Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Concise Synthesis of a Pateamine A Analogue with In Vivo Anticancer Activity Based on an Iron-Catalyzed Pyrone Ring Opening/Cross-Coupling

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Crystallographic Information

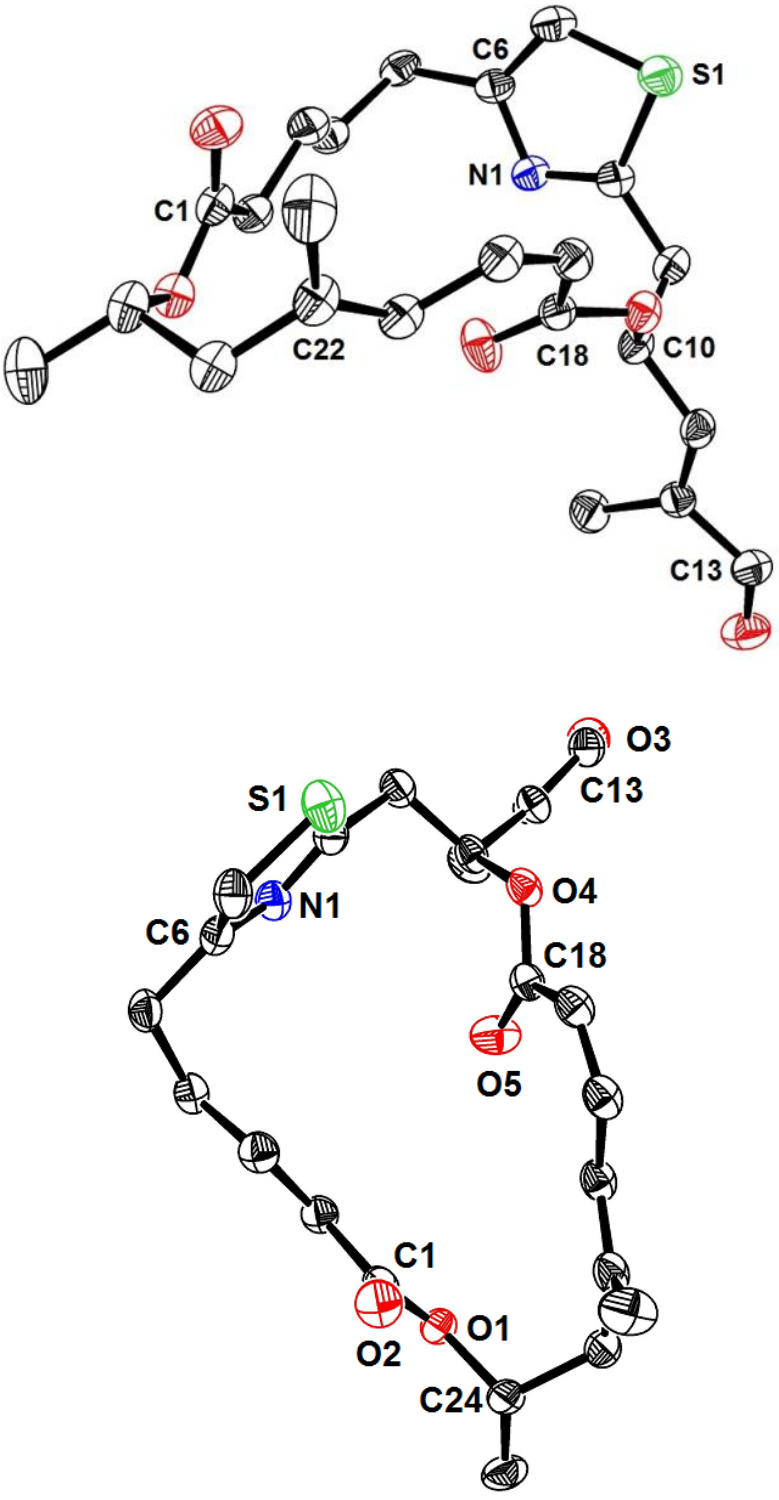


Figure S1. Structure of compound **21** in the solid state in two different orientations

X-ray Crystal Structure Analysis of Compound 21: $C_{23}H_{29}NO_5S$, M_r = 431.53 g · mol^{-1}, colorless prism, crystal size 0.258 x 0.199 x 0.060 mm^3, monoclinic, space group *C2*, *a* = 20.625(3) Å, *b* = 7.8102(11) Å, *c* = 14.940(2) Å, *β* = 102.870(3)°, *V* = 2346.3(6) Å^3, *T* = 100 K, *Z* = 4, D_{calc} = 1.222 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.170 mm^{-1}, Gaussian absorption correction (T_{min} = 0.97, T_{max} = 0.99), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 3.795 < θ < 30.746°, 33814 measured reflections, 7294 independent reflections, 6008 reflections with $I > 2\sigma(I)$, R_{int} = 0.038. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.037 [$I > 2\sigma(I)$], wR_2 = 0.092, 273 parameters, H atoms riding, *S* = 1.020, residual electron density 0.2 / -0.2 e Å^{-3}. **CCDC 1454695**

Experimental details and characterization data

General. Unless stated otherwise, all reactions were carried out in flame-dried glassware using anhydrous solvents under argon. The solvents were purified by distillation over the following drying agents and were transferred under argon: THF, Et_2O (Mg/anthracene), CH_2Cl_2, toluene (Na/K), MeOH (Mg, stored over MS 3 Å); DMF, DMSO, Et_3N and pyridine were dried by an adsorption solvent purification system based on molecular sieves; anhydrous (99.9%) cyclopentyl methyl ether (CPME) purchased from Aldrich was kept in a flame-dried Schlenk flask containing MS 4 Å under argon. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM®SIL/UV254); Preparative TLC: Macherey-Nagel precoated plates (SIL G-100 UV 254; silica gel layer: 1.0 mm); Flash chromatography: Merck silica gel 60 (40–63 µm) with predistilled or HPLC grade solvents; Celite® was dried at 170 °C for 48 h under high vacuum (1 × 10^{-3} mbar) and stored under argon. NMR: Spectra were recorded on Bruker DPX 300, AV 400, AV 500 or AVIII 600 spectrometers 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 = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; C_6D_6: δ_C = 128.06 ppm; residual C_6D_5H: δ_H = 7.16 ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FTMS (7 T magnet) or Mat 95 (Finnigan). Optical rotations ($[\alpha]_D^{20}$ =) were measured with a Perkin-Elmer Model 343 polarimeter. LC-MS analyses were conducted on a Shimadzu LC-MS 2020 instrument (pumps LC-20AD, autosampler SIL-20AC, column oven CTO-20AC, diode array detector SPD-M20A, controller CBM-20A, ESI detector and software Labsolutions) with a ZORBAX Eclipse Plus column (C18 1.8 µm, 3.0 or 4.6 mm ID × 50 mm (Agilent)) or a YMC-Pack Pro C18 column (S-5 µm, 120 Å, 2.1 mm ID × 150 mm). A binary gradient of MeCN or MeOH in water, aq. triethylammonium acetate buffer (10 mmol, pH 8) or aq. trifluoroacetatic acid buffer (0.1 %) were used as eluents at a flow rate of 0.2 mL/min (2.1 mm ID), 0.5 mL/min (3.0 mm ID) or 0.8 mL/min (4.6 mm ID). The oven temperature was kept at 35 °C and the detection wave length at 228 nm or 258 nm. Conditions for each compound are specified below. Chiral HPLC analyses were conducted on a Shimadzu LC 20 instrument (pumps LC-20AB, autosampler SIL-20AC, column oven CTO-20AC, diode array detector SPD-M20A, controller CBM-20A, and software Labsolutions) with a Daicel Chiralpak IC-3 column (4.6 mm × 150 mm). Unless stated otherwise, all commercially available compounds (Alfa Aesar, Aldrich, TCI, Strem Chemicals) were used as received.

***tert*-Butyl (*Z*)-3-iodoacrylate** (**12**).[1] *tert*-Butyl propiolate (15.4 mmol, 1.94 g) was added to a solution of NaI (23.5 mmol, 3.53 g) in acetic acid (9 mL) and the resulting mixture was stirred at 70 °C for 16 h. The mixture was cooled to room temperature before it was diluted with water (30 mL) and diethyl ether (30 mL). The aqueous phase was extracted with Et_2O (4 × 30 mL). The combined extracts were neutralized with aq. KOH (3 M), washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated in vacuum. Purification of the residue on silica gel by flash chromatography (hexane/EtOAc = 100/1 to 50/1) gave the product as a pale yellow oil (3.17 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 1.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 131.3, 92.9, 81.8, 28.1. IR (film, cm^{-1}): 3003, 2978, 2933, 1721, 1708, 1596, 1368, 1323, 1215, 1139, 946, 810, 528. MS (EI): *m*/*z* (%) 254 (12), 198 (100), 181 (93), 153 (17), 127 (19), 71 (7), 56 (69), 41 (41), 29 (12). HRMS (ESI): *m*/*z*: calcd for $C_7H_{11}O_2INa$ [*M* +*Na*$^+$]: 276.96960, found: 276.96940.

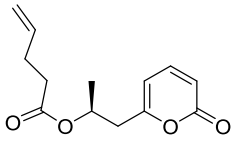
***tert*-Butyl (*S*, *Z*)-7-hydroxyoct-2-en-4-ynoate** (**13**). *Step 1*: (*S*)-2-Methyloxirane (49.6 mmol, 3.47 mL) was added dropwise at 0 °C to a suspension of lithium acetylide-ethylene diamine complex (54.7 mmol, 5.6 g, 90%) in DMSO (50 mL). Once the addition was complete, the mixture was stirred at RT for 15 h. The mixture was poured onto ice and the resulting solution was extracted with Et_2O (4 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford alkyne **10** as a yellow volatile oil, which was used in the next step without further purification.[2]

Step 2: *tert*-Butyl (*Z*)-3-iodoacrylate (**12**) (5.09 mmol, 1.29 g) and the crude **10** (6.2 mmol, 558.7 mg, 94% in Et_2O) were added successively to a stirred solution of CuI (0.28 mmol, 54.2 mg) and $Pd(PPh_3)_4$ (0.25 mmol, 288 mg) in Et_3N (20 mL). Stirring was continued in a sealed Schlenk tube at 30 °C for 70 h. The mixture was diluted with *tert*-butyl methyl ether (20 mL) and the reaction was quenched with H_2O (15 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 30 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by flash chromatography on silica gel (hexane/EtOAc = 20/1 to 10/1) to yield the title compound as a yellow oil (992.2 mg, 93%). $[\alpha]_D^{20}$ = +49.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.05 (s, 2H), 4.09-4.00 (m, 1H), 3.82 (d, *J* = 4.4 Hz, 1H), 2.61 (dd, *J* = 16.8, 4.0 Hz, 1H), 2.47 (dd, *J* = 16.8, 7.6 Hz, 1H), 1.48 (s, 9H), 1.28 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 130.4, 122.8, 100.0, 81.1, 80.9, 66.2, 30.8, 28.1, 22.1. IR (film, cm^{-1}): 3461, 2976, 2931, 2208, 1702, 1605, 1480, 1456, 1408, 1367, 1303, 1237, 1210, 1147, 1084, 1060, 1029, 959, 938, 869, 856, 817, 759, 728, 541, 477, 444, 429. MS (EI): *m*/*z* (%) 154 (6), 137 (21), 110 (100), 92 (19), 82 (64), 65 (15), 57 (63), 45 (31), 41 (26), 39 (17), 29 (16). HRMS (ESI): *m*/*z*: calcd for: $C_{12}H_{18}O_3Na$ [*M*+*Na*$^+$]: 233.11481, found: 233.11480.

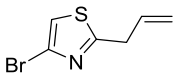
(*S*)-6-(2-Hydroxypropyl)-2*H*-pyran-2-one (**14**). [(Xphos)AuNTf$_2$] (0.039 mmol, 37.1 mg) was added to a solution of compound **13** (3.5 mmol, 743 mg) in $MeNO_2$ (5.7 mL) and HOAc (1.4 mL) and the resulting mixture was stirred for 23 h. The mixture was adsorbed on silica which was loaded on top of a flash column filled with silica, and the product was eluted with hexane/EtOAc (4/1 to 1/3). The desired product was obtained as a yellow oil (484 mg, 89%). $[\alpha]_D^{20}$ = +121.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (dd, *J* = 9.6, 6.8 Hz, 1H), 6.17 (dd, *J* = 9.2, 0.89 Hz, 1H), 6.09 (dt, *J* = 6.8, 0.8 Hz, 1H), 4.30-4.17 (m, 1H), 2.66-2.53 (m, 2H), 2.38 (br s, 1H), 1.27 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.4, 162.9, 143.8, 113.5, 104.7, 65.4, 43.3, 23.3. IR

(film, cm^{-1}): 3412, 2974, 2934, 1725, 1633, 1558, 1384, 1174, 1103, 940, 914, 804, 726, 697, 544. MS (EI): *m*/*z* (%) 154 (10), 110 (100), 95 (44), 82 (33), 68 (5), 54 (7), 45 (30), 39 (68), 27 (12). HRMS (EI): *m*/*z*: calcd for: $C_8H_{10}O_3$ [*M*]: 154.06300, found: 154.06284.

(*S*)-1-(2-Oxo-2*H*-pyran-6-yl)propan-2-yl pent-4-enoate (**15**). 2,4,6-Trichlorobenzoyl chloride (4.8 mmol, 0.75 mL) was slowly added to a stirred solution of 4-pentenoic acid (4.8 mmol, 481 mg) and Et_3N (4.8 mmol, 0.66 mL) in toluene (60 mL) at 0 °C. After stirring at RT for 1.5 h, the mixture was cooled to 0 °C and DMAP (7.2 mmol, 886.8 mg) was added, followed by a solution of compound **14** (4 mmol, 617.8 mg) in toluene (20 mL) (the flask was rinsed with 2 × 2.5 mL of THF). After stirring for 1 h at RT, the reaction was quenched with water (20 mL). The aqueous phase was extracted with EtOAc (3 × 30 mL) and the combined extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 8/1 to 2/1) to yield the title compound as a pale yellow oil (913.3 mg, 97%). $[\alpha]_D^{20}$ = +49.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.19 (dd, *J* = 9.6, 1.2 Hz, 1H), 6.01 (dd, *J* = 6.4, 1.2 Hz, 1H), 5.82-5.72 (m, 1H), 5.26-5.18 (m, 1H), 5.04-4.96 (m, 2H), 2.77-2.66 (m, 2H), 2.39-2.30 (m, 4H), 1.30 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.2, 162.3, 162.1, 143.3, 136.4, 115.5, 114.0, 104.3, 68.0, 40.0, 33.5, 28.7, 19.9. IR (film, cm^{-1}): 3081, 2981, 2935, 1723, 1637, 1558, 1365, 1170, 1086, 913, 797, 548. MS (EI): *m*/*z* (%) 236 (0.3), 153 (1.1), 136 (100), 108 (42), 55 (32), 39 (8). HRMS (ESI): *m*/*z*: calcd for: $C_{13}H_{16}O_4Na$ [*M*+Na^+]: 259.09408, found: 259.09393.



2-Allyl-4-bromothiazole (**5**). Anhydrous LiCl (16.9 mmol, 717 mg) was placed in a Schlenk tube under argon and was dried for 10 min at 300 °C (heat gun) in vacuum (2 × 10^{-3} mbar). Zinc powder (18.2 mmol, 1.19 g) was added and the mixture was dried again for 10 min at 300 °C (heat gun) in vacuum (2 × 10^{-3} mbar). The flask was evacuated and refilled with argon twice before THF (15 mL) was introduced. The suspension was stirred at 50 °C when $BrCH_2CH_2Br$ (0.56 mmol, 48 µL) was added to activate the Zn dust. The mixture was cooled to RT before Me_3SiCl (0.23 mmol, 28.5 µL) and 2,4-dibromothiazole (11.2 mmol, 2.73 g) were successively added and stirring was continued for 7 h. At this time, the resulting solution of the organozinc compound in THF was filtered through a pad of dry Celite (see General) under argon into a new dried and Ar-flushed Schlenk tube, rinsing the reaction vessel with THF (2 × 5 mL). The solution was cooled to 0 °C before allyl bromide (18.0 mmol, 1.55 mL) was added, followed by CuCN (0.56 mmol, 50.3 mg). The mixture was stirred at 0 °C for 1 h before the reaction was quenched with sat. aq. NH_4Cl (20 mL). The mixture was diluted with Et_2O (20 mL), the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with sat. aq. NaCl, dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by flash chromatography on silica gel (pentane/Et_2O = 250/1 to 50/1) to yield the title compound as a colorless oil (2.05 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (s, 1H), 6.01 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.31-5.24 (m, 2H), 3.76 (dt, *J* = 6.8, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 132.8, 124.4, 119.3, 116.5, 37.8. IR (film, cm^{-1}): 3122, 3083, 2981, 2904, 1640, 1477, 1250, 1076, 921, 834, 726. MS (EI): *m*/*z* (%) 204 (100), 179 (16), 138 (27), 124 (20), 97 (17), 80 (22), 57 (47). HRMS (ESI): *m*/*z*: calcd for: $C_6H_6NBrSNa$ [*M*+Na^+]: 225.92967, found: 225.92947.



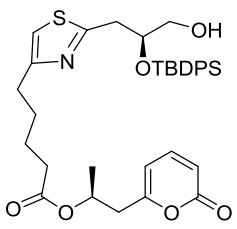
(*S*)-3-(4-Bromothiazol-2-yl)propane-1,2-diol (**6**). A pressure tube equipped with a magnetic stir bar was charged with $Pt(dba)_3$ (0.065 mmol, 58.2 mg), ligand **8** (0.076 mmol, 68.8 mg), and $B_2(pin)_2$ (3.85 mmol, 978 mg). The tube was evacuated and refilled with argon. THF (2.8 mL) was added via syringe and the resulting solution stirred at 80 °C for 30 min. The tube was cooled to room temperature before compound **5** (2.75 mmol, 560.6 mg, freshly distilled before use) was introduced. The tube was sealed and stirring continued at 60 °C for 14 h. For work up, the mixture was cooled to RT and transferred into a 100 mL two-necked round bottom flask, rinsing with THF (2 × 2 mL). The mixture was cooled to 0 °C before aq. NaOH (3 M, 6.8 mL) was added, followed by dropwise addition of hydrogen peroxide (30% *w/w*, 3.5 mL). The mixture was gradually warmed to room temperature and stirred for 4 h before the reaction was quenched at 0 °C by dropwise addition of sat. aq. sodium thiosulfate (2.8 mL) over 5 minutes. The mixture was diluted with ethyl acetate and aqueous layer extracted with ethyl acetate (6 × 20 mL). The combined extracts were dried over $MgSO_4$, filtered, and concentrated, and the residue was purified by flash chromatography on silica gel (hexane/EtOAc = 1/1 to 1/3, then EtOAc/MeOH = 25/1) to yield the title compound as a white solid (598 mg, 91%, 91% ee). [Conditions for HPLC analysis: Daicel Chiralpak IC-3 (4.6 mm × 150 mm), *n*-heptane/2-propanol = 80/20, *v* = 1.0 mL·min^{-1}, λ = 250 nm, t (minor) = 8.02 min, t (major) = 5.81 min]; m.p. = 67.8-68.6 °C; $[\alpha]_D^{20} = -13.0$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (s, 1H), 4.19-4.13 (m, 1H), 3.74 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.66 (br. s, 1H), 3.60 (dd, *J* = 11.2, 6.0 Hz, 1H), 3.18 (d, *J* = 6.0 Hz, 2H), 2.67 (br. s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 124.3, 116.6, 70.8, 65.6, 36.6. IR (film, cm^{-1}): 3341, 3167, 3125, 3063, 2918, 2863, 1477, 1256, 1072, 1035, 899, 624, 436. MS (EI): *m*/*z* (%) 239 (1.5), 208 (65), 179 (100), 138 (10), 99 (12). HRMS (ESI): *m*/*z*: calcd for: $C_6H_8NO_2BrSNa$ [*M*+Na^+]: 259.93515, found: 259.93503.

(S)-1-(4-Bromothiazol-2-yl)-3-((*tert*-butyldiphenylsilyl)oxy)propan-2-ol (**7**). TBDPSCl (3.70 mmol, 0.96 mL) was added dropwise at 0 °C to a solution of compound **6** (3.25 mmol, 774 mg), Et_3N (9.75 mmol, 1.76 mL) and DMAP (0.33 mmol, 40 mg) in CH_2Cl_2 (33 mL). After stirring for 48 h, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate (3 × 20 mL) and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by flash chromatography on silica gel (hexane/EtOAc = 15/1 to 6/1) to yield the title compound as a viscous yellow oil (1.54 g, quant.). $[\alpha]_D^{20} = -6.2$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73-7.57 (m, 4H), 7.49-7.33 (m, 6H), 7.11 (s, 1H), 4.21-4.08 (m, 1H), 3.70 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.65 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.23 (dd, *J* = 15.2, 4.0 Hz, 1H), 3.13 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.03 (d, *J* = 4.4 Hz, 1H), 1.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 135.5, 132.82, 132.79, 129.9, 127.8, 124.2, 116.6, 70.9, 66.7, 37.0, 26.8, 19.2. IR (film, cm^{-1}): 3392, 3070, 3048, 2929, 2857, 1474, 1255, 1110, 1079, 739, 612, 503. MS (ESI): *m*/*z*: 474 [*M*-H^+]. HRMS (ESI): *m*/*z*: calcd for: $C_{22}H_{25}NO_2BrSSi$ [*M*-H^+]: 474.05643, found: 474.05645.

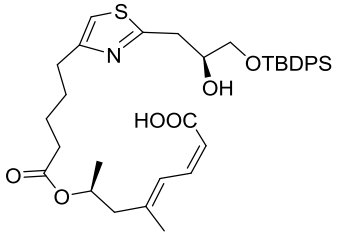
Compound 16. 9-BBN (0.5 M in degassed THF, 9 mL) was added dropwise at 0 °C to a solution of compound **15** (3.44 mmol, 812.7 mg) in degassed THF (15 mL). The mixture was stirred for 6 h before degassed H_2O (80 μL) was added and stirring continued for 15 min to quench the excess borane. In a second Schlenk tube, compound **7** (2.64 mmol, 1.258 g), RuPhos (0.264 mmol, 123.2 mg), $Pd(OAc)_2$ (0.135 mmol, 30.3 mg), and K_3PO_4 (8.45 mmol, 1.793 g) were dissolved in

degassed THF (8.6 mL). The mixture was vigorously stirred for 10 min before the borane solution was slowly added via canula (rinsing with 2 × 1 mL of THF). The resulting mixture was stirred at 50 °C for 30 min before it was diluted with EtOAc (25 mL) and the reaction was quenched with H_2O (10 mL). The aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic phases were washed with sat. aq. NaCl (20 mL), dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc = 8/1 to 1/1) to yield the title compound as a yellow oil (1.37 g, 82%). Small amounts of the isomeric product **S1** were obtained as a yellow oil when the eluent was switched to hexane/EtOAc = 1/1 to 1/3. The ratio **16:S1** in the crude material was determined as 88/12 by LC-MS analysis [50 × 3.0 mm Zorbax Eclipse Plus C18, 1.8µm, Nr USUYA03995, MeCN/H_2O (0.1% TFA) = 60:40, *v* = 0.5 mL/min, λ = 228 nm, 35 °C, 120 bar]. $[\alpha]_D^{20}$ = +15.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.56 (m, 4H), 7.48-7.31 (m, 6H), 7.21 (dd, *J* = 9.6, 6.8 Hz, 1H), 6.75 (s, 1H), 6.15 (d, *J* = 9.2 Hz, 1H), 5.99 (d, *J* = 6.8 Hz, 1H), 5.27-5.16 (m, 1H), 4.17-4.10 (m, 1H), 3.84 (br s, 1H), 3.76-3.57 (m, 2H), 3.22 (dd, *J* = 15.2, 3.6 Hz, 1H), 3.11 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.78-2.60 (m, 4H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.72-1.54 (m, 4H), 1.30 (d, *J* = 6.4 Hz, 3H), 1.06 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 167.0, 162.2, 162.1, 156.4, 143.2, 135.5, 133.0, 129.7, 127.7, 114.0, 112.4, 104.3, 71.1, 67.9, 66.7, 40.1, 36.4, 34.1, 31.0, 28.4, 26.8, 24.4, 19.9, 19.2. IR (film, cm^{-1}): 3430, 3071, 2930, 2857, 1730, 1636, 1558, 1427, 1110, 1079, 1059, 799, 702, 504. MS (ESI): *m*/*z*: 656 [*M*+Na^+]. HRMS (ESI): *m*/*z*: calcd for: $C_{35}H_{43}NO_6SSiNa$ [*M*+Na^+]: 656.24726, found: 656.24715.

Isomer S1. $[\alpha]_D^{20}$ = +32.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 4H), 7.46-7.35 (m, 6H), 7.21 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.73 (s, 1H), 6.16 (dd, *J* = 9.2, 0.8 Hz, 1H), 5.99 (dd, *J* = 6.8, 0.8 Hz, 1H), 5.25-5.17 (m, 1H), 4.26-4.09 (m, 1H), 3.56-3.37 (m, 2H), 3.19-3.10 (m, 2H), 2.78-2.63 (m, 4H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.69-1.58 (m, 5H), 1.30 (d, *J* = 6.4 Hz, 3H), 1.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 165.9, 162.2, 156.4, 143.2, 135.8, 135.7, 133.6, 133.4, 129.9, 127.8, 127.7, 114.0, 112.9, 104.3, 72.5, 68.0, 65.3, 40.1, 37.6, 34.1, 30.9, 28.5, 26.9, 24.4, 19.9, 19.2. IR (film, cm^{-1}): 3429, 3071, 2930, 2856, 1730, 1636, 1558, 1427, 1105, 1056, 799, 702, 505. MS (ESI): *m*/*z*: 656 [*M*+Na^+]. HRMS (ESI): *m*/*z*: calcd for: $C_{35}H_{43}NO_6SSiNa$ [*M*+Na^+]: 656.24726, found: 656.24735.

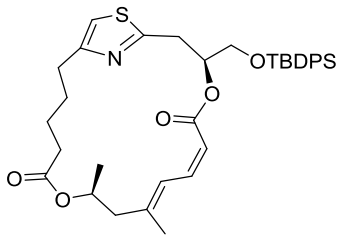


Seco-Acid 17. MeMgBr (0.56 M in Et_2O, 1.8 mL) was added via syringe pump over 76 min to a solution of $Fe(acac)_3$ (0.035 mmol, 12.4 mg) and compound **16** (0.122 mmol, 77.0 mg) in Et_2O/cyclopentyl methyl ether (1/1, 4.8 mL) at −30 °C. Stirring was continued for 140 min at this temperature before the reaction was quenched with aq. sat. NH_4Cl and the pH of the aqueous layer was adjusted to ~2-3 upon addition of aq. HCl (1 M). The aqueous layer was extracted with EtOAc (5 × 25 mL) and the combined organic layers were washed with sat. aq. NaCl, dried over $MgSO_4$, filtered and concentrated to an oily residue, which was purified by preparative TLC (hexane/EtOAc = 1/1) to yield the title compound as a yellow oil (59 mg, 75%). [Conditions for LC-MS analysis: 2.1 × 150 mm YMC-Pack Pro C18 S-5 µm, MeCN/H_2O (0.1% TFA) = 70:30, *v* = 0.2 mL/min, λ = 228 nm, 35 °C, 40 bar]; $[\alpha]_D^{20}$ = −52.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 4H), 7.48-7.32 (m, 6H), 7.15 (d, *J* = 12.0 Hz, 1H), 6.86 (t, *J* = 11.6 Hz, 1H), 6.76 (s, 1H), 5.59 (d, *J* = 11.6 Hz, 1H), 5.71-4.98 (br s, 1H), 5.16-5.08 (m, 1H), 4.18-4.12 (m, 1H), 3.75-3.53 (m, 3H), 3.26 (dd,



J = 11.2, 3.2 Hz, 1H), 3.15 (dd, *J* = 15.2, 8.4 Hz, 1H), 2.81-2.61 (m, 2H), 2.44 (dd, *J* = 14.4, 8.8 Hz, 1H), 2.35-2.23 (m, 3H), 1.87 (s, 3H), 1.72-1.57 (m, 4H), 1.24 (d, *J* = 6.4 Hz, 3H), 1.06 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 170.4, 167.6, 156.3, 145.3, 140.6, 135.5, 133.1, 133.0, 129.8, 127.7, 124.1, 116.1, 112.6, 71.2, 68.3, 66.7, 46.8, 36.3, 34.2, 30.6, 28.7, 26.8, 24.2, 20.2, 19.2, 17.2. IR (film, cm^{-1}): 3433, 3070, 2932, 2858, 1728, 1632, 1428, 1111, 828, 701, 503. MS (ESI): *m*/*z*: 672 [*M*+Na^+]. HRMS (ESI): *m*/*z*: calcd for: $C_{36}H_{47}NO_6SSiNa$ [*M*+Na^+]: 672.27856, found: 672.27890.

Compound 19. 2-Bromo-1-ethyl-pyridinium tetrafluoroborate (6.4 mmol, 1.75 g) was added to a solution of compound **17** (0.26 mmol, 166.2 mg) and $NaHCO_3$ (63.9 mmol, 5.37 g) in CH_2Cl_2 (470 mL). The mixture was stirred for 45 h in the dark. The reaction was quenched with H_2O (50 mL), the aqueous layer was extracted with *tert*-butyl methyl ether (4 × 50 mL) and the combined organic phases were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash chromatography on silica gel (hexane/Et_2O = 8/1 to 3/1) to yield the title compound as a colorless oil (114.3 mg, 71%).



$[\alpha]_D^{20} = -211.3$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72-7.58 (m, 4H), 7.48-7.33 (m, 6H), 7.00 (d, *J* = 12.0 Hz, 1H), 6.70 (s, 1H), 6.69 (t, *J* = 11.5 Hz, 1H), 5.66-5.49 (m, 1H), 5.41 (d, *J* = 11.5 Hz, 1H), 5.21-5.06 (m, 1H), 3.83 (dd, *J* = 11.0, 5.0 Hz, 1H), 3.77 (d, *J* = 10.5, 4.5 Hz, 1H), 3.31 (dd, *J* = 14.5, 3.0 Hz, 1H), 3.23 (dd, *J* = 14.5, 11.5 Hz, 1H), 2.83 (dddd, *J* = 15.5, 6.0, 4.5, 1.5 Hz, 1H), 2.59 (ddd, *J* = 14.5, 10.0, 4.5 Hz, 1H), 2.39-2.23 (m, 2H), 2.22-2.08 (m, 2H), 1.83 (s, 3H), 1.82-1.78 (m, 1H),1.72-1.65 (m, 1H), 1.41-1.32 (m, 1H), 1.30-1.24 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 3H), 1.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 165.9, 164.7, 156.4, 145.5, 140.9, 135.6, 135.5, 133.13, 133.11, 129.7, 127.72, 127.69, 124.0, 114.8, 113.3, 72.3, 67.1, 65.4, 48.2, 35.0, 34.7, 30.7, 28.1, 26.8, 23.2, 21.2, 19.3, 16.7. IR (film, cm^{-1}): 3071, 2931, 2857, 1719, 1632, 1427, 1161, 1112, 814, 731, 701, 504. MS (ESI): *m*/*z*: 654 [*M*+Na^+]. HRMS (ESI): *m*/*z*: calcd for: $C_{36}H_{45}NO_5SSiNa$ [*M*+Na^+]: 654.26799, found: 654.26771.

Scalable Procedure for the Preparation of 19. MeMgBr (0.56 M in Et_2O, 6.06 mL) was added via syringe pump over 3.5 h to a solution of $Fe(acac)_3$ (0.12 mmol, 42.8 mg) and compound **16** (0.40 mmol, 256.1 mg) in Et_2O/cyclopentyl methyl ether (1/1, 16.2 mL) at −30 °C. Stirring was continued for 2.5 h at this temperature before the reaction was quenched with aq. sat. NH_4Cl and the pH of the aqueous layer was adjusted to ~2-3 upon addition of aq. HCl (1 M). The aqueous phase was extracted with EtOAc (5 × 30 mL). The combined organic layers were washed with sat. aq. NaCl, dried over $MgSO_4$, filtered and concentrated to an oily residue, which was dried in high vacuum for 1 h. This crude material was directly used in the next step.

2-Bromo-1-ethyl-pyridinium tetrafluoroborate (9.95 mmol, 2.73 g) was added to a solution of the crude material and $NaHCO_3$ (103.3 mmol, 8.68 g) in CH_2Cl_2 (680 mL). The mixture was stirred for 43 h in the dark before the reaction was quenched with H_2O (80 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (4 × 70 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash chromatography on silica gel (hexane/Et_2O = 8/1 to 3/1) to yield the title compound as a colorless oil (139 mg, 55%). Unreacted starting material **16** was recovered in 14% yield (34.8 mg) when the eluent was switched to hexane/EtOAc = 2/1 to 1/1.

Compound 20. TBAF (0.42 mmol, 1 M in THF, 0.42 mL) was slowly added to a solution of compound **19** (0.21 mmol, 131.9 mg) in THF (3 mL) and acetic acid (1.02 mmol, 58.7 µL). After stirring for 16 h, the mixture was poured into a mixed solution of ethyl acetate (5 mL) and sat. aq. $NaHCO_3$ (5 mL). The aqueous layer was extracted with ethyl acetate (5 × 10 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified by flash column chromatography on silica gel (hexane/EtOAc = 2/1 to 1/2) to yield the title compound as a colorless oil (82.1 mg, quant.). $[\alpha]_D^{20}$ = −273.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, *J* = 11.6 Hz, 1H), 6.69 (t, *J* = 11.6 Hz, 1H), 6.68 (s, 1H), 5.59-5.46 (m, 1H), 5.40 (d, *J* = 11.2 Hz, 1H), 5.19-5.05 (m, 1H), 3.89-3.70 (m, 2H), 3.27-3.19 (m, 2H), 2.82 (dt, *J* = 14.4, 4.8 Hz, 1H), 2.62-2.51 (m, 1H), 2.45 (br s, 1H), 2.36-2.21 (m, 2H), 2.19-2.10 (m, 2H), 1.82 (s, 3H), 1.80-1.72 (m, 1H), 1.69-1.60 (m, 1H), 1.40-1.13 (m, 1H), 1.26-1.14 (m, 1H), 1.23 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 165.7, 165.0, 156.4, 146.1, 141.4, 123.9, 114.3, 113.3, 73.0, 67.1, 64.5, 48.2, 34.6, 34.5, 30.6, 28.0, 23.1, 21.1, 16.8. IR (film, cm^{-1}): 3308, 2931, 2868, 1714, 1631, 1427, 1201, 1155, 1048, 814, 750. MS (ESI): *m*/*z*: 416 [*M*+Na^+]. HRMS (ESI): *m*/*z*: calcd for: $C_{20}H_{27}NO_5SNa$ [*M*+Na^+]: 416.15022, found: 416.15025.

Compound 21. Sulfur trioxide pyridine complex (0.301 mmol, 47.9 mg) and anhydrous *i*Pr_2NEt (0.74 mmol, 128.2 µL) were successively added to a solution of compound **20** (0.104 mmol, 40.8 mg) in CH_2Cl_2 (1.6 mL) at −20 °C. The resulting mixture was stirred for 5 min before anhydrous DMSO (1.05 mmol, 74 µL) was added dropwise. Stirring was continued for 40 min at −20 °C before the solution was poured into a mixture of *tert*-butyl methyl ether (10 mL) and aq. phosphate buffer (pH 7, 10 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 15 mL) and the combined organic phases were washed with phosphate buffer, dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to an oily residue, which was dried in vacuum for 2 h (2 × 10^{-3} mbar). The crude material was directly used in the next step.

2-(Triphenylphosphoranylidene)-propionaldehyde (0.13 mmol, 39.9 mg) was added to a solution of the crude product in toluene (5 mL) and the resulting solution was stirred at 80 °C for 2 h. Once the reaction was complete (monitored by TLC), the mixture was allowed to reach ambient temperature before the reaction was quenched by H_2O (5 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (4 × 10 mL) and the combined extracts were dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (hexane/Et_2O = 8/1 to 2/3) to yield the title compound as a white solid (38.6 mg, 86%). $[\alpha]_D^{20}$ = −320.3 (*c* = 1.0, $CHCl_3$); m.p. = 134.7-135.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.46 (s, 1H), 6.97 (d, *J* = 12.0 Hz, 1H), 6.72 (s, 1H), 6.71 (dd, *J* = 12.0, 11.2 Hz, 1H), 6.49-6.26 (m, 2H), 5.36 (d, *J* = 11.2 Hz, 1H), 5.16-5.08 (m, 1H), 3.24-3.19 (m, 2H), 2.85 (dt, *J* = 14.4, 4.8 Hz, 1H), 2.57 (ddd, *J* = 14.8, 10.4, 4.4 Hz, 1H), 2.41-2.05 (m, 4H), 1.96 (d, *J* = 1.2 Hz, 3H), 1.87-1.78 (m, 1H), 1.83 (s, 3H), 1.71-1.51 (m, 1H), 1.42-1.35 (m, 1H), 1.24-1.17 (m, 1H), 1.21 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.4, 173.0, 164.3, 163.9, 156.9, 147.8, 146.5, 141.7, 140.7, 123.8, 113.9, 113.5, 68.5, 67.1, 48.3, 37.3, 34.6, 30.7, 28.0, 23.1, 21.1, 16.8, 9.9. IR (film, cm^{-1}): 2964, 2931, 2857, 1713, 1687, 1651, 1424,

1144, 1114, 812, 752. MS (ESI): *m*/*z*: 432 [*M*+H$^+$]. HRMS (ESI): *m*/*z*: calcd for: $C_{23}H_{30}NO_5S$ [*M*+H$^+$]: 432.18392, found: 432.18422.

Compound 22. A mixture of CHI_3 (0.42 mmol, 166 mg) and compound **21** (61.6 µmol, 26.6 mg) in degassed THF (1.4 mL, rinsing the flask with 2 × 0.5 mL of THF) was added dropwise to a slurry of $CrCl_2$·1.05 THF (1.65 mmol, 322 mg) in degassed THF (1.5 mL) at 0 °C. The mixture was stirred at this temperature for 1.5 h. Once the reaction was complete (monitored by TLC), the mixture was diluted with *tert*-butyl methyl ether (5 mL) and H_2O (5 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (3 × 10 mL) and the combined extracts were dried over $MgSO_4$, filtered, and evaporated. The crude material was purified by flash chromatography on silica (hexane/Et_2O = 10/1 to 2/1) to yield the title compound as a yellow oil (31.2 mg, 91%, product/Σ of isomers = 94/6) [Conditions for LC-MS analysis: 2.1 × 150 mm YMC-Pack Pro C18 S-5 µm, MeOH/H_2O = 90:10, *v* = 0.2 mL/min, λ = 228 nm, 35 °C, 64 bar]; $[\alpha]_D^{20} = -412.7$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 14.5 Hz, 1H), 6.99 (d, *J* = 12.0 Hz, 1H), 6.99 (s, 1H), 6.67 (t, *J* = 11.5 Hz, 1H), 6.44 (d, *J* = 14.5 Hz, 1H), 6.20 (td, *J* = 9.0, 5.0 Hz, 1H), 5.48 (d, *J* = 8.5 Hz, 1H), 5.34 (d, *J* = 11.0 Hz, 1H), 5.20-5.03 (m, 1H), 3.19-3.12 (m, 2H), 2.85 (dt, *J* = 14.5, 5.0 Hz, 1H), 2.58 (ddd, *J* = 15.0, 10.5, 4.5 Hz, 1H), 2.37- 2.24 (m, 2H), 2.22-2.06 (m, 2H), 1.95 (s, 3H), 1.88-1.79 (m, 1H), 1.83 (s, 3H), 1.70-1.63 (m, 1H), 1.41-1.34 (m, 1H), 1.23 (d, *J* = 8.5 Hz, 3H), 0.95-0.79 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.1, 164.9, 164.4, 156.7, 148.5, 145.8, 141.0, 138.0, 129.9, 123.9, 114.6, 113.3, 77.6, 68.6, 67.1, 48.3, 38.4, 34.7, 30.8, 28.1, 23.2, 21.2, 16.8, 12.8. IR (film, cm^{-1}): 2975, 2930, 2856, 1714, 1631, 1427, 1152, 1116, 860, 751. MS (EI): *m*/*z* (%) 555 (49), 428 (100), 305 (12), 276 (22), 258 (12), 250 (18), 232 (14), 199 (15), 135 (47), 107 (33), 91 (22), 79 (18). HRMS (ESI): *m*/*z*: calcd for: $C_{24}H_{30}NO_4SINa$ [*M*+Na$^+$]: 578.08325, found: 578.08409.

DMDA-Pat A (2). Flame-dried [$Ph_2PO_2^-$][NBu_4^+] (0.089 mmol, 41.0 mg) was dissolved in degassed DMF (0.3 mL) and the resulting solution was added to a Schlenk tube containing compound **22** (0.045 mmol, 25.0 mg) (rinsing with 2 × 0.15 mL DMF). (*E*)-*N*,*N*-Dimethyl-3-(tributylstannyl)but-2-en-1-amine (**23**)[3] (0.072 mmol, 28.0 mg) and copper thiophene carboxylate (CuTC, 0.068 mmol, 12.9 mg) were then introduced, followed by $Pd(PPh_3)_4$ (0.0045 mmol, 5.2 mg). The resulting mixture was stirred for 1 h before the reaction was quenched with water (5 mL). After dilution with EtOAc (5 mL), the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined extracts were washed with sat. aq. NaCl, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash chromatography on silica (pretreated with 1% Et_3N in hexane, hexane/EtOAc = 1/1 then EtOAc/Et_3N = 120/1 to 50/1) to yield the title compound as a yellow oil (19.7 mg, 83%). $[\alpha]_D^{20} = -379.7$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.47 (d, *J* = 11.8 Hz, 1H), 6.70 (ddd, *J* = 9.1, 8.7, 5.6 Hz, 1H), 6.47 (dd, *J* = 11.8, 11.4 Hz, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.21 (d, *J* = 15.9 Hz, 1H), 6.20 (d, *J* = 0.8 Hz, 1H), 5.69 (t, *J* = 6.8 Hz, 1H), 5.55 (d, *J* = 11.4 Hz, 1H), 5.50 (dd, *J* = 9.1, 1.1 Hz, 1H), 5.15 (dqd, *J* = 10.9, 6.4, 1.6 Hz, 1H), 3.07 (dd, *J* = 14.5, 5.6 Hz, 1H), 3.06 (dd, *J* = 14.5, 8.7 Hz, 1H), 2.93 (d, *J* = 6.8 Hz, 2H), 2.78 (dt, *J* = 14.4, 4.0 Hz, 1H), 2.45 (ddd, *J* = 16.3, 10.3,

6.5 Hz, 1H), 2.35 (ddd, *J* = 4.0, 10.5, 14.3 Hz, 1H), 2.17-2.02 (m, 3H), 2.12 (s, 6H), 1.91 (d, *J* = 1.1 Hz, 3H), 1.71 (s, 3H), 1.65 (dd, *J* = 12.9, 1.6 Hz, 1H), 1.57-1.43 (m, 3H), 1.55 (s, 3H), 0.96 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.5, 165.2, 164.9, 157.4, 145.6, 141.3, 138.4, 135.9, 134.3, 131.5, 131.2, 129.3, 124.6, 115.5, 113.1, 69.8, 66.8, 57.6, 48.5, 45.5, 39.0, 35.0, 31.2, 28.5, 23.7, 21.2, 16.7, 13.3, 12.9. IR (film, cm^{-1}): 2973, 2932, 2856, 2814, 2764, 1729, 1713, 1631, 1427, 1154, 1112, 814, 750, 539. MS (ESI): *m*/*z*: 527 [*M*+H$^+$]. HRMS (ESI): *m*/*z*: calcd for: $C_{30}H_{43}N_2O_4S$ [*M*+H$^+$]: 527.29381, found: 527.29421.

Signal assignment of DMDA-PatA : Graphical Representation of NOE and ^{3}J Coupling Patterns

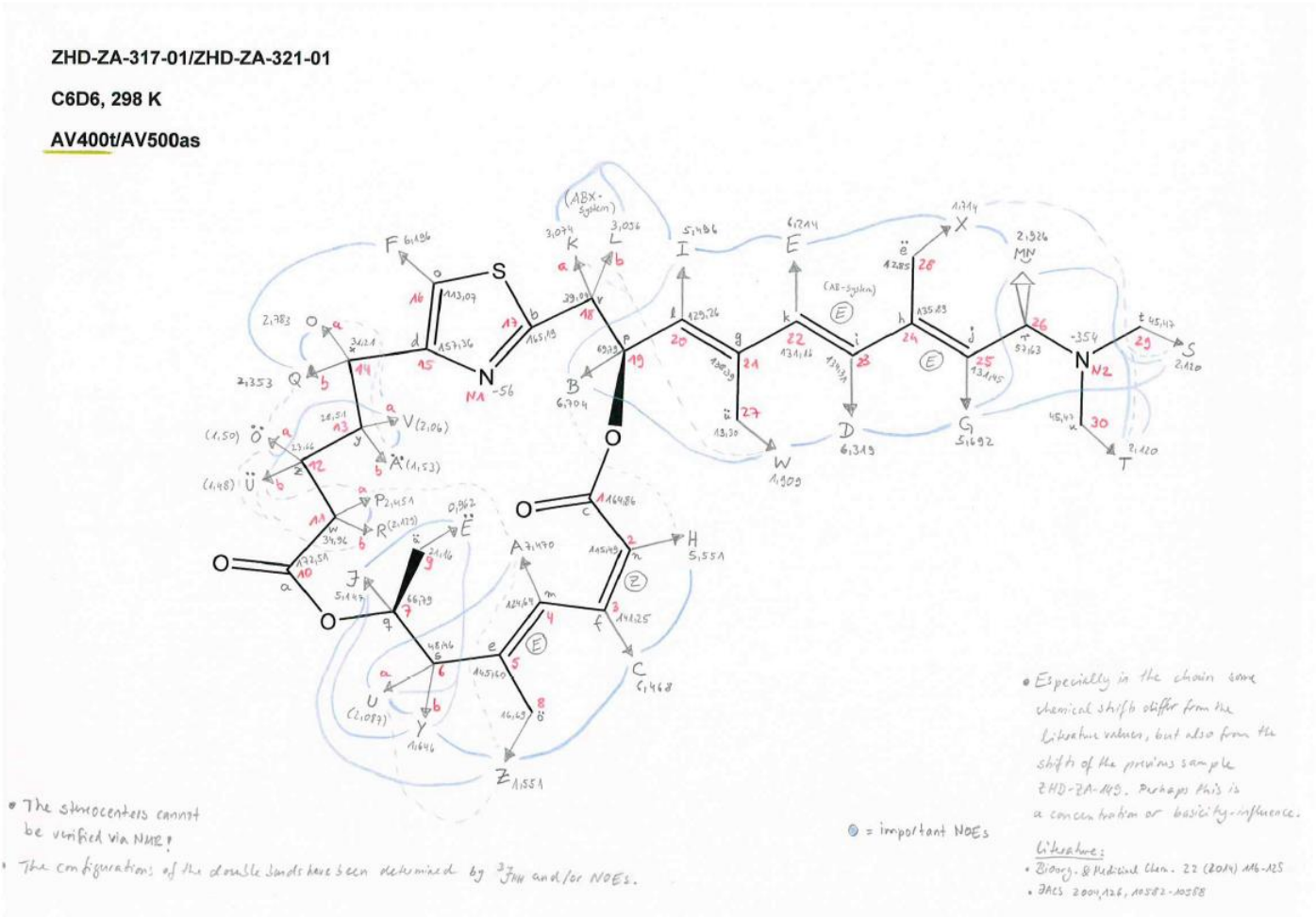


Table S-1. Signal assignment for DMDA-Pat A (**2**); arbitrary numbering scheme as shown in the Insert

Position	^{13}C NMR, δ (ppm)	^{1}H NMR, δ (ppm)
10	172.5	-
17	165.2	-
1	164.9	-
15	157.4	-
5	145.6	-
3	141.3	6.47
21	138.4	-
24	135.9	-
23	134.3	6.32
25	131.5	5.69
22	131.2	6.21
20	129.3	5.50
4	124.6	7.47
2	115.5	5.55
16	113.1	6.20
19	69.8	6.70
7	66.8	5.15
26	57.6	2.93
6	48.5	2.09, 1.65
29, 30	45.5	2.12
18	39.0	3.07, 3.06
11	35.0	2.45, 2.13
14	31.2	2.78, 2.35
13	28.5	2.06, 1.53
12	23.7	1.50, 1.48
9	21.2	0.96
8	16.7	1.55
27	13.3	1.91
28	12.9	1.71

Table S-2. Comparison of the ^{1}H NMR data of DMDA-Pat A (**2**) (ca. 15 mg in 0.5 mL of C_6D_6) with those reported in the literature

Literature[4]		This work		
δ (ppm)	***J* (Hz)**	**δ (ppm)**	***J* (Hz)**	**Δδ (ppm)**
7.47	12.0	7.47	11.8	0
6.71	5.0, 9.0	6.70	5.6, 8.7, 9.1	0.01
6.45	11.5	6.47	11.4, 11.8	0.02
6.32	16.0	6.32	15.9	0
6.21	16.0	6.21	15.9	0
6.17	-	6.20	0.8	0.03
5.69	7.0	5.69	6.8	0
5.55	11.5	5.55	11.4	0
5.49	9.0	5.50	1.1, 9.1	0.01
5.19-5.11	-	5.15	1.6, 6.4, 10.9	-
3.08-3.01	-	3.07	5.6, 14.5	-
		3.06	8.7, 14.5	-
2.91	6.5	2.93	6.8	0.02
2.78	4.5, 14.0	2.78	4.0, 14.4	0
2.48-2.42	-	2.45	6.5, 10.3, 16.3	-
2.33	4.0, 10.0, 14.5	2.35	4.0, 10.5, 14.3	0.02
2.11	-	2.12	-	0.01
2.16-2.03	-	2.17-2.02	-	0.01
1.90	1.0	1.91	1.1	0.01
1.71	-	1.71	-	0
1.64-1.61	-	1.65	1.6, 12.9	-
1.56-1.43	-	1.57-1.43	-	0.01
1.54	-	1.55	-	0.01
0.96-0.81	-	-	-	-
0.95	6.5	0.96	6.4	0.01

Table S-3. Comparison of the ^{13}C NMR data of DMDA-Pat A (**2**) in C_6D_6 (ca. 15 mg in 0.5 mL of C_6D_6) with the data reported in the literature

Literature[5] δ (ppm)	this work δ (ppm)	Δδ (ppm)
172.5	172.5	0
165.2	165.2	0
164.9	164.9	0
157.4	157.4	0
145.9	145.6	0.3
141.4	141.3	0.1
138.1	138.4	0.3
133.8	135.9	2.1
133.1	134.3	1.2
130.8	131.5	0.7
-	131.2	-
126.9	129.3	2.4
124.6	124.6	0
122.1	-	-
115.3	115.5	0.2
113.2	113.1	0.1
69.7	69.8	0.1
66.8	66.8	0
55.1	57.6	2.5
48.5	48.5	0
42.3	45.5	3.2
38.9	39.0	0.1
35.0	35.0	0
31.2	31.2	0
30.2	-	-
28.5	28.5	0
23.7	23.7	0
21.2	21.2	0
16.7	16.7	0
13.4	13.3	0.1
13.1	12.9	0.2

References:

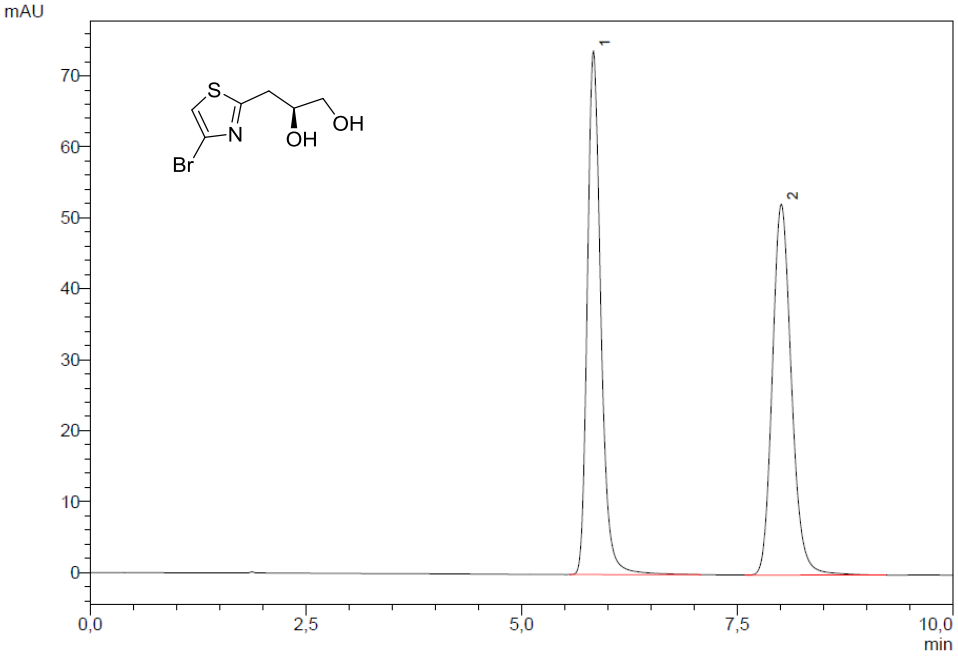
[1] N.-W. Tseng, M. Lautens, *J. Org. Chem.* **2009***, 74,* 2521-2526.

[2] T.-Y. Yuen, M. A. Brimble, *Org. Lett.* **2012**, *14*, 5154-5157.

[3] a) L. Otero, B. Vaz, R. Álvarez, Á. R. de Lera, *Chem. Commun.* **2013**, *49*, 5043-5045; b) G. Pattenden, D. J. Critcher, M. Remuiñán, *Can. J. Chem*. **2004**, *82*, 353-365.

[4] D. Romo, N. S. Choi, S. Li, I. Buchler, Z. Shi, J. O. Liu, *J. Am. Chem. Soc*. **2004**, *126*, 10582-10588.

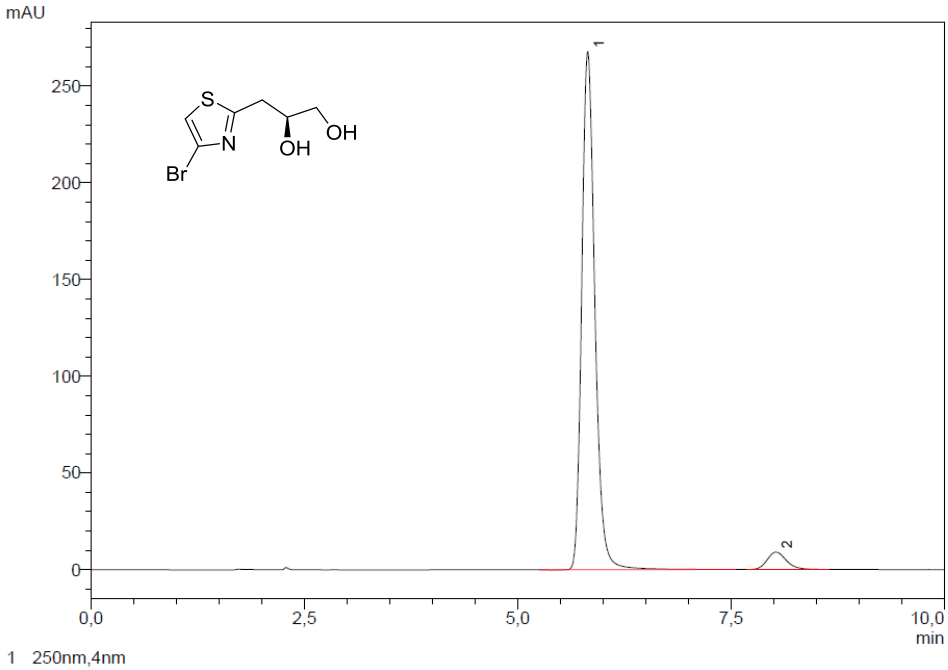
[5] W.-K. Low, J. Li, M. Zhu, S. S. Kommaraju, J. Shah-Mittal, K. Hull, J. O. Liu, D. Romo, *Bioorg. Med. Chem*. **2014**, *22*, 116-125.



1 250nm,4nm

PDA Ch1 250nm

Peak #	Ret. Time	Area %	Name
1	5,83	49,97	
2	8,01	50,03	
Total		100,00	



1 250nm,4nm

PDA Ch1 250nm

Peak #	Ret. Time	Area %	Name
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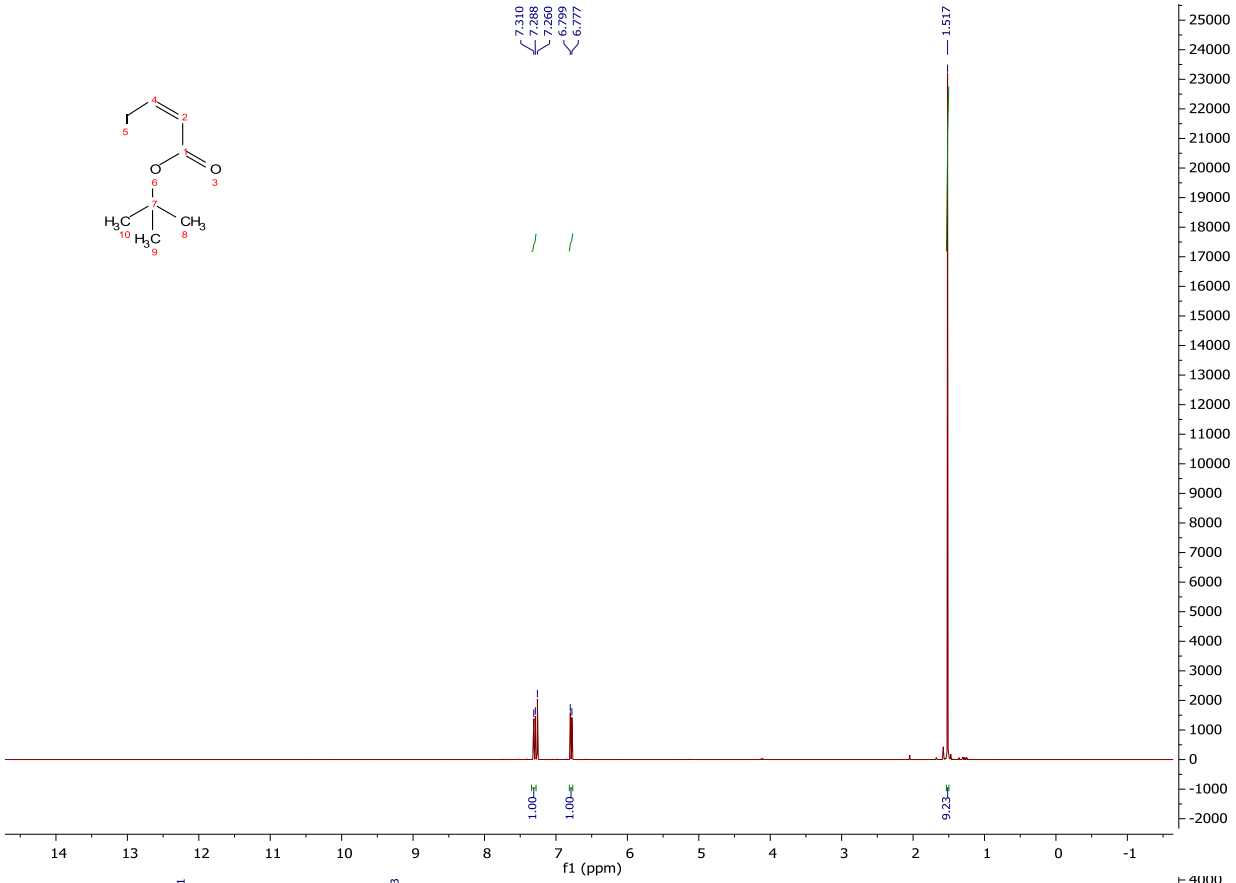
2	8,02	4,71	
Total		100,00	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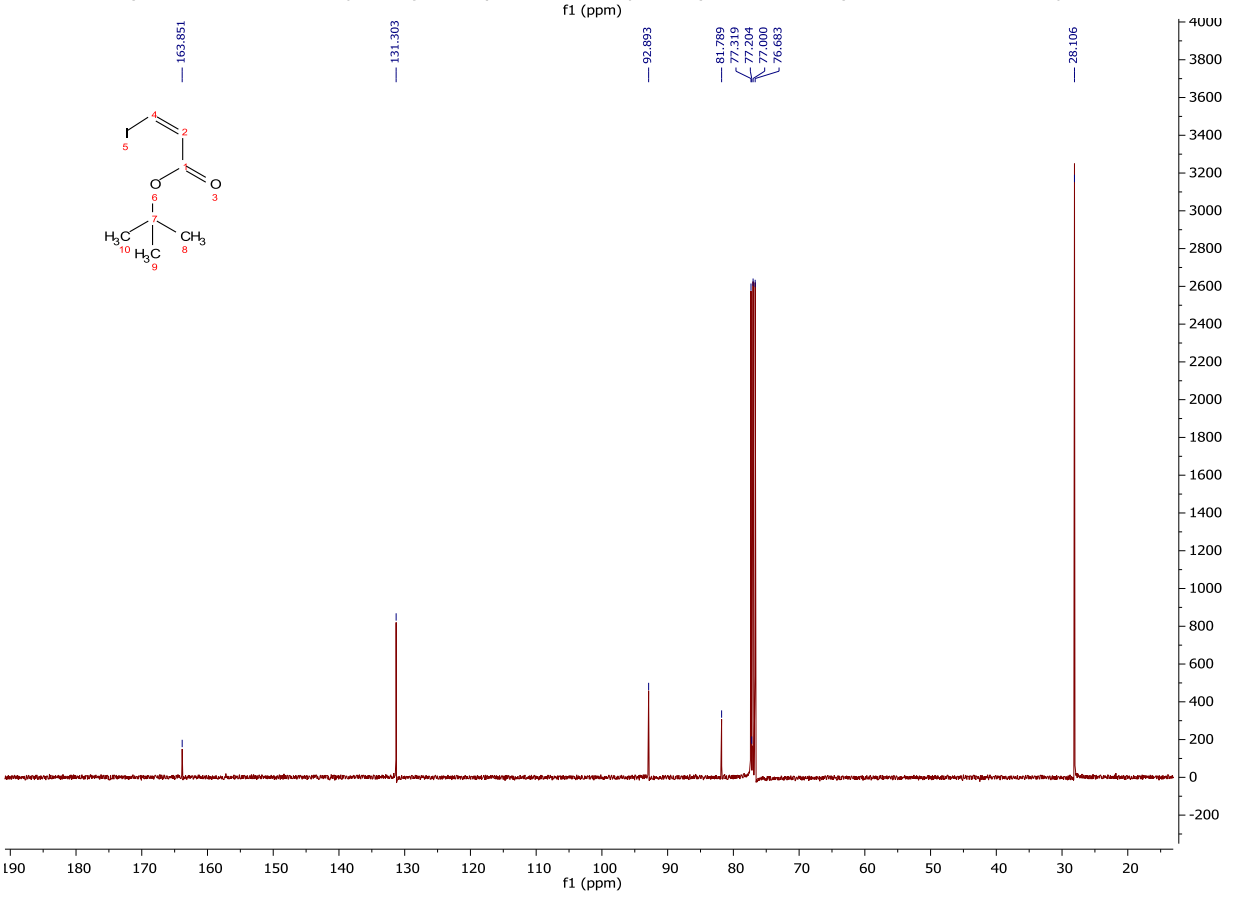
6.777
1.517
1.00
1.00
9.23
f1 (ppm)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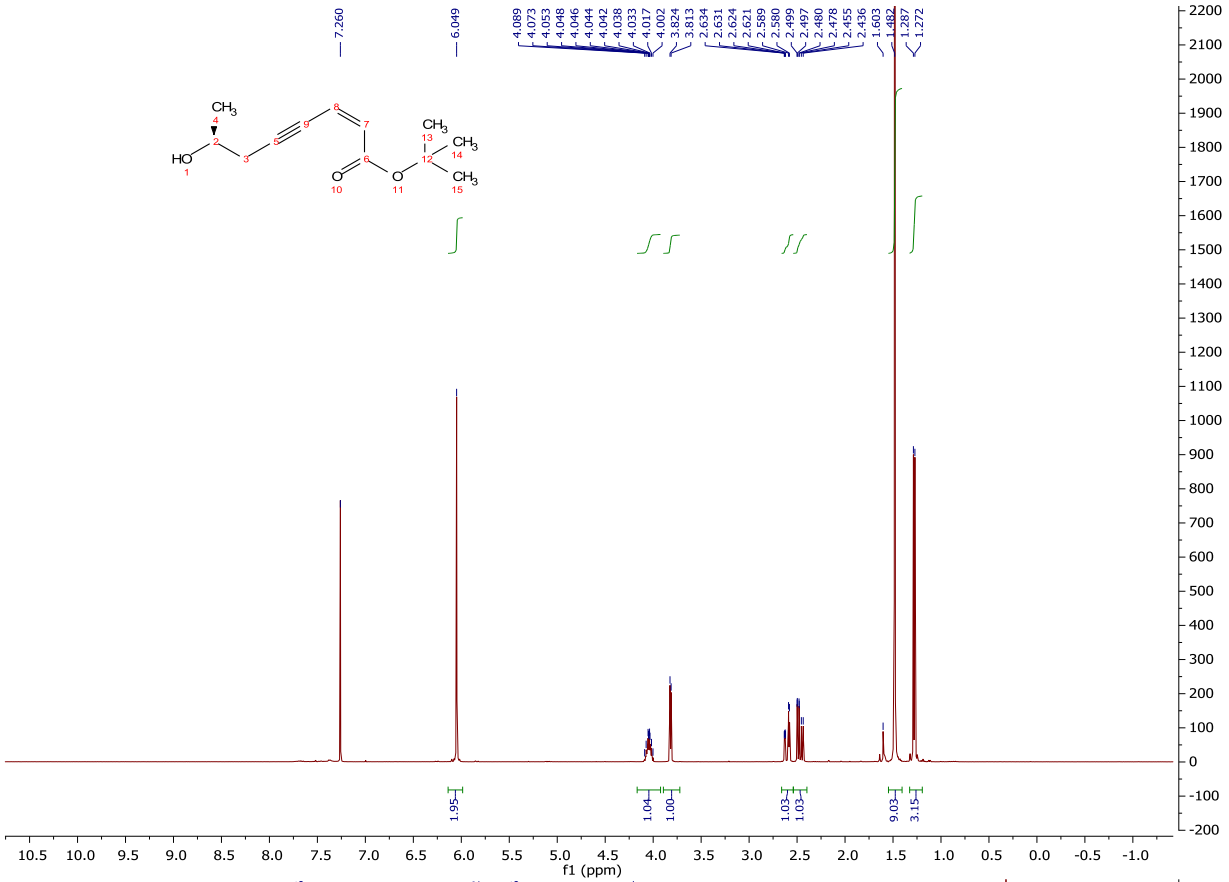
77.319
77.204
77.000
76.683
28.106
f1 (ppm)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4.048
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4.038
4.033
4.017
4.002
3.824
3.813
2.634
2.631
2.624
2.621
2.589
2.580
2.499
2.497
2.480
2.478
2.455
2.436
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1.04
1.00
1.03
1.03
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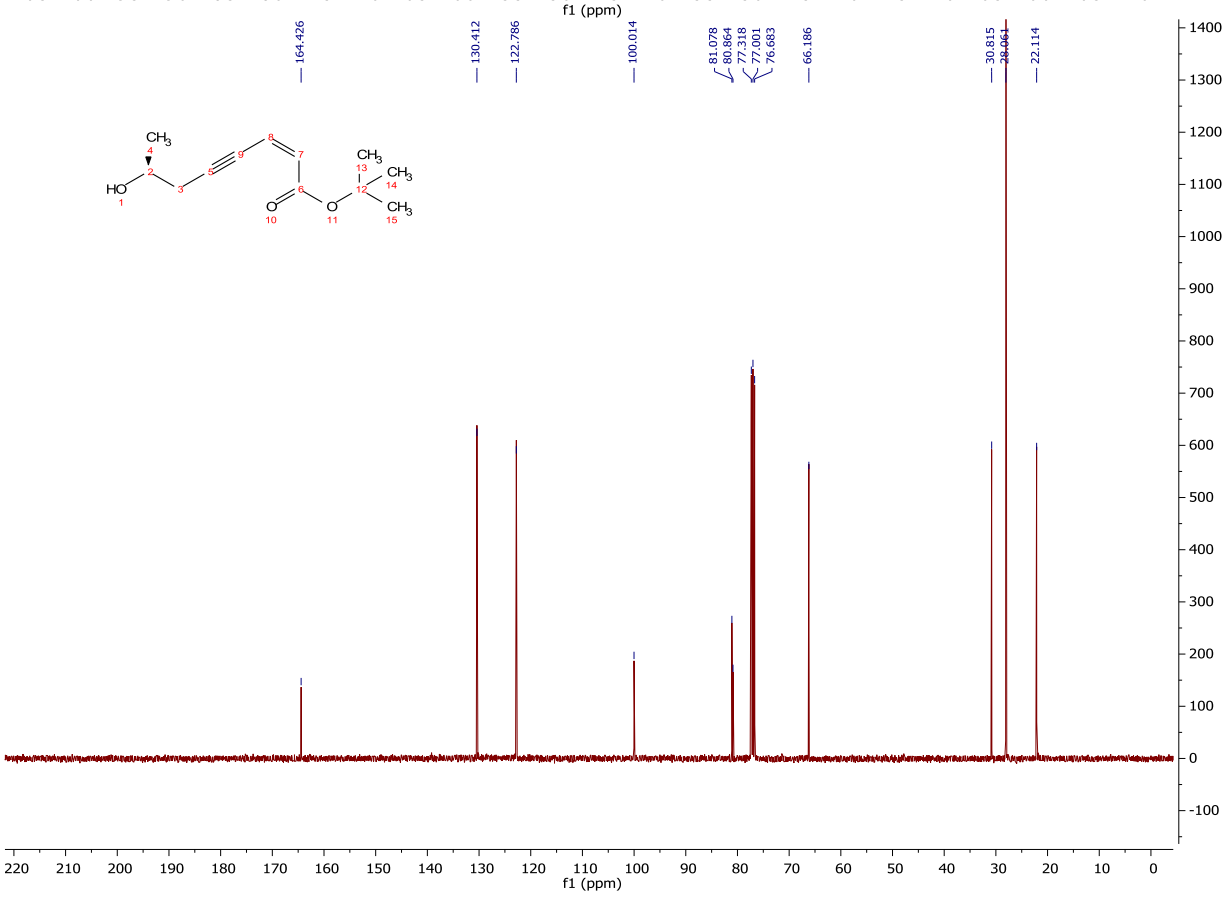
3.15
f1 (ppm)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77.001
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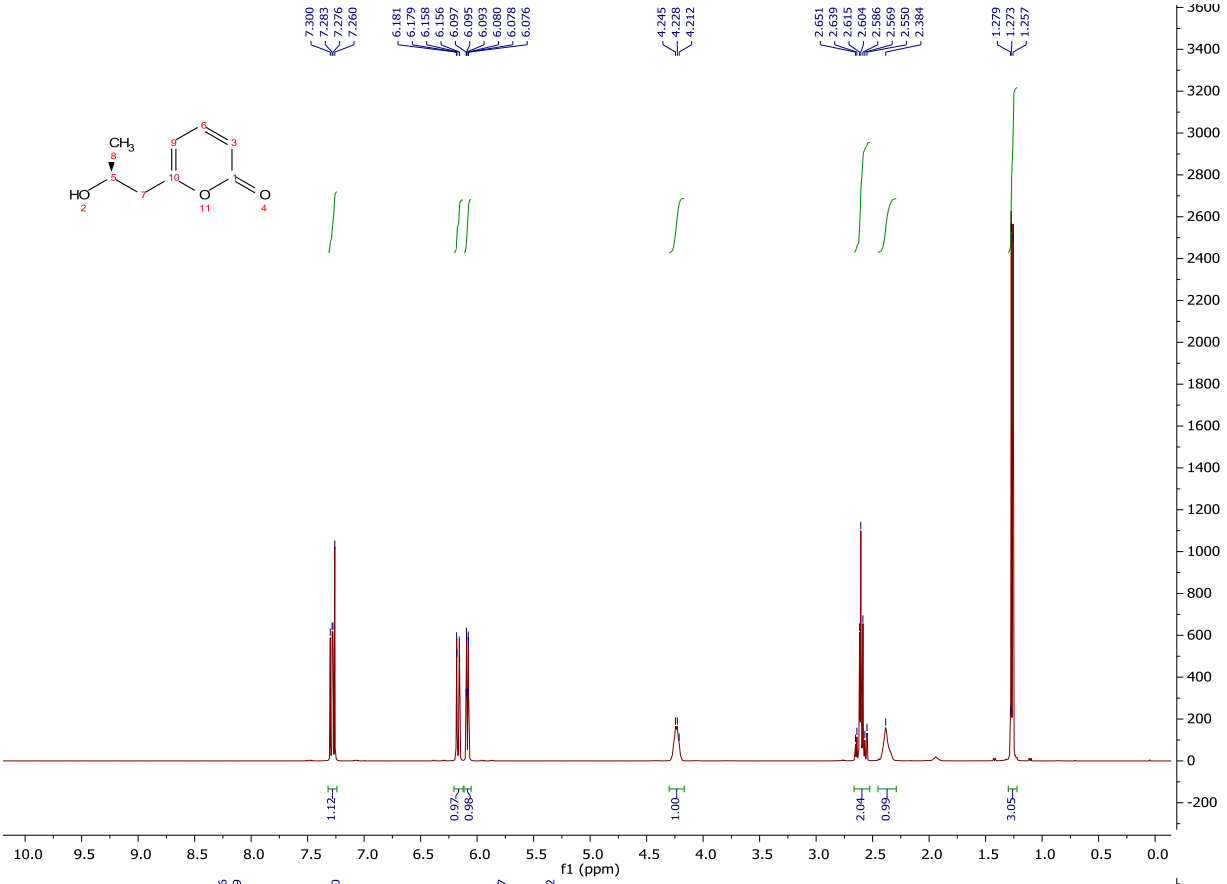
30.815
28.061
22.114
f1 (ppm)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6.179
6.158
6.156
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6.095
6.093
6.080
6.078
6.076
4.245
4.228
4.212
2.651
2.639
2.615
2.604
2.586
2.569
2.550
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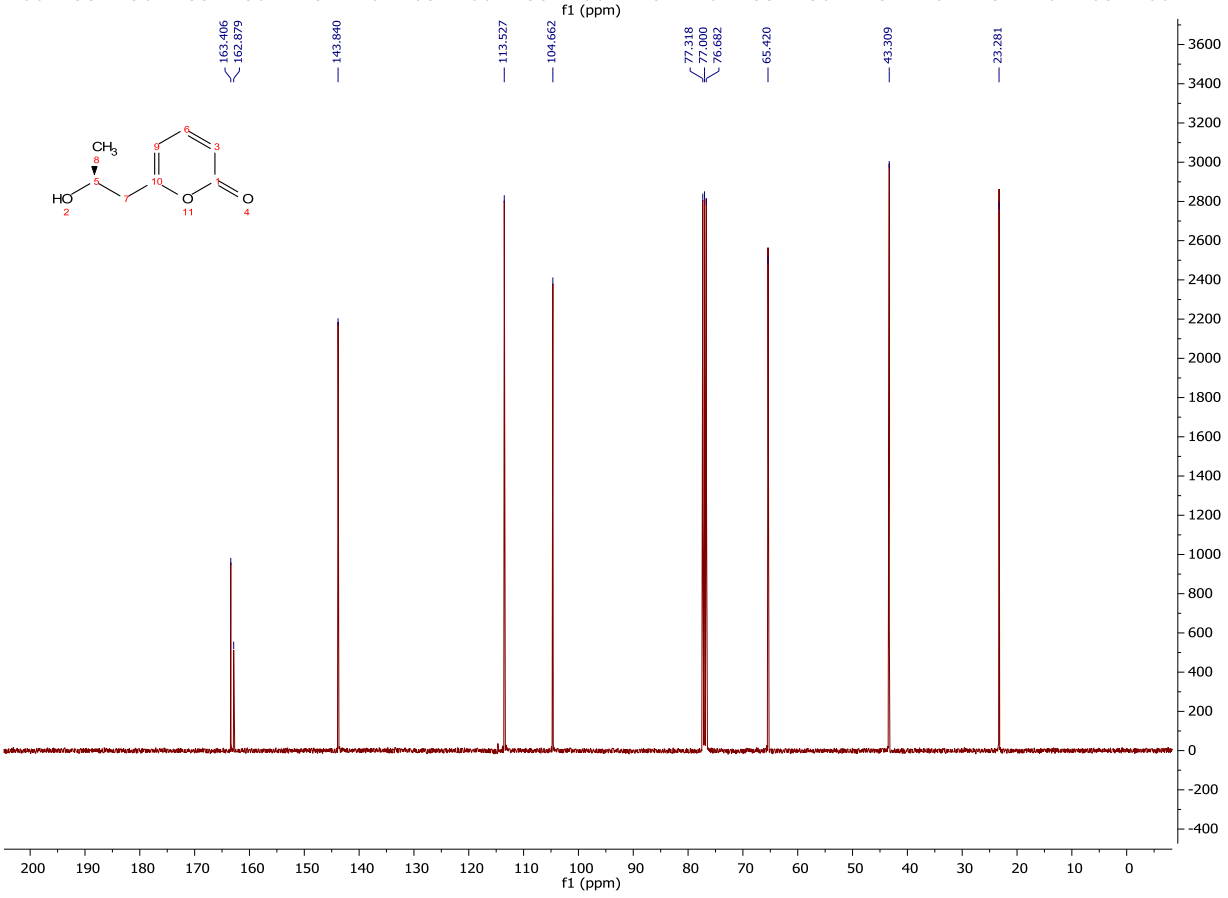
f1 (ppm)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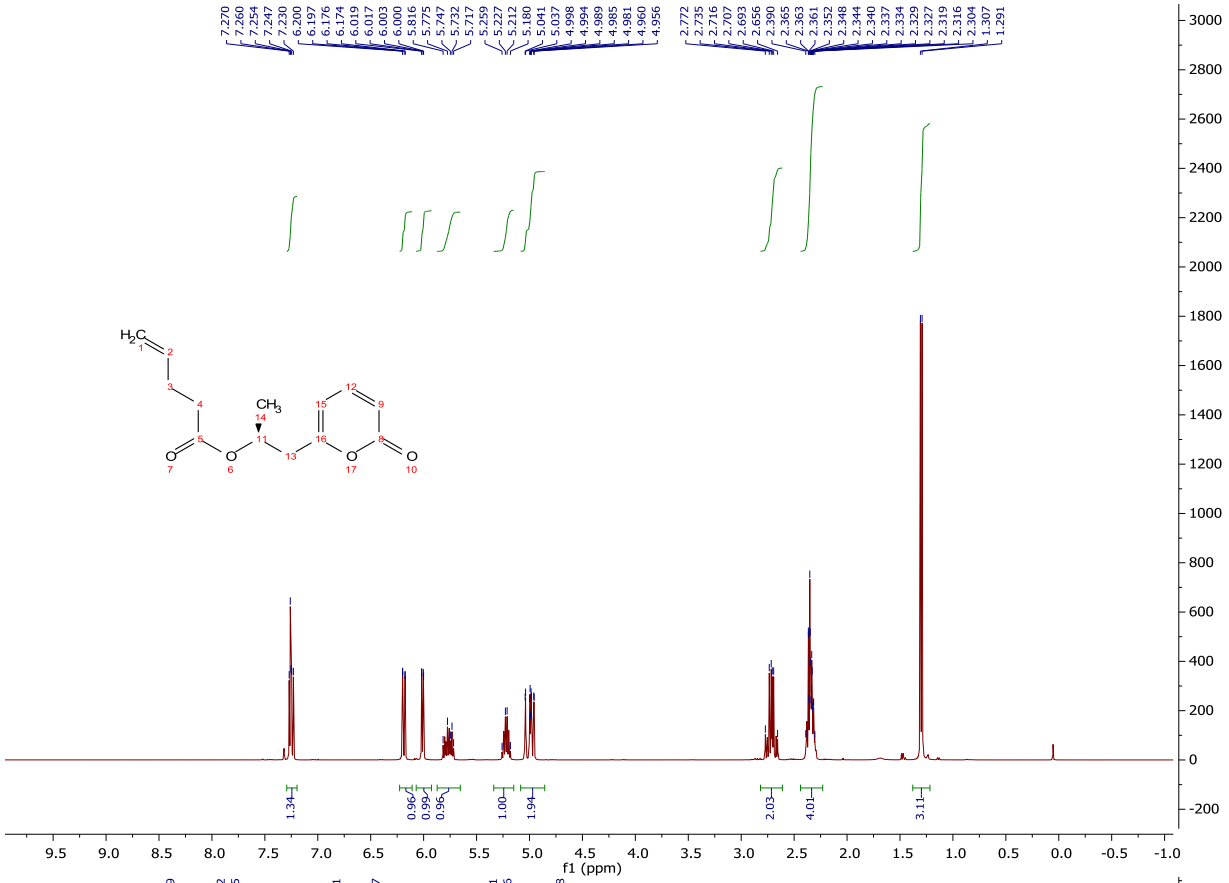
23.281
f1 (ppm)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6.000
5.816
5.775
5.747
5.732
5.717
5.259
5.227
5.212
5.180
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5.037
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4.994
4.989
4.985
4.981
4.960
4.956
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2.707
2.693
2.656
2.390
2.365
2.363
2.361
2.352
2.348
2.344
2.340
2.337
2.334
2.329
2.327
2.319
2.316
2.304
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0.96
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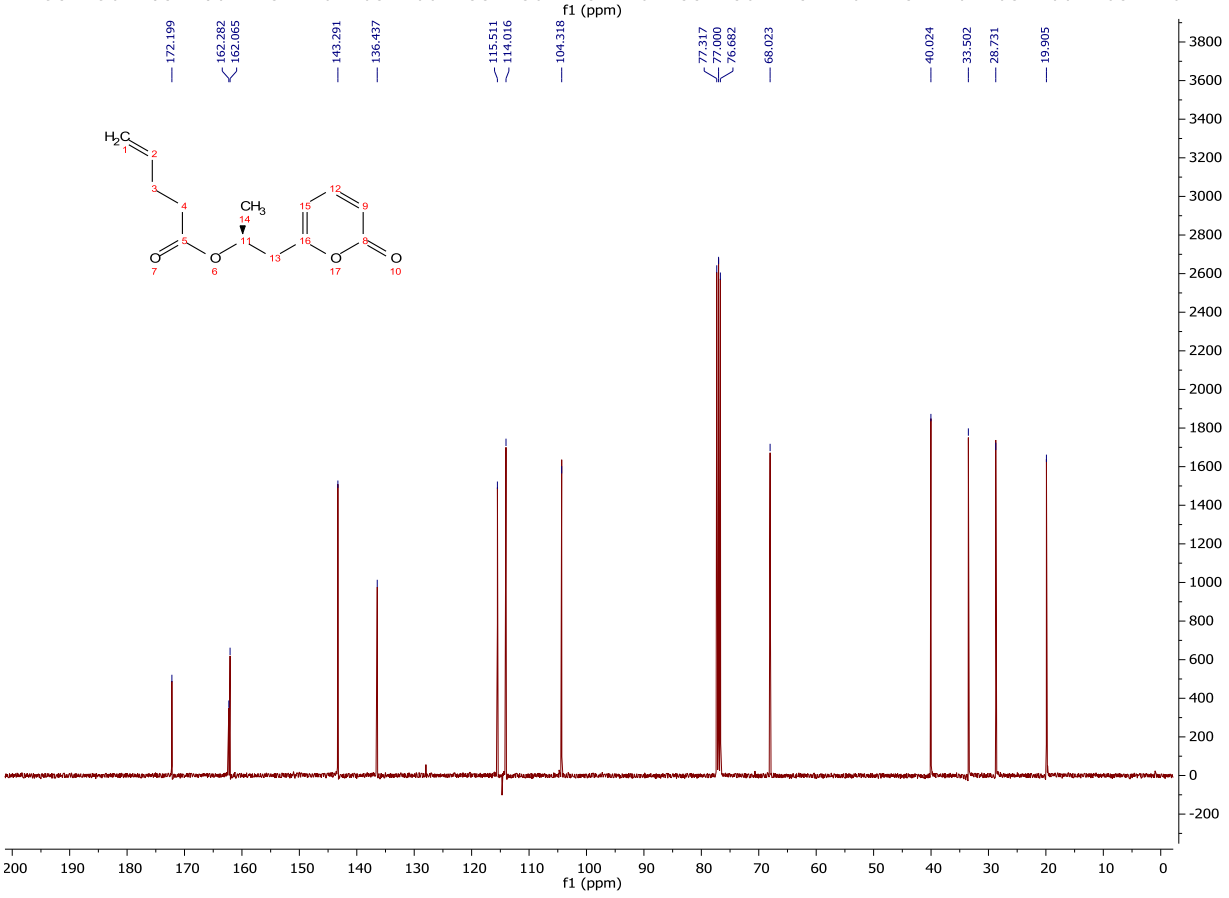
4.01
3.11
f1 (ppm)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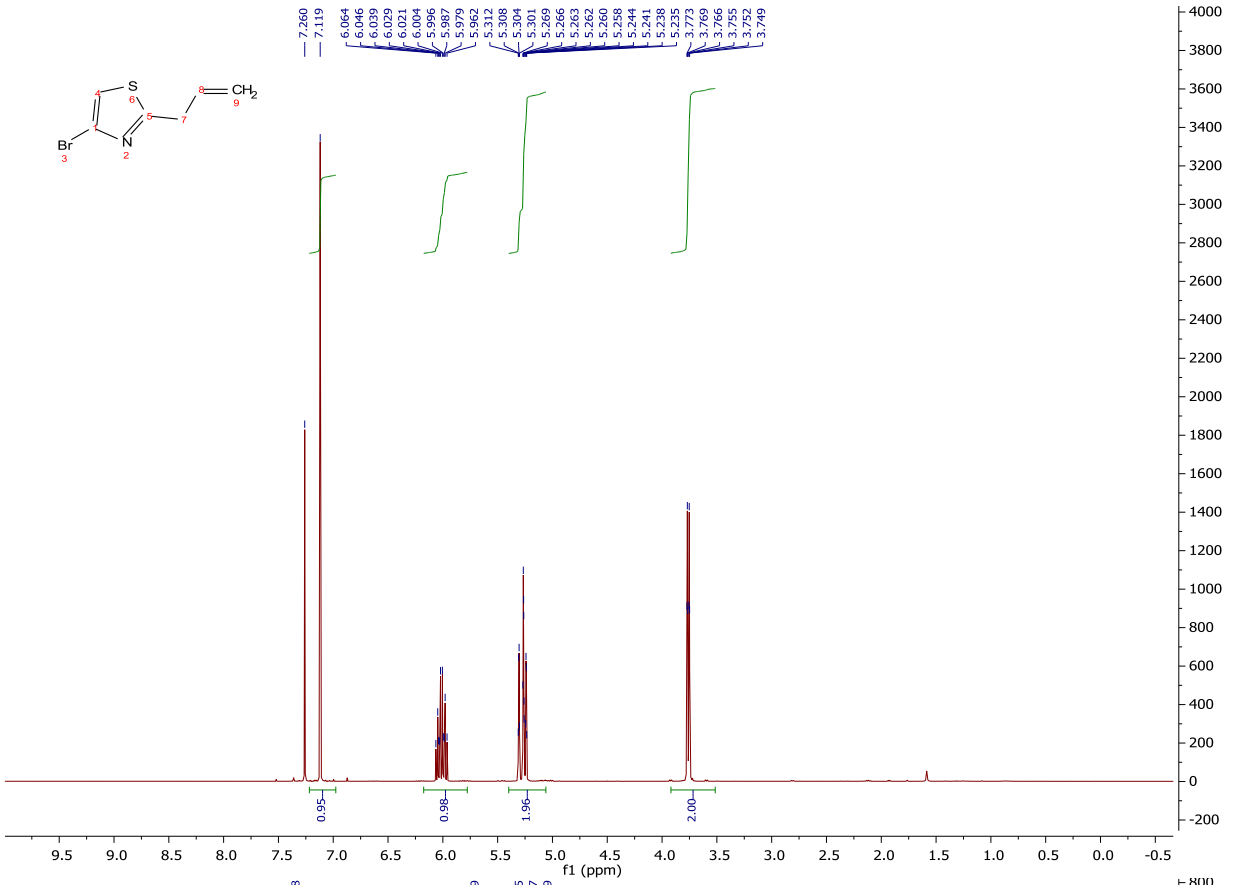
19.905
f1 (ppm)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5.308
5.304
5.301
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5.262
5.260
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5.244
5.241
5.238
5.235
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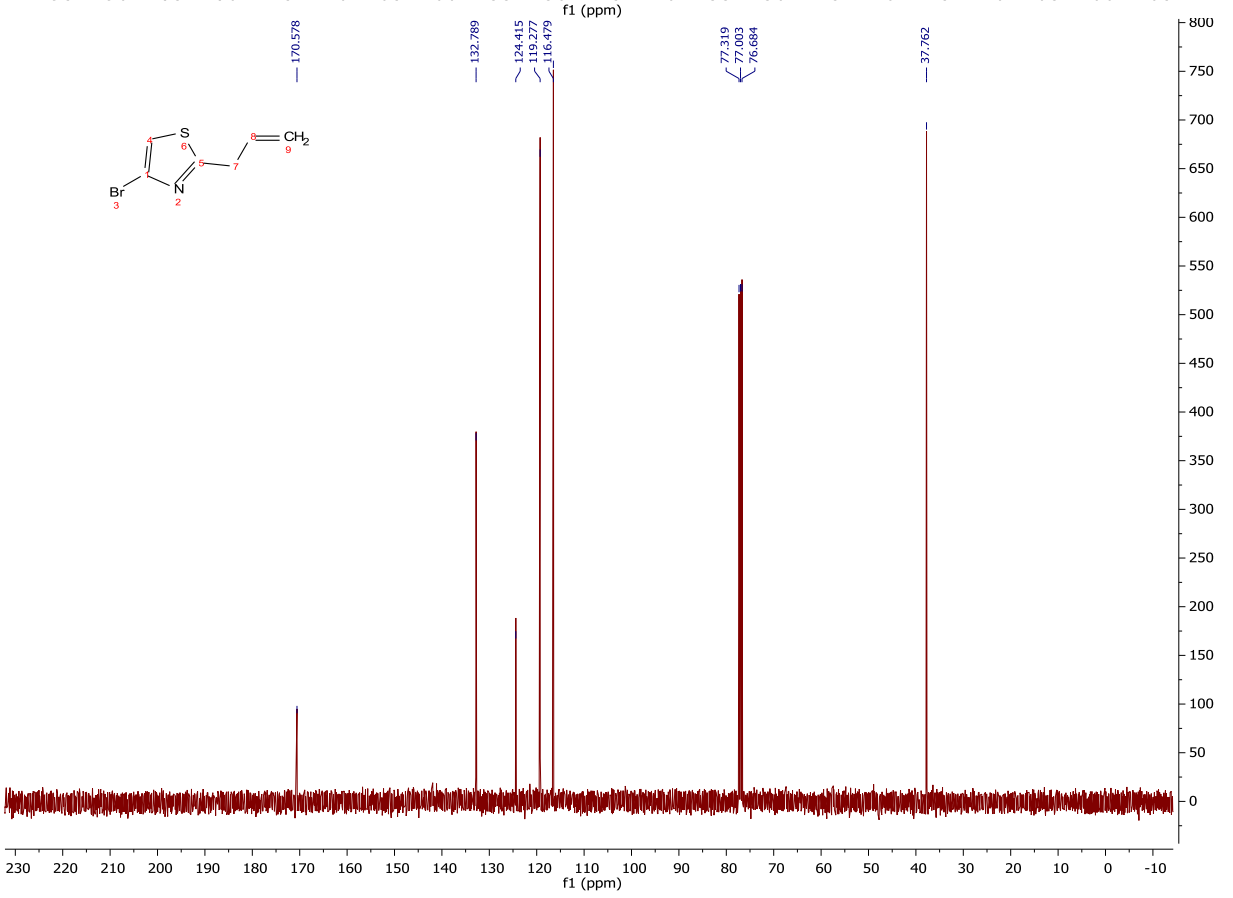
2.00
f1 (ppm)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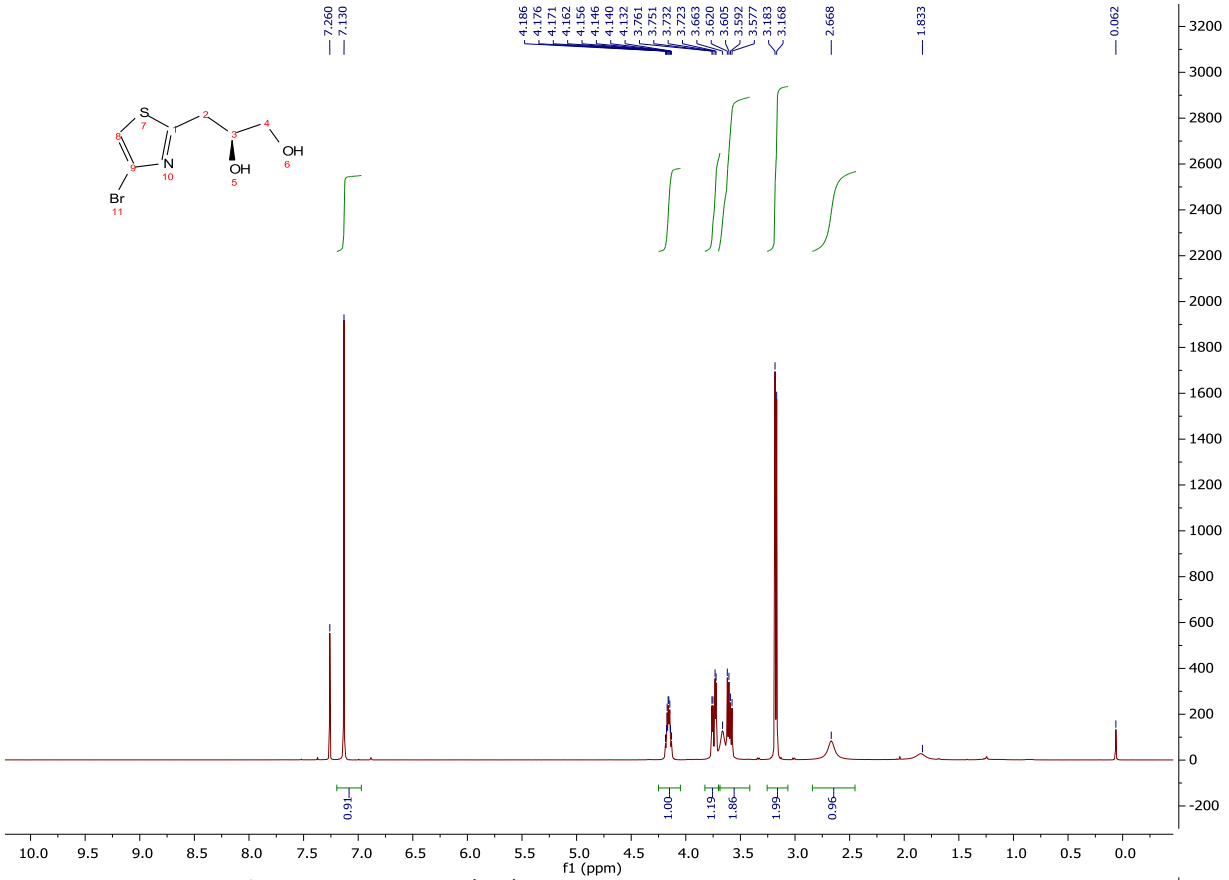
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3.663
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3.605
3.592
3.577
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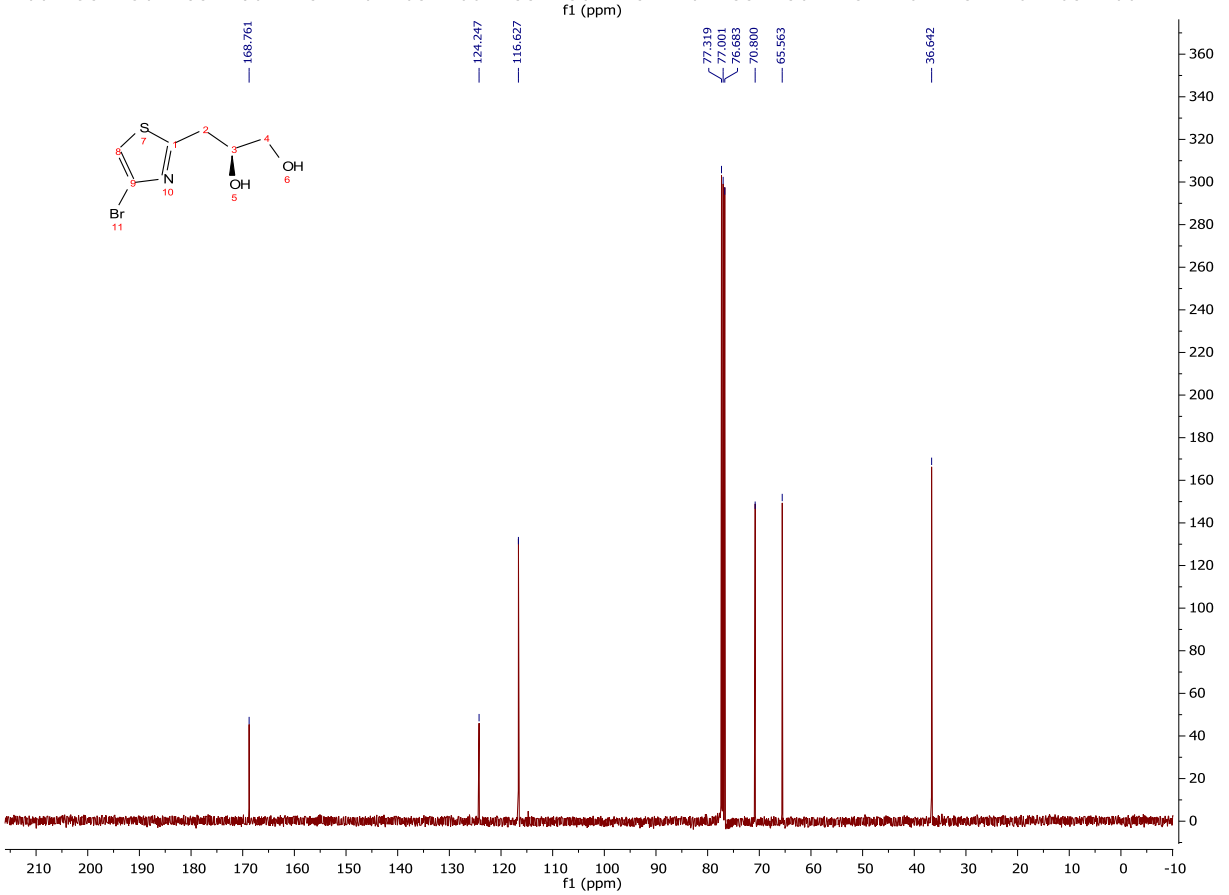
f1 (ppm)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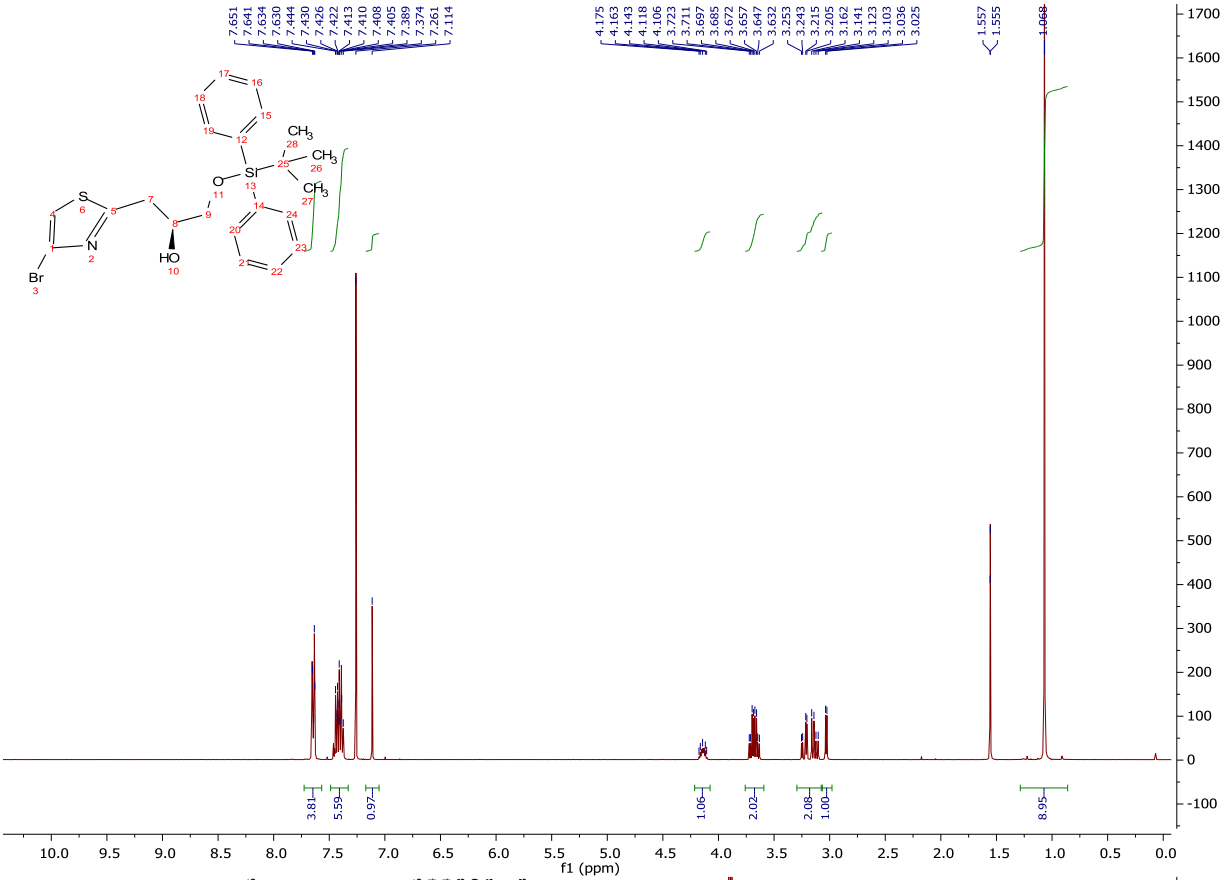
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7.261
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3.723
3.711
3.697
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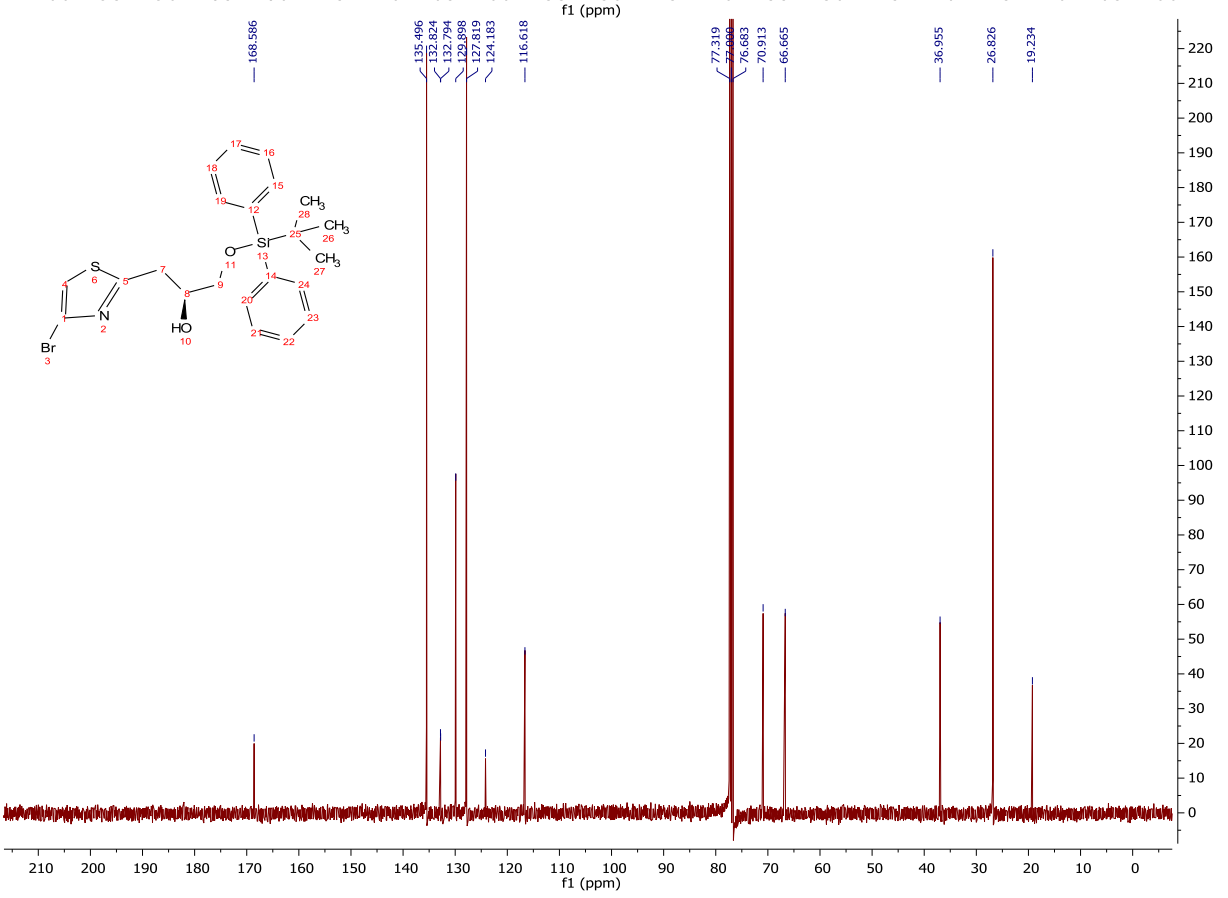
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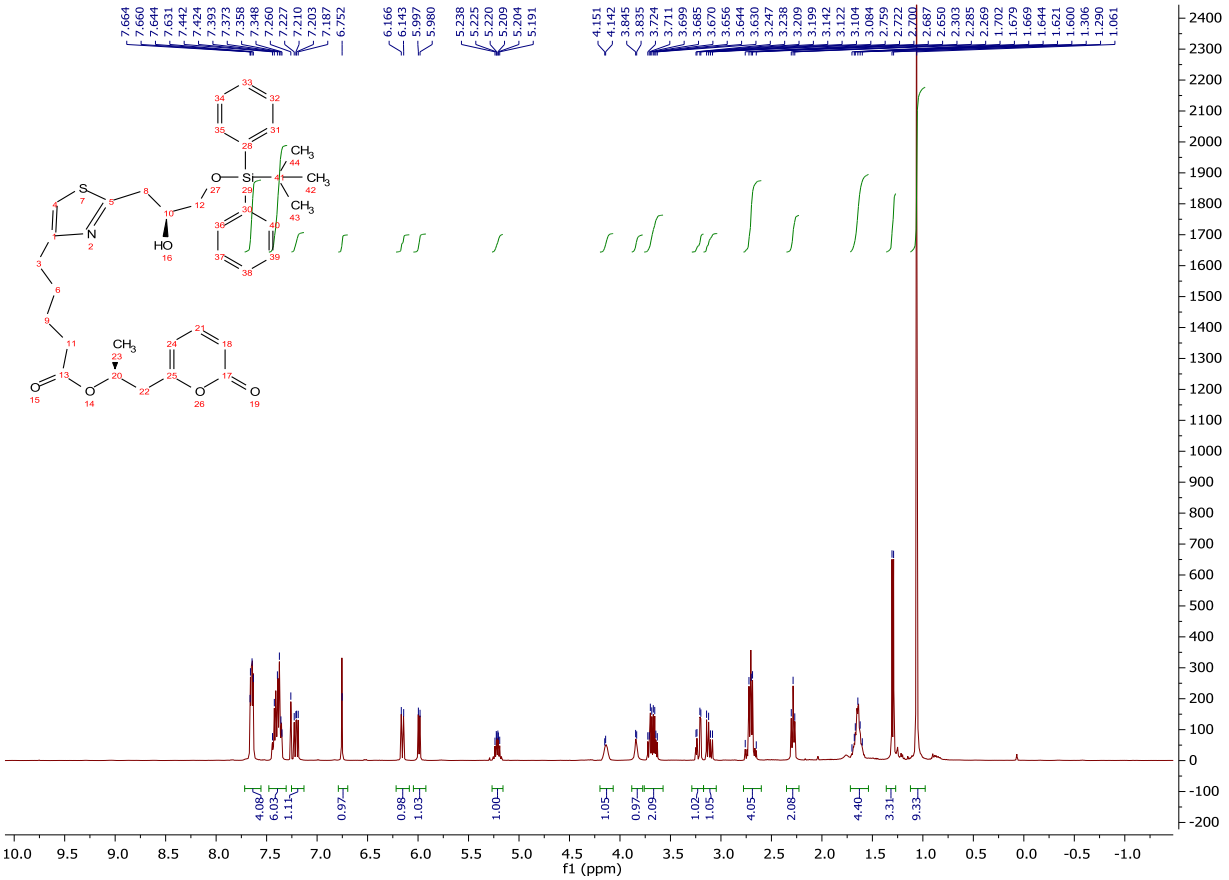
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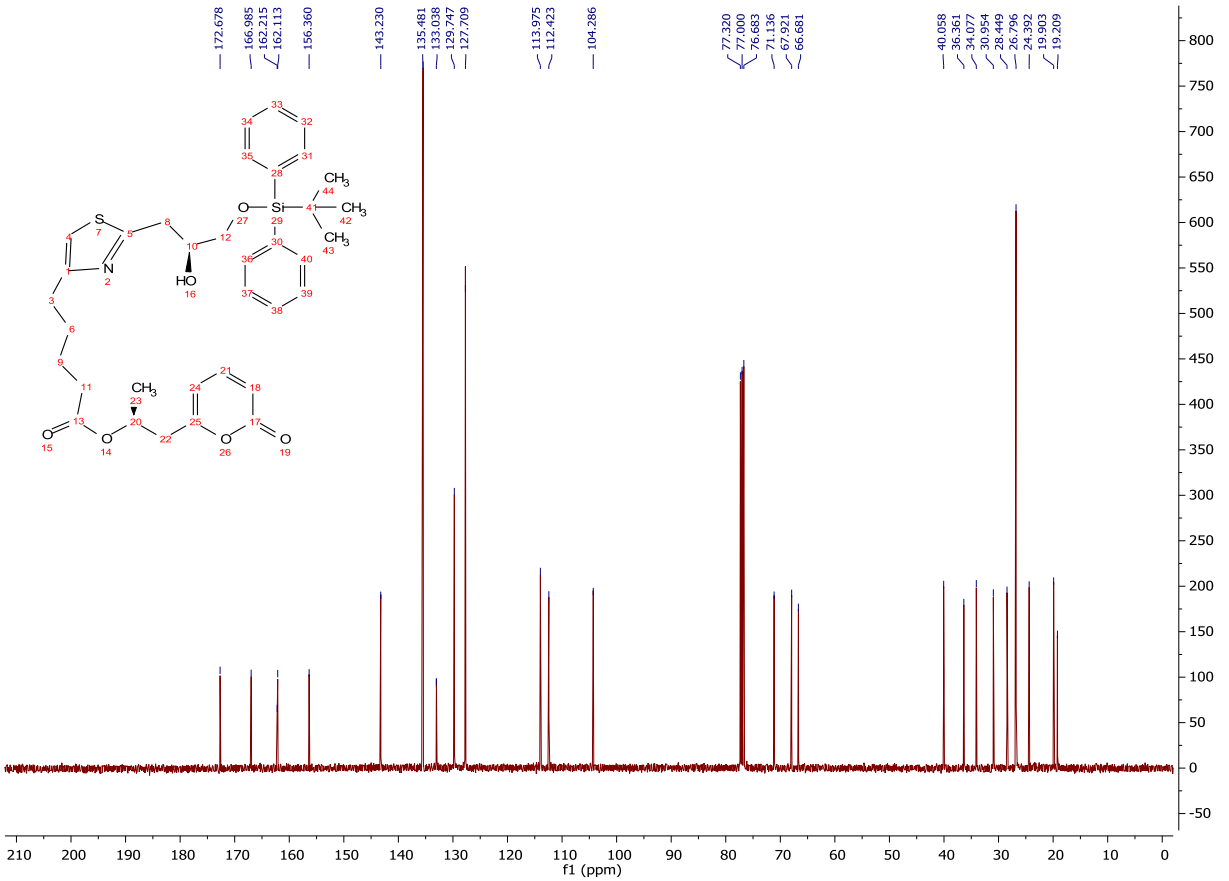
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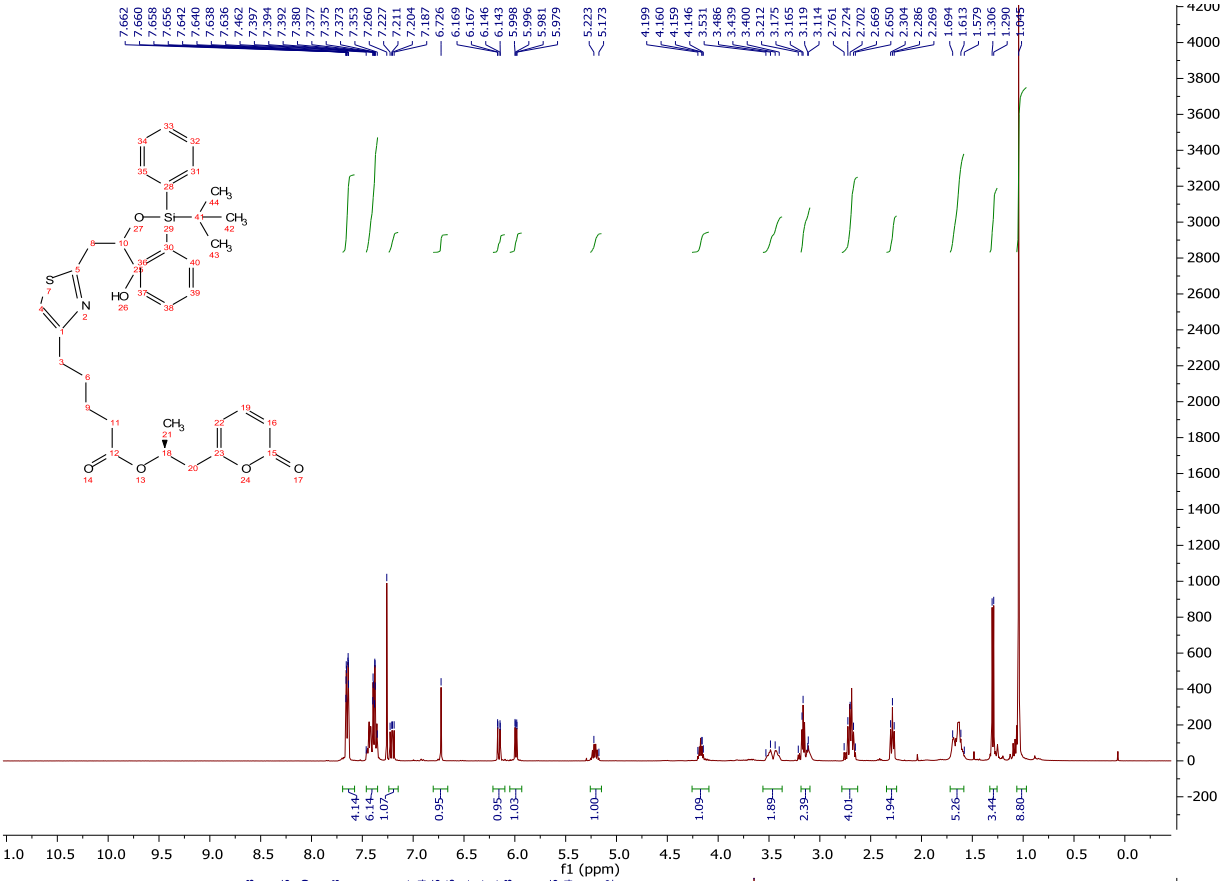
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7.187
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6.143
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5.173
4.199
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6.14
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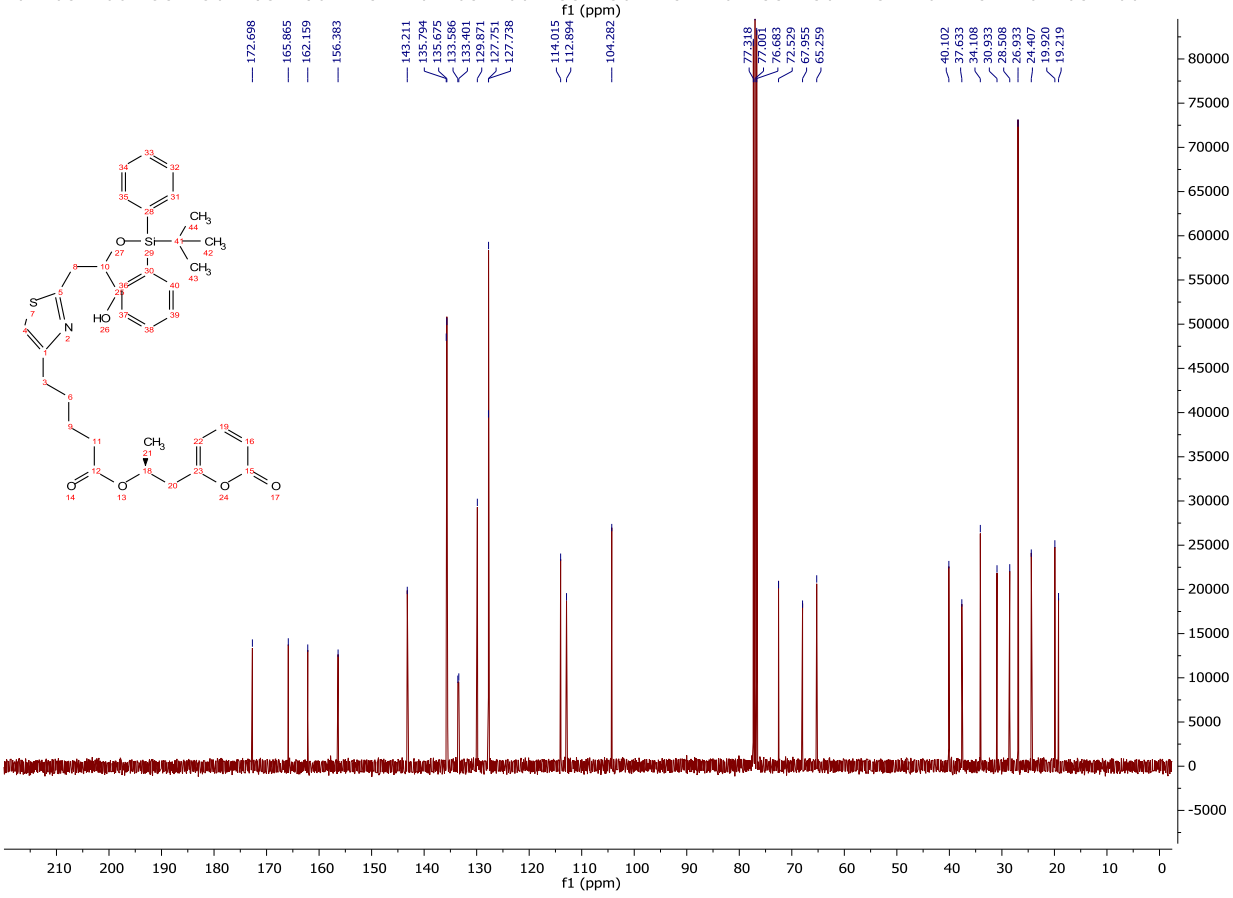
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112.894
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77.318
77.001
76.683
72.529
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65.259
40.102
37.633
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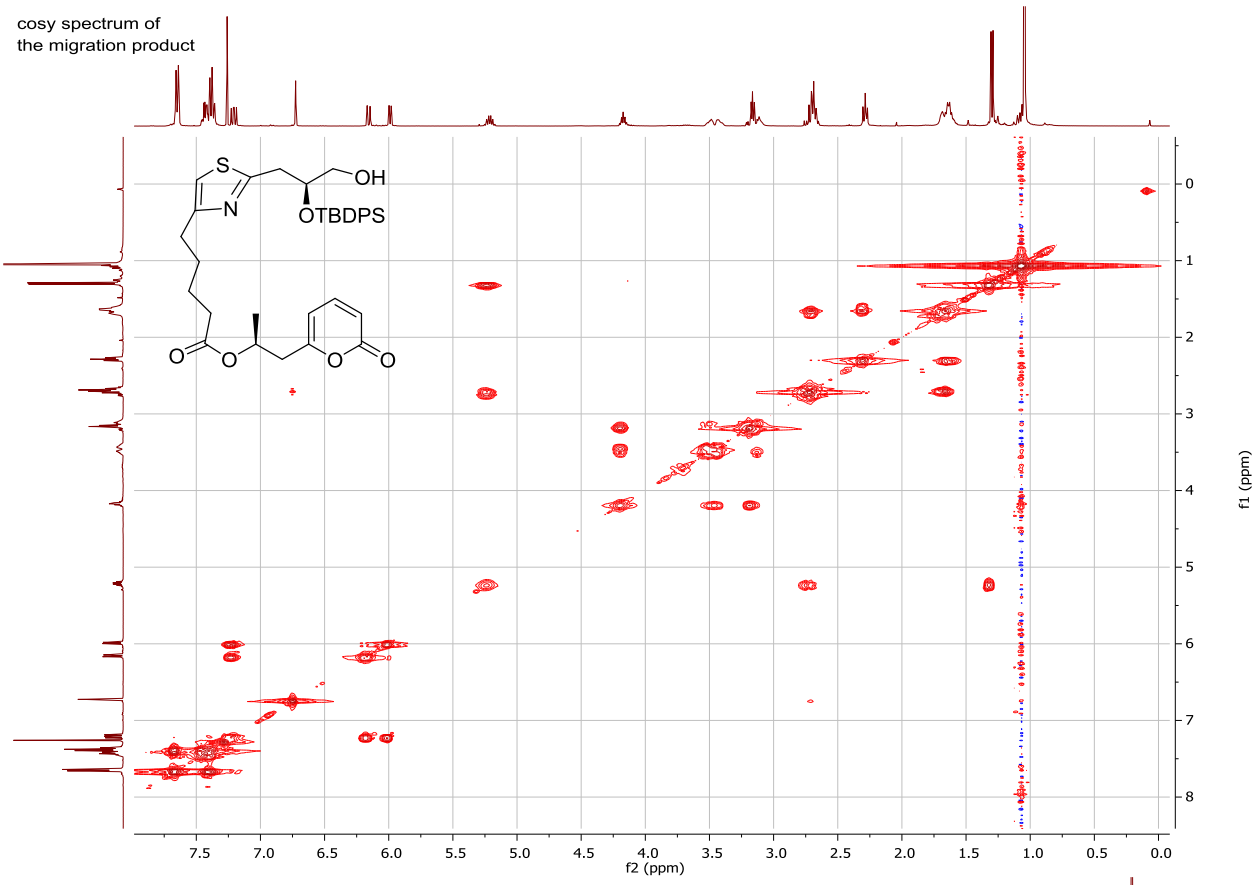
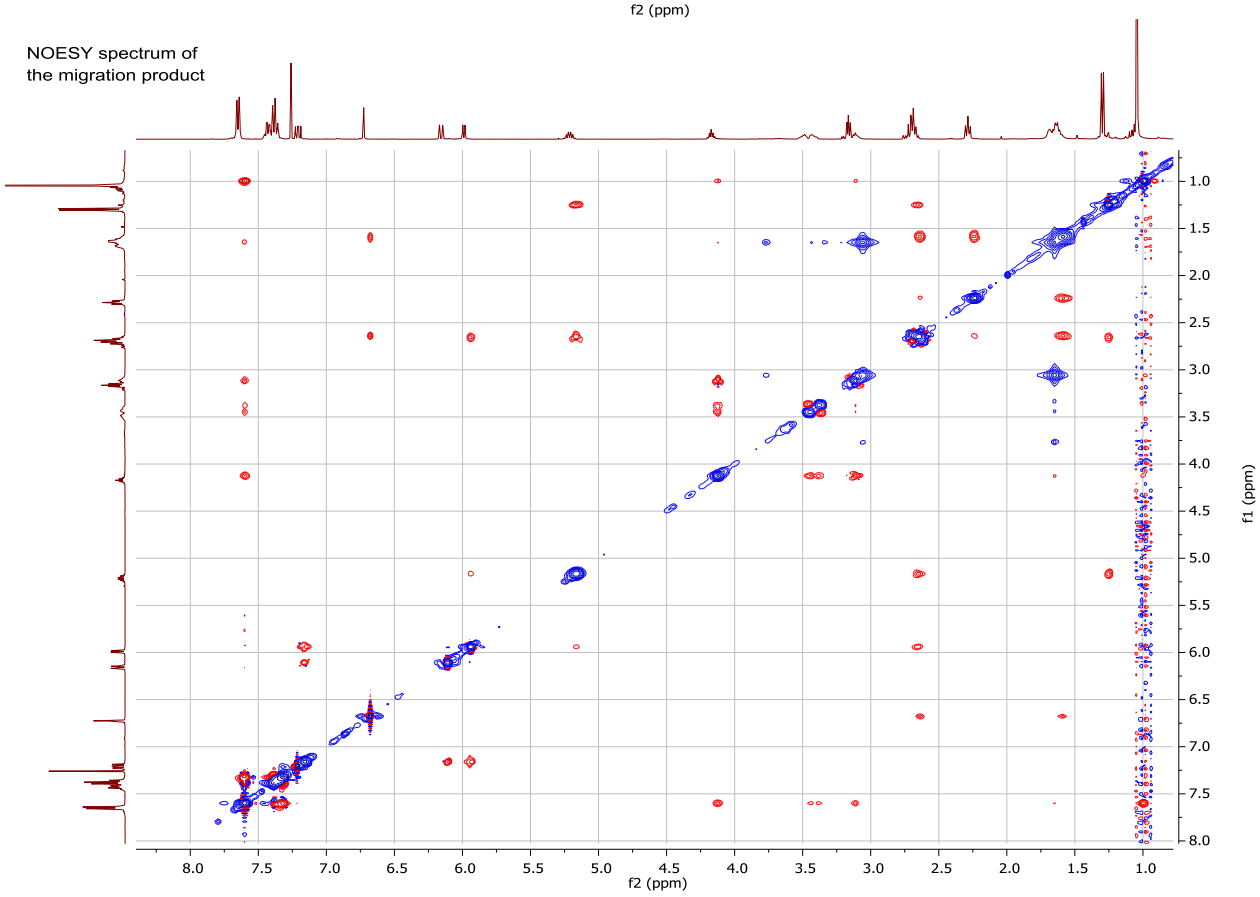
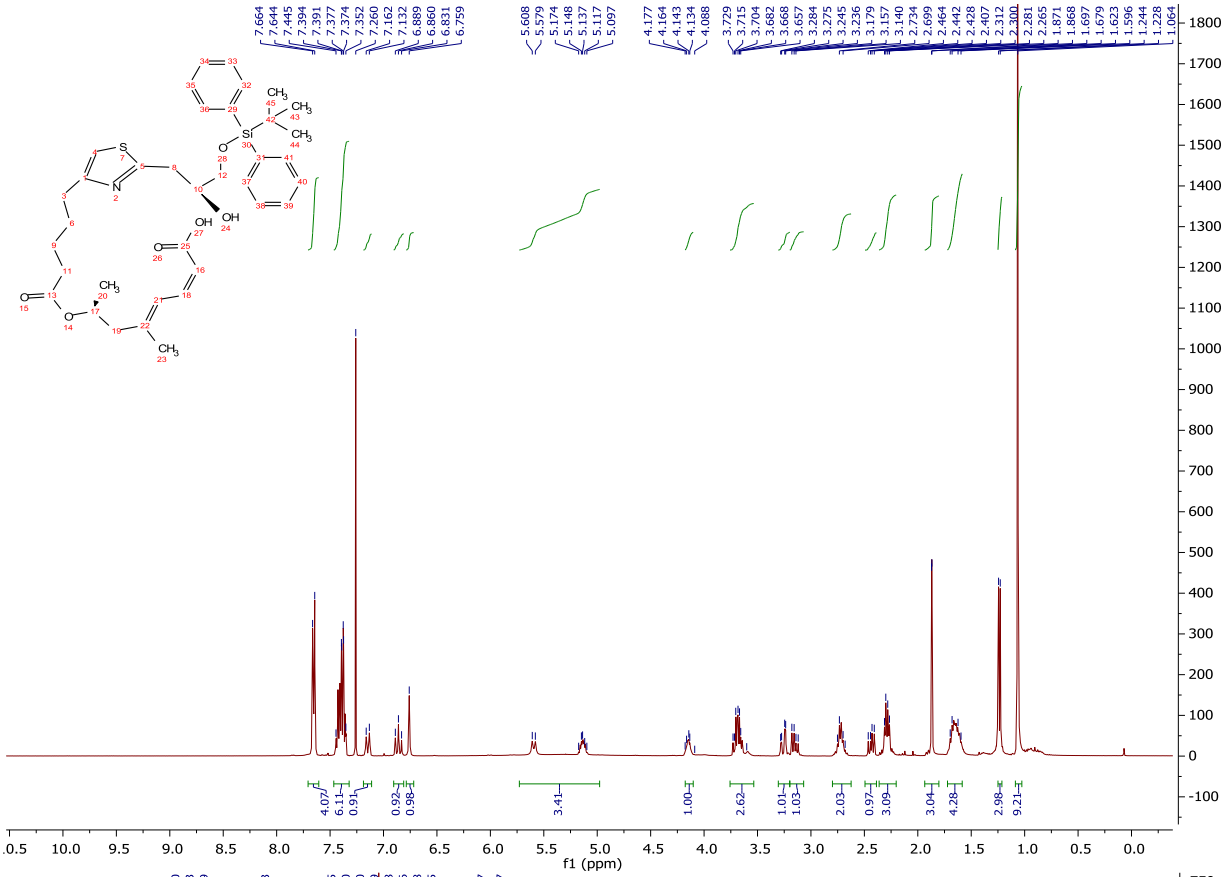
30.933
28.508
26.933
24.407
19.920
19.219
f1 (ppm)

cosy spectrum of
the migration product



NOESY spectrum of
the migration product

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6.860
6.831
6.759
5.608
5.579
5.174
5.148
5.137
5.117
5.097
4.177
4.164
4.143
4.134
4.088
3.729
3.715
3.704
3.682
3.668
3.657
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3.245
3.236
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1.244
1.228
1.064
4.07
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0.92
0.98
3.41
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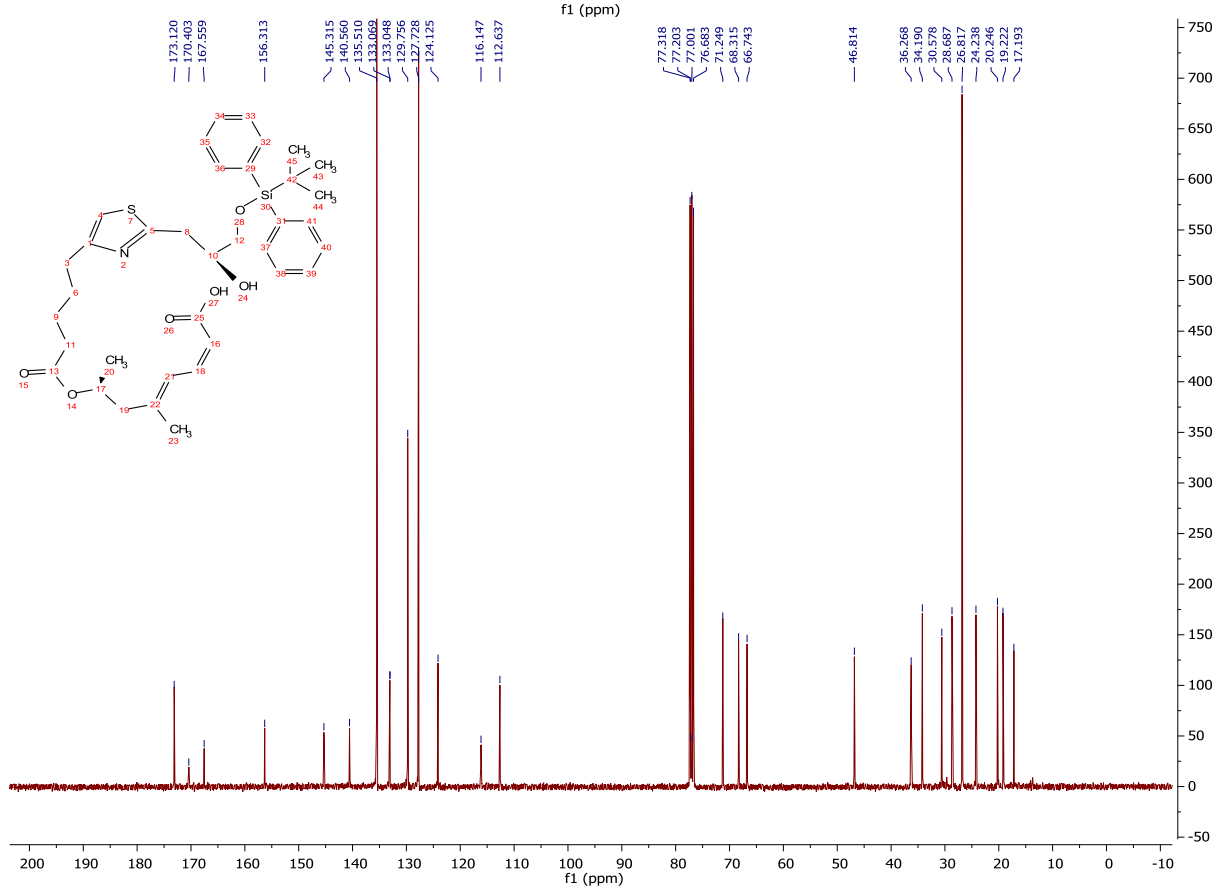
f1 (ppm)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77.318
77.203
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71.249
68.315
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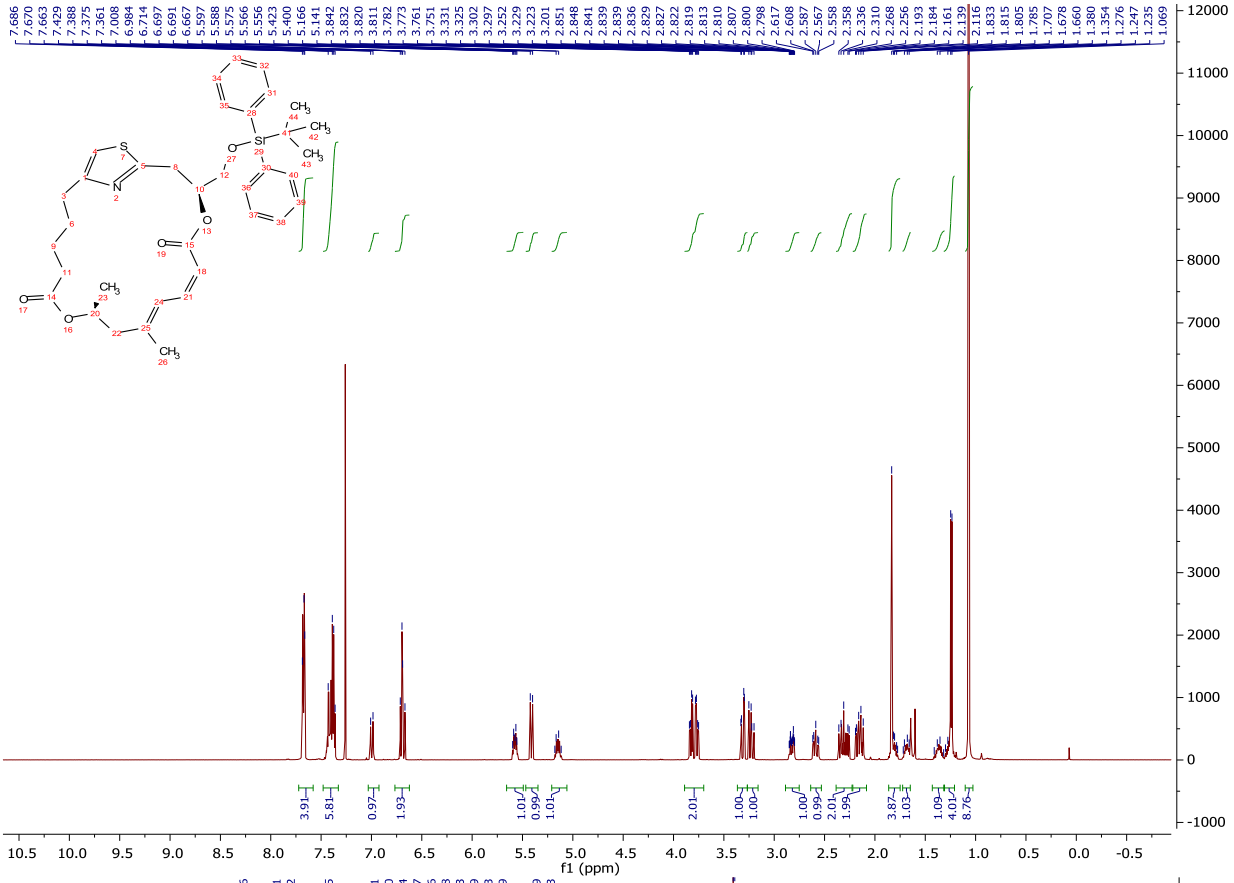
20.246
19.222
17.193
f1 (ppm)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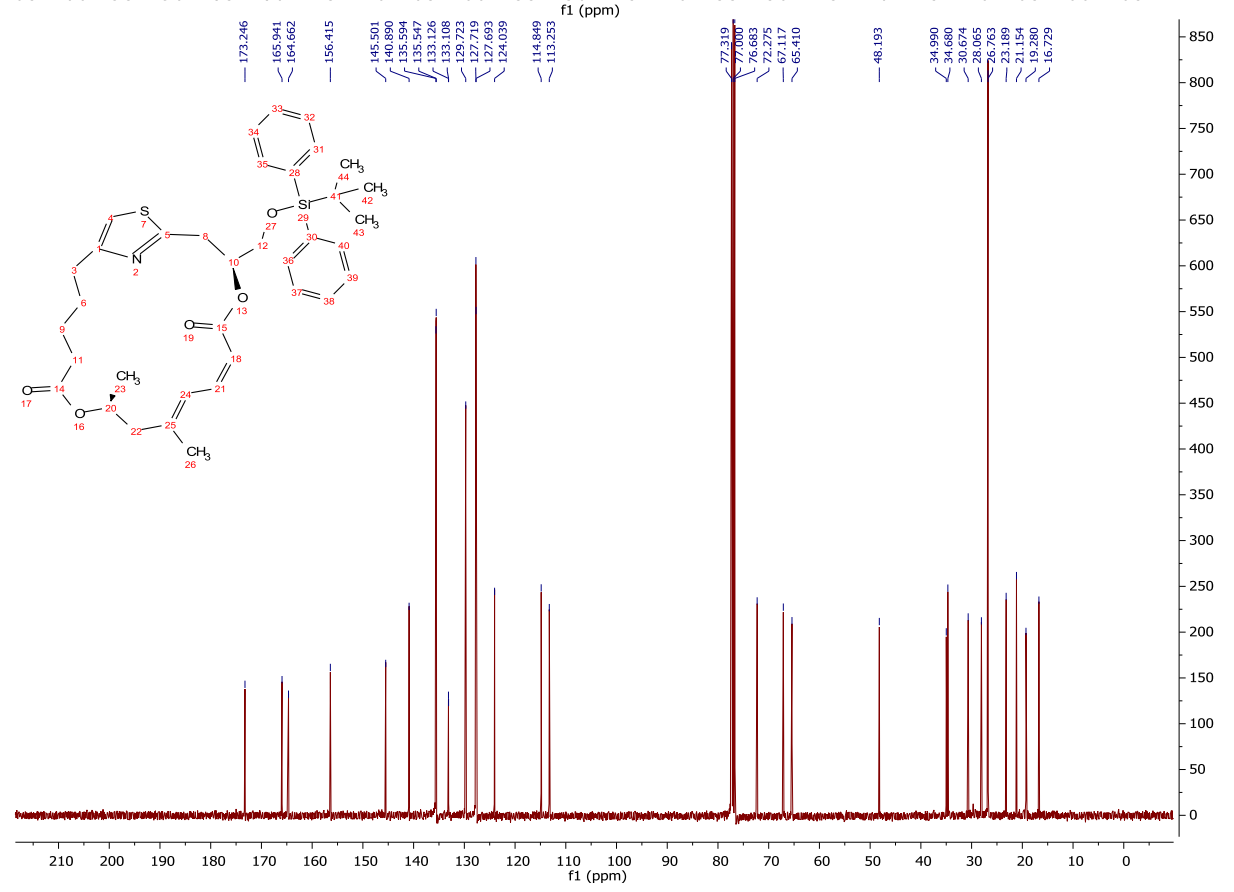
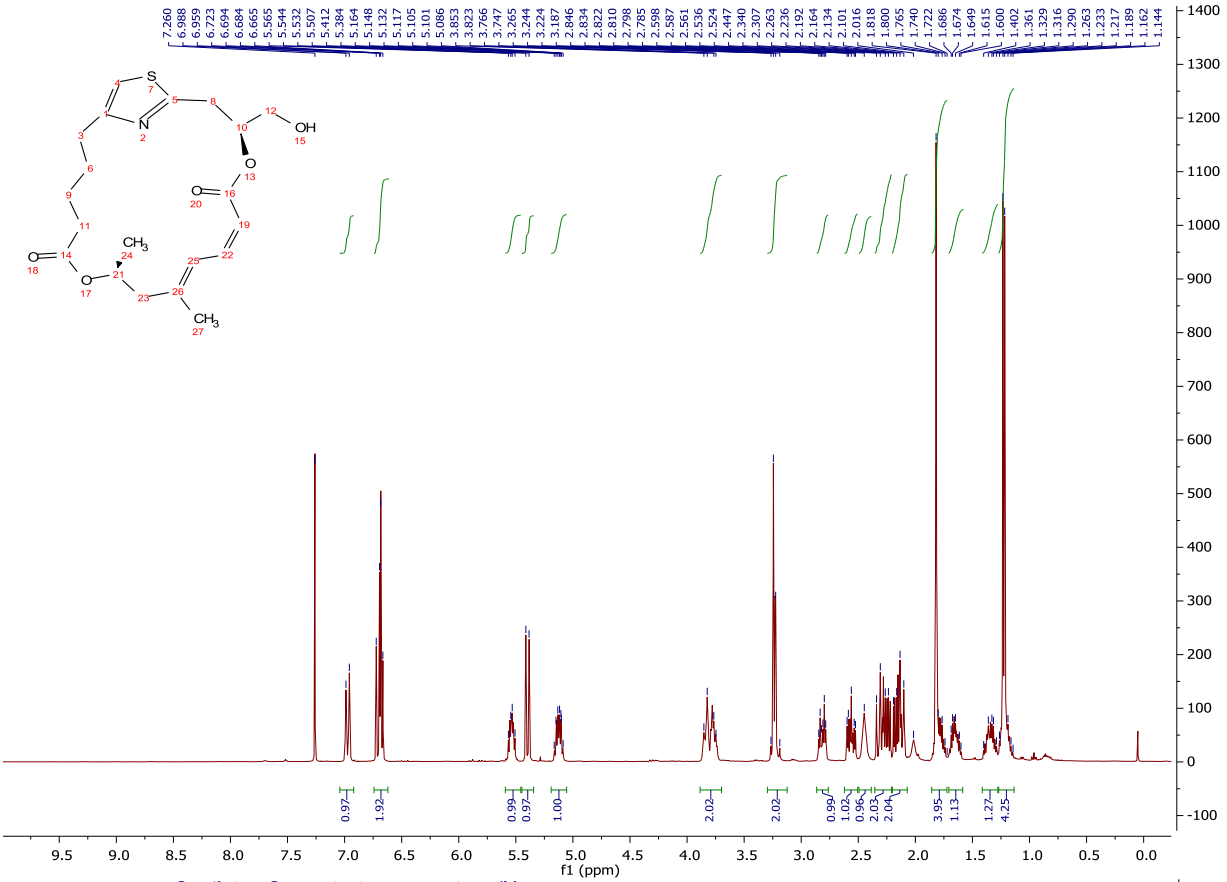
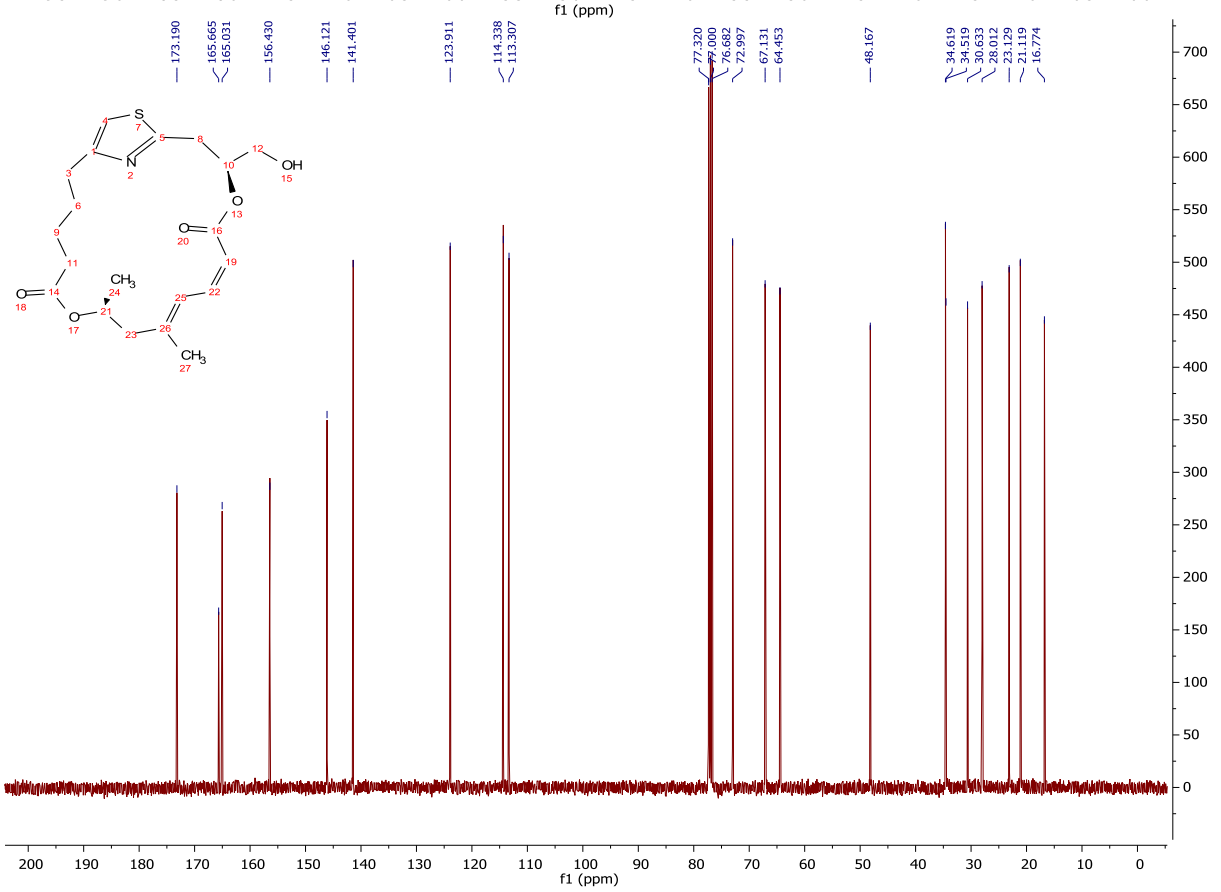
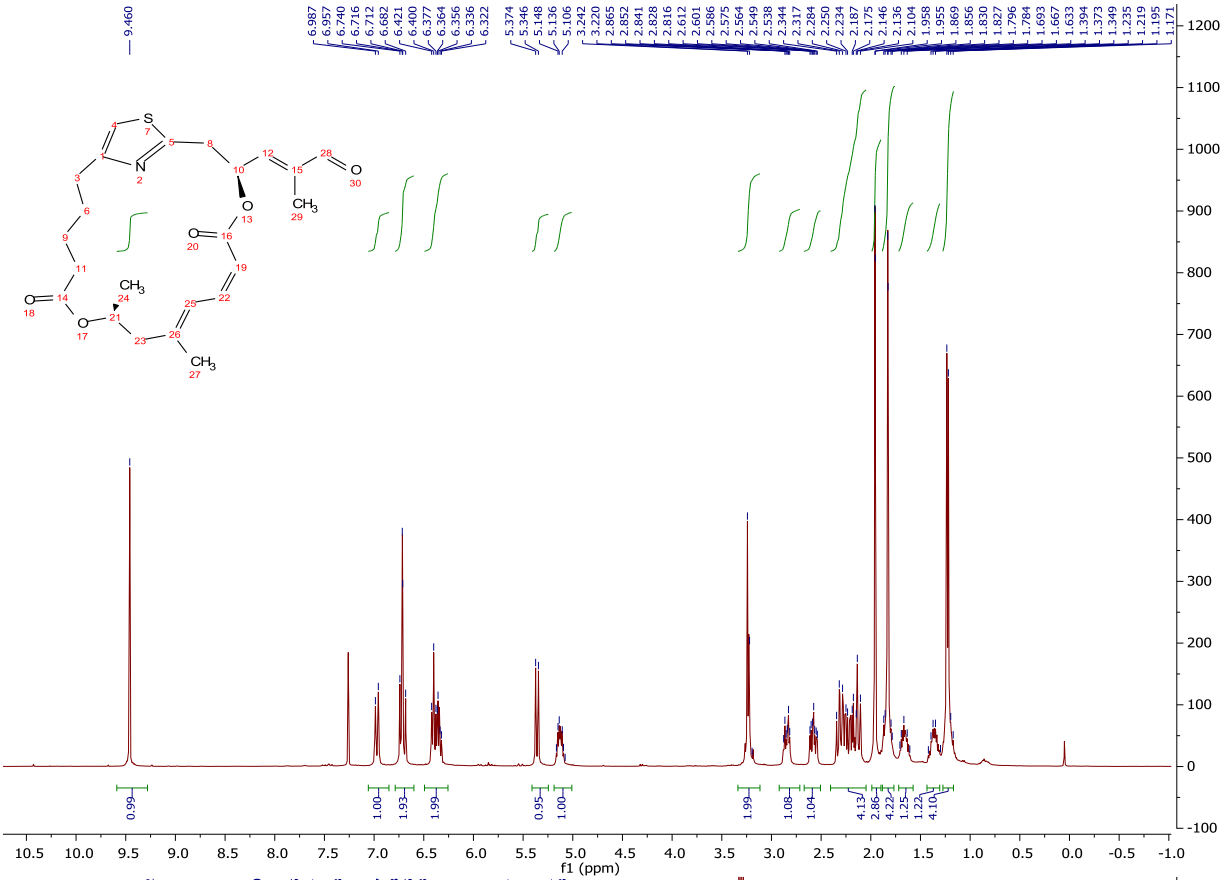
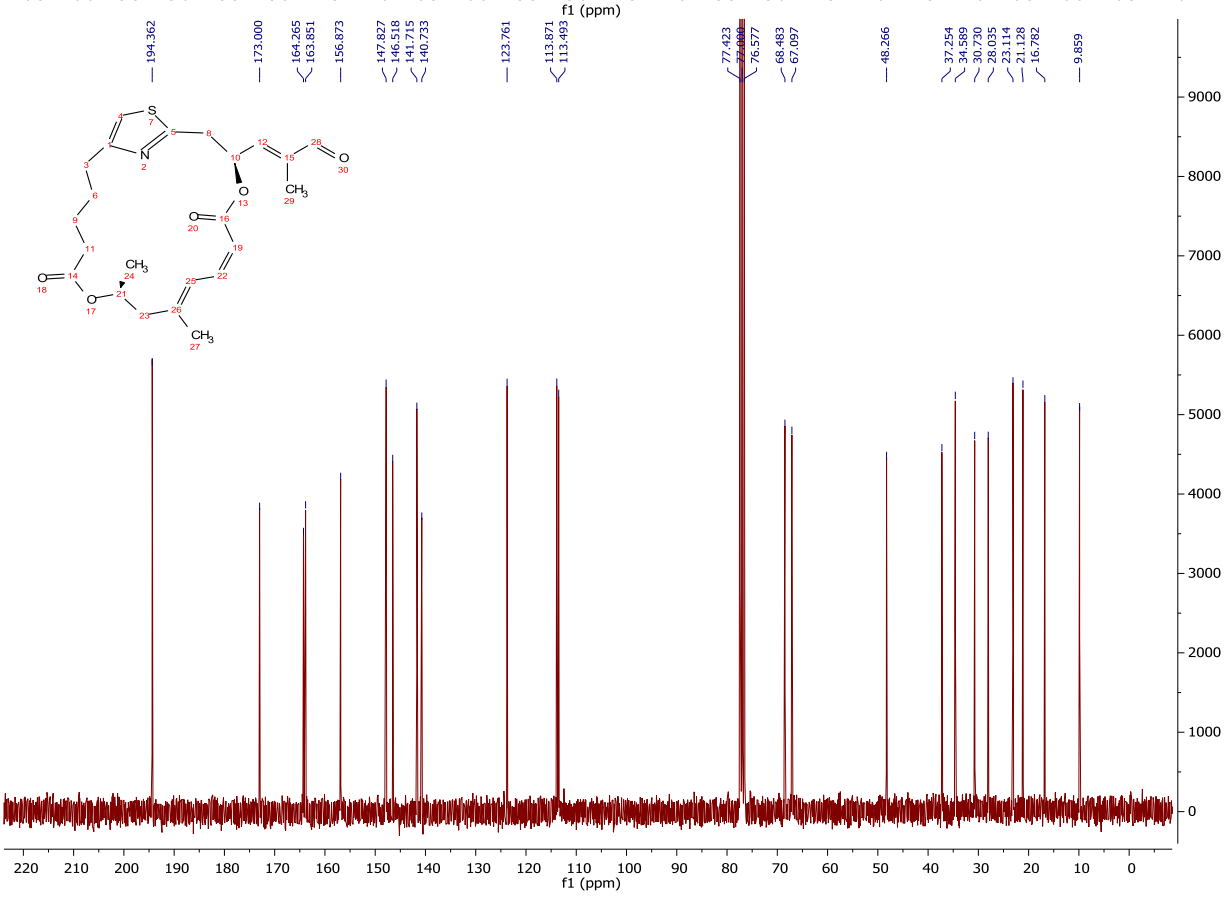
3.91 5.81 0.97 1.93 1.01 0.99 1.01 2.01 1.00 1.00 1.00 0.99 2.01 1.99 3.87 1.03 1.09 4.01 8.76
f1 (ppm)

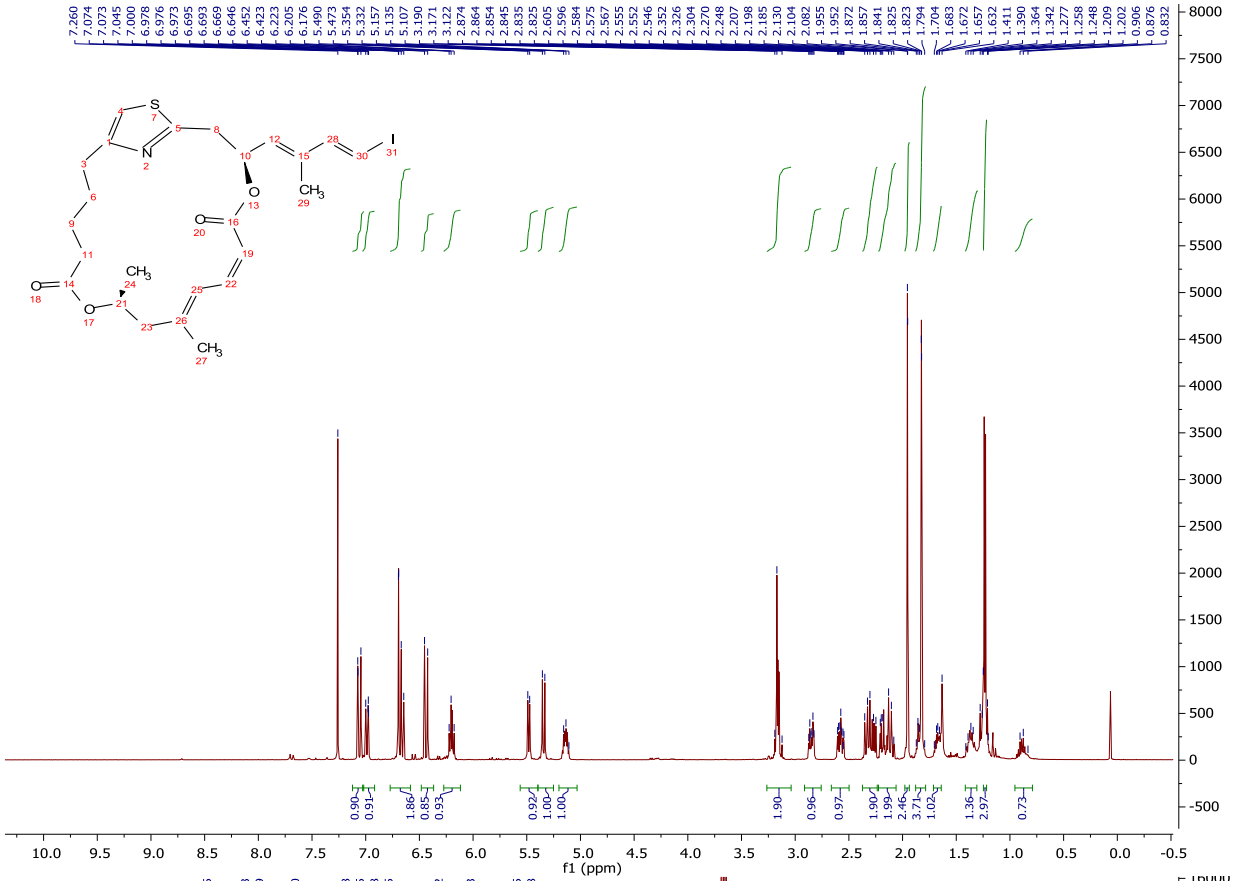

173.246 165.941 164.662 156.415 145.501 140.890 135.594 135.547 133.126 133.108 129.723 127.719 127.693 124.039 114.849 113.253 77.319 77.000 76.683 72.275 67.117 65.410 48.193 34.990 34.680 30.674 28.065 26.763 23.189 21.154 19.280 16.729
f1 (ppm)

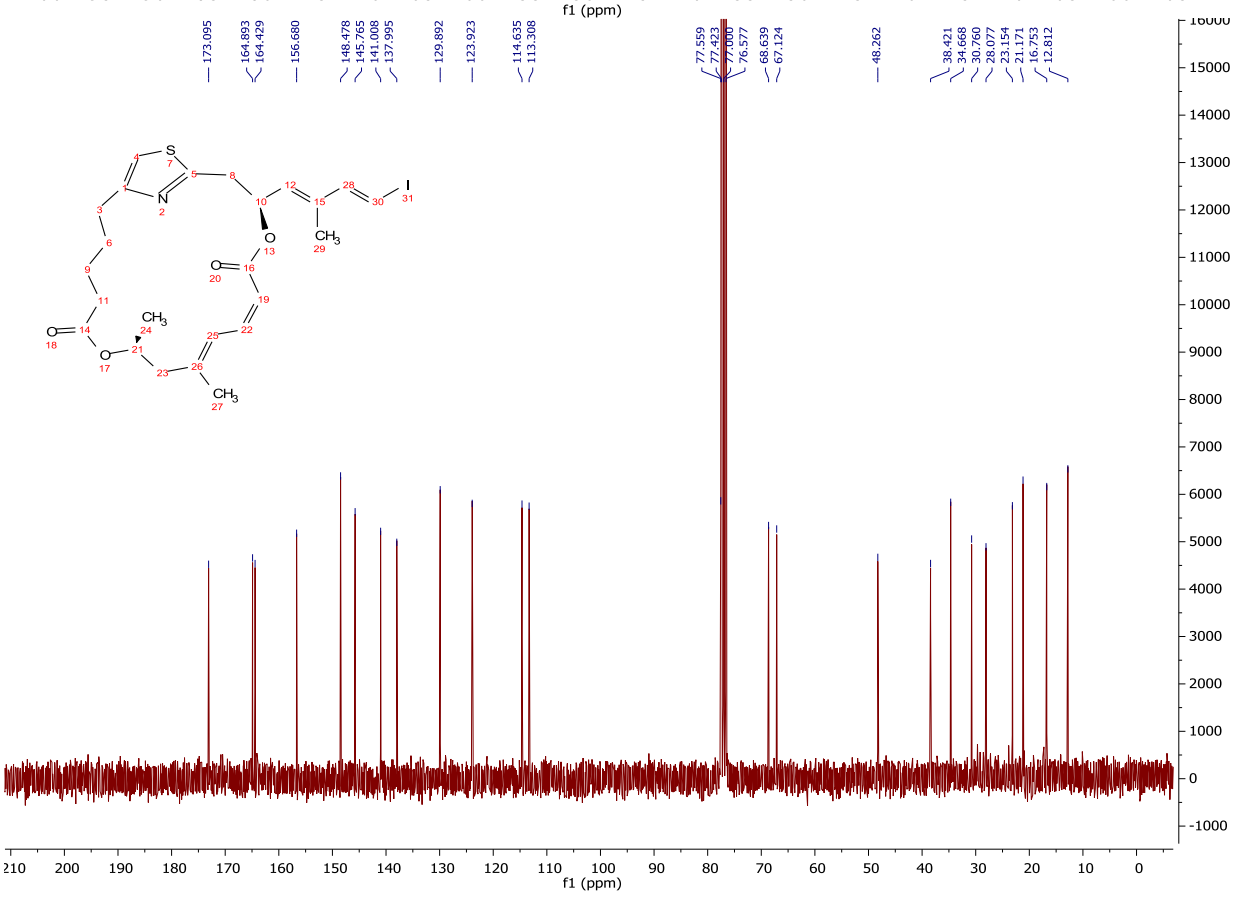

7.260 6.988 6.959 6.723 6.694 6.684 6.665 5.565 5.544 5.532 5.507 5.412 5.384 5.164 5.148 5.132 5.117 5.105 5.101 5.086 3.853 3.823 3.766 3.747 3.265 3.244 3.224 3.187 2.846 2.834 2.822 2.810 2.798 2.785 2.598 2.587 2.561 2.536 2.524 2.447 2.340 2.307 2.263 2.236 2.192 2.164 2.134 2.101 2.016 1.818 1.800 1.765 1.740 1.722 1.686 1.674 1.649 1.615 1.600 1.402 1.361 1.329 1.316 1.290 1.263 1.233 1.217 1.189 1.162 1.144
0.97 1.92 0.99 0.97 1.00 2.02 2.02 0.99 1.02 0.96 2.03 2.04 3.95 1.13 1.27 4.25
f1 (ppm)

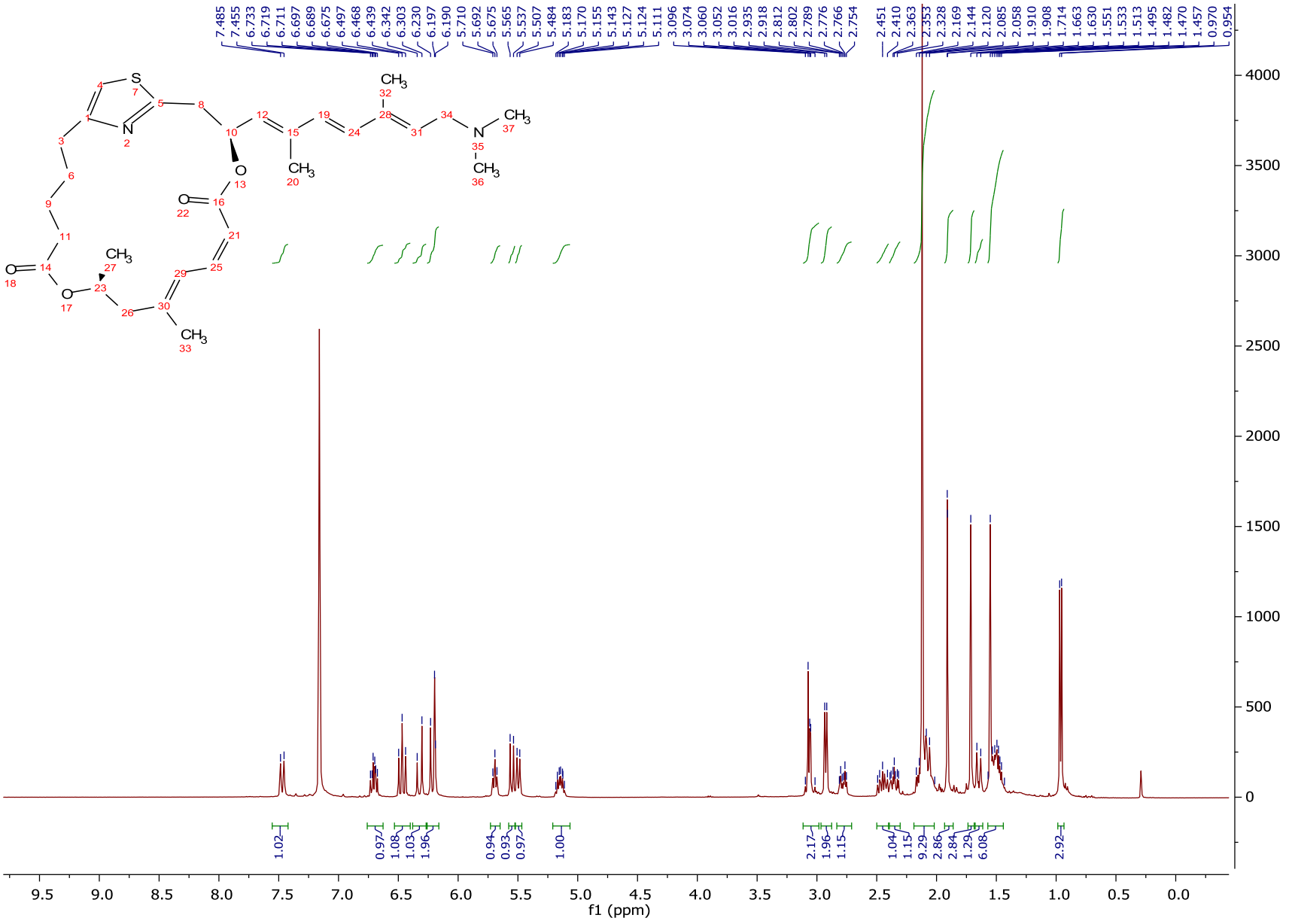

173.190 165.665 165.031 156.430 146.121 141.401 123.911 114.338 113.307 77.320 77.000 76.682 72.997 67.131 64.453 48.167 34.619 34.519 30.633 28.012 23.129 21.119 16.774
f1 (ppm)

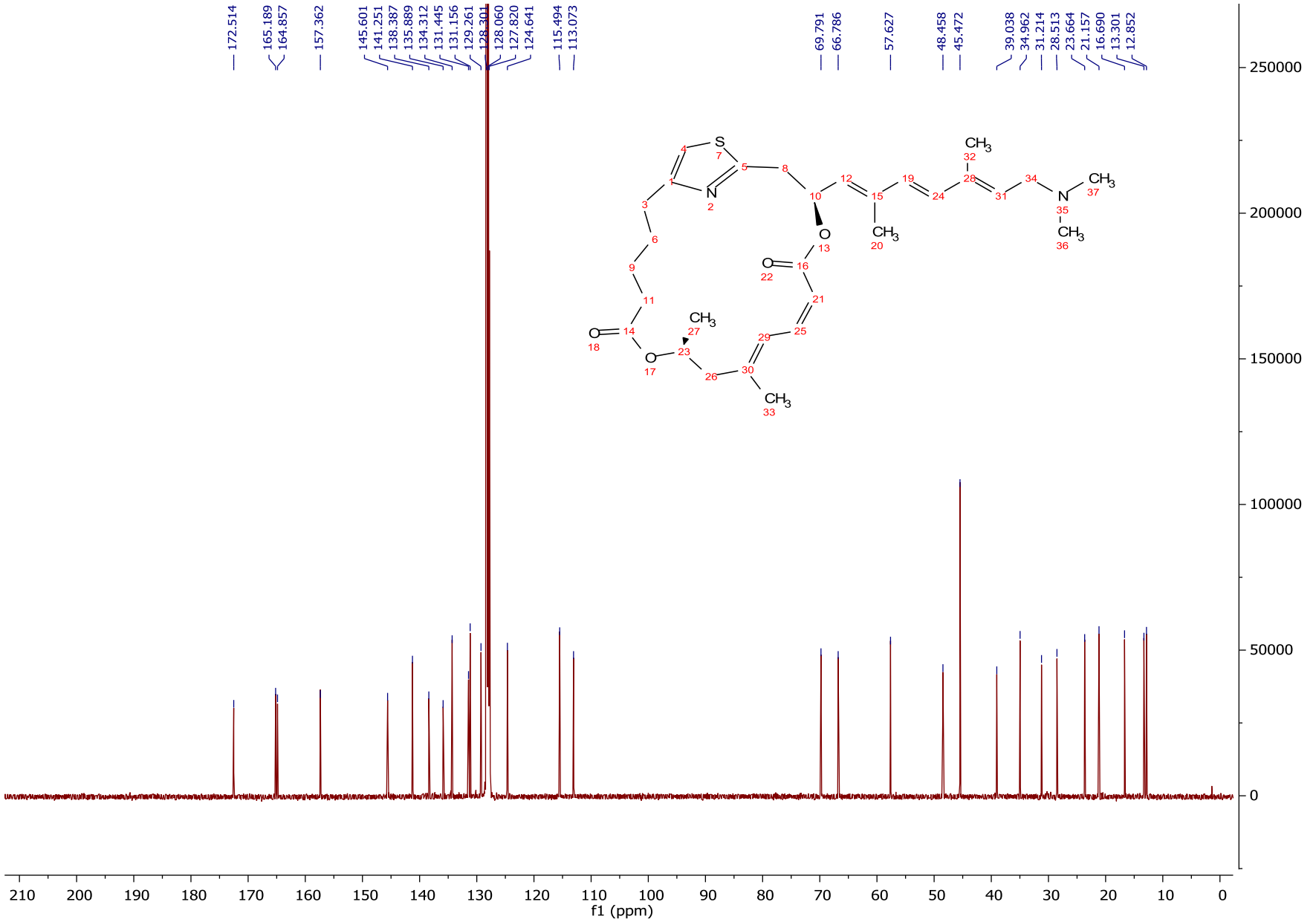

9.460
6.987
6.957
6.740
6.716
6.712
6.682
6.421
6.400
6.377
6.364
6.356
6.336
6.322
5.374
5.346
5.148
5.136
5.106
3.242
3.220
2.865
2.852
2.841
2.828
2.816
2.612
2.601
2.586
2.575
2.564
2.549
2.538
2.344
2.317
2.284
2.250
2.234
2.187
2.175
2.146
2.136
2.104
1.958
1.955
1.869
1.856
1.830
1.827
1.796
1.784
1.693
1.667
1.633
1.394
1.373
1.349
1.235
1.219
1.195
1.171
0.99
1.00
1.93
1.99
0.95
1.00
1.99
1.08
1.04
4.13
2.86
4.22
1.25
1.22
4.10
f1 (ppm)

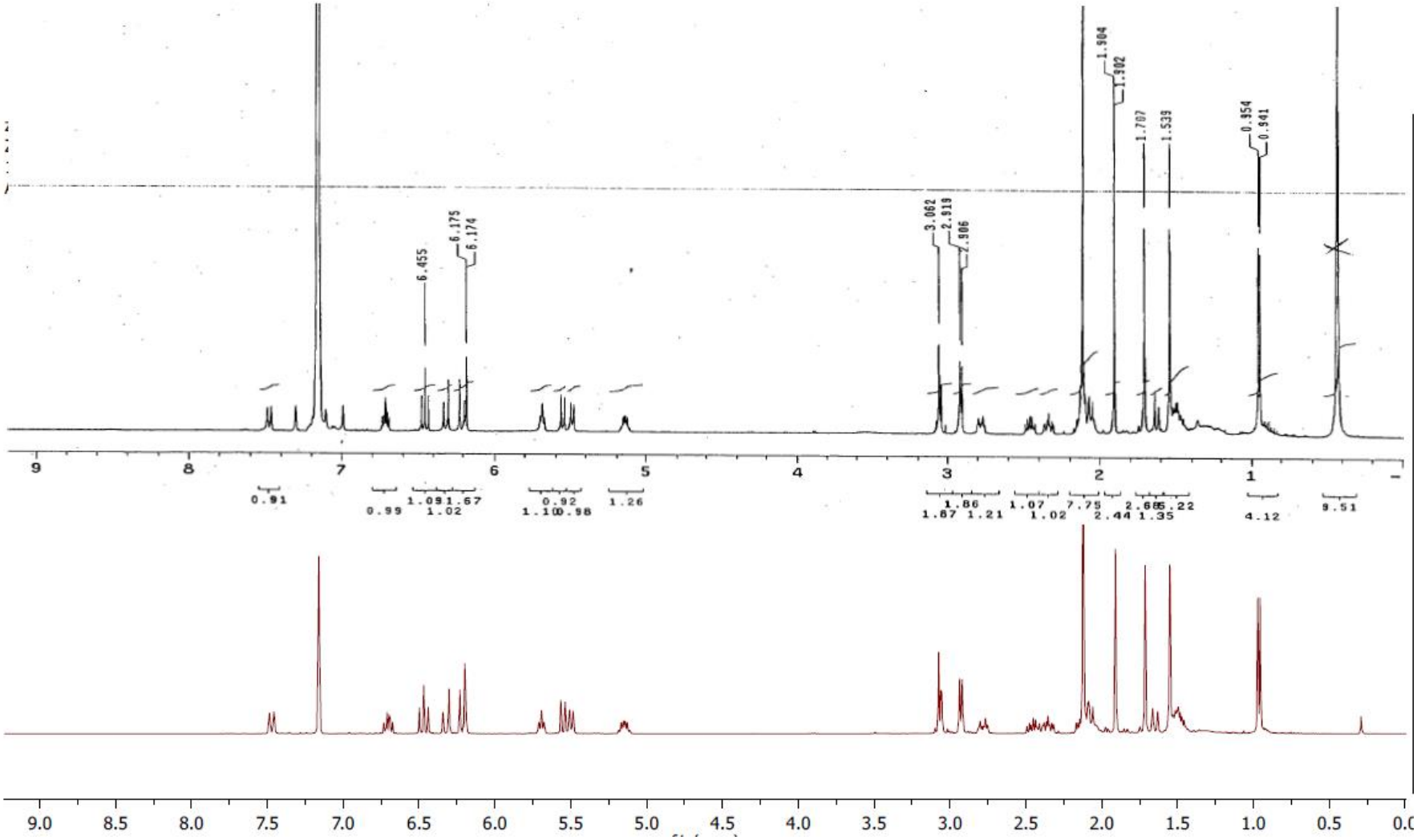

194.362
173.000
164.265
163.851
156.873
147.827
146.518
141.715
140.733
123.761
113.871
113.493
77.423
77.000
76.577
68.483
67.097
48.266
37.254
34.589
30.730
28.035
23.114
21.128
16.782
9.859
f1 (ppm)


f1 (ppm)

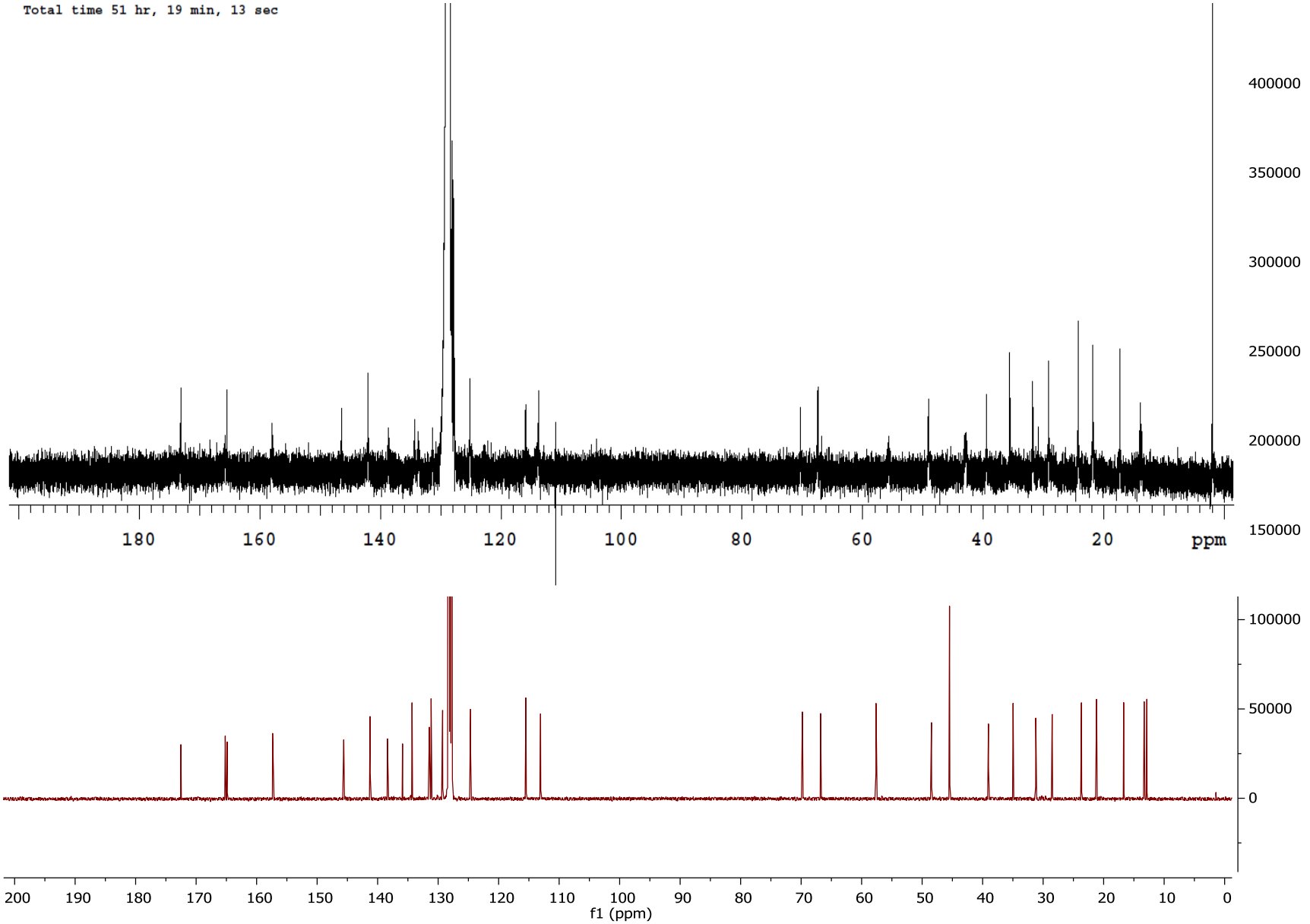

f1 (ppm)


7.485 7.455 6.733 6.719 6.711 6.697 6.689 6.675 6.497 6.468 6.439 6.342 6.303 6.230 6.197 6.190 5.710 5.692 5.675 5.565 5.537 5.507 5.484 5.183 5.170 5.155 5.143 5.127 5.124 5.111 3.096 3.074 3.060 3.052 3.016 2.935 2.918 2.812 2.802 2.789 2.776 2.766 2.754 2.451 2.410 2.363 2.353 2.328 2.169 2.144 2.120 2.085 2.058 1.910 1.908 1.714 1.663 1.630 1.551 1.533 1.513 1.495 1.482 1.470 1.457 0.970 0.954
4000
3500
3000
2500
2000
1500
1000
500
0
1.02 0.97 1.08 1.03 1.96 0.94 0.93 0.97 1.00 2.17 1.96 1.15 1.04 1.15 9.29 2.86 2.84 1.29 6.08 2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.514
165.189
164.857
157.362
145.601
141.251
138.387
135.889
134.312
131.445
131.156
129.261
128.301
128.060
127.820
124.641
115.494
113.073
69.791
66.786
57.627
48.458
45.472
39.038
34.962
31.214
28.513
23.664
21.157
16.690
13.301
12.852
250000
200000
150000
100000
50000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



Comparison of Romo's ^{1}H NMR (top) and Fürstner's (bottom)



Comparison of Romo's ^{13}C NMR (top) and Fürstner's (bottom)