Supplementary Information

Ten-step Asymmetric Total Syntheses of Potent Antibiotic Anthracimycin and Anthracimycin B

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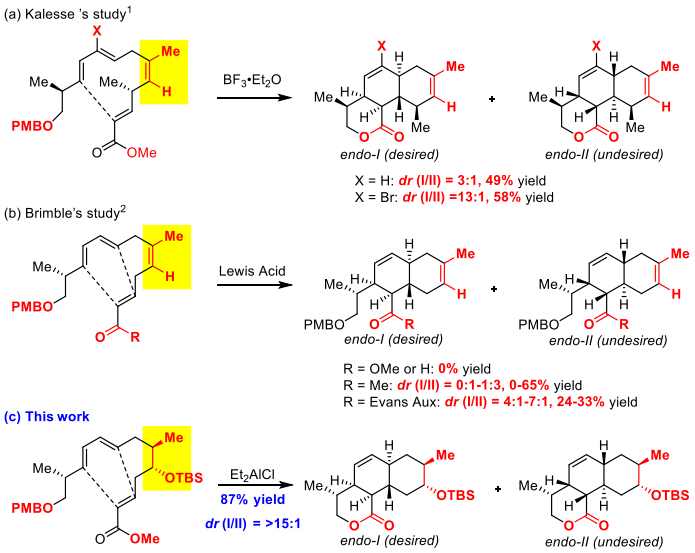
General Information

Reactions were carried out in oven-dried glassware under an argon atmosphere, unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as indicator. Dichloromethane was freshly distilled before use from calcium hydride (CaH_2). Solvents used in workup, extraction and column chromatography were used as received from commercial suppliers without further purification. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC, 0.25 mm) on Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Grace. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) as values relative to residual chloroform peaks (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Optical rotations were measured on a JASCO Perkin-Elmer model P-2000 polarimeter and RUDOLPH API, A28576-T-LED. High resolution mass spectra were measured at the Hong Kong University of Science and Technology Mass Spectrometry Service Center on either an Agilent GC/MS 5975C system or an API QSTAR XL System.

Comparison of intramolecular Diels–Alder reaction

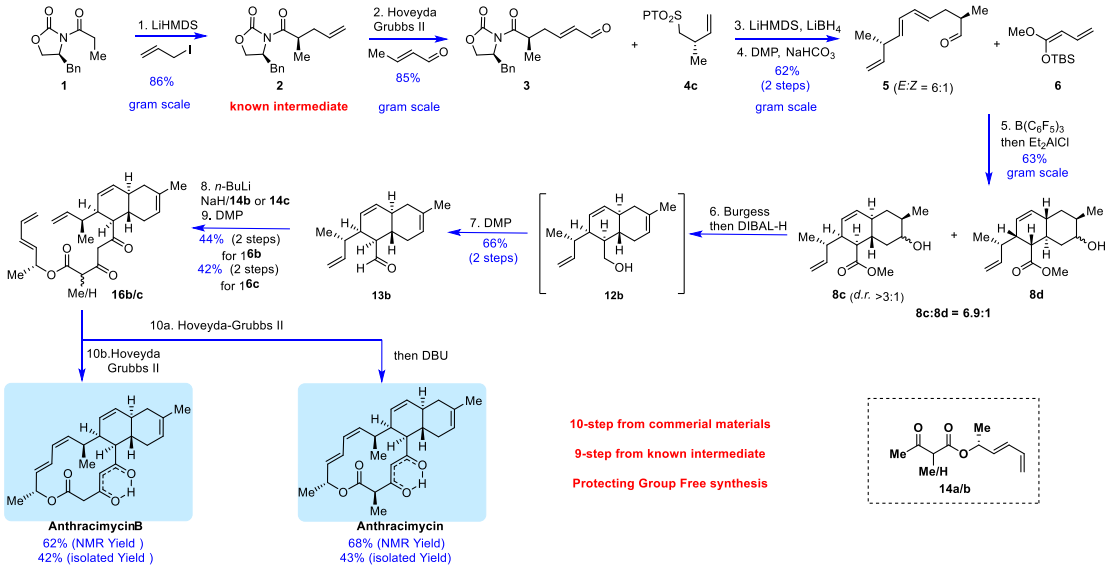
To address the challenge of the bioinspired intramolecular Diels-Alder reaction of tetraene substrates employed by Kalesse[1] and Brimble[2] and highlight our design of the intramolecular Diels–Alder reaction substrate, we summarized these results in Scheme S1. Kalesse *et al*. found the bromodiene enhanced yield and selectivity, while Brimble *et al*. identified Evans chiral auxiliary to be advantageous for the bioinspired Diels–Alder reaction. Our strategically designed substrate delivered the desired decalin with excellent yield (87%) and high selectivity (*d.r.*>15:1).



Scheme S1. Construction of the *trans*-decalin core through Diels–Alder reaction

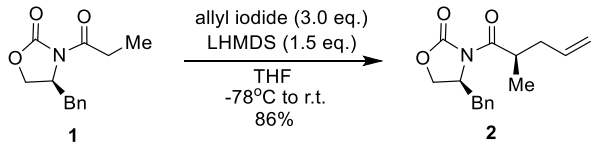
Ten-step synthetic route for anthracimycin and anthracimycin B

With our optimized synthesis of decalin intermediate **13b**, the total number of steps for anthracimycin and anthracimycin B was reduced to 10 without using any protecting groups and with substantially improved overall yield (>3%) (Scheme S2).



Scheme S2. Ten-step synthetic route for anthracimycin and anthracimycin B

Preparation of Compound 2



Compound **2** was prepared according to a slightly modified procedure described by Liu and coworkers[3]. To a solution of compound **1** (25.00 g, 107.2 mmol, 1.0 equiv.) in 250 mL THF at -78°C was added LHMDS (1.0 M in THF, 160.7 mL, 160.7 mmol, 1.5 equiv. , dropwise). After the reaction mixture was stirred at the same temperature for 2 hours, allyl iodide (29.4 mL, 321.5 mmol, 3 equiv.) was added and the resulting solution was stirred for 10 hours. The reaction was allowed to warm up to room temperature and stirred for another 30 mintues before being quenched with sat. aq. NH_4Cl (100 mL). The two phases was separated and the aqueous phase was extracted with EtOAc (3 × 150 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane, 1/15 to 1/10) to give compound **2** (25.2 g, 86%) as a colorless oil.

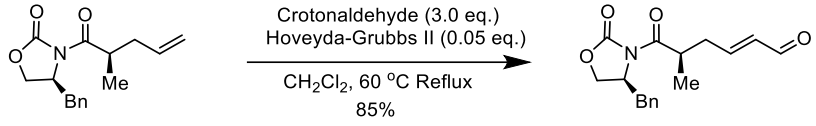
$[\alpha]_D^{25}$ = +31.60 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.14 (m, 5H), 5.94 – 5.71 (m, 1H), 5.27 – 4.97 (m, 2H), 4.80 – 4.59 (m, 1H), 4.29 – 4.08 (m, 2H), 3.96 – 3.74 (m, 1H), 3.29 (dd, *J* = 13.3, 3.4 Hz, 1H), 2.71 (dd, *J* = 13.3, 9.8 Hz, 1H), 2.63 – 2.37 (m, 1H), 2.30 – 2.15 (m, 1H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.4, 153.0, 135.3, 135.2, 129.3, 128.8, 127.2, 117.1, 65.9, 55.3, 38.0, 37.9, 37.1, 16.3.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{17}H_{19}NO_4+Na]^+$ 296.1257, found 296.1259.

Preparation of Compound 3



2 **3**

A solution of compound **2** (25.2 g, 92.2 mmol, 1.0 equiv.) in 460 mL CH_2Cl_2, was degassed with argon sparging for 5 minutes. Then crotonaldehyde (22.8 ml, 276.9 mmol, 3.0 equiv.) and Hoveyda Grubbs II catalyst (2.89 g, 4.6 mmol, 0.05 equiv.) were added sequentially to the solution. The reaction mixture was heated to reflux for 3 days, and then cooled to room temperature. The CH_2Cl_2 solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane, 1/10 to 1/3) to give compound **3** (27.8 g, 85%) as a brown oil.

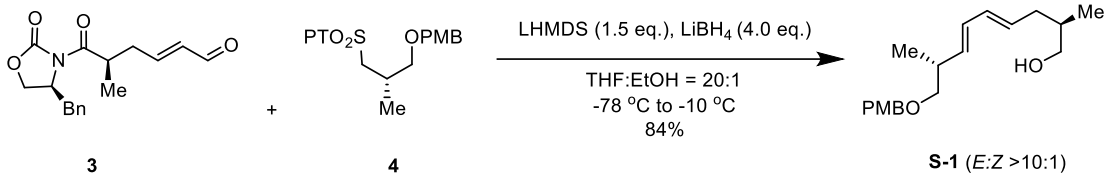
$[\alpha]_D^{25}$ = +32.10 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.21 – 7.14 (m, 2H), 6.85 (dt, *J* = 15.7, 7.1 Hz, 1H), 6.24 – 6.10 (m, 1H), 4.72 – 4.62 (m, 1H), 4.26 – 4.14 (m, 2H), 4.00 – 3.90 (m, 1H), 3.24 (dd, *J* = 13.3, 3.4 Hz, 1H), 2.86 – 2.68 (m, 2H), 2.48 (dtd, *J* = 14.5, 7.1, 1.4 Hz, 1H), 1.23 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 193.6, 175.3, 154.6, 153.1, 135.0, 134.7, 129.3, 128.9, 127.4, 66.2, 55.4, 37.9, 36.7, 36.3, 16.8.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{17}H_{19}NO_4+Na]^+$ 324.1206, found 324.1211.

Preparation of Compound S-1



3 + **4** → **S-1** (*E*:*Z* >10:1)

To a solution of aldehyde **3** (4.91 g, 16.3 mmol, 1.0 equiv.) and sulfone **4**[4] (7.87 g, 19.6 mmol, 1.2 equiv.) in 160 mL THF at -78 ℃ was added dropwise LHMDS (1.0 M in THF, 21.2 mL, 21.2 mmol, 1.3 equiv.). The reaction mixture was stirred at -78 ℃ for 2 hours before adding 8.2 mL ethanol. Then reaction mixture was allowed to warm up to -10 ℃ and then $LiBH_4$ (2.0 M in THF, 32.6 mL, 65.2 mmol, 4.0 equiv.) was added dropwise to the reaction mixture. After stirring for another 2 hours or until completion of the reaction as indicated by TLC, the reaction was allowed to warm up to 0 ℃ and quenched with 1 *N* NaOH (70 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (3 × 100 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane, 1/5 to 1/2) to give compound **S-1** (4.15 g, 84%) as a light yellow oil.

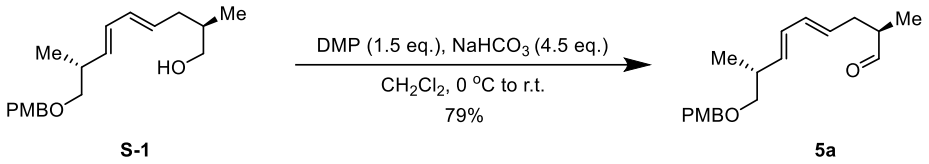
$[\alpha]_D^{25}$ = -0.15 (*c* 2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.21 (m, 2H), 6.94 – 6.85 (m, 2H), 6.14 – 5.98 (m, 2H), 5.68 – 5.49 (m, 2H), 4.47 (s, 2H), 3.83 (s, 3H), 3.59 – 3.43 (m, 2H), 3.32 (ddd, *J* = 32.6, 9.2, 6.7 Hz, 2H), 2.60 – 2.46 (m, 1H), 2.26 – 2.15 (m, 1H), 2.04 – 1.92 (m, 1H), 1.82 – 1.65 (m, 1H), 1.54 (s, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 134.9, 132.0, 130.6, 130.1, 129.7, 129.2, 113.7, 74.9, 72.6, 67.9, 55.2, 36.8, 36.5, 36.1, 17.0, 16.5.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{19}H_{28}O_3+Na]^+$ 327.1931, found 327.1932.

Preparation of Compound 5a



S-1 **5a**

To a solution of alcohol **S-1** (4.15 g, 13.6 mmol, 1.0 equiv.) in 136 mL CH_2Cl_2 at 0 ℃ were added $NaHCO_3$ (5.15 g, 61.3 mmol, 4.5 equiv.) and Dess-Martin periodinane (8.67 g, 20.4 mmol, 1.5 equiv.). The reaction mixture was stirred at 0 ℃ for 2 hours, and then the reaction was quenched by addition of sat. aq. $NaHCO_3$ (30 mL) and sat. aq. $Na_2S_2O_3$ (60 mL). The reaction mixture was stirred for another 30 minutes. The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 60 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane, 1/5) to afford aldehyde **5a** (3.26 g, 79%) as a pale-yellow oil.

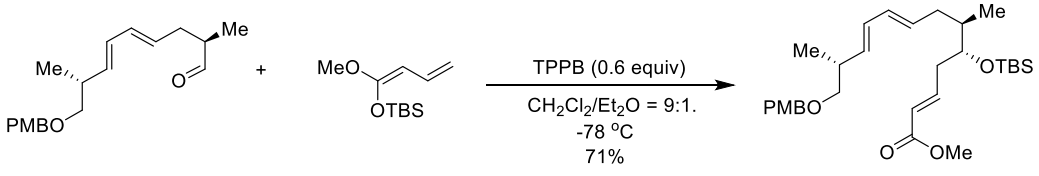
$[\alpha]_D^{25}$ = -0.40 (*c* 2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (d, *J* = 1.4 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.12 – 5.96 (m, 2H), 5.65 – 5.45 (m, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.33 (dd, *J* = 9.1, 6.6 Hz, 1H), 3.26 (dd, *J* = 9.1, 6.8 Hz, 1H), 2.58 – 2.36 (m, 3H), 2.22 – 2.10 (m, 1H), 1.10 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 204.6, 159.0, 135.8, 1323.0, 130.6, 129.3, 129.1, 128.3, 113.7, 74.7, 72.5, 55.2, 46.2, 36.8, 33.6, 17.0, 13.1.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{19}H_{26}O_3+Na]^+$ 325.1774, found 325.1776.

Preparation of Compound 7



5a **6** **7** (*d.r.* > 6:1)

To a solution of aldehyde **5a** (112 mg, 0.37 mmol, 1.0 equiv.) and compound **6** (159 mg, 0.74 mmol, 2.0 equiv.) in 3.7 mL CH_2Cl_2/Et_2O (9:1) at -78 ℃ was added tris(pen-

tafluorophenyl)borane (114 mg, 0.22 mmol, 0.6 equiv.). The reaction mixture was stirred at -78 ℃ for 2 hours, and then the reaction was quenched by addition of sat. aq. $NaHCO_3$ (10 mL). The organic phase was collected, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane, 1/50) to afford ester **7** (136 mg, 71%) as a colorless oil.

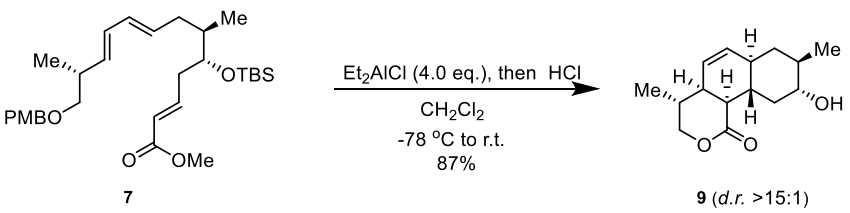
$[\alpha]_D^{25}$ = +2.33 (*c* 0.3, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 7.1 Hz, 2H), 6.99 – 6.91 (m, 1H), 6.91 – 6.86 (m, 2H), 6.10 – 5.95 (m, 2H), 5.91 – 5.81 (m, 1H), 5.63 – 5.45 (m, 2H), 4.45 (s, 2H), 3.81 (s, 3H), 3.74 (s, 3H), 3.72 – 3.66 (m, 1H), 3.35 (dd, *J* = 9.1, 6.4 Hz, 1H), 3.27 (dd, *J* = 9.1, 7.0 Hz, 1H), 2.57 – 2.46 (m, 1H), 2.39 – 2.29 (m, 2H), 2.28 – 2.16 (m, 1H), 1.93 – 1.77 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 1.0 Hz, 9H), 0.86 (dd, *J* = 6.7, 4.0 Hz, 4H), 0.04 (t, *J* = 1.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.8, 159.1, 146.6, 134.7, 131.8, 131.4, 130.7, 129.8, 129.2, 122.7, 113.71, 74.91, 74.46, 72.59, 55.25, 51.41, 38.67, 37.08, 36.81, 35.85, 25.84, 17.07, 13.97, -4.28, -4.53.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{30}H_{48}SiO_5+Na]^+$ 539.3163, found 539.3171.

Preparation of Compound 9



7 **9** (*d.r.* >15:1)

To a solution of ester **7** (3.72 g, 7.20 mmol, 1.0 equiv.) in 150 mL CH_2Cl_2 at -78 ℃ was added dropwise Et_2AlCl (2.0 M in hexane, 14.4mL, 28.8 mmol, 4.0 equiv.). The reaction mixture was allowed to gradually warm up to room temperature, and stirred

for 18 hours before addition of 1.0 mL H_2O and 15.0 mL concentrated HCl at 0 ℃. The reaction mixture was stirred for another 10 hours before addition of 2 *N* NaOH (100 mL). The organic phase was collected, and the aqueous phase was extracted by CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The resulting residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane, 1/2) to afford lactone **9** (1.58 g, 87%) as a white solid.

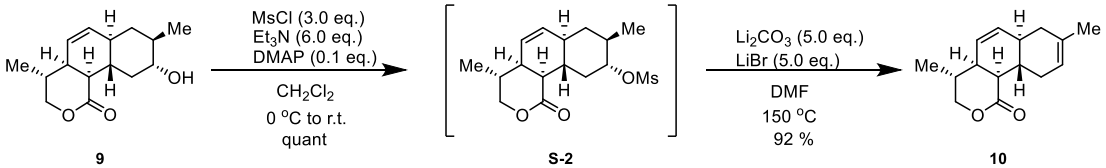
$[\alpha]_D^{25}$ = -26.67 (*c* 0.3, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74 – 5.65 (m, 1H), 5.61 (d, *J* = 10.0 Hz, 1H), 4.28 (dd, *J* = 11.3, 4.7 Hz, 1H), 3.87 (t, *J* = 11.0 Hz, 1H), 3.25 – 3.12 (m, 1H), 2.61 (dd, *J* = 11.2, 6.0 Hz, 1H), 2.30 – 2.18 (m, 1H), 2.09 – 1.91 (m, 2H), 1.91 – 1.74 (m, 2H), 1.52 – 1.42 (m, 2H), 1.39 – 1.24 (m, 1H), 1.03 (dd, *J* = 15.6, 6.5 Hz, 6H), 0.88 (q, *J* = 12.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 132.8, 126.0, 76.0, 74.2, 45.4, 41.7, 39.8, 39.6, 39.2, 37.0, 32.1, 18.2, 14.3.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{15}H_{22}O_3+Na]^+$ 273.1461, found 273.1461.

Preparation of Compound 10



To a solution of lactone **9** (1.58 g, 6.31 mmol, 1.0 equiv.), DMAP (77 mg, 0.63 mmol, 0.1 eq) and Et_3N (8.8 mL, 63.3mmol, 10.0 eq.) in 63 mL CH_2Cl_2 was added dropwise MsCl (2.45 mL, 31.6 mmol, 5.0 equiv.) at 0 ℃. The reaction mixture was stirred for 18 hours at room temperature before quenching by addition of sat. aq. $NHCl_4$ (30 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with brine and dried over Na_2SO_4, concentrated under reduced pressure. The residue was dissolved in 32.0 mL DMF, and Li_2CO_3 (2.34 g, 31.7 mmol, 5.0 equiv.) and LiBr

(2.75 g, 31.7 mmol, 5.0 equiv.) were added. The reaction mixture was heated to 150 ℃ for 1 hour and then cooled to room temperature. 250 mL Et_2O was added to the reaction mixture. The organic phase was washed with H_2O (3 × 30 mL), dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane, 1/5) to give lactone **10** (1.35 g, 92%) as a white solid.

See **X-Ray** crystal structure analysis in page-35 (CCDC 2175241)

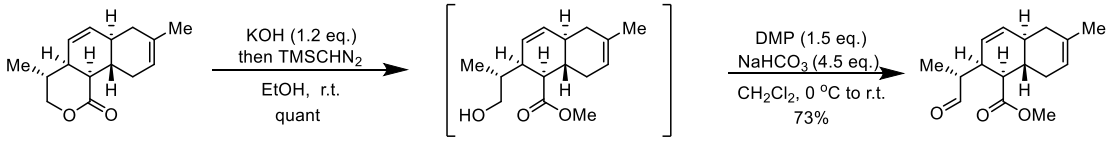
$[\alpha]_D^{25}$ = +94.10 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 – 5.71 (m, 1H), 5.71 – 5.61 (m, 1H), 5.45 – 5.38 (m, 1H), 4.29 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.85 (t, *J* = 11.0 Hz, 1H), 2.56 (dd, *J* = 11.6, 5.5 Hz, 1H), 2.27 – 2.16 (m, 1H), 2.17 – 1.93 (m, 5H), 1.85 – 1.70 (m, 1H), 1.72 – 1.62 (m, 3H), 1.01 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 133.1, 132.8, 125.7, 121.0, 74.6, 45.2, 40.0, 38.4, 37.3, 34.6, 32.1, 30.5, 23.2, 14.3.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{15}H_{20}O_2+Na]^+$ 255.1356, found 255.1361.

Preparation of Compound11



To a stirred solution of lactone **10** (112 mg, 0.48 mmol, 1.0 equiv.) in 2.5 mL EtOH was added 4 *N* KOH (0.15mL, 0.58 mmol, 1.2 equiv.). The reaction mixture was stirred for 14 hours at room temperature, then EtOH was removed under reduced pressure. The residue was suspended in H_2O (4 mL) and treated with 1 *N* HCl (2.3 ml) until pH of 4-5. The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic phases were washed with H_2O (3 × 30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was dissolved in 24.0 mL MeOH/EtOAc (2:1) and a solution of $TMSCHN_2$ (2.0 M hexane, 1.0 mL, 2 mmol, 4.2 equiv.) was added dropwise into the reaction mixture until the solution became

yellow and persisted for 1 minute. After the reaction solvent and excess of $TMSCHN_2$ were removed under reduced pressure, 5 mL CH_2Cl_2 was added to the residue. The resulting solution was cooled down to 0 ℃, and then $NaHCO_3$ (182 mg, 2.17 mmol, 4.5 equiv.) and Dess-Martin periodinane (307 mg, 0.72 mmol, 1.5 equiv.) were added. The reaction mixture was stirred for another 1.5 hours at room temperature before addition of sat. aq. $NaHCO_3$ (2 mL) and sat. aq. $Na_2S_2O_3$ (5 mL) with stirring for another 30 minutes. The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified through flash chromatography (eluent: EtOAc/hexane, 1/50) to afford aldehyde **11** (92 mg, 73%) as a colourless oil.

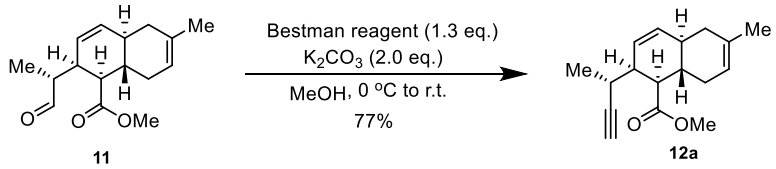
$[\alpha]_D^{25}$ = +249.9 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 5.65 (d, *J* = 10.0 Hz, 1H), 5.43 – 5.34 (m, 1H), 5.31 (d, *J* = 5.4 Hz, 1H), 3.60 (s, 3H), 3.19 – 3.12 (m, 1H), 2.64 (dd, *J* = 11.6, 6.3 Hz, 1H), 2.56 – 2.42 (m, 1H), 2.22 – 2.12 (m, 1H), 2.03 – 1.91 (m, 2H), 1.84 – 1.48 (m, 6H), 1.06 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 203.3, 174.2, 133.6, 133.1, 124.9, 120.5, 51.3, 48.7, 47.9, 37.3, 36.8, 35.1, 33.9, 30.4, 23.2, 11.2.

HRMS (TOF, CI$^+$) m/z calculated for $[C_{16}H_{22}O_3+Na]^+$ 285.1461, found 285.1467.

Preparation of Compound 12a



To a stirred solution of aldehyde **11** (380 mg, 1.45 mmol, 1.0 equiv.) in 20 mL MeOH at 0 ℃ were added K_2CO_3 (401 mg, 2.90 mmol, 2.0 equiv.) and dimethyl (1-diazo-2-oxopropyl)phosphonate (0.29 mL, 1.89 mmol, 1.3 equiv.). After the reaction mixture was allowed to warm to room temperature and stirred for 2 hours. The solvent was removed under reduced pressure. The residue was dissolved in

EtOAc (30 mL) and washed with sat. aq. $NaHCO_3$ (10 mL). The organic phase was concentrated under reduced pressure and purified via flash chromatography (eluent: EtOAc/hexane, 1/80) to afford alkyne **12a** (288 mg, 77%) as a colourless oil.

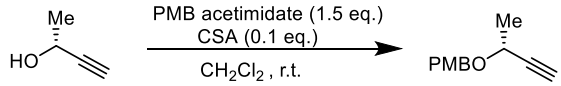
$[\alpha]_D^{25}$ = +230.33 (*c* 0.3, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 – 5.77 (m, 1H), 5.77 – 5.68 (m, 1H), 5.38 – 5.27 (m, 1H), 3.69 (d, *J* = 4.6 Hz, 3H), 2.86 – 2.76 (m, 1H), 2.64 (dd, *J* = 11.9, 6.8 Hz, 1H), 2.57 – 2.43 (m, 1H), 2.30 (dd, *J* = 16.9, 6.0 Hz, 1H), 2.06 (d, *J* = 2.4 Hz, 1H), 2.05 – 1.92 (m, 2H), 1.83 – 1.69 (m, 2H), 1.66 – 1.62 (m, 3H), 1.61 – 1.48 (m, 1H), 1.16 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.7, 133.7, 133.1, 124.8, 120.7, 88.7, 68.5, 51.3, 49.2, 40.8, 37.3, 37.1, 33.8, 30.8, 27.8, 23.3, 17.8.

HRMS (TOF, CI$^+$) m/z calculated for $[C_{17}H_{22}O_2+H]^+$ 259.1693, found 259.1693.

Preparation of Compound S-4



S-3 **S-4**

To a stirred solution of alkyne **S-3** (1.50 g, 21.4 mmol, 1.0 equiv.) and *para*-methoxy benzyl acetimidate (9.07 g, 32.1 mmol, 1.5 equiv.) in 107 mL CH_2Cl_2 was added camphorsulfonic acid (497 mg,2.14 mmol, 0.1 equiv.). The reaction mixture was stirred at room temperature for 15 hours before quenched with sat. aq. $NaHCO_3$ (50 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified through flash chromatography (eluent: EtOAc/hexane, 1/50) to afford alkyne **S-4** (3.63 g, 89%) as a yellow oil.

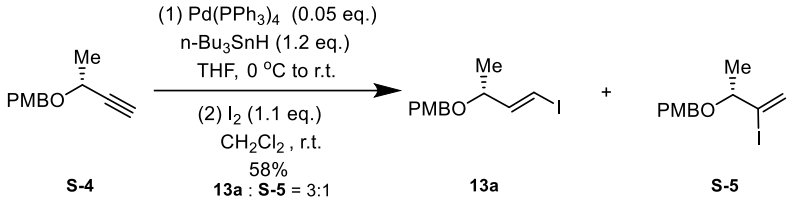
$[\alpha]_D^{25}$ = +133.60 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.30 (m, 2H), 6.99 – 6.82 (m, 2H), 4.78 (d, *J* = 11.3 Hz, 1H), 4.49 (d, *J* = 11.3 Hz, 1H), 4.28 – 4.18 (m, 1H), 3.83 (s, 3H), 2.53 (d, *J* = 2.0 Hz, 1H), 1.51 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.2, 129.6, 113.7, 83.7, 73.0, 70.0, 63.7, 55.1, 21.9.

HRMS (TOF, CI$^+$) m/z calculated for $[C_{12}H_{14}O_2]^+$ 190.0988, found 190.0996.

Preparation of Compound 13a



To a stirred solution of alkyne **S-4** (3.63 g, 19.1 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ in 95.0 mL THF at 0 °C was added ^{n}Bu$_3$SnH (6.16 mL, 22.9 mmol, 1.2 equiv.). After the reaction mixture was allowed to warm to room temperature and stirred for 10 hours. The solvent was removed under reduced pressure. The residue was dissolved in 100 mL CH_2Cl_2 and titrated with a solution of I_2 (2.67 g, 21.0 mmol, 1.1 equiv.) in THF (30 mL) until the reddish color persisted. The reaction was quenched with sat. aq. $Na_2S_2O_3$ (50 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified through flash chromatography (eluent: EtOAc/hexane, 1/100) to afford vinyl iodide **13a** (3.52 g, 58%) as a yellow oil.

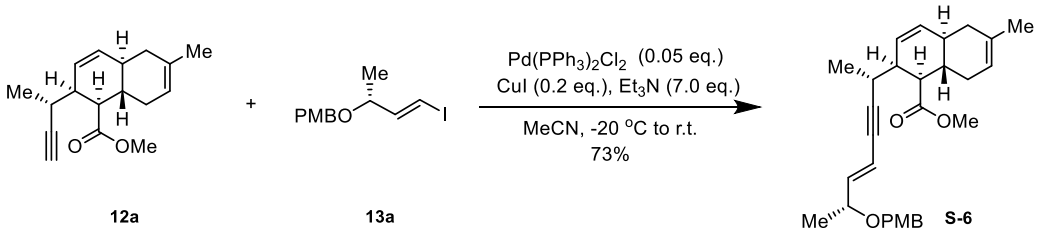
$[\alpha]_D^{25}$ = +71.20 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.98 – 6.91 (m, 2H), 6.57 (dd, *J* = 14.5, 7.3 Hz, 1H), 6.36 (dd, *J* = 14.5, 0.8 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.37 (d, *J* = 11.5 Hz, 1H), 3.99 – 3.87 (m, 1H), 3.83 (s, 3H), 1.32 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.9, 147.8, 129.0, 113.6, 79.4, 76.6, 69.7, 55.0, 20.6.

HRMS (TOF, CI$^+$) m/z calculated for $[C_{12}H_{15}IO_2]^+$ 318.0111, found 318.0113.

Preparation of Compound S-6



To a solution of alkyne **12a** (130 mg, 0.50 mmol, 1.0 equiv.) and vinyl iodide **13a** (304mg, 0.96 mmol, 1.9 equiv.) in 15 mL anhydrous acetonitrile at -78 ℃ were added $Pd(PPh_3)Cl_2$ (18mg, 0.03mmol, 0.05 equiv.) and CuI (19mg, 0.1mmol, 0.2 equiv.). The reaction solution was degassed with argon. The reaction mixture under argon atmosphere was allowed to warm up to -20 ℃ before triethylamine (0.49ml, 3.52 mmol, 7.0 equiv.) was added. The reaction mixture was stirred for 30 minutes and then warmed to room temperature and stirred for another 30 minutes before the reaction was quenched with phosphate buffer (pH 7, 10 mL). EtOAc (15 mL) was added, and the reaction mixture was stirred at room temperature for 20 minutes. The organic phase was collected and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified through flash chromatography (eluent: EtOAc/hexane, 1/50) to afford compound **S-6** (165 mg, 73%) as a colourless oil.

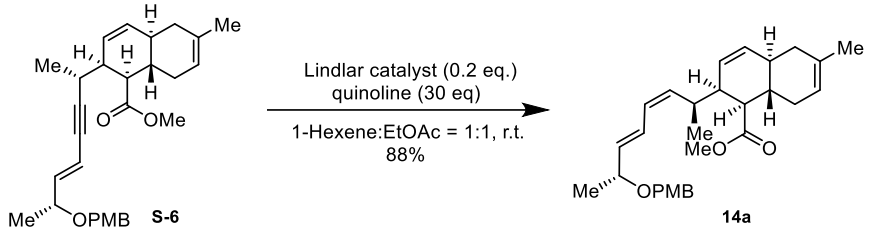
$[\alpha]_D^{25}$ = +172.00 (*c* 0.2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.20 (m, 2H), 6.91 – 6.83 (m, 2H), 5.98 (dd, *J* = 15.9, 7.4 Hz, 1H), 5.89 – 5.76 (m, 1H), 5.73 (d, *J* = 10.1 Hz, 1H), 5.65 (dd, *J* = 15.9, 1.7 Hz, 1H), 5.42 – 5.33 (m, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.29 (d, *J* = 11.5 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.80 (s, 3H), 3.70 (d, *J* = 1.7 Hz, 3H), 2.88 – 2.79 (m, 1H), 2.70 – 2.56 (m, 2H), 2.33 (d, *J* = 16.7 Hz, 1H), 2.09 – 1.93 (m, 2H), 1.84 – 1.77 (m, 1H), 1.77 – 1.68 (m, 1H), 1.64 (d, *J* = 14.7 Hz, 3H), 1.61 – 1.53 (m, 1H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.8, 143.7, 133.7, 133.0, 130.6, 129.2, 125.1, 120.8, 113.8, 111.4, 74.8, 69.8, 55.2, 51.3, 49.3, 41.0, 37.4, 37.1, 33.8, 30.9, 28.7, 23.3, 21.3, 17.9.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{29}H_{36}O_4+Na]^+$ 471.2506, found 471.2510.

Preparation of Compound 14a



To a stirred solution of **S-6** (80 mg, 0.18 mmol, 1.0 equiv.) in 14 mL EtOAc/1-Hexene (1:1) were added quinoline (0.63 mL, 5.3 mmol, 30.0 equiv.) and Lindlar catalyst (Aldrich, 5 % Pd on $CaCO_3$ poisoned with Pb, 80 mg). The reaction mixture was stirred under H_2 (1 atm) atmosphere for 2.5 hours. The reaction mixture was passed through a plug of SiO_2 (eluent: EtOAc). The filtrates were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/hexane, 1/50) to afford compound **14a** (70 mg, 88%) as a colourless oil.

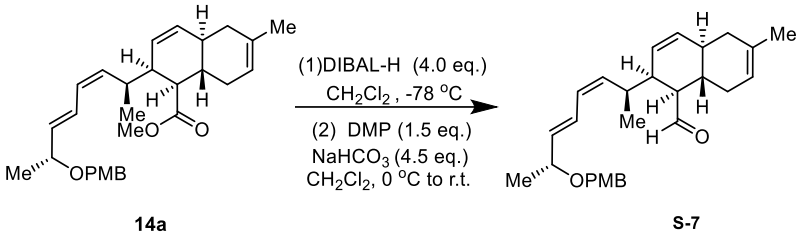
$[\alpha]_D^{25}$ = +101.25 (*c* 0.8, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.21 (m, 2H), 6.87 (dd, *J* = 9.0, 2.5 Hz, 2H), 6.40 – 6.28 (m, 1H), 5.97 – 5.85 (m, 1H), 5.77 – 5.54 (m, 3H), 5.45 – 5.32 (m, 2H), 4.50 (dd, *J* = 11.5, 9.0 Hz, 1H), 4.41 – 4.25 (m, 1H), 4.00 – 3.87 (m, 1H), 3.80 (s, 3H), 3.72 – 3.59 (m, 3H), 2.62 (dd, *J* = 9.7, 4.9 Hz, 2H), 2.52 – 2.41 (m, 1H), 2.11 – 1.95 (m, 2H), 1.83 (t, *J* = 4.4 Hz, 2H), 1.70 – 1.66 (m, 3H), 1.61 – 1.49 (m, 1H), 1.35 – 1.23 (m, 3H), 1.23 – 1.11 (m, 1H), 1.00 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.8, 159.0, 137.8, 135.6, 133.7, 132.5, 130.8, 129.4, 126.9, 126.4, 125.4, 121.0, 113.7, 74.9, 69.3, 55.2, 51.0, 49.5, 42.6, 37.5, 37.2, 34.1, 33.7, 31.1, 23.3, 21.6, 17.9.

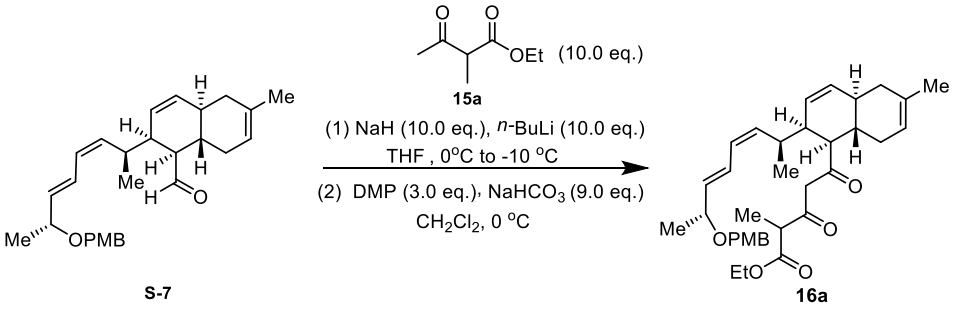
HRMS (TOF, ES$^+$) m/z calculated for $[C_{29}H_{38}O_4+Na]^+$ 473.2662, found 473.2665.

Preparation of Compound S-7



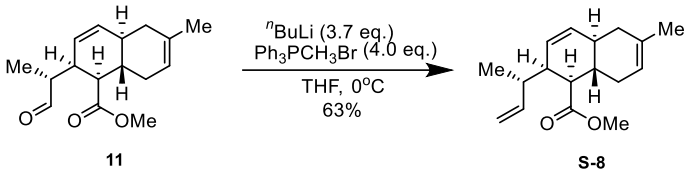
To a stirred solution of **14a** (70 mg, 0.16 mmol, 1.0 equiv.) in 3.0 mL CH_2Cl_2 at -78 ℃ was added dropwise DIBAL-H (1.0 M in hexane, 0.6 mL, 0.6 mmol, 4.0 equiv.). The reaction mixture was stirred for 2 hours and then quenched by 2 *N* HCl (5 mL). The resulting solution was stirred at room temperature for another 30 minutes. The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was dissolved in 3.0 mL CH_2Cl_2 was cooled down to 0 ℃, and $NaHCO_3$ (59 mg, 0.70 mmol, 4.5 equiv.) and Dess-Martin periodinane (99 mg, 0.23 mmol, 1.5 equiv.) were added. The reaction mixture was stirred for another 1.5 hours at room temperature before sat. aq. $NaHCO_3$ (3 mL) and sat. aq. $Na_2S_2O_3$ (3 mL) were added. The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in 0.5 mL EtOAc and the suspension was filtered through a plug of SiO_2 (eluent: EtOAc/hexane, 1/5). The filtrates were concentrated under reduced pressure. The crude product **S-7** (56 mg, check by ^{1}H NMR) was used directly in the next step without other purifications.

Preparation of Compound 16a



To a stirred suspension of sodium hydride (60% dispersion in mineral oil, 53 mg, 1.33 mmol, 10.0 equiv.) in 4.5mL THF at 0 °C was added a solution of **15a** (192 mg, 1.33 mmol, 10.0 equiv. , dropwise) in 4.5 mL THF. The reaction mixture was stirred for 30 minutes and then cooled to -10 °C before ^{n}BuLi (2.5 M in hexane, 0.53 mL, 1.33 mmol, 10.0 equiv. , dropwise) was added. After stirring for another 30 minutes at -10 °C, a solution of the crude product **S-7** (56 mg, 0.13 mmol, 1 equiv. , dropwise) in 2.0 mL THF was then added. The reaction mixture was stirred for 2 hours at the same temperature before water (2 mL) was added to quench the reaction. The reaction mixture was diluted with Et_2O (10 mL), and acidified with 1 *N* HCl until pH of 4-5. The organic layer was collected and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The crude product dissolved in CH_2Cl_2 (5 mL) was cooled to 0° C and then $NaHCO_3$ (98 mg, 1.17 mmol, 9.0 equiv.) and Dess-Martin periodinane (166 mg, 0.40 mmol, 3.0 equiv.) were added. The reaction mixture was stirred for another 1.5 hours at 0 °C (the product decomposed if the reaction mixture was allowed to warm to room temperature) before sat. aq. $NaHCO_3$ (2 mL) and sat. aq. $Na_2S_2O_3$ (5 mL) were added to quench the reaction. The resulting reaction mixture was allowed to warm to room temperature and stirred for another 30 minutes. The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue dissolved in 0.5 mL EtOAc was filtered through a plug of SiO_2 (eluent: EtOAc/hexane, 1/5). The filtrates were concentrated under reduced pressure. The crude product **16a** (6 mg, check by ^{1}H NMR) was used directly in the next step without other purifications.

Preparation of Compound S-8



To a stirred suspension of Ph_3PCH_3Br (381 mg, 1.08 mmol, 4.0 equiv.) in 11 mL THF at 0 °C was added ^{n}BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol, 3.7 equiv. , dropwise). The reaction mixture was allowed to warm to room temperature. After stirring for 1 hour at room temperature, the solution was cooled to -78 °C and a solution of aldehyde **11** (56 mg, 0.13 mmol, 1.0 equiv. , dropwise) in 2.7 mL THF was added. The reaction mixture was allowed to warm to 0 °C and stirred for another 1 hour before quenching with sat. aq. NH_4Cl (10 mL). The organic phase was collected and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified through flash chromatography (eluent: EtOAc/hexane, 1/50) to afford compound **S-8** (35 mg, 63%) as a colourless oil.

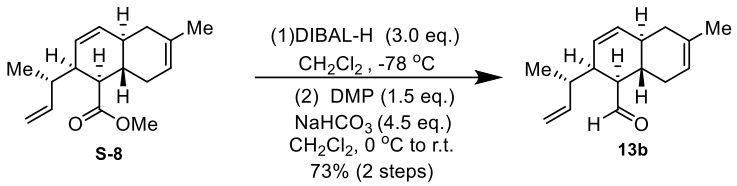
$[\alpha]_D^{25}$ = +271.6 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 – 5.77 (m, 1H), 5.66 (d, *J* = 10.2 Hz, 1H), 5.62 – 5.51 (m, 1H), 5.39 – 5.32 (m, 1H), 5.03 – 4.88 (m, 2H), 3.68 (s, 3H), 2.70 – 2.60 (m, 2H), 2.43 – 2.33 (m, 1H), 2.20 – 2.12 (m, 1H), 2.07 – 1.90 (m, 2H), 1.79 (tdd, *J* = 14.8, 8.2, 4.9 Hz, 2H), 1.69 – 1.64 (m, 3H), 1.60 – 1.47 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.1, 143.6, 133.7, 132.5, 125.0, 120.9, 113.2, 51.1, 49.7, 41.2, 38.9, 37.4, 37.2, 33.8, 31.1, 23.3, 15.6.

HRMS (TOF, CI$^+$) m/z calculated for $[C_{17}H_{24}O_2+H]^+$ 261.1849, found 261.1855.

Preparation of Compound 13b



To a stirred solution of compound **S-8** (528 mg, 2.03 mmol, 1.0 equiv.) in 10 mL CH_2Cl_2 at -78 °C was added dropwise DIBAL-H (1.0 M in hexane, 6.1 mL, 6.10 mmol, 3.0 equiv.). The reaction mixture was stirred for 2 hours at -78 °C and then quenched with 2 *N* HCl (10 mL). The resulting mixture was stirred at room temperature for another 30 minutes. The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was dissolved in 10 mL CH_2Cl_2 cooled down to 0 ℃ and then $NaHCO_3$ (767 mg, 9.13 mmol, 4.5 equiv.) and Dess-Martin periodinane (1.29 g, 3.04 mmol, 1.5 equiv.) were added. The reaction mixture was stirred for another 1.5 hours at room temperature before quenching with sat. aq. $NaHCO_3$ (3 mL) and sat. aq. $Na_2S_2O_3$ (3 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: EtOAc/hexane, 1/60) to afford compound **13b** (341 mg, 73%) as a colourless oil.

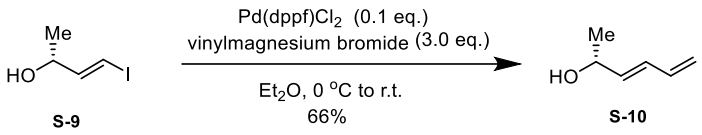
$[\alpha]_D^{25}$ = +41.80 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (d, *J* = 3.9 Hz, 1H), 5.86 – 5.71 (m, 1H), 5.70 – 5.59 (m, 2H), 5.37 (dd, *J* = 5.1, 2.6 Hz, 1H), 5.06 – 4.92 (m, 2H), 2.75 – 2.66 (m, 1H), 2.51 – 2.34 (m, 2H), 2.34 – 2.23 (m, 1H), 2.10 – 1.87 (m, 3H), 1.83 (d, *J* = 13.9 Hz, 1H), 1.67 (d, *J* = 2.4 Hz, 3H), 1.64 – 1.57 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 205.6, 143.8, 134.2, 132.5, 126.0, 120.5, 114.2, 55.8, 41.9, 39.3, 37.5, 36.9, 32.8, 30.8, 23.4, 17.2.

HRMS (TOF, ES$^-$) m/z calculated for $[C_{17}H_{24}O_2\text{-}H]^+$ 229.1587, found 229.1601.

Preparation of Compound S-10



To a stirred solution of known vinyl iodide **S-9**[5] (2.56 g, 12.9 mmol, 1.0 equiv.) in 65 mL Et_2O at 0 °C were added dropwise $Pd(dppf)Cl_2$ (946 mg, 0.13 mmol, 0.1 equiv.) and vinylmagnesium bromide (1.0 M in THF, 38.8 mL, 38.8 mmol, 3 equiv.). The resulting mixture was allowed to warm to room temperature over 15 hours before the reaction was diluted with Et_2O (50 mL) and quenched with H_2O (50 mL) at 0 °C. The organic phase was collected and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: Et_2O/Hexane, 1/3) to afford compound **S-10** (836 mg, 66%) as a colourless oil.

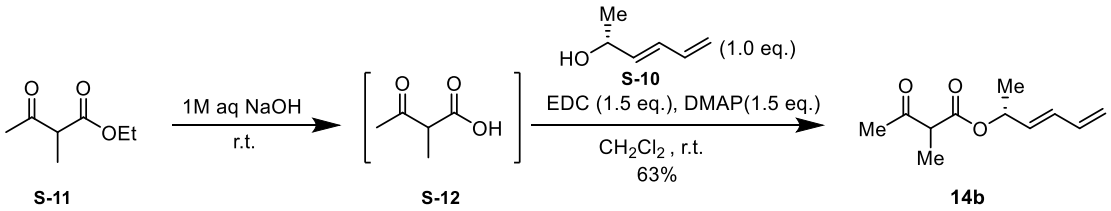
$[\alpha]_D^{25}$ = -6.00 (*c* 0.35, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 – 6.18 (m, 1H), 6.12 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.73 – 5.62 (m, 1H), 5.29 – 4.98 (m, 2H), 4.31 – 4.20 (m, 1H), 1.20 (dd, *J* = 6.5, 2.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.7, 136.3, 129.6, 129.6, 117.0, 67.8, 67.8, 22.9.

HRMS (TOF, CI$^+$) m/z calculated for $[C_6H_{10}O]^+$ 98.0732, found 98.0734.

Preparation of Compound 14b



The solution of ethyl-2-methylacetoacetate **S-11** (3.65 g, 25.3 mmol, 1 equiv.) in 35 mL 1 *N* NaOH was stirred vigorously at room temperature for 16 h. The reaction mixture was cooled to 0 °C and acidified with 1 *N* HCl until pH of 3-4. The reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were

washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure at 10 °C. To the solution of the crude product **S-12** (2.36 g, 20.3 mmol, 1.5 equiv.) and alcohol **S-10** (1.33 g, 13.6 mmol, 1 equiv.) in 136 mL CH_2Cl_2 were added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride salt (3.89 g, 20.3 mmol, 1.5 equiv.) and 4-dimethylaminopyridine (2.48 g, 20.3 mmol, 1.5 equiv.). The reaction mixture was stirred for 18 hours before it was diluted with addition of CH_2Cl_2 (150 mL). The reaction solution was washed by sat. aq. NH_4Cl (3 × 50 mL). The organic phase was collected, washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (eluent: Et_2O/Hexane, 1/5) to afford compound **14b** (1.68 g, 63%, 1:1 mixture of diastereomers) as a colourless oil.

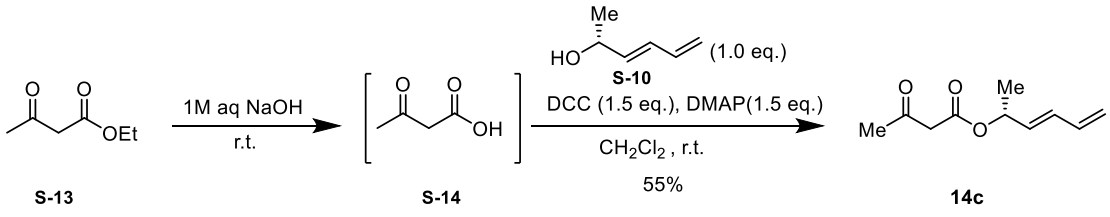
$[\alpha]_D^{25}$ = +20.70 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, CDCl3): δ 6.30 – 6.00 (m, 2H), 5.62 – 5.48 (m, 1H), 5.39 – 5.24 (m, 1H), 5.17 – 5.07 (m, 1H), 5.07 – 4.96 (m, 1H), 3.45 – 3.33 (m, 1H), 2.10 (dd, *J* = 5.8, 1.3 Hz, 3H), 1.35 – 1.11 (m, 6H).

^{13}C NMR (101 MHz, CDCl3): δ 203.0, 203.0, 169.4, 169.3, 135.6, 132.4, 132.3, 131.8, 131.7, 118.4, 71.2, 53.4, 53.4, 28.1, 28.0, 19.7, 19.6, 12.3, 12.3.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{11}H_{16}O_3+Na]^+$ 219.0992, found 219.0992.

Preparation of Compound 14c



Following the same procedure for preparation of **14a**, compound **14c** (1.03 g, 55%) was obtained as a colourless oil from ethyl acetoacetate **S-13** (2.53 g, 19.4 mmol, 1 equiv.) and alcohol **S-10** (1.01 g, 10.3 mmol, 1 equiv.).

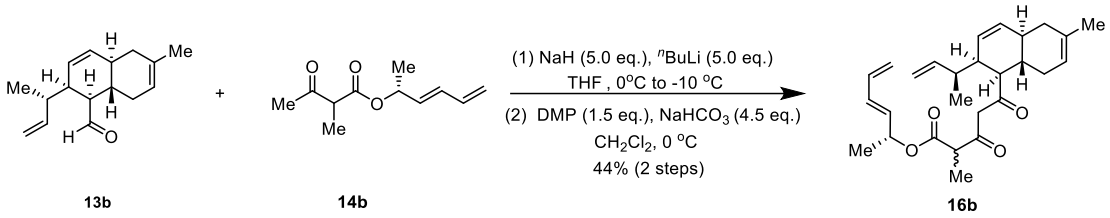
$[\alpha]_D^{25}$ = +44.90 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 – 6.16 (m, 2H), 5.70 – 5.57 (m, 1H), 5.47 – 5.34 (m, 1H), 5.25 – 5.15 (m, 1H), 5.14 – 5.04 (m, 1H), 3.39 (s, 2H), 2.21 (s, 3H), 1.30 (dd, *J* = 6.5, 2.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.4, 166.2, 135.7, 132.5, 131.9, 118.6, 71.6, 50.2, 30.0, 19.9.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{11}H_{16}O_3+Na]^+$ 205.0835, found 205.0830.

Preparation of Compound 16b



13b 14b 16b

Following the same procedure for preparation of compound **16a**, compound **16b** (45 mg, 44%) was obtained as a colourless oil from **14b** (234 mg, 1.19 mmol, 5.0 equiv.) and aldehyde **13b** (55 mg, 0.24 mmol, 1 equiv.).

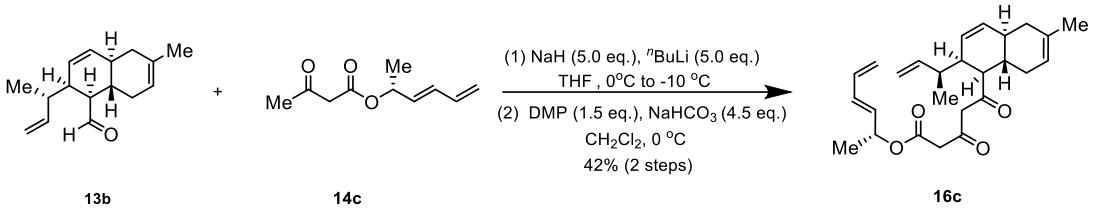
[α]$_D^{25}$ = +82.4 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 15.34 (brs, 1H), 6.36 – 6.17 (m, 2H), 5.87 – 5.73 (m, 1H), 5.70 – 5.60 (m, 3H), 5.59 – 5.52 (m, 1H), 5.50 – 5.37 (m, 1H), 5.37 – 5.31 (m, 1H), 5.30 – 5.21 (m, 1H), 5.21 – 5.06 (m, 1H), 5.00 – 4.87 (m, 2H), 3.43 – 3.32 (m, 1H), 2.55 – 2.45 (m, 2H), 2.31 (d, *J* = 17.8 Hz, 2H), 2.25 – 2.08 (m, 2H), 2.02 (d, *J* = 15.0 Hz, 1H), 2.00 – 1.93 (m, 1H), 1.83 (d, *J* = 4.2 Hz, 1H), 1.76 – 1.69 (m, 1H), 1.66 (s, 3H), 1.45 – 1.37 (m, 3H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.00 – 0.94 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$):δ 193.6, 193.5, 192.3, 192.0, 170.1, 170.0, 143.9, 135.9, 133.8, 133.8, 132.6, 132.5, 132.5, 132.5, 132.1, 132.1, 125.2, 125.1, 120.9, 120.9, 118.7, 118.7, 113.1, 100.0, 99.9, 77.3, 77.0, 76.7, 71.6, 71.5, 52.1, 49.6, 49.5, 43.2, 37.9, 37.9, 37.7, 37.3, 33.6, 33.5, 31.1, 23.3, 20.1, 19.9, 15.5, 15.4, 13.9, 13.8.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{27}H_{36}O_4+Na]^+$ 447.2506, found 447.2509.

Preparation of Compound 16c



13b 14c 16c

Following the same procedure for preparation of compound **16a**, compound **16c** (32 mg, 42%) was obtained as a colourless oil from **14c** (172 mg, 0.94 mmol, 5.0 equiv.) and aldehyde **13b** (43 mg, 0.19 mmol, 1 equiv.).

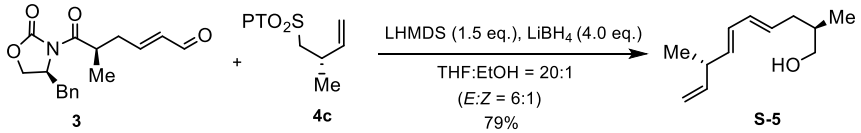
[α]$_D^{25}$ = +48.30 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 15.35 (brs, 1H), 6.37 – 6.20 (m, 2H), 5.82 (ddd, *J* = 16.8, 10.6, 6.1 Hz, 1H), 5.71 – 5.64 (m, 3H), 5.60 – 5.53 (m, 1H), 5.45 (p, *J* = 6.7 Hz, 1H), 5.35 (s, 1H), 5.32 – 5.21 (m, 1H), 5.15 (ddd, *J* = 8.8, 4.9, 1.7 Hz, 1H), 4.98 – 4.89 (m, 2H), 3.35 (d, *J* = 5.1 Hz, 2H), 2.57 – 2.47 (m, 2H), 2.35 (s, 1H), 2.30 (s, 1H), 2.07 – 1.90 (m, 3H), 1.90 – 1.77 (m, 2H), 1.35 (t, *J* = 6.7 Hz, 3H), 1.07 – 0.94 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.5, 186.9, 166.8, 143.9, 135.9, 133.8, 132.7, 132.5, 132.0, 125.1, 120.9, 118.8, 113.1, 101.6, 71.8, 52.4, 45.4, 43.1, 37.9, 37.7, 37.3, 33.6, 31.1, 23.3, 20.1, 15.4.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{26}H_{34}O_4+Na]^+$ 433.2349, found 433.2353.

Preparation of Compound S-5



3 4c S-5

To a solution of aldehyde **3** (2.58 g, 8.6 mmol, 1.0 equiv. .) and sulfone **4c**[6] (2.86 g, 10.3 mmol, 1.2 equiv. .) in 43 mL THF at -78 ℃ was added dropwise LHMDS (1.0 M in THF, 11.2 mL, 11.2 mmol, 1.3 equiv. .). The reaction mixture was stirred at -78 ℃ for 2 hours and then 2.2 mL ethanol was added. The reaction mixture was allowed to warm up to -10 ℃ and $LiBH_4$ (2.0 M in THF, 34.3 mL, 34.3 mmol, 4.0 equiv. .) was added dropwise into the reaction mixture. After the reduction was completed as

indicated by TLC (~2 hours), the reaction mixture was allowed to warm up to 0 ℃ and then quenched with 1 *N* NaOH (30 mL). The organic phase was collected and the aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel (eluent: EtOAc/hexane, 1/20) to give compound **S-5** (1.22 g, 79%) as a light yellow oil.

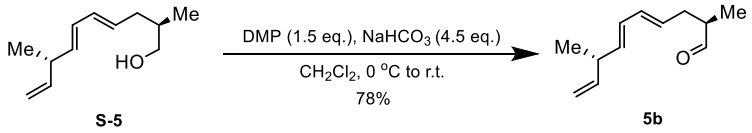
$[\alpha]_D^{25}$ = +8.20 (*c* 2, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09 – 5.89 (m, 2H), 5.85 – 5.70 (m, 1H), 5.67 – 5.47 (m, 2H), 4.98 (t, *J* = 15.1 Hz, 2H), 3.52 – 3.37 (m, 2H), 2.95 – 2.82 (m, 1H), 2.39 – 2.08 (m, 2H), 1.92 (dtt, *J* = 14.3, 7.4, 3.0 Hz, 1H), 1.77 – 1.65 (m, 1H), 1.14 – 1.05 (m, 3H), 0.94 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.4, 135.8, 131.8, 130.7, 128.9, 112.9, 67.6, 40.1, 36.4, 35.9, 19.6, 16.4.

HRMS (TOF, CI$^+$) m/z calculated for $[C_{12}H_{20}O]^+$ 180.1514, found 180.1517.

Preparation of Compound 5b



S-5 5b

To a solution of alcohol **S-5** (1.22 g, 6.8 mmol, 1.0 equiv.) in 34 mL CH_2Cl_2 at 0 ℃ were added $NaHCO_3$ (2.56 g, 30.5 mmol, 4.5 equiv.) and Dess-Martin periodinane (4.31 g, 10.2 mmol, 1.5 equiv.). The reaction mixture was stirred at 0 ℃ for 2 hours and then quenched by addition of sat. aq. $NaHCO_3$ (20 mL) and sat. aq. $Na_2S_2O_3$ (20 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: EtOAc/hexane, 1/50) to afford aldehyde **5b** (941 mg, 79%) as a pale-yellow oil.

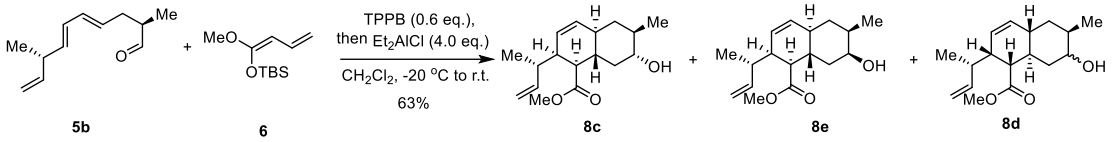
$[\alpha]_D^{25}$ = +0.20 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (d, *J* = 1.3 Hz, 1H), 6.09 – 5.85 (m, 2H), 5.81 – 5.67 (m, 1H), 5.66 – 5.44 (m, 2H), 5.01 – 4.87 (m, 2H), 2.91 – 2.78 (m, 1H), 2.54 – 2.33 (m, 2H), 2.23 – 2.06 (m, 1H), 1.07 (dd, *J* = 6.9, 2.6 Hz, 6H).

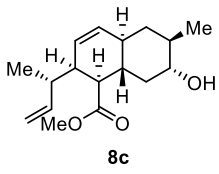
^{13}C NMR (101 MHz, $CDCl_3$): δ 204.4, 142.2, 136.7, 132.8, 128.4, 128.3, 113.0, 46.1, 40.1, 33.5, 19.5, 13.0.

HRMS (TOF, CI$^+$) m/z calculated for $[C_{12}H_{18}O]^+$ 178.1358, found 178.1356.

Preparation of Compound 8c and 8e



To a solution of aldehyde **5b** (1.16 g, 6.51 mmol, 1.0 equiv.) and compound **6** (2.79 g, 13.0 mmol, 2.0 equiv.) in 65 mL CH_2Cl_2 at -20 ℃ was added tris(pentafluorophenyl)-borane (2.00 g, 3.91 mmol, 0.6 equiv.). The reaction mixture was stirred at -20 ℃ for 30 minutes before Et_2AlCl (2.0 M in hexane, 13.0 mL, 26.0 mmol, 4.0 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 13 hours before 1.0 mL H_2O and 8.0 mL concentrated HCl was added at 0 ℃. The reaction mixture was stirred for another 10 hours before quenching by addition of 2 *N* NaOH (50 mL). The organic phase was collected and the aqueous phase was extracted by CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: EtOAc/hexane, 1/20) to afford **8c** (998 mg, 55%) as a colourless oil (mixed with **8d** inseparable, **8c**:**8d** > 3:1) and **8e** (145 mg, 8%) as a colourless oil.



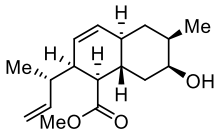
[α]$_D^{25}$ = +26.0 (*c* 0.1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 – 5.77 (m, 1H), 5.63 – 5.56 (m, 1H), 5.56 – 5.47 (m, 1H), 5.04 – 4.89 (m, 2H), 3.69 (d, *J* = 3.0 Hz, 3H), 3.34 – 3.22 (m, 1H), 2.74 – 2.64 (m, 1H), 2.64 – 2.50 (m, 1H), 2.29 – 2.19 (m, 1H), 2.19 – 2.05 (m, 1H), 1.95 – 1.80 (m, 1H), 1.80 – 1.65 (m, 2H), 1.65 – 1.51

(m, 1H), 1.51 – 1.37 (m, 1H), 1.05 (dd, *J* = 6.8, 3.2 Hz, 3H), 0.97 (dd, *J* = 7.1, 1.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.8, 143.5, 132.2, 125.3, 113.4, 76.1, 51.2, 49.4, 40.8, 40.7, 40.1, 39.4, 39.2, 38.8, 36.4, 18.3, 15.3.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{17}H_{26}O_3+Na]^+$ 301.1774, found 301.1772.



8e

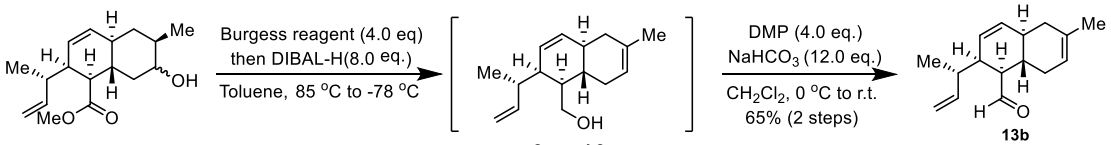
[α]$_D^{25}$ = -28.00 (*c* 0.25, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86 – 5.67 (m, 1H), 5.61 – 5.53 (m, 1H), 5.51 – 5.41 (m, 1H), 5.00 – 4.87 (m, 2H), 3.89 – 3.79 (m, 1H), 3.66 (d, *J* = 3.7 Hz, 3H), 2.66 – 2.51 (m, 2H), 2.18 – 2.06 (m, 2H), 1.95 – 1.86 (m, 1H), 1.73 – 1.64 (m, 1H), 1.64 – 1.54 (m, 1H), 1.51 – 1.41 (m, 1H), 1.30 – 1.21 (m, 1H), 1.13 – 1.06 (m, 1H), 1.05 – 1.01 (m, 1H), 0.99 – 0.94 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.0, 143.6, 133.0, 125.0, 113.2, 70.5, 51.1, 49.5, 41.3, 41.1, 38.8, 38.0, 36.9, 34.6, 31.1, 18.0, 15.5.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{17}H_{26}O_3+Na]^+$ 301.1774, found 301.1775.

Preparation of Compound 13b



8c and 8e **8c and 8e** **13b**

To a solution of **8c**/**8e** (52 mg, 0.19 mmol, 1.0 equiv.) in 9.4 mL toluene was added Burgess reagent (178 mg, 0.75 mmol, 4.0 equiv.). The reaction mixture was heated to 85 ℃ for 2 hours. It was cooled to -78 ℃ and DIBAL-H (1.0 M in hexane, 1.5 mL, 1.5 mmol, 8.0 equiv.) was added dropwise. After stirring for 2 hours, the reaction was quenched by addition of 1 *N* HCl (10 mL). The organic phase was collected and the aqueous phase was extracted by EtOAc (3 × 15 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue in 1.9 mL CH_2Cl_2 was cooled to 0 ℃ and $NaHCO_3$ (189 mg, 2.25 mmol, 12.0 equiv.) and Dess-Martin periodinane (359 mg, 0.85 mmol, 4.5

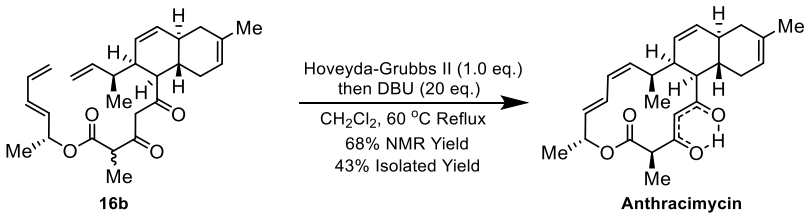
equiv.) were added. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 hours before quenching with sat. aq. $NaHCO_3$ (1 mL) and sat. aq. $Na_2S_2O_3$ (2 mL). The organic phase was collected and the aqueous phase was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: EtOAc/hexane, 1/50) to afford aldehyde **13b** (31 mg, 65%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 – 9.81 (m, 1H), 5.83 – 5.70 (m, 1H), 5.66 – 5.63 (m, 1H), 5.40 – 5.31 (m, 1H), 5.06 – 4.91 (m, 2H), 2.74 – 2.62 (m, 1H), 2.51 – 2.37 (m, 2H), 2.37 – 2.23 (m, 1H), 2.08 – 1.88 (m, 3H), 1.88 – 1.77 (m, 1H), 1.67 (dd, *J* = 2.6, 1.4 Hz, 3H), 1.64 – 1.55 (m, 1H), 1.07 (dd, *J* = 6.9, 0.8 Hz, 1H), 1.01 (dd, *J* = 7.0, 2.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 205.5, 143.7, 134.1, 132.4, 126.0, 120.4, 114.2, 55.8, 41.8, 39.2, 37.5, 36.9, 32.7, 30.7, 23.4, 17.1.

HRMS (TOF, ES$^-$) m/z calculated for $[C_{17}H_{24}O_2\text{-}H]^+$ 229.1587, found 229.1601.

Preparation of Anthracimycin



The solution of compound **16b** (45 mg, 0.11 mmol, 1.0 equiv.) in 21 mL CH_2Cl_2 was degassed with argon sparging for 5 minutes and the Hoveyda Grubbs II catalyst (67 mg, 0.11 mmol, 1.0 equiv.) was added. The reaction mixture was heated to reflux for 3 hours and then cooled to room temperature. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.32 mL, 2.14 mmol, 20.0 equiv.) was added to the reaction mixture, which was stirred at room temperature for another 30 minutes. The solvent was removed under reduced pressure to provide the crude anthracimycin with 68% yield based on ^{1}H NMR analysis using 1,3,5-trimethoxybenzene (6 mg, 0.036 mmol, 0.33 equiv.) as the internal standand. The crude anthracimycin was purified by column

chromatography on reversed-phase silica gel (water/acetonitrile, 10:1 to 0:1) to afford anthracimycin (18 mg, 43%) as a light brown solid. For biological testing, the sample was further purified by the reverse-phase HPLC (Phenomenex Luna ® C18 column, 100 Å, 250 x 4.6 mm, 5μm) using a gradient of H_2O: MeCN = 10:90 over 1 hour, the flow rate was 1 mL/min, with UV detection under 280nm wavelength (Waters 2998 Photodiode Array Detector; Milford, USA). Pure anthracimycin (11 mg) was collected at 44.0 min as a white solid. Total 25 mg of anthracimycin was obtained from two batches. A single crystal suitable for X-Ray diffraction analysis was obtained (see page 36) with CCDC deposition number 2194803.

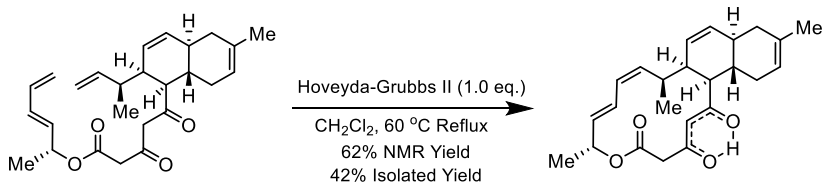
$[\alpha]_D^{25}$ = -144.00 (*c* 1, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 15.45 (s, 1H), 6.53 – 6.38 (m, 1H), 5.96 (s, 1H), 5.87 (t, *J* = 11.1 Hz, 1H), 5.72 (d, *J* = 10.2 Hz, 1H), 5.60 – 5.51 (m, 3H), 5.46 – 5.32 (m, 2H), 3.53 (q, *J* = 6.9 Hz, 1H), 2.75 – 2.49 (m, 3H), 2.39 (d, *J* = 17.4 Hz, 1H), 2.11 – 1.88 (m, 3H), 1.81 (d, *J* = 7.1 Hz, 1H), 1.67 (s, 3H), 1.57 – 1.49 (m, 1H), 1.45 – 1.37 (m, 3H), 1.34 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 194.2, 190.8, 168.9, 139.1, 134.0, 133.0, 131.7, 126.1, 124.9, 123.8, 121.0, 103.0, 70.0, 52.7, 49.2, 46.0, 37.5, 37.4, 33.0, 32.8, 31.4, 23.5, 21.0, 16.4, 11.8.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{25}H_{32}O_4+Na]^+$ 419.2193, found 419.2197.

Preparation of Anthracimycin B



16c **AnthracimycinB**

Following the same procedure for preparation of anthracimycin, anthracimycin B (7 mg, 42% yield; 62% NMR yield) was obtained from compound **16c** (18 mg, 0.04 mmol, 1.0 equiv.) and Hoveyda Grubbs II catalyst (28 mg, 0.04 mmol, 1.0 equiv.) as a light green solid. Anthracimycin B was further purified by reverse-phase HPLC (Phenomenex Luna ® C18 column, 100 Å, 250 x 4.6 mm, 5μm) using a gradient of

H_2O: MeCN =10:90 over 1 hour, the flow rate was 1 mL/min, with UV detection under 280nm wavelength (Waters 2998 Photodiode Array Detector; Milford, USA). Anthracimycin B (4.5 mg) as a white solid was collected at 45.7 min. Total 14 mg of anthracimycin B was obtained from two batches.

$[\alpha]_D^{25}$ = -169.00 (*c* 0.45, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 15.37 (s, 1H), 6.50 – 6.47 (m, 1H), 5.96 (s, 1H), 5.90 (t, *J* = 10.7 Hz, 1H), 5.73 (d, *J* = 10.0 Hz, 1H), 5.57 – 5.54 (m, 3H), 5.42 – 5.37 (m, 2H), 3.50 (d, *J* = 11.5 Hz, 1H), 3.22 (d, *J* = 11.4 Hz 1H), 2.63 – 2.61 (m, 3H), 2.43 (d, *J* = 17.4 Hz, 1H), 2.05 – 2.02 (m, 2H), 1.99 – 1.90 (m, 1H), 1.87 – 1.74 (m, 1H), 1.67 (s, 3H), 1.51 (d, *J* = 24.0 Hz, 1H), 1.35 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.5, 184.8, 165.4, 138.9, 133.8, 133.0, 131.3, 125.9, 124.6, 123.5, 120.9, 102.8, 70.0, 53.1, 46.5, 45.5, 37.3, 37.3, 32.8, 32.7, 31.2, , 23.4, 20.7, 16.2.

HRMS (TOF, ES$^+$) m/z calculated for $[C_{24}H_{30}O_4+Na]^+$ 405.2036, found 405.2040.

NMR comparison of natural and synthetic anthracimycin and anthracimycin B

Table S1 ^{1}H NMR comparison of natural and synthetic Anthracimycin

Natural sample[7] δ_H **(500 MHz, $CDCl_3$)**	**Brimble's synthetic sample[2]** δ_H **(500 MHz, $CDCl_3$)**	**Our synthetic sample** δ_H **(400 MHz, $CDCl_3$)**
Not observed	15.45 (brs)	15.45 (brs)
6.45 (dd, 15.2, 11.0)	6.46 (ddd, 15.4, 11.6, 1.8)	6.46 (m)
5.96 (s)	5.96 (s)	5.96 (s)
5.87 (dd, 11.0, 10.5)	5.87 (app. t, 10.9)	5.87 (t, 11.1)
5.71 (d, 10.0)	5.72 (d, 10.4)	5.72 (d, 10.2)
5.57 (dq, 6.5, 2.4)	5.58-5.56 (m) [b]	5.60 – 5.51 (m) [b]
5.56 (dd, 15.2, 2.4)	5.58-5.56 (m) [b]	5.60 – 5.51 (m) [b]
5.53 (dd, 10.0, 5.0)	5.54-5.52 (m)	5.60 – 5.51 (m) [b]
5.40 (dd, 10.5, 9.8)	5.40 (app. t, 9.4)	5.48 – 5.32 (m)
5.36 (brd, 4.5)	5.36 (brd, 4.6)	5.48 – 5.32 (m)
3.53 (q, 7.0)	3.53 (q, 7.0)	3.53 (q, 6.9)
2.64 [a]	2.66-2.57 (m) [b]	2.75 – 2.49 (m) [b]
2.60 [a]	2.66-2.57 (m) [b]	2.75 – 2.49 (m) [b]
2.58 (11.8, 6.7)	2.66-2.57 (m) [b]	2.75 – 2.49 (m) [b]
2.39 (ddd,16.0, 4.5, 4.5)	2.39 (brd, 18.6)	2.39 (d, 17.4)
2.02 (dd, 16.5, 4.0)	2.03 (brd, 5.3)	2.11 – 1.88 (m) [b]
1.98 (ddd, 14.5, 12.5, 11.8)	2.00-1.97 (m)	2.11 – 1.88 (m) [b]
1.93 (m)	1.93 (dd, 10.6, 4.2)	2.11 – 1.88 (m) [b]
1.82 (dd, 16.5, 10.3)	1.85-1.81 (m)	1.81 (d, 7.1)
1.67 (s)	1.67 (s)	1.67 (s)
1.52(ddd, 16.0, 10.5, 4.5)	Not observed [c]	1.57 – 1.49 (m)
1.39 (d, 7.0)	1.40 (d, 6.8)	1.45 – 1.37 (m)
1.33 (d, 6.5)	1.34 (d, 6.8)	1.34 (d, 6.7)
0.94 (d, 7.0)	0.95 (d, 6.6)	0.95 (d, 6.6)

[a]The coupling constant was not measured because of overlapping signals

[b]Unresolved signals

[c] Not observed due to overlapping water signal.

Table S2 ^{13}C NMR comparison of natural and synthetic Anthracimycin

Natural sample[7] δ_C **(125 MHz,** $CDCl_3$**)**	**Brimble's synthetic sample[2]** δ_C **(125 MHz,** $CDCl_3$**)**	**Our synthetic sample** δ_C **(101 MHz,** $CDCl_3$[a]**)**
194.1	194.2	194.2
190.9	190.8	190.8
168.9	168.9	168.9
139.1	139.1	139.1
134.0	134.0	134.0
133.0	133.0	133.0
131.7	131.7	131.7
126.1	126.1	126.1
124.9	124.9	124.9
123.7	123.8	123.8
121.0	121.0	121.0
103.0	103.0	103.0
70.0	70.0	70.0
52.6	52.7	52.7
49.2	49.2	49.2
46.0	46.0	46.0
37.5	37.5	37.5
37.4	37.4	37.4
33.0	33.0	33.0
32.8	32.8	32.8
31.4	31.4	31.4
23.5	23.5	23.5
21.0	21.0	21.0
16.4	16.4	16.4

[a] Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform 77.16 ppm for ^{13}C

Table S3 ^{1}H NMR comparison of natural and synthetic Anthracimycin B

Natural sample[8] δ_H **(500 MHz, $CDCl_3$)**	**Our synthetic sample** δ_H **(400 MHz, $CDCl_3$)**
15.35 (brs)	15.37 (brs)
6.48 (dd, 13.0, 12.7)	6.50 – 6.47 (m)
5.96 (brs)	5.96 (s)
5.88 (dd, 10.8, 10.8)	5.90H(t, 10.7)
5.73 (d, 10.0)	5.73 (d, 10.0)
5.57 (m)	5.57 – 5.54 (m)[a]
5.55 (m)	5.57 – 5.54 (m)[a]
5.40 (m)	5.42 – 5.37 (m)[a]
5.37 (m)	5.42 – 5.37 (m)[a]
3.50 (d, 11.3)	3.50 (d, 11.5)
3.22 (d, 11.3)	3.22 (d, 11.4)
2.65 (m)	2.63-2.61 (m)[a]
2.64 (m)	2.63-2.61 (m)[a]
2.63 (m)	2.63-2.61 (m)[a]
2.42 (brd, 15.4)	2.43 (d, 17.4)[a]
2.05 (m)	2.05-2.02 (m)[a]
1.99 (m)	1.99-1.90 (m)[a]
1.96 (m)	1.96-1.93 (m)[a]
1.82 (brd, 16.9)	1.87-1.74 (m)[a]
1.68 (s)	1.67 (s)
1.51 (m)	1.51 (m)
1.35 (d, 6.7)	1.35 (d, 6.6)
0.95 (d, 6.0)	0.95 (d, 6.6)

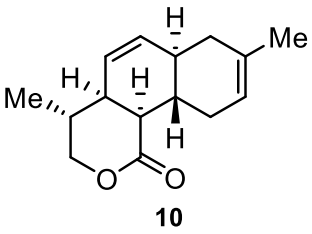
[a]Unresolved signals

Table S4 ^{13}C NMR comparison of natural and synthetic Anthracimycin

Natural sample[8] δ_C **(125 MHz, $CDCl_3$)**	**Our synthetic sample** δ_C **(101 MHz, $CDCl_3$ [a])**
196.5	196.5
184.7	184.8
165.5	165.4
139.0	138.9
133.8	133.8
133.0	133.0
131.3	131.3
125.9	125.9
124.6	124.6
123.6	123.5
120.9	120.9
102.8	102.8
70.0	70.0
53.1	53.1
46.5	46.5
45.5	45.5
37.3	37.3
37.3	32.3
32.9	32.8
32.7	32.7
31.2	31.2
23.4	23.4
20.7	20.7
16.3	16.2

[a] Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform 77.00 ppm for ^{13}C

X-Ray Crystal Structure of compound 10



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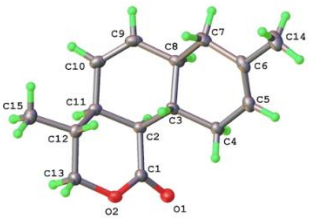
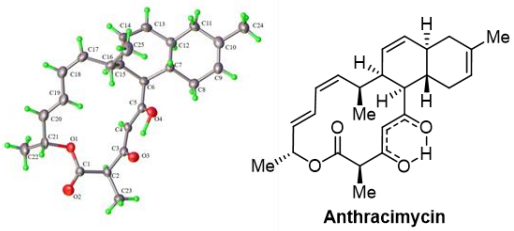


(Probabililty ellipsoid level: 40%; CCDC Deposition Number 2175241)

Compound	**ptian3CuLT**
Formula	$C_{15}H_{20}O_2$
$D_{calc.}$/ g cm^{-3}	1.204
m/mm^{-1}	0.615
Formula Weight	232.31
Colour	colourless
Shape	needle
Size/mm^3	0.40×0.08×0.07
T/K	99.97(10)
Crystal System	orthorhombic
Flack Parameter	0.12(9)
Hooft Parameter	0.12(9)
Space Group	$P2_12_12_1$
a/Å	5.60939(10)
b/Å	10.26643(19)
c/Å	22.2551(4)
a/°	90
b/°	90
g/°	90
V/Å^3	1281.64(4)
Z	4
Z′	1
Wavelength/Å	1.54184
Radiation type	CuK_a
Q_{min}/°	3.973
Q_{max}/°	76.640
Measured Refl.	7631
Independent Refl.	2639
Reflections with I > 2(I)	2612
R_{int}	0.0230
Parameters	156
Restraints	0
Largest Peak	0.426
Deepest Hole	-0.170
GooF	1.057
wR_2 (all data)	0.0912
wR_2	0.0910
R_1 (all data)	0.0351
R_1	0.0348



Anthracimycin

(Probabililty ellipsoid level: 50%; CCDC Deposition Number 2194803)

Crystal data and structure refinement	
Identification code	pre_Dr. WANG_s sample_auto
Empirical formula	$C_{25}H_{32}O_4$
Formula weight	396.50
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.5419(2)
b/Å	15.3789(5)
c/Å	25.7913(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2198.15(13)
Z	4
ρ_{calc}g/cm^3	1.198
μ/mm^{-1}	0.634
F(000)	856.0
Crystal size/mm^3	0.12 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.95 to 155.176
Index ranges	$-6 \le h \le 6$, $-18 \le k \le 9$, $-31 \le l \le 31$
Reflections collected	7767
Independent reflections	3739 [R_{int} = 0.0906, R_{sigma} = 0.0855]
Data/restraints/parameters	3739/0/270
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0709, wR_2 = 0.1844
Final R indexes [all data]	R_1 = 0.0797, wR_2 = 0.1917
Largest diff. peak/hole / e Å^{-3}	0.42/-0.38
Flack parameter	-0.1(3)

An issue was encountered during data collection for this crystal because the crystal specimen was decaying fast.

Antibacterial assays

The antibacterial activity of anthracimycin and anthracimycin B was examined with several pathogenic strains including gram-negative strains--*A. baumannii* B-65371, *E. cloacae* NRRL-B-425, *E. coli* k12, *K. pneumoniae* NRRL-B-408, and gram-positive strains-- MRSA ATCC 43300, MRSA ATCC 29213, MRSA Sa115, *S. aureus* ATCC 25923, *S. aureus* R22952, *B. subtilis* zk31 and *Micrococcus luteus* ATCC 10040. The minimal inhibition concentration (MIC) was determined using the broth microdilution method according to CLSI guidelines. The tested bacteria were overcultured and inoculated into $1x10^5$ CFU/mL in MHB media; samples were injected into 96-well plates with different concentrations. Plates were incubated at 37 °C for 24 hours.

The minimum biofilm inhibitory concentration (MBIC) was measured by MTT (3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) staining assays. Similar to cytotoxicity tests, MTT could be reduced from bright yellow to blueviolet formazan. The color intensity was correlated to the number of live cells in the remaining biofilm, which dissolves in DMSO and can be quantified with 550 nm wavelength. The overnight cultured MRSA ATCC 29213 was diluted into $1x10^7$CFU/mL in LB broth with 0.5% glucose. Compounds with different concentration gradient were injected in to the diluted cultures in 96-well plates and incubated for 24 hours at 37 °C. Then each well was rinsed with 1X PBS in order to remove the planktonic and non-adhering cells. Inject 20 uL of MTT(5mg/mL) and 80 uL of 1X PBS to each well and keep incubation for another 2 hours, 100 uL DMSO was then added to dissolve the formazan. MBIC was determined as the minimum concentration with no violet color development.

Vancomycin Anthricimycin Anthricimycin B.

↓ ↓ ↓

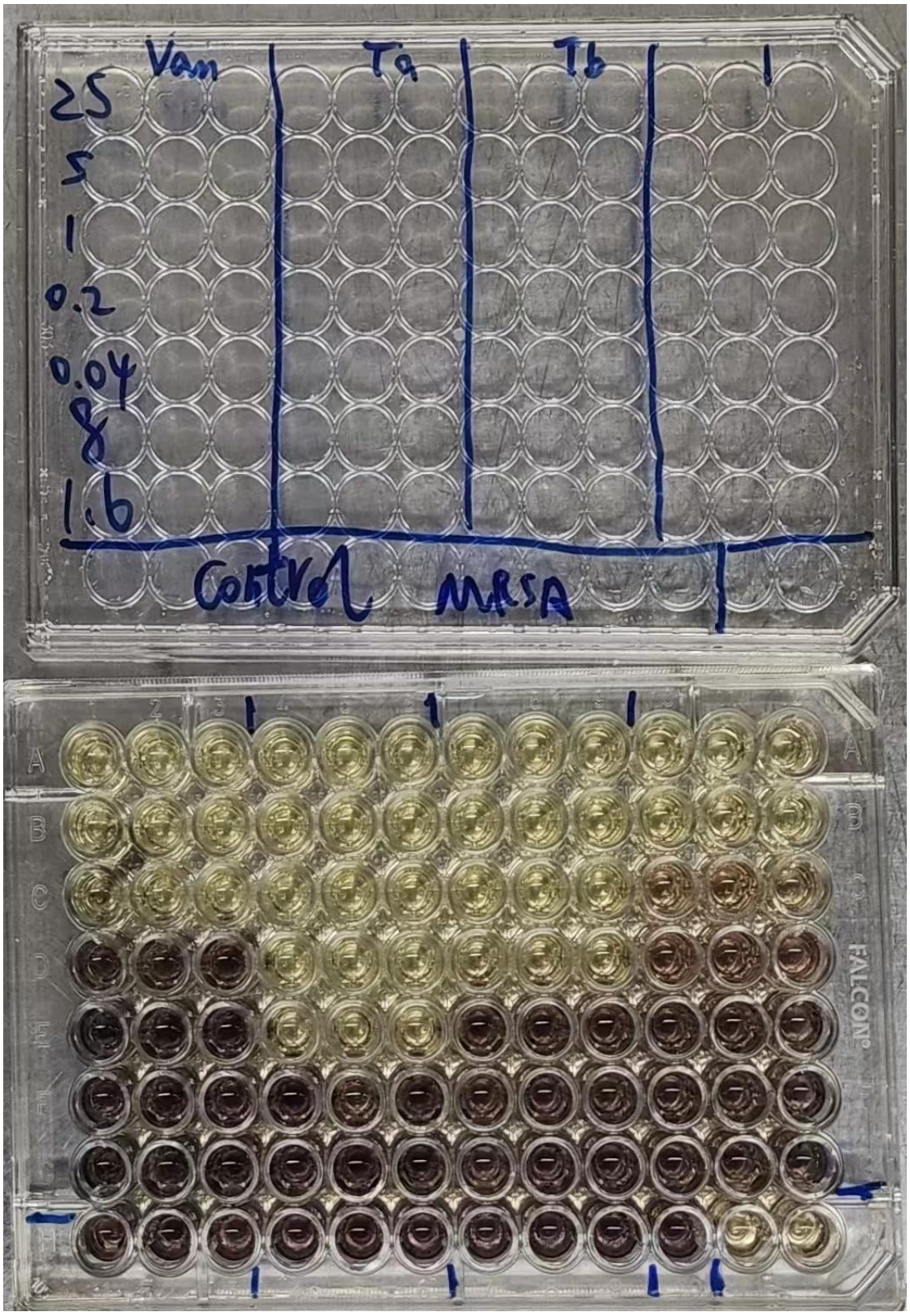


Figure S1. Inhibition effect of anthracimycins on biofilm formation

Cytotoxicity assays

Human epidermal keratinocyte cell line HaCaT cells were used in the MTT assays to evaluate samples' cytotoxicities. Cells were grown in DMEM with 10% fetal bovine serum and 1% penicillin and streptomycin at 37 °C with 5% CO_2. Each well of the 96-well plates was seeded with $5x10^3$ cells and incubated for 1 day. Then injection of compounds into each well achieved different concentrations and cultured for another 24 hours. After injecting 20uL of 5mg/mL MTT into each well for 3 hours at 37 °C, the culture liquid was removed and 100 uL DMSO was added to dissolve formazan MTT. The absorbance was measured at 570 nm wavelength using the Multiskan^{TM} FC microplate photometer, and the IC_{50} data was analyzed using GraphPad Prism software.

Table S5 Antimicrobial and cytotoxic activities of compounds

Strains/Cells	Anthracimycin (μg/mL)	Anthracimycin B (μg/mL)	vancomycin (μg/mL)
A. baumannii B65371 (-)	>40	>40	>40
E.cloacae NRRL-B-425 (-)	>40	>40	>40
E. coli K12 (-)	>40	>40	>40
K. pneumoniae NRRL-B-408 (-)	>40	>40	>40
MRSA ATCC43300 (+)	0.03	0.7	0.8
MRSA ATCC29213 (+)	0.04	1.0	0.4
MRSA ATCC29213 Biofilm	0.02	0.6	1.2
MRSA Sa115 (+)	0.04	1.0	0.4
S. aureus ATCC 25923 (+)	0.04	0.3	0.8
S. aureus R2952 (+)	0.04	1.0	0.4
B. subtilis zk31 (+)	0.04	0.5	0.07
M. luteus ATCC 10040 (+)	0.02	0.8	1.6
HaCaT cells	14.74	14.90	

Note: (-) represents Gram-negative strains, and (+) for positive. The experimental results are expressed as MIC, MBIC and IC_{50} (ug/mL). All the bioactivity assays of compounds were performed three times. In antimicrobial experiments, kanamycin and vancomycin were used as positive controls.

References:

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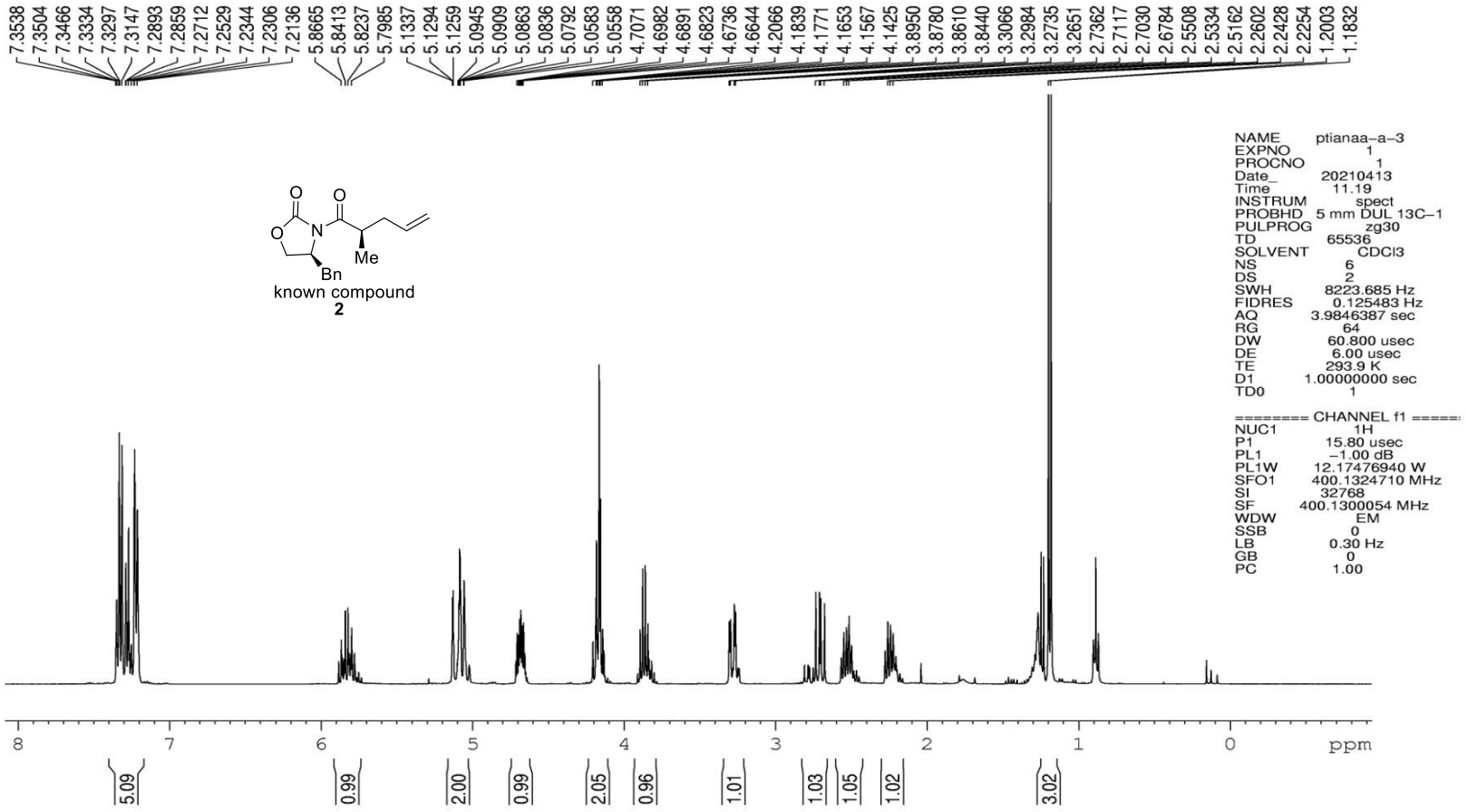
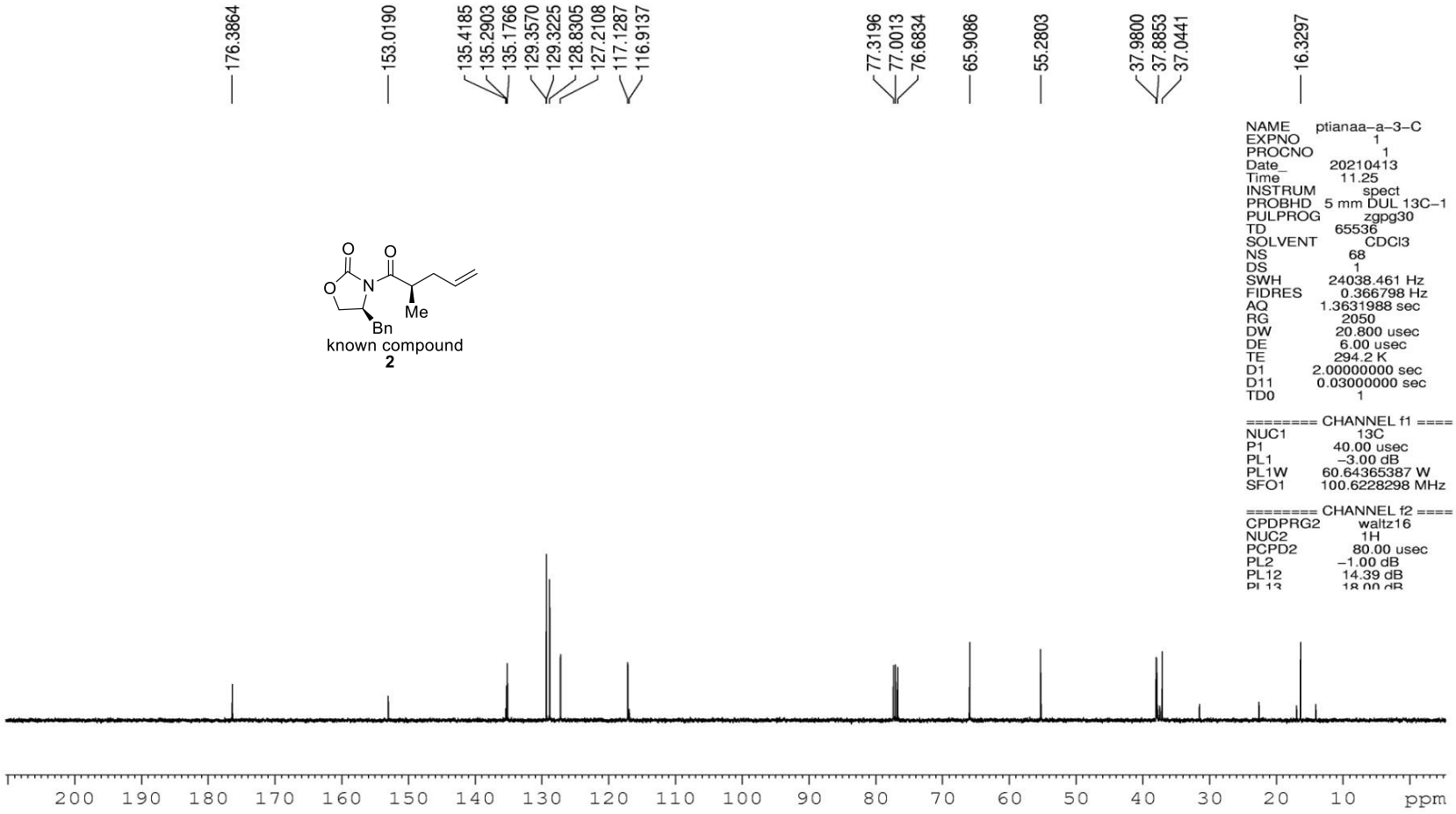
^{1}H and ^{13}C NMR Spectra

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D11 0.03000000 sec
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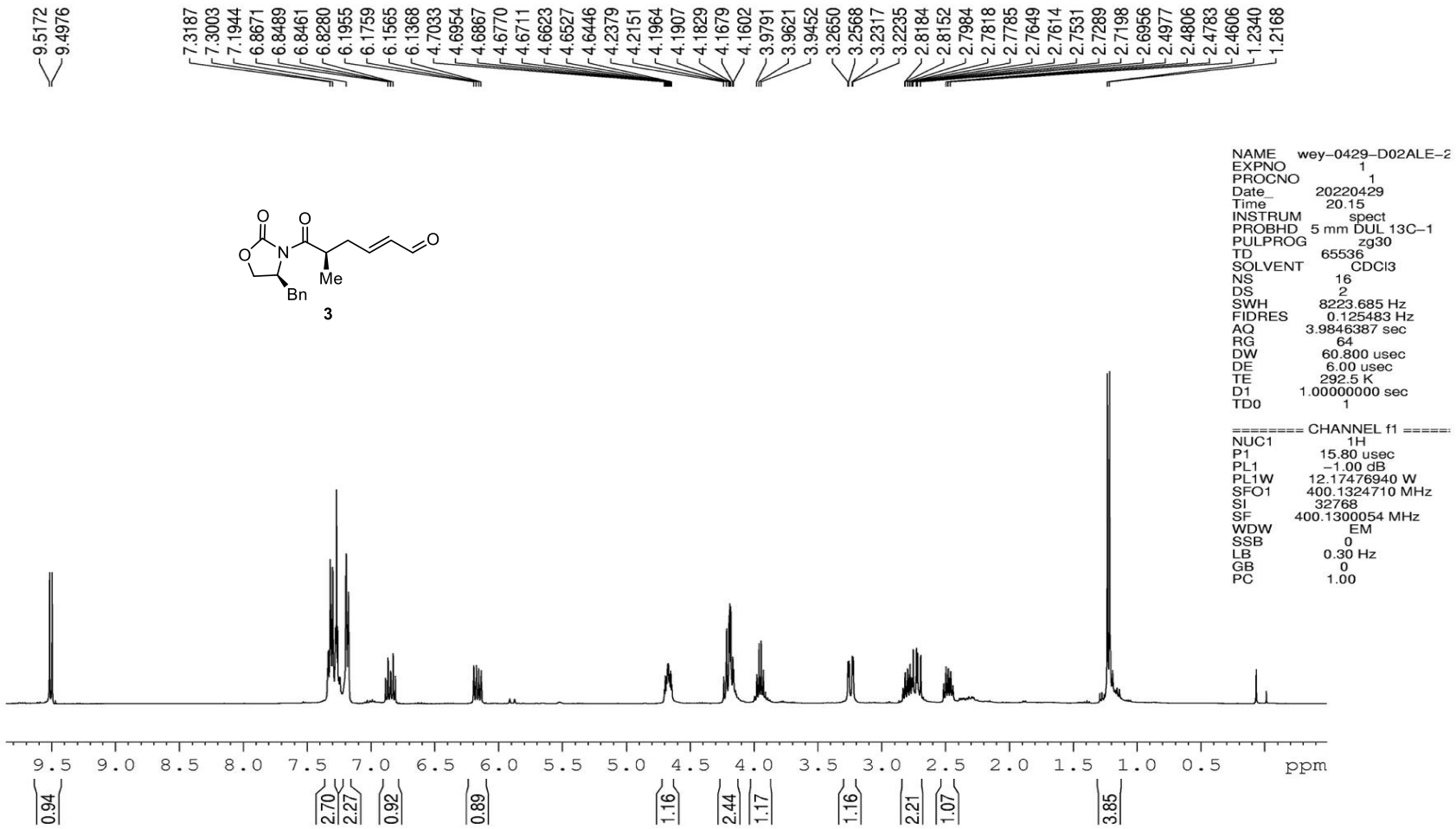
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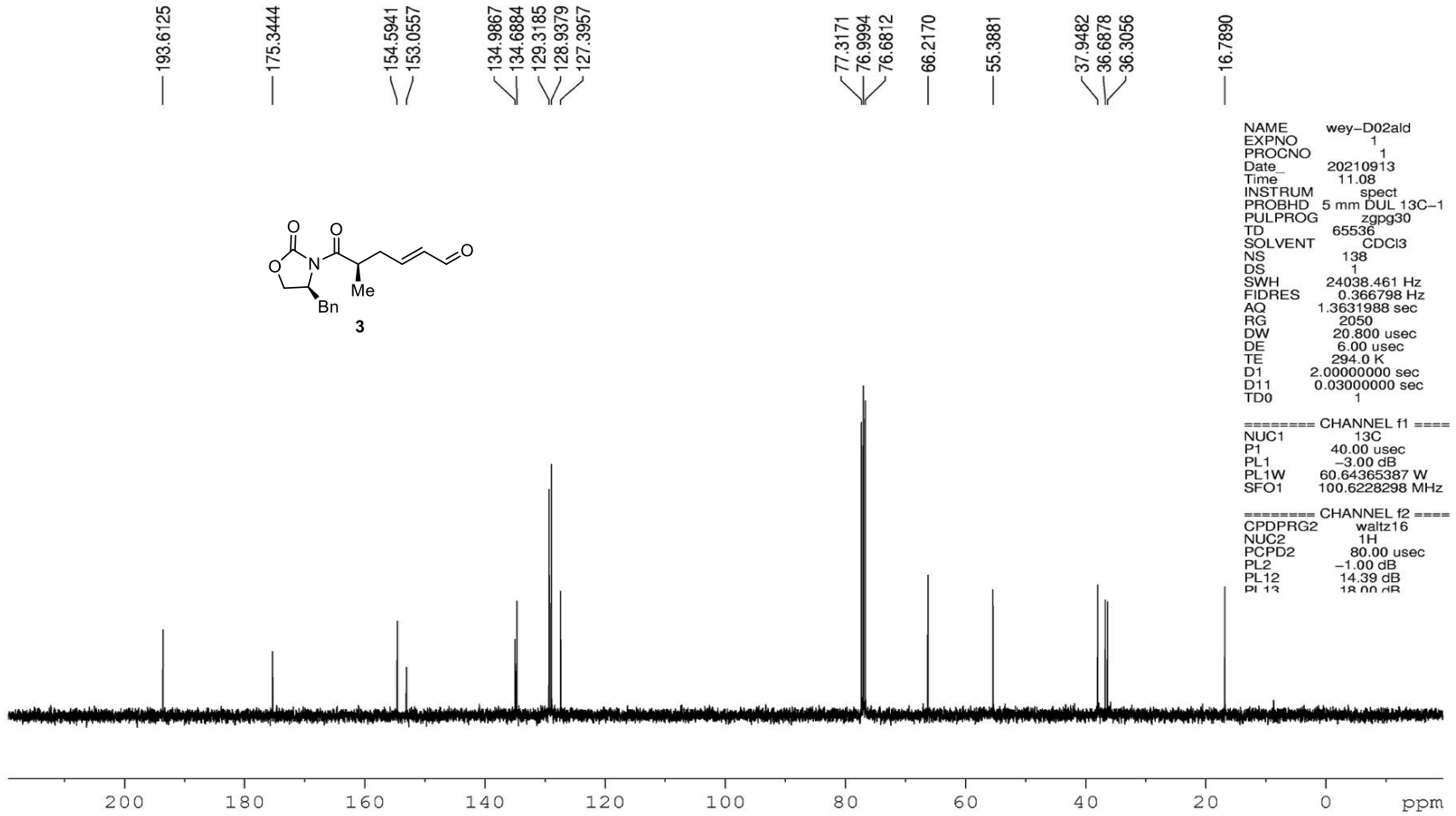
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D11 0.03000000 sec
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PL1 -3.00 dB
PL1W 60.64365387 W
SFO1 100.6228298 MHz
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NUC2 1H
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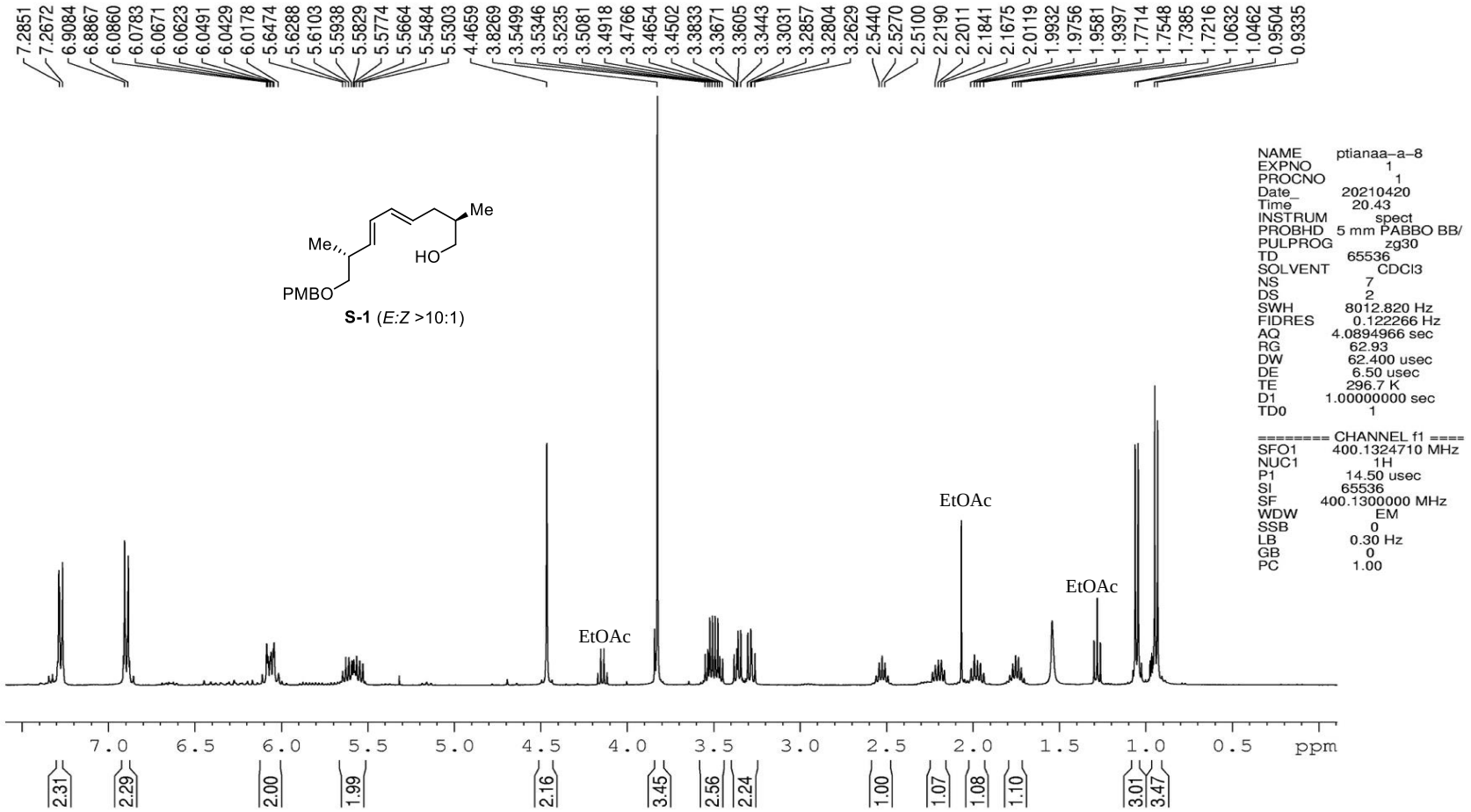
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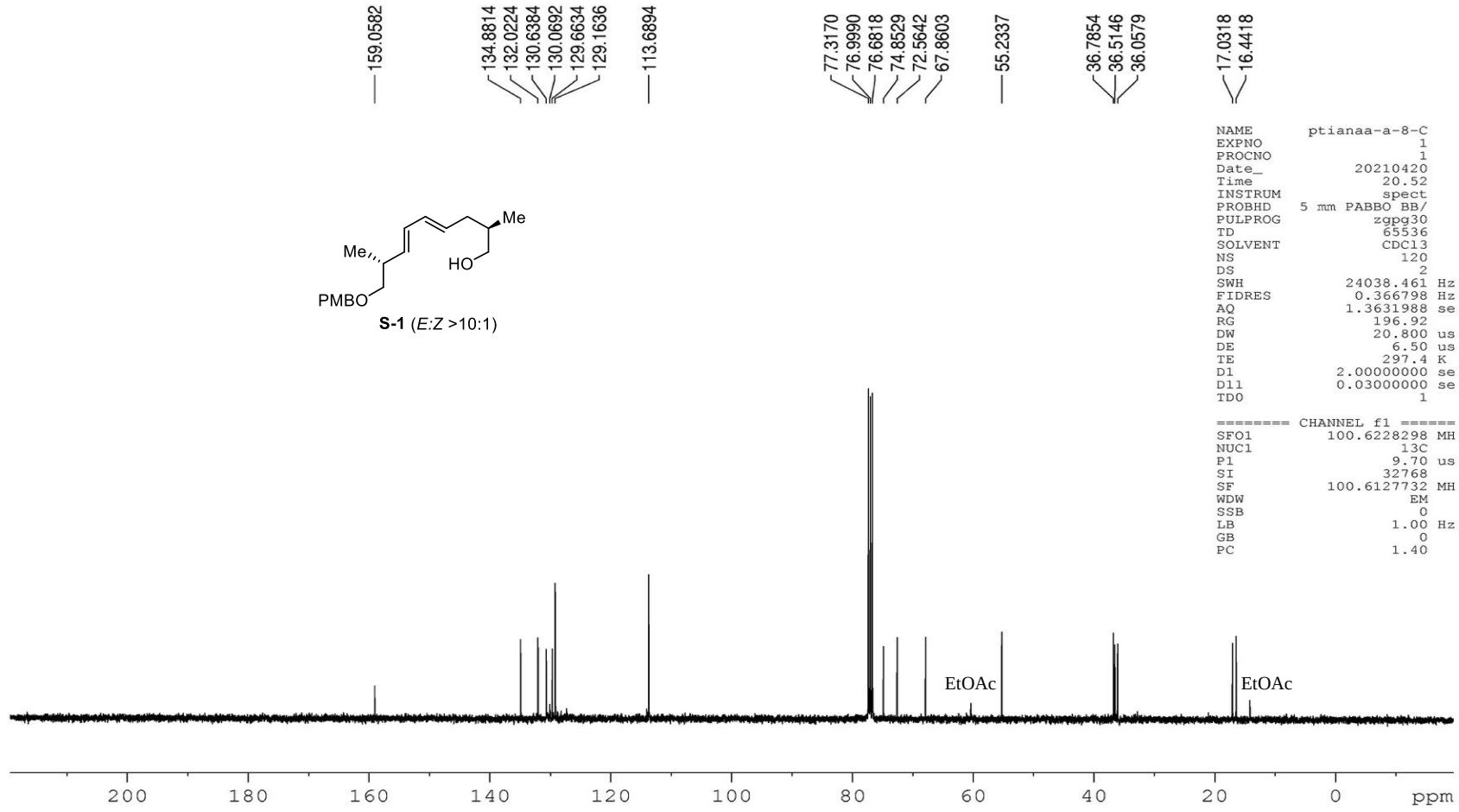
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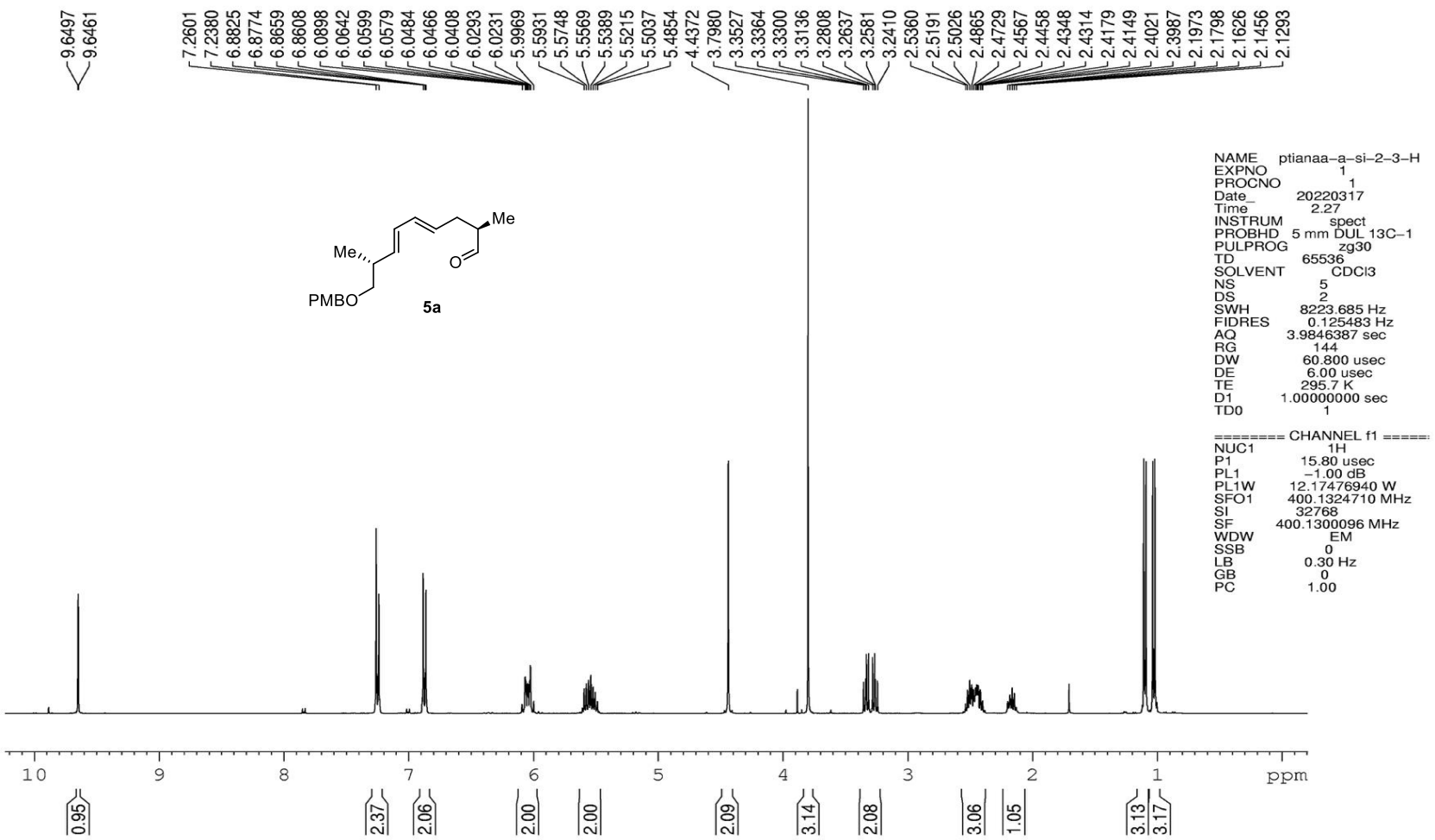
TE 297.4 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127732 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
EtOAc
EtOAc
200
180
160
140
120
100
80
60
40
20
0
ppm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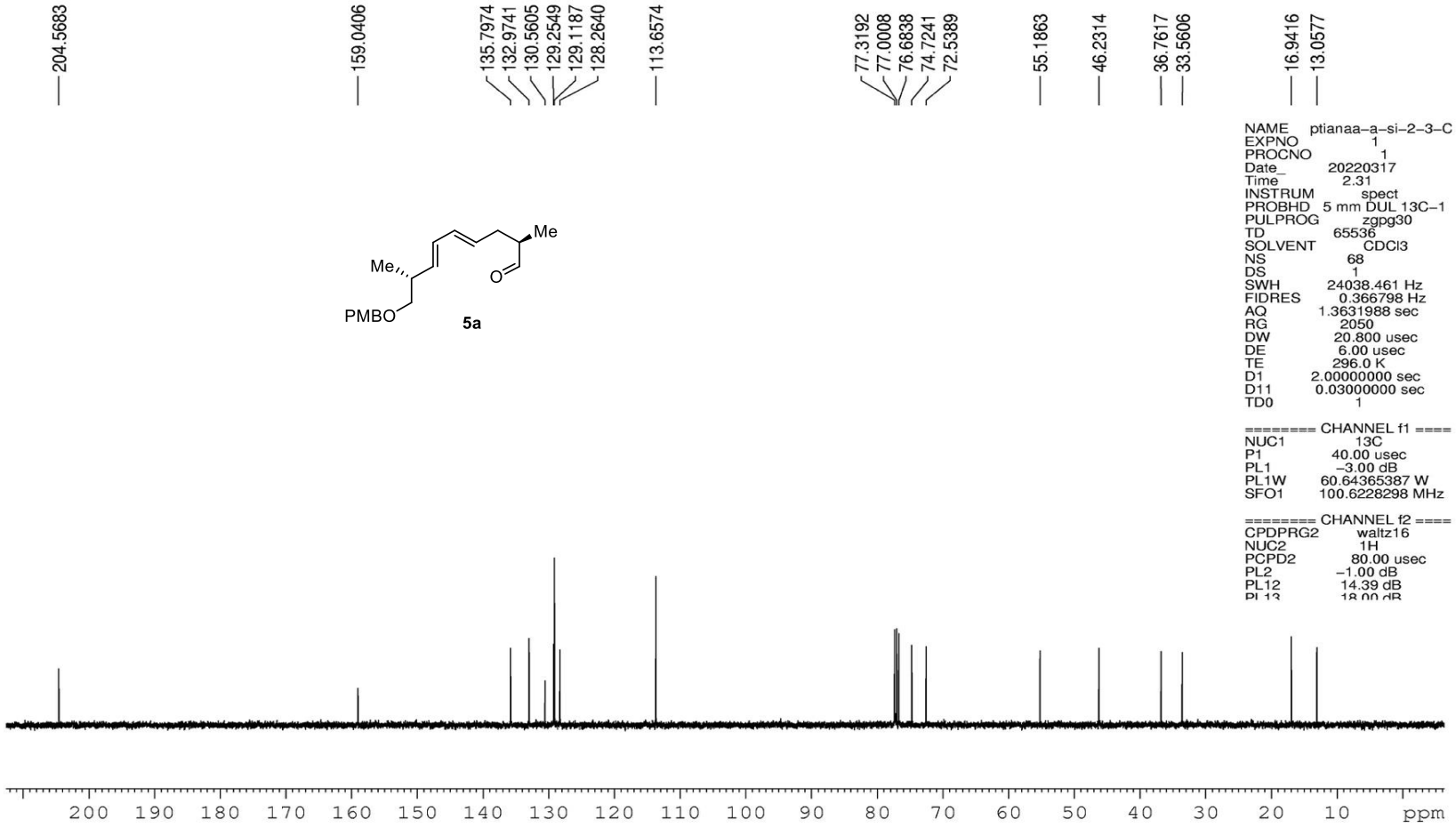
7.2380
6.8825
6.8774
6.8659
6.8608
6.0898
6.0642
6.0599
6.0579
6.0484
6.0466
6.0408
6.0293
6.0231
5.9969
5.5931
5.5748
5.5569
5.5389
5.5215
5.5037
5.4854
4.4372
3.7980
3.3527
3.3364
3.3300
3.3136
3.2808
3.2637
3.2581
3.2410
2.5360
2.5191
2.5026
2.4865
2.4729
2.4567
2.4458
2.4348
2.4314
2.4179
2.4149
2.4021
2.3987
2.1973
2.1798
2.1626
2.1456
2.1293
Me
Me
O
PMBO
5a
NAME ptianaa-a-si-2-3-H
EXPNO 1
PROCNO 1
Date_ 20220317
Time 2.27
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 144
DW 60.800 usec
DE 6.00 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
ppm
0.95
2.37
2.06
2.00
2.00
2.09
3.14
2.08
3.06
1.05
3.13
3.17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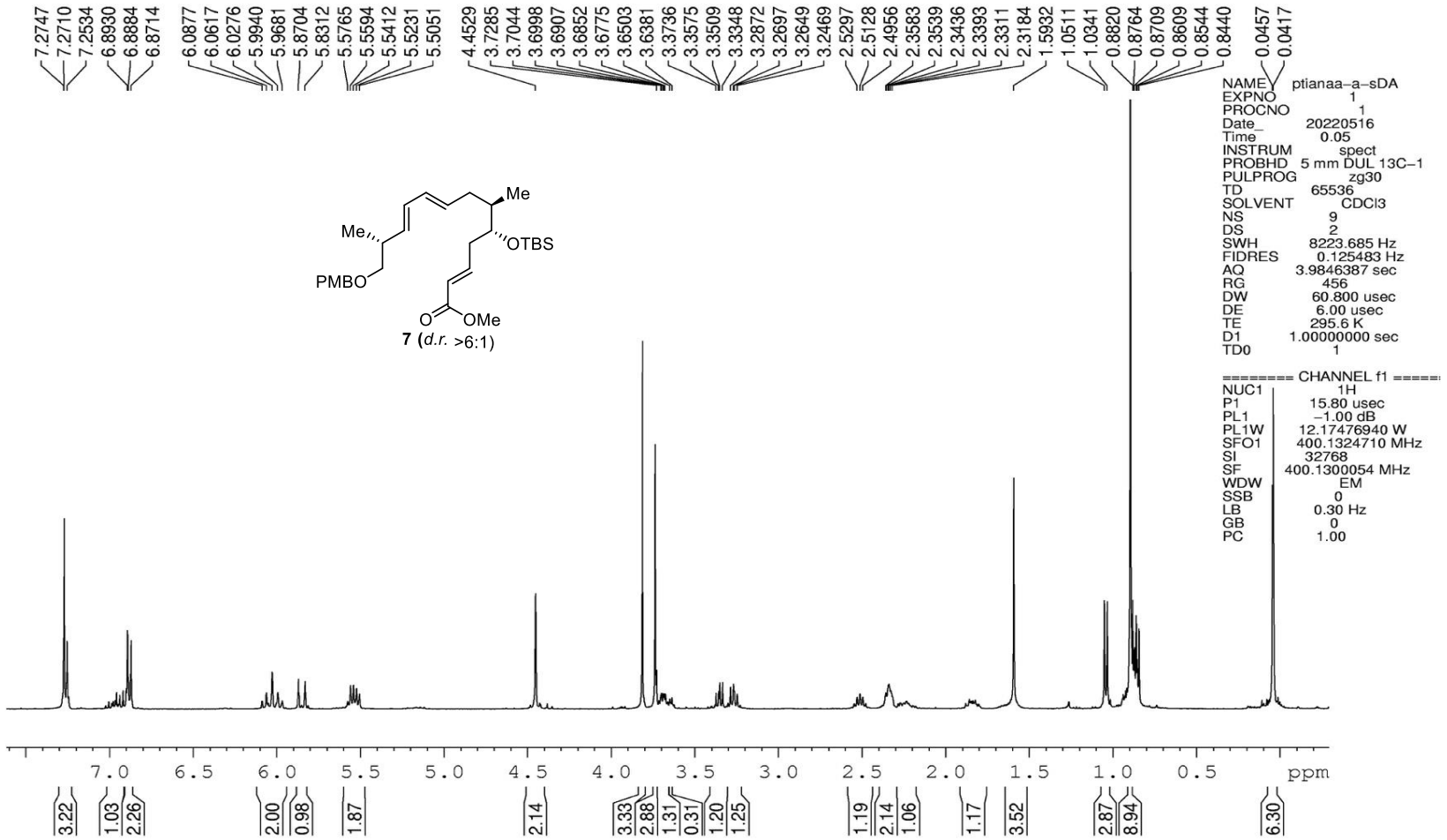
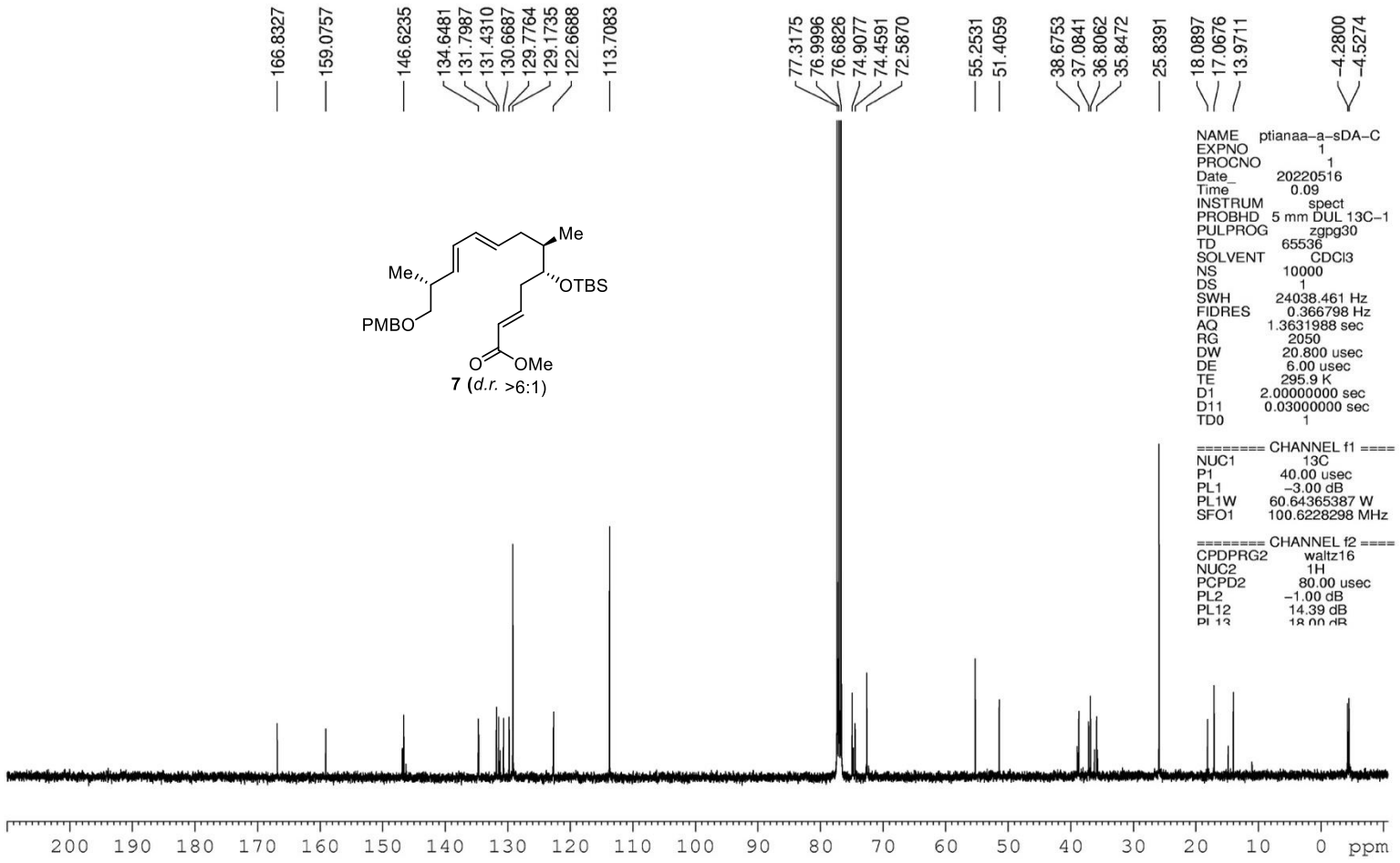
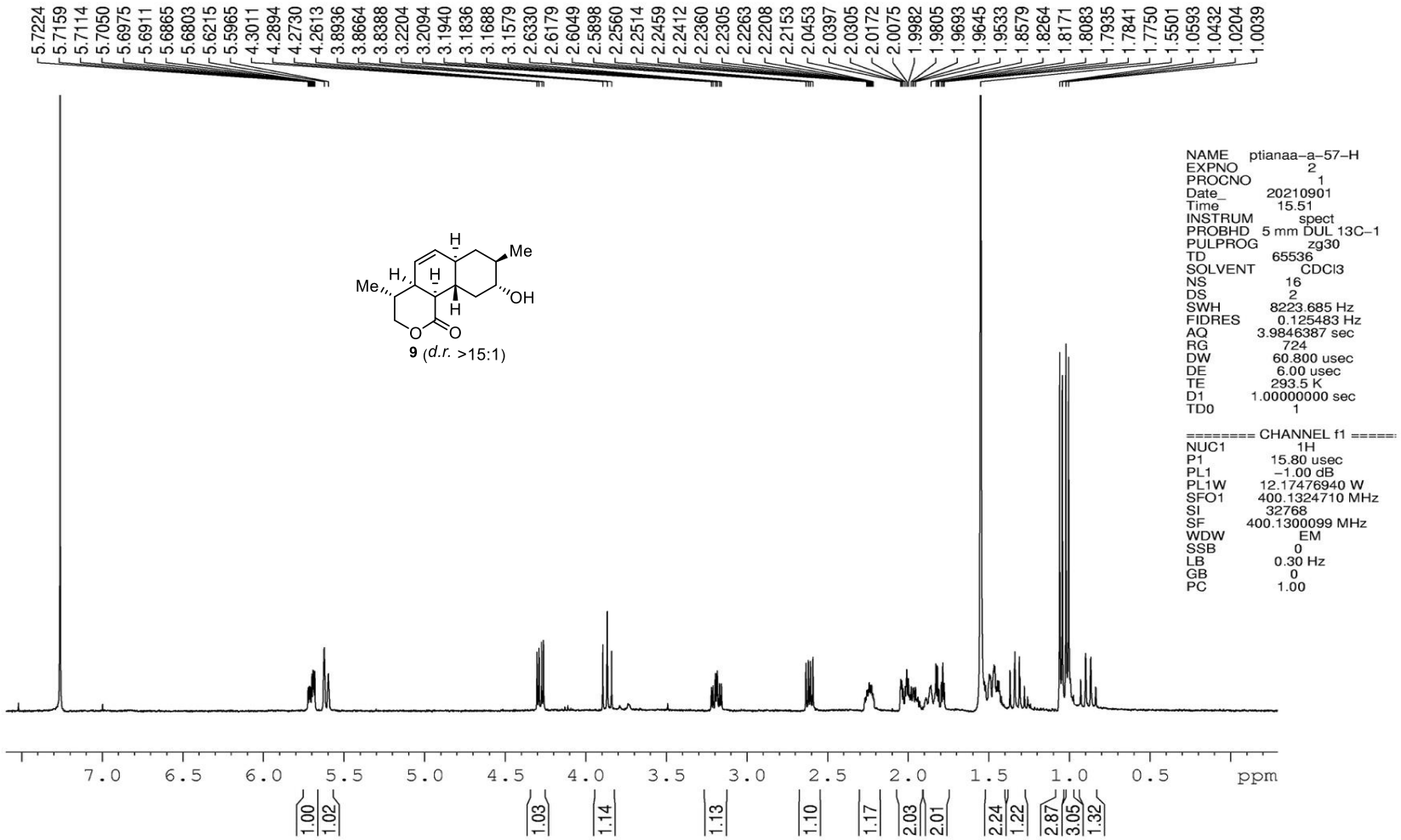
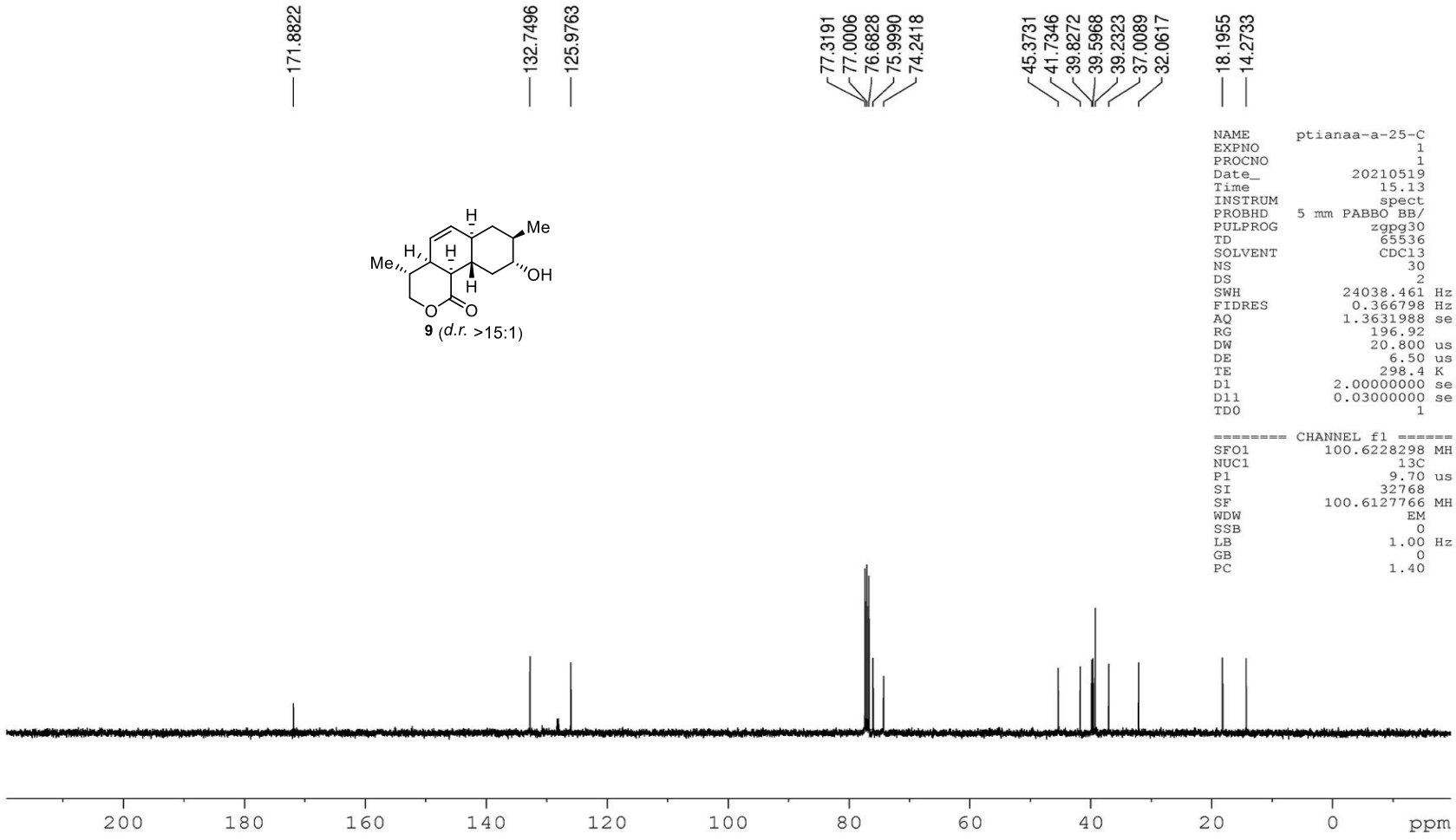
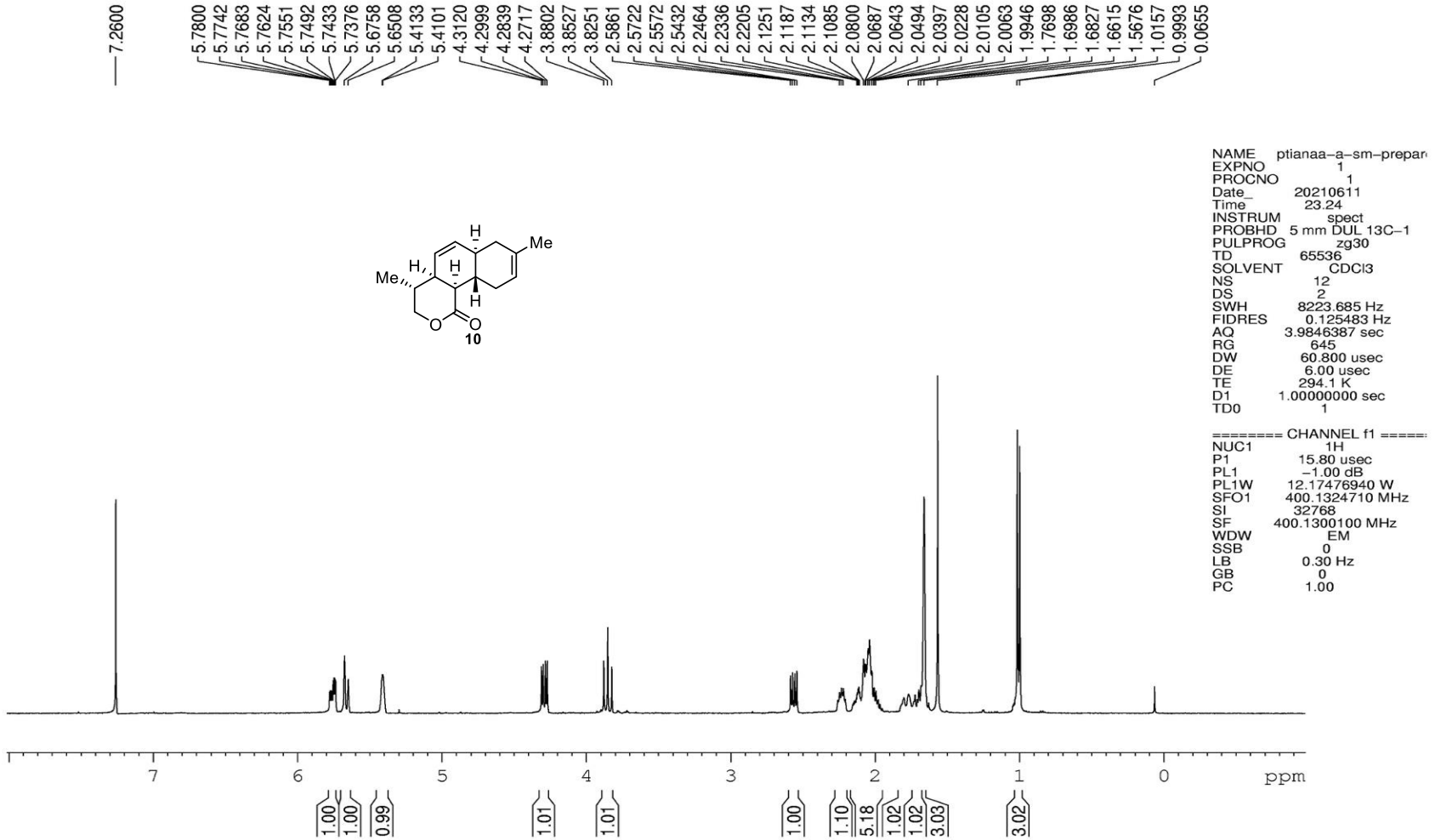
135.7974
132.9741
130.5605
129.2549
129.1187
128.2640
113.6574
77.3192
77.0008
76.6838
74.7241
72.5389
55.1863
46.2314
36.7617
33.5606
16.9416
13.0577
Me
Me
O
PMBO
5a
NAME ptianaa-a-si-2-3-C
EXPNO 1
PROCNO 1
Date_ 20220317
Time 2.31
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 68
DS 1
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.00 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ====
NUC1 13C
P1 40.00 usec
PL1 -3.00 dB
PL1W 60.64365387 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.39 dB
PL13 18.00 dB
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

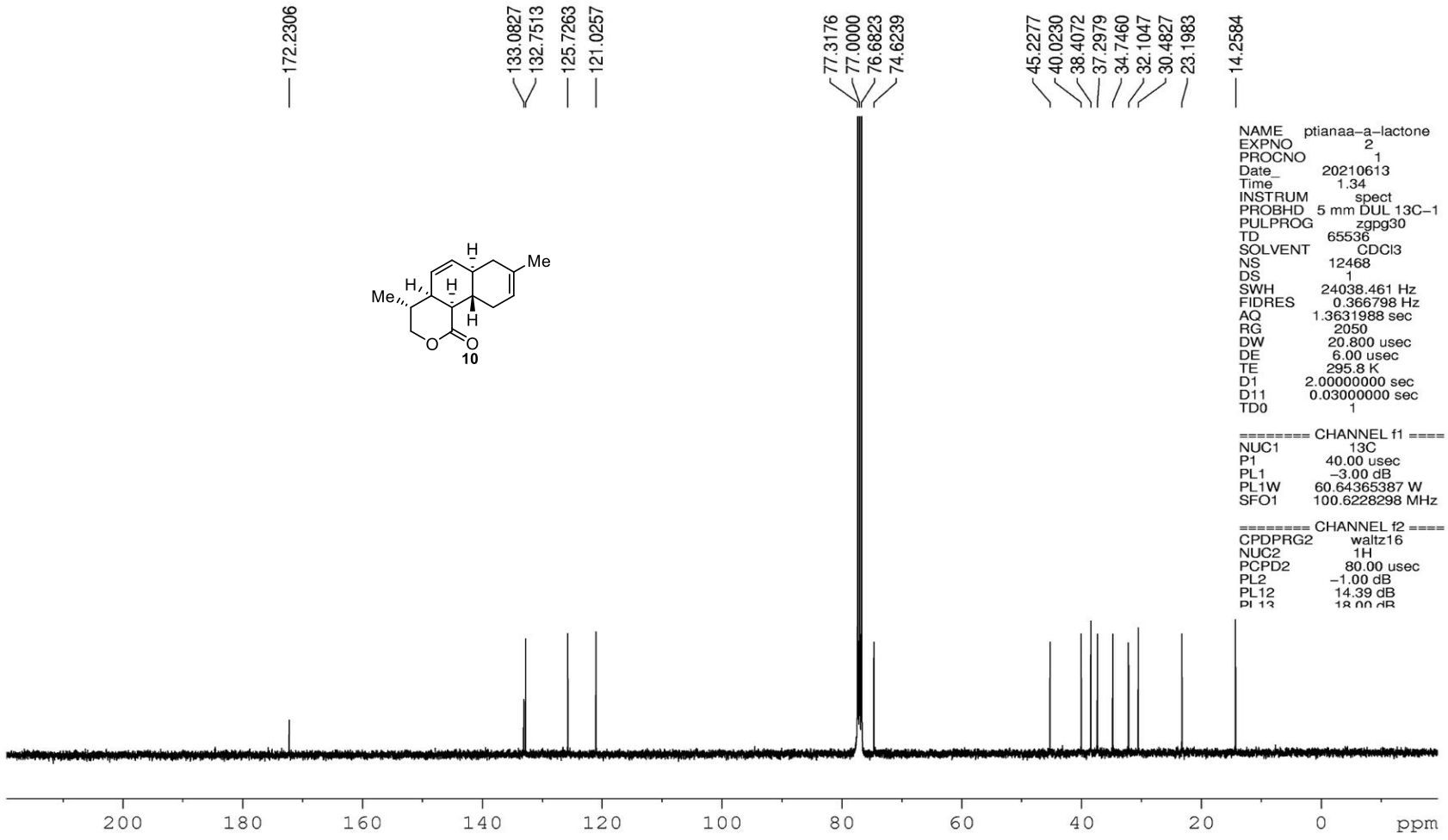

7.2747
7.2710
7.2534
6.8930
6.8884
6.8714
6.0877
6.0617
6.0276
5.9940
5.9681
5.8704
5.8312
5.5765
5.5594
5.5412
5.5231
5.5051
4.4529
3.7285
3.7044
3.6998
3.6907
3.6852
3.6775
3.6503
3.6381
3.3736
3.3575
3.3509
3.3348
3.2872
3.2697
3.2649
3.2469
2.5297
2.5128
2.4956
2.3583
2.3539
2.3436
2.3393
2.3311
2.3184
1.5932
1.0511
1.0341
0.8820
0.8764
0.8709
0.8609
0.8544
0.8440
0.0457
0.0417
Me
Me
OTBS
PMBO
O
OMe
7 (d.r. >6:1)
NAME ptianaa-a-sDA
EXPNO 1
PROCNO 1
Date_ 20220516
Time 0.05
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 456
DW 60.800 usec
DE 6.00 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
3.22
1.03
2.26
2.00
0.98
1.87
2.14
3.33
2.88
1.31
0.31
1.20
1.25
1.19
2.14
1.06
1.17
3.52
2.87
8.94
6.30

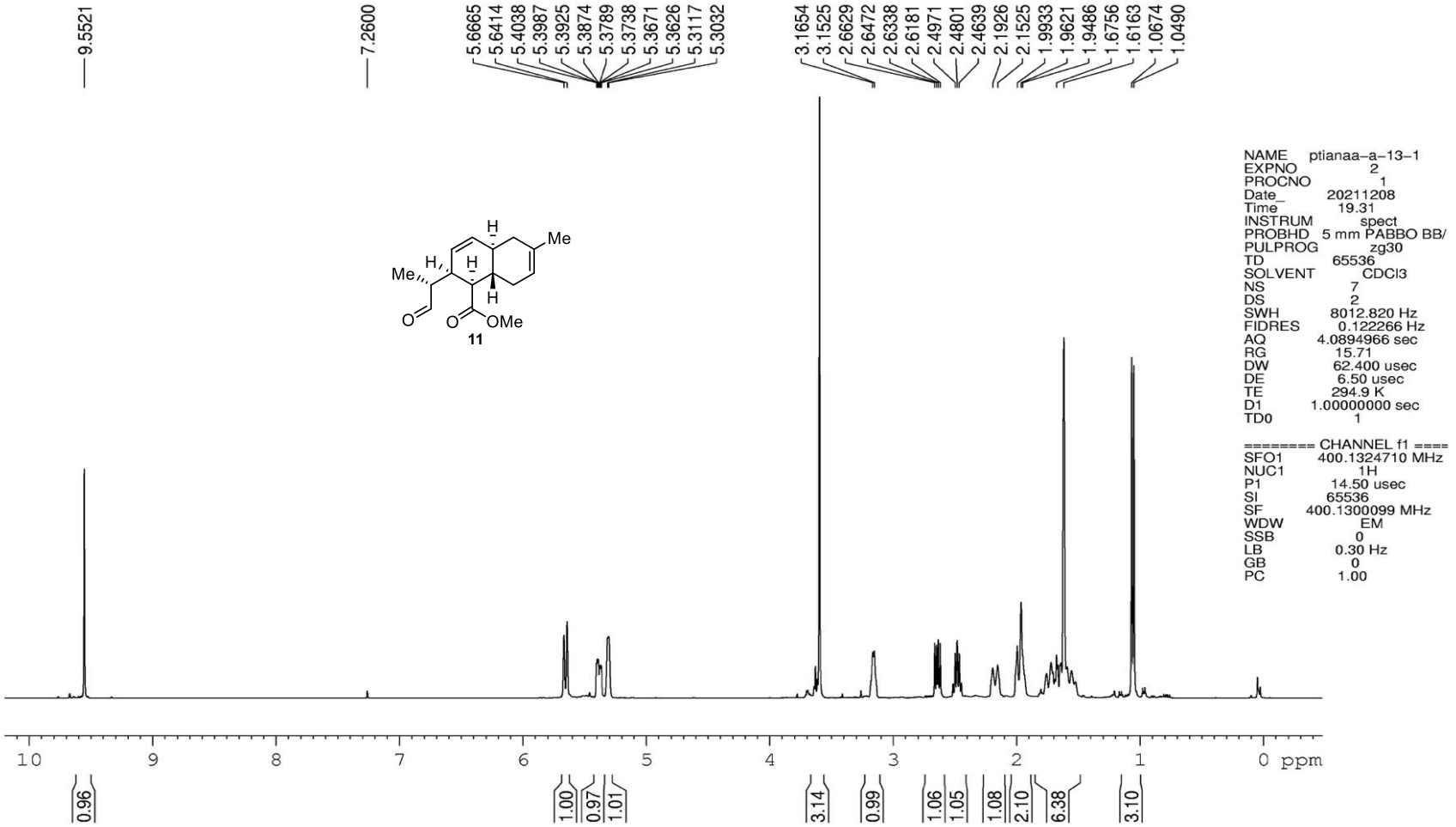

166.8327
159.0757
146.6235
134.6481
131.7987
131.4310
130.6687
129.7764
129.1735
122.6688
113.7083
77.3175
76.9996
76.6826
74.9077
74.4591
72.5870
55.2531
51.4059
38.6753
37.0841
36.8062
35.8472
25.8391
18.0897
17.0676
13.9711
-4.2800
-4.5274
Me
Me
OTBS
PMBO
O
OMe
7 (d.r. >6:1)
NAME ptianaa-a-sDA-C
EXPNO 1
PROCNO 1
Date_ 20220516
Time 0.09
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10000
DS 1
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.00 usec
TE 295.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ====
NUC1 13C
P1 40.00 usec
PL1 -3.00 dB
PL1W 60.64365387 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.39 dB
PL13 18.00 dB
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


5.7224
5.7159
5.7114
5.7050
5.6975
5.6911
5.6865
5.6803
5.6215
5.5965
4.3011
4.2894
4.2730
4.2613
3.8936
3.8664
3.8388
3.2204
3.2094
3.1940
3.1836
3.1688
3.1579
2.6330
2.6179
2.6049
2.5898
2.2560
2.2514
2.2459
2.2412
2.2360
2.2305
2.2263
2.2208
2.2153
2.0453
2.0397
2.0305
2.0172
2.0075
1.9982
1.9805
1.9693
1.9645
1.9533
1.8579
1.8264
1.8171
1.8083
1.7935
1.7841
1.7750
1.5501
1.0593
1.0432
1.0204
1.0039
Me
H
H
Me
OH
H
O
O
9 (d.r. >15:1)
NAME ptianaa-a-57-H
EXPNO 2
PROCNO 1
Date_ 20210901
Time 15.51
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 724
DW 60.800 usec
DE 6.00 usec
TE 293.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
1.00
1.02
1.03
1.14
1.13
1.10
1.17
2.03
2.01
2.24
1.22
2.87
3.05
1.32


171.8822
132.7496
125.9763
77.3191
77.0006
76.6828
75.9990
74.2418
45.3731
41.7346
39.8272
39.5968
39.2323
37.0089
32.0617
18.1955
14.2733
NAME ptianaa-a-25-C
EXPNO 1
PROCNO 1
Date_ 20210519
Time 15.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 30
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 298.4 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127766 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
H
H
H
Me
OH
O
O
9 (d.r. >15:1)
200
180
160
140
120
100
80
60
40
20
0
ppm


7.2600
5.7800
5.7742
5.7683
5.7624
5.7551
5.7492
5.7433
5.7376
5.6758
5.6508
5.4133
5.4101
4.3120
4.2999
4.2839
4.2717
3.8802
3.8527
3.8251
2.5861
2.5722
2.5572
2.5432
2.2464
2.2336
2.2205
2.1251
2.1187
2.1134
2.1085
2.0800
2.0687
2.0643
2.0494
2.0397
2.0228
2.0105
2.0063
1.9946
1.7698
1.6986
1.6827
1.6615
1.5676
1.0157
0.9993
0.0655
Me
H
H
Me
H
O
O
10
NAME ptianaa-a-sm-prepar
EXPNO 1
PROCNO 1
Date_ 20210611
Time 23.24
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 645
DW 60.800 usec
DE 6.00 usec
TE 294.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7
6
5
4
3
2
1
0
ppm
1.00
1.00
0.99
1.01
1.01
1.00
1.10
5.18
1.02
1.02
3.03
3.02


172.2306
133.0827
132.7513
125.7263
121.0257
77.3176
77.0000
76.6823
74.6239
45.2277
40.0230
38.4072
37.2979
34.7460
32.1047
30.4827
23.1983
14.2584
Me
Me
H
H
H
H
O
O
10
NAME ptianaa-a-lactone
EXPNO 2
PROCNO 1
Date_ 20210613
Time 1.34
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 12468
DS 1
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.00 usec
TE 295.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ====
NUC1 13C
P1 40.00 usec
PL1 -3.00 dB
PL1W 60.64365387 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.39 dB
200
180
160
140
120
100
80
60
40
20
0
ppm


9.5521
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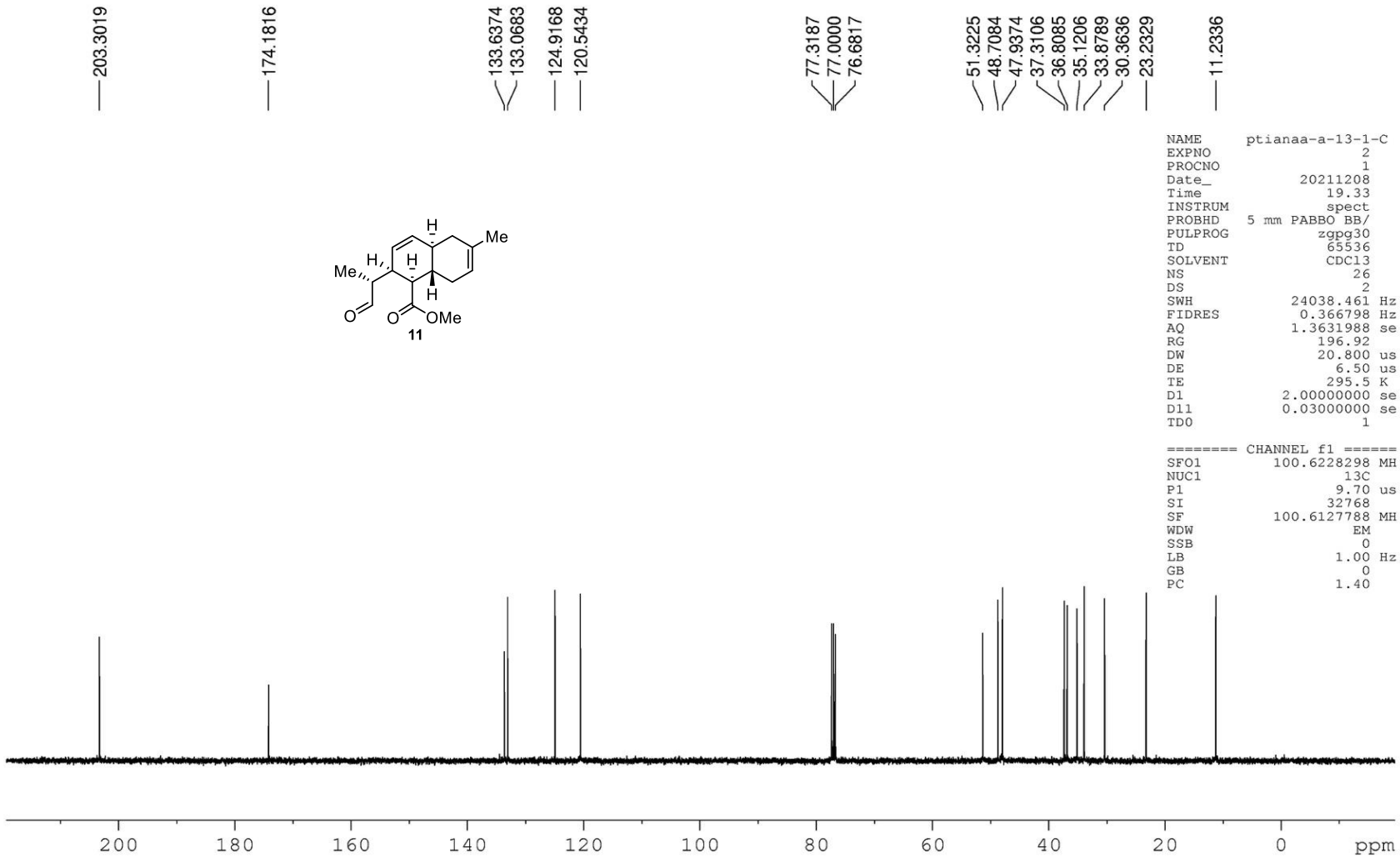
5.6665
5.6414
5.4038
5.3987
5.3925
5.3874
5.3789
5.3738
5.3671
5.3626
5.3117
5.3032
3.1654
3.1525
2.6629
2.6472
2.6338
2.6181
2.4971
2.4801
2.4639
2.1926
2.1525
1.9933
1.9621
1.9486
1.6756
1.6163
1.0674
1.0490
Me
H
H
H
Me
H
O
O
OMe
11
NAME ptianaa-a-13-1
EXPNO 2
PROCNO 1
Date_ 20211208
Time 19.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 7
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 15.71
DW 62.400 usec
DE 6.50 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
0.96
1.00
0.97
1.01
3.14
0.99
1.06
1.05
1.08
2.10
6.38
3.10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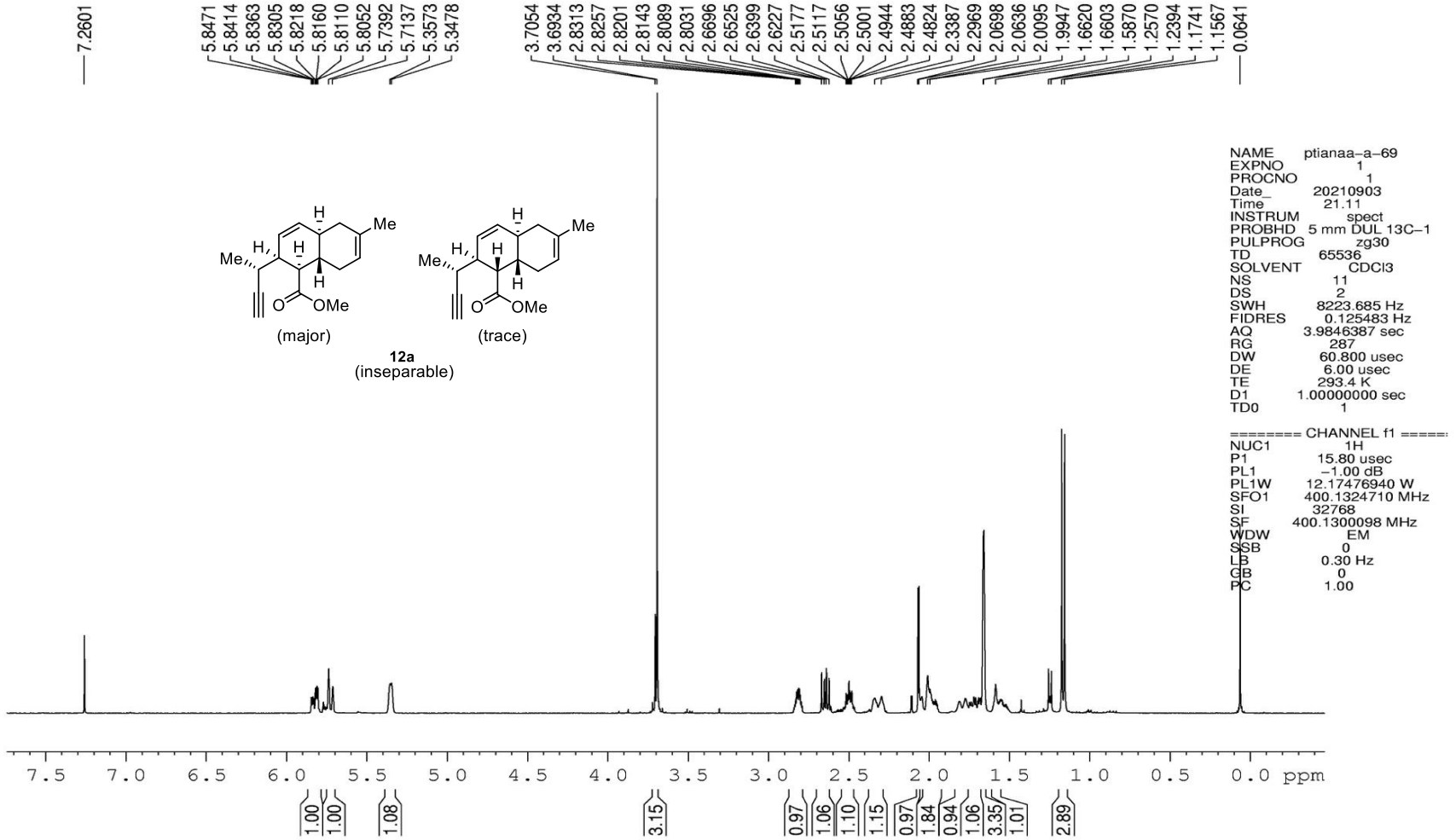
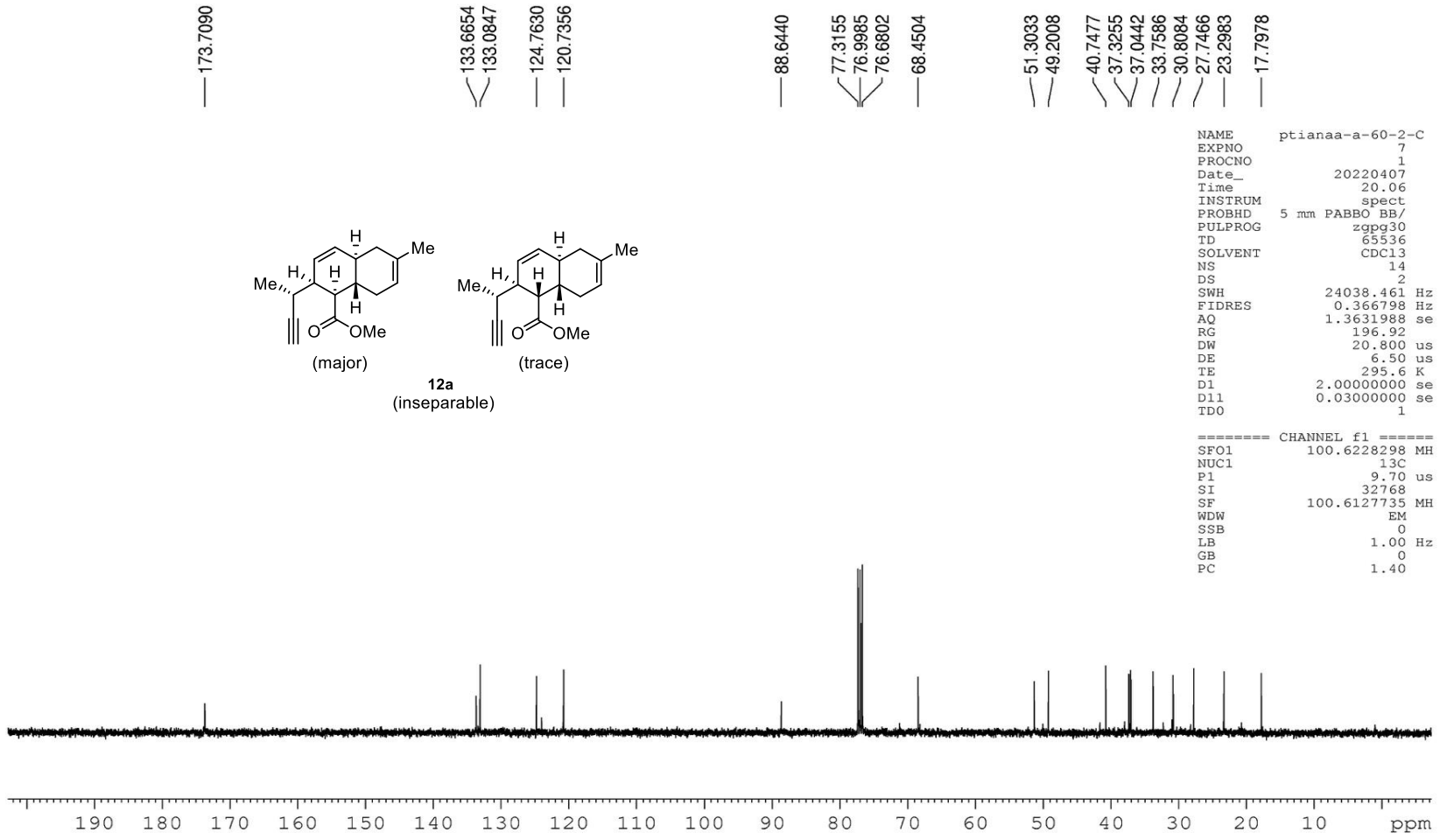
174.1816
133.6374
133.0683
124.9168
120.5434
77.3187
77.0000
76.6817
51.3225
48.7084
47.9374
37.3106
36.8085
35.1206
33.8789
30.3636
23.2329
11.2336
NAME ptianaa-a-13-1-C
EXPNO 2
PROCNO 1
Date_ 20211208
Time 19.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 26
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 295.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127788 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
H
H
H
Me
O
O
OMe
11
200
180
160
140
120
100
80
60
40
20
0
ppm


7.2601
5.8471
5.8414
5.8363
5.8305
5.8218
5.8160
5.8110
5.8052
5.7392
5.7137
5.3573
5.3478
3.7054
3.6934
2.8313
2.8257
2.8201
2.8143
2.8089
2.8031
2.6696
2.6525
2.6399
2.6227
2.5177
2.5117
2.5056
2.5001
2.4944
2.4883
2.4824
2.3387
2.2969
2.0698
2.0636
2.0095
1.9947
1.6620
1.6603
1.5870
1.2570
1.2394
1.1741
1.1567
0.0641
(major)
(trace)
12a
(inseparable)
NAME ptianaa-a-69
EXPNO 1
PROCNO 1
Date_ 20210903
Time 21.11
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 287
DW 60.800 usec
DE 6.00 usec
TE 293.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
1.08
3.15
0.97
1.06
1.10
1.15
0.97
1.84
0.94
1.06
3.35
1.01
2.89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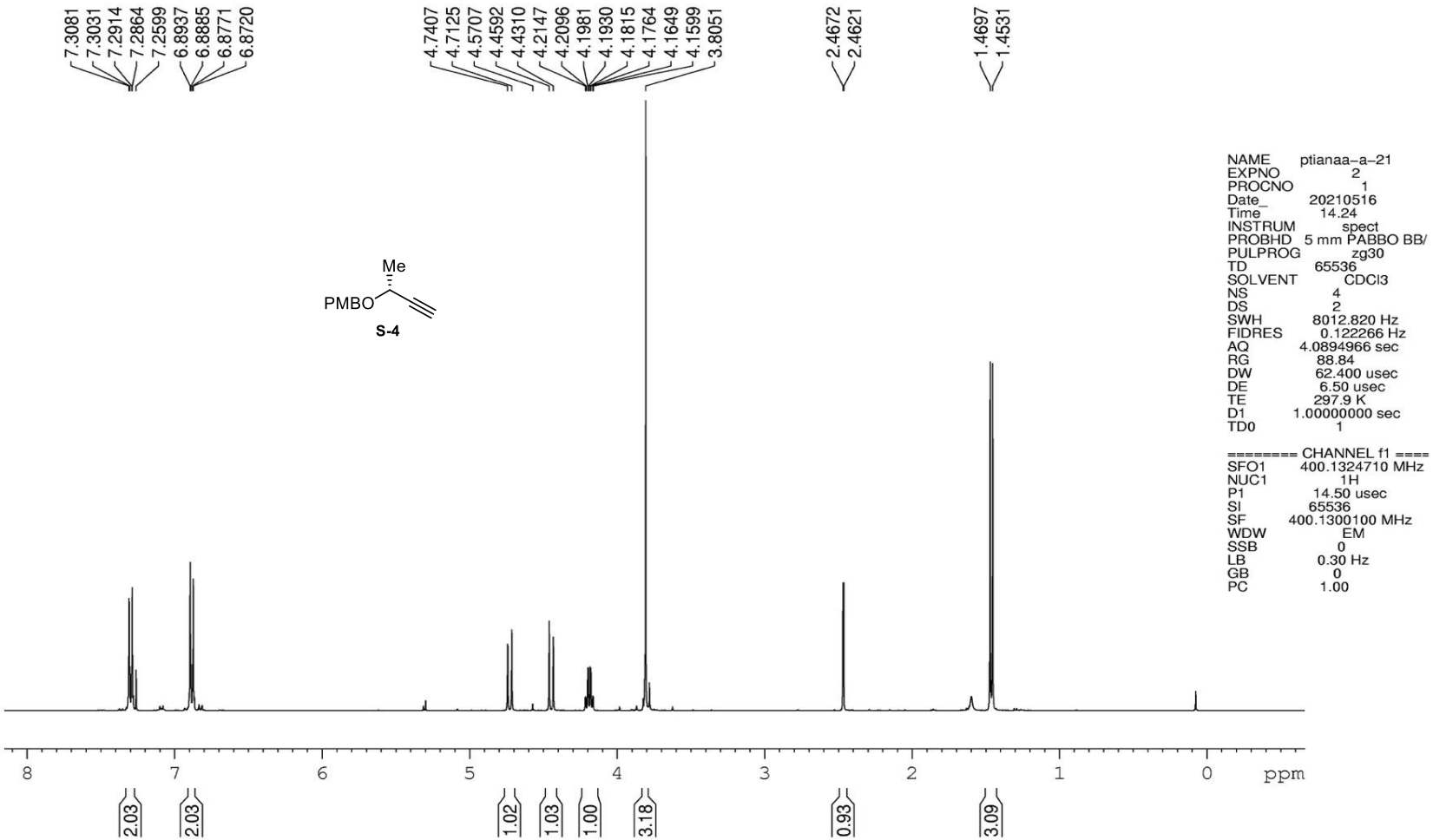
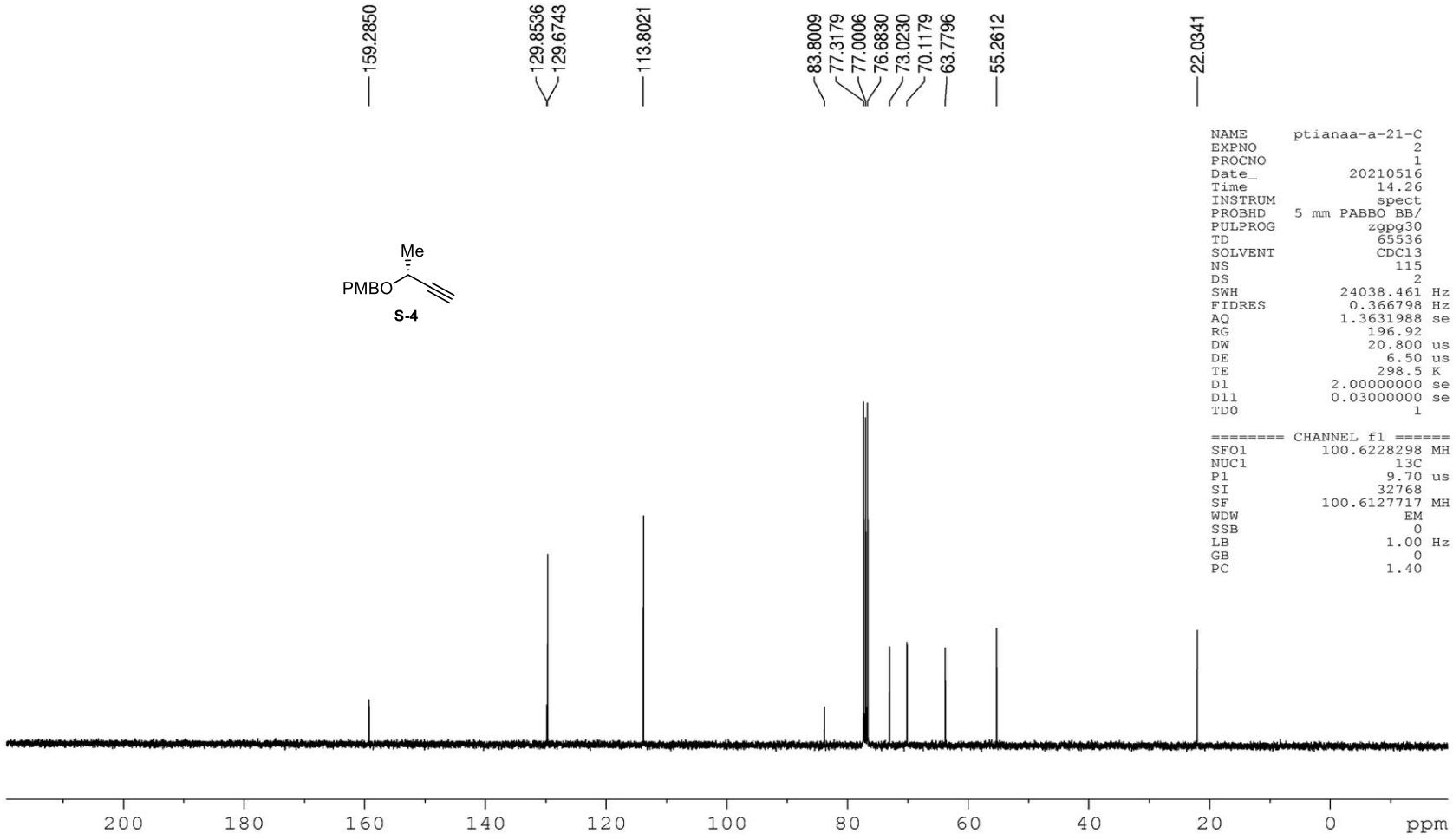
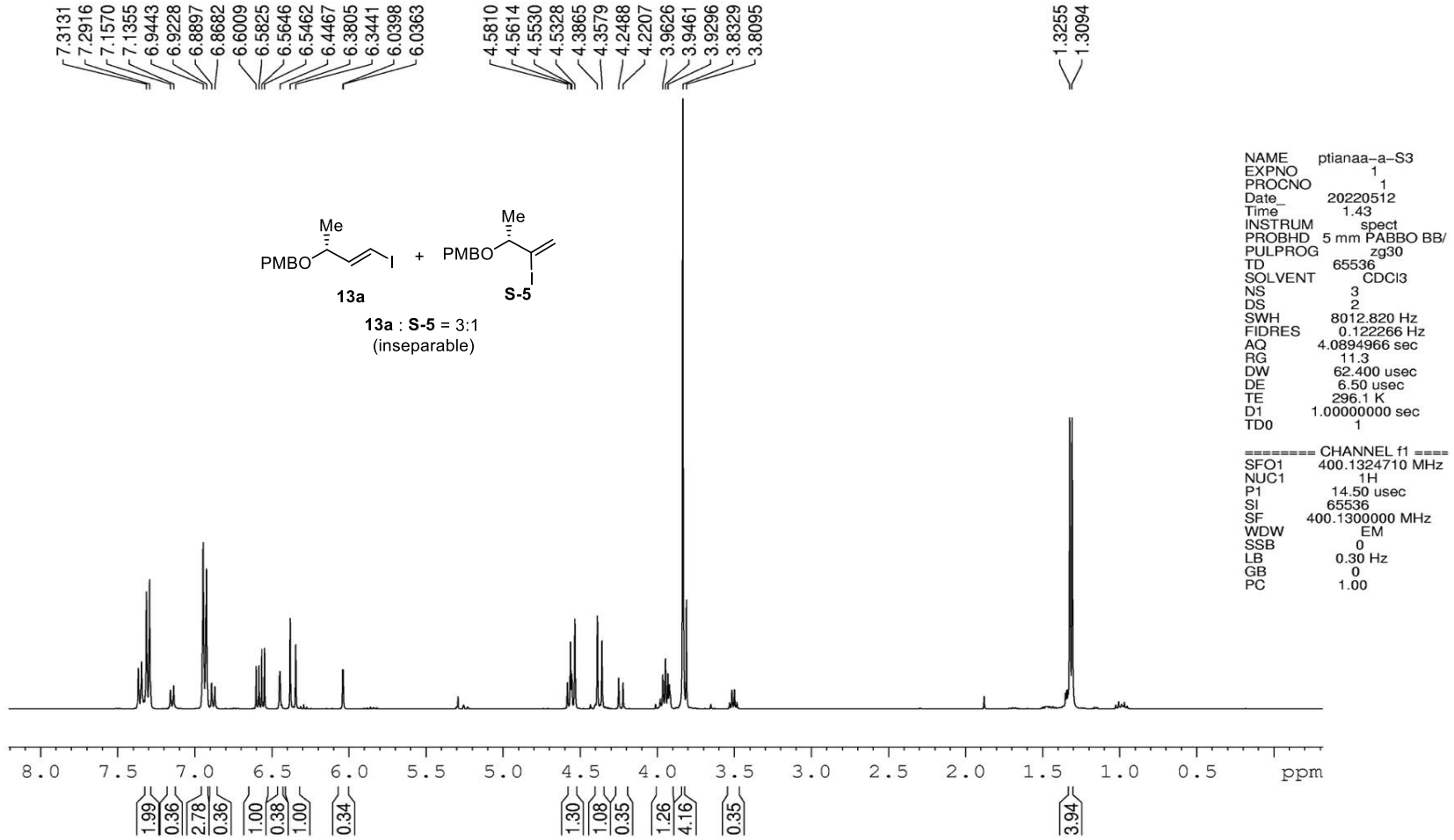
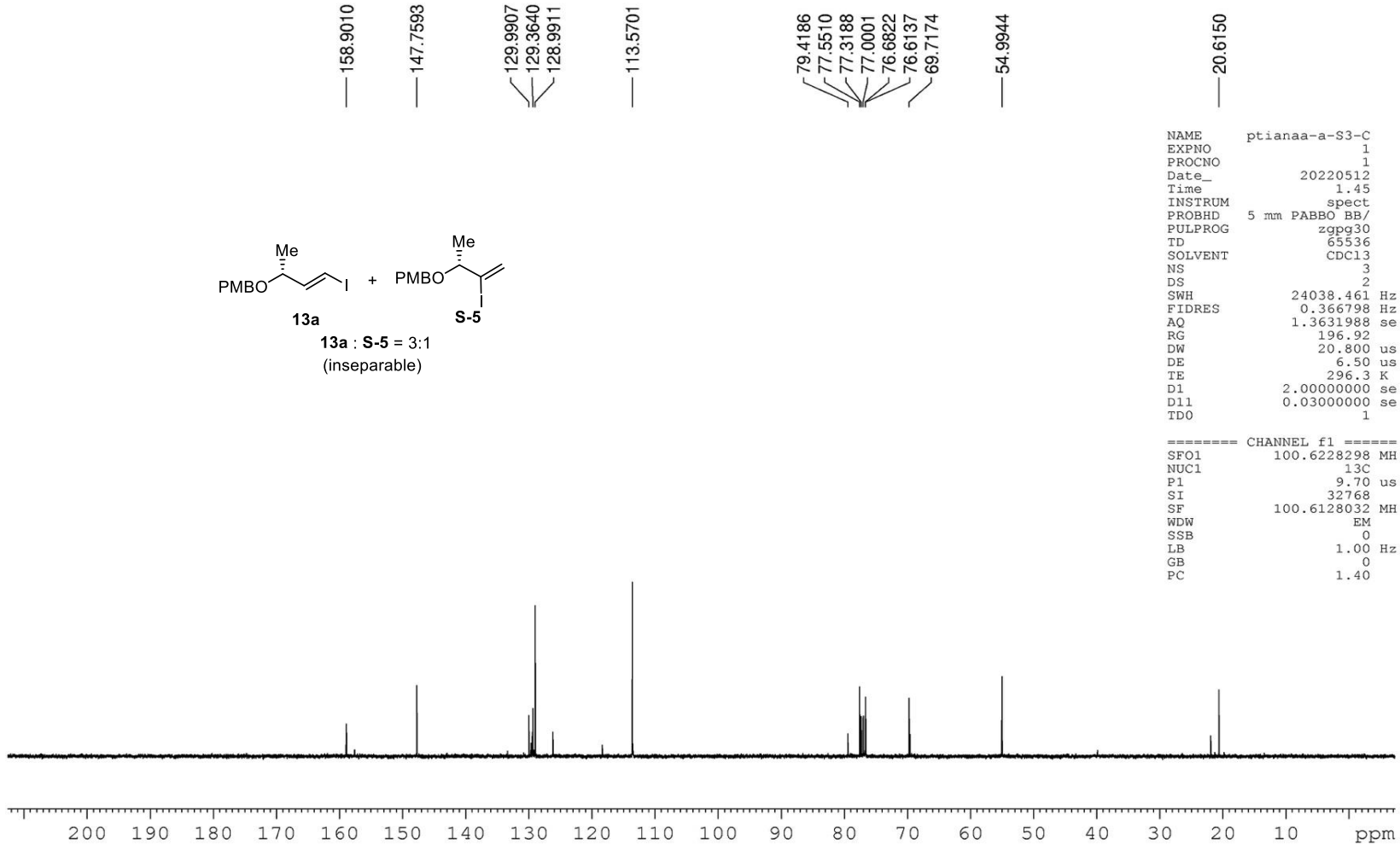
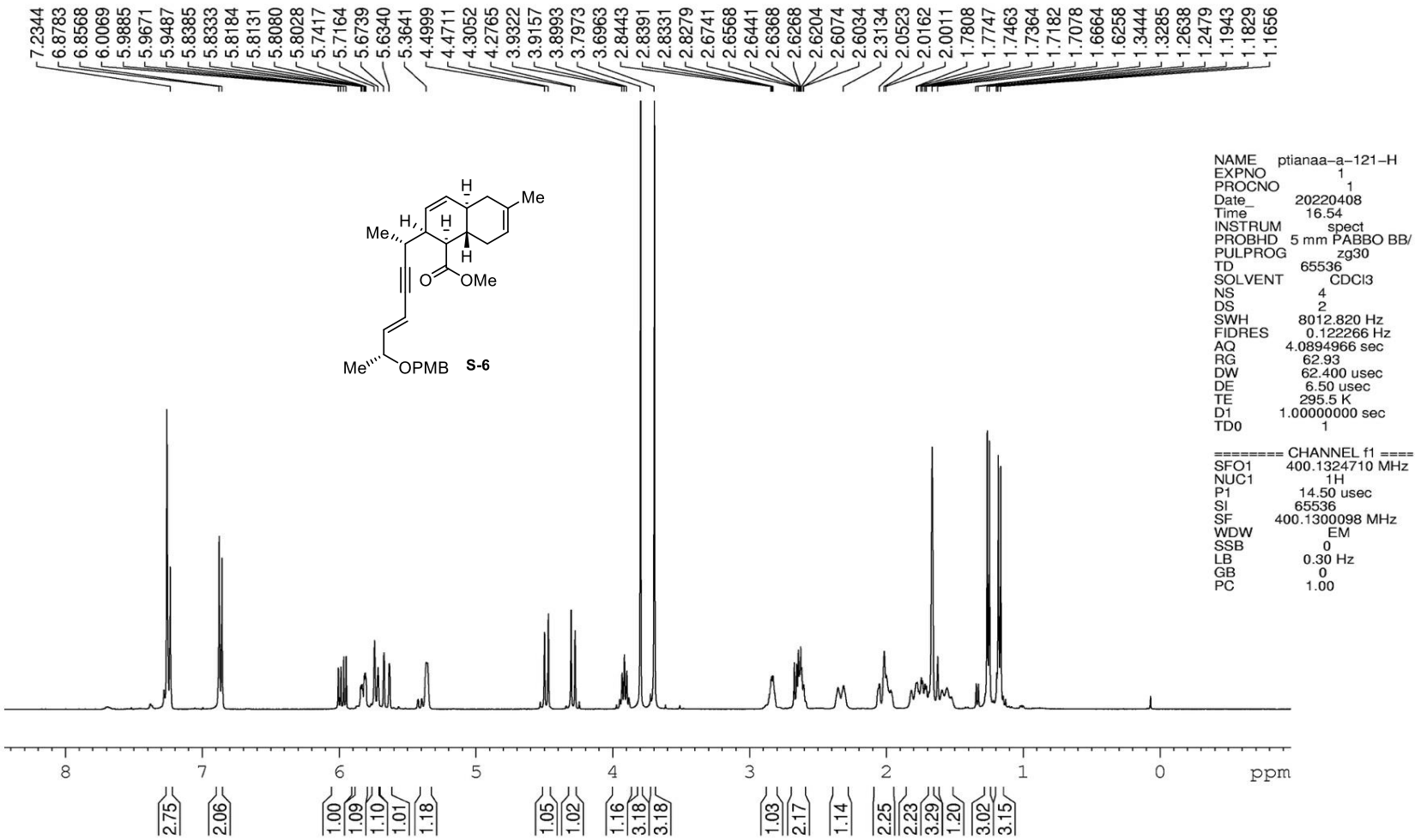
133.6654
133.0847
124.7630
120.7356
88.6440
77.3155
76.9985
76.6802
68.4504
51.3033
49.2008
40.7477
37.3255
37.0442
33.7586
30.8084
27.7466
23.2983
17.7978
NAME ptianaa-a-60-2-C
EXPNO 7
PROCNO 1
Date_ 20220407
Time 20.06
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 14
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 295.6 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127735 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
OMe
(major)
(trace)
12a
(inseparable)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.3081
7.3031
7.2914
7.2864
7.2599
6.8937
6.8885
6.8771
6.8720
4.7407
4.7125
4.5707
4.4592
4.4310
4.2147
4.2096
4.1981
4.1930
4.1815
4.1764
4.1649
4.1599
3.8051
2.4672
2.4621
1.4697
1.4531
Me
PMBO
S-4
NAME ptianaa-a-21
EXPNO 2
PROCNO 1
Date_ 20210516
Time 14.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 88.84
DW 62.400 usec
DE 6.50 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
2.03
2.03
1.02
1.03
1.00
3.18
0.93
3.09


159.2850
129.8536
129.6743
113.8021
83.8009
77.3179
77.0006
76.6830
73.0230
70.1179
63.7796
55.2612
22.0341
Me
PMBO
S-4
NAME ptianaa-a-21-C
EXPNO 2
PROCNO 1
Date_ 20210516
Time 14.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 115
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 298.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127717 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm


7.3131
7.2916
7.1570
7.1355
6.9443
6.9228
6.8897
6.8682
6.6009
6.5825
6.5646
6.5462
6.4467
6.3805
6.3441
6.0398
6.0363
4.5810
4.5614
4.5530
4.5328
4.3865
4.3579
4.2488
4.2207
3.9626
3.9461
3.9296
3.8329
3.8095
1.3255
1.3094
Me
PMBO
I
13a
+
Me
PMBO
I
S-5
13a : S-5 = 3:1
(inseparable)
NAME ptianaa-a-S3
EXPNO 1
PROCNO 1
Date_ 20220512
Time 1.43
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 3
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 11.3
DW 62.400 usec
DE 6.50 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
1.99
0.36
2.78
0.36
1.00
0.38
1.00
0.34
1.30
1.08
0.35
1.26
4.16
0.35
3.94


158.9010
147.7593
129.9907
129.3640
128.9911
113.5701
79.4186
77.5510
77.3188
77.0001
76.6822
76.6137
69.7174
54.9944
20.6150
Me
PMBO
I
13a
+
Me
PMBO
I
S-5
13a : S-5 = 3:1
(inseparable)
NAME ptianaa-a-S3-C
EXPNO 1
PROCNO 1
Date_ 20220512
Time 1.45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 296.3 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6128032 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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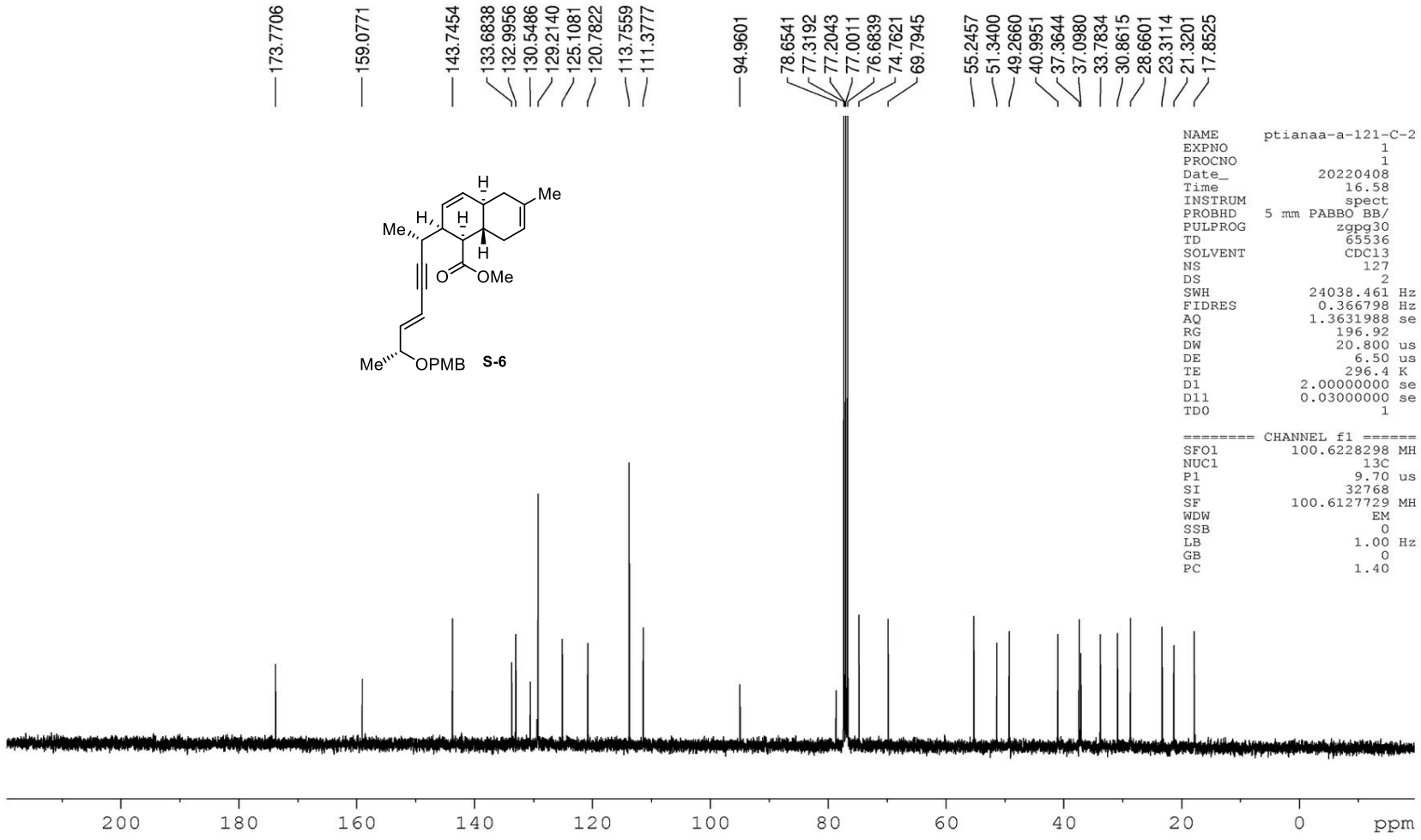
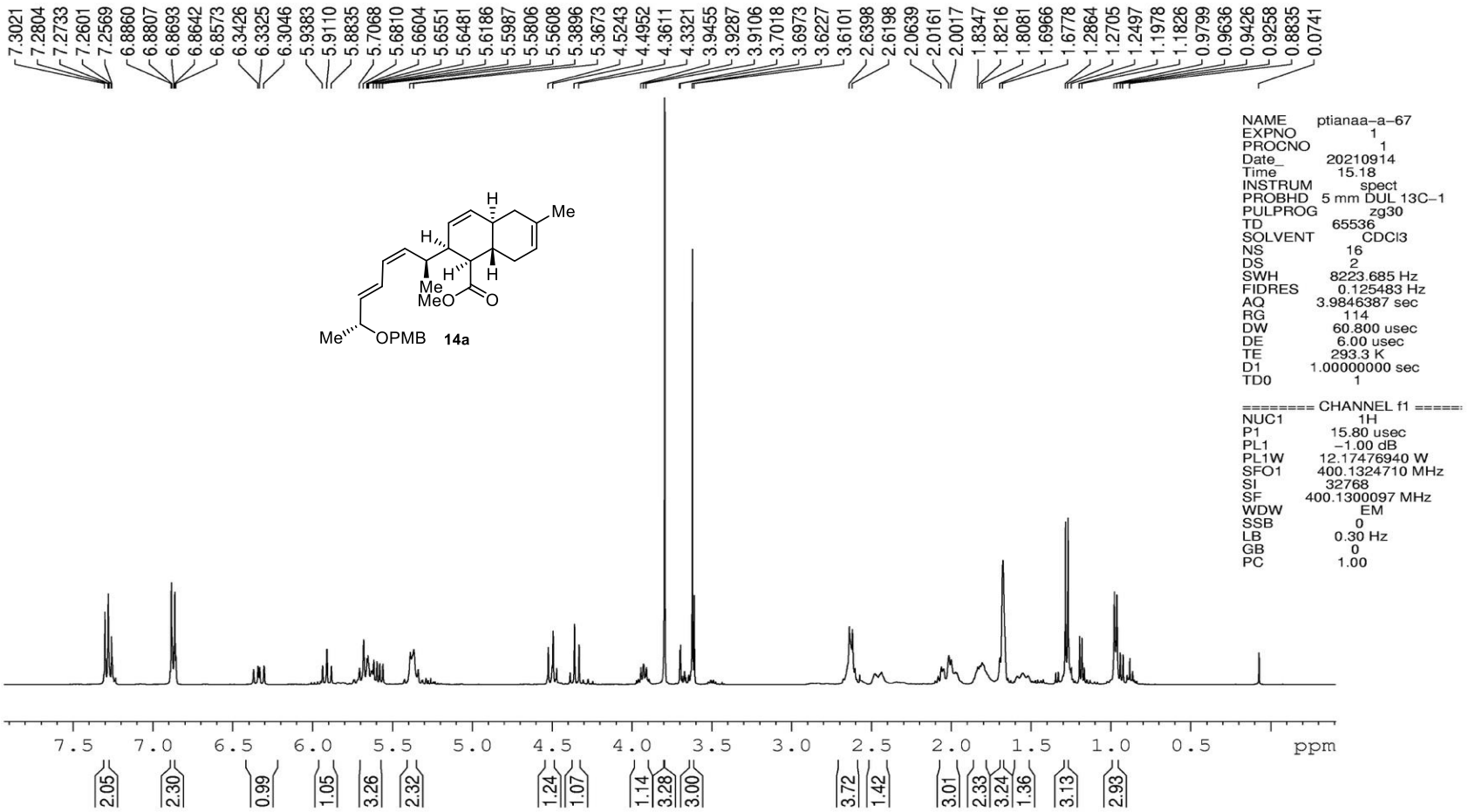
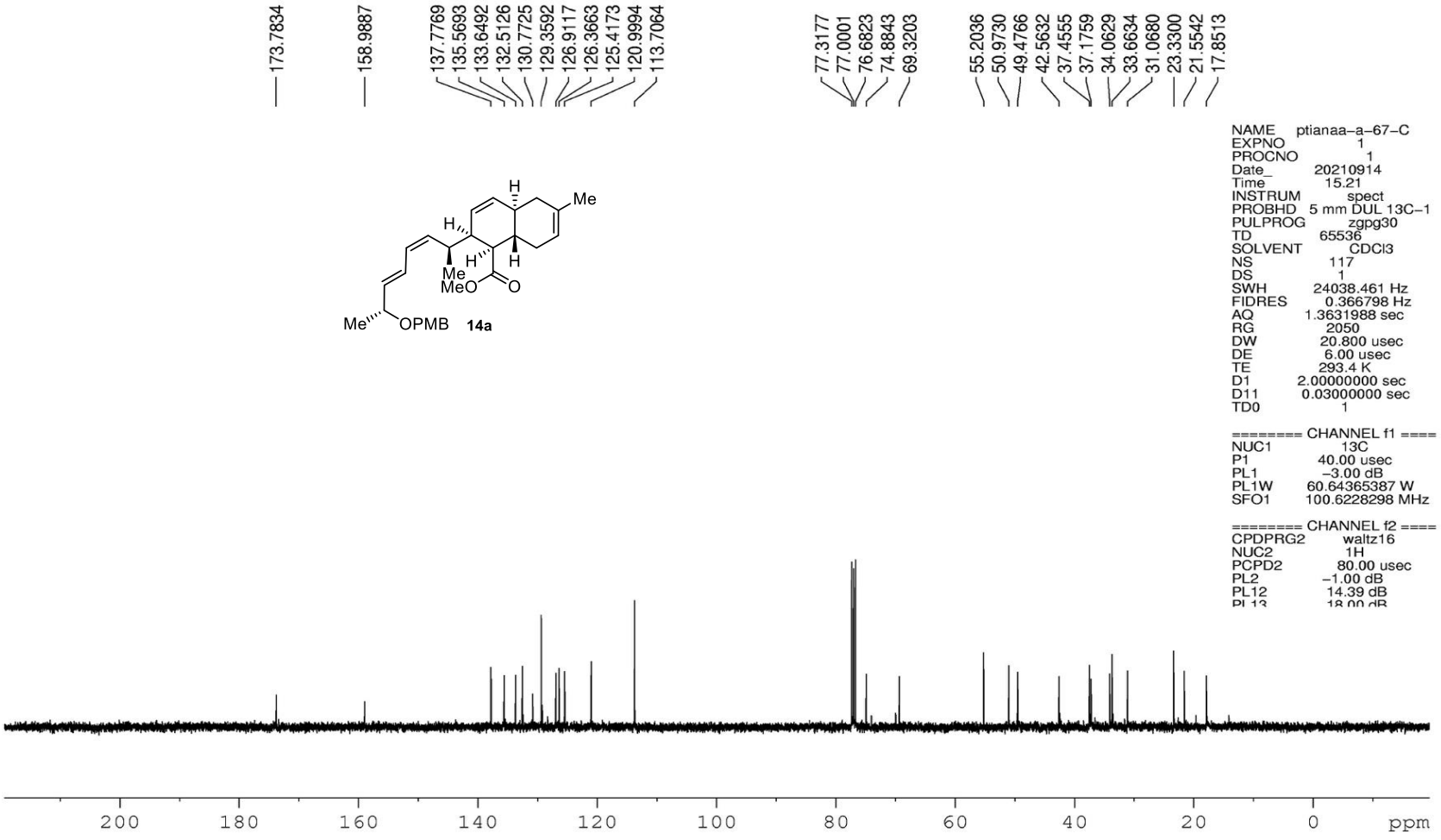
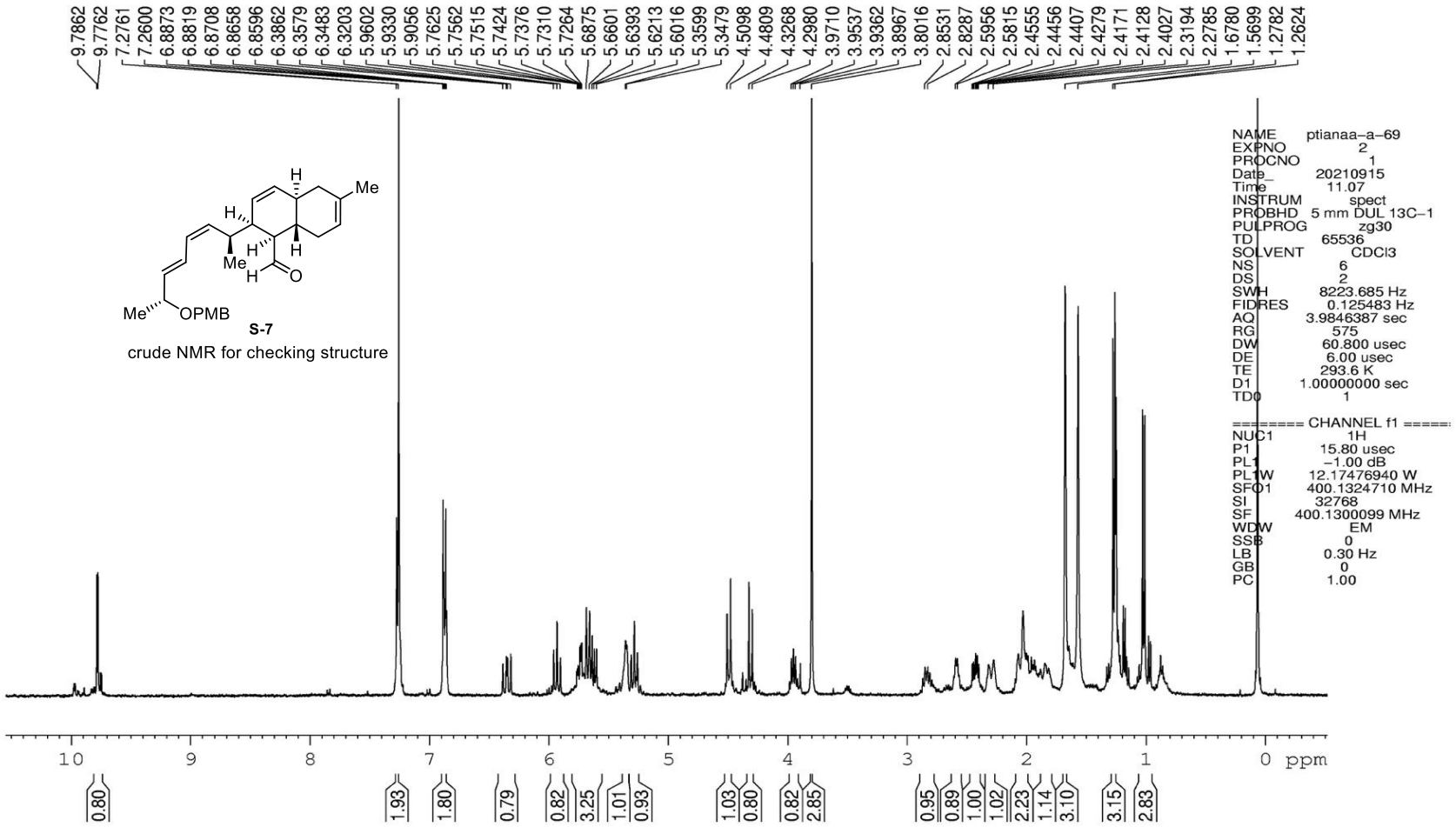
6.8783
6.8568
6.0069
5.9885
5.9671
5.9487
5.8385
5.8333
5.8184
5.8131
5.8080
5.8028
5.7417
5.7164
5.6739
5.6340
5.3641
4.4999
4.4711
4.3052
4.2765
3.9322
3.9157
3.8993
3.7973
3.6963
2.8443
2.8391
2.8331
2.8279
2.6741
2.6568
2.6441
2.6368
2.6268
2.6204
2.6074
2.6034
2.3134
2.0523
2.0162
2.0011
1.7808
1.7747
1.7463
1.7364
1.7182
1.7078
1.6664
1.6258
1.3444
1.3285
1.2638
1.2479
1.1943
1.1829
1.1656
Me
H
H
H
Me
H
O
OMe
Me
OPMB
S-6
NAME ptianaa-a-121-H
EXPNO 1
PROCNO 1
Date_ 20220408
Time 16.54
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 62.93
DW 62.400 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
2.75
2.06
1.00
1.09
1.10
1.01
1.18
1.05
1.02
1.16
3.18
3.18
1.03
2.17
1.14
2.25
2.23
3.29
1.20
3.02
3.15


173.7706
159.0771
143.7454
133.6838
132.9956
130.5486
129.2140
125.1081
120.7822
113.7559
111.3777
94.9601
78.6541
77.3192
77.2043
77.0011
76.6839
74.7621
69.7945
55.2457
51.3400
49.2660
40.9951
37.3644
37.0980
33.7834
30.8615
28.6601
23.3114
21.3201
17.8525
NAME ptianaa-a-121-C-2
EXPNO 1
PROCNO 1
Date_ 20220408
Time 16.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 127
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 296.4 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127729 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
H
H
H
Me
O
OMe
Me
OPMB
S-6
200
180
160
140
120
100
80
60
40
20
0
ppm


7.3021 7.2804 7.2733 7.2601 7.2569 6.8860 6.8807 6.8693 6.8642 6.8573 6.3426 6.3325 6.3046 5.9383 5.9110 5.8835 5.7068 5.6810 5.6604 5.6551 5.6481 5.6186 5.5987 5.5806 5.5608 5.3896 5.3673 4.5243 4.4952 4.3611 4.3321 3.9455 3.9287 3.9106 3.7018 3.6973 3.6227 3.6101 2.6398 2.6198 2.0639 2.0161 2.0017 1.8347 1.8216 1.8081 1.6966 1.6778 1.2864 1.2705 1.2497 1.1978 1.1826 0.9799 0.9636 0.9426 0.9258 0.8835 0.0741
H
Me
H
H
Me
MeO
O
Me
OPMB
14a
NAME ptianaa-a-67
EXPNO 1
PROCNO 1
Date_ 20210914
Time 15.18
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.00 usec
TE 293.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 2.30 0.99 1.05 3.26 2.32 1.24 1.07 1.14 3.28 3.00 3.72 1.42 3.01 2.33 3.24 1.36 3.13 2.93


173.7834
158.9887
137.7769
135.5693
133.6492
132.5126
130.7725
129.3592
126.9117
126.3663
125.4173
120.9994
113.7064
77.3177
77.0001
76.6823
74.8843
69.3203
55.2036
50.9730
49.4766
42.5632
37.4555
37.1759
34.0629
33.6634
31.0680
23.3300
21.5542
17.8513
H
Me
H
H
H
Me
MeO
O
Me
OPMB
14a
NAME ptianaa-a-67-C
EXPNO 1
PROCNO 1
Date_ 20210914
Time 15.21
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 117
DS 1
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.00 usec
TE 293.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ====
NUC1 13C
P1 40.00 usec
PL1 -3.00 dB
PL1W 60.64365387 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.39 dB
200
180
160
140
120
100
80
60
40
20
0
ppm


9.7862
9.7762
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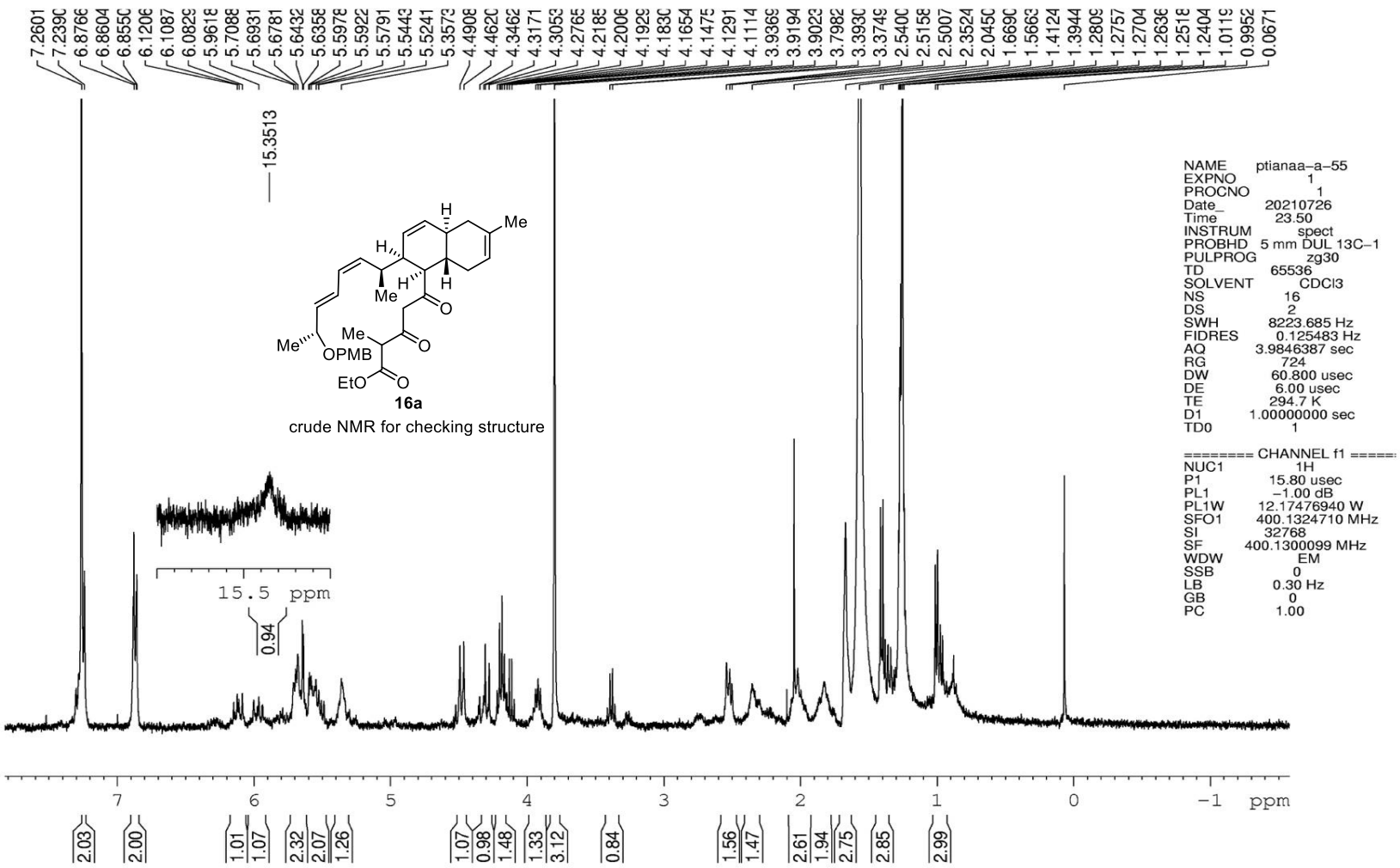
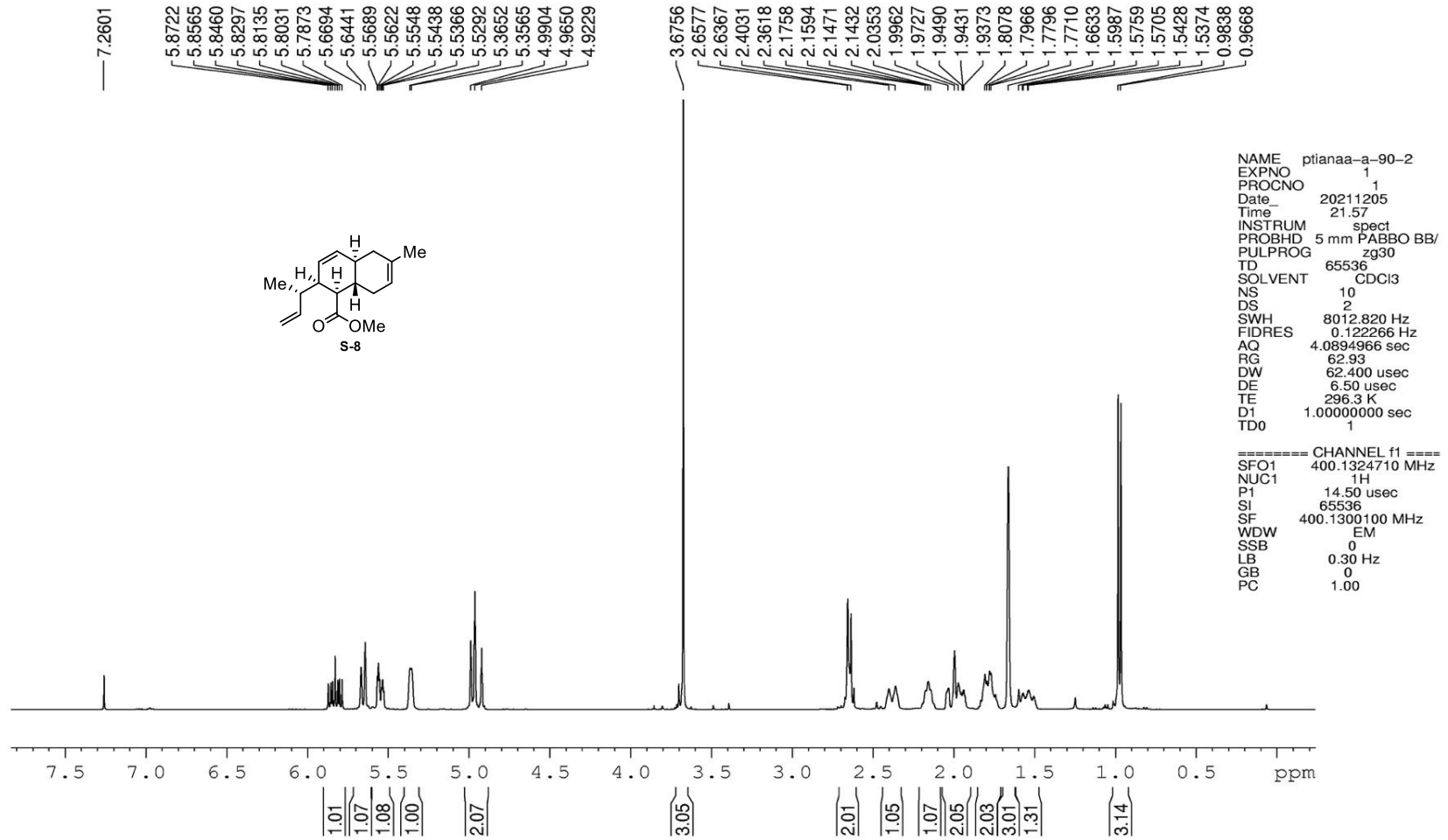
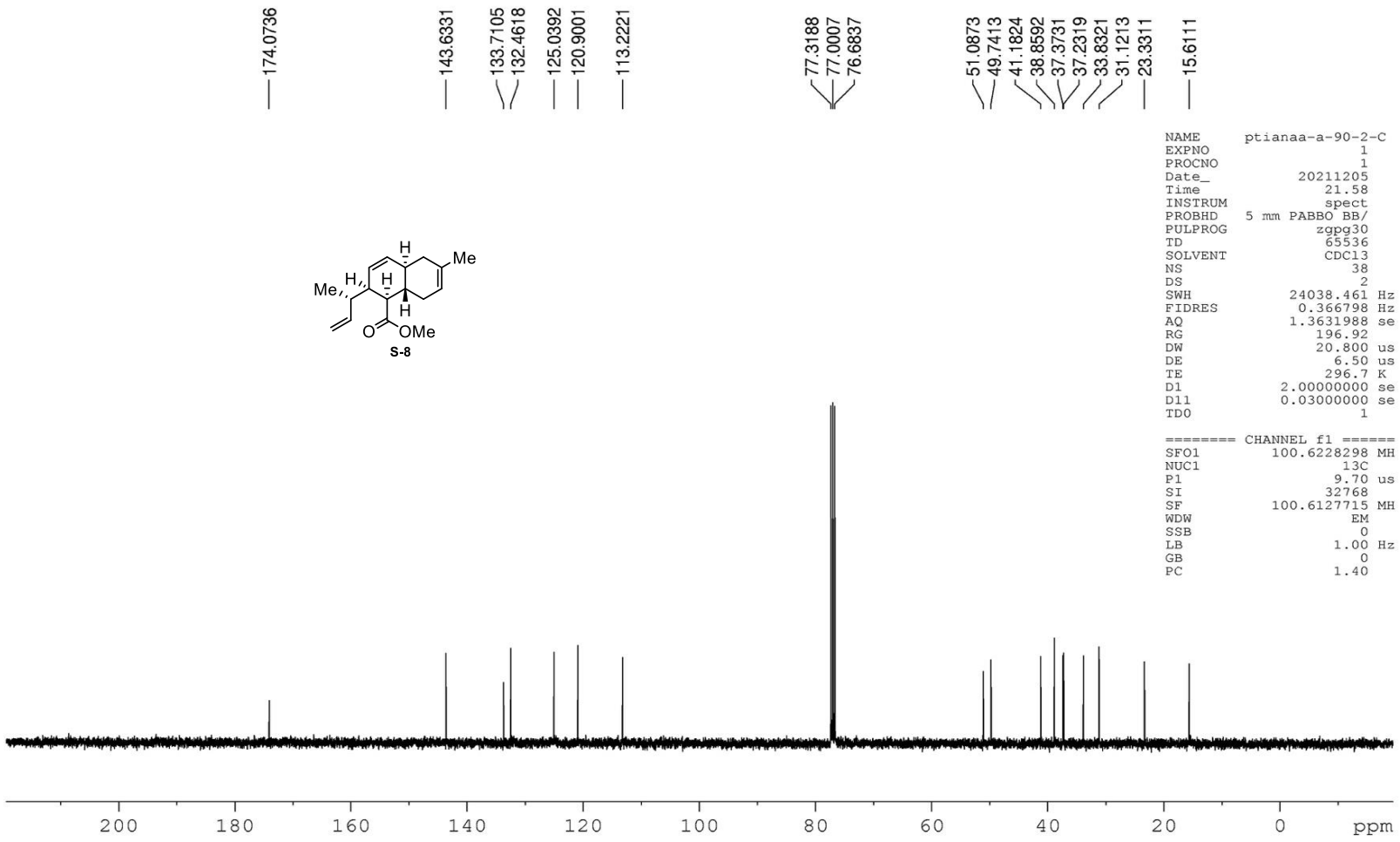
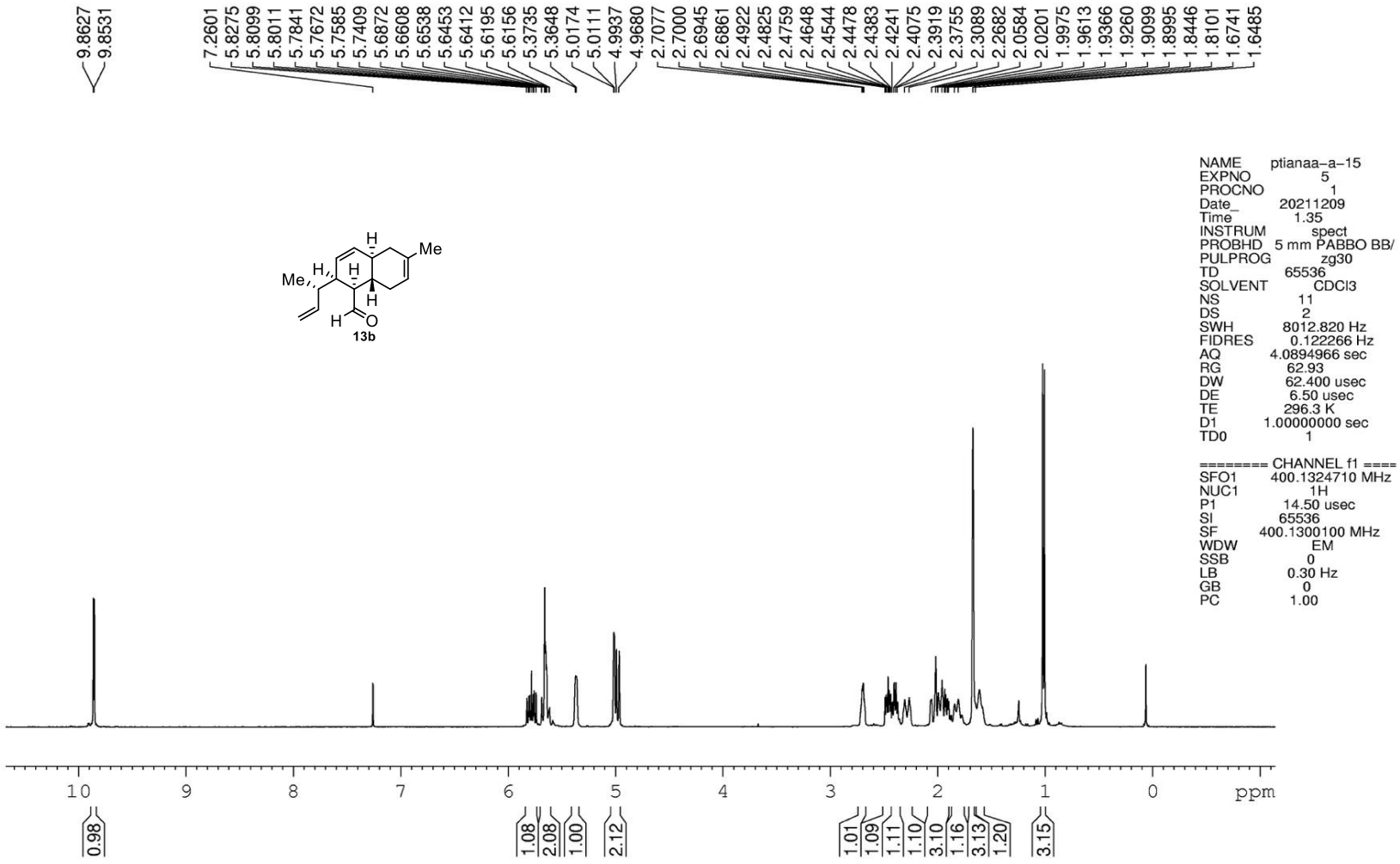
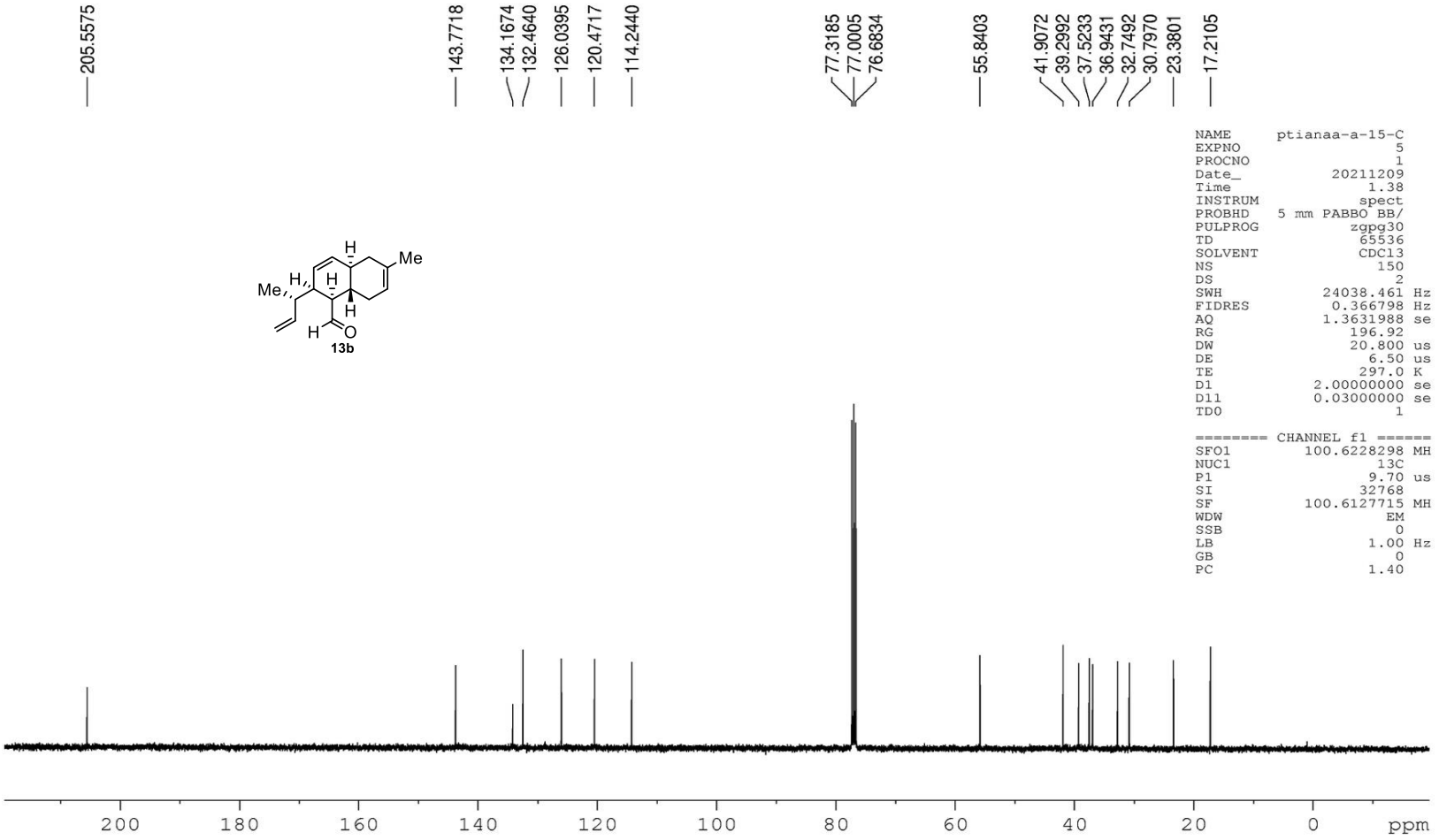
7.2600
6.8873
6.8819
6.8708
6.8658
6.8596
6.3862
6.3579
6.3483
6.3203
5.9602
5.9330
5.9056
5.7625
5.7562
5.7515
5.7424
5.7376
5.7310
5.7264
5.6875
5.6601
5.6393
5.6213
5.6016
5.3599
5.3479
4.5098
4.4809
4.3268
4.2980
3.9710
3.9537
3.9362
3.8967
3.8016
2.8531
2.8287
2.5956
2.5815
2.4555
2.4456
2.4407
2.4279
2.4171
2.4128
2.4027
2.3194
2.2785
1.6780
1.5699
1.2782
1.2624
Me
H
H
Me
H
H
H
O
Me
OPMB
S-7
crude NMR for checking structure
NAME ptianaa-a-69
EXPNO 2
PROCNO 1
Date_ 20210915
Time 11.07
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 6
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 575
DW 60.800 usec
DE 6.00 usec
TE 293.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
0.80
1.93
1.80
0.79
0.82
3.25
1.01
0.93
1.03
0.80
0.82
2.85
0.95
0.89
1.00
1.02
2.23
1.14
3.10
3.15
2.83

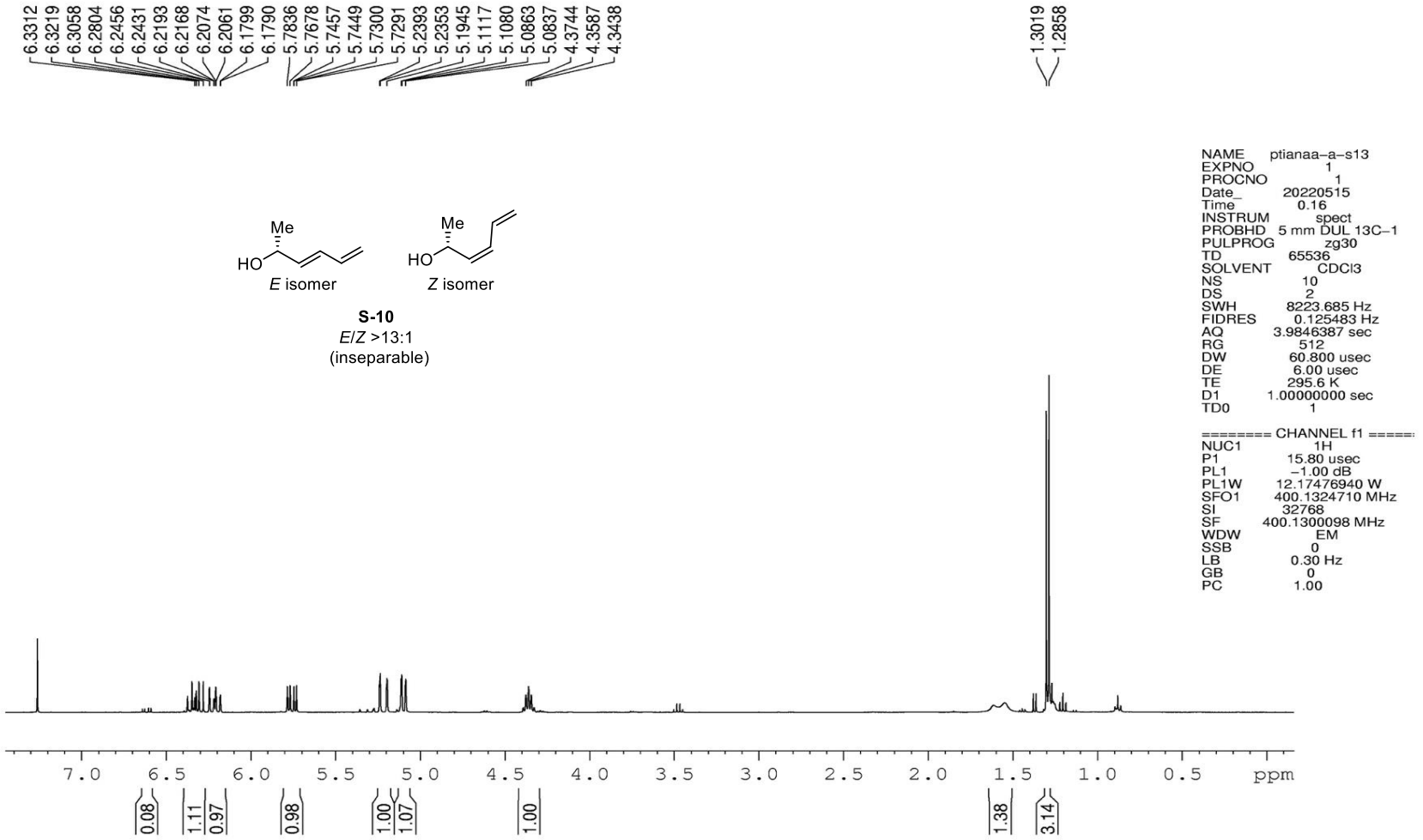

15.3513
16a
crude NMR for checking structure
15.5 ppm
0.94
NAME ptianaa-a-55
EXPNO 1
PROCNO 1
Date_ 20210726
Time 23.50
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 724
DW 60.800 usec
DE 6.00 usec
TE 294.7 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

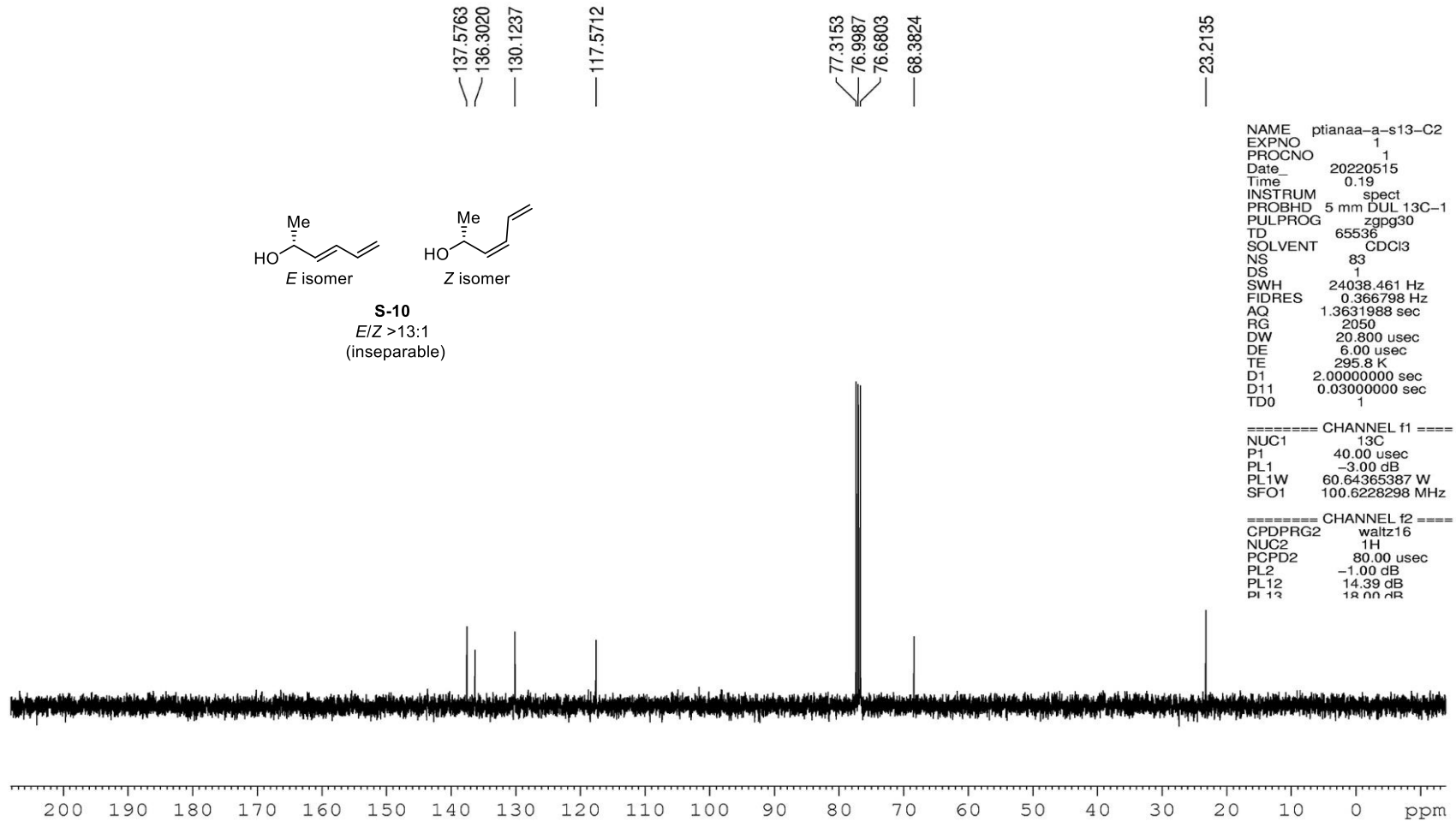

7.2601
5.8722
5.8565
5.8460
5.8297
5.8135
5.8031
5.7873
5.6694
5.6441
5.5689
5.5622
5.5548
5.5438
5.5366
5.5292
5.3652
5.3565
4.9904
4.9650
4.9229
3.6756
2.6577
2.6367
2.4031
2.3618
2.1758
2.1594
2.1471
2.1432
2.0353
1.9962
1.9727
1.9490
1.9431
1.9373
1.8078
1.7966
1.7796
1.7710
1.6633
1.5987
1.5759
1.5705
1.5428
1.5374
0.9838
0.9668
Me
H
H
Me
H
OMe
O
S-8
NAME ptianaa-a-90-2
EXPNO 1
PROCNO 1
Date_ 20211205
Time 21.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 62.93
DW 62.400 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
1.01
1.07
1.08
1.00
2.07
3.05
2.01
1.05
1.07
2.05
2.03
3.01
1.31
3.14

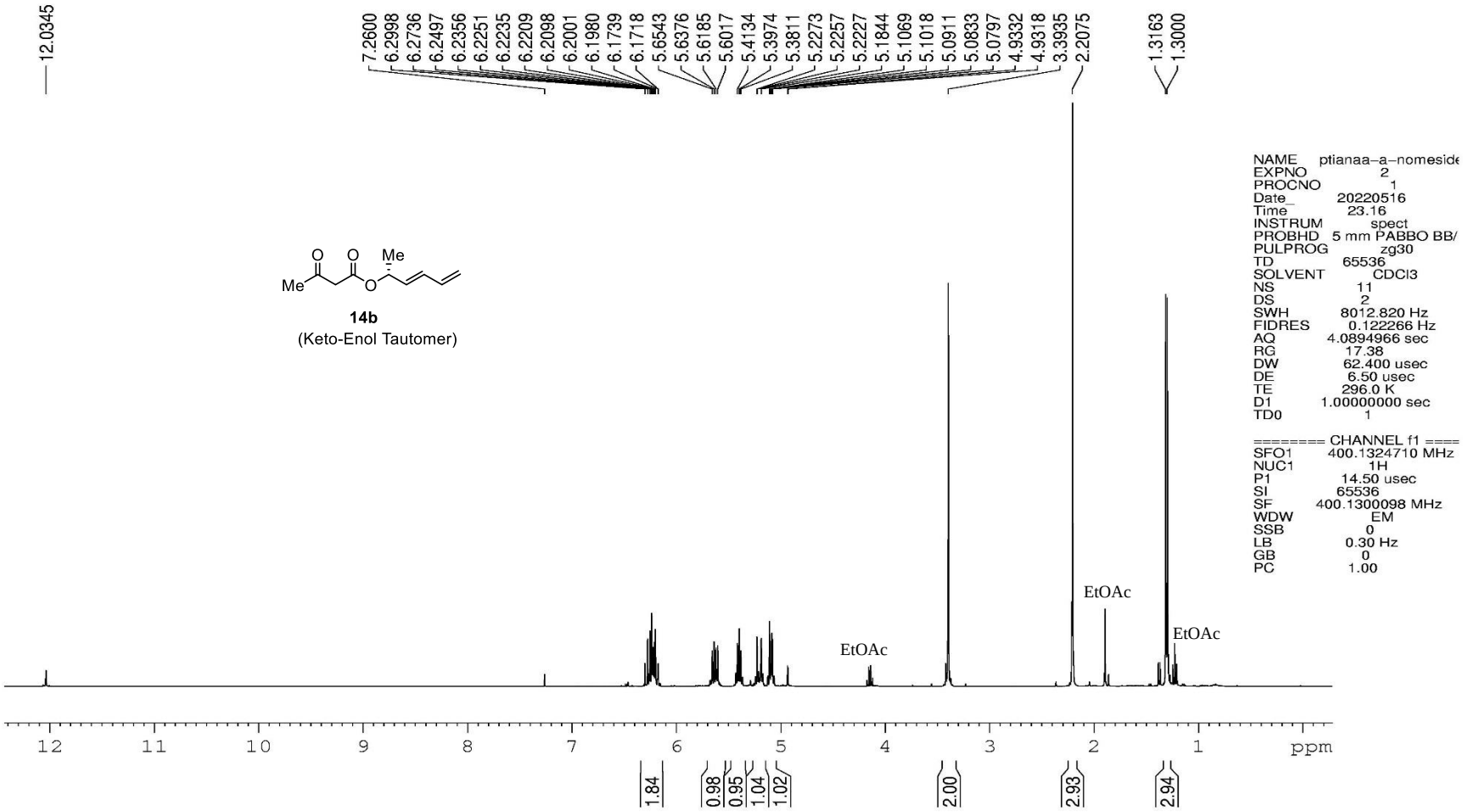

174.0736
143.6331
133.7105
132.4618
125.0392
120.9001
113.2221
77.3188
77.0007
76.6837
51.0873
49.7413
41.1824
38.8592
37.3731
37.2319
33.8321
31.1213
23.3311
15.6111
NAME ptianaa-a-90-2-C
EXPNO 1
PROCNO 1
Date_ 20211205
Time 21.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 38
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 296.7 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127715 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
H
H
H
Me
O
OMe
S-8
200
180
160
140
120
100
80
60
40
20
0
ppm

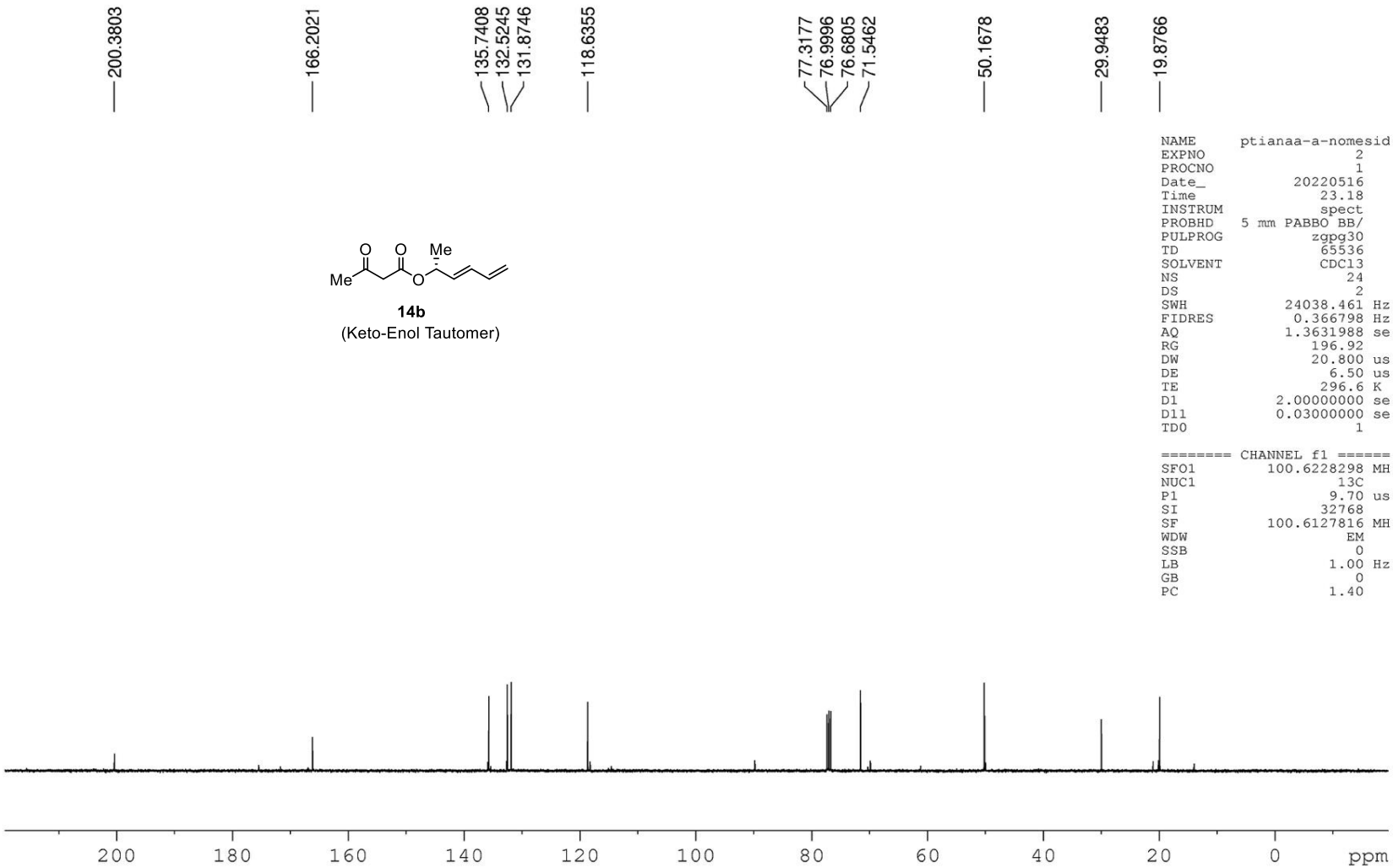

9.8627
9.8531
7.2601
5.8275
5.8099
5.8011
5.7841
5.7672
5.7585
5.7409
5.6872
5.6608
5.6538
5.6453
5.6412
5.6195
5.6156
5.3735
5.3648
5.0174
5.0111
4.9937
4.9680
2.7077
2.7000
2.6945
2.6861
2.4922
2.4825
2.4759
2.4648
2.4544
2.4478
2.4383
2.4241
2.4075
2.3919
2.3755
2.3089
2.2682
2.0584
2.0201
1.9975
1.9613
1.9366
1.9260
1.9099
1.8995
1.8446
1.8101
1.6741
1.6485
Me
Me
H
H
H
H
O
13b
NAME ptianaa-a-15
EXPNO 5
PROCNO 1
Date_ 20211209
Time 1.35
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 62.93
DW 62.400 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.08
2.08
1.00
2.12
1.01
1.09
1.11
1.10
3.10
1.16
3.13
1.20
3.15

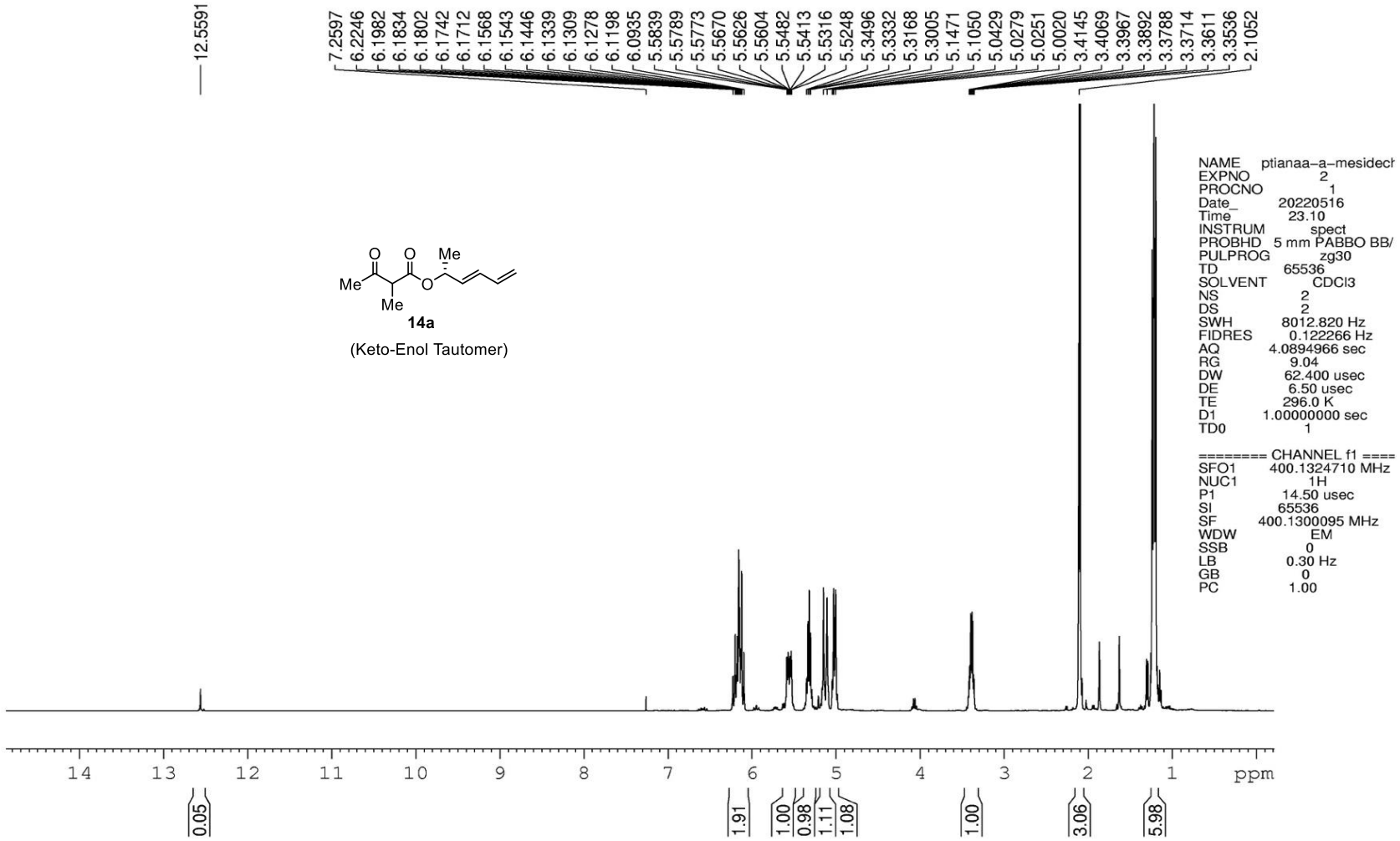

205.5575
143.7718
134.1674
132.4640
126.0395
120.4717
114.2440
77.3185
77.0005
76.6834
55.8403
41.9072
39.2992
37.5233
36.9431
32.7492
30.7970
23.3801
17.2105
Me
Me
H
H
H
H
H
O
13b
NAME ptianaa-a-15-C
EXPNO 5
PROCNO 1
Date_ 20211209
Time 1.38
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 150
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 297.0 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127715 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

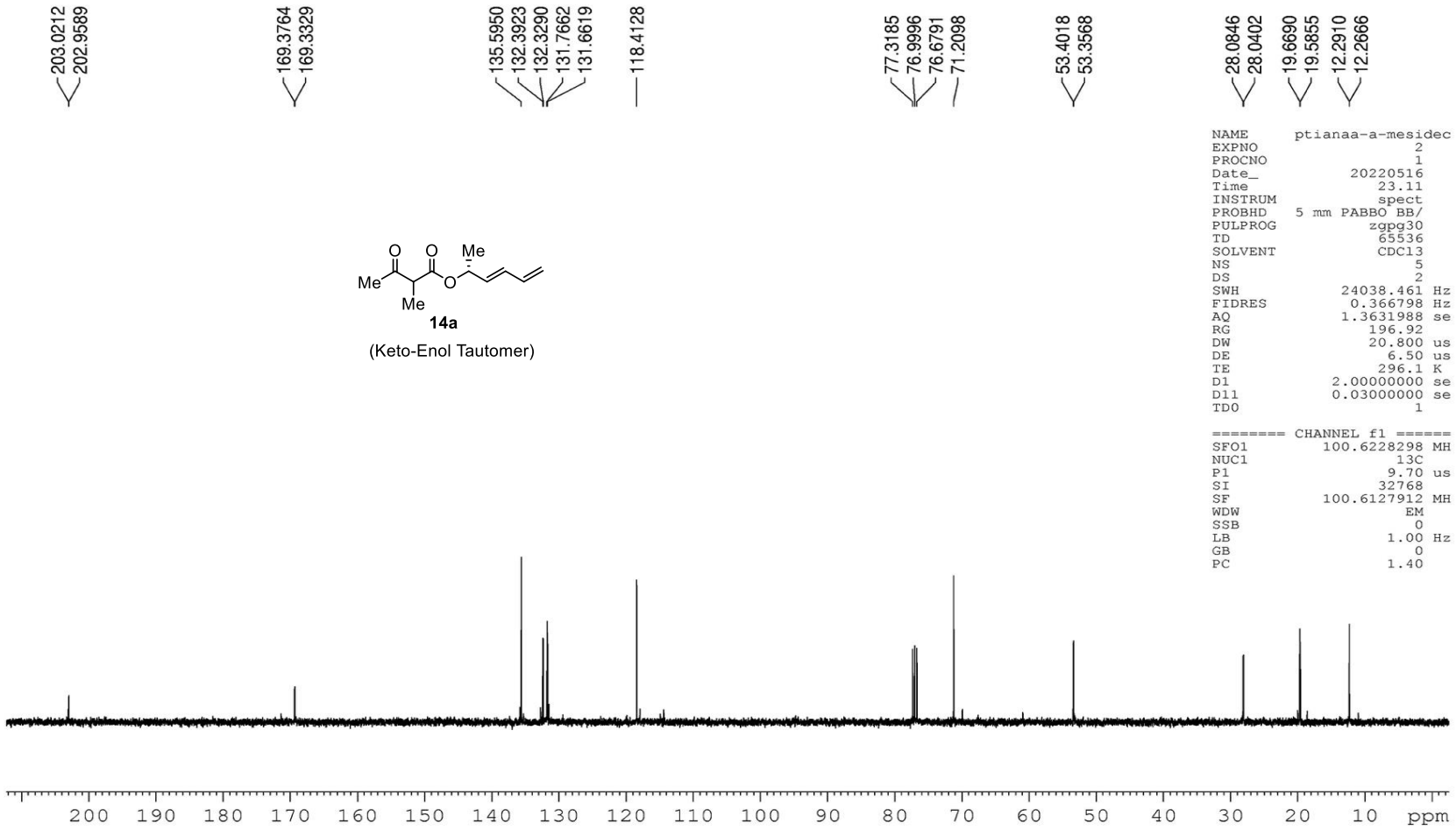

6.3312
6.3219
6.3058
6.2804
6.2456
6.2431
6.2193
6.2168
6.2074
6.2061
6.1799
6.1790
5.7836
5.7678
5.7457
5.7449
5.7300
5.7291
5.2393
5.2353
5.1945
5.1117
5.1080
5.0863
5.0837
4.3744
4.3587
4.3438
1.3019
1.2858
Me
HO
E isomer
Me
HO
Z isomer
S-10
E/Z >13:1
(inseparable)
NAME ptianaa-a-s13
EXPNO 1
PROCNO 1
Date_ 20220515
Time 0.16
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 512
DW 60.800 usec
DE 6.00 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
0.08
1.11
0.97
0.98
1.00
1.07
1.00
1.38
3.14

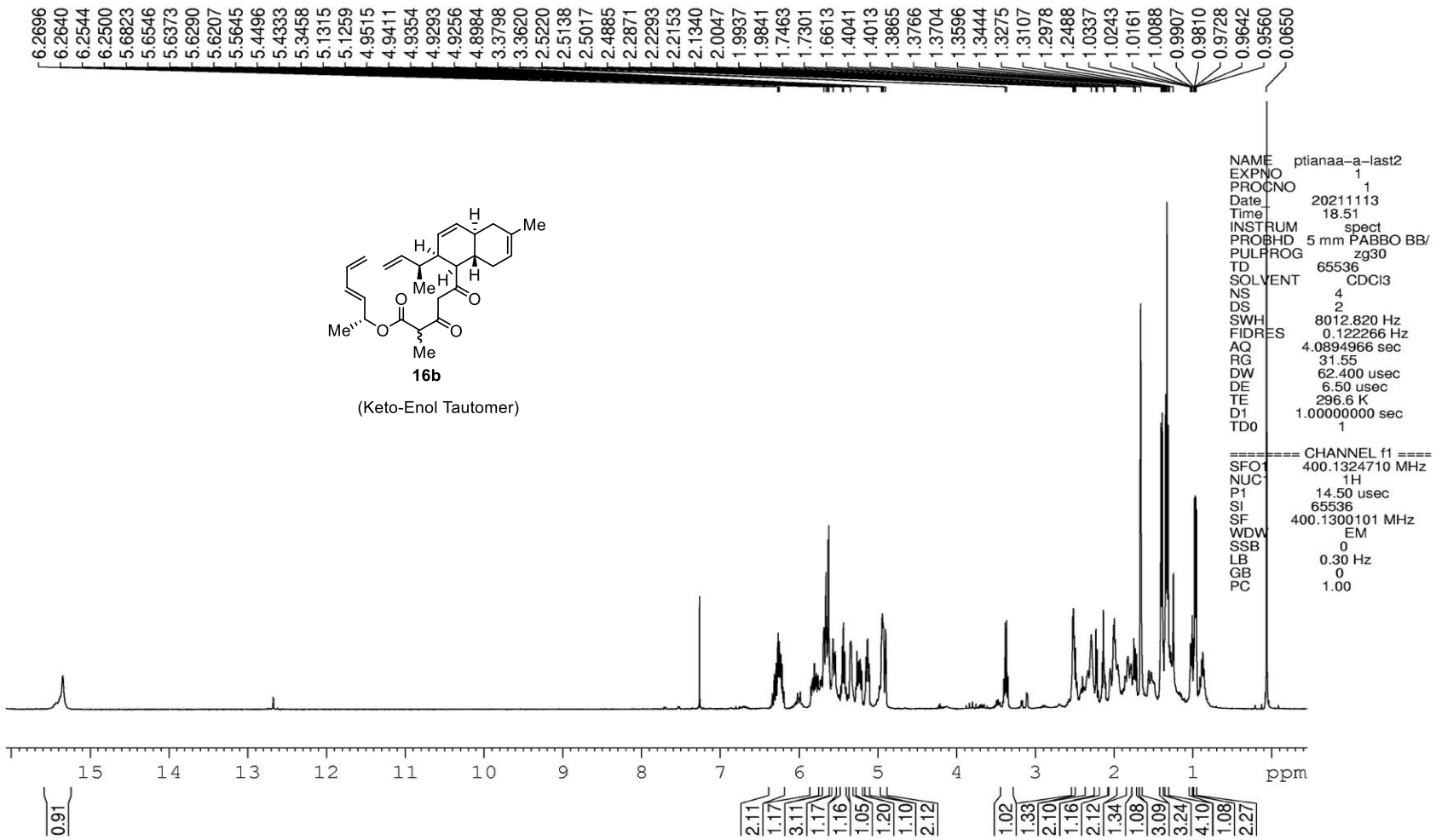

137.5763
136.3020
130.1237
117.5712
77.3153
76.9987
76.6803
68.3824
23.2135
Me
HO
E isomer
Me
HO
Z isomer
S-10
E/Z >13:1
(inseparable)
NAME ptianaa-a-s13-C2
EXPNO 1
PROCNO 1
Date_ 20220515
Time 0.19
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 83
DS 1
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.00 usec
TE 295.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ====
NUC1 13C
P1 40.00 usec
PL1 -3.00 dB
PL1W 60.64365387 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.39 dB
PL13 18.00 dB
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

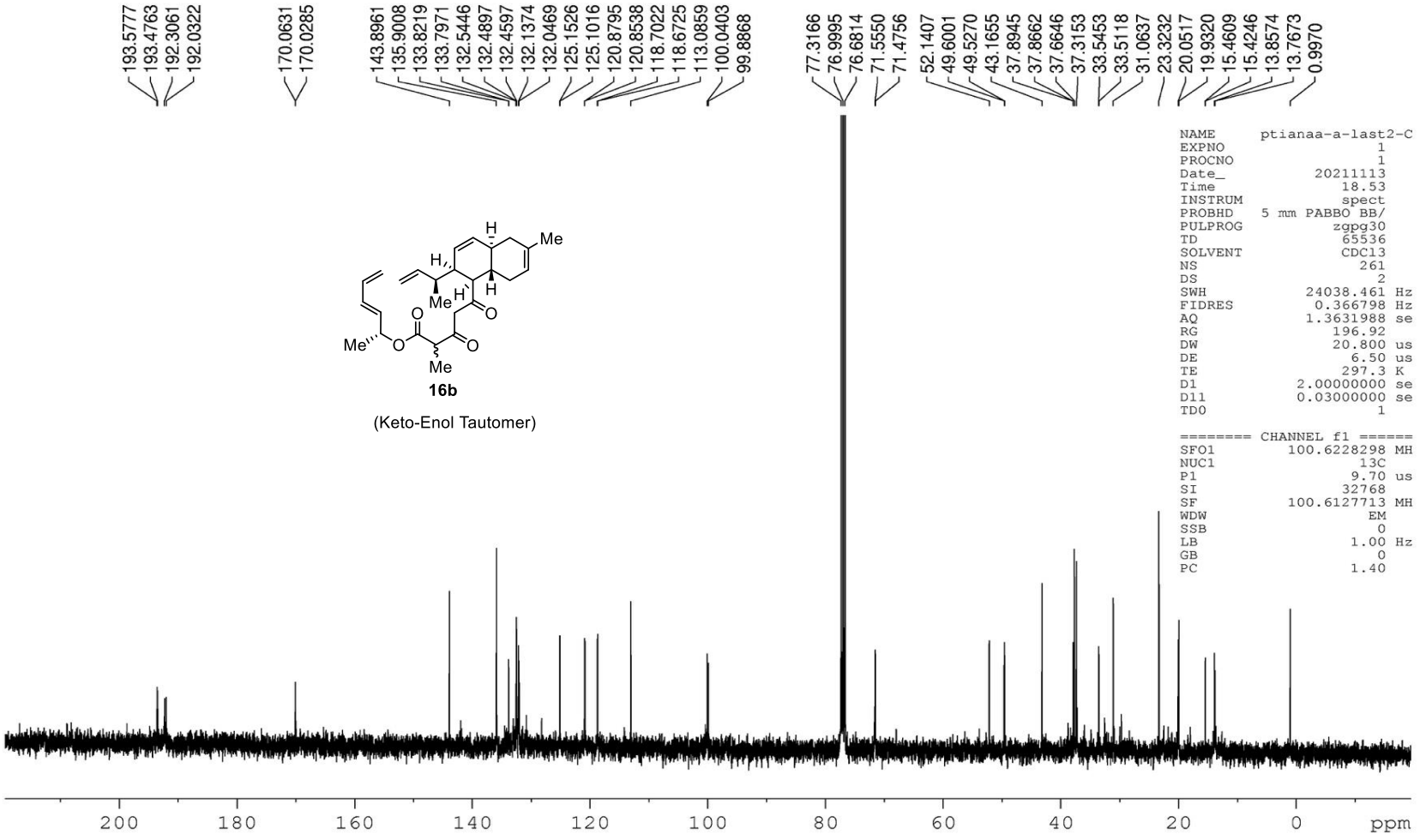

12.0345
7.2600
6.2998
6.2736
6.2497
6.2356
6.2251
6.2235
6.2209
6.2098
6.2001
6.1980
6.1739
6.1718
5.6543
5.6376
5.6185
5.6017
5.4134
5.3974
5.3811
5.2273
5.2257
5.2227
5.1844
5.1069
5.1018
5.0911
5.0833
5.0797
4.9332
4.9318
3.3935
2.2075
1.3163
1.3000
Me
O
O
Me
O
14b
(Keto-Enol Tautomer)
NAME ptianaa-a-nomeside
EXPNO 2
PROCNO 1
Date_ 20220516
Time 23.16
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 17.38
DW 62.400 usec
DE 6.50 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
EtOAc
EtOAc
EtOAc
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.84
0.98
0.95
1.04
1.02
2.00
2.93
2.94


200.3803
166.2021
135.7408
132.5245
131.8746
118.6355
77.3177
76.9996
76.6805
71.5462
50.1678
29.9483
19.8766
O
O
Me
Me
O
14b
(Keto-Enol Tautomer)
NAME ptianaa-a-nomesid
EXPNO 2
PROCNO 1
Date_ 20220516
Time 23.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 24
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 296.6 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127816 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm


12.5591
7.2597
6.2246
6.1982
6.1834
6.1802
6.1742
6.1712
6.1568
6.1543
6.1446
6.1339
6.1309
6.1278
6.1198
6.0935
5.5839
5.5789
5.5773
5.5670
5.5626
5.5604
5.5482
5.5413
5.5316
5.5248
5.3496
5.3332
5.3168
5.3005
5.1471
5.1050
5.0429
5.0279
5.0251
5.0020
3.4145
3.4069
3.3967
3.3892
3.3788
3.3714
3.3611
3.3536
2.1052
Me
O
O
Me
Me
O
Me
14a
(Keto-Enol Tautomer)
NAME ptianaa-a-mesitech
EXPNO 2
PROCNO 1
Date_ 20220516
Time 23.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 9.04
DW 62.400 usec
DE 6.50 usec
TE 296.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.05
1.91
1.00
0.98
1.11
1.08
1.00
3.06
5.98

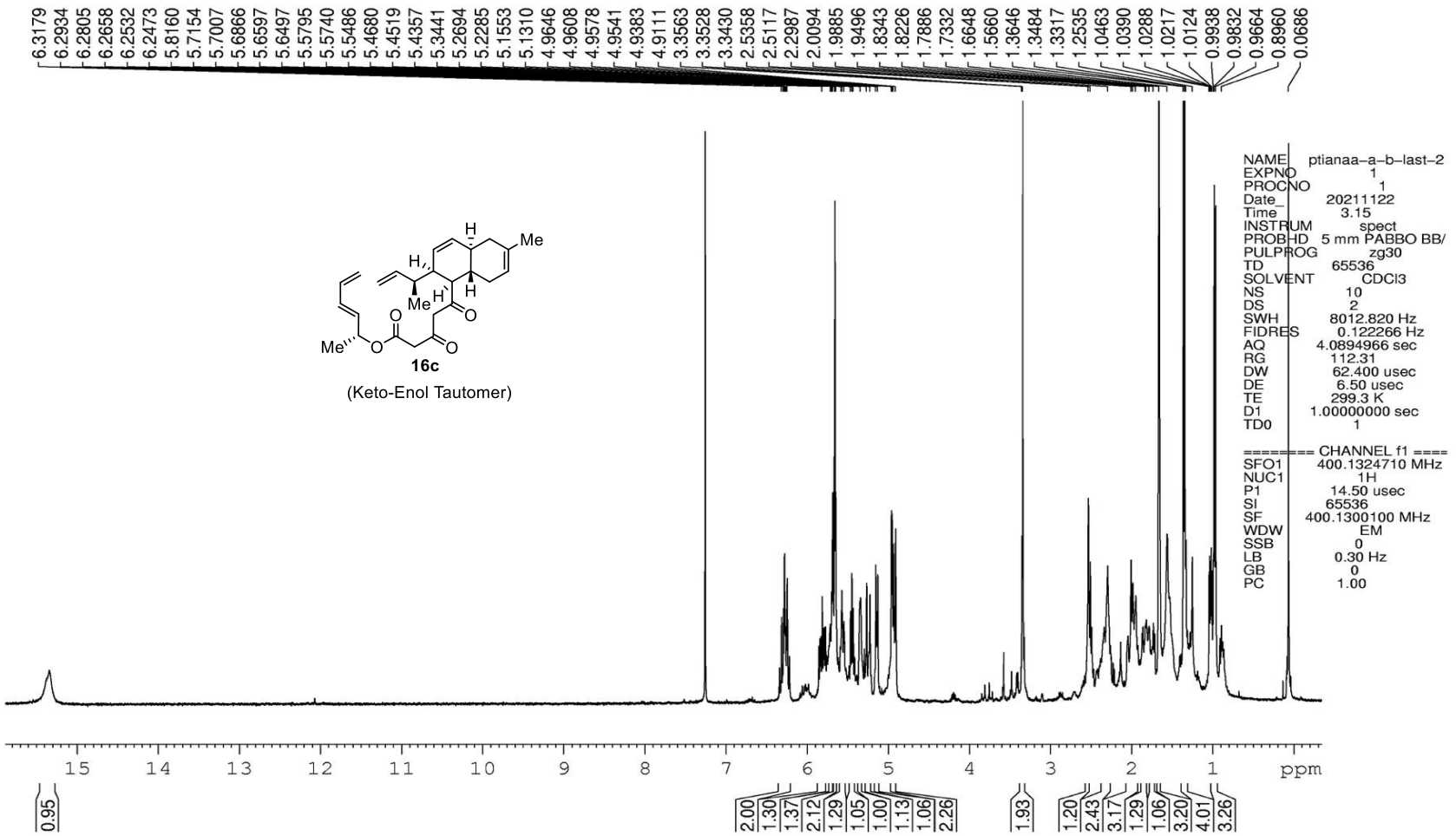

203.0212
202.9589
169.3764
169.3329
135.5950
132.3923
132.3290
131.7662
131.6619
118.4128
77.3185
76.9996
76.6791
71.2098
53.4018
53.3568
28.0846
28.0402
19.6690
19.5855
12.2910
12.2666
Me
Me
Me
14a
(Keto-Enol Tautomer)
NAME ptianaa-a-mesidec
EXPNO 2
PROCNO 1
Date_ 20220516
Time 23.11
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 296.1 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127912 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

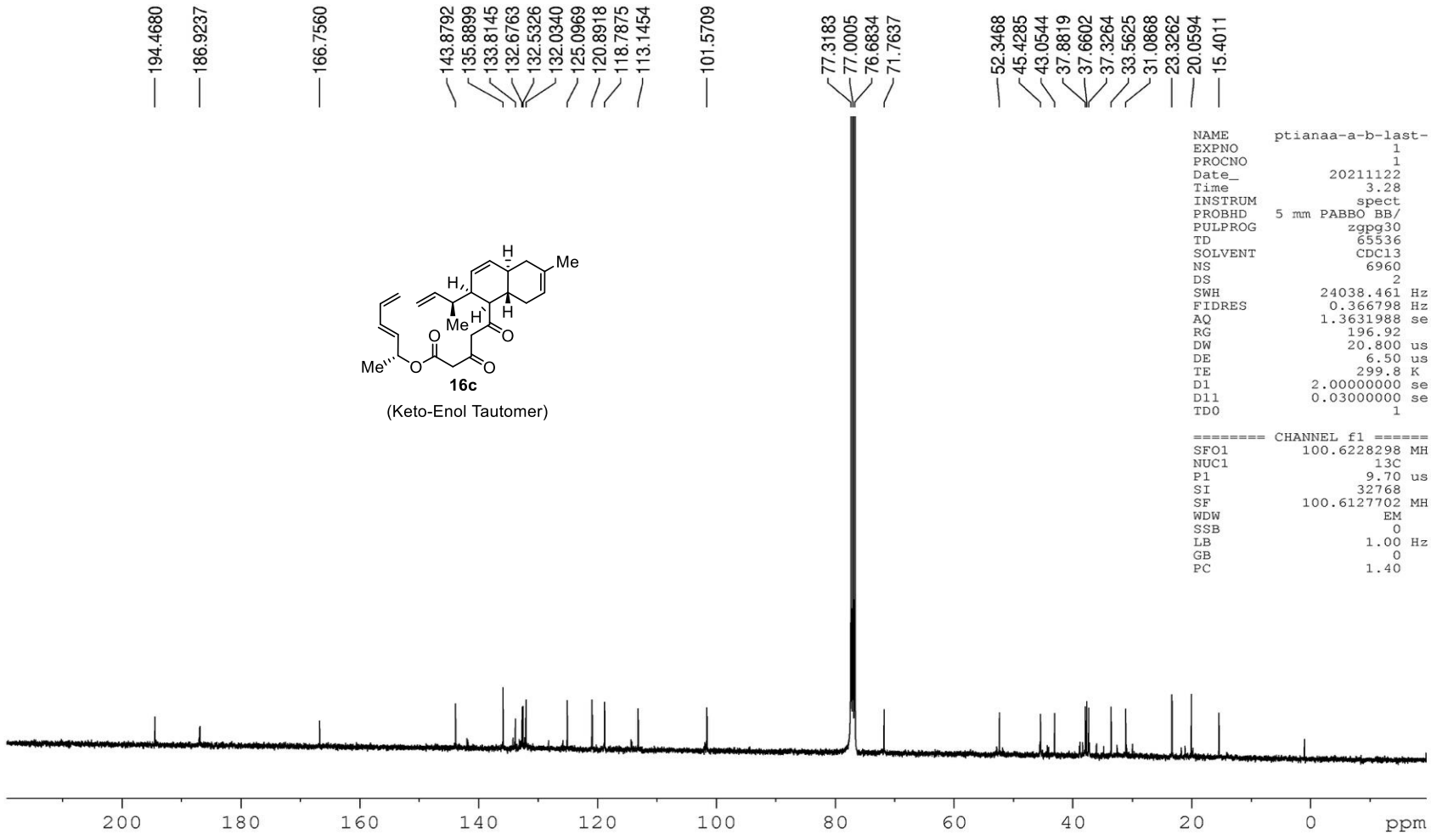

6.2696
6.2640
6.2544
6.2500
6.6823
6.6546
6.6373
6.6290
6.6207
6.5645
6.5496
6.4333
6.3458
6.1315
6.1259
4.9515
4.9411
4.9354
4.9293
4.9256
4.8984
3.3798
3.3620
2.5220
2.5138
2.5017
2.4885
2.2871
2.2293
2.2153
2.1340
2.0047
1.9937
1.9841
1.7463
1.7301
1.6613
1.4041
1.4013
1.3865
1.3766
1.3704
1.3596
1.3444
1.3275
1.3107
1.2978
1.2488
1.0337
1.0243
1.0161
1.0088
0.9907
0.9810
0.9728
0.9642
0.9560
0.0650
Me
H
H
Me
H
H
O
O
O
Me
O
Me
16b
(Keto-Enol Tautomer)
NAME ptianaa–a–last2
EXPNO 1
PROCNO 1
Date 20211113
Time 18.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 31.55
DW 62.400 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC 1H
P1 14.50 usec
SI 65536
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.91
2.11
1.17
3.11
1.17
1.16
1.05
1.20
1.10
2.12
1.02
1.33
2.10
1.16
2.12
1.34
1.08
3.09
3.24
4.10
1.08
2.27

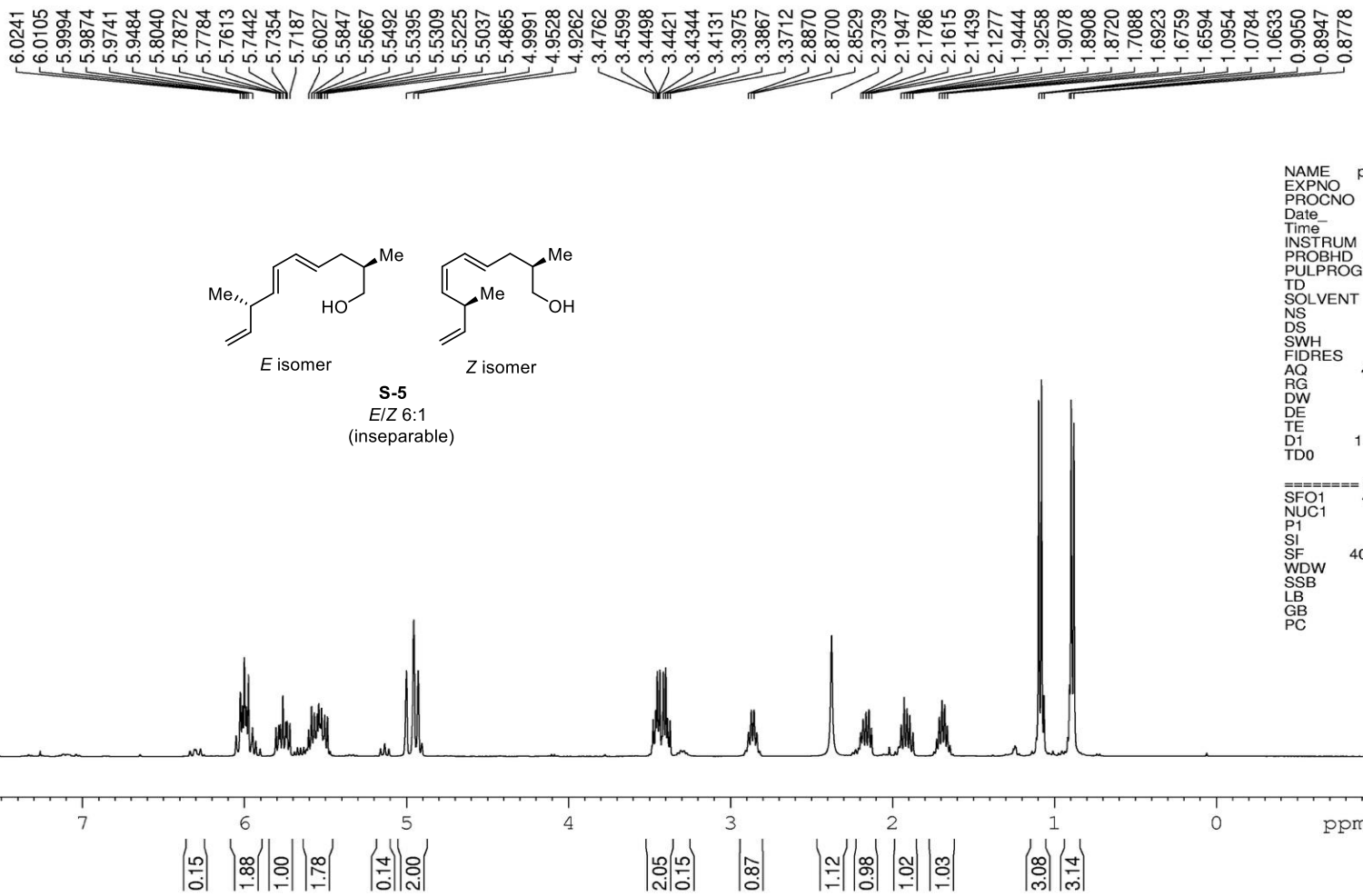


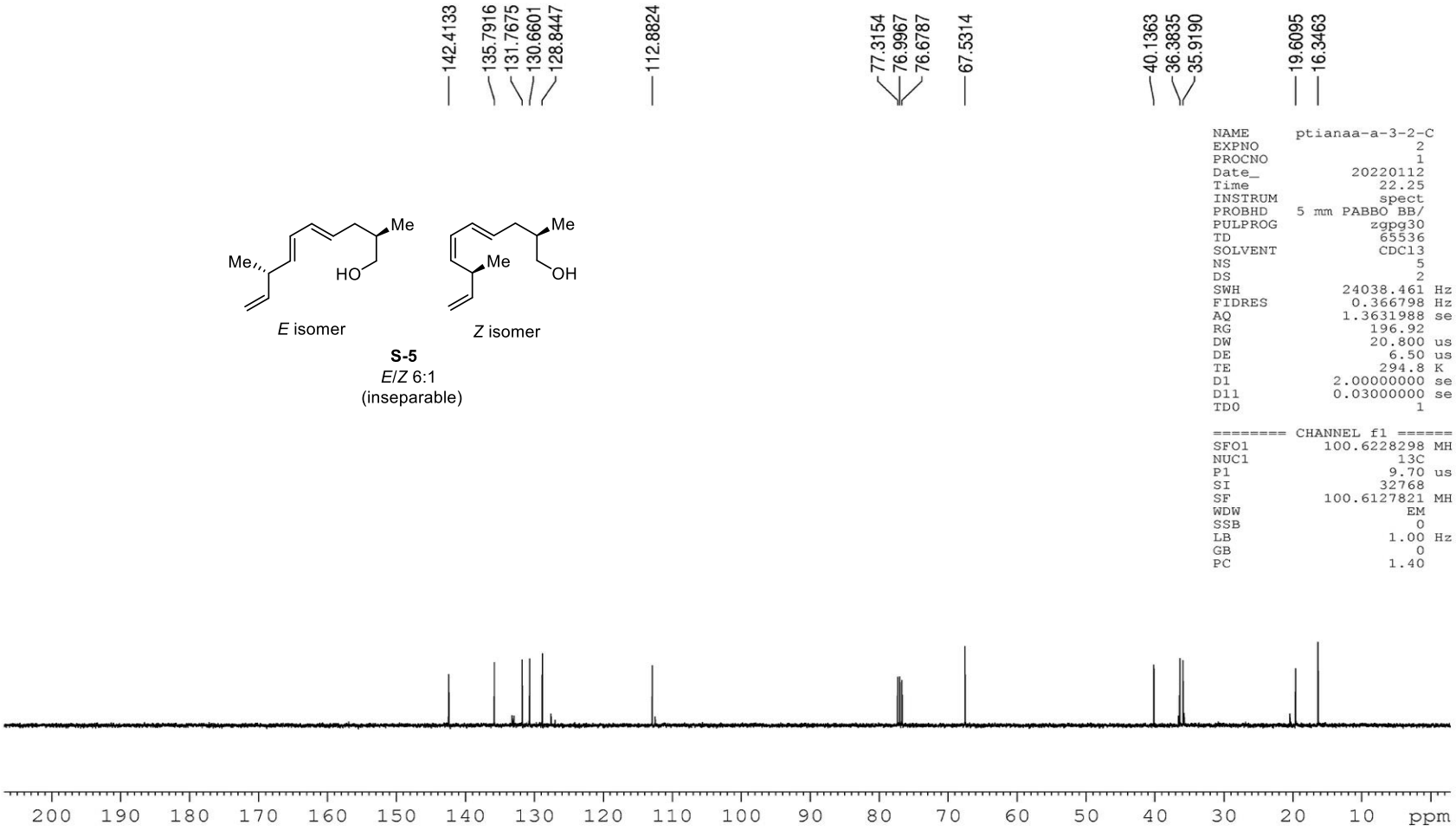
16b

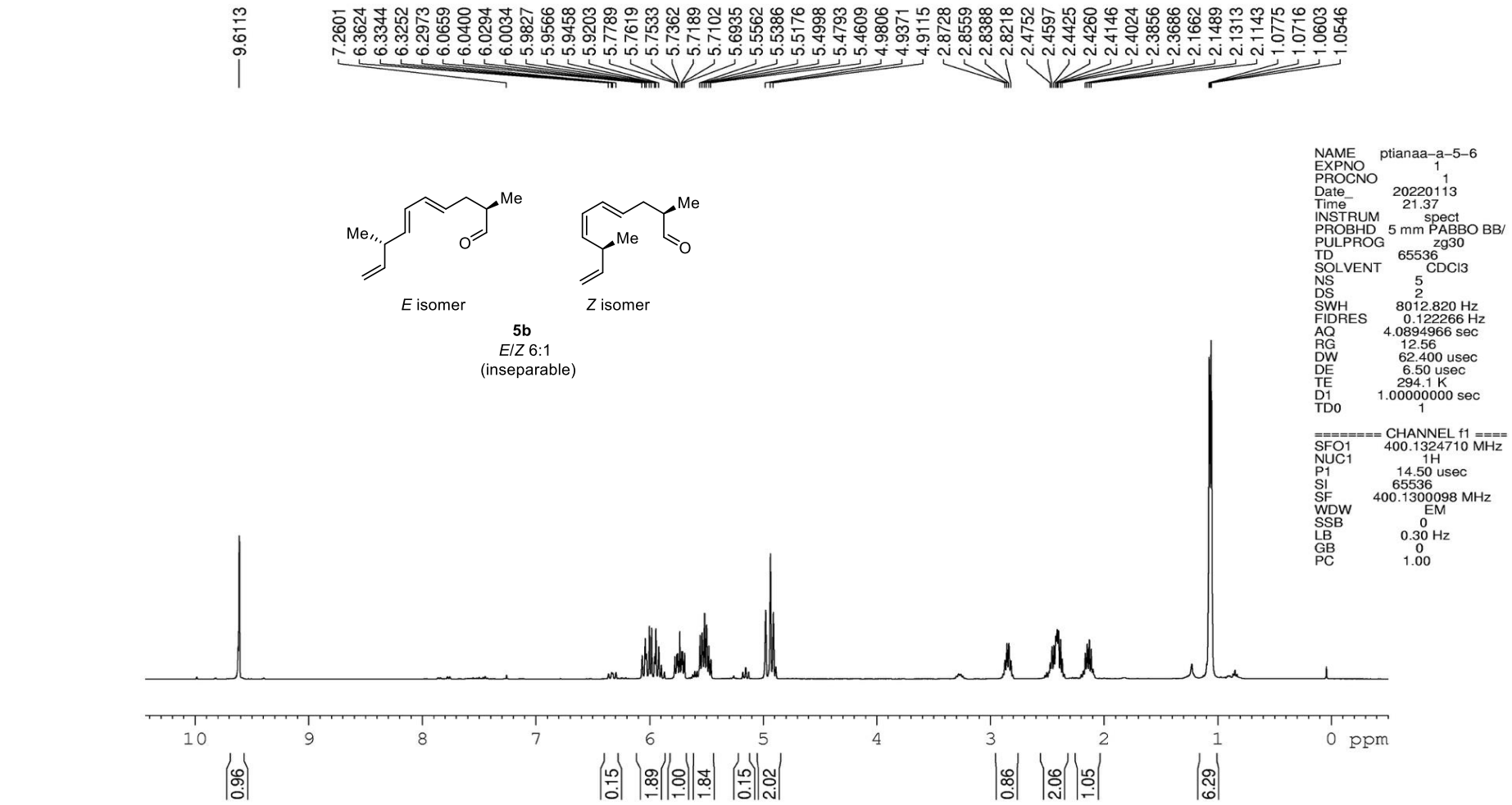
(Keto-Enol Tautomer)

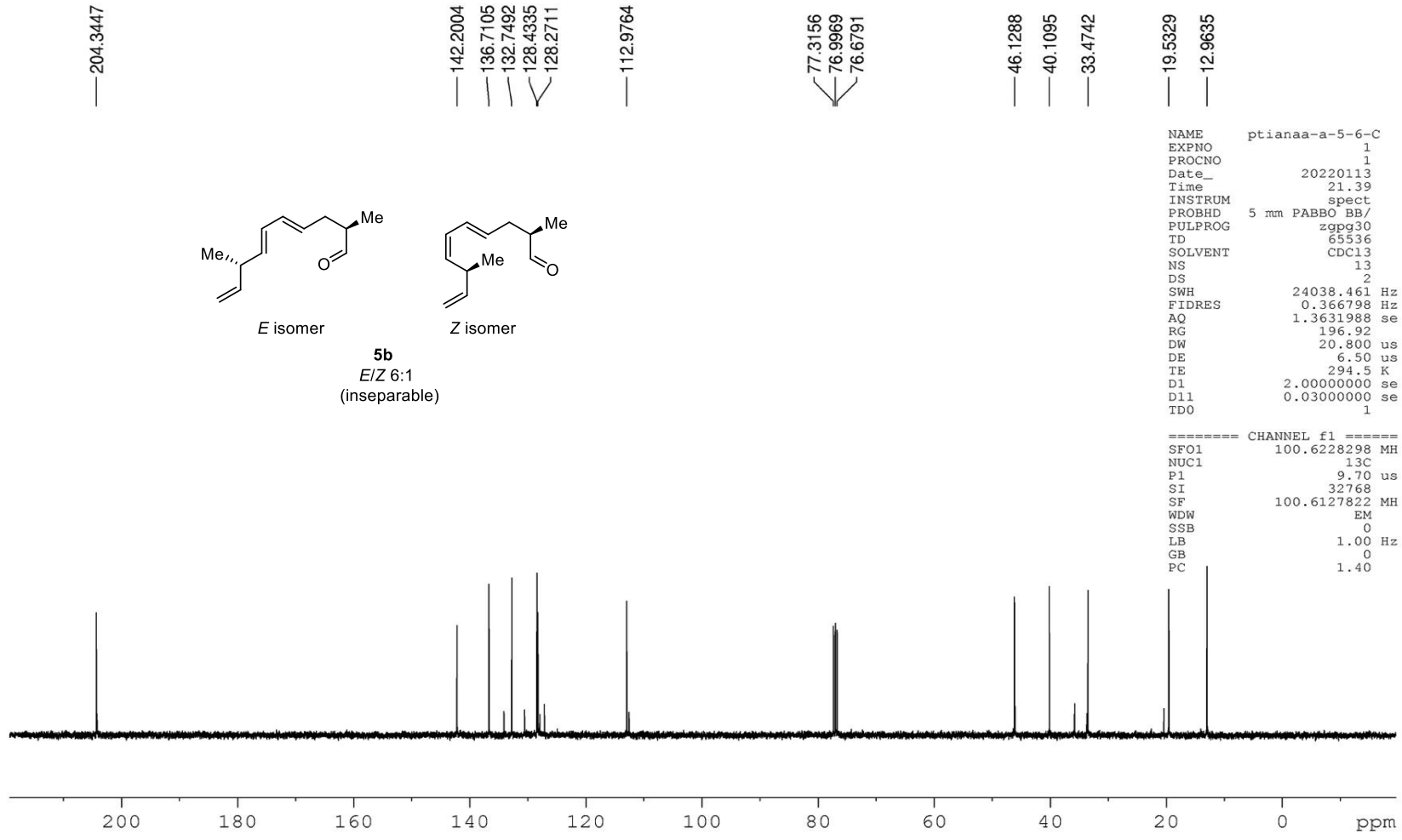

6.3179
6.2934
6.2805
6.2658
6.2532
6.2473
5.8160
5.7154
5.7007
5.6866
5.6597
5.6497
5.5795
5.5740
5.5486
5.4680
5.4519
5.4357
5.3441
5.2694
5.2285
5.1553
5.1310
4.9646
4.9608
4.9578
4.9541
4.9383
4.9111
3.3563
3.3528
3.3430
2.5358
2.5117
2.2987
2.0094
1.9885
1.9496
1.8343
1.8226
1.7886
1.7332
1.6648
1.5660
1.3646
1.3484
1.3317
1.2535
1.0463
1.0390
1.0288
1.0217
1.0124
0.9938
0.9832
0.9664
0.8960
0.0686
Me
H
H
H
Me
H
O
O
O
Me
O
16c
(Keto-Enol Tautomer)
NAME ptianaa–a–b–last–2
EXPNO 1
PROCNO 1
Date_ 20211122
Time 3.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 112.31
DW 62.400 usec
DE 6.50 usec
TE 299.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.95
2.00
1.30
1.37
2.12
1.29
1.05
1.00
1.13
1.06
2.26
1.93
1.20
2.43
3.17
1.29
1.06
3.20
4.01
3.26

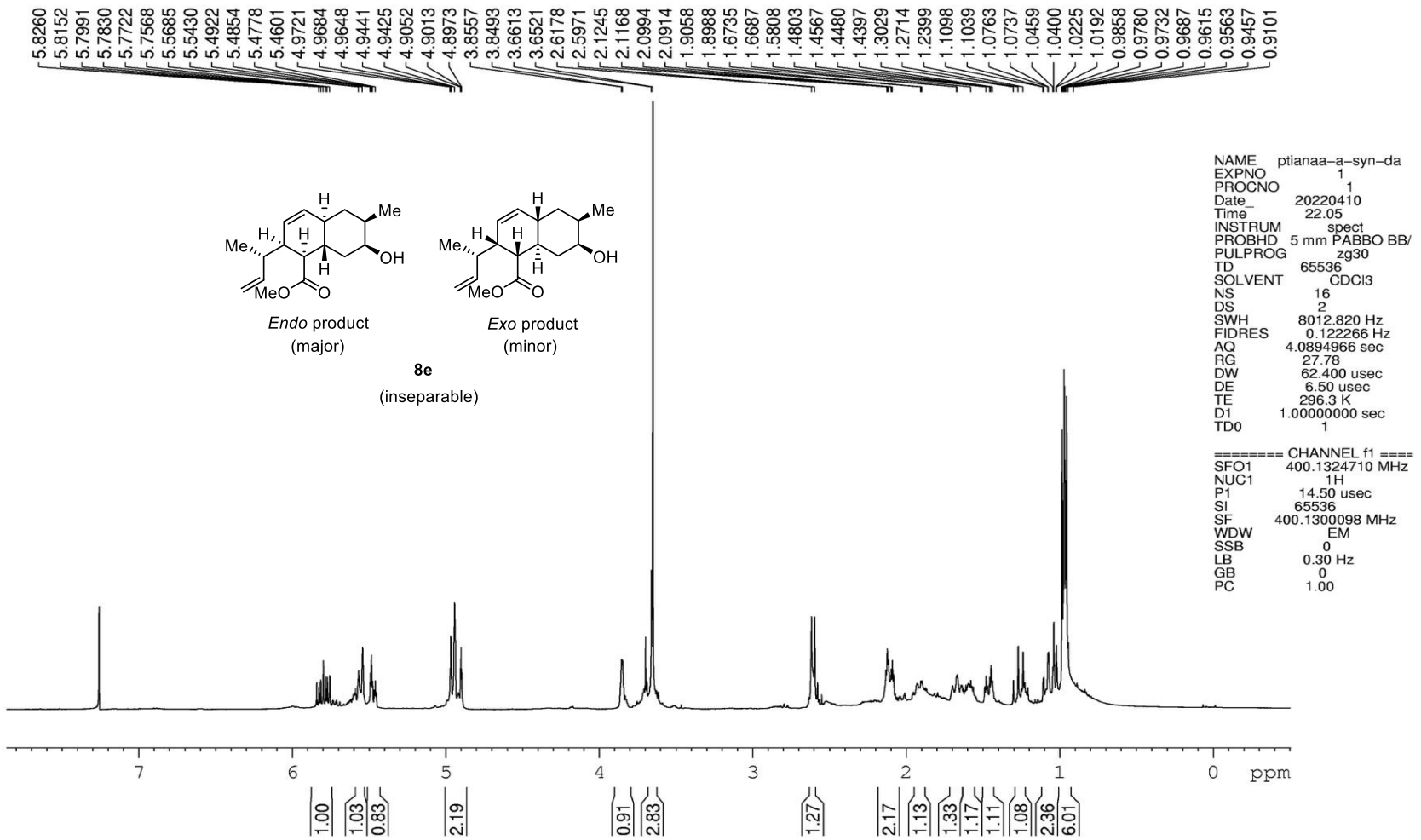

194.4680
186.9237
166.7560
143.8792
135.8899
133.8145
132.6763
132.5326
132.0340
125.0969
120.8918
118.7875
113.1454
101.5709
77.3183
77.0005
76.6834
71.7637
52.3468
45.4285
43.0544
37.8819
37.6602
37.3264
33.5625
31.0868
23.3262
20.0594
15.4011
NAME ptianaa-a-b-last-
EXPNO 1
PROCNO 1
Date_ 20211122
Time 3.28
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6960
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 299.8 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127702 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
16c
(Keto-Enol Tautomer)
200
180
160
140
120
100
80
60
40
20
0
ppm

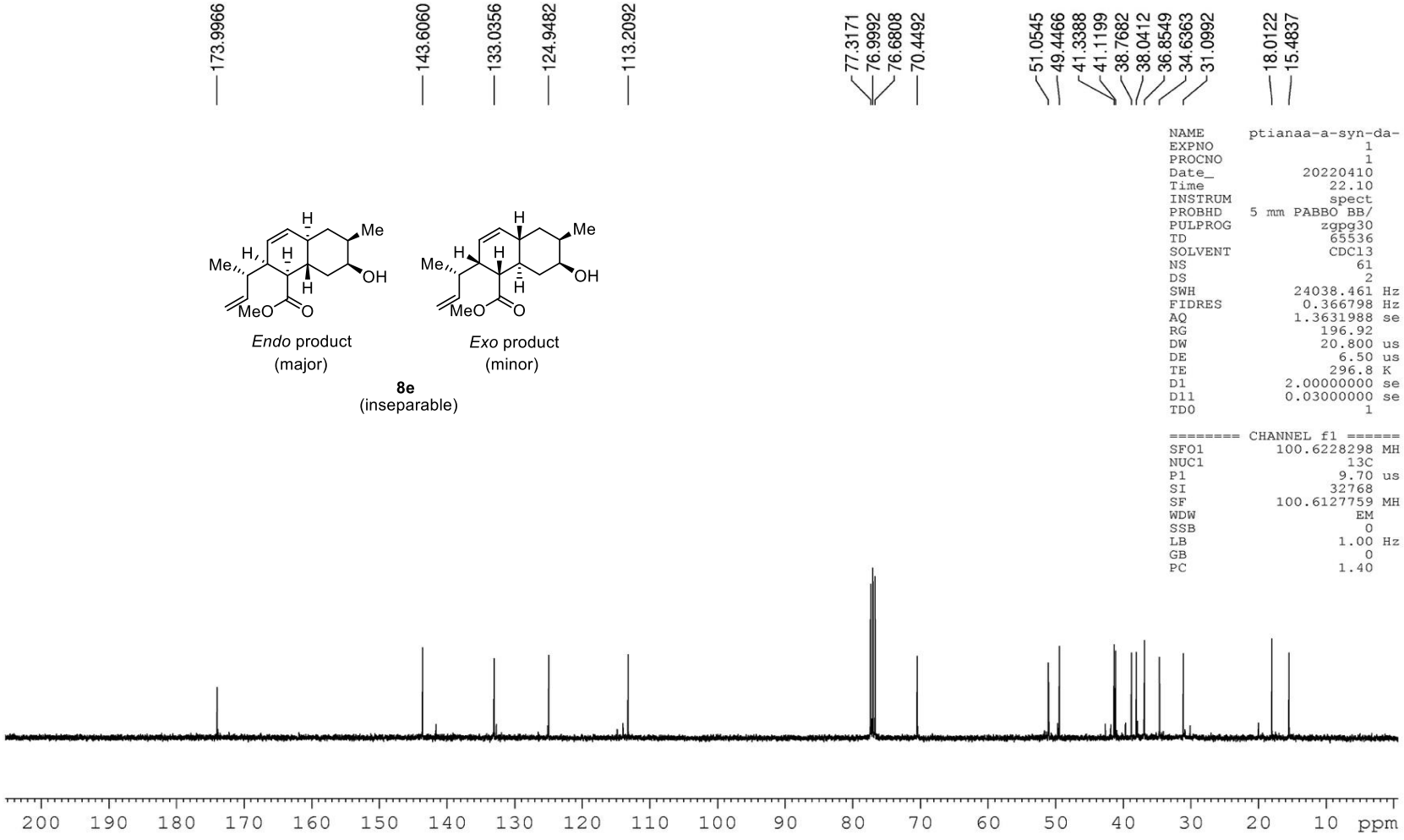

6.0241
6.0105
5.9994
5.9874
5.9741
5.9484
5.8040
5.7872
5.7784
5.7613
5.7442
5.7354
5.7187
5.6027
5.5847
5.5667
5.5492
5.5395
5.5309
5.5225
5.5037
5.4865
4.9991
4.9528
4.9262
3.4762
3.4599
3.4498
3.4421
3.4344
3.4131
3.3975
3.3867
3.3712
2.8870
2.8700
2.8529
2.3739
2.1947
2.1786
2.1615
2.1439
2.1277
1.9444
1.9258
1.9078
1.8908
1.8720
1.7088
1.6923
1.6759
1.6594
1.0954
1.0784
1.0633
0.9050
0.8947
0.8778
Me
Me
HO
Me
Me
OH
E isomer
Z isomer
S-5
E/Z 6:1
(inseparable)
NAME ptianaa–a–3–2
EXPNO 2
PROCNO 1
Date_ 20220112
Time 22.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 11.3
DW 62.400 usec
DE 6.50 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7
6
5
4
3
2
1
0
ppm
0.15
1.88
1.00
1.78
0.14
2.00
2.05
0.15
0.87
1.12
0.98
1.02
1.03
3.08
3.14


142.4133
135.7916
131.7675
130.6601
128.8447
112.8824
77.3154
76.9967
76.6787
67.5314
40.1363
36.3835
35.9190
19.6095
16.3463
Me
Me
HO
Me
Me
OH
E isomer
Z isomer
S-5
E/Z 6:1
(inseparable)
NAME ptianaa-a-3-2-C
EXPNO 2
PROCNO 1
Date_ 20220112
Time 22.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 294.8 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127821 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


9.6113
7.2601
6.3624
6.3344
6.3252
6.2973
6.0659
6.0400
6.0294
6.0034
5.9827
5.9566
5.9458
5.9203
5.7789
5.7619
5.7533
5.7362
5.7189
5.7102
5.6935
5.5562
5.5386
5.5176
5.4998
5.4793
5.4609
4.9806
4.9371
4.9115
2.8728
2.8559
2.8388
2.8218
2.4752
2.4597
2.4425
2.4260
2.4146
2.4024
2.3856
2.3686
2.1662
2.1489
2.1313
2.1143
1.0775
1.0716
1.0603
1.0546
Me
Me
O
Me
Me
O
E isomer
Z isomer
5b
E/Z 6:1
(inseparable)
NAME ptianaa–a–5–6
EXPNO 1
PROCNO 1
Date_ 20220113
Time 21.37
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 12.56
DW 62.400 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
0.96
0.15
1.89
1.00
1.84
0.15
2.02
0.86
2.06
1.05
6.29


204.3447
142.2004
136.7105
132.7492
128.4335
128.2711
112.9764
77.3156
76.9969
76.6791
46.1288
40.1095
33.4742
19.5329
12.9635
Me
Me
O
Me
Me
O
E isomer
Z isomer
5b
E/Z 6:1
(inseparable)
NAME ptianaa-a-5-6-C
EXPNO 1
PROCNO 1
Date_ 20220113
Time 21.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 13
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 294.5 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127822 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

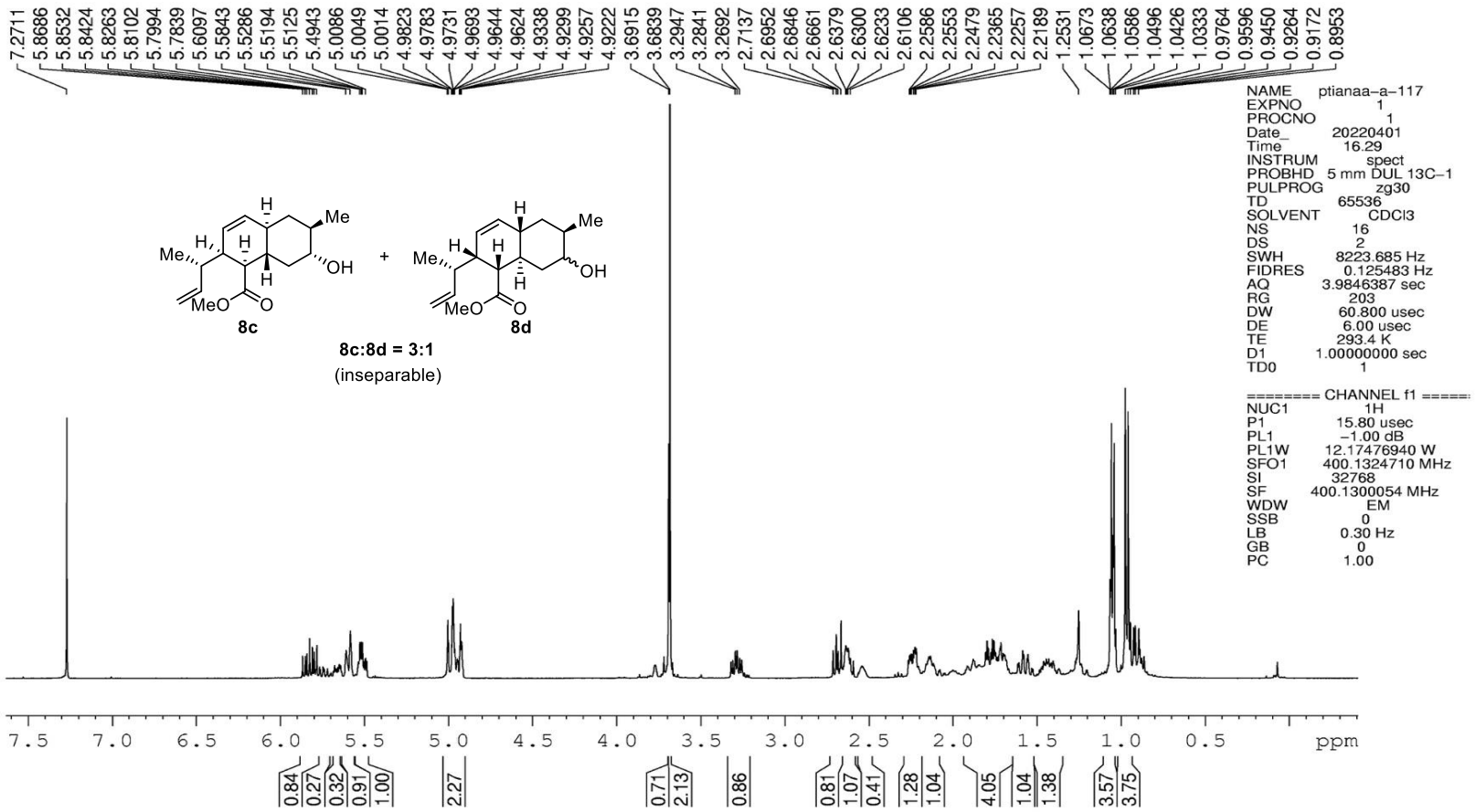

5.8260
5.8152
5.7991
5.7830
5.7722
5.7568
5.5685
5.5430
5.4922
5.4854
5.4778
5.4601
4.9721
4.9684
4.9648
4.9441
4.9425
4.9052
4.9013
4.8973
3.8557
3.8493
3.6613
3.6521
2.6178
2.5971
2.1245
2.1168
2.0994
2.0914
1.9058
1.8988
1.6735
1.6687
1.5808
1.4803
1.4567
1.4480
1.4397
1.3029
1.2714
1.2399
1.1098
1.1039
1.0763
1.0737
1.0459
1.0400
1.0225
1.0192
0.9858
0.9780
0.9732
0.9687
0.9615
0.9563
0.9457
0.9101
NAME ptianaa-a-syn-da
EXPNO 1
PROCNO 1
Date_ 20220410
Time 22.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 27.78
DW 62.400 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Endo product
(major)
Exo product
(minor)
8e
(inseparable)
7
6
5
4
3
2
1
0
ppm
1.00
1.03
0.83
2.19
0.91
2.83
1.27
2.17
1.13
1.33
1.17
1.11
1.08
2.36
6.01



Endo product
(major)

Exo product
(minor)

8e
(inseparable)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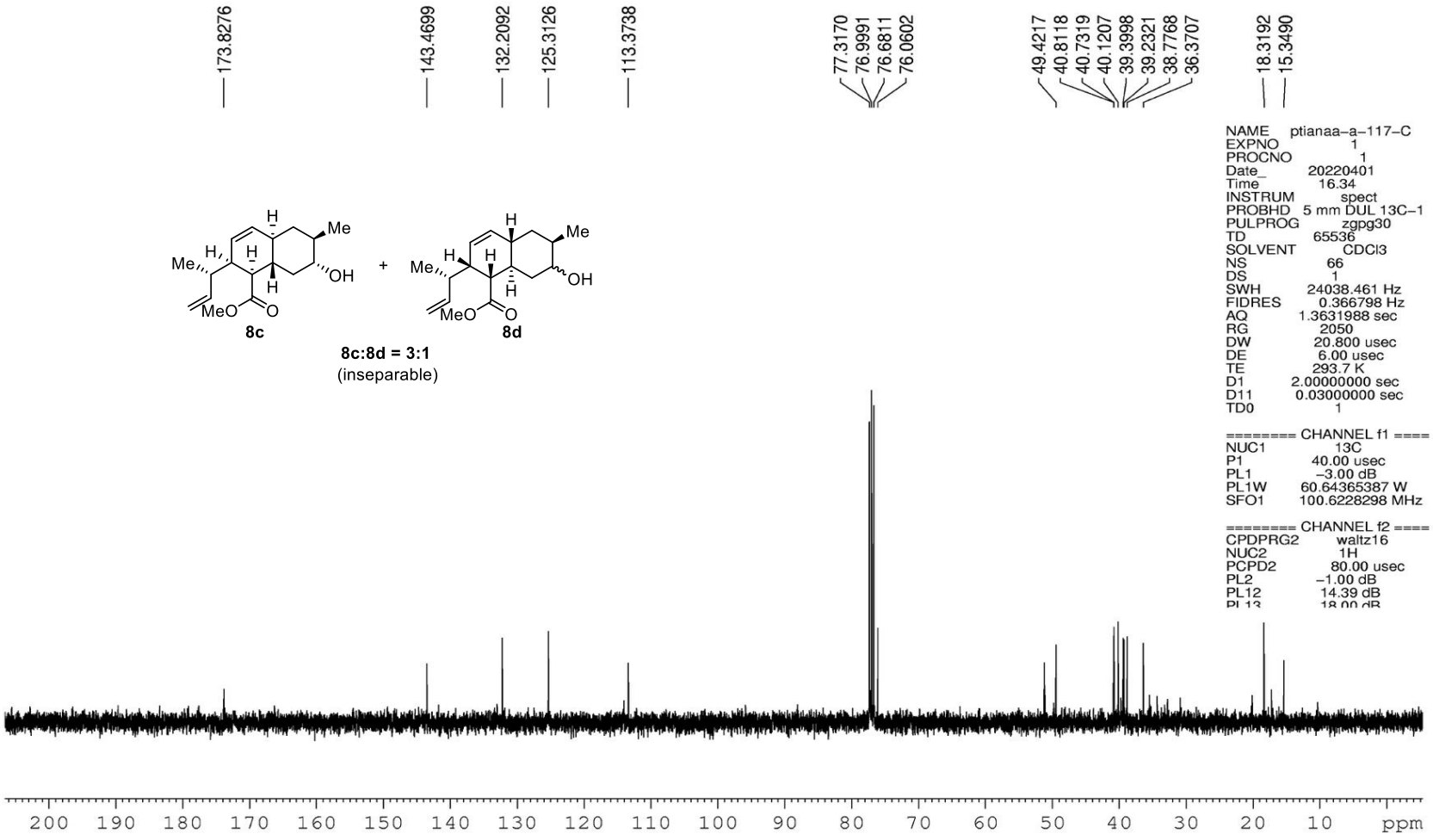
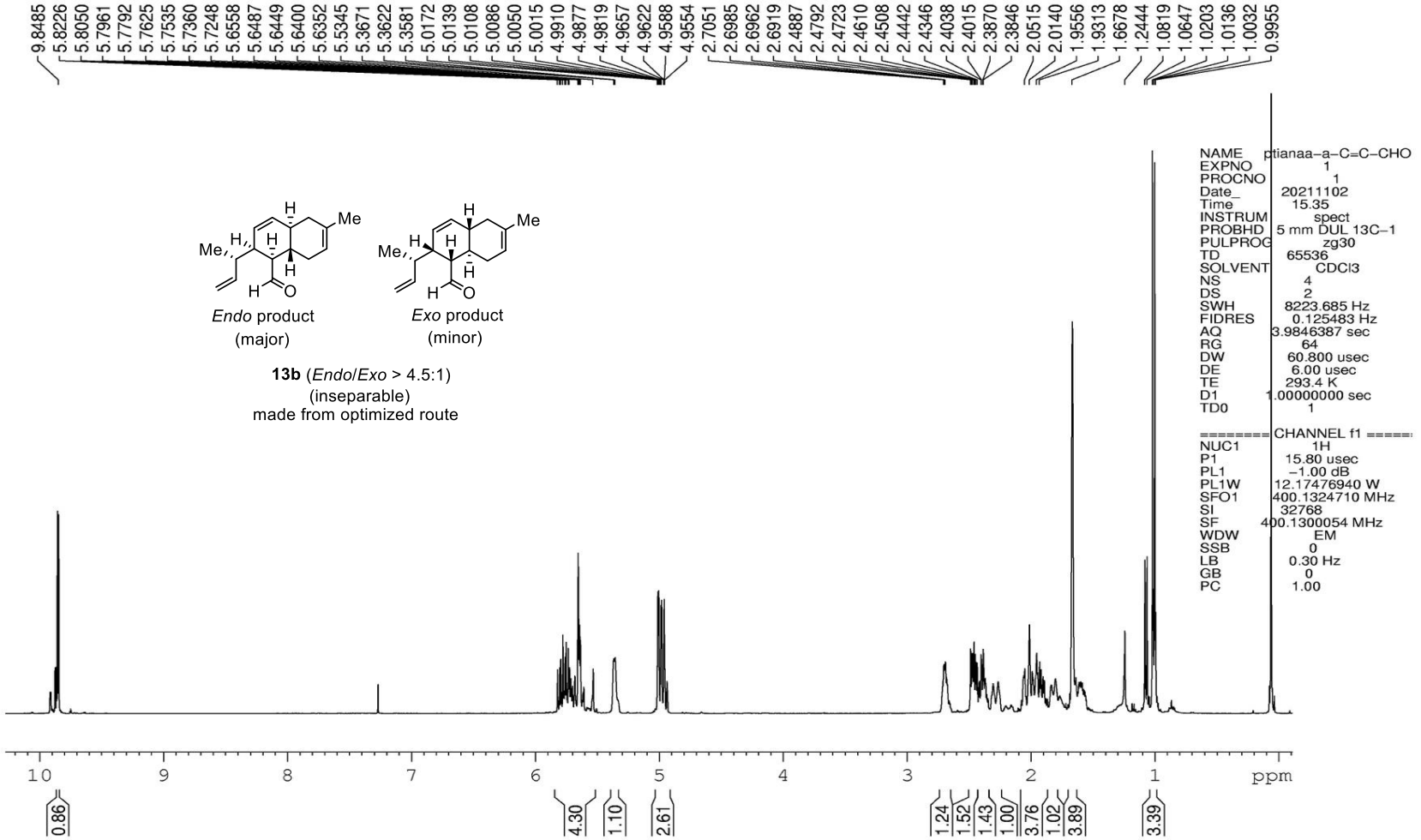
5.8686
5.8532
5.8424
5.8263
5.8102
5.7994
5.7839
5.6097
5.5843
5.5286
5.5194
5.5125
5.4943
5.0086
5.0049
5.0014
4.9823
4.9783
4.9731
4.9693
4.9644
4.9624
4.9338
4.9299
4.9257
4.9222
3.6915
3.6839
3.2947
3.2841
3.2692
2.7137
2.6952
2.6846
2.6661
2.6379
2.6300
2.6233
2.6106
2.2586
2.2553
2.2479
2.2365
2.2257
2.2189
1.2531
1.0673
1.0638
1.0586
1.0496
1.0426
1.0333
0.9764
0.9596
0.9450
0.9264
0.9172
0.8953
NAME ptianaa-a-117
EXPNO 1
PROCNO 1
Date_ 20220401
Time 16.29
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.00 usec
TE 293.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8c
8d
8c:8d = 3:1
(inseparable)
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
0.84
0.27
0.32
0.91
1.00
2.27
0.71
2.13
0.86
0.81
1.07
0.41
1.28
1.04
4.05
1.04
1.38
3.57
3.75



8c + 8d

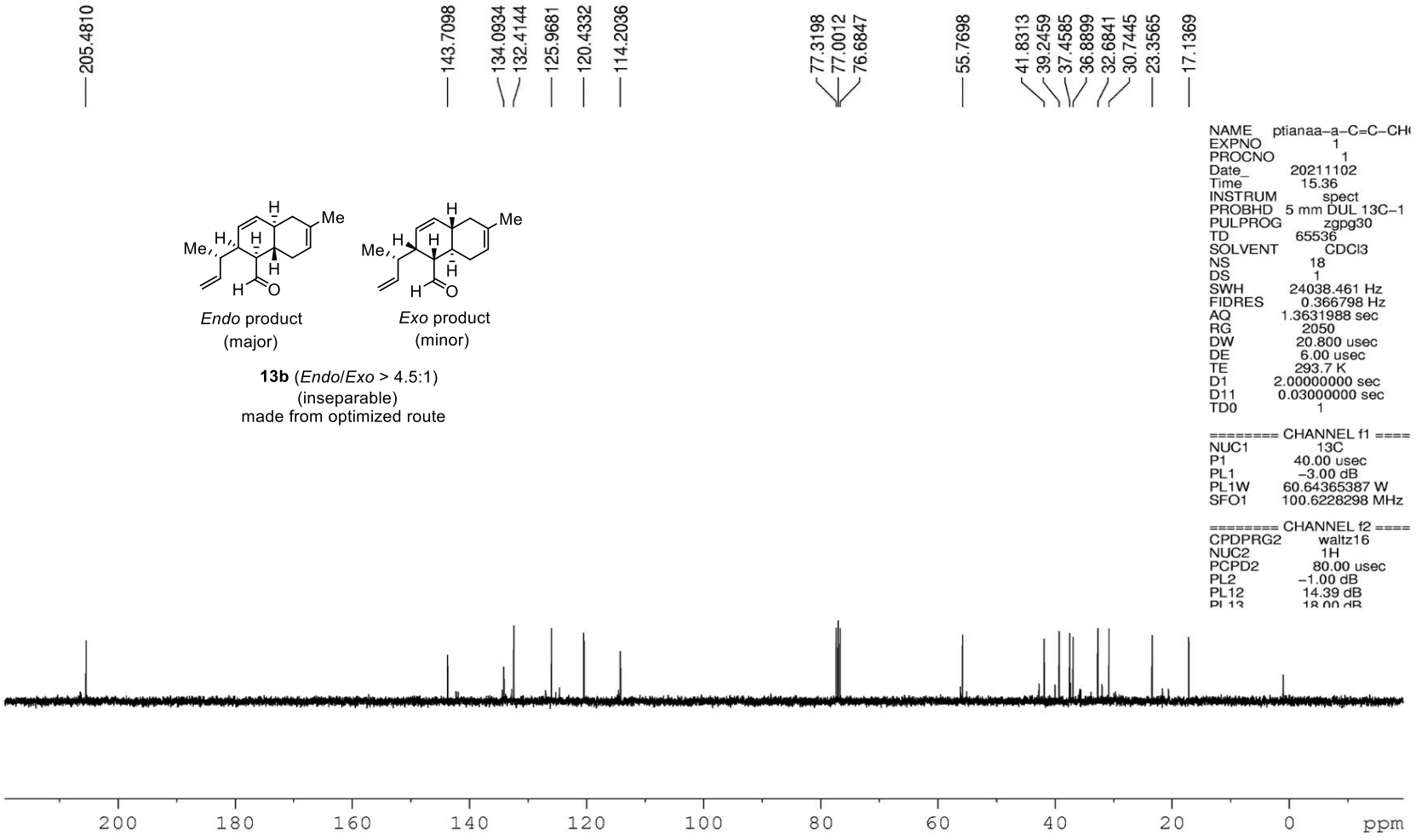
8c:8d = 3:1
(inseparable)



Endo product
(major)

Exo product
(minor)

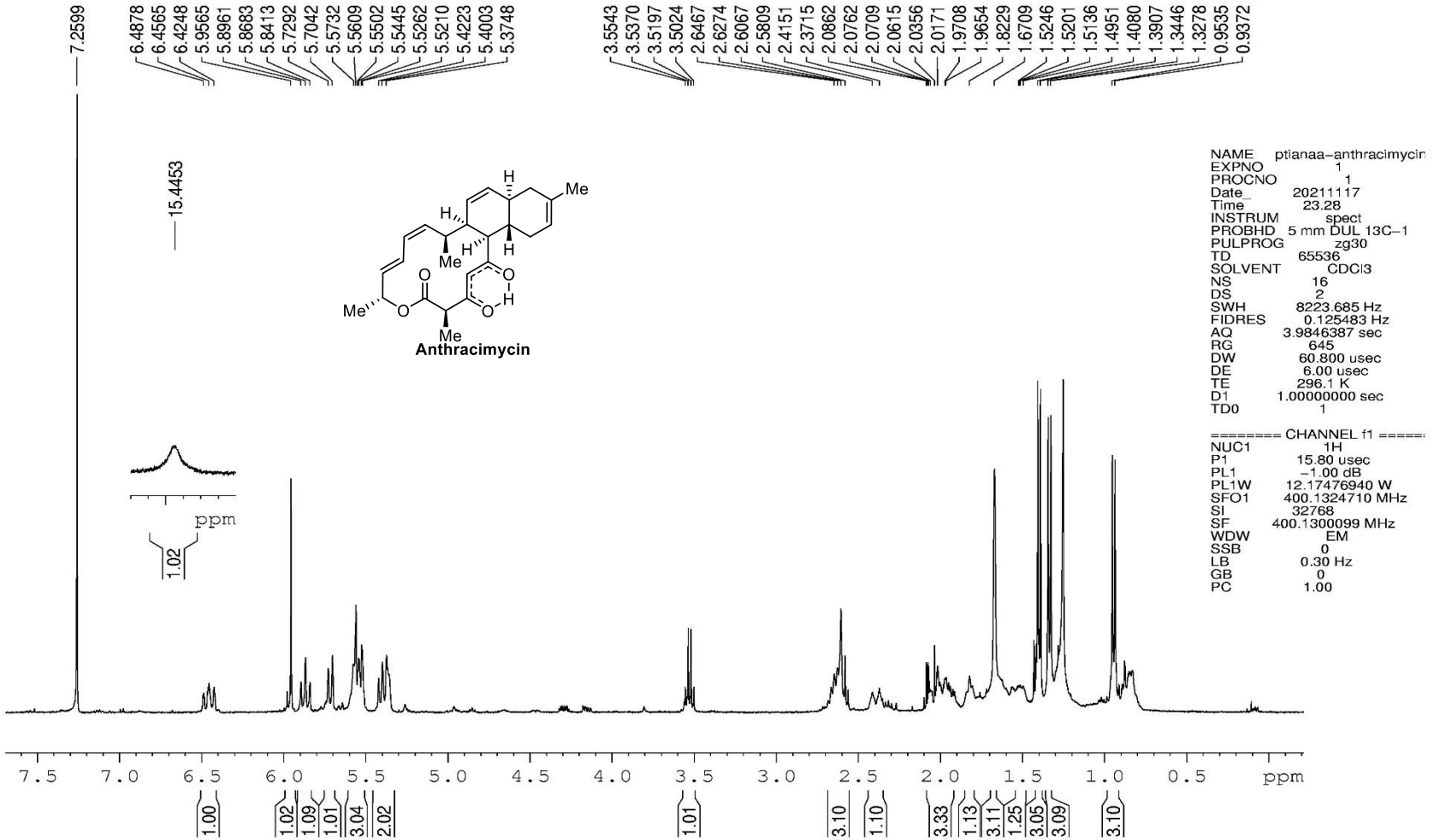
13b (*Endo*/*Exo* > 4.5:1)
(inseparable)
made from optimized route

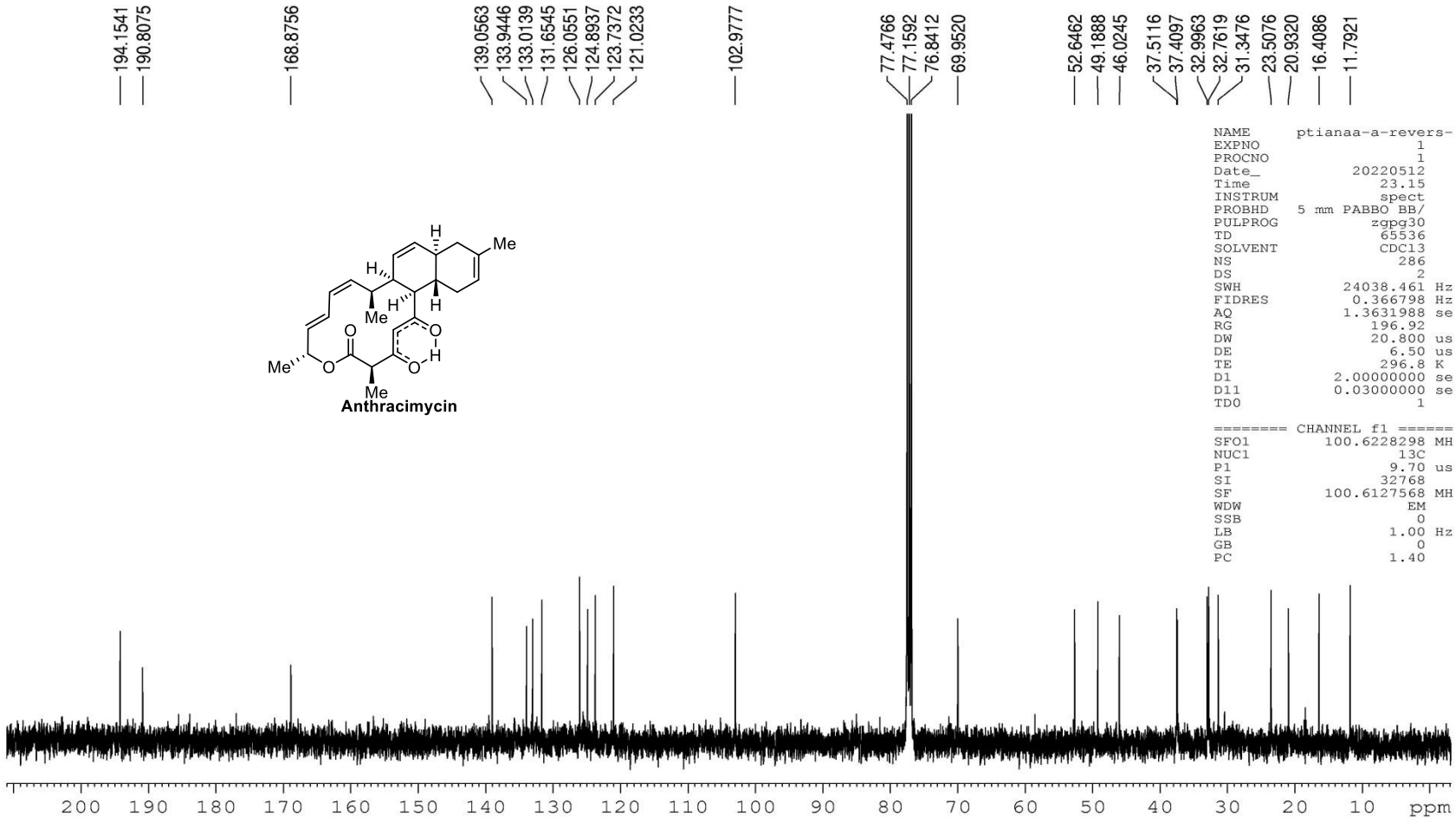


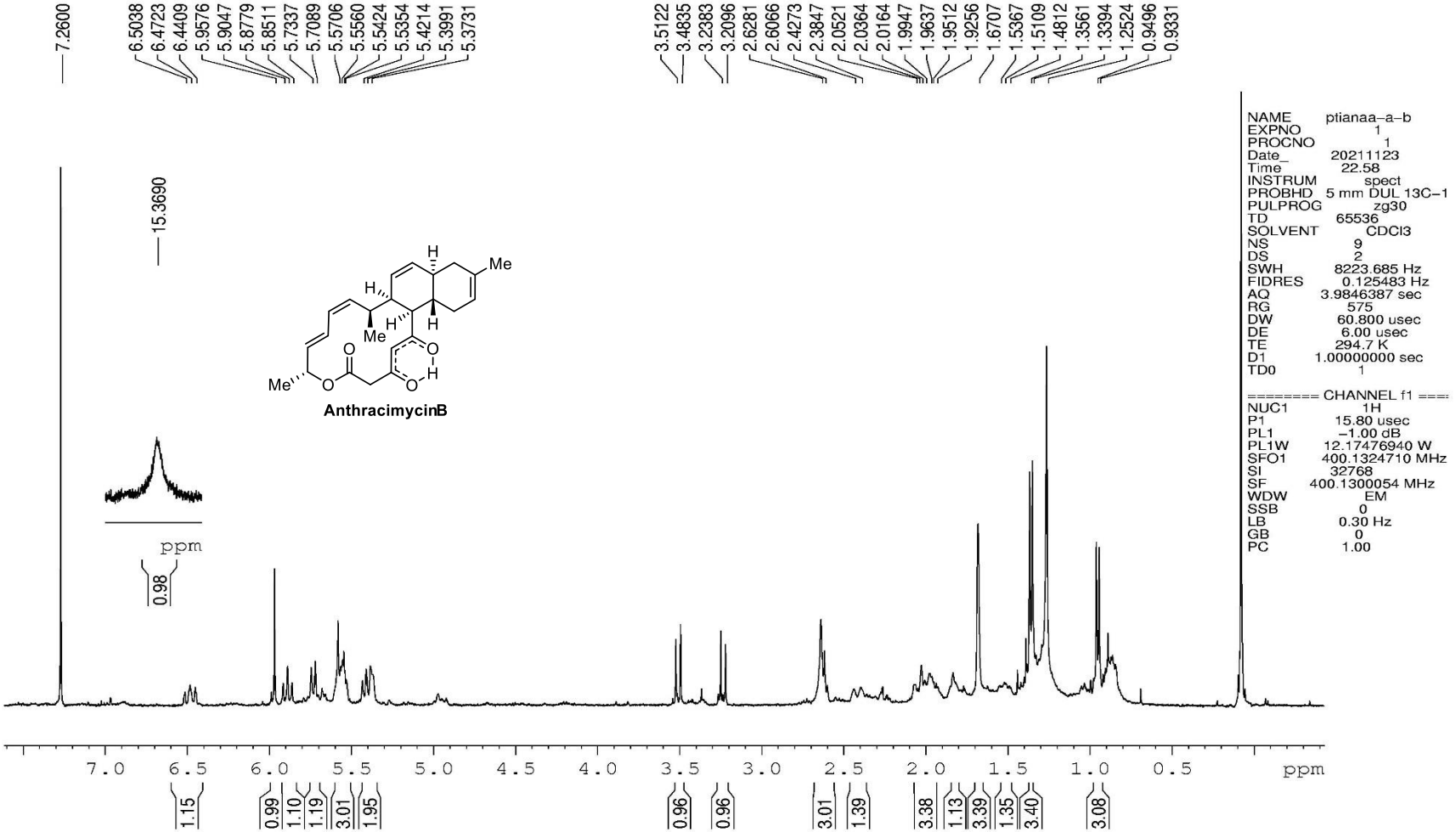
Endo product
(major)

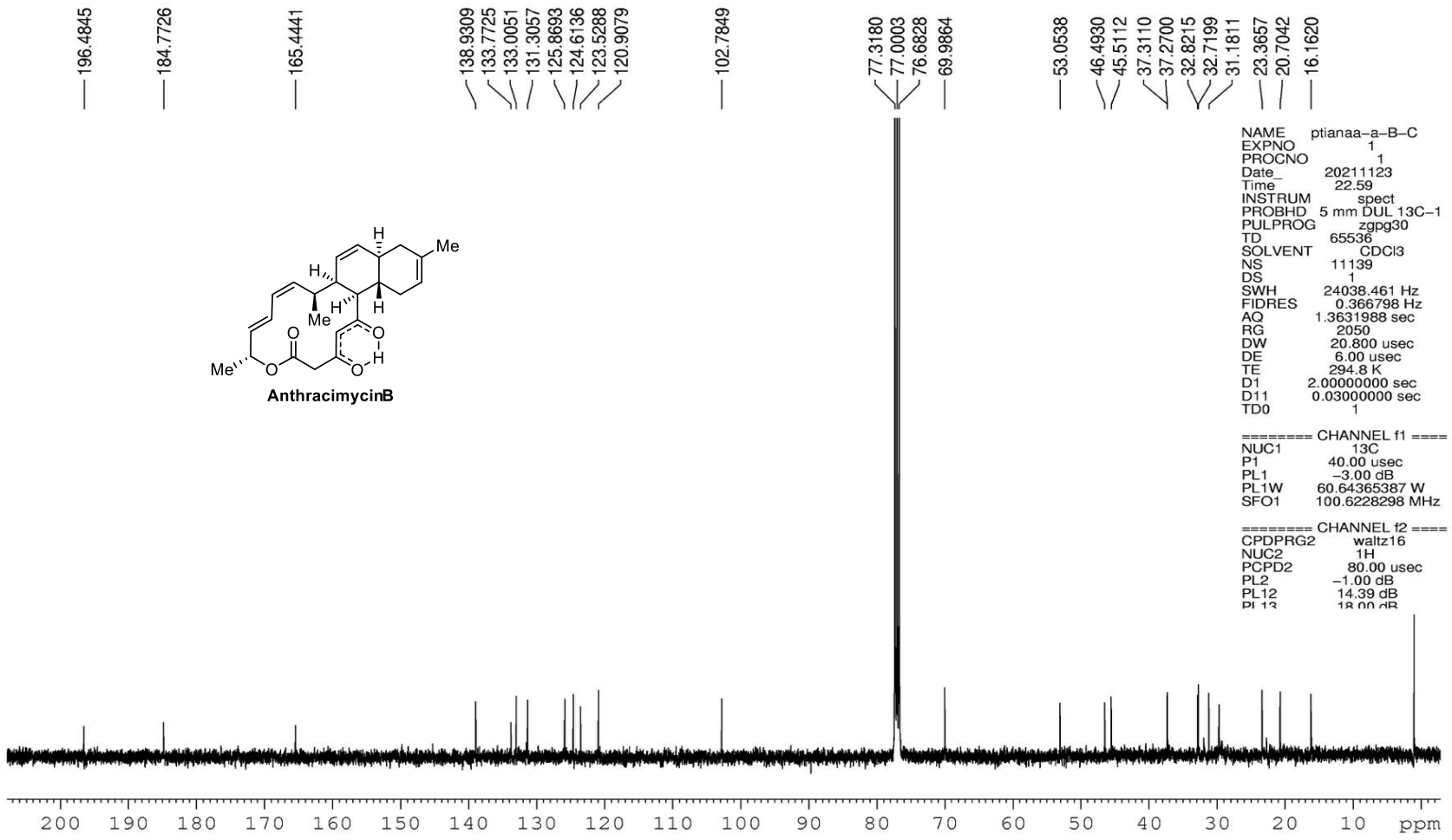
Exo product
(minor)

13b (*Endo*/*Exo* > 4.5:1)
(inseparable)
made from optimized route


7.2599
6.4878
6.4565
6.4248
5.9565
5.8961
5.8683
5.8413
5.7292
5.7042
5.5732
5.5609
5.5502
5.5445
5.5262
5.5210
5.4223
5.4003
5.3748
3.5543
3.5370
3.5197
3.5024
2.6467
2.6274
2.6067
2.5809
2.4151
2.3715
2.0862
2.0762
2.0709
2.0615
2.0356
2.0171
1.9708
1.9654
1.8229
1.6709
1.5246
1.5201
1.5136
1.4951
1.4080
1.3907
1.3446
1.3278
0.9535
0.9372
15.4453
Anthracimycin
ppm
1.02
NAME ptianaa-anthracimycin
EXPNO 1
PROCNO 1
Date_ 20211117
Time 23.28
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 645
DW 60.800 usec
DE 6.00 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
1.00
1.02
1.09
1.01
3.04
2.02
1.01
3.10
1.10
3.33
1.13
3.11
1.25
3.05
3.09
3.10


194.1541
190.8075
168.8756
139.0563
133.9446
133.0139
131.6545
126.0551
124.8937
123.7372
121.0233
102.9777
77.4766
77.1592
76.8412
69.9520
52.6462
49.1888
46.0245
37.5116
37.4097
32.9963
32.7619
31.3476
23.5076
20.9320
16.4086
11.7921
NAME ptianaa-a-revers-
EXPNO 1
PROCNO 1
Date_ 20220512
Time 23.15
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 286
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 196.92
DW 20.800 us
DE 6.50 us
TE 296.8 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
SFO1 100.6228298 MH
NUC1 13C
P1 9.70 us
SI 32768
SF 100.6127568 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Anthracimycin
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.2600
6.5038
6.4723
6.4409
5.9576
5.9047
5.8779
5.8511
5.7337
5.7089
5.5706
5.5560
5.5424
5.5354
5.4214
5.3991
5.3731
3.5122
3.4835
3.2383
3.2096
2.6281
2.6066
2.4273
2.3847
2.0521
2.0364
2.0164
1.9947
1.9637
1.9512
1.9256
1.6707
1.5367
1.5109
1.4812
1.3561
1.3394
1.2524
0.9496
0.9331
15.3690
AnthracimycinB
ppm
0.98
NAME ptianaa-a-b
EXPNO 1
PROCNO 1
Date_ 20211123
Time 22.58
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 9
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 575
DW 60.800 usec
DE 6.00 usec
TE 294.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ====
NUC1 1H
P1 15.80 usec
PL1 -1.00 dB
PL1W 12.17476940 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300054 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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
1.15
0.99
1.10
1.19
3.01
1.95
0.96
0.96
3.01
1.39
3.38
1.13
3.39
1.35
3.40
3.08


196.4845
184.7726
165.4441
138.9309
133.7725
133.0051
131.3057
125.8693
124.6136
123.5288
120.9079
102.7849
77.3180
77.0003
76.6828
69.9864
53.0538
46.4930
45.5112
37.3110
37.2700
32.8215
32.7199
31.1811
23.3657
20.7042
16.1620
AnthracimycinB
NAME ptianaa-a-B-C
EXPNO 1
PROCNO 1
Date_ 20211123
Time 22.59
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 11139
DS 1
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.00 usec
TE 294.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ====
NUC1 13C
P1 40.00 usec
PL1 -3.00 dB
PL1W 60.64365387 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.39 dB
PL13 18.00 dB
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm