Supporting Information for

$BF_3 \cdot Et_2O$ Mediated Cascade Cyclizations: Synthesis of Schweinfurthins F and G.

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5–Bromo–3,4–bis(methoxymethoxy)benzyloxy–*tert*–butyldimethylsilane (25). To a solution of benzyl alcohol **24** (4.11 g, 13.4 mmol) in CH_2Cl_2 at 0 °C was added *tert*-butyldimethylsilyl chloride (2.28 g, 15.1 mmol) in one portion. Imidazole (2.77 g, 40.8 mmol) was added in one portion to the cooled solution and the reaction was allowed to warm to room temperature and then stirred for 15 h. The reaction was quenched by addition of H_2O and extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O and brine, dried ($MgSO_4$), and concentrated *in vacuo* to afford silane **25** (5.61 g, 99 %) as a pale yellow liquid: ^{1}H NMR δ 7.18 (d, *J* = 2.1 Hz, 1H), 7.08 (d, *J* = 1.5 Hz, 1H), 5.18 (s, 2H), 5.16 (s, 2H), 4.64 (s, 2H), 3.66 (s, 3H), 3.49 (s, 3H), 0.94 (s, 9H), 0.09 (s, 6H); ^{13}C NMR δ 151.0, 142.9, 139.1, 123.8, 117.7, 113.7, 99.0, 95.4, 64.0, 58.1, 56.4, 26.0 (3C), 18.5, –5.2 (2C); HRMS (EI^+) *m/z* calcd for $C_{17}H_{29}O_5BrSi$ (M^+) 420.0968, found 420.0962.

5–((2*E*)–3,7–Dimethyl–2,6–octadienyl)–3,4–bis(methoxymethoxy)benzyloxy–*tert*–butyldimethylsilane (26). To a solution of bromoarene **25** (4.40 g, 10.5 mmol) in THF at –78 °C was added *n*–BuLi (5.1 mL, 2.3 M in hexanes, 11.6 mmol) dropwise and the resulting solution was stirred for 0.5 h. Geranyl bromide (2.3 mL, 11.6 mmol) was added dropwise to the cooled solution and the resulting solution was allowed to warm to room temperature and stirred for an additional 16 h. The reaction was quenched by addition of H_2O and extracted with EtOAc. The combined organic extracts were washed with H_2O and brine, dried ($MgSO_4$), and concentrated *in vacuo* to give a yellow oil. Final purification by flash column chromatography (3% EtOAc in hexanes) afforded compound **26** (4.40 g, 86%) as a colorless liquid: ^{1}H NMR δ 6.98 (d, *J* = 1.2 Hz, 1H), 6.79 (d, *J* = 1.2 Hz, 1H), 5.31 (t, *J* = 7.2 Hz, 1H), 5.18 (s, 2H), 5.11–5.08 (m, 1H), 5.09

(s, 2H), 4.65 (s, 2H), 3.60 (s, 3H), 3.49 (s, 3H), 3.41 (d, *J* = 7.2 Hz, 2H), 2.11–1.96 (m, 4H), 1.70 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H), 0.93 (s, 9H), 0.09 (s, 6H); ^{13}C NMR δ 150.0, 143.6, 137.6, 136.4, 135.8, 131.5, 124.4, 122.7, 120.6, 112.2, 99.2, 95.3, 64.8, 57.6, 56.2, 39.9, 37.6, 28.5, 26.8, 26.0 (3C), 25.8, 18.5, 17.8, 16.3, –5.2 (2C). Anal. Calcd for $C_{27}H_{46}O_5Si$: C, 67.74; H, 9.68. Found: C, 67.65; H, 9.77.

Phosphonate 38. To a solution of alcohol **37** (135 mg, 0.39 mmol) in THF at 0 ºC was added triethylamine (0.23 mL, 1.7 mmol). After methanesulfonyl chloride (0.13 mL, 1.7 mmol) was added dropwise, the solution was stirred for 4 h. The reaction was quenched by addition of H_2O and extracted with EtOAc. The combined organic layers were washed with NH_4Cl (sat.) and brine, dried ($MgSO_4$), and concentrated *in vacuo* to give a yellow oil, which was then dissolved in acetone and treated with sodium iodide (234 mg, 1.6 mmol) for 15 h. The solvent was removed *in vacu*o and the red oily residue was extracted with EtOAc. The organic layers were washed with H_2O, $NaHCO_3$ (sat.) and then $Na_2S_2O_3$ until the reddish color dissipated. The combined aqueous layers were extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and concentrated to give a yellow oil which was subsequently treated with $P(OEt)_3$ (0.27 mL, 1.6 mmol). This solution was heated for 8 h at 80 ºC, then stirred at room temperature for 15 h, and finally quenched by addition of H_2O and extracted with EtOAc. The organic extracts were washed with H_2O and brine, dried ($MgSO_4$) and concentrated *in vacuo* to give a yellow liquid. Final purification by flash column chromatography (50% EtOAc in hexanes) yielded phosphonate **38** (68 mg, 37%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.61 (d, *J* = 1.8 Hz, 1H), 6.58 (d, *J* = 2.1 Hz, 1H), 4.74 (d, *J* = 6.9 Hz, 1H), 4.62 (d, *J* = 6.9 Hz, 1H), 4.04–3.96 (m, 4H), 3.80 (s, 3H), 3.38 (s, 3H), 3.24 (dd, *J* = 11.7, 4.2 Hz,

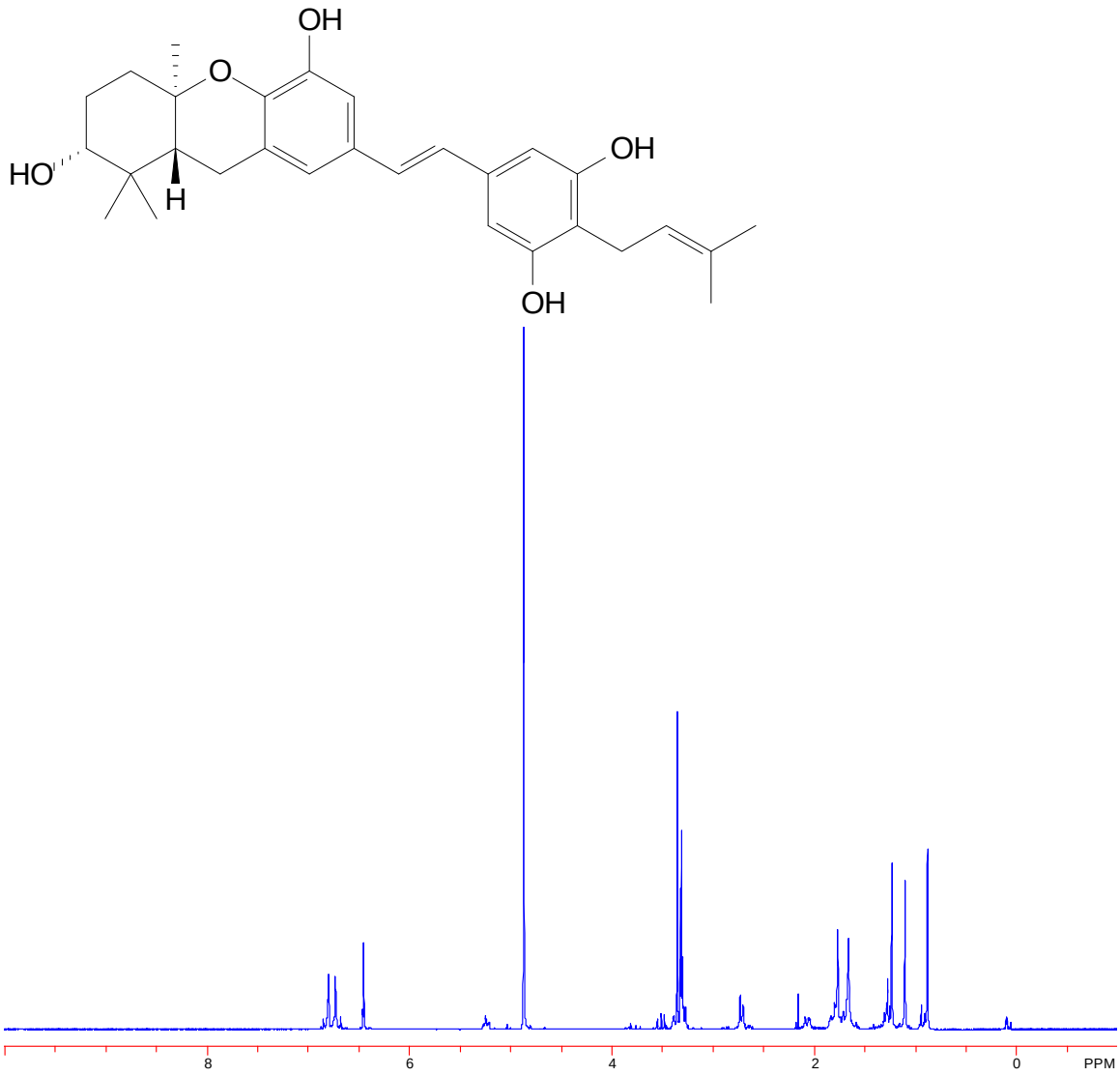
1H), 2.99 (d, J_{PH} = 21.3 Hz, 2H), 2.65 (s, 1H), 2.63–2.60 (m, 1H), 2.15–1.95 (m, 3H), 1.80–1.70 (m, 2H), 1.23 (t, J = 7.2 Hz, 6H), 1.21 (s, 3H), 1.05 (s, 3H), 0.86 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 148.7, (d, J_{CP} = 3.2 Hz), 141.7 (d, J_{CP} = 3.7 Hz), 126.5, 122.9 (d, J_{CP} = 7.4 Hz), 122.2 (d, J_{CP} = 9.2 Hz), 110.9 (d, J_{CP} = 5.6 Hz), 96.3, 84.2, 77.6, 62.2 (d, J_{CP} = 3.1 Hz), 62.2 (d, J_{CP} = 3.1 Hz), 56.1, 55.8, 47.1, 38.3, 37.7, 33.2 (d, J_{CP} = 138.7 Hz), 27.5, 25.4, 23.2, 19.8, 16.5 (d, J_{CP} = 5.7 Hz), 16.5 (d, J_{CP} = 5.7 Hz), 15.2; ^{31}P NMR δ 27.7; HRMS (EI$^+$) *m/z* calcd for $C_{24}H_{39}O_7P$ (M^+) 470.2433, found 470.2434.

Aldehyde 39. To a solution of the corresponding benzyl alcohol[11] (56 mg, 0.16 mmol) in CH_2Cl_2 was added MnO_2 (327 mg, 3.2 mmol). The resulting mixture was allowed to stir for 19 h and then filtered through celite. The solvent was removed *in vacuo* to obtain a yellow liquid and final purification by flash column chromatography (20% EtOAc in hexanes) afforded aldehyde **39**[22] (39 mg, 69%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 9.88 (s, 1H), 7.29 (s, 2H), 5.27 (s, 4H), 5.18 (t, J = 6.3 Hz, 1H), 5.05 (t, J = 6.3 Hz, 1H), 3.49 (s, 6H), 3.48–3.46 (m, 2H), 2.08–2.02 (m, 2H), 2.00–1.94 (m, 2H), 1.79 (s, 3H), 1.63 (s, 3H), 1.56 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 191.9, 156.1 (2C), 135.9, 135.6, 131.5, 127.6, 124.3, 121.3, 109.0 (2C), 94.5 (2C), 56.3 (2C), 39.9, 26.8, 25.8, 23.3, 17.8, 16.3.

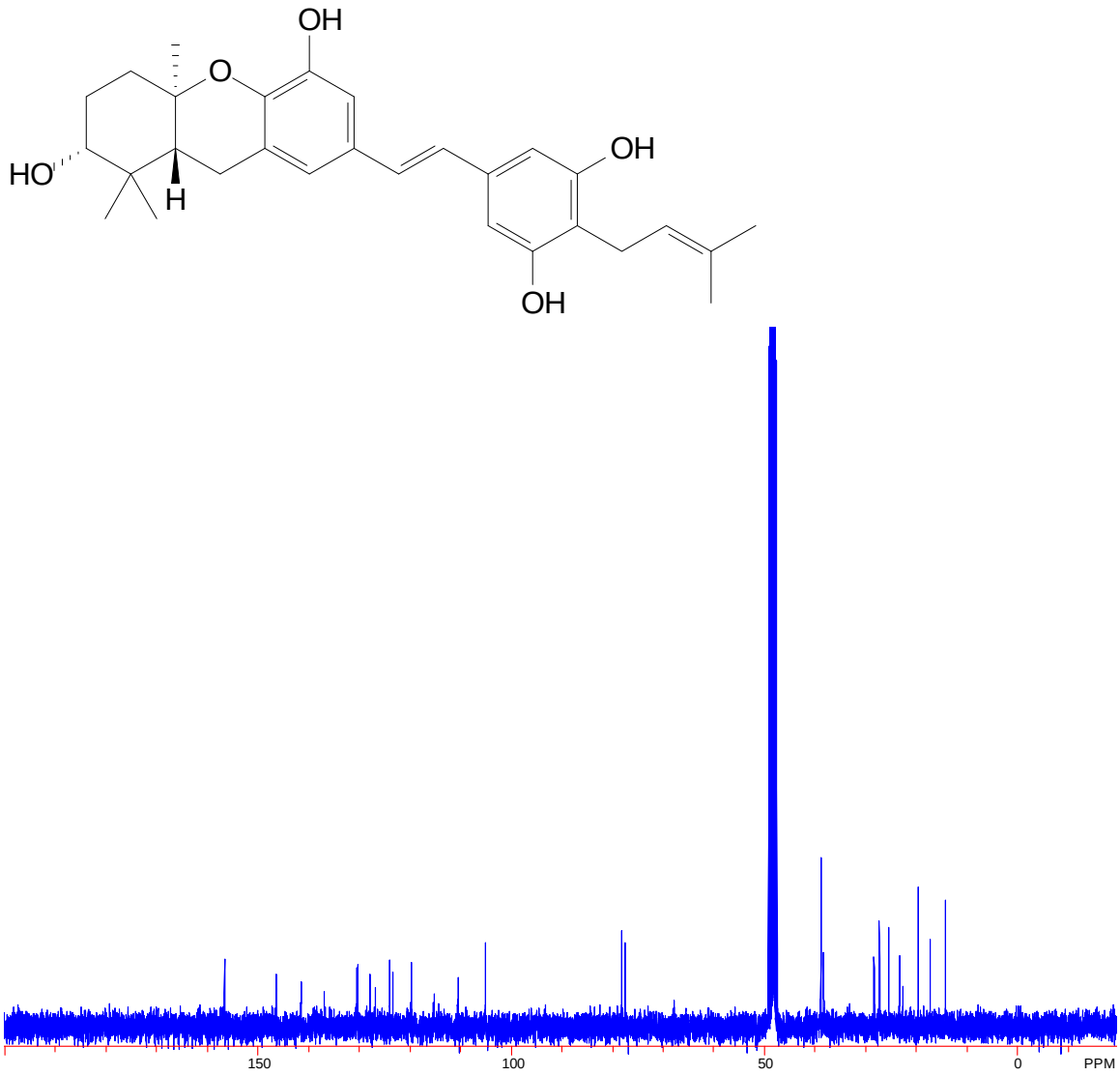
(2*R*,4*aR*,9*aR*)–O–2,5',7'–Tri(methoxymethyl)–3–deoxyschweinfurthin B (40). To a suspension of NaH (40 mg, 1.01 mmol, 60% oil dispersion) and 15–crown–5 (0.01 mL, 0.05 mmol) in THF at 0 ºC was added a solution of phosphonate **38** (20 mg, 0.04 mmol) and aldehyde **39** (17 mg, 0.04 mmol) in THF. The reaction was allowed to warm to room temperature and stirred for 26 h. The reaction was quenched by addition of H_2O and extracted with EtOAc. The organic extracts were washed with H_2O and brine, dried ($MgSO_4$), concentrated *in vacuo* to give a yellow liquid, and purified by flash column

chromatography (15% EtOAc in hexanes) to afford compound **40** (14 mg, 49%) as a colorless oil: $[\alpha]^{26.4}_{D}$ = +62.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.94–6.89 (m, 4H), 6.88 (d, *J* = 1.5 Hz, 1H), 6.86–6.84 (m, 1H), 5.25–5.22 (m, 5H), 5.10–5.06 (m, 1H), 4.77 (d, *J* = 6.9 Hz, 1H), 4.65 (d, *J* = 7.2 Hz, 1H), 3.90 (s, 3H), 3.50 (s, 6H), 3.41 (s, 3H), 3.41–3.37 (m, 2H), 3.27 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.73–2.68 (m, 2H), 2.15–1.95 (m, 6H), 1.79 (s, 3H), 1.75–1.70 (m, 3H), 1.64 (s, 3H), 1.56 (s, 3H), 1.26 (s, 3H), 1.09 (s, 3H), 0.91 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 156.0 (2C), 149.1, 142.8, 136.8, 134.8, 131.4, 129.0, 128.4, 126.5, 124.5, 122.8, 122.8, 122.7, 120.7, 119.6, 106.1 (2C), 96.3, 94.6 (2C), 84.2, 77.4, 56.1 (2C), 55.8, 47.2, 40.0, 38.4, 37.7, 27.5, 26.9, 25.8, 25.4, 23.2, 22.8, 21.4, 20.0, 17.8, 16.2, 15.3; HRMS (EI^+) *m/z* calcd for $C_{41}H_{58}O_8$ (M^+) 678.4132, found 678.4139.

(2*R*,*4aR*,*9aR*)–3–Deoxyschweinfurthin B (11). To a solution of stilbene **40** (8 mg, 0.01 mmol) in MeOH was added TsOH (11 mg, 0.06 mmol) at room temperature and the solution was stirred for 92 h. The reaction was quenched by addition of H_2O and extracted with EtOAc. The organic extracts were washed with H_2O, $NaHCO_3$ (sat.) and brine, dried ($MgSO_4$), and concentrated *in vacuo* to afford a yellow oil. Final purification by flash column chromatography (3:2 hexanes/EtOAc) afforded stilbene **11** (5 mg, 81%) as a yellow oil with spectral data matching previously reported data and 94% ee by HPLC.[13]



^{1}H NMR for compound **8** (300 MHz)



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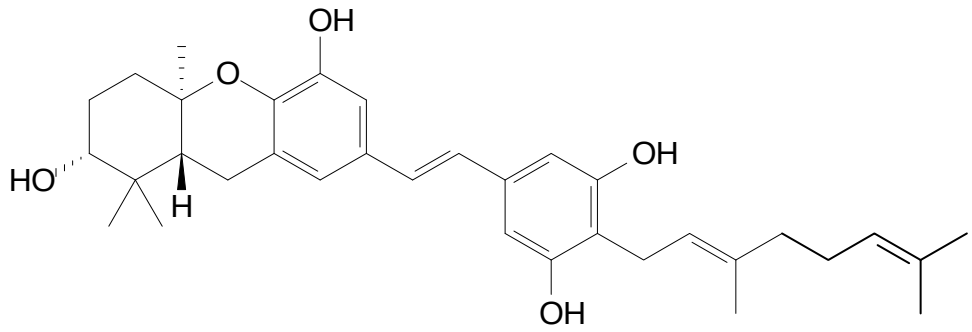

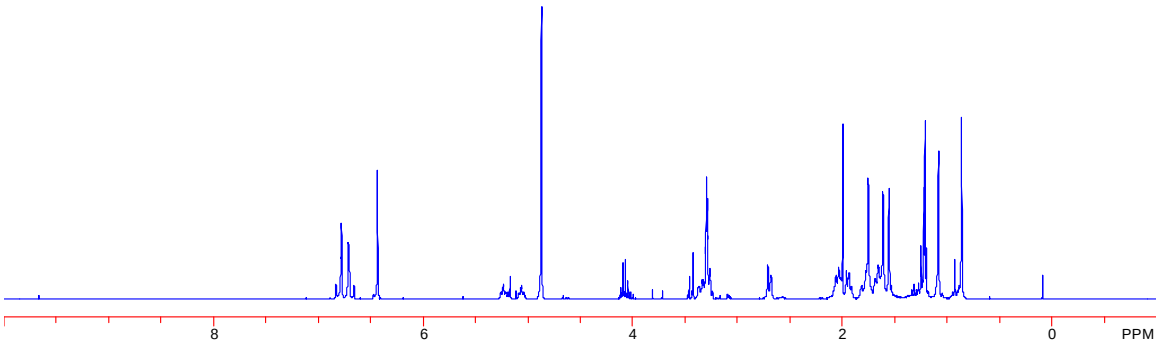

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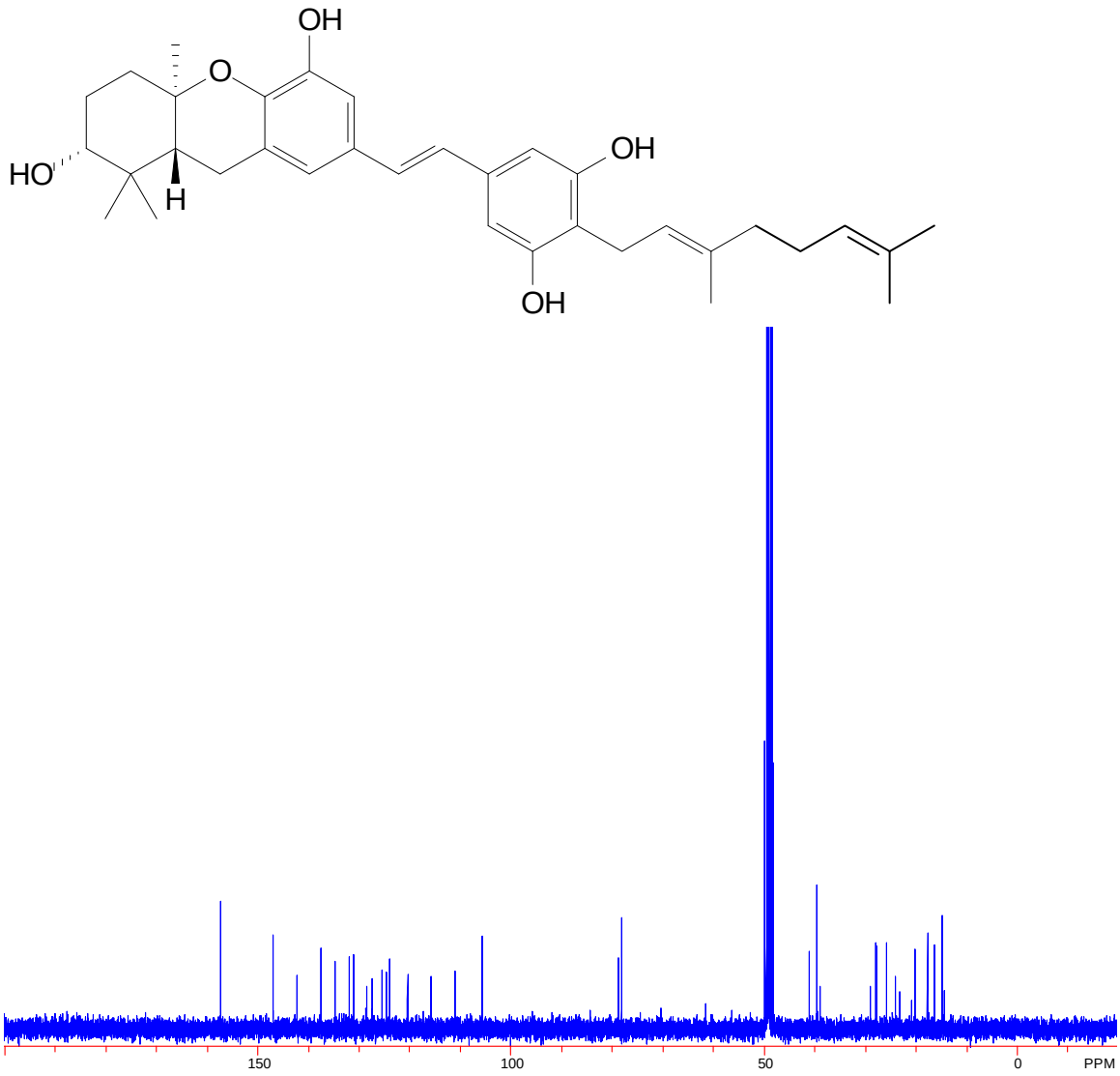

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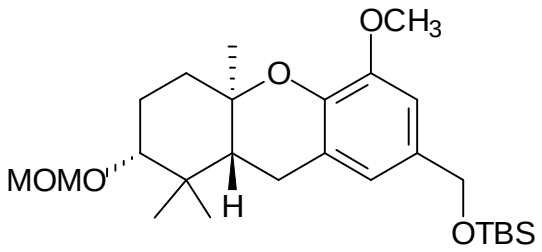

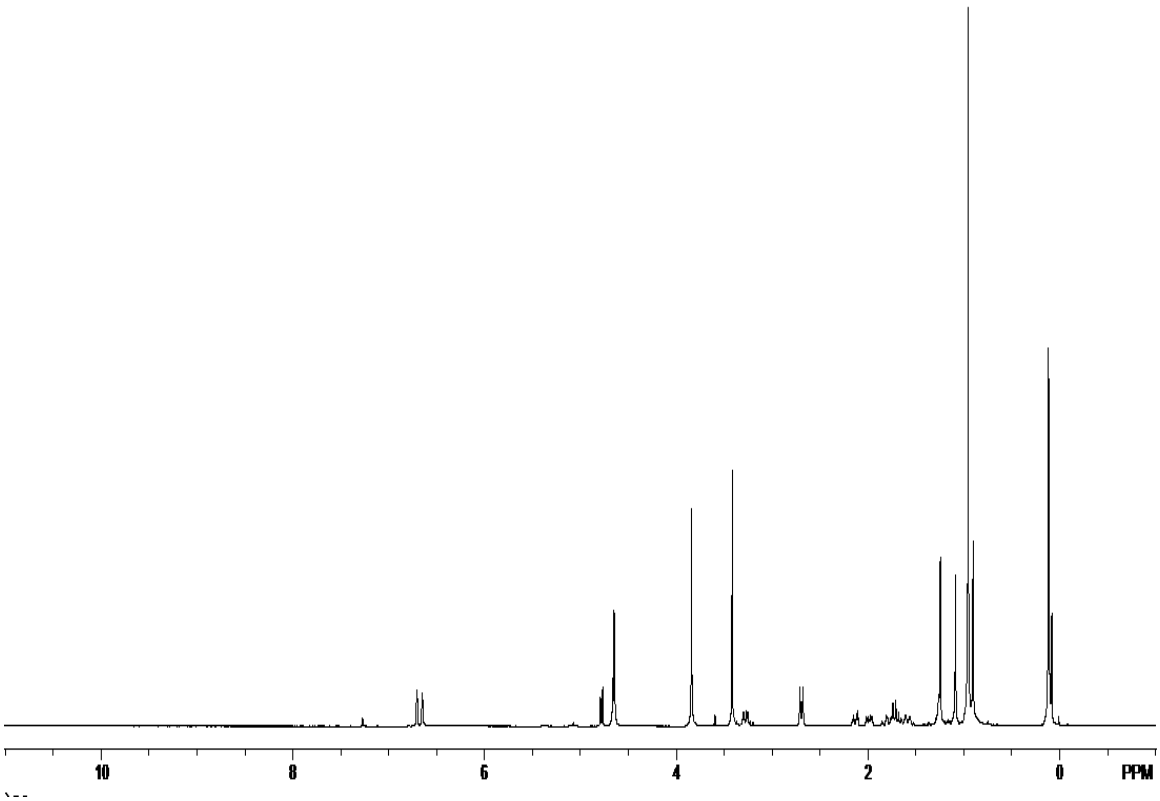

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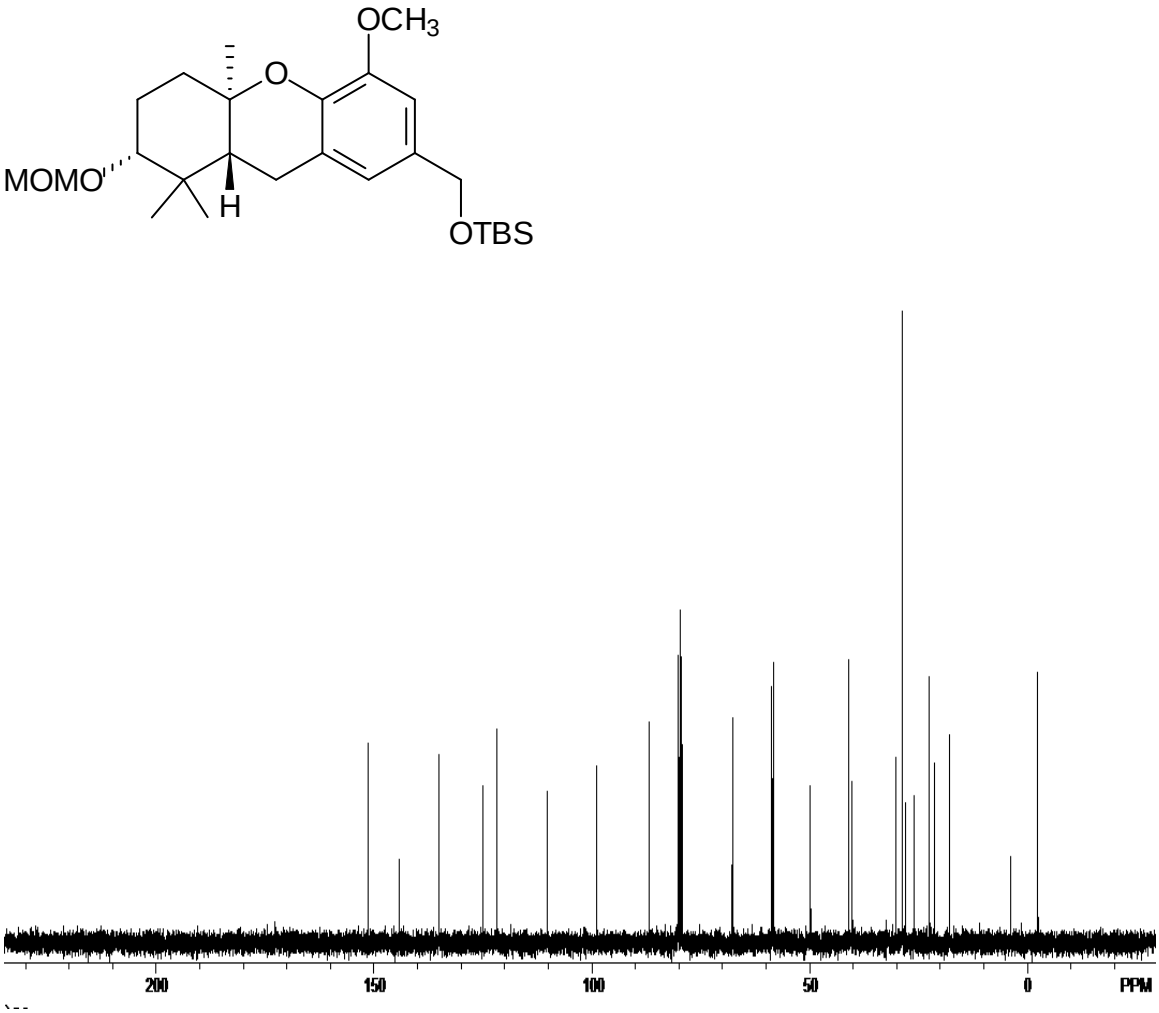

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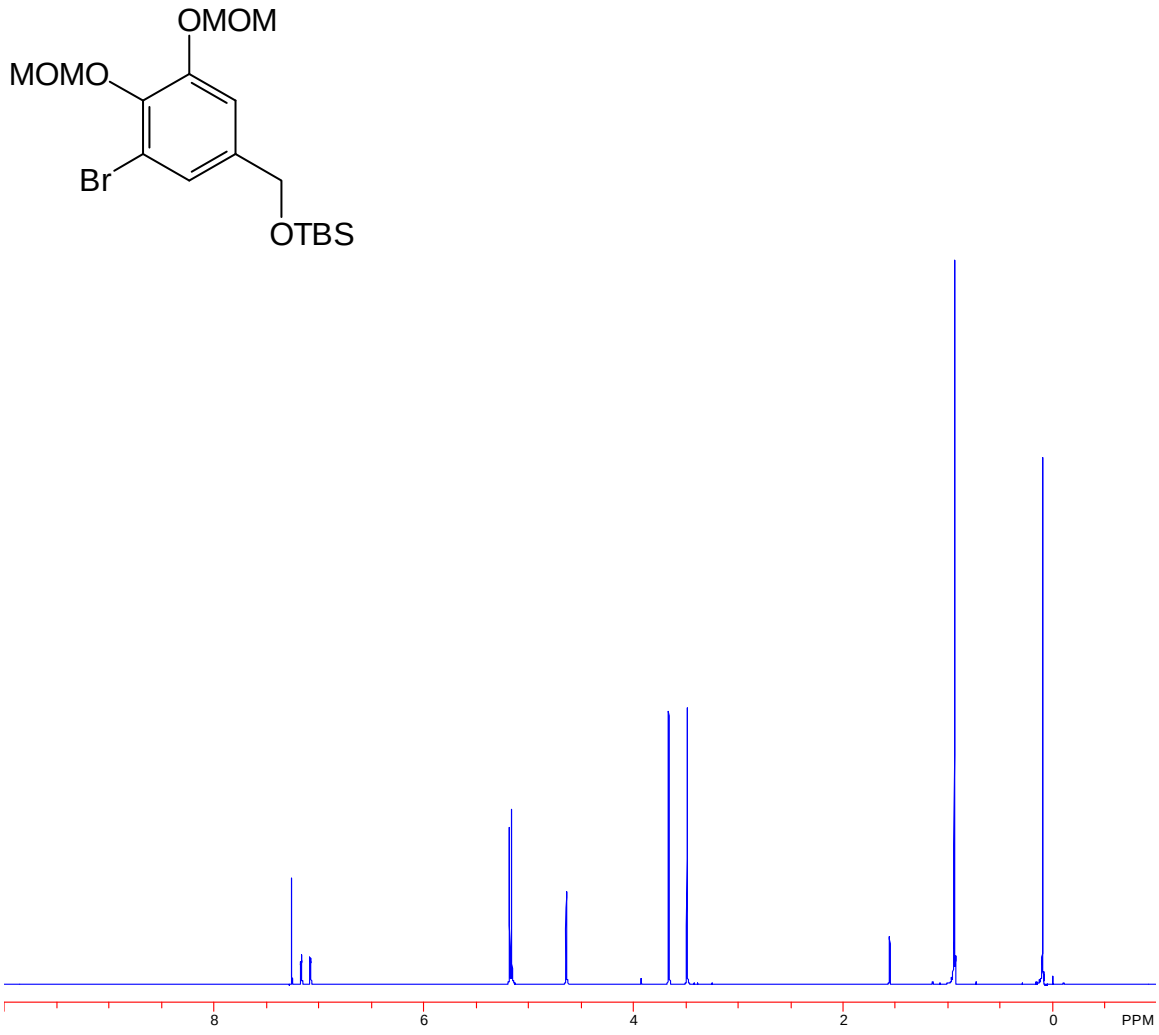

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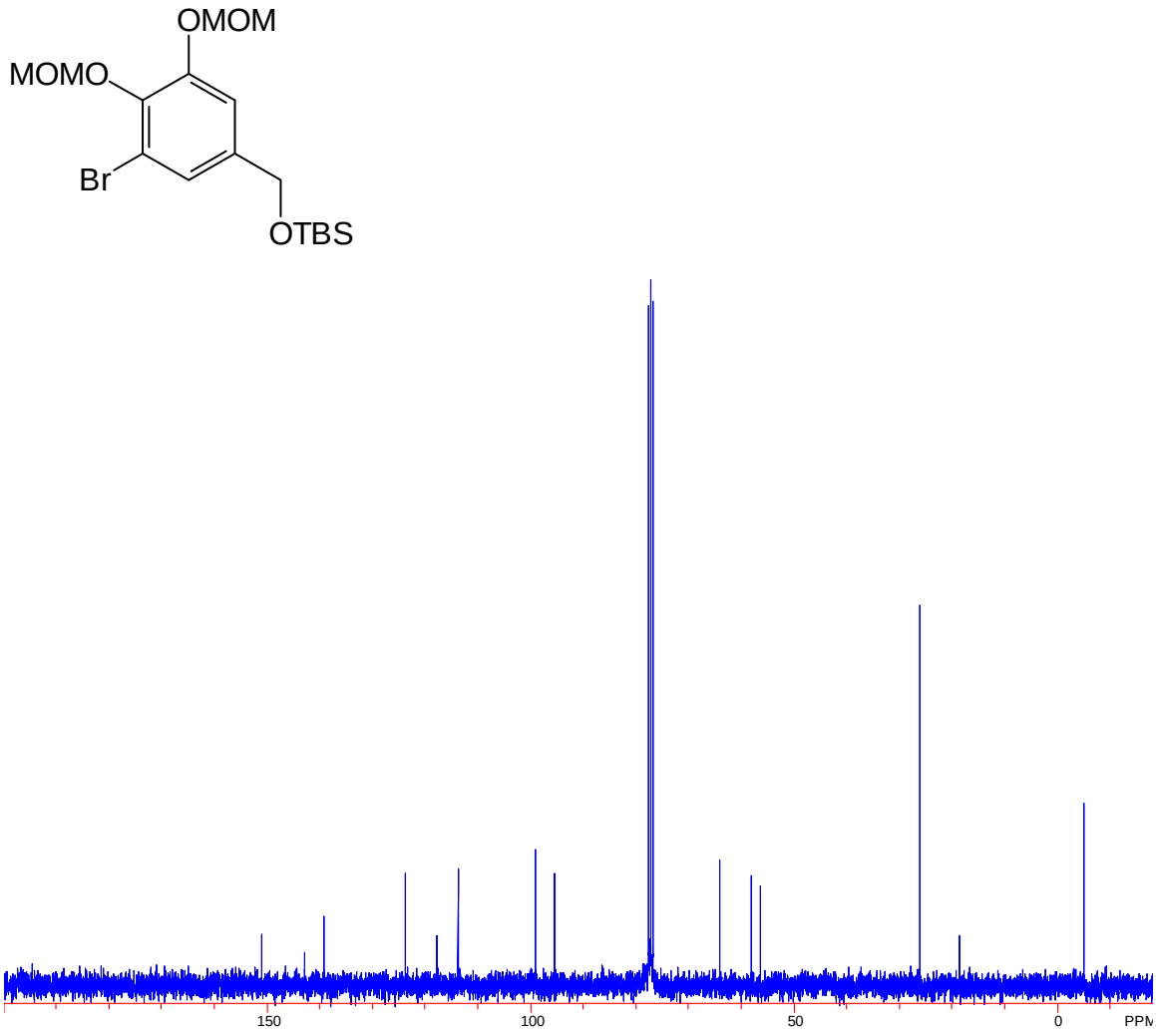

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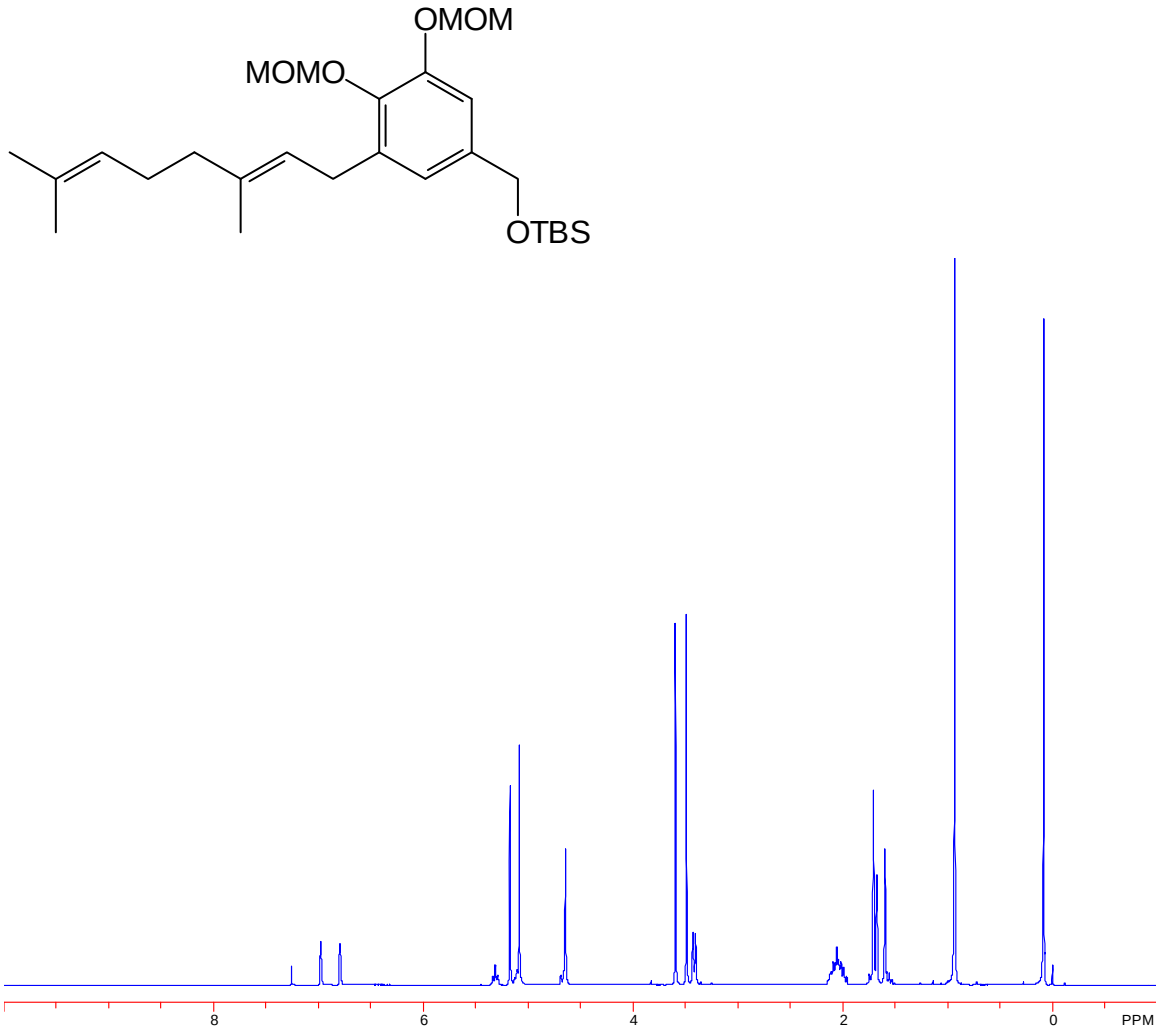

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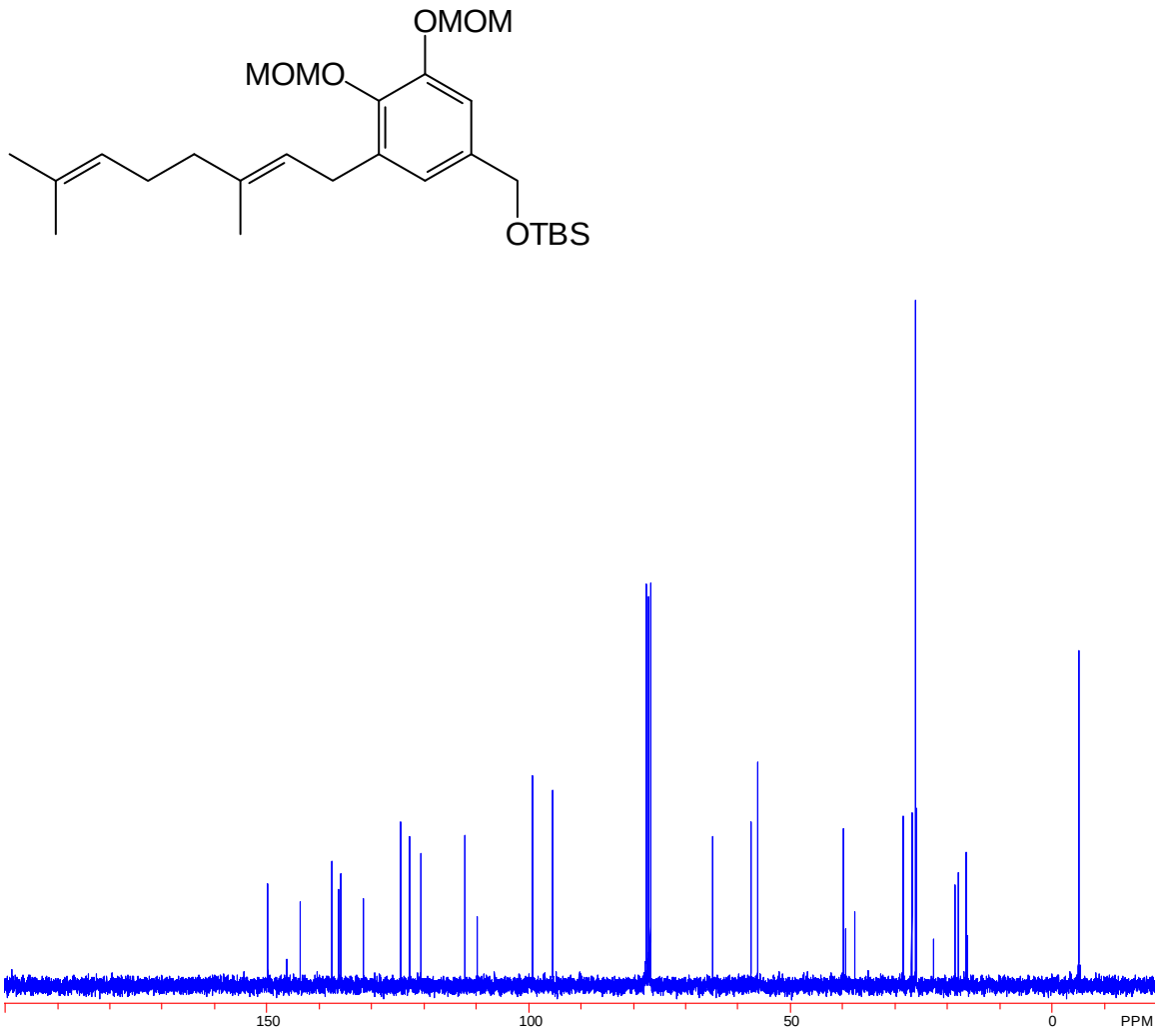

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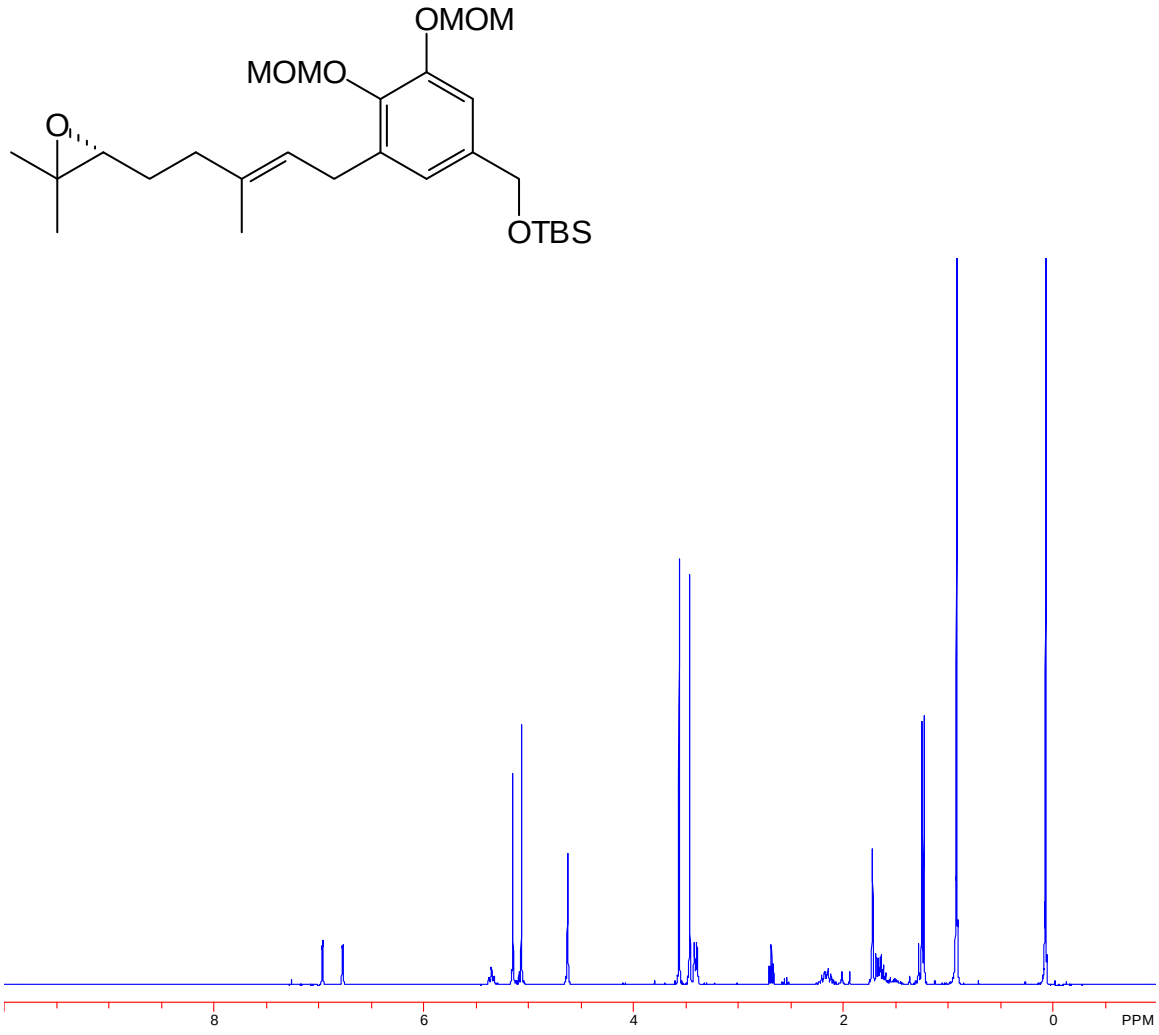

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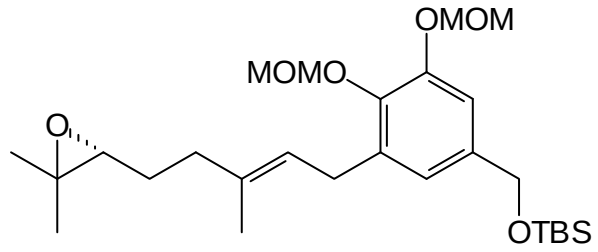

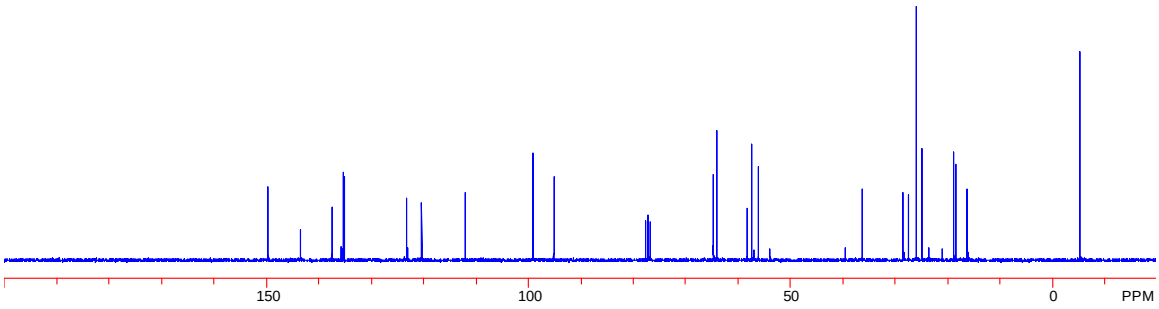

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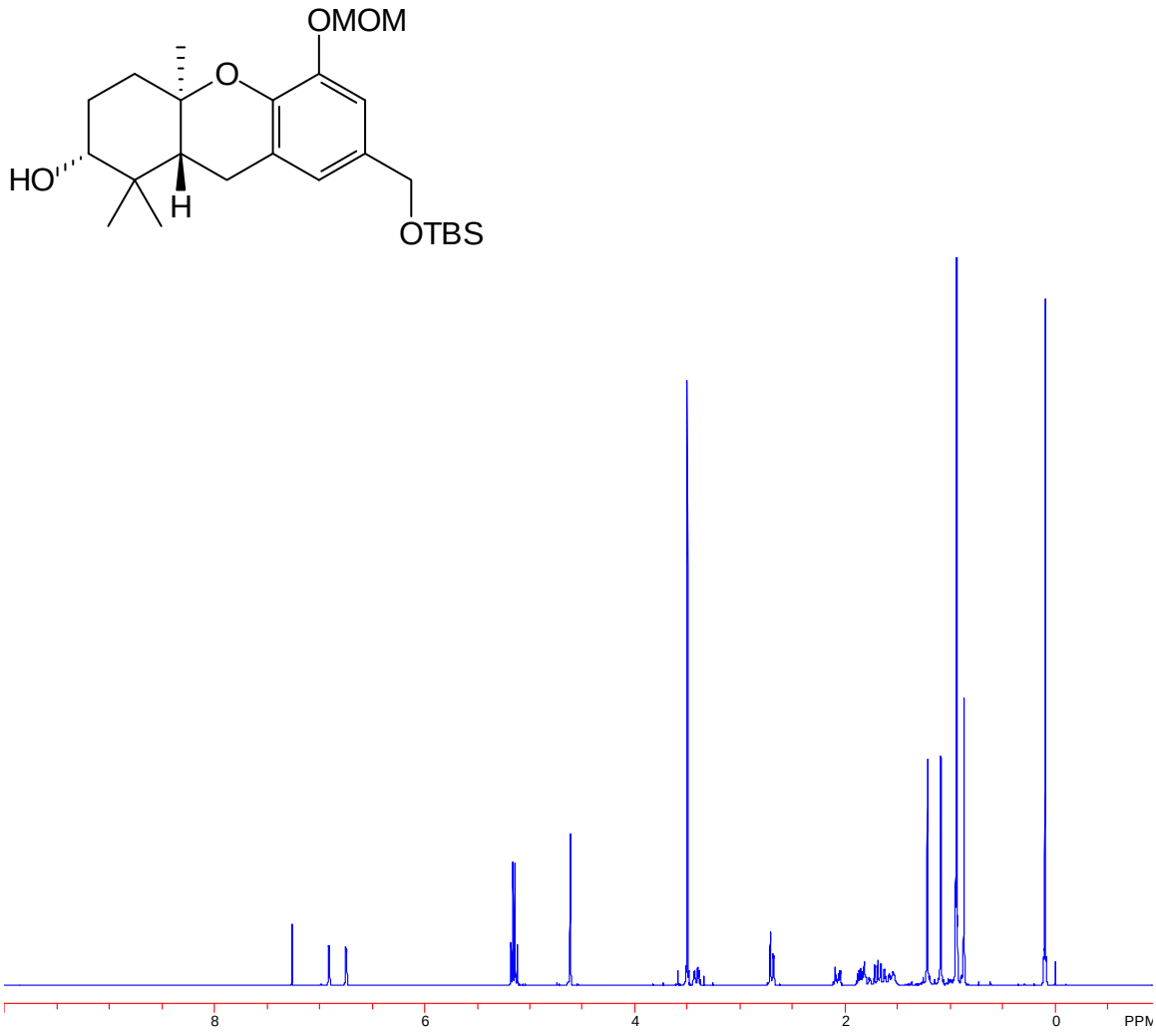

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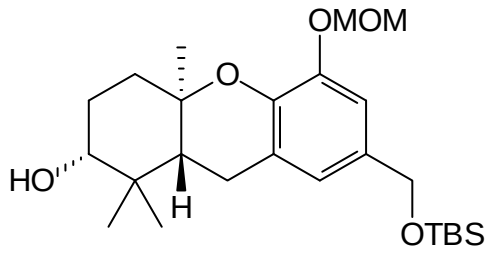

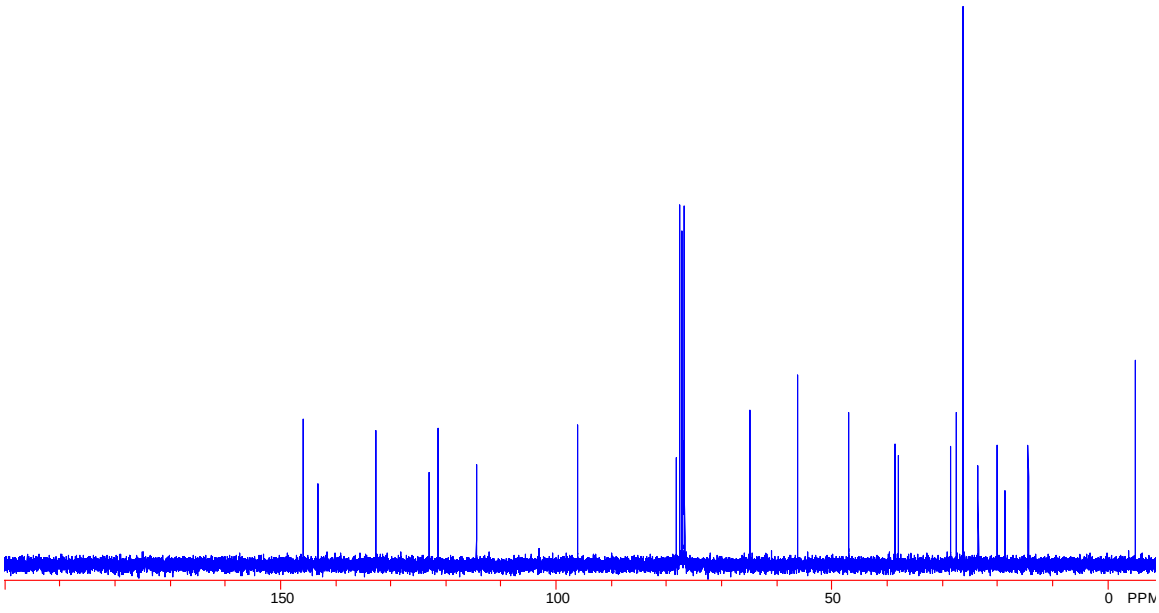

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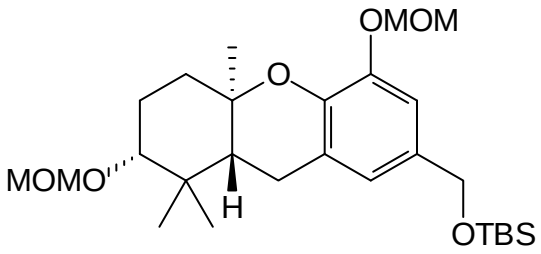

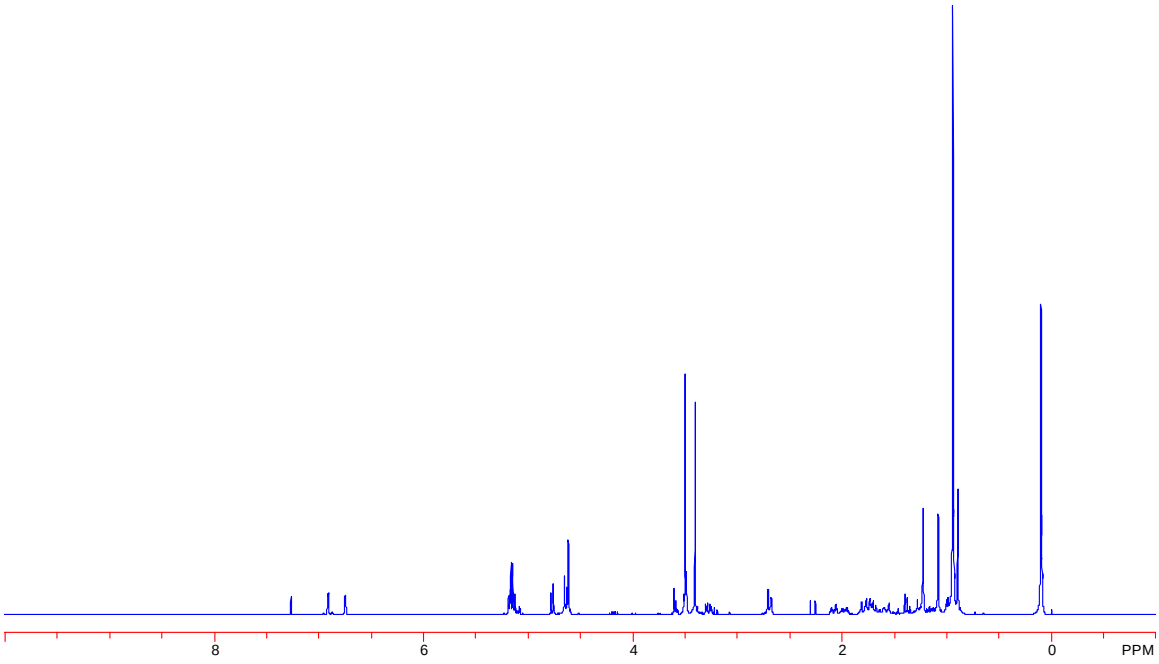

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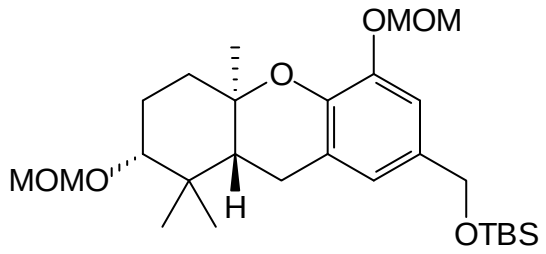

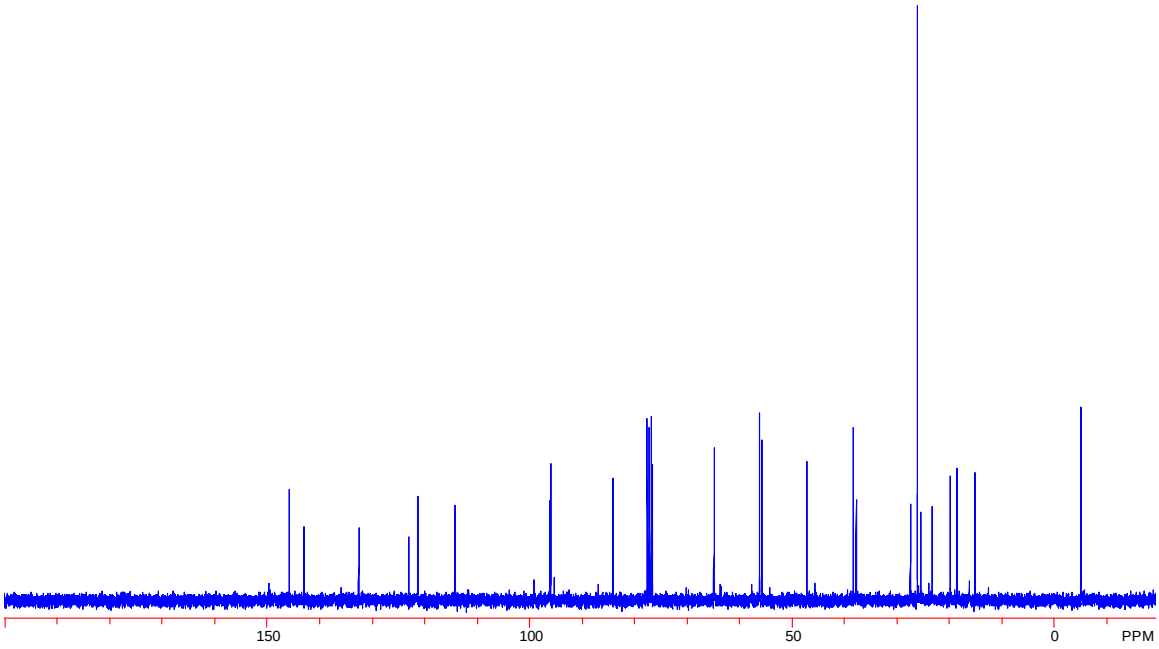

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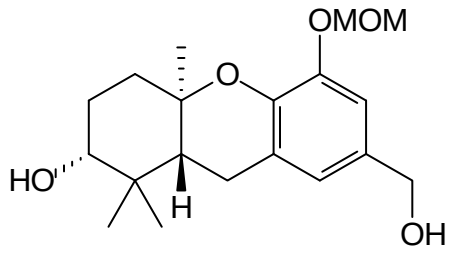

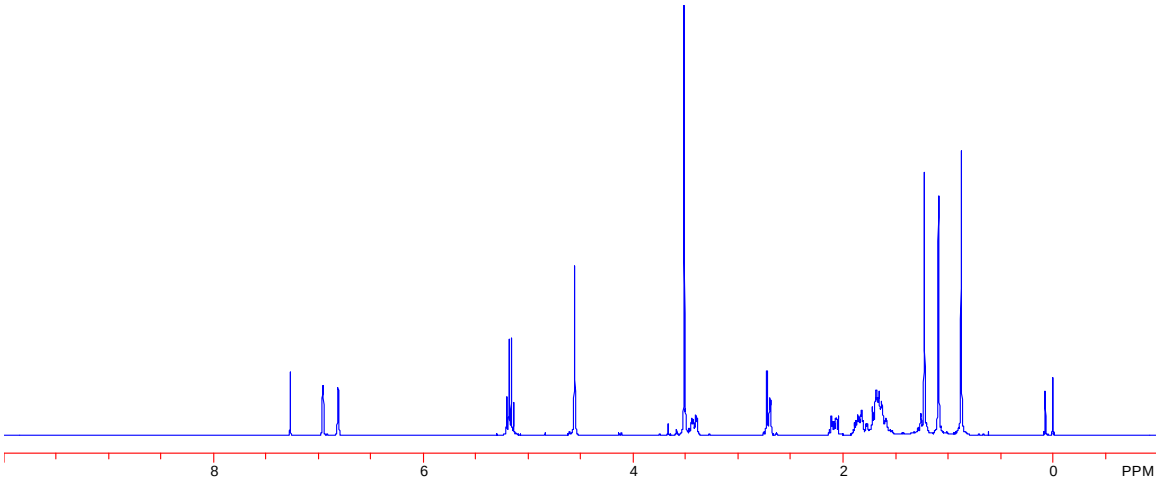

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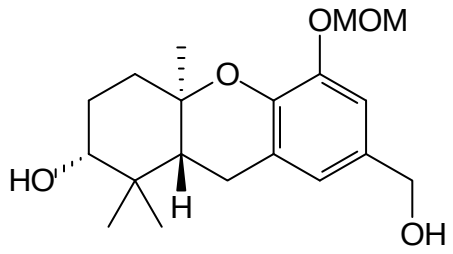

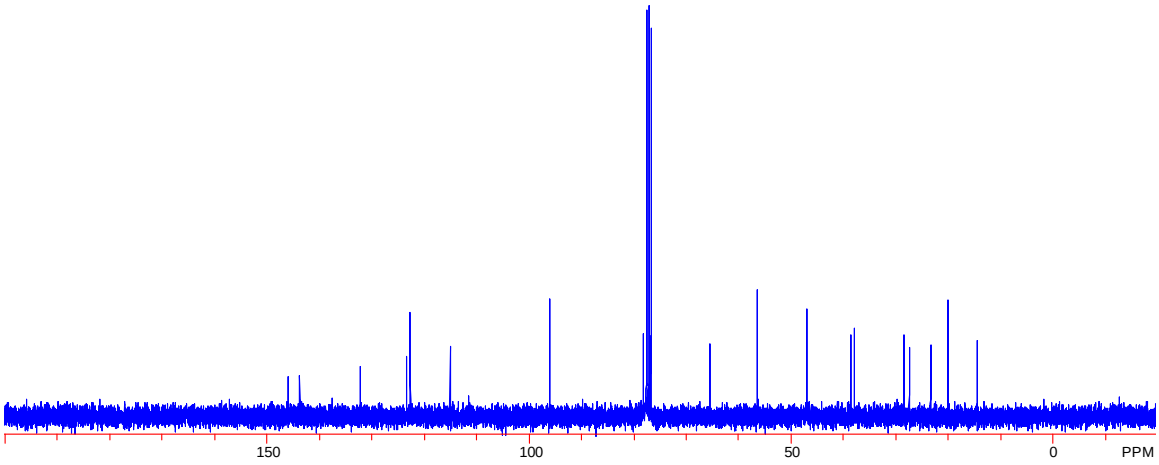

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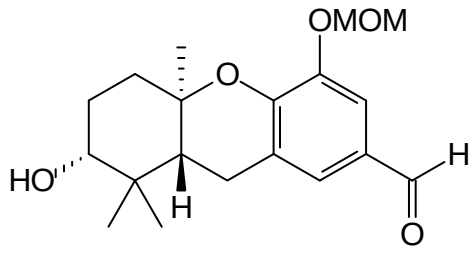

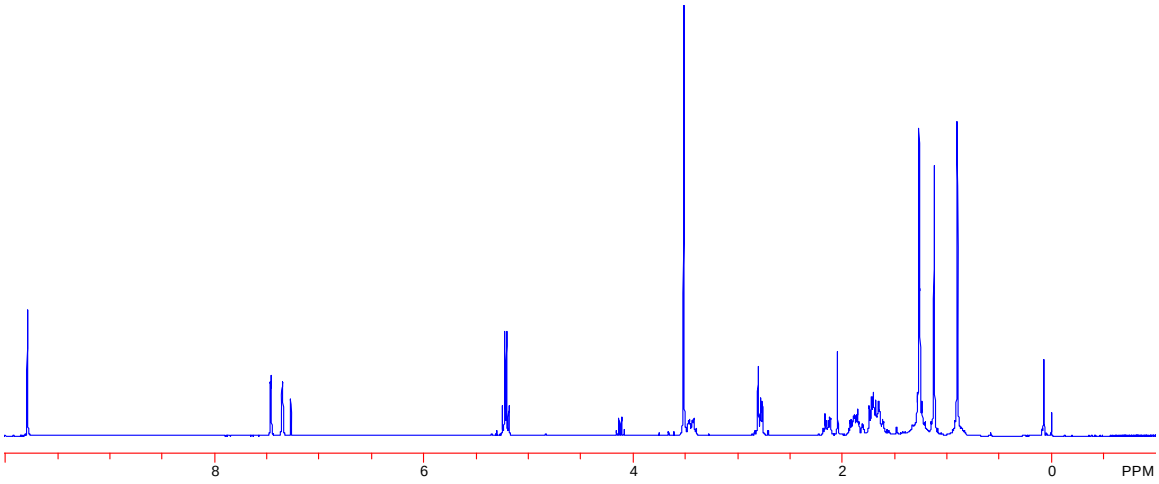

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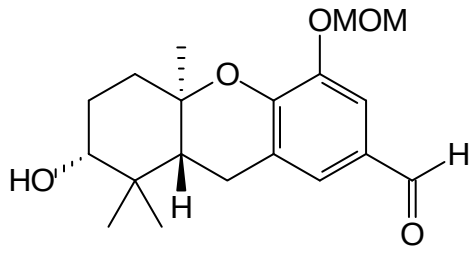

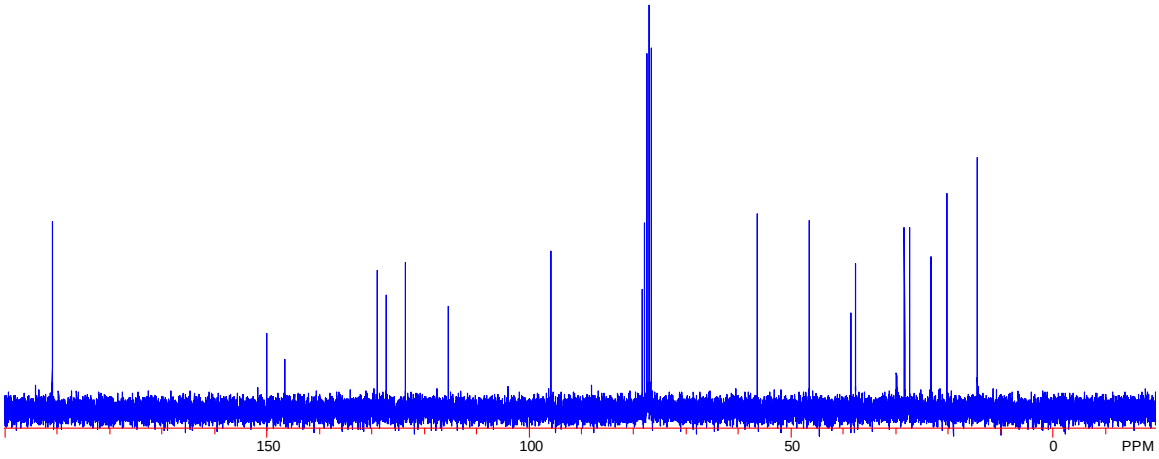

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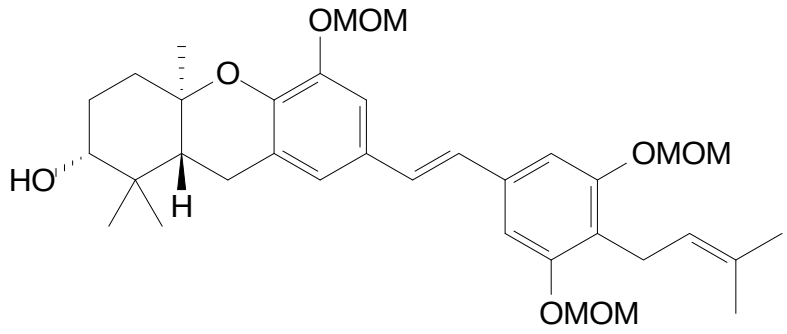

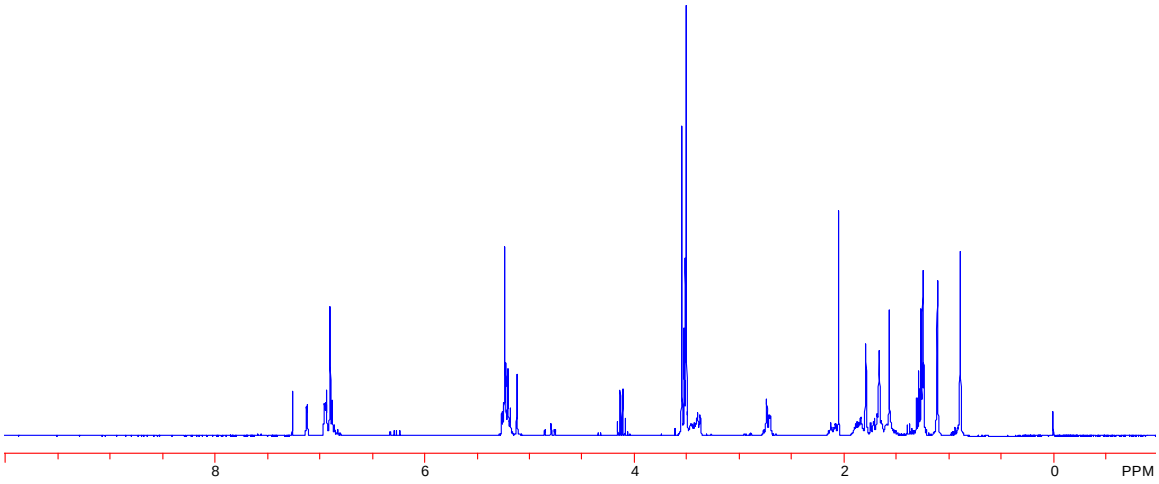

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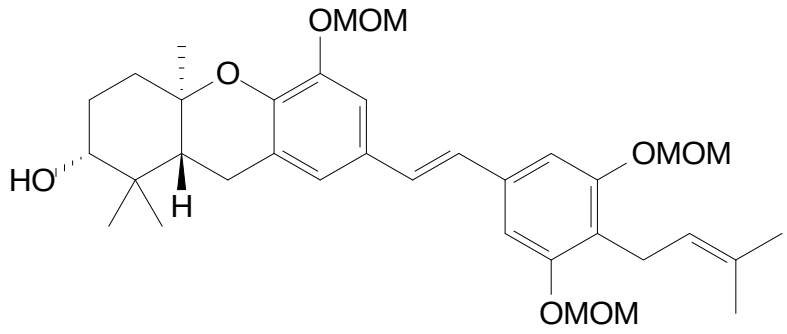
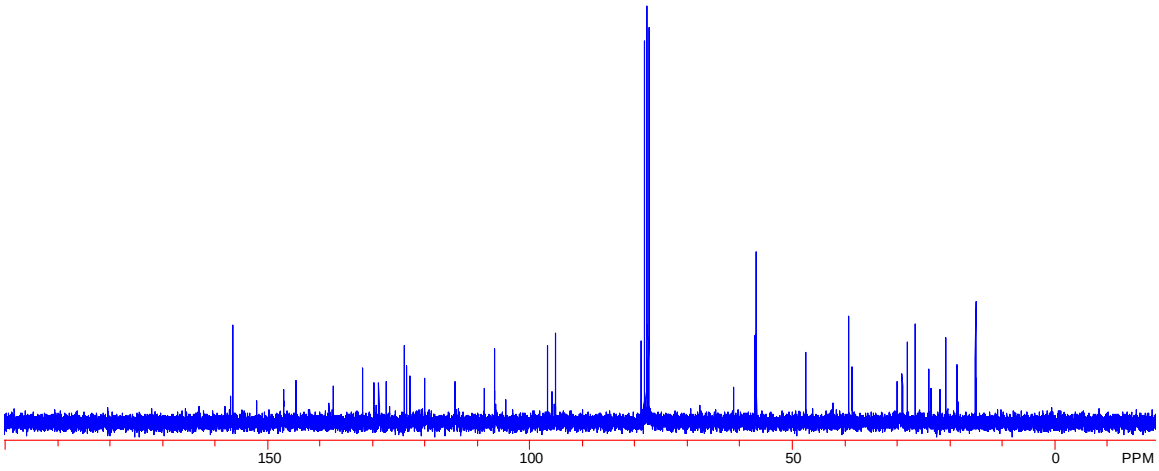
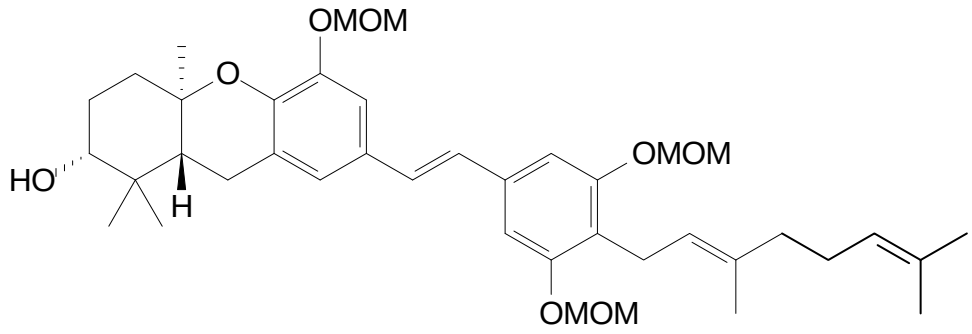
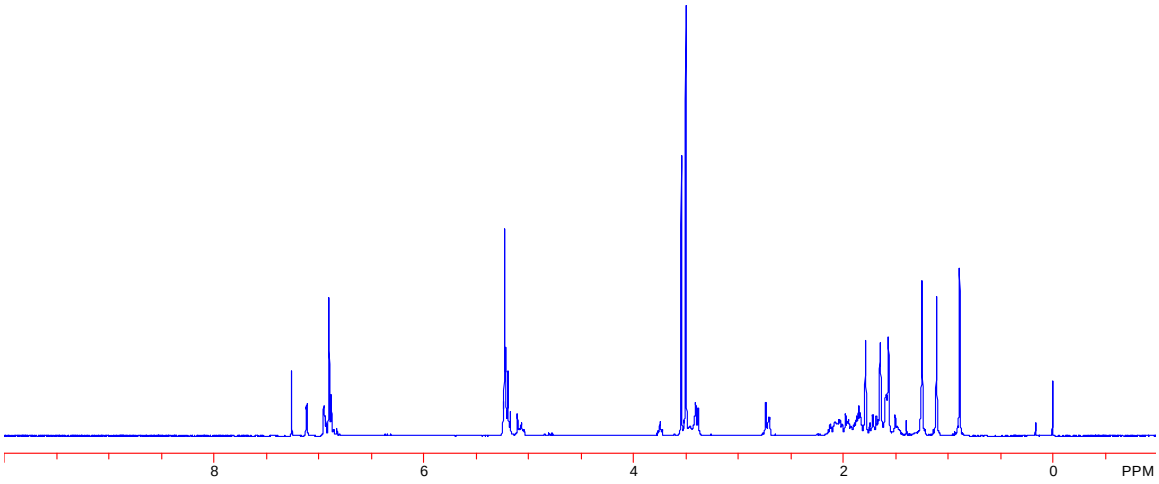


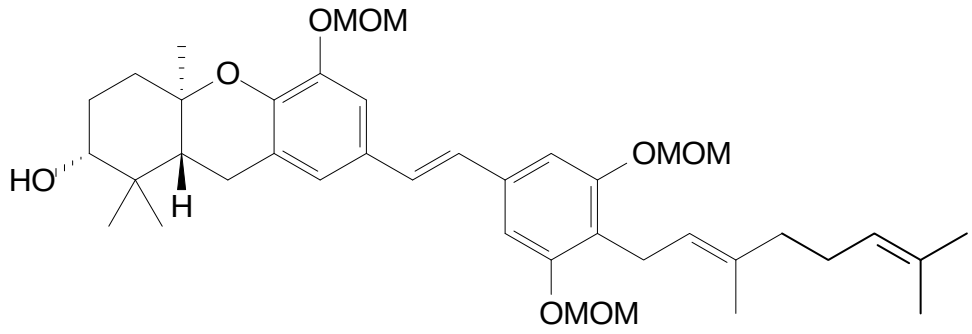


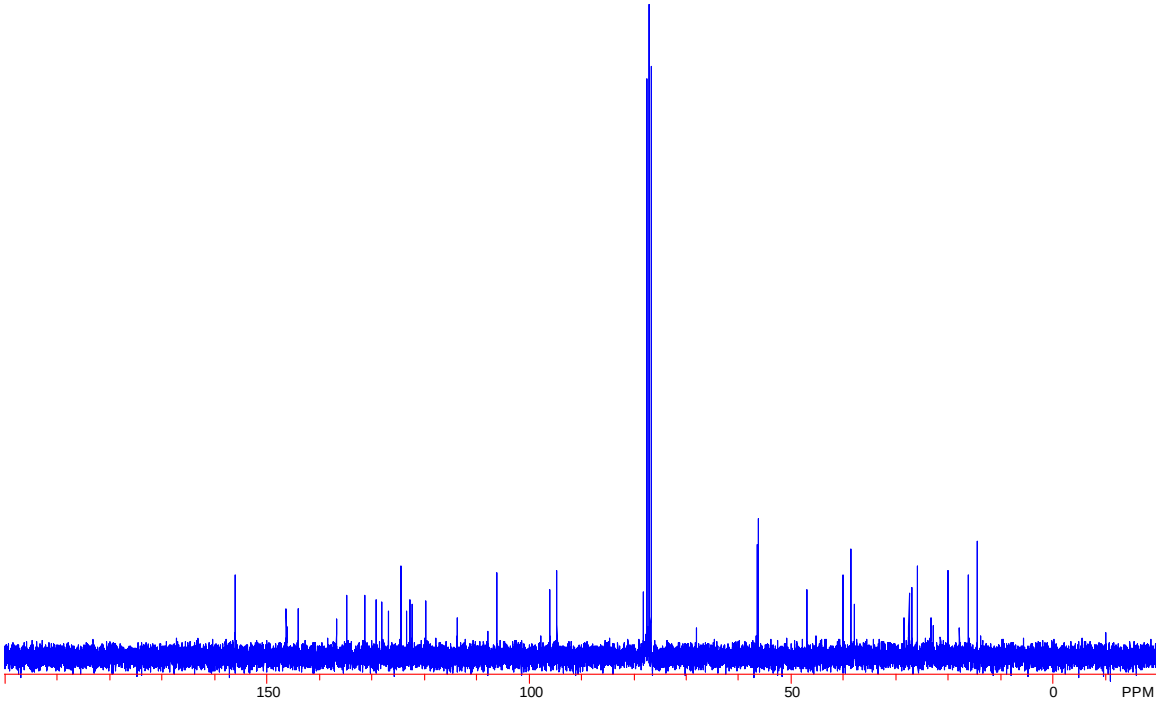
^{13}C NMR for compound **34** (75 MHz)



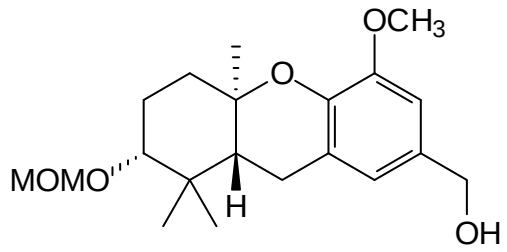


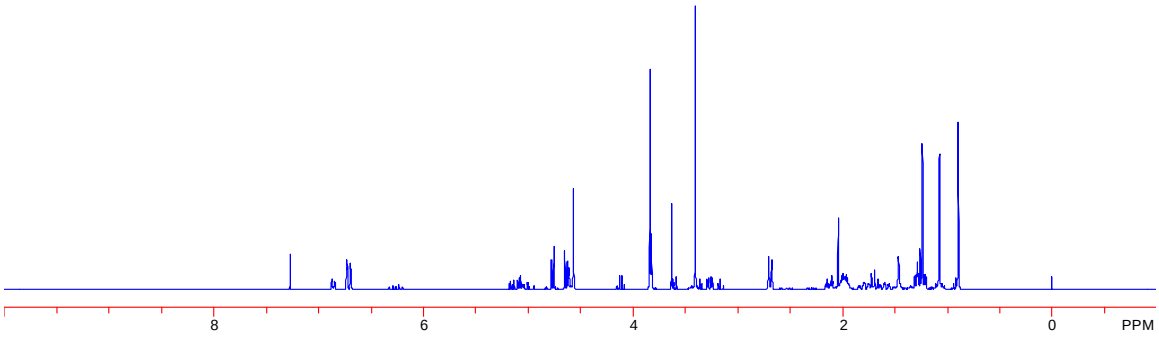
^{1}H NMR for compound **36** (300 MHz)



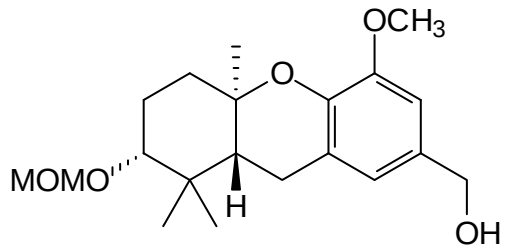


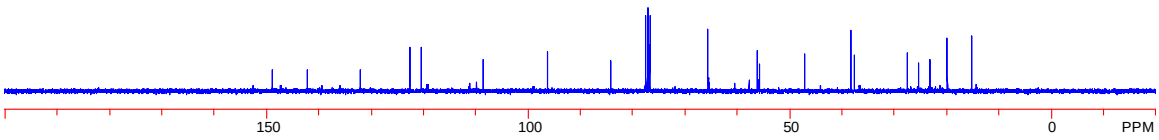
^{13}C NMR for compound **36** (75 MHz)



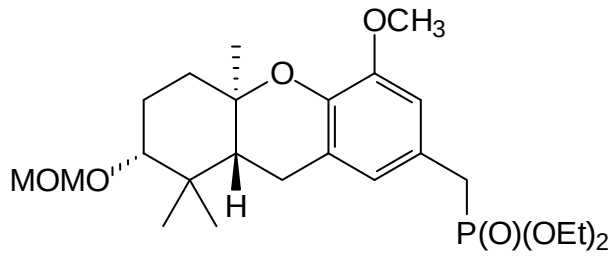


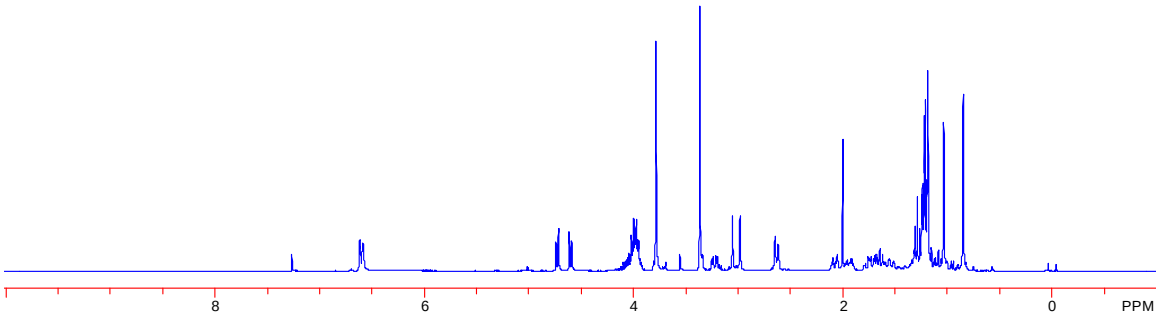
^{1}H NMR for compound **37** (300 MHz)



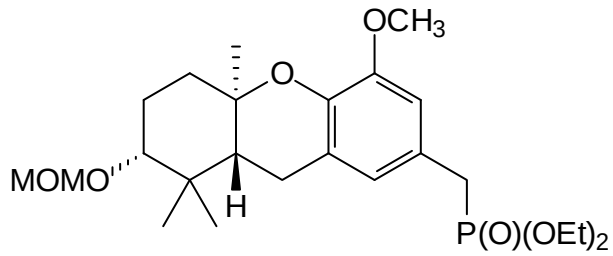


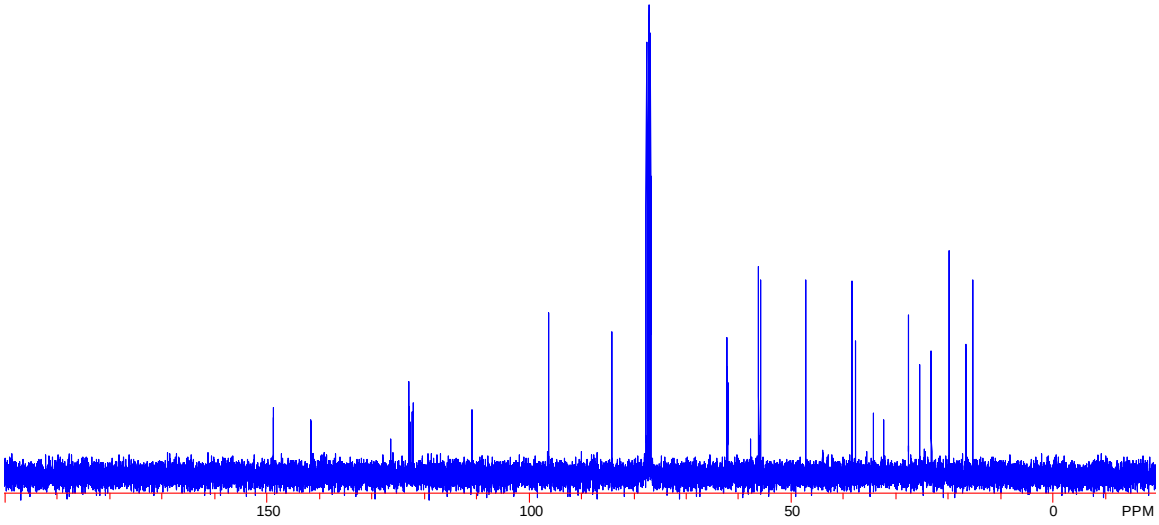
^{13}C NMR for compound **37** (75 MHz)



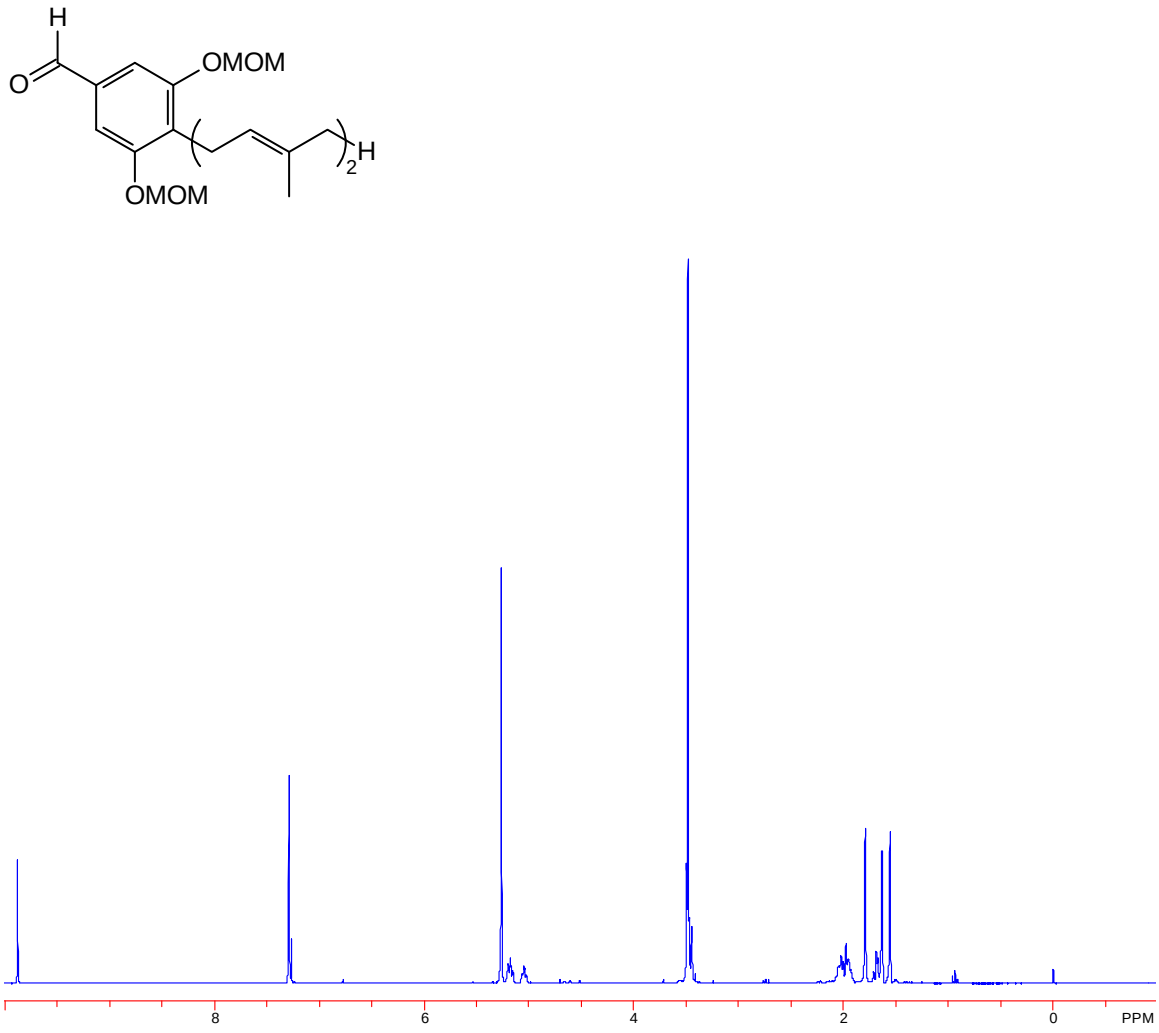


^{1}H NMR for compound **38** (300 MHz)

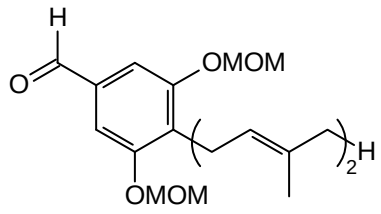


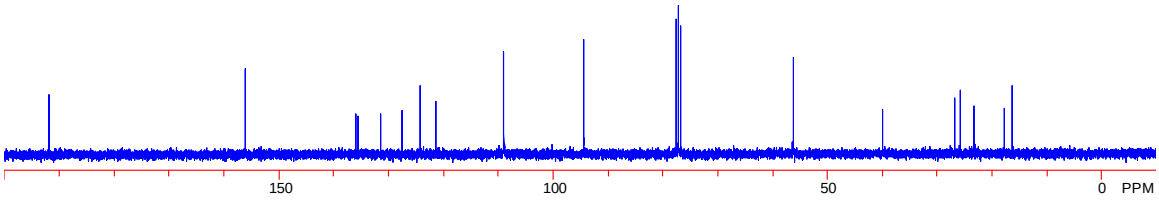


^{13}C NMR for compound **38** (75 MHz)

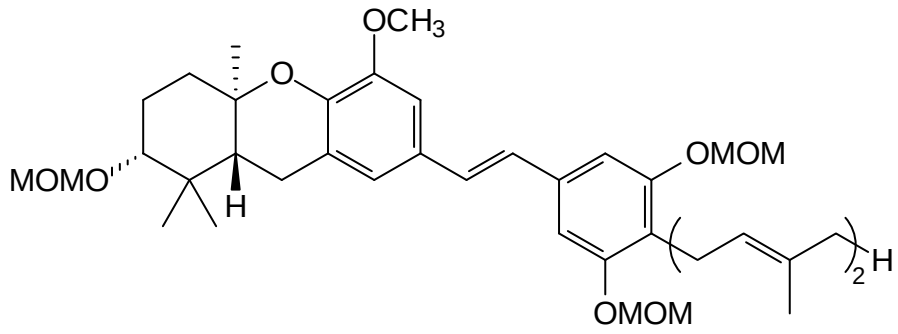


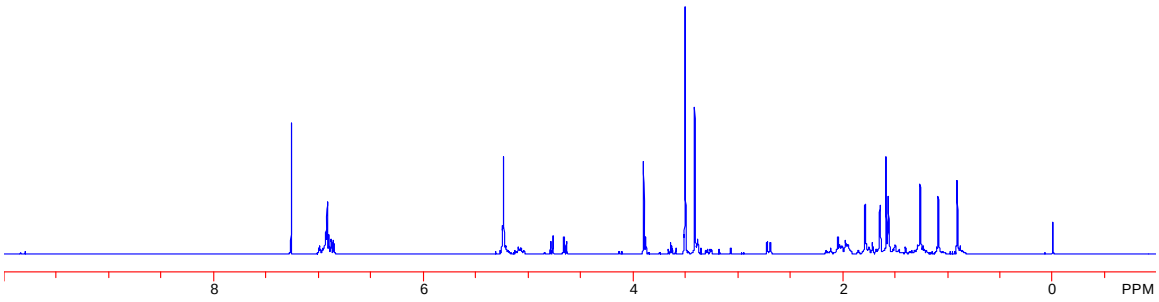
^{1}H NMR for compound **39** (300 MHz)



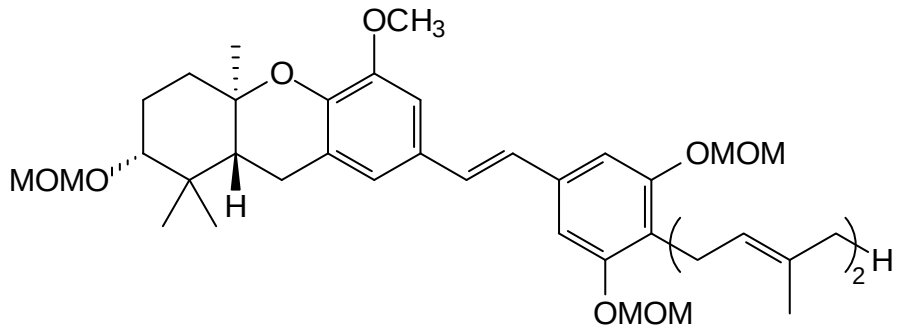


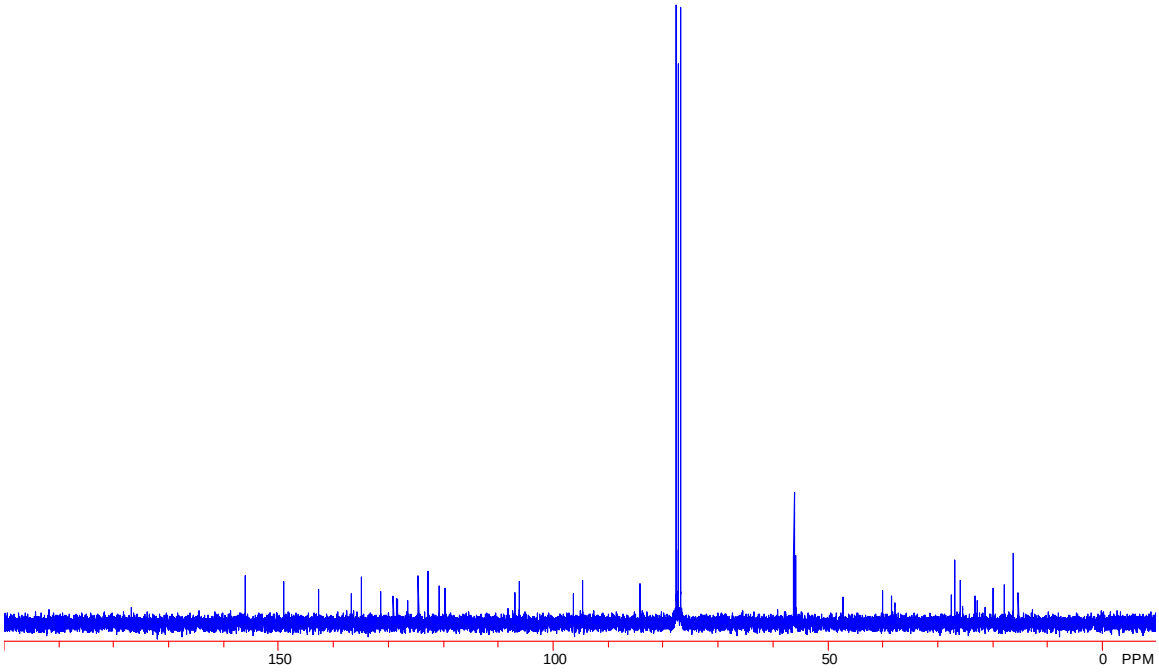
^{13}C NMR for compound **39** (75 MHz)



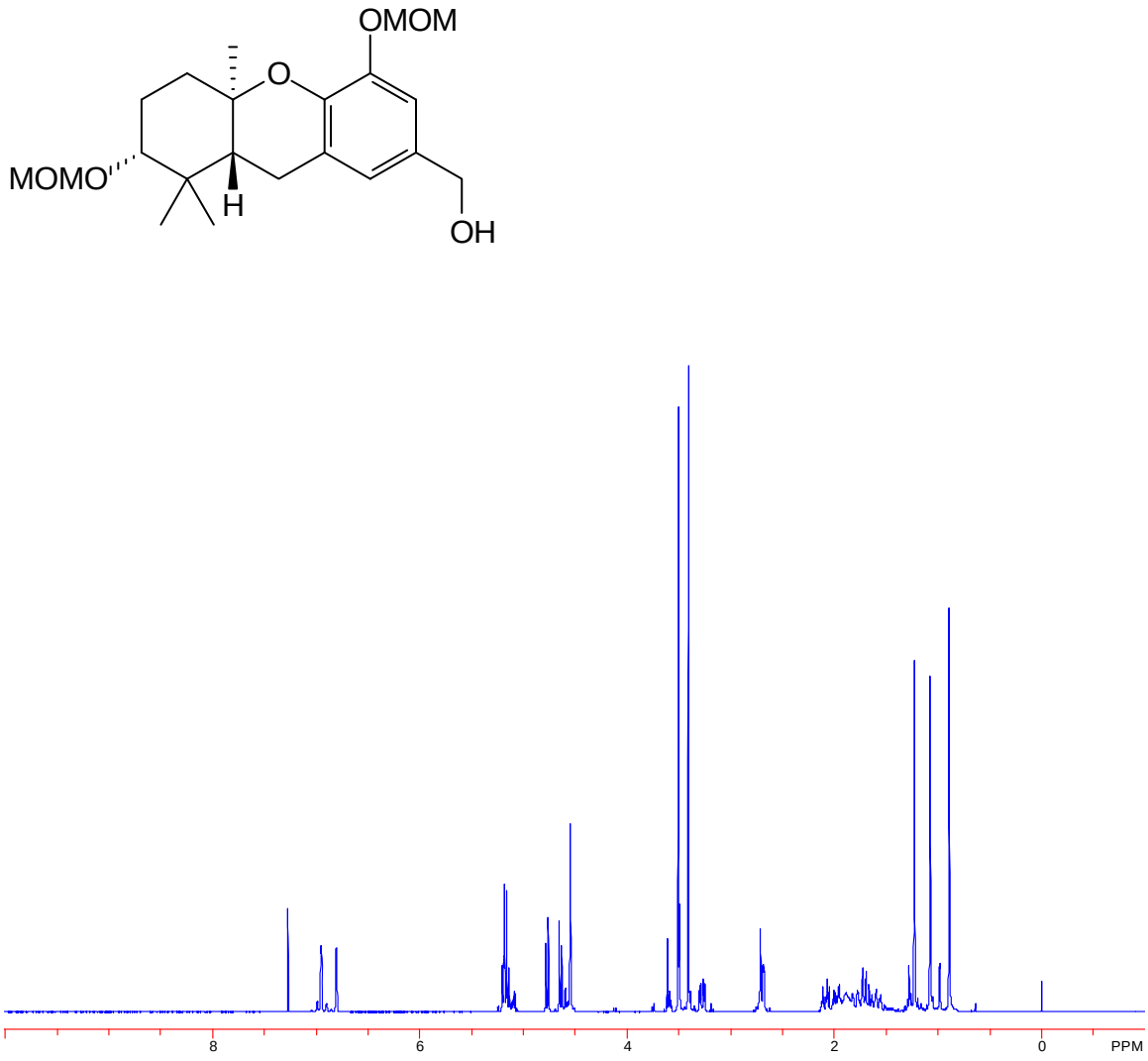


^{1}H NMR for compound **40** (300 MHz)

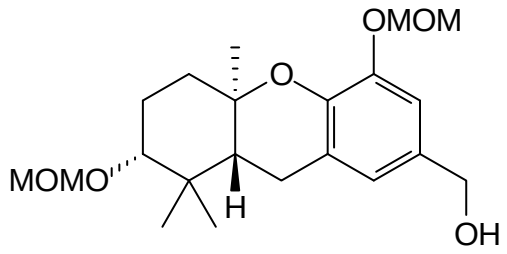


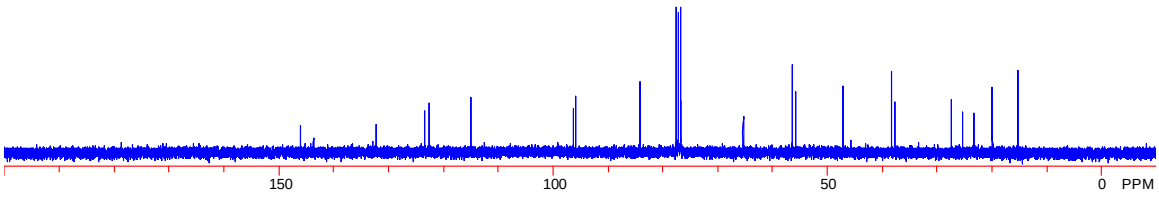


^{13}C NMR for compound **40** (75 MHz)

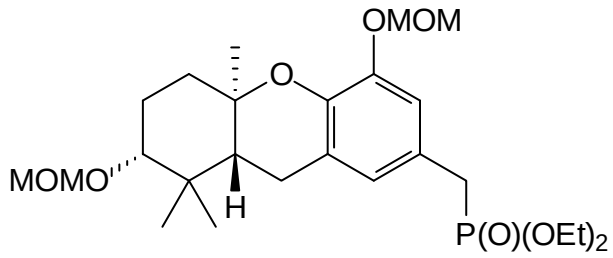


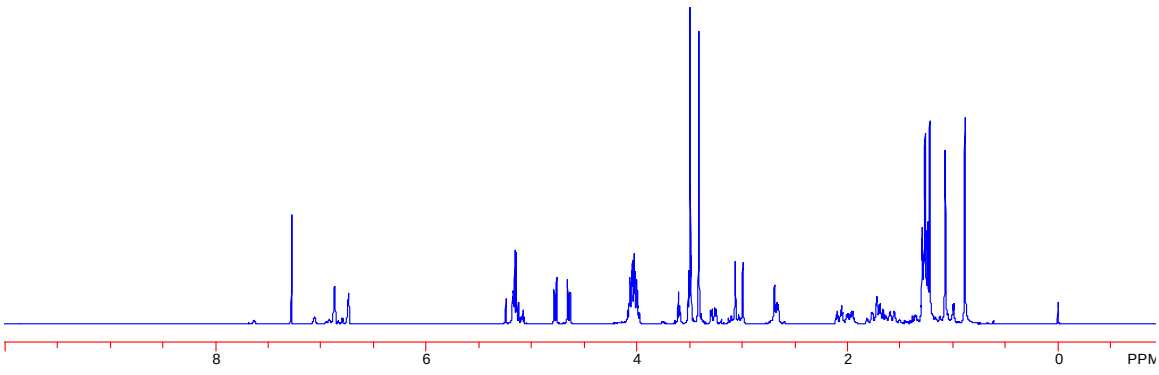
^{1}H NMR for compound **41** (300 MHz)



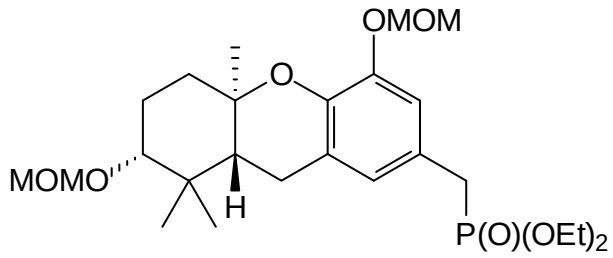


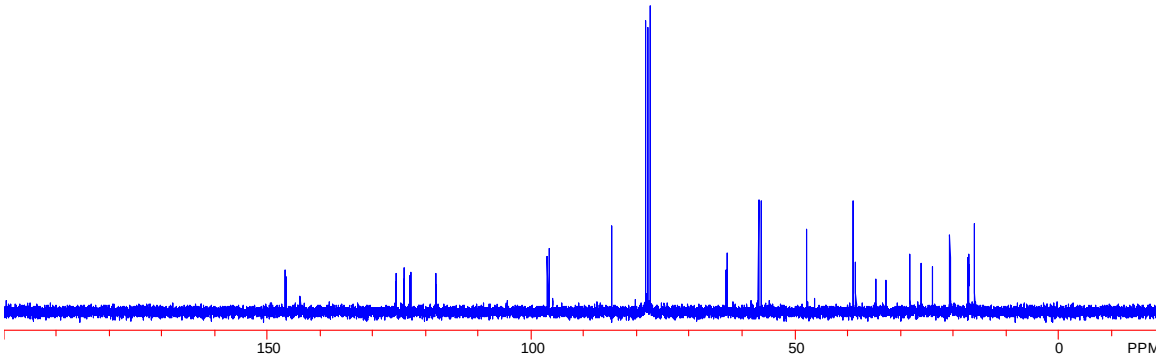
^{13}C NMR for compound **41** (75 MHz)



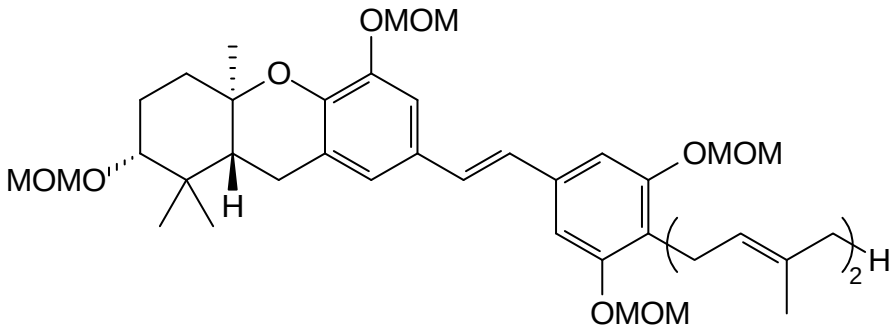


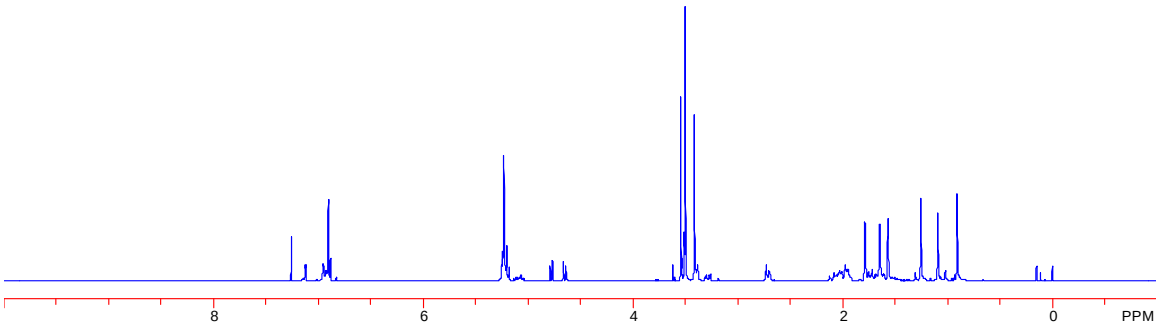
^{1}H NMR for compound **42** (300 MHz)



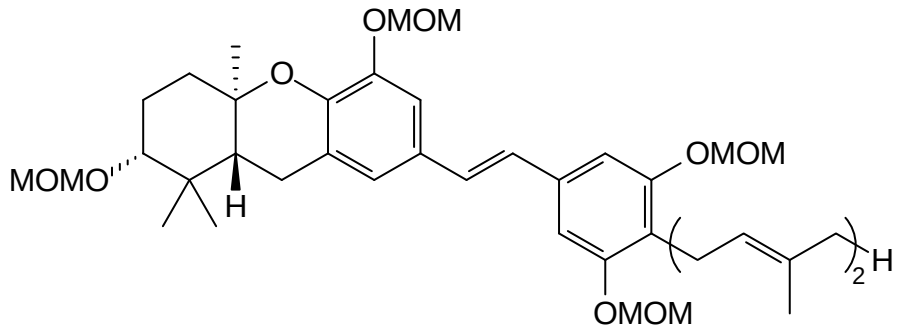


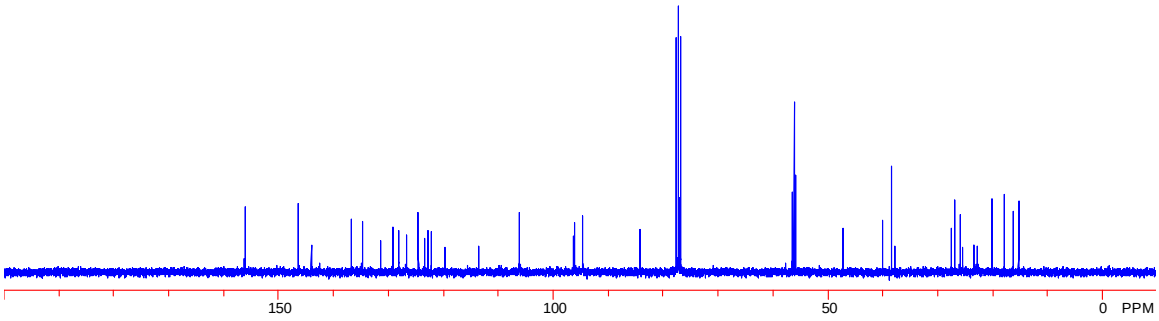
^{13}C NMR for compound **42** (75 MHz)



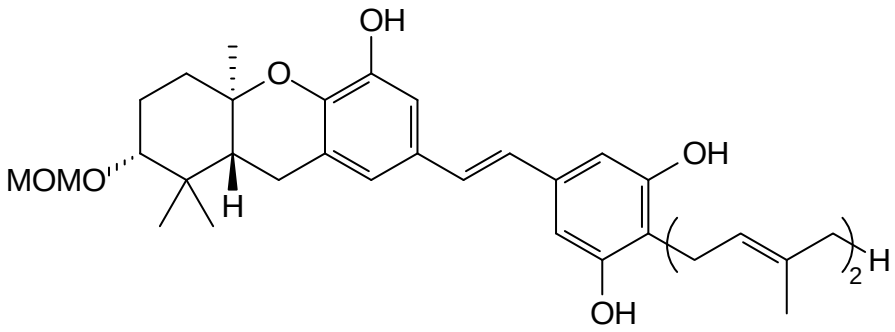


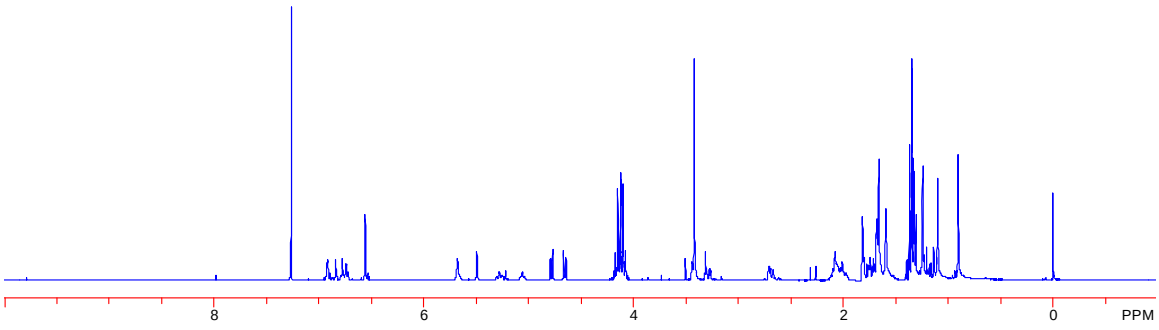
^{1}H NMR for compound **43** (300 MHz)



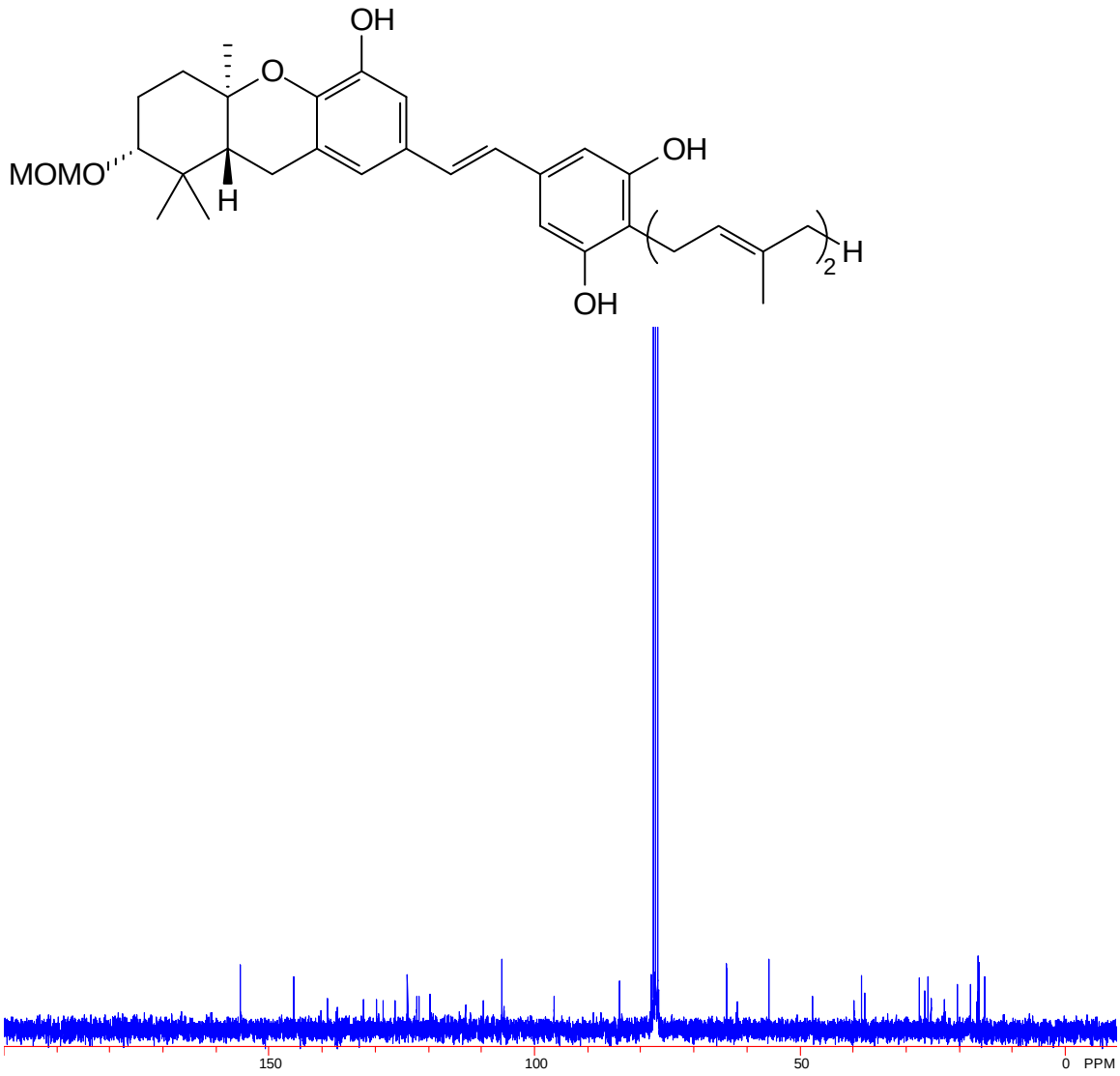


^{13}C NMR for compound **43** (75 MHz)





^{1}H NMR for compound **44** (300 MHz)



^{13}C NMR for compound **44** (75 MHz)