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Visible-Light Photocatalytic Oxidation of 1,3-Dicarbonyl Compounds and Carbon-Carbon Bond Formation

Marion Daniel,[ab] *Louis Fensterbank,**[ab] *Jean-Philippe Goddard**[abc] *and Cyril Ollivier**[ab]

[a] Sorbonne Universités UPMC Univ Paris 06, UMR 8232, Institut Parisien de Chimie Moléculaire, 4 place Jussieu, C. 229, F-75005 Paris, France. Fax: 33(0)44277360

[b] CNRS, UMR 8232, Institut Parisien de Chimie Moléculaire, 4 place Jussieu, C. 229, F-75005 Paris, France.

[c] Laboratoire de Chimie Organique et Bioorganique EA 4566, Université de Haute-Alsace, Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue Alfred Werner, F-68093 Mulhouse Cedex, France.

E-mail: louis.fensterbank@upmc.fr, jean-philippe.goddard@uha.fr, cyril.ollivier@upmc.fr

Contents

1. General Remarks

All reagents were purchased from commercial sources and were used as received, unless noted otherwise. 2-Diazobenzophenone tetrafluoroborate was prepared as described previously.[1] Unless special mention, all reactions were carried out under an argon atmosphere and in anhydrous solvents. Solvents and liquid reagents were distilled under an argon atmosphere prior to use, particularly: CH_3CN and CH_2Cl_2 from calcium hydride. DMF was used from the bottle without any further purification. TLC were performed on Merck 60 F254 silica gel and revealed with either a ultra-violet lamp (λ = 254 nm) or a specific color reagent (potassium permanganate). A silica gel Merck Geduran SI 60 (35-70 µm) was used for flash column chromatography (FC) using Still's method.[2] PE refers to petroleum ether. The melting points were measured with an Electrothermal IA9100 Melting Point apparatus and are uncorrected. ^1H, ^{13}C and ^{19}F spectra were recorded at 300 and 400 MHz using Bruker AVANCE spectrometers. Chemical shifts are given in parts per million (ppm) using the $CDCl_3$ residual chloroform signal as reference (δ^1H = 7.26 ppm, $\delta^{13}C$ = 77.16 ppm). Otherwise noted, NMR spectra were recorded in $CDCl_3$ at 300 K. The terms m, s, d, t, q and dd represent multiplet, singlet, doublet, triplet, quadruplet, quintuplet, and doublet of doublets respectively. Coupling constants (*J*) are given in Hertz (Hz). IR spectra were recorded with a Tensor 27 (ATR diamond) Bruker spectrometer. IR was reported as characteristic bands (cm^{-1}). High resolution mass spectra (HRMS) were recorded at the Institut de Chimie Moléculaire (FR 2769) of our university (electrospray source).

2. General Procedures

General Procedure 1 (GP1). *Dimerization procedure*. A Schlenk flask was charged with $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (0.037 g, 0.05 mmol, 10 mol %), K_2CO_3 (0.083 g, 0.6 mmol, 1.2 equiv.) and triphenylcarbenium tetrafluoroborate (0.165 g, 0.5 mmol, 1 equiv.). Then, β-ketoester **1a-g** (0.5 mmol) in DMF (5 mL) was added. The solution was allowed to stir under air atmosphere (Schlenk with open tap) and exposed to a 14 W fluorescent light-bulb (~ 2 cm away from the glassware) for 24h to 48h at RT. The light was then switched off, water (5 mL) was added to the mixture and diluted with Et_2O. The aqueous phase was extracted with Et_2O (×3). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated under reduce pressure to give the crude product. The residue was purified by FC on silica gel (pentane or petroleum ether/Et_2O).

General Procedure 2 (GP2). *Allylation procedure.* A Schlenk flask was charged with $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (0.037 g, 0.05 mmol, 10 mol %), K_2CO_3 (0.083 g, 0.6 mmol, 1.2 equiv.) and triphenylcarbenium tetrafluoroborate (0.165 g, 0.5 mmol, 1 equiv.). Then, ethyl 2-benzoylacetate **1a** (0.09 mL, 0.096 g, 0.5 mmol) and allylstannane or allylsulfone (5 mmol, 10 equiv.) in DMF (5 mL) was added. The solution was allowed to stir under air atmosphere (Schlenk with open tap) and exposed to a 14 W fluorescent light-bulb (~ 2 cm away from the glassware) for 24h to

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[1] A. H. Lewin, R. J. Michl, *J. Org. Chem.* **1973**, *38*, 1126-1130.
[2] W. C. Still, M. Khan, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.

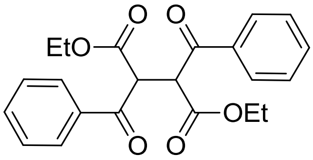
48h at RT. The light was then switched off, water (5 mL) was added to the mixture and diluted with Et_2O. The aqueous phase was extracted with Et_2O (×3). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated under reduce pressure to give the crude product. The residue was purified by FC on silica gel (pentane or petroleum ether/Et_2O).

General Procedure 3 (GP3). A 100 mL round-bottomed flask was charged with NaH (60 % in oil, 1.04 g, 26 mmol, 1.2 equiv.) and THF (50 mL). 1-Phenyl-butane-1,3-dione (3.406 g, 21 mmol, 1 equiv.) in THF (5 mL) was added dropwise at 0°C and the solution was stirred for 5 min at 0°C, then 15 min at room temperature. Then, n-BuLi (2.2 M in hexane, 9.5 mL, 21 mmol, 1 equiv.) was added dropwise over 15 min and the solution was stirred for 20 min at 0°C. Finally, the alkylbromide (23 mmol, 1.1 equiv.) was added dropwise at 0°C and the solution was stirred several hours at room temperature. The solution was cooled to 0°C and treated by conc. HCl (4 mL), water (5 mL) and Et_2O (20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by FC on silica gel (pentane/Et_2O).

General Procedure 4 (GP4). *Cascade procedure.* A Schlenk flask was charged with $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (0.037 g, 0.05 mmol, 10 mol %), K_2CO_3 (0.083 g, 0.6 mmol, 1.2 equiv.) and triphenylcarbenium tetrafluoroborate (0.330 g, 1 mmol, 2 equiv.). Then, 1,3-diketone **6** or **8** (0.5 mmol) in DMF (5 mL) was added. The solution was allowed to stir under air atmosphere (Schlenk with open tap) and exposed to a 14 W fluorescent light-bulb (~ 2 cm away from the glassware) for 24h at RT. The light was then switched off, water (5 mL) was added to the mixture and diluted with Et_2O. The aqueous phase was extracted with Et_2O (×3). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product. The residue was purified by FC on silica gel (pentane/Et_2O).

3. Dimerization Reactions

Diethyl-2,3-dibenzoylsuccinate (2a)



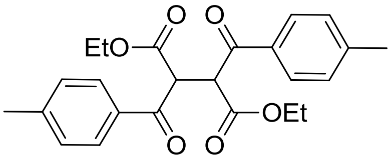
$C_{22}H_{22}O_6$

M = 382.14 g/mol

Following **GP1** with ethyl 2-benzoylacetate **1a** (0.09 mL, 0.096 g, 0.5 mmol). Flash column chromatography (8:2 pentane/Et_2O) afforded **2a** (0.096 g, 0.25 mmol, > 98%) in a 1:1 diastereomeric ratio (estimated from crude ^1H NMR) as a white solid. Spectral and physical data are in accordance with those reported in the literature.[3]

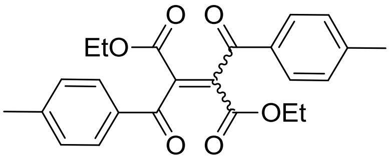
Both diastereoisomers: Mp = 126 °C (lit.[3] Mp = 127-129 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 8.19-8.16 (m, 4H), 8.13-8.09 (m, 4H), 7.61-7.56 (m, 4H), 7.54-7.45 (m, 8H), 5.61 (s, 2H), 5.54 (s, 2H), 4.14 (q, J = 7.1 Hz, 4H), 3.97 (q, J = 7.1 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H), 0.96 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1 (2C), 193.2 (2C), 167.6 (2C), 167.2 (2C), 136.2 (2C), 135.8 (2C), 133.9 (2C), 133.8 (2C), 129.5 (4C), 129.4 (4C), 128.7 (8C), 62.1 (4C), 54.3 (2C), 53.3 (2C), 13.9 (2C), 13.7 (2C). IR (neat) 1734, 1680, 1596, 1579, 1448 cm^{-1}. HRMS calculated for $C_{22}H_{22}O_6Na$ ($[M + Na]^+$) 405.1309, found 405.1324.

Diethyl-2,3-bis(4-methylbenzoyl)succinate (1b)



$C_{24}H_{26}O_6$

M = 410.46 g/mol



Overoxidation side product of **1b**

Following **GP1** with ethyl 2-(4-methylbenzoyl)acetate **1b** (0.10 mL, 0.103 g, 0.5 mmol). Flash column chromatography (10:1 pentane/Et_2O) afforded **2b** (0.088 g, 0.21 mmol, 85%) in a 0.92:1 diastereomeric ratio (estimated from crude ^1H NMR) as a white solid, contaminated by ca. 10% (estimated by ^1H NMR) of a byproduct which may result from overoxidation of **1b**. Spectral data are in accordance with those reported in the literature.[3]

Both diastereoisomers: Mp = 127 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 4H), 7.93 (d, J = 8.3 Hz, 4H), 7.23 (d, J = 8.3 Hz, 4H), 7.18 (d, J = 8.3 Hz, 4H), 5.50 (s, 2H), 5.43 (s, 2H), 4.05 (q, J = 7.1 Hz, 4H), 3.88 (q, J = 7.1 Hz, 4H), 2.35 (s, 6H), 2.33 (s, 6H), 1.08 (t, J = 7.1 Hz, 6H), 0.89 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6 (2C), 192.7 (2C), 167.8 (2C), 167.3 (2C), 144.9 (2C), 144.8 (2C), 133.8 (2C), 133.4 (2C), 129.7

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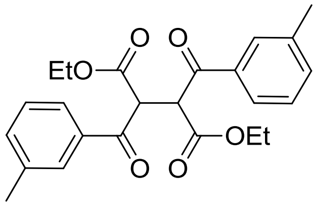
[3] J. Song, H. Zhang, X. Chen, X. Li, D. Xu, *Synthetic Communications* **2010**, 40, 1847-1855.

(4C), 129.6 (4C), 129.4 (4C), 129.3 (4C), 62.0 (2C), 62.0 (2C), 54.1 (2C), 53.3 (2C), 21.8 (4C), 14.0 (2C), 13.7 (2C). IR (neat) 2981, 2923, 2853, 1732, 1673, 1604, 1572 cm^{-1}. HRMS calculated for $C_{24}H_{26}O_6Na$ ([M + Na]$^+$) 433.1622, found 433.1635.

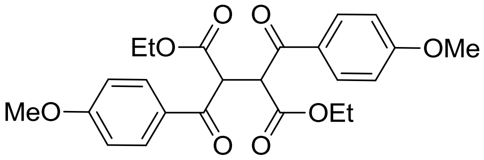
2,3-Bis-(3-methyl-benzoyl)-succinic acid diethyl ester (1c)



$C_{24}H_{26}O_6$
M = 410.46 g/mol

Following **GP1** with ethyl 2-(3-methylbenzoyl)acetate **1c** (0.10 mL, 0.103 g, 0.5 mmol). Flash column chromatography (10:1 pentane/Et_2O) afforded **2c** (0.044 g, 0.107 mmol, 43%) in a 0.87:1 diastereomeric ratio (estimated from crude ^{1}H NMR) as a yellow solid.
Both diastereoisomers: Mp = 124°C. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.99-7.89 (m, 8H), 7.44-7.34 (m, 8H), 5.59 (s, 2H), 5.52 (s, 2H), 4.18-4.10 (m, 4H), 4.00 (qd, *J* = 7.1, 0.8 Hz, 4H), 2.45 (s, 6H), 2.41 (s, 6H), 1.16 (t, *J* = 7.1 Hz, 6H, dia 2), 0.98 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 194.3 (2C), 193.4 (2C), 167.8 (2C), 167.3 (2C), 138.5 (2C), 138.5 (2C), 136.4 (2C), 136.0 (2C), 134.7 (2C), 134.7 (2C), 130.0 (2C), 129.9 (2C), 128.6 (2C), 128.6 (2C), 126.8 (2C), 126.8 (2C), 62.1 (2C), 62.1 (2C), 54.4 (2C), 53.5 (2C), 21.5 (2C), 21.4 (2C), 14.0 (2C), 13.7 (2C). IR (neat) 2981, 2958, 2923, 2853, 1730, 1680, 1603, 1585 cm^{-1}. HRMS calculated for $C_{24}H_{26}O_6Na$ ([M + Na]$^+$) 433.1622, found 433.1630.

Diethyl-2,3-bis(4-methoxybenzoyl)succinate (1d)

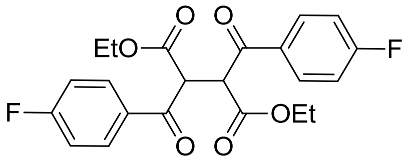


$C_{24}H_{26}O_8$
M = 442.46 g/mol

Following **GP1** with ethyl (4-methoxybenzoyl)acetate **1d** (0.10 mL, 0.111 g, 0.5 mmol). Flash column chromatography (5:2 then 1:1 petroleum ether/Et_2O) afforded **2d** (0.088 g, 0.20 mmol, 80%) in a 0.87:1 diastereomeric ratio (estimated from crude ^{1}H NMR) as a yellow solid.
Mp = 92°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.9 Hz, 4H), 8.10 (d, *J* = 8.9 Hz, 4H), 6.99-6.92 (m, 8H), 5.54 (s, 2H), 5.49 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 4H), 3.96 (q, *J* = 7.1 Hz, 4H), 3.88 (s, 6H), 3.86 (s, 6H), 1.16 (t, *J* = 7.1 Hz, 6H), 0.97 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 192.3 (2C), 191.4 (2C), 168.0 (2C), 167.4

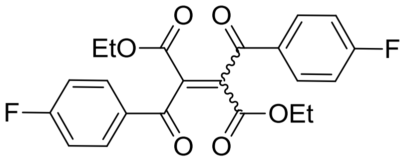
(2C), 164.2 (2C), 164.2 (2C), 132.0 (4C), 131.9 (4C), 129.2 (2C), 128.9 (2C), 113.9 (4C), 113.8 (4C), 62.0 (2C), 61.9 (2C), 55.6 (4C), 53.9 (2C), 53.1 (2C), 14.0 (2C), 13.8 (2C). IR (neat) 2980, 2938, 2842, 1731, 1667, 1596, 1573, 1510 cm^{-1}. HRMS calculated for $C_{24}H_{26}O_8Na$ ($[M + Na]^+$) 465.1525, found 465.1481.

Diethyl-2,3-bis(4-fluorobenzoyl)succinate (1e)



$C_{22}H_{20}F_2O_6$

M = 418.39 g/mol



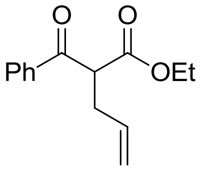
Overoxidation side product of **1e**

Following **GP1** with ethyl (4-fluorobenzoyl)acetate **1e** (0.09 mL, 0.105 g, 0.5 mmol). Flash column chromatography (10:1 pentane/Et_2O) afforded **2e** (0.073 g, 0.17 mmol, 70%) in a 1:0.86 diastereomeric ratio (estimated from crude ^{1}H NMR) as a white solid, contaminated by ca. 10% (estimated by ^{1}H NMR) of a byproduct which may result from overoxidation of **1e**.

Both diastereoisomers: Mp = 122°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17-8.12 (m, 4H), 8.10-8.05 (m, 4H), 7.15-7.05 (m, 8H), 5.49 (s, 2H), 5.42 (s, 2H), 4.08 (q, *J* = 7.1 Hz, 4H), 3.92 (q, *J* = 7.1 Hz, 4H), 1.09 (t, *J* = 7.1 Hz, 6H), 0.91 (t, *J* = 7.12 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5 (2C), 191.7 (2C), 167.4 (2C), 167.0 (2C), 166.4 (d, J_{CF} = 254.7 Hz, 2C), 166.3 (d, J_{CF} = 254.6 Hz, 2C), 132.7 (2C), 132.7 (2C), 132.4 (2C), 132.4 (2C), 132.3 (2C), 132.3 (2C), 116.1 (4C), 115.8 (4C), 62.3 (4C), 54.3 (2C), 53.3 (2C), 13.9 (2C), 13.8 (2C). IR (neat) 3077, 2983, 2926, 1732, 1678, 1594, 1507 cm^{-1}. HRMS calculated for $C_{22}H_{20}F_2O_6Na$ ($[M + Na]^+$) 441.1120, found 441.1136.

4. Allylation Reactions

2-Benzoyl-pent-4-enoic acid ethyl ester (4a)



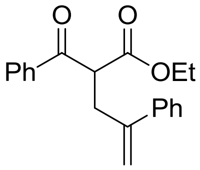
$C_{14}H_{16}O_3$

M = 232.28 g/mol

Following **GP2** with allyltributyltin **3a** (1.55 mL, 1.656 g, 5 mmol, 10 equiv.). Flash column chromatography (9:1 petroleum ether/Et_2O) afforded **4a** (0.032 g, 0.14 mmol, 28%) as a colorless oil contaminated by ca. 10% (estimated by ^1H NMR) of triphenylmethanol as a byproduct. Spectral data are in accordance with those reported in the literature.[4]

^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.61-7.59 (m, 1H), 7.53-7.48 (m, 2H), 5.90-5.80 (m, 1H), 5.18-5.09 (m, 2H), 4.42 (t, *J* = 7.2 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.81-2.76 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6 (1C), 169.5 (1C), 136.3 (1C), 134.6 (1C), 133.6 (1C), 128.8 (2C), 128.7 (2C), 117.3 (1C), 61.5 (1C), 54.0 (1C), 33.1 (1C), 14.1 (1C). IR (neat) 2981, 2933, 1734, 1685, 1643, 1597, 1580 cm^{-1}. HRMS calculated for $C_{14}H_{16}O_3Na$ ($[M + Na]^+$) 255.0992 , found 255.0987.

2-Benzoyl-4-phenyl-pent-4-enoic acid ethyl ester (4b)



$C_{20}H_{20}O_3$

M = 308.37 g/mol

Following **GP2** with 2-phenyl-allyltributyltin **3b** (2.03 g, 5 mmol, 10 equiv.) or 2-phenyl allyl p-tolyl sulfone **3e** (1.36 g, 5 mmol, 10 equiv.) as acceptor. Flash column chromatography (19:1 pentane/Et_2O) afforded **4b** (0.066 g, 0.021 mmol, 43%) or (0.046 g, 0.15 mmol, 30%) respectively as a colorless oil.

^1H NMR: (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.59-7.55 (m, 1H), 7.45-7.28 (m, 7H), 5.29 (s, 1H), 5.15 (s, 1H), 4.48 (t, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.26 (dd, *J* = 7.4, 4.4 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 194.9 (1C), 169.5 (1C), 145.2 (1C), 140.3 (1C), 136.4 (1C), 133.6 (2C), 128.7 (4C),

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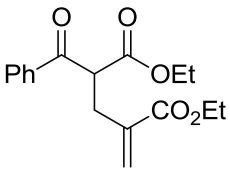
[4] D. F. Gonzales, J. P. Brand, J. Waser, *Chem. Eur. J.* **2010**, 16, 9457-9461.

128.6 (2C), 126.5 (2C), 115.2 (1C), 61.6 (1C), 53.0 (1C), 34.8 (1C), 14.1 (1C). IR (neat) 3058, 2981, 2934, 1732, 1684, 1629, 1596, 1580 cm^{-1}. HRMS calculated for $C_{20}H_{20}O_3Na$ ($[M + Na]^+$) 331.1305, found 331.1314.

2-Benzoyl-4-methylene-pentanedioic acid diethyl ester (4c)



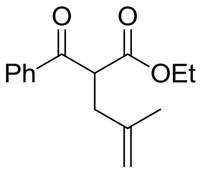
$C_{17}H_{20}O_5$

M = 304.34 g/mol

Following **GP2** with ethyl α-tributyltinmethacrylate **3c** (2.016 g, 5 mmol, 10 equiv.) or ethyl α-*p*-toluenesulfonylmethacrylate **3f** (1.422 g, 5 mmol, 10 equiv.) of as the acceptor. Flash column chromatography (10:1 pentane/Et_2O) afforded **4c** (0.097 g, 0.319 mmol, 64% or 0.094 g, 0.309 mmol, 62%) as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.02 (m, 2H), 7.57-7.55 (m, 1H), 7.48-7.44 (m, 2H), 6.20 (s, 1H), 5.70 (s, 1H), 4.73 (t, *J* = 7.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.98 (d, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8 (1C), 169.3 (1C), 166.6 (1C), 136.8 (1C), 136.1 (1C), 133.7 (1C), 128.9 (2C), 128.8 (2C), 128.5 (1C), 61.5 (1C), 61.0 (1C), 53.1 (1C), 32.0 (1C), 14.3 (1C), 14.1 (1C). IR (neat) 3062, 2983, 2939, 2907, 1737, 1712, 1687, 1631, 1597, 1581 cm^{-1}. HRMS calculated for $C_{17}H_{20}O_5Na$ ($[M + Na]^+$) 327.1203, found 327.1208.

2-Benzoyl-4-methyl-pent-4-enoic acid ethyl ester (4d)



$C_{15}H_{18}O_3$

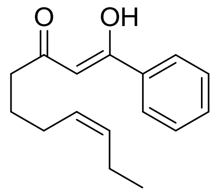
M = 246.30 g/mol

Following **GP2** with methallyltributyltin **3d** (1.726 g, 5 mmol, 10 equiv.) as the acceptor. Flash column chromatography (10:1 pentane/Et_2O) afforded **4d** (0.089 g, 0.36 mmol, 72%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2H), 7.60-7.57 (m, 1H), 7.51-7.47 (m, 2H), 4.79 (t, *J* = 0.6 Hz, 1H), 4.73 (s, 1H), 4.57 (t, *J* = 7.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.77-2.72 (m, 2H), 1.78 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6 (1C), 169.6 (1C), 142.2 (1C), 136.3 (1C), 133.6 (1C), 128.8 (2C), 128.7 (2C), 112.3 (1C), 61.5 (1C), 52.9 (1C), 36.6 (1C), 22.7 (1C), 14.1 (1C). IR (neat) 3077, 2979, 2937, 1735, 1686, 1650, 1597, 1581, 1448 cm-1. HRMS calculated for $C_{15}H_{18}O_3Na$ ($[M + Na]^+$) 269.1148, found 269.1143.

5. Intramolecular Cascade Reactions

1-Hydroxy-1-phenyl-deca-1,7-dien-3-one (5)[5]

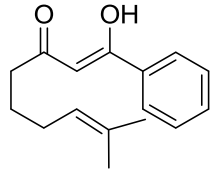


$C_{16}H_{20}O_2$
M = 244.33 g/mol

Following **GP3** with 1-phenyl-butane-1,3-dione (3.406 g, 21 mmol, 1 equiv.) and 1-bromo-hex-3-ene (3.749 g, 23 mmol, 1.1 equiv.). Flash column chromatography (20:1 pentane/Et_2O) afforded **5** (1.546 g, 6.33 mmol, 30%) as a colorless oil consisting of a 12:1 mixture of enol and keto tautomers. Spectral data are in accordance with those reported in the literature.[5]

Enol form of ***5***: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.54 – 7.42 (m, 3H), 6.17 (s, 1H), 5.47 – 5.29 (m, 2H), 2.44 (t, J = 7.4 Hz, 2H), 2.14 – 2.00 (m, 4H), 1.75 (quint., J = 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H), the OH signal is missing. ^{13}C NMR: (100 MHz, $CDCl_3$) δ 196.8 (1C), 183.6 (1C), 135.2 (1C), 132.9 (1C), 132.3 (1C), 128.7 (2C), 128.0 (1C), 127.1 (2C), 96.24 (1C), 38.7 (1C), 26.7 (1C), 25.9 (1C), 20.7 (1C), 14.4 (1C). *Characteristic signals of the keto form of* ***5***: 4.08 (s, 2H), 2.59 (t, J = 7.4 Hz, 2H), 1.67 (quint., J = 7.4 Hz, 2H). IR (neat) 3061, 3003, 2959, 2934, 2869, 1603, 1459, 1268 cm^{-1}. HRMS calculated for $C_{16}H_{20}O_2Na$ ($[M + Na]^+$) 267.13555, found 267.13604.

1-Hydroxy-8-methyl-1-phenyl-nona-1,7-dien-3-one (7)



$C_{16}H_{20}O_2$
M = 244.33 g/mol

Following **GP3** with 1-phenyl-butane-1,3-dione (3.406 g, 21 mmol, 1 equiv.) and 5-bromo-2-methyl-pent-2-ene (3.749 g, 23 mmol, 1.1 equiv.). Flash column chromatography (60:1 pentane/Et_2O) afforded **7** (1.082 g, 4.43 mmol, 21%) as a colorless oil consisting of a 12:1 mixture of enol and keto tautomers.

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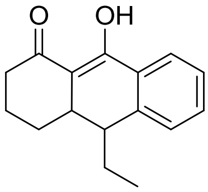
[5] B. B. Snider, Q. Zhang, M. A. Dombroski, *J. Org. Chem.*, 1992, 57, 4195-4205.

*Enol form of **7***: ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.53 – 7.42 (m, 3H), 6.17 (s, 1H), 5.15 – 5.10 (m, 1H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.07 (q, *J* = 7.4 Hz, 2H), 1.73 (quint., *J* = 7.4 Hz, 2H), 1.70 (s, 3H), 1.63 (s, 3H), the OH signal is missing. *Characteristic signals of the keto form of **7***: 4.08 (s, 2H), 2.57 (t, *J* = 7.4 Hz, 2H), 1.99 (q, *J* = 7.4 Hz, 2H), 1.41 (quint., *J* = 7.4 Hz, 2H). ^{13}C NMR: (100 MHz, $CDCl_3$) δ 197.0 (1C), 183.6 (1C), 135.1 (1C), 132.2 (1C), 128.7 (2C), 128.2 (1C), 127.1 (2C), 123.7 (1C), 96.2 (1C), 38.8 (1C), 27.6 (1C), 26.1 (1C), 25.9 (1C), 17.9 (1C). IR (neat) 2964, 2929, 2912, 2855, 1598, 1572, 1491, 1452 cm^{-1}. HRMS calculated for $C_{16}H_{20}O_2Na$ ([M + Na]$^+$) 267.1353, found 267.1356.

10-Ethyl-9-hydroxy-3,4,4a,10-tetrahydro-2H-anthracen-1-one (6)[5]

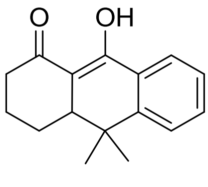


$C_{16}H_{18}O_2$
M = 242.31 g/mol

Following **GP4** with 1-phenyl-dec-7-ene-1,3-dione **5** (0.122 g, 0.5 mmol, 1 equiv.). Flash column chromatography (20:1 pentane/ diethyl ether) afforded **6** (0.035 g, 0.14 mmol, 29% yield) as a yellow solid. Spectral data are in accordance with those reported in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 1H), 7.52-7.48 (m, 1H), 7.38-7.32 (m, 2H), 2.70-2.58 (m, 2H), 2.49-2.46 (m, 2H), 2.22-2.16 (m, 2H), 2.04-1.92 (m, 2H), 1.70-1.58 (m, 1H), 1.35-1.21 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1 (1C), 182.1 (1C), 143.3 (1C), 132.6 (1C), 132.4 (1C), 126.8 (1C), 126.6 (1C), 125.2 (1C), 108.3 (1C), 42.5 (1C), 34.5 (1C), 32.7 (1C), 27.9 (1C), 21.1 (1C), 18.8 (1C), 7.9 (1C). IR (neat) 2958, 2931, 2871, 1712, 1679, 1598, 1448 cm-1. HRMS calculated for $C_{16}H_{18}O_2Na$ ([M + Na]$^+$) 265.1199, found 265.1202.

9-Hydroxy-10,10-dimethyl-3,4,4a,10-tetrahydro-2H-anthracen-1-one (8)

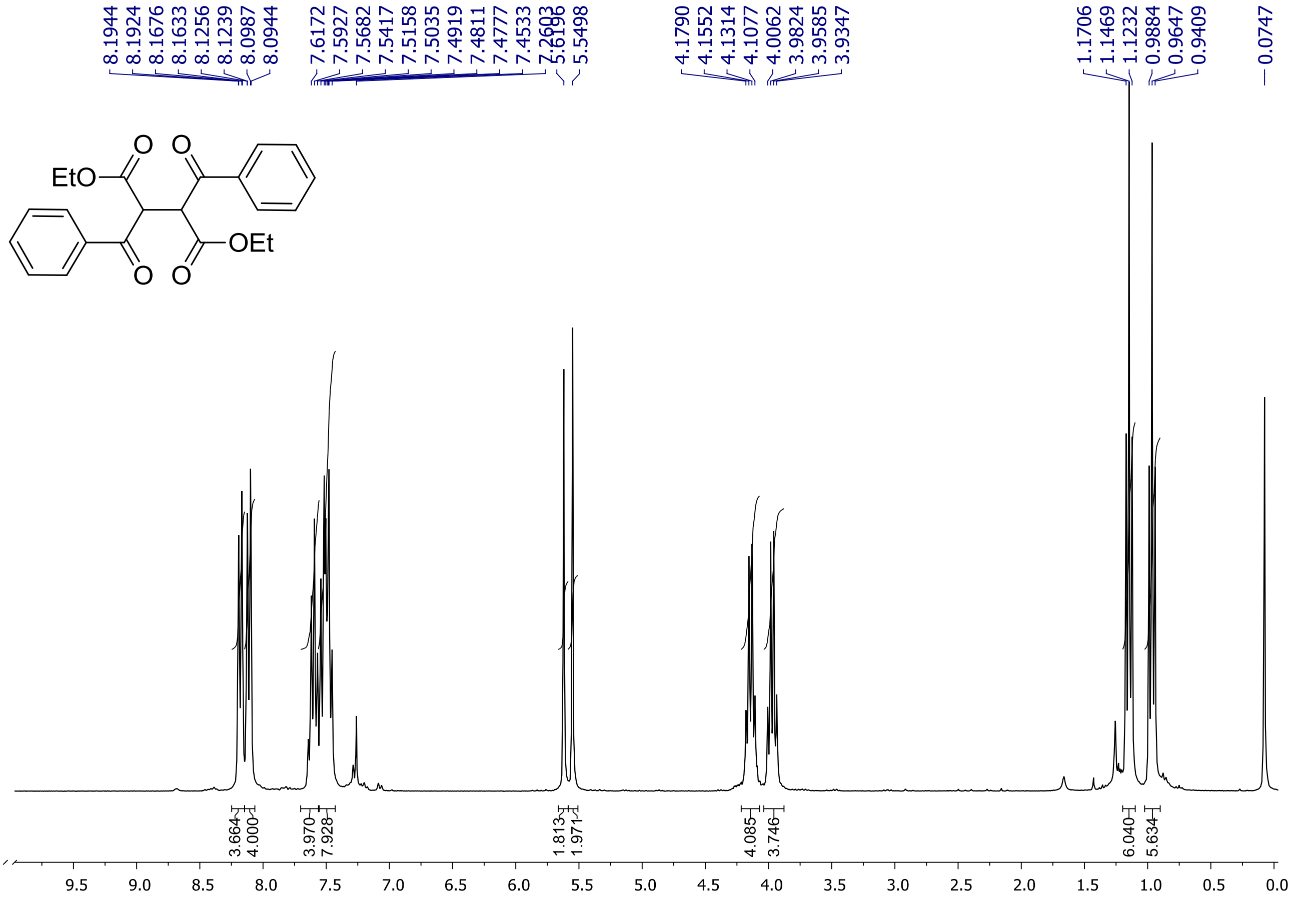


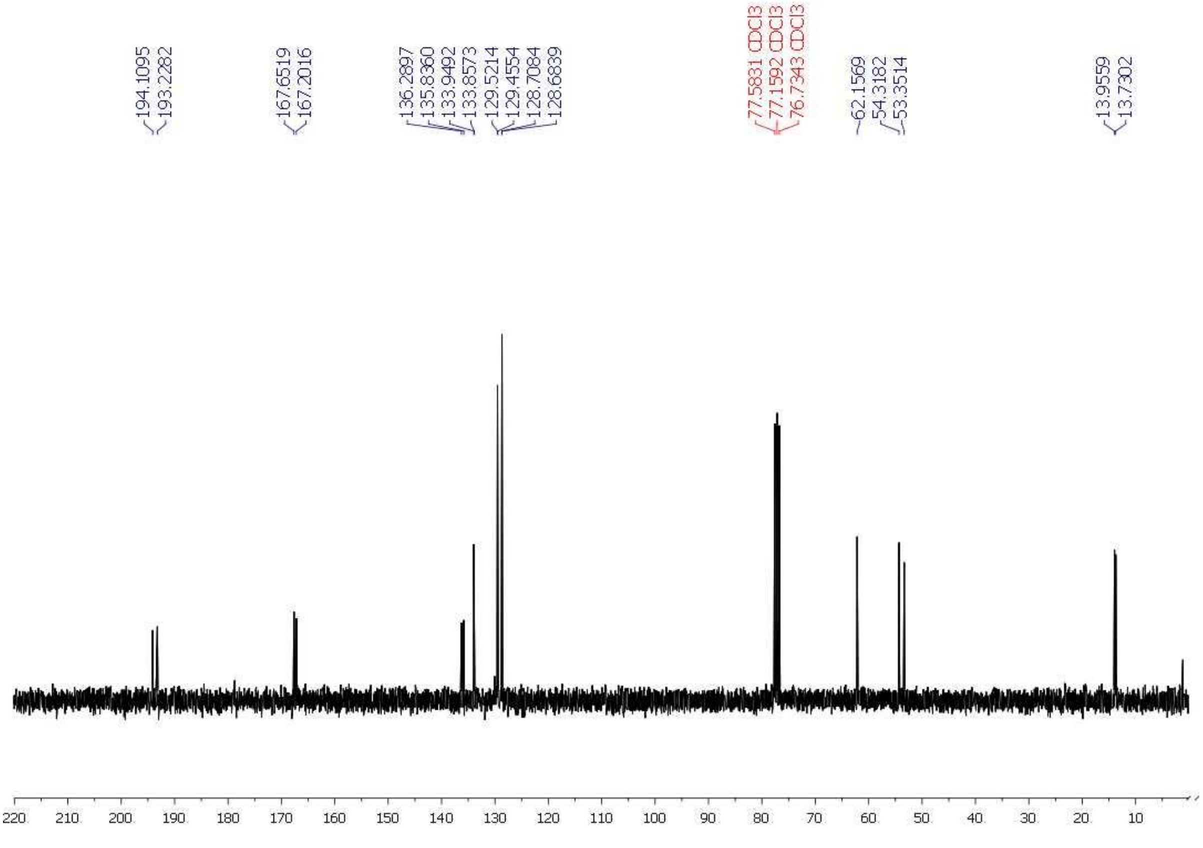
$C_{16}H_{18}O_2$
M = 242.31 g/mol

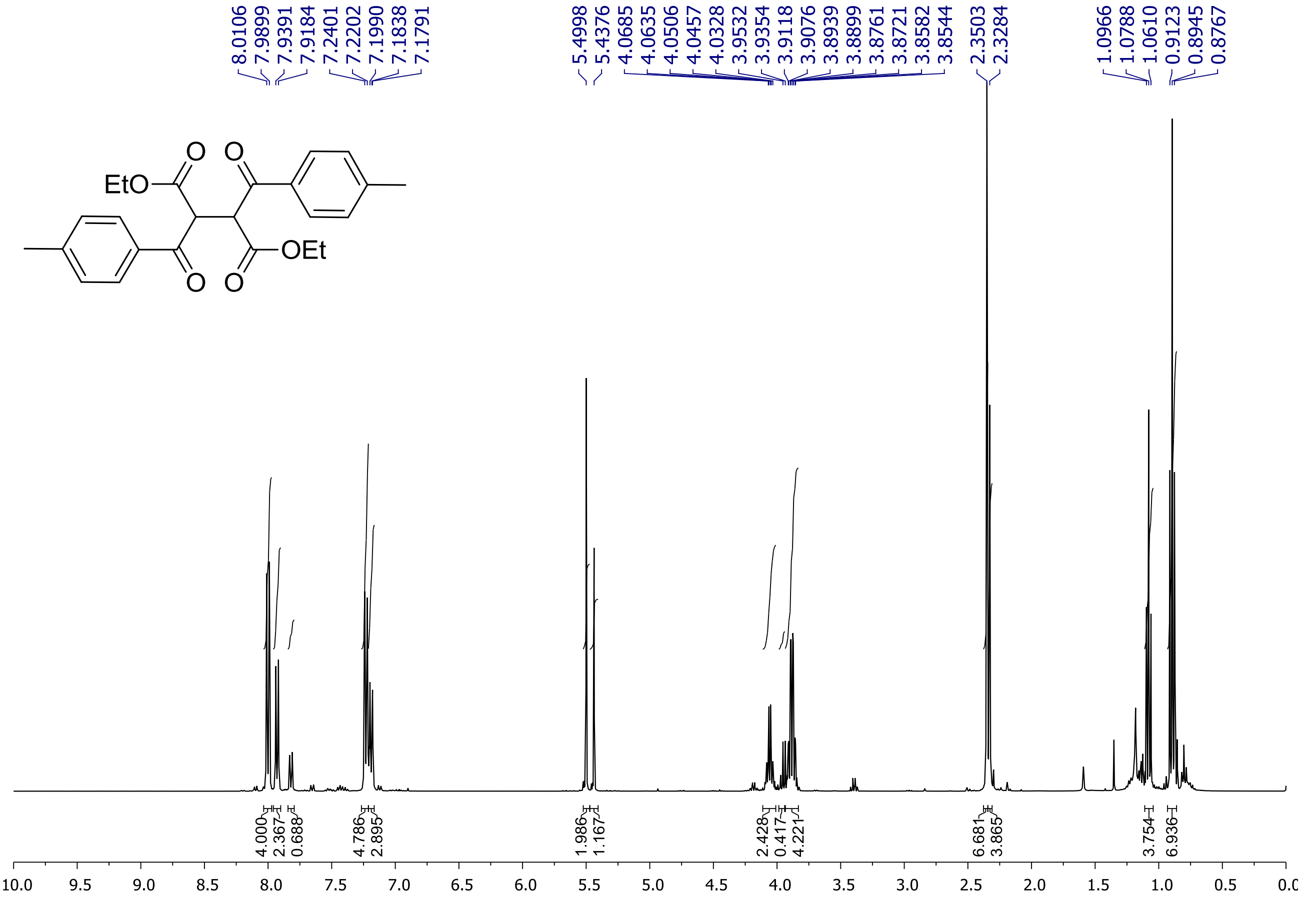
Following **GP4** with 8-methyl-1-phenyl-non-7-ene-1,3-dione **7** (0.122 g, 0.5 mmol, 1 equiv.). Flash column chromatography (20:1 pentane/ diethyl ether) afforded **8** (0.038 g, 0.16 mmol, 31% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 1H), 7.51-7.47 (m, 1H), 7.44-7.41 (m, 1H), 7.35-7.31 (m, 1H), 2.69-2.65 (m, 1H), 2.46-2.43 (m, 2H), 2.09-1.98 (m, 2H), 1.68-1.57 (m, 1H), 1.50-1.39 (m, 1H), 1.45 (s, 3H), 0.99 (s, 3H), the OH signal is missing. ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5 (1C), 183.4 (1C), 151.5 (1C), 133.1 (1C), 130.5 (1C), 126.8 (1C), 126.7 (1C), 123.8 (1C), 106.8 (1C), 42.3 (1C), 37.2 (1C), 32.5 (1C), 24.2 (1C), 24.1 (1C), 23.7 (1C), 21.0 (1C). IR (neat) 3067, 2934, 2868, 1590, 1561, 1467, 1413 cm^{-1}. HRMS calculated for $C_{16}H_{18}O_2Na$ ($[M + Na]^+$) 265.1199, found 265.1204.

6. ^{1}H and ^{13}C NMR Spectra



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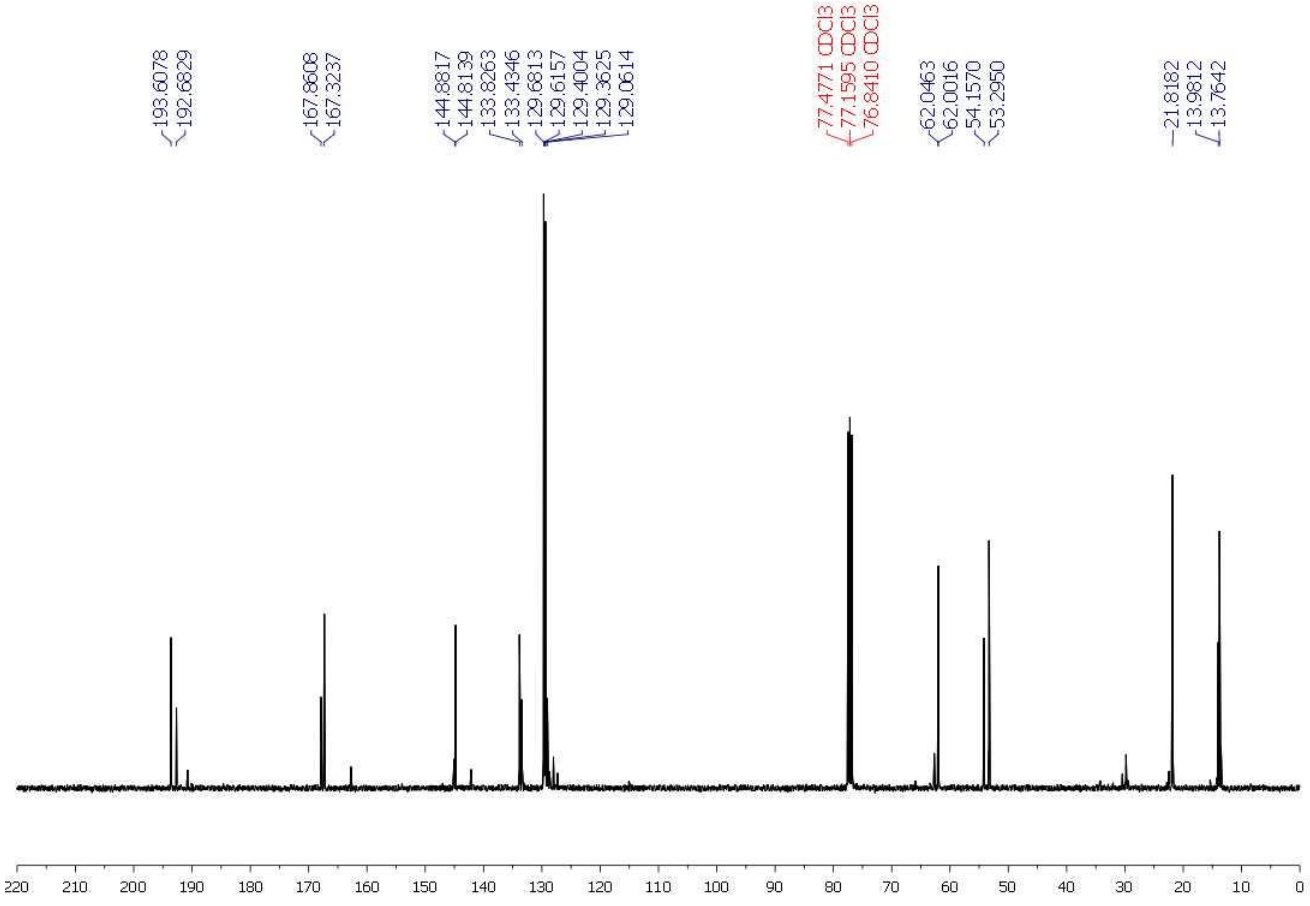
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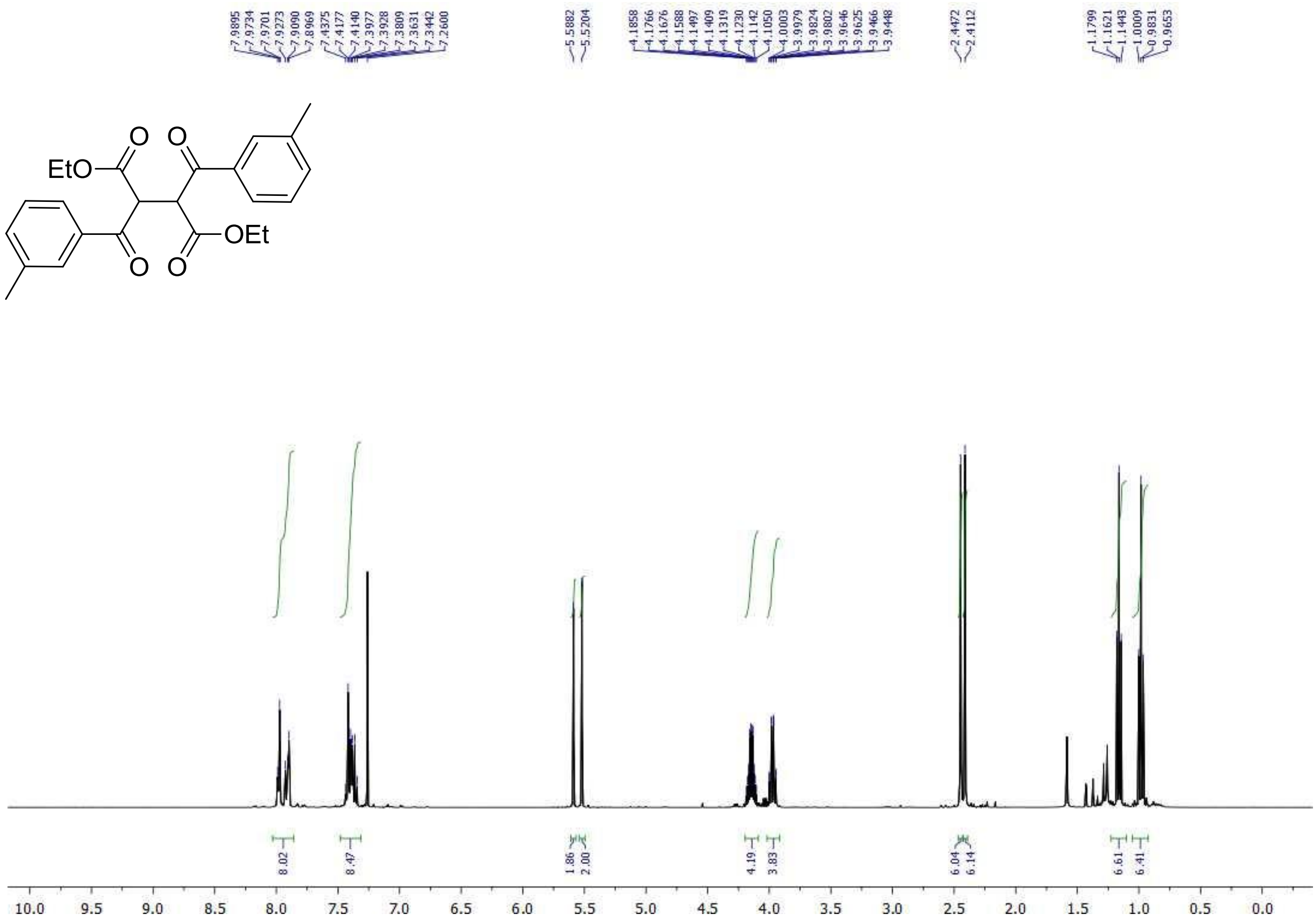
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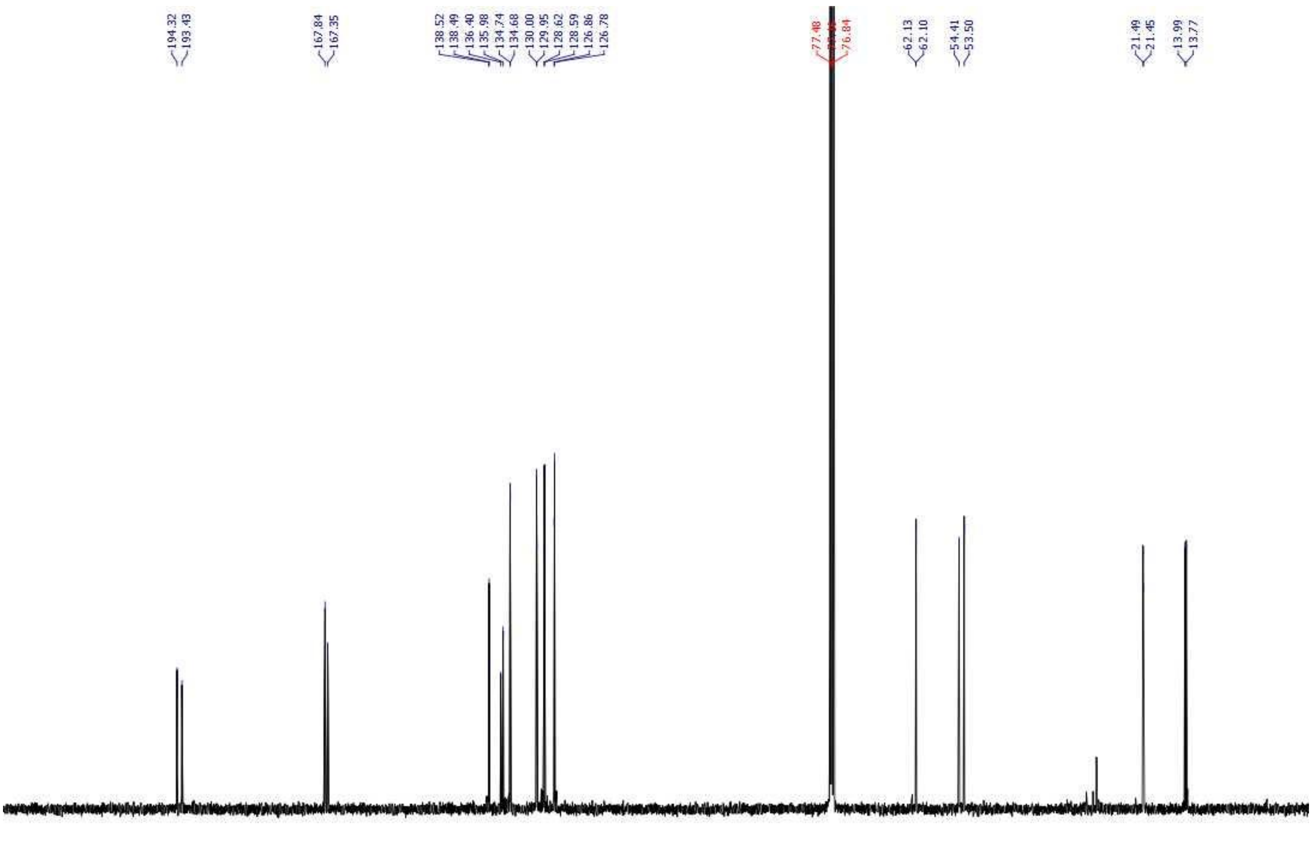
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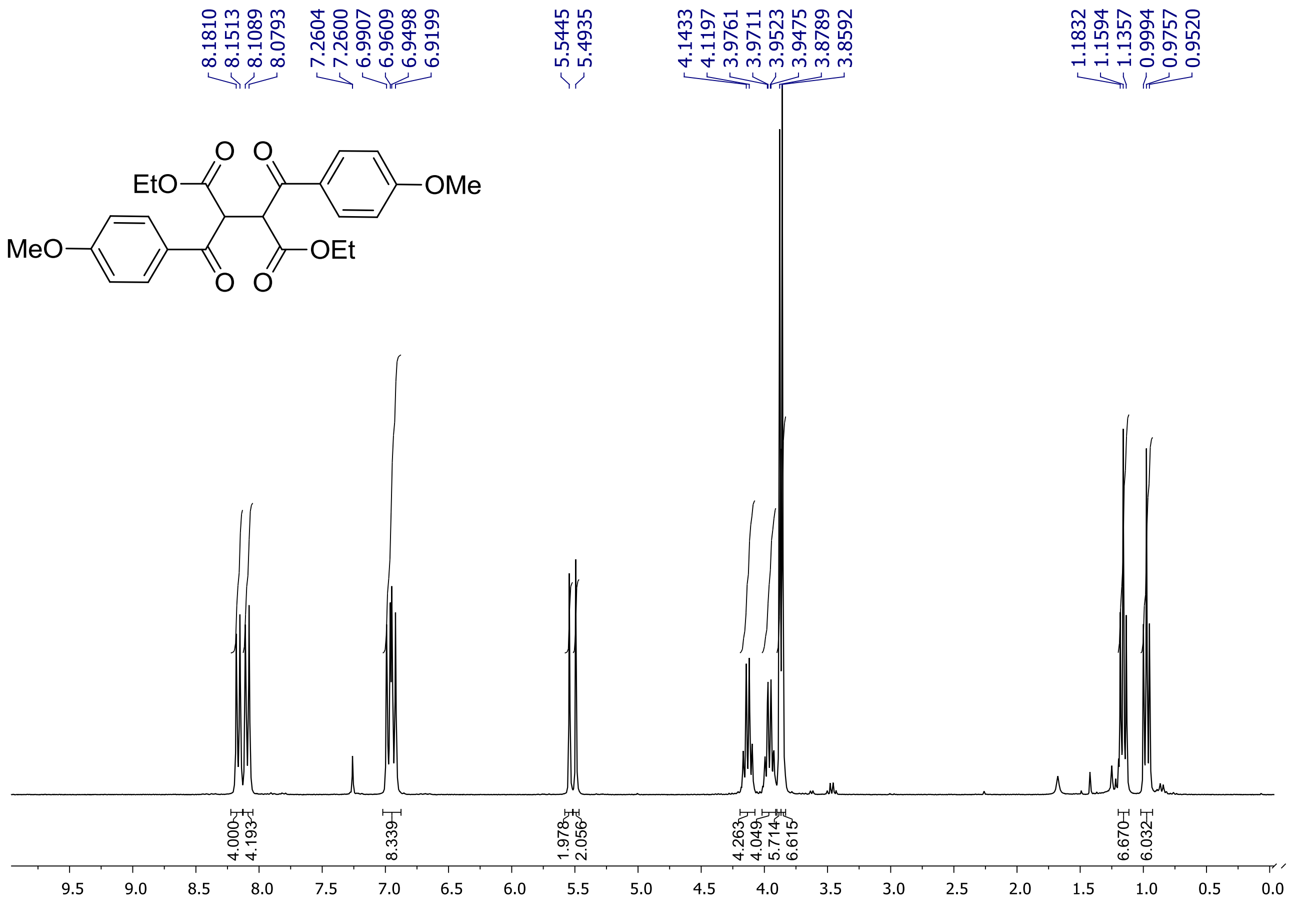
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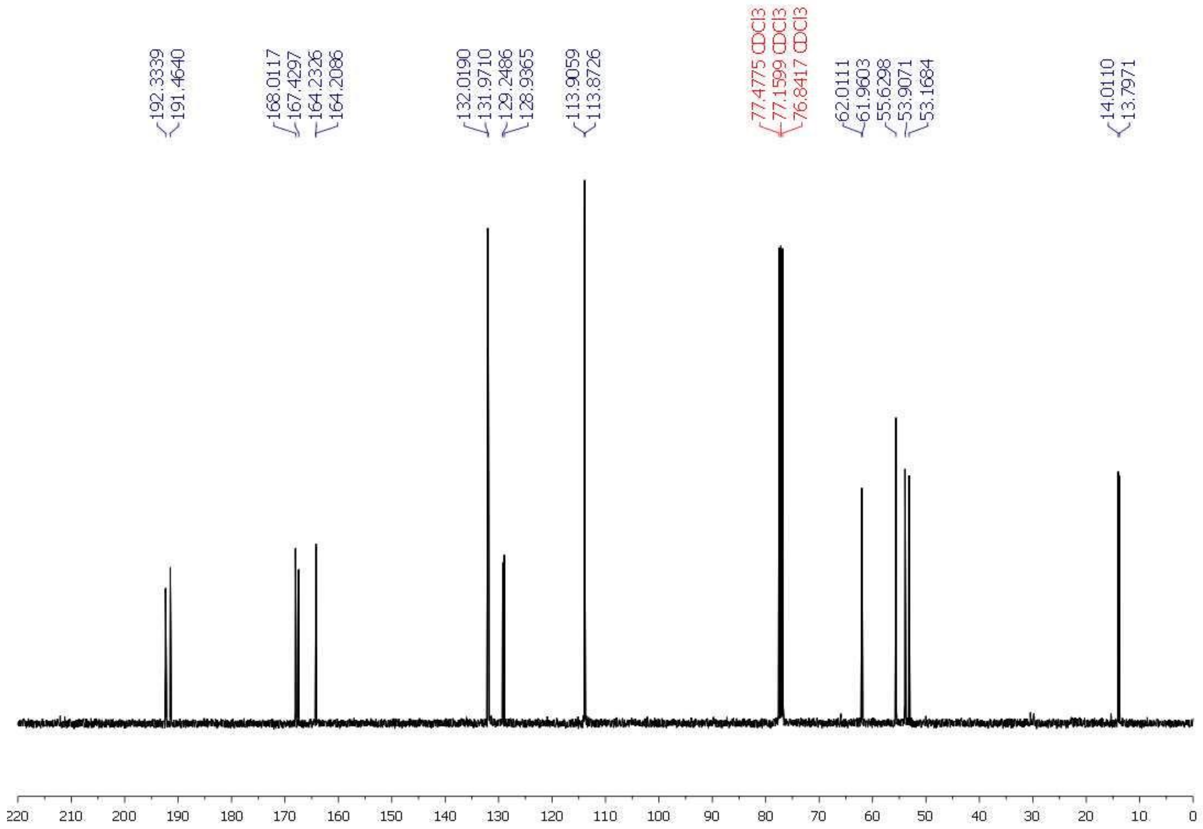
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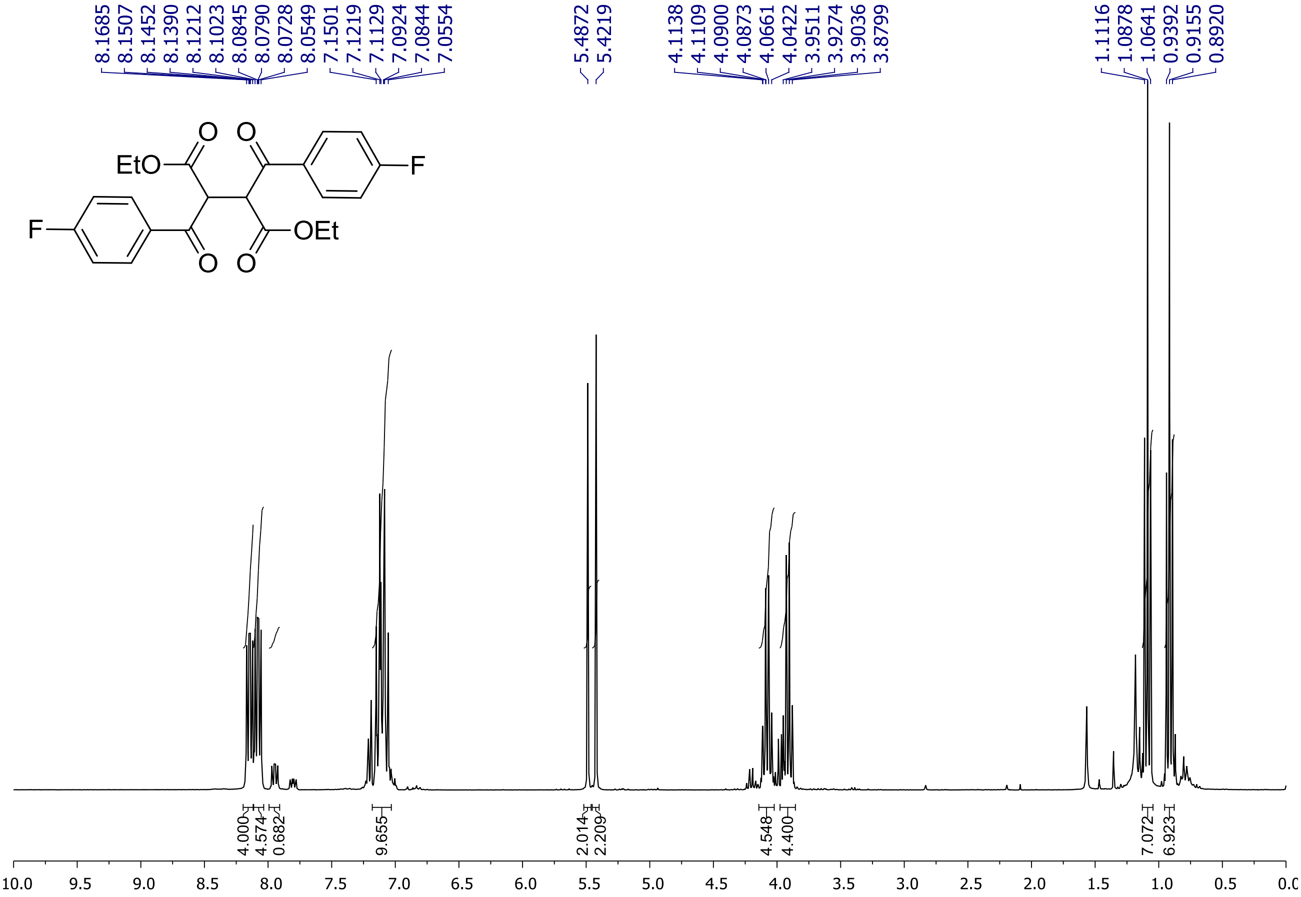
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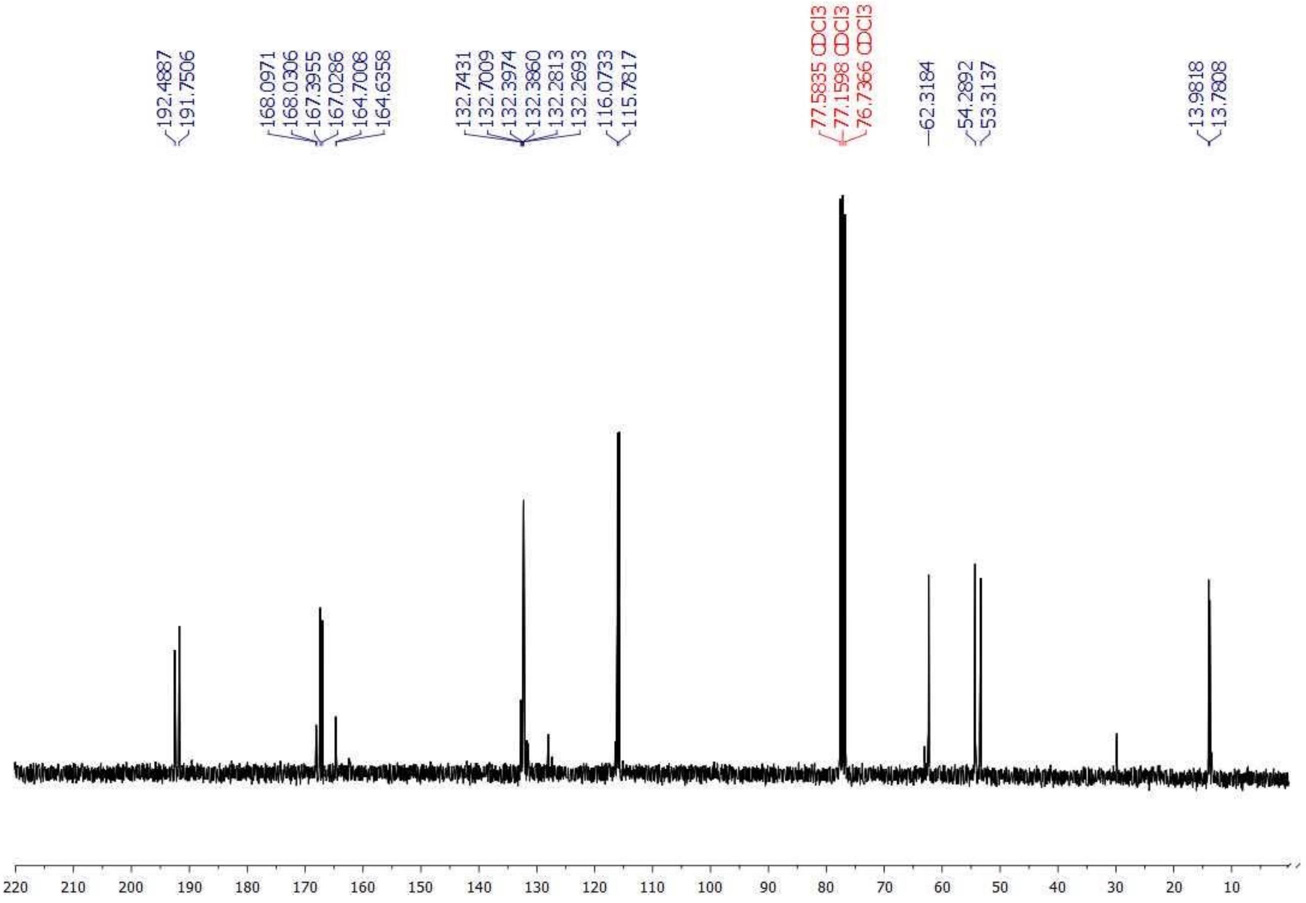
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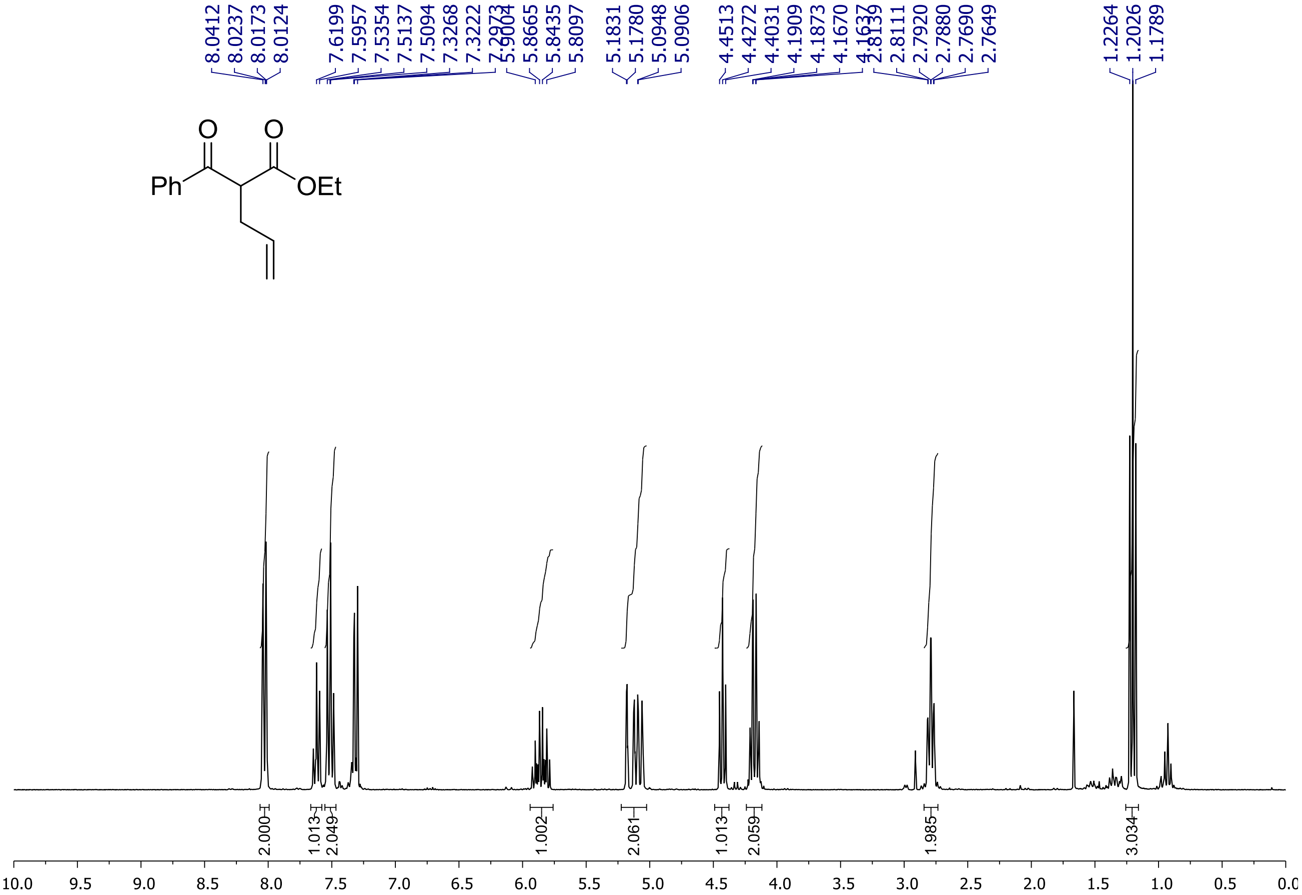
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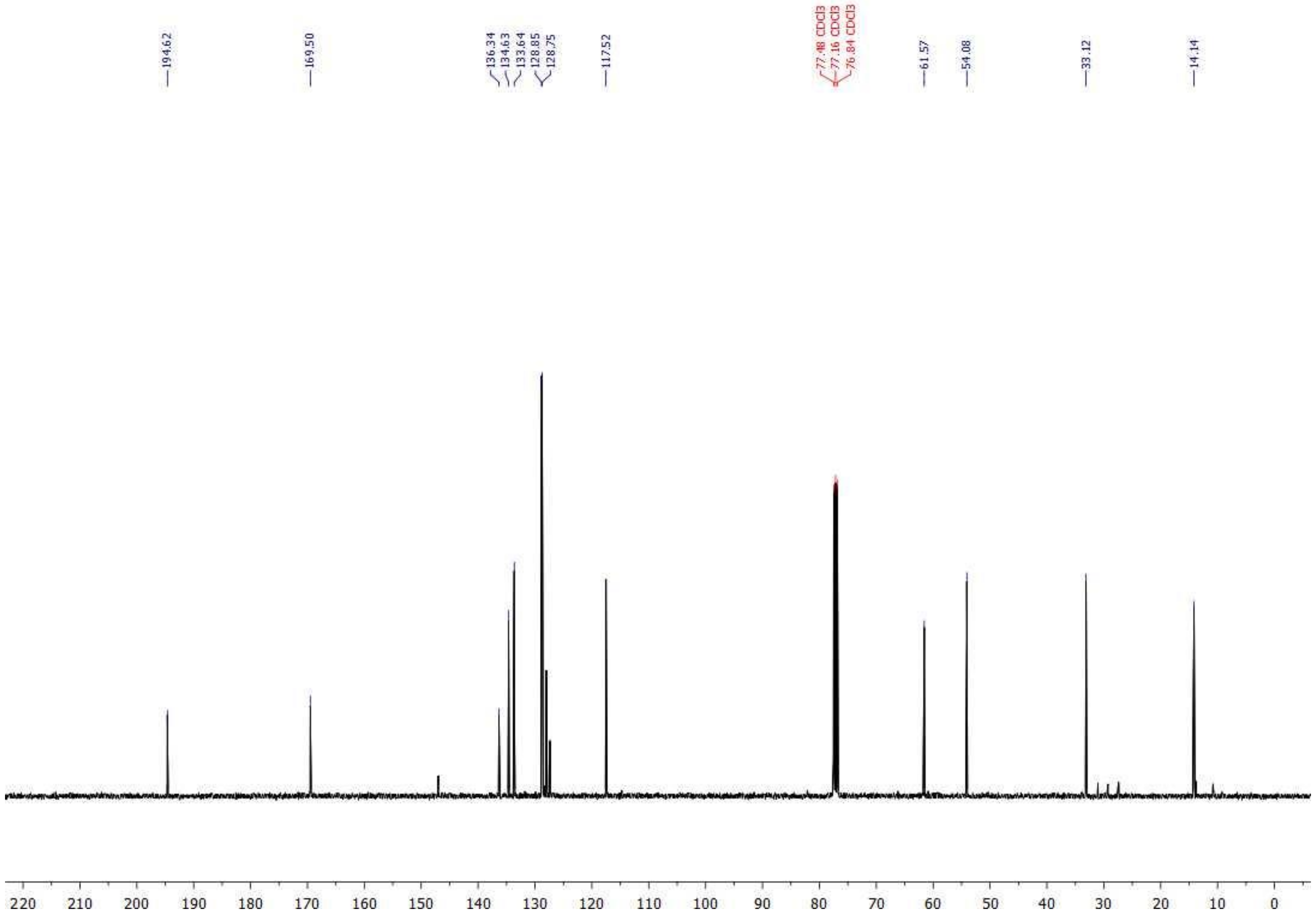
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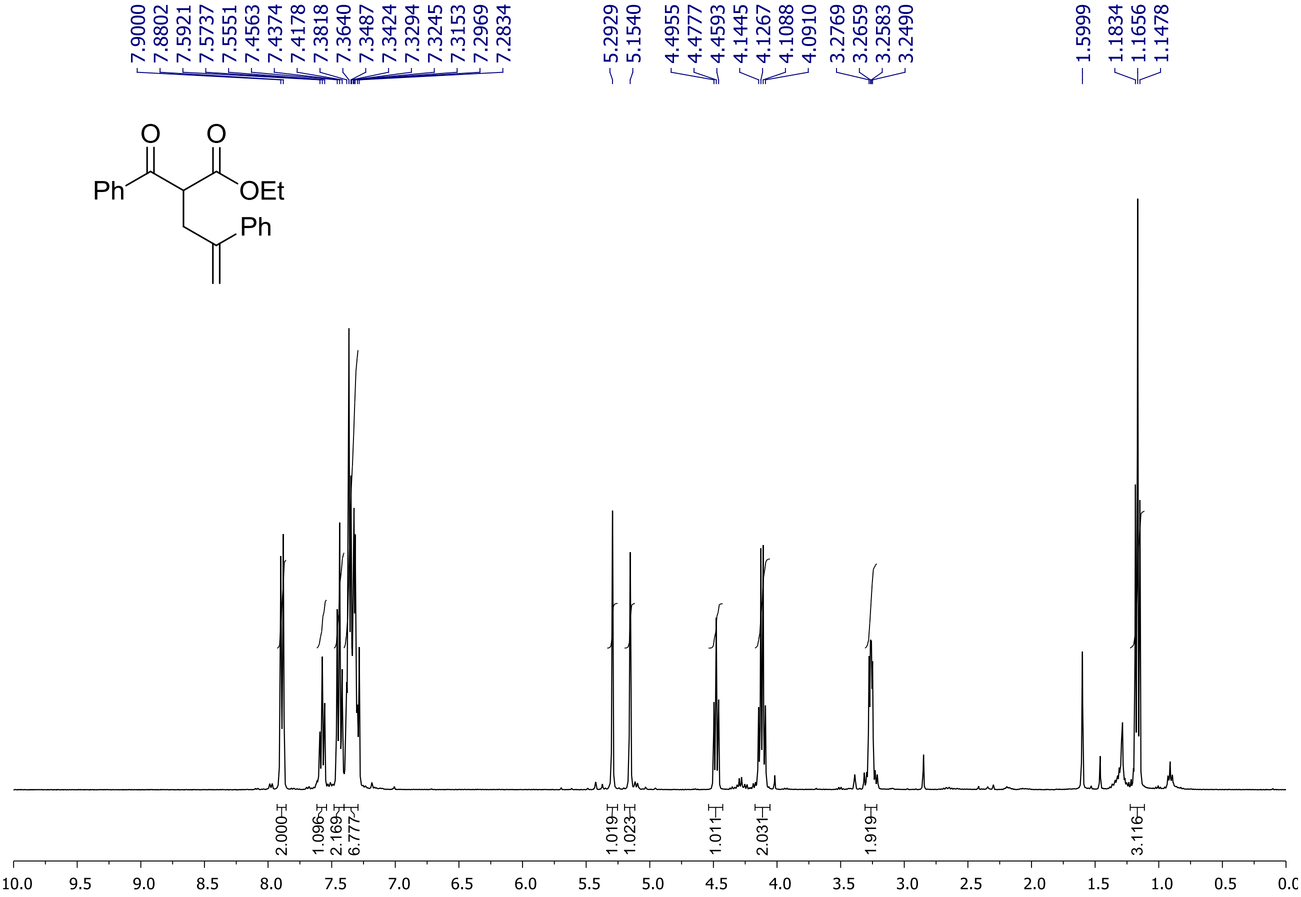
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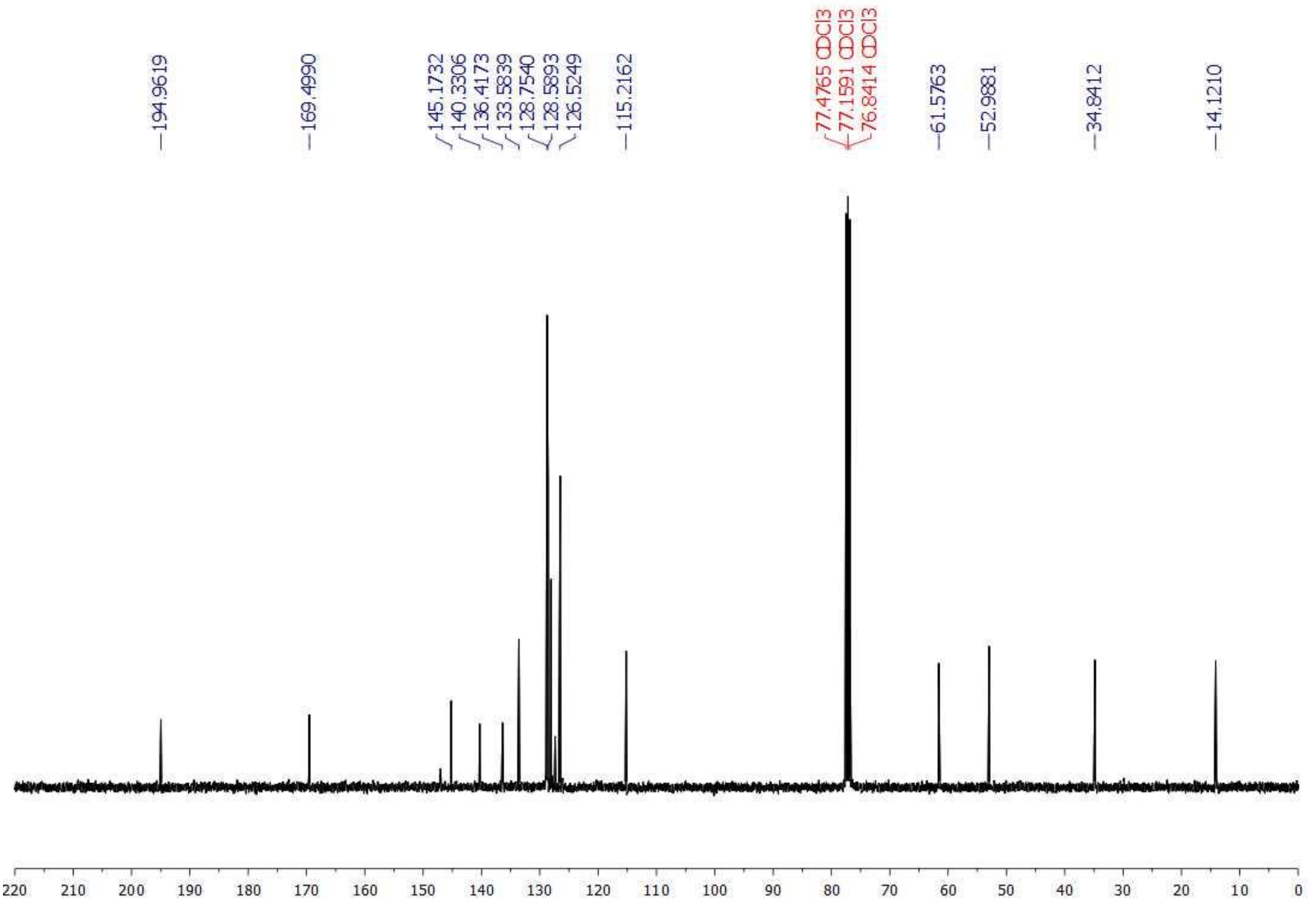
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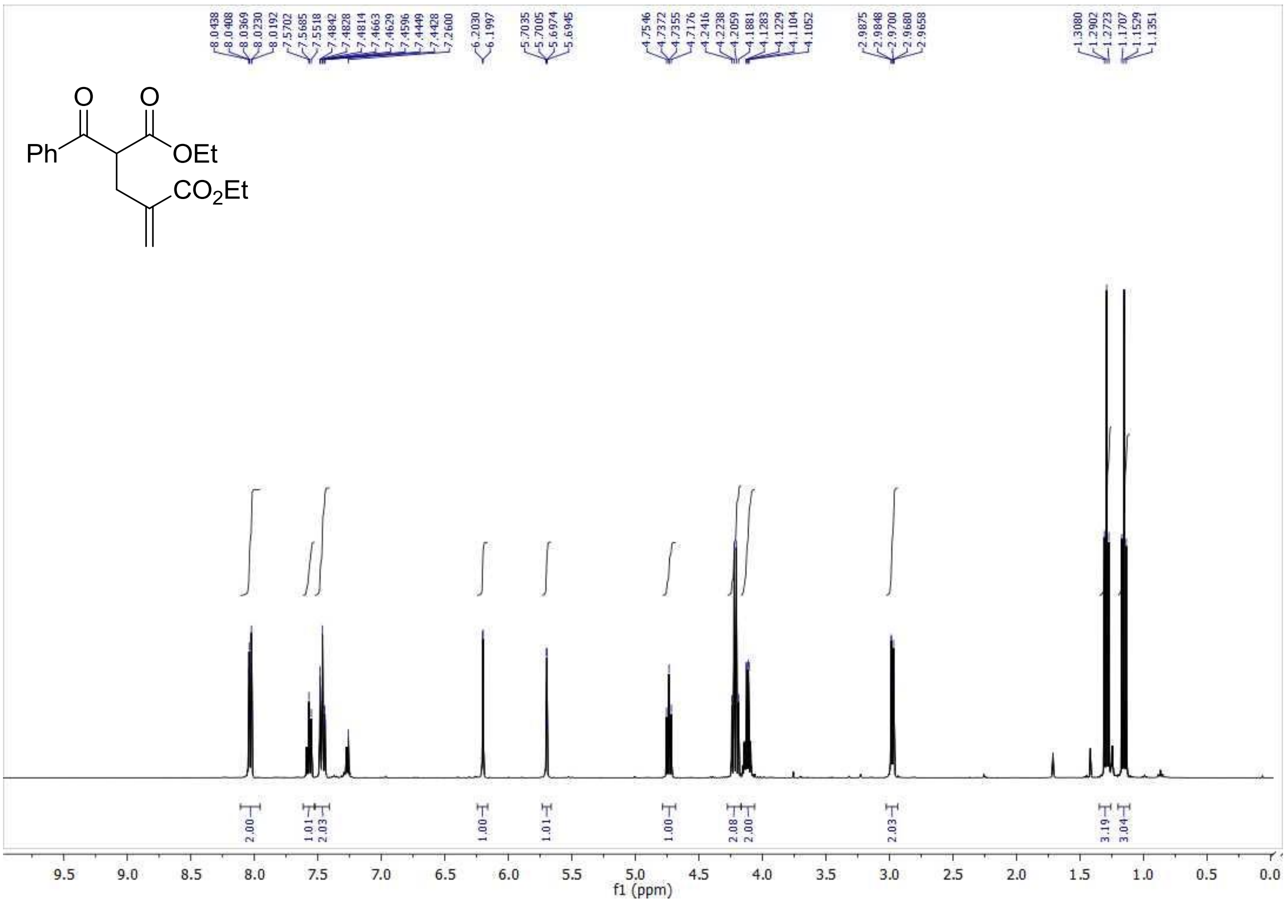
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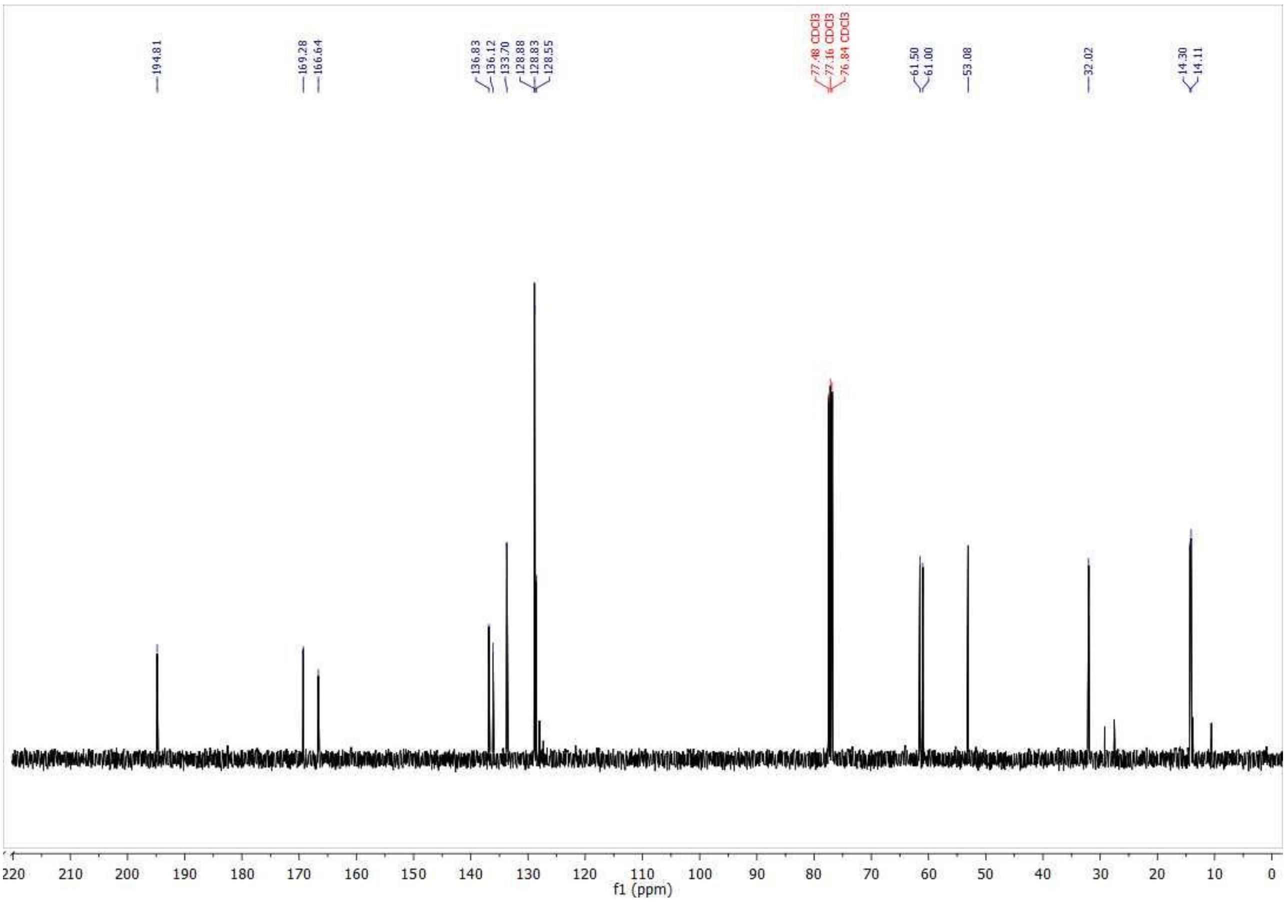
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180
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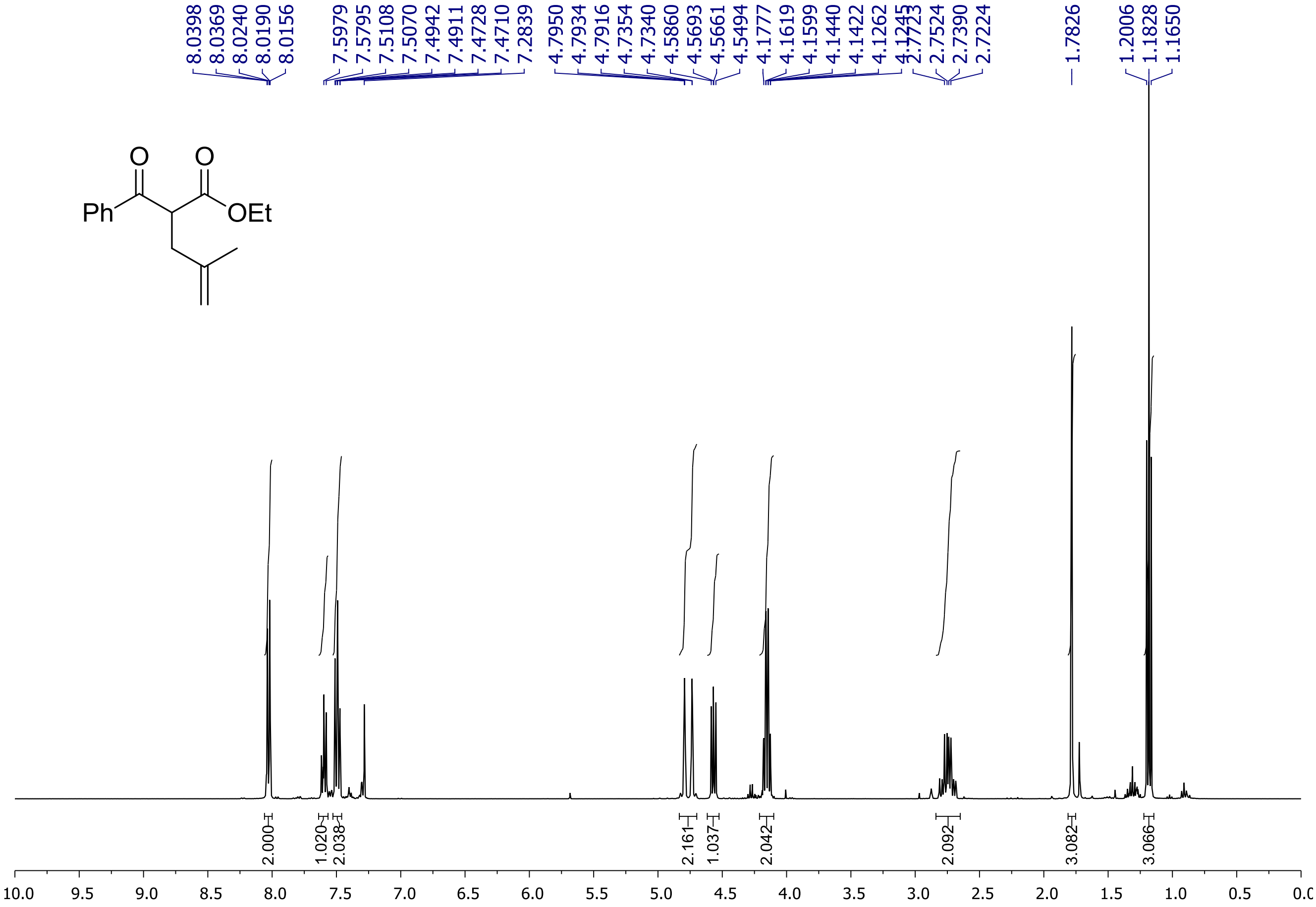
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4.1422
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4.1245
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2.7224
1.7826
1.2006
1.1828
1.1650
O
O
Ph
OEt
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1.020
2.038
2.161
1.037
2.042
2.092
3.082
3.066
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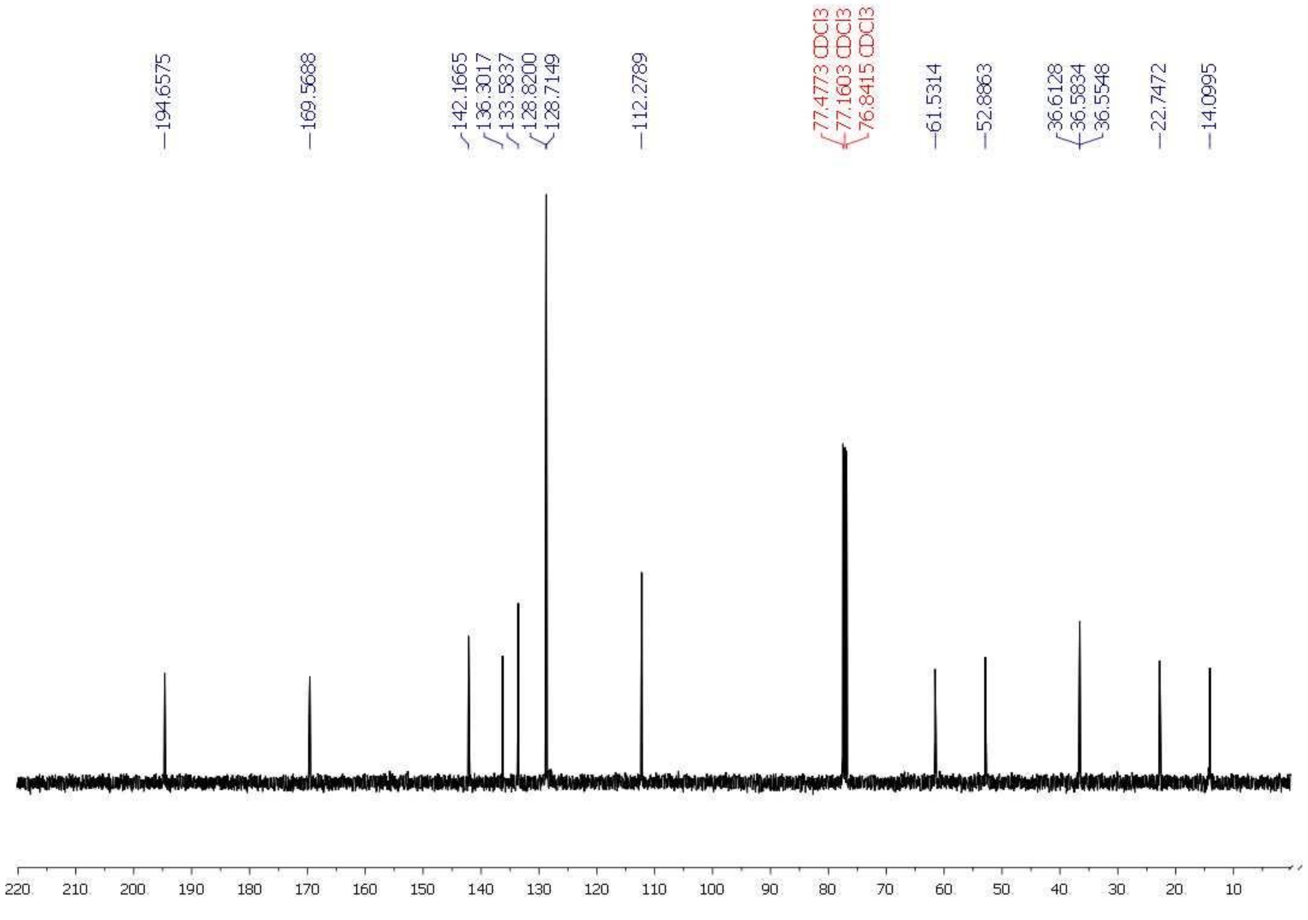
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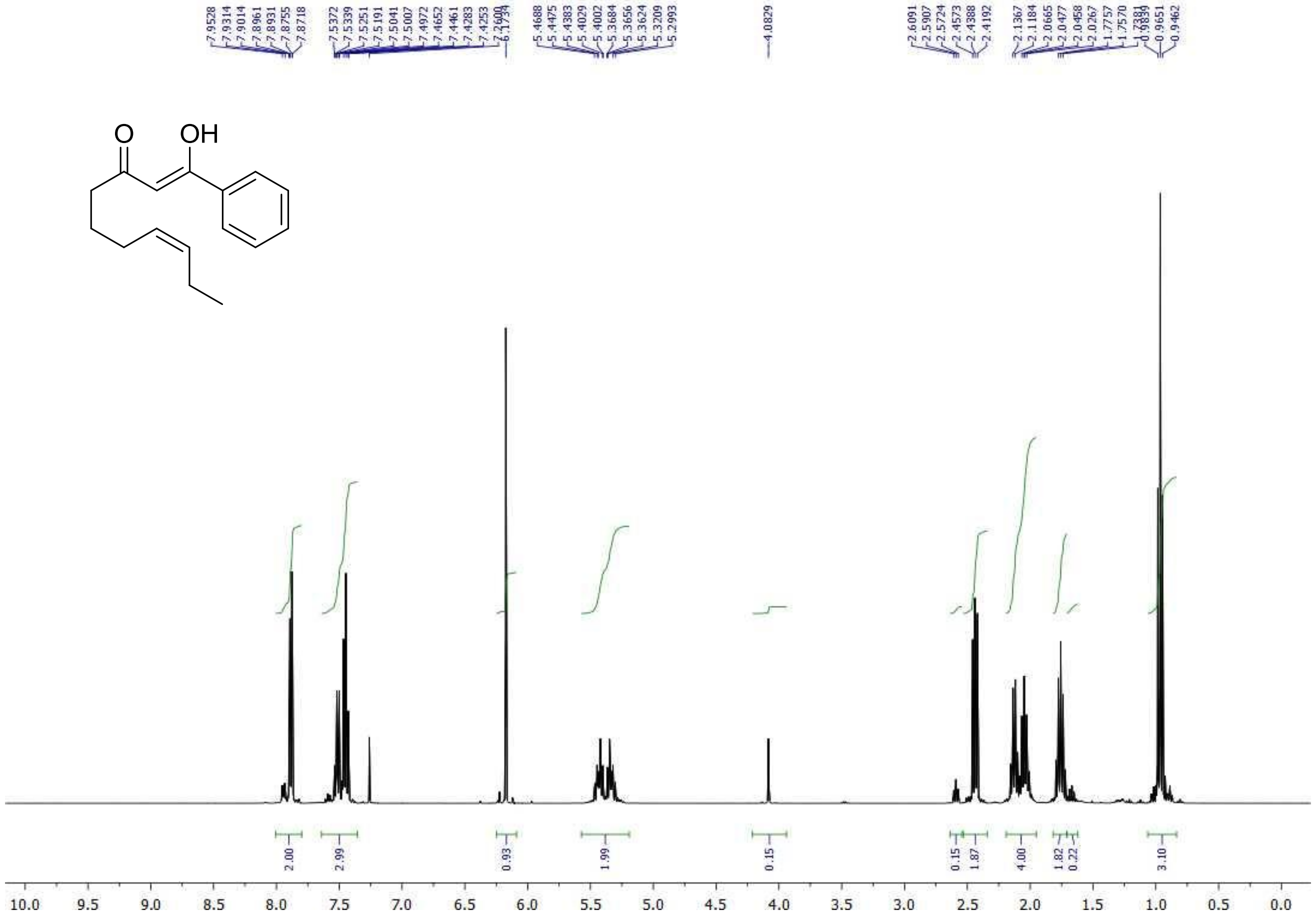
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6.1734
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OH
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9.5
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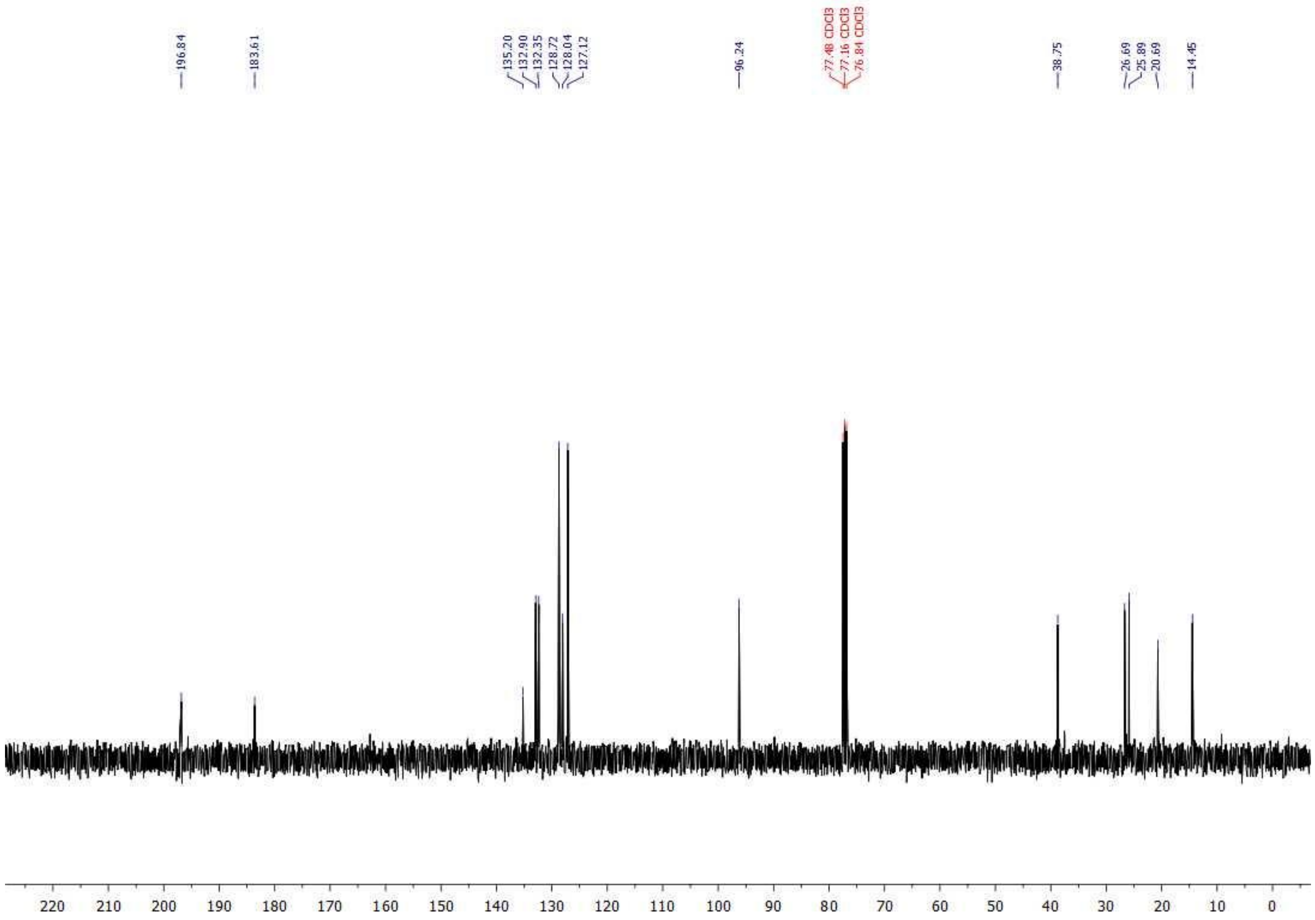
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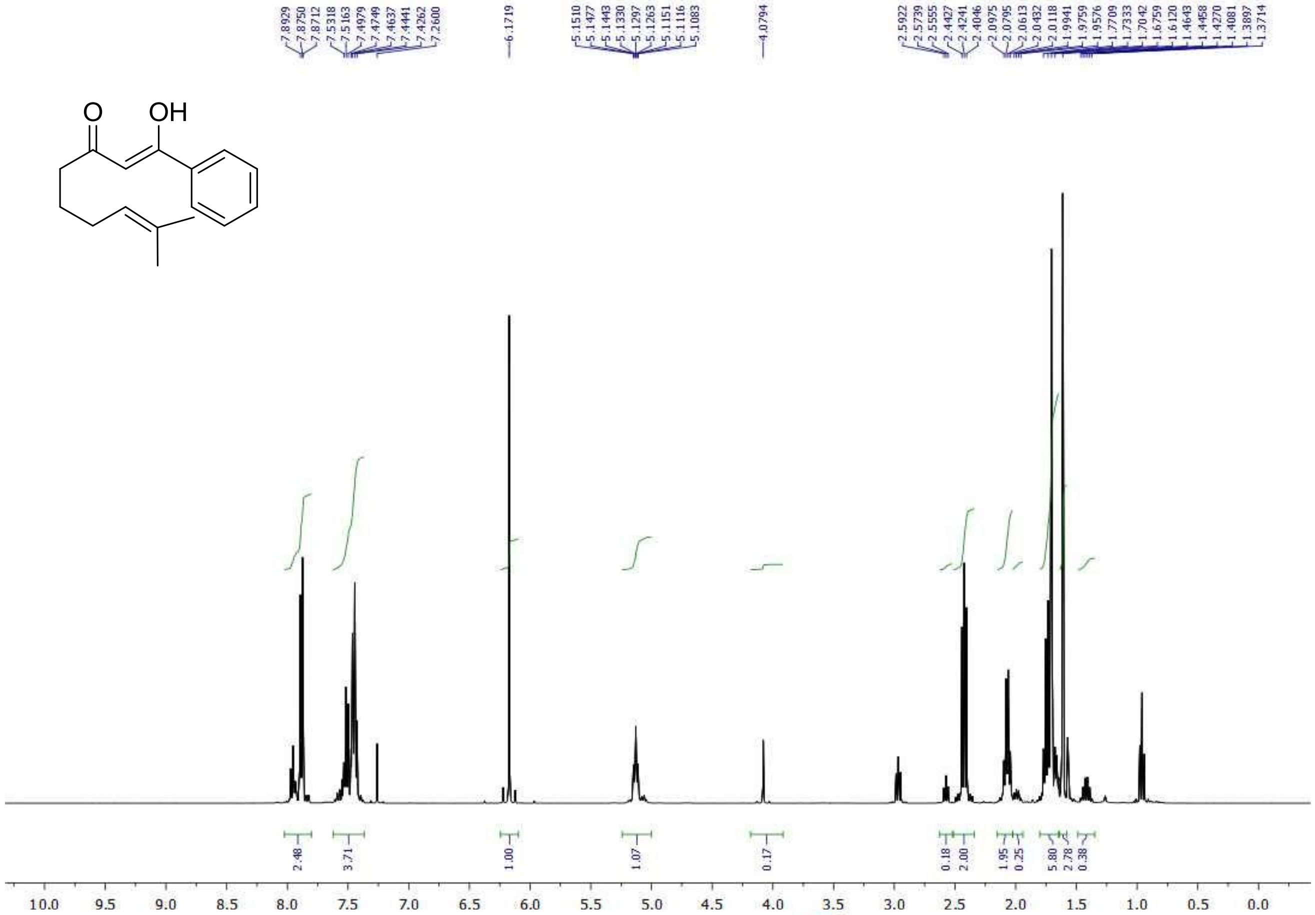
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5.1151
5.1116
5.1083
4.0794
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2.5739
2.5555
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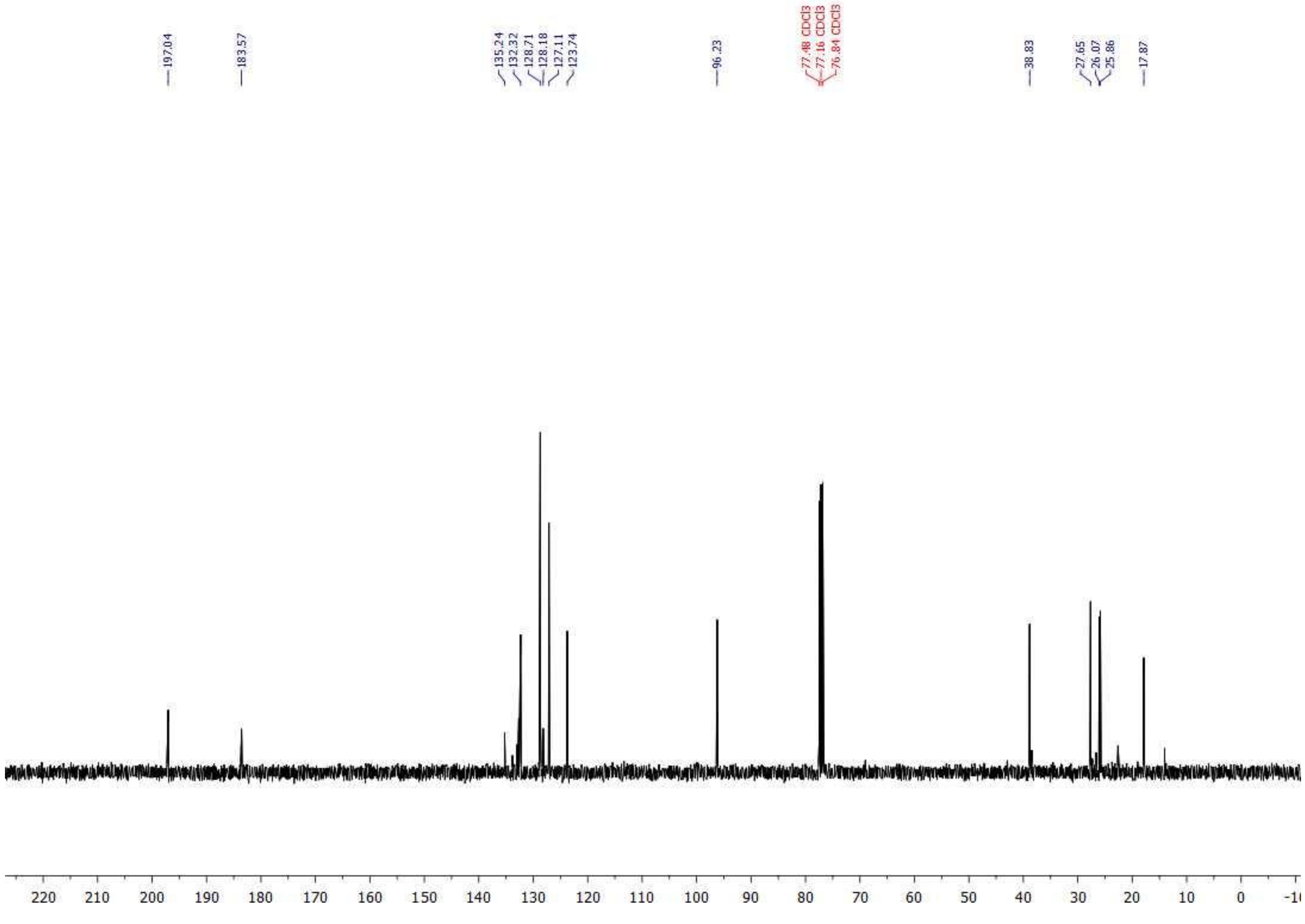
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26.07
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200
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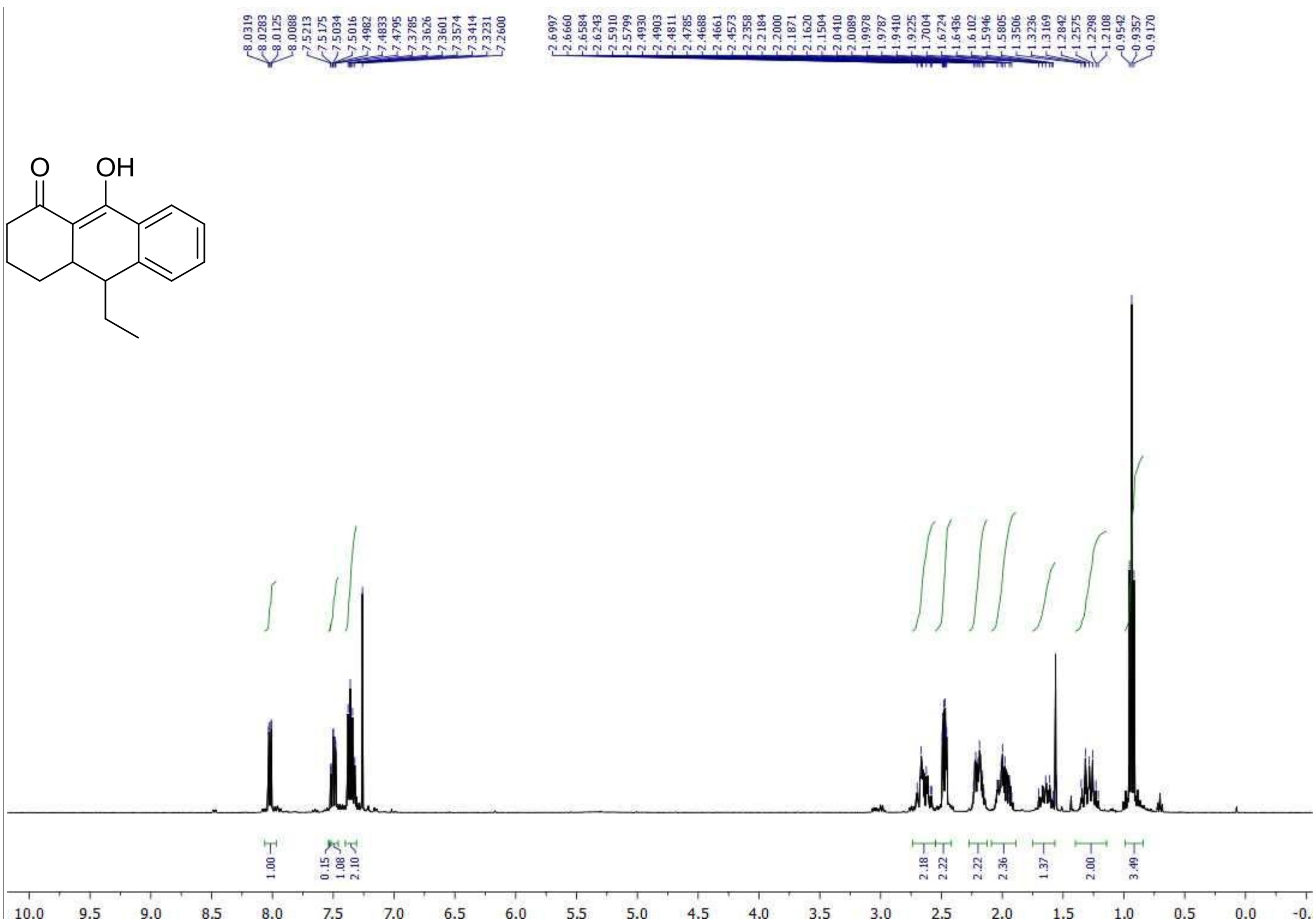
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7.3601
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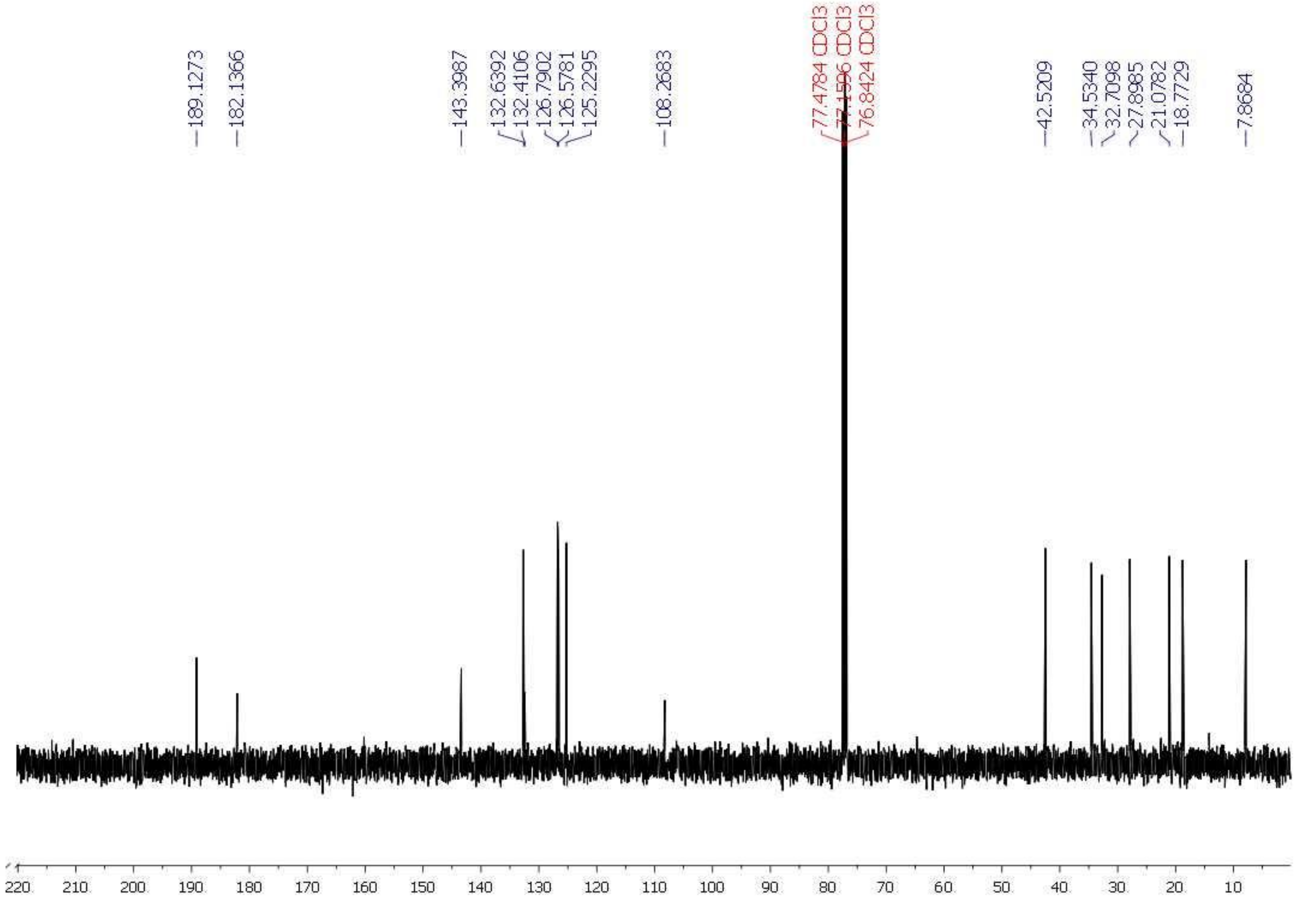
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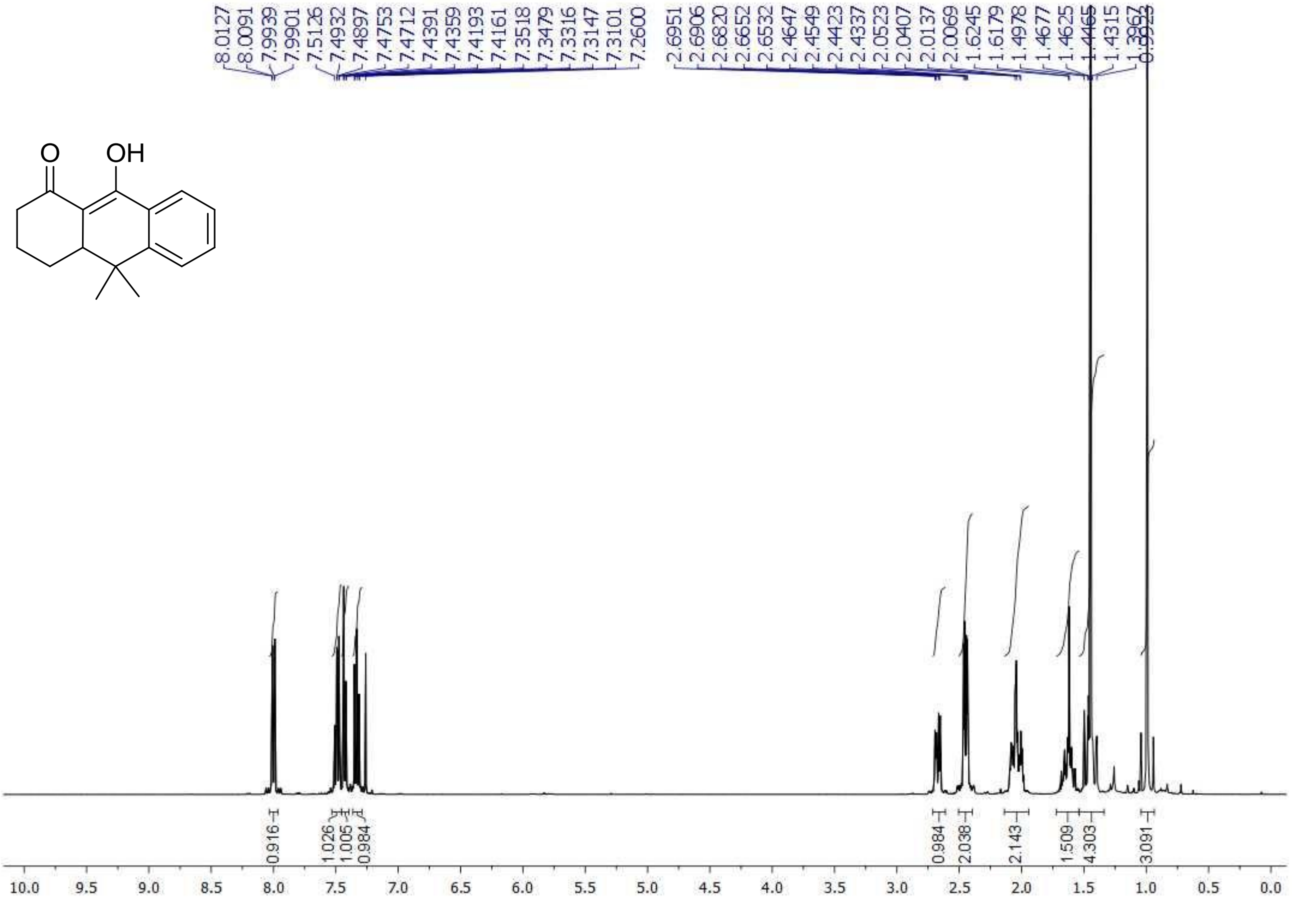
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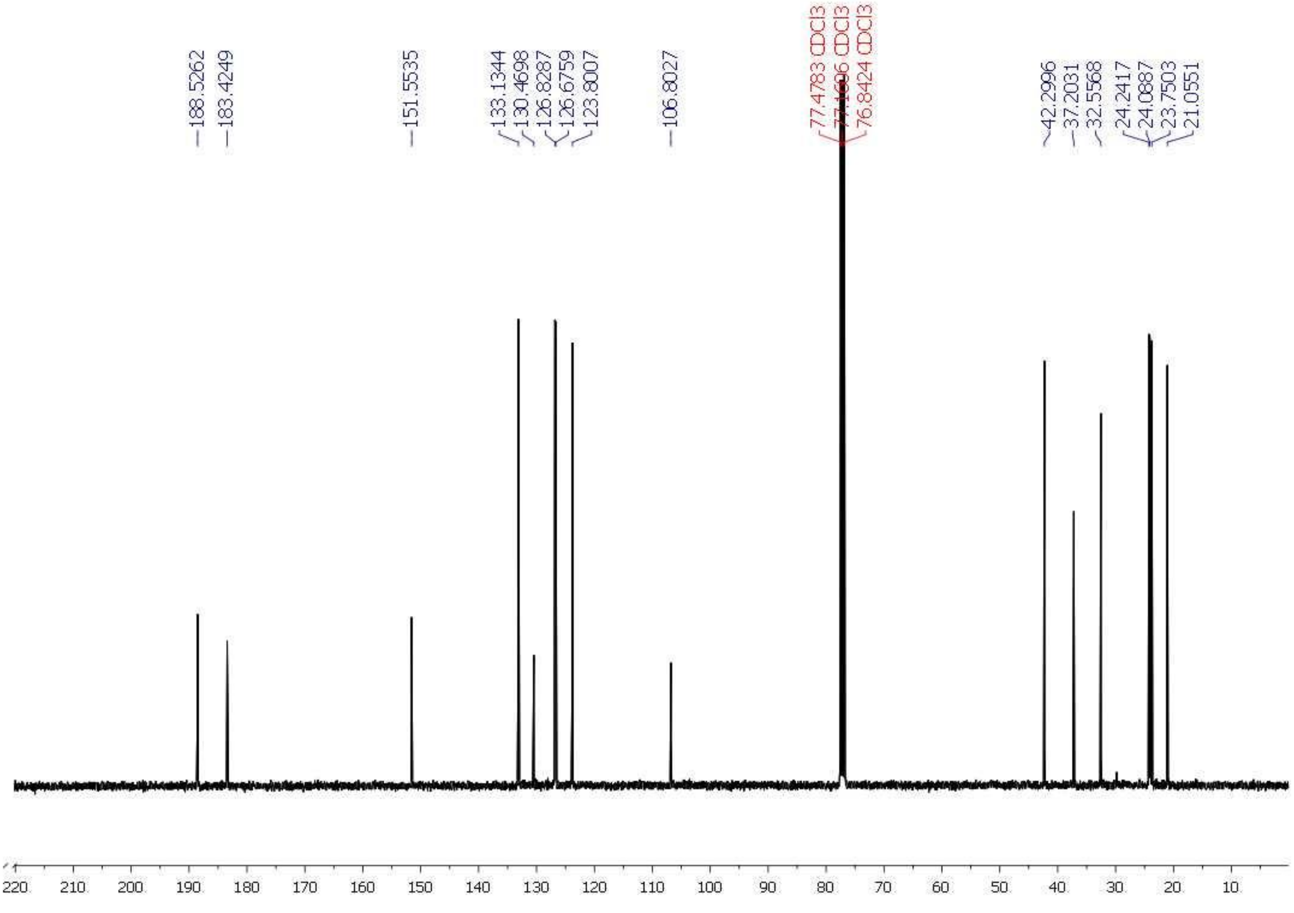
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