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Supporting Information

Gold- or Silver-Catalyzed Syntheses of Pyrones and Pyridine Derivatives: Mechanistic and Synthetic Aspects

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Crystallographic Section

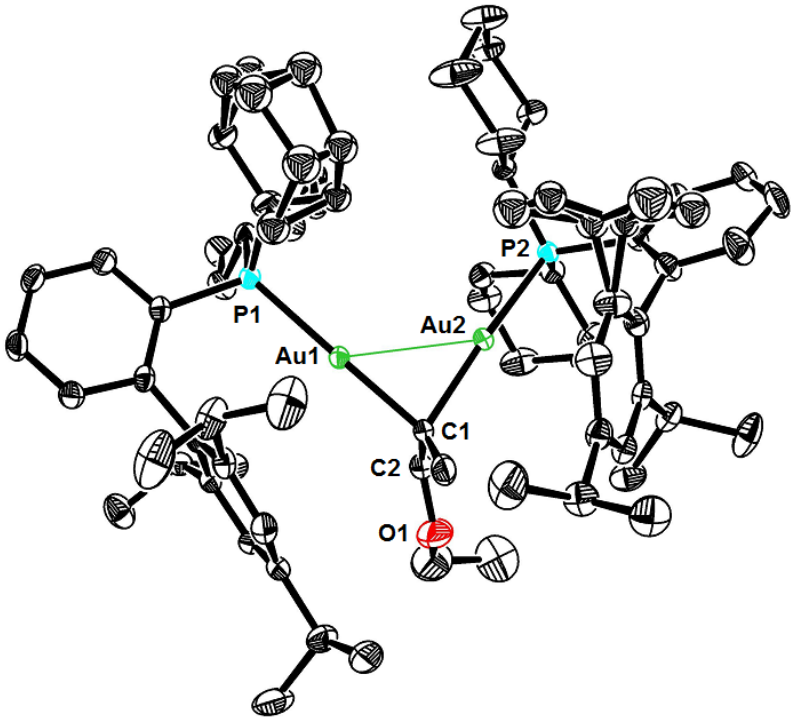


Figure S-1. Structure of complex **12b** (L = XPhos) in the solid state; only the complex cation is depicted, whereas the escorting $[NTf_2]^-$ anion as well as co-crystallized CH_2Cl_2 are omitted for clarity.

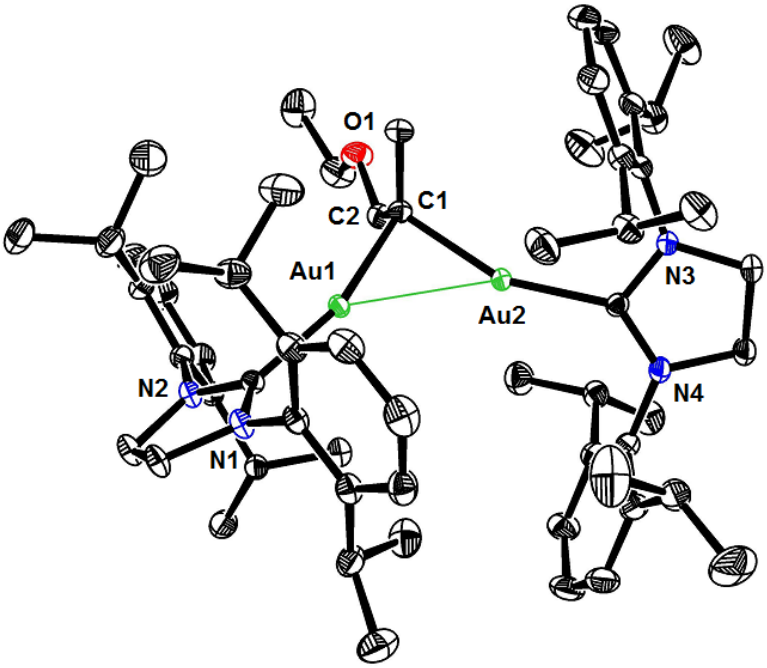


Figure S-2. Structure of complex **12c** (L = SIPr) in the solid state; only the complex cation is depicted, whereas the escorting $[NTf_2]^-$ anion as well as co-crystallized CH_2Cl_2 are omitted for clarity

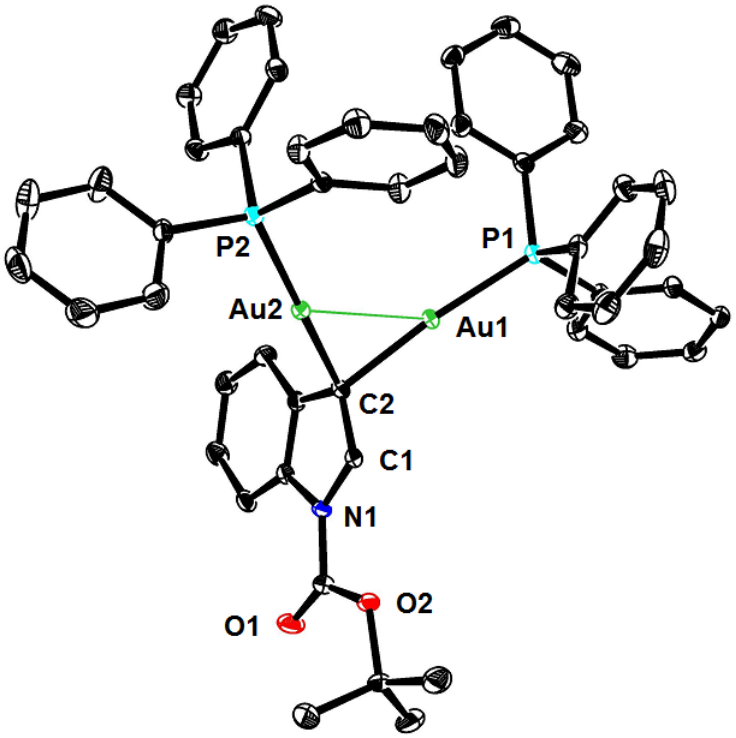


Figure S-3. Structure of complex **15** in the solid state; only the complex cation is depicted for clarity

X-ray Crystal Structure Analysis of Complex 12b: $C_{74}H_{109}Au_2Cl_2F_6NO_5P_2S_2$, M_r = 1797.52 g·mol^{-1}, colorless needle, crystal size 0.23 x 0.05 x 0.04 mm, monoclinic, space group $P2_1/c$, a = 14.610(3) Å, b = 19.683(4) Å, c = 27.269(5) Å, β = 100.485(3)°, V = 7711(3) Å^3, T = 100 K, Z = 4, D_{calc} = 1.548 g·cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 4.028 mm^{-1}, Multi-Scan absorption correction (T_{min} = 0.49, T_{max} = 0.88), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 1.75 < θ < 27.50°, 176078 measured reflections, 17692 independent reflections, 15300 reflections with $I > 2\sigma(I)$; structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.030 [$I > 2\sigma(I)$], wR_2 = 0.079, 856 parameters, H atoms riding, S = 1.041, residual electron density +2.7 / −1.5 e Å^{-3}. **CCDC 1417652**

X-ray Crystal Structure Analysis of Complex 12c: $C_{61.64}H_{86.27}Au_2Cl_{1.27}F_6N_5O_5S_2$, M_r = 1594.32 g·mol^{-1}, colorless plate, crystal size 0.24 x 0.17 x 0.06 mm, orthorhombic, space group *Pbca*, a = 22.049(4) Å, b = 23.9661(14) Å, c = 25.927(5) Å, V = 13700(4) Å^3, T = 100 K, Z = 8, D_{calc} = 1.546 g·cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 4.453 mm^{-1}, Multi-Scan absorption correction (T_{min} = 0.40, T_{max} = 0.73), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.63 < θ < 35.01°, 264725 measured reflections, 30068 independent reflections, 21100 reflections with $I > 2\sigma(I)$; structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.041 [$I > 2\sigma(I)$], wR_2 = 0.102, absolute structure parameter = −0.2(6), 813 parameters, H atoms riding, S = 1.120, residual electron density +2.6 / −2.4 e Å^{-3}. **CCDC 1417653**

X-ray Crystal Structure Analysis of Complex 15: $C_{51}H_{44}Au_2F_6N_2O_6P_2S_2$, M_r = 1414.88 g·mol^{-1}, colorless

plate, crystal size 0.09 x 0.08 x 0.02 mm, triclinic, space group *P1*, a = 12.074(3) Å, b = 14.204(3) Å, c = 16.028(3) Å, α = 80.320(4)°, β = 85.057(4)°, γ = 67.709(4)°, V = 2506.6(9) Å^3, T = 100 K, Z = 2, D_{calc} = 1.875 g·cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 6.067 mm^{-1}, Multi-Scan absorption correction (T_{min} = 0.57, T_{max} = 0.89), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 1.29 < θ < 31.03°, 73431 measured reflections, 15987 independent reflections, 13402 reflections with $I > 2\sigma(I)$; structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.022 [$I > 2\sigma(I)$], wR_2 = 0.058, 643 parameters, H atoms riding, S = 1.085, residual electron density +1.4 / −1.3 e Å^{-3}. **CCDC 1417651**

General. All reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: THF, Et_2O (Mg/anthracene), MeCN, CH_2Cl_2 (CaH_2), MeOH (Mg), hexane (Na/K), toluene (Na/K). DMF, pyridine and NEt_3 were dried by an absorption solvent purification system based on molecular sieves. HMPA and iPr$_2$NH were purified by distillation over CaH_2 and transferred under Ar. CH_3NO_2 and HOAc were used as received. Flash chromatography: Merck silica gel 60 (40–63 μm). NMR: Spectra were recorded a Bruker DPX 300, AV 400, AV 500 or AV 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C ≡ 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H ≡ 7.26 ppm; CD_2Cl_2: δ_C ≡ 53.84 ppm; residual CH_2Cl_2 in CD_2Cl_2: δ_H ≡ 5.32 ppm; C_6D_6 δ_H ≡ 7.15 ppm, δ_C ≡ 128.00 ppm; [D_6]-DMSO: δ_H ≡ 2.50 ppm, δ_C ≡ 39.5 ppm; [D_5]-pyridine: δ_H ≡ 8.74, 7.58, 7.22 ppm, δ_C ≡ 150.35, 135.91, 123.87 ppm; D_3COD: δ_H ≡ 3.31 ppm, δ_C ≡ 49.00 ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich, Strem) were used as received. TeocCl,[1] (*E*)-1,1-dibromopenta-1,3-diene,[2] and [LAuNTf$_2$][3] (L = PPh_3, SPhos, XPhos, SIPr) were prepared in analogy to literature procedures.

Gold Complexes

Representative Procedure for the Preparation of *gem*-Diaurated Complexes. Preparation of Complex 12a (L = PPh$_3$). [(Ph_3P)AuNTf$_2$] (828 mg, 1.12 mmol) was added to a solution of compound **10** (114 mg, 0.56 mmol) and Cs_2CO_3 (182 mg, 0.56 mmol) in THF (5 mL) and the resulting mixture was stirred at ambient temperature for 1 h. At this point, inspection of the reaction mixture by ^{31}P NMR showed the formation of a major product (δ_P = 37.1 ppm, ca. 90 %), together with small amounts of unreacted [(Ph_3P)AuNTf$_2$] (δ_P = 31.0 ppm, ca. 7 %) and [(Ph_3P)$_2$Au][NTf$_2$] (δ_P = 45.3 ppm, ca. 3 %). For work up, all volatile materials were distilled off under vacuum (15 mbar) and the residue was passed through a short silica gel column (ca. 10 cm, ∅ 2 cm), eluting with CH_2Cl_2 (200 mL). The combined product-containing fractions were evaporated and the residue dried in vacuo to give complex **12a** as a colorless oil (383 mg), which contained trace impurities of [(Ph_3P)$_2$Au][NTf$_2$] and (Ph_3P)AuCl (likely formed by activation of CH_2Cl_2 during the work up, δ_P = 33.8 ppm). Crystals suitable for X-ray diffraction were grown by slowly

1 M. Sekine, M. Tobe, T. Nagayama, T. Wada, *Lett. Org. Chem.* **2004**, *1*, 179–182.

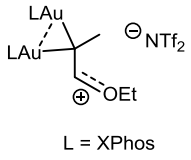
2 H. J. Bestmann, H. Frey, *Liebigs Ann. Chem.* **1980**, 2061–2071.

3 N. Mézailles, L. Ricard, F. Gagosz, *Org. Lett.* **2005,** *7*, 4133–4136.

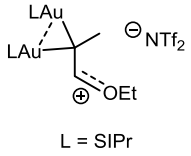
cooling a solution of the complex in CH_2Cl_2, layered with cold pentane, to –78°C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.70 – 7.33 (m, 30-35H),[4] 7.30 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.09 (q, *J* = 1.5 Hz, 3H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 174.8 (t, $^3J_{PC}$ = 2.4 Hz), 134.4 (d, $^2J_{PC}$ = 13.8 Hz), 132.5 (d, $^4J_{PC}$ = 2.6 Hz), 129.8 (d, $^3J_{PC}$ = 11.5 Hz), 129.3 (d, J_{PC} = 56.7 Hz), 120.4 (q, J_{CF} = 322 Hz), 116.6 (t, J_{PC} = 60.6 Hz), 71.8, 20.3, 15.4; ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 37.5; MS (ESI): *m/z* 1003 (M^+ – NTf_2); 721 [$(Ph_3P)_2Au^+$]; 280 (NTf_2^-); HRMS (ESI): *m/z*: calcd. for $C_{41}H_{39}Au_2OP_2$ [M^+]: 1003.1801, found: 1003.1792.

The following complexes were prepared analogously:

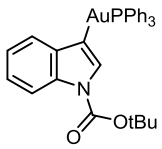
Complex 12b (L = XPhos): colorless solid (142 mg, 87%); crystals suitable for X-ray diffraction were grown from CH_2Cl_2/pentane; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.69 – 7.61 (m, 2H), 7.54 – 7.46 (m, 4H), 7.05 – 6.99 (m, 4H), 6.97 (d, *J* = 1.7 Hz, 2H), 6.24 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.88 (sept., *J* = 6.9 Hz, 2H), 2.39 (sept., *J* = 6.7 Hz, 4H), 2.22 (sept., *J* = 6.7 Hz, 2H), 2.20 – 1.63 (m, 24H), 1.37 (t, *J* = 7.1 Hz, 3H), [1.48 – 1.06 (m), 1.31 (d, *J* = 6.9 Hz), 1.28 (d, *J* = 6.9 Hz), 1.22 (d, *J* = 6.9 Hz), 1.17 (d, *J* = 6.9 Hz), 42H], 0.94 (d, *J* = 6.7 Hz, 6H), 0.93 (m, 3H), 0.86 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 169.8 (t, $^3J_{PC}$ = 1.8 Hz), 149.2, 147.5 (d, J_{PC} = 15.2 Hz), 147.0, 146.8, 136.4 (d, J_{PC} = 5.4 Hz), 134.8 (d, J_{PC} = 8.4 Hz), 133.6, 131.2 (d, J_{PC} = 2.2 Hz), 127.8 (d, J_{PC} = 6.8 Hz), 126.8 (d, J_{PC} = 45.8 Hz), 122.2, 121.5, 120.4 (d, J_{CF} = 320 Hz), 117.2 (t, J_{PC} = 58.7 Hz), 70.6, 38.4 (d, J_{PC} = 28.8 Hz), 37.4 (d, J_{PC} = 30.4 Hz), 34.2, 31.6 (d, J_{PC} = 3.9 Hz), 31.3, 31.1, 30.6, 30.4, 30.3, 27.44 (d, J_{PC} = 11.8 Hz), 27.39 (d, J_{PC} = 13.2 Hz), 27.01 (d, J_{PC} = 12.5 Hz), 26.95 (d, J_{PC} = 13.5 Hz), 26.4, 26.2, 25.4, 25.3, 24.5, 23.8, 23.3, 22.9, 20.3, 15.4; ^{31}P NMR (162 MHz CD_2Cl_2): δ = 38.7; MS (ESI): *m/z* 1431 [M^+ - NTf_2]; HRMS (ESI): *m/z* calcd for $C_{71}H_{107}Au_2OP_2$ [M^+ - NTf_2]: 1431.7123, found: 1431.7113;



Complex 12c (L = SIPr): pale yellow solid (141 mg (73%); crystals suitable for X-ray diffraction were grown from CH_2Cl_2/pentane; ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.38 (t, *J* = 7.7 Hz, 4H), 7.16 (d, *J* = 7.7 Hz, 8H), 5.31 (q, *J* = 1.4 Hz, 2H), 3.95 (s, 8H), 3.54 (q, *J* = 7.1 Hz, 1H), [2.90 (sept., *J* = 6.9 Hz), 2.89 (sept., *J* = 6.9 Hz) 8H], 1.250 (d, *J* = 6.9 Hz, 12H), 1.247 (d, *J* = 6.9 Hz, 12H), 1.06 (d, *J* = 6.9 Hz, 12H), 1.05 (t, *J* = 7.1 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 12H), 0.51 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 206.4, 170.1, 146.99, 146.92, 134.6, 130.0, 124.78, 124.73, 120.3 (q, J_{CF} = 322 Hz), 103.9, 70.0, 54.1, 29.12, 29.02, 25.04, 24.97, 24.40, 24.15, 19.4, 15.3; MS (ESI): *m/z* 1259 [M^+ - NTf_2]; 280 [NTf_2^-]; HRMS (ESI): *m/z*: calcd. for $C_{59}H_{85}Au_2N_4O$ [M^+ - NTf_2]: 1259.6049, found: 1259.6062.



Complex 14. A solution of boronate **13** (227 mg, 0.66 mmol),[5] Cs_2CO_3 (215 mg, 0.66 mmol) and $(Ph_3P)AuNTf_2$ (488 mg, 0.66 mmol) in THF (3 mL) was stirred for 2 h before all volatile materials were evaporated. The residue was suspended in CH_2Cl_2 (3 mL), insoluble materials were filtered off and the filtrate was evaporated. The residue was suspended in pentane (10 mL) and the suspension stirred for 1 h. Insoluble materials were filtered off, the filtrate was evaporated and the residue dried in vacuo (10^{-3} mbar) to give the title complex as a colorless solid material (357 mg, 80%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.10 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), [7.69 – 7.6 (m), 7.6 – 7.47 (m); 15H], 7.40 (s, 1H), 7.22 – 7.11 (m, 2H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 150.3, 145.5 (br), 141.3, 136.5, 134.7 (d, J_{PC} = 13.8 Hz), 133.1, 131.8 (d, J_{PC} = 2.2

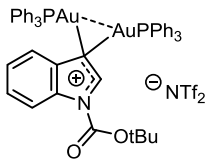


[4] Because of the mentioned trace impurities, the integral for the aromatic protons is variable and slightly higher than expected.

[5] V. A. Kallepalli, F. Shi, S. Paul, E. N. Onyeozili, R. E. Maleczka, Jr., M. R. Smith, *J. Org. Chem*. **2009**, *74*, 9199–9201.

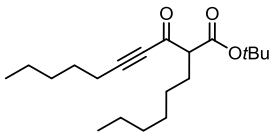
Hz), 131.1 (d, J_{PC} = 51.6 Hz), 129.6 (d, J_{PC} = 11 Hz), 124.6, 123.5, 121.9, 115.1, 82.8, 28.4; ^{31}P NMR (162 MHz CD_2Cl_2): δ = 45.7; MS (EI): *m/z* 619 (≤ 1), 459 (4), 432 (6), 320 (34), 276 (21), 262 (100), 232 (20), 183 (65), 108 (28), 57 (43).

Complex 15. A solution of complex **14** (184 mg, 0.27 mmol) and $(Ph_3P)AuNTf_2$ (201 mg, 0.27 mmol) in CH_2Cl_2 (3 mL) was stirred for 1 h. The mixture was filtered through a short plug of Celite and the filtrate was evaporated to give the title complex as a colorless solid material (357 mg, 93%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.56 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.8 – 7.3 (m, 32H), 1.74 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2, −50° C): δ = 153.1 (br), 147.9 (br), 141.9 (br), 136.7 (br), 133.8 (d, J_{PC} = 13.8 Hz), 132.1 (d, J_{PC} = 2.3 Hz), 129.4 (d, J_{PC} = 11.6 Hz), 128.0 (d, J_{PC} = 58.5 Hz), 125.8, 124.0, 123.8, 119.5 (q, J_{CF} = 320 Hz), 116.3 (t, J_{PC} = 62.3 Hz), 115.8; ^{31}P NMR (162 MHz CD_2Cl_2): δ = 38.1; MS (ESI): *m/z* 1134 [M^+ - NTf_2]; HRMS (ESI): *m/z*: calcd. for $C_{49}H_{44}Au_2NO_2P_2$ [M^+ - NTf_2]: 1134.2173, found 1134.2182; Crystals suitable for X-ray diffraction were grown from CH_2Cl_2/pentane.

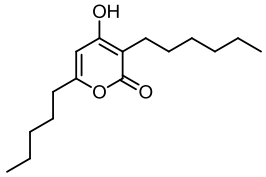


Preparation of 4-Hydroxy-2-Pyrones

Representative Procedure for the Preparation of a Cyclization Precursor by Claisen Condensation: *tert*-Butyl 2-Hex-3-oxodec-4-ynoate. *t*-Butyl octanoate (1.0 g, 0.5 mmol) was added dropwise to a stirred solution of LDA (0.5 M in THF, 10 mL, 5 mmol) at –78 °C. The mixture was stirred at this temperature for 30 min before methyl 2-octynoate (771 mg, 0.5 mmol) was slowly introduced and stirring continued at –78 °C for 2 h. The mixture was poured into aq. sat. NH_4Cl (50 mL) and the organic phase extracted with Et_2O (3 x 50 mL), dried (Na_2SO_4) and concentrated. Flash chromatography of the residue (hexanes/EtOAc, 99:1 → 95:5) gave the title compound as a colorless oil (1.34 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of keto/enol tautomers): δ = 0.85-0.93 (m, 6H), 1.23-1.43 (m, 12H), 1.46 & 1.50 (s each, Σ 9H), 1.53-1.62 (m, 2H), 1.80-1.93 (m, 1H), 2.22-2.29 (m, 1H), 2.36 (t, *J* = 7.1, 1H), 2.40 (t, *J* = 7.1, 1H), 3.33 (t, *J* = 7.4 Hz, 0.5H), 12.33 (s, 0.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 13.9, 14.0, 14.0, 19.0, 19.4, 22.0, 22.1, 22.5, 22.6, 27.0, 17.3, 27.8, 27.8, 27.9, 28.1, 28.2, 28.9, 29.0, 29.6, 30.9, 31.0, 31.5, 31.6, 61.9, 75.0, 79.6, 81.6, 81.7, 96.3, 99.2, 109.4, 152.3, 168.2, 172.8, 183.3. IR (film): $\tilde{\nu}$ = 2957, 2929, 2859, 2214, 1736, 1677, 1633, 1598, 1457, 1369, 1358, 1250, 1150, 1128, 845, 820 cm^{-1}; MS (EI): *m/z* (%) 322 (4), 266 (45), 249 (15), 238 (5), 223 (23), 210 (13), 195 (23), 177 (20), 139 (11), 123 (95), 98 (71), 82 (9), 67 (23), 57 (100), 41 (38); HRMS (EI): *m/z*: calcd for $C_{20}H_{34}O_3Na$ [*M+Na*$^+$]: 345.24001, found: 345.23988.



Representative Procedure for the Preparation of 4-Hydroxy-2-pyrones. Synthesis of Pseudopyronine A. A solution of *tert*-butyl 2-hex-3-oxodec-4-ynoate (325 mg, 1.0 mmol) and [$SPhosAuNTf_2$] (9 mg, 10 µmol, 1 mol%) in HOAc (5 mL) was stirred for 24 h before the acid was distilled off and the residue purified by flash chromatography (hexane/HOAc, 4:1) to afford pseudopyronine A as a white solid (257 mg, 96%). Mp = 111.5-112.5 °C (lit. 106-108 °C).[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86-0.93 (m, 6H), 1.24-1.38 (m, 10H), 1.44-1.54 (m, 2H), 1.58-1.68 (m, 2H), 2.40-2.48 (m,



[6] A. C. Giddens, L. Nielsen, H. I. Boshoff, D. Tasdemir, R. Perozzo, M. Kaiser, F. Wang, J. C. Sacchettini, B. R. Copp, *Tetrahedron* **2008**, *64*, 1242–1249.

4H), 6.20 (s, 1H), 10.19 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 14.1, 22.3, 22.7, 23.1, 26.5, 28.0, 29.3, 31.1, 31.8, 33.5, 100.9, 103.4, 163.6, 167.2, 168.4; ^{1}H NMR (400 MHz, CD_3OD): δ = 0.89 (t, J = 7.0 Hz, 3H), 0.92 (t, J = 7.0 Hz, 3H), 1.32-1.40 (m, 10H), 1.40-1.50 (m, 2H), 1.60-1.70 (m, 2H), 2.37 (t, J = 7.5 Hz, 2H), 2.46 (t, J = 7.6 Hz, 2H), 4.89 (br s, 1H), 5.98 (s, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ = 14.2, 14.4, 23.4, 23.7, 23.9, 27.6, 29.0, 30.2, 32.2, 32.9, 34.2, 101.0, 103.9, 165.1, 167.7, 168.8; IR (film): $\tilde{\nu}$ = 2955, 2926, 2872. 2858, 2643, 1663, 1630, 1556, 1433, 1407, 1292, 1256, 1172, 1130, 992, 856, 758 cm^{-1}; MS (EI): *m/z* (%) 266 (17), 249 (3), 237 (3), 223 (11), 209 (14), 195 (100), 182 (9), 168 (19), 153 (10), 140 (15), 126 (11), 111 (7), 99 (11), 83 (4), 69 (10), 55 (21), 43 (21); HRMS (ESI–): *m/z*: calcd for $C_{16}H_{25}O_3$ [M-H]$^-$: 265.18092, found: 265.18085.

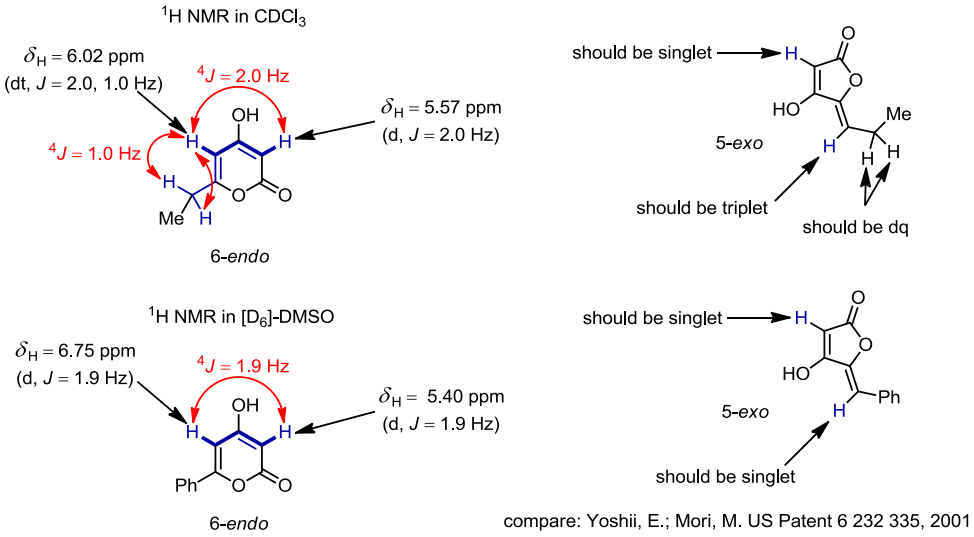
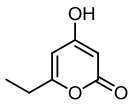
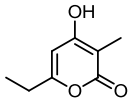


Figure S1. Analysis of the ^{1}H NMR data of two representative products formed by gold catalyzed 6-*endo-dig* cyclization; the comparison with the known data for the corresponding tetronic acids (5-*exo* products) corroborates the structure assignment.



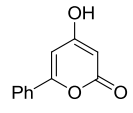
Prepared analogously as colorless crystals (655 mg, 94%); after washing with Et_2O, the material was found analytically pure, thus requiring no flash chromatography. Mp = 106–107 °C (lit:[7a] 83 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.33 (br s, 1H), 6.02 (dt, J = 2.0, 1.0 Hz, 1H), 5.59 (d, J = 2.0 Hz, 1H), 2.52 (q, J = 7.5 Hz, 2H), 1.20 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9 (C), 168.5 (C), 168.3 (C), 100.6 (CH), 89.7 (CH), 26.8 (CH_2), 10.8 (CH_3); IR (film): $\tilde{\nu}$ = 2984, 2950, 2566, 1650, 1614, 1574, 1543, 1446, 1383, 1366, 1311, 1283, 1266, 1242, 1203, 1139, 937, 883, 835, 808, 782, 693, 661 cm^{-1}; MS (EI): *m/z* (%): 140 (37) [M^+], 111 (70), 99 (16), 69 (100), 57 (26), 29 (24); HRMS (EI): *m/z*: calcd for $C_7H_8O_3$ [M^+]: 140.0473, found: 140.0472. The spectroscopic data are in good agreement with the data reported in the literature.[7]



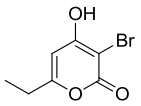
Prepared analogously as a white solid (14.9 mg, 97%); after washing with Et_2O, the material was found analytically pure, thus requiring no flash chromatography. ^{1}H NMR (400 MHz, [D_6]-DMSO): δ = 11.08 (br s, 1H), 5.96 (br s, 1H), 2.43 (q, J = 7.5 Hz, 2H), 1.74 (s,

7 a) D. Schmidt, J. Conrad, I. Klaiber, U. Beifuss *Chem. Commun.* **2006**, 4732–4734; b) X. Zhang, M. McLaughlin, R. L. P. Muñoz, R. P. Hsung, J. Wang, J. Swidorski, Synthesis **2007**, 749–753.

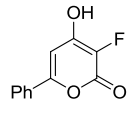
3H), 1.09 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, [D$_6$]-DMSO): $\delta = 165.0$ (C), 164.9 (C), 163.8 (C), 98.2 (CH), 96.5 (C), 25.9 (CH$_2$), 10.9 (CH$_3$), 8.3 (CH$_3$); IR (film): $\tilde{\nu}$ = 2984, 2967, 2914, 2690, 1671, 1634, 1574, 1508, 1428, 1399, 1373, 1353, 1315, 1238, 1180, 1122, 1088, 1056, 1020, 947, 930, 845, 831, 752, 743, 667 cm^{-1}; MS (EI): *m*/*z* (%): 154 (88) [M^+], 126 (79), 111 (100), 99 (59), 83 (14), 69 (94); HRMS (EI): *m*/*z*: calcd for $C_8H_{10}O_3$ [M^+]: 154.0630, found: 154.0631.



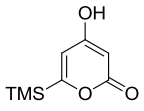
Prepared analogously as a white solid (18.7 mg, 99%); after washing with Et$_2$O, the material was found analytically pure, thus requiring no flash chromatography. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): $\delta = 11.85$ (br s, 1H), 7.84 (m, 2H), 7.51 (m, 3H), 6.75 (d, $J = 1.9$ Hz, 1H), 5.40 (d, $J = 1.9$ Hz, 1H); ^{13}C NMR (100 MHz, [D$_6$]-DMSO): $\delta = 170.5$ (C), 163.0 (C), 160.1 (C), 131.1 (C), 130.9 (CH), 129.1 (2 × CH), 125.5 (2 × CH), 98.4 (CH), 89.6 (CH). The analytical data matched those reported in the literature.[7a,8]



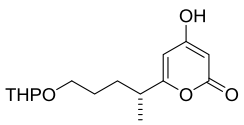
Prepared analogously as a white solid (18.6 mg, 82%); after washing with Et$_2$O, the material was found analytically pure, thus requiring no flash chromatography. Mp = 187-195 °C (decomp.); ^{1}H NMR (400 MHz, [D$_6$]-DMSO): $\delta = 1.11$ (t, J = 7.5 Hz, 3H), 2.48 (dq, J = 7.5, 0.8 Hz, 2H), 6.08 (t, J = 0.8 Hz, 1H), 12.53 (br s, 1H); ^{13}C NMR (100 MHz, [D$_6$]-DMSO): $\delta = 10.7$, 25.7, 84.9, 98.2, 160.4, 165.8, 166.7; IR (film): $\tilde{\nu}$ = 3082, 1656, 1565, 1428, 1411, 1380, 1326, 1222, 1157, 1048, 971, 943, 844, 791, 773, 741, 683758 cm^{-1}; MS (EI): *m*/*z* (%) 220 (96), 218 (97), 192 (53), 190 (57), 177 (15), 175 (16), 163 (21), 161 (22), 135 (36), 133 (35), 122 (12), 120 (11), 111 (8), 99 (100), 83 (11), 69 (25), 57 (30), 53 (29), 39 (12), 29 (27); HRMS (EI): *m*/*z*: calcd for $C_7H_6O_3Br$ [M+Na^+]: 216.95059, found: 216.95071.



Prepared analogously as a white solid (17.5 mg, 85%); after washing with Et$_2$O, the material was found analytically pure, thus requiring no flash chromatography. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): $\delta = 12.38$ (br s, 1H), 7.78 (m, 2H), 7.51 (m, 3H), 6.83 (d, $J = 5.3$ Hz, 1H); ^{13}C NMR (100 MHz, [D$_6$]-DMSO): $\delta = 157.1$ (d, $J_{CF} = 23.7$ Hz, C), 154.9 (d, $J_{CF} = 6.0$ Hz, C), 153.8 (d, $J_{CF} = 9.2$ Hz, C), 133.0 (C), 130.7 (CH), 130.4 (C), 129.1 (2 × CH), 125.3 (2 × CH), 98.9 (CH), IR (film): $\tilde{\nu}$ = 2885, 2641, 2587, 2551, 1625, 1577, 1549, 1495, 1453, 1399, 1356, 1174, 1071, 1048, 910, 859, 824, 770, 734, 685, 658 cm^{-1}; MS (EI): *m*/*z* (%): 206 (100) [M^+], 178 (27), 149 (21), 130 (18), 105 (42), 77 (53), 51 (27); HRMS (ESI+): *m*/*z*: calcd for $C_{11}H_7O_3FNa$ [$M^+ + Na$]: 229.0271, found: 229.0274.



Prepared analogously as a white solid (8.3 mg, 45%). Mp = 116-118 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.27$ (s, 9H), 5.66 (d, J = 2.3 Hz, 1H), 6.36 (d, J = 2.3 Hz, 1H), 11.00 (br s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = –2.9, 92.5, 112.1, 169.7, 170.1, 175.1; IR (film): $\tilde{\nu}$ = 3133, 2961, 1681, 1650, 1631, 1571, 1421, 1283, 1243, 1222, 1188, 1088, 988, 921, 869, 839, 826, 702 cm^{-1}; MS (EI): *m*/*z* (%) 184 (22), 169 (81), 156 (2), 143 (10), 127 (6), 111 (6), 99 (20), 83 (8), 73 (100), 69 (21), 66 (3), 55 (4), 45 (16), 29 (3); HRMS (EI): *m*/*z*: calcd for $C_8H_{12}O_3Si$ [M+Na^+]: 184.05558, found: 184.05542.



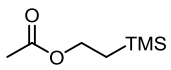
Prepared analogously as a yellow oil (mixture of diastereoisomers, 69 mg, 83%). $[\alpha]_D^{20}$: –9.4 (c = 1, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.09 (bs, 1H), 5.90 (d, J = 1.8 Hz, 1H), 5.41 (d, J = 1.8 Hz, 1H), 4.57 – 4.50 (m, 1H), 3.88 – 3.77 (m, 1H), 3.75 – 3.65 (m, 1H), 3.51 – 3.43 (m, 1H), 3.39 – 3.13 (m, 1H), 2.60 – 2.50 (m, 1H), 1.83 – 1.43 (m, 10H), 1.20 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 170.2, 170.7, 167.8, 100.3, 99.32, 99.31, 90.0, 67.50, 67.45, 62.78, 62.75, 38.4, 38.3, 31.14, 31.09, 30.8, 27.5, 27.4, 25.5, 19.8, 18.4; IR

[8] A. R. Katritzky, Z. Wang, M. Wang, C. D. Hall, K. Suzuki *J. Org. Chem.* **2005**, *70*, 4854–4856.

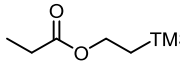
(film): $\tilde{\nu}$ = 2941, 2870, 1665, 1567, 1439, 1367, 1258, 1057, 1022 cm^{-1}. HRMS (ESI): *m/z*: calcd. for $C_{15}H_{22}O_5Na$ [M^++Na]: 305.13600, found 305.13594.

The Trimethylsilylethyl 3-Oxoalkanoate Series

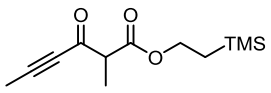
2-(Trimethylsilyl)ethyl acetate.[9] 2-Trimethylsilyl-ethanol (7.5 mL, 52.33 mmol) was added dropwise to a solution of $Mg(ClO_4)_2$ (117 mg, 0.52 mmol) in Ac_2O (5.0 mL, 52.90 mmol) and the resulting mixture was stirred for 4 h. The reaction was quenched with sat. aq. $NaHCO_3$ and the aqueous layer extracted with *tert*-butyl methyl ether. The combined extracts were washed twice with sat. aq. $NaHCO_3$, dried over $MgSO_4$, and evaporated to give the title compound as a colorless liquid which was pure enough for further use (7.67 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 – 4.10 (m, 2H), 2.03 (s, 3H), 1.01 – 0.95 (m, 2H), 0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 62.8, 21.4, 17.4, –1.4. IR (film): $\tilde{\nu}$ = 2254, 1730, 1251, 903 cm^{-1}. HRMS (ESI): *m/z*: calcd. for $C_7H_{16}O_2SiNa^+$: 183.08127; found: 183.08118.



2-(Trimethylsilyl)ethyl propionate. Prepared analogously from propionic anhydride (5.0 mL, 39.07 mmol) as a colorless liquid (5.32 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 – 4.12 (m, 2H), 2.29 (q, *J* = 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H), 1.00 – 0.94 (m, 2H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 62.6, 27.9, 17.4, 9.3, –1.4. IR (film): $\tilde{\nu}$ = 2254, 1725, 1251, 1180, 903 cm^{-1}. HRMS (ESI): *m/z*: calcd. for $C_8H_{18}O_2SiNa^+$: 197.09690; found: 197.09683.



2-(Trimethylsilyl)ethyl 2-methyl-3-oxohex-4-ynoate. *n*BuLi (1.6 M in hexanes, 3.6 mL, 5.76 mmol) was added dropwise to a solution of *i*Pr_2NH (1.0 mL, 7.14 mmol) in THF (11.5 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C before it was cooled to –78 °C. 2-(Trimethylsilyl)ethyl propionate (1.0 g, 5.74 mmol) was added dropwise and stirring continued at −78°C for 30 min before ethyl-2-butynoate (0.5 mL, 4.23 mmol) was slowly added. After stirring at this temperature for 3 h, the reaction was quenched with sat. aq. NH_4Cl and the aqueous layer extracted with *tert*-butyl methyl ether. The extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 20:1) gave the title compound as a colorless liquid (942 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of keto/enol tautomers): δ = 12.18 (s, 0.8 H, enol); 4.32 – 4.20 (m, 2H, ketone+enol); 3.52 (q, J = 7.2 Hz, 0.2H, ketone); 2.08 (s, 2.4 H, enol); 2.04 (s, 0.5 H, ketone); 1.87 (s, 2.4 H, enol); 1.41 (d, *J* = 7.1 Hz, 0.5 H, ketone); 1.09 – 0.96 (m, 2H, ketone+enol); 0.05 (s, 7H, enol); 0.04 (s, 1.8H, ketone). ^{13}C NMR (101 MHz, $CDCl_3$, mixture of keto/enol tautomers): δ = 183.3 (ketone), 173.5 (enol), 170.0 (ketone), 152.3 (enol), 103.3 (enol), 95.9 (enol), 92.9 (ketone), 78.9 (ketone), 74.3 (enol), 64.0 (ketone), 63.3 (enol), 55.0 (ketone), 17.41 (enol), 17.35 (ketone), 13.1 (enol), 13.0 (ketone), 4.7 (enol), 4.4 (ketone), –1.36 (enol), –1.41 (ketone). IR (film): $\tilde{\nu}$ = 2254, 1638, 1603, 1392, 1335, 1253, 1161, 1120, 903 cm^{-1}. HRMS (ESI): *m/z*: calcd. for $C_{12}H_{20}O_3SiNa^+$: 263.10742; found: 263.10739.



[9] E. Knobloch, R. Brückner *Synthesis* **2008**, *14*, 2229–2246.

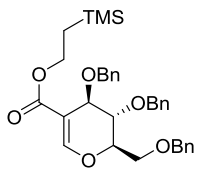
2-(Trimethylsilyl)ethyl 2-methyl-3-oxo-5-phenylpent-4-ynoate. Prepared analogously as a colorless liquid (627 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of keto/enol tautomers): δ = 13.47 (s, 0.9 H, enol); 7.64 – 7.46 (m, 2H, ketone+enol); 7.46 – 7.27 (m, 3H, ketone+enol); 4.35 -4.24 (m, 2H, ketone+enol); 3.66 (q, *J* = 7.3 Hz, 0.1H, ketone); 2.00 (s, 2.7 H, enol); 1.50 (d, *J* = 7.3 Hz, 0.3H, ketone); 1.11 – 1.03 (m, 2H, ketone+enol); 0.07 (s, 8H, enol); 0.02 (s, 1H, ketone). ^{13}C NMR (101 MHz, $CDCl_3$, enol form): δ = 173.3, 152.0, 132.1, 129.8, 128.6, 121.4, 104.5, 97.8, 83.1, 63.5, 17.5, 13.4, –1.3. IR (film): $\tilde{\nu}$ = 2954, 2215, 1738, 1638, 1605, 1591, 1390, 1336, 1278, 1190, 1060 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{17}H_{22}O_3SiNa^+$: 325.123010; found: 325.123043.

(2*R*,3*S*,4*R*)-3,4-bis(Benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carbaldehyde (S-1).[10] $POCl_3$ (2.45 mL, 26.16 mmol) was added dropwise over 1 h to a solution of tri-*O*-benzyl-D-glucal (1.00 g, 2.4 mmol) in DMF (4 mL) at 0°C. The mixture was stirred for 24 h while slowly warming to room temperature. The reaction was quenched with sat. aq. $NaHCO_3$ and the aqueous layer was extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$, the drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 5:1) afforded the title compound (807 mg, 76%). $[\alpha]_D^{20}$: +2.1 (c = 1, $CHCl_3$; Lit.:[10] $[\alpha]_D^{25}$: +6.8, c = 0.34, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (s, 1H), 7.42 – 7.20 (m, 15H), 4.77 – 4.71 (m, 1H), 4.71 – 4.44 (m, 7H), 4.42 (t, *J* = 2.3 Hz, 1H), 3.84 (t, *J* = 2.3 Hz, 1H), 3.80 (dd, *J* = 10.9, 7.8 Hz, 1H), 3.63 (dd, 10.7, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.5, 164.4, 138.3, 137.8, 137.3, 128.7, 128.6, 128.5, 128.2, 128.0, 127.93, 127.87, 127.8, 117.9, 79.5, 73.5, 72.6, 71.8, 71.5, 68.5, 65.4. IR (film): $\tilde{\nu}$ = 3064, 3031, 2866, 1673, 1626, 1454, 1294, 1199, 1089, 1072 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{28}H_{28}O_5Na^+$: 467.18306; found: 467.18289.

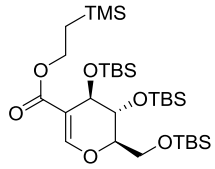
(2*R*,3*S*,4*R*)-3,4-bis(Benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylic acid (S-2). NaH_2PO_4 (5.60 g, 46.68 mmol) and H_2O_2 (7.5 mL, 77.17 mmol, 35% in H_2O) were added to a solution of **S-1** (6.45 g, 15.49 mmol) in CH_3CN/*t*BuOH/H_2O (2:2:1, 70 mL) at 0°C. The mixture was stirred for 5 min before $NaClO_2$ (8.4 g, 92.88 mmol) was added. Stirring was then continued for 16 h at room temperature before the mixture was diluted with water and the aqueous phase was extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 5:1) afforded the title compound (5.60 g, 79%). $[\alpha]_D^{20}$: –4.2 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.39 – 7.21 (m, 15H), 4.72 – 4.63 (m, 2H), 4.59 – 4.49 (m, 4H), 4.44 (d, *J* = 12.1 Hz, 1H), 4.34 (t, *J* = 2.3 Hz, 1H), 3.82 (t, *J* = 2.2 Hz, 1H), 3.78 (dd, *J* = 10.7, 7.7 Hz, 1H), 3.62 (dd, *J* = 10.7, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9, 157.6, 138.3, 137.8, 137.5, 128.7, 128.6, 128.5, 128.15, 128.11, 127.91, 127.88, 127.85, 127.1, 104.7, 77.5, 73.5, 72.4, 71.6, 71.4, 68.4, 67.8. IR (film): $\tilde{\nu}$ = 3063, 3030, 2863, 1647, 1453, 1362, 1238, 1097, 1069, 1047, 1027 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{28}H_{28}O_6Na^+$: 483.17805; found: 483.17781.

[10] N.G. Ramesh, K.K. Balasubramanian *Tetrahedron Lett.* **1991**, *32*, 3875–3878.

2-(Trimethylsilyl)ethyl (2*R*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylate (S-3). DEAD (6.70 mL, 36.77 mmol) was added dropwise over 60 min to a solution of compound **S-2** (5.60 g, 12.15 mmol), 2-(TMS)-ethanol (4.5 mL, 31.39 mmol) and PPh_3 (11.50 g, 43.84 mmol) in THF (60 mL) at 0°C. After stirring for 16 h at room temperature, the reaction was quenched with sat. aq. NH_4Cl and the aqueous phase extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 10:1) afforded the title compound (5.25 g, 77%). $[\alpha]_D^{20}$: −15.8 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.39 – 7.20 (m, 15H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.64 – 4.59 (m, 1H), 4.58 – 4.47 (m, 4H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.35 (t, *J* = 2.1 Hz, 1H), 4.29 – 4.21 (m, 2H), 3.80 (t, *J* = 2.3 Hz, 1H), 3.76 (dd, *J* = 10.6, 7.6 Hz, 1H), 3.61 (dd, *J* = 10.7, 4.9 Hz, 1H), 1.06 – 0.98 (m, 2H), 0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.5, 155.3, 138.4, 137.9, 137.6, 128.7, 128.6, 128.5, 128.12, 128.10, 127.92, 127.86, 127.8, 105.7, 77.1, 73.5, 72.5, 71.61, 71.56, 68.4, 68.1, 62.5, 17.6, −1.3. IR (film): $\tilde{\nu}$ = 3031, 2952, 2897, 1701, 1633, 1454, 1293, 1275, 1250, 1195, 1071, 1028 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{33}H_{40}O_6SiNa^+$: 583.24854; found: 583.24864.

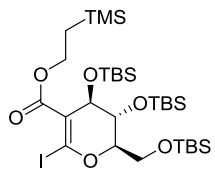


2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*R*)-3,4-bis((tert-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylate (S-4). $Pd(OH)_2$/C (375 mg, 10% *w/w*) was added to a solution of compound **S-3** (3.75 g, 6.69 mmol) in CH_3OH (66 mL). The solution was purged with H_2 and stirred for 15 h under a H_2 atmosphere (1 atm). The mixture was then filtered through a plug of Celite® and the filtrate was concentrated.



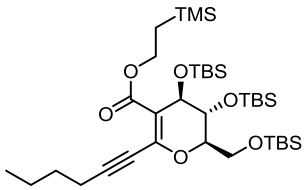
TBSOTf (6.20 mL, 26.99 mmol) was added to a solution of the crude triol in CH_2Cl_2 (16.5 mL) and pyridine (6.5 mL) at 0 °C. The mixture was stirred for 16 h while warming to room temperature, before the reaction was quenched with sat. aq. NH_4Cl and the aqueous phase extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 60:1) furnished the title compound (3.72 g, 88%). $[\alpha]_D^{20}$: +4.3 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1H), 4.36 – 4.20 (m, 3H), 4.20 – 4.08 (m, 1H), 3.93 (dd, *J* = 11.6, 8.1 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.73 (dd, *J* = 11.7, 3.9 Hz, 1H), 1.07 – 0.97 (m, 2H), 0.89 (s, 9H), 0.84 (s, 18H), 0.15 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), 0.04 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7, 154.4, 106.7, 82.3, 68.3, 63.8, 62.3, 62.1, 26.1, 25.84, 25.78, 18.5, 18.13, 18.10, 17.5, −1.3, −4.6, −4.67 (2 C), −4.71, −5.05, −5.14. IR (film): $\tilde{\nu}$ = 2954, 2930, 2896, 2858, 1706, 1635, 1472, 1252, 1197, 1076 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{30}H_{64}O_6Si_4Na^+$: 655.36777; found: 655.36722.

2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*R*)-3,4-bis((tert-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-6-iodo-3,4-dihydro-2*H*-pyran-5-carboxylate (S-5). *n*BuLi (1.6 M in hexanes, 1.60 mL, 2.56 mmol) was added dropwise to a solution of *i*Pr_2NH (0.50 mL, 3.57 mmol) in THF (5.70 mL) at 0°C and the resulting mixture was stirred for 15 min before it was cooled to −78°C. A solution of compound **S-4** (540 mg, 0.85 mmol) in THF (5.70 mL) was added dropwise and the resulting mixture was stirred for 1.5 h. A solution of iodine (1.08 g, 4.26 mmol) in THF (5.70 mL) was then added dropwise and stirring

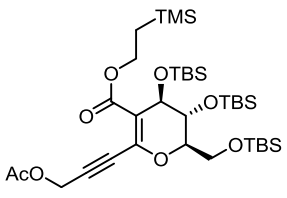


was continued for 30 min. The reaction was quenched with sat. aq. $Na_2S_2O_3$ and the aqueous layer extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$, the drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 20:1) afforded the title compound (598 mg, 92%). $[\alpha]_D^{20}$: +4.2 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.45 (t, *J* = 2.4 Hz, 1H), 4.41 – 4.32 (m, 1H), 4.32 – 4.26 (m, 1H), 4.15 – 4.06 (m, 1H), 4.02 – 3.94 (m, 2H), 3.79 (dd, *J* = 11.5, 4.9 Hz, 1H), 1.06 (dd, *J* = 9.6, 8.1 Hz, 2H), 0.89 (s, 9H), 0.85 (s, 9H), 0.83 (s, 9H), 0.11 (s, 3H), 0.08 (s, 9H), 0.06 – 0.02 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 119.6, 112.7, 87.1, 67.9, 66.5, 63.0, 61.7, 26.1, 25.78, 25.76, 18.5, 18.10, 18.07, 17.6, −1.4, −4.4, −4.5, −4.6, −4.8, −5.0, −5.2. IR (film): $\tilde{\nu}$ = 2953, 2929, 2894, 2857, 1698, 1584, 1471, 1521, 1113, 1064 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{30}H_{63}O_6Si_4INa^+$: 781.26417; found: 781.26387.

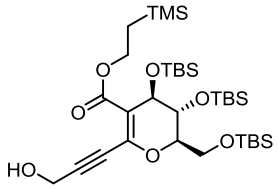
2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*R*)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-6-(hex-1-yn-1-yl)-3,4-dihydro-2*H*-pyran-5-carboxylate. 1-Hexyne (0.1 mL, 0.87 mmol) was added to a degassed solution of **S-5** (100 mg, 0.13 mmol) and NEt_3 (2.5 mL, 17.94 mmol) in THF (0.9 mL) at room temperature, followed by CuI (5 mg, 0.03 mmol, 20 mol%) and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.01 mmol, 10 mol%). The mixture was stirred for 15 h before it was filtered through a plug of Celite®. The filtrate was diluted with sat. aq. NH_4Cl and the aqueous phase extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$, the drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 60:1) afforded the title compound as a colorless syrup (88 mg, 93%). $[\alpha]_D^{20}$: +2.3 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.46 (t, *J* = 2.4 Hz, 1H), 4.41 – 4.30 (m, 1H), 4.29 – 4.21 (m, 1H), 4.19 – 4.08 (m, 1H), 3.94 (dd, *J* = 2.8, 1.5 Hz, 1H), 3.90 (dd, *J* = 11.4, 7.6 Hz, 1H), 3.80 (dd, *J* = 11.3, 5.4 Hz, 1H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.64 – 1.54 (m, 2H), 1.50 – 1.39 (m, 2H), 1.10 – 1.00 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.89 (s, 9H), 0.86 (s, 9H), 0.83 (s, 9H), 0.14 (s, 3H), 0.09 – 0.06 (m, 12H), 0.06 – 0.03 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.3, 144.2, 109.9, 96.9, 82.5, 75.9, 67.7, 65.6, 62.4, 62.0, 30.3, 26.1, 25.9, 25.8, 22.3, 19.5, 18.5, 18.2, 17.7, 13.8, −1.4, −4.46, −4.53, −4.6, −4.7, −5.0, −5.2. IR (film): $\tilde{\nu}$ = 2954, 2930, 2858, 1689, 1602, 1471, 1389, 1251, 1112, 1069 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{36}H_{72}O_6Si_4Na^+$: 735.42997; found: 735.42982.



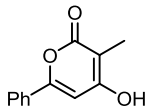
2-(Trimethylsilyl)ethyl (2*R*,3*S*,4*R*)-6-(3-acetoxyprop-1-yn-1-yl)-3,4-bis(benzyloxy)-2-((benzyloxy)-methyl)-3,4-dihydro-2*H*-pyran-5-carboxylate. Prepared analogously from propargyl acetate (33 µL, 0.33 mmol) and **S-5** (50 mg, 0.07 mmol) (42 mg, 87%). $[\alpha]_D^{20}$: +3.5 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.88 (s, 2H), 4.44 (t, *J* = 2.3 Hz, 1H), 4.39 – 4.30 (m, 1H), 4.29 – 4.23 m, 1H), 4.19 – 4.09 (m, 1H), 3.94 (dd, *J* = 2.8, 1.5 Hz, 1H), 3.88 (dd, *J* = 11.4, 7.6 Hz, 1H), 3.79 (dd, *J* = 11.4, 5.6 Hz, 1H), 2.10 (s, 3H), 1.09 – 1.01 (m, 2H), 0.88 (s, 9H), 0.85 (s, 9H), 0.83 (s, 9H), 0.13 (s, 3H), 0.08 – 0.07 (m, 6H), 0.07 – 0.05 (m, 6H), 0.04 (s, 9H), 0.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.3, 166.7, 143.0, 111.6, 88.3, 82.7, 81.3, 67.5, 65.3, 62.8, 61.8, 52.6, 26.1, 25.82, 25.76, 20.9, 18.5, 18.1, 17.4, −1.4, −4.5, −4.58, −4.62, −4.8, −5.1, −5.2. IR (film): $\tilde{\nu}$ = 2953, 2929, 2857, 1753, 1692, 1607, 1472, 1389, 1321, 1250, 1217, 1111, 1067 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{35}H_{68}O_8Si_4Na^+$: 751.38857; found: 751.38835.



2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*R*)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-6-(3-hydroxyprop-1-yn-1-yl)-3,4-dihydro-2*H*-pyran-5-carboxylate. Prepared analogously from **S-5** (147 mg, 0.19 mmol) and propargylic alcohol (36 µL, 0.62 mmol) (116 mg, 87%). $[\alpha]_D^{20}$: +6.9 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.50 – 4.45 (m, 2H), 4.45 (t, *J* = 2.4 Hz, 1H), 4.40 – 4.31 (m, 1H), 4.29 – 4.22 (m, 1H), 4.16 – 4.07 (m, 1H), 3.95 (dd, *J* = 2.6, 1.4 Hz, 1H), 3.88 (dd, *J* = 11.2, 7.4 Hz, 1H), 3.80 (dd, *J* = 11.4, 5.5 Hz, 1H), 2.26 (bs, 1H), 1.04 (dd, *J* = 9.5, 7.9 Hz, 1H), 0.88 (s, 9H), 0.85 (s, 9H), 0.83 (s, 9H), 0.13 (s, 3H), 0.08 (s, 6H), 0.06 (s, 6H), 0.04 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 143.6, 111.1, 93.1, 82.6, 80.6, 67.5, 65.3, 62.8, 61.8, 51.6, 26.1, 25.81, 25.75, 18.5, 18.1, 17.5, 1.2, −1.4, −4.4, −4.58, −4.63, −4.8, −5.1, −5.2. IR (film): $\tilde{\nu}$ = 3429, 2953, 2930, 2896, 2857, 1692, 1601, 1472, 1389, 1251, 1220, 1070 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{33}H_{66}O_7Si_4Na^+$: 709.37782; found: 709.37779.

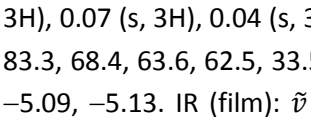


3,6-Dimethyl-4-hydroxy-2-pyrone. SPhosAuNTf$_2$ (4 mg, 0.005 mmol, 1 mol%) was added to a solution of 2-(trimethylsilyl)ethyl 2-methyl-3-oxohex-4-ynoate (120 mg, 0.5 mmol) in HOAc (2.5 mL) and the resulting mixture was stirred for 2 h. The solvent was evaporated and the residue washed with Et_2O to yield the title compound as a white solids in analytically pure form (68 mg, 97%). ^{1}H NMR (400 MHz, CD_3OD): δ = 5.99 (s, 1H), 2.20 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD): δ = 169.1, 167.9, 161.4, 101.5, 98.7, 19.5, 8.2. IR (film): $\tilde{\nu}$ = 2958, 2926, 2856, 2672, 1729, 1638, 1582, 1404, 1251, 1131 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_7H_8O_3Na^+$: 163.03661; found: 163.03656.

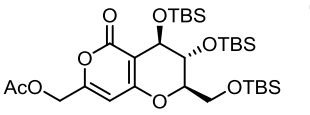


3-Methyl-6-phenyl-4-hydroxy-2-pyrone. Prepared analogously as a white solid (126 mg, 94%). ^{1}H NMR (400 MHz, [D$_5$]-pyridine): δ = 7.87 – 7.77 (m, 2H), 7.36 – 7.26 (m, 3H), 6.82 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, [D$_5$]-pyridine): δ = 166.0, 165.4, 157.6, 132.2, 130.5, 129.1, 125.6, 99.9, 98.7, 9.4. IR (film): $\tilde{\nu}$ = 2877, 2650, 2543, 1612, 1560, 1395, 1372, 1260, 1229, 1154 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{12}H_{10}O_3Na^+$: 225.05221; found: 225.05224.

(2*R*,3*R*,4*R*)-7-Butyl-3,4-bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-3,4-dihydro-2H,5*H*-pyrano[4,3-b]pyran-5-one. Prepared analogously using CH_3NO_2 as the solvent (50 mg, 83%). $[\alpha]_D^{20}$: +34.1 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.75 (s, 1H), 4.31-4.12(m, 2H), 4.01 – 3.92 (m, 2H), 3.80 (dd, *J* = 11.6, 4.0 Hz, 1H), 2.44 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.57 (m, 2H), 1.36 (hex, *J* = 7.4 Hz, 2H), 0.92(t, *J* = 7.3 Hz, 3H), 0.89 (s, 9H), 0.86 (s, 9H), 0.82 (s, 9H), 0.21 (s, 3H), 0.16 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.5, 164.8, 163.4, 99.5, 98.6, 83.3, 68.4, 63.6, 62.5, 33.5, 28.7, 26.04, 25.94, 25.80, 22.2, 18.5, 18.2, 18.1, 13.9, −4.5, −4.6, −4.7, −4.9, −5.09, −5.13. IR (film): $\tilde{\nu}$ = 2954, 2929, 2857, 1721, 1652, 1588, 1433, 1523, 1105, 1071 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{31}H_{60}O_6Si_3Na^+$: 635.35868; found: 635.35899.



((2*R*,3*R*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-oxo-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-7-yl)methyl acetate. Prepared analogously in CH_3NO_2 as the solvent (18 mg, 91%). $[\alpha]_D^{20}$: +38.8 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.01 (s, 1H), 4.82 (s, 2H), 4.42 – 4.32 (m, 2H), 3.98 (dd, *J* = 2.5, 1.8 Hz, 1H), 3.94 (dd, *J* = 11.6, 8.1 Hz, 1H), 3.82 (dd, *J* = 11.6, 4.3 Hz, 1H), 2.15 (s, 3H), 0.89 (s, 9H), 0.86 (s, 9H), 0.83 (s, 9H), 0.21 (s, 3H), 0.16 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.2, 163.5, 162.7, 157.9, 101.0, 100.4, 83.5, 68.2, 63.5, 62.3, 61.6, 26.0, 25.9, 25.8, 20.8, 18.5, 18.2, 18.1, −4.5, −4.7, −4.8, −4.9, −5.11, −5.14. IR (film): $\tilde{\nu}$ =

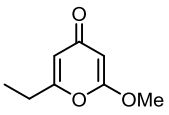


2953, 2923, 2857, 1754, 1727, 1662, 1591, 1431, 1252, 1219, 1071 cm^{-1}. HRMS (ESI): *m/z*: calcd. for $C_{30}H_{56}O_8Si_3Na^+$: 651.31722; found: 671.31753.

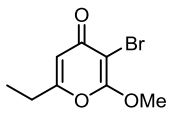
(2*R*,3*R*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-7-(hydroxymethyl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one. Prepared analogously in CH_3NO_2 as the solvent (100 mg, 89%). $[\alpha]_D^{20}$: +41.1 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.11 (s, 1H), 4.44 – 4.32 (m, 4H), 4.00 – 3.97 (m, 1H), 3.95 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.81 (dd, *J* = 11.6, 4.3 Hz, 1H), 3.13 (bs, 1H), 0.88 (s, 9H), 0.85 (s, 9H), 0.81 (s, 9H), 0.19 (s, 3H), 0.14 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.3, 163.5, 163.2, 99.5, 99.2, 83.5, 68.1, 63.4, 62.4, 61.1, 26.0, 25.8, 25.7, 18.4, 18.2, 18.0, −4.6, −4.7, −4.8, −5.0, −5.1, −5.2. IR (film): $\tilde{\nu}$ = 3413, 2953, 2926, 2857, 1724, 1697, 1587, 1472, 1432, 1254, 1077 cm^{-1}. HRMS (ESI): *m/z*: calcd. for $C_{28}H_{54}O_7Si_3Na^+$: 609.30704; found: 609.30696.

Preparation of 2-Alkoxy-4-pyrones.

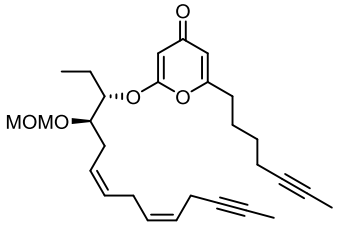
2-Ethyl-6-methoxy-4*H*-pyran-4-one. $SPhosAuNTf_2$ (1.3 mg, 1.5 μmol) was added to a solution of methyl 3-oxohept-4-ynoate (21.8 mg, 0.141 mmol) in HOAc (0.5 mL). The mixture was stirred for 24 h and concentrated, and the residue was purified by flash chromatography (hexanes/EtOAc, 1:1 → 0/1) to give the title compound as a colorless solid (19.4 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 1.20 (t, *J* = 7.5 Hz, 3H), 2.49 (dq, *J* = 7.5, 0.7 Hz, 2H), 3.84 (s, 3H), 5.43 (d, *J* = 1.8 Hz, 1H), 5.97 (dt, *J* = 1.8, 0.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 10.8, 26.3, 56.2, 89.6, 111.1, 166.4, 168.3, 182.0; IR (film): $\tilde{\nu}$ = 3074, 2972, 2941, 1657, 1611, 1576, 1455, 1393, 1241, 1161, 1054, 985, 961, 918, 882, 839 cm^{-1}; MS (EI): *m/z* (%) 154 (76), 139 (3), 126 (12), 111 (72), 101 (11), 83 (12), 69 (100), 59 (12), 39 (15), 33 (1), 29 (21); HRMS (EI): *m/z*: calcd for $C_8H_{10}O_3$ [M^+]: 154.06300, found: 154.06313.

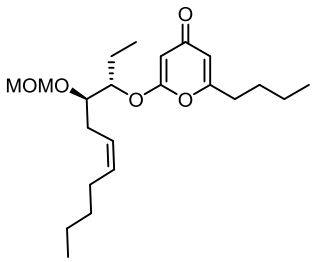


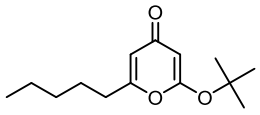
3-Bromo-6-ethyl-2-methoxy-4*H*-pyran-4-one. Prepared analogously as a as a colorless solid (16.9 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 1.25 (t, *J* = 7.5 Hz, 3H), 2.57 (dq, *J* = 7.5, 0.8 Hz, 2H), 4.08 (s, 3H), 6.12 (t, *J* = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 10.8, 25.9, 56.7, 90.3, 110.5, 162.7, 164.5, 175.6; IR (film): $\tilde{\nu}$ = 2961, 1660, 1633, 1571, 1466, 1420, 1373, 1347, 1293, 1246, 1146, 1102, 1062, 1024, 977, 913, 847, 727 cm^{-1}; MS (EI): *m/z* (%) 234 (98), 232 (100), 219 (5), 217 (5), 191 (20), 189 (21), 180 (65), 178 (68), 149 (16), 147 (14), 121 (14), 106 (5), 93 (15), 81 (18), 69 (46), 59 (55), 53 (39), 43 (17), 39 (40); HRMS (ESI+): *m/z*: calcd for $C_8H_9BrNaO_3$ [$M+Na^+$]: 254.96274, found: 254.96275.



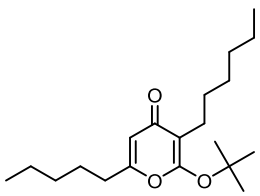
2-(Benzyloxy)-6-ethyl-2*H*-pyran-4-one. Prepared analogously as a white solid (21.6 mg, 94%). Mp = 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 1.21, (t, *J* = 7.5 Hz, 3H), 2.51 (dt, *J* = 7.5, 0.5 Hz, 2H), 5.09 (s, 2H), 5.54 (d, *J* = 1.8 Hz, 1H), 5.99 (m, *J* = 1.8 Hz, 1H), 7.35-7.44 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$): *δ* = 10.7, 26.2, 71.2, 90.9, 111.1, 127.9, 128.9, 129.0, 133.7, 166.4, 167.1, 181.9; IR (film): $\tilde{\nu}$ = 3051, 2973, 2914, 1656, 1615, 1589, 1575, 1500, 1455, 1416, 1380, 1366, 1302, 1251, 1226, 103, 1157, 1091, 1059, 1029, 1005, 978, 924, 898, 800, 787, 740, 691, 681, 670 cm^{-1}; MS (EI): *m/z* (%) 230 (1) 174 (1), 132 (15), 91 (100), 77 (1), 65 (9), 51 (1), 40 (3), 29 (2) HRMS (EI): *m/z*: calcd for $C_{14}H_{14}O_3Na$ [$M+Na^+$]: 253.08351, found: 253.08334.

2-(Hept-5-yn-1-yl)-6-{[(3*S*,4*R*,6*Z*,9*Z*)-4-(methoxymethoxy)tetradeca-6,9-dien-12-yn-3-yl]oxy}-4*H*-pyran-4-one.  Prepared analogously in MeCN/HOAc (5:1) as a colorless oil (27.5 mg, 86%). $[\alpha]_D^{25}$ = −22.7 (c = 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 3H), 1.49-1.58 (m, 2H), 1.69-1.89 (m, 4H), 1.77 (t, *J* = 2.5 Hz, 3H), 1.77 (t, *J* = 2.5 Hz, 3H), 2.13-2.21 (m, 2H), 2.29-2.46 (m, 2H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.76-2.83 (m, 2H), 2.86-2.93 (m, 2H), 3.36 (s, 3H), 3.82 (dt, *J* = 6.3, 3.3 Hz, 1H), 4.36 (dt, *J* = 8.0, 3.8 Hz, 1H), 4.64 (d, *J* = 6.9 Hz, 1H), 4.66 (d, *J* = 6.9 Hz, 1H), 5.33-5.56 (m, 5H), 5.99 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.6, 3.6, 10.2, 17.3, 18.5, 22.6, 25.8, 25.8, 28.2, 28.7, 32.6, 56.0, 75.7, 76.3, 76.8, 77.4, 78.4, 83.4, 91.6, 96.2, 112.3, 125.0, 125.8, 128.7, 130.6, 164.9, 167.1, 182.0; IR (film): $\tilde{\nu}$ = 2921, 1661, 1625, 1581, 1398, 1241, 1149, 1100, 1031, 918, 855, 751 cm^{-1}; MS (EI): *m/z* (%) 454 (3), 409, (1), 383 (2), 352 (2), 321 (4), 263 (2), 251 (31), 219 (9), 207 (21), 177 (9), 117 (15), 91 (18), 71 (14), 45 (100); HRMS (ESI): *m*/*z*: calcd. for $C_{28}H_{38}NaO_5$ [*M+Na*$^+$]: 477.26114, found: 477.26141.

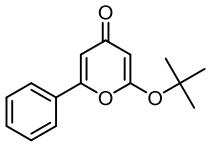
2-(Heptyl)-6-[(3*S*,4*R*,6*Z*)-4-(methoxymethoxy)-undecene-2-yl]-4*H*-pyran-4-one.  Prepared analogously in MeCN/HOAc (3:1) as a colorless oil (95 mg, 95%). $[\alpha]_D^{20}$ = −14.3 (c = 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (s, 1H), 5.55-5.35 (m, 3H), 4.64 (dd, *J* = 15.6, 6.9 Hz, 2H), 4.37-4.33 (m, 1H), 3.83-3.79 (m, 1H), 3.35 (s, 3H), 2.45-2-27 (m, 4H), 2.03-1.99 (m, 2H), 1.88-1.57 (m, 4H), 1.43-1.29 (m, 6H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.5, 174.5, 167.2, 165.5, 133.4, 124.0, 112.0, 96.1, 91.5, 83.5, 76.8, 55.8, 32.7, 31.7, 28.7, 27.2, 22.4, 22.3, 22.1, 14.0, 13.7, 10.1; IR (film): $\tilde{\nu}$ = 2957, 2929, 1719, 1661, 1579, 1402, 1245, 1090, 920, 855 cm^{-1}; MS (ESI+): [*M+Na*$^+$]: 403; HRMS (ESI): *m*/*z*: calcd. for $C_{22}H_{36}O_5$[*M+Na*$^+$]: 403.24549, found: 403.24553.

Representative Procedure for the Silver-Catalyzed Preparation of 2-*tert*-Butoxy-4-pyrones. 2-(tert-Butoxy)-6-pentyl-4*H*-pyran-4-one.  *N,N'*-Dimethylethylenediamine (DMEDA, 4.4 mg, 0.05 mmol, 5 mol%) and AgOTs (14 mg, 0.05 mmol, 5 mol%) were successively added to a solution of *tert*-butyl-3-oxodec-4-ynoate (238.3 mg, 0.5 mmol) in chloroform (5 mL).[11] The mixture was stirred until TLC showed complete conversion of the substrate (ca. 24 h). The mixture was filtered through a plug of silica, eluting with *tert*-butyl methyl ether, and the filtrate was evaporated. Flash chromatography (silica) furnished the title compound as a colorless oil (203 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$):[11] δ = 5.98 (d, 1H, *J* = 1.9 Hz), 5.56 (d, 1H, *J* = 2.0 Hz), 2.45 (t, 2H, *J* = 7.5 Hz), 1.67-1.59 (m, 2H), 1.48 (s, 9H), 1.35-1.29 (m, 4H), 0.89 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$):[11] δ = 182.4, 165.7, 165.5, 112.4, 98.3, 85.3, 33.1, 30.9, 28.7, 26.3, 22.2, 13.8; IR (film): $\tilde{\nu}$ = 2932, 2863, 1657, 1626, 1586, 1370, 1246, 1136, 932, 857, 752 cm^{-1}; MS (EI) *m/z* (%): 238 (3), 183 (15), 182 (34), 154 (3), 140 (11), 127 (7), 126 (100), 122 (6), 112 (4), 111 (51), 98 (33), 97 (10), 71 (5), 69 (29), 57 (53), 56 (9), 55 (17), 43 (16), 41 (45), 39 (16), 29 (17), 27 (8); HRMS (ESI): *m*/*z*: calcd. for $C_{14}H_{22}O_3Na$ [*M*$^+$*+Na*]: 261.14611, found 261.14613.

[11] $CDCl_3$ was desactivated prior to use by filtration over a plug anhydrous potassium carbonate.



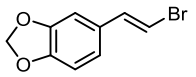
Prepared analogously as a colorless oil (142 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.99 (s, 1H), 2.43 (t, 2H, *J* = 7.5 Hz), 2.30 (t, 2H, *J* = 7.4 Hz), 1.66-1.55 (m, 2H), 1.47 (s, 9H), 1.45-1.37 (m, 2H), 1.35-1.20 (m, 10H), 0.88 (t, 3H, *J* = 6.9 Hz), 0.85 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.6, 163.6, 162.6, 112.0, 110.7, 84.4, 32.9, 31.6, 30.8, 29.2, 28.1, 26.3, 22.6, 22.4, 22.2, 14.0, 13.8; IR (film): $\tilde{\nu}$ = 2956, 2927, 2858, 1660, 1627, 1589, 1400, 1370, 1263, 1144, 836, 741, 710 cm^{-1}; MS (EI) *m*/*z* (%): 322 (6), 267 (17), 266 (31), 265 (8), 249 (5), 237 (5), 224 (20), 223 (22), 210 (11), 209 (20), 197 (12), 195 (100), 168 (26), 167 (7), 153 (9), 141 (8), 140 (12), 126 (9), 111 (4), 99 (10), 71 (4), 57 (51), 55 (6), 43 (10), 41 (14), 29 (5); HRMS (ESI): *m*/*z*: calcd. for $C_{20}H_{34}O_3Na$ [M^++*Na*]: 345.24001, found 345.24029.



Prepared analogously as a white solid (106 mg, 87 %). Mp = 63-64 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71-7.67 (m, 2H), 7.47-7.42 (m, 3H), 6.62 (d, 1H, *J* = 1.9 Hz), 5.68 (d, 1H, *J* = 2.0 Hz), 1.53 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.1, 165.3, 160.8, 131.1, 131.0, 129.0, 125.7, 110.4, 99.3, 85.6, 28.7; IR (film): $\tilde{\nu}$ = 3069, 2978, 2932, 1649, 1587, 1449, 1371, 1334, 1229, 1138, 939, 876, 837, 766, 682, 633, 510, 450 cm^{-1}; MS (EI) *m*/*z* (%): 244 (5), 188 (51), 161 (11), 160 (100), 147 (8), 131 (11), 105 (41), 104 (6), 103 (7), 77 (28), 69 (18), 57 (17), 56 (11), 55 (6), 51 (8); HRMS (ESI): *m*/*z*: calcd. for $C_{15}H_{16}O_3Na$ [M^++*Na*]: 267.09916, found 267.09926.

Hispidine and Phellinin A

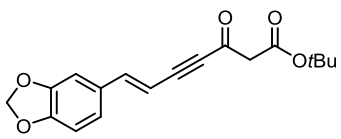
Compound 20. Et_3N (70 µL, 0.95 mmol, 5 mol%) was added to a stirred suspension of 3,4-(methylenedioxy)cinnamic acid (1.92 g, 10 mmol) in CH_3CN/H_2O (9:1, 30mL), followed by portionwise addition of NBS (2.1 g, 12 mmol). The mixture was stirred for 15 min (after a few minutes, all starting material had dissolved). For work up, the mixture was poured into water (100 mL), the aqueous layer was repeatedly extracted with Et_2O, and the combined extracts were dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (hexanes/CH_2Cl_2, 3:1) gave the title compound in the form of white crystals. (2.07 g, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.96 (s, 2H), 6.59 (d, *J* = 13.9 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.75 (s, 1H), 6.81 (d, *J* = 0.8 Hz, 1H), 7.0 (d, *J* = 13.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.3, 104, 5, 105.4, 108.4, 120.9, 130.3, 136.7, 147.8, 148.1.



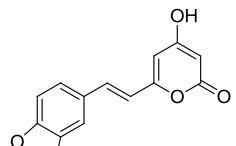
Compound 21. Ethyl propiolate (253 µL, 2.5 mmol) was added dropwise to a stirred solution of LDA (0.5 M in THF, 5 mL, 2.5 mmol,) at −78 °C. The mixture was stirred at this temperature for 30 min before a solution of $ZnBr_2$ (1 M in THF, 2.5 mL, 2.5 mmol) was introduced. The mixture was warmed to 0°C and stirring continued for 15 min. Compound **20** (228 mg, 1.0 mmol) and $Pd(PPh_3)_4$ (62 mg, 53 µmol, 5 mol%) were added and stirring continued for another 18 h at ambient temperature. The mixture was poured into aq. sat. NH_4Cl (20 mL), the aqueous layer was extracted with Et_2O (3 x 30 mL), and the combined extracts were dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc, 95:5 → 9:1) gave the title compound as a white solid (165 mg, 68%). Mp = 79-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.1 Hz, 3H), 4.26 (q, *J* = 7.1 Hz, 2H), 5.99 (s, 2H), 6.00 (d, *J* = 16.2 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 7.14 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 61.9, 82.1, 86.3, 101.5, 102.5, 105.4, 108.5, 123.0, 129.6, 147.3, 148.4, 149.3, 154.1; IR

(film): $\tilde{\nu}$ = 2197, 1710, 1621, 1595, 1503, 1490, 1442, 1366, 1248, 1194, 1131, 1094, 1037, 1011, 946, 932, 852, 800, 742 cm^{-1}; MS (EI) *m/z* (%): 244 (100), 229 (5), 216 (7), 199 (61), 185 (4), 171 (66), 157 (3), 141 (12), 129 (3), 113 (41), 99 (34), 87 (10), 75 (6), 63 (24), 51 (5), 39 (5), 29 (11); HRMS (EI): *m/z*: calcd. for $C_{14}H_{12}O_4Na$ [$M+Na^+$]: 267.06278, found: 267.06258.

Compound 22. *t*-Butyl acetate (234 mg, 2 mmol) was added dropwise to a stirred solution of LDA (0.5 M in THF, 4 mL, 2.0 mmol) at −78 °C. The mixture was stirred at this temperature for 30 min before a solution of compound **21** (244 mg, 1.0 mmol) in THF (1 ml) was added. Stirring was continued at −78 °C for 3 h before the reaction was quenched with sat. aq. NH_4Cl (20 mL). The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined extracts were dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (hexanes/EtOAc, 9:1→4:1) gave the title compound as a yellow oil (280 mg, 89%). ^{1}H NMR (ketone form, 400 MHz, $CDCl_3$): δ = 1.49 (s, 9H), 3.52 (s, 2H), 6.00 (s, 2H), 6.05 (d, *J* = 16.2 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.95 (d, *J* = 1.6 Hz, 1H), 7.16 (d, *J* = 16.2 Hz, 1H); characteristic signals of the enol form: δ = 1.50 (s, 9H), 5.28 (s, 1H), 5.98 (s, 2H), 6.07 (d, *J* = 16.2 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.93 (d, *J* = 1.6 Hz, 1H), 7.02 (d, *J* = 16.2 Hz, 1H), 12.05 (s, 1H); ^{13}C NMR (ketone form, 100 MHz, $CDCl_3$): δ = 27.9, 52.6, 82.2, 89.4, 93.0, 101.6, 102.6, 105.5, 108.6, 123.4, 129.5, 148.4, 148.4, 149.6, 165.4, 179.0; characteristic signals of the enol form: δ = 28.3, 80.4, 82.2, 85.3, 98.3,101.4, 103.9, 105.3, 108.5, 122.6, 130.1, 144.6, 148.3, 148.9, 154.9, 172.0; IR (film): $\tilde{\nu}$ = 2979, 2903, 2170, 1729, 1663, 1619, 1589, 1504, 1490, 1447, 1392, 1366, 1287, 1250, 1148, 1102, 1035, 952, 928, 893, 833, 798, 761 cm^{-1}; MS (EI) *m/z* (%): 314 (29), 258 (100), 240 (19), 227 (3), 214 (19), 199 (88), 188 (31), 169 (32), 157 (15), 141 (11), 127 (14), 113 (31), 99 (16), 87 (6), 77 (5), 63 (12), 57 (63), 41 (20), 29 (14); HRMS (EI): *m/z*: calcd. for $C_{18}H_{18}O_5Na$ [$M+Na^+$]: 337.10465, found: 337.10462.

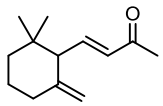


Compound 23. The solution of compound **22** (386 mg 1.23 mmol) and $SPhosAuNTf_2$ (22 mg, 25 µmol, 2 mol%) in acetic acid (8 mL) was stirred for 2 h. The mixture was concentrated and the resulting solid was rinsed with cold Et_2O (3 x 5 mL) and dried under vacuum to give the title compound as a yellow solid (286 mg, 90%). Because of the low solubility, flash chromatography results in loss of material. Mp = 239-242°C (decomp.); ^{1}H NMR (400 MHz, [D_6]-DMSO): δ = 5.30 (d, *J* = 2.0 Hz, 1H), 6.07 (s, 2H), 6.13 (d, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.23 (d, *J* = 16.0 Hz, 1H), 7.33 (d, *J* = 1.4 Hz, 1H), 11.69 (br s, 1H); ^{13}C NMR (100 MHz, [D_6]-DMSO): δ = 89.6, 101.1, 101.4, 106.0, 108.5, 118.0, 123.6, 129.7, 133.9, 148.0, 148.4, 159.4, 162.9, 170.1; IR (film): $\tilde{\nu}$ = 1699, 1631, 1606, 1555, 1499, 1479, 1443, 1357, 1299, 1254, 1241, 1157, 1100, 1036, 1009, 959, 924, 840, 815, 796, 683 cm^{-1}; MS (EI) *m/z* (%): 258 (100), 241 (7), 230 (6), 214 (21), 199 (11), 188 (45), 175 (30), 160 (25), 145 (25), 130 (16), 117 (16), 102 (12), 89 (35), 77 (6), 69 (26), 51 (10), 39 (11), 29 (5); HRMS (ESI): *m/z*: calcd. for $C_{14}H_{10}O_5Na$ [$M+Na^+$]: 281.0420, found: 281.0421.



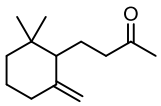
Compound S-6. $LiAlH_4$ (4.15 g, 109.1 mmol) was added in portions to a cold (0°C) solution of ester **27** (10.0 g, 54.5 mmol) in THF (200 mL). Stirring was continued for 2 h at 0°C before the mixture is allowed to reach ambient temperature. The reaction was carefully quenched by slow addition of water (4 mL) and aq. NaOH (15% *w/w*, 4 mL). The resulting mixture was vigorously stirred for 1 h before the insoluble material was filtered off and carefully rinsed with EtOH (ca. 50 mL). The combined filtrates were evaporated and the residue was purified by distillation, collecting

the fraction boiling at 76-80°C (10 mbar). The product was thus obtained as a colorless liquid (7.56 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.94 (d, *J* = 1.8 Hz, 1H), 4.74 (d, *J* = 1.8 Hz, 1H), 3.69 (b, 1H), 3.61 (t, *J* = 10.6 Hz, 1H), 2.10 (t, *J* = 6.4 Hz, 2H), 2.03 (dd, *J* = 10.8 Hz, 4.8 Hz, 1H), 1.62-1.48 (m, 2H), 1.45-1.35 (m, 2H), 1.29-1.22 (m, 1H), 0.94 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.5, 111.7, 59.6, 56.4, 36.3, 33.8, 31.8, 29.8, 26.5, 23.1; MS (EI) *m*/*z* (%): 139 (6) [M^+ - Me], 136 (36), 121 (62), 109 (34), 95 (25), 93 (83), 81 (54), 79 (30), 69 (100), 67 (34), 55 (26), 53 (12), 41 (52), 29 (11).

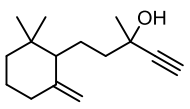


Compound S-7. Oxalyl chloride (10.1 mL, 117.6 mmol) was added dropwise to a solution of DMSO (13.9 mL, 196.1 mmol) in CH_2Cl_2 (120 mL) at −78°C. The mixture was stirred for 15 min at this temperature before a solution of compound **S-6** (12.1 g, 78.4 mmol) in CH_2Cl_2 (5 mL) was added over the course of 5 min. Stirring was continued at −78°C for 3 h before Et_3N (44 mL, 313.7 mmol) was introduced and the mixture allowed to reach ambient temperature. The reaction was then quenched with water (200 mL), the aqueous phase was repeatedly extracted with *tert*-butyl methyl ether, and the combined organic layers were dried over Na_2SO_4 and evaporated.

The residue was dissolved in toluene (200 mL) and Ph_3P=CC(O)Me (34.9 g, 109.8 mmol) was added. The resulting mixture was stirred at reflux temperature for 16 h. After reaching ambient temperature, hexane (60 mL) was introduced and the precipitate was filtered off. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 20:1) to give the title compound as a colorless liquid (10.1 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93 (dd, *J* = 15.8 Hz, 10.0 Hz, 1H), 6.08 (d, *J* = 15.8 Hz, 1H), 4.79 (t, *J* = 1.1 Hz, 1H), 4.54 (s, 1H), 2.58 (d, *J* = 10.0 Hz, 1H), 2.31-2.21 (m, 1H), 2.26 (s, 3H), 2.11-2.01 (m, 1H), 1.63-1.55 (m, 2H), 1.54-1.45 (m, 1H), 1.40-1.29 (m, 1H), 0.90 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 148.3, 147.1, 132.7, 109.6, 57.5, 38.6, 35.5, 34.1, 29.2, 27.2, 23.9, 23.1; IR (film): $\tilde{\nu}$ = 3077, 2930, 2867, 1697, 1672, 1644, 1624, 1437, 1386, 1361, 1252, 1231, 1176, 1139, 988, 889, 849, 705 cm^{-1}; MS (EI) *m*/*z* (%): 192 (17) [M^+], 177 (17), 164 (12), 149 (64), 135 (9), 121 (47), 109 (39), 93 (22), 81 (45), 69 (56), 65 (13), 53 (14), 43 (100), 27 (15).



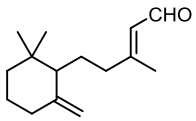
Compound S-8. Bu_3SnH (2.3 mL, 8.47 mmol) was added over 20 min to a solution of compound **S-7** (814 mg, 4.24 mmol), $(Ph_3P)_2PdCl_2$ (150 mg, 0.21 mmol, 5 mol%), NH_4Cl (522 mg, 9.75 mmol) and water (206 mg, 11.45 mmol) in THF (50 mL). The resulting mixture was stirred for 3 h before it was diluted with Et_2O (50 mL) and brine (30 mL). The organic phase was evaporated and the residue was dissolved in EtOAc (25 mL). An aq. sat. solution of NaF (30 mL) was added and the resulting mixture was vigorously stirred for 5 h. Insoluble materials were then filtered off. The organic phase was separated and concentrated, and the residue was purified by flash chromatography (hexanes/EtOAc, 20:1) to give the title compound as a pale yellow liquid (623 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.78 (t, *J* = 1.0 Hz, 1H), 4.49 (d, *J* = 2.4 Hz, 1H), 2.38-2.31 (m, 1H), 2.30-2.24 (m, 1H), 2.09 (s, 3H), 2.02-1.94 (m, 2H), 1.84-1.73 (m, 1H), 1.71-1.64 (m, 1H), 1.60-1.42 (m, 4H), 1.23-1.15 (m, 1H), 0.90 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 149.0, 109.4, 53.4, 42.3, 35.7, 34.8, 32.0, 30.1, 28.2, 26.5, 23.5, 20.2; MS (EI) *m*/*z* (%): 194 (4) [M^+], 176 (31), 161 (29), 147 (2), 136 (100), 121 (70), 109 (28), 105 (51), 95 (52), 79 (32), 67 (13), 55 (13), 43 (56), 27 (5); HRMS (EI): *m*/*z*: calcd. 194.1669; found: 194.1671.



Compound 28. A solution of ethynylmagnesium bromide (0.5 M in THF, 9.6 mL, 4.8 mmol) was slowly added to a solution of compound **S-8** (623 mg, 3.21 mmol) in THF (30 mL) at 0°C. The ice bath was removed and the mixture stirred for 30 min. The reaction was quenched with sat. aq. NH_4Cl (30 mL), the aqueous phase was repeatedly extracted with EtOAc, the

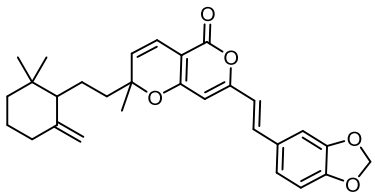
combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 10:1) to give the title compound as a colorless liquid (670 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 4.78 – 4.73 (m, 1H), 4.58 – 4.54 (m, 1H), 2.43 (s, 1H), 2.078 – 1.87 (m, 3H); 1.74 – 1.36 (m, 8H), 1.48 (d, *J* = 0.8 Hz, 3H), 1.24 – 1.19 (m, 1H), 0.93 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.1, 109.13 109.1, 87.9, 87.8, 71.2, 68.22, 68.16, 54.1, 54.0, 42.2, 42.1, 36.23, 36.2, 35.0, 32.42, 32.37, 30.0, 29.7, 28.39, 28.38, 26.2, 23.65, 23.64, 21.20, 21.15. MS (EI) *m/z* (%): 205 (5), 187 (27), 177 (4), 159 (18), 145 (17), 131 (30), 121 (30), 109 (47), 93 (50), 81 (42), 69 (100), 55 (32), 41 (61), 29 (10); HRMS (EI): *m/z*: calcd. for [M^++H]: 221.1903; found: 221.1905.

Compound 29. A sealed flask containing a solution of compound **28** (626 mg, 2.84 mmol), $(Ph_3SiO)_3V{=}O$

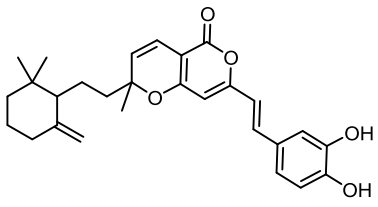


(127 mg, 0.14 mmol, 5 mol%) and Ph_3SiOH (24 mg, 0.09 mmol, 3mol%) in toluene (7.5 mL) was heated in a microwave oven at 120°C for 1.5 h. For work up, all volatile materials were evaporated and the residue was purified by flash chromatography (hexanes/EtoAc, 20:1) to give the title compound as a pale yellow liquid (509 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.89 (d, *J* = 8.3 Hz, 1H), 5.85 (d, *J* = 8.2 Hz, 1H), 4.83 (d, *J* = 1.0 Hz, 1H), 4.57 (d, *J* = 1.1 Hz, 1H), 2.09-2.01 (m, 2H), 1.97 (s, 3H), 1.77-1.39 (m, 7H), 1.29-1.17 (m, 2H), 0.93 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 165.1, 148.6, 128.4, 109.7, 53.8, 36.2, 34.9, 32.4, 31.3, 28.3, 26.1, 25.6, 24.9, 23.6; MS (EI) *m/z* (%): 220 (3) [M^+], 205 (24), 187 (11), 176 (61), 161 (39), 149 (9), 137 (36), 121 (36), 109 (58), 105 (34), 95 (74), 81 (100), 69 (89), 55 (43), 41 (89), 29 (17); HRMS (EI): *m/z*: calcd. 220.1828; found: 220.1827.

Compound 25. A solution of aldehyde **29** (163 mg, 0.74 mmol), acetic acid anhydride (97 mg, 0.96 mmol) and piperidine (82 mg, 0.96 mmol) in EtOAc (35 mL) was stirred in a closed pressure flask at 85°C bath temperature for 1 h. A solution of pyrone **23** (190 mg, 0.74 mmol) in EtOAc (15 mL) was then added and stirring continued at 85°C for another 3 h. After reaching ambient temperature, the solvent was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 10:1) to give the title compound as a 1:1 mixture of diastereomers in the form of a yellow solid (280 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 15.8 Hz, 1H), 7.00 (s, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 10.1 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.00 (s, 2H), 5.90 (s, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 4.79 – 4.73 (m, 1H), 4.54 (d, *J* = 2.2 Hz, 1H), 2.09 – 2.12 (m, 2H), 1.80 – 1.33 (m, 8H), 1.41 (s, 3H), 1.27 – 1.16 (m, 1H), 0.91 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.3, 164.2, 161.8, 158.9, 149.11, 149.08, 149.0, 148.5, 135.3, 129.9, 124.6, 124.4, 123.7, 117.3, 117.10, 117.06, 109.4, 109.3, 108.8, 105.9, 101.6, 100.81, 100.78, 99.3, 83.2, 83.0, 54.21, 54.15, 40.6, 40.5, 36.4, 36.2, 35.14, 35.07, 32.6, 32.4, 28.50, 28.48, 27.7, 27.5, 26.4, 26.2, 23.72, 23.70, 20.5, 20.4; MS (EI) *m/z* (%): 460 (34) [M^+], 337 (3), 309 (100), 271 (11), 175 (11), 145 (6), 117 (3), 89 (3), 69 (3), 41 (4); HRMS (ESI): *m/z*: calcd. for [M^+ + Na]: 483.2138; found: 483.2142.



Compound 26. BCl_3 (1 M in CH_2Cl_2, 250 µL, 0.25 mmol) was added to a solution of compound **25** (23 mg, 0.05 mmol) and the resulting mixture was stirred at 50°C for 16 h. After reaching ambient temperature, MeOH (1 mL) was introduced and stirring continued for 1 h at 40°C. Next, all volatile materials were evaporated and the residue was purified by flash chromatography (hexanes/acetone, 1:1) to give the product as an inseparable 1:1



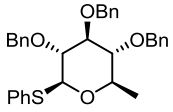
mixture of diastereoisomers in the form of a yellow, sparingly soluble solid material (8 mg, 36%). ^{1}H NMR (600 MHz, CD_3OD): δ = 7.29 (d, *J* = 15.9 Hz, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.94 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.40 (dd, *J* = 10.2, 3.4 Hz, 1H), 6.14 (d, *J* = 2.6 Hz, 1H), 5.48 (d, *J* = 10.1 Hz, 1H), 5.44 (d, *J* = 10.1 Hz, 1H), 4.78 – 4.76 (m, 1H), 4.58 – 4.54 (m, 1H), 2.05 -2.02 (m, 1H), 1.79 – 1.38 (m, 9H), 1.42 (s, 3H), 1.26 – 1.18 (m, 1H), 0.92 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (150 MHz, CD_3OD): δ = 166.70, 166.67, 163.86, 163.85, 161.4, 150.4, 148.8, 146.8, 137.37, 137.36, 128.9, 126.1, 125.9, 122.1, 117.4, 117.3, 116.83, 116.81, 116.6, 114.9, 110.0, 109.9, 101.1, 99.4, 84.6, 84.5, 55.43, 55.42, 41.62, 41.59, 37.3, 37.2, 35.9, 35.8, 33.4, 33.3, 28.84, 28.83, 27.9, 27.8, 26.7, 24.7, 21.6, 21.5; MS (EI) *m/z* (%): 471 (100) [M^+ + Na]; HRMS (ESI): *m/z:* calcd. for [M^+ + Na]: 471.2146; found: 471.2142.

The Radicinol Family

6-(4-Methylbenzenesulfonate)-phenyl-1-thio-β-D-glucopyranoside (S-9). Tosyl chloride (10.50 g, 55.08 mmol) was added in one portion to a solution of compound **33** (10.00 g, 57.06 mmol) in pyridine (65 mL) at 0°C. The mixture was stirred for 13 h at 0°C before it was concentrated. The residue was dissolved in CH_2Cl_2 and the organic phase was washed with sat. aq. $NaHCO_3$ and brine, dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (CH_2Cl_2/CH_3OH, 1:0 to 6:1) to give the title compound as a white foam (10.66 g, 68%). $[\alpha]_D^{20}$: –36.7 (c = 1, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 – 7.78 (m, 2H), 7.50 – 7.45 (m, 2H), 7.36 – 7.26 (m, 5H), 4.46 (d, *J* = 9.8 Hz, 1H), 4.36 – 4.27 (m, 2H), 3.59 – 3.45 (bm, 3H), 3.32 – 3.24 (m, 1H), 3.13 – 2.98 (bm, 1H), 2.97 – 2.85 (bm, 1H), 2.71 – 2.60 (bm, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.2, 133.1, 132.8, 131.4, 130.1, 129.2, 238.5, 128.2, 88.0, 77.5, 77.2, 71.7, 69.2, 21.8. IR (film): $\tilde{\nu}$ = 3392, 1480, 1440, 1360, 1190, 1175, 1095, 1042, 1020, 973, 903, 814, 724, 650 cm^{-1}. HRMS (ESI): *m/z*: calcd. for $C_{19}H_{22}O_7S_2Na^+$: 449.06992; found: 449.06992.

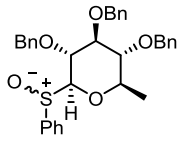
6-(4-Methylbenzenesulfonate)-2,3,4-tris-*O*-benzyl-phenyl-1-thio-β-D-glucopyranoside (34). NaH (1.90 g, 79.14 mmol) was added in portions to a solution of compound **S-9** (8.27 g, 19.38 mmol) in DMF (100 mL) at 0°C. The mixture was stirred at 0°C for 1 h before benzyl bromide (10 mL, 171.04 mmol) was slowly added. Stirring was continued for 18 h at ambient temperature. For work up, the solvent was removed in vacuo and the residue was dissolved in *tert*-butyl methyl ether. The organic layer was washed with sat. aq. NH_4Cl and brine, dried over $MgSO_4$, and evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 5:1) afforded the title compound as a white solid (11.75 g, 87%). $[\alpha]_D^{20}$: –0.1 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 7.81 – 7.76 (m, 2H), 7.53 – 7.45 (m, 2H), 7.39-7.26 (m, 18H), 7.21 – 7.16 (m, 2H), 4.87 (t, *J* = 10.1 Hz, 2H), 4.81 (dd, *J* = 10.9, 2.5 Hz, 2H), 4.69 (d, *J* = 10.3 Hz, 1H), 4.56 (d, *J* = 9.8 Hz, 1H), 4.53 (d, *J* = 10.8 Hz, 1H), 4.30 – 4.23 (m, 1H), 4.20 – 4.15 (m, 1H), 3.69 – 3.62 (m, 1H), 3.54 – 3.46 (m, 2H), 3.46 – 3.38 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0, 138.3, 138.0, 137.6, 133.2, 132.9, 132.4, 130.0, 129.1, 128.7, 128.64, 128.60, 128.4, 128.3, 128.2, 128.1, 128.0, 127.91, 127.86, 87.4, 86.6, 80.6, 76.9, 76.6, 76.0, 75.6, 75.3, 68.5, 21.8. IR (film): $\tilde{\nu}$ = 3063, 3030, 1598, 1585, 1454, 1363, 1190, 1177, 1093, 1067, 1028 cm^{-1}. HRMS (ESI): *m/z*: calcd. for $C_{40}H_{40}O_7S_2Na^+$: 719.21077; found: 719.21077.

6-Deoxy-2,3,4-tris-*O*-benzyl-phenyl-1-thio-β-D-glucopyranoside (S-10). $LiAlH_4$ (2.02 g, 53.16 mmol) was



added in one portion to a solution of compound **34** (9.26 g, 13.29 mmol) in THF (133 mL) and the resulting mixture was stirred at reflux temperature for 2 h. After cooling to room temperature, the reaction was quenched by the careful addition of EtOAc and water. The aqueous phase was extracted with *tert*-butyl methyl ether, the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 10:1) afforded the title compound as a white solid (6.23 g, 89%). $[a]_D^{20}$: +10.8 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 – 7.52 (m, 2H), 7.41–7.26 (m, 18H), 4.94 – 4.82 (m, 4H), 4.74 (d, *J* = 10.4 Hz, 1H), 4.66 (d, *J* = 10.1 Hz, 2H), 3.68 (t, *J* = 9.0 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.45 – 3.38 (m, 1H), 3.23 (t, *J* = 9.3 Hz, 1H), 1.35 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 138.2, 134.0, 132.0, 129.1, 128.6, 128.6, 128.4, 128.2, 128.03, 128.00, 127.9, 127.6, 87.6, 86.7, 83.4, 81.4, 76.0, 75.8, 75.6, 75.5, 18.3. IR (film): $\tilde{\nu}$ = 3062, 3030, 2900, 2867, 1584, 1497, 1454, 1360, 1130, 1089, 1069, 737, 697 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{33}H_{34}O_4SNa^+$: 549.20700; found: 549.20700.

6-Deoxy-2,3,4-tris-*O*-benzyl-1-(phenylsulfinyl)-β-D-glucopyranoside (35a,b). A solution of *m*CPBA (1.25

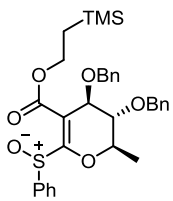


g, 5.58 mmol) in CH_2Cl_2 (30 mL) was added dropwise over 30 min to a solution of **S-10** (2.10 g, 3.99 mmol) in CH_2Cl_2 (30 mL) at –20°C. The resulting mixture was stirred at −20°C for 12 h before the reaction was quenched with sat. aq. $Na_2S_2O_3$. The mixture was warmed to RT and extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 5:1) afforded the diastereomeric sulfoxides **35a** (730 mg) and **35b** (1.31 g) as white solids each (94%, d.r.: 1:1.8).

Analytical and spectral data of the minor isomer **35a:** $[a]_D^{20}$: +21.4 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (m, 2H), 7.46-7.21 (m, 16H), 7.12 (m, 2H), 4.82 (m, 5H), 4.61 (d, *J* = 10.9 Hz, 1H), 4.67 (m, 1H), 3.78 (m, 2H), 3.52 (m, 1H), 3.12 (m, 1H), 1.31 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.2, 138.1, 137.8, 131.0, 128.8, 128.6, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 125.5, 95.3, 86.5, 83.0, 76.5, 76.2, 75.6, 75.4, 74.1, 17.9. IR (film): $\tilde{\nu}$ = 3062, 3030, 2872, 1497, 1454, 1360, 1131, 1086, 1046, 1029, 999, 735, 696 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{33}H_{34}O_5SNa^+$: 565.20192; found: 565.20192.

Analytical and spectral data of the major isomer **35b:** $[a]_D^{20}$: –83.0 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (m, 2H), 7.50 (m, 3H), 7.42 - 7.22 (m, 15H), 4.99 (q, *J* = 9.9 Hz, 2H), 4.93 (q, *J* = 10.2 Hz, 2H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.62 (d, *J* = 10.8 Hz, 1H), 4.08 (t, *J* = 9.3 Hz, 1H), 3.88 (d, *J* = 10.9 Hz, 1H), 3.74 (t, *J* = 9.0 Hz, 1H), 3.28 (t, *J* = 9.1 Hz, 1H), 3.20 (m, 1H), 1.11 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.8, 138.4, 137.9, 137.7, 131.1, 128.9, 128.7, 128.66, 128.61, 128.5, 128.3, 128.1, 127.9, 127.8, 125.4, 93.6, 86.5, 82.9, 77.2, 76.8, 76.0, 75.8, 75.5, 17.6. IR (film): $\tilde{\nu}$ = 3063, 3031, 2873, 1497, 1445, 1361, 1211, 1136, 1088, 1049, 745, 697 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{33}H_{34}O_5SNa^+$: 565.20192; found: 565.20192.

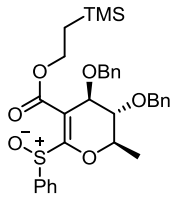
1,5-Anhydro-2,6-dideoxy-2-(2-trimethylsilyl-ethoxycarbonyl)-3,4-bis-*O*-benzyl-1-*C*-(phenylsulfinyl)-D-



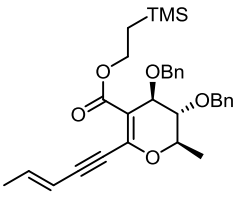
arabino-hex-1-enitol (37a). *n*BuLi (1.6 M in hexanes, 3.3 mL, 5.28 mmol) was added dropwise to a solution of diisopropylamine (890 µL, 6.35 mmol) in THF (59 mL) at 0°C and the resulting mixture was stirred for 15 min at this temperature. The mixture was then cooled to –78°C and a solution of **35a** (570 mg, 1.05 mmol) in THF (117 mL) was added dropwise over 30 min. Stirring was continued at this temperature for 1 h before

HMPA (183 µL, 1.05 mmol) was injected, followed by TeocCl (573 µL, 3.15 mmol). After stirring for an additonal 1.5 h at –78 °C, the reaction was quenched with sat. aq. NH_4Cl, the mixture was warmed to room temperature and the aqueous layer extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 2:1) afforded product **37a** as a colorless solid (600 mg, 99%). $[\alpha]_D^{20}$: –265.2 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.91 (m, 2H), 7.51 – 7.42 (m, 2H), 7.40 – 7.26 (m, 9H), 7.22 – 7.14 (m, 2H), 4.82 – 4.73 (m, 1H), 4.61 – 4.47 (m, 4H), 4.45 (dd, *J* = 2.5, 1.8 Hz, 1H), 4.36 – 4.21 (m, 2H), 3.52 (t, *J* = 2.6 Hz, 1H), 1.14 – 0.96 (m, 5H), 0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.9, 165.7, 143.4, 138.0, 137.5, 131.0, 129.0, 128.7, 128.6, 128.1, 128.05, 127.96, 127.9, 125.7, 106.8, 76.7, 75.0, 73.0, 72.5, 71.7, 63.8, 17.8, 14.9, –1.4. IR (film): $\tilde{\nu}$ = 2952, 1695, 1600, 1454, 1381, 1298, 1250, 1205, 1140, 1083, 1055 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{32}H_{38}O_6SSiNa^+$: 601.20506; found: 601.20506.

1,5-Anhydro-2,6-dideoxy-2-(2-trimethylsilyl-ethoxycarbonyl)-3,4-bis-*O*-benzyl-1-*C*-(phenylsulfinyl)-D-arabino-hex-1-enitol (37b, diastereomeric sulfoxide). Prepared analogously starting from **35b** (778 mg, 1.43 mmol) as a colorless syrup (796 mg, 96%). $[\alpha]_D^{20}$: +71.5 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (m, 2H), 7.40 (tt, *J* = 7.3, 1.6 Hz, 1H), 7.36-7.26 (m, 10H), 7.03 (m, 2H), 4.83 (qt, *J* = 2.3, 1.9 Hz, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.33 (d, *J* = 11.6 Hz, 1H), 4.29 (t, *J* = 2.4 Hz, 1H), 4.16 (m, 2H), 3.58 (t, *J* = 2.3 Hz, 1H), 1.52 (d, *J* = 7.3 Hz, 3H), 0.96 (m, 2H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 166.3, 144.4, 138.1, 137.6, 131.1, 129.1, 128.6, 128.5, 128.13, 128.08, 127.9, 127.3, 126.6, 104.7, 77.7, 74.9, 73.2, 71.3, 71.2, 63.4, 17.6, 16.1, –1.4. IR (film): $\tilde{\nu}$ = 3062, 3030, 2953, 1694, 1597, 1454, 1298, 1261, 1207, 1073, 1056 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{32}H_{38}O_6SSiNa^+$: 601.20506; found: 601.20506.

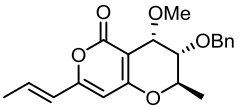


1,5-Anhydro-2,6-dideoxy-2-(2-trimethylsilyl-ethoxycarbonyl)-3,4-bis-*O*-benzyl-1-*C*-((*E*)-pent-3-en-1-yn)-D-arabino-hex-1-enitol (39). *This reaction was performed in the dark*. *n*BuLi (1.6 M in hexanes, 3.00 mL, 4.80 mmol) was added dropwise to a solution of (*E*)-1,1-dibromopenta-1,3-diene (537 mg, 2.38 mmol)[2] in THF (3 mL) at –78°C. The mixture was stirred at –78 °C and at 0 °C for 1 h each. After re-cooling to –78°C, a solution of **37a** (275 mg, 0.48 mmol) in THF (3 mL) was added dropwise and stirring was continued at –78°C for 30 min and at –55°C for an additional 16 h. The reaction was quenched with sat. aq. NH_4Cl while cold, the mixture was warmed to room temperature and the aqueous layer was extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 10:1) afforded the title compound as a yellow oil (203 mg, 82%).

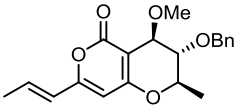


When applied to compound **37b** (248 mg, 0.43 mmol), the same product was obtained in 85% yield (190 mg). $[\alpha]_D^{20}$: –13.0 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.26 (m, 10H), 6.36 (dq, *J* = 15.7, 6.9 Hz, 1H), 5.69 (dq, *J* = 15.7, 1.7 Hz, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 6.64 – 4.55 (m, 3H), 4.55 – 4.52 (m, 1H), 4.50 – 4.42 (m, 1H), 4.31 – 4.20 (m, 2H), 3.59 (t, *J* = 3.4 Hz, 1H), 1.84 (dd, *J* = 7.1, 1.8 Hz, 3H), 1.40 (d, *J* = 7.1 Hz, 3H), 1.06 – 0.99 (m, 2H), 0.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 144.8, 143.5, 138.7, 137.9, 128.6, 128.4, 128.0, 127.9, 127.74, 127.70, 110.1, 109.8, 94.3, 82.3, 75.7, 74.8, 72.7, 72.2, 71.9, 62.7, 19.1, 17.7, 16.7, –1.4. IR (film): $\tilde{\nu}$ = 2951, 2208, 1688, 1594, 1454, 1381, 1324, 1249, 1146, 1069 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{31}H_{38}O_5SiNa^+$: 541.23107; found: 541.23807.

(2*R*,3*R*,4*S*)-3-(Benzyloxy)-4-methoxy-2-methyl-7-((*E*)-prop-1-en-1-yl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-b]-pyran-5-one (42b, R = Me) and (2*R*,3*R*,4*R*)-3-(benzyloxy)-4-methoxy-2-methyl-7-((*E*)-prop-1-en-1-yl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one (*epi*-42b, R = Me). SPhosAuNTf$_2$ (1.6 mg, 0.002 mmol, 1 mol%) was added to a solution of compound **39** (100 mg, 0.19 mmol) in CH_3OH (1.85 mL). The mixture was stirred for 2 h before conc. HCl (50 µL, 0.61 mmol) was added dropwise. Stirring was continued for 18 h. The reaction was quenched with sat. aq. NH_4Cl and the aqueous layer extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 5:1) afforded **42b** (R = Me, 44 mg, 67%) and ***epi*-42b** (R = Me, 16 mg, 24%).

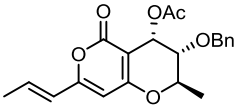


Analytical and spectral data of **42b (R = Me):** $[\alpha]_D^{20}$: +58.2 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.41 – 7.28 (m, 5H), 6.66 (dq, *J* = 15.5, 6.9 Hz, 1H), 5.98 (dq, *J* = 15.4, 1.6 Hz, 1H), 5.71 (s, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 3.0 Hz, 1H), 4.29 (dq, *J* = 10.4, 6.3 Hz, 1H), 3.55 (s, 3H), 3.34 (dd, *J* = 10.2, 2.9 Hz, 1H), 1.90 (dd, *J* = 7.1, 1.8 Hz, 3H), 1.45 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 166.2, 164.1, 159.4, 138.1, 135.5, 128.8, 128.3, 128.2, 123.2, 99.04, 98.99, 78.0, 72.1, 71.6, 67.3, 59.0, 18.6, 17.9. IR (film): $\tilde{\nu}$ = 2930, 1714, 1660, 1617, 1572, 1421, 1262, 1153, 1110, 1075 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{20}H_{22}O_5Na^+$: 365.13591; found: 365.13594.

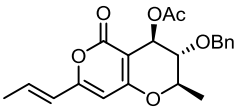


Analytical and spectral data of ***epi*-42b (R = Me):** $[\alpha]_D^{20}$: –4.2 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.28 (m, 5H), 6.70 (dq, *J* = 15.3, 7.0 Hz, 1H), 5.94 (dq, *J* = 15.3, 1.5 Hz, 1H), 5.72 (s, 1H), 4.73 – 4.57 (m, 3H), 4.31 (t, *J* = 2.2 Hz, 1H), 3.71 (t, *J* = 2.4 Hz, 1H), 3.48 (s, 3H), 1.89 (dd, *J* = 6.8, 1.5 Hz, 3H), 1.40 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.32, 164.27, 158.7, 137.4, 135.1, 128.7, 128.2, 128.0, 122.9, 99.4, 97.7, 75.5, 73.8, 71.6, 69.8, 57.9, 18.6, 16.9. IR (film): $\tilde{\nu}$ = 3031, 2934, 1717, 1660, 1618, 1572, 1424, 1212, 1152, 1082, 1023 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{20}H_{22}O_5Na^+$: 365.135910; found: 365.135944.

(2*R*,3*R*,4*S*)-3-(Benzyloxy)-2-methyl-5-oxo-7-((*E*)-prop-1-en-1-yl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-b]-pyran-4-yl acetate (42a, R = Ac) and (2*R*,3*R*,4*R*)-3-(benzyloxy)-2-methyl-5-oxo-7-((*E*)-prop-1-en-1-yl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-b]pyran-4-yl acetate (*epi*-42a, R = Ac). SPhosAuNTf$_2$ (1.4 mg, 0.002 mmol, 1 mol%) was added to a solution of compound **39** (80 mg, 0.15 mmol) in glacial acetic acid (1.6 mL) and the resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with sat. aq. $NaHCO_3$ and the aqueous phase extracted with *tert*-butyl methyl ether. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 5:1) afforded **42a** (R = Ac, 42 mg, 74%) and ***epi*-42a** (R = Ac, 5 mg, 9%).

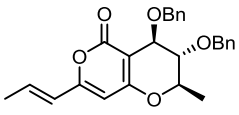


Analytical and spectral data of **42a (R = Ac):** $[\alpha]_D^{20}$: +138.1 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.28 (m, 5H), 6.73 (dq, *J* = 15.2, 7.1 Hz, 1H), 6.37 (d, *J* = 3.3 Hz, 1H), 5.94 (dq, *J* = 15.4, 1.6 Hz, 1H), 5.70 (s, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 4.48 (d, *J* = 11.4 Hz, 1H), 4.30 (dq, *J* = 10.4, 6.2 Hz, 1H), 3.40 (dd, *J* = 10.1, 3.5 Hz, 1H), 2.09 (s, 3H), 1.90 (dd, *J* = 7.1, 1.5 Hz, 3H), 1.42 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.1, 166.9, 162.7, 159.7, 137.2, 136.2, 128.8, 128.6, 128.2, 122.8, 98.4, 96.8, 75.8, 72.19, 72.18, 59.9, 21.2, 18.6, 17.7. IR (film): $\tilde{\nu}$ = 3064, 3031, 2936, 1744, 1720, 1658, 1616, 1573, 1425, 1380, 1224, 1153, 1010 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{21}H_{22}O_6Na^+$: 393.13086; found: 393.13086.



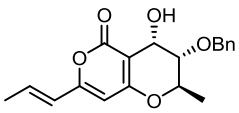
Analytical and spectral data of ***epi*-42a (R = Ac):** $[\alpha]_D^{20}$: –26.2 (c = 1, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.27 (m, 5H), 6.72 (dq, *J* = 15.3, 7.1 Hz, 1H), 5.96 (dq, *J* = 15.7, 1.6 Hz, 1H), 5.89 (t, *J* = 2.1 Hz, 1H), 5.75 (s, 1H), 4.81 (d, *J* = 12.1 Hz, 1H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.54 (qt, *J* = 2.3, 2.2 Hz, 1H), 3.69 (t, *J* = 2.5 Hz, 1H), 2.07 (s, 3H), 1.90 (dd, *J* = 7.0, 1.6 Hz, 3H), 1.34 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.5, 165.1, 162.9, 159.3, 137.5, 135.7, 128.6, 128.2, 128.1, 122.9, 99.1, 95.4, 75.6, 74.3, 71.9, 62.7, 21.1, 18.6, 16.7. IR (film): $\tilde{\nu}$ = 2960, 2936, 1715, 1660, 1618, 1575, 1427, 1372, 1226, 1153, 1090, 1023 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{21}H_{22}O_6Na^+$: 393.13086; found: 393.13086.

(2*R*,3*R*,4*R*)-3,4-Bis(benzyloxy)-2-methyl-7-((*E*)-prop-1-en-1-yl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-b]-



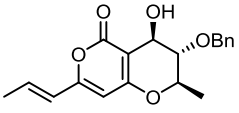
pyran-5-one (40). $SPhosAuNTf_2$ (0.4 mg, 0.0004 mmol, 1 mol%) was added to a solution of compound **39** (25 mg, 0.048 mmol) in nitromethane (0.4 mL) and the resulting mixture was stirred for 24 h. The reaction was quenched with sat. aq. $NaHCO_3$ and the aqueous phase was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 5:1) afforded the title compound (19 mg, 94%). $[\alpha]_D^{20}$: +13.7 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.27 (m, 9H), 7.25 – 7.23 (m, 1H), 6.71 (dq, *J* = 15.3, 7.0 Hz, 1H), 5.95 (dq, *J* = 15.5, 1.5 Hz, 1H), 5.73 (s, 1H), 4.87 (d, *J* = 11.6 Hz, 1H), 4.72 (d, *J* = 11.4 Hz, 1H), 4.63 – 4.55 (m, 3H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.68 (t, *J* = 2.4 Hz, 1H), 1.90 (dd, *J* = 7.1, 1.5 Hz, 3H), 1.44 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.4, 164.3, 158.7, 138.8, 137.6, 135.1, 128.7, 128.5, 128.13, 128.08, 127.9, 127.7, 123.0, 99.4, 98.1, 75.7, 75.1, 73.9, 71.7, 68.3, 18.6, 17.2. IR (film): $\tilde{\nu}$ = 3031, 2934, 1706, 1660, 1618, 1573, 1424, 1211, 1152, 1090, 1067, 1025 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{26}H_{26}O_5Na^+$: 441.16750; found: 441.16724.

(2*R*,3*S*,4*S*)-3-(Benzyloxy)-4-hydroxy-2-methyl-7-((*E*)-prop-1-en-1-yl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-b]-



pyran-5-one (S-11). K_2CO_3 (109 mg, 0.79 mmol) was added in one portion to a solution of **42a** (R = Ac, 29 mg, 0.08 mmol) in MeOH/H_2O (1:1, 0.9 mL) and the resulting mixture was stirred at room temperature for 18 h. The mixture was diluted with water and the aqueous phase extracted with EtOAc. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (pentanes/EtOAc, 2:1) afforded the title compound as a colorless oil (23 mg, 90%). $[\alpha]_D^{20}$: +61.7 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.30 (m, 5H), 6.72 (dq, *J* = 15.1, 7.1 Hz, 1H), 5.94 (dq, *J* = 15.5, 1.5 Hz, 1H), 5.71 (s, 1H), 4.94 (d, *J* = 3.8 Hz, 1H), 4.82 (d, *J* = 11.9 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.40 (dq, *J* = 9.9, 6.3 Hz, 1H), 3.77 (dd, *J* = 9.8, 3.6 Hz, 1H), 2.74 (bs, 1H), 1.89 (dd, *J* = 6.8, 1.5 Hz, 3H), 1.46 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1, 164.1, 159.3, 137.1, 135.8, 128.8, 128.4, 128.3, 122.8, 99.8, 98.7, 76.8, 71.6, 71.4, 58.7, 18.6, 17.5. IR (film): $\tilde{\nu}$ = 3443, 2932, 1690, 1659, 1617, 1572, 1428, 1265, 1151, 1086, 1056 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{20}O_5Na^+$: 351.12029; found: 351.12029.

(2*R*,3*S*,4*R*)-3-(Benzyloxy)-4-hydroxy-2-methyl-7-((*E*)-prop-1-en-1-yl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-b]-



pyran-5-one (S-12). Prepared analogously from compound ***epi*-42a** (R = Ac, 14 mg, 0.04 mmol); colorless oil (12 mg, 97%). $[\alpha]_D^{20}$: +12.6 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.29 (m, 5H), 6.71 (dq, *J* = 15.0, 7.1 Hz, 1H), 5.96 (dq, *J* = 15.6, 1.6 Hz, 1H), 5.76 (s, 1H), 5.01 (d, *J* = 11.4 Hz, 1H), 4.83 (d, *J* = 6.3 Hz, 1H), 4.76 (d, *J* = 11.4 Hz, 1H),

4.18 (dq, *J* = 8.1, 6.6 Hz, 1H), 4.18 – 4.03 (bs, 1H), 3.55 (dd, *J* = 8.3, 6.1 Hz, 1H), 1.91 (dd, *J* = 6.8, 1.5 Hz, 3H), 1.46 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.7, 164.3, 158.7, 138.0, 135.6, 128.6, 128.3, 128.0, 122.7, 101.2, 99.0, 78.8, 75.7, 73.9, 67.6, 18.6, 17.4. IR (film): $\tilde{\nu}$ = 3460, 2927, 1687, 1573, 1428, 1378, 1322, 1276, 1211, 1154, 1096, 1021 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{20}O_5Na^+$: 351.12029; found: 351.12029.

(+)-3-Methoxy-3-*epi*-radicinol (*ent*-32). BCl_3 (1 M in CH_2Cl_2, 0.2 mL, 0.2 mmol) was added dropwise to a solution of **42b** (R = Me, 22 mg, 0.06 mmol) in CH_2Cl_2 (0.6 mL) at –78°C. The mixture was stirred for 1 h at –78°C before the reaction was quenched with methanol and sat. aq. NH_4Cl. The aqueous layer was extracted with EtOAc and the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (pentanes/EtOAc, 5:1) afforded ***ent*-32** as a colorless oil (8 mg, 72%). $[\alpha]_D^{20}$: +43.5 (c = 0.5, $CHCl_3$) [Lit.[12] for **32**: $[\alpha]_D$: –65 (c = 5.8, $CHCl_3$)]; for the NMR-spectroscopic data, see Table S-1; IR (film): $\tilde{\nu}$ = 3428, 2926, 2855, 1709, 1572, 1426, 1366, 1261, 1203, 1082, 1063 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{13}H_{16}O_5Na^+$: 275.08892; found: 275.08899.

Table S-1. Assigned spectral data ($CDCl_3$, 500 MHz/126 MHz) of 3-methoxy-3-*epi*-radicinol (*ent*-32) and graphical representation of key NOE contacts; arbitrary numbering scheme as shown in the Insert. The comparison with the literature data for the enantiomer (32) show certain discrepancies, thus raising questions as to the original structure assignment of the natural metabolite

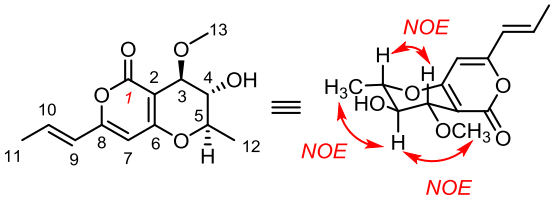
Position	^{13}C NMR		^{1}H NMR	
	synthetic *ent*-32	lit[13] for 32	synthetic *ent*-32	lit[13] for 32
1	166.6	165.4		
2	98.5	99.1		
3	69.7	68.0	4.40 (d, *J* = 3.8 Hz, 1H)	4.33 (d, *J* = 3.8 Hz, 1H)
4	70.0	72.5	3.44 (dd, *J* = 10.4, 3.5 Hz, 1H)	3.40 (dt, *J* = 8.2, 3.8 Hz, 1H)
5	73.2	76.8	4.14 (dq, *J* = 10.4, 6.4 Hz, 1H)	4.12 (dq, *J* = 8.2, 6.9 Hz, 1H)
6	164.3	n.r.		
7	98.8	100.4	5.71 (s, 1H)	5.68 (s, 1H)
8	159.3	158.9		
9	122.8	122.7	5.95 (dq, *J* = 15.4, 1.6 Hz, 1H)	5.90 (d, *J* = 13.9 Hz, 1H)
10	135.8	135.7	6.73 (dq, *J* = 15.4, 7.0 Hz, 1H)	6.68 (dq, *J* = 13.9, 7.5 Hz, 1H)
11	18.6	18.4	1.90 (dd, *J* = 7.0, 1.6 Hz, 3H)	1.86 (d, *J* = 7.5 Hz, 3H)
12	17.7	17.1	1.48 (d, *J* = 6.3 Hz, 3H)	1.38 (d, *J* = 6.9 Hz, 3H)
13	59.1	55.2	3.61 (s, 3H)	3.65 (s, 3H)
OH			2.64 (bs, 1H)	2.50 (bs, 1H)

[12] M. Solfrizzo, C. Vitti, A. De Girolamo, A. Visconti, A. Logrieco, F.P. Fanizzi *J. Agric. Food. Chem.* **2004**, *52*, 3655–3660.

[13] H. Sheridan, A.-M. Canning, *J. Nat. Prod.* **1999**, *62*, 1568–1569.

(+)-3-Methoxy-radicinol (S-13). Prepared analogously starting from **42b** (R = Me, 15 mg, 0.04 mmol); colorless oil (7.6 mg, 69%). $[\alpha]_D^{20}$: +40.8 (c = 1, $CHCl_3$). For the NMR-spectroscopic data, see Table S-2; IR (film): $\tilde{\nu}$ = 3402, 2934, 1682, 1659, 1617, 1569, 1427, 1152, 1084, 1021 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{13}H_{16}O_5Na^+$: 275.08906; found: 275.08899.

Table S-2. Assigned spectral data ($CDCl_3$, 500 MHz/126 MHz) of 3-methoxy-radicinol (S-13) and graphical representation of key NOE contacts; arbitrary numbering scheme as shown in the Insert

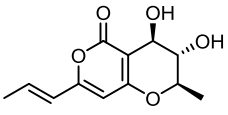


Position	^{13}C NMR	^{1}H NMR
1	164.7	
2	97.6	
3	73.0	4.21 (dd, *J* = 3.3, 1.5 Hz, 1H)
4	68.5	4.03 (t, *J* = 3.3 Hz, 1H)
5	77.4	4.50 (qdd, *J* = 7.0, 3.1, 1.7 Hz, 1H)
6	164.1	
7	99.2	5.72 (s, 1H)
8	158.9	
9	122.8	5.94 (dq, *J* = 15.4, 1.6 Hz, 1H)
10	135.5	6.70 (dq, *J* = 15.4, 7.0 Hz, 1H)
11	18.6	1.89 (dd, *J* = 7.0, 1.6 Hz, 3H)
12	16.7	1.45 (d, *J* = 7.1 Hz, 3H)
13	58.3	3.56 (s, 3H)

(+)-3-*epi*-Radicinol (*ent*-29). BCl_3 (1 M in CH_2Cl_2, 0.17 mL, 0.17 mmol,) was added to a solution of **S-11** (17 mg, 0.05 mmol) in CH_2Cl_2 (0.5 mL) at –78°C and the resulting mixture was stirred for 1.5 h at this temperature. The reaction was quenched with sat. aq. NH_4Cl and the aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (pentanes/EtOAc, 1:1) afforded the title compound as a colorless oil (11 mg, 91%). $[\alpha]_D^{20}$: +13.0 (c = 1, $CHCl_3$) [Lit.[14] for **29**: $[\alpha]_D^{25}$: –10.7 (c = 0.0014, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (dq, *J* = 15.3, 7.0 Hz, 1H), 5.96 (dq, *J* = 15.4, 1.4 Hz, 1H), 5.76 (s 1H), 4.76 (d, *J* = 4.3 Hz, 1H), 4.28 (dq, *J* = 8.1, 6.6 Hz, 1H), 3.76 (bs, 1H), 3.65 (dt, *J* = 7.6, 4.3 Hz, 1H), 2.98 (d, *J* = 7.3 Hz, 1H), 1.90 (dd, *J* = 7.1, 1.5 Hz, 3H), 1.45 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.6, 164.6, 135.9, 122.7, 100.0, 99.1, 74.0, 69.3, 60.9, 18.6, 17.0. IR (film): $\tilde{\nu}$ = 3444, 2924, 2854, 1688, 1572, 1429, 1378, 1262, 1159, 1053 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{12}H_{14}O_5Na^+$: 261.07334; found: 261.07334.

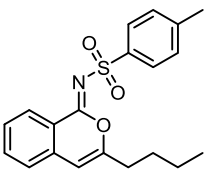
[14] G. B. Varma, M. O. Fatope, R. G. Marwah, M. E. Deadman, F. K. Al-Rawahi, *Phytochemistry* **2006**, *67*, 1925–1930.

(+)-Radicinol (*ent*-27). BCl_3 (1 M in CH_2Cl_2, 0.18 mL, 0.18 mmol) was added dropwise to a solution of compound **40** (25 mg, 0.06 mmol) in CH_2Cl_2 (0.6 mL) at –78°C and the resulting mixture was stirred for 3 h at this temperature. The reaction was quenched with sat. aq. NH_4Cl and the aqueous layer was extracted with EtOAc. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (pentanes/EtOAc, 1:1) afforded the title compound (14 mg, 88%). $[\alpha]_D^{20}$: +46.9 (c = 1, $CHCl_3$) [Lit.[15] for **27**: $[\alpha]_D^{28}$: –92 (c = 0.48, $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (dq, *J* = 15.3, 7.0 Hz, 1H), 5.96 (dq, *J* = 15.6, 1.6 Hz, 1H), 5.76 (s, 1H), 4.63 (d, *J* = 7.6 Hz, 1H), 4.59 (bs, 1H), 4.11 (dq, *J* = 9.1, 6.5 Hz, 1H), 3.66 (dd, *J* = 9.5, 7.7 Hz, 1H), 3.01 (bs, 1H), 1.90 (dd, *J* = 7.0, 1.6 Hz, 3H), 1.51 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.1, 164.2, 158.9, 135.8, 122.6, 100.4, 98.9, 76.3, 73.1, 68.5, 18.6, 17.2. IR (film): $\tilde{\nu}$ = 3410, 2953, 2924, 2854, 1683, 1617, 1570, 1428, 1378, 1277, 1157, 1055, 1019 cm^{-1}. HRMS (ESI): *m*/*z*: calcd. for $C_{12}H_{14}O_5Na^+$: 261.07334; found: 261.07334.



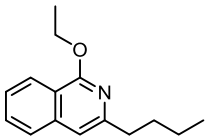
Preparation of N-Heterocycles

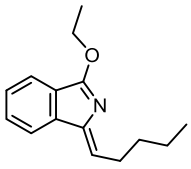
Compound 53. [(Johnphos)Au]SbF_6 (0.005 mmol, 4.0 mg, 5 mol%) was added to a solution of compound **52** (36 mg, 0.1 mmol) in acetic acid (0.5 mL) and the resulting mixture was stirred for 24 h. The solvent was distilled off and the residue purified by flash chromatography (hexanes/*tert*-butyl methyl ether, 1:1) to yield the title compound as a white waxy solid (24.0 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, 1H, *J* = 7.6 Hz), 7.94 (d, 2H, *J* = 8.3 Hz), 7.64 (td, 1H, *J* = 7.8 and 1.3 Hz), 7.40 (t, 1H, *J* = 7.8 Hz), 7.30-7.26 (m, 3H), 6.31 (s, 1H), 2.47 (t, 2H, *J* = 7.4 Hz), 2.39 (s, 3H), 1.59 (quint, 2H, *J* = 7.6 Hz), 1.41-1.31 (m, 2H), 0.92 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 157.6, 142.9, 139.3, 135.5, 135.3, 129.1, 128.9, 128.3, 127.3, 125.1, 120.2, 104.5, 32.4, 28.8, 22.1, 21.5, 13.6; IR (film): $\tilde{\nu}$ = 2960, 1703, 1355, 1257, 1167, 1087, 1034, 814, 703, 658, 569 cm^{-1}; MS (EI) *m*/*z* (%): 1088, 733, 378; HRMS (ESI): *m*/*z*: calcd. for $C_{20}H_{21}NO_3SNa$ [M^++*Na*]: 378.11343, found 378.11378.

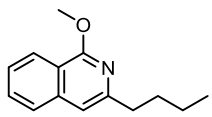


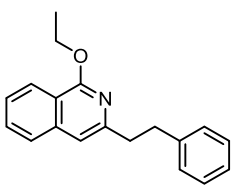
Compound 55. Prepared analogously starting from compound **54** and using $MeNO_2$/water (4:1) as the solvent; white solid (54 mg, 80%). Mp = 112-114 °C; $[\alpha]_{20}^{D}$ = +209.3 (c = 0.89, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, 1H, *J* = 8.1 Hz), 7.63 (t, 1H, *J* = 7.6 Hz), 7.47 (d, 1H, *J* = 7.9 Hz), 7.41 (t, 1H, *J* = 8.1 Hz), 7.33-7.30 (m, 2H), 7.26-7.22 (m, 3H), 6.46 (s, 1H), 5.61 (br. s, 1H), 4.72-4.67 (m, 1H), 4.45 (dd, 1H, *J* = 12.0, 3.4 Hz), 2.70-2.64 (m, 2H), 1.65-1.59 (m, 2H), 1.42 (sext, 2H, *J* = 7.3 Hz), 0.93 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 143.8, 137.2, 136.7, 132.6, 128.5, 127.9, 127.1, 126.2, 126.1, 125.1, 106.8, 64.0, 62.4, 33.7, 31.0, 22.3, 13.7; IR (film): $\tilde{\nu}$ = 3448, 2960, 2928, 2861, 1647, 1617, 1592, 1457, 1378, 1301, 1162, 1046, 988, 749, 725, 696, 574 cm^{-1}; MS (EI) *m*/*z* (%): 322 (5), 321 (14), 303 (10), 274 (5), 262 (9), 261 (39), 260 (7), 246 (5), 202 (36), 201 (11), 172 (9), 160 (11), 159 (100), 158 (12), 142 (7), 131 (9), 130 (7), 120 (5), 116 (7), 115 (8), 103 (14), 91 (15), 89 (5), 77 (7), 31 (6); HRMS (ESI): *m*/*z*: calcd. for $C_{21}H_{23}NO_2Na$ [M^++*Na*]: 344.16210, found 344.16195.

[15] M. Nukina, S. Marumo, *Tetrahedron Lett*. **1977**, *18*, 3271–3272.

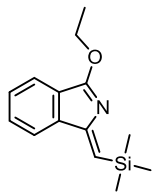
Representative Procedure for the Synthesis of 1-Alkoxyisoquinolines. 3-Butyl-1-ethoxyisoquinoline (58).  Triethyloxonium tetrafluoroborate (1.14 g, 6 mmol) was added to a solution of 2-(hex-1-yn-1-yl)benzamide (1.208 g, 6 mmol) in dichloromethane (30 mL). The resulting mixture was stirred overnight and then concentrated. The residue was taking up with *tert*-butyl methyl ether (60 mL) and triethylamine (9 mL) was added (if necessary, a little bit of dichloromethane can be added to help solubilize the intermediate imidate). The mixture was stirred for 10 min before it was filtered through a plug of cotton which was carefully rinsed with *tert*-butyl methyl ether. The combined filtrates were evaporated and the resulting imidate dissolved in chloroform (30 mL). This solution was added to a solution of AgOTs (83.7 mg, 0.3 mmol, 5 mol%) and DMEDA (26.4 mg, 0.3 mmol, 5 mol%) in chloroform (15 mL) at 0°C. The ice bath was removed and the mixture allowed to stir at ambient temperature overnight. The mixture was filtered through a plug of silica, which was rinsed with *tert*-butyl methyl ether. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexane/*tert*-butyl methyl ether, 94:4) to afford the title compound as a colorless oil (1.102 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, 1H, *J* = 8.3 Hz), 7.61 (d, 1H, *J* = 8.0 Hz), 7.55 (td, 1H, *J* = 6.7, 1.2 Hz), 7.40 (ddd, 1H, *J* = 8.2, 6.8, 1.3 Hz), 6.97 (s, 1H), 4.55 (q, 2H, *J* = 7.1 Hz), 2.74 (t, 2H, *J* = 7.5 Hz), 1.74 (quint, 2H, *J* = 7.5 Hz), 1.47 (t, 3H, *J* = 7.0 Hz), 1.38 (sext, 2H, *J* = 7.6 Hz), 0.94 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 153.1, 138.6, 130.0, 125.6, 125.3, 124.1, 118.1, 111.5, 61.6, 37.6, 31.5, 22.4, 14.6, 14.0; IR (film): $\tilde{\nu}$ = 2955, 2929, 2859, 1628, 1572, 1497, 1407, 1376, 1318, 1155, 1104, 1024, 838, 750, 670 cm^{-1}; MS (EI) *m*/*z* (%): 229 (22), 214 (22), 201 (6), 200 (14), 188 (14), 187 (100), 186 (9), 172 (10), 160 (7), 159 (68), 158 (25), 143 (5), 142 (5), 131 (12), 130 (7), 128 (5), 116 (8), 115 (11), 103 (10), 89 (10), 77 (5), 29 (9), 27 (6); HRMS (ESI): *m*/*z*: calcd. for $C_{15}H_{20}NO$ [M^++*H*]: 230.15394, found 230.15413.

 The minor isomer (**59**) analyzed as follows: colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, 1H, *J* = 7.5 Hz), 7.51 (d, 1H, *J* = 7.4 Hz), 7.37 (td, 1H, *J* = 7.3, 1.1 Hz), 7.29 (td, 1H, *J* = 7.4, 1.0 Hz), 6.16 (t, 1H, *J* = 7.7 Hz), 4.59 (q, 2H, *J* = 7.1 Hz), 2.72 (q, 2H, *J* = 7.4 Hz), 1.59-1.35 (m, 4H), 1.46 (t, 3H, *J* = 7.1 Hz), 0.94 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7, 146.2, 141.5, 131.3, 128.9, 127.0, 124.5, 119.8, 119.1, 64.4, 31.7, 27.5, 22.4, 14.6, 13.9; IR (film): $\tilde{\nu}$ = 2955, 2926, 2857, 1540, 1406, 1377, 1340, 1140, 1091, 1023, 881, 757, 686 cm^{-1}; MS (EI) *m*/*z* (%): 229 (9), 201 (8), 200 (48), 188 (5), 187 (37), 186 (11), 172 (7), 159 (13), 158 (100), 146 (16), 145 (13), 131 (7), 130 (16), 129 (5), 128 (5), 115 (7), 103 (11), 102 (6), 77 (6), 76 (5); HRMS (ESI): *m*/*z*: calcd. for $C_{15}H_{19}NONa$ [M^++*Na*]: 252.13588, found 252.13606.

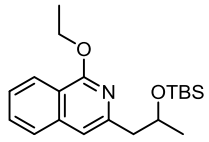
 Colorless oil (33 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, 1H, *J* = 8.2 Hz), 7.62 (d, 1H, *J* = 8.0 Hz), 7.57 (t, 1H, *J* = 7.6 Hz), 7.42 (t, 1H, *J* = 7.6 Hz), 7.00 (s, 1H), 4.12 (s, 3H), 2.78 (t, 2H, *J* = 7.5 Hz), 1.78 (quint, 2H, *J* = 7.5 Hz), 1.41 (sext, 2H, *J* = 7.5 Hz), 0.97 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 153.0, 138.6, 130.1, 125.6, 125.4, 124.0, 118.1, 111.7, 53.4, 37.6, 31.5, 22.4, 14.0; IR (film): $\tilde{\nu}$ = 2954, 2858, 1629, 1573, 1497, 1451, 1367, 1331, 1156, 1101, 986, 839, 750, 670, 556, 524 cm^{-1}; MS (EI) *m*/*z* (%): 216 (4), 215 (21), 200 (7), 186 (8), 174 (12), 173 (100), 172 (8), 158 (24), 131 (4), 115 (5), 103 (4); HRMS (ESI): *m*/*z*: calcd. for $C_{14}H_{18}NO$ [M^++*H*]: 216.13829, found 216.13815.

 Colorless oil (34.5 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, 1H, *J* = 8.2 Hz), 7.60-7.53 (m, 2H), 7.42 (ddd, 1H, *J* = 8.1, 6.6, 1.5 Hz), 7.28-7.20 (m, 4H), 7.16 (t, 1H, *J* = 7.6 Hz), 6.94 (s, 1H), 4.59 (q, 2H, *J* = 7.1 Hz), 3.14-3.09 (m, 2H), 3.08-3.03 (m,

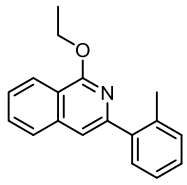
2H), 1.49 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 151.7, 142.2, 138.5, 130.1, 128.5, 128.2, 125.7, 125.6, 125.5, 124.1, 118.3, 111.8, 61.7, 39.6, 35.5, 14.6; IR (film): $\tilde{\nu}$ = 2978, 1627, 1572, 1495, 1408, 1377, 1319, 1154, 1099, 1024, 840, 748, 697, 670 cm^{-1}; MS (EI) *m*/*z* (%): 278 (22), 277 (100), 276 (6), 263 (9), 262 (46), 250 (5), 249 (29), 248 (50), 233 (5), 232 (6), 231 (7), 230 (5), 206 (8), 200 (6), 186 (27), 172 (9), 171 (5), 159 (5), 158 (39), 145 (6), 142 (8), 140 (5), 131 (21), 130 (6), 115 (13), 103 (20), 91 (37), 89 (14), 77 (11), 65 (9), 63 (5), 29 (7); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{20}NO$ [M^++*H*]: 278.15394, found 278.15398.



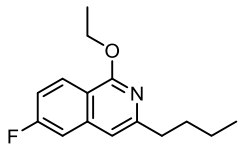
Colorless oil (198 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, 1H, *J* = 7.1 Hz), 7.48 (d, 1H, *J* = 7.4 Hz), 7.39 (td, 1H, *J* = 7.4, 1.1 Hz), 7.33 (td, 1H, *J* = 7.4, 1.0 Hz), 6.24 (s, 1H), 4.59 (q, 2H, *J* = 7.1 Hz), 1.48 (t, 3H, *J* = 7.1 Hz), 0.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 158.7, 141.0, 131.5, 129.1, 127.9, 121.8, 120.3, 119.5, 64.7, 14.5, 0.2; IR (film): $\tilde{\nu}$ = 2954, 1725, 1537, 1406, 1377, 1342, 1322, 1243, 1088, 1011, 836, 759, 689 cm^{-1}; MS (EI) *m*/*z* (%): 246 (5), 245 (22), 231 (9), 230 (45), 218 (5), 217 (19), 216 (100), 202 (20), 201 (5), 186 (9), 115 (4), 103 (24), 100 (4), 77 (4), 76 (8), 75 (79), 73 (4), 59 (6), 45 (4); HRMS (ESI): *m*/*z*: calcd. for $C_{14}H_{20}NOSi$ [M^++*H*]: 246.13087, found 246.13100.



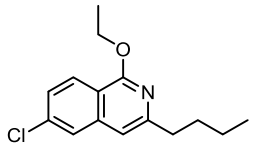
Colorless oil (37 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, 1H, *J* = 8.2 Hz), 7.61 (d, 1H, *J* = 7.9 Hz), 7.56 (td, 1H, *J* = 6.7, 1.2 Hz), 7.42 (ddd, 1H, *J* = 8.2, 6.8, 1.3 Hz), 6.99 (s, 1H), 4.55 (q, 2H, *J* = 7.0 Hz), 4.33 (sext, 1H, *J* = 6.6 Hz), 2.88 (dd, 1H, *J* = 13.0, 6.9 Hz), 2.77 (dd, 1H, *J* = 13.0, 5.8 Hz), 1.47 (t, 3H, *J* = 7.1 Hz), 1.21 (d, 3H, *J* = 6.1 Hz), 0.79 (s, 9H), −0.06 (s, 3H), −0.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 149.9, 138.5, 130.1, 125.6, 125.5, 124.0, 118.2, 113.6, 68.7, 61.6, 48.5, 25.8, 23.9, 18.1, 14.7, −4.8, −5.1; IR (film): $\tilde{\nu}$ = 2954, 2926, 2856, 1629, 1573, 1498, 1409, 1376, 1321, 1253, 1097, 999, 834, 773, 750, 672 cm^{-1}; MS (ESI) *m*/*z* : 368, 345; HRMS (ESI): *m*/*z*: calcd. for $C_{20}H_{32}NO_2Si$ [M^++*H*]: 346.21968, found 346.21927.



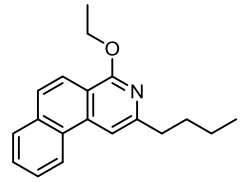
Colorless oil (35 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, 1H, *J* = 8.3 Hz), 7.75 (d, 1H, *J* = 8.1 Hz), 7.65 (td, 1H, *J* = 6.9, 1.2 Hz), 7.56-7.51 (m, 2H), 7.31-7.28 (m, 4H), 4.62 (q, 2H, *J* = 7.1 Hz), 2.50 (s, 3H), 1.51 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 150.9, 140.6, 138.4, 136.4, 130.8, 130.3, 129.9, 127.8, 126.3, 126.2, 125.8, 124.2, 118.4, 114.1, 62.0, 20.9, 14.7; IR (film): $\tilde{\nu}$ = 2977, 1625, 1569, 1498, 1406, 1376, 1319, 1162, 1100, 1023, 931, 875, 847, 752, 725, 666, 534 cm^{-1}; MS (EI) *m*/*z* (%): 264 (8), 263 (30), 248 (8), 235 (20), 234 (100), 232 (7), 218 (5), 217 (6), 216 (16), 204 (6), 189 (5), 178 (4), 89 (5); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{18}NO$ [M^++*H*]: 264.13829, found 264.13806.



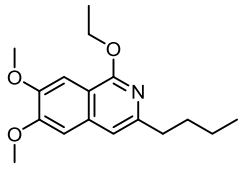
Colorless oil (40 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (dd, 1H, *J* = 9.0, 5.8 Hz), 7.20 (dd, 1H, *J* = 9.7, 2.5 Hz), 7.13 (td, 1H, *J* = 8.8, 2.5 Hz), 6.91 (s, 1H), 4.55 (q, 2H, *J* = 7.1 Hz), 2.73 (t, 2H, *J* = 7.6 Hz), 1.75 (quint, 2H, *J* = 7.4 Hz), 1.47 (t, 3H, *J* = 7.1 Hz), 1.39 (sext, 2H, *J* = 7.6 Hz), 0.95 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6 (d, $J_{C\text{-}F}$ = 248.3 Hz), 159.8, 154.6, 140.3 (d, $J_{C\text{-}F}$ = 10.2 Hz), 127.1 (d, $J_{C\text{-}F}$ = 9.7 Hz), 115.1, 115.0 (d, $J_{C\text{-}F}$ = 24.7 Hz), 111.2 (d, $J_{C\text{-}F}$ = 4.1 Hz), 109.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 61.8, 37.6, 31.4, 22.4, 14.6, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −109.4; IR (film): $\tilde{\nu}$ = 2956, 2930, 2872, 1633, 1574, 1501, 1407, 1376, 1322, 1226, 1133, 1105, 1025, 964, 869, 824, 771, 665 cm^{-1}; MS (EI) *m*/*z* (%): 248 (8), 247 (21), 232 (21), 219 (5), 218 (9), 206 (13), 205 (100), 204 (8), 190 (8), 177 (55), 176 (15), 159 (5), 149 (10), 134 (5), 133 (7), 121 (5), 107 (8); HRMS (ESI): *m*/*z*: calcd. for $C_{15}H_{19}NOF$ [M^++*H*]: 248.14452, found 248.14467.



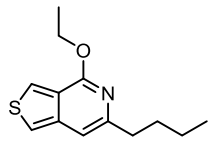
White solid (42 mg, 80%). Mp = 25-26 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, 1H, *J* = 8.8 Hz), 7.57 (d, 1H, *J* = 2.0 Hz), 7.33 (dd, 1H, *J* = 8.8, 2.0 Hz), 6.87 (s, 1H), 4.54 (q, 2H, *J* = 7.1 Hz), 2.73 (t, 2H, *J* = 7.5 Hz), 1.74 (quint, 2H, *J* = 7.4 Hz), 1.47 (t, 3H, *J* = 7.1 Hz), 1.38 (sext, 2H, *J* = 7.6 Hz), 0.95 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 154.7, 139.5, 136.2, 126.1, 125.9, 124.5, 116.3, 110.6, 61.8, 37.6, 31.4, 22.4, 14.6, 14.0; IR (film): $\tilde{\nu}$ = 2978, 2954, 2925, 2870, 1625, 1567, 1474, 1409, 1374, 1315, 1194, 1015, 872, 829, 772, 664, 594 cm^{-1}; MS (EI) *m*/*z* (%): 263 (13), 250 (7), 248 (23), 234 (13), 223 (31), 222 (16), 221 (100), 220 (12), 206 (12), 195 (28), 194 (16), 193 (84), 192 (22), 190 (5), 177 (7), 175 (5), 167 (6), 166 (5), 165 (14), 164 (6), 158 (5), 152 (8), 150 (5), 141 (7), 140 (13), 137 (7), 128 (6), 127 (5), 123 (14), 115 (9), 114 (10), 102 (10), 101 (8), 89 (6), 27 (6); HRMS (ESI): *m*/*z*: calcd. for $C_{15}H_{19}NOCl$ [M^{+}+*H*]: 264.11497, found 264.11507.



White solid (45 mg, 81%). Mp = 51-52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60-8.56 (m, 1H), 8.12 (d, 1H, *J* = 9.0 Hz), 7.91-7.86 (m, 1H), 7.78 (s, 1H), 7.70 (d, 1H, *J* = 9.0 Hz), 7.65-7.60 (m, 2H), 4.59 (q, 2H, *J* = 7.0 Hz), 2.87 (t, 2H, *J* = 7.6 Hz), 1.82 (quint, 2H, *J* = 7.5 Hz), 1.50 (t, 3H, *J* = 7.1 Hz), 1.42 (sext, 2H, *J* = 7.6 Hz), 0.96 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 155.1, 137.2, 133.7, 128.5, 128.4, 127.8, 126.3, 125.8, 123.5, 121.2, 114.8, 107.4, 61.8, 38.1, 31.8, 22.5, 14.7, 14.0; IR (film): $\tilde{\nu}$ = 2959, 2926, 1621, 1577, 1515, 1428, 1373, 1327, 1084, 1045, 1027, 825, 756, 740, 556 cm^{-1}; MS (EI) *m*/*z* (%): 280 (9), 279 (40), 265 (5), 264 (26), 251 (7), 250 (9), 238 (18), 237 (100), 236 (8), 222 (8), 209 (42), 208 (41), 190 (9), 181 (5), 180 (8), 178 (5), 166 (5), 165 (14), 153 (11), 152 (10), 151 (5), 139 (11), 29 (10); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{22}NO$ [M^{+}+*H*]: 280.16959, found 280.16980.

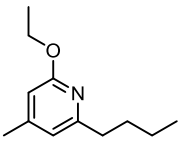


White solid (50 mg, 86%). Mp = 58-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 1H), 6.90 (s, 1H), 6.86 (s, 1H), 4.54 (q, 2H, *J* = 7.1 Hz), 3.98 (s, 3H), 3.95 (s, 3H), 2.70 (t, 2H, *J* = 7.5 Hz), 1.73 (quint, 2H, *J* = 7.4 Hz), 1.46 (t, 3H, *J* = 7.0 Hz), 1.37 (sext, 2H, *J* = 7.6 Hz), 0.93 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 152.5, 151.7, 148.6, 134.9, 112.5, 110.7, 104.5, 102.8, 61.4, 55.9, 55.8, 37.4, 31.5, 22.3, 14.7, 14.0; IR (film): $\tilde{\nu}$ = 2954, 2923, 1625, 1578, 1508, 1423, 1316, 1256, 1215, 1164, 1091, 1026, 860, 774, 642 cm^{-1}; MS (EI) *m*/*z* (%): 290 (9), 289 (44), 275 (5), 274 (30), 261 (8), 260 (11), 248 (15), 247 (100), 246 (10), 232 (7), 219 (24), 218 (72), 204 (6), 174 (6), 29 (7); HRMS (ESI): *m*/*z*: calcd. for $C_{17}H_{23}NO_3Na$ [M^{+}+*Na*]: 312.15701, found 312.15711.

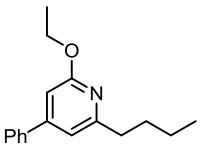


This compound is air-sensitive and must be handled with care. No chromatography was made for its isolation; rather, the crude material was dissolved in hexane/*tert*-butyl methyl ether (95/5) and the solution quickly filtered through a short plug of silica. Evaporation of the filtrate gave compound of sufficient purity. The low integrals for the two protons of the thiophene core are ascribed to issues with their relaxation time. Yellow oil (45 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (dd, 0.6 H, *J* = 3.2, 1.0 Hz), 7.33 (d, 0.8H, *J* = 3.2 Hz), 6.75 (s, 1H), 4.53 (q, 2H, *J* = 7.1 Hz), 2.62 (t, 2H, *J* = 7.6 Hz), 1.70 (quint, 2H, *J* = 7.4 Hz), 1.45 (t, 3H, *J* = 7.1 Hz), 1.38 (sext, 2H, *J* = 7.4 Hz), 0.94 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 150.2, 141.5, 126.0, 120.6, 114.0, 105.6, 61.4, 37.3, 31.2, 22.4, 14.6, 14.1; IR (film): $\tilde{\nu}$ = 2956, 2930, 2859, 1697, 1614, 1525, 1498, 1367, 1311, 1104, 1074, 1019, 861, 831, 804, 751, 732 cm^{-1}; MS (EI) *m*/*z* (%): 236 (5), 235 (35), 220 (18), 207 (7), 206 (25), 195 (5), 194 (12), 193 (100), 192 (14), 190 (6), 178 (17),

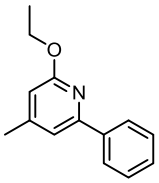
177 (6), 166 (10), 165 (89), 164 (47), 149 (6), 148 (6), 137 (25), 136 (5), 124 (5), 122 (13), 121 (7), 109 (8), 45 (9), 27 (6); HRMS (EI): *m*/*z*: calcd. for $C_{13}H_{17}NOS$ [M^+]: 235.10308, found 235.10333.



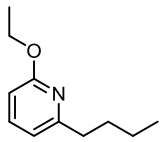
Colorless oil (55 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.50 (s, 1H), 6.30 (s, 1H), 4.28 (q, 2H, *J* = 7.1 Hz), 2.60 (t, 2H, *J* = 7.6 Hz), 2.22 (s, 3H), 1.65 (quint, 2H, *J* = 5.8 Hz), 1.38-1.29 (m, 2H), 1.35 (t, 3H, *J* = 7.0 Hz), 0.91 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 160.0, 149.8, 116.5, 107.2, 61.4, 37.5, 31.6, 22.4, 20.9, 14.7, 14.0; IR (film): $\tilde{\nu}$ = 2956, 2930, 2860, 1612, 1568, 1429, 1337, 1214, 1149, 1096, 1058, 835 cm^{-1}; MS (EI) *m*/*z* (%): 193 (3), 178 (34), 164 (14), 151 (100), 150 (10), 136 (12), 123 (70), 77 (7), 67 (4), 53 (10), 41 (6), 27 (6); HRMS (ESI): *m*/*z*: calcd. for $C_{12}H_{20}NO$ [M^++*H*]: 194.15393, found 194.15394.



Colorless oil (101 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dd, 2H, *J* = 6.7, 1.5 Hz), 7.48-7.34 (m, 3H), 6.96 (d, 1H, *J* = 1.3 Hz), 6.78 (d, 1H, *J* = 1.3 Hz), 4.44 (q, 2H, *J* = 7.0 Hz), 2.77 (t, 2H, *J* = 7.6 Hz), 1.79 (quint, 2H, *J* = 7.6 Hz), 1.49-1.40 (m, 2H), 1.45 (t, 3H, *J* = 7.0 Hz), 1.00 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 160.8, 151.3, 138.9, 128.8, 128.6, 126.9, 113.6, 105.0, 61.5, 37.8, 31.6, 22.4, 14.7, 14.0; IR (film): $\tilde{\nu}$ = 2955, 2929, 2860, 1610, 1553, 1411, 1374, 1339, 1204, 1047, 856, 761, 694, 538 cm^{-1}; MS (EI) *m*/*z* (%): 256 (5), 255 (7), 240 (21), 226 (10), 214 (15), 213 (100), 198 (6), 185 (34), 167 (5), 156 (6), 115 (8); HRMS (ESI): *m*/*z*: calcd. for $C_{17}H_{22}NO$ [M^++*H*]: 256.16958, found 256.16968.

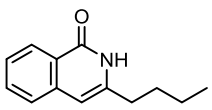


Colorless oil (66 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, 2H, *J* = 7.1 Hz), 7.44 (t, 2H, *J* = 7.6 Hz), 7.38 (t, 1H, *J* = 7.2 Hz), 7.16 (s, 1H), 6.50 (s, 1H), 4.49 (q, 2H, *J* = 7.1 Hz), 2.34 (s, 3H), 1.44 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 154.3, 150.1, 139.2, 128.5, 128.4, 126.6, 114.2, 109.4, 61.3, 21.0, 14.7; IR (film): $\tilde{\nu}$ = 2978, 1610, 1563, 1430, 1411, 1380, 1336, 1227, 1155, 1052, 836, 771, 691, 561 cm^{-1}; MS (EI) *m*/*z* (%): 214 (11), 213 (40), 212 (6), 199 (14), 198 (100), 186 (4), 185 (32), 184 (7), 170 (5), 169 (21), 168 (21), 167 (4), 157 (17), 156 (23), 154 (10), 141 (4), 129 (5), 128 (8), 127 (4), 115 (6), 84 (6), 77 (5), 53 (6), 51 (6), 49 (7), 29 (5), 27 (5); HRMS (EI): *m*/*z*: calcd. for $C_{14}H_{15}NO$ [M^+]: 213.11536, found 213.11510.



Colorless oil (55 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (dd, 1H, *J* = 8.1, 7.4 Hz), 6.65 (d, 1H, *J* = 7.2 Hz), 6.48 (d, 1H, *J* = 8.2 Hz), 4.31 (q, 2H, *J* = 7.1 Hz), 2.65 (t, 2H, *J* = 7.6 Hz), 2.65 (quint, 2H, *J* = 7.4 Hz), 1.40-1.30 (m, 2H), 1.37 (t, 3H, *J* = 7.0 Hz), 0.91 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4, 160.4, 138.6, 114.9, 107.1, 61.4, 37.6, 31.6, 22.4, 14.7, 14.0; IR (film): $\tilde{\nu}$ = 2956, 2930, 2860, 1595, 1578, 1446, 1282, 1258, 1042, 988, 789 cm^{-1}; MS (EI) *m*/*z* (%): 179 (4), 165 (4), 164 (28), 151 (4), 150 (13), 137 (100), 136 (11), 135 (6), 134 (4), 123 (4), 122 (16), 109 (85), 106 (8), 104 (8), 93 (7), 92 (6), 91 (17), 81 (8), 80 (12), 79 (5), 77 (7), 66 (7), 65 (8), 53 (8), 41 (5), 39 (12), 29 (5), 27 (6); HRMS (EI): *m*/*z*: calcd. for $C_{11}H_{17}NO$ [M^+]: 179.13101, found 179.13107.

Representative Procedure for the Deprotection.[16] **Preparation of 3-Butylisoquinolin-1(2*H*)-one.** An



aliquot of a stock solution of TMSCl (3.4 mL, 0.26 mmol) [50 µL of TMSCl in 5 mL of MeCN] was added to a solution of 3-butyl-1-ethoxyisoquinoline (46 mg, 0.2 mmol) and NaI (30 mg, 0.2 mmol) in MeCN (13 mL). The resulting mixture is stirred for 2 h at reflux temperature. Additional NaI (15 mg, 0.1 mmol) and TMSCl (16 µL, 0.13 mmol) were added and heating continued for additional 30 min. After reaching ambient temperature, the reaction was quenched with water and the aqueous layer repeatedly extracted with EtOAc. The combined extracts

[16] C. González, E. Guitián, L. Castedo, *Tetrahedron* **1999**, *55*, 5195–5206.

were washed with water, aq. $Na_2S_2O_3$ (10 mol%) and brine before they were dried over $MgSO_4$ and evaporated to give the title compound (41 mg, quant.). The spectroscopic data were in good agreement with those reported in the literature.[17]

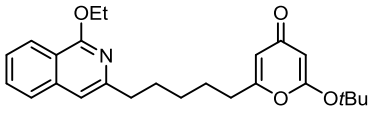
Double Cyclization

Methyl deca-2,9-diynoate. A solution of MeMgCl in THF (2.76 M, 5.8 mL, 16 mmol) was added dropwise to a solution of 1,8-nonadiyne (2.40 mL, 16.0 mmol) in THF (80 mL) at −20°C. The cold bath was removed and the mixture stirred for 5 h at room temperature before it was cooled again to −20°C. Methyl chloroformate (80 mmol, 6.2 mL) was added and stirring continued for 1 h at ambient temperature. The reaction was quenched with aq. sat. NH_4Cl, the aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were washed with water and brine before they were dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (hexanes/*tert*-butyl methyl ether, 85:15) gave the title compound as a colorless oil (1.48 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 3H), 2.29 (t, 2H, *J* = 6.8 Hz), 2.16-2.12 (m, 2H), 1.89 (t, 1H, *J* = 2.6 Hz), 1.58-1.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 89.3, 84.0, 72.9, 68.4, 52.4, 27.8, 27.7, 26.9, 18.4, 18.1; IR (film): $\tilde{\nu}$ = 3294, 2942, 2864, 2236, 1710, 1434, 1249, 1076, 752, 634 cm^{-1}; MS (EI) *m*/*z* (%): 149 (5), 147 (5), 135 (9), 119 (20), 118 (9), 117 (43), 115 (7), 111 (6), 107 (10), 105 (20), 103 (8), 93 (7), 92 (11), 91 (100), 81 (25), 79 (67), 77 (37), 69 (5), 68 (6), 67 (14), 66 (26), 65 (13), 59 (21), 55 (16), 53 (39), 51 (18), 41 (51), 39 (47), 38 (6), 29 (8), 27 (14); HRMS (ESI): *m*/*z*: calcd. for $C_{11}H_{14}O_2Na$ [M^++*Na*]: 201.08860, found 201.08870.

Compound 63. A solution of 2-iodobenzamide (1.065 g, 4.3 mmol), triethylamine (2.40 mL, 17.2 mmol), $PdCl_2(PPh_3)_2$ (106 mg, 0.15 mmol, 3.5 mol%) and copper iodide (66 mg, 0.08 mmol, 8 mol%) in DMF (16 mL) was stirred for 1 h before a solution of methyl deca-2,9-diynoate (922 mg, 5.17 mmol) in DMF (4.0 mL + 1.5 mL for rinsing) was added. The resulting mixture was stirred for 4 d. For work up, the mixture was poured into water, the aqueous phase was repeatedly extracted with EtOAc, and the combined extracts were washed with water and brine before they were dried (Na_2SO_4) and concentrated. Purification of the residue by flash chromatography (*tert*-butyl methyl ether/hexanes, 95:5) furnished the title compound as a yellow solid (932 mg, 73%). Mp = 63-64°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.43 (dd, 1H, *J* = 6.8, 2.5 Hz), 7.53 (br. s, 1H), 7.49-7.45 (dd, 1H, *J* = 6.6, 2.4 Hz), 7.41-7.34 (m, 2H), 6.01 (br. s, 1H), 3.72 (s, 3H), 2.49 (t, 2H, *J* = 6.6 Hz), 2.36 (t, 2H, *J* = 6.4 Hz), 1.66-1.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 154.1, 134.2, 133.8, 130.9, 130.1, 128.1, 120.8, 97.0, 89.3, 79.9, 73.1, 52.6, 28.0, 27.8, 26.9, 19.5, 18.5; IR (film): $\tilde{\nu}$ = 3361, 3171, 2943, 2233, 1707, 1637, 1594, 1450, 1398, 1252, 1076, 815, 779, 749, 631 cm^{-1}; MS (EI) *m*/*z* (%): 239 (7), 238 (25), 237 (5), 236 (7), 224 (13), 223 (11), 222 (13), 221 (22), 220 (11), 219 (8), 210 (7), 209 (10), 208 (11), 207 (8), 205 (6), 203 (8), 200 (18), 196 (12), 195 (14), 194 (15), 193 (13), 192 (6), 191 (8), 183 (8), 182 (10), 181 (14), 180 (12), 179 (8), 178 (13), 173 (5), 172 (26), 168 (5), 167 (8), 166 (8), 165 (24), 160 (9), 159 (100), 158 (26), 155 (11), 154 (7), 153 (9), 152 (8), 146 (8), 144 (5), 143 (6), 141 (9), 140 (12), 133 (7), 132 (6), 131 (7), 130 (42), 129 (8), 128 (16), 127 (17), 126 (5), 117 (5), 116 (7), 115 (29), 114 (13), 113 (6), 105 (9), 104 (12), 103 (19), 102 (9), 101 (7), 91 (9), 89 (7), 88 (6), 79 (11), 77 (29), 75 (5), 66 (8), 65 (6), 63 (8), 55 (7), 53 (8), 52 (6), 51 (9), 44 (8), 43 (7), 41 (6), 39 (10), 29 (8); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{19}NO_3Na$ [M^++*Na*]: 320.12571, found 320.12572.

[17] H. Gao, J. Zhang, *Adv. Synth. Catal.* **2009**, *351*, 85–88.

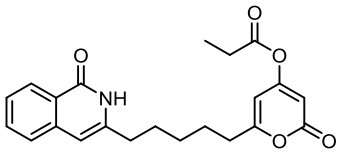
Compound 65. *tert*-Butyl acetate (176 µL, 1.3 mmol) was added to a freshly prepared solution of LDA (1.0 M in THF, 1.2 mL, 1.2 mmol) at −78°C. The mixture was stirred for 30 min at this temperature before a solution of compound **63** (149 mg, 0.5 mmol) in THF (1.2 mL) was added dropwise. Stirring was continued for 4 h at −78°C. The reaction was quenched with aq. sat. NH_4Cl and the aqueous phase extracted with *tert*-butyl methyl ether. The combined extracts were washed with water and brine before they were dried (Na_2SO_4) and gently concentrated. The resulting product is instable; attempted chromatography (silica) results in extensive degradation. The product should be carefully handled and directly used in the next step.



Triethyloxonium tetrafluoroborate (95 mg, 0.5 mmol) was added to a solution of the crude material in dichloromethane (2.5 mL). The mixture was stirred for 2 h before triethylamine (70 µL, 0.5 mmol) and ether (1.0 mL) were added. After 5 min, the mixture was filtered through a plug of silica, which was carefully rinsed with *tert*-butyl methyl ether. The combined filtrates were concentrated and the residue dissolved in chloroform (1.0 mL).

This solution of the crude imidate was added at 0°C to a solution of AgOTs (14 mg, 0.05 mmol, 10 mol%) and DMEDA (5.4 µL, 0.05 mmol, 10 mol%) in chloroform (1.0 mL + 0.5 for rising). The ice bath was removed and the mixture stirred overnight before it was filtered through a plug of silica that was carefully rinsed with *tert*-butyl methyl ether. The combined filtrates were concentrated and the residue purified by flash chromatography (*tert*-butyl methyl ether/CH_2Cl_2, 4:1) to give the title compound as a pale yellow oil (137 mg, 67%). At this stage, trace amounts of an inseparable impurity were present which could be removed in the next step. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, 1H, *J* = 8.2 Hz), 7.62-7.53 (m, 2H), 7.41 (ddd, 1H, *J* = 8.2, 6.5, 1.6 Hz), 6.95 (s, 1H), 5.98 (d, 1H, *J* = 1.9 Hz), 5.55 (d, 1H, *J* = 2.0 Hz), 4.54 (q, 2H, *J* = 7.1 Hz), 2.73 (t, 2H, *J* = 7.4 Hz), 2.46 (t, 2H, *J* = 7.5 Hz), 1.80 (quint, 2H, *J* = 7.6 Hz), 1.73-1.63 (m, 2H), 1.49-1.40 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.4, 165.7, 165.5, 160.0, 152.3, 138.5, 130.1, 125.5, 125.4, 124.0, 118.2, 112.4, 111.6, 98.2, 85.3, 61.6, 37.5, 33.1, 28.8, 28.6, 28.4, 26.6, 14.6; IR (film): $\tilde{\nu}$ = 2979, 2932, 2859, 1657, 1626, 1572, 1372, 1320, 1247, 1137, 1101, 1023, 930, 840, 753, 671 cm^{-1}; MS (EI) *m*/*z* (%): 411 (5), 410 (29), 409 (97), 294 (6), 353 (8), 352 (9), 338 (8), 335 (9), 324 (19), 310 (6), 289 (5), 238 (7), 228 (14), 215 (12), 214 (9), 212 (5), 201 (18), 200 (92), 198 (13), 188 (13), 187 (100), 186 (26), 185 (6), 184 (14), 173 (8), 172 (32), 171 (10), 167 (8), 160 (5), 159 (42), 158 (31), 154 (10), 143 (6), 142 (5), 141 (5), 131 (11), 130 (5), 116 (5), 115 (7), 103 (7), 69 (9), 57 (51), 41 (9), 29 (12); HRMS (ESI): *m*/*z*: calcd. for $C_{25}H_{31}NO_4Na$ [M^++*Na*]: 432.21453, found 432.21482.

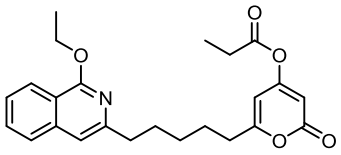
Compound 67. An aliquot of a stock solution of TMSCl (5.3 mL, 0.84 mmol, 2.6 eq) [200 µL of TMSCl in 10 mL of MeCN] was added to a solution of compound **63** (132 mg, 0.32 mmol) and NaI (96 mg, 0.64 mmol) in MeCN (21 mL). The mixture was then stirred for 3 h at reflux temperature. After reaching ambient temperature, the reaction was quenched with water and the aqueous layer was repeatedly extracted with EtOAc. The combined extracts were successively washed with water, aq. $Na_2S_2O_3$ (10 mol%) and water.

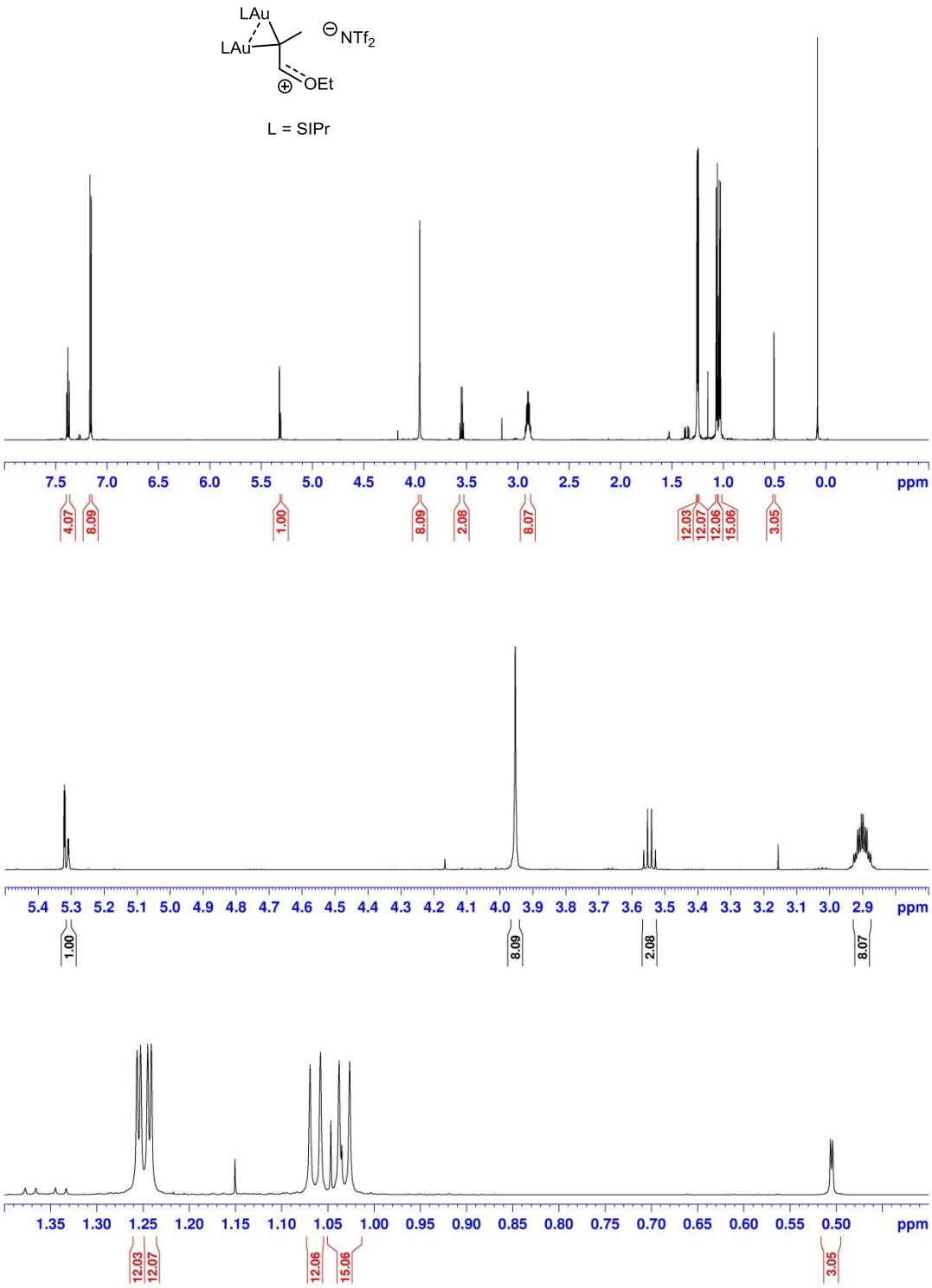


The insoluble material was filtered off, and the organic phase was concentrated. The residue was dried in high vacuum for 1 h before it was suspended in CH_2Cl_2 (28 mL). Triethylamine (1.82 mL, 13.0 mmol) was added at 0°C, followed by propionic anhydride (1.26 mL, 9.8 mmol). The mixture was stirred for 3 h at this temperature before water was

introduced. The aqueous layer was repeatedly extracted with CH_2Cl_2, the combined organic phases were washed with water and brine, dried (Na_2SO_4) and concentrated. The crude material still contained anhydride which was pumped off in high vacuum before the residue was purified by flash chromatography (EtOAc/*tert*-butyl methyl ether, 4:1) to give the title compound as a yellow solid (95 mg, 77%), Mp = 130-131°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.44 (br. s, 1H), 8.32 (d, 1H, *J* = 8.0 Hz), 7.59 (t, 1H, *J* = 7.2 Hz), 7.46 (d, 1H, *J* = 7.6 Hz), 7.40 (t, 1H, *J* = 7.9 Hz), 6.29 (s, 1H), 6.01 (d, 1H, *J* = 2.0 Hz), 5.89 (d, 1H, *J* = 2.0 Hz), 2.63 (t, 2H, *J* = 7.5 Hz), 2.54-2.46 (m, 4H), 1.78 (quint, 2H, *J* = 7.6 Hz), 1.71 (quint, 2H, *J* = 7.6 Hz), 1.45 (quint, 2H, *J* = 7.1 Hz), 1.19 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 166.6, 163.8, 163.1, 141.6, 138.7, 132.6, 127.1, 125.8, 125.7, 104.0, 101.0, 100.7, 33.6, 33.1, 28.2, 27.9, 27.8, 26.3, 8.6; IR (film): $\tilde{\nu}$ = 2920, 1781, 1712, 1638, 1567, 1462, 1345, 1164, 1100, 1068, 855, 800, 762, 688, 580, 469 cm^{-1}; MS (EI) *m*/*z* (%): 382 (18), 381 (38), 326 (10), 325 (33), 200 (13), 198 (5), 187 (17), 186 (8), 184 (5), 173 (22), 172 (100), 171 (8), 160 (11), 159 (96), 158 (17), 131 (10), 103 (6), 89 (5), 69 (6), 57 (27), 29 (20), 27 (5); HRMS (ESI): *m*/*z*: calcd. for $C_{22}H_{23}NO_5Na$ [$M+Na^+$]: 404.14684, found 404.14688.

Compound 66. A solution of boron tribromide (1.0 M, 0.62 mmol, 624 µL) was added to a solution of compound **65** (64 mg, 0.16 mmol) in CH_2Cl_2 (4.7 mL) at 0°C. The ice bath was removed and the mixture stirred for 1 d at ambient temperature. The reaction was quenched at 0°C with water and the aqueous layer was repeatedly extracted with CH_2Cl_2. The combined extracts were washed with water and brine, dried (Na_2SO_4) and concentrated. The residue was dissolved in CH_2Cl_2 (11 mL). Triethylamine (344 µL, 2.5 mmol) was added at 0°C followed by propionic anhydride (172 µL, 1.3 mmol). The mixture was stirred overnight while reaching ambient temperature. The reaction was carefully quenched with aq. sat. $NaHCO_3$ and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with water and brine, dried (Na_2SO_4) and concentrated. Excess anhydride was pumped off in vacuum before the residue was purified by flash chromatography (*tert*-butyl methyl ether/hexane, 3:2) to give the title compound as a yellow solid (24 mg, 38%), Mp = 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, 1H, *J* = 8.2 Hz), 7.61 (d, 1H, *J* = 8.0 Hz), 7.46 (ddd, 1H, *J* = 8.0, 6.7, 1.2 Hz), 7.41 (ddd, 1H, *J* = 8.2, 6.8, 1.4 Hz), 6.95 (s, 1H), 6.01 (d, 1H, *J* = 2.0 Hz), 5.89 (d, 1H, *J* = 2.0 Hz), 4.54 (q, 2H, *J* = 7.1 Hz), 2.73 (t, 2H, *J* = 7.4 Hz), 2.53 (q, 2H, *J* = 7.5 Hz), 2.47 (t, 2H, *J* = 7.7 Hz), 1.79 (quint, 2H, *J* = 7.6 Hz), 1.70 (quint, 2H, *J* = 7.7 Hz), 1.48-1.39 (m, 2H), 1.47 (t, 3H, *J* = 7.0 Hz), 1.21 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 167.0, 163.8, 163.1, 159.9, 152.4, 138.5, 130.1, 125.6, 125.4, 124.0, 118.2, 111.6, 100.9, 100.5, 61.6, 37.4, 33.8, 28.7, 28.5, 27.8, 26.5, 14.6, 8.6; IR (film): $\tilde{\nu}$ = 2937, 2862, 2360, 1774, 1714, 1640, 1570, 1404, 1381, 1336, 1317, 1149, 1088, 1071, 1026, 854, 834, 759, 675 cm^{-1}; MS (ESI) *m*/*z*: 841, 432; HRMS (ESI): *m*/*z*: calcd. for $C_{24}H_{27}NO_5Na$ [M^++*Na*]: 432.17814, found 432.17790.

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LAu
⊖NTf2
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4.07 8.09 1.00 8.09 2.08 8.07 12.03 12.07 12.06 15.06 3.05
5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 ppm
1.00 8.09 2.08 8.07
1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 0.70 0.65 0.60 0.55 0.50 ppm
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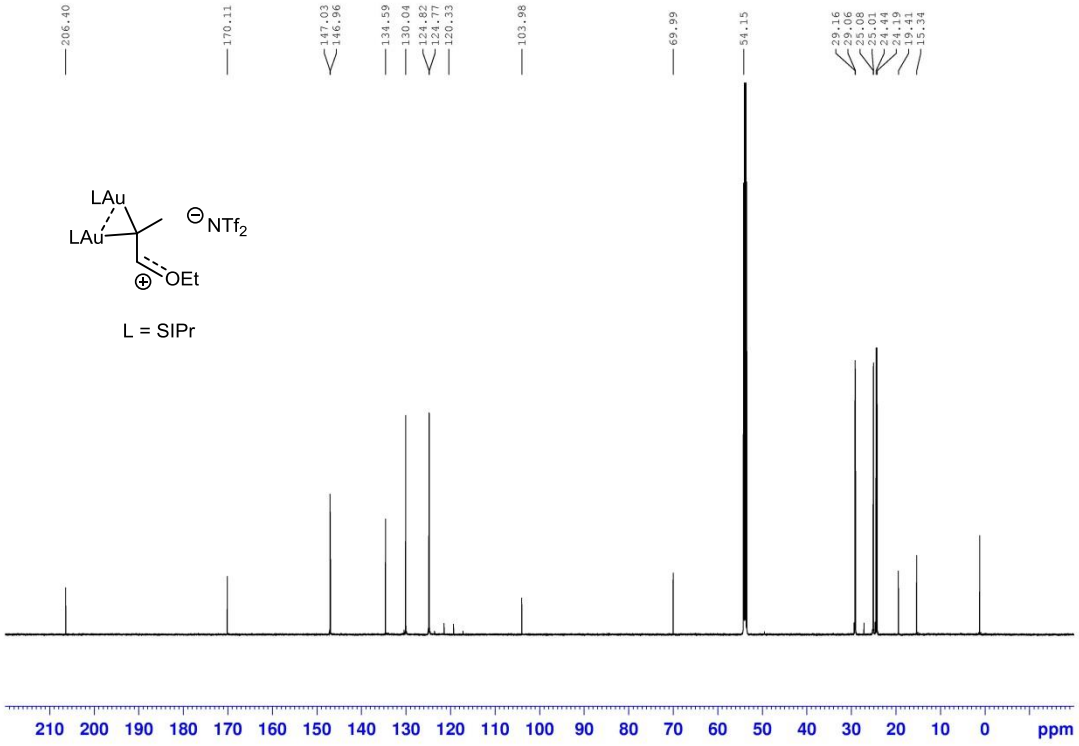
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29.06
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25.01
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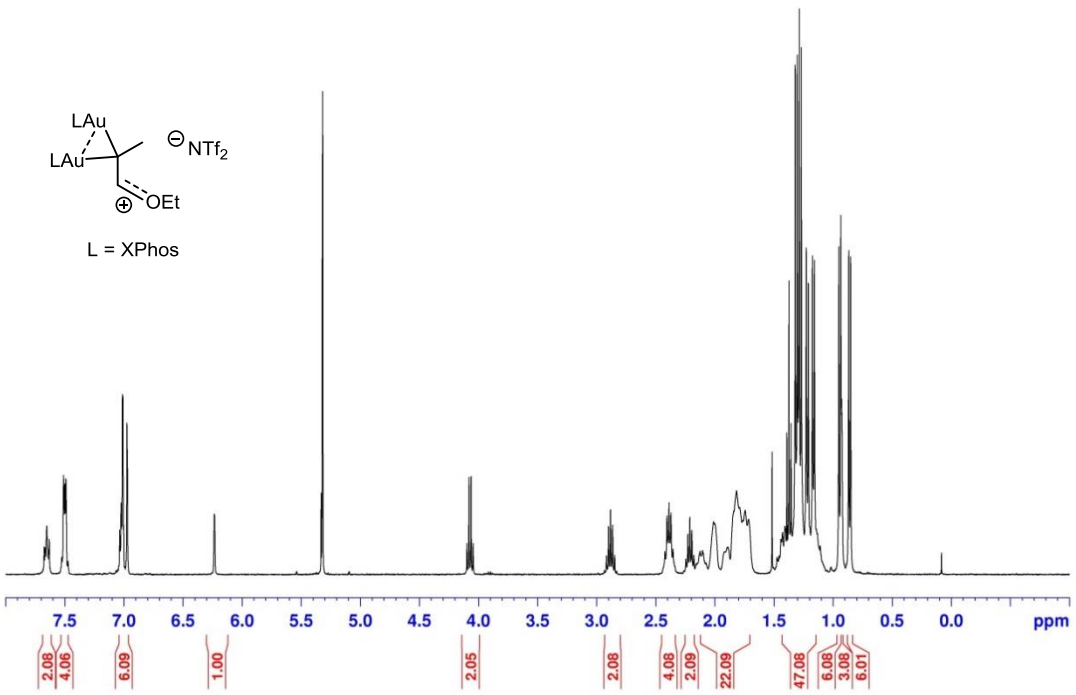
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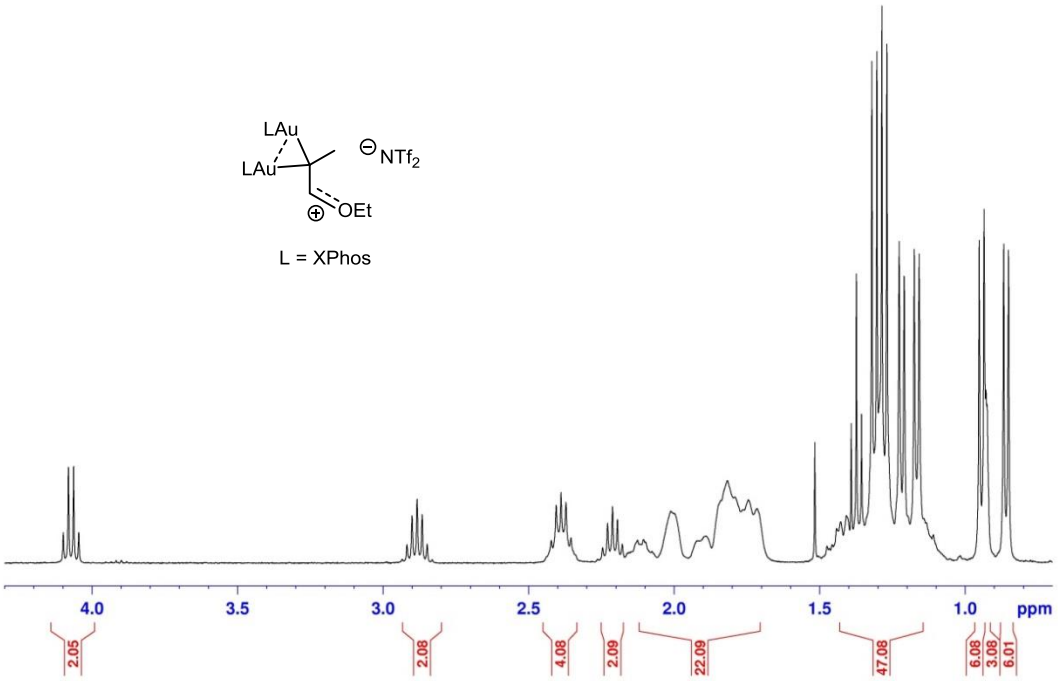
6.01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ppm
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2.08
4.08
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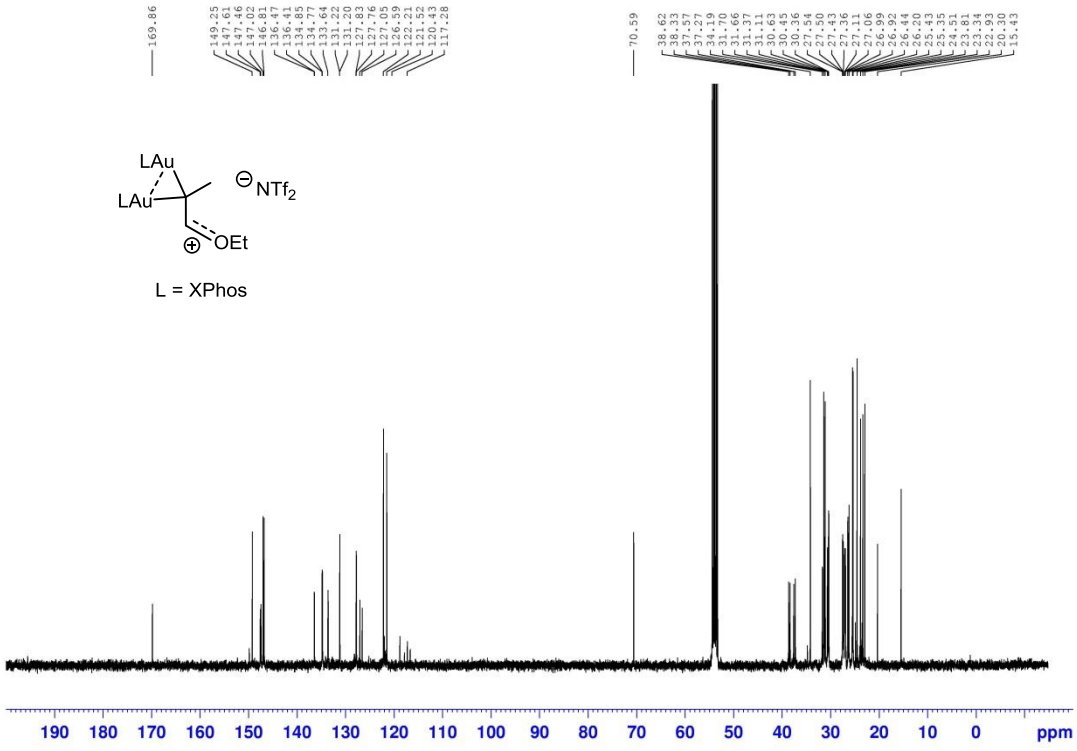
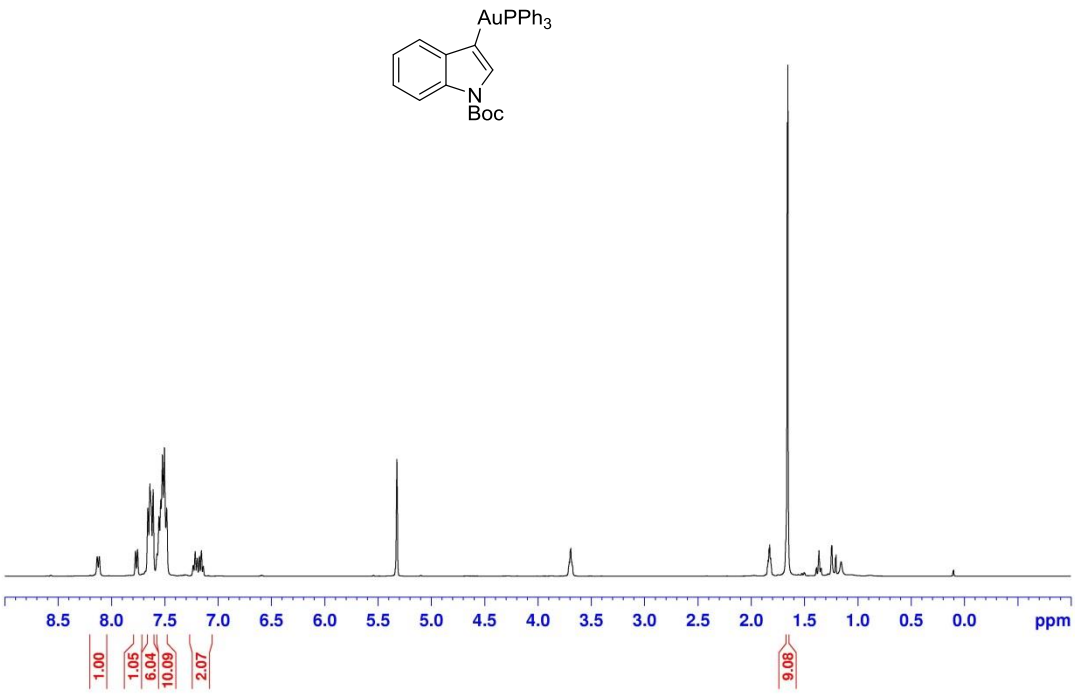
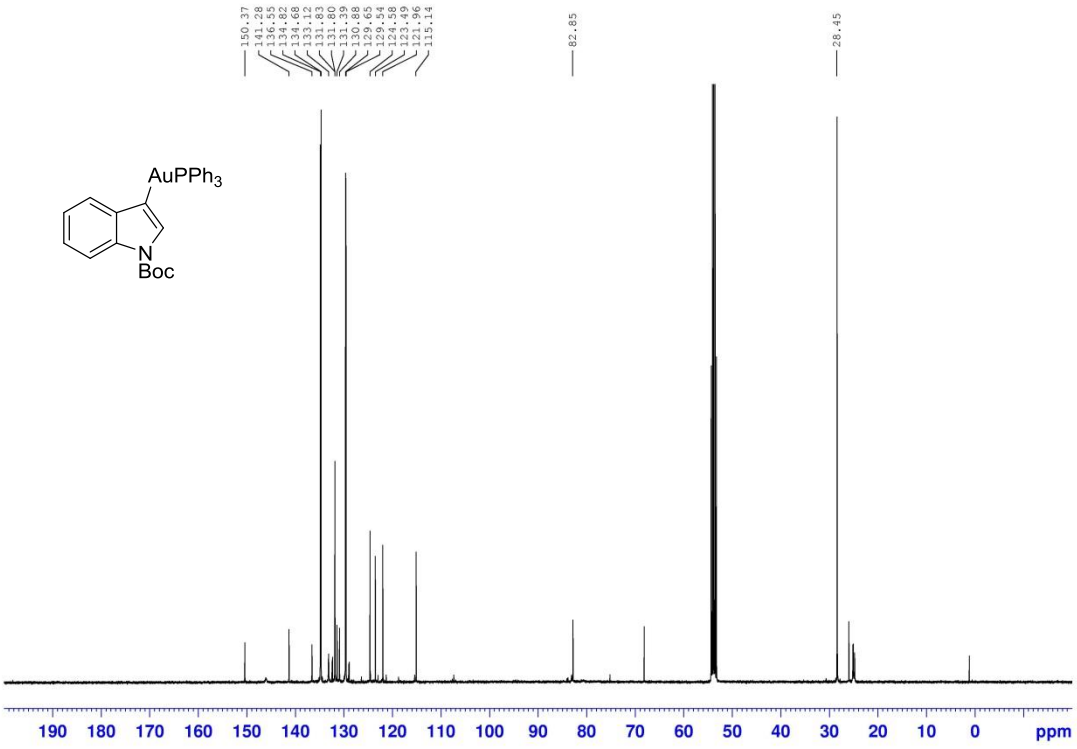
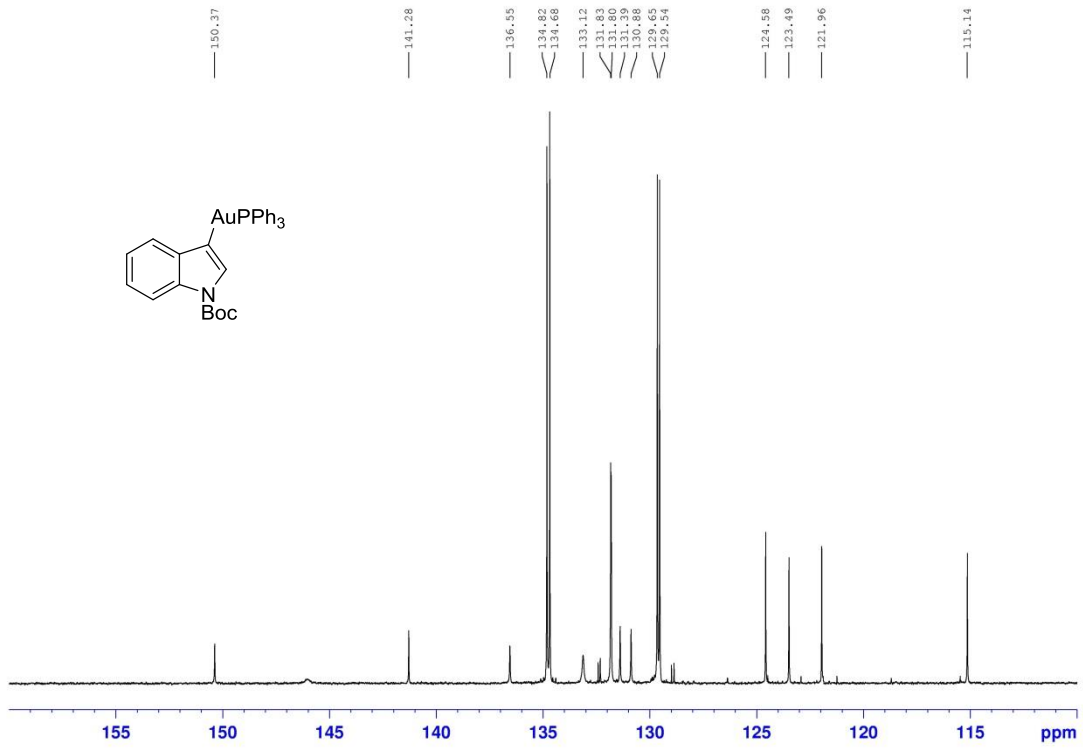
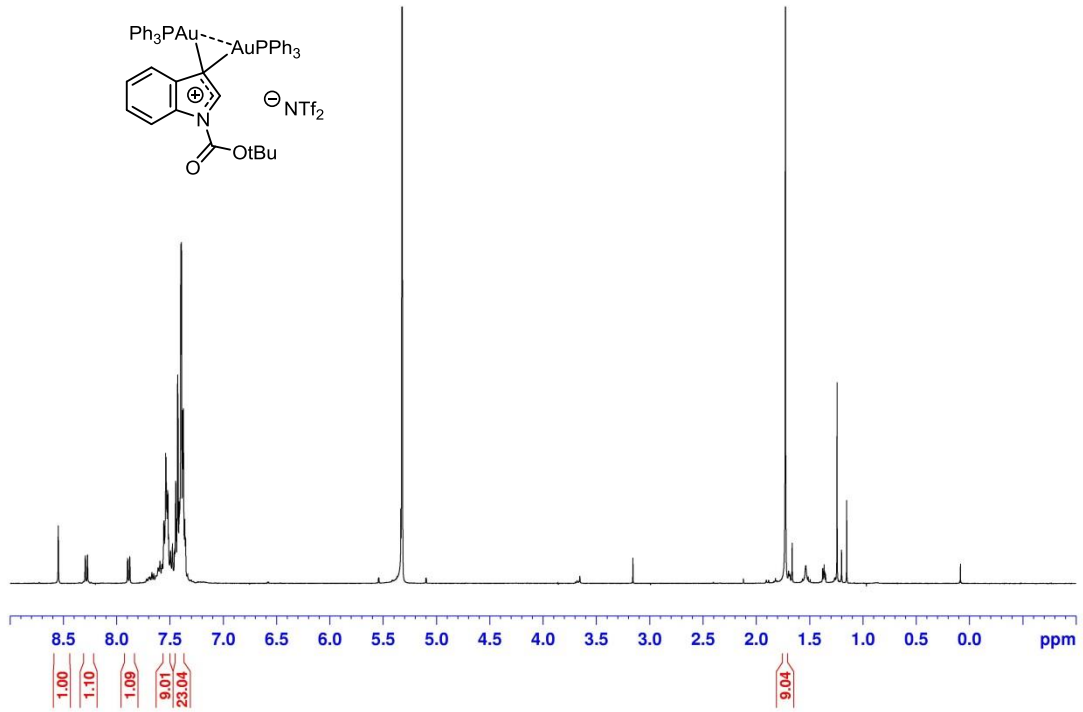
22.09
47.08
6.08
3.08
6.01

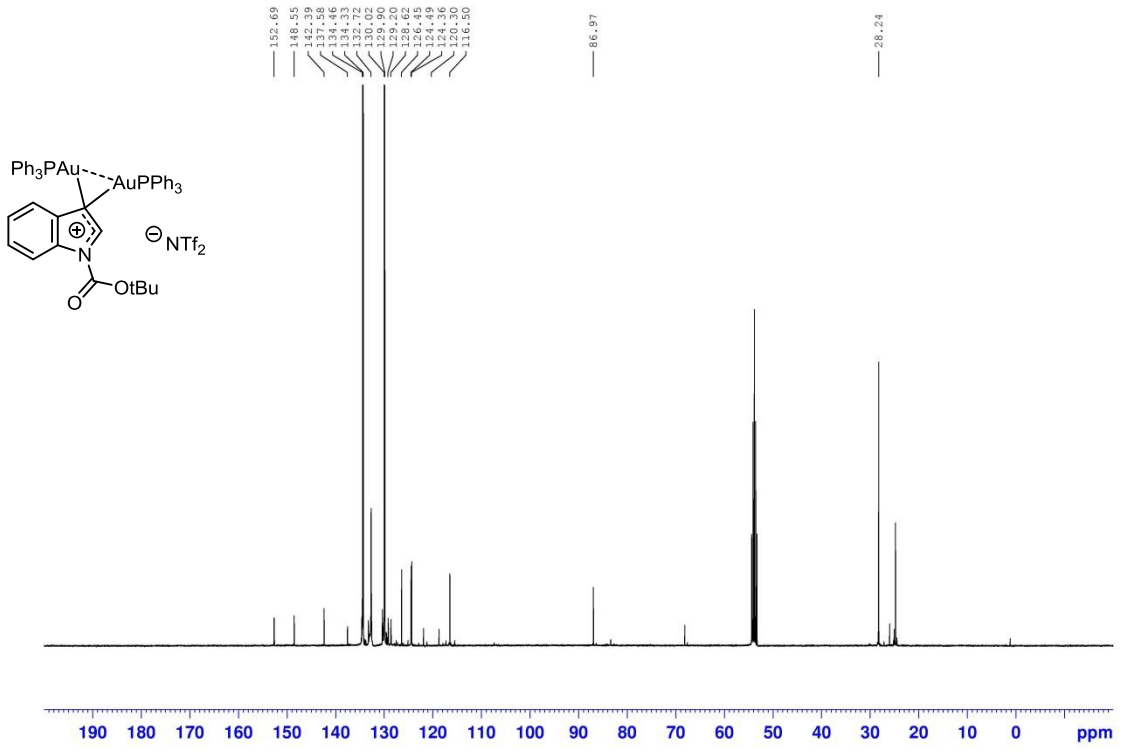

169.86
149.25
147.61
147.46
147.02
136.81
136.47
136.41
134.85
134.77
133.64
131.22
131.20
127.83
127.76
127.05
126.59
122.21
121.52
120.43
117.28
70.59
38.62
38.33
37.57
37.27
34.19
31.70
31.66
31.37
31.11
30.63
30.45
30.36
27.54
27.40
27.43
27.36
27.11
27.06
26.99
26.92
26.44
26.40
26.43
25.35
24.51
23.81
23.34
22.93
20.30
15.43
LAu
LAu
⊖NTf2
⊕OEt
L = XPhos
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

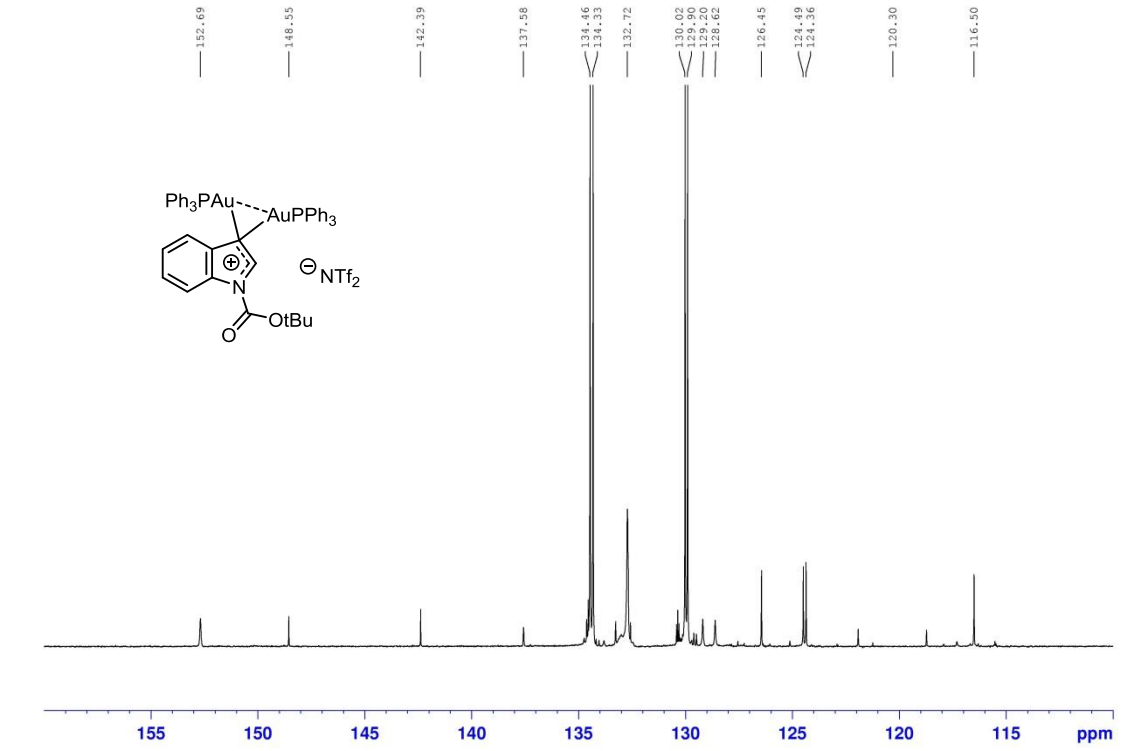

AuPPh3
N
Boc
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.05
6.04
10.09
2.07
9.08

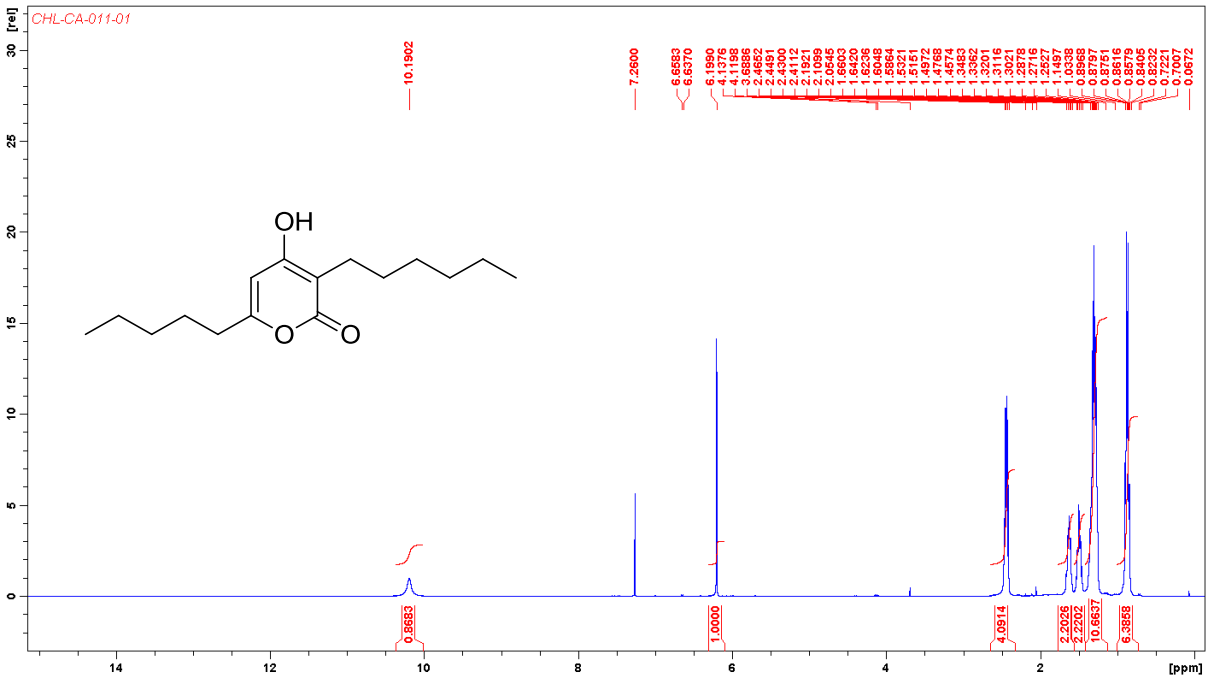

150.37
141.28
136.55
134.82
134.68
133.12
131.83
131.80
131.39
130.88
129.65
129.54
124.58
123.49
121.96
115.14
82.85
28.45
AuPPh3
N
Boc
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

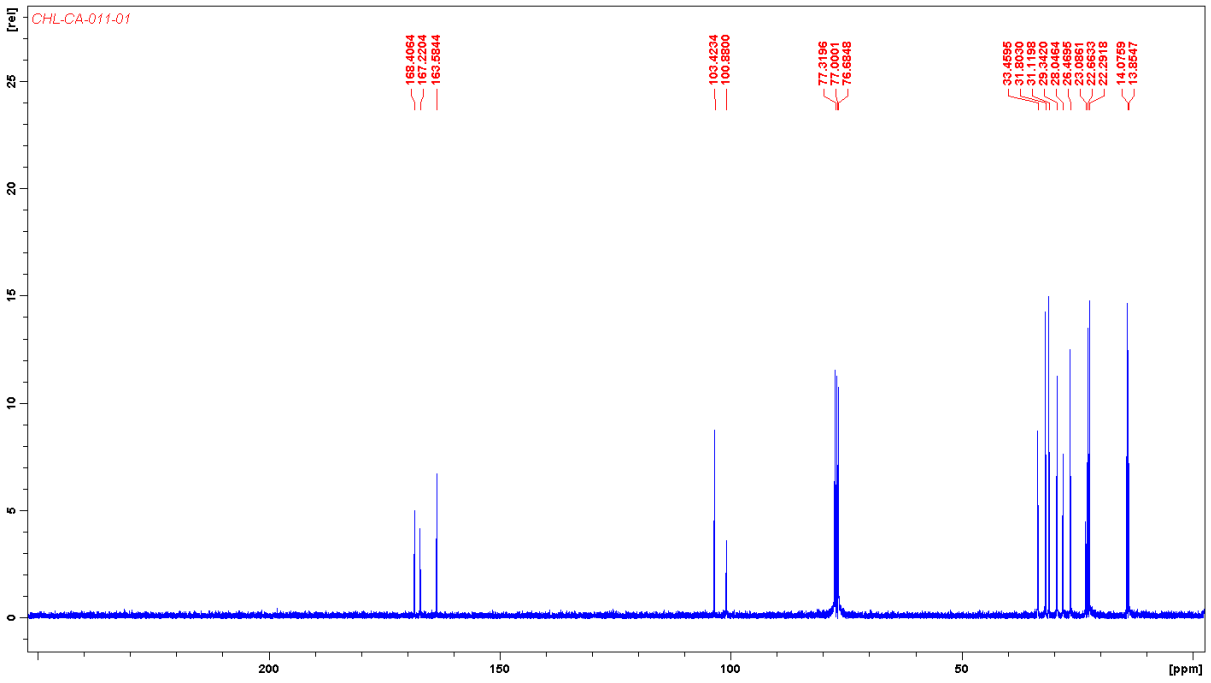

150.37
141.28
136.55
134.82
134.68
133.12
131.83
131.80
131.39
130.88
129.65
129.54
124.58
123.49
121.96
115.14
AuPPh3
N
Boc
155
150
145
140
135
130
125
120
115
ppm

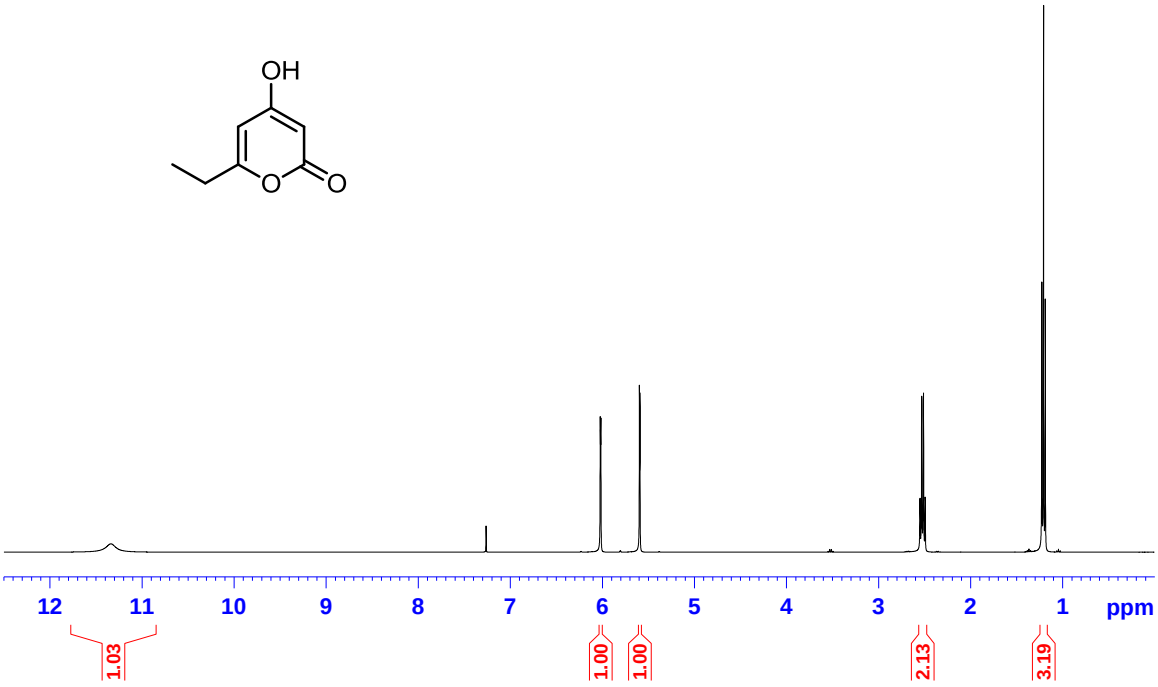

Ph3PAu
AuPPh3
NTf2
N
O
OtBu
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.10
1.09
9.01
23.04
9.04

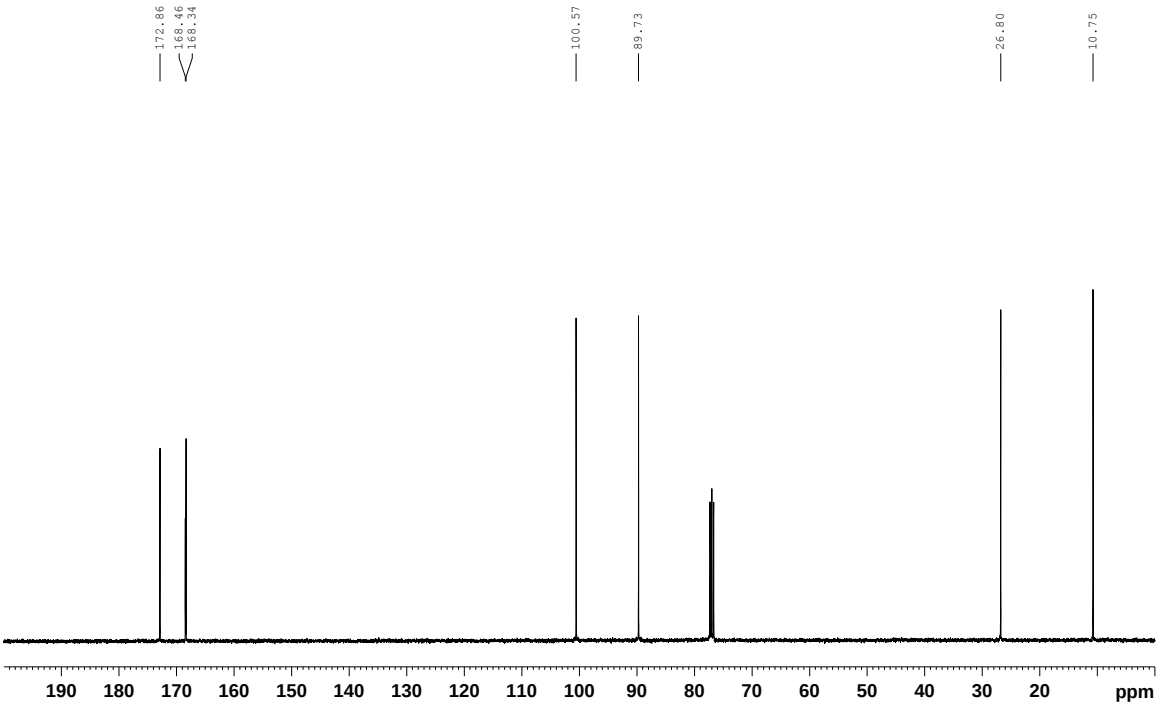

152.69
148.55
142.39
137.58
134.46
134.33
132.72
130.02
129.90
129.20
128.62
126.45
124.49
124.36
120.30
116.50
86.97
28.24
Ph3PAu
AuPPh3
NTf2
N
O
OtBu
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

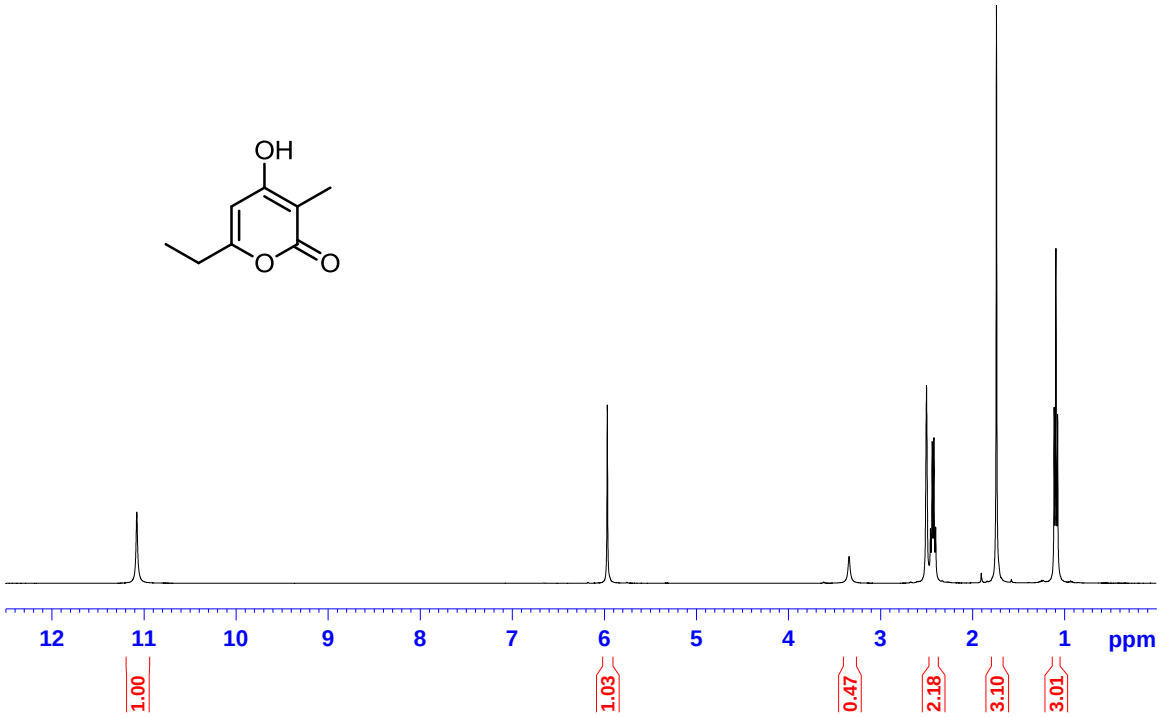

152.69
148.55
142.39
137.58
134.46
134.33
132.72
130.02
129.90
129.20
128.62
126.45
124.49
124.36
120.30
116.50
Ph3PAu
AuPPh3
NTf2
N
O
OtBu
155 150 145 140 135 130 125 120 115 ppm

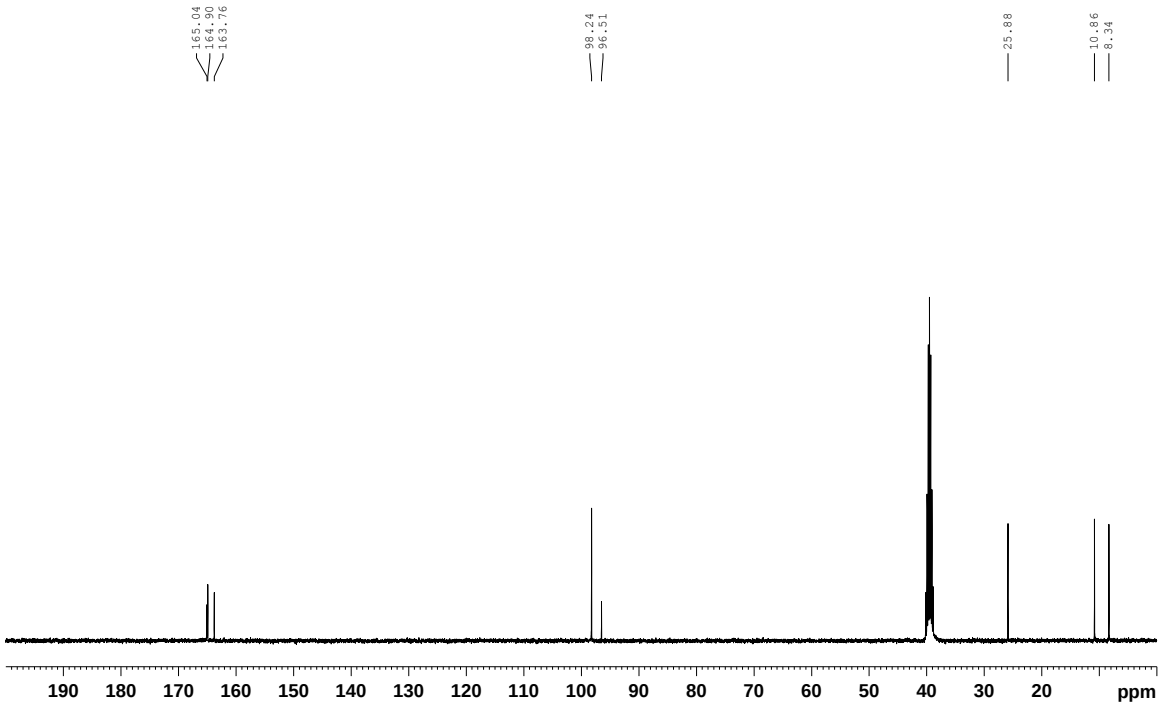

CHL-CA-011-01
[rel]
[ppm]
OH
O
O
10.1902
7.2600
6.6583
6.6370
6.1990
4.1376
4.1198
3.6886
2.4652
2.4491
2.4300
2.4112
2.1921
2.1099
2.0545
1.9603
1.6429
1.6228
1.6048
1.5984
1.5321
1.5151
1.4972
1.4758
1.4574
1.3483
1.3362
1.3201
1.3116
1.3021
1.2873
1.2718
1.2527
1.1497
1.0338
0.8968
0.8797
0.8731
0.8618
0.8579
0.8405
0.8232
0.7221
0.7007
0.6672
0.9683
1.0000
4.0914
2.2026
2.2202
10.6637
6.3858

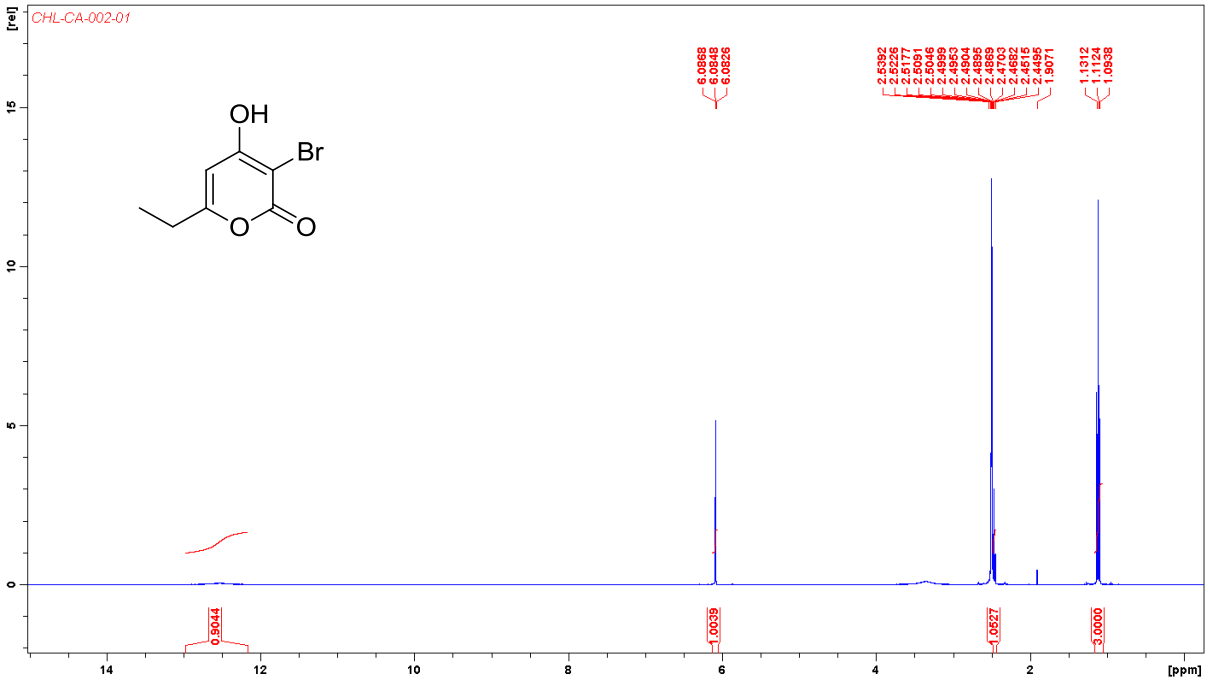

CHL-CA-011-01
[rel]
[ppm]
168.4064
167.2204
163.5844
103.4234
100.3800
77.3196
77.0001
76.6848
33.4656
31.8030
31.1198
29.3420
28.0464
26.4695
23.0861
22.6653
22.2918
14.0759
13.8547

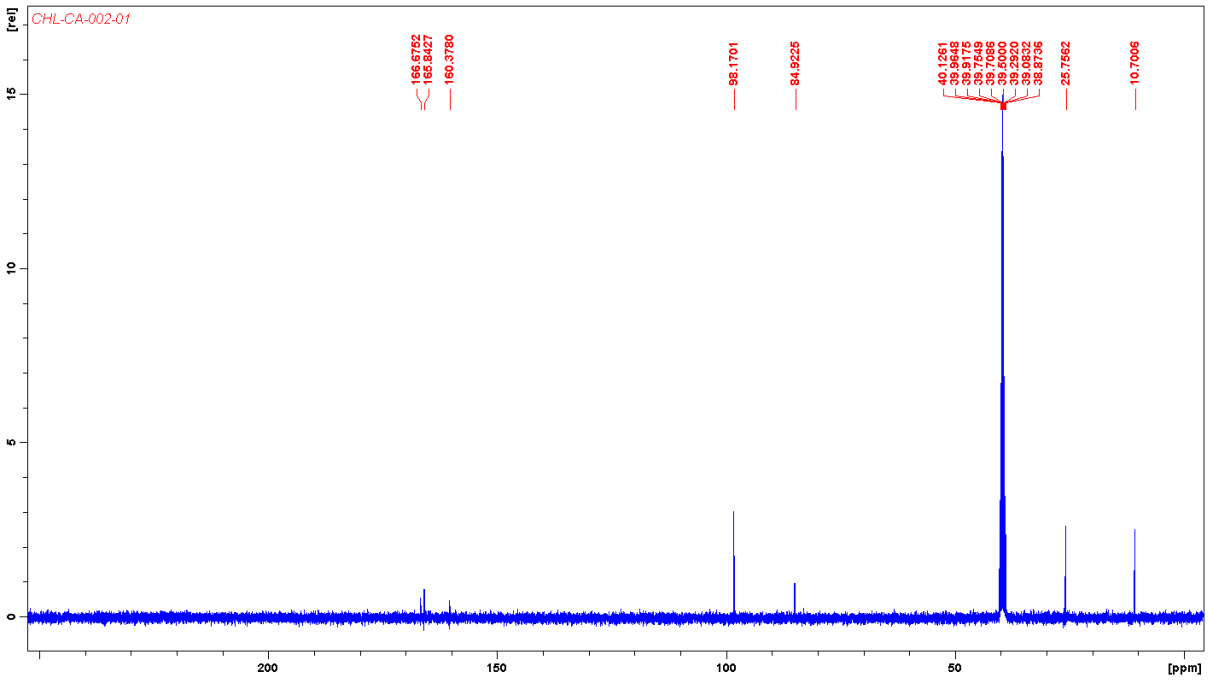

OH
O
O
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.03
1.00
1.00
2.13
3.19

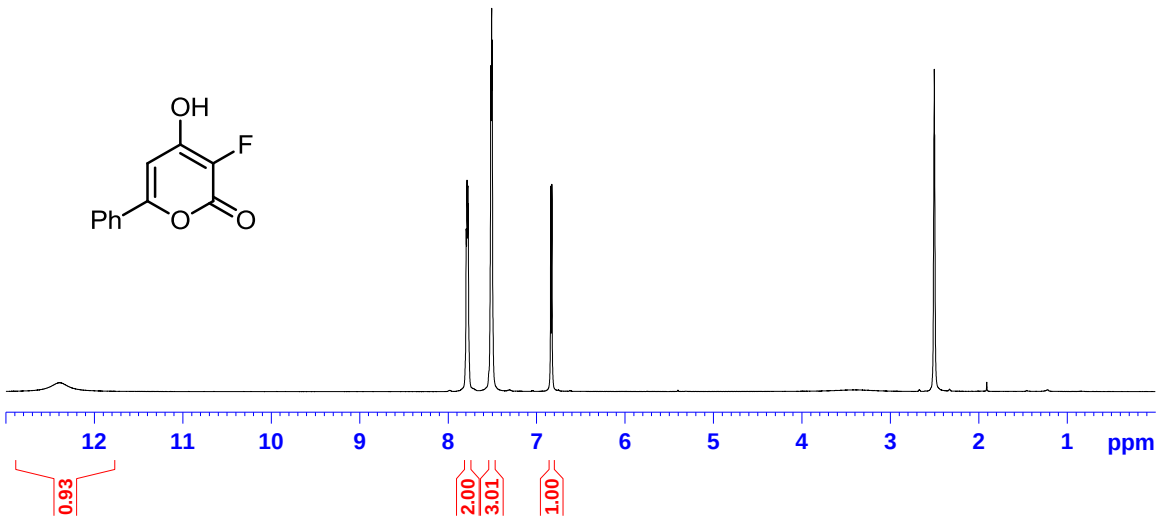

172.86
168.46
168.34
100.57
89.73
26.80
10.75
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

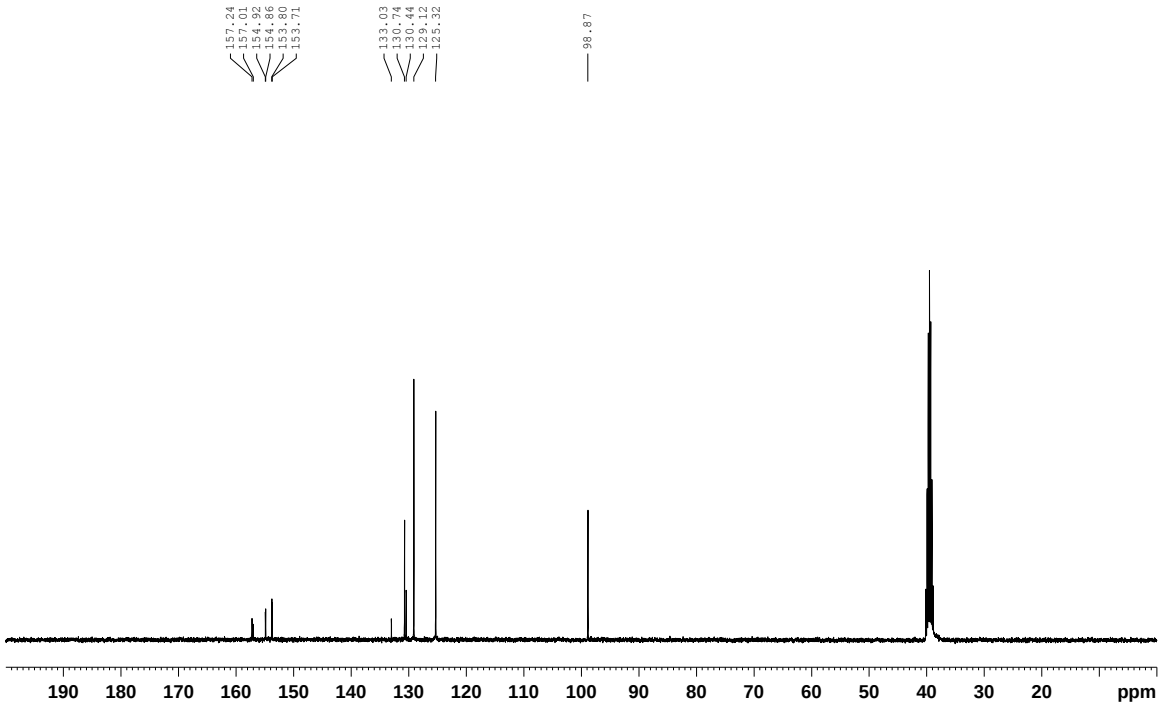

OH
O
O
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
0.47
2.18
3.10
3.01

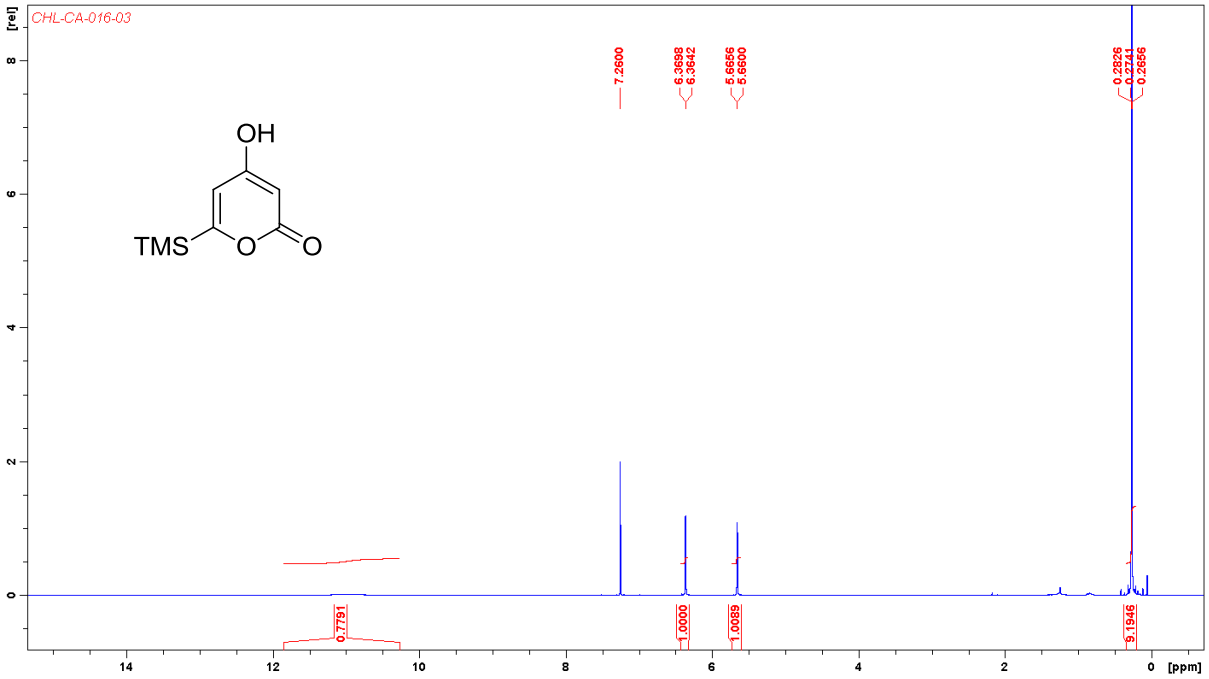

165.04
164.90
163.76
98.24
96.51
25.88
10.86
8.34
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

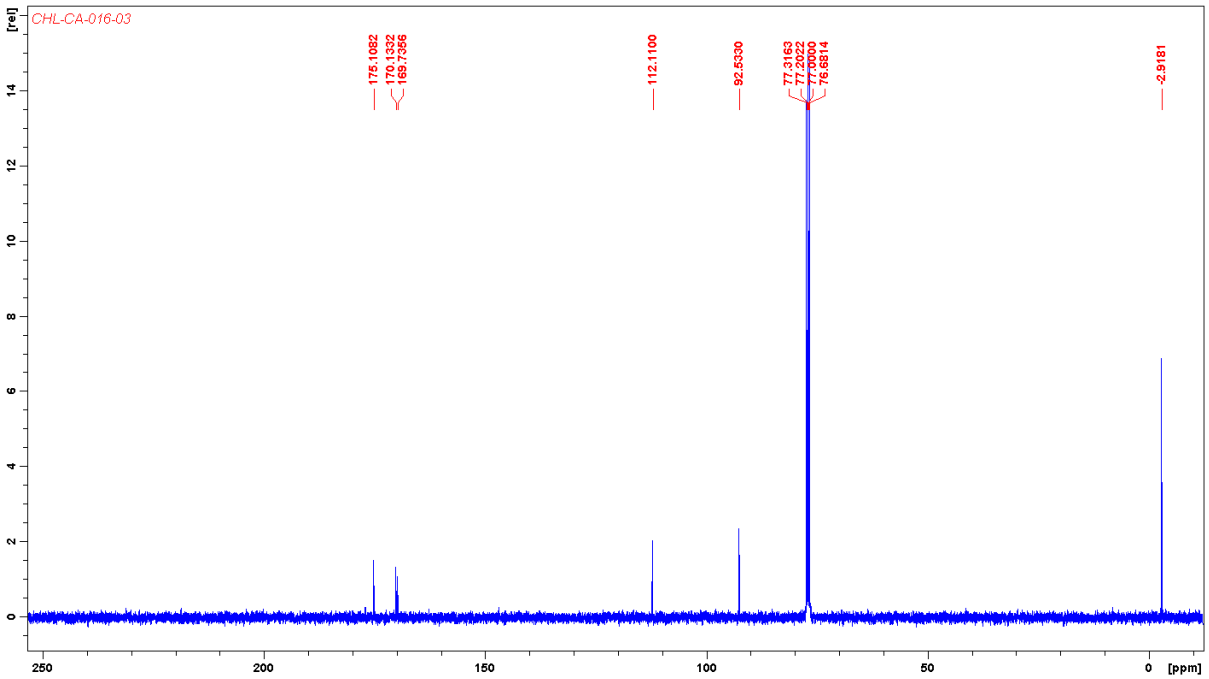

CHL-CA-002-01
[rel]
OH
Br
O
O
6.0868
6.0848
6.0828
2.5392
2.5226
2.5177
2.5091
2.5046
2.4999
2.4953
2.4904
2.4855
2.4809
2.4703
2.4682
2.4515
2.4495
1.9071
1.1312
1.1124
1.0938
0.5044
1.0039
1.0527
3.0000
[ppm]

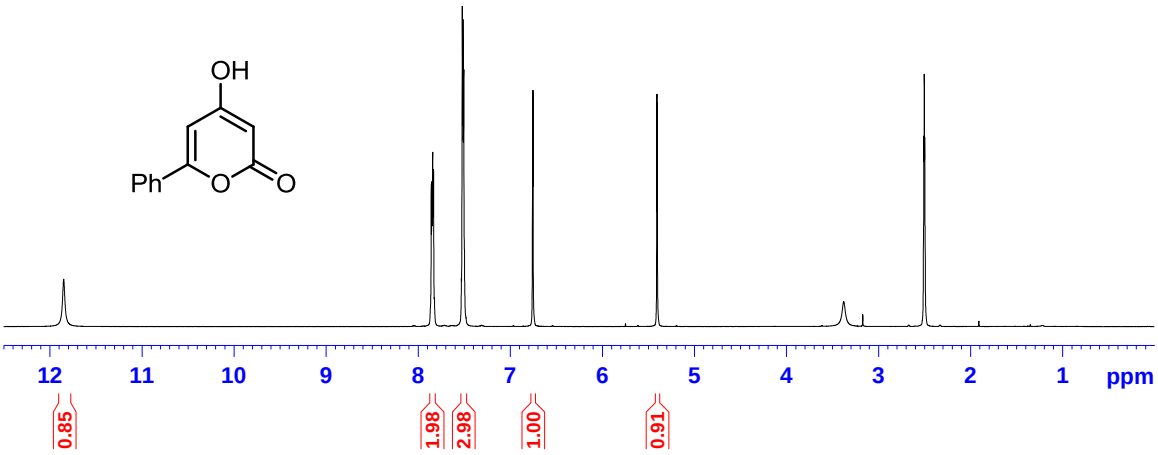

CHL-CA-002-01
[rel]
166.6762
165.8427
160.3780
98.1701
84.9225
40.1261
39.9648
39.9175
39.7648
39.7086
39.5000
39.2920
39.0832
38.8736
25.7562
10.7006
[ppm]

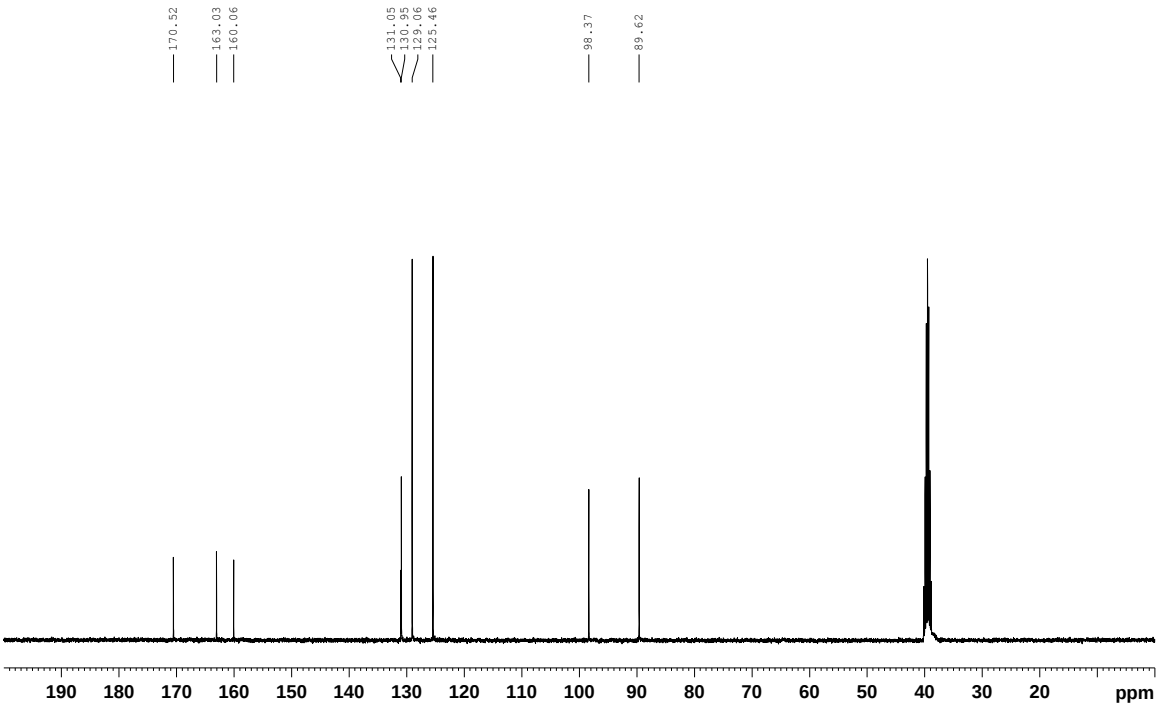

OH
F
Ph
O
O
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.93
2.00
3.01
1.00

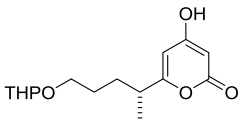

157.24
157.01
154.92
154.86
153.80
153.71
133.03
130.74
130.44
129.12
125.32
98.87
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

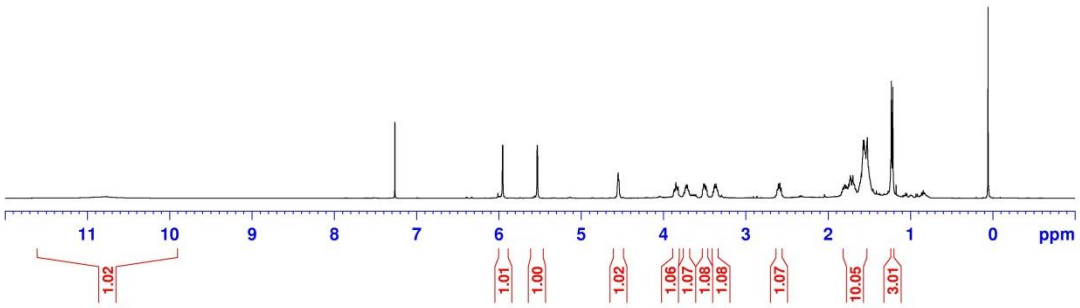

CHL-CA-016-03
[rel]
7.2600
6.3698
6.3642
5.6656
5.6600
0.2826
0.2741
0.2656
OH
TMS
O
O
0.7791
1.0000
1.0089
9.1946
[ppm]

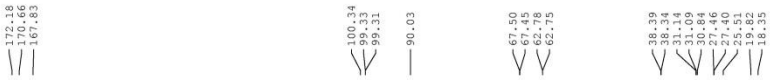

CHL-CA-016-03
[rel]
175.1082
170.1332
169.7356
112.1100
92.5330
77.3163
77.2022
77.0880
76.6814
-2.9181
[ppm]

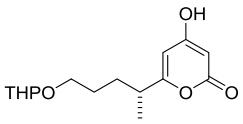

OH
Ph
O
O
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.85
1.98
2.98
1.00
0.91

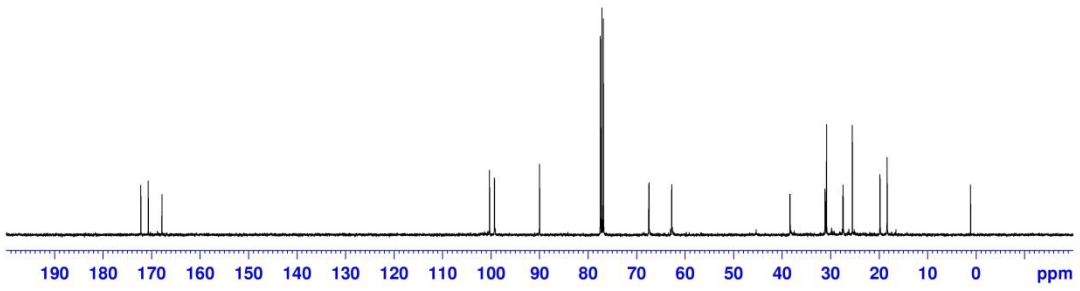

170.52
163.03
160.06
131.05
130.95
129.06
125.46
98.37
89.62
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

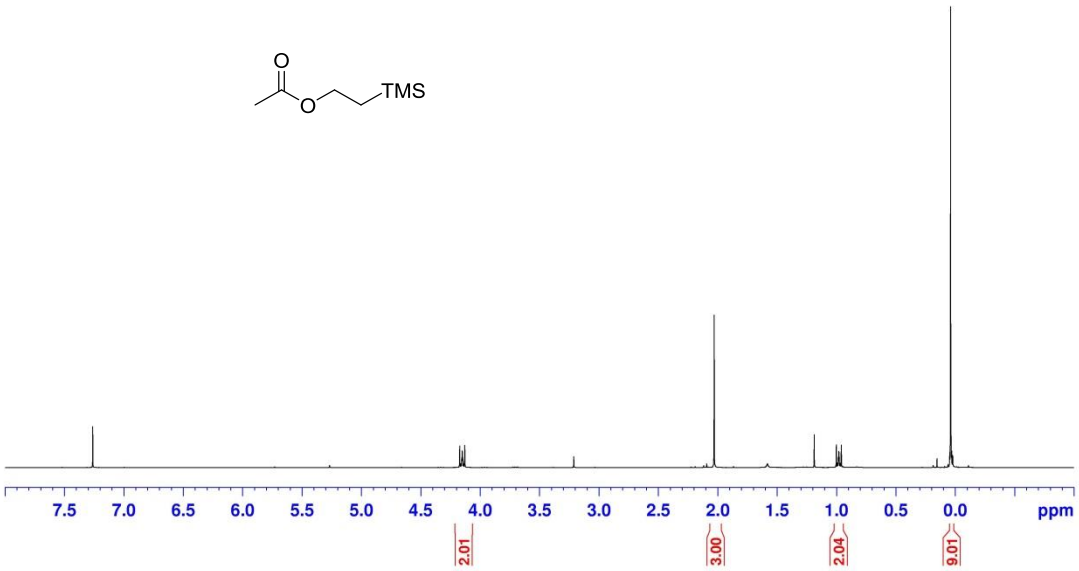

OH
THPO
O
O

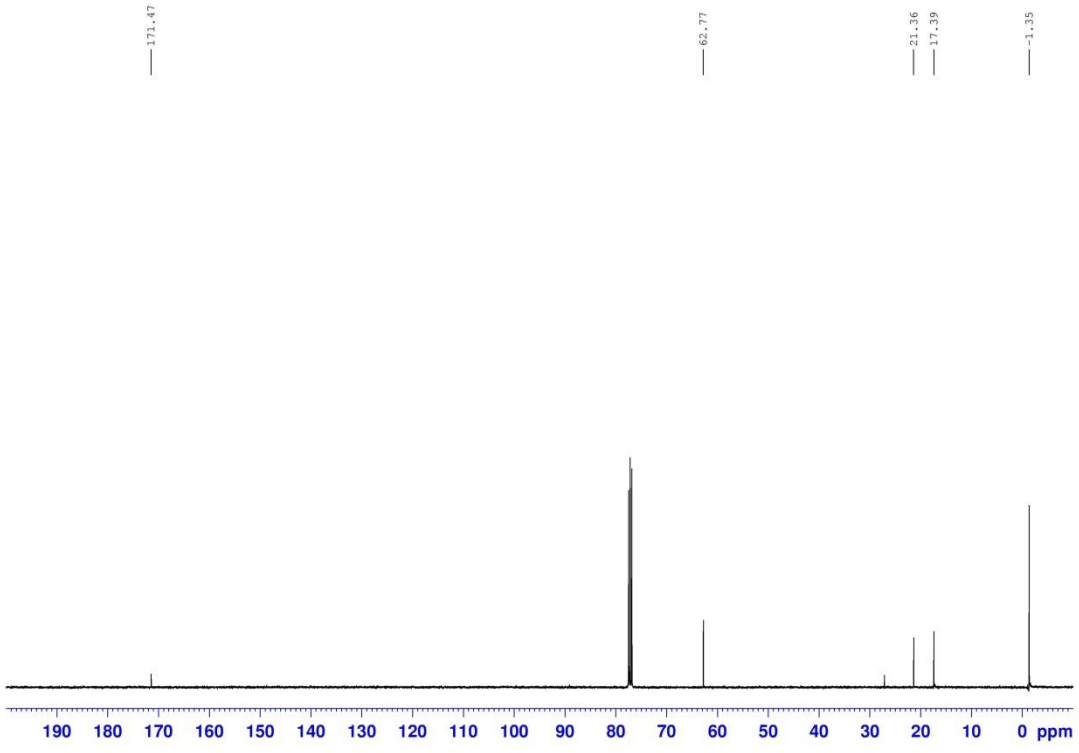

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.01
1.00
1.02
1.06
1.07
1.08
1.08
1.07
10.05
3.01

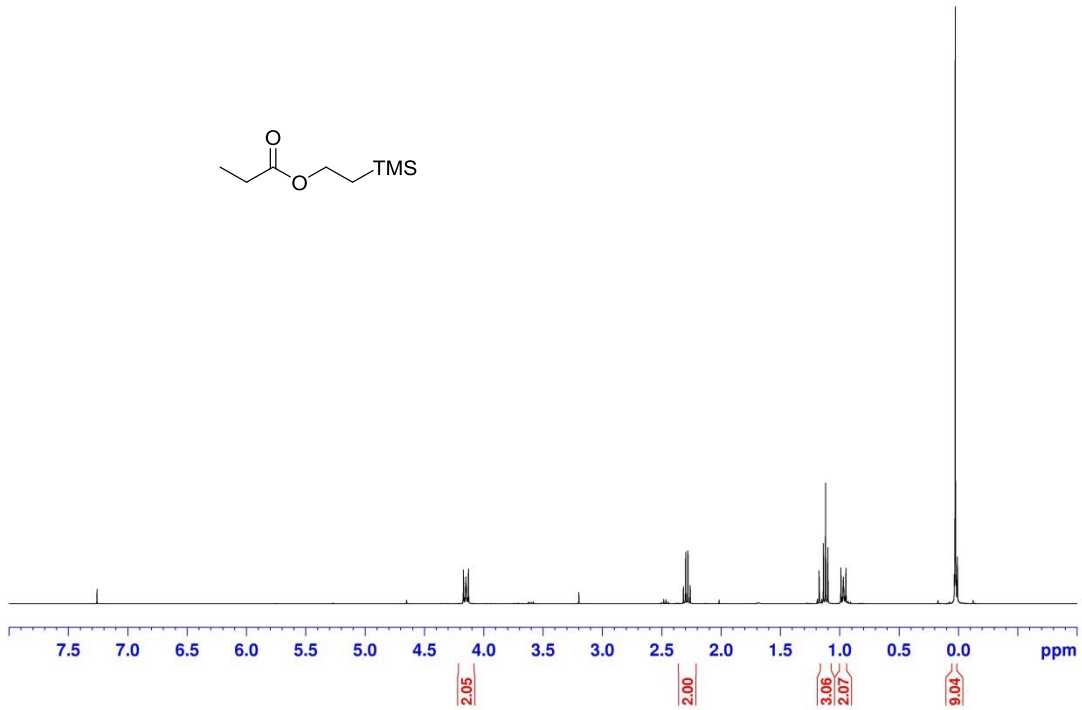

172.18
170.66
167.83
100.34
99.33
99.31
90.03
67.50
67.45
62.78
62.75
38.39
38.34
31.14
31.09
30.84
27.46
27.40
25.51
19.82
18.35

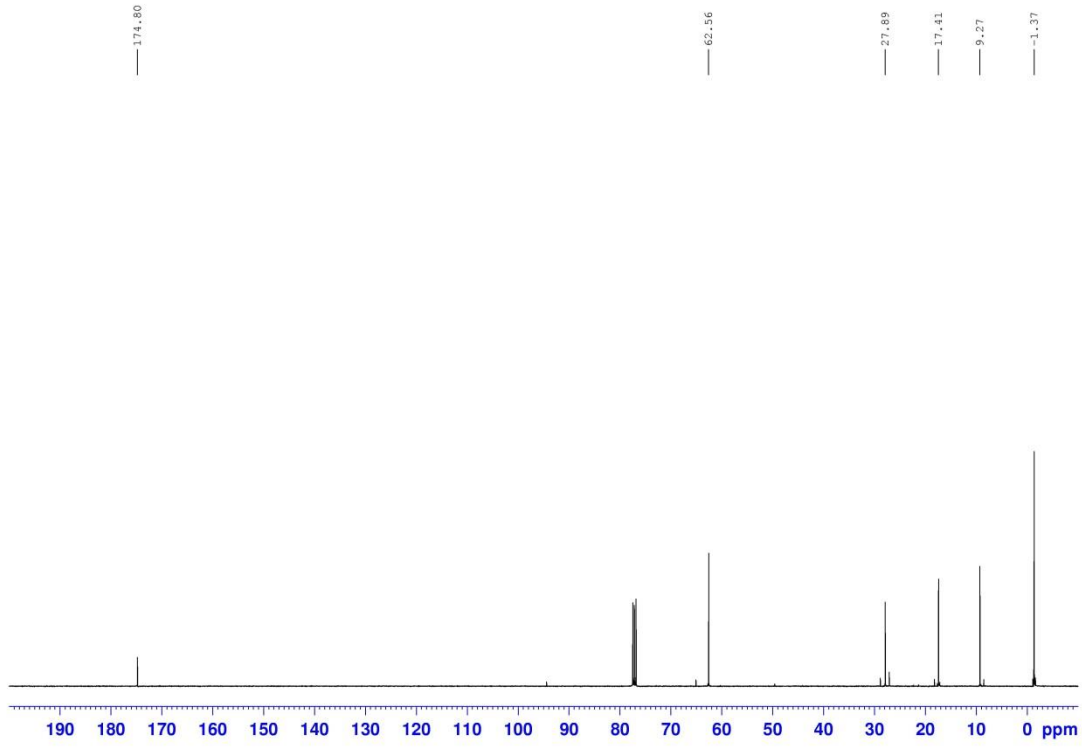

OH
THPO
O
O

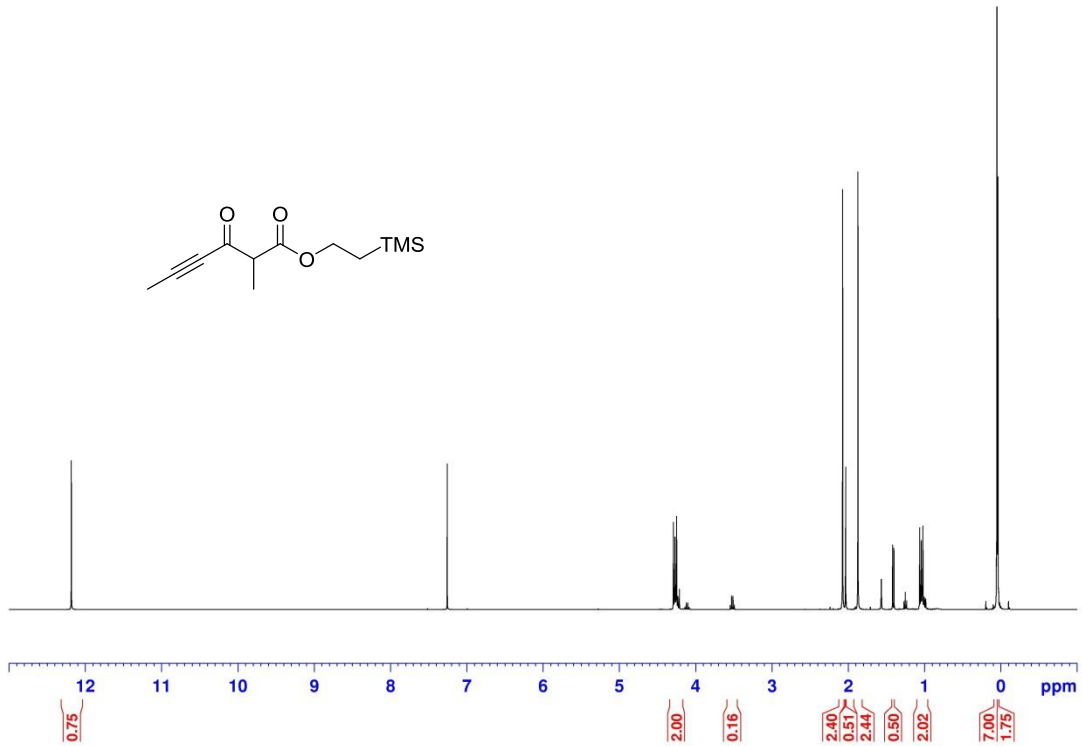

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

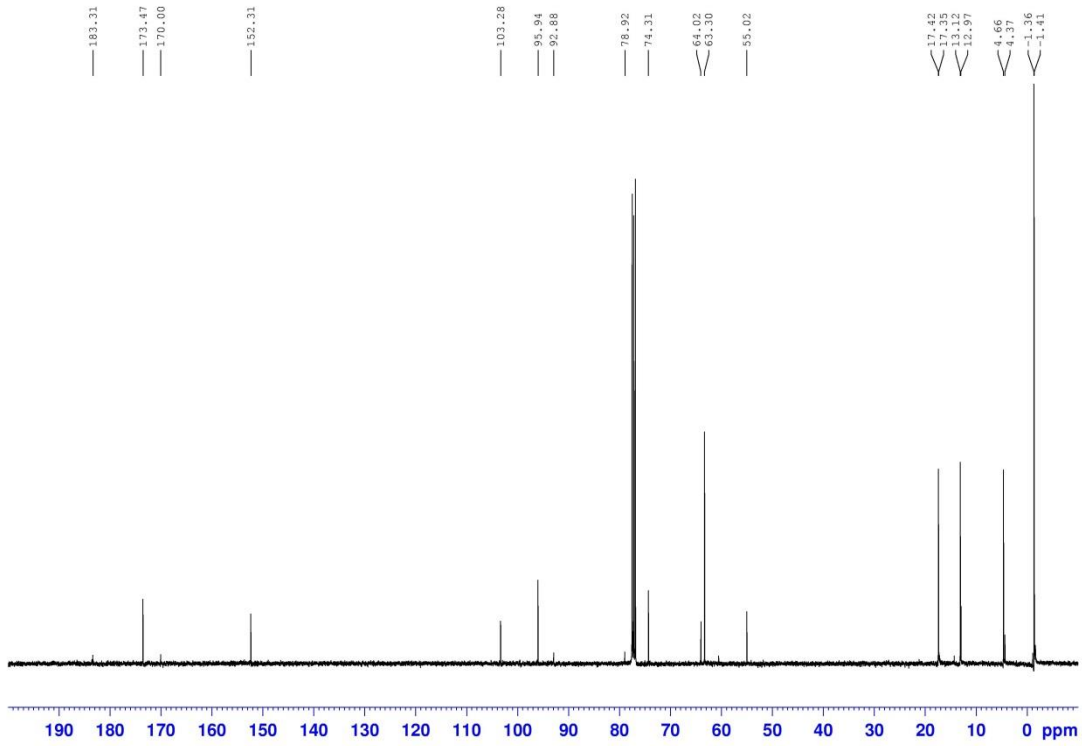

O
O
TMS
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
3.00
2.04
9.01

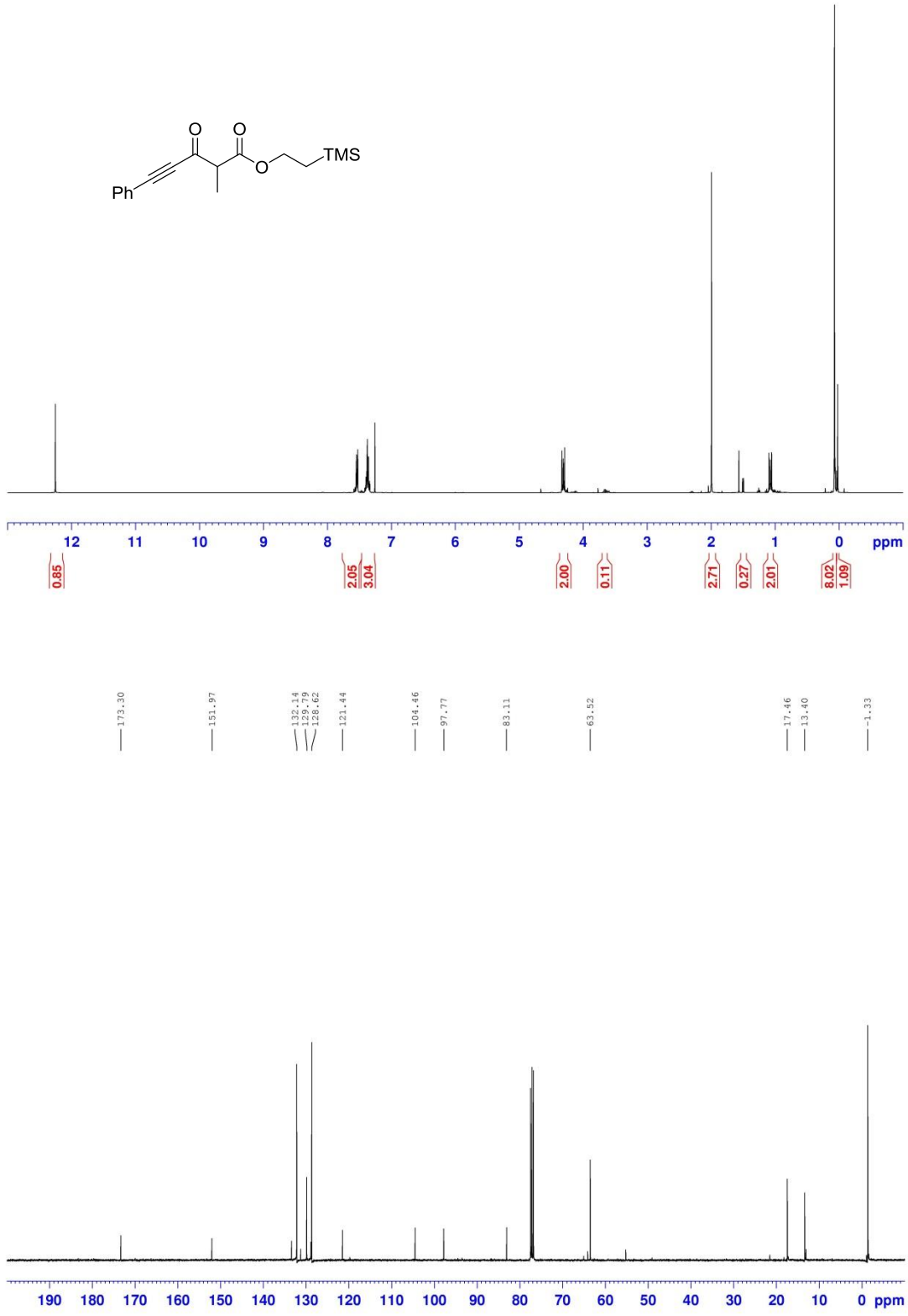

171.47
62.77
21.36
17.39
-1.35
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

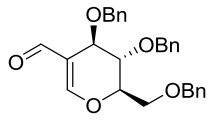

O
O
TMS
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05
2.00
3.06
2.07
9.04

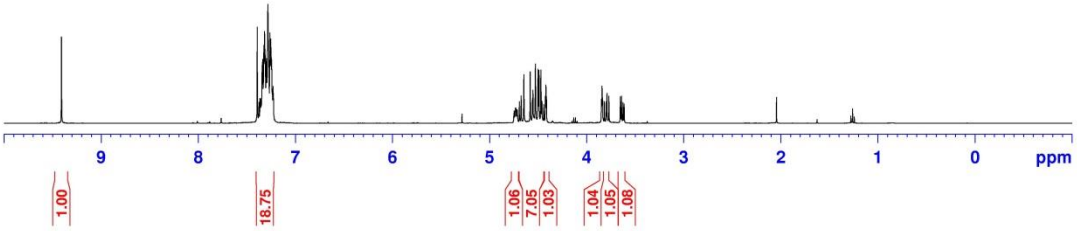

174.80
62.56
27.89
17.41
9.27
-1.37
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

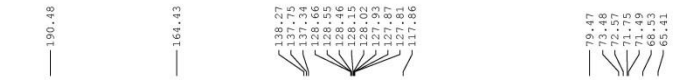

O
O
O
TMS
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.75
2.00
0.16
2.40
0.51
2.44
0.50
2.02
7.00
1.75

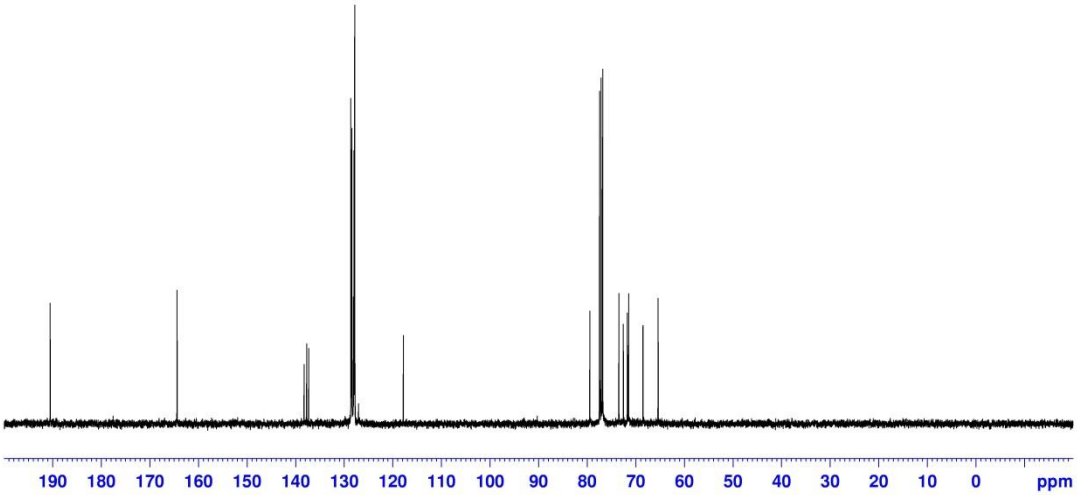

183.31
173.47
170.00
152.31
103.28
95.94
92.88
78.92
74.31
64.02
63.30
55.02
17.42
17.35
13.12
12.97
4.66
4.37
-1.36
-1.41
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

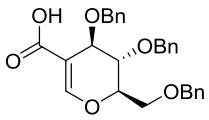

O
O
O
TMS
Ph
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.85
2.05
3.04
2.00
0.11
2.71
0.27
2.01
8.02
1.09
173.30
151.97
132.14
129.79
128.62
121.44
104.46
97.77
83.11
63.52
17.46
13.40
-1.33
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

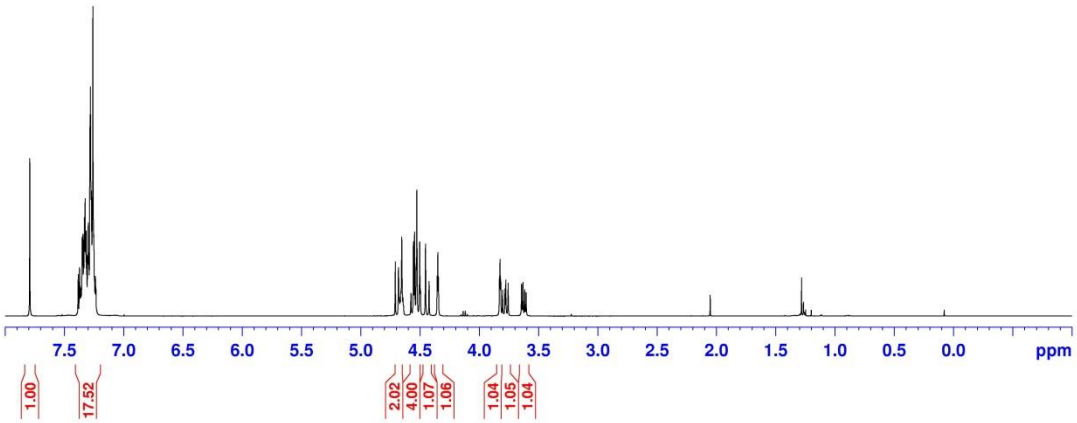

OBn
OBn
OBn
O
O

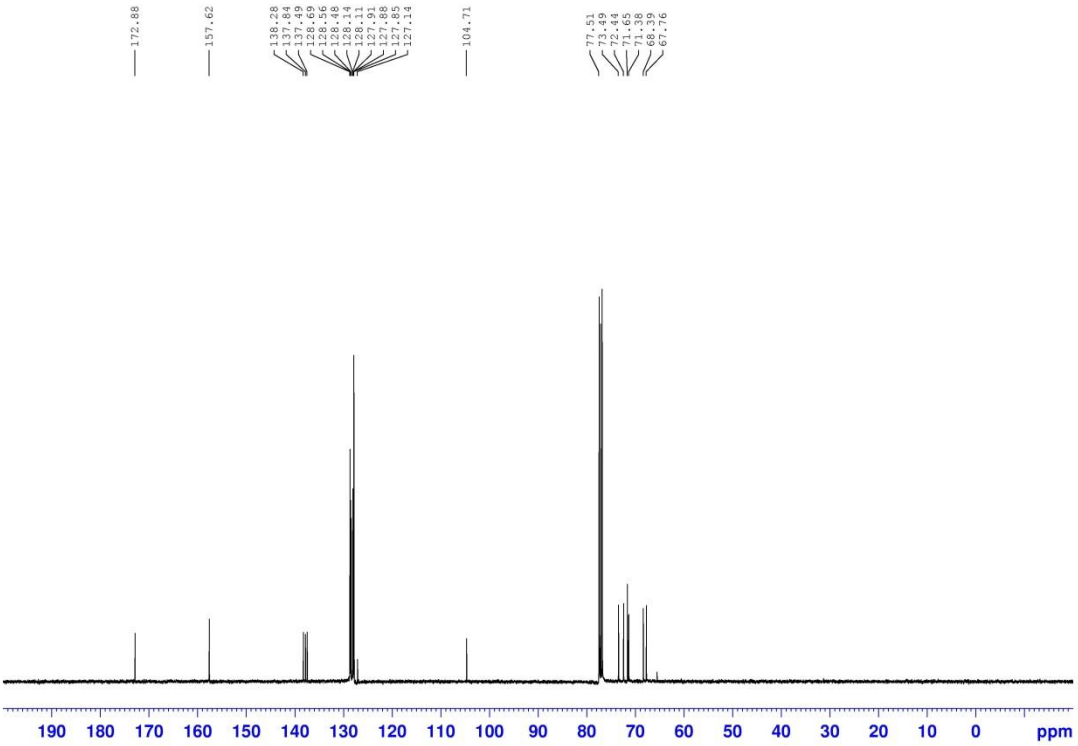

9
8
7
6
5
4
3
2
1
0
ppm
1.00
18.75
1.06
7.05
1.03
1.04
1.05
1.08

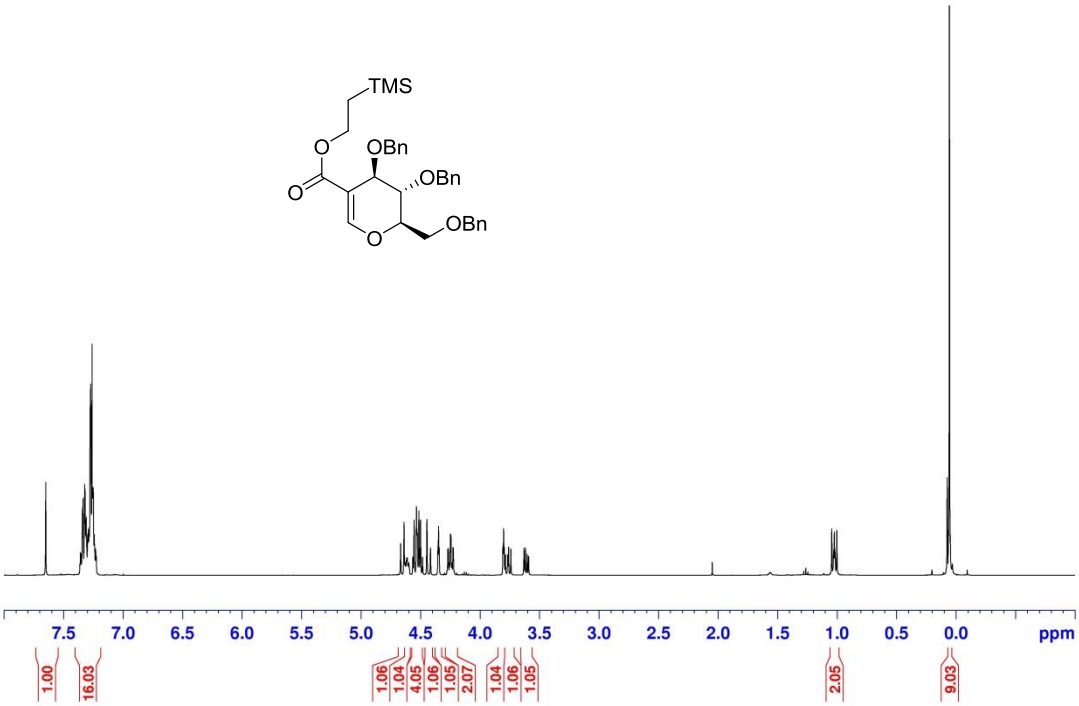

190.48
164.43
138.27
137.75
137.34
128.66
128.55
128.46
128.15
128.02
127.93
127.87
127.81
117.86
79.47
73.48
72.57
71.75
71.49
68.53
65.41

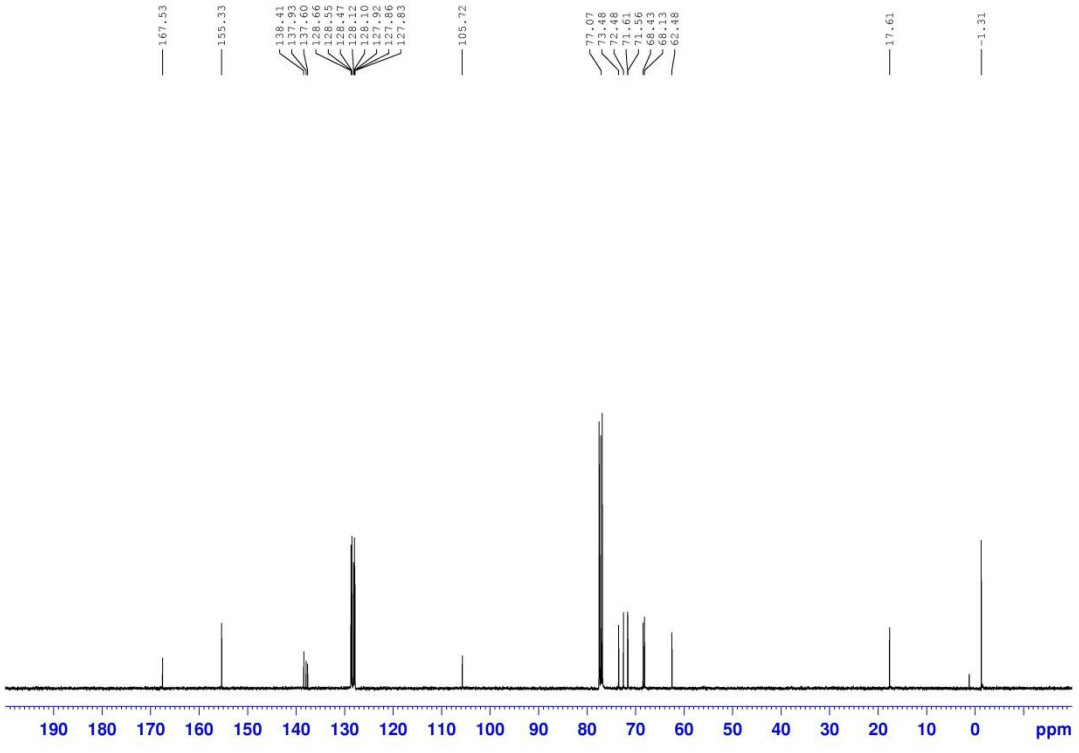

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

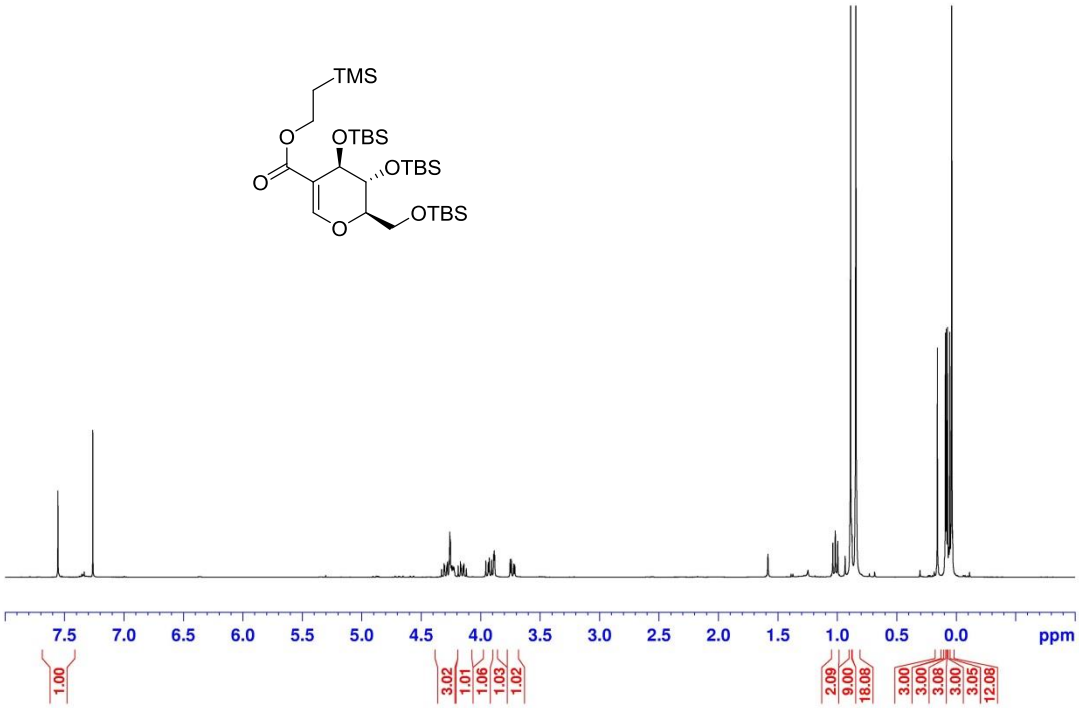

OH
OBn
OBn
OBn
O
O

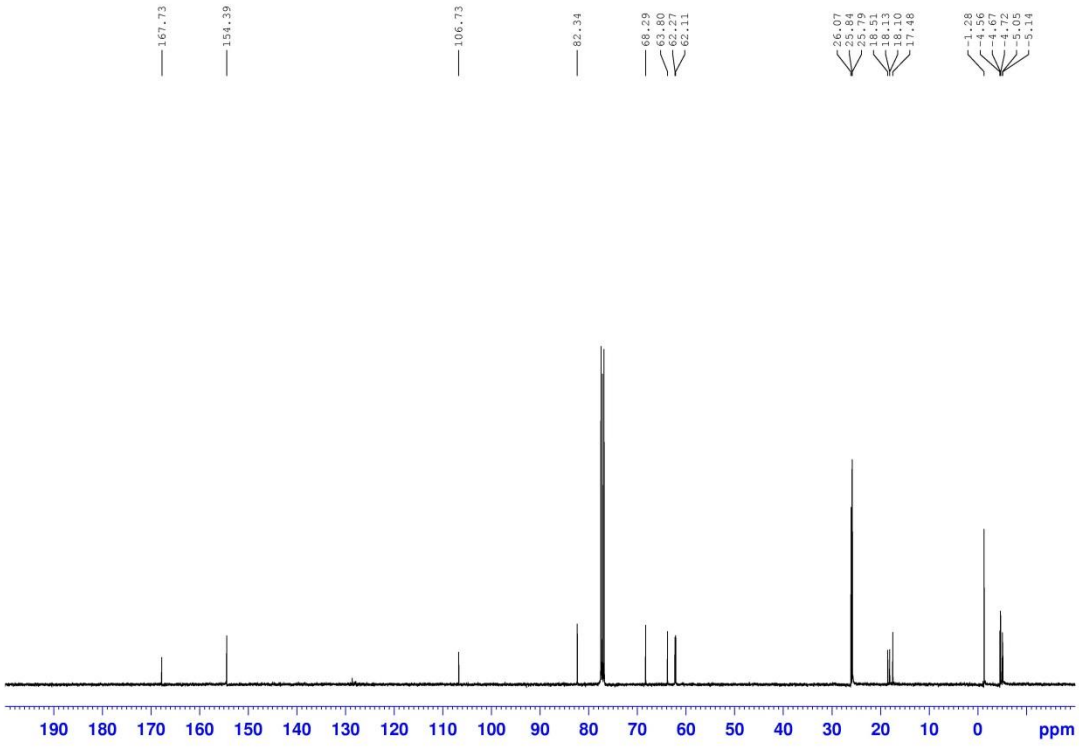

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
17.52
2.02
4.00
1.07
1.06
1.04
1.05
1.04

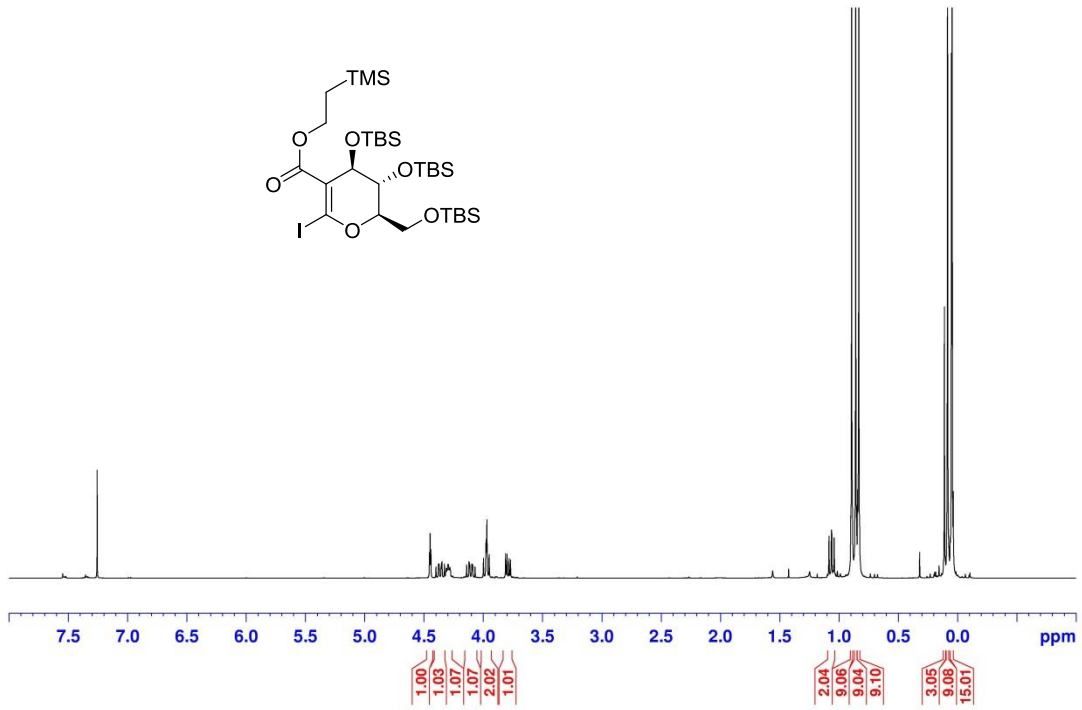

172.88
157.62
138.28
137.84
137.49
128.69
128.56
128.48
128.14
128.11
127.91
127.88
127.85
127.14
104.71
77.51
73.49
72.44
71.65
71.38
68.39
67.76
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

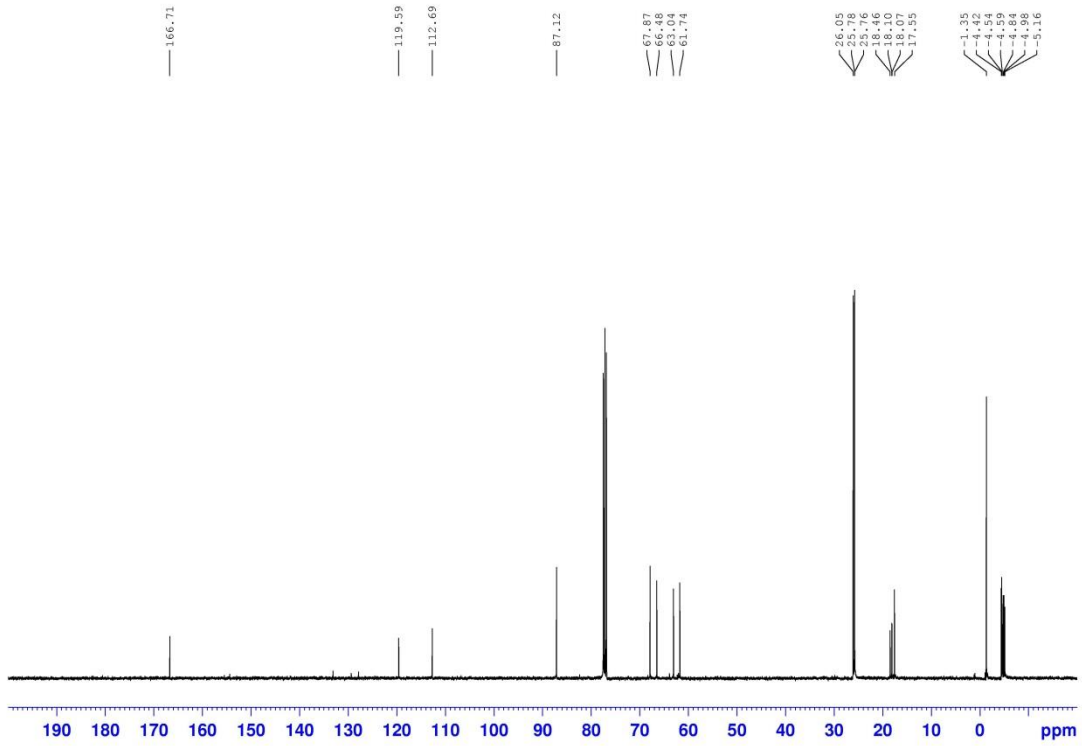

TMS
O
OBn
OBn
O
OBn
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
16.03
1.06
1.04
4.05
1.06
1.05
2.07
1.04
1.06
1.05
2.05
9.03

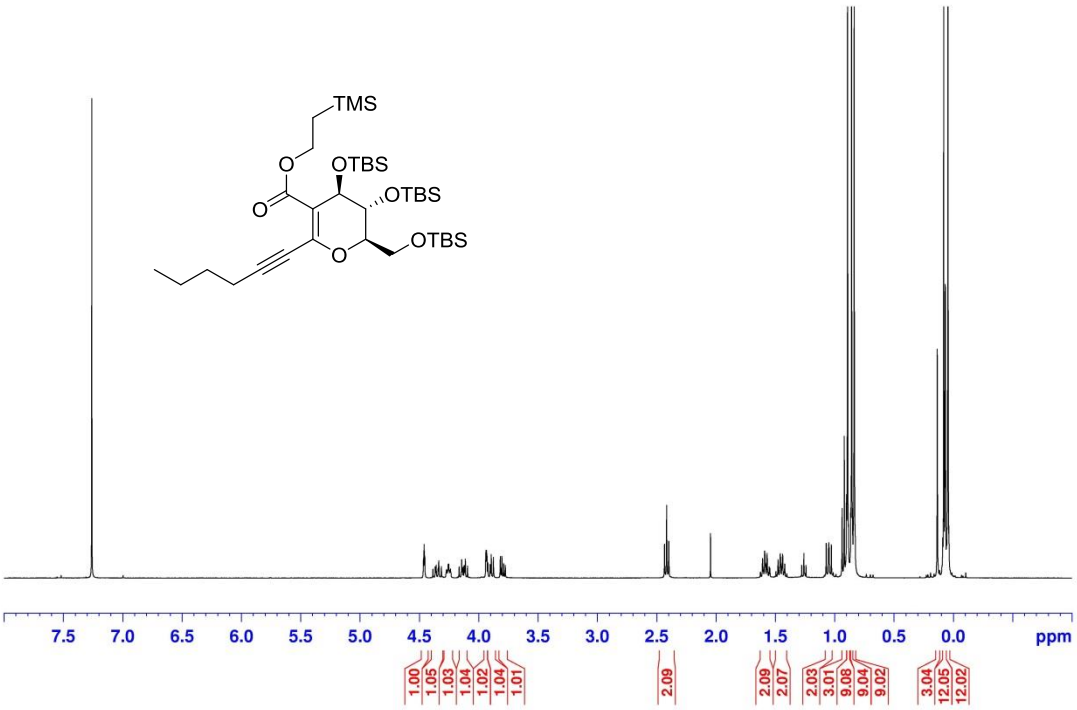

167.53
155.33
138.41
137.93
137.60
128.66
128.55
128.47
128.12
128.10
127.92
127.86
127.83
105.72
77.07
73.48
72.48
71.61
71.56
68.33
68.13
62.48
17.61
-1.31
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

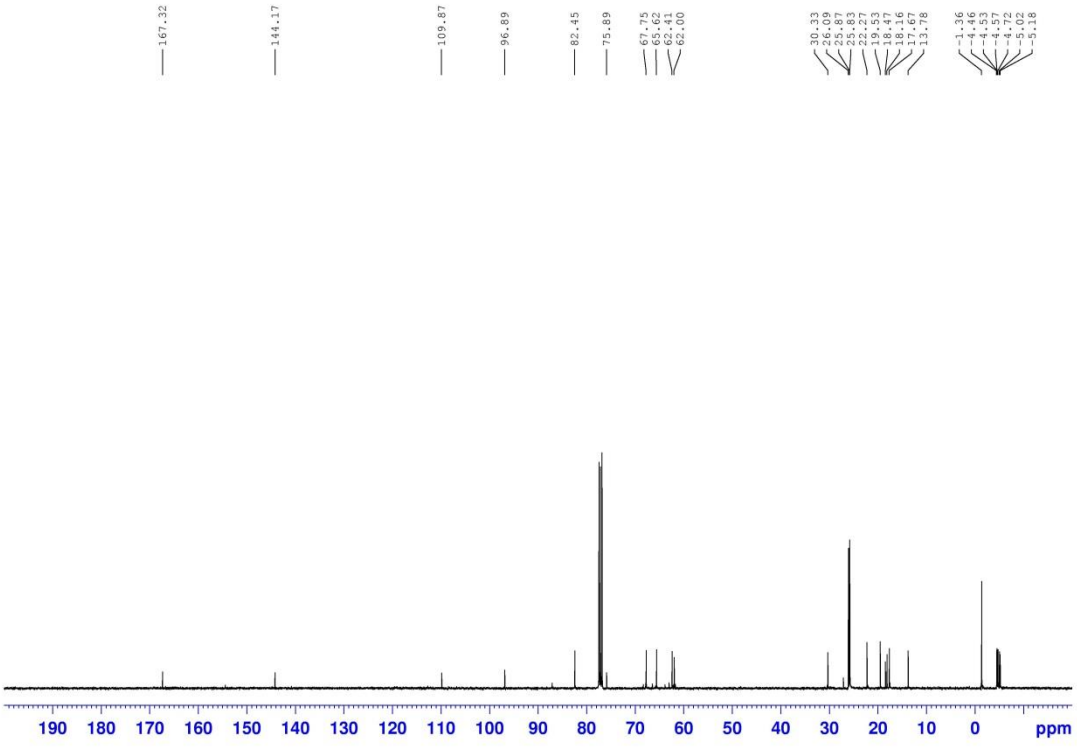

TMS
O
OTBS
O
OTBS
OTBS
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
3.02
1.01
1.06
1.03
1.02
2.09
9.00
18.08
3.00
3.00
3.08
3.00
3.05
12.08

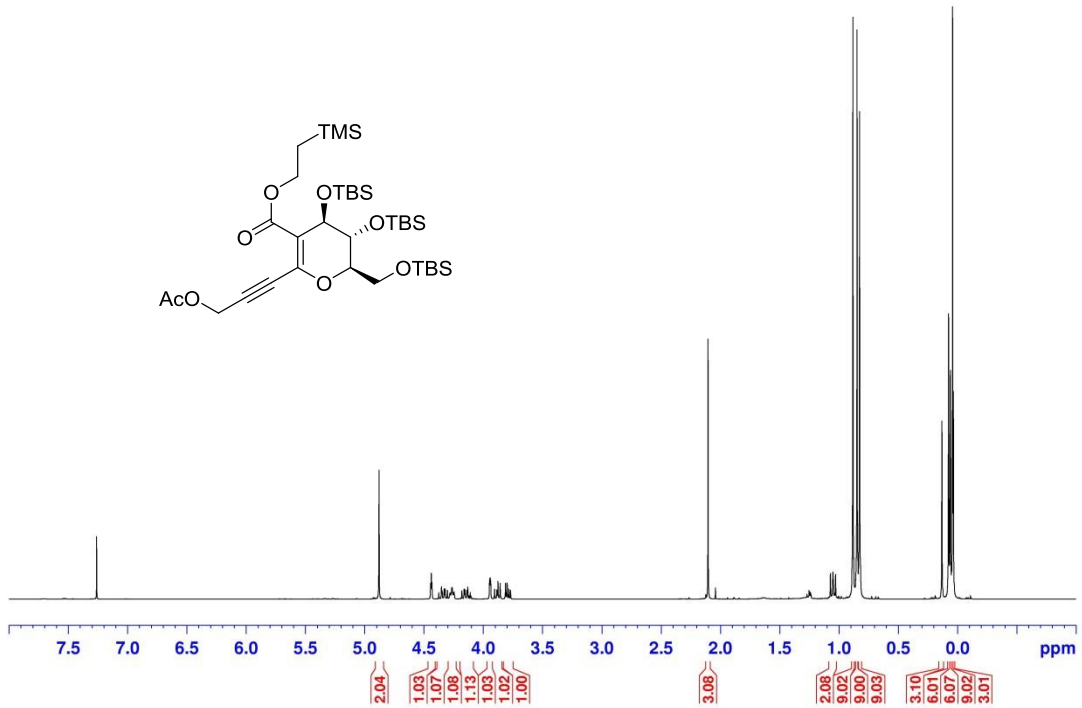

167.73
154.39
106.73
82.34
68.29
63.80
62.27
62.11
26.07
25.84
25.79
25.71
18.13
18.10
17.48
-1.28
-4.56
-4.67
-4.72
-5.05
-5.14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

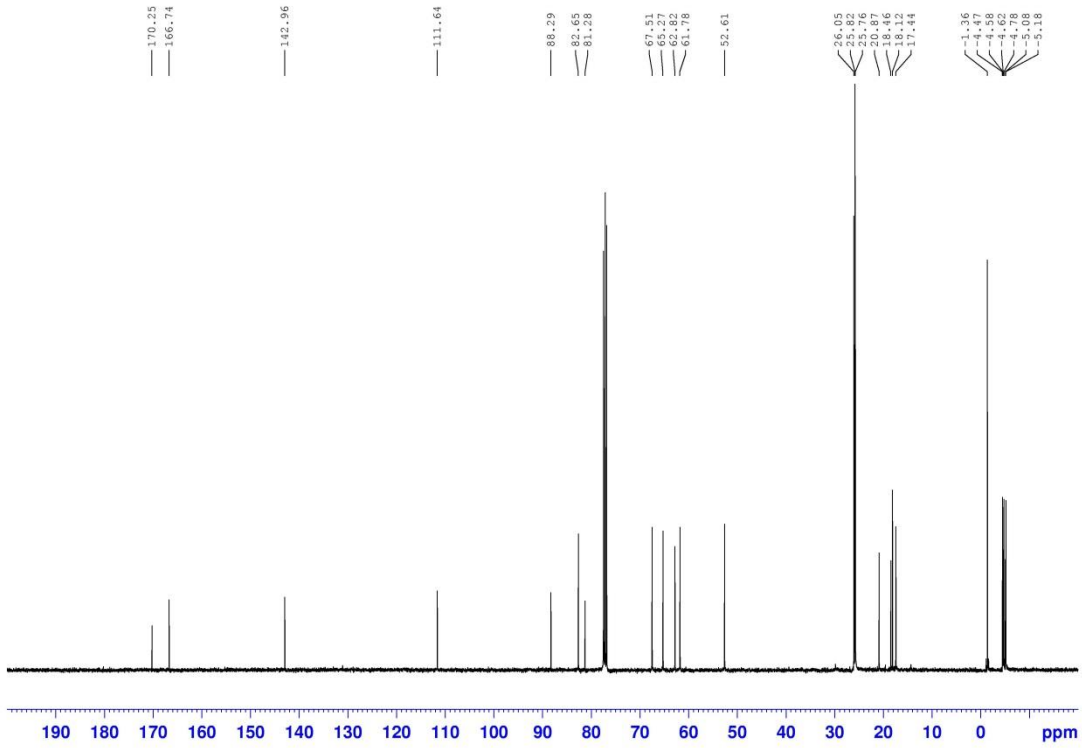

TMS
OTBS
OTBS
OTBS
O
O
O
I
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.03 1.07 1.07 2.02 1.01
2.04 9.06 9.04 9.10
3.05 9.08 15.01

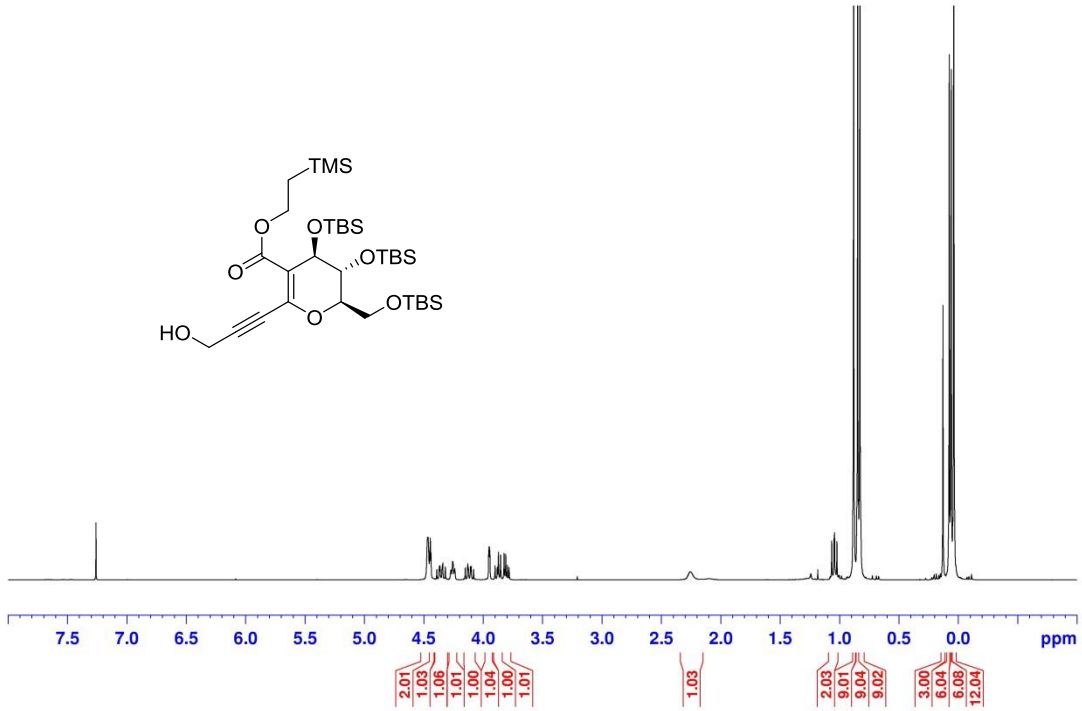

166.71
119.59
112.69
87.12
67.87
66.48
63.04
61.74
26.05
25.78
25.76
18.46
18.10
18.07
17.55
-1.35
-4.42
-4.54
-4.59
-4.84
-4.98
-5.16
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

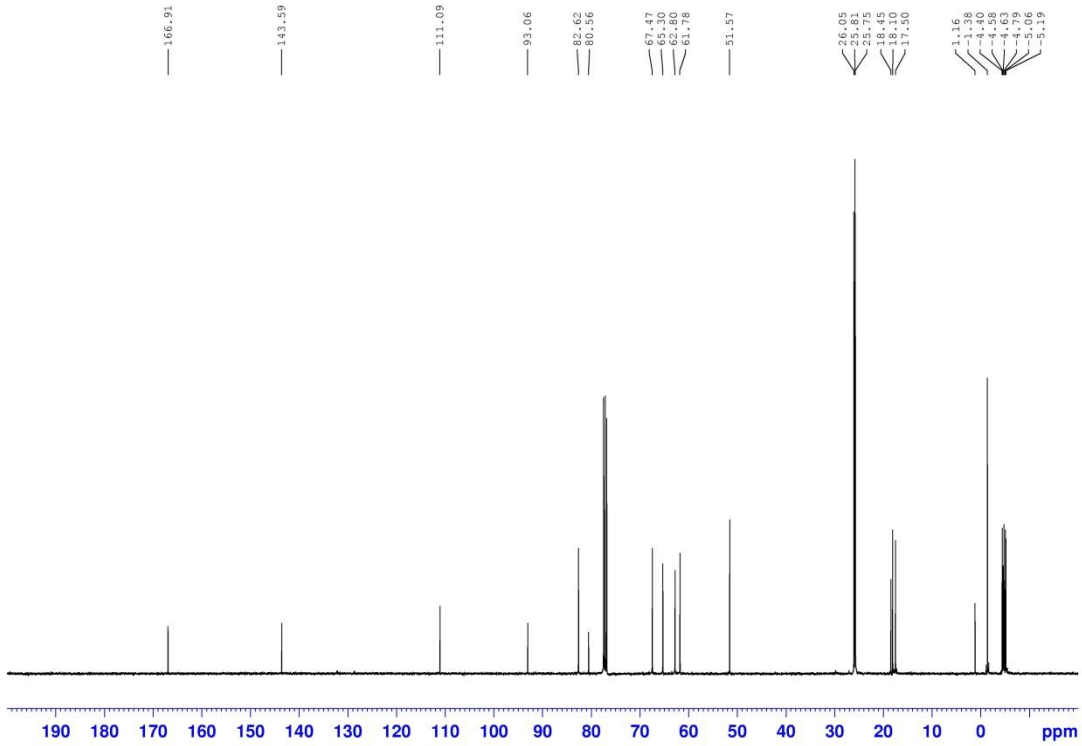

TMS
O
OTBS
O
OTBS
OTBS
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.05 1.03 1.04 1.02 1.04 1.01 2.09 2.09 2.07 2.03 3.01 9.08 9.04 9.02 3.04 12.05 12.02

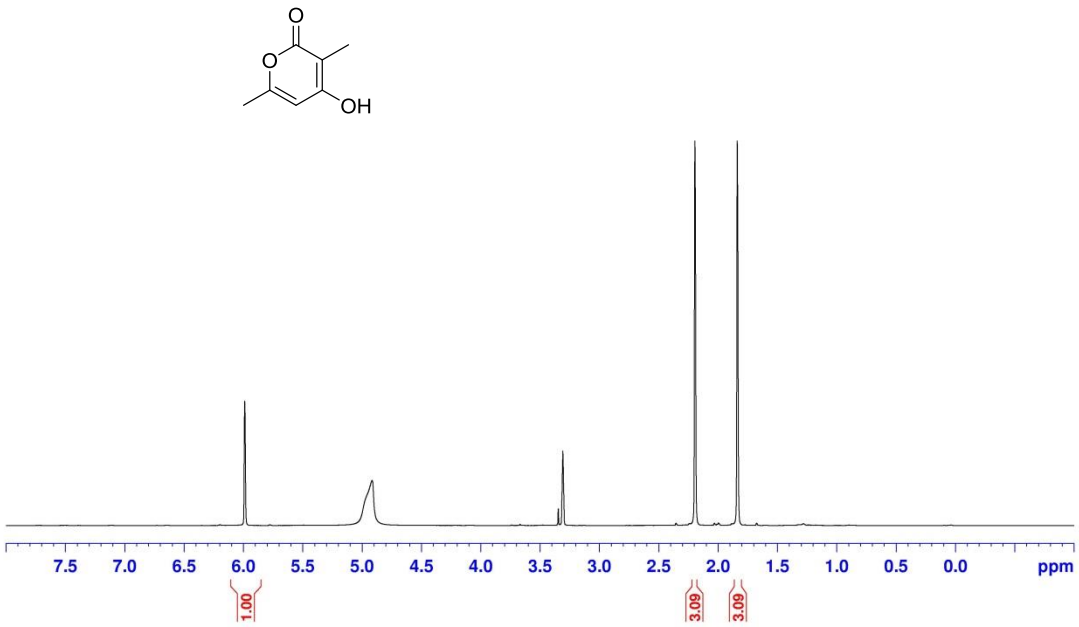

167.32
144.17
109.87
96.89
82.45
75.89
67.75
65.62
62.41
62.00
30.33
26.09
25.87
25.83
22.27
19.53
18.47
18.16
17.67
13.78
-1.36
-4.46
-4.53
-4.57
-4.72
-5.02
-5.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

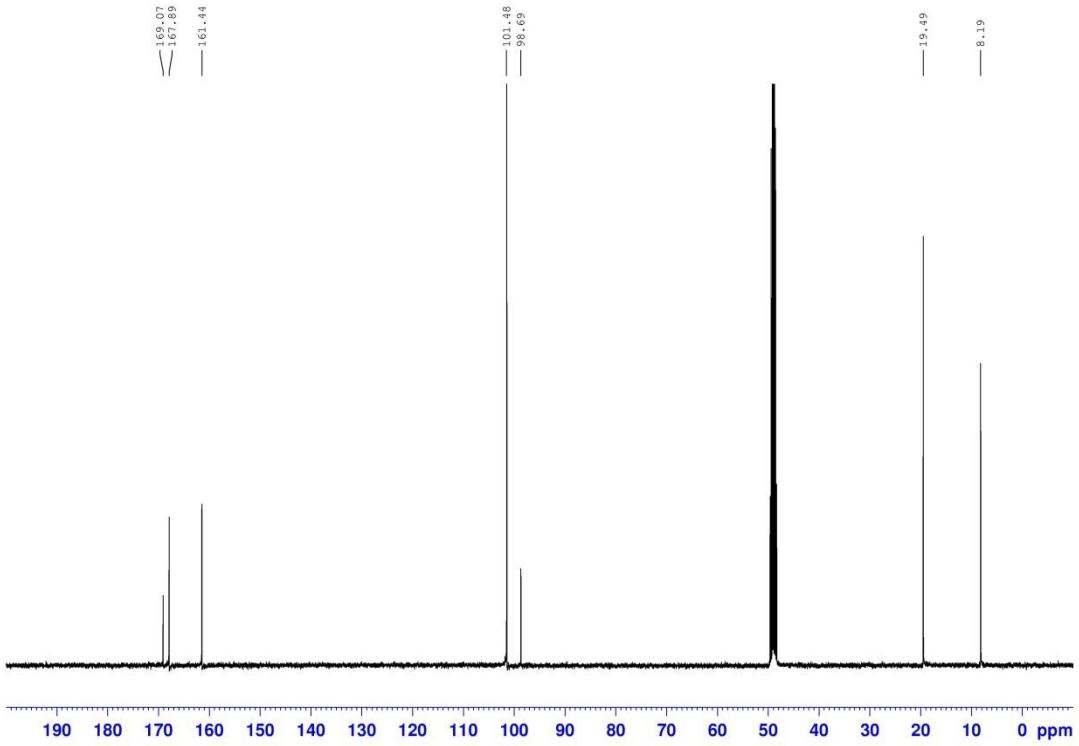

TMS
O
OTBS
O
OTBS
OTBS
O
AcO
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.04 1.03 1.07 1.08 1.13 1.03 1.02 1.00 3.08 2.08 9.02 9.00 9.03 3.10 6.01 6.07 9.02 3.01

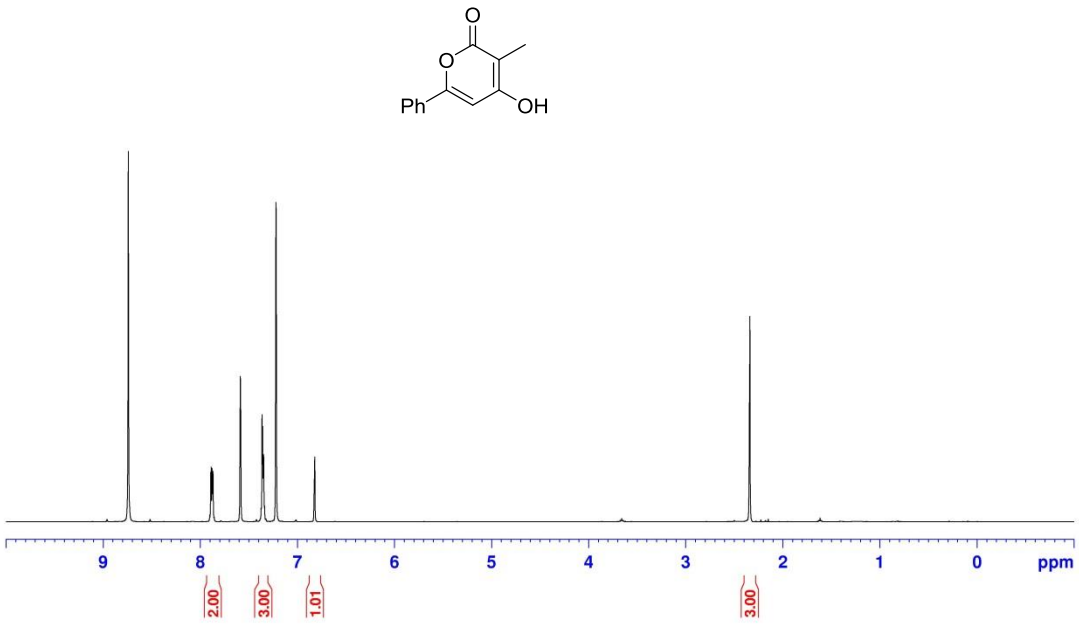

170.25
166.74
142.96
111.64
88.29
82.65
81.28
67.51
65.27
62.82
61.78
52.61
26.05
25.72
25.56
20.87
18.46
18.12
17.44
-1.36
-4.47
-4.88
-4.62
-4.78
-5.08
-5.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

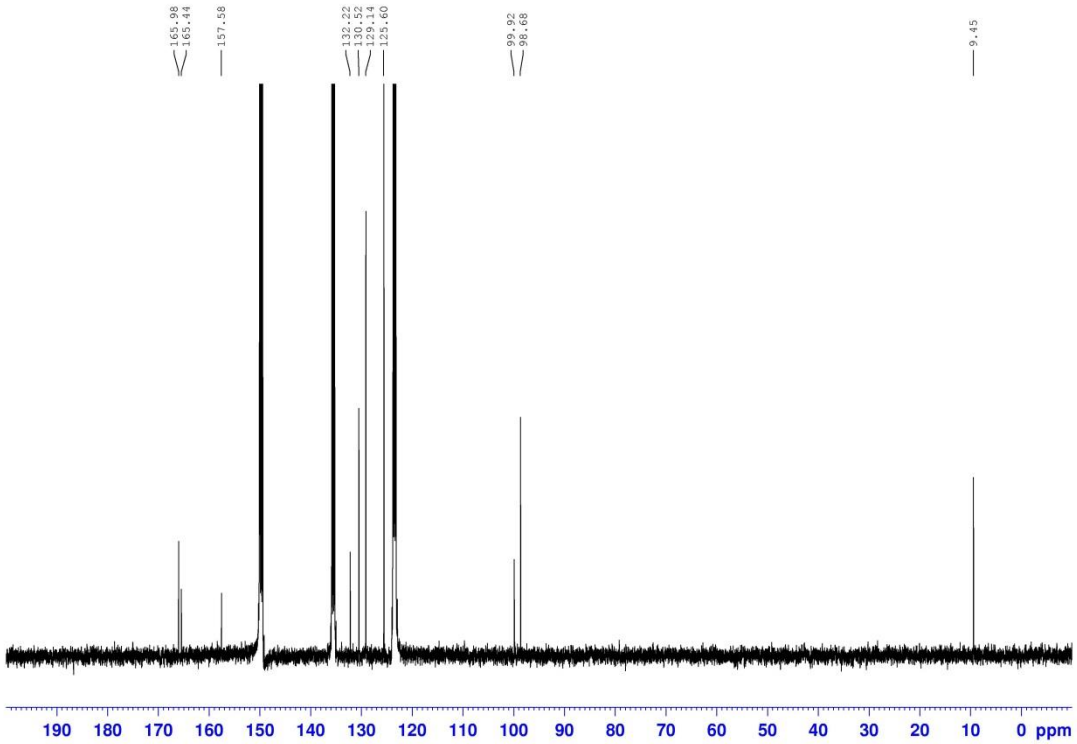

TMS
O
OTBS
OTBS
O
OTBS
O
HO
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01 1.03 1.06 1.01 1.00 1.04 1.00 1.01
1.03
2.03 9.01 9.04 9.02
3.00 6.04 6.08 12.04

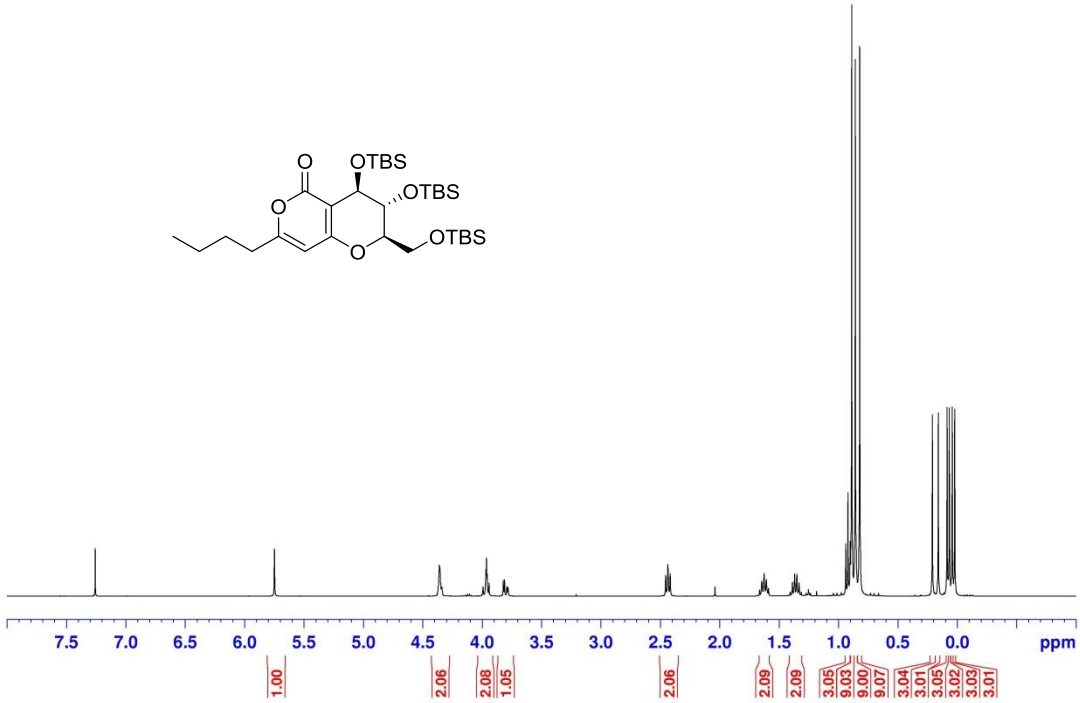

166.91
143.59
111.09
93.06
82.62
80.56
67.47
65.30
62.80
61.78
51.57
26.05
25.81
25.75
18.45
18.10
17.50
1.16
-1.38
-4.10
-4.58
-4.63
-4.79
-5.06
-5.19
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

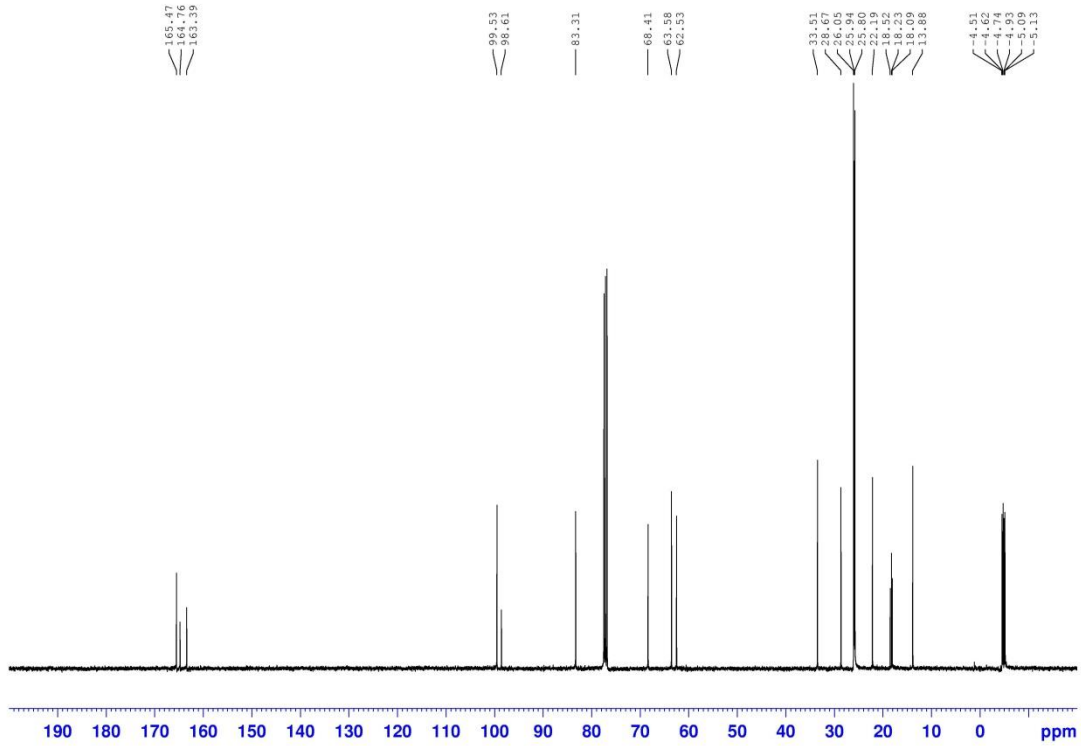

O
O
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
3.09
3.09

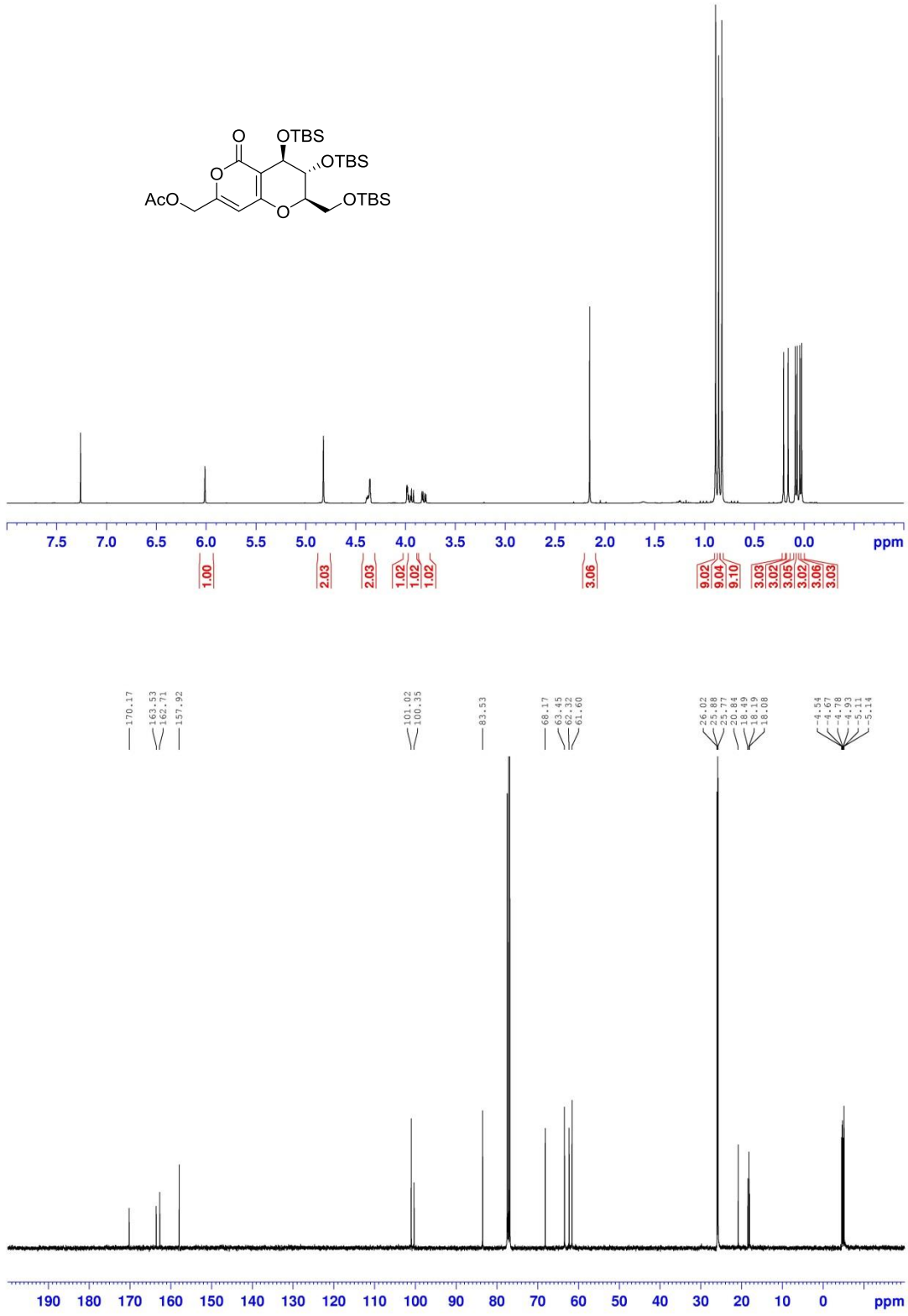

169.07
167.89
161.44
101.48
98.69
19.49
8.19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

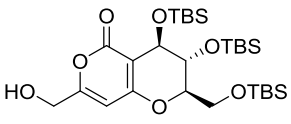

O
O
Ph
OH
9
8
7
6
5
4
3
2
1
0
ppm
2.00
3.00
1.01
3.00

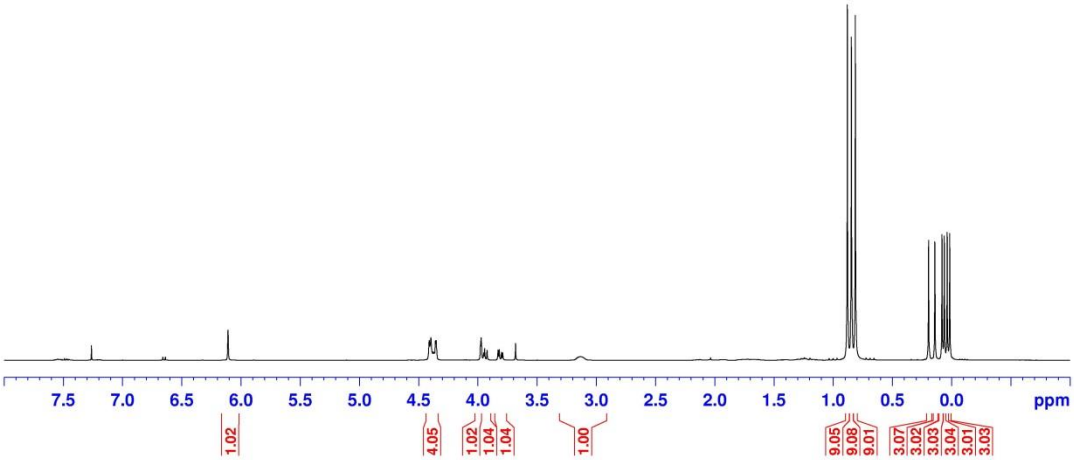

165.98
165.44
157.58
132.22
130.52
129.14
125.60
99.92
98.68
9.45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


O
OTBS
OTBS
O
OTBS
O
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 ppm
1.00 2.06 2.08 1.05 2.06 2.09 2.09 3.05 9.03 9.00 9.07 3.04 3.01 3.05 3.02 3.03 3.01


165.47
164.76
163.39
99.53
98.61
83.31
68.41
63.58
62.53
33.51
28.67
26.05
25.84
25.80
22.19
18.52
18.23
18.09
18.09
13.88
-4.51
-4.62
-4.74
-4.93
-5.09
-5.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OTBS
OTBS
OTBS
AcO
O
O
O
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 ppm
1.00 2.03 2.03 1.02 1.02 1.02 3.06 9.02 9.04 9.10 3.03 3.02 3.05 3.02 3.06 3.03
170.17 163.53 162.71 157.92 101.02 100.35 83.53 68.17 63.45 62.32 61.60 26.02 25.98 25.77 20.84 18.49 18.19 18.08 -4.54 -4.67 -4.78 -4.93 -5.11 -5.14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
OTBS
OTBS
O
HO
O
OTBS


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 ppm
1.02
4.05
1.02
1.04
1.04
1.00
9.05
9.08
9.01
3.07
3.02
3.03
3.04
3.01
3.03


164.33
163.53
163.18
99.49
99.17
83.46
68.14
63.42
62.43
61.11
25.99
25.84
25.73
18.44
18.15
18.04
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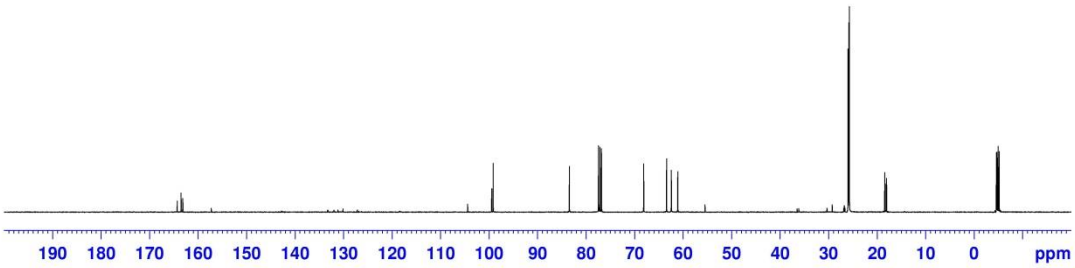
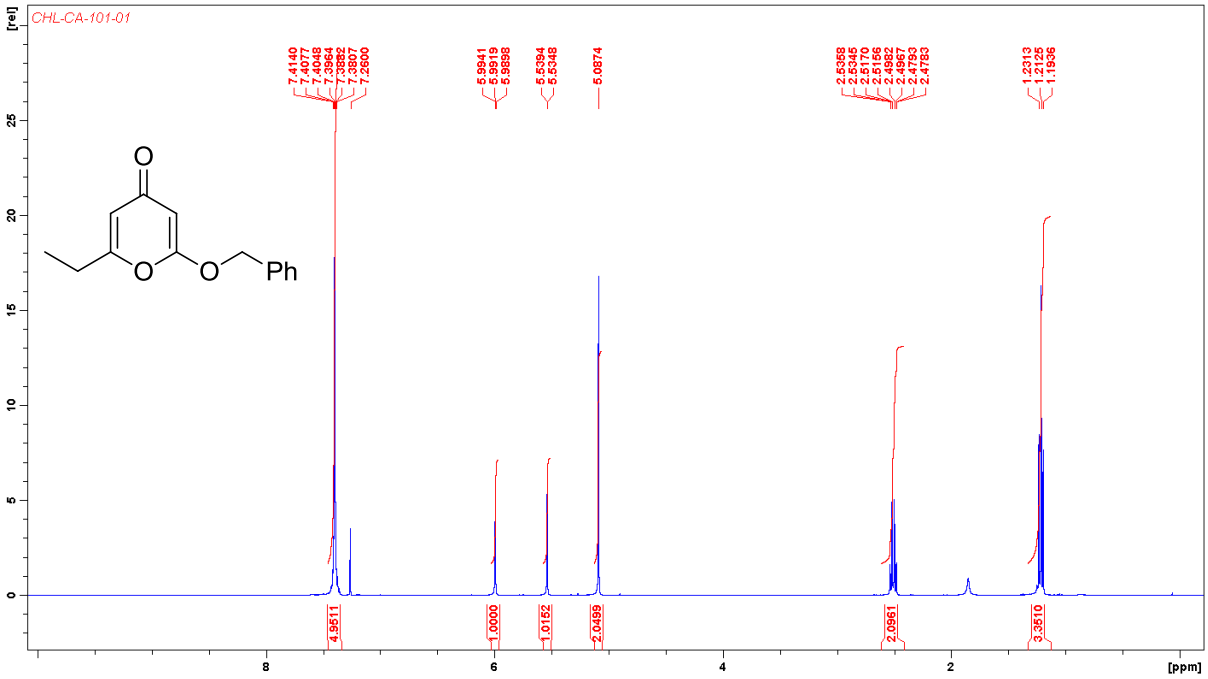
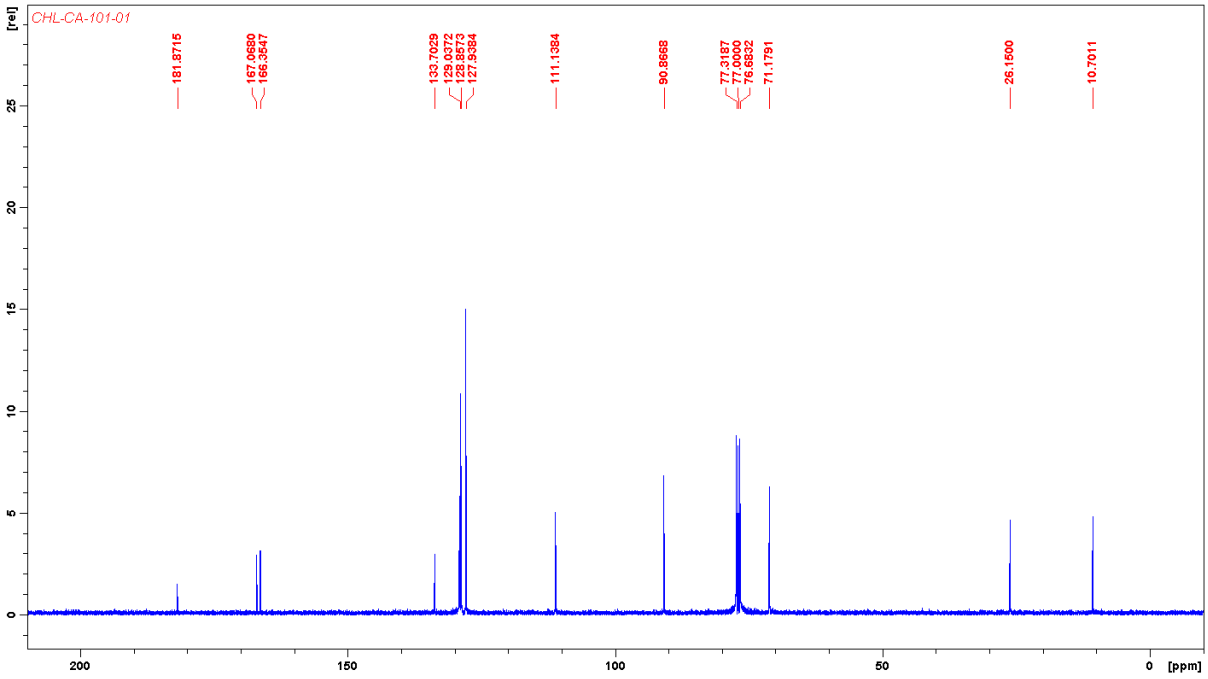
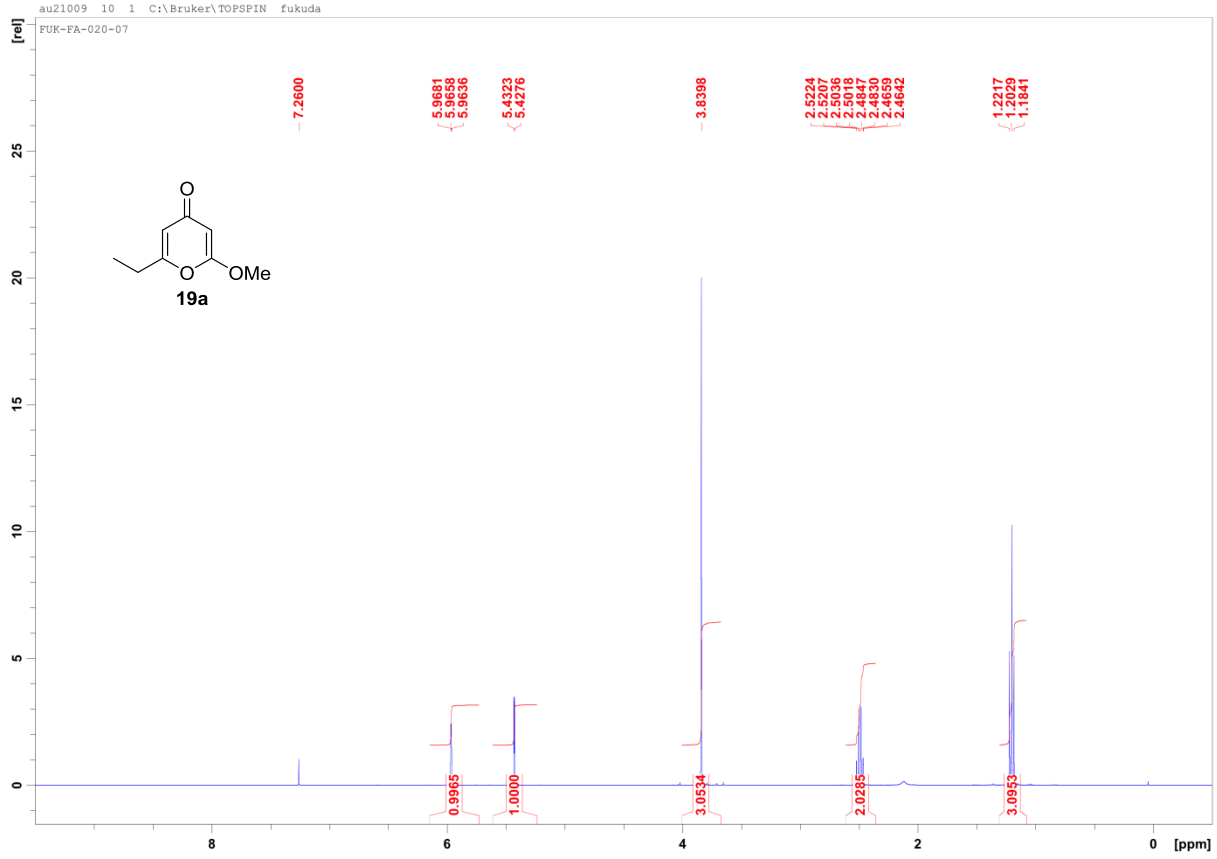
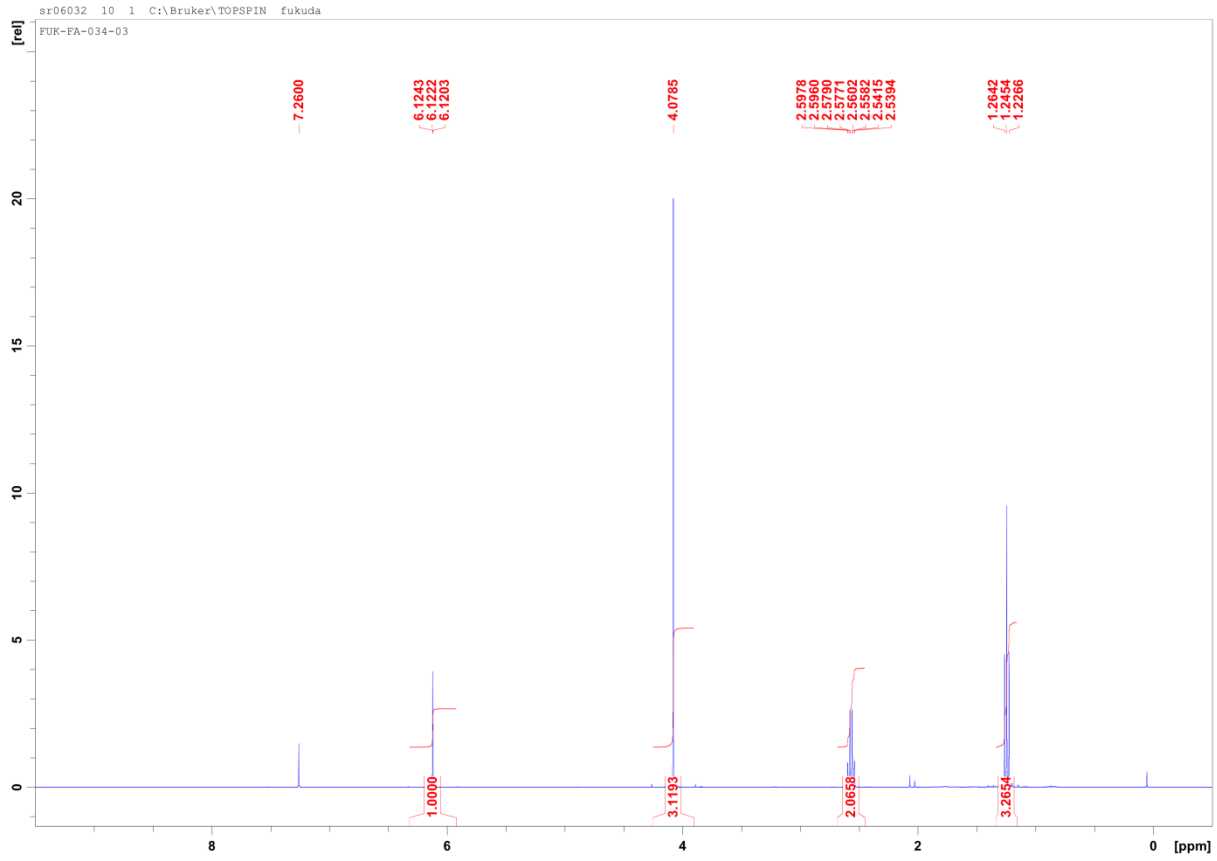
-4.70
-4.80
-4.95
-5.10
-5.18

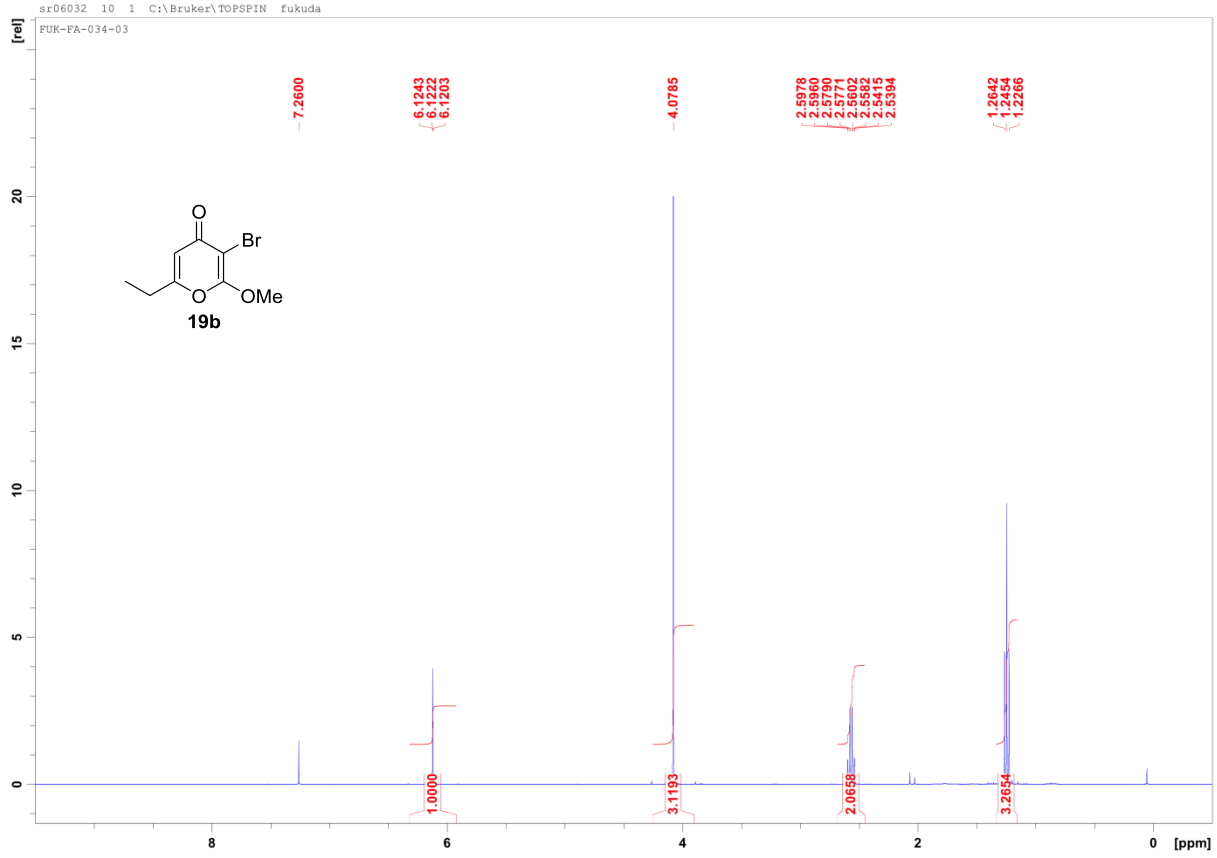

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

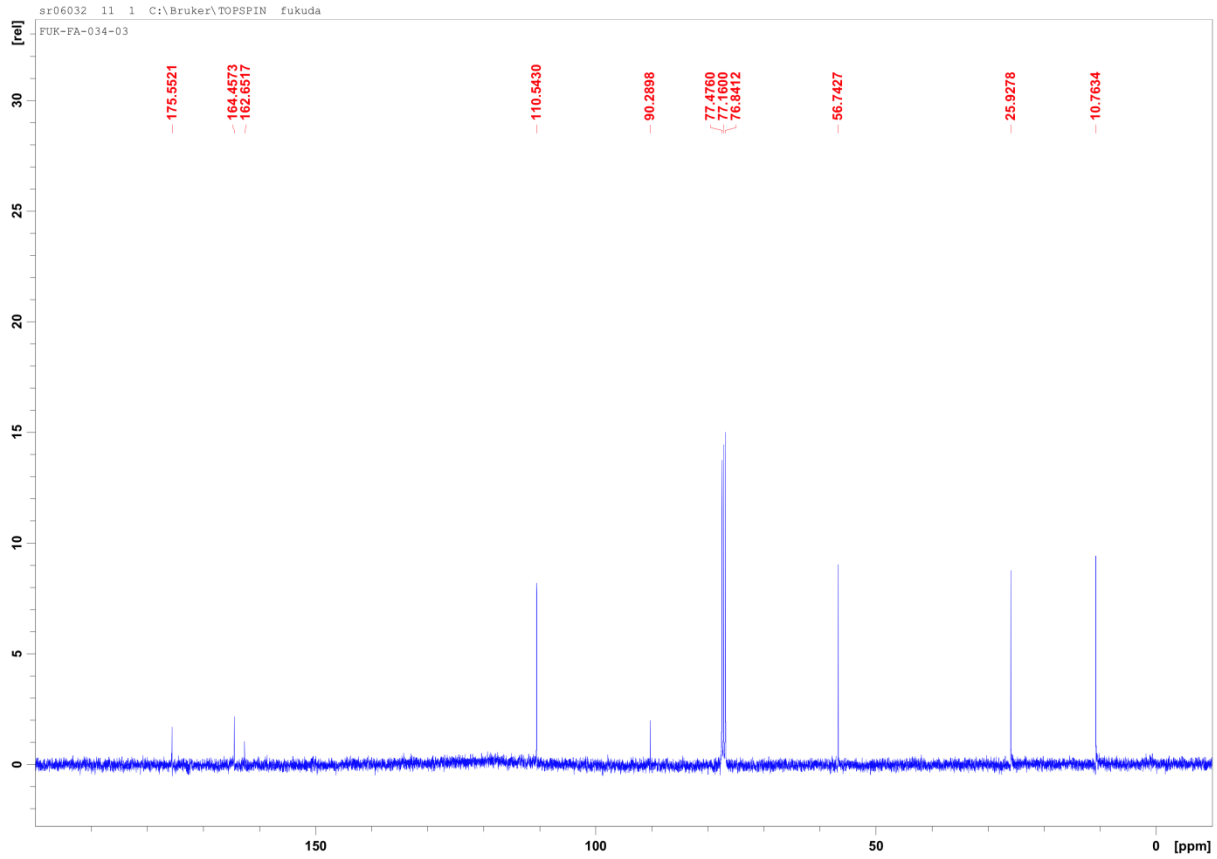

CHL-CA-101-01
[rel]
7.4140
7.4077
7.4048
7.3964
7.3882
7.3807
7.2600
5.9941
5.9919
5.9898
5.5394
5.5348
5.0874
2.5358
2.5345
2.5170
2.5156
2.4982
2.4967
2.4793
2.4783
1.2313
1.2125
1.1936
4.9511
1.0000
1.0152
2.0499
2.0961
3.3510
O
O
O
Ph
8
6
4
2
[ppm]

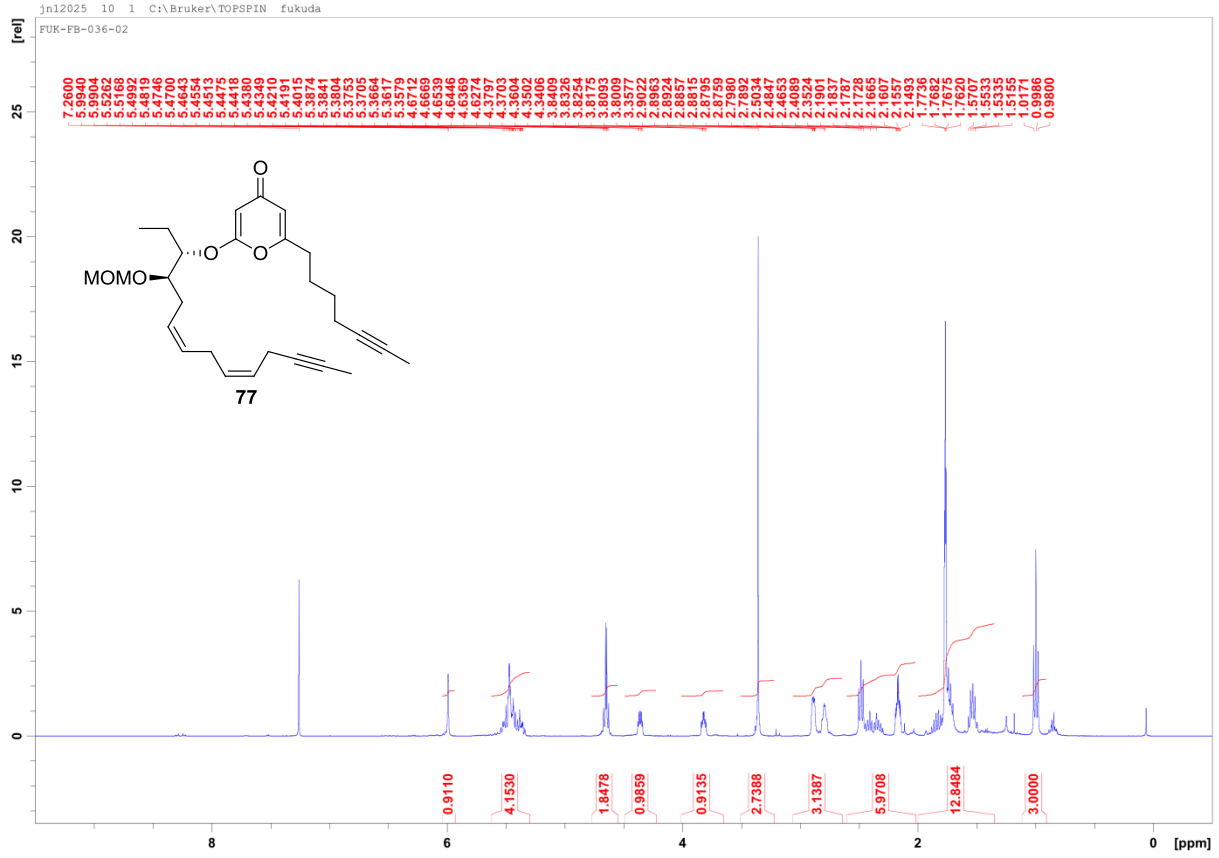

CHL-CA-101-01
[rel]
181.8715
167.0680
166.3547
133.7029
129.0372
128.6573
127.9384
111.1384
90.8668
77.3187
77.0000
76.6832
71.1791
26.1500
10.7011
200
150
100
50
0
[ppm]

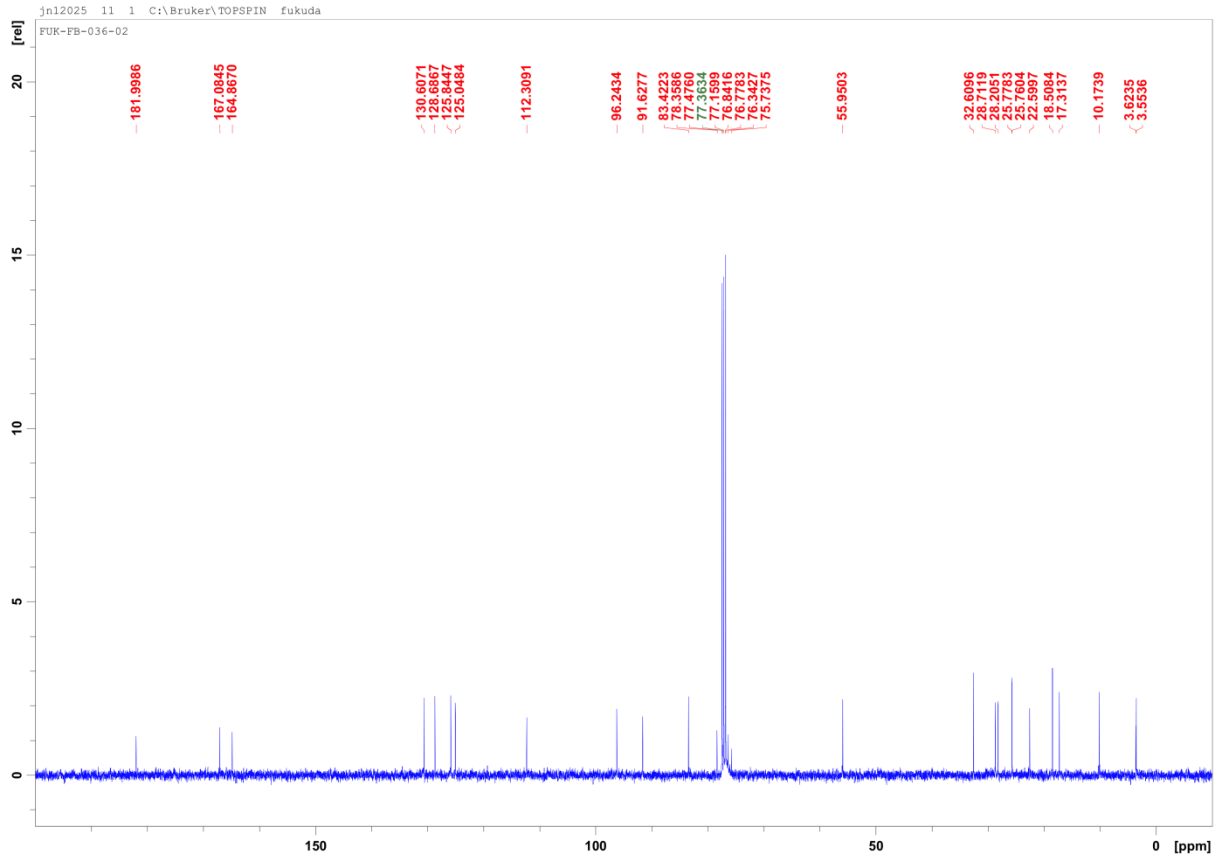

au21009 10 1 C:\Bruker\TOPSPIN fukuda
FUK-FA-020-07
[rel]
7.2600
5.9681
5.9658
5.9636
5.4323
5.4276
3.8398
2.5224
2.5207
2.5018
2.4847
2.4830
2.4659
2.4642
1.2217
1.2029
1.1841
O
O
OMe
19a
0.9965
1.0000
3.0534
2.0285
3.0953
[ppm]

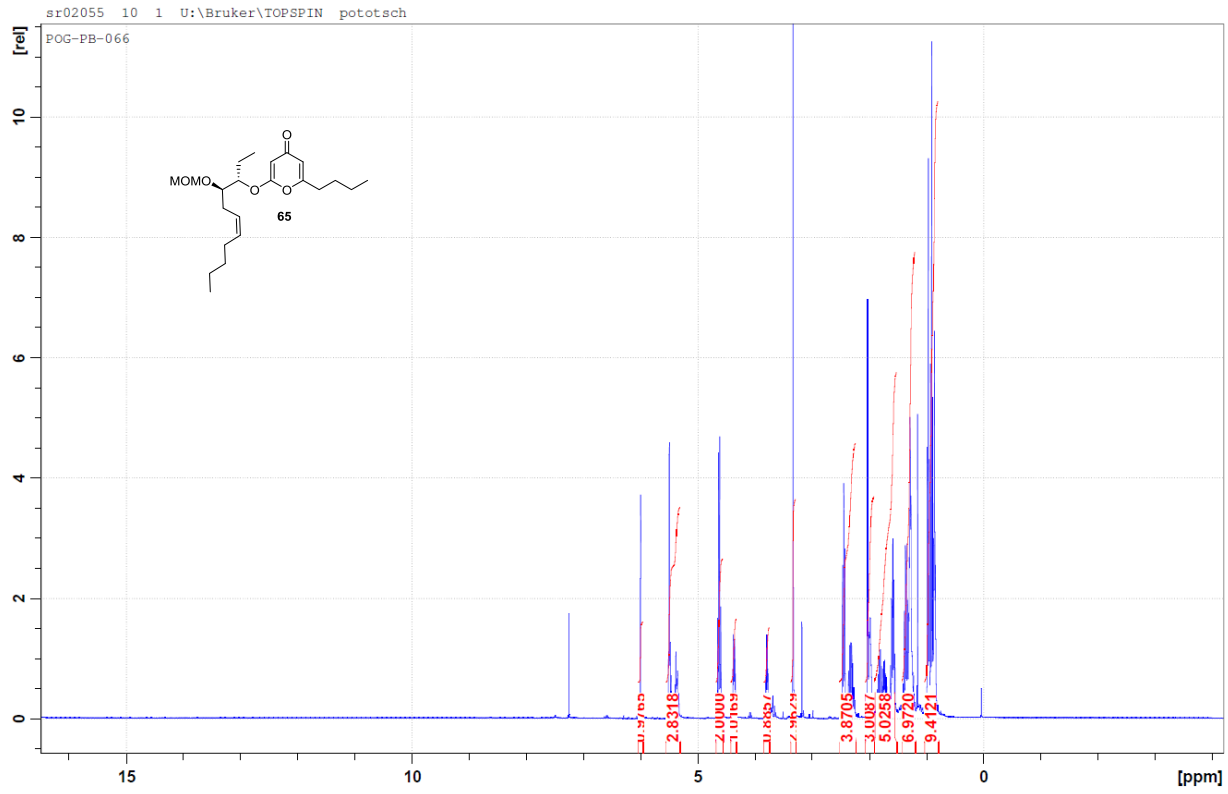

sr06032 10 1 C:\Bruker\TOPSPIN fukuda
FUK-FA-034-03
[rel]
7.2600
6.1243
6.1222
6.1203
4.0785
2.5978
2.5960
2.5790
2.5771
2.5602
2.5582
2.5415
2.5394
1.2642
1.2454
1.2266
1.0000
3.1193
2.0658
3.2654
[ppm]

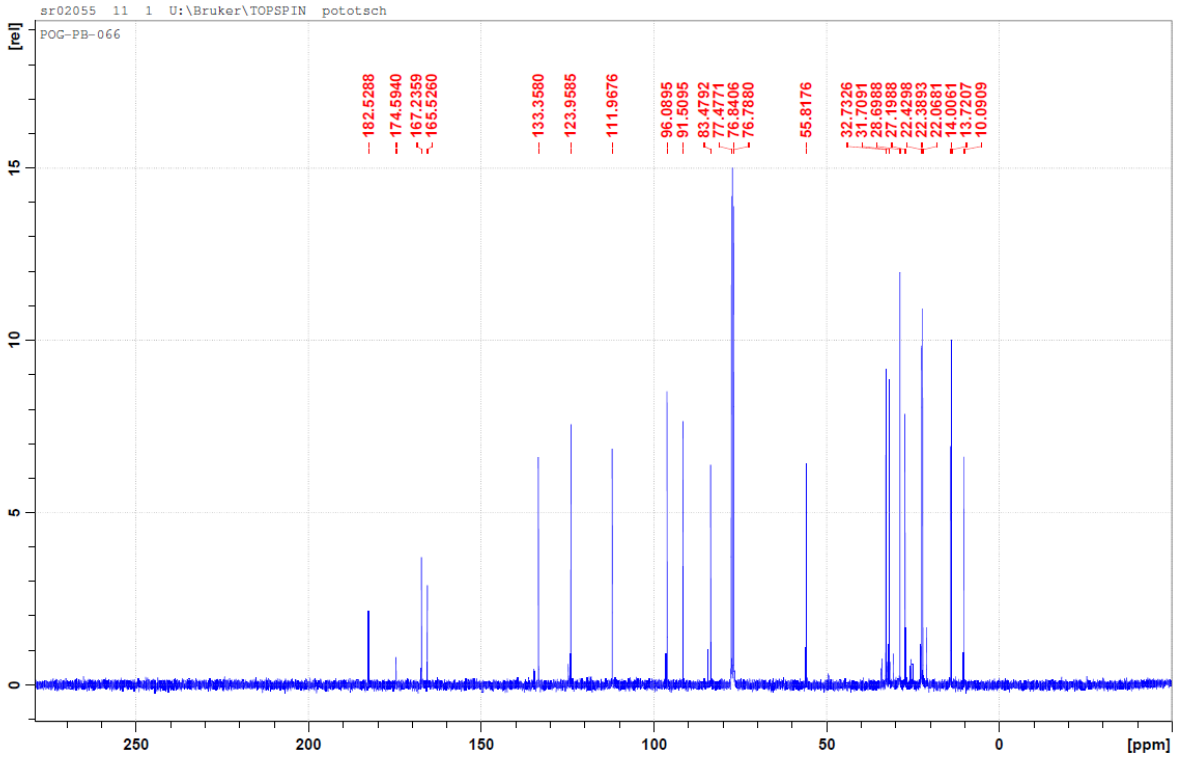

sr06032 10 1 C:\Bruker\TOPSPIN fukuda
FUK-FA-034-03
[rel]
7.2600
6.1243
6.1222
6.1203
4.0785
2.5978
2.5960
2.5790
2.5771
2.5602
2.5352
2.5415
2.5394
1.2642
1.2454
1.2266
1.0000
3.1193
2.0658
3.2654
[ppm]
O
Br
O
OMe
19b

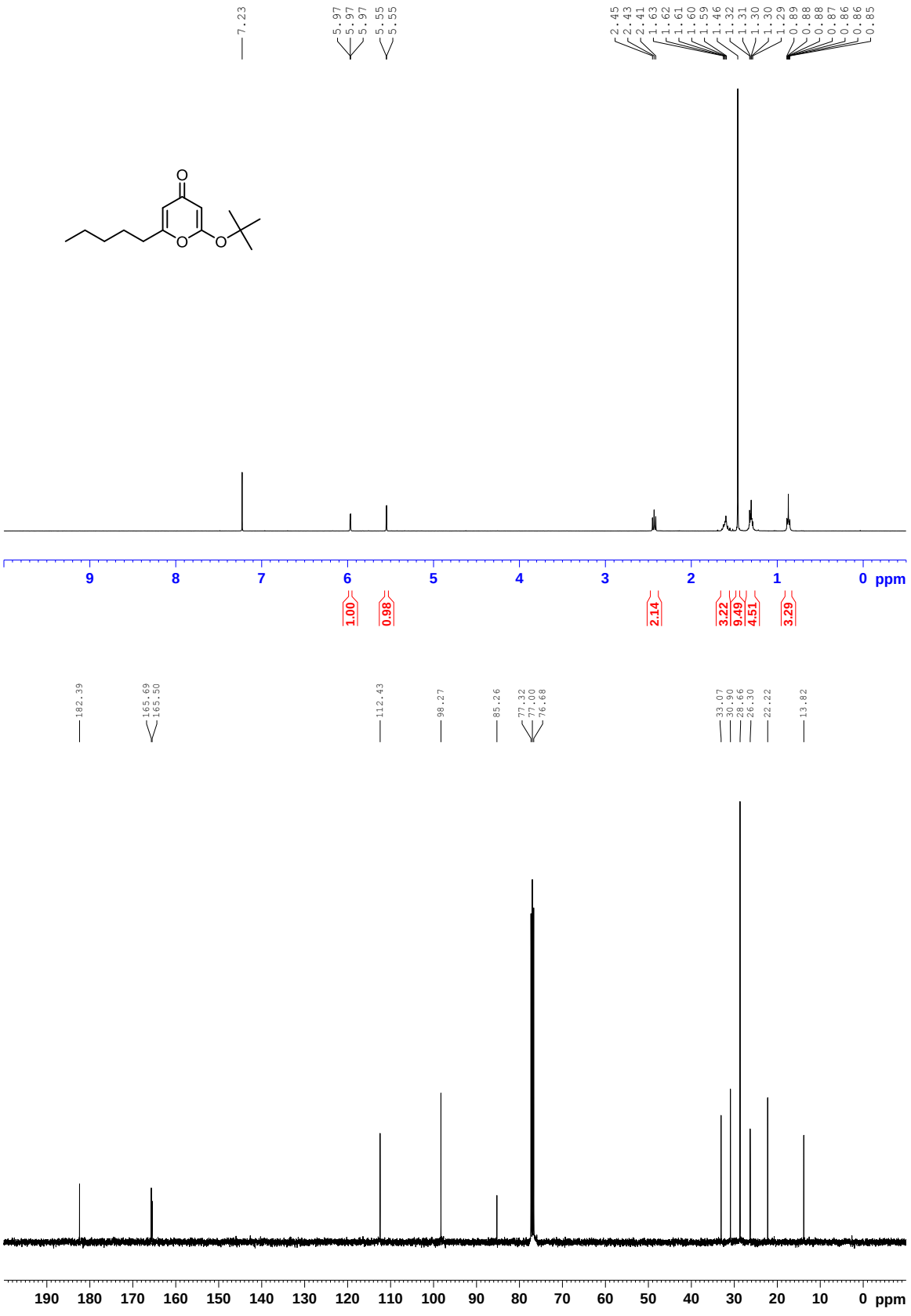

sr06032 11 1 C:\Bruker\TOPSPIN fukuda
FUK-FA-034-03
[rel]
175.5521
164.4573
162.6517
110.5430
90.2898
77.4760
77.1600
76.8412
56.7427
25.9278
10.7634
[ppm]

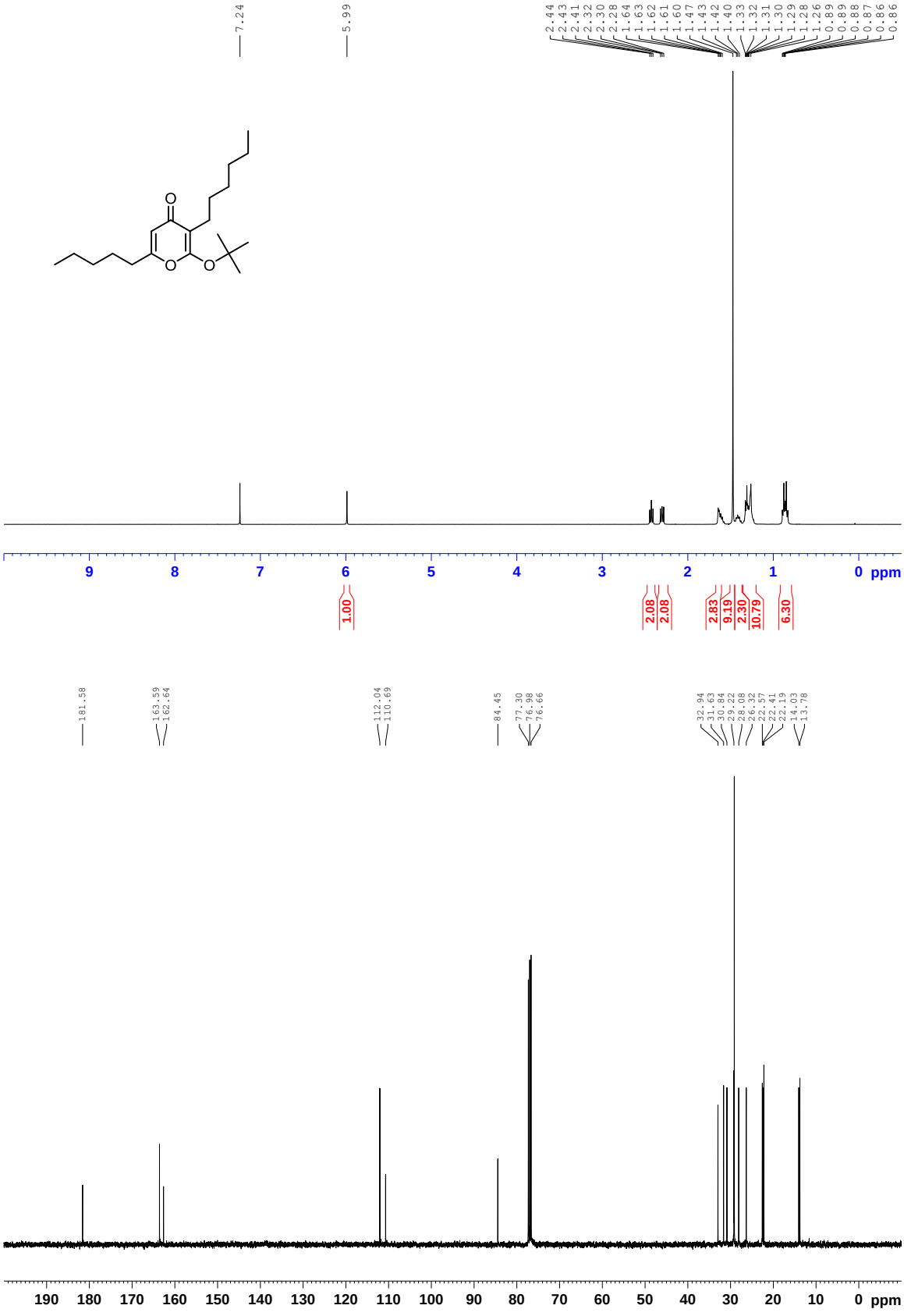

jn12025 10 1 C:\Bruker\TOPSPIN fukuda
FUK-FB-036-02
[rel]
MOMO
77
0.9110
4.1530
1.8478
0.9859
0.9135
2.7388
3.1387
5.9708
12.8484
3.0000
[ppm]

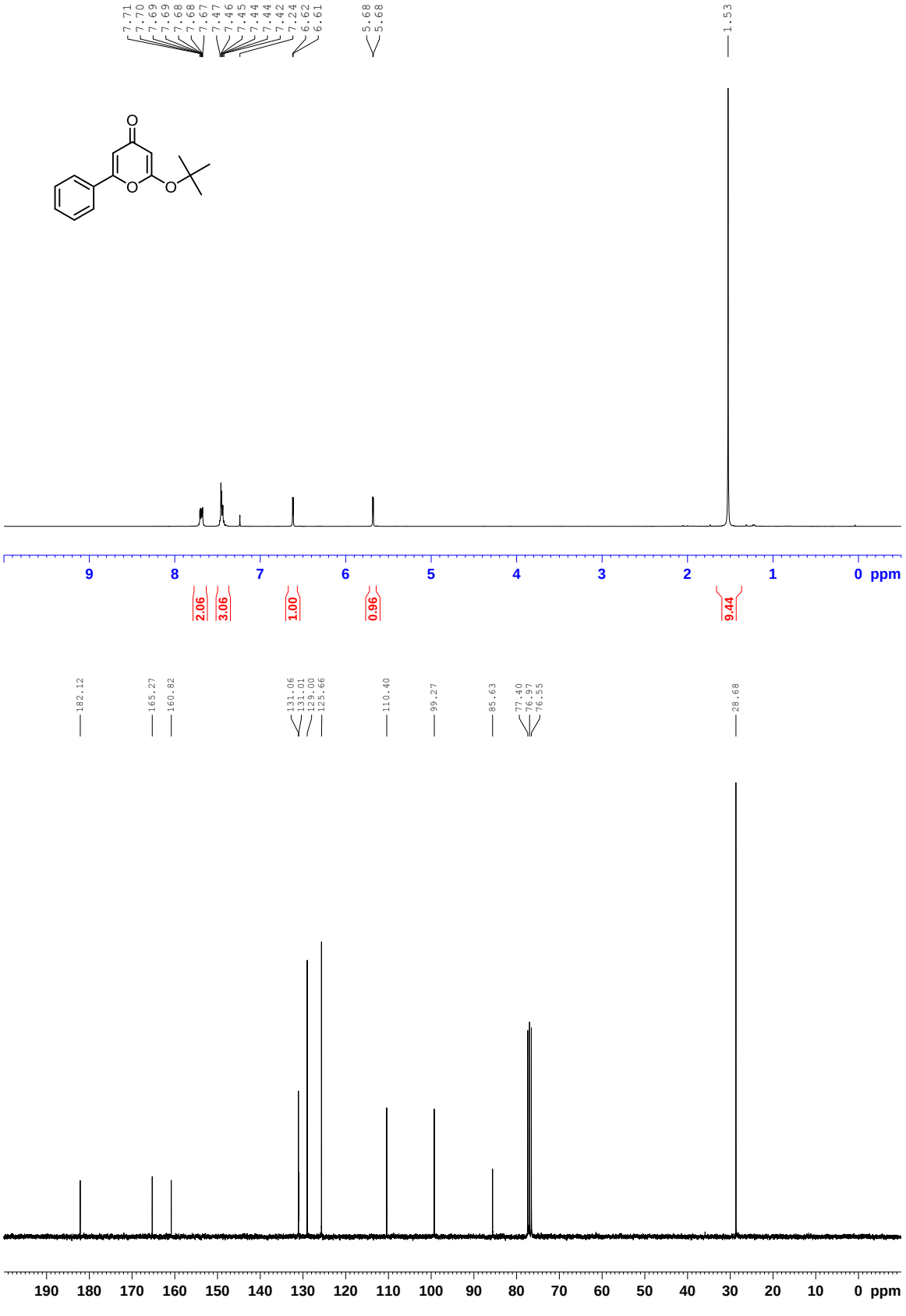

jn12025 11 1 C:\Bruker\TOPSPIN fukuda
FUK-FB-036-02
[rel]
181.9986
167.0845
164.8670
130.6071
128.6867
125.8447
125.0484
112.3091
96.2434
91.6277
83.4223
78.3586
77.4760
77.3634
77.1599
76.8416
76.7783
76.3427
75.7375
55.9503
32.6096
28.7119
28.2051
25.7783
25.7604
22.9997
18.5084
17.3137
10.1739
3.6235
3.5536
[ppm]

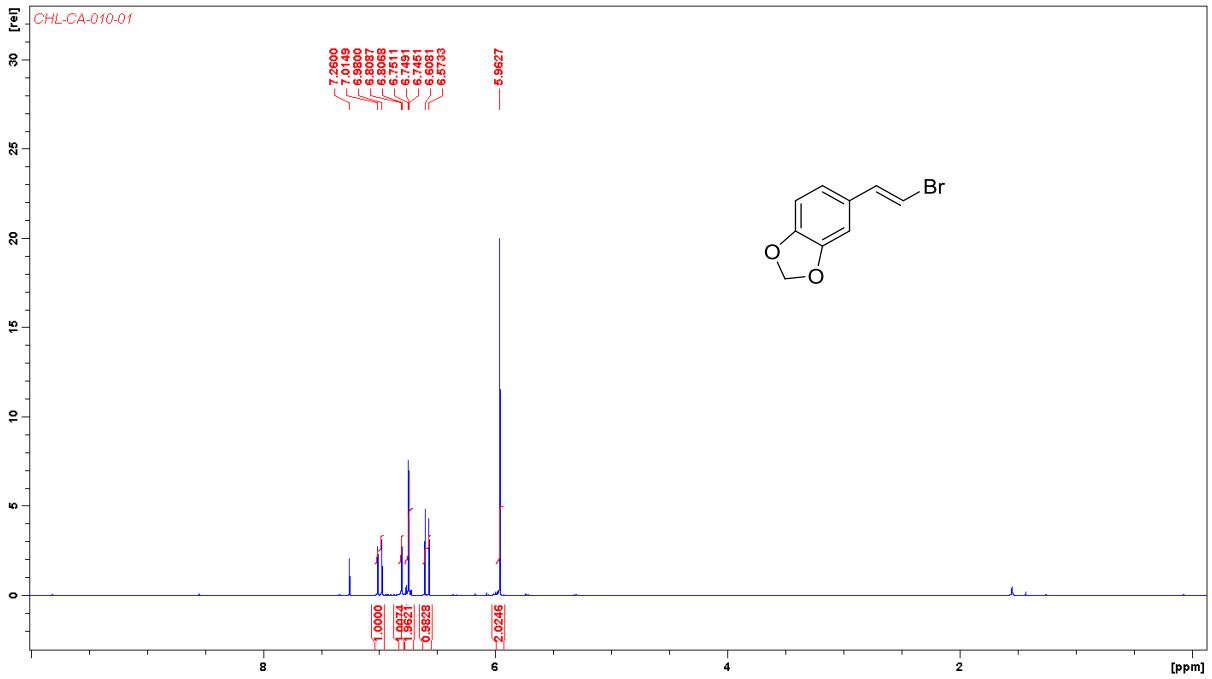

sr02055 10 1 U:\Bruker\TOPSPIN pototsch
POG-PB-066
[rel]
MOMO
O
O
O
65
2.8318
3.8705
5.0258
6.9720
9.4121
15
10
5
0
[ppm]

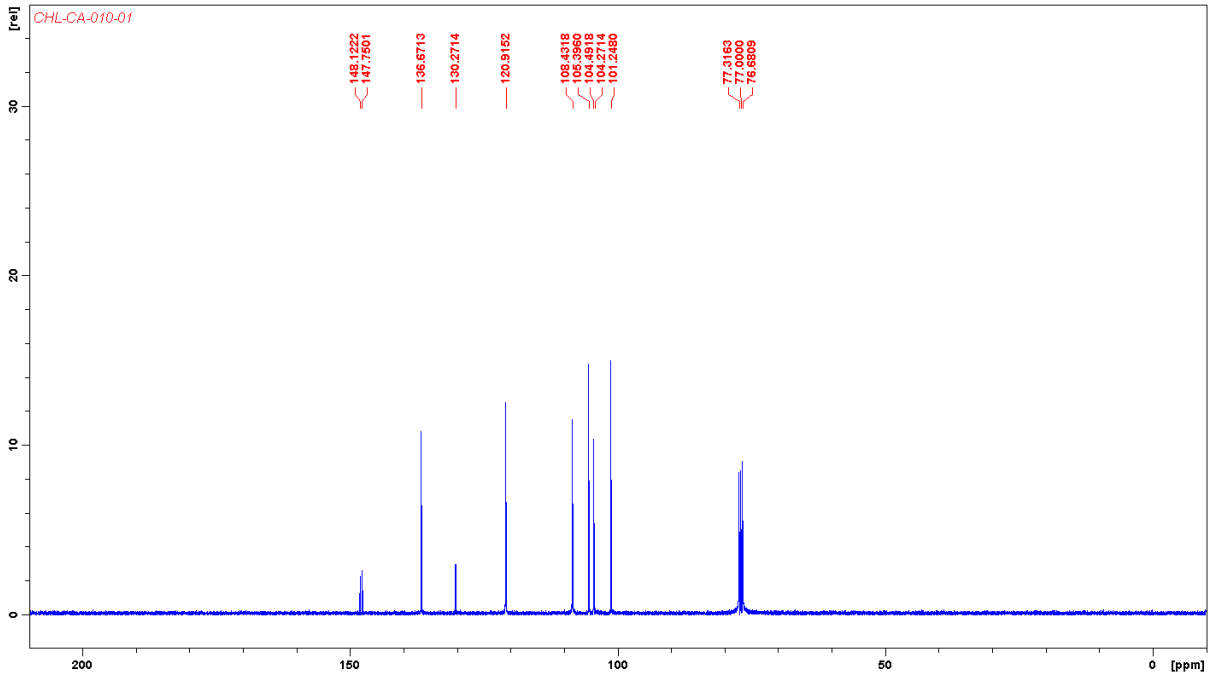

sr02055 11 1 U:\Bruker\TOPSPIN pototsch
POG-PB-066
[rel]
182.5288
174.5940
167.2359
165.5260
133.3580
123.9585
111.9676
96.0895
91.5095
83.4792
77.4771
76.8406
76.7880
55.8176
32.7326
31.7091
28.6988
27.1988
22.4298
22.3893
22.0681
14.0061
13.7207
10.0909
250
200
150
100
50
0
[ppm]

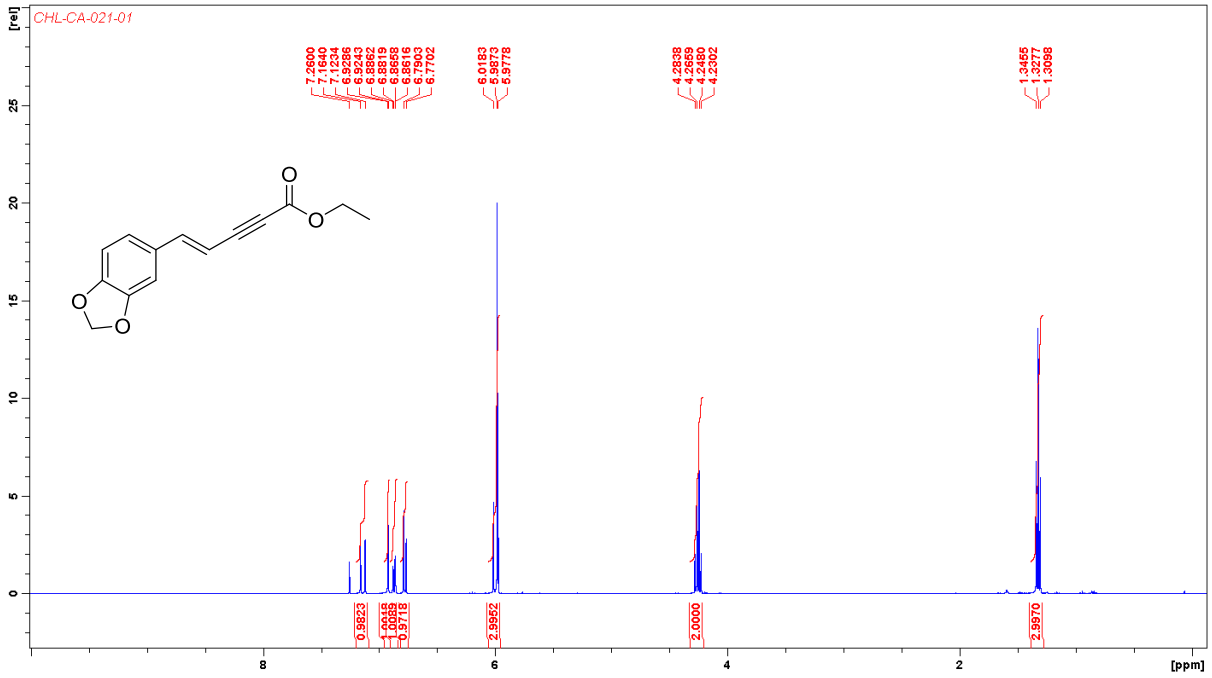

7.23
5.97
5.97
5.97
5.55
5.55
2.45
2.43
2.41
1.63
1.62
1.61
1.60
1.59
1.46
1.32
1.31
1.30
1.29
0.89
0.88
0.88
0.87
0.86
0.86
0.85
O
O
O
9
8
7
6
5
4
3
2
1
0 ppm
1.00
0.98
2.14
3.22
9.49
4.51
3.29
182.39
165.69
165.50
112.43
98.27
85.26
77.32
77.00
76.68
33.07
30.90
28.66
26.30
22.22
13.82
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

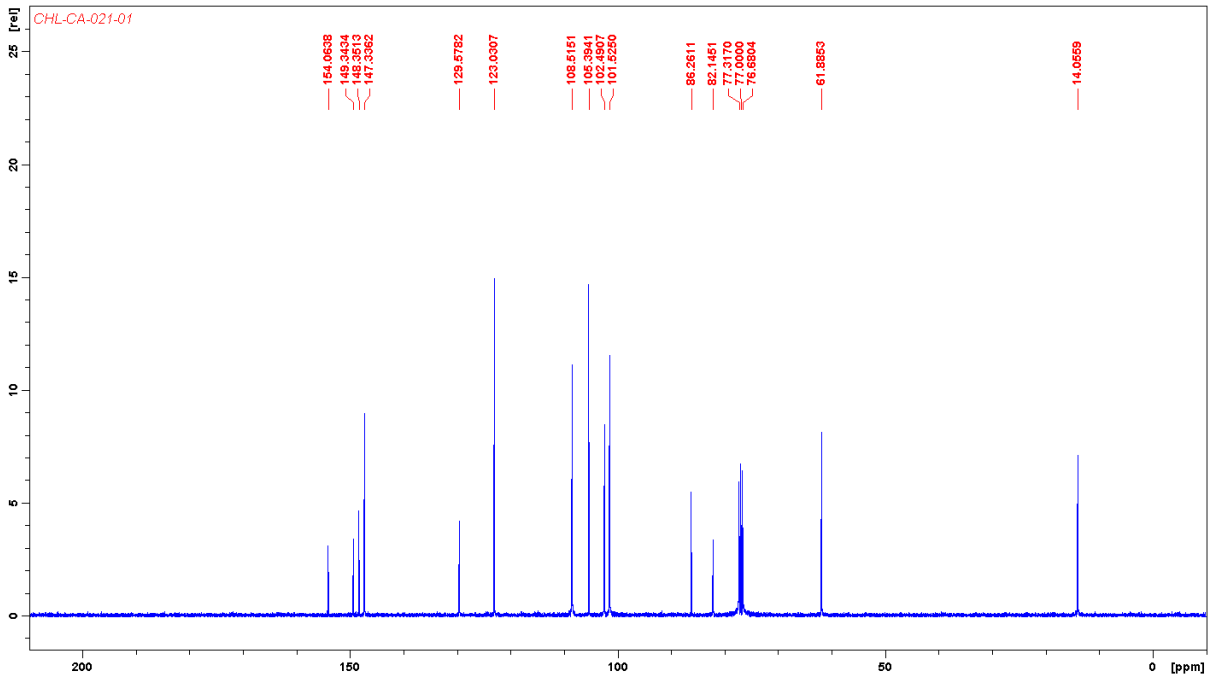

7.24
5.99
2.44
2.43
2.41
2.32
2.30
2.28
1.64
1.63
1.62
1.61
1.60
1.47
1.43
1.42
1.40
1.33
1.32
1.31
1.30
1.29
1.28
1.26
0.89
0.89
0.88
0.87
0.86
0.86
O
O
O
9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.08
2.08
2.83
9.19
2.30
10.79
6.30
181.58
163.59
162.64
112.04
110.69
84.45
77.30
76.98
76.66
32.94
31.63
30.84
29.22
28.08
26.32
22.57
22.41
22.19
14.03
13.78
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

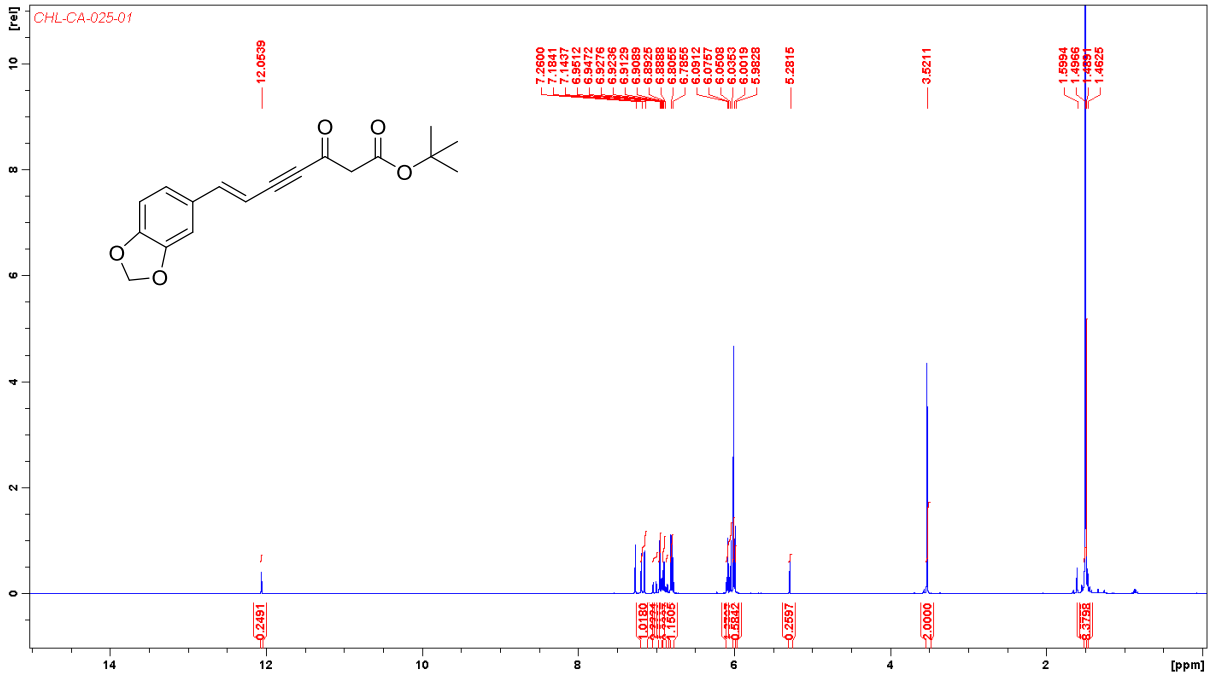

7.71
7.70
7.69
7.69
7.68
7.68
7.67
7.47
7.46
7.45
7.44
7.44
7.42
7.24
6.62
6.61
5.68
5.68
1.53
O
O
O
9
8
7
6
5
4
3
2
1
0 ppm
2.06
3.06
1.00
0.96
9.44
182.12
165.27
160.82
131.06
131.01
129.00
125.66
110.40
99.27
85.63
77.40
76.97
76.55
28.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

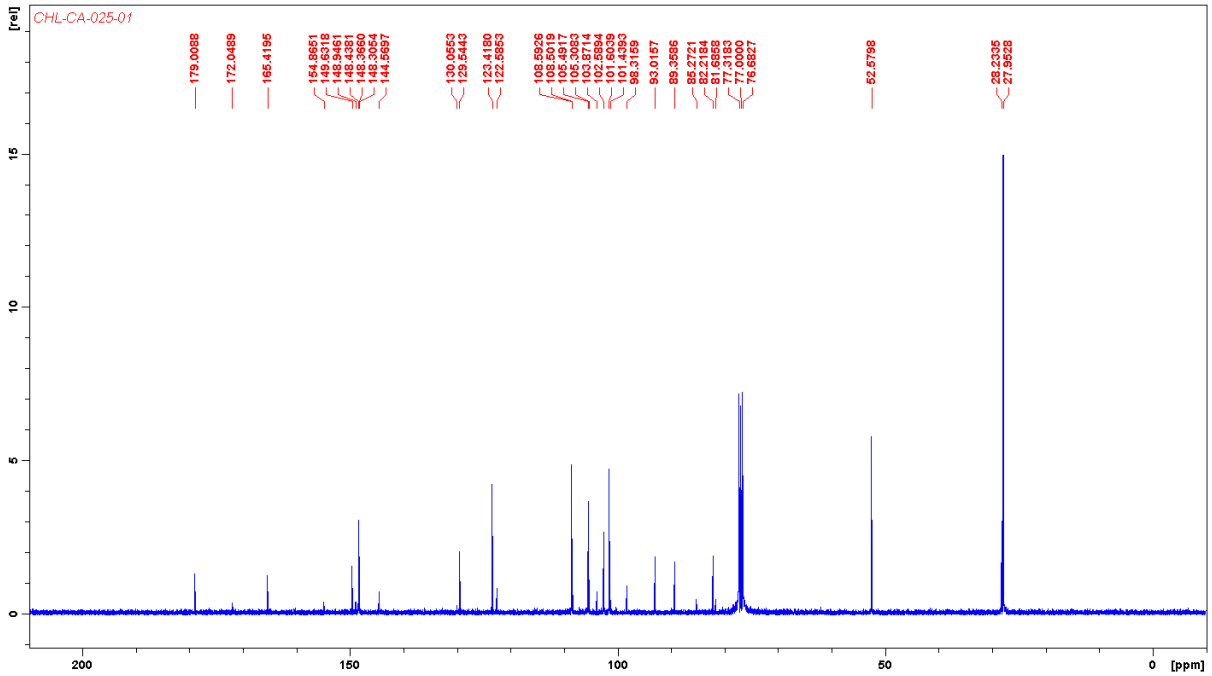

CHL-CA-010-01
[rel]
7.2600
7.0149
6.9800
6.8097
6.8068
6.7511
6.7491
6.7451
6.6081
6.5733
5.9627
Br
O
O
1.0000
1.9824
1.9821
0.9828
2.0246
[ppm]

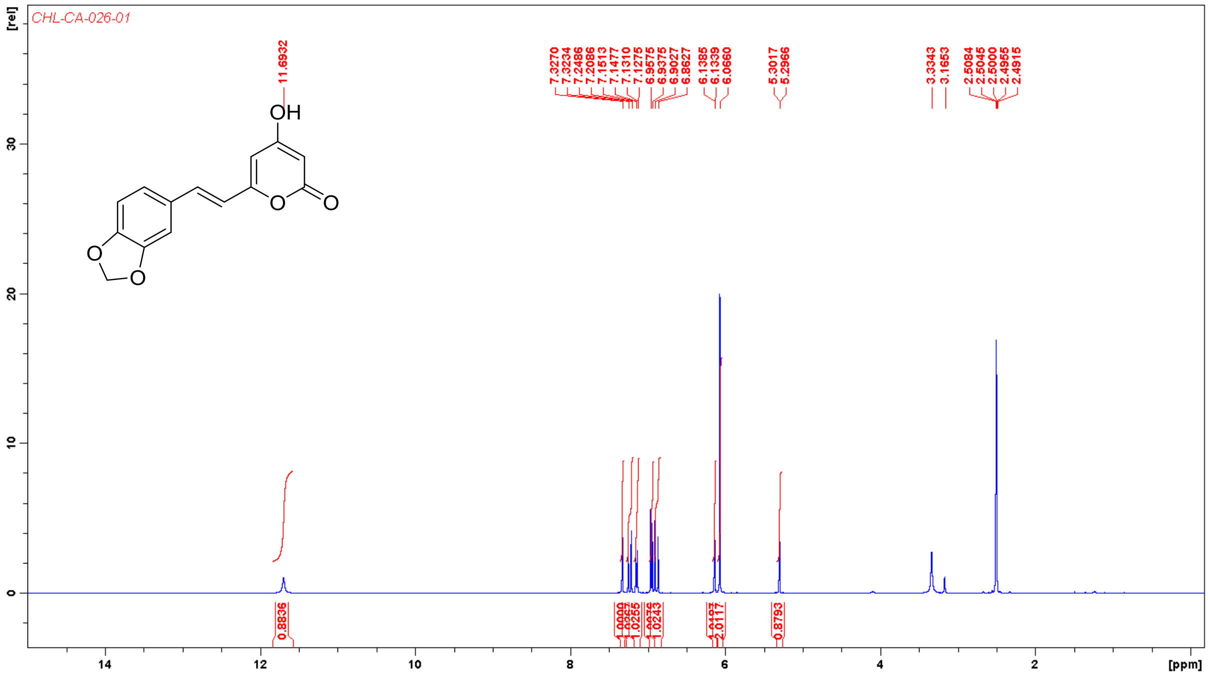

CHL-CA-010-01
[rel]
148.1222
147.7501
136.6713
130.2714
120.9152
108.4318
105.3960
104.4918
104.2714
101.2480
77.3163
77.0000
76.6809
[ppm]

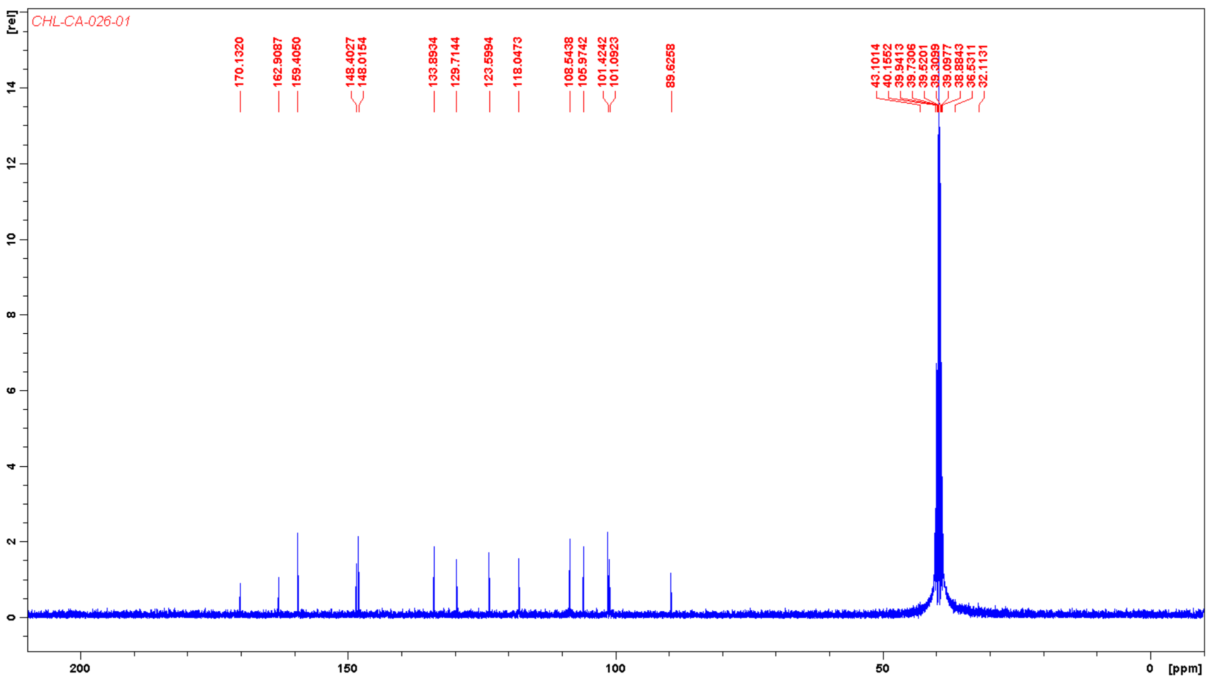

CHL-CA-021-01
[rel]
7.2600
7.1640
7.1234
6.9286
6.9243
6.8892
6.8849
6.8688
6.8616
6.7903
6.7702
6.0193
5.9973
5.9778
4.2838
4.2659
4.2480
4.2302
1.3455
1.3277
1.3098
0.9823
1.0000
1.0058
0.9718
2.9952
2.0000
2.9970
[ppm]

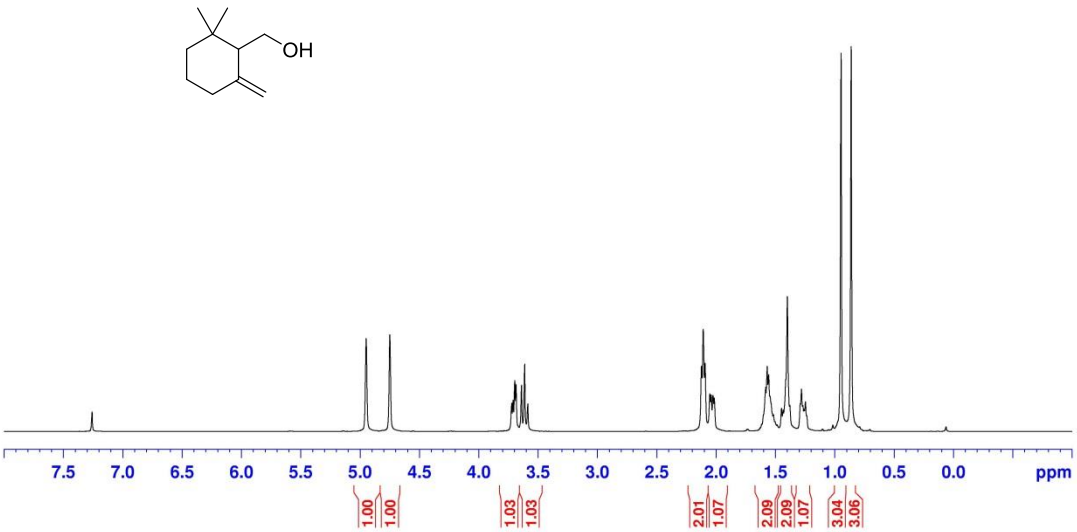

CHL-CA-021-01
[rel]
154.0638
149.3434
148.3513
147.3362
129.5782
123.0307
108.5151
105.3941
102.4907
101.5250
86.2611
82.1451
77.3170
77.0000
76.6804
61.8853
14.0559
[ppm]

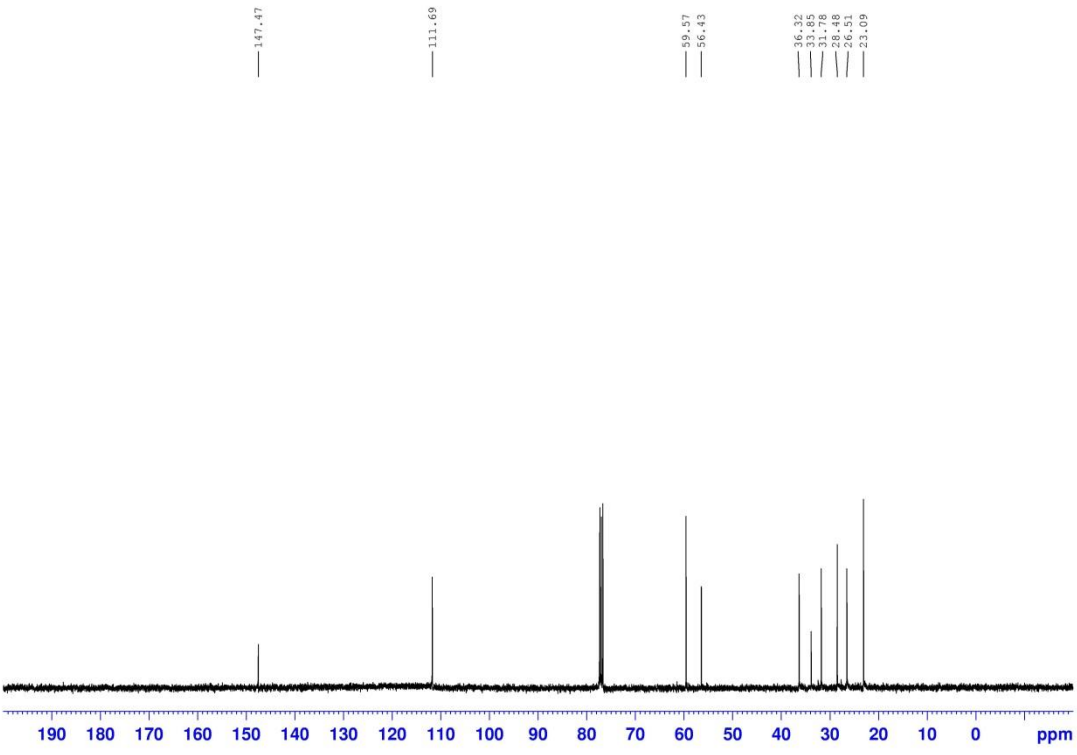

CHL-CA-025-01
[rel]
[ppm]
12.0539
7.2600
7.1841
7.1477
6.9512
6.9472
6.9276
6.9236
6.9129
6.9089
6.8925
6.8888
6.8055
6.7855
6.0912
6.0757
6.0568
6.0353
6.0019
5.9828
5.2815
3.5211
1.5994
1.4966
1.4891
1.4625
0.2491
1.0180
1.1605
0.5842
0.2697
2.0000
8.3758

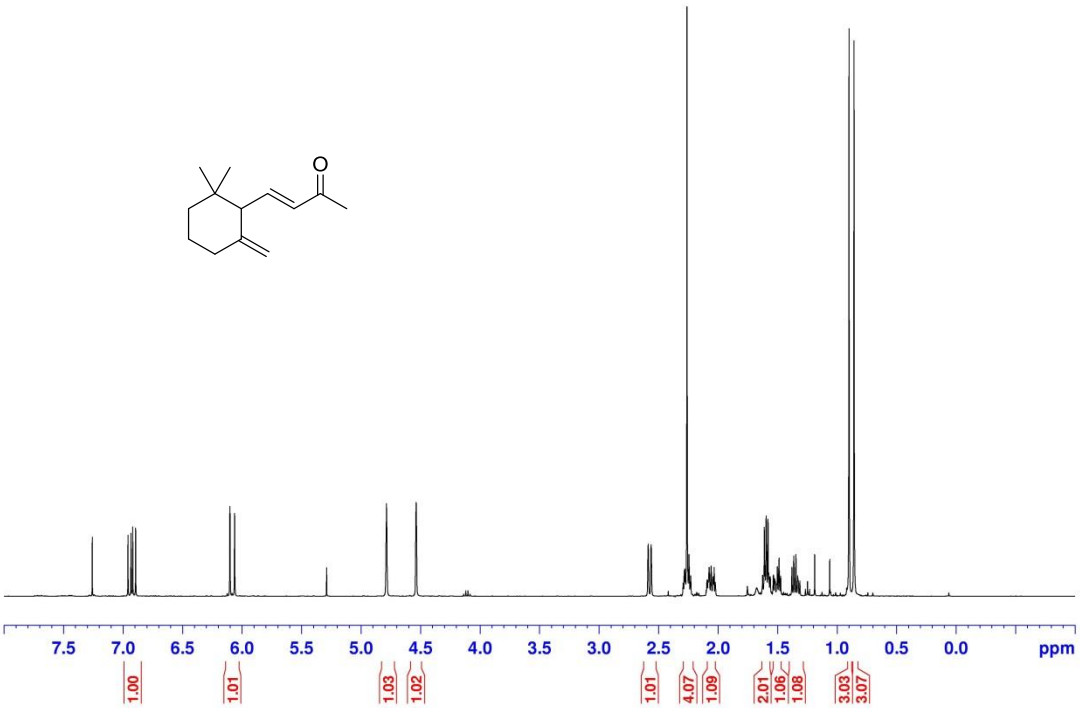

CHL-CA-025-01
[rel]
[ppm]
179.0088
172.0489
165.4195
154.9651
149.6318
148.9461
148.4381
148.3660
148.3054
144.5697
130.0553
129.5443
123.4180
122.5853
108.5926
108.5519
105.4917
105.3083
103.8714
102.5894
101.6039
101.4393
93.3159
93.0157
89.3586
86.2721
85.2154
81.6858
77.3183
77.0000
76.6827
52.5798
28.2335
27.9528

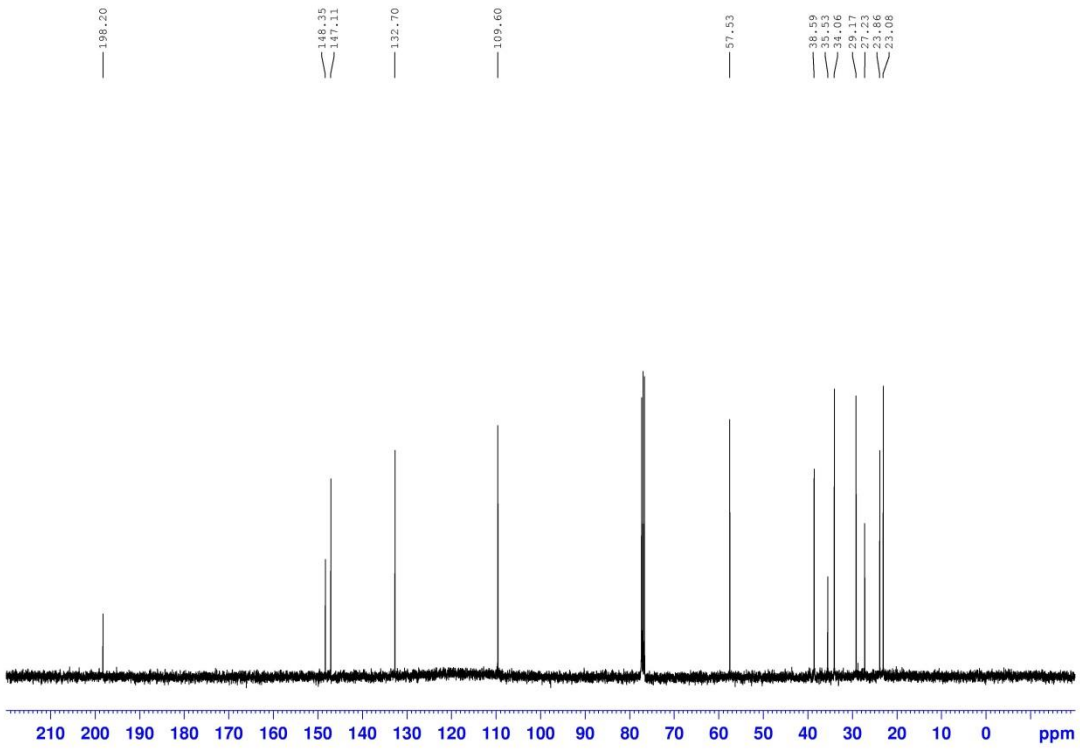


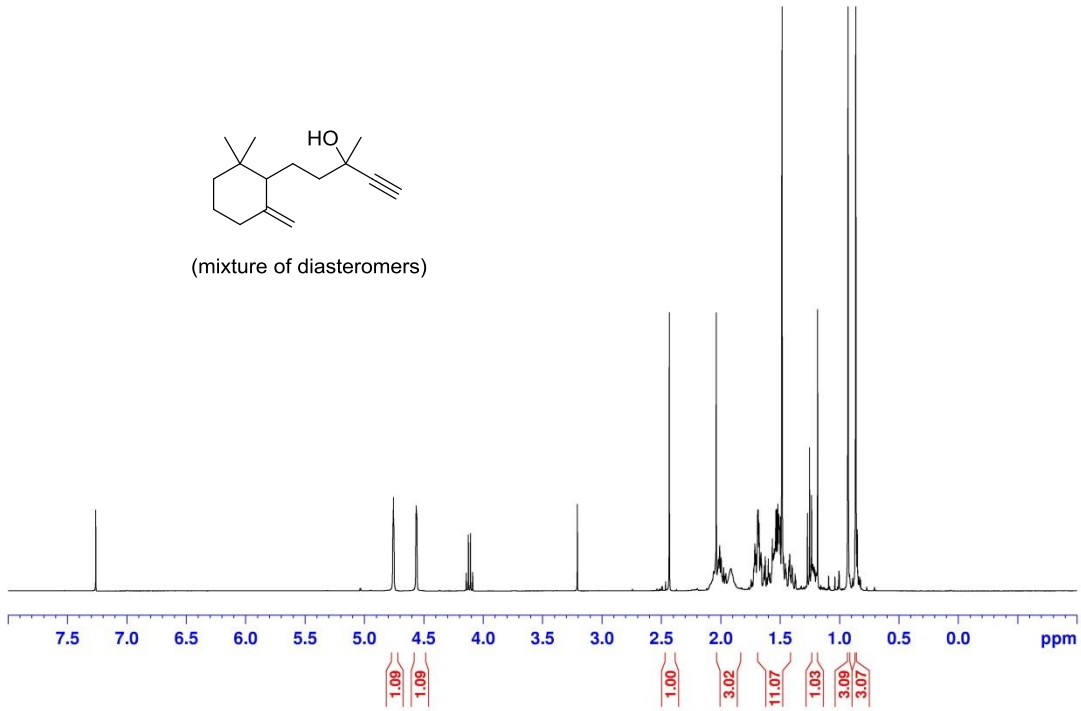


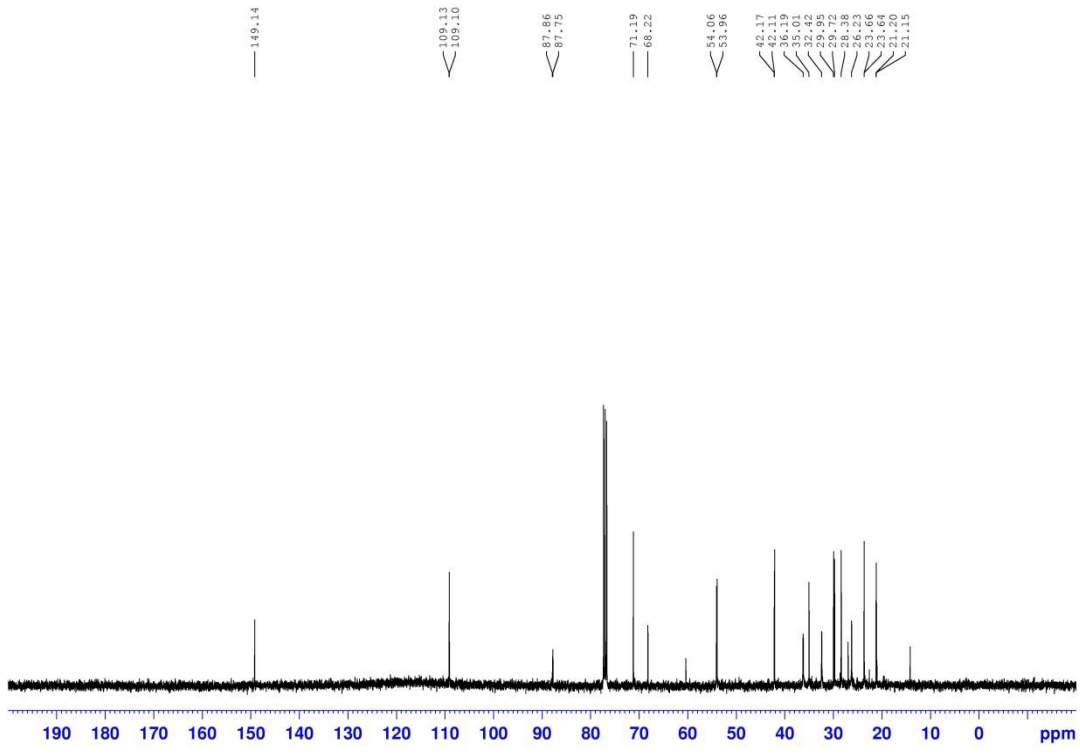

OH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.00 1.03 1.03 2.01 1.07 2.09 2.09 1.07 3.04 3.06

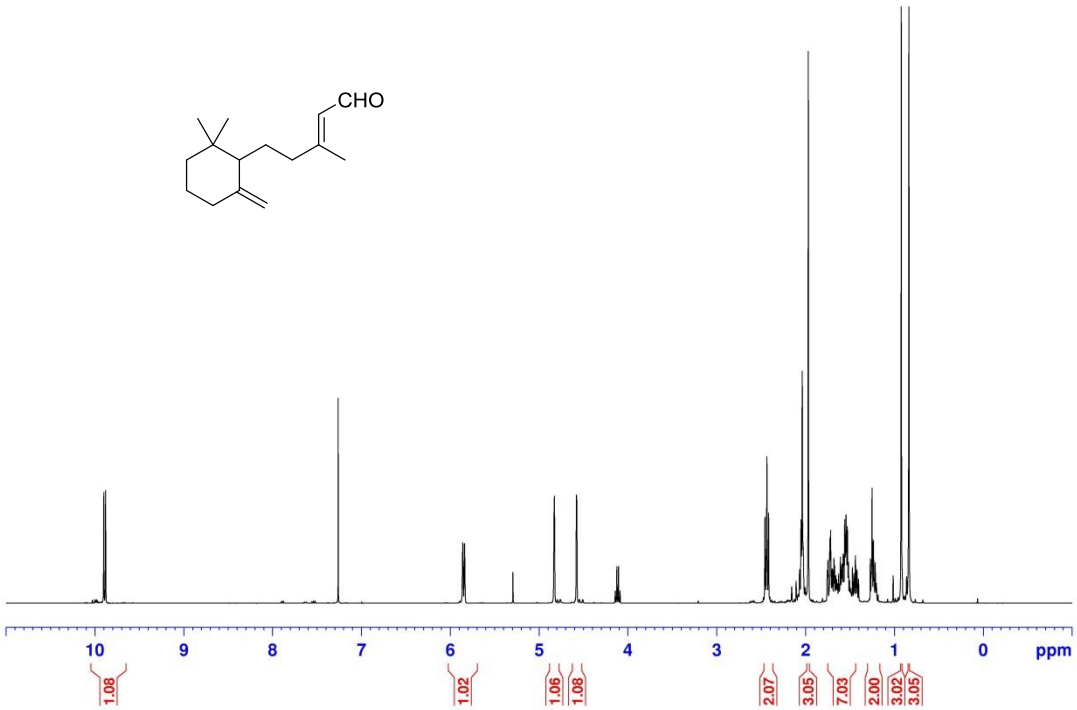

147.47
111.69
59.57
56.43
36.32
33.85
31.78
28.48
26.51
23.09
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

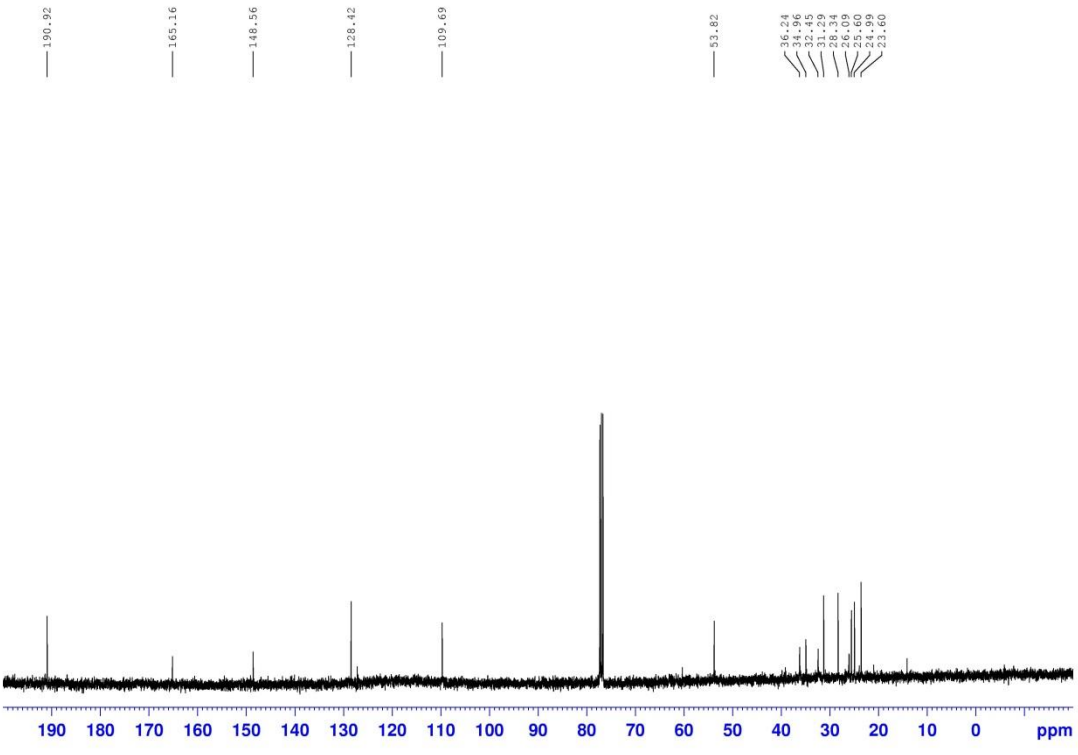

O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.01 1.03 1.02 1.01 4.07 1.09 2.01 1.06 1.08 3.03 3.07

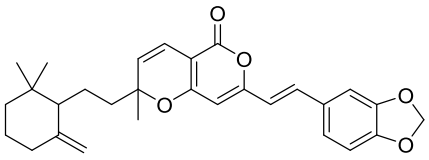

198.20
148.35
147.11
132.70
109.60
57.53
38.59
35.53
34.06
29.17
27.23
23.66
23.08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


HO
(mixture of diasteromers)
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 ppm
1.09 1.09 1.00 3.02 11.07 1.03 3.09 3.07

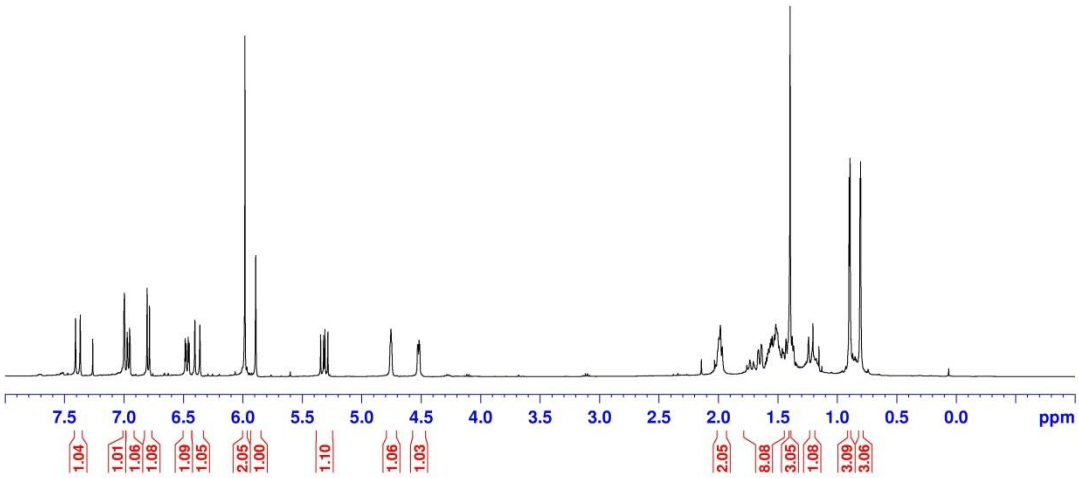

149.14
109.13
109.10
87.86
87.75
71.19
68.22
54.06
53.96
42.17
42.11
36.19
35.01
33.42
33.35
29.72
28.38
26.23
23.66
23.64
21.20
21.15
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

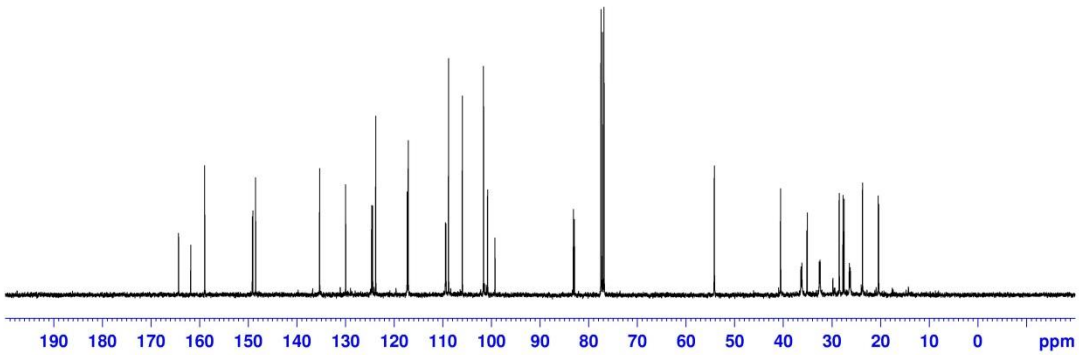

CHO
10
9
8
7
6
5
4
3
2
1
0
ppm
1.08
1.02
1.06
1.08
2.07
3.05
7.03
2.00
3.02
3.05

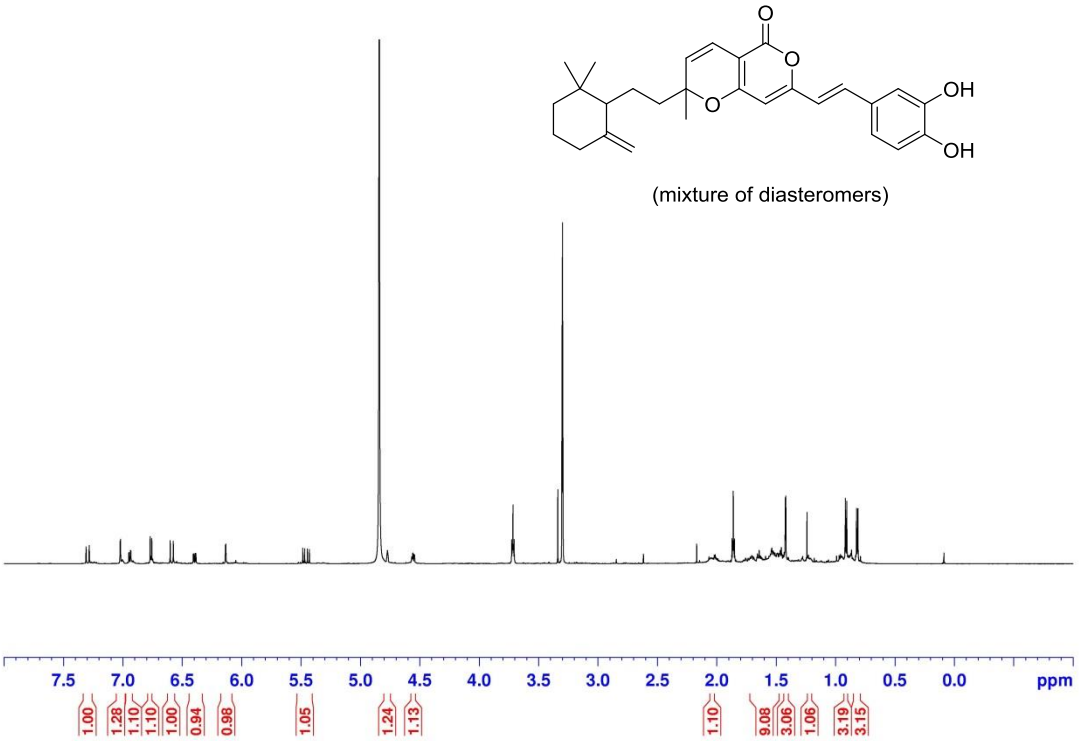

190.92
165.16
148.56
128.42
109.69
53.82
36.24
34.96
32.45
31.29
28.34
26.89
25.60
24.99
23.60
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

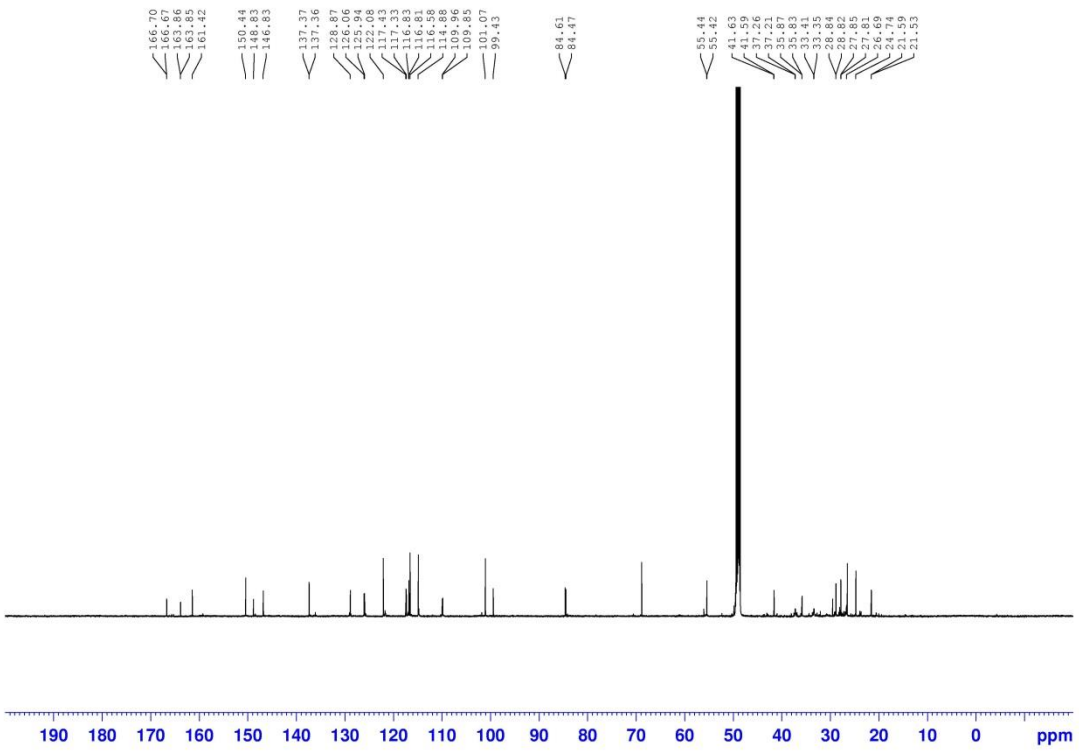


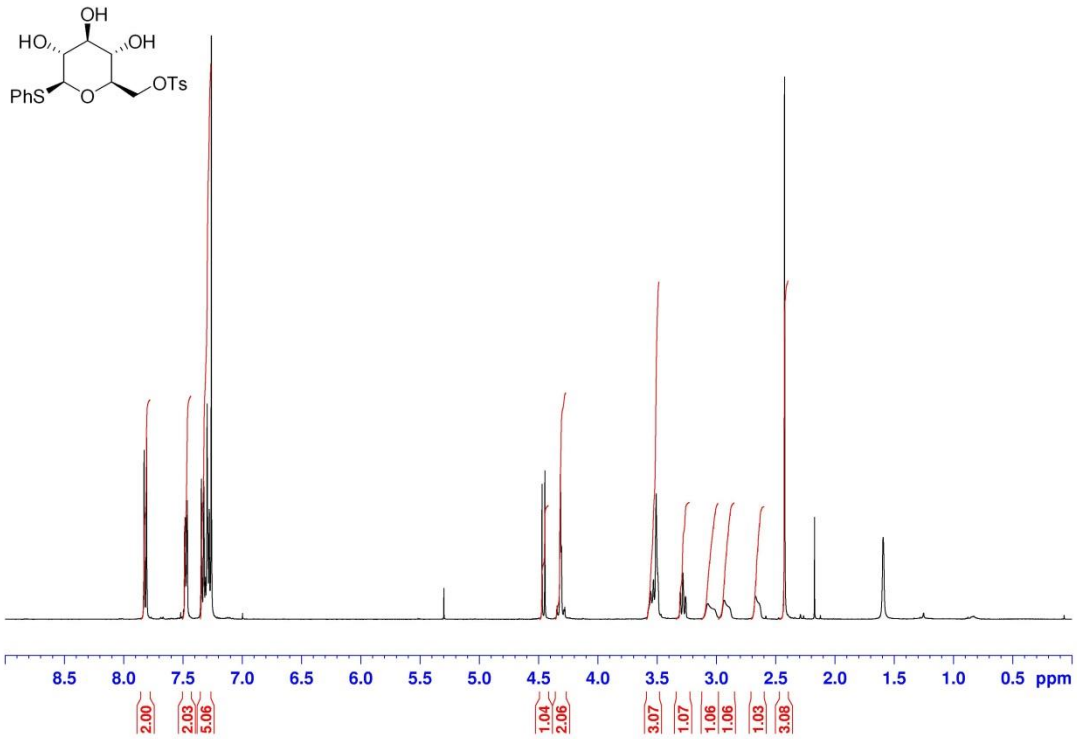
(mixture of diasteromers)

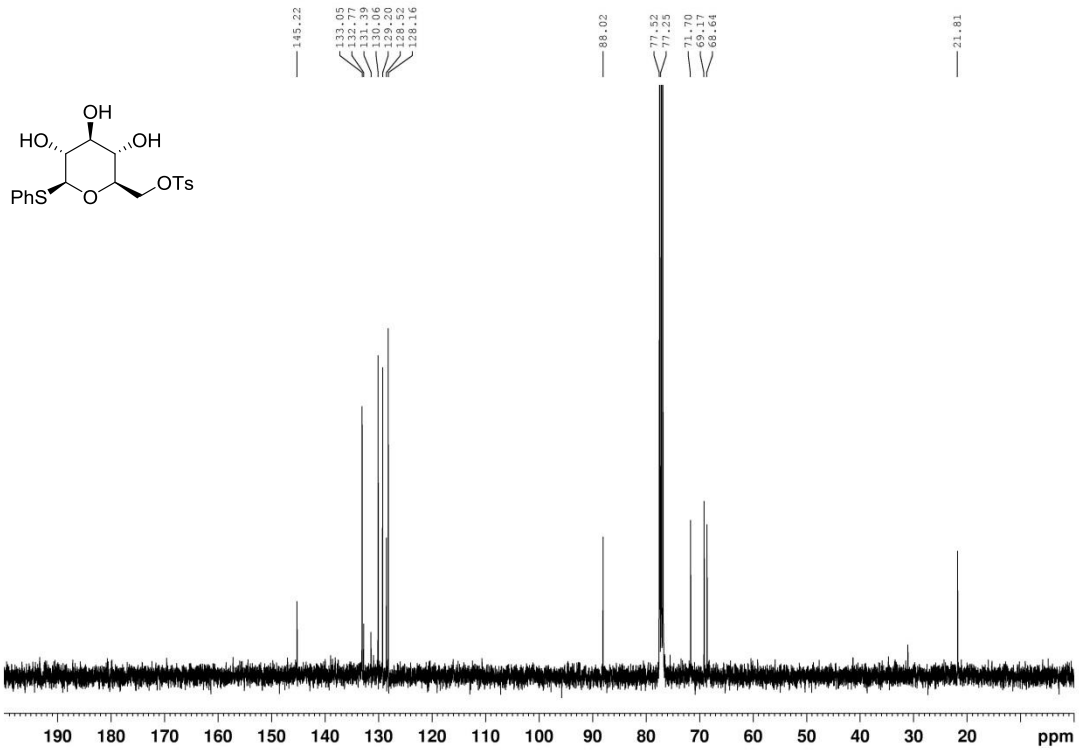


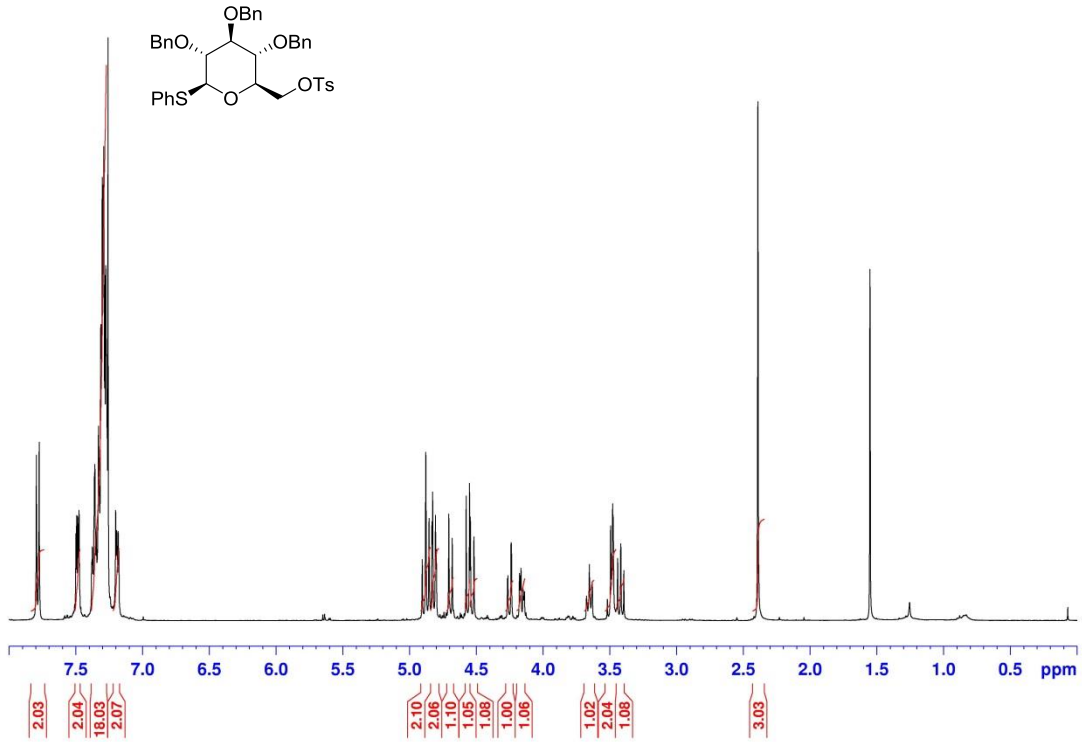


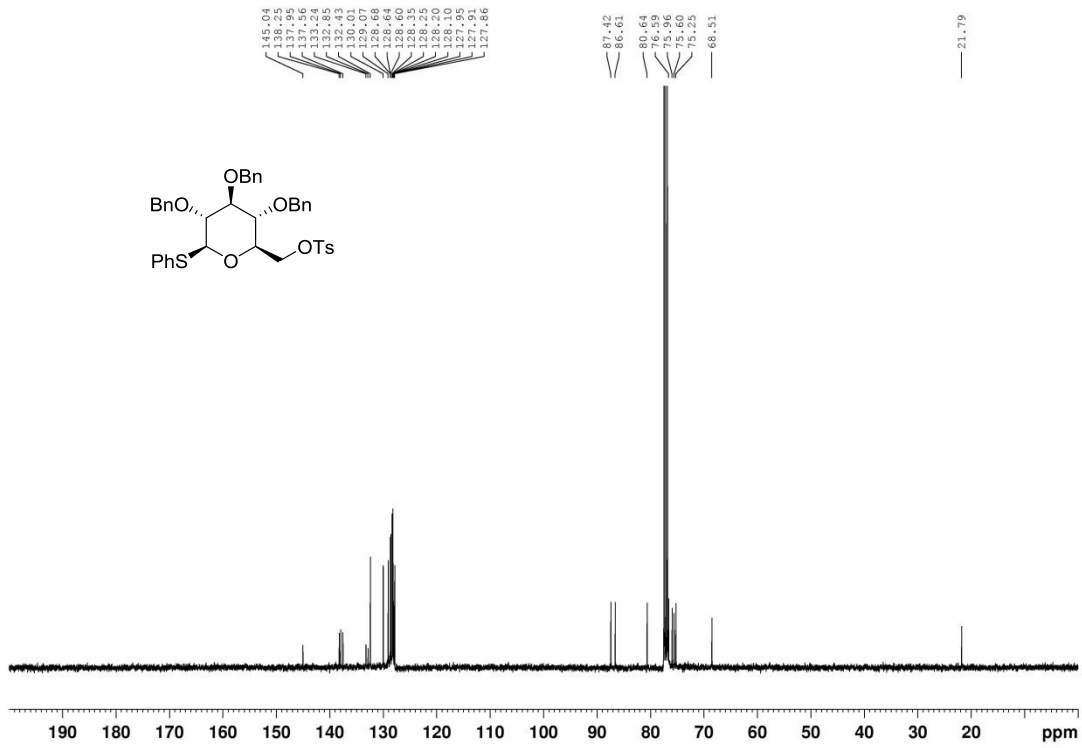

O
O
O
OH
OH
(mixture of diasteromers)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.28 1.10 1.10 1.00 0.94 0.98 1.05 1.24 1.13 1.10 9.08 3.06 1.06 3.19 3.15

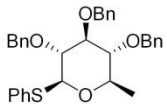

166.70 166.67 163.86 163.85 161.42
150.44 148.83 146.83
137.37 137.36
128.87 126.06 125.94 122.08 117.43 117.33 116.83 116.81 116.58 114.88 109.96 109.86 101.07 99.43
84.61 84.47
55.44 55.42
41.63 41.59 37.26 37.21 35.87 35.63 33.11 33.05 28.84 28.82 27.85 27.81 26.69 24.74 21.89 21.53
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

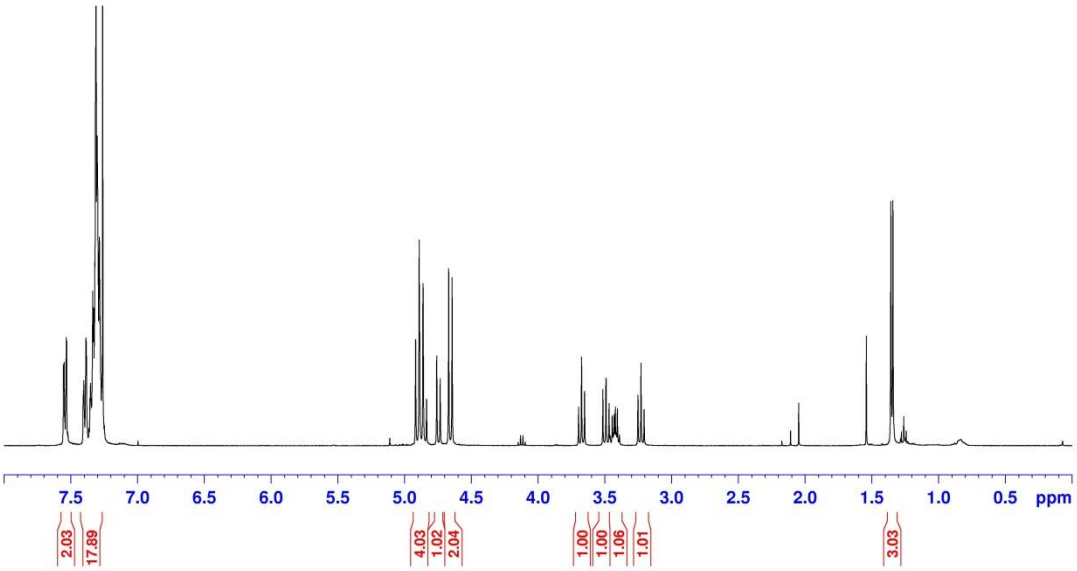

OH
HO
OH
PhS
O
OTs
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 2.03 5.06 1.04 2.06 3.07 1.07 1.06 1.06 1.03 3.08

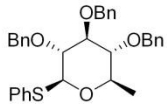

145.22
133.05
132.77
131.39
130.06
129.20
128.52
128.16
88.02
77.52
77.25
71.70
69.17
68.64
21.81
OH
HO
OH
PhS
O
OTs
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

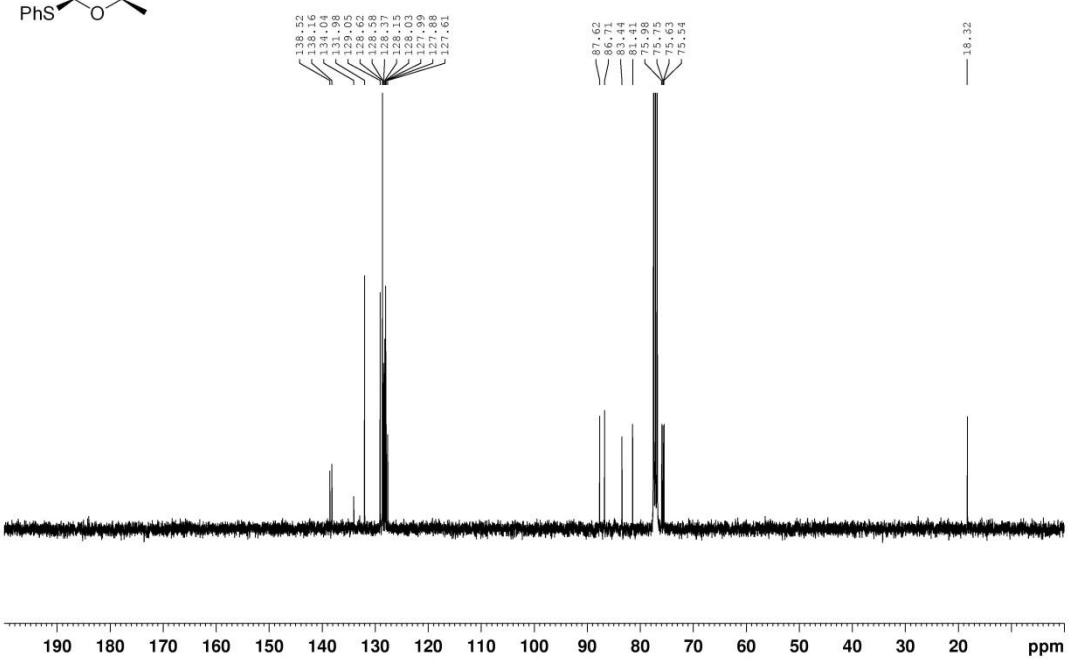

OBn
BnO
OBn
PhS
O
OTs
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
2.04
18.03
2.07
2.10
2.06
1.10
1.05
1.08
1.00
1.06
1.02
2.04
1.08
3.03

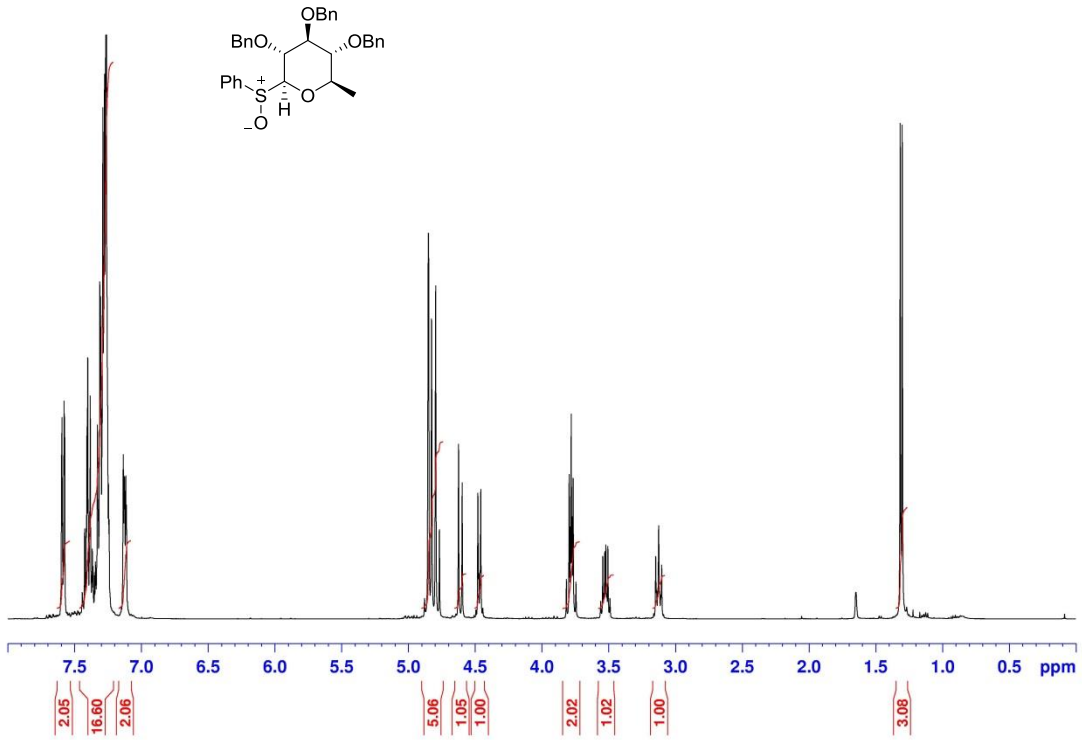

145.04
138.25
137.95
137.86
133.24
132.85
132.43
130.01
129.07
128.68
128.60
128.60
128.35
128.25
128.20
128.10
127.95
127.91
127.86
87.42
86.61
80.64
76.59
75.56
75.60
75.25
68.51
21.79
OBn
BnO
OBn
PhS
O
OTs
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

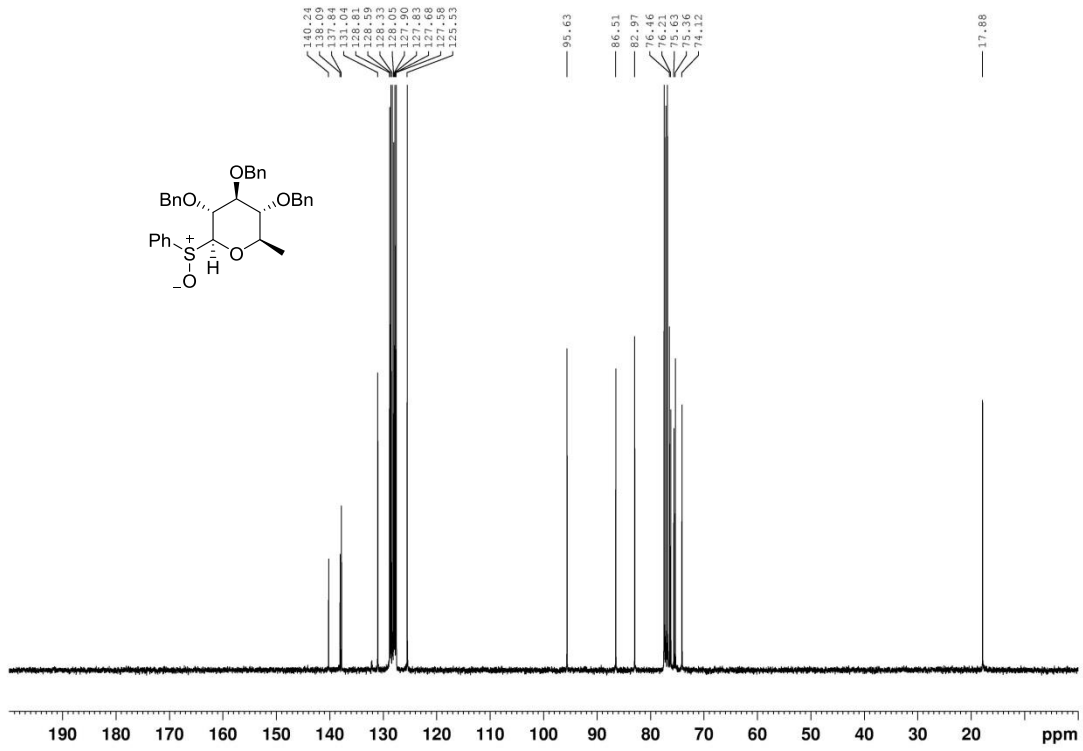

OBn
BnO
OBn
PhS
O

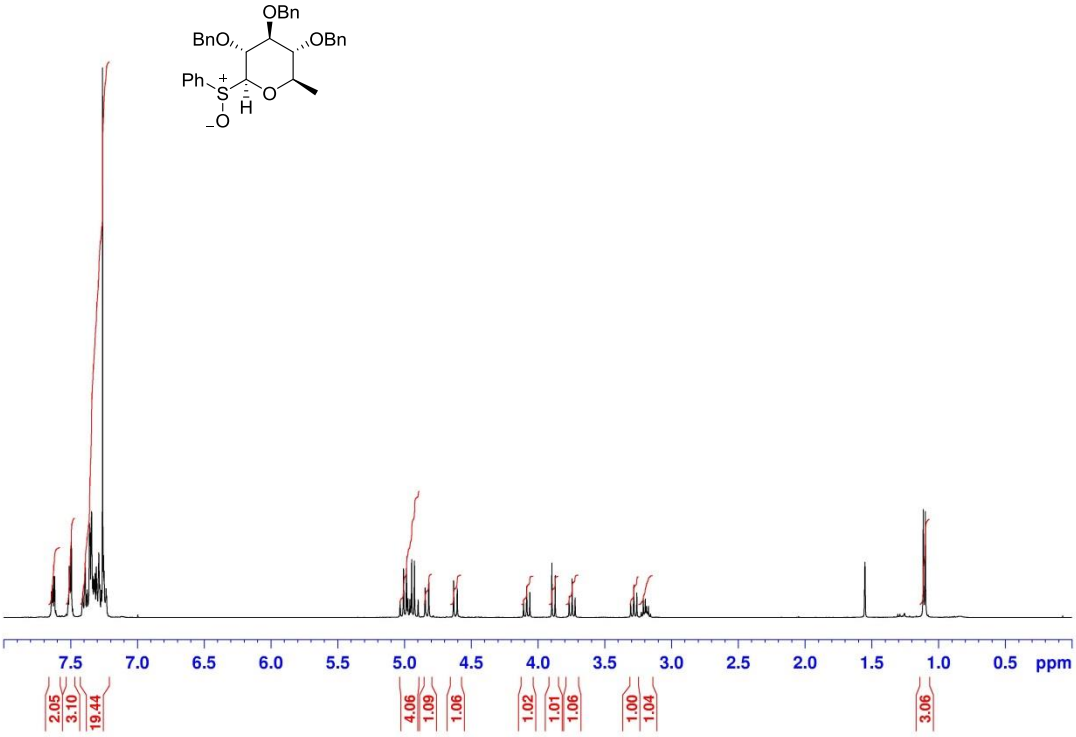

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
17.89
4.03
1.02
2.04
1.00
1.00
1.06
1.01
3.03

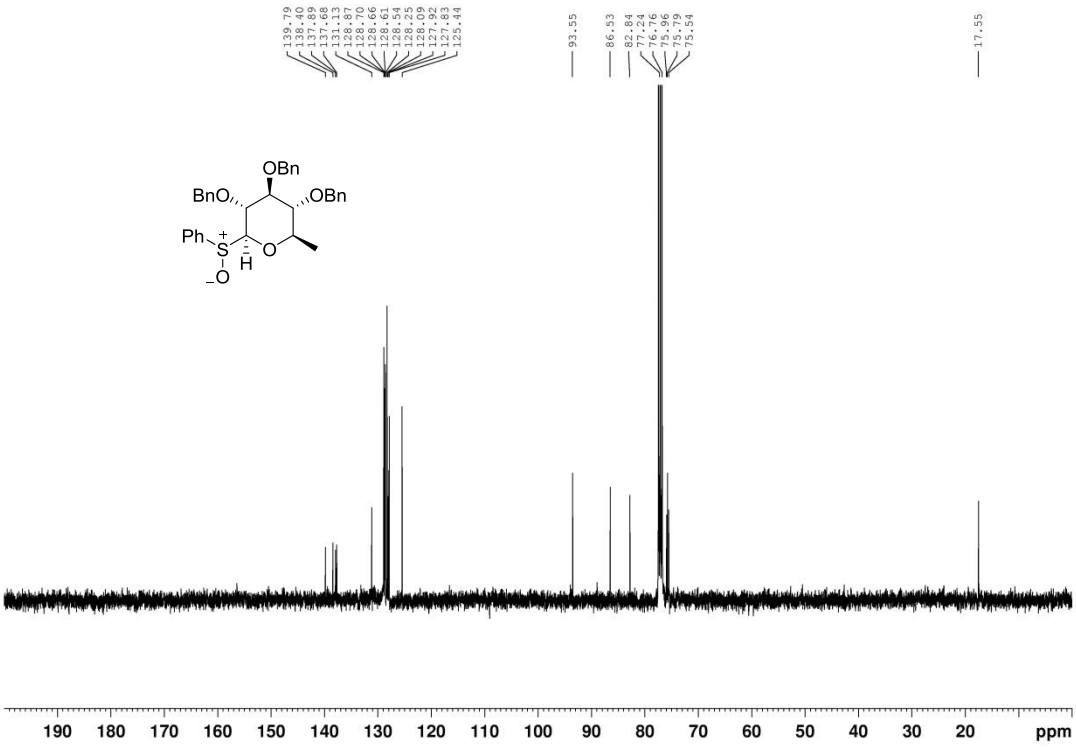

OBn
BnO
OBn
PhS
O

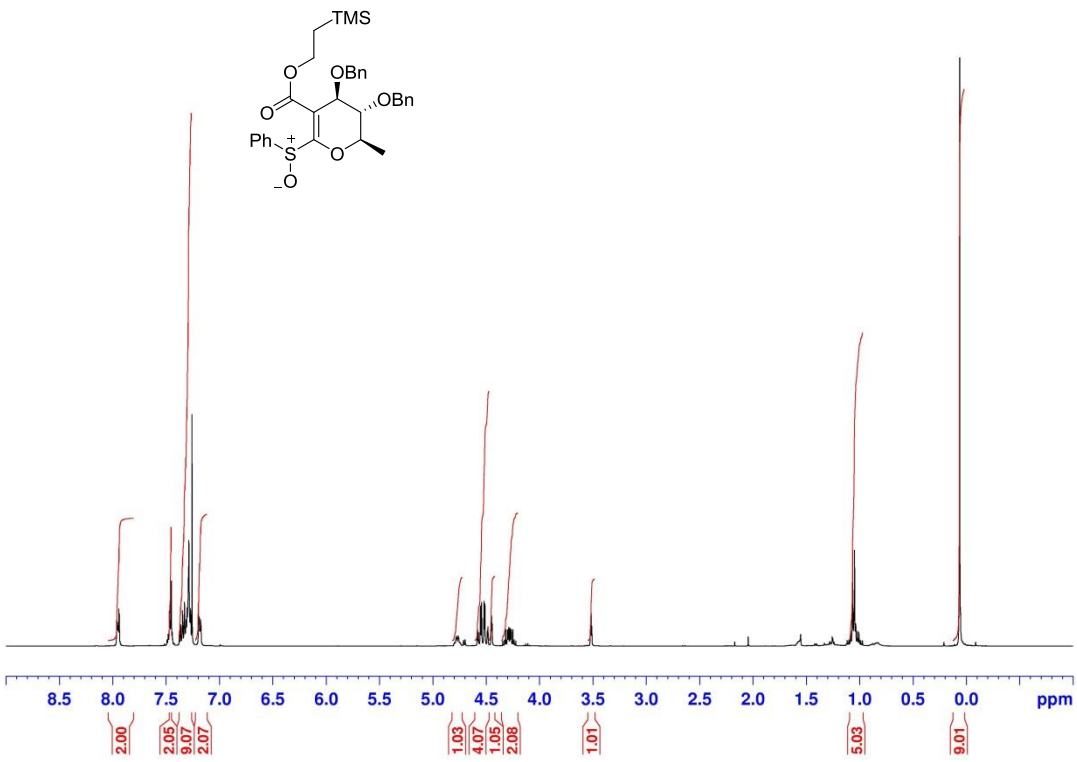

138.52
138.16
134.04
131.98
129.05
128.62
128.58
128.37
128.15
128.03
127.99
127.88
127.61
87.62
86.71
83.44
81.41
81.38
75.75
75.63
75.54
18.32
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

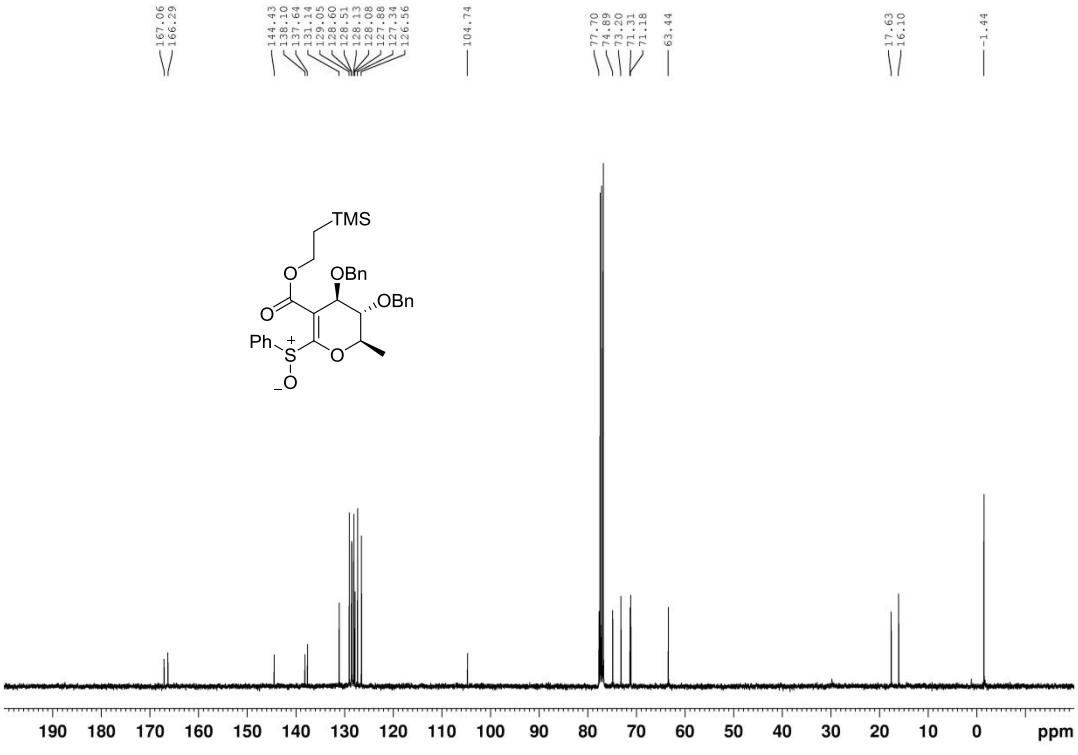

OBn
BnO
OBn
Ph
S
O
H
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
16.60
2.06
5.06
1.05
1.00
2.02
1.02
1.00
3.08

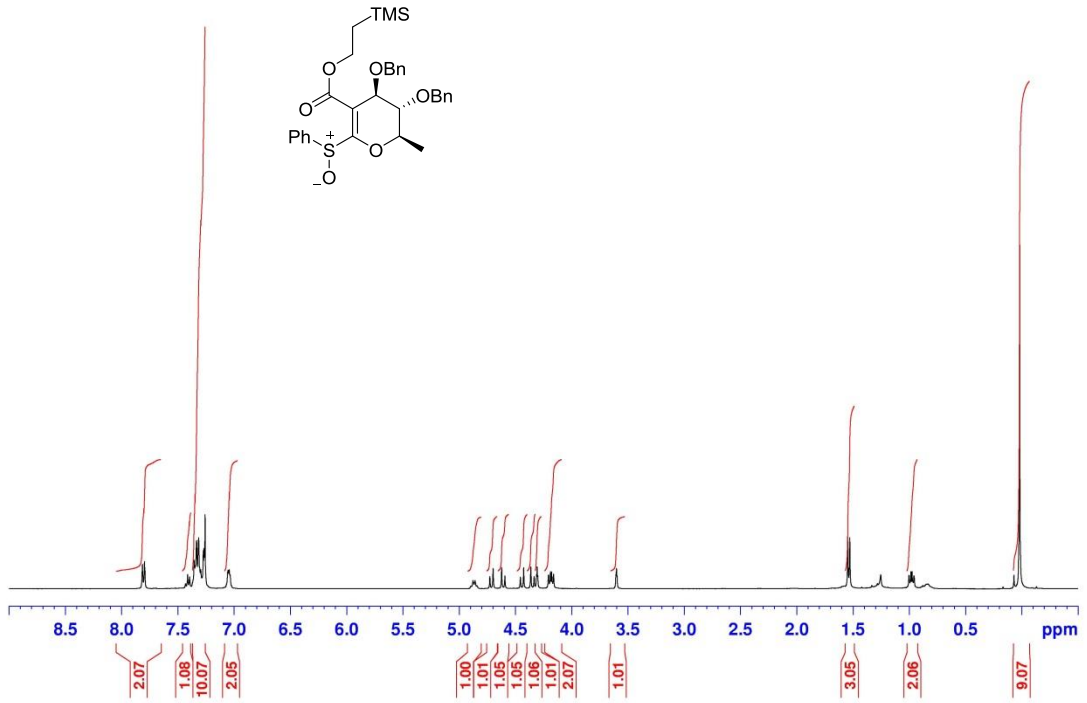

140.24
138.09
137.84
131.04
128.81
128.59
128.33
128.05
127.90
127.83
127.68
127.58
125.53
95.63
86.51
82.97
76.46
76.21
75.63
75.36
74.12
17.88
OBn
BnO
OBn
Ph
S
O
H
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

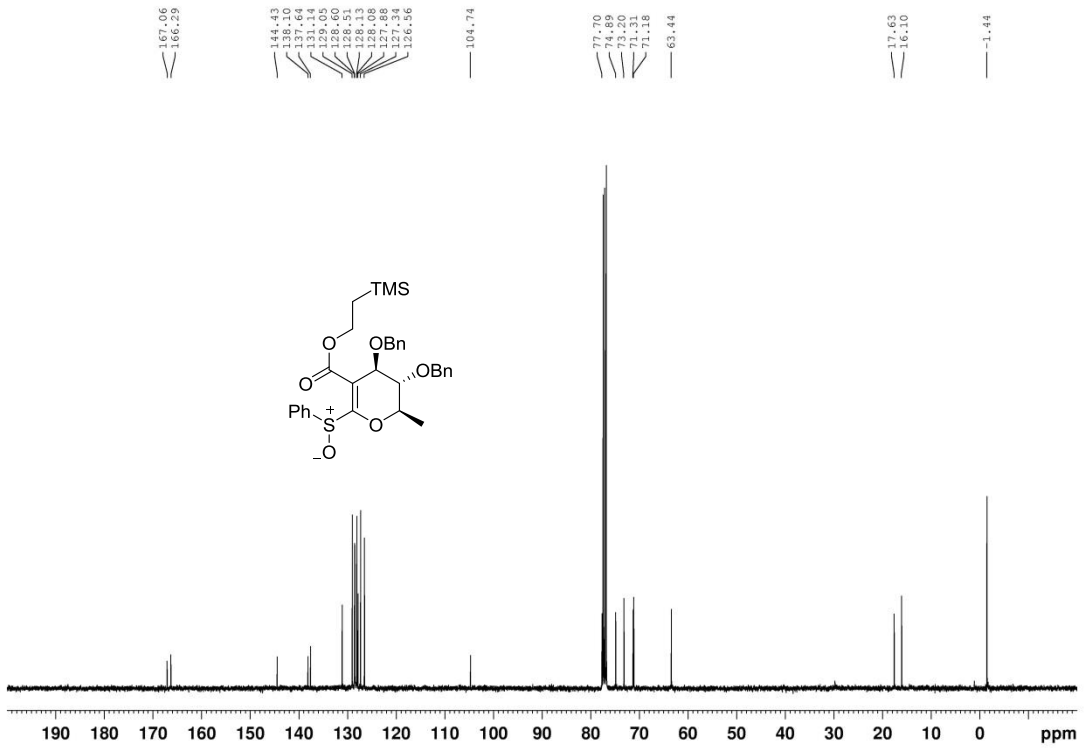

OBn
BnO
OBn
Ph
S
O
H
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
3.10
19.44
4.06
1.09
1.06
1.02
1.01
1.06
1.00
1.04
3.06

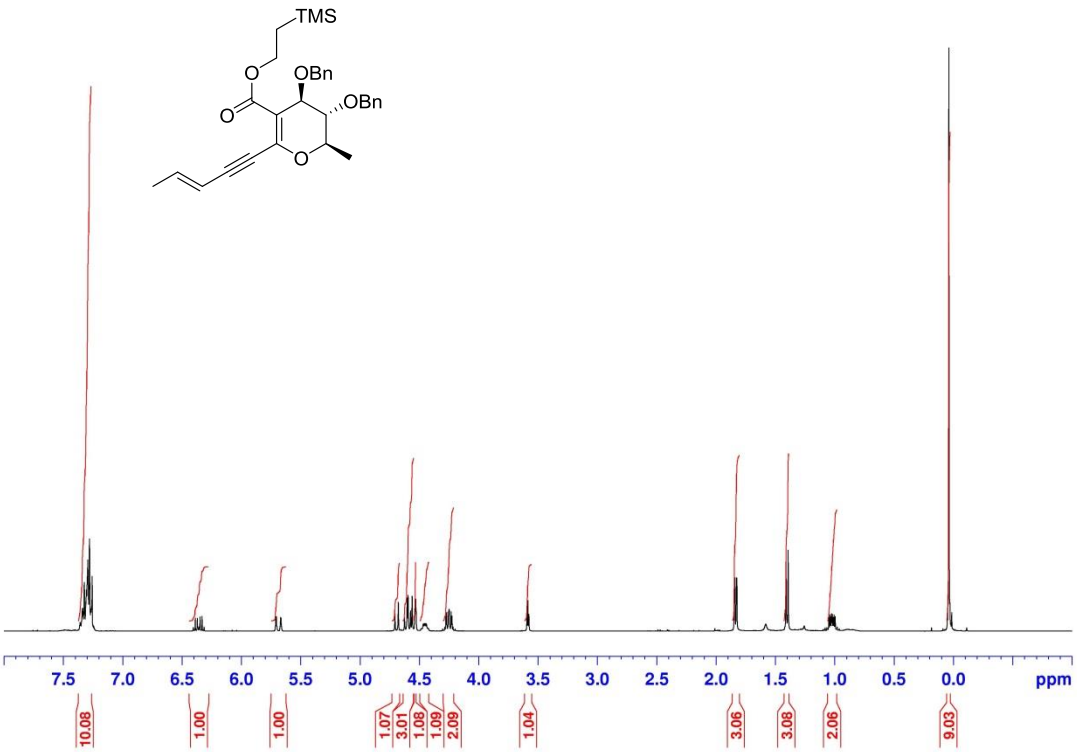

139.79
139.40
137.88
137.68
131.13
128.87
128.70
128.66
128.61
128.54
128.25
128.09
127.92
127.83
125.44
93.55
86.53
82.84
77.24
76.76
75.96
75.79
75.54
17.55
OBn
BnO
OBn
Ph
S
O
H
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

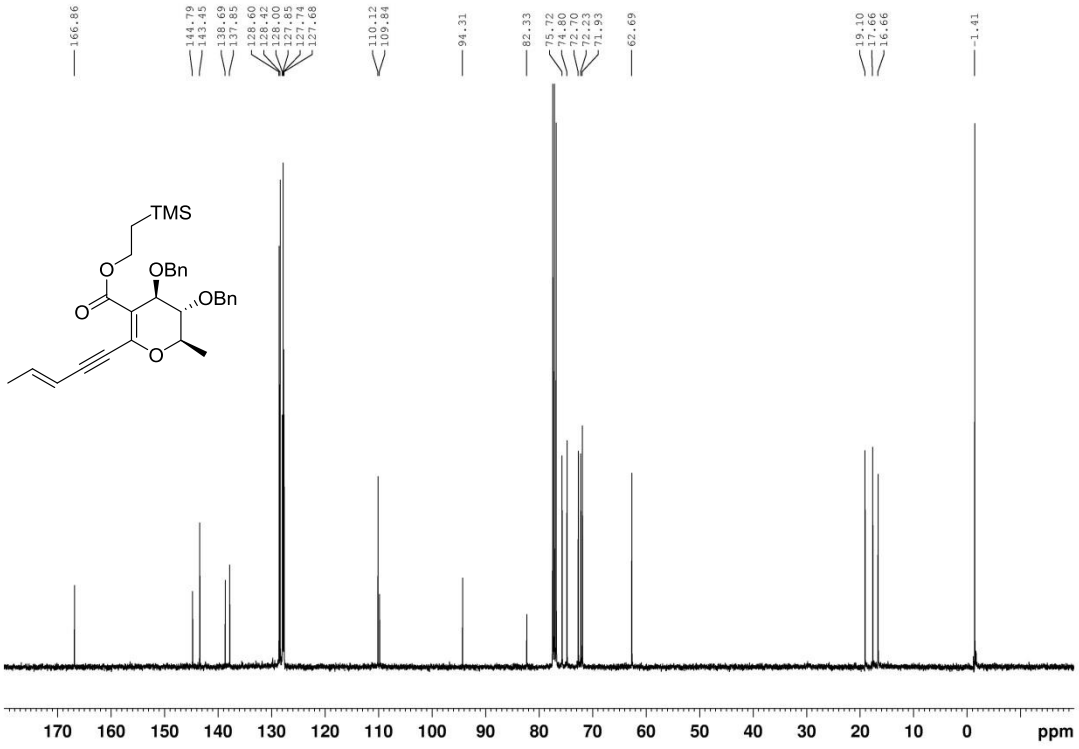

TMS
OBn
OBn
Ph
S
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00 2.05 9.07 2.07 1.03 4.07 1.05 2.08 1.01 5.03 9.01

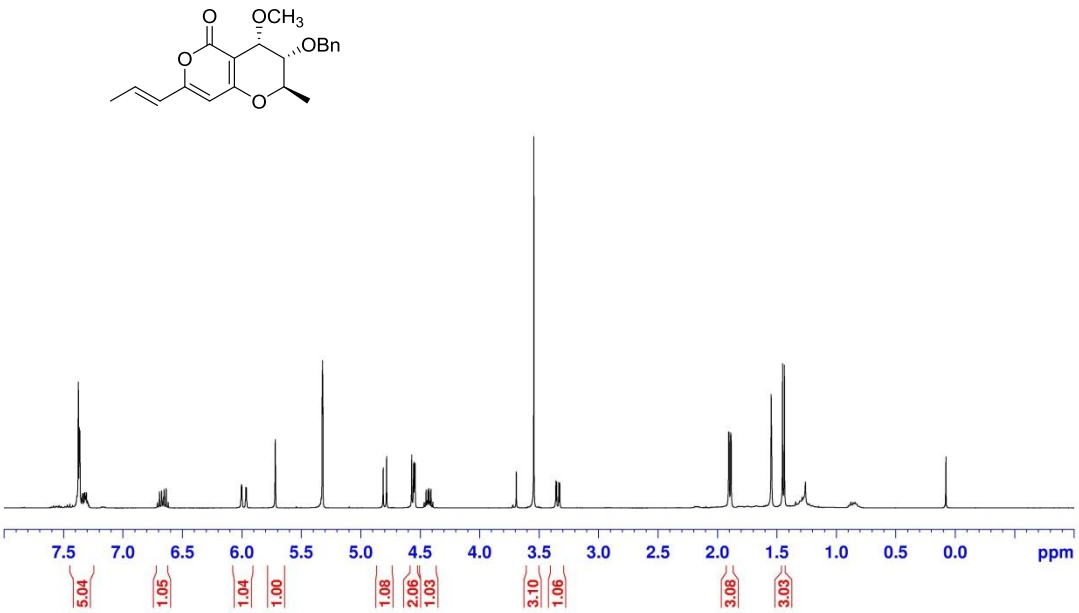

167.06
166.29
144.43
138.10
137.64
131.14
129.05
128.60
128.51
128.13
128.03
127.88
127.34
126.56
104.74
77.70
74.89
73.20
71.31
71.18
63.44
17.63
16.10
-1.44
TMS
OBn
OBn
Ph
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

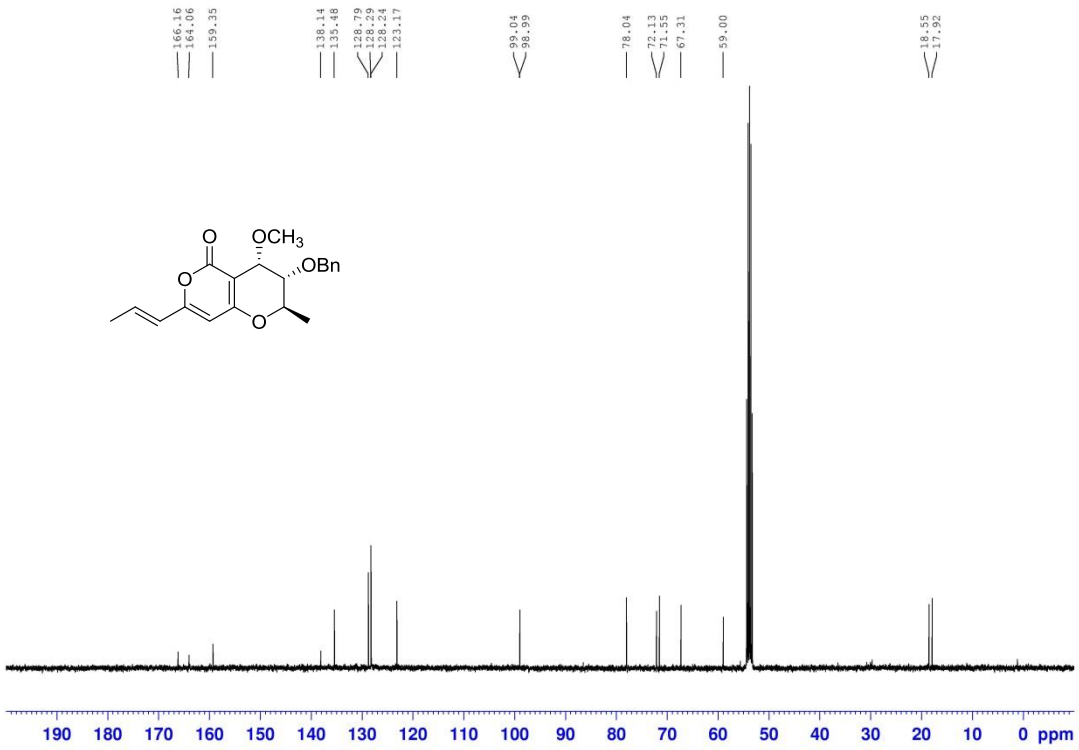

TMS
OBn
OBn
Ph
S
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.07 1.08 10.07 2.05 1.00 1.01 1.05 1.05 1.06 1.01 2.07 1.01 3.05 2.06 9.07

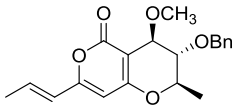

TMS
OBn
OBn
Ph
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

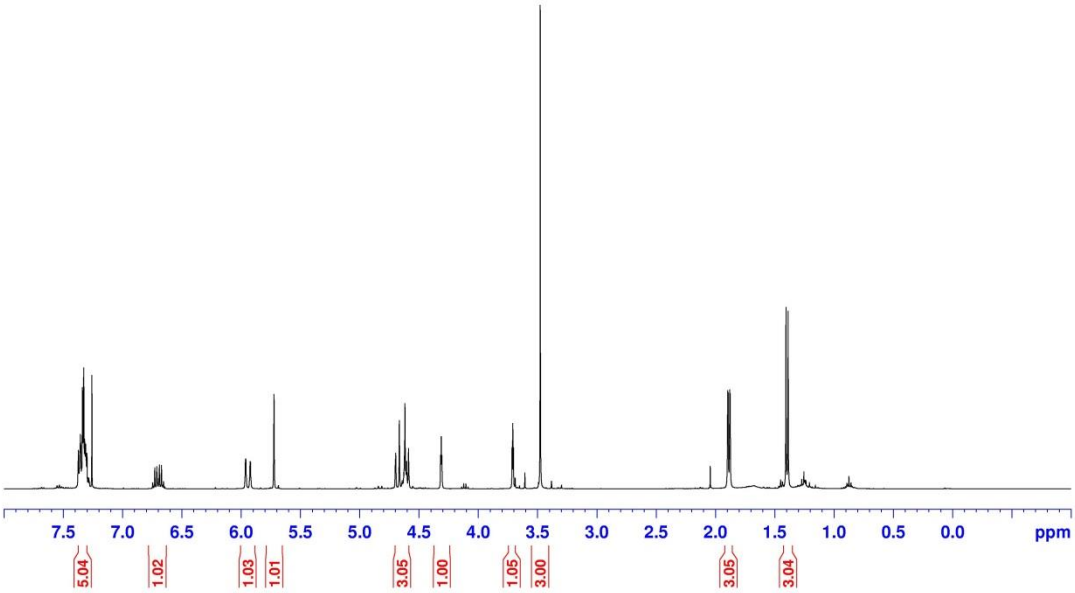

TMS
O
OBn
OBn
O
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
10.08
1.00
1.00
1.07
3.01
1.08
1.09
2.09
1.04
3.06
3.08
2.06
9.03


166.86
144.79
143.45
138.69
137.85
128.60
128.42
128.00
127.85
127.74
127.68
110.12
109.84
94.31
82.33
75.72
74.80
72.70
72.23
71.93
62.69
19.10
17.66
16.66
-1.41
TMS
O
OBn
OBn
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

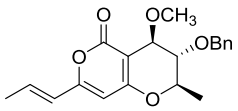

O
OCH3
OBn
O
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.04
1.05
1.04
1.00
1.08
2.06
1.03
3.10
1.06
3.08
3.03

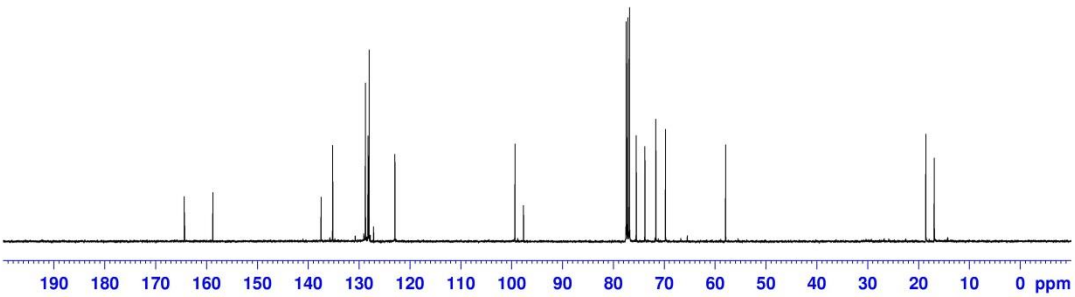

166.16
164.06
159.35
138.14
135.48
128.79
128.29
128.24
123.17
99.04
98.99
78.04
72.13
71.55
67.31
59.00
18.55
17.92
O
OCH3
OBn
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

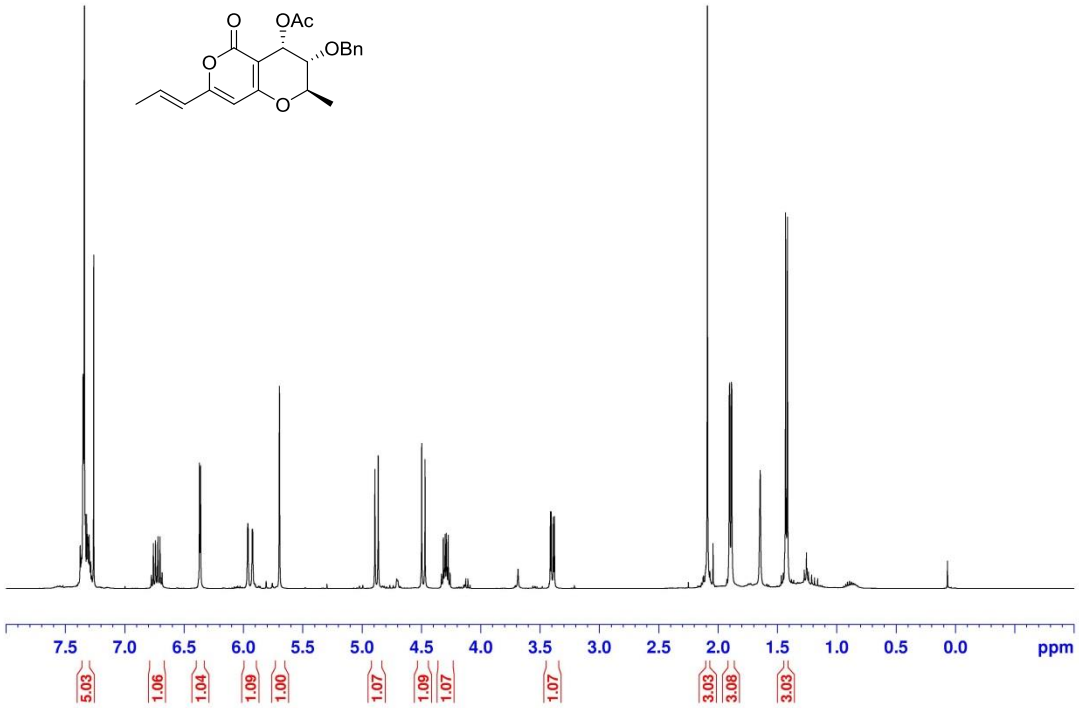

O
OCH3
OBn
O
O

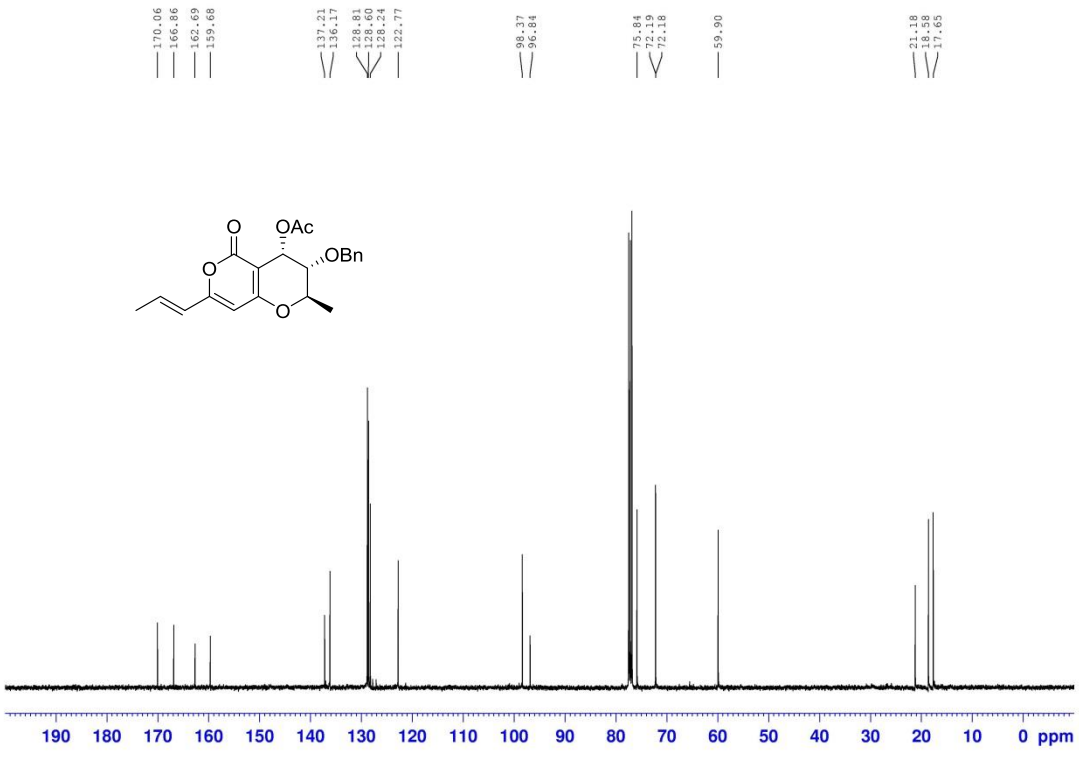

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.04
1.02
1.03
1.01
3.05
1.00
1.05
3.00
3.05
3.04

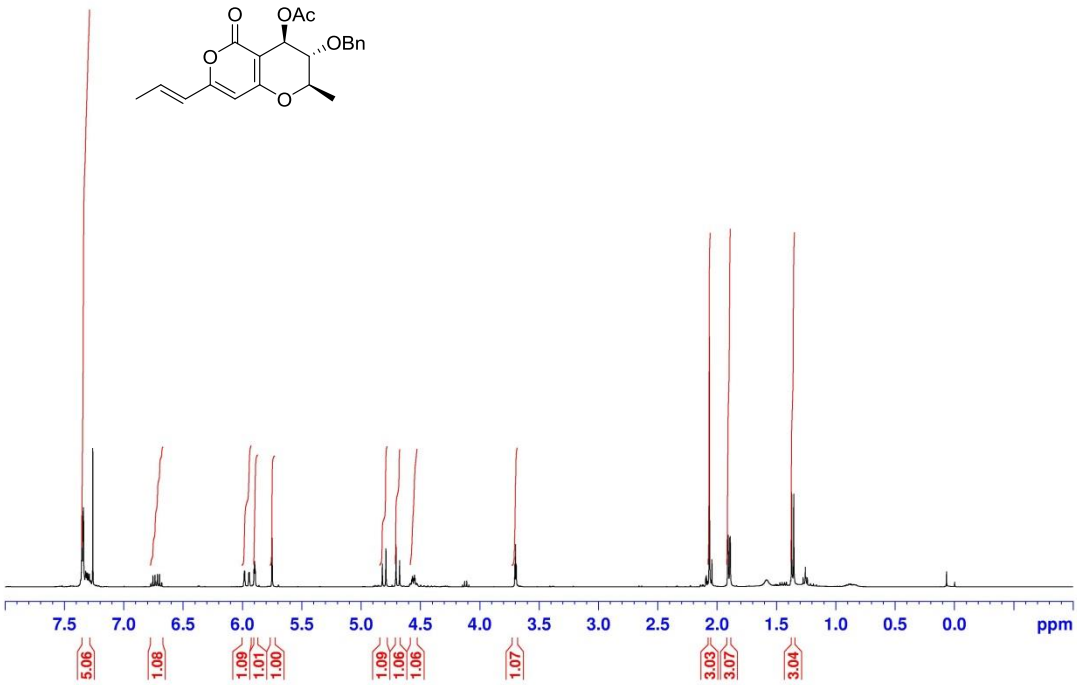

164.32
164.27
158.70
137.43
135.14
128.70
128.18
127.96
122.90
99.36
97.67
75.50
73.79
71.65
69.76
57.93
18.57
16.90

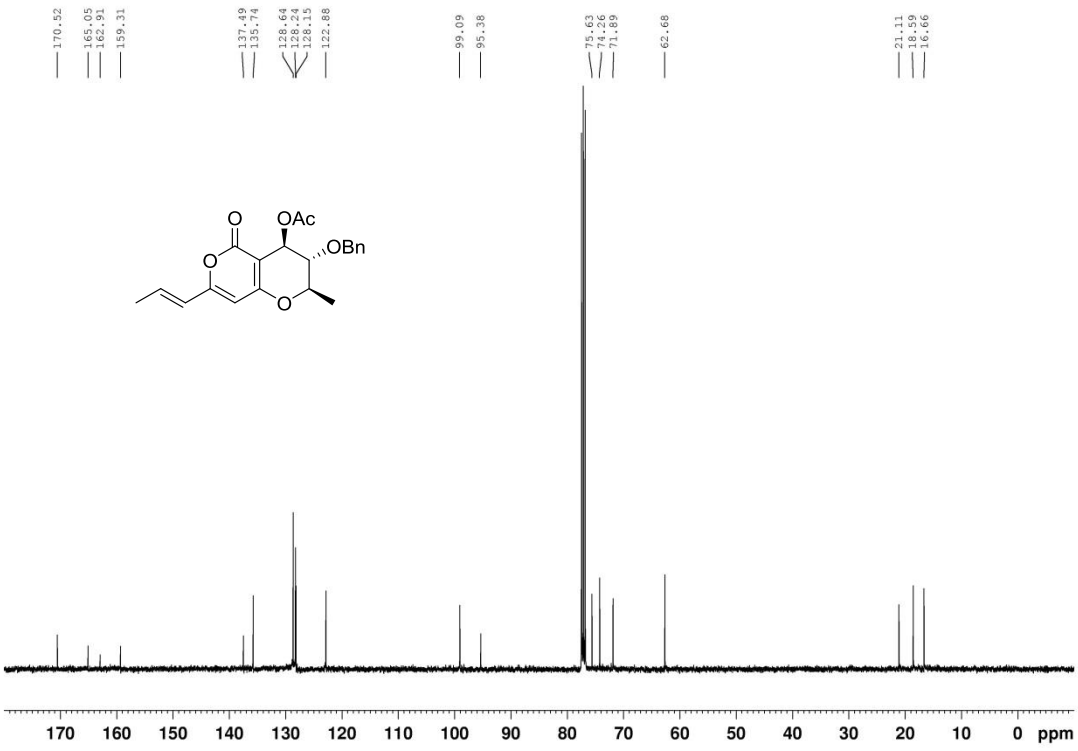

O
OCH3
OBn
O
O

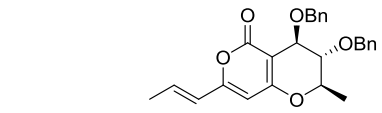

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

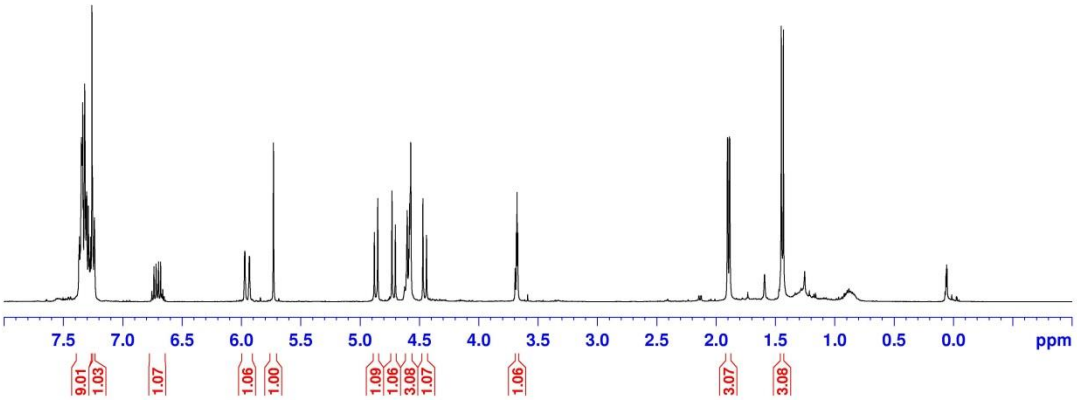

O
OAc
OBn
O
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.03 1.06 1.04 1.09 1.00 1.07 1.09 1.07 1.07 3.03 3.08 3.03


O
OAc
OBn
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
OAc
OBn
O
O
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
ppm
5.06
1.08
1.09
1.01
1.00
1.09
1.06
1.06
1.07
3.03
3.07
3.04


170.52
165.05
162.91
159.31
137.49
135.74
128.64
128.24
128.15
122.88
99.09
95.38
75.63
74.26
71.89
62.68
21.11
18.59
16.66
O
OAc
OBn
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
OBn
OBn
O
O


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
ppm
9.01
1.03
1.07
1.06
1.00
1.09
1.06
3.08
1.07
1.06
3.07
3.08


164.35
164.33
158.68
138.76
137.55
135.05
128.68
128.47
128.13
128.08
127.91
127.74
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99.44
98.13
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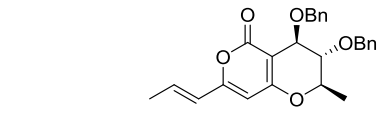
75.06
73.09
71.74
68.32
18.56
17.22


O
OBn
OBn
O
O

190
180
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150
140
130
120
110
100
90
80
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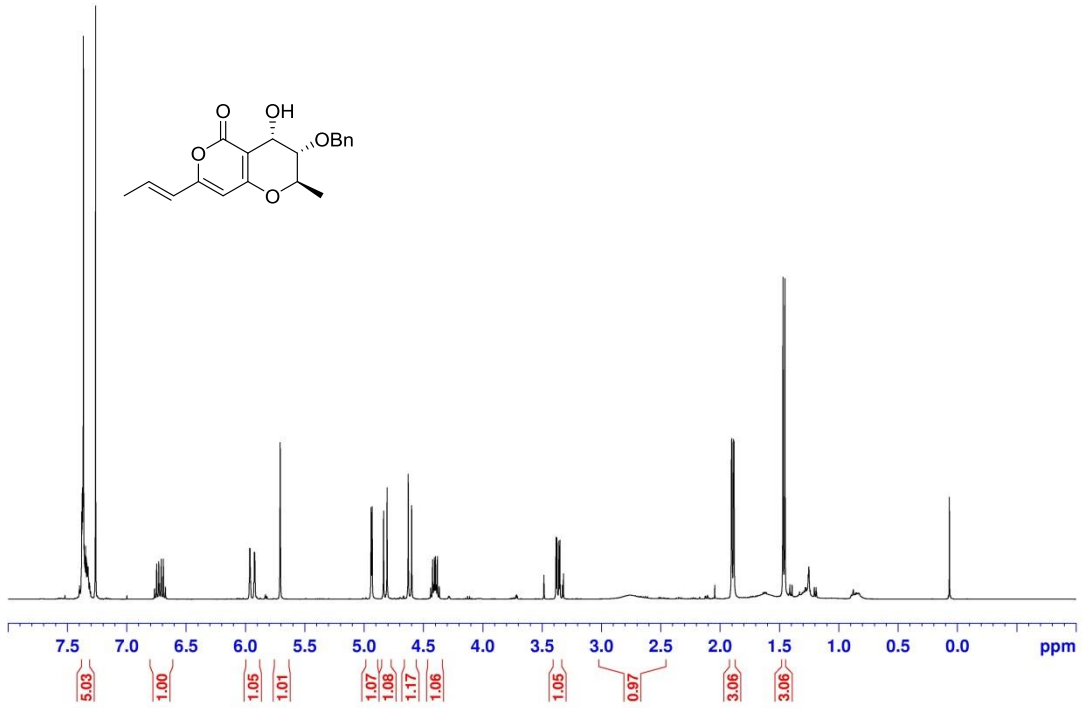
60
50
40
30
20
10
0 ppm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OH
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O
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6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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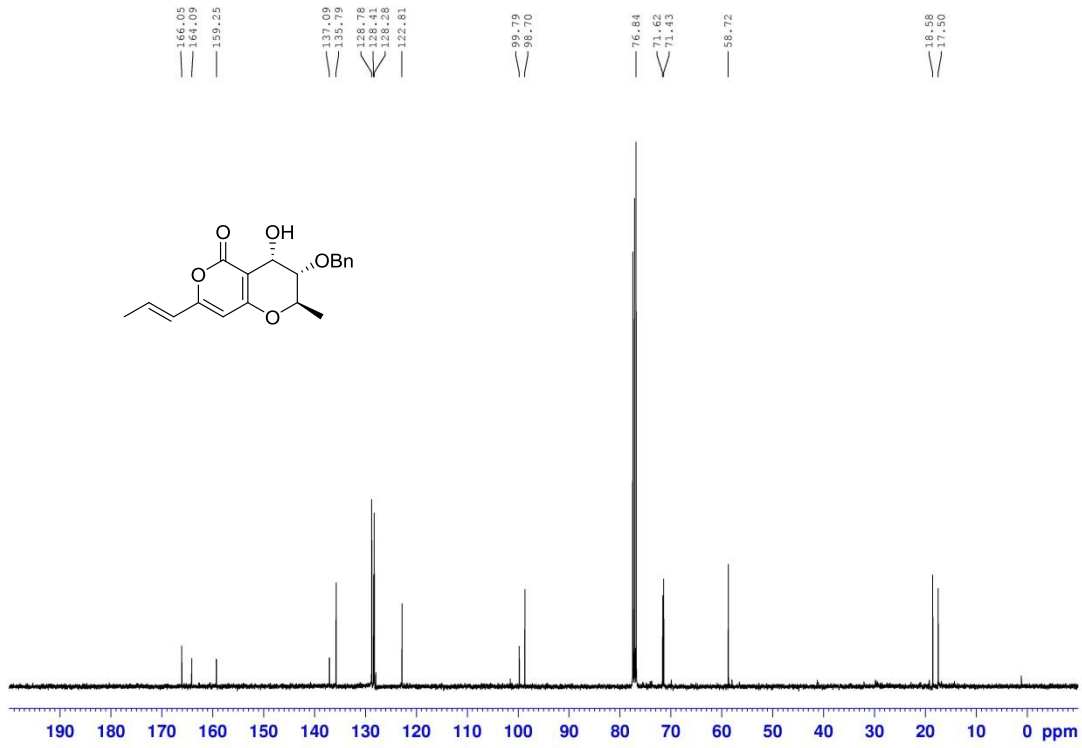
1.00
1.05
1.01
1.07
1.08
1.17
1.06
1.05
0.97
3.06
3.06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164.09
159.25
137.09
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128.78
128.41
128.28
122.81
99.79
98.70
76.84
71.62
71.43
58.72
18.58
17.50
O
OH
OBn
O
O
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180
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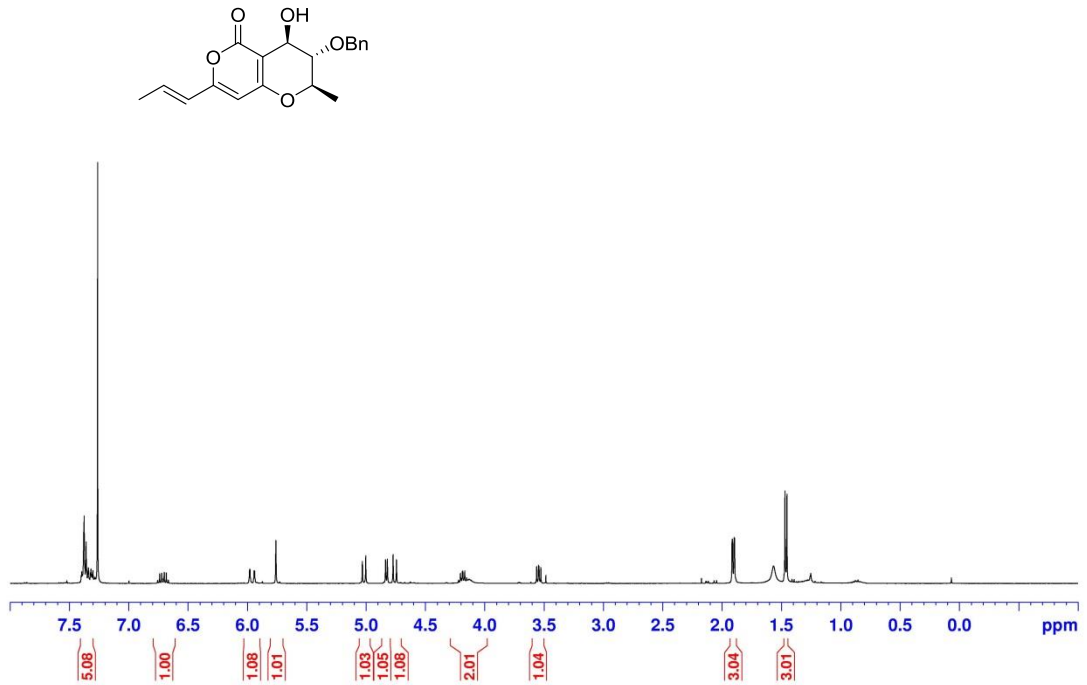
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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OH
OBn
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O
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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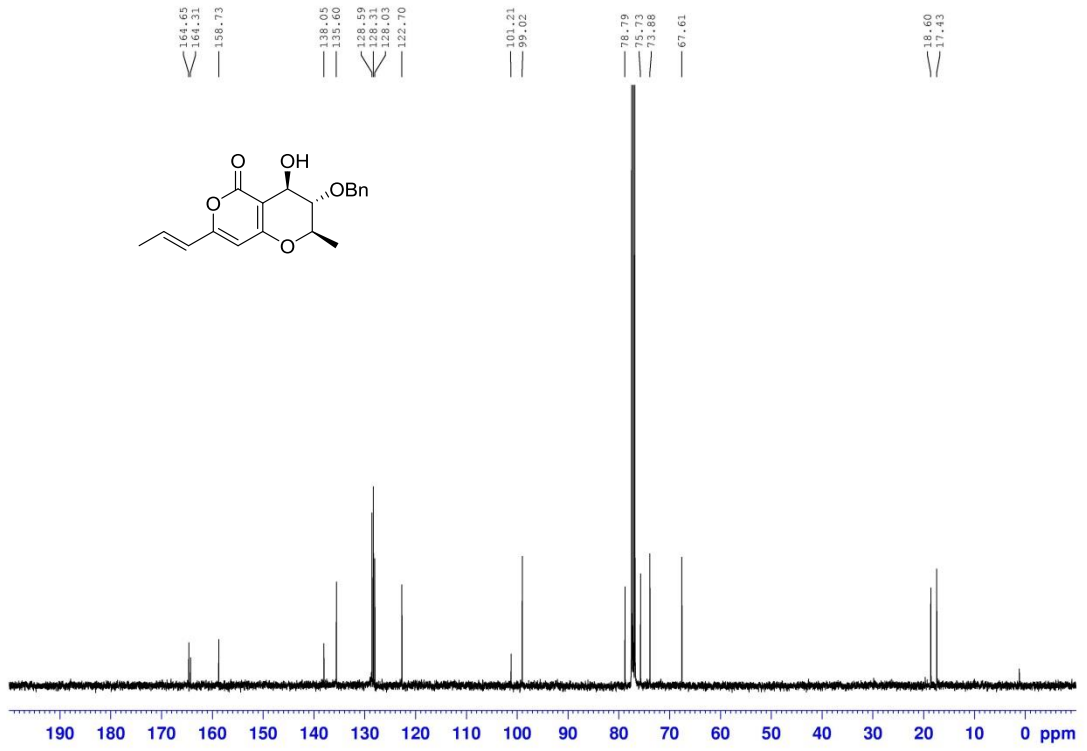
1.08
1.01
1.03
1.05
1.08
2.01
1.04
3.04
3.01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164.31
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135.60
128.59
128.31
128.03
122.70
101.21
99.02
78.79
75.73
73.88
67.61
18.60
17.43
O
OH
OBn
O
O
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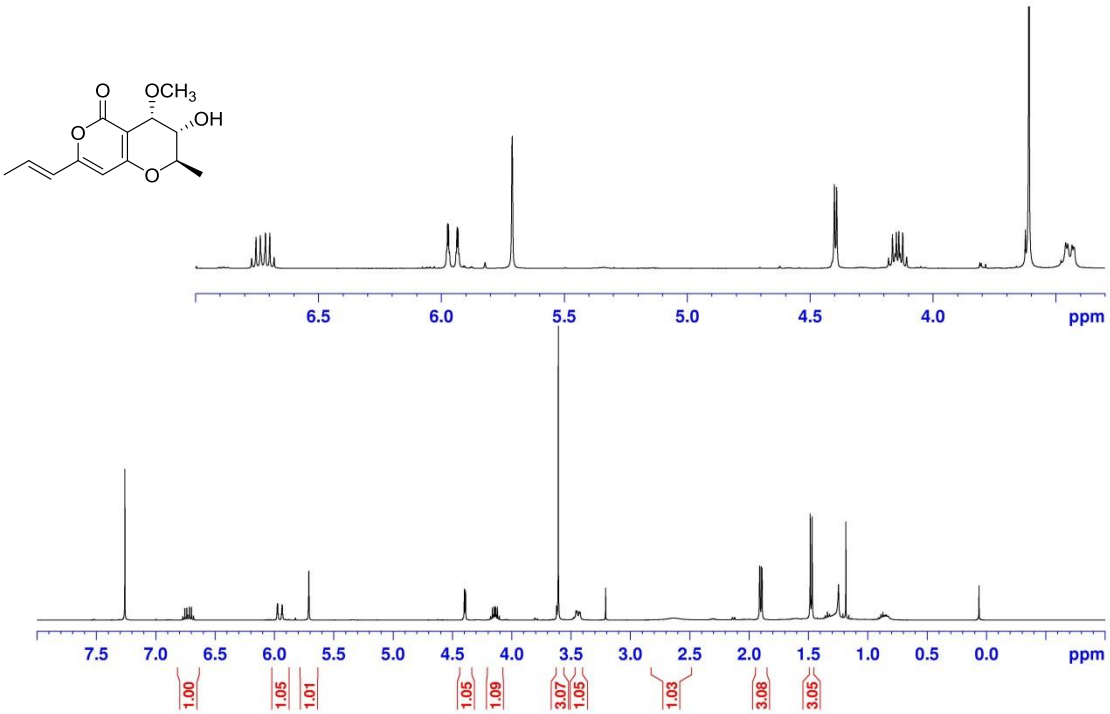
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


OCH3
OH
O
O
O
6.5
6.0
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5.0
4.5
4.0
ppm
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
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ppm
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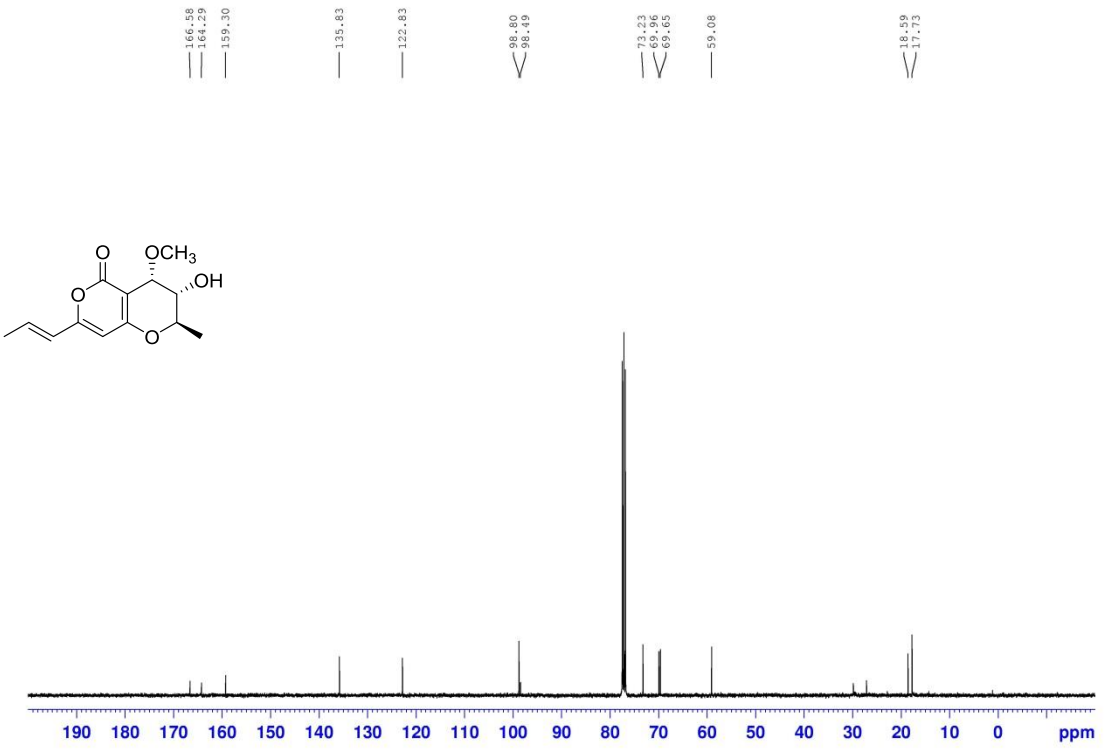
1.05
1.01
1.05
1.09
3.07
1.05
1.03
3.08
3.05

)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164.29
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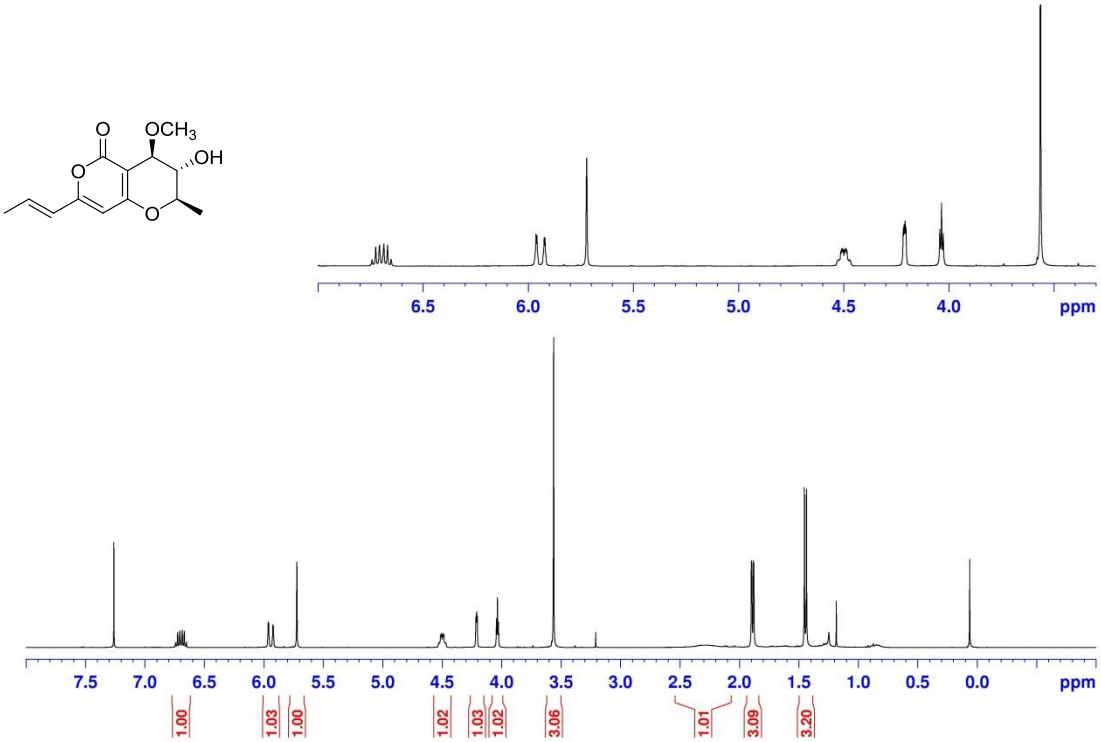
122.83
98.80
98.49
73.23
69.96
69.65
59.08
18.59
17.73
OCH3
OH
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
OCH3
OH
O
O
6.5
6.0
5.5
5.0
4.5
4.0
ppm
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
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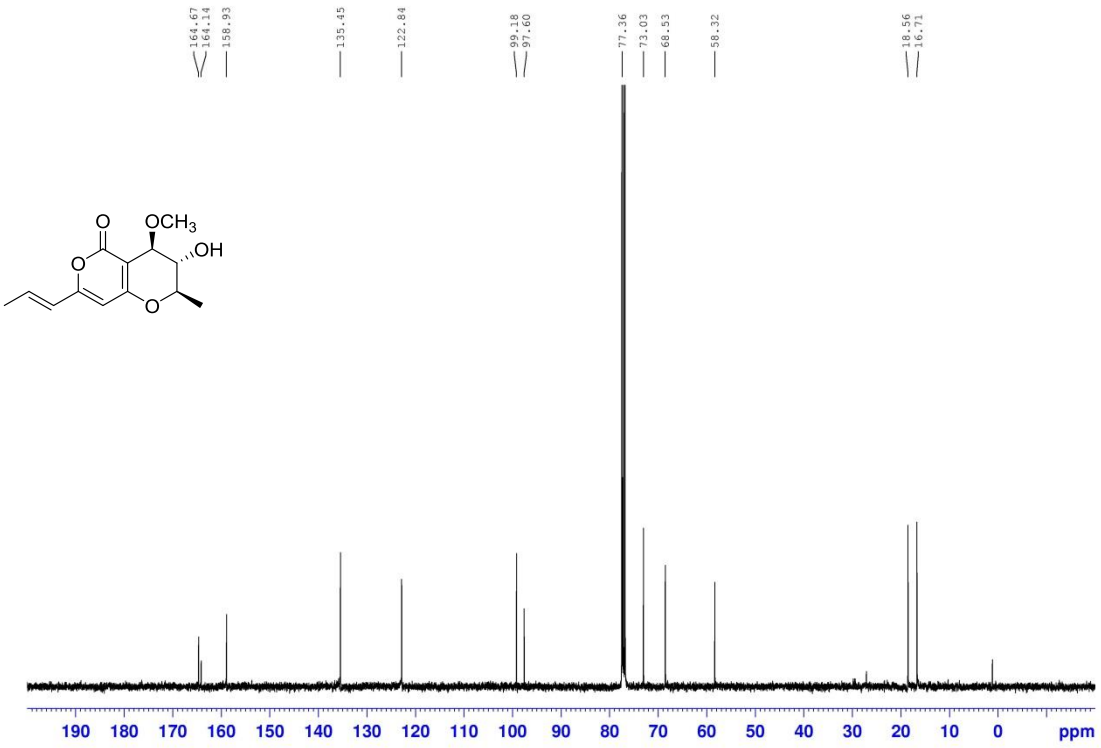
1.03
1.00
1.02
1.03
1.02
3.06
1.01
3.09
3.20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164.14
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99.18
97.60
77.36
73.03
68.53
58.32
18.56
16.71
O
OCH3
OH
O
O
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180
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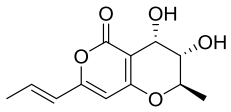
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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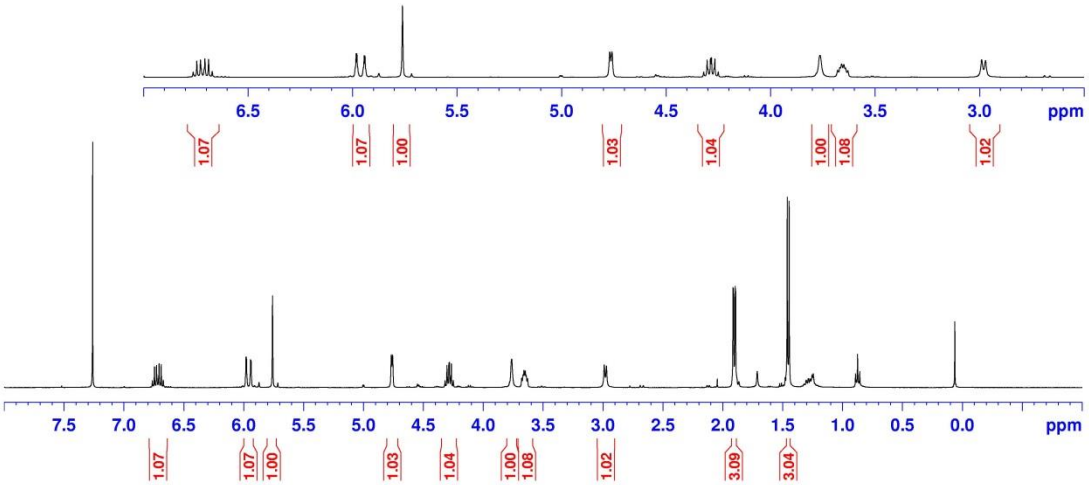
OH
O
OH
O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6.0
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5.0
4.5
4.0
3.5
3.0
ppm
1.07
1.07
1.00
1.03
1.04
1.00
1.08
1.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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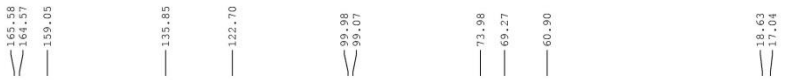
1.07
1.00
1.03
1.04
1.00
1.08
1.02
3.09
3.04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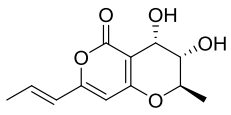
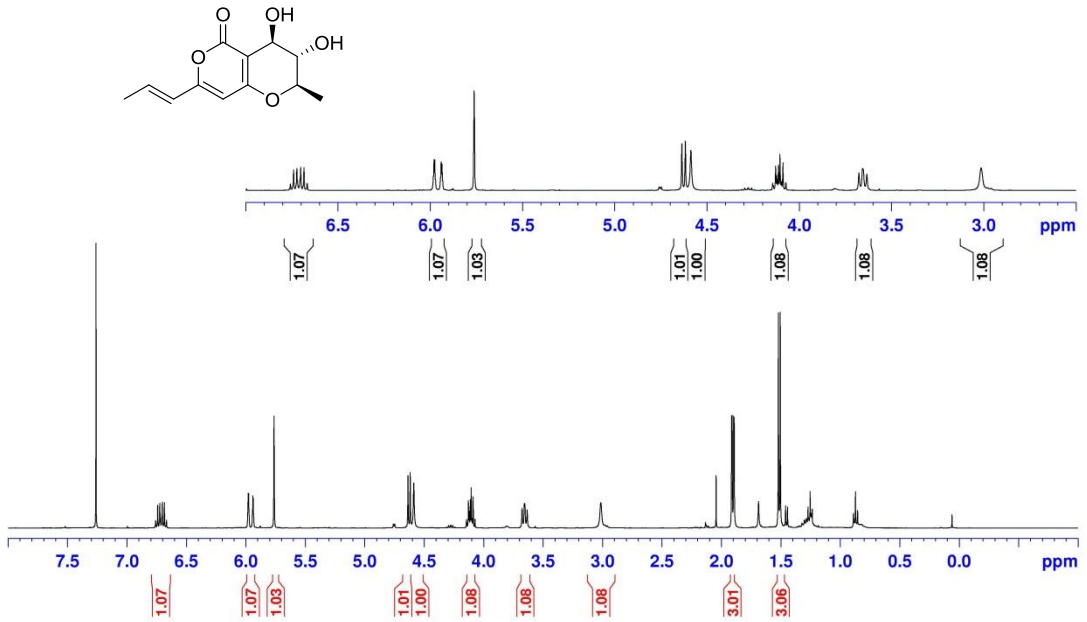
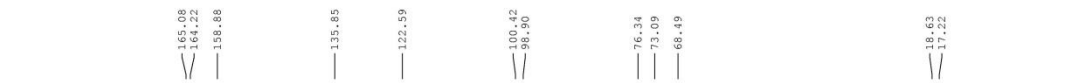
99.98
99.07
73.98
69.27
60.90
18.63
17.04


O
OH
O
OH
O

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


O
OH
OH
O
O
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
1.07
1.07
1.03
1.01
1.00
1.08
1.08
1.08
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
ppm
1.07
1.07
1.03
1.01
1.00
1.08
1.08
1.08
3.01
3.06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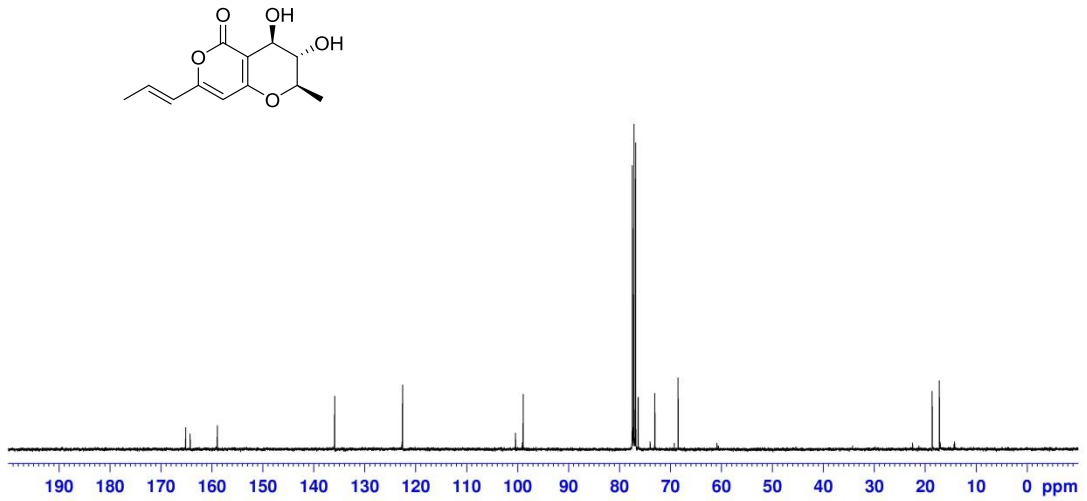
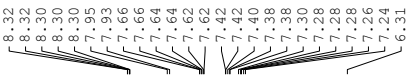
98.90
76.34
73.09
68.49
18.63
17.22


O
OH
OH
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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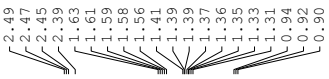
8.32
8.30
8.30
8.30
7.95
7.93
7.66
7.66
7.64
7.64
7.62
7.62
7.42
7.40
7.38
7.38
7.30
7.28
7.28
7.28
7.26
7.24
6.31


2.49
2.47
2.45
2.39
1.63
1.61
1.59
1.58
1.56
1.41
1.39
1.39
1.37
1.36
1.35
1.33
1.31
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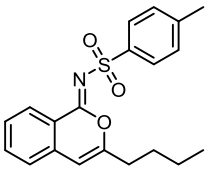
0.92
0.90


O
S
O
N
O

9
8
7
6
5
4
3
2
1
0 ppm
0.99
1.97
1.04
1.11
3.02
1.00
2.04
3.07
2.08
2.65
3.05


159.89
157.61
142.89
139.32
135.53
135.25
129.12
128.85
128.31
127.27
125.14
120.18
104.50
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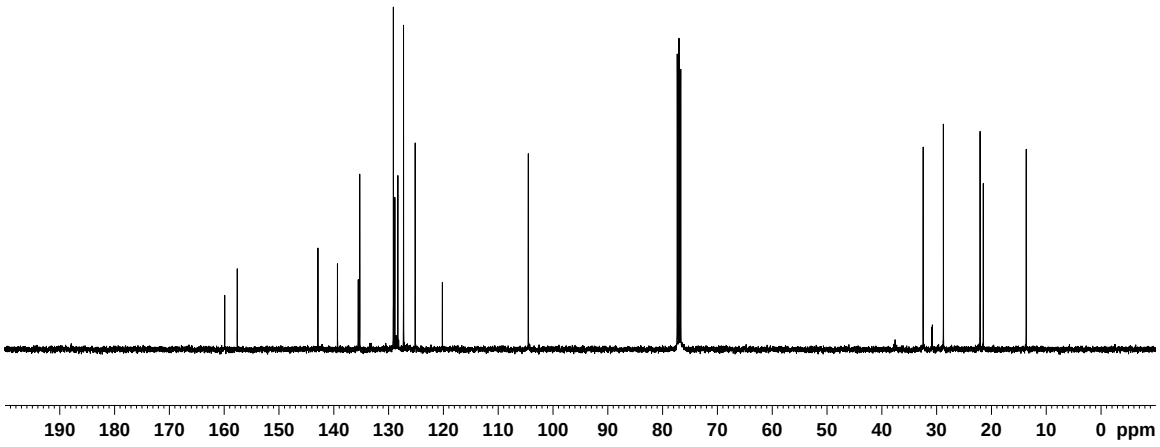
77.00
76.68
32.45
28.76
22.06
21.48
13.65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180
170
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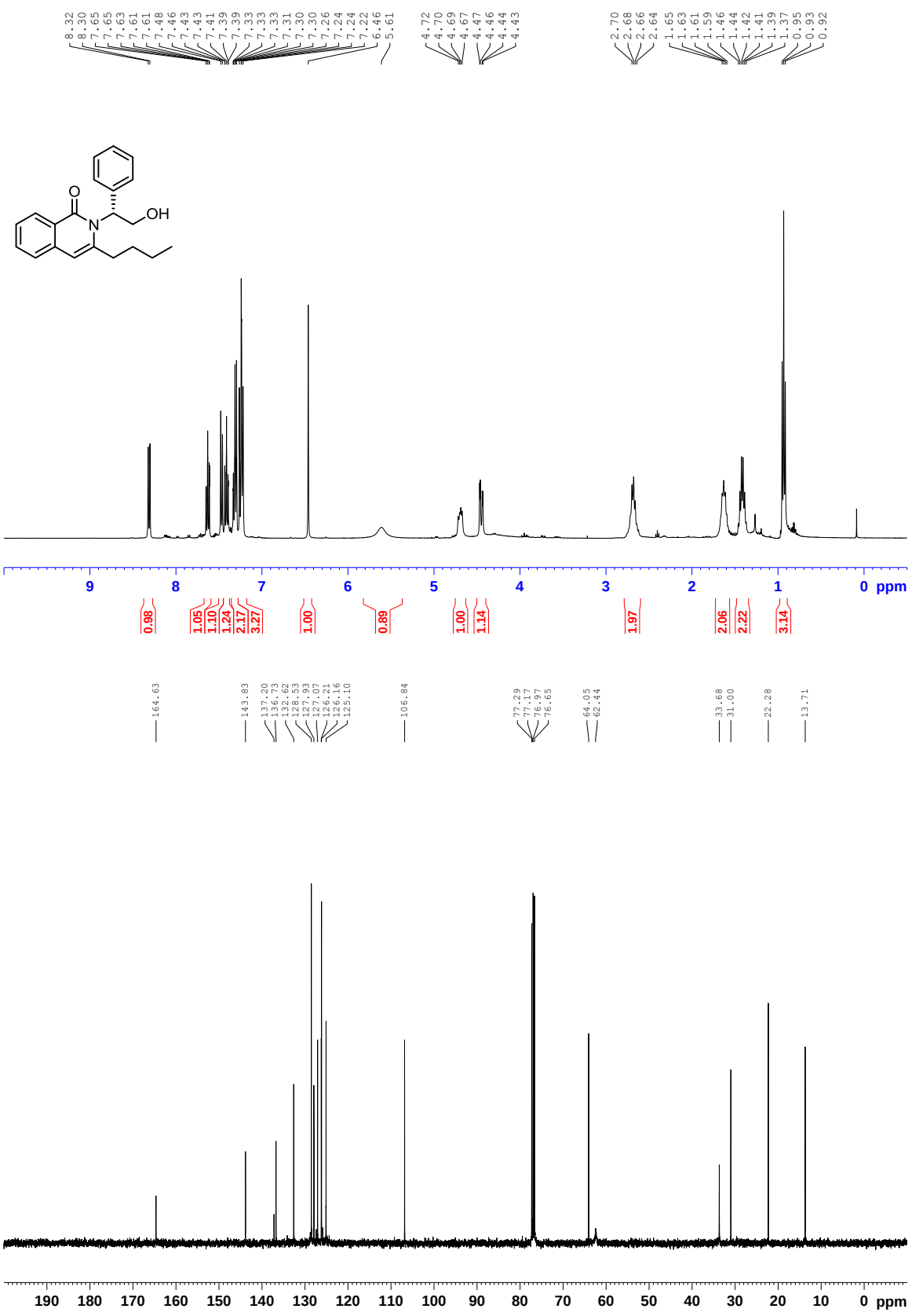
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.43
7.43
7.41
7.39
7.39
7.33
7.33
7.31
7.30
7.30
7.26
7.24
7.24
7.22
6.46
5.61
4.72
4.70
4.69
4.67
4.47
4.46
4.44
4.43
2.70
2.68
2.66
2.64
1.65
1.63
1.61
1.59
1.46
1.44
1.42
1.41
1.39
1.37
0.95
0.93
0.92
O
N
OH
9
8
7
6
5
4
3
2
1
0 ppm
0.98
1.05
1.10
1.24
2.17
3.27
1.00
0.89
1.00
1.14
1.97
2.06
2.22
3.14
164.63
143.83
137.20
136.73
132.62
128.53
127.93
127.07
126.21
126.16
125.10
106.84
77.29
77.17
76.97
76.65
64.05
62.44
33.68
31.00
22.28
13.71
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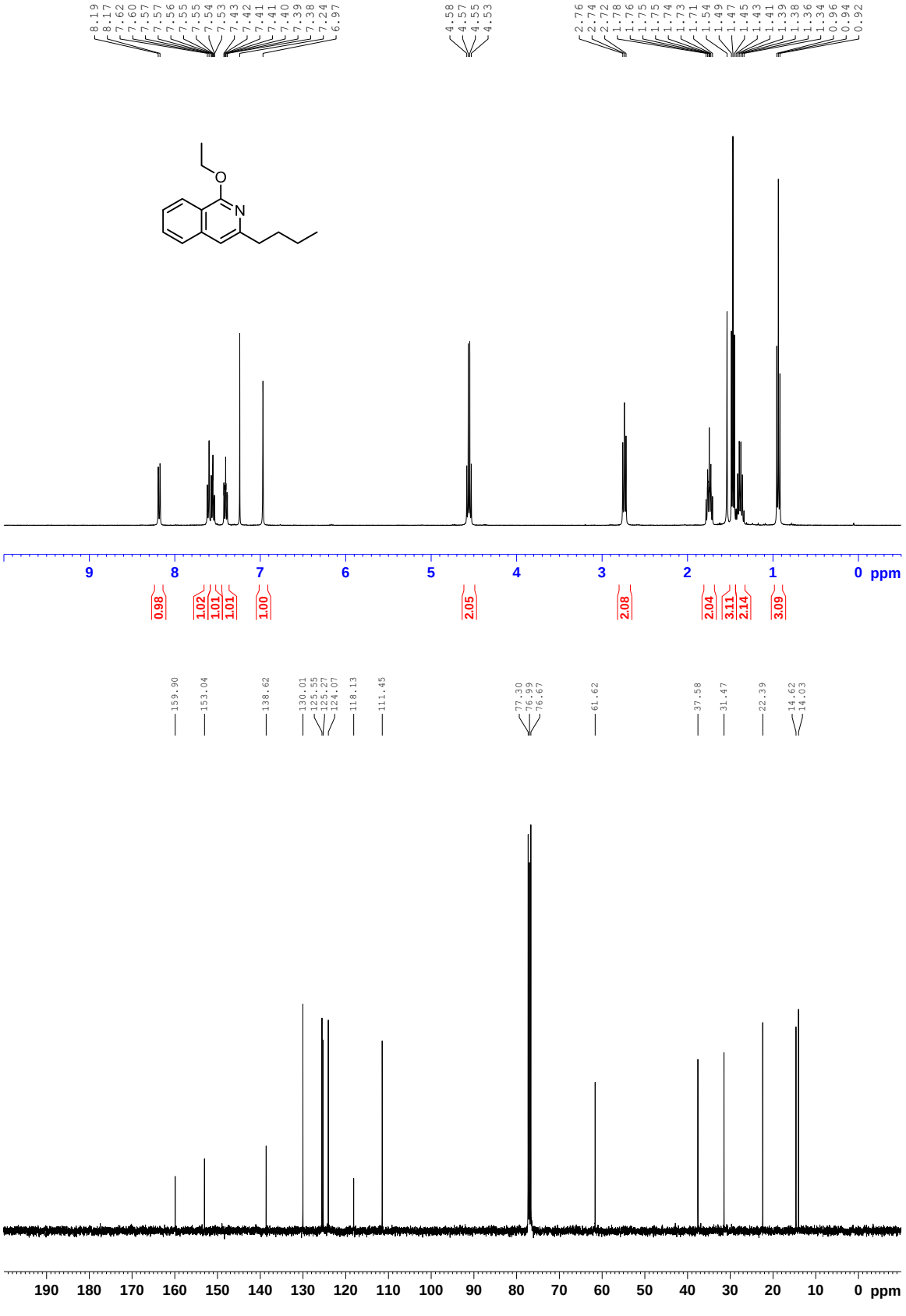
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.54
7.53
7.43
7.42
7.41
7.41
7.40
7.39
7.38
7.24
6.97
4.58
4.57
4.55
4.53
2.76
2.74
2.72
1.78
1.76
1.75
1.75
1.74
1.73
1.71
1.54
1.49
1.47
1.45
1.43
1.41
1.39
1.38
1.36
1.34
0.96
0.94
0.92
O
N
9
8
7
6
5
4
3
2
1
0 ppm
0.98
1.02
1.01
1.01
1.00
2.05
2.08
2.04
3.11
2.14
3.09
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138.62
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125.55
125.27
124.07
118.13
111.45
77.30
76.99
76.67
61.62
37.58
31.47
22.39
14.62
14.03
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180
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150
140
130
120
110
100
90
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70
60
50
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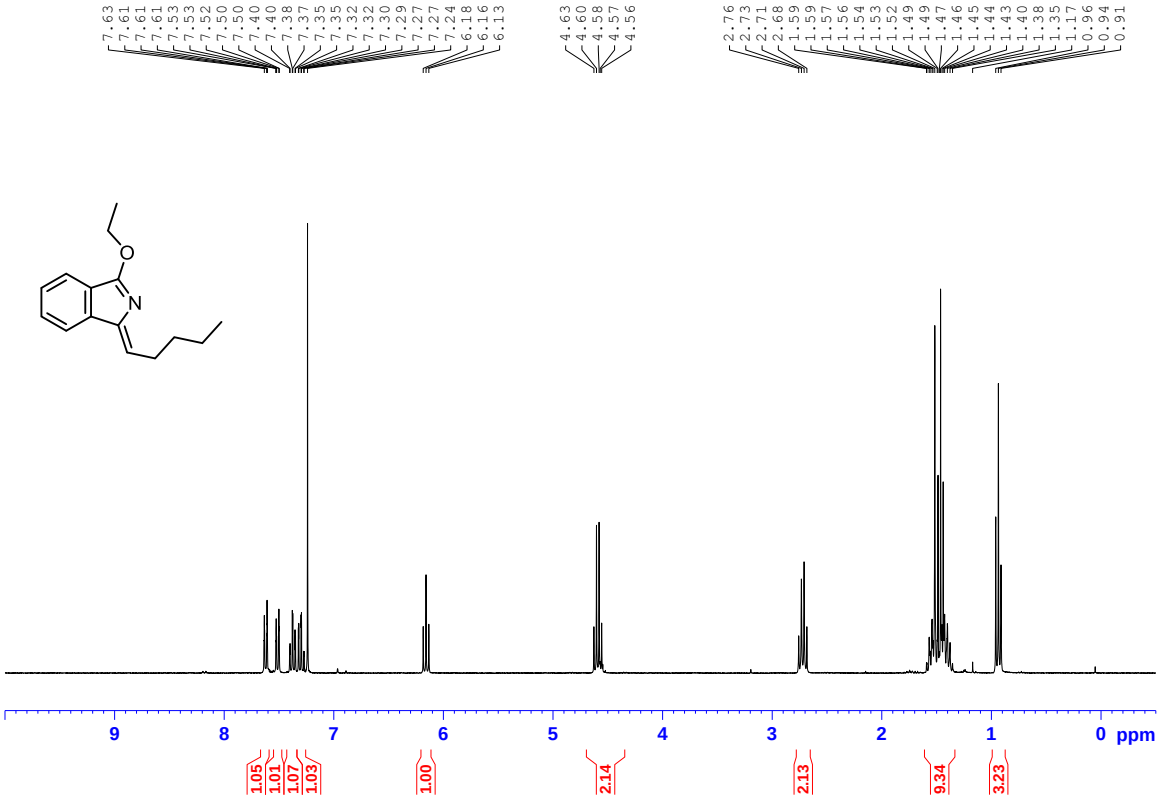
30
20
10
0 ppm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7.61
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7.61
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7.52
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7.40
7.38
7.37
7.35
7.35
7.32
7.32
7.30
7.29
7.27
7.27
7.24
6.18
6.16
6.13
4.63
4.60
4.58
4.57
4.56
2.76
2.73
2.71
2.68
1.59
1.59
1.57
1.56
1.54
1.53
1.52
1.49
1.49
1.47
1.46
1.45
1.44
1.43
1.40
1.38
1.35
1.17
0.96
0.94
0.91
O
N
9
8
7
6
5
4
3
2
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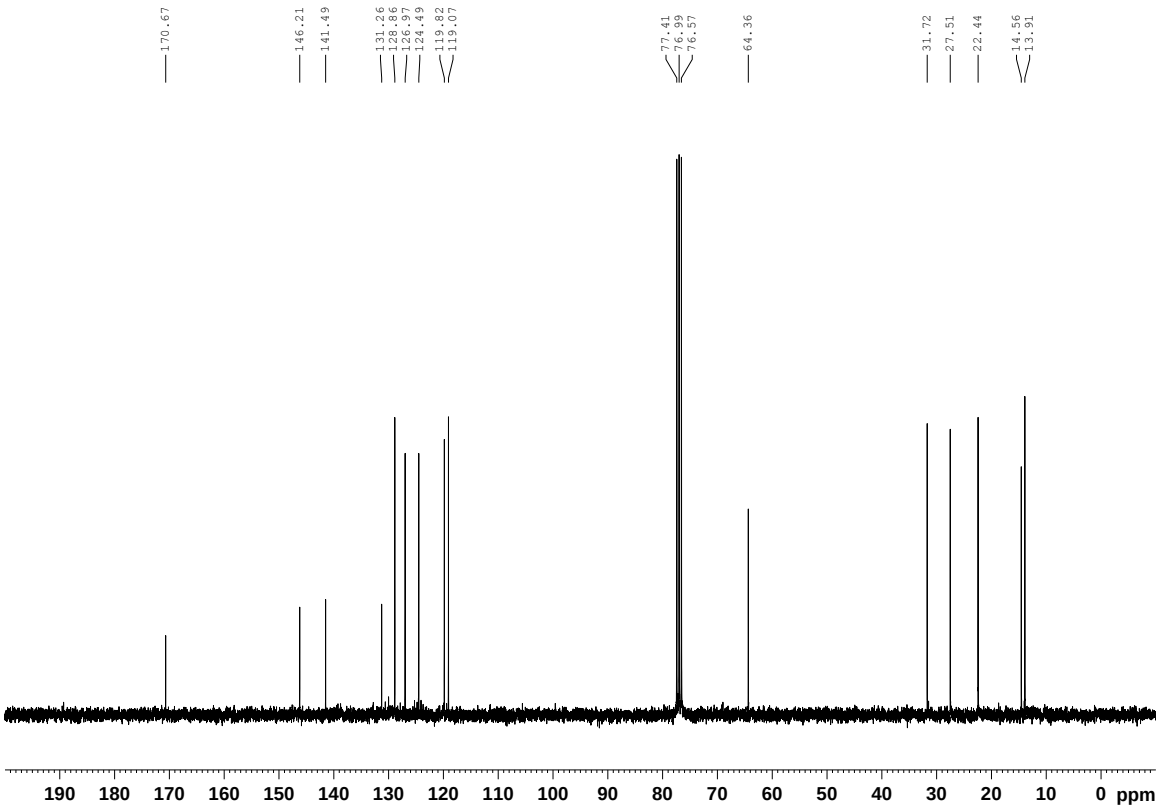
0 ppm
1.05
1.01
1.07
1.03
1.00
2.14
2.13
9.34
3.23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119.82
119.07
77.41
76.99
76.57
64.36
31.72
27.51
22.44
14.56
13.91
190
180
170
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150
140
130
120
110
100
90
80
70
60
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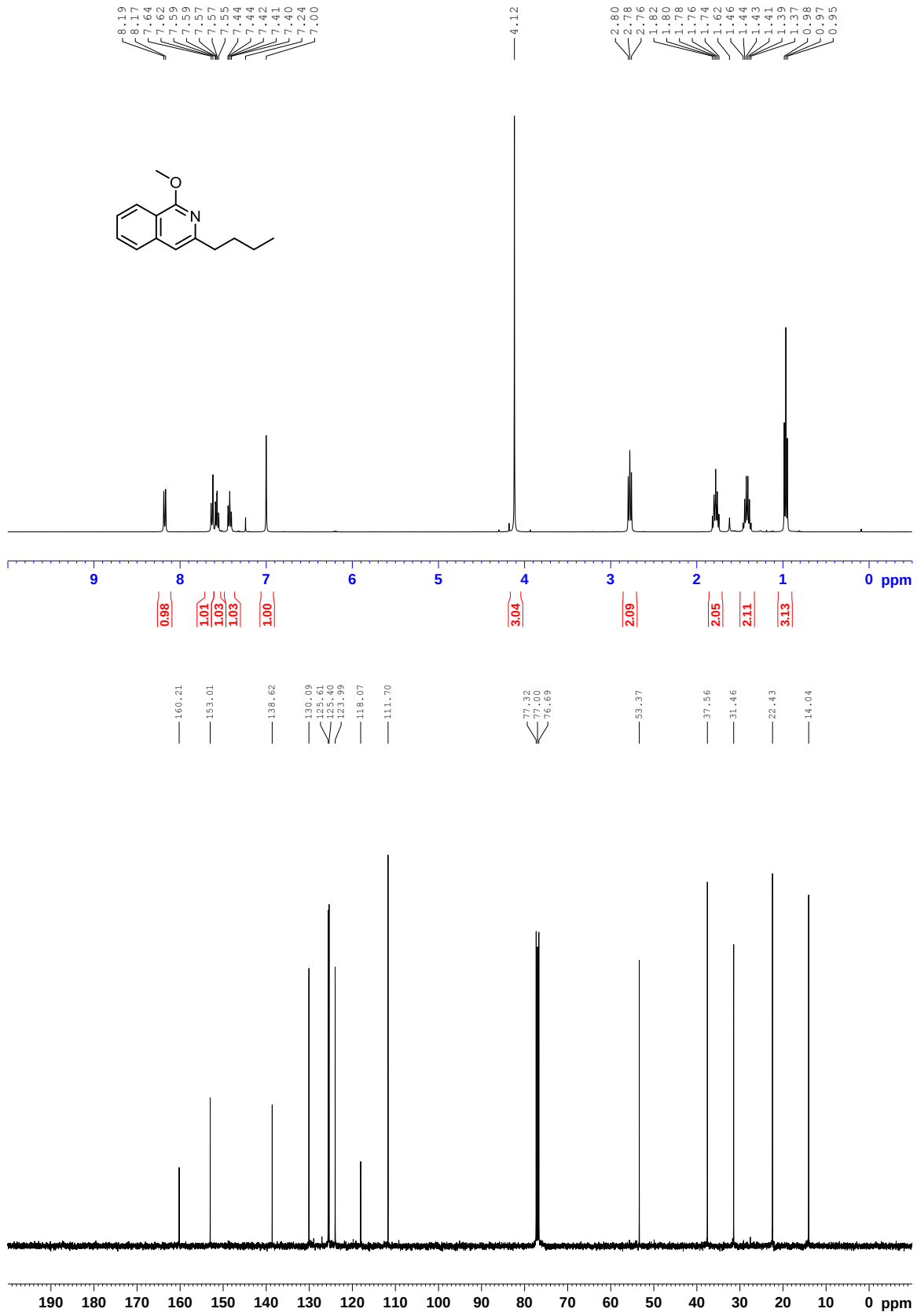
30
20
10
0 ppm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7.59
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7.57
7.55
7.44
7.44
7.42
7.41
7.40
7.24
7.00
4.12
2.80
2.78
2.76
1.82
1.80
1.78
1.76
1.74
1.62
1.46
1.44
1.43
1.41
1.39
1.37
0.98
0.97
0.95
O
N
9
8
7
6
5
4
3
2
1
0 ppm
0.98
1.01
1.03
1.03
1.00
3.04
2.09
2.05
2.11
3.13
160.21
153.01
138.62
130.09
125.61
125.40
123.99
118.07
111.70
77.32
77.00
76.69
53.37
37.56
31.46
22.43
14.04
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150
140
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120
110
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90
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70
60
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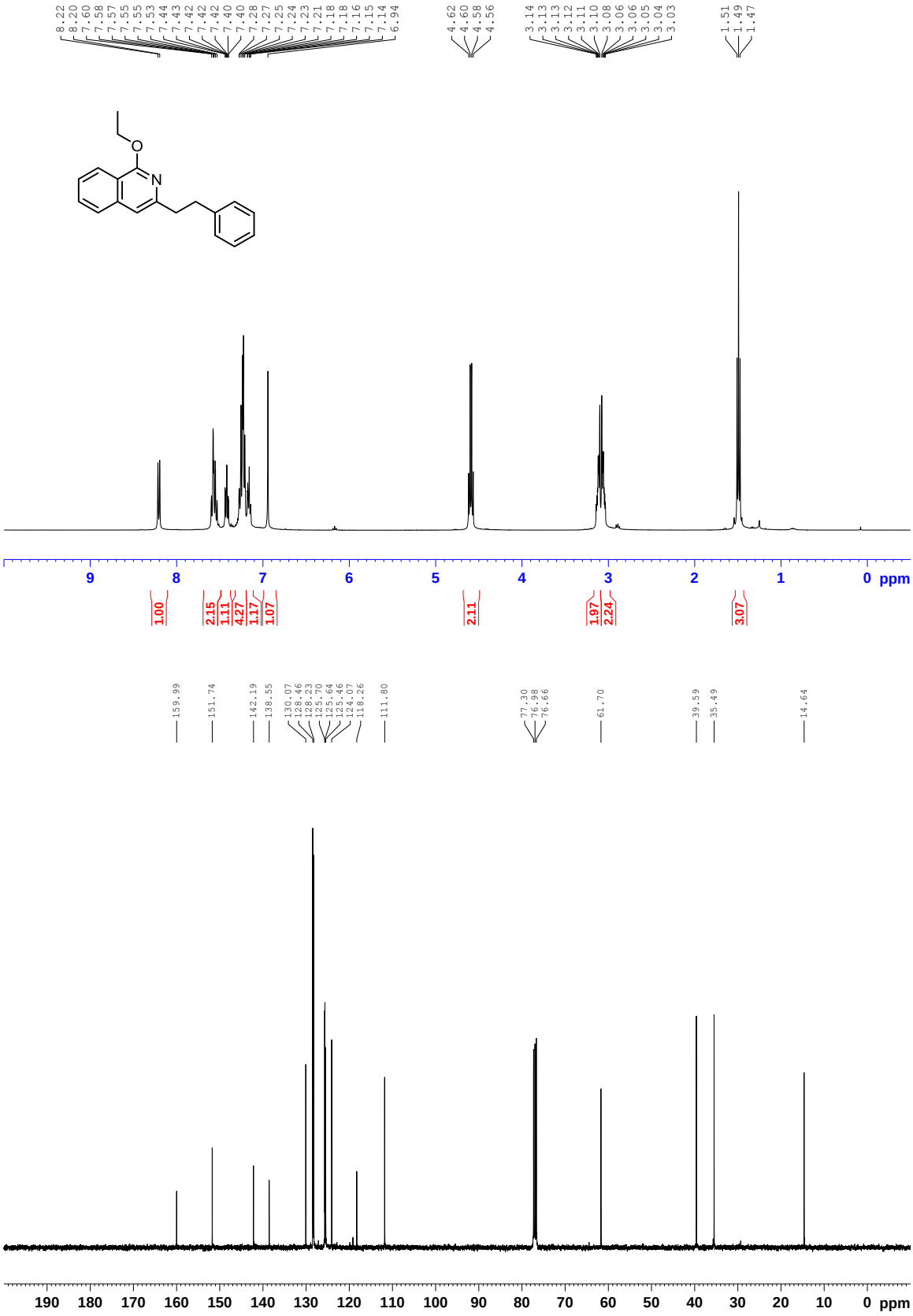
30
20
10
0 ppm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7.58
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7.55
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7.53
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.28
7.27
7.25
7.24
7.23
7.21
7.18
7.18
7.16
7.15
7.14
6.94
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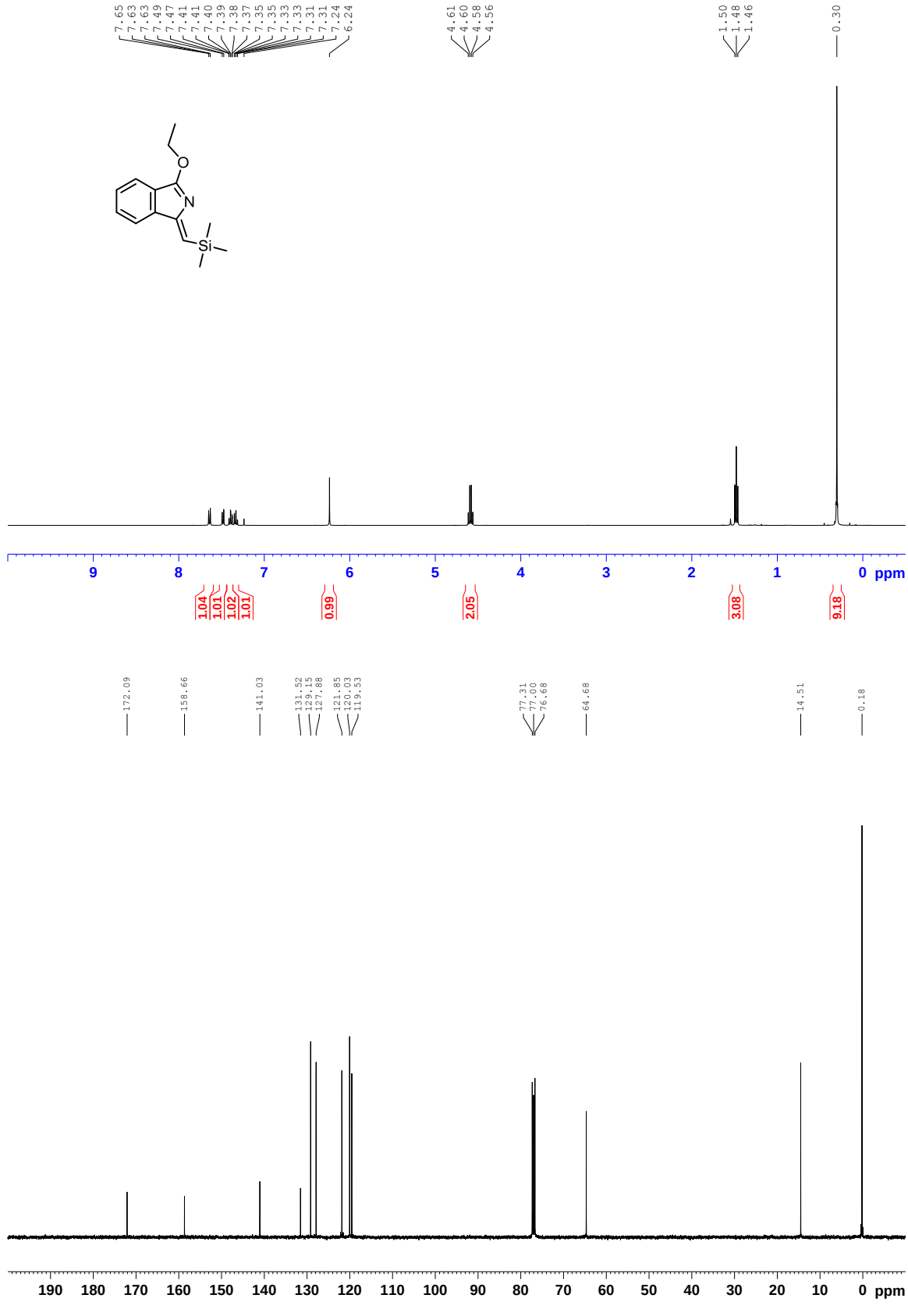
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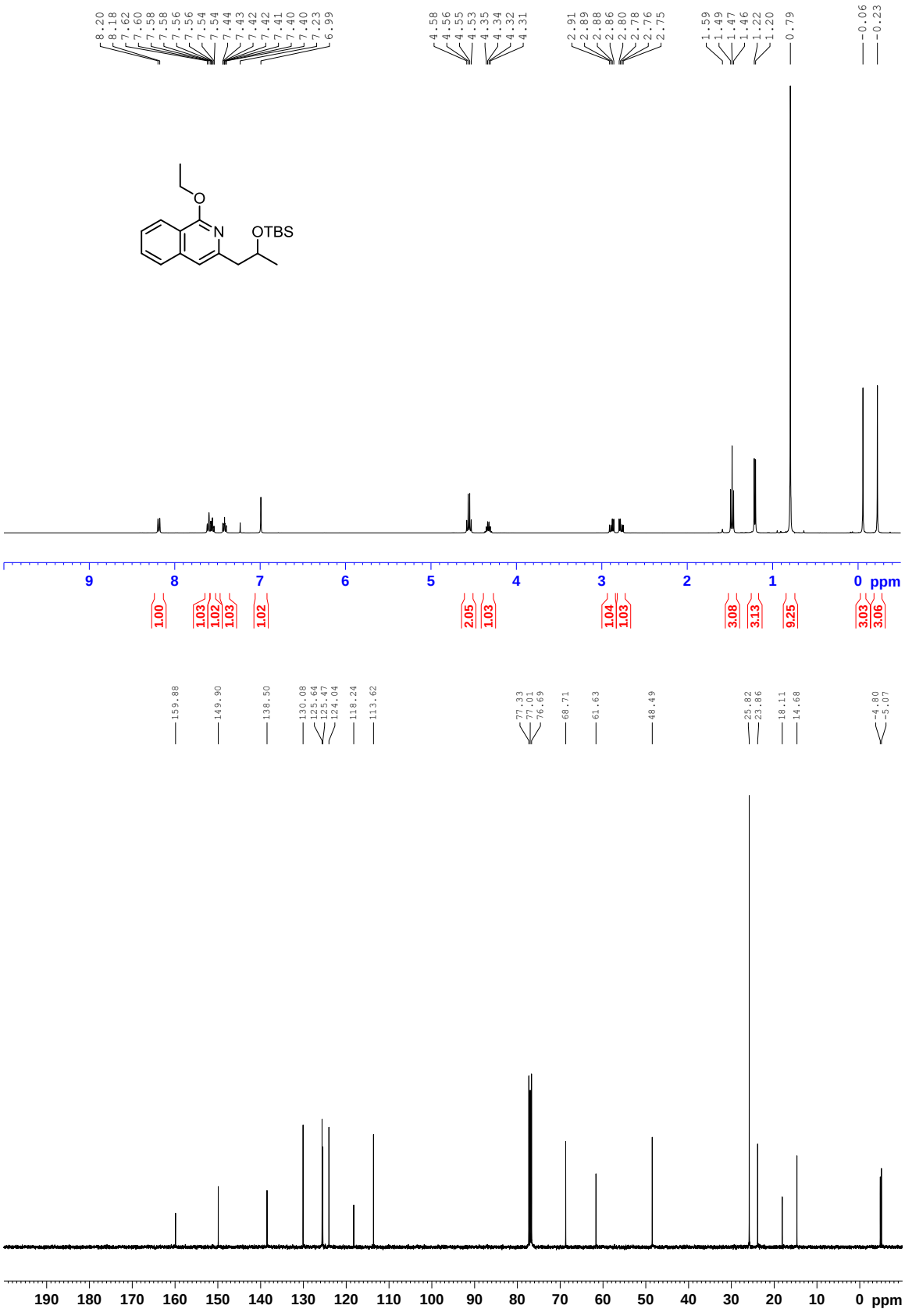
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N
OTBS
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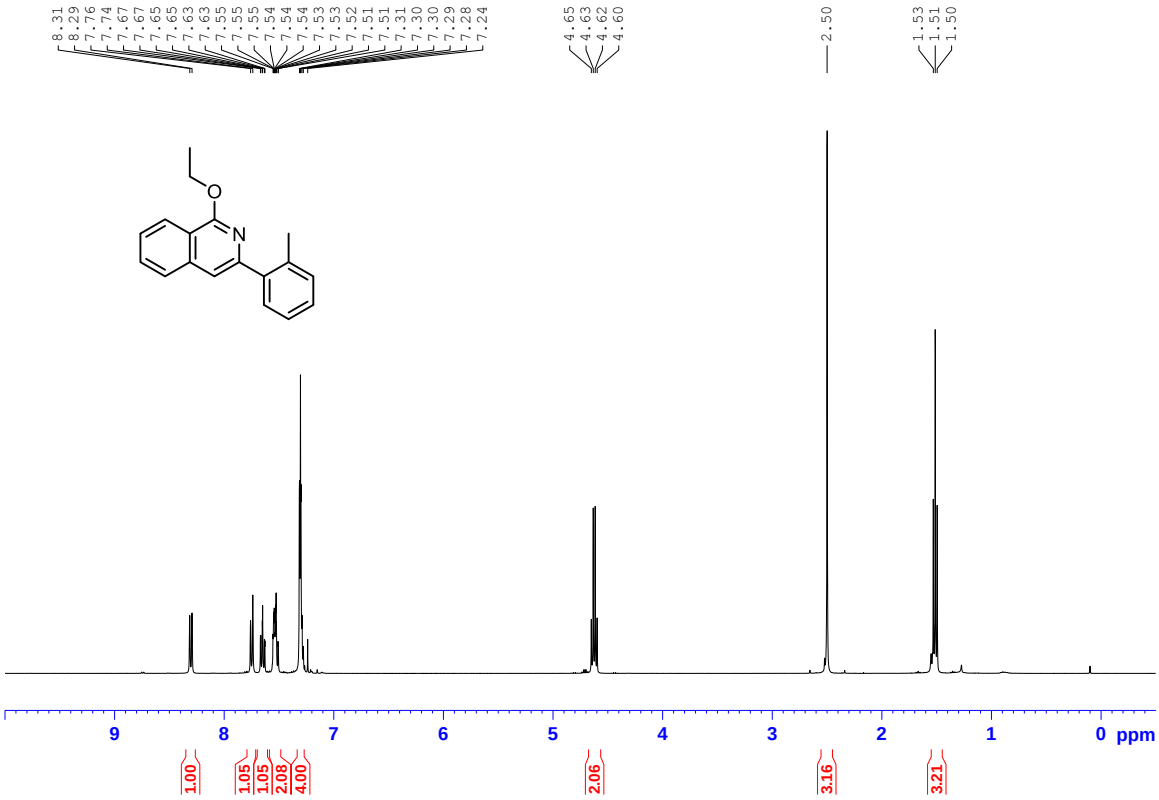
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4.62
4.60
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O
N
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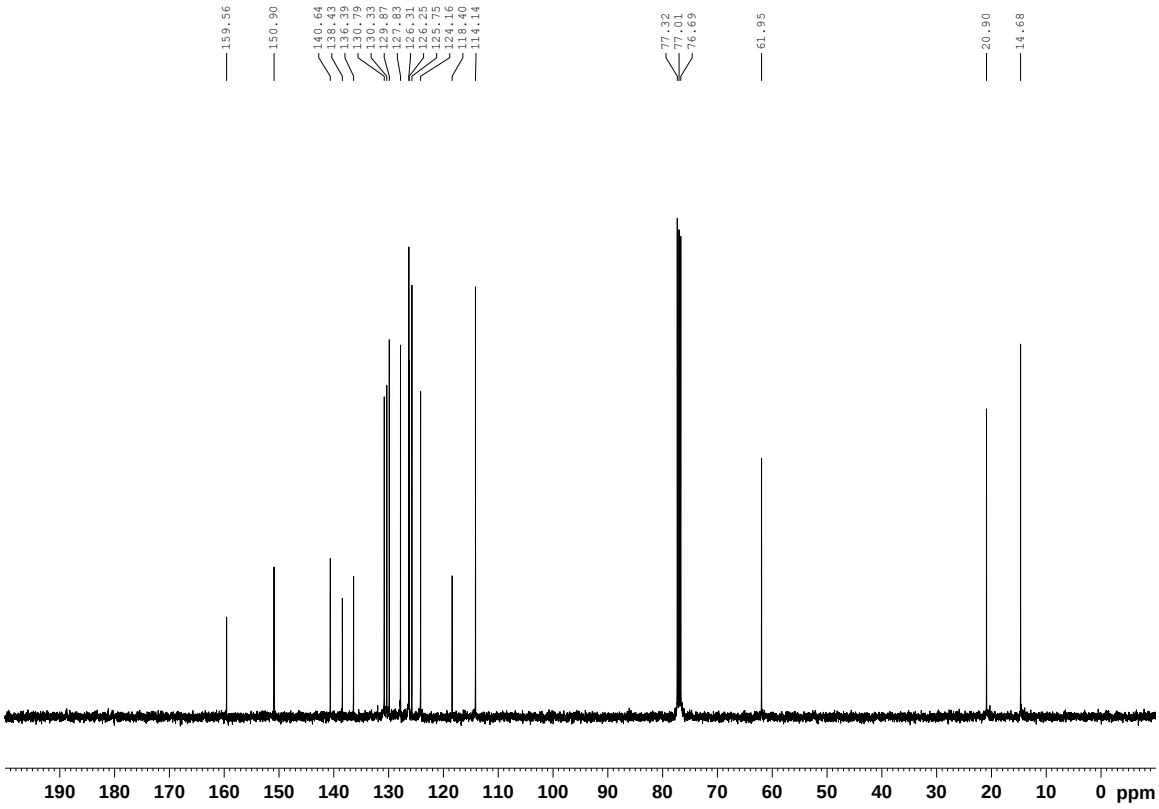
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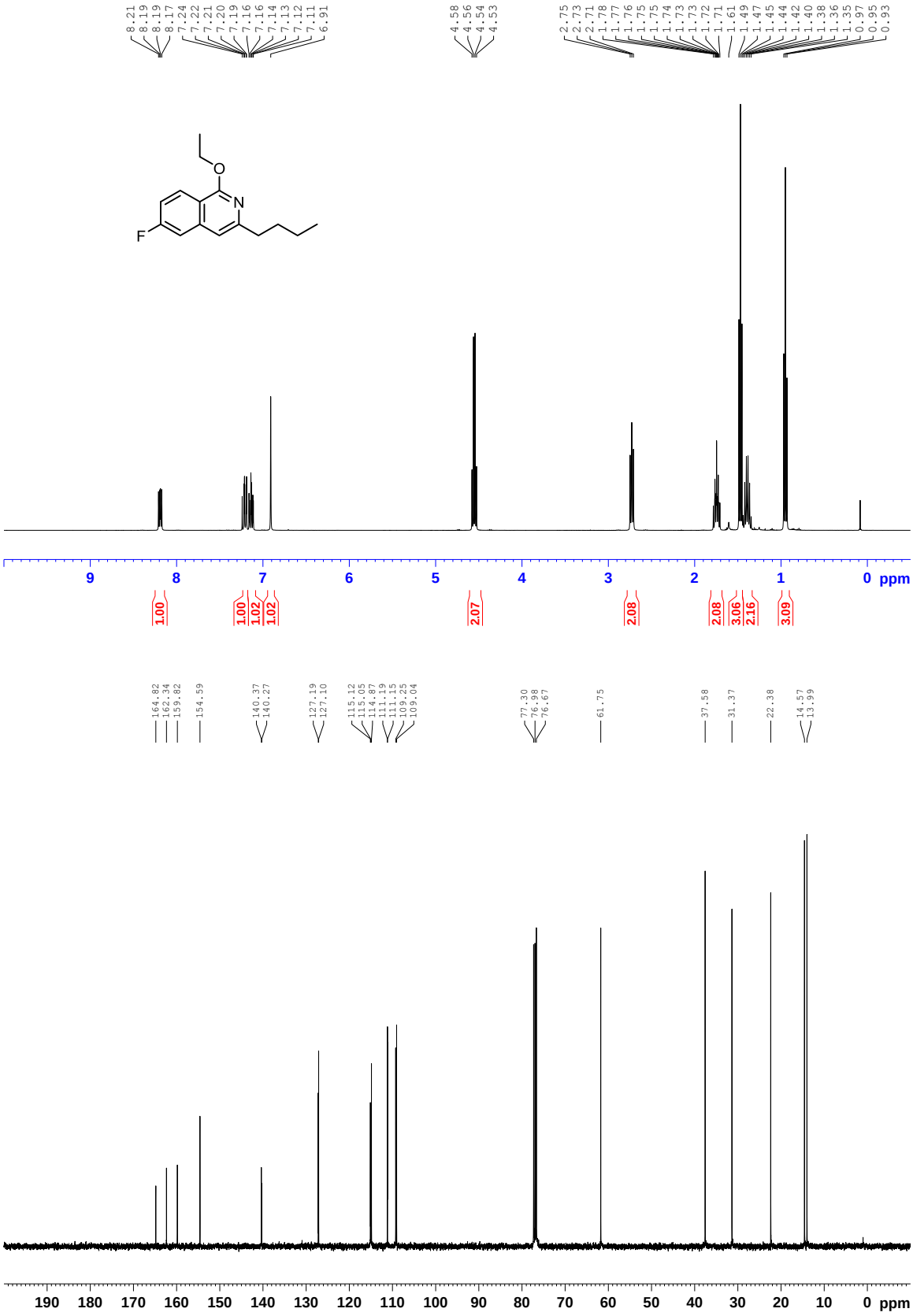
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0.93
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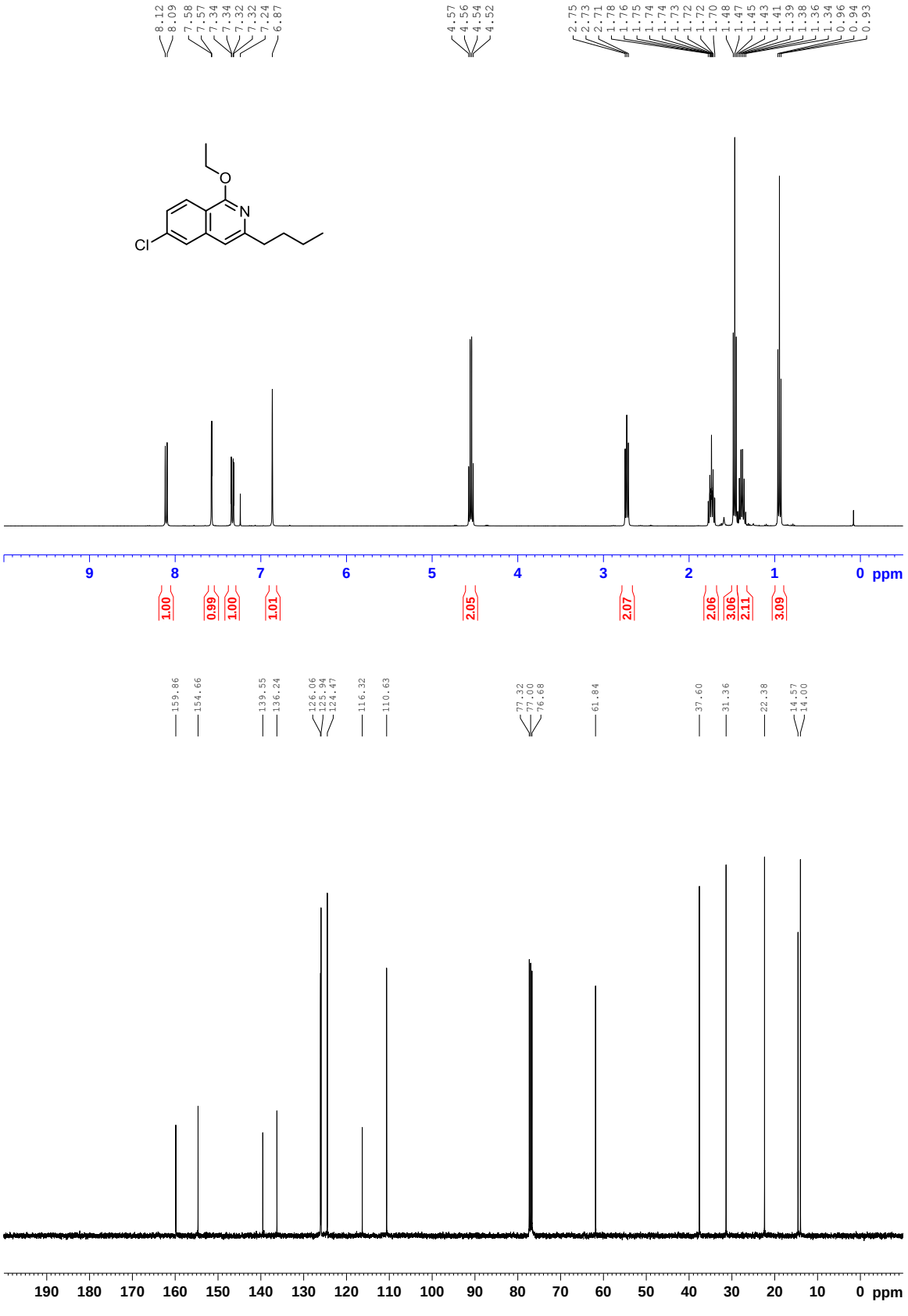
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2.71
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1.75
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0.93
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N
Cl
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0.99
1.00
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2.06
3.06
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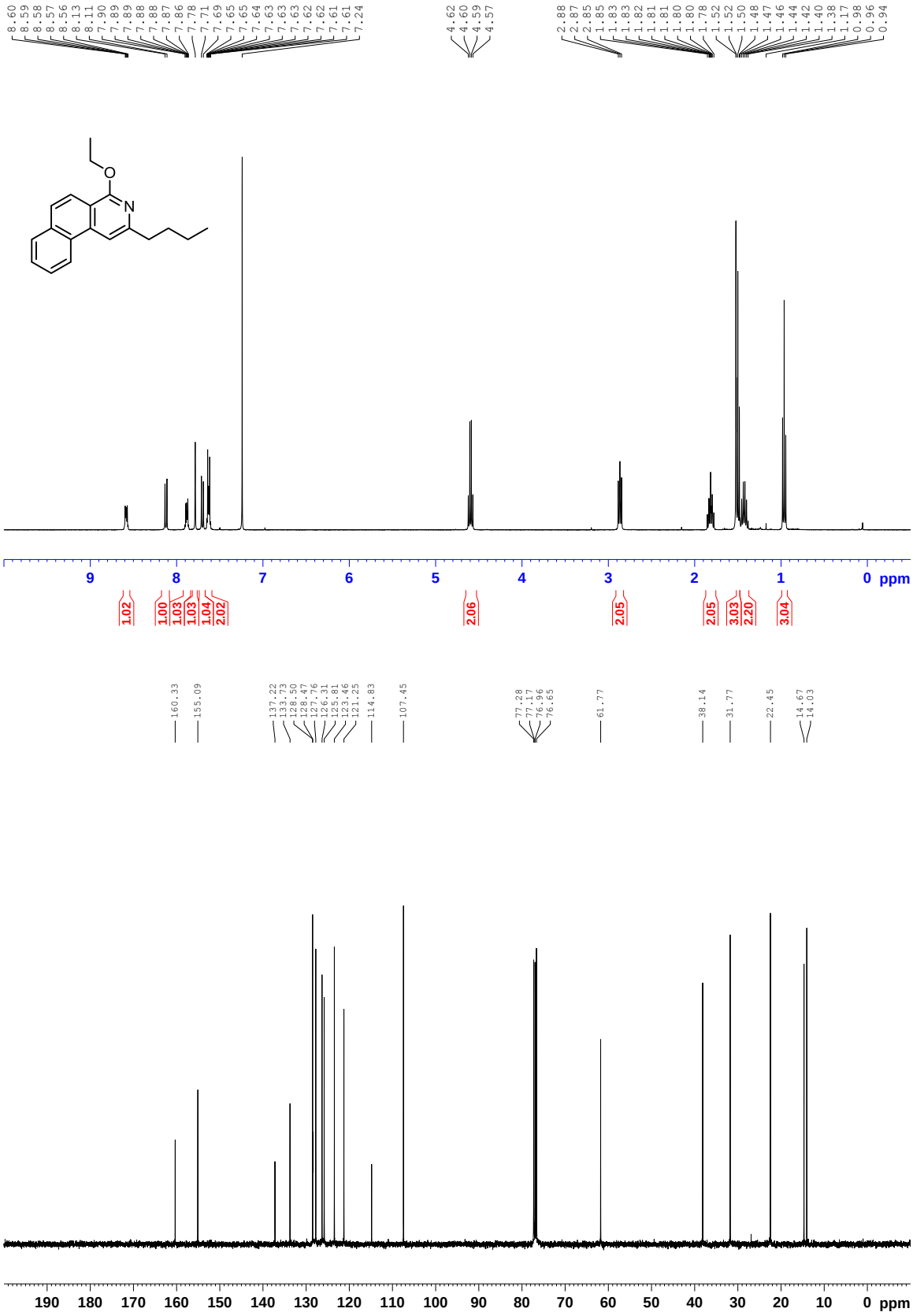
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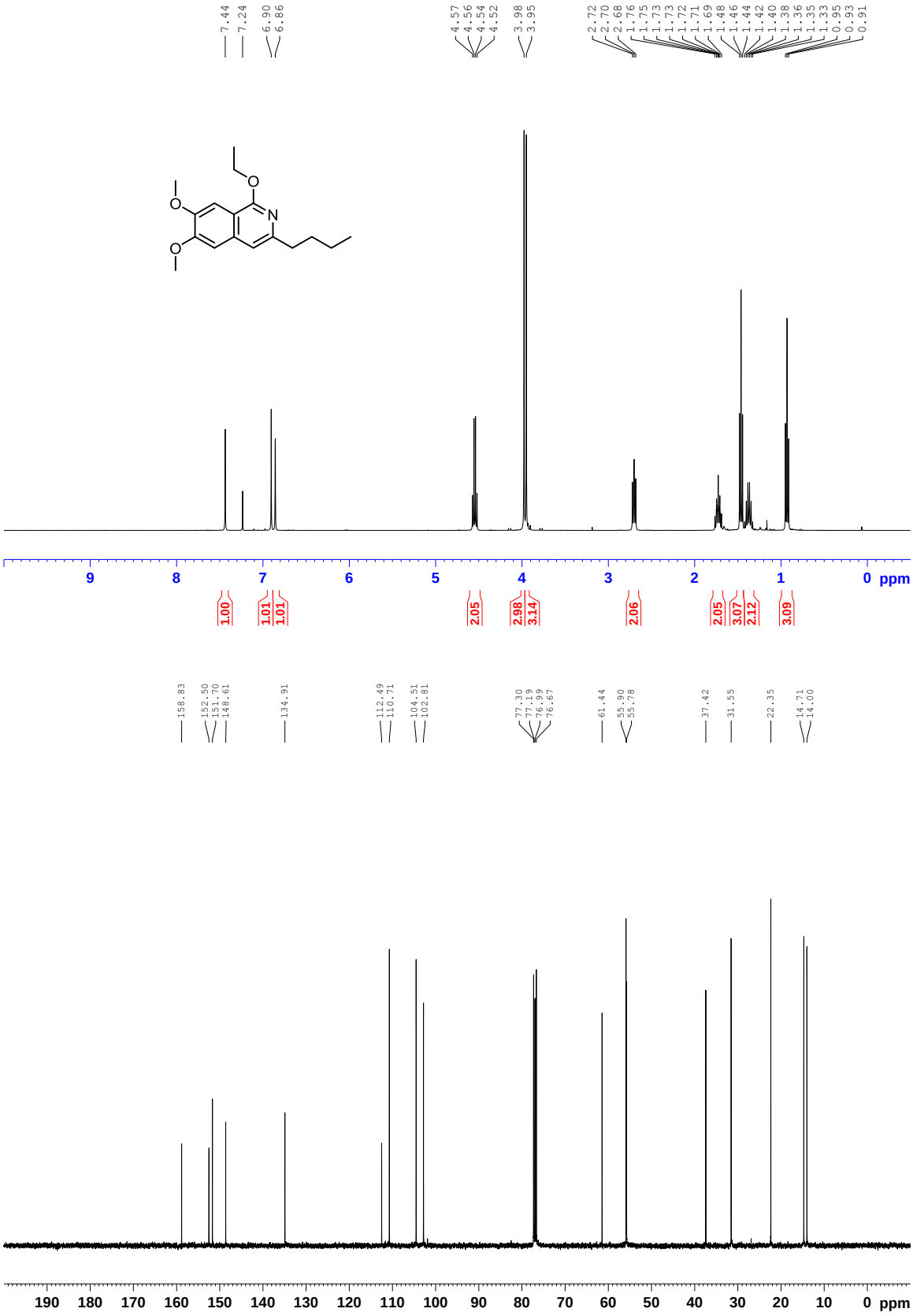
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1.44
1.42
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1.38
1.36
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1.33
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O
O
N
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5
4
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3.07
2.12
3.09
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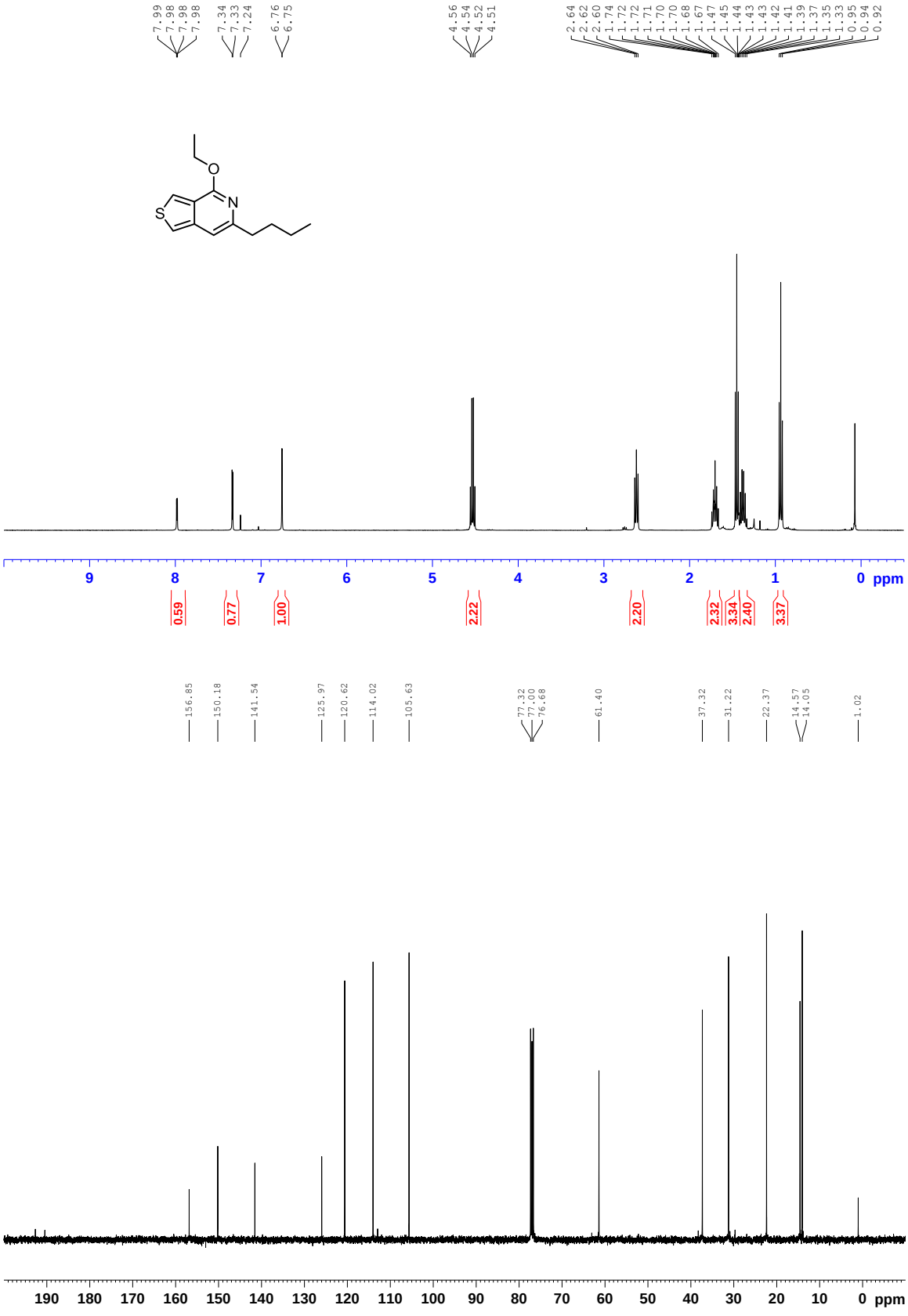
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N
S
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37.32
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22.37
14.57
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1.02
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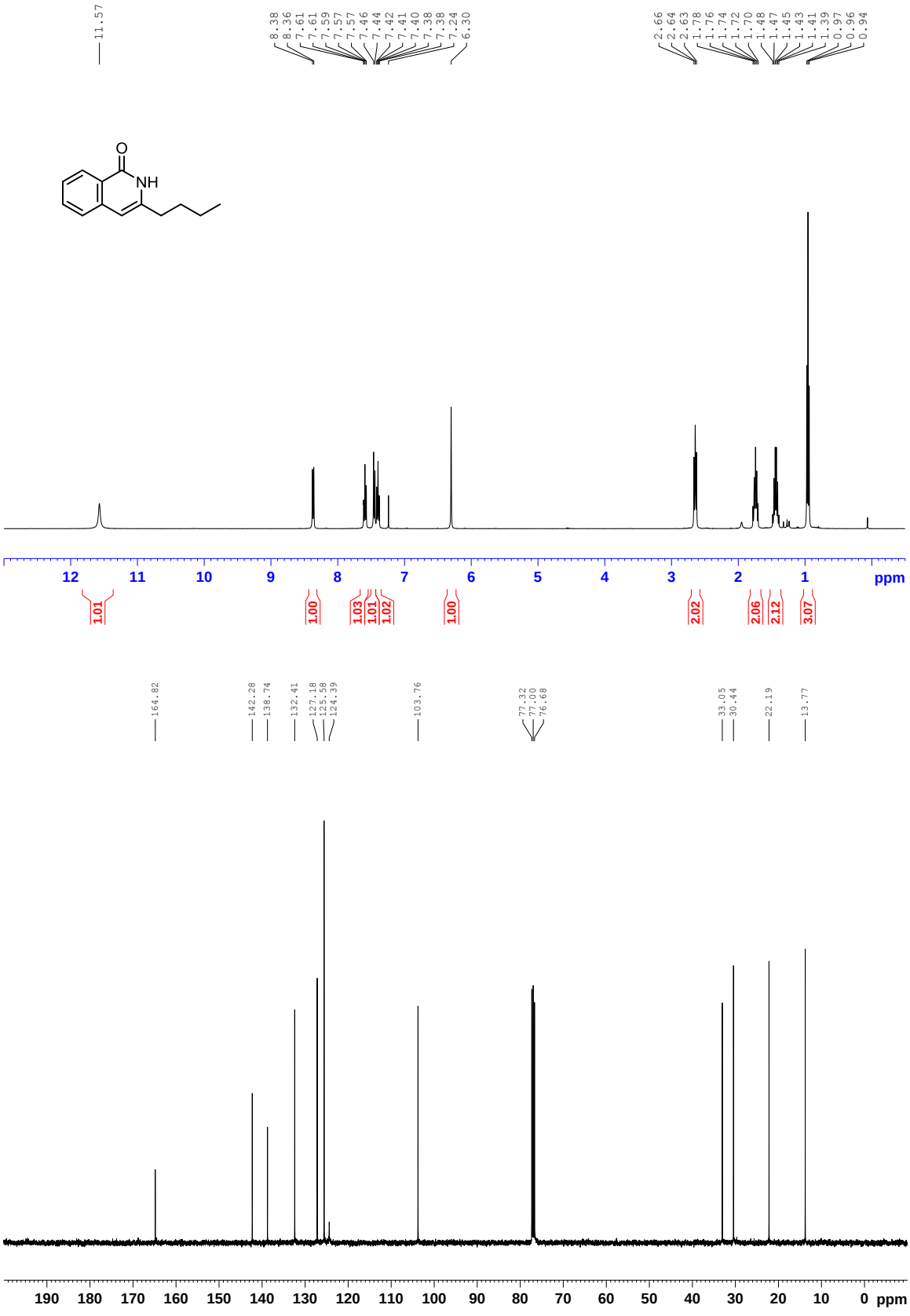
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0.94
O
NH
12
11
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8
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6
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4
3
2
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ppm
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1.00
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1.01
1.02
1.00
2.02
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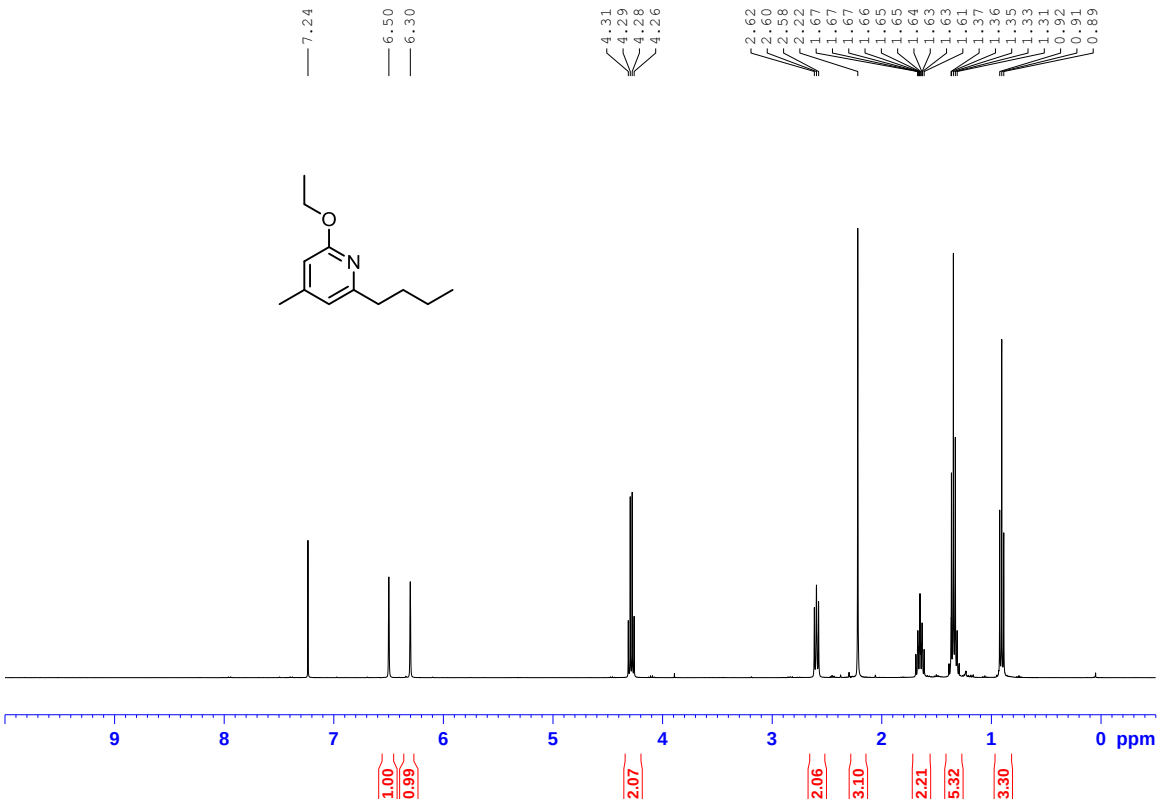
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1.61
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0.89
O
N
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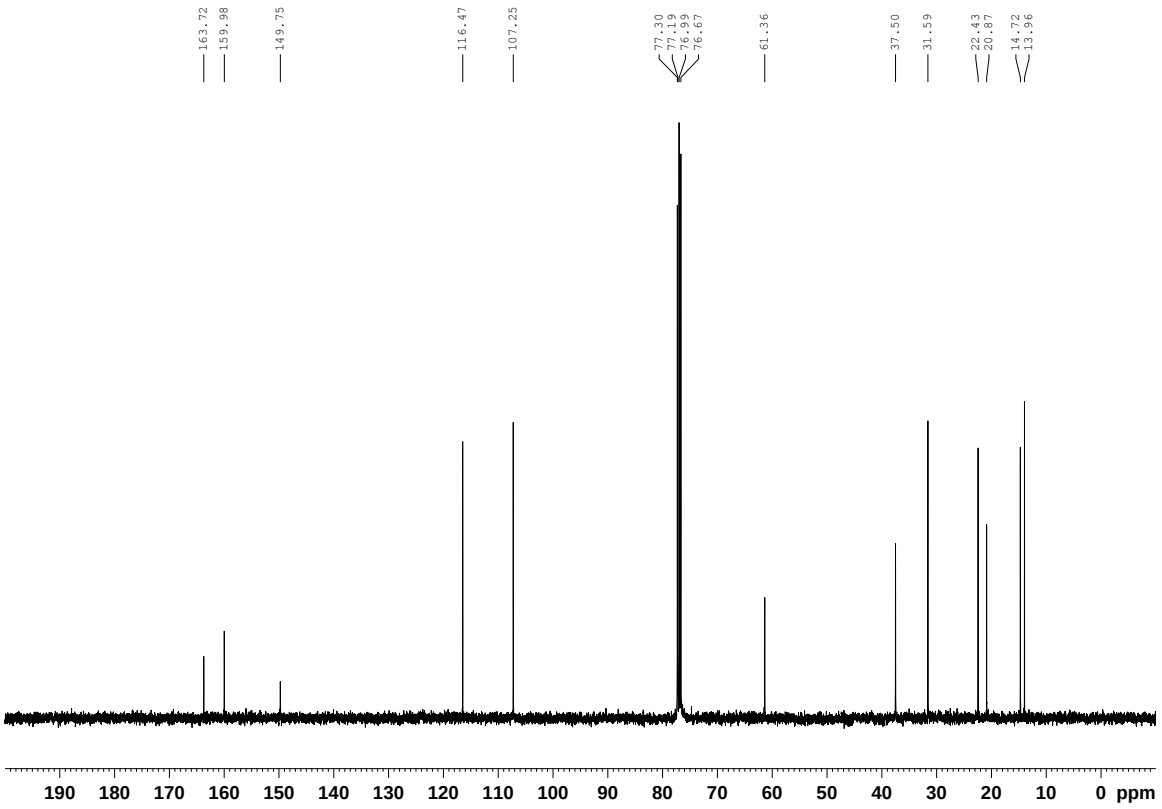
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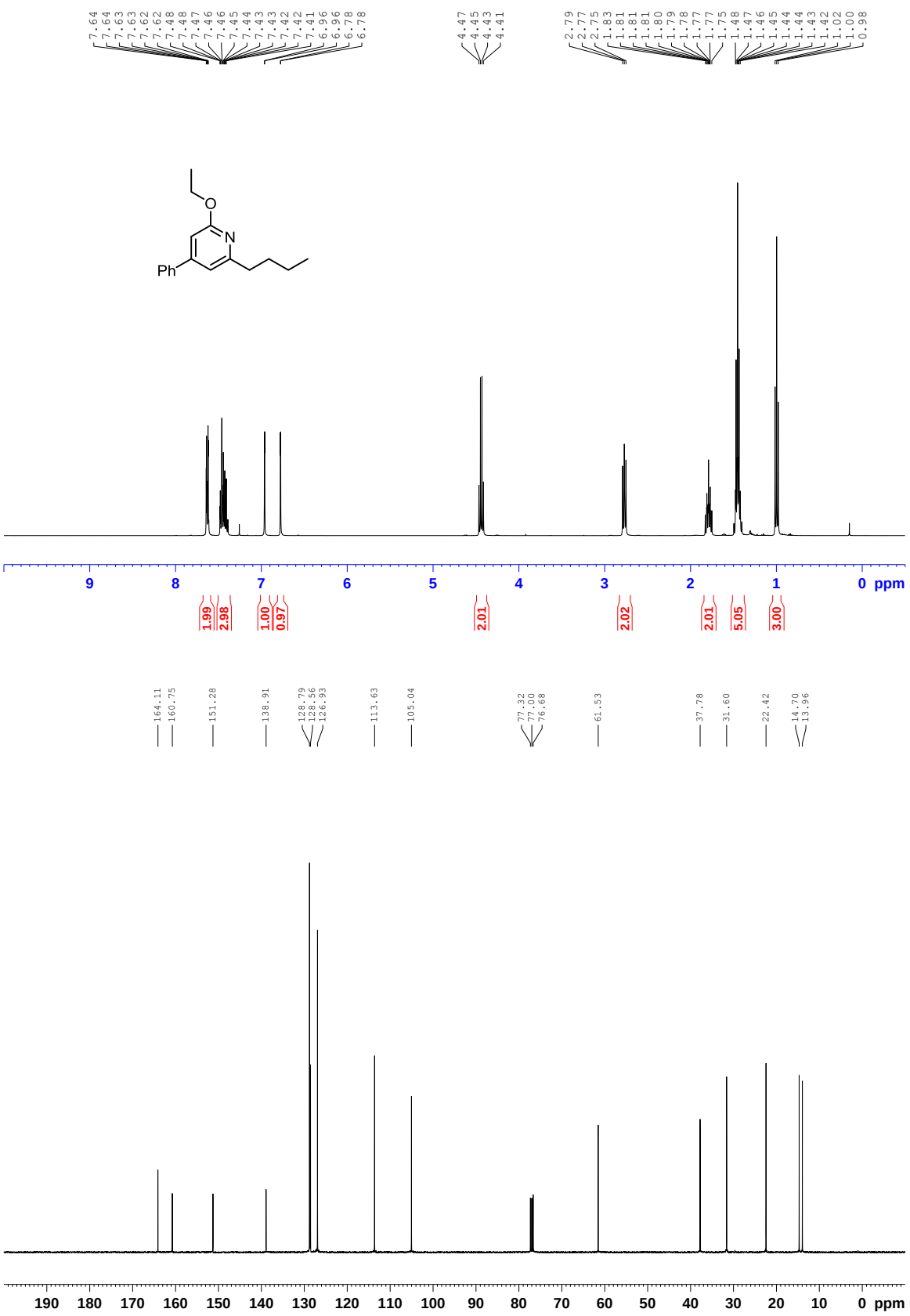
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N
Ph
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2.98
1.00
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2.01
2.02
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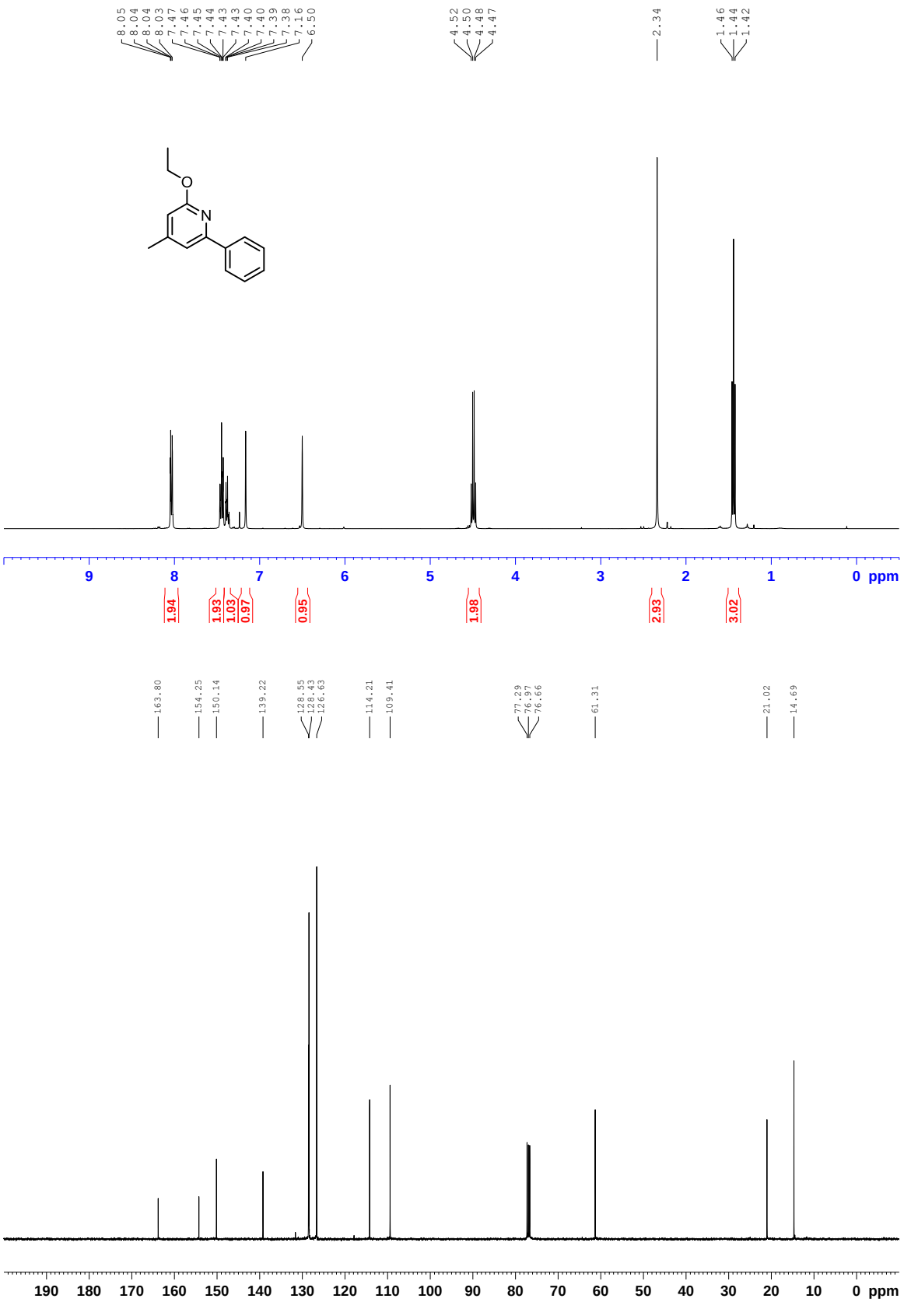
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N
9
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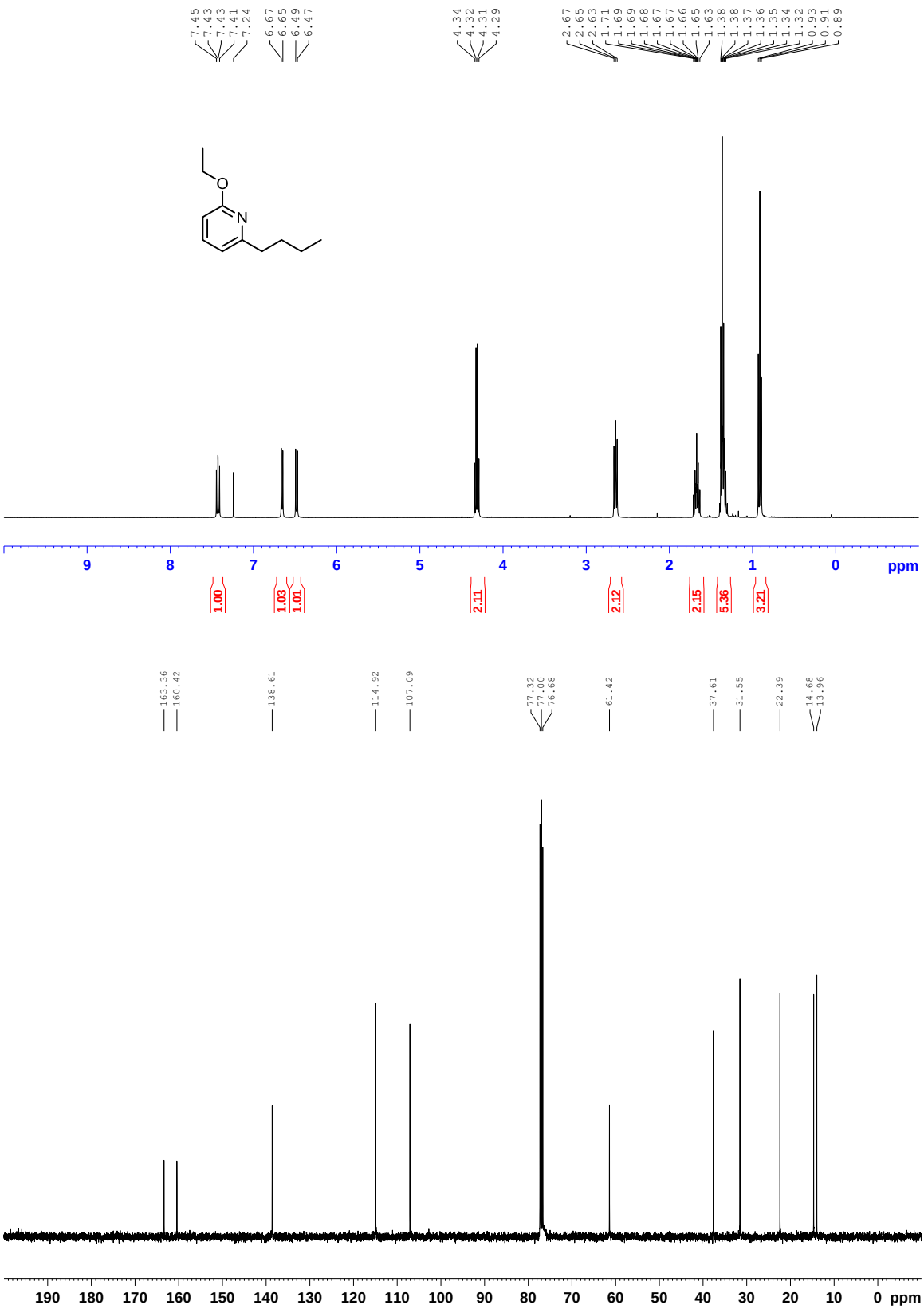
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ppm
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1.01
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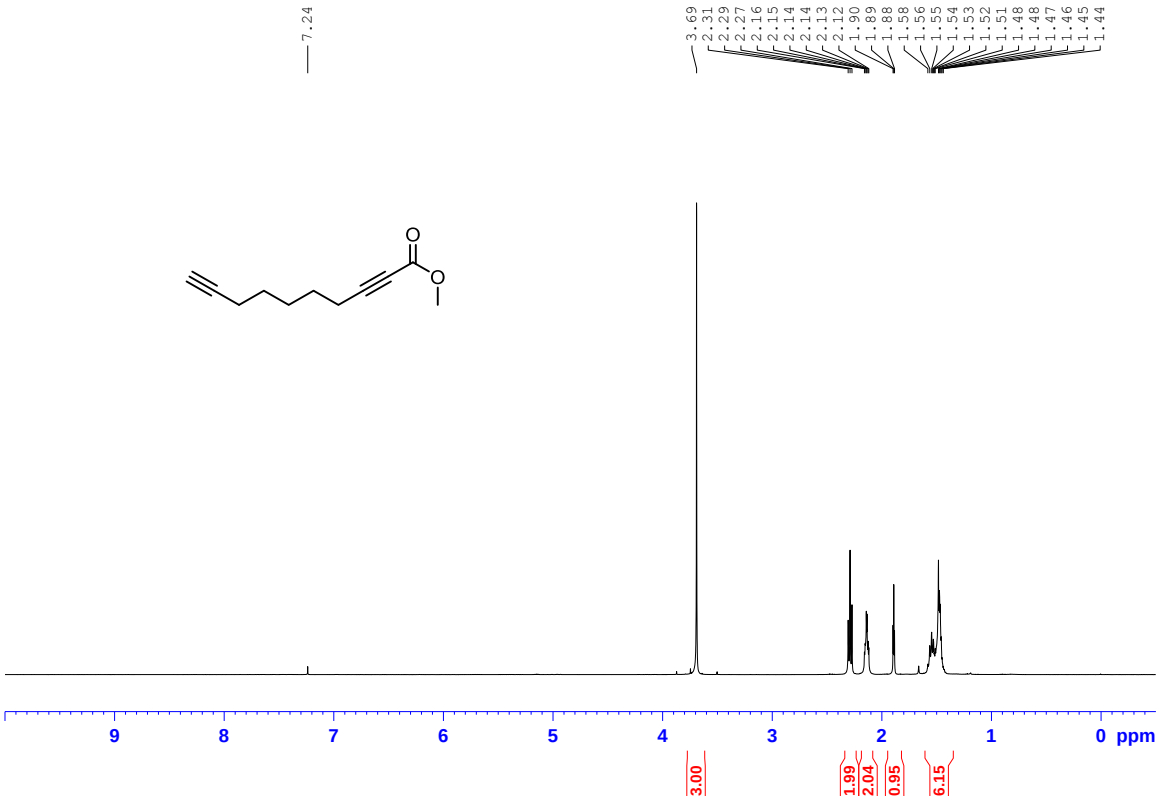
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1.51
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1.46
1.45
1.44
O
O
9
8
7
6
5
4
3
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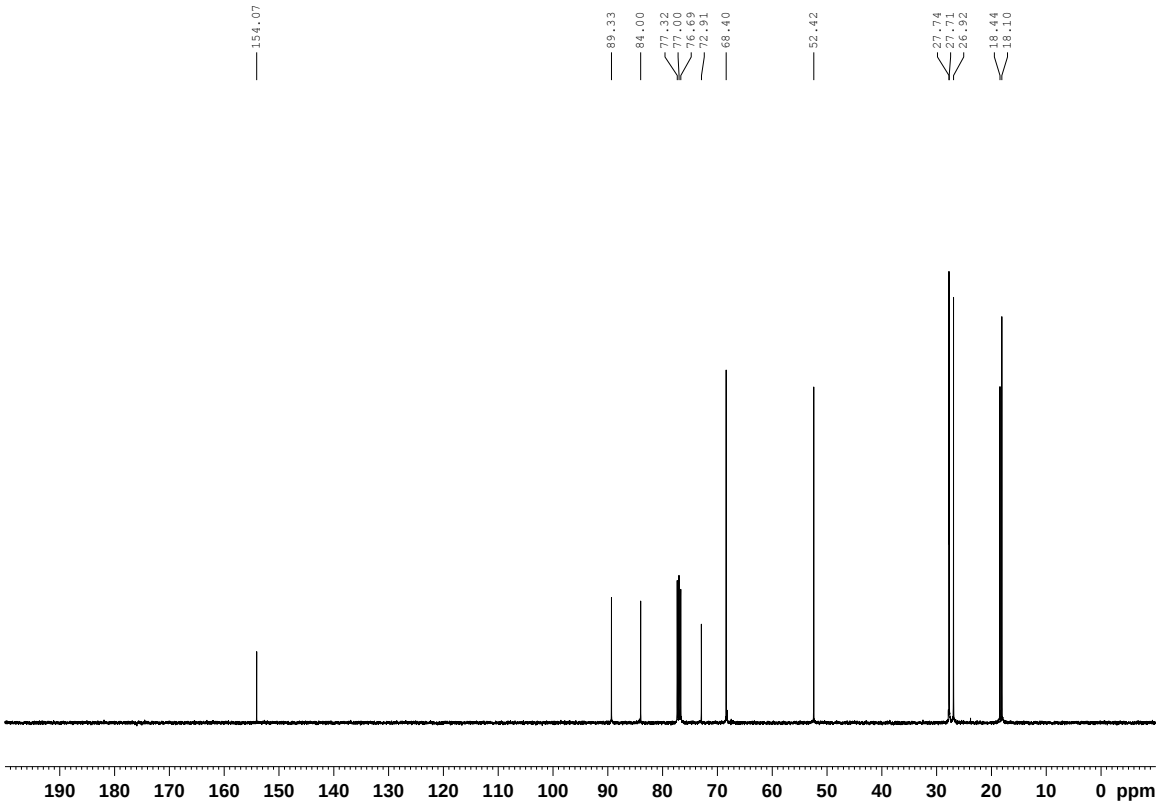
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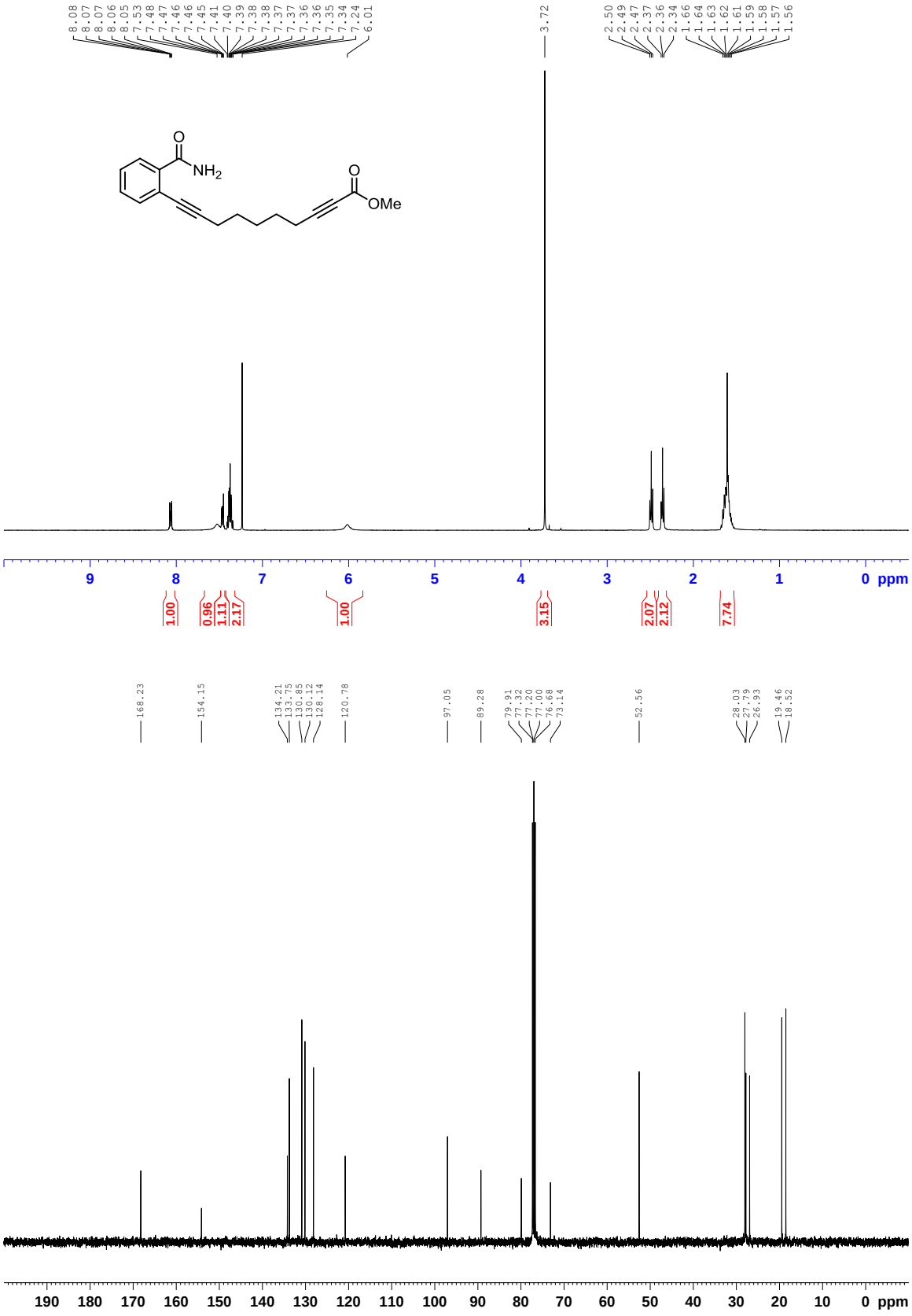
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154.15
134.21
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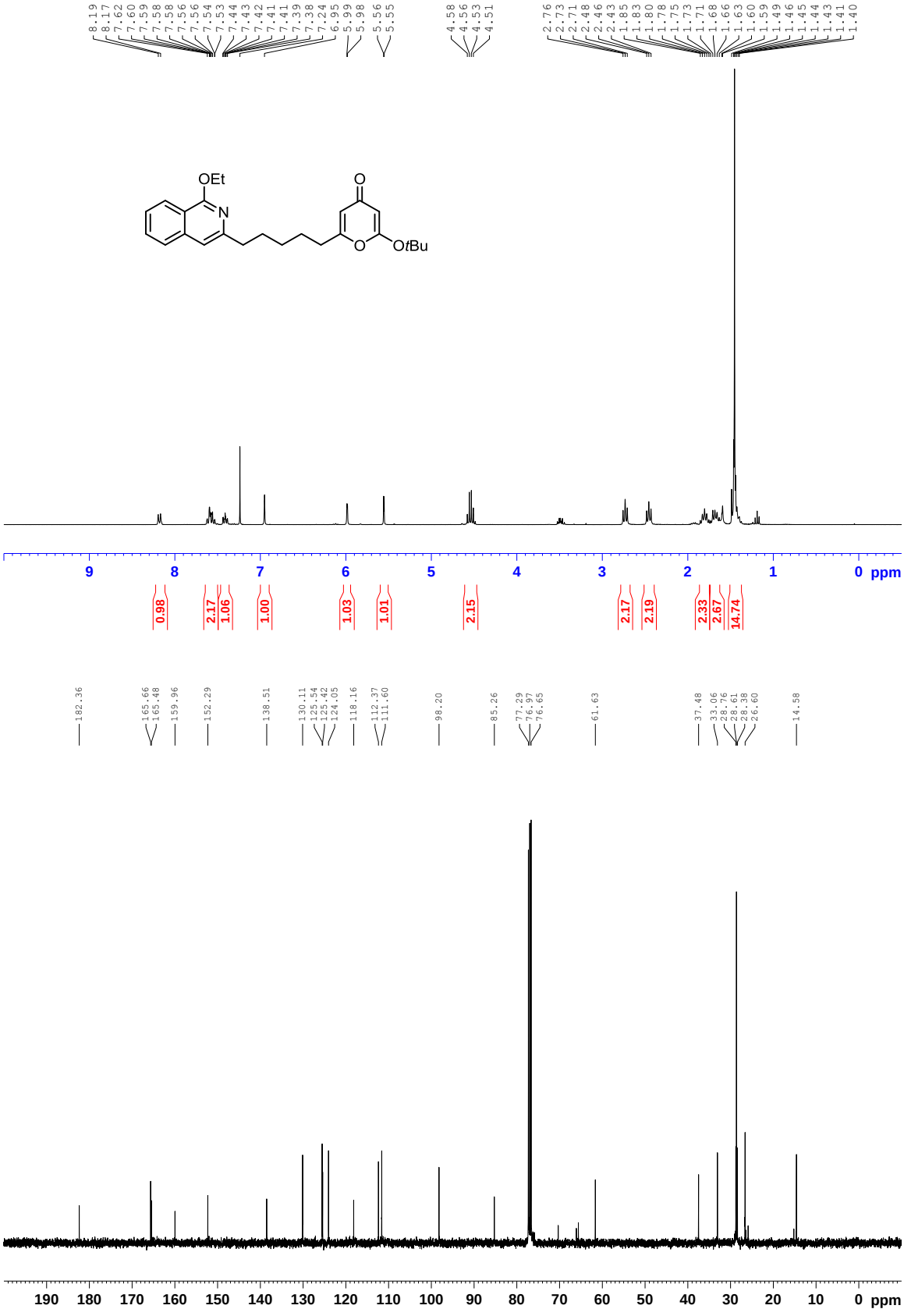
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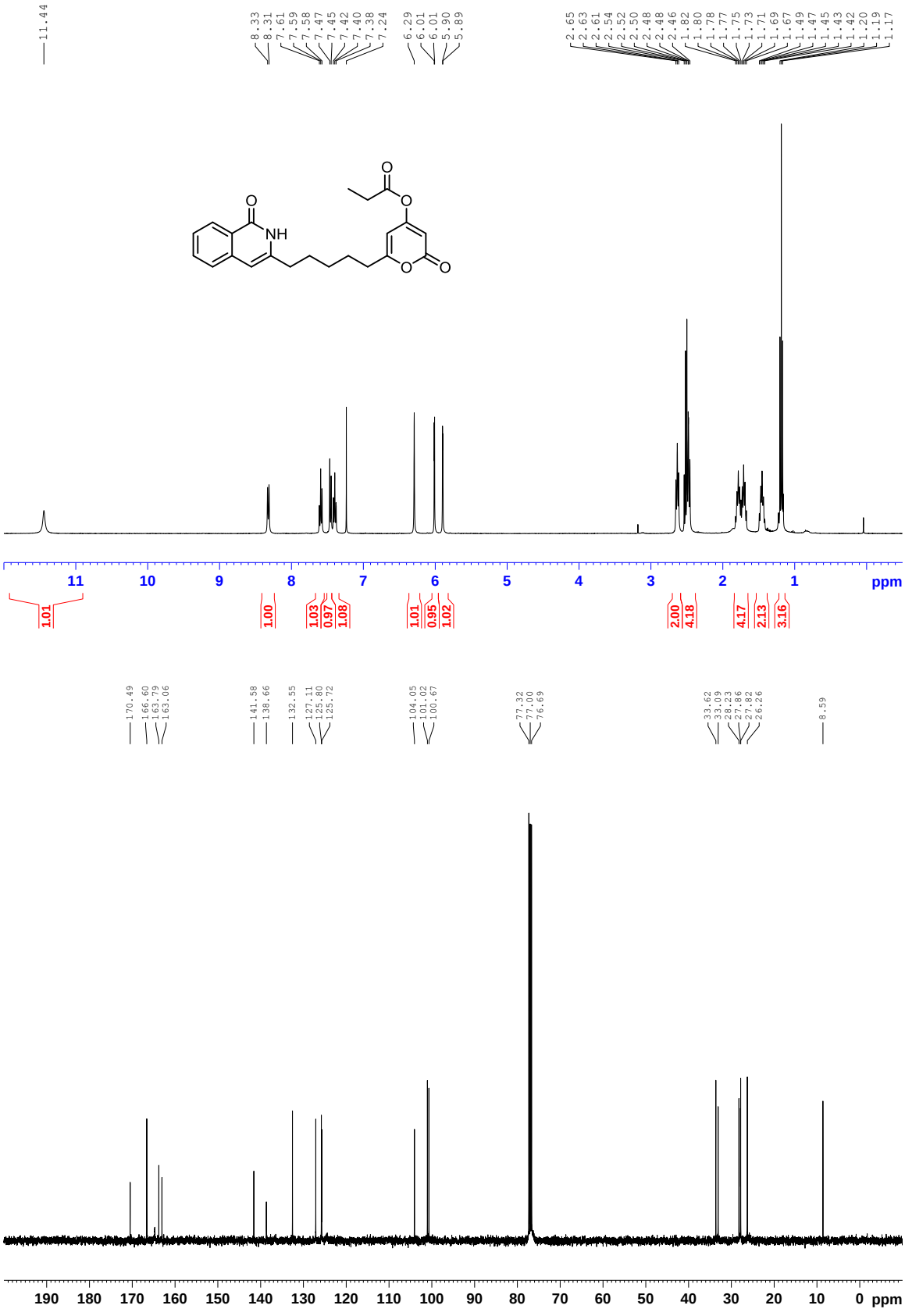
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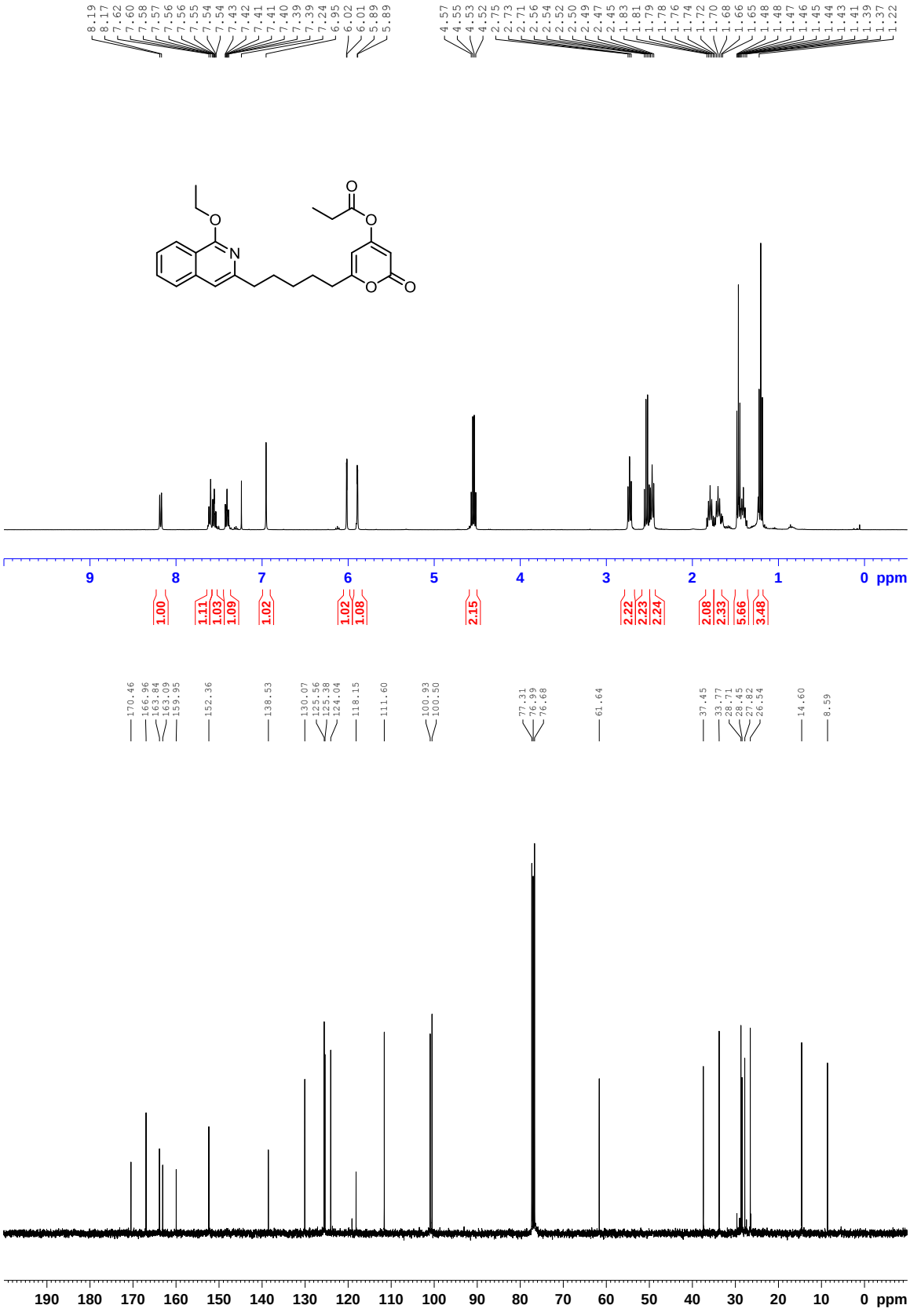
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