Electronic Supporting Information

Total Synthesis and Structural Revision of Biyouyanagin B

K. C. Nicolaou,* Silvano Sanchini, T. Robert Wu, and David Sarlah

Contribution from the Department of Chemistry and The Skaggs Institute for Chemical Biology, The Scripps Research Institute, 10550 N. Torrey Pines Road, La Jolla, CA 92037 (USA), and Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093 (USA)

E-mail: kcn@scripps.edu

I. Experimental Procedures and Spectroscopic Data for Compounds

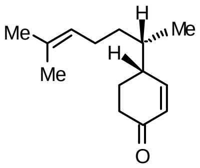
General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), toluene, benzene, diethyl ether (Et_2O) and methylene chloride (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography.

NMR spectra were recorded on Bruker DRX-600 or DRX-500 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad.

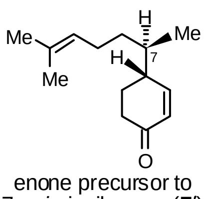
Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Melting points are uncorrected and were measured on a Thomas- Hoover Unimelt capillary melting point apparatus. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-ZSE mass spectrometer using MALDI (matrix-assisted laser-desorption ionization) or ESI (electrospray ionization).

Enone precursor to zingiberene (3′): To a mixture of (*R*)-2-(methoxydiphenylmethyl)pyrrolidine (267 mg, 1.0 mmol, 5 mol%) and ethyl 3,4-dihydroxy benzoate (729 mg, 4.0 mmol, 20 mol%) at 0 °C was added a pre-cooled mixture of *S*-citronellal (3.09 g, 20.0 mmol) and methyl vinyl ketone (2.10 g, 30.0 mmol, 1.5 equiv). The resulting homogeneous solution was stirred at 4 °C for 48 h and the reaction mixture was directly subjected to flash column chromatography (silica gel, ether/hexanes, 1:5) to give the corresponding keto-aldehyde as colorless oil (3.59 g, 16.0 mmol, 80%, ca 10:1 dr). After dissolving the resulting keto-aldehyde (2.24 g, 10.0 mmol) in *i*Pr-O H (33 mL) was added LiOH × H_2O (0.042 g, 1.0 mmol) and the mixture was stirred for 24 h. The mixture was then extracted with Et_2O (3 × 100 mL), and the combined organic phase was washed with brine (100 mL), dried with Na_2SO_4 and concentrated in vacuo. The residue so-obtained was subjected to flash column chromatography (silica gel, EtOAc:hexanes, 1:12) to give the title compound (1.75 g, 8.50 mmol, 81%, ca 10:1 dr). **3′**: R_f = 0.62 (silica gel, EtOAc:hexanes 1:2); $[\alpha]_D^{25}$ = –38.3 (*c* = 0.80, $CHCl_3$); IR ν_{max} (film): 3017, 2961, 2925, 2873, 2858, 1683, 1451, 1381, 755 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 6.83 (dt, *J* = 10.2, 1.9 Hz, 1 H), 6.01 (dd, *J* = 10.2, 2.5 Hz, 1 H), 5.09 (m, 1 H), 2.50 (dt, *J* = 16.6, 3.9 Hz, 1 H), 2.43 (m, 1 H), 2.33 (m, 1 H), 2.05 (td, *J* = 14.7, 6.8 Hz, 1 H), 1.95 (m, 2 H), 1.77 (ddd, *J* = 13.6, 8.9, 3.5 Hz, 1 H), 1.69 (s, 3 H), 1.61 (s, 3 H), 1.41 (m, 1 H), 1.23 (m, 1 H), 0.89 (d, *J* = 6.9 Hz, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.17, 155.46, 131.80, 129.65, 124.09, 41.03, 37.49, 36.09, 34.09, 25.82, 25.69, 23.94, 17.67, 15.97 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{14}H_{23}O$ ($M+H^+$): 207.1671; found 207.1745.



enone precursor to zingiberene (**3′**)

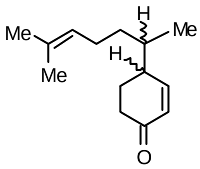
Enone precursor to 7-*epi*-zingiberene (7′): The same procedure for the preparation of the enone precursor of zingiberene (**3**) was followed using *R*-citronellal (2.24 g, 10.0 mmol) as starting material. The title compound was obtained as a colorless oil (1.73 g, 8.40 mmol, 78%, ca 8:1 dr). **7′**: R_f = 0.60 (silica gel, EtOAc:hexanes 1:2); $[\alpha]_D^{25}$ = –53.6 (*c* = 1.00, $CHCl_3$); IR ν_{max} (film): 3029, 2962, 2926, 2873,



enone precursor to 7-*epi*-zingiberene (**7′**)

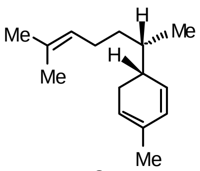
2858, 1683 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.87 (d, *J* = 10.3 Hz, 1 H), 6.02 (dd, *J* = 10.3, 2.7 Hz, 1 H), 5.08 (t, *J* = 6.5 Hz, 1 H), 2.50 (dt, *J* = 16.6, 3.9 Hz, 1 H), 2.42 (m, 1 H), 2.34 (m, 1 H), 2.06 (td, *J* = 14.4, 6.6 Hz, 1 H), 1.95 (m, 2 H), 1.80 (m, 1 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.39 (m, 1 H), 1.25 (m, 1 H), 0.93 (d, *J* = 6.8 Hz, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.15, 154.36, 131.82, 129.91, 124.12, 41.60, 37.68, 36.03, 33.88, 25.82, 25.78, 25.69, 17.67, 16.50 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{14}H_{23}O$ (M+H^+): 207.1671; found 207.1748.

Enone precursor to racemic zingiberene (3′, *ent*-3′, 7′, *ent*-7′) (equimolar mixture of all four possible isomers): This compound was prepared from the piperidine enamine of racemic citronellal following the procedure reported by Croft et al.[1] Spectroscopic data are in accord to those reported in the literature.[1]



enone precursor to racemic zingiberene **3′**, *ent*-**3′**, **7′**, *ent*-**7′**

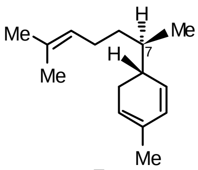
Zingiberene (3): To a stirring solution of its precursor enone (2.20 g, 10.7 mmol) and Comins reagent (6.32 g, 18.2 mmol, 1.7 equiv) in THF (200 mL) at –78 °C was added KHMDS (0.5 M in toluene, 32.1 mL, 16.1 mmol, 1.5 equiv). The resulting orange solution was stirred at –78 °C for 0.5 h. Upon completion (TLC analysis), the reaction was quenched at –78 °C with saturated aqueous $NaHCO_3$ solution (100 mL) and, upon warming to ambient temperature, was extracted with Et_2O (3 × 100 mL). The combined organic phases were washed with brine (30 mL), dried with Na_2SO_4, and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (30 mL) and passed through a short silica gel pad. After concentration, the resulting crude triflate was dissolved in THF (80 mL). To this solution at 0 °C was added CuI (95 mg, 0.50 mmol, 5 mol%) and then MeMgBr (3.0 M in ether, 5.0 mL, 15.0 mmol, 1.5 equiv) in the dark. After stirring at 0 °C for 30 min, the reaction was quenched with saturated aqueous NH_4Cl solution (50 mL) and extracted with ether (3 × 50 mL). The combined organic phases were washed with brine (100 mL), dried with Na_2SO_4 and carefully concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel, pentane) to give the



3

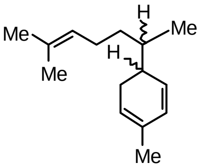
title compound (1.75 g, 8.56 mmol, 91% for the two steps). This compound is rather labile at room temperature and was used immediately. **3**: R_f = 0.39 (hexanes); $[\alpha]_D^{25}$ = –111.3 (*c* = 0.70, $CHCl_3$); IR ν_{max} (film): 3020, 2996, 2917, 2859, 2858, 1215, 754 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 5.77 (d, *J* = 9.7 Hz, 1 H), 5.64 (dd, *J* = 9.7, 2.9 Hz, 1 H), 5.45 (s, 1 H), 5.10 (t, *J* = 7.1 Hz, 1 H), 2.27 (m, 1 H), 2.03 (m, 3 H), 1.93 (m, 1 H), 1.72 (d, *J* = 1.1 Hz, 3 H), 1.69 (s, 3 H), 1.61 (s, 3 H), 1.56 (m, 1 H), 1.41 (ddd, *J* = 15.0, 11.2, 5.9 Hz, 1 H), 1.18 (m, 1 H), 0.87 (d, *J* = 6.8 Hz, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 131.21, 131.06, 127.84, 124.80, 120.38, 38.01, 35.99, 34.23, 25.92, 25.71, 24.38, 21.10, 17.65, 16.54 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{15}H_{25}$ $(M+H^+)$: 205.1878; found 205.1951.

7-*epi*-zingiberene (7′): The same procedure for the preparation of zingiberene (**3**) was followed using the appropriate enone (2.24 g, 10.0 mmol) as starting material. The title compound was obtained as colorless oil (1.73 g, 8.40 mmol, 78%). **7′**: R_f = 0.60 (silica gel, EtOAc:hexanes 1:2); $[\alpha]_D^{25}$ = –101.9 (*c* = 0.71, $CHCl_3$); IR ν_{max} (film): 3025, 2996, 2917, 2859, 2823, 759 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 5.79 (dd, *J* = 9.7, 1.5 Hz, 1 H), 5.67 (dd, *J* = 9.8, 3.0 Hz, 1 H), 5.46 (d, *J* = 0.8 Hz, 1 H), 5.11 (m, 1 H), 2.26 (m, 1 H), 2.06 (m, 1 H), 1.93 (m, 1 H), 1.72 (d, *J* = 1.7 Hz, 1 H), 1.69 (d, *J* = 0.5 Hz, 1 H), 1.61 (s, 1 H), 1.50 (m, 1 H), 1.42 (m, 1 H), 1.18 (m, 1 H), 0.89 (d, *J* = 6.8 Hz, 1 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 131.21, 131.08, 129.71, 128.19, 124.83, 120.57, 38.37, 36.00, 34.12, 26.33, 25.89, 25.71, 21.09, 17.65, 16.70 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{15}H_{25}$ $(M+H^+)$: 205.1878; found 205.1951.



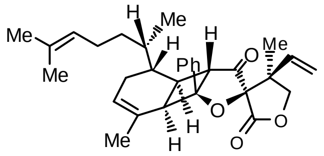
7

Racemic zingiberene: The same procedure for the preparation of zingiberene (**3**) was followed using the appropriate enone[1] (2.24 g, 10.0 mmol) as starting material. Spectroscopic data are in accord to those reported in literature.[2]



racemic zingiberene

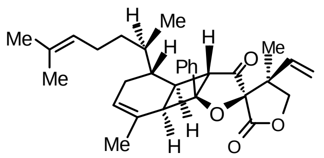
Biyouyanagin 6: Obtained from 4-*epi*-hyperolactone C (**5**)[3] and zingiberene (**3**) in 52% yield. **6**:



6

R_f = 0.28 (silica gel, pure benzene); $[\alpha]_D^{25}$ = +153.0 (*c* = 0.50, $CHCl_3$); IR ν_{max} (film): 2966, 2922, 2857, 1792, 1742, 1108, 756, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.32 (m, 5 H), 5.96 (dd, *J* = 17.5, 10.9 Hz, 1 H), 5.48 (m, 1 H), 5.30 (d, *J* = 10.9 Hz, 1 H), 5.11 (m, 1 H), 5.11 (d, *J* = 17.5 Hz, 1 H), 4.48 (d, *J* = 8.8 Hz, 1 H), 4.19 (d, *J* = 8.8 Hz, 1 H), 3.44 (d, *J* = 8.4 Hz, 1 H), 3.20 (dd, *J* = 6.2, 1.2 Hz, 1 H), 3.09 (m, 1 H), 2.15 (m, 1 H), 2.04 (m, 1 H), 2.01 (m, 1 H), 1.91 (m, 1 H), 1.73 (m, 1 H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.43 (m, 2 H), 1.18 (m, 1 H), 0.96 (s, 3 H), 0.82 (d, *J* = 6.8 Hz, 3 H), 0.67 (s, 3 H) ppm; NMR (150 MHz, $CDCl_3$) δ = 209.85, 171.62, 139.29, 137.59, 131.49, 131.37, 127.81, 127.71, 125.96, 124.52, 123.76, 115.55, 92.28, 89.35, 72.97, 52.60, 50.32, 48.74, 38.68, 36.12, 35.18, 34.92, 25.82, 25.68, 23.47, 21.59, 17.65, 16.83, 15.26 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ (M+ H^+): 475.2843; found 475.2844.

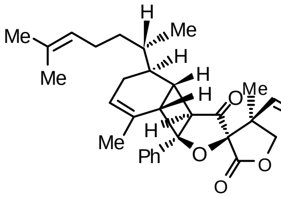
Biyouyanagin 8: Obtained from 4-*epi*-hyperolactone C (**5**)[3] and 7-*epi*-zingiberene (**7**) in 37% yield. **8**:



8

R_f = 0.29 (silica gel, pure benzene); $[\alpha]_D^{25}$ = +214.4 (*c* = 0.13, $CHCl_3$); IR ν_{max} (film): 2964, 2926, 1793, 1742, 1108, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.31 (m, 5 H), 5.96 (dd, *J* = 17.5, 10.9 Hz, 1 H), 5.48 (m, 1 H), 5.31 (d, *J* = 10.9 Hz, 1 H), 5.11 (d, *J* = 17.5 Hz, 1 H), 5.07 (m, 1 H), 4.49 (d, *J* = 8.9 Hz, 1 H), 4.20 (d, *J* = 8.9 Hz, 1 H), 3.41 (d, *J* = 8.3 Hz, 1 H), 3.23 (d, *J* = 6.4 Hz, 1 H), 3.18 (m, 1 H), 2.23 (m, 1 H), 2.05 (m, 1 H), 2.00 (m, 1 H), 1.87 (m, 1 H), 1.69 (m, 1 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 1.41 (m, 1 H), 1.37 (m, 1 H), 1.15 (m, 1 H), 0.95 (s, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H), 0.66 (s, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 209.84, 171.69, 139.29, 137.60, 131.50, 131.39, 127.85, 127.74, 126.00, 124.61, 123.58, 115.59, 92.33, 89.32, 73.00, 52.38, 50.14, 48.75, 38.76, 35.48, 35.01, 34.67, 25.71, 25.52, 25.22, 21.68, 17.66, 17.25, 15.26 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ (M+H^+): 475.2843; found 475.2849.

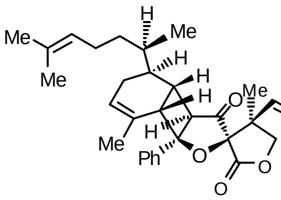
Biyouyanagin 9: Obtained from 4-*epi*-hyperolactone C (**5**)[3] and *ent*-7-*epi*-zingiberene (*ent*-**7**)[4] in



9

39% yield. **9**: R_f = 0.38 (silica gel, pure benzene); $[\alpha]_D^{25}$ = +241.8 (*c* = 0.17, $CHCl_3$); IR ν_{max} (film): 3022, 2968, 2917, 1791, 1741, 1215, 1107, 755, 701, 669 cm^{-1}; NMR (600 MHz, $CDCl_3$) δ = 7.29 (m, 5 H), 5.92 (dd, *J* = 17.5, 10.9 Hz, 1 H), 5.55 (d, *J* = 6.7 Hz, 1 H), 5.28 (d, *J* = 10.9 Hz, 1 H), 5.11 (m, 1 H), 5.05 (d, *J* = 17.5 Hz, 1 H), 4.46 (d, *J* = 8.8 Hz, 1 H), 4.16 (d, *J* = 8.8 Hz, 1 H), 3.64 (m, 1 H), 3.35 (m, 2 H), 2.33 (m, 1 H), 2.02 (m, 1 H), 1.92 (m, 1 H), 1.85 (m, 1 H), 1.70 (s, 3 H), 1.61 (s, 3 H), 1.50 (m, 1 H), 1.43 (m, 1 H), 1.35 (m, 1 H), 1.19 (m, 1 H), 0.93 (s, 3 H), 0.87 (d, *J* = 6.6 Hz, 3 H), 0.54 (s, 3 H) ppm; NMR (150 MHz, $CDCl_3$) δ = 209.70, 171.54, 138.99, 137.59, 131.61, 131.35, 127.99, 127.65, 126.28, 124.71, 124.64, 115.52, 92.54, 89.27, 72.97, 50.98, 48.63, 47.24, 37.83, 35.16, 34.21, 33.79, 26.01, 25.74, 24.72, 22.09, 17.68, 17.01, 15.18 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ ($M+H^+$): 475.2843; found 475.2846.

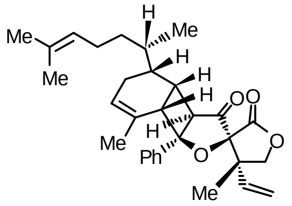
Biyouyanagin 10: Obtained from 4-*epi*-hyperolactone C (**5**)[3] and *ent*-zingiberene (*ent*-**3**)[4] in 44%



10

yield. **10**: R_f = 0.37 (silica gel, pure benzene); $[\alpha]_D^{25}$ = +65.7 (*c* = 0.21, $CHCl_3$); IR ν_{max} (film): 2964, 2921, 2852, 1793, 1741, 1148, 1379, 1106, 1018, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.29 (m, 5 H), 5.92 (dd, *J* = 17.5, 10.9 Hz, 1 H), 5.56 (d, *J* = 6.8 Hz, 1 H), 5.28 (d, *J* = 10.9 Hz, 1 H), 5.09 (m, 1 H), 5.05 (d, *J* = 17.5 Hz, 1 H), 4.46 (d, *J* = 8.8 Hz, 1 H), 4.16 (d, *J* = 8.8 Hz, 1 H), 3.63 (m, 1 H), 3.34 (m, 2 H), 2.28 (m, 2 H), 1.92 (m, 2 H), 1.69 (s, 3 H), 1.60 (s, 3 H), 1.42 (m, 2 H), 1.35 (m, 1 H), 1.05 (m, 1 H), 0.95 (d, *J* = 6.7 Hz, 3 H), 0.93 (s, 3 H), 0.53 (s, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 209.48, 171.48, 139.01, 137.62, 131.64, 131.34, 127.98, 127.64, 126.28, 124.75, 124.47, 115.49, 92.51, 89.27, 72.92, 51.08, 48.63, 47.35, 37.82, 35.61, 34.25, 34.17, 25.71, 25.37, 25.04, 22.09, 17.49, 16.42, 15.16 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ ($M+H^+$): 475.2843; found 475.2833

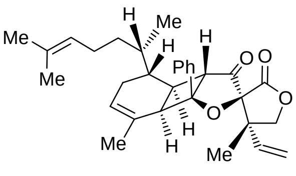
Biyouyanagin 11: Obtained from hyperolactone C (**4**)[4] and zingiberene (**3**)[4] in 54% yield. **11**: R_f



11

= 0.33 (silica gel, pure benzene); $[\alpha]_D^{25}$ = –199.2 (*c* = 0.60, $CHCl_3$); IR ν_{max} (film): 3020, 2926, 2855, 1791, 1741, 1215, 1104, 754, 668 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.28 (m, 3 H), 7.24 (m, 2 H), 5.52 (d, *J* = 6.9 Hz, 1 H), 5.08 (m, 1 H), 5.06 (dd, *J* = 17.6, 10.9 Hz, 1 H), 4.68 (d, *J* = 8.7 Hz, 1 H), 4.66 (d, *J* = 11.0 Hz, 1 H), 4.46 (d, *J* = 17.6 Hz, 1 H), 3.93 (d, *J* = 8.6 Hz, 1 H), 3.57 (m, 1 H), 3.36 (d, *J* = 7.8 Hz, 1 H), 3.32 (d, *J* = 7.4 Hz, 1 H), 2.25 (m, 1 H), 1.98 (m, 1 H), 1.89 (m, 1 H), 1.81 (m, 1 H), 1.69 (s, 3 H), 1.60 (s, 3 H), 1.41 (m, 2 H), 1.34 (m, 1 H), 1.25 (s, 3 H), 1.04 (m, 1 H), 0.95 (s, 3 H), 0.93 (d, *J* = 6.7 Hz, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 209.11, 171.44, 139.39, 134.25, 131.63, 131.31, 127.86, 127.61, 126.11, 124.71, 124.50, 118.18, 93.27, 89.50, 73.58, 50.90, 48.89, 46.54, 37.82, 35.40, 34.26, 34.11, 25.71, 25.32, 25.04, 22.17, 20.03, 17.50, 16.41 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ ($M+H^+$): 475.2843; found 475.2837.

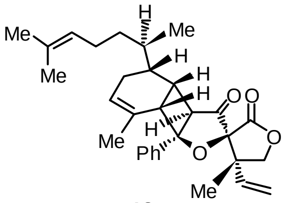
Biyouyanagin 12: Obtained from hyperolactone C (**4**)[4] and zingiberene (**3**)[4] in 4% yield. **12**: R_f =



12

0.27 (silica gel, pure benzene); $[\alpha]_D^{25}$ = –6.1 (*c* = 0.65, $CHCl_3$); IR νmax (film): 2954, 2929, 2857, 1795, 1742, 1215, 1100, 835 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.40 (m, 5 H), 6.10 (dd, *J* = 17.5, 10.8 Hz, 1 H), 5.50 (m, 1 H), 5.44 (m, 2 H), 5.08 (m, 1 H), 4.75 (d, *J* = 8.7 Hz, 1 H), 4.00 (d, *J* = 8.7 Hz, 1 H), 3.12 (dd, *J* = 5.6, 1.1 Hz, 1 H), 2.99 (d, *J* = 8.9 Hz, 1 H), 2.78 (m, 1 H), 2.13 (m, 1 H), 2.03 (m, 1 H), 1.94 (m, 2 H), 1.71 (m, 1 H), 1.69 (s, 3 H), 1.60 (s, 3 H), 1.50 (s, 3 H), 1.41 (m, 2 H), 1.17 (m, 1 H), 1.00 (s, 3 H), 0.84 (d, *J* = 6.7 Hz, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 209.67, 171.14, 139.12, 135.88, 131.55, 131.47, 127.50, 127.46, 125.83, 124.46, 123.86, 119.43, 92.74, 88.69, 74.07, 53.55, 51.21, 48.84, 39.30, 34.87, 34.48, 33.26, 29.70, 25.83, 25.72, 23.83, 21.45, 18.92, 17.74, 16.63 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ ($M+H^+$): 475.2843; found 475.2851.

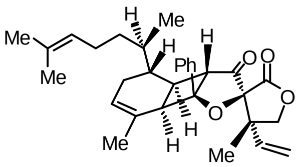
Biyouyanagin 13: Obtained from hyperolactone C (**4**)[4] and 7-*epi*-zingiberene (**7**) in 37% yield. **13**: R_f = 0.32 (silica gel, pure benzene); $[\alpha]_D^{25}$ = –115.0 (*c* = 0.1, $CHCl_3$); IR ν_{max} (film): 3020,



13

2927, 2857, 1789, 1743, 1215, 1214, 753 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27 (m, 5 H), 5.52 (d, *J* = 6.8 Hz, 1 H), 5.10 (m, 1 H), 5.06 (dd, *J* = 17.6, 10.9 Hz, 1 H), 4.67 (m, 2 H), 4.46 (d, *J* = 17.6 Hz, 1 H), 3.93 (d, *J* = 8.6 Hz, 1 H), 3.58 (m, 1 H), 3.37 (d, *J* = 7.8 Hz, 1 H), 3.31 (d, *J* = 7.4 Hz, 1 H), 2.30 (m, 1 H), 2.01 (m, 1 H), 1.90 (m, 1 H), 1.81 (m, 1 H), 1.69 (s, 3 H), 1.61 (s, 3 H), 1.49 (s, 1 H), 1.42 (s, 1 H), 1.33 (s, 1 H), 1.25 (s, 3 H), 1.17 (s, 1 H), 0.96 (s, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 209.34, 171.52, 139.37, 134.24, 131.61, 131.34, 127.62, 126.12, 124.72, 124.61, 118.21, 93.31, 89.52, 73.63, 50.81, 48.89, 46.43, 37.86, 34.93, 34.15, 33.80, 29.70, 25.97, 25.74, 24.72, 22.18, 20.04, 17.68, 16.99 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ (M+H$^+$): 475.2843; found 475.2853.

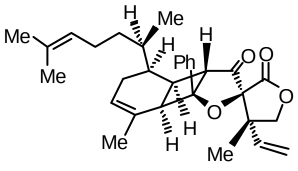
Biyouyanagin 14: Obtained from hyperolactone C (**4**)[4] and 7-*epi*-zingiberene (**7**) in 19% yield.



14

14: R_f = 0.26 (silica gel, pure benzene); $[\alpha]_D^{25}$ = +15.6 (*c* = 0.08, $CHCl_3$); IR ν_{max} (film): 3020, 2926, 2855, 1791, 1741, 1215, 1104, 754, 668 cm^{-1}; NMR (600 MHz, $CDCl_3$) δ = 7.36 (m, 5 H), 6.10 (dd, *J* = 17.5, 10.8 Hz, 1 H), 5.50 (m, 1 H), 5.46 (d, *J* = 17.5 Hz, 1 H), 5.43 (d, *J* = 11.2 Hz, 1 H), 5.08 (m, 1 H), 4.74 (d, *J* = 8.7 Hz, 1 H), 4.00 (d, *J* = 8.7 Hz, 1 H), 3.15 (d, *J* = 5.8 Hz, 1 H), 2.97 (d, *J* = 8.9 Hz, 1 H), 2.84 (m, 1 H), 2.23 (m, 1 H), 2.02 (m, 1 H), 1.92 (m, 2 H), 1.71 (m, 1 H), 1.69 (s, 3 H), 1.61 (s, 3 H), 1.50 (s, 3 H), 1.41 (m, 1 H), 1.37 (m, 1 H), 1.16 (m, 1 H), 0.97 (s, 3 H), 0.88 (d, *J* = 6.8 Hz, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 209.60, 171.12, 139.11, 135.95, 131.55, 131.39, 127.46, 125.82, 124.48, 123.84, 119.41, 92.78, 88.60, 74.07, 53.39, 51.06, 48.86, 39.29, 35.80, 34.64, 32.52, 29.70, 25.72, 25.53, 25.50, 21.49, 18.88, 17.70, 17.30 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ (M+H$^+$): 475.2843; found 475.2839.

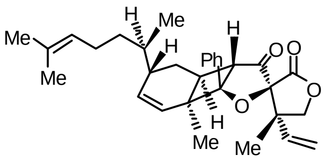
Biyouyanagin B (2): Obtained from hyperolactone C (**4**)[4] and *ent*-zingiberene (*ent*-**3**)[4] in 3% yield. **2**: R_f = 0.26 (silica gel, pure benzene); mp 125–126 °C, CH_2Cl_2/hexanes; $[\alpha]_D^{25}$ = –1.8 (*c* = 0.33, $CHCl_3$); {lit., $[\alpha]_D^{25}$ = –5.9 (*c* = 0.20, $CHCl_3$)}; IR ν_{max} (film): 3021, 2970, 2915, 1792, 1741,



2: biyouyanagin B

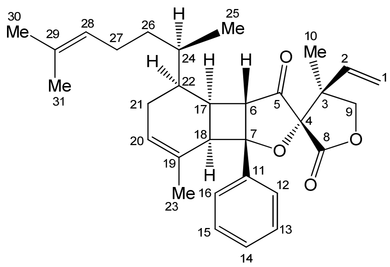
1216, 1101, 756 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.26 (m, 5 H), 6.07 (dd, *J* = 17.5, 10.8 Hz, 1 H), 5.57 (d, *J* = 6.9 Hz, 1 H), 5.44 (d, *J* = 17.5 Hz, 1 H), 5.38 (d, *J* = 10.8 Hz, 1 H), 5.11 (t, *J* = 7.0 Hz, 1 H), 4.72 (d, *J* = 8.7 Hz, 1 H), 3.97 (d, *J* = 8.7 Hz, 1 H), 3.29 (m, 2 H), 3.03 (d, *J* = 7.4 Hz, 1 H), 2.29 (m, 1 H), 2.01 (m, 1 H), 1.94 (m, 1 H), 1.83 (m, 1 H), 1.70 (s, 3 H), 1.64 (s, 3 H), 1.51 (s, 3 H), 1.47 (m, 2 H), 1.27 (m, 1 H), 1.08 (m, 1 H), 0.96 (d, *J* = 6.7 Hz, 3 H), 0.92 (s, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 209.39, 170.92, 138.72, 136.22, 131.77, 131.20, 127.40, 127.13, 126.06, 124.77, 124.66, 119.26, 92.68, 88.60, 74.03, 51.19, 48.83, 47.18, 37.89, 34.37, 33.92, 33.08, 25.74, 25.53, 24.90, 22.23, 18.84, 17.74, 16.65 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ ($M+H^+$): 475.2843; found 475.2834.

Biyouyanagin C (15): Obtained from hyperolactone C (**4**)[4] and *ent*-zingiberene (*ent*-**3**)[4] in 2% yield. **15**: R_f = 0.25 (silica gel, pure benzene); $[\alpha]_D^{25}$ = +27.6 (*c* = 0.50, $CHCl_3$); IR ν_{max} (film): 3020, 2972, 2921, 2855, 1792, 1741, 1215, 1100, 754 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32 (m, 3 H), 7.15 (m, 2 H), 6.07 (dd, *J* = 17.5, 10.7 Hz, 1 H), 5.48 (d, *J* = 10.5 Hz, 1 H), 5.45 (d, *J* = 4.3 Hz, 1 H), 5.43 (d, *J* = 1.9 Hz, 1 H), 5.10 (m, 1 H), 4.88 (m, 1 H), 4.69 (d, *J* = 8.7 Hz, 1 H), 3.92 (d, *J* = 8.7 Hz, 1 H), 3.32 (d, *J* = 7.4 Hz, 1 H), 2.87 (m, 1 H), 2.12 (m, 1 H), 2.05 (m, 1 H), 1.94 (m, 1 H), 1.69 (s, 3 H), 1.65 (m, 1 H), 1.62 (s, 3 H), 1.55 (m, 1 H), 1.49 (s, 3 H), 1.38 (m, 1 H), 1.26 (s, 3 H), 1.28 (m, 1 H), 1.19 (m, 1 H), 0.83 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 209.42, 170.94, 138.89, 136.27, 131.94, 131.60, 131.54, 127.54, 127.52, 127.46, 126.16, 124.47, 119.55, 92.63, 90.08, 48.86, 47.02, 45.55, 37.68, 36.05, 35.24, 34.15, 26.07, 25.73, 21.94, 19.10, 18.94, 17.69, 15.56 ppm; HRMS (ESI-TOF): *m/z* calcd for $C_{31}H_{39}O_4$ ($M+H^+$): 475.2843; found 475.2839.



15: biyouyanagin C

Table 1. ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectroscopic data comparison for natural[5] versus synthetic biyouyanagin B (**2**).



biyouyanagin B (**2**)

Position	**Natural**[5] δ ^{1}H [ppm, mult, *J* (Hz)] 400 MHz	**Synthetic** δ ^{1}H [ppm, mult, *J* (Hz)] 600 MHz	**Natural**[5] δ ^{13}C [ppm, mult, *J* (Hz)] 100 MHz	**Synthetic** δ ^{13}C [ppm, mult, *J* (Hz)] 150 MHz
1	5.39 (d, 10.8, 1 H) 5.44 (d, 16.8, 1 H)	5.38 (d, *J* = 10.8, 1 H) 5.44 (d, *J* = 17.5, 1 H)	119.1	119.26
2	6.08 (dd, 17.6, 10.8, 1 H)	6.07 (dd, *J* = 17.5, 10.8, 1 H)	136.2	136.22
3			48.7	48.83
4			92.6	92.68
5			209.3	209.39
6	3.30 (m, 1 H)	3.29 (1 H, m)	48.7	48.83
7			88.5	88.60
8			170.8	170.92
9	3.98 (d, 8.8, 1 H) 4.73 (d, 8.8, 1 H)	3.97 (d, *J* = 8.7, 1 H) 4.72 (d, *J* = 8.7, 1 H)	73.9	74.03
10	1.52 (s, 3 H)	1.51 (s, 3 H)	18.8	18.84
11			138.6	138.89
12	7.28 (m, 1 H)	7.28 (m, 1 H)	126.0	126.16
13	7.28 (m, 1 H)	7.28 (m, 1 H)	127.0	127.46
14	7.28 (m, 1 H)	7.28 (m, 1 H)	127.3	127.52
15	7.28 (m, 1 H)	7.28 (m, 1 H)	127.0	127.46
16	7.28 (m, 1 H)	7.28 (m, 1 H)	126.0	126.16
17	3.30 (m, 1 H)	3.29 (m, 1 H)	33.0	33.08
18	3.04 (brd, 6.4, 1 H)	3.03 (d, *J* = 7.4, 1 H)	51.1	51.19
19			131.7	131.77
20	5.58 (brd, 6.4, 1 H)	5.57 (d, *J* = 6.9, 1 H)	124.7	124.77
21	1.82 (m, 1 H) 2.29 (m, 1 H)	1.83 (m, 1 H) 2.29 (m, 1 H)	25.4	25.53
22	1.28 (m, 1 H)	1.27 (m, 1 H)	37.8	37.89
23	0.93 (s, 3 H)	0.92 (3 H, s)	22.1	22.23
24	1.47 (m, 1 H)	1.47 (m, 1 H)	33.9	33.92
25	0.97 (3 H, d, 6.8)	0.96 (d, *J* = 6.7, 3 H)	16.5	16.65
26	1.08 (m, 1 H) 1.47 (m, 1 H)	1.08 (m, 1 H) 1.47 (m, 1 H)	34.3	34.37
27	1.98 (m, 2 H)	1.94 (m, 1 H) 2.01 (m, 1 H)	24.8	24.90
28	5.12 (t, 6.4, 1 H)	5.11 (t, *J* = 7.0, 1 H)	124.6	124.66
29			131.1	131.20
30	1.71 (s, 3 H)	1.70 (s, 3 H)	25.6	25.73
31	1.65 (s, 3 H)	1.64 (s, 3 H)	17.6	17.69

II. References

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[3] K. C. Nicolaou, T. R. Wu, D. Sarlah, D. M. Shaw, E. Rowcliffe, D. R. Burton, *J. Am. Chem. Soc.* **2008**, *130*, 11114–11121.

[4] K. C. Nicolaou, D. Sarlah, D. M. Shaw, *Angew. Chem.* **2007**, *119*, 4792–4795; *Angew. Chem. Int. Ed.* **2007**, *46*, 4708–4711.

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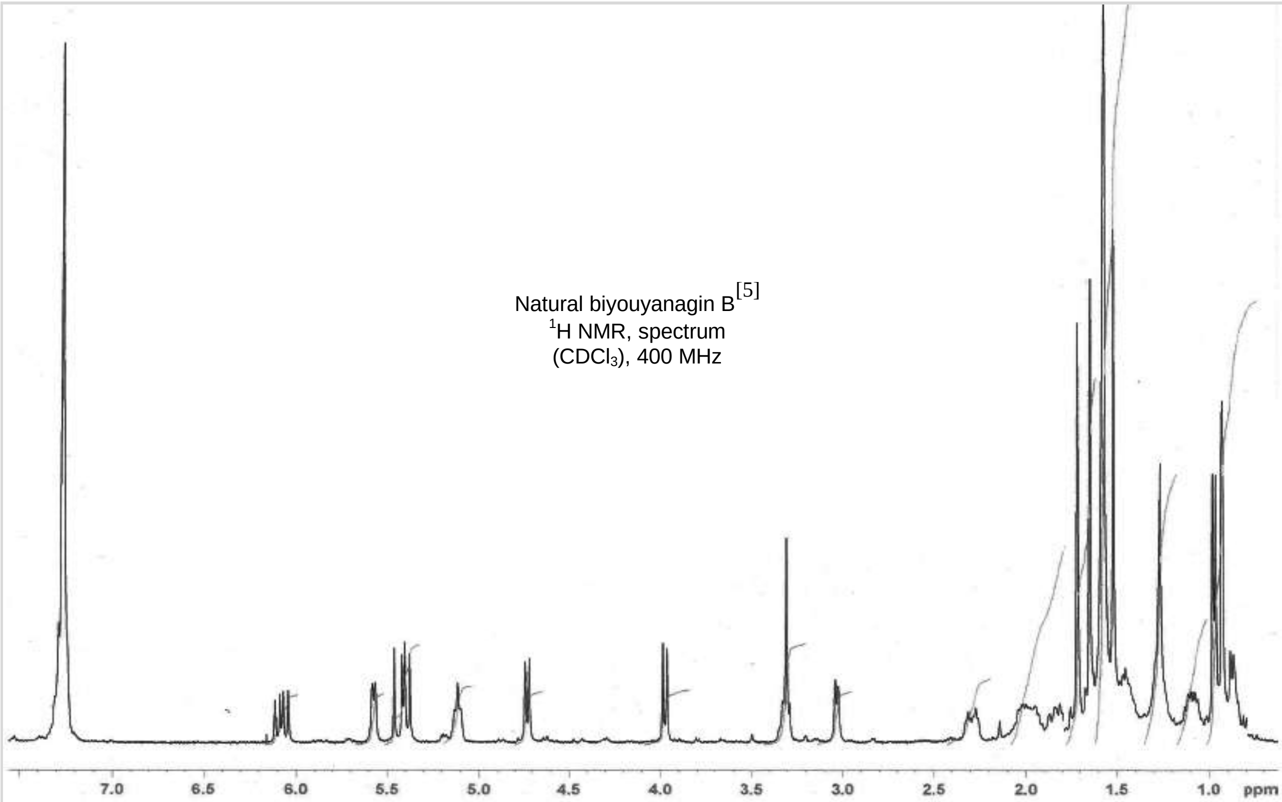
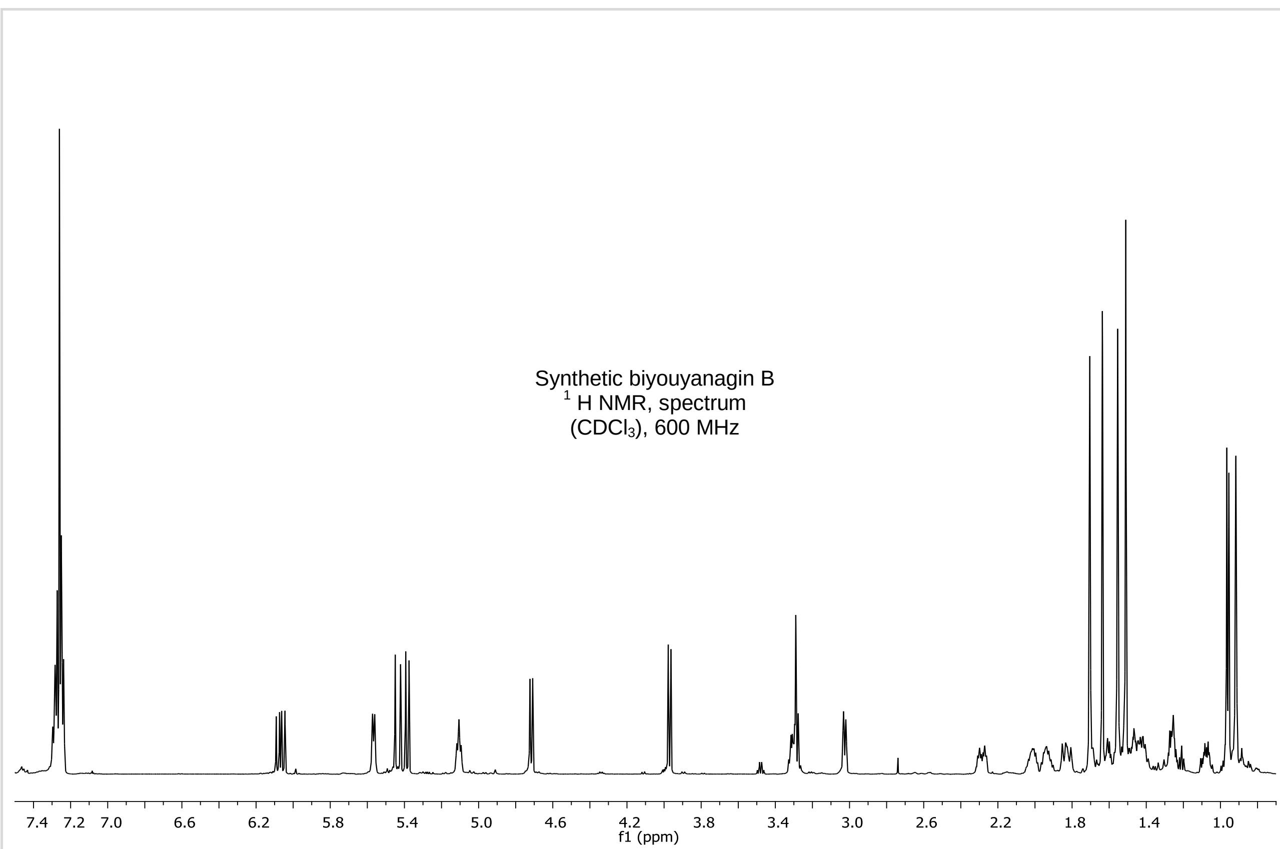
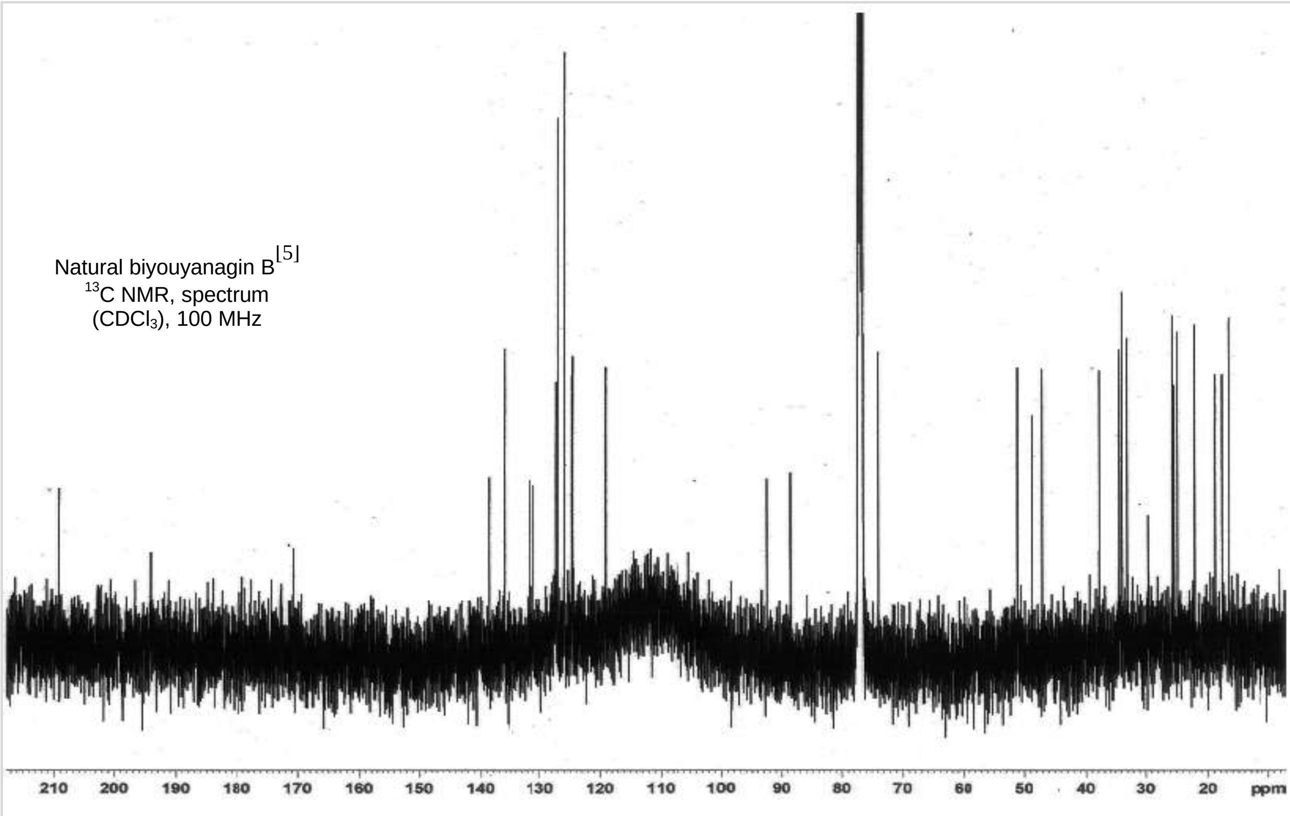
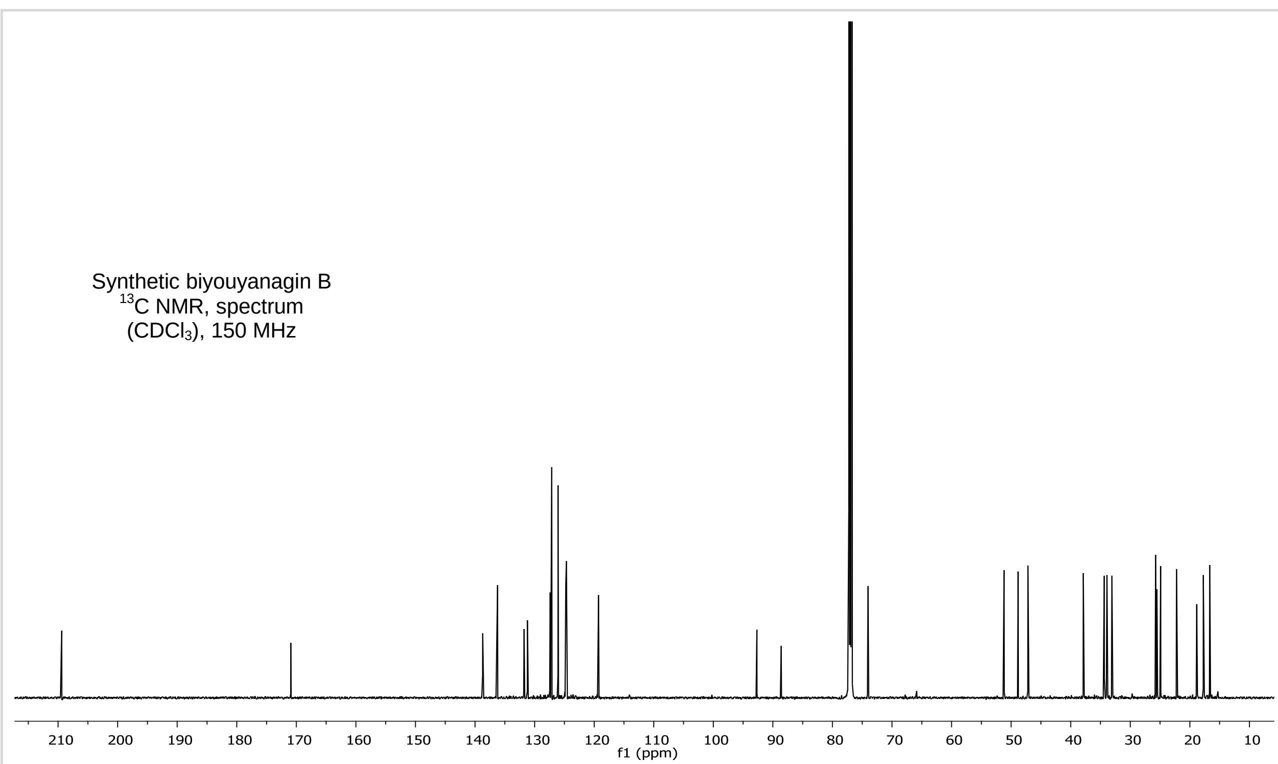
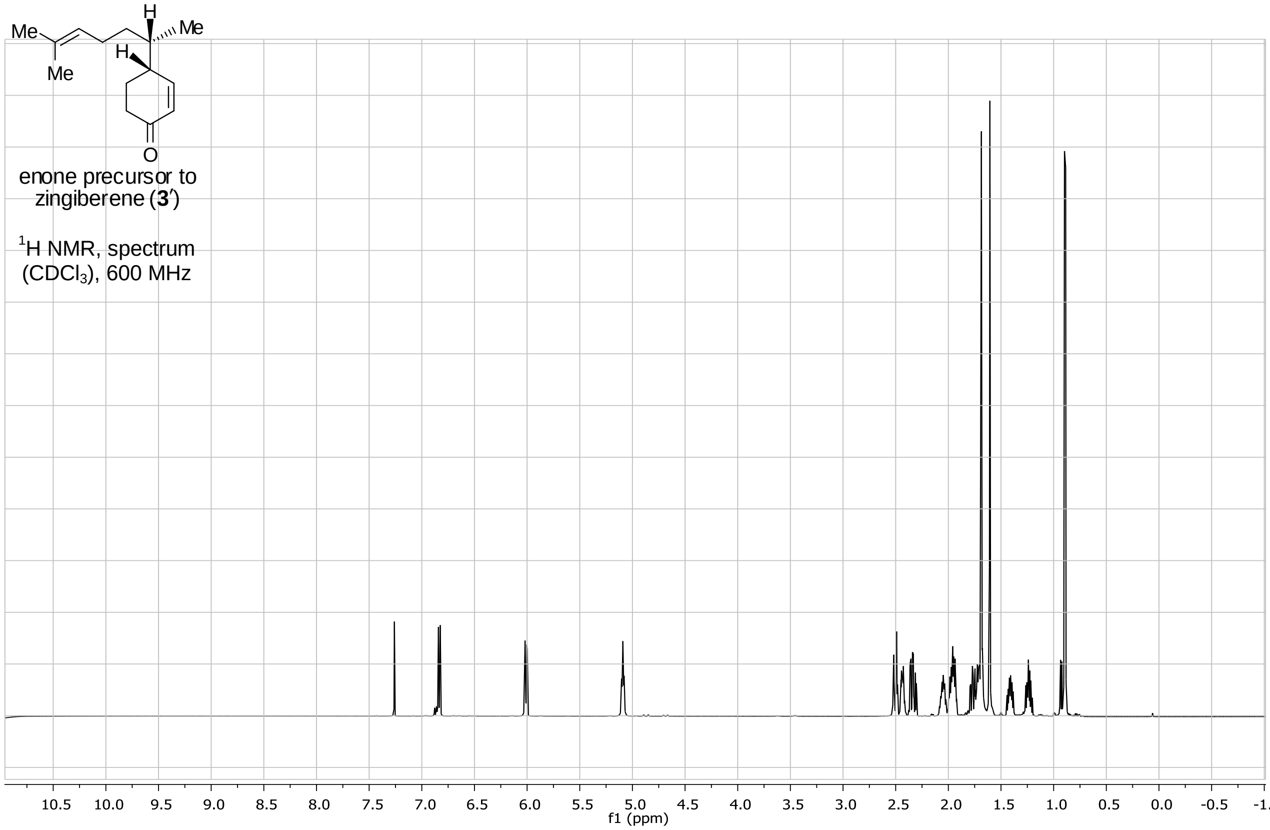
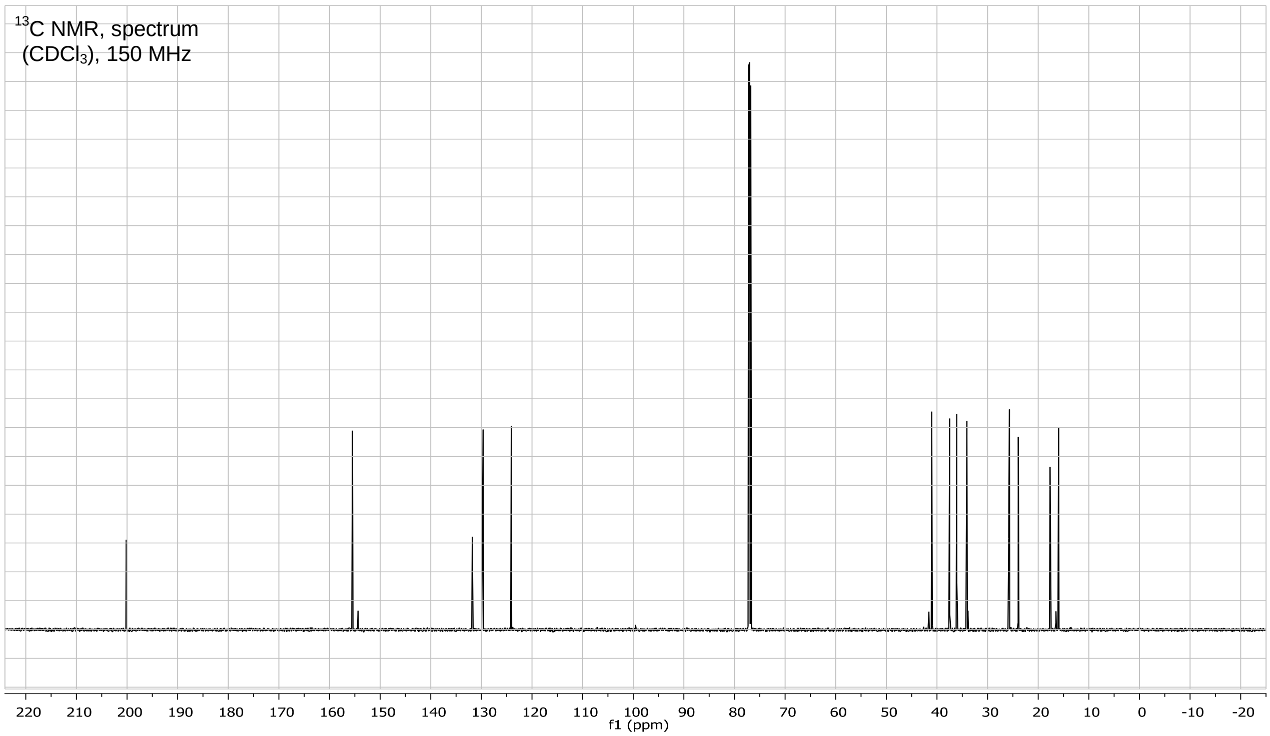

Natural biyouyanagin B[5]
¹H NMR, spectrum
(CDCl₃), 400 MHz
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

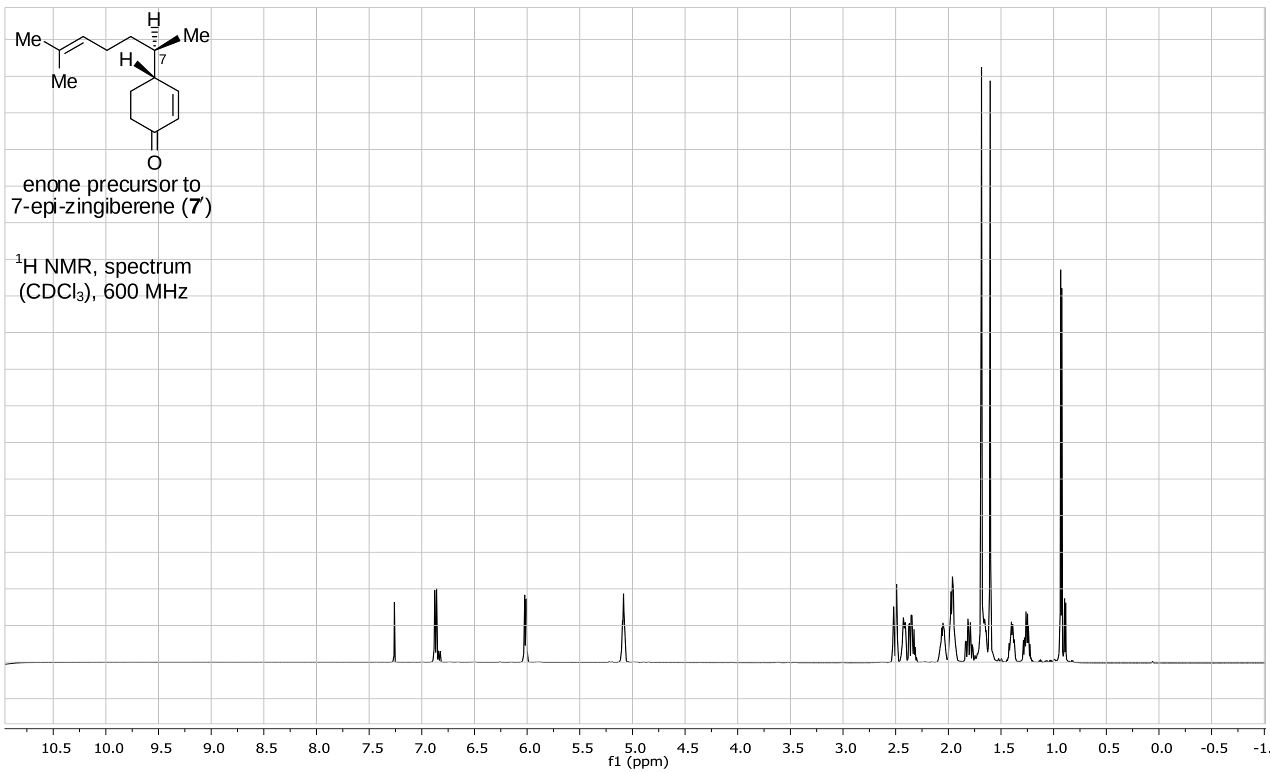

Synthetic biyouyanagin B
¹ H NMR, spectrum
(CDCl₃), 600 MHz
7.4
7.2
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
f1 (ppm)

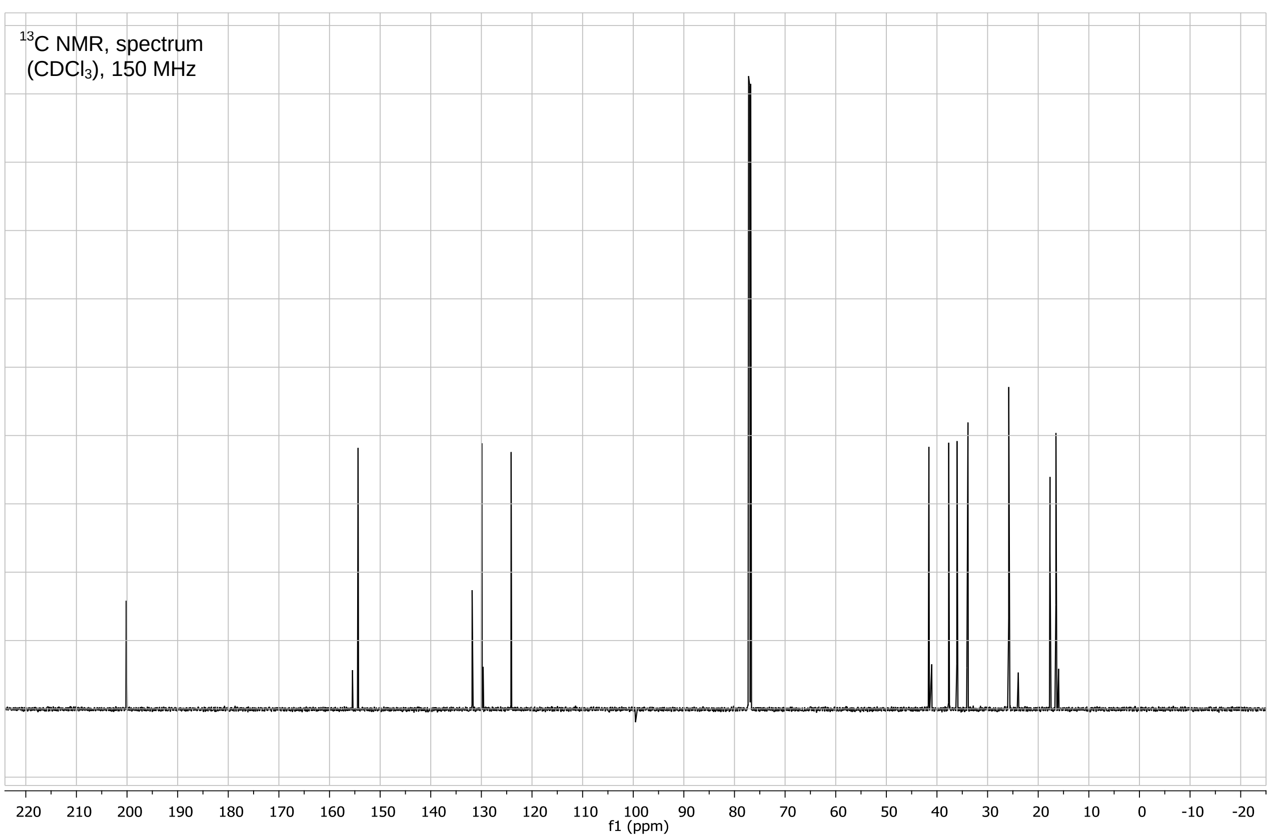

Natural biyouyanagin B[5]
^{13}C NMR, spectrum
($CDCl_3$), 100 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

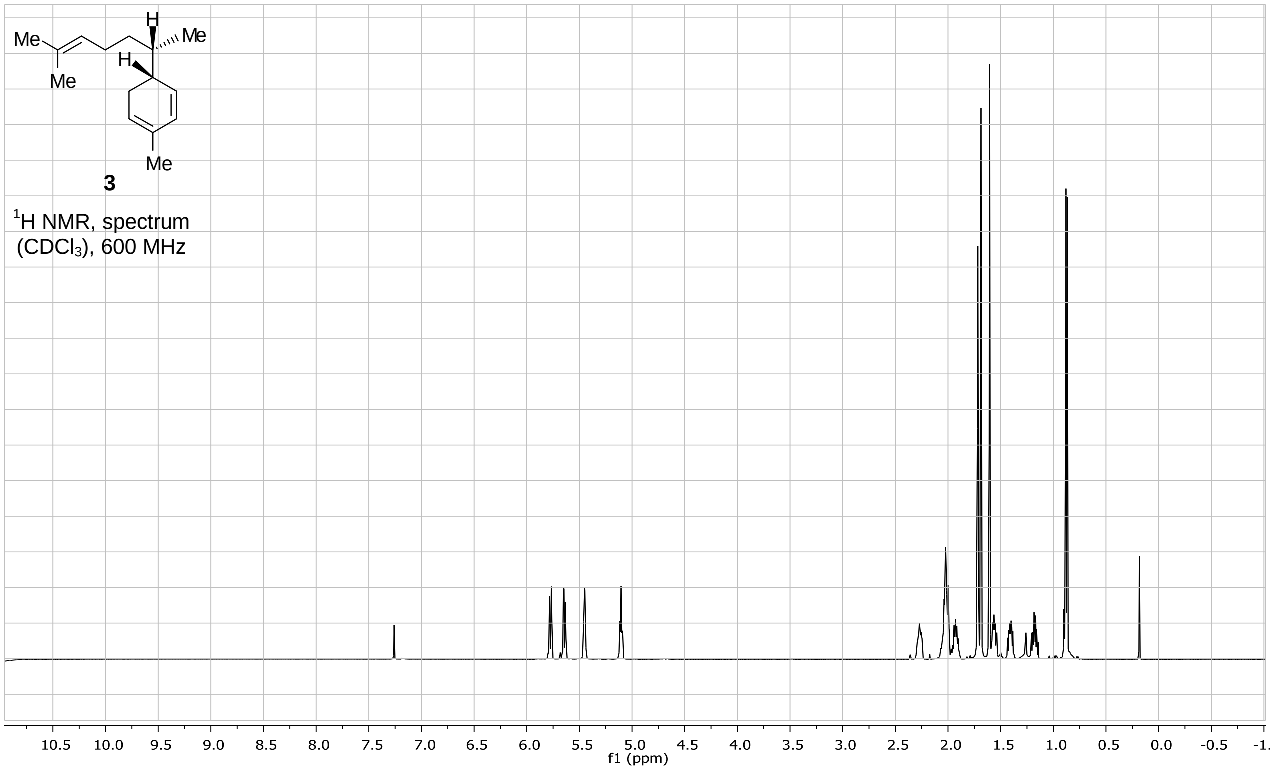

Synthetic biyouyanagin B
^{13}C NMR, spectrum
($CDCl_3$), 150 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me
Me
H
Me
H
O
enone precursor to zingiberene (3′)
1H NMR, spectrum (CDCl3), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

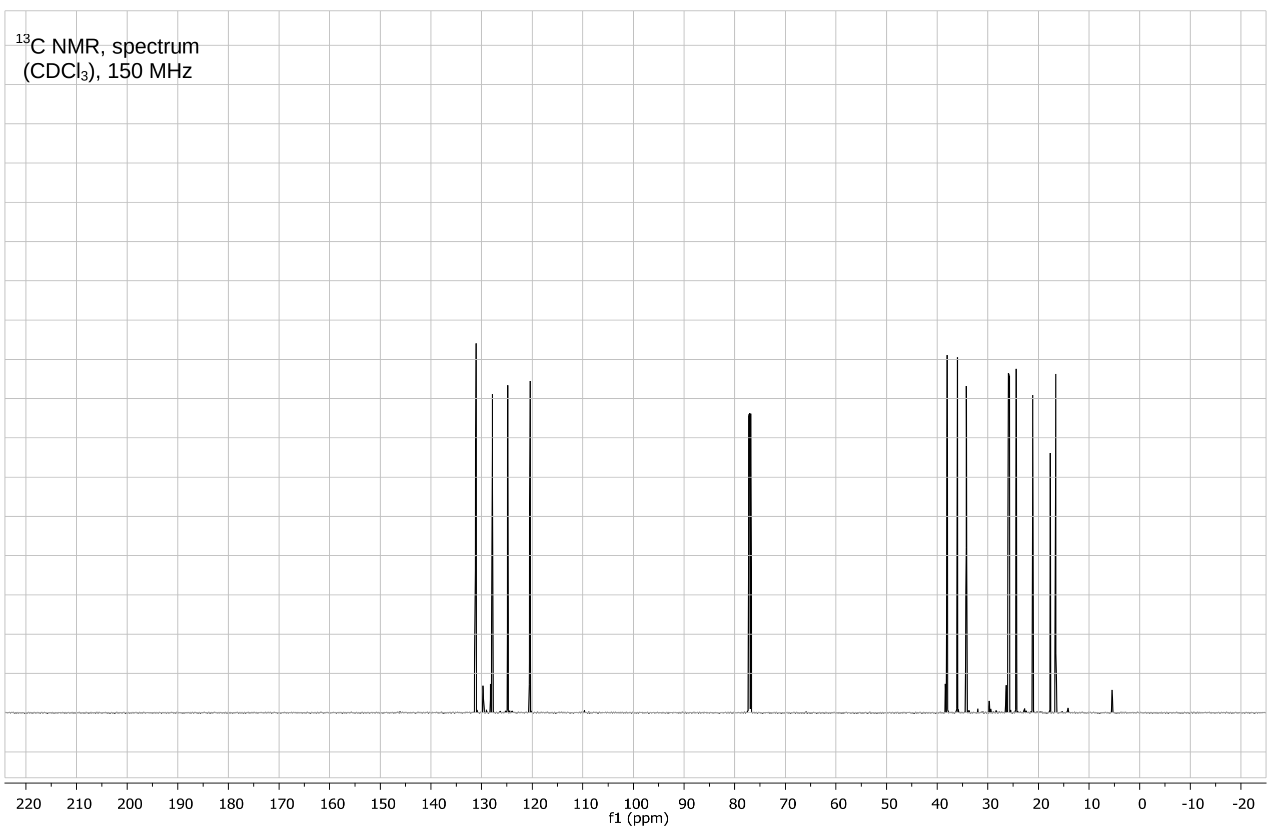

13C NMR, spectrum (CDCl3), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Me
Me
H
Me
H
7
O
enone precursor to
7-epi-zingiberene (7′)
1H NMR, spectrum
(CDCl3), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

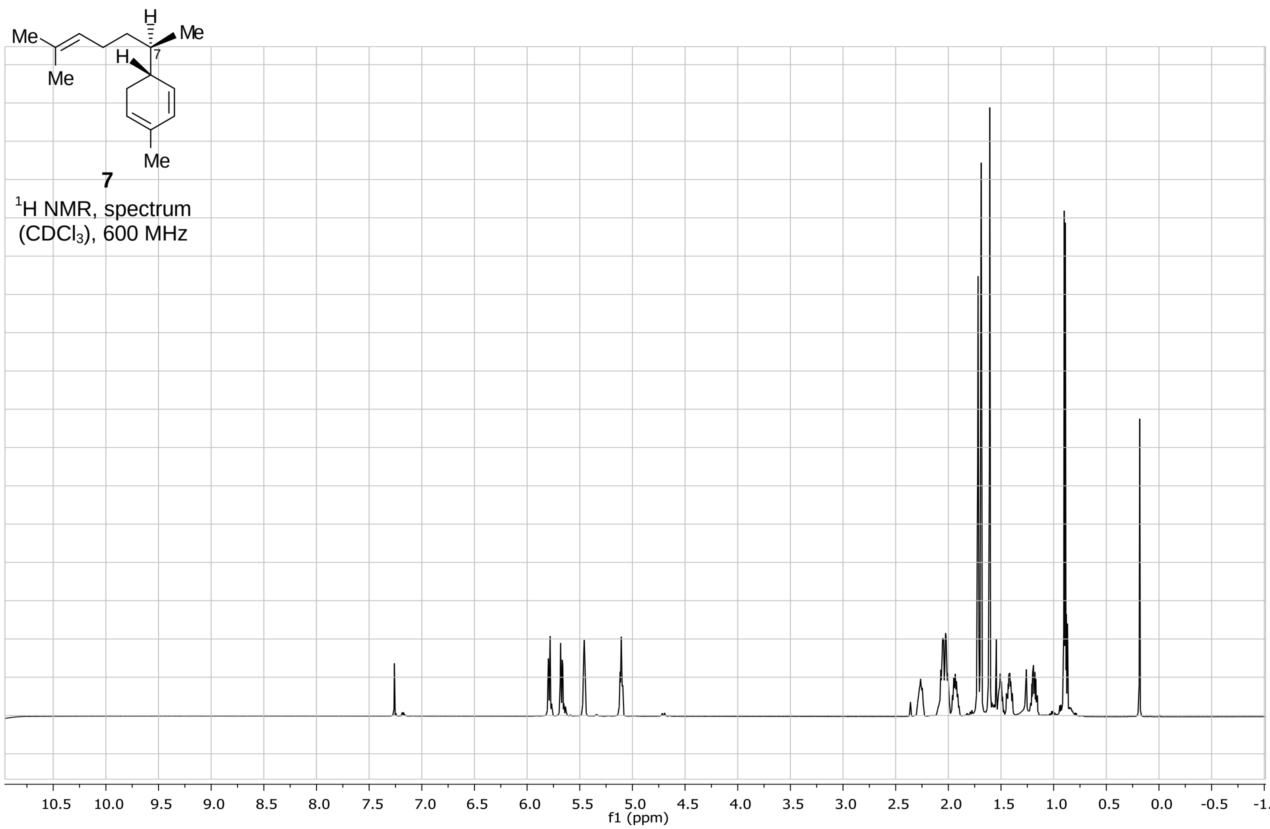

13C NMR, spectrum
(CDCl3), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

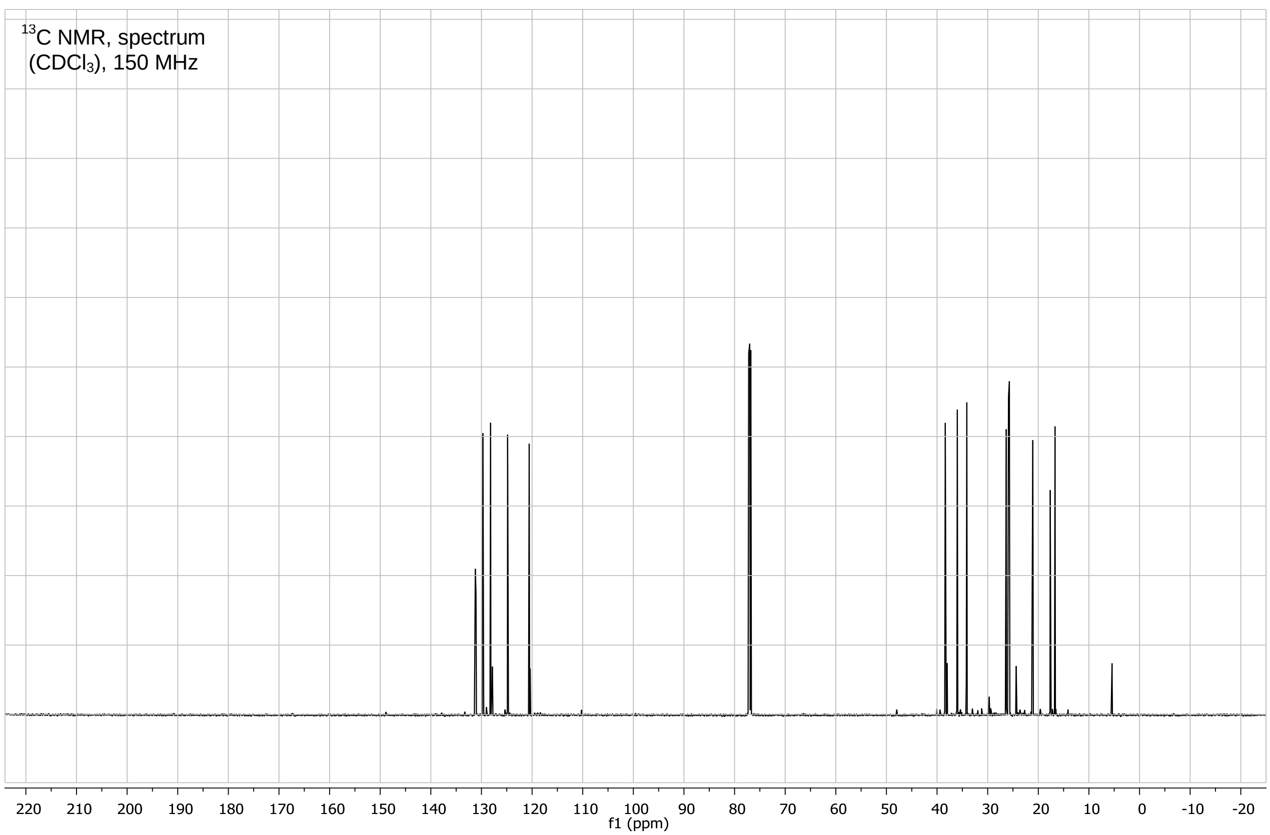


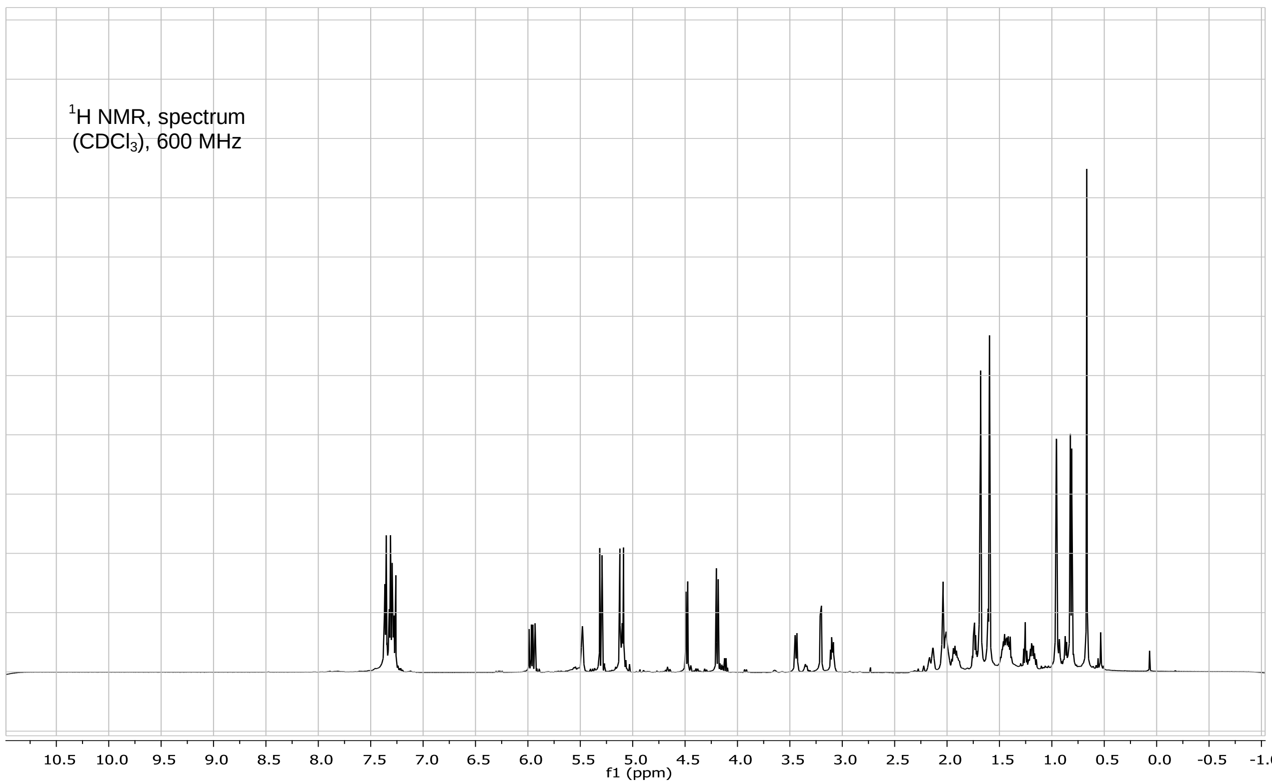
Me
Me
H
Me
H
Me
3
^{1}H NMR, spectrum
($CDCl_3$), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

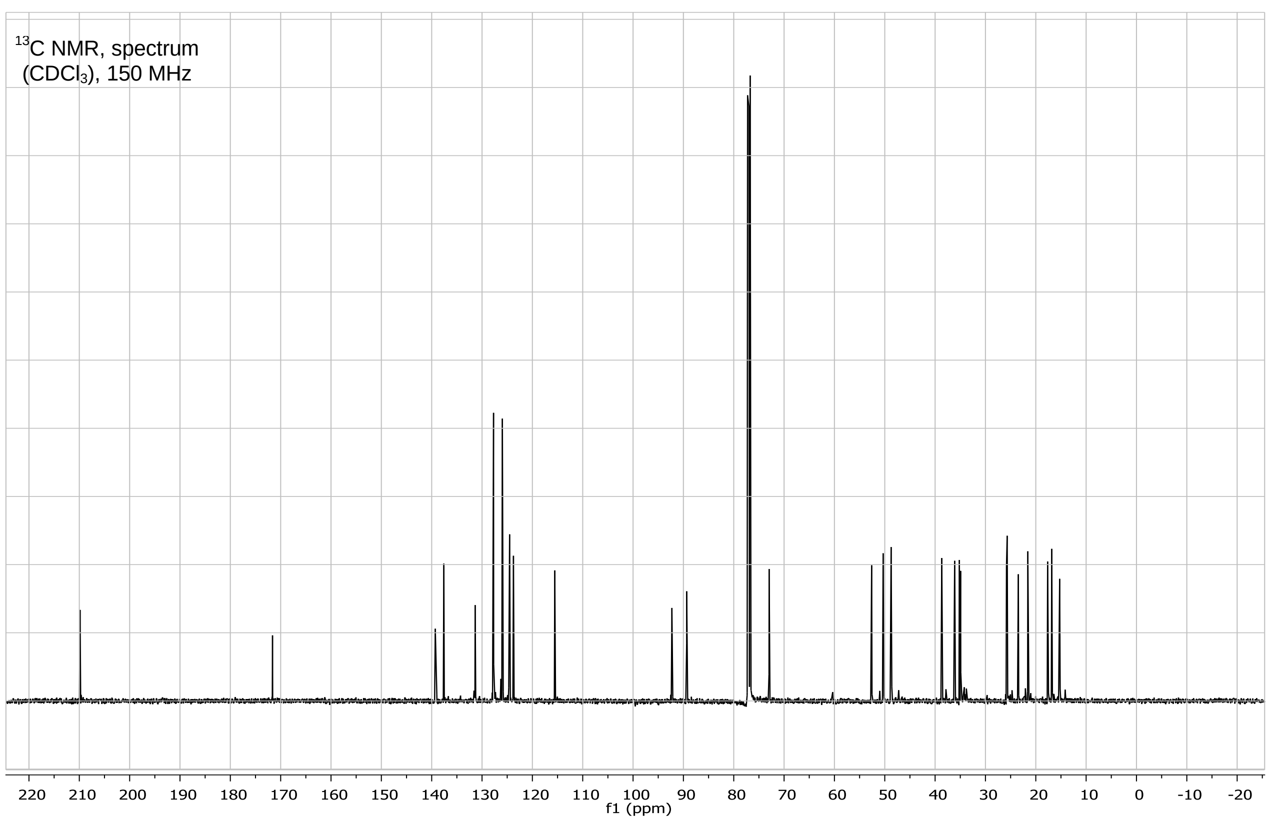


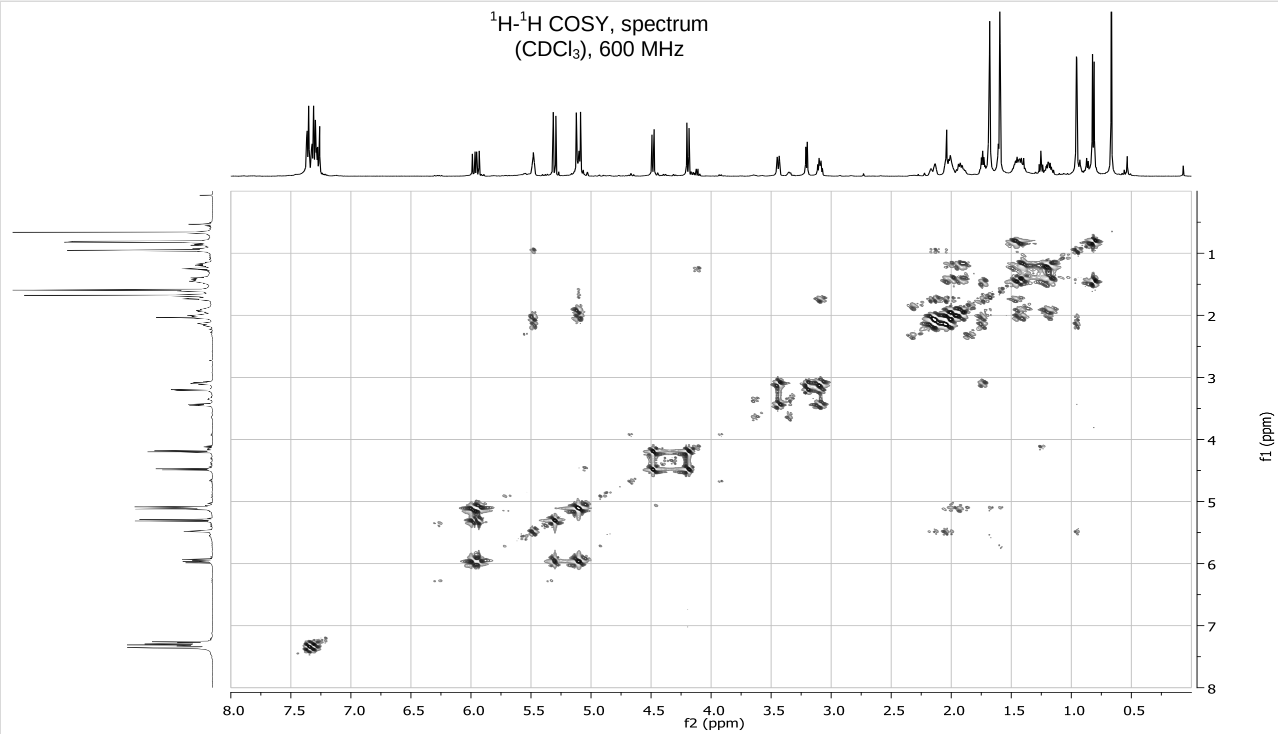
^{13}C NMR, spectrum
($CDCl_3$), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

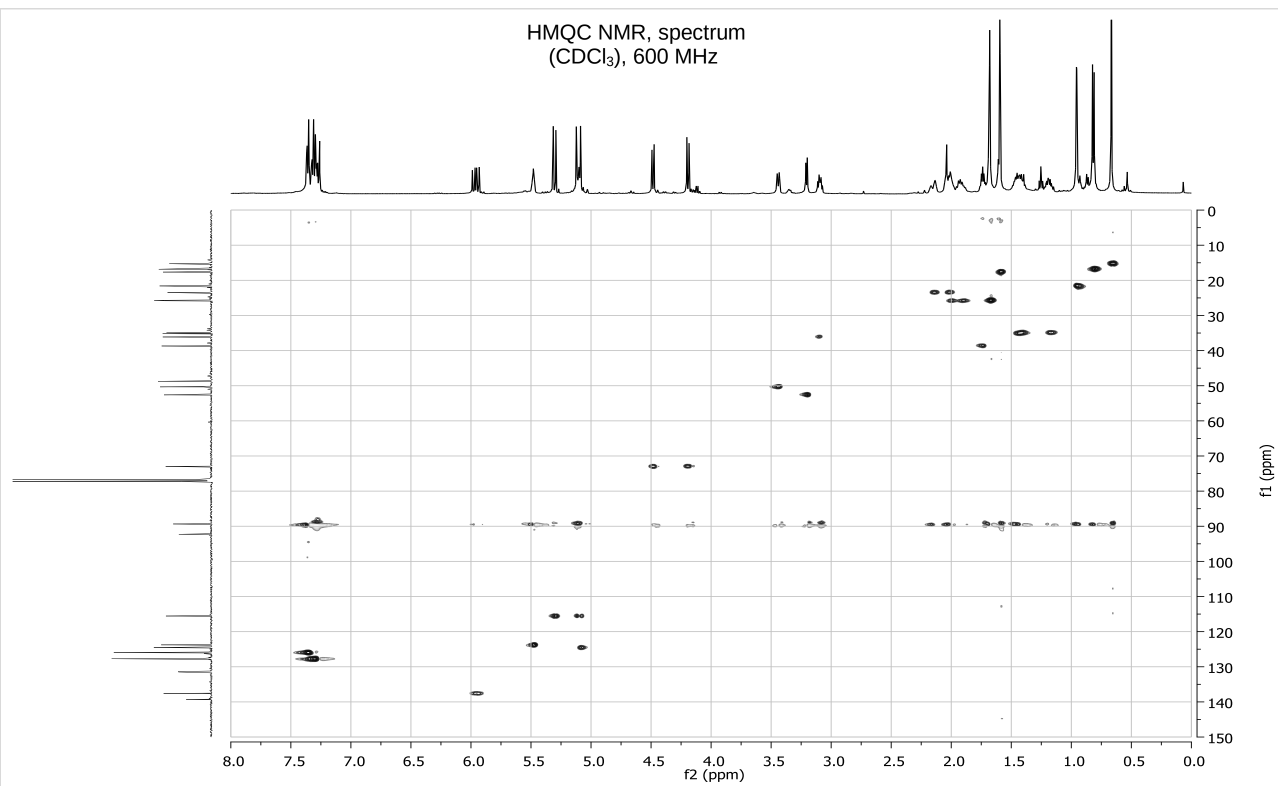

Me
Me
H
Me
7
H
Me
7
^{1}H NMR, spectrum
(CDCl$_3$), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

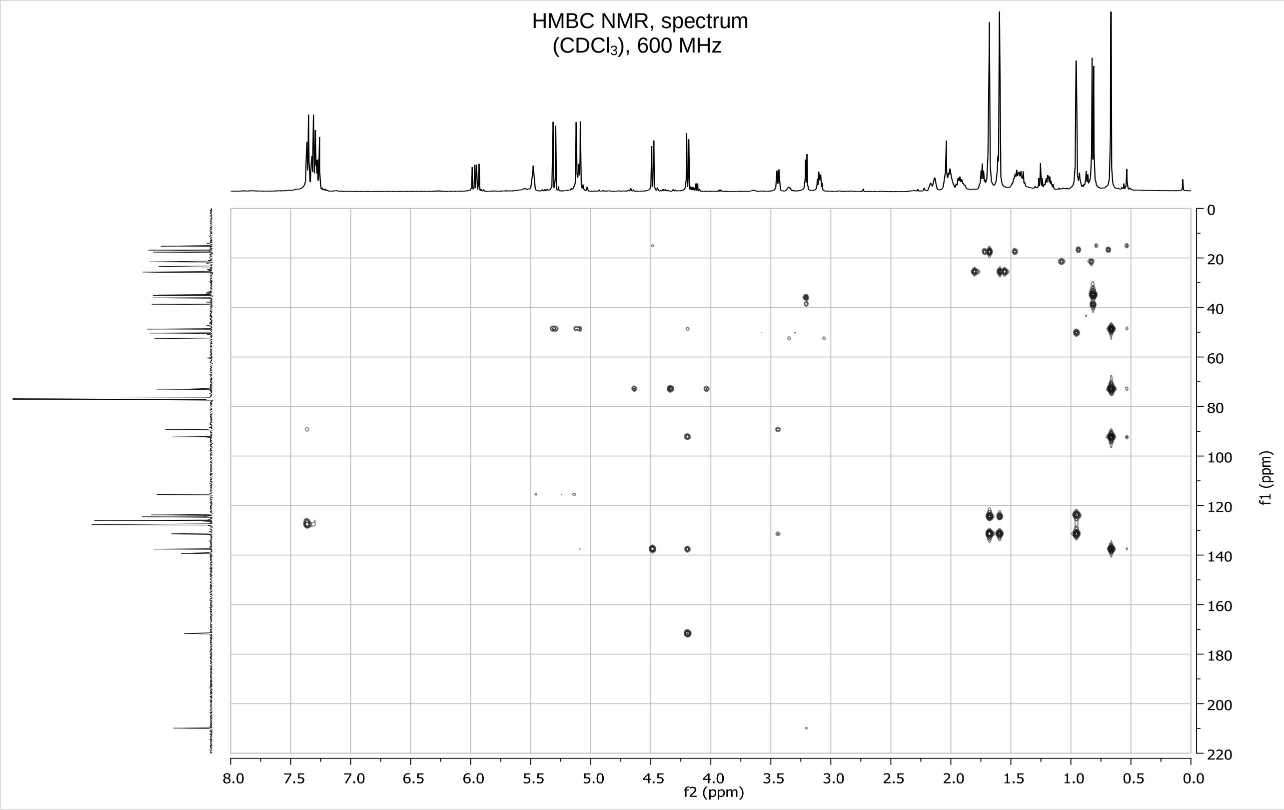

^{13}C NMR, spectrum
(CDCl$_3$), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

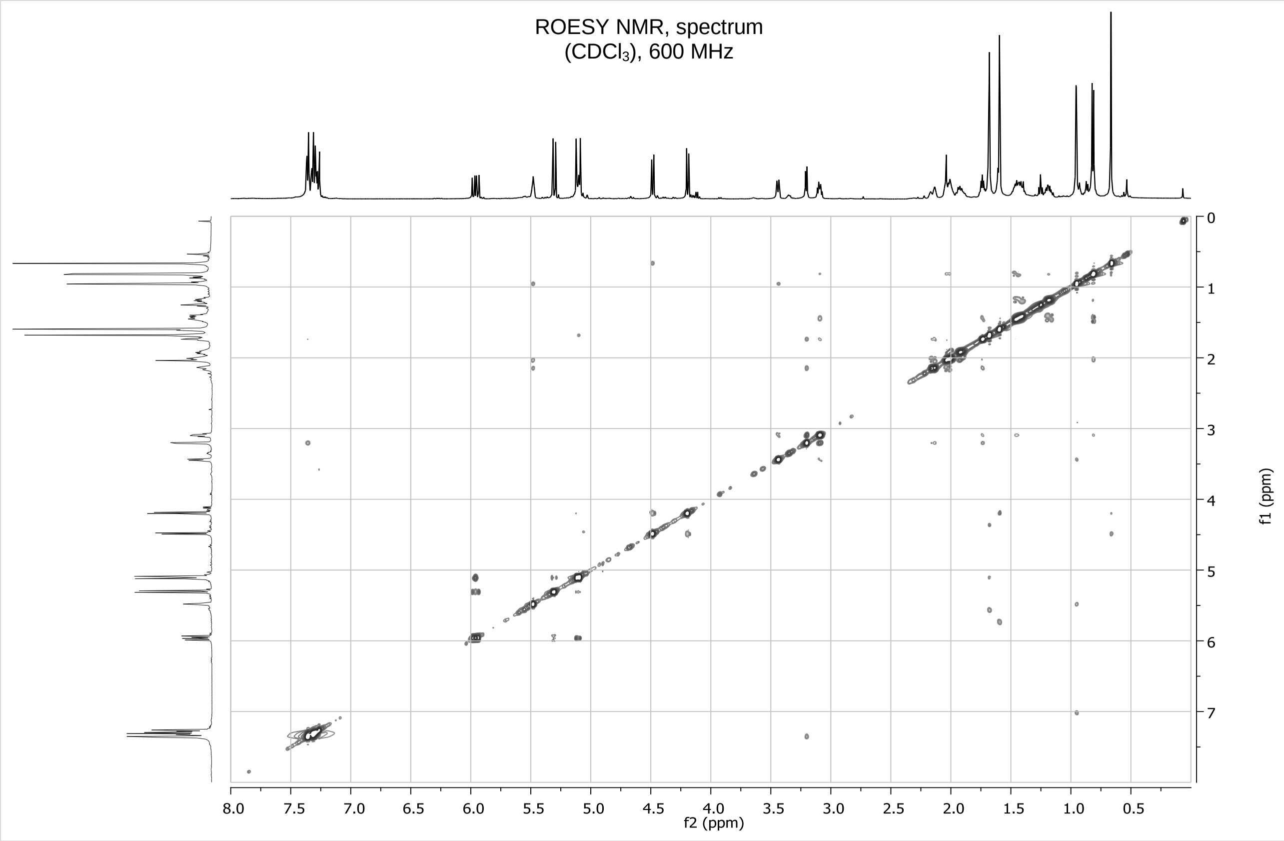

1H NMR, spectrum
(CDCl3), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

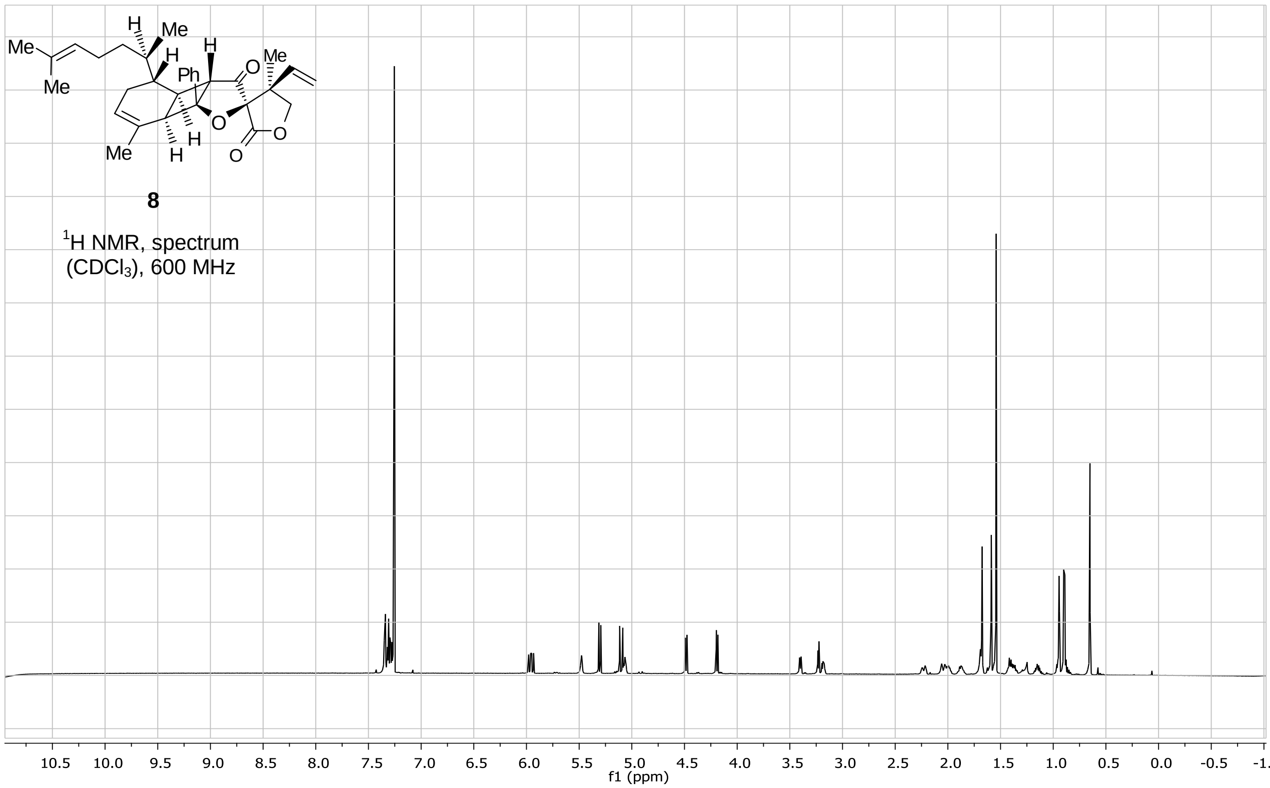

13C NMR, spectrum
(CDCl3), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

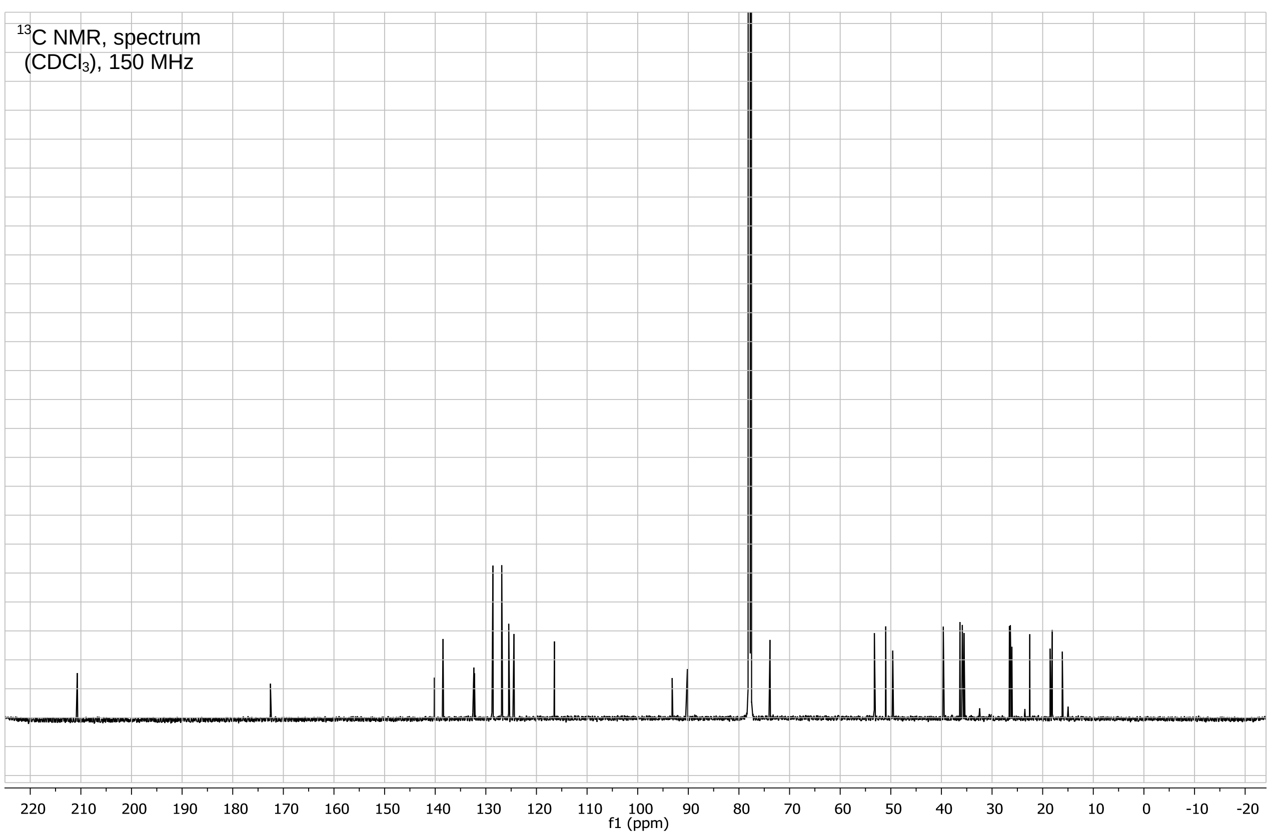

^{1}H-^{1}H COSY, spectrum
($CDCl_3$), 600 MHz
f2 (ppm)
f1 (ppm)

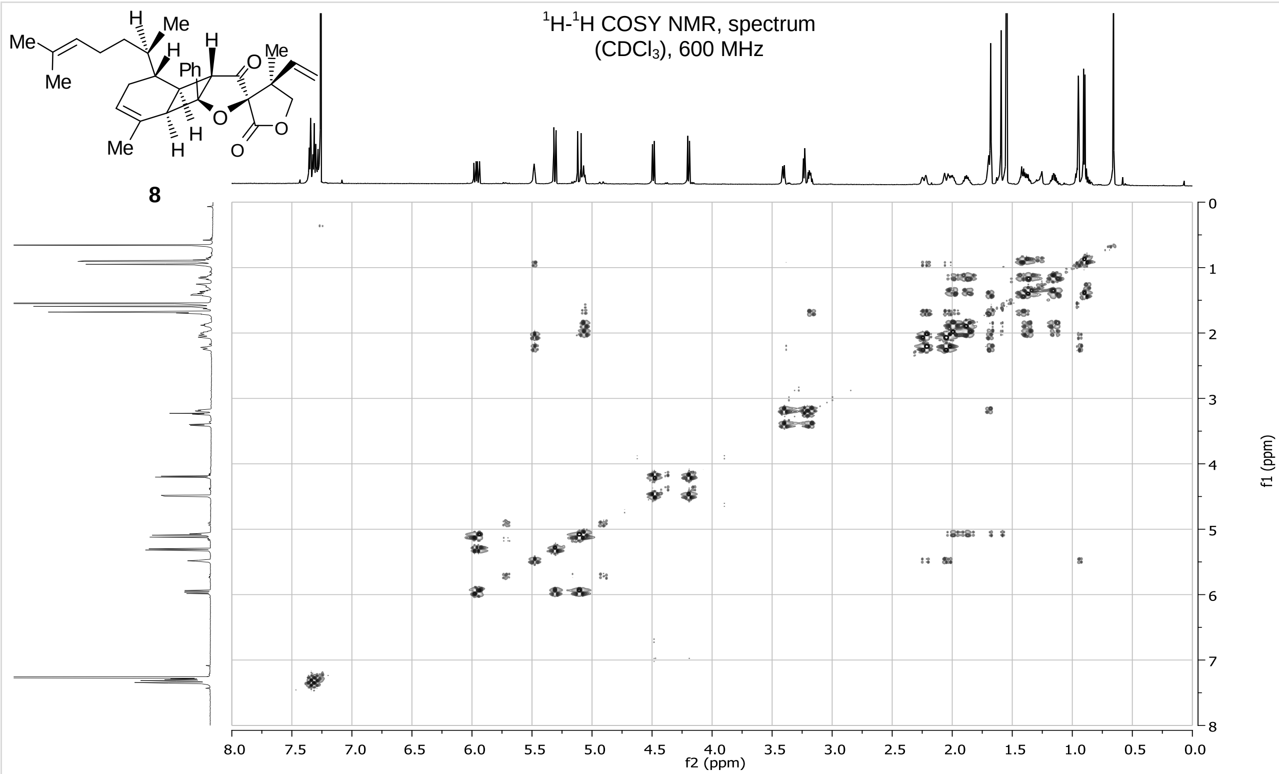

HMQC NMR, spectrum
($CDCl_3$), 600 MHz
f2 (ppm)
f1 (ppm)


HMBC NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)

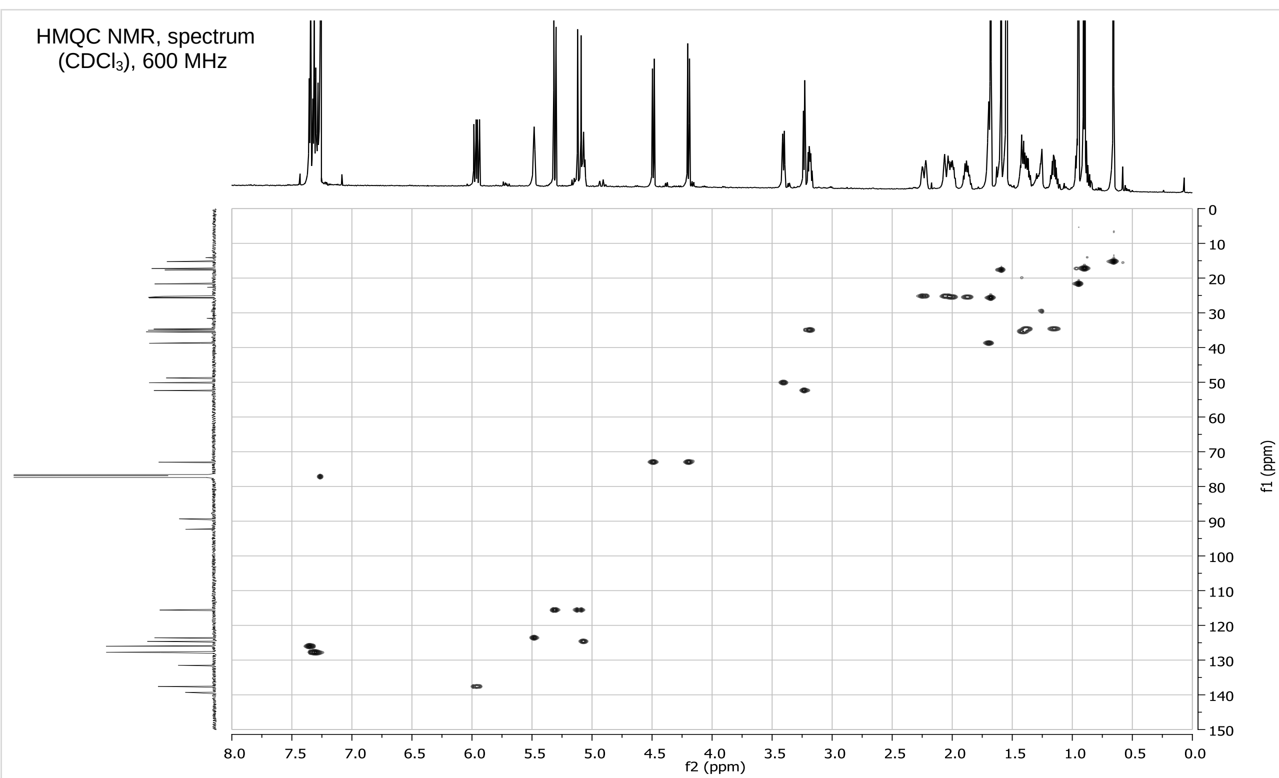

ROESY NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)


8
1H NMR, spectrum
(CDCl3), 600 MHz
f1 (ppm)

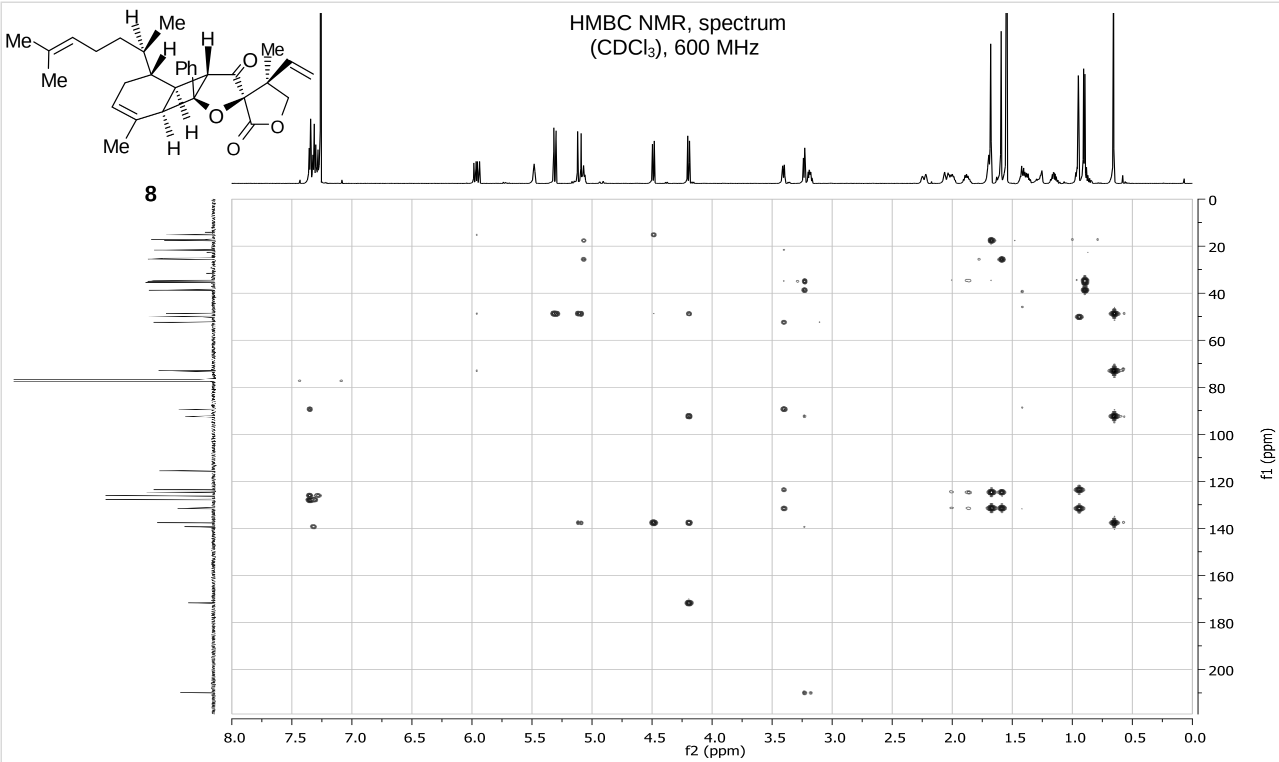

13C NMR, spectrum
(CDCl3), 150 MHz
f1 (ppm)

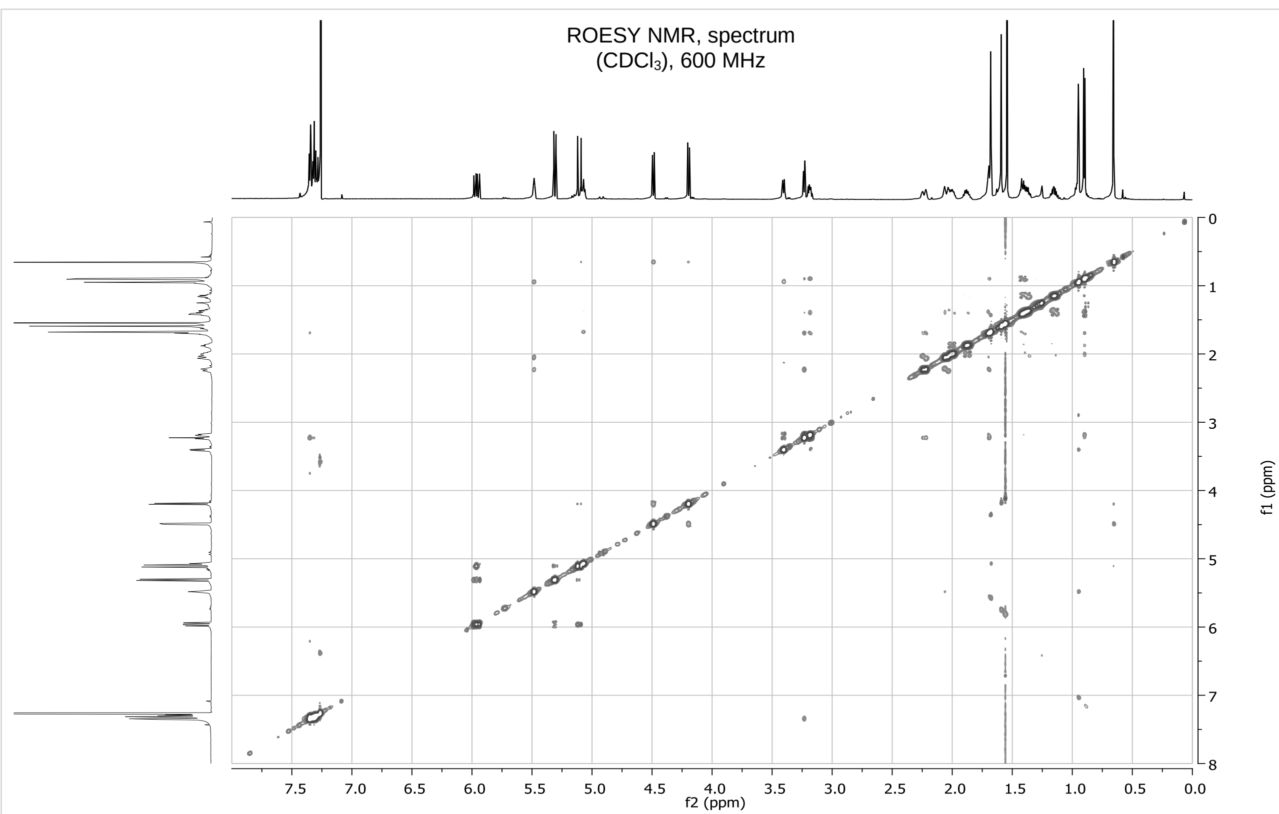


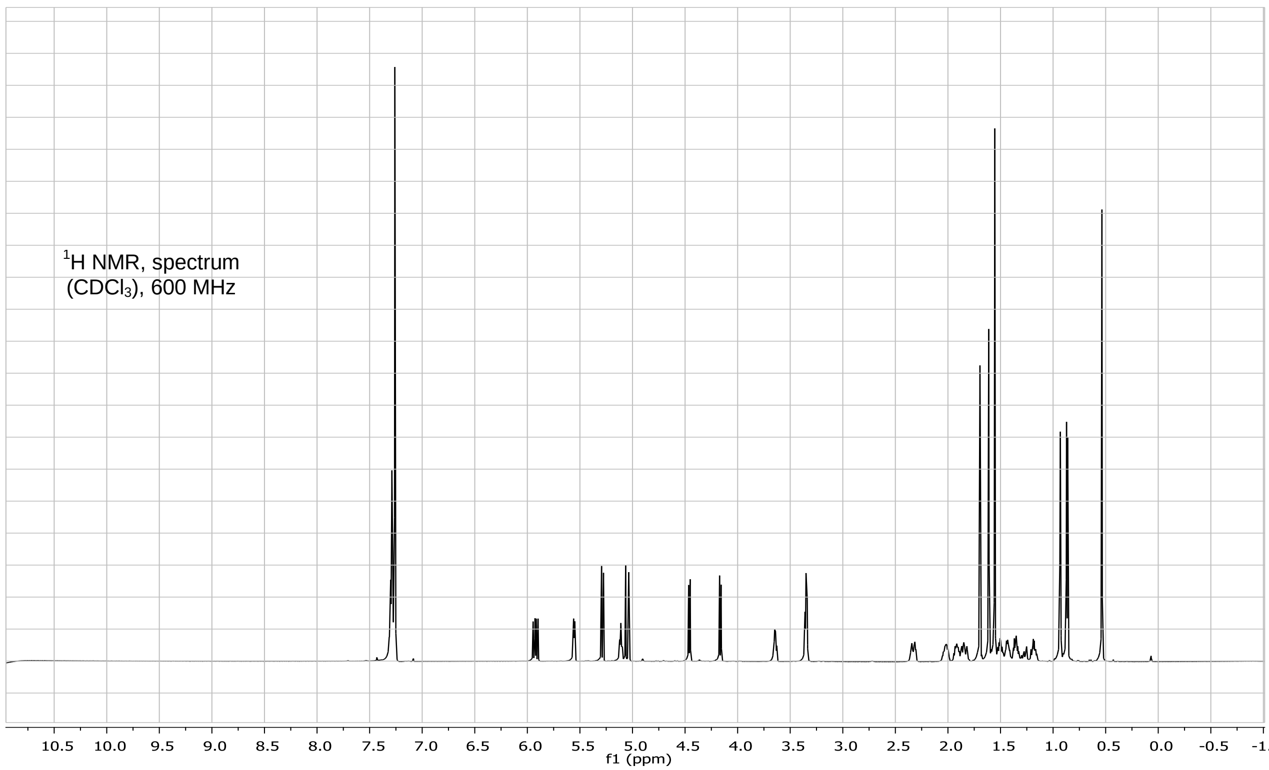
^{1}H-^{1}H COSY NMR, spectrum
($CDCl_3$), 600 MHz
8
f2 (ppm)
f1 (ppm)

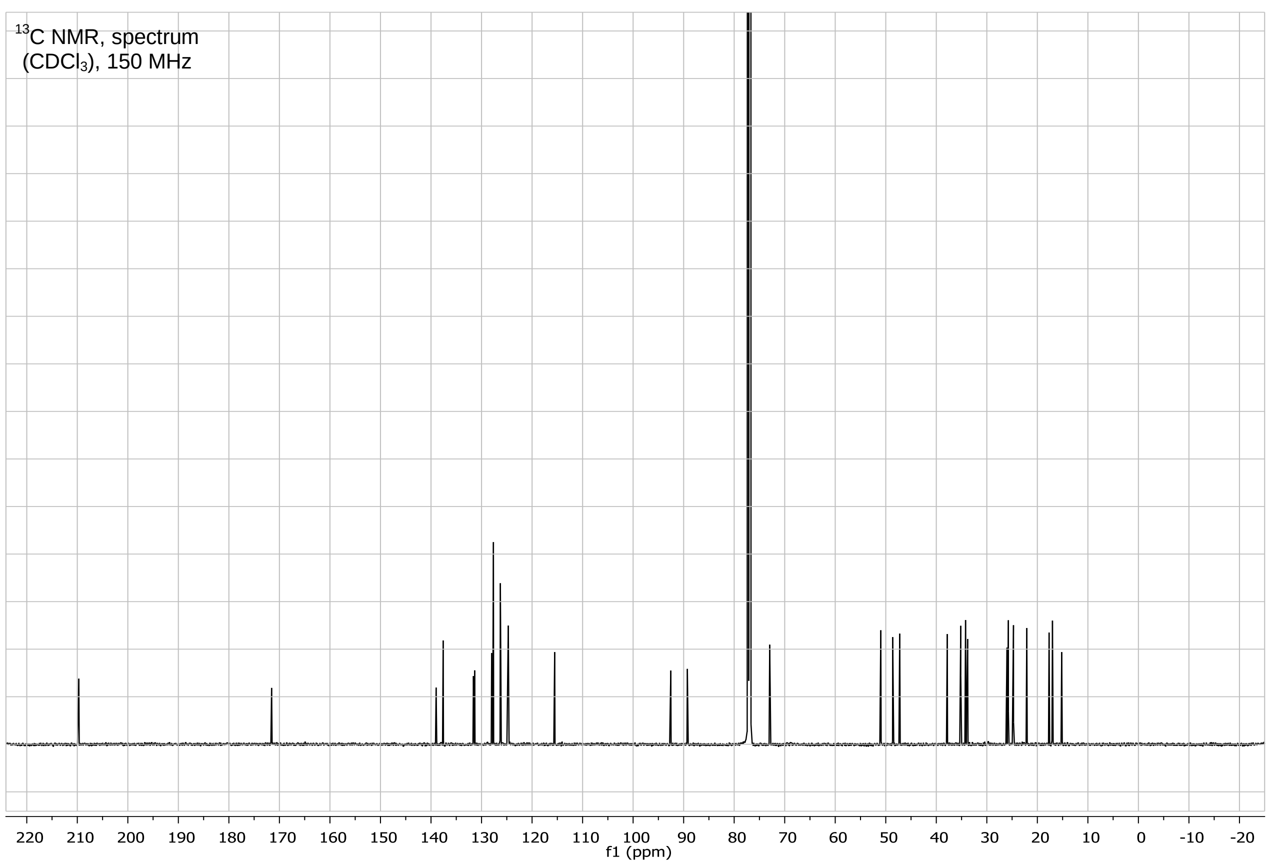


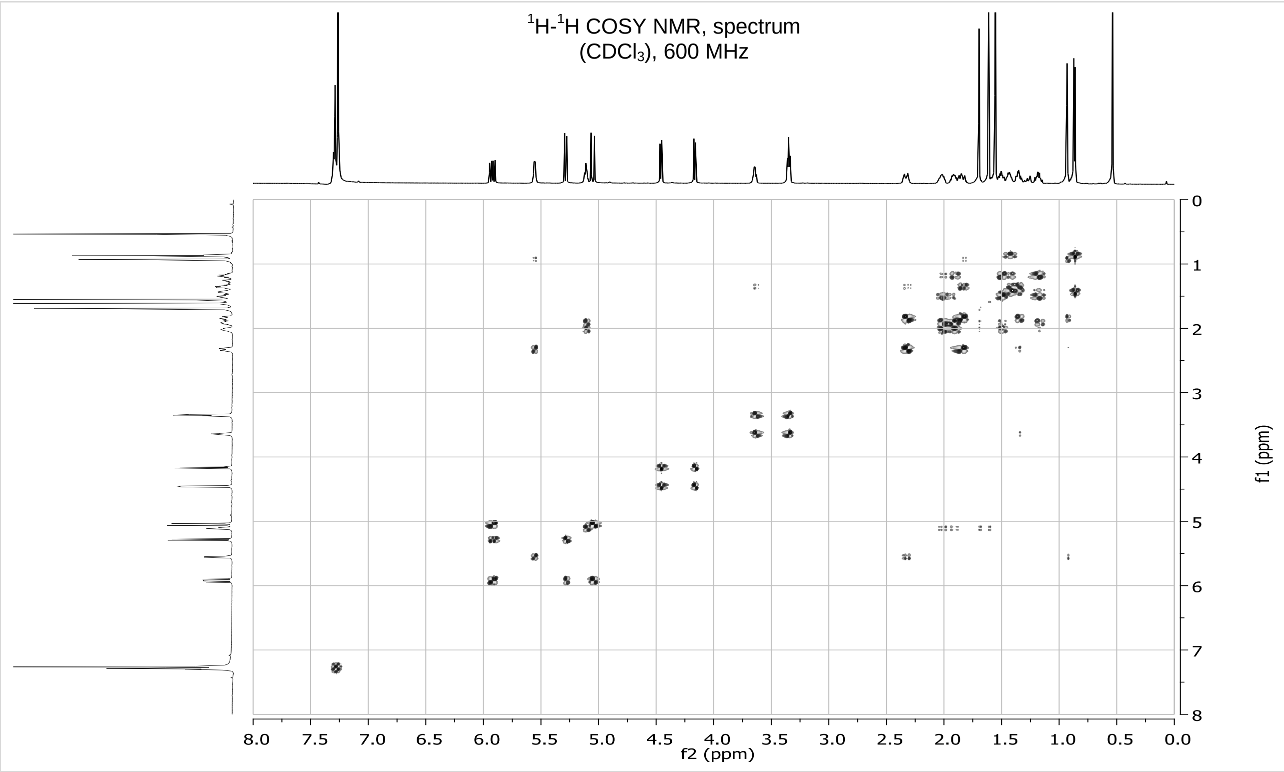
HMQC NMR, spectrum
($CDCl_3$), 600 MHz
f2 (ppm)
f1 (ppm)

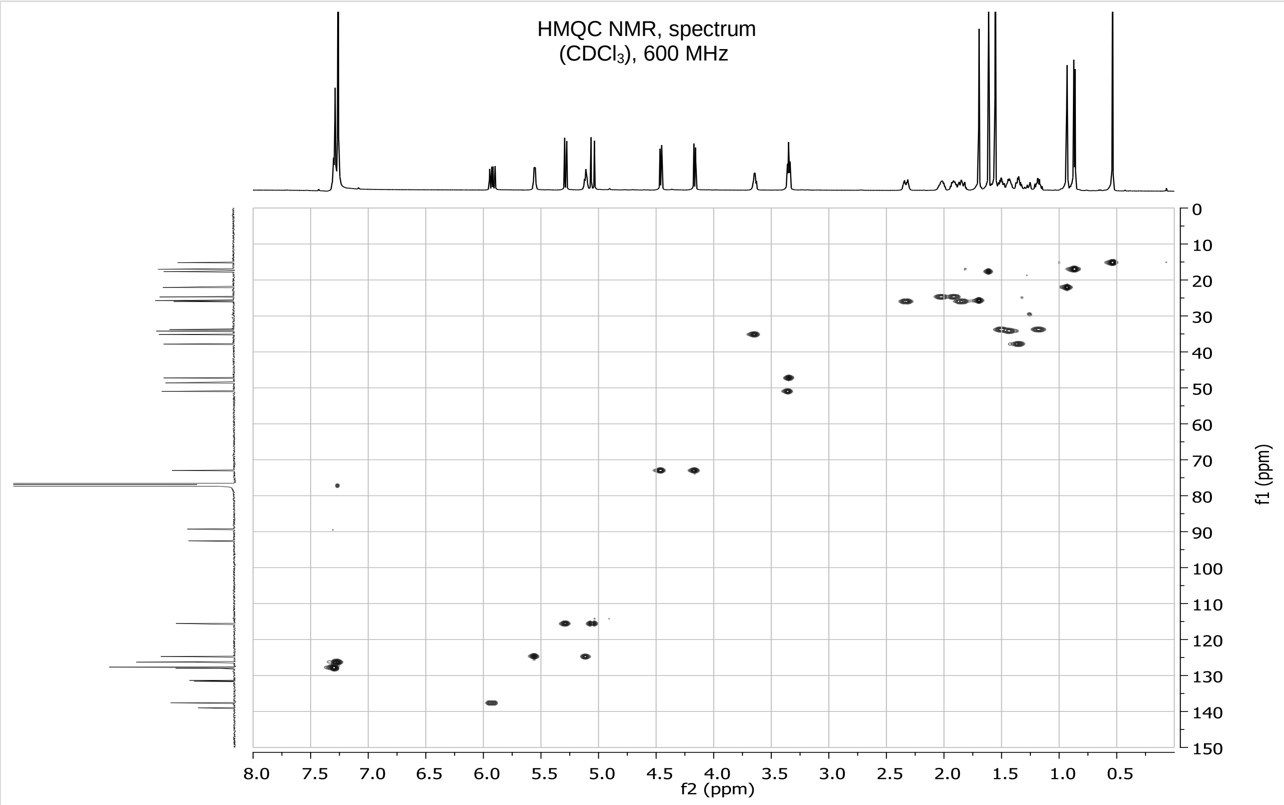

HMBC NMR, spectrum
(CDCl3), 600 MHz
8
f2 (ppm)
f1 (ppm)

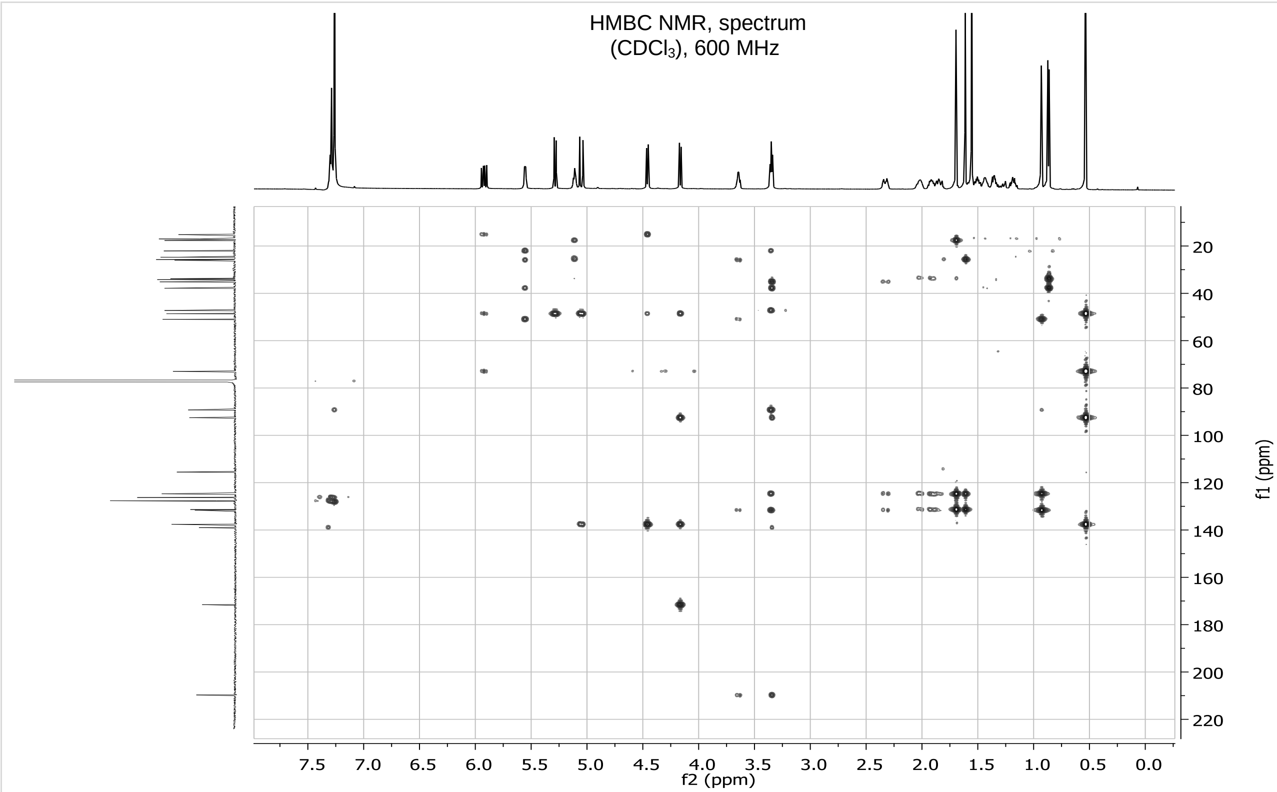

ROESY NMR, spectrum
(CDCl3), 600 MHz
f2 (ppm)
f1 (ppm)

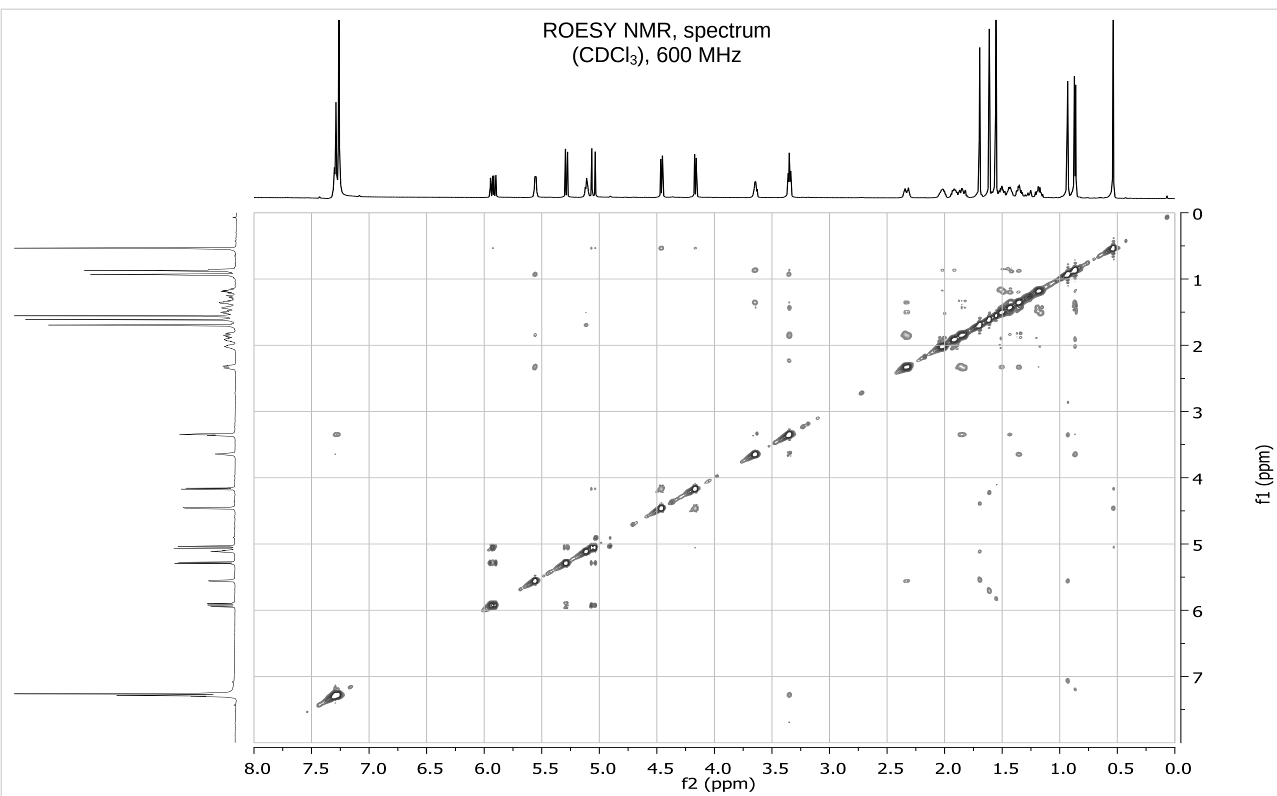

1H NMR, spectrum
(CDCl3), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

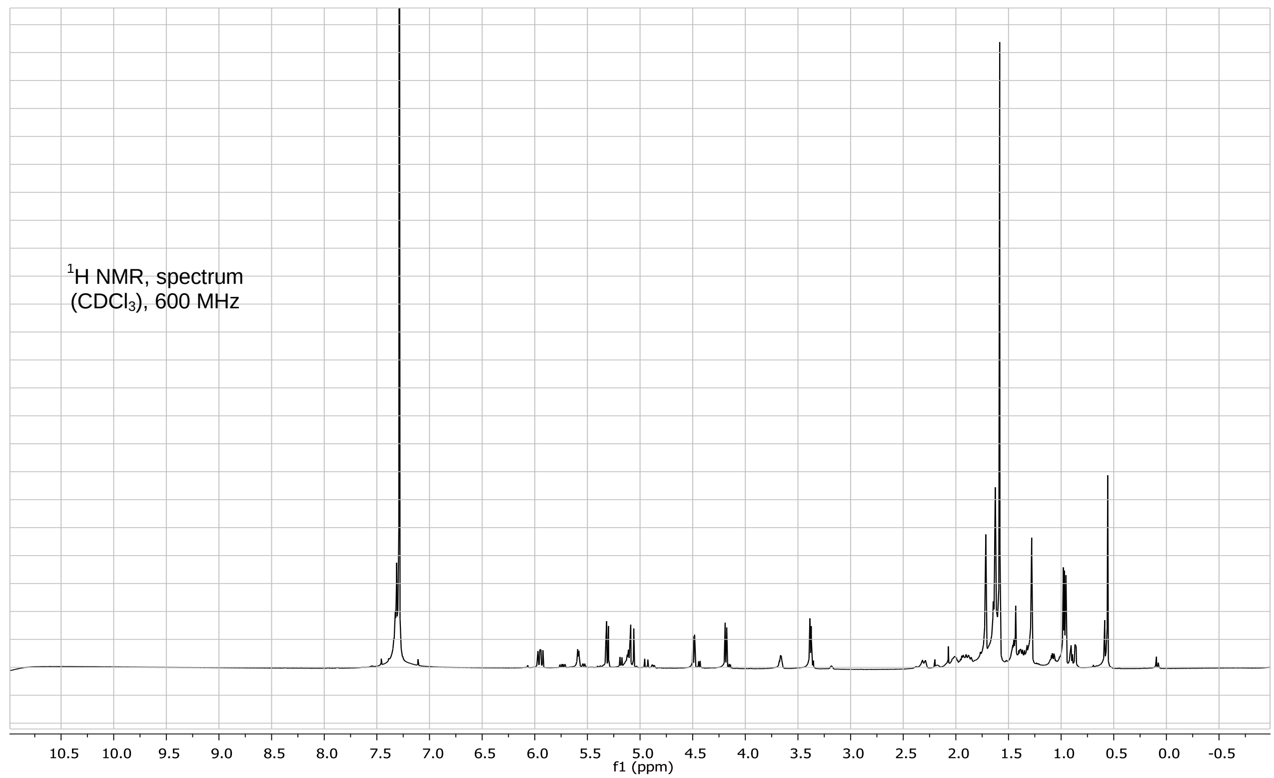

13C NMR, spectrum
(CDCl3), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


^{1}H-^{1}H COSY NMR, spectrum
($CDCl_3$), 600 MHz
f2 (ppm)
f1 (ppm)

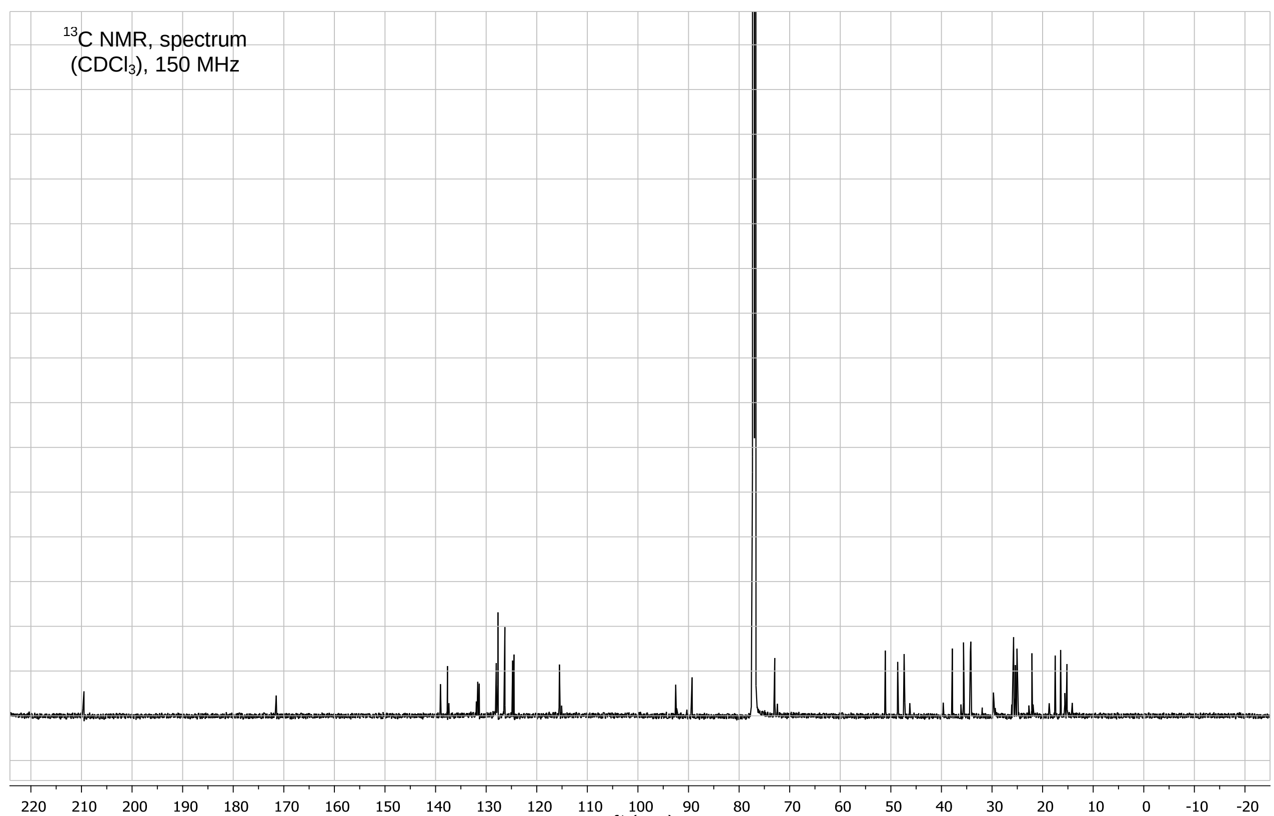

HMQC NMR, spectrum
($CDCl_3$), 600 MHz
f2 (ppm)
f1 (ppm)


HMBC NMR, spectrum
(CDCl3), 600 MHz
f1 (ppm)
f2 (ppm)

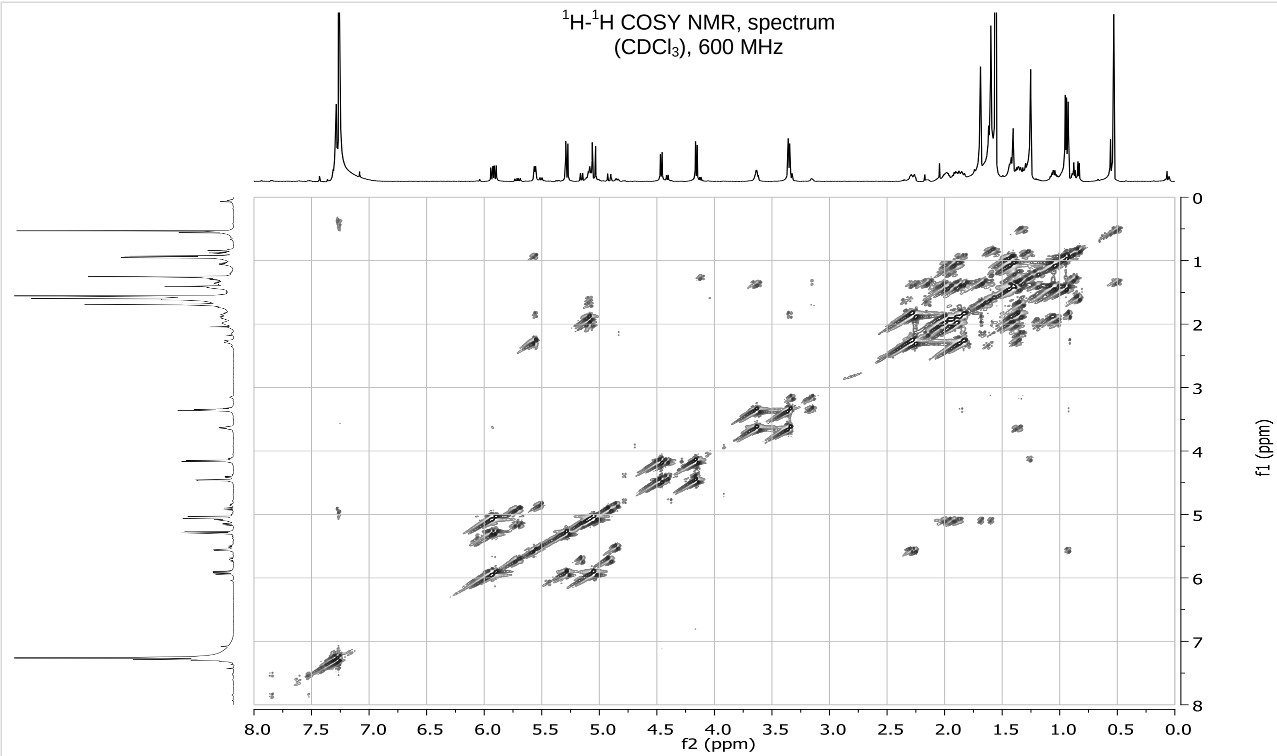

ROESY NMR, spectrum
(CDCl3), 600 MHz
f1 (ppm)
f2 (ppm)



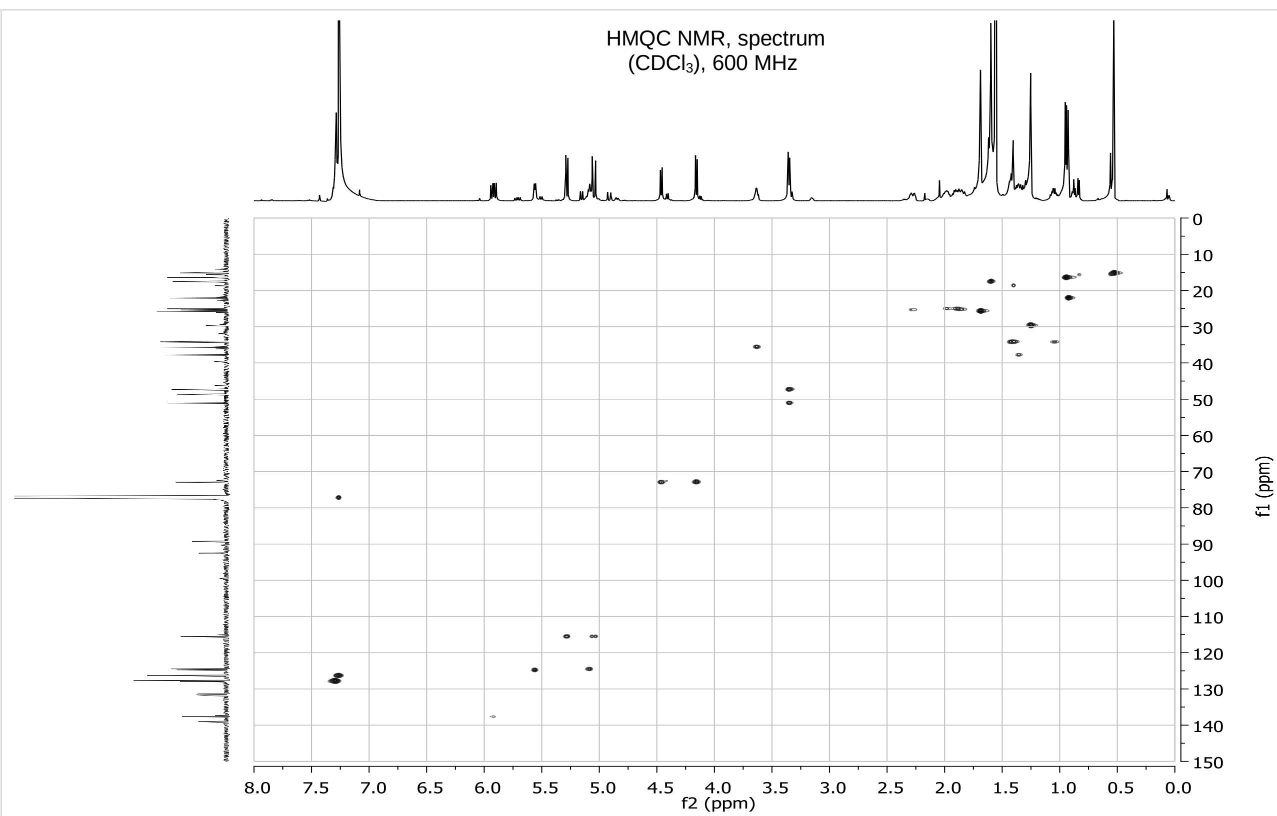
^{1}H NMR, spectrum
($CDCl_3$), 600 MHz
f1 (ppm)



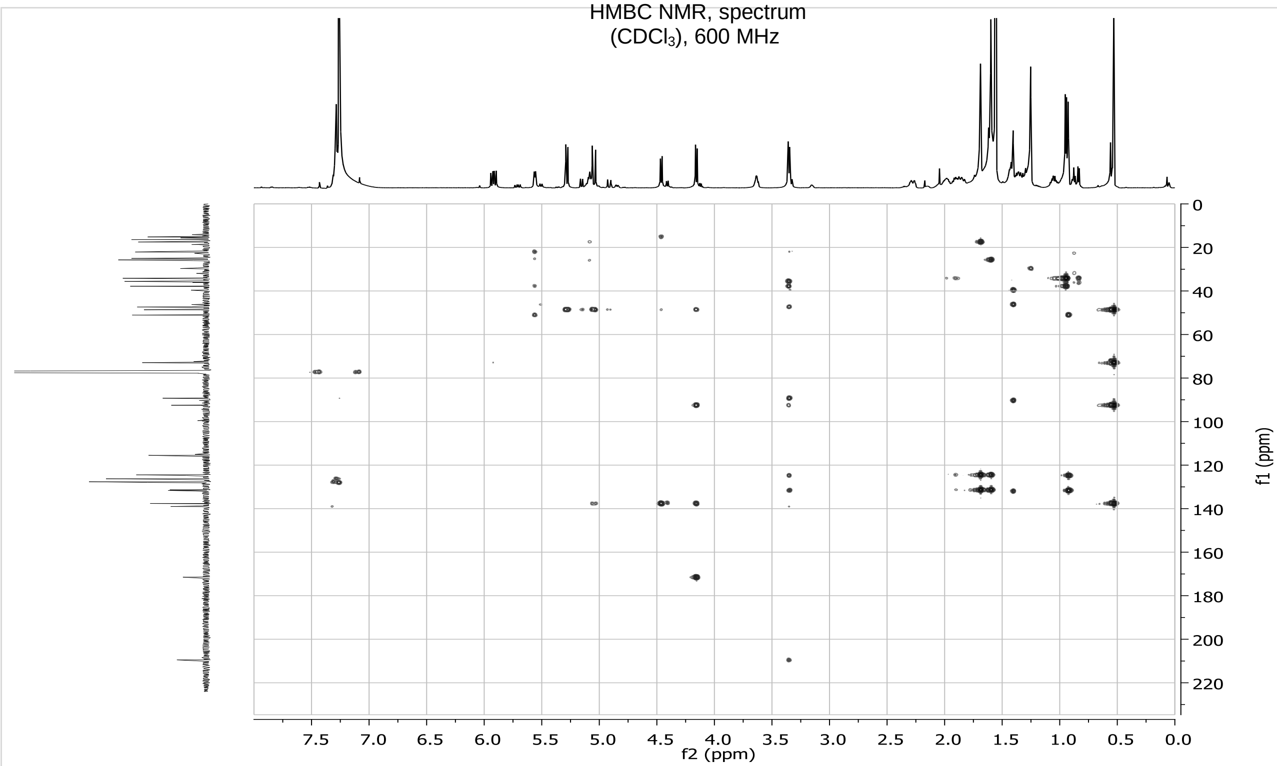
^{13}C NMR, spectrum
($CDCl_3$), 150 MHz
f1 (ppm)

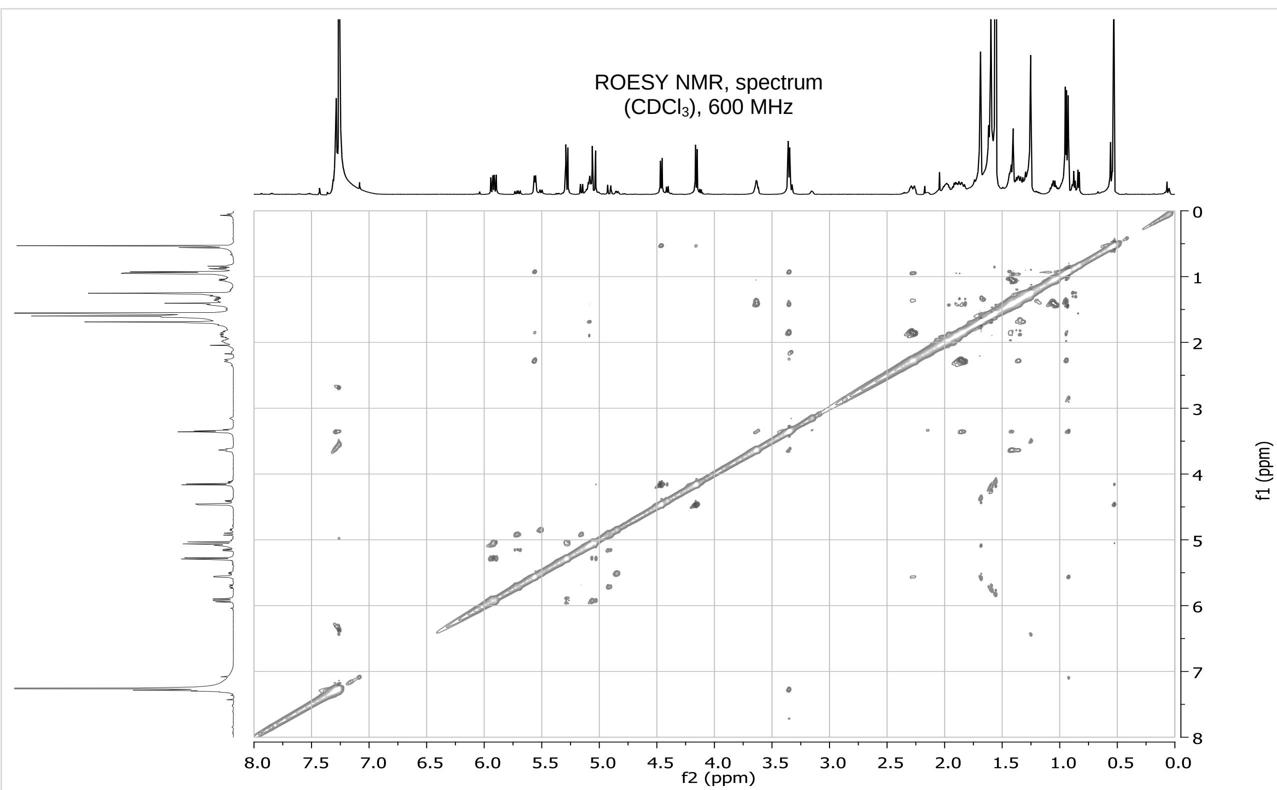


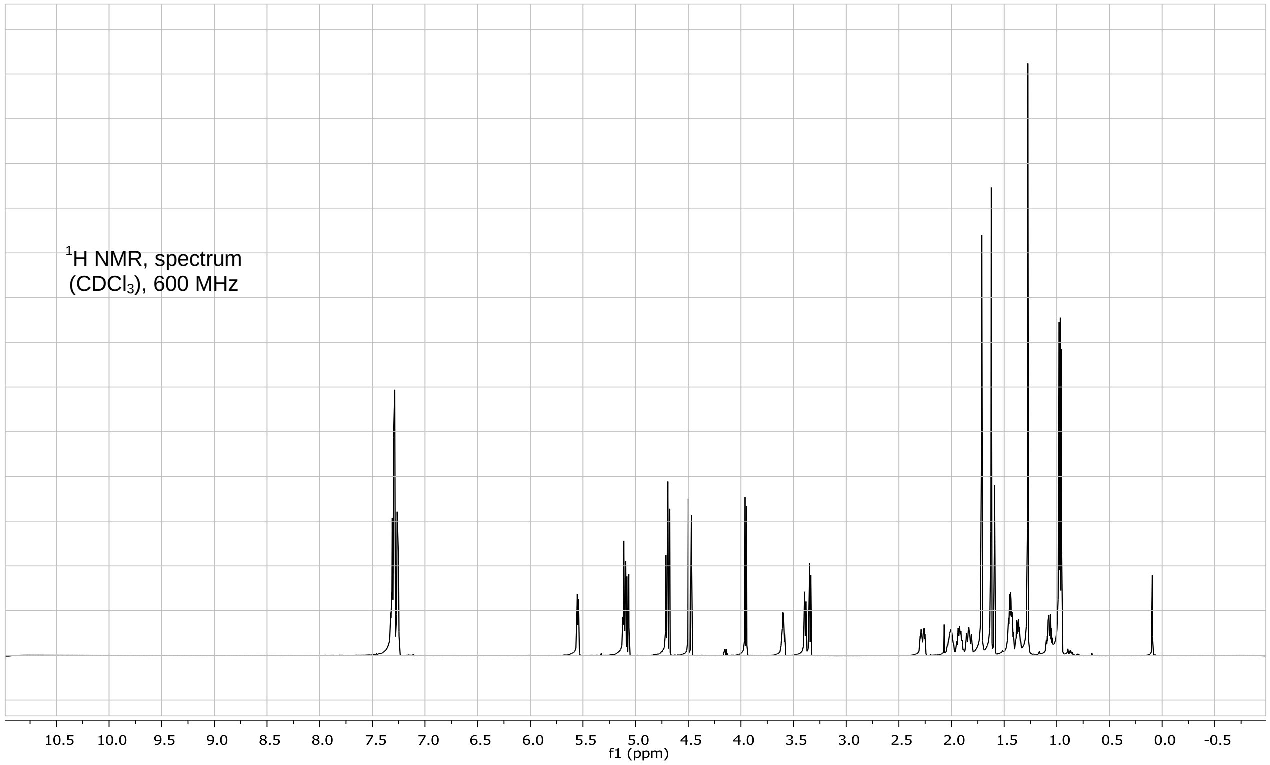
[1]H-[1]H COSY NMR, spectrum
($CDCl_3$), 600 MHz
f1 (ppm)
f2 (ppm)



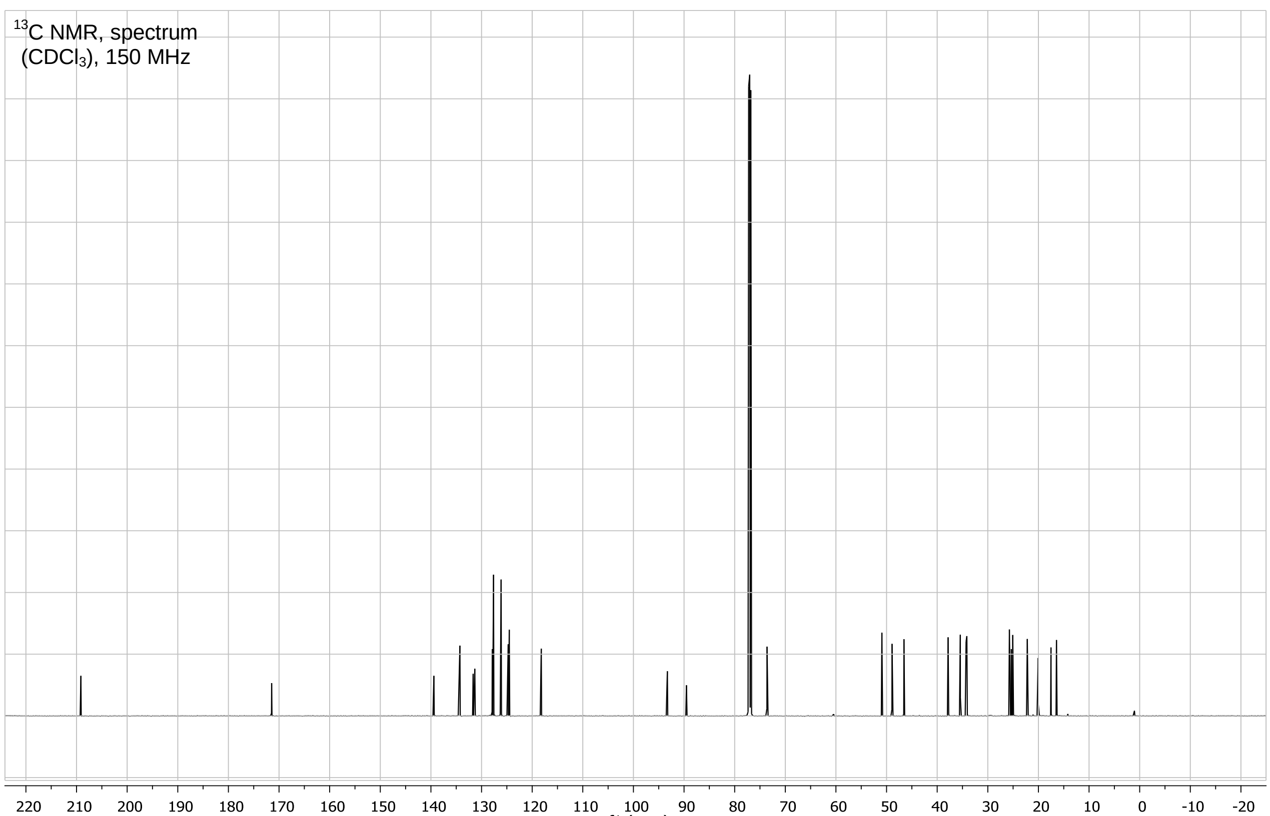
HMQC NMR, spectrum
($CDCl_3$), 600 MHz
f1 (ppm)
f2 (ppm)


HMBC NMR, spectrum
(CDCl3), 600 MHz
f2 (ppm)
f1 (ppm)

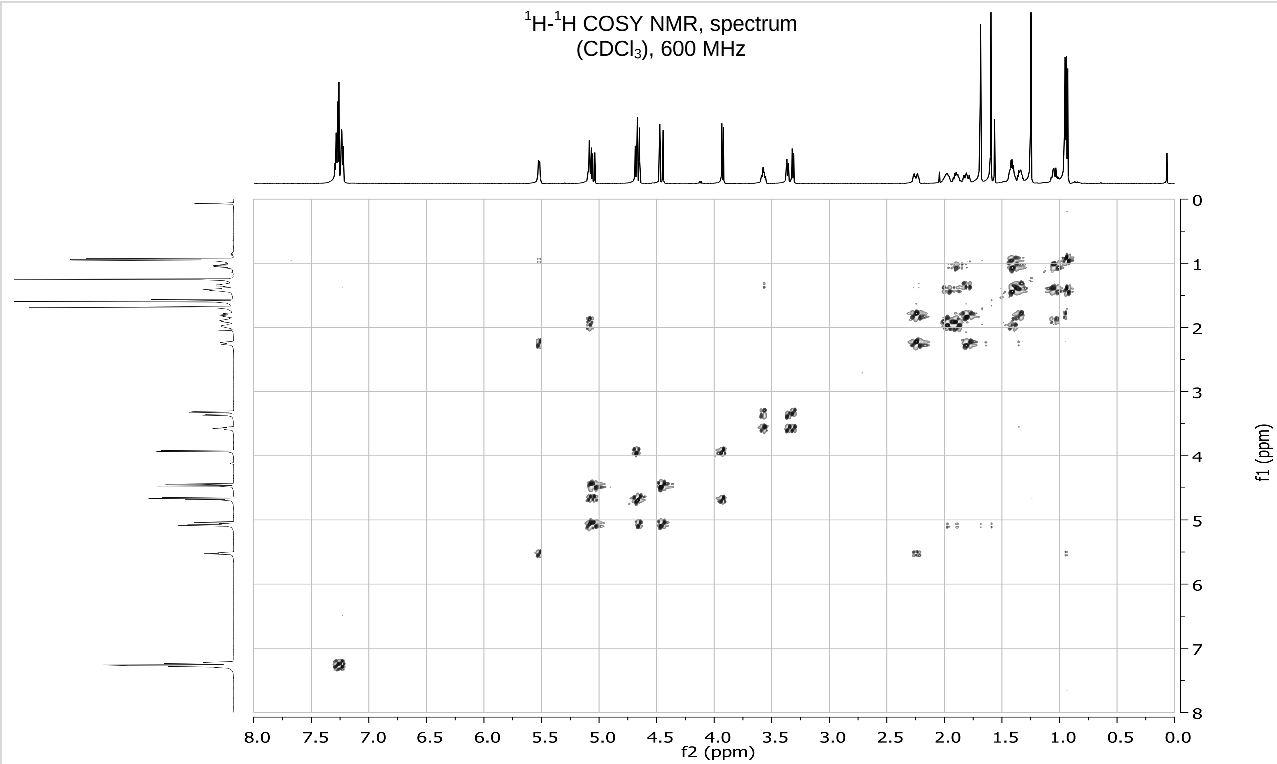

ROESY NMR, spectrum
(CDCl3), 600 MHz
f2 (ppm)
f1 (ppm)



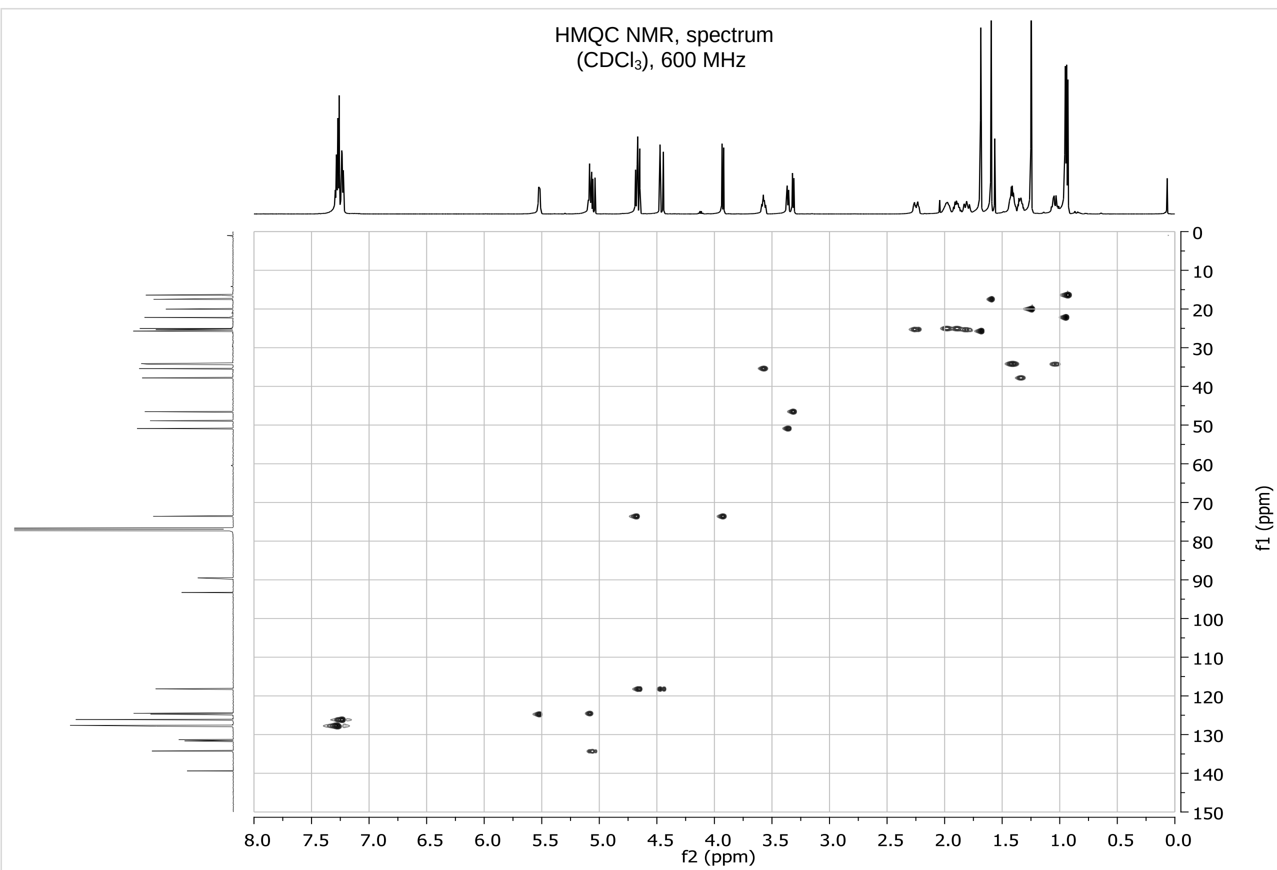
^{1}H NMR, spectrum
($CDCl_3$), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



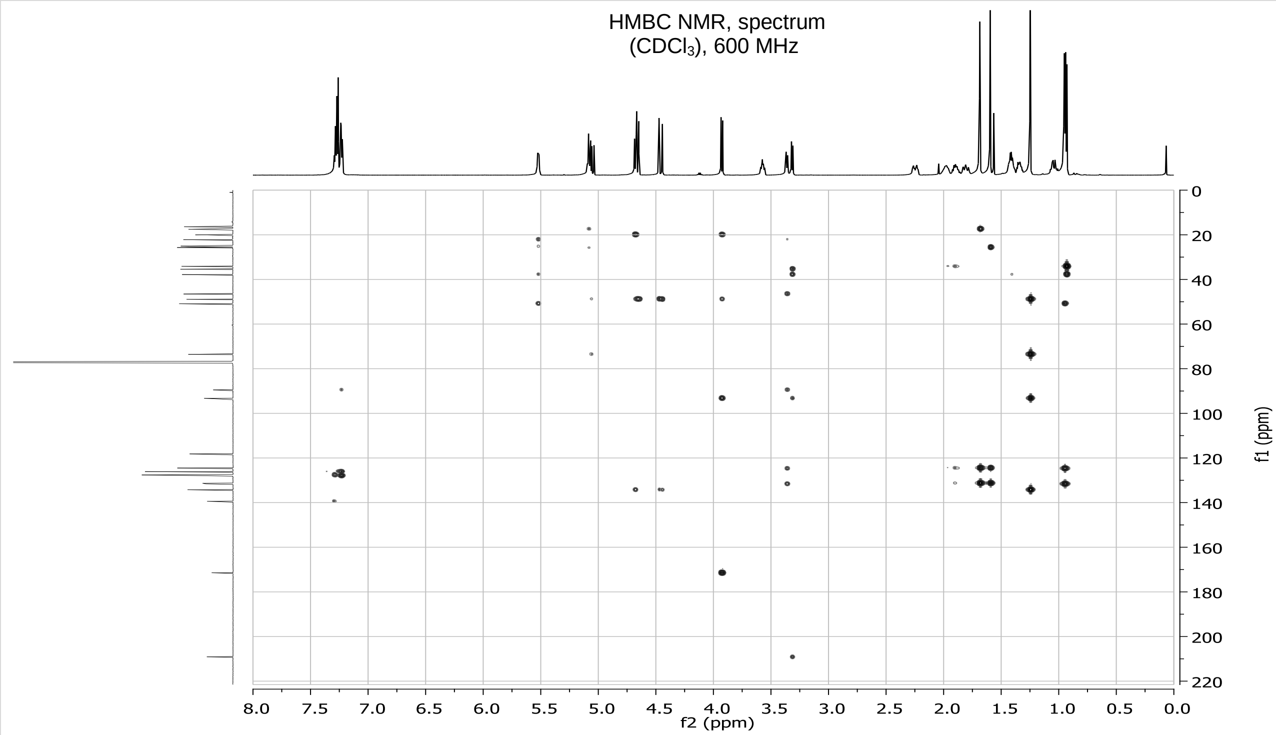
^{13}C NMR, spectrum
($CDCl_3$), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

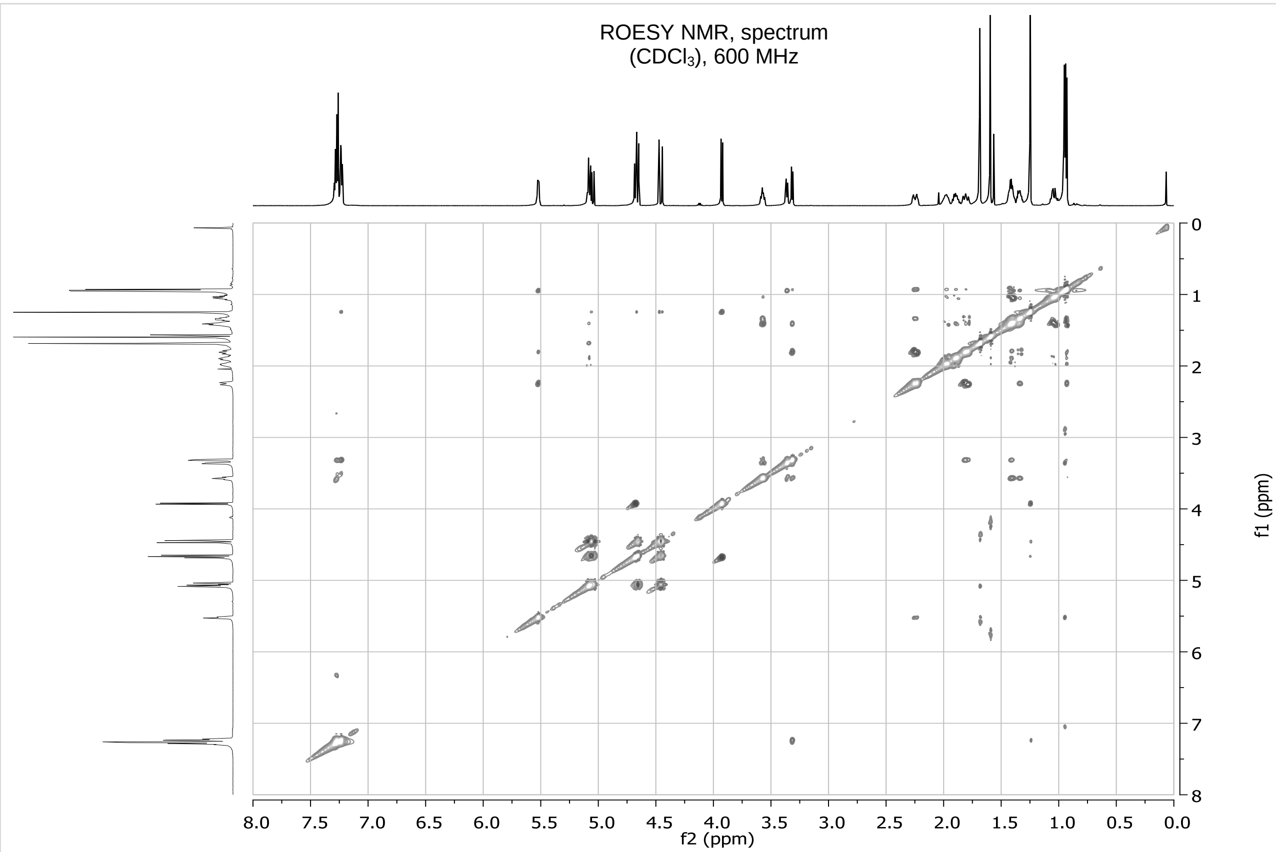


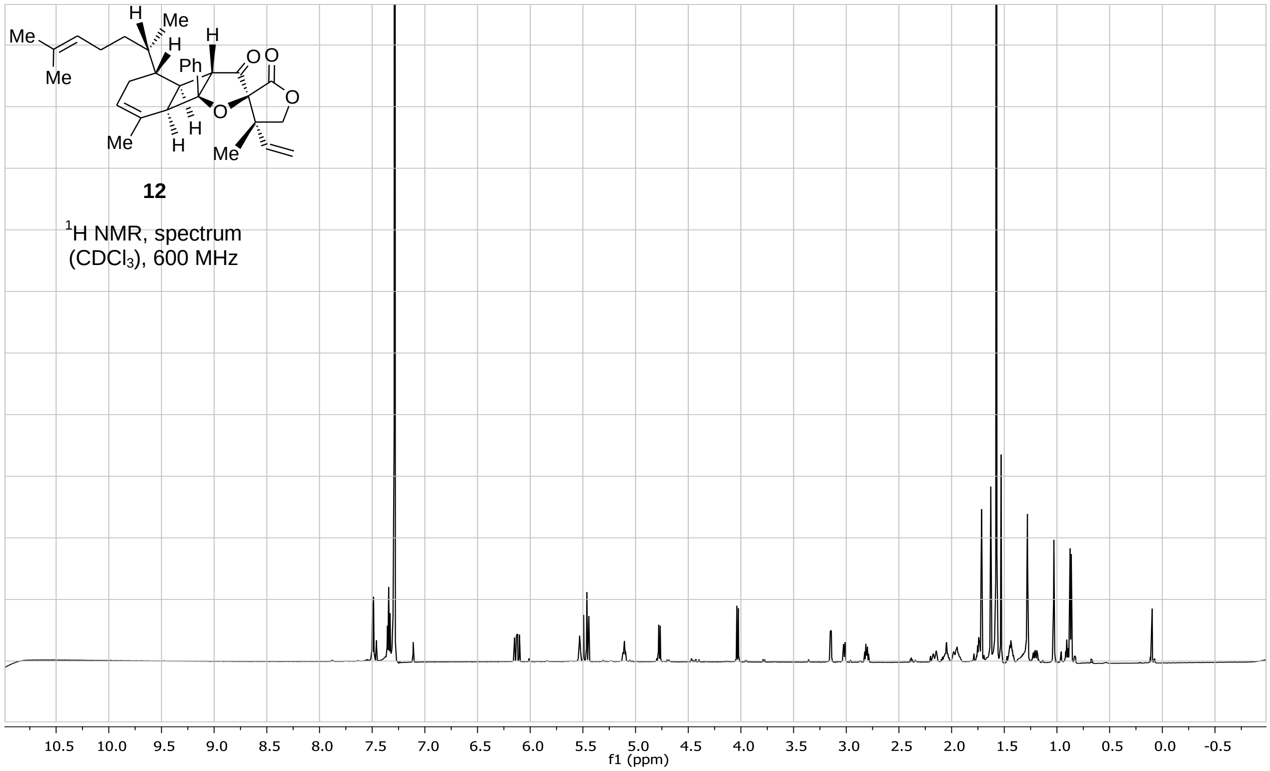
^{1}H-^{1}H COSY NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)

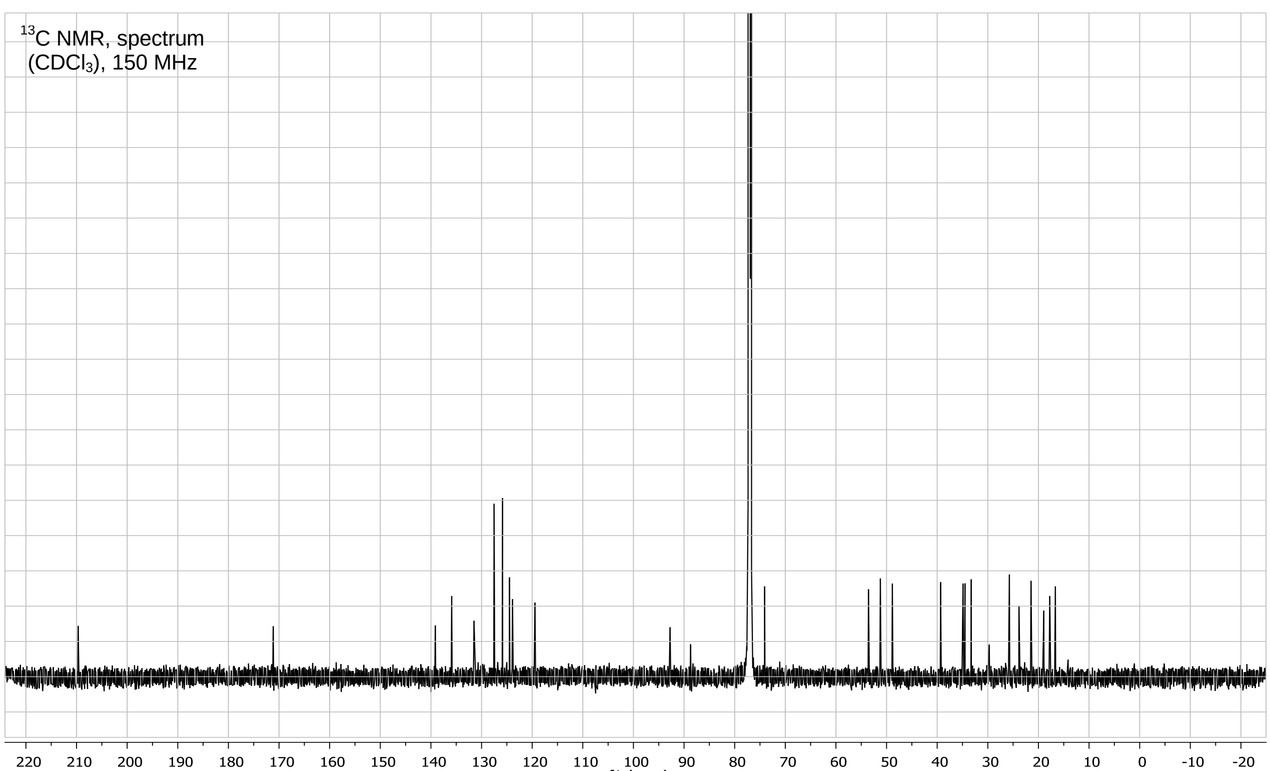


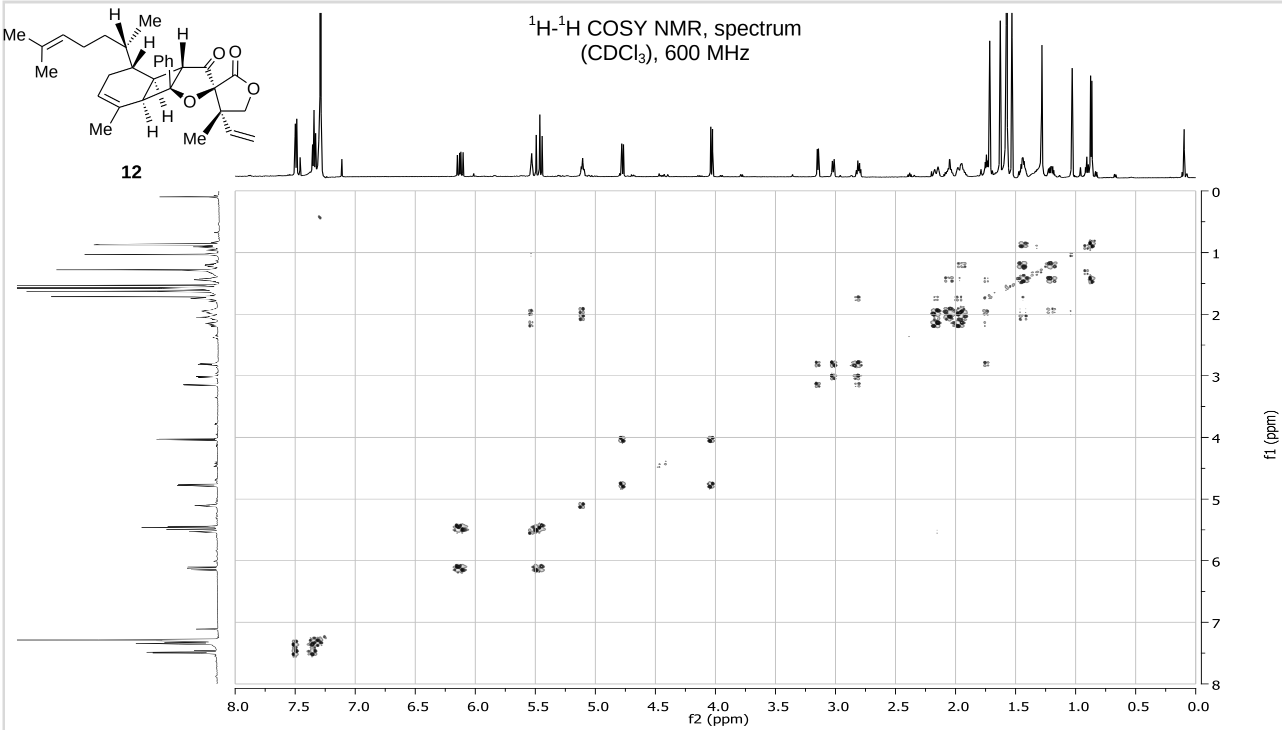
HMQC NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)


HMBC NMR, spectrum
(CDCl3), 600 MHz
f2 (ppm)
f1 (ppm)

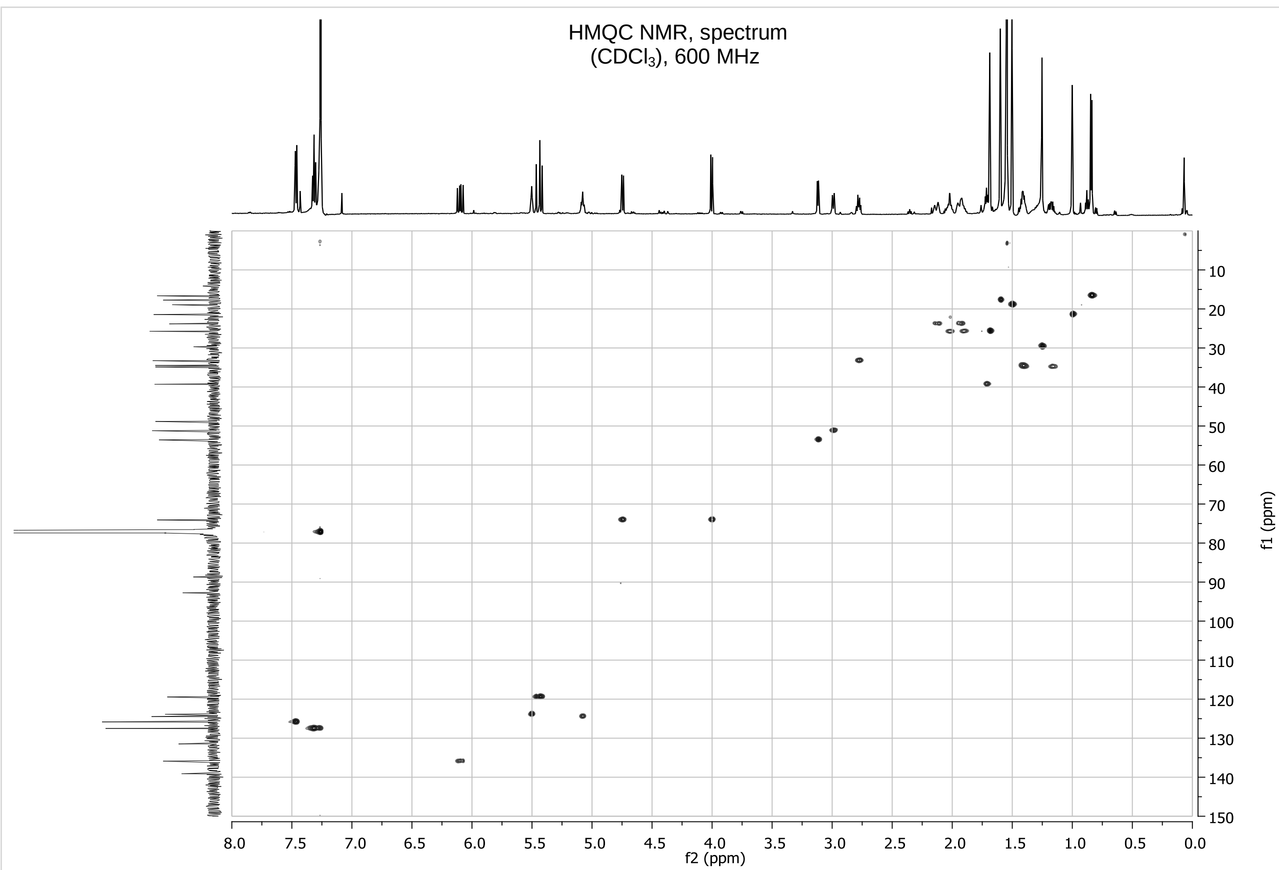

ROESY NMR, spectrum
(CDCl3), 600 MHz
f2 (ppm)
f1 (ppm)


12
^{1}H NMR, spectrum
($CDCl_3$), 600 MHz
f1 (ppm)

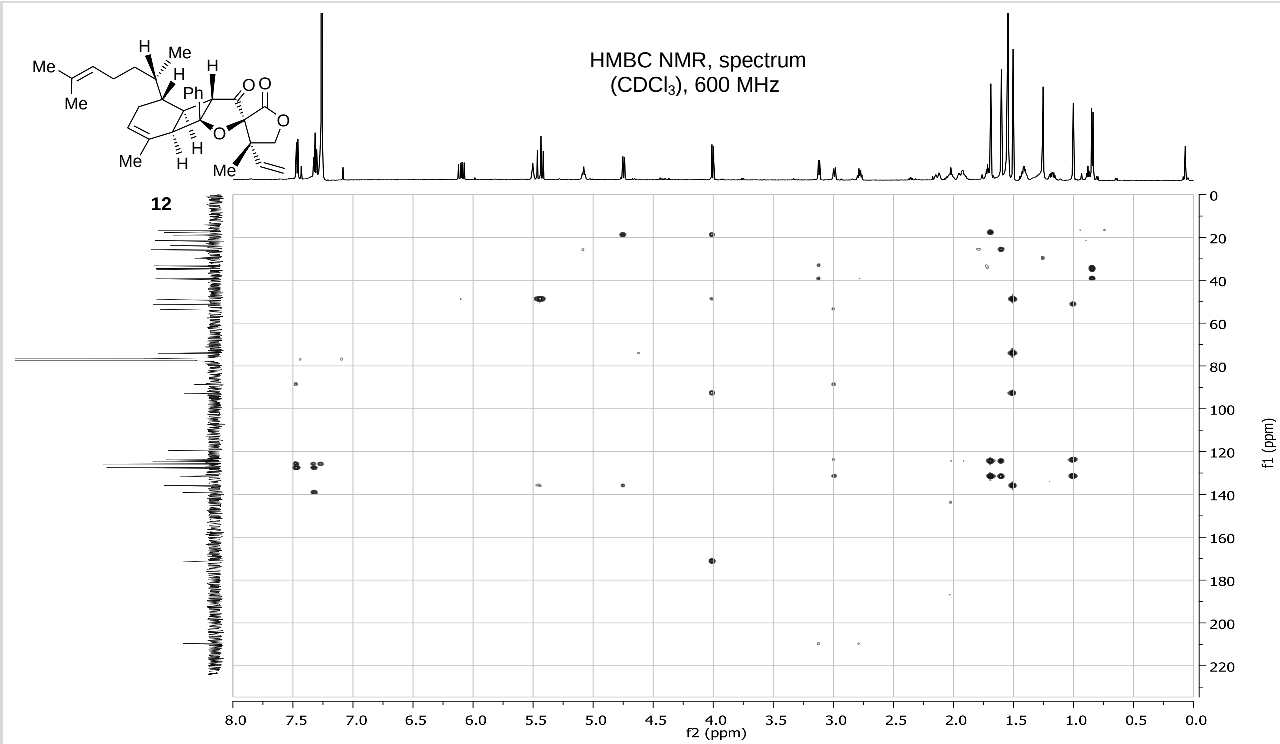

^{13}C NMR, spectrum
($CDCl_3$), 150 MHz
f1 (ppm)

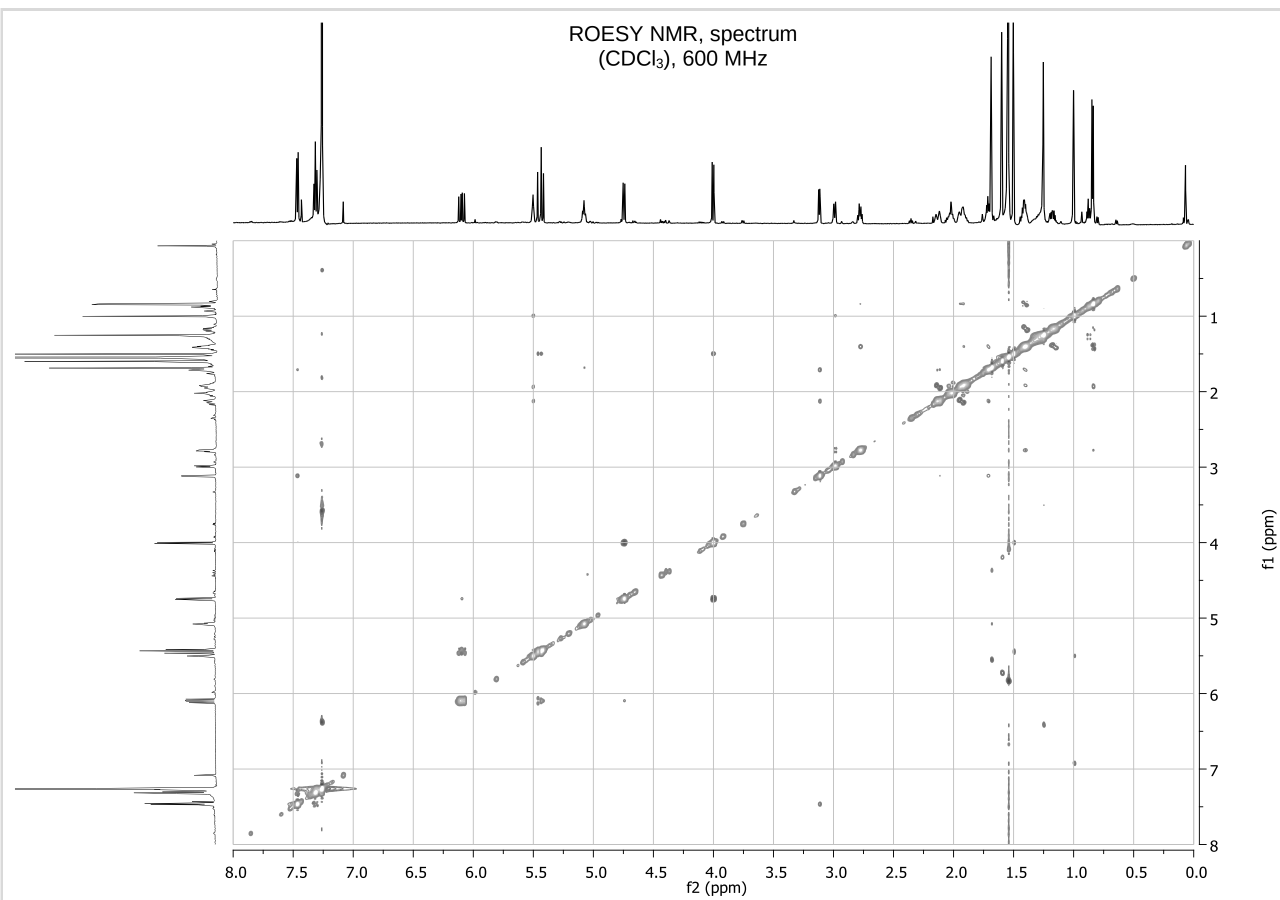


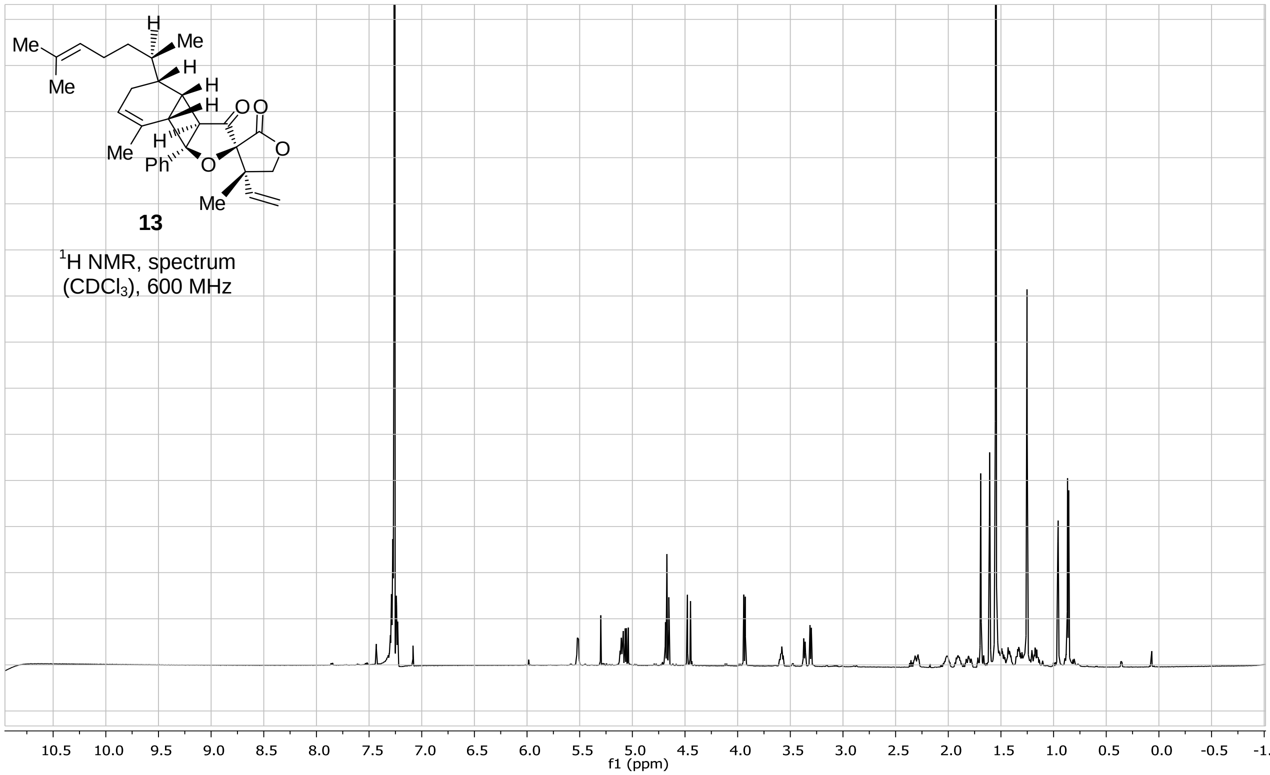
Me
Me
H
Me
H
H
Ph
O
O
O
O
Me
H
H
Me
12
^{1}H-^{1}H COSY NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)

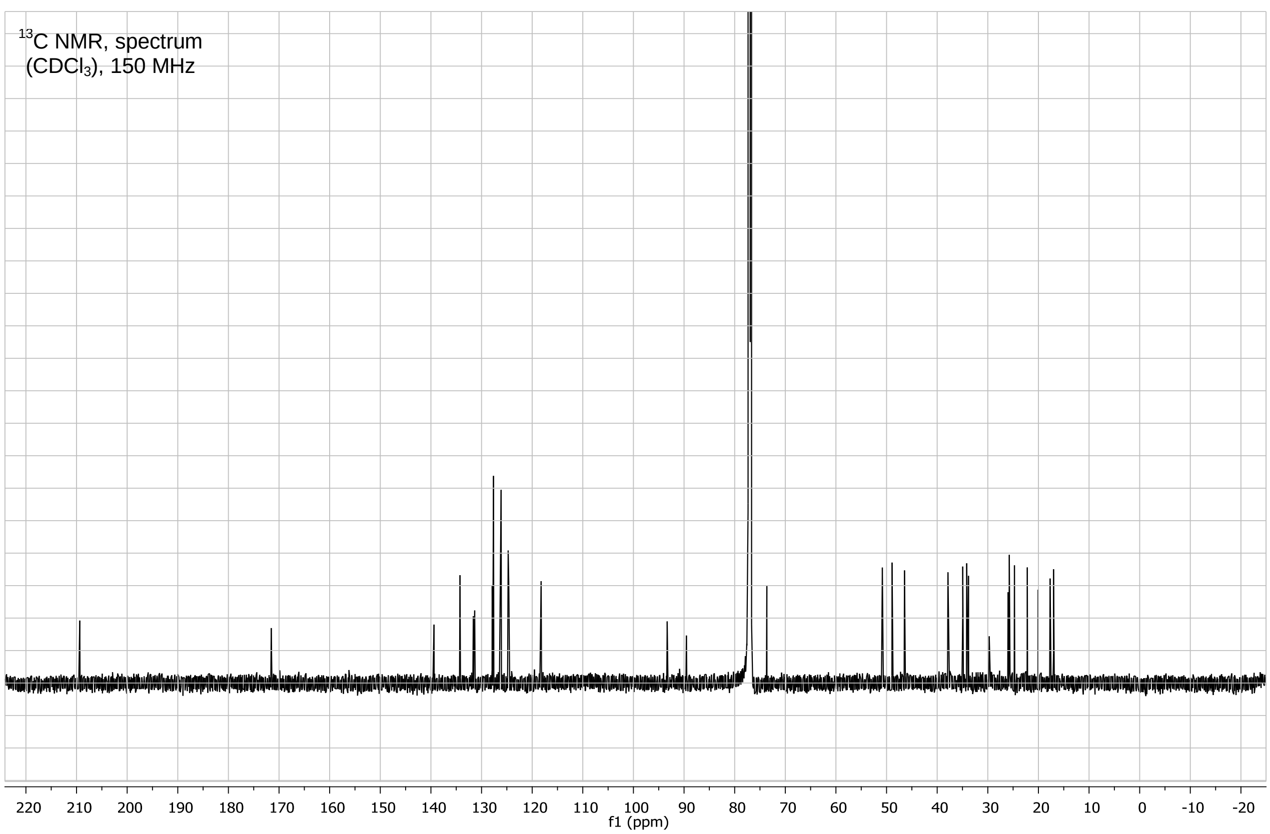


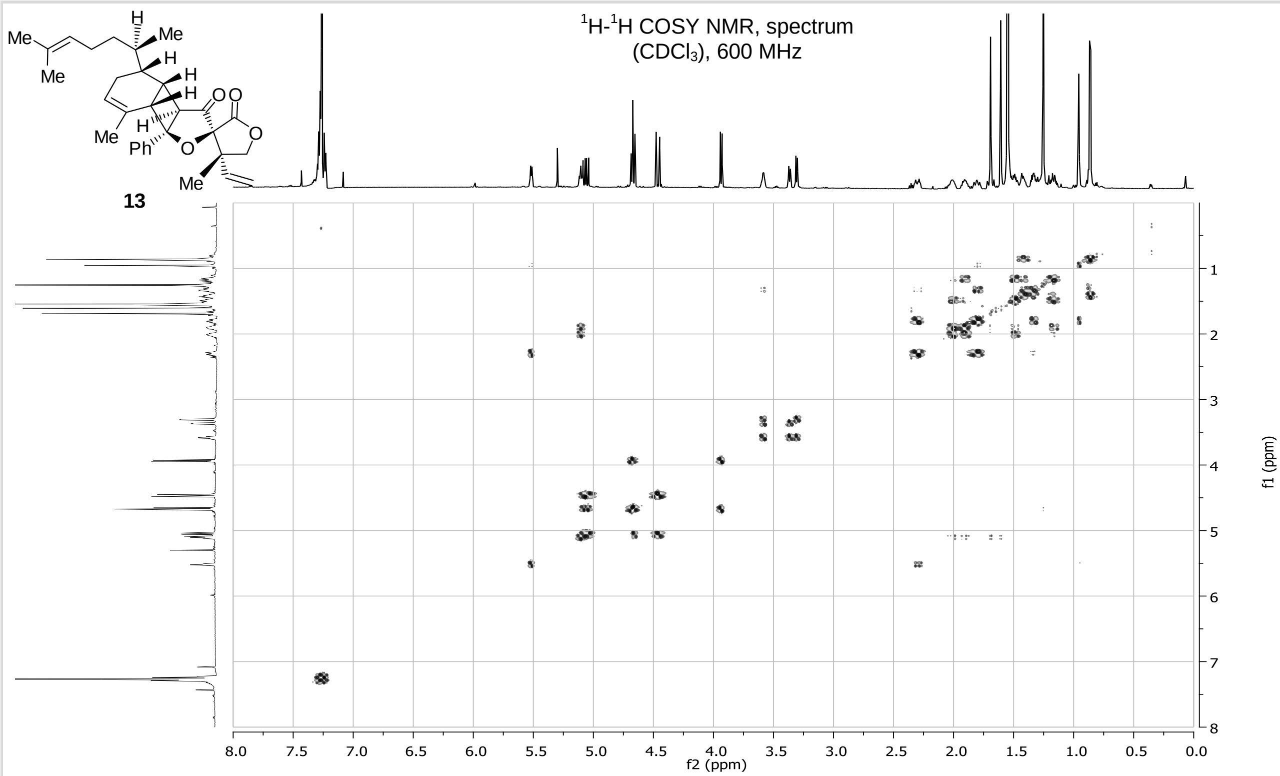
HMQC NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)

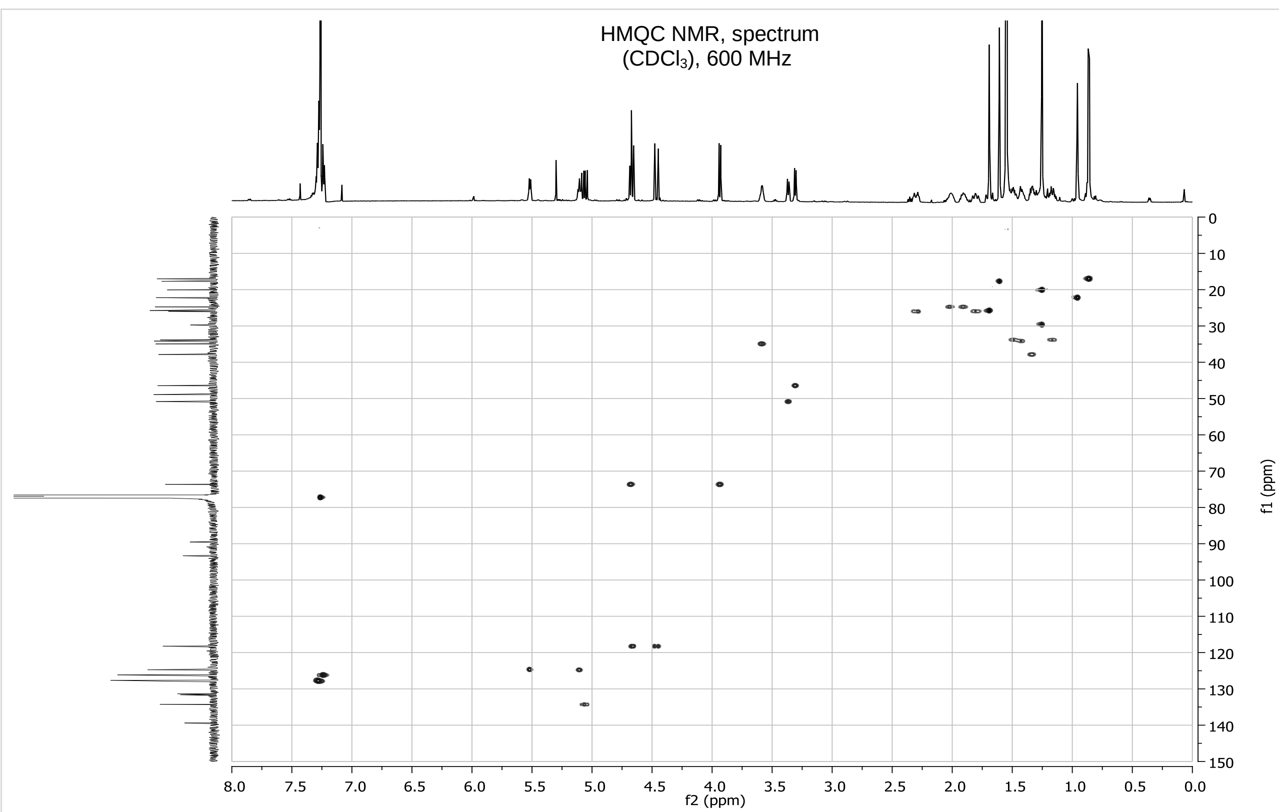

HMBC NMR, spectrum
(CDCl3), 600 MHz
12
Me
Me
H
Me
H
H
Ph
O
O
O
O
H
Me
H
Me
f1 (ppm)
f2 (ppm)

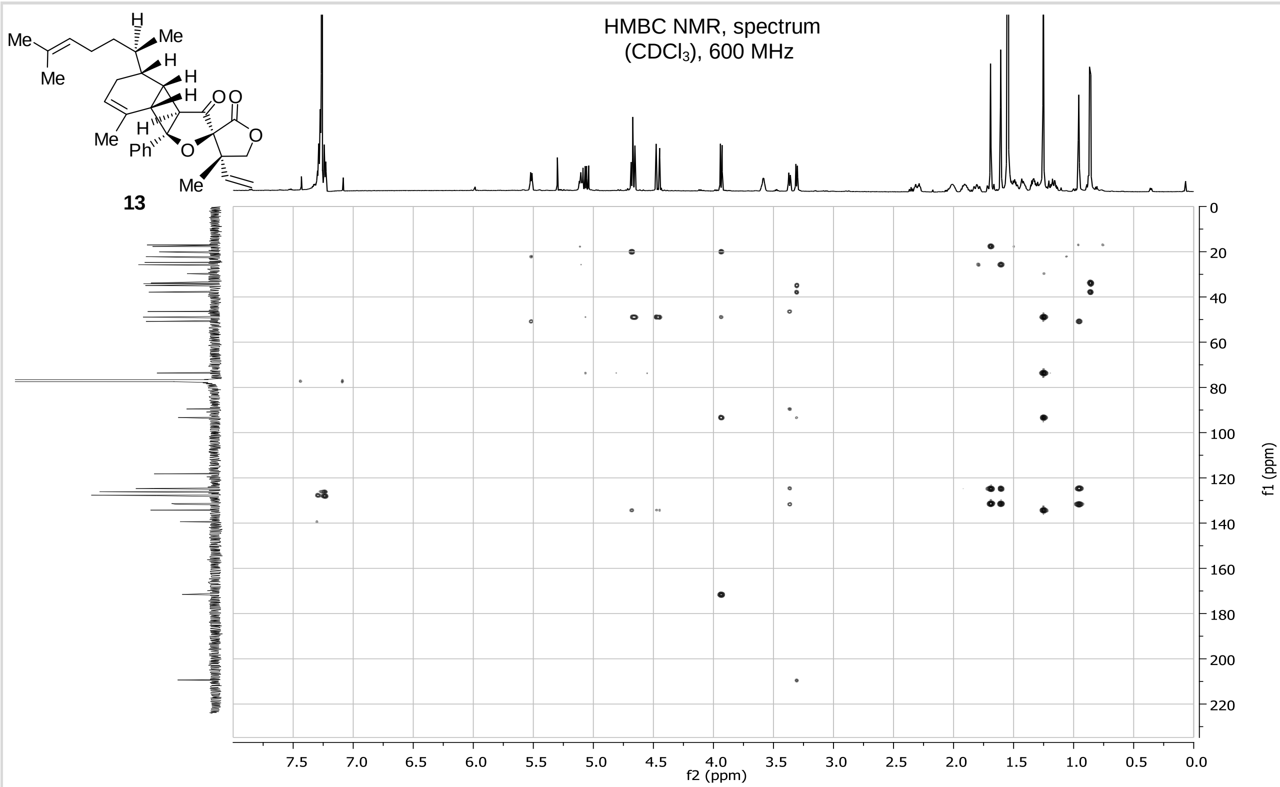

ROESY NMR, spectrum
(CDCl3), 600 MHz
f1 (ppm)
f2 (ppm)

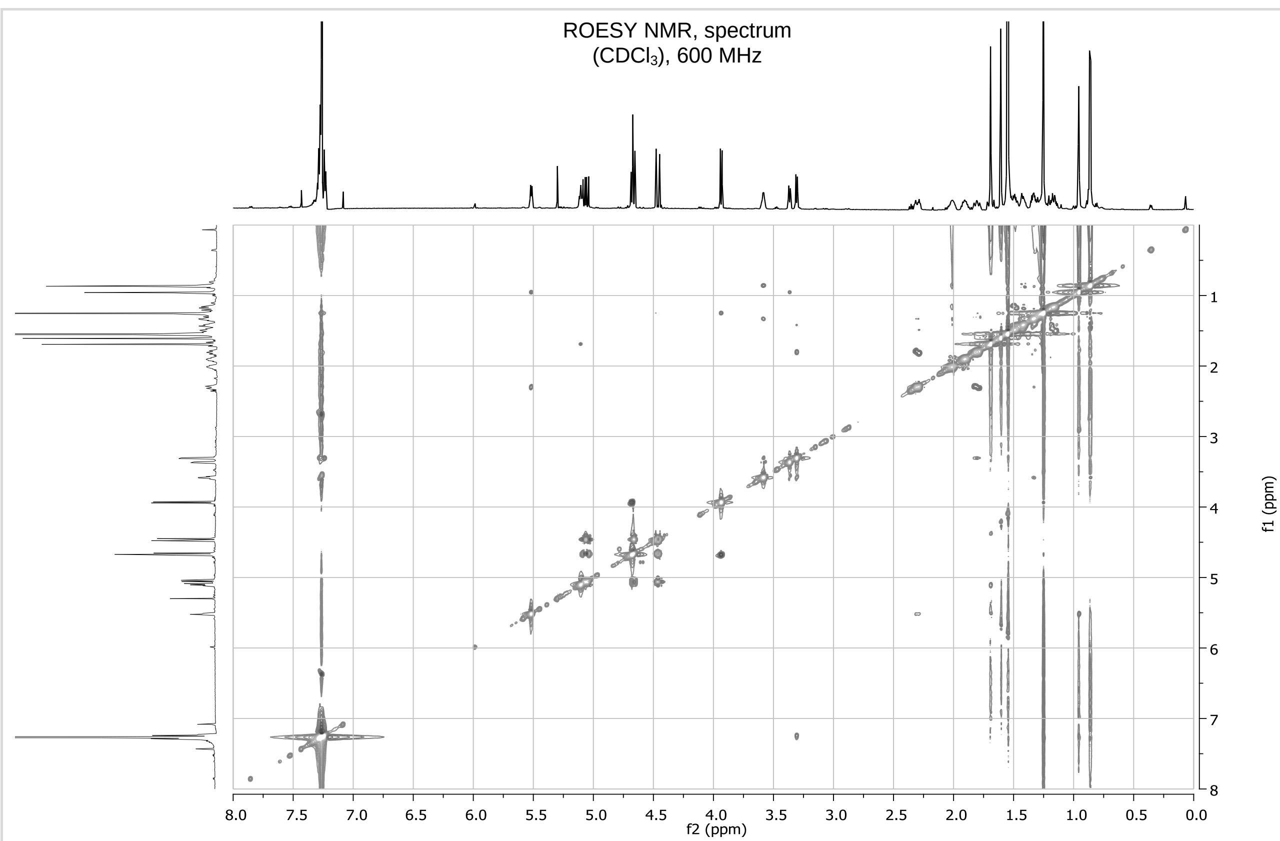

13
1H NMR, spectrum
(CDCl3), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

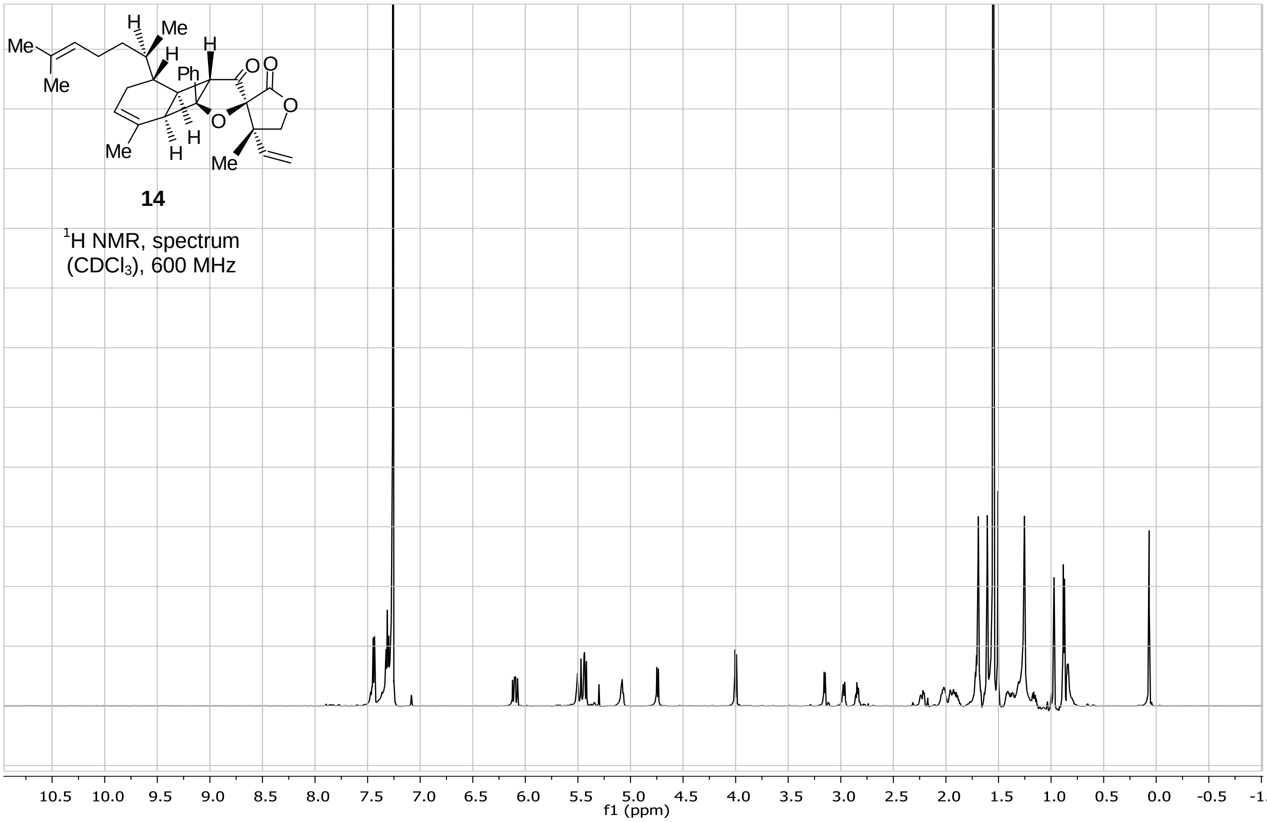

13C NMR, spectrum
(CDCl3), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

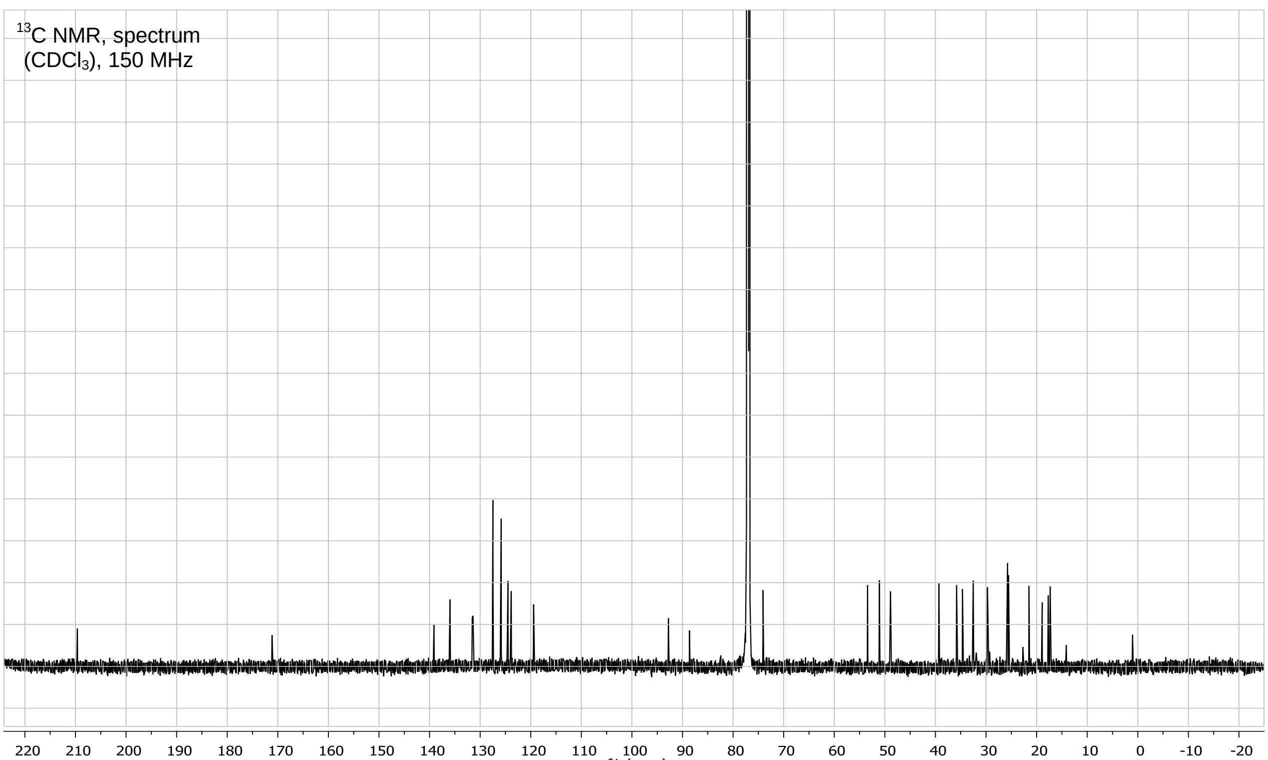

^{1}H-^{1}H COSY NMR, spectrum
(CDCl$_3$), 600 MHz
13
Me
Me
H
Me
H
H
H
O
O
O
H
Me
Ph
O
Me
f2 (ppm)
f1 (ppm)

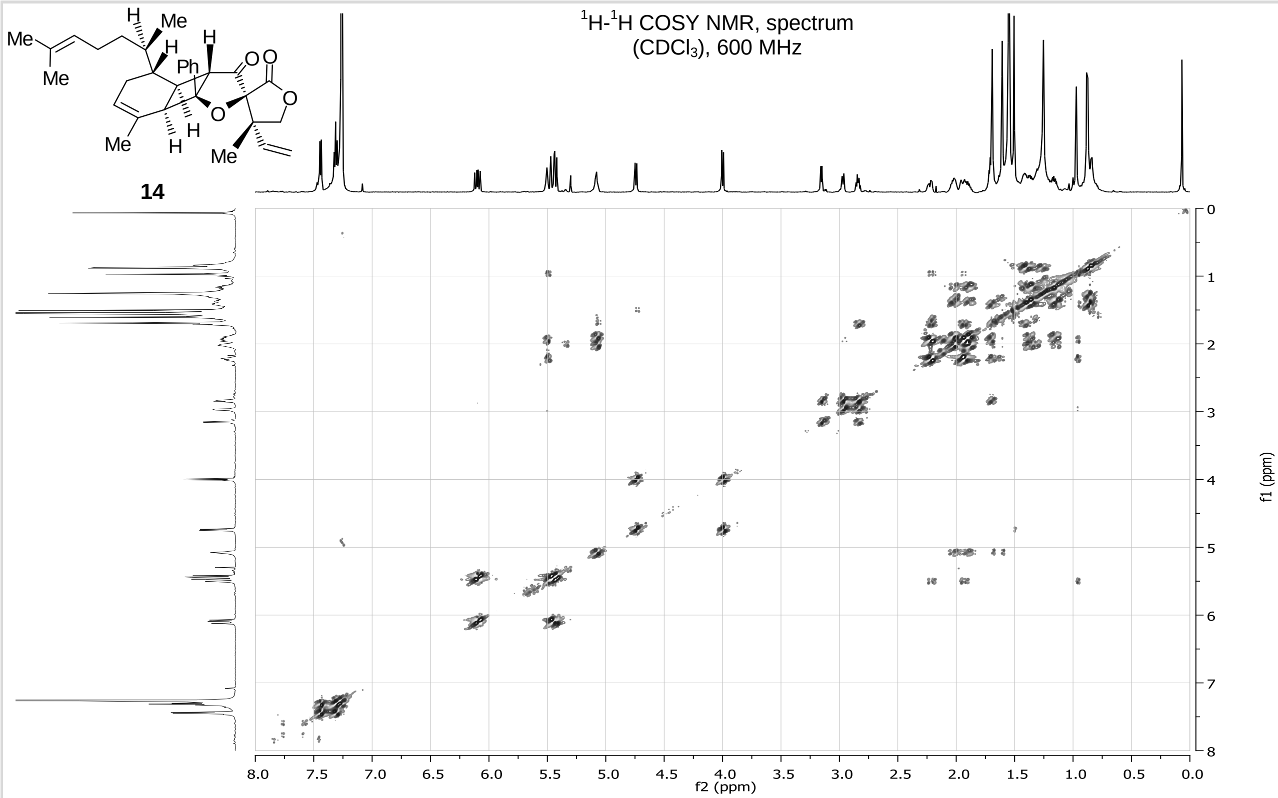

HMQC NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)


HMBC NMR, spectrum
(CDCl3), 600 MHz
13
f2 (ppm)
f1 (ppm)

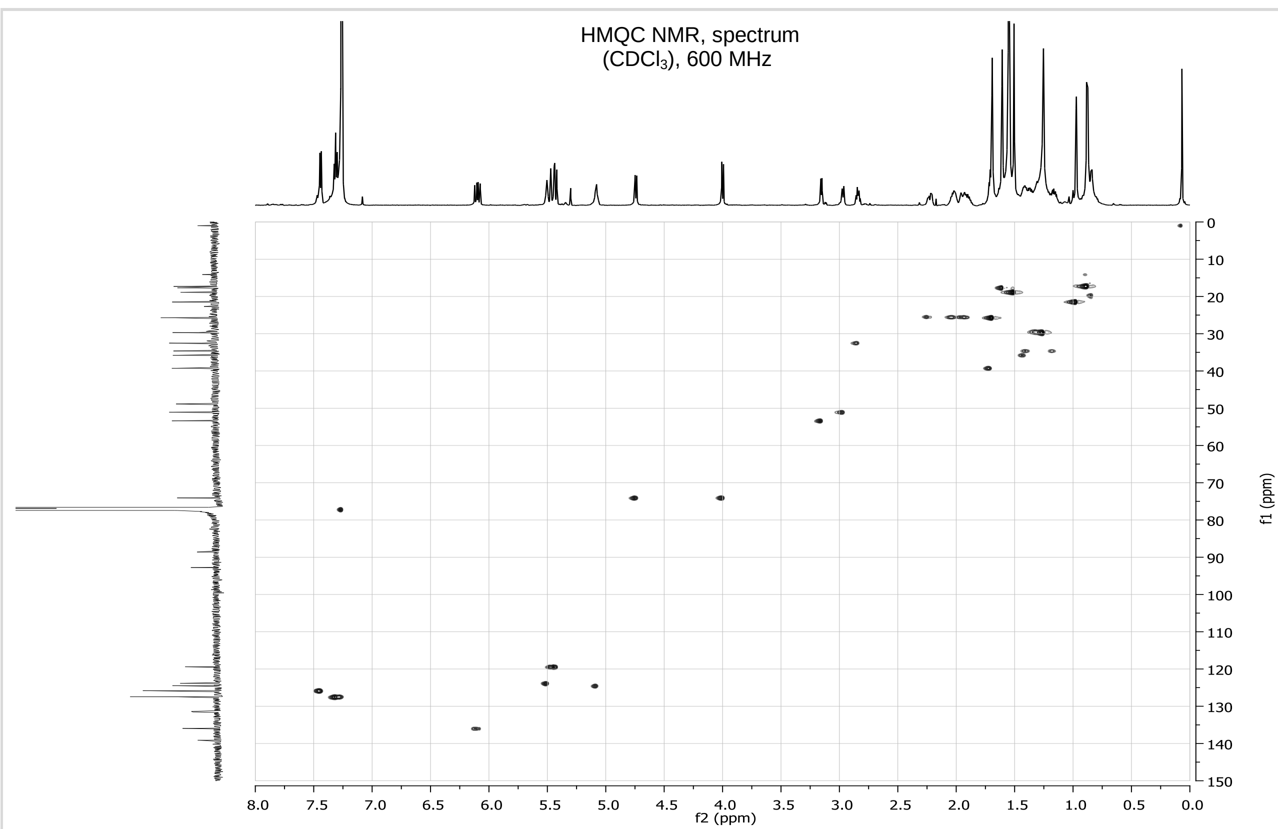

ROESY NMR, spectrum
(CDCl3), 600 MHz
f2 (ppm)
f1 (ppm)


14
^{1}H NMR, spectrum
($CDCl_3$), 600 MHz
f1 (ppm)

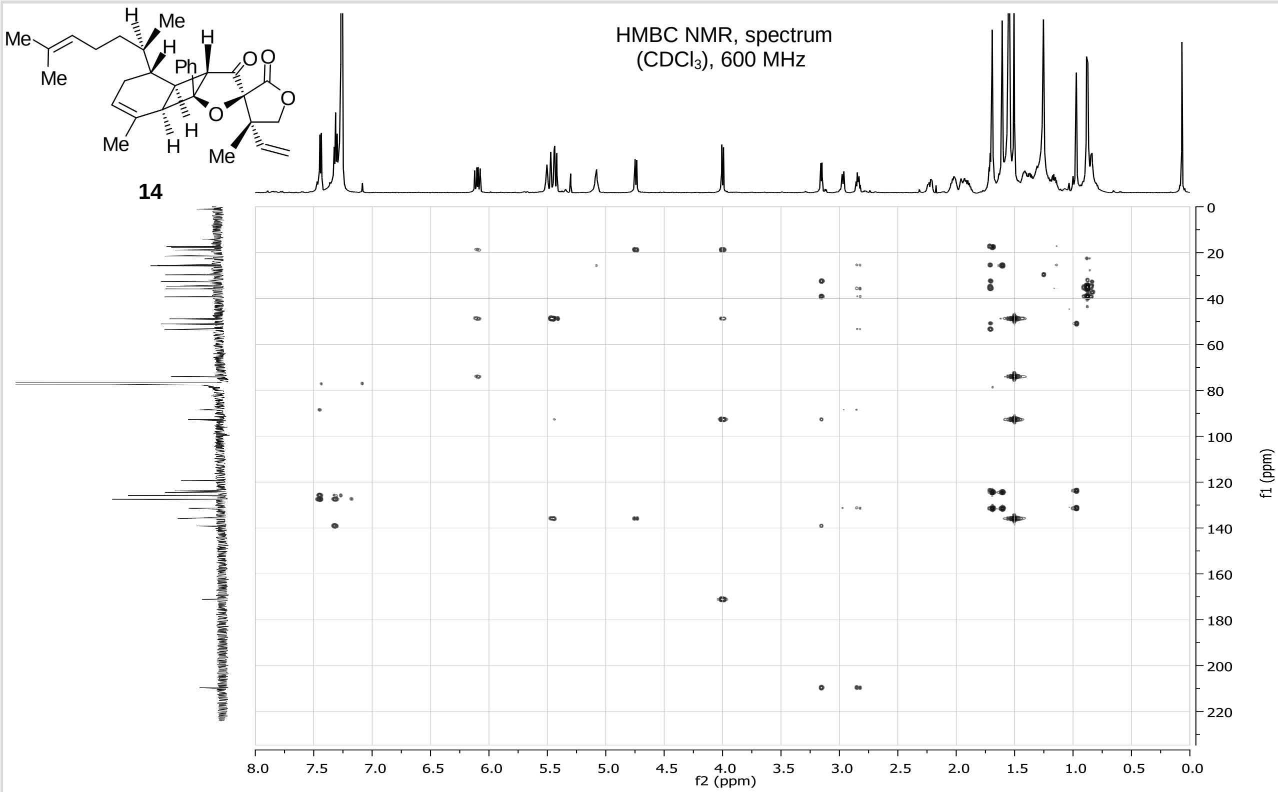

^{13}C NMR, spectrum
($CDCl_3$), 150 MHz
f1 (ppm)

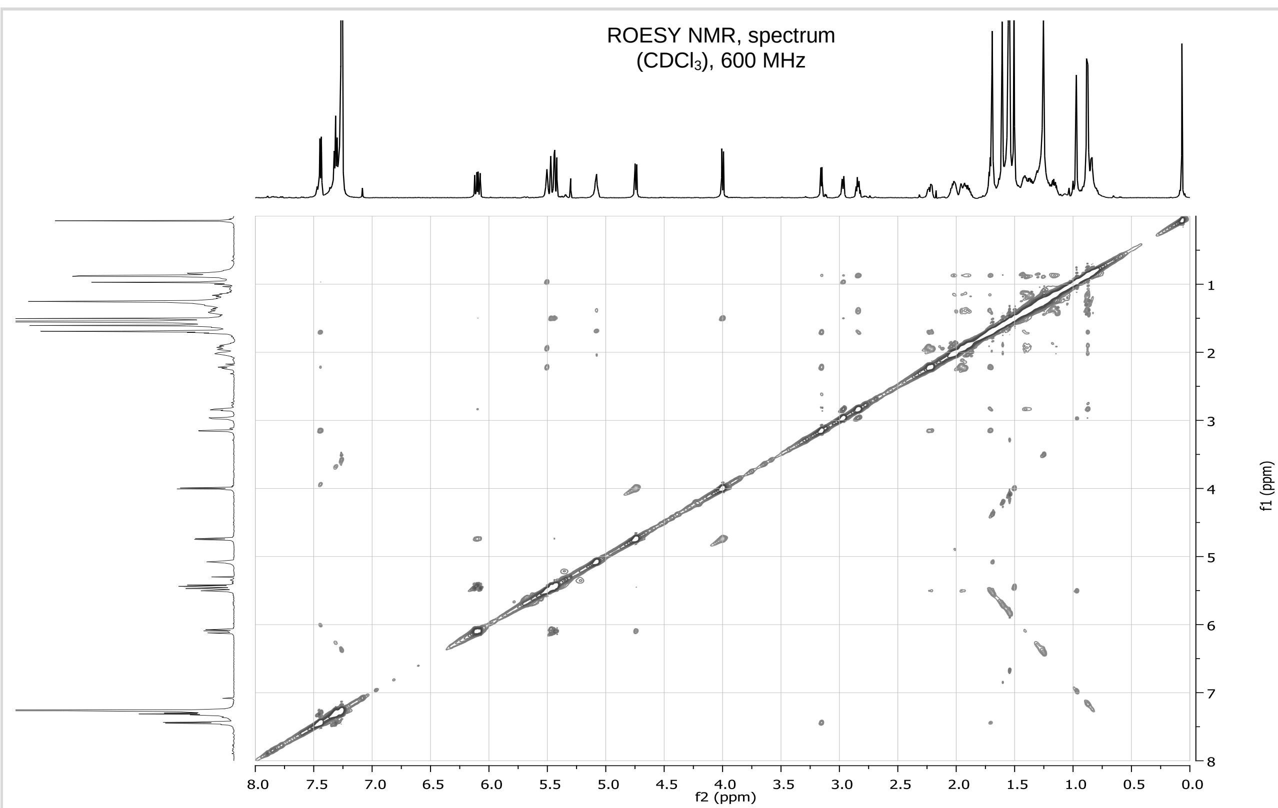


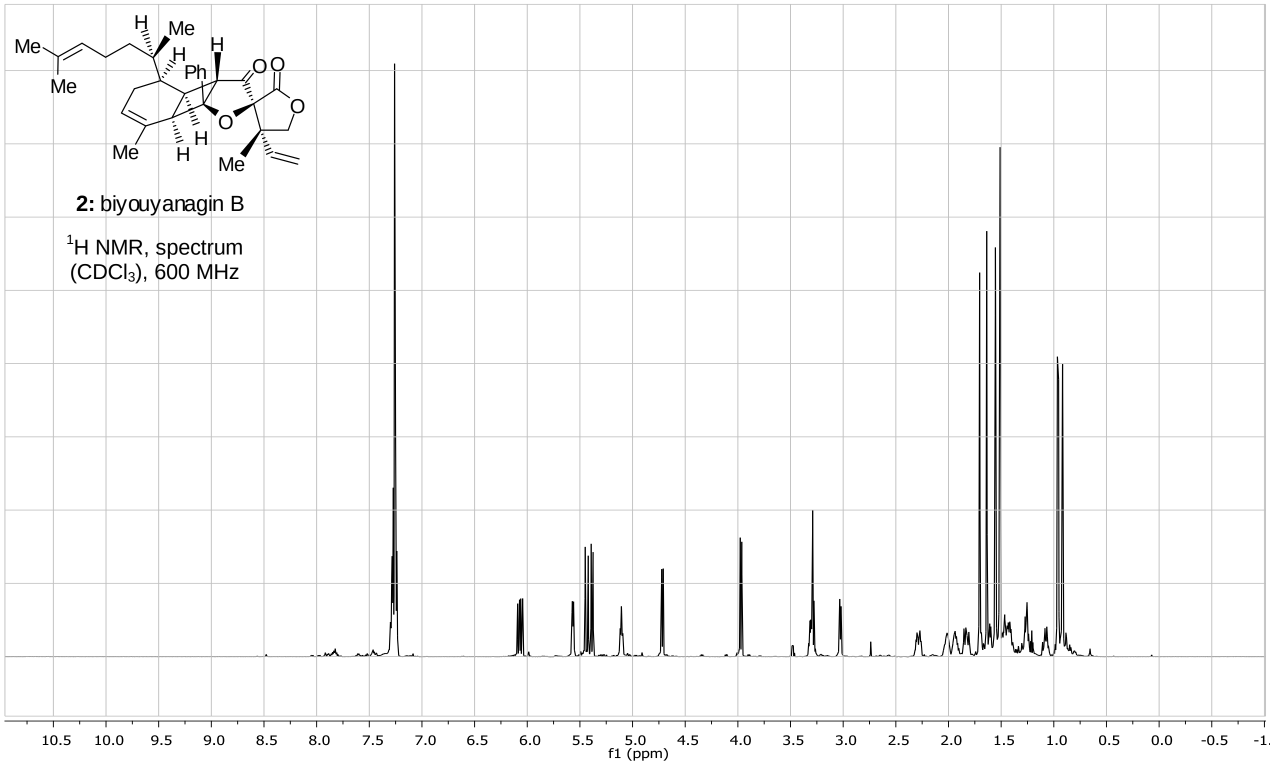
Me
Me
H
Me
H
H
Ph
O
O
O
O
H
H
Me
H
Me
14
^{1}H-^{1}H COSY NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)

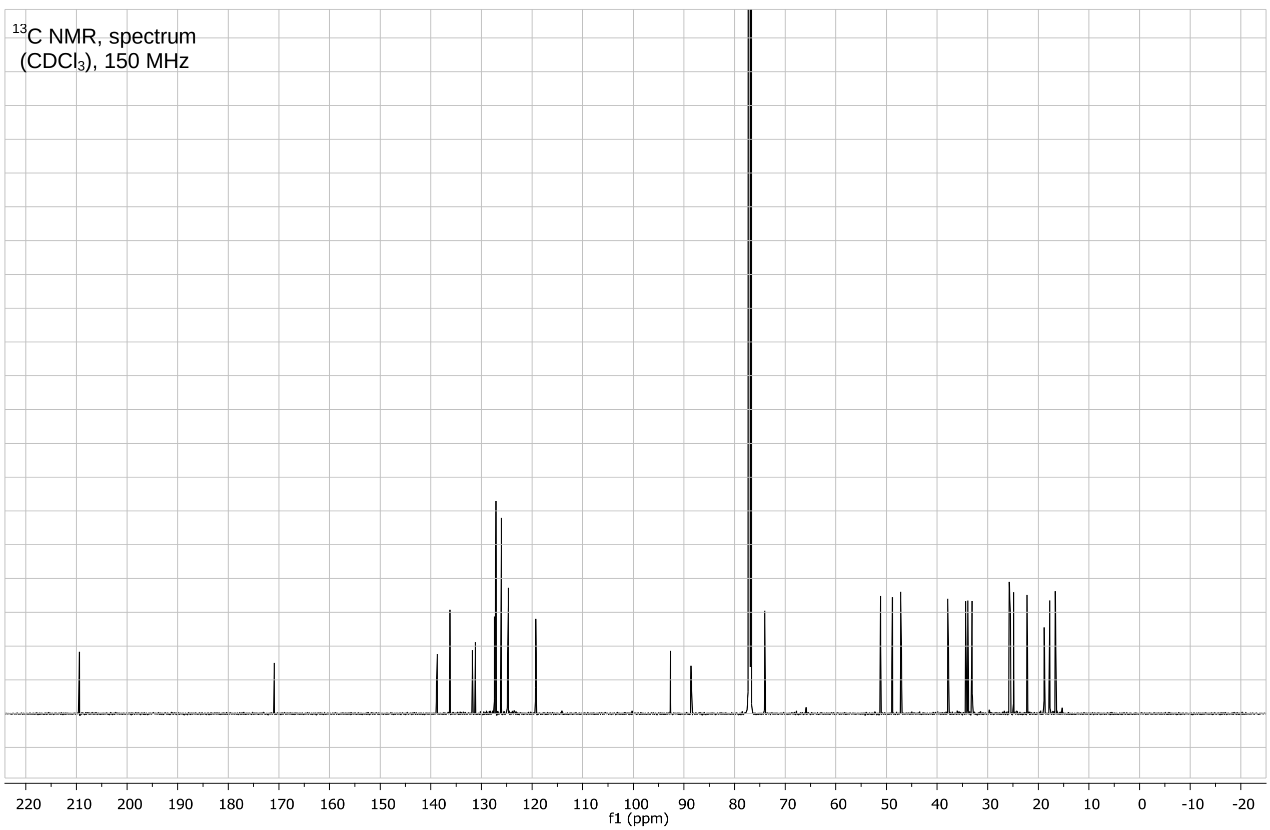


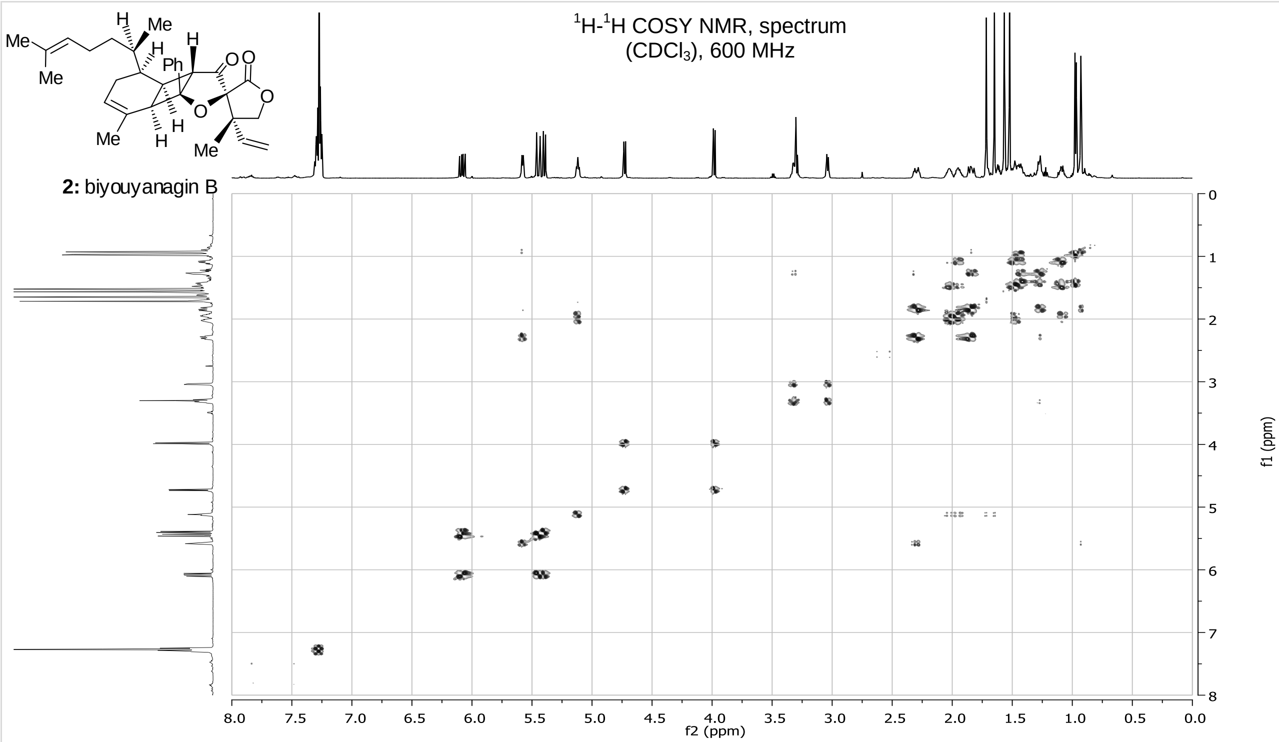
HMQC NMR, spectrum
(CDCl$_3$), 600 MHz
f2 (ppm)
f1 (ppm)


HMBC NMR, spectrum
(CDCl3), 600 MHz
Me
H
Me
H
H
Ph
O
O
O
Me
H
H
Me
H
Me
14
f2 (ppm)
f1 (ppm)

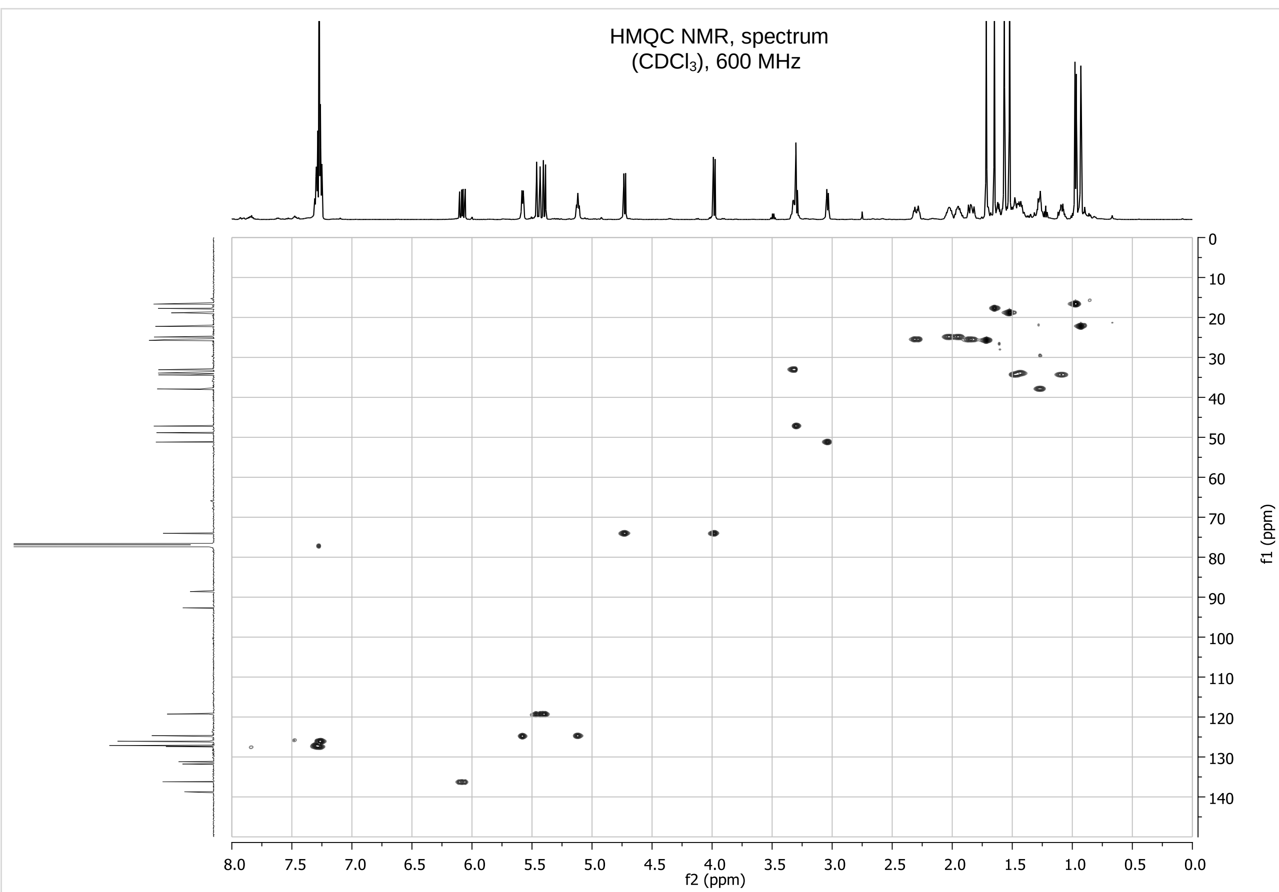

ROESY NMR, spectrum
(CDCl3), 600 MHz
f2 (ppm)
f1 (ppm)

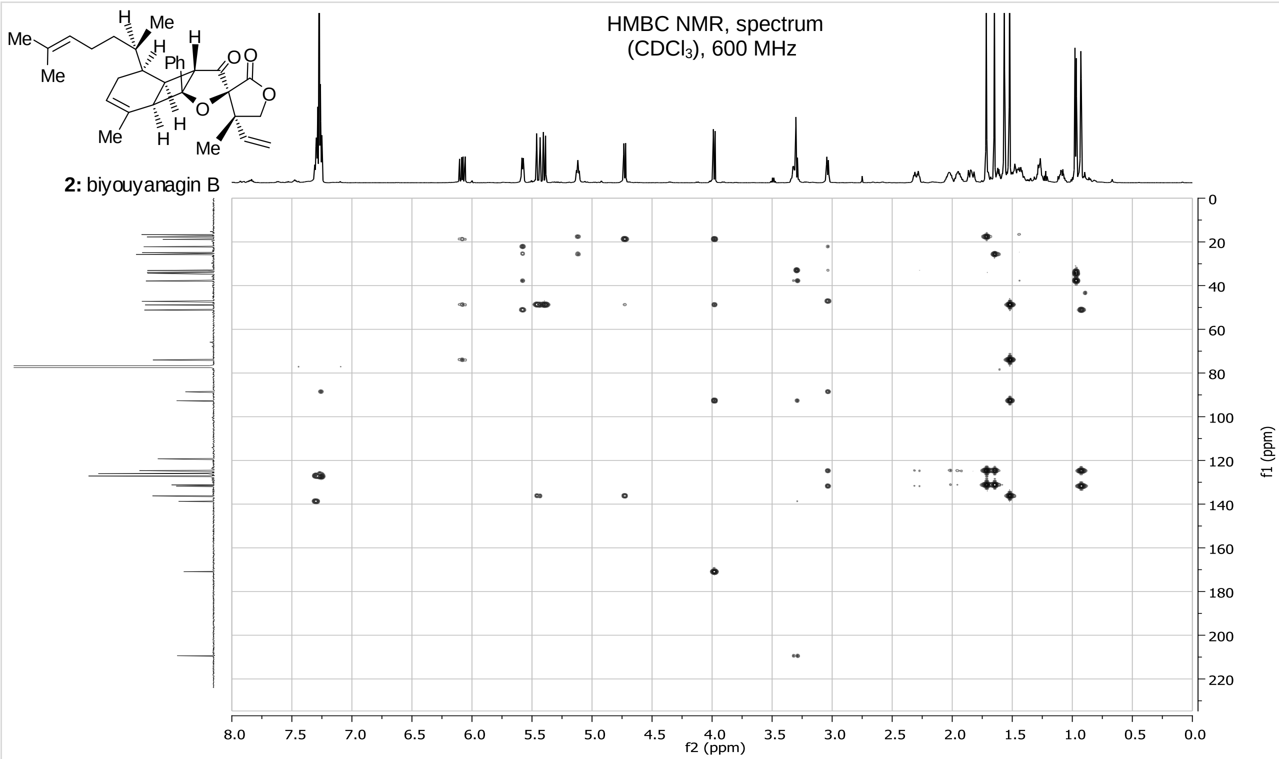

2: biyouyanagin B
^{1}H NMR, spectrum
($CDCl_3$), 600 MHz
f1 (ppm)

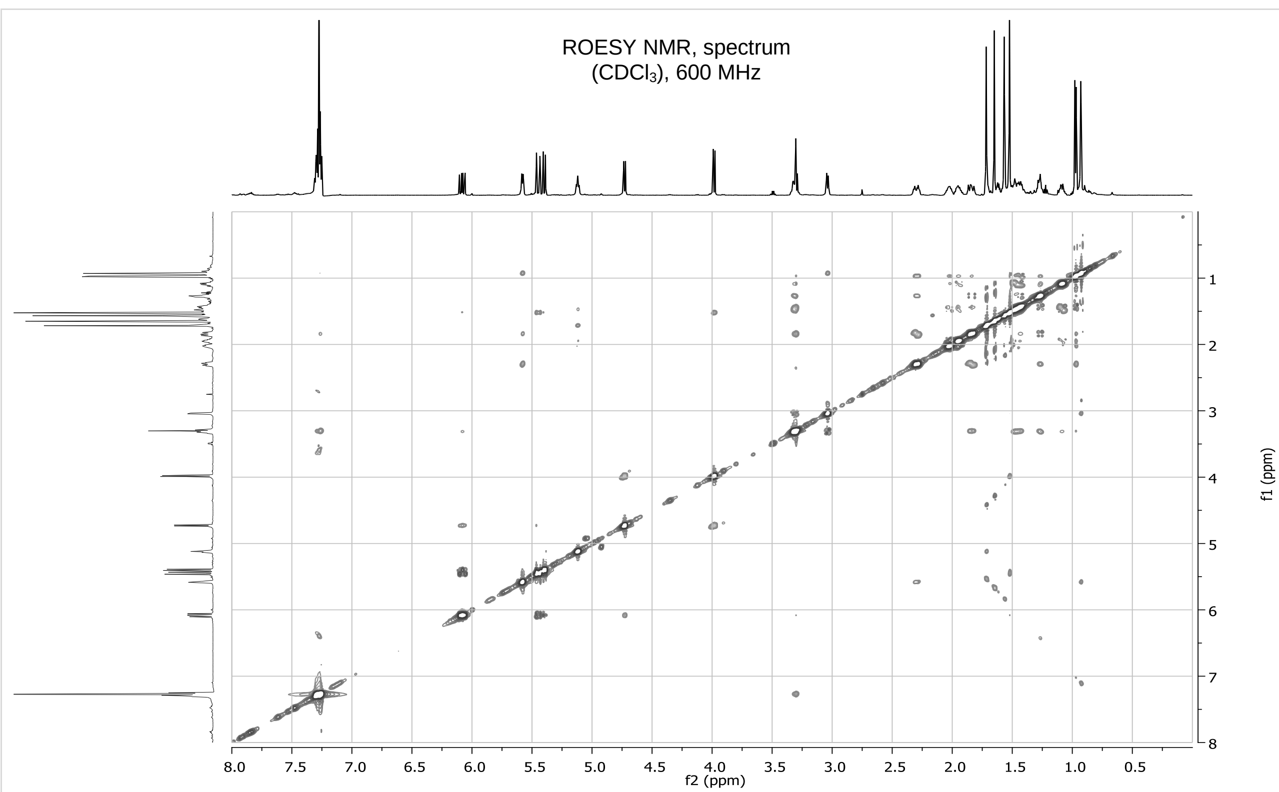

^{13}C NMR, spectrum
($CDCl_3$), 150 MHz
f1 (ppm)

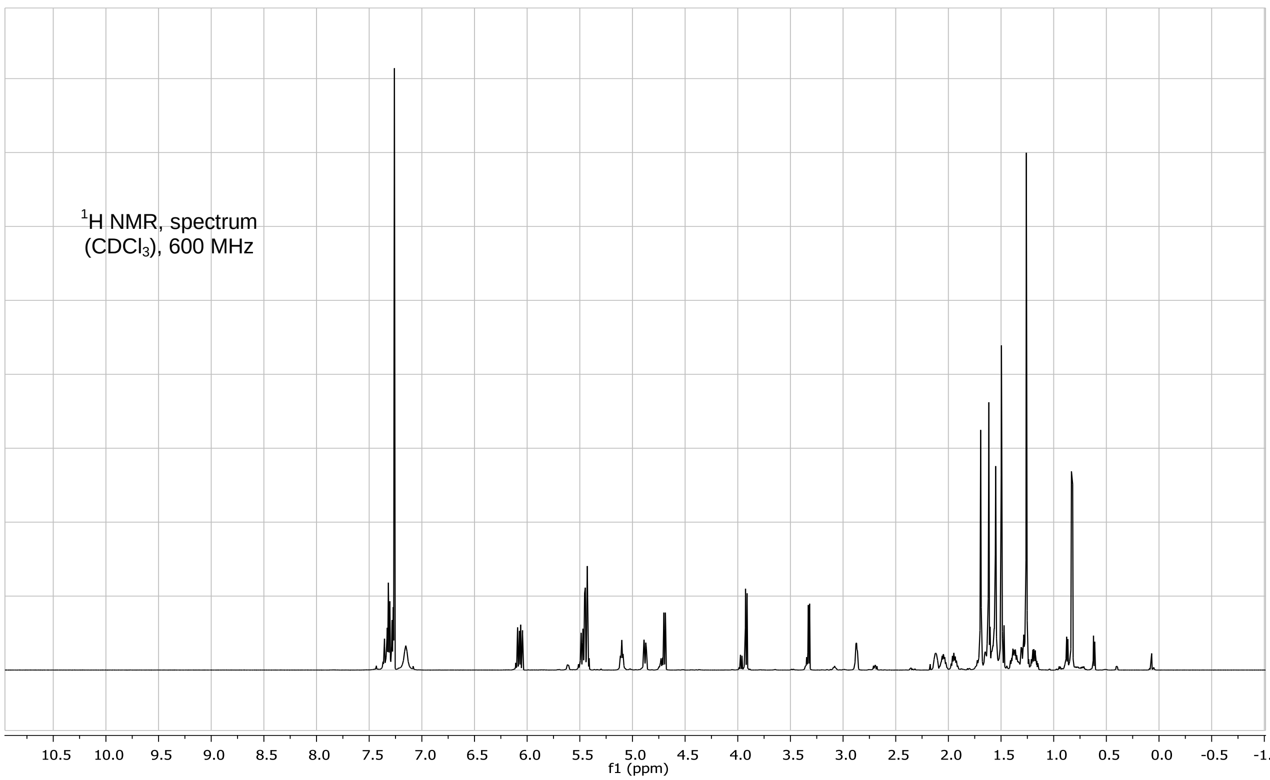


2: biyouyanagin B

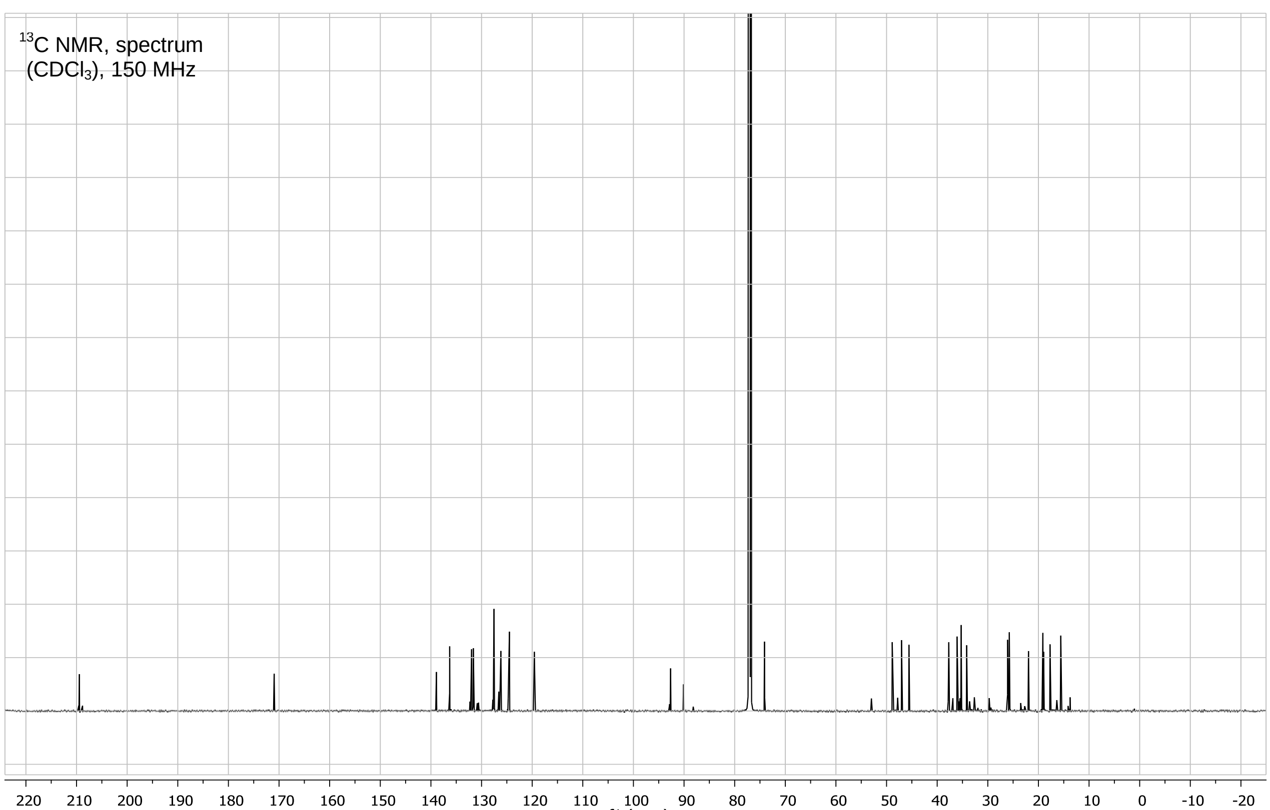



HMBC NMR, spectrum
($CDCl_3$), 600 MHz
2: biyouyanagin B
f2 (ppm)
f1 (ppm)

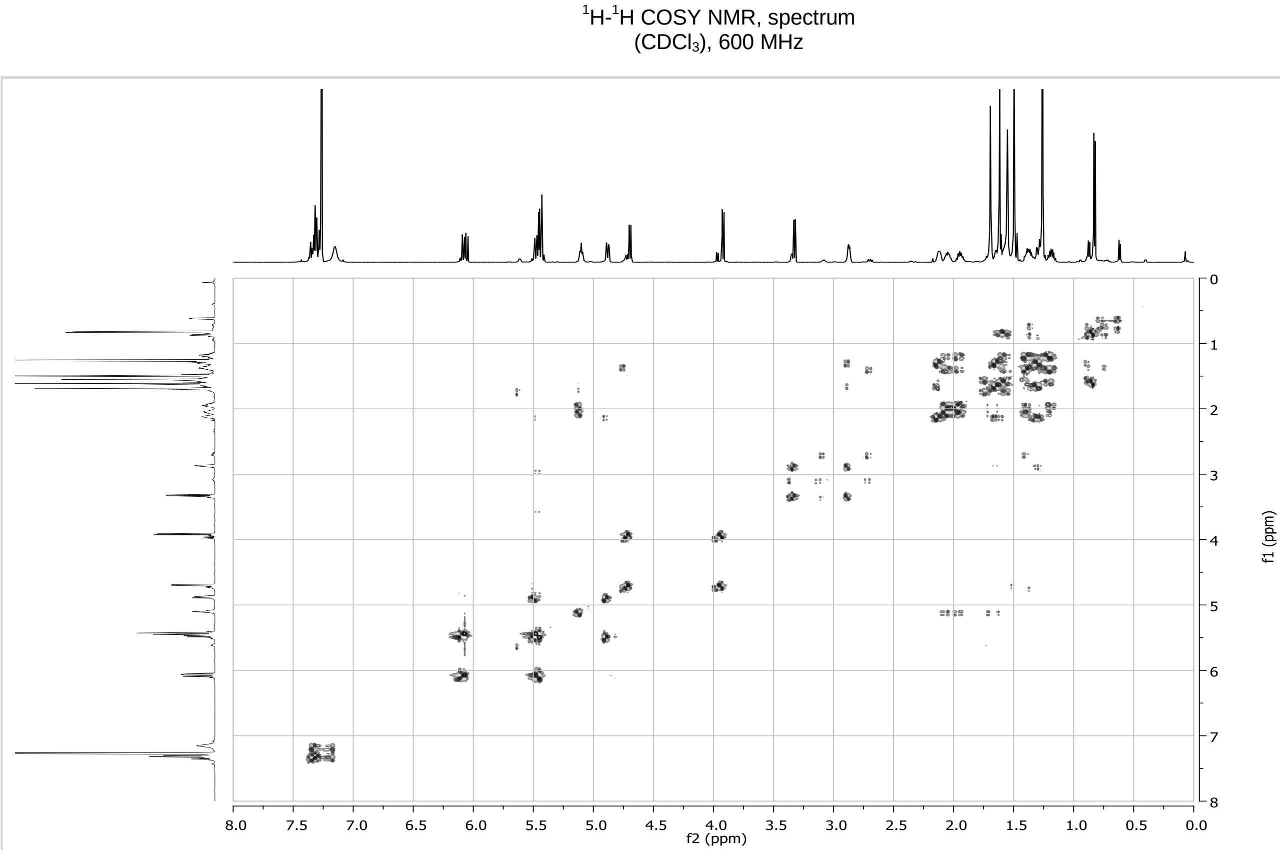

ROESY NMR, spectrum
($CDCl_3$), 600 MHz
f2 (ppm)
f1 (ppm)

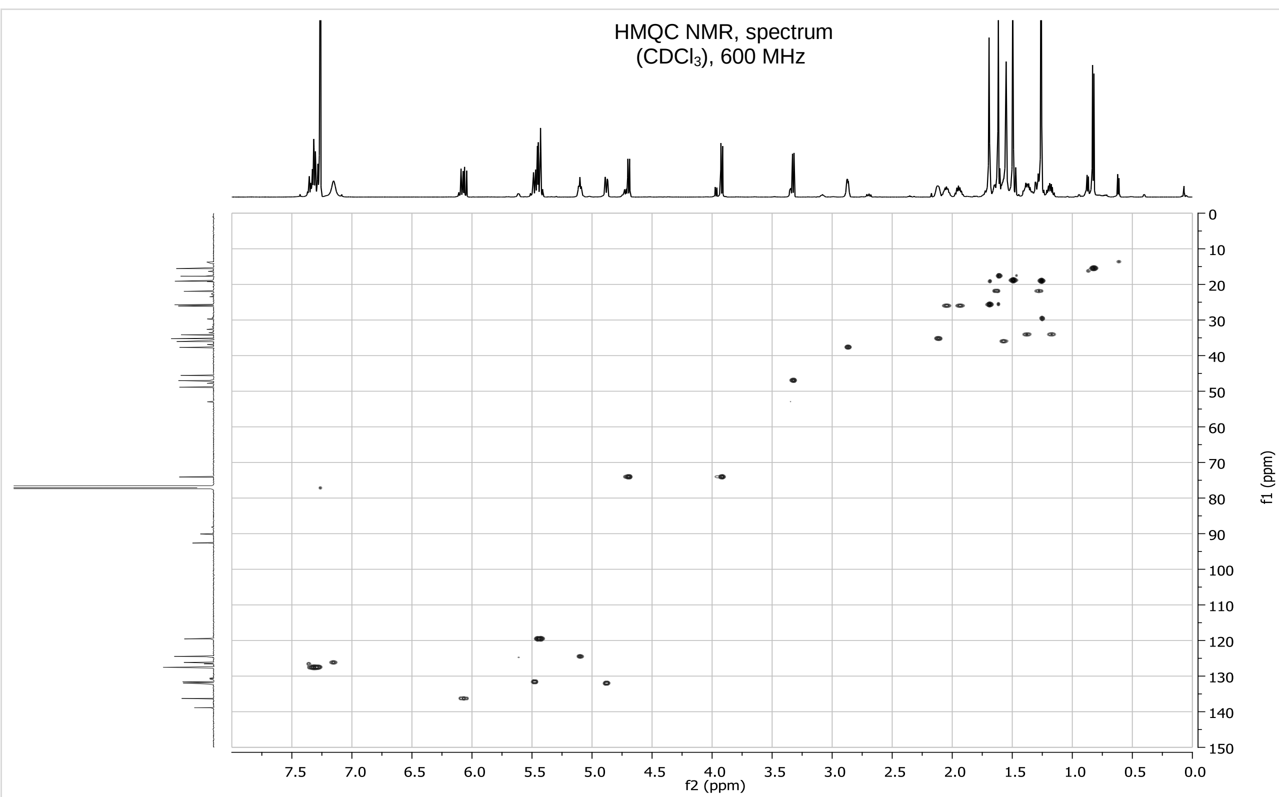


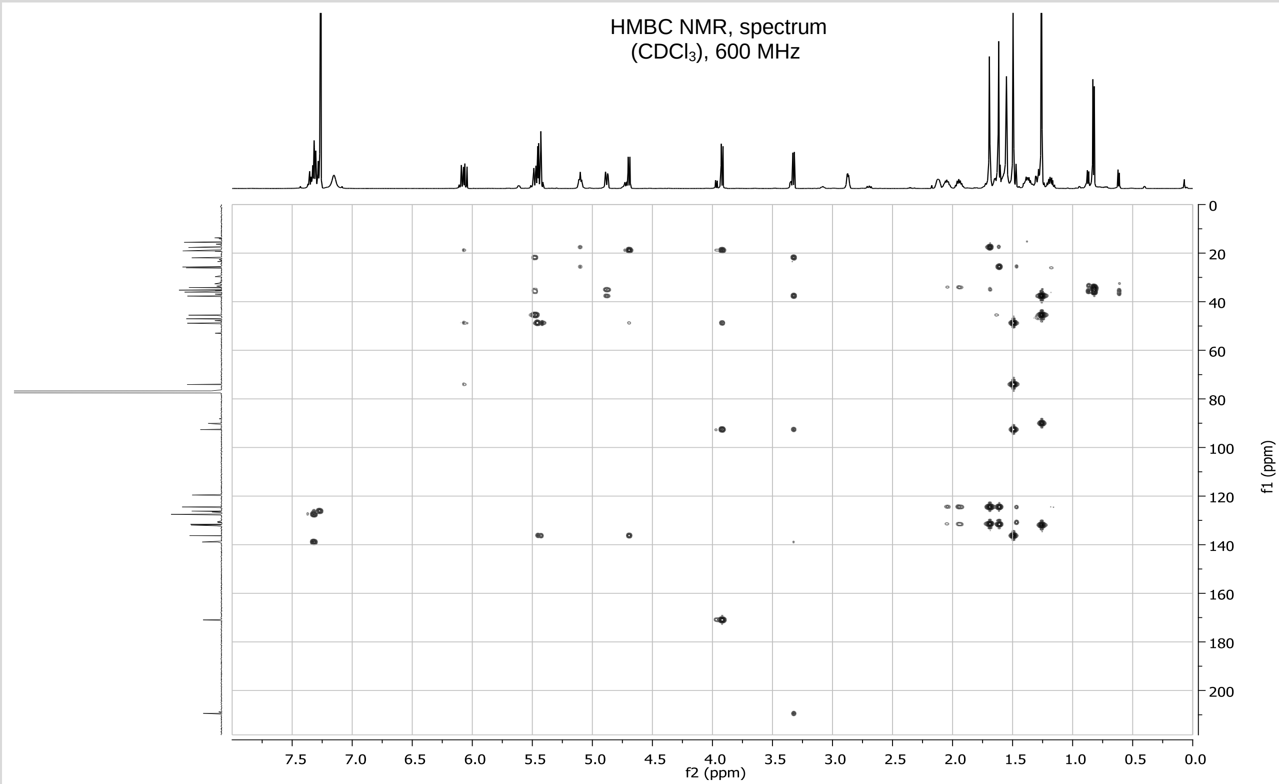
[1]H NMR, spectrum
($CDCl_3$), 600 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

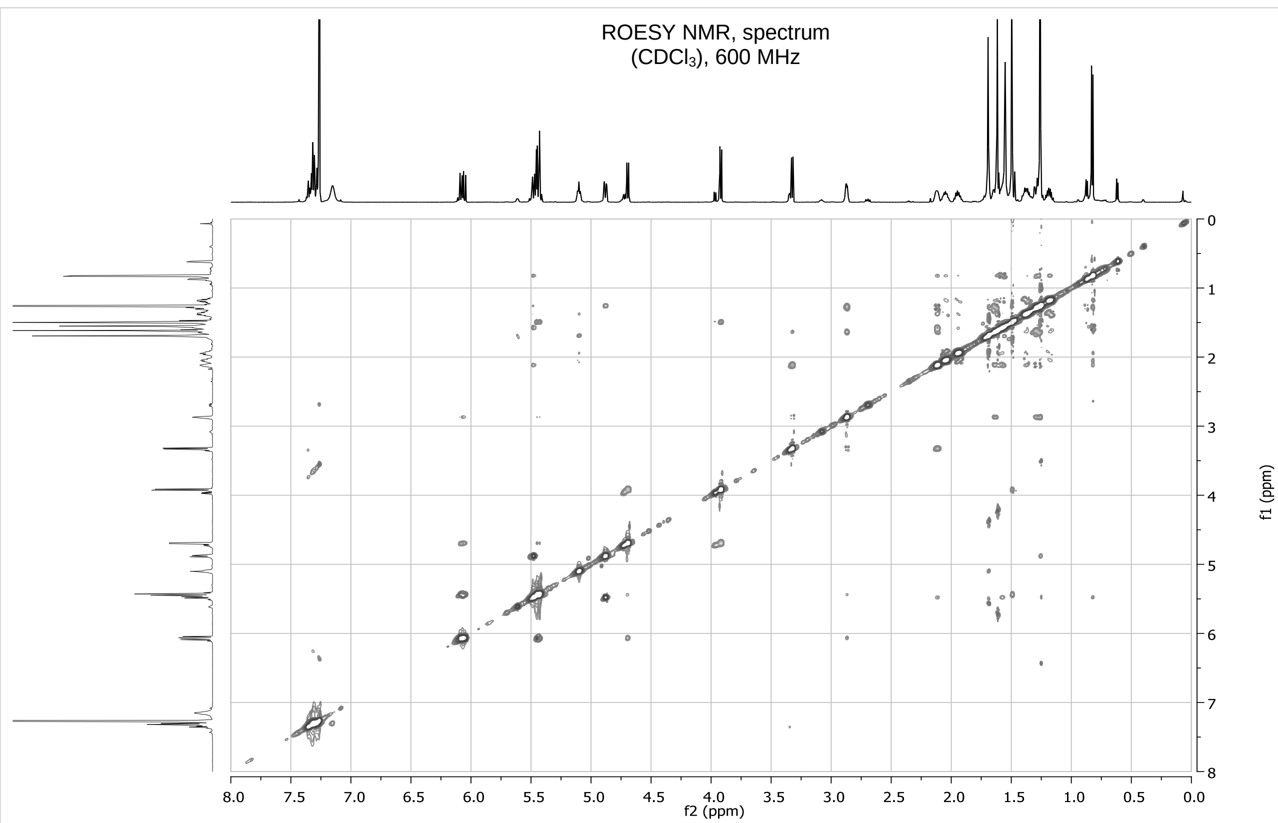


[13]C NMR, spectrum
($CDCl_3$), 150 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


^1H-^1H COSY NMR, spectrum
($CDCl_3$), 600 MHz
f2 (ppm)
f1 (ppm)


HMQC NMR, spectrum
($CDCl_3$), 600 MHz
f2 (ppm)
f1 (ppm)


HMBC NMR, spectrum
(CDCl3), 600 MHz
f1 (ppm)
f2 (ppm)


ROESY NMR, spectrum
(CDCl3), 600 MHz
f1 (ppm)
f2 (ppm)