Supporting Information

For

Direct Entry to Erythronolides via a Cyclic Bis[Allene]

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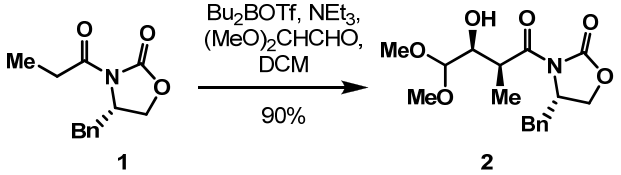
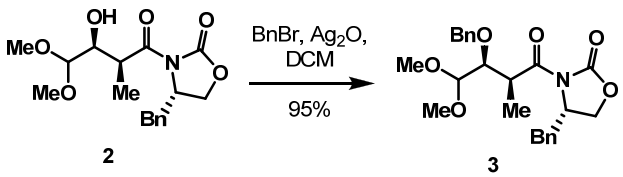
General Procedure: Starting materials, reagents and solvents were purchased from commercial suppliers (Aldrich, Strem, TCI America and Ochem.) and used without further purification unless otherwise stated. All reactions were conducted in oven-dried (135 °C) glassware under an inert atmosphere of argon. The progress of reactions was monitored by silica gel thin layer chromatography (TLC) plates (mesh size 250 um with F-254 indicator, Dynamic Adsorbent), visualized under UV and charred using anisaldehyde or ceric ammonium molybdate (CAM) stain. Products were purified by flash column chromatography (FCC) on 120-400 mesh silica gel (Fisher). Infrared (FTIR) spectra were recorded on an ATI Mattson Genesis Series FTInfrared spectrophotometer. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on either a Varian-600 instrument (600 MHz) or a Varian-500 instrument (500MHz). Chemical shifts are reported in ppm relative to residual $CHCl_3$ signal. Data is reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet), coupling constant (Hz), and integration. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded on either a Varian-600 instrument (150 MHz) or a Varian-500 instrument (125 MHz). Mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer. Optical rotations were recorded at rt using the sodium D line (589 nm), on a Perkin Elmer 343 Polarimeter.

Procedures and characterization data for 1-22



1 2

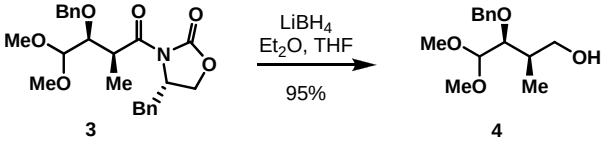
To a solution of 4(***S***)-benzyl *N*-propionyl oxazolidinone **1** (16.0 g, 68.6 mmol) in dichloromethane (DCM) (343 mL) was added dibutylboron triflate (75.0 mL, 75.0 mmol) and triethylamine (TEA) (9.72 g, 96.0 mmol) sequentially at −78 °C. The reaction mixture was then warmed to 0 °C and stirred for 1 h then cooled back to −78 °C. A DCM solution (1.0 M) of 1,1-dimethoxy acetaldehyde (100 mL, 100 mmol) was added to the reaction mixture slowly at −78 °C. The mixture was slowly warmed to 0 °C over 1 h and then stirred for 1 h. The reaction was then quenched with 100 mL solution of methanol and pH=7.4 phosphate buffer (1:3 ratio) at 0 °C, followed by addition of 100 mL solution of 30% H_2O_2 and methanol (1:2 ratio). The mixture was then stirred for 10 min at 0 °C then diluted with 200 mL DCM. The organic layer was separated, washed with water (2 x 100 mL), dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure to give the crude product, which was purified by FCC using 40% ethyl acetate in hexane to afford aldol product **2** as white crystalline (20.9 g, 90% yield). $[\alpha]^{25}_D$= +50.0 (*c* = 0.01, $CHCl_3$); M.P. 67 °C; IR ν_{max}(neat)/cm^{-1} 3485, 2937, 1778, 1696, 1386; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.25 (m, 3H,), 7.21 (d, *J* = 7.0 Hz, 2H), 4.72-4.65 (m. 1H), 4.33 (d, *J* = 6.0 Hz, 1H), 4.23- 4.15 (m, 2H), 4.05-3.96 (m, 1H), 3.42 (s, 3H), 3.38 (s, 3H), 3.26 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.78 (dd, *J* = 13.5, 10 Hz, 1H), 2.68-2.60 (bs, 1H), 1.32 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 153.2, 135.4, 129.6 (2), 129.1 (2), 127.5, 104.9, 71.4, 66.3, 55.4, 54.9, 54.4, 39.2, 38.1, 12.8; MS (ESI+) calculated for $[C_{17}H_{23}NO_6+Na]^+$: 360.2, found: 360.2



2 3

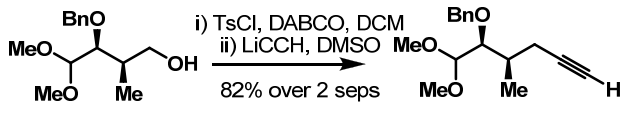
Powdered 4Å molecular sieves (20.0 g) and Ag_2O (35.0 g, 151 mmol) were combined under inert atmosphere (glove bag) and then taken up in anhydrous DCM (150 mL) followed by addition of **2** (17.0 g, 50.4 mmol) in anhydrous DCM (100 mL). After stirring for 10 min at room temperature

(rt) BnBr (18.5 g, 108 mmol) was added to this heterogeneous mixture. The system was then wrapped in aluminum foil and stirred for 2 days under inert atmosphere in the dark at rt. The mixture was then filtered over celite and the solid residue was rinsed with DCM (3 x 100 mL). The organic filtrate was concentrated under reduced pressure to give crude product, which was purified by FCC using 20% ethyl acetate in hexane to afford **3** as a colorless oil (20.4 g, 95% yield). $[\alpha]^{25}_{D}$= +21.0 (*c* = 0.01, $CHCl_3$); IR ν_{max}(neat)/cm^{-1} 2934, 1778, 1698, 1383, 1107; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.23 (m, 8H), 7.19 (d, *J* = 7.0 Hz, 2H), 4.81 (d, *J* = 11.5 Hz, 1H), 4.64 (*J* = 11.5 Hz, 1H), 4.59- 4.53 (m, 1H), 4.34 (d, *J* = 6.0 Hz, 1H), 4.14-4.03 (m, 3H), 3.84 (dd, *J* = 7.5, 6.5 Hz, 1H), 3.43 (s, 3H), 3.34 (s, 3H), 3.24 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.75 (dd, *J* = 13.5, 9.5 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 153.3, 138.6, 135.5, 129.6 (2), 129.0 (2), 128.4 (2), 128.2 (2), 127.8, 127.4, 107.0, 79.8, 74.4, 66.1, 55.5, 55.4, 55.2, 39.5, 38.1, 13.8; MS (ESI+) calculated for $[C_{24}H_{29}NO_6+Na]^+$: 450.2, found: 450.2;.



3 4

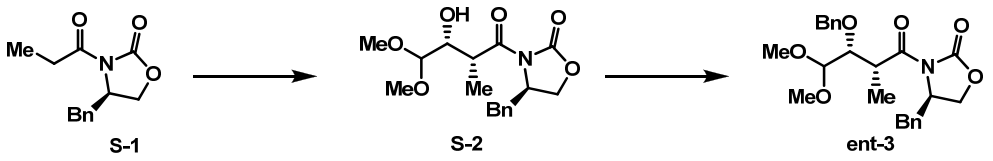
To a solution of **3** (17.8 g, 41.6 mmol) in diethyl ether (200 mL) was added methanol (5 mL). The reaction mixture was cooled to 0 °C and then $LiBH_4$ [33.2 mL of 2.5 M solution in tetrahydrofuran (THF) 83.0 mmol] was added slowly under argon. The resulting solution was stirred at 0 °C for 2 h then quenched with aqueous NH_4Cl (50 mL) and extracted with ethyl acetate (3 x 200 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and then concentrated under reduced pressure to give crude product, which was purified by FCC using 15% ethyl acetate in hexane to afford **4** as colorless oil (10.1 g, 95% yield). $[\alpha]^{25}_{D}$= –33.0 (*c* = 0.01, $CHCl_3$); IR ν_{max}(neat)/cm^{-1} 3431, 2934, 1454, 1071; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.32 (m, 4H), 7.30-7.25 (m, 2H), 4.82(d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 6.5 Hz, 1H), 3.59 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.59-3.46 (m, 2H), 3.49 (s, 3H), 3.41 (s, 3H), 2.02-1.96 (m, 1H), 1.90 (bs, 1H), 0.94 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 128.5 (2), 128.2 (2), 127.8, 106.5, 79.6, 74.1, 65.8, 56.2, 54.6, 36.9, 11.4; MS (ESI+) calculated for $[C_{14}H_{22}O_4+Na]^+$: 277.2, found: 277.2.



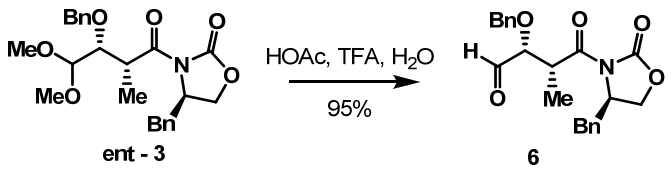
4 5

To a solution of **4** (7.30 g, 28.7 mmol) in DCM (150 mL) was added DABCO (3.22 g, 28.7 mmol). The reaction mixture was cooled to 0 °C and then tosyl chloride (5.47 g, 28.7 mmol) was added. The resulting solution was warmed to rt, stirred for 1 h, then diluted with 150 mL of DCM, washed with saturated NH_4Cl (3 x 50 mL) and water (50 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give crude tosylate, which was taken on without further purification as described below.

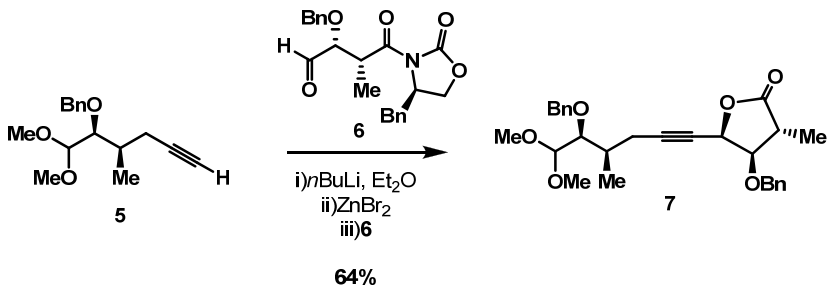
The above tosylate was dissolved in anhydrous DMSO (70 mL), and then lithium acetylide-ethylenediamine (4.76 g, 52.9 mmol) solution in DMSO (30 mL) was added. The resulting mixture was stirred for 3 h at rt, then cooled to 10 °C then carefully quenched with aqueous NH_4Cl (50 mL) such that the temperature of the solution was maintained below 20 °C. The quenched solution was then diluted with ethyl acetate (300 ml) and washed with water (3 x 100 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure to give crude product, which was purified by FCC using 3% ethyl acetate in hexane to afford **5** as colorless oil (5.95 g, 82% yield). $[\alpha]^{25}_D$= –39.0 (*c* = 0.01, $CHCl_3$); IR ν_{max}(neat)/cm^{-1} 3295, 2935, 2116, 1096; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.28-7.22 (m, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.56 (d, *J* = 11.5 H, 1H), 4.36 (d, *J* = 7.0 Hz, 1H), 3.65 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.47 (s, 3H), 3.38 (s, 3H), 2.23- 2.12 (m, 2H), 2.10- 2.00 (m, 2H), 1.96 (t, *J* = 7.5 Hz, 1H), 0.98 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 128.4 (2), 127.9 (2), 127.6, 106.4, 83.7, 80.3, 74.8, 69.6, 56.0, 53.8, 34.4, 23.5, 14.0; MS (ESI+) calculated for $[C_{16}H_{22}O_3+Na]^+$: 285.1, found: 285.2.



Compound **S-2** and *ent-**3*** were prepared following the same procedure used for the synthesis of their antipods **2** and **3** respectively. The observed optical rotation ($[\alpha]^{25}_D$) for the compound **S-2** and ent-**3** are –50.0 (*c* = 0.01, $CHCl_3$), and –21.0 (*c* = 0.01, $CHCl_3$) respectively.

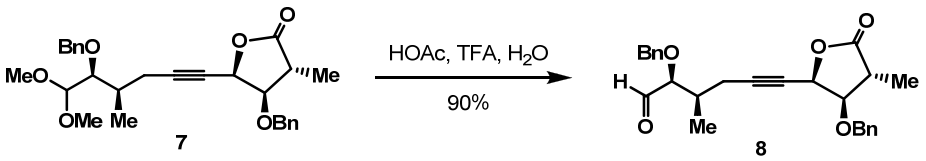


*Ent-**3*** (1.00 g, 2.34 mmol) was dissolved in 10 mL water: acetic acid:trifluoroacetic acid = 1:4:1 mixed solution at rt for 3 h and 30 mins. The acidic solvent was azatropically removed with toluene (5 x 20 mL) under reduced pressure and the resulting crude product was taken on without further purification as described below. It could also be further purified by FCC using 15% ethyl acetate in hexane to afford **6** as colorless viscous oil (847 mg, 95% yield). $[\alpha]^{25}_{D}$= –30.0 (*c* = 0.01, $CHCl_3$); IR ν_{max}(neat)/cm^{-1} 1778, 1730, 1693, 1390, 1212; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.38-7.22 (m, 8H), 7.17 (d, *J* = 7.0 Hz, 2H), 4.75 (d, *J* = 12.5 Hz, 1H), 4.64-4.54 (m, 1H), 4.59 (d, *J* = 12.5 Hz, 1H), 4.32-4.24 (m, 1H), 4.16-4.06 (m, 2H), 3.92 (d, *J* = 6.0 Hz, 1H), 3.20 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.76 (dd, *J* = 13.5, 10 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.0, 173.8, 153.1, 137.2, 135.1, 129.6 (2), 129.1 (2), 128.7 (2), 128.4, 128.3 (2), 127.5, 83.3, 73.1, 66.4, 55.4, 41.5, 37.8, 13.4; MS (ESI+) calculated for $[C_{22}H_{23}NO_5+Na]^+$: 404.2, found: 404.2.

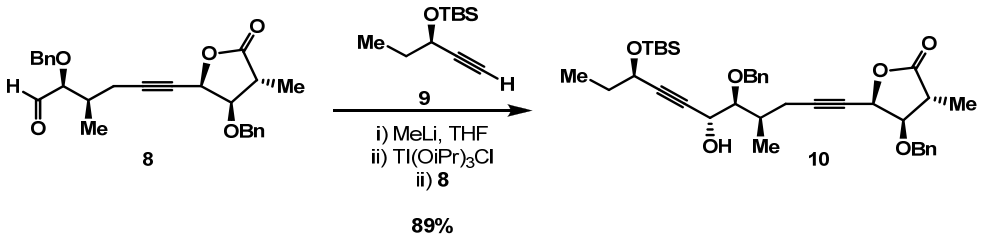


A solution of alkyne **5** (2.04 g, 7.76 mmol) in diethyl ether (40 mL) was cooled to –78 °C and then *n*-BuLi (3.10 mL, 7.76 mmol) was added slowly. The reaction mixture was stirred at –78 °C for 1 h and then a solution of $ZnBr_2$ (1.75 g, 7.76 mmol) in diethyl ether (20 mL) was added. The resulting milky white solution was stirred for 10 mins at –78 °C then warmed to 0 °C and then a solution of above aldehyde **6** (0.804 g, 2.1 mmol) in diethyl ether (15 mL) was added drop wise using a syringe pump for 2 h. The solution was then stirred for another 4 h then quenched with aqueous NH_4Cl (50 mL) at 0 °C, diluted with ethyl acetate (200 ml) and washed with water (2 x 50 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure to give the crude product (8:1 ratio by ^{1}H NMR), which was purified by FCC using 10% ethyl acetate in hexane to afford major isomer of **7** as colorless oil (570 mg, 58% yield). $[\alpha]^{25}_{D}$= +18.0 (*c* = 0.01, $CHCl_3$); IR ν_{max}(neat)/cm^{-1} 2935, 2238, 1786, 1454; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.24 (m, 10H), 5.12 (td, *J* = 2.0 Hz, 6.5 Hz, 1H), 4.82 (d, *J* =11.5 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.35 (d, *J* = 6.9 Hz, 1H), 3.88 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.57 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.47 (s,

3H), 3.37 (s, 3H), 2.86-2.76 (m, 1H), 2.38-2.20 (m, 2H), 2.10-2.00 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 139.1, 137.1, 128.8 (2), 128.5 (2), 128.4, 128.1 (2), 127.9 (2), 127.7, 106.4, 90.5, 81.0, 80.5, 74.7, 73.9, 72.4, 70.5, 56.1, 54.1, 39.4, 34.4, 24.0, 14.0, 12.7; MS (ESI+) calculated for $[C_{28}H_{34}O_6+Na]^+$: 489.3, found: 489.2.



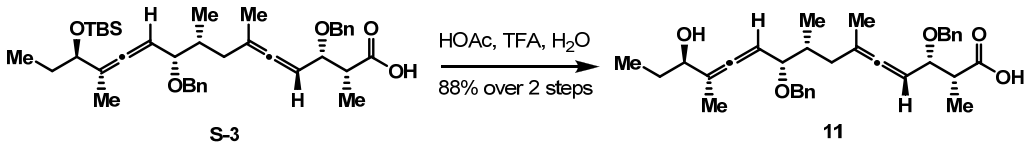
Alkyne **7** (280 mg, 0.600 mmol) was dissolved in 20 mL mixed solution of acetic acid, TFA and water (4:1:1) at rt and stirred for 14 h. The acidic solvent was removed with toluene (5 x 100 mL) under reduced pressure to afford the crude product, which was taken on without further purification as described below. It could also be further purified by FCC using 12% ethyl acetate in hexane to afford **8** as colorless viscous oil (227 mg, 90% yield). $[\alpha]^{25}_D$= +22.0 (*c* = 0.01, $CHCl_3$); IR ν_{max}(neat)/cm^{-1} 2935, 2240, 1786, 1730, 1455; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.4-7.25 (m, 10H), 5.11 (d, *J* = 6 Hz, 1H), 4.67 (d, *J* = 13 Hz, 2H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.46 (d, *J* = 12 Hz, 1H), 3.95-3.85 (m, 2H), 2.85-2.75 (m, 1H), 2.48-2.26 (m, 2H), 2.26- 2.16 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.3, 175.9, 137.6, 137.1, 128.8 (2), 128.7 (2), 128.5, 128.3, 128.2 (2), 128.0 (2), 89.2, 85.1, 81.0, 74.9, 73.4, 72.4, 70.4, 39.4, 35.2, 23.1, 14.5, 12.7; MS (ESI+) calculated for $[C_{26}H_{28}O_5+Na]^+$: 443.2, found: 443.2.



A solution of **9** (594 mg, 3.00 mmol) in THF (25 mL) was cooled to −78 °C and then a solution of MeLi in diethyl ether (1.4 mL, 2.25 mmol) was added slowly. (The preparation of compound **9** can be found in the supporting information of: Ghosh, P.; Lotesta, S. D.; Williams, L. J. *J. Am. Chem. Soc.* **2007**, *129*, 2438.) The reaction mixture was stirred for 1 h and then a 1 M hexane solution of chlorotriisopropoxytitanium (IV) (3.00 mL, 3.00 mmol) was added. The solution was slowly warmed to –40 °C and then a solution of aldehyde **8** (315 g, 0.749 mmol) in THF (10 mL) was added slowly at –40 °C. The mixture was warmed slowly to –20 °C over 2 h, diluted with ethyl

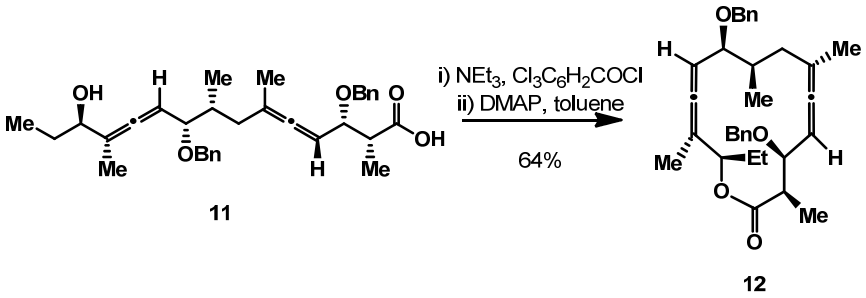
acetate (200 ml) and washed with water (50 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure to give the crude product (6:1 ratio by ^{1}H NMR) which was purified by FCC using 10% ethyl acetate in hexane to afford major isomer of **10** as colorless oil (411 mg, 89% combined yield for both diastereomers). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.44 (m, 1H), 5.11 (td, *J* = 2.1 Hz, 6.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.53 (*J* = 12.0 Hz, 1H), 4.43-4.54 (m, 1H), 4.32 (t, *J* = 6.6 Hz, 1H), 3.87 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.58 (dd, *J* = 5.4, 5.4 Hz, 1H), 2.88-2.76 (m, 1H), 2.46-2.13 (m, 1H), 1.75- 1.60 (m, 1H), 1.24 (d, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.87 (s, 9H), 0.08 (s, 3H), 0.10 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 138.5, 137.1, 128.8, 128.6, 128.5, 128.1, 127.9, 127.90, 89.8, 88.5 83.5, 82.7, 81.0, 77.5, 77.2, 77.0, 74.6, 74.4, 72.4, 70.5, 64.4, 63.5, 39.4, 34.7, 31.9, 26.0, 23.8, 18.5, 15.0, 12.7, 9.9, 0.2, -4.3, -4.8; MS (ESI+) calculated for $[C_{37}H_{50}O_6Si+Na]^+$: 641.3, found: 641.3.

To a solution of **10** (1.53 g, 2.47 mmol) in 50mL anhydrous diethyl ether was added Et_3N (377 mg, 3.71 mmol) and MsCl (424 mg, 3.71 mmol) respectively at 0 °C. The reaction mixture was warmed to rt and stirred for 1 h at rt. The solution was then cooled to –20 °C and then a solution of methyl cyanocuprate was added, prepared from CuCN (1.32 g, 14.8 mmol) and MeLi (9.2 mL, 14.7 mmol) in 75 mL Et_2O at –20 °C. The reaction mixture was then warmed to rt and stirred for 2 h, quenched with aqueous NH_4Cl (50 mL), extracted in diethyl ether (3 x 100 mL) and washed with water (100 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure to give crude product which was then taken on without further purification as described below.



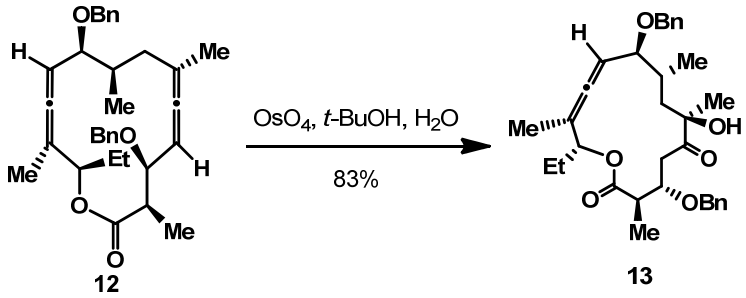
The above acid **S-3** (1.39 g, 2.20 mmol) was dissolved in 80% acetic acid (50 mL) and stirred for 8 h at rt. The solvent 80% acetic acid was removed with toluene (3 x 50 mL) under reduced pressure

and the resulting crude product was purified by FCC using 50% ethyl acetate in hexane to afford **11** as colorless oil (1.14 g, 88% yield). $[\alpha]^{25}_{D}$= +45.0 (*c* = 0.01, $CHCl_3$); IR ν_{max}(neat)/cm^{-1} 3388, 2933, 1965, 1710, 1454; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.27 (m, 10H), 5.18-5.10 (m, 1H), 5.08-5.02 (m, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.04 (dd, *J* = 7.0, 7.0 Hz, 1H), 3.99 (t, *J* = 6.5 Hz, 1H), 3.69 (dd, *J* = 8.5, 5 Hz, 1H), 2.84-2.76 (m, 1H), 2.38-2.32 (m, 1H), 1.94-1.84 (m, 1H), 1.75 (d, *J* = 3 Hz, 3H), 1.67 (d, *J* = 2.5 Hz, 3H), 1.66-1.50 (m, 2H), 1.23 (d, *J* = 7 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.90 (t, *J* = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 201.7, 175.7, 138.9, 137.7, 128.7 (2), 128.5 (2), 128.1, 128.1 (2), 127.8 (2), 127.7, 103.4, 100.6, 92.5, 88.0, 82.1, 79.3, 74.2, 70.7, 70.4, 44.4, 37.6, 37.0, 27.9, 19.4, 15.4, 15.1, 13.3, 9.8; MS (ESI+) calculated for $[C_{33}H_{42}O_5+Na]^+$: 541.3, found: 541.3.

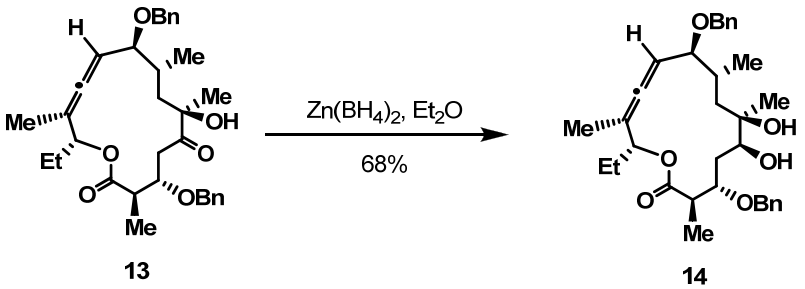


Seco acid **11** (280 mg, 0.540 mmol) was taken up in 20 mL toluene, then triethylamine (273 mg, 2.7 mmol) and 2,4,6-trichlorobenzoyl chloride (658 mg, 2.7 mmol) were added at rt. The reaction mixture was then stirred for 6 h at rt. The resulting solution was delivered dropwise by syringe pump over 2 h into a solution of DMAP (659 mg, 5.40 mmol) in toluene (150 mL) at 80 °C. The mixture was then cooled to rt and quenched with aqueous NH_4Cl (100 mL). The organic layer was separated, washed with water (2 x 100 mL), dried over anhydrous Na_2SO_4, filtered, and then concentrated under reduced pressure to give the crude product which upon FCC purification using 5% ethyl acetate in hexanes to afford macrolactone **12** (172 mg, 64% yield) as a colorless oil. IR ν_{max}(neat)/cm^{-1} 2970, 1961, 1731, 1454, 1248; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.22 (m, 10H), 5.33 (m, 1H), 5.26 (dt, *J* = 6.8, 1.1 Hz, 1H), 5.13 (m, 1H), 4.64 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.7 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 3.95 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.74 (dd, *J* = 7.8, 7.2 Hz, 1H), 2.78 (dq, *J* = 8.4, 7.1 Hz, 1H), 2.18 (m, 1H), 1.96 (m, 1H), 1.71 (d, *J* = 2.9 Hz, 3H), 1.70 (d, *J* = 2.9 Hz, 3H), 1.69-1.67 (m, 2H), 1.61 (m, 1H), 1.26 (d, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.7, 201.4,

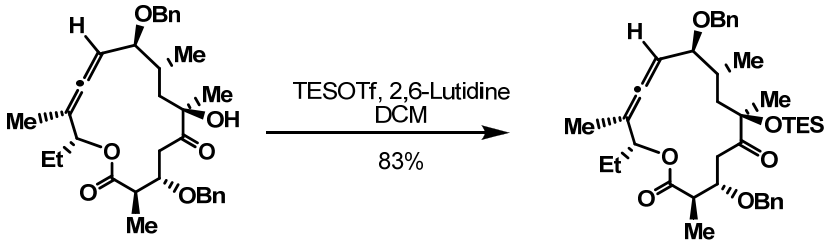
174.1, 139.3, 138.8, 128.5, 128.4, 128.0, 127.9, 127.7, 127.5, 102.6, 99.2, 92.0, 90.8, 81.8, 77.0, 75.7, 70.7, 68.9, 45.2, 37.9, 36.1, 25.2, 20.4, 15.5, 14.3, 9.9; MS (ESI+) calculated for $[C_{33}H_{40}O_4+Na]^+$: 523.3, found: 523.3.



The macrolactone **12** (26 mg, 0.052mmol) was dissolved in 2 mL 1:1 mixture of *t*-BuOH and water. To this solution was added OsO_4 (0.50 ml, 4% wt. water solution, 0.078mmol) at rt, stirred for 45 min then quenched by 20 mL saturated sodium sulfite solution, extracted with diethyl ether (2 x 20 mL). The organic layer was separated, dried over Na_2SO_4, filtered, and then concentrated under reduced pressure to give the crude product, which was purified by FCC using 10% ethyl acetate in hexane to afford the macrolactone **13** as a light yellowish oil (23 mg, 0.043 mmol, 83% yield): IR ν_{max}(neat)/cm^{-1} 3475, 2930, 2872, 1966, 1739, 1496, 1455, 1370; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.38 (m, 10H), 5.15 (m, 1H), 4.94 (m, 1H), 4.74 (d, *J* =11.6 Hz, 1H), 4.60 (d, *J* =12.2 Hz, 1H), 4.56 (d, *J* =11.6 Hz, 1H), 4.34 (d, *J* =12.2 Hz, 1H), 4.15 (m, 1H), 3.44 (dd, *J* =6.8, 8.1 Hz, 1H), 2.96 (dd, *J* = 6.9, 17.7 Hz, 1H), 2.93 (dd, *J* =3.8, 17.7 Hz, 1H), 2.58 (m, 1H), 1.9 (dd, *J* =6.6, 15.1 Hz, 1H), 1.79 (d, *J* =2.9 Hz, 1H), 1.73 (m, 1H), 1.69 (m, 2H), 1.54 (dd, *J* =3.2, 15.1 Hz, 1H), 1.32 (s, 3H), 1.30 (d, *J* =6.8 Hz, 3H), 1.05 (d, *J* =6.8 Hz, 3H), 0.90 (t, *J* =7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.1, 204.0, 173.8, 138.6, 138.4, 128.6, 128.5, 128.1, 127.9, 127.7, 126.1, 99.8, 96.7, 82.3, 78.9, 76.5, 76.0, 73.8, 70.0, 45.6, 43.0, 42.6, 34.2, 27.4, 25.3, 18.6, 15.5, 13.7, 9.6; MS (ESI+) calculated for $[C_{33}H_{42}O_6+Na]^+$: 557.3, found: 557.3. $[\alpha]^{25}_D$ = -32.6° (c = 0.004, $CHCl_3$)



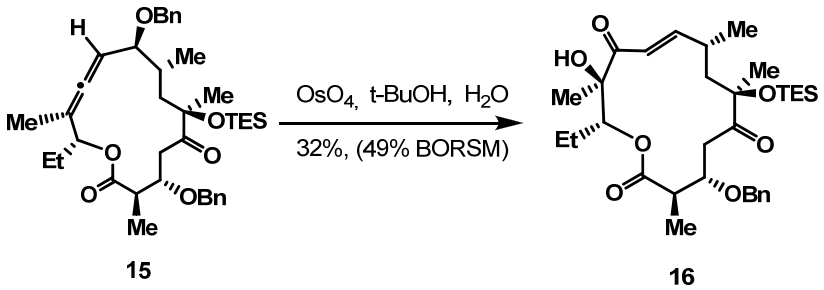
The hydroxyl ketone **13** (8.0 mg, 0.015 mmol) was dissolved in 1 mL anhydrous diethyl ether, cooled to 0 °C, then a 0.1 M solution of zinc borohydride (1 mL, 0.1 mmol) was added, stirred for 30 min then quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and then concentrated under reduced pressure to give a crude product which was purified by FCC using 20% ethyl acetate in hexane to afford **14** as a colorless oil (5.4 mg, 0.010mmol, 68% yield) as product: IR ν_{max} (neat)/cm^{-1} 3454, 2968, 2933, 2875, 1729, 1455, 1371, 1182, 1067; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.27 (m, 10H), 5.38 (m, 1H), 5.21 (m, 1H), 4.74 (d, *J* = 12.3 Hz, 1H), 4.60 (d, *J* = 11.1, 1H), 4.59 (d, *J* = 11.1, 1H), 4.42 (d, *J* = 12.3 Hz, 1H), 3.92 (m, 1H), 3.69 (dd, *J* = 7.5, 5.5 Hz, 1H), 3.59 (m, 1H), 2.89 (s, 1H), 2.76 (dq, *J* = 7.2, 6.9 Hz, 1H), 2.06 (m, 1H), 1.99 (dd, *J* = 14.8, 5.3 Hz, 1H), 1.86 (dd, *J* = 15.0, 3.4 Hz, 1H), 1.83 (dd, J=15.0, 7.1 Hz, 1H), 1.74 (d, *J* = 3.0 Hz, 3H), 1.72 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.16 (s, 3H), 1.07 (dd, *J* = 14.8, 3.8 Hz, 1H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 204.2, 174.8, 138.3, 138.0, 128.7, 128.6, 128.2, 128.1(2), 127.8, 99.5, 91.7, 80.6, 79.7, 76.3, 74.6, 73.7, 73.1, 70.6, 44.0, 39.8, 34.1, 33.5, 27.1, 25.2, 19.9, 14.6, 14.2, 9.7; MS (ESI+) calculated for $[C_{33}H_{44}O_6+Na]^+$: 559.30, found: 559.30; $[\alpha]^{25}_D$ = -3.1° (c = 0.003, $CHCl_3$).



13 **15**

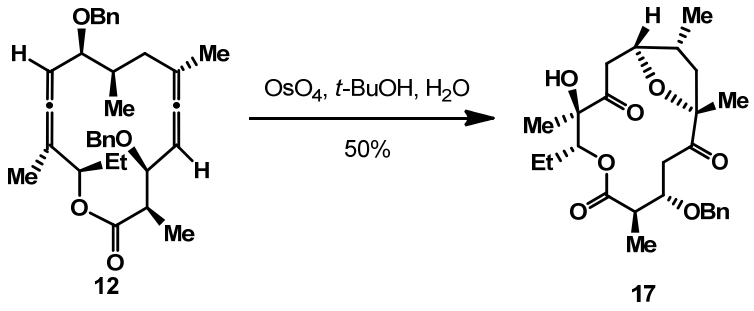
The macrolactone **13** (6.0 mg, 0.011 mmol) was dissolved in 1 mL DCM then 2,6-lutidine and TESOTf was added respectively at rt, stirred for 20 min at rt, and then quenched by addition of excess aqueous NH_4Cl solution. The organic layer was diluted with 10 mL DCM, separated, and then concentrated under reduced pressure to give the crude product which was purified with FCC (3% ethyl acetate in hexane) to afford the product **15** as a colorless oil (6.0 mg, 0.0093mmol, 83% yield): IR ν_{max}(neat)/cm^{-1} 2957, 2934, 2875, 1726, 1455, 1370, 1167, 1072; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.14 (m, 10H), 5.16 (dd, *J* = 6.2, 5.0 Hz, 1H), 5.04 – 4.90 (m, 1H), 4.60 (q, *J* = 11.0 Hz, 2H), 4.47 (d, *J* = 12.1 Hz, 1H), 4.22 (ddd, *J* = 19.7, 10.9, 5.9 Hz, 1H), 4.12 (d, *J* = 12.0 Hz, 1H), 4.05 (ddd, *J* = 8.3, 6.0, 4.3 Hz, 1H), 3.49 – 3.35 (m, 1H), 3.15 (dd, *J* = 16.9, 8.4 Hz, 1H), 2.88 – 2.82 (m, 1H), 2.82 – 2.75 (m, 1H), 1.91 (dt, *J* = 10.2, 4.7 Hz, 2H), 1.78 – 1.74 (m, 2H), 1.73

– 1.63 (m,2H), 1.39 (s, 3H), 1.35 – 1.28 (m, 3H), 1.28 – 1.23 (m, 3H), 1.21 (d, *J* = 7.0 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.98 (dt, *J* = 6.4, 5.6 Hz, 6H), 0.72 – 0.60 (m, 6H), 0.57 – 0.47 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.9, 204.1, 174.1, 139.2, 138.6, 128.4, 128.4, 128.3, 128.0, 127.8, 127.5, 98.9, 92.4, 83.2, 82.4, 77.4, 76.4, 72.9, 70.3, 45.3, 42.7, 41.6, 34.3, 26.9, 25.1, 18.1, 15.7, 13.1, 9.3, 7.5, 7.1; MS (ESI+) calculated for $[C_{39}H_{56}O_6Si+Na]^+$: 671.3, found: 671.3. $[\alpha]^{25}_D$ = -33.7° (c = 0.004, $CHCl_3$)

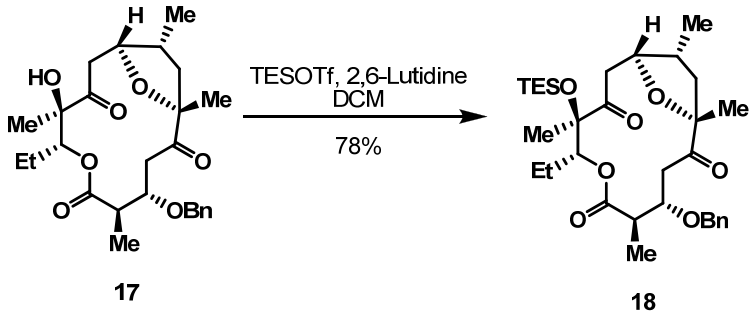


15 **16**

The protected ketoalcohol **15** (12.8 mg, 0.0200 mmol) was dissolved in 1 mL *t*-BuOH followed by the addition of citric acid (8.0 mg, 0.040 mmol) and the osmium tetroxide solution (0.13 mL, 4% wt. in water). The resulting dark purple solution was then stirred at rt for 3 h then the reaction was stopped by adding 10 mL saturated solution of sodium sulfite and extracted with 20 mL ethyl acetate. The organic layer was separated and then concentrated under reduced pressure to give a crude product which was purified by FCC using 10% ethyl acetate in hexane to afford product **16** as a colorless oil: (3.7 mg, 0.0064 mmol, 32% yield, 4.5 mg starting material recovered, 49% BORSM) IR ν_{max}(neat)/cm^{-1} 3479, 2921, 2876, 2850, 1731, 1698, 1623, 1455, 1367; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.28 (m, 5H); 6.64 (d, *J* =15.5 Hz, 1H), 6.60 (dd, *J* =8.2, 15.5 Hz, 1H), 4.89 (dd, *J* =2.5, 11.3 Hz, 1H), 4.56 (d, *J* =11.6 Hz, 1H), 4.49 (d, *J* =11.6 Hz, 1H), 3.68 (m, 1H), 3.60 (m, 1H), 3.42 (dd, *J* =4.3, 18.8 Hz, 1H), 2.58 (m, 1H), 2.44 (dd, *J* =3.4, 18.8 Hz, 1H), 2.29 (dd, *J* =10.2, 14.3 Hz, 1H), 2.02 (m, 1H), 1.78 (m, 1H), 1.45 (dd, *J* =2.1, 14.3 Hz, 1H), 1.31 (s, 3H), 1.23 (s, 3H), 1.21 (d, *J* =7.0 Hz, 3H), 1.02 (d, *J* =6.6 Hz, 3H), 1.01 (t, *J* =7.9, 9H), 0.88 (t, *J* =7.4 Hz, 3H), 0.66 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.5, 202.7, 178.5, 154.9, 138.5, 128.6, 128.3, 128.0, 122.7, 84.4, 82.4, 80.8, 77.1, 73.0 46.3, 43.0, 37.6, 33.3, 28.3, 23.6, 23.0, 22.5, 16.0, 10.9, 7.5, 7.0; MS (ESI+) calculated for $[C_{32}H_{50}O_7Si+Na]^+$: 597.3, found: 597.3

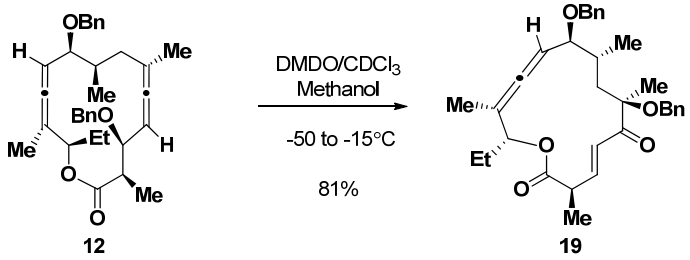


The macrolactone **12** (10 mg, 0.02 mmol) was dissolved in a 1:1 mixture solution of *t*-BuOH and water (1 mL), then 0.28 mL OsO_4 solution (4% wt. in water) was added at rt, stirred for 4 h then quenched with 15 mL saturated sodium sulfite solution, and then extracted with diethyl ether (2 x 20 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and then concentrated under reduced pressure to give a crude product, which was purified by FCC using 20% ethyl acetate and hexane to afford macrolactone **17** as a colorless oil: (4.4 mg, 0.0092 mmol, 46% yield) IR ν_{max}(neat)/cm^{-1} 3477, 2971, 2934, 2878, 1735, 1711, 1455, 1382; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.30(m, 5H), 4.89 (dd, *J* = 9.0, 3.4 Hz, 1H), 4.63 (m, 1H), 4.57 (d, *J* = 11.6Hz 1H), 4.59(d, *J* = 11.6 Hz 1H), 3.86 (m, *J* = 11.1, 4.7 Hz, 1H), 3.37 (dd, *J* = 14.5, 6.4 Hz, 1H), 3.08 (dd, *J* = 18.7, 10.2 Hz, 1H), 2.98 – 2.82 (m, 1H), 2.51 – 2.36 (m, 1H), 2.29 (dd, *J* = 4.7, 14.5 Hz, 1H), 1.97 (m, 1H), 1.89 (dd, *J* = 12.9, 9.1 Hz, 1H), 1.79 (dd, *J* = 12.9, 7.3 Hz, 1H), 1.55 (m, 1H), 1.38 (s, 3H), 1.27 (s, 3H), 1.21 (d, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.67 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 213.3, 212.6, 173.2, 137.5, 128.8, 128.4, 128.0, 88.5, 78.9, 78.4, 77.8, 76.3, 72.0, 42.1, 40.5, 39.6, 35.4, 34.9, 25.2, 23.1, 17.0, 15.0, 14.2, 11.0; MS (ESI+) calculated for $[C_{26}H_{36}O_7+Na]^+$: 483.3, found: 483.3.

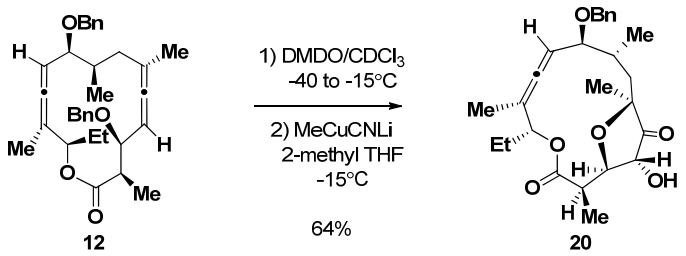


The keto-alcohol **17** (4.0 mg, 0.0082 mmol) was dissolved in 1.5 mL DCM then 2,6-lutidine (100 mg) and TESOTf (120 mg) was added respectively at rt, stirred at rt for 30 min then quenched by 10 mL saturated NH_4Cl solution. Organic layer was diluted with 10 mL DCM, separated then concentrated under reduced pressure to give the crude product, which was Further purified by FCC

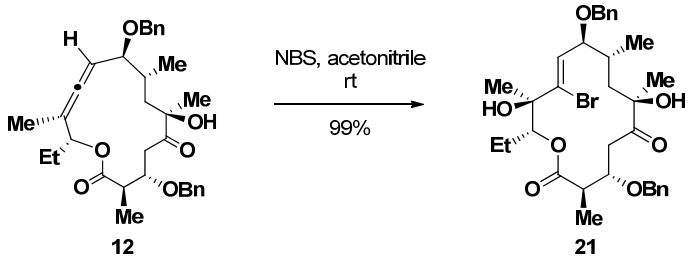
using 10% ethyl acetate in hexane to afford the product **18** as a colorless oil (4.0 mg, 78% yield), which could be converted to a white crystalline by slow evaporation at rt in 1 mL 30% ethyl acetate in hexane: IR ν_{max}(neat)/cm^{-1} 3444, 2954, 2928, 2875, 1738, 1716, 1456, ,1378, 1183, 1164; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.30 (m, 5H), 5.2 (dd, *J* =2.9, 9.5 Hz, 1H), 4.6 (d, *J* =10.4 Hz, 1H), 4.48 (m, 1H), 4.44 (d, *J* =10.4 Hz, 1H), 3.87 (m, 1H), 3.26 (dd, *J* =9.6, 14.9 Hz, 1H), 2.92 (m, 1H), 2.78 (dd, *J* =10.5, 19.0 Hz, 1H), 2.35 (dd, *J* =1.5, 19.0 Hz, 1H), 2.24 (m, 1H), 2.17 (dd, *J* =3.8, 14.9 Hz, 1H), 1.89 (m, 1H), 1.81 (dd, *J* =11.4, 12.6 Hz, 1H), 1.73 (dd, *J* =7.0, 12.6 Hz, 1H), 1.46 (m, 1H), 1.33 (s, 3H), 1.28 (s, 3H), 1.14 (d, *J* =7.0 Hz, 3H), 0.91 (t, *J* =7.2 Hz, 3H), 0.89 (dd, *J* =7.8, 8.2 Hz, 9H), 0.68 (d, *J* =6.9 Hz, 3H), 0.56-0.54 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 215.5, 211.4, 172.9, 137.7, 129.1, 128.5, 128.3, 88.6, 79.6 (2), 79.4, 78.1, 72.5, 41.6, 41.2, 39.8, 36.3, 35.0, 25.5, 22.7, 17.0, 14.8, 13.9, 11.1, 7.2, 6.4; MS (ESI+) calculated for $[C_{32}H_{50}O_7Si+Na]^+$: 597.3, found: 597.3.



To a solution of macrolactone **12** (12 mg, 0.020 mmol) in methanol (3.0 mL) was added a solution of DMDO (0.38 mL, 0.14 mmol) dropwise at −50 °C. The solution was stirred under inert atmosphere and warmed to −15 °C over 1.5 h. The mixture was then concentrated under reduced pressure to give the crude product, which was purified by FCC using 5% ethyl acetate in hexane to afford **19** as colorless oil (10 mg, 81%). For detailed NMR analysis, see page S28. IR νmax (neat)/cm^{-1} 3442, 3062, 2956, 2922, 2850, 1728, 1711, 1454, 1376, 1165, 1070; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48-7.17 (m, 10H), 7.05 (dd, J = 15.7, 1.2 Hz, 1H), 6.73 (dd, *J* = 15.7, 8.3 Hz, 1H), 4.71 (m, 1H), 4.62 (m, 1H), 4.57 (d, *J* = 11.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.26 (d, *J* = 11.5 Hz, 1H), 4.24 (d, *J* = 11.5 Hz, 1H), 3.30 (m, 1H), 3.24 (t, *J* = 9.1 Hz, 1H), 1.95 (dd, *J* = 14.2 Hz, 1H), 1.82 (d, *J* = 2.9 Hz, 3H), 1,78-1.68 (m, 2H), 1.48 (dd, *J* = 14.4, 6.9 Hz, 1H), 1.44 (s, 3H), 1.41 (m, 1H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.6, 202.1, 171.9, 145.3, 138.6, 138.6, 128.4, 128.3, 128.2, 127.8, 127.5, 127.4, 127.2, 101.1, 93.9, 84.9, 83.0, 75.8, 69.8, 66.3, 42.3, 41.4, 33.5, 26.4, 19.9, 18.0, 17.4, 14.6, 9.7; MS (ESI+) calculated for $[C_{33}H_{40}O_5+Na]^+$: 539.3, found: 539.3; $[\alpha]^{25}_D$ = 3.3° (c = 0.005, $CHCl_3$).

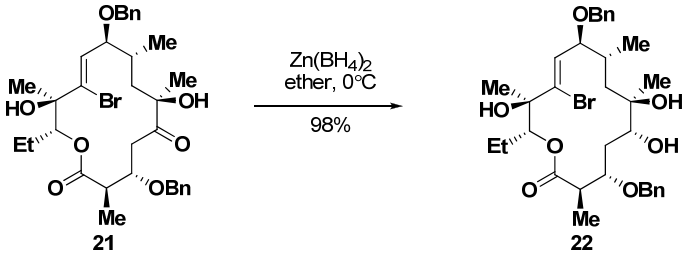


To a solution of macrolactone **12** (17.7 mg, 0.0340 mmol) in $CDCl_3$ (0.5 mL) was added a solution of DMDO (0.56 mL, 0.21 mmol) dropwise at –40 °C, warmed up to –15 °C over 30 min, then lower order methyl cyanocuprate (MeCuCNLi, 0.71 mmol) was added, prepared by addition of MeLi (0.44 mL, 0.71 mmol) to a slurry of CuCN (63 mg, 0.71 mmol) in 2-methyl THF (5.99 mL) at –78 °C and then warming to –15 °C. The mixture was warmed to –2 °C over 1.5 h, quenched with saturated aqueous solution of NH_4OH and NH_4Cl (1:4 ratio) and then extracted with diethyl ether. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and then concentrated under reduced pressure to give the crude product, which was purified by FCC using 15% ethyl acetate in hexane to afford **20** (10 mg, 64% yield) as a colorless oil. For detailed NMR analysis, see page S30. IR νmax (neat)/cm^{-1} 3434, 2968, 2925, 1959, 1764, 1725, 1452, 1370, 1155; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 5.60 (dd, *J* = 8.1, 6.3 Hz, 1H), 5.07 (m, 2H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.36 (d, *J* = 12.1 Hz, 1H), 3.90 (dd, *J* = 8.7, 4.4 Hz, 1H), 3.83 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.06 (m, 1H), 1.87 (dd, *J* = 15.0, 5.8 Hz, 1H), 1.80 (d, *J* = 2.8 Hz, 3H), 1.70 (m, 2H), 1.65 (m, 2H), 1.35 (d, *J* = 7.4 Hz, 2H), 1.14 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 218.9, 206.6, 171.0, 138.9, 128.2, 127.7, 127.3, 99.0, 90.7, 83.4, 82.3, 79.7, 76.6, 72.5, 70.2, 42.9, 40.2, 34.0, 24.3, 22.8, 14.5, 13.8, 13.6, 10.0; MS (ESI+) calculated for $[C_{26}H_{34}O_6+Na]^+$: 465.2, found: 465.5; $[\alpha]^{25}_D$ = 5.9° (c = 0.005, $CHCl_3$).



To a stirred solution of macrolactone **12** (7.8 mg, 0.015 mmol) in 1.0 mL of acetonitrile was added *N*-bromosuccinimide (34 mg, 0.19 mmol) at rt then stirred for 5 min. The reaction mixture was quenched with 1 mL of saturated aqueous solution of $Na_2S_2O_3$ and then extracted with diethyl ether (2 x 5 mL). The organic layer was separated and then concentrated under reduced pressure to

give the crude product which was purified by FCC using 14% ethyl acetate in hexane to afford **21** as colorless oil: (9.1 mg, 99% yield). For detailed NMR analysis, see page S32. IR νmax (neat)/cm^{-1} 3442, 3062, 2956, 2922, 2850, 1728, 1711, 1454, 1376, 1165, 1070; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.24 (m, 10H), 6.14 (d, *J* = 8.4 Hz, 1H), 4.89 (dd, *J* = 10.9, 2.4 Hz, 1H), 4.64 (d, *J* = 11.1 Hz, 1H), 4.52 (m, 2H), 4.40 (d, *J* = 12.3 Hz, 1H), 4.34 (m, 1H), 4.00 (dd, *J* = 8.3, 6.1 Hz, 1H), 3.11 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.56 (q, *J* = 6.9 Hz, 1H), 2.47 (dd, *J* = 15.6, 5.7 Hz, 1H), 1.85 (m, 1H), 1.82 (m, 1H), 1.79 (dd, *J* = 14.4 Hz, 1H), 1.55 (m, 1H), 1.45 (dd, *J* = 14.4, 5.9 Hz, 1H), 1.44 (s, 3H), 1.23 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.7, 174.6, 138.7, 138.4, 134.2, 131.2, 128.3(2), 128.1, 127.7(2), 127.5, 84.0, 79.4, 79.3, 77.1, 76.1, 73.3, 72.2, 44.8, 42.5, 41.3, 35.0, 26.8, 25.1, 24.4, 19.6, 12.6, 11.1; MS (ESI+) calculated for $[C_{33}H_{43}BrO_7+Na]^+$: 653.3, 655.3, found: 653.2, 655.2; $[\alpha]^{25}_D$ = 7.6° (c = 0.005, $CHCl_3$).

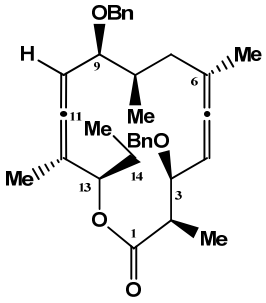


To a stirred solution of macrolactone **21** (5.0 mg, 0.0079 μmol) in 1.00 mL of anhydrous diethyl ether was added 0.13 M $Zn(BH_4)_2$ solution in anhydrous diethyl ether (0.090 ml, 0.012 mmol) at 0 °C. The mixture was stirred for 30mins at 0 °C, quenched with 1 mL of saturated aqueous solution of NH_4Cl, then extracted with diethyl ether (2 x 5 mL). The organic layer was separated, dried over Na_2SO_4, filtered then concentrated under reduced pressure to give the crude product, which was purified by FCC 20% ethyl acetate in hexane to afford **22** (4.9 mg, 98% yield) as an oil. For detailed NMR analysis, see page S34. IR νmax (neat)/cm^{-1} 2925, 2851, 1729, 1450, 1375, 1164, 1068; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.23 (m, 10H) 6.38 (d, *J* = 8.6 Hz, 1H), 4.88 (dd, *J* = 11.0, 2.3 Hz, 1H), 4.58 (m, 2H), 4.51 (d, *J* = 10.7 Hz, 1H), 4.47 (d, *J* = 12.4 Hz, 1H), 4.36 (m, 1H), 4.11 (dd, *J* = 8.6, 6.6 Hz, 1H), 3.51 (dd, *J* = 7.0, 2.4 Hz, 1H), 2.65 (m, 1H), 2.31 (m, 1H), 1.85 (m, 2H), 1.83 (dd, *J* = 15.0, 3.0 Hz, 1H), 1.77 (dd, *J* = 15.0, 3.0 Hz, 1H), 1.61 (dd, *J* = 14.7, 6.1 Hz, 1H), 1.50 (s, 3H), 1.28 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.17 (dd, *J* = 14.9, 7.0 Hz, 1H), 1.12 (d, *J* = 6.7 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 139.0, 137.9, 133.0, 131.4, 128.3, 128.1, 128.0, 127.9, 127.6, 126.5, 84.7, 81.3, 78.2, 77.6, 75.2, 73.7, 73.1, 71.9, 44.8,

40.8, 35.9, 34.6, 27.7, 26.0, 24.7, 20.0, 12.4, 11.4; MS (ESI+) calculated for $[C_{33}H_{45}O_7+Na]^+$: 655.2, 657.2, found: 655.2, 657.2; $[\alpha]^{25}_D = 5.8°$ (c = 0.005, $CHCl_3$).

Detailed ^{1}H, ^{13}C, and selected NOE and HMBC data for 12-22

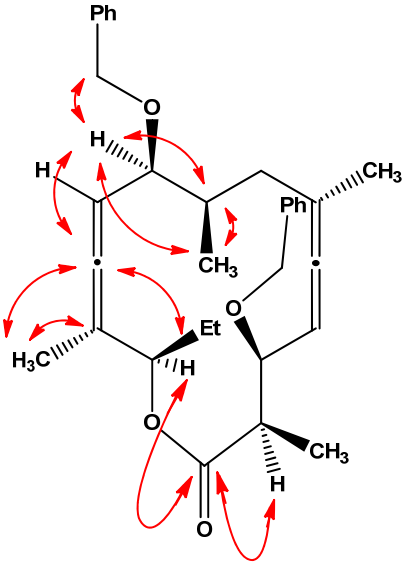
Detailed NMR analysis for compounds 12



12

1H NMR chemical shifts (d/ppm) and coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)
2.78 (dq, $J_{H2, H3}$ = 8.4Hz, $J_{H2, 2\text{-}CH3}$ = 7.1Hz, H2)	173.8 ----- C1
1.26 (d, $J_{2\text{-}CH3, H2}$ = 7.1Hz, 2-CH_3)	44.5 ----- C2
3.95 (dd, $J_{H3, H2}$ = 8.4Hz, $J_{H3, H4}$ = 4.0Hz, H3)	77.2 ----- C3
5.33 (m, $J_{H4, H3}$ = 4.0Hz, $J_{H4,6\text{-}CH3}$=2.9Hz, $J_{H4,H7\alpha}$=2.7Hz, $J_{H4, H7\beta}$ = 3.4Hz, H4)	90.5 ----- C4
	201.2 ----- C5
1.70 (d, 6-CH_3)	102.4 ----- C6
1.61 (m, $J_{H7\beta, H8}$ = 5.4Hz, $J_{H7\beta, H7\alpha}$ = 15.4Hz, $J_{H4, H7\beta}$ = 3.4Hz, H7β)	37.7 ----- C7
	35.9 ----- C8
2.18 (m, $J_{H7\alpha, H8}$ = 5.7Hz, $J_{H7\alpha, H7\beta}$ = 15.4Hz, $J_{H4,H7\alpha}$=2.7Hz, H7α)	81.6 ----- C9
	91.7 ----- C10
1.96 (m, $J_{H7\alpha, H8}$ = 5.7Hz, $J_{H7\beta, H8}$ = 5.4Hz, $J_{H8, 8\text{-}CH3}$ = 6.7Hz, $J_{H8, H9}$ = 7.2Hz, H8)	203.4 ----- C11
	99.0 ----- C12
1.05 (d, $J_{8\text{-}CH3, H8}$ = 6.7Hz, 8-CH_3)	75.5 ----- C13
3.74 (dd, $J_{H9, H8}$ = 7.2Hz, $J_{H9, H10}$= 7.8Hz, H9)	24.9 ----- C14
5.13 (m, $J_{H9,H10}$= 7.8Hz, $J_{H10,12\text{-}CH3}$ = 2.9Hz, $J_{H10\text{-}H13}$=1.1Hz, H10)	15.2 ----- 2-CH_3
	20.2 ----- 6-CH_3
1.71 (d, $J_{H10,12\text{-}CH3}$ = 2.9Hz, 12-CH_3)	17.6 ----- 8-CH_3
5.26 (dt, $J_{H10\text{-}H13}$=1.1Hz, $J_{H13, H14}$ = 6.8Hz, H13)	14.0 ----- 12-CH_3
1.69, 1.67 (m, 14-CH_2)	9.6 ----- 14-CH_3
0.90 (t, $J_{14\text{-}CH3, H14}$ = 7.5Hz, 14-CH_3)	
4.64 (d, J=11.7Hz, 3-Bn-CH_2a)	
4.48 (d, J=11.7Hz, 3-Bn-CH_2b)	
4.54 (d, J=11.9Hz, 9-Bn-CH_2a)	
4.34 (d, J=11.9Hz, 9-Bn-CH_2b)	
7.22-7.35 (two phenyl)	

HMBC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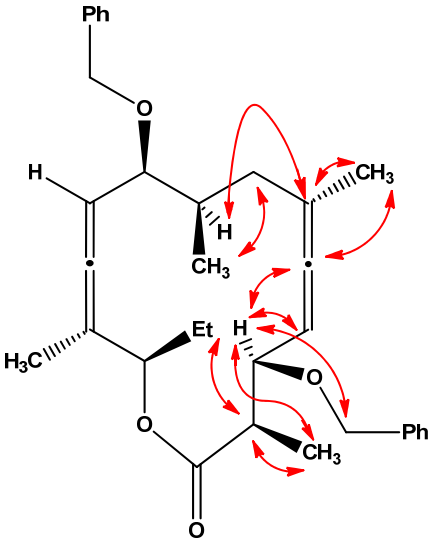
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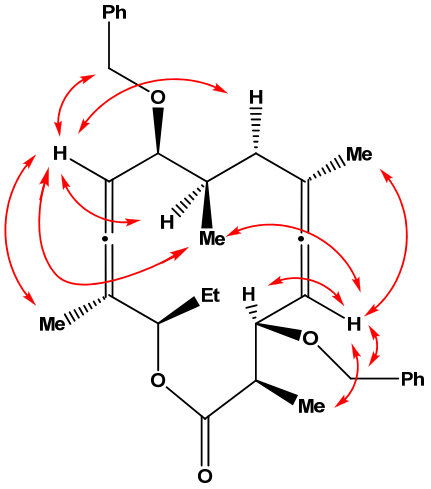
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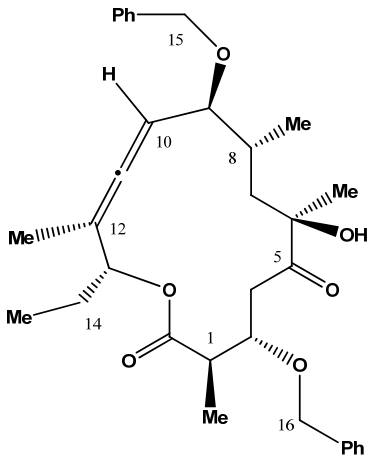
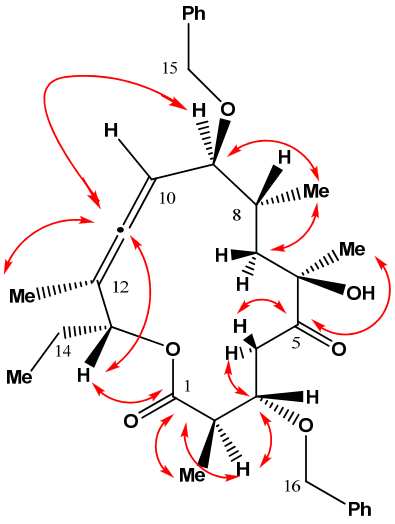
Detailed NMR analysis for compounds 13



1H NMR chemical shifts (d/ppm) and coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)
2.58 (dq, $J_{H2, H3}$ = 8.7Hz, $J_{H2, 2\text{-}CH3}$ = 6.8Hz, H2)	173.84 —— C1
1.30 (d, $J_{2\text{-}CH3, H2}$ = 6.8Hz, 2-CH_3)	45.56 —— C2
4.15 (m, $J_{H3, H2}$ = 8.7Hz, $J_{H3, H4\alpha}$ = 3.8Hz, $J_{H3, H4\beta}$ = 6.9Hz, H3)	76.0 —— C3
2.93 (dd, $J_{H4\alpha, H3}$ = 3.8Hz, $J_{H4\alpha, H4\beta}$ = 17.7, H4α)	42.6 —— C4
2.96 (dd, $J_{H4\beta, H3}$ = 6.9Hz, $J_{H4\alpha, H4\beta}$ = 17.7, H4β)	212.1 —— C5
1.32 (s, 6-CH_3)	78.9 —— C6
1.90 (dd, $J_{H7\beta, H8}$ = 6.6Hz, $J_{H7\beta, H7\alpha}$ = 15.1Hz, H7β)	43.0 —— C7
1.54 (dd, $J_{H7\alpha, H8}$ = 3.2Hz, $J_{H7\alpha, H7\beta}$ = 15.1Hz, H7α)	34.2 —— C8
1.69 (m, $J_{H7\alpha, H8}$ = 3.2Hz, $J_{H7\beta, H8}$ = 6.6Hz, $J_{H8, 8\text{-}CH3}$ = 6.8Hz, $J_{H8, H9}$ = 6.8Hz, H8)	82.3 —— C9
	96.7 —— C10
	204.0 —— C11
1.05 (d, $J_{8\text{-}CH3, H8}$ = 6.8Hz, 8-CH_3)	99.8 —— C12
3.44 (dd, $J_{H9, H8}$ = 6.8Hz, $J_{H9, H10}$ = 8.1Hz, H9)	76.5 —— C13
4.94 (m, $J_{H9,H10}$ = 8.1Hz, $J_{H10,H13}$=1.1Hz, $J_{H10,12\text{-}CH3}$=2.9Hz, H10)	25.3 —— C14
1.79 (d, $J_{H10,12\text{-}CH3}$=2.9Hz, 12-CH_3)	13.7 —— 2-CH_3
5.15 (m, $J_{H13, H14}$ = 7.0 Hz, $J_{H10,H13}$=1.1Hz H13)	27.4 —— 6-CH_3
1.69, 1.73 (m, 14-CH_2)	18.6 —— 8-CH_3
0.90 (t, $J_{14\text{-}CH3, H14}$ = 7.4Hz, 14-CH_3)	15.5 —— 12-CH_3
4.34 (d, $J_{H15a,H15b}$= 12.2, H15a)	9.6 —— 14-CH_3
4.60 (d, $J_{H15a,H15b}$= 12.2, H15b)	73.8 —— C16
4.56 (d, J=11.6Hz, H16a)	70.0 —— C15
4.74 (d, J=11.6Hz, H16b)	138.6 —— ^{ipso}C-15
7.26-7.38 (m, 10H, two phenyl)	128.1 —— ^{ortho}C-15
	128.6 —— ^{meta}C-15
	127.9 —— ^{para}C-15
	138.4 —— ^{ipso}C-16
	126.1 —— ^{ortho}C-16
	128.5 —— ^{meta}C-16
	127.7 —— ^{para}C-16

HMBC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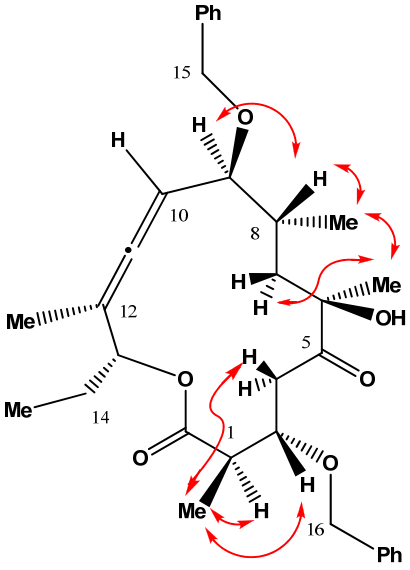
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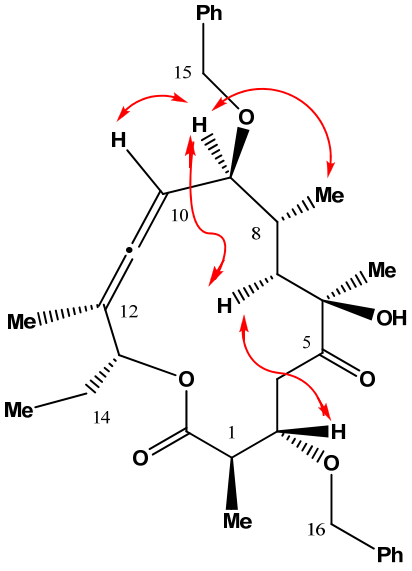
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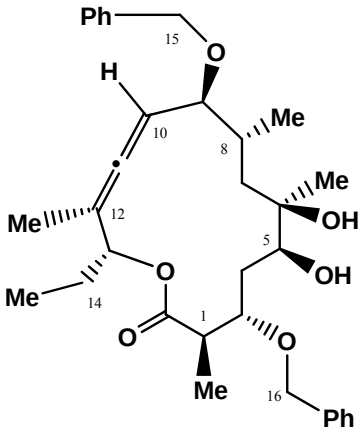
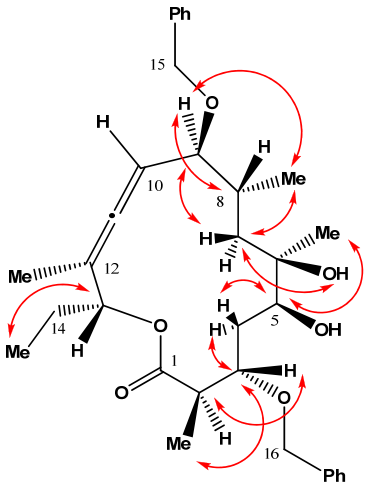
Detailed NMR analysis for compounds 14



14

1H NMR chemical shifts (d/ppm) and coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)
2.76 (dq, $J_{H2, H3}$ = 7.2Hz, $J_{H2, 2\text{-}CH3}$ = 6.9Hz, H2)	174.8 ----- C1
1.24 (d, $J_{2\text{-}CH3, H2}$ = 6.Hz, 2-CH_3)	44.0 ----- C2
3.92 (m, $J_{H3, H2}$ = 7.2Hz, $J_{H3, H4\alpha}$ = 3.4Hz, $J_{H3, H4\beta}$ = 7.1Hz, H3)	79.7 ----- C3
1.86 (dd, $J_{H4\alpha, H3}$ = 3.4Hz, $J_{H4\alpha, H4\beta}$ = 15.0, H4α)	33.5 ----- C4
1.83 (dd, $J_{H4\beta, H3}$ = 7.1Hz, $J_{H4\alpha, H4\beta}$ = 15.0, H4β)	74.6 ----- C5
3.59 (m, $J_{H4\alpha, H5}$ = 9.6Hz, $J_{H4\beta, H5}$ = 2.1Hz, $J_{H5\text{-}5\text{-}OH}$=6.21Hz, H5)	73.7 ----- C6
1.16 (s, 6-CH_3)	39.8 ----- C7
2.89 (s, 6-OH)	34.1 ----- C8
1.99 (dd, $J_{H7\beta, H8}$ = 5.3Hz, $J_{H7\beta, H7\alpha}$ = 14.8Hz, H7β)	80.6 ----- C9
1.07 (dd, $J_{H7\alpha, H8}$ = 3.8Hz, $J_{H7\alpha, H7\beta}$ = 14.8Hz, H7α)	91.7 ----- C10
2.06 (m, $J_{H7\alpha, H8}$ = 3.8Hz, $J_{H7\beta, H8}$ = 5.3Hz, $J_{H8, 8\text{-}CH3}$ = 6.9Hz, $J_{H8, H9}$ = 5.5Hz, H8)	204.2 ----- C11
1.00 (d, $J_{8\text{-}CH3, H8}$ = 6.9Hz, 8-CH_3)	99.5 ----- C12
3.69 (dd, $J_{H9, H8}$ = 5.5Hz, $J_{H9, H10}$ =7.5Hz, H9)	76.3 ----- C13
5.21 (m, $J_{H9,H10}$ = 7.5Hz, $J_{H10,H13}$=1.2Hz, $J_{H10,12\text{-}CH3}$=3.0Hz, H10)	25.2 ----- C14
1.74 (d, $J_{H10,12\text{-}CH3}$=3.0Hz, 12-CH_3)	14.2 ----- 2-CH_3
5.38 (m, $J_{H13, H14}$ = 6.8 Hz, $J_{H10,H13}$=1.2Hz H13)	27.1 ----- 6-CH_3
1.72 (m, 14-CH_2)	19.9 ----- 8-CH_3
0.91 (t, $J_{14\text{-}CH3, H14}$ = 7.3Hz, 14-CH_3)	14.6 ----- 12-CH_3
4.59 (d, $J_{H15a,H15b}$= 11.1, H15a)	9.7 ----- 14-CH_3
4.60 (d, $J_{H15a,H15b}$= 11.1, H15b)	73.1 ----- C16
4.42 (d, J=12.3Hz, H16a)	70.6 ----- C15
4.74 (d, J=12.3Hz, H16b)	
7.27-7.37 (m, 10H, two phenyl)	

HMBC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8
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H
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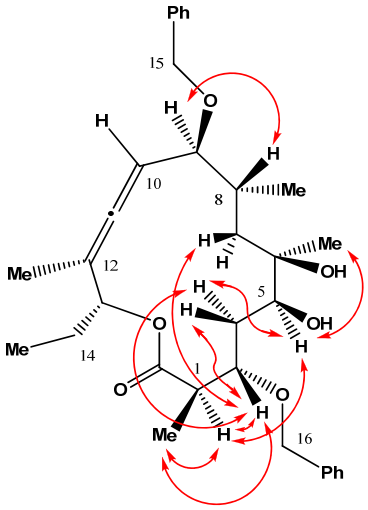
H
1
O
H
O
Me
H
16
Ph

NOESY


Ph
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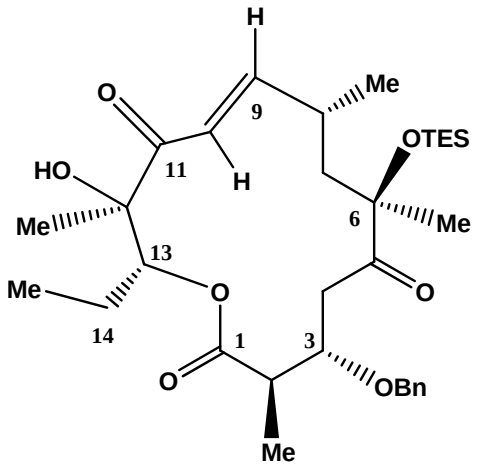
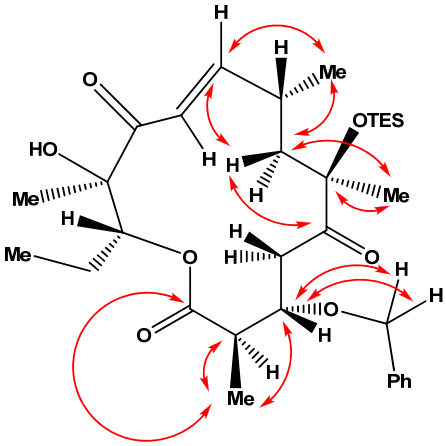
Ph

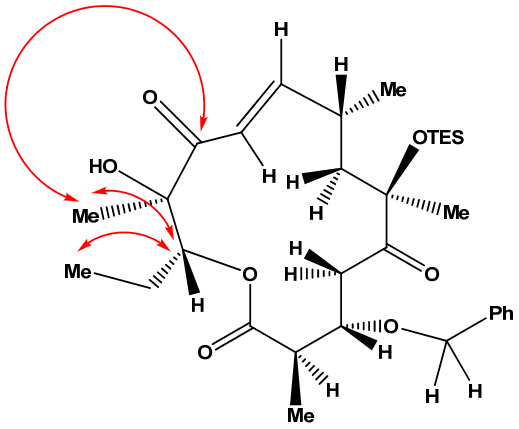
Detailed NMR analysis for compounds 16



1H NMR chemical shifts (d/ppm) and coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)
3.60 (dq, $J_{H2, H3}$ = 9.7Hz, $J_{H2, 2\text{-}CH3}$ = 7.0Hz, H2)	178.5 ----- C1
1.21 (d, $J_{2\text{-}CH3, H2}$ = 7.0Hz, 2-CH_3)	43.0 ----- C2
3.68 (ddd, $J_{H3, H2}$ = 9.7Hz, $J_{H3, H4\alpha}$ = 3.4Hz, $J_{H3, H4\beta}$ = 4.3Hz, H3)	77.1 ----- C3
2.44 (dd, $J_{H4\alpha, H3}$ = 3.4Hz, $J_{H4\alpha, H4\beta}$ = 18.8, H4α)	37.6 ----- C4
3.42 (dd, $J_{H4\beta, H3}$ = 4.3Hz, $J_{H4\beta, H4\alpha}$ = 18.8, H4β)	212.5 ----- C5
1.23 (s, 6-CH_3)	82.4 ----- C6
2.29 (dd, $J_{H7\beta, H8}$ = 10.2Hz, $J_{H7\beta, H7\alpha}$ = 14.3Hz, H7β)	46.3 ----- C7
1.45 (dd, $J_{H7\alpha, H8}$ = 2.1Hz, $J_{H7\alpha, H7\beta}$ = 14.3Hz, H7α)	33.3 ----- C8
2.58 (m, $J_{H8, 8\text{-}CH3}$ = 6.6Hz, $J_{H8, H9}$ = 8.2Hz, H8)	154.9 ----- C9
1.02 (d, $J_{8\text{-}CH3, H8}$ = 6.6Hz, 8-CH_3)	122.7 ----- C10
6.60 (dd, $J_{H9, H8}$ = 8.2Hz, $J_{H9, H10}$ = 15.5 Hz, H9)	202.7 ----- C11
6.64 (d, $J_{H9,H10}$ = 15.5Hz, H10)	80.8 ----- C12
1.31 (s, 12-CH_3)	84.4 ----- C13
4.89 (dd, $J_{H13, H14}$ = 2.5, 11.3Hz, H13)	23.6 ----- C14
1.78, 2.02 (m, 14-CH_2)	16.0 ----- 2-CH_3
0.88 (t, $J_{14\text{-}CH3, H14}$ = 7.4Hz, 14-CH_3)	28.3 ----- 6-CH_3
4.49 (d, J=11.6Hz, Bn-CH_2a)	22.5 ----- 8-CH_3
4.56 (d, J=11.6Hz, Bn-CH_2b)	23.0 ----- 12-CH_3
0.66 (m, J=7.9, 15.1, TES-CH_2)	10.9 ----- 14-CH_3
1.01 (t, J=7.9, TES-CH_3)	138.1 ----- ^{ipso}C
	128.3 ----- ^{ortho}C
	128.6 ----- ^{meta}C
	128.0 ----- ^{para}C
	7.01 ----- TES-CH_2
	7.45 ----- TES-CH_3

HMBC





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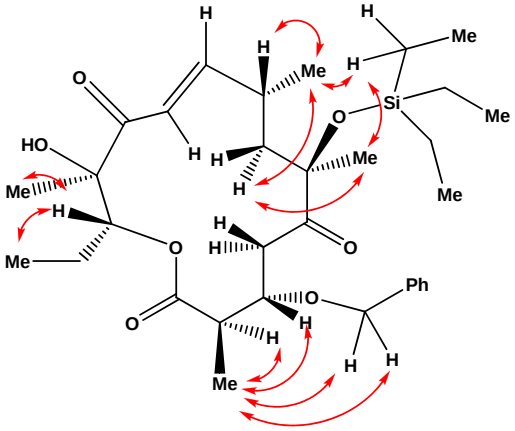
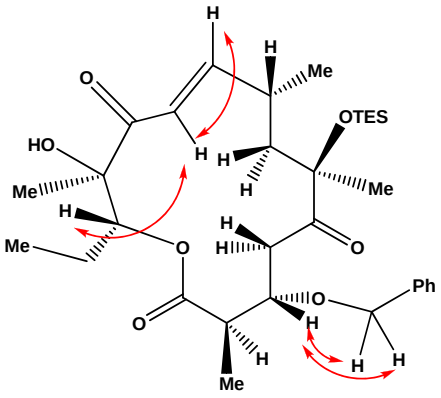
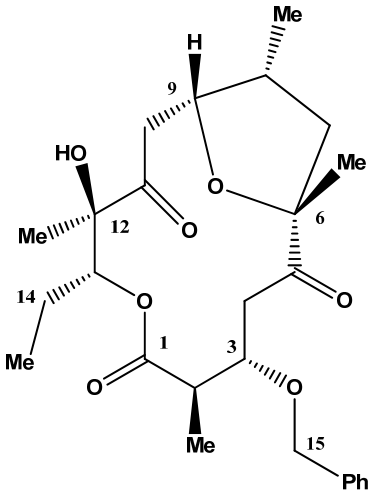


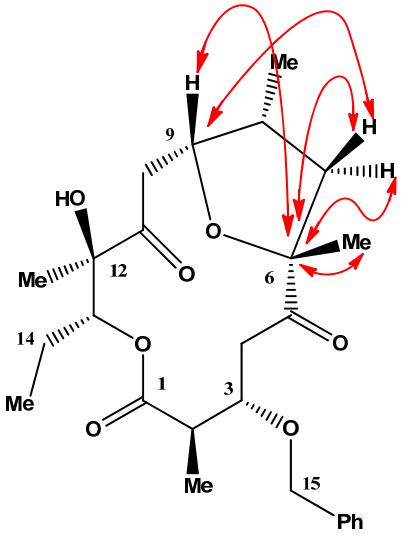


Detailed NMR analysis for compounds 17



1H NMR chemical shifts (d/ppm) and coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)		
2.89 (dq, $J_{H2, H3}$ = 11.1Hz, $J_{H2, 2\text{-}CH3}$ = 7.3Hz, H2)	173.2	-----	C1
1.21 (d, $J_{2\text{-}CH3, H2}$ = 7.3Hz, 2-CH_3)	42.1	-----	C2
3.86 (m, $J_{H3, H2}$ = 11.1Hz, $J_{H3, H4\alpha}$ = 4.7Hz, $J_{H3, H4\beta}$ = 6.4Hz, H3)	78.4	-----	C3
2.29 (dd, $J_{H4\alpha, H3}$ = 4.7Hz, $J_{H4\alpha, H4\beta}$ = 14.5, H4α)	35.4	-----	C4
3.37 (dd, $J_{H4\beta, H3}$ = 6.4Hz, $J_{H4\alpha, H4\beta}$ = 14.5, H4β)	212.6	-----	C5
1.27 (s, 6-CH_3)	88.5	-----	C6
1.89 (dd, $J_{H7\beta, H8}$ = 9.1Hz, $J_{H7\beta, H7\alpha}$ = 12.9Hz, H7β)	40.5	-----	C7
1.79 (dd, $J_{H7\alpha, H8}$ = 7.3Hz, $J_{H7\alpha, H7\beta}$ = 12.9Hz, H7α)	34.9	-----	C8
2.40 (m, $J_{H7\alpha, H8}$ = 7.3Hz, $J_{H7\beta, H8}$ = 9.1Hz,	76.3	-----	C9
$J_{H8, 8\text{-}CH3}$ = 7.0Hz, $J_{H8, H9}$ = 6.9Hz, H8)	39.6	-----	C10
0.67 (d, $J_{8\text{-}CH3, H8}$ = 7.0Hz, 8-CH_3)	213.3	-----	C11
4.63 (ddd, $J_{H9, H8}$ = 6.9Hz, $J_{H9, H10\alpha}$ = 10.2Hz,	77.8	-----	C12
$J_{H9, H10\beta}$ = 1.5Hz H9)	78.9	-----	C13
3.08 (dd, $J_{H9,H10\beta}$ = 10.2Hz, $J_{10\beta,H10\alpha}$ = 18.7Hz H10β)	23.1	-----	C14
2.29 (dd, $J_{H9,H10\alpha}$ = 1.5Hz, $J_{10\alpha,H10\beta}$ = 18.7Hz H10α)	15.0	-----	2-CH_3
1.38 (s, 12-CH_3)	25.2	-----	6-CH_3
4.89 (dd, $J_{H13, H14}$ = 3.4,9.0 Hz, H13)	14.2	-----	8-CH_3
1.55, 1.97 (m, 14-CH_2)	17.0	-----	12-CH_3
0.93 (t, $J_{14\text{-}CH3, H14}$ = 7.5Hz, 14-CH_3)	11.0	-----	14-CH_3
4.57 (d, J=11.6Hz, Bn-CH_2a)	137.5	-----	^{ipso}C
4.59 (d, J=11.6Hz, Bn-CH_2b)	128.8	-----	^{ortho}C
7.35 (^{o}H/Ph)	128.4	-----	^{meta}C
7.34 (^{m}H/Ph)	128.0	-----	^{para}C
7.30 (^{p}H/Ph)	72.0	-----	15-CH_2

HMBC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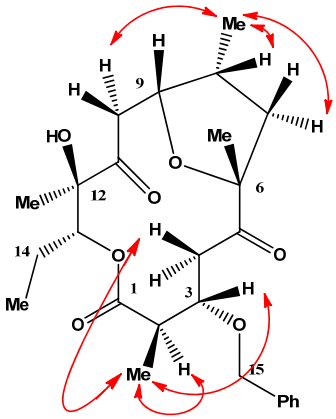
15
Ph

NOESY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Me
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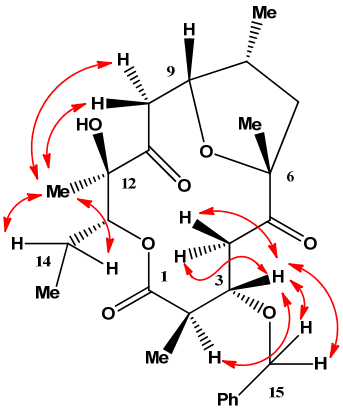
1
3
H
O
O
Me
H
15
Ph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Me
H
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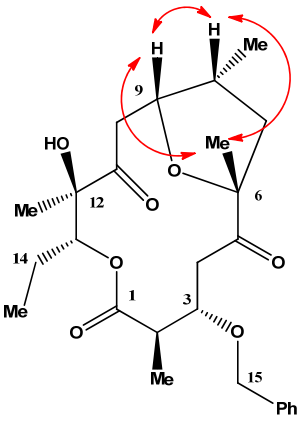
Ph
15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1
3
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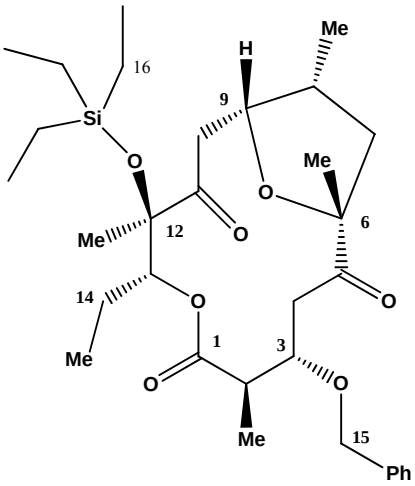
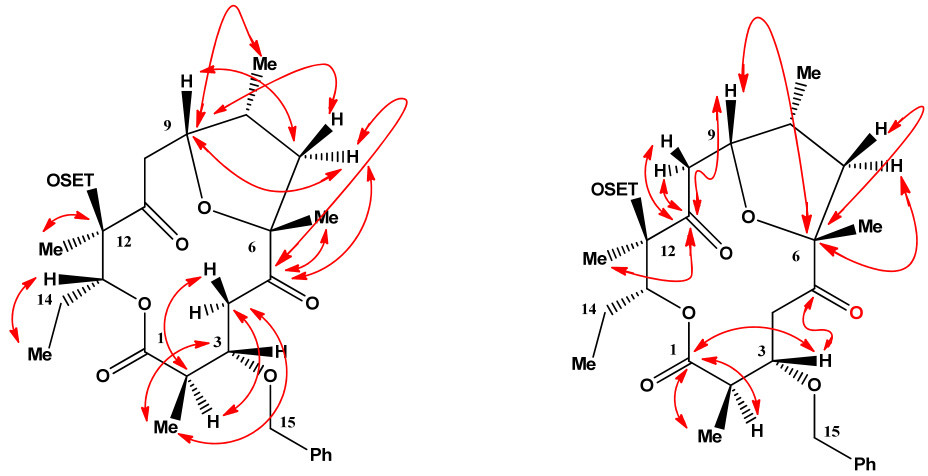
Me
15
Ph

Detailed NMR analysis for compounds 18



1H NMR chemical shifts (d/ppm) and coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)
2.92 (dq, $J_{H2, H3}$ = 5.0Hz, $J_{H2, 2\text{-}CH3}$ = 7.0Hz, H2)	172.9 ----- C1
1.14 (d, $J_{2\text{-}CH3, H2}$ = 7.0Hz, 2-CH_3)	41.6 ----- C2
3.87 (m, $J_{H3, H2}$ = 5.0Hz, $J_{H3, H4\alpha}$ = 3.8Hz, $J_{H3, H4\beta}$ = 9.6Hz, H3)	79.6 ----- C3
2.17 (dd, $J_{H4\alpha, H3}$ = 3.8Hz, $J_{H4\alpha, H4\beta}$ = 14.9, H4α)	36.3 ----- C4
3.26 (dd, $J_{H4\beta, H3}$ = 9.6Hz, $J_{H4\alpha, H4\beta}$ = 14.9, H4β)	215.5 ----- C5
1.28 (s, 6-CH_3)	88.6 ----- C6
1.73 (dd, $J_{H7\beta, H8}$ = 7.0Hz, $J_{H7\beta, H7\alpha}$ = 12.6Hz, H7β)	41.2 ----- C7
1.81 (dd, $J_{H7\alpha, H8}$ = 11.4Hz, $J_{H7\alpha, H7\beta}$ = 12.6Hz, H7α)	35.0 ----- C8
2.24 (m, $J_{H7\alpha, H8}$ = 11.4Hz, $J_{H7\beta, H8}$ = 7.0Hz, $J_{H8, 8\text{-}CH3}$ = 6.9Hz, $J_{H8, H9}$ = 7.4Hz, H8)	78.1 ----- C9
	39.8 ----- C10
0.68 (d, $J_{8\text{-}CH3, H8}$ = 6.9Hz, 8-CH_3)	211.4 ----- C11
4.48 (ddd, $J_{H9, H8}$ = 7.4Hz, $J_{H9, H10\alpha}$ = 1.5Hz, $J_{H9, H10\beta}$ = 10.5Hz H9)	79.4 ----- C12
	79.6 ----- C13
2.78 (dd, $J_{H9,H10\beta}$ = 10.5Hz, $J_{10\beta,H10\alpha}$ = 19.0Hz H10β)	22.7 ----- C14
2.35 (dd, $J_{H9,H10\alpha}$ = 1.5Hz, $J_{10\alpha,H10\beta}$ = 19.0Hz H10α)	14.8 ----- 2-CH_3
1.33 (s, 12-CH_3)	25.5 ----- 6-CH_3
5.20 (dd, $J_{H13, H14}$ = 2.9,9.5 Hz, H13)	13.9 ----- 8-CH_3
1.46, 1.89 (m, 14-CH_2)	17.0 ----- 12-CH_3
0.91 (t, $J_{14\text{-}CH3, H14}$ = 7.2, 7.6Hz, 14-CH_3)	11.1 ----- 14-CH_3
4.44 (d, J=10.4Hz, Bn-CH_2a)	137.7 ----- ^{ipso}C
4.60 (d, J=10.4Hz, Bn-CH_2b)	129.1 ----- ^{ortho}C
0.54, 0.56(m, H16)	128.5 ----- ^{meta}C
0.89 (dd, J= 8.2, 7.8Hz, 16-CH_3)	128.3 ----- ^{para}C
7.33 (^{o}H/Ph)	72.5 ----- 15-CH_2
7.33 (^{m}H/Ph)	6.4 ----- C16
7.30 (^{p}H/Ph)	7.2 ----- 16-CH_3

HMBC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H
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Ph
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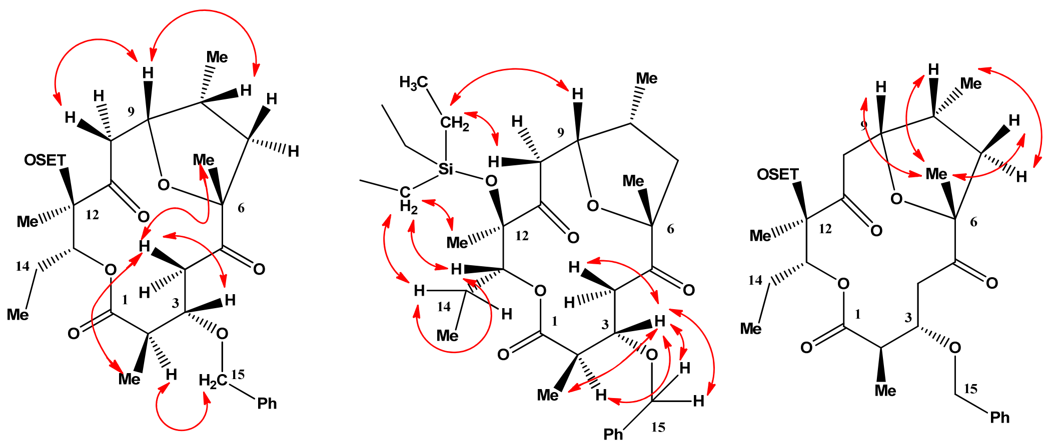
15

NOESY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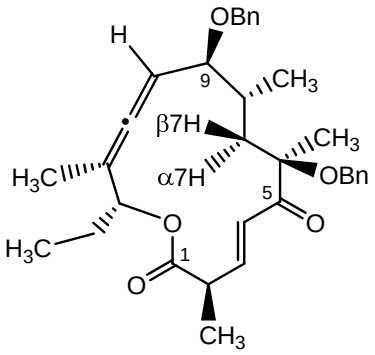
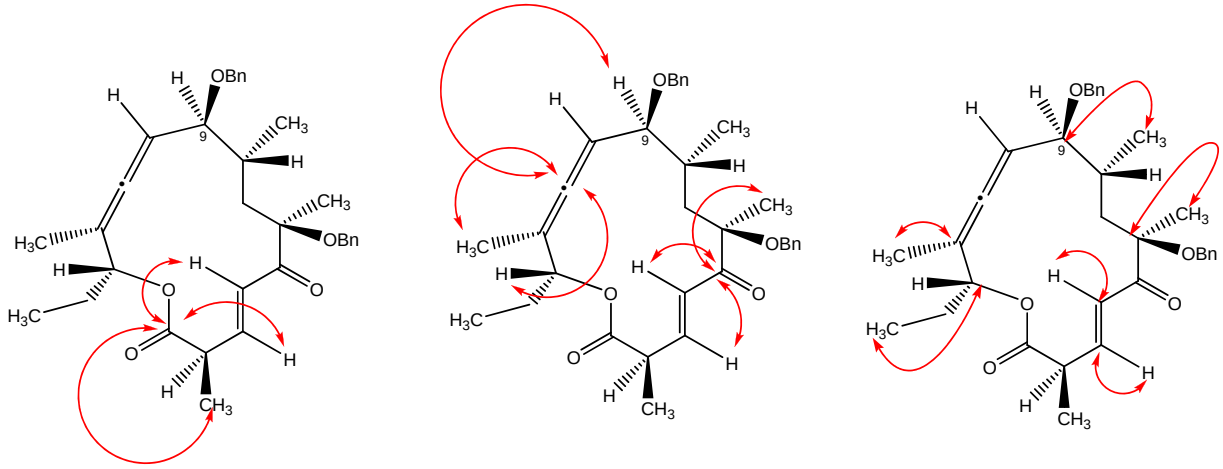
9
12
14
15

Detailed NMR analysis for compound 19.



1H NMR chemical shifts (d/ppm) & coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)
3.30 (ddd, $J_{H2, H3}$ = 8.2Hz, $J_{H2, 2\text{-}CH3}$ = 6.8Hz, $J_{H2, H4}$ = 1.1Hz, H2)	171.9 ----- C1
1.32 (d, $J_{2\text{-}CH3, H2}$ = 6.8Hz, 2-CH_3)	42.3 ----- C2
6.73 (dd, $J_{H3, H4}$ = 15.7Hz, $J_{H3, H2}$ = 8.3Hz, H3)	145.3 ----- C3
7.05 (dd, $J_{H4, H3}$ = 15.7Hz, $J_{H4, H2}$ = 1.2Hz, H4)	127.8 ----- C4
1.44 (s, 6-CH_3)	202.1 ----- C5
4.26 (d, J_{AB} = 11.5Hz, 6-OCH_2)	84.9 ----- C6
4.56 (d, J_{AB} = 12.0Hz, 6-OCH_2)	41.4 ----- C7
1.95 (dd, $J_{H7\alpha, H7\beta}$ = 14.2Hz, H7β)	33.5 ----- C8
1.48 (dd, $J_{H7\beta, H8}$ = 6.85 Hz, $J_{H7\beta, H7\alpha}$ = 14.4Hz, H7α)	83.0 ----- C9
1.41 (m, H8)	93.9 ----- C10
1.09 (d, $J_{8\text{-}CH3, H8}$ = 6.6Hz, 8-CH_3)	202.6 ----- C11
3.24 (t, $J_{H9, H8}$ = 9.1Hz, H9)	101.1 ----- C12
4.24 (d, J_{AB} = 11.5Hz, 9-OCH_2)	75.8 ----- C13
4.57 (d, J_{AB} = 11.0Hz, 9-OCH_2)	26.4 ----- C14
4.62 (dq, J = 9.31Hz, H10)	14.6 ----- 2-CH_3
1.82 (d, $J_{12\text{-}CH3, H10}$ = 2.9Hz, 12-CH_3)	17.4 ----- 6-CH_3
4.71 (ddd, $J_{H13, 14\text{-}CH2}$ = 6.6Hz, $J_{H13, H10}$ = 1.6Hz, H13)	19.9 ----- 8-CH_3
1.68 - 1.78 (m, 14-CH_2)	18.0 ----- 12-CH_3
0.99 (t, $J_{14\text{-}CH3, 13\text{-}CH2}$ = 7.3Hz, 14-CH_3)	9.7 ----- 14-CH_3
7.48 - 7.17 (m, 8H, Ph)	66.3 ----- 6-OCH_3
	69.8 ----- 9-OCH_3

HMBC



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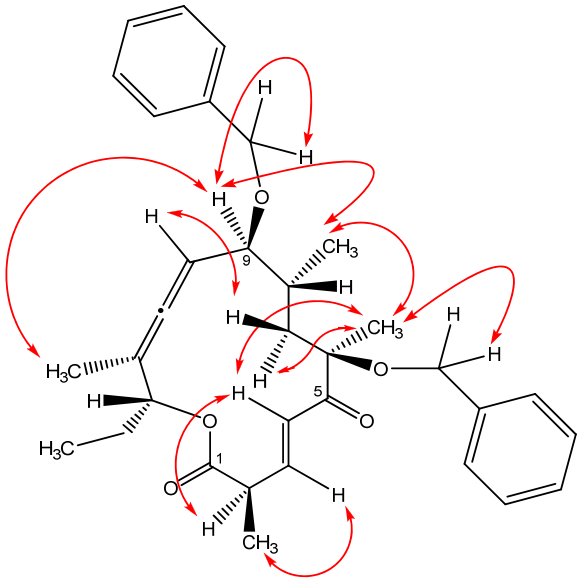
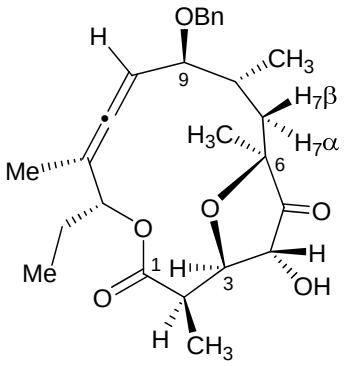
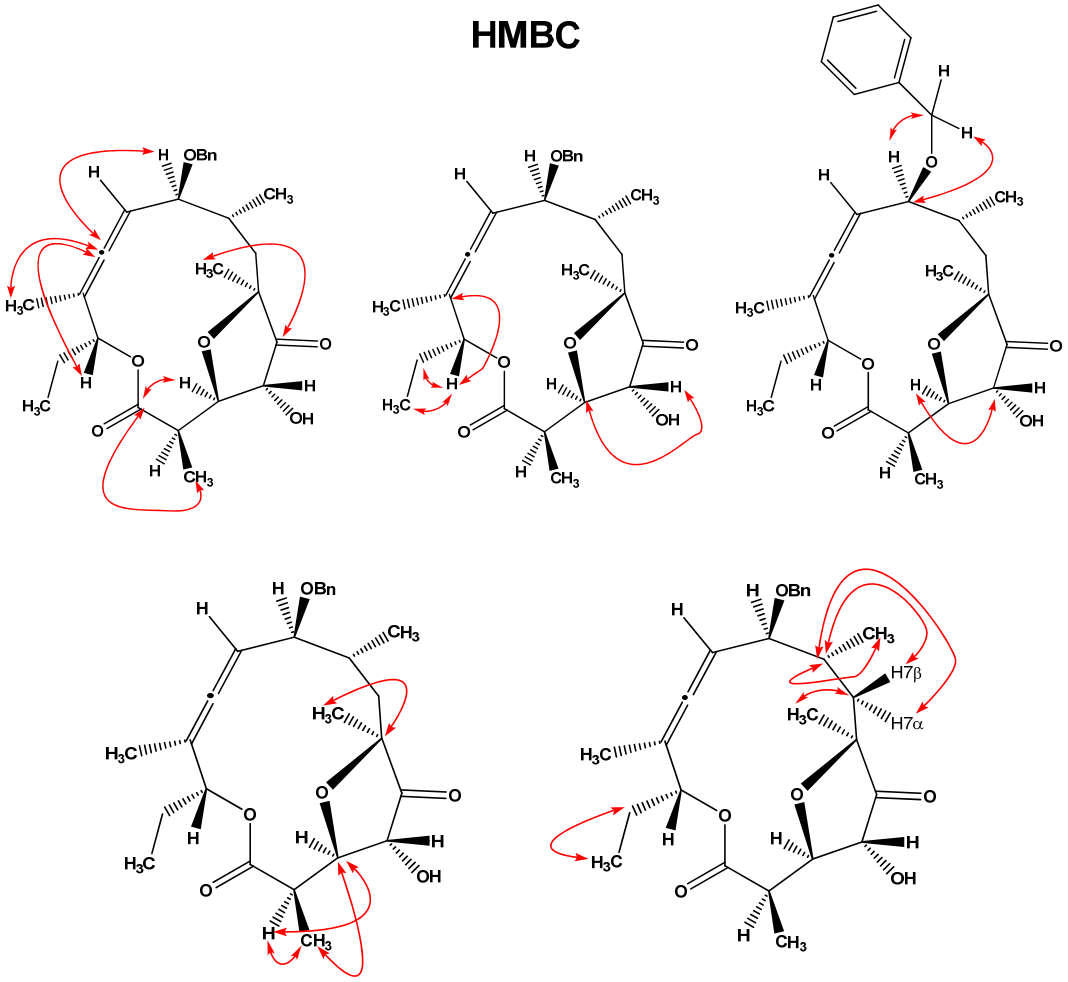


Detailed NMR analysis for compound 20



1H NMR chemical shifts (d/ppm) & coupling constant (J/Hz)	**13C NMR chemical shift (d/ppm)**
3.06 dq, $J_{H2, H3}$ = 4.4Hz, $J_{H2, 2\text{-}CH3}$ = 7.4Hz, **H2**)	171.0 ----- C1
1.35 (d, $J_{2\text{-}CH3, H2}$ = 7.4Hz, **2-CH_3**)	40.2 ----- C2
3.90 (dd, $J_{H3, H2}$ = 4.4Hz, $J_{H3, H4}$ = 8.7Hz, **H3**)	79.7 ----- C3
5.07 (d, $J_{H4, H3}$ = 8.7Hz, **H4**)	72.5 ----- C4
1.14 (s, **6-CH_3**)	218.9 ----- C5
1.65 (dd, $J_{H7\beta, H8}$ = 3.9 Hz, $J_{H7\beta, H7\alpha}$ = 15.0Hz, **H7β**)	83.4 ----- C6
1.87 (dd, $J_{H7\alpha, H8}$ = 5.8 Hz, $J_{H7\alpha, H7\beta}$ = 15.0Hz, **H7α**)	42.9 ----- C7
1.70 (m, **H8**)	34.0 ----- C8
0.88 (d, $J_{8\text{-}CH3, H8}$ = 7.0Hz, **8-CH_3**)	82.3 ----- C9
3.83 (dd, $J_{H9, H8}$ = 2.6Hz, $J_{H9, H10}$ = 8.1Hz, **H9**)	90.7 ----- C10
4.62, 4.36 (d, J_{AB} = 12.1Hz, **9-OCH_2**)	206.6 ----- C11
5.07 (qd, **H10**)	99.0 ----- C12
1.80 (d, **12-CH_3**)	76.6 ----- C13
5.60 (dd, $J_{H13, H14}$ = 6.3, 8.1Hz, **H13**)	24.3 ----- C14
1.65, 1.70 (m, **14-CH_2**)	13.8 ----- 2-CH_3
0.93 (t, $J_{14\text{-}CH3, H14}$ = 7.6Hz, **14-CH_3**)	22.8 ----- 6-CH_3
	14.5 ----- 8-CH_3
	13.6 ----- 12-CH_3
	10.0 ----- 14-CH_3
	70.2 ----- 9-OCH_3

HMBC



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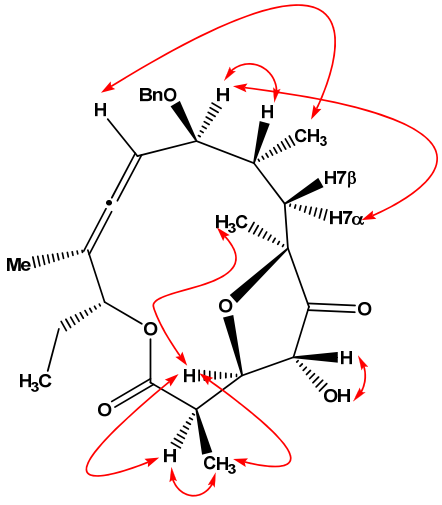
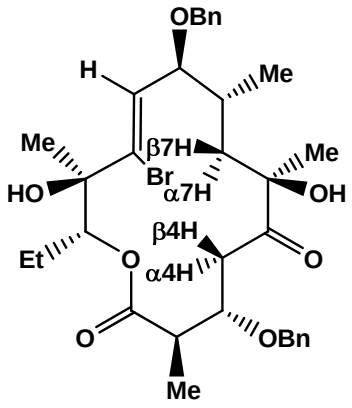
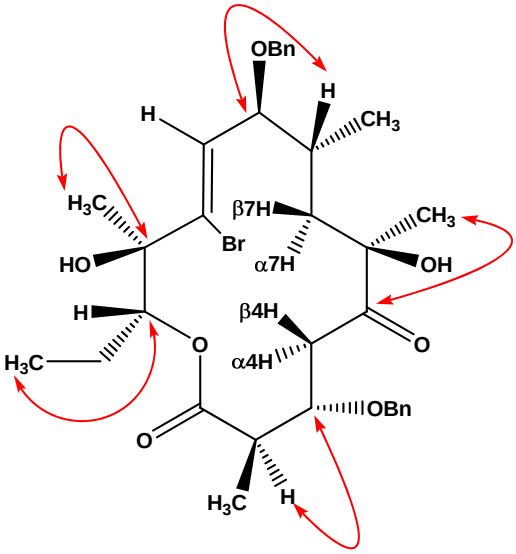


Detailed NMR analysis for compound 21

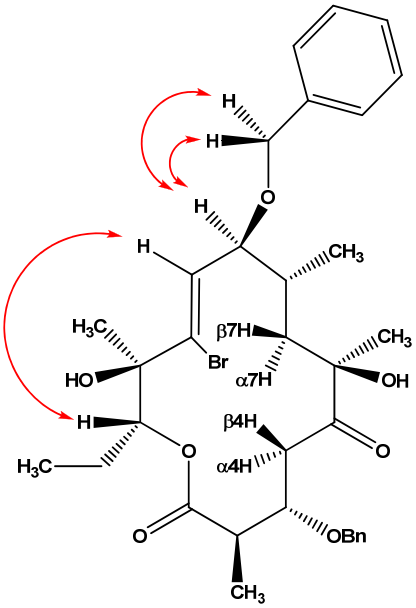


1H NMR chemical shifts (d/ppm) & coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)
2.56 (quintet, $J_{H2,\ 2\text{-}CH3}$ = 6.9Hz, H2)	174.6 ----- C1
1.20 (d, $J_{2\text{-}CH3,\ H2}$ = 6.9Hz, 2-CH_3)	42.5 ----- C2
4.34 (m, H3)	76.1 ----- C3
4.64, 4.52 (d, J_{AB} = 11.1Hz, C3-OCH_2)	44.8 ----- C4
3.11 (dd, $J_{H4\alpha,\ H4\beta}$ = 15.6Hz, $J_{H4\alpha,\ H3}$ = 6.4Hz, H4α)	212.7 ----- C5
2.47 (dd, $J_{H4\beta,\ H4\alpha}$ = 15.6Hz, $J_{H4\beta,\ H3}$ = 5.7Hz, H4β)	79.4 ----- C6
1.23 (s, 6-CH_3)	41.3 ----- C7
1.79 (dd, $J_{H7\beta,\ H7\alpha}$ = 14.4Hz, H7β)	35.0 ----- C8
1.45 ($J_{H7\alpha,\ H8}$ = 5.90 Hz, $J_{H7\alpha,\ H7\beta}$ = 14.4Hz, H7α)	84.0 ----- C9
1.70-1.85 (m, H8)	131.2 ----- C10
1.05 (d, $J_{8\text{-}CH3,\ H8}$ = 6.6Hz, 8-CH_3)	134.2 ----- C11
4.00 (dd, $J_{H9,\ H10}$ = 8.3Hz, $J_{H9,\ H8}$ = 6.1Hz, H9)	77.1 ----- C12
4.52, 4.40 (d, J_{AB} = 12.3Hz, 9-OCH_2)	79.3 ----- C13
6.14 (d, J = 8.4Hz, H10)	24.4 ----- C14
1.44 (s, 12-CH_3)	12.6 ----- 2-CH_3
4.89 (dd, $J_{H13,\ H14}$ = 2.4, 10.9Hz, H13)	26.8 ----- 6-CH_3
1.75-1.82, 1.47-1.55 (m, 14-CH_2)	19.6 ----- 8-CH_3
0.80 (t, $J_{14\text{-}CH3,\ H14}$ = 7.4Hz, 14-CH_3)	25.1 ----- 12-CH_3
	11.1 ----- 14-CH_3
	73.3 ----- 6-OCH_3
	72.2 ----- 9-OCH_3

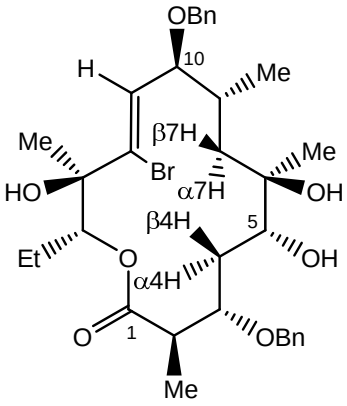
HMBC


OBn
H
H
CH3
H3C
β7H
CH3
Br
HO
α7H
OH
H
β4H
O
O
H3C
α4H
O
OBn
H3C
H

NOESY

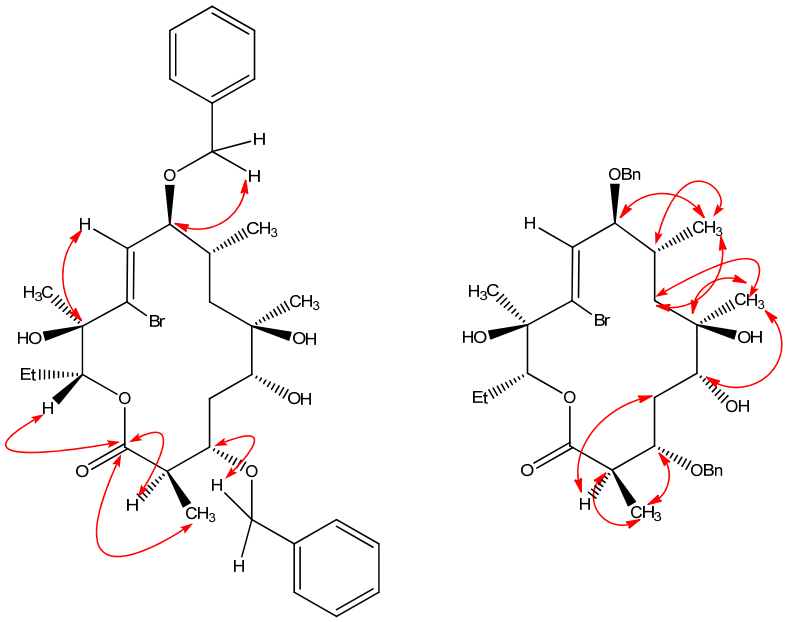

H
H
O
H
H
CH3
H3C
β7H
CH3
Br
HO
α7H
OH
H
β4H
O
O
H3C
α4H
O
OBn
CH3

Detailed NMR analysis for compound 22

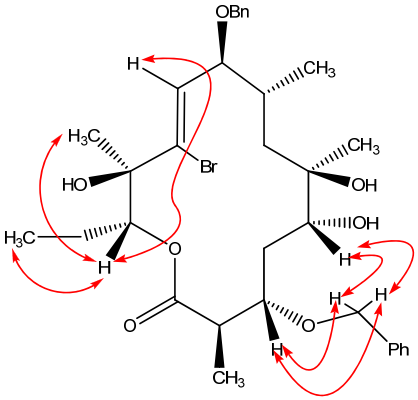


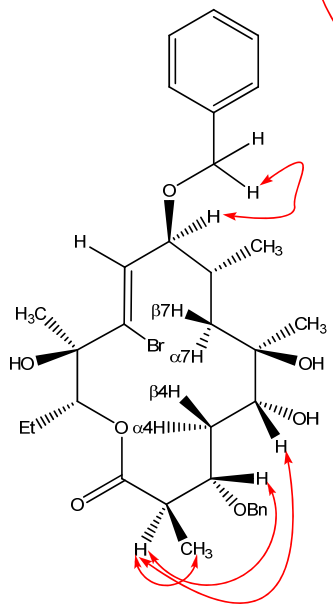
1H NMR chemical shifts (d/ppm) & coupling constant (J/Hz)	13C NMR chemical shift (d/ppm)
2.65 (qd, $J_{H2,\ 2\text{-}CH3}$ = 6.9Hz, $J_{H2,\ H3}$ = 13.4Hz, H2)	176.8 ----- C1
1.27 (d, $J_{2\text{-}CH3,\ H2}$ = 7.0Hz, 2-CH_3)	44.8 ----- C2
4.36 (ddd. $J_{H3,\ H2}$ = 8.6Hz, $J_{H3,\ H4\alpha}$ = 6.2Hz, $J_{H3,\ H4\beta}$ = 2.9Hz, H3)	78.2 ----- C3
4.58, 4.51 (d, J_{AB} = 10.7Hz, C3-OCH_2)	35.9 ----- C4
1.83 (dd, $J_{H4\alpha,\ H4\beta}$ = 15.0Hz, $J_{H4\alpha,\ H3}$ = 8.5 Hz, H4α)	75.2 ----- C5
1.77 (dd, $J_{H4\beta,\ H4\alpha}$ = 15.0Hz, $J_{H4\beta,\ H3}$ = 3.0 Hz, H4β)	73.7 ----- C6
3.51 (dd, $J_{H5,\ H4\alpha}$ = 2.4 Hz, $J_{H5,\ H4\beta}$ = 7.0 Hz, H5)	40.8 ----- C7
1.28 (s, 6-CH_3)	34.6 ----- C8
1.61 (dd, $J_{H7\beta,\ H8}$ = 6.1 Hz, $J_{H7\beta,\ H7\alpha}$ = 14.7Hz, H7β)	84.7 ----- C9
1.17 (dd, $J_{H7\alpha,\ H8}$ = 7.0 Hz, $J_{H7\alpha,\ H7\beta}$ = 14.9Hz, H7α)	131.4 ----- C10
2.31 (dt, $J_{H8,8\text{-}CH3}$ = 6.4Hz, H8)	133.0 ----- C11
1.12 (d, $J_{8\text{-}CH3,\ H8}$ = 6.7Hz, 8-CH_3)	77.6 ----- C12
4.11 (dd, $J_{H9,\ H10}$ = 8.6Hz, $J_{H9,\ H8}$ = 6.6Hz, H9)	81.3 ----- C13
4.58, 4.47 (d, J_{AB} = 12.4Hz, 9-OCH_2)	24.7 ----- C14
6.38 (d, $J_{H10,\ H9}$ = 8.6Hz, H10)	12.4 ----- 2-CH_3
1.50 (s, 12-CH_3)	27.7 ----- 6-CH_3
4.88 (dd, $J_{H13,\ H14}$ = 2.3, 11.0Hz, H13)	20.0 ----- 8-CH_3
1.73-1.85 (m, 14-CH_2)	26.0 ----- 12-CH_3
0.89 (t, $J_{14\text{-}CH3,\ H14}$ = 7.4Hz, 14-CH_3)	11.4 ----- 14-CH_3
	73.1 ----- 6-OCH_3
	71.9 ----- 9-OCH_3
	137.9, 139.0 ----- ^{ipso}C (C_3, C_9)
	128.1, 128.0 ----- $^{ortho}C$ (C_3, C_9)
	126.5, 128.3 ----- ^{meta}C (C_3, C_9)
	127.9, 127.6 ----- ^{para}C (C_3, C_9)

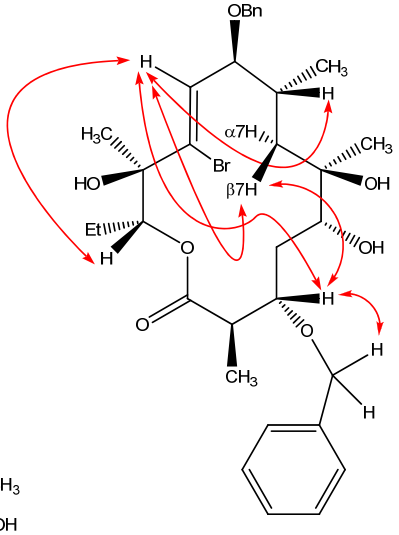
HMBC



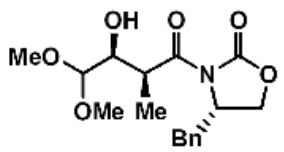
NOESY







^{1}H NMR (500MHz, $CDCl_3$)



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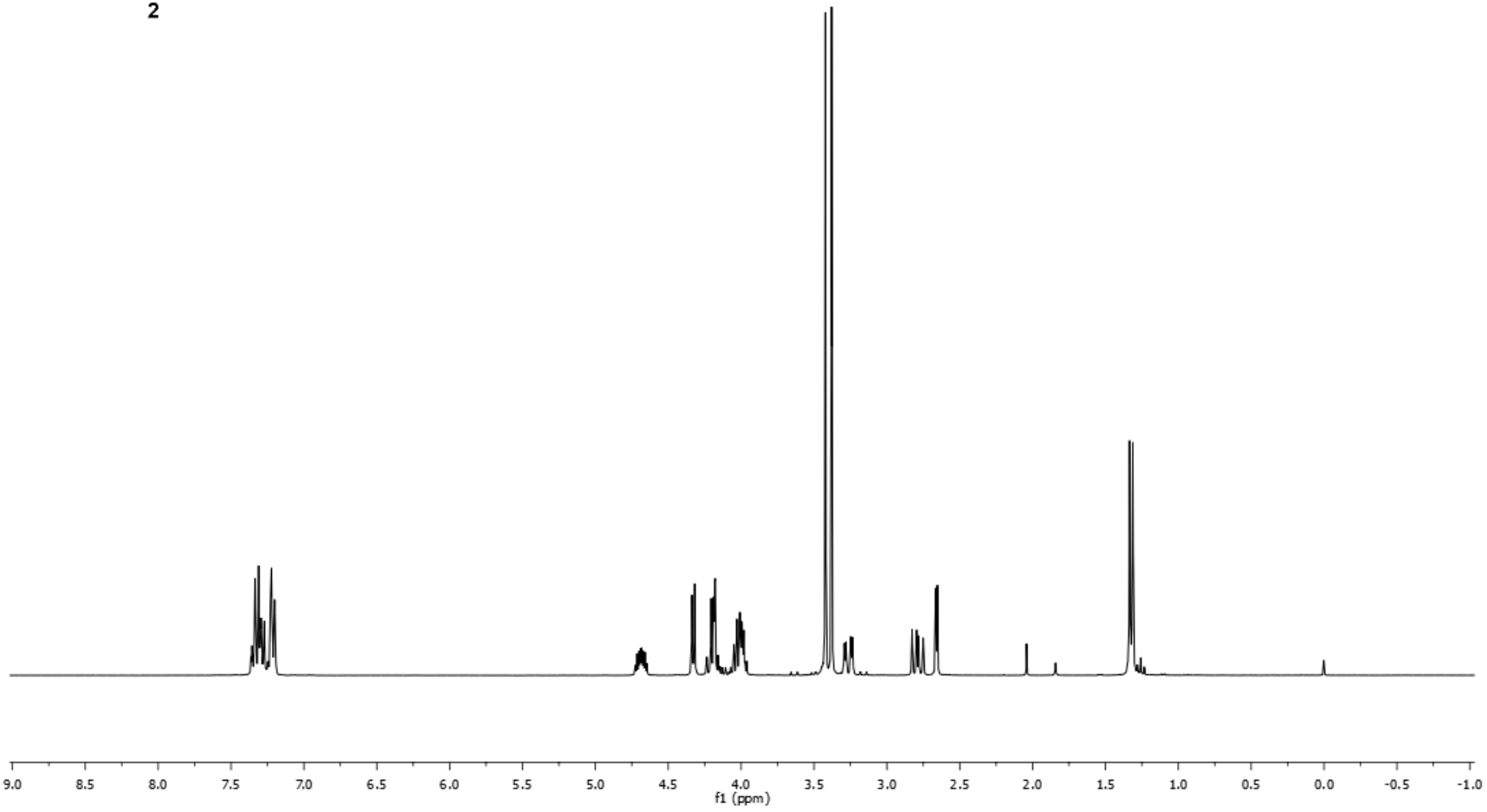
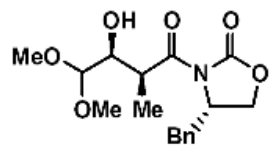
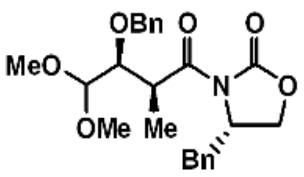


^{13}C NMR (125MHz, $CDCl_3$)



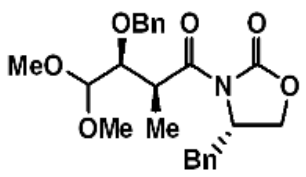
2

^{1}H NMR (500MHz, $CDCl_3$)



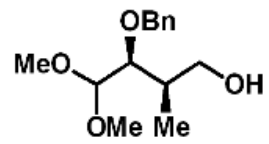
3

^{13}C NMR (125MHz, $CDCl_3$)



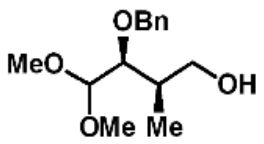
3

^{1}H NMR (500MHz, $CDCl_3$)



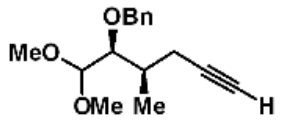
4

^{13}C NMR (125MHz, $CDCl_3$)



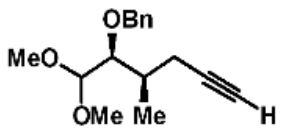
4

^{1}H NMR (500MHz, $CDCl_3$)



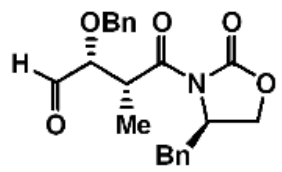
5

^{13}C NMR (125MHz, $CDCl_3$)



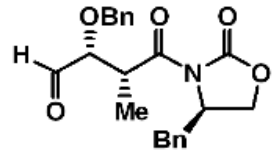
5

^{1}H NMR (500MHz, $CDCl_3$)



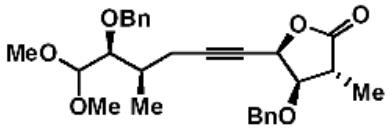
6

^{13}C NMR (125MHz, $CDCl_3$)



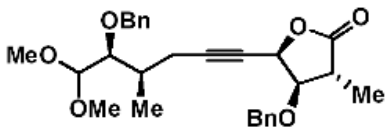
6

^{1}H NMR (500MHz, $CDCl_3$)



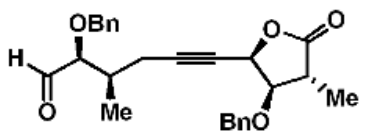
7

^{13}C NMR (125MHz, $CDCl_3$)



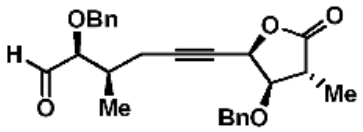
7

^{1}H NMR (500MHz, $CDCl_3$)



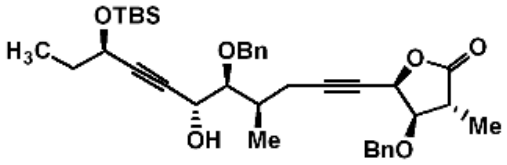
8

^{13}C NMR (125MHz, $CDCl_3$)



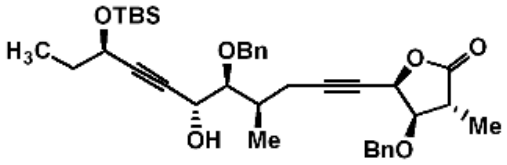
8

^{1}H NMR (500MHz, $CDCl_3$)



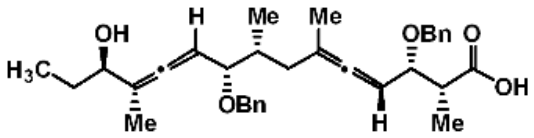
10

^{13}C NMR (125MHz, $CDCl_3$)

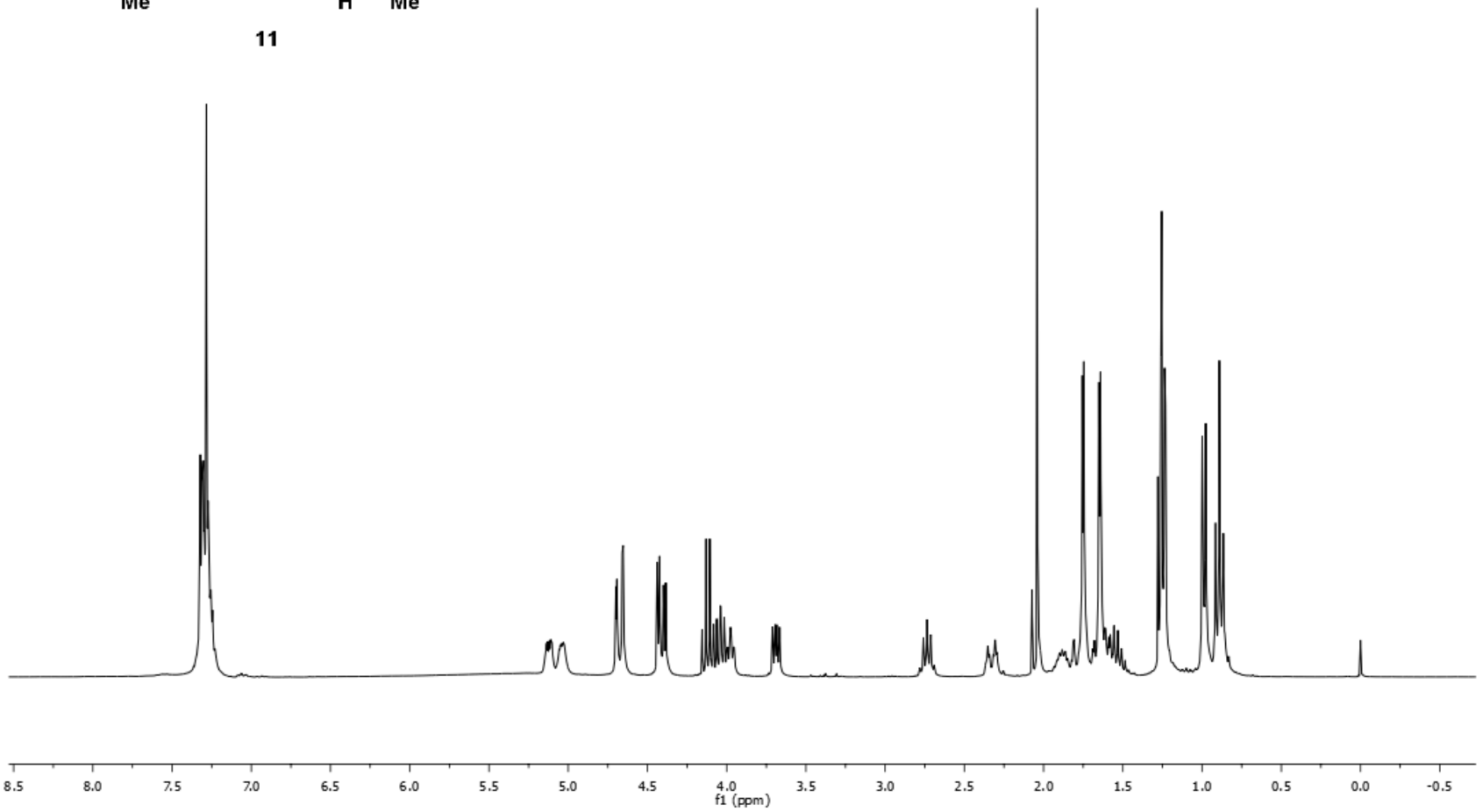


10

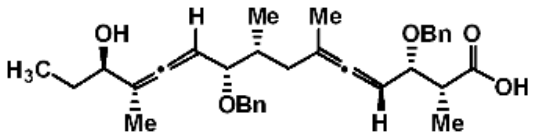
^{1}H NMR (500MHz, $CDCl_3$)



11

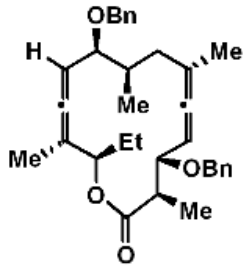


^{13}C NMR (125MHz, $CDCl_3$)

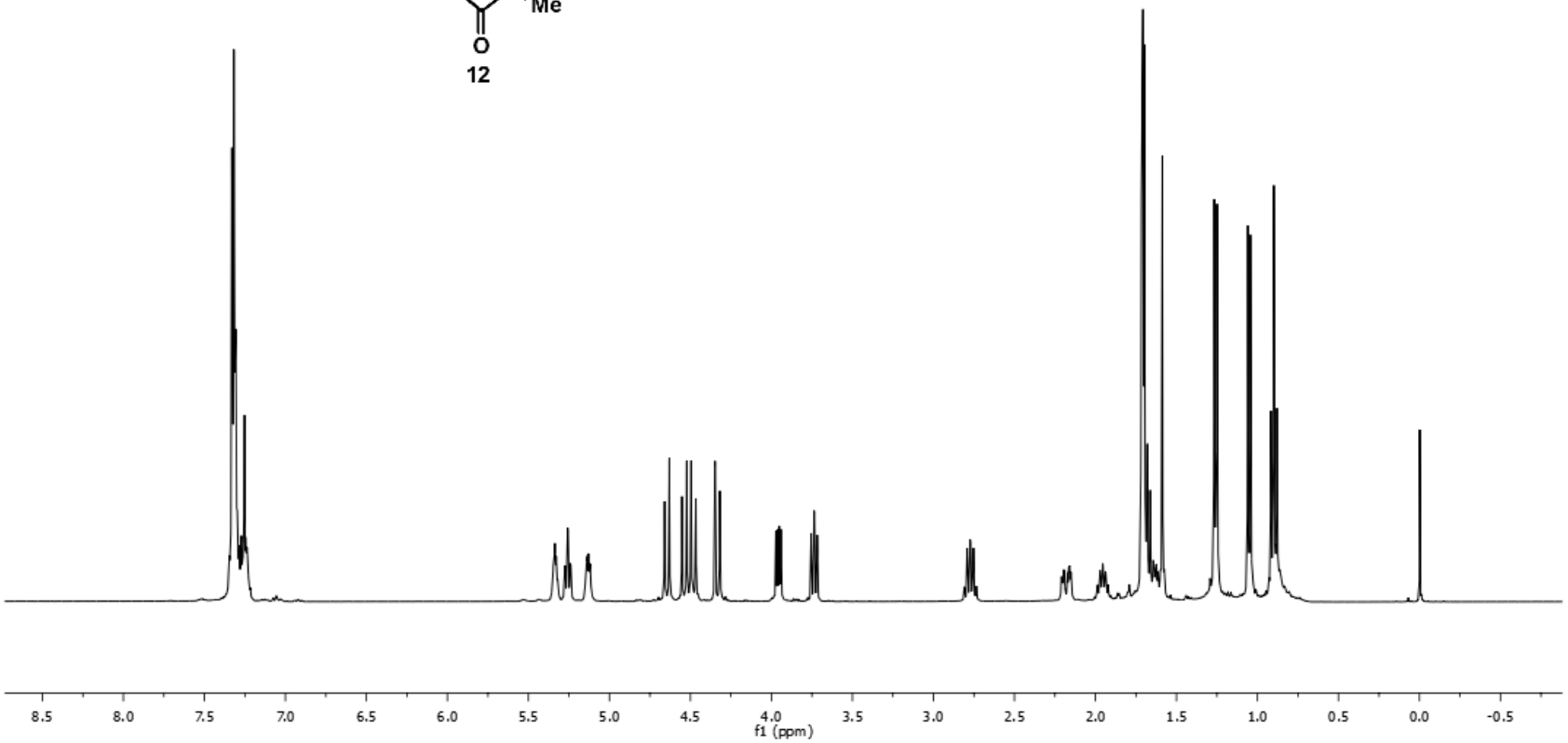


11

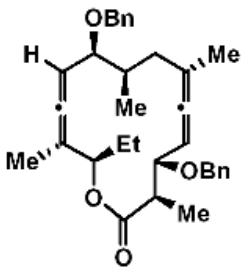
^{1}H NMR (500MHz, $CDCl_3$)



12

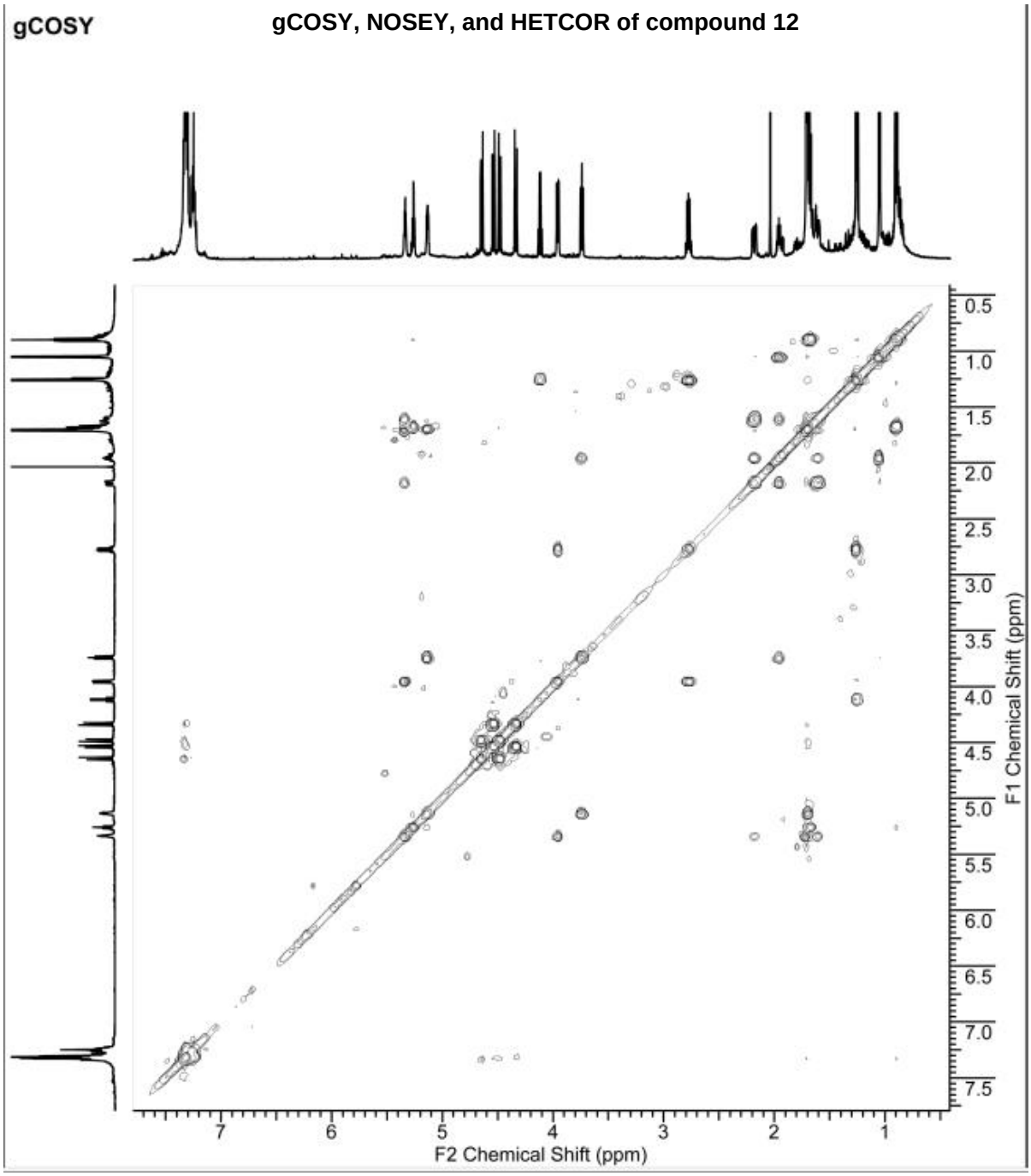


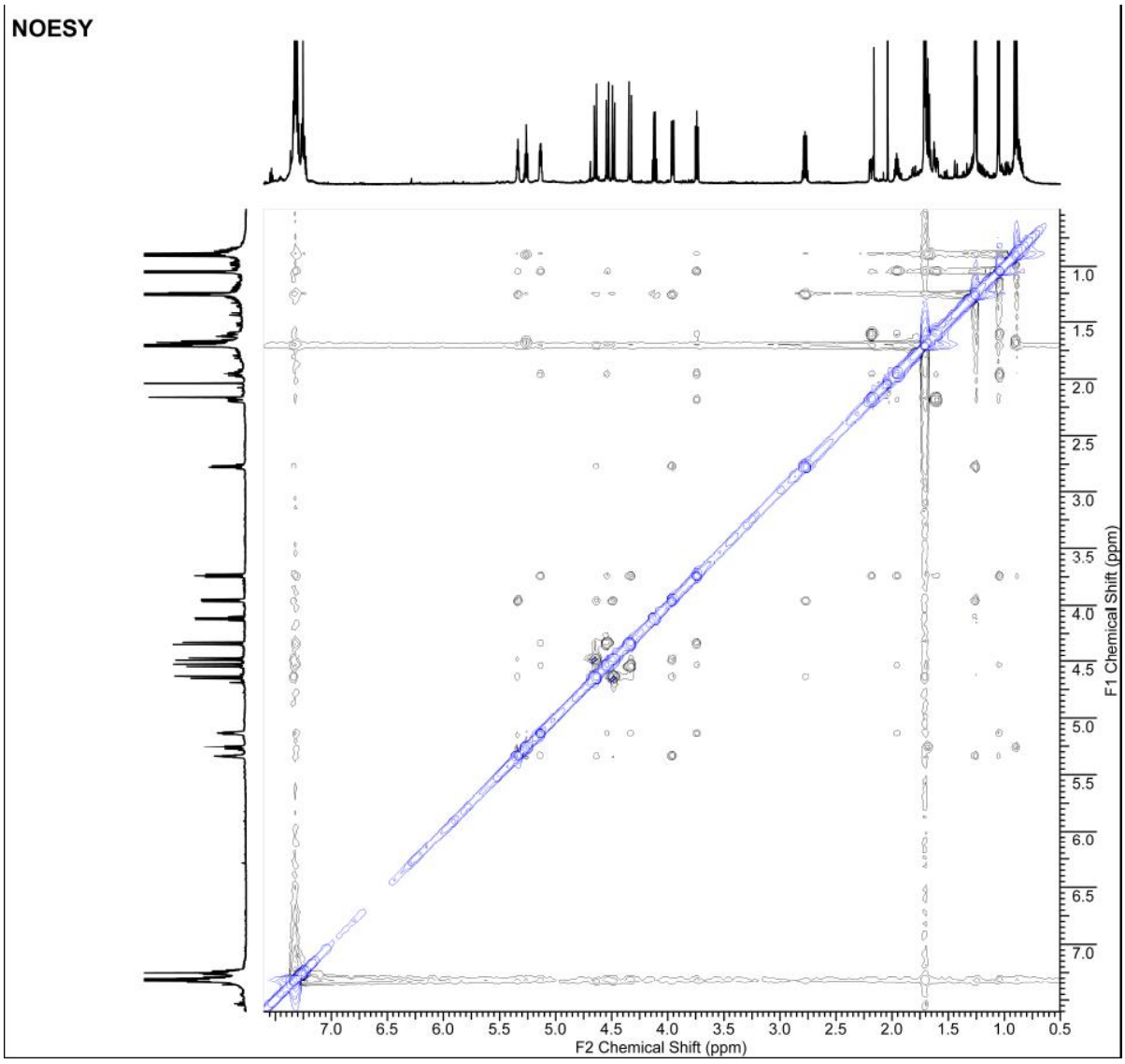
^{13}C NMR (125MHz, $CDCl_3$)

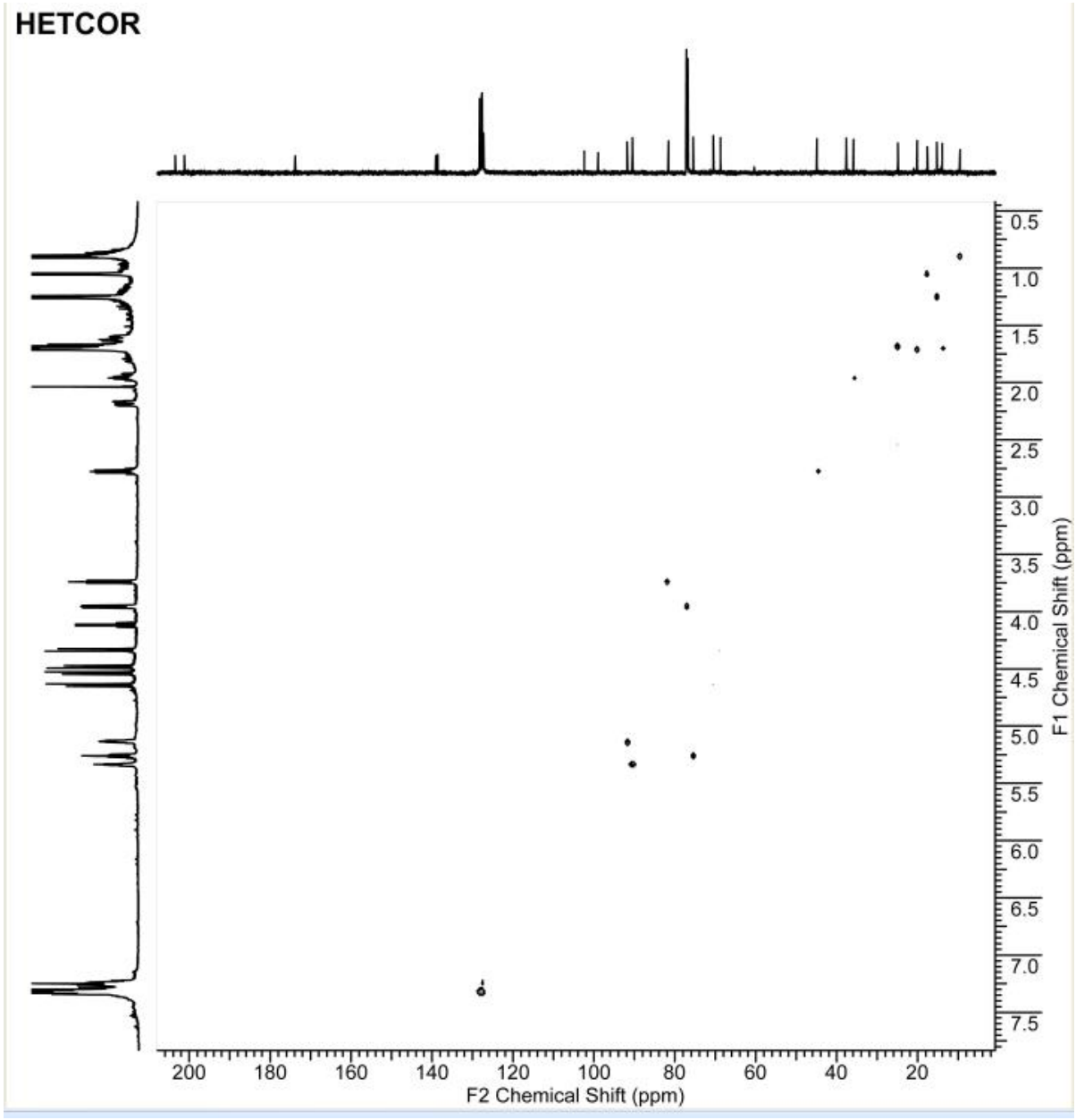


12

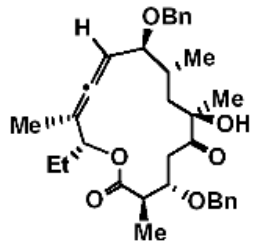
gCOSY, NOSEY, and HETCOR of compound 12




NOESY
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
F2 Chemical Shift (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
F1 Chemical Shift (ppm)

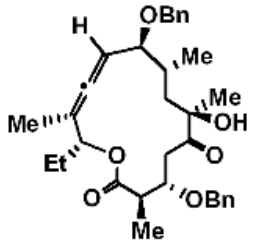

HETCOR
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
F1 Chemical Shift (ppm)
200
180
160
140
120
100
80
60
40
20
F2 Chemical Shift (ppm)

^{1}H NMR (500MHz, $CDCl_3$)



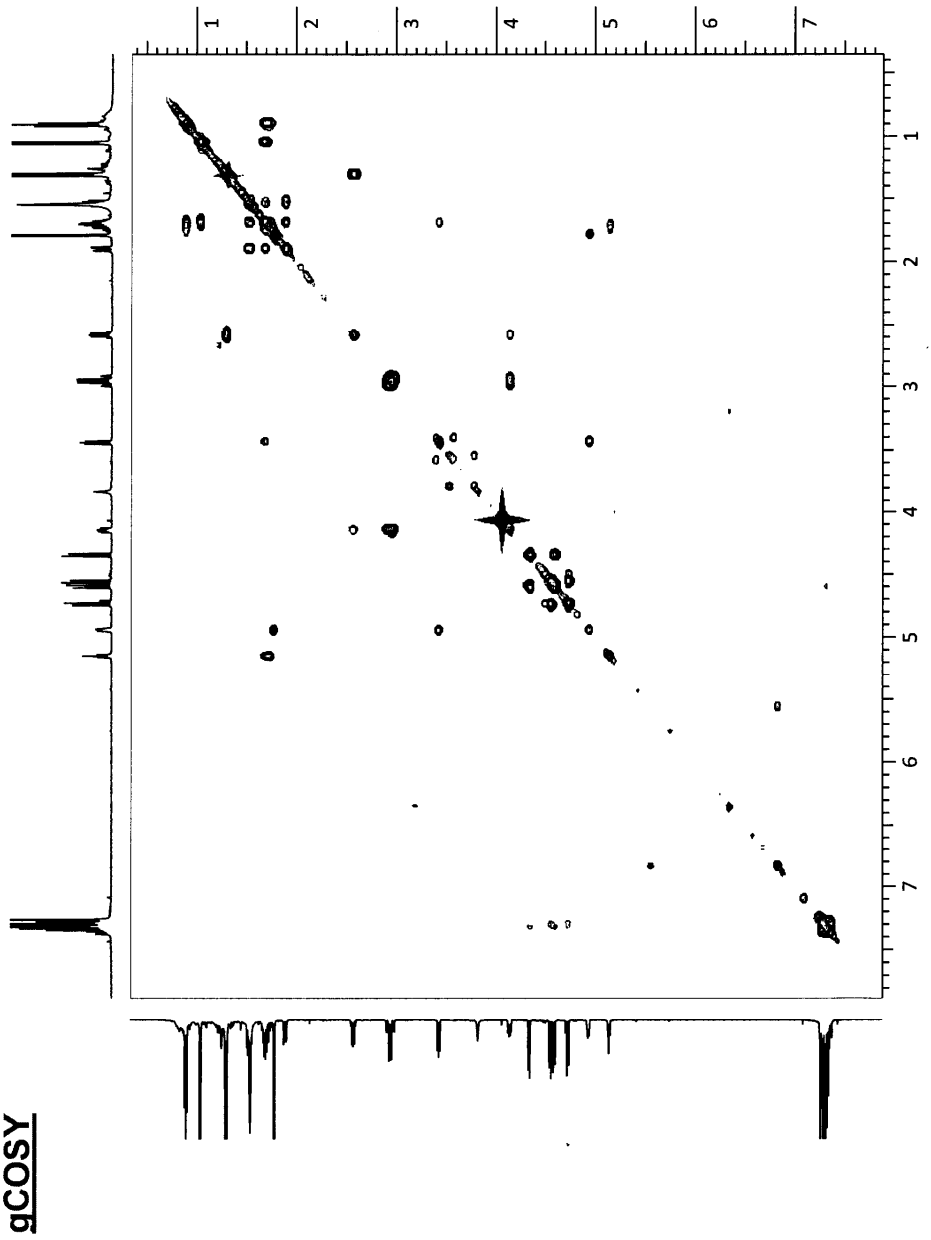
13

^{13}C NMR (125MHz, $CDCl_3$)

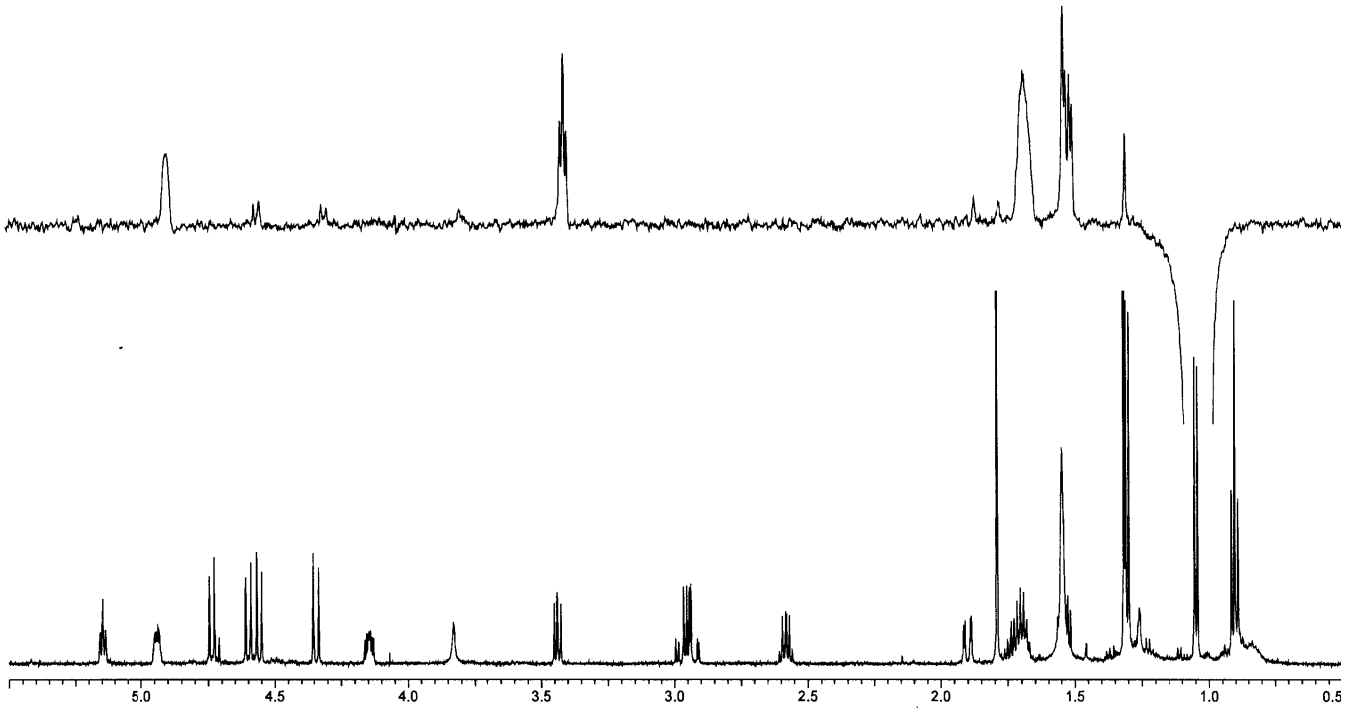


13

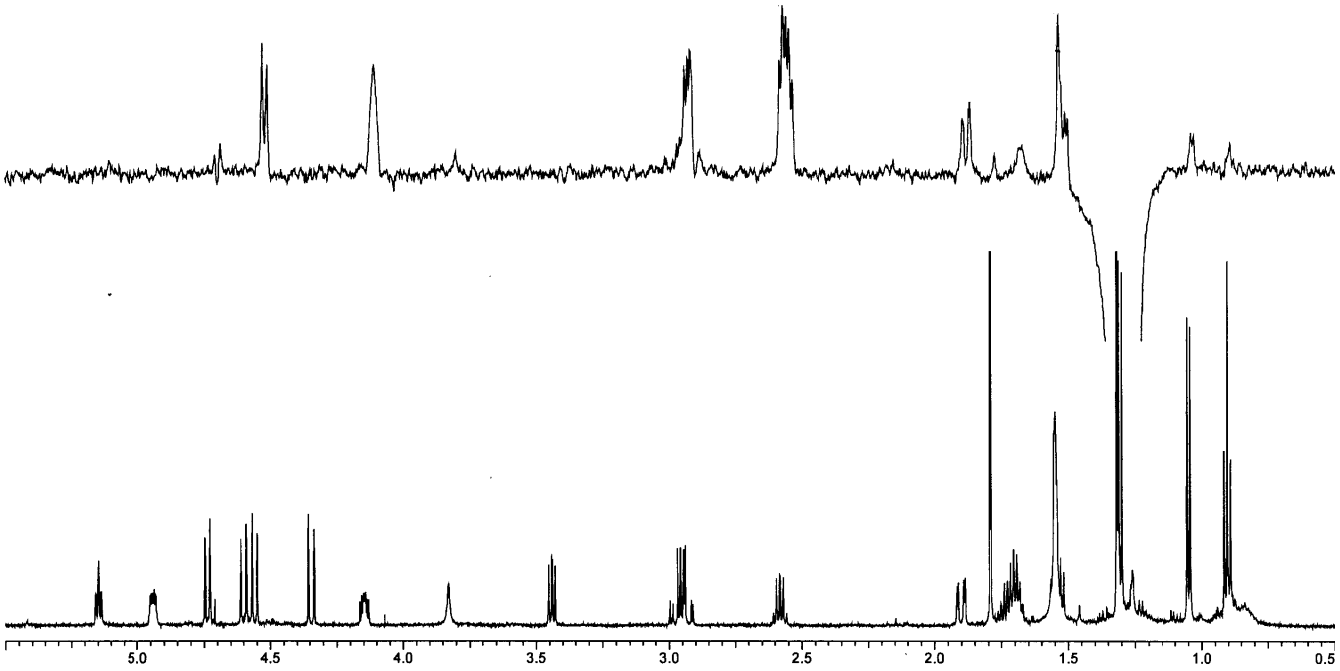
gCOSY, DPFGSENOE, gHMBC and HETCOR of compound 13

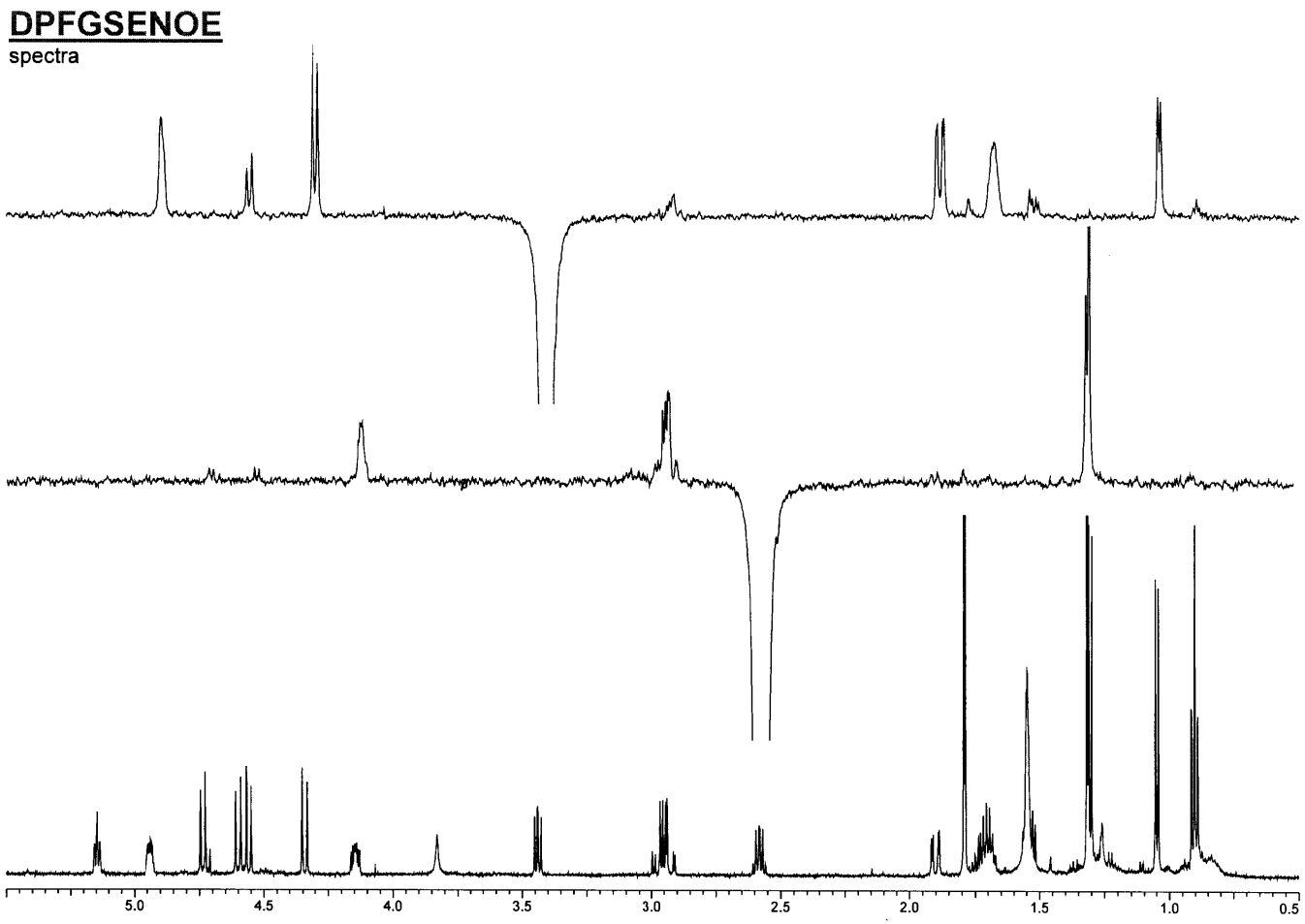


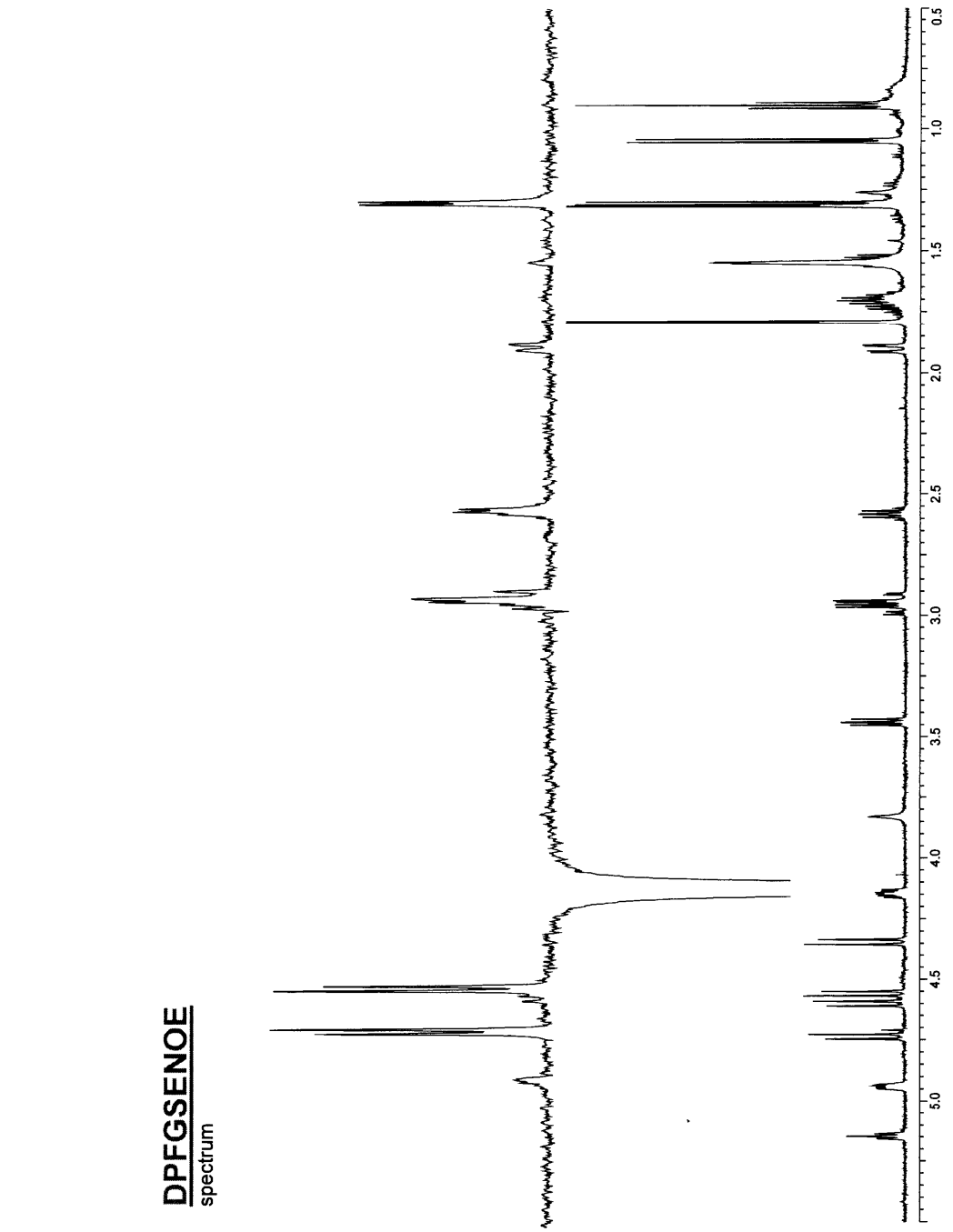
DPFGSENOE
spectrum

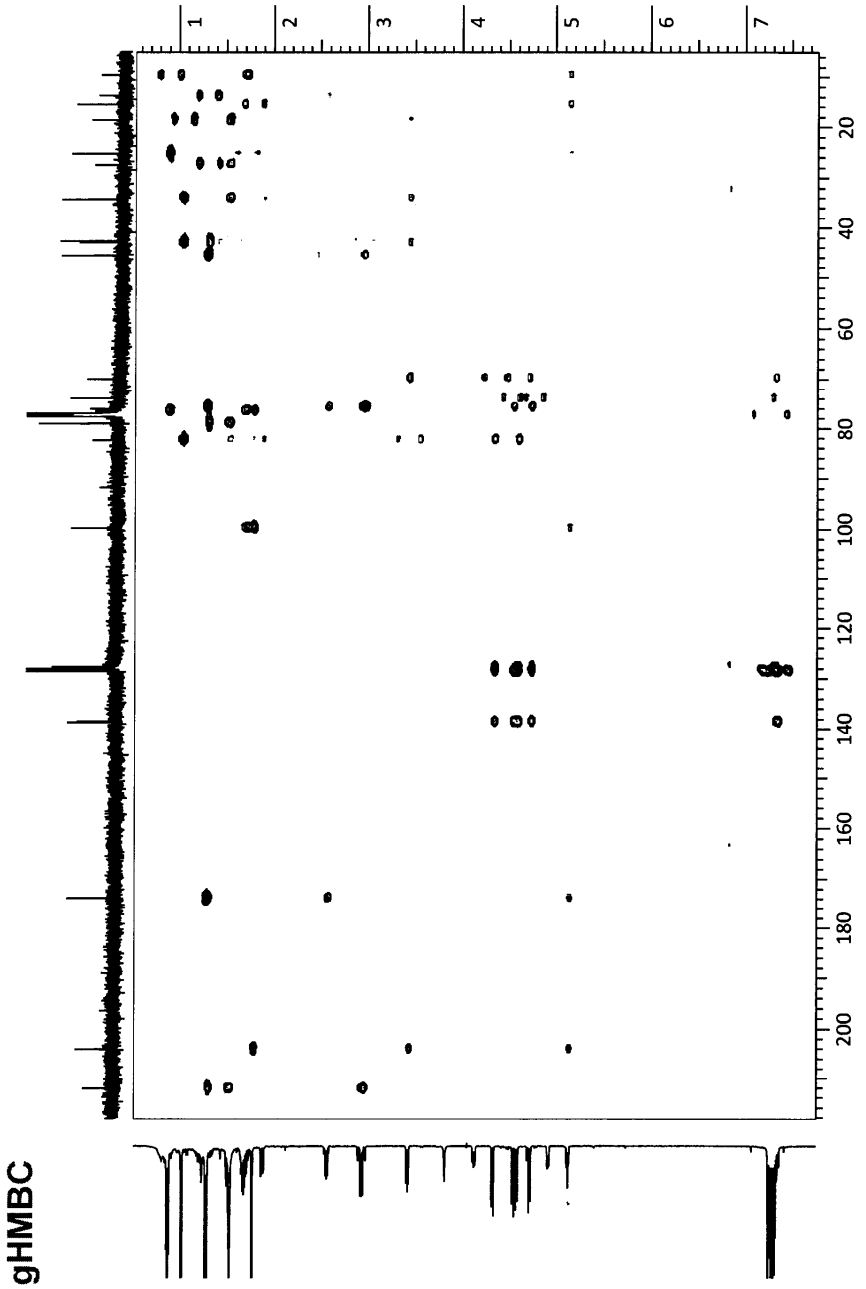


DPFGSENOE
spectrum

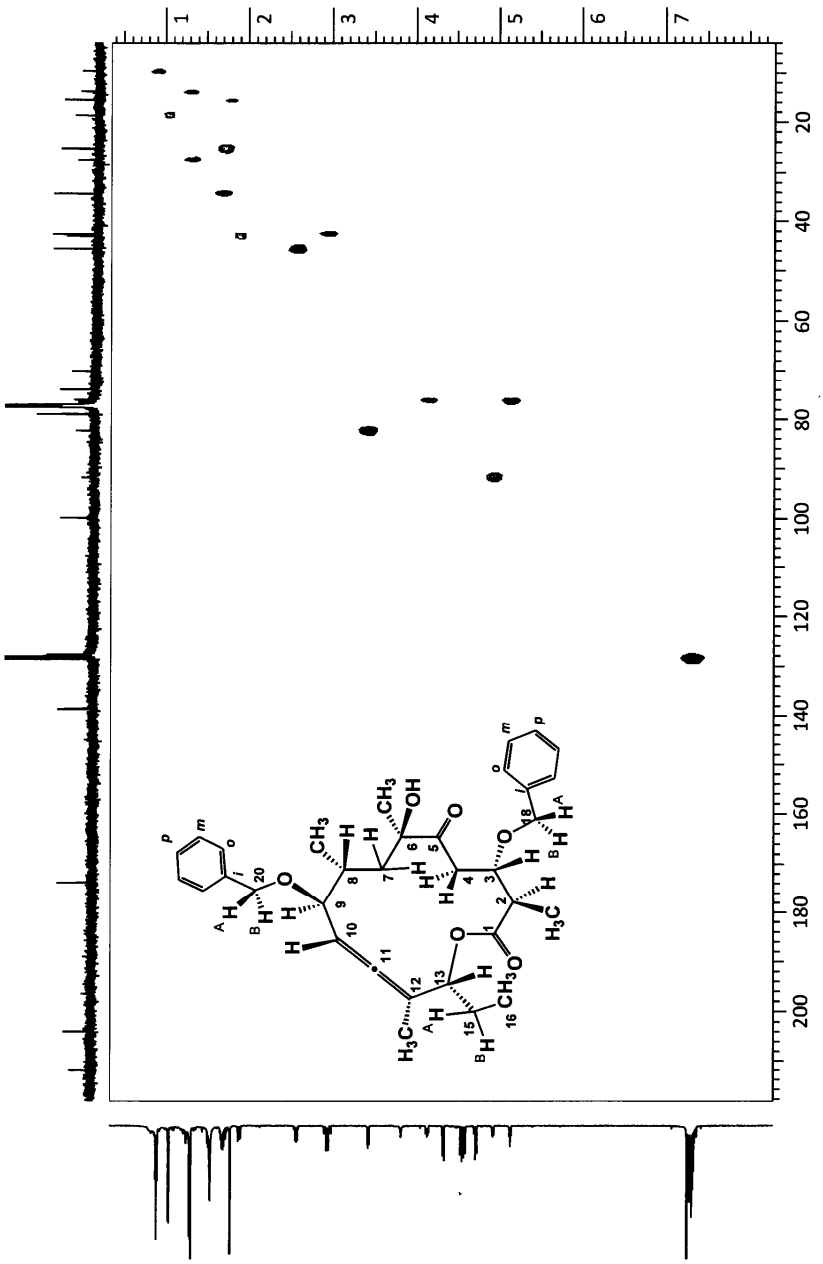



DPFGSENOE
spectra
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


DPFGSENOE
spectrum
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

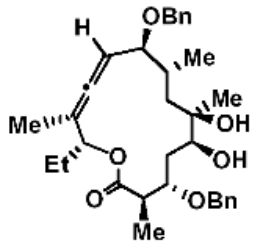

gHMBC
1
2
3
4
5
6
7
20
40
60
80
100
120
140
160
180
200

HETCOR



Jun22nd-H1-KL-2-027
Std proton

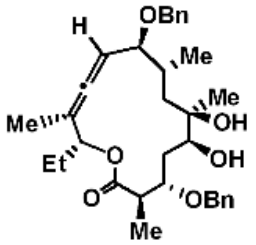
^{1}H NMR (500MHz, $CDCl_3$)



14

Jun22nd-C13-KL-2-027
Std proton

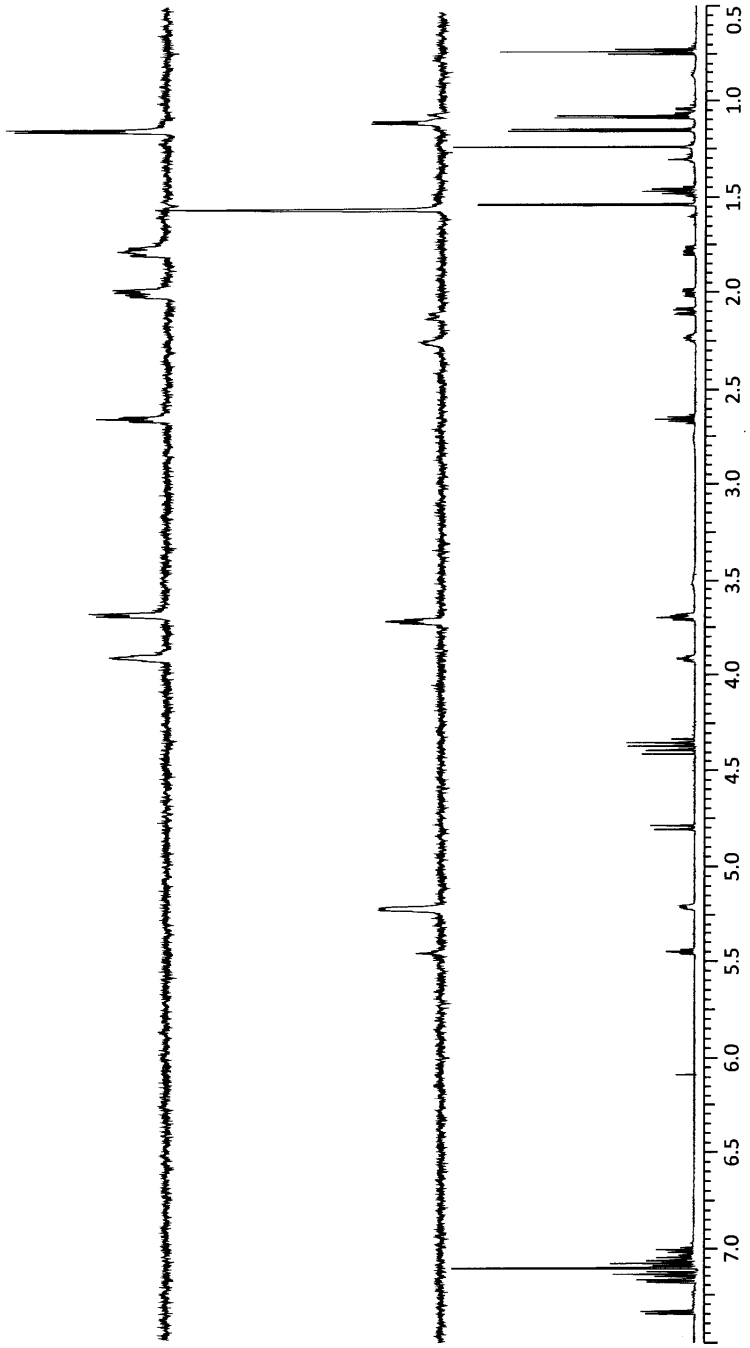
^{13}C NMR (125MHz, $CDCl_3$)

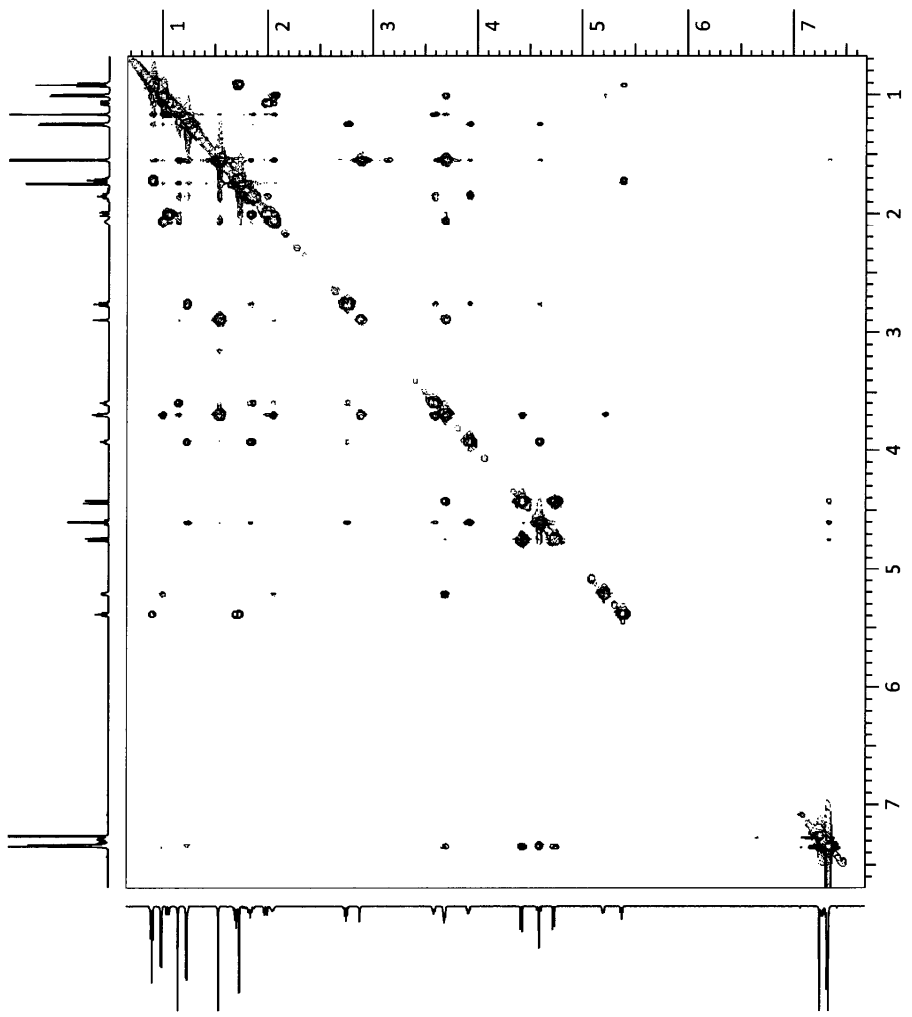


14

1DTOCSY, NOSEY and gHMBC of compound 14

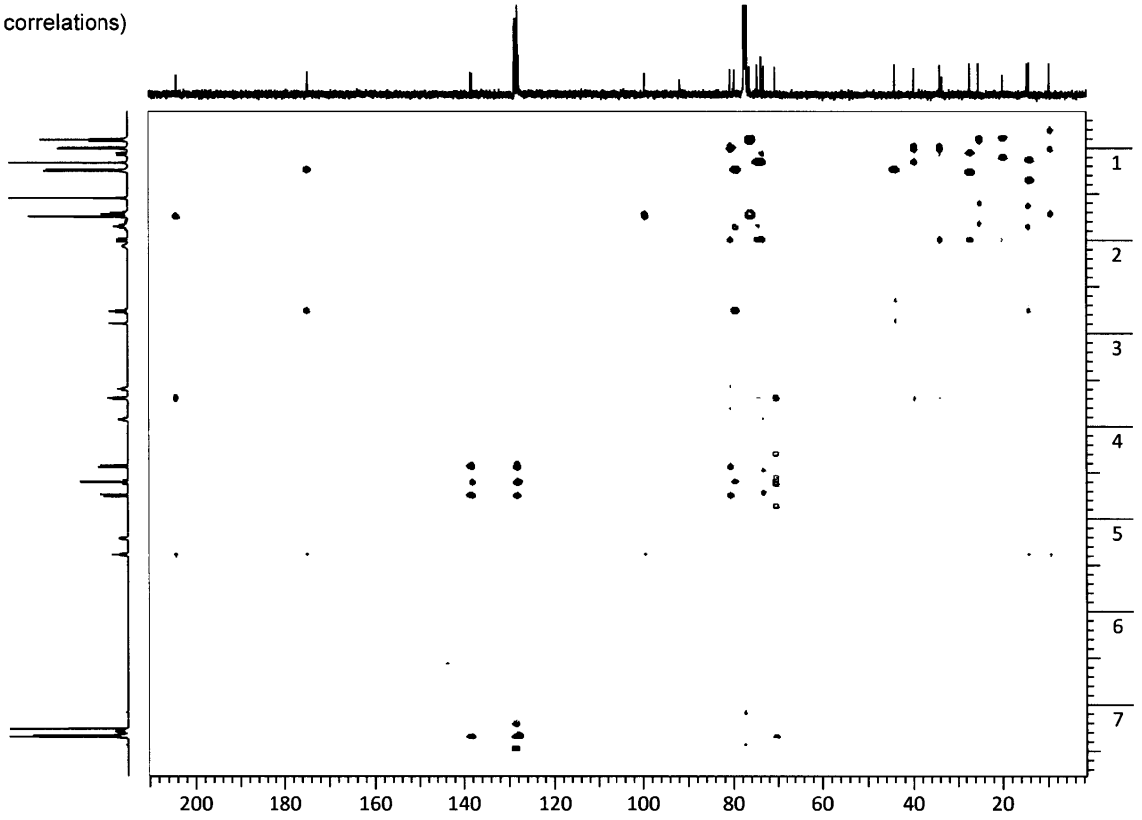
1D TOCSY spectra



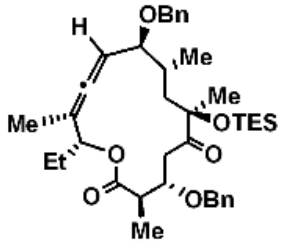


NOESY

gHMBC
(long-range correlations)

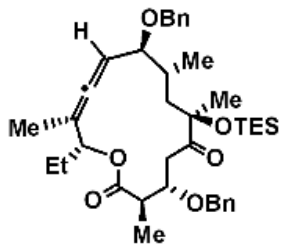


^{1}H NMR (500MHz, $CDCl_3$)



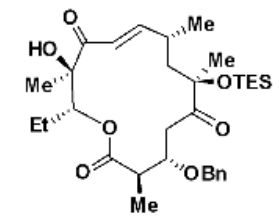
15

^{13}C NMR (125MHz, $CDCl_3$)



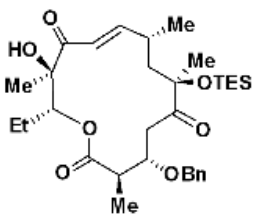
15

^{1}H NMR (500MHz, $CDCl_3$)



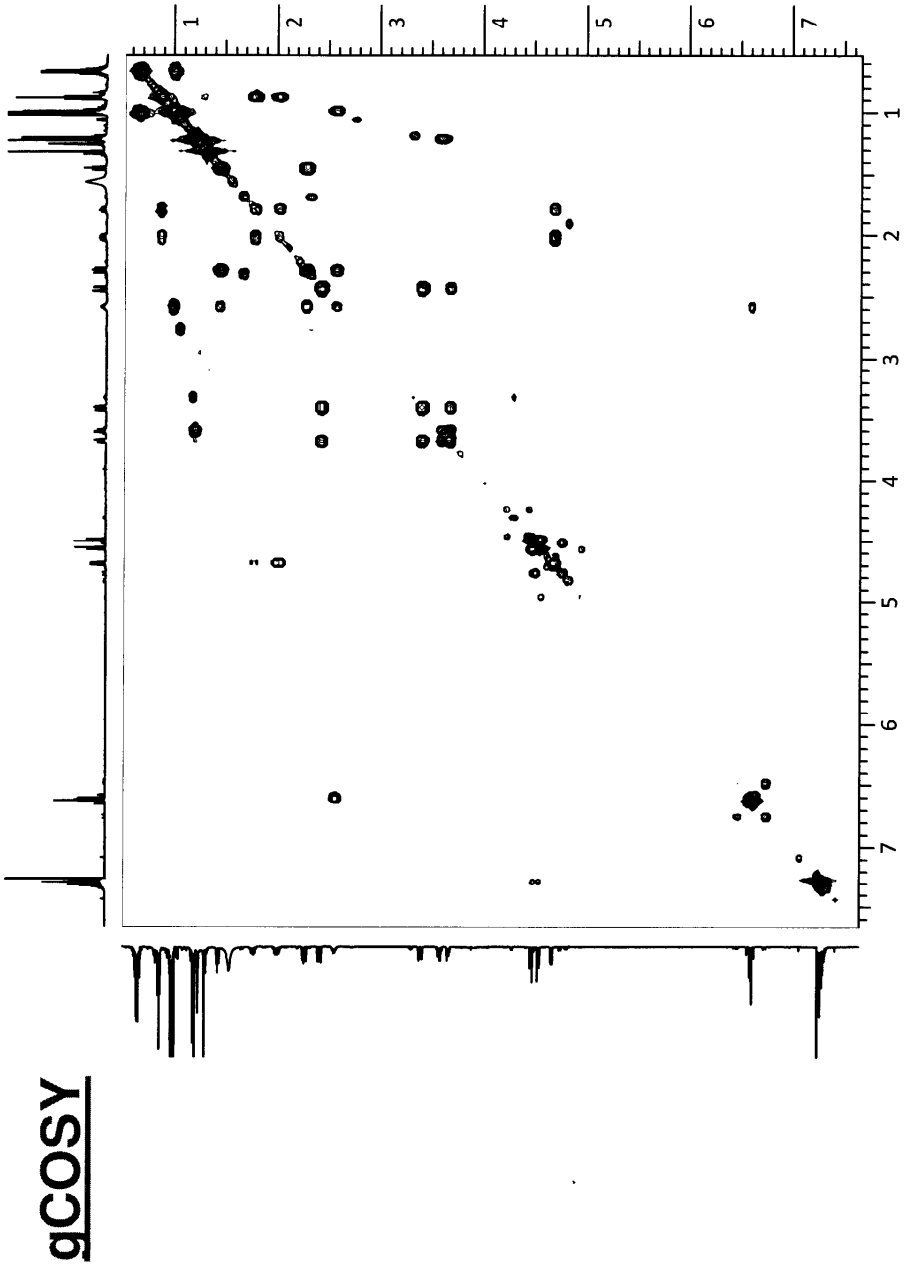
16

^{13}C NMR (125MHz, $CDCl_3$)

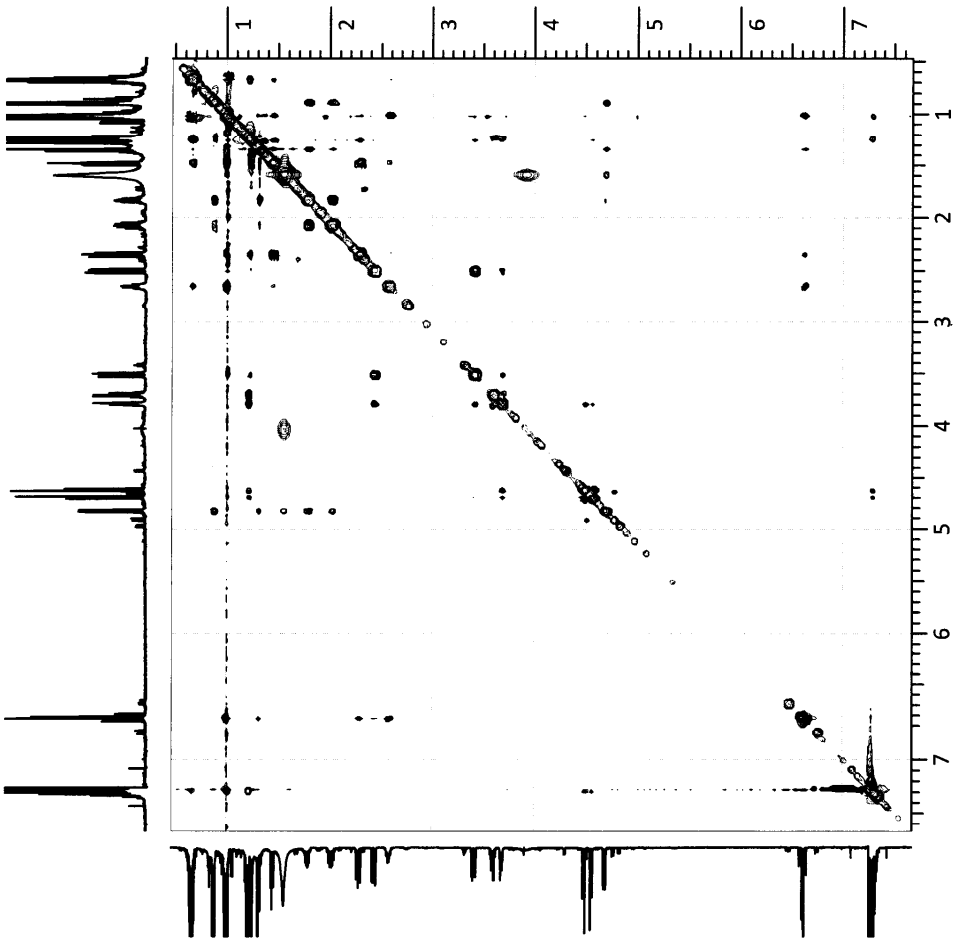


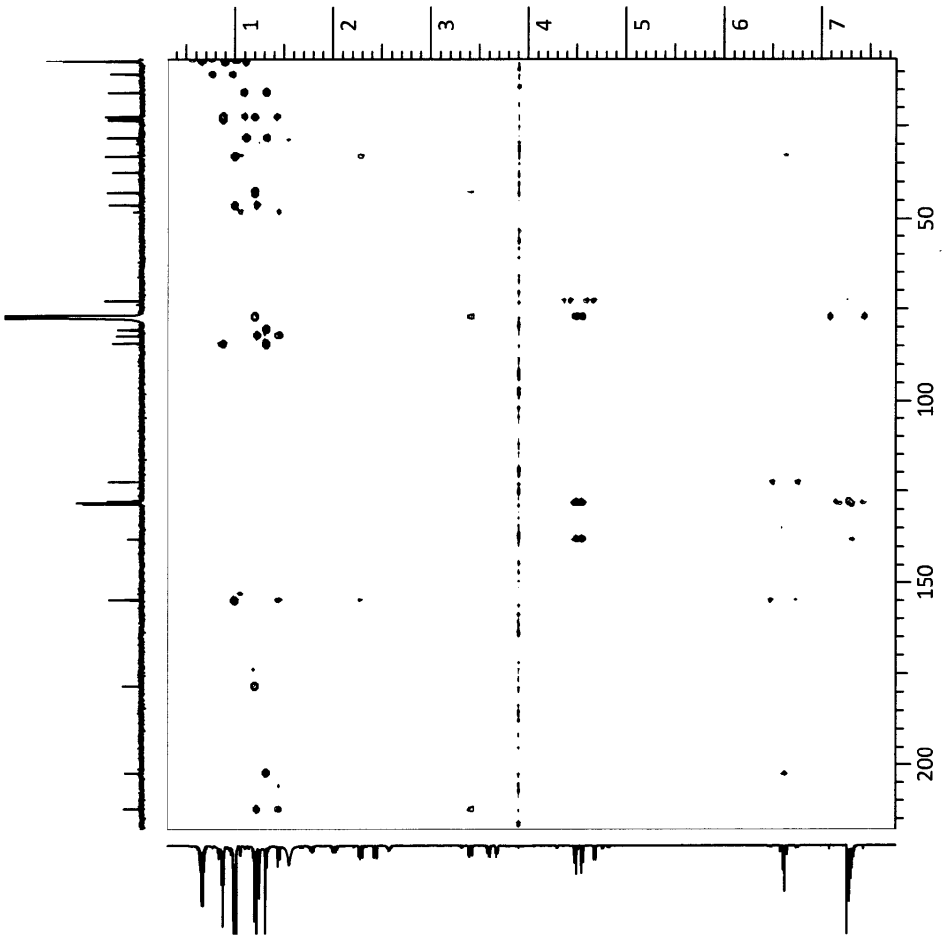
16

gCOSY, NOSEY and gHMBC of compound 16

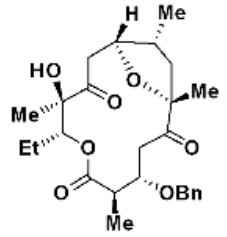


NOSEY



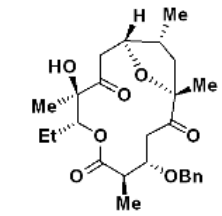

gHMBC
1
2
3
4
5
6
7
50
100
150
200

^{1}H NMR (500MHz, $CDCl_3$)



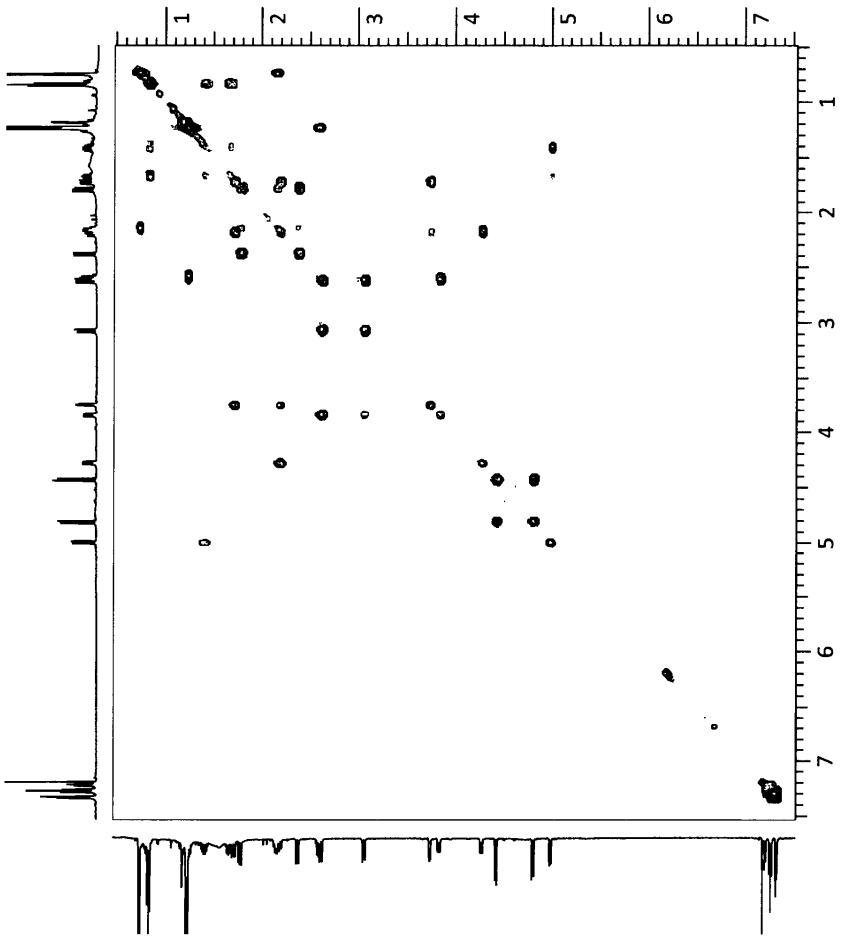
17

^{13}C NMR (125MHz, $CDCl_3$)



17

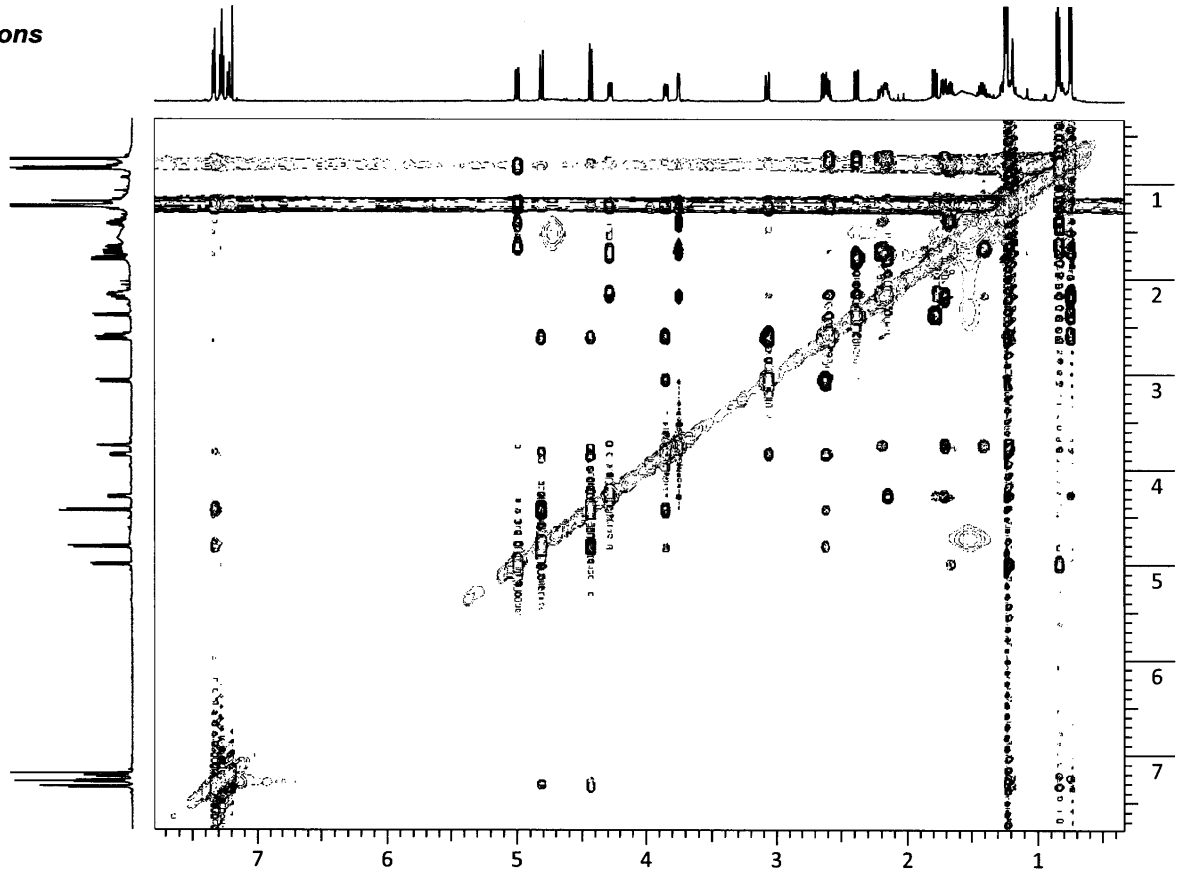
gCOSY, NOSEY and gHMBC of compound 17



gCOSY

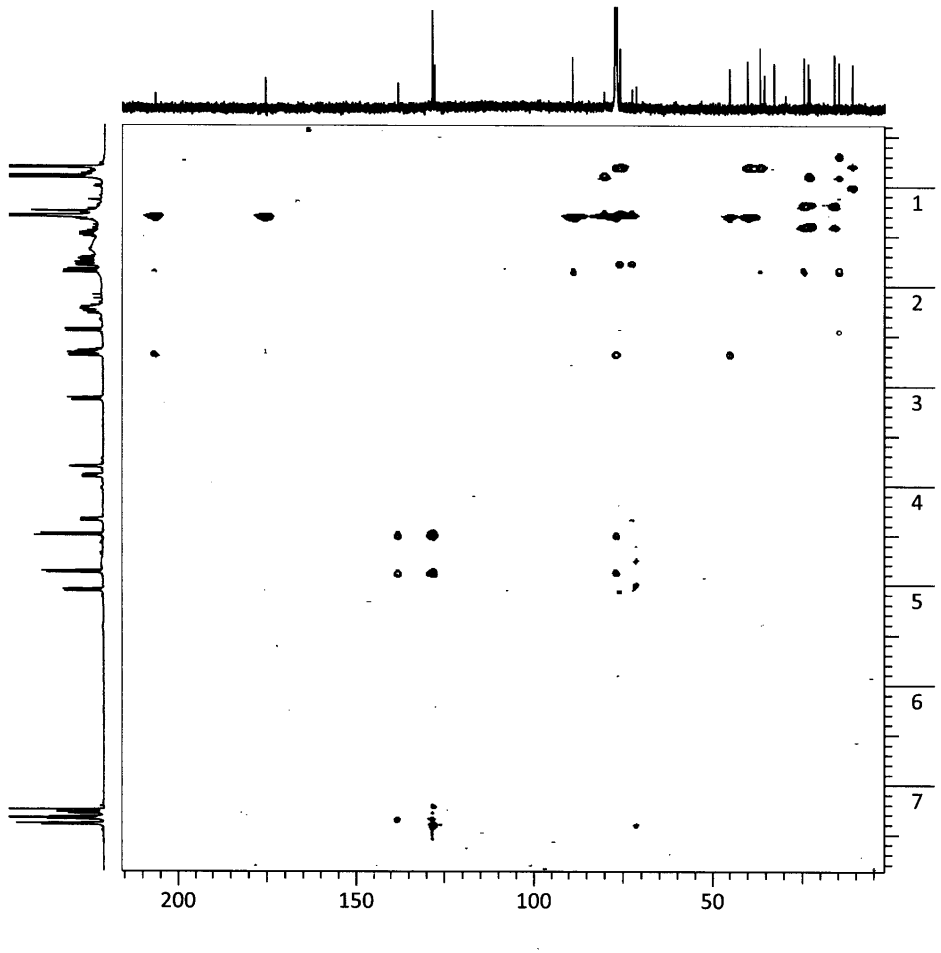
NOESY

correlations

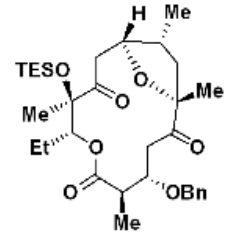


gHMBC

correlations

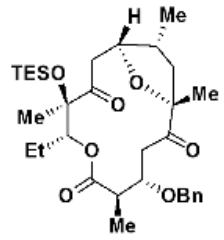


^{1}H NMR (500MHz, $CDCl_3$)



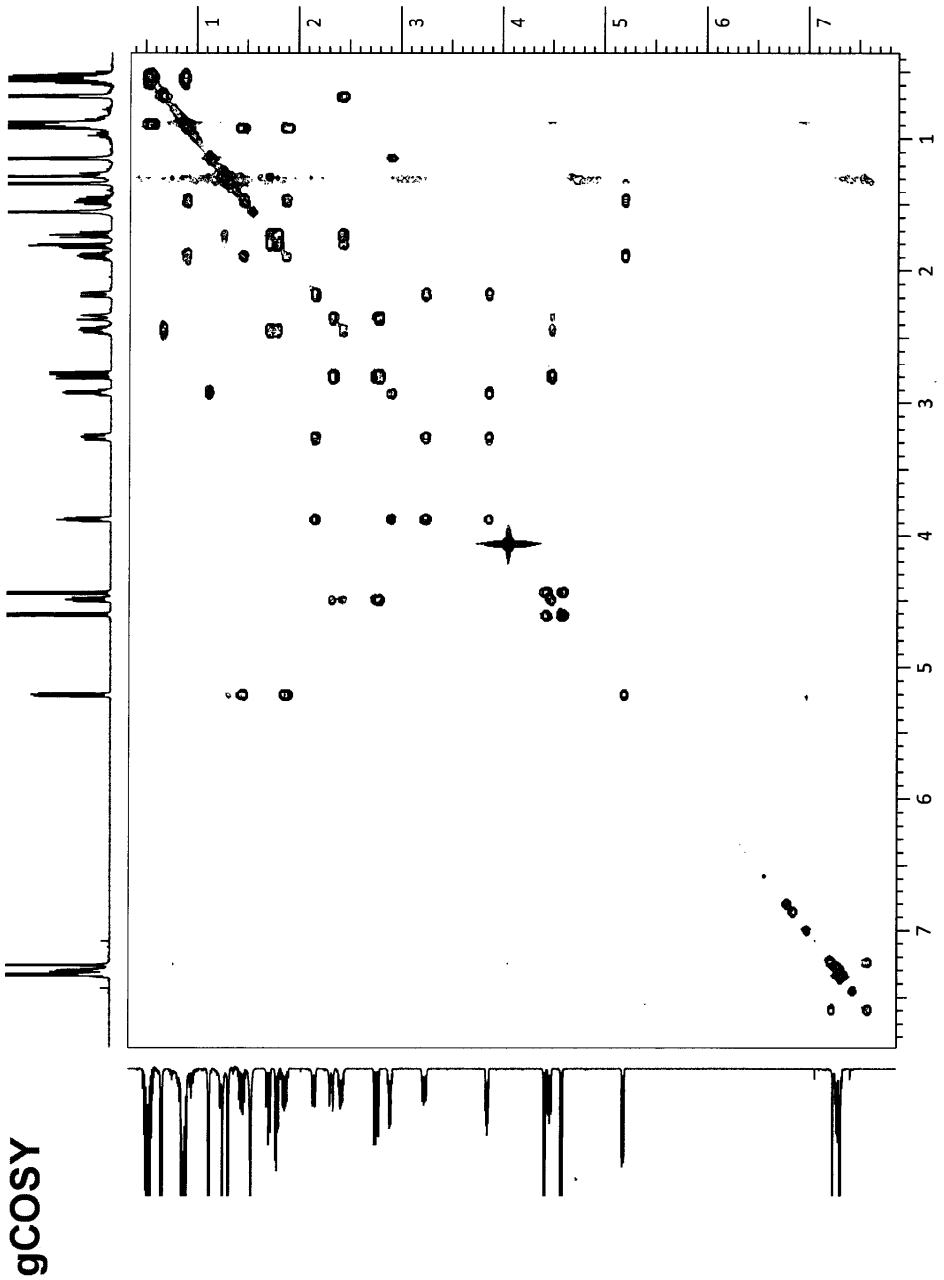
18

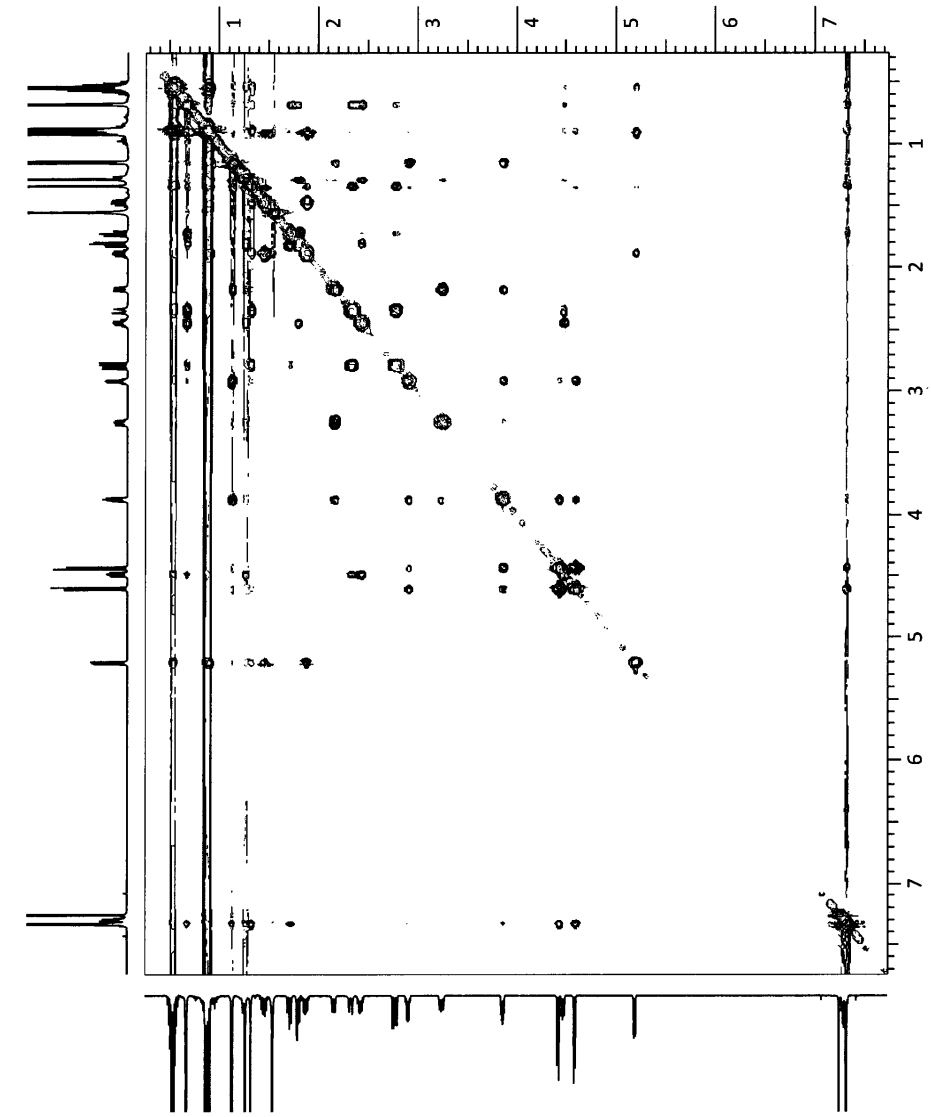
^{13}C NMR (125MHz, $CDCl_3$)

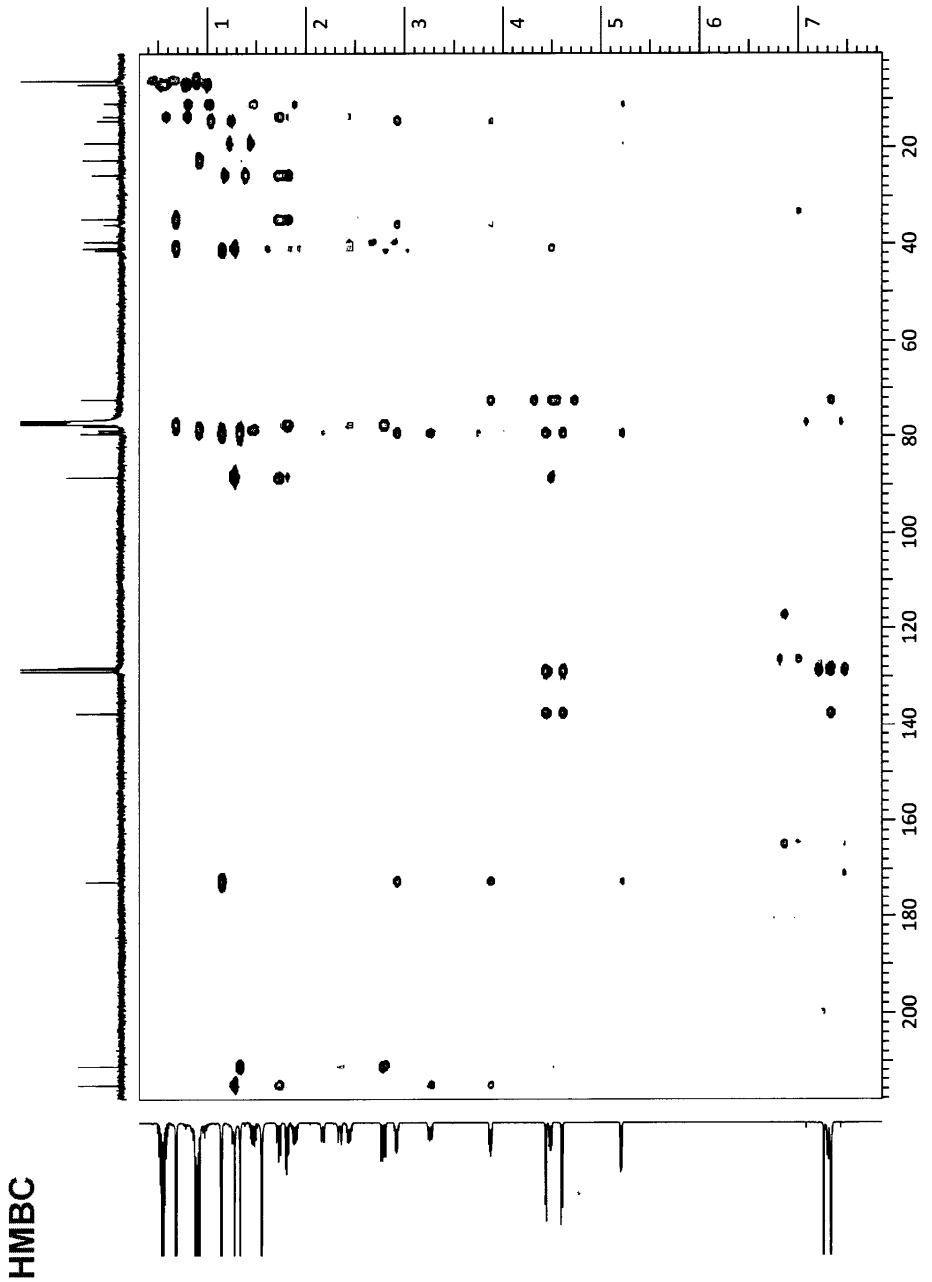


18

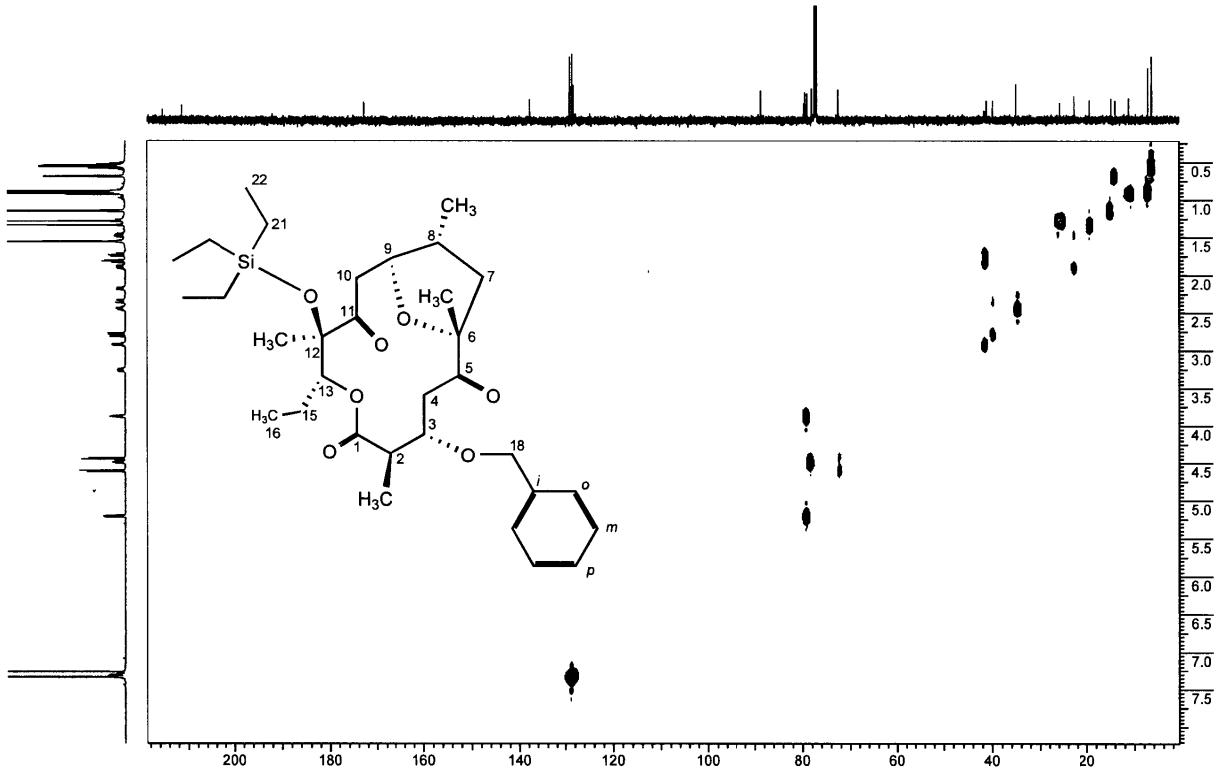
gCOSY, NOSEY, gHMBC and HETCOR of compound 18

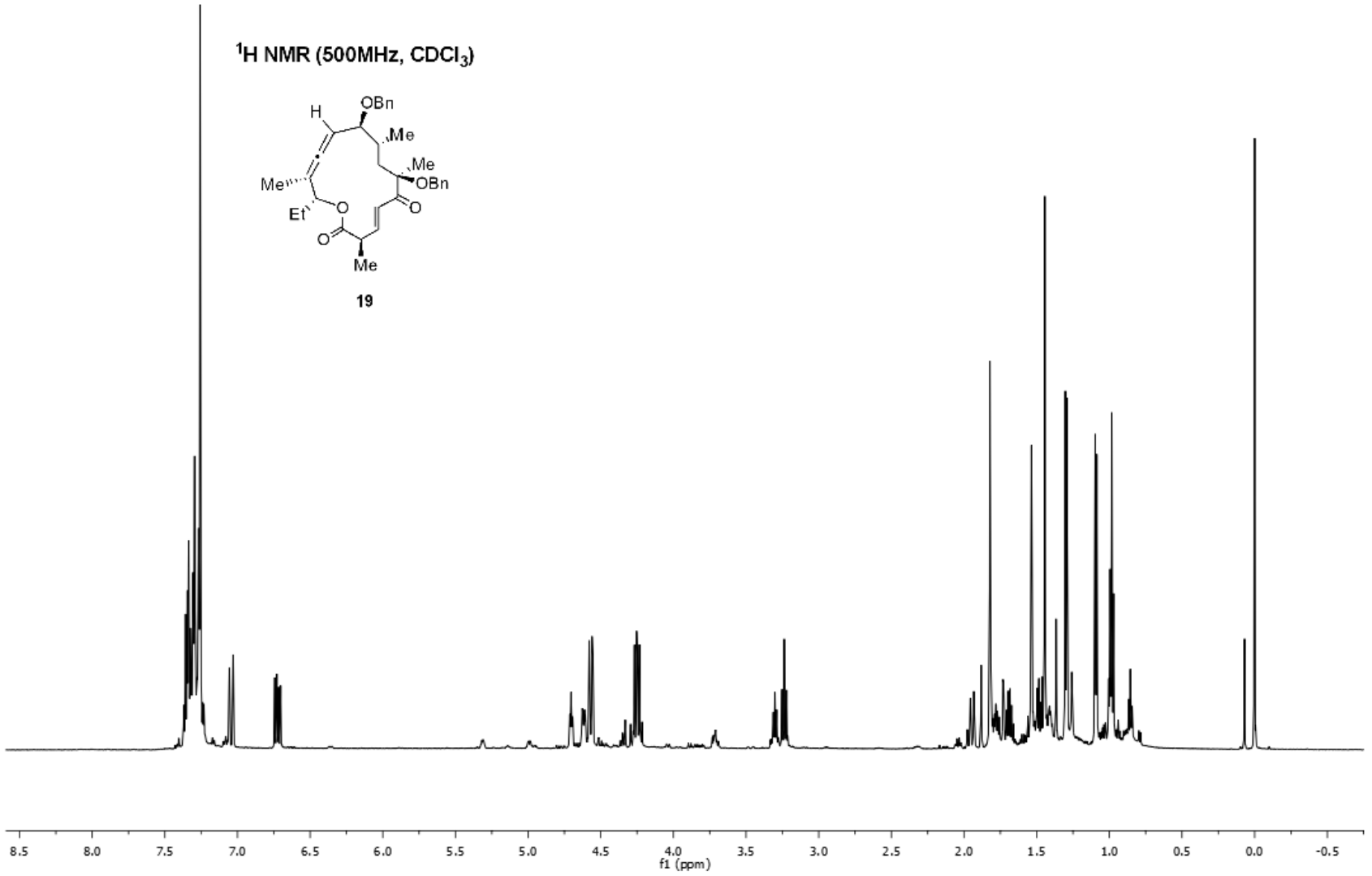



NOESY
1
2
3
4
5
6
7

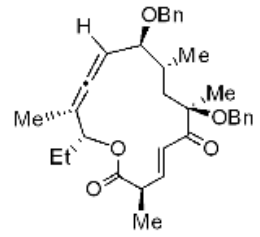

HMBC
1
2
3
4
5
6
7
20
40
60
80
100
120
140
160
180
200

One-bond heterocorrelation (HETCOR) spectrum



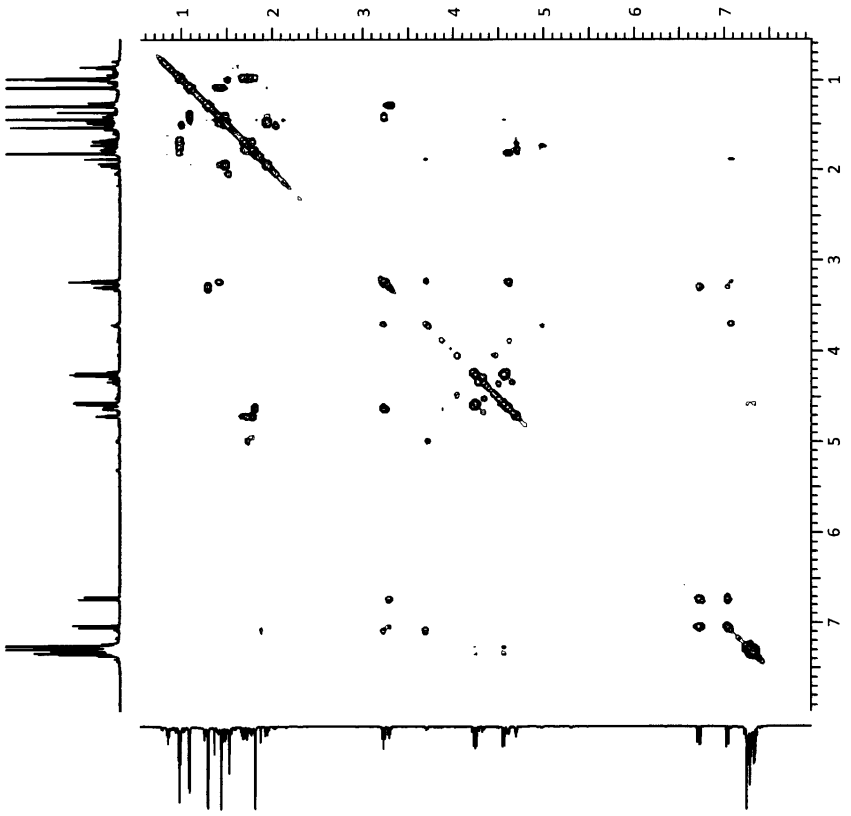

^{1}H NMR (500MHz, CDCl$_3$)
OBn
H
Me
Me
OBn
Me
Et
O
O
O
Me
19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

^{13}C NMR (125MHz, $CDCl_3$)

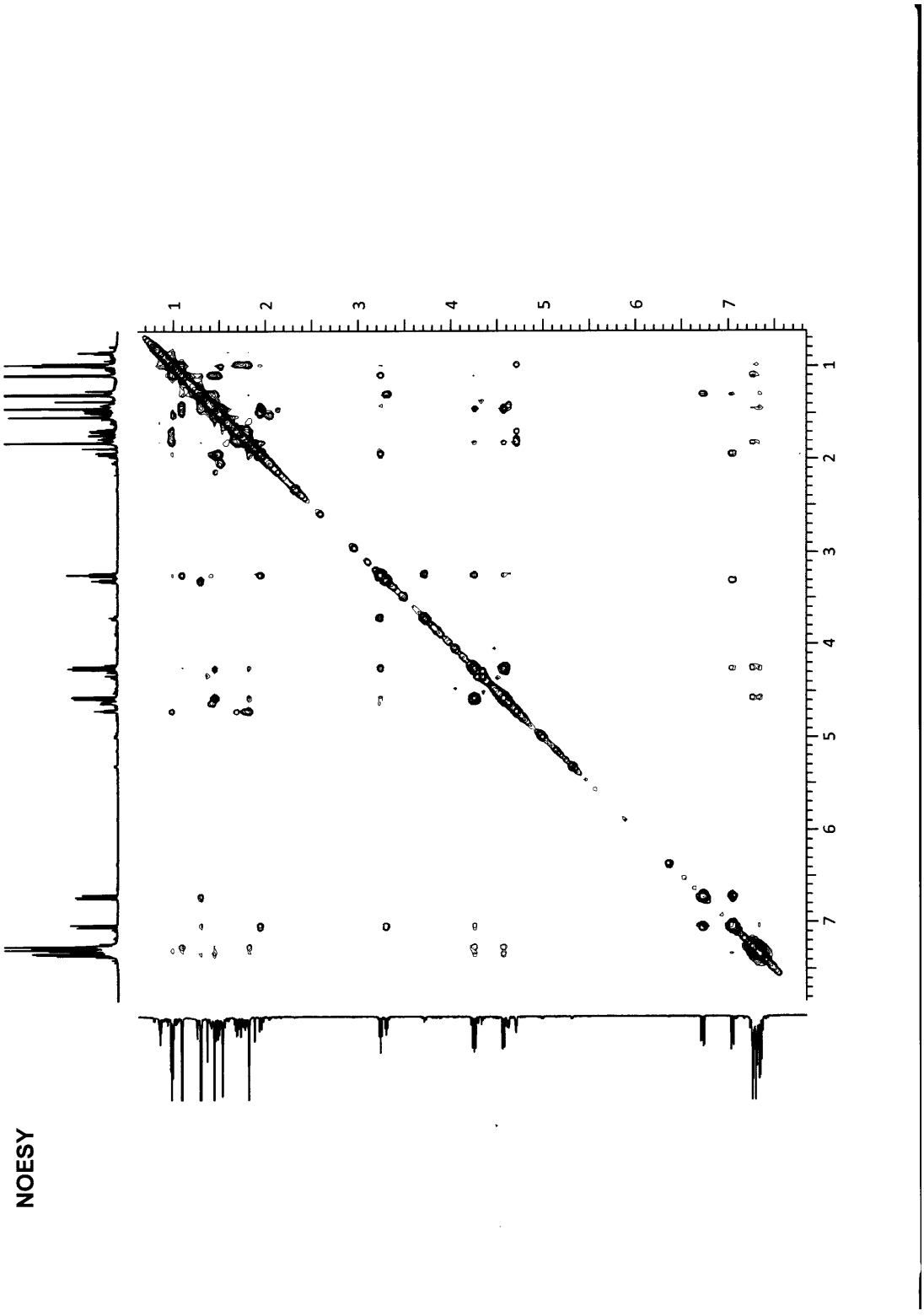


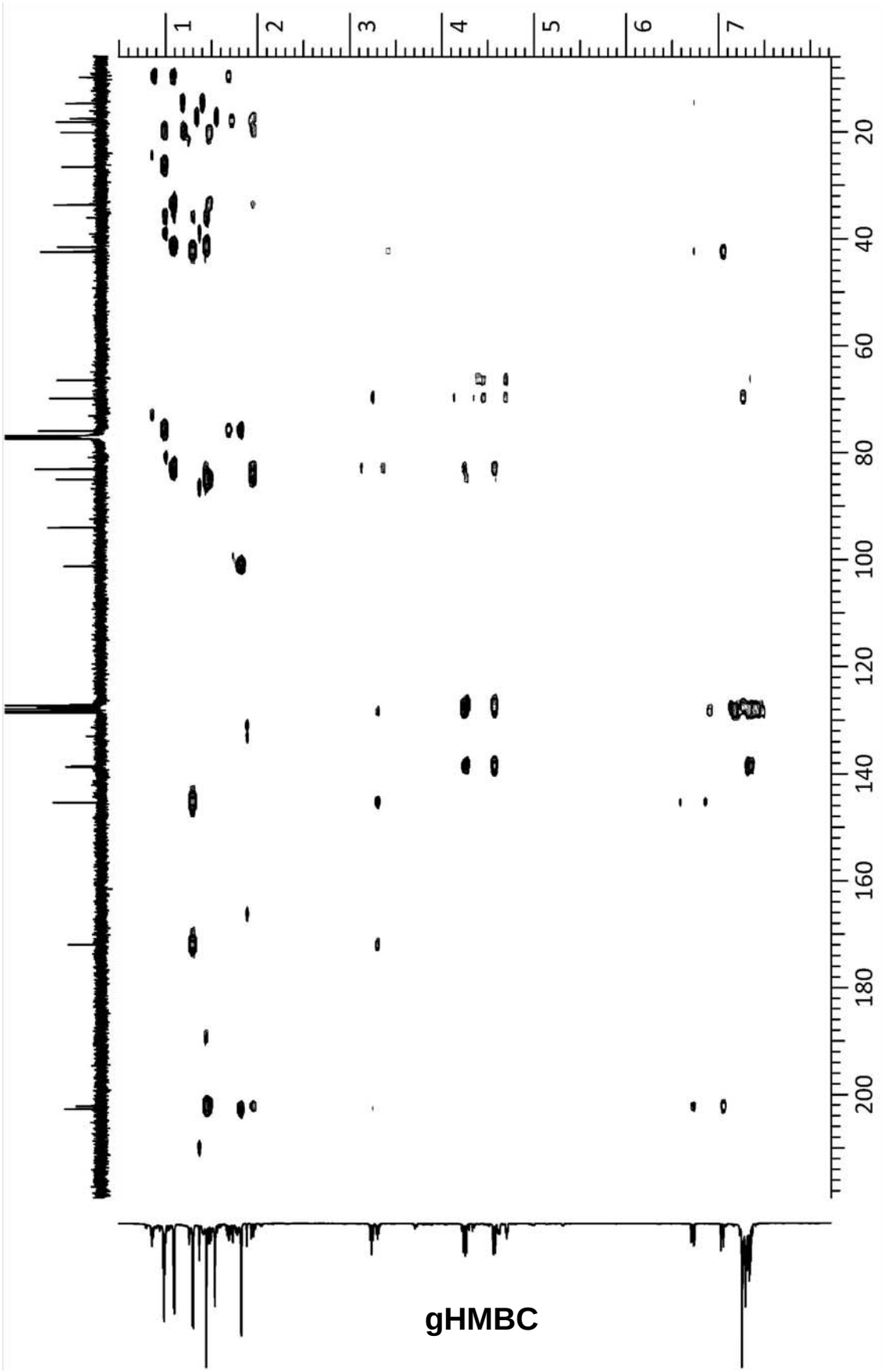
19

gCOSY, NOSEY, and gHMBC of compound 19

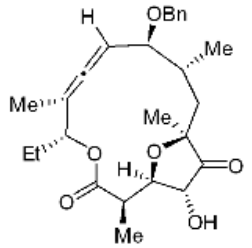


gCOSY


NOESY
1
2
3
4
5
6
7

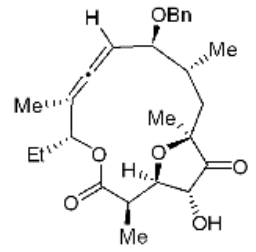

1
2
3
4
5
6
7
20
40
60
80
100
120
140
160
180
200
gHMBC

^{1}H NMR (500MHz, $CDCl_3$)



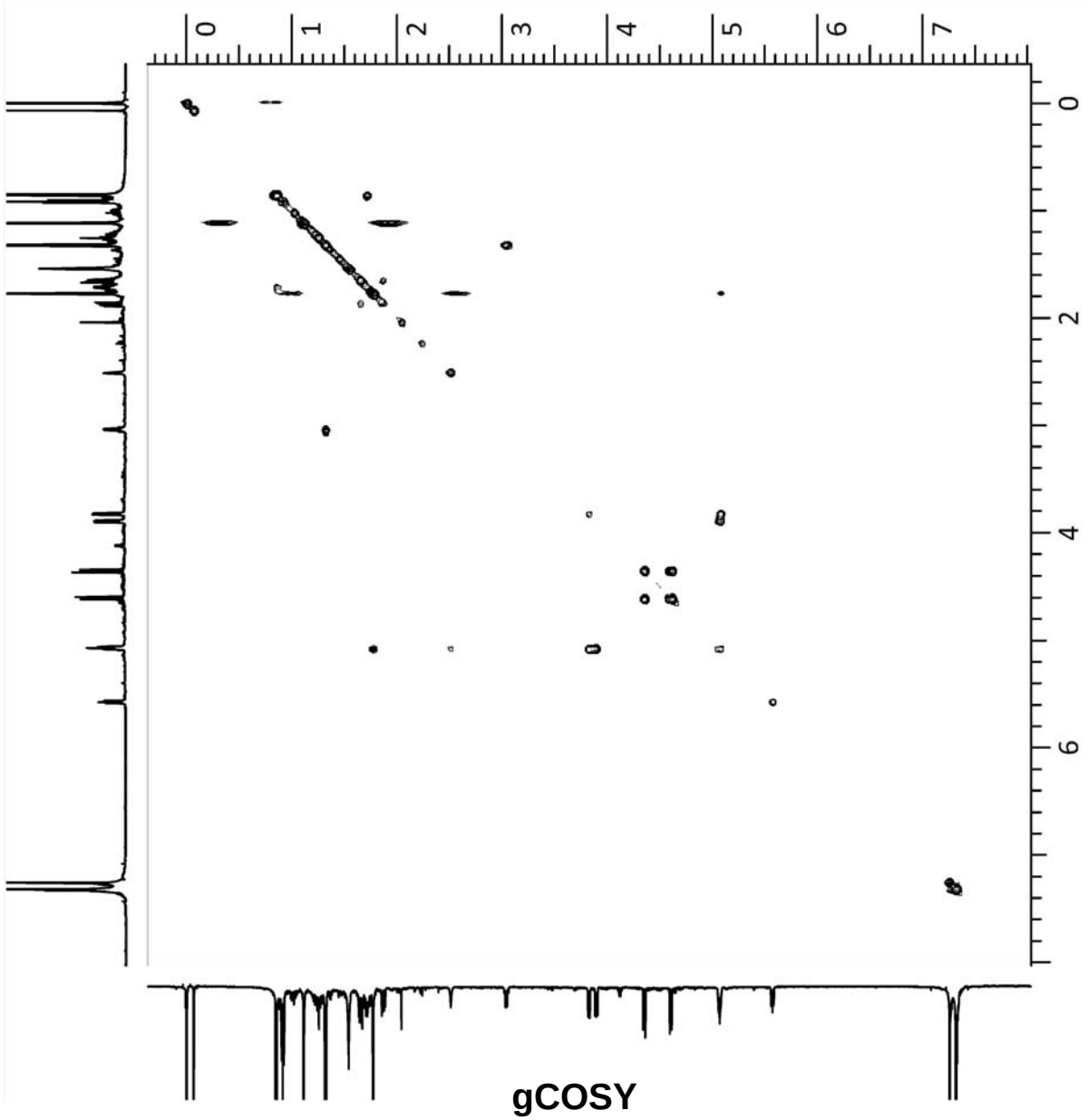
20

^{13}C NMR (125MHz, $CDCl_3$)

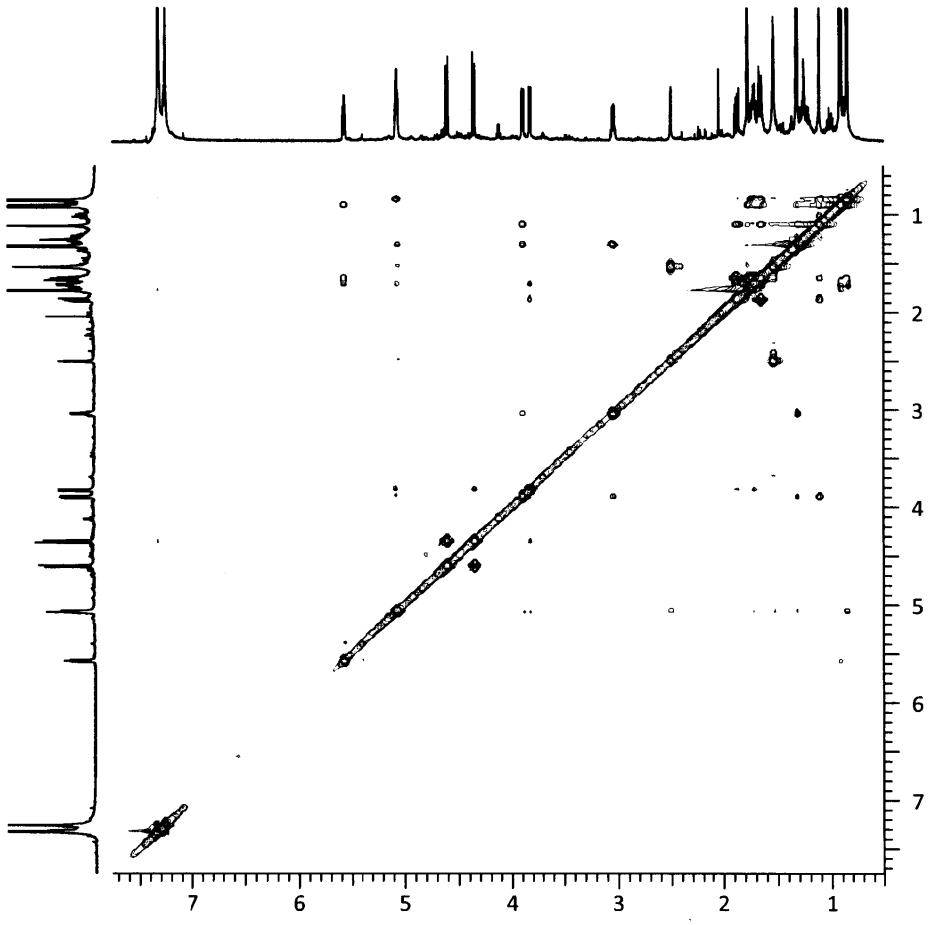


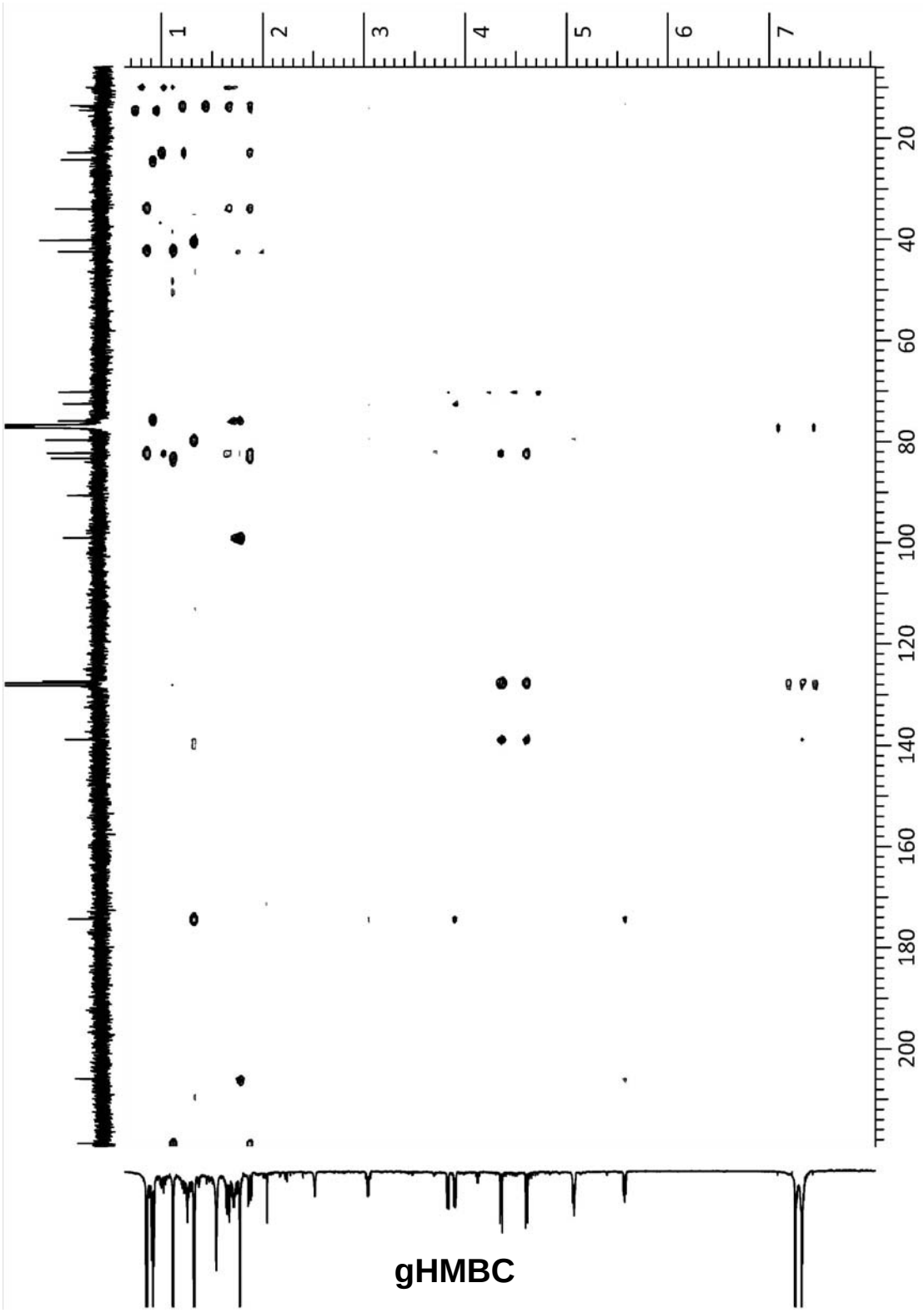
20

gCOSY, NOSEY, and gHMBC of compound 20

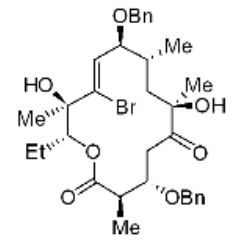


NOESY



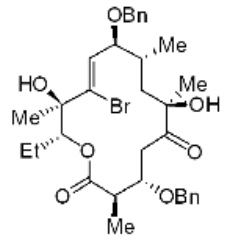

1
2
3
4
5
6
7
20
40
60
80
100
120
140
160
180
200
gHMBC

^{1}H NMR (500MHz, $CDCl_3$)



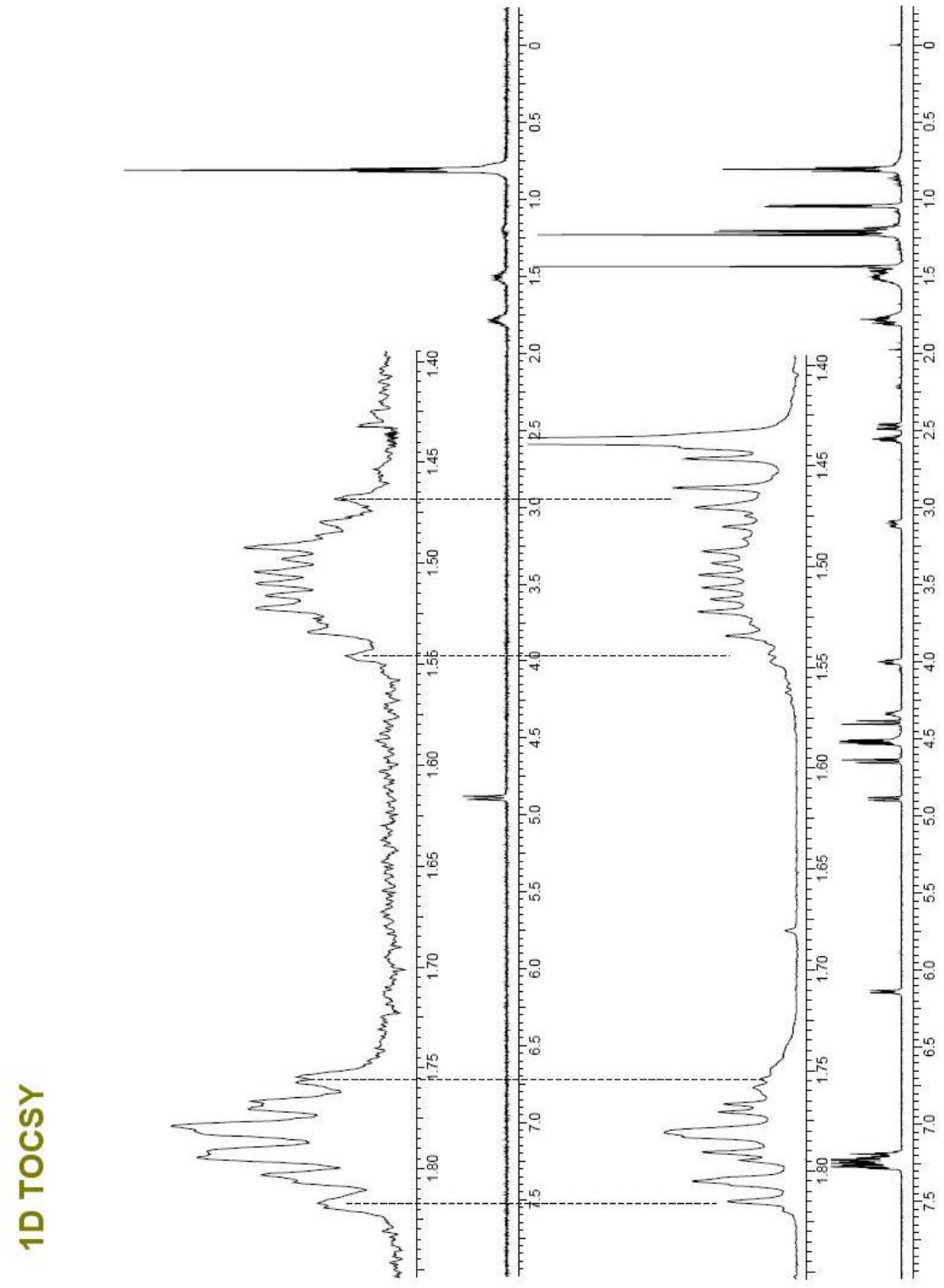
21

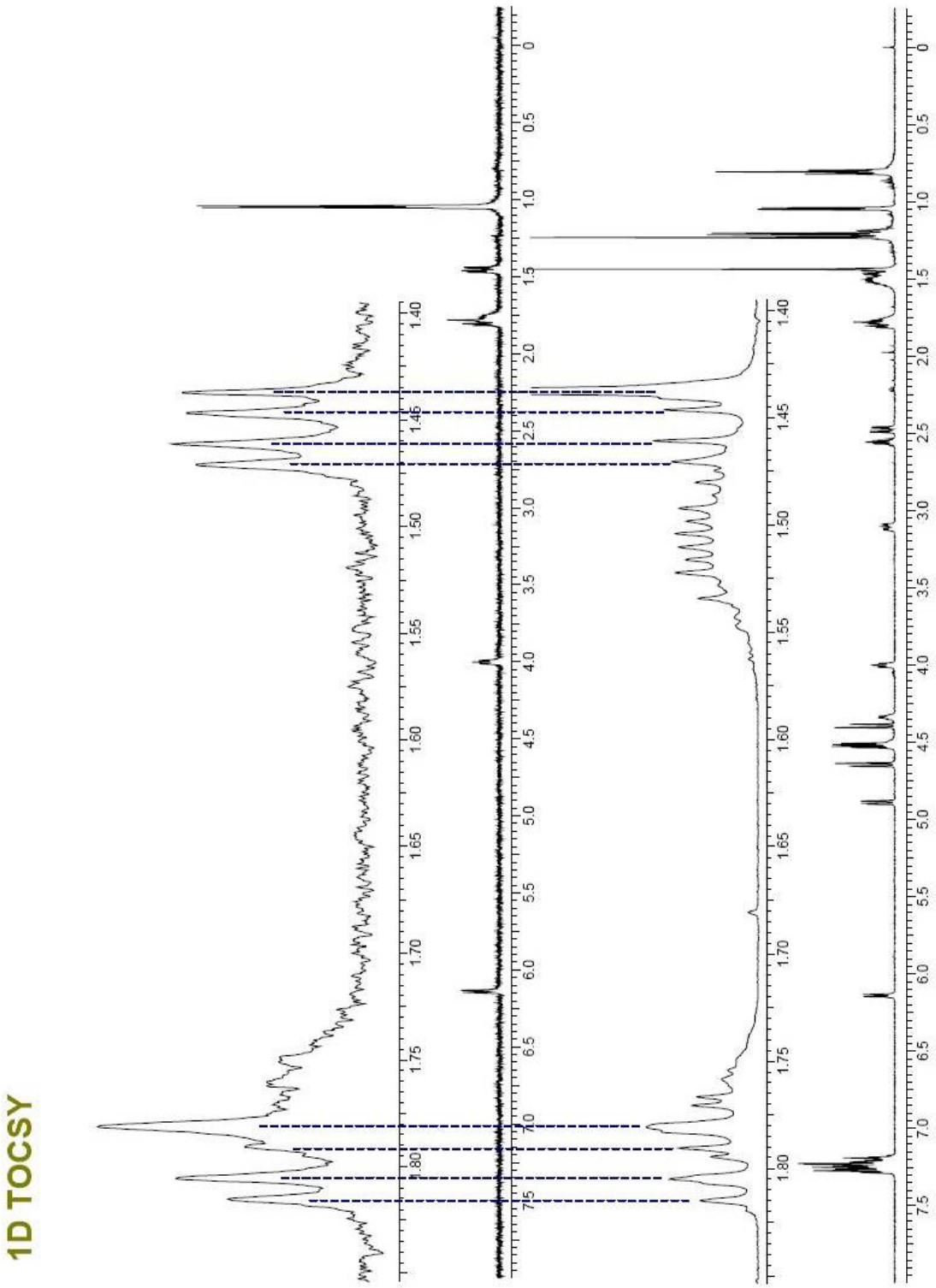
^{13}C NMR (125MHz, $CDCl_3$)



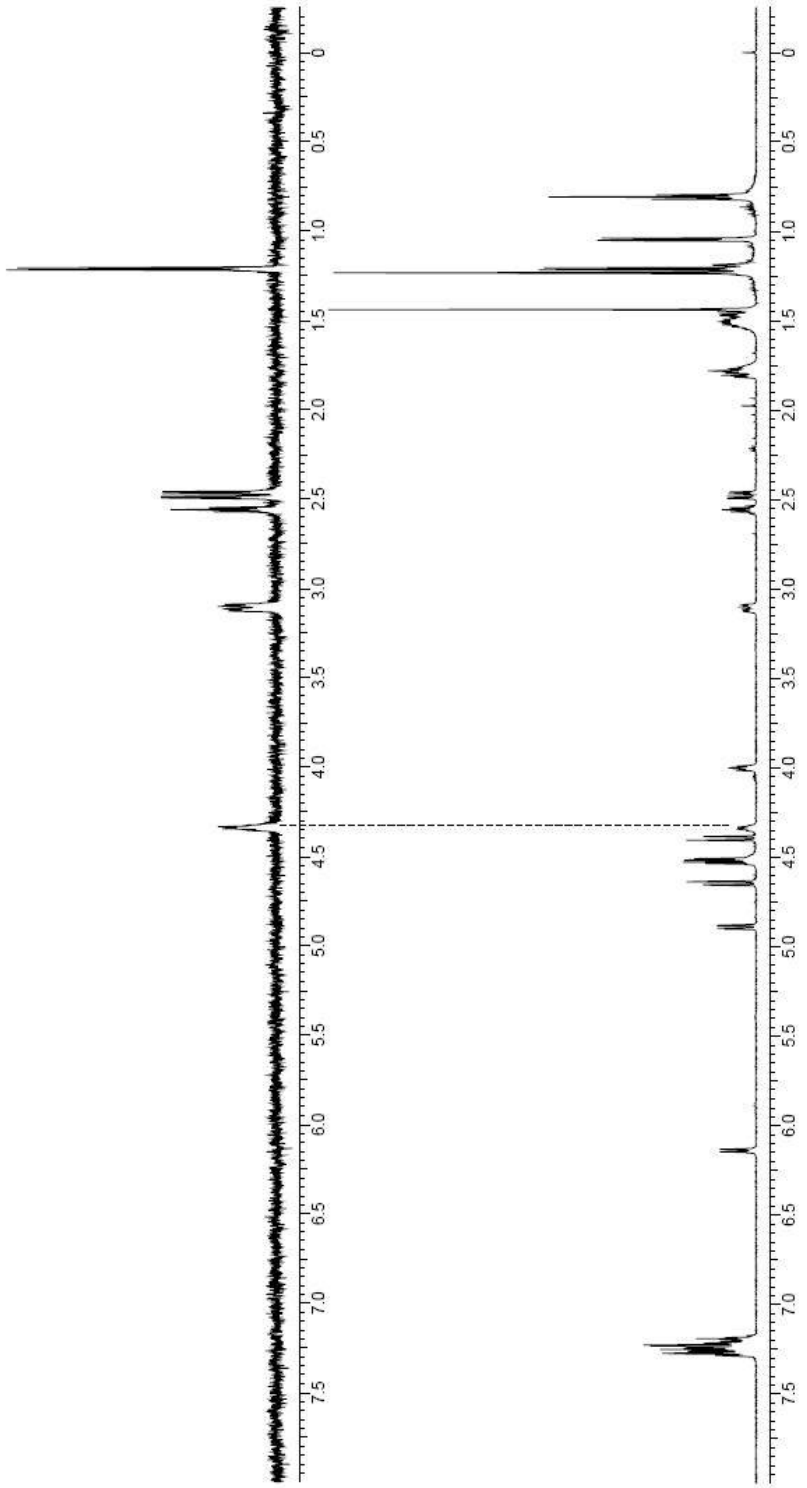
21

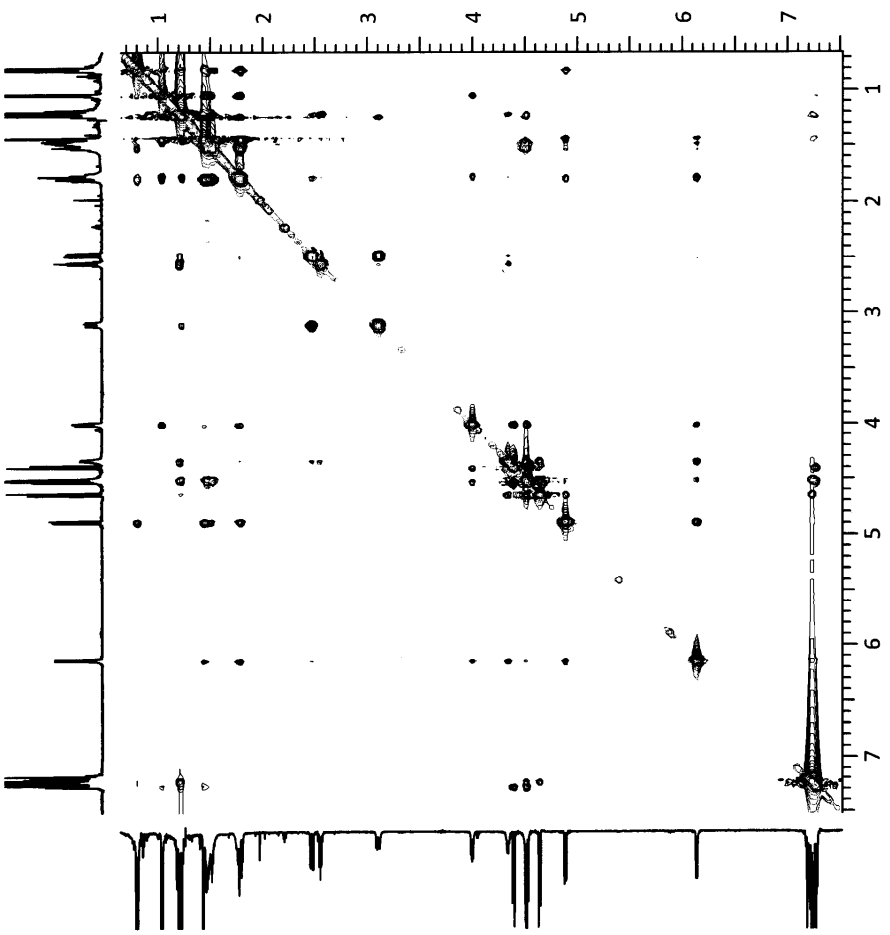
1DTOCSY, NOSEY, and gHMBC of compound 21

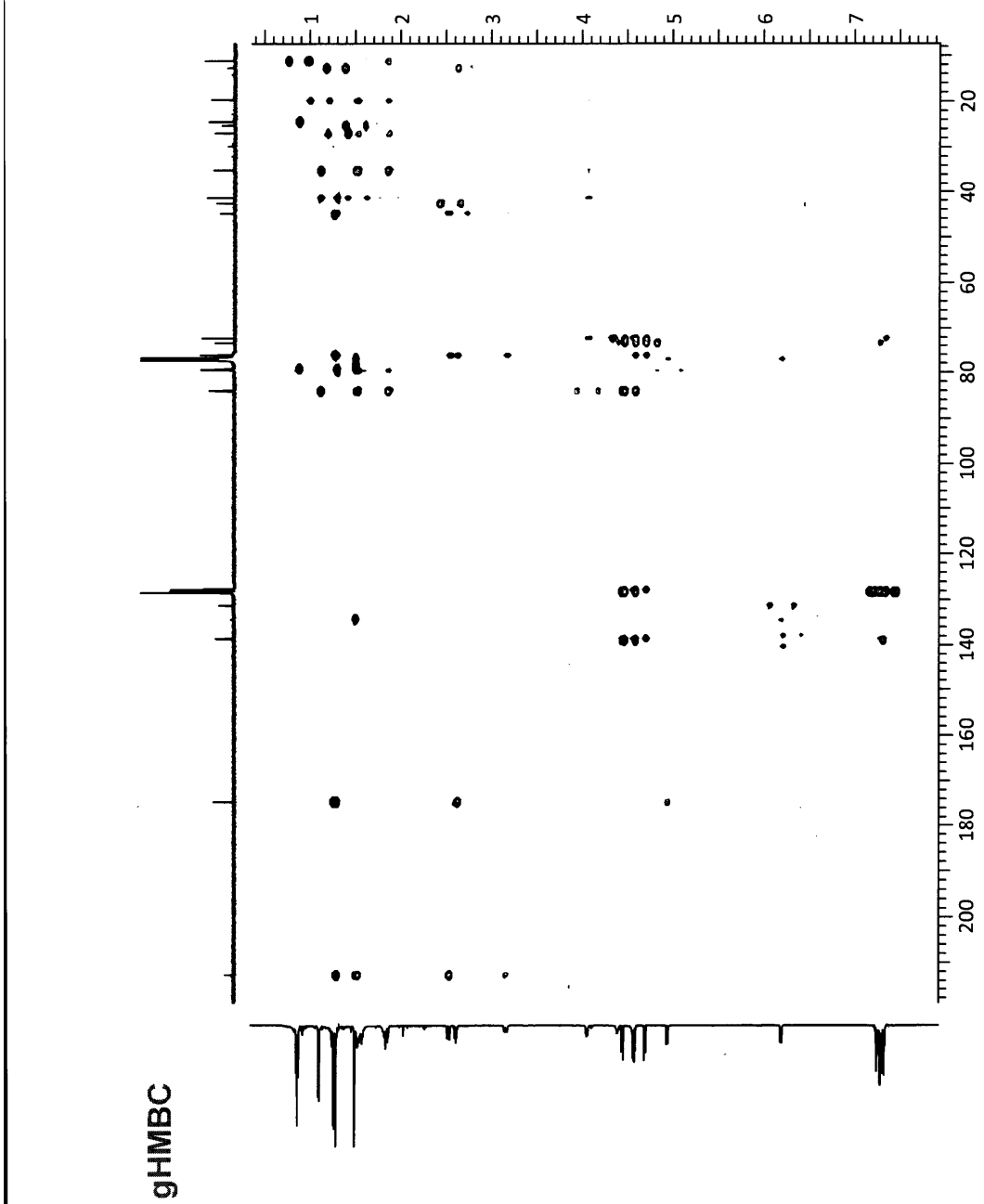



1D TOCSY

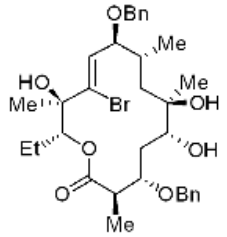
1D TOCSY




NOESY
1
2
3
4
5
6
7

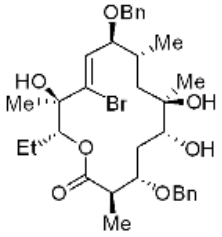

gHMBC
1
2
3
4
5
6
7
20
40
60
80
100
120
140
160
180
200

^{1}H NMR (500MHz, $CDCl_3$)



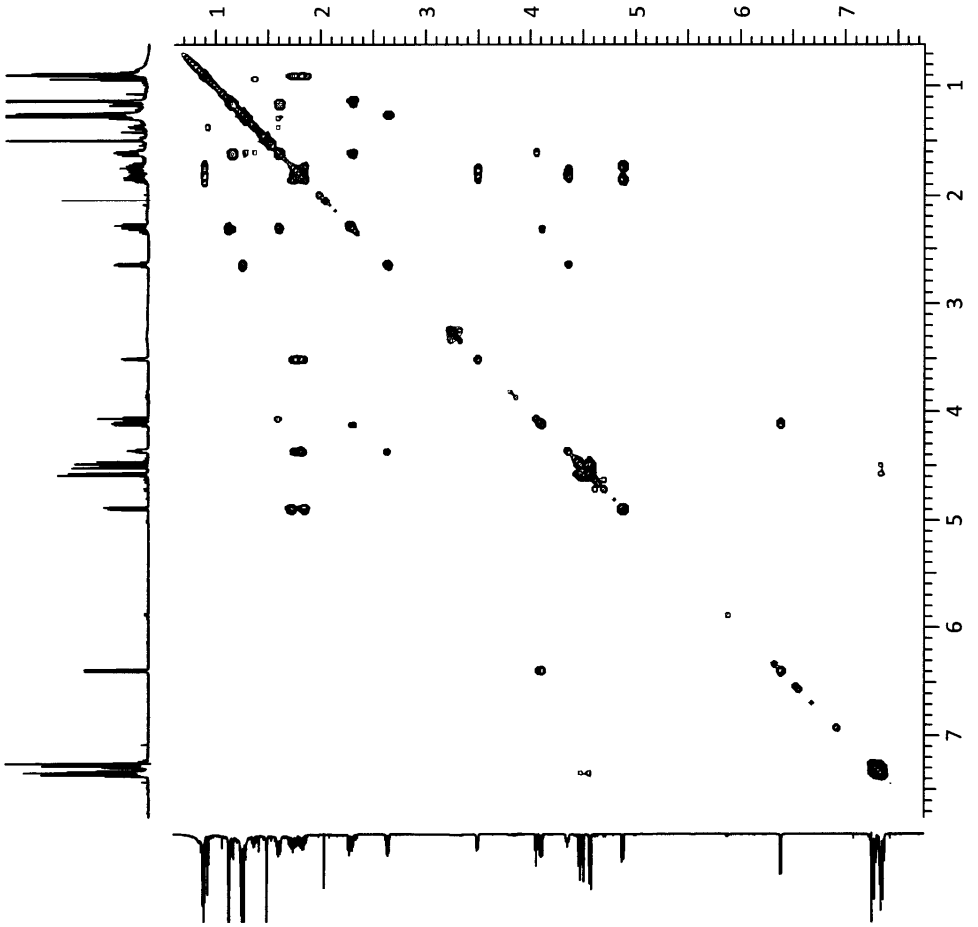
22

^{13}C NMR (125MHz, $CDCl_3$)



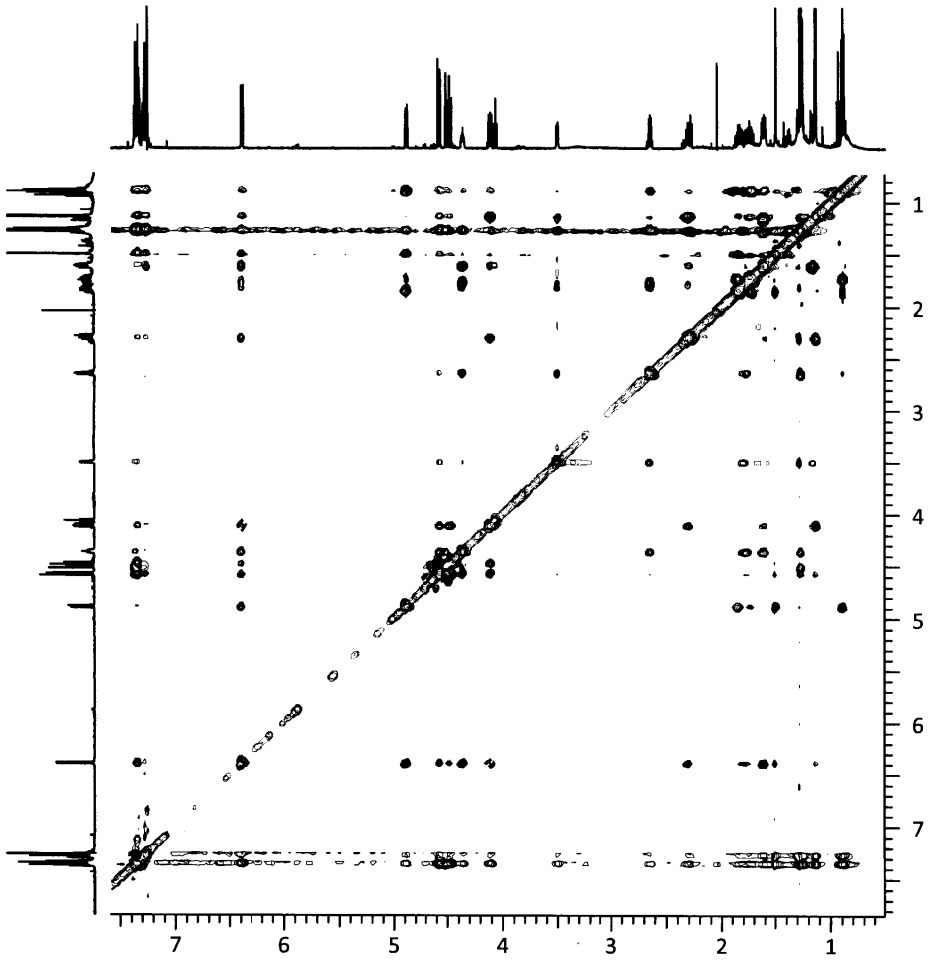
22

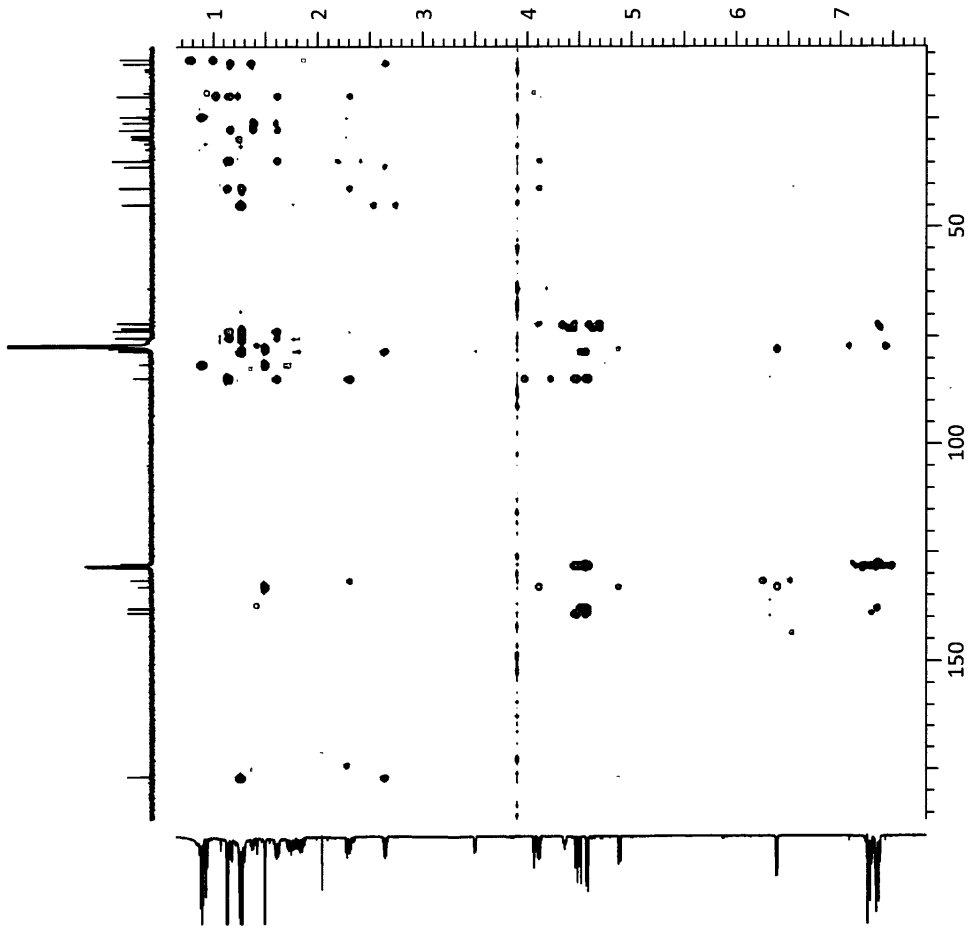
gCOSY, NOSEY, and gHMBC of compound 22



gCOSY

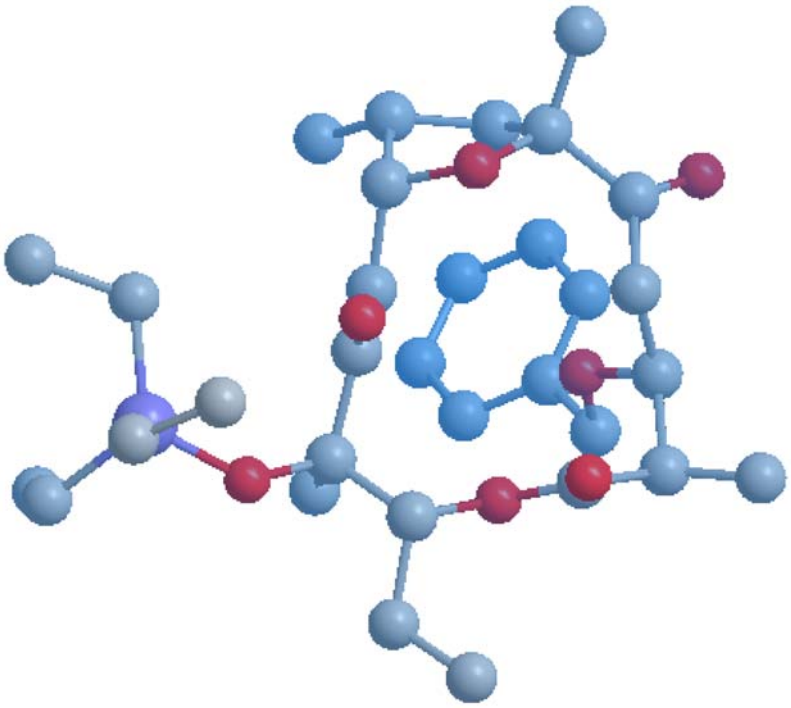
NOESY



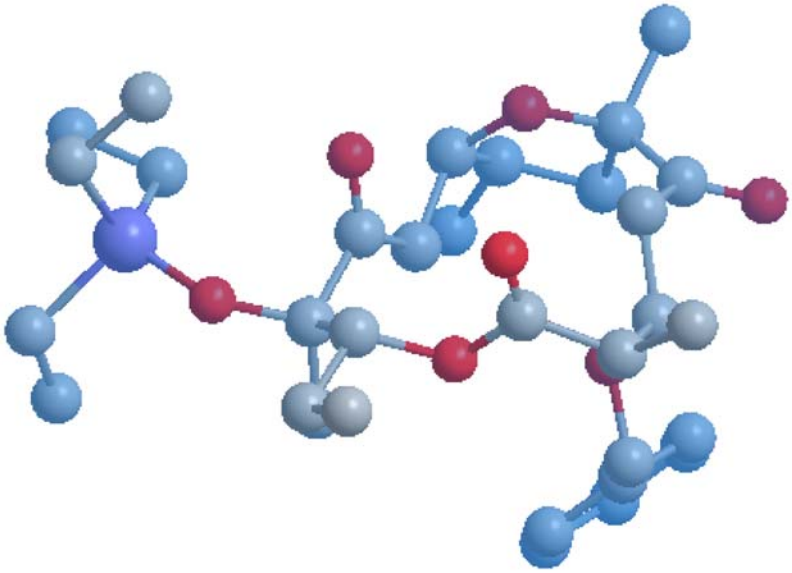


gHMBC

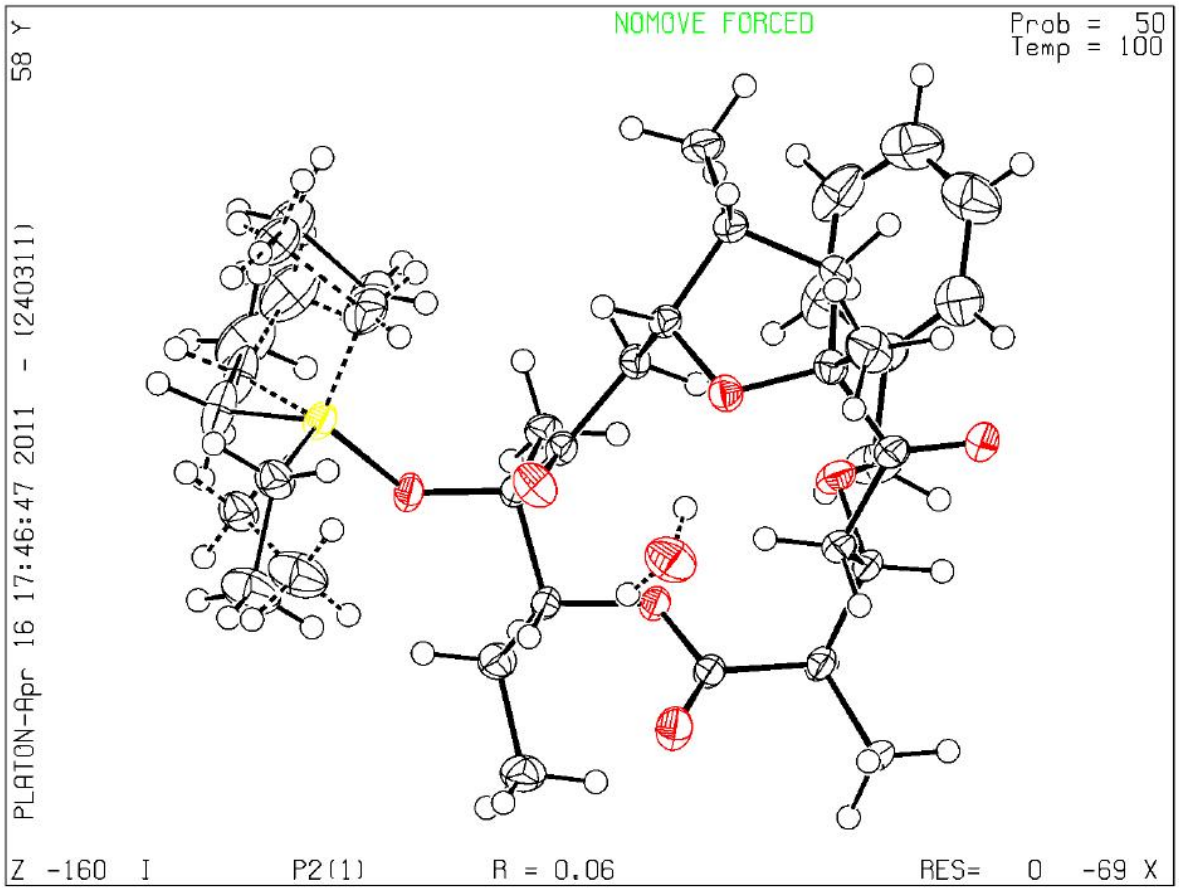
Crystal structure of compound 18



Crystal structure of compound 18 (From different angle)



Ellipsoid plot of compound 18



See .cif file for compound coordinates

Full list of authors in reference **6i-6k**

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