Supporting Information
Oxidation of Hindered Allylic C-H Bonds with Applications to the Functionalization of Complex Molecules

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A. General Experimental Details

All air-sensitive manipulations were conducted in a nitrogen-filled glovebox or by standard Schlenk technique under nitrogen. All glassware was heated in an oven and cooled under an inert atmosphere prior to use. Vials (4 mL) were used as reaction vessels and were sealed with Teflon-lined caps. Products were visualized on TLC plates with an anisaldehyde stain and a heat gun. NMR spectra were acquired on 300 MHz, 400 MHz, 500 MHz, or 600 MHz Bruker instruments at the University of California. Flash chromatography was performed with a Teledyne ISCO CombiFlash RF 200 with Gold-Top silica. NMR spectra were processed with MestReNova 5.0 (Mestrelab Research SL). Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H and 77.16 ppm for ^{13}C). Coupling constants are reported in hertz. NMR yields were determined by ^1H NMR spectroscopy with 1,3,5-Tribromo-2-methoxybenzene as an internal standard. High-resolution mass spectra were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

Solvents and Reagents for Catalytic Oxidation Reaction

Tert-butyl benzoyl peroxide (98%) was purchased as a solution from Sigma-Aldrich and filtered through a plug of basic alumina before use. Palladium benzoate was purchased from Strem Chemicals Inc or prepared from commercial palladium acetate as previously described.[1] Benzoquinone was purchased from Sigma-Aldrich, dissolved in DCM, and filtered through a plug of basic alumina. The solvent was removed under high vacuum. 4,5-Diazafluoren-9-one (98%) was purchased from Alfa Aesar.

B. General Procedures

General allylation procedure I: Substrate Synthesis

To a dry 20 mL vial under N_2 containing a magnetic stir bar, substrate (5.00 mmol, 1.00 equiv) and THF (5 mL) were added, and the vial was sealed with a rubber septum. To a dry 100 mL flask containing a stir bar under N_2, LiHMDS (6.25 mmol, 1.25 equiv) and THF (15 mL) were added. The solution in the 100 mL flask was cooled to -78 °C in a bath of dry ice and acetone, and the solution from the vial was added slowly under N_2. The resulting mixture was allowed to stir for 1 h at -78 °C, and then allyl bromide (10.0 mmol, 2.00 equiv) was added dropwise. The flask was allowed to warm slowly to room temperature and stirred for 12 h. The reaction mixture was poured into a separatory funnel containing 200 mL of a saturated NH_4Cl solution and extracted with ether (3 x 40 mL). Anhydrous Na_2SO_4 was added to the combined organic layers. The resulting slurry was filtered through a frit containing additional anhydrous Na_2SO_4, and the remaining slurry was washed with ether (3 x 20 mL) and repeatedly filtered. The dried organic layer was concentrated in vacuo and purified via combiflash using a mixture of ethyl acetate and hexanes.

The relative quantitates of reagents were maintained when this procedure was conducted at varying scales.

General alkylation procedure II: Substrate Synthesis

To a dry 20 mL vial under N_2 containing a magnetic stir bar, were added substrate (10.0 mmol, 1.00 equiv) and THF (10 mL), and the vial was sealed with a rubber septum. To a dry 100 mL flask containing a stir bar under N_2, LiHMDS (12.5 mmol, 1.25 equiv) and THF (30 mL)

were added. The solution in the 100 mL flask was cooled to -78 °C in a bath of dry ice and acetone, and the solution from the vial was added slowly under N_2. The resulting solution was allowed to stir for 1 h at -78 °C, and then the appropriate alkyl iodide (12.0-14.0 mmol, 1.20-1.40 equiv) was added dropwise. The flask was allowed to warm slowly to room temperature and stirred for 12 h. The reaction mixture was poured into a separatory funnel containing 200 mL of a saturated NH_4Cl solution and extracted with ether (3 x 40 mL). Anhydrous Na_2SO_4 was added to the combined organic layers. The resulting solution was filtered through a frit containing additional anhydrous Na_2SO_4, and the remaining slurry was washed with ether (3 x 20 mL) and repeatedly filtered. The dried organic layer was concentrated in vacuo and purified via combiflash using a mixture of ethyl acetate and hexanes.

The relative quantitates of reagents were maintained when this procedure was conducted at varying scales.

Benzoylation Procedure III on a 0.2 mmol scale:

To a dry 4 mL vial under N_2 containing a magnetic stir bar, $Pd(OBz)_2$ (0.020 mmol, 0.10 equiv), 4,5-diazafluoren-9-one (0.020 mmol, 0.10 equiv), and benzoquinone (0.020 mmol, 0.10 equiv) were added. Substrate was layered on the bottom of the vial (0.20 mmol, 1.0 equiv), and then (0.40 mmol, 2.0 equiv) of *tert*-butyl benzoyl peroxide was added. The reaction vial was sealed with a Teflon-lined cap and heated at 65 °C for 3-15 hours. Solid substrates rapidly dissolved in the reaction mixture upon heating. Upon completion, DCM was added, and the resulting brown oil was filtered through a silica plug. The filtrate was concentrated under vacuum, loaded onto silica, and purified via combiflash using a mixture of ethyl acetate and

hexanes.

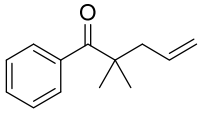
The relative quantitates of reagents were maintained when this procedure was conducted at a 0.10 mmol scale.

Large Scale Benzoylation Procedure IV:

To a dry 4 mL vial under N_2 containing a magnetic stir bar, $Pd(OBz)_2$ (0.17 mmol, 0.050 equiv), 4,5-diazafluoren-9-one (0.17 mmol, 0.050 equiv), and benzoquinone (0.70 mmol, 0.20 equiv) were added. Substrate **1g** was deposited on the bottom of the vial (3.49 mmol, 1.00 equiv), and then (6.98 mmol, 2.00 equiv) *tert*-butyl benzoyl peroxide was added. The reaction vial was sealed with a Teflon-lined cap and heated at 65 °C for 9 hours. Solid substrates rapidly dissolved in the reaction mixture upon heating. Upon completion, DCM was added, and the resulting brown oil was filtered through a silica plug. The filtrate was concentrated under vacuum, loaded onto silica, and purified via combiflash using a mixture of ethyl acetate and hexanes.

C. Synthesis of Starting Materials

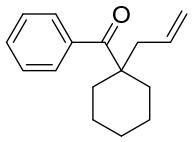
Substrate (1a) 2,2-dimethyl-1-phenylpent-4-en-1-one



Substrate **1a** was prepared on a 3.37 mmol scale according to General Allylation Procedure I from commercially available 2-methyl-1-phenylpropan-1-one. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 0:100 to 5:95 EtOAc:Hexanes) to afford 2,2-dimethyl-1-phenylpent-4-en-1-one as a colorless oil (0.531 g, 2.82 mmol, 84% yield). The ^{1}H NMR spectrum matches that previously reported.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.46 (m, 1H), 7.41 (m, 2H), 5.72 (m, 1H), 5.03 (m, 2H), 2.49 (dt, *J* = 7.3, 1.0 Hz, 2H), 1.32 (s, 6H).

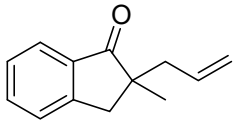
Substrate (1b) (1-allylcyclohexyl)(phenyl)methanone



Substrate **1b** was prepared on a 5.00 mmol scale according to General Allylation Procedure I from commercially available cyclohexyl(phenyl)methanone. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 0:100 to 5:95 EtOAc:Hexanes) to afford (1-allylcyclohexyl)(phenyl)methanone as a colorless oil (0.939 g, 4.11 mmol, 82% yield). The ^{1}H NMR spectrum matches that previously reported.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (m, 2H), 7.45 (m, 1H), 7.38 (m, 2H), 5.71 (m, 1H), 5.04 (m, 2H), 2.55 (dt, *J* = 7.3, 1.0 Hz, 2H), 2.20 (m, 2H), 1.64-1.22 (m, 8H).

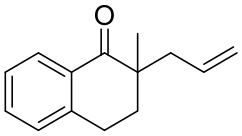
Substrate (1c) 2-allyl-2-methyl-2,3-dihydro-1H-inden-1-one



Substrate **1c** was prepared on a 5.00 mmol scale according to General Allylation Procedure I from commercially available 2-methyl-2,3-dihydro-1H-inden-1-one. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 0:100 to 5:95 EtOAc:Hexanes) to afford 2-allyl-2-methyl-2,3-dihydro-1H-inden-1-one as a colorless oil (0.786 g, 4.22 mmol, 84% yield). The ^{1}H NMR spectrum matches that previously reported.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.59 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 5.66 (m, 1H), 5.10-4.98 (m, 2H), 3.16 (d, *J* = 17.2 Hz, 1H), 2.84 (d, *J* = 17.2 Hz, 1H), 2.38 (m, 1H), 2.29 (m, 1H), 1.23 (s, 3H).

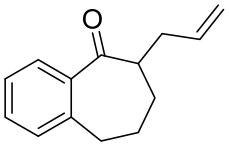
Substrate (1d) 2-allyl-2-methyl-3,4-dihydronaphthalen-1(2H)-one



Substrate **1d** was prepared on a 5.80 mmol scale according to General Allylation Procedure I from commercially available 2-methyl-3,4-dihydronaphthalen-1(2H)-one. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 0:100 to 5:95 EtOAc:Hexanes) to afford 2-allyl-2-methyl-3,4-dihydronaphthalen-1(2H)-one as a colorless oil (1.003 g, 5.010 mmol, 86% yield). The ^{1}H NMR spectrum matches that previously reported.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.45 (td, *J* = 7.4, 1.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.6, 1H), 5.79 (m, 1H), 5.09 (m, 2H), 2.98 (m, 2H), 2.46 (m, 1H), 2.28 (m, 1H), 2.08 (m, 1H), 1.90 (m, 1H), 1.19 (s, 3H).

6-allyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one



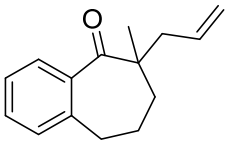
6-allyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one was synthesized from commercially available 6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one on a 10 mmol scale according to a

modified version of General Allylation Procedure I:

To a dry 20 mL vial under N_2 containing a magnetic stir bar, substrate (10.0 mmol, 1.00 equiv) and THF (10 mL) were added, and the vial was sealed with a rubber septum. To a dry 100 mL flask containing a stir bar under N_2, LiHMDS (10.0 mmol, 1.00 equiv) and THF (30 mL) were added. The solution in the 100 mL flask was cooled to -78 °C in a bath of dry ice and acetone, and the solution from the vial was added slowly under N_2. The resulting mixture was allowed to stir for 1 h, and then allyl bromide (10.0 mmol, 1.00 equiv) was added dropwise. The flask was allowed to warm slowly to room temperature and stirred for 12 h. The reaction mixture was poured into a separatory funnel containing 200 mL of a saturated NH_4Cl solution and extracted with ether (3 x 40 mL). Anhydrous Na_2SO_4 was added to the combined organic layers. The resulting solution was filtered through a frit containing additional anhydrous Na_2SO_4, and the remaining slurry was washed with ether (3 x 20 mL) and repeatedly filtered. The dried organic layer was concentrated in vacuo and purified via combiflash using a mixture of ethyl acetate and hexanes (gradient 0:100 to 5:95 EtOAc:Hexanes). After the removal of di-allylated product 6-allyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one was obtained as a colorless oil (0.675 g, 3.37 mmol, 34% yield). The ^{1}H NMR spectrum matches that previously reported.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.37 (td, *J* = 7.6, 1.0 Hz, 1H), 7.27 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 5.77 (m, 1H), 5.03 (m, 2H), 2.94 (m, 3H), 2.68 (m, 1H), 2.23 (m, 1H), 2.06 (m, 1H), 1.96 (m, 1H), 1.69 (m, 1H), 1.59 (m, 1H).

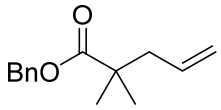
Substrate (1e) 6-allyl-6-methyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one



Substrate **1e** was prepared from 6-allyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one on a 3.37 mmol scale according to General Alkylation Procedure I with 4.00 equiv (13.5 mmol) of methyl iodide. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 0:100 to 5:95 EtOAc:Hexanes) to afford 6-allyl-6-methyl-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one as a colorless oil (0.540 g, 2.52 mmol, 75% yield). The ^{1}H NMR spectrum matches that previously reported.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 1H), 7.27 (dd, *J* = 4.9, 0.9 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 5.75 (m, 1H), 5.07 (m, 2H), 2.80 (m, 2H), 2.34 (m, 2H), 1.93 (m, 2H), 1.78 (m, 1H), 1.62 (m, 1H), 1.20 (s, 3H).

Substrate (1f) benzyl 2,2-dimethylpent-4-enoate



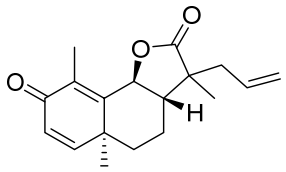
Substrate **1f** was prepared on a 5.00 mmol scale according to General Allylation Procedure I from commercially available benzyl isobutyrate. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 0:100 to 5:95 EtOAc:Hexanes) to afford benzyl 2,2-dimethylpent-4-enoate as a colorless oil (0.670 g, 3.07 mmol, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 5H), 5.70 (m, 1H), 5.11 (s, 2H), 5.02 (m, 2H), 2.30 (d, *J* = 7.2 Hz, 2H), 1.20 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.3, 136.3, 134.1, 128.5, 128.0, 127.9, 118.0, 66.1, 44.7, 42.4, 24.8.

HRMS (EI+): *m/z* for $C_{14}H_{18}O_2$ $[M]^+$ calculated: 218.1307, found: 218.1312.

Substrate (1g) Allyl-santonin - (3aR,5aR,9bR)-3-allyl-3,5a,9-trimethyl-3a,5,5a,9b-tetrahydronaphtho[1,2-b]furan-2,8(3H,4H)-dione



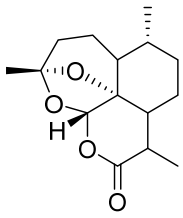
Substrate **1g** was prepared on a 5.00 mmol scale according to General Allylation Procedure I from commercially available (-)-α-Santonin. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 5:95 to 50:50 EtOAc:Hexanes) to afford allyl-santonin as a tan solid (1.263 g, 4.410 mmol, 88% yield). The ^{1}H NMR spectrum has been previously reported, and the absolute configuration was assigned.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, *J* = 9.8 Hz, 1H), 6.25 (d, *J* = 9.8, 1H), 5.86 (m, 1H), 5.21 (m, 2H), 5.05 (dd, *J* = 11.5, 1.3 Hz, 1H), 2.42 (m, 1H), 2.27 (m, 1H), 2.14 (d, *J* =1.3 Hz, 3H), 1.99 (m, 1H), 1.91 (m, 1H), 1.81 (m, 2H), 1.48 (m, 1H), 1.29 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 186.4, 179.2, 154.8, 151.8, 132.8, 128.9, 126.2, 119.5, 79.3, 56.7, 45.1, 41.5, 38.1, 36.9, 25.2, 22.1, 19.1, 11.1.

HRMS (EI+): *m/z* for $C_{18}H_{22}O_3$ $[M]^+$ calculated: 286.1569, found: 286.1572.

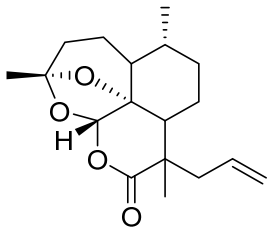
Deoxy-artemisinin



Deoxy-artemisinin was prepared commercially available artemisinin. To a dry 250 mL flask, 1.010 g (3.580 mmol, 1.000 equiv) of artemisinin and 55 mL of MeOH were added. The solution was degassed with N_2, and a slurry with 0.0270 g of 10% Pd/C in 4 mL of MeOH was added under N_2. The solution was purged twice with a balloon filled with hydrogen. Two hydrogen balloons were attached, and the reaction was allowed to stir at room temp for 24 h. At this time, the balloons were removed, and 0.0231 g of *p*-toluene sulfonic acid in 20 mL of toluene was added. The reaction was stirred until no diol remained as indicated by TLC (bottom spot disappears in approx. 2 h). The reaction mixture was filtered and concentrated under vacuum. The crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 0:100 to 10:90 EtOAc:Hexanes) to afford deoxy-artemisinin as a white solid (0.854 g, 3.21 mmol, 90% yield). The ^{1}H NMR spectrum matches that previously reported.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (s, 1H), 3.19 (m, 1H), 2.00 (ddd, *J* = 12.1, 4.4, 4.4 Hz, 1H), 1.90 (m, 2H), 1.78 (m, 2H), 1.60 (m, 1H), 1.53 (s, 3H), 1.25 (m, 3H), 1.20 (d, *J* = 7.3, 3H), 1.09 (m, 2H), 0.94 (d, 5.3 Hz, 3H).

Substrate (1h) (3a1R,6R,9S,10aR)-3-allyl-3,6,9-trimethyloctahydro-10aH-3a1,9-epoxyoxepino[4,3,2-ij]isochromen-2(3H)-one



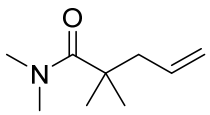
Substrate **1h** was prepared on a 3.00 mmol scale according to General Allylation Procedure I from deoxy-artemisinin. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 0:100 to 10:90 EtOAc:Hexanes) to afford allyl-deoxy-artemisinin as a white solid (0.572 g, 1.87 mmol, 62% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.5, 10.2, 7.5 Hz, 1H), 5.74 (s, 1H), 5.15 (m, 2H), 3.01 (dd, *J* = 13.3, 7.5 Hz, 1H), 2.48 (dd, *J* = 13.3, 7.5 Hz, 1H), 2.04 (dd, *J* = 12.5, 4.2 Hz, 1H), 1.89 (m, 2H), 1.75 (m, 2H), 1.60 (m, 1H), 1.53 (s, 3H), 1.29 (m, 3H), 1.19 (s, 3H), 1.10 (m, 2H), 0.92 (d, *J* = 6.2, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 133.5, 119.5, 109.8, 99.9, 83.4, 45.5, 44.6, 43.3, 41.5, 35.7, 34.3, 33.9, 26.8, 24.3, 23.4, 22.4, 18.9.

HRMS (EI+): *m/z* for $C_{18}H_{26}O_4$ $[M]^+$ calculated 306.1831, found: 306.1836.

Substrate (1i) N,N,2,2-tetramethylpent-4-enamide



Substrate **(1i)** was prepared according to the following procedure on a 7.74 mmol scale from commercially available N,N-dimethylisobutyramide.

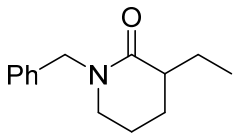
To a dry 100 mL flask under N_2 containing a magnetic stir bar, 1.6 mL of diisopropylamine (11.4 mmol 1.50 equiv) and anhydrous THF (6 mL) were added, and the flask was sealed with a rubber septum. The solution in the flask was cooled to 0 °C, and 4.6 mL of a 2.5 M *n*-butyllithium (11.5 mmol, 1.50 equiv) solution in hexanes was added. This solution was stirred for 20 min at 0 °C. To a second dry 100 mL flask under N_2 containing a magnetic stir bar, 1 mL of *N*,*N*-dimethylisobutyramide and 24 mL of anhydrous THF were added. This solution was cooled to 0 °C, and the solution from the first flask was added. The mixture was allowed to stir for 45 min at 0 °C, and then it was cooled to -78 °C. At this temperature, 4 mL (46.2 mmol, 6.00 equiv) of allyl bromide was added dropwise. The flask was allowed to warm slowly to room temperature and stirred for 12 h. The solution was poured into a separatory funnel containing 200 mL of a saturated NH_4Cl solution and extracted with ether (3 x 40 mL). Anhydrous Na_2SO_4 was added to the combined organic layers. The resulting solution was filtered through a frit containing additional anhydrous Na_2SO_4, and the remaining slurry was washed with ether (3 x 20 mL) and repeatedly filtered. The dried organic layer was concentrated in vacuo and purified via combiflash using a mixture of ethyl acetate and hexanes (gradient 5:95 to 20:80 EtOAc:Hexanes) to afford N,N,2,2-tetramethylpent-4-enamide as a clear oil (0.314 g, 2.02 mmol, 26% yield).[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (m, 1H), 5.03 (m, 2H), 3.04 (s, 6H), 2.39 (dt, J = 7.2, 1.0 Hz, 2H), 1.27 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 135.0, 117.5, 45.23, 42.4, 38.4, 26.4.

HRMS (EI+): *m/z* for $C_9H_{17}NO$ $[M]^+$ calculated 155.1310, found 155.1310.

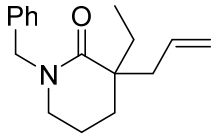
1-benzyl-3-ethylpiperidin-2-one



To a dry 20 mL vial under N_2 containing a magnetic stir bar, substrate (6.14 mmol, 1.00 equiv) and THF (6 mL) were added, and the vial was sealed with a rubber septum. To a dry 100 mL flask containing a stir bar under N_2, KHMDS (7.68 mmol, 1.25 equiv) and THF (18 mL) were added. The solution in the 100 mL flask was cooled to -78 °C in a bath of dry ice and acetone, and the solution from the vial was added slowly under N_2. The resulting solution was allowed to stir for 1 h, and then ethyl iodide (7.38 mmol, 1.20 equiv) was added dropwise. The flask was allowed to warm slowly to room temperature and was stirred for 12 h. The solution was poured into a separatory funnel containing 200 mL of a saturated NH_4Cl solution and extracted with ether (3 x 40 mL). Anhydrous Na_2SO_4 was added to the combined organic layers. The resulting solution was filtered through a frit containing additional anhydrous Na_2SO_4, and the remaining slurry was washed with ether (3 x 20 mL) and repeatedly filtered. The dried organic layer was concentrated in vacuo and purified via combiflash using a mixture of ethyl acetate and hexanes (gradient 5:95 to 20:80 EtOAc:Hexanes) to afford 1-benzyl-3-ethylpiperidin-2-one as a clear oil (0.447 g, 2.06 mmol, 34% yield). The ^1H NMR spectrum matches that previously reported.[9]

^1H NMR (400 MHz, $CDCl_3$) δ 7.3 (m, 2H), 7.24 (m, 3H), 4.59 (s, 2H), 3.19 (m, 2H) 2.30 (m, 1H), 1.95 (m, 2H), 1.84 (m, 1H), 1.70 (m, 1H), 1.59 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H)

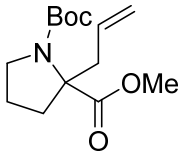
Substrate (1j) 3-allyl-1-benzyl-3-ethylpiperidin-2-one 1-Benzyl-2-piperidone



Substrate **1j** was prepared on a 2.05 mmol scale according to General Allylation Procedure I from benzyl-3-ethylpiperidin-2-one. After workup, the crude product was purified via combiflash with ethyl acetate and hexanes as eluents (gradient 5:95 to 20:80 EtOAc:Hexanes) to afford 3-allyl-1-benzyl-3-ethylpiperidin-2-one as a colorless oil (0.263 g, 1.02 mmol, 50% yield). The ^{1}H NMR spectrum matches that previously reported.[10]

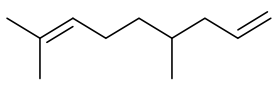
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.25 (m, 3H), 5.79 (m, 1H), 5.06 (m, 2H), 4.60 (m, 2H), 3.17 (m, 2H), 2.55 (ddt, *J* = 13.4, 6.7, 1.3 Hz, 1H), 2.21 (ddt, *J* = 13.5, 8.0, 1.1 Hz, 1H), 1.83 (m, 1H), 1.74 (m, 4H), 1.52 (m, 1H), 0.89 (t, *J* = 7.5 Hz, 3H).

Substrate (1k) 1-(tert-butyl) 2-methyl 2-allylpyrrolidine-1,2-dicarboxylate



Substrate **(1k)** was prepared as previously described as a mixture of two rotomers in a 1:2 ratio.[11] ^{1}H NMR matches that previously reported. See Ref. 11 for extensive characterization.

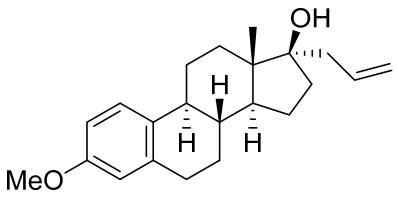
Substrate (1l) 4,8-dimethylnona-1,7-diene



Substrate **(1l)** was prepared as previously described.[12] The ^{1}H NMR spectrum matches that previously reported.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (m, 1H), 5.10 (m, 1H), 4.99 (m, 2H), 1.98 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.54 (m, 1H), 1.34 (m, 1H), 1.15 (m, 1H), 0.87 (br, 3H).

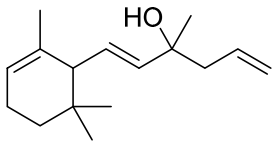
Substrate (1n) (8R,9S,13S,14S,17R)-17-allyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-ol



To a dry 100 mL flask under N_2 containing a magnetic stir bar, 3 mL of 1 M solution of allyl magnesium bromide in diethyl ether (3.00 mmol, 3.00 equiv) was added. To a dry 20 mL vial under N_2 containing a magnetic stir bar, methoxy estrone (1.00 mmol, 1.00 equiv) was added, along with 6 mL of benzene. The allyl magnesium bromide solution was cooled to 0 °C , and the solution from the vial containing methoxy estrone was added dropwise to the flask containing the allyl magnesium bromide solution. An additional 3 mL of benzene was added to the 20 mL vial, and this solution was also transferred to the flask containing Grignard solution. The resulting solution was warmed to rt and stirred for 4 h. The solution was poured into a separatory funnel containing 100 mL of a saturated NH_4Cl solution and extracted with DCM (3 x 20 mL). Anhydrous Na_2SO_4 was added to the combined organic layers was added. The resulting solution was filtered through a frit containing additional anhydrous Na_2SO_4, and the remaining slurry was washed with ether (3 x 20 mL) and repeatedly filtered. The dried organic layer was concentrated in vacuo and purified via combiflash using a mixture of ethyl acetate and hexanes (gradient 0:100 to 10:90 EtOAc:Hexanes) to afford **1n** (0.281 g, 0.861 mmol, 86% yield). The ^{1}H NMR spectrum matches that previously reported.[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 8.7 Hz, 1H), 6.71 (dd, J = 8.6, 2.9 Hz, 1H), 6.63 (d, J = 2.9 Hz, 1H), 6.01 (m, 1H), 5.20 (m, 2H), 3.78 (s, 3H), 2.86 (m, 2H), 2.35 (m, 2H), 2.27 (m, 1H), 2.17 (m, 1H), 2.00 (m, 1H), 1.89 (m, 1H), 1.70-1.26 (10 H), 0.93 (s, 3H).

Substrate (1o) (E)-3-methyl-1-(2,6,6-trimethylcyclohex-2-en-1-yl)hexa-1,5-dien-3-ol



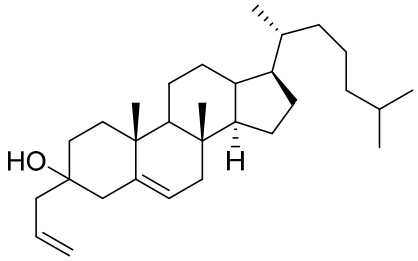
To a dry 100 mL flask under N_2 containing a magnetic stir bar, 22 mL of 1M solution of allyl magnesium bromide in diethyl ether (22.0 mmol, 1.51 equiv) was added. To a second dry 100 mL flask under N_2 containing a magnetic stir bar, α-ionone (14.6 mmol, 1.00 equiv) was added along with 40 mL of anhydrous toluene. The allyl magnesium bromide solution was cooled to 0 °C, and the solution containing α-ionone was added dropwise under N_2. The resulting solution was warmed to rt and stirred for 12 h. The solution was poured into a separatory funnel containing 200 mL of a saturated NH_4Cl solution and extracted with ether (3 x 20 mL). Anhydrous Na_2SO_4 was added to the combined organic layers. The resulting solution was filtered through a frit containing additional anhydrous Na_2SO_4, and the remaining slurry was washed with ether (3 x 20 mL) and repeatedly filtered. The dried organic layer was concentrated in vacuo and purified via combiflash using a mixture of ethyl acetate and hexanes (gradient 0:100 to 5:95 EtOAc:Hexanes) to afford **1o** (2.710 g, 11.60 mmol, 79% yield) as a mixture of diastereomers.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (m, 1H), 5.45 (m, 1H), 5.40 (m, 2H), 5.11 (m, 2H), 2.34 (m, 1H), 2.27 (m, 1H), 2.09 (d, *J* = 8.9 Hz, 1H), 1.99 (bs, 2H), 1.57 (m, 4H), 1.43 (m, 1H), 1.29 (s, 3H), 1.17 (m, 1H), 0.88 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ [138.44, 138.40], [134.30, 134.24], [134.18, 134.14], [128.98, 128.94], 121.11, [118.99, 118.91], [72.35, 72.33], [54.20, 54.18], [47.63, 47.60], [32.19, 32.12], [31.77, 31.75], [28.33, 28.32], [27.83, 27.71], [27.15, 27.14], 23.23, [23.08, 23.01].

HRMS (EI+): *m/z* for $C_{16}H_{26}O$ $[M]^+$ calculated: 234.1984, found: 234.1981.

Substrate (1p) (8S,9S,10R,13R,14S,17R)-3-allyl-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol.



To a dry 100 mL flask under N_2 containing a magnetic stir bar, 3 mL of 1M solution of allyl magnesium bromide in diethyl ether (1.15 mmol, 1.50 equiv) was added. To a dry 20 mL vial under N_2 containing a magnetic stir bar, 5-cholesten-3-one (0.764 mmol, 1.00 equiv) was added along with 6 mL of toluene. The allyl magnesium bromide solution was cooled to 0 °C, and the solution containing 5-cholesten-3-one was added dropwise. An additional 3 mL of toluene was added to the 20 mL vial, and this solution was transferred to the flask containing the Grignard reagent. The resulting solution was warmed to rt and stirred for 4 h. The solution was poured into a separatory funnel containing 100 mL of a saturated NH_4Cl solution and extracted with DCM (3 x 20 mL). Anhydrous Na_2SO_4 was added to the combined organic layers. The resulting solution was filtered through a frit containing additional anhydrous Na_2SO_4, and the remaining slurry was washed with ether (3 x 20 mL) and repeatedly filtered. The dried organic layer was concentrated in vacuo and purified via combiflash using a mixture of ethyl acetate and hexanes (gradient 0:100 to 10:90 EtOAc:Hexanes) to afford **1p** (0.165 g, 0.387 mmol, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.85 (ddt, *J* = 17.6, 10.2, 7.5 Hz, 1H), 5.31 (dt, *J* = 4.9, 2.1 Hz, 1H), 5.17 (m, 1H), 5.12 (ddt, *J* = 17.1, 2.3, 1.3 Hz, 1H), 2.40 (dq, *J* = 13.4, 2.8 Hz, 1H), 2.18 (m, 2H), 2.00 (m, 3H), 1.84 (m, 1H), 1.74 (m, 1H), 1.71-1.05 (m, 20H), 1.03 (m, 3H), 1.01-0.94 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.7 Hz, 6H), 0.68 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.90, 133.82, 122.40, 119.12, 73.04, 56.97, 56.39, 50.73, 45.53, 42.52, 41.13, 39.98, 39.69, 36.76, 36.54, 36.38, 35.97, 34.26, 32.16, 32.15, 28.40, 28.18, 24.47, 24.03, 22.97, 22.72, 21.24, 19.67, 18.89, 12.02.

HRMS (EI+): *m/z* for $C_{30}H_{50}O$ $[M]^+$ calculated: 426.3862, found: 426.3864.

D. Procedures and Spectral Data for Isolated Products

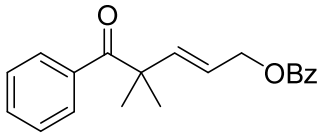
Benzoylation Procedure III on a 0.2 mmol scale:

To a dry 4 mL vial under N_2 containing a small magnetic stir bar, $Pd(OBz)_2$ (0.020 mmol, 0.10 equiv), 4,5-diazafluoren-9-one (0.020 mmol, 0.10 equiv), and benzoquinone (0.020 mmol, 0.10 equiv) were added. Substrate was layered on the bottom of the vial (0.20 mmol, 1.0 equiv), and then (0.40 mmol, 2.0 equiv) of *tert*-butyl benzoyl peroxide was added. The reaction vial was sealed with a Teflon-lined cap and heated at 65 °C for 3-15 hours. Solid substrates rapidly dissolved in the reaction mixture upon heating. Upon completion, the resulting brown oil was cooled to room temperature, and a solution consisting of 2,4,6-tribromoanisole dissolved in EtOAc was added (as an internal standard). DCM was added to the crude reaction mixture, and the resulting solution was filtered through a silica plug. The filtrate was concentrated under vacuum, and a proton NMR spectrum was acquired. Then the crude product was loaded onto silica and purified via combiflash using a mixture of ethyl acetate and hexanes.

Table S1 - Summary of 0.2 mmol Benzoylation and Isolation

Code	Shorthand	Page	Mass SM	Mass Prod	MW React	MW Prod	Mol Int Standard	React/Stand	Prod/Stand	NMR % Yield	Isolated % Yield	Time
2a	DM Ketone	5_280 A	0.0365	0.0407	188.27	308.38	2.13E-05	9.08	7.41	82	68	10h
2b	Cy Ketone	5_280 C	0.046	0.0464	228.333	348.44	2.13E-05	9.44	7.50	79	66	10h
2c	5 Ketone	5_210 D	0.0376	0.0437	186.253	306.36	2.26E-05	8.92	7.77	87	71	15h
2d	6 Ketone	5_210 E	0.0416	0.0435	200.283	320.39	2.26E-05	9.18	7.22	79	65	15h
2e	7 Ketone	5_210 F	0.0437	0.041	214.313	334.42	2.26E-05	9.01	6.44	71	60	15h
2f	Ester	5_210 C	0.0436	0.0458	218.293	338.4	2.26E-05	8.82	6.97	79	68	15h
2g	Allyl Sant	5_215 A	0.0579	0.0597	286.373	406.48	2.13E-05	9.51	7.30	77	73	5h
2h	Artemis	5_285 B	0.0633	0.0467	306.403	426.51	2.16E-05	9.58	6.87	72	53	10h
2i	Amide	6_19 A	0.0322	0.0404	155.243	275.35	2.13E-05	9.72	7.35	76	71	5h
2j	Lactam	5_210 I	0.0505	0.0426	257.373	377.48	2.26E-05	8.67	5.71	66	58	15h
2k	Proline	5_210 H	0.0555	0.0478	269.343	389.45	2.26E-05	9.10	5.18	57	60	15h
2l	Cit	5_223 A	0.0316	0.0344	152.283	272.39	2.40E-05	8.64	6.72	78	61	5h
2m	OHPH	5_266 A	0.0323	0.0343	162.233	282.34	1.23E-05	16.19	11.65	72	61	3h
2n	Estrone	5_293 A	0.0649	0.065	326.483	446.59	2.19E-05	9.07	7.45	82	73	5h
2o	ionone	5_299 A	0.0469	0.0337	234.383	354.49	2.16E-05	9.27	6.38	69	48	3h
2p	cholestrone	5_258 A	0.0836	0.0535	426.733	546.84	3.25E-05	6.03	3.99	66	50	3h

Product (2a) (E)-4,4-dimethyl-5-oxo-5-phenylpent-2-en-1-yl benzoate



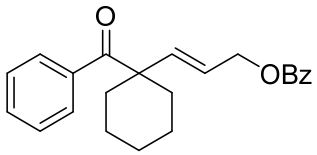
Product **2a** was synthesized according to General Benzoylation Procedure III with 0.0365 g of **1a** (0.194 mmol). The reaction duration was 10 h. A ^{1}H NMR yield of 82% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 2.5:97.5 EtOAc:Hexanes), and **2a** was obtained in a yield of 68% (0.0407 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.84 (m, 2H), 7.57 (m , 1H), 7.45 (t, *J* = 7.63 Hz, 3H), 7.34 (m, 2H), 6.22 (d, *J* = 15.9 Hz, 1H), 5.86 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.85 (dd, *J* = 6.2, 3.1 Hz, 2H), 1.42 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 204.14, 166.22, 140.74, 136.87, 132.96, 131.64, 130.11, 129.59, 129.15, 128.32, 127.94, 123.56, 65.07, 49.38, 26.20.

HRMS (ESI+): *m/z* for $C_{20}H_{20}O_3Na$ $[M+Na]^+$ calculated: 331.1305, found: 331.1299.

Product (2b) (E)-3-(1-benzoylcyclohexyl)allyl benzoate



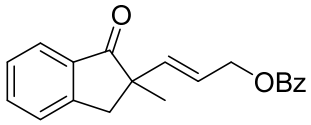
Product **2b** was synthesized according to General Benzoylation Procedure III with 0.0460 g of **1b** (0.201 mmol). The reaction duration was 10 h. A ^{1}H NMR yield of 79% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 2.5:97.5 EtOAc:Hexanes), and **2b** was obtained in a yield of 66% (0.0464 g).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 2H) 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 6.16 (d, *J* = 16.0 Hz, 1H), 5.81 (dt, *J* = 16.0, 6.2 Hz, 1H), 4.85 (dd, *J* = 5.9, 1.4 Hz, 2H), 2.17 (m, 2H), 1.66 (m, 2H), 1.58-1.44 (m, 3H), 1.35 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 205.21, 166.41, 139.79, 138.19, 133.14, 131.34, 130.31, 129.76, 128.76, 128.51, 128.03, 125.59, 65.33, 53.69, 35.32, 25.81, 22.86.

HRMS (ESI+): *m/z* for $C_{23}H_{24}O_3Na$ $[M+Na]^+$ calculated: 371.1618, found: 371.1613.

Product (2c) (E)-3-(2-methyl-1-oxo-2,3-dihydro-1H-inden-2-yl)allyl benzoate



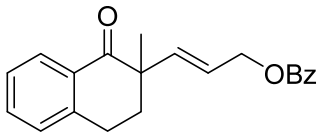
Product **2c** was synthesized according to General Benzoylation Procedure III with 0.0376 g of **1c** (0.202 mmol). The reaction duration was 15 h. A ^{1}H NMR yield of 87% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 10:90 EtOAc:Hexanes), and **2c** was obtained in a yield of 71% (0.0437 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.54 (m, 1H), 7.42 (m, 4H), 5.98 (dt, *J* = 15.7, 1.3 Hz, 1H), 5.85 (dt, *J* = 15.7, 6.0 Hz, 1H), 4.80 (m, 2H), 3.34 (d, *J* = 17.2 Hz, 1H), 3.05 (d, *J* = 17.2 Hz, 1H), 1.40 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 207.71, 166.34, 152.02, 137.55, 135.21, 135.18, 133.02, 130.25, 129.72, 128.40, 127.76, 126.66, 124.83, 123.88, 65.31, 51.52, 41.28, 23.94.

HRMS (ESI+): *m/z* for $C_{20}H_{18}O_3Na$ $[M+Na]^+$ calculated: 329.1148, found: 329.1143.

Product (2d) (E)-3-(2-methyl-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)allyl benzoate



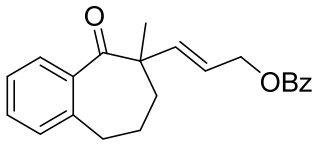
Product **2d** was synthesized according to General Benzoylation Procedure III with 0.0416 g of **1d** (0.208 mmol). The reaction duration was 15 h. A ^{1}H NMR yield of 79% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 10:90 EtOAc:Hexanes), and **2d** was obtained in a yield of 65% (0.0435 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 3H), 7.54 (m, 1H), 7.43 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 6.06 (dt, *J* = 15.9, 1.3 Hz, 1H), 5.65 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.77 (m, 2H), 3.04 (m, 1H), 2.95 (m, 1H), 2.13 (m, 2H), 1.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.06, 166.38, 143.56, 137.59, 133.42, 133.05, 131.85, 130.33, 129.76, 128.81, 128.45, 128.17, 126.85, 124.37, 65.41, 47.88, 35.45, 25.98, 23.69.

HRMS (ESI+): *m/z* for $C_{21}H_{21}O_3$ $[M+H]^+$ calculated: 321.1485, found: 321.1480.

Product (2e) (E)-3-(6-methyl-5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulen-6-yl)allyl benzoate



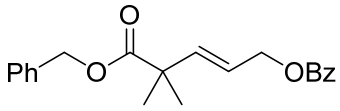
Product **2e** was synthesized according to General Benzoylation Procedure III with 0.0437 g of **1e** (0.204 mmol). The reaction duration was 15 h. A ^{1}H NMR yield of 71% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 5:95 EtOAc:Hexanes), and **2e** was obtained in a yield of 60% (0.0410 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (m, 2H), 7.59 (m, 1H), 7.47 (m, 2H), 7.38 (m, 1H), 7.33 (m, 1H), 7.29 (m, 1H), 7.15 (m, 1H), 6.11 (dt, *J* = 15.9, 1.4 Hz, 1H), 5.82 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.84 (dd, *J* = 6.1, 1.4 Hz, 2H), 2.81 (m, 2H), 2.00 (m, 1H), 1.92 (m, 2H), 1.81 (m, 1H), 1.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 211.73, 166.39, 140.81, 138.24, 137.57, 133.05, 131.23, 130.37, 129.75, 128.65, 128.47, 127.60, 126.72, 123.93, 65.55, 51.69, 35.34, 32.40, 25.12, 22.99.

HRMS (ESI+): *m/z* for $C_{22}H_{22}O_3Na$ $[M+Na]^+$ calculated: 357.1461, found: 357.1457.

Product (2f) (E)-5-(benzyloxy)-4,4-dimethyl-5-oxopent-2-en-1-yl benzoate



Product **2f** was synthesized according to General Benzoylation Procedure III with 0.0436 g of **1f** (0.200 mmol). The reaction duration was 15 h. A ^{1}H NMR yield of 79% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 5:95

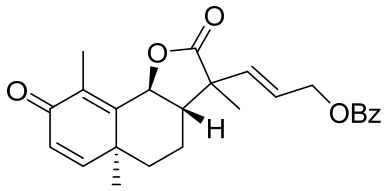
EtOAc:Hexanes), and **2f** was obtained in a yield of 68% (0.0458 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.57 (m, 1H), 7.44 (m, 2H), 7.33 (m, 5H), 6.09 (dt, *J* = 15.8, 1.4 Hz, 1H), 5.76 (dt, *J* = 15.8, 6.2 Hz, 1H), 5.14 (s, 2H), 4.81 (dd, *J* = 6.2, 1.4 Hz, 2H), 1.37 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.84, 166.40, 139.19, 136.20, 133.07, 130.32, 129.76, 128.62, 128.47, 128.18, 127.84, 122.90, 66.60, 65.35, 44.42, 25.00.

HRMS (ESI+): *m/z* for $C_{21}H_{22}O_4Na$ $[M+Na]^+$ calculated: 361.1410, found: 361.1406.

Product (2g) (E)-3-((3aR,5aR,9bR)-3,5a,9-trimethyl-2,8-dioxo-2,3,3a,4,5,5a,8,9b-octahydronaphtho[1,2-b]furan-3-yl)allyl benzoate



Product **2g** was synthesized according to General Benzoylation Procedure III with 0.0579 g of **1g**. (0.202 mmol). The reaction duration was 5 h. A ^{1}H NMR yield of 77% was measured. The product was purified with flash column silica chromatography (gradient 15:85 to 40:60 EtOAc:Hexanes), and **2g** was obtained in a yield of 73% (0.0597 g).

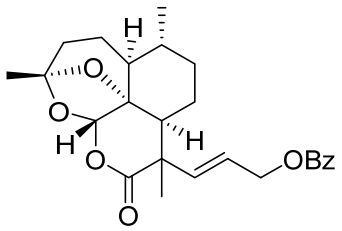
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.56 (m, 1H), 7.43 (m, 2H), 6.64 (d, *J* = 9.9 Hz, 1H), 6.21 (d, *J* = 9.8 Hz, 1H), 5.77 (s, 2H), 4.84 (m, 3H), 2.12 (s, 3H), 1.97 (td, *J* = 12.0, 3.8 Hz, 1H), 1.84 (m, 1H), 1.78 (m, 1H), 1.73 (m, 1H), 1.45 (td, *J* = 13.1, 5.1 Hz, 1H), 1.37 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 186.28, 177.53, 166.33, 154.82, 151.24, 133.39, 130.14, 130.05, 129.75, 129.30, 128.62, 127.59, 126.12, 79.36, 64.61, 56.89, 49.24, 41.40, 37.75, 24.94, 21.34,

19.11, 11.16.

HRMS (ESI+): *m/z* for $C_{25}H_{27}O_5$ $[M+H]^+$ calculated: 407.1853, found: 407.1851.

Product (2h) (E)-3-((3aS,3a1R,6R,6aS,9S,10aR)-3,6,9-trimethyl-2-oxodecahydro-10aH-3a1,9-epoxyoxepino[4,3,2-ij]isochromen-3-yl)allyl benzoate



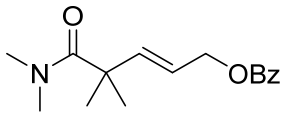
Product **2h** was synthesized according to General Benzoylation Procedure III with 0.0633 g of **1h** (0.207 mmol). The reaction duration was 10 h. A ^{1}H NMR yield of 72% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 20:80 EtOAc:Hexanes), and **2h** was obtained in a yield of 53% (0.0467 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.53 (m, 1H), 7.40 (m, 2H), 6.04 (dd, *J* = 15.9, 1.7 Hz, 1H), 5.70 (s, 1H), 5.63 (dtd, *J* = 15.9, 6.4, 1.7 Hz, 1H), 4.77 (m, 2H), 2.05 (m, 1H), 2.00 (m, 1H), 1.87 (m, 1H), 1.78 (m, 1H), 1.66 (m, 1H), 1.53 (m, 1H), 1.39 (s, 3H), 1.31 (s, 3H), 1.23 (m, 3H), 1.08 (m, 2H), 0.90 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.68, 166.36, 141.51, 132.96, 130.30, 129.69, 128.36, 119.40, 110.15, 99.99, 82.60, 65.49, 46.50, 45.89, 45.23, 35.40, 33.99, 33.94, 25.79, 25.19, 23.51, 22.25, 18.66.

HRMS (ESI+): *m/z* for $C_{25}H_{30}O_6Na$ $[M+Na]^+$ calculated: 449.1935, found: 449.1926.

Product (2i) (E)-5-(dimethylamino)-4,4-dimethyl-5-oxopent-2-en-1-yl benzoate



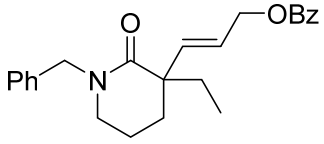
Product **2i** was synthesized according to General Benzoylation Procedure III with 0.0322 g of **1i** (0.207 mmol). The reaction duration was 5 h. A ^{1}H NMR yield of 76% was measured. The product was purified with flash column silica chromatography (gradient 5:95 to 50:50 EtOAc:Hexanes), and **2i** was obtained in a yield of 71% (0.0404 g).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.57 (m, 1H), 7.45 (m, 2H), 6.06 (dt, *J* = 15.9, 1.4 Hz, 1H), 5.70 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.83 (dd, *J* = 6.2, 1.4 Hz, 2H), 2.96, (s, 6H), 1.34 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.17, 166.45, 141.26, 133.18, 130.33, 129.72, 128.56, 121.97, 65.37, 44.47, 26.80. (1 peak overlap)

HRMS (ESI+): *m/z* for $C_{16}H_{21}NO_3$ $[M+Na]^+$ calculated: 298.1414, found: 298.1408.

Product (2j) (E)-3-(1-benzyl-3-ethyl-2-oxopiperidin-3-yl)allyl benzoate



Product **2j** was synthesized according to General Benzoylation Procedure III with 0.0505 g of **1j** (0.196 mmol). The reaction duration was 15 h. A ^{1}H NMR yield of 66% was measured. The product was purified with flash column silica chromatography (gradient 5:95 to 40:60 EtOAc:Hexanes), and **2j** was obtained in a yield of 58% (0.0426 g).

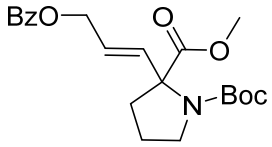
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 2H), 7.60 (m, 1H), 7.48 (m, 2H), 7.37-7.24 (m, 5H), 6.03 (dt, *J* = 15.9, 1.4 Hz, 1H), 5.80 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.88 (d, *J* = 6.2 Hz, 2H), 4.62 (m, 2H),

3.23 (m, 2H), 1.91 (m, 1H), 1.83 (m, 3H), 1.71 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.73, 166.46, 139.79, 137.67, 133.00, 130.51, 129.78, 128.68, 128.45, 128.12, 127.38, 123.87, 65.69, 50.71, 48.61, 47.84, 31.99, 29.34, 19.43, 8.66.

HRMS (ESI+): *m/z* for $C_{24}H_{28}O_3$ $[M+H]^+$ calculated: 378.2064, found: 378.2063.

Product (2k) 1-(tert-butyl) 2-methyl (E)-2-(3-(benzoyloxy)prop-1-en-1-yl)pyrrolidine-1,2-dicarboxylate



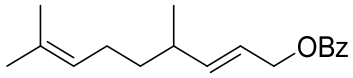
Product **2k** was synthesized according to General Benzoylation Procedure III with 0.0555 g of **1k** (0.206 mmol). The reaction duration was 15 h. A ^{1}H NMR yield of 57% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 20:80 EtOAc:Hexanes), and **2k** was obtained in a yield of 60% (0.0478 g) as a mixture of rotomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (m, 2H), 7.55 (m, 1H), 7.42 (m, 2H), 6.37 (d, *J* = 15.7 Hz, 1H), 5.69 (dt, *J* = 15.7, 6.3 Hz, 1H), 4.85 (m, 2H), 3.73 (m, 3H), 3.70-3.49 (m, 2H), 2.20 (m, 1H), 2.03 (m, 1H), 1.88 (m, 2H), 1.43 (s, 3H), 1.32 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.64, 173.46, 166.42, 166.32, 153.70, 153.42, 134.38, 133.48, 133.10, 133.02, 130.25, 129.76, 129.72, 128.45, 122.99, 122.93, 80.24, 80.09, 68.94, 68.71, 65.01, 64.87, 52.62, 52.47, 48.13, 47.98, 39.60, 38.29, 28.47, 28.28, 23.06, 22.18.

HRMS (ESI+): *m/z* for $C_{21}H_{28}NO_6$ $[M+H]^+$ calculated: 390.1911, found: 390.1905.

Product (2l) (E)-4,8-dimethylnona-2,7-dien-1-yl benzoate



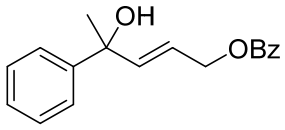
Product **2l** was synthesized according to General Benzoylation Procedure III with 0.0316 g of **1l** (0.208 mmol). The reaction duration was 5 h. A ^{1}H NMR yield of 78% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 5:95 EtOAc:Hexanes), and **2l** was obtained in a yield of 61% (0.0344 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.54 (m, 1H), 7.43 (m, 2H), 5.69 (m, 2H), 5.09 (tdt, *J* = 7.4, 3.1, 1.6 Hz, 1H), 4.77 (d, *J* = 6.1 Hz, 2H), 2.19 (m, 1H), 1.97 (q, *J* = 7.5 Hz, 2H), 1.68 (s, 3H), 1.58 (s, 3H), 1.32 (m, 2H), 1.02 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.58, 142.25, 132.96, 131.58, 130.58, 129.74, 128.44, 124.59, 122.42, 65.97, 36.86, 36.15, 25.86, 20.30, 17.84. (1 peak overlap)

HRMS (EI+): *m/z* for $C_{18}H_{24}O_2$ $[M]^+$ calculated: 272.1776, found: 272.1746.

Product (2m) (E)-4-hydroxy-4-phenylpent-2-en-1-yl benzoate



Product **2m** was synthesized according to General Benzoylation Procedure III with 0.0323 g of **1m** (0.199 mmol). The reaction duration was 3 h. A ^{1}H NMR yield of 72% was measured. The product was purified with flash column silica chromatography (5:95 EtOAc:Hexanes), and **2m** was obtained in a yield of 61% (0.0343 g).

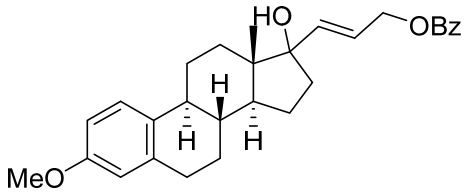
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.57 (m, 1H), 7.51 (m, 2H), 7.46 (m, 2H), 7.36 (m, 2H), 7.27 (m, 1H), 6.18 (dt, *J* = 15.6, 1.4 Hz, 1H), 5.97 (dt, *J* = 15.6, 6.0 Hz, 1H), 4.86 (dd, *J* =

6.0, 1.4 Hz, 2H), 2.11 (br s, 1H), 1.70 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, CDCl3) δ 166.45, 146.31, 141.03, 133.14, 130.28, 129.79, 128.51, 128.49, 127.31, 125.28, 122.50, 74.34, 64.96, 29.80.

HRMS (ESI+): *m/z* for $C_{18}H_{18}O_3Na$ $[M+Na]^+$ calculated: 305.1148, found: 305.1145.

Product (2n) (E)-3-((8R,9S,13S,14S)-17-hydroxy-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)allyl benzoate



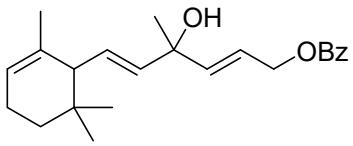
Product **2n** was synthesized according to General Benzoylation Procedure III with 0.0649 g of **1n** (0.199 mmol). The reaction duration was 5 h. A ^{1}H NMR yield of 82% was measured. The product was purified with flash column neutral alumina chromatography (gradient 0:100 to 15:85 EtOAc:Hexanes), and **2n** was obtained in a yield of 73% (0.0650 g).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.56 (m, 1H), 7.44 (m, 2H), 7.18 (d, J = 8.6 Hz, 1H), 6.71 (dd, J = 8.6, 2.7 Hz, 1H), 6.63 (d, J = 2.7 Hz, 1H), 6.13 (d, J = 15.6 Hz, 1H), 5.89 (dt, J = 15.6, 6.2 Hz, 1H), 4.89 (m, 2H), 3.78 (s, 3H), 2.86 (m, 2H), 2.28 (m, 1H), 2.13 (m, 1H), 2.04 (m, 1H), 1.90 (m, 2H), 1.75 (m, 1H), 1.60 (m, 3H), 1.46 (m, 3H), 1.40 (m, 1H), 1.34 (m, 1H), 0.95 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.53, 157.62, 140.19, 138.09, 133.10, 132.73, 130.47, 129.77, 128.52, 126.45, 122.15, 113.97, 111.63, 83.79, 65.43, 55.36, 49.43, 47.16, 43.87, 39.65, 36.99, 32.48, 29.98, 27.61, 26.45, 23.44, 14.21.

HRMS (EI+): *m/z* for $C_{29}H_{34}O_4$ $[M]^+$ calculated: 446.2457, found: 446.2460.

Product (2o) (2E,5E)-4-hydroxy-4-methyl-6-(2,6,6-trimethylcyclohex-2-en-1-yl)hexa-2,5-dien-1-yl benzoate



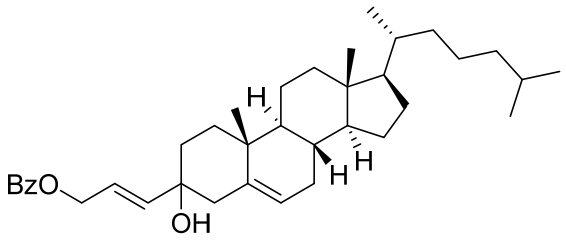
Product **2o** was synthesized according to General Benzoylation Procedure III with 0.0469 g of **1o** (0.200 mmol). The reaction duration was 3 h. A ^{1}H NMR yield of 69% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 20:80 EtOAc:Hexanes), and **2o** was obtained in a yield of 48% (0.0337 g) as a mixture of diastereomers.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.56 (m, 1H), 7.44 (m, 2H), 5.97 (dd, *J* = 15.7, 2.3 Hz, 1H), 5.90 (dt, *J* = 15.7, 5.4 Hz, 1H), 5.58 (d, *J* = 15.5 Hz, 1H), 5.46 (m, 1H), 5.39 (br s, 1H), 4.83, (d, *J* = 5.4 Hz, 2H), 2.10 (d, *J* = 9.2 Hz, 1H), 1.99 (br s, 2H), 1.64 (s, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 1.25 (m, 1H), 1.16 (m, 1H), 0.88 (s, 3H), 0.80 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.23, [140.72, 140.63], 136.90, [133.80, 133.76], 132.88, 130.20, [129.93, 129.85], 129.57, 128.27, [121.95, 121.91], [121.10, 121.09], 72.63, 64.79, 53.91, [32.01, 31.99], 31.49, [28.33, 28.27], [27.54, 27.51], 26.89, 22.99, [22.83, 22.81].

HRMS (EI+): *m/z* for $C_{23}H_{30}O_3$ $[M]^+$ calculated: 354.2195, found: 354.2186.

Product (2p) (R)-3-((8S,9S,10R,13R,14S,17R)-3-hydroxy-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)allyl benzoate



Product **2p** was synthesized according to General Benzoylation Procedure III with 0.0836 g of **1p** (0.196 mmol). The reaction duration was 3 h. A ^{1}H NMR yield of 66% was measured. The product was purified with flash column silica chromatography (gradient 0:100 to 10:90 EtOAc:Hexanes), and **2p** was obtained in a yield of 50% (0.0535 g).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.56 (m, 1H), 7.44 (m, 2H), 6.05 (d, *J* = 15.9 Hz, 1H), 5.97 (dt, *J* = 15.9, 4.8 Hz, 1H), 5.33 (d, *J* = 4.8 Hz, 1H), 4.82 (d, *J* = 4.8 Hz, 2H), 2.54 (m, 1H), 2.17 (dd, *J* = 13.4, 2.7 Hz, 1H), 2.05-0.96 (m, 30H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.4 Hz, 6H), 0.67 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.41, 140.23, 139.13, 133.09, 130.48, 129.79, 128.51, 123.24, 122.95, 100.15, 73.05, 65.33, 56.88, 56.38, 50.44, 45.97, 42.48, 39.92, 39.68, 36.65, 36.38, 36.33, 36.06, 35.97, 32.04, 28.40, 28.18, 24.42, 24.04, 22.98, 22.72, 21.20, 19.67, 18.88, 12.01.

HRMS (ESI+): *m/z* for $C_{37}H_{54}O_3Na$ $[M+Na]^+$ calculated: 569.3965, found: 569.3970.

E. Raw Data For Tables 1 and 2

Table S2 – Masses of Substrate and Internal Standard for Table 1. Oxidation of Model Ketone 1b.

Exp	Sub	Mass	MW	Mol Sub	R/S Mol	P/S (NMR)	R/S (NMR)
A-1	1b	0.0236	228.34	0.000103	5.210	0	5.431
B-2	1b	0.0232	228.34	0.000102	5.122	0	1.140
C-3	1b	0.0233	228.34	0.000102	5.144	3.031	0
D-4	1b	0.0235	228.34	0.000103	5.188	2.998	0
E-5	1b	0.0229	228.34	0.0001	5.056	2.781	0
F-6	1b	0.0232	228.34	0.000102	5.122	2.643	1.081
G-7	1b	0.0232	228.34	0.000102	5.122	3.766	0
H-8	1b	0.0231	228.34	0.000101	5.100	3.987	0
I-9	1b	0.0233	228.34	0.000102	5.144	4.149	0
J-10	1b	0.0233	228.34	0.000102	5.144	3.943	0

Table S3 – Yields and Conversions for Table 1. Oxidation of Model Ketone 1b.

Exp	Sub	Yield	Remaining Reactant	Pd(Obz)2	DAFO	BQ	Time	Temp °C
A-1	1b	0	104%	X	10%	X	20h	65
B-2	1b	0	22%	10%	X	X	20h	65
C-3	1b	59%	0	10%	10%	X	20h	65
D-4	1b	58%	0	10%	10%	X	20h	65
E-5	1b	55%	0	20%	20%	X	20h	65
F-6	1b	52%	21%	10%	10%	X	20h	65
G-7	1b	74%	0	10%	10%	10%	20h	65
H-8	1b	78%	0	10%	10%	50%	20h	65
I-9	1b	81%	0	10%	10%	10%	10h	65
J-10	1b	77%	0	10%	10%	10%	10h	65
IJAVG	1b	79%	0	10%	10%	10%	10h	66

S = Internal Standard Tribromoanisole
R = Substrate **(1b)**
P = product **(2b)**
Cy = **1b**

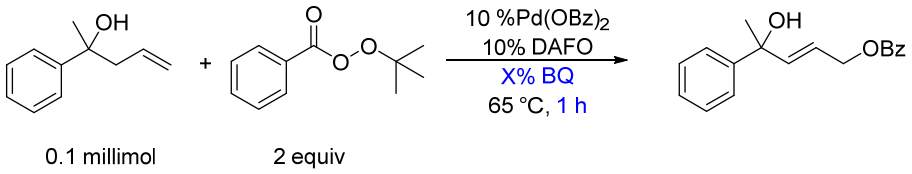
Table S4 – Masses of Substrate and Internal Standard for Table 2. Oxidation of Homoallylic Alcohol 1m

Exp	Exp #	Sub	Mass	MW	Mol Sub	R/S Mol	P/S (NMR)	R/S (NMR)
6_51 E	1	1m	0.0162	162.23	0.000100	4.8059	1.3222	2.2160
6_52B	2	1m	0.0165	162.23	0.000102	4.8949	1.3842	2.2768
6_51C	3	1m	0.0166	162.23	0.000102	4.9245	1.2271	0.0000
6_51F	4	1m	0.0170	162.23	0.000105	5.0432	3.5158	0.0000
6_51G	5	1m	0.0162	162.23	0.000100	4.8059	3.3408	0.0000
6_51H	6	1m	0.0165	162.23	0.000102	4.8949	3.3525	0.0000
6_52A	7	1m	0.0172	162.23	0.000106	5.1025	3.4990	0.0000

Table S5 – Yields and Conversions for Table 2. Oxidation of Homoallylic Alcohol 1m

Exp	Sub		Yield	Remaining Reactant	Pd(Obz)2	DAFO	BQ	Time	Temp °C
1	1m		28%	46%	10%	10%	X	1 h	65
2	1m		28%	47%	10%	10%	X	3 h	65
3	1m		25%	0%	10%	10%	X	48 h	65
4	1m		70%	0%	10%	10%	5%	1 h	65
5	1m		70%	0%	10%	10%	10%	1 h	65
6	1m		69%	0%	10%	10%	50%	1 h	65
7	1m		69%	0%	10%	10%	10%	3 h	65

F. Investigation of the Effects of Additives on the Rate and Yield of C-H Oxidation



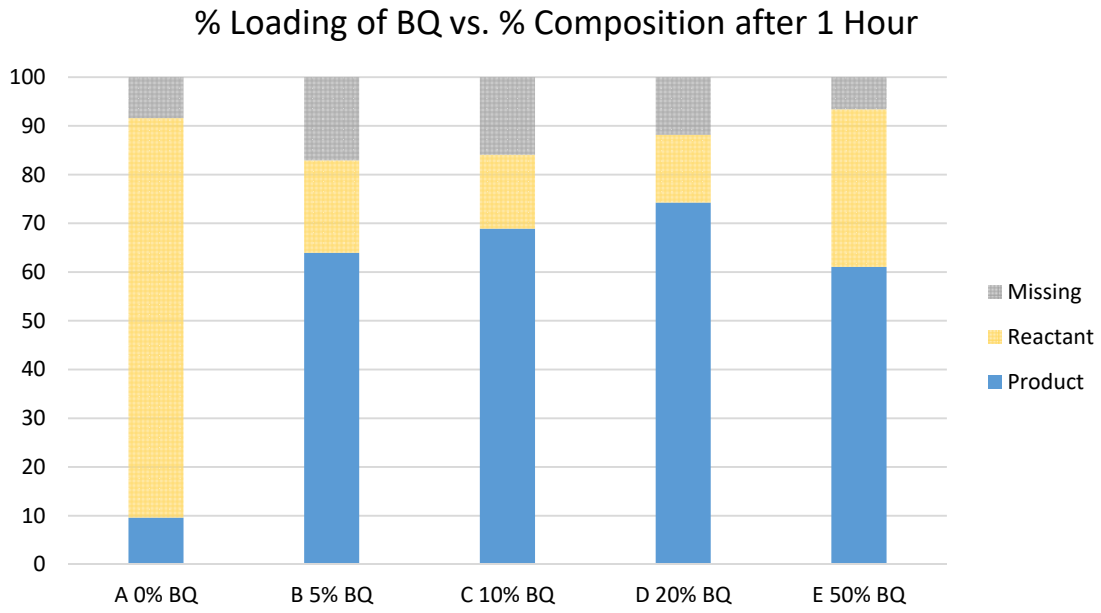
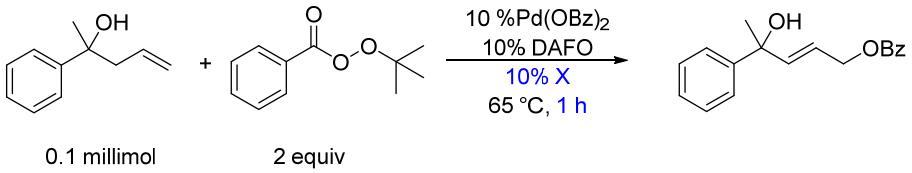


Figure S1 – The Effect of Varying the Loading of BQ on the Yield of 2m and Conversion of 1m



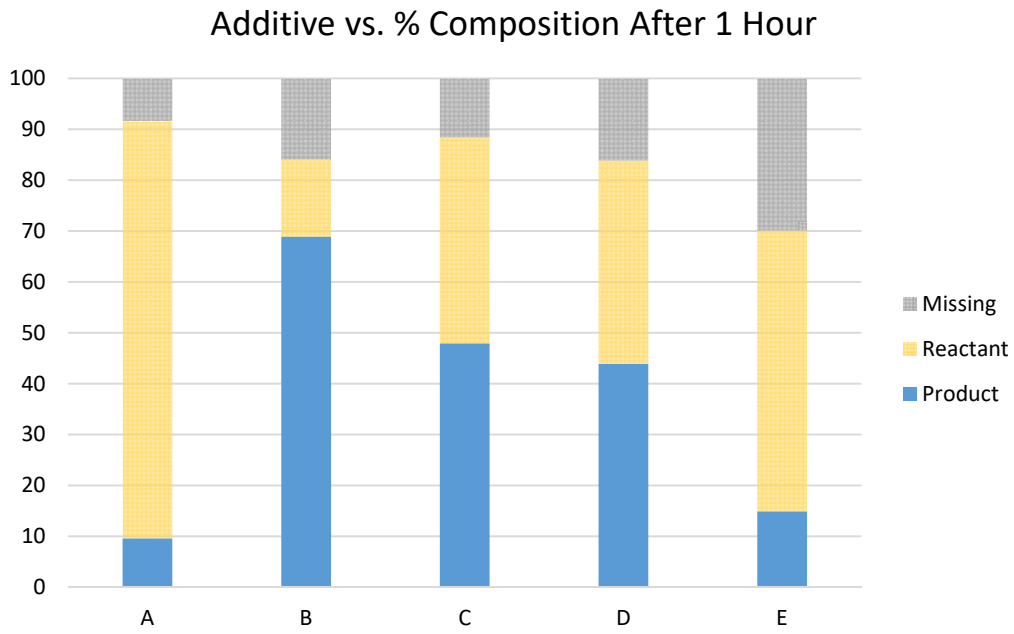


Figure S2 – The Effect of Varying the Structure of the Quinones on the Yield of 2m and Conversion of 1m

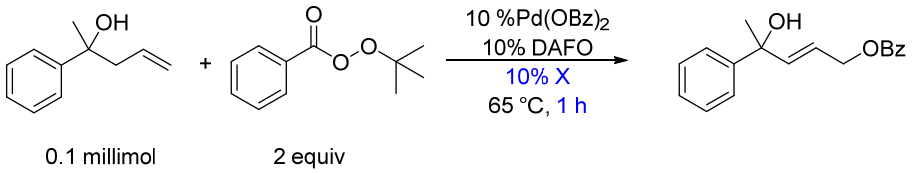
A = Control - no Additive

B = 10% Benzoquinone

C = 10% 2,6-dimethylcyclohexa-2,5-diene-1,4-dione

D = 10% 2,5-dimethylcyclohexa-2,5-diene-1,4-dione

E = 10% 2,3,5,6-tetrafluorocyclohexa-2,5-diene-1,4-dione



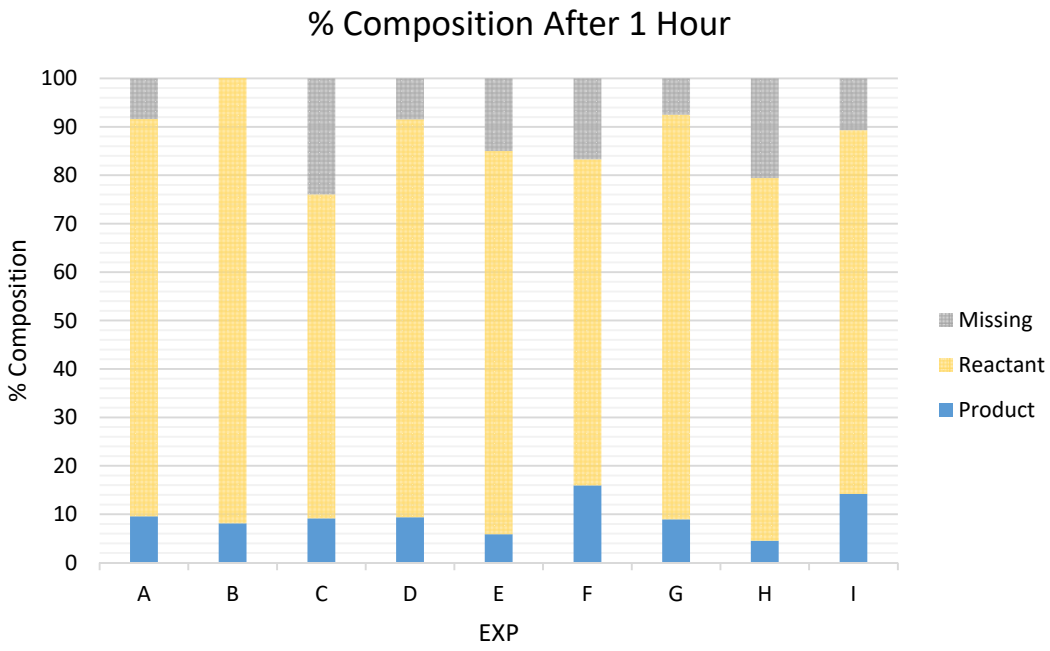


Figure S3 – The Effect of Metal Salts on the Yield of 2m and Conversion of 1m

A = CTRL no additive

B = 10% $NaVO_3$

C = 10% $VO(acac)_2$

D = 10% Fe_2O_3

E = 10% $Fe(acac)_3$

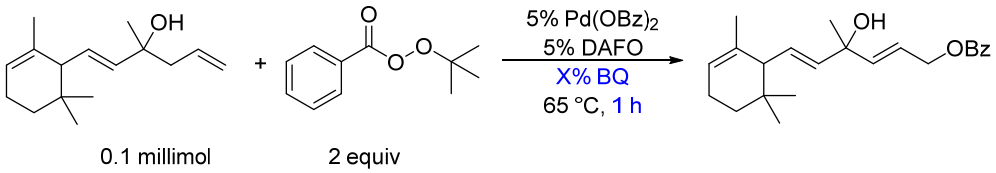
F = 10% Cu(O)

G = 10% (Co)Salophen (CAS 14167-18-1)

H = 10% $Fe(acac)_2$

I = Ferrocenium tetrafluoroborate (CAS: 1282-37-7)

G. Optimization of Conditions for Large Scale Reaction



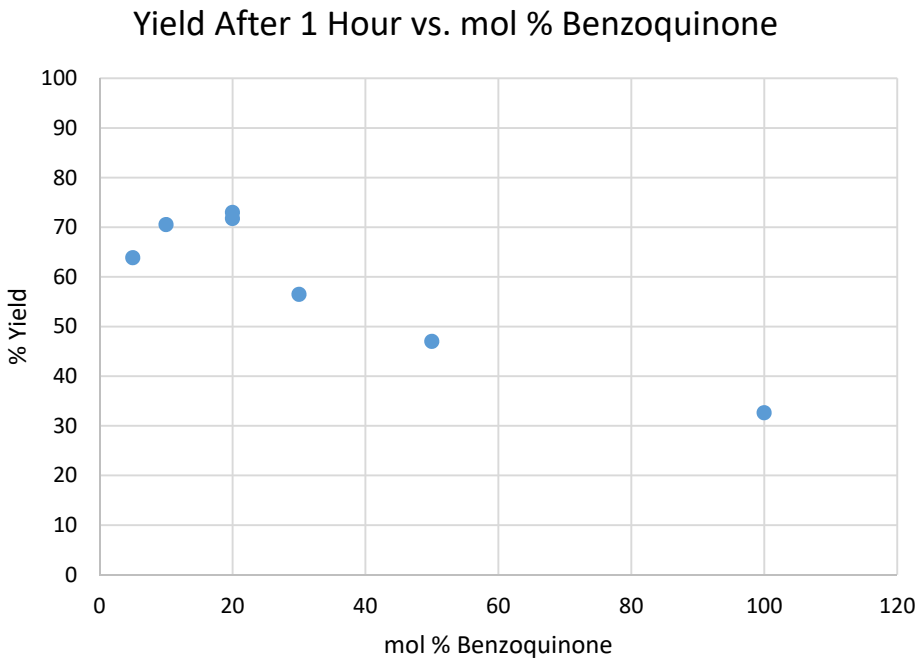


Figure S4 – The Effect of Varying the BQ Loading on the Yield of 2o and Conversion of 1o with 5 mol % $Pd(OBz)_2$ and DAFO

H. Crude NMR from the Oxidation of 1m

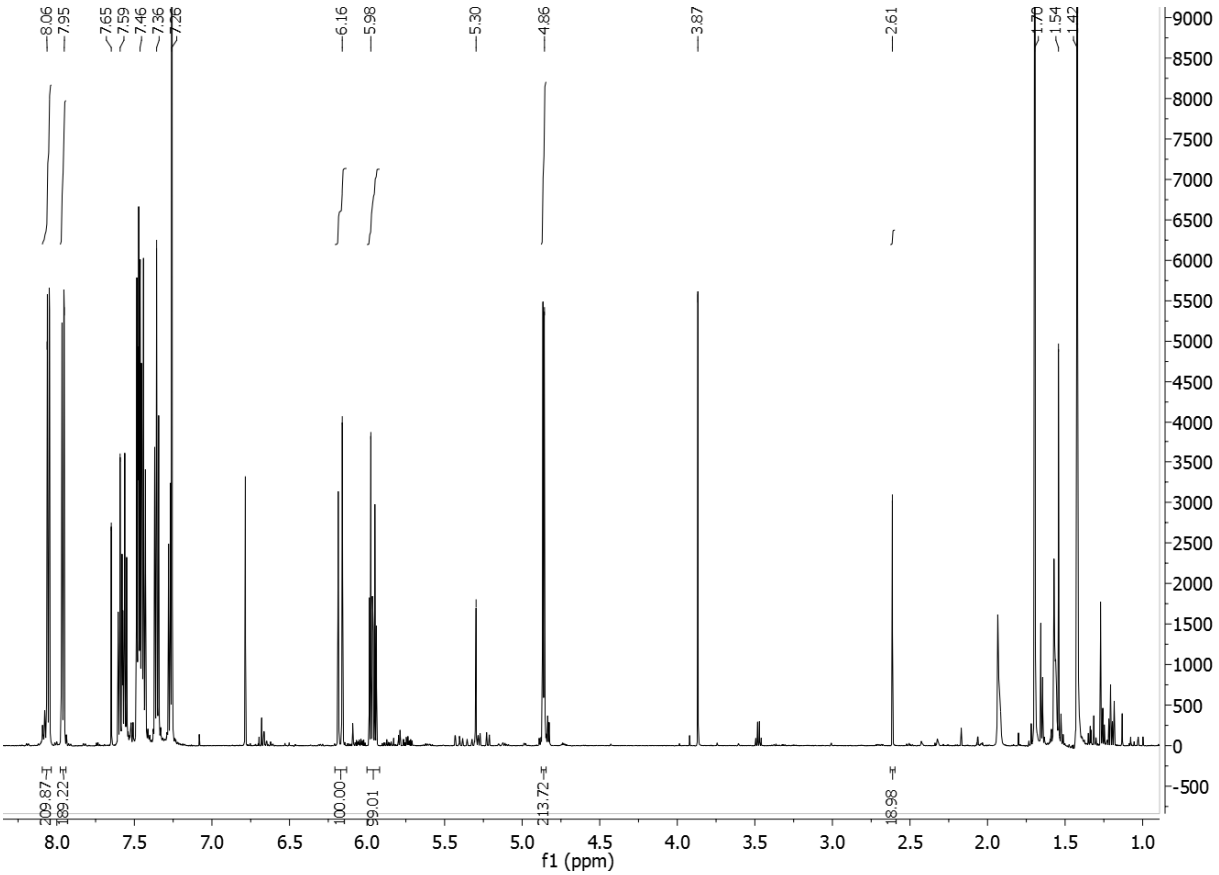


Figure S5 - Representative Crude ^{1}H NMR Spectrum for the Oxidation of 1m

I. Possible Catalytic Cycle for Allylic Oxidation

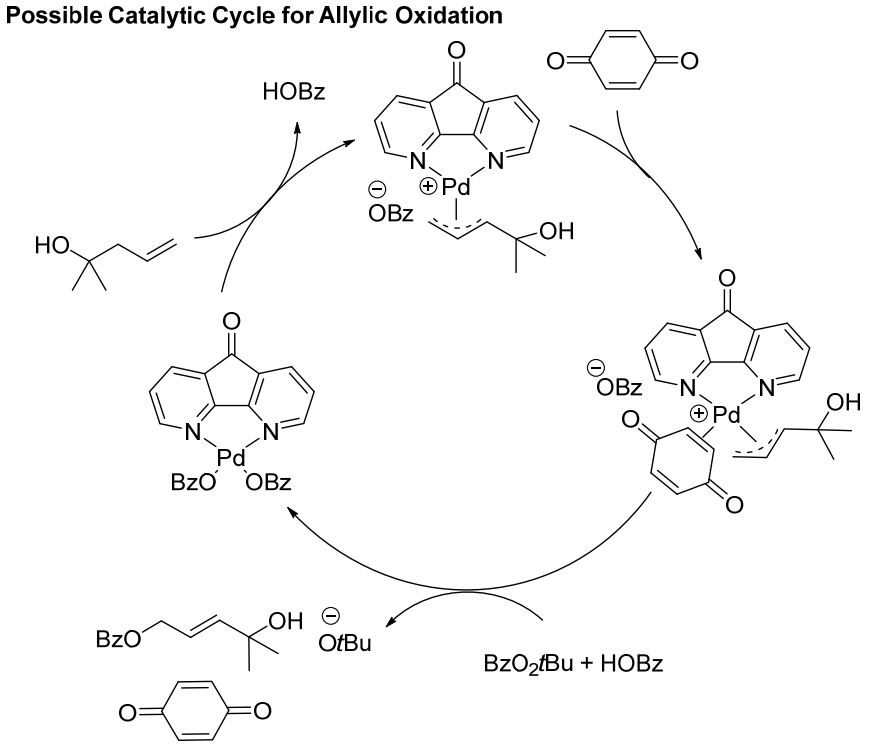


Figure S6 – Possible Catalytic Cycle for Allylic Oxidation

J. References

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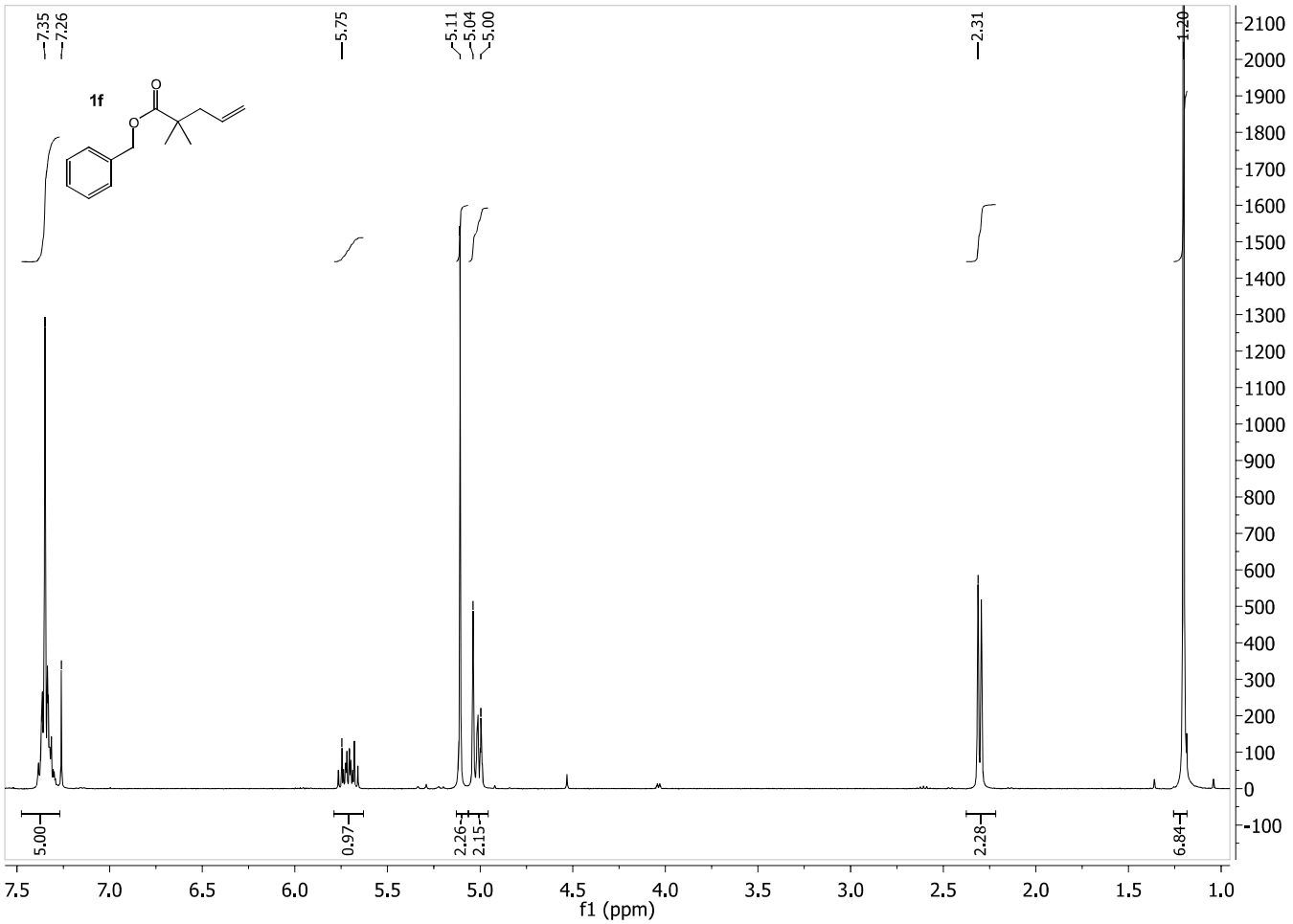
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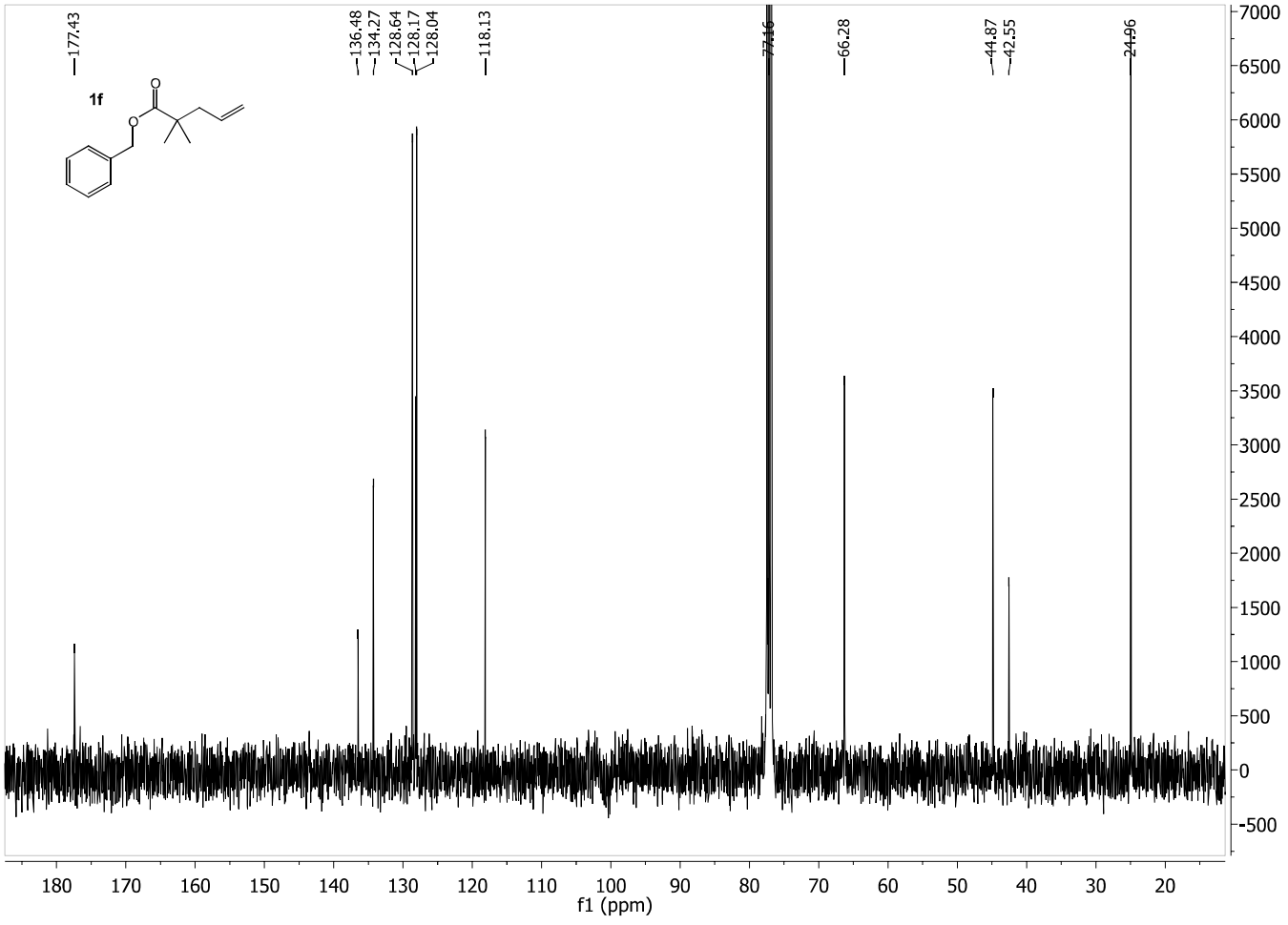
5.75
5.11
5.04
5.00
2.31
1.20
1f
5.00
0.97
2.26
2.15
2.28
6.84
f1 (ppm)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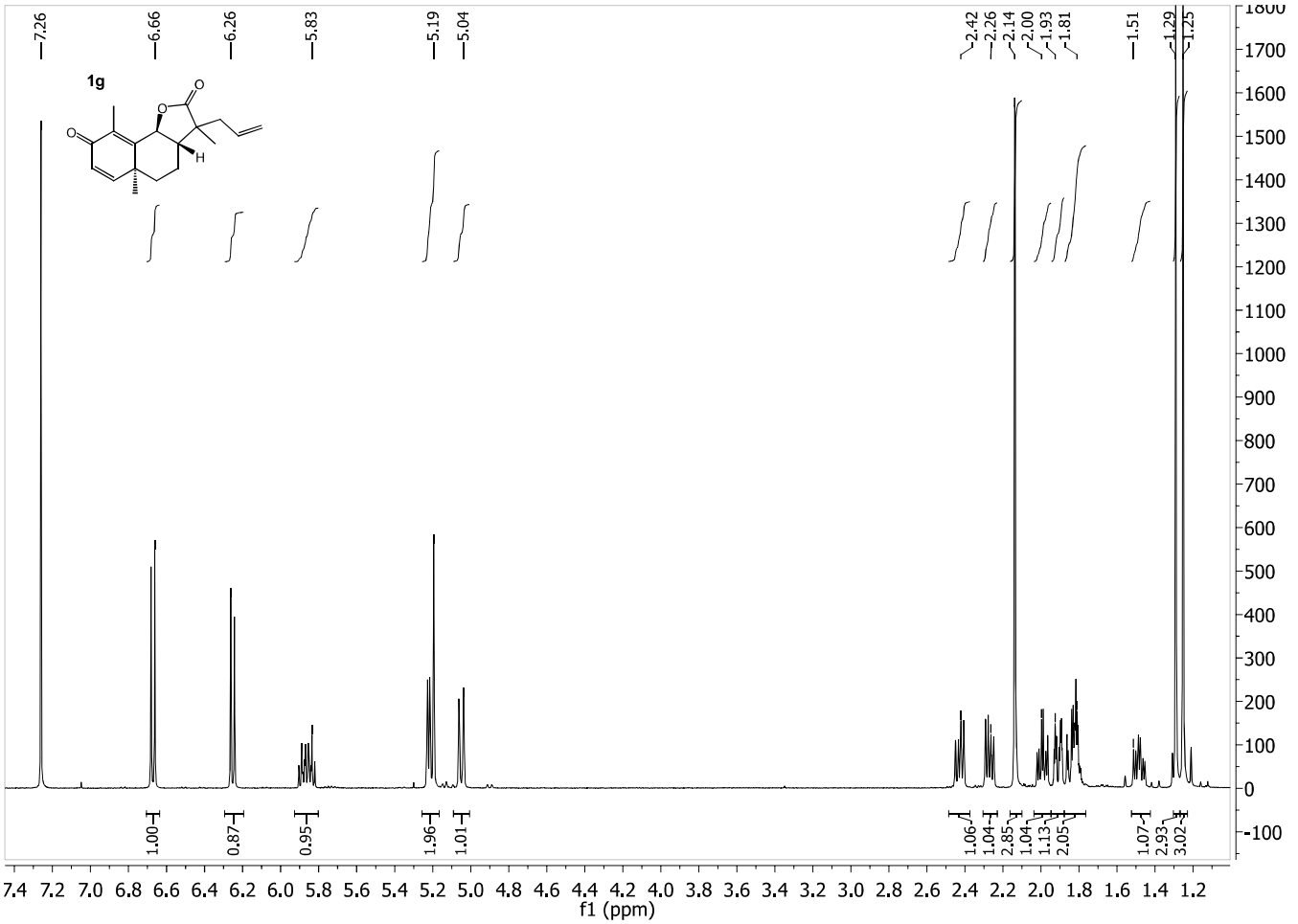
42.55
24.96
1f
f1 (ppm)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6.26
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5.19
5.04
2.42
2.26
2.14
2.00
1.93
1.81
1.51
1.29
1.25
1g
1.00
0.87
0.95
1.96
1.01
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1.04
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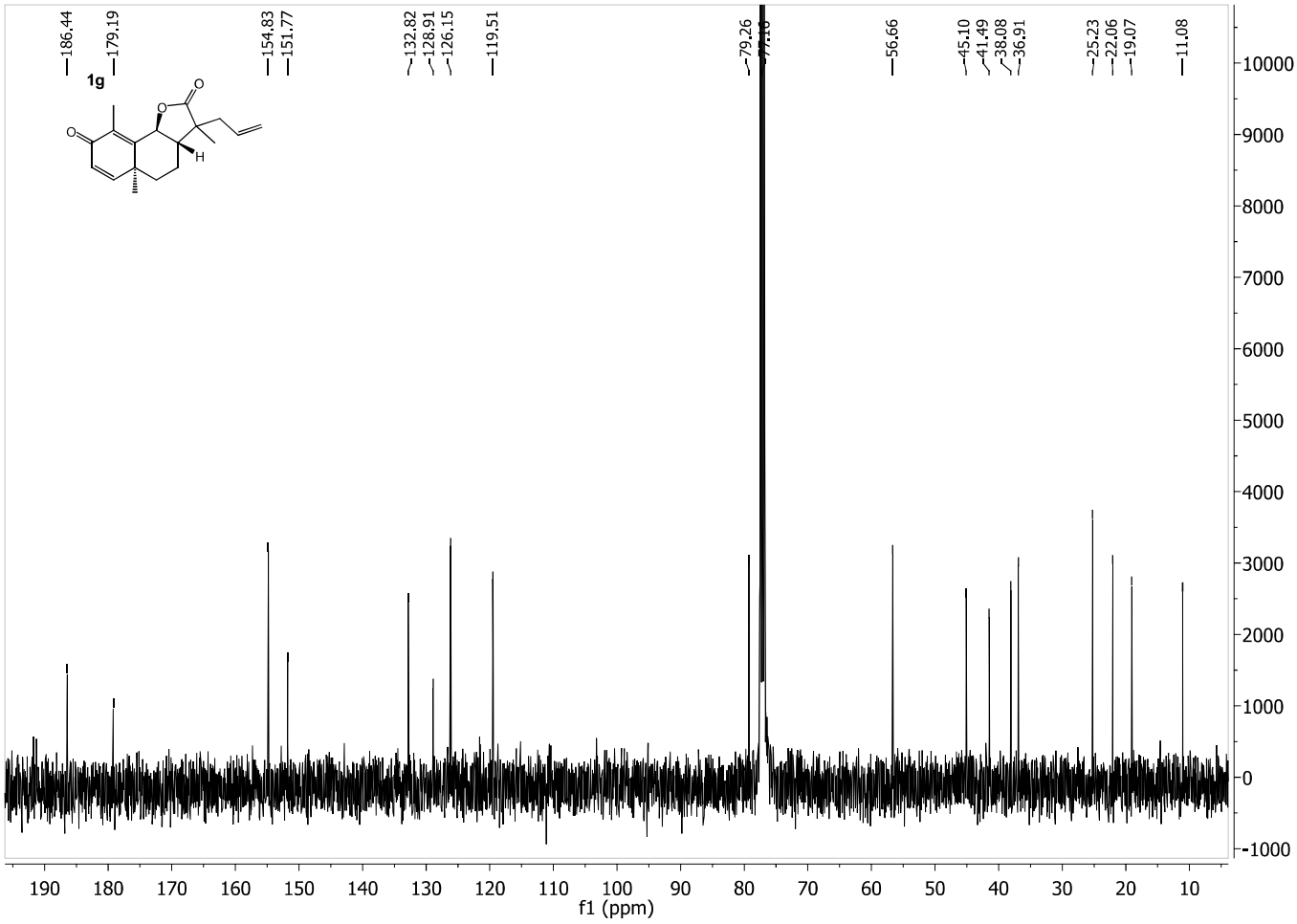
1.04
1.13
2.05
1.07
2.93
3.02
f1 (ppm)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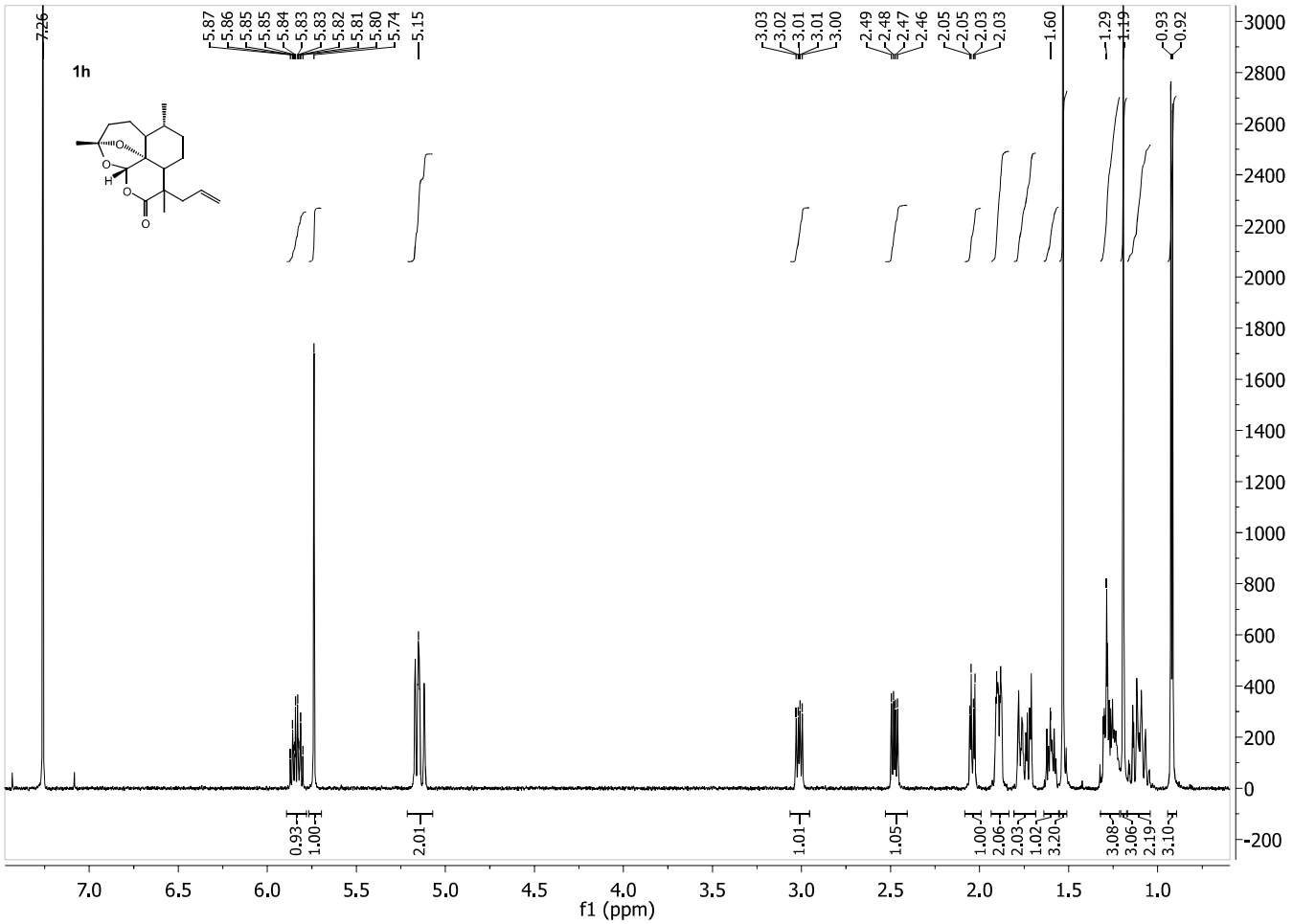
19.07
11.08
1g
f1 (ppm)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5.74
5.15
3.03
3.02
3.01
3.01
3.00
2.49
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2.47
2.46
2.05
2.05
2.03
2.03
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1.29
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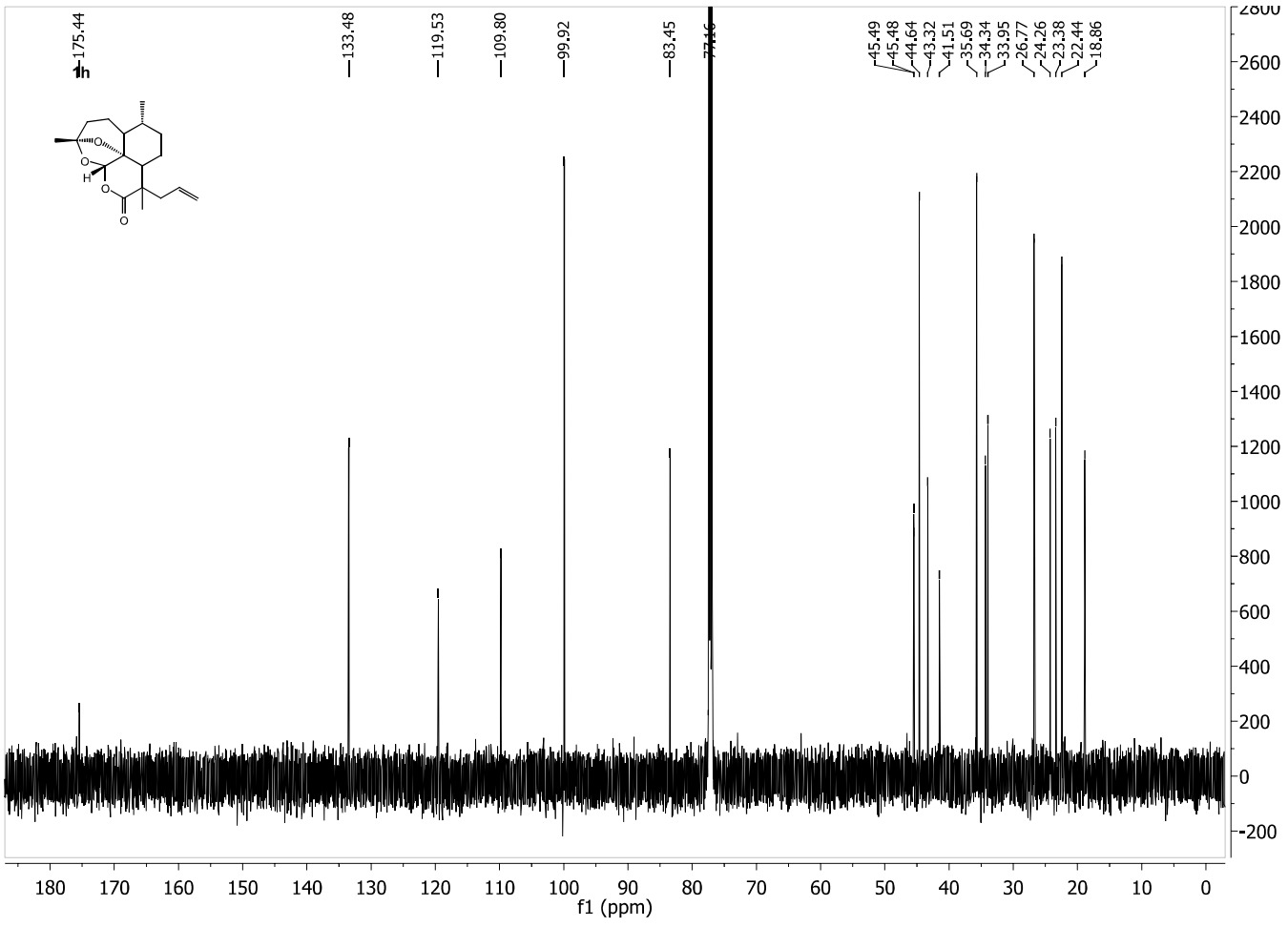
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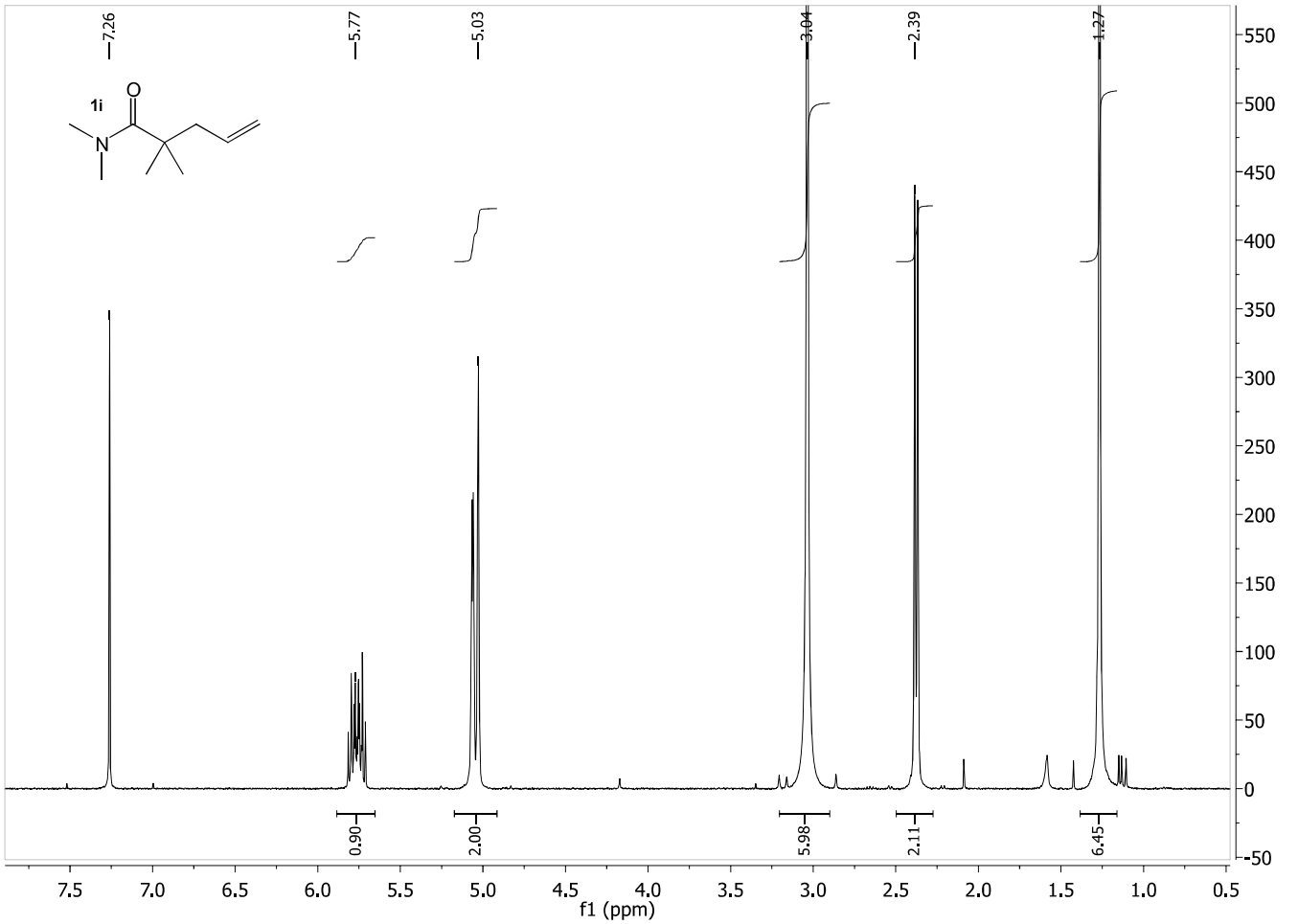
f1 (ppm)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O
N
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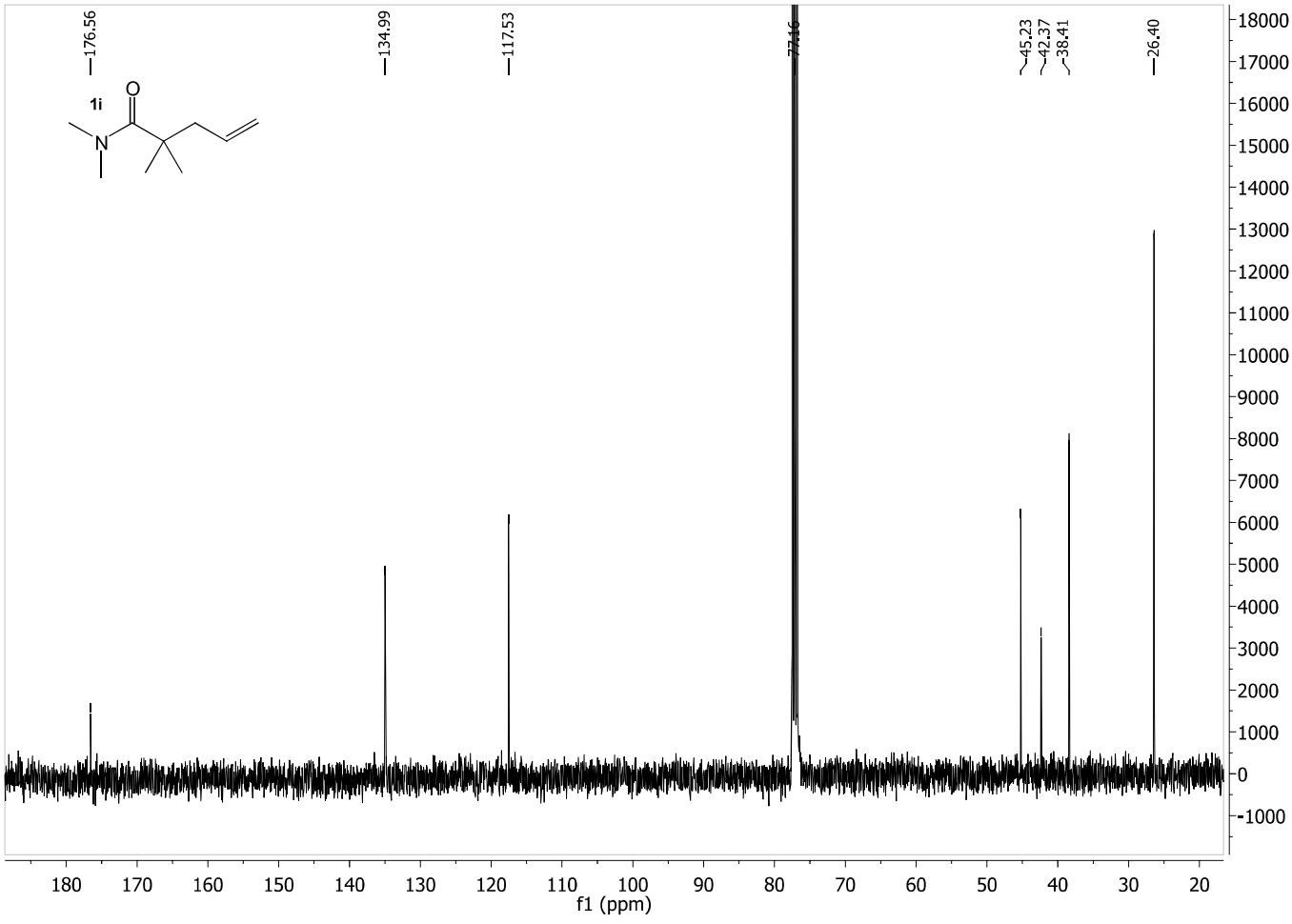
f1 (ppm)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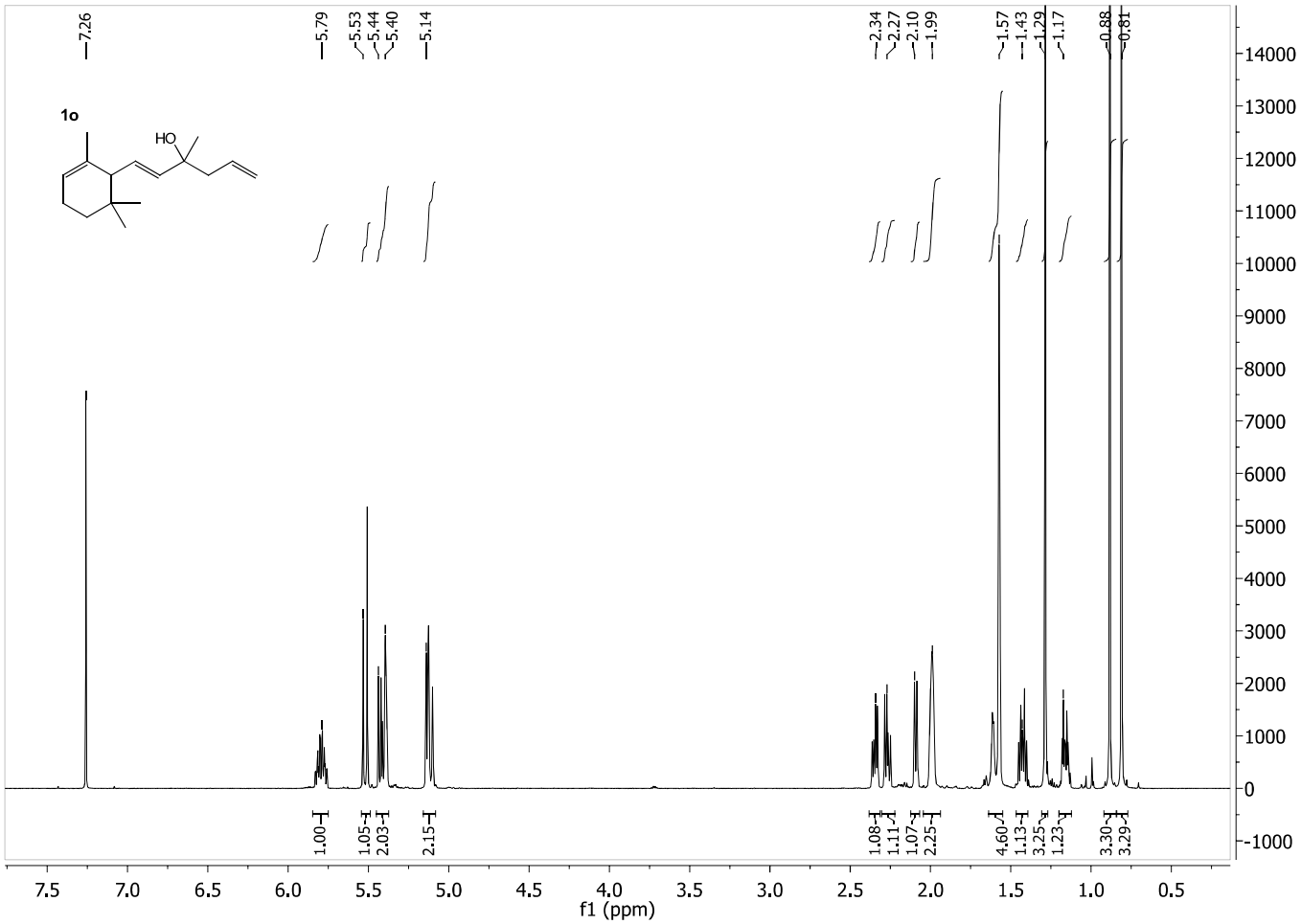
O
N
f1 (ppm)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0.81
1o
HO
1.00
1.05
2.03
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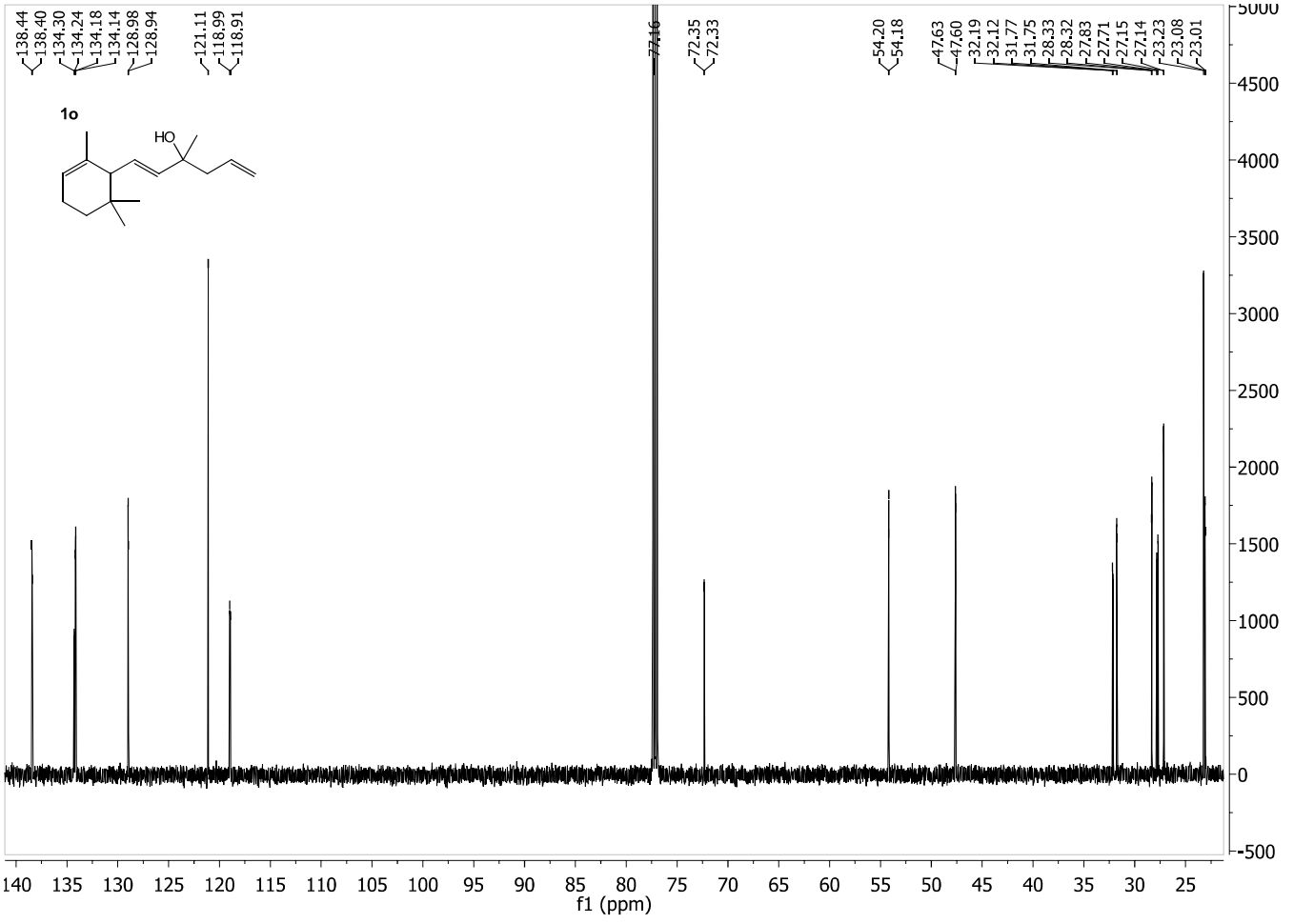
f1 (ppm)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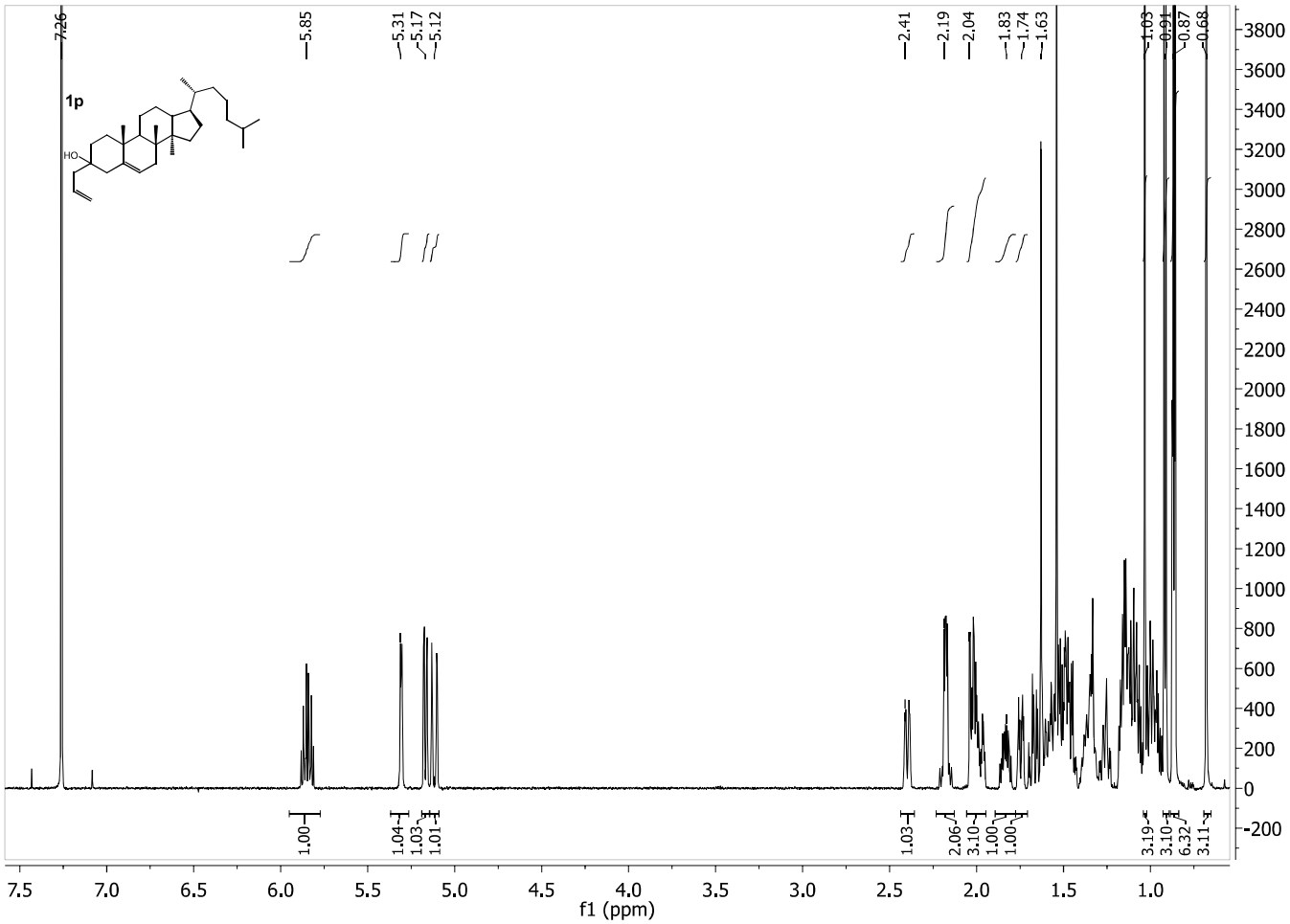
f1 (ppm)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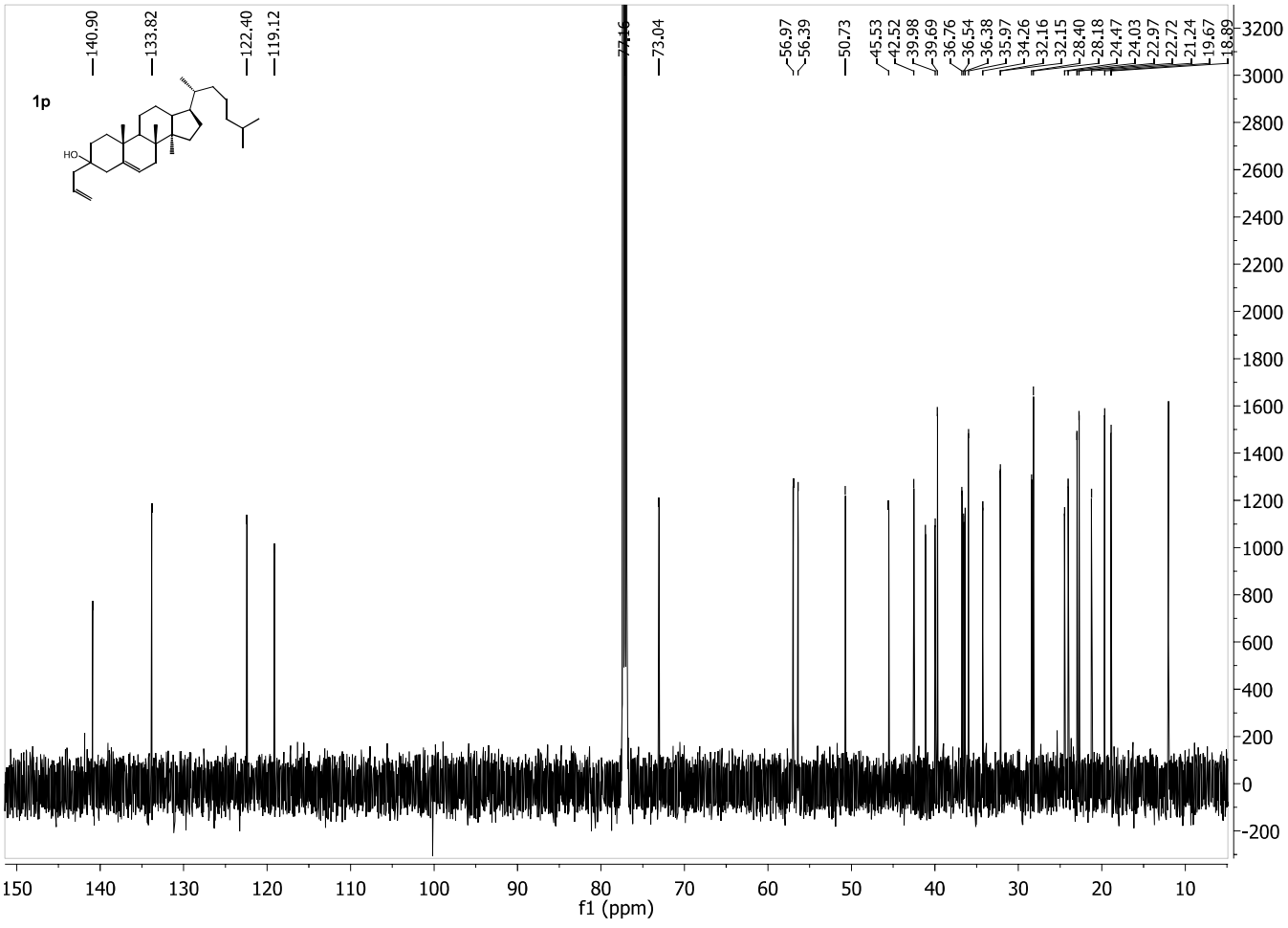
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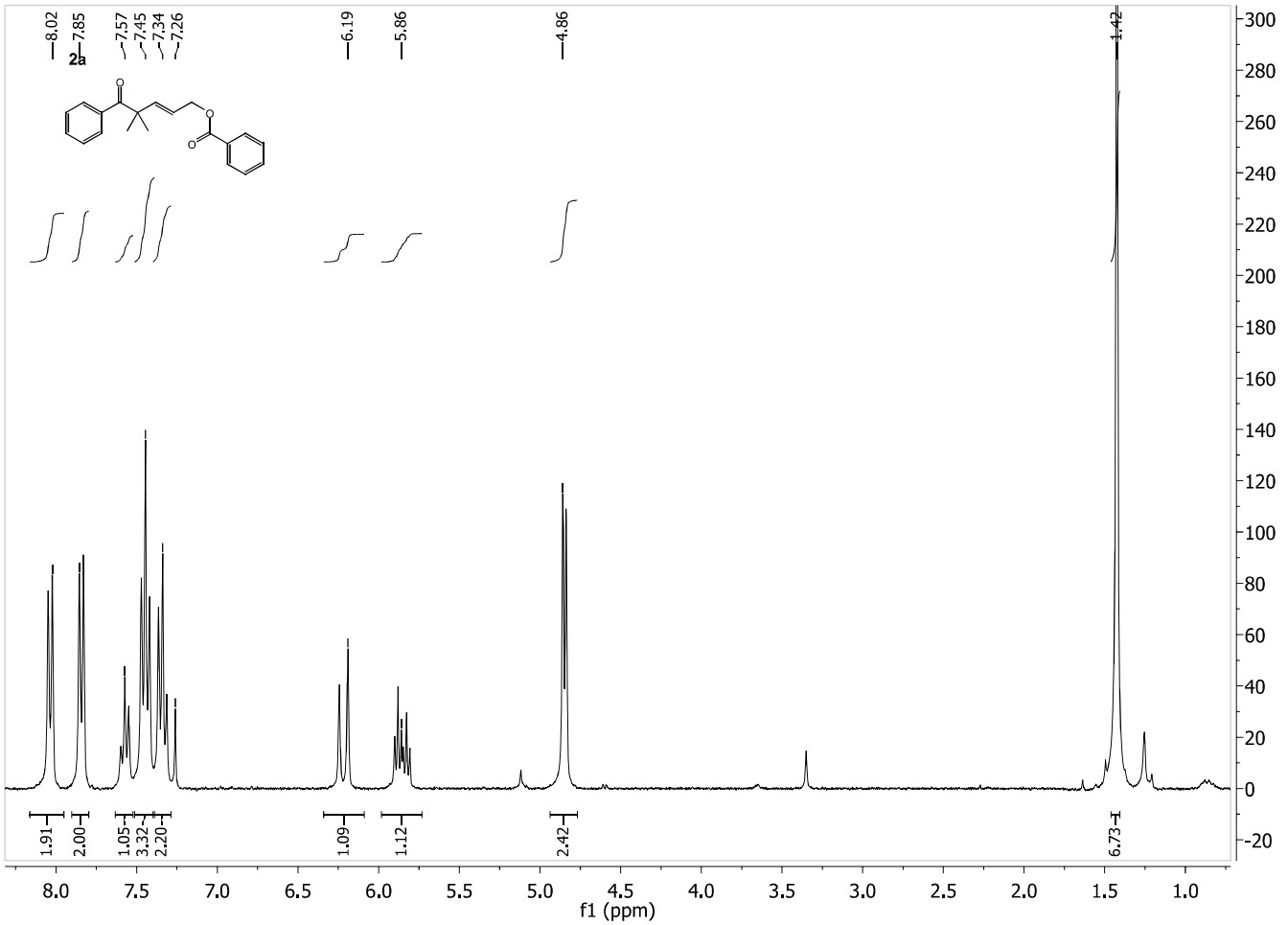
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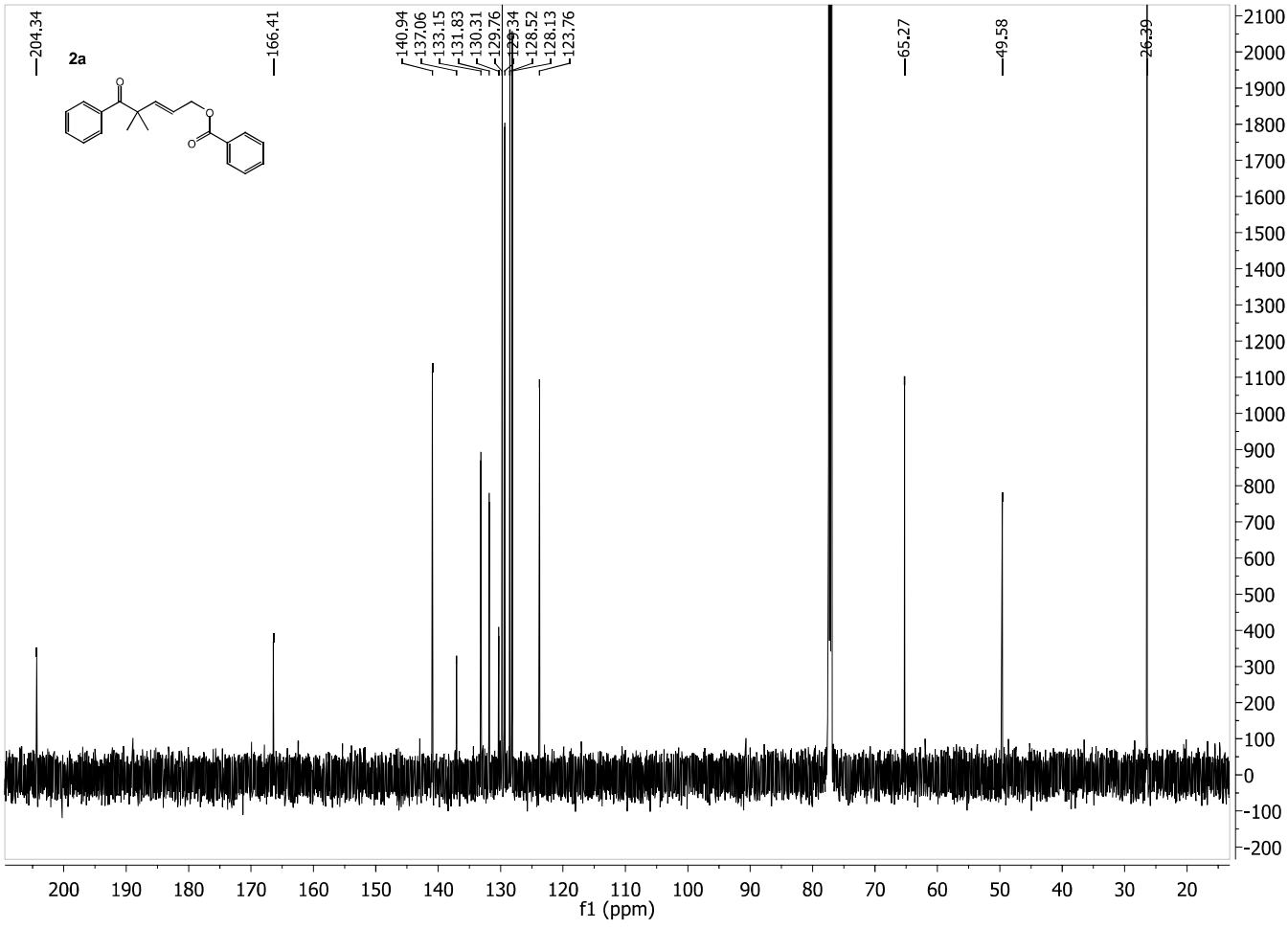
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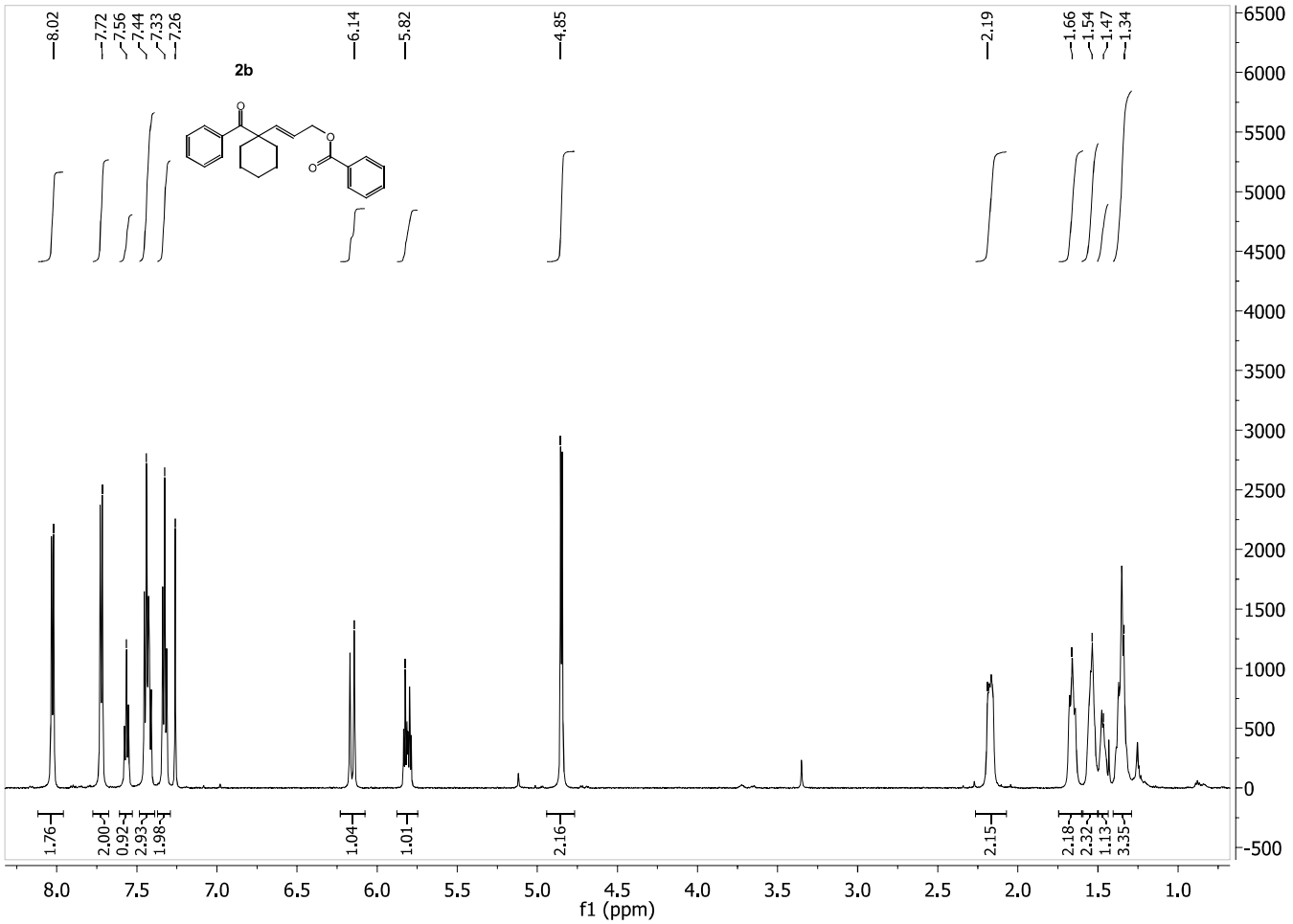
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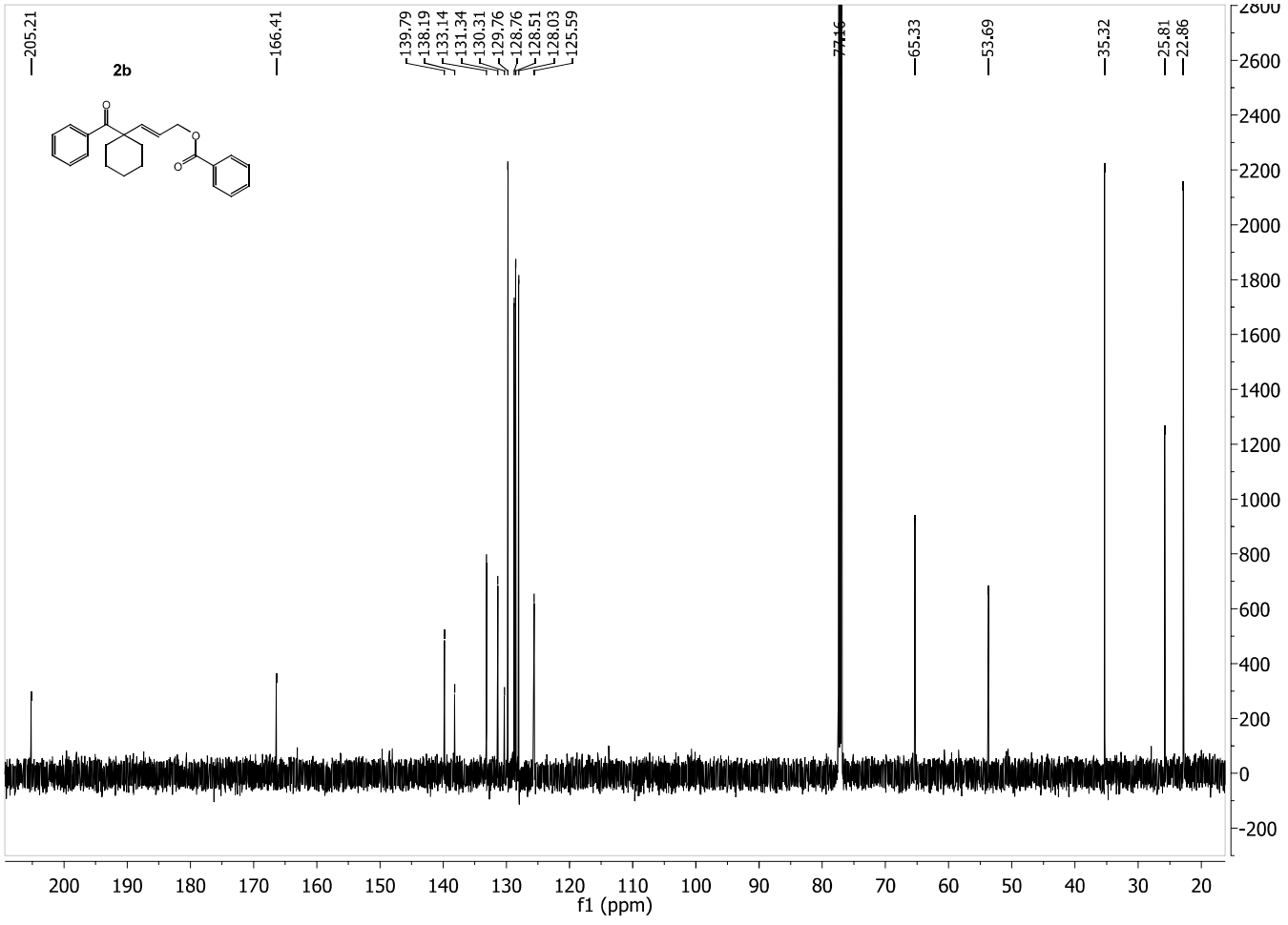
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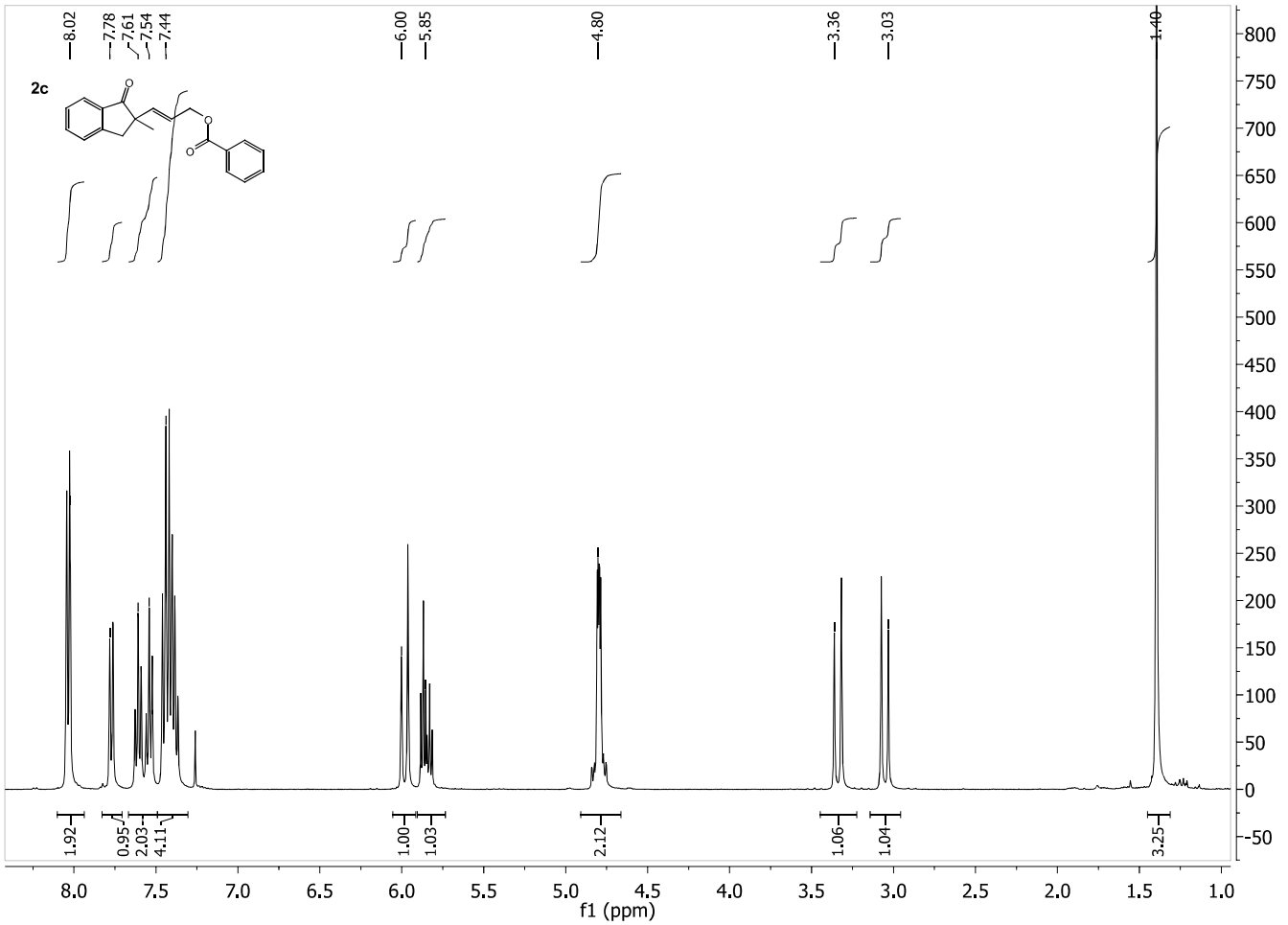
f1 (ppm)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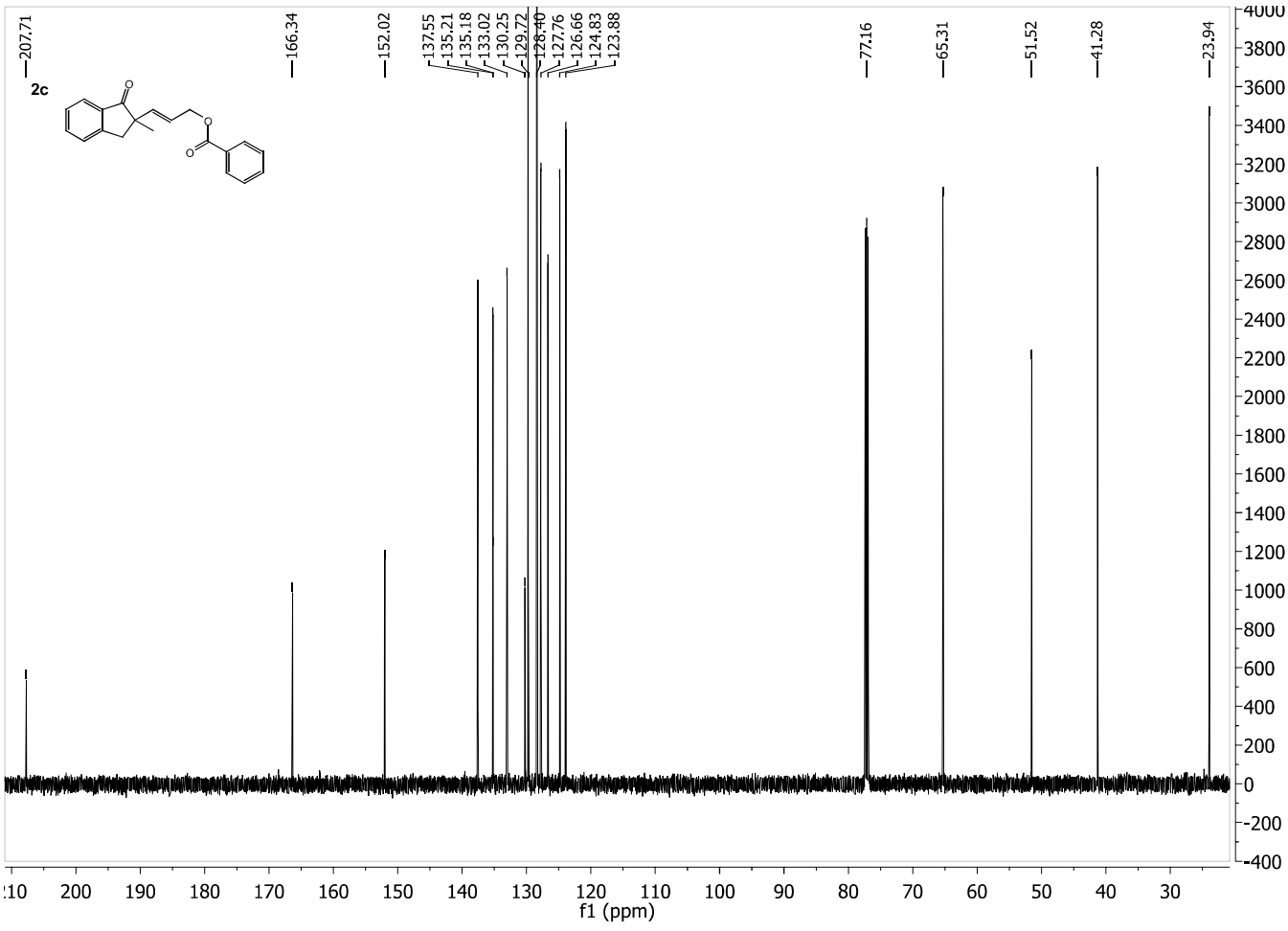
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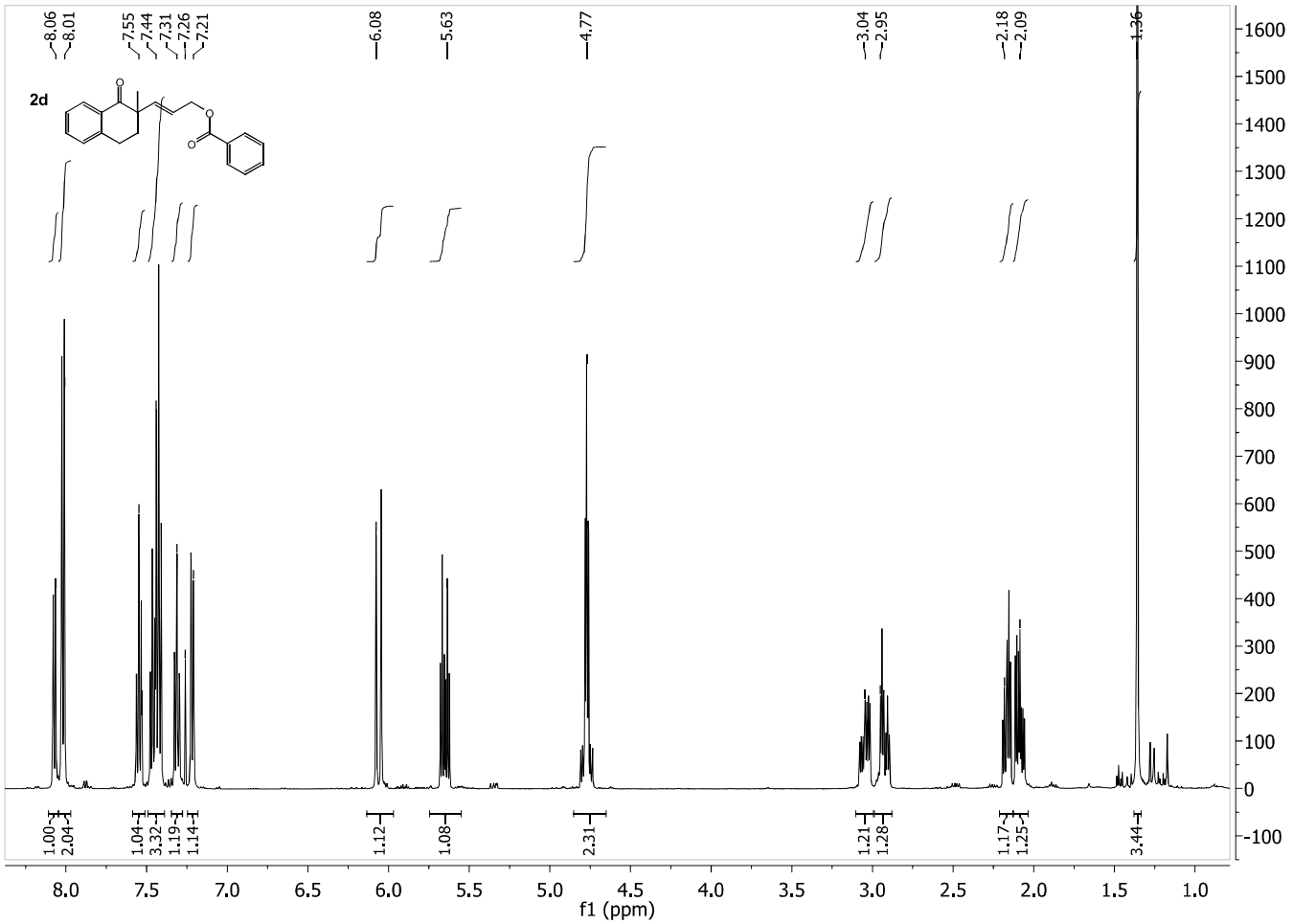
2c
f1 (ppm)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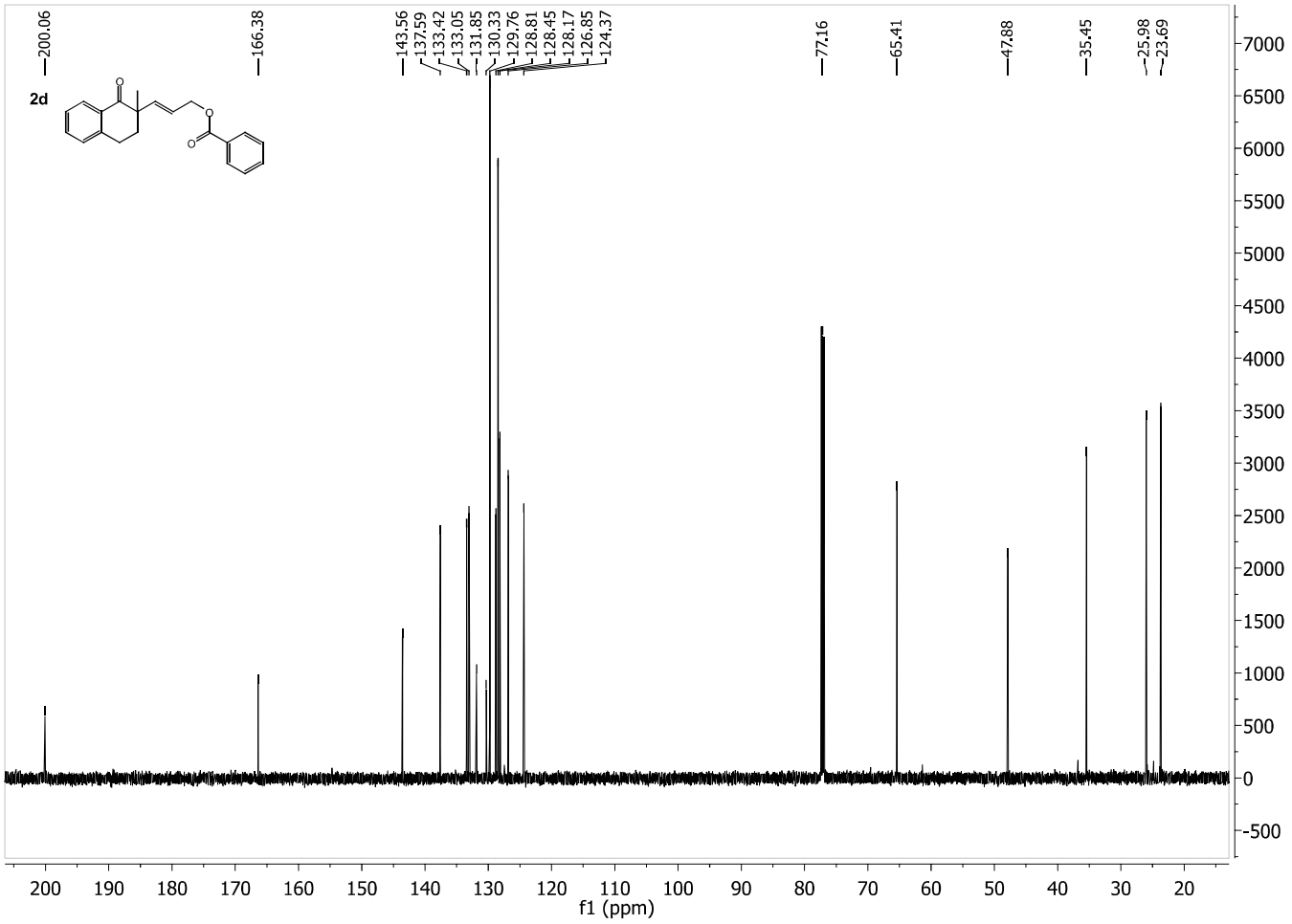
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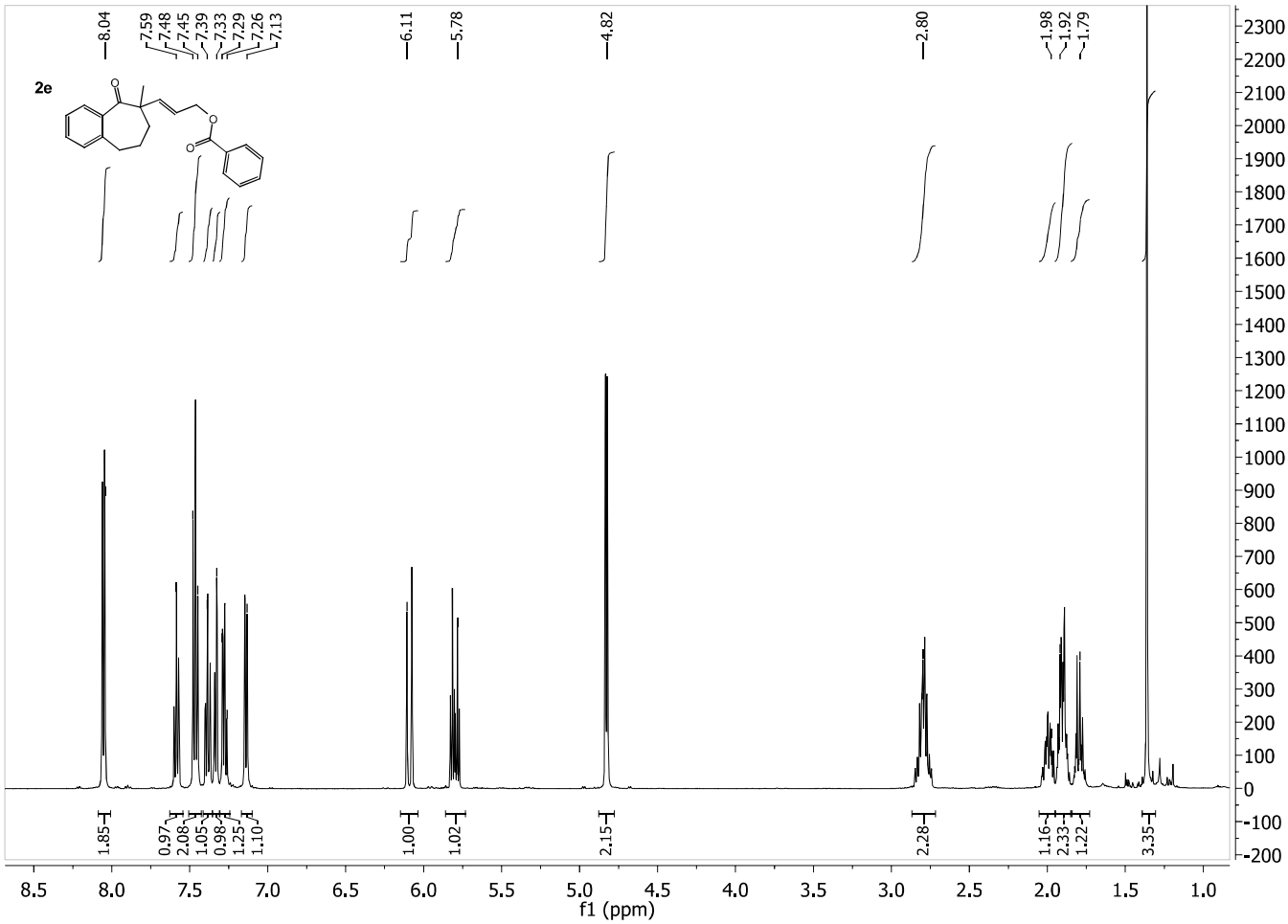
130.33
129.76
128.81
128.45
128.17
126.85
124.37
77.16
65.41
47.88
35.45
25.98
23.69
2d
f1 (ppm)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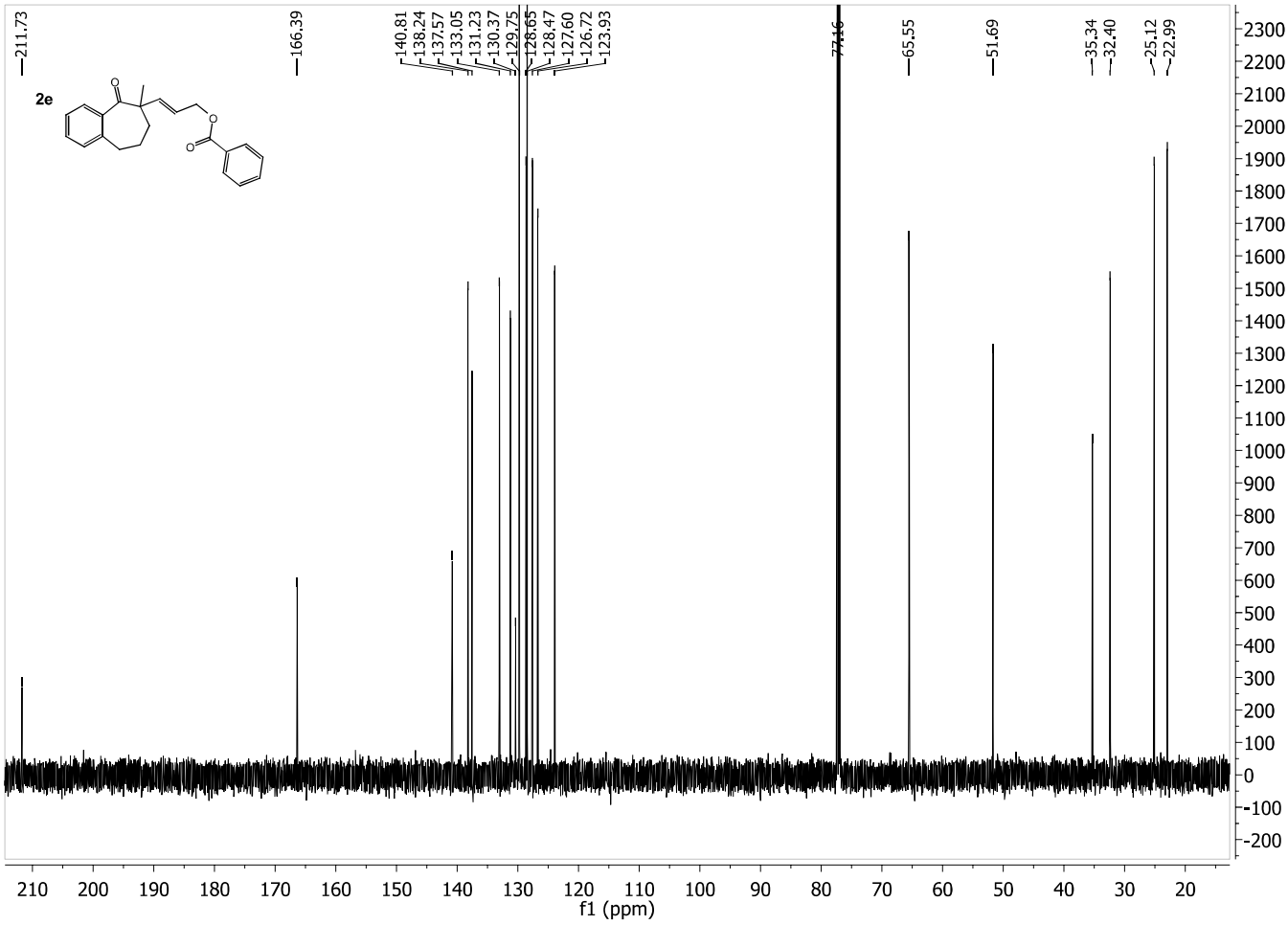
7.45
7.39
7.33
7.29
7.26
7.13
6.11
5.78
4.82
2.80
1.98
1.92
1.79
2e
1.85
0.97
2.08
1.05
0.98
1.25
1.10
1.00
1.02
2.15
2.28
1.16
2.33
1.22
3.35
f1 (ppm)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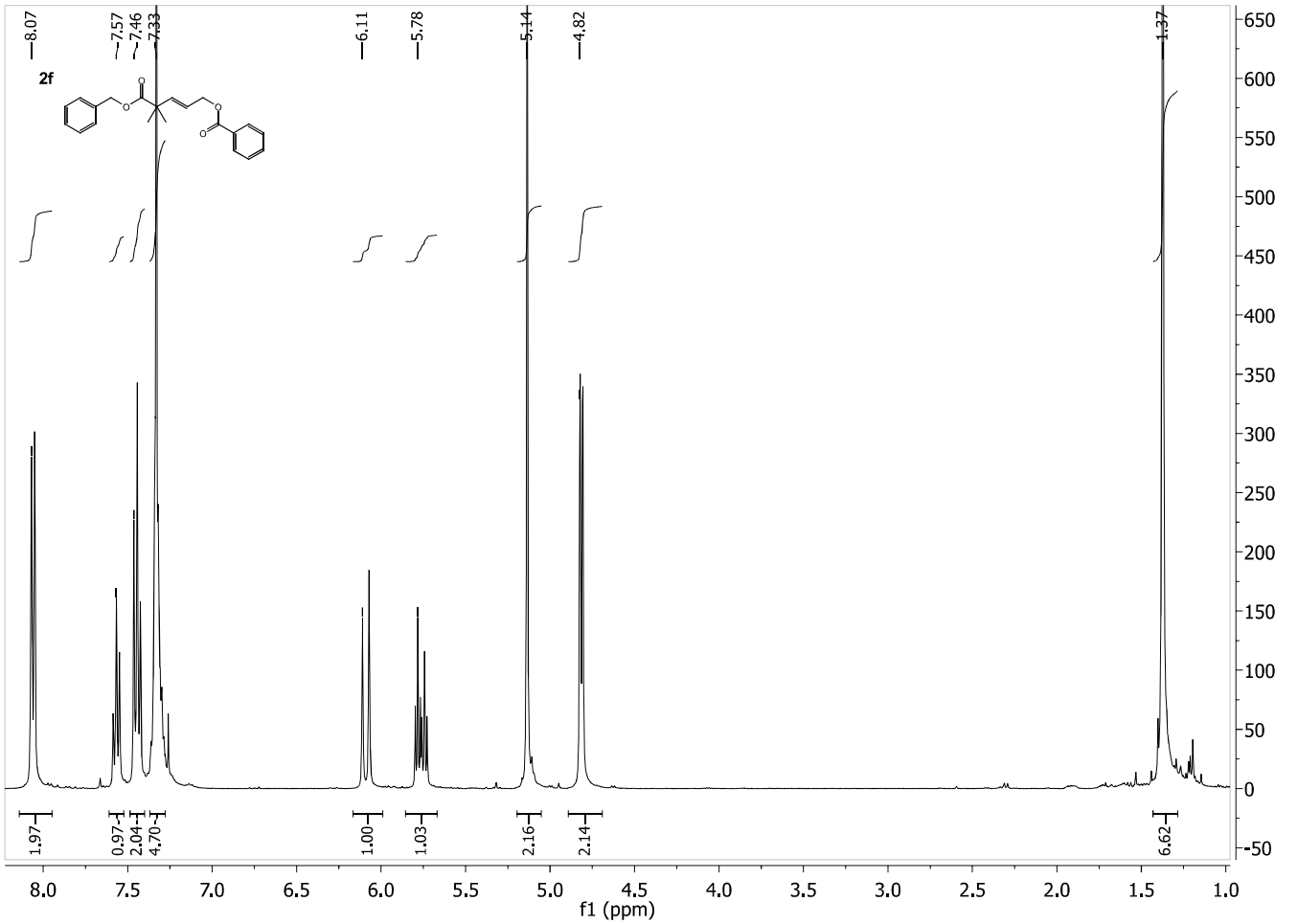
138.24
137.57
133.05
131.23
130.37
129.75
128.65
128.47
127.60
126.72
123.93
77.16
65.55
51.69
35.34
32.40
25.12
22.99
2e
f1 (ppm)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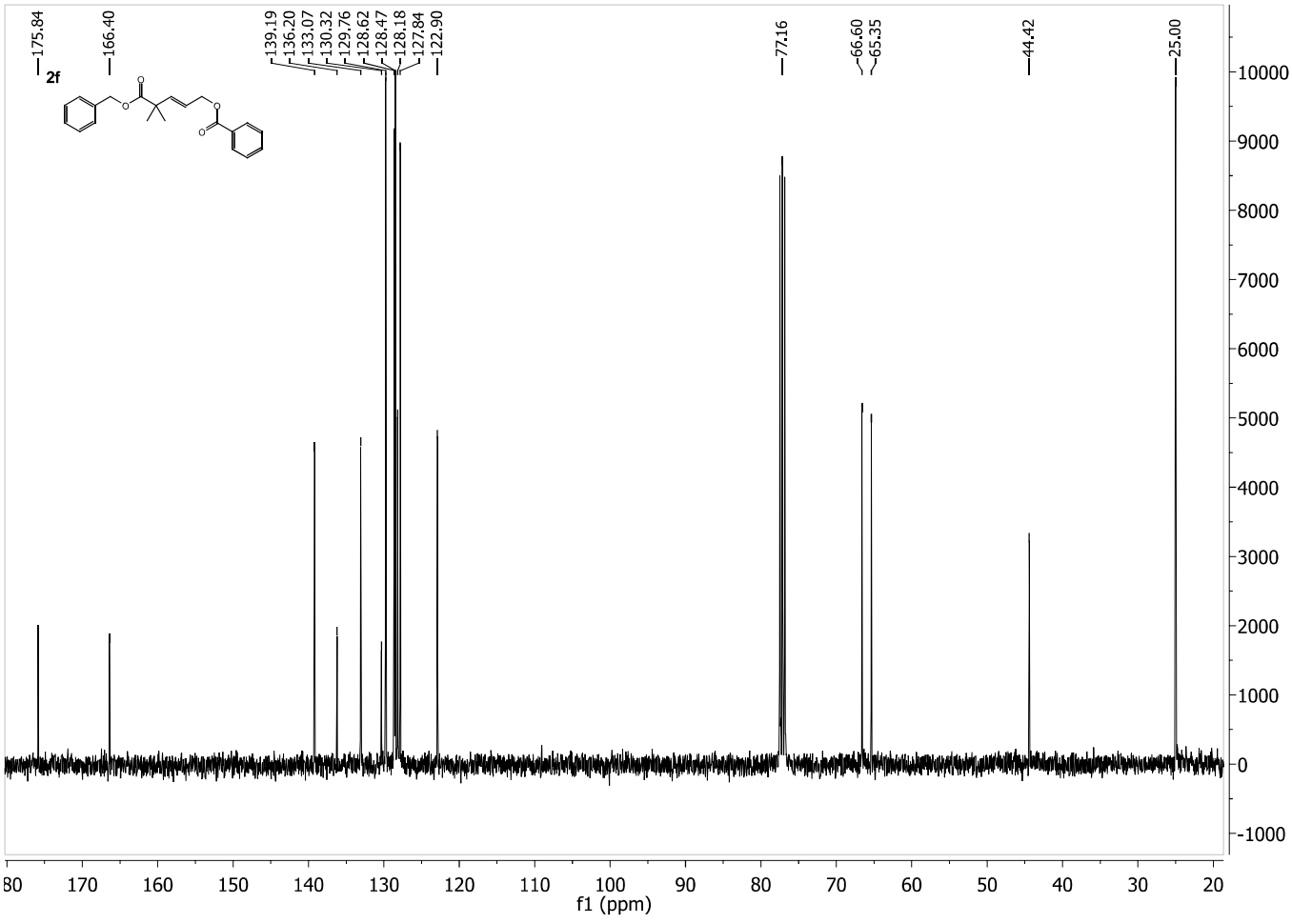
7.57
7.46
7.33
6.11
5.78
5.14
4.82
1.37
2f
1.97
0.97
2.04
4.70
1.00
1.03
2.16
2.14
6.62
f1 (ppm)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139.19
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133.07
130.32
129.76
128.62
128.47
128.18
127.84
122.90
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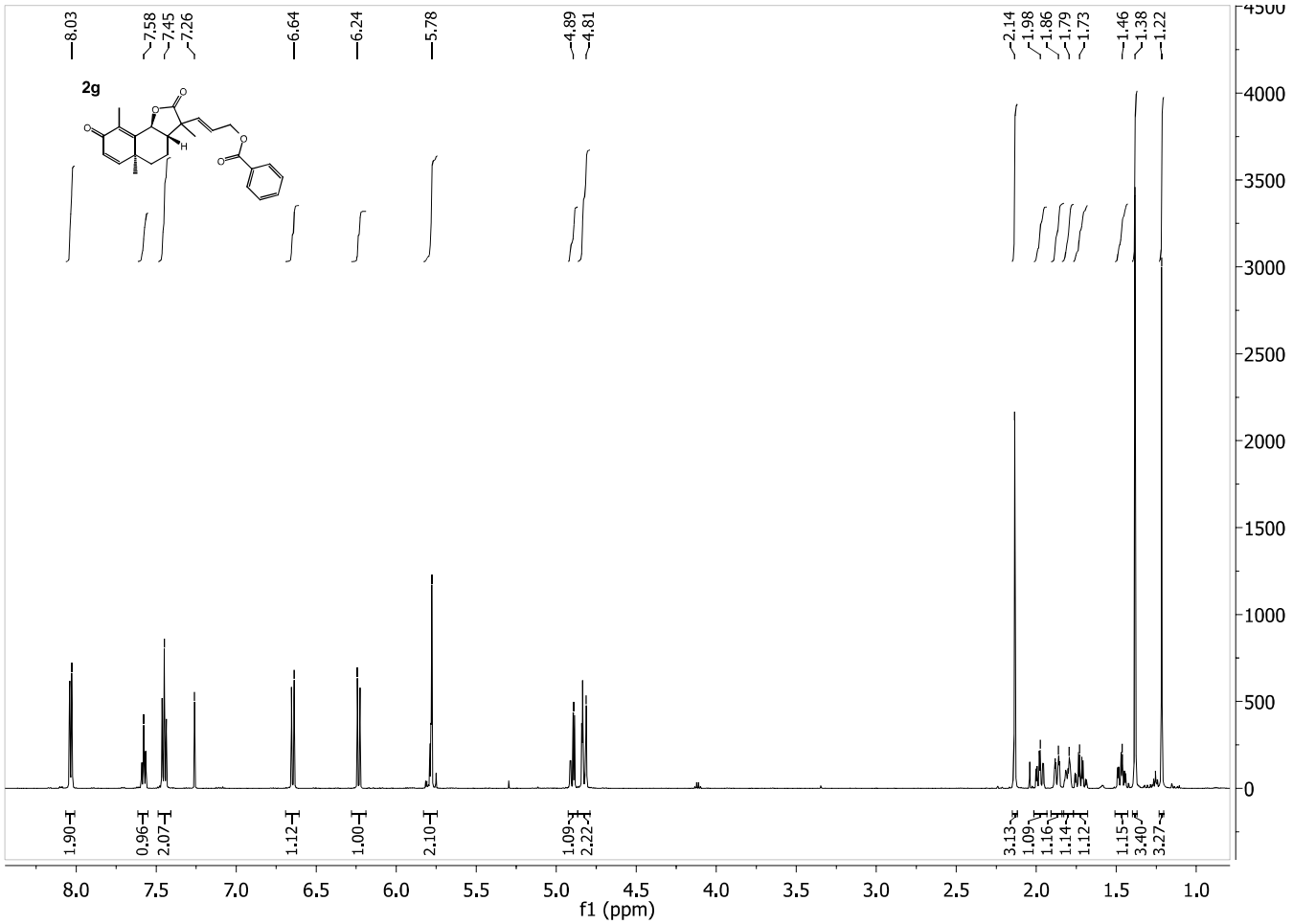
65.35
44.42
25.00
2f
f1 (ppm)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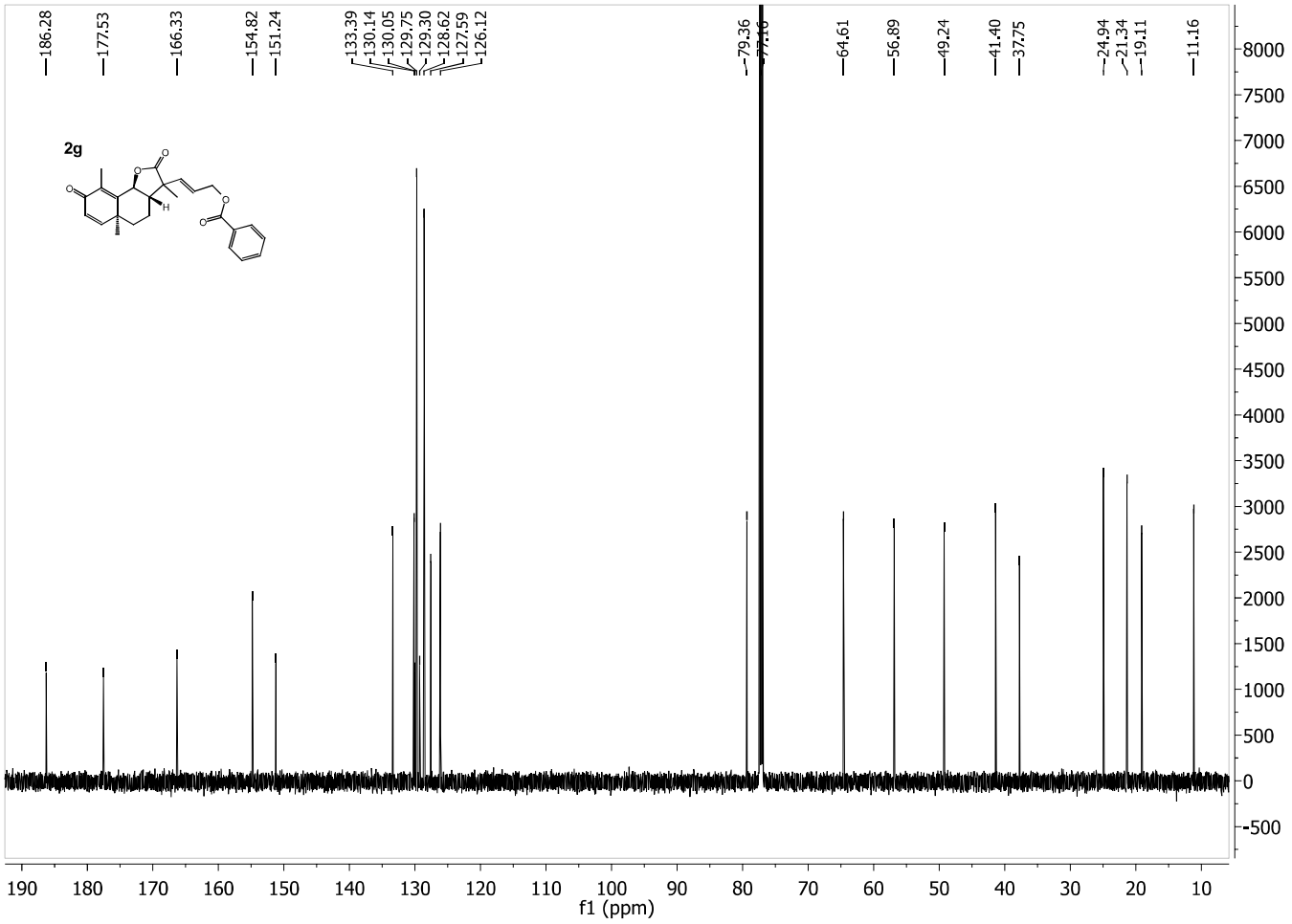
7.58
7.45
7.26
6.64
6.24
5.78
4.89
4.81
2.14
1.98
1.86
1.79
1.73
1.46
1.38
1.22
2g
1.90
0.96
2.07
1.12
1.00
2.10
1.09
2.22
3.13
1.09
1.16
1.14
1.12
1.15
3.40
3.27
f1 (ppm)


186.28
177.53
166.33
154.82
151.24
133.39
130.14
130.05
129.75
129.30
128.62
127.59
126.12
79.36
77.16
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49.24
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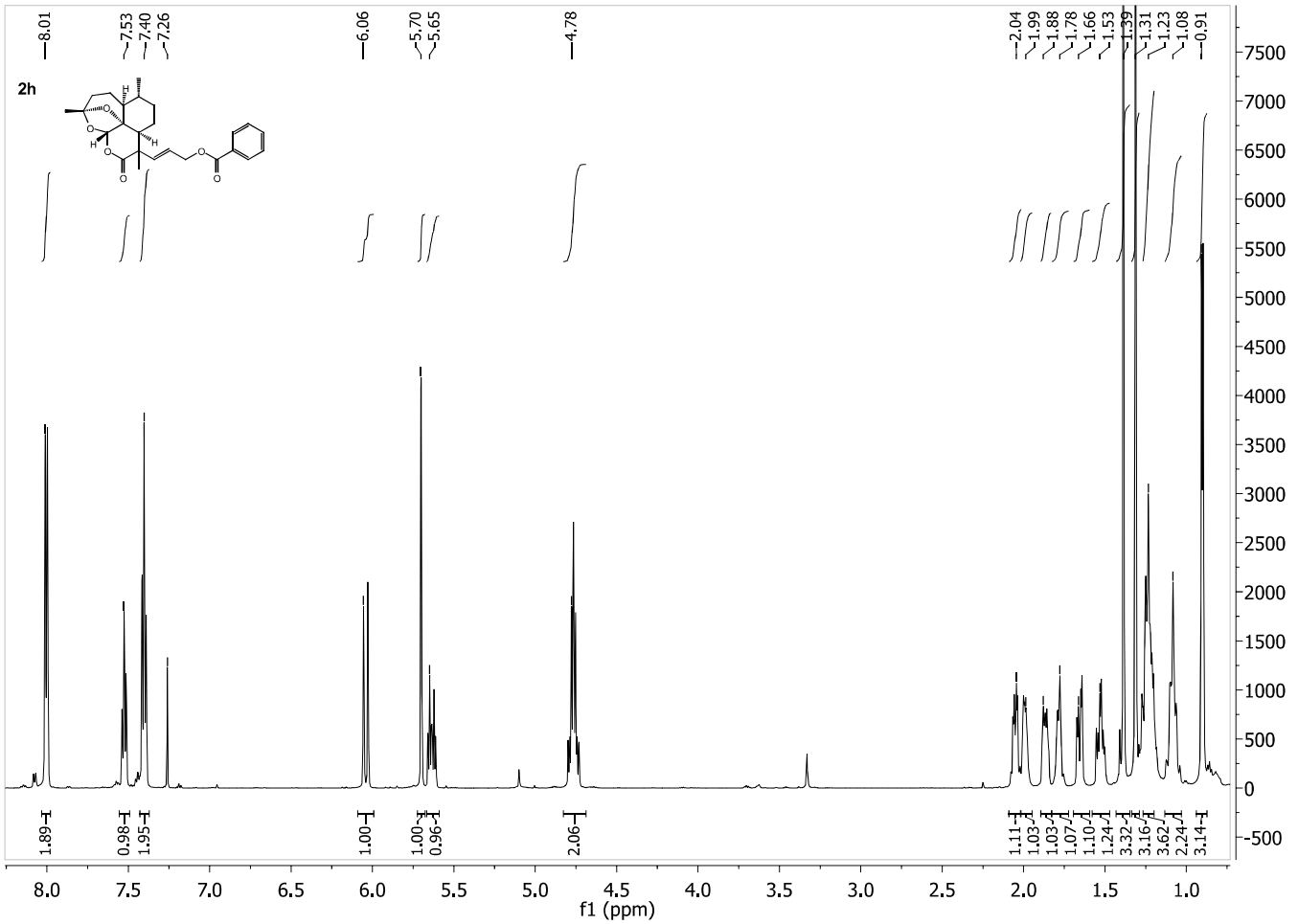
24.94
21.34
19.11
11.16
2g
f1 (ppm)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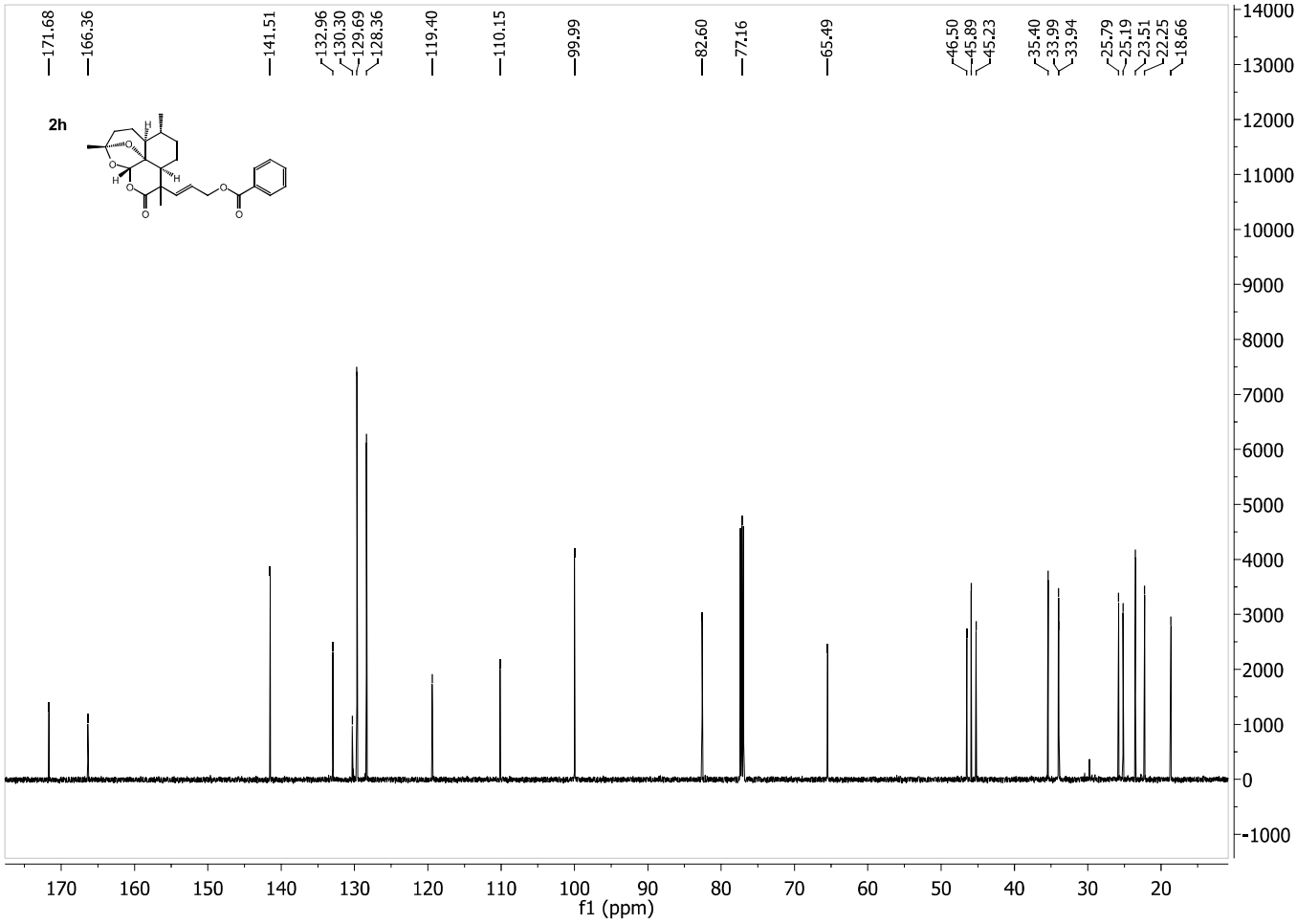
7.26
6.06
5.70
5.65
4.78
2.04
1.99
1.88
1.78
1.66
1.53
1.39
1.31
1.23
1.08
0.91
2h
1.89
0.98
1.95
1.00
1.00
0.96
2.06
1.11
1.03
1.03
1.07
1.10
1.24
3.32
3.16
3.62
2.24
3.14
f1 (ppm)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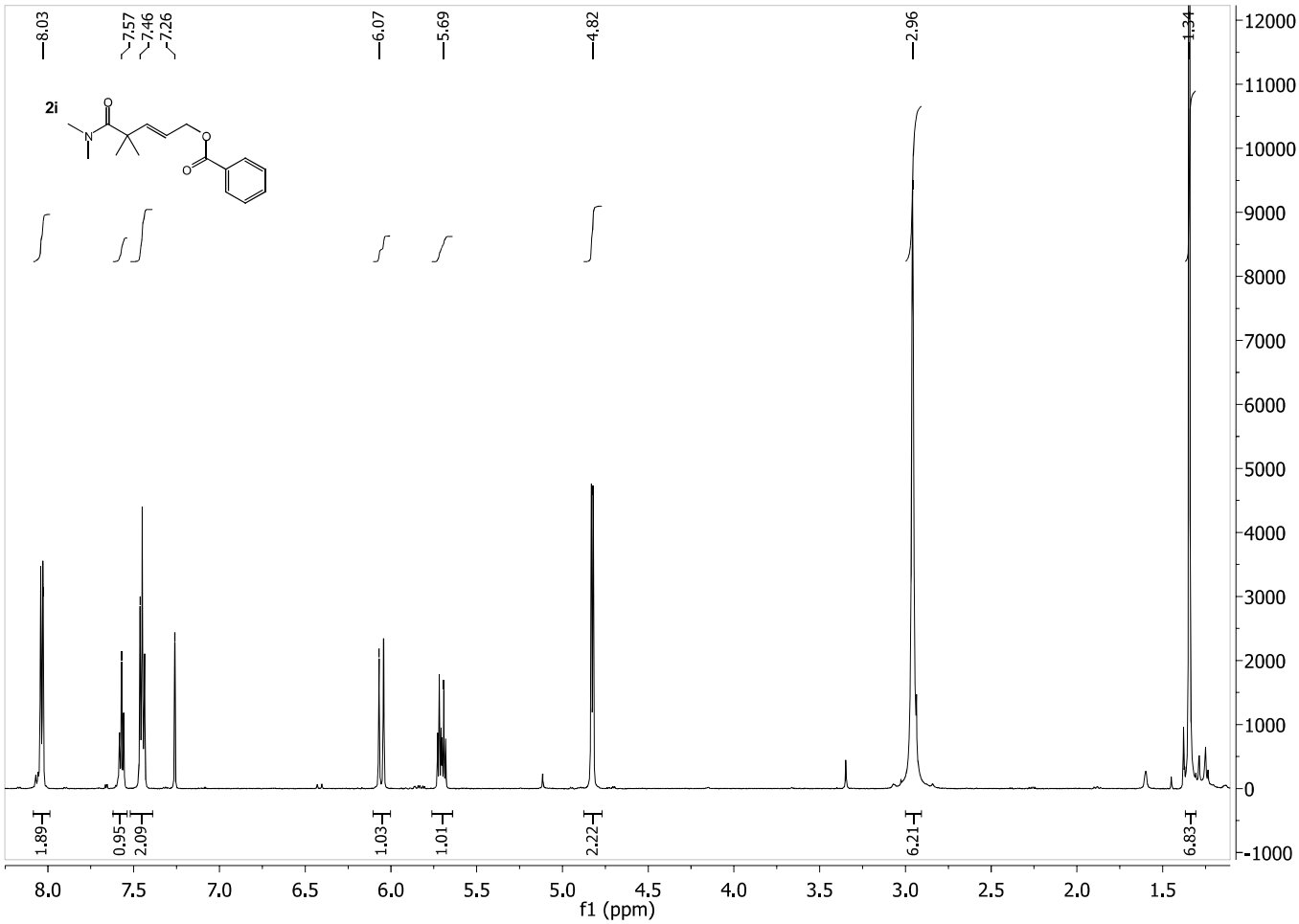
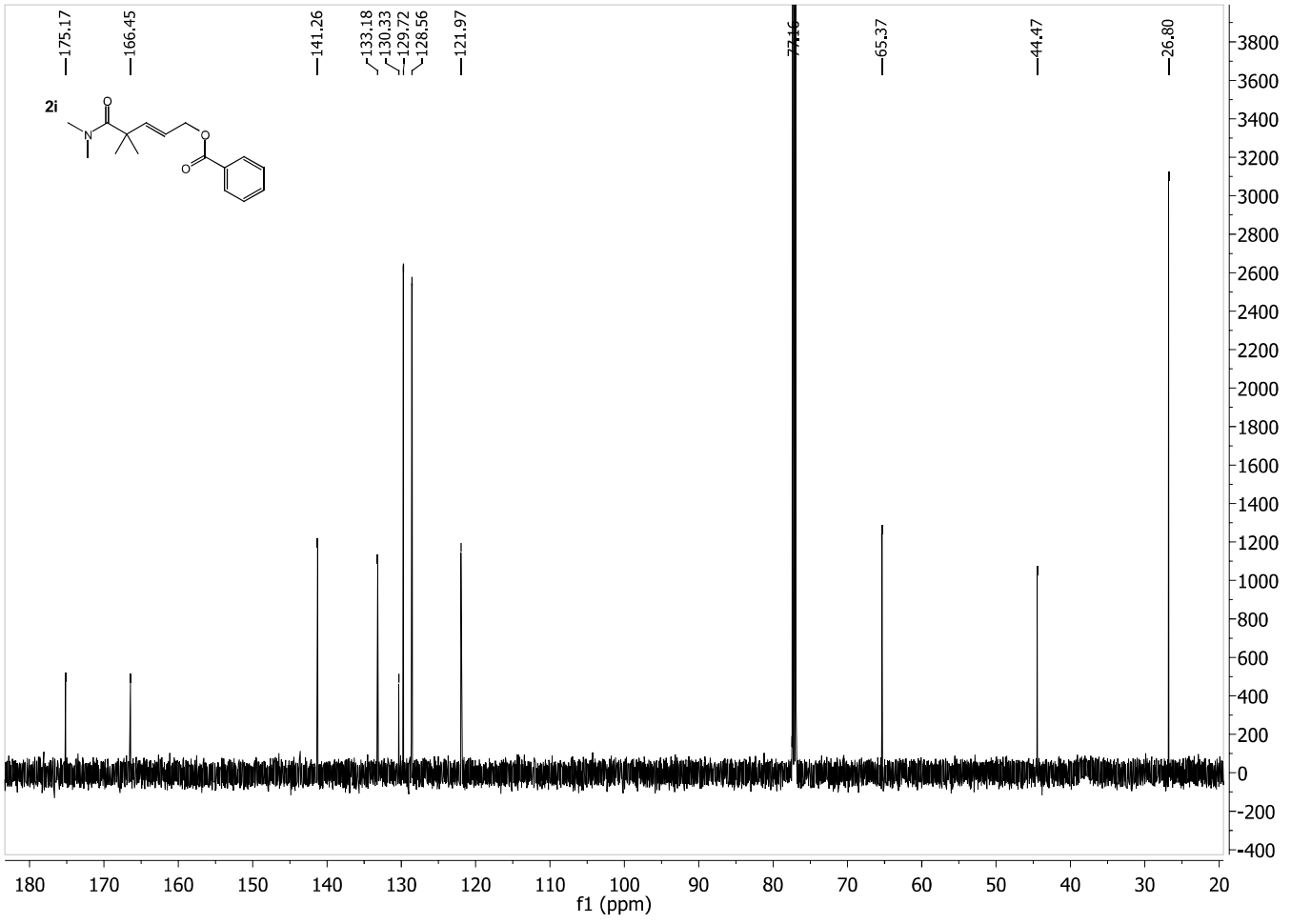
132.96
130.30
129.69
128.36
119.40
110.15
99.99
82.60
77.16
65.49
46.50
45.89
45.23
35.40
33.99
33.94
25.79
25.19
23.51
22.25
18.66
2h
f1 (ppm)


8.03
7.57
7.46
7.26
6.07
5.69
4.82
2.96
1.34
2i
1.89
0.95
2.09
1.03
1.01
2.22
6.21
6.83
f1 (ppm)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166.45
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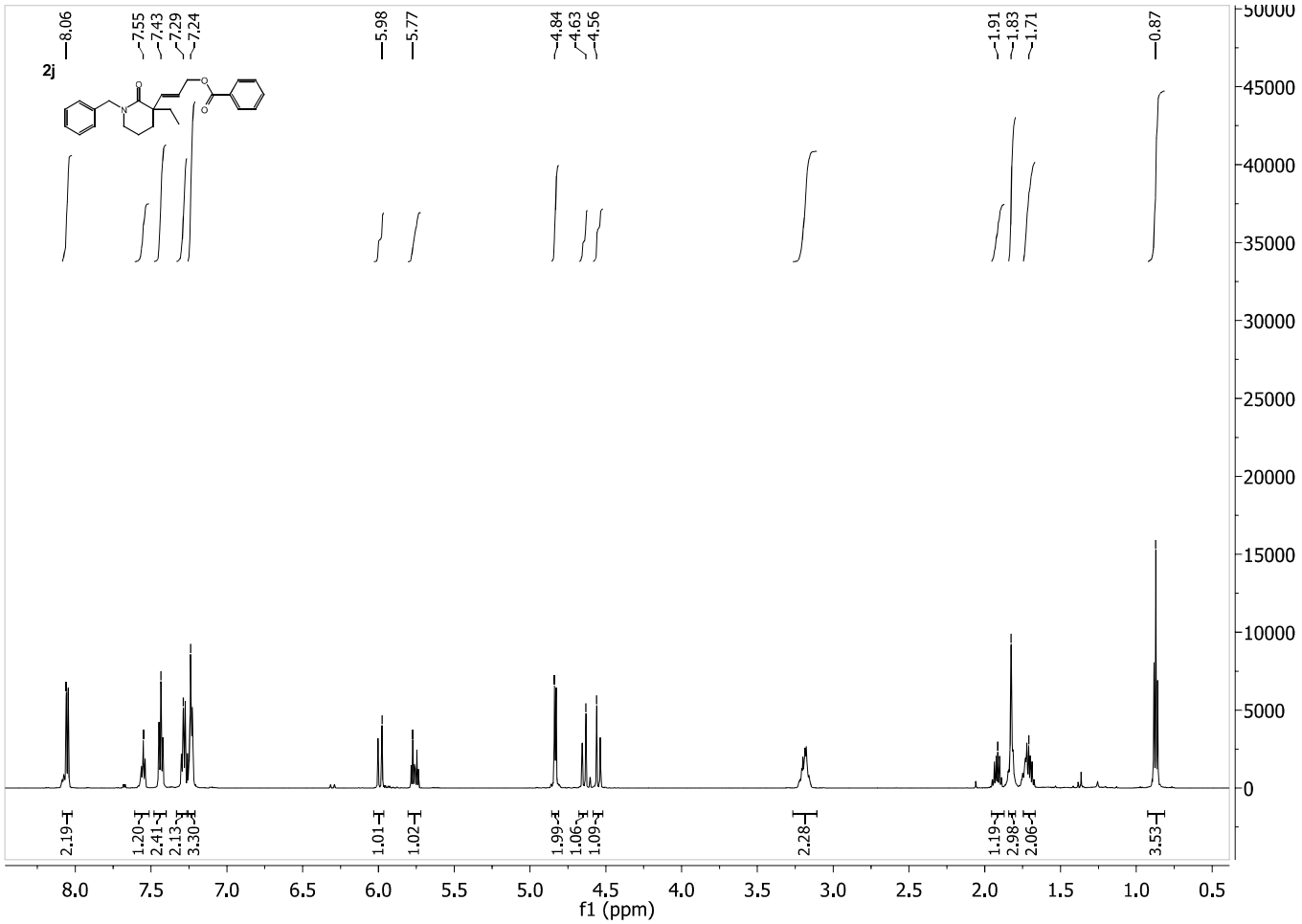
129.72
128.56
121.97
77.16
65.37
44.47
26.80
2i
f1 (ppm)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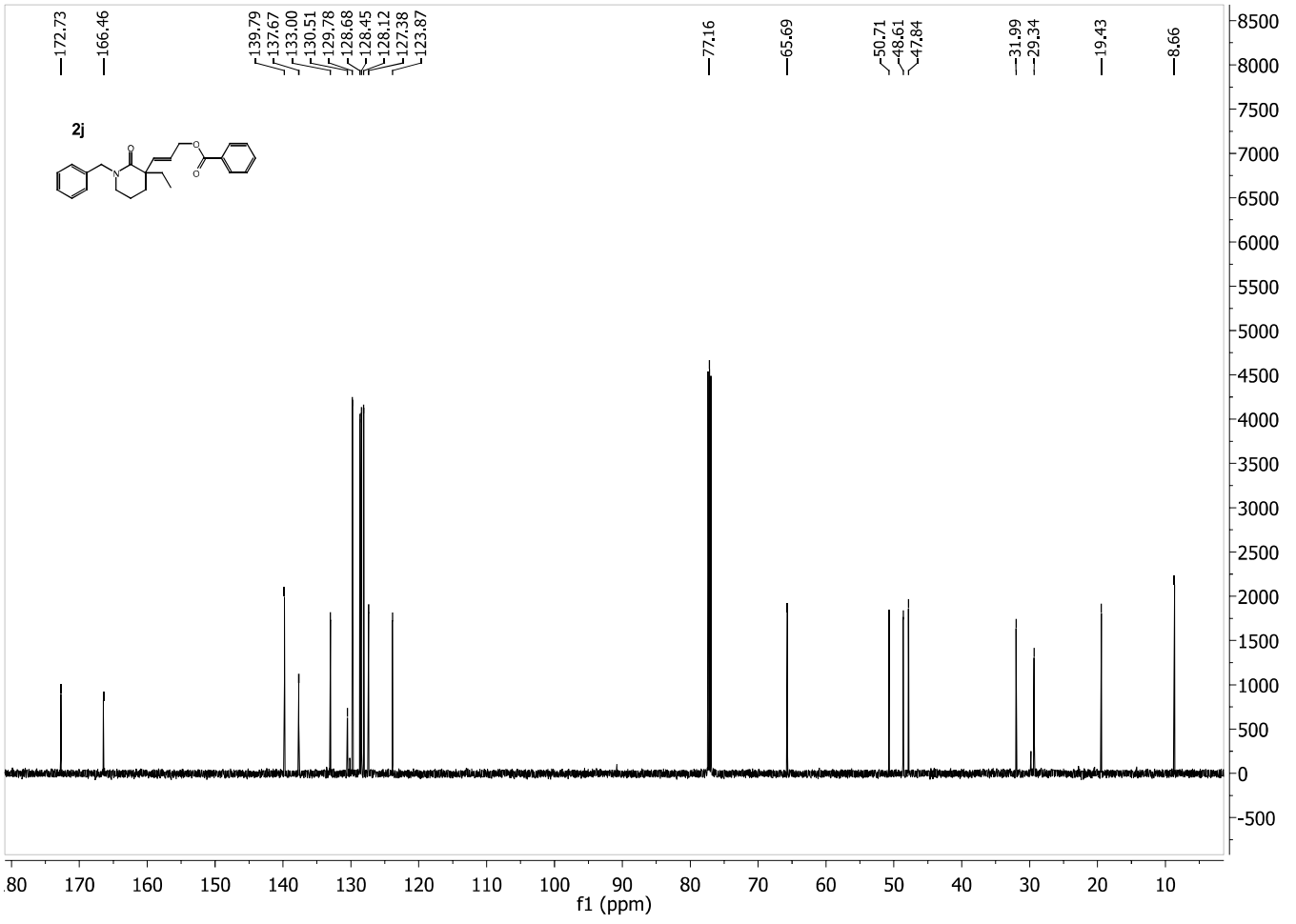
7.55
7.43
7.29
7.24
5.98
5.77
4.84
4.63
4.56
1.91
1.83
1.71
0.87
2j
2.19
1.20
2.41
2.13
3.30
1.01
1.02
1.99
1.06
1.09
2.28
1.19
2.98
2.06
3.53
f1 (ppm)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130.51
129.78
128.68
128.45
128.12
127.38
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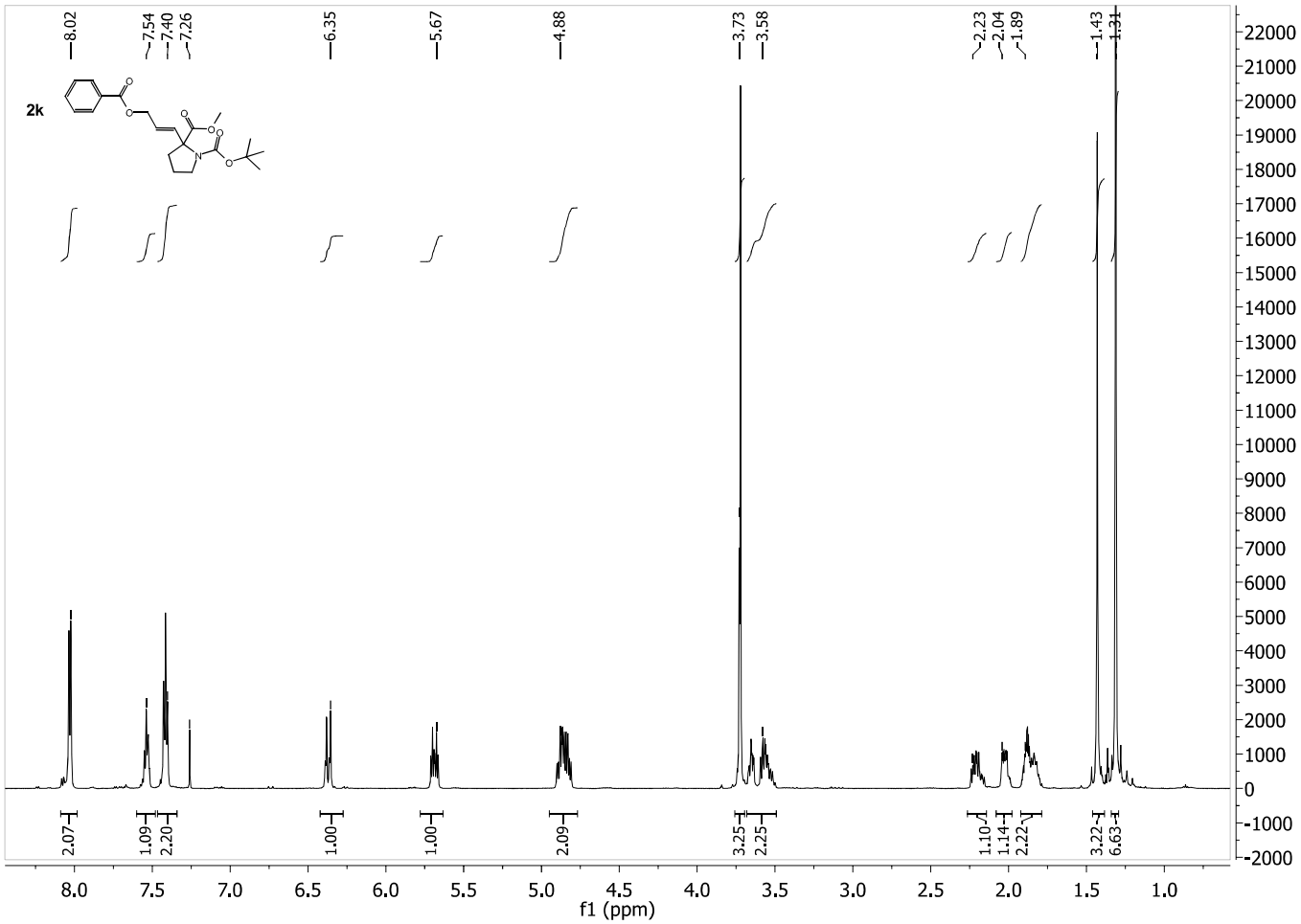
65.69
50.71
48.61
47.84
31.99
29.34
19.43
8.66
2j
f1 (ppm)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4.88
3.73
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2.23
2.04
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1.43
1.31
2k
2.07
1.09
2.20
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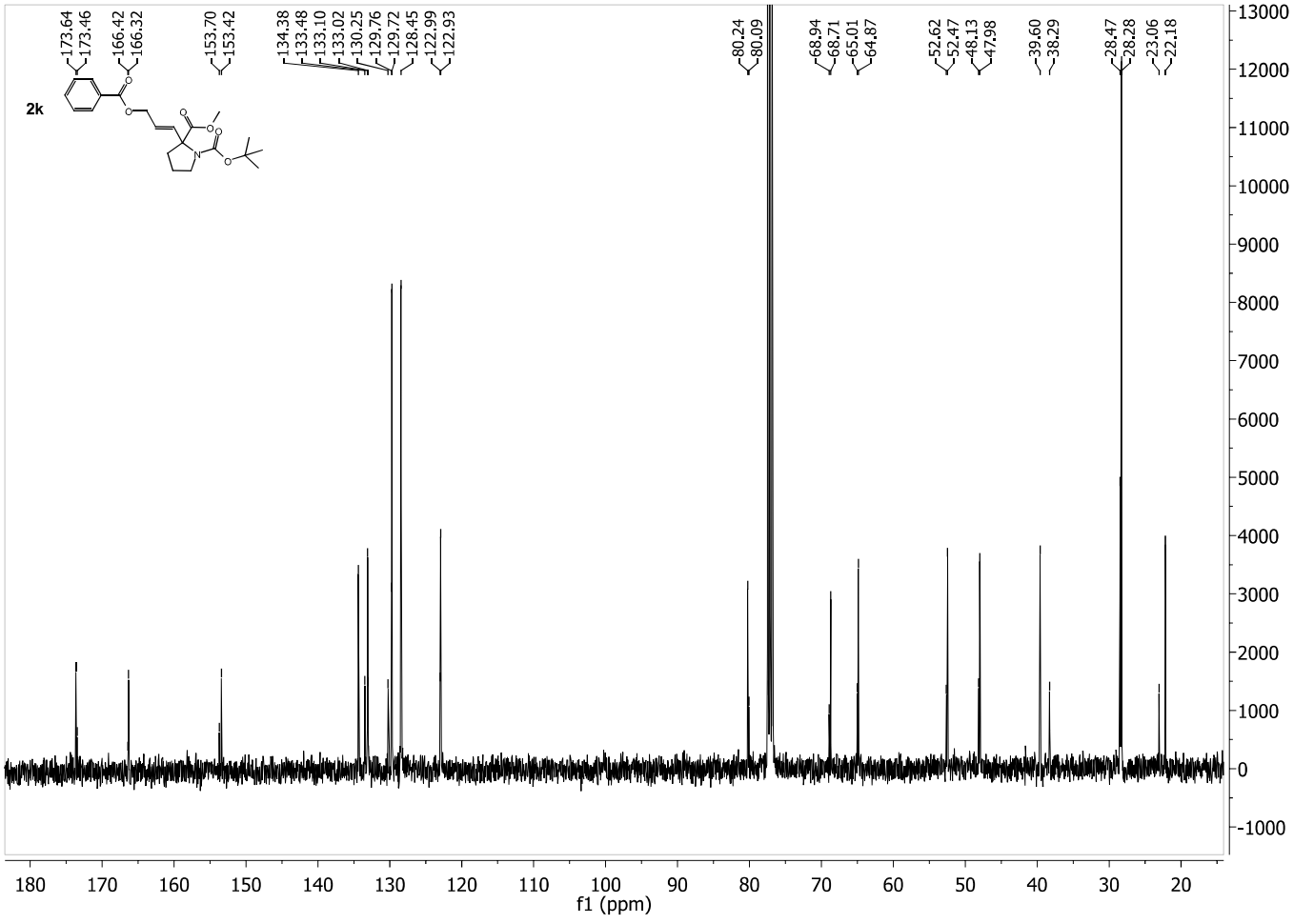
1.00
2.09
3.25
2.25
1.10
1.14
2.22
3.22
6.63
f1 (ppm)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166.32
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153.42
134.38
133.48
133.10
133.02
130.25
129.76
129.72
128.45
122.99
122.93
80.24
80.09
68.94
68.71
65.01
64.87
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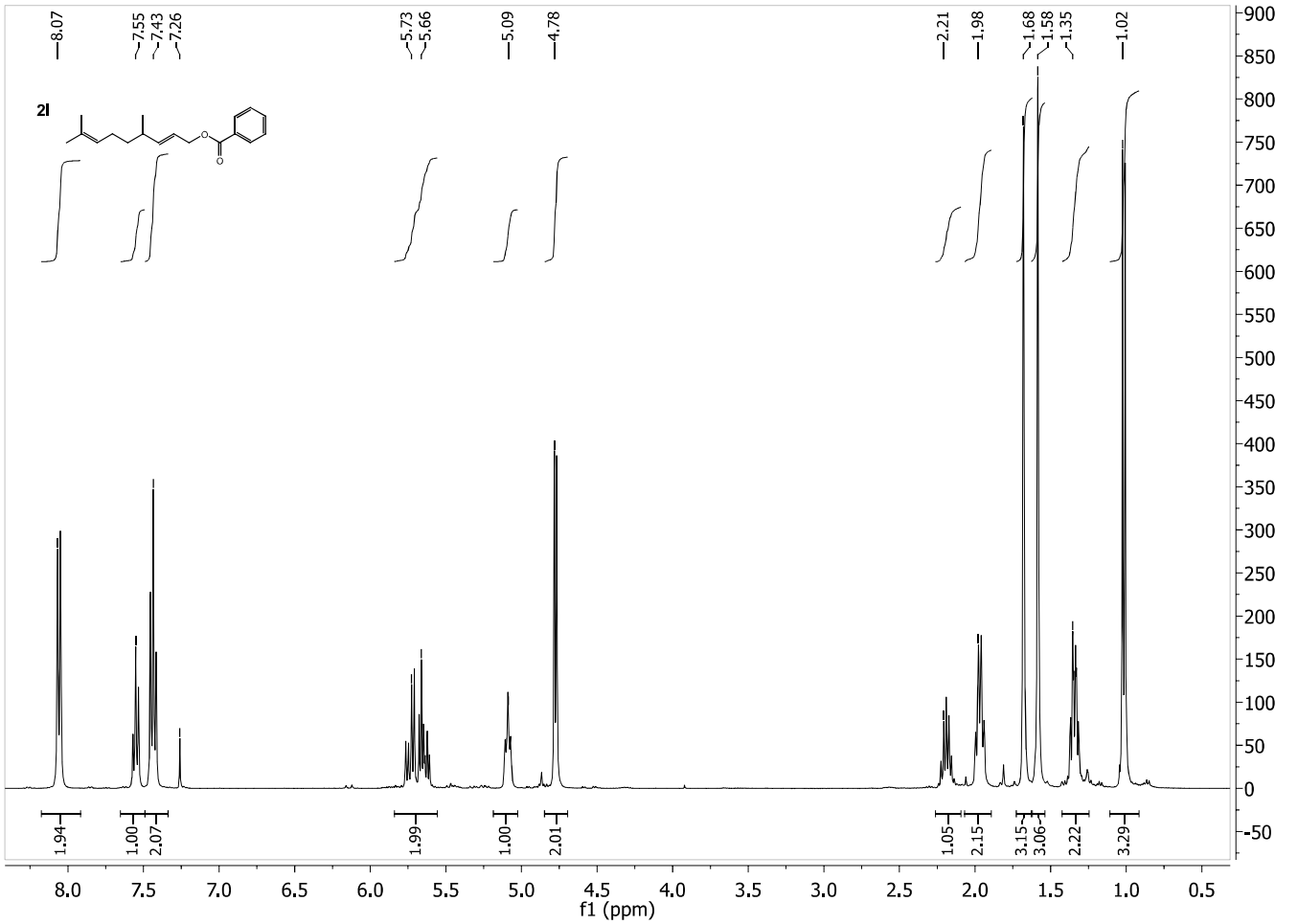
28.28
23.06
22.18
2k
f1 (ppm)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7.43
7.26
5.73
5.66
5.09
4.78
2.21
1.98
1.68
1.58
1.35
1.02
2l
1.94
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1.00
2.01
1.05
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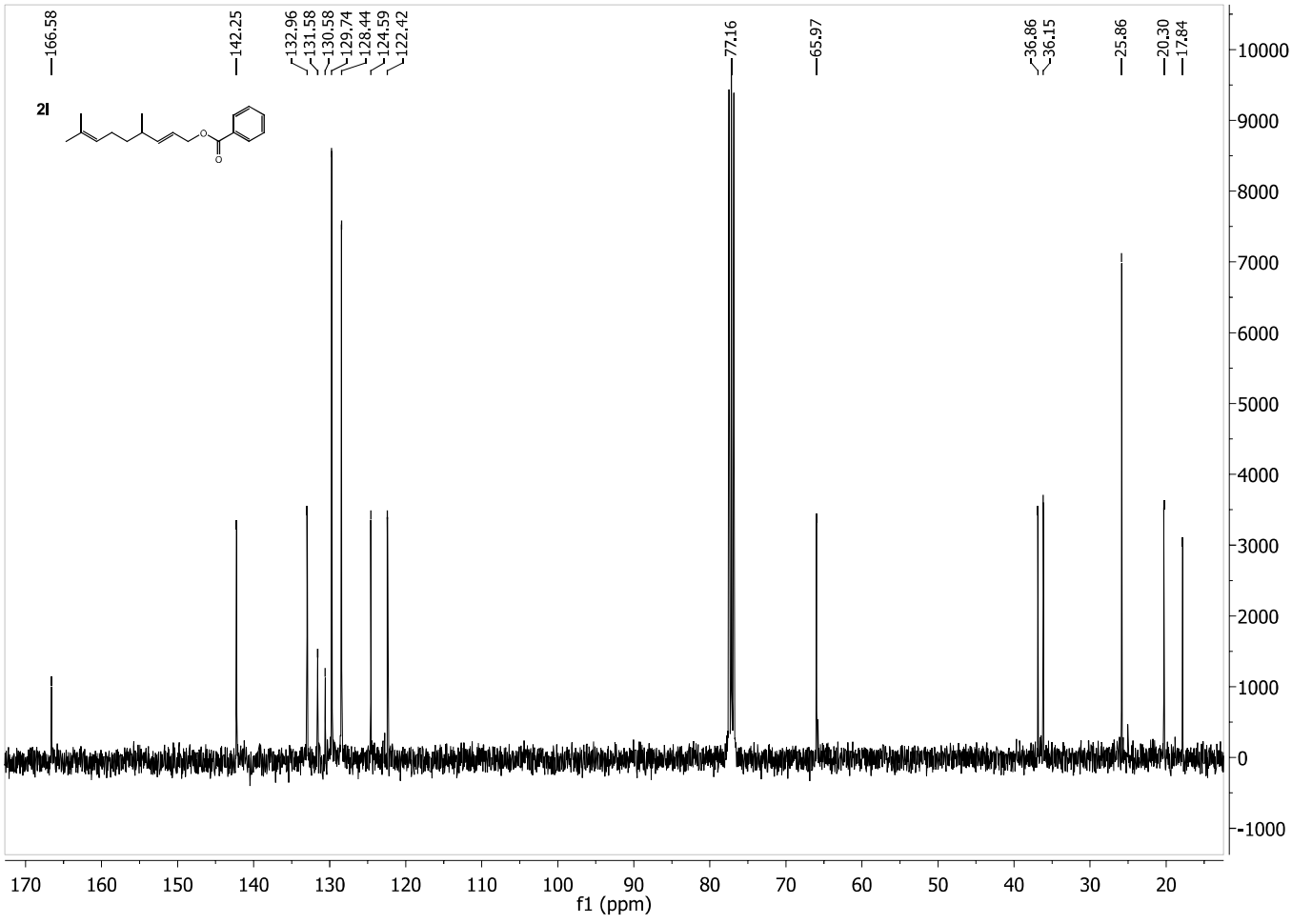
3.15
3.06
2.22
3.29
f1 (ppm)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77.16
65.97
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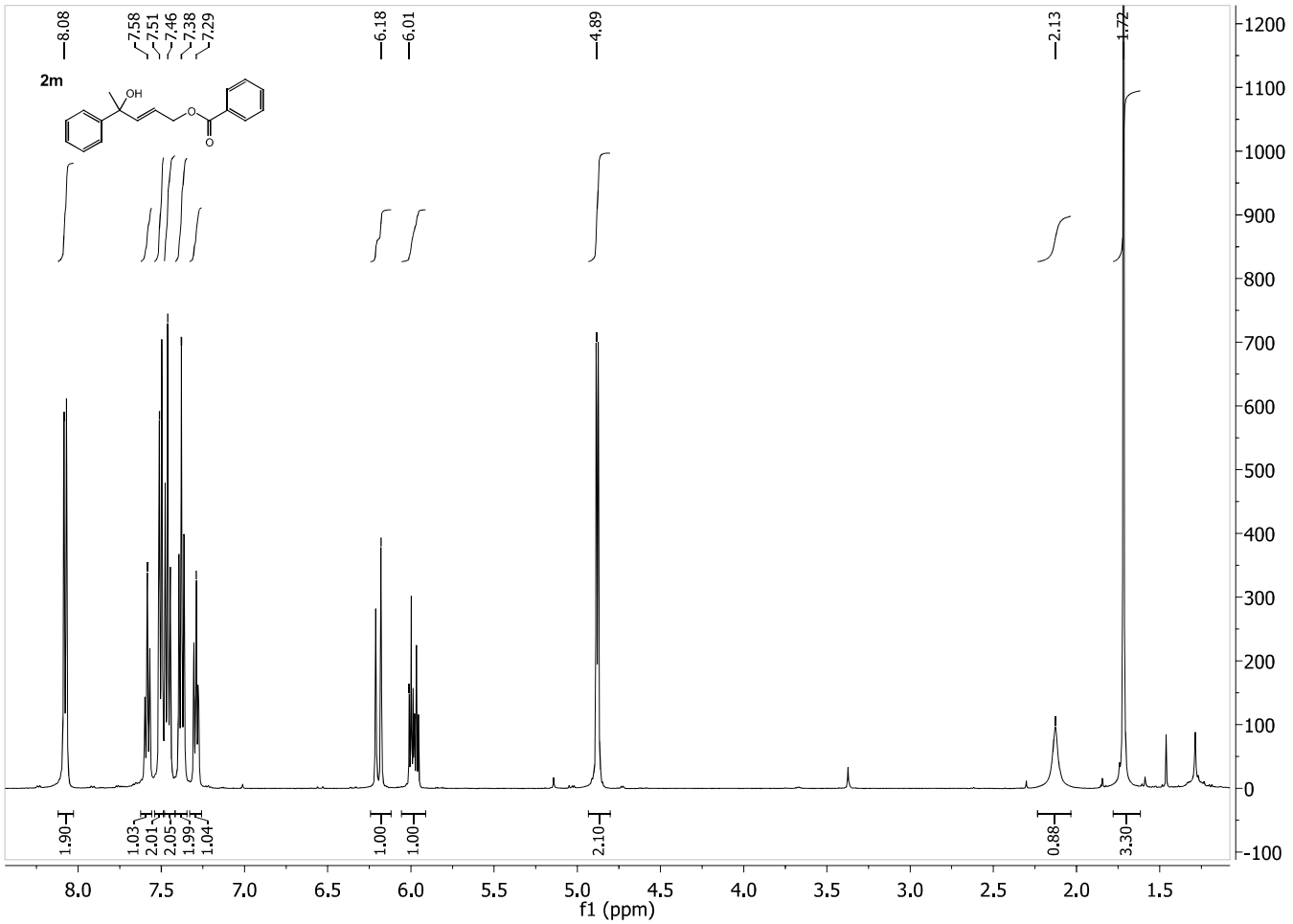
25.86
20.30
17.84
2l
f1 (ppm)


2m
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7.51
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7.38
7.29
6.18
6.01
4.89
2.13
1.72
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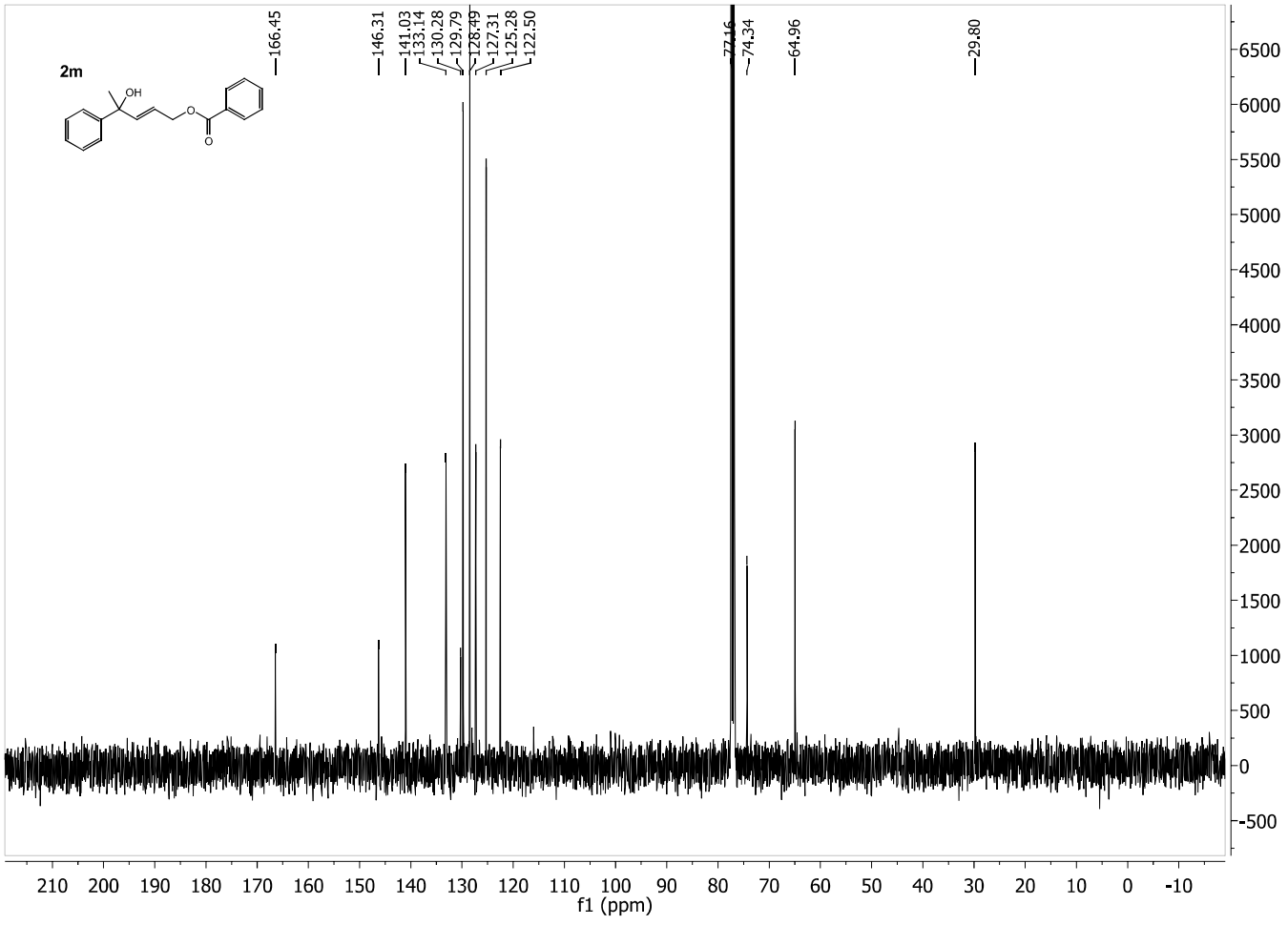
1.03
2.01
2.05
1.99
1.04
1.00
1.00
2.10
0.88
3.30
f1 (ppm)


2m
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141.03
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125.28
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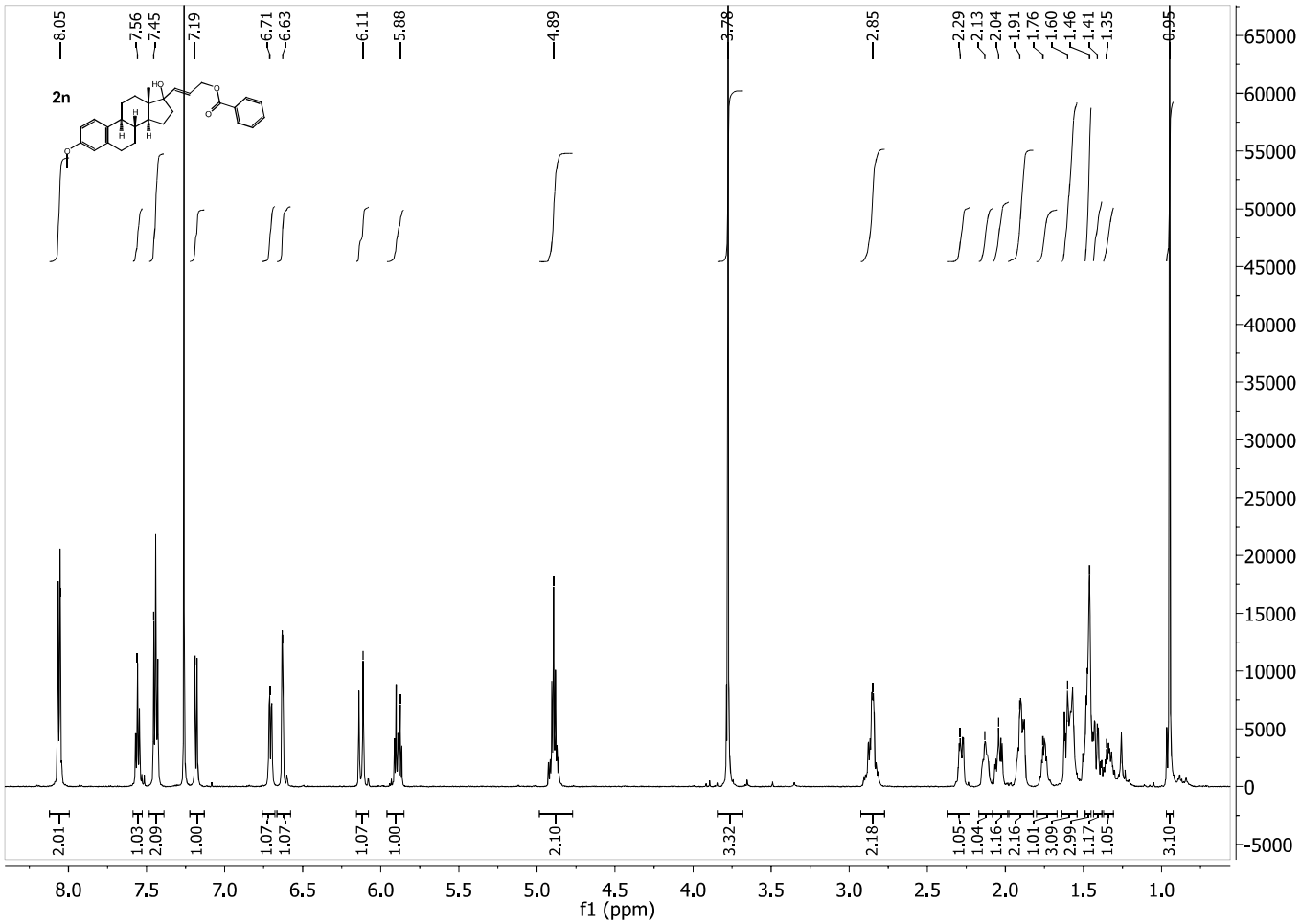
74.34
64.96
29.80
f1 (ppm)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4.89
3.78
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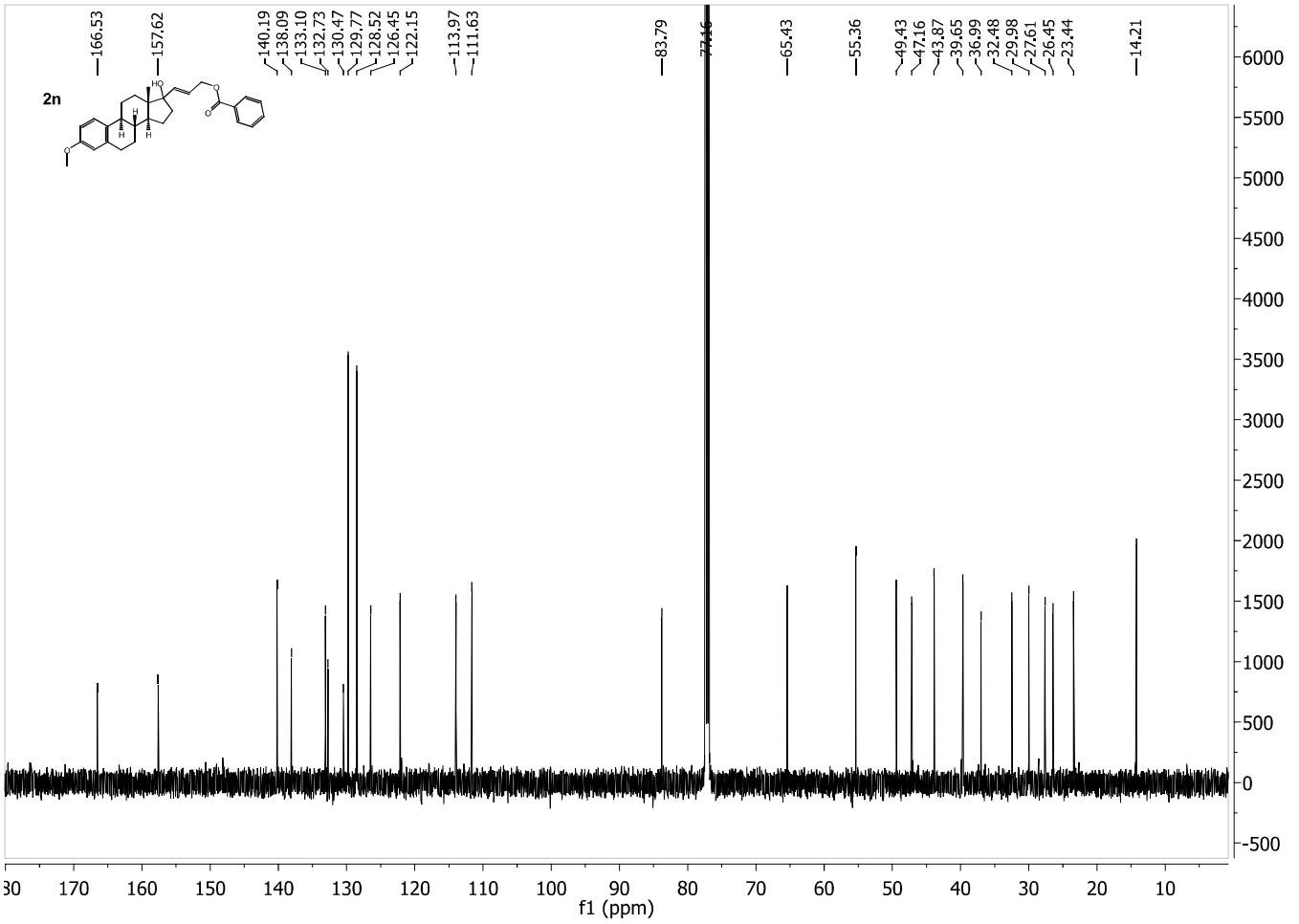
2.29
2.13
2.04
1.91
1.76
1.60
1.46
1.41
1.35
0.95
2n
2.01
1.03
2.09
1.00
1.07
1.07
1.07
1.00
2.10
3.32
2.18
1.05
1.04
1.16
2.16
1.01
3.09
2.99
1.17
1.05
3.10
f1 (ppm)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129.77
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126.45
122.15
113.97
111.63
83.79
77.16
65.43
55.36
49.43
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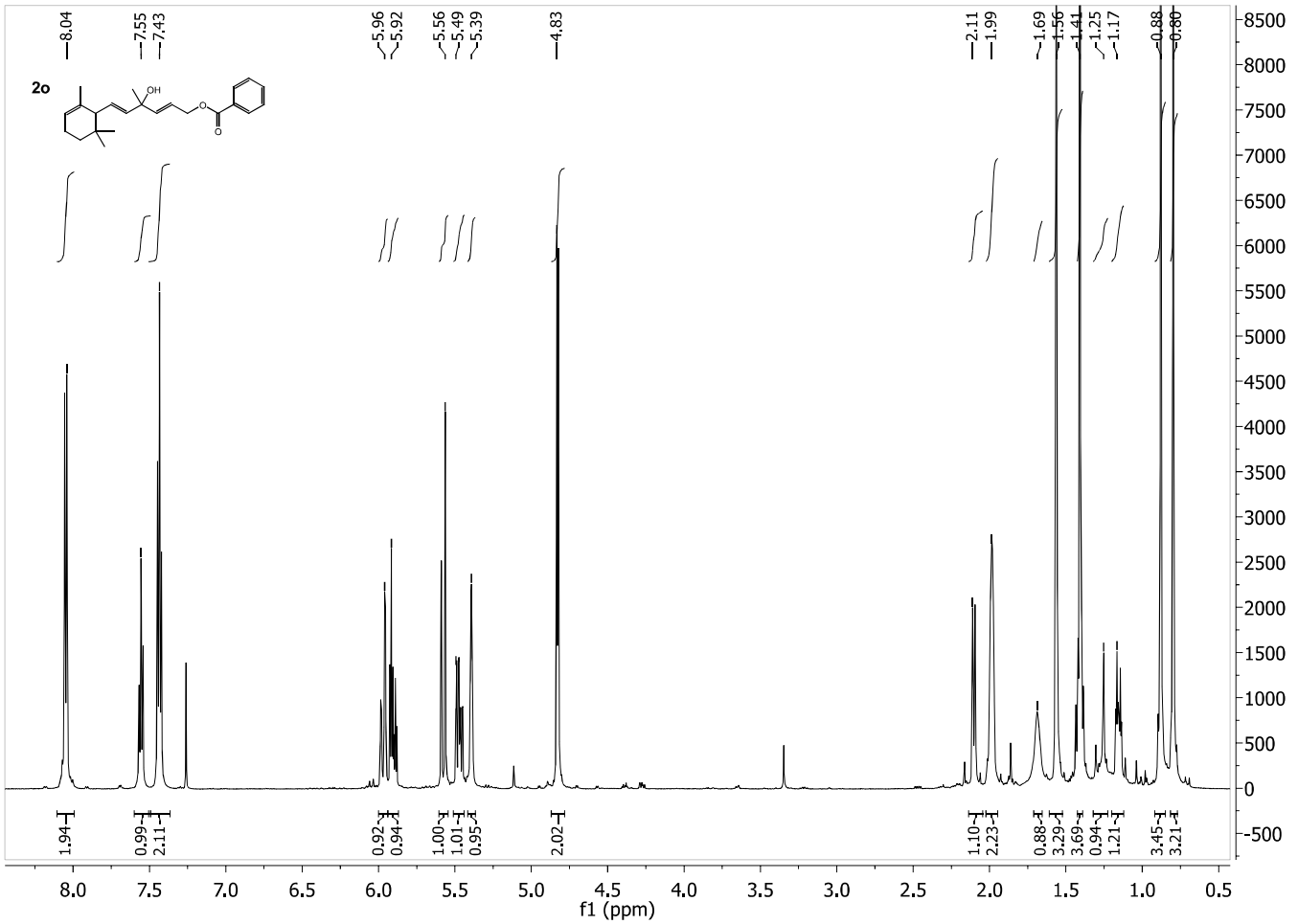
39.65
36.99
32.48
29.98
27.61
26.45
23.44
14.21
2n
f1 (ppm)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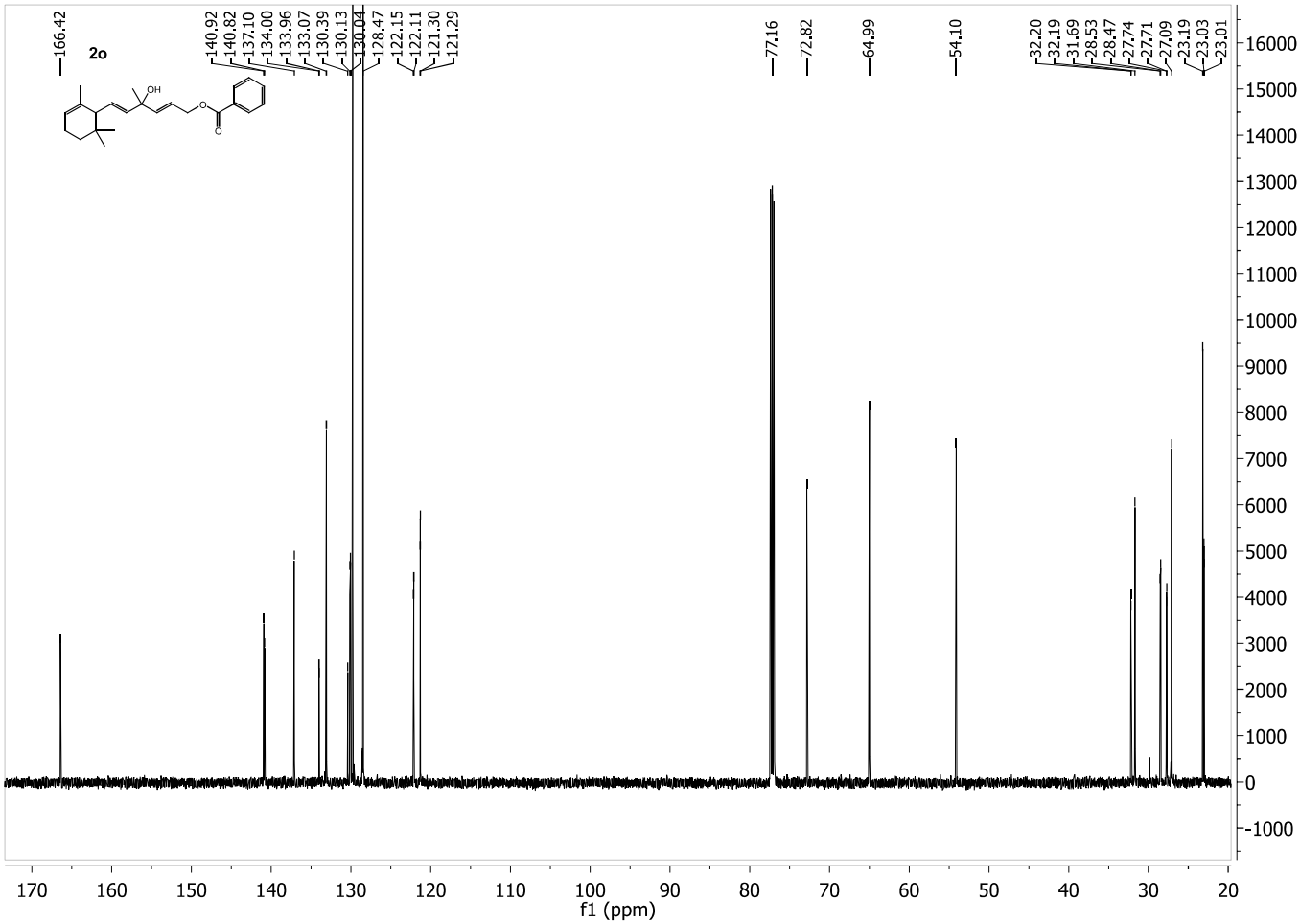
5.49
5.39
4.83
2.11
1.99
1.69
1.56
1.41
1.25
1.17
0.88
0.80
1.94
0.99
2.11
0.92
0.94
1.00
1.01
0.95
2.02
1.10
2.23
0.88
3.29
3.69
0.94
1.21
3.45
3.21
f1 (ppm)


2o
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133.96
133.07
130.39
130.13
130.04
128.47
122.15
122.11
121.30
121.29
77.16
72.82
64.99
54.10
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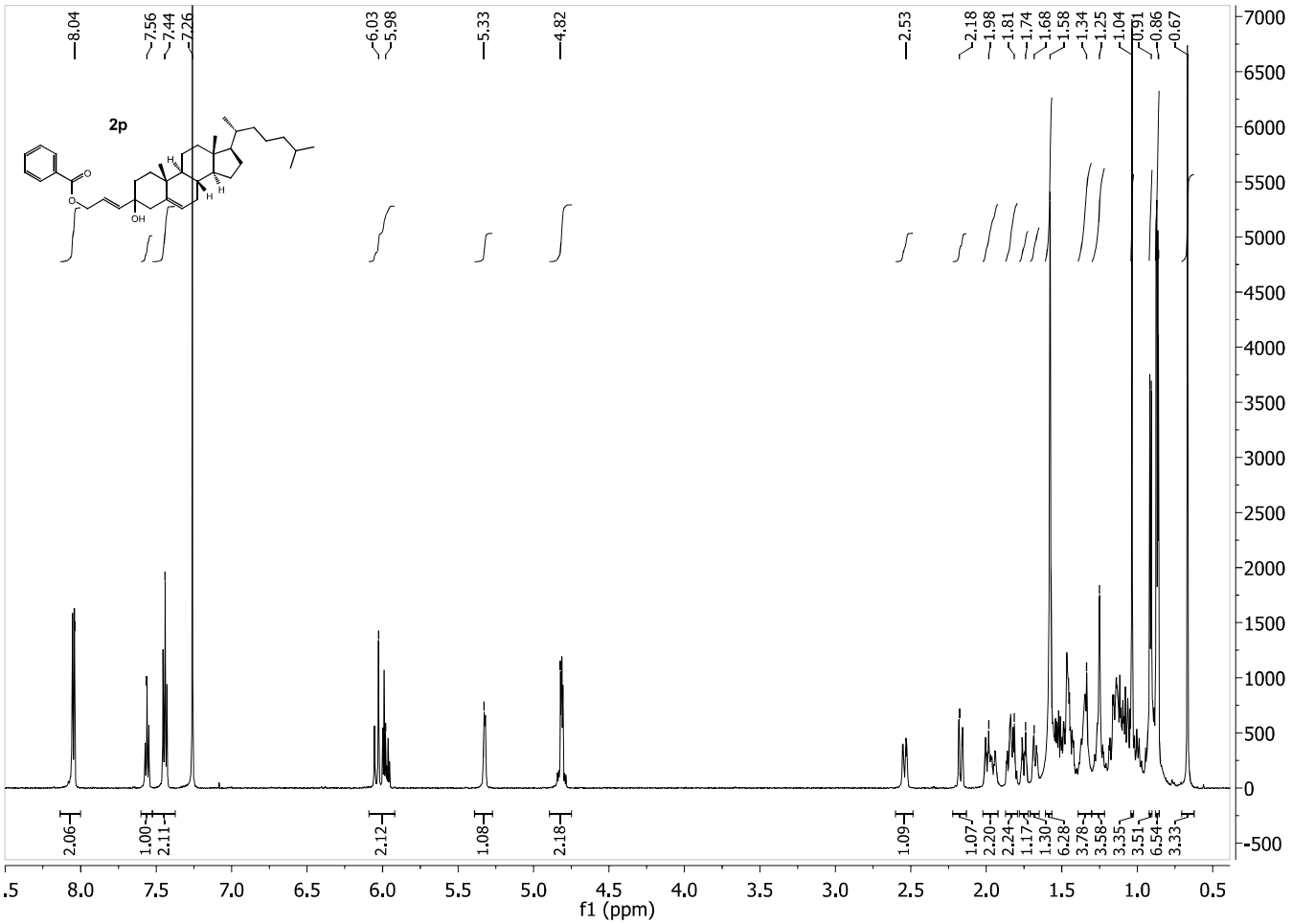
32.19
31.69
28.53
28.47
27.74
27.71
27.09
23.19
23.03
23.01
f1 (ppm)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4.82
2.53
2.18
1.98
1.81
1.74
1.68
1.58
1.34
1.25
1.04
0.91
0.86
0.67
2p
OH
2.06
1.00
2.11
2.12
1.08
2.18
1.09
1.07
2.20
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1.30
6.28
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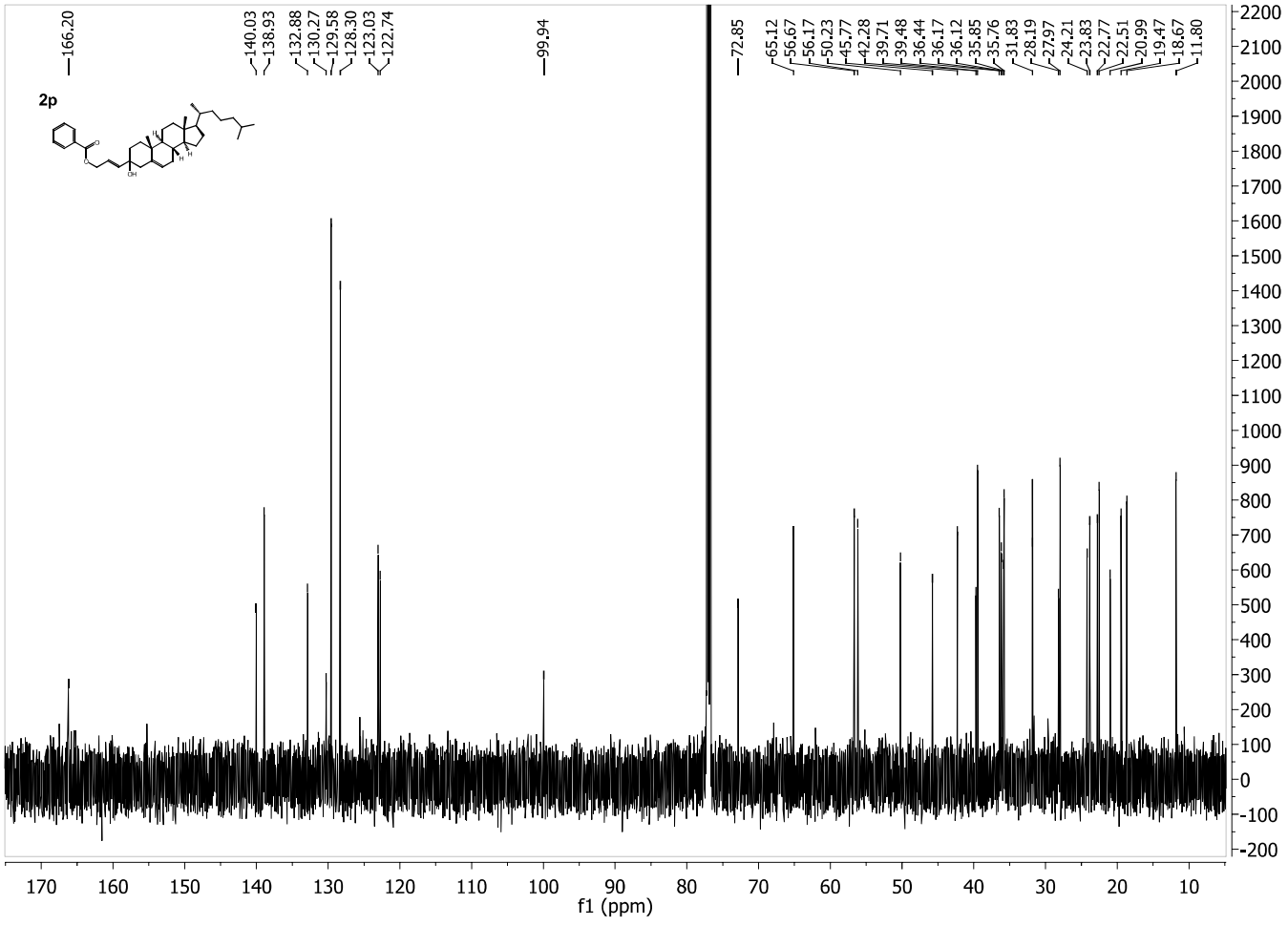
3.58
3.35
3.51
6.54
3.33
f1 (ppm)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129.58
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123.03
122.74
99.94
72.85
65.12
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56.17
50.23
45.77
42.28
39.71
39.48
36.44
36.17
36.12
35.85
35.76
31.83
28.19
27.97
24.21
23.83
22.77
22.51
20.99
19.47
18.67
11.80
2p
OH
f1 (ppm)