Decarboxylative Allylations of Ester Enolate Equivalents

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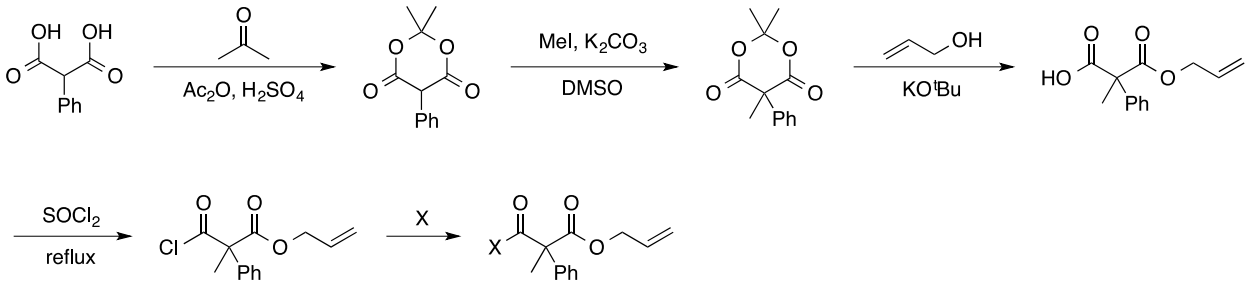
Table of Contents

General experimental:

All reactions were run in flame-dried glassware under Argon atmosphere. Commercially available reagents and anhydrous benzene were used without further treatment. Compound purification was effected by flash chromatography using 230x400 mesh, 60Å porosity, silica obtained from Sorbent Technologies. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance 400 or Bruker Avance 500 DRX spectrometer and were referenced to residual protio solvent signals. Structural assignments were based on ^{1}H, ^{13}C, DEPT-135, COSY, HSQC, and FT-IR spectroscopies. Mass spectrometry was run using ESI techniques.

Procedure for the synthesis of α,α-disubstituted di-ester equivalents:

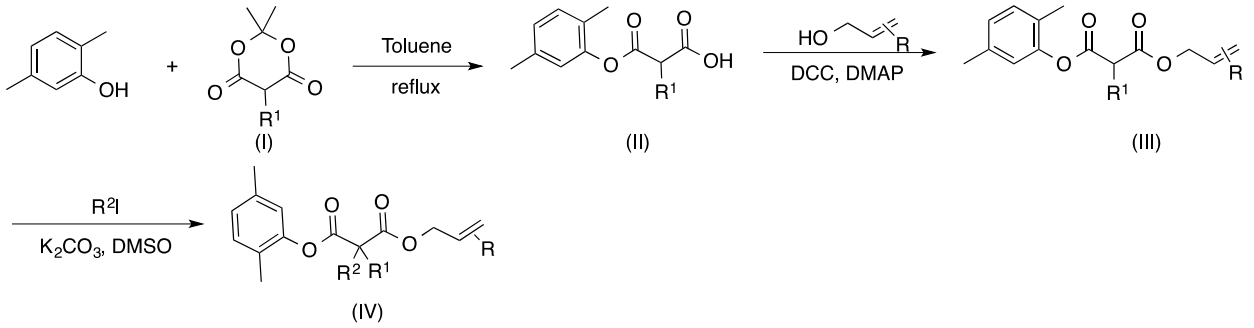


2,2-dimethyl-5-phenyl-1,3-dioxane-4,6-dione (II)[1] and 2,2,5-trimethyl-5-phenyl-1,3-dioxane-4,6-dione (III)[2] were prepared according to the literature procedures, starting from commercially available 2-phenylmalonic acid (I). Synthesis of 3-(allyloxy)-2-methyl-3-oxo-2-phenylpropanoic acid (IV) was carried out according to the literature procedure[3] and characterization data were identical to reported data.[3] (IV) converted to the acid chloride (V) in refluxing $SOCl_2$ and treatment of the acid chloride with suitable amine[6, 7], Lithium pyrrolide[4], phenol[5] or thio-phenol[5] provided the required diester compounds.

Synthesis of Lithium Pyrrolide

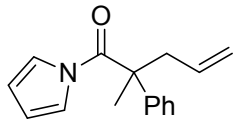
In a flame–dried Schlenk tube under argon, freshly distilled pyrrole (1g, 14.9 mmol, 1.0 eq.) in 25 mL of anhydrous ether was cooled to -20°C and n-BuLi (9.3 mL, 14.9 mmol, 1.0 eq.) was added in batches of 0.5 ml. The resulting solution was warmed to room temperature and stirring was continued for 4 hours. The white precipitate of lithium pyrollide was filtered, washed with ether, dried under an inert atmosphere and stored in a glove box. Same procedure was followed to prepare lithium indolide except the indolide was prepared at -78°C. Characterization data were identical to previously reported data in literature.[4]

General procedure for the synthesis of α,α-disubstituted phenolic esters.



A solution of Meldrum's acid (I) in Toluene was refluxed for 2 hours with 2,5-dimethylphenol[8] to obtain required propanoic acid (II) and used in standard DCC, DMAP coupling[9] with corresponding allyl alcohol to obtain α mono-substituted di-ester (III). Additional α-alkylation was carried out according to the literature procedure to obtain (IV). [10]

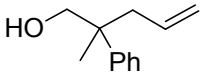
Representative procedure for Palladium catalyzed decarboxylative allylation.



In a flame-dried schlenk flask under argon, $Pd(PPh_3)_4$ (40.8 mg, 0.035 mmol, 0.10 eq.) and 9 mL anhydrous benzene (0.04M w.r.t. the ester) was added to allyl 2-methyl-3-oxo-2-phenyl-3-(1H-pyrrol-1-yl)propanoate (100 mg, 0.35 mmol, 1.0 eq.) and stirred for 25 minutes at room temperature. Reaction was concentrated *in-vacuo* and purified *via* flash chromatography using 5% EtOAc and Hexane to obtain colorless oil (81 mg, 97%).

Transformations of Acyl pyrrole

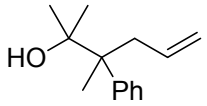
2-methyl-2-phenylpent-4-en-1-ol.



In a flame-dried schlenk flask under argon, $NaBH_4$ (9.5 mg, 0.25 mmol, 2.0 eq.) was added to a solution of 2-methyl-2-phenyl-1-(1H-pyrrol-1-yl)pent-4-en-1-one(acyl pyrrole) (30 mg, 0.13 mmol, 1.0 eq.) in 1 mL of THF at 0°C. Solution was stirred 4 hours at 0°C and overnight at room temperature. Saturated K_2CO_3 (10 mL) was added and extracted with EtOAc (3x10mL). Dried over anhyd. $MgSO_4$ and concentrated *in-vacuo* and purified *via* flash chromatography using 5% EtOAc and Hexane to obtain colorless oil (17 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 4H), 7.18 – 7.14 (m, 1H), 5.52 (m, 1H), 4.95 (dddt, *J* = 24.0, 10.1, 2.0, 1.2 Hz, 2H), 3.68 (dd, *J* = 10.9, 2.1 Hz, 1H), 3.54 (dd, *J* = 10.8, 5.4 Hz, 1H), 2.49 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.34 – 2.25 (m, 1H), 1.27 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 134.5, 128.5, 126.7, 126.3, 117.6, 71.8, 43.2, 42.9, 21.9 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3396, 2920, 1027, 906, 692 Calcd. HRMS for $C_{12}H_{17}O$ (M+H) – 177.1279, found 177.1333

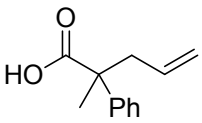
2,3-dimethyl-3-phenylhex-5-en-2-ol.



In a flame-dried schlenk flask under argon, MeLi (1 mL, excess) was added to a solution of 2-methyl-2-phenyl-1-(1H-pyrrol-1-yl)pent-4-en-1-one (acyl pyrrole) (50 mg, 0.21 mmol, 1.0 eq.) in 1 mL of THF at 0˚C. The reaction mixture was stirred overnight at room temperature. Quenched with water and extracted with EtOAc (3x10 mL). Dried over anhyd. $MgSO_4$ and concentrated *in-vacuo* and purified *via* flash chromatography using 5% EtOAc and Hexane to obtain colorless oil (40 mg, 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dt, *J* = 8.4, 1.7 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.18 – 7.13 (m, 1H), 5.41 (m, 1H), 4.98 (ddd, *J* = 17.0, 3.0, 2.1 Hz, 1H), 4.84 (dd, *J* = 10.2, 0.8 Hz, 1H), 3.09 (dd, *J* = 14.2, 5.0 Hz, 1H), 2.25 (dd, *J* = 14.3, 8.5 Hz, 1H), 1.30 (d, *J* = 0.6 Hz, 3H), 1.12 (s, 3H), 1.02 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 135.9, 128.9, 127.7, 126.1, 117.1, 74.7, 48.3, 39.7, 25.9, 25.5, 21.2 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3366, 3448, 2985, 1637, 1375, 908, 702 Calcd. HRMS for $C_{14}H_{20}OLi$ (M+Li) – 211.1674, found 211.0926

2-methyl-2-phenylpent-4-enoic acid.



A Flame dried-schlenk flask under argon, was charged with 2-methyl-2-phenyl-1-(1H-pyrrol-1-yl)pent-4-en-1-one (acyl pyrrole) (50 mg, 0.21 mmol, 1.0 eq.) in THF (2mL) and H_2O (0.5 mL). The solution was cooled to 0˚C and was added H_2O_2 (30% in H_2O, 0.1 mL) followed by $LiOH•H_2O$ (44 mg, 1 mmol, 5.0 eq.) Reaction mixture was stirred overnight at room temperature. $Na_2S_2O_3$ (0.7 M, 1mL) and $NaHCO_3$ (0.5 N, 2 mL) were added and THF was removed *in-vacuo*. The aqueous layer was acidified with 2M HCl (monitored by pH papers) and extracted with EtOAc (3x10mL). Solvent was removed in-vacuo and purified *via* flash chromatography using 5%-15% EtOAc and Hexane to obtain colorless oil (34 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 7.29

(ddd, J = 8.4, 4.6, 1.4 Hz, 1H), 5.64 (ddt, J = 17.3, 10.1, 7.2 Hz, 1H), 5.16 – 5.04 (m, 2H), 2.84 (dd, J = 13.8, 7.4 Hz, 1H), 2.71 (dd, J = 13.8, 7.1 Hz, 1H), 1.59 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.8, 142.4, 133.7, 128.5, 127.1, 126.2, 118.7, 49.7, 43.5, 22.2 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3076, 1697, 1446, 1277, 918 Calcd. HRMS for $C_{12}H_{14}O_2Na$ (M+Na) 213.0892, found 213.0823

1. Loev, B.; Macko, E.; Fried, I. M. *J. Med. Chem*. **1969**, *12*, 854.

2. Fillion, E.; Dumas, A. M. *J. Org. Chem*. **2008**, *73*, 2920.

3. Imao, D.; Itoi, A.; Yamazaki, A.; Shirakura, M.; Ohtoshi, R.; Ogata, K.; Ohmori, Y.; Ohta, T.; Ito, Y. *J. Org. Chem.* **2007**, *72*, 1652.

4. Franzel, A.; Gluth, M.; Herbst-Irmer, R.; Klingebiel, U. *J. Organomet. Chem*. **1996**, *514*, 281.

5. Sauer, S. J.; Garnsey, M. R.; Coltart, D. M. *J. Am. Chem. Soc*. **2010**, *132*, 13997.

6. Weinreb, S. M.; Nahm, S. *Tetrahedron Lett*. **1981**, *22*, 3815.

7. Evans, D. A.; Borg, G.; Scheidt, K. A. *Angew. Chem. Int. Ed*. **2002**, *41*, 3188.

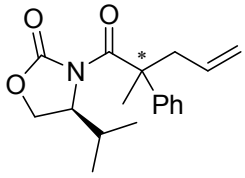
8. Blaquiere, N.; Shore, D. G.; Rousseaux, S.; Fagnou. K. *J. Org. Chem*. **2009**, *74*, 6190.

9. Neises, B.; Steglich, W. *Angew.Chem. Int. Ed. Eng*. **1978**, *17*, 522.

10. Torregrosa, R. R. P.; Ariyarathna, Y.; Chattopadhyay, K.; Tunge, J. A. *J. Am. Chem. Soc.* **2010,** *132*, 9280.

Spectral Characterization

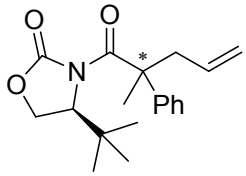
Spectral Characterization of **1a** (4S)-4-isopropyl-3-(2-methyl-2-phenylpent-4-enoyl)oxazolidin-2-one



major, minor

Major isomer - ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 10.4, 4.8 Hz, 3H), 7.17 – 7.04 (m, 3H)- Ar-H major and minor are overlapped, 5.56 (m, 1H), 5.07 – 4.93 (m, 2H), 4.49 – 4.41 (m, 1H), 4.13 – 3.99 (m, 2H), 3.25 (dd, *J* = 13.7, 8.1 Hz, 1H), 2.58 (dd, *J* = 13.8, 6.5 Hz, 1H), 2.35 (dqd, *J* = 13.9, 7.0, 3.4 Hz, 1H), 1.53 (s, 3H), 0.86 (d, *J* = 7.1 Hz, 3H), 0.76 (d, *J* = 6.9 Hz, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 151.4, 143.3, 133.9, 128.1, 126.4, 125.5, 118.6, 62.8, 60.1, 52.9, 43.2, 28.4, 24.4, 18.3, 14.7 Minor- ^{1}H NMR (500 MHz, $CDCl_3$) δ Ar-H are overlapped with major isomer, 5.54 – 5.44 (m, 1H-overlapped with major isomer), 5.07 – 4.97 (m, overlapped with major isomer, 4.12 – 3.99 (m, overlapped with major isomer), 2.93 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.53 (dd, *J* = 13.8, 6.4 Hz, overlapped with major isomer), 1.64 (s, 3H), 0.79 (d, *J* = 6.9 Hz, 6H - overlapped with major isomer) ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 134.2, 118.4, 63.1, 59.9, 52.9, 44.5, 28.6, 23.1, 18.1, 14.9 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3055, 2975, 1689, 1598, 1380, 703 Calcd. HRMS for $C_{18}H_{23}NO_3Na$ (M+Na) – 324.1576, found 324.1541

Spectral Characterization of **1b** (4S)-4-(tert-butyl)-3-(2-methyl-2-phenylpent-4-enoyl)oxazolidin-2-one

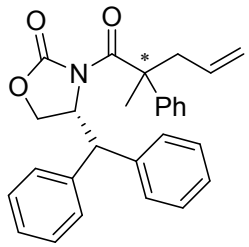


major, minor

Major isomer - ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.20 (m, 3H), 7.15 – 7.06 (m, 2H + minor isomer), 5.73 (m, 1H), 5.12 (ddd, *J* = 16.9, 3.1, 1.6 Hz, 1H), 5.08 – 5.02 (m, 1H), 4.43 (dd, *J* = 7.4, 1.4 Hz, 1H), 4.10 – 4.01 (m, 2H), 3.71 – 3.55 (m, 1H), 2.67 (ddt, *J* = 13.7, 6.2, 1.4 Hz, 1H), 1.47 (s, 3H), 0.87 (s, 9H + minor isomer). Minor isomer - ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 - 7.15 (Ar-H - overlapped with major isomer), 5.51 – 5.42 (m, 1H), 4.94 (s, 1H), 4.93 – 4.90 (m, 1H), 4.52 (dd, *J* = 7.4, 1.6 Hz, 1H), 4.32 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.14 (dd, *J* = 9.3, 1.4 Hz, 1H), 2.74 (dd, *J* = 13.8, 8.1 Hz, 1H), 2.48 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.75 (s, 3H), 0.89 (^{t}Bu – overlapped with major isomer) ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7(major), 174.8 (minor), 152.6 (major), 152.0 (minor), 144.1 (major), 142.3 (minor), 134.4 (minor), 134.1 (major), 128.6 (minor), 128.3 (major), 128.1 (minor), 127.2 (minor), 126.4 (major), 125.5 (minor), 125.2 (major), 119.0 (major), 118.3 (minor), 64.9 (major), 63.2 (major), 62.1 (minor), 61.4 (minor),

53.4 (major), 52.9 (minor), 42.9 (minor), 41.6 (major), 35.9 (major), 35.8 (minor), 27.5 (minor), 26.1 (major), 25.7 (major), 20.1 (minor) FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3060, 2973, 1690, 1590, 1370, 700 Calcd. HRMS for $C_{19}H_{25}NO_3Na$ (M+Na) – 338.1732, found 338.1701

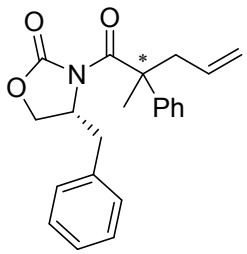
Spectral Characterization of **1c** (4R)-4-benzhydryl-3-(2-methyl-2-phenylpent-4-enoyl)oxazolidin-2-one



major, minor

^1H NMR (500 MHz, $CDCl_3$) Ar-H major isomer + minor isomer δ 7.30 – 7.22 (m, 4H), 7.22 – 7.17 (m, 6H), 7.17 – 7.12 (m, 7H), 7.10 (ddd, *J* = 8.3, 4.4, 2.1 Hz, 3H), 6.93 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.90 – 6.86 (m, 2H), 5.39 (td, *J* = 7.4, 2.8 Hz, 1H), 5.31 (ddd, *J* = 7.4, 6.3, 3.1 Hz, 1H), 5.29 – 5.18 (m, 1H), 4.96 – 4.83 (m, 3H), 4.69 (d, *J* = 6.2 Hz, 1H), 4.54 (d, *J* = 7.3 Hz, 1H), 4.20 – 4.10 (m, 3H), 3.03 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.63 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.51 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.41 – 2.35 (m, 1H), 1.46 (s, 3H), 1.44 (s, 2H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7 (major), 175.2 (minor), 151.3 (major), 150.9 (minor), 142.7 (major), 142.1 (minor), 139.9 (major), 139.7 (minor), 138.6 (minor), 138.5 (major), 134.4 (minor), 134.0 (major); Ar-C; major+ minor 129.07 (Ar-C), 129.05 (Ar-C), 129.01 (Ar-C), 128.9 (Ar-C), 128.8 (Ar-C), 128.7 (Ar-C), 128.69 (Ar-C), 128.6 (Ar-C), 128.05 (Ar-C), 128.02 (Ar-C), 127.7 (Ar-C), 127.68 (Ar-C), 127.1 (Ar-C), 126.3 (Ar-C), 126.27 (Ar-C), 125.7 (Ar-C), 125.6 (Ar-C), 118.4 (major), 118.1 (minor), 65.4 (minor), 65.1 (major), 58.7 (major), 57.9 (minor), 52.7 (major), 52.6 (minor), 52.5 (minor), 51.9 (major) FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3060, 2977, 1789, 1681, 1600, 1496, 1242, 918, 700 Calcd. HRMS for $C_{28}H_{27}NO_3Na$ (M+Na) – 448.1889, found 448.1931

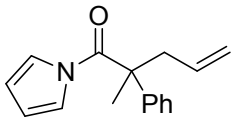
Spectral Characterization of **1d** (4R)-4-benzyl-3-(2-methyl-2-phenylpent-4-enoyl)oxazolidin-2-one



major, minor

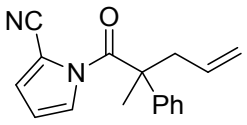
^{1}H NMR (500 MHz, $CDCl_3$) δ Ar-H major isomer + minor isomer 7.29 – 7.20 (m, 6H), 7.20 – 7.17 (m, 4H), 7.17 – 7.12 (m, 2H), 7.12 – 7.07 (m, 3H), 5.64 (m, *J* = 16.7, 10.1, 8.3, 6.4 Hz, 1H), 5.55 – 5.48 (m, minor isomer), 5.10 – 4.93 (m, 2H + minor isomer), 4.70 – 4.62 (m, 1H + minor isomer), 4.00 – 3.93 (m, 2H + minor isomer), 3.40 – 3.26 (m, 2H + minor isomer), 3.00 – 2.95 (m, minor isomer), 2.68 – 2.55 (m, 1H + minor isomer), 2.50 (dd, *J* = 13.1, 10.8 Hz, 1H, major isomer), 1.65 (s, minor isomer), 1.56 (s, 3H, major isomer). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8 (minor), 175.5 (major), 150.8 (major), 143.2 (major), 142.6 (minor), 135.8 (major), 135.6 (minor), 134.1 (minor), 133.9 (major), 129.5 (minor), 129.4 (major), 129.0 (major), 128.9 (major), 128.2 (major), 128.2 (minor), 127.3 (minor), 127.28 (major), 126.4 (major), 125.6 (minor), 125.5 (major), 118.8 (major), 118.5 (minor), 65.9 (minor), 65.8 (major), 57.3 (major), 57.0 (minor), 52.8 (minor), 52.7 (major), 44.2 (minor), 42.7 (major), 37.9 (minor), 37.8 (major) FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3026, 2977, 1789, 1681, 1236, 700 Calcd. HRMS for $C_{22}H_{24}NO_3$ (M+H) – 350.1756, found 350.1743

Spectral Characterization of **2a** 2-methyl-2-phenyl-1-(1H-pyrrol-1-yl)pent-4-en-1-one



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dt, *J* = 9.7, 1.9 Hz, 2H), 7.23 – 7.15 (m, 3H), 6.92 – 6.87 (m, 2H), 5.97 (d, *J* = 2.4 Hz, 2H), 5.48 (m, 1H), 4.99 – 4.94 (m, 1H), 4.88 (ddd, *J* = 17.0, 3.2, 1.4 Hz, 1H), 2.81 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.71 (dd, *J* = 13.7, 6.6 Hz, 1H), 1.60 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 142.3, 132.1, 128.1, 126.2, 124.8, 119.6, 118.1, 110.8, 51.0, 44.0, 23.6 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3020, 1704, 1494, 1465, 1213, 1155, 700, 503 Calcd. HRMS for $C_{16}H_{17}NO$ (M+) – 239.1310, found 239.1245

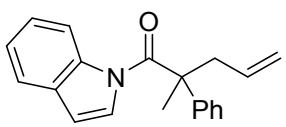
Spectral Characterization of **2b** 1-(2-methyl-2-phenylpent-4-enoyl)-1H-pyrrole-2-carbonitrile



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 3H), 7.22 – 7.10 (m, 3H), 6.81 (dd, *J* = 3.6, 1.4 Hz, 1H), 6.53 (dd, *J* = 3.4, 1.4 Hz, 1H), 5.94 (t, *J* = 3.5 Hz, 1H), 5.50 (m, 1H), 5.03 – 4.97 (m, 1H), 4.86 (ddd, *J* = 16.9, 3.1, 1.4 Hz, 1H), 2.85 – 2.70 (m, 2H), 1.63 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 142.1, 132.3,

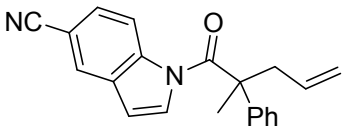
129.5, 127.9, 125.9, 125.6, 125.1, 119.8, 113.4, 112.3, 104.4, 52.7, 44.8, 24.4 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3057, 2200, 1725, 1450, 1150, 725 Calcd. HRMS for $C_{17}H_{16}N_2ONa$ (M+Na) – 287.1160, found 287.1161

Spectral Characterization of **2c** 1-(1H-indol-1-yl)-2-methyl-2-phenylpent-4-en-1-one



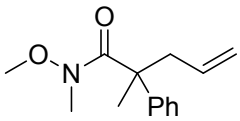
^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.21 (dd, *J* = 6.2, 5.2 Hz, 3H), 7.18 (ddd, *J* = 8.3, 5.3, 1.1 Hz, 2H), 6.79 (d, *J* = 3.9 Hz, 1H), 6.21 (d, *J* = 3.6 Hz, 1H), 5.52 (m, 1H), 4.98 – 4.86 (m, 2H), 2.88 (dd, *J* = 13.7, 7.9 Hz, 1H), 2.77 (dd, *J* = 13.7, 6.7 Hz, 1H), 1.66 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 143.8, 136.5, 133.3, 129.5, 129.2, 127.3, 126.2, 125.8, 125.0, 123.7, 120.5, 119.1, 117.2, 108.2, 52.8, 45.3, 24.7 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3068, 2989, 1704, 1539, 1494, 1379, 1321, 1207, 1145, 931, 767 Calcd. HRMS for $C_{20}H_{19}NOLi$ (M+Li) – 296.1627, found 296.1648

Spectral Characterization of **2d** 1-(2-methyl-2-phenylpent-4-enoyl)-1H-indole-5-carbonitrile



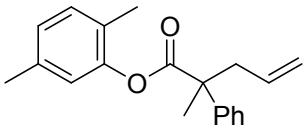
^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 1.1 Hz, 1H), 7.53 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.31 (dt, *J* = 9.7, 1.8 Hz, 2H), 6.91 (d, *J* = 3.9 Hz, 1H), 6.27 (d, *J* = 4.4 Hz, 1H), 5.50 (m, 1H), 4.98 – 4.92 (m, 1H), 4.87 (ddd, *J* = 17.0, 2.9, 1.3 Hz, 1H), 2.82 (ddd, *J* = 20.3, 13.7, 7.3 Hz, 2H), 1.66 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 143.1, 138.4, 132.8, 129.5, 128.2, 127.6, 125.7, 125.2, 119.6, 119.5, 117.9, 107.7, 107.0, 53.1, 45.0, 24.6 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3058, 2875, 2360, 1751, 1639, 1512, 1249, 1116, 916, 698 Calcd. HRMS for $C_{21}H_{18}N_2OLi$ (M+Li) – 321.1579, found 321.1531

Spectral Characterization of **2e** N-methoxy-N,2-dimethyl-2-phenylpent-4-enamide



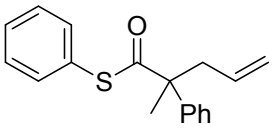
^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (tt, *J* = 3.6, 1.8 Hz, 2H), 7.21 – 7.10 (m, 3H), 5.49 (m, 1H), 5.01 – 4.91 (m, 2H), 3.03 (s, 3H), 2.90 (dd, *J* = 13.6, 8.1 Hz, 1H), 2.60 – 2.50 (m, 4H), 1.45 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.0, 144.8, 134.5, 128.2, 126.2, 125.9, 118.1, 58.9, 49.9, 43.1, 33.3, 22.9 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3064, 2935, 1654, 1490, 1379, 999, 698 Calcd. HRMS for $C_{14}H_{20}NO_2$ (M+H) – 234.1494 found 234.1520

Spectral Characterization of **2f** 2,5-dimethylphenyl 2-methyl-2-phenylpent-4-enoate



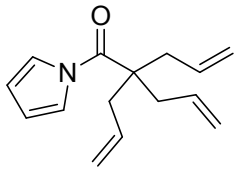
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.16 (m, 5H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 5.64 (ddt, *J* = 14.5, 10.1, 7.2 Hz, 1H), 5.14 – 4.98 (m, 2H), 2.91 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.73 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.20 (s, 3H), 1.80 (s, 3H), 1.65 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 146.9, 140.3, 134.4, 131.5, 128.6, 126.5, 126.3, 124.9, 124.6, 124.4, 123.9, 119.8, 116.6, 47.7, 41.3, 20.0, 18.6, 13.3 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3078, 2980, 1735, 1598, 1508, 1492, 1240, 1198, 1128, 925, 700 Calcd. HRMS for $C_{20}H_{23}O_2$ (M+H) – 295.1698, found 295.1670

Spectral Characterization of **2g** S-phenyl 2-methyl-2-phenylpent-4-enethioate



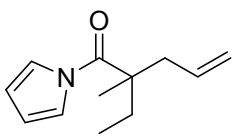
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 10H), 5.55 – 5.43 (m, 1H), 5.07 – 4.95 (m, 2H), 2.77 (ddd, *J* = 20.7, 13.9, 7.2 Hz, 2H), 1.61 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.5, 141.6, 134.8, 133.4, 129.1, 128.6, 128.3, 127.4, 127.2, 118.8, 57.1, 43.7, 22.7 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3058, 2985, 1780, 1697, 1440, 952, 703 Calcd. HRMS for $C_{18}H_{19}OS$ (M+H) – 283.1157, found 283.1202

Spectral characterization of **2h** 2,2-diallyl-1-(1H-pyrrol-1-yl)pent-4-en-1-one



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 6.21 – 6.18 (m, 2H), 5.62 (ddt, *J* = 17.5, 10.2, 7.4 Hz, 3H), 5.05 – 4.94 (m, 6H), 2.53 (d, *J* = 7.4 Hz, 6H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 132.6, 120.2, 119.4, 112.2, 51.7, 39.2 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3072, 2941, 1704, 1637, 1467, 1284, 1255, 1103, 921, 736 Calcd. HRMS for $C_{15}H_{20}NO$ (M+H) – 230.1545, found 230.1539

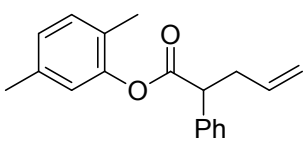
Spectral characterization of **2i** 2-ethyl-2-methyl-1-(1H-pyrrol-1-yl)pent-4-en-1-one



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 6.31 – 6.24 (m, 2H), 5.80 – 5.65 (m, 1H), 5.11 – 4.97 (m, 2H), 2.71 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.43 (dd, *J* = 14.1, 7.7 Hz, 1H), 2.08 – 1.92 (m, 1H), 1.79 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.39 (s, 3H), 0.89 (t, *J* = 7.5 Hz, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 132.1, 119.2, 117.7, 110.9, 47.7, 42.6, 31.3, 22.2, 7.8 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 2966, 2949, 1760,

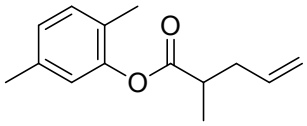
1664, 1517, 1463, 1163, 919, 734 Calcd. HRMS for $C_{12}H_{18}NO$ (M+H) – 192.1388, found 192.1443

Spectral characterization of **3a** 2,5-dimethylphenyl 2-phenylpent-4-enoate



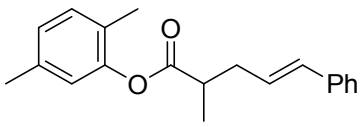
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.63 (s, 1H), 5.76 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.15 – 4.97 (m, 2H), 3.83 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.90 (dddt, *J* = 14.4, 8.5, 7.1, 1.1 Hz, 1H), 2.56 (dtt, *J* = 14.5, 6.7, 1.3 Hz, 1H), 2.19 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 147.9, 137.1, 135.7, 134.1, 129.7, 127.7, 127.1, 126.6, 125.8, 125.7, 121.1, 116.3, 50.4, 36.2, 19.8, 14.5; FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3070, 2920, 1755, 1508, 1454, 1242, 1134, 1110, 918 Calcd. HRMS for $C_{19}H_{21}O_2$ (M+H) – 281.1542, found 281.1497

Spectral characterization of **3b** 2,5-dimethylphenyl 2-methylpent-4-enoate



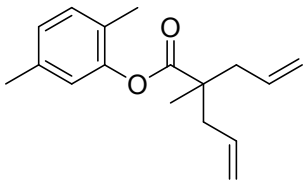
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.71 (s, 1H), 5.79 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.13 – 5.01 (m, 2H), 2.73 (h, *J* = 7.0 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.30 – 2.24 (m, 1H), 2.24 (d, *J* = 3.4 Hz, 3H), 2.05 (s, 3H), 1.26 (d, *J* = 7.0 Hz, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 149.1, 136.9, 135.3, 130.8, 126.7, 122.3, 117.3, 39.4, 37.8, 20.9, 16.8, 15.9 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3072, 2869, 1753, 1623, 1510, 1244,1114, 918 Calcd. HRMS for $C_{14}H_{19}O_2$ (M+H) – 219.1385, found 219.1384

Spectral characterization of **3c** (E)-2,5-dimethylphenyl 2-methyl-5-phenylpent-4-enoate



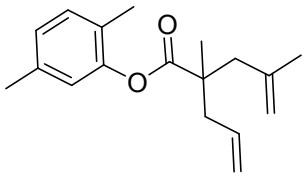
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.24 (dd, *J* = 10.3, 4.9 Hz, 2H), 7.17 – 7.13 (m, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.19 (dt, *J* = 15.7, 7.2 Hz, 1H), 2.90 – 2.75 (m, 1H), 2.66 (dtd, *J* = 8.6, 7.3, 1.3 Hz, 1H), 2.43 (dtd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 2.19 (s, 3H), 2.03 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 149.1, 137.3, 136.9, 132.6, 130.8, 128.6, 127.3, 126.1, 122.4, 39.9, 37.1, 20.8, 16.9, 15.8 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3033, 2975, 2933, 1755, 1506, 1456, 1377, 1247,1143, 1114, 968 Calcd. HRMS for $C_{20}H_{22}O_2Na$ (M+Na) – 317.1518, found 317.1529

Spectral characterization of **3d** 2,5-dimethylphenyl 2-allyl-2-methylpent-4-enoate



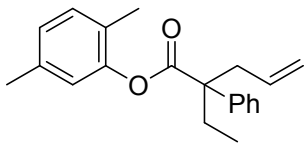
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 5.90 (ddt, *J* = 16.8, 10.4, 7.3 Hz, 2H), 5.24 – 5.13 (m, 4H), 2.59 (ddd, *J* = 13.8, 7.1, 0.8 Hz, 2H), 2.42 (ddd, *J* = 13.8, 7.5, 0.9 Hz, 2H), 2.34 (s, 3H), 2.16 (s, 3H), 1.34 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 148.3, 135.7, 132.5, 129.8, 125.6, 121.3, 117.6, 44.9, 41.8, 20.6, 19.9, 15.0 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3076, 2983, 1751, 1641, 1510, 1242, 1199, 1116, 1000, 919 Calcd. HRMS for $C_{17}H_{23}O_2$ (M+H) – 259.1698, found 259.1711.

Spectral characterization of **3e** 2,5-dimethylphenyl 2-allyl-2,4-dimethylpent-4-enoate



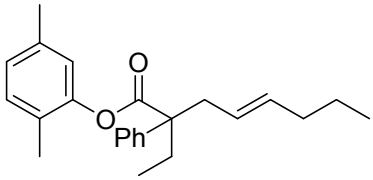
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.74 (s, 1H), 5.86 – 5.74 (m, 1H), 5.15 – 5.04 (m, 2H), 4.87 – 4.82 (m, 1H), 4.73 (d, *J* = 0.9 Hz, 1H), 2.55 (dd, *J* = 13.9, 5.6 Hz, 2H), 2.29 (ddd, *J* = 13.8, 4.0, 3.4 Hz, 2H), 2.23 (s, 3H), 2.07 (s, 3H), 1.73 (s, 3H), 1.24 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 149.3, 141.9, 136.7, 133.7, 130.9, 126.6, 126.5, 122.2, 118.8, 114.9, 46.5, 45.9, 44.0, 24.4, 21.6, 20.9, 16.1 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3072, 2985, 2919, 1750, 1644, 1507, 1454, 1244, 1194, 1115, 897 Calcd. HRMS for $C_{18}H_{25}O_2$ (M+H) – 273.1855, found 273.1848.

Spectral characterization of **3f** 2,5-dimethylphenyl 2-ethyl-2-phenylpent-4-enoate



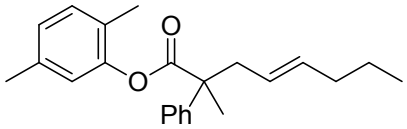
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dt, *J* = 3.0, 1.7 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.62 (s, 1H), 5.60 – 5.50 (m, 1H), 5.14 – 5.00 (m, 2H), 2.96 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.82 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.24 (dd, *J* = 14.3, 7.1 Hz, 1H), 2.20 (s, 3H), 2.10 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.76 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 149.2, 141.5, 136.6, 133.4, 130.8, 128.5, 127.0, 126.9, 126.7, 126.5, 122.1, 118.5, 53.9, 37.9, 26.4, 20.9, 15.6, 8.4 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3076, 2979, 1737, 1598, 1508, 1496, 1242, 1188, 1118, 923, 702 Calcd. HRMS for $C_{21}H_{24}O_2Na$ (M+Na) – 331.1674, found 331.1682.

Spectral characterization of **3g** (E)-2,5-dimethylphenyl 2-ethyl-2-phenyloct-4-enoate

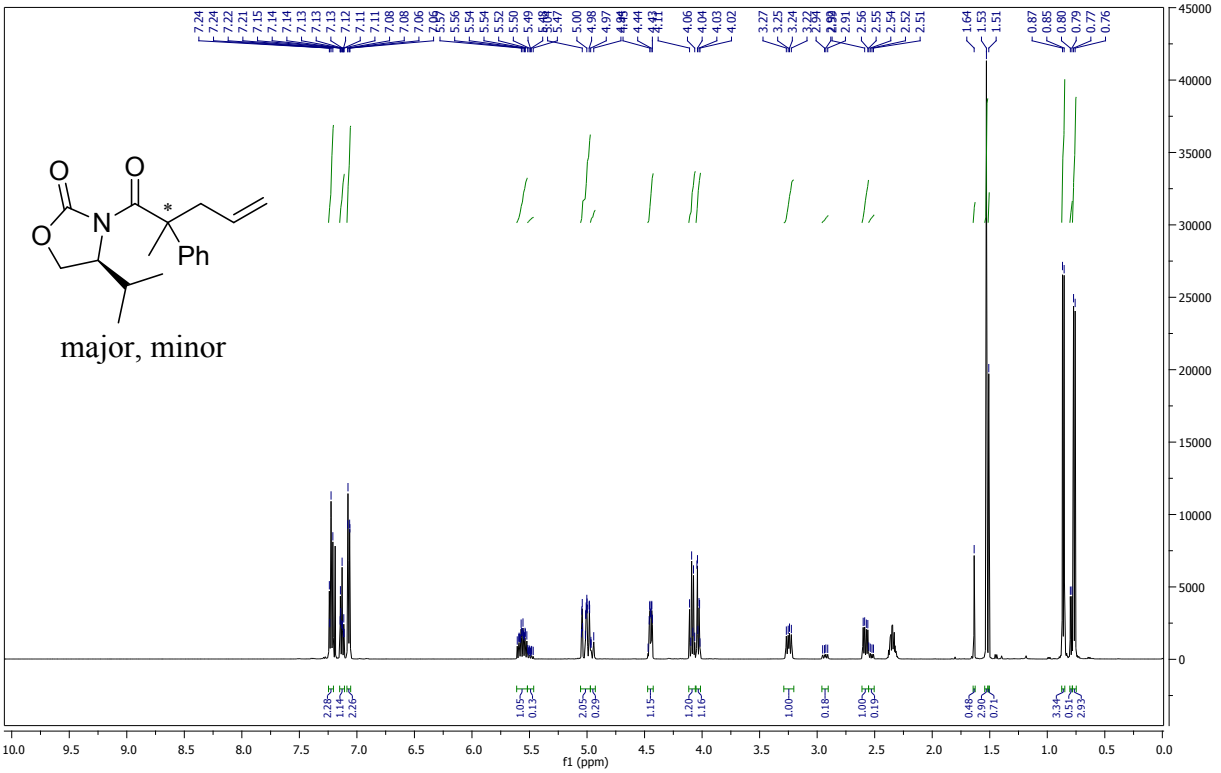


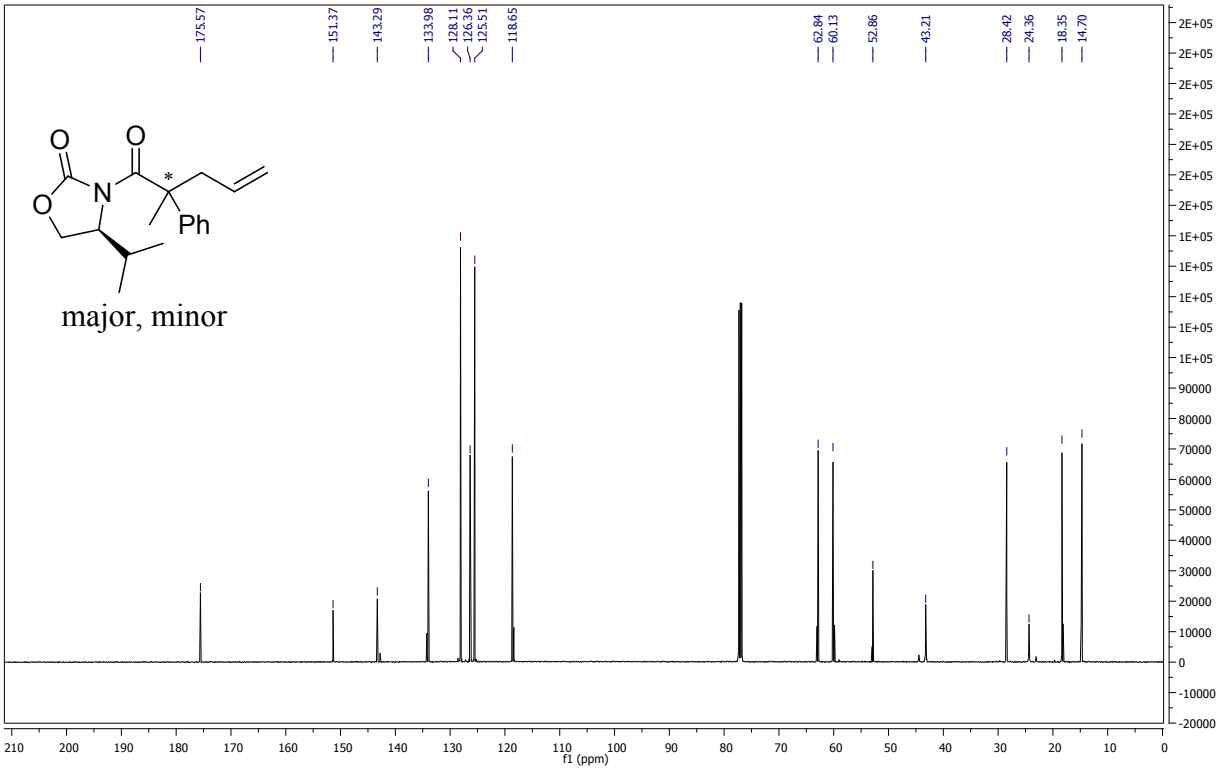
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.68 (s, 1H), 5.54 (dt, *J* = 13.9, 6.8 Hz, 1H), 5.23 (dt, *J* = 14.5, 6.7 Hz, 1H), 2.97 (dd, *J* = 14.1, 7.7 Hz, 1H), 2.80 (dd, *J* = 14.1, 6.6 Hz, 1H), 2.30 – 2.23 (m, 4H), 2.18 – 2.12 (m, 1H), 1.95 (q, *J* = 7.1 Hz, 2H), 1.82 (s, 3H), 1.39 – 1.29 (m, 2H), 0.85 (td, *J* = 7.4, 5.7 Hz, 6H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 149.2, 141.8, 136.6, 134.6, 130.8, 128.4, 126.8, 126.5, 124.5, 122.1, 54.2, 36.6, 34.8, 26.5, 22.6, 20.9, 15.6, 13.6, 8.3 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 3020, 2958, 2927, 2871, 1508, 1750, 1203, 1151, 1108, 804, 698 Calcd. HRMS for $C_{24}H_{30}O_2Na$ (M+Na) – 373.2144, found 373.2149.

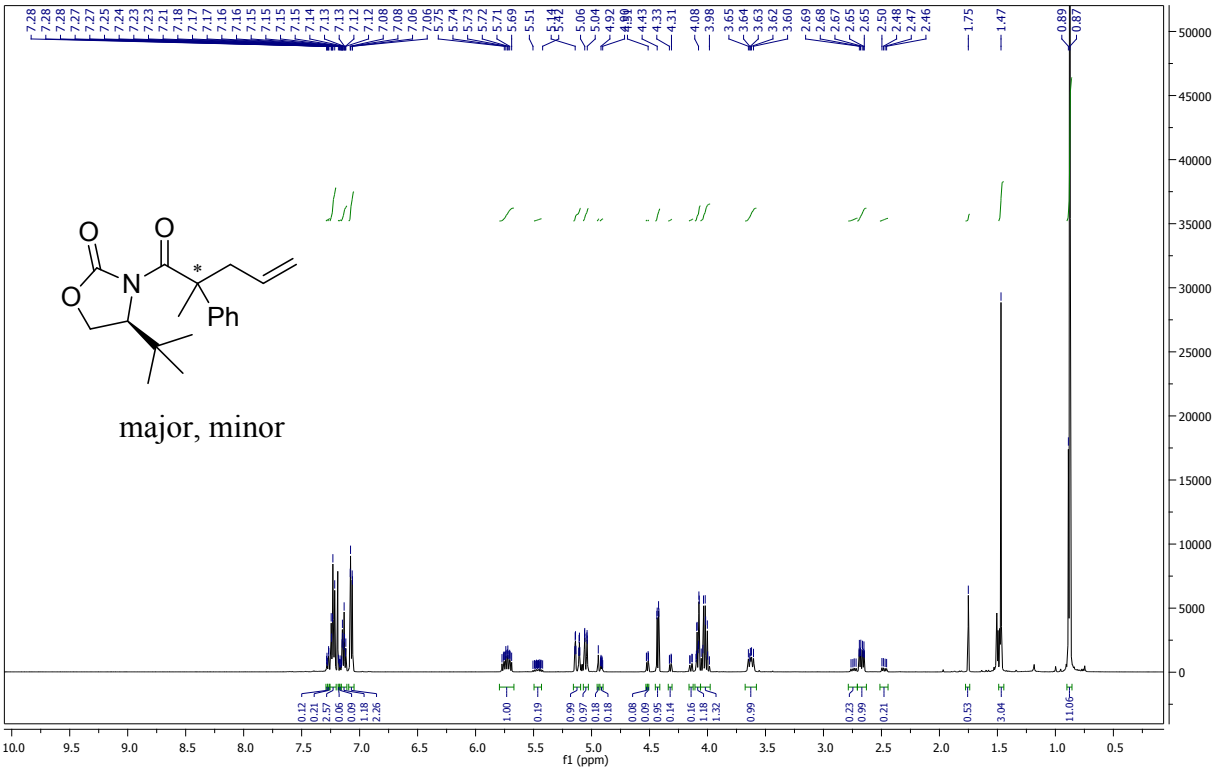
Spectral characterization of **3h** (E)-2,5-dimethylphenyl 2-methyl-2-phenyloct-4-enoate

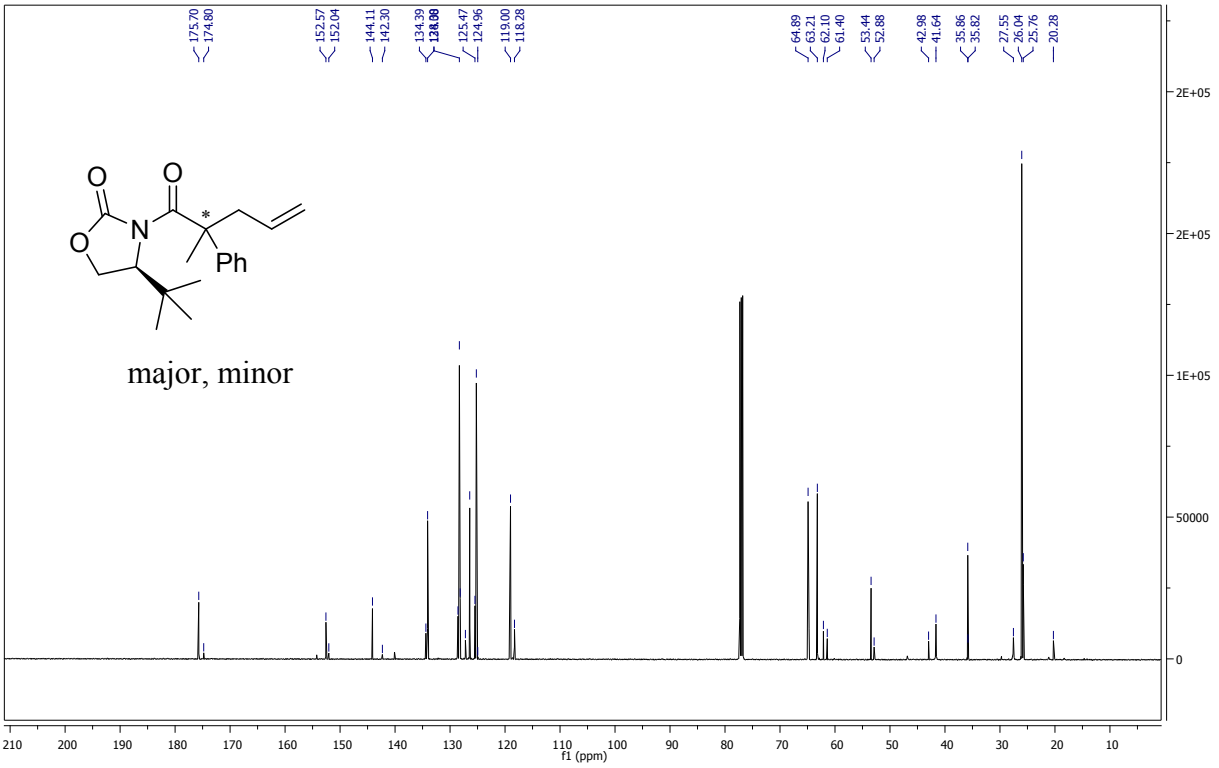


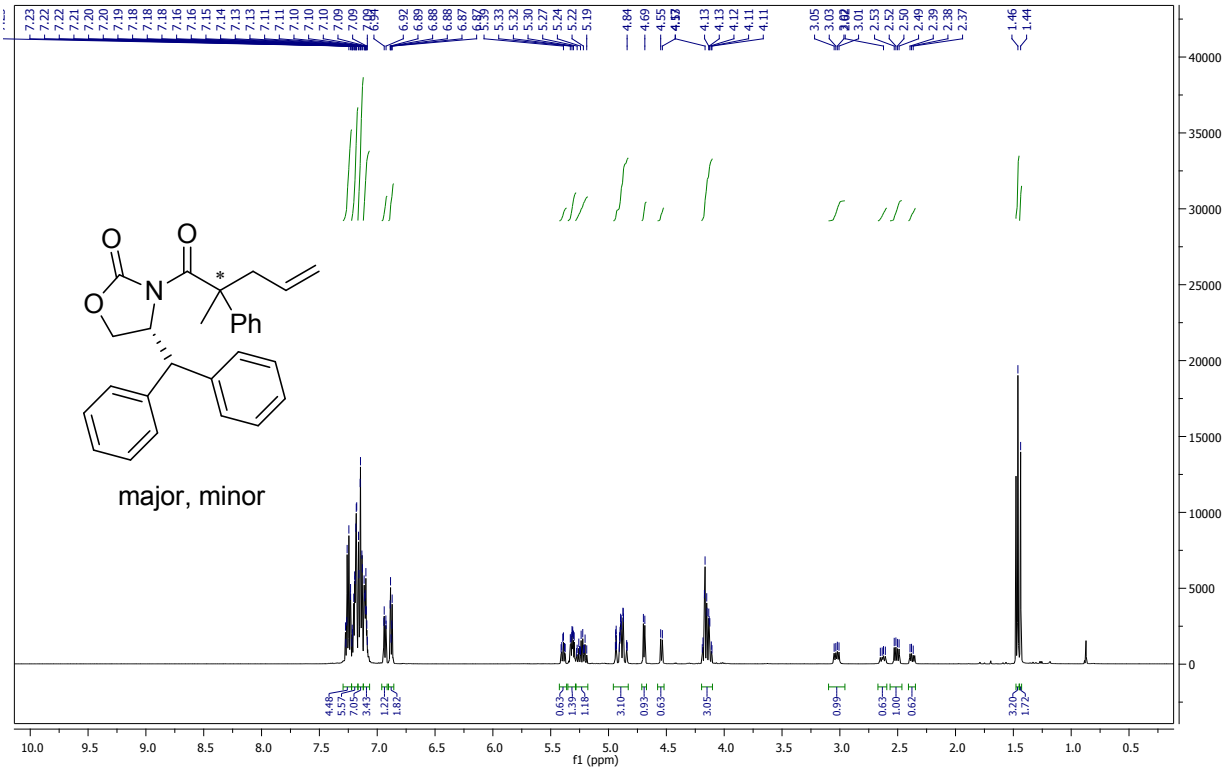
^{1}H NMR (400 MHz, CDCl3) δ 7.47 – 7.42 (m, 2H), 7.40 – 7.33 (m, 2H), 7.27 (dt, J = 3.9, 1.7 Hz, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.67 (s, 1H), 5.52 (dt, J = 14.8, 6.7 Hz, 1H), 5.39 – 5.22 (m, 1H), 2.92 (dd, J = 13.9, 7.4 Hz, 1H), 2.70 (dd, J = 13.7, 6.9 Hz, 1H), 2.26 (s, 3H), 1.95 (q, J = 7.0 Hz, 2H), 1.86 (s, 3H), 1.67 (s, 3H), 1.40 – 1.29 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H) ^{13}C NMR (126 MHz, CDCl3) δ 174.5, 149.4, 143.1, 136.8, 135.2, 130.9, 128.6, 127.1, 126.8, 126.5, 125.2, 122.3, 50.4, 42.5, 34.9, 22.8, 22.7, 21.1, 15.8, 13.9 FT-IR (CH_2Cl_2) υ_{max} cm^{-1} 2968, 2920, 1749, 1502, 1430, 1238, 1110, 692 Calcd. HRMS for $C_{23}H_{28}O_2$ (M+Na) – 359.1987 found 359.1989.

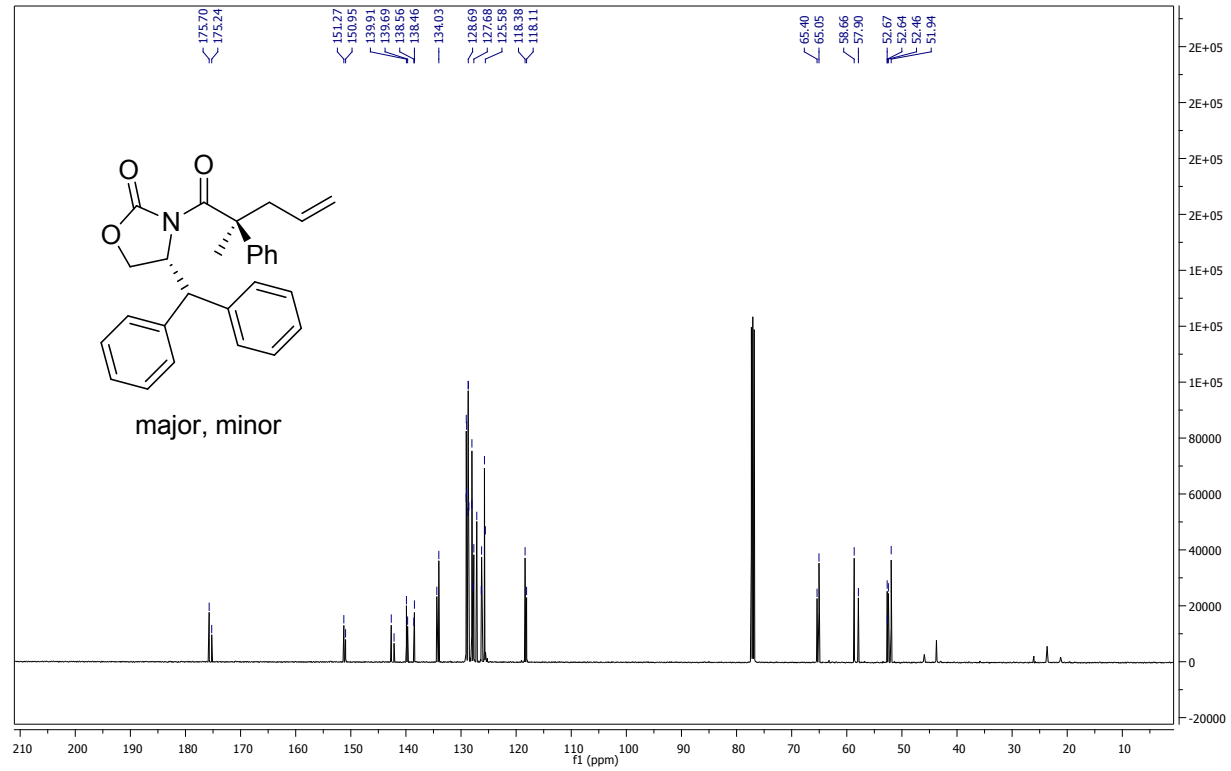

major, minor
f1 (ppm)

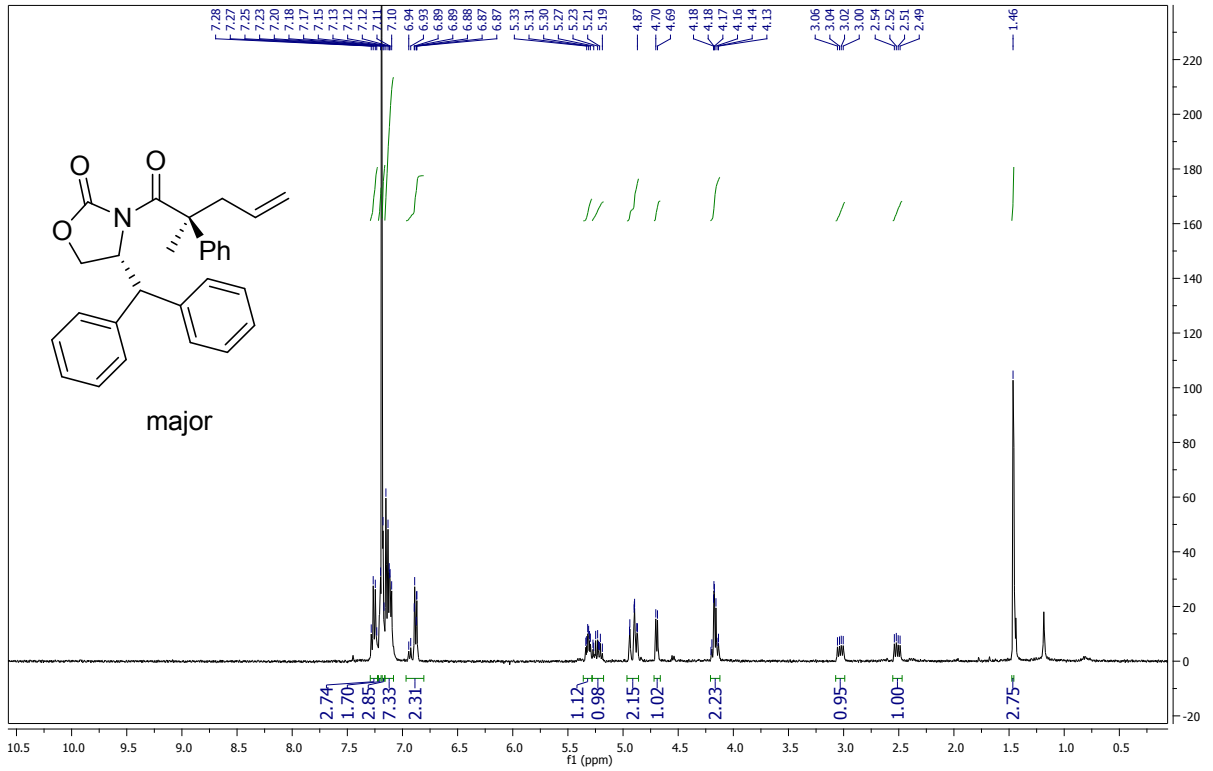

major, minor
f1 (ppm)

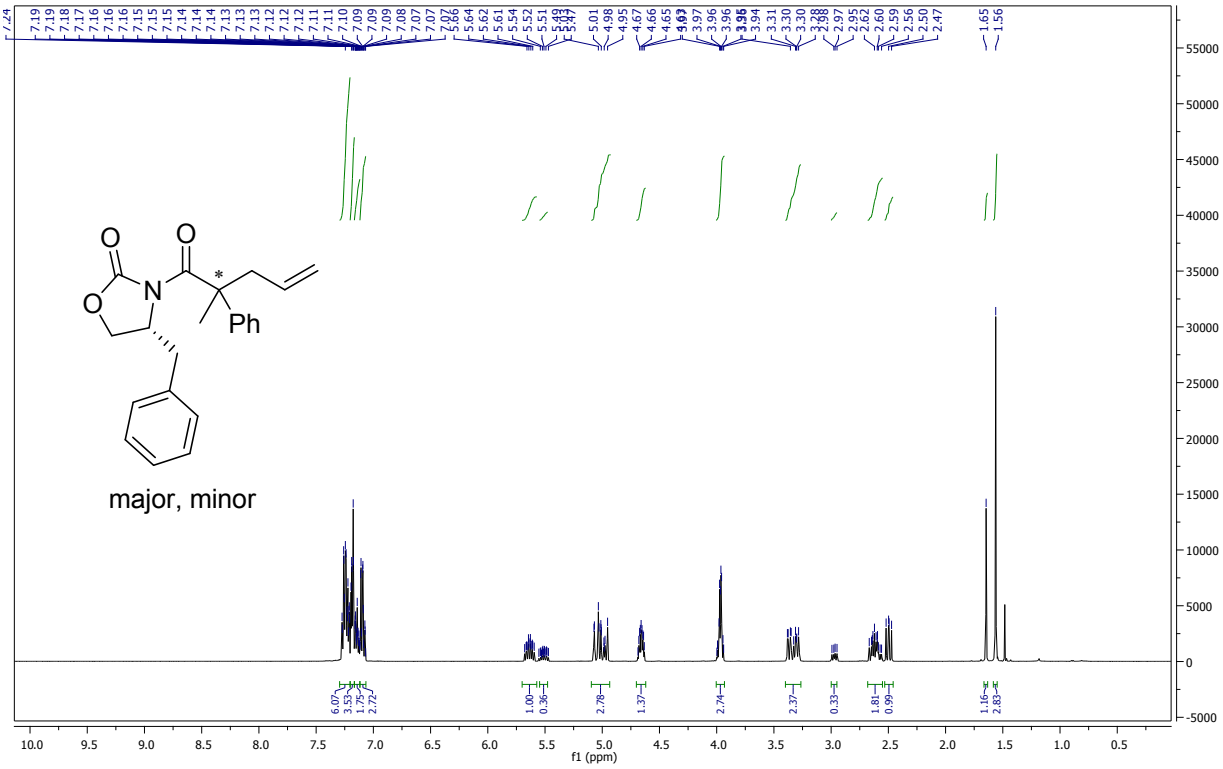

major, minor
f1 (ppm)

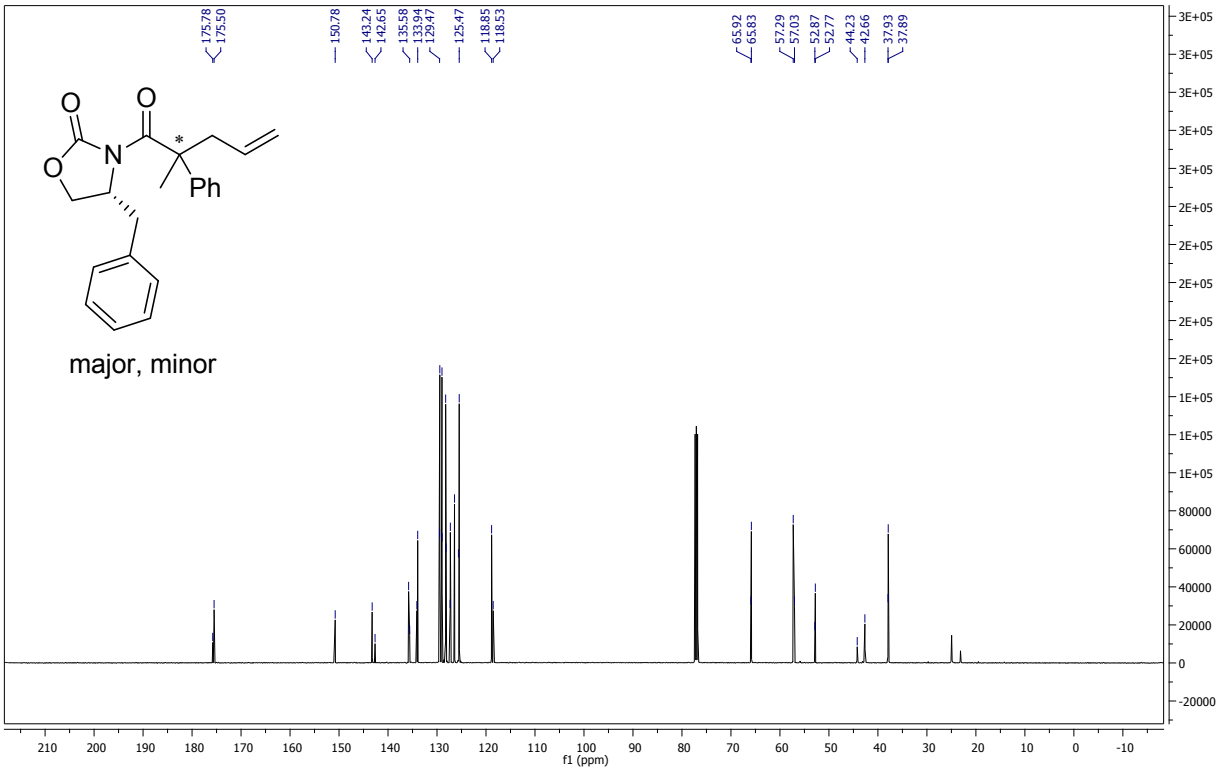

major, minor
f1 (ppm)

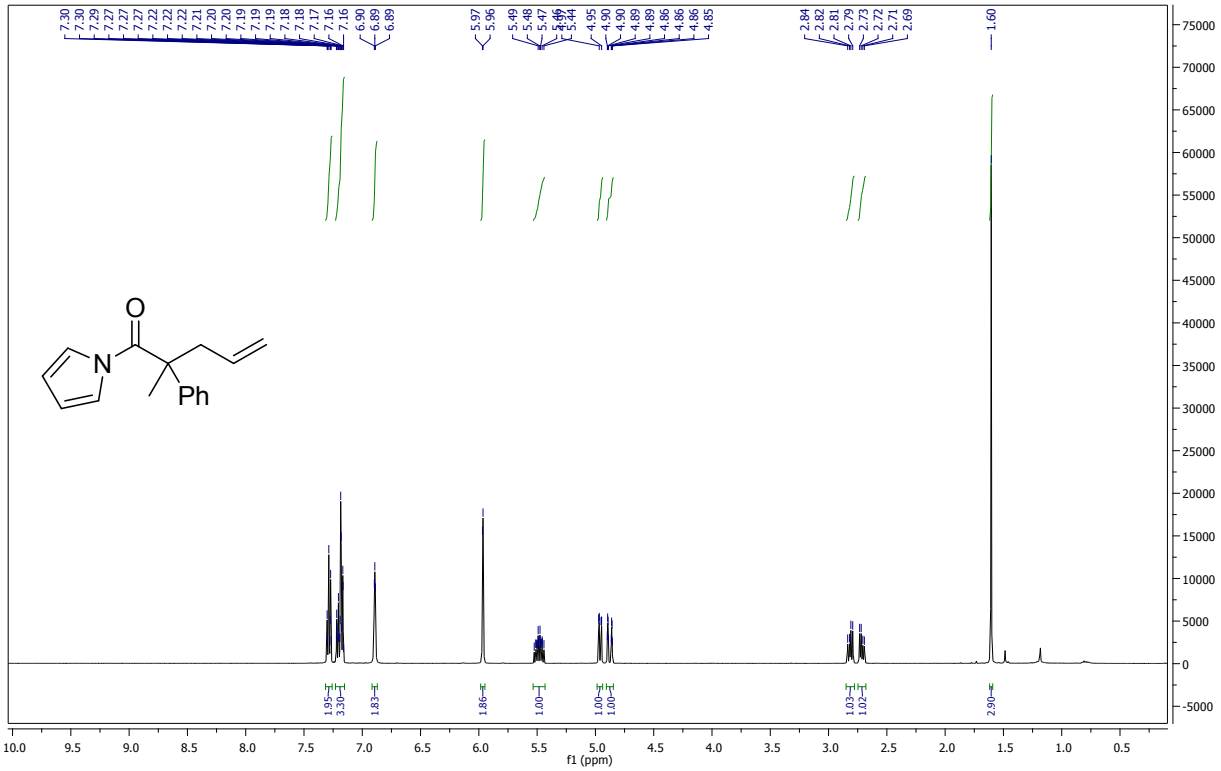

major, minor
f1 (ppm)


major, minor
f1 (ppm)


major
f1 (ppm)


major, minor
f1 (ppm)


major, minor
f1 (ppm)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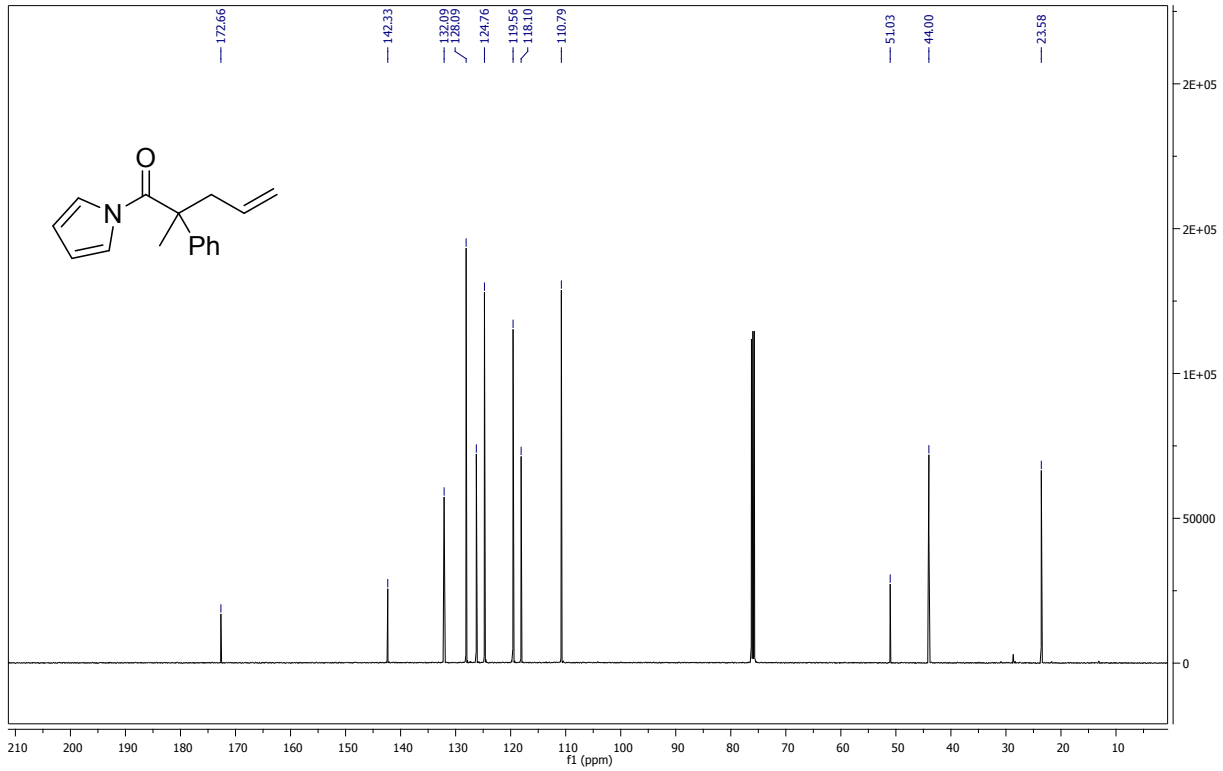
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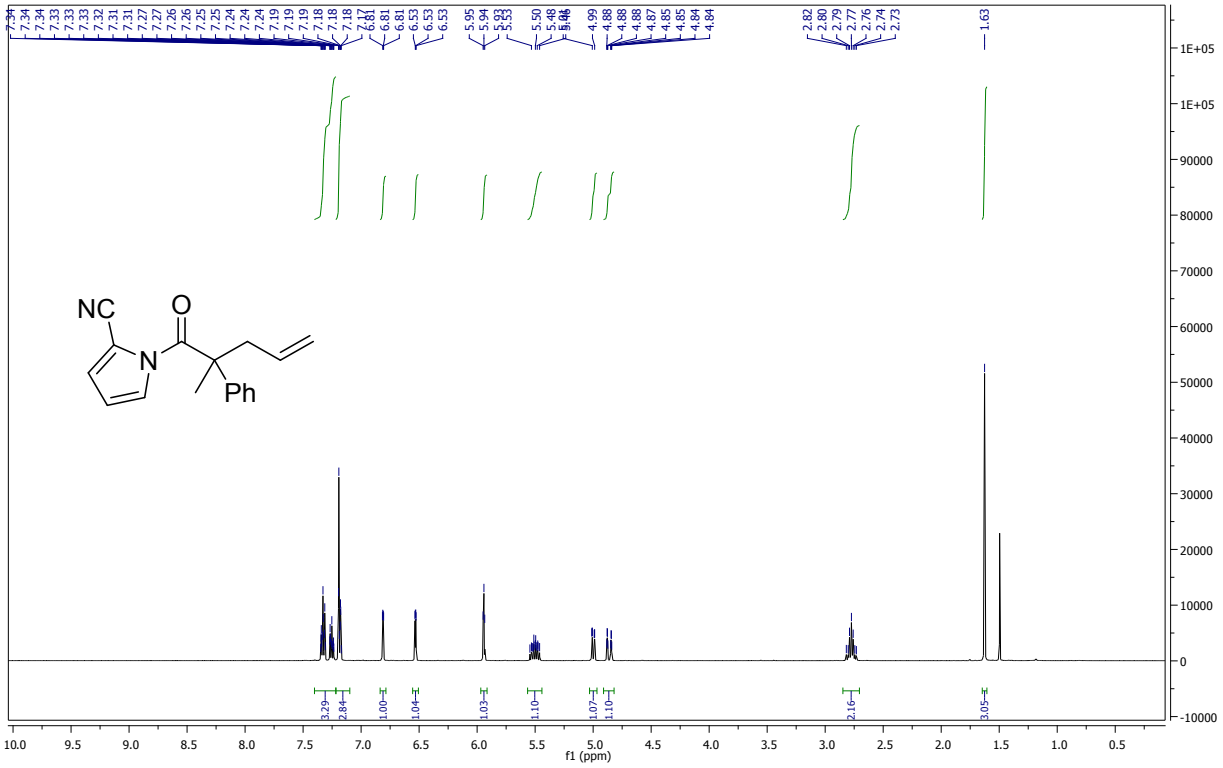
132.09
128.09
124.76
119.56
118.10
110.79
51.03
44.00
23.58
O
N
Ph
f1 (ppm)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O
N
Ph
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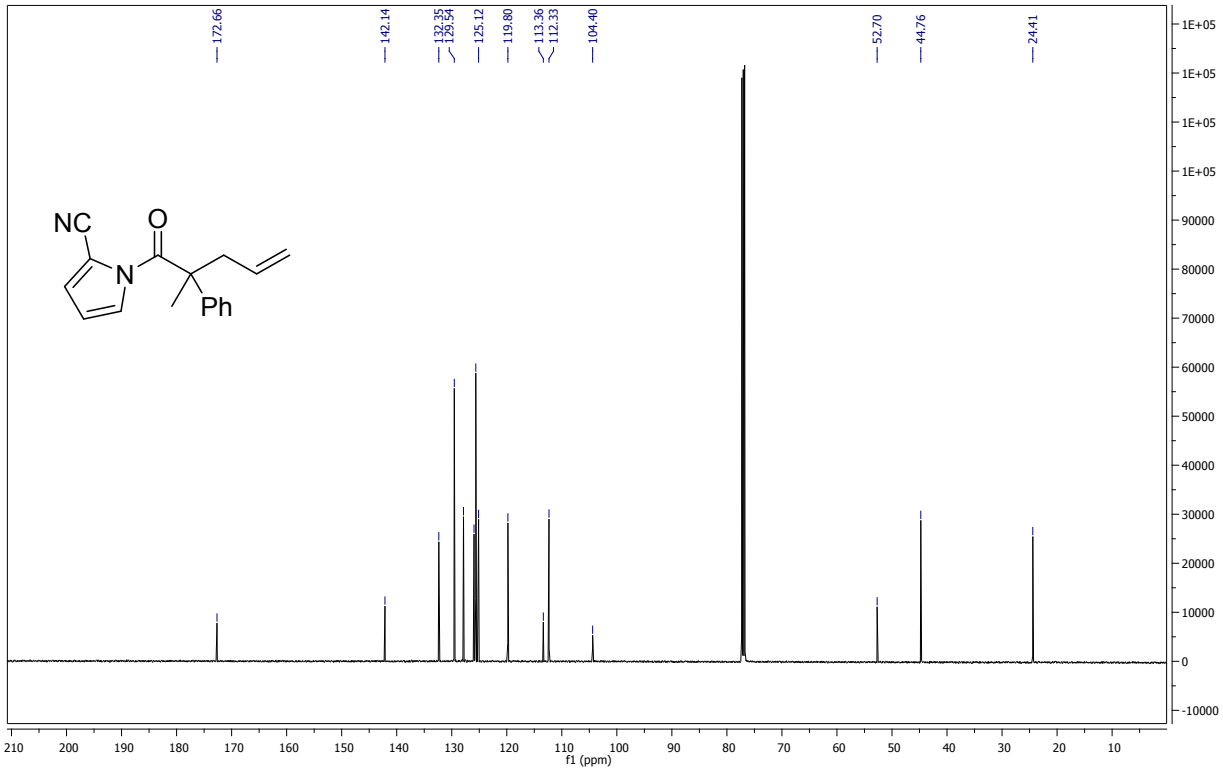
1.04
1.03
1.10
1.07
1.10
2.16
3.05
f1 (ppm)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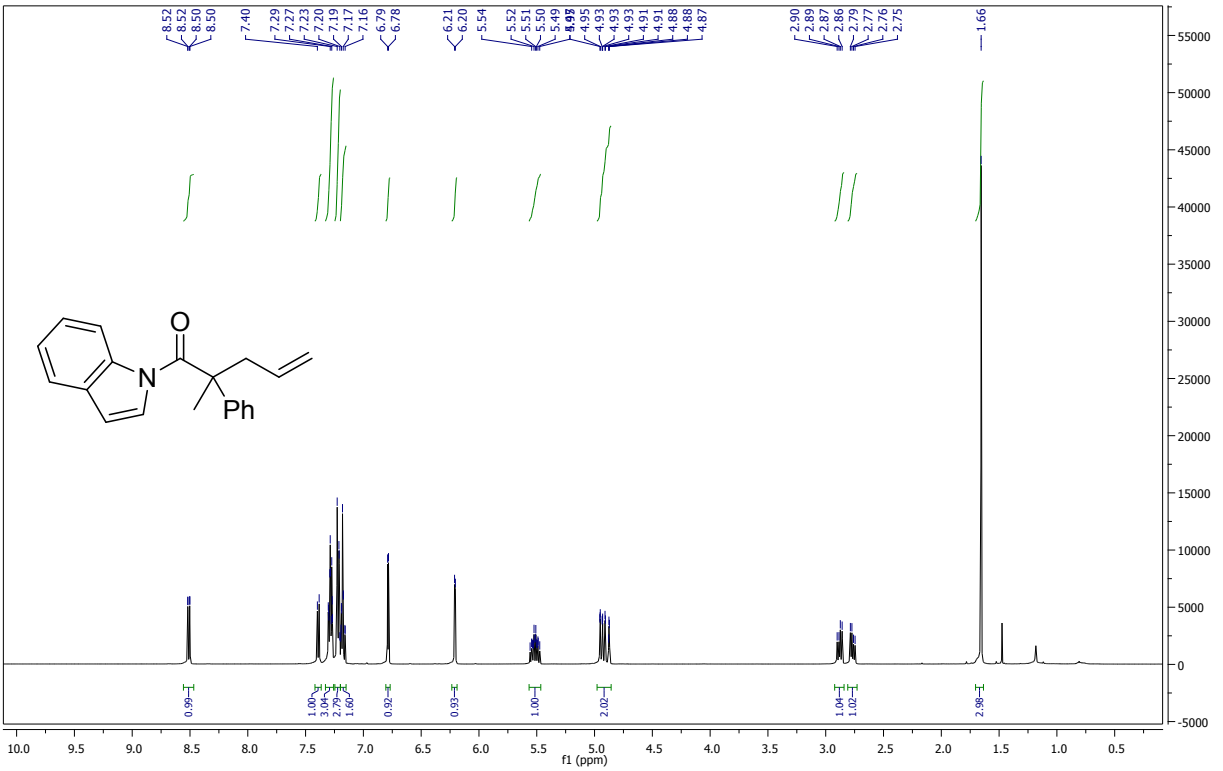
24.41
NC
O
N
Ph
f1 (ppm)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8.52
8.50
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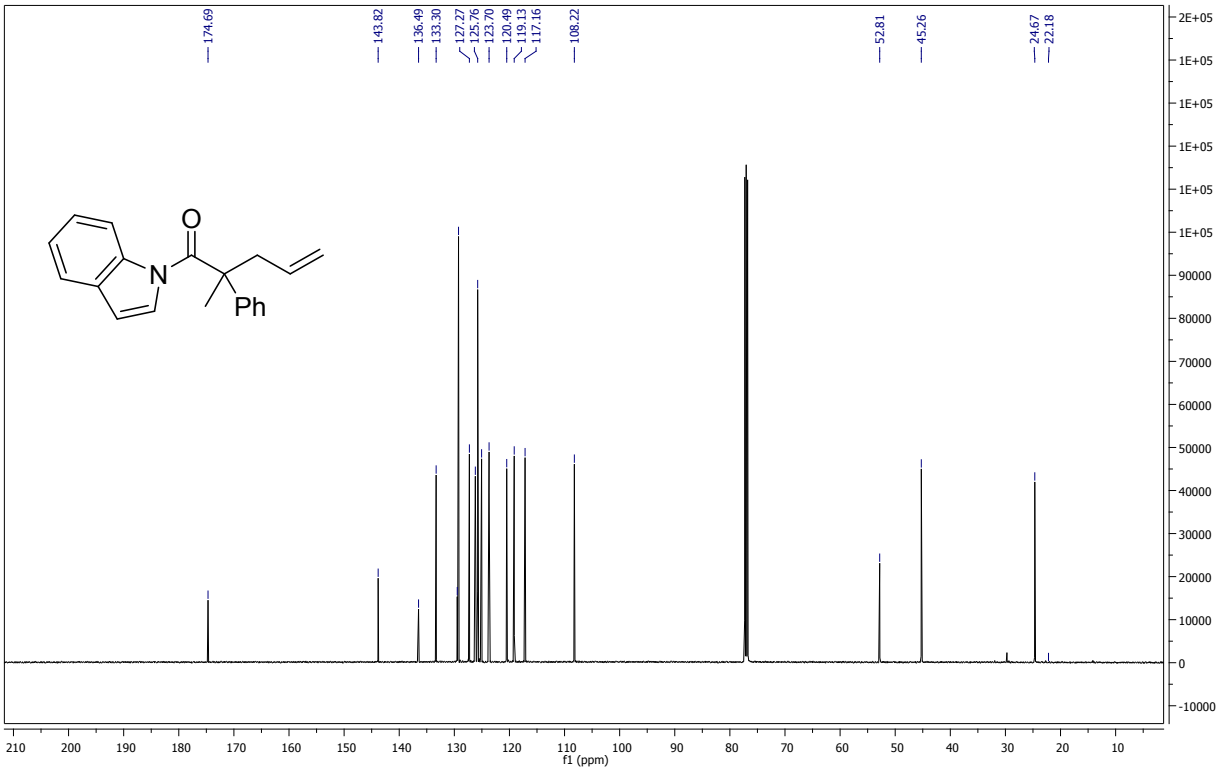
7.40
7.29
7.27
7.23
7.20
7.19
7.17
7.16
6.79
6.78
6.21
6.20
5.54
5.52
5.51
5.50
5.49
4.95
4.93
4.93
4.91
4.91
4.88
4.88
4.87
2.90
2.89
2.87
2.86
2.79
2.77
2.76
2.75
1.66
O
N
Ph
0.99
1.00
3.04
2.79
1.60
0.92
0.93
1.00
2.02
1.04
1.02
2.98
f1 (ppm)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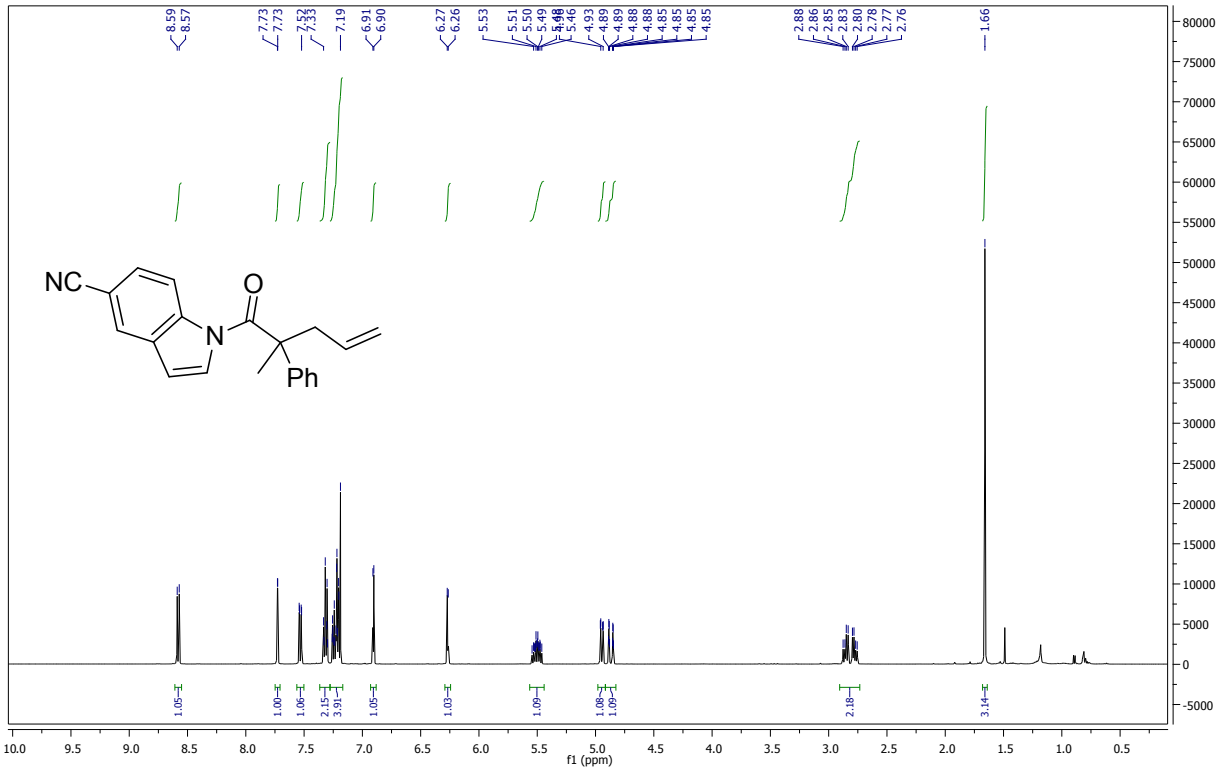
133.30
127.27
125.76
123.70
120.49
119.13
117.16
108.22
52.81
45.26
24.67
22.18
O
N
Ph
f1 (ppm)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8.57
7.73
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7.52
7.33
7.19
6.91
6.90
6.27
6.26
5.53
5.51
5.50
5.49
5.46
4.93
4.89
4.89
4.88
4.88
4.85
4.85
4.85
4.85
2.88
2.86
2.85
2.83
2.80
2.78
2.77
2.76
1.66
NC
O
N
Ph
1.05
1.00
1.06
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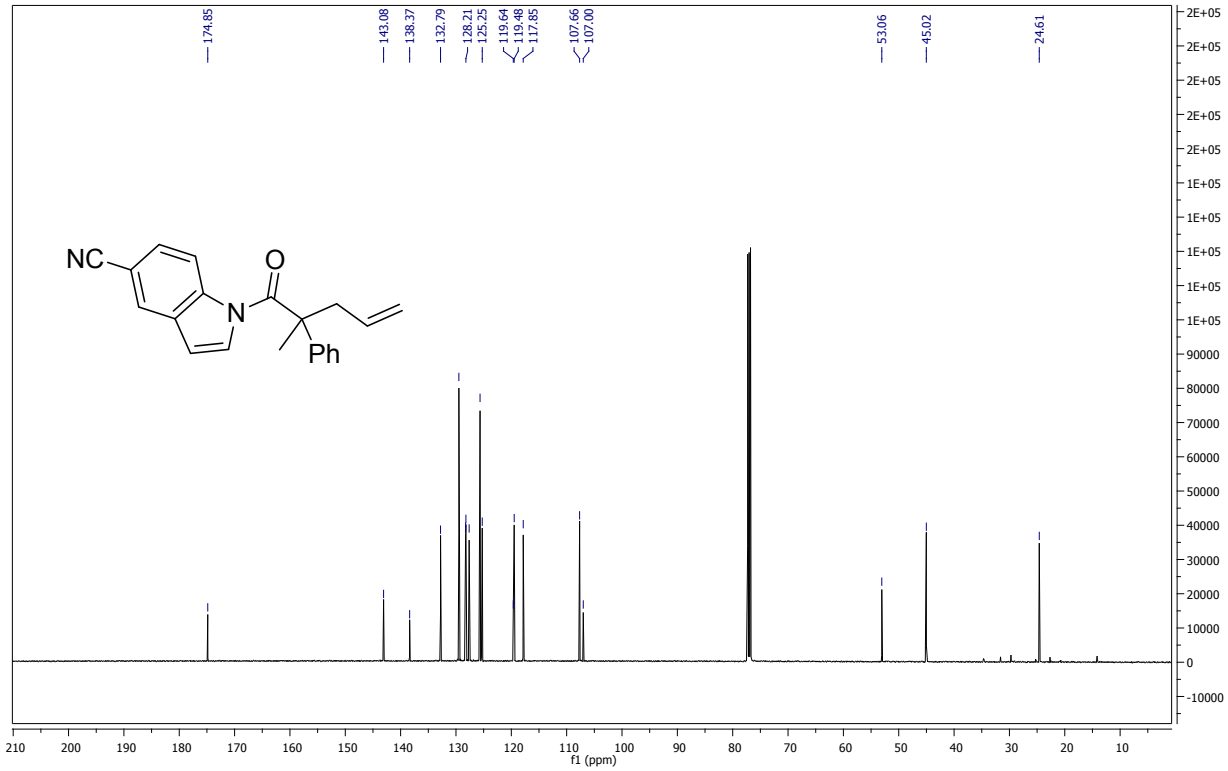
3.91
1.05
1.03
1.09
1.08
1.09
2.18
3.14
f1 (ppm)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143.08
138.37
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128.21
125.25
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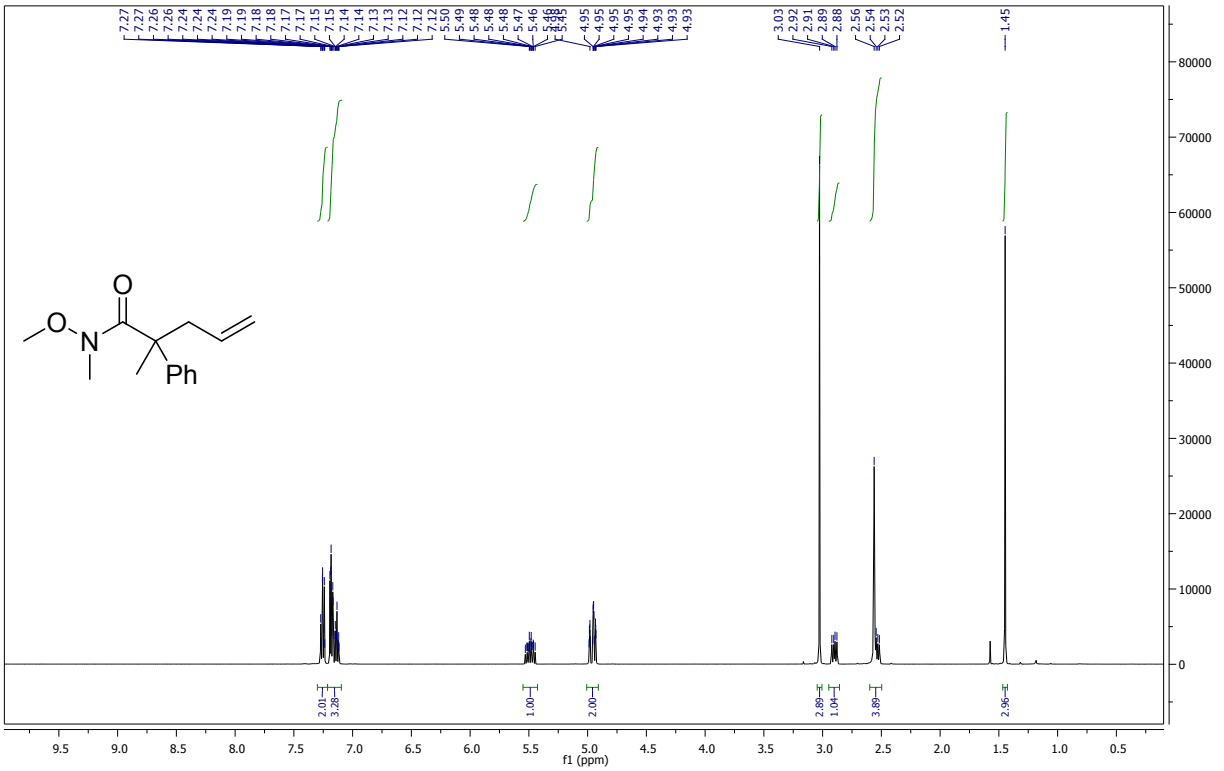
107.66
107.00
53.06
45.02
24.61
NC
O
N
Ph
f1 (ppm)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7.17
7.15
7.14
7.13
7.12
5.50
5.49
5.48
5.47
5.46
4.95
4.94
4.93
3.03
2.92
2.91
2.89
2.88
2.56
2.54
2.53
2.52
1.45
O
O
N
Ph
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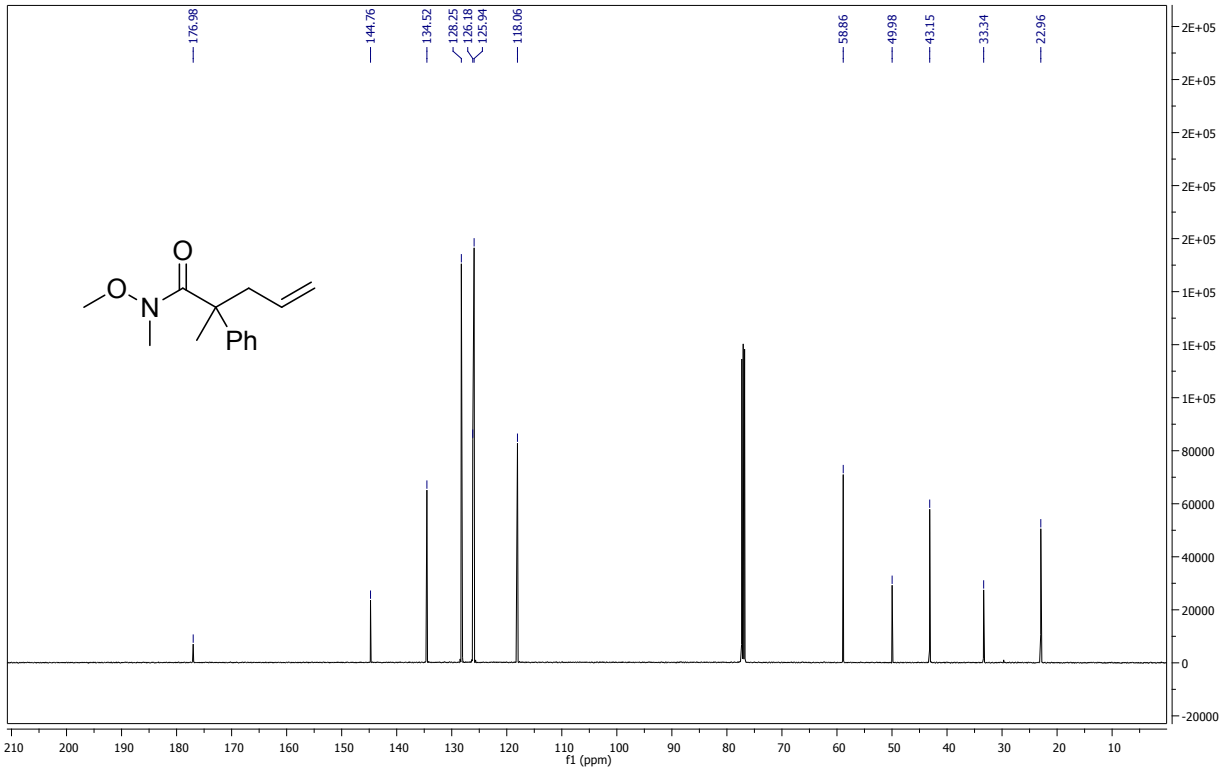
3.28
1.00
2.00
2.89
1.04
3.89
2.96
f1 (ppm)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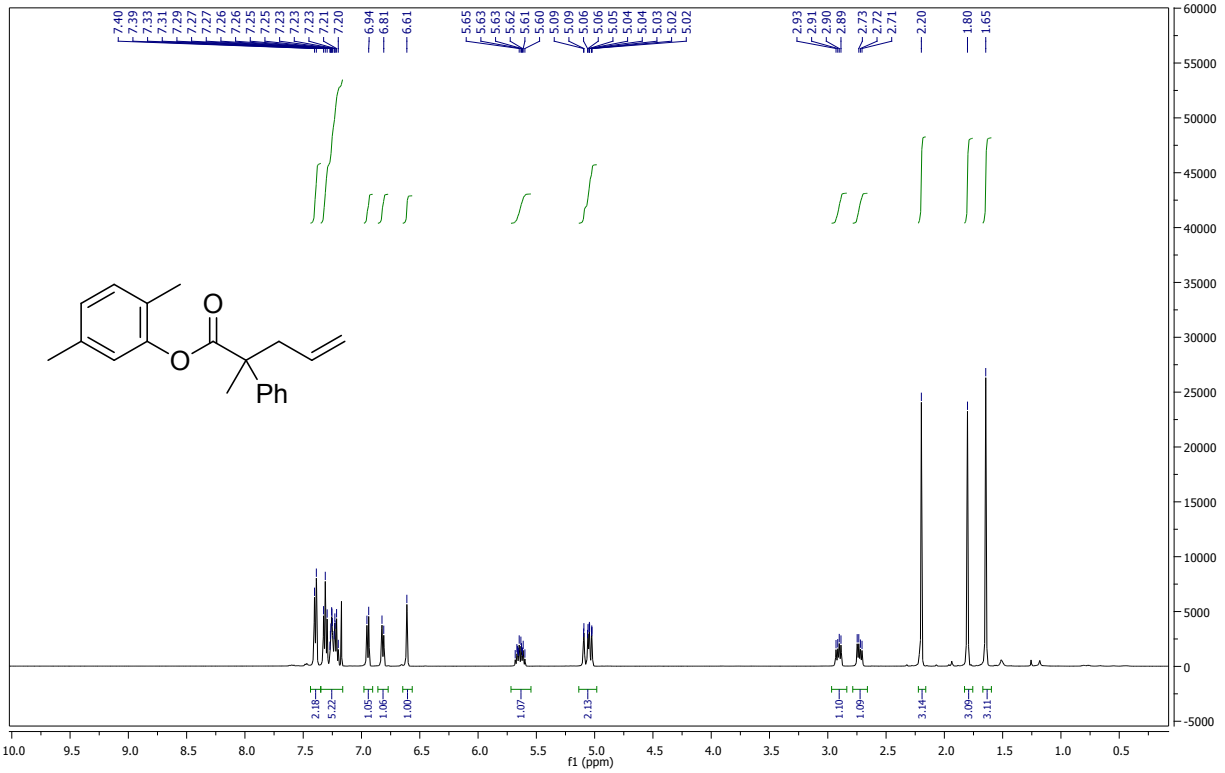
144.76
134.52
128.25
126.18
125.94
118.06
58.86
49.98
43.15
33.34
22.96
O
O
N
Ph
f1 (ppm)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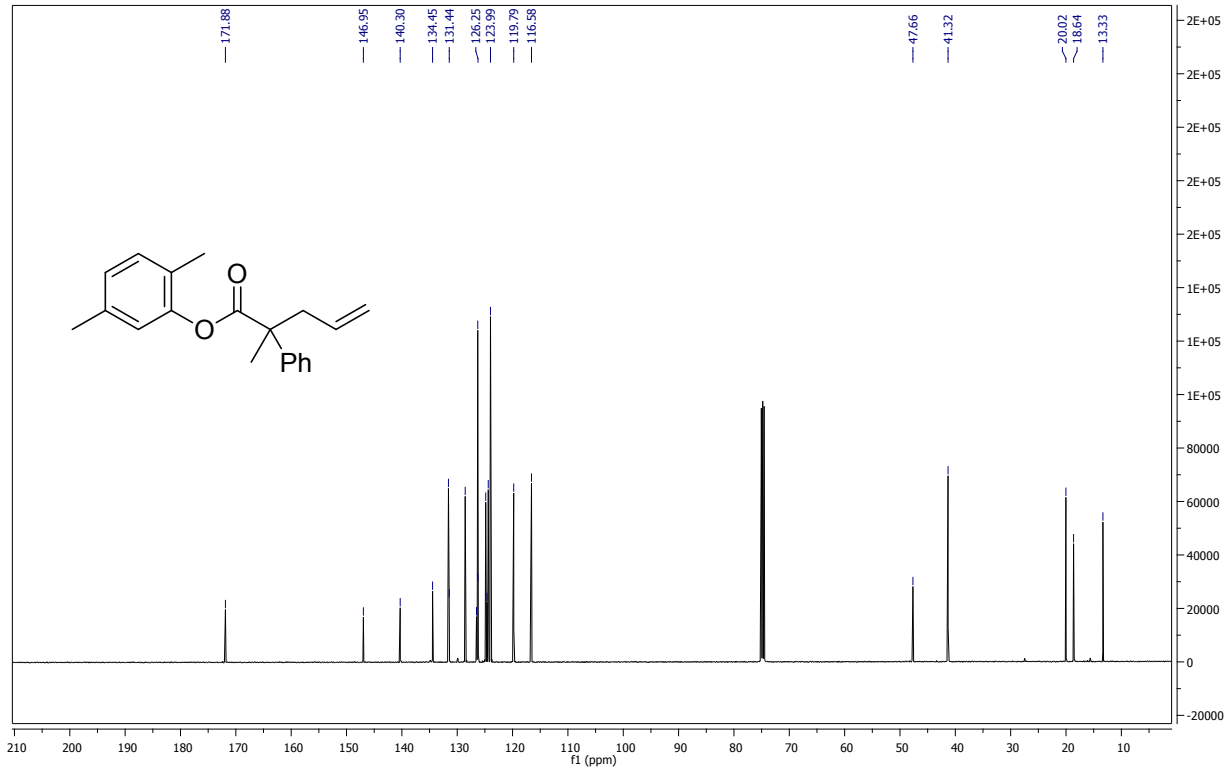
7.23
7.23
7.21
7.20
6.94
6.81
6.61
5.65
5.63
5.63
5.62
5.61
5.60
5.09
5.09
5.06
5.06
5.05
5.04
5.04
5.03
5.02
5.02
2.93
2.91
2.90
2.89
2.73
2.72
2.71
2.20
1.80
1.65
O
O
Ph
2.18
5.22
1.05
1.06
1.00
1.07
2.13
1.10
1.09
3.14
3.09
3.11
f1 (ppm)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41.32
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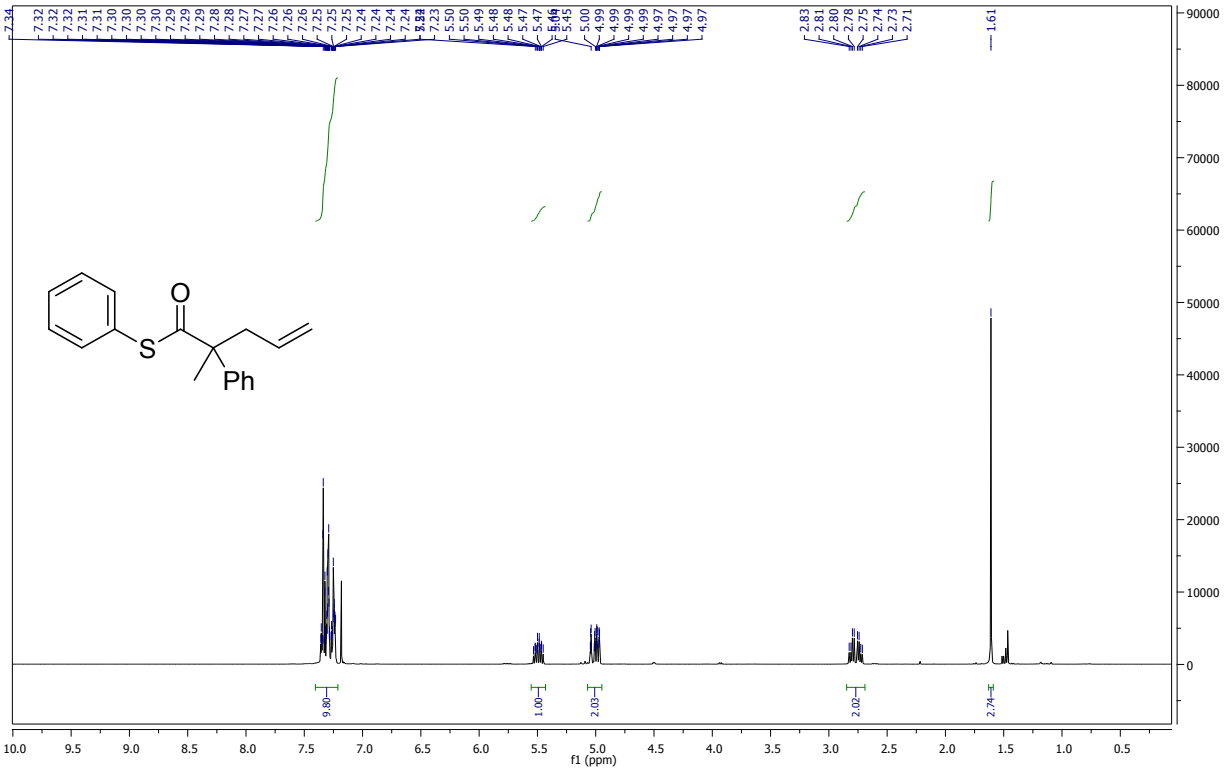
13.33
O
O
Ph
f1 (ppm)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S
Ph
9.80
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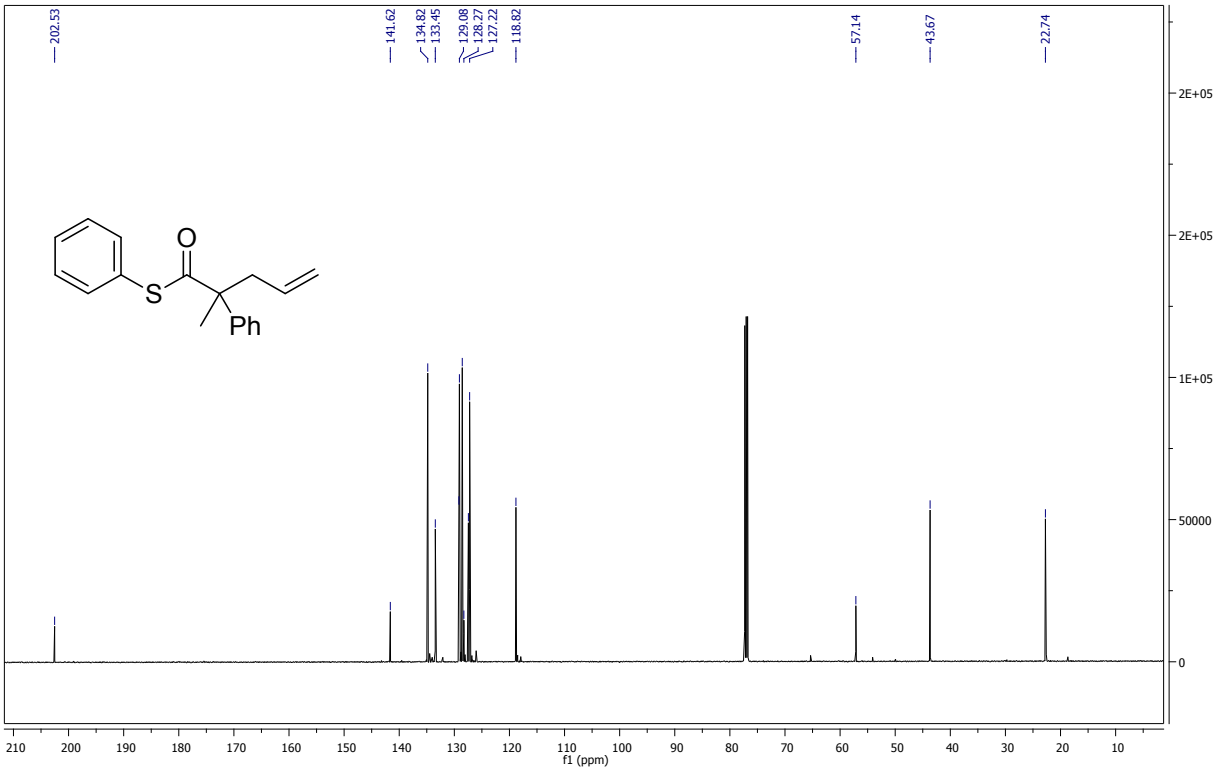
2.74
f1 (ppm)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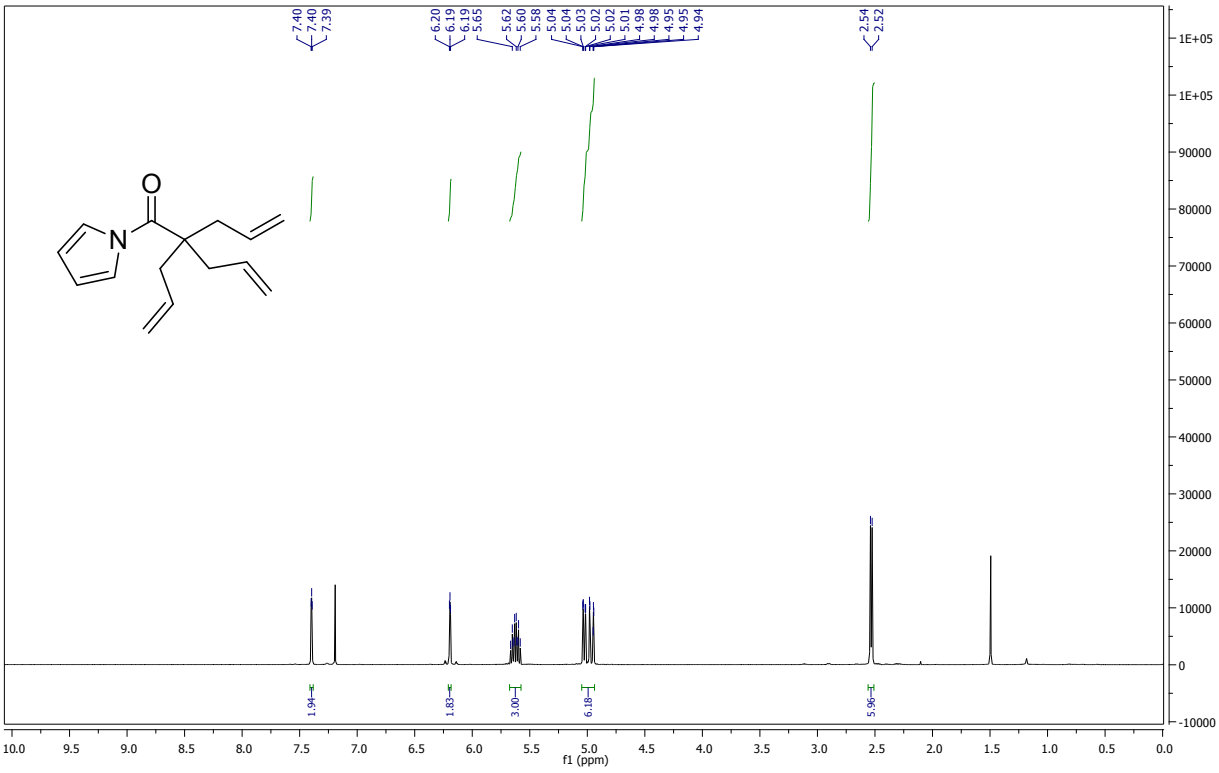
118.82
57.14
43.67
22.74
O
S
Ph
f1 (ppm)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5.62
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5.58
5.04
5.04
5.03
5.02
5.02
5.01
4.98
4.98
4.95
4.95
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2.54
2.52
O
N
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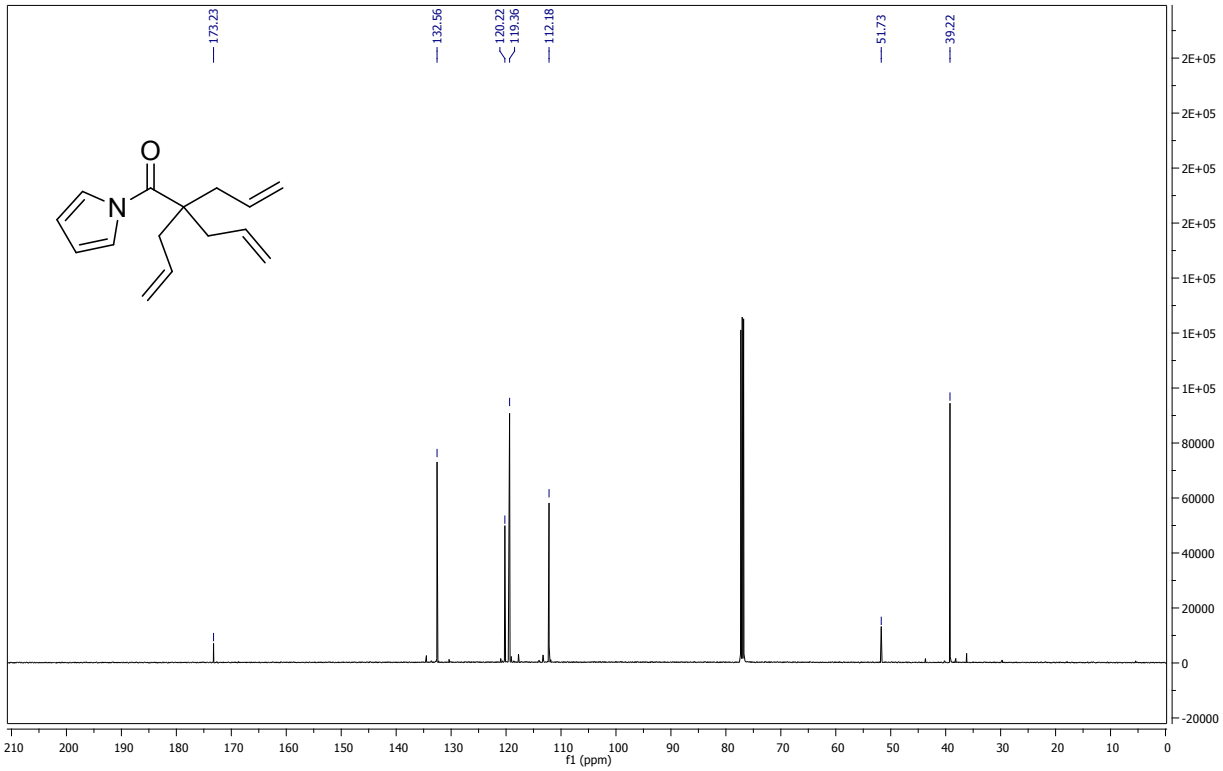
1.83
3.00
6.18
5.96
f1 (ppm)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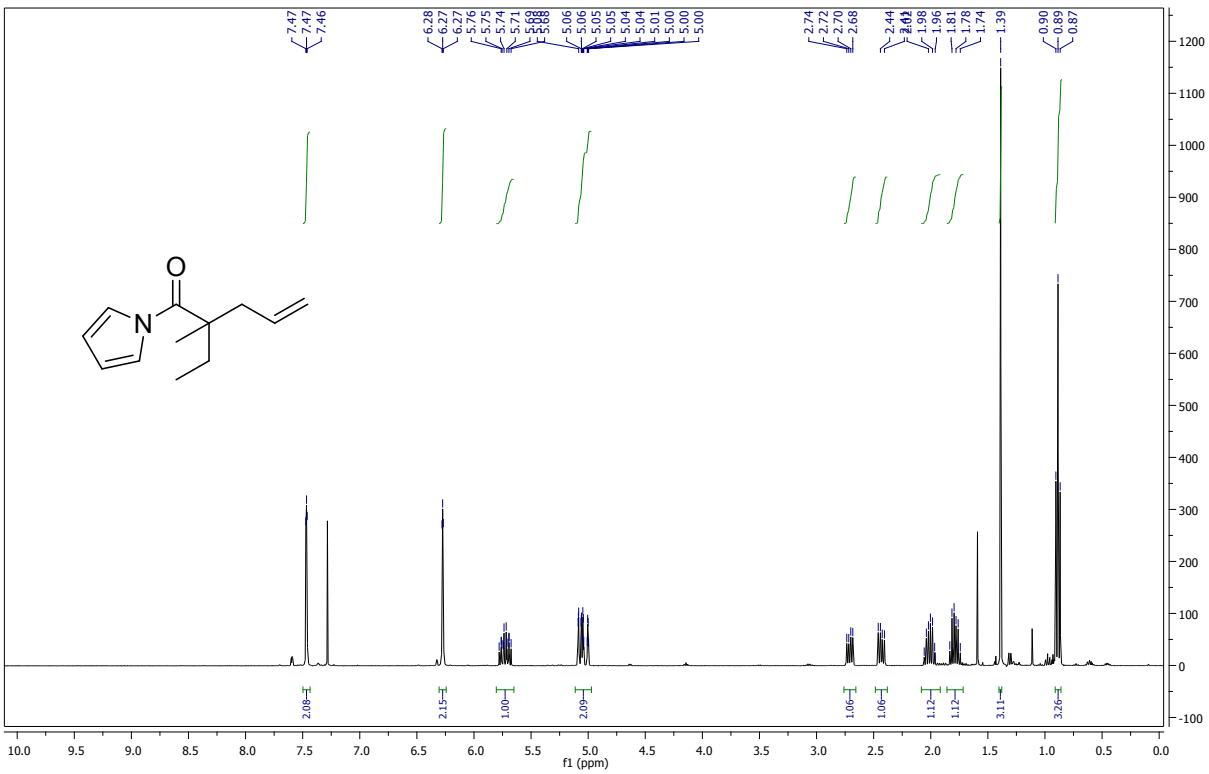
119.36
112.18
51.73
39.22
O
N
f1 (ppm)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5.06
5.06
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5.05
5.04
5.04
5.01
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5.00
5.00
2.74
2.72
2.70
2.68
1.96
1.81
1.78
1.74
1.39
0.90
0.89
0.87
2.08
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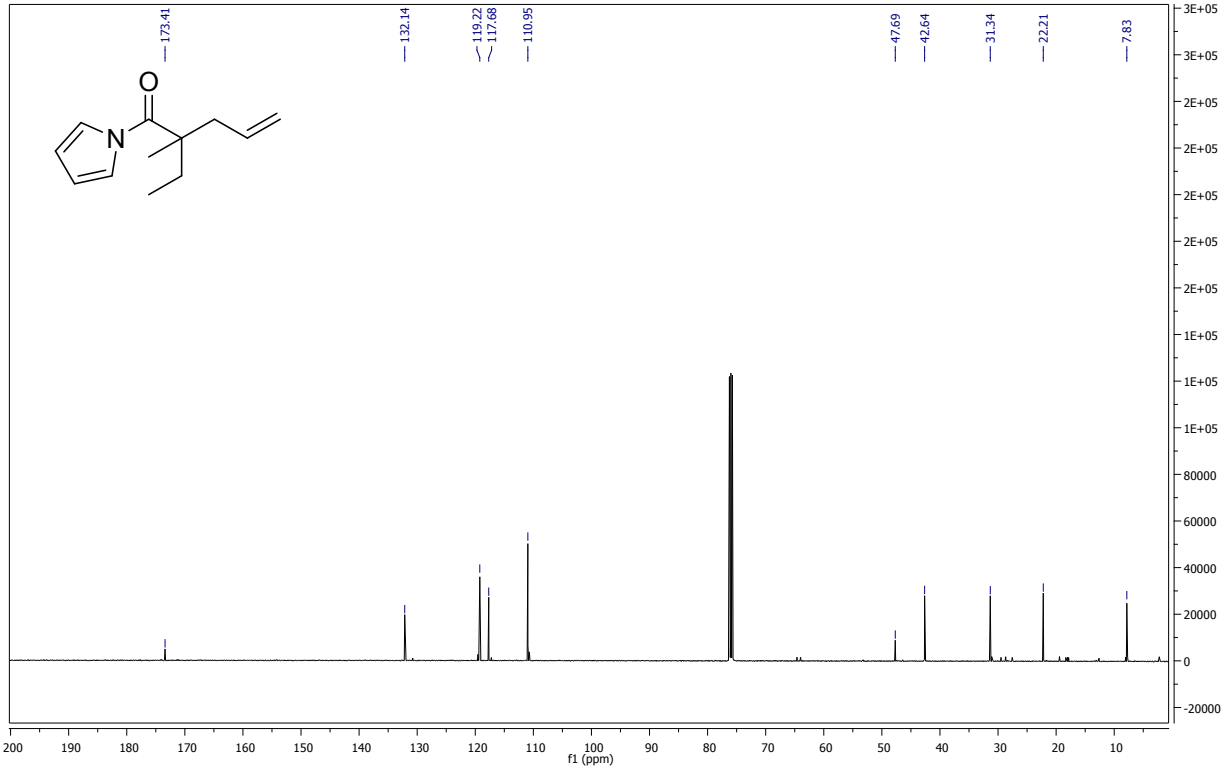
2.09
1.06
1.06
1.12
1.12
3.11
3.26
O
N
f1 (ppm)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22.21
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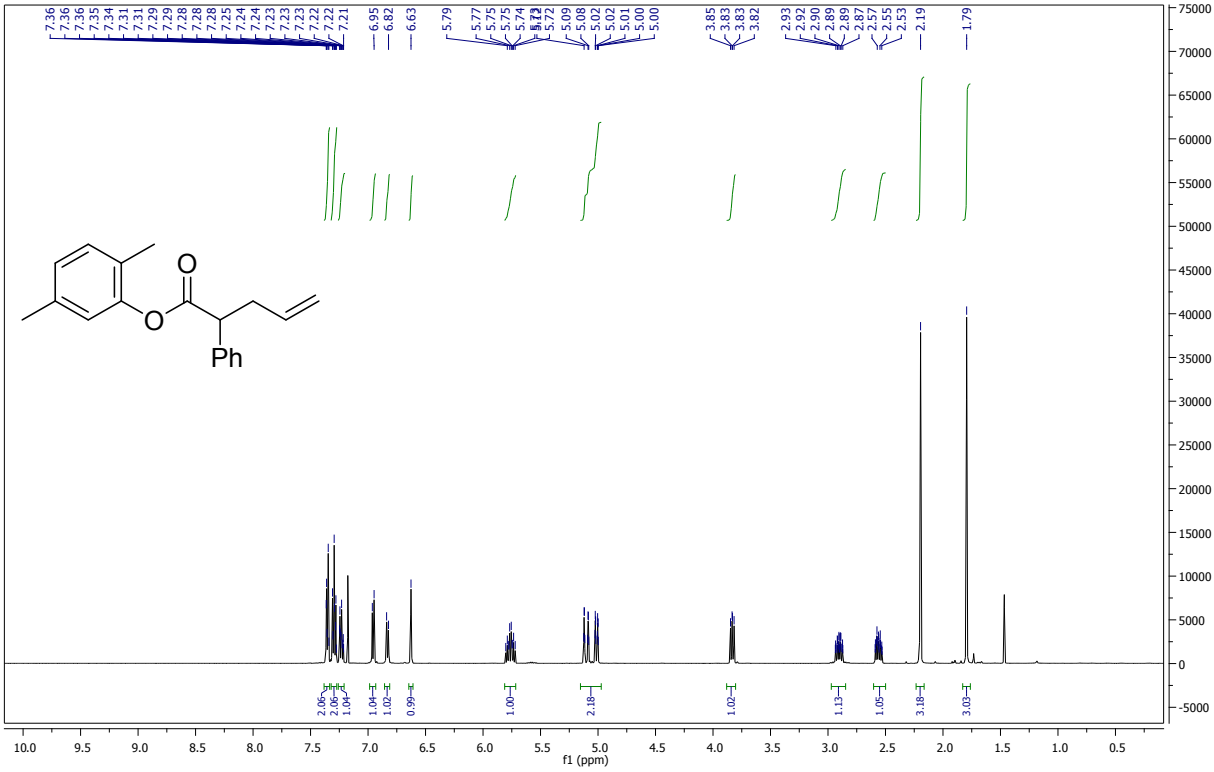
N
f1 (ppm)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7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
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6.82
6.63
5.79
5.77
5.75
5.75
5.74
5.72
5.09
5.08
5.02
5.02
5.01
5.00
5.00
3.85
3.83
3.83
3.82
2.93
2.92
2.90
2.89
2.89
2.87
2.57
2.55
2.53
2.19
1.79
O
O
Ph
2.06
2.06
1.04
1.04
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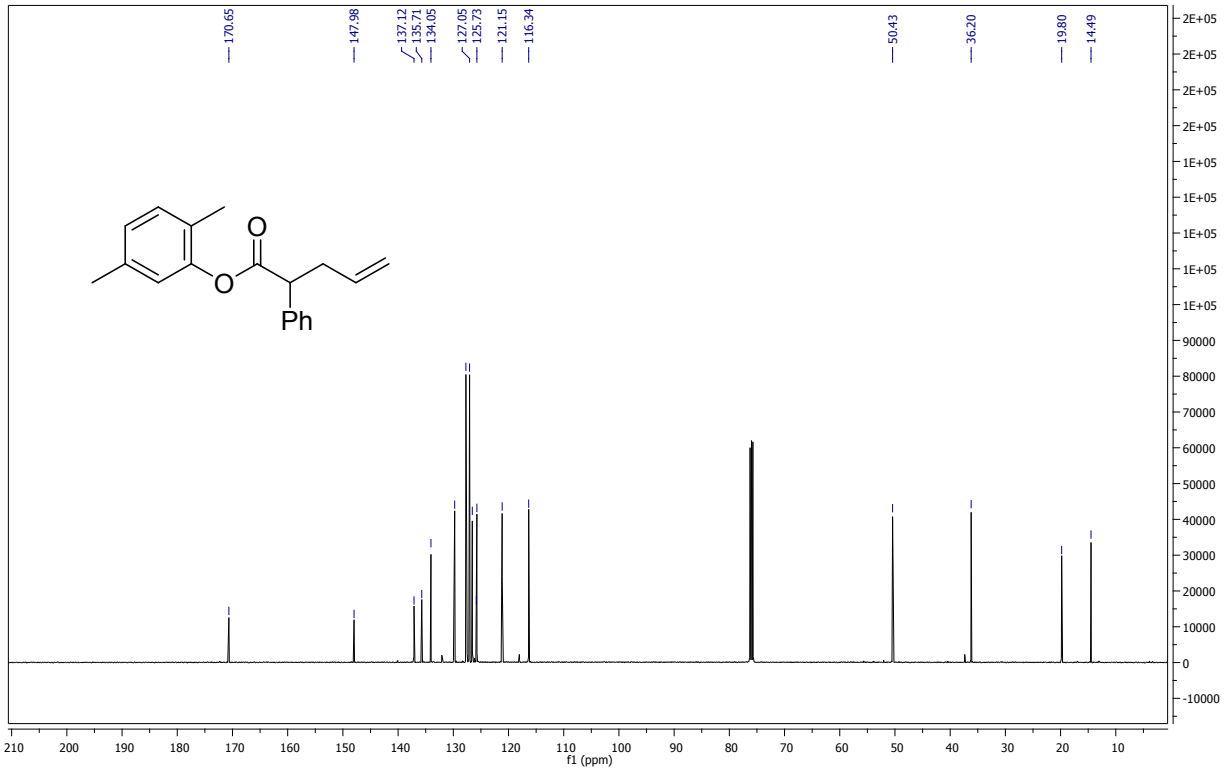
1.00
2.18
1.02
1.13
1.05
3.18
3.03
f1 (ppm)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116.34
50.43
36.20
19.80
14.49
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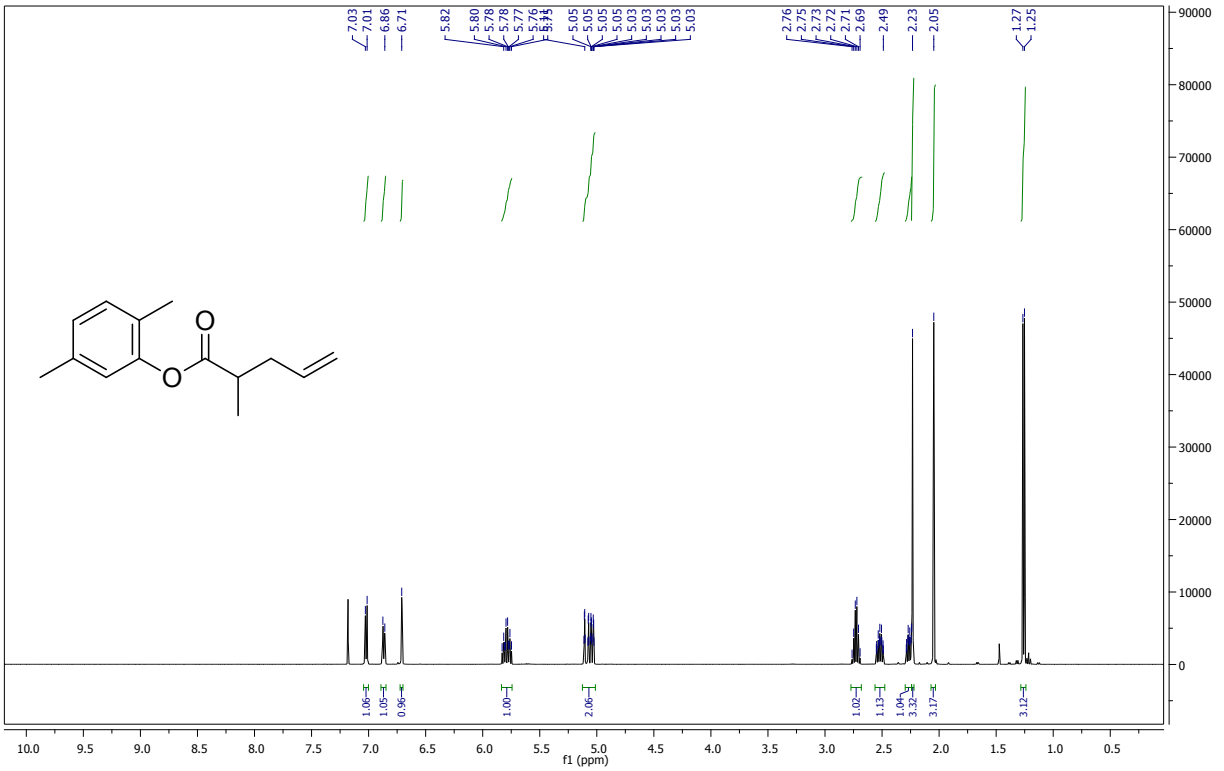
O
Ph
f1 (ppm)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5.03
2.76
2.75
2.73
2.72
2.71
2.69
2.49
2.23
2.05
1.27
1.25
1.06
1.05
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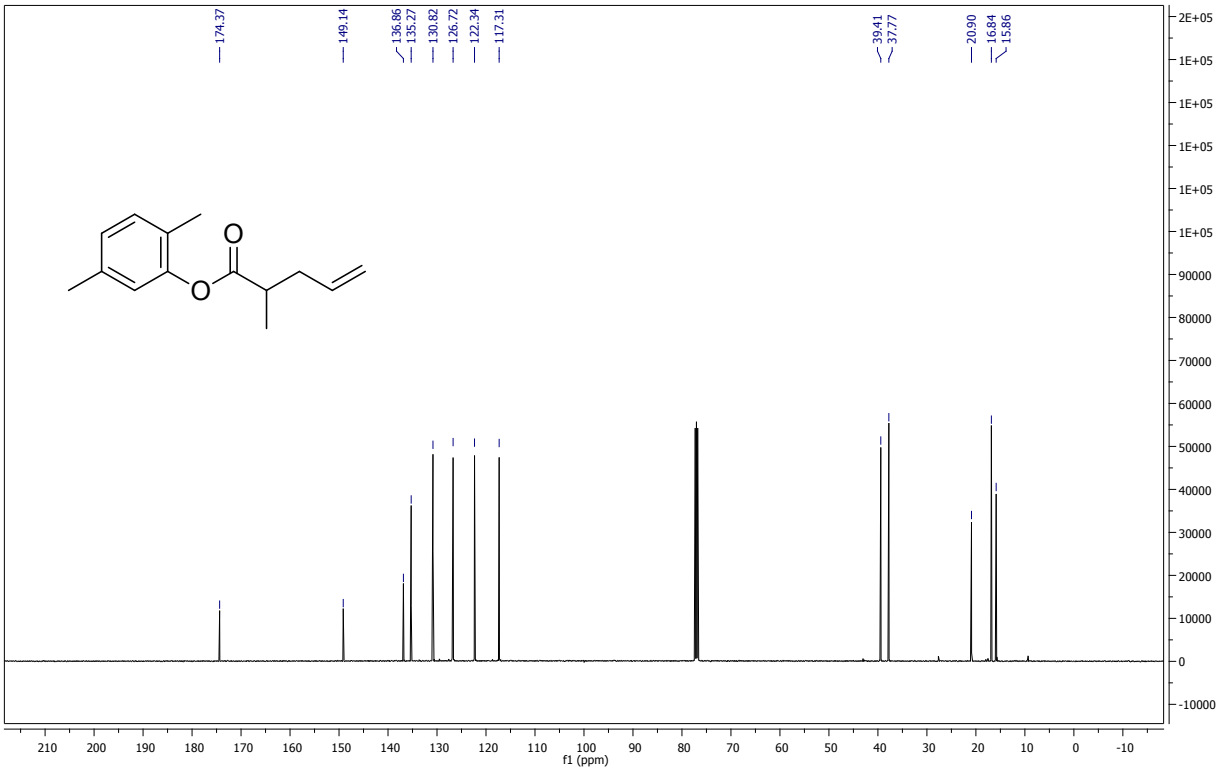
2.06
1.02
1.13
1.04
3.32
3.17
3.12
O
O
f1 (ppm)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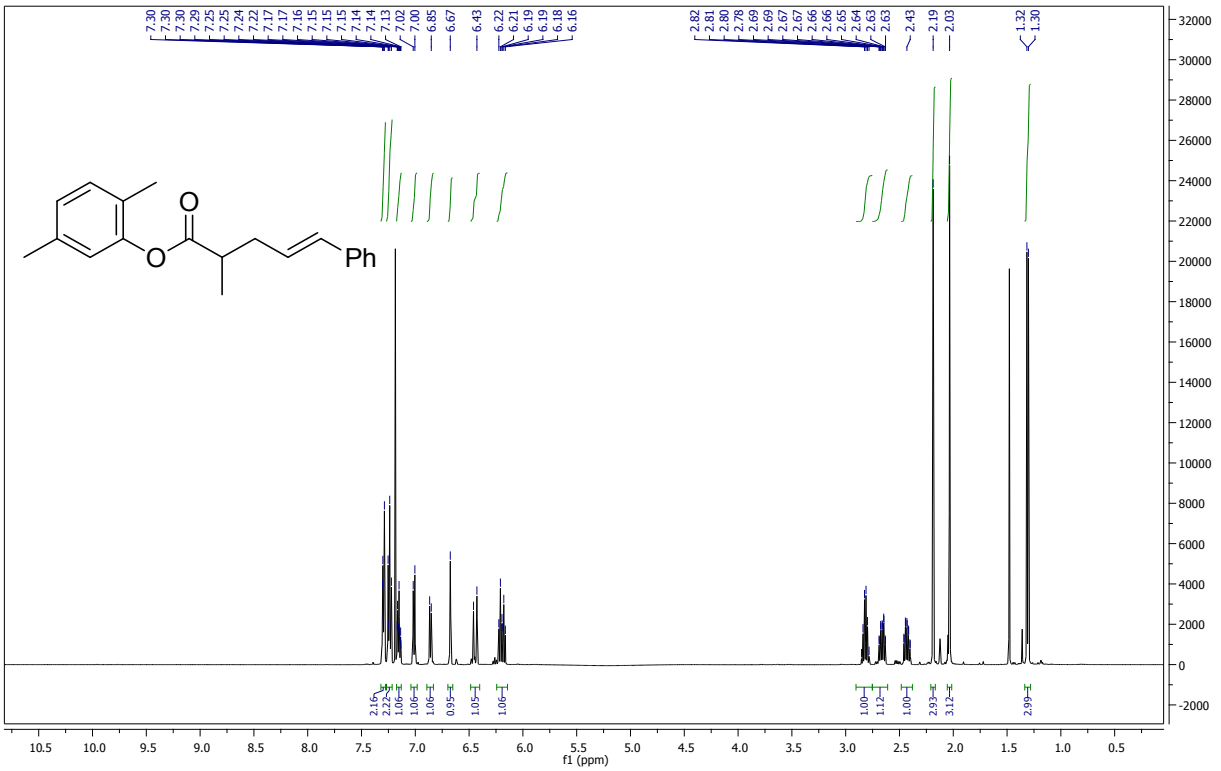
16.84
15.86
O
O
f1 (ppm)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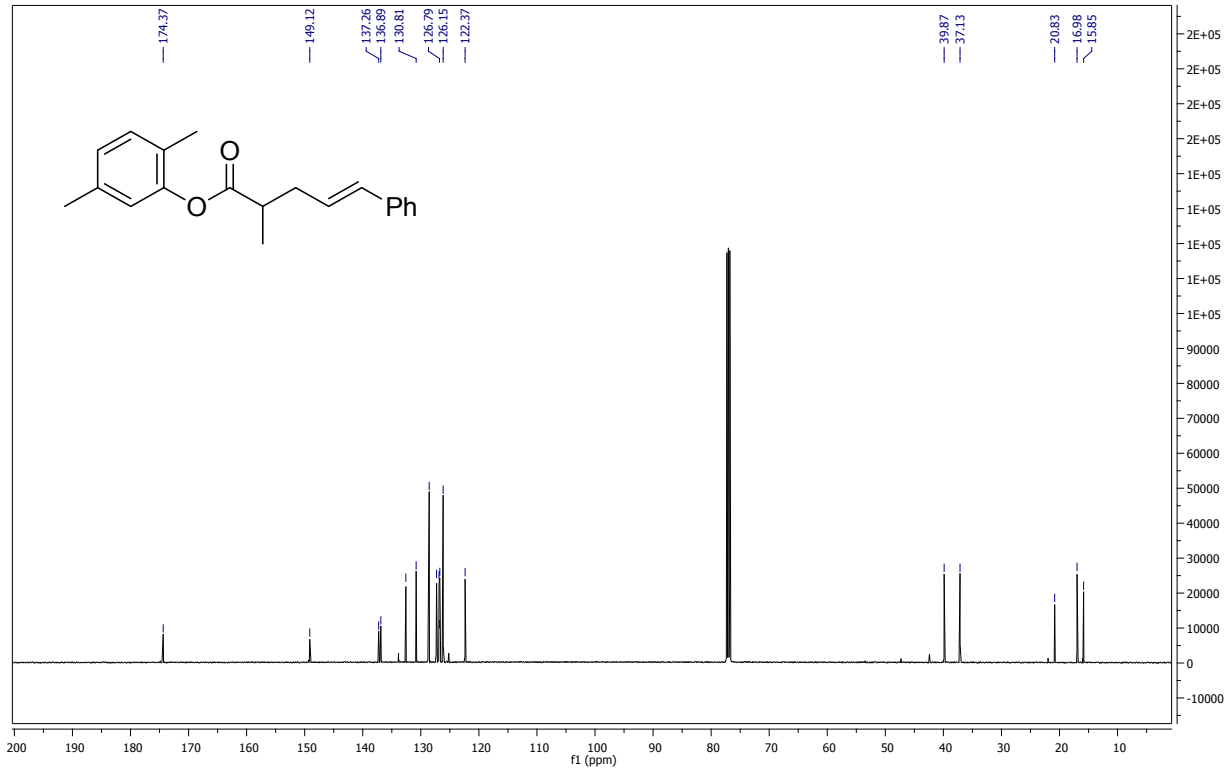
O
Ph
f1 (ppm)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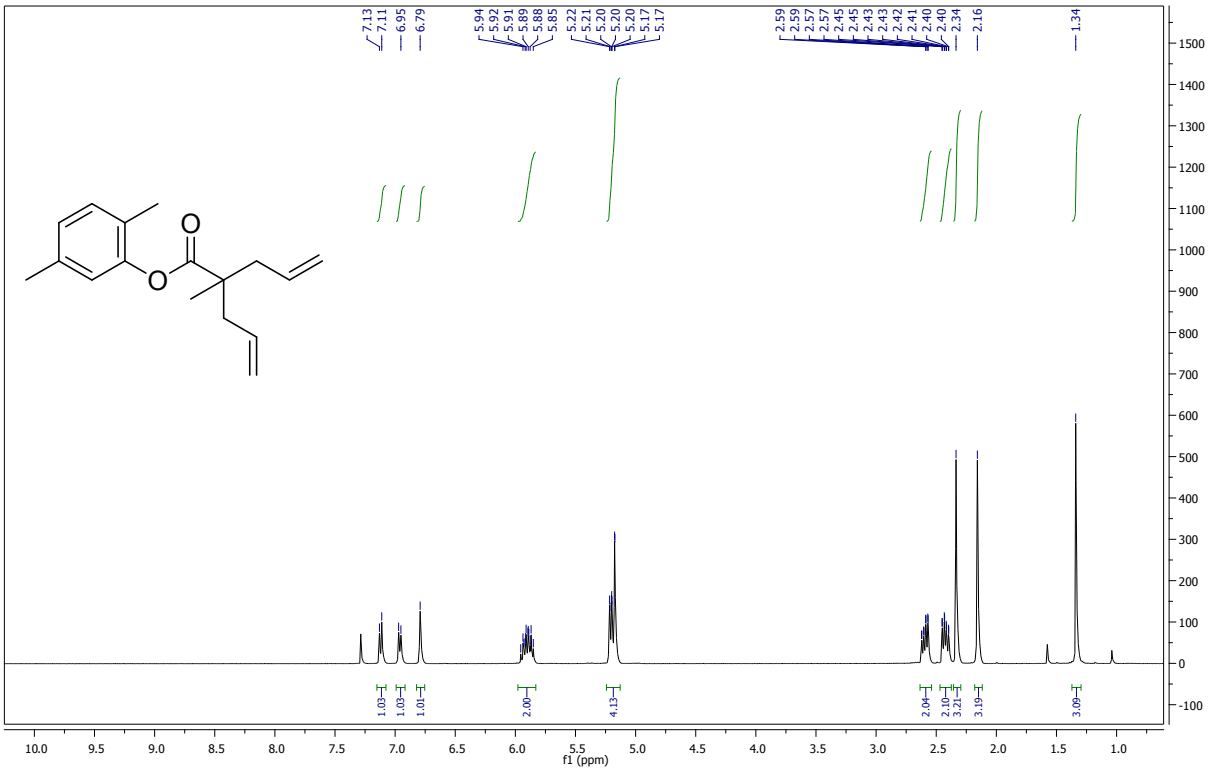
122.37
39.87
37.13
20.83
16.98
15.85
O
O
Ph
f1 (ppm)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5.85
5.22
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5.20
5.20
5.20
5.17
5.17
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2.59
2.57
2.57
2.45
2.45
2.43
2.43
2.42
2.41
2.40
2.40
2.34
2.16
1.34
1.03
1.03
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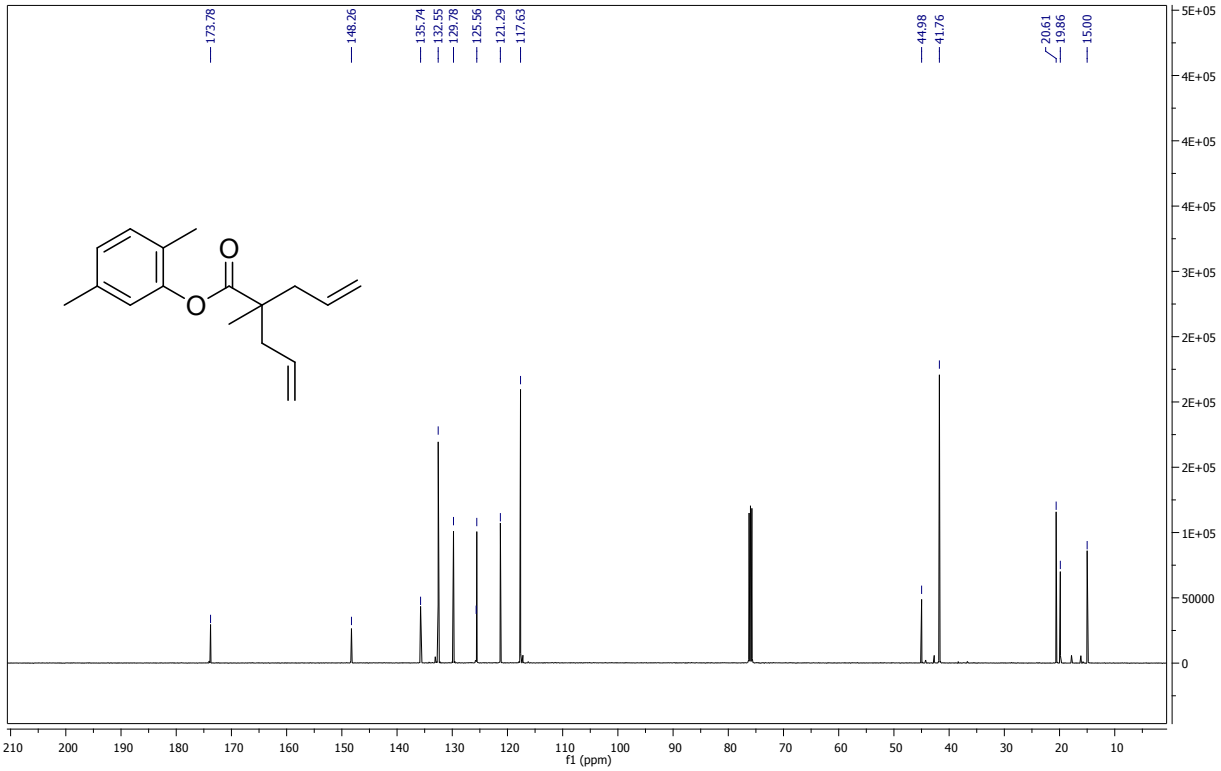
2.00
4.13
2.04
2.10
3.21
3.19
3.09
O
O
f1 (ppm)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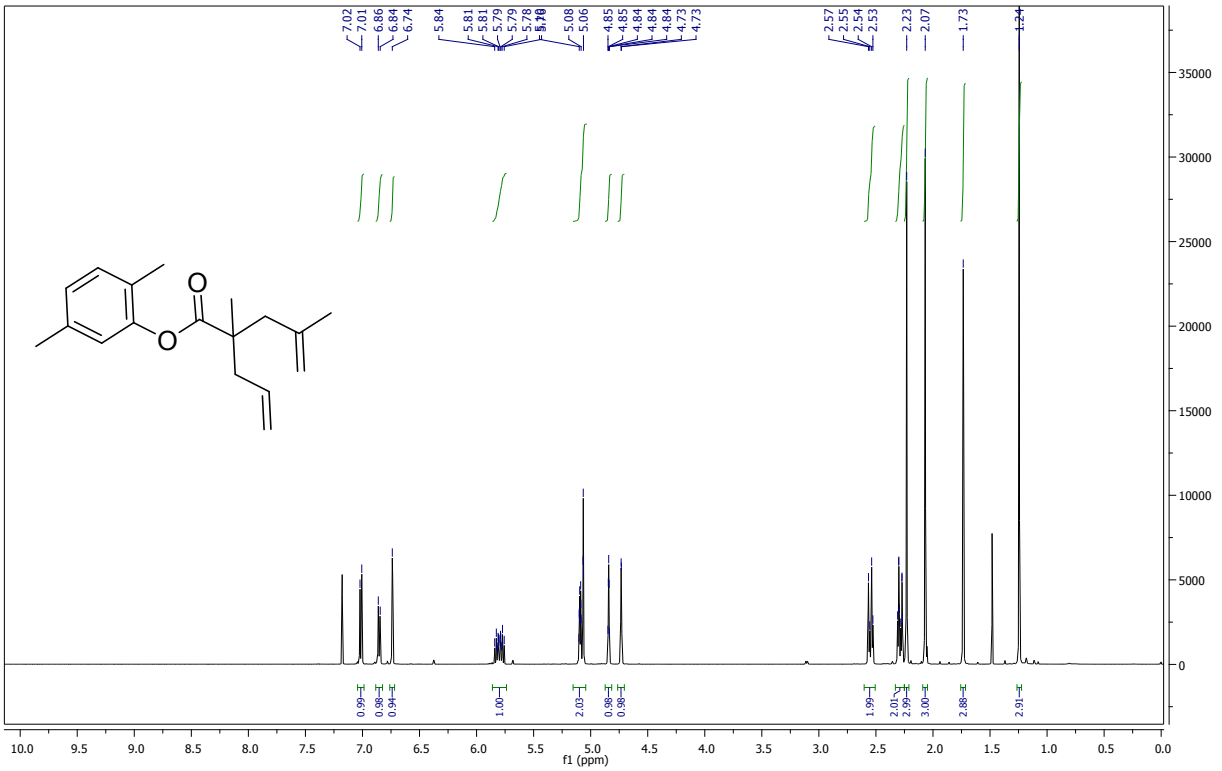
20.61
19.86
15.00
f1 (ppm)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5.84
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5.81
5.79
5.79
5.78
5.08
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4.84
4.73
4.73
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2.55
2.54
2.53
2.23
2.07
1.73
1.24
0.99
0.98
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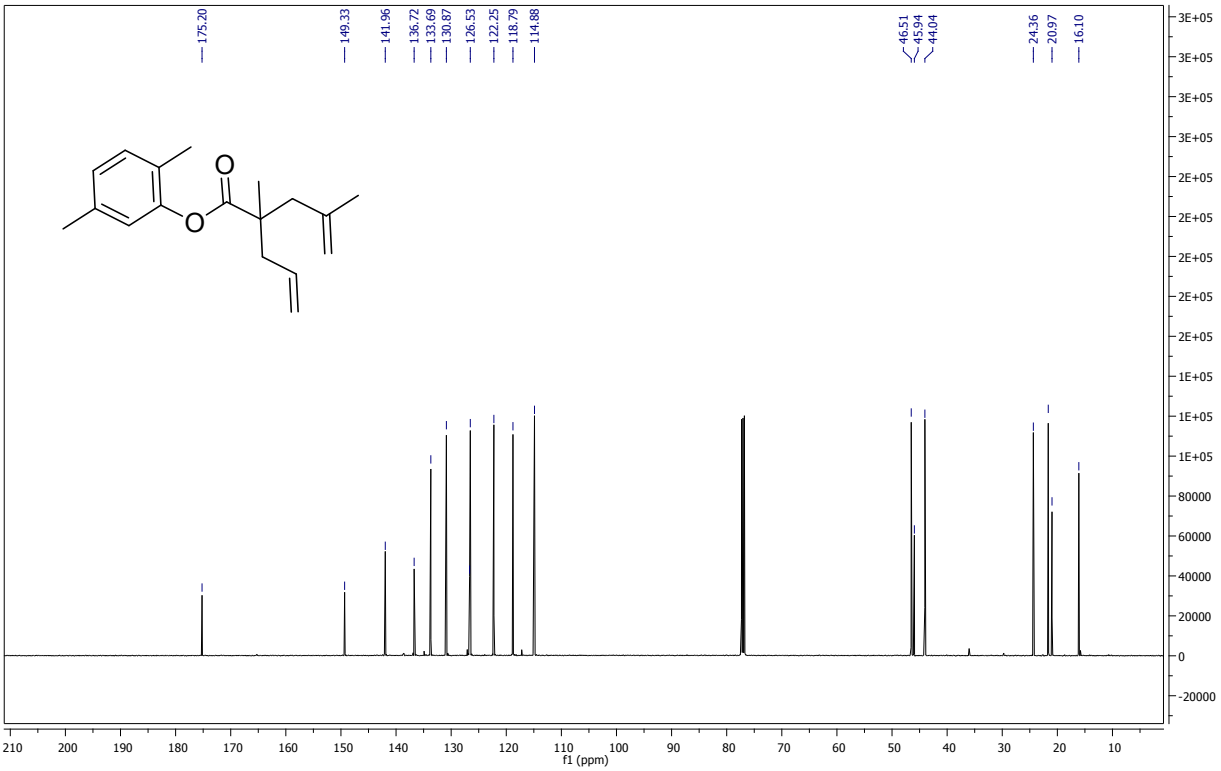
0.98
1.99
2.01
2.99
3.00
2.88
2.91
f1 (ppm)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122.25
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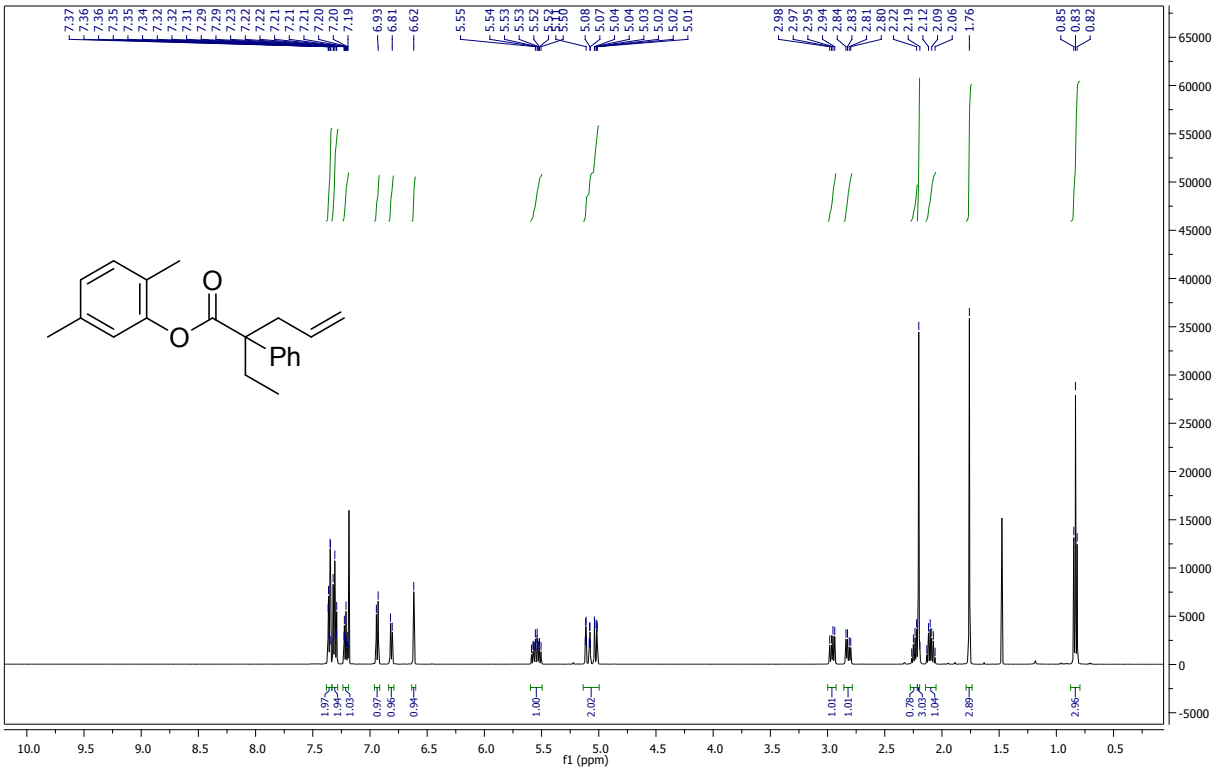
114.88
46.51
45.94
44.04
24.36
20.97
16.10
O
O
f1 (ppm)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7.32
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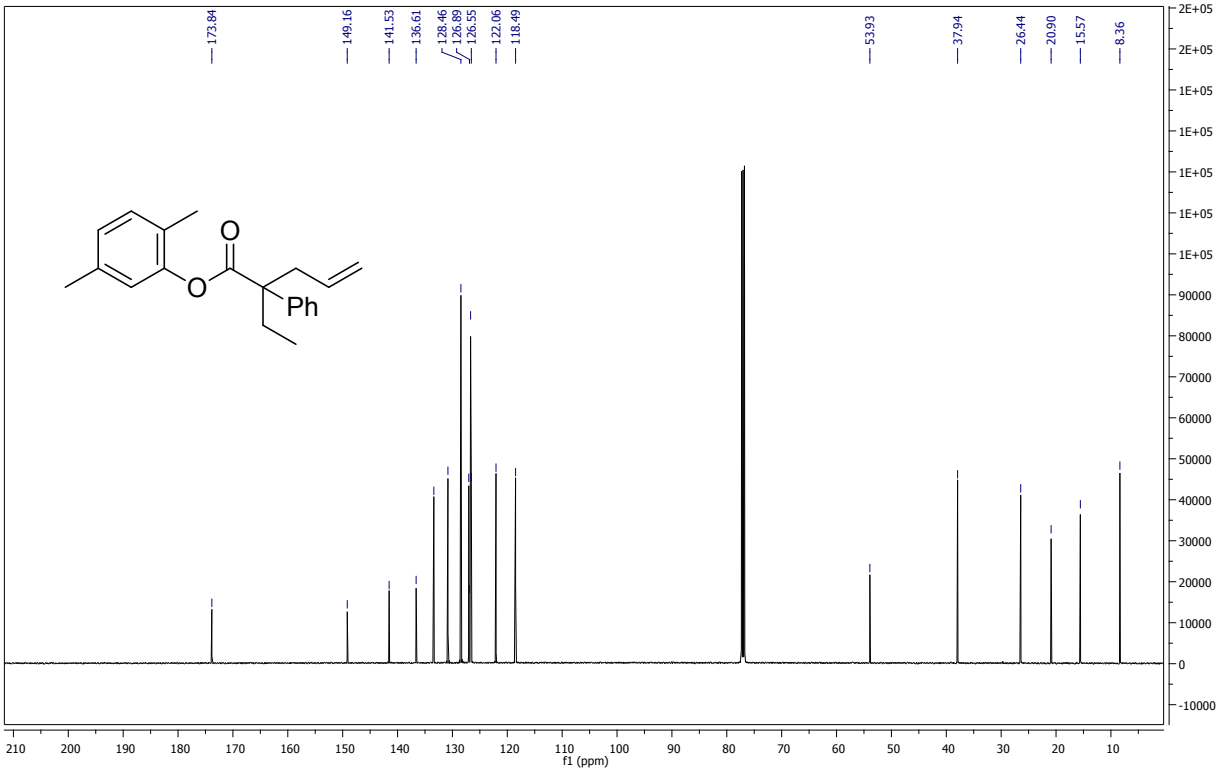
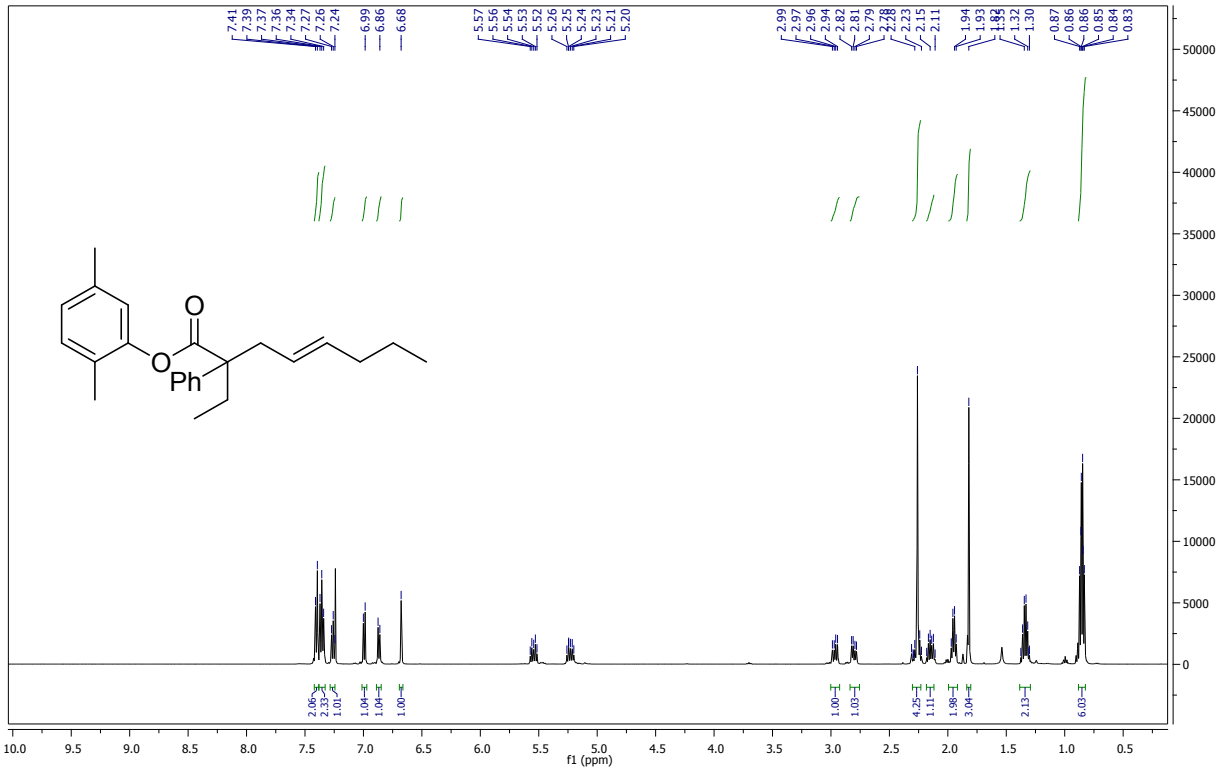
7.29
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.19
6.93
6.81
6.62
5.55
5.54
5.53
5.53
5.52
5.52
5.50
5.08
5.07
5.04
5.04
5.03
5.02
5.02
5.01
2.98
2.97
2.95
2.94
2.84
2.83
2.81
2.80
2.22
2.19
2.12
2.09
2.06
1.76
0.85
0.83
0.82
O
O
Ph
1.97
1.94
1.03
0.97
0.96
0.94
1.00
2.02
1.01
1.01
0.78
3.03
1.04
2.89
2.96
f1 (ppm)


173.84
149.16
141.53
136.61
128.46
126.89
126.55
122.06
118.49
53.93
37.94
26.44
20.90
15.57
8.36
O
O
Ph
f1 (ppm)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7.36
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7.27
7.26
7.24
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6.86
6.68
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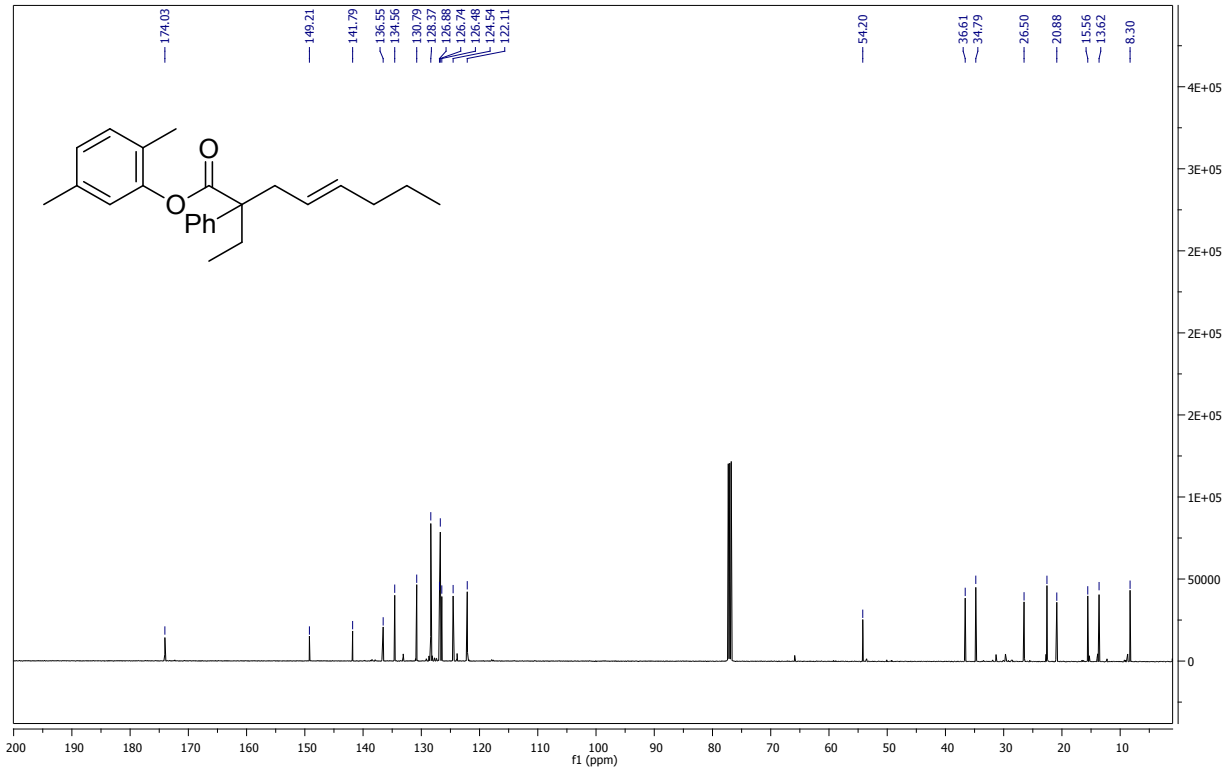
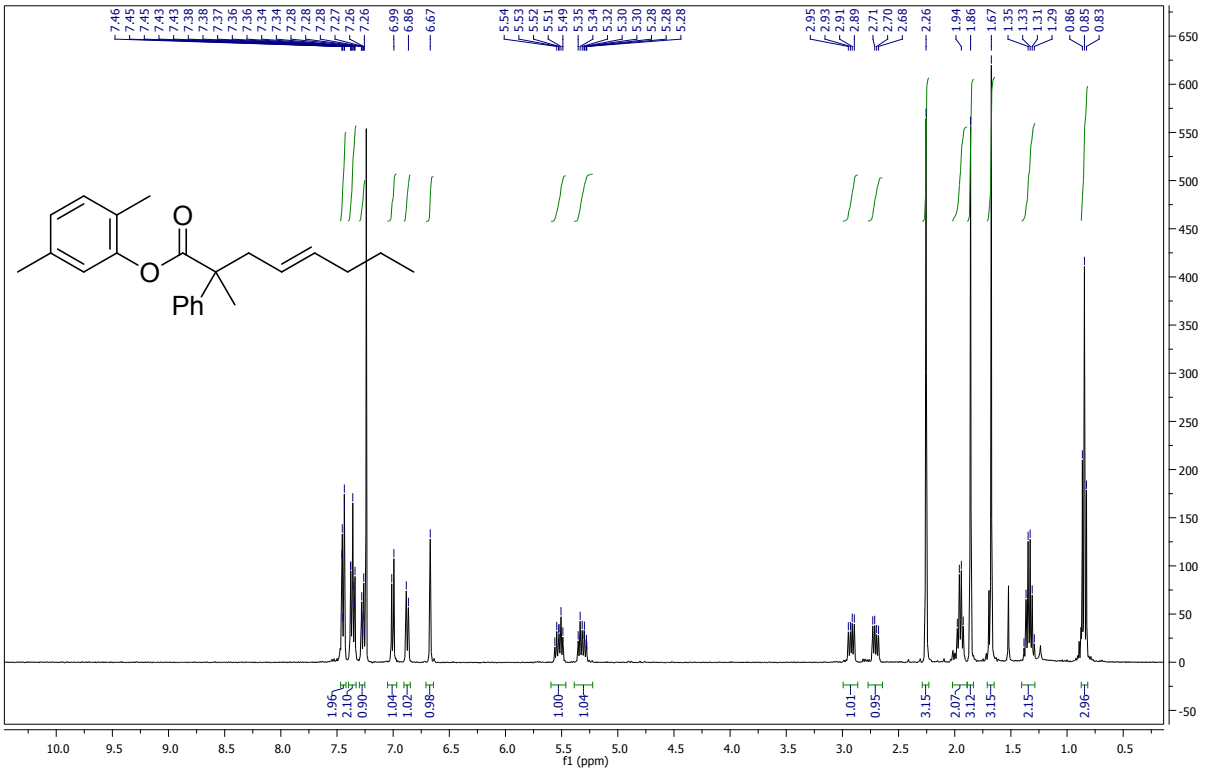
5.56
5.54
5.53
5.52
5.26
5.25
5.24
5.23
5.21
5.20
2.99
2.97
2.96
2.94
2.82
2.81
2.79
2.23
2.15
2.11
1.94
1.93
1.32
1.30
0.87
0.86
0.86
0.85
0.84
0.83
O
O
Ph
f1 (ppm)


174.03
149.21
141.79
136.55
134.56
130.79
128.37
126.88
126.74
126.48
124.54
122.11
54.20
36.61
34.79
26.50
20.88
15.56
13.62
8.30
O
O
Ph
f1 (ppm)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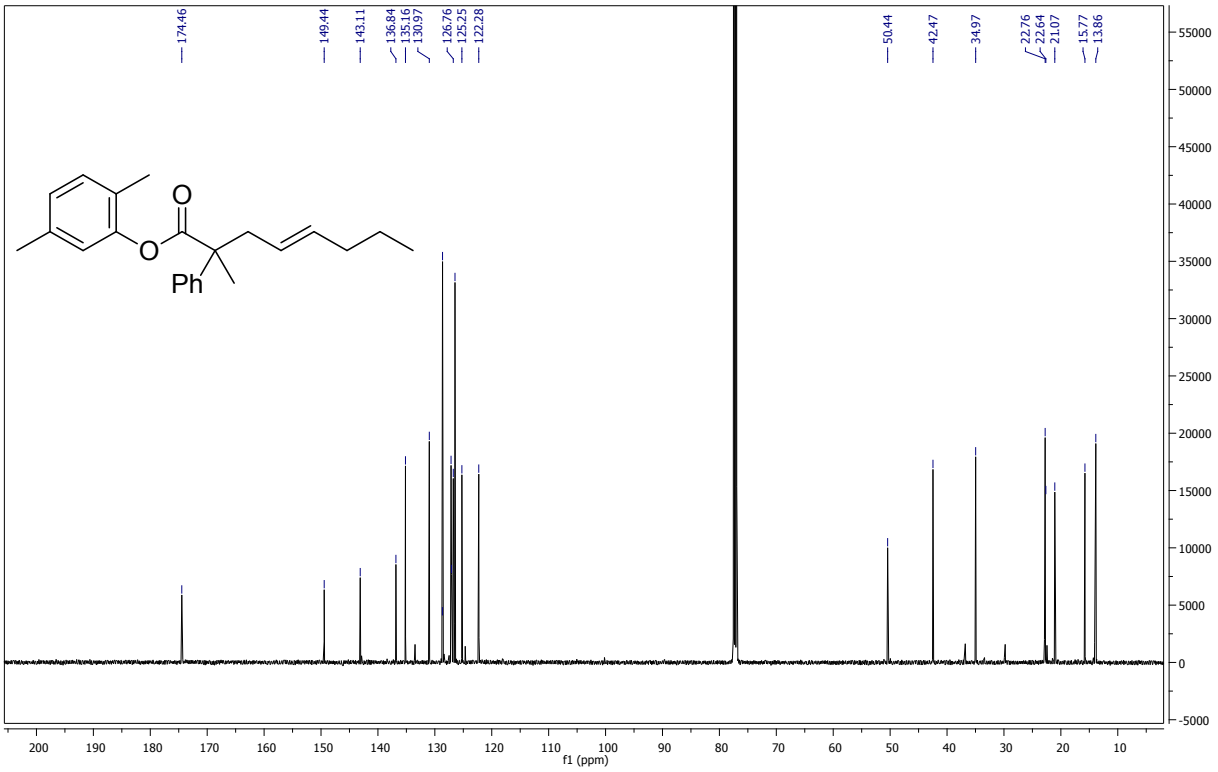
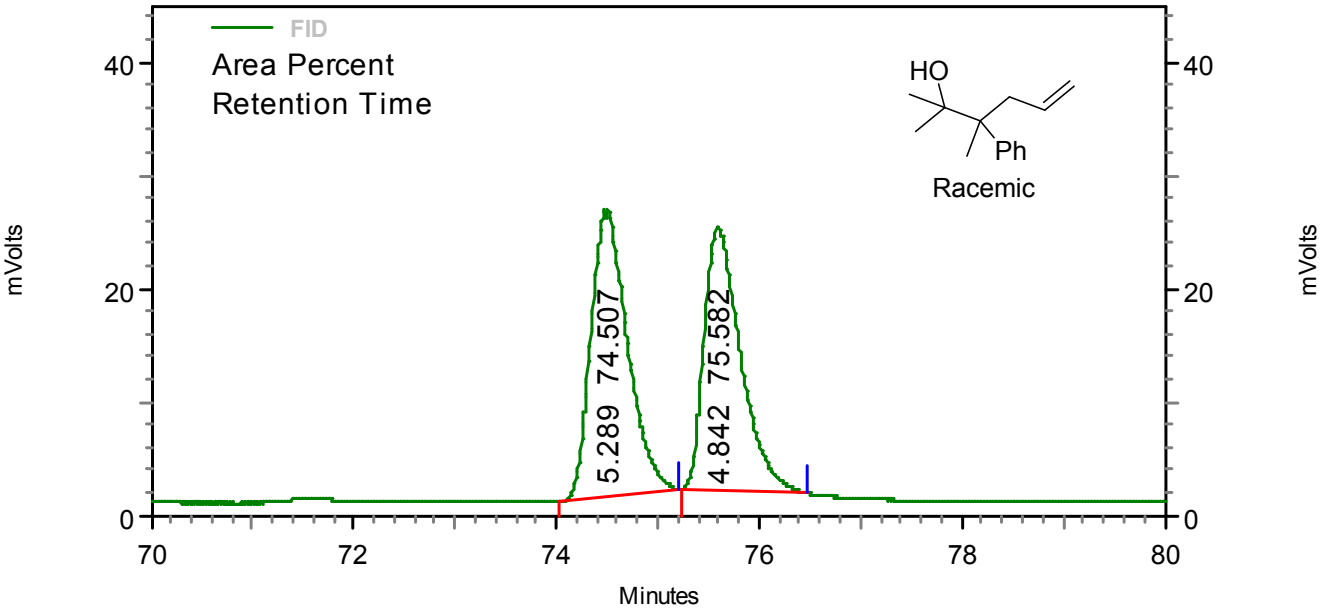
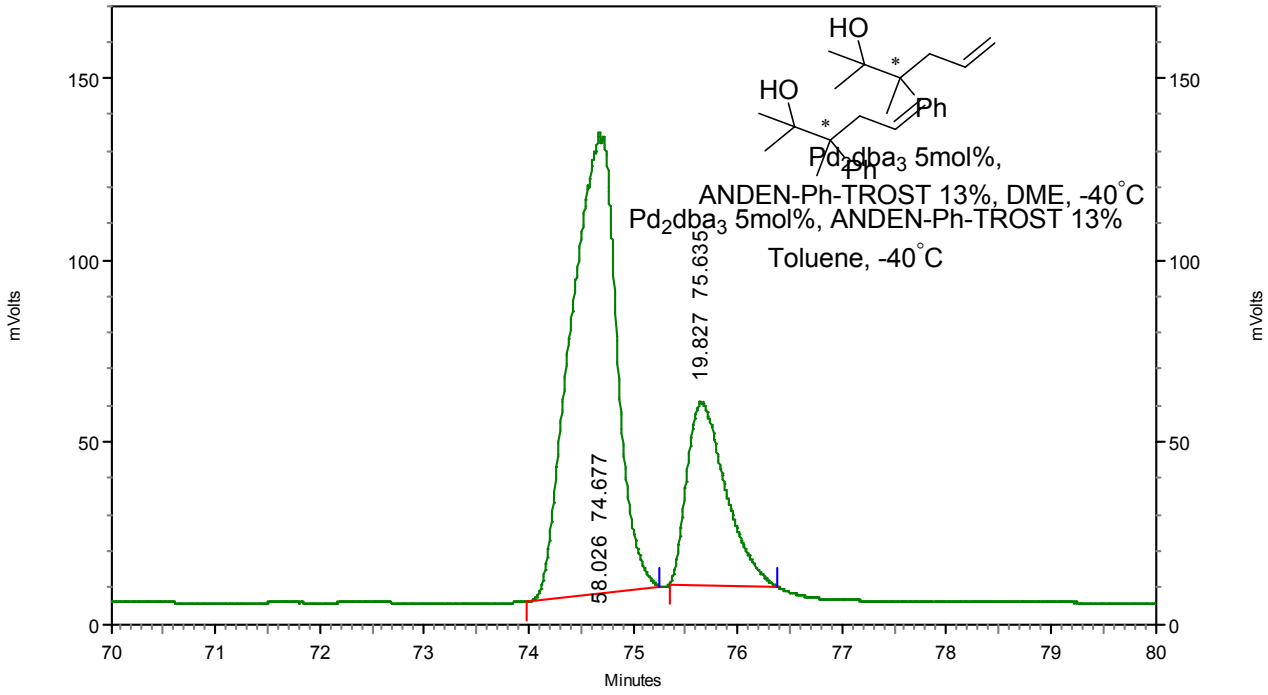
7.45
7.45
7.43
7.43
7.38
7.38
7.37
7.36
7.36
7.34
7.34
7.28
7.28
7.28
7.27
7.26
7.26
6.99
6.86
6.67
5.54
5.53
5.52
5.51
5.49
5.35
5.34
5.32
5.30
5.30
5.28
5.28
5.28
2.95
2.93
2.91
2.89
2.71
2.70
2.68
2.26
1.94
1.86
1.67
1.35
1.33
1.31
1.29
0.86
0.85
0.83
1.96
2.10
0.90
1.04
1.02
0.98
1.00
1.04
1.01
0.95
3.15
2.07
3.12
3.15
2.15
2.96
O
O
Ph
f1 (ppm)

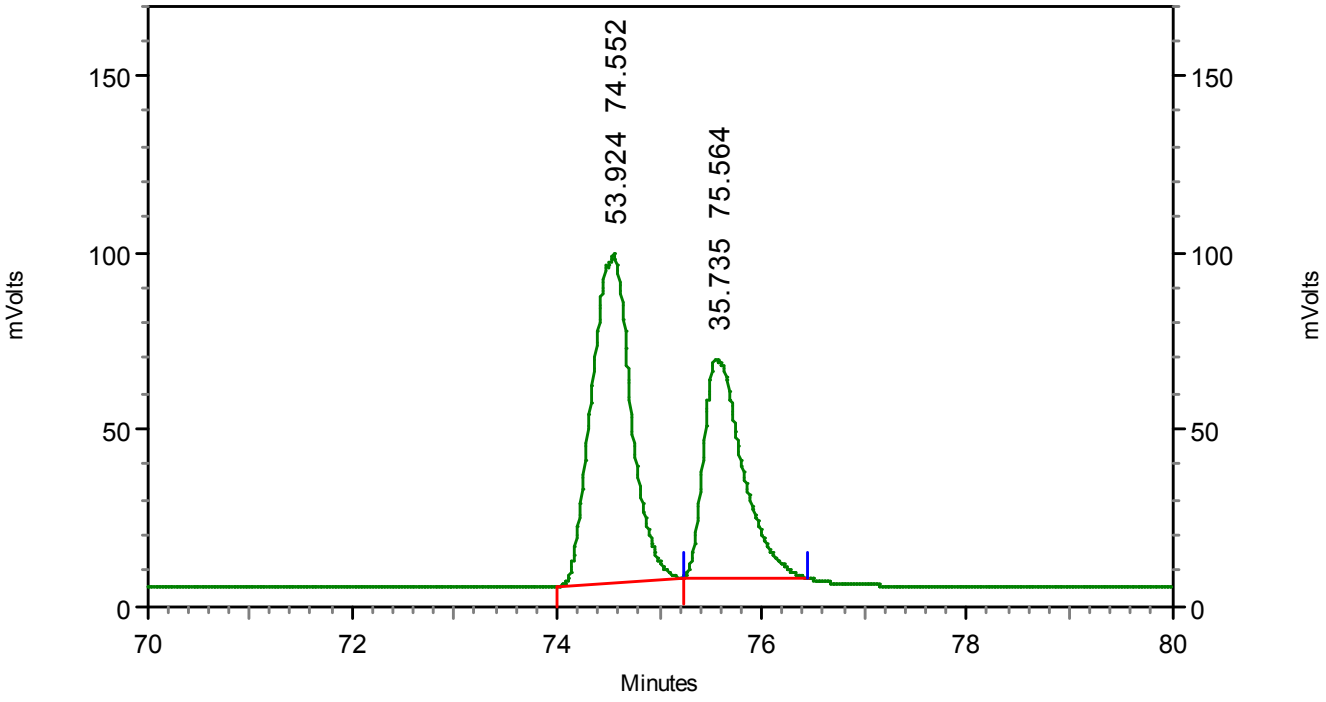

174.46
149.44
143.11
136.84
135.16
130.97
126.76
125.25
122.28
50.44
42.47
34.97
22.76
22.64
21.07
15.77
13.86
O
O
Ph
f1 (ppm)

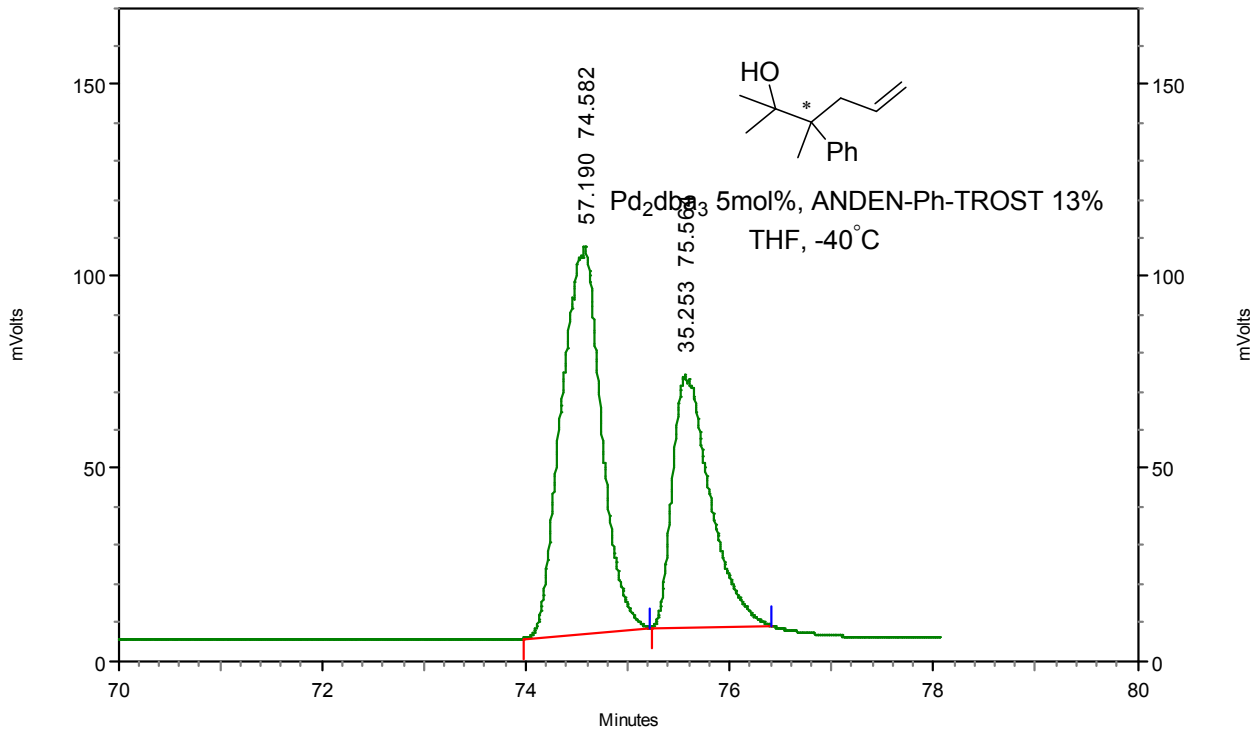
GC data

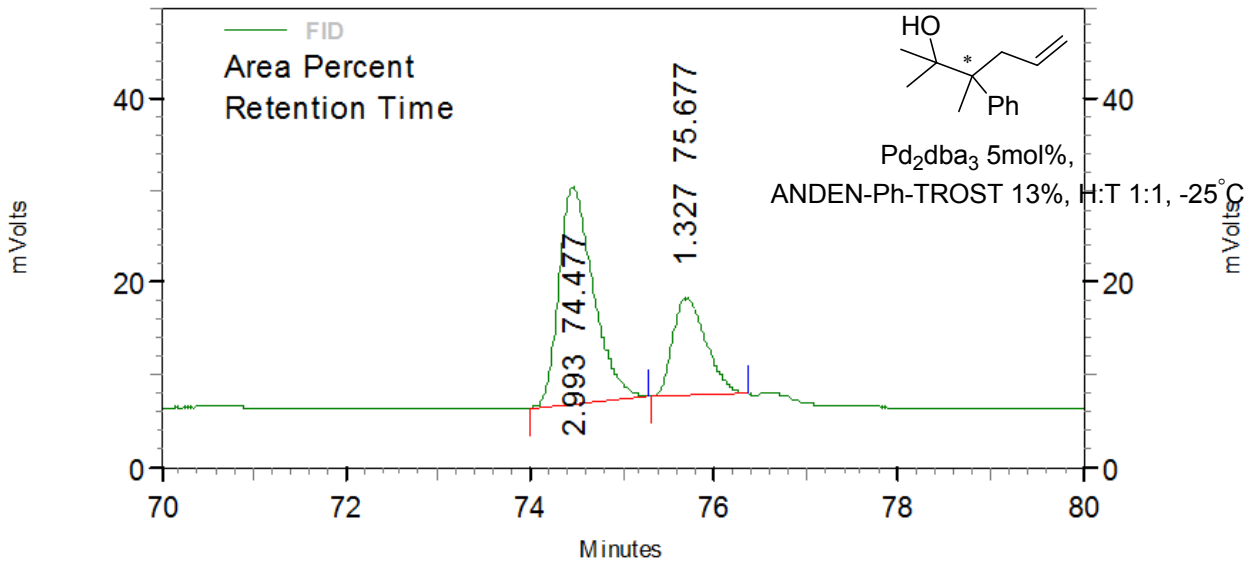
Chiral GC analysis was done using Astec CHIRALDEX B-DM column, 107-115°C at 0.1°C/min. Prior to analysis Acyl pyrrole substrates were transformed in to tertiary alcohols using MeLi.



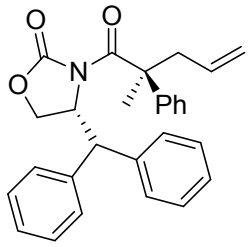



53.924 74.552
35.735 75.564
mVolts
Minutes
150
100
50
0
70
72
74
76
78
80


HO
*
Ph
Pd2dba3 5mol%, ANDEN-Ph-TROST 13%
THF, -40°C
57.190 74.582
35.253 75.563
mVolts
Minutes
150
100
50
0
70
72
74
76
78
80



Crystal structure



major