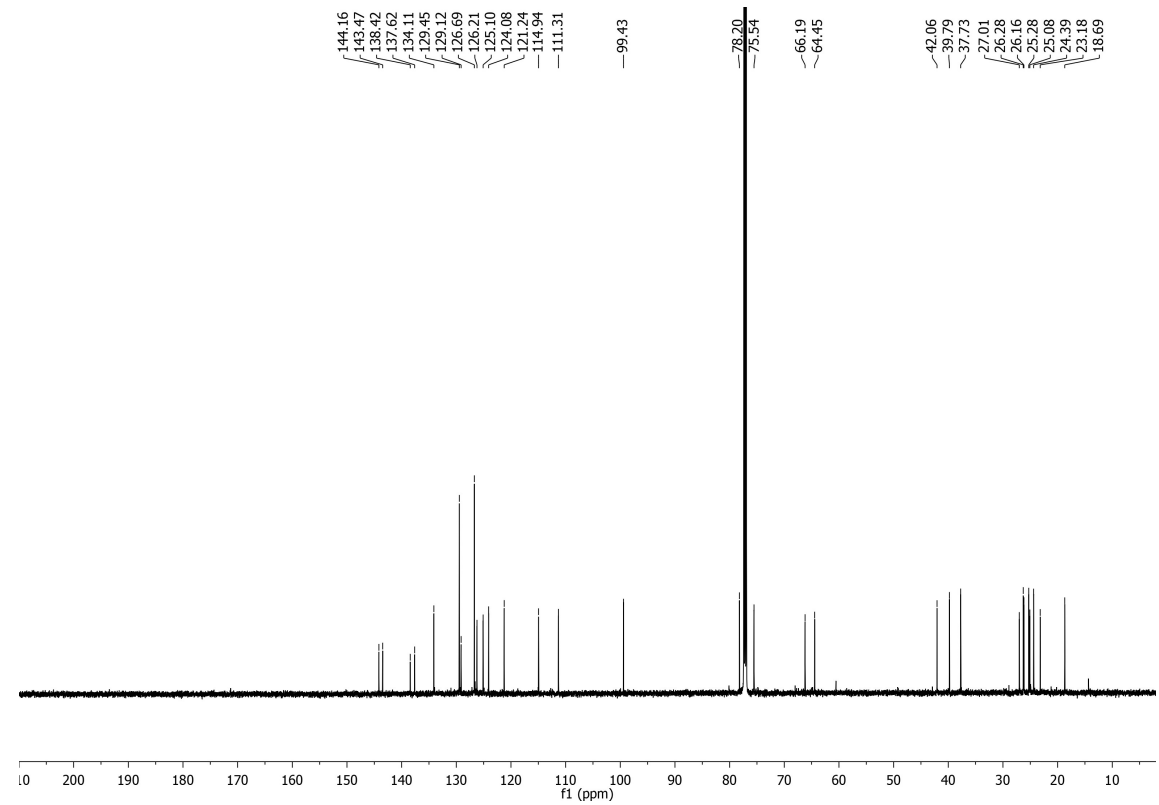
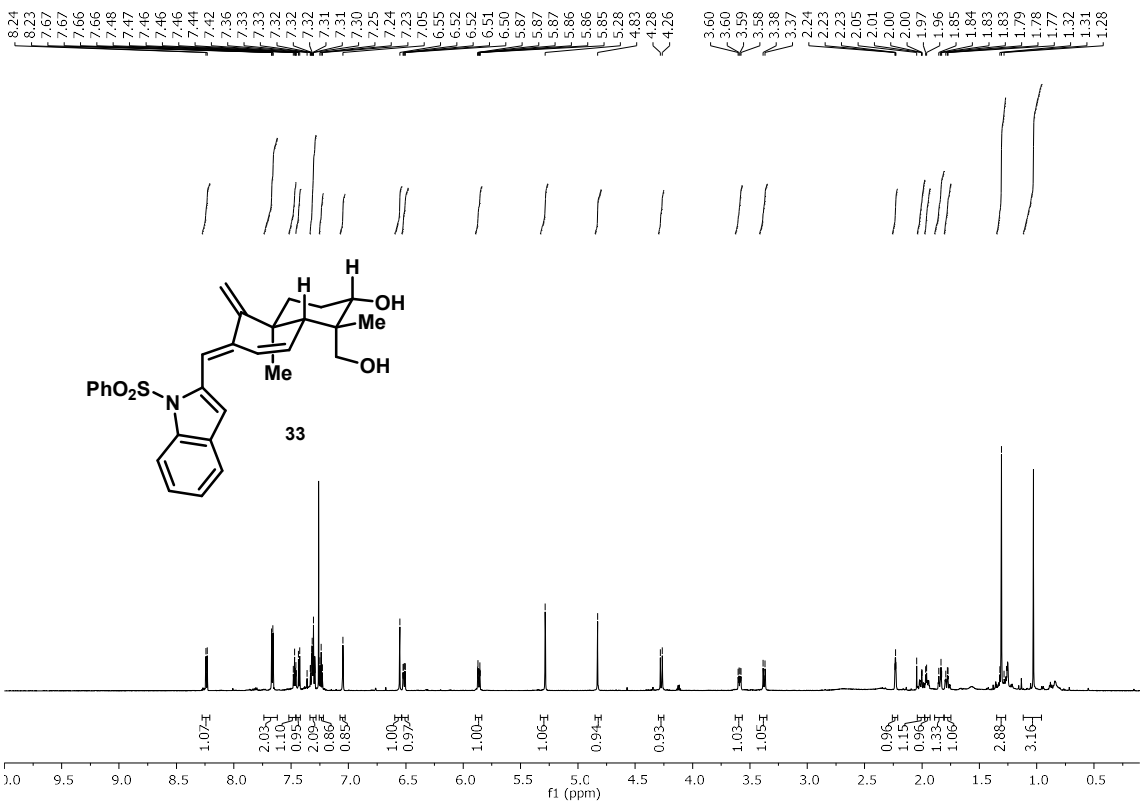
1.00
1.00
1.11
1.13
0.94
f1 (ppm)


196.24
151.67
144.98
99.27
76.08
75.61
64.00
41.22
39.01
37.32
26.45
26.33
26.08
25.17
24.92
24.87
18.18
f1 (ppm)


Me
H
H
O
HO
Me
HO
Me
Me
O
Me
PhO2S
N
31
f1 (ppm)
f1 (ppm)


8.09 8.07 7.84 7.84 7.83 7.82 7.82 7.55 7.54 7.53 7.53 7.52 7.51 7.47 7.46 7.46 7.44 7.44 7.43 7.42 7.41 7.40 7.31 7.31 7.29 7.29 7.29 7.26 7.25 7.24 7.23 6.78 6.06 6.05 5.83 5.82 5.82 4.09 4.07 3.55 3.55 3.54 3.53 3.23 3.21 2.96 2.95 1.95 1.94 1.91 1.76 1.75 1.73 1.73 1.72 1.67 1.66 1.64 1.62 1.59 1.58 1.57 1.57 1.56 1.45 1.42 1.38 1.18 1.16
Me
H
H
O
Me
HO
HO
Me
Me
O
Me
PhO2S
N
31
1.00 1.96 1.20 3.18 1.16 0.85 0.88 0.93 0.93 1.03 1.13 0.97 0.90 1.10 3.30 2.31 2.34 8.75 6.13
f1 (ppm)


144.16 143.47 138.42 137.62 134.11 129.45 129.12 126.69 126.21 125.10 124.08 121.24 114.94 111.31 99.43 78.20 75.54 66.19 64.45 42.06 39.79 37.73 27.01 26.28 26.16 25.28 25.08 24.39 23.18 18.69
f1 (ppm)


8.24
8.23
7.67
7.67
7.66
7.66
7.48
7.47
7.46
7.46
7.46
7.44
7.42
7.36
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.25
7.24
7.23
7.05
6.55
6.52
6.52
6.51
6.50
5.87
5.87
5.87
5.86
5.86
5.85
5.28
4.83
4.28
4.26
3.60
3.60
3.59
3.58
3.38
3.37
2.24
2.23
2.23
2.05
2.01
2.00
2.00
1.97
1.96
1.85
1.84
1.83
1.83
1.79
1.78
1.77
1.32
1.31
1.28
H
H
OH
Me
Me
OH
PhO2S
N
33
1.07
2.03
1.10
0.95
2.09
0.86
0.85
1.00
0.97
1.00
1.06
0.94
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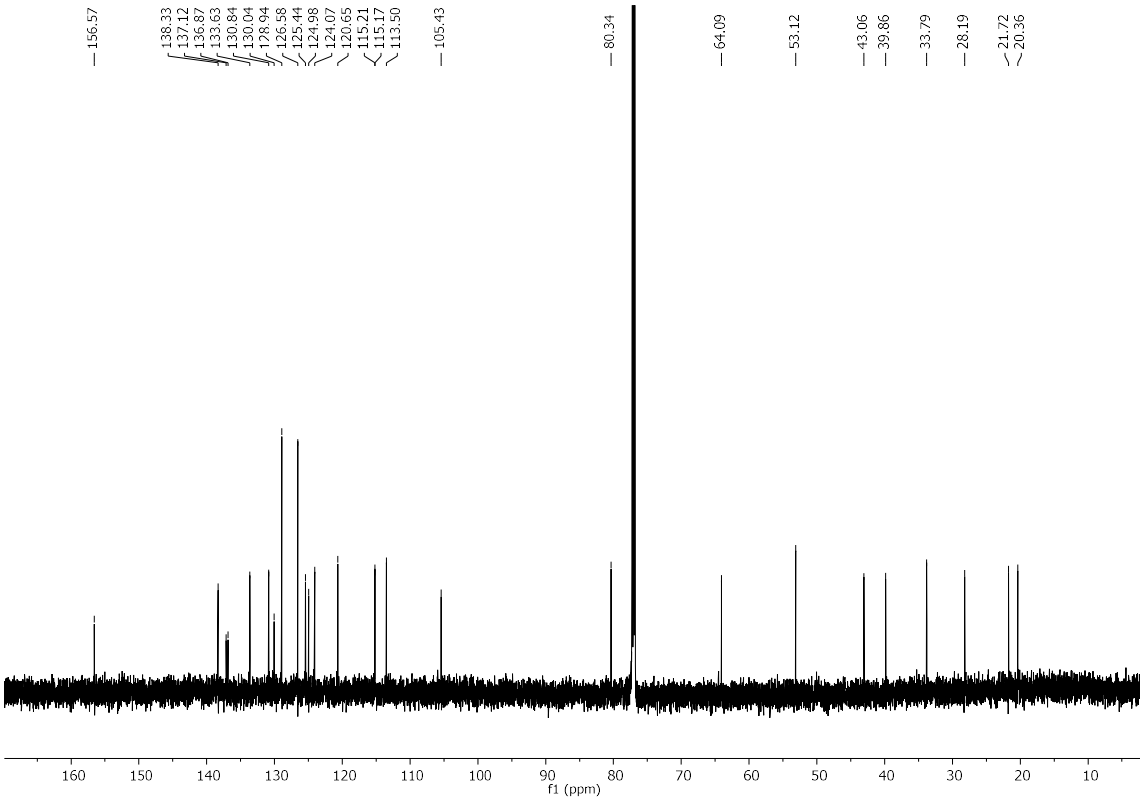
0.96
1.33
1.06
2.88
3.16
f1 (ppm)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133.63
130.84
130.04
128.94
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125.44
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124.07
120.65
115.21
115.17
113.50
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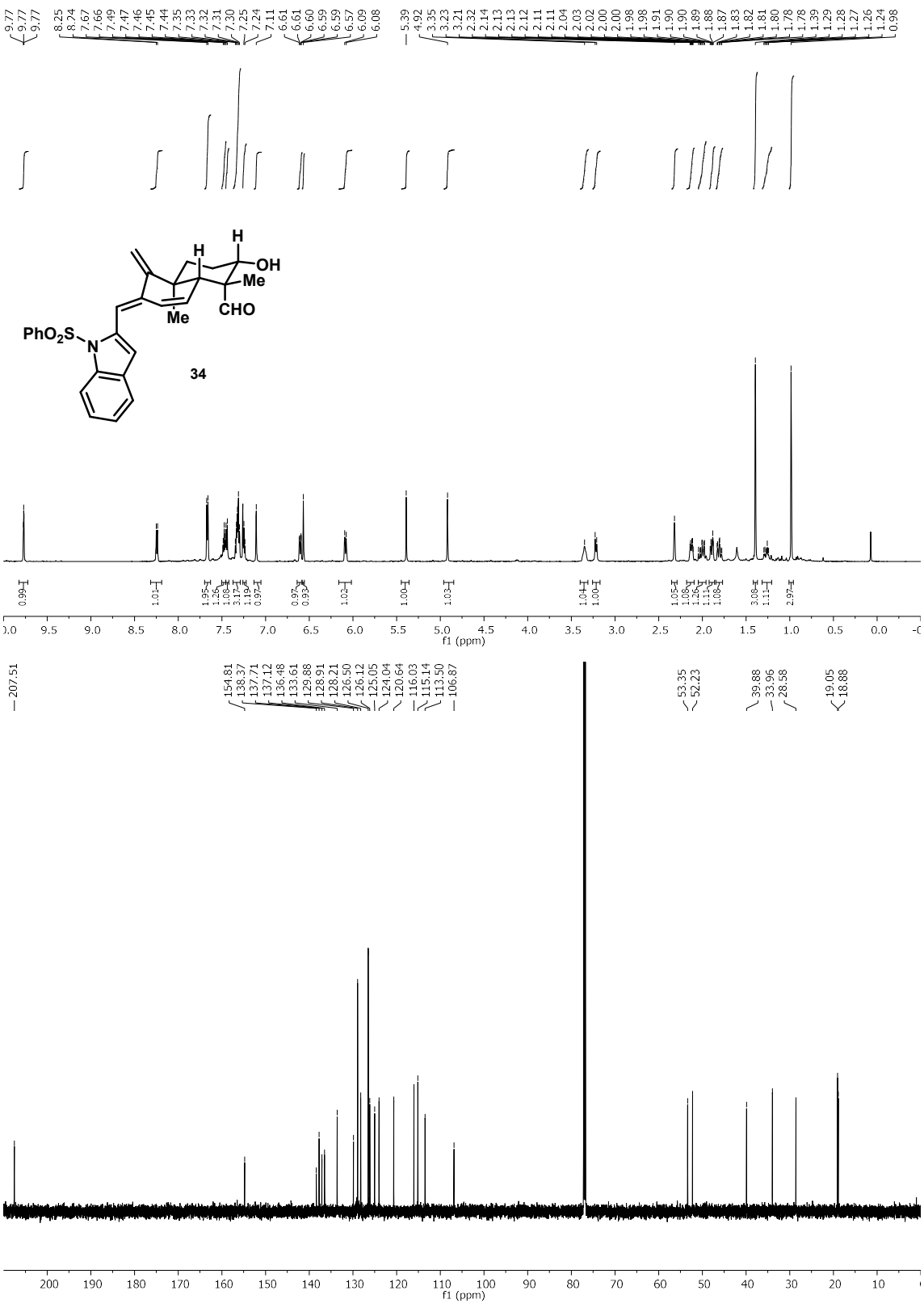
43.06
39.86
33.79
28.19
21.72
20.36
f1 (ppm)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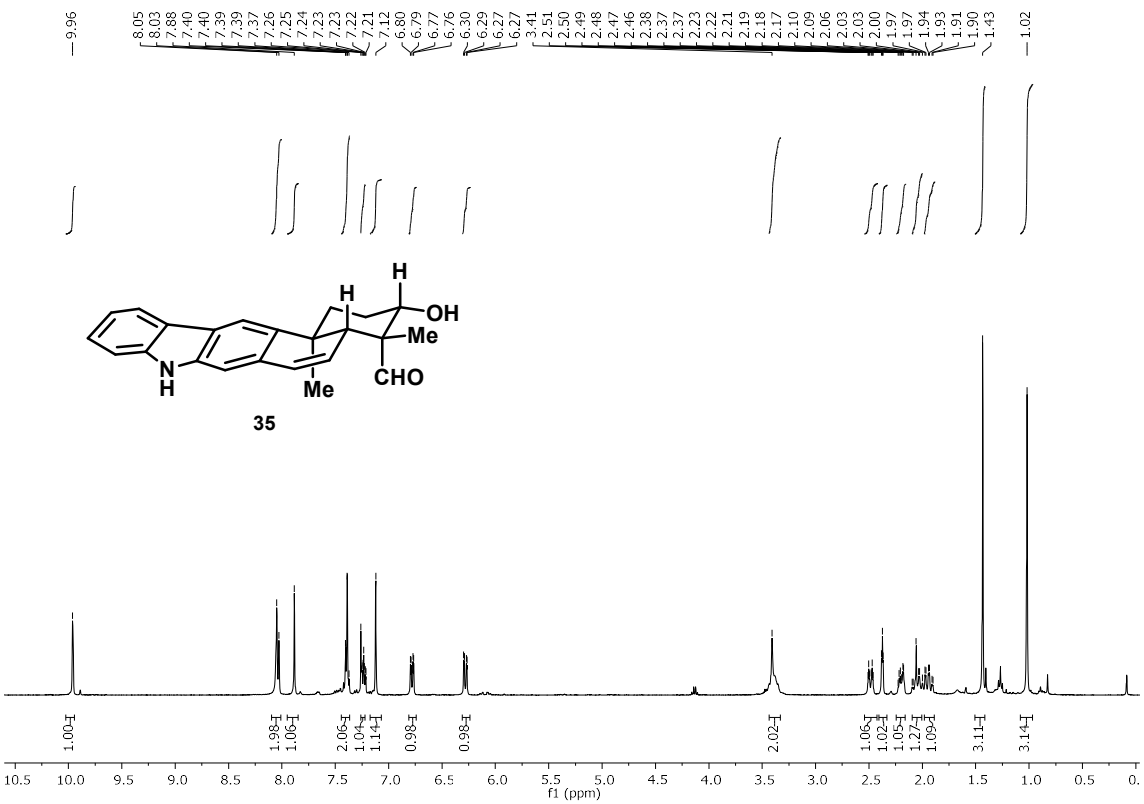
H
OH
Me
CHO
Me
PhO2S
N
34
f1 (ppm)
f1 (ppm)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8.05
8.03
7.88
7.40
7.40
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7.39
7.37
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7.25
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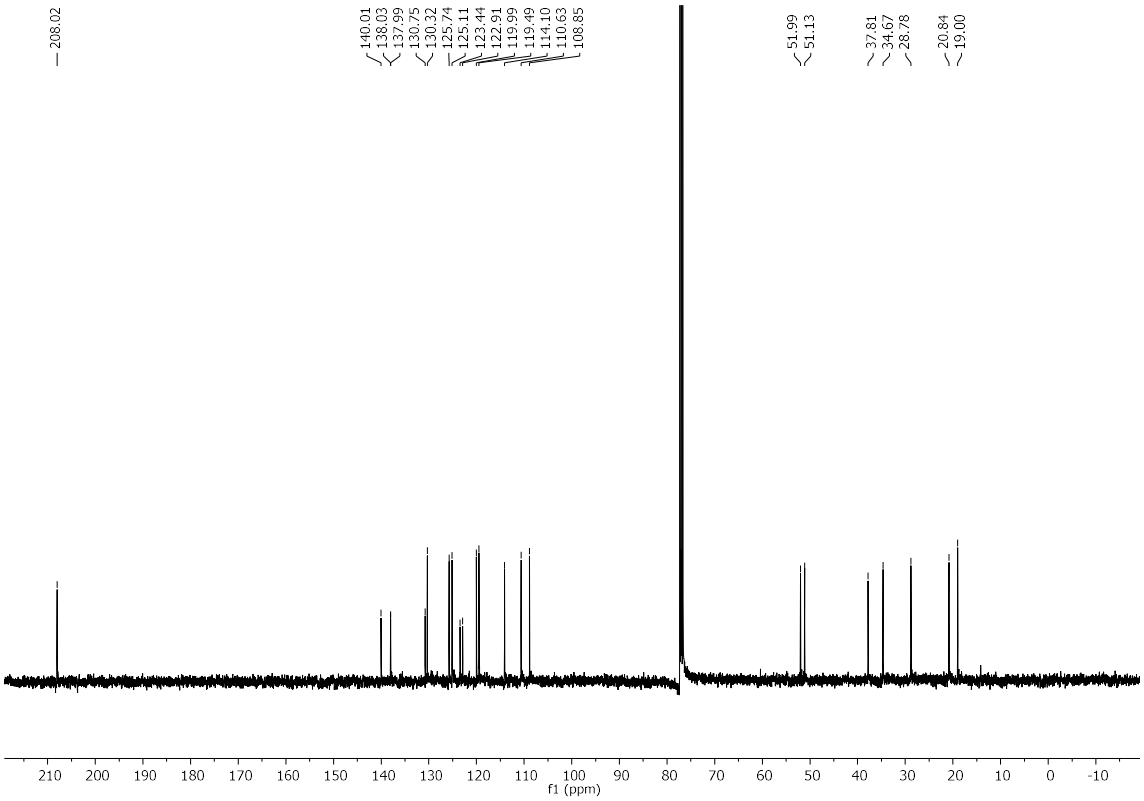
7.23
7.23
7.22
7.21
7.12
6.80
6.79
6.77
6.76
6.30
6.29
6.27
6.27
3.41
2.51
2.50
2.49
2.48
2.47
2.46
2.38
2.37
2.37
2.23
2.22
2.21
2.19
2.18
2.17
2.10
2.09
2.06
2.03
2.03
2.00
1.97
1.97
1.94
1.93
1.91
1.90
1.43
1.02
H
H
OH
Me
CHO
N
H
Me
35
1.00
1.98
1.06
2.06
1.04
1.14
0.98
0.98
2.02
1.06
1.02
1.05
1.27
1.09
3.11
3.14
f1 (ppm)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138.03
137.99
130.75
130.32
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125.11
123.44
122.91
119.99
119.49
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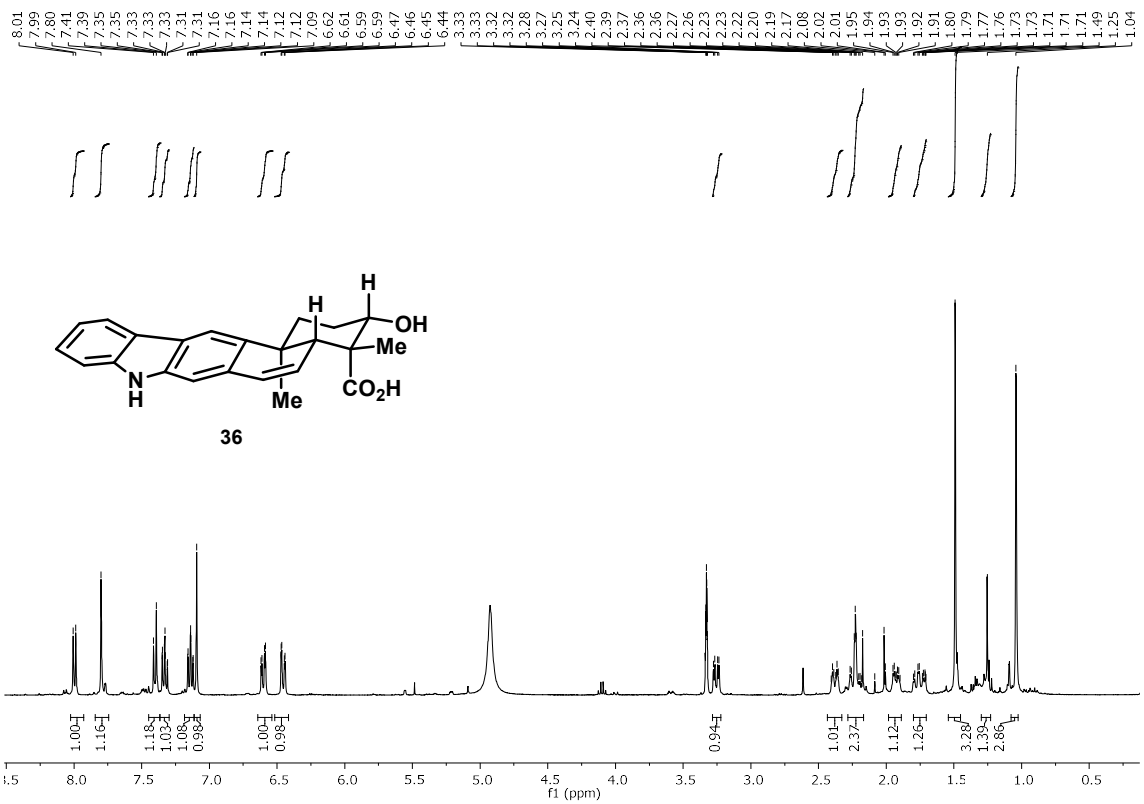
51.99
51.13
37.81
34.67
28.78
20.84
19.00
f1 (ppm)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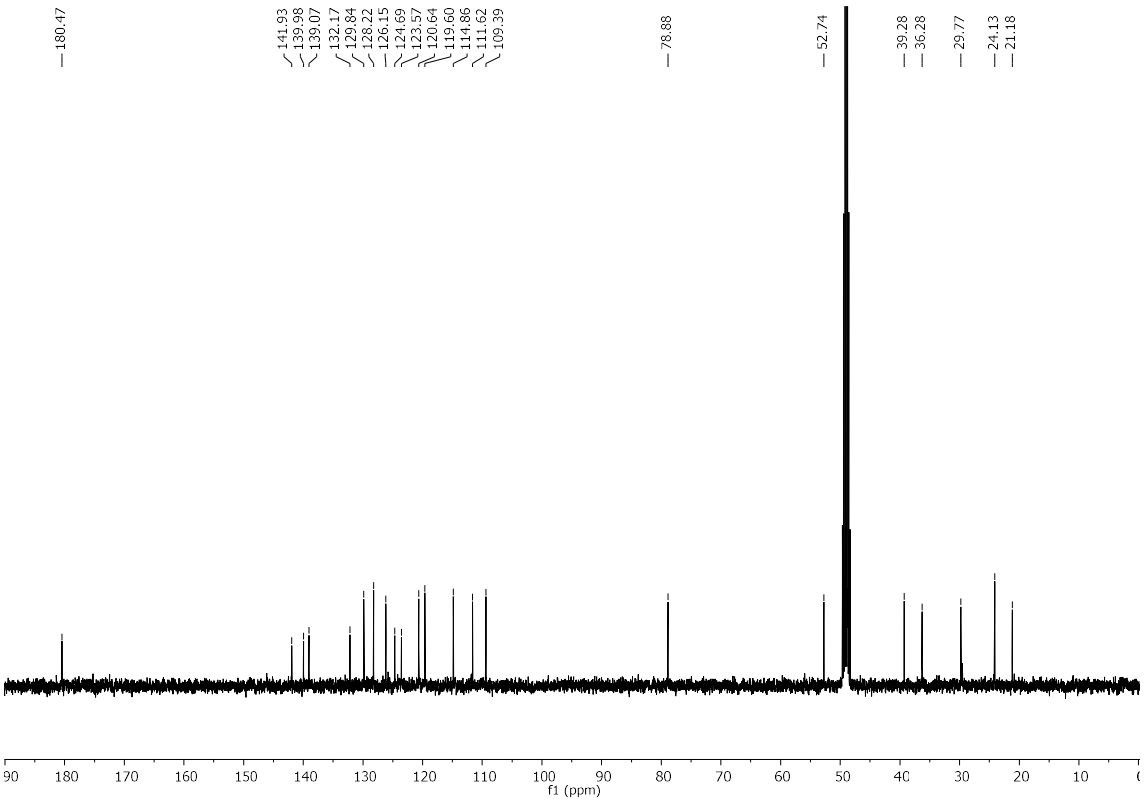
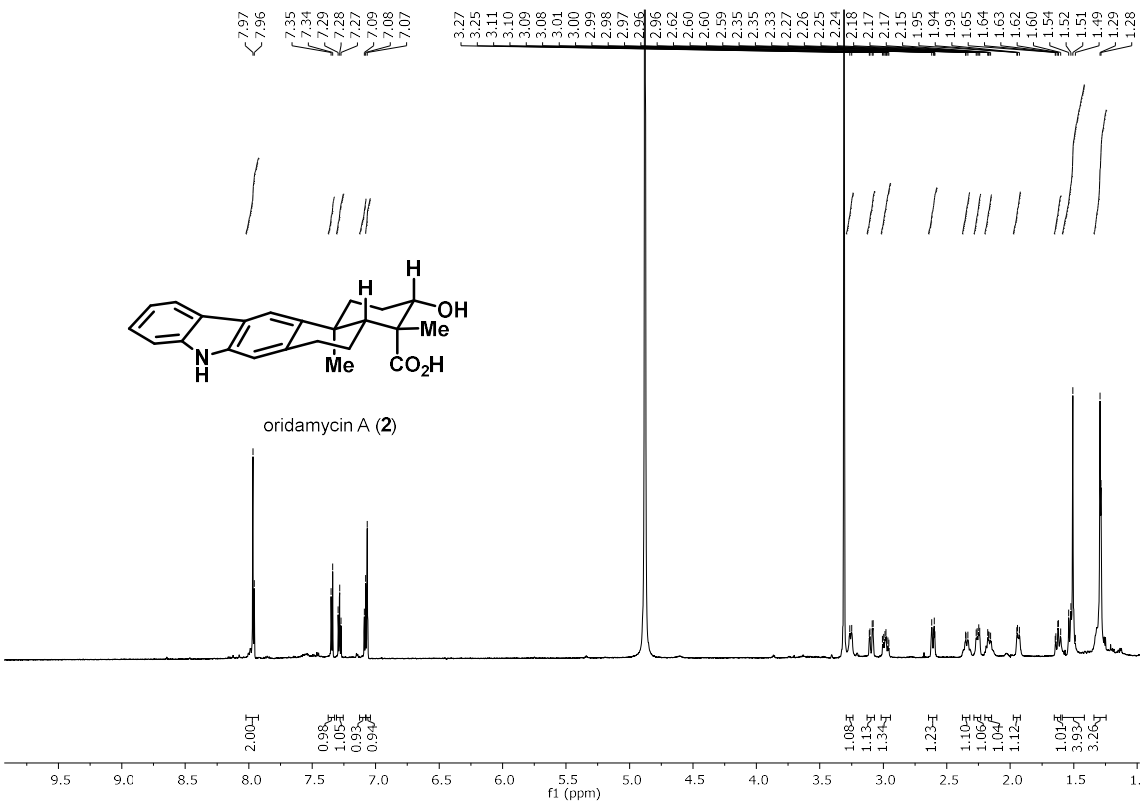
3.33 3.33 3.32 3.32 3.28 3.27 3.25 3.24 2.40 2.39 2.37 2.36 2.36 2.27 2.26 2.23 2.23 2.22 2.20 2.19 2.17 2.08 2.02 2.01 1.95 1.94 1.93 1.93 1.92 1.91 1.80 1.79 1.77 1.76 1.73 1.73 1.71 1.71 1.71 1.49 1.25 1.04
H
H
OH
Me
N
H
Me
CO2H
36
1.00 1.16 1.18 1.03 1.08 0.98 1.00 0.98 0.94 1.01 2.37 1.12 1.26 3.28 1.39 2.86
f1 (ppm)


180.47
141.93 139.98 139.07 132.17 129.84 128.22 126.15 124.69 123.57 120.64 119.60 114.86 111.62 109.39
78.88
52.74
39.28 36.28 29.77 24.13 21.18
f1 (ppm)


7.97
7.96
7.35
7.34
7.29
7.28
7.27
7.09
7.08
7.07
3.27
3.25
3.11
3.10
3.09
3.08
3.01
3.00
2.99
2.98
2.97
2.96
2.96
2.62
2.60
2.60
2.59
2.35
2.35
2.33
2.27
2.26
2.25
2.24
2.18
2.17
2.17
2.15
1.95
1.94
1.93
1.65
1.64
1.63
1.62
1.60
1.54
1.52
1.51
1.49
1.29
1.28
H
H
OH
Me
Me
CO2H
N
H
oridamycin A (2)
2.00
0.98
1.05
0.93
0.94
1.08
1.13
1.34
1.23
1.10
1.06
1.04
1.12
1.01
3.93
3.26
9.5
9.0
8.5
8.0
7.5
7.0
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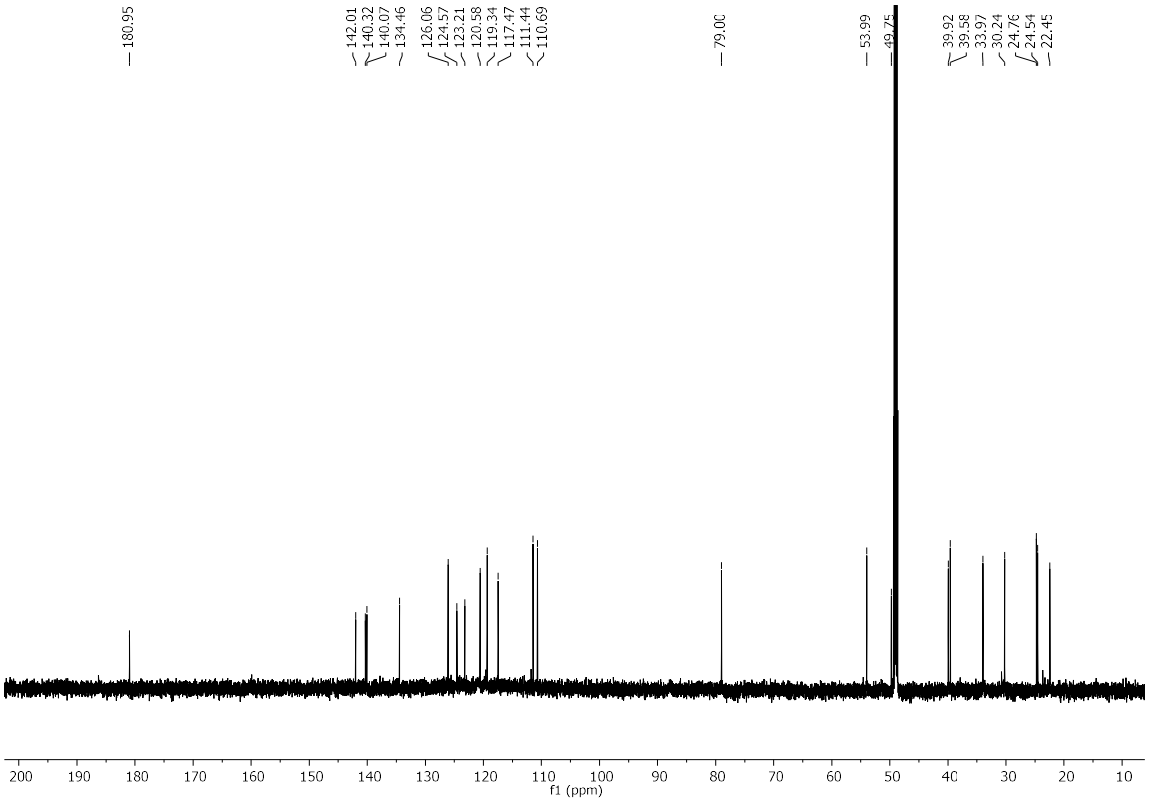
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


180.95
142.01
140.32
140.07
134.46
126.06
124.57
123.21
120.58
119.34
117.47
111.44
110.69
79.00
53.99
49.75
39.92
39.58
33.97
30.24
24.76
24.54
22.45
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)